

Hard versus Soft Reactivity of Lewis Acidic Boranes

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Abstract

This work outlines the use of Lewis acidic boranes in a variety of different reactions, mainly in the activation of unsaturated substrates such as allenes, alkynes, ketones, aldehydes and imines.

The activation of allenes toward frustrated Lewis pairs showed that a formal 1,4-addition product prevails, trapping the product as the zwitterionic *s-cis* diene species. Conversely, reacting these same substrates with $B(C_6F_5)_3$ alone allows two distinct reactive pathways; either σ -activation to yield the scarcely observed 1,2-carboboration product or π -activation followed by dealkylation to generate the γ -lactone. Following this second activation mode, the reaction between propargyl esters, amides, carbamates and carbonates with a variety of homo- and hetero-leptic boranes as well as borocations promotes the 5-*exo-dig* cyclisation which, depending on the substrate, was either isolated as the oxazolium or dioxaborinine heterocycle. In addition, utilising the Lewis acid $PhBCl_2$ in this reaction interestingly produces the hitherto unreported 1,3-haloboration of alkynes.

$B(C_6F_5)_3$ was also shown to be hugely successful in a number of other ring closing reactions, specifically the 6-*endo-dig* cyclisation of alkynyl ester derivatives to form various pyrones, isocoumarins and pyryliums. Of particular interest is the development of a new methodology for catalytic carbon-carbon bond formation through alkyl group transfer. In this case, benzyl, α -methylbenzyl and benzhydryl functionalised alkynyl esters underwent the expected cyclisation using catalytic $B(C_6F_5)_3$ to form the lactone however, 1,5-migration occurs from oxygen to carbon to generate the corresponding γ -functionalised pyrones and isocoumarins.

Finally, a diverse array of reduction chemistry was performed by attenuating the Lewis acidity at boron to specialise its function in catalysis. Other work focused on the exploitation of novel processing technologies to improve conventional batch-type main group reactivity *via* continuous-flow chemistry. Additionally, biologically inspired dihydropyridines were used in the formation of thermally stable borohydrides as well as elemental hydrogen surrogates in boron mediated transfer hydrogenation pathways.

Contents

	Acknowledgements	i
	Abstract	ii
	List of Publications	vi
	List of Abbreviations	viii
Chapter 1	Introduction	1
1.1	Scope of This Work	1
1.2	Background	2
Chapter 2	Activation of Allenyl Ketones and Esters using Cooperative Lewis Pairs and Boron Lewis Acids	7
2.1	Introduction	7
2.1.1	Aims of This Chapter	11
2.2	Results and Discussion	11
2.2.1	Cooperative Lewis Pair Reactions with Allenes	11
2.2.2	1,2-Carboration of Allenes using $B(C_6F_5)_3$	16
2.3	Conclusions	21
Chapter 3	The Propargyl Rearrangement: Cyclisations, 1,1-Carbaborations and 1,3-Haloborations of Homoleptic and Heteroleptic Boranes	22
3.1	Introduction	22
3.1.1	Aims of This Chapter	28
3.2	Results and Discussion	29
3.2.1	The Propargyl Rearrangement of Amides, Carbamates and Carbonates	29
3.2.1.1	Reactivity of Dipropargyl Amides	29
3.2.1.2	Reactivity of Propargyl Ureas	32
3.2.1.3	Reactivity of Propargyl Carbamates	34
3.2.1.4	Reactivity of propargyl carbonates	39
3.2.2	Use of Heteroleptic Boranes for Selective Migratory Group Transfer	41
3.2.3	Divergent Elementoboration using Heteroleptic Boranes in the Propargyl Rearrangement	49
3.3	Conclusions	54
Chapter 4	Formation of 6-Membered Heterocycles via Alkyne Activation: Carbon-Element Bond Creation through Cyclisations	56
4.1.1	Aims of This Chapter	61
4.2	Results and Discussion	61
4.2.1	Formation of Zwitterionic Pyrylium Borates using $B(C_6F_5)_3$	61
4.2.2	Divergent Reactivity of Hard and Soft Lewis Acids: 6-endo-dig vs. 5-exo-dig	66
4.2.3	Stoichiometric and Catalytic Pyrone and Isocoumarin Formation via C–H and C–C Bond Formation	71
4.3	Conclusions	82
Chapter 5	Boron Mediated and Catalysed Reduction Reactions: Emerging Catalysts, Novel Processing Techniques and Transfer Hydrogenation	83
5.1	Introduction	83

5.1.1	Aims of This Chapter	91
5.2	Results and Discussion.....	92
5.2.1	Tempering Lewis Acidity of Boranes for General Hydroboration Reactions ..	92
5.2.2	Novel Processing Methods in the Hydrosilylation of Aldehydes, Ketones and Imines.....	98
5.2.3	Biologically Inspired Borohydride Sources and Subsequent Transfer Hydrogenation Reactions.....	104
5.3	Conclusions.....	110
Chapter 6	Experimental	112
6.1	General Experimental	112
6.2	Activation of Allenyl Ketones and Esters using Cooperative Lewis Pairs and Boron Lewis Acids	113
6.2.1	Synthesis of Starting Materials	113
6.2.2	Synthesis of Products	113
6.2.3	Computational Studies	122
6.2.4	Crystallographic Studies	122
6.3	The Propargyl Rearrangement: Cyclisations and 1,1-Carboborations of Homoleptic and Heteroleptic Boranes	125
6.3.1	The Propargyl Rearrangement of Esters, Amides, Carbamates and Carbonates.....	125
6.3.1.1	Synthesis of Starting Materials	125
6.3.1.2	Synthesis of Products	130
6.3.2	Use of Heteroleptic Boranes for Selective Migratory Group Transfer	137
6.3.2.1	Synthesis of Starting Materials	137
6.3.2.2	Synthesis of Products	144
6.3.3	Divergent Elementoboration using Heteroleptic Boranes in the Propargyl Rearrangement	151
6.3.3.1	Synthesis of Starting Materials	151
6.3.3.2	Synthesis of Products	153
6.3.4	Crystallographic Studies	155
6.4	Formation of 6-Membered Heterocycles via Alkyne Activation: Carbon-Element Bond Creation through Cyclisations	160
6.4.1	Formation of Zwitterionic Pyrylium Borates using $B(C_6F_5)_3$	160
6.4.1.1	Synthesis of Starting Materials	160
6.4.1.2	Synthesis of Products	160
6.4.2	Divergent Reactivity of Hard and Soft Lewis Acids: 6-endo-dig vs. 5-exo-dig.	162
6.4.2.1	Synthesis of Starting Materials	162
6.4.2.2	Synthesis of Products	164
6.4.3	Stoichiometric and Catalytic Pyrone and Isocoumarin Formation via C–H and C–C Bond Formation	166
6.4.3.1	Synthesis of Starting Materials	166
6.4.3.2	Synthesis of Products	185

6.4.5	Computational Studies	208
6.4.6	Crystallographic Studies	208
6.5	Boron Mediated and Catalysed Reduction Reactions: Emerging Catalysts, Novel Processing Techniques and Transfer Hydrogenation	211
6.5.1	Tempering Lewis Acidity of Boranes for General Hydroboration Reactions	211
6.5.1.1	Synthesis of Starting Materials	211
6.5.1.2	Synthesis of Products	216
6.5.2	Novel Processing Methods in the Hydrosilylation of Aldehydes, Ketones and Imines.....	232
6.5.2.1	Synthesis of Products	232
6.5.3	Biologically Inspired Borohydride Sources and Subsequent Transfer Hydrogenation Reactions.....	239
6.5.3.1	Synthesis of Starting Materials	239
6.5.3.2	Synthesis of Products	242
6.5.4	Computational Studies	245
6.5.5	Crystallographic Studies	245
References	247

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List of Abbreviations

4-DMAP	4-(<i>N,N</i> -dimethylamino)pyridine
9-BBN	9-borabicyclo[3.3.1]nonane
ASAP.....	atmospheric solids analysis probe
cod	1,5-cyclooctadiene
COSY	correlation spectroscopy
DFT	density functional theory
DMSO.....	dimethylsulfoxide
EI.....	electron impact
ES.....	electrospray ionisation
FLP	frustrated Lewis pair
HBCat	catecholborane
HBPin	pinacolborane
HOESY.....	heteronuclear Overhauser effect spectroscopy
HMBC.....	heteronuclear multiple bond correlation
HRMS	high resolution mass spectrometry
HSQC	heteronuclear single quantum correlation
IR	infra-red
NBO	natural bond order
NHC	N-heterocyclic carbene
NICS	nucleus independent chemical shift
NMR	nuclear magnetic resonance
ppm	parts per million
RMS	root mean square
THF	tetrahydrofuran
TMS	trimethylsilyl

Chapter 1

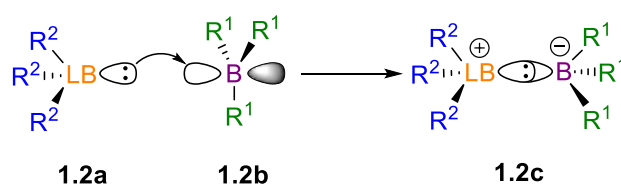
Introduction

1.1 Scope of This Work

As the implementation of boron Lewis acids has exploded over the past few decades, new avenues of reactivity that were previously thought to be unobtainable have become accessible to the synthetic chemist. The following work described in this thesis highlights this fact through the reactions of Lewis acidic boranes and borocations in various transformations such as electrophilic cyclisations, carboborations, haloborations as well as reduction of unsaturated substrates. **Chapter 1** gives an introduction to boranes and borocations as Lewis acids including their synthesis and reactivity. **Chapter 2** shows the rearrangement reactions of allenyl ketones and esters when exposed to the Lewis acid *tris*(pentafluorophenyl) borane. These same reagents are then subjected to frustrated Lewis pair chemistry with the heterocyclic products being elucidated and studied. **Chapter 3** outlines further application of the propargyl rearrangement mechanism discovered within the Melen group previously. Various homo- and hetero-leptic boranes as well as borocations are used in regioselective functional group transfer of a number of propargyl esters, amides, carbamates and carbonates. **Chapter 4** targets the application of *p*-block Lewis acids in the cyclisation of alkynyl esters and carboxylic acids *via* π -activation. Dialkynyl systems are then explored using two different Lewis acids of differing chemical hardness. Finally, **Chapter 5** focuses on boron mediated and catalysed reduction chemistry across three main themes; attenuating the Lewis acidity at boron through aryl group substitution to improve reactivity over perfluorinated counterparts; the use of novel processing technologies in hydrosilylation reactions and comparisons to batch-type reactions; the use of biologically inspired hydride sources as potential borohydride precursors as well as their applications in boron mediated transfer hydrogenation reactions.

1.2 Background

The concept of Lewis acidity arose in 1923 in opposition to the Brønsted-Lowry definition of the time which stated that acids and bases are proton acceptors and donors respectively. Lewis proposed an alternative definition whereby the movement of a lone pair of electrons describes their basicity and acidity with a Lewis base acting as a lone pair donor (**1.2a**) and a Lewis acid acting as a lone pair acceptor (**1.2b**, Scheme 1.1).^[1] Using this parlance, Brønsted-Lowry and Lewis bases are in essence the same, with only the definition of the Lewis acidic component changing. This theory may then be divided further into their hard and soft definitions. For instance, hard Lewis acids and bases tend to have small atomic radii with high charge density. This results in low polarisability leading to predominantly ionic-type bonding. Conversely, softer Lewis acids and bases tend to have lower oxidation states and charge densities with larger atomic radii and are therefore more polarisable giving rise to predominantly covalent-type bonding. This in turn explains why hard acids tend to bind to hard bases and conversely, soft acids tend to bind to soft bases.



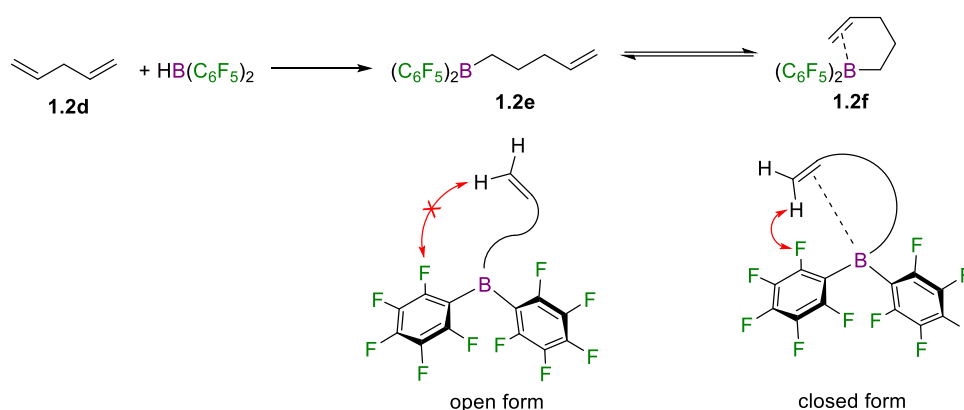
Scheme 1.1: General reactivity of boranes with Lewis bases.

Table 1.1: Atomic characteristic according to hard soft acid base (HSAB) theory

Characteristic	Hard	Soft
Polarisability	low	high
Atomic radii	small	large
Charge density	high	low
Affinity	ionic	covalent

As the vast majority of the following work concerns the implementation of highly electrophilic boron Lewis acids in various organic transformations, the Lewis acidity of such compounds is paramount to their reactivity. Indeed, the reactivity of these electron deficient group 13 Lewis acids relies on the availability of a vacant p_z orbital on boron to accept a lone pair of electrons from a Lewis base (Scheme 1.1). With regard to softer Lewis basic centres, specifically alkenes and alkynes, it is proposed that an initial encounter complex is formed between the π -electron rich multiple bond

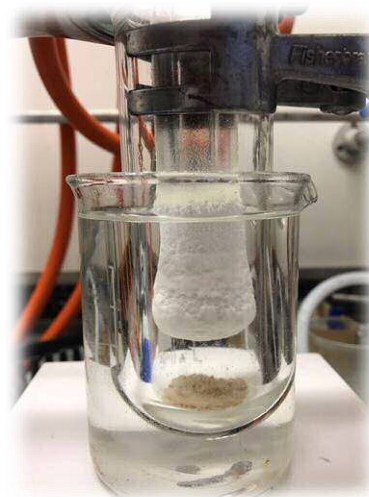
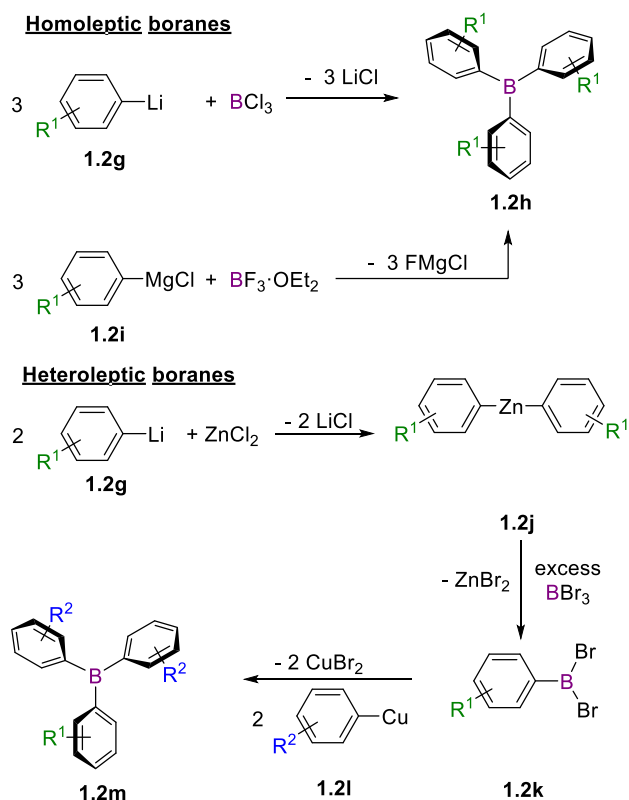
and the borane. This hypothesis is supported experimentally by Stephan *et al.* whereby a borane tethered alkene **1.2e** is synthesised by exposing Piers' borane to 1,4-pentadiene **1.2d** with the reaction coordinate being monitored *via* low temperature $^1\text{H}\{^{19}\text{F}\}$ HOESY NMR spectroscopy.^[2] Using this technique, significant through space cross-relaxation between the olefinic protons and the *ortho*-fluorine atoms of $\text{B}(\text{C}_6\text{F}_5)_2$ was seen indicating a 'closed' form of alkenyl borane **1.2f** (Scheme 1.2). These cross-signals in the 2D NMR spectrum disappeared upon heating to ambient temperature as the small dissociation energy of the van der Waals encounter complex was overcome. The same effect was observed upon addition of acetonitrile as the favourable nitrogen-boron adduct is formed preferentially over alkene coordination. These experimental findings agree with theoretical work by Guo and Li who also found that a similar transitional van der Waals complex is formed between ethylene and $\text{B}(\text{C}_6\text{F}_5)_3$ before nucleophilic attack by phosphorus in an FLP reaction.^[3]



Scheme 1.2: Depiction of closed (**1.2e**) and open (**1.2f**) forms in the detection of van der Waals interactions *via* HOESY.

With regard to their synthesis, several paths to generate trivalent boranes **1.2h** exist for example; boron trihalides may undergo salt metathesis reactions *via* either a Grignard^[4] or organolithium^[5] reagent (**1.2g** and **1.2i** respectively) to form the homoleptic borane with elimination of either LiX or MgX_2 (Scheme 1.3, top). Sublimation of the product under reduced pressure and elevated temperatures is a convenient method for purification of broad variety of perfluorinated aryl boranes such as $\text{B}(\text{C}_6\text{F}_5)_3$ (Scheme 1.3, inset). Recent work by Ashley and Wildgoose *et al.* used a similar method in pursuit of heteroleptic boranes whereby the diarylated zinc reagent **1.2j** (formed *via* salt metathesis) was then reacted with excess boron tribromide to yield the mono-arylated borane **1.2k**. Further reaction with an arylated copper reagent **1.2l** garners the requisite heteroleptic borane with a general structure similar to that of **1.2m** (Scheme 1.3, bottom). While syntheses to similar heteroleptic boranes are

laborious, the final yield was remarkably good at 81%, paving the way for further derivatisation using a similar method.^[6]



Scheme 1.3: Salt metathesis routes to homo- and hetero-leptic boranes. Inset shows the sublimation of $\text{B}(\text{C}_6\text{F}_5)_3$.

Other common synthetic methodologies involve the use of routes such as the hydroboration of alkenes and alkynes in the analogous reaction seen earlier in Scheme 1.2. Some of the more prominent borane reagents used in recent years such as those from Erker^[7] and Du^[8] *inter alia*^[9] have used this technique to garner highly electrophilic heteroleptic boranes for use in a plethora of areas of synthetic chemistry such as small molecule activation as well as highly important enantioselective transformations using unsaturated chiral backbones.

Following on from electrophilic boranes, borocations have seen great promise over recent years with their implementation in catalysis seeing marked improvements since the first structural example of a boronium cation was revealed by Parry *et al.*^[10] Koelle and Nöth provide an in-depth review of structural aspects of borocations which summarise the three types of borocation; the two-coordinate borinium, the three-coordinate borenium and the four-coordinate boronium.^[11] In terms of reactivity, the *sp* hybridised borinium cation is the most reactive, featuring two X-type ligands leaving two empty *p*-orbitals for bonding. These tend to be highly unstable, requiring

electronically stabilising π -donors such as amines and significantly bulky ligands to sterically protect the vacant orbitals at the boron centre (**1.2n–o**, Figure 1.1).^[12] On the other end of the spectrum exists the boronium cations featuring sp^3 hybridised boron centre with the general formula of $[BX_2L_2]^+$. In this case, the boron centre still features a formal positive charge however, it is coordinatively saturated (**1.2r–s**, Figure 1.1). The increase in stability over the borinium cation is mitigated by a partial quenching of reactivity due to the two L-type donors. Nevertheless, they are still common motifs in borylation chemistry, often being described as ‘masked boroniums’ on account of a weakly bound ligand in the fourth coordination site whose lability opens up the boron centre toward reaction.^[13] A compromise between the two extremes of the borinium and boronium is possible through the use of boronium cations, a three coordinate borocation with the general structure $[BX_2L]^+$ (**1.2p–q**, Figure 1.1).^[14] These offer a highly Lewis acidic boron centre as a result of the formal positive charge, as well as the availability of the vacant p_z orbital on boron.

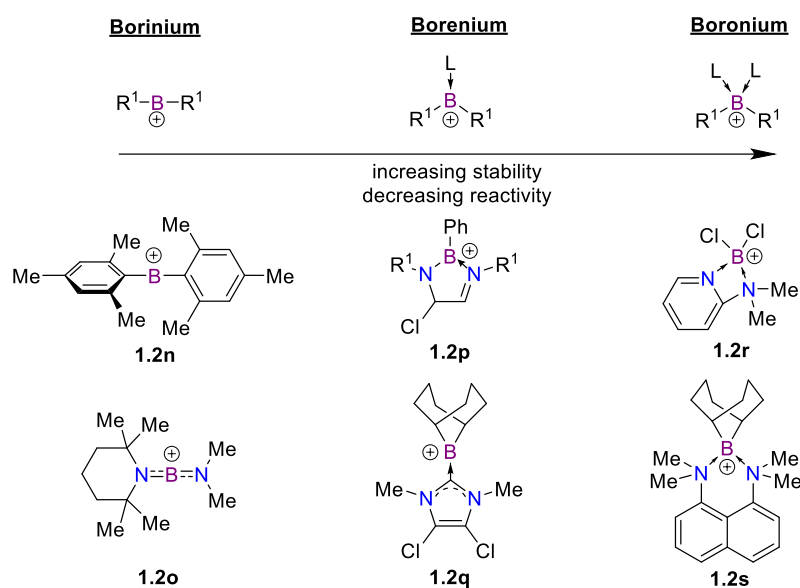


Figure 1.1: Trend in borocation reactivity and select examples.

The use of boranes in synthetic chemistry has been a staple for many decades now, with a small selection being shown in Figure 1.2. To expand, a vast range of reactions are possible using boron reagents with aryl and vinyl boranes proving to be powerful precursors for carbon-carbon bond formation through the Suzuki-Miyaura cross-coupling reaction.^[15] This transformation is of such importance that the 2010 Nobel Prize in Chemistry was awarded to the pioneers for their contributions to organic synthesis, highlighting the influence that boron reagents have in synthetic chemistry. Similar reactivity of aryl boronic acids was revealed in the Chan-Lam

cross-coupling using a copper (II) acetate catalyst to form oxygen or nitrogen bridged diaryl systems under aerobic conditions.^[16] Allylboron reagents also have a prominent position in allylation reactions, sharing this mantle with other famous main group compounds such as allylstannanes as well as metal derivatives, for example organochromium,^[17] zinc^[18] and indium compounds.^[19] This reaction is particularly useful in the installation of allyl alcohol derivatives, with a surprising amount of molecular complexity being possible using synthetically accessible boron reagents.^[20] The bulky Lewis acid $B(C_6F_5)_3$ has also been used industrially as a co-catalyst in the Ziegler-Natta polymerisation of alkenes. In this case, the borane is used as an abstraction agent to remove a methyl group from the zirconium centre to leave a vacant site at the metal. This is then ready for alkene coordination and subsequent propagation to generate the requisite polymer. More pertinent to the work outlined within this thesis, trivalent boranes have been recently adopted to great effect in carbo- halo- and hydroborations which are explored in-depth throughout this work. Therefore, the exploitation of commercially available or readily synthesisable boranes in new reactivity is of utmost importance to the scientific community. To that end, the utilisation of these highly reactive electron-deficient group 13 reagents for use in new synthetic methodologies such as carboborations, cyclisations, haloborations, hydroboration, hydrosilylations and hydrogenations comprise the major focus of this thesis (Chapters 2–5).

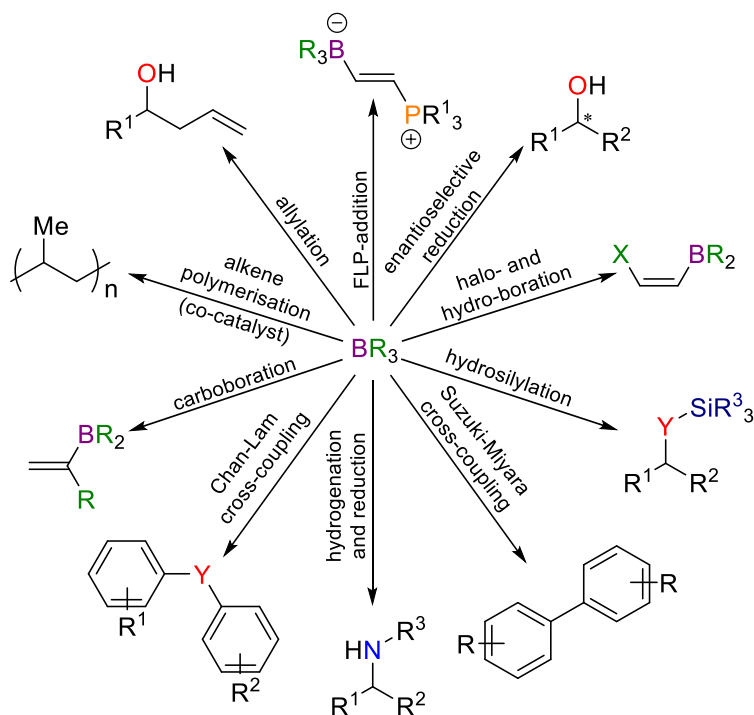


Figure 1.2: Selection of boron mediated or catalysed reactions.

Chapter 2

Activation of Allenyl Ketones and Esters using Cooperative Lewis Pairs and Boron Lewis Acids

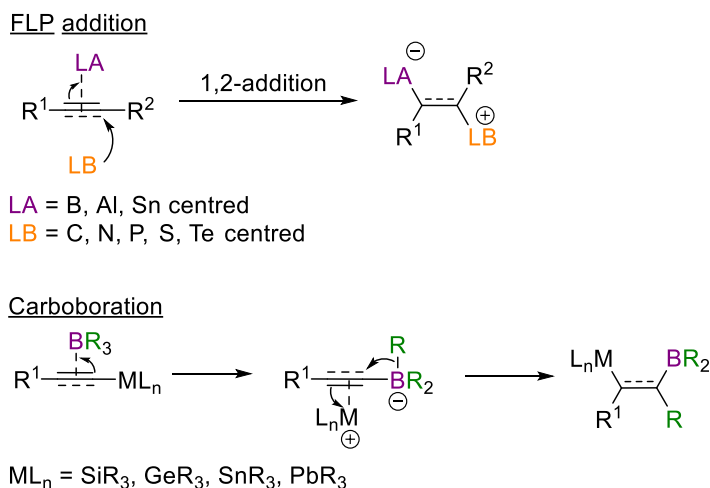
Publications from this work

1. R. L. Melen,* L. C. Wilkins, B. M. Kariuki, H. Wadepl, L. H. Gade, A. S. K. Hashmi, D. W. Stephan, M. M. Hansmann,* “Diverging Pathways in the Activation of Allenes with Lewis Acids and Bases: Addition, 1,2-Carboboration and Cyclization”, *Organometallics*, **2015**, *34*, 4127.

2.1 Introduction

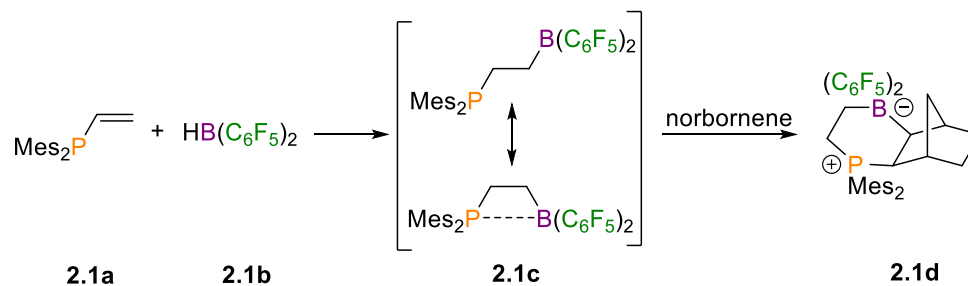
Two main reactions are discussed within the chapter; frustrated Lewis pair-type chemistry and 1,n-carboborations. Regarding the former, frustrated Lewis pair chemistry has seen an exponential increase in interest since the initial discovery by Stephan *et al.* in 2006.^[9c, 9e, 21] As discussed earlier, the combination of a sterically encumbered Lewis acid and base leads to unquenched reactivity. This ‘frustrated’ reactivity has seen particular interest in the activation of small molecule such as N₂O, SO₂, CO₂, CO and H₂ with molecular hydrogen perhaps being one of the most synthetically, and industrially useful.^[9g] More pertinent to this work though, the application of an FLP system to unsaturated carbon-carbon frameworks, leads to a 1,2-addition reaction across the double- or triple-bond. This has been shown with a variety of Lewis acid/base combinations such as boranes, alanes and stannanes as the Lewis acid, with amines, phosphines and sulfides amongst others being used as the base (Scheme 2.1, top).^[9d, 22]

The activation of carbon-element double bonds (C = X where X = N, O) with main group compounds has been extensively pursued in a variety of reduction reactions such as hydrosilylations,^[23] hydroborations^[24] and hydrogenations^[9a, 25] with the activation of carbon-carbon double bonds being slightly less well explored due to the inherent lower polarity compared with the heteroatom congeners. In this context, one of the earlier examples of metal-free main group reactivity with alkenes was in the synthesis of intramolecular FLPs by Erker.^[7a, 7c] It was shown that the reaction of dimesitylvinylphosphine (**2.1a**) with Piers’ borane HB(C₆F₅)₂ (**2.1b**) proceeded to yield the selective anti-Markovnikov product as the ethylene-bridged B/P frustrated Lewis pair **2.1c**.



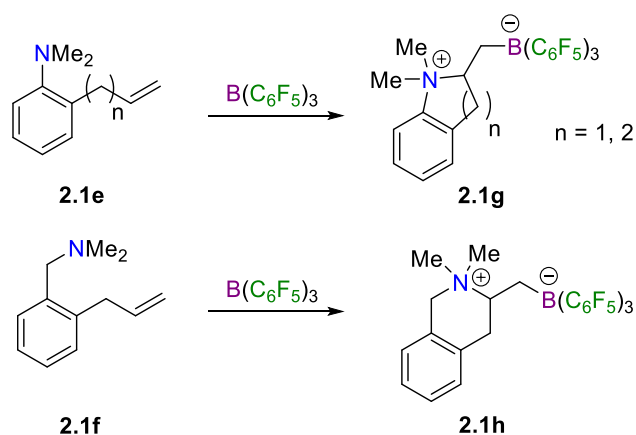
Scheme 2.1: Activation of carbon-carbon multiple bonds by FLPs (top) boranes (bottom).

This has seen numerous applications as an effective FLP catalyst in a number of reactions such as small molecule activation, but also as an alkene activator itself. When exposed to norbornene a formal 1,2-addition takes place to garner the *exo*-2,3-adduct **2.1d** in 72% yield (Scheme 2.2). Other work by Wang *et al.* showed how Piers' borane can also readily undergo a reduction reaction of an 'unactivated' olefin to the alkylborane which can then participate in subsequent hydrogenolysis to furnish the requisite alkane regenerating the Piers' borane in a catalytic fashion.^[26]

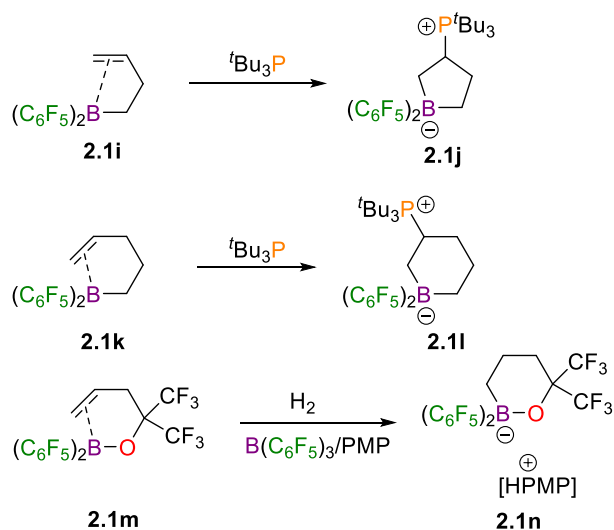


Scheme 2.2: Hydroboration of a vinylphosphine to form an intramolecular FLP with subsequent alkene activation.

Some examples exist of borylation reactions of alkenes however, many incorporate early transition metals such as copper, nickel or a bimetallic Cu/Pd system to yield the alkyl boronate esters.^[27] To counter this trend, Erker and Stephan have been at the forefront of the movement to utilise metal-free routes to activate alkenes such as the cycloamination of *o*-allyl dimethylaniline derivatives **2.1e–f** to yield the zwitterionic indoline and quinoline derivatives **2.1g–h** (Scheme 2.3).^[28]

Scheme 2.3: Cycloamination of *o*-allyl anilines using $B(C_6F_5)_3$.

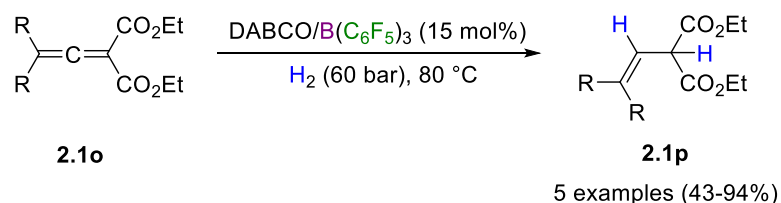
This is similar in nature to further research conducted by Stephan *et al.* whereby various boranes with pendant olefinic units (**2.1i**, **2.1k**) undergo an FLP-1,2-addition reaction upon exposure to the bulky Lewis base P^tBu_3 to generate either the zwitterionic 5- or 6-membered *B*-heterocycles **2.1j** and **2.1l** respectively (Scheme 2.4). In addition, the combination of the bulky amine base pentamethylpiperidine (PMP) with the alkoxyborane **2.1m** furnished a similar 6-membered heterocyclic ring, this time with the incorporation of oxygen to generate the ammonium borate salt **2.1n** (Scheme 2.4).^[29] Similar examples exist using 1,3-dienes,^[30] 1,3-enynes or 1,3-diynes also.^[31]



Scheme 2.4: Cyclisation of allylboranes by FLP-1,2-addition and hydrogenation.

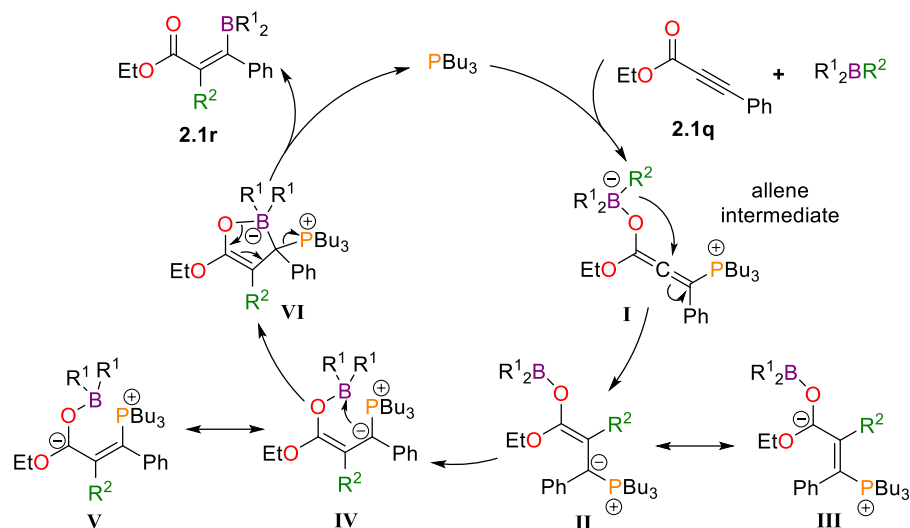
While alkynes, and to a lesser extent alkenes, have received the majority of the attention, there is a surprising lack of interest in the literature regarding the reactivity of allenes toward main group compounds. With regard to this, a few examples exist

such as the hydrostannation of various alkyl allenes to yield the vinyl tin reagents in relatively good yields, however, *E/Z* selectivity of the resulting alkene was poor ranging from 1:99 to 42:58.^[32] Subsequent work by Alcarazo observed the FLP hydrogenation of electron deficient allenyl malonates **2.1o** using various amine and phosphine bases alongside B(C₆F₅)₃. Pressurising the system with H₂ (60 bar) showed hydrogenation of the olefinic unit proximal to the malonate functional group.^[33] Expanding the substrate scope with various electron rich and poor groups appended to the terminal carbon of the allene whilst using DABCO as the Lewis base garnered the reduced products **2.1p** in good to excellent yields however, long reaction times of 72 hours were noted (Scheme 2.5). Interestingly, the exposure of these allenes to the FLP system in the absence of hydrogen was not trialed.



Scheme 2.5: Hydrogenation of allenyl malonates using FLPs.

Remarkably, carboborations of alkenes appear to be seldom found in the literature whilst their alkyne counterparts have found endless success in a variety of 1,*n*-carboboration reactions. The topic of carboboration of alkynes is extensively covered during the course of this work (see Chapters 3 and 4) therefore extensive discussion of alkyne activation can be found in these sections. Nevertheless there was an interesting report from Ohmiya and Sawamura *et al.* who demonstrated an elegant method to carry out a 1,2-*trans*-carboboration of ethyl 3-phenylpropiolate **2.1q** *via* an allenyl phosphonium borate intermediate **I** (Scheme 2.6).^[34] This reaction proceeds *via* a 1,4-alkyl migration to the α -carbon to yield the resonance structures of the allylide intermediate **II** and **III**. This then undergoes a conformational change to **IV–V** with concomitant ring-closing to form the cyclic phosphonium borate **VI**. Subsequent ring-opening with loss of the phosphine fragment generates the *trans*-carboboration product **2.1r** as a result of molecular templating from the carbonyl oxygen.

Scheme 2.6: 1,2-*trans*-carbo-boration of ethylpropiolates *via* allene intermediates.

2.1.1 Aims of This Chapter

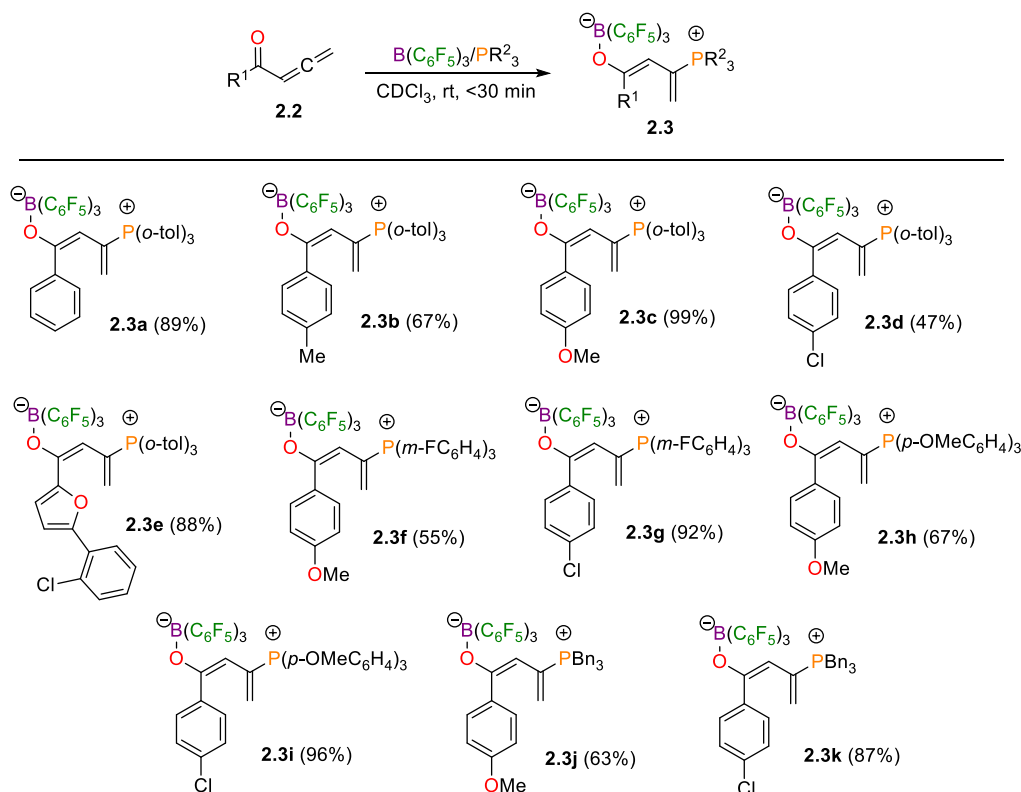
The reaction of allenes with FLPs and boranes to yield various borylated products is notably scarce in the literature therefore investigations into these systems are incredibly desirable. Additionally, given the high reactivity of these systems it is anticipated that interesting reactivity should result from this work. Herein, the reactivity of these allene systems toward Lewis acids and bases will be probed with an examination of the reaction pathway taking place *via* spectroscopic, solid-state and computational analyses.

2.2 Results and Discussion

2.2.1 Cooperative Lewis Pair Reactions with Allenes

Initial investigations pursued the addition of sterically demanding Lewis acids and bases to the various allenyl ketone reagents **2.2** with the preliminary expectation that a simple 1,2-*trans*-addition across the distal olefinic unit would occur, similar to that witnessed previously with other unsaturated carbon-carbon frameworks as discussed above. The allenyl ketones **2.2** were reacted with a combination of the Lewis acid $B(C_6F_3)_3$ and various tertiary phosphines ($P(o\text{-tol})_3$; $P(m\text{-FC}_6\text{H}_4)_3$; $P(p\text{-OMeC}_6\text{H}_4)_3$; PBn_3) in a 1:1:1 ratio. Once mixed, the reaction progress was assessed *via in situ* NMR spectroscopy (1H , ^{19}F , ^{11}B , ^{13}C , ^{31}P) which revealed an almost instantaneous and quantitative conversion to a new product **2.3** which was determined to be the

product of a 1,4-addition (Scheme 2.7). The recovered yields were of the crystalline products hence lower than the NMR spectroscopic conversions. Diagnostically, the ^{11}B NMR spectra invariably all displayed resonances at *ca.* $\delta = -4.0$ ppm which is synonymous with the formation of an oxygen bound borate moiety.^[35]



Scheme 2.7: Reactions of allenyl ketones **2.2** with FLPs to give **2.3**.

As expected, all ^{19}F NMR spectra exhibited three multiplet signals in a 2:1:2 ratio arising from the *ortho* ($\delta = -132.7$ to -133.3 ppm), *para* ($\delta = -160.1$ to -161.2 ppm) and *meta* ($\delta = -164.9$ to -165.9 ppm) fluorine atoms of the perfluorophenyl rings of the borane. In addition, the ^{19}F NMR spectra of **2.3f** and **2.3g** showed resonances at $\delta = -105.5$ and -105.2 ppm respectively as a result of the *m*-fluorine atoms on the phosphine derivative that was used. The singlet resonance observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra varied according to the phosphine that was utilised in the reaction: for **2.3a–e** and **2.3f–g** where $\text{P}(\text{o-tol})_3$ and $\text{P}(\text{m-FC}_6\text{H}_5)_3$ were used respectively, the chemical shift was observed at *ca.* $\delta = 23$ ppm. Similarly, for **2.3h–i** where $\text{P}(\text{p-OMeC}_6\text{H}_5)_3$ was used, a resonance at $\delta = 22$ ppm was seen and finally for **2.3j–k** using PBn_3 , a singlet shift was observed at *ca.* $\delta = 25$ ppm.

For many of these addition products, single crystals could be obtained directly from the reaction mixture after storing at ambient temperature for 2–8 h. Single crystal X-ray diffraction measurements were performed on the crystals **2.3a–c**, **2.3f** and **2.3j–**

k which confirmed the molecular structure as the result of a 1,4-addition of the boron to oxygen, and the phosphine to the β -carbon of the allene unit to form the *s-cis* conformer (Figure 2.1). The bond lengths of the solid-state structures are all similar regardless of the ketone substituent and phosphine used (Table 2.1). However, differences do arise between the structures when comparing the dihedral angles $C^1=C^2$ and $C^3=C^4$ subunits.

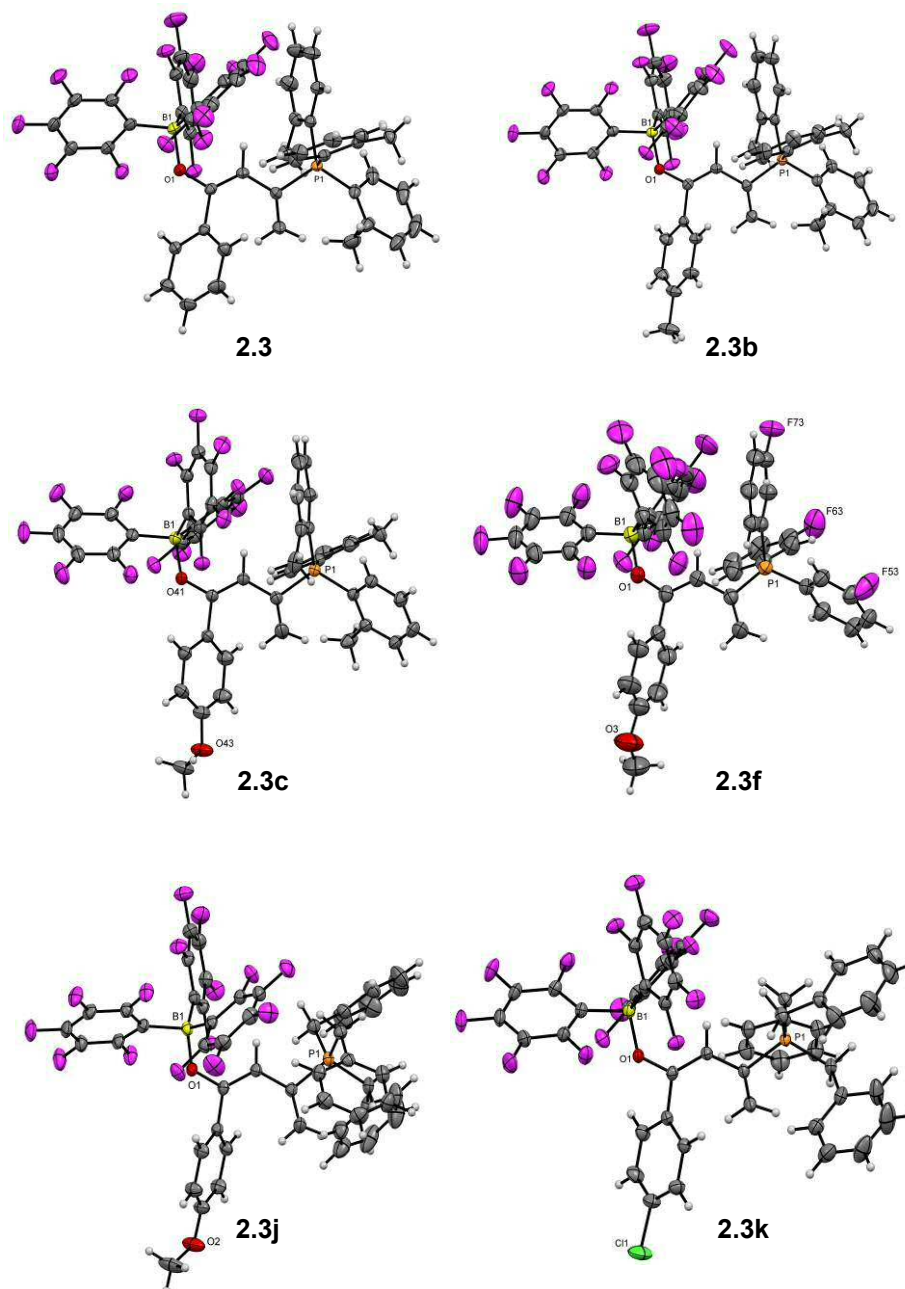
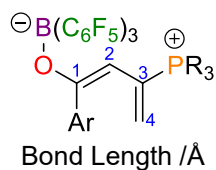


Figure 2.1: Solid-state molecular structures of **2.3a–c**, **2.3f** and **2.3j–k**. C: grey, O: red, B: yellow-green, F: pink, P: orange, Cl: green. Thermal ellipsoids drawn at 50% probability.

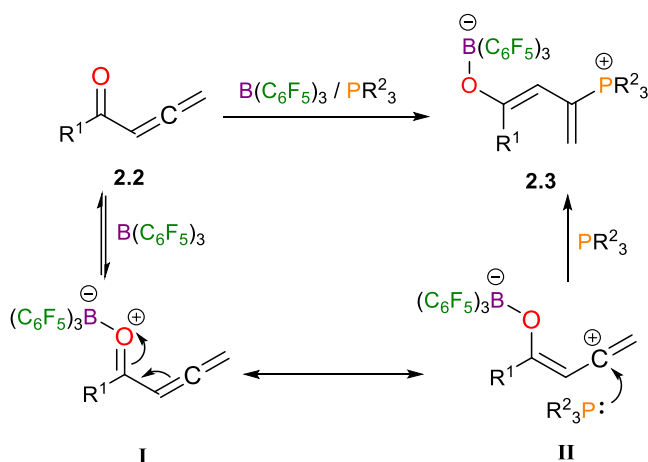
Although a conjugated π -system is present, the two olefinic fragments are out of plane by anywhere between $14.2(4)^\circ$ and $29.5(3)^\circ$ thus reducing effective orbital overlap and reducing the extent of delocalisation across the system. Further to this, the R^1 phenyl substituent appears to rotate out of the diene plane in the solid-state, further hindering the delocalisation of the conjugated π -system which is thought to be a combination of steric obstruction as well as an artifact of crystal packing.

Table 2.1: Experimental bond lengths in **2.3a–c**, **2.3f** and **2.3j–k**.

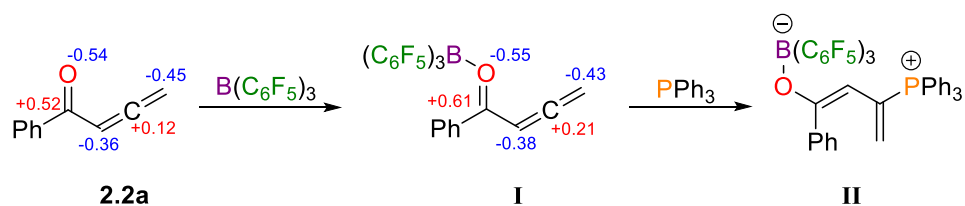


Bond	2.3a	2.3b	2.3c	2.3f	2.3j	2.3k
C ¹ –C ²	1.347(2)	1.352(4)	1.356(2)	1.356(3)	1.359(3)	1.353(2)
C ² –C ³	1.465(3)	1.468(4)	1.464(2)	1.460(3)	1.463(3)	1.466(2)
C ³ –C ⁴	1.337(3)	1.332(5)	1.340(2)	1.339(3)	1.337(3)	1.335(2)
C ¹ –O	1.339(2)	1.334(4)	1.336(2)	1.337(3)	1.339(2)	1.335(2)
O–B	1.495(3)	1.493(4)	1.489(2)	1.499(3)	1.490(2)	1.493(2)
C ³ –P	1.818(2)	1.825(3)	1.811(1)	1.811(2)	1.800(2)	1.804(1)

Mechanistically it is proposed that the reaction is initiated by the formation of the hard Lewis acid/base adduct between the borane and carbonyl oxygen *via* σ -activation. This initial adduct formation is in-keeping with previous reports whereby the borane primarily forms this Lewis adduct however, the relatively facile nature of the B–O bond cleavage enables the borane to activate other functional groups.^[23a, 23b, 36] In this instance however, upon coordination there is a build-up of partial positive charge on the β -carbon of the allene (**I**, Scheme 2.8) allowing subsequent conjugate addition to occur through nucleophilic attack by the external phosphine (**II**, Scheme 2.8) to furnish the diene product **2.3** (Scheme 2.8). Whilst it may be feasible that the phosphine addition may occur reversibly in the absence of the borane, *in situ* NMR spectroscopic studies show no indication of activation on an NMR timescale, signifying that the borane is necessary to isolate the product.

Scheme 2.8: Reactions of allenyl ketones **2.2** with Lewis acid/base pairs.

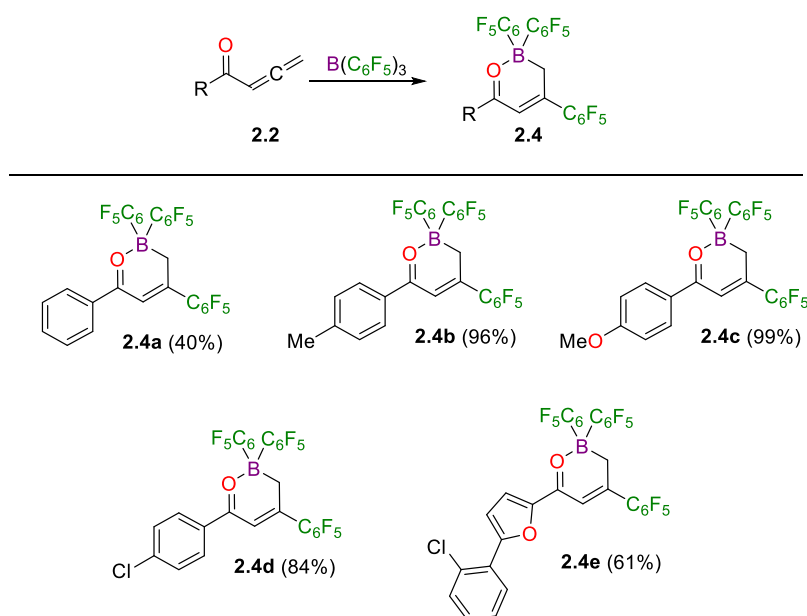
To probe this further, thermodynamic calculations were carried out using the allenyl ketone **2.2a** as a model in the sequential addition of $B(C_6F_5)_3$ then PPh_3 in order to assess the energetics of each reaction step. The enthalpy, entropy and Gibbs energy changes were calculated at 298 K alongside NBO analysis to calculate partial charges on each atom of the allene substrate.^[37] As expected, this supports the experimental findings showing a large increase in positive charge on the β -carbon upon borane addition in **I** from +0.12 to +0.21. Additionally, the thermodynamic data supports this theory showing favourable energetics upon borane binding with a further decrease in ΔG once conjugate addition has taken place (Table 2.2).

Table 2.2: Thermodynamic data and NBO charge distributions (e^-) for the reaction of **2.2a** with $B(C_6F_5)_3$ and PPh_3 using B3LYP/6-311G*+ level of theory.

Compound	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol.K)
2.2a	-1210463	-1210344	0.398505
$B(C_6F_5)_3$	-5799279	-5799045	0.785245
PPh_3	-2720657	-2720496	0.539788
I	-7009704	-7009412	0.977920
II	-9730353	-9729963	1.304974

2.2.2 1,2-Carboration of Allenes using $B(C_6F_5)_3$

Once it was established that allene reagents will react with cooperative Lewis pairs, it was postulated that these reactive functional groups should react directly with the Lewis acidic component on its own. Therefore, the same allenyl ketones (**2.2**) as outlined above in Section 2.2 were subjected to a stoichiometric amount of $B(C_6F_5)_3$. Once again, these reactions were complete within a 30 minute timeframe at room temperature to yield a single product when observed by NMR spectroscopy. The ^{11}B NMR spectra for products **2.4** showed a broad singlet resonance at $\delta = 2$ ppm, consistent with chelating heterocyclic adducts observed in the literature.^[20, 36b, 36d] Perhaps more revealing was the presence of a new set of peaks in the ^{19}F NMR spectra. Two sets of 2:1:2 resonances were present in a 1:2 ratio indicating the presence of two equivalent perfluorophenyl rings and one inequivalent suggesting a carboboration reaction had occurred. With the above information to hand, coupled with the presence of a vinylic proton at $\delta = 7.3$ ppm and an alkyl CH_2 fragment at $\delta = 2.7$ ppm in the 1H NMR spectra, it was anticipated that the reaction undergoes a regioselective formal 1,2-carboration of the terminal olefinic unit of the allene to form the *E*-isomer of the chelating α,β -unsaturated ketone **2.4** (Scheme 2.9).



Scheme 2.9: Reactions of $B(C_6F_5)_3$ with allenyl ketones **2.2** to give **2.4**.

The proposed product was confirmed in the solid-state through X-ray diffraction studies of crystals grown from a saturated toluene/hexane solution stored at -40 °C. Indeed, the structure was that of a formal 1,2-carboration whereby a C_6F_5 has been

installed in the β -position with the boron fragment being located at the γ -position to the carbonyl functionality (Figure 2.2). Metrics are summarised in Table 2.3, showing bond lengths are the same within error for the two structural derivatives.

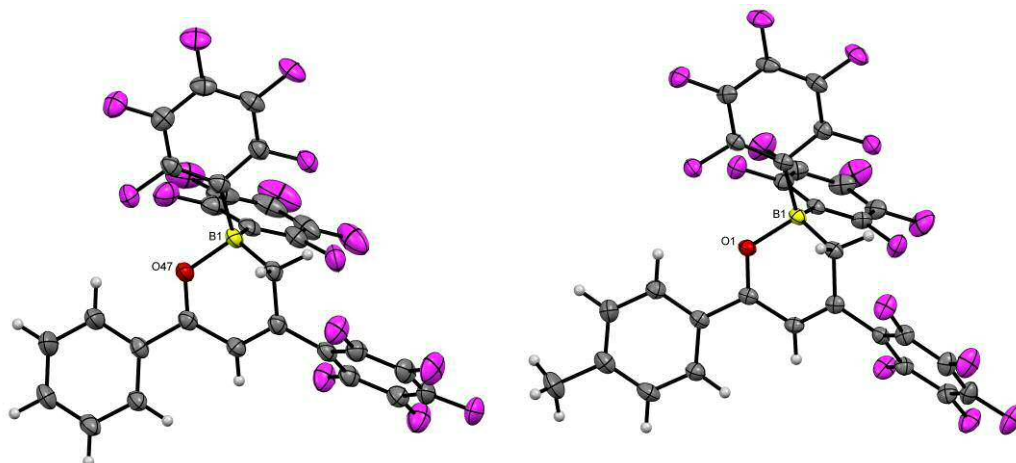
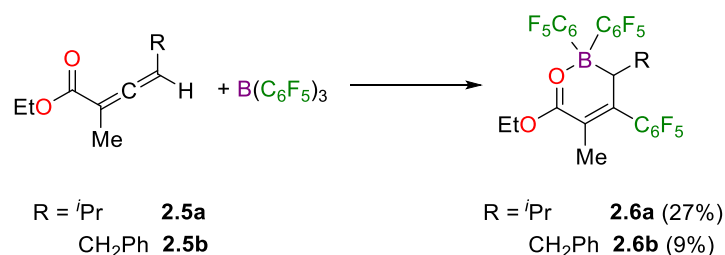


Figure 2.2: Solid-state molecular structures of **2.4a** (left) and **2.4b** (right). C: grey, O: red, B: yellow-green, F: pink. Thermal ellipsoids drawn at 50% probability.

As this chemistry appeared to work well with allenyl ketones, it was posited that allenyl esters would show similar reactivity (Scheme 2.10). Unfortunately, the reaction between $\text{B}(\text{C}_6\text{F}_5)_3$ and the ester derivatives **2.5a–b** did not proceed as smoothly with *in situ* spectroscopic analyses showing an intractable mixture of products. However, a small crop of crystals suitable for X-ray diffraction could be isolated from a scale-up reaction by slow evaporation of either a CH_2Cl_2 /hexane (**2.5a**) or toluene/hexane (**2.5b**) solution to reveal the solid-state structure of **2.6a–b** as the product of a 1,2-carboboration process (Figure 2.3, Table 2.3). As with the allenyl ketones, the isolated structures show σ -activation with a subsequent 1,5- C_6F_5 migration followed by a sigmatropic 1,5-boron migration to form the stable intramolecular 6-membered chelate **2.6**. This was again confirmed by the ^{11}B NMR spectra of the isolated crystals with broad singlet resonances arising at *ca.* $\delta = 4.5$ ppm, again indicative of these intramolecularly coordinated oxaborinine compounds.^[20, 36b, 36d]



Scheme 2.10: Reactions of $\text{B}(\text{C}_6\text{F}_5)_3$ with allenyl esters **2.5**.

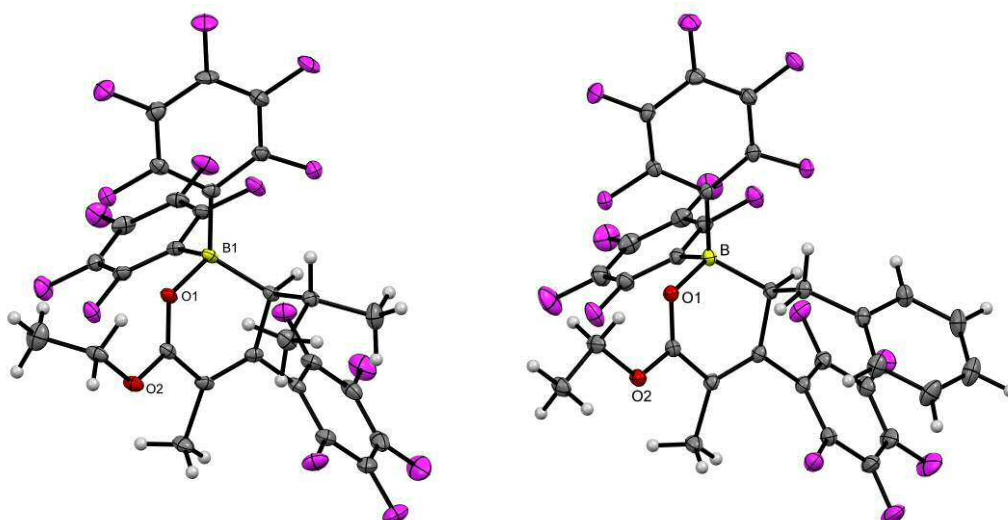
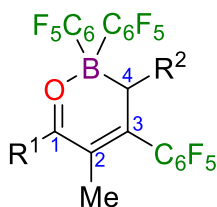


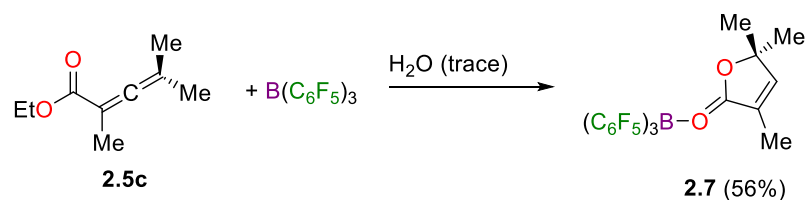
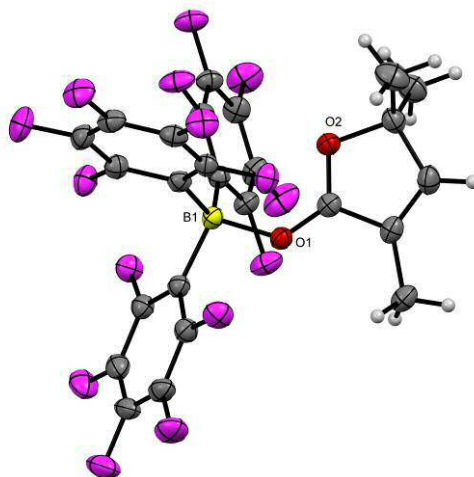
Figure 2.3: Solid-state molecular structures of **2.6a** (left) and **2.6b** (right). C: grey, O: red, B: yellow-green, F: pink. Thermal ellipsoids drawn at 50% probability.

Table 2.3: Experimental bond lengths in **2.4a–b** and **2.6a–b**.

Bond	Bond Length /Å			
	2.4a	2.4b	2.6a	2.6b
C ¹ –C ²	1.437(4)	1.440(3)	1.4636(3)	1.4655(16)
C ² –C ³	1.352(3)	1.355(2)	1.3482(3)	1.3565(16)
C ³ –C ⁴	1.496(3)	1.497(3)	1.5180(3)	1.5235(17)
C ¹ –O	1.268(3)	1.277(2)	1.2557(2)	1.2613(15)
O–B	1.569(3)	1.565(2)	1.5723(3)	1.5660(16)
B–C ⁴	1.604(3)	1.603(3)	1.6148(3)	1.6136(17)

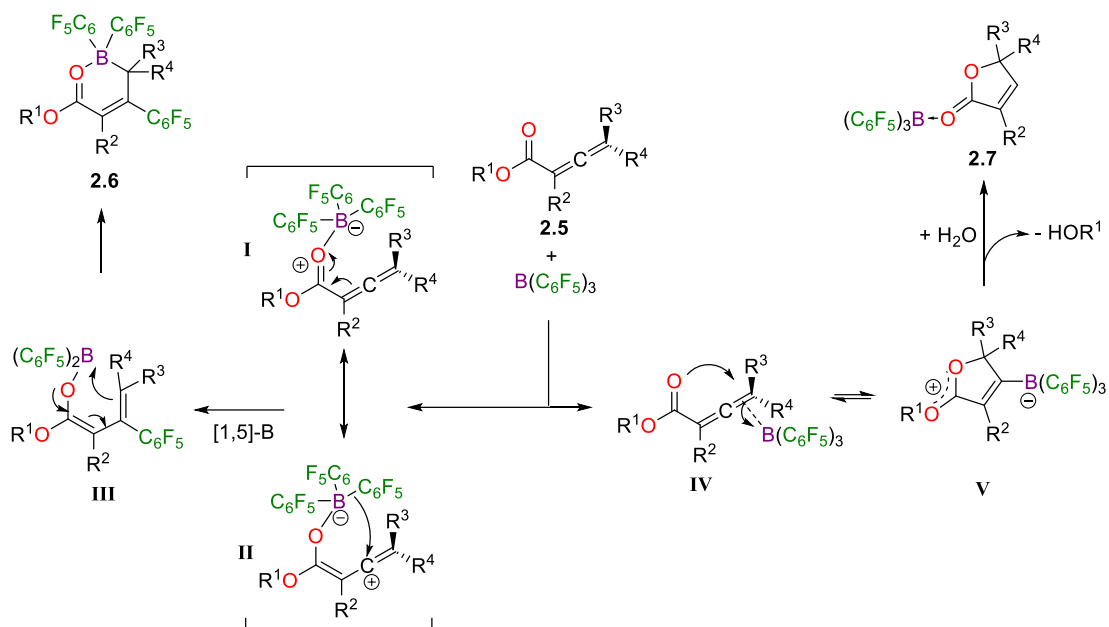


As described earlier, $B(C_6F_5)_3$ has displayed the proclivity to undergo certain π -binding modes instead of the traditional σ -activation mode. This was evident when combining the trimethylated allenyl ketone **2.5c**, in the presence of trace water, which afforded the γ -lactone **2.7** as the product of a *5-endo-trig* cyclisation with borane coordinated to the carbonyl oxygen in a moderately good yield of 56% (Scheme 2.11). This was confirmed *via* X-ray diffraction as seen in Figure 2.4. Of note is the similarity of this reaction to others conducted with coinage and platinum group metals such as gold or palladium, setting an interesting prospect for boranes to act as transition metal mimics.^[38]

Scheme 2.11: Reactions of $\text{B}(\text{C}_6\text{F}_5)_3$ with allenyl ester **2.5c**.Figure 2.4: Solid-state structure of compound **2.7**. C: grey, O: red, B: yellow-green, F: pink. Thermal ellipsoids drawn at 50% probability.

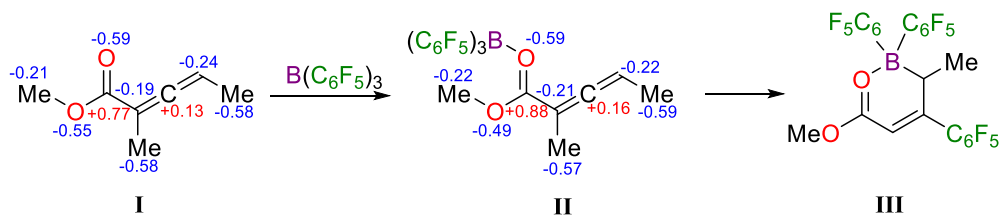
With regard to possible mechanistic pathways, it is understood that these allenyl esters may undergo either a σ -activation mode of the carbonyl oxygen, or π -activation of the distal olefinic fragment with each drastically changing the product which is formed. Whilst no formal η -2-type complex has been isolated showing side-on activation of the π -system, recent analyses indicate that weak van der Waals interactions may exist between the π -bond and the borane (see Scheme 1.2).^[2] This is more evident in the case of the allenyl ketones whereby the inherent polarity of the carbonyl bond is more pronounced, with significantly more positive charge located on the β -carbon. If this is diminished, as is the case with allenyl ester derivatives, then alternative π -activation pathways may predominate. If the σ -activation pathway prevails, then the activation of the β -carbon occurs through the conjugated system (**I** and **II**, Scheme 2.12) allowing a 1,5- C_6F_5 migration to occur followed by the sigmatropic 1,5-boron migration of the intermediate diene unit **III** to the α,β -unsaturated ester **2.6** featuring the chelating O–B motif. Alternatively, if π -activation is invoked (**IV**, Scheme 2.12) then depletion of electron density on the terminal carbon of the allene allows for nucleophilic attack to form the furanium borate intermediate **V**. This may be evidenced in the ^{11}B NMR spectrum where a sharp singlet is observed at $\delta = -16$ ppm.^[39] This step is presumably reversible however, when trace water is

present dealkylation of the ester moiety may occur driving the reaction toward the lactone **2.7** via concurrent protodeboration, similar in fashion to related chemistry of palladium or gold systems through protodemetalation mechanisms.^[38]



Scheme 2.12: Proposed mechanism for σ - vs. π -activation of allenyl esters.

Table 2.4: Thermodynamic data and NBO partial charges (e^-) for the reaction of **I** with $B(C_6F_5)_3$ and its subsequent rearrangement to **III**.



Compound	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol.K)
$B(C_6F_5)_3$	-5799279	-5799045	0.785245
I	-1111010	-1110888	0.410736
II	-6910240	-6909945	0.988575
III	-6910341	-6910056	0.957191

To explore this phenomenon further, representative computational analyses were conducted of the prototypical allenyl ester (**I**, Table 2.4). In this case, the depletion of electron density on the central carbon of the allene unit is far less pronounced upon borane coordination compared to the ketone derivative, increasing from +0.13 to only +0.16 according to NBO partial charge analysis. Thermodynamic data was also calculated revealing that this process is far less thermodynamically favourable than the ketone counterpart with the Gibbs free energy of the cyclised chelate product **III** being essentially iso-energetic to the σ -activated intermediate **II**.

2.3 Conclusions

The application of cooperative Lewis pairs to allenyl ketones results in the 1,4-addition product through O–B coordination and nucleophilic attack of the β -carbon by the phosphine. If a Lewis base is absent from the reaction, then a net 1,2-carboboration pathway prevails through a series of steps; 1) borane coordination to the carbonyl oxygen; 2) 1,5- C_6F_5 migration from boron to the β -carbon and; 3) a sigmatropic 1,5-boron migration to garner the heterocyclic 6-membered allylboron chelate. However, when allenyl esters are used, there are two pathways by which the reaction may proceed. Firstly, σ -activation follows the same pathway as before to yield the 6-membered heterocycles however, in the presence of water the second pathway may proceed *via* π -activation. In this case activation of the distal olefin results in a 1,2-addition followed by dealkylation and protodeboration to reveal the γ -lactone product. The latter reactivity mimics that of π -Lewis acidic late transition metals such as palladium, platinum and gold revealing new applications of boranes in carbon-carbon multiple bond activation, a topic that is discussed in the following chapters.

Chapter 3

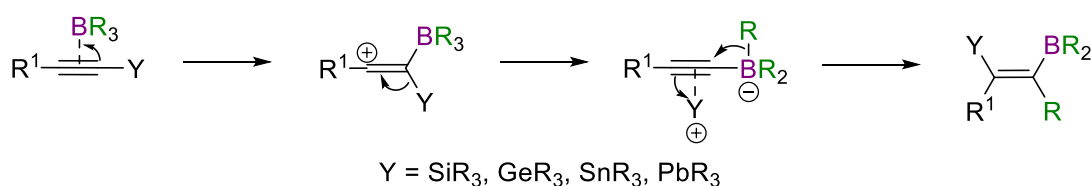
The Propargyl Rearrangement: Cyclisations, 1,1-Carbaborations and 1,3-Haloborations of Homoleptic and Heteroleptic Boranes

Publications from this work

1. L. C. Wilkins, P. Wieneke, P. D. Newman, F. Rominger, A. S. K. Hashmi, M. M. Hansmann*, R. L. Melen,* "Pathways to Functionalized Heterocycles: The Propargyl Rearrangement Using B(C₆F₅)₃", *Organometallics*, **2015**, *34*, 5298.
2. L. C. Wilkins, J. R. Lawson, P. Wieneke, F. Rominger, A. S. K. Hashmi, M. M. Hansmann*, R. L. Melen,* "The Propargyl Rearrangement to Functionalised Allyl- Boron and Borocation Compounds", *Chem. Eur. J.*, **2016**, *22*, 14618.

3.1 Introduction

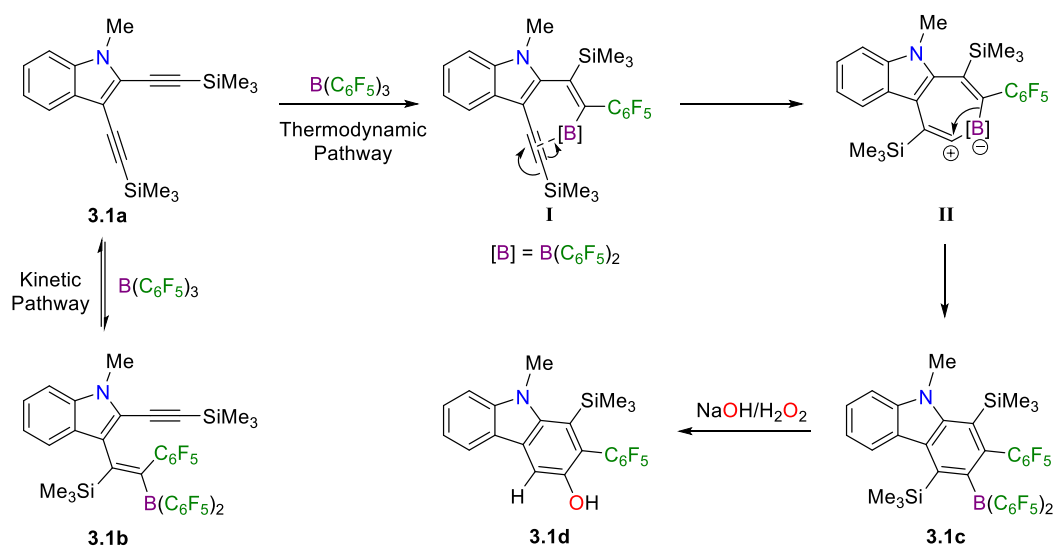
One powerful subset of carbon-element bond forming reactions is the 1,*n*-carbaboration where main group centred reagents have been used extensively with many applications in benzannulations^[40] and cyclisations,^[41] amongst others.^[42] Wrackmeyer's seminal work, which is also briefly described in Chapter 2, describes how an 'activated' alkyne undergoes a 1,1-carbaboration reaction through π -activation of the electron rich carbon-carbon triple bond (Scheme 3.1).^[43]



Scheme 3.1: General carboboration mechanism.

In light of Wrackmeyer's discoveries, Erker *et al.* utilised this powerful method to affect benzannulation reactions through a series of carboboration steps using dialkynyl precursors in conjunction with B(C₆F₅)₃. In this case, a functionalised indole derivative **3.1a**, featuring trimethylsilyl groups in the terminal positions of the alkynes, undergoes a cascade reaction to garner the 6,5,6-tricyclic 14 π Hückel aromatic compound **3.1c**.^[40] This was then extended to thiophene and pyridine backbones to

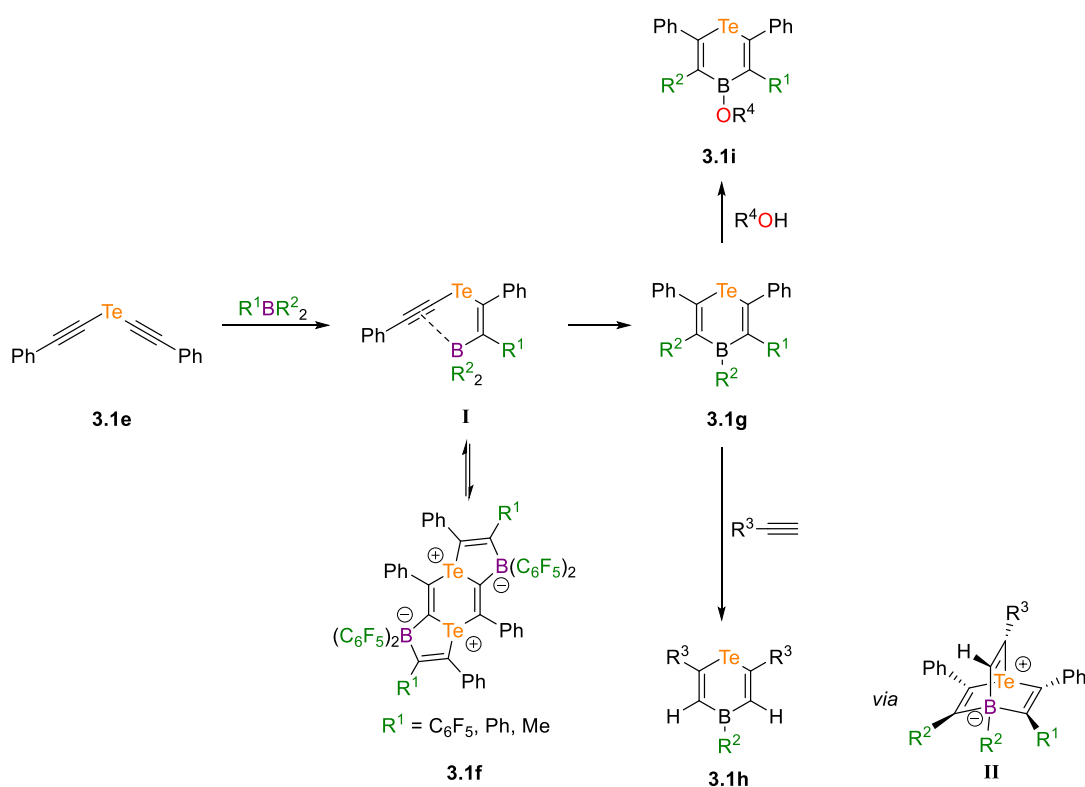
generate the corresponding benzothiophenes and quinoline derivatives. These cyclized products were then subjected to oxidative workup using NaOH/H₂O₂ to remove the boron fragment however, this workup also cleaved the adjacent C–Si bond to give the resultant benzannulation products such as **3.1d** in a modest yield of 52–58% (Scheme 3.2). This reaction is posited to proceed *via* the mono-carbaboration of the alkyne proximal to the heteroatom to give the selective *Z* intermediate **I** (thermodynamic pathway). If the distal alkyne is activated (kinetic pathway), it was seen through the solid-state structure of **3.1b** that the second alkyne activation may not proceed due to the boron centre not being in the vicinity of the second alkyne π -bond. Nevertheless, once the thermodynamic product **I** is formed, a 1,1-alkenylboration reaction from **II** takes place to generate the desired carbazole product **3.1c**.



Scheme 3.2: Benzannulation reaction of diynes using B(C₆F₅)₃.

Other work in this area from Stephan *et al.* used telluroethers in a series of carboboration reactions to produce a range of 1-telluro-4-boracyclohexadienes. In the earliest report, a dialkynyl telluroether **3.1e** was combined with a number of boranes (B(C₆F₅)₃, PhB(C₆F₅)₂ and BPh₃), triggering a double 1,1-carbaboration reminiscent of the work by Erker above.^[44] Following the first 1,1-carbaboration (**I**, Scheme 3.3), it appears as though the reaction can follow one of two pathways; the first pathway is the reversible intermolecular FLP addition to generate an extensively conjugated dizwitterion **3.1f**. However, this is in equilibrium and thus collapses back to the native carboboration intermediate **I** that undergoes a second irreversible 1,1-carbaboration furnishing the 6-membered borotellurocycle **3.1g** which were all confirmed spectroscopically as well as in the solid-state. Interestingly, it was shown that when

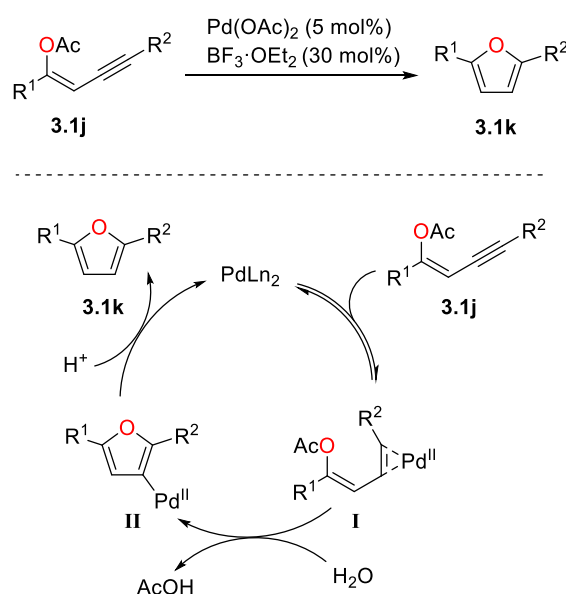
tetrasubstituted olefinic substituents are incorporated, a substitution reaction may occur upon addition of a terminal alkyne such as phenylacetylene (Scheme 3.3). Due to the increased steric crowding afforded by the quaternisation and the substituent adjacent to boron (**II**, Scheme 3.3), the internal alkynyl equivalent is expelled to garner the less hindered heterocycle **3.1h**.^[45] Conversely, if an alcohol is applied to the intermediate **3.1g** then a substitution reaction ensues that affords a variety of unsymmetrically substituted tellurium boron heterocycles **3.1i**.^[46] Further to this, using monofunctionalised telluroethers gave the mono-carbaboration products which are then susceptible to further FLP-type addition reaction toward alkynes to give the zwitterionic borotellurocycle.^[22a] This work has particularly interesting prospects as tellurium-doped heterocycles possess interesting photophysical properties^[47] and photo-reactivity^[48] as well as applications in optoelectronics^[49] and photodynamic therapy.^[50]



Scheme 3.3: Formation of various boron tellurium heterocycles *via* 1,1-carbaboration.

With regard to the target cyclisation products, specifically oxazoles, oxazolines and dioxaborinines, the synthesis of such functionalisable heterocycles are key in various areas of chemistry with application in a diverse range of fields such as pharmaceuticals,^[51] coordination chemistry^[52] as well as protecting groups.^[53] With specific focus on their use in pharmaceuticals, searching for procedures that negate

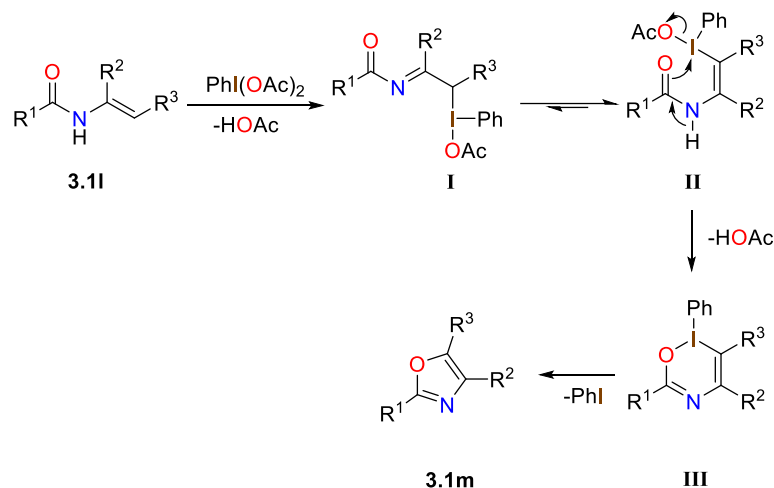
the use of heavy metals and replacing them with less toxic, more abundant main group reagents is of particular interest. Traditionally, many of the methods used to undergo similar cyclisations to form oxazoles, furans and lactones use late transition metals such as gold,^[54] palladium^[55] or silver^[56] as soft π -Lewis acids. One example of many is the use of a Pd (II) catalyst in work by Liu *et al.* whereby an enynyl acetate reagent (**3.1j**) undergoes a 5-*endo-dig* cyclisation reaction to generate the 2,5-substituted furans **3.1k** through a π -activation process (Scheme 3.4). In this case, the formation of an η -2 metal complex (**I**, Scheme 3.4) activates the alkyne toward nucleophilic attack by the acetate moiety. This in turn releases the palladium substituted furan (**II**, Scheme 3.4) through dealkylation of the acetate group to form acetic acid with concomitant protodemetalation to give the substituted furan **3.1k**. Similar work in their group previously found that the same reaction could be conducted using elemental iodine to form the iodonium electrophile *in situ* resulting in the substituted furans, thus precluding the use of expensive transition metal catalysts.^[57]



Scheme 3.4: Palladium catalysed intramolecular cyclisation to form furan derivatives.

This original discovery using main group elements showcases how many transformations that are carried out by transition metals may also be effectively carried out using more abundant and potentially less toxic *p*-block elements. With the revelation that main group compounds are useful in carbon-carbon triple bond activation, contrary to traditional thought, a number of other procedures having been put forward using elemental iodine and hypervalent iodine (III) reagents.^[58]

Specifically, work conducted by Du and Zhao *et al.* utilised the Lewis acidity of phenyliodine diacetate, $\text{PhI}(\text{OAc})_2$, in the oxidative intramolecular cyclisation of enamides (**3.1l**) to form the target oxazoles **3.1m** (Scheme 3.5).^[59] This proceeds through a number of complex rearrangement steps with one proposed pathway proceeding through alkene activation by the hypervalent iodine with subsequent isomerisation (**I**, Scheme 3.5). This then undergoes substitution at iodine to give the iodine-containing heterocycle (**III**, Scheme 3.5) followed by reductive elimination of iodobenzene to form the new carbon-oxygen bond of the oxazole.

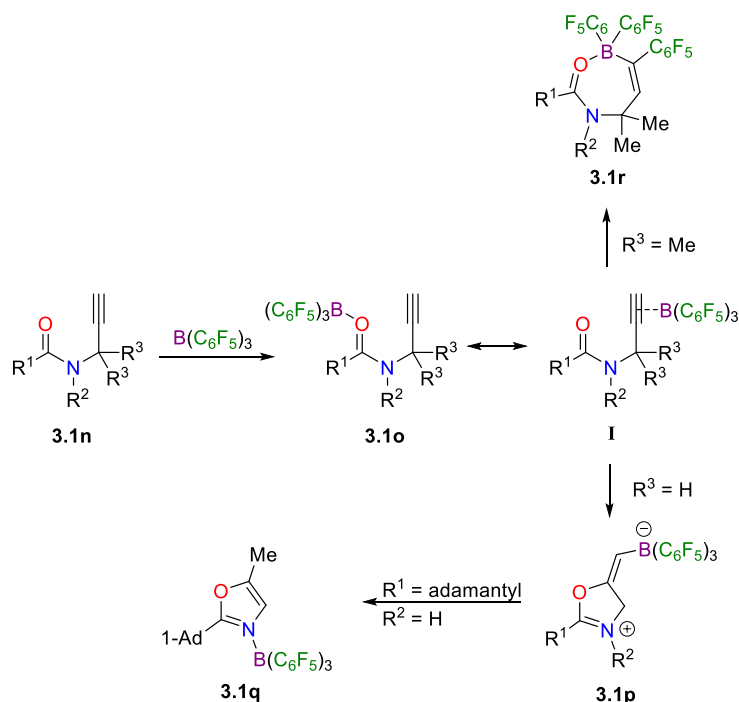


Scheme 3.5: Hypervalent iodine mediated cyclisation of enamides to form oxazoles.

Recent work within the Melen group combined both these practices of cyclisations and 1,1-carbaborations utilising main group compounds in the formation of a number of oxazoles, oxazoliums and dioxoliums through the use of boron Lewis acids. Some of the earlier research in the area used propargyl amides **3.1n** in combination with the archetypal bulky Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ producing similar results as those utilising π -Lewis acidic gold complexes.^[60] In this case, using the borane in a stoichiometric manner initiated the 5-*exo-dig* cyclisation when heated to 45 °C to yield a range of oxazolium borate zwitterions (**3.1p**, Scheme 3.6).^[39a] It was noted that a reactivity series could be established whereby depletion of electron density of the carbonyl through the R^1 substituent could enhance reactivity by increasing the lability of the boron adduct of **3.1o**, resulting in more 'free' borane to activate the alkyne. This is a trend that holds true with a lot of early main group reactivity, with specific mention to reduction reactions whereby hydrosilylation occurs fastest with electron deficient carbonyls and conversely, the poorest reactivity is imparted by electron rich substrates.^[23a, 24a, 61]

Many of the examples used in this early work feature a tertiary amine in the backbone however, if a secondary amine is used then catalytic turnover to the oxazole

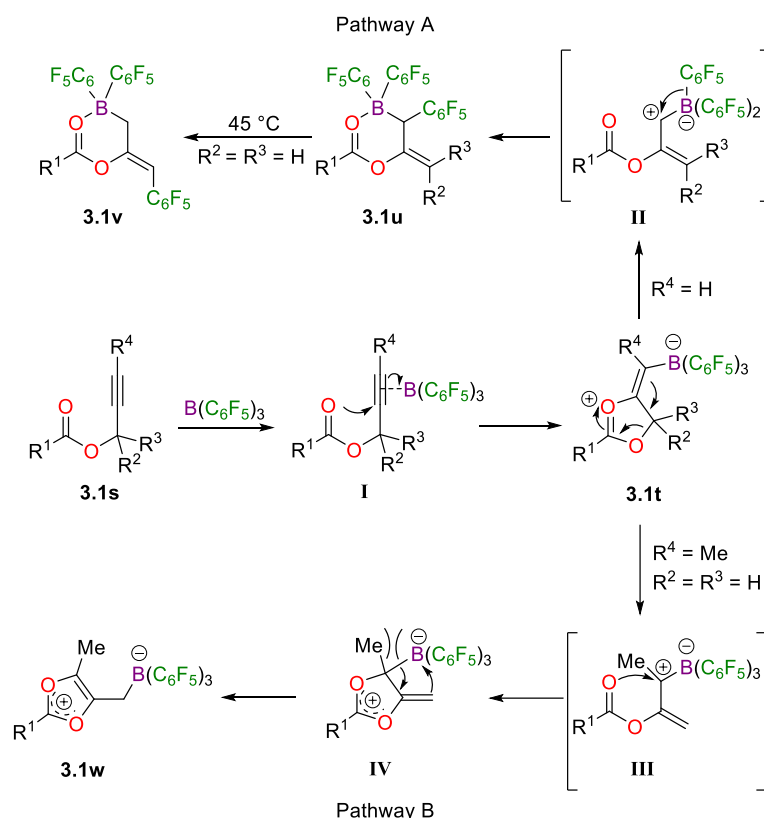
can be observed when a sufficiently bulky adamantyl group is incorporated into the R¹ position. While the reaction is slow under harsh reaction conditions (10 days at 100 °C) the oxazole **3.1q** could be produced in 83% yield setting an encouraging precedent for main group catalysts (Scheme 3.6). When the substrates were functionalised with methyl groups in the propargylic position, then an alternative reaction pathway prevailed producing a 7-membered chelating 1,1-carboboration product **3.1r**. This is posited as being the result of allylic strain between the adjacent bulky C₆F₅ groups on boron and the dimethyl backbone in the oxazolium borate resulting in the carboboration pathway triumphing over the cyclisation route (Scheme 3.6).



Scheme 3.6: Varying reactivity of propargyl amides with $\text{B}(\text{C}_6\text{F}_5)_3$.

In an extension to this, simply switching out the amide unit for an ester drastically changes the outcome of the reaction with a complex rearrangement process occurring coined as the ‘propargyl rearrangement’ (Pathway A, Scheme 3.7). Early examples of this divergent reactivity from Melen *et al.* used various substitution patterns of propargyl esters in conjunction with $\text{B}(\text{C}_6\text{F}_5)_3$ to form the similar 5-membered zwitterionic **3.1t** however, due to the instability of the dioxolium salt, this undergoes a ring-opening reaction with π -bond migration generating a build-up of positive charge on the carbon adjacent to the boron centre (**II**, Scheme 3.7). This is followed by a 1,2-C₆F₅ shift which, upon conformational change, forms a stable 6-membered dioxaborinine **3.1u**. When heated, this may then undergo a 1,3-boron shift to give the less hindered product **3.1v**. Yet, in a similar vein to the propargyl amides,

functionalising the propargyl reagent drastically affects the reactivity as seen when the terminal alkyne is altered to an internal variant featuring either Me or ⁿPr groups in the R⁴ position. In this system, instead of the propargyl rearrangement taking place, a stable tertiary carbocation (**III**, Scheme 3.7) is formed which undergoes a new ring-closing reaction by nucleophilic attack of the carbonyl oxygen. A subsequent 1,3-boron shift and carbon-carbon double bond migration generates the stable dioxolium zwitterions **3.1w** (Pathway B, Scheme 3.7). This is particularly interesting as very few isolable examples of such dioxoliums exist in the literature owing to their inherent instability.^[20, 62]



Scheme 3.7: Varying reactivity of propargyl esters with B(C₆F₅)₃.

3.1.1 Aims of This Chapter

Combining the above topics and methodologies to synthesise evermore complex and synthetically useful heterocyclic structures is of massive importance to the synthetic chemist. Additionally, developing these systems to deliver groups other than perfluorinated aryl rings is a challenge that is prime for exploitation. To this end, and building on other contemporary works in this area, this chapter aims to expand the substrate scope of these propargyl systems to include ureas, carbamates and carbonates as well as utilising heteroleptic boranes to deliver synthetically more useful R-groups to the heterocyclic products.

3.2 Results and Discussion

3.2.1 The Propargyl Rearrangement of Amides, Carbamates and Carbonates

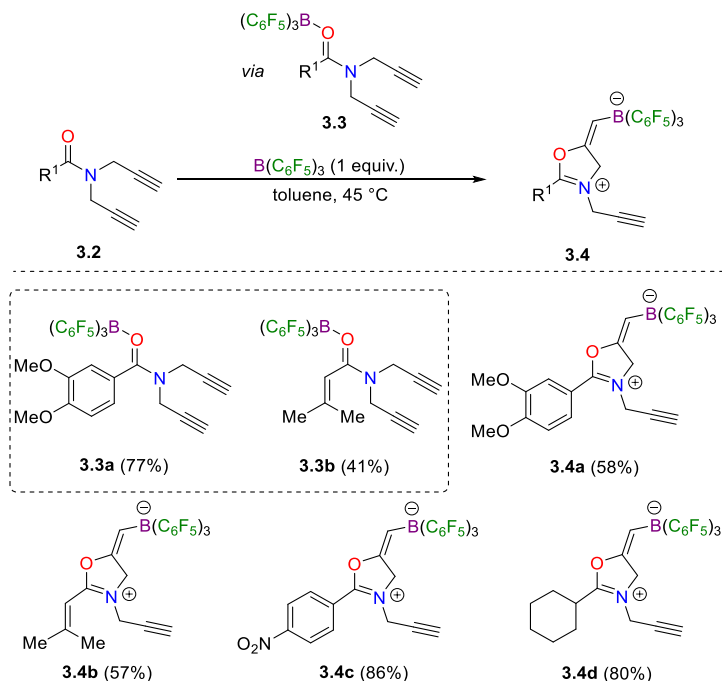
3.2.1.1 Reactivity of Dipropargyl Amides

Building on previous work within the group, we aimed to react dipropargyl amides with $B(C_6F_5)_3$ in a bid to promote a cyclisation reaction. Initially it was uncertain as to whether the diyne cyclisation would occur to form the carboboration product similar to those seen in the synthesis of boroles, phospholes *inter alia*,^[41, 63] or whether it would follow the analogous propargyl amide cyclisation pathway seen before with gold and boron reagents to form the oxazolium salt.^[39a, 64] Indeed, there is the prospect for the pendant alkyne fragment to undergo additional tandem reactions differing from previous mono-alkyne reagents.

It was observed that the 1:1 stoichiometric reaction between *N,N*-dipropargyl amides **3.2** with $B(C_6F_5)_3$ at mild temperatures resulted in a single product being formed. Interestingly, it was solely the 5-*exo-dig* cyclisation pathway that prevailed to form the oxazolium zwitterion **3.4** while leaving the second alkyne fragment untouched (Scheme 3.8). This presumably follows the same mechanistic pathway observed previously whereby the 1,2-*trans*-addition of the carbonyl oxygen and borane to the alkyne occur *via* the initial Lewis adduct **3.3**.^[39a] Two examples of this Lewis adduct intermediate **3.3a–b** could be isolated by crystallisation from a saturated toluene solution stored at -40 °C in 77% and 41% yield respectively, which could be measured by single crystal X-ray diffraction (*vide infra*). The ensuing cyclisation to form the 5-alkylidene-4,5-dihydrooxazolium borate products **3.4** *via* π -activation could be initiated by heating to 45 °C for 48 hours garnering the products in generally good yields of 57–86% (Scheme 3.8). It appears the best conversions were as a result of the incorporation of mesomerically electron-withdrawing *p*-nitrophenyl group (**3.4c**) presumably reducing the nucleophilicity of the carbonyl oxygen. This in turn increases the lability of the O–B adduct, leaving more ‘free’ borane available to activate the alkyne toward nucleophilic attack. This general trend is congruent with other findings within the group.^[39a]

The proposed transformation is evidenced by the ^{11}B NMR spectra whereby a broad singlet is seen at $\delta = -0.5$ ppm for the B–O adduct which then gives rise to another sharp singlet resonance at $\delta = -17$ ppm post cyclisation, which is indicative of similar vinyl borate moieties.^[39, 62] This is further reinforced by the ^{19}F NMR spectra which showed that upon quaternisation of the borane, a diagnostic upfield shift of the

p-F atoms are observed revealing the three resonances in a 2:1:2 ratio for *ortho* (ca. $\delta = -132.8$ ppm), *para* (ca. $\delta = -160.5$ ppm) and *meta* (ca. $\delta = -165.0$ ppm) fluorine atoms of the perfluorophenyl rings.



Scheme 3.8: Reactions of dipropargyl amide derivatives with $\text{B}(\text{C}_6\text{F}_5)_3$.

Solid-state analysis of the Lewis adducts **3.3a–b** reveals that both structures present similar bond lengths which are all within anticipated ranges however, a slight shortening of the C–N bond is seen as a result of the stabilizing effect of the cationic carbonyl fragment (ca. 1.324 Å vs. 1.346 Å for a C–N single bond). The resulting *cis* configuration displays a slight bent geometry with regard to the dihedral angle between B–O–C–C of 18.71(16)° for **3.3a** and 7.88(17)° for **3.3b**. Subsequent solid-state analyses on **3.4c–d** reveal as expected, the heterocyclic oxazolium borate. Similar in nature to the adduct, the delocalisation of positive charge that is formed through the cyclisation step is now more pronounced with further contraction of the C–N bond (ca. 1.302 Å) compared to a formal C–N single bond at 1.346 Å.^[65]

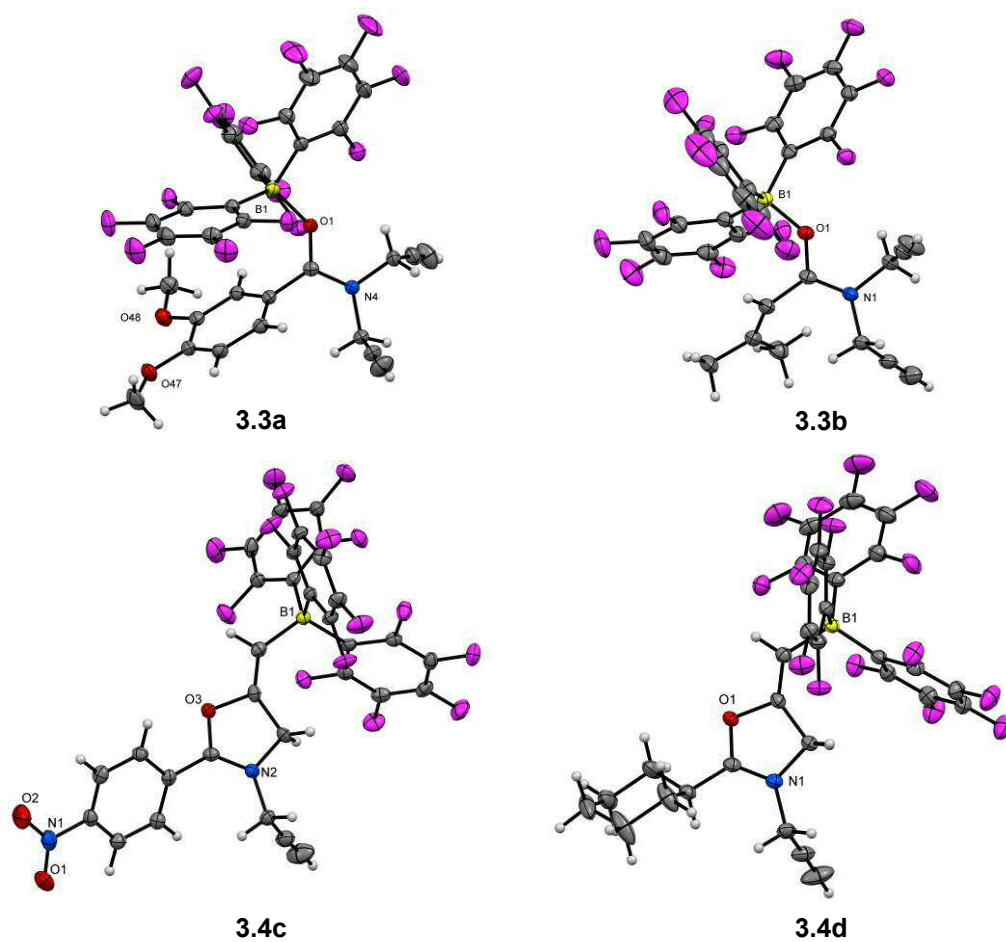
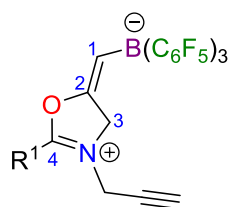


Figure 3.1: Solid-state structures of **3.3a–b** and **3.4c–d**. Toluene solvent omitted for clarity. C: grey, B: yellow-green, N: blue, F: pink, O: red. Thermal ellipsoids shown at 50% probability.

Table 3.1: Experimental bond lengths for **3.4c** and **3.4d**.

Bond	Bond Length /Å	
	3.4c	3.4d
C ¹ –C ²	1.305(9)	1.315(2)
C ² –C ³	1.499(8)	1.510(2)
C ³ –C	1.489(7)	1.475(2)
C ⁴ –C	1.306(6)	1.298(2)
C ⁴ –N	1.466(7)	1.489(2)
C ² –O	1.471(5)	1.459(2)
C ⁴ –O	1.303(8)	1.307(2)
C ¹ –B	1.619(8)	1.628(2)



Both structures also display remarkable planarity regardless of the lack of aromaticity with root mean square (RMS) deviation values of 0.024 and 0.037 for **3.4c** and **3.4d** respectively as a result of four of the five atoms in the ring system being predominantly sp^2 in character. Additionally, in the solid-state, the oxazoline fragment lies in the equatorial position of the cyclohexyl group of **3.4d**, theorised to be as a means to reduce the steric occlusion between the adjacent unreacted propargyl moiety (Figure 3.1).

3.2.1.2 Reactivity of Propargyl Ureas

In an extension to the work conducted previously into the dipropargyl amides and the lability of the B–O adduct, attenuation of the carbonyl oxygen donor ability was probed through the use of propargyl urea substrates. If this reaction follows the same 5-*exo-dig* cyclisation pathway, then it should be expected that 5-alkylidene-4,5-dihydrooxazol-2-amino borate products will predominate. Indeed, when the substrates **3.5** were subjected to one equivalent of $B(C_6F_5)_3$, a broad singlet was observed in the ^{11}B NMR spectrum at $\delta = -1.9$ ppm indicating adduct formation.^[66] Upon heating to 50 °C a new resonance at $\delta = -17.0$ ppm was observed in the ^{11}B NMR after 7 days (**3.6a**) or 14 days (**3.6b**) which was attributed to the target vinyl borate species (Scheme 3.9). These could both be isolated in 31% yield as crystalline solids from the reaction mixtures upon cooling.

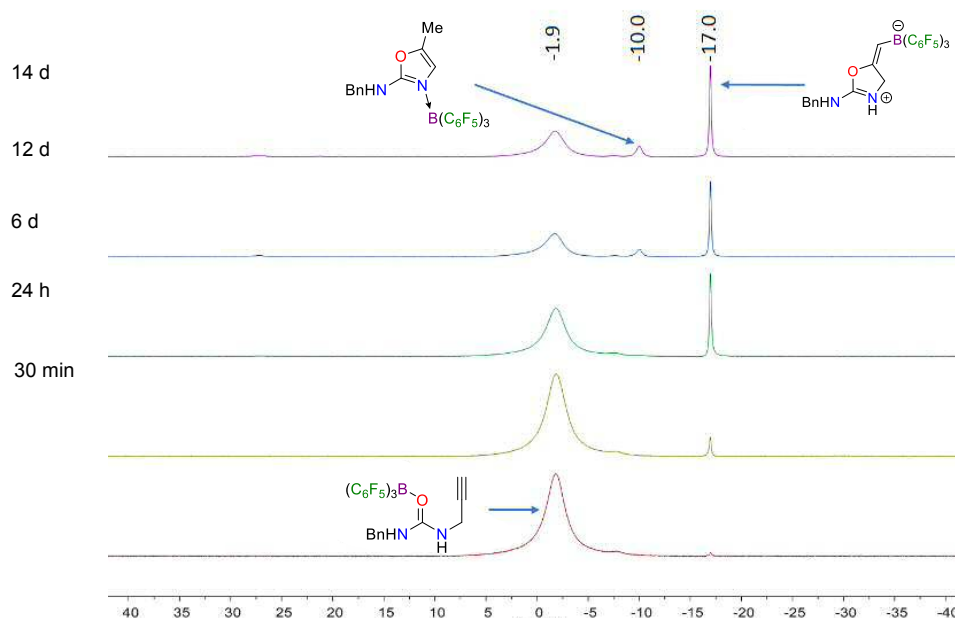
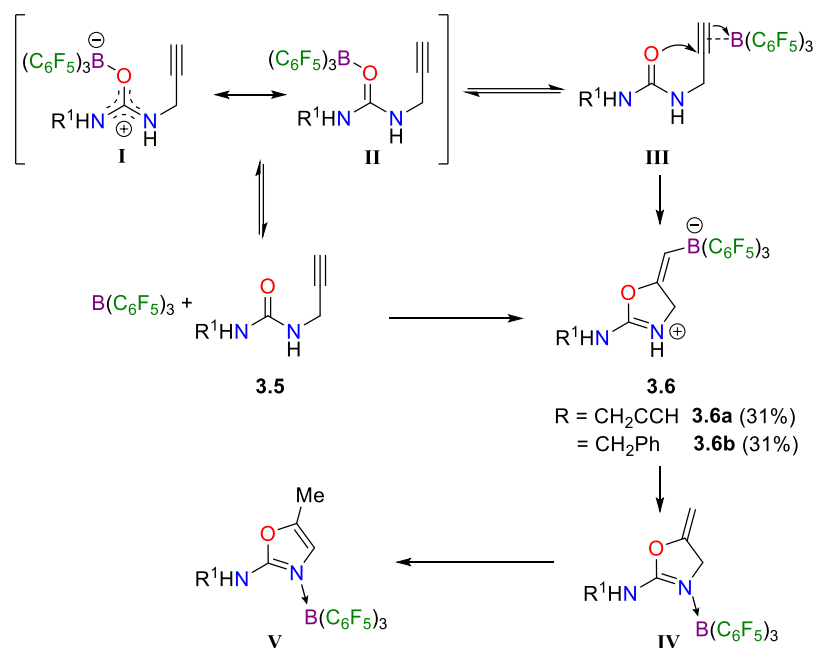


Figure 3.2: *In situ* ^{11}B NMR spectra of the reaction between **3.5b** and $B(C_6F_5)_3$.

Further support could be offered by the ^{19}F NMR spectra, revealing a similar theme in the form of the three resonances in a 2:1:2 ratio for the *ortho* ($\delta = -132.4$ ppm), *para* ($\delta = -161.2$ ppm) and *meta* ($\delta = -165.1$ ppm) fluorine atoms. This upfield shift of the *para*-fluorine atom is again indicative of a four-coordinate borate which is consistent with similar motifs found in the literature.^[67] It was also noted that a side product was emerging in the ^{11}B NMR at $\delta = -10.0$ ppm which is attributed to the formation of the oxazole *via* a protodeboration and tautomerisation rearrangement with the borane coordinating to the imine nitrogen (Figure 3.2, Scheme 3.9).

The reduced reaction rate of the urea derivatives compared to the amide precursors may be attributed to the stronger donor character of the carbonyl oxygen due to the urea scaffold in addition to poor solubility of the urea reagents. The delocalised positive charge about the N_2CO fragment is more stabilised than in the amide example leading to lower concentrations of 'free' borane in solution, therefore reduced rates of alkyne activation. These factors may be partially mitigated through the use of more harsh reaction conditions to ensure that the oxazoline products **3.6** could be furnished in modest yields.



Scheme 3.9: Proposed mechanistic pathway of the reaction between propargyl ureas and $\text{B}(\text{C}_6\text{F}_5)_3$.

As stated earlier, the positive charge that is delocalised about the N_2CO fragment is elucidated when addressing the solid-state metrics of the cyclised oxazoline products **3.6**. The data summarised in Table 3.2 showcases this with a noticeable

contraction of both C–N bonds (1.313(3) and 1.317(3) Å) as well as the C–O bond (1.304(3) Å) which are all intermediate between formal single and double bonds.^[65] Again, the planarity of the 5-membered oxazoline ring system is almost completely planar with a RMS of 0.026.

Table 3.2: Experimental bond lengths for **3.6a–b**.

Bond	Bond Length / Å	
	3.6a	3.6b
C ¹ -C ²	1.309(3)	1.310(4)
C ² -C ³	1.512(3)	1.508(5)
C ³ -N ¹	1.465(2)	1.455(4)
C ⁴ -N ²	1.313(3)	1.312(5)
C ⁴ -N	1.317(2)	1.309(5)
C ² -O	1.461(2)	1.460(4)
C ⁴ -O	1.304(2)	1.309(4)
C ¹ -B	1.619(3)	1.618(5)

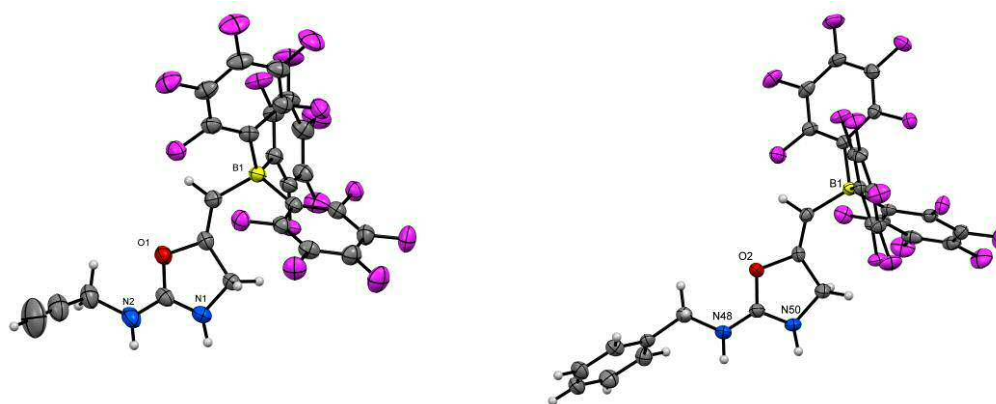
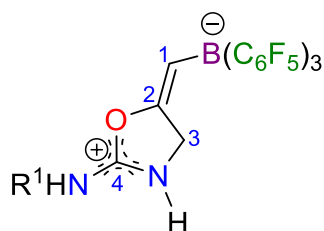
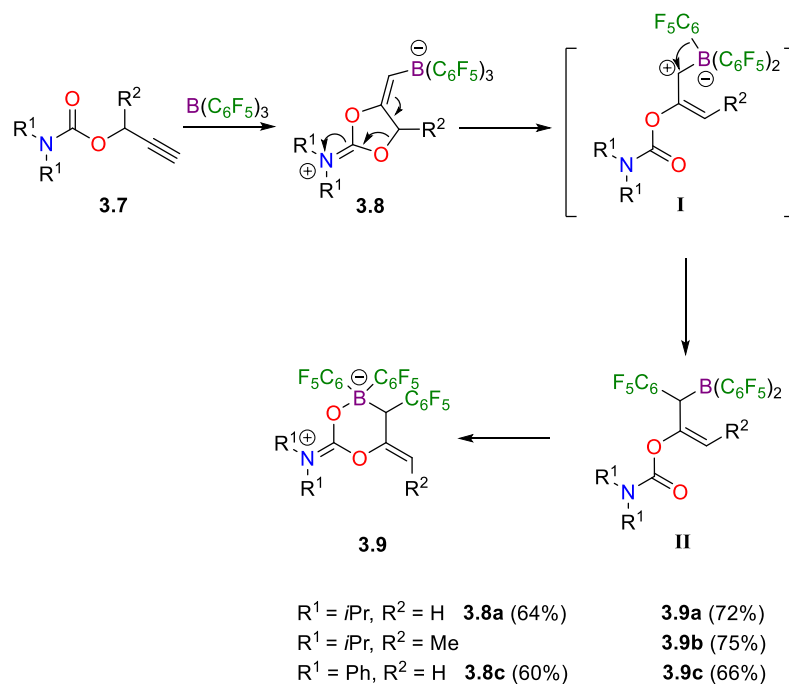


Figure 3.3: Solid-state molecular structures of **3.6a** (left) and **3.6b** (right). C: grey, B: yellow-green, N: blue, F: pink, O: red. Thermal ellipsoids shown at 50% probability.

3.2.1.3 Reactivity of Propargyl Carbamates

Moving along the series in varying the heteroatoms flanking the carbonyl moiety, O-propargyl carbamates **3.7** were used in a stoichiometric amount with $B(C_6F_5)_3$ to affect the propargyl rearrangement to yield the heterocyclic chelating 1,1-carbaboration product **3.9**. While the first part of the mechanism involves the formation of the dioximinolium borate **3.8**, similar to those seen in Sections 3.2.1 and 3.2.2, a subsequent rearrangement *via* a ring-opening/1,2- C_6F_5 migration

mechanism occurs (**I** and **II**, Scheme 3.10) to generate the allylboron **3.9** which is analogous to the reaction between propargyl esters with $B(C_6F_5)_3$. This initial cyclisation readily occurs at room temperature, assumedly due to lower nucleophilicity of the NCO_2 moiety when compared to the urea derivative, which could be isolated in 64% and 60% yield respectively. However, to secure the final allylboron products **3.9**, extended reaction times of 24–120 h were necessary although increasing reaction temperature to 50 °C saw the products being furnished in as little as 16 h in yields of 66–75% (Scheme 3.10). With regard to mechanistic insight, conducting the initial cyclisation step at low temperature precludes the ring-opening step, allowing the 2-amino-1,3-dihydrooxolium zwitterions **3.8** to be isolated. Whilst other unstabilised dioxolium compounds rapidly undergo the ring-opening step making isolation near impossible with a few exceptions,^[20] the stabilisation offered by the amido nitrogen of the carbamate allowed for easy isolation of these intermediates as crystalline solids.



Scheme 3.10: Reaction between **3.7** and $B(C_6F_5)_3$ to give **3.8** and **3.9**.

Multinuclear NMR spectroscopic analysis of the intermediates presented the characteristic resonance in the ^{11}B NMR spectra at $\delta = -17.0$ ppm for the quaternised vinyl borate fragment with a similar motif in the ^{19}F NMR spectra for the *ortho*- ($\delta = -132.8$ ppm), *para*- ($\delta = -161.1$ ppm) and *meta*- ($\delta = -165.5$ ppm) fluorine atoms of the pentafluorophenyl rings in a 2:1:2 ratio. Indeed, when these are then heated to initiate

the ring-opening step, the formation of the allylboron products **3.9** are readily identified by a broad resonance at $\delta = ca. 0$ ppm in the ^{11}B NMR spectra which is indicative of the new chelating B–O adduct. Another diagnostic NMR handle is the formation of the *exo*-alkene moiety. These vinylic protons present as a pair of doublets for the unsubstituted propargyl carbamates (**3.9a,c**) at $\delta = 4.3\text{--}5.0$ ppm in the ^1H NMR, or a doublet and quartet for the methyl derivative (**3.9b**). Instead of observing three resonances in the ^{19}F NMR as is the case with the vinylborate intermediates **3.8**, the juxtaposition of one of the C_6F_5 rings as a result of the carboboration reaction leads to all three perfluorophenyl rings being inequivalent hence nine distinct resonances for **3.9**.

From the reactivity so far, a trend can be identified whereby an increase in the stabilisation from heteroatoms that flank the carbonyl moiety, the more Lewis basic the carbonyl oxygen and hence the slower the cyclisation is due to borane sequestration. An argument could be made that a stronger Lewis basic oxygen could undergo a more rapid cyclisation due to an increase in nucleophilic behaviour once B–O dissociation occurs however, it appears that adduct cleavage is the rate determining step leading to slower reaction times and more harsh reaction conditions being necessary for appreciable conversion to the heterocyclic product. Additionally, the extra stabilisation that is afforded by the amido nitrogen also stabilises the intramolecular chelate formed in **3.9** as prolonged heating at 60°C did not undergo a 1,3-boron shift to yield the 1,3-carboboration product as seen in Scheme 3.7, which requires this O–B bond to be cleaved.^[20] Whilst these compounds were fully characterised *via* multinuclear NMR spectroscopy, the solid-state structures could also be measured by single crystal X-ray diffraction to unambiguously verify the formation of the zwitterionic 5-membered oxazolium borate **3.8** and 6-membered allylboron chelate **3.9** (Figure 3.4). The metrics are outlined in Table 3.3. Comparing the C–N bond length of the urea product **3.6** to that of **3.8** shows a contraction (1.313(3) vs. 1.290(3) Å) which is consistent with the positive charge being located primarily on the nitrogen atom hence, a decrease in the number of stabilising nitrogen atoms leads to shorter bond lengths of any remaining C–N bonds. Confirmation of the molecular structure of **3.9b–c** was seen through single crystal X-ray diffraction, revealing the heterocyclic 6-membered allylboron product. The metrics in this case were as expected with the $\text{C}^2\text{--C}^3$ bond displaying typical double bond sp^2 character (1.324(7) and 1.309(3) Å) alongside a contracted $\text{C}^4\text{--N}$ bond in agreement with prior observations regarding bond order (Table 3.3).

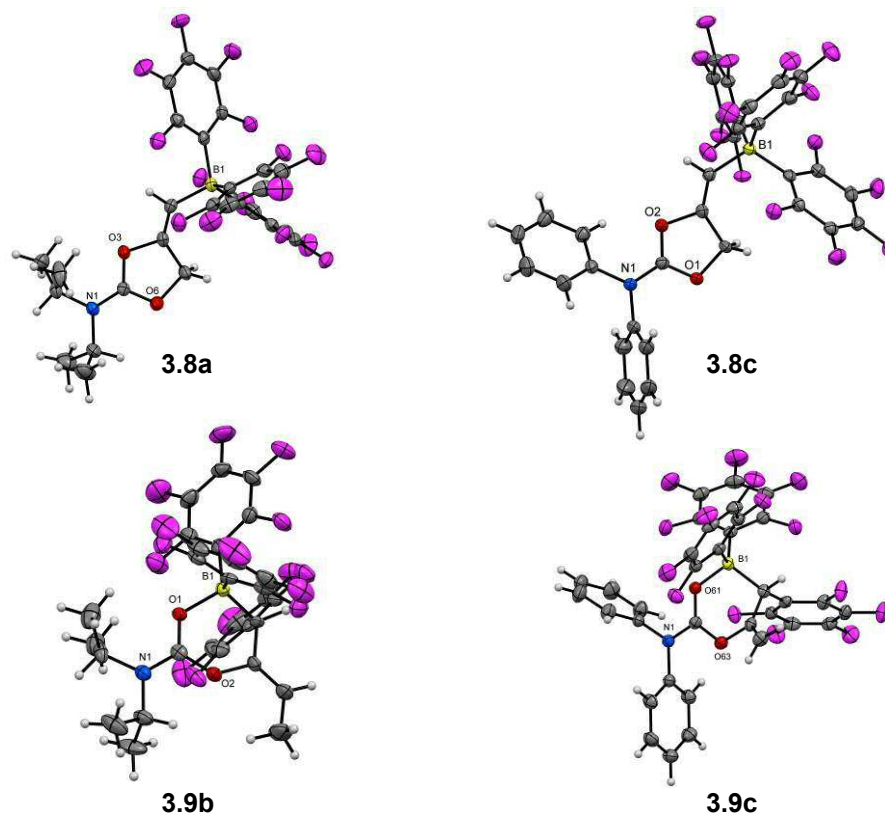


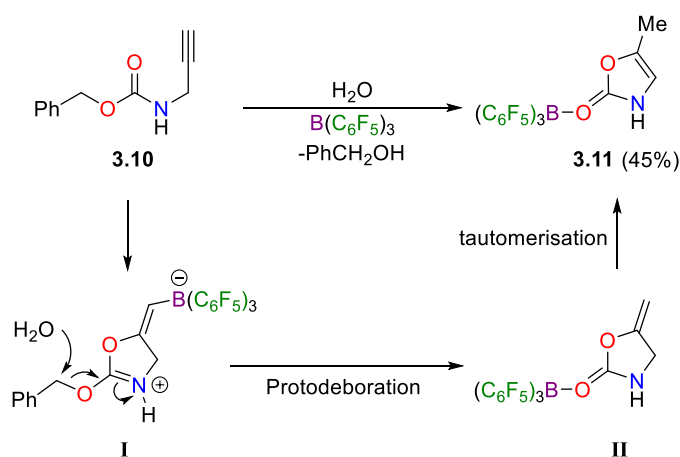
Figure 3.4: Solid-state molecular structures of **3.8a,c**, **3.9b–c**. C: grey, B: yellow-green, N: blue, F: pink, O: red. Thermal ellipsoids shown at 50% probability.

Table 3.3: Experimental bond lengths for **3.8** and **3.9**.

Bond	Bond Length / Å		Bond	Bond Length (Å)	
	3.8a	3.8c		3.9b	3.9c
C ⁴ -C ⁵	1.302(3)	1.304(4)	C ⁵ -C ⁶	1.498(6)	1.492(3)
C ⁴ -C ⁶	1.509(3)	1.505(4)	C ⁶ -C ⁷	1.324(7)	1.309(3)
C ⁶ -O ⁷	1.468(3)	1.466(4)	C ⁶ -O ⁸	1.438(5)	1.436(2)
C ² -O ⁷	1.309(3)	1.297(3)	C ² -O ³	1.280(6)	1.263(3)
C ² -N ¹	1.290(3)	1.305(3)	C ² -O ⁸	1.332(6)	1.315(3)
C ⁴ -O ³	1.440(3)	1.464(3)	C ² -N ¹	1.325(6)	1.320(3)
C ² -O ³	1.307(3)	1.305(3)	C ⁵ -B ⁴	1.633(7)	1.647(4)
C ⁵ -B	1.616(4)	1.627(4)	O ³ -B ⁴	1.570(6)	1.555(2)

While the former carbamate substrates featured the propargyl functionality tethered to the oxygen atom, the reverse was then investigated through the use of the *N*-propargyl carbamate **3.10** (Scheme 3.11). Upon exposure to one equivalent of $B(C_6F_5)_3$ the anticipated oxazolium borate was unexpectedly absent when observing the *in situ* multinuclear NMR spectra. Instead, the ^{11}B NMR spectrum showed a resonance at $\delta = 0.7$ ppm indicating a coordinative B–O bond. This information, coupled with the 1H NMR spectrum where resonances at $\delta = 2.18$ ppm and $\delta = 6.56$ ppm were observed indicating methyl and vinyl environments, suggested that the compound was a product of the aforementioned protodeboration/tautomerisation step to form the corresponding 5-methyl-2-(3*H*)-oxazolone borane adduct **3.11**. This was then reinforced through single crystal X-ray diffraction confirming the molecular connectivity as being the oxazolone heterocycle. It is posited that trace amounts of water prompt the dealkylation of the benzyl protecting group with concurrent protodeboration/tautomerisation to generate the oxazolone **3.11**.

As the product sequesters the borane as the Lewis adduct, it was thought that this reaction could be conducted catalytically. Attempting this reaction using 10 mol% $B(C_6F_5)_3$ in the presence of one equivalent of water shows the presence of a singlet in the 1H NMR spectrum at $\delta = 4.63$ ppm, indicating the formation of benzyl alcohol as a result of the dealkylation step. However, the *in situ* NMR spectroscopic data could not reliably confirm the success of this reaction due to a mixture of other products being present. This does however demonstrate the potential that the strong Lewis acid $B(C_6F_5)_3$ poses as a transition metal mimic as similar transformations to oxazolone products exist using late coinage and platinum group metals such as palladium or gold.^[68]



Scheme 3.11: Oxazolone synthesis from the reaction between $B(C_6F_5)_3$ and **3.10**.

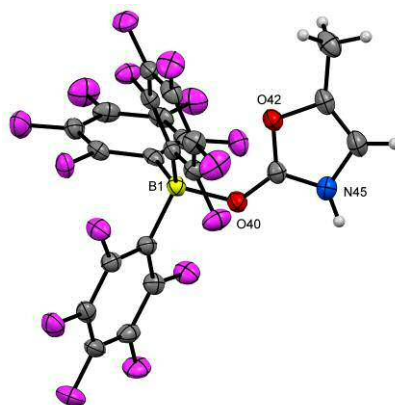


Figure 3.5: Solid-state molecular structure of **3.11**, C: grey, B: yellow-green, N: blue, F: pink, O: red. Thermal ellipsoids shown at 50% probability.

3.2.1.4 Reactivity of propargyl carbonates

To fully extend the series of flanking heteroatoms, propargyl carbonates were subsequently examined. Indeed, the stoichiometric mixture of the propargyl carbonate **3.12** with $B(C_6F_5)_3$ led to the formation of the 6-membered allylboron heterocycle in 81% yield *via* the propargyl rearrangement with relatively long reaction times of 72 hours being noted (Scheme **3.12**). All NMR spectroscopy revealed the expected chemical shifts with the indicative ^{11}B NMR resonance presenting as a broad singlet at $\delta = ca. 0$ ppm. Subsequent solid-state analysis through single crystal X-ray diffraction again confirmed the molecular structure (Figure 3.6). Additionally, it was observed that all three C–O bond lengths were similar in nature, varying by only *ca.* 0.05 Å (1.246(2), 1.298(2) and 1.292(2) Å for C–O¹, C–O² and C–O³ respectively) showing the positive charge is delocalised almost equally about the CO₃ fragment.

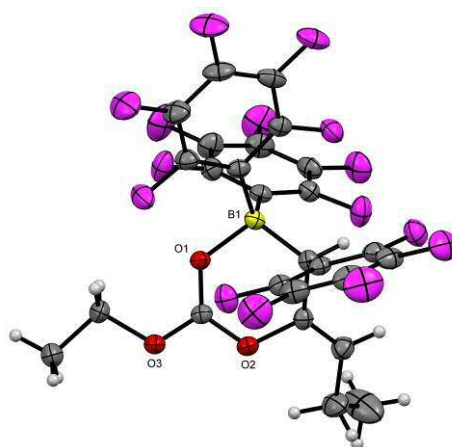
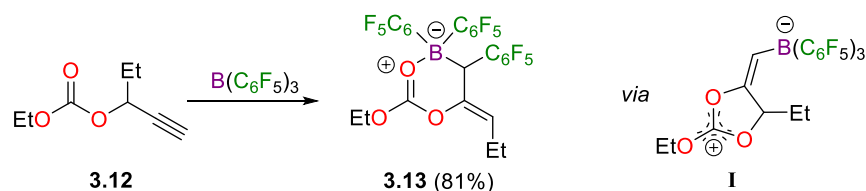
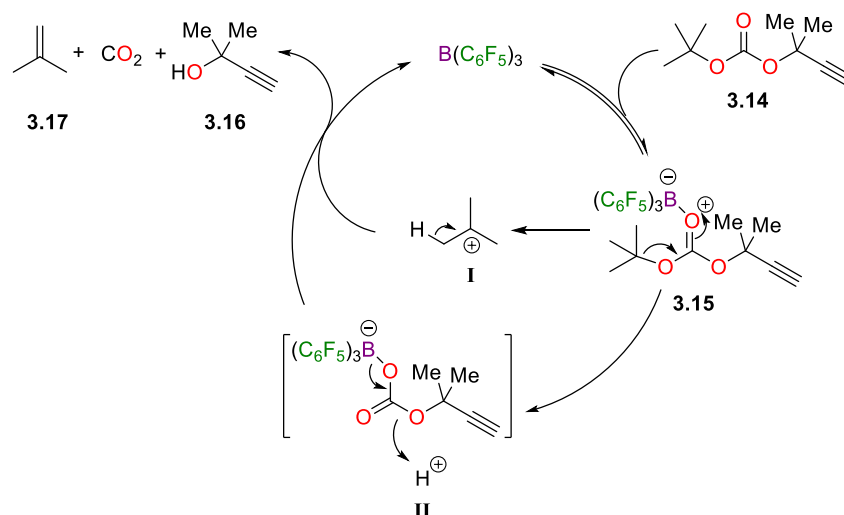


Figure 3.6: Solid-state molecular structure of **3.13**, C: grey, B: yellow-green, F: pink, O: red. Thermal ellipsoids shown at 50% probability.



Scheme 3.12: Reactions of propargyl carbonate **3.12** in propargyl rearrangements with $B(C_6F_5)_3$.

In an interesting turn from the reactivity observed with these types of reagents, a completely new avenue was unlocked when the ^tbutyl derivative **3.14** was used. Instead of the anticipated 1,1-carbaboration product prevailing, the *in situ* 1H NMR spectrum revealed a more interesting fate. The use of $B(C_6F_5)_3$ resulted in the complete deprotection of the the Boc group to generate isobutylene as well as the propargyl alcohol starting material (Scheme 3.13). Analysis of the 1H NMR spectrum over time when using 10 mol% $B(C_6F_5)_3$ loading at ambient temperature showed almost complete deprotection of the Boc group after 17 hours, with the diagnostic isobutylene septet at $\delta = 4.64$ ppm being identified (Figure 3.7). In addition to this, the methyl groups of the alcohol moiety undergo a slight downfield shift in the 1H NMR spectrum from $\delta = 1.67$ to 1.70 ppm.



Scheme 3.13: Proposed mechanism for Boc deprotection of propargyl carbonate **3.14** using 10 mol% $B(C_6F_5)_3$.

Indeed, this deprotection is an incredibly common method in synthetic chemistry, more often catalysed by the addition of a strong Brønsted acid e.g. HCl/acetic acid or trifluoroacetic acid however, if certain acid sensitive functionalities are present in reagent, this method may provide a slightly milder approach to catalytic Boc group

deprotection.^[69] It is also true that this transformation has been conducted by other main group centred compounds^[70] nonetheless, according to an exhaustive literature survey, this is one of the first examples where $B(C_6F_5)_3$ has been used for the catalytic deprotection of Boc groups.

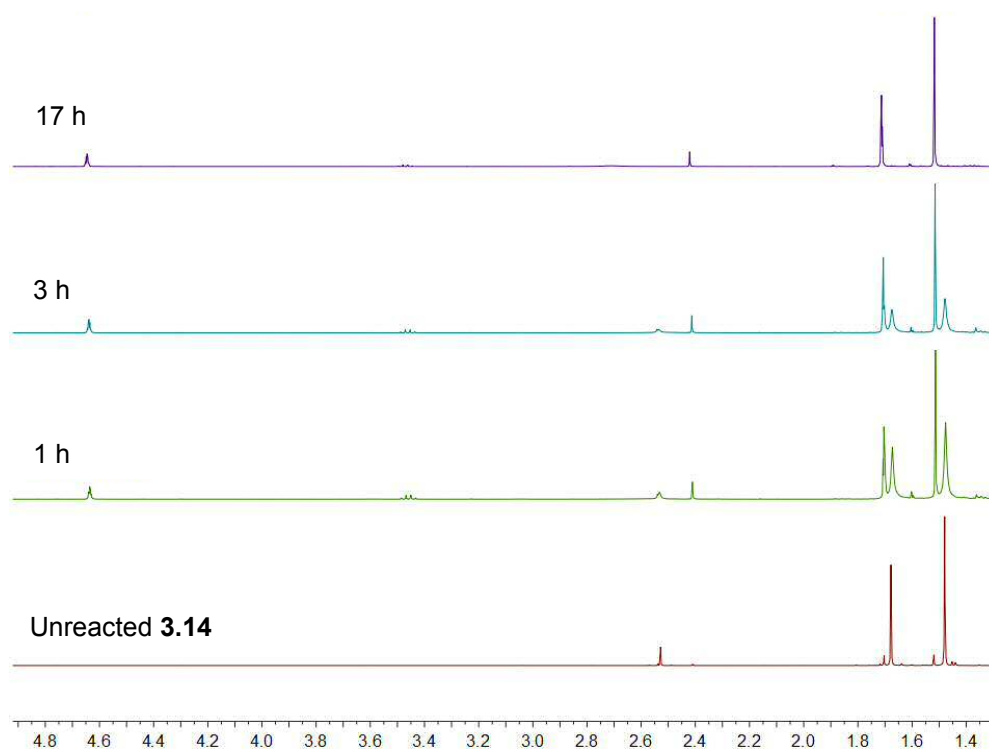


Figure 3.7: Stacked *in situ* ¹H NMR spectra for the catalytic Boc deprotection of propargyl carbonate **3.14** using 10 mol% $B(C_6F_5)_3$.

3.2.2 Use of Heteroleptic Boranes for Selective Migratory Group Transfer

The use of boranes, specifically $B(C_6F_5)_3$, as a carboboration reagent was outlined in the previous section however, the transfer of a C_6F_5 group is of limited synthetic use with only a handful of practical uses, such as their applications in biological systems.^[71] It would be of greater significance to transfer 'R'-groups other than these perfluorophenyl rings. To this end, other electrophilic boranes were synthesised to be utilised in the propargyl rearrangement as a way of installing new functionality in a one-pot multistep process. Boranes of the general structure $R-B(C_6F_5)_2$ were used for example, those synthesised by Erker through the salt metathesis of $PhBCl_2$ and LiC_6F_5 to yield $PhB(C_6F_5)_2$ ^[72] (**3.18**) as well as the hydroboration of styrene using Piers' borane $(HB(C_6F_5)_2)$ ^[24a] to generate the

phenylethyl borane **3.19**.^[24b, 73] Additional transfer reagents such as the borenium cation **3.21** reported by Ingleson *et al.* were also utilised in this work as selective carboboration reagents (Figure 3.8).^[74]

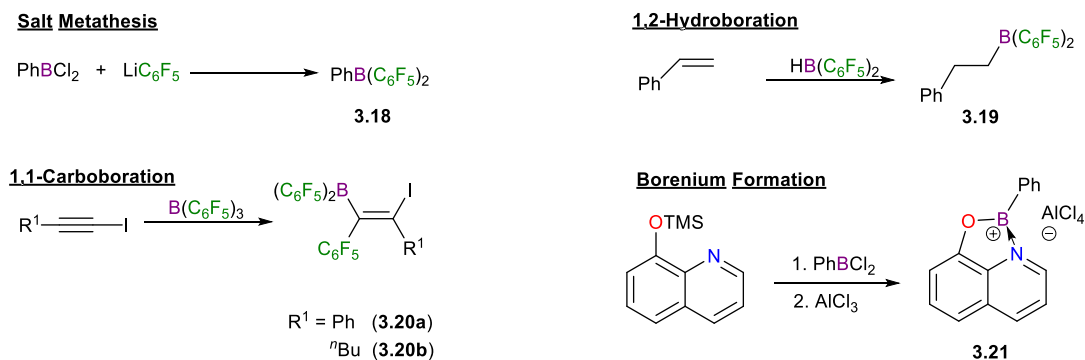


Figure 3.8: Electrophilic borane and borenium Lewis acids used as R-group transfer reagents.

It was also identified that iodoalkynes of the general structure R-C≡C-I (R = Ph, ⁿBu) are excellent candidates to undergo carboboration reactions due to their similarity to Wrackmeyer's 'activated' alkynes. Indeed, when exposed to B(C₆F₅)₃, such iodoalkynes undergo rapid 1,1-carboboration (<10 mins) to garner the iodoalkenylboranes **3.20** quantitatively and in excellent stereoselectivities of *ca.* 98:2 *E/Z* of the product **3.20a** as determined by *in situ* multinuclear NMR spectroscopy. Equally, the ⁿBu derivative gave similarly high yields however, slightly lower selectivities were noted giving a *ca.* 80:20 mixture of the *E/Z* isomers of **3.20b**. This is a surprisingly high degree of selectivity when compared to 'normal' alkynes (terminal alkyl/aryl groups), where the *E/Z* isomers are formed in a *ca.* 1:1 ratio.^[73] This selectivity, and purity, could be readily assessed through the ¹⁹F NMR spectra which give rise to six resonances for the *ortho* (δ = -127.0 (4F), -137.5 (2F) ppm), *para* (δ = *ca.* -144.5 (2F), -152.6 (1F) ppm) and *meta* (δ = *ca.* -160.5 (6F) ppm) fluorine atoms. The small number of residual resonances observed in the ¹⁹F NMR spectrum of **3.20b** are attributed to the minor isomer of the carboboration step. Additional multinuclear NMR spectroscopic data confirms these findings with **3.20a–b** presenting a broad singlet resonance in the ¹¹B NMR spectrum at δ = 57.9 ppm and δ = 58.4 ppm respectively which is congruent with other similar scaffolds.^[75] Work in the area by Erker showcased how irradiation of the stereoisomeric sample could promote photolytic interconversion to a single isomer however, after being irradiated with UV light (HPK 125, pyrex filter)^[73] a mixture of stereoisomers persisted. Of note is the prospect of employing these iodine-functionalised reagents in further reactivity

such as the synthetically important carbon-carbon bond forming reactions for instance, Sonogashira or Suzuki-Miyaura cross-coupling as well as Heck reactions.

The borane and borenium reagents **3.18–3.21** were then implemented as transfer reagents to assess their alkyl, alkenyl and aryl migratory aptitudes when subjected to various propargyl esters and carbamates which have to date only seen reaction with $B(C_6F_5)_3$.^[20, 36d] The first reagent that was trialed was $PhB(C_6F_5)_2$ **3.18** in conjunction with the propargyl ester **3.22f** in a stoichiometric ratio. Initial results from this reaction were less than impressive with a mixture of products being observed, most likely arising from an unselective migration of either a C_6F_5 or phenyl moiety. Similarly, the reaction using the ethylphenylborane **3.19** with the ester **3.22f** again gave an intractable mixture of products, presumably showing how lability of each group (C_6F_5 vs. alkyl) is similar in this instance, which is interestingly in contradiction to previous reports.^[75] While this reaction proved to be unselective (64:36 alkyl: C_6F_5 transfer) single crystals of the major isomer could be obtained which were suitable for X-ray diffraction showing transfer of the alkyl group (Figure 3.9).

As a side note, a 1,1-hydroboration reaction was also attempted using Piers' borane to see whether the propargyl rearrangement could be affected with subsequent 1,2-hydride shift from boron to carbon however, the clean 1,2-hydroboration of the alkyne proceeded within minutes thus signifying that the hydroboration reaction occurs much more rapidly than the propargyl rearrangement.

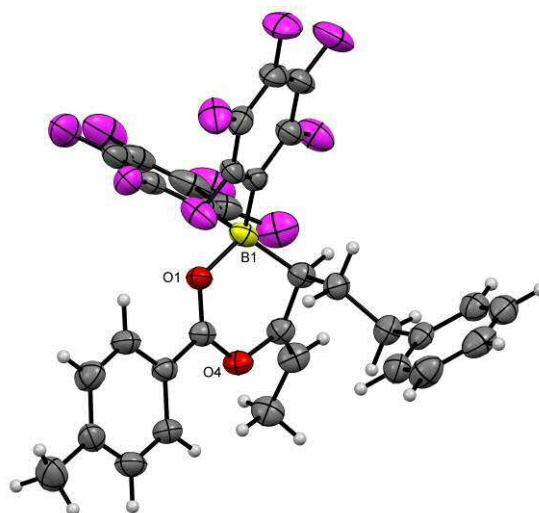
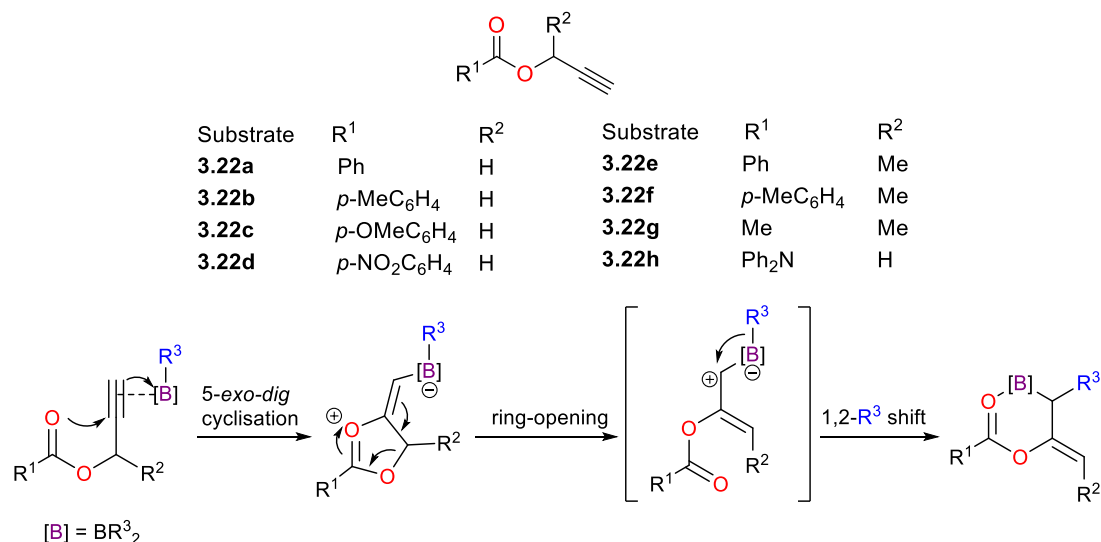
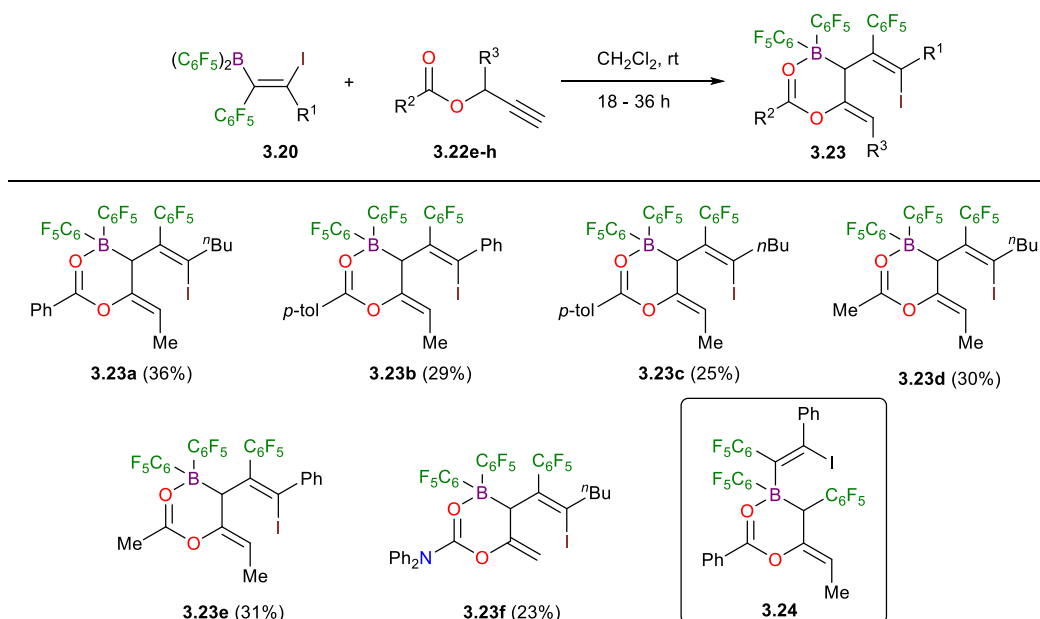


Figure 3.9: Solid-state structure of reaction between **3.22f** and **3.19**. C: grey, H: white, O: red, B: yellow-green, F: pink. Thermal ellipsoids drawn at 50% probability.



Scheme 3.14: General mechanism for the propargyl rearrangement using boron centered reagents.

Moving forward with the novel iodoalkenylboranes **3.20** in these carboboration reactions, it was observed that the proclivity of the alkene to migrate was superior to that of the C₆F₅ moiety. With these favourable results in hand, the reaction scope was expanded to various other substituted aryl esters **3.22e–f**, acetyl ester **3.22g** and carbamate **3.22h** to give a range of various highly functionalised allylboron products **3.23a–e** (Scheme 3.15). Through *in situ* multinuclear NMR spectroscopy, it was observed that these reactions had reached completion within approximately 18 hours at ambient temperature to yield **3.23**. This could be discerned through the ¹¹B NMR spectra which showed a broad singlet at $\delta = 2.0$ ppm, which is characteristic of these 6-membered dioxaborinine derivatives. The selective transfer of the alkene moiety was further verified by scrutinising the ¹⁹F NMR spectra whereby the introduced inequivalence of the perfluorophenyl rings confirms selective transfer. In addition to the inequivalence that is noted in previous examples to give six resonances, the juxtaposition of the sterically encumbered alkene fragment precludes the free rotation of the C₆F₅ rings further, therefore presenting as ten resonances instead. This is rationalised as four *ortho*-fluorine resonances ($\delta = ca. -130$ to -140 ppm (6F)), three *para*-fluorine resonances ($\delta = ca. -150$ to -160 ppm, (3F)) and a further three *meta*-fluorine resonances ($\delta = ca. -160$ to -165 ppm (6F)). Supplementary verification was shown through the presence of the proton on the carbon adjacent to boron as a broad singlet in the ¹H NMR spectra at $\delta = ca. 5$ ppm.



Scheme 3.15: Rearrangement products (**3.23a–f**) from vinyl group transfer. **3.24** shows minor product from C_6F_5 -migration.

Additionally, the presence of a quartet $\delta = 5.5$ ppm is characteristic of the vinyl group *exo* to the dioxaborinine ring being formed as a result of the cyclisation process. In the case where the carbamate precursor **3.22h** was used, instead of the methylvinyl group being generated, a simple vinylic fragment is noted with the presence of a pair of doublets at $\delta = 4.72$ and 5.00 ppm in the ^1H NMR for **3.23f**.

Storing the samples **3.23a–c** and **3.23e–f** as saturated CH_2Cl_2 /hexane solutions at -40 °C led to the formation of a crop of crystals whose structure could be determined by single-crystal X-ray diffraction (Figure 3.10). Using this method revealed the iodinated olefinic fragment to be the *E*-isomer in all structures however, the stereochemistry of the adjacent sp^3 carbon centre is formed as a racemic mixture of the *R*- and *S*-enantiomers. In the case of **3.24**, a very small number of crystals could be collected of the minor product whereby a C_6F_5 fragment was transferred instead of the olefinic unit.

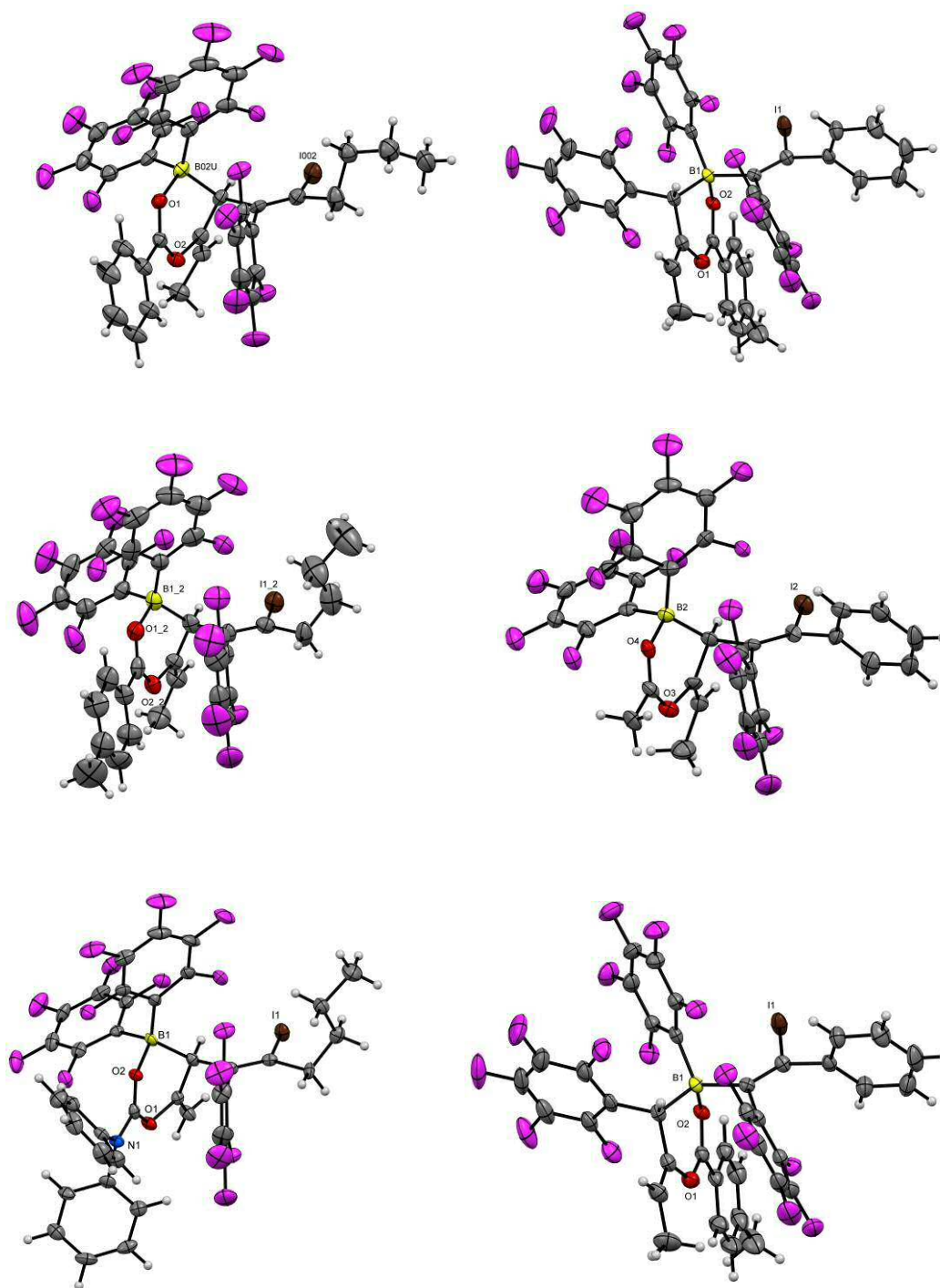
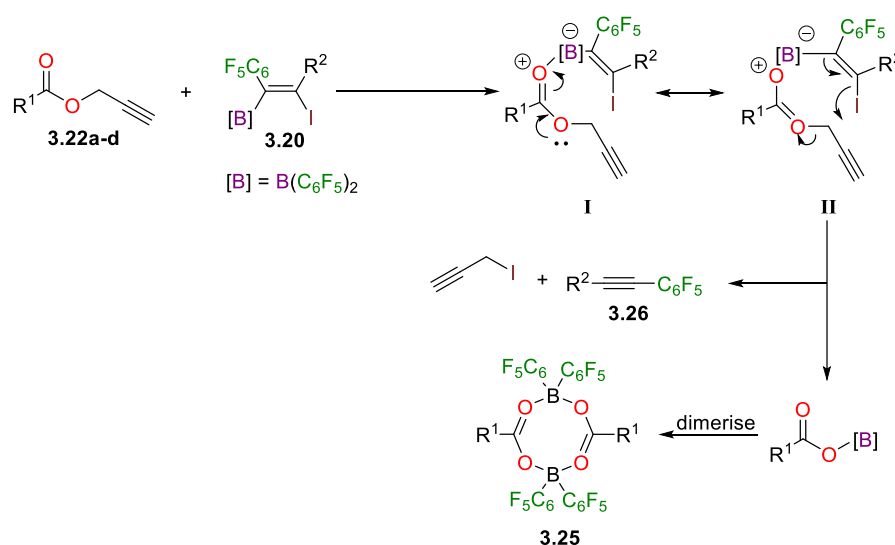


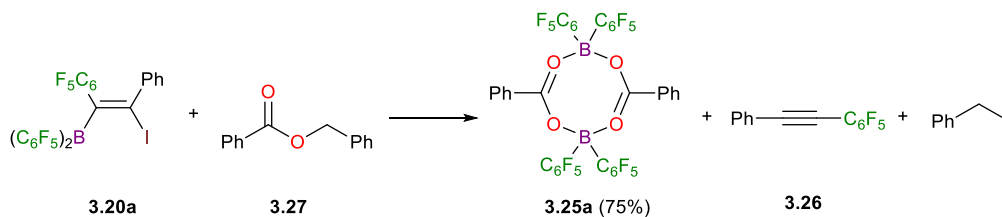
Figure 3.10: Solid-state structure of **3.23a–c**, **3.23e–f** and **3.24**. C: grey, H: white, O: red, B: yellow-green, F: pink, I: brown, N: blue. Thermal ellipsoids drawn at 50% probability.

The propargyl esters used so far feature a methyl group in the propargylic position however, when this is replaced with a proton to give the methylene esters **3.22a–d** (Scheme 3.14), an entirely different rearrangement mechanism is observed. While a familiar resonance was present in the ^{11}B NMR at $\delta = 2.0$ ppm, indicating

adduct formation of a trivalent species, when observing the ^1H NMR spectra the presence of the vinylic protons were noticeably absent. Fortunately, two sets of single crystals could be harvested from the reaction between **3.22d** and **3.20** which were unambiguously determined as the *bis*(perfluorophenyl)boranyl ester dimer **3.25** in addition to the substituted (pentafluorophenylethynyl)benzene **3.26** as a result of an elimination reaction (Scheme 3.16, Figure 3.11). Mechanistically, it is presumed that the initial B–O Lewis adduct is formed which in turn activates the propargylic position to undergo nucleophilic attack *via* iodine transfer. With the loss of propargyliodide, the B–C bond cleavage occurs to produce the (pentafluorophenylethynyl)benzene fragment **3.26** alongside the *bis*(pentafluorophenyl)boranyl ester which dimerises as observed in the solid-state (Figure 3.11). To further test this hypothesis, benzyl benzoate **3.27** was trialed with the iodovinylborane **3.20a** with the corresponding borane dimer **3.25a** prevailing as determined by X-ray crystallography. This alternative reaction pathway is presumed to arise due to the lack of steric encumbrance in the propargylic position as the inclusion of a bulkier group in this position impedes the intramolecular halide shift.



Scheme 3.16: Alternative reactivity of propargyl esters **3.22a–d** with vinyl boranes **3.20**.



Scheme 3.17: Reaction of **3.20a** with benzyl benzoate to generate the dimeric boranylester **3.25a**. Conversion given as *in situ* NMR spectroscopic measurement.

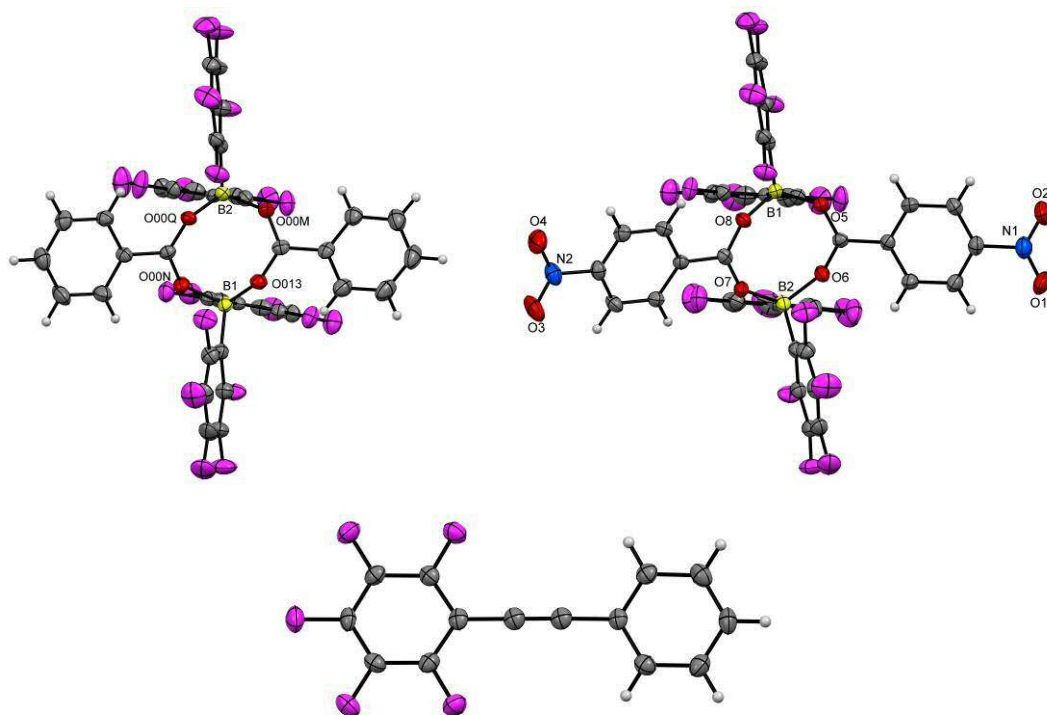
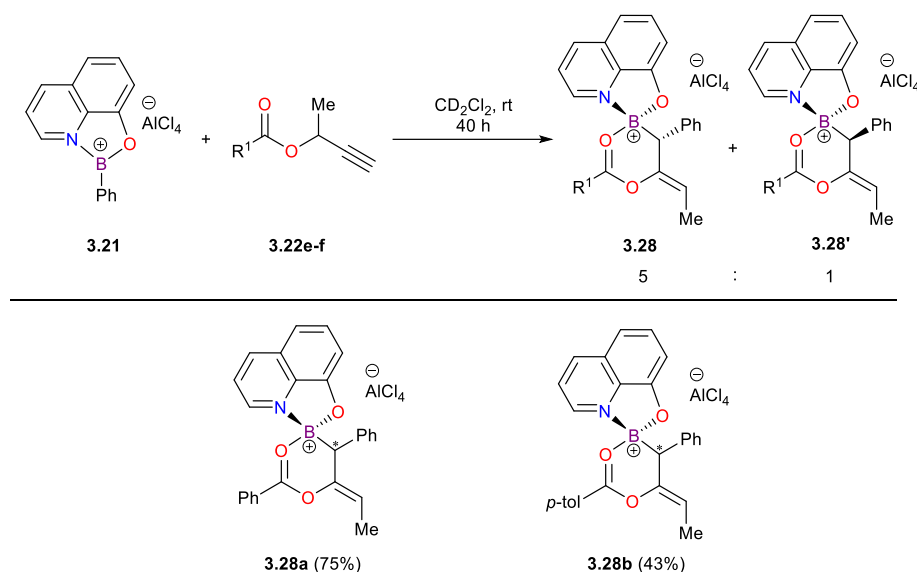


Figure 3.11: Solid-state structure of **3.25a**, **3.25b** and **3.26**. C: grey, H: white O: red, B: yellow-green, F: pink, N: blue. Thermal ellipsoids drawn at 50% probability.

As the approaches used so far show varying degrees of successful alkyl, vinyl or aryl group transfer, focus was then shifted to the 8-oxy-quinolatoroborene salts **3.21** reported by Ingleson, which have proven to be effective migratory group transfer reagents.^[74] This was selected due to the bidentate nature of the quinoline backbone which promotes the exclusive transfer of the aryl substituent on boron. Monitoring the reaction between the propargyl esters **3.22e–f** and the borene cation **3.21** showed that indeed the phenyl group was transferred exclusively to garner the allylboronium salts **3.28**. These were formed in 43% and 75% respectively as measured *via in situ* conversions. The resultant ¹H NMR spectra for **3.28a–b** were perhaps more complicated than first assumed due to the formation of a diastereomeric mixture of the (*R,R*) and (*R,S*) conformers in a 5:1 ratio as a result of the *spiro*-centre formed at boron and adjacent chiral *sp*³ centre. Single crystals could be grown of the (*R,R*) diastereomer which unequivocally shows molecular connectivity of the boronium cation **3.28b** (Figure 3.12).



Scheme 3.18: Propargyl rearrangements with borenium cations **3.21**. Conversion to both diastereoisomers **3.28** and **3.28'** determined by *in situ* NMR spectroscopy.

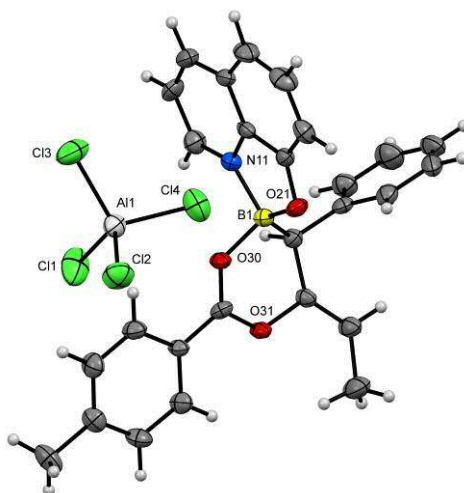


Figure 3.12: Solid-state structure of **3.28b**. C: grey, H: white O: red, N: blue, B: yellow-green, Al: light grey, Cl: green. Thermal ellipsoids drawn at 50% probability.

3.2.3 Divergent Elementoboration using Heteroleptic Boranes in the Propargyl Rearrangement

In the previous sections, various boranes and borocation have been discussed as 'R'-group transfer reagents in a bid to increase molecular complexity in the products of the propargyl rearrangement. While both sections outline a powerful method of transferring various groups, there are certain pitfalls such as the restrictive nature of transferring C_6F_5 groups using $\text{B}(\text{C}_6\text{F}_5)_3$, or the synthetically intensive routes to form the alkyl, vinyl and aryl boron centred reagents in section 3.3. It was therefore

proposed that another commercially available borane could be used to affect the same transformation while simultaneously transferring a synthetically more useful R-group. To this end, dichlorophenylborane PhBCl₂ was targeted as a good candidate for this transformation.

To trial this borane in the propargyl rearrangement, the model ester **3.29a** was mixed with PhBCl₂ in a 1:1 ratio to affect what was suspected to be the formation of the dioxaborinine heterocycle similar to previous examples however, detailed 2D NMR spectroscopy (COSY, HSQC, HMBC) did not correlate with the anticipated structure. Instead of the expected 1,1-carboration product prevailing, it was revealed that a formal 1,3-haloboration reaction had taken place to furnish the product as the α,β -unsaturated ester **3.31** as indicated by the resonance at $\delta = 6.6$ ppm for the vinylic proton, and $\delta = 4.7$ ppm for the methylene protons. Interestingly there are no reported 1,3-haloboration reactions of alkynes with only one being reported for alkenes.^[76] With this alternative reactivity being confirmed, the substrate scope was expanded to include a small number of substituted phenyl groups with the target products being identified by *in situ* NMR spectroscopy in generally >90% conversion.

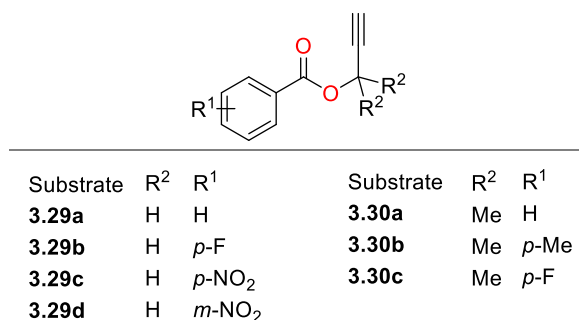
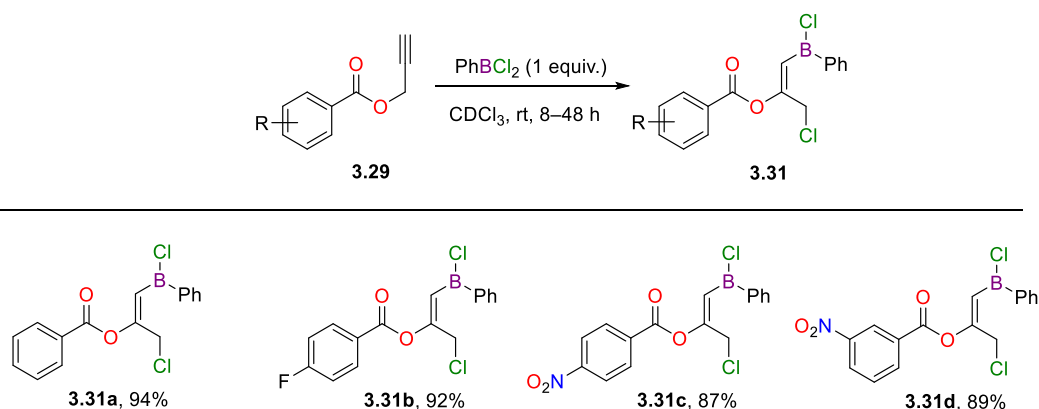


Figure 3.13: Propargyl ester substrates used in this work.



Scheme 3.19: Reaction between PhBCl₂ and **3.29** to give 1,3-haloboration products **3.31**. Values are given as *in situ* NMR conversions.

In the case of the *p*-nitro derivative **3.31c** it was possible to obtain single crystals from a saturated CH₂Cl₂/hexane solution stored at -40 °C which unambiguously confirmed the molecular structure to be that of a formal 1,3-haloboration reaction, agreeing with conclusions from NMR spectroscopic methods (Figure 3.14). It was possible to elucidate the stereochemistry of the resulting olefin to be the *trans*-product. Earlier work by Erker showcased similar vinylboranes which may be subject to photoinduced isomerisation between the *E/Z* conformers when irradiated with UV light.^[73] Attempts to induce this interconversion here to form the intramolecular chelate were met with limited success as no clear alteration could be noted when scrutinising the ¹¹B NMR spectrum. A brief optimisation of solvent systems was implemented with all common halogenated and non-halogenated solvents (chloroform, dichloromethane, chlorobenzene, benzene and toluene) garnering the product in quantitative conversion in 9 hours. Conversely, when coordinating solvents such as diethylether and tetrahydrofuran were used, reactivity was completely quenched with a singlet resonance at $\delta = 15$ ppm persisting in the ¹¹B NMR spectra indicating the favourable O–B Lewis adduct was formed, precluding alkyne activation.

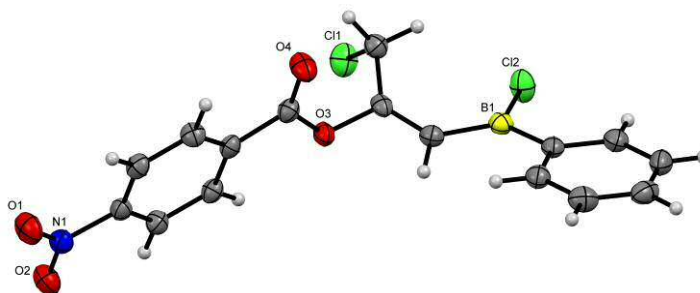
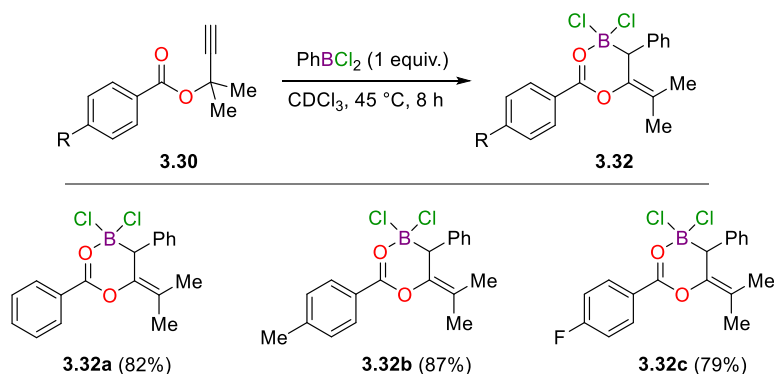


Figure 3.14: Solid-state structure of compound **3.31c**, C: grey, H: white, N: blue, O: red, B: yellow-green, Cl: green. Thermal ellipsoids shown at 50% probability.

The scope was then expanded to include various propargyl esters featuring methyl groups in the propargylic position (**3.30**) instead of the protons seen in **3.29** (Figure 3.13). Interestingly, once these new reagents were exposed to PhBCl₂ in a 1:1 ratio, the *in situ* multinuclear NMR spectra were not consistent with the formation of structures analogous to **3.31**. Instead, new resonances arose in the ¹H NMR spectrum at $\delta = 3.8$ ppm and the ¹¹B NMR spectra at $\delta = 8.0$ ppm, both indicating the generation of a dioxaborinine scaffold *via* 1,1-carbaboration, similar in nature to those outlined earlier in this chapter (Scheme 3.20). This could be confirmed further by looking at the ¹³C NMR spectra whereby the vinyl *sp*² carbon of the 1,3-haloboration product **3.31** gives rise to a resonance at δ ca. = 120 ppm whereas the *sp*³ carbon

formed in **3.32** is as expected at $\delta = \text{ca. } 40 \text{ ppm}$. This reactivity was then expanded to other substituted propargyl esters featuring moderately electron withdrawing/donating functionalities. However, it appears that this system suffers from decomposition when using strongly electron deficient propargyl systems as an intractable mixture of products prevails from the reaction. Fortunately, storing a saturated CH_2Cl_2 /hexane solution of **3.32a–c** at $-40 \text{ }^\circ\text{C}$ resulted in the formation of a crop of crystals suitable for X-ray diffraction which confirmed the 1,1-carboboration products (Figure 3.15). From the solid-state structure it was possible to gain insight into the regioselectivity of this reaction with the selective transfer of the aryl group being preferable to the chloride fragment.^[36d] Detailed 2D NMR spectroscopic studies could again confirm that the bulk sample is in agreement with the solid-state structure.



Scheme 3.20: Reaction between PhBCl_2 and **3.30** to give 1,1-carboboration products **3.32**. Yields are given as isolated yields.

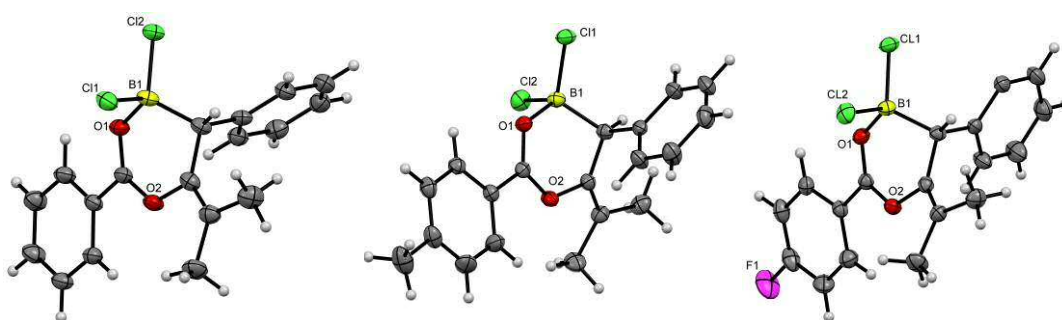


Figure 3.15: Solid-state structure of compounds **3.32a–c**, C: grey, H: white, O: red, B: yellow-green, Cl: green, F: pink. Thermal ellipsoids shown at 50% probability.

In order to probe the mechanism of these transformations, the terminal position of the alkyne **3.29a** was selectively deuterated using a polystyrene immobilised amine base (WA50) according to a process proposed by Yamada *et al.*^[77] For the ^1H NMR

of the unaltered compound **3.31**, a resonance is seen at $\delta = 6.6$ ppm for the proton of the newly formed olefin however, when conducting this reaction with **3.29a^D** this peak is no longer present although it is seen in the ^2H NMR spectrum at the same chemical shift of $\delta = 6.6$ ppm (Figure 3.16).

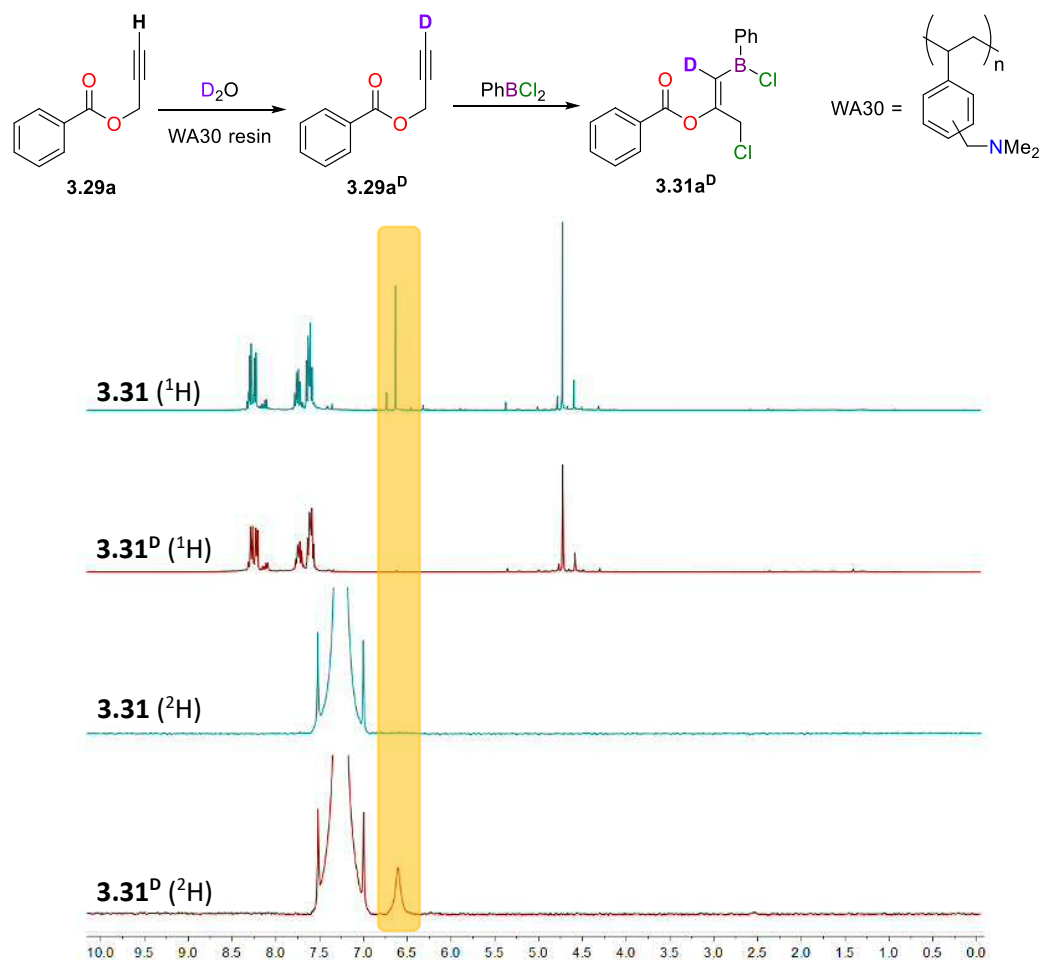
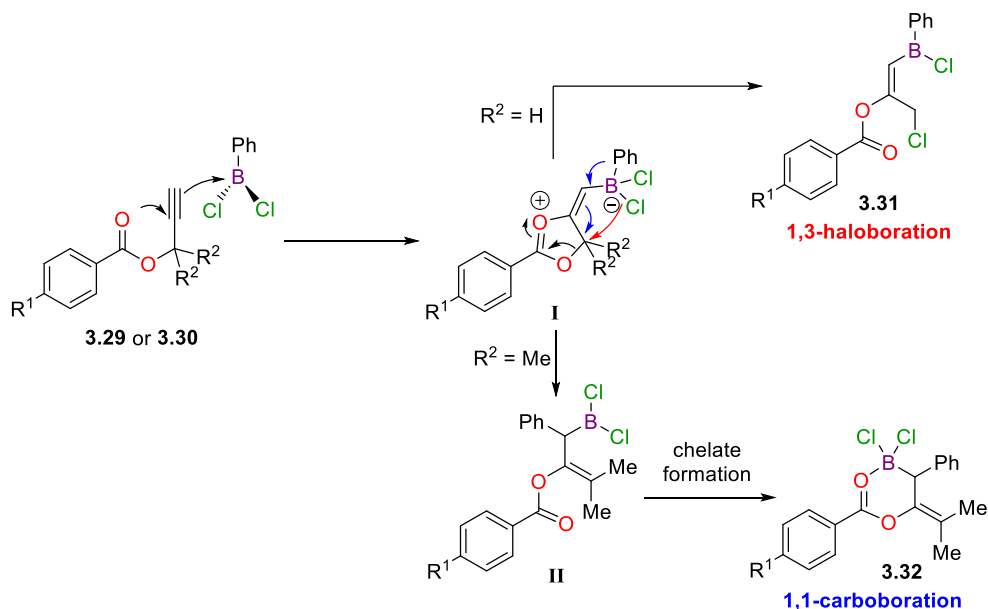


Figure 3.16: Stacked *in situ* spectra for the reaction between propargyl ester **3.29a** or **3.29a^D** with PhBCl_2 .

Comparison of the diverging elementoboration witnessed in this chapter is posited to be as a result of the varying steric encumbrance encountered at the propargylic position. Taking into account the deuterium labelling experiments above, mechanistically it is proposed that initially a 1,2-*trans*-oxyboration reaction occurs to generate the dioxolium borate intermediate (**I**, Scheme 3.21).^[20, 62] From this point, the reaction may proceed one of two ways depending on the group featured on the backbone. If hydrogen atoms occupy the propargylic position, then the partial positive charge that builds here may be quenched by a 1,4-chloride migration to generate the 1,3-haloboration product **3.31** (Scheme 3.21). Counter to this, if more sterically

demanding methyl groups are featured, then the stabilised positive charge cannot be quenched leading to the ring-opening rearrangement leaving a build-up of positive charge on the carbon adjacent to boron. In this case, a 1,2-aryl group migration occurs to furnish the 1,1-carboboration product as the intramolecular chelate **3.32** (Scheme 3.21).



Scheme 3.21: Proposed mechanism for the divergent elementoboration of **3.29** or **3.30** using PhBCl_2 .

3.3 Conclusions

The addition of various boranes to propargyl ester and amide derivatives spawn a variety of differing reactivities stemming from the simple cyclisation of amide derivatives, such as ureas and carbamates, to give oxazolium salts. Alternatively, the use of ester variants undergo the propargyl rearrangement *via* 1,1-carboboration to give 6-membered heterocyclic dioxaborinine products. In the case of $\text{B}(\text{C}_6\text{F}_5)_3$ these reactions simply transfer a synthetically benign C_6F_5 group however, using various heteroleptic boranes, other functionalities have been transferred including alkyl, vinyl and aryl groups. These reagents then possess a multitude of reactive sites including allylboron units, vinyl iodide fragments as well as boronic ester-type functionality all leading to potential further reactivity from allylations, crotylations, Heck couplings or Suzuki-Miyaura cross-coupling. Further to this, the use of commercially available boranes, specifically PhBCl_2 , has been shown to effectively carry out the propargyl rearrangement to garner the dichloroboronate ester. Slight modification of the propargyl reagents that were used completely alters the reactivity with the hitherto

unreported 1,3-haloboration pathway prevailing over the traditional 1,1-carbaboration. These reactions show how versatile boron reagents are in the transformation of simple alkynyl substrates to much more complex and synthetically useful products.

Chapter 4

Formation of 6-Membered Heterocycles *via* Alkyne Activation: Carbon-Element Bond Creation through Cyclisations

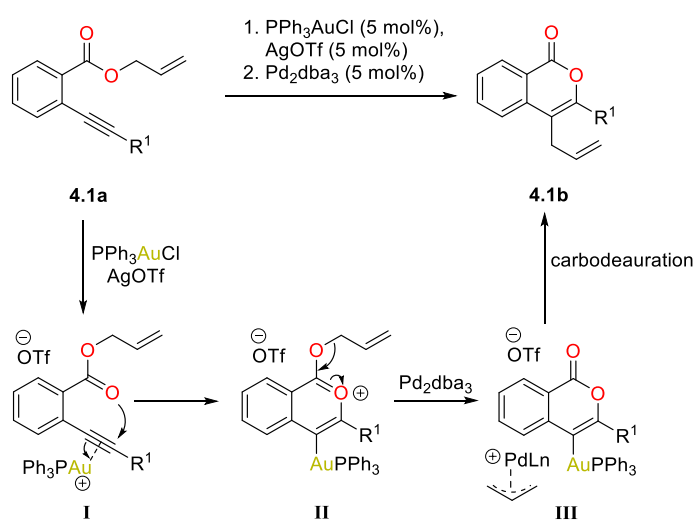
Publications from this work

1. L. C. Wilkins, H. B. Hamilton, B. M. Kariuki, A. S. K. Hashmi, M. M. Hansmann, R. L. Melen,* "Lewis Acid-Base 1,2-Addition Reactions: Synthesis of Pyrylium Borates from En-ynoate Precursors", *Dalton Trans.* **2016**, 45, 5929.
2. L. C. Wilkins, B. A. R. Günther, M. Walther, J. R. Lawson, T. Wirth, R. L. Melen,* "Contrasting Frustrated Lewis Pair Reactivity Using Selenium and Boron-Based Lewis Acids", *Angew. Chem., Int. Ed.* **2016**, 55, 11292.
3. Y. Soltani,[†] L. C. Wilkins,[†] R. L. Melen,* "Stoichiometric and Catalytic C–C and C–H Bond Formation with B(C₆F₅)₃ *via* Cationic Intermediates", *Angew. Chem. Int. Ed.* **2017**, 56, 11995. [†]equal contribution.

4.1 Introduction

The use of boron Lewis acids in cyclisation reactions has seen exceptional uptake in the synthesis of a vast range of compounds such as many common heterocyclic motifs seen in a number of biologically active compounds specifically pyrones, isocoumarins and pyryliums. These compounds are of particular interest due to their wide-ranging physicochemical properties,^[78] making them ideal candidates for antimicrobial,^[79] anti-inflammatory,^[80] antibiotic,^[81] antiviral,^[82] and antispasmodic^[83] agents. Additionally, there are many recorded cases where they also act as a non-steroidal antagonist to a number of androgen^[84] or pregnane X receptors.^[85] Of equal interest is their use as enzyme inhibitors such as that of serine proteases.^[86] Due to their plethora of applications,^[86] many synthetic methodologies have been developed over the past few decades from intermolecular approaches such as cascade reactions of alkynes with propiolic acids or esters using late transition metal catalysts such as ruthenium^[87] catalysts or a more elegant gold/silver bimetallic coupling system.^[88] Alternative methods involve ring expansion of β -lactones as well as inverse Diels-Alder-type chemistry based on reports by Boger and Mullican,^[89] which were subsequently expanded by Yamashita *et al.*^[90]

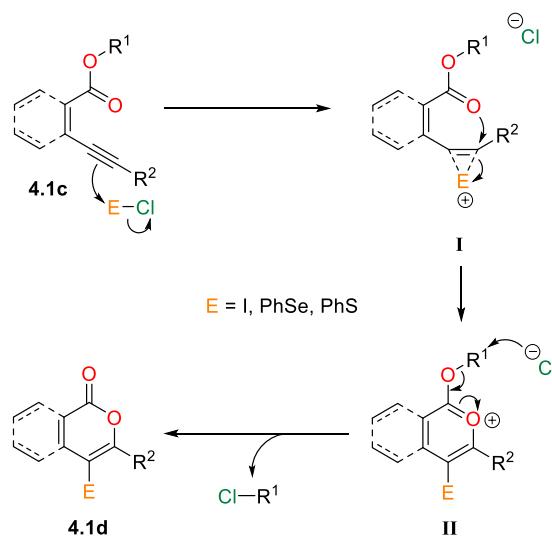
Another approach is the intramolecular cyclisation of esters featuring pendant alkenes or alkynes using π -Lewis acids, for example the bimetallic system set forth by Blum *et al.* whereby a gold/palladium cooperative system was used to affect a tandem cyclisation/alkyl migration to generate complex γ -functionalised isocoumarins (Scheme 4.1).^[91] In this case the π -Lewis acidic Au (I) centre successfully activates the alkyne of **4.1a** toward cyclisation by the ester carbonyl to generate the oxonium triflate ion pair intermediate **II**. The activated ester substituent is then primed to undergo a carbodeauration mechanism *via* the η -3 allyl palladium intermediate **III** to furnish the final substituted product **4.1b** using a relatively low catalyst loading of 5 mol% with excellent isolated yields of 83–98%.



Scheme 4.1: Dual catalytic cyclisation/allyl transfer mechanism using a bimetallic catalyst.

While the use of transition metals in this sector has seen extensive application, other groups have dedicated their research to main group alternatives. One of the prototypical examples is that of Gandour *et al.* whereby an electrophilic bromonium ion is generated *in situ* which was able to affect a formal 6-*endo-dig* cyclisation of intramolecular alkynyl esters to the corresponding bromo-functionalised isocoumarin.^[92] This was then extended by Larock *et al.* where other main group electrophiles such phenylselenenyl chloride, phenylsulfenylchloride and iodine monochloride were used to affect the analogous transformation as that set forth by Gandour to generate the respective isocoumarin **4.1d** with concomitant loss of the ester substituent as an alkyl halide (Scheme 4.2).^[93] This reaction was thought to proceed *via* three key steps; 1) activation of the alkyne of **4.1c** to form the cationic η -2 selenonium, sulfonium or iodonium intermediate **I** followed by; 2) nucleophilic attack of the carbonyl oxygen to the activated alkyne through a 6-*endo-dig* cyclisation

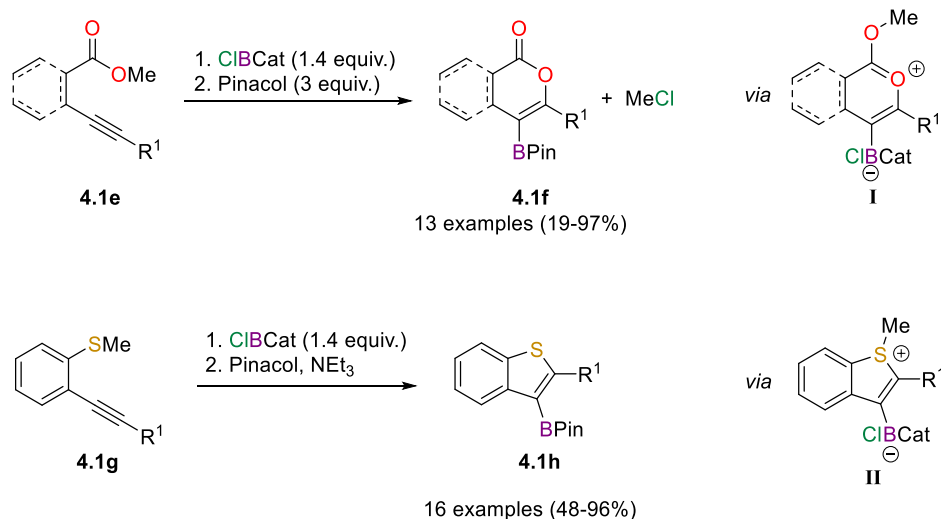
pathway resulting in the pyrylium intermediate **II** and; 3) dealkylation of the ester substituent by the generated halide anion to liberate the γ -functionalised isocoumarin **4.1d** with the simultaneous loss of the alkyl halide by-product (Scheme 4.2)



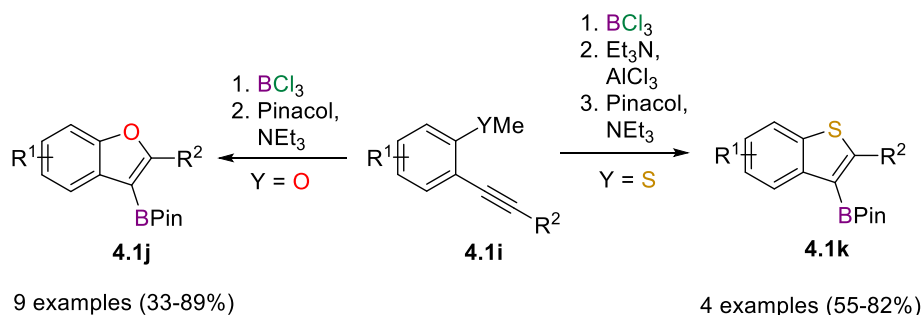
Scheme 4.2: Proposed general mechanism for electrophilic cyclisation of alkynyl esters.

Katzenellenbogen *et al.* also implemented a similar methodology using mercury (II) acetate to promote the cyclisation with successive addition of two equivalents of copper (II) chloride to displace the pendant mercurial group in the γ -position leaving the chlorinated isocoumarin.^[94] While this work further highlights the use of main group compounds in cyclisation reactions, the use of toxic mercury compounds combined with the use of superstoichiometric amounts of reagent make this route less attractive to the synthetic chemist.

In a bid to focus on metal-free cyclisation methods Blum and co-workers, building on work outlined later in this chapter (see Section 4.2.1) and their own previous findings,^[95] reported the stoichiometric use of *B*-chlorocatechol borane to promote the cyclisation of methyl pent-4-ynoate **4.1e** to their respective lactone products **4.1f** (Scheme 4.3, top). In this instance, the 1,2-*trans*-oxyboration cyclisation forms the pyrylium borate zwitterion which provides a suitable nucleophile in the form of a chloride ion to undergo alkyl abstraction of the ester substituent (**I**, Scheme 4.3).^[96] The intermediate catechol boronate ester was then *trans*-esterified to garner the stable γ -functionalised isocoumarin **4.1f** which provides an excellent scaffold for further derivatisation through Suzuki-Miyaura cross-coupling reactions. The same *B*-chlorocatecholborane reagent was then applied to alkynyl thioethers **4.1g** to furnish the functionalised benzothiophene products **4.1h** in generally good to excellent yields of 48–96% *via* a similar zwitterionic intermediate (**II**, Scheme 4.3).^[97]

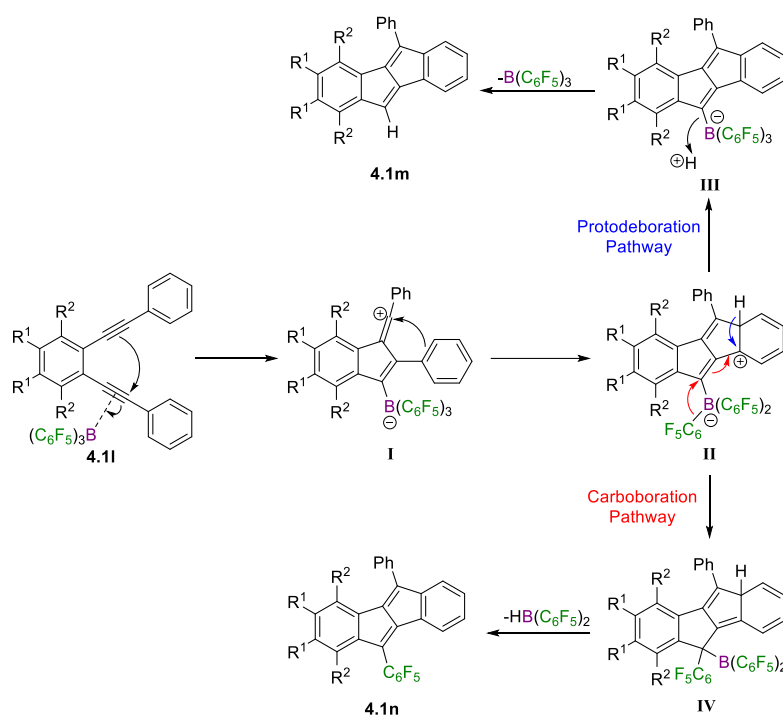
Scheme 4.3: Reactivity of alkynyl methyl esters and thioethers with *B*-chlorocatechol borane.

Ingleson *et al.* showed in simultaneous work that the commercially available boron trichloride was also an extremely useful reagent for the cyclisation of similar alkynyl ethers and thioethers to generate a series of benzofurans and benzothiophenes respectively.^[98] The combination of the alkynyl ethers **4.1i** (Scheme 4.4, Y = O) with this borane led to rapid cyclisation and loss of chloromethane to generate the borylated benzofuran in as little as five minutes. This vinylchloroborane was then esterified due to the inherent instability of the dichloro species to furnish the bench stable vinyl boronate ester (Scheme 4.4), which was subsequently applied to further cross-coupling reactions to generate the arylated benzofuran in a one-pot reaction. This cyclisation methodology could also be applied to thioethers **4.1i** (Scheme 4.4, Y = S) however, the demethylation step did not occur under the standard conditions. In this case, the addition of NEt₃ and AlCl₃ was necessary to drive the reaction forward with the products **4.1k** being isolated in 55–82% yield after conversion to the pinacol boronate ester.



Scheme 4.4: Oxy- and thio-boration using boron trichloride.

Interesting work by Erker *et al.* further demonstrates the use of boron Lewis acids in alkyne activation through annulation reactions of diynes to generate a number of dibenzopentalenes. Initial reactions using the tetrafluoro derivative of **4.11** ($R^1 = R^2 = F$, Scheme 4.5) showed how a 1:1 amount of $B(C_6F_5)_3$ could induce the intramolecular cyclisation reaction to garner the requisite 6,5,5,6-tetracyclic system **4.1m** in moderately good yields of 58%. Altering the backbone of the diyne to include either protons or methyl groups in the R^1 position instead of the tetrafluoro motif allowed a different reaction pathway to ensue. In these cases, a mixture of products were recorded, most notably **4.1m** which is the analogous product to that observed before, and the monoarylated species **4.1n**. Mechanistically it was proposed that the initial tandem activation of the diyne leads to the intermediate **I** (Scheme 4.5), which can then follow one of two paths. Either protodeboration occurs to generate the final product *via* the vinylborate intermediate **III** or double bond migration followed by carboboration may occur followed by deborylation to the C_6F_5 functionalised product **4.1n**.



Scheme 4.5: Synthesis of dibenzopentalenes using $B(C_6F_5)_3$.

Research outlined earlier in Chapters 2 and 3, as well as examples in the literature, have shown how the strong Lewis acid $B(C_6F_5)_3$ is capable of operating as a π -Lewis acid in a range of transformations such as *trans*-oxyborations,^[36d] annulations^[99] and cycloaminations^[28a] *inter alia*,^[42, 63, 100] in essence mimicking the reactivity of late coinage and platinum group metals. As $B(C_6F_5)_3$ is characterised as

a particularly hard Lewis acid, such high reactivity with both hard Lewis basic carbonyls as well as soft π -Lewis basic centres is an interesting phenomena. This 'dual activity' is not too dissimilar from research by Takaki *et al.* whereby a bismuth (III) acetate catalyst is used in similar cyclisations to yield functionalised pyrones however, this softer Lewis acid was described as activating the ester and alkyne simultaneously in a bifunctional manner however, due to the limited availability of the vacant p_z orbital on boron, only one activation mode may be in operation at any moment.^[101]

4.1.1 Aims of This Chapter

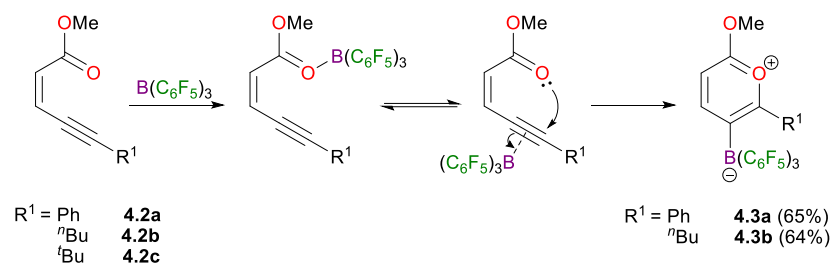
There are numerous examples of the strong Lewis acid $B(C_6F_5)_3$ acting as a hard Lewis acid in the activation of various substrates through a σ -binding mode however, π -activation was observed less frequently until recent years. This chapter exploits new findings where $B(C_6F_5)_3$ is effective in 1,2-addition reactions across alkynes to form new heterocyclic products such as pyryliums, indenenes, pyrones and isocoumarins. Using this method, this chapter explores new methods to form C–H, C–C and C–O bonds as well as demonstrating this boranes application in tandem reactivity. As a contrast, softer period 4 Lewis acids will also be compared to the reactivity of their lighter group 13 congeners.

4.2 Results and Discussion

4.2.1 Formation of Zwitterionic Pyrylium Borates using $B(C_6F_5)_3$

Reagents featuring alkynyl and carbonyl functionalities tethered by a vinylic backbone were targeted as potentially useful starting materials in cyclisation reactions due to the driving force of forming a 6π aromatic pyrylium species. Therefore, enynoates **4.2a–c** were synthesised by literature methods^[102] with subsequent reaction with the strong Lewis acid $B(C_6F_5)_3$ which resulted in a rapid colour change from off-yellow to a dark orange/red colour at ambient temperatures. *In situ* multinuclear NMR spectroscopic studies indicated that a new product had been formed in as little as 1 h in quantitative conversion. Storing a saturated CH_2Cl_2 /hexane solution at $-40\text{ }^\circ\text{C}$ resulted in a crop of colourless crystals that could be isolated in 65% and 64% yield for **4.3a** and **4.3b** respectively. Interrogation of the NMR spectroscopic data indicated that a 6-*endo-dig* cyclisation reaction had occurred to generate the 6-membered pyrylium borate derivatives (Scheme 4.6). This was

evidenced by a distinct downfield shift of the vinylic proton on the β -carbon to the ester ($\delta = 6.37$ to 8.65 ppm (**4.3a**), $\delta = 6.15$ to 8.47 ppm (**4.3b**)). Due to the sterically demanding borane used in this transformation, restricted movement of the R^1 substituent is seen upon cyclisation (supported by the solid-state structure, see below). This was the most pronounced when looking at the ^1H NMR spectrum of **4.3b** whereby the two proximal methylene unit of the ^nBu unit are inequivalent, presenting as two broad 1:1 singlets at $\delta = 1.43$ and 0.64 ppm.



Scheme 4.6: Proposed mechanistic pathway of the reaction between $\text{B}(\text{C}_6\text{F}_5)_3$ and methyl enynoates.

This restricted movement was also observed in the ^{19}F NMR spectra whereby the 'normal' 2:1:2 *o*-F:*p*-F:*m*-F motif is replaced by a more complex picture (Figure 4.1). In the case of **4.3a**, eight peaks are witnessed for the respective *ortho* ($\delta = -128.6$ (1F), -130.3 (4F) and -131.1 ppm (1F)), *para* ($\delta = -159.2$ (1F) and -160.0 ppm (2F)) and *meta* ($\delta = -163.5$ (1F), -164.7 (1F) and -165.4 ppm (4F)) fluorine atoms. This pattern indicates that two of the perfluorophenyl rings are equivalent and one inequivalent which contrasts with the ^nBu derivative which is far more complex. For **4.3b**, fifteen resonances are seen in total for the *ortho* ($\delta = -128.2$ to -135.0 ppm (6F)), *para* ($\delta = -158.9$ to -159.9 ppm (3F)) and *meta* ($\delta = -162.8$ to -165.3 ppm (6F)) fluorine atoms with each fluorine atom being chemically inequivalent. Perhaps the most indicative evidence for the formation of the pyrylium borate scaffold was the sharp singlet resonance seen in the ^{11}B NMR at $\delta = -14.4$ and -14.5 ppm for **4.3a** and **4.3b** respectively which is indicative of the formation of formally four-coordinate vinyl borate species.^[39a, 103] Attempts to use variable temperature NMR experiments to overcome the rotational energy barrier were unfortunately met with little success as heating a d_8 -toluene solution of **4.3b** to 80 °C resulted in no coalescence of the proximal methylene protons in the ^1H NMR spectrum.

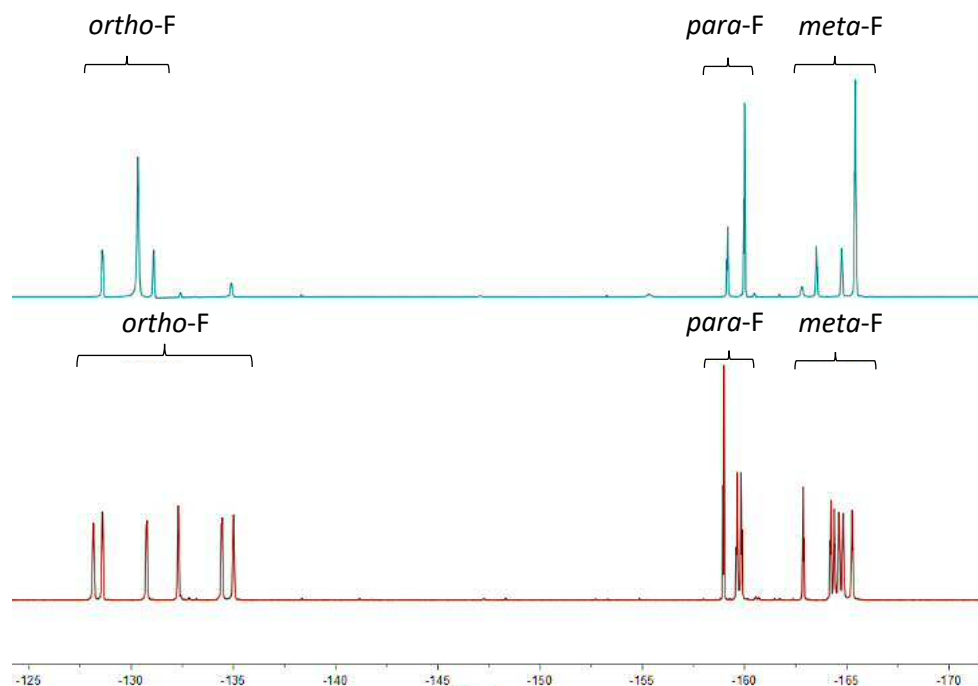


Figure 4.1: Stacked ^{19}F NMR spectra of **4.3a** (top) and **4.3b** (bottom).

Additionally, no coalescence of the fluorine resonances in the ^{19}F NMR spectrum was apparent indicating that a substantial energy barrier is present in the rotation of the C_6F_5 -groups and the R^1 substituent. With regard to steric occlusion in the R^1 position, if a more sterically demanding $t\text{Bu}$ group is included, then reactivity is completely quenched as the Lewis acid/base adduct between the carbonyl and borane predominates.

As stated, both structures could be isolated as single crystals which could be measured *via* X-ray diffraction to unambiguously verify the formation of the 6-membered heterocyclic pyrylium borate **4.3a–b** (Figure 4.2). As seen in the solid-state structure for **4.3a** where $\text{R}^1 = \text{Ph}$, an extended conjugated system is prevented as the phenyl unit rotates out of the plane of aromatic pyrylium ring by $58.4(2)^\circ$. This is in contrast to the cationic 5-membered dioxolium examples whereby coplanar orbital overlap is necessary between the $[\text{CO}_2]^+$ fragment and the adjoining aromatic substituent to stabilise the positive charge.^[62] As proposed earlier it is presumed that steric congestion about the boron centre is the chief factor for this phenyl group rotation, which is clearly evident in the space-filling models (Figure 4.3). In the solid-state there appears to be a displaced π -stacking interaction between this rotated phenyl substituent and one of the perfluorophenyl groups on boron with a centroid \cdots centroid distance of $3.6421(10)$ Å. This stacking leads to an eclipsed geometry of the $\text{B}-\text{C}_6\text{F}_5$ bond and the adjacent $\text{C}-\text{C}_6\text{H}_5$ bond which deviate by a mere $0.11(14)^\circ$. Conversely, **4.3b** displays lower symmetry, consistent with the NMR

spectroscopic data, giving a B–C₆F₅/C–ⁿBu deviation of 49.9(2)° showing the intersection of the ⁿBu group between two perfluorophenyl rings which is again, more evident in the space filling model (Figure 4.3). Other metric parameters of the two structures **4.3a–b** are similar to one another with C–C bond lengths in the main residue of 1.372(3)–1.410(3) Å (Table 4.1) being intermediate between formal single (ca. 1.53 Å) and double (ca. 1.33 Å) bonds, and consistent with aromatic systems (ca. 1.38 Å).^[65] Additionally, both C–O bonds *exo* and *endo* to the ring system are statistically equivalent within error (1.303(2)–1.316(2) Å), again intermediate to formal single and double C–O bond lengths (ca. 1.42 and 1.23 Å respectively).^[65] Further to this, the planarity of the heterocycle could be examined through root mean square (RMS) deviation calculations which show the 6-membered cyclic structure being near perfectly planar with RMS values of 0.023 (**4.3a**) and 0.013 (**4.3b**).

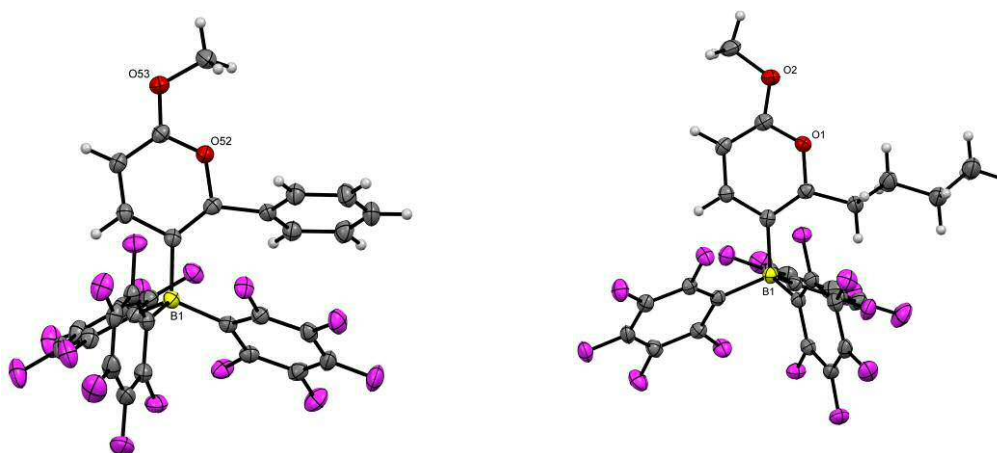


Figure 4.2: Solid-state structures of **4.3a** (left) and **4.3b** (right). C: grey, O: red, B: yellow-green, F: pink, H: white. Thermal ellipsoids shown at 50% probability.

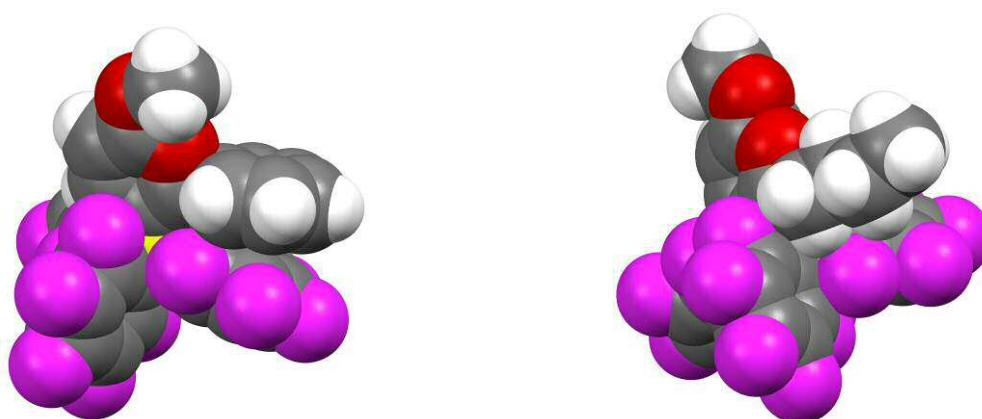


Figure 4.3: Space-filling representation of structures **4.3a** (left) and **4.3b** (right). C: grey, O: red, B: yellow-green, F: pink, H: white.

Computational studies were then undertaken to further investigate these pyrylium structures through natural bond order (NBO)^[37] and nucleus independent chemical

shift analysis (NICS(0)) using the B3LYP/6-311G* level of theory.^[104] The converged energy minima structure agrees well with metrics obtained through experimental means with similar bond lengths being observed between theoretical and experimental methods (Table 4.1). NBO analysis shows clear delocalisation about the heterocyclic ring however, a more localised cationic motif is observed about the CO₂ fragment with Wiberg bond indices for each C–O bond being similar (Figure 4.4). Due to the increased electronegativity of the oxygen atoms, a strong bond polarisation of the σ -system is observed through large partial charge build up on the carbon atoms bonded to oxygen in addition to the oxygen atoms themselves. This accumulation of positive charge is predominantly based on the carbon bonded to both oxygens however, second order perturbation analysis indicates how some of this effect is mitigated through π -back donation to the carbocationic centre. NICS(0) calculations clearly demonstrated that **4.3a** (-3.93 ppm) and **4.3b** (-4.86 ppm) are both aromatic although, are both markedly less aromatic in character compared to the benzene with a NICS(0) chemical shift of -8.91 ppm (Figure 4.5). This clearly indicates that the inclusion of a secondary oxygen atom external to the pyrylium ring disturbs the overall aromaticity, which is congruent with other similar systems.^[105]

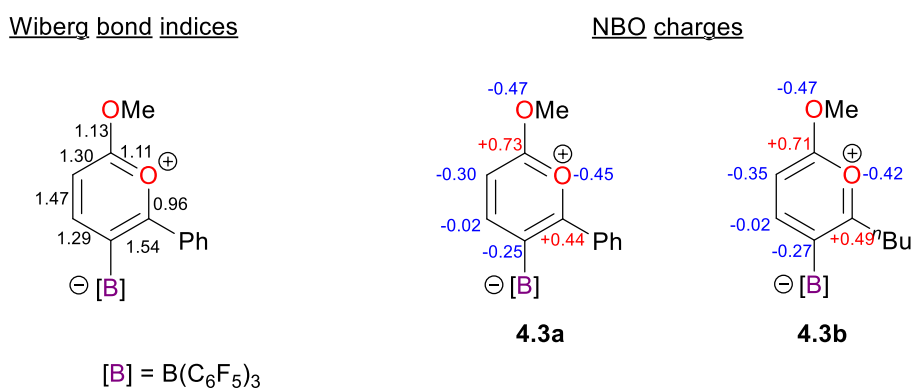


Figure 4.4: Wiberg bond indices for **4.3a** and NBO charges for the pyrylium cations **4.3a** and **4.3b**.

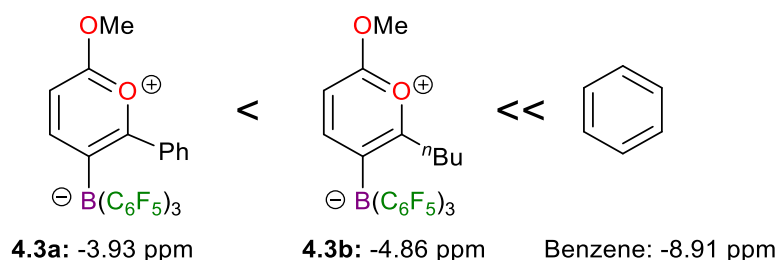
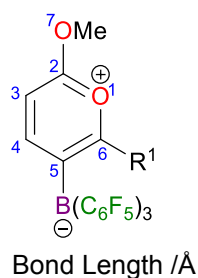


Figure 4.5: Aromaticity of compounds **4.3** relative to benzene using NICS(0) calculations.

Table 4.1: Experimental and calculated bond lengths for **4.3a** and **4.3b**

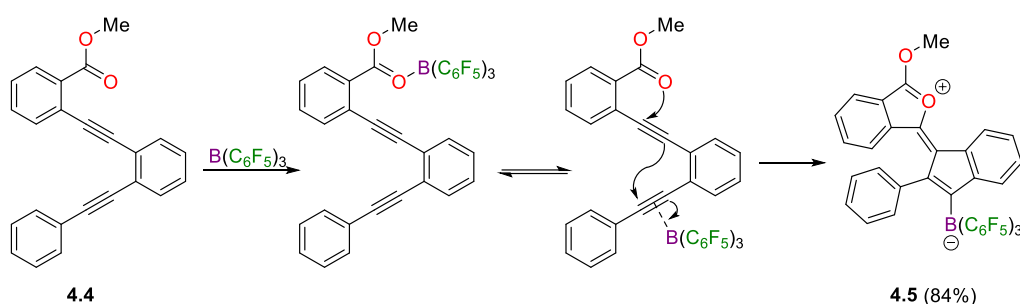
Bond	4.3a		4.3b	
	Experimental	Calculated	Experimental	Calculated
C ² –C ³	1.371(3)	1.386	1.374(3)	1.378
C ³ –C ⁴	1.362(3)	1.384	1.382(3)	1.390
C ⁴ –C ⁵	1.430(2)	1.423	1.410(3)	1.410
C ⁵ –C ⁶	1.361(2)	1.377	1.372(3)	1.384
C ² –O ¹	1.316(2)	1.319	1.316(3)	1.320
C ⁶ –O ¹	1.404(2)	1.391	1.370(3)	1.370
C ² –O ⁷	1.306(2)	1.316	1.311(3)	1.316
C ⁵ –B	1.665(2)	1.671	1.657(3)	1.673

This reaction is assumed to proceed *via* a 1,2-addition of the Lewis basic carbonyl oxygen and the Lewis acidic borane to the alkyne in a 6-*endo-dig* cyclisation mechanism reminiscent to that observed in the literature. [20, 39a, 62, 95-96, 106] It was seen that the formation of the 6-membered, planar, 6 π Hückel aromatic system is preferred over the alternative 5-*exo-dig* cyclisation and the 1,1-carboboration pathways which are also prevalent in the literature.^[75] Indeed, the resultant furanium derivative as a result of a potential 5-*exo-dig* cyclisation is considered to be less stable than the pyrylium counterpart however, examples of such cationic motifs do exist (*vide infra*).^[107]

4.2.2 Divergent Reactivity of Hard and Soft Lewis Acids: 6-*endo-dig* vs. 5-*exo-dig*

With the previous work into cyclisations of enynyl esters to hand, similar reactivity was applied to the conjugated diynyl methyl ester **4.4**. Upon mixing this substrate with B(C₆F₅)₃ in a 1:1 ratio, an immediate colour change was noted, changing from a yellow/orange solution to dark green from which a crop of red block-shaped crystals could be harvested in very good yields of 84%. Single crystal X-ray diffraction studies of these crystals uncovered the solid-state structure to be that of the extensively

conjugated olefin bridged indene-benzofuranium zwitterion product **4.5** (Scheme 4.7, Figure 4.6). It is posited that, contrary to the pyrylium scaffolds witnessed in Section 4.2, a tandem *5-exo-dig*/*5-endo-dig* tandem cyclisation reaction occurs through π -activation of the sterically less encumbered alkyne distal to the ester. This triggers the nucleophilic attack of the proximal alkyne by the carbonyl oxygen, which then itself acts as the nucleophile, undergoing a 1,2-trans addition to the distal alkyne (Scheme 4.7). It is of note that while a gamut of cascade reactions are known within the biomedical field, the use of Lewis acidic boranes in similar domino annulation reactions are more rare with only a few examples existing in the literature.^[108]



Scheme 4.7: Reaction of **4.4** with $B(C_6F_5)_3$.

When scrutinising the solid-state structure, it is seen that while the indene and furan subunits are adjoined through an olefin bridge and are thus conjugated, they are not coplanar in the solid-state with a twist angle of 17.99(11). Interestingly, a similar trope to the pyrylium borate products (see Section 4.2.1) is observed in this structure whereby the steric occlusion brought about by the juxtaposition of the borane and olefin phenyl substituent causes a loss of symmetry as observed in the ^{19}F NMR spectrum. Alongside this, π -stacking of the phenyl substituent and one of the C_6F_5 rings occurs adopting a near coplanar geometry with a fold angle of just 12.52(9) $^\circ$. This π -stacking is shown to have a centroid \cdots centroid distance of 3.4785(16) Å which is slightly shorter than that exhibited by **4.3a** mentioned in Section 4.2.1.^[39b]

Bulk sample analysis *via* multinuclear NMR spectroscopy agreed with the proposed structure of **4.5** with the ^{11}B NMR spectrum displaying a sharp singlet resonance at $\delta = -15.8$ ppm, typical of such four-coordinate vinyl borates.^[36b] As indicated with the solid-state structure, the steric encumbrance brought about by the bulky Lewis acid causes restricted rotation of the perfluorophenyl groups leading to chemical inequivalence hence, a more complex ^{19}F NMR spectrum than initially anticipated. Three discrete resonances are observed in the ^{19}F NMR spectrum for both the *para*- ($\delta = -160.8 - -162.7$ ppm (3F)) and *meta*- ($\delta = -164.9 - -166.6$ ppm

(6F)) fluorine atoms with each of the *ortho*-fluorine atoms also being inequivalent, resulting in six distinct signals ($\delta = -123.0 - -136.2$ ppm (6F)). In a similar fashion to the pyrylium borate products **4.3**, the space-filling model elucidates the steric encumbrance about the lower part of the molecule where the indene subunit interlocks between two of the C₆F₅-rings as well as the π -stacking motif of the remaining C₆F₅-ring and the phenyl substituent (Figure 4.6).

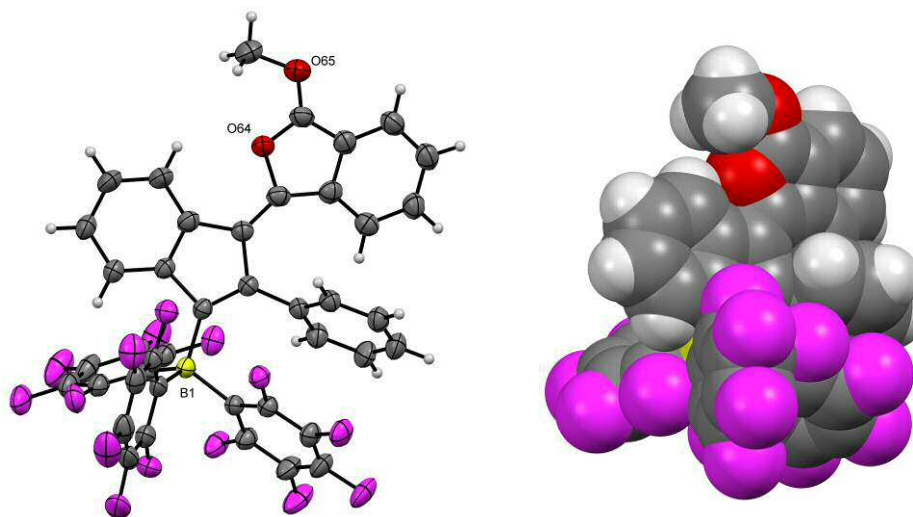


Figure 4.6: Solid-state structure of **4.5** (left). C: grey, H: white, O: red, B: yellow-green, F: pink. Thermal ellipsoids shown at 50% probability. Space-filling model of **4.5** (right).

To contrast the reactivity of the archetypal hard Lewis acid, B(C₆F₅)₃, the softer phenylselenenylchloride was used as it has been utilised in similar cyclisations to form the corresponding selenolactones through a selenirenium intermediate.^[109] Upon mixing the same diyne starting material **4.4** with PhSeCl in a 1:1 ratio, instead of the cascade reaction observed with B(C₆F₅)₃, the monocyclisation reaction with the alkyne proximal to the ester took place, garnering the isocoumarin appended selenyl ether in 68% yield, leaving the distal alkyne untouched (Scheme 4.8). This could be verified by the loss of the diagnostic methyl group of the ester moiety which appears in the ¹H NMR spectrum at $\delta = 3.89$ ppm in **4.6** alongside the downfield shift of the aromatic protons on the phenyl backbone. In an attempt to incorporate both Lewis acidic centres into the product, the isocoumarin **4.6** was then reacted with one equivalent of B(C₆F₅)₃ to promote π -activation of the second alkyne subunit. Unfortunately, this second activation was not observed with the simple hard Lewis acid adduct between the carbonyl oxygen and borane prevailing (**4.7**, Scheme 4.8). This could be readily identified through the ¹¹B NMR spectrum revealing a broad singlet at $\delta = -0.5$ ppm alongside a pattern in the ¹⁹F NMR spectrum in which the *para*- and

meta-fluorine resonances do not indicate formal quaternisation as $\Delta\delta_{p-m} = ca. 8$ ppm rather than that of $\Delta\delta_{p-m} = ca. 3$ ppm for formal anionic borate species.^[67]

This was further corroborated through X-ray crystallographic studies which clearly identified the structure to be that of the Lewis adduct (Figure 4.7). This is not dissimilar to other systems whereby extended chain alkynyl benzoates prefer this adduct formation over alkyne activation.^[36c] Interestingly though, heating a toluene solution of **4.6** to reflux for several days still did not produce any indication of alkyne activation with the ⁷⁷Se NMR spectrum retaining the singlet resonance at $\delta = 289.5$ ppm which is comparable to similar selanyl compounds reported in the literature.^[110]

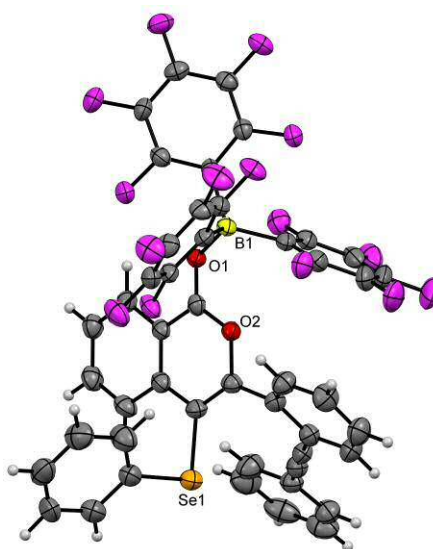


Figure 4.7: Solid-state structure of **4.6**. C: grey, H: white, O: red, B: yellow-green, F: pink, Se: orange. Thermal ellipsoids shown at 50% probability.

In light of this reluctance to react with a hard Lewis acid, a further two equivalents of PhSeCl were added to the isocoumarin intermediate **4.6** (Scheme 4.8). Fortunately, the solid-state structure could be elucidated by X-ray crystallography of crystals which were isolated in 37% yield by slow evaporation of the solvent (Figure 4.8). The structure was that of a tetracyclic conjugated salt **4.7** which comprised a selenium atom in three separate environments; 1) a cationic selenonium; 2) neutral selene and 3) anionic selenate counterion. Due to poor solubility of the salt, the ⁷⁷Se NMR spectrum could not be measured however, both high resolution mass spectrometry and elemental analysis support the proposed product.

With regard to the solid-state structure of **4.7**, while the isocoumarin scaffold is essentially planar, the selenocycle disrupts this planarity through the adoption of a tetragonal geometry consisting of C–Se–C bond angles of $96.57(12)^\circ$ and $100.86(12)^\circ$. This is further evidenced when looking at the intracyclic C–Se bond

lengths of 1.912(2)–1.939(3) Å which are consistent with Se–C single bonds, indicating that although the tetracyclic unit is fully conjugated, the aromaticity does not extend across the entire structure. Remarkably, there have been very few reports of the [PhSeCl₂][−] counterion in the literature however, the metrics that are observed in this work are similar to those encountered previously with the counterion adopting a T-shape geometry featuring axial chloride atoms.^[111] As expected, the C–Se–Cl bond angles are near perpendicular (90.47(10)° and 90.72(10)°) with Se–Cl bond lengths of lengths 2.445(1) and 2.457(1) Å.

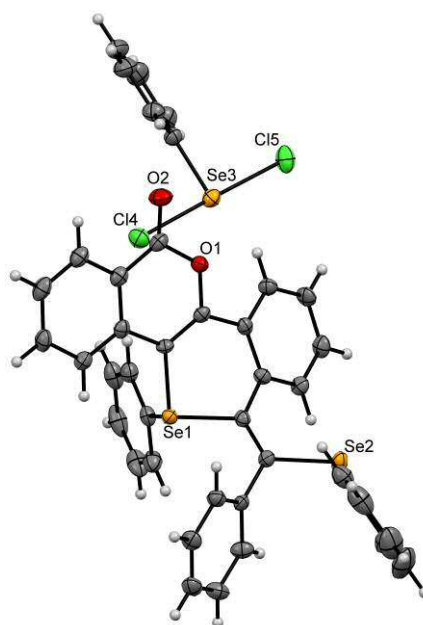
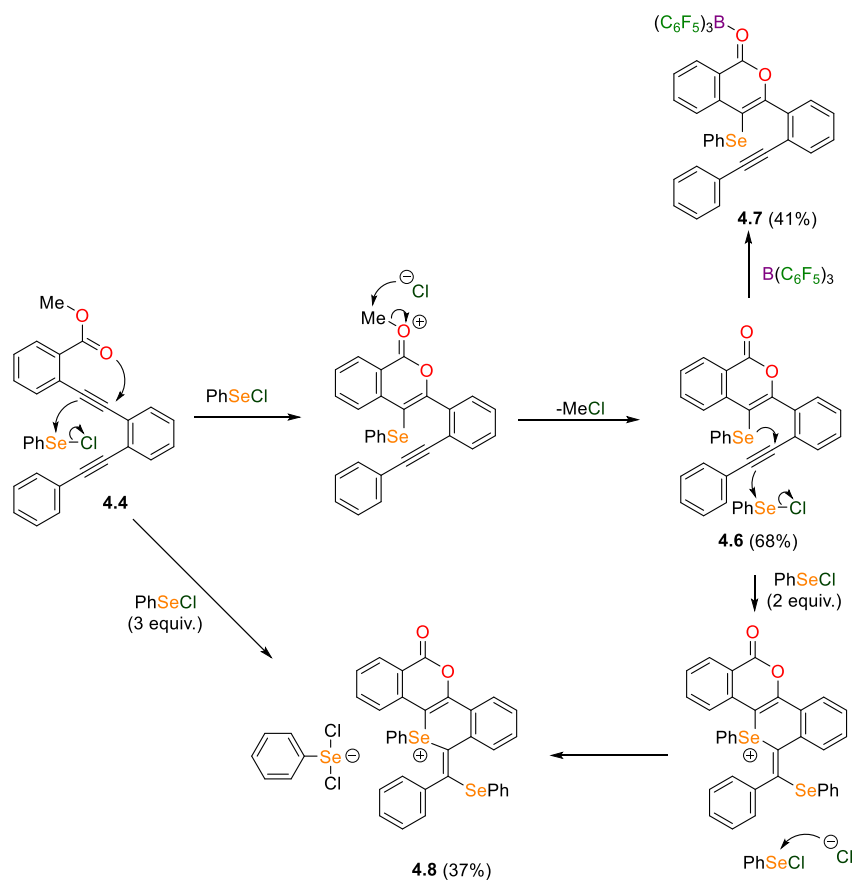


Figure 4.8: Solid-state structure of **4.7**. Chloroform solvate molecule omitted for clarity. C: grey, H: white, O: red, Se: orange. Thermal ellipsoids shown at 50% probability.

It was then seen as to whether the tetracyclic salt **4.7** could be formed in a single step through the addition of three equivalents of PhSeCl to the diyne precursor **4.4**. Indeed, multinuclear spectroscopy could confirm the formation of **4.7** along with the concomitant loss of chloromethane ($\delta_{\text{H}} = 3.05$ ppm, $\delta_{\text{C}} = 21.5$ ppm).^[112] Mechanistic considerations propose that the selenium reagent initially acts as the electrophile to activate the alkyne forming the aforementioned selenirenium cation intermediate which undergoes nucleophilic attack by the carbonyl oxygen. Once the intermediate salt is formed (**I**, Scheme 4.8), the chloride ion then dealkylates the ester forming chloromethane and the selenyl isocoumarin **4.6**. This type of reactivity has been applied more recently to other cyclisation reactions, such as those highlighted by Blum and Ingleson in the formation of benzofurans and benzothiophenes.^[97-98] A second PhSeCl equivalent then activates the distal alkyne with the isocoumarin

tethered selenyl ether acting as the nucleophile in an FLP-type 1,2-*trans*-addition step with the third equivalent of PhSeCl accepting the chloride ion to generate the $[\text{PhSeCl}_2]^-$ anion alongside the tetracyclic product **4.8** (Scheme 4.8).



Scheme 4.8: Reactions of **1** with phenylselenenyl chloride (PhSeCl) to generate **4.6–4.8**.

4.2.3 Stoichiometric and Catalytic Pyrone and Isocoumarin Formation via C–H and C–C Bond Formation

The substitution of different groups in the R^1 position of various alkynyl acids (**4.9**) and esters (**4.10**) was then tested to see whether the requisite pyrone or isocoumarin product could be formed. To that end, various alkynyl carboxylic acid and esters (Figure 4.9) which were prepared by literature methods^[101] were exposed to $\text{B}(\text{C}_6\text{F}_5)_3$ to promote the 6-*endo-dig* cyclisation, similar to that observed earlier with the pyrylium borates (see section 4.2.1). Indeed, the exposure of neutral and electron rich alkynyl carboxylic acids **4.9a–c** produced the pyrones **4.11a–c** in near quantitative conversions within 30 minutes as noted in the *in situ* NMR spectra with excellent isolated yields between 93% and 96% (Scheme 4.9). When the dimethyl backbone was altered to include a phenyl scaffold, the reactivity was hindered with the

corresponding isocoumarins **4.11d–e** being isolated in only 45 and 52% yield respectively. Nevertheless, storing a saturated CH_2Cl_2 /hexane solution of **4.11a** and **4.11d–e** at $-40\text{ }^\circ\text{C}$ resulted in a crop of colourless crystals which were suitable for single crystal X-ray diffraction (Figure 4.10)

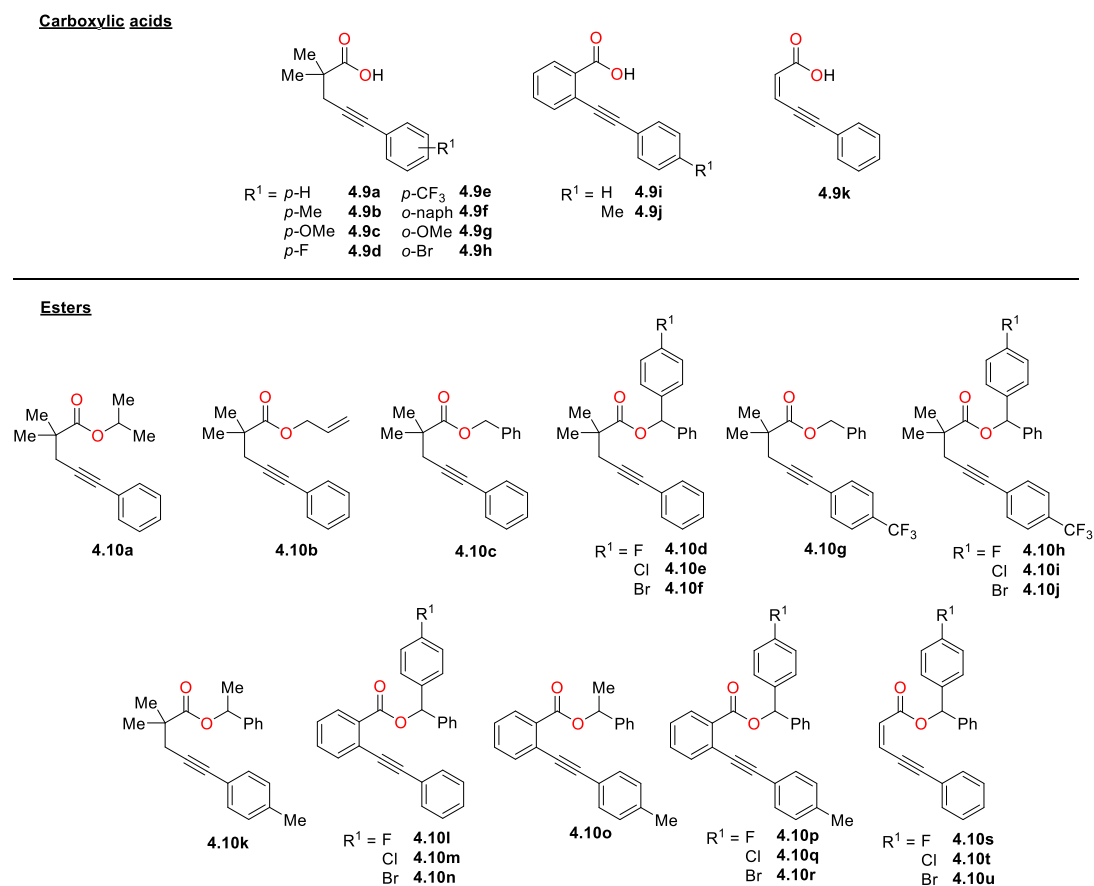


Figure 4.9: Substrates **4.9** and **4.10** used in this study.

The results from the carboxylic acid reagents were particularly noteworthy as boranes, $\text{B}(\text{C}_6\text{F}_5)_3$ in particular, tend to undergo various decomposition pathways such as protonolysis when exposed to Brønsted acids. There are however a very limited number of examples of their successful reactivity, for example $\text{B}(\text{C}_6\text{F}_5)_3$ catalysed deoxygenations in addition to structural investigations.^[113] Unfortunately, electron poor or *ortho*-substituted alkynyl carboxylic acids **4.9d–h** were less successful with the target molecule only being observed as the minor component of an otherwise intractable mixture of products.

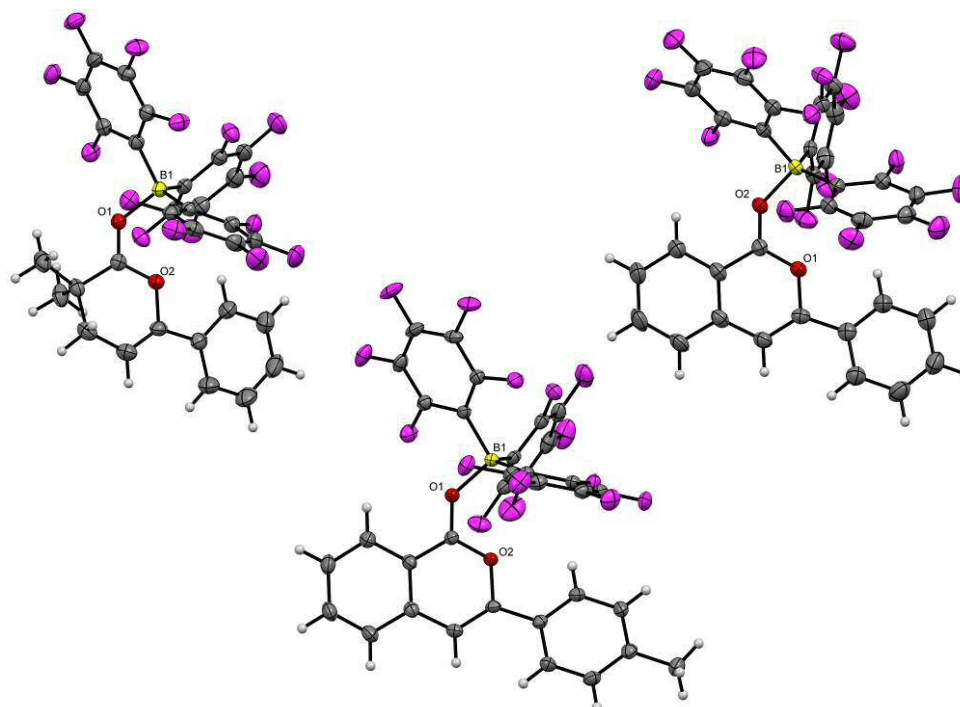


Figure 4.10: Solid-state structure of compound **4.11a**, **4.11d** and **4.11e**. C: grey, H: white, B: yellow-green, O: red, F: pink. Thermal ellipsoids shown at 50% probability.

With this, the R^1 substituent was then exchanged for various ester groups which led to more intricate pyrone and isocoumarin products resulting from the cyclisation process (Scheme 4.9). Whilst it was hoped that simple isopropyl or allyl groups appended to the ester could be transferred (**4.10a–b**), no cyclised product was formed with the Lewis adduct prevailing in the reaction mixture. Fortuitously, altering the ester substituent for a benzyl, α -methylbenzyl or benzhydryl derivative spurred the same cyclisation witnessed with the carboxylic acids whereby the ester substituent is transferred to the γ -position of the lactone with the borane being bound to the carbonyl oxygen. While the majority of products featuring a phenyl or *p*-tolyl group in the R^2 position produced the pyrone and isocoumarin derivatives in very good to excellent yields (81–97%) in as little as 30 minutes, the formation of **4.11f** and **4.11k** took considerably longer at 24 h however, excellent yields were also reported at 91% and 92% respectively. To confirm the anticipated structure, the solid-state structures could be elucidated for **4.11h–i**, **4.11m** and **4.11v** clearly showing the γ -functionalised heterocycle (Figure 4.11). Identifiable spectroscopic changes include the upfield shift of the benzhydryl proton from $\delta = ca.$ 6.8 ppm to $\delta = 5.0$ ppm consistent with the migration away from the electron withdrawing ester oxygen. Additionally, the ^{11}B NMR spectra showed the characteristic broad singlet at $\delta = 0.0$ ppm for the B–O adduct

formation. One of the most indicative changes was the loss of the alkyne resonances in the ^{13}C NMR between $\delta = \text{ca. } 81\text{--}89$ ppm alongside the appearance of new vinylic signals in the region between $\delta = \text{ca. } 115\text{--}140$ ppm.

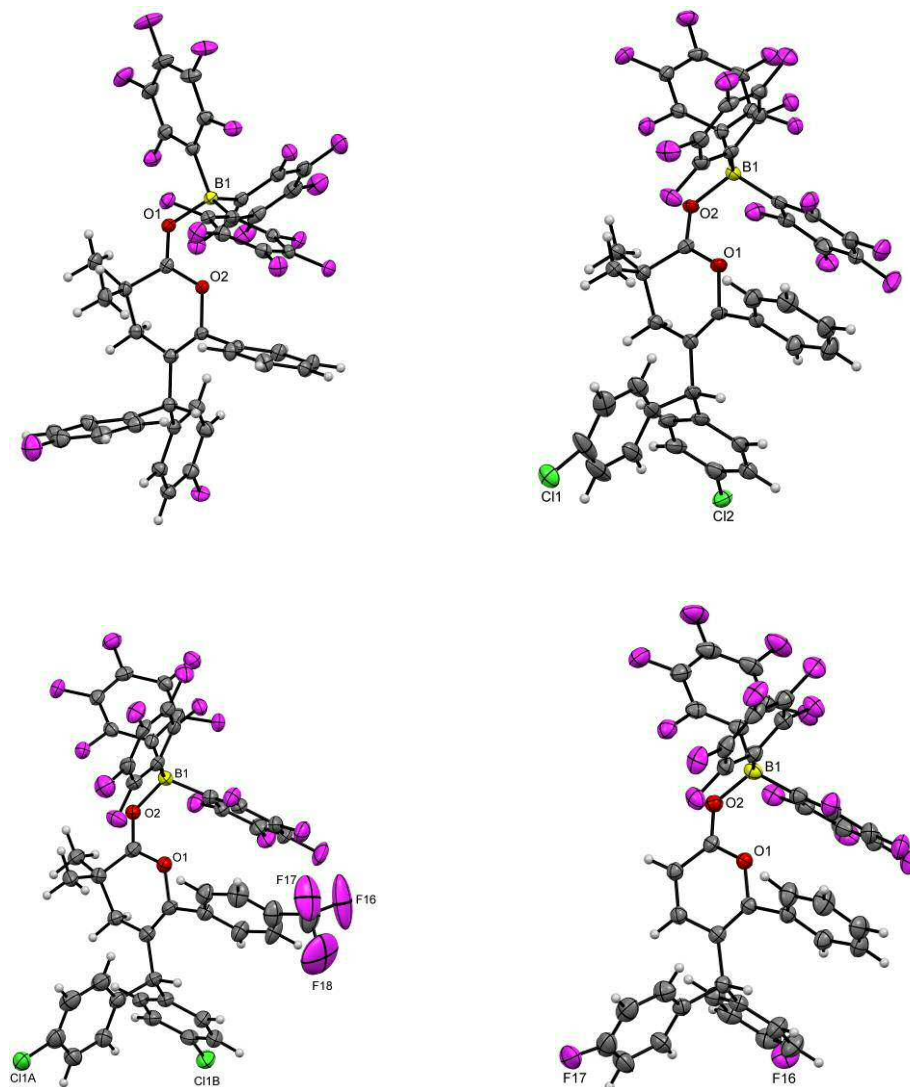
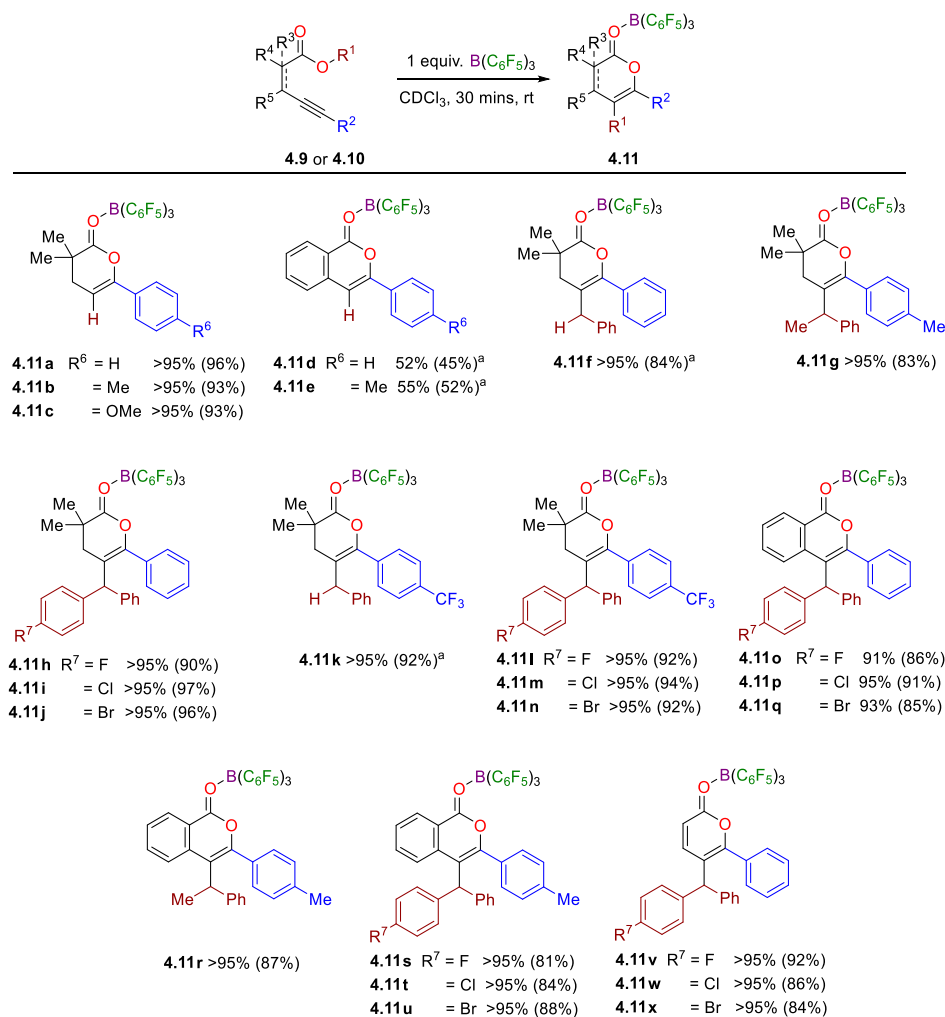


Figure 4.11: Solid-state structure of compound **4.11h**, **4.11i**, **4.11m** and **4.11v**. Disordered F and Cl atoms modelled over two sites. C: grey, H: white, B: yellow-green, O: red, F: pink, Cl: green. Thermal ellipsoids shown at 50% probability.



Scheme 4.9: Substrate scope for the cyclisation reaction of **4.9** or **4.10** with $\text{B(C}_6\text{F}_5)_3$. *In situ* NMR conversion (isolated yield). ^a 24 h reaction time.

As noted earlier, the final products of the stoichiometric reactions result in the sequestration of the borane as the Lewis adduct with the carbonyl oxygen therefore, it was proposed that this weak boron-oxygen bond could be thermolytically cleaved to allow the borane to activate other alkynyl precursors in a catalytic fashion. Fortuitously, when using the substrate **4.10d** in CDCl_3 and 10 mol% $\text{B(C}_6\text{F}_5)_3$, the product **4.12c** could be observed in >95% conversion after 6 h at 70 °C. This protocol then underwent optimisation *viz.* solvent, catalyst loading and borane catalyst (Table 4.2). Through these optimisations it was seen that less Lewis acidic boranes (BPh_3 , $\text{B(2,6-F}_2\text{C}_6\text{H}_3)_3$ and $\text{B(2,4,6-F}_3\text{C}_6\text{H}_2)_3$)^[114] were ineffective, with no conversion being noted after 24 h (entries 1–3, Table 4.2). The slightly less Lewis acidic,^[19] and less bulky $\text{BF}_3 \cdot \text{OEt}_2$ also showed very little reactivity giving **4.12c** in only 7% conversion (entry 4, Table 4.2). On the other hand, it was noted that $\text{B(C}_6\text{F}_5)_3$ was an extremely effective catalyst even when used in only 1 mol%, giving almost quantitative

conversion within 6 hours however, 5 mol% was used for the proceeding experiments to ensure maximum conversion for the least active reagents as well as for use in tandem reactivity explored later in this chapter (entries 5–7, Table 4.2). This reaction appears to be tolerant of most common solvents such as CDCl_3 , CH_2Cl_2 , Et_2O and toluene generating the product in >95% conversions however, strongly coordinating solvents (THF and 1,4-dioxane) fared less well presumably due to catalyst deactivation through borane-solvent coordination (entries 5, 8–12, Table 4.2). These optimised conditions were then applied to the electron-rich carboxylic acid substrate **4.9c** which found that the same trend is followed whereby **4.12a** was formed quantitatively (entry 13, Table 4.2). To examine whether this reaction is Brønsted acid catalysed as a result of borane coordination to the carboxylic acid carbonyl oxygen, trifluoroacetic acid and the stronger trifluoromethanesulfonic acid were trialled with little success (entries 14–15, table 4.2).

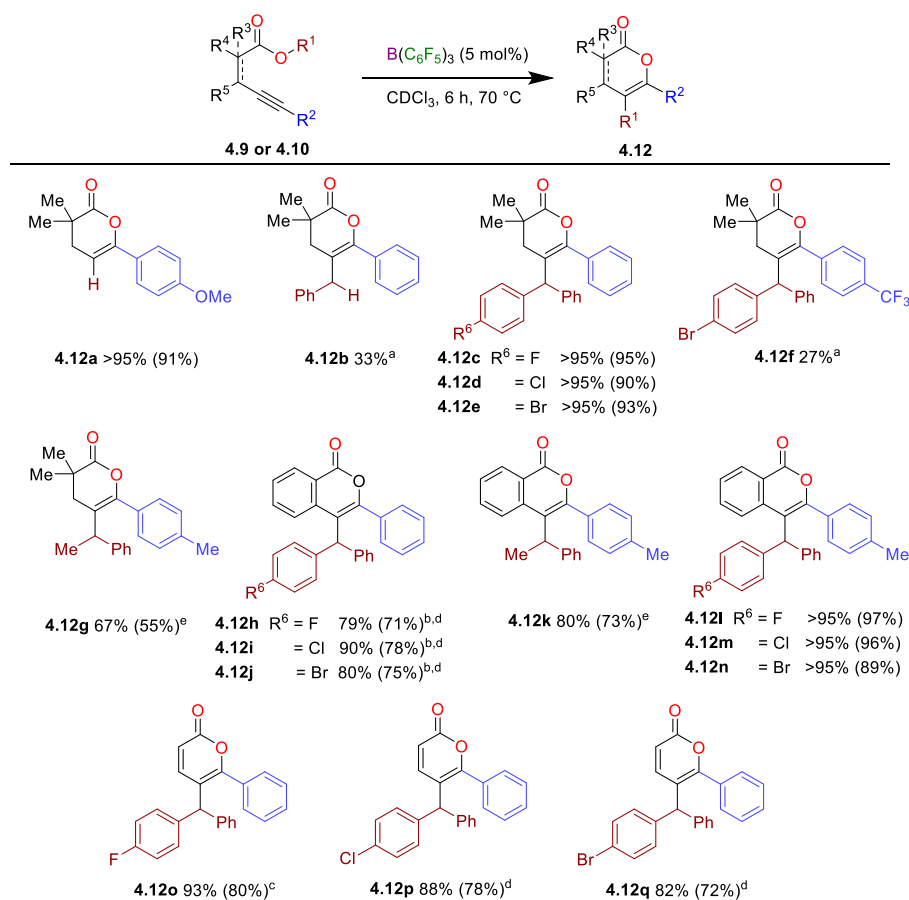
Table 4.2: Optimisation for the catalytic cyclisation of **4.9c** and **4.10d** to give **4.12c** and **4.12a**.

Entry	Catalyst	Solvent	Loading (mol%)	Conv. (%) ^a	Product
1	BPh_3	CDCl_3	10	<5	4.12c
2	$\text{B}(2,6\text{-F}_2\text{C}_6\text{H}_3)_3$	CDCl_3	10	<5	4.12c
3	$\text{B}(2,4,6\text{-F}_3\text{C}_6\text{H}_2)_3$	CDCl_3	10	<5	4.12c
4	$\text{BF}_3 \cdot \text{OEt}_2$	CDCl_3	10	7	4.12c
5	$\text{B}(\text{C}_6\text{F}_5)_3$	CDCl_3	10	>95	4.12c
6	$\text{B}(\text{C}_6\text{F}_5)_3$	CDCl_3	5	>95	4.12c
7	$\text{B}(\text{C}_6\text{F}_5)_3$	CDCl_3	1	>95	4.12c
8	$\text{B}(\text{C}_6\text{F}_5)_3$	THF	10	52	4.12c
9	$\text{B}(\text{C}_6\text{F}_5)_3$	1,4-Dioxane	10	54	4.12c
10	$\text{B}(\text{C}_6\text{F}_5)_3$	Toluene	10	>95	4.12c
11	$\text{B}(\text{C}_6\text{F}_5)_3$	Et_2O	10	>95	4.12c
12	$\text{B}(\text{C}_6\text{F}_5)_3$	CH_2Cl_2	10	>95	4.12c
13	$\text{B}(\text{C}_6\text{F}_5)_3$	CDCl_3	5	>95	4.12a
14	$\text{CF}_3\text{CO}_2\text{H}$	CDCl_3	5	0	4.12a
15	$\text{CF}_3\text{SO}_3\text{H}$	CDCl_3	5	Traces ^b	4.12a

^a *In situ* NMR conversion after 6 hours at 70 °C. ^b Multiple products observed.

Using these optimised conditions, various alkynyl carboxylic acids and esters were then reacted to obtain the respective pyrone or isocoumarin products. As before, the most electron-rich carboxylic acid **4.12a** could be isolated in an excellent yield of 91% however, all other less electron-rich derivatives **4.9a–b**, and the sterically encumbered variants **4.9d–e** showed no appreciable conversion. Nevertheless, when

using the ester substrates, the vast majority could be isolated in excellent yields although lower conversions were noted for the benzyl derivative **4.12b** and the electron-poor alkyne variant **4.12f** which were isolated in 33% and 27% respectively (Scheme 4.10). An increase in catalyst loading to 10 mol% was necessary in the conversion of the conjugated substrates **4.12h–j** garnering the products in reasonably good yields of 71–78%. Confirmation of these lactone products could be gathered from the solid-state structure by storing saturated CH_2Cl_2 /hexane solutions at $-40\text{ }^\circ\text{C}$ to yield a crop of colourless crystals (Figure 4.12)



Scheme 4.10: Catalytic formation of **4.12** using $\text{B}(\text{C}_6\text{F}_5)_3$. *In situ* NMR conversion (isolated yield). ^a Isolated yield after 120 h. ^b 10 mol% catalyst. ^c 16 h reaction time. ^d 24 h reaction time. ^e 48 h reaction time.

Further to this work, it was anticipated that the borane may act as a dual catalyst for the one-pot tandem cyclisation/hydrosilylation from the alkynyl ester reagent **4.10d** through to the γ -functionalised cyclic silylacetals (Scheme 4.11). Indeed, the latter hydrosilylation step is well-known in the literature, hence it was expected that this reduction reaction should proceed in a facile manner.^[23c-e, 115] It was found that after using the optimised conditions to form the lactone **4.12**, the addition of one equivalent

of silane (HSiPh_3 or HSiEt_3) and heating to 70 °C for 6 h showed quantitative conversion to the reduced silylacetal **4.13a–f**, which could be isolated in excellent yields of 90–95%.

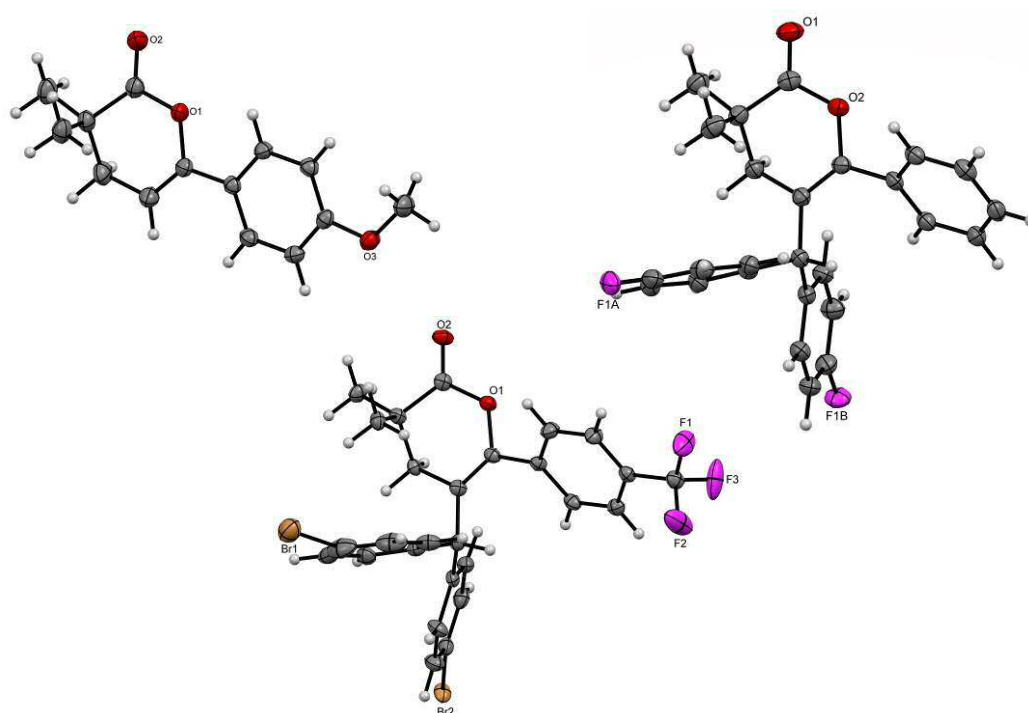
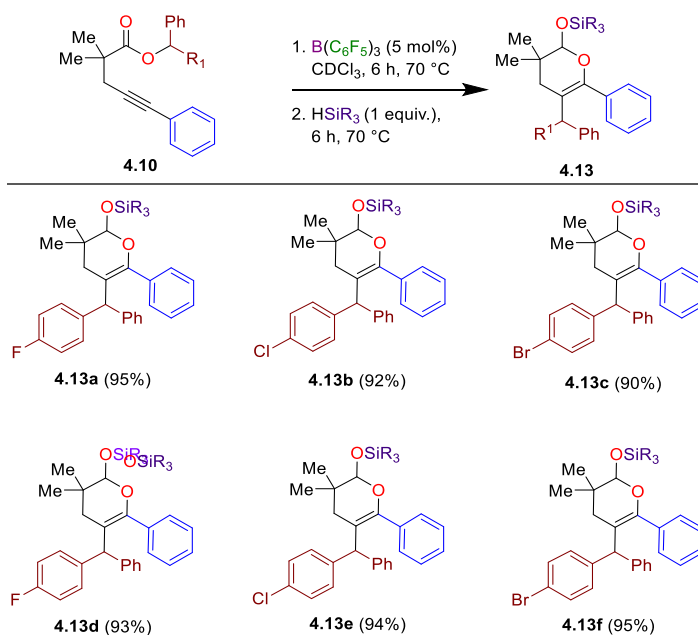


Figure 4.12: Solid-state structure of compound **4.12a**, **4.12c** and **4.12f**. Disordered F and Br atoms modelled over two sites. C: grey, H: white, B: yellow-green, O: red, F: pink, Br: brown. Thermal ellipsoids shown at 50% probability.



Scheme 4.11: Catalytic tandem one-pot cyclisation/hydrosilylation to yield **4.13**.

This was evident by the new resonance in the ^{29}Si NMR spectra at $\delta = \text{ca. } 11.8$ ppm (SiPh_3) and $\delta = \text{ca. } 19.8$ ppm (SiEt_3). This was seen alongside the new singlet resonance at $\delta = \text{ca. } 5.0$ ppm in the ^1H NMR spectrum corresponding to the newly introduced hydride to the CO_2 unit. Whilst there is the opportunity to reduce at different sites within the lactone, this reaction appears to be regioselective for the carbonyl over the alkene which was confirmed through the solid-state structure (Figure 4.13).

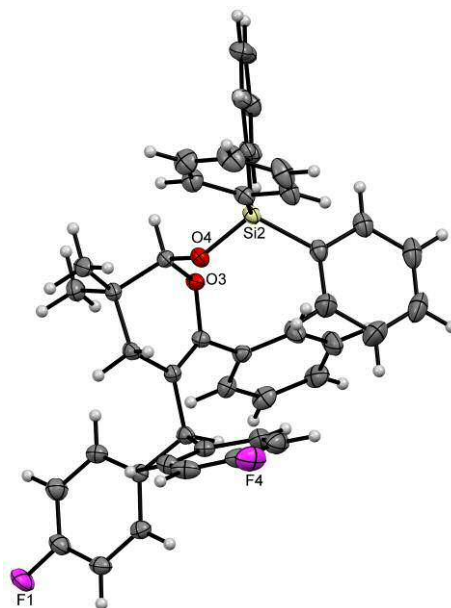


Figure 4.13: Solid-state structure of compound **4.13a**. Disordered F atoms modelled over two sites. C: grey, H: white, B: yellow-green, O: red, F: pink, Si: light grey. Thermal ellipsoids shown at 50% probability.

One mechanistic aspect that was investigated was whether the 1,5-migration of the ester moiety proceeds *via* an *intra*- or *inter*-molecular pathway. To probe this, a 1:1 mixture of **4.10f** and **4.10h** was combined with two equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ with the reaction being monitored through multinuclear NMR spectroscopy (Figure 4.14, crossover A). It was seen that a mixture of all four possible products prevailed indicating a scrambling of the cationic benzhydryl fragment occurred by way of an intermolecular pathway. To confirm this, a second crossover was performed using **4.10d** and **4.10j** again with two equivalents of borane. Indeed, a similar scrambling pattern was observed, supporting the previous findings whereby a transient carbenium ion is generated leading to intermolecular transfer (Figure 4.14, crossover B). On further inspection, crossover A showed essentially even formation of the four products **4.11h**, **4.11j**, **4.11l** and **4.11n** whereas crossover B showed that **4.11h** predominated over the other three products. It is assumed that the more electron-rich

alkyne **4.10d** reacts preferentially over the electron-poor variant **4.10j**, which also explains the lowered reactivity of the CF₃ substituted alkynyl esters earlier. In addition, the Hammett parameter for *para*-F is greater than that of *para*-Br suggesting a more stable carbenium ion is formed with the fluorinated substrate, resulting in faster reaction of the substrate **4.10d**.^[116]

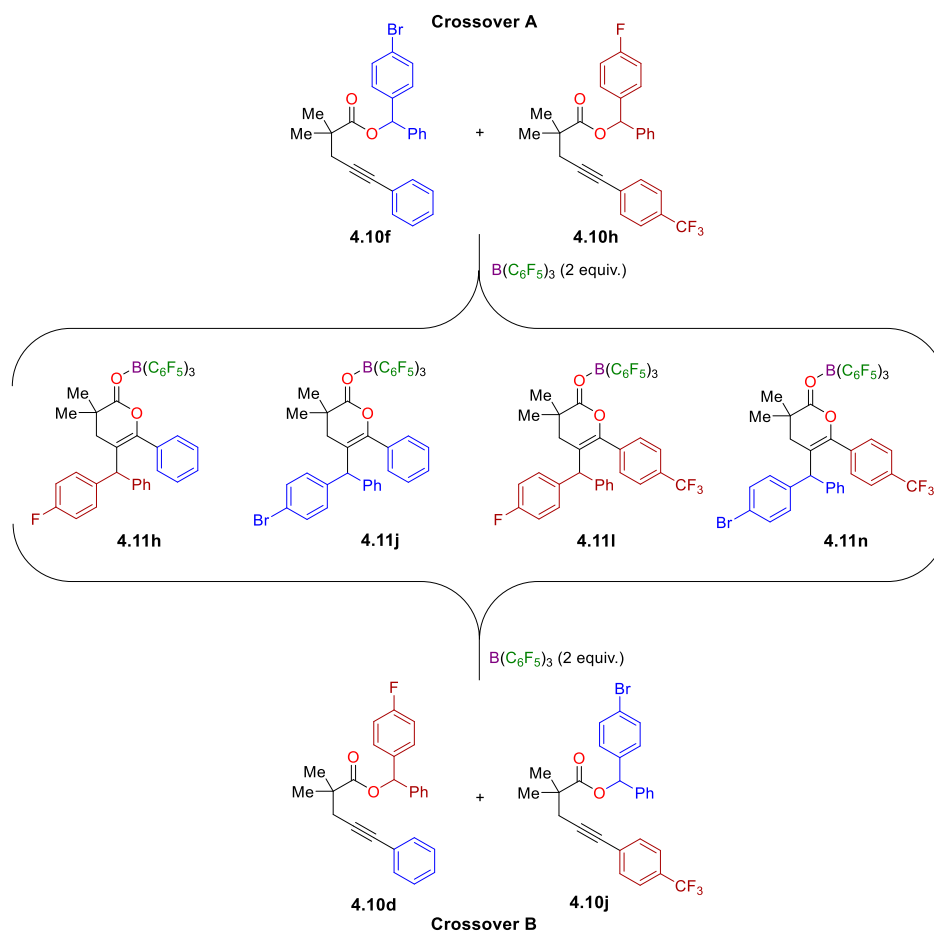
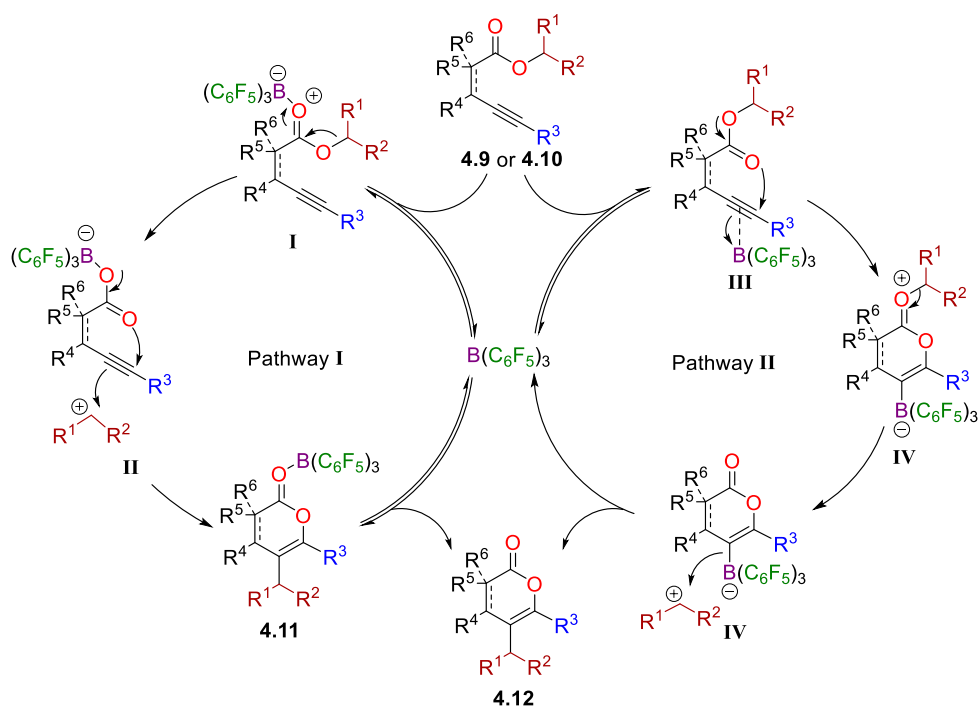


Figure 4.14: Crossover reactions to probe inter- vs. *intra*-molecular pathway.

As mentioned in Chapters 2 and 3, there are two independent modes by which the borane may activate these types of alkynyl esters, either σ - or π -activation. With the former, activation of the carbonyl by the borane promotes the elimination of the carbenium ion with concomitant 6-*endo-dig* cyclisation (Pathway I, Scheme 4.12). Conversely, π -activation promotes the 1,2-*trans*-addition of the borane and carbonyl oxygen across the triple bond with subsequent proto- or carbo-deboration (Pathway II, Scheme 4.12). Both such pathways have precedence in the literature and other work mentioned in Chapters 2 and 3. For instance, the catalytic deprotection of Boc groups using B(C₆F₅)₃ outlined in Chapter 3 follows a very similar premise to that proposed here,^[36b] while the 6-*endo-dig* mechanism posited in Pathway II has been

elucidated earlier in Section 4.2.1 as well as by others in the literature in the synthesis of pyryliums, lactones *inter alia*.^[39b, 96]

It may be assumed that the hard Lewis acid/base adduct between the carbonyl and borane is preferred over the softer alkyne site as described by hard soft acid base (HSAB) theory. While this initial activation mode undoubtedly takes place as indicated by a broad singlet resonance at $\delta = \text{ca. } 40 \text{ ppm}$ in the ^{11}B NMR spectrum, a transient sharp singlet is also observed at $\delta = -15 \text{ ppm}$ indicating that Pathway II is also taking place. Further evidence for the reaction proceeding *via* Pathway II may be inferred from the lack of reactivity of the *ortho*-substituted carboxylic acid derivatives **4.9d–h** as other electronically similar *para*-substituted derivatives were shown to react. This increased steric crowding about the alkyne may preclude this activation pathway leading to reduced reactivity. The assumption that the reaction proceeds *via* a carbenium ion intermediate is reinforced by the lack or lower reactivity of less stabilised carbeniums (i.e. ^iPr , allyl, benzyl) compared to the more stable ethyl phenyl or benzhydryl derivatives. Other mechanistic observations include the lack of reactivity with the Brønsted acids trifluoroacetic acid and trifluoromethylsulfonic acid. If σ -activation does take place then presumably this would create a fairly potent Brønsted acid source which could in turn affect the cyclisation. Both catalytic and stoichiometric amounts of Brønsted acid failed to form the desired heterocycle perhaps indicating that the latter π -activation pathway may predominate in the formation of the pyrone and isocoumarin products.



Scheme 4.12: Proposed mechanistic pathways for the catalytic formation of **4.12**.

4.3 Conclusions

Within this chapter it has been shown how the strong Lewis acid $B(C_6F_5)_3$ can undergo π -activation of alkynes to affect *5-exo-dig* and *6-endo-dig* cyclisations to form various pyryliums, pyrones and isocoumarins as well as promote annulation reactions. Indeed, the synthesis of such compounds have extensive uses as synthetic intermediates as well as in biologically active agents therefore are of great importance to the synthetic chemist. It is also important to note the divergent reactivity between soft and hard Lewis acids, altering the electrophile in this instance has a dramatic influence on the proceeding reaction. Additionally, the use of softer Lewis acids in these FLP-type 1,2-addition reactions is comparatively rare in the literature with this work providing much needed exposure. Additionally, the use of electron deficient boranes in new C–H and C–C bond forming reactions as well as tandem catalysis is an area of main group chemistry that is now beginning to expand, with work showcased above displaying excellent atom efficiency in a range of transformations.

Chapter 5

Boron Mediated and Catalysed Reduction Reactions: Emerging Catalysts, Novel Processing Techniques and Transfer Hydrogenation

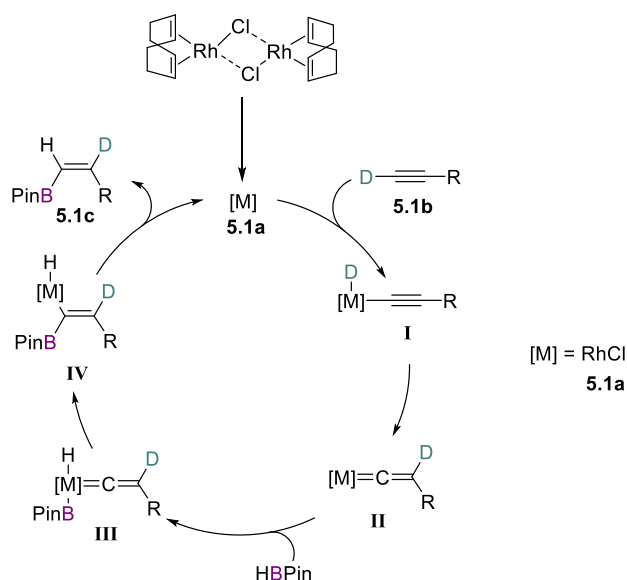
Publications from this work

1. J. R. Lawson,[†] L. C. Wilkins,[†] R. L. Melen,* “Tris(2,4,6-trifluorophenyl) borane: An Efficient Hydroboration Catalyst”, *Chem. Eur. J.*, **2017**, *23*, 10997. [†]equal contribution
2. L. C. Wilkins, J. H. Howard, S. Burger, L. Frenzel-Beyme, D. L. Browne,* R. L. Melen,* “Exploring Multistep Continuous Flow Hydrosilylation Reactions Catalyzed by Tris(pentafluorophenyl)borane”, *Adv. Synth. Catal.*, **2017**, *359*, 2580.
3. L. C. Wilkins, N. Santi, L. Y. P. Luk, R. L. Melen,* “Reactions of Biologically Inspired Hydride Sources with B(C₆F₅)₃”, *Phil. Trans. R. Soc. A*, **2017**, *375*, 20170009.

5.1 Introduction

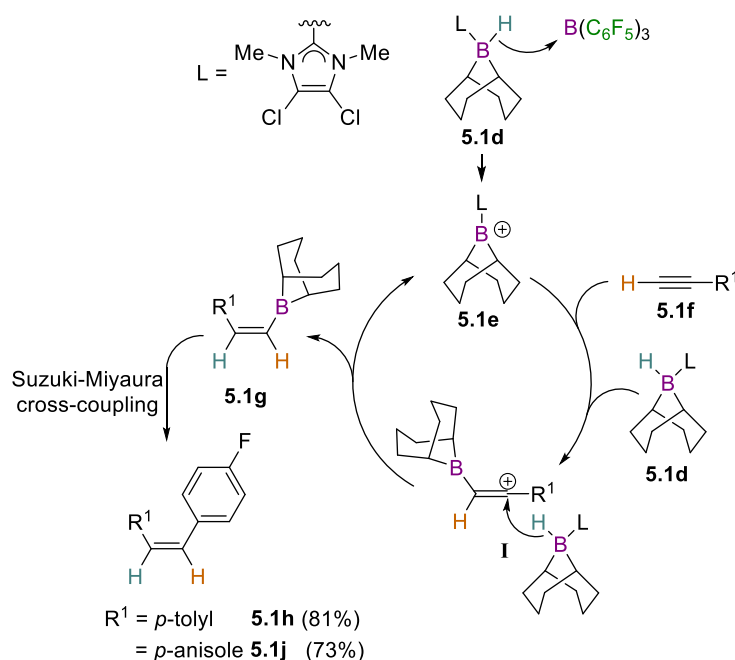
The hydroboration reaction is one of the most well-known applications for boranes dating back to the 1950's, with H. C. Brown being awarded the Nobel Prize in Chemistry for his work in the synthesis of organoboranes through the hydroboration of alkenes.^[117] One of the many advantages of the hydroboration reaction is the atom-efficiency, rendering the borylated product with little to no side-products with good control over regioselectivity as well as the variability in the borane that can be used; e.g. pinacol borane (HBPin),^[118] 9-BBN^[119] or the strongly Lewis acidic Piers' borane [HB(C₆F₅)₂].^[24a, 24b] The hydroboration of alkenes and alkynes using boranes (R₂BH) tend to proceed *via* a concerted *syn*-addition giving the anti-Markovnikov product on account of the greater electronegativity of hydrogen over boron. More recently, a bevy of examples have included transition metals such as rhodium, palladium and platinum as the active catalyst in the hydroboration of unsaturated substrates.^[120] For example, work by Miyaura *et al.* described how the catalyst [Rh(cod)Cl]₂ could affect the alternative 1,1-hydroboration of various alkynes to the (*Z*)-alkene in up to 99% yield.^[120a] This follows a proposed mechanism that is perhaps more complex than first

envisaged. Initial oxidative addition of the alkyne to the metal (**I**, Scheme 5.1) is followed by tautomerisation to the alkyldiene intermediates (**II**, Scheme 5.1). A subsequent second oxidative addition of the borane to the metal, with the borane moiety occurs to undergo a 1,2-migration furnishing the vinyl intermediate **IV**. Reductive elimination of the product **5.1c** garners the (*Z*)-stereoisomer with concomitant regeneration of the metal catalyst.



Scheme 5.1: Isotope labelled mechanism for the transition metal catalysed hydroboration of alkynes.

In recent years however, metal-free catalysts have been developed for this purpose from both *s*-block^[121] and *p*-block^[122] elements to great effect. Indeed, this success has proliferated over the last few decades in a bid to compete with transition metal catalysts, particularly in the development of pharmaceutical precursors where trace-metal impurities are heavily restricted.^[123] One interesting example reported by Ingleson *et al.* shows how using a borenium-based system, initiated by $B(C_6F_5)_3$, the stereoselective *trans*-1,2-addition of alkynes can occur vs. the conventional *syn*-1,2-addition (Scheme 5.2).^[124] In this case, it is proposed that the NHC stabilised 9-BBN undergoes hydride abstraction by the $B(C_6F_5)_3$ initiator leaving the borenium borate ion pair **5.1e**. Activation of an alkyne substrate by **5.1e** forms the unstable vinylic cation **I** which is then reduced by a hydride from another equivalent of **5.1d** to give the borylated product **5.1g**, whilst reforming the borenium cation to enter the cycle again.

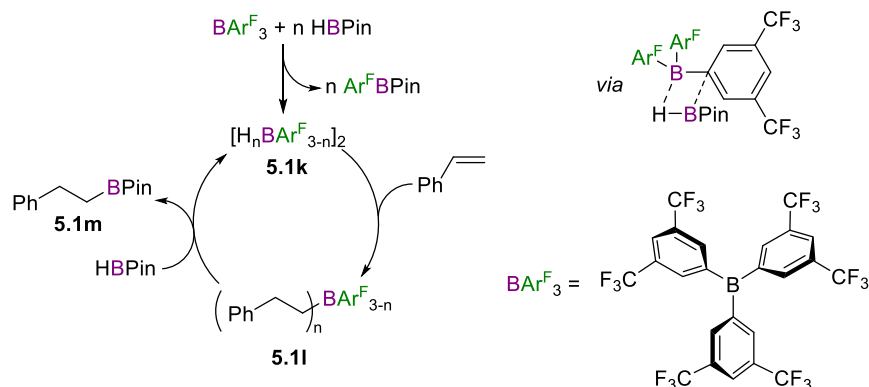


Scheme 5.2: Mechanism for the metal-free 1,2-*trans*-hydroboration of alkynes. $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ counterion omitted for clarity.

A series of products could be synthesised using this methodology to include a large number of styrene derivatives as well as vinylthiophene, vinylcyclohexenyl and isoprene-type moieties in generally excellent yields (56–97%). As stated throughout this work, such borylated products are excellent candidates for further functionalisation such as cross-coupling reactions to more complex polyaromatic compounds.^[15] Indeed, Ingleson showed that the vinylic boranes **5.1h–j** (where R = *p*-tol or *p*-anisole) were susceptible to a Suzuki-Miyaura cross-coupling reaction to provide the *cis*-stilbene derivative in 81% and 73% yield respectively in a one-pot synthesis.

Additionally, reduction of unactivated alkenes has been shown by Oestreich and co-workers using the highly Lewis acidic borane *tris*[3,5-*bis*(trifluoromethyl)phenyl] borane (BAr^{F_3}).^[125] In this case, the reduction capability of BAr^{F_3} was found to be even greater than that of the archetypal Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$. Whilst initial observations may indicate the simple hydroboration *via* catalytic hydride shuttling by BAr^{F_3} , the proposed mechanism, supported by literature precedence and kinetic experiments indicated a more complex mechanism was occurring.^[24a, 126] The BAr^{F_3} in this case may be thought of as a precatalyst as the combination with HBPIn results in ligand exchange through σ -bond metathesis to generate the active catalyst **5.1k** (Scheme 5.3). This active catalyst, similar to Piers' borane, then undergoes the expected 1,2-hydroboration to generate the alkyl borane **5.1l**. A second ligand metathesis reaction

occurs upon reaction with another equivalent of HBPin, regenerating **5.1k** while garnering the requisite pinacol boronate ester **5.1m**. Whilst transition metal catalysts have been used in the hydroboration of other unsaturated moieties such as imines^[127] and aldehydes,^[128] the incorporation of metal-free variations are seldom reported however, traction has certainly built in this area over the past decade.^[24c, 129]

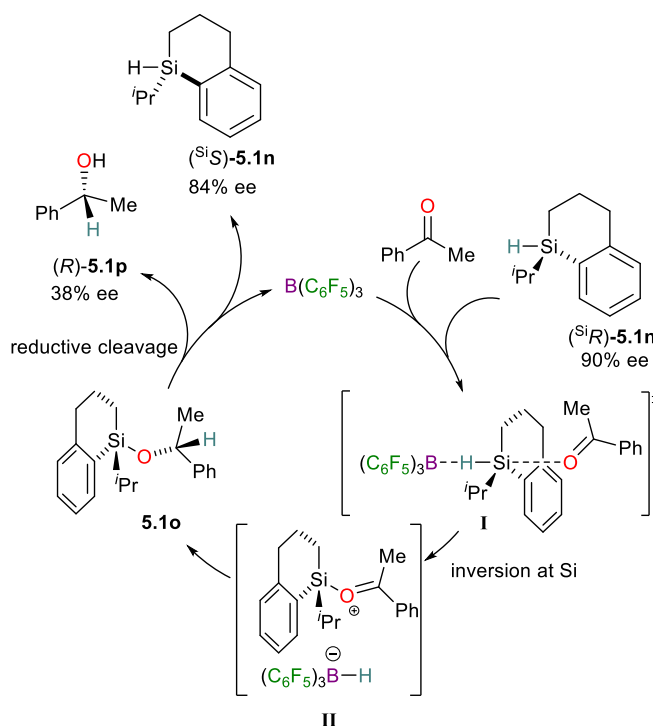


Scheme 5.3: Proposed mechanism for the hydroboration of alkenes using BAr^{F}_3 via ligand redistribution through σ -bond metathesis.

Another common reaction in the reduction of unsubstituted scaffolds is the hydrosilylation reaction. Silanes of the general structure R_3SiH as well as others such as tetramethyldisiloxane (TMDS) are commonly used in this transformation as the reductant to form silyl protecting groups *en route* to liberation of the free alcohol or amine. Whilst the most popular is the simple 1,2-addition to $\text{C}=\text{X}$ bonds such as carbonyls, other addition patterns are routine such as the 1,4-addition to α,β -unsaturated ketones, in a conjugate addition reaction. The common Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ has once again shown prominence in the catalytic formation of new $\text{O}-\text{Si}$,^[23a] $\text{C}-\text{Si}$ ^[130] as well as $\text{N}-\text{Si}$ bonds (*en route* to various hydrogenation products by hydrolysis).^[23b, 131]

Seminal work in this field by Piers *et al.* using $\text{B}(\text{C}_6\text{F}_5)_3$ showed how aldehydes, ketones and esters could be readily reduced in the presence of various silanes.^[23a] In these initial reactions a number of carbonyl containing substrates could be converted to the corresponding silylether, which underwent hydrolysis to form the alcohol in good to excellent yields (*ca.* 80%). Further studies by Piers uncovered how the conventional reactivity series whereby aldehydes are the most reactive, and esters are the least reactive is in fact reversed.^[23b]^[132] Extensive kinetic work described how the reaction proceeds *via* the initial silane-borane encounter complex ($\text{Si}-\text{H}\cdots\text{B}$) with subsequent nucleophilic attack of the silane by the carbonyl followed by hydride delivery by $\text{B}(\text{C}_6\text{F}_5)_3$. To reason this inverse reactivity, it was posited that the more

basic the functional group (aldehyde>ketone>ester) the stronger the adduct formation with the Lewis acid. Therefore, it is necessary to have an electron-deficient heteroatom to increase the availability of 'free' borane in solution to abstract the hydride upon coordination of the silane to the carbonyl. These findings were supported in further work by Oestreich and co-workers using a chiral silane reagent, and tracking the final configuration (and purity) of the product by chiral HPLC and optical rotation measurements.^[115b] Employing this methodology, it was found that using an enantioenriched silane (^{Si}R)-**5.1n** (90% enantiomeric excess (*ee*)) in the hydrosilylation of the prochiral acetophenone resulted in the almost complete inversion of the silane producing (^{Si}S)-**5.1n** (84% *ee*), as well as generating the alcohol in 38% *ee*. This complete inversion at silicon is only possible if the reaction proceeds through a Walden inversion transition state in an overall S_N2 reaction. If this reaction were to occur by the formation of a silylium intermediate as a result of an S_N1 reaction, then presumably a racemic mixture would result. This hypothesis was reinforced by theoretical work carried out by Fujimoto *et al.* confirming this S_N2 reaction at silicon reaction by initial Si–H activation by the borane.^[115c]



Scheme 5.4: S_N2 silylation reaction mechanism proposed by Oestreich.

Interestingly, while contemporary main group chemistry, including borane catalysed hydrosilylation, has become more mainstream over the past two decades, there appears to be little crossover with other fields or processing technologies. In nearly all cases other than very recent reports by Stephan *et al.*^[133] the use of *p*-block

catalysts in continuous-flow chemistry has been all but ignored. Indeed, flow chemistry has seen increased adoption across many diverse fields^[134] in both industry and academia however, main group chemistry appears to be behind this trend.^[135]

The need to expand implementation of continuous-flow chemistry is paramount to many processes as the symbiotic relationship of traditional methods coupled with novel processing methods often leads to increased conversion, reaction rates and selectivities. Perhaps more significantly, flow chemistry allows for a modular and adaptable approach to synthesis thus increasing automation^[136] and sanctioning multistep processes in a single reaction setup.^[137] Using these new methods, expansive libraries of compounds may be synthesised whilst reducing manual intervention.^[138] Another facet to continuous-flow processing is the ability to conduct reactions at significantly higher temperatures and pressures than is normally allowed when using a traditional batch-type setup. By incorporating other fixtures such as back-pressure regulators (BPR), the superheating of solvents at high pressure almost invariably leads to increased reaction rates, providing a very attractive methodology for rapid throughput to the synthetic chemist (Figure 5.1).^[139] Using such fixtures also explicates one of the other critical benefits to using flow chemistry; the increased safety profile. Using this technology increases the safety profile through increased thermal control, lower risk of concentration hotspots of reactive intermediates as well as working with smaller volumes during the active step, e.g. the reactive step is contained to a continuously-fed 5 ml reactor coil rather than a static larger volume flask. This means that more capricious reactions may be conducted in a laboratory setting with a vastly increased safety profile.^[140]

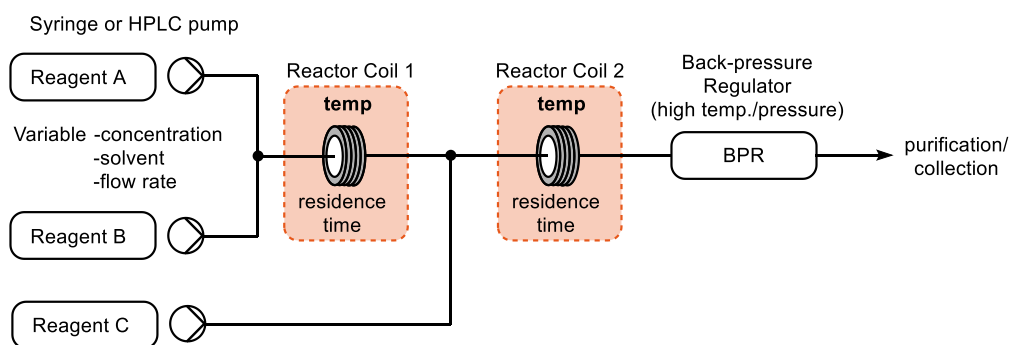
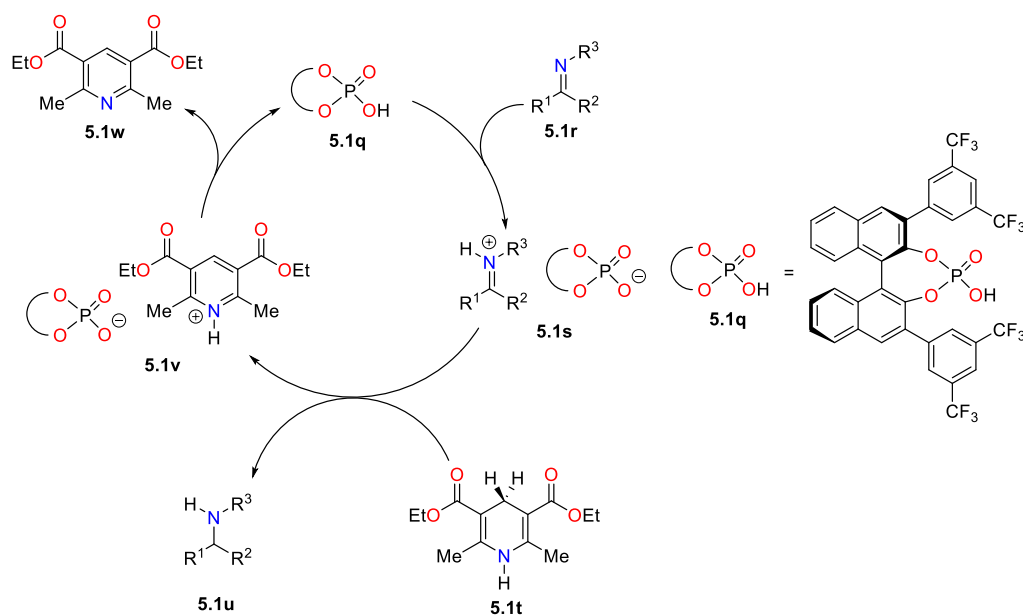


Figure 5.1: General flow set-up for a multi-step synthesis.

Another area of main group chemistry that has seen great expansion in the past decade has been that of small molecule activation, specifically hydrogenation. This was mainly promulgated through frustrated Lewis pair chemistry in seminal work by

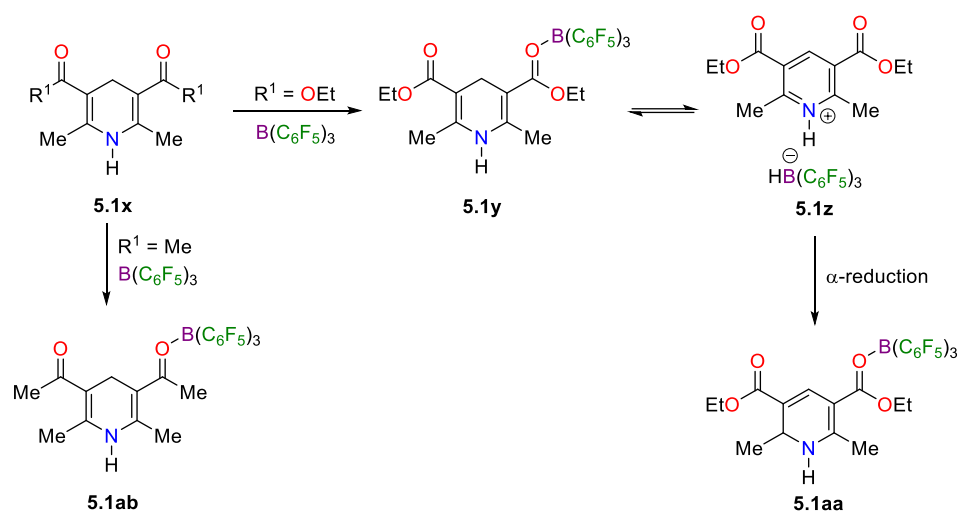
Stephan *et al.* using both *intra*- and *inter*-molecular phosphine/borane combinations to heterolytically cleave dihydrogen.^[9a-c, 21, 141] While dihydrogen has received massive amounts of attention, alternative dihydrogen and hydride sources have been overlooked in the literature with only a handful of reports in this area. Hantzsch esters are great hydrogen equivalents due to its ease of manipulation when compared to gaseous hydrogen, with access to both the protic and hydridic components being possible through simple activation by a Lewis acid.^[142] Other routes have been implemented to access the H₂ equivalent stored in Hantzsch esters, such as the organocatalytic method introduced by Rueping *et al.* whereby a phosphoric acid **5.1q** is used as the proton source to form the iminium intermediate **5.1s** with subsequent reduction by the hydride on the Hantzsch ester to garner the secondary amine **5.1u**. The pyridinium **5.1v** that is formed reprotonates the phosphate anion to regenerate the organocatalyst while garnering the aromatic pyridine **5.1n** as a by-product (Scheme 5.5).^[143]



Scheme 5.5: Work by Rueping into organocatalytic reduction of imines using Hantzsch esters as hydrogen storage mediums.

Other than the above examples or those catalysed by transition metals, only a couple of studies exist of inorganic main group chemistry being applied to this area.^[144] One of these few examples is reported by Stephan and Crudden *et al.* who used these Hantzsch esters as a hydride source to form borohydrides for subsequent reduction reactions (Scheme 5.6).^[145] In this case, when traditional Hantzsch esters are used ($R^1 = \text{OEt}$), an equilibrium is established between the carbonyl/borane Lewis

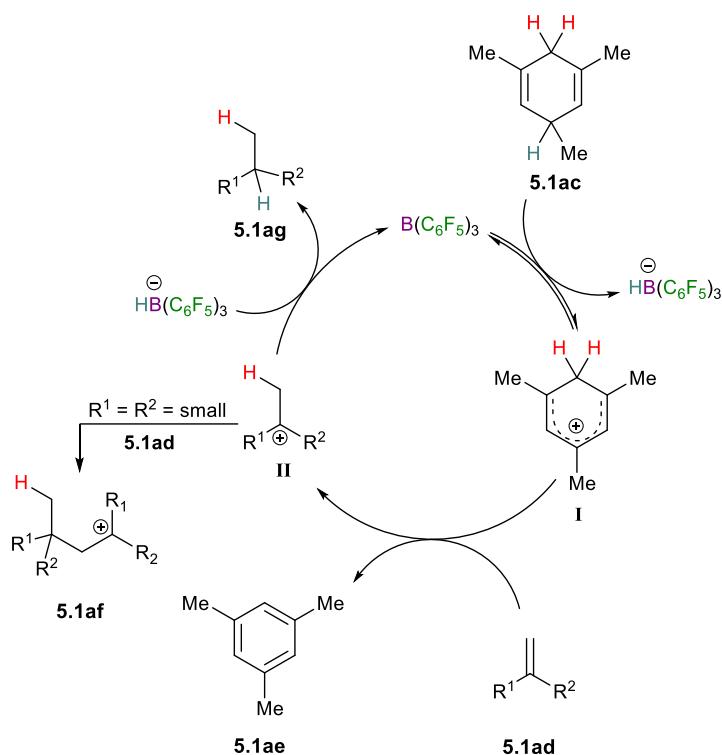
adduct **5.1y** and the pyridinium hydridoborate **5.1z** *via* hydride abstraction. Whilst this could be isolated at low temperatures and characterised by single crystal X-ray diffraction, it was found that above -20°C a secondary reduction reaction may occur. In this case the hydridoborate moiety reduces the pyridinium at the α -position to furnish the 2,3-dihydropyridine **5.1aa**. This was deemed to be as a result of the B–O adduct formation being the energetically more favourable product. Further to this, when a ketone was used ($\text{R}^1 = \text{Me}$) instead of an ester, then the adduct **5.1ab** was the sole product of the reaction with no hydride abstraction taking place. The reason for this relates to similar observations outlined in chapters 2 and 3, as well as by Piers and Oestreich whereby the stronger Lewis basic ketone sequesters the borane preferentially over other reactivity.



Scheme 5.6: Recent work from Stephan and Cruden using Hantzsch ester and derivatives as hydride sources for borohydride formation.

Oestreich pursued similar reactivity through the reaction of cyclohexa-1,4-diene derivatives with $\text{B}(\text{C}_6\text{F}_5)_3$ in the transfer-hydrogenation of alkenes (Scheme 5.7).^[146] With 1,1-diphenylethylene being selected as a model substrate, a series of substituted cyclohexa-1,4-dienes were trialled for reactivity with the optimal hydrogen source being determined as 1,3,5-trimethylcyclohexa-1,4-diene **5.1ac** garnering the reduced product **5.1ag** in 97% yield after just 1 h using 5 mol% borane loading. Following this, an extensive substrate scope was tested with generally excellent yields being recovered across the board however, smaller substituents in the R^1 and R^2 position tended to give lower conversions due to competitive side-reactions such as dimerisation with another equivalent of **5.1ad**. Increasing the steric bulk about the alkene terminus reduces the possibility for this dimerisation to occur hence garnering higher yields with bulkier substituents. Regarding the posited mechanism for this

reaction, it is believed that initial borohydride formation occurs to form the Wheland intermediate **I** which then protonates the alkene substrate generating the aromatised mesitylene as a side-product. At this point, the carbenium intermediate **II** may then undergo the dimerisation to form **5.1af** or reduction by the hydridoborate to garner the desired alkane **5.1ag** however, according to *in silico* studies, the former pathway is energetically less favoured due to the steric encumbrance about the cationic centre.



Scheme 5.7: Proposed mechanism for catalytic transfer hydrogenation of alkenes using cyclohexa-1,4-dienes.

5.1.1 Aims of This Chapter

This chapter explores new reactivity in boron mediated reduction reactions using several new approaches. Firstly, attenuation of the Lewis acidity has been shown as an effective way of modulating reactivity to suit a certain purpose. To that end, adapting boranes for the reduction of unsaturated substrates is an area of main group catalysis that is currently being exploited to increase their effectiveness and competitiveness. Secondly, novel processing methods are a fascinating competitor to conventional batch-type reactions, with there being more adoption across several fields in academia and industry of late. However, the combination of main group catalysis and continuous-flow processing technologies has rarely been investigated, hence studies in this topic will provide much-needed insight into this synergistic pairing. This drive to pair such technologies are spurred by the adaptability of

continuous-flow methodologies to undergo reactions at far higher temperatures and pressures than those seen in batch-type reactions, allowing main group catalysts to be applied to a wider range of substrates with greater success. Finally, the use of borohydrides are ubiquitous in organic synthesis with their syntheses relying mainly on salt metathesis reactions however, very few examples are presented in the literature whereby biological analogues are used as hydride donors. Analogues of the biologically sourced nicotinamide adenine dinucleotide phosphate (NADPH), such as 1-benzyl-1,4-dihydronicotinamide, are considered to be artificial mimics with similar hydride donor properties to NADPH. Reactions of these mimics, and derivatives thereof, should provide an interesting basis for merging main group and biological chemistry.

5.2 Results and Discussion

5.2.1 Tempering Lewis Acidity of Boranes for General Hydroboration Reactions

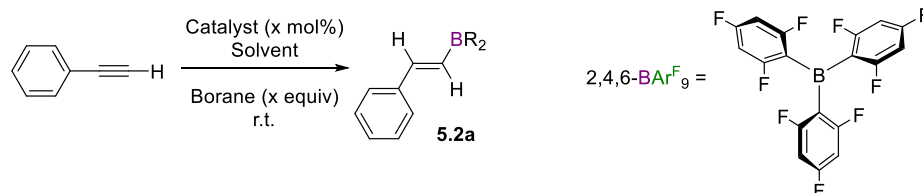
As stated earlier, the use of boranes and other main group compounds for reduction reactions has been exploited to great effect in recent years, with one of the most established being the hydroboration of carbon-element multiple bonds. Herein the focus of this work was to find a highly Lewis acidic borane that was capable of reducing C–X (X = C, N, O) multiple bonds in a facile manner with high functional group tolerance. It is well known that both tris(3,5-bis(trifluoromethyl)phenyl) borane and tris(pentafluorophenyl) borane are prime examples of strongly electrophilic boranes that are capable of catalysing the swift reduction of unsaturated systems however, in certain circumstances such examples shown earlier (see chapters 2–4), $B(C_6F_5)_3$ specifically is prone to react with such unsaturated systems in carboboration reactions. To this end, the less Lewis acidic borane *tris*(2,4,6-trifluorophenyl)borane ($2,4,6-BAr^F_9$) was targeted as a good candidate for this reaction owing in part to its lower Lewis acidity while retaining a sufficiently encumbered boron centre.^[114]

Fortuitously, the 1:1 stoichiometric combination of $2,4,6-BAr^F_9$ and the model alkyne, phenylacetylene, displayed no reactivity even when heated to 60 °C for five days. This is in distinct contrast to $B(C_6F_5)_3$ which undergoes a 1,1-carboboration reaction with the same substrate at ambient temperature within minutes.^[75, 147] Work by Alcarazo outlined the relative Lewis acidity of these common Lewis acids *via* Child's method showing that $B(C_6F_5)_3$ (100%) > $2,4,6-BAr^F_9$ (70%) > $2,6-BAr^F_9$ (56%) which may in part help explain the reactivity observed here.^[114] In addition to the lack

of reactivity of 2,4,6-BAr^F₉ toward alkynes, no ligand scrambling occurred when exposed to equimolar amounts of HBPin presumably as a result of the *ortho*-fluorine atoms blocking this redistribution.^[125a] The reaction conditions were then optimised *viz.* borane substrate, solvent and reaction time as well as control reactions of other more and less Lewis acidic boranes with the conversion of phenylacetylene to the corresponding pinacol boronate ester **5.2a** being measured *via in situ* NMR spectroscopy. It was observed that tuning the Lewis acidity was essential to the general applicability of the borane with more and less electrophilic boranes (2,6-BAr^F₆, B(C₆F₅)₃, BPh₃) performing poorly in comparison (entry 1–3, Table 5.1) whereas 2,4,6-BAr^F₉ showed complete conversion to **5.2a** within 5 hours at 5 mol% catalyst loading (entry 4, Table 5.1).

Altering the solvent from CH₂Cl₂ to toluene had no effect on reactivity whereas the use of coordinating ethereal solvents completely quenched the reaction presumably due to borane sequestration (entries 4–7, Table 5.1). The final parameters that were optimised were borane catalyst and reagent loading. Reducing the catalyst loading to 1 mol% could still garner the product **5.2a** in 99% conversion however, an extended reaction time of 18 h was noted.

Table 5.1: Optimisation of reaction conditions.

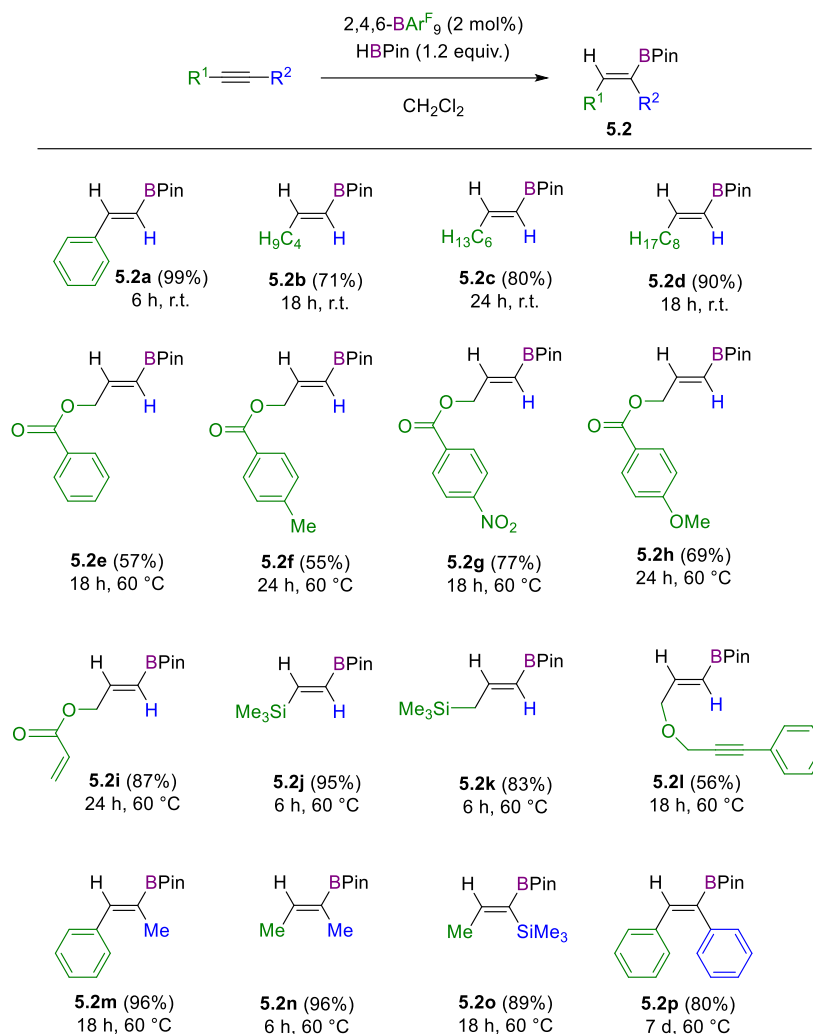


Entry	Catalyst	Loading (mol%)	Borane (equiv.)	Solvent	Time (h)	Conversion ^a (%)
1	B(C ₆ F ₅) ₃	5	HBPin (1)	CH ₂ Cl ₂	18	59
2	2,6-BAr ^F ₆	5	HBPin (1)	CH ₂ Cl ₂	18	62
3	BPh ₃	5	HBPin (1)	CH ₂ Cl ₂	18	31
4	2,4,6-BAr ^F ₉	5	HBPin (1)	CH ₂ Cl ₂	5	99
5	2,4,6-BAr ^F ₉	5	HBPin (1)	Toluene	5	99
6	2,4,6-BAr ^F ₉	5	HBPin (1)	THF	18	0
7	2,4,6-BAr ^F ₉	5	HBPin (1)	Et ₂ O	18	0
8	2,4,6-BAr ^F ₉	1	HBPin (1)	CH ₂ Cl ₂	18	99
9	2,4,6-BAr ^F ₉	2	HBPin (1)	CH ₂ Cl ₂	6	99
10	2,4,6-BAr ^F ₉	10	HBPin (1)	CH ₂ Cl ₂	4	99
11	2,4,6-BAr ^F ₉	2	HBPin (1.2)	CH ₂ Cl ₂	6	99
12	2,4,6-BAr ^F ₉	2	HBPin (2)	CH ₂ Cl ₂	6	99
13	2,4,6-BAr ^F ₉	2	HBPin (5)	CH ₂ Cl ₂	5	99
14	2,4,6-BAr ^F ₉	2	HBCat (1.2)	CH ₂ Cl ₂	6	85

^a Conversion measured *via in situ* ¹H NMR spectroscopy.

Conversely, increasing the catalyst loading to 10 mol% had a negligible positive effect on conversion giving quantitative conversions in 4 h. It was therefore decided that 2 mol% represented a good compromise between low catalyst loading and appreciably swift reaction times (entry 8-10, Table 5.1). Changing the stoichiometry of the borane reagent between 1 and 5 equivalents showed almost no difference in reaction rate therefore, a slight excess of 1.2 equivalents was used to furnish maximum conversion as any excess borane was readily removed under reduced vacuum (entry 11–13, Table 5.1). Catecholborane (HBCat) was also tested as an alternative to pinacolborane however, its performance was subpar, generating the boronate ester in conversions of only 85% after 6 h (entry 14, Table 5.1)

Once the optimised conditions had been realised, other alkyne substrates were then trialled such as terminal aryl and alkyl substrates which generated the reduced products **5.2a–d** in excellent yields of 71–99%. Propargyl esters were then reacted which revealed the selective hydroboration of the alkyne moiety over the ester carbonyl giving the expected anti-Markovnikov product in 55–77% yield (**5.2e–h**). Propargyl acrylate also shows the same regioselectivity as neither the olefin or ester were reduced, leading to the alkyne being the sole reduction site garnering the borylated product **5.2i** in 87% yield. It was observed that selective reduction of terminal alkynes occurs when a combination of both terminal and internal alkynes are featured in the same substrate furnishing the styryl derivative **5.2l** in 56% yield. With this in mind, other internal alkynes were then trialled to find any limitations of this catalytic system. Fortunately, all cases where either aryl, alkyl or silyl termini are present on the internal alkyne, the hydroborated products **5.2m–p** could be formed in generally excellent yields ranging between 80 to 96%. Interestingly, when asymmetric internal alkynes were utilised, *in situ* NMR spectroscopic studies indicate the two regioisomers are formed in a *ca.* 10:1 ratio with the borane and phenyl substituent lying *trans* to one another in **5.2m**, and *trans* to the methyl group in **5.2o**. It was possible to isolate single crystals of **5.2k** and **5.2p** by storing a saturated CH₂Cl₂ solution at -40 °C. Measuring the solid-state structure by X-ray diffraction unambiguously determined the structure to be the product of the expected *syn*-hydroboration (Figure 5.2).



Scheme 5.8: Hydroboration of various terminal and internal alkynes. Conditions for given isolated yield noted.

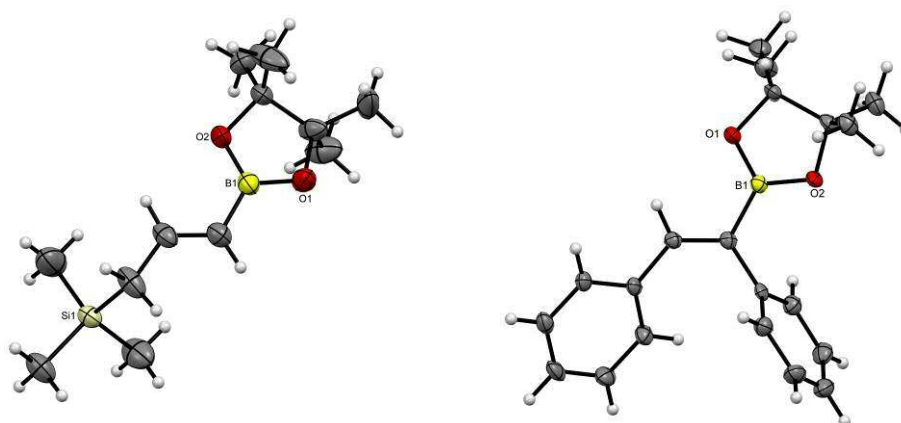
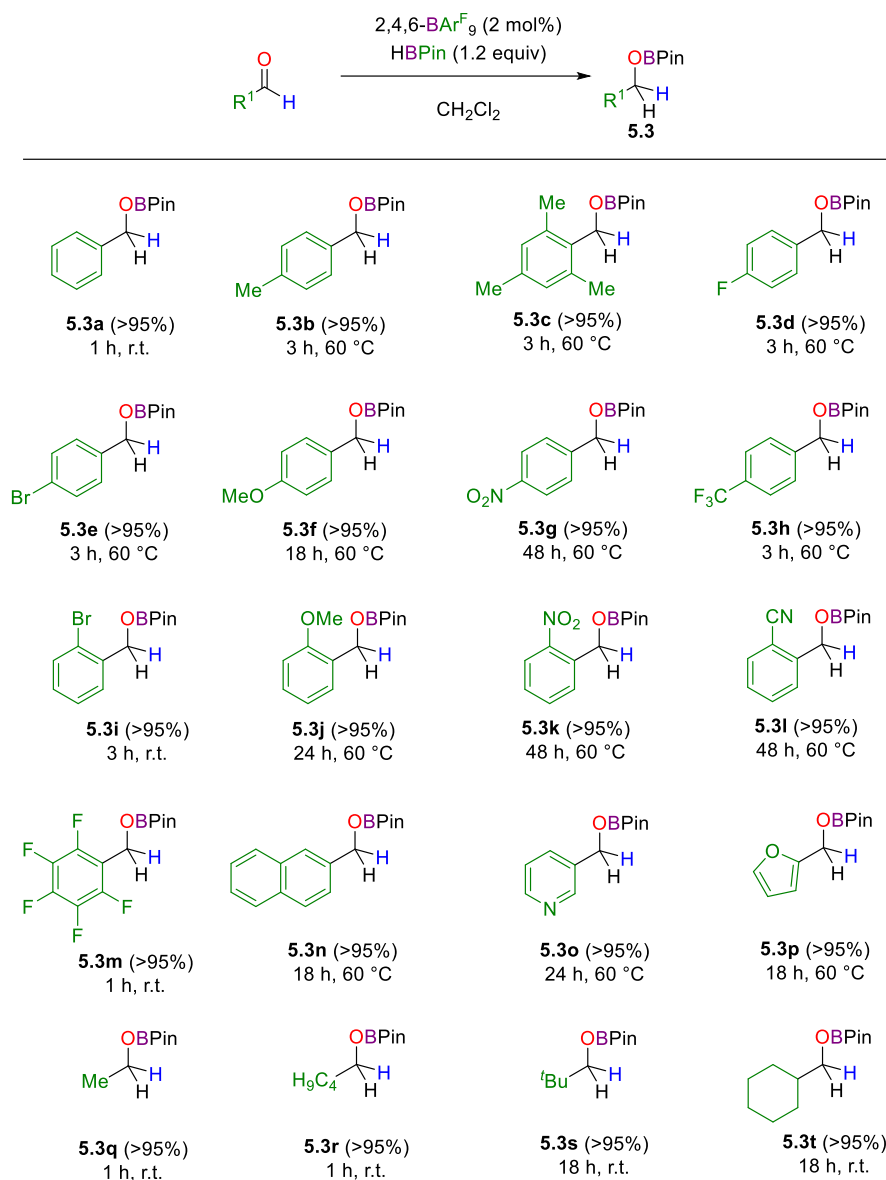


Figure 5.2: Solid-state structure of **5.2k** and **5.2p**. C: grey, H: white, O: red, B: yellow green, Si: grey. Thermal ellipsoids shown at 50% probability.

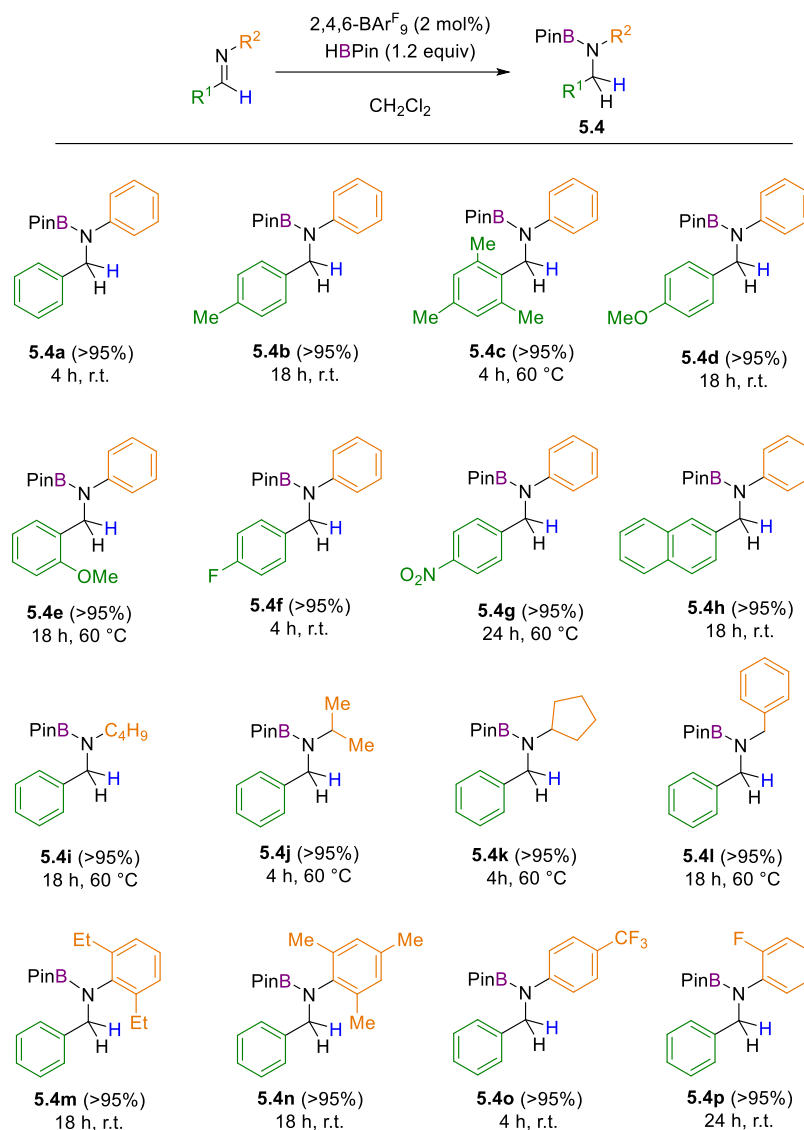
Using the same optimised reaction conditions from before, the hydroboration of various aldehydes was then undertaken. Through *in situ* NMR spectroscopic studies, it was observed that benzaldehyde was converted to the borate ester **5.3a** quantitatively within 1 h. Confirmation of **5.3a** was possible through multinuclear NMR spectroscopy by removing the volatiles under reduced pressure and redissolving in CDCl_3 . Following this successful result, the substrate scope was expanded to incorporate a broad spectrum of functional groups (Scheme 5.9). It was shown that benzaldehyde derivatives which included either electron withdrawing or donating groups e.g. NO_2 , CN, F, CF_3 , OMe, Me in the *para*- or *ortho*-position could be quantitatively converted to the borate esters **5.3a–m** in as little as 3 h however, $-\text{M}$ electronic functionalities required increased reaction times of 48 h.



Scheme 5.9: Hydroboration of aldehydes. Conditions indicated to reach quantitative conversion by *in situ* ^1H NMR spectroscopy.

The inclusion of heteroarenes also posed few obstacles with pyridine and furan derivatives furnishing the reduced products **5.3o–p** within 24 h showing that coordinating substrates may reversibly sequester the borane catalyst and/or reagent with little impingement on reactivity. Various other functionalities such as fused aryl moieties (**5.3n**) alkyl groups (**5.3q–s**) in addition to cyclic aliphatics all performed well producing the hydroborated species quantitatively in as little as 1 h at ambient temperature. This methodology is extremely portable to many different substituted aldehydes with quantitative conversion being seen in all cases however, in certain instances slightly elevated temperatures are required with somewhat increased reaction times being observed.

Moving on to other unsaturated frameworks, aldimines were then targeted for hydroboration using the same procedure. Initial tests using *N*-benzylideneaniline again showed very favourable results with the resulting borolanamine **5.4a** being formed rapidly in quantitative conversions. To expand the substrate scope, a number of other aldimines were synthesised according literature procedures to include various substitution patterns at both the nitrogen and carbon centres.^[148] Facile hydroboration of these imines was achieved using the standard conditions, with the exception of some examples which required mild heating, to produce the tertiary amines quantitatively within 4 to 24 h. *C*-functionalisation with electron-poor aromatics appeared to slow the reaction slightly taking the full 24 h (**5.4g**), while the electron-rich derivatives **5.4b–e** were formed in slightly shorter times of between 4 and 18 h. Additionally, sterically encumbered groups were also tolerated nicely as well as *o*-functionalised aromatic systems (**5.4c**, **5.4e**). *N*-functionalisation also showed little impediment to reactivity with both derivatised aromatics and aliphatic groups giving optimal conversions **5.4i–l**. Again, sterically demanding groups are also tolerated well in this position with no impact on reactivity showing the general applicability of this catalyst and procedure toward reduction reactions. For the purpose of complete characterisation, some borolanamine products were converted to the secondary amines taking advantage of their proclivity to undergo protodeborative decomposition during work-up (**5.4d–g**, **5.4p**).



Scheme 5.10: Hydroboration of imines. Conditions indicated to reach quantitative conversion by *in situ* ^1H NMR spectroscopy.

5.2.2 Novel Processing Methods in the Hydrosilylation of Aldehydes, Ketones and Imines

The synthetically useful $\text{B}(\text{C}_6\text{F}_5)_3$ catalysed hydrosilylation process was used in this section to reduce various aldehydes and ketones to their constituent silyl ethers, as well as in the tandem reductive amination of aldehydes and amines to their respective secondary amines under continuous-flow conditions. A benchmark for the hydrosilylation reaction conditions were established using a conventional batch reaction methodology. In this reaction, acetophenone was used as the model substrate with stoichiometric amounts of the commercially available triphenylsilane and 2 mol% borane catalyst loading. This was conducted at concentrations of 0.2 M

in toluene as reactions at higher concentrations and/or using CH_2Cl_2 as a solvent resulted in precipitate formation which may lead to failure of the injection apparatus when adapted to the flow procedure. Using this system, the silylether **5.5a** could be isolated in 78% yield after 30 minutes at ambient temperatures.

In order to replicate these conditions for use under continuous-flow conditions, a 0.4 M ketone/aldehyde solution and an 8 mM (2 mol%) $\text{B}(\text{C}_6\text{F}_5)_3$ solution were prepared with 5 ml aliquots of each being used for the reaction. The reagent streams were injected using syringe pumps and mixed using a T-piece at a flow rate of 0.083 ml/min giving a combined flow rate of 0.166 ml/min at the requisite concentration of 0.2 M. The combined reagents continued to a 5 ml reactor coil giving a residence time of 30 minutes, then to the quench reagent. Once the reaction had commenced, it was allowed to reach steady-state conditions for 6 minutes then allowed to flow for the designated residence time before collection commenced. Analysing the collected product upon dissolution in CDCl_3 via ^1H NMR spectroscopy showed that the silylether **5.5a** was present in very good conversions of 85%, a slight improvement over the batch reaction. Increasing the reaction temperature to 60 °C showed the reduced product **5.5a** in essentially quantitative conversions of 98%. With these encouraging results, the method to quench the reaction was optimised to ensure that the conversion that was measured was as a result of the flow process alone, rather than a combination of the flow process and the continued reaction in the collection flask.

Three possible quench methods were proposed to deactivate irreversibly the borane catalyst; 1) dropping the product stream into water; 2) dropping into a MeCN/CsF slurry or; 3) filtration through a short silica gel plug (Figure 5.3). Interestingly, the reaction appeared to continue while using the first two quench methods with time-dependent NMR studies showing continued product formation post-quench. This is perhaps not unexpected as recent reports by Ingleson and Ashley explicated how $\text{B}(\text{C}_6\text{F}_5)_3$ shows surprising stability and cooperative reactivity when in the presence of water in certain instances.^[149] Conversely, when filtering through a short silica gel plug, all remnants of the borane catalyst had been removed per ^{11}B and ^{19}F NMR spectroscopy with no further catalytic activity being recorded.

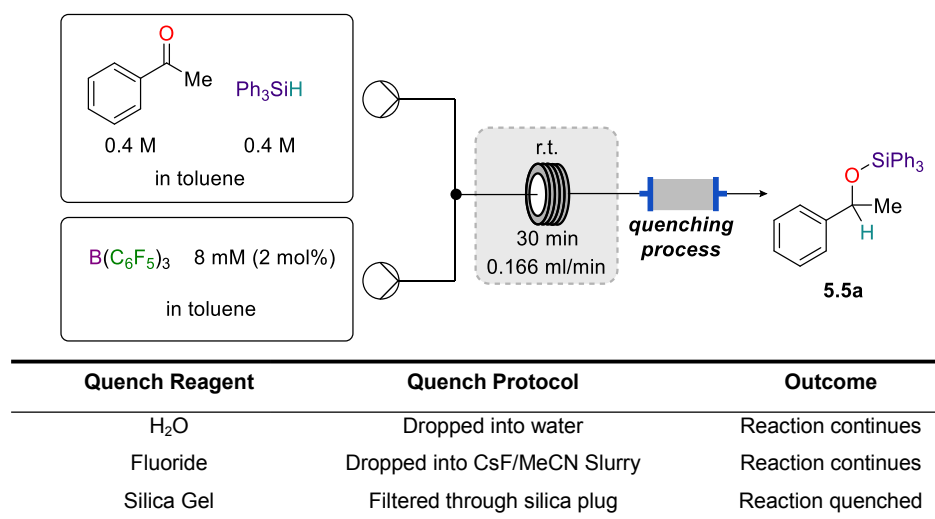


Figure 5.3: Quenching protocols to terminate catalytic activity.

Once the optimised conditions had been established, including the quench protocol, a range of ketones and aldehydes featuring various electronic and steric differentiated aryl substituents as well as aliphatic groups were then tested under these continuous-flow conditions. Generally the silylethers **5.5** and **5.6** could be generated in conversions greater than 90% with few exceptions. As noted in earlier work by Piers, ketones undergo the reduction reaction faster than the aldehydes hence the slightly lower conversions noted for compound **5.6** compared to **5.5**. This is reasoned as the effect of the more Lewis basic carbonyl sequestering the borane catalyst hence reducing catalytic activity. Conversely, the least Lewis basic derivative allows there to be more ‘free’ borane to activate the silane in an S_N2 reaction with the carbonyl. This difference in reactivity between aldehydes and ketones is more pronounced in the mesityl examples where identical reaction conditions gave the ketone derivative **5.5d** in 87% conversion whereas the aldehyde variant **5.6d** only reached 62% (Figures 5.4 and 5.5). Furthermore, lower conversions of 78% and 58% were noted for the electron rich *para*-methoxy functionalised systems **5.5g** and **5.6g** respectively, agreeing with the premise that electron poor carbonyl units, or significantly increased borane concentrations, are required for facile hydride transfer.^[23a]

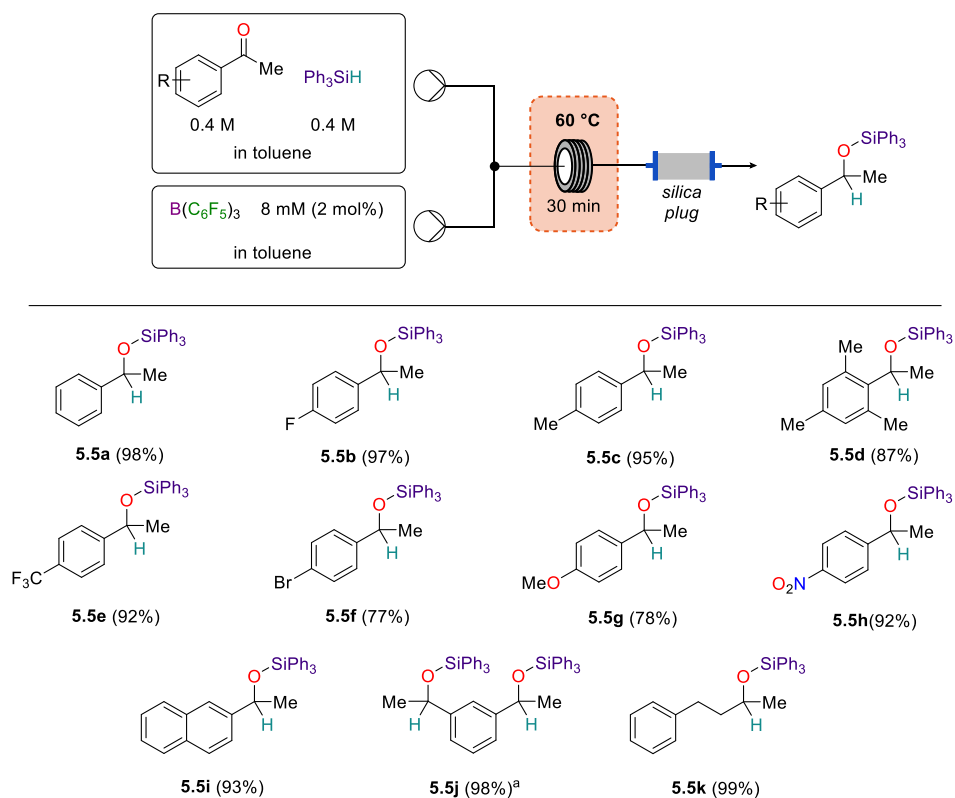


Figure 5.4: Continuous-flow hydrosilylation of ketones. Conversion measured via ^1H NMR spectroscopy. ^a Using the same reaction conditions with 2 equivalents of silane.

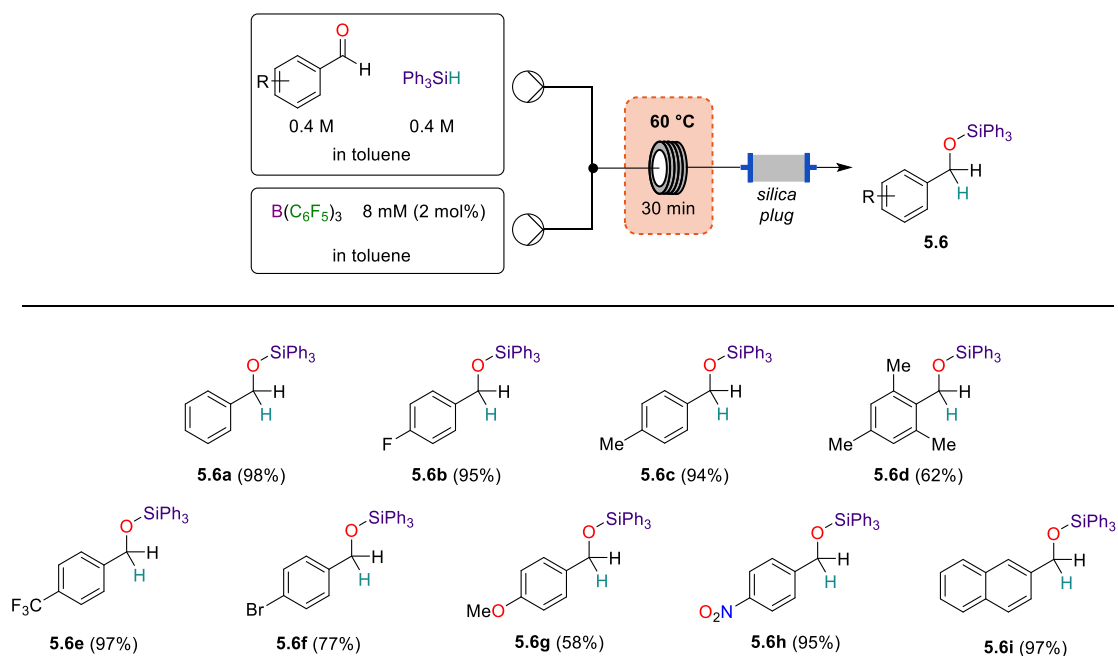


Figure 5.5: Continuous-flow hydrosilylation of aldehydes. Conversion measured via ^1H NMR spectroscopy.

Whilst these results are certainly encouraging as there are very few reports of using electron rich acetophenone or benzaldehyde derivatives in borane catalysed hydrosilylation due to their poor reactivity, it was decided to attempt to push these results further by embracing more facets of this novel processing technology. Therefore, simple modifications to the setup such as the use of high pressure HPLC pumps and a back-pressure regulator (BPR) allowed higher temperatures and pressures to be reached. Using this adapted apparatus the most problematic substrate, *p*-anisaldehyde, could form the silylether **5.6g** in a conversion of 67% in just 5 minutes at 150 °C and 130 PSI (Figure 5.6)

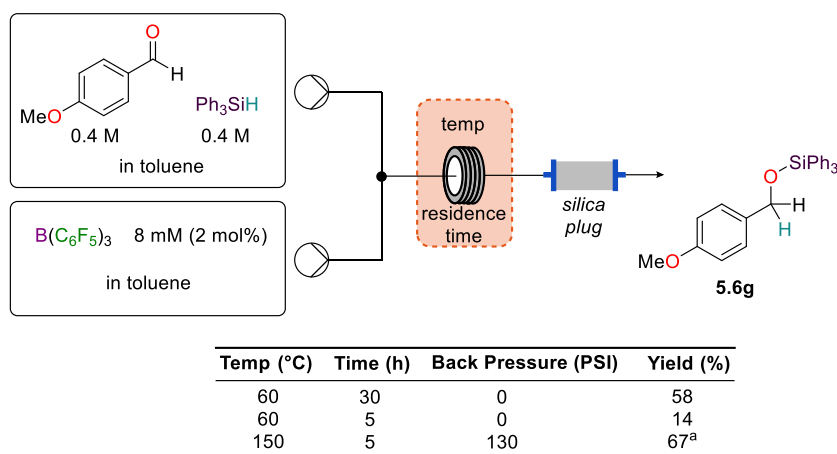


Figure 5.6: Comparison between low pressure/temperature and high pressure/temperature systems. ^a Using a back-pressure regulator, HPLC pumps and stainless steel reactor coil.

Combining ideas from Chapter 4 regarding tandem reactivity (see 4.2.3), as well as observations made earlier on the surprising observation that $B(C_6F_5)_3$ may remain catalytically active when exposed to water, it was proposed that the tandem imine formation and reductive hydrosilylation reaction could be conducted in flow.^[149] To affect this reaction, more adaptations were made to the setup to include a third reagent stream.^[137] The rationale being that the combination of the silane, amine and aldehyde should form the aldimine *in situ* alongside one equivalent of water in the first reactor coil, followed by the injection of the borane to carry out the hydrosilylation of the imine to the secondary amine in the second reactor coil (Figure 5.7). In this instance, the less sterically demanding silane Me_2PhSiH was utilised to reduce the steric occlusion between the silane and the substituent on nitrogen upon coordination.^[23c, 150] The reaction setup followed the general scheme; a combination of aldehyde (0.4 M) and silane (0.48 M) in toluene was mixed with the aniline derivative (0.48 M) in toluene using a T-piece adapter. Following a short residence time in the first reactor coil (40 s), the borane catalyst (8 mM) was injected, which then proceeded the second reactor coil. This was heated to 150 °C for 10 minutes

before passing through a cooling coil to leave the product stream at ambient temperature which could then pass through a silica gel plug before being collected.

The target amines **5.7** could be produced in good yields up to 89% with various arylated substituents on either the C or N terminus (Scheme 5.7). Notable exceptions to this are where strongly electron donating or withdrawing functionalities are installed at nitrogen such as *p*-OMe (**5.7f**) and *p*-CF₃ (**5.7g**) which gave the secondary amine in yields of 45% and 34% respectively (Figure 5.7). In this latter case, hydrosilylated aldehyde was also detected in the product stream as a result of poor imine formation. Due to the modular and adaptable format of continuous-flow chemistry, this trait could easily be remedied in future by increasing residence time or temperature of reactor coil 1 to ensure complete conversion to the imine takes place. As mentioned earlier, regardless of the formation of water as a side-product, the borane suffers no deleterious effects during this process opening more avenues for a merger between main group chemistry and this emergent processing technology. As can be seen below, comparison of results between the batch and flow methodologies clearly show advantages to using latter process (Figure 5.8). This radial diagram shows a number of comparative parameters by which to judge the effectiveness of each approach. Evidently, the continuous-flow method allows modularity and easy access to more forcing reaction conditions such as high pressures and temperatures thus leading to product formation in much faster times whilst greatly increasing the yield with the same catalyst loading.

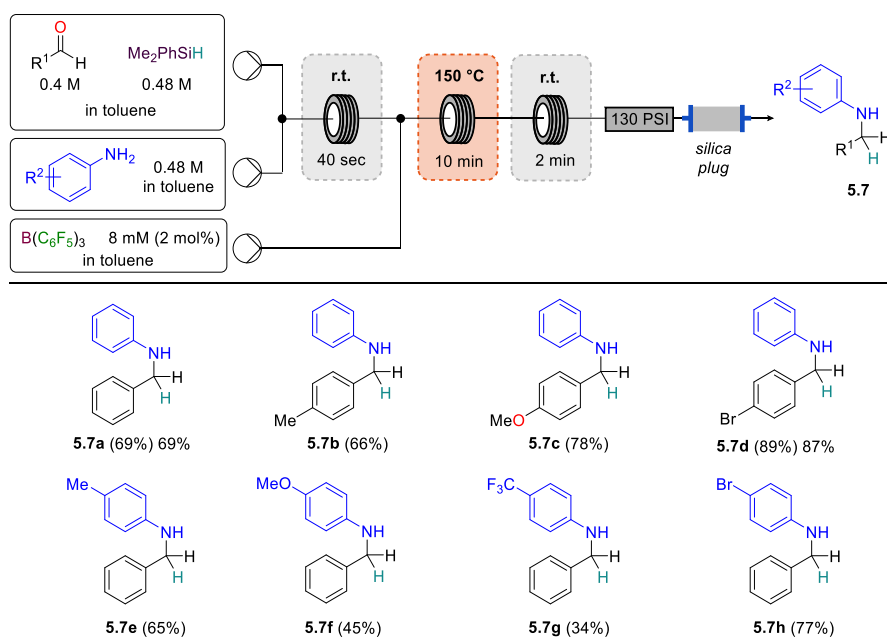


Figure 5.7: Tandem B(C₆F₅)₃ catalysis to give **5.7**. Conversion measured via ¹H NMR spectroscopy in parenthesis with isolated yields indicated for **5.7a** and **5.7d**.

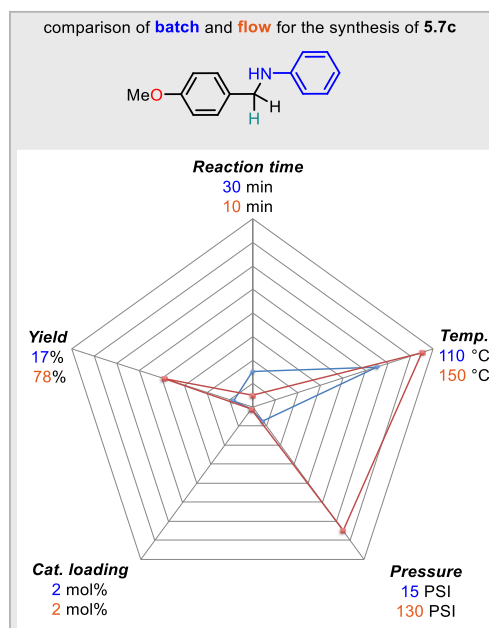


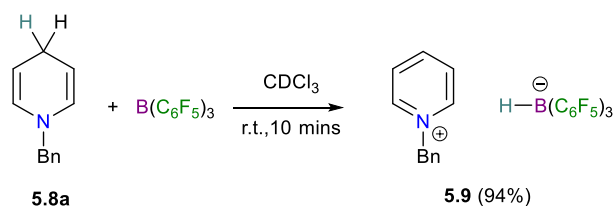
Figure 5.8: Radial chart comparing batch and flow systems in the synthesis of **5.7c**.

5.2.3 Biologically Inspired Borohydride Sources and Subsequent Transfer Hydrogenation Reactions

Initial bids to form borohydrides from biologically inspired hydride donors involved the reaction of $B(C_6F_5)_3$ with the NADPH analogue, 1-benzyl-1,4-dihydropyridine **5.8a**. Monitoring the reaction progress *via in situ* NMR spectroscopy revealed the formation of an aromatic pyridinium motif within 10 mins. This was evidenced by the 1H NMR spectrum with new diagnostic peaks observed at $\delta = 8.65$, 8.43 and 7.97 ppm for the *ortho*-, *para*- and *meta*-protons of the newly formed aromatic ring. This was corroborated in the ^{11}B NMR spectrum whereby a sharp doublet resonance was observed at $\delta = -25.2$ ppm ($^1J_{BH} = 66$ Hz), synonymous with the tris(pentafluorophenyl)hydridoborate anion, $[HB(C_6F_5)_3]^-$.^[151] This rapid quantitative conversion, taking less than 10 minutes, to the pyridinium borate was accompanied by a stark colour change from an off yellow solution to a dark crimson once the reaction had completed with the product being isolated in 94% yield. Conversely, the use of the less Lewis acidic 2,4,6- BAr^F_9 showed much slower reactivity in forming the hydridoborate species however, much lower conversions were measured with a number of other by-products persisting. Additionally, BPh_3 was also trialled with very little success, with barely any activation being observed.

Unfortunately, repeated efforts to obtain single crystals of **5.9** were met with little success with a red oil resulting from each attempt. Interestingly, the pyridinium borate salt **5.9** was stable in solution at elevated temperatures of 70 °C for over 3 hours

which is in contrast to similar systems reported recently whereby warming the Hantzsch ester ion pair to room temperature results in the reduction of the pyridinium ring at the *ortho*-position furnishing the 1,2-dihydropyridine borane adduct (see Scheme 5.6).^[145] According to these reports, this is posited to be driven by the formation of a favourable hard Lewis adduct between the borane and the ester carbonyl oxygen. This particular reversible reduction pathway is avoided through the exclusion of such coordinating functional groups alongside the slight steric congestion brought about by the amine substituent, thus allowing the equilibrium to favour the formation of the pyridinium borate.

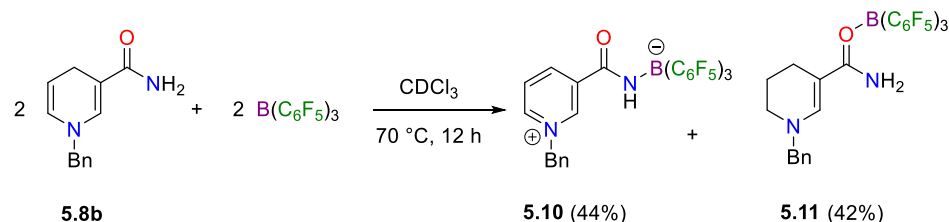


Scheme 5.11: Synthesis of pyridinium borate **5.9**.

Further investigations sought to compare the results from the native dihydropyridine **5.8a** with that of the C3-functionalised amidodihydropyridine **5.8b**. The proceeding 1:1 reaction between **5.8b** and $\text{B}(\text{C}_6\text{F}_5)_3$ shows that initially a strong amide-borane adduct is formed as evidenced by the *in situ* ^{11}B NMR spectrum, presenting a broad singlet resonance at $\delta = -2.4$ ppm, which is similar in nature to others reported previously.^[36b] Monitoring the ^{11}B NMR spectrum after 1 h showed a new sharp resonance emerging at $\delta = -10.9$ ppm indicating a new tetrahedral borate species. Heating the reaction to 70°C for 12 h produced a white crystalline solid that could be isolated in 44% yield.

Solid-state analyses *via* X-ray diffraction showed the product of the reaction to be the zwitterionic pyridinium amidoborate **5.10** which supports the chemical shift seen in the ^{11}B NMR spectrum as well as the downfield shift of the dihydropyridine backbone protons as a result of aromatisation (Scheme 5.12). Initial speculation regarding the mechanism proposed that the reaction proceeds *via* a dehydrogenative pathway through hydride abstraction by the borane, followed by dehydrocoupling to form the pyridinium amidoborane **5.10**. However, closer inspection of the multinuclear NMR spectra of the mother liquor exposed a new boron-containing compound in the ^{11}B NMR spectrum as well as newly formed aliphatic proton signals in the ^1H NMR spectrum. The new resonances were ascribed to the partially hydrogenated amidotetrahydropyridine borane adduct **5.11** which could be isolated as a pale green solid in a moderate yield of 42% to give a combined total yield for the reaction of 86%.

A deshielding effect is observed through the conjugated system as a result of borane coordination resulting in a downfield shift of the vinylic proton to $\delta = 7.92$ ppm in the ^1H NMR spectrum. Additionally, the newly formed aliphatic sp^3 signals arise as triplets at $\delta = 3.15$ and 2.11 ppm as well as a pentet at $\delta = 1.91$ ppm.



Scheme 5.12: Reaction between **5.8b** and $\text{B}(\text{C}_6\text{F}_5)_3$ to give 1:1 mixture of **5.10** and **5.11**.

Analysing the solid-state structure of **5.10** unambiguously confirmed the formation of the pyridinium heterocycle. With regard to the metric parameters, the C–C bonds lengths (1.369(5)–1.389(3) Å) and C–N bond lengths (1.345(3)–1.351(3) Å) of the heterocycle are consistent with literature values of similar nitrogen containing heterocyclic structures (Figure 5.9, Table 5.2).^[65] Other traits include the rotation of the amide fragment out of the plane of the heterocyclic ring by $34.3(3)^\circ$ thus reducing the effective orbital overlap and hindering conjugation. This is thought to arise as a result of the repulsion between the amide N–H proton and the aromatic C–H proton which features a distance of only 2.23(17) Å in the solid-state. When observing packing features in the solid-state, short intermolecular contacts are seen between the carbonyl oxygen and the electron deficient *ortho*-H atom of the pyridinium ring and one of the benzylic protons (Figure 5.10).

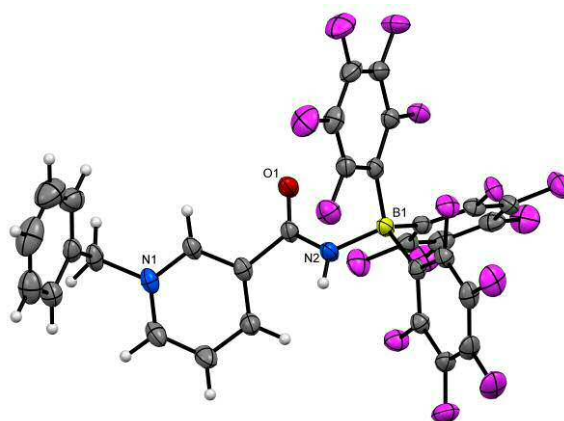


Figure 5.9: Solid-state structure of **5.10**. C: grey, H: white, N: blue, O: red, B: yellow-green, F: pink. Thermal ellipsoids shown at 50% probability.

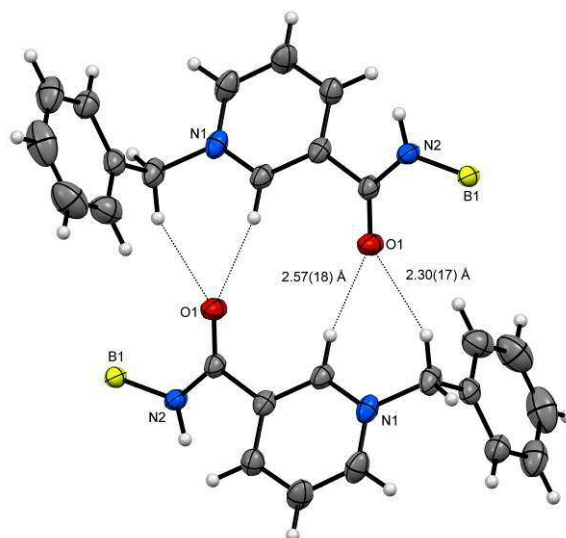
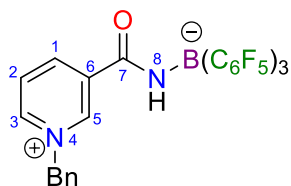


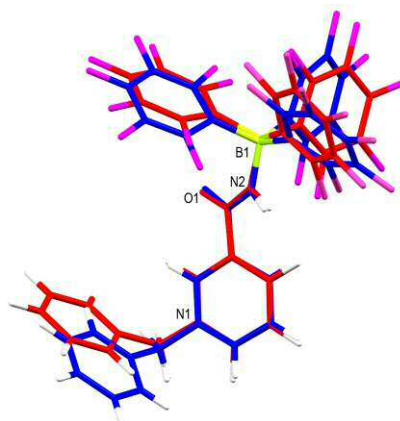
Figure 5.10: Solid-state packing of **5.10** depicting close intermolecular contacts. C₆F₅-groups omitted from boron atom for clarity. C: grey, O: red, N: blue, B: yellow-green. Thermal ellipsoids shown at 50% probability.

Theoretical studies at the B3LYP/6-31G* level of theory^[152] showed that the geometry optimised structure agreed well for the most part with the experimental solid-state structure as all calculated bond lengths were the same within error as the experimental data (Table 5.2). A slight difference arose when comparing the rotation of the nitrogen appended benzyl group, as the solid-state twist angle between the pyridinium ring and phenyl group was measured at 11.1(7)° whereas the *in silico* study calculated this to be more pronounced at 64.6° (Figure 5.11) presumed to be an artefact of packing effects in the solid-phase vs. gas-phase calculations.

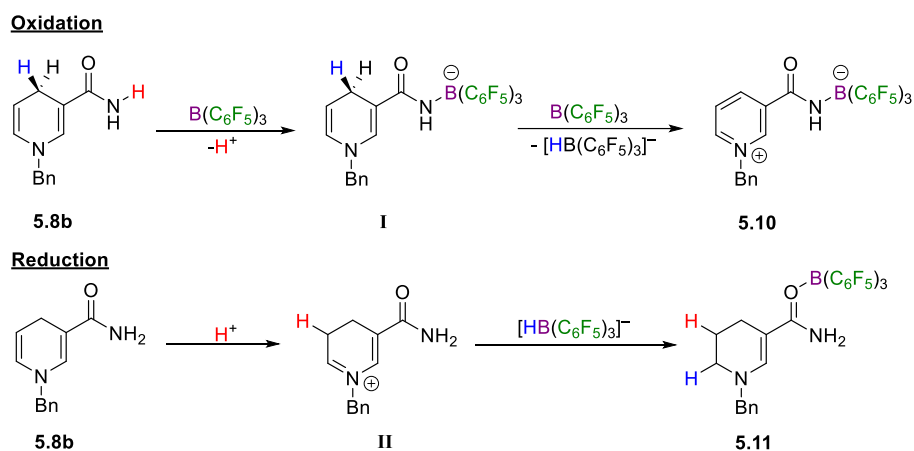
Table 5.2. Calculated and experimental bond distances for **5.10**.

Bond	Bond lengths (Å)	
	Experimental	Calculated
C ¹ -C ²	1.389(4)	1.399
C ² -C ³	1.369(5)	1.382
C ³ -N ⁴	1.345(3)	1.358
C ⁵ -N ⁴	1.351(3)	1.348
C ⁵ -C ⁶	1.379(4)	1.389
C ⁶ -C ¹	1.390(3)	1.398
C ⁶ -C ⁷	1.516(4)	1.528
C ⁷ -O	1.228(3)	1.234
C ⁷ -N ⁸	1.329(3)	1.333
N ⁸ -B	1.557(4)	1.570

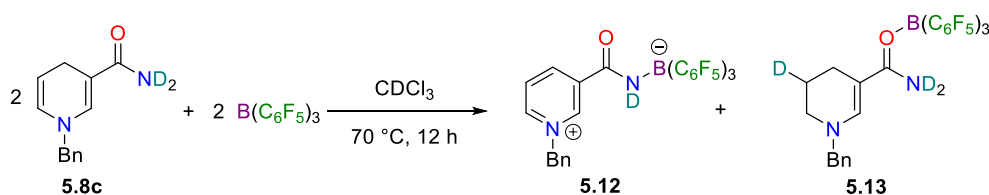


Figure 5.11: Overlay of experimental structure (blue) and calculated structure (red) of **5.10**.

With regard to the mechanism, it was posited that the initial adduct formation between the amide oxygen atom and boron causes the NH_2 protons to become more acidic. This in turn protonates the alkenyl functionality distal to the amide of another dihydropyridine equivalent with boron migration from oxygen to nitrogen to garner the intermediate **I**. Subsequent hydride migration from **I** to the iminium intermediate **II** generates the tetrahydropyridine borane adduct **5.11** and the zwitterionic pyridinium borate **5.10** in a 1:1 molar ratio (Scheme 5.13). It was hoped that using half an equivalent of the borane could also produce the desired product as half the supplied borane forms the simple Lewis adduct **5.11** which may be recycled upon heating. Unfortunately, a mixture of products were observed according to *in situ* NMR spectroscopy when using this new 1:2 borane to substrate stoichiometry. This result indicates that ‘free’ borane is essential for the desired reactivity to proceed *via* borane mediated hydride shuttling (Scheme 5.13). Alternatively, coordination of $\text{B}(\text{C}_6\text{F}_5)_3$ to the carbonyl oxygen of intermediate **II** promotes reduction of the iminium by an equivalent of **I**.

Scheme 5.13: Proposed mechanistic pathway for the disproportionation reaction between **5.8b** and $\text{B}(\text{C}_6\text{F}_5)_3$.

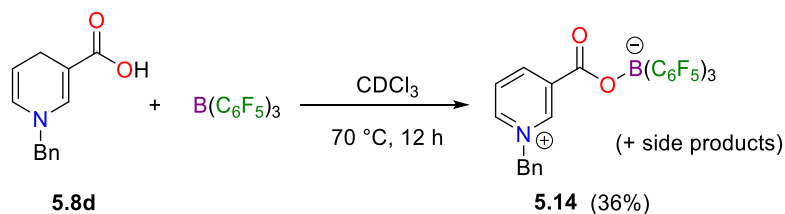
To understand further the reaction mechanism, isotopic labelling of the amide protons was conducted in a bid to ascertain what, if any, regiocontrol this reaction follows. The deuterated amide **5.8c**, synthesised by exposing **5.8b** to MeOD, was exposed to $B(C_6F_5)_3$ in a 1:1 stoichiometric ratio and heated to 70 °C in $CDCl_3$ for 12 h. The resulting NMR spectra showed that a single regioisomer was formed for the isolated compounds of **5.12** and **5.13** with selective deuteration at the β -position to the nitrogen of the heterocyclic ring (Scheme 5.14). Instead of the previously observed triplets, doublets now prevailed at $\delta = 3.15$ ppm and 2.10 ppm for the methylene protons adjacent to the deuterated position. Further to this, the pentet that was observed previously endured however, with an integral of 1 at $\delta = 1.91$ ppm.



Scheme 5.14: Deuterium labelling studies into the hydrogen transfer reaction of **5.8c**.

This reaction was then repeated in the presence of a reducible reagent (4-fluorobenzaldehyde) however, no alcoholic product was observed with the aldehyde resonance remaining completely unaltered. Following the reaction coordinate by *in situ* NMR spectroscopy indicated that the reaction proceeds as seen in Scheme 5.12, with the two compounds **5.10** and **5.11** being observed, albeit amongst a small amount of side products.

Further work altered the functional group on the dihydropyridine backbone to a carboxylic acid in a bid to affect the same transformation as seen before. Indeed, applying the same conditions to the reaction with **5.8d** garnered the expected product **5.14**, which could be isolated in 36% yield (Scheme 5.15). Confirmation could be obtained by the presence of the aromatic motif in the 1H NMR spectrum alongside the diagnostic sharp singlet resonance of $\delta = -4.0$ ppm in the ^{11}B NMR spectrum. Unfortunately, the reduced product could not be isolated from the reaction mixture as a number of side reactions occurred according to spectroscopic analysis of the mother liquor. This reaction further reinforces new ground-breaking group 13 Lewis acid chemistry as carboxylic acids are not normally tolerated by similar highly electrophilic boranes, as set out in Chapter 4. These new examples of previously forbidden chemistry continue to push the boundaries of main group compounds and their applications in more diverse fields.

Scheme 5.15: Reaction between 1-benzyl-1,4-dihyronicotinic acid **5.8d** and $\text{B}(\text{C}_6\text{F}_5)_3$.

5.3 Conclusions

This chapter has shown how tailoring the Lewis acidity at boron can vastly change the reactivity and effectiveness in reduction reactions, specifically hydroborations. By attenuating the electrophilicity of the Lewis acid it was demonstrated that side reactions may be precluded while still remaining catalytically active in the hydroboration of a vast number of unsaturated reagents, such as alkynes, aldehyde and aldimines with tolerance to a plethora of electronic and steric functional groups. Pleasingly, low catalyst loading is required to produce the majority of these pinacol boronate esters in quantitative yields using only mild reaction conditions and relatively short reaction times. In addition to this, simple purification *via* either removal of volatiles under reduced pressure and/or filtering through a silica gel plug rendered this catalytic system incredibly useful in the hydroboration of a range of unsaturated substrates.

With regard to the continuous-flow aspect, this work has shown how there is significant benefit through the synergistic combination of novel processing methods and main group catalysis to affect hydrosilylation reactions. This has not only allowed the hydrosilylation of more problematic electron rich substrates which are not possible under traditional batch-type conditions, but also permitted the multi-step synthesis of secondary amines *via* a $\text{B}(\text{C}_6\text{F}_5)_3$ catalysed condensation reaction in a single procedure.

Finally, with only a small number of examples where biological inspired systems have been merged with main group chemistry, this work built upon this premise to develop thermally stable borohydrides from nicotinamide adenine dinucleotide phosphate (NADPH) mimics. Functionalisation of these dihydropyridines with either an amide or carboxylic acid moiety leads to a transfer hydrogenation-type reaction whereby one equivalent undergoes an oxidation to form the pyridinium borate whereas the second equivalent is reduced to the tetrahydropyridine. It was hypothesised that in this case the borane acts in a bifunctional manner, not only acting

as an initiator to promote the protonation of the alkene, but also to promote hydride transfer to reduce one equivalent of the dihydropyridine.

This chapter has shown how the combination of different fields can effectively overcome many hurdles in main group chemistry, paving the way for further bridging themes to tackle current pitfalls in early *p*-block reactivity.

Chapter 6

Experimental

6.1 General Experimental

With the exception of the synthesis of starting materials, all reactions and manipulations were carried out under an atmosphere of dry, O₂-free nitrogen using standard double-manifold techniques with a rotary oil pump. A nitrogen-filled glove box (MBraun) was used to manipulate solids including the storage of starting materials, room temperature reactions, product recovery and sample preparation for analysis. All solvents (toluene, CH₂Cl₂, hexane, pentane, THF, 1,4-dioxane, Et₂O) were dried by employing a Grubbs-type column system (Innovative Technology) or a solvent purification system MB SPS-800 and stored under a nitrogen atmosphere. Deuterated solvents were distilled and/or dried over molecular sieves before use. Chemicals were purchased from commercial suppliers and used as received. ¹H, ¹¹B, ¹³C, ¹⁹F, ²⁷Al, ²⁹Si and ⁷⁷Se NMR spectra were recorded on a Bruker Avance 300, Bruker Avance II 400 or Bruker Avance 500 spectrometers. ¹³C NMR spectra were recorded as ¹H decoupled. Chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS) and are referenced to CDCl₃ (7.26/77.16 ppm) as internal standards. NMR spectra were referenced to CFCI₃ (¹⁹F), BF₃·Et₂O/CDCl₃ (¹¹B), Al(NO₂)₃ (²⁷Al), TMS/CDCl₃ (²⁹Si) and Me₂Se (⁷⁷Se). The description of signals include: s = singlet, d = doublet, t = triplet, q = quartet, pent. = pentet, sext. = sextet, sept. = septet, m = multiplet and br. = broad. All coupling constants are absolute values and are expressed in Hertz (Hz). Yields are given as isolated yields unless otherwise states. All spectra were analysed assuming a first order approximation. IR-Spectra were measured on a Shimadzu IRAffinity-1 photospectrometer where intensity is denoted by s = strong, m = medium, w = weak and br. = broad. Mass spectra were measured on a Waters LCT Premier/XE or a Waters GCT Premier. Elemental Analysis was performed by Mr Stephen Boyer of London Metropolitan University.

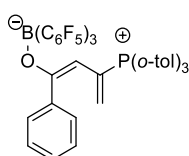
6.2 Activation of Allenyl Ketones and Esters using Cooperative Lewis Pairs and Boron Lewis Acids

6.2.1 Synthesis of Starting Materials

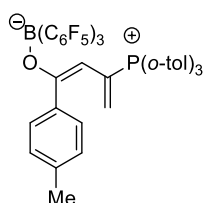
Allenyl ketones and esters **2.2** and **2.5** respectively were synthesised by Dr. Max. M. Hansmann using literature procedures.^[153]

6.2.2 Synthesis of Products

General Procedure 1: PR₃ (0.1 mmol, 1 equiv.) in CDCl₃ (0.5 ml) was added to B(C₆F₅)₃ (51 mg, 0.1 mmol, 1 equiv.) to give a pale yellow solution which was then transferred to **2.2** (0.1 mmol, 1 equiv.) to give a red solution. The mixture was transferred to an NMR tube and the ¹H, ¹³C ¹¹B, ³¹P and ³¹P{¹H} NMR spectra were measured. Multinuclear *in situ* NMR reaction spectra for **2.3a** were not recorded due to rapid crystal formation upon reaction, similarly *in situ* ¹³C NMR spectrum was not recorded for **2c** for the same reason. Crystals of **2.3a**, **2.3b**, **2.3c**, **2.3f**, **2.3j** and **2.3k** suitable for X-ray diffraction were grown from CDCl₃. The remaining solid was washed with hexane (3 x 2 ml) and dried *in vacuo* to give the pure product with isolated yields indicated. For **2.3d**, **2.3e**, **2.3g**, **2.3h** and **2.3i**, the volatiles were removed under reduced pressure to yield a solid which was washed with hexane (3 x 2 ml) and dried *in vacuo* to give the product with isolated yields indicated.

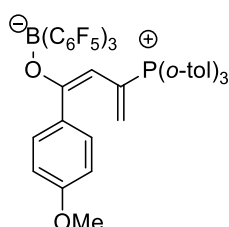


2.3a: Synthesised according to *General Procedure 1* using **2.2a** (14 mg, 0.1 mmol) tri(*o*-tol)phosphine (30 mg, 0.1 mmol). Yield: 58.3 mg, 88.9 μmol, 89%. **IR** ν_{\max} (cm⁻¹): 3054, 2987, 2685, 2412, 2305, 1642, 1558, 1515, 1466, 1423, 1266, 1087, 980, 896, 747, 735, 706. **HRMS** (ES⁻) *m/z* calculated for [M-H]⁻ [C₄₉H₂₈BF₁₅OP]⁻: 958.1768, found: 958.1782.

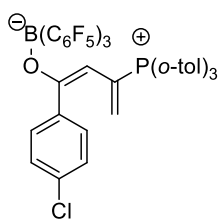


2.3b: Synthesised according to *General Procedure 1* using **2.2b** (16 mg, 0.1 mmol) tri(*o*-tol)phosphine (30 mg, 0.1 mmol). Yield: 65 mg, 66.7 μmol, 67%. Melting point: 178-193 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 7.37-7.07 (m, 12H, phosphine C-H), 7.37-7.07 (m, 4H, Ar-H), 5.40 (d, ³J_{HP} = 53 Hz, 1H, C-H), 5.22 (d, ³J_{HP} = 26 Hz, 1H, =C-H), 4.34 (d, ³J_{HP} = 11 Hz, 1H, =CH) 2.45 (br. s, 3H, Ar-CH₃), 2.25 (br. s, 3H, phosphine CH₃), 1.78 (br. s, 3H, phosphine CH₃), 1.59 (br. s, 3H, phosphine CH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 165.2 (s), 151.5 (s), 148.9

(s), 146.9 (s), 138.4 (s), 137.5 (s), 134.9 (s), 133.6 (s), 132.2 (s), 130.9 (s), 129.7 (s), 127.7 (s), 93.7 (s), 22.6 (s), 21.5 (s). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: -4.0 (br. s). **¹⁹F NMR** (282 MHz, CDCl₃, 298 K) δ/ppm: -132.7 (m, 2F, *o*-F), -161.1 (t, ³J_{FF} = 20 Hz, 1F, *p*-F), -165.9 (m, 2F, *m*-F). **³¹P NMR** (202 MHz, CDCl₃, 298 K) δ/ppm: 22.9 (br. s). **³¹P{¹H} NMR** (202 MHz, CDCl₃, 298 K) δ/ppm: 23.0 (s). **IR** ν_{max} (cm⁻¹): 3055, 2987, 2925, 2853, 2687, 2412, 2306, 1643, 1586, 1558, 1513, 1465, 1423, 1390, 1373, 1266, 1202, 1137, 1114, 1087, 997, 980, 927, 897, 836, 809, 742, 707. **HRMS** (ES⁻) *m/z* calculated for [M-H]⁻ [C₅₀H₃₀BF₁₅OP]⁻: 972.1924, found: 972.1971. **Elemental analysis** (%) calculated for C₅₀H₃₁BF₁₅OP: C 61.62, H 3.21, found: C 61.68, H: 3.14.

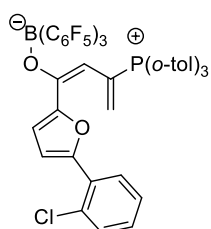


2.3c: Synthesised according to *General Procedure 1* using **2.2c** (17 mg, 0.1 mmol) tri(*o*-tol)phosphine (30 mg, 0.1 mmol). Yield: 47 mg, 47.4 μmol, 47%. Melting point: 176-187 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.28-7.14 (m, 12H, phosphine C-H), 7.52 (d, ³J_{HH} = 8.7 Hz, 2H, *o*-H), 6.89 (d, ³J_{HH} = 8.7 Hz, 2H, *m*-H), 5.54 (d, ³J_{HP} = 52 Hz, 1H, C-H), 5.35 (d, ³J_{HP} = 26 Hz, 1H, =C-H), 4.42 (d, ³J_{HP} = 11 Hz, 1H, =C-H), 3.79 (s, 3H, Ar-OCH₃), 2.45 (br. s, 3H, phosphine CH₃), 1.85 (br. s, 3H, phosphine CH₃), 1.65 (br. s, 3H, phosphine CH₃). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: -4.0 (br. s). **¹⁹F NMR** (282 MHz, CDCl₃, 298 K) δ/ppm: -132.7 (m, 2F, *o*-F), -161.1 (t, ³J_{FF} = 21 Hz, 1F, *p*-F), -165.9 (m, 2F, *m*-F). **³¹P NMR** (202 MHz, CDCl₃, 298 K) δ/ppm: 22.7 (br. s). **³¹P{¹H} NMR** (202 MHz, CDCl₃, 298 K) δ/ppm: 22.8 (s). **IR** ν_{max} (cm⁻¹): 3055, 2988, 2931, 2856, 2687, 2524, 2411, 2306, 1713, 1643, 1610, 1587, 1557, 1513, 1465, 1423, 1390, 1373, 1267, 1175, 1138, 1088, 1032, 980, 925, 908, 897, 842, 808, 756, 724, 706. **HRMS** (ES⁻) *m/z* calculated for [M-H]⁻ [C₅₀H₃₀BF₁₅O₂P]⁻: 988.1873, found 988.1891. **Elemental analysis** (%) calculated for C₅₀H₃₁BF₁₅O₂P·CDCl₃: C 55.14, H: 2.99, found: C 55.07, H 2.26.

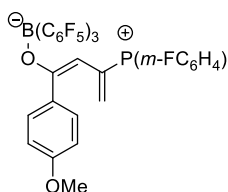


2.3d: Synthesised according to *General Procedure 1* using **2.2d** (18 mg, 0.1 mmol) tri(*o*-tol)phosphine (30 mg, 0.1 mmol). Yield: 98 mg, 98.5 μmol, 99%. Melting point: 186-194 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.15-7.17 (m, 12H, phosphine C-H), 7.53 (d, ³J_{HH} = 8.5 Hz, *o*-H), 7.34 (d, ³J_{HH} = 8.5 Hz, *m*-H), 5.52 (d, ³J_{HP} = 52 Hz, 1H, =C-H), 5.38 (d, ³J_{HP} = 25 Hz, 1H, =C-H), 4.48 (d, ³J_{HP} = 10 Hz, 1H, C-H), 2.44 (br. s, 3H, phosphine CH₃), 1.83 (br. s, 3H, phosphine CH₃), 1.66 (br. s, 3H, phosphine CH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 163.8 (m), 149.1 (s),

147.2 (s), 143.9 (s), 143.2 (s), 143.2 (s), 139.0 (s), 137.8 (s), 135.3 (s), 134.7 (s), 134.0 (s), 133.5 (s), 130.0 (s), 129.7 (s), 129.5 (s), 129.3 (s), 126.6 (s), 113.5 (s), 94.6 (m), 26.0 (s), 22.8 (br. s), 21.5 (s), 19.4 (s). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: -3.9 (br. s). **¹⁹F NMR** (282 MHz, CDCl₃, 298 K) δ/ppm: -132.9 (m, 2F, *o*-F), -160.8 (t, ³J_{FF} = 20 Hz, 1F, *p*-F), -165.6 (m, 2F, *m*-F). **³¹P NMR** (202 MHz, CDCl₃, 298 K) δ/ppm: 23.0 (br. s). **³¹P{¹H} NMR** (202 MHz, CDCl₃, 298 K) δ/ppm: 23.1 (s). **IR** ν_{max} (cm⁻¹): 3055, 2987, 2685, 2412, 2308, 1644, 1585, 1556, 1515, 1488, 1466, 1422, 1390, 1371, 1296, 1267, 1202, 1171, 1136, 1122, 1088, 1032, 1016, 996, 979, 926, 910, 898, 844, 808, 750, 729, 706. **HRMS** (ES⁻) *m/z* calculated for [M-H]⁻ [C₄₉H₂₇BClF₁₅OP]⁻: 992.1378, found: 992.1411.

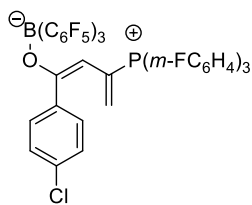


2.3e: Synthesised according to *General Procedure 1* using **2.2d** (24 mg, 0.1 mmol) tri(*o*-tol)phosphine (30 mg, 0.1 mmol). Yield: 100 mg, 88.1 μmol, 88%. Melting point: 98-115 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.59-6.84 (m, 12H, phosphine C-H), 7.59-6.84 (m, 4H, Ar-H), 7.59-6.84 (br. m, 2H, furan C-H), 5.87 (d, ³J_{HP} = 50 Hz, 1H, C-H), 5.63 (d, ³J_{HP} = 23 Hz, 1H, =C-H), 4.36 (d, ³J_{HP} = 7.4 Hz, 1H, =C-H), 2.30 (s, 3H, phosphine CH₃), 1.79 (s, 3H, phosphine CH₃), 1.58 (s, 3H, phosphine CH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 151.5 (s), 150.7 (m), 148.3 (s), 147.7 (s), 145.8 (s), 138.6 (s), 136.5 (s), 133.9 (s), 129.8 (s), 128.1 (s), 127.4 (s), 126.8 (s), 125.3 (s), 114.1 (s), 112.2 (s), 95.2 (m), 21.6 (s), 20.0 (m). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: -3.6 (br. s). **¹⁹F NMR** (282 MHz, CDCl₃, 298 K) δ/ppm: -132.9 (m, 2F, *o*-F), -161.2 (t, ³J_{FF} = 21 Hz, 1F, *p*-F), -165.7 (m, 2F, *m*-F). **³¹P NMR** (202 MHz, CDCl₃, 298 K) δ/ppm: 23.7 (s), 19.7 (br. s). **³¹P{¹H} NMR** (202 MHz, CDCl₃, 298 K) δ/ppm: 23.6 (s), 19.7 (br. s). **IR** ν_{max} (cm⁻¹): 3055, 2988, 2686, 2522, 2412, 2306, 1712, 1645, 1593, 1566, 1555, 1514, 1466, 1424, 1368, 1265, 1223, 1170, 1137, 1087, 1025, 978, 897, 808, 753, 723, 705. **HRMS** (ES⁻) *m/z* calculated for [M-H]⁻ [C₅₃H₂₉BClF₁₅O₂P]⁻: 1058.1484, found: 1058.1536.

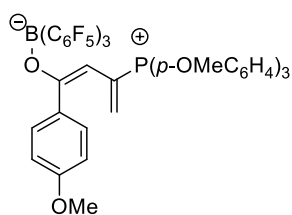


2.3f: Synthesised according to *General Procedure 1* using **2.2c** (17 mg, 0.1 mmol) tris(*m*-FC₆H₄) phosphine (32 mg, 0.1 mmol). Yield: 55 mg, 54.9 μmol, 55%. Melting point: 151-164 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.51-7.48 (m, 3H, phosphine C-H), 7.39 (br. t, ³J_{HH} = 8.1 Hz, 3H, phosphine C-H), 7.34 (d, ³J_{HH} = 8.2 Hz, 2H, *o*-H), 7.16 (m, 3H, phosphine C-H), 7.05 (m, 3H, phosphine C-H), 6.74 (d, ³J_{HH} = 8.2 Hz, 2H, *m*-H), 5.63 (d, ³J_{HP} = 53 Hz, 1H, =C-H), 5.06 (d, ³J_{HP} = 25 Hz, 1H, =C-H), 4.45 (d, ³J_{HP} = 9.8 Hz, 1H, =C-H), 3.67 (s, 3H, OCH₃). **¹³C NMR**

(126 MHz, CDCl₃, 298 K) δ /ppm: 166.0 (m), 163.8 (m), 161.9 (m), 160.0 (s), 148.6 (s), 139.6 (s), 137.5 (m), 135.4 (m), 132.9 (s), 132.6 (m), 131.1 (s), 129.7 (s), 129.7 (s), 129.4 (s), 123.1 (m), 120.6 (m), 119.4 (s), 118.8 (s), 114.0 (s), 92.3 (m), 55.1 (s). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: -3.8 (br. s). **¹⁹F NMR** (282 MHz, CDCl₃, 298 K) δ /ppm: -105.5 (m, 1F, phosphine), -133.2 (d, ³J_{FF} = 22 Hz, 2F, *o*-F), -160.8 (t, ³J_{FF} = 21 Hz, 1F, *p*-F), -165.6 (t, ³J_{FF} = 21 Hz, 2F, *m*-F). **³¹P NMR** (202 MHz, CDCl₃, 298 K) δ /ppm: 22.6 (s). **³¹P{¹H} NMR** (202 MHz, CDCl₃, 298 K) δ /ppm: 22.7 (s). **IR** ν_{\max} (cm⁻¹): 3055, 2987, 2686, 2411, 2306, 1644, 1610, 1585, 1556, 1514, 1480, 1465, 1423, 1270, 1262, 1237, 1175, 1098, 1090, 1033, 999, 981, 925, 897, 844, 794, 757, 723, 706. **HRMS** (AP⁺) *m/z* calculated for [M]⁺ [C₄₇H₂₂BF₁₈O₂P]⁺: 1002.1163, found: 1002.1166. **Elemental analysis** (%) calculated for C₄₇H₂₂BF₁₈O₂P: C 56.31, H 2.21, found: C 56.27, H 2.18.

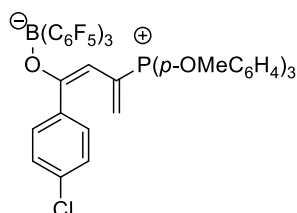


2.3g: Synthesised according to *General Procedure 1* using **2.2d** (18 mg, 0.1 mmol) tris(*m*-FC₆H₄)phosphine (32 mg, 0.1 mmol). Yield: 93 mg, 92.4 μ mol, 92%. Melting point: 119-141 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 7.02-7.54 (m, 12H, phosphine C-H) 7.02-7.54 (m, 4H, Ar-H), 5.62 (d, ³J_{HH} = 53 Hz, 1H, =C-H), 5.11 (d, ³J_{HH} = 25 Hz, 1H, =C-H), 4.52 (d, ³J_{HH} = 9.4 Hz, 1H, =CH). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 165.3 (m), 164.4 (m), 162.3 (m), 149.1 (m), 147.2 (m), 140.2 (m), 137.9 (m), 137.7 (s), 135.8 (m), 135.2 (s), 134.2 (m), 133.1 (m), 130.8 (m), 130.0 (m), 129.4 (m), 127.9 (s), 127.3 (s), 123.8 (m), 121.2 (m), 119.7 (m), 119.0 (m), 117.0 (m), 93.6 (m). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: -3.8 (br. s). **¹⁹F NMR** (282 MHz, CDCl₃, 298 K) δ /ppm: -105.2 (m, 1F, P(*m*-FC₆H₄)₃), -133.3 (m, 2F, *o*-F), -160.4 (t, ³J_{FF} = 20.3 Hz, 1F, *p*-F), -165.4 (m, 2F, *m*-F). **³¹P NMR** (202 MHz, CDCl₃, 298 K) δ /ppm: 22.9 (br. s). **³¹P{¹H} NMR** (202 MHz, CDCl₃, 298 K) δ /ppm: 22.8 (s). **IR** ν_{\max} (cm⁻¹): 3055, 2988, 2964, 2932, 2874, 2861, 2686, 2411, 2307, 1720, 1682, 1644, 1585, 1556, 1514, 1480, 1465, 1424, 1370, 1267, 1235, 1100, 1056, 1015, 998, 979, 966, 926, 898, 843, 794, 752, 731, 707. **HRMS** (ES⁻) *m/z* calculated for [M-H]⁻ [C₄₆H₁₈BClF₁₈OP]⁻: 1004.0626, found: 1004.0672.

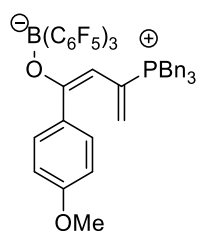


2.3h: Synthesised according to *General Procedure 1* using **2.2c** (17 mg, 0.1 mmol) tris(*p*-OMeC₆H₄)phosphine (35 mg, 0.1 mmol). Yield 70 mg, 67.4 μ mol, 67%. Melting point: 110-122 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 7.32 (d, ³J_{HH} = 8.4 Hz, 2H, Ar *o*-H), 7.24 (m, 6H, phosphine *m*-H), 6.89 (dd, ³J_{HH} = 8.8 Hz, ⁴J_{HH} = 2.5 Hz, 6H, phosphine *o*-H), 6.70 (d, ³J_{HH} = 8.7 Hz, 2H,

Ar *m*-H), 5.47 (d, $^3J_{\text{HP}} = 50$ Hz, 1H, =C-H), 5.00 (d, $^3J_{\text{HP}} = 24$ Hz, 1H, =C-H), 4.47 (d, $^3J_{\text{HP}} = 9.0$ Hz, 1H, =CH), 3.77 (s, 9H, phosphine CH₃), 3.66 (s, 3H, OCH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 164.8 (s), 164.11 (m), 159.9 (s), 149.0 (br. s), 147.1 (br. s), 137.7 (m), 135.8 (m), 132.0 (s), 131.7 (s), 130.8 (s), 129.9 (s), 115.8 (m), 113.9 (s), 109.2 (s), 108.4 (s), 94.0 (m), 55.7 (s), 55.3 (s). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: -3.8 (br. s). **¹⁹F NMR** (282 MHz, CDCl₃, 298 K) δ /ppm: -133.0 (m, 2F, *o*-F), -161.2 (t, $^3J_{\text{FF}} = 21$ Hz, 1F, *p*-F), -165.8 (t, $^3J_{\text{FF}} = 21$ Hz, 2F, *m*-F). **³¹P NMR** (202 MHz, CDCl₃, 298 K) δ /ppm: 21.8 (br. s). **³¹P{¹H} NMR** (202 MHz, CDCl₃, 298 K) δ /ppm: 21.7 (s). **IR** ν_{max} (cm⁻¹): 3055, 2988, 2845, 2687, 2410, 2307, 1713, 1643, 1596, 1568, 1513, 1505, 1464, 1443, 1423, 1364, 1297, 1267, 1184, 1170, 1112, 1084, 1026, 966, 897, 834, 805, 753, 728, 705. **HRMS** (ES⁻) *m/z* calculated for [M-H]⁻ [C₅₀H₃₀BF₁₅O₅P]⁻: 1036.1721, found: 1036.1725.

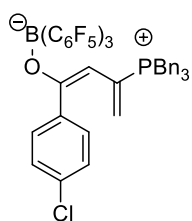


2.3i: Synthesised according to *General Procedure 1* using **2.2d** (18 mg, 0.1 mmol) tris(*p*-OMeC₆H₄)phosphine (35 mg, 0.1 mmol). Yield: 100 mg, 95.9 μ mol, 96%. Melting point: 87-99 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 7.30 (d, $^3J_{\text{HH}} = 8.8$ Hz, 2H, Ar *o*-H), 7.24-7.20 (m, 6H, phosphine C-H), 7.12 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H, Ar *m*-H), 6.92-6.91 (m, 6H, phosphine C-H), 5.47 (d, $^3J_{\text{HP}} = 49$ Hz, 1H, =C-H), 5.06 (d, $^3J_{\text{HP}} = 23$ Hz, 1H, =C-H), 4.54 (d, $^3J_{\text{HP}} = 8.6$ Hz, 1H, =CH), 3.78 (s, 9H, phosphine CH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 164.6 (m), 148.8 (m), 146.7 (m), 136.0 (m), 135.5 (m), 129.8 (s), 129.1 (s), 128.9 (s), 128.5 (s), 128.1 (s), 125.2 (s), 116.6 (m), 115.7 (m), 108.6 (m), 107.9 (m), 55.6 (m), 31.5 (s), 22.6 (s), 21.3 (s), 14.0 (s). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: -3.8 (br. s). **¹⁹F NMR** (282 MHz, CDCl₃, 298 K) δ /ppm: -133.1 (m, 2F, *o*-F), -160.9 (t, $^3J_{\text{FF}} = 20.7$ Hz, 1F, *p*-F), -165.6 (m, 2F, *m*-F). **³¹P NMR** (202 MHz, CDCl₃, 298 K) δ /ppm: 21.6 (s). **³¹P{¹H} NMR** (202 MHz, CDCl₃, 298 K) δ /ppm: 21.7 (s). **IR** ν_{max} (cm⁻¹): 3054, 2988, 2846, 2685, 2309, 1713, 1644, 1594, 1567, 1514, 1504, 1465, 1422, 1366, 1300, 1265, 1223, 1184, 1113, 1088, 1024, 979, 965, 896, 835, 806, 739, 706. **HRMS** (ES⁻) *m/z* calculated for [M-H]⁻ [C₄₉H₂₇BClF₁₅O₄P]⁻: 1040.1225, found: 1040.1245.



2.3j: Synthesised according to *General Procedure 1* using **2.2c** (17 mg, 0.1 mmol) tribenzylphosphine (30 mg, 0.1 mmol). Yield: 62 mg, 62.6 μ mol, 63%. Melting point: 168-181 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 7.34-7.39 (m, 9H, phosphine C-H), 7.34-7.39 (m, 2H, Ar *o*-H) 6.89 (m, 6H, phosphine C-H), 6.80 (d, $^3J_{\text{HH}} = 8.8$

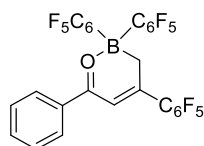
Hz, 2H, Ar *m*-H), 5.58 (d, $^3J_{\text{HP}} = 47$ Hz, 1H, =C-H), 5.19 (d, $^3J_{\text{HP}} = 20$ Hz, 1H, =C-H), 4.87 (d, $^3J_{\text{HP}} = 8.3$ Hz, 1H, =CH), 3.78 (s, 3H, OCH₃), 3.20 (d, $^3J_{\text{HP}} = 13$ Hz, 6H, phosphine CH₂). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 196.9 (s), 164.5 (m), 149.1 (br. s) 147.2 (br. s) 137.9 (br. s), 137.3 (s), 135.9 (m), 134.7 (s), 133.3 (s), 130.3 (m), 129.2 (m), 128.7 (m), 126.1 (s), 91.3 (m), 28.6 (m), 26.0 (m). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: -3.57 (br. s). **¹⁹F NMR** (282 MHz, CDCl₃, 298 K) δ /ppm: -132.9 (m, 2F, *o*-F), -160.3 (t, $^3J_{\text{FF}} = 21.1$, 1F, *p*-F), 165.1 (m, 2F, *m*-F). **³¹P NMR** (202 MHz, CDCl₃, 298 K) δ /ppm: 25.1 (m). **³¹P{¹H} NMR** (202 MHz, CDCl₃, 298 K) δ /ppm: 25.0 (s). **IR** ν_{max} (cm⁻¹): 3055, 2987, 2961, 2926, 2855, 2687, 2411, 2359, 2308, 1716, 1643, 1609, 1588, 1565, 1514, 1498, 1465, 1423, 1365, 1266, 1175, 1088, 1032, 980, 925, 896, 865, 845, 808, 751, 730, 706. **HRMS** (ES⁻) *m/z* calculated for [M-H]⁻ [C₅₀H₃₀BF₁₅O₂P]⁻: 988.1873, found: 988.1896. **Elemental analysis** (%) calculated for C₅₀H₃₀BF₁₅O₂P: C 60.63, H 3.15, found: C 60.48, H 2.94.



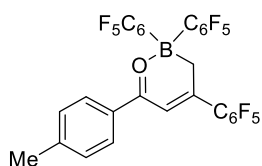
2.3k: Synthesised according to *General Procedure 1* using **2.2d** (18 mg, 0.1 mmol) tribenzylphosphine (30 mg, 0.1 mmol). Yield: 87 mg, 87.4 μmol , 87%. Melting point: 91-103 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 7.29-7.21 (m, 9H, phosphine C-H), 7.29-7.21 (m, 2H, Ar *o*-H), 7.14 (m, 2H, Ar *m*-H), 6.77 (m, 6H, phosphine C-H), 5.42 (d, $^3J_{\text{HP}} = 47$ Hz, 1H, =C-H), 5.09 (d, $^3J_{\text{HP}} = 20$ Hz, 1, =C-H), 4.8 (d, $^3J_{\text{HP}} = 8.1$ Hz, 1H, =CH), 3.13 (d, $^3J_{\text{HP}} = 13$ Hz, 6H, phosphine CH₂). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 186.7 (s), 167.5 (s), 155.9 (s), 148.3 (s), 139.8 (s), 138.1 (s), 130.3 (m), 129.6 (m), 128.8 (m), 126.2 (s), 93.6 (s), 34.5 (m), 22.4 (m). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: -3.5 (br. s). **¹⁹F NMR** (282 MHz, CDCl₃, 298 K) δ /ppm: -132.9 (m, 2F, *o*-F), -160.1 (t, $^3J_{\text{FF}} = 20.6$ Hz, 1F, *p*-F), -164.9 (m, 2F, *m*-F). **³¹P NMR** (202 MHz, CDCl₃, 298 K) δ /ppm: 25.4 (m). **³¹P{¹H} NMR** (202 MHz, CDCl₃, 298 K) δ /ppm: 25.2 (s). **IR** ν_{max} (cm⁻¹): 3055, 2987, 2927, 2854, 2687, 2412, 2361, 2307, 1714, 1678, 1645, 1589, 1515, 1464, 1423, 1364, 1266, 1222, 1088, 978, 964, 897, 751, 728, 707. **HRMS** (ES⁻) *m/z* calculated for [M-H]⁻ [C₄₉H₂₇BClF₁₅OP]⁻: 992.1378, found: 992.1357. **Elemental analysis** (%) calculated for C₄₉H₂₈BClF₁₅OP: C 59.15, H 2.84, found: C 59.02, H 2.86.

General procedure 2: B(C₆F₅)₃ (51 mg, 0.1 mmol, 1 equiv.) in CDCl₃ (0.5 ml) was added to **2.2** (0.1 mmol, 1 equiv.) and transferred to an NMR tube and the ¹H, ¹¹B, ¹³C and ¹⁹F NMR spectra were measured. Upon completion, the solvent was removed under reduced pressure yielding an oil which was washed with hexane (3 x 2 ml) and

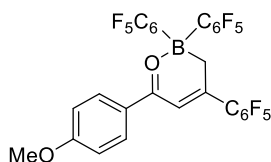
dried *in vacuo* to give a solid with isolated yields indicated. Crystals of **2.4a** and **2.4b** suitable for X-ray diffraction were obtained by dissolving in a few drops of toluene with the addition of 1 drop of hexane and leaving at -40 °C.



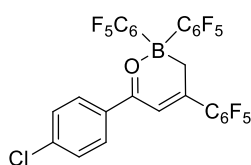
2.4a: Synthesised according to *General Procedure 2* using **2.2a** (14 mg, 0.1 mmol). Yield: 26 mg, 39.6 μmol , 40%. Melting point: 48-51 °C. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ /ppm: 8.26 (d, $^3J_{\text{HH}} = 7.7$ Hz, 2H, *o*-H), 7.88 (t, $^3J_{\text{HH}} = 7.6$ Hz, 1H, *p*-H), 7.67 (t, $^3J_{\text{HH}} = 7.7$ Hz, 2H, *m*-H), 7.33 (s, C-H), 2.74 (s, 2H, CH_2). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3 , 298 K) δ /ppm: 192.6 (s), 169.1 (s), 147.9 (dm, $^1J_{\text{CF}} = 255$ Hz), 144.3 (dm, $^1J_{\text{CF}} = 245$ Hz), 140.2 (dm, $^1J_{\text{CF}} = 255$ Hz), 140.0 (dm, $^1J_{\text{CF}} = 255$ Hz), 138.6 (s), 138.3 (dm, $^1J_{\text{CF}} = 245$ Hz), 137.3 (dm, $^1J_{\text{CF}} = 258$ Hz), 132.9 (s), 131.9 (s), 130.1 (s), 121.2 (s), 27.2 (m). **$^{11}\text{B NMR}$** (160 MHz, CDCl_3 , 298 K) δ /ppm: 2.7 (br. s). **$^{19}\text{F NMR}$** (282 MHz, CDCl_3 , 298 K) δ /ppm: -135.1 (m, 4F, *o*-F), -138.2 (m, 2F, *o*-F), -149.1 (t, $^3J_{\text{FF}} = 20.5$ Hz, 1F, *p*-F), -157.6 (t, $^3J_{\text{FF}} = 20.7$ Hz, 2F, *p*-F), -159.7 (m, 2F, *m*-F), -163.6 (m, 4F, *m*-F). **IR** ν_{max} (cm^{-1}): 3055, 2988, 2689, 2365, 2307, 1736, 1719, 1651, 1520, 1473, 1422, 1270, 1262, 1096, 982, 897, 759, 721, 708. **HRMS** (ES^-) m/z calculated for $[\text{M-H}]^- [\text{C}_{28}\text{H}_7\text{BF}_{15}\text{O}]^-$: 654.0387, found: 654.0378.



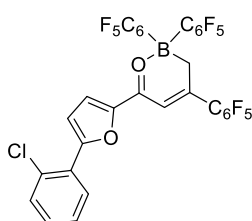
2.4b: Synthesised according to *General Procedure 2* using **2.2b** (16 mg, 0.1 mmol). Yield: 64 mg, 95.5 μmol , 96%. Melting point: 48-52 °C. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ /ppm: 8.19 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H, *o*-H), 7.46 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H, *m*-H), 7.29 (s, C-H), 2.71 (s, 2H, CH_2), 2.54 (s, 3H, CH_3). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3 , 298 K) δ /ppm: 191.8 (s), 168.1 (s), 151.7 (s), 148.1 (dm, $^1J_{\text{CF}} = 242$ Hz), 144.5 (dm, $^1J_{\text{CF}} = 250$ Hz), 142.7 (dm, $^1J_{\text{CF}} = 253$ Hz), 140.1 (dm, $^1J_{\text{CF}} = 255$ Hz), 138.7 (dm, $^1J_{\text{CF}} = 245$ Hz), 137.7 (dm, $^1J_{\text{CF}} = 255$ Hz), 132.4 (s), 131.2 (s), 130.6 (s), 121.4 (s), 116.4 (m), 22.8 (s). **$^{11}\text{B NMR}$** (160 MHz, CDCl_3 , 298 K) δ /ppm: 2.2 (br. s). **$^{19}\text{F NMR}$** (282 MHz, CDCl_3 , 298 K) δ /ppm: -135.1 (m, 4F, *o*-F), -138.5 (m, 2F, *o*-F), -149.6 (t, $^3J_{\text{FF}} = 20.1$ Hz, 1F, *p*-F), -157.8 (t, $^3J_{\text{FF}} = 20.6$ Hz, 2F, *p*-F), -159.9 (m, 2F, *m*-F), -163.7 (m, 4F, *m*-F). **IR** ν_{max} (cm^{-1}): 3055, 2983, 2686, 2411, 2360, 2343, 2307, 1714, 1650, 1606, 1520, 1486, 1422, 1364, 1319, 1268, 1264, 1223, 1184, 1093, 980, 896, 754, 726, 704. **HRMS** (ES^-) m/z calculated for $[\text{M-H}]^- [\text{C}_{29}\text{H}_9\text{BF}_{15}\text{O}]^-$: 668.0543, found: 668.0535. **Elemental analysis** (%) calculated for $\text{C}_{29}\text{H}_{10}\text{BF}_{15}\text{O}$: C 51.97, H 1.50, found: C 51.86, H 1.46.



2.4c: Synthesised according to *General Procedure 2* using **2.2c** (17 mg, 0.1 mmol). Yield: 68 mg, 99.1 μmol , 99%. Melting point: 64-71 $^{\circ}\text{C}$. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ/ppm : 8.30 (d, $^3J_{\text{HH}} = 8.6$ Hz, 2H, *o*-H), 7.23 (s, C-H), 7.11 (d, $^3J_{\text{HH}} = 8.6$ Hz, 2H, *m*-H), 4.00 (s, 3H, CH_3), 2.66 (s, 2H, CH_2). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3 , 298 K) δ/ppm : 189.0 (s), 168.8 (s), 165.8 (s), 148.0 (dm, $^1J_{\text{CF}} = 248$ Hz), 144.2 (dm, $^1J_{\text{CF}} = 251$ Hz), 140.1 (dm, $^1J_{\text{CF}} = 248$ Hz), 139.8 (dm, $^1J_{\text{CF}} = 250$ Hz), 138.2 (dm, $^1J_{\text{CF}} = 248$ Hz), 137.2 (dm, $^1J_{\text{CF}} = 255$ Hz), 135.2 (s), 125.5 (s), 120.9 (s), 115.8 (s), 56.4 (s), 26.9 (br. s). **$^{11}\text{B NMR}$** (160 MHz, CDCl_3 , 298 K) δ/ppm : 1.7 (br. s). **$^{19}\text{F NMR}$** (282 MHz, CDCl_3 , 298 K) δ/ppm : -135.2 (m, 4F, *o*-F), -138.9 (m, 2F, *o*-F), -150.3 (t, $^3J_{\text{FF}} = 20.9$ Hz, 1F, *p*-F), -158.2 (t, $^3J_{\text{FF}} = 21.0$ Hz, 2F, *p*-F), -160.2 (m, 2F, *m*-F), -163.9 (m, 4F, *m*-F). **IR** ν_{max} (cm^{-1}): 3056, 2989, 2687, 2413, 2361, 2308, 1713, 1649, 1593, 1572, 1518, 1496, 1465, 1427, 1384, 1271, 1264, 1178, 1095, 1050, 1019, 993, 978, 922, 897, 845, 758, 722, 706. **HRMS** (ES^-) m/z calculated for $[\text{M}-\text{H}]^-$ [$\text{C}_{29}\text{H}_9\text{BF}_{15}\text{O}_2$] $^-$: 684.0605, found: 684.0624.

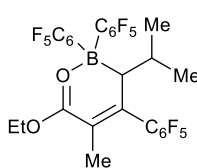


2.4d: Synthesised according to *General Procedure 2* using **2.2d** (18 mg, 0.1 mmol). Yield: 58 mg, 84.0 μmol , 84%. Melting point: 61-66 $^{\circ}\text{C}$. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ/ppm : 8.22 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H, *o*-H), 7.64 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H, *m*-H), 7.28 (s, 1H, C-H), 2.75 (s, 2H, CH_2). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3 , 298 K) δ/ppm : 191.4 (s), 170.1 (s), 148.0 (dm, $^1J_{\text{CF}} = 260$ Hz), 146.1 (s), 144.3 (dm, $^1J_{\text{CF}} = 252$ Hz), 142.8 (dm, $^1J_{\text{CF}} = 245$ Hz), 140.0 (dm, $^1J_{\text{CF}} = 248$ Hz), 138.4 (dm, $^1J_{\text{CF}} = 259$ Hz), 137.3 (dm, $^1J_{\text{CF}} = 256$ Hz), 133.0 (s), 131.2 (s), 130.6 (s), 120.8 (s), 27.3 (s). **$^{11}\text{B NMR}$** (160 MHz, CDCl_3 , 298 K) δ/ppm : 2.1 (br. s). **$^{19}\text{F NMR}$** (282 MHz, CDCl_3 , 298 K) δ/ppm : -135.2 (m, 4F, *o*-F), -138.0 (m, 2F, *o*-F), -148.7 (t, $^3J_{\text{FF}} = 21.1$ Hz, 1F, *p*-F), -157.4 (t, $^3J_{\text{FF}} = 20.7$ Hz, 2F, *p*-F), -159.6 (m, 2F, *m*-F), -163.5 (m, 4F, *m*-F). **IR** ν_{max} (cm^{-1}): 3055, 2988, 2686, 2362, 2343, 2307, 1712, 1669, 1651, 1520, 1484, 1423, 1363, 1320, 1266, 1223, 1093, 980, 896, 749 732, 706. **HRMS** (ES^-) m/z calculated for $[\text{M}-\text{H}]^-$ [$\text{C}_{28}\text{H}_6\text{BClF}_{15}\text{O}$] $^-$: 687.9997, found: 687.9984.

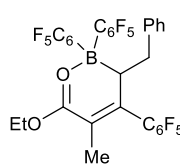


2.4e: Synthesised according to *General Procedure 2* using **2.2e** (24 mg, 0.1 mmol). Yield: 46 mg, 60.8 μmol , 61%. Melting point: 58-63 $^{\circ}\text{C}$. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ/ppm : 8.04 (br. s, 1H, C-H), 7.81 (m, 1H, C-H), 7.47 (m, 2H, Ar-H), 7.36 (m, 2H, Ar-H), 7.16 (s, 1H, C-H), 2.60 (s, 2H, CH_2). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3 , 298 K) δ/ppm : 176.1 (br. s), 166.5 (br. s), 161.9 (br. s), 148.0 (dm,

$^1J_{CF} = 262$ Hz), 144.2 (dm, $^1J_{CF} = 254$ Hz), 140.3 (dm, $^1J_{CF} = 247$ Hz), 139.9 (dm, $^1J_{CF} = 255$ Hz), 138.2 (dm, $^1J_{CF} = 260$ Hz), 137.3 (dm, $^1J_{CF} = 256$ Hz), 134.4 (s), 133.0 (s), 132.6 (s), 132.3 (s), 132.1 (s), 131.7 (s), 129.8 (s), 127.7 (br. s), 126.6 (s), 120.5 (s), 27.3 (br. s). **^{11}B NMR** (160 MHz, CDCl_3 , 298 K) δ /ppm: 1.9 (br. s). **^{19}F NMR** (282 MHz, CDCl_3 , 298 K) δ /ppm: -135.1 (m, 4F, *o*-F), -138.3 (m, 2F, *o*-F), -149.9 (t, $^3J_{FF} = 21$ Hz, 1F, *p*-F), -158.1 (t, $^3J_{FF} = 21$ Hz, 2F, *p*-F), -160.1 (m, 2F, *m*-F), -163.9 (m, 4F, *m*-F). **IR** ν_{max} (cm^{-1}): 3055, 2987, 2686, 2411, 2361, 2343, 2307, 1714, 1651, 1519, 1493, 1482, 1422, 1365, 1320, 1266, 1186, 1093, 1029, 982, 897, 752, 728, 706. **Elemental analysis** (%) calculated for $\text{C}_{32}\text{H}_9\text{BClF}_{15}\text{O}_2$: C 50.80, H 1.20, found: C 50.74, H 1.12.

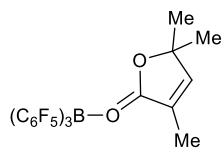


2.6a: $\text{B}(\text{C}_6\text{F}_5)_3$ (103 mg, 0.2 mmol) was dissolved in toluene (1 ml) and was added to ethyl 2,5-dimethylhexa-2,3-dienoate (**2.5a**) (34 mg, 0.2 mmol) in toluene (1 ml). The reaction was left to stand at room temperature for 24 h giving an orange solution. Removal of the solvent afforded a dark orange oil. Addition of hexane (2 ml) and a small amount of DCM (ca. 0.5 ml to solubilise the oil) followed by slow evaporation of the solvent afforded colourless crystals of the product. The remaining solution was decanted off and the solid product washed with pentane (3 x 2 ml) and dried *in vacuo* to give the crude mixture. **^{11}B NMR** (128 MHz, CDCl_3 , 298 K) δ /ppm: 4.2 (br. s). (Due to intractable mixture of products analysis *via* ^1H , ^{13}C and ^{19}F NMR spectroscopy was not possible, however ^{11}B NMR spectra has been identified to show the desired broad singlet of the chelating boron).



2.6b: $\text{B}(\text{C}_6\text{F}_5)_3$ (103 mg, 0.2 mmol) was dissolved in toluene (1 ml) and was added to ethyl 2-methyl-5-phenylpenta-2,3-dienoate (**2.5b**) (43 mg, 0.2 mmol) in toluene (1 ml) giving a yellow solution upon addition. The reaction was left to stand at room temperature for 24 h. Removal of the solvent afforded a dark orange oil. Addition of hexane (2 ml) and a small amount of toluene (ca. 0.5 ml to solubilise the oil) followed by slow evaporation of the solvent afforded colourless crystals of the product. The remaining solution was decanted off and the solid product washed with pentane (3 x 2 ml) and dried *in vacuo* to give the pure product (13.7 mg, 9%, 0.02 mmol). **^1H NMR** (400 MHz, C_6D_6 , 298 K) δ /ppm: 7.08-7.07 (m, 3H, *o*-H and *p*-H), 6.95 (d, $^3J_{\text{HH}} = 6.6$ Hz, 2H, *m*-H), 4.68 and 4.43 (m, 2H, CH_2 diastereotopic), 3.08 and 2.65 (m, 2H, CH_2 diastereotopic), 1.78 (d, $^4J_{\text{HH}} = 2$ Hz, 3H, CH_3), 1.51 (t, $^3J_{\text{HH}} = 7.1$ Hz, 3H, CH_3), 0.88 (t, $^3J_{\text{HH}} = 7.1$ Hz, 1H, CH). **^{11}B NMR** (128 MHz, C_6D_6 , 298 K) δ /ppm: 4.5 (br. s). **^{19}F NMR** (282 MHz, C_6D_6 , 298 K) δ /ppm: -132.9 (m, 2F, *o*-F), -133.2 (m, 1F, *o*-F), -137.5 (br. s, 2F, *o*-F), -139.3 (m,

1F, *o*-F), -152.2 (t, $^3J_{FF} = 21$ Hz, 1F, *p*-F), -157.2 (t, $^3J_{FF} = 21$ Hz, 1F, *p*-F), -157.8 (t, $^3J_{FF} = 20$ Hz, 1F, *p*-F), -160.4 (m, 1F, *m*-F), -161.5 (m, 1F, *m*-F), -163.3 (m, 2F, *m*-F), -163.6 (m, 2F, *m*-F).



2.7: B(C₆F₅)₃ (102 mg, 0.2 mmol) was dissolved in toluene (2 ml) and added to ethyl 2,4-dimethylpenta-2,3-dienoate (**2.5c**) (31 mg, 0.2 mmol) to give a brown solution. After the addition of 1 equiv. H₂O the reaction was left at room temperature for 72 h. Slow evaporation of the solvent gave large brown crystals that were suitable for X-ray diffraction. The remaining solid was washed with hexane (3 x 2 ml) and dried *in vacuo* to give the pure product. (72 mg, 0.12 mmol, 56%). **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.42 (s, 1H, =CH), 2.03 (s, 3H, CH₃), 1.43 (s, 6H, (CH₃)₂). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 160.9 (s), 148.8 (s), 146.8 (s), 138.9 (s), 137.8 (s), 135.8 (s), 128.7 (s), 23.7 (s), 17.0 (s), 9.6 (s). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 40.4 (br. s), 26.2 (br. s), 1.1 (br. s, B–O adduct), -3.6 (br. s). **¹⁹F NMR** (282 MHz, CDCl₃, 298 K) δ/ppm: -134.7 (d, $^3J_{FF} = 21$ Hz, 2F, *o*-F), -157.3 (t, $^3J_{FF} = 21$ Hz, 1F, *p*-F), -164.2 (t, $^3J_{FF} = 21$ Hz, 2F, *m*-F). **HRMS** (ES⁺) *m/z* calculated for [M-B(C₆F₅)₃]⁺ [C₇H₁₀O₂]⁺: 126.0681, found: 126.0683.

6.2.3 Computational Studies

All geometry optimisations were undertaken using the B3LYP functional^[152a] and 6-31G* basis set^[154] within Jaguar.^[155] Subsequent single point calculations were undertaken using the B3LYP functional and larger 6-311G*+ basis set.

6.2.4 Crystallographic Studies

Single crystals of **2.3**, **2.4**, **2.6** and **2.7** were grown under an inert atmosphere. Intensity data sets were collected at low temperature with an Agilent Dual SuperNova diffractometer using monochromatic Cu-Kα radiation (1.54184 Å) and a CCD area detector. The data was collected at Data collection and processing implemented CrysAlisPro^[156] and a gaussian absorption correction applied within the CrysAlisPro suite. The structures were solved by direct methods and refined against *F*² using the SHELXTL package.^[157] The structures have been deposited with the Cambridge Structural Database (CCDC deposition numbers 1062326-1062327 and 1062523-1062531).

Table 6.2.1 Crystallographic data for compounds **2.3**, **2.4**, **2.6** and **2.7**.

Compound	2.3a	2.3b	2.3c	2.3f
Empirical Formula	C ₅₀ H ₃₀ BCl ₃ F ₁₅ OP	C ₅₀ H ₃₁ BF ₁₅ OP	C ₅₀ H ₃₁ BF ₁₅ O ₂ P	C ₄₇ H ₂₂ BF ₁₈ O ₂ P
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	13.00937(15)	12.9285(2)	11.7467(2)	12.68853(19)
<i>b</i> /Å	20.5826(2)	20.8057(3)	22.3776(4)	18.3742(3)
<i>c</i> /Å	17.61995(18)	20.3530(3)	17.2697(3)	17.9394(3)
α /°	90	90	90	90
β /°	102.1504(10)	107.5893(18)	105.0260(18)	99.2369(16)
γ /°	90	90	90	90
<i>V</i> /Å ³	4612.34(9)	5218.72(15)	4384.36(13)	4128.17(12)
<i>Z</i>	4	4	4	4
<i>T</i> /K	150(2)	150(2)	150(2)	150(2)
<i>D</i> _c /g.cm ⁻³	1.555	1.544	1.501	1.613
Crystal size/mm	0.400 x 0.220 x 0.110	0.280 x 0.100 x 0.090	0.240 x 0.1.00 x 0.070	0.270 x 0.080 x 0.050
Total data	18570	21771	18384	17523
Unique data	8002	10346	8680	8156
<i>R</i> _{int}	0.0212	0.0385	0.0268	0.0290
<i>R</i> ₁ [<i>F</i> ² >2 σ (<i>F</i> ²)]	0.0424	0.0651	0.0357	0.0450
w <i>R</i> ₂ (all data)	0.1131	0.1931	0.0950	0.1326
GoF	1.044	1.040	1.021	1.033
$\rho_{\min}/\rho_{\max}/\text{e}\text{\AA}^{-3}$	-0.534/0.732	-1.147/1.287	-0.344/0.377	-0.292/0.662
CCDC code	1062523	1062524	1062525	1062526

Compound	2.3j	2.3k	2.4a	2.4b
Empirical Formula	C ₅₀ H ₃₁ BF ₁₅ O ₂ P	C ₄₉ H ₂₈ BClF ₁₅ OP	C ₂₈ H ₈ BF ₁₅ O	C ₃₆ H ₁₈ BF ₁₅ O
Crystal System	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
<i>a</i> /Å	13.0028(3)	13.0092(2)	11.1762(5)	11.3113(4)
<i>b</i> /Å	15.1522(3)	15.1502(2)	15.7904(6)	11.5408(5)
<i>c</i> /Å	23.0392(5)	22.7586(3)	14.5984(6)	12.6612(5)
α /°	90	90	90	105.469(4)
β /°	103.336(2)	104.4200(16)	109.641(5)	96.466(3)
γ /°	90	90	90	91.745(3)
<i>V</i> /Å ³	4416.79(16)	4344.22(12)	2426.40(19)	1579.64(11)
<i>Z</i>	4	4	4	2
<i>T</i> /K	150(2)	151(2)	150(2)	150(2)
<i>D</i> _c /g.cm ⁻³	1.490	1.521	1.796	1.603
Crystal size/mm	0.290 x 0.050 x 0.030	0.190 x 0.130 x 0.070	0.280 x 0.160 x 0.080	0.360 x 0.110 x 0.070
Total data	18440	17446	11576	14168
Unique data	8711	8580	5768	7467
<i>R</i> _{int}	0.0442	0.0224	0.0454	0.0582
<i>R</i> ₁ [<i>F</i> ² >2 σ (<i>F</i> ²)]	0.0421	0.0312	0.0546	0.0499
w <i>R</i> ₂ (all data)	0.1127	0.0820	0.1439	0.1388
GoF	1.023	1.032	1.046	1.078
$\rho_{\min}/\rho_{\max}/\text{e}\text{\AA}^{-3}$	-0.318/0.330	-0.343/0.259	-0.247/0.292	-0.306/0.330
CCDC code	1062527	1062528	1062529	1062530

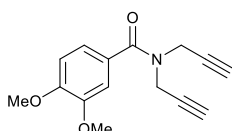
Compound	2.6a	2.6b	2.7
Empirical Formula	C ₂₈ H ₁₆ BF ₁₅ O ₂	C ₃₂ H ₁₆ BF ₁₅ O ₂	C ₂₅ H ₁₀ BF ₁₅ O ₂
Crystal System	Monoclinic	Orthorhombic	Monoclinic
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P bca</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	14.643(7)	14.550(8)	16.8686 (3)
<i>b</i> /Å	18.428(8)	14.952(7)	11.05869 (18)
<i>c</i> /Å	19.621(9)	7.128(13)	27.6059 (4)
α /°	90	90	90
β /°	90.098(14)	90	105.3765 (18)
γ /°	90	90	90
<i>V</i> /Å ³	5295(4)	5902(5)	4965.39
<i>Z</i>	8	8	8
<i>T</i> /K	100(1)	100(1)	150(2)
<i>D</i> _c /g.cm ⁻³	1.707	1.639	1.707
Crystal size/mm	0.240 x 0.180 x 0.090	0.260 x 0.190 x 0.120	0.270 x 0.200 x 0.140
Total data	117383	145467	21050
Unique data	13680	10197	9823
<i>R</i> _{int}	0.0645	0.0549	0.0266
<i>R</i> ₁ [<i>F</i> ² >2 σ(<i>F</i> ²)]	0.0386	0.0396	0.0339
w <i>R</i> ₂ (all data)	0.0915	0.1056	0.0945
GoF	1.015	1.030	1.015
ρ _{min} / ρ _{max} /eÅ ⁻³	-0.234/0.314	-0.234/0.457	-0.223/0.261
CCDC code	1062326	1062327	1062531

6.3 The Propargyl Rearrangement: Cyclisations and 1,1-Carbaborations of Homoleptic and Heteroleptic Boranes

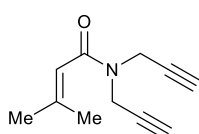
6.3.1 The Propargyl Rearrangement of Esters, Amides, Carbamates and Carbonates

6.3.1.1 Synthesis of Starting Materials

General Procedure 1. *N,N*-Dipropargylcarboxamides were prepared according to literature methods.^[64] Et₃N (1.39 ml, 10 mmol, 2 equiv.) and 4-DMAP (12 mg, 98 μmol, 2 mol%) were added to a solution of *N,N*-dipropargylamine hydrochloride (0.645 g, 5 mmol, 1 equiv.) in CH₂Cl₂ at room temperature under a nitrogen atmosphere and the resulting solution was stirred for 15 min. The solution was then cooled to 0 °C and the corresponding acyl chloride (5 mmol, 1 equiv.) was added dropwise and stirred for 30 min at this temperature. The reaction mixture was then allowed to warm to room temperature and was stirred for a further 3 h. The reaction was then quenched with water and the aqueous layer extracted with CH₂Cl₂ (x2) and the combined organic phases washed with brine. The organic phase was then dried with Na₂SO₄ and filtered. Removal of the solvent yielded the crude product which was purified by column chromatography.

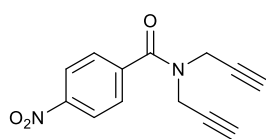


3.2a: Synthesised according to *General Procedure 1* using 3,4-dimethoxybenzoyl chloride (1.0 g, 5 mmol, 1 equiv.). The crude product was purified by column chromatography (SiO₂, Pet. ether/ethyl acetate, 6:4). Yield: 0.926 g, 3.6 mmol, 72%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.22 (dd, ³J_{HH} = 8.2 Hz, ⁴J_{HH} = 1.9 Hz, 1H, Ar-H), 7.17 (d, ⁴J_{HH} = 1.9 Hz, 1H, Ar-H), 6.89 (d, ³J_{HH} = 8.2 Hz, 1H, Ar-H), 4.33 (br. s, 4H, N-CH₂), 3.91 (s, 3H, OCH₃), 3.91 (s, 3H, OCH₃), 2.33 (br. s, 2H, ≡CH). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 170.8 (s), 151.0 (s), 148.8 (s), 126.7 (s), 120.8 (s), 111.0 (s), 110.6 (s), 78.6 (br. s), 72.8 (br. s), 56.1 (s).

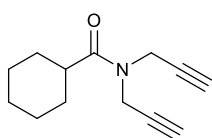


3.2b: Synthesised according to *General Procedure 1* using 3-methylbut-2-enoyl chloride (0.590 g, 5 mmol, 1 equiv.). The crude product was purified by column chromatography (SiO₂, Pet. ether/ethyl acetate, 7:3). Yield: 0.578 g, 3.3 mmol, 65%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 5.82 (m, 1H, =CH), 4.33 (s, 2H, N-CH₂), 4.21 (s, 2H, N-CH₂), 2.28 (s, 1H, ≡CH), 2.21 (s, 1H, ≡CH), 1.93 (d, ⁴J_{HH} = 1.1, 3H, CH₃), 1.86 (d, ⁴J_{HH} = 1.1 Hz, 3H,

CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 167.6 (s), 149.6 (s), 116.8 (s), 78.6 (s), 78.1 (s), 73.0 (s), 72.1 (s), 36.8 (br. s), 33.3 (br. s), 26.6 (br. s), 20.5 (br. s).

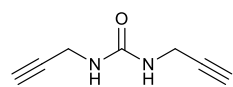


3.2c: Synthesised according to *General Procedure 1* using 4-nitrobenzoyl chloride (0.925 g, 5 mmol, 1 equiv.). The crude product was purified by column chromatography (SiO₂, Pet. ether/ethyl acetate, 7:3). Yield: 1.02 g, 4.2 mmol, 84%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 8.31 (d, ³J_{HH} = 8.8 Hz, 2H, Ar-H), 7.74 (d, ³J_{HH} = 8.6 Hz, 2H, Ar-H), 4.50 (br. s, 2H, N-CH₂), 4.10 (br. s, 2H, N-CH₂), 2.40 (br. s, 1H, ≡CH), 2.32 (br. s, 1H, ≡CH). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 168.7 (s), 150.0 (s), 140.7 (s), 128.4 (s), 124.1 (s), 77.4 (s), 74.2 (s), 73.2 (s), 38.3 (s), 34.0 (s).



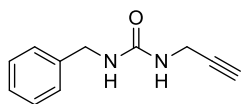
3.2d: Synthesised according to *General Procedure 1* using cyclohexanecarbonyl chloride (0.730 g, 5 mmol, 1 equiv.). The crude product was purified by column chromatography. (SiO₂, Pet. ether/ethyl acetate, 7:3). Yield: 548 mg, 2.7 mmol, 54%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 4.31 (d, ⁴J_{HH} = 2.1 Hz, 2H, N-CH₂), 4.23 (d, ⁴J_{HH} = 2.1 Hz, 2H, N-CH₂), 2.50 (m, 1H, ≡CH), 2.30 (br. s, 1H, ≡CH), 2.20 (m, 1H, cyclohex.), 1.84-1.72 (m, 4H, cyclohex.), 1.86 (m, 1H, cyclohex.), 1.48 (m, 2H, cyclohex.), 1.34-1.16 (m, 3H, cyclohex.). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 175.6 (s), 78.8 (s), 78.3 (s), 72.9 (s), 72.2 (s), 41.0 (s), 36.1 (s), 33.9 (s), 29.4 (s), 25.8 (s). **HRMS** (EI⁺) *m/z* calculated for [M]⁺ [C₁₃H₁₇NO]⁺: 203.1306, found 203.1310. **IR** ν_{max} (cm⁻¹): 3281, 3223, 2926, 2922, 2855, 1728, 1643, 1452, 1435, 1418, 1343, 1310, 1290, 1273, 1265, 1244, 1204, 1175, 1136, 953, 922, 893, 856, 640.

General Procedure 2. Propargyl ureas were prepared according to similar literature methods.^[158] To the amine (1 equiv.) dissolved in water (ca. 50 ml) at 4 °C was added carbonyldiimidazole (CDI) (2 equiv.) and the resulting mixture stirred for 1 h at this temperature. The solution was then allowed to warm up to room temperature and after complete formation of the carbonylimidazolide, propargyl amine (1 equiv.) was added and the mixture stirred at room temperature for ca. 2 h until the reaction was complete. The product was isolated by filtration, washed with cold water and dried *in vacuo* to give a white solid.



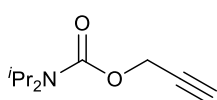
3.5a: Synthesised according to *General Procedure 2* using propargylamine (1.1 g, 20.2 mmol, 2 equiv.). Yield: 1.4 g, 10.3 mmol, 51%. Melting point: 178-184 °C. **¹H NMR** (500 MHz, DMSO-d₆, 298 K) δ/ppm:

6.32 (t, $^3J_{\text{HH}} = 5.8$ Hz, 2H, NH), 3.78 (dd, $^3J_{\text{HH}} = 5.8$ Hz, $^4J_{\text{HH}} = 2.5$ Hz, 4H, CH₂), 3.04 (t, $^4J_{\text{HH}} = 2.5$ Hz, 2H, $\equiv\text{CH}$). **¹³C NMR** (126 MHz, DMSO-d₆, 298 K) δ /ppm: 156.9 (s), 82.3 (s), 72.5 (s), 28.8 (s). **HRMS** (EI⁺) m/z calculated for [M]⁺ [C₇H₉N₂O]⁺: 137.0715, found: 137.0711.

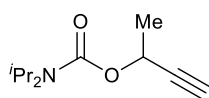


3.5b: Synthesised according to *General Procedure 2* using benzylamine (1.1 g, 10.2 mmol, 1 equiv.) and propargylamine (0.55 g, 10.2 mmol, 1 equiv.). Yield: 3.4 g, 18 mmol, 91%, Melting point: 117–120 °C. **¹H NMR** (500 MHz, DMSO-d₆, 298 K) δ /ppm: 7.29-7.17 (m, 5H, Ar-H), 6.39 (t, $^3J_{\text{HH}} = 5.4$ Hz, 1H, NH), 6.20 (t, $^3J_{\text{HH}} = 5.4$ Hz, 1H, NH), 4.22 (d, $^3J_{\text{HH}} = 5.9$ Hz, 2H, CH₂), 3.82 (m, 2H, CH₂), 2.81 (s, 1H, $\equiv\text{CH}$). **¹³C NMR** (126 MHz, DMSO-d₆, 298 K) δ /ppm: 157.4 (s), 140.3 (s), 127.9 (s), 126.9 (s), 126.4 (s), 82.0 (s), 71.9 (s), 42.9 (s), 28.8 (s). **HRMS** (EI⁺) m/z calculated for [M]⁺ [C₁₁H₁₂N₂O]⁺: 188.0950, found: 188.0941.

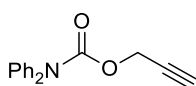
General procedure 3. Propargyl carbamates were synthesised by the following method. Carbamoyl chloride (1 equiv.) and 4-DMAP (0.05 equiv.) were added to a solution of propargyl alcohol (1 equiv.) in pyridine (5 ml) and the resulting mixture heated overnight at 80 °C. The reaction mixture was quenched with saturated NH₄Cl solution (10 ml) and the aqueous phase extracted with diethyl ether (3 x 20 ml). The combined organic phases were then washed further with saturated NH₄Cl solution (3 x 20 ml), dried over sodium sulfate, filtered and the solvent removed *in vacuo*.



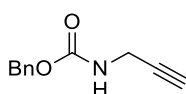
3.7a: Synthesised according to *General Procedure 3* using *N,N*-diisopropylcarbamoyl chloride and propargyl alcohol. Purification by column chromatography gave a colourless oil. (SiO₂, Pet. ether/EtOAc, 95:5). Yield: 0.35 g, 1.64 mmol, 67%. $R_f = 0.44$ (SiO₂, Pet. ether/EtOAc, 80:20). **¹H NMR** (300 MHz, CDCl₃, 298 K) δ /ppm: 4.70 (d, $^4J_{\text{HH}} = 2.5$ Hz, 2H), 4.92 (br. s, 2H), 2.42 (t, $^4J_{\text{HH}} = 2.5$ Hz, 1H), 1.22 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H). **¹³C NMR** (75 MHz, CDCl₃, 298 K) δ /ppm: 154.8 (s), 79.1 (s), 74.1 (s), 52.2 (s), 46.2 (br. s), 21.1 (br. s). **IR** ν_{max} (cm⁻¹): 3247, 2971, 1702, 1443, 1370, 1310, 1294, 1219, 1160, 1136, 1069, 960, 771, 719, 624, 606. MS-EI: 183.1 (13), 169.1 (11), 168.1 (100), 161.9 (6), 151.0 (6), 126.1 (39), 102.1(5), 82.1 (11), 70.0 (11). **HRMS** (EI⁺) m/z calculated for [M+H]⁺ [C₁₀H₁₇NO₂]⁺: 183.1259, found: 183.1239.



3.7b: Synthesised according to *General Procedure 3* using *N,N*-diisopropyl carbamoyl chloride and but-3-yn-2-ol. Purification by column chromatography gave a colourless oil. (SiO₂, Pet. ether/EtOAc, 95:5). Yield: 0.61 g, 3.10 mmol, 62%. R_f = 0.33 (SiO₂, Pet. ether/EtOAc, 95:5). **¹H NMR** (300 MHz, CDCl₃, 298 K) δ/ppm: 5.42 (dq, ³J_{HH} = 6.7 Hz, ⁴J_{HH} = 2.1 Hz, 1H), 4.28-3.55 (m, 2H), 2.40 (d, ⁴J_{HH} = 2.1 Hz, 1H), 1.50 (d, ³J_{HH} = 6.7 Hz, 3H), 1.21-1.18 (m, 12H). **¹³C NMR** (75 MHz, CDCl₃, 298 K) δ/ppm: 154.6 (s), 83.3 (s), 72.3 (s), 60.2 (s), 46.0 (br. s), 21.8 (s), 21.1 (br. s). **IR** ν_{max} (cm⁻¹): 3312, 3248, 2972, 2937, 2876, 2121, 1694, 1437, 1370, 1344, 1319, 1284, 1210, 1191, 1158, 1133, 1091, 1045, 918, 768, 661. MS ESI: 197.1 (31), 183.1 (12), 182.1 (100), 161.9 (5), 150.9 (5), 138.1 (5), 130.0 (35), 128.1 (11), 102.0 (11), 96 (18), 88.0 (17), 86.1 (23), 86.0 (19). **HRMS** (EI⁺) *m/z* calculated for [M+H]⁺ [C₁₁H₁₉NO₂]⁺: 197.1416, found: 197.1422.

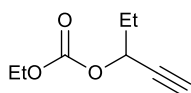


3.7c: Synthesised according to *General Procedure 3* using *N,N*-diphenyl carbamoyl chloride and propargyl alcohol. Purification by recrystallisation from petroleum ether 40-60 with a few drops of Et₂O to solubilise the solid at -40 °C gave a pale yellow solid. Yield: 1.07 g, 4.26 mmol, 71%. Melting point: 128–133 °C. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.28–7.13 (m, 10H, Ar-H), 4.68 (s, 2H, CH₂), 2.37 (s, 1H, ≡CH). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 154.1 (s), 142.4 (s), 129.1 (s), 127.1 (s), 126.5 (s), 78.2 (s), 74.9 (s), 53.5 (s). **IR** ν_{max} (cm⁻¹): 3087, 3062, 3027, 2950, 2922, 2870, 1944, 1861, 1803, 1730, 1605, 1495, 1461, 1379, 1304, 1210, 1180, 1083, 1059, 1031, 896, 735. **HRMS** (AP⁺) *m/z* calculated for [M+H]⁺ [C₁₆H₁₄NO₂]⁺: 252.1025, found: 252.1017.

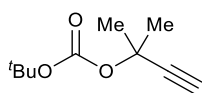


3.10: The propargyl carbamate was synthesised by the following method. Propargylamine (0.51 ml, 8 mmol) was added to a solution of chloroformate (1.2 ml, 8 mmol) and NaHCO₃ (0.67 g, 8 mmol) in 10 ml EtOH/H₂O (1:1) at 0 °C. The solution was allowed to warm up to room temperature and stirred overnight. The solution was diluted with EtOH/H₂O and the aqueous phase extracted with diethyl ether (3 x 20 ml). The combined organic phases were then washed with saturated NH₄Cl solution (3 x 20 ml), dried over sodium sulfate, filtered and the solvent removed *in vacuo*. The crude product was purified by recrystallisation from petroleum ether 40-60 with a few drops of Et₂O to solubilise the solid left at -40 °C. Yield: 1.48 g, 7.82 mmol, 98%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.36 (m, 5H, Ar-H), 5.13 (s, 2H, CH₂-O), 4.98 (br. s, 1H, NH), 4.00 (s, 2H, N-CH₂), 2.24 (t, ⁴J_{HH} = 2.5 Hz, 1H, ≡CH). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm:

156.0 (s), 136.2 (s), 128.6 (s), 128.3 (m), 127.1 (s), 79.8 (s), 71.7 (s), 67.2 (s), 30.9 (s). **IR** ν_{\max} (cm⁻¹): 3421, 3308, 3087, 3064, 3030, 2982, 2922, 2875, 2739, 2123, 1950, 1864, 1811, 1732, 1606, 1511, 1457, 1381, 1353, 1325, 1227, 1176, 1141, 1085, 1047, 987, 939, 908, 870, 775. **HRMS** (EI⁺) m/z calculated for [M]⁺ [C₁₁H₁₁NO₂]⁺: 189.0785, found: 189.0790.



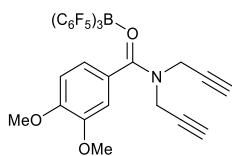
3.12a: ⁿBuLi (2.00 ml, 2.5 M in hexane, 5.00 mmol) was added to a solution of 1-pentyne-3-ol (0.43 ml, 5.00 mmol) in THF (10-20 ml) at -78 °C and the resulting solution stirred for 1 h. Diethylpyrocarbonate (0.73 ml, 5.00 mmol) in 20 ml THF was then added to the cooled solution and the mixture allowed to warm to room temperature and subsequently stirred for 12-24 h. The reaction mixture was quenched with saturated NH₄Cl solution (20 ml) and the aqueous phase extracted with diethyl ether (3 x 20 ml). The combined organic phases were then washed with saturated NH₄Cl solution (3 x 20 ml), dried over NaSO₄, filtered and the solvent removed *in vacuo*. The product was purified by column chromatography using SiO₂ (SiO₂, pet. ether/EtOAc 95:5 to 80:20) to give the pure product. Yield: 0.57 g, 5.00 mmol, 100%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 5.09 (dt, ³J_{HH} = 6.5 Hz, ⁴J_{HH} = 1.3 Hz, 1H, CH), 4.22 (q, ³J_{HH} = 7.2 Hz, 2H, CH₂), 2.50 (d, ⁴J_{HH} = 1.3 Hz, 1H, ≡CH), 1.88-1.81 (m, 2H, CH₂), 1.32 (t, ³J_{HH} = 7.2 Hz, 3H, CH₃), 1.04 (t, ³J_{HH} = 7.4 Hz, 3H, CH₃). **¹³C NMR** (125 MHz, CDCl₃, 298 K) δ /ppm: 154.7 (s), 80.8 (s), 74.7 (d), 69.0 (d), 64.7 (t), 28.2 (t), 14.6 (q), 9.5 (q). **IR** ν_{\max} (cm⁻¹): 3293, 2979, 2940, 2882, 2358, 2125, 1756, 1515, 1465, 1396, 1373, 1342, 1302, 1275, 1177, 1094, 1062, 1046, 1007, 948, 932, 893, 857, 791, 670. MS-EI: 128.0 (39), 127.0 (8), 91.0 (12), 84.1 (7), 83.1 (51), 69.0 (30), 67.1 (82), 66.0 (100), 63.0 (20). **HRMS** (EI⁺) m/z calculated for [M-C₂H₄]⁺ [C₆H₈O₃]⁺: 128.0473, found: 128.0487.



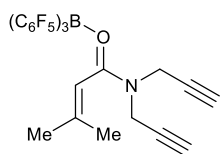
3.14: Synthesised according to a similar literature method.^[28] Propargyl alcohol (1.7 ml, 30 mmol) was dissolved in dichloromethane in combination with Hünig's base (13.1 ml, 75 mmol) alongside 4-DMAP (10 mol%). After cooling to 0 °C, Boc anhydride (8.51 g, 39 mmol) was added portionwise ensuring reaction is not allowed to reflux, then stirred until completion. The resultant solution was quenched with saturated NH₄Cl solution (20 ml) and the aqueous phase extracted with dichloromethane (3 x 20 ml). The combined organic phases were then washed with 1M HCl, sat. NaHCO₃ solution and brine (all 2 x 20 ml) then dried over MgSO₄, filtered and the solvent removed *in vacuo* to give a colourless oil. The product was sufficiently pure for subsequent reactions. Yield: 3.4 g, 21.8 mmol, 73%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 2.53 (s, 1H,

$\equiv\text{CH}$), 1.68 (s, 6H, CH_3), 1.48 (s, 9H, CH_3). ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ /ppm: 151.5 (s), 84.6 (s), 82.4 (s), 73.0 (s), 72.5 (s), 29.0 (s), 28.0 (s).

6.3.1.2 Synthesis of Products

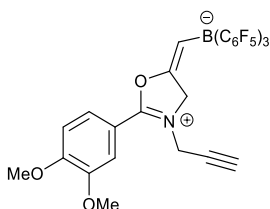


3.3a: 3,4-dimethoxy-*N,N*-di(prop-2-yn-1-yl)benzamide **3.2a** (52 mg, 0.2 mmol) was dissolved in toluene (2 ml) and added to $\text{B}(\text{C}_6\text{F}_5)_3$ (102 mg, 0.2 mmol) to give a yellow solution. After 1 h small crystals formed which were redissolved by briefly warming the solution slightly and adding a few drops of CH_2Cl_2 . Upon cooling large colourless blocks of the adduct formed which were suitable for X-ray diffraction. The crystals were washed with petroleum ether 40-60 (3 x 3 ml) to give the adduct **3.3a**. Yield: 119 mg, 77%, 0.15 mmol. ^1H NMR (400 MHz, CDCl_3 , 298 K) δ /ppm: 6.70 (dd, $^3J_{\text{HH}} = 8.4$ Hz, $^4J_{\text{HH}} = 1.9$ Hz, 1H, Ar-H), 6.63 (d, $^3J_{\text{HH}} = 8.4$ Hz, 1H, Ar-H), 6.50 (d, $^4J_{\text{HH}} = 1.9$ Hz, 1H, Ar-H), 4.64 (br. s, 2H, N- CH_2), 4.17 (d, $^4J_{\text{HH}} = 2.3$ Hz, 2H, N- CH_2), 3.79 (s, 3H, OCH₃), 3.61 (s, 3H, OCH₃), 2.46 (t, $^4J_{\text{HH}} = 2.3$ Hz, 1H, $\equiv\text{CH}$), 2.40 (t, $^4J_{\text{HH}} = 2.4$ Hz, 1H, $\equiv\text{CH}$). ^{11}B NMR (160 MHz, CDCl_3 , 298 K) δ /ppm: 0.5 (br. s). ^{19}F NMR (283 MHz, CDCl_3 , 298 K) δ /ppm: -133.6 (d, $^3J_{\text{FF}} = 20.6$ Hz, 2F, *o*-F), -157.5 (t, $^3J_{\text{FF}} = 20.5$ Hz, 1F, *p*-F), -164.1 (m, 2F, *m*-F). The product could not be fully characterised in solution as subsequent dissociation of boron from the amide oxygen atom followed by cyclisation to yield **3.4a** occurs. IR ν_{max} (cm^{-1}): 2359, 2340, 2322, 1647, 1560, 1560, 1516, 1464, 1456, 1273, 1258, 1240, 1099, 978. **Elemental analysis** (%) calculated for $\text{C}_{33}\text{H}_{15}\text{BF}_{15}\text{NO}_3$: C 51.52, H 1.97, N 1.82, found: C 51.49, H 1.85, N 1.82.

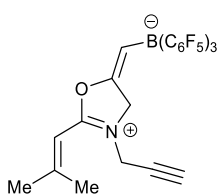


3.3b: 3-methyl-*N,N*-di(prop-2-yn-1-yl)but-2-enamide **3.2b** (36 mg, 0.2 mmol) was dissolved in toluene (ca. 2 ml) and added to $\text{B}(\text{C}_6\text{F}_5)_3$ (102 mg, 0.2 mmol) to give a yellow solution. The reaction was left at room temperature without stirring for 30 min. Slow evaporation of the solvent yielded large colourless blocks of the product which could be characterised by X-ray diffraction. The remaining solvent was decanted off and the product washed with petroleum ether (3 x 3 ml) and dried *in vacuo* to give pure **3.3b**. Yield: 57 mg, 0.08 mmol, 41%. ^1H NMR (400 MHz, CDCl_3 , 298 K) δ /ppm: 5.32 (br. s, 1H, =CH), 4.49 (d, $^4J_{\text{HH}} = 2.2$ Hz, 2H, N- CH_3), 4.28 (d, $^4J_{\text{HH}} = 2.2$ Hz, 2H, N- CH_3), 2.38 (t, $^4J_{\text{HH}} = 2.2$ Hz, 1H, $\equiv\text{CH}$), 2.24 (t, $^4J_{\text{HH}} = 2.2$ Hz, 1H, $\equiv\text{CH}$), 1.48 (s, 3H, CH_3), 1.24 (s, 3H, CH_3). ^{11}B NMR (160 MHz, CDCl_3 , 298 K) δ /ppm: -0.5 (br. s). ^{19}F NMR (283 MHz, CDCl_3 , 298 K) δ /ppm: -134.1 (d, $^3J_{\text{FF}} = 20.1$ Hz, 2F, *o*-F), -157.4 (t, $^3J_{\text{FF}} = 20.5$ Hz, 1F, *p*-F), -164.0 (m, 2F, *m*-F). The product could not be fully

characterised in solution as subsequent dissociation of boron from the amide oxygen atom followed by cyclisation to yield **3.4b** occurs. **IR** ν_{\max} (cm^{-1}): 2361, 2340, 2322, 1647, 1559, 1516, 1456, 1281, 1257, 1092, 980, 868, 806, 766, 729, 690, 682. **Elemental analysis** (%) calculated for $\text{C}_{29}\text{H}_{13}\text{BF}_{15}\text{NO}$: C 50.68, H 1.91, N 2.04, found: C 50.83, H 1.82, N 2.11.

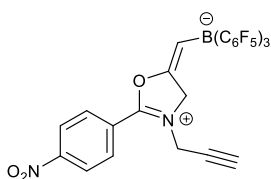


3.4a: 3,4-dimethoxy-*N,N*-di(prop-2-yn-1-yl)benzamide **3.2a** (52 mg, 0.2 mmol) was dissolved in toluene (8 ml) and added to $\text{B}(\text{C}_6\text{F}_5)_3$ (102 mg, 0.2 mmol) to give a yellow solution. The reaction was heated to 45 °C for 2 days without stirring whereupon CH_2Cl_2 (ca. 0.5 ml) was added. Upon cooling small colourless crystals of the product formed. The remaining solvent was decanted off and the crystals washed with petroleum ether (3 x 3 ml) and then dried under vacuum to give colourless crystals of the pure product Yield: 89 mg, 58%, 0.12 mmol. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ/ppm : 7.59 (dd, $^3J_{\text{HH}} = 8.6$ Hz, $^4J_{\text{HH}} = 2.2$ Hz, 1H, Ar-H), 7.35 (d, $^4J_{\text{HH}} = 2.2$ Hz, 1H, Ar-H), 7.10 (d, $^3J_{\text{HH}} = 8.6$ Hz, 1H, Ar-H), 6.64 (br. s, 1H, =CH), 4.54 (d, $^4J_{\text{HH}} = 2.6$ Hz, 2H, N- CH_2), 4.38 (d, $^4J_{\text{HH}} = 2.6$ Hz, 2H, CH_2), 4.04 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 2.75 (t, $^4J_{\text{HH}} = 2.2$ Hz, 1H, $\equiv\text{CH}$). **$^{11}\text{B NMR}$** (160 MHz, CDCl_3 , 298 K) δ/ppm : -16.9 (s). **$^{19}\text{F NMR}$** (283 MHz, CDCl_3 , 298 K) δ/ppm : -132.7 (d, $^3J_{\text{FF}} = 22.4$ Hz, 2F, *o*-F), -160.8 (t, $^3J_{\text{FF}} = 20.8$ Hz, 1F, *p*-F), -165.0 (m, 2F, *m*-F). **Elemental analysis** (%) calculated for $\text{C}_{33}\text{H}_{15}\text{BF}_{15}\text{NO}_3$: C 51.52, H 1.97, N 1.82, found: C 51.50, H 1.89, N 1.91. **IR** ν_{\max} (cm^{-1}): 2357, 2342, 1613, 1597, 1512, 1458, 1437, 1396, 1348, 1284, 1271, 1080, 961, 810, 768.

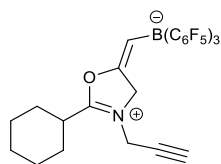


3.4b: 3-methyl-*N,N*-di(prop-2-yn-1-yl)but-2-enamide **3.2b** (36 mg, 0.2 mmol) was dissolved in toluene (8 ml) and added to $\text{B}(\text{C}_6\text{F}_5)_3$ (102 mg, 0.2 mmol) to give a yellow solution. The reaction was heated to 45 °C for 2 days without stirring giving an orange solution. Upon cooling small colourless acicular crystals of the product formed. The remaining solvent was decanted off and the crystals washed with petroleum ether (3 x 3ml) and dried under vacuum to give colourless crystals of the pure product. Yield: 79 mg, 57%, 0.11 mmol. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ/ppm : 6.53 (br. s, 2H, =CH), 5.96 (br. s, 1H, =CH), 4.32 (d, $^4J_{\text{HH}} = 2.4$ Hz, 2H, N- CH_2), 4.15 (d, $^4J_{\text{HH}} = 2.4$ Hz, 2H, CH_2), 2.62 (t, $^4J_{\text{HH}} = 2.5$ Hz, 1H, $\equiv\text{CH}$), 2.39 (s, 3H, CH_3), 2.27 (s, 3H, CH_3). **$^{11}\text{B NMR}$** (160 MHz, CDCl_3 , 298 K) δ/ppm : -16.9 (s). **$^{19}\text{F NMR}$** (283 MHz, CDCl_3 , 298 K) δ/ppm : -132.7 (d, $^3J_{\text{FF}} = 21.9$ Hz, 2F, *o*-F), -160.9 (t, $^3J_{\text{FF}} = 20.8$ Hz, 1F, *p*-F), -165.1 (m, 2F, *m*-F). **HRMS** (EI⁺) m/z calculated for $[\text{M}-\text{H}]^- [\text{C}_{29}\text{H}_{12}\text{BF}_{15}\text{NO}]^-$: 686.0772,

found: 686.0799. **IR** ν_{\max} (cm⁻¹): 2359, 2334, 2322, 1636, 1512, 1456, 1271, 1262, 1080, 974, 963, 806.

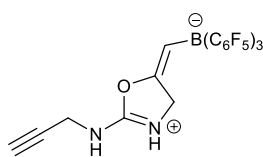


3.4c: 4-nitro-*N,N*-di(prop-2-yn-1-yl)benzamide **3.2c** (48 mg, 0.2 mmol) was dissolved in toluene (3 ml) and was added to B(C₆F₅)₃ (102 mg, 0.2 mmol) to give a yellow solution. The reaction was left at room temperature for 1 h and CH₂Cl₂ (ca. 1ml) was added and the solvent was allowed to evaporate slowly to give small acicular colourless crystals of the product which were suitable for X-ray diffraction. The remaining solvent was decanted off and the crystals washed with petroleum ether (3 x 3ml) and then dried under vacuum to give colourless crystals of the pure product. Yield: 130 mg, 86%, 0.17 mmol. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 8.51 (d, ³*J*_{HH} = 8.9 Hz, 2H, Ar-H), 8.08 (d, ³*J*_{HH} = 8.9 Hz, 2H, Ar-H), 6.69 (s, 1H, =CH), 5.23 (s, 2H, CH₂), 4.47 (br. d, ⁴*J*_{HH} = 2.4 Hz, 2H, N-CH₂), 2.78 (t, ⁴*J*_{HH} = 2.4 Hz, 1H, \equiv CH). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: -16.9 (s). **¹⁹F NMR** (283 MHz, CDCl₃, 298 K) δ /ppm: -132.7 (d, ³*J*_{FF} = 22.5 Hz, 2F, *o*-F), -160.3 (t, ³*J*_{FF} = 21.1 Hz, 1F, *p*-F), -164.7 (m, 2F, *m*-F). **Elemental analysis** (%) calculated for C₃₁H₁₀BF₁₅N₂O₃: C 49.37, H 1.34, N 3.71, found: C 52.50, H 1.64, N 3.52. **IR** ν_{\max} (cm⁻¹): 2361, 2341, 1653, 1636, 1597, 1533, 1512, 1456, 1445, 1400, 1358, 1296, 1267, 1258, 1084, 978, 961, 928, 891, 866, 808, 770, 739, 716, 692, 669.

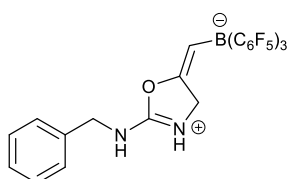


3.4d: *N,N*-di(prop-2-yn-1-yl)cyclohexanecarboxamide **3.2d** (40 mg, 0.2 mmol) was dissolved in toluene (2 ml) and added to B(C₆F₅)₃ (102 mg, 0.2 mmol) to give a cloudy yellow solution. Leaving the solution to stand for 10 min resulted in the formation of a white precipitate which was redissolved by gentle heating with the addition of a few drops of CH₂Cl₂. The reaction was left for 2 days and then the solvent was allowed to evaporate slowly to give colourless crystals of the product which were suitable for X-ray diffraction. The remaining solvent was decanted off and the crystals washed with petroleum ether (3 x 3 ml) and then dried under vacuum to give colourless crystals of the pure product. Yield: 114 mg, 80%, 0.15 mmol. **¹H NMR** (400 MHz, DMSO-*d*₆, 298 K) δ /ppm: 6.31 (s, 1H, =CH), 4.51 (s, 2H, CH₂), 4.06 (s, 2H, CH₂), 2.78 (t, ⁴*J*_{HH} = 2.5 Hz, 1H, \equiv CH), 1.90-1.68 (m, 5H, cyclohex.), 1.53-1.45 (m, 2H, cyclohex.), 1.33-1.17 (m, 4H, cyclohex.). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: -17.0 (s). **¹⁹F NMR** (283 MHz, CDCl₃, 298 K) δ /ppm: -132.8 (d, ³*J*_{FF} = 22.4 Hz, 2F, *o*-F), -160.9 (t, ³*J*_{FF} = 20.4 Hz, 1F, *p*-F), -165.3 (m, 2F, *m*-F). **Elemental analysis** (%) calculated for C₃₁H₁₇BF₁₅NO: C 52.06, H 2.40, N 1.96, found: C 51.94, H 2.24, N

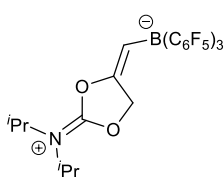
1.94. **HRMS** (EI⁺) m/z calculated for [M]⁺ [C₃₁H₁₆BF₁₅NO]⁻: 714.1085, found: 714.1079. **IR** ν_{\max} (cm⁻¹): 2363, 2342, 2322, 1630, 1512, 1454, 1437, 1304, 1260, 1233, 1180, 1138, 1113, 1078, 978, 961, 883, 841, 818, 806, 768, 669.



3.6a: B(C₆F₅)₃ (51 mg, 0.1 mmol) was dissolved in CDCl₃ (ca. 0.5 ml) and added to 1,3-di(prop-2-yn-1-yl)urea **3.5a** (14 mg, 0.1 mmol). The reaction was heated at 50 °C for 7 d to give a yellow solution and a crop of needle shaped crystals which were suitable for X-ray diffraction. The remaining solvent was decanted off and the product was washed with hexane (4 x 2 ml) and dried *in vacuo* to give pure **9a**. Yield: 20 mg, 0.03 mmol, 31%. Melting point: 178–184 °C. **¹H NMR** (500 MHz, DMSO-d₆, 298 K) δ /ppm: 10.01 (br. s, 1H, NH), 5.91 (s, 1H, NH), 5.65 (s, 1H, =CH), 4.07 (d, ⁴J_{HH} = 2.0 Hz, 2H, CH₂), 3.64 (s, 2H, CH₂), 3.30 (br. s, 1H, CH). **¹¹B NMR** (160 MHz, DMSO-d₆, 298 K) δ /ppm: -17.0 (s). **¹⁹F NMR** (283 MHz, DMSO-d₆, 298 K) δ /ppm: 132.1 (d, ³J_{FF} = 22.2 Hz, 2F, *o*-F), 161.3 (t, ³J_{FF} = 22.2 Hz, 1F, *p*-F), 165.2 (t, ³J_{FF} = 22.2 Hz, 2F, *m*-F). **IR** ν_{\max} (cm⁻¹): 3085, 3061, 3029, 2922, 2876, 1708, 1672, 1643, 1607, 1572, 1545, 1514, 1495, 1460, 1380, 1280, 1082, 1030, 977, 729, 695. **HRMS** (ES⁻) m/z calculated for [M-H]⁻ [C₂₅H₇BN₂OF₁₅]⁻: 646.0448, found: 646.0445.

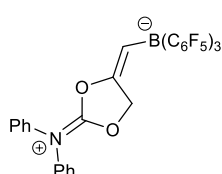


3.6b: B(C₆F₅)₃ (51 mg, 0.1 mmol) was dissolved in CDCl₃ (ca. 0.5 ml) and added to 1-benzyl-3-(prop-2-yn-1-yl)urea **3.5b** (19 mg, 0.1 mmol). The reaction was heated to 50 °C for 14 d to give a pale yellow solution. The solvent was removed *in vacuo*, leaving a white solid, which was recrystallised from hexane with a drop of toluene at -40 °C to give colourless crystals of **9b**. Yield: 43 mg, 0.06 mmol, 31%. Melting point: 182–190 °C. **¹H NMR** (500 MHz, DMSO-d₆, 298 K) δ /ppm: 10.11 (br. s, 1H, NH), 7.39–7.30 (m, 5H, Ar-H), 5.90 (br. s, 1H, NH), 5.74 (s, 1H, =CH), 4.43 (br. s, 2H, CH₂), 3.65 (br. s, 2H, CH₂). **¹¹B NMR** (160 MHz, DMSO-d₆, 298 K) δ /ppm: -16.9 (br. s). **¹⁹F NMR** (283 MHz, DMSO-d₆, 298 K) δ /ppm: -132.1 (d, ³J_{FF} = 21.3 Hz, 2F, *o*-F), -161.1 (t, ³J_{FF} = 21.0 Hz, 1F, *p*-F), -165.1 (t, ³J_{FF} = 21.0 Hz, 2F, *m*-F). **IR** ν_{\max} (cm⁻¹): 3088, 3062, 3029, 2923, 2783, 1944, 1865, 1808, 1648, 1605, 1519, 1495, 1469, 1380, 1287, 1101, 1067, 1032, 981, 872, 819, 771, 733, 695, 616. **HRMS** (ES⁻) m/z calculated for [M-H]⁻ [C₂₉H₁₁BN₂OF₁₅]⁻: 698.0761, found: 698.0790.

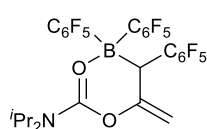


3.8a: Prop-3-yn-2-yl-diisopropylcarbamate **3.7a** (18.3 mg, 0.1 mmol) and B(C₆F₅)₃ (51.2 mg, 0.1 mmol) were dissolved in CD₂Cl₂ (0.5 ml) and the mixture left for 24 h. The progress of the reaction was monitored by ¹H-, ¹¹B- and ¹⁹F-NMR spectroscopy. The

solution was concentrated and when complete, layered with pentane and stored at -20 °C, whereby the product crystallised out. The remaining solution was decanted off and the resulting solid washed with cold pentane (3 x 2ml). Drying *in vacuo* afforded the product as a white crystalline solid. Yield: 44.5 mg, 0.06 mmol, 64%. **¹H NMR** (500 MHz, CD₂Cl₂, 298 K) δ/ppm: 6.46 (s, 1H, =CH), 4.85 (d, ⁴J_{HH} = 2.1 Hz, 2H, CH₂), 4.22 (sept., ³J_{HH} = 6.9 Hz, 1H, CH ⁱPr), 4.07 (sept., ³J_{HH} = 6.9 Hz, 1H, CH ⁱPr), 1.39 (d, ³J_{HH} = 6.9 Hz, 6H, CH₃ ⁱPr), 1.36 (d, ³J_{HH} = 6.9 Hz, 6H, CH₃ ⁱPr). **¹¹B NMR** (96 MHz, CD₂Cl₂, 298 K) δ/ppm: -17.0 (s). **¹⁹F NMR** (282 MHz, CD₂Cl₂, 298 K) δ/ppm: -133.0 (d, ³J_{FF} = 22 Hz, 6F, *o*-F), -161.9 (t, ³J_{FF} = 20 Hz, 3F, *p*-F), -166.2 (m, 6F, *m*-F). **¹³C NMR** (125 MHz, CD₂Cl₂, 298 K) δ/ppm: 160.9 (s), 148.7 (dm, ¹J_{CF} = 245 Hz), 140.5 (m), 139.1 (dm, ¹J_{CF} = 245 Hz), 137.2 (dm, ¹J_{CF} = 245 Hz), 119.4 (m), 71.6 (s), 51.7 (s), 20.2 (s). **IR** ν_{max} (cm⁻¹): 1716, 1663, 1643, 1512, 1457, 1442, 1404, 1379, 1363, 1264, 1144, 1079, 1066, 978, 959, 902, 867, 844, 804, 763, 747, 736, 704, 675, 658, 642, 607. **HRMS** (ES⁺) *m/z* calculated for [M+H]⁺ [C₂₈H₁₈BF₁₅NO₂]⁺: 696.1191, found: 696.1183.

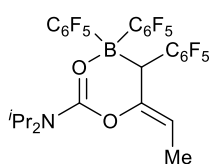


3.8c: Prop-2-yn-1-yl diphenylcarbamate **3.7c** (50 mg, 0.2 mmol) and B(C₆F₅)₃ (102 g, 0.2 mmol) were dissolved in toluene (2 ml) to give a clear colourless solution. This was immediately cooled to -40 °C and left for 5 days to give a crop of small pale yellow crystals suitable for X-ray diffraction. The solution was decanted and the solid was washed with hexane (3 x 2 ml) and dried *in vacuo* to afford the product as a white solid. Yield: 91 mg, 0.12 mmol, 60%. Melting point: 65-72 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.46-7.25 (m, 10H, Ar-H), 6.43 (s, 1H, =CH), 4.9 (s, 2H, CH₂). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 162.3 (s), 148.2 (dm, ¹J_{CF} = 252 Hz), 139.9 (m), 140.3 (s), 138.9 (dm, ¹J_{CF} = 255 Hz), 136.9 (dm, ¹J_{CF} = 247 Hz), 130.1 (s), 129.9 (s), 126.7 (s), 110.2 (s), 73.0 (s). **¹¹B NMR** (160 MHz, CDCl₃, 298 K), -17.1 (s) **¹⁹F NMR** (282 MHz, CDCl₃, 298 K) δ/ppm: -132.6 (d, ³J_{FF} = 21.3 Hz, 2F, *o*-F), -160.5 (t, ³J_{FF} = 21.2 Hz, 1F, *p*-F), -164.9 (t, ³J_{FF} = 21.2 Hz, 2F, *m*-F). **IR** ν_{max} (cm⁻¹): 3088, 3046, 3016, 2915, 2873, 2739, 1946, 1861, 1806, 1737, 1616, 1584, 1518, 1476, 1381, 1319, 1287, 1251, 1212, 1179, 1101, 1088, 1029, 973, 898, 774, 739, 719, 702, 689. **HRMS** (EI) *m/z* calculated for [M-H]⁻ [C₃₄H₁₂BNO₂F₁₅]⁻: 761.0785, found: 761.0775.



3.9a: Prop-3-yn-2-yl-diisopropylcarbamate **3.7a** (18 mg, 0.1 mmol) and B(C₆F₅)₃ (51 mg, 0.1 mmol) were dissolved C₆D₆ (0.5 ml) and the reaction left at 60 °C for 15 h. The progress of the reaction was monitored by ¹H-, ¹¹B- and ¹⁹F-NMR spectroscopy. The solution was concentrated,

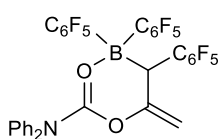
when complete and layered with pentane then stored at $-20\text{ }^{\circ}\text{C}$ whereby the product crystallised out. The remaining solution was decanted off and the resulting solid washed with cold pentane (3 x 2 ml). Drying *in vacuo* afforded the product as a white crystalline solid. Yield: 50.4 mg, 0.07 mmol, 72%. **^1H NMR** (600 MHz, C_6D_6 , 298 K) δ/ppm : 4.55 (d, $^4J_{\text{HH}} = 2.6\text{ Hz}$, 1H, =CH), 4.48 (br. s, 1H, CH), 4.38 (d, $^4J_{\text{HH}} = 2.6\text{ Hz}$, 1H, =CH), 3.06 (br. s, 2H, CH i Pr), 0.89 (d, $^3J_{\text{HH}} = 6.8\text{ Hz}$, 3H, CH_3), 0.86 (d, $^3J_{\text{HH}} = 6.6\text{ Hz}$, 3H, CH_3), 0.83 (d, $^3J_{\text{HH}} = 6.8\text{ Hz}$, 3H, CH_3), 0.80 (d, $^3J_{\text{HH}} = 6.8\text{ Hz}$, 3H, CH_3). **^{11}B NMR** (96 MHz, C_6D_6 , 298 K) δ/ppm : 0.8 (br. s). **^{19}F NMR** (282 MHz, C_6D_6 , 298 K) δ/ppm : -134.8 (br. d, 2F, *o*-F), -136.0 (m, 2F, *o*-F), -143.0 (m, 2F, *o*-F), -156.8 (m, 2F, *p*-F), -157.6 (t, $^3J_{\text{FF}} = 21.7\text{ Hz}$, 1F, *p*-F), -162.9 (br. s, 2F, *m*-F), -163.4 (m, 2F, *m*-F), -163.7 (m, 2F, *m*-F). **^{13}C NMR** (150 MHz, C_6D_6 , 298 K) δ/ppm : 156.4 (s), 155.8 (s), 148.4 (dm, $^1J_{\text{CF}} = 245\text{ Hz}$), 147.9 (dm, $^1J_{\text{CF}} = 245\text{ Hz}$), 145.3 (dm, $^1J_{\text{CF}} = 245\text{ Hz}$), 140.4 (dm, $^1J_{\text{CF}} = 245\text{ Hz}$), 139.3 (dm, $^1J_{\text{CF}} = 245\text{ Hz}$), 137.7 (dm, $^1J_{\text{CF}} = 245\text{ Hz}$), 98.9 (s), 49.7 (s), 47.3 (s), 29.0 (br. s), 20.6 (s), 20.1 (s).



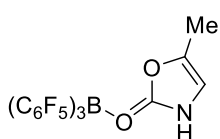
3.9b: But-3-yn-2-yl-diisopropylcarbamate **3.7b** (19.7 mg, 0.1 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (51.2 mg, 0.1 mmol) were dissolved in CD_2Cl_2 (0.5 ml) and the reaction left for 24 h. The completion of the reaction was monitored by ^1H -, ^{11}B - and ^{19}F -NMR spectroscopy.

The solution was concentrated, and when complete layered with pentane and stored at $-20\text{ }^{\circ}\text{C}$ resulting in crystallisation on the product. The remaining solution was decanted off and the solid was washed with cold pentane (3 x 2 ml). Drying *in vacuo* afforded the product as a white crystalline solid. Yield: 54.7 mg, 0.08 mmol, 75%. **^1H NMR** (300 MHz, CD_2Cl_2 , 298 K) δ/ppm : 5.04 (q, $^3J_{\text{HH}} = 6.9\text{ Hz}$, 1H, =CH), 4.68-4.64 (m, 1H, CH), 4.34 (s, 1H, CH), 4.00-3.91 (m, 1H, CH), 1.70 (d, $^3J_{\text{HH}} = 6.9\text{ Hz}$, 3H, CH_3), 1.44-1.30 (m, 12H, CH_3). **^{13}C NMR** (125 MHz, CD_2Cl_2 , 298 K) δ/ppm : 156.7 (s), 149.1 (m), 148.4 (dm, $^1J_{\text{CF}} = 245\text{ Hz}$), 147.8 (dm, $^1J_{\text{CF}} = 245\text{ Hz}$), 145.4 (dm, $^1J_{\text{CF}} = 245\text{ Hz}$), 140.4 (dm, $^1J_{\text{CF}} = 245\text{ Hz}$), 140.1 (s), 139.3 (dm, $^1J_{\text{CF}} = 245\text{ Hz}$), 137.9 (s), 137.6 (dm, $^1J_{\text{CF}} = 245\text{ Hz}$), 137.3 (s), 110.2 (s), 50.1 (s), 48.1 (s), 29.4 (br. s), 21.1 (s), 20.5 (s), 11.0 (s). **^{11}B NMR** (96 MHz, CD_2Cl_2 , 298 K) δ/ppm : 0.0 (br. s). **^{19}F NMR** (282 MHz, CD_2Cl_2 , 298 K) δ/ppm : -135.0 (br. s, 2F, *o*-F), -136.3 (m, 2F, *o*-F), -143.1 (d, $^3J_{\text{FF}} = 20.6\text{ Hz}$, 2F, *o*-F), -158.7 (t, $^3J_{\text{FF}} = 20.7\text{ Hz}$, 1F, *p*-F), -159.0 (t, $^3J_{\text{FF}} = 20.0\text{ Hz}$, 1F, *p*-F), -159.7 (t, $^3J_{\text{FF}} = 20.8\text{ Hz}$, 1F, *p*-F), -163.9 (m, 2F, *m*-F), -164.8 (m, 2F, *m*-F), -165.0 (m, 2F, *m*-F), all C_6F_5 -rings are inequivalent. **IR** ν_{max} (cm^{-1}): 2993, 2978, 1702, 1644, 1614, 1517, 1494, 1464, 1393, 1374, 1284, 1250, 1215, 1182, 1157, 1091, 1068, 1039, 993, 974, 956, 934, 904, 873, 860, 824, 777, 751, 737, 720, 699,

686, 663, 629, 617. **HRMS** (ES⁺) *m/z* calculated for [M+NH₄]⁺ [C₂₉H₂₃BF₁₅N₂O₂]⁺: 727.1613, found: 727.1601.

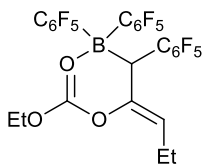


3.9c: Prop-2-yn-1-yl diphenylcarbamate **3.7c** (50 mg, 0.2 mmol) and B(C₆F₅)₃ (102 mg, 0.2 mmol) were dissolved in toluene (0.5 ml) to give a clear colourless solution. After 5 d at room temperature a few drops of CH₂Cl₂ were added and the solvent left to evaporate to give large pale yellow blocks suitable for X-ray diffraction. The solution was decanted and the solid washed with hexane (3 x 2 ml). This was then dried *in vacuo* to yield the pure product as a white solid. Yield: 101 mg, 0.13 mmol, 66%. Melting point: 137-146 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) 7.50-7.35 (m, 10H, Ar-H), 4.73 (d, ²J_{HH} = 2.5 Hz, 1H, =C-H), 4.66 (d, ²J_{HH} = 2.5 Hz, 1H, =C-H), 4.39 (s, 1H, B-C-H). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 157.2 (s), 155.6 (s), 130.1 (s), 129.9 (s), 129.4 (s), 129.5 (s), 126.7 (s), 126.6 (s), 100.5 (s), note: carbon environments of C₆F₅ groups not reported due to extensive line broadening. **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 1.4 (br. s). **¹⁹F NMR** (282 MHz, CDCl₃, 298 K) δ/ppm: -134.0 (d, ³J_{FF} = 21.5 Hz, 2F, *o*-F), -135.5 (d, ³J_{FF} = 21.5 Hz, 2F, *o*-F), -141.4 (br. s, 1F, *o*-F), -143.2 (br. s, 1F, *o*-F), -156.6 (t, ³J_{FF} = 21.2 Hz, 1F, *p*-F), -157.0 (t, ³J_{FF} = 21.2 Hz, 2F, *p*-F), -161.2 (br. s, 1F, *m*-F), -162.0 (br. s, 1F, *m*-F), -163.0 (m, 2F, *m*-F) -163.8 (m, 2F, *m*-F). All C₆F₅ rings are inequivalent. **IR** ν_{max} (cm⁻¹): 3055, 2987, 2686, 2359, 2307, 1673, 1647, 1618, 1582, 1519, 1496, 1487, 1465, 1423, 1384, 1289, 1273, 1260, 1209, 1161, 1107, 1092, 1026, 998, 972, 896, 759, 738, 717, 699. **HRMS** (EI⁺) *m/z* calculated for [M+Na]⁺ [C₃₄H₁₃BF₁₅NO₂Na]⁺: 785.0734, found 785.0711.



3.11: With less stringent exclusion of water, benzyl-prop-2-yn-1-ylcarbamate **3.10** (38 mg, 0.2 mmol) was added to B(C₆F₅)₃ (102 mg, 0.2 mmol) in 2 ml toluene to give a slight yellow solution. After reaction for 4 d at room temperature the solution was concentrated *in vacuo*, layered with hexane and left at -40 °C to produce yellow/orange blocks suitable for X-ray diffraction. Yield: 55 mg, 0.09 mmol, 45%. Melting point: 95-102 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.29 (br. s, 1H, NH), 6.56 (s, 1H, =CH), 2.18 (s, 3H, CH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 157.9 (s), 148.0 (br. s), 147.1 (br. s), 141.3 (m), 139.3 (m), 138.2 (m), 136.2 (m), 108.8 (s), 53.6 (s), 11.2 (s). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 0.7 (br. s). **¹⁹F NMR** (282 MHz, CDCl₃, 298 K) δ/ppm: -134.7 (m, 2F, *o*-F), -156.8 (m, 1F, *p*-F), -163.7 (s, 2F, *m*-F). **IR** ν_{max} (cm⁻¹): 3380, 3088, 3062, 3028, 2922, 2873, 1943, 1863, 1806, 1731, 1697, 1674, 1648, 1604, 1519, 1496,

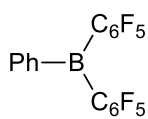
1470, 1379, 1291, 1105, 1085, 1033, 979, 774, 736, 725, 697, 625. **HRMS** (EI⁻) *m/z* calculated for [M-H]⁻ [C₂₂H₄BNO₂F₁₅]⁻: 609.0132, found: 609.0142.



3.13: Ethyl-pent-1-yn-3-yl-carbonate **3.12** (15.6 mg, 0.1 mmol) and B(C₆F₅)₃ (51.2 mg, 0.1 mmol) were dissolved in 0.6 ml CD₂Cl₂ and left for 66 h at room temperature. The completion of the reaction was monitored by ¹H-, ¹¹B- and ¹⁹F-NMR spectroscopy. Removal of the solvent *in vacuo* afforded the crude product as a brown solid. Product was recrystallised by slow evaporation of toluene to yield a small crop of colourless plates. Yield: 53.9 mg, 0.08 mmol, 81%. **¹H NMR** (400 MHz, CD₂Cl₂, 298 K) δ/ppm: 5.20 (t, ³J_{HH} = 7.5 Hz, 1H), 4.80 (dq, ³J_{HH} = 7.1 Hz, ⁴J_{HH} = 1.4 Hz, 2H), 4.48 (s, 1H), 2.23-2.04 (m, 2H), 1.55 (t, ³J_{HH} = 7.1 Hz, 3H), 0.93 (t, ³J_{HH} = 7.5 Hz, 3H); **¹¹B NMR** (96 MHz, CD₂Cl₂, 298 K) δ/ppm: -0.9 (br. s). **¹⁹F NMR** (282 MHz, CD₂Cl₂, 298 K) δ/ppm: -139.2 (m, 2F, *o*-F), -139.8 (m, 2F, *o*-F), -147.0 (br. s, 2F, *o*-F), -161.2 (t, ³J_{FF} = 20.2 Hz, 1F, *p*-F), -161.7 (t, ³J_{FF} = 20.6 Hz, 1F, *p*-F), -162.2 (t, ³J_{FF} = 20.6 Hz, 1F, *p*-F), -166.7 (br. m, 2F, *m*-F), -168.2 (m, 4F, *m*-F). **¹³C NMR** (100 MHz, CD₂Cl₂, 298) δ/ppm: 159.4 (s), 148.5 (dm, ¹J_{CF} = 245 Hz), 147.8 (dm, ¹J_{CF} = 245 Hz), 145.5 (dm, ¹J_{CF} = 245 Hz), 140.9 (dm, ¹J_{CF} = 245 Hz), 140.6 (dm), 139.8 (dm, ¹J_{CF} = 245 Hz), 138.3 (s), 138.1 (s), 137.7 (dm, ¹J_{CF} = 245 Hz), 120.6 (s), 117.6 (t), 117.1 (m), 71.8 (s), 27.9 (br. s), 18.8 (s), 14.2 (s), 13.6 (s). **IR** ν_{max} (cm⁻¹): 3293, 2979, 2940, 2882, 2358, 2125, 1756, 1515, 1465, 1396, 1373, 1342, 1302, 1275, 1177, 1094, 1062, 1007, 948, 939, 893, 857, 7901, 670.

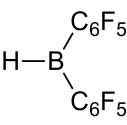
6.3.2 Use of Heteroleptic Boranes for Selective Migratory Group Transfer

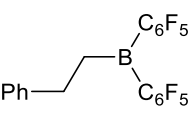
6.3.2.1 Synthesis of Starting Materials



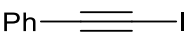
3.18: ⁿBuLi (7.5 ml, 1.6 M in hexanes, 12 mmol) was added drop wise to a solution of C₆F₅Br (1.5 ml, 12 mmol) in hexane (45 ml) at -78 °C. The reaction mixture was stirred for 40 minutes before dichlorophenylborane (0.78 ml, 6 mmol) was added, and the mixture warmed to 25 °C over a period of 12 h, at which point the generated LiCl was removed *via* cannula filtration. Evaporation of the filtrate afford a white solid, which was then sublimed at 100 °C (1 x 10⁻³ mbar) over 12 h to afford the desired triarylborane as white crystals (750 mg, 1.8 mmol, 30%). **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.68 – 7.62 (m, 3H, Ar-H), 7.43 (t, ³J_{HH} = 7.6 Hz, 2H, Ar-H). Partial **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 139.5 (s), 136.8 (s), 128.6 (s). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 64.6 (br. s). **¹⁹F NMR** (470 MHz, CDCl₃, 298 K) δ/ppm: -128.6 (dd, ³J_{FF} = 24.0 Hz, ⁴J_{FF}

= 8.6 Hz, 4F, *o*-F), -148.3 (t, $^3J_{\text{FF}} = 20.0$ Hz, 2F, *p*-F), -160.6 (td, $^3J_{\text{FF}} = 22.4$ Hz, $^4J_{\text{FF}} = 8.5$ Hz, 4F, *m*-F). Analytical data agrees with values previously reported.^[72]

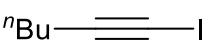

 HB(C₆F₅)₂: B(C₆F₅)₃ (0.77 g, 1.50 mmol, 1.0 equiv.) and triethylsilane (0.24 ml, 1.50 mmol, 1.0 equiv.) were dissolved in toluene (10 ml). The solution was heated at 60 °C for 5 days and then cooled to -20 °C upon which the desired product HB(C₆F₅)₂ crystallised as colourless needles. The remaining solvent was removed *via* cannula and the crystals washed with cold toluene (3 x 2 ml). Drying *in vacuo* afforded the desired product as a colourless crystalline solid (164 mg, 0.47 mmol, 32%). **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 4.10 (br. s, 1H). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 19.7 (br. s). **¹⁹F NMR** (376 MHz, CDCl₃, 298 K) δ/ppm: -132.3 (d, $^3J_{\text{FF}} = 15.1$ Hz, 4F, *o*-F), -147.2 (t, $^3J_{\text{FF}} = 20.2$ Hz, 2F, *p*-F), -158.9 (td, $^3J_{\text{FF}} = 21.0$ Hz, $^4J_{\text{FF}} = 7.6$ Hz, 4F, *m*-F). The spectral data is in accordance with literature reports.^[24a]


3.19: HB(C₆F₅)₂ (35 mg, 0.1 mmol) and styrene (10 mg, 0.1 mmol) were dissolved in toluene (2 ml). After 30 minutes the solvent was removed *in vacuo* to yield a white solid, which was washed with hexane and dried to give **2**. Yield: 26 mg, 0.057 mmol, 57%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.29 – 7.25 (m, 2H, Ar-H), 7.20 – 7.13 (m, 3H, Ar-H), 2.89 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H, CH₂), 2.47 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H, CH₂). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 74.0 (br. s). **¹⁹F NMR** (376 MHz, CDCl₃, 298 K) δ/ppm: -129.6 (dt, $^3J_{\text{FF}} = 21.2$ Hz, $^4J_{\text{FF}} = 6.6$ Hz, 4F, *o*-F), -147.0 (t, $^3J_{\text{FF}} = 19.8$ Hz, 2F, *p*-F), -160.6 (m, 4F, *m*-F). Spectral data is in accordance with literature reports.^[159]

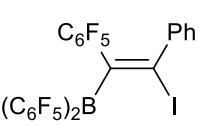
General procedure 4: Synthesised in a similar procedure set out Lal *et al.*^[160] Terminal alkyne (20 mmol, 1 equiv.) dissolved in 50 ml of THF was cooled to -78 °C in a flame-dried Schlenk flask. To this ⁿBuLi 1.6 M in hexane solution (13.1 ml, 21 mmol, 1.05 equiv.) was added dropwise and left to stir at this temperature for 30 minutes. A solution of I₂ (5.33 g, 21 mmol, 1.05 equiv.) in 30 ml of THF was added portionwise to give an orange solution. Once warmed to room temperature, the mixture was immediately washed with H₂O, extracted with hexane (iodoethynyl-benzene) or diethyl ether (1-iodohex-1-yne) and the organic fractions combined and washed with 10% Na₂S₂O₃ solution then saturated NaCl solution. Volatiles were removed *in vacuo* to give a yellow/orange oil which were suitably pure for subsequent reactions.

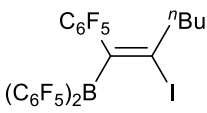

3.20a': Synthesised according to *General Procedure 4* using phenyl acetylene (2.19 ml, 20 mmol, 1 equiv.) as terminal alkyne. Yield: 4.39 g, 19.26 mmol,

96%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.46-7.41 (m, 2H, Ar-H), 7.34-7.29 (m, 3H, Ar-H). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 132.4 (s), 128.9 (s), 128.3 (s), 123.4 (s), 94.2 (s), 6.7 (s). Analytical data agrees with previously reported values.^[161]

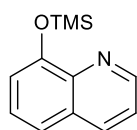
 **3.20b'**: Synthesised according to *General Procedure 4* using 1-hexyne (2.3 ml, 20 mmol, 1 equiv.) as terminal alkyne. Yield: 3.46 g, 16.7 mmol, 83%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 2.36 (t, ³J_{HH} = 7.0 Hz, 2H, CH₂), 1.55-1.47 (m, 2H, CH₂), 1.44-1.38 (m, 2H, CH₂), 0.91 (t, ³J_{HH} = 7.3 Hz, 3H, CH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 95.0 (s), 30.7 (s), 22.0 (s), 20.7 (s), 13.7 (s), -7.6 (s). Analytical data agrees with previously reported values.^[162]

General Procedure 5: The iodoalkyne reagent **3.20'** (0.2 mmol, 1 equiv.) was dissolved in CH₂Cl₂ (2 ml) with the subsequent addition of B(C₆F₅)₃ (102 mg, 0.2 mmol, 1 equiv.). Removal of solvent *in vacuo* gave the pure product as a dark orange-brown oil within 10 minutes at room temperature as confirmed by multinuclear NMR spectroscopy.

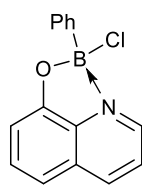
 **3.20a**: Synthesised using *General Procedure 5* with **3.20a'** (45 mg, 0.2 mmol, 1 equiv.) Yield: 147 mg, 0.2 mmol, quant. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.22 – 7.16 (m, 5H, Ar-H). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 149.1 (dm, ¹J_{CF} = ~250 Hz) 143.9 (dm, ¹J_{CF} = ~250 Hz), 143.9 (dm, ¹J_{CF} = 250 Hz), 143.1 (s), 137.7 (dm, ¹J_{CF} = ~250 Hz) 130.4 (s), 129.2 (s), 128.4 (s), 119.7 (s), 116.4 (m), 112.8 (m). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 57.9 (br. s). **¹⁹F NMR** (283 MHz, CDCl₃, 298 K) δ/ppm: -127.2 (d, ³J_{FF} = 21.7 Hz, 4F, *o*-F), -137.3 (d, ³J_{FF} = 18.5 Hz, 2F, *o*-F), -144.0 (t, ³J_{FF} = 21.0 Hz, 2F, *p*-F), -152.6 (t, ³J_{FF} = 21.6 Hz, 1F, *p*-F), -160.2 (td, ³J_{FF} = 21.7 Hz, ⁴J_{FF} = 8.9 Hz, 4F, *m*-F), -160.6 (t, ³J_{FF} = 18.5 Hz, 2F, *m*-F). **Elemental analysis** (%) calculated for C₂₆H₅BF₁₅I: C 42.20, H 0.68, found: C 41.97, H 0.72.

 **3.20b**: Synthesised using *General Procedure 5* with **3.20b'** (42 mg, 0.2 mmol, 1 equiv.). Yield 144 mg, 0.2 mmol, quant. Major stereoisomer reported: **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 2.52 (t, ³J_{HH} = 7.3 Hz, 2H, CH₂), 1.70 – 1.56 (m, 2H, CH₂), 1.37 – 1.29 (m, 2H, CH₂), 0.88 (t, ³J_{HH} = 7.3 Hz, 3H, CH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 148.6 (dm, ¹J_{CF} = ~250 Hz), 145.7 (dm, ¹J_{CF} = ~250 Hz), 144.7 (dm, ¹J_{CF} = ~250 Hz), 142.7 (dm, ¹J_{CF} = ~250 Hz), 137.7 (dm, ¹J_{CF} = ~250 Hz), 127.9 (s), 114.8 (m), 113.3 (m),

47.6 (s), 43.3 (s), 34.0 (s), 31.8 (s), 21.7 (s), 21.5 (s), 13.8 (s), 13.6 (s). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 58.4 (br. s). **¹⁹F NMR** (283 MHz, CDCl₃, 298 K) δ/ppm: -127.1 (d, ³J_{FF} = 19.6 Hz, 4F, *o*-F), -137.7 (m, 2F, *o*-F), -144.9 (t, ³J_{FF} = 21.1 Hz, 2F, *p*-F), -152.8 (t, ³J_{FF} = 21.1 Hz, 1F, *p*-F), -160.73 – -160.55 (m, 6F, *m*-F). **Elemental analysis** (%) calculated for C₂₄H₉BF₁₅I: C 40.04, H 1.26, found: C 39.95, H 1.20.

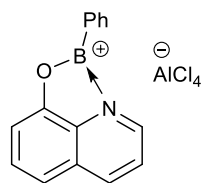


8-((trimethylsilyl)oxy)quinoline: Prepared according to literature methods.^[163] To a solution of 8-hydroxyquinoline (4.79 g, 33.0 mmol) and imidazole (2.36 g, 34.7 mmol) in 50 ml CH₂Cl₂, trimethylsilyl chloride (4.62 ml, 36.4 mmol) was added and stirred overnight at room temperature. The resulting cloudy orange solution was diluted with diethyl ether (100 ml) and filtered. The organic layer was dried with Na₂SO₄ and the volatiles removed *in vacuo*. The resulting brown oil was left to stand for 24 h whereby the resulting orange/brown oil was decanted from the brown crystalline solid to give the pure product as a brown oil. Yield: 3.33 g, 15.3 mmol, 46%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.89 (dd, ³J_{HH} = 4.2 Hz, ⁴J_{HH} = 1.7 Hz, 1H, quinoline Ar-H), 8.12 (dd, ³J_{HH} = 8.1 Hz, ⁴J_{HH} = 1.7 Hz, 1H, quinoline Ar-H), 7.42 (s, 1H, Ar-H), 7.41 (d, ³J_{HH} = 2.6 Hz, 1H, Ar-H), 7.37 (q, ³J_{HH} = 4.1 Hz, 1H, Ar-H), 7.16 (dd, ³J_{HH} = 5.7 Hz, ³J_{HH} = 3.2 Hz, 1H, Ar-H), 0.36 (s, 9H, SiMe₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 152.2 (s), 148.7 (s), 142.0 (s), 135.8 (s), 129.7 (s), 126.8 (s), 121.2 (s), 120.5 (s), 117.6 (s), 1.1 (s). **HRMS** (EI⁺) *m/z* calculated for [C₁₂H₁₅NOSi]⁺ [M]⁺: 217.0923, found: 217.0922. Characterisation agrees with previous literature findings.^[74]



3.21': Prepared in a procedure set out by Ingleson *et al.*^[74] To a solution of 8-((trimethylsilyl)oxy)quinoline (1 ml, 4.6 mmol, 1 equiv.) in 10 ml of CH₂Cl₂, dichlorophenyl borane (PhBCl₂) (0.73 ml, 4.6 mmol, 1 equiv.) was added dropwise to give an instant colour change from an orange to a dark green solution. This was left at room temperature for 1 h whereby bright yellow crystals formed. The remaining solution was decanted and the resulting solid dried *in vacuo*. The crude product was washed with cold CH₂Cl₂ (1 x 2 ml) then hexane (3 x 2 ml) and dried under reduced pressure to afford the pure product as a bright yellow crystalline solid. Yield: 1.20 g, 4.49 mmol, 98%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.64 (dd, ³J_{HH} = 5.2 Hz, ⁴J_{HH} = 0.9 Hz, 1H, Ar-H), 8.53 (dd, ³J_{HH} = 8.3 Hz, ⁴J_{HH} = 0.9 Hz, 1H, Ar-H), 7.76-7.71 (m, 4H, Ar-H), 7.42 (d, ³J_{HH} = 8.4 Hz, 1H, Ar-H), 7.38-7.29 (m, 4H, Ar-H). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 156.3 (s), 140.5 (s), 140.4 (s), 136.2 (s), 133.0 (s), 131.8 (s), 128.3 (s), 128.1 (s), 127.9 (s), 123.4 (s), 114.4 (s), 111.2 (s). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 12.3 (br. s). **HRMS**

(EI⁺) m/z calculated for [C₁₅H₁₁BCINO]⁺ [M]⁺: 266.0659, found: 266.0658. Characterisation agrees with previous literature findings.^[74]

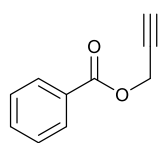


3.21: Prepared in a procedure set out by Ingleson *et al.*^[74] The oxazaboroloquinoline precursor **3.21'** (0.60 g, 2.25 mmol, 1 equiv.) was dissolved in CH₂Cl₂ (25 ml) with subsequent addition of AlCl₃ (0.30 g, 2.25 mmol, 1 equiv.) instantly yielding a yellow-green precipitate. The mixture was stirred for a further 20 minutes then left to settle. The solution was decanted with the solid residue being washed with hexane (3 x 5 ml) to give the product (**3.21**) as a bright yellow powder. Yield: 653 mg, 1.68 mmol, 73%. ¹H NMR (500 MHz, CH₂Cl₂ d₆-DMSO insert, 298 K) δ/ppm: 9.79 (br. s, 1H, Ar-H), 9.43 (d, ³J_{HH} = 6.8 Hz, 1H, Ar-H), 8.53 (br. s, 1H, Ar-H), 8.35 (br. d, ³J_{HH} = 6.1 Hz, 2H, Ar-H), 8.2 (br. d, ³J_{HH} = 7.6 Hz, 1H, Ar-H), 8.12 – 8.07 (m, 2H, Ar-H), 7.84 (br. s, 1H, Ar-H), 7.71 (t, ³J_{HH} = 7.5 Hz, 2H, Ar-H). ¹¹B NMR (160 MHz, CH₂Cl₂ d₆-DMSO insert, 298 K) δ/ppm: 34.5 (br. s). HRMS (EI⁺) m/z calculated for [C₁₅H₁₁BNO]⁺ [M]⁺: 231.0970, found: 231.0960. Characterisation agrees with previous literature findings.^[74]

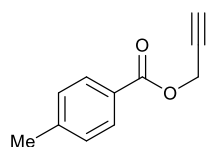
General Procedure 6: Synthesised using an adapted procedure from Lam *et al.*^[164] Propargyl alcohol (0.72 ml, 12.5 mmol, 1 equiv.) was dissolved in 100 ml CH₂Cl₂ and cooled to -78 °C. Tetramethylethylenediamine (TMEDA) (1.12 ml, 7.5 mmol, 0.6 equiv.) was added followed by dropwise addition of acyl chloride (13.8 mmol, 1.1 equiv.). After stirring at this temperature for 30 minutes the reaction was warmed to room temperature and quenched with saturated NH₄Cl solution. The aqueous phase was extracted with CH₂Cl₂ (3 x 30 ml) with the combined organic phases being washed with H₂O then dried over K₂CO₃ and Na₂SO₄. Removal of volatiles under reduced pressure gave the crude product as a pale yellow oil. This was purified by either recrystallisation or column chromatography.

General Procedure 7: Synthesised using a procedure similar to that reported by Stephan *et al.*^[20] The acyl chloride (15 mmol, 1.2 equiv.) and triethylamine (TEA) (3.5 ml, 25 mmol, 2 equiv.) were dissolved in 50 ml CH₂Cl₂ and cooled to 0 °C. Propargyl alcohol (12.5 mmol, 1 equiv.) was added dropwise at this temperature and the mixture stirred at room temperature for 10 h. The resulting solution was washed with 100 ml H₂O with the aqueous phase being extracted with CH₂Cl₂ (3 x 50 ml). The combined organic fractions were washed with saturated NaCl solution (100 ml) and dried over MgSO₄ with the volatiles being removed *in vacuo*. The crude product was purified by either recrystallisation or column chromatography.

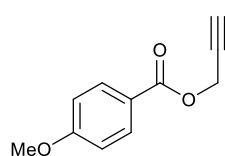
General procedure 8: Synthesised using a procedure adapted from Stephan *et al.*^[20] Triethylamine (1.0 equiv.) and 4-dimethylaminopyridine (4-DMAP) (0.02 equiv.) were added to a solution of the propargyl alcohol (1.0 equiv.) in CH₂Cl₂ (ca. 20 ml) and was stirred for 5 min. The solution was cooled to 0 °C and the acyl chloride (1.0 equiv.) added dropwise. The resulting mixture was stirred at this temperature for 30 min and was then allowed to warm to room temperature and was stirred for a further 3-48 h. The reaction was quenched with water and the aqueous layer extracted twice with CH₂Cl₂. The collective organic phases were washed with brine, dried with MgSO₄, filtered, and the solvent was removed under vacuum and the product purified by column chromatography or recrystallisation as necessary.



3.22a: Synthesised according to *General Procedure 6* using benzoyl chloride (1.60 ml, 13.8 mmol, 1.1 equiv.). Purification *via* column chromatography (hexane/ethyl acetate, 20:1) gave the pure product as a colourless oil. Yield: 1.82 g, 11.4 mmol, 91%. Spectroscopic data agrees with literature values.^[165] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.09 – 8.07 (m, 2H, Ar-H), 7.58 (tt, ³J_{HH} = 7.5 Hz, ⁴J_{HH} = 1.3 Hz, 1H, Ar-H), 7.45 (t, ³J_{HH} = 7.6 Hz, 2H, Ar-H), 4.93 (d, ⁴J_{HH} = 2.5 Hz, 2H, CH₂), 2.52 (t, ⁴J_{HH} = 2.5 Hz, 1H, ≡CH). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 165.9 (s), 133.5 (s), 130.0 (s), 129.6 (s), 128.6 (s), 77.9 (s), 75.1 (s), 52.6 (s).

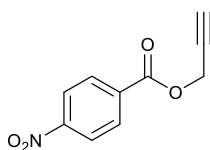


3.22b: Synthesised according to *General Procedure 6* using *p*-toluoyl chloride (1.82 ml, 13.8 mmol, 1.1 equiv.). Recrystallisation from hexane by slow evaporation afforded the product as a white crystalline solid. Yield: 2.17 g, 12.5 mmol, 100%. Spectroscopic data agrees with literature values.^[20] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.96 (d, ³J_{HH} = 8.1 Hz, 2H, Ar-H), 7.25 (d, ³J_{HH} = 8.1 Hz, 2H, Ar-H), 4.91 (d, ⁴J_{HH} = 2.5 Hz, 2H, CH₂), 2.51 (t, ⁴J_{HH} = 2.5 Hz, 1H, ≡CH), 2.41 (s, 3H, Ar-Me). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 166.3 (s), 144.5 (s), 130.3 (s), 129.6 (s), 127.1 (s), 78.3 (s), 75.2 (s), 52.7 (s), 22.1 (s).



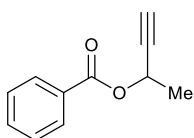
3.22c: Synthesised according to *General Procedure 7* using *p*-anisoyl chloride (2.03 ml, 15 mmol, 1.2 equiv.). Purification *via* column chromatography (hexane/ethyl acetate, 5:1) gave the pure product as a colourless oil. Yield: 1.98 g, 10.4 mmol, 83%. Spectroscopic data agrees with literature values.^[166] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.02 (dt, ³J_{HH} = 9.0 Hz, ⁴J_{HH} = 2.2 Hz, 2H, Ar-H), 6.92 (dt, ³J_{HH} = 9.0 Hz,

$^4J_{\text{HH}} = 2.2$ Hz, 2H, Ar-H), 4.89 (d, $^4J_{\text{HH}} = 2.4$ Hz, 2H, CH₂), 3.86 (s, 3H, OMe), 2.50 (t, $^4J_{\text{HH}} = 2.4$ Hz, 1H, $\equiv\text{CH}$). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 165.7 (s), 163.9 (s), 132.0 (s), 122.0 (s), 113.9 (s), 78.2 (s), 74.9 (s).



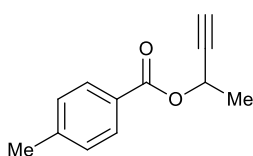
3.22d: Synthesised according to *General Procedure 7* using *p*-nitrobenzoylchloride (2.77 g, 15 mmol, 1.2 equiv.). Recrystallisation *via* slow evaporation of CH₂Cl₂ gave the pure product as a yellow crystalline solid. Yield: 2.36 g, 11.5 mmol, 96%.

Spectroscopic data agrees with literature values.^[167] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 8.30 (dt, $^3J_{\text{HH}} = 9.0$ Hz, $^4J_{\text{HH}} = 2.2$ Hz, 2H, Ar-H), 8.23 (dt, $^3J_{\text{HH}} = 9.0$ Hz, $^4J_{\text{HH}} = 2.2$ Hz, 2H, Ar-H), 4.97 (d, $^4J_{\text{HH}} = 2.5$ Hz, 2H, CH₂), 2.56 (t, $^4J_{\text{HH}} = 2.5$ Hz, 1H, $\equiv\text{CH}$). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 164.0 (s), 151.0 (s), 134.9 (s), 131.1 (s), 123.8 (s), 77.1 (s), 75.8 (s), 53.4 (s).



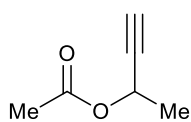
3.22e: Synthesised according to *General Procedure 7* using benzoyl chloride (1.74 ml, 15 mmol, 1.2 equiv.) and but-3-yn-2-ol (0.92 ml, 12.5 mmol). Purification *via* column chromatography (hexane/ethyl acetate, 10:1) gave the product as a white solid. Yield: 1.54 g, 8.9 mmol, 71%.

Spectroscopic data agrees with literature values.^[20] **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 8.07 (d, $^3J_{\text{HH}} = 7.8$ Hz, 2H, Ar-H), 7.57 (t, $^3J_{\text{HH}} = 7.8$ Hz, 1H, Ar-H), 7.45 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H, Ar-H), 5.68 (q, $^3J_{\text{HH}} = 6.8$ Hz, 1H, OCH(Me)), 2.49 (s, 1H, $\equiv\text{CH}$), 1.65 (d, $^3J_{\text{HH}} = 6.8$ Hz, 3H, OCH(Me)). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 165.6 (s), 133.3 (s), 129.9 (s), 129.9 (s), 128.5 (s), 82.3 (s), 73.1 (s), 60.8 (s), 21.5 (s).

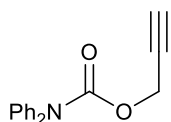


3.22f: Synthesised according to *General Procedure 8*, but-3-yn-2-ol (1.56 ml, 19.8 mmol), 4-DMAP (488 mg), NEt₃ (2.72 ml, 31.4 mmol) and *p*-toluoyl chloride (2.60 ml, 19.5 mmol) were reacted in 50 ml CH₂Cl₂. Purification by column chromatography on SiO₂ (hexane:EtOAc, 19:1) afforded the product as a white crystalline solid.

Yield: 2.67 g, 14.2 mmol, 73%. Spectroscopic data agrees with literature values.^[20] **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 7.96 (d, $^3J_{\text{HH}} = 8.30$ Hz, 2H, *o*-H), 7.24 (d, $^3J_{\text{HH}} = 8.30$ Hz, 2H, *m*-H), 5.67 (qd, $^3J_{\text{HH}} = 6.68$ Hz, $^4J_{\text{HH}} = 2.18$ Hz, 1H, -CH), 2.48 (d, $^4J_{\text{HH}} = 2.18$ Hz, 1H, -C \equiv CH), 2.41 (s, 3H, -CH₃), 1.64 (d, $^3J_{\text{HH}} = 6.68$ Hz, 3H, -CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 156.7 (s), 144.1 (s), 130.0 (s), 129.2 (s), 127.2 (s), 82.5 (s), 73.1 (s), 60.6 (s), 21.9 (s), 21.5 (s).

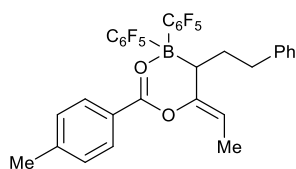


3.22g: But-3-yn-2-ol (0.8 ml, 10 mmol, 1 equiv.) dissolved in 10 ml of CH_2Cl_2 along with triethylamine (2.1 ml, 15 mmol, 1.5 equiv.). Subsequent addition of acetic anhydride (1.04 ml, 11 mmol, 1.1 equiv.) and 4-dimethylamino pyridine (0.12 g, 1 mmol, 0.1 equiv.) gave a pale yellow solution. This was left to stir at rt for 12 h. The resulting solution was washed with saturated NH_4Cl solution (10 ml) then saturated NaCl solution (10 ml). The solution was dried over MgSO_4 and volatiles removed *in vacuo* to give the pure product as an off yellow oil which was suitable pure without any further purification. Yield: 0.84 g, 7.5 mmol, 75%. Spectroscopic data agrees with literature values.^[168] **$^1\text{H NMR}$** (400 MHz, CDCl_3 , 298 K) δ /ppm: 5.42 (q, $^3J_{\text{HH}} = 6.7$ Hz, 1H, $\text{OCH}(\text{Me})$), 2.45 (s, 1H, $\equiv\text{CH}$), 2.08 (s, 3H, CO_2Me), 1.50 (d, $^3J_{\text{HH}} = 6.7$ Hz, 3H, $\text{OCH}(\underline{\text{Me}})$). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3 , 298 K) δ /ppm: 169.8 (s), 82.2 (s), 72.9 (s), 60.0 (s), 21.2 (s).



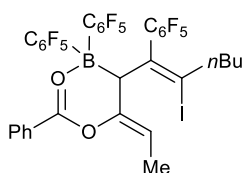
3.22b: Diphenyl carbamoyl chloride (1.15 g, 5 mmol 1 equiv.) and 4-dimethylamino pyridine (0.05 equiv.) were added to a solution of propargyl alcohol (0.29 ml, 5 mmol, 1 equiv.) in pyridine (5 ml) and the resulting mixture heated overnight at 80 °C. The reaction mixture was quenched with saturated NH_4Cl solution (10 ml) and the aqueous phase extracted with diethyl ether (3 x 20 ml). The combined organic phases were then washed with saturated NH_4Cl solution (3 x 20 ml), dried over sodium sulfate, filtered and the solvent removed *in vacuo*. Purification by recrystallisation from petroleum ether with a few drops of Et_2O to solubilise the solid at -40 °C gave a pale yellow solid. Yield: 1.07 g, 4.26 mmol, 71%. Spectroscopic data agrees with literature values.^[36b] **$^1\text{H NMR}$** (400 MHz, CDCl_3 , 298 K) δ /ppm: 7.28–7.13 (m, 10H, Ar-H), 4.68 (s, 2H, CH_2), 2.37 (s, 1H, $\equiv\text{CH}$). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3 , 298 K) δ /ppm: 154.1 (s), 142.4 (s), 129.1 (s), 127.1 (s), 126.5 (s), 78.2 (s), 74.9 (s), 53.5 (s).

6.3.2.2 Synthesis of Products

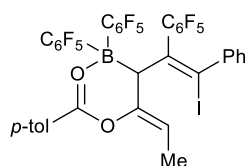


$\text{HB}(\text{C}_6\text{F}_5)_2$ (35 mg, 0.1 mmol) and styrene (10 mg, 0.1 mmol) were dissolved in toluene (2 ml). After 35 minutes but-3-yn-2-yl 4-methylbenzoate (**3.22f**) (19 mg, 0.1 mmol) was added. The reaction was stirred for 40 h, and volatiles removed *in vacuo* to give a white solid. Yield: 60 mg, 0.09 mmol, 94%. (combined mixture regioisomers in 2:1 ratio, $(\text{CH}_2)_2\text{Ph}$ vs. C_6F_5 migration). **$^1\text{H NMR}$** (400 MHz, CDCl_3 , 298 K) δ /ppm: 8.17 (d, $^3J_{\text{HH}} = 8.3$ Hz, 2H, Ar-H), 7.43 (d, $^3J_{\text{HH}} = 8.1$ Hz, 2H, Ar-H), 7.24 – 7.20 (m, 2H, Ar-H), 7.09 (d, $^3J_{\text{HH}} = 7.3$ Hz, 3H, Ar-H), 5.06 (q, $^3J_{\text{HH}} = 7.0$

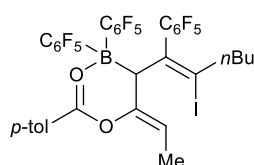
Hz, 1H, =CH), 2.73 – 2.69 (m, 2H, CH₂), 2.53 (s, 3H, Ph-Me), 2.63 – 2.59 (m, 1H, BCH), 1.79 (d, ³J_{HH} = 7.0 Hz, 3H, =CMe), 1.41 – 1.27 (m, 2H, CH₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 172.1 (s), 152.9 (s), 149.6 (s), 147.1 (dm, ¹J_{CF} = 237 Hz, *o*-C, C₆F₅), 142.2 (s), 140.0 (dm, ¹J_{CF} = 248 Hz, *p*-C, C₆F₅), 137.3 (dm, ¹J_{CF} = 247 Hz, *m*-C, C₆F₅), 131.5 (s), 130.5 (s), 128.5 (s), 126.0 (s), 122.5 (s), 109.5 (s), 35.3 (s), 29.7 (s), 22.4 (s), 10.4 (s). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 3.5 (br. s). **¹⁹F NMR** (376 MHz, CDCl₃, 298 K) δ/ppm: -134.7 – -135.0 (m, 4F, *o*-F), -157.6 (dt, ³J_{FF} = 20.4 Hz, 1F, *p*-F), -157.9 (dt, ³J_{FF} = 20.3 Hz, 1F, *p*-F), -163.7 (tdd, ³J_{FF} = 22.8 Hz, ⁴J_{FF} = 9.1 Hz, 4F, *m*-F). Note: Overlapping of both rearrangement products present (C₆F₅ vs. (CH₂)₂Ph) leading to split patterns observed particularly for *p*-F of C₆F₅ rings. Clear major/minor peaks identified in a ratio of *ca.* 2:1. **Elemental analysis** (%) calculated for C₃₂H₂₁BF₁₀O₂: C 60.21, H 3.32, found: C 60.30, H 3.28.



3.23a: B(C₆F₅)₃ (102 mg, 0.2 mmol, 1.0 equiv.) was dissolved in CH₂Cl₂ (5 ml) and 1-iodohex-1-yne (42 mg, 0.2 mmol, 1.0 equiv.) added at room temperature. After 10 min but-3-yn-2-yl benzoate (**3.22e**) (34 mg, 0.2 mmol, 1.0 equiv.) was added and the reaction stirred for 18 h. The solvent was partially removed, layered with hexane and stored at -40 °C to give colourless crystals. The remaining solvent was removed and the crystals washed with cold hexane (3 x 2 ml). Drying in vacuum affords the desired product as an off-white solid. Yield: 70 mg, 0.071 mmol, 36%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 8.04 (d, ³J_{HH} = 7.7 Hz, 2H, Ar-H), 7.86 (t, ³J_{HH} = 7.6 Hz, 1H, Ar-H), 7.61 (t, ³J_{HH} = 7.6 Hz, 2H, Ar-H), 5.59 (q, ³J_{HH} = 7.4 Hz, 1H, =CH), 4.90 (s, 1H, BCH), 2.08 (t, ³J_{HH} = 7.4 Hz, 2H, CH₂), 1.80 (d, ³J_{HH} = 7.1 Hz, 3H, =CMe), 1.38 (pent., ³J_{HH} = 7.4 Hz, 2H, CH₂), 1.08 (sxt, ³J_{HH} = 7.3 Hz, 2H, CH₂), 0.74 (t, ³J_{HH} = 7.2 Hz, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 172.3 (s), 151.2 (s), 138.2 (s), 130.8 (s), 129.8 (s), 128.5 (s), 124.2 (s), 116.1 (s), 112.6 (s), 45.3 (s), 42.9 (s), 31.7 (s), 21.4 (s), 13.9 (s), 10.4 (s). note: carbons of C₆F₅ groups not reported due to extensive line broadening. **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 2.7 (br. s). **¹⁹F NMR** (376 MHz, CDCl₃, 298 K) δ/ppm: -132.0 (br. s, 2F, *o*-F), -134.1 (d, ³J_{FF} = 26.3 Hz, 1F, *o*-F), -135.5 (br. s, 2F, *o*-F), -137.5 (d, ³J_{FF} = 24.0 Hz, 1F, *o*-F), -153.8 (t, ³J_{FF} = 20.7 Hz, 1F, *p*-F), -156.8 (t, ³J_{FF} = 20.7 Hz, 1F, *p*-F), -157.4 (t, ³J_{FF} = 20.7 Hz, 1F, *p*-F), -160.8 – -161.0 (m, 2F, *m*-F), -162.8 – -162.9 (m, 2F, *m*-F), -164.1 – -164.3 (m, 2F, *m*-F). **Elemental analysis** (%) calculated for C₃₅H₁₉BF₁₅O₂: C 47.01, H 2.14, found: C 46.98, H 2.22.

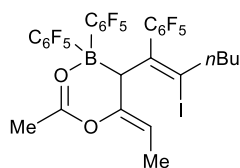


3.23b: $B(C_6F_5)_3$ (51 mg, 0.1 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (0.6 ml) and (iodoethynyl)benzene (23 mg, 0.1 mmol, 1.0 equiv.) added at room temperature. After 10 min but-3-yn-2-yl 4-methylbenzoate (**3.22f**) (19 mg, 0.1 mmol, 1.0 equiv.) was added and the reaction stirred for 18 h. The solvent was partially removed, layered with pentane and stored at $-20\text{ }^\circ\text{C}$ to give colourless crystals. The remaining solvent was removed *via* cannula, the crystals washed with cold pentane (3 x 2 ml). Drying in vacuum affords the desired product as a white solid. Yield: 27.0 mg, 0.029 mmol, 29%. **1H NMR** (300 MHz, $CDCl_3$, 298 K) δ /ppm: 7.88 (d, $^3J_{HH} = 8.2$ Hz, 2H), 7.35 (d, $^3J_{HH} = 8.2$ Hz, 2H), 7.11-7.01 (m, 3H), 6.95 (d, $^3J_{HH} = 7.3$ Hz, 2H), 5.62 (q, $^3J_{HH} = 7.1$ Hz, 1H), 4.92 (s, 1H), 2.49 (s, 3H), 1.83 (d, $^3J_{HH} = 7.1$ Hz, 3H). **^{11}B NMR** (96 MHz, $CDCl_3$, 298 K) δ /ppm: 2.22 (br. s). **^{19}F NMR** (282 MHz, $CDCl_3$, 298 K) δ /ppm: -131.9 (br. s., 2F, *o*-F), -133.4 (dm, $^3J_{FF} = 25.3$ Hz, 1F, *o*-F), -135.9 (m, 2F, *o*-F), -137.5 (dm, $^3J_{FF} = 26.0$ Hz, 1F, *o*-F), -154.1 (t, $^3J_{FF} = 20.8$ Hz, *p*-F), -156.9 (t, $^3J_{FF} = 19.5$ Hz, *p*-F), -157.3 (t, $^3J_{FF} = 20.3$ Hz, *p*-F), -161.9 (m, 2F, *m*-F), -162.9 (m, 2F, *m*-F), -164.1 (m, 2F, *m*-F). **^{13}C NMR** (150 MHz, $CDCl_3$, 298 K) δ /ppm: 172.4 (s), 150.8 (s), 150.7 (s), 147.8 (dm, $^1J_{CF} = 250$ Hz), 147.4 (dm, $^1J_{CF} = 250$ Hz), 144.3 (s), 143.0 (dm, $^1J_{CF} = 250$ Hz), 140.1 (dm, $^1J_{CF} = 250$ Hz), 137.3 (dm, $^1J_{CF} = 250$ Hz), 132.5 (s), 130.9 (s), 130.4 (s), 128.3 (s), 128.2 (s), 126.6 (s), 121.3 (s), 118.7 (m), 116.1 (m), 112.5 (s), 112.6 (m), 107.2 (s), 45.2 (br. s), 22.4 (s), 10.4, (s). **HRMS** (ES⁺) *m/z* calculated for $[C_{38}H_{21}BF_{15}INO_2]^+ [M+NH_4]^+$, calculated for 946.0471; found, 946.0460.

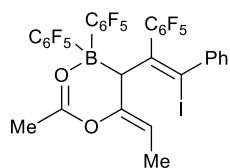


3.23c: $B(C_6F_5)_3$ (51 mg, 0.1 mmol, 1.0 equiv.) was dissolved in CD_2Cl_2 (0.6 ml) and 1-iodohex-1-yne (21 mg, 0.1 mmol, 1.0 equiv.) added at room temperature. After 10 min but-3-yn-2-yl 4-methylbenzoate (**3.22f**) (19 mg, 0.1 mmol, 1.0 equiv.) was added and the reaction stirred for 18 h. The solvent was partially removed, layered with pentane and stored at $-20\text{ }^\circ\text{C}$ to give colourless crystals. The remaining solvent was removed *via* cannula, the crystals washed with cold pentane (3 x 2 ml). Drying in vacuum affords the desired product as white solid. Yield: 22 mg, 0.025 mmol, 25%. **1H NMR** (600 MHz, $CDCl_3$, 298 K) δ /ppm: 7.91 (d, $^3J_{HH} = 8.1$ Hz, 2H), 7.38 (d, $^3J_{HH} = 8.1$ Hz, 2H), 5.54 (q, $^3J_{HH} = 7.00$ Hz, 1H), 4.88 (s, 1H), 2.53 (s, 3H), 2.08 (t, $^3J_{HH} = 7.1$ Hz, 2H), 1.78 (d, $^3J_{HH} = 7.1$ Hz, 3H), 1.43-1.35 (m, 2H), 1.11-1.03 (m, 2H), 0.75 (t, $^3J_{HH} = 7.8$ Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, 298 K) δ /ppm: 172.2 (s), 151.0 (s), 150.6 (s), 147.7 (dm, $^1J_{CF} = 246$ Hz), 147.3 (dm, $^1J_{CF} = 239$ Hz), 143.2 (dm, $^1J_{CF} = 241$ Hz), 140.1 (dm, $^1J_{CF} = 250$ Hz), 137.2 (dm, $^1J_{CF} = 250$ Hz), 131.6 (s), 130.9 (s), 130.5 (s), 128.6 (s), 121.3 (s), 118.5 (m), 115.8 (s), 116.2 (m), 112.44 (m), 112.2 (s),

45.4 (br. s), 42.9 (s), 31.7 (s), 22.5 (s), 21.4 (s), 13.9 (s), 10.4 (s). **¹¹B NMR** (96 MHz, CDCl₃, 298 K) δ/ppm: 1.92 (br. s). **¹⁹F NMR** (282 MHz, CDCl₃, 298 K) δ/ppm: -132.0 (br. s, 2F, *o*-F), -134.1 (d, ³J_{FF} = 24.7 Hz, 1F, *o*-F), -135.5 (m, 2F, *o*-F), -137.5 (d, ³J_{FF} = 24.7 Hz, 1F, *o*-F), -154.1 (t, ³J_{FF} = 21.0 Hz, *p*-F), -157.0 (t, ³J_{FF} = 21.2 Hz, *p*-F), -157.7 (t, ³J_{FF} = 20.6 Hz, *p*-F), -161.1 (m, 2F, *m*-F), -163.0 (m, 2F, *m*-F), -164.3 (m, 2F, *m*-F). **HRMS** (ES⁺) *m/z* calculated for [C₃₆H₂₅BF₁₅INO₂]⁺ [M+NH₄]⁺: 926.0784; found, 926.0770.

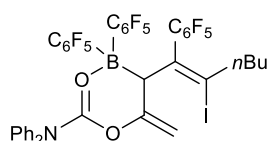


3.23d: B(C₆F₅)₃ (102 mg, 0.2 mmol, 1.0 equiv.) was dissolved in CH₂Cl₂ (5 ml) and 1-iodohex-1-yne (42 mg, 0.2 mmol, 1.0 equiv.) added at room temperature. After 10 min but-3-yn-2-yl acetate (**3.22g**) (22 mg, 0.2 mmol, 1.0 equiv.) was added and the reaction stirred for 18 h. The solvent was partially removed, layered with hexane and stored at -40 °C to give colourless crystals. The remaining solvent was removed and the crystals washed with cold hexane (3 x 2 ml). Drying in vacuum affords the desired product as an off-white solid. Yield: 50 mg, 0.06 mmol, 30%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 5.53 (q, ³J_{HH} = 7.0 Hz, 1H, =CH), 4.70 (s, 1H, CH), 2.20 (s, 3H, MeCO₂), 2.10 (t, ³J_{HH} = 8.3 Hz, 2H, CH₂), 1.67 (d, ³J_{HH} = 7.1 Hz, 3H, =CMe), 1.40 (pent., ³J_{HH} = 7.6 Hz, 2H, CH₂), 1.10 (sext., ³J_{HH} = 7.3 Hz, 2H, CH₂), 0.77 (t, ³J_{HH} = 7.2 Hz, 3H, CH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 180.6 (s), 151.0 (s), 128.0 (s), 117.8 (s), 112.9 (s), 77.4 (s), 43.0 (s), 31.8 (s), 21.6 (s), 21.5 (s), 13.9 (s), 10.3 (s). Note: Partial spectrum, Carbon resonances of C₆F₅-groups unobserved due to extensive line broadening as a result of C–F coupling. **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 2.4 (br. s). **¹⁹F NMR** (378 MHz, CDCl₃, 298 K) δ/ppm: -131.98 (br. s, 2F, *o*-F), -133.9 (d, ³J_{FF} = 23.4 Hz, 1F, *o*-F), -136.1 (d, ³J_{FF} = 17.3 Hz, 2F, *o*-F), -136.9 (d, ³J_{FF} = 23.0 Hz, 1F, *o*-F), -152.3 (t, ³J_{FF} = 21.0 Hz, 1F, *p*-F), -156.6 (t, ³J_{FF} = 21.1 Hz, 1F, *p*-F), -157.0 (t, ³J_{FF} = 21.1 Hz, 1F, *p*-F), -159.5 (td, ³J_{FF} = 22.6 Hz, ⁴J_{FF} = 8.1 Hz, 1F, *m*-F), -161.3 (td, ³J_{FF} = 22.6 Hz, ⁴J_{FF} = 8.3 Hz, 1F, *m*-F), -162.7 (td, ³J_{FF} = 22.1 Hz, ⁴J_{FF} = 9.2 Hz, 2F, *m*-F), -164.2 (td, ³J_{FF} = 22.1 Hz, ⁴J_{FF} = 9.1 Hz, 2F, *m*-F). **Elemental analysis** (%) calculated for C₃₀H₁₇BF₁₅O₂: C 43.30, H 2.06, found: C 43.16, H 1.96.



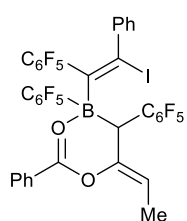
3.23e: B(C₆F₅)₃ (102 mg, 0.2 mmol, 1.0 equiv.) was dissolved in CH₂Cl₂ (5 ml) and 1-(iodoethynyl)benzene (46 mg, 0.2 mmol, 1.0 equiv.) added at room temperature. After 10 min but-3-yn-2-yl acetate (**3.22g**) (22 mg, 0.2 mmol, 1.0 equiv.) was added and the reaction stirred for 18 h. The solvent was partially removed, layered with hexane and

stored at $-40\text{ }^{\circ}\text{C}$ to give colourless crystals. The remaining solvent was removed and the crystals washed with cold hexane (3 x 2 ml). Drying in vacuum affords the desired product as an off-white solid. Yield: 52 mg, 0.06 mmol, 31%. **^1H NMR** (400 MHz, CDCl_3 , 298 K) δ /ppm: 7.06 – 7.00 (m, 3H, Ar-H), 6.92 – 6.90 (m, 2H, Ar-H), 5.55 (q, $^3J_{\text{HH}} = 7.0$ Hz, 1H, =CH), 4.70 (s, 1H, CH), 2.10 (s, 3H, Me), 1.65 (d, $^3J_{\text{HH}} = 7.0$ Hz, 3H, =CMe). **^{13}C NMR** (101 MHz, CDCl_3 , 298 K) δ /ppm: 180.8 (s), 150.6 (s), 144.2 (s), 128.5 (s), 128.3 (s), 128.1 (s), 126.6 (s), 125.9 (s), 114.6 (s), 113.2 (s), 21.5 (s), 10.4 (s). Note: Partial spectrum, Carbon resonances of C_6F_5 -groups unobserved due to extensive line broadening due to C–F coupling. **^{11}B NMR** (128 MHz, CDCl_3 , 298 K) δ /ppm: 2.4 (br. s). **^{19}F NMR** (378 MHz, CDCl_3 , 298 K) δ /ppm: -132.1 (br. s, 2F, o-F), -134.2 (d, $^3J_{\text{FF}} = 22.0$ Hz, 1F, o-F), -135.6 (br. s, 2F, o-F), -137.6 (d, $^3J_{\text{FF}} = 25.5$ Hz, 1F, o-F), -153.8 (t, $^3J_{\text{FF}} = 21.2$ Hz, 1F, p-F), -156.9 (t, $^3J_{\text{FF}} = 20.5$ Hz, 1F), -157.5 (t, $^3J_{\text{FF}} = 21.1$ Hz, 1F, p-F), -160.8 – -161.1 (m, 2F, m-F), -162.9 (td, $^3J_{\text{FF}} = 22.0$ Hz, $^4J_{\text{FF}} = 8.8$ Hz, 2F, m-F), -164.3 (td, $^3J_{\text{FF}} = 21.9$ Hz, $^4J_{\text{FF}} = 8.9$ Hz, 2F, m-F). **Elemental analysis** (%) calculated for $\text{C}_{32}\text{H}_{13}\text{BF}_{15}\text{O}_2$ 0.5 equiv. CH_2Cl_2 : C: 43.63, H: 1.58. Found: C: 43.39, H: 1.66.



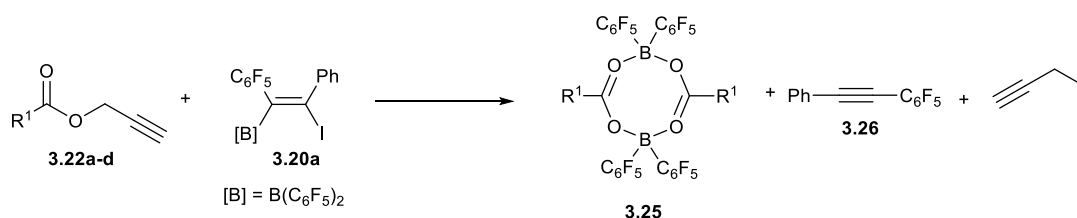
3.23f: $\text{B}(\text{C}_6\text{F}_5)_3$ (102 mg, 0.2 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (5 ml) and 1-iodohex-1-yne (42 mg, 0.2 mmol, 1.0 equiv.) added at room temperature. After 10 min prop-2-yn-1-yl diphenylcarbamate (**3.22h**) (50 mg, 0.2 mmol, 1.0 equiv.) was added and the reaction stirred for 18 h. The solvent was partially removed, layered with hexane and stored at $-40\text{ }^{\circ}\text{C}$ to give colourless crystals. The remaining solvent was removed and the crystals washed with cold hexane (3 x 2 ml). Drying in vacuum affords the desired product as an off-white solid. Yield: 44 mg, 0.05 mmol, 23%. **^1H NMR** (500 MHz, CD_2Cl_2 , 298 K) δ /ppm: 7.52 – 7.22 (m, 9H, Ar-H), 7.06 (d, $^3J_{\text{HH}} = 7.4$ Hz, 1H, Ar-H), 5.00 (d, $^2J_{\text{HH}} = 2.4$ Hz, 1H, = CH_2), 4.72 (s, 1H, CH), 4.64 (d, $^2J_{\text{HH}} = 2.4$ Hz, 1H, = CH_2), 2.17 (t, $^3J_{\text{HH}} = 6.8$ Hz, 2H, CH_2), 1.46 (pent., $^3J_{\text{HH}} = 7.3$ Hz, 2H, CH_2), 1.15 (sext., $^3J_{\text{HH}} = 7.3$ Hz, 2H, CH_2), 0.81 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H, CH_3). **^{13}C NMR** (126 MHz, CD_2Cl_2 , 298 K) δ /ppm: 158.0 (s), 157.2 (s), 138.9 (s), 138.8 (s), 130.5 (s), 130.0 (s), 129.7 (s), 129.5 (s), 128.9 (s), 126.8 (s), 126.5 (s), 118.3 (s), 99.6 (s), 46.4 (s), 43.4 (s), 32.3 (s), 21.9 (s), 14.0 (s). Note: Partial spectrum, Carbon resonances of C_6F_5 -groups unobserved due to extensive line broadening due to C–F coupling. **^{11}B NMR** (160 MHz, CD_2Cl_2 , 298 K) δ /ppm: 2.0 (br. s). **^{19}F NMR** (282 MHz, CD_2Cl_2 , 298 K) δ /ppm: -131.8 (s, 2F, o-F), -134.5 (d, $^3J_{\text{FF}} = 23.7$ Hz, 1F, o-F), -136.1 – -136.2 (m, 3F, o-F), -154.0 (t, $^3J_{\text{FF}} = 21.2$ Hz, 1F, p-F), -158.4 (t, $^3J_{\text{FF}} = 20.2$ Hz, 1F, p-F), -158.9 (t, $^3J_{\text{FF}} = 20.2$ Hz, 1F, p-F), -161.1 (td, $^3J_{\text{FF}} = 22.5$ Hz, $^4J_{\text{FF}} = 6.2$ Hz, 1F,

m-F), -161.3 (td, $^3J_{FF} = 22.5$ Hz, $^4J_{FF} = 6.2$ Hz, 1F, *m*-F), -164.0 (dt, $^3J_{FF} = 22.2$ Hz, $^4J_{FF} = 8.4$ Hz, 2F, *m*-F), -165.7 (td, $^3J_{FF} = 22.2$ Hz, $^4J_{FF} = 8.2$ Hz, 2F, *m*-F). **Elemental analysis** (%) calculated for C₄₀H₂₂BF₁₅I₂NO₂: C 49.46, H 2.28, N 1.44, found: C 49.36, H 2.31, N 1.49.



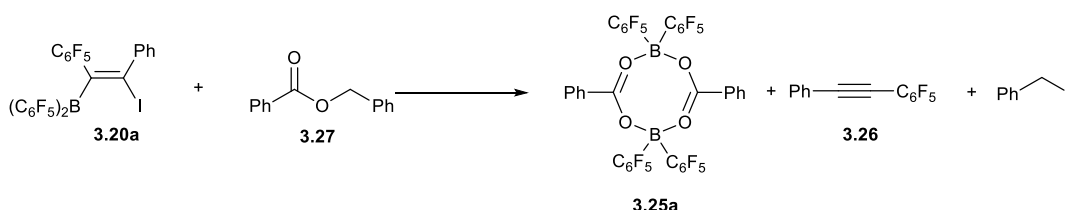
3.24: B(C₆F₅)₃ (102 mg, 0.2 mmol, 1.0 equiv.) was dissolved in CH₂Cl₂ (5 ml) and (iodoethynyl)benzene (46 mg, 0.2 mmol, 1.0 equiv.) added at room temperature. After 10 min but-3-yn-2-yl benzoate (**3.22e**) (34 mg, 0.2 mmol, 1.0 equiv.) was added and the reaction stirred for 18 h. The solvent was partially removed, layered with hexane and stored at -40 °C to give a few colourless crystals which could be characterised by X-ray diffraction.

Reactions of methylene propargyl esters **3.22a–d** with vinyl borane **3.20a**



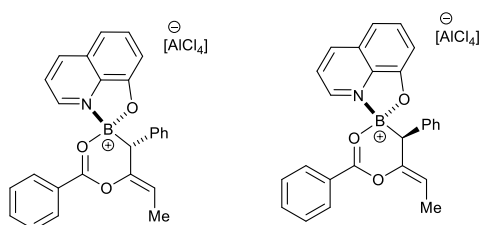
General Procedure 9: B(C₆F₅)₃ (51 mg, 0.1 mmol, 1.0 equiv.) was dissolved in CH₂Cl₂ (0.6 ml) and (iodoethynyl)benzene (23 mg, 0.1 mmol, 1.0 equiv.) added at room temperature. After 10 min the propargyl ester **3.22a–d** (0.1 mmol, 1.0 equiv.) was added and the reaction stirred for up to 7 days. A mixture of products were produced as observed by *in situ* NMR spectroscopic experiments, however *o*-, *p*-, *m*-fluorine atoms of Ph-C≡C-C₆F₅ were clearly visible. The solvent was partially removed, layered with pentane and stored at -20 °C to give a very small crop of colourless crystals of the bis(perfluorophenyl)boranyl ester **3.25** and/or (perfluorophenylethynyl)benzene **3.26** suitable for X-ray diffraction.

Reaction of benzyl benzoate with **3.20a**

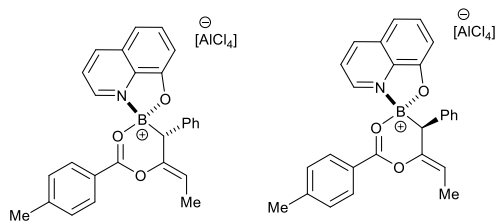


B(C₆F₅)₃ (51 mg, 0.1 mmol) was added to (iodoethynyl)benzene **3.20a'** (46 mg, 0.1 mmol) in CDCl₃ (0.5 ml) and left at ambient temperature for 10 minutes. Benzyl

benzoate (21 mg, 0.1 mmol) was then added with the mixture then being transferred to an NMR tube. Multinuclear NMR spectroscopy (^1H , ^{11}B and ^{19}F) was conducted *in situ* over the course of 5 days.



3.28a: To a solution of **3.21** (40 mg, 0.1 mmol, 1 equiv.) in CD_2Cl_2 (0.6 ml) in CD_2Cl_2 (0.6 ml) but-3-yn-2-ylbenzoate **3.22e** (17 mg, 0.10 mmol, 1.0 equiv.) was added upon which after 40 h at room temperature a diastereomer mixture of **3.28a** and **3.28a'** is generated (based on *in situ* monitoring by NMR). The remaining solution was removed under reduced vacuum and the residue washed with cold hexane (3 x 2 ml) and dried *in vacuo* to give the desired product as yellow solid. Conversion calculated using *in situ* ratio between integral of starting material and combined diastereoisomers. Diastereoisomers of **3.28a** formed in approximately a 5:1 ratio with the major diastereoisomer being reported. Conversion: 75%. $^1\text{H NMR}$ (500 MHz, CDCl_3 , 298 K) δ /ppm: 9.29 (d, $^3J_{\text{HH}} = 5.0$ Hz, 1H, Ar-H), 8.74 (d, $^3J_{\text{HH}} = 8.0$ Hz, 1H, Ar-H), 8.26 (dd, $^3J_{\text{HH}} = 9.6$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 2H, Ar-H), 8.08 – 8.05 (m, 1H, Ar-H), 7.86 (tt, $^3J_{\text{HH}} = 7.4$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 1H, Ar-H), 7.73 (t, $^3J_{\text{HH}} = 7.6$ Hz, 1H, Ar-H), 7.60 (t, $^3J_{\text{HH}} = 7.6$ Hz, 2H, Ar-H), 7.44 (t, $^3J_{\text{HH}} = 7.9$ Hz, 1H, Ar-H), 7.35 (d, $^3J_{\text{HH}} = 7.1$ Hz, 2H, Ar-H), 7.30 (d, $^3J_{\text{HH}} = 7.6$ Hz, 1H, Ar-H), 7.15 (t, $^3J_{\text{HH}} = 7.7$ Hz, 2H, Ar-H), 7.07 (t, $^3J_{\text{HH}} = 7.1$ Hz, 1H, Ar-H), 5.20 (qd, $^3J_{\text{HH}} = 7.1$ Hz, $^4J_{\text{HH}} = 2.2$ Hz, 1H, =CH), 4.01 (br. t, $^4J_{\text{HH}} = 2.2$ Hz, 1H, BCH), 2.0 (dd, $^3J_{\text{HH}} = 7.1$ Hz, $^4J_{\text{HH}} = 2.4$ Hz, 3H, =CMe). $^{11}\text{B NMR}$ (160 MHz, CD_2Cl_2 , 298 K) δ /ppm: 10.1 (br. s). $^{27}\text{Al NMR}$ (104 MHz, CDCl_3 , 298 K) δ /ppm: 104.0 (s, AlCl_4). **Elemental analysis** (%) calculated for $\text{C}_{26}\text{H}_{21}\text{AlBCl}_4\text{NO}_3$: C 54.31, H 3.68, N 2.44, found C 54.13, H 3.72, N 2.36.



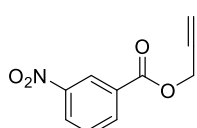
3.28b: To a solution of **3.21** (40 mg, 0.1 mmol, 1 equiv.) in CD_2Cl_2 (0.6 ml) but-3-yn-2-yl 4-methylbenzoate **3.22f** (18.8 mg, 0.10 mmol, 1.0 equiv.) was added upon which after 40 h at room temperature a diastereomer mixture of **3.28a** and **3.28a'** is generated (based on *in situ* monitoring by NMR). The solvent was partially removed to give a saturated solution which was layered with pentane. Crystals of diastereoisomer **3.28a** were formed from the solution at -20 °C. The remaining solution was removed and the crystals washed with cold pentane (3 x 2 ml) and dried *in vacuo* to give the desired product a yellow

crystalline solid. Conversion calculated using *in situ* ratio of integrals of starting material and combined diastereoisomers. Conversion calculated using *in situ* ratio between integral of starting material and combined diastereoisomers. Diastereoisomers of **3.28b** formed in approximately a 5:1 ratio with the major diastereoisomer being reported. Conversion: 49%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 9.29 (d, ³J_{HH} = 5.0 Hz, 1H, Ar-H), 8.73 (d, ³J_{HH} = 8.0 Hz, 1H, Ar-H), 8.15 (d, ³J_{HH} = 8.4 Hz, 2H, Ar-H), 7.72 (m, 2H, Ar-H), 7.52 (d, ³J_{HH} = 8.2 Hz, 1H, Ar-H), 7.39 (d, ³J_{HH} = 8.1 Hz, 2H, Ar-H), 7.34 (d, ³J_{HH} = 7.1 Hz, 2H, Ar-H), 7.29 (d, ³J_{HH} = 7.3 Hz, 2H, Ar-H), 7.15 (t, ³J_{HH} = 7.4 Hz, 2H, Ar-H), 5.18 (qd, ³J_{HH} = 7.1 Hz, ⁴J_{HH} = 2.2 Hz, 1H, =CH), 4.01 (br. t, ⁴J_{HH} = ~2 Hz, 1H, BCH), 2.49 (s, 3H, Ph-Me), 1.98 (dd, ³J_{HH} = 7.1 Hz, ⁴J_{HH} = 2.3 Hz, 3H, =CMe). **¹¹B NMR** (160 MHz, CD₂Cl₂, 298 K) δ/ppm: 10.4 (br. s). **²⁷Al NMR** (104 MHz, CDCl₃, 298 K) δ/ppm: 104.0 (s, AlCl₄). **Elemental analysis** (%) calculated for C₂₇H₂₃AlBCl₄NO₃: C 55.05, H 3.94, N: 2.38, found: C 54.87, H 4.06, N 2.52.

6.3.3 Divergent Elementoboration using Heteroleptic Boranes in the Propargyl Rearrangement

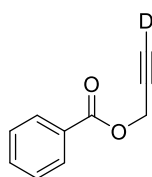
6.3.3.1 Synthesis of Starting Materials

General Procedure 10: Synthesised using a procedure similar to that reported by Stephan *et al.*^[20] The acyl chloride (15 mmol, 1.2 equiv.) and triethylamine (TEA) (3.5 ml, 25 mmol, 2 equiv.) were dissolved in 50 ml CH₂Cl₂ and cooled to 0 °C. Propargyl alcohol (0.73 ml, 12.5 mmol, 1 equiv.) or 2-methylbut-3-yn-2-ol (1.21 ml, 12.5 mmol, 1 equiv.) was added dropwise at this temperature and the mixture stirred at room temperature for 10 h. The resulting solution was washed with 100 ml H₂O with the aqueous phase being extracted with CH₂Cl₂ (3 x 50 ml). The combined organic fractions were washed with saturated NaCl solution (100 ml) and dried over MgSO₄ with the volatiles being removed *in vacuo*. The crude product was purified by either recrystallisation or column chromatography.

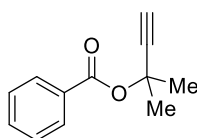


3.29d: Synthesised according to *General Procedure 10* using *m*-nitrobenzoyl chloride (2.78 g, 15 mmol, 1.2 equiv.). Yield: 1.67 g, 8.13 mmol, 65%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 8.90 (dd, ⁴J_{HH} = 2.9, ⁴J_{HH} = 1.1 Hz, 1H, Ar-H), 8.45 (ddd, ³J_{HH} = 8.2, ⁴J_{HH} = 2.3, ⁴J_{HH} = 1.1 Hz, 1H, Ar-H), 8.43 – 8.38 (m, 1H, Ar-H), 7.72 – 7.65 (m, 1H, Ar-H), 4.99 (d, ⁴J_{HH} = 2.5 Hz, 2H, CH₂), 2.57 (t, ⁴J_{HH} = 2.5 Hz, 1H, ≡CH). **¹³C NMR** (101 MHz, CDCl₃, 298 K)

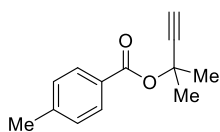
δ /ppm: 163.9 (s), 148.4 (s), 135.6 (s), 131.3 (s), 129.9 (s), 127.9 (s), 125.0 (s), 77.1 (s), 75.9 (s), 53.4 (s).



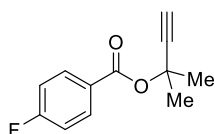
3.29a^D: Synthesised using similar methods to that reported in the literature^[77] whereby the proto-derivative **3.29a** (0.336 g, 2.1 mmol) was dissolved in D₂O at which point the WA30 resin (38 mg) was added and stirred under ambient conditions for 18 h. At this point the resin was filtered off, and the filtrate was extracted with Et₂O (10 ml). This was washed with water (10 ml) with the aqueous phase being extracted with Et₂O (3 x 10 ml). The combined organic phases were dried over MgSO₄ with the volatiles then being removed *in vacuo* to give the pure deuterated compound. The ¹H and ¹³C NMR data agree with the literature reported values.^[77] Yield: 0.267 g, 1.87 mmol, 88%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 8.02 – 7.97 (m, 2H, Ar-H), 7.53 – 7.48 (m, 1H, Ar-H), 7.40 – 7.34 (m, 2H, Ar-H), 4.85 (s, 2H, CH₂). **²H NMR** (61 MHz, CDCl₃, 298 K) δ /ppm: 2.53 (s, 1H, \equiv CD). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 165.9 (s), 133.5 (s), 130.0 (s), 129.5 (s), 128.6 (s), 77.5 (s), 74.9 (t, ¹J_{CD} = 38.9 Hz), 52.6 (s).



3.30a: Synthesised according to *General Procedure 10* using benzoyl chloride (1.74 ml, 15 mmol, 1.2 equiv.). Yield: 0.352 g, 1.89 mmol, 15%. Spectroscopic data agrees with literature known values.^[169] **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 8.05 – 8.01 (m, 1H, Ar-H), 7.57 – 7.52 (m, 1H, Ar-H), 7.46 – 7.40 (m, 1H, Ar-H), 2.59 (s, 1H, \equiv CH), 1.82 (s, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 165.0 (s), 133.1 (s), 130.9 (s), 129.8 (s), 128.4 (s), 84.8 (s), 72.7 (s), 72.4 (s), 29.2 (s).



3.30b: Synthesised according to *General Procedure 10* using 4-toluoyl chloride (1.98 ml, 15 mmol, 1.2 equiv.). Yield: 1.31 g, 6.5 mmol, 52%. Spectroscopic data agrees with literature known values.^[20] **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 7.90 (d, ³J_{HH} = 8.2 Hz, 1H, Ar-H), 7.21 (d, ³J_{HH} = 8.1 Hz, 2H, Ar-H), 2.57 (s, 1H, \equiv CH), 2.38 (s, 3H, Ar-CH₃), 1.80 (s, 6H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 164.0 (s), 142.6 (s), 128.7 (s), 128.0 (s), 127.1 (s), 83.9 (s), 71.5 (s), 71.0 (s), 28.1 (s), 20.7 (s).



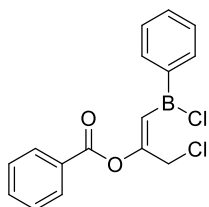
3.30c: Synthesised according to *General Procedure 10* using 4-fluorobenzoyl chloride (1.77 ml, 15 mmol, 1.2 equiv.). Yield: 1.78 g, 8.62 mmol, 69%. **¹H NMR** (400 MHz, CDCl₃, 298 K) 8.05 – 8.01 (m, 2H, Ar-H), 7.11 – 7.06 (m, 2H, Ar-H), 2.59 (s, 1H, \equiv CH), 1.81

(s, 6H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) 165.8 (d, ¹J_{CF} = 253.7 Hz), 164.0 (s), 132.3 (d, ³J_{CF} = 9.3 Hz), 127.1 (d, ⁴J_{CF} = 3.0 Hz), 115.5 (d, ²J_{CF} = 22.0 Hz), 84.7 (s), 72.8 (s), 72.5 (s), 29.1 (s). **¹⁹F NMR** (376 MHz, CDCl₃, 298 K) δ/ppm: -105.8 (s).

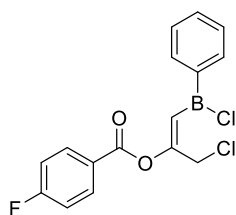
6.3.3.2 Synthesis of Products

General Procedure 11: Terminal alkyne **3.29** (0.2 mmol, 1 equiv.) was added to PhBCl₂ (32 mg, 0.2 mmol, 1 equiv.) in CDCl₃ (0.5 ml) in an NMR tube, with the progress being monitored *via in situ* multinuclear NMR spectroscopy. Connectivity was confirmed through HSQC and HMBC spectroscopy due to difficulty in obtaining HRMS or elemental analysis in spite of repeated attempts. In addition other spectroscopic data such as IR were inaccessible due to stability issues.

General Procedure 12: Terminal alkyne **3.30** (0.2 mmol, 1 equiv.) was added to PhBCl₂ (32 mg, 0.2 mmol, 1 equiv.) in CDCl₃ (0.5 ml) in an NMR tube, with the progress being monitored *via in situ* multinuclear NMR spectroscopy. At the point the reaction was complete, the solvents were removed *in vacuo* with the residue being washed with cold hexane (3 x 1 ml). This was then dissolved in a CH₂Cl₂/hexane solution and stored at -40 °C overnight to yield a crop of white crystals suitable for X-ray diffraction. The solid was isolated and dried to yield the pure product as a white solid.

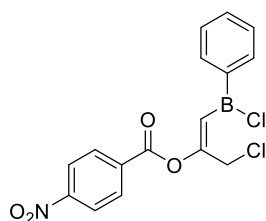


3.31a: Synthesised according to *General Procedure 11* using **3.29a** (37 mg, 0.2 mmol). Conversion: 94%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 8.12 – 8.00 (m, 3H, Ar-H), 7.59 – 7.51 (m, 2H, Ar-H), 7.46 – 7.36 (m, 5H, Ar-H), 6.44 (s, 1H, =CH), 4.55 (s, 2H, CH₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 164.3 (s), 160.0 (s), 137.2 (s), 136.6 (s), 134.7 (s), 134.1 (s), 130.4 (s), 128.8 (s), 128.4 (s), 128.0 (s), 119.1 (br. s), 41.8 (s). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 59.0 (br. s).

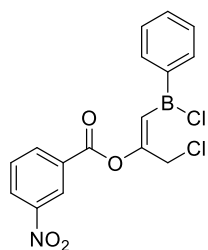


3.31b: Synthesised according to *General Procedure 11* using **3.29b** (41 mg, 0.2 mmol). Conversion: 92%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 8.11 – 8.06 (m, 2H, Ar-H), 8.02 – 7.99 (m, 2H, Ar-H), 7.55 – 7.50 (m, 1H, Ar-H), 7.41 – 7.36 (m, 2H, Ar-H), 7.11 – 7.06 (m, 2H, Ar-H), 6.42 (s, 1H, =CH), 4.53 (s, 2H, CH₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 166.5 (d, ¹J_{CF} = 255.9 Hz), 163.3 (s), 159.7 (s), 136.9 (s), 136.6 (s), 134.7 (s), 133.1 (d, ³J_{CF} = 9.6 Hz), 128.4 (s), 125.3 (d, ⁴J_{CF} =

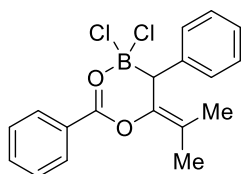
3.0 Hz), 116.1 (d, $^2J_{CF} = 22.1$ Hz), 41.8 (s). ^{19}F NMR (376 MHz, CDCl_3 , 298 K) δ/ppm : -103.5 (s). ^{11}B NMR (128 MHz, CDCl_3 , 298 K) δ/ppm : 59.33 (br. s).



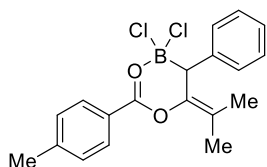
3.31c: Synthesised according to *General Procedure 11* using **3.29c** (47 mg, 0.2 mmol). Conversion: 87%. ^1H NMR (400 MHz, CDCl_3 , 298 K) δ/ppm : 8.27 – 8.25 (m, 4H, Ar-H), 8.12 – 8.10 (m, Hz, 2H, Ar-H), 7.67 – 7.63 (m, 1H, Ar-H), 7.53 – 7.48 (m, 2H, Ar-H), 6.55 (s, 1H, =CH), 4.63 (s, 2H, CH_2). ^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ/ppm : 162.4 (s), 158.7 (s), 151.1 (s), 136.6 (s), 134.9 (s), 131.5 (s), 128.4 (s), 123.9 (s), 119.6 (s), 41.6 (s). ^{11}B NMR (128 MHz, CDCl_3 , 298 K) δ/ppm : 59.9 (br. s).



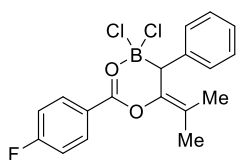
3.31d: Synthesised according to *General Procedure 11* using **3.29d** (47 mg, 0.2 mmol). Conversion: 89%. ^1H NMR (400 MHz, CDCl_3 , 298 K) δ/ppm : 9.03 – 8.94 (m, 1H, Ar-H), 8.52 – 8.48 (m, 2H, Ar-H), 8.14 – 8.10 (m, 2H, Ar-H), 7.77 – 7.73 (m, 1H, Ar-H), 7.68 – 7.63 (m, 1H, Ar-H), 7.54 – 7.49 (m, 2H, Ar-H), 6.55 (s, 1H, =CH), 4.65 (s, 2H, CH_2). ^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ/ppm : 162.2 (s), 158.8 (s), 148.5 (s), 137.0 (s), 136.7 (s), 135.9 (s), 134.9 (s), 130.8 (s), 130.2 (s), 128.5 (s), 128.3 (s), 125.3 (s), 119.7 (s), 41.6 (s). ^{11}B NMR (128 MHz, CDCl_3 , 298 K) δ/ppm : 60.0 (br. s).



3.32a: Synthesised according to *General Procedure 12* using **3.30a** (37 mg, 0.2 mmol, 1 equiv.). Yield: 57 mg, 0.16 mmol, 82%. ^1H NMR (400 MHz, CDCl_3 , 298 K) δ/ppm : 8.23 (d, $^3J_{\text{HH}} = 7.5$ Hz, 2H, Ar-H), 7.79 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H, Ar-H), 7.56 (t, $^3J_{\text{HH}} = 7.9$ Hz, 2H, Ar-H), 7.13 (t, $^3J_{\text{HH}} = 7.5$, 2H, Ar-H), 7.06 (t, $^3J_{\text{HH}} = 7.3$ Hz, 1H, Ar-H), 6.98 (d, $^3J_{\text{HH}} = 7.4$ Hz, 2H, Ar-H), 3.84 (s, 1H, CH), 1.97 (s, 3H, CH_3), 1.78 (s, 3H, CH_3). ^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ/ppm : 171.4 (s), 147.8 (s), 141.1 (s), 138.1 (s), 131.6 (s), 129.8 (s), 128.4 (s), 127.5 (s), 125.9 (s), 124.7 (s), 122.5 (s), 39.51 (br. s), 18.7 (s), 17.7 (s). ^{11}B NMR (128 MHz, CDCl_3 , 298 K) δ/ppm : 8.7 (s). IR ν_{max} (cm^{-1}): 3201 (w), 2993 (w), 2916 (w), 1689 (m), 1597 (m), 1535 (s), 1496 (m), 1450 (m), 1404 (s), 1311 (m), 1242 (m), 1180 (s), 1056 (m), 1026 (w), 987 (w), 933 (w), 879 (w), 833 (w), 802 (m), 740 (s), 694 (s).



3.32b: Synthesised according to *General Procedure 12* using **3.30b** (40 mg, 0.2 mmol, 1 equiv.). Yield: 67 mg, 0.17 mmol, 87%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 8.20 (d, ³J_{HH} = 8.3 Hz, 2H, Ar-H), 7.44 (d, ³J_{HH} = 8.1 Hz, 2H, Ar-H), 7.21 (t, ³J_{HH} = 7.5 Hz, 2H, Ar-H), 7.14 (t, ³J_{HH} = 7.3 Hz, 1H, Ar-H), 7.06 (d, ³J_{HH} = 7.4 Hz, 2H, Ar-H), 3.90 (s, 1H, CH), 2.53 (s, 3H, Ar-CH₃), 2.03 (s, 3H, CH₃), 1.86 (s, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 171.3 (s), 150.4 (s), 147.6 (s), 141.2 (s), 131.7 (s), 130.6 (s), 128.4 (s), 127.5 (s), 125.9 (s), 122.0 (s), 121.8 (s), 39.6 (br. s), 22.5 (s), 18.6 (s), 17.7 (s). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 8.64 (s). **IR** ν_{max} (cm⁻¹): 2160 (w), 1666 (w), 1605 (w), 1581 (w), 1527 (s), 1504 (m), 1412 (s), 1296 (m), 1249 (m), 1172 (m), 1134 (m), 1080 (m), 1049 (m), 972 (w), 933 (w), 910 (w), 879 (w), 833 (m), 763 (s), 740 (s), 648 (m).



3.32c: Synthesised according to *General Procedure 12* using **3.30c** (41 mg, 0.2 mmol, 1 equiv.). Yield: 58 mg, 0.16 mmol, 79%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 8.37 – 8.34 (m, 2H, Ar-H), 7.33 (t, ³J_{HF} = 8.5 Hz, 2H, Ar-H), 7.22 (t, ³J_{HH} = 7.4 Hz, 2H, Ar-H), 7.15 (t, ³J_{HH} = 7.3 Hz, 1H, Ar-H), 7.05 (d, ³J_{HH} = 7.3 Hz, 1H, Ar-H), 3.91 (s, 1H, Ar-H), 2.03 (s, 3H, CH₃), 1.86 (s, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 170.3, (s), 168.9 (d, ¹J_{CF} = 264.1 Hz), 147.9 (s), 140.9 (s), 134.8 (d, ³J_{CF} = 10.6 Hz), 128.5 (s), 127.5 (s), 126.0 (s), 122.6 (s), 121.0 (d, ⁴J_{CF} = 2.7 Hz), 117.6 (d, ²J_{CF} = 22.6 Hz), 39.6 (br. s), 18.7 (s), 17.7 (s). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 8.8 (s). **¹⁹F NMR** (376 MHz, CDCl₃, 298 K) δ/ppm: -94.5 (dt, ³J_{HF} = 8.5 Hz, ⁴J_{HF} = 5.4 Hz, 1F, *p*-F). **IR** ν_{max} (cm⁻¹): 3201 (w), 3086 (w), 2916 (w), 1697 (w), 1597 (m), 1535 (m), 1504 (m), 1404 (s), 1311 (m), 1242 (s), 1157 (s), 1049 (m), 972 (w), 933 (w), 910 (w), 879 (w), 833 (m), 763 (s), 725 (s), 695 (s), 648 (m).

6.3.4 Crystallographic Studies

Crystallographic studies were undertaken on single crystal mounted in paratone and studied on an Agilent SuperNova Dual three-circle diffractometer using Cu-Kα or Mo-Kα radiation and a CCD detector. Measurements were typically made at 150(1) K with temperatures maintained using an Oxford cryostream. Data were collected and integrated and data corrected for absorption using a numerical absorption correction based on gaussian integration over a multifaceted crystal model within CrysAlisPro.^[156] The structures were solved by direct methods and refined against *F*² within SHELXL-2013.^[170] The structures have been deposited with the Cambridge

Structural Database (CCDC deposition numbers 1413179-1413189, 1429175, 1475828-1475835, 147641715-1476417, 1582714-1582717).

Table 6.3.1 Crystallographic data for compounds **3.3–3.32**.

Compound	3.3a	3.3b	3.4c	3.4d
Empirical Formula	C _{36.5} H ₁₉ BF ₁₅ NO ₃	C _{32.5} H ₁₇ BF ₁₅ NO	C ₃₆ H ₁₈ BF ₁₅ N ₂ O ₃	C ₃₁ H ₁₇ BF ₁₅ NO
Crystal System	Triclinic	Triclinic	Monoclinic	Monoclinic
Space Group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	10.1170(3)	9.7542(3)	14.4138(10)	11.92043(19)
<i>b</i> /Å	11.1727(3)	12.6233(4)	12.2486(7)	11.60613(16)
<i>c</i> /Å	15.4493(4)	13.5710(5)	20.8864(15)	21.1674(3)
α /°	85.231(2)	69.527(3)	90	90
β /°	81.224(2)	78.068(3)	110.078(8)	105.0293(15)
γ /°	88.399(3)	85.081(3)	90	90
<i>V</i> /Å ³	1719.66(9)	1531.47(9)	3463.4(4)	2828.33(7)
<i>Z</i>	2	2	4	4
<i>T</i> /K	150(2)	150(2)	150(2)	150(2)
<i>D</i> _c /g.cm ⁻³	1.575	1.590	1.623	1.680
Crystal size/mm	0.200 x 0.100 x 0.050	0.200 x 0.100 x 0.050	0.558 x 0.386 x 0.030	0.370 x 0.150 x 0.100
Total data	12184	10274	10549	10705
Unique data	6754	6006	5514	5571
<i>R</i> _{int}	0.0189	0.0157	0.0457	0.0234
<i>R</i> ₁ [<i>F</i> ² >2 σ(<i>F</i> ²)]	0.0379	0.0358	0.0436	0.0347
w <i>R</i> ₂ (all data)	0.0976	0.0913	0.1075	0.0934
GoF	1.026	0.965	1.045	1.035
$\rho_{\min}/\rho_{\max}/\text{e}\text{\AA}^{-3}$	-0.385/0.514	-0.294/0.232	-0.316/0.314	-0.307/0.306
CCDC code	1413182	1413181	1413189	1413183

Compound	3.6a	3.6b	3.8a	3.8c
Empirical Formula	C ₂₅ H ₈ BF ₁₅ N ₂ O	C _{30.5} H ₁₅ BCl ₃ F ₁₅ N ₂ O	C ₂₈ H ₁₇ BF ₁₅ NO ₂	C ₄₁ H ₂₁ BF ₁₅ NO ₂
Crystal System	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	9.2926(2)	12.6397(5)	8.3006(6)	13.4550(5)
<i>b</i> /Å	10.8449(3)	12.0585(4)	12.1237(8)	12.8454(4)
<i>c</i> /Å	24.2433(7)	21.4952(7)	14.8933(10)	21.5470(7)
α /°	90	90	99.1451(17)	90
β /°	99.850(3)	105.440(4)	98.9427(16)	106.721(4)
γ /°	90	90	107.2389(16)	90
<i>V</i> /Å ³	2407.17(12)	3158.0(2)	1380.26(16)	3566.6(2)
<i>Z</i>	4	4	2	4
<i>T</i> /K	150(2)	150(2)	200(2)	151(2)
<i>D</i> _c /g.cm ⁻³	1.788	1.741	1.673	1.593
Crystal size/mm	0.250 x 0.060 x 0.040	0.160 x 0.160 x 0.030	0.130 x 0.080 x 0.040	0.250 x 0.180 x 0.090
Total data	8952	20172	13263	20811
Unique data	4723	7650	4928	8638
<i>R</i> _{int}	0.0357	0.0440	0.0979	0.0365
<i>R</i> ₁ [<i>F</i> ² >2 σ(<i>F</i> ²)]	0.0477	0.0664	0.0468	0.0574
w <i>R</i> ₂ (all data)	0.1423	0.1889	0.1200	0.1600
GoF	1.035	1.026	1.063	1.071
$\rho_{\min}/\rho_{\max}/\text{e}\text{\AA}^{-3}$	-0.262/0.440	-1.285/0.667	-0.312/0.287	-0.312/0.385
CCDC code	1413184	1413188	1413180	1413186

Compound	3.22 major	3.23a	3.23b	3.23c
Empirical Formula	C ₃₂ H ₂₁ BF ₁₀ O ₂	C ₃₅ H ₁₉ BF ₁₅ I ₂ O ₂	C ₃₈ H ₁₇ BF ₁₅ I ₂ O ₂	C _{37.25} H ₂₄ BF ₁₅ I ₂ O ₂
Crystal System	Triclinic	Monoclinic	Monoclinic	Triclinic
Space Group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1
<i>a</i> /Å	10.0350(10)	18.1962(7)	11.5090(4)	9.1636(7)
<i>b</i> /Å	12.4428(12)	18.0826(7)	18.3922(9)	18.4314(14)
<i>c</i> /Å	13.2197(13)	21.6291(11)	16.6568(6)	22.5357(16)
α /°	70.067(2)	90	90	79.537(2)
β /°	68.606(3)	103.640(5)	95.446(3)	78.435(2)
γ /°	73.250(2)	90	90	89.862(5)
<i>V</i> /Å ³	1419.3(2)	6916.0(5)	3509.9(3)	3664.7(5)
<i>Z</i>	2	8	4	4
<i>T</i> /K	200(2)	150(2)	150(2)	200(2)
<i>D</i> _c /g.cm ⁻³	1419.3(2)	1.718	1.757	1.679
Crystal size/mm	0.170 x 0.110 x 0.100	0.259 x 0.177 x 0.137	0.368 x 0.197 x 0.051	0.260 x 0.050 x 0.030
Total data	4991	31196	19770	33796
Unique data	4991	12137	8421	12051
<i>R</i> _{int}	0.0478	0.0773	0.0451	0.1300
<i>R</i> ₁ [<i>F</i> ² >2 σ(<i>F</i> ²)]	0.0575	0.0771	0.0359	0.0613
w <i>R</i> ₂ (all data)	0.1387	0.2067	0.0876	0.1543
GoF	1.108	1.069	1.024	1.016
$\rho_{\min}/\rho_{\max}/\text{e}\text{\AA}^{-3}$	-0.236/0.214	-0.763/1.957	-0.617/0.494	-0.588/0.727
CCDC code	1476417	1475828	1475829	1476415

Compound	3.9b	3.9c	3.11	3.13
Empirical Formula	C ₂₉ H ₁₉ BF ₁₅ NO ₂	C ₃₄ H ₁₃ BF ₁₅ NO ₂	C ₂₂ H ₅ BF ₁₅ NO ₂	C ₂₆ H ₁₂ BF ₁₅ O ₃
Crystal System	Triclinic	Monoclinic	Triclinic	Triclinic
Space Group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	9.254(3)	8.7141(5)	8.2180(5)	9.6463(4)
<i>b</i> /Å	11.596(4)	31.5529(12)	10.6283(8)	12.1922(5)
<i>c</i> /Å	14.792(6)	11.7474(5)	13.5393(7)	12.2500(5)
α /°	102.195(8)	90	92.431(5)	96.542(3)
β /°	93.271(9)	109.032(5)	100.822(5)	91.236(3)
γ /°	108.528(8)	90	108.692(6)	97.100(3)
<i>V</i> /Å ³	1457.9(9)	3053.4(3)	1093.56(12)	1419.43(10)
<i>Z</i>	2	4	2	2
<i>T</i> /K	200(2)	150(2)	150(2)	150(2)
<i>D</i> _c /g.cm ⁻³	1.616	1.660	1.856	1.563
Crystal size/mm	0.150 x 0.150 x 0.150	0.300 x 0.180 x 0.110	0.290 x 0.160 x 0.030	0.308 x 0.213 x 0.079
Total data	8328	16328	9676	13642
Unique data	4035	7195	5157	6742
<i>R</i> _{int}	0.1076	0.0581	0.0635	0.0378
<i>R</i> ₁ [<i>F</i> ² >2 σ(<i>F</i> ²)]	0.0632	0.0511	0.0545	0.0452
w <i>R</i> ₂ (all data)	0.1222	0.1134	0.1366	0.1170
GoF	1.019	1.031	1.043	0.991
$\rho_{\min}/\rho_{\max}/\text{e}\text{\AA}^{-3}$	-0.247/0.230	-0.237/0.299	-0.327/0.484	-0.250/0.301
CCDC code	1413179	1413185	1413187	1429175

Compound	3.25b	3.26	3.28b	3.31d
Empirical Formula	C ₃₈ H ₁₀ B ₂ F ₂₀ O ₄	C ₁₄ H ₅ F ₅	C _{28.50} H ₂₆ AlBCl ₇ NO ₃	C ₁₆ H ₁₂ BCl ₂ NO ₄
Crystal System	Monoclinic	Triclinic	Triclinic	Triclinic
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	11.7827(5)	6.1216(7)	9.6723(7)	7.1918(4)
<i>b</i> /Å	25.3378(13)	7.2354(5)	12.0596(10)	10.3441(6)
<i>c</i> /Å	12.0166(5)	12.7503(10)	16.3280(12)	13.0804(7)
α /°	90	85.263(6)	89.278(2)	96.791(4)
β /°	102.193(4)	84.938(9)	74.351(2)	100.323(5)
γ /°	90	85.921(8)	66.729(2)	92.295(4)
<i>V</i> /Å ³	3506.6(3)	559.45(9)	1675.2(2)	948.75(9)
<i>Z</i>	4	2	2	2
<i>T</i> /K	150(2)	150(2)	200(2)	150(2)
<i>D</i> _c /g.cm ⁻³	1.766	1.592	1.420	1.274
Crystal size/mm	0.385 x 0.311 x 0.104	0.353 x 0.094 x 0.079	0.120 x 0.110 x 0.090	0.413 x 0.324 x 0.274
Total data	18566	4678	14673	6804
Unique data	8387	2563	5144	4012
<i>R</i> _{int}	0.0555	0.0806	0.0797	0.0401
<i>R</i> ₁ [<i>F</i> ² >2 σ(<i>F</i> ²)]	0.0526	0.0594	0.0565	0.0381
w <i>R</i> 2 (all data)	0.1359	0.1747	0.1261	0.0930
GoF	1.060	1.000	1.038	1.022
$\rho_{\min}/\rho_{\max}/e\text{\AA}^{-3}$	-0.270/0.272	-0.284/0.374	-0.512/0.579	-0.291/0.266
CCDC code	1475834	1475835	1476416	1582714

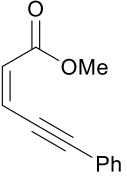
Compound	3.23e	3.23f	3.24	3.25a
Empirical Formula	C ₃₂ H ₁₃ BF ₁₅ I ₂ O ₂	C ₄₀ H ₂₂ BF ₁₅ INO ₂	C ₃₇ H ₁₅ BF ₁₅ O ₂	C ₃₉ H ₁₀ B ₂ C ₁₂ F ₂₀ N ₂ O ₈
Crystal System	Triclinic	Monoclinic	Monoclinic	Triclinic
Space Group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1
<i>a</i> /Å	9.3179(14)	9.1197(4)	11.5171(5)	11.3389(5)
<i>b</i> /Å	10.4144(4)	14.8775(8)	18.0090(9)	12.9856(6)
<i>c</i> /Å	32.2014(13)	27.7753(12)	16.5168(6)	15.3040(7)
α /°	91.978(3)	90	90	111.693(4)
β /°	93.889(7)	98.246(4)	94.905(4)	92.064(3)
γ /°	90.052(8)	90	90	102.822(4)
<i>V</i> /Å ³	3115.8(5)	3729.5(3)	3413.2(3)	2024.17(16)
<i>Z</i>	4	4	4	2
<i>T</i> /K	150(2)	150(2)	150(2)	150(2)
<i>D</i> _c /g.cm ⁻³	1.817	1.730	1.779	1.816
Crystal size/mm	0.284 x 0.138 x 0.082	0.291 x 0.055 x 0.042	0.241 x 0.179 x 0.147	0.283 x 0.117 x 0.034
Total data	21940	17237	15712	20253
Unique data	21940	6541	6000	9562
<i>R</i> _{int}	0.0747	0.0744	0.0469	0.0568
<i>R</i> ₁ [<i>F</i> ² >2 σ(<i>F</i> ²)]	0.0563	0.0438	0.0437	0.0732
w <i>R</i> 2 (all data)	0.1528	0.0916	0.1301	0.1882
GoF	1.059	1.038	0.924	1.074
$\rho_{\min}/\rho_{\max}/e\text{\AA}^{-3}$	-1.587/1.395	-0.681/0.715	-1.098/1.236	-0.718/0.526
CCDC code	1475830	1475831	1475832	1475833

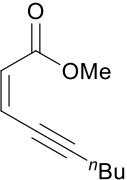
Compound	3.32a	3.32b	3.32c
Empirical Formula	C ₁₈ H ₁₇ BCl ₂ O ₂	C ₁₉ H ₁₉ BCl ₂ O ₂	C ₁₈ H ₁₆ BCl ₂ FO ₂
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	13.1814(5)	10.8458(4)	10.4734(3)
<i>b</i> /Å	8.4219(4)	13.8708(5)	14.0452(4)
<i>c</i> /Å	15.3446(8)	12.3961(5)	12.0480(4)
α /°	90	90	90
β /°	97.278(4)	103.821(4)	100.970(3)
γ /°	90	90	90
<i>V</i> /Å ³	1689.71(13)	1810.89(12)	1739.88(9)
<i>Z</i>	4	4	4
<i>T</i> /K	150(2)	150(2)	150(2)
<i>D</i> _c /g.cm ⁻³	1.364	1.324	1.393
Crystal size/mm	0.232 x 0.203 x 0.055	0.257 x 0.182 x 0.154	0.237 x 0.217 x 0.096
Total data	5940	6210	6325
Unique data	3173	3409	3073
<i>R</i> _{int}	0.0460	0.0253	0.0233
<i>R</i> ₁ [<i>F</i> ² >2 σ(<i>F</i> ²)]	0.0457	0.0336	0.0296
w <i>R</i> 2 (all data)	0.1304	0.0954	0.0787
GoF	1.043	1.033	1.045
$\rho_{\text{min}}/\rho_{\text{max}}/e\text{\AA}^{-3}$	-0.408/0.446	-0.349/0.349	-0.253/0.291
CCDC code	1582715	1582716	1582717

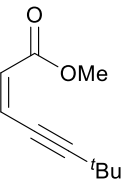
6.4 Formation of 6-Membered Heterocycles via Alkyne Activation: Carbon-Element Bond Creation through Cyclisations

6.4.1 Formation of Zwitterionic Pyrylium Borates using $B(C_6F_5)_3$.

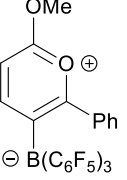
6.4.1.1 Synthesis of Starting Materials.

 **4.2a:** Synthesised using a literature known procedure.^[102] The 1H and ^{13}C NMR data agree with the literature reported values confirming the isolation of the product.^[102] **1H NMR** (500 MHz, $CDCl_3$, 298 K) δ /ppm: 7.55-7.53 (m, 2H, Ar-H), 7.35 (m, 3H, Ar-H), 6.37 (d, $^3J_{HH} = 11.4$ Hz, 1H, =CH), 6.15 (d, $^3J_{HH} = 11.4$ Hz, 1H, =CH), 3.80 (s, 3H, OCH_3). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ /ppm: 165.3 (s), 132.2 (s), 129.3 (s), 128.5 (s), 127.9 (s), 123.3 (s), 122.8 (s), 101.5 (s), 86.5 (s), 51.6 (s).

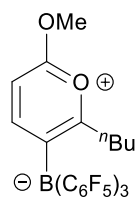
 **4.2b:** synthesised using similar methods to that reported in the literature.^[102] The 1H and ^{13}C NMR data agree with the literature reported values confirming the isolation of the product.^[102] **1H NMR** (500 MHz, $CDCl_3$, 298 K) δ /ppm: 6.16-6.13 (dt, $^3J_{HH} = 11.4$ Hz, $^4J_{HH} = 2.4$ Hz, 1H, =CH), 6.02 (d, $^3J_{HH} = 11.4$ Hz, 1H, =CH), 3.74 (s, 3H, OCH_3), 2.45 (td, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 2.4$ Hz, 2H, CH_2), 1.60-1.54 (m, 2H, CH_2), 1.49-1.43 (m, 2H, CH_2), 0.92 (t, $^3J_{HH} = 7.2$ Hz, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ /ppm: 165.5 (s), 127.1 (s), 124.3 (s), 104.5 (s), 77.8 (s), 51.4 (s), 30.6 (s), 22.1 (s), 19.9 (s), 13.7 (s).

 **4.2c:** Compound **1c** was synthesised using similar methods to that reported in the literature.^[102] The 1H NMR data agrees with the literature reported values confirming the isolation of the product.^[102] **1H NMR** (500 MHz, $CDCl_3$, 298 K) δ /ppm: 6.14 (d, $^3J_{HH} = 11.5$ Hz, 1H, =CH), 6.01 (d, $^3J_{HH} = 11.5$ Hz, 1H, =CH), 3.75 (s, 3H, OCH_3), 1.30 (s, 9H, tBu).

6.4.1.2 Synthesis of Products

 **4.3a:** (*Z*)-methyl 5-phenylpent-2-en-4-ynoate (**4.2a**) (37 mg, 0.2 mmol) was dissolved in toluene (ca. 2 ml) and was added to $B(C_6F_5)_3$ (102 mg, 0.2 mmol) to give a yellow solution. The reaction was left at room

temperature without stirring for 12 h. Slow evaporation of the solvent yielded colourless crystals of the product which could be characterised by single crystal X-ray diffraction. The remaining solvent was decanted off and the product was washed with petroleum ether (3 x 3 ml) and dried *in vacuo*. Yield: 91 mg, 0.13 mmol, 65%. Melting point: 194–198 °C. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 8.65 (br. s, 1H, pyrylium CH), 7.44–7.40 (m, 1H, Ar-H), 7.27–7.25 (m, 2H, Ar-H), 7.23–7.20 (m, 2H, Ar-H), 7.06 (d, ³J_{HH} = 9.0 Hz, 1H, pyrylium CH), 4.34 (s, 3H, CH₃). **¹³C NMR partial** (126 MHz, CDCl₃, 298 K) δ/ppm: 168.8 (s), 167.9 (s), 167.1 (s), 131.4 (s), 130.9 (s), 128.7 (s), 127.8 (s), 106.4 (s), 58.3 (s). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: -14.4. **¹⁹F NMR** (565 MHz, CDCl₃, 298 K) δ/ppm: -128.6 (d, ³J_{FF} = 20.6 Hz, 1F, *o*-F), -130.3 (br. s, 4F, *o*-F), -131.1 (d, ³J_{FF} = 20.6 Hz, 1F, *o*-F), -159.2 (t, ³J_{FF} = 20.3 Hz, 1F, *p*-F), -160.0 (t, ³J_{FF} = 20.3 Hz, 2F, *p*-F), -163.5 (br. t, 1F, ³J_{FF} = 18.8 Hz, *m*-F), -164.7 (br. t, ³J_{FF} = 18.8 Hz, 1F, *m*-F), -165.4 (t, ³J_{FF} = 18.8 Hz, 4F, *m*-F). **IR** ν_{max} (cm⁻¹): 1643, 1616, 1599, 1550, 1515, 1492, 1436, 1385, 1346, 1273, 1242, 1192, 1081, 965, 841, 833, 792, 771, 761, 703, 694, 679, 664, 640, 629. **Elemental analysis** (%) calculated for C₃₀H₁₀BF₁₅O₂: C 51.61, H 1.44, found: C 51.64 H 1.44.

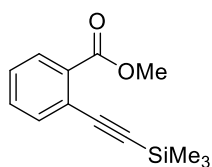


4.3b: (*Z*)-methyl non-2-en-4-ynoate (**4.2b**) (33 mg, 0.2 mmol) was dissolved in toluene (2 ml) and added to B(C₆F₅)₃ (102 mg, 0.2 mmol) to give an orange solution. The reaction mixture was left at room temperature for 30 min before being cooled to -40 °C for 18 h. The product could be recrystallised from the slow evaporation of a toluene/petroleum ether solution to give small colourless crystals of the product suitable for X-ray diffraction. The remaining solvent was removed and the crystals were washed with petroleum ether 40-60 (3 x 3ml) to give the product as a pale green solid. Yield: 87 mg, 64%, 0.13 mmol. Melting point: 191–194 °C. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 8.47 (s, 1H, =CH), 6.90 (d, ³J_{HH} = 8.8 Hz, 1H, =CH), 4.36 (s, 3H, O-CH₃), 2.92–2.80 (m, 2H, CH₂), 1.43 (br. s, 1H, CH), 1.31–1.19 (m, 2H, CH₂), 0.80 (t, ³J_{HH} = 7.3 Hz, 3H, CH₃) 0.64 (br. s, 1H, CH) (two α-protons of *n*Bu are diastereotopic). **¹³C NMR partial** (126 MHz, CDCl₃, 298 K) δ/ppm: 175.8 (s), 168.5 (s), 165.0 (s), 104.4 (s), 58.2 (s), 33.4 (s), 29.2 (s), 22.5 (s), 13.4 (s). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: -14.5. **¹⁹F NMR** (565 MHz, CDCl₃, 298 K) δ/ppm: -128.2 (br. s, 1F, *o*-F), -128.6 (br. s, 1F, *o*-F), -130.8 (br. d, ³J_{FF} = 19.3 Hz, 1F, *o*-F), -132.3 (br. s, 1F, *o*-F), -134.4 (br. d, ³J_{FF} = 19.3 Hz, 1F, *o*-F), -135.0 (br. s, 1F, *o*-F), -159.0 (t, ³J_{FF} = 20.3 Hz, 1F, *p*-F), -159.6 (t, ³J_{FF} = 20.3 Hz, 1F, *p*-F), -159.8 (t, ³J_{FF} = 20.3 Hz, 1F, *p*-F), -162.9 (br. t, ³J_{FF} = 22.9 Hz, 1F, *m*-F), -164.2 (br. dt, ³J_{FF} = 23.1 Hz, ⁴J_{FF} = 8.3 Hz, 1F, *m*-F), -164.39 (br. t, ³J_{FF} = 19.6 Hz, 1F, *m*-F), -164.6 (m, 1F, *m*-F), -164.8 (m, 1F, *m*-F), -165.3 (br. t, ³J_{FF} = 19.6 Hz,

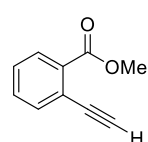
1F, *m*-F). IR ν_{\max} (cm⁻¹): 2957, 2936, 2877, 2863, 1643, 1606, 1551, 1515, 1498, 1453, 1346, 1276, 1081, 1002, 966, 864, 824, 794, 771, 760, 749, 679, 632, 557. HRMS (ES⁻) *m/z* calculated for [M-H]⁻ [C₂₈H₁₃BF₁₅O₂]⁻: 676.0805, found: 676.0806. Elemental analysis (%) calculated for C₂₈H₁₄BF₁₅O₂: C 49.59, H 2.08, found: C 49.64, H 1.97. Note: Partial ¹³C NMR spectra recorded for **4.3a,b** due to broad resonances observed for fluorine coupled carbon nuclei of C₆F₅-rings.

6.4.2 Divergent Reactivity of Hard and Soft Lewis Acids: 6-*endo-dig* vs. 5-*exo-dig*.

6.4.2.1 Synthesis of Starting Materials.

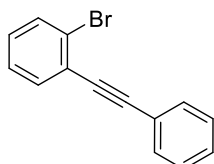


Methyl 2-((trimethylsilyl)ethynyl)benzoate: Prepared according to literature methods.^[171] To a solution of methyl 2-iodobenzoate (2.52 g, 9.60 mmol), copper iodide (73.3 mg, 385 μ mol) and PdCl₂(PPh₃)₂ (135 mg, 193 μ mol) in THF (25 ml) was added triethylamine (2.67 ml, 19.3 mmol). A solution of ethynyltrimethylsilane (1.42 g, 14.5 mmol) in THF (5 ml) was added dropwise and the reaction mixture was stirred for 19 h at 23 °C. The mixture was filtered through Celite and diluted with water (150 ml). The phases were separated and the aqueous layer was extracted with diethyl ether (3 x 50 ml). The combined organic layers were washed with aq. NaCl solution (3 x 50 ml) and dried over MgSO₄. The solvent was removed *in vacuo* yielding methyl 2-((trimethylsilyl)ethynyl)benzoate as a brown oil. The NMR data is in agreement with that reported in the literature.^[171] Yield: 2.13 g, 9.18 mmol, 95%. ¹H NMR (500 MHz, CDCl₃, 298 K) δ /ppm: 7.90 (dd, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.2 Hz, 1H), 7.58 (dd, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.2 Hz, 1H), 7.44 (td, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.2 Hz, 1H), 7.37 (td, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.2 Hz, 1H), 3.92 (s, 3H), 0.27 (s, 9H).

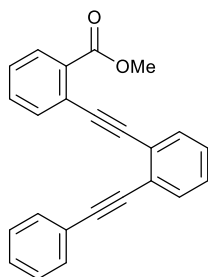


Methyl 2-ethynylbenzoate: Prepared according to literature methods.^[171] To a solution of methyl 2-((trimethylsilyl)ethynyl)benzoate (2.13 g, 9.18 mmol) in MeOH (20 ml) and CH₂Cl₂ (10 ml) was added K₂CO₃ (3.86 g, 27.60 mmol). The reaction mixture was stirred for 13 h at 23 °C, upon completion the reaction mixture was diluted with water (50 ml). The layers were separated and the aqueous phase was extracted with diethyl ether (3 x 30 ml). The combined organic layers were washed with saturated aq. NaCl solution (3 x 30 ml) and dried over MgSO₄. The solvent was removed *in vacuo* yielding methyl 2-ethynylbenzoate as a brown oil. Yield: 1.19 g, 7.40 mmol, 81%. The NMR data is in agreement with that

reported in the literature.^[171] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.94 (dd, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.1 Hz, 1H), 7.63 (dd, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.1 Hz, 1H), 7.48 (td, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.4 Hz, 1H), 7.41 (td, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.3 Hz, 1H), 3.93 (s, 3H), 3.40 (s, 1H).

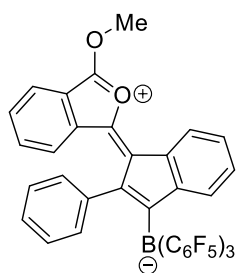


1-bromo-2-(phenylethynyl)benzene: Prepared according to literature methods.^[171] To a solution of 1-bromo-2-iodobenzene (1.40 g, 4.93 mmol), copper iodide (37.6 mg, 197 μmol) and PdCl₂(PPh₃)₂ (69.2 mg, 98.6 μmol) in THF (15 ml) was added triethylamine (1.37 ml, 9.86 mmol). A solution of phenylacetylene (756 mg, 7.40 mmol) in THF (3 ml) was added dropwise and the reaction mixture was stirred for 16 h at 23 °C. The mixture was filtered through Celite and diluted with water (150 ml). The phases were separated and the aqueous layer was extracted with diethyl ether (3 x 50 ml). The combined organic layers were washed with saturated aq. NaCl solution (3 x 50 ml) and dried over MgSO₄. The solvent was removed *in vacuo* with the crude oil being purified by column chromatography (silica, eluent: *n*-hexane), yielding 1-bromo-2-(phenylethynyl)benzene as a brown oil. Yield: 0.83 g, 3.20 mmol, 65%. The NMR data is in agreement with that reported in the literature.^[171] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: = 7.52 – 7.63 (m, 4H), 7.36 – 7.37 (m, 3H), 7.30 (td, ³J_{HH} = 7.4 Hz, ⁴J_{HH} = 1.2 Hz, 1H), 7.18 (td, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.6 Hz, 1H).

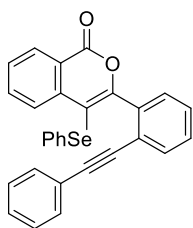


4.4: Prepared according to literature methods.^[171] To a solution of 1-bromo-2-(phenylethynyl)benzene (829 mg, 3.22 mmol), copper iodide (12 mg, 64.4 μmol), Pd(PPh₃)₄ (74 mg, 64.4 μmol) and *n*-butylamine (1.29 ml, 13.0 mmol) in dry diethyl ether (10 ml) was added methyl 2-ethynylbenzoate (516 mg, 3.22 mmol). The resulting mixture was heated to 60 °C and stirred for 17 h. After cooling to rt, the mixture was quenched with saturated aq. NH₄Cl solution (20 ml). The layers were separated and the aqueous layer was extracted with diethyl ether (3 x 10 ml). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The crude oil was purified by column chromatography to give **4.4**. Yield: 396 mg, 0.97 mmol, 30%. The NMR data is in agreement with that reported in the literature.¹ **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.99 (dd, ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 1.4 Hz, 1H), 7.71 (dd, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.4 Hz, 1H), 7.61 – 7.63 (m, 1H), 7.55 – 7.59 (m, 3H), 7.47 (td, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.4 Hz, 1H), 7.39 (td, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.4 Hz, 1H), 7.32 – 7.35 (m, 5H), 3.89 (s, 3H).

6.4.2.2 Synthesis of Products

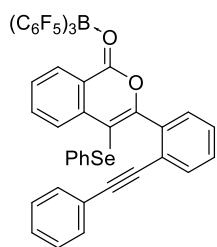


4.5: Methyl-2-((2-(phenylethynyl)phenyl)ethynyl)benzoate (**4.4**) (67 mg, 0.2 mmol) and $B(C_6F_5)_3$ (102 mg, 0.2 mmol) were dissolved in toluene (1 ml) to give a yellow solution, which quickly changed colour to a very dark green. The reaction mixture was left at room temperature for 4 h. During this time crystals were formed, which were suitable for X-ray diffraction. The solvent was evaporated and the remaining crystals were washed with hexane (6 x 2 ml) to give the product **4.5** as a dark green solid. Yield: 142 mg, 0.17 mmol, 84%. Melting point: 175 – 180 °C (dec.). **1H NMR** (500 MHz, $CDCl_3$, 298 K) δ /ppm: 7.99 (d, $^3J_{HH} = 7.8$ Hz, 1H), 7.75 (d, $^3J_{HH} = 7.4$ Hz, 1H), 7.53 (t, $^3J_{HH} = 7.7$ Hz, 1H), 7.45 (d, $^3J_{HH} = 7.7$ Hz, 1H), 7.40 (t, $^3J_{HH} = 7.8$ Hz, 1H), 7.12 – 7.29 (m, 5H), 7.01 – 7.07 (m, 2H), 4.91 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ /ppm: 175.0 (s), 144.9 (s), 140.7 (s), 140.0 (s), 139.8 (s), 137.6 (s), 136.7 (s), 135.0 (s), 134.2 (s), 132.3 (s), 132.1 (s), 131.8 (s), 130.6 (s), 128.6 (s), 128.5 (s), 128.2 (s), 127.4 (s), 127.3 (s), 127.1 (s), 126.2 (s), 126.1 (s), 125.5 (s), 117.4 (s), 63.4 (s). Note: carbon atoms of C_6F_5 groups not reported due to extensive line broadening. **^{11}B NMR** (160 MHz, $CDCl_3$, 298 K) δ /ppm: -15.8 (s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ /ppm: -123.03 (br. s, 1F, *o*-F), -125.19 (br. d, $^3J_{FF} = 20.3$ Hz, 1F, *o*-F), -129.18 (br. d, $^3J_{FF} = 20.3$ Hz, 1F, *o*-F), -129.62 (br. s, 1F, *o*-F), -131.98 (br. m, 1F, *o*-F), -136.14 (br. s, 1F, *o*-F), -160.78 (t, $^3J_{FF} = 20.7$ Hz, 1F, *p*-F), -161.72 (t, $^3J_{FF} = 20.8$ Hz, 1F, *p*-F), -162.68 (t, $^3J_{FF} = 20.8$ Hz, 1F, *p*-F), -164.87 (t, $^3J_{FF} = 24.2$ Hz, 1F, *m*-F), -165.49 (m, 1F, *m*-F), -166.58 (m, 4F, *m*-F). **HRMS** (ES⁺) *m/z* calculated for [M]⁺ [$C_{42}H_{16}BF_{15}O_2$]⁺: 848.1004; observed: 848.1016.

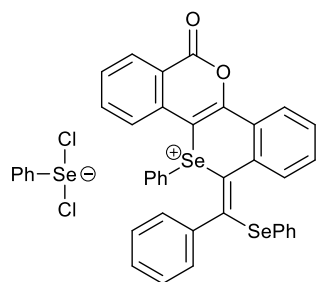


4.6: A solution of phenylselenenyl chloride (38 mg, 0.2 mmol) in toluene (1 ml) was added to methyl-2-((2-(phenylethynyl)phenyl)ethynyl)benzoate (**4.4**) (67 mg, 0.2 mmol) and the reaction left overnight at room temperature. The solvent was then removed and the crude product washed with hot *n*-hexane. Drying *in vacuo* afforded the pure product. Yield: 65 mg, 0.14 mmol, 68%. **1H NMR** (500 MHz, $CDCl_3$, 298 K) δ /ppm: 8.39 (dd, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.0$ Hz, 1H), 8.05 (d, $^3J_{HH} = 8.0$ Hz, 1H), 7.71 (td, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.3$ Hz, 1H), 7.64 (dd, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.0$ Hz, 1H), 7.55 (t, $^3J_{HH} = 7.7$ Hz, 1H), 7.51 (dd, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.0$ Hz, 1H), 7.45 (td, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.6$ Hz, 1H), 7.39 (td, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.2$ Hz, 1H), 7.33 – 7.31 (m, 2H), 7.27 – 7.22 (m, 5H), 7.09 – 7.04 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ /ppm: 161.8 (s), 158.5 (s), 138.0 (s), 137.9 (s), 136.7 (s), 135.3 (s), 132.0 (s), 131.6 (s), 131.4 (s),

129.9 (s), 129.9 (s), 129.8 (s), 129.7 (s), 129.1 (s), 128.8 (s), 128.5 (s), 128.3 (s), 128.2 (s), 128.1 (s), 127.9 (s), 126.6 (s), 125.3 (s), 123.9 (s), 122.8 (s), 121.2 (s), 107.7 (s), 94.3 (s), 87.4 (s). **⁷⁷Se NMR** (95 MHz, CDCl₃, 298 K) δ/ppm: 289.5. **HRMS** (ES⁺) *m/z* calculated [C₂₉H₁₈O₂Se]⁺ [M]⁺: 478.0472, found: 478.0475.



4.7: A solution of phenylselenenyl chloride (19 mg, 0.1 mmol) in CDCl₃ (0.5 ml) was added to methyl-2((2-phenylethynyl)phenylethynyl) benzoate (**4.4**) (34 mg, 0.1 mmol). After 3 h tris(pentafluorophenyl)borane (51 mg, 0.1 mmol) was added which was accompanied by a colour change from an orange solution to dark red/black. The reaction mixture was heated to 40 °C for 3 d. The dark red solution was concentrated *in vacuo*, washed with *n*-hexane and concentrated again *in vacuo*. Recrystallisation from CH₂Cl₂ and *n*-hexane yielded the product as red-brown crystals which could be characterised by single crystal X-ray diffraction. Yield: 41 mg, 0.4 mmol, 41%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.60 (d, ³J_{HH} = 8.2 Hz, 1H), 8.23 (d, ³J_{HH} = 8.2 Hz, 1H), 8.00 (t, ³J_{HH} = 7.7 Hz, 1H), 7.79 (t, ³J_{HH} = 7.7 Hz, 1H), 7.54 (d, ³J_{HH} = 7.2 Hz, 1H), 7.45 (t, ³J_{HH} = 8.2 Hz, 1H), 7.29 (t, ³J_{HH} = 7.7 Hz, 1H), 7.20 (t, ³J_{HH} = 8.2 Hz, 1H), 6.92 – 7.15 (m, 10H). **¹³C NMR partial** (126 MHz, CDCl₃, 298 K) δ/ppm: 170.2 (s), 156.4 (s), 148.0 (m), 140.0 (s), 139.9 (s), 137.3 (m), 133.0 (s), 132.4 (s), 131.5 (s), 131.2 (s), 131.1 (s), 129.8 (s), 129.4 (s), 129.2 (s), 129.1 (s), 129.1 (s), 128.5 (s), 128.4 (s), 128.0 (s), 124.0 (s), 121.9 (s), 117.7 (s), 116.5 (m), 95.1 (s), 85.7 (s). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: -0.51 (br. s). **¹⁹F NMR** (283 MHz, CDCl₃, 298 K) δ/ppm: -135.0 (d, ³J_{FF} = 20.5 Hz, 6F, *o*-F), -157.3 (t, ³J_{FF} = 18.8 Hz, 3F, *p*-F), -163.8 (t, ³J_{FF} = 21.7 Hz, 6F, *m*-F). **⁷⁷Se NMR** (95 MHz, CDCl₃, 298 K) δ/ppm: 289.4 (s). **IR** ν_{max} (cm⁻¹): 2916 (w, br.), 1493 (m), 725 (s), 698 (s) cm⁻¹. **HRMS** (ES⁺) *m/z* calculated for [C₄₇H₁₈BF₁₅O₂Se]⁺ [M]⁺: 990.0326, found: 990.0338.

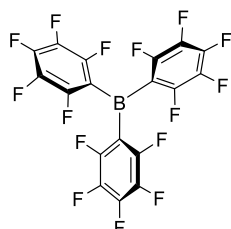


4.8: A solution of phenylselenenyl chloride (29.1 mg, 150 μmol, 3 equiv.) in CDCl₃ (0.5 ml) was added to methyl-2((2-phenylethynyl)phenylethynyl) benzoate (**4.4**) (17 mg, 50.0 μmol, 1 equiv.). Slow evaporation of the solvent yielded orange crystals which could be characterised by single crystal X-ray diffraction. The crystals were washed with *n*-hexane (2 x 3 ml) and dried *in vacuo* to give the pure product. Yield: 16 mg, 18.6 μmol, 37%. Melting point: 128 – 133 °C. **¹H NMR** (400 MHz, CD₂Cl₂, 298 K) δ/ppm: 8.39 (d, ³J_{HH} = 7.8 Hz, 1H), 8.16 (dd, ³J_{HH} = 7.0 Hz, ⁴J_{HH} = 1.4 Hz, 1H), 8.09 (dd, ³J_{HH}

= 7.3 Hz, $^4J_{\text{HH}} = 1.8$ Hz, 1H), 7.84 (t, $^3J_{\text{HH}} = 7.3$ Hz, 1H), 7.77 (d, $^3J_{\text{HH}} = 7.8$ Hz, 2H), 7.69 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 7.59 – 7.56 (m, 2H), 7.54 – 7.38 (m, 11H), 7.30 (d, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 7.21 – 7.20 (m, 4H), 7.06 (t, $^3J_{\text{HH}} = 7.6$ Hz, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2 , 298 K) δ/ppm : 163.5 (s), 159.2 (s), 153.3 (s), 137.8 (s), 137.5 (s), 136.6 (s), 136.3 (br. s), 134.0 (s), 133.3 (s), 133.0 (s), 132.1 (s), 132.0 (s), 132.0 (s), 131.9 (s), 131.8 (s), 131.5 (s), 130.4 (s), 130.3 (s), 130.1 (s), 130.1 (s), 129.8 (s), 129.9 (s), 129.7 (s), 129.7 (s), 129.6 (s), 129.0 (br. s), 128.6 (br. s), 127.9 (s), 127.9 (s), 127.7 (s), 127.4 (s), 124.7 (s), 120.8 (s), 114.1 (s), 104.9 (s). IR ν_{max} (cm^{-1}): 3052 (w), 1263 (s), 1263 (s), 895 (w), 746 (s), 702 (s) cm^{-1} . HRMS (ES⁺) m/z calculated for $[\text{C}_{35}\text{H}_{23}\text{O}_2\text{Se}_2]^+$ $[\text{M-PhSeCl}_2]^+$: 635.0028, found 635.0037. Note: Sparse solubility of selenocyclic salt **2** resulted in a very weak ^{77}Se NMR spectrum. Trials in many different deuterated solvents did not lead to a sample sufficiently concentrated enough to carry out this spectroscopic method.

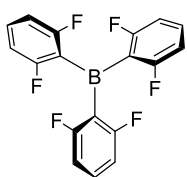
6.4.3 Stoichiometric and Catalytic Pyrone and Isocoumarin Formation via C–H and C–C Bond Formation

6.4.3.1 Synthesis of Starting Materials

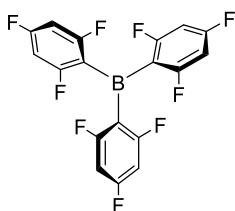


Tris(pentafluorophenyl)borane: Synthesised in a procedure adapted from Lancaster *et al.*^[4] whereby magnesium turnings (1.1 g, 45 mmol, 3 equiv.) was suspended in Et_2O (100 ml). $\text{C}_6\text{F}_5\text{Br}$ (5.6 ml, 45 mmol, 3 equiv.) was added dropwise over the course of 30 minutes whilst stirring, without allowing the mixture to reach reflux. After stirring at ambient temperature for 30 mins, this mixture was transferred *via* filter cannula to a stirred solution of $\text{BF}_3 \cdot \text{OEt}_2$ (1.9 ml, 15 mmol, 1 equiv.) in toluene (100 ml). The excess Et_2O solvent was removed under vacuum leaving the mixture as a toluene solution. The reaction was then set to react at 100 °C for 1 h then left to cool to ambient temperature. The remaining solvent was removed under reduced pressure whilst gently heating in an oil bath until a brown cake remains. This was the subject to a two-fold sublimation (110 °C, 1×10^{-3} mbar) whereupon the pure $\text{B}(\text{C}_6\text{F}_5)_3$ was collected as a white microcrystalline solid. Yield: 6.7 g, 13.2 mmol, 88%. The spectroscopic data agrees with literature established values.^[4] ^{11}B NMR (128 MHz, CDCl_3 , 298 K) δ/ppm : 59.6 (br. s). ^{19}F NMR (471 MHz, CDCl_3 , 298 K) δ/ppm : -127.73 (br. s, 6F, *o*-F), -142.46 (br. s, 3F, *p*-F), -159.83 (br. s, 6F, *m*-F).

General Procedure 1: According to the literature,^[114] the corresponding di- or tri-fluoro-substituted bromobenzene (3 equiv.) was dissolved in freshly distilled THF (100 ml) and cooled to -20 °C. At this temperature ⁱPrMgCl (3 equiv., 2.0 M in THF) was added dropwise. The reaction mixture was then allowed to reach 0 °C and after 1 h at this temperature cooled again to -50 °C. Subsequently, BF₃·Et₂O (1 equiv.) was added dropwise and after 1 h the cooling bath was removed and the reaction mixture warmed to room temperature within another hour. Removal of all volatiles and a two-fold sublimation of the remaining solid (120 °C, 1 x 10⁻³ mbar) afforded the desired boranes as white solids.



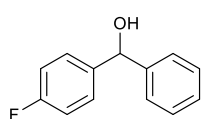
Tris(2,6-difluorophenyl)borane: Synthesised in accordance with *General Procedure 1* using 1-bromo-2,6-difluorobenzene (3.39 ml, 30 mmol, 3 equiv.), ⁱPrMgCl (15 ml, 30 mmol, 3 equiv.) and BF₃·Et₂O (1.23 ml, 10 mmol, 1 equiv.) to give the pure product (2.14 g, 6.1 mmol, 61%). Spectroscopic analyses agree with literature established values.^[114] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.59–7.20 (m, 3H, aryl), 6.87 (t, ³J_{HH} = 7.8 Hz, 6H, aryl). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: -62.8 (br. s). **¹⁹F NMR** (471 MHz, CDCl₃, 298 K) δ/ppm: -99.05.



Tris(2,4,6-trifluorophenyl)borane: Synthesised in accordance with *General Procedure 1* using 1-bromo-2,4,6-trifluorobenzene (3.50 ml, 30 mmol, 3 equiv.), ⁱPrMgCl (15 ml, 30 mmol, 3 equiv.) and BF₃·Et₂O (1.23 ml, 10 mmol, 1 equiv.) to give the pure product (3.35 g, 8.3 mmol, 83%). Spectroscopic analyses agree with literature established values.^[114] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 6.64 (t, ³J_{HH} = 8.3 Hz, 6H, aryl). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 58.4 (br. s). **¹⁹F NMR** (471 MHz, CDCl₃, 298 K) δ/ppm: -95.75 (d, ³J_{HF} = 10.4 Hz, 6F, *o*-F), -100.31 (t, ³J_{HF} = 10.4 Hz, 3F, *p*-F).

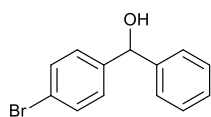
General Procedure 2: In accordance with the literature,^[172] magnesium turnings (1 equiv.) were stirred in THF (15 ml) with 1,2-dibromoethane (0.1 ml) being added and the solution was cooled to 0 °C. After stirring for 5 minutes, a solution of a halo-benzene (0.9 equiv.) in THF (20 ml) was added through a dropping funnel. The ice bath was removed and the mixture was stirred for 1 h. After cooling the reaction down to 0 °C again, a solution of a benzaldehyde derivative (0.8 equiv.) in THF (20 ml) was added through a dropping funnel and the reaction mixture was stirred overnight. The reaction was then quenched with saturated NH₄Cl solution (50 ml) and the organic

phase was separated. The aqueous phase was extracted with Et₂O (3 x 15 ml). The combined organic layers were dried *in vacuo* yielding the desired compound which was sufficiently pure for subsequent use.



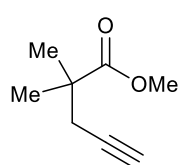
4-Fluorobenzhydryl: Synthesised by *General Procedure 2* using magnesium (0.8 g, 32.9 mmol), 1-bromo-4-fluoro-benzene (5.3 g, 3.3 ml, 30.3 mmol,) and benzaldehyde (2.69 g, 2.6 ml, 25.3 mmol).

The spectroscopic data agrees with literature established values.^[172] Yield: 4.36 g, 21.6 mmol, 83%. ¹H NMR (500 MHz, CDCl₃, 298 K) δ/ppm: 7.39–7.32 (m, 4H, Ar-H), 7.31–7.27 (m, 3H, Ar-H), 7.02 (t, ³J_{HH} = 8.6 Hz, 2H, Ar-H), 5.83 (s, 1H, C(H)Ar₂), 2.26 (br. s, 1H, OH). ¹⁹F NMR (471 MHz, CDCl₃, 298 K) δ/ppm: -115.05 – -115.11 (br. m, 1F, Ar-F).



4-Bromobenzhydryl: Synthesised by *General Procedure 2* using magnesium (0.5 g, 22.3 mmol), bromobenzene (3.49 g, 22.3 mmol, 3.3 ml) and 4-bromo-benzaldehyde (3.2 g, 17.1 mmol). The

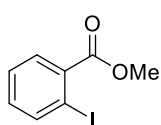
spectroscopic data agrees with literature established values.^[172] Yield: 3.52 g, 13.4 mmol, 78%. ¹H NMR (300 MHz, CDCl₃, 298 K) δ/ppm: 7.46 (d, ³J_{HH} = 8.4 Hz, 2H, Ar-H), 7.37–7.28 (m, 5H, Ar-H), 7.26 (d, ³J_{HH} = 8.3 Hz, 2H, Ar-H), 5.80 (s, 1H, C(H)Ar₂), 2.23 (br. s, 1H, OH).



Methyl 2,2-dimethylpent-4-ynoate: Diisopropylamine (20 ml, 0.14 mol) was cooled to -78 °C in THF (40 ml), at which point ⁿBuLi (1.6 M in hexanes, 79.2 ml, 0.13 mol) was added and the reaction was stirred for 1 h. The freshly prepared lithium diisopropylamide was then added

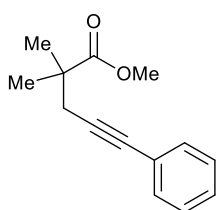
to a solution of methyl isobutyrate (13.2 ml, 0.12 mol) in THF (30 ml) through a dropping funnel over 2 h whilst stirring at 0 °C. After complete addition, the reaction mixture was stirred for 1 h at room temperature before cooling back to 0 °C. A solution of propargyl bromide (80 wt% in toluene, 12.2 ml, 0.12 mmol) in THF (10 ml) was then added dropwise. The mixture was warmed to room temperature and then stirred for 18 h. After quenching with water, the organic phase was separated and the aqueous layer extracted with Et₂O (3 x 20 ml). The combined organic layers were washed with a saturated aqueous NaCl solution, dried over MgSO₄, filtered and concentrated *in vacuo*. The obtained oil was distilled (50 °C, 15 mmHg) to give the desired product as a colourless oil. The spectroscopic data agrees with literature established values.^[101, 173] Yield: 12.9 g, 42 mol, 84%. ¹H NMR (300 MHz, CDCl₃, 298 K) δ/ppm:

3.70 (s, 3H, OCH₃), 2.44 (d, ⁴J_{HH} = 2.6 Hz, 2H, CH₂), 2.00 (t, ⁴J_{HH} = 2.6 Hz, 1H, ≡CH), 1.28 (s, 6H, C(CH₃)₂).

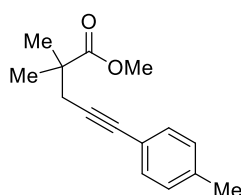


Methyl 2-iodobenzoate: 2-Iodo-benzoic acid (15 g, 60.5 mmol, 1 equiv.) was dissolved in methanol (50 ml). The mixture was stirred for 10 min to dissolve the acid. After cooling the clear solution to 0 °C, concentrated sulphuric acid (2.5 ml, 46.9 mmol, 0.8 equiv.) was added. The mixture was allowed to warm to room temperature and was refluxed over-night. The reaction mixture was cooled to room temperature and neutralised with saturated aqueous NaHCO₃ solution (150 ml) and the product was extracted with hexane (3 x 50 ml). The combined organic phases were dried over MgSO₄, filtered over a short silica plug and dried *in vacuo* to yield the product as a yellow oil. The spectroscopic data agrees with literature established values.^[174] Yield: 15.4 g, 58.7 mmol, 97%. ¹H NMR (300 MHz, CDCl₃, 298 K) δ/ppm: 7.99 (d, ³J_{HH} = 7.9 Hz, 1H, Ar-H), 7.80 (d, ³J_{HH} = 7.8 Hz, 1H, Ar-H), 7.40 (t, ³J_{HH} = 7.6 Hz, 1H, Ar-H), 7.15 (t, ³J_{HH} = 7.7 Hz, 1H, Ar-H), 3.93 (s, 3H, OCH₃).

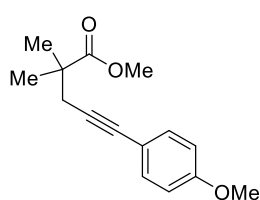
General Procedure 3: Methyl 2,2-dimethylpent-4-ynoate (0.8 g, 5.7 mmol, 1 equiv.) was added to a solution of THF (10 ml), NEt₃ (6 ml, 42 mmol, 7 equiv.) and iodobenzene derivative (1 equiv.). Pd(PPh₃)₂Cl₂ (58 mg, 1 mol%), CuI (23 mg, 2 mol%) and PPh₃ (60 mg, 4 mol%) were added. The reaction mixture was set to reflux for 10 h. After cooling and quenching with water, the organic layer was separated and extracted with Et₂O (3 x 20 ml). The combined organic layers were washed with saturated aqueous NaCl solution, dried over MgSO₄, filtered and dried *in vacuo*. The obtained material was purified by column chromatography to afford the product as an oil.^[101]



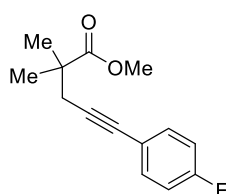
4.9a': Synthesised according to *General Procedure 3* using iodobenzene (0.63 ml, 5.7 mmol, 1 equiv.) The spectroscopic data agrees with literature established values.^[101] R_f value: 0.11 (SiO₂, 2:1 hexane/CHCl₃). Yield: 1.16 g, 5.4 mmol, 95%. ¹H NMR (300 MHz, CDCl₃, 298 K) δ/ppm: 7.43–7.23 (m, 5H, Ar-H), 3.71 (s, 3H, OCH₃), 2.66 (s, 2H, CH₂), 1.34 (s, 6H, C(CH₃)₂).



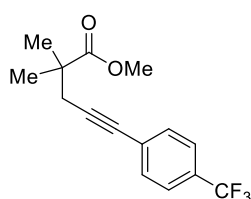
4.9b^f: Synthesised according to *General Procedure 3* using 4-iodotoluene (1.24 g, 5.7 mmol, 1 equiv). R_f value: 0.13 (SiO_2 , 2:1 hexane/ CHCl_3). Yield: 670 mg, 2.91 mmol, 49%. **¹H NMR** (400 MHz, CDCl_3 , 298 K) δ /ppm: 7.27 (d, $^3J_{\text{HH}} = 8.0$ Hz, 2H, Ar-H), 7.08 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H, Ar-H), 3.71 (s, 3H, OCH_3), 2.64 (s, 2H, CH_2), 2.33 (s, 3H, Ar-Me), 1.33 (s, 6H, $\text{C}(\text{CH}_3)_2$). **¹³C NMR** (101 MHz, CDCl_3 , 298 K) δ /ppm: 177.5 (s), 137.9 (s), 131.6 (s), 129.1 (s), 120.7 (s), 85.9 (s), 82.9 (s), 52.2 (s), 42.7 (s), 30.7 (s), 24.8 (s), 21.6 (s). **HRMS** (EI^+) m/z calculated for $[\text{C}_{15}\text{H}_{18}\text{O}_2]^+ [\text{M}]^+$: 230.1307, found: 230.1306.



4.9c^f: Synthesised according to *General Procedure 3* using 4-(methoxy)iodobenzene (1.32 g, 5.7 mmol, 1 equiv). R_f value: 0.19 (SiO_2 , 2:1 hexane/ CHCl_3). Yield: 532 mg, 2.17 mmol, 32%. **¹H NMR** (500 MHz, CDCl_3 , 298 K) δ /ppm: 7.32 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H, Ar-H), 6.81 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H, Ar-H), 3.80 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 2.64 (s, 2H, CH_2), 1.33 (s, 6H, $\text{C}(\text{CH}_3)_2$). **¹³C NMR** (126 MHz, CDCl_3 , 298 K) δ /ppm: 177.5 (s), 159.3 (s), 133.1 (s), 116.0 (s), 113.9 (s), 85.1 (s), 82.6 (s), 55.4 (s), 52.2 (s), 42.7 (s), 30.7 (s), 24.8 (s). **HRMS** (AP^+) m/z calculated for $[\text{C}_{15}\text{H}_{19}\text{O}_3]^+ [\text{M}+\text{H}]^+$: 247.1334, found: 247.1324.

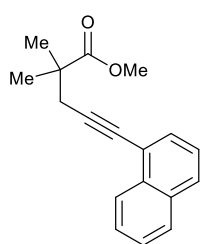


4.9d^f: Synthesised according to *General Procedure 3* using 4-fluoroiodobenzene (1.27 g, 5.7 mmol, 1 equiv). R_f value: 0.09 (SiO_2 , 3:1 hexane/ CHCl_3). Yield: 934 mg, 3.99 mmol, 70%. **¹H NMR** (400 MHz, CDCl_3 , 298 K) δ /ppm: 7.35 (dd, $^3J_{\text{HH}} = 8.8$ Hz, $^4J_{\text{HF}} = 5.5$ Hz, 2H, Ar-H), 6.97 (t, $^3J_{\text{HH}} = 8.8$ Hz, 2H, Ar-H), 3.71 (s, 3H, OCH_3), 2.64 (s, 2H, CH_2), 1.33 (s, 6H, $\text{C}(\text{CH}_3)_2$). **¹³C NMR** (101 MHz, CDCl_3 , 298 K) δ /ppm: 177.3 (s), 162.3 (d, $^1J_{\text{CF}} = 249$ Hz), 133.5 (d, $^3J_{\text{CF}} = 8.3$ Hz), 119.8 (s), 115.6 (d, $^2J_{\text{CF}} = 22.0$ Hz), 86.4 (s), 81.8 (s), 52.2 (s), 42.7 (s), 30.7 (s), 24.8 (s). **¹⁹F NMR** (376 MHz, CDCl_3 , 298 K) δ /ppm: -111.97 (s, 1F, p -F). **HRMS** (AP^+) m/z calculated for $[\text{C}_{14}\text{H}_{16}\text{O}_2\text{F}]^+ [\text{M}+\text{H}]^+$: 235.1134, found: 235.1125.

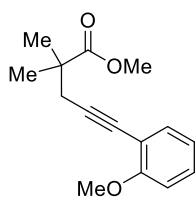


4.9e^f: Synthesised according to *General Procedure 3* using 4-(trifluoromethyl)iodobenzene (1.55 g, 0.84 ml, 5.7 mmol, 1 equiv). R_f value: 0.15 (SiO_2 , 2:1 hexane/ CHCl_3). Yield: 1.59 g, 5.6 mmol, 98%. **¹H NMR** (300 MHz, CDCl_3 , 298 K) δ /ppm: 7.50 (dd, $^3J_{\text{HH}} = 8.09$ Hz, $^3J_{\text{HH}} = 8.07$ Hz, 4H, Ar-H), 3.72 (s, 3H,

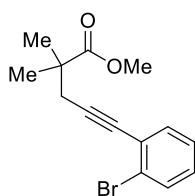
OCH₃), 2.67 (s, 2H, CH₂), 1.34 (s, 6H, C(CH₃)₂). **¹⁹F NMR** (376 MHz, CDCl₃, 298 K) δ/ppm: -62.79 (s, 3F, CF₃).



4.9f: Synthesised according to *General Procedure 3* using 1-iodonaphthalene (0.83 ml, 5.7 mmol, 1 equiv.) R_f value: 0.14 (SiO₂, 2:1 hexane/CHCl₃). Yield: 505 mg, 1.89 mmol, 33%. **¹H NMR** (300 MHz, CDCl₃, 298 K) δ/ppm: 8.30 (d, ³J_{HH} = 8.3 Hz, 1H, Ar-H), 7.83 (d, ³J_{HH} = 7.8 Hz, 1H, Ar-H), 7.79 (d, ³J_{HH} = 8.3 Hz, 1H, Ar-H), 7.62 (d, ³J_{HH} = 7.1 Hz, 1H, Ar-H), 7.58–7.48 (m, 2H, Ar-H), 7.40 (dd, ³J_{HH} = 8.1 Hz, ³J_{HH} = 7.3 Hz, 1H, Ar-H), 3.75 (s, 3H, OCH₃), 2.83 (s, 2H, CH₂), 1.42 (s, 6H, C(CH₃)₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 177.4 (s), 133.6 (s), 133.3 (s), 130.4 (s), 128.3 (s), 128.3 (s), 126.7 (s), 126.4 (s), 126.3 (s), 125.3 (s), 121.5 (s), 91.8 (s), 80.9 (s), 52.3 (s), 42.9 (s), 31.2 (s), 25.0 (s). **HRMS** (EI⁺) *m/z* calculated for [C₁₈H₁₈O₂]⁺ [M]⁺: 266.1307, found: 266.1312.

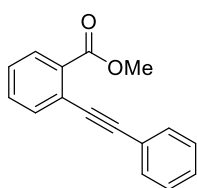


4.9g: Synthesised according to *General Procedure 3* using 2-(methoxy)iodobenzene (0.74 ml, 5.7 mmol, 1 equiv). R_f value: 0.18 (SiO₂, 2:1 hexane/CHCl₃). Yield: 746 mg, 3.03 mmol, 53%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.35 (dd, ³J_{HH} = 7.5 Hz, ⁴J_{HH} = 1.6 Hz, 1H, Ar-H), 7.25 (td, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.7 Hz, 1H, Ar-H), 6.89–6.84 (m, 2H, Ar-H), 3.86 (s, 3H, OCH₃), 3.71 (s, 3H, OCH₃), 2.72 (s, 2H, CH₂), 1.35 (s, 6H, C(CH₃)₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 177.5 (s), 160.1 (s), 133.7 (s), 129.2 (s), 120.5 (s), 113.0 (s), 110.7 (s), 91.0 (s), 79.0 (s), 55.9 (s), 52.1 (s), 42.7 (s), 31.0 (s), 24.7 (s). **HRMS** (ES⁺) *m/z* calculated for [C₁₅H₁₈O₃]⁺ [M]⁺: 246.1256, found: 246.1250.

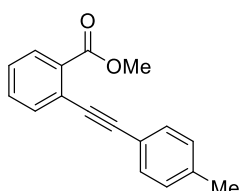


4.9h: Synthesised according to *General Procedure 3* using 1-bromo-2-iodobenzene (1.61 g, 5.7 mmol, 1 equiv). R_f value: 0.18 (SiO₂, 2:1 hexane/CHCl₃). Yield: 1.20 g, 4.07 mmol, 71%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.55 (dd, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 1.1 Hz, 1H, Ar-H), 7.42 (dd, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.6 Hz, 1H, Ar-H), 7.22 (td, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.1 Hz, 1H, Ar-H), 7.12 (td, ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 1.7 Hz, 1H, Ar-H), 3.72 (s, 3H, OCH₃), 2.72 (s, 2H, CH₂), 1.38 (s, 6H, C(CH₃)₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 177.4 (s), 133.6 (s), 132.4 (s), 129.0 (s), 127.0 (s), 125.9 (s), 125.6 (s), 91.9 (s), 81.5 (s), 52.3 (s), 42.7 (s), 30.8 (s), 24.9 (s). **HRMS** (EI⁺) *m/z* calculated for [C₁₄H₁₅BrO₂]⁺ [M]⁺: 294.0255, found: 294.0258.

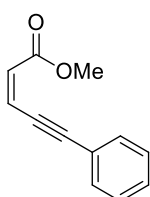
General Procedure 4: Methyl 2-iodobenzoate (2.24 ml, 4.00 g, 15.3 mmol, 1 equiv.), Pd(PPh₃)₂Cl₂ (220 mg, 0.3 mmol, 2 mol%) and CuI (120 mg, 0.6 mmol, 4 mol%) were mixed. NEt₃ (50 ml) and THF (20 ml) was subsequently added. The mixture was stirred for 5 mins. The terminal alkyne (1.2 equiv.) was added and the reaction was heated under reflux for 16 h. After allowing the mixture to cool, the reaction was quenched with water (100 ml) and extracted with CH₂Cl₂ (3 x 60 ml). The combined organic layers were dried over MgSO₄, filtered, concentrated and purified by flash column chromatography using a gradient of EtOAc/hexane (0-5%) as eluent to afford the product.



4.9i': Synthesised according to *General Procedure 4* using phenylacetylene (1.9 ml, 17.71 mmol, 1.16 equiv). The spectroscopic data agrees with literature established values.^[175] R_f value: 0.18 (SiO₂, hexane/EtOAc 95:5) Yield: 3.27 g, 13.84 mmol, 91%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.98 (dd, ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 0.9 Hz, 1H, Ar-H), 7.65 (dd, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 0.8 Hz, 1H, Ar-H), 7.60–7.56 (m, 2H, Ar-H), 7.50 (td, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.4 Hz, 1H, Ar-H), 7.41–7.34 (m, 4H, Ar-H), 3.97 (s, 3H, OCH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 166.9 (s), 134.1 (s), 132.0 (s), 131.9 (s), 131.9 (s), 130.6 (s), 128.7 (s), 128.5 (s), 128.0 (s), 123.8 (s), 123.4 (s), 94.5 (s), 88.3 (s), 52.4 (s).



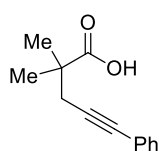
4.9j': Synthesised according to *General Procedure 4* using 4-ethynyltoluene (2.25 ml, 17.71 mmol, 1.16 equiv). R_f value: 0.29 (SiO₂, 90:10, hexane/EtOAc). Yield: 3.78 g, 15.1 mmol, 99%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.97 (dd, ³J_{HH} = 7.9, ⁴J_{HH} = 0.9 Hz, 1H, Ar-H), 7.64 (dd, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 0.7 Hz, 1H, Ar-H), 7.51–7.45 (m, 3H, Ar-H), 7.37 (td, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.2 Hz, 1H, Ar-H), 7.17 (d, ³J_{HH} = 7.9 Hz, 2H, Ar-H), 3.97 (s, 3H, OCH₃), 2.38 (s, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 166.9 (s), 138.8 (s), 134.0 (s), 131.8 (s), 131.7 (s), 131.7 (s), 130.5 (s), 129.2 (s), 127.7 (s), 123.9 (s), 120.2 (s), 94.6 (s), 87.6 (s), 52.2 (s), 21.6 (s). **HRMS** (ES⁺) *m/z* calculated for [C₁₇H₁₄O₂]⁺ [M+H] 250.0994, found 250.0987.



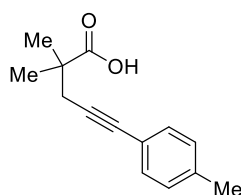
4.9k': Methyl 3-iodoacrylate (6.00 g, 28.30 mmol, 1 equiv.), phenylacetylene (2.96 ml, 26.56 mmol, 1.16 equiv.), Pd(PPh₃)₂Cl₂ (322 mg, 0.45 mmol, 2 mol%) and CuI (175 mg, 0.92 mmol, 4 mol%) were dissolved in NEt₃ (50 ml) and THF (20 ml) and stirred over night. The black suspension was quenched with saturated NH₄Cl (50 mL) and the

mixture was extracted with ethyl acetate (3 x 40 ml). After being concentrated *in vacuo*, the residue was purified by flash column chromatography (SiO₂, 50:1, hexane/EtOAc) to afford the product as an orange oil. The spectroscopic data agrees with literature established values.^[176] R_f value: 0.07 (SiO₂, 50:1, hexane/EtOAc) Yield: 4.27 g, 22.93 mmol, 81%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.58–7.51 (m, 2H, Ar-H), 7.36 (s, 3H, Ar-H), 6.37 (d, ³J_{HH} = 11.4 Hz, 1H, =CH), 6.15 (d, ³J_{HH} = 11.3 Hz, 1H, =CH), 3.81 (s, 3H, OCH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 165.3 (s), 132.2 (s), 129.3 (s), 128.4 (s), 127.8 (s), 123.2 (s), 122.6 (s), 101.4 (s), 86.3 (s), 51.5 (s).

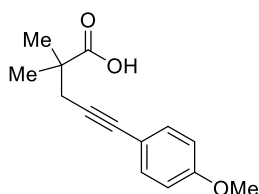
General Procedure 5: In a procedure similar to that outlined by Takaki *et al.*,^[101] to a solution of NaOH (5 equiv.) in methanol (20 ml), a solution of methyl ester in methanol (25 ml) was added. The mixture was heated at 80 °C for 16 h. After cooling to room temperature, the crude mixture was concentrated and then diluted with H₂O (25 ml). The aqueous mixture was extracted with Et₂O (3 x 20 ml). The aqueous layer was acidified with concentrated HCl and extracted with Et₂O. The combined extracts were washed with saturated aqueous NaCl solution, dried over MgSO₄, filtered and dried *in vacuo* to give the carboxylic acid.



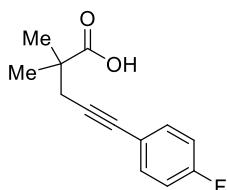
4.9a: Synthesised according to *General Procedure 5* using **4.9a'** (1.16 g, 5.4 mmol, 1 equiv.) to give an off-white solid. The spectroscopic data agrees with literature established values.^[101] Yield: 1.15 g, 5.4 mmol, 99%. **¹H NMR** (300 MHz, CDCl₃, 298 K) δ/ppm: 7.39 (br. s, 2H, Ar-H), 7.27 (br. s, 3H, Ar-H), 2.69 (s, 2H, CH₂), 1.37 (s, 6H, C(CH₃)₂). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 182.7 (s), 131.8 (s), 128.3 (s), 127.9 (s), 123.7 (s), 86.4 (s), 83.1 (s), 42.5 (s), 30.4 (s), 24.6 (s).



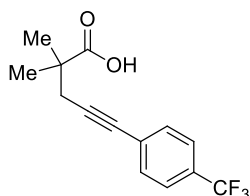
4.9b: Synthesised according to *General Procedure 5* using **4.9b'** (670 mg, 2.91 mmol, 1 equiv.) to give an off-white solid. Melting point: 92–98 °C. Yield: 629 mg, 2.91 mmol, 99%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.29 (d, ³J_{HH} = 8.0 Hz, 2H, Ar-H), 7.08 (d, ³J_{HH} = 7.9 Hz, 2H, Ar-H), 2.67 (s, 2H, CH₂), 2.33 (s, 3H, Ph-Me), 1.37 (s, 6H, C(CH₃)₂). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 183.8 (s), 137.9 (s), 131.6 (s), 129.1 (s), 120.7 (s), 85.6 (s), 83.1 (s), 42.5 (s), 30.4 (s), 24.6 (s), 21.6 (s). **HRMS** (ES⁺) *m/z* calculated for [C₁₄H₁₆O₂]⁺ [M]⁺: 216.1150, found: 216.1151.



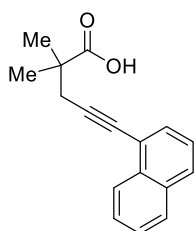
4.9c: Synthesised according to *General Procedure 5* using **4.9c'** (532 mg, 2.17 mmol, 1 equiv.) to give an off-white solid. Melting point: 104–108 °C. Yield: 501 mg, 2.17 mmol, 99%. **¹H NMR** (300 MHz, CDCl₃, 298 K) δ/ppm: 7.32 (d, ³J_{HH} = 8.0 Hz, 2H, Ar-H), 6.80 (d, ³J_{HH} = 7.9 Hz, 2H, Ar-H), 3.79 (s, 3H, OCH₃), 2.66 (s, 2H, CH₂), 1.36 (s, 6H, C(CH₃)₂). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 183.8 (s), 159.3 (s), 133.1 (s), 115.9 (s), 114.0 (s), 84.8 (s), 82.8 (s), 55.4 (s), 42.5 (s), 30.4 (s), 24.6 (s). **HRMS** (ES⁻) *m/z* calculated for [C₁₄H₁₅O₃]⁻ [M-H]⁻: 231.1021, found: 231.1015.



4.9d: Synthesised according to *General Procedure 5* using **4.9d'** (934 mg, 3.99 mmol, 1 equiv.) to give an off-white solid. Melting point: 77–82 °C. Yield: 879 mg, 3.99 mmol, 99%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.36 (dd, ³J_{HH} = 8.6 Hz, ⁴J_{HF} = 5.5 Hz, 2H, Ar-H), 6.96 (t, ³J_{HH} = 8.7 Hz, 2H, Ar-H), 2.67 (s, 2H, CH₂), 1.37 (s, 6H, C(CH₃)₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 182.7 (s), 162.4 (d, ¹J_{CF} = 250 Hz), 133.6 (d, ³J_{CF} = 8.3 Hz), 119.7 (s), 115.6 (d, ²J_{CF} = 22.0 Hz), 86.0 (s), 82.0 (s), 42.5 (s), 30.4 (s), 24.6 (s). **¹⁹F NMR** (376 MHz, CDCl₃, 298 K) δ/ppm: -111.84 (s, 1F, *p*-F). **HRMS** (EI⁺) *m/z* calculated for [C₁₃H₁₃O₂F]⁺ [M]⁺: 220.0900, found: 220.0898.

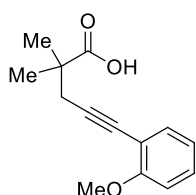


4.9e: Synthesised according to *General Procedure 5* using **4.9e'** (1.59 g, 5.6 mmol, 1 equiv.) to give an off-white solid. Melting point: 80–86 °C. Yield: 1.51 g, 5.6 mmol, 97%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.53–7.48 (m, 4H, Ar-H), 2.70 (s, 2H, CH₂), 1.37 (s, 6H, C(CH₃)₂). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 183.2 (s), 132.0 (s), 127.5 (s), 125.3 (q, ³J_{CF} = 3.8 Hz), 123.0 (s), 89.3 (s), 81.9 (s), 42.5 (s), 30.4 (s), 24.7 (s). **¹⁹F NMR** (471 MHz, CDCl₃, 298 K) δ/ppm: -62.80 (s, 3F, CF₃). **HRMS** (AP⁺) *m/z* calculated for [C₁₄H₁₄O₂F₃]⁺ [M+H]⁺: 271.0946, found: 271.0933.

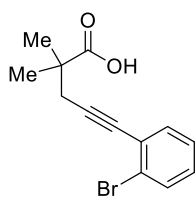


4.9f: Synthesised according to *General Procedure 5* using **4.9f'** (505 mg, 1.89 mmol, 1 equiv.) to give an off-white solid. Melting point: 118–122 °C. Yield: 476 mg, 1.89 mmol, 99%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 8.31 (d, ³J_{HH} = 8.3 Hz, 1H, Ar-H), 7.81 (d, ³J_{HH} = 8.0 Hz, 1H, Ar-H), 7.77 (d, ³J_{HH} = 8.2 Hz, 1H, Ar-H), 7.62 (d, ³J_{HH} = 7.0 Hz, 1H, Ar-H), 7.54 (t, ³J_{HH} = 7.1 Hz, 1H, Ar-H), 7.47 (d, ³J_{HH} = 7.1 Hz, 1H, Ar-H), 7.37 (d, ³J_{HH} = 7.7 Hz, 1H, Ar-H), 2.84 (s, 2H, CH₂), 1.44 (s, 6H, C(CH₃)₂). **¹³C NMR**

(126 MHz, CDCl₃, 298 K) δ /ppm: 183.7 (s), 133.6 (s), 133.3 (s), 130.4 (s), 128.3 (s), 128.3 (s), 126.8 (s), 126.4 (s), 126.4 (s), 125.3 (s), 121.4 (s), 91.5 (s), 81.1 (s), 42.7 (s), 30.8 (s), 24.8 (s). **HRMS** (EI⁺) m/z calculated for [C₁₇H₁₆O₂]⁺ [M]⁺: 252.1150, found: 252.1149.

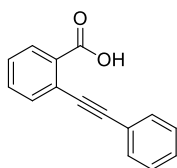


4.9g: Synthesised according to *General Procedure 5* using **4.9g'** (746 mg, 3.03 mmol, 1 equiv.) to give an off-white solid. Melting point 90–94 °C. Yield: 696 mg, 42.5 mmol, 99%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 7.36 (dd, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.5 Hz, 1H, Ar-H), 7.25 (td, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.6 Hz, 1H, Ar-H), 6.89–6.83 (m, 2H, Ar-H), 3.86 (s, 3H, OCH₃), 2.75 (s, 2H, CH₂), 1.40 (s, 6H, C(CH₃)₂). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 183.8 (s), 160.2 (s), 133.6 (s), 129.3 (s), 120.5 (s), 112.9 (s), 110.7 (s), 90.7 (s), 79.3 (s), 55.9 (s), 42.6 (s), 30.6 (s), 24.5 (s). **HRMS** (EI⁺) m/z calculated for [C₁₄H₁₆O₃]⁺ [M]⁺: 232.1099, found: 232.1095.

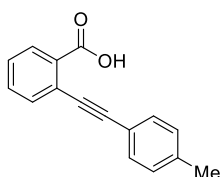


4.9h: Synthesised according to *General Procedure 5* using **4.9h'** (1.20 g, 4.07 mmol, 1 equiv.) to give an off-white solid. Melting point: 44–48 °C. Yield: 1.13 g, 4.07 mmol, 99%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 7.55 (dd, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 0.9 Hz, 1H, Ar-H), 7.43 (dd, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.5 Hz, 1H, Ar-H), 7.22 (td, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.1 Hz, 1H, Ar-H), 7.12 (td, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.6 Hz, 1H, Ar-H), 2.75 (s, 2H, CH₂), 1.42 (s, 6H, C(CH₃)₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 182.6 (s), 133.6 (s), 132.4 (s), 129.1 (s), 127.0 (s), 125.8 (s), 125.6 (s), 91.5 (s), 81.7 (s), 42.5 (s), 30.6 (s), 24.7 (s). **HRMS** (EI⁺) m/z calculated for [C₁₃H₁₃O₂Br]⁺ [M]⁺: 280.0099, found: 280.0090.

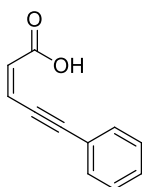
General Procedure 6: To a stirred solution of the ester in methanol (60 ml) was added aqueous NaOH (1.0 M, 2.7 equiv.) at ambient temperature and the reaction was stirred for 14 h. The reaction mixture was concentrated under reduced pressure. This was subsequently diluted with water (120 ml) and washed with Et₂O (3 x 30 ml). The aqueous phase was acidified (pH = 1–2) with HCl (1 M) and extracted with EtOAc (3 x 50 ml). The combined organic extracts were dried over MgSO₄, filtered and concentrated under reduced pressure to afford the pure free acid.



4.9i: Synthesised according to *General Procedure 6* using **4.9i'** (3.27 g, 13.84 mmol). The spectroscopic data agrees with literature established values.^[175] R_f value: 0.18 (SiO₂, CHCl₃). Yield: 2.84 g, 12.78 mmol, 92%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 8.15 (dd, ³ J_{HH} = 7.9, 1H, Ar-H), 7.70 (d, ³ J_{HH} = 7.7 Hz, 1H, Ar-H), 7.61–7.54 (m, 3H, Ar-H), 7.44 (td, ³ J_{HH} = 7.8, ⁴ J_{HH} = 1.2 Hz, 1H, Ar-H), 7.36–7.28 (m, 3H, Ar-H). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 171.1 (s), 134.2 (s), 132.6 (s), 131.8 (s), 131.4 (s), 130.5 (s), 128.7 (s), 128.4 (s), 128.0 (s), 124.4 (s), 123.1 (s), 95.5 (s), 88.0 (s).



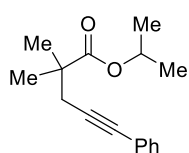
4.9j: Synthesised according to *General Procedure 6* using **4.9j'** (3.78 g, 15.1 mmol). R_f value: 0.23 (SiO₂, CHCl₃). Yield: 3.47 g, 15.1 mmol, 93%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 8.14 (d, ³ J_{HH} = 7.8 Hz, 1H, Ar-H), 7.68 (d, ³ J_{HH} = 7.5 Hz, 1H, Ar-H), 7.55 (t, ³ J_{HH} = 7.6 Hz, 1H, Ar-H), 7.47 (d, ³ J_{HH} = 7.7 Hz, 2H, Ar-H), 7.42 (t, ³ J_{HH} = 7.6 Hz, 1H, Ar-H), 7.12 (d, ³ J_{HH} = 7.7 Hz, 2H, Ar-H), 2.35 (s, ³ J_{HH} = 13.8 Hz, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 171.8 (s), 138.9 (s), 134.2 (s), 132.7 (s), 131.8 (s), 131.5 (s), 130.6 (s), 129.3 (s), 127.9 (s), 124.8 (s), 120.2 (s), 95.9 (s), 87.6 (s), 21.7 (s).



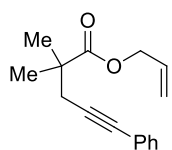
4.9k: Synthesised by dissolving **4.9k'** in THF (50 ml) and treating with 1M LiOH solution (50 ml, 21.00 mmol 2.38 equiv.). The mixture was stirred vigorously overnight. The solution was concentrated under vacuum and cooled down to 0 °C. Sulfuric acid (1 M) was added dropwise until a pH of 1 is reached. The suspension was extracted with ethylacetate (3 x 50 ml) and dried with MgSO₄ and concentrated under vacuum to obtain the product as bright yellow crystals. The spectroscopic data agrees with literature established values.^[177] Yield: 3.55 g, 20.6 mmol, 98%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 7.52 (d, ³ J_{HH} = 6.9 Hz, 2H, Ar-H), 7.40–7.29 (m, 3H, Ar-H), 6.49 (d, ³ J_{HH} = 11.3 Hz, 1H, Ar-H), 6.19 (d, ³ J_{HH} = 11.3 Hz, 1H, Ar-H). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 169.2 (s), 132.2 (s), 129.5 (s), 128.5 (s), 127.3 (s), 125.2 (s), 122.4 (s), 103.2 (s), 86.2 (s).

General Procedure 7: The carboxylic acid (1 equiv.) was dissolved in CH₂Cl₂. After addition of 4-dimethylaminopyridine (7 mol%) and the alcohol (1–3 equiv.), the reaction mixture was cooled down to 0 °C and *N,N'*-dicyclohexylcarbodiimide (1.1 equiv.) was added. After 5 minutes the solution was warmed to room temperature, and stirred for 3 h. The mixture was filtered to remove the resulting urea. The filtrate

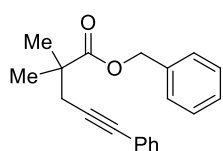
was washed twice with aq. HCl (0.5 M), then washed with a saturated aq. NaHCO₃ solution and dried using MgSO₄. The obtained residue was purified by column chromatography (SiO₂, 100% chloroform) to give the ester.



4.10a: Synthesised according to *General Procedure 7* using compound **4.9a** (750 mg, 3.7 mmol, 1 equiv.) and 2-propanol (11.1 mmol, 1.2 g, 3 equiv.) giving a yellow oil. R_f value: 0.64. Yield: 115 mg, 0.47 mmol, 13%. ¹H NMR (500 MHz, CDCl₃, 298 K) δ/ppm: 7.43–7.21 (m, 5H, Ar-H), 5.01 (hept, ³J_{HH} = 6.2 Hz, 1H, CH(CH₃)₂), 2.62 (s, 2H, CH₂), 1.30 (s, 6H, C(CH₃)₂), 1.23 (d, ³J_{HH} = 6.3 Hz, 6H, OC(CH₃)₂). ¹³C NMR (126 MHz, CDCl₃, 298 K) δ/ppm: 176.4 (s), 131.7 (s), 128.3 (s), 127.8 (s), 123.9 (s), 87.0 (s), 82.7 (s), 67.9 (s), 42.5 (s), 30.7 (s), 24.7 (s), 21.9 (s). IR ν_{max} (cm⁻¹): 2981 (m), 1723 (s), 1601 (w), 1491 (m), 1471 (m), 1391 (w), 1385 (m), 1375 (m), 1302 (w), 1249 (w), 1199 (m), 1143 (m), 1106 (s), 1023 (w), 927 (w), 877 (w), 831 (w), 755 (s), 692 (s), 526 (m). HRMS (ES⁺) *m/z* calculated for [C₁₆H₂₁O₂]⁺ [M+H]⁺: 245.1542, found: 245.1536.

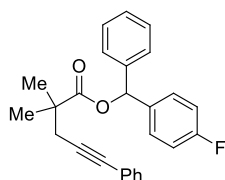


4.10b: Synthesised according to *General Procedure 7* using compound **4.9a** (500 mg, 2.5 mmol, 1 equiv.) and allyl alcohol (0.80 g, 7.4 mmol, 3 equiv.) to give a yellow oil. R_f value: 0.67. Yield: 334 mg, 1.38 mmol, 56%. ¹H NMR (500 MHz, CDCl₃, 298 K) δ/ppm: 7.42–7.24 (m, 5H, Ar-H), 5.97–5.88 (m, 1H, -CH=), 5.28 (dd, ²J_{HH} = 61.3 Hz ³J_{HH} = 13.9 Hz 2H, =CH₂), 4.62 (d, ³J_{HH} = 5.4 Hz 2H, OCH₂-), 2.68 (s, 2H, CH₂), 1.36 (s, 6H, C(CH₃)₂). ¹³C NMR (126 MHz, CDCl₃, 298 K) δ/ppm: 176.5 (s), 132.4 (s), 131.7 (s), 128.3 (s), 127.9 (s), 123.8 (s), 117.9 (s), 86.8 (s), 82.9 (s), 65.4 (s), 42.8 (s), 30.7 (s), 24.8 (s). IR ν_{max} (cm⁻¹): 2977 (w), 1730 (s), 1650 (w), 1597 (w), 1488 (m), 1471 (m), 1388 (w), 1365 (w), 1322 (m), 1246 (m), 1196 (m), 1130 (s), 1070 (w), 984 (m), 924 (m), 848 (w), 755 (s), 692 (s), 526 (w). HRMS (ES⁺) *m/z* calculated for [C₁₆H₁₉O₂]⁺ [M+H]⁺: 243.1385, found: 243.1380.

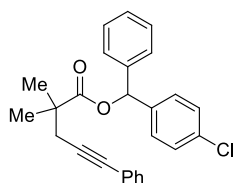


4.10c: Synthesised according to *General Procedure 7* using compound **4.9a** (2.0 g, 9.89 mmol, 1 equiv.) and benzyl alcohol (3.2 g, 30 mmol, 3 equiv.) to give a yellow oil. R_f value: 0.85. Yield: 1.85 g, 6.34 mmol, 64%. ¹H NMR (500 MHz, CDCl₃, 298 K) δ/ppm: 7.37–7.23 (m, 10H, Ar-H), 5.15 (s, 2H, OCH₂-), 2.68 (s, 2H, CH₂), 1.35 (s, 6H, C(CH₃)₂). ¹³C NMR (126 MHz, CDCl₃, 298 K) δ/ppm: 176.6 (s), 136.2 (s), 131.6 (s), 128.5 (s), 128.2 (s), 128.0 (s), 127.8 (s), 127.7 (s), 123.6 (s), 86.6 (s), 82.8 (s), 66.5

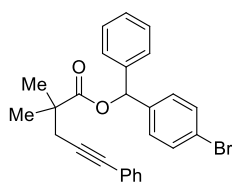
(s), 42.7 (s), 30.6 (s), 24.7 (s). **IR** ν_{\max} (cm^{-1}): 2974 (w), 1730 (s), 1597 (w), 1491 (m), 1458 (m), 1388 (w), 1319 (w), 1299 (w), 1246 (w), 1193 (m), 1126 (s), 984 (w), 751 (s), 692 (s), 529 (m). **HRMS** (ES^+) m/z calculated for $[\text{C}_{20}\text{H}_{21}\text{O}_2]^+$ $[\text{M}+\text{H}]^+$: 292.1463, found: 292.1452.



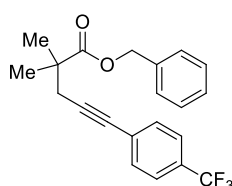
4.10d: Synthesised according to *General Procedure 7* using compound **4.9a** (800 mg, 3.96 mmol, 1 equiv.) and 4-fluorobenzhydryl (840 mg, 4.15 mmol, 1.05 equiv.) giving a white solid. R_f value: 0.72. Yield: 605 mg, 1.57 mmol, 40%. Melting point: 79–85 °C. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ/ppm : 7.37–7.25 (m, 12, Ar-H), 6.98–6.90 (m, 2H, Ar-H), 6.85 (s, 1H, C(H)Ar₂), 2.71 (s, 2H, CH₂), 1.37 (s, 6H, C(CH₃)₂). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3 , 298 K) δ/ppm : 175.7 (s), 162.4 (d, $^1J_{\text{CF}} = 246$ Hz), 140.2 (s), 136.3 (s), 131.7 (s), 129.1 (d, $^4J_{\text{CF}} = 8.2$ Hz), 128.5 (d, $^2J_{\text{CF}} = 50.2$ Hz), 128.0 (d, $^3J_{\text{CF}} = 16.8$ Hz), 127.0 (s), 123.6 (s), 115.5 (s), 115.3 (s), 86.5 (s), 83.0 (s), 42.9 (s), 31.1 (s), 30.7 (s), 24.9 (s), 24.8 (s). **$^{19}\text{F NMR}$** (471 MHz, CDCl_3 , 298 K) δ/ppm : -114.33 (s, 1F, *p*-F). **IR** ν_{\max} (cm^{-1}): 2977 (w), 1727 (s), 1607 (w), 1511 (s), 1491 (m), 1468 (w), 1455 (w), 1388 (w), 1368 (w), 1322 (m), 1305 (m), 1226 (m), 1199 (s), 1163 (s), 1133 (s), 1103 (w), 1073 (w), 1023 (w), 1000 (w), 917 (w), 861 (w), 828 (m), 811 (w), 788 (m), 758 (s), 741 (m), 692 (s), 645 (w), 629 (w), 582 (m), 556 (s), 506 (m). **HRMS** (ES^+) m/z calculated for $[\text{C}_{26}\text{H}_{24}\text{FO}_2]^+$ $[\text{M}+\text{H}]^+$: 387.1759, found: 387.1760.



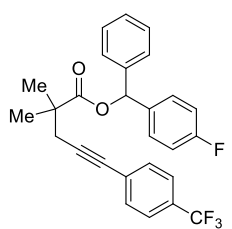
4.10e: Synthesised according to *General Procedure 7* using compound **4.9a** (900 mg, 4.5 mmol, 1 equiv.) and 4-chlorobenzhydryl (1.07 g, 4.89 mmol, 1.1 equiv.) to give a white solid. R_f value: 0.83. Yield: 452 mg, 1.12 mmol, 26%. Melting point: 62–67 °C. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ/ppm : 7.37–7.27 (m, 14H, Ar-H), 6.85 (s, 1H, C(H)Ar₂), 2.73 (s, 2H, CH₂), 1.40 (s, 6H, C(CH₃)₂). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3 , 298 K) δ/ppm : 175.6 (s), 139.9 (s), 139.0 (s), 133.9 (s), 131.7 (s), 128.8 (s), 128.7 (s), 128.6 (s), 128.3 (s), 128.2 (s), 127.9 (s), 127.0 (s), 123.6 (s), 86.6 (s), 83.1 (s), 76.6 (s), 43.0 (s), 30.7 (s), 24.9 (s), 24.9 (s). **IR** ν_{\max} (cm^{-1}): 2977 (w), 1723 (s), 1601 (w), 1494 (s), 1458 (w), 1388 (w), 1302 (m), 1193 (s), 1166 (m), 1133 (s), 1093 (m), 1020 (m), 997 (m), 987 (m), 914 (q), 858 (q), 814 (m), 788 (m), 758 (s), 721 (m), 698 (s), 642 (w), 622 (w), 582 (m), 549 (w), 516 (m), 489 (m), 413 (w). **HRMS** (ES^+) m/z calculated for $[\text{C}_{26}\text{H}_{24}\text{O}_2\text{Cl}]^+$ $[\text{M}+\text{H}]^+$: 403.1465, found: 403.1452.



4.10f: Synthesised according to *General Procedure 7* using compound **4.9a** (800 mg, 3.96 mmol, 1 equiv.) and 4-bromobenzhydrol (1.1 g, 4.15 mmol, 1.05 equiv.) to give a white solid. R_f value: 0.72. Yield: 795 mg, 1.78 mmol, 45%. Melting point: 70–76 °C **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ /ppm: 7.32 (d, $^3J_{\text{HH}} = 8.3$ Hz, 2H, Ar-H), 7.27–7.18 (m, 10H, Ar-H), 7.15 (d, $^3J_{\text{HH}} = 8.3$ Hz, 2H, Ar-H), 6.74 (s, 1H, C(H)Ar₂), 2.64 (s, 2H, CH₂), 1.30 (s, 6H, C(CH₃)₂) **$^{13}\text{C NMR}$** (126 MHz, CDCl_3 , 298 K) δ /ppm: 175.6 (s), 139.8 (s), 139.5 (s), 131.8 (s), 131.7 (s), 129.0 (s), 128.7 (s), 128.3 (s), 128.2 (s), 128.0 (s), 127.0 (s), 123.6 (s), 122.0 (s), 86.6 (s), 83.2 (s), 76.6 (s), 43.0 (s), 30.8 (s), 24.9 (s), 24.9 (s). **IR** ν_{max} (cm⁻¹): 2984 (w), 1727 (s), 1601 (w), 1487 (s), 1469 (w), 1456 (w), 1444 (w), 1397 (w), 1388 (w), 1325 (w), 1316 (w), 1296 (w), 1195 (s), 1162 (m), 1135 (s), 1071 (m), 1023 (w), 1001 (m), 916 (w), 859 (w), 814 (w), 785 (m), 753 (s), 711 (w), 702 (s), 693 (s), 666 (w), 625 (w), 583 (m), 548 (w), 523 (w), 506 (w), 477 (w). **HRMS** (ES⁺) m/z calculated for [C₂₆H₂₄O₂Br]⁺ [M+H]⁺: 447.0960, found: 447.0962.

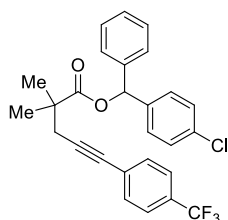


4.10g: Synthesised according to *General Procedure 7* using compound **4.9e** (1.0 g, 3.7 mmol, 1 equiv.) and benzylalcohol (420 mg, 3.89 mmol, 1.05 equiv.) to give a yellow oil. R_f value: 0.76. Yield: 805 mg, 2.23 mmol, 61%. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ /ppm: 7.55–7.38 (m, 4H, Ar-H), 7.38–7.28 (m, 5H, Ar-H), 5.16 (s, 2H, OCH₂-), 2.70 (s, 2H, CH₂), 1.37 (s, 6H, C(CH₃)₂). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3 , 298 K) δ /ppm: 176.4 (s), 136.2 (s), 132.0 (s), 129.6 (q, $^2J_{\text{CF}} = 32.6$ Hz), 128.6 (s), 128.3 (s), 128.2 (s), 128.0 (s), 125.2 (q, $^3J_{\text{CF}} = 3.8$ Hz), 89.7 (s), 81.8 (s), 66.6 (s), 42.8 (s), 42.8 (s), 30.8 (s), 24.9 (s). **$^{19}\text{F NMR}$** (471 MHz, CDCl_3 , 298 K) δ /ppm: -62.77 (s, 3F, CF₃). **IR** ν_{max} (cm⁻¹): 2977 (w), 1730 (s), 1617 (w), 1471 (w), 1458 (w), 1405 (w), 1322 (s), 1242 (w), 1166 (m), 1123 (s), 1066 (s), 1017 (w), 841 (m), 741 (w), 695 (m), 599 (w). **HRMS** (ES⁺) m/z calculated for [C₂₁H₂₀O₂F₃]⁺ [M+H]⁺: 361.1415, found: 361.1418.



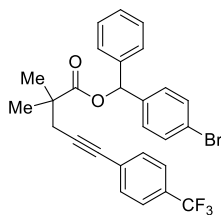
4.10h: Synthesised according to *General Procedure 7* using compound **4.9e** (1.0 g, 3.70 mmol, 1 equiv.) and 4-fluorobenzhydrol (790 mg, 3.89 mmol, 1.05 equiv.) to give a white solid. R_f value: 0.78. Yield: 405 mg, 1.68 mmol, 24%. Melting point: 68–75 °C. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ /ppm: 7.54–7.47 (m, 2H, Ar-H), 7.37–7.27 (m, 9H, Ar-H), 7.01–6.92 (m, 2H, Ar-H), 6.86 (s, 1H, C(H)Ar₂), 2.72 (s, 2H, CH₂), 1.38 (s, 6H, C(CH₃)₂). **$^{13}\text{C NMR}$** *partial* (126 MHz, CDCl_3 , 298 K) δ /ppm: 175.4 (s), 162.3 (d, $^1J_{\text{CF}} = 246$ Hz), 140.1 (s), 136.2 (s), 132.0 (s), 129.1

(d, $^3J_{\text{CF}} = 8.1$ Hz), 128.7 (s), 128.1 (s), 127.4 (s), 127.0 (s), 125.2 (q, $^3J_{\text{CF}} = 3.9$ Hz), 115.6 (d, $^2J_{\text{CF}} = 21.6$ Hz), 89.5 (s), 82.0 (s), 76.6 (s), 42.9 (s), 31.1 (s), 30.8 (s), 24.9 (s), 24.9 (s). **^{19}F NMR** (471 MHz, CDCl_3 , 298 K) δ/ppm : -62.78 (s, 3F, CF_3), -114.33 (s, 1F, *p*-F). **IR** ν_{max} (cm^{-1}): 2974 (w), 1733 (m), 1717 (m), 1611 (w), 1511 (m), 1471 (w), 1451 (w), 1405 (w), 1322 (s), 1229 (m), 1166 (s), 1126 (s), 1103 (s), 1066 (s), 1017 (m), 987 (m), 911 (w), 841 (s), 828 (m), 788 (w), 765 (w), 738 (m), 698 (s), 649 (w), 625 (w), 599 (m), 556 (m), 509 (m).



4.10i: Synthesised according to *General Procedure 7* using compound **4.9e** (1.0 g, 3.7 mmol, 1 equiv.) and 4-chlorobenzhydrol (850 mg, 3.9 mmol, 1.05 equiv.) to give a white solid. R_f value: 0.74. Yield: 750 mg, 1.59 mmol, 43%. Melting point: 67–74 °C. **^1H NMR** (500 MHz, CDCl_3 , 298 K) δ/ppm : 7.53

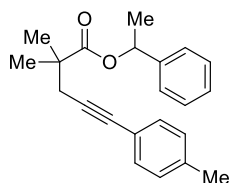
(br. s, 2H, Ar-H), 7.33–7.29 (m, 11H, Ar-H), 6.87 (s, 1H, C(H)Ar₂), 2.74 (s, 2H, CH₂), 1.40 (s, 6H, C(CH₃)₂). **^{13}C NMR** (126 MHz, CDCl_3 , 298 K) δ/ppm : 175.4 (s), 139.8 (s), 138.9 (s), 134.0 (s), 131.9 (s), 128.9 (s), 128.8 (s), 128.7 (s), 128.2 (s), 127.0 (s), 89.4 (s), 76.6 (s), 42.9 (s), 30.8 (s), 25.0 (s), 24.9 (s). **^{19}F NMR** (376 MHz, CDCl_3 , 298 K) δ/ppm : -62.69 (s, 3F, CF_3). **IR** ν_{max} (cm^{-1}): 2978 (w), 1731 (s), 1614 (w), 1494 (m), 1471 (w), 1451 (w), 1404 (w), 1394 (w), 1324 (s), 1301 (m), 1194 (m), 1164 (s), 1120 (s), 1104 (s), 1067 (s), 1020 (m), 1000 (m), 960 (w), 910 (w), 844 (s), 817 (s), 787 (m), 760 (m), 717 (m), 697 (s), 620 (w), 597 (w), 570 (m), 517 (m), 490 (m).



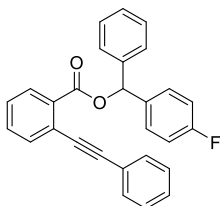
4.10j: Synthesised according to *General Procedure 7* using compound **4.9e** (1.0 g, 3.7 mmol, 1 equiv.) and 4-bromobenzhydrol (3.89 mmol, 1.0 g, 1.05 equiv.) R_f value: 0.61. Yield: 577 mg, 1.12 mmol, 31%. Melting point: 74–80 °C. **^1H NMR** (500 MHz, CDCl_3 , 298 K) δ/ppm : 7.51 (d, $^3J_{\text{HH}} = 8.1$ Hz, 2H, Ar-

H), 7.39 (d, $^3J_{\text{HH}} = 8.1$ Hz, 2H, Ar-H), 7.33–7.27 (m, 7H, Ar-H), 7.39 (d, $^3J_{\text{HH}} = 8.3$ Hz, 2H, Ar-H), 6.82 (s, 1H, C(H)Ar₂), 2.72 (s, 2H, CH₂), 1.38 (s, 6H, C(CH₃)₂). **^{13}C NMR partial** (126 MHz, CDCl_3 , 298 K) δ/ppm : 175.4 (s), 139.8 (s), 139.4 (s), 131.9 (s), 131.8 (s), 129.0 (s), 128.8 (s), 128.2 (s), 127.0 (s), 125.2 (q, $^3J_{\text{CF}} = 3.8$ Hz), 122.1 (s), 89.4 (s), 82.0 (s), 76.7 (s), 43.0 (s), 30.8 (s), 25.0 (s), 24.9 (s). **^{19}F NMR** (376 MHz, CDCl_3 , 298 K) δ/ppm : -62.77 (s, 3F, CF_3). **IR** ν_{max} (cm^{-1}): 2987 (w), 1730 (w), 1617 (w), 1491 (w), 1475 (w), 1455 (w), 1405 (w), 1388 (w), 1322 (s), 1302 (m), 1196 (m), 1163 (s), 1116 (s), 1106 (s), 1066 (s), 1017 (m), 997 (m), 957 (w), 914 (w), 841 (s), 818 (m), 788 (w), 751 (s), 715 (m), 698 (m), 672 (w), 622 (w), 599 (m), 572 (m), 519

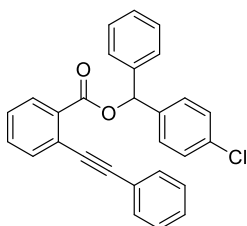
(w), 506 (m), 493 (m). **HRMS** (ES)⁺ *m/z* calculated for [C₂₆H₂₃O₂]⁺ [M+H]⁺: 515.0834, found: 515.0834.



4.10k: Synthesised according to *General Procedure 7* using compound **4.9b** (0.216 g, 1.07 mmol) *N,N'*-dicyclohexylcarbodiimide (0.243 g, 1.18 mmol, 1.1 equiv.), 4-dimethylaminopyridine (9 mg, 7 mol%) and 1-phenylethanol (0.14 ml, 0.143 g, 1.17 mmol, 1.1 equiv.) giving a colourless oil. *R_f* value: 0.26 (SiO₂, 1:1, hexane/CHCl₃) Yield: 82 mg, 0.26 mmol, 24%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.42–7.24 (m, 7H, Ar-H), 7.10 (d, ³*J*_{HH} = 5.8 Hz, 2H, Ar-H), 5.98–5.89 (m, 1H, C(H)CH₃), 2.70 (s, 2H, CH₂), 2.36 (s, 3H, CH₃), 1.61–1.58 (m, 3H, CH₃), 1.38 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 176.1 (s), 142.0 (s), 137.8 (s), 131.6 (s), 129.1 (s), 128.6 (s), 127.8 (s), 126.0 (s), 120.7 (s), 86.0 (s), 82.9 (s), 72.6 (s), 42.7 (s), 30.7 (s), 24.8 (s), 24.8 (s), 22.5 (s), 21.6 (s). **HRMS** (ES⁺) *m/z* calculated for [C₂₂H₂₄O₂]⁺ [M+H]⁺: 321.1855, found 321.1842.

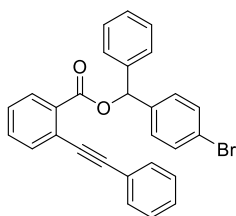


4.10l: Synthesised according to *General Procedure 7* using compound **4.9i** (0.60 g, 2.7 mmol) and 4-fluorobenzhydrol (0.610 g, 2.97 mmol, 1.1 equiv.) giving a colourless oil. *R_f* value: 0.63 (SiO₂, CHCl₃). Yield: 0.876 g, 2.16 mmol, 80%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 8.06 (d, ³*J*_{HH} = 8.0 Hz, 1H, Ar-H), 7.67 (d, ³*J*_{HH} = 7.0 Hz, 1H, Ar-H), 7.52 (t, ³*J*_{HH} = 7.4 Hz, 1H, Ar-H), 7.48–7.27 (m, 13H, Ar-H), 7.16 (s, 1H, C(H)Ar₂), 6.95 (t, ³*J*_{HH} = 8.1 Hz, 2H, Ar-H). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 165.5 (s), 162.5 (d, ¹*J*_{CF} = 247 Hz), 140.1 (s), 136.2 (d, ⁴*J*_{CF} = 3.2 Hz), 134.6 (s), 132.1 (s), 131.8 (s), 131.6 (s), 131.0 (s), 129.36 (d, ³*J*_{CF} = 8.2 Hz), 128.7 (s), 128.6 (s), 128.4 (s), 128.1 (s), 128.1 (s), 127.3 (s), 124.0 (s), 123.3 (s), 115.5 (d, ²*J*_{CF} = 21.6 Hz), 94.8 (s), 88.5 (s), 77.4 (s). **¹⁹F NMR** (376 MHz, CDCl₃, 298 K) δ/ppm: -114.31 (s, 1F, *p*-F). **HRMS** (ES⁺) *m/z* calculated for [C₂₈H₂₀FO₂]⁺ [M+H]⁺: 407.1447, found: 407.1441.

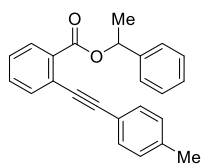


4.10m: Synthesised according to *General Procedure 7* using compound **4.9i** (0.60 g, 2.7 mmol) and 4-chlorobenzhydrol (0.650 g, 2.97 mmol, 1.1 equiv.) giving a colourless oil. *R_f* value: 0.64 (SiO₂, CHCl₃). Yield: 1.06 g, 2.51 mmol, 93%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 8.06 (d, ³*J*_{HH} = 7.8 Hz, 1H, Ar-H), 7.67 (d, ³*J*_{HH} = 7.6 Hz, 1H, Ar-H), 7.52 (t, ³*J*_{HH} = 7.5 Hz, 1H, Ar-H), 7.47–7.21 (m, 16H, Ar-H), 7.13 (s, 1H, C(H)Ar₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 165.4 (s),

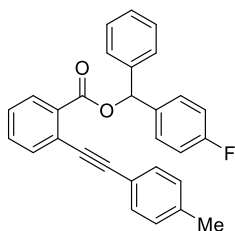
139.8 (s), 138.9 (s), 134.6 (s), 134.0 (s), 132.1 (s), 131.8 (s), 131.6 (s), 131.0 (s), 128.9 (s), 128.8 (s), 128.8 (s), 128.7 (s), 128.4 (s), 128.2 (s), 128.2 (s), 127.3 (s), 124.0 (s), 123.2 (s), 94.8 (s), 88.5 (s), 77.5 (s). **HRMS** (ES⁺) *m/z* calculated for [C₂₈H₂₀ClO₂]⁺ [M+H]⁺: 423.1152, found: 423.1164.



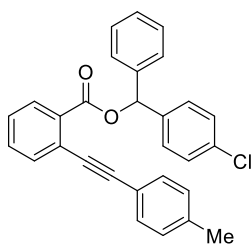
4.10n: Synthesised according to *General Procedure 7* using compound **4.9i** (0.60 g, 2.7 mmol) and 4-bromobenzhydrol (0.790 g, 2.97 mmol, 1.1 equiv.) giving a colourless oil. R_f value: 0.65 (SiO₂, CHCl₃). Yield: 1.04 g, 2.23 mmol, 83%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 8.05 (d, ³J_{HH} = 7.8 Hz, 1H, Ar-H), 7.67 (d, ³J_{HH} = 7.5 Hz, 1H, Ar-H), 7.52 (t, ³J_{HH} = 7.6 Hz, 1H, Ar-H), 7.36 (dd, ³J_{HH} = 13.8, ³J_{HH} = 7.0 Hz, 16H, Ar-H), 7.11 (s, 1H, C(H)Ar₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 165.5 (s), 139.7 (s), 139.4 (s), 134.6 (s), 132.1 (s), 131.8 (s), 131.8 (s), 131.5 (s), 131.0 (s), 129.2 (s), 129.2 (s), 128.8 (s), 128.7 (s), 128.4 (s), 128.2 (s), 128.2 (s), 127.3 (s), 124.0 (s), 123.2 (s), 122.1 (s), 94.8 (s), 88.5 (s), 77.5 (s). **HRMS** (ES⁺) *m/z* calculated for [C₂₈H₂₀BrO₂]⁺ [M+H]⁺: 467.0647, found: 467.0668.



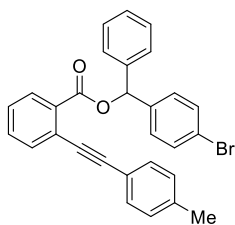
4.10o: Synthesised according to *General Procedure 7* using compound **4.9j** (0.750 g, 3.18 mmol), *N,N*-dicyclohexylcarbodiimide (0.720 g, 3.50 mmol, 1.1 equiv.), 4-dimethylaminopyridine (27 mg, 7 mol%) and 1-phenylethanol (0.42 ml, 0.426 g, 3.49 mmol, 1.1 equiv.) giving a very light pink solid. R_f value: 0.25 (SiO₂, 1:1, hexane/CHCl₃) Yield: 657 mg, 2.01 mmol, 63%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.99 (dd, ³J_{HH} = 7.6, ⁴J_{HH} = 2.7 Hz, 1H, Ar-H), 7.65 (dd, ³J_{HH} = 7.5, ⁴J_{HH} = 2.6 Hz, 1H, Ar-H), 7.52–7.44 (m, 3H, Ar-H), 7.44–7.25 (m, 7H, Ar-H), 7.15 (d, ³J_{HH} = 5.1 Hz, 2H, Ar-H), 6.23–6.14 (m, 1H, C(H)CH₃), 2.37 (d, ³J_{HH} = 2.9 Hz, 3H, CH₃), 1.71–1.65 (m, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 165.8 (s), 141.8 (s), 138.7 (s), 134.3 (s), 132.2 (s), 131.7 (s), 131.7 (s), 130.7 (s), 129.2 (s), 128.6 (s), 127.9 (s), 127.9 (s), 126.4 (s), 124.0 (s), 120.4 (s), 94.7 (s), 87.9 (s), 73.5 (s), 22.7 (s), 21.7 (s). **HRMS** (ES⁺) *m/z* calculated for [C₂₄H₂₀O₂]⁺ [M+H]⁺: 341.1542, found: 341.1538.



4.10p: Synthesised according to *General Procedure 7* using compound **4.9j** (0.60 g, 2.54 mmol) and 4-fluorobenzhydrol (0.570 g, 2.79 mmol, 1.1 equiv.) giving a colourless oil. R_f value: 0.65 (SiO₂, CHCl₃). Yield: 0.725 g, 1.72 mmol, 68%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 7.98 (d, $^3J_{\text{HH}} = 7.9$ Hz, 1H, Ar-H), 7.59 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H, Ar-H), 7.43 (t, $^3J_{\text{HH}} = 7.3$ Hz, 1H, Ar-H), 7.41–7.15 (m, 10H, Ar-H), 7.08 (s, 1H, C(H)Ar₂), 7.03 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H, Ar-H), 6.88 (t, $^3J_{\text{HH}} = 8.3$ Hz, 2H, Ar-H), 2.29 (s, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 165.5 (s), 162.5 (d, $^1J_{\text{CF}} = 247$ Hz), 140.1 (s), 138.8 (s), 136.2 (d, $^4J_{\text{CF}} = 3.2$ Hz), 134.5 (s), 132.0 (s), 131.7 (s), 131.5 (s), 131.0 (s), 129.4 (d, $^3J_{\text{CF}} = 8.2$ Hz), 129.2 (s), 128.7 (s), 128.1 (s), 127.9 (s), 127.3 (s), 124.2 (s), 120.2 (s), 115.5 (d, $^2J_{\text{CF}} = 21.6$ Hz), 95.1 (s), 88.0 (s), 77.4 (s), 21.7 (s). **¹⁹F NMR** (376 MHz, CDCl₃, 298 K) δ /ppm: -114.36 (s). **HRMS** (ES⁺) m/z calculated for [C₂₉H₂₂FO₂]⁺ [M+H]⁺: 421.1604, found: 421.1604.

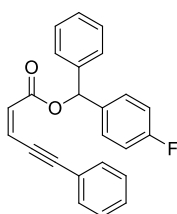


4.10q: Synthesised according to *General Procedure 7* using compound **4.9j** (0.60 g, 2.54 mmol) and 4-chlorobenzhydrol (0.61 g, 2.79 mmol, 1.1 equiv.) giving a colourless oil. R_f value: 0.67 (SiO₂, CHCl₃). Yield: 1.07 g, 2.45 mmol, 96%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 8.07 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H, Ar-H), 7.68 (d, $^3J_{\text{HH}} = 7.6$ Hz, 1H, Ar-H), 7.53 (t, $^3J_{\text{HH}} = 7.6$ Hz, 1H, Ar-H), 7.49–7.22 (m, 12H, Ar-H), 7.14 (d, $^3J_{\text{HH}} = 8.3$ Hz, 2H, Ar-H), 7.11 (s, 1H, C(H)Ar₂), 2.39 (s, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 165.5 (s), 139.9 (s), 138.9 (s), 138.9 (s), 134.5 (s), 133.9 (s), 132.1 (s), 131.7 (s), 131.5 (s), 131.0 (s), 129.2 (s), 129.0 (s), 128.8 (s), 128.8 (s), 128.2 (s), 128.0 (s), 127.3 (s), 124.2 (s), 120.2 (s), 95.1 (s), 87.9 (s), 77.5 (s), 21.7 (s). **HRMS** (ES⁺) m/z calculated for [C₂₉H₂₂ClO₂]⁺ [M+H]⁺: 437.1309, found: 437.1308.

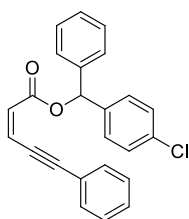


4.10r: Synthesised according to *General Procedure 7* using compound **4.9j** (0.600 g, 2.54 mmol) and 4-bromobenzhydrol (0.740 g, 2.79 mmol, 1.1 equiv.) giving a colourless oil. R_f value: 0.70 (SiO₂, CHCl₃). Yield: 1.18 g, 15.1 mmol, 97%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 8.07 (d, $^3J_{\text{HH}} = 7.9$ Hz, 1H, Ar-H), 7.68 (d, $^3J_{\text{HH}} = 7.9$ Hz, 1H, Ar-H), 7.53 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H, Ar-H), 7.49–7.23 (m, 15H, Ar-H), 7.14 (s, 2H, Ar-H), 7.12 (s, 1H, C(H)Ar₂), 2.39 (s, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 165.5 (s), 139.8 (s), 139.4 (s), 138.9 (s), 134.5 (s), 132.1 (s), 131.8 (s), 131.7 (s), 131.5 (s), 131.0 (s), 129.2 (s), 128.8 (s), 128.2 (s), 128.0 (s),

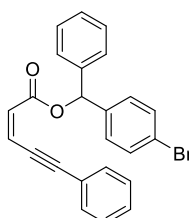
127.3 (s), 124.2 (s), 122.1 (s), 120.2 (s), 95.1 (s), 87.9 (s), 77.5 (s), 21.7 (s). **HRMS** (ES⁺) *m/z* calculated for [C₂₉H₂₂BrO₂]⁺ [M+H]⁺: 481.0803, found: 481.0825.



4.10s: Synthesised according to *General Procedure 7* using compound **4.9k** (0.500 g, 2.9 mmol) and 4-fluorobenzhydrol (0.646 g, 3.19 mmol, 1.1 equiv.) giving a yellow oil. R_f value: 0.44 (chloroform). Yield: 0.946 g, 2.65 mmol, 91%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.46–7.27 (m, 12H, Ar-H), 7.01 (s, 1H, C(H)Ar₂), 6.97 (t, ³J_{HH} = 8.2 Hz, 2H, Ar-H), 6.44 (d, ³J_{HH} = 11.7 Hz, 1H, =CH), 6.21 (d, ³J_{HH} = 11.5 Hz, 1H, =CH). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 163.9 (s), 162.5 (d, ¹J_{CF} = 247 Hz), 140.1 (s), 136.2 (d, ⁴J_{CF} = 3.1 Hz), 132.1 (s), 129.4 (s), 129.3 (d, ³J_{CF} = 8.2 Hz), 128.7 (s), 128.5 (s), 128.1 (s), 127.9 (s), 127.3 (s), 123.7 (s), 122.6 (s), 115.5 (d, ²J_{CF} = 21.6 Hz), 102.1 (s), 86.6 (s), 76.6 (s). **¹⁹F NMR** (376 MHz, CDCl₃, 298 K) δ/ppm: -114.30 (s, 1F, *p*-F). **HRMS** (ES⁺) *m/z* calculated for [C₂₄H₁₇FO₂]⁺ [M]⁺: 356.1213, found: 356.1210.



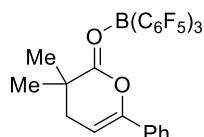
4.10t: Synthesised according to *General Procedure 7* using compound **4.9k** (0.500 g, 2.9 mmol) and 4-chlorobenzhydrol (0.699 g, 3.19 mmol, 1.1 equiv.) giving a yellow oil. R_f value: 0.49 (SiO₂, CHCl₃). Yield: 0.797 g, 2.14 mmol, 74%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.41–7.26 (m, 14H, Ar-H), 6.99 (s, 1H, C(H)Ar₂), 6.45 (d, ³J_{HH} = 11.5 Hz, 1H, =CH), 6.21 (d, ³J_{HH} = 11.6 Hz, 1H, =CH). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 163.9 (s), 139.8 (s), 138.9 (s), 133.9 (s), 132.1 (s), 129.4 (s), 128.8 (s), 128.8 (s), 128.8 (s), 128.5 (s), 128.2 (s), 127.8 (s), 127.3 (s), 123.8 (s), 122.6 (s), 102.1 (s), 86.6 (s), 76.6 (s). **HRMS** (ES⁺) *m/z* calculated for [C₂₄H₁₇ClO₂]⁺ [M]⁺: 372.0917, found: 372.0919.



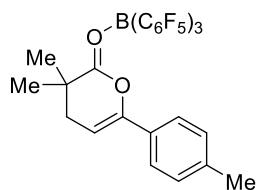
4.10u: Synthesised according to *General Procedure 7* using compound **4.9k** (0.500 g, 2.9 mmol) and 4-bromobenzhydrol (0.841 g, 3.19 mmol, 1.1 equiv.) giving a yellow oil. R_f value: 0.53 (SiO₂, CHCl₃). Yield: 0.641 g, 1.54 mmol, 53%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.44–7.27 (m, 14H, Ar-H), 6.97 (s, 1H, C(H)Ar₂), 6.45 (d, ³J_{HH} = 11.5 Hz, 1H, =CH), 6.21 (d, ³J_{HH} = 11.5 Hz, 1H, =CH). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 163.7 (s), 139.6 (s), 139.2 (s), 132.0 (s), 131.7 (s), 129.3 (s), 129.0 (s), 128.6 (s), 128.4 (s), 128.1 (s), 127.6 (s), 127.2 (s), 123.7 (s), 122.4 (s), 121.9 (s), 102.0 (s), 86.4 (s), 76.5 (s). **HRMS** (ES⁺) *m/z* calculated for [C₂₈H₁₇FO₂]⁺ [M]⁺: 416.0412, found: 416.0415.

6.4.3.2 Synthesis of Products

General Procedure 8: Carboxylic acid **4.9** or ester **4.10** (0.1 mmol, 1 equiv.) was dissolved in CDCl_3 (0.5 ml) with subsequent addition of $\text{B}(\text{C}_6\text{F}_5)_3$ (0.1 mmol, 1 equiv.). After 15 minutes (unless stated otherwise) multinuclear NMR spectroscopy showed full conversion at which point solvent was removed *in vacuo* and the residue was washed with cold hexane (2 x 1 ml) to give the compound **4.11**.

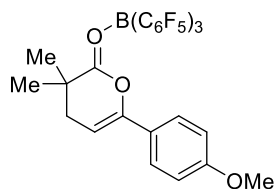


4.11a: Synthesised according to *General Procedure 8* using **4.9a** (20 mg, 0.1 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (51 mg, 0.1 mmol) to give a white solid that was recrystallised by slow evaporation of a saturated CH_2Cl_2 /hexane solution. Yield: 68 mg, 0.09 mmol, 96%. Melting point: 70–76 °C. **^1H NMR** (500 MHz, CDCl_3 , 298 K) δ /ppm: 7.38–7.30 (m, 3H, Ar-H), 7.07 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2H, Ar-H), 5.95 (t, $^3J_{\text{HH}} = 4.0$ Hz, 1H, =CH), 2.54 (d, $^3J_{\text{HH}} = 3.8$ Hz, CH_2), 1.46 (s, 6H, $\text{C}(\text{CH}_3)_2$). **^{13}C NMR** (126 MHz, CDCl_3 , 298 K) δ /ppm: 150.5 (s), 147.9 (dm, $^1J_{\text{CF}} \approx 240$ Hz), 140.3 (dm, $^1J_{\text{CF}} \approx 240$ Hz), 137.3 (dm, $^1J_{\text{CF}} \approx 250$ Hz), 130.5 (s), 129.3 (s), 129.0 (s), 124.4 (s), 103.2 (s), 37.6 (s), 32.8 (s), 24.0 (s). **^{11}B NMR** (128 MHz, CDCl_3 , 298 K) δ /ppm: 2.0 (br. s). **^{19}F NMR** (471 MHz, CDCl_3 , 298 K) δ /ppm: -135.04 (d, $^3J_{\text{FF}} = 15.9$ Hz, 6F, *o*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -156.64 (br. s, 3F, *p*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -163.63 (br. s, 6F, *m*-F $\text{B}(\text{C}_6\text{F}_5)_3$). **IR** ν_{max} (cm^{-1}): 2982 (w), 2936 (w), 1716 (m), 1678 (m), 1647 (m), 1557 (m), 1518 (s), 1465 (s), 1389 (m), 1342 (w), 1287 (m), 1275 (m), 1209 (w), 1099 (s), 1055 (w), 970 (s), 893 (w), 791 (m), 760 (m), 746 (m), 689 (m), 613 (w), 576 (w). **HRMS** (AP^+) m/z calculated for $[\text{C}_{14}\text{H}_{16}\text{O}_2]^+$ $[\text{M}+\text{H}-(\text{B}(\text{C}_6\text{F}_5)_3)]^+$: 203.1072, found: 203.1079.

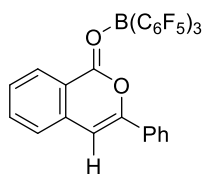


4.11b: Synthesised according to *General Procedure 8* using **4.9b** (22 mg, 0.1 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (51 mg, 0.1 mmol) to give a white solid. Yield: 68 mg, 0.09 mmol, 93%. Melting point: 75–81 °C. **^1H NMR** (500 MHz, CDCl_3 , 298 K) δ /ppm: 7.10 (d, $^3J_{\text{HH}} = 7.7$ Hz, 2H, Ar-H), 7.01 (d, $^3J_{\text{HH}} = 7.3$ Hz, 2H, Ar-H), 5.87 (t, $^3J_{\text{HH}} = 4.5$ Hz, 1H, =CH), 2.49 (s, 2H, CH_2), 2.35 (s, 3H, *p*-Me), 1.44 (s, 6H, $\text{C}(\text{CH}_3)_2$). **^{13}C NMR** (126 MHz, CDCl_3 , 298 K) δ /ppm: 150.5 (s), 148.0 (dm, $^1J_{\text{CF}} \approx 240$ Hz), 140.8 (s), 140.2 (dm, $^1J_{\text{CF}} \approx 250$ Hz), 137.3 (dm, $^1J_{\text{CF}} \approx 250$ Hz), 129.6 (s), 126.8 (s), 124.3 (s), 101.9 (s), 37.5 (s), 32.8 (s), 24.1 (s), 21.4 (s). **^{11}B NMR** (128 MHz, CDCl_3 , 298 K) δ /ppm: 1.5 (br. s). **^{19}F NMR** (471 MHz, CDCl_3 , 298 K) δ /ppm: -135.05 (d, $^3J_{\text{FF}} = 18.5$ Hz, 6F, *o*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -156.86 (t, $^3J_{\text{FF}} = 19.2$ Hz, 3F, *p*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -163.74 (br. s, 6F, *m*-F $\text{B}(\text{C}_6\text{F}_5)_3$). **IR** ν_{max} (cm^{-1}): 2955 (w), 2910 (w), 2876 (w), 1726 (w), 1678 (m), 1599

(s), 1576 (m), 1510 (m), 1483 (w), 1418 (w), 1368 (w), 1317 (m), 1261 (m), 1171 (s), 1072 (w), 1032 (w), 1004 (m), 976 (w), 907 (m), 841 (m), 841 (m). **HRMS** (ES⁺) *m/z* calculated for [C₁₄H₁₆O₂]⁺ [M-B(C₆F₅)₃]⁺: 216.1150, found 216.1149.

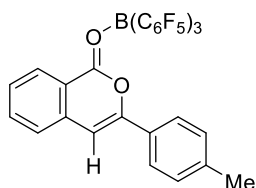


4.11c: Synthesised according to *General Procedure 8* using **4.9c** (23 mg, 0.1 mmol) and B(C₆F₅)₃ (51 mg, 0.1 mmol) to give a white solid. Yield: 69 mg, 0.09 mmol, 93%. Melting point: 80–87 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 6.99 (d, ³J_{HH} = 8.3 Hz, 2H, Ar-H), 6.79 (d, ³J_{HH} = 8.3 Hz, 2H, Ar-H), 5.77 (t, ³J_{HH} = 4.3 Hz, 1H, =CH), 3.79 (s, 3H, OCH₃), 2.48 (d, ³J_{HH} = 4.2 Hz, 2H, CH₂), 1.43 (s, 6H, C(CH₃)₂). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 161.3 (s), 150.4 (s), 148.0 (dm, ¹J_{CF} ≈ 240 Hz), 140.3 (dm, ¹J_{CF} ≈ 250 Hz), 137.2 (dm, ¹J_{CF} ≈ 250 Hz), 126.0 (s), 121.8 (s), 114.3 (s), 101.1 (s), 55.5 (s), 37.6 (s), 32.7 (s), 24.0 (s). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 1.4 (br. s). **¹⁹F NMR** (471 MHz, CDCl₃, 298 K) δ/ppm: -135.03 (d, ³J_{FF} = 19.4 Hz, 6F, *o*-F B(C₆F₅)₃), -156.84 (t, ³J_{FF} = 20.3 Hz, 3F, *p*-F B(C₆F₅)₃), -163.72 (t, ³J_{FF} = 18.2 Hz, 6F, *m*-F B(C₆F₅)₃). **IR** ν_{max} (cm⁻¹): 2982 (w), 2845 (w), 1705 (w), 1647 (m), 1611 (m), 1516 (s), 1460 (s), 1381 (m), 1287 (m), 1271 (m), 1251 (m), 1238 (m), 1178 (m), 1099 (s), 1033 (w), 972 (s), 891 (m), 864 (m), 835 (w), 793 (w), 775 (w), 764 (w), 746 (w), 685 (w), 673 (w), 608 (w). **HRMS** (AP⁺) *m/z* calculated for [C₁₄H₁₇O₃]⁺ [M+H-(B(C₆F₅)₃)]⁺: 233.1178, found: 233.1183.

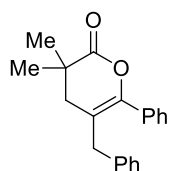


4.11d: Synthesised according to *General Procedure 8* using **4.9i** (22 mg, 0.1 mmol) and B(C₆F₅)₃ (51 mg, 0.1 mmol) to give a pale green solid that was recrystallised by slow evaporation of a saturated CH₂Cl₂/hexane solution. Yield: 33 mg, 0.05 mmol, 45%. Melting point: 205–211 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.57 (d, ³J_{HH} = 8.1 Hz, 1H, Ar-H), 8.09 (t, ³J_{HH} = 7.6 Hz, 1H, Ar-H), 7.89–7.70 (m, 2H, Ar-H), 7.57–7.48 (m, 1H, Ar-H), 7.47–7.32 (m, 5H, Ar-H). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 154.7 (s), 148.1 (dm, ¹J_{CF} = 244 Hz), 140.0 (dm, ¹J_{CF} = 247 Hz), 139.3 (s), 139.2 (s), 137.2 (dm, ¹J_{CF} = 253 Hz), 131.8 (s), 130.9 (s), 130.6 (s), 129.4 (s), 127.0 (s), 125.6 (s), 117.4 (s), 106.5 (s). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 0.8 (br. s). **¹⁹F NMR** (471 MHz, CDCl₃, 298 K) δ/ppm: -134.77 (d, ³J_{FF} = 19.6 Hz, 6F, *o*-F B(C₆F₅)₃), -157.14 (t, ³J_{FF} = 19.9 Hz, 3F, *p*-F B(C₆F₅)₃), -163.79 (t, ³J_{FF} = 17.7 Hz, 6F, *m*-F B(C₆F₅)₃). **IR** ν_{max} (cm⁻¹): 2160 (w), 1681 (m), 1645 (m), 1606 (m), 1564 (m), 1517 (s), 1426 (s), 1379 (m), 1344 (w), 1286 (m), 1242 (m), 1159 (w), 1089 (s), 1029 (w), 968 (s), 879 (w), 798 (w), 765 (m), 688 (s), 673 (s), 621 (w), 574 (w), 538 (w), 524

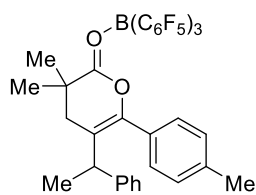
(w). **HRMS** (ES⁺) m/z calculated for [C₁₅H₁₁O₂]⁺ [M+H-(B(C₆F₅)₃)]⁺: 223.0759, found: 223.0760.



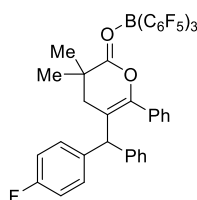
4.11e: Synthesised according to *General Procedure 8* using **4.9j** (24 mg, 0.1 mmol) and B(C₆F₅)₃ (51 mg, 0.1 mmol) to give a pale green solid that was recrystallised by slow evaporation of a saturated CH₂Cl₂/hexane solution. Yield: 39 mg, 0.05 mmol, 52%. Melting point: 187–192 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.55 (d, ³J_{HH} = 8.2 Hz, 1H, Ar-H), 8.07 (t, ³J_{HH} = 7.8 Hz, 1H, Ar-H), 7.85–7.64 (m, 2H, Ar-H), 7.38 (s, 1H, =CH), 7.25 (q, ³J_{HH} = 8.3 Hz, 4H), 2.41 (s, 3H, CH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 154.9 (s), 147.9 (dm, ¹J_{CF} = 241 Hz), 142.5 (s), 140.0 (dm, ¹J_{CF} = 246 Hz), 139.3 (s), 139.2 (s), 137.0 (dm, ³J_{CF} = 253 Hz), 130.5 (s), 130.4 (s), 130.0 (s), 126.7 (s), 125.3 (s), 117.0 (s), 105.6 (s), 21.5 (s). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 0.7 (br. s). **¹⁹F NMR** (471 MHz, CDCl₃, 298 K) δ/ppm: -134.76 (d, ³J_{FF} = 18.0 Hz, 6F, *o*-F B(C₆F₅)₃), -157.27 (t, ³J_{FF} = 20.3 Hz, 3F, *p*-F B(C₆F₅)₃), -163.86 (t, ³J_{FF} = 18.3 Hz, 6F, *m*-F B(C₆F₅)₃). **IR** ν_{max} (cm⁻¹): 2362 (w), 2160 (w), 1647 (m), 1606 (m), 1579 (m), 1558 (m), 1517 (s), 1458 (s), 1381 (m), 1340 (m), 1286 (m), 1244 (w), 1192 (w), 1163 (w), 1101 (s), 984 (s), 881 (w), 854 (w), 831 (w), 817 (m), 796 (m), 773 (s), 752 (s), 696 (s), 677 (s), 630 (w), 582 (m), 524 (s). **HRMS** (ES⁺) m/z calculated for [C₁₆H₁₃O₂]⁺ [M+H-(B(C₆F₅)₃)]⁺: 237.0916, found: 237.0920.



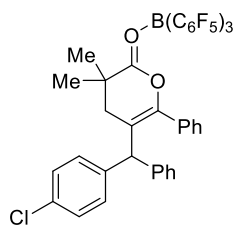
4.11f: Synthesised according to *General Procedure 8* using **4.10c** (57 mg, 0.2 mmol) and B(C₆F₅)₃ (100 mg, 0.2 mmol) however, this compound was purified by column chromatography after 24 h using 100% chloroform to yield compound **4.11f** as a yellow oil. R_f value: 0.49 (SiO₂, CHCl₃). Yield: 48 mg, 0.17 mmol, 84%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.54–7.49 (m, 2H, Ar-H), 7.42–7.29 (m, 5H, Ar-H), 7.21–7.15 (m, 3H, Ar-H), 3.55 (s, 2H, CH₂), 2.18 (s, 2H, CH₂), 1.26 (s, 6H, C(CH₃)₂). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 174.2 (s), 146.8 (s), 138.7 (s), 133.0 (s), 129.1 (s), 128.8 (s), 128.8 (s), 128.7 (s), 128.5 (s), 112.3 (s), 38.7 (s), 37.8 (s), 36.5 (s), 24.9 (s). **IR** ν_{max} (cm⁻¹): 2980 (w), 2361 (w), 1717 (m), 1647 (m), 1517 (s), 1460 (s), 1379 (m), 1344 (m), 1287 (m), 1211 (w), 1101 (s), 1053 (w), 965 (s), 868 (w), 789 (w), 764 (m), 746 (w), 700 (m), 678 (m), 625 (w), 577 (w), 517 (w), 444 (w). **HRMS** (ES⁺) m/z calculated for [C₂₀H₂₀O₂]⁺ [M+H]⁺: 292.1463, found: 292.1462.



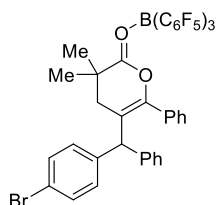
4.11g: Synthesised according to *General Procedure 8* using **4.10k** (64 mg, 0.2 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (100 mg, 0.2 mmol) to yield compound as a yellow oil. Yield: 138 mg, 0.17 mmol, 83%. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ /ppm: 7.26–7.20 (m, 2H, Ar-H), 7.16 (d, $^3J_{\text{HH}} = 7.3$ Hz, 1H, Ar-H), 7.12 (d, $^3J_{\text{HH}} = 7.8$ Hz, 2H, Ar-H), 7.01 (d, $^3J_{\text{HH}} = 7.5$ Hz, 2H, Ar-H), 6.85 (d, $^3J_{\text{HH}} = 8.1$ Hz, 2H, Ar-H), 3.82 (q, $^3J_{\text{HH}} = 7.1$ Hz, 1H, C(H)(Me)Ar), 2.32 (s, 3H, CH_3), 2.23 (d, $^2J_{\text{HH}} = 17.4$ Hz, 1H, CH_2), 1.94 (d, $^2J_{\text{HH}} = 17.2$ Hz, 1H, CH_2), 1.36 (d, $^3J_{\text{HH}} = 7.2$ Hz, 3H, C(H)(Me)Ar), 1.29 (s, 3H, CH_3), 1.07 (s, 3H, CH_3). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3 , 298 K) δ /ppm: 147.8 (d, $^1J_{\text{CF}} = 239$ Hz), 145.8 (s), 141.3 (s), 140.8 (s), 140.1 (d, $^1J_{\text{CF}} = 249$ Hz), 137.1 (d, $^1J_{\text{CF}} = 247$ Hz), 129.7 (s), 128.9 (s), 128.5 (s), 127.4 (s), 127.2 (s), 126.1 (s), 122.9 (s), 38.3 (s), 37.3 (s), 32.2 (s), 23.4 (s), 23.2 (s), 21.5 (s), 16.7 (s). **$^{11}\text{B NMR}$** (160 MHz, CDCl_3 , 298 K) δ /ppm: 1.2 (br. s). **$^{19}\text{F NMR}$** (376 MHz, CDCl_3 , 298 K) δ /ppm: -135.33 (d, $^3J_{\text{FF}} = 17.7$ Hz, 6F, *o*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -157.45 (t, $^3J_{\text{FF}} = 20.0$ Hz, 3F, *p*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -163.84 – -164.48 (m, 6F, *m*-F $\text{B}(\text{C}_6\text{F}_5)_3$). **IR** ν_{max} (cm^{-1}): 2976 (w), 1705 (m), 1645 (m), 1605 (w), 1517 (s), 1458 (s), 1379 (m), 1348 (w), 1286 (m), 1224 (w), 1174 (w), 1099 (m), 1068 (m), 1024 (w), 989 (s), 869 (w), 804 (w), 773 (m), 738 (w), 700 (m), 678 (m), 617 (w). **HRMS** (EI⁺) m/z calculated for $[\text{C}_{22}\text{H}_{24}\text{O}_2]^+ [\text{M}-\text{B}(\text{C}_6\text{F}_5)_3]^+$: 320.1776, found: 320.1776.



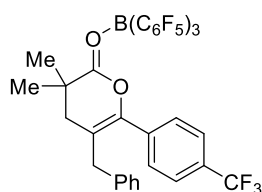
4.11h: Synthesised according to *General Procedure 8* using compound **4.10d** (39 mg, 0.1 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (51 mg, 0.1 mmol). Yield: 81 mg, 0.09 mmol, 90%. Melting point: 168–175 °C. **$^1\text{H NMR}$** (400 MHz, CDCl_3 , 298 K) δ /ppm: 7.45 (d, $^3J_{\text{HH}} = 7.5$ Hz, 1H, Ar-H), 7.34 (pent., $^3J_{\text{HH}} = 6.5$ Hz, 5H, Ar-H), 7.06–7.03 (m, 6H, Ar-H), 6.99 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H, Ar-H), 5.14 (s, 1H, $\text{CH}(\text{Ar})_2$), 2.42–2.32 (m, 2H, CH_2), 1.25 (d, $^4J_{\text{HH}} = 4.0$ Hz, 6H, $\text{C}(\text{CH}_3)_2$). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3 , 298 K) δ /ppm: 162.0 (d, $^1J_{\text{CF}} = 245$ Hz), 148.0 (dm, $^1J_{\text{CF}} = 250$ Hz), 140.4 (s), 140.1 (dm, $^1J_{\text{CF}} = 245$ Hz), 137.1 (dm, $^1J_{\text{CF}} = 245$ Hz), 136.6 (s), 130.5 (s), 129.01 (s), 129.0 (d, $^3J_{\text{CF}} = 7.4$ Hz), 128.9 (s), 128.3 (s), 127.6 (s), 50.7 (s), 37.0 (s), 34.6 (s), 23.9 (s), 23.8 (s). **$^{11}\text{B NMR}$** (160 MHz, CDCl_3 , 298 K) δ /ppm: 1.6 (br. s). **$^{19}\text{F NMR}$** (376 MHz, CDCl_3 , 298 K) δ /ppm: -114.56 (s, 1F, *p*-F), -135.31 – -135.36 (m, 6F, *o*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -157.08 (t, $^3J_{\text{FF}} = 20.5$ Hz, 3F, *p*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -163.85 (td, 6F, $^3J_{\text{FF}} = 23.9$ Hz, $^4J_{\text{FF}} = 8.3$ Hz, *m*-F $\text{B}(\text{C}_6\text{F}_5)_3$). **IR** ν_{max} (cm^{-1}): 2982 (w), 1763 (w), 1647 (w), 1611 (m), 1518 (m), 1506 (m), 1467 (s), 1408 (m), 1383 (w), 1366 (w), 1331 (w), 21283 (w), 1227 (m), 1227 (m), 1105 (m), 1049 (w), 976 (s), 937 (w), 885 (w), 856 (w), 841 (w), 831 (w), 808 (w), 789 (m), 775 (w), 765 (m), 745 (w), 727 (w), 696 (m), 681 (m), 667 (m), 624 (w), 610 (w). **HRMS** (ES⁺) m/z calculated for $[\text{C}_{26}\text{H}_{24}\text{O}_2\text{F}]^+ [(\text{M}-\text{B}(\text{C}_6\text{F}_5)_3)+\text{H}]^+$: 387.1760, found: 387.1752.



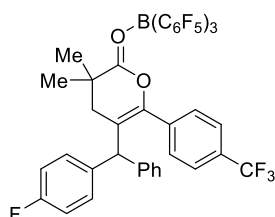
4.11i: Synthesised according to *General Procedure 8* using compound **4.10e** (40 mg, 0.1 mmol) and $B(C_6F_5)_3$ (51 mg, 0.1 mmol). Yield: 88 mg, 0.09 mmol, 97%. Melting point: 149–155 °C. **1H NMR** (400 MHz, $CDCl_3$, 298 K) δ /ppm: 7.38 (t, $^3J_{HH} = 7.5$ Hz, 1H, Ar-H), 7.30 – 7.22 (m, 7H, Ar-H), 6.99 – 6.90 (m, 4H, Ar-H), 6.86 (d, $^3J_{HH} = 7.3$ Hz, 2H, Ar-H), 5.05 (s, 1H, C(H)Ar₂), 2.32 (s, 2H, CH₂), 1.22 (s, 3H, CH₃), 1.19 (s, 3H, CH₃). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ /ppm: 186.2 (s), 147.8 (dm, $^1J_{CF} \approx 250$ Hz), 147.5 (s), 140.0 (dm, $^1J_{CF} \approx 250$ Hz), 139.6 (s), 138.6 (s), 137.1 (dm, $^1J_{CF} \approx 250$ Hz), 133.6 (s), 131.0 (s), 130.2 (s), 129.3 (s), 129.2 (s), 129.1 (s), 128.8 (s), 128.2 (s), 127.9 (s), 119.4 (s), 50.7 (s), 37.4 (s), 34.1 (s), 23.6 (s), 23.4 (s). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ /ppm: 1.4 (br. s). **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ /ppm: -135.31 (d, $^3J_{FF} = 18.5$ Hz, 6F, *o*-F $B(C_6F_5)_3$), -157.03 (t, $^3J_{FF} = 20.3$ Hz, 3F, *p*-F $B(C_6F_5)_3$), -163.66 – -163.94 (m, 6F, *m*-F $B(C_6F_5)_3$). **IR** ν_{max} (cm⁻¹): 2982 (w), 2361 (w), 1647 (w), 1611 (s), 1518 (s), 1491 (m), 1462 (s), 1406 (m), 1381 (m), 1364 (m), 1331 (w), 1283 (m), 1229 (m), 1091 (s), 1048 (m), 1015 (w), 976 (s), 935 (w), 885 (w), 856 (w), 839 (w), 824 (w), 789 (m), 766 (m), 698 (s), 681 (m), 665 (m), 625 (m), 610 (m). **HRMS** (ES⁺) *m/z* calculated for $[C_{26}H_{24}O_2Cl]^+$ [(M- $B(C_6F_5)_3$)+H]⁺: 403.1465, found: 403.1455.



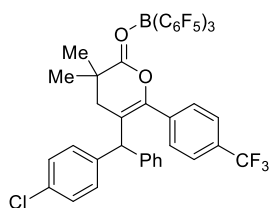
4.11j: Synthesised according to *General Procedure 8* using compound **4.10f** (45 mg, 0.1 mmol) and $B(C_6F_5)_3$ (51 mg, 0.1 mmol). Yield: 92 mg, 0.09 mmol, 96%. Melting point: 154–159 °C. **1H NMR** (400 MHz, $CDCl_3$, 298 K) δ /ppm: 7.43–7.35 (m, 3H, Ar-H), 7.31–7.19 (m, 5H, Ar-H), 6.96 (d, $^3J_{HH} = 7.1$ Hz, 2H, Ar-H), 6.87 (d, $^3J_{HH} = 8.4$ Hz, 4H, Ar-H), 5.04 (s, 1H, C(H)Ar₂), 2.32 (s, 2H, CH₂), 1.22 (s, 3H, CH₃), 1.19 (s, 3H, CH₃). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ /ppm: 147.8 (dm, $^1J_{CF} \approx 240$ Hz), 147.6 (s), 140.2 (dm, $^1J_{CF} \approx 250$ Hz), 140.2 (d, $^3J_{CF} = 47.6$ Hz), 137.1 (dm, $^1J_{CF} \approx 250$ Hz), 132.0 (s), 130.7 (s), 130.26 (s), 129.0 (s), 128.9 (s), 128.9 (s), 128.3 (s), 127.5 (s), 121.3 (s), 51.1 (s), 36.7 (s), 34.9 (s), 24.1 (s), 24.0 (s). **^{11}B NMR** (160 MHz, $CDCl_3$, 298 K) δ /ppm: 1.5 (br. s). **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ /ppm: -135.32 (d, $^3J_{FF} = 16.9$ Hz, 6F, *o*-F $B(C_6F_5)_3$), -157.02 (t, $^3J_{FF} = 20.5$ Hz, 3F, *p*-F $B(C_6F_5)_3$), -163.79 (td, $^3J_{FF} = 23.9$, $^4J_{FF} = 8.2$ Hz, *m*-F $B(C_6F_5)_3$). **IR** ν_{max} (cm⁻¹): 2982 (w), 2361 (w), 1647 (w), 1611 (s), 1518 (s), 1487 (m), 1462 (s), 1406 (m), 1381 (m), 1364 (m), 1331 (w), 1283 (m), 1229 (m), 1101 (s), 1047 (m), 1011 (m), 976 (s), 885 (w), 856 (w), 837 (w), 789 (m), 775 (m), 766 (m), 721 (m), 696 (s), 680 (m), 671 (m), 624 (w), 610 (w). **HRMS** (ES⁺) *m/z* calculated for $[C_{26}H_{24}O_2Br]^+$ [(M- $B(C_6F_5)_3$)+H]⁺: 447.0960, found: 447.0947.



4.11k: Synthesised according to *General Procedure 8* using compound **4.10g** (45 mg, 0.1 mmol) and $B(C_6F_5)_3$ (51 mg, 0.1 mmol). Yield: 89 mg, 0.09 mmol, 92%. Melting point: 80–86 °C. **1H NMR** (400 MHz, $CDCl_3$, 298 K) δ /ppm: 7.68 (d, $^3J_{HH} = 8.0$ Hz, 2H, Ar-H), 7.38–7.34 (m, 2H, Ar-H), 7.25–7.18 (m, 3H, Ar-H), 7.10 (d, $^3J_{HH} = 7.2$ Hz, 2H, Ar-H), 3.52 (s, 2H, CH_2Ph), 2.38 (s, 2H, CH_2), 1.38 (s, 6H, $C(CH_3)_2$). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ /ppm: 1.7 (br. s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ /ppm: -63.30 (s, 3F, CF_3), -134.94 (br. s, 6F, *o*-F- $B(C_6F_5)_3$), -156.30 (br. s, 3F, *p*-F $B(C_6F_5)_3$), -163.44 (br. s, 6F, *m*-F $B(C_6F_5)_3$). **IR** ν_{max} (cm^{-1}): 2936 (w), 2361 (w), 2332 (w), 1717 (w), 1647 (w), 1618 (w), 1541 (w), 1518 (s), 1461 (s), 1406 (w), 1381 (w), 1323 (s), 1288 (m), 1169 (m), 1103 (s), 1067 (s), 1018 (w), 972 (s), 845 (w), 793 (w), 775 (w), 745 (w), 700 (w), 673 (w), 609 (w), 577 (w). **HRMS** (ES^+) m/z calculated for $[C_{23}H_{23}F_3NO_2]^+$ [$M+MeCN+H-(B(C_6F_5)_3)$] $^+$: 402.1681, found: 402.1674.

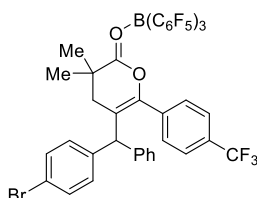


4.11i: Synthesised according to *General Procedure 8* using compound **4.10h** (45 mg, 0.1 mmol) and $B(C_6F_5)_3$ (51 mg, 0.1 mmol). Yield: 89 mg, 0.09 mmol, 92%. Melting point: 165–171 °C. **1H NMR** (400 MHz, $CDCl_3$, 298 K) δ /ppm: 7.55 (d, $^3J_{HH} = 8.3$ Hz, 2H), 7.33–7.27 (m, 3H, Ar-H), 7.19 (d, $^3J_{HH} = 6.5$ Hz, 2H, Ar-H), 7.03–6.97 (m, 5H, Ar-H), 5.03 (s, 1H, $C(H)Ar_2$), 2.41–2.39 (m, 2H, CH_2), 1.29 (s, 3H, CH_3), 1.28 (s, 3H, CH_3). **^{13}C NMR** *partial* (126 MHz, $CDCl_3$, 298 K) δ /ppm: 148.1 (dm, $^1J_{CF} = 245$ Hz), 147.9 (s), 140.1 (s), 139.1 (s), 137.3 (dm, $^1J_{CF} = 250$ Hz), 134.0 (s), 131.3 (s), 130.1 (s), 129.6 (s), 129.6 (s), 129.5 (s), 129.2 (s), 128.6 (s), 128.3 (s), 51.1 (s), 37.7 (s), 34.5 (s), 24.0 (s), 23.92 (s). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ /ppm: 0.0 (br. s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ /ppm: -63.04 (s, 3F, CF_3), -114.76 (m, 1F, *p*-F Ph), -138.45 (dd, $^3J_{FF} = 21.7$ Hz, $^4J_{FF} = 8.5$ Hz, 6F, *o*-F $B(C_6F_5)_3$), -153.49 (br. s, $^3J_{FF} = 20.1$ Hz, $^4J_{FF} = 6.9$ Hz, 3F, *p*-F $B(C_6F_5)_3$), -161.81 – -161.94 (m, 6F, *m*-F $B(C_6F_5)_3$).

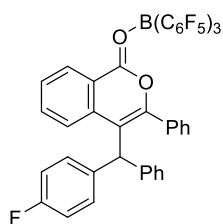


4.11m: Synthesised according to *General Procedure 8* using compound **4.10i** (47 mg, 0.1 mmol) and $B(C_6F_5)_3$ (51 mg, 0.1 mmol). Yield: 92 mg, 0.09 mmol, 94%. Melting point: 160–168 °C. **1H NMR** (400 MHz, $CDCl_3$, 298 K) δ /ppm: 7.54 (d, $^3J_{HH} = 8.2$ Hz, 2H, Ar-H), 7.26–7.24 (m, 4H, Ar-H), 7.00–6.90 (m, 8H, Ar-H), 4.99 (s, 1H, $C(H)Ar_2$), 2.35 (s, 2H, CH_2), 1.26 (s, 3H, CH_3), 1.23 (s, 3H, CH_3). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ /ppm: 2.6 (br. s). **^{13}C NMR** (126 MHz, $CDCl_3$,

298 K) δ /ppm: 188.0 (s), 146.6 (dm, $^1J_{CF} = 240$ Hz), 144.8 (s), 140.6 (s), 138.9 (dm, $^1J_{CF} = 245$ Hz), 138.5 (s), 137.4 (s), 136.0 (dm, $^1J_{CF} = 245$ Hz), 132.6 (s), 129.0 (s), 128.4 (s), 128.2 (s), 128.1 (s), 128.2 (s), 127.6 (s), 127.6 (s), 126.8 (s), 124.9 (q, $^3J_{CF} = 3.5$ Hz), 49.7 (s), 36.0 (s), 33.6 (s), 22.6 (s), 22.6 (s). **^{19}F NMR** (376 MHz, CDCl_3 , 298 K) δ /ppm: -63.39 (s, 3F, CF_3), -135.12 (d, $^3J_{FF} = 18.3$ Hz, 6F, *o*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -156.46 (s, 3F, *p*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -163.58 (t, $^3J_{FF} = 17.7$ Hz, 6F, *m*-F $\text{B}(\text{C}_6\text{F}_5)_3$). **IR** ν_{max} (cm^{-1}): 2982 (w), 2359 (w), 2332 (w), 1716 (m), 1647 (m), 1616 (w), 1518 (s), 1462 (s), 1406 (m), 1381 (m), 1323 (s), 1288 (m), 1225 (w), 1169 (m), 1101 (s), 1067 (s), 1016 (m), 972s, 847 (m), 791 (w), 775 (w), 744 (w), 704w, 679 (m), 608 (w), 579 (w), 561 (w). **HRMS** (ES^+) m/z calculated for $[\text{C}_{27}\text{H}_{23}\text{O}_2\text{F}_3\text{Cl}]^+ [(\text{M}-\text{B}(\text{C}_6\text{F}_5)_3)+\text{H}]^+$: 471.1339, found: 471.1330.

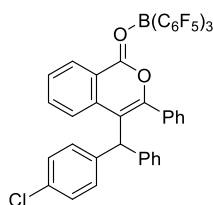


4.11n: Synthesised according to *General Procedure 8* using compound **4.10j** (51 mg, 0.1 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (51 mg, 0.1 mmol). Yield: 93 mg, 0.09 mmol, 92%. Melting point: 105–110 °C. **^1H NMR** (400 MHz, CDCl_3 , 298 K) δ /ppm: 7.48 (d, $^3J_{\text{HH}} = 8.2$ Hz, 2H, Ar-H), 7.35 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H, Ar-H), 7.23–7.21 (m, 3H, Ar-H), 6.94–6.88 (m, 4H, Ar-H), 6.79 (d, $^3J_{\text{HH}} = 8.3$ Hz, 2H, Ar-H), 4.91 (s, 1H, C(H)Ar₂), 2.30 (s, 2H, CH₂), 1.21 (s, 3H, CH₃), 1.18 (s, 3H, CH₃). **^{13}C NMR** (126 MHz, CDCl_3 , 298 K) δ /ppm: 189.2 (s), 147.9 (dm, $^1J_{CF} = 245$ Hz), 146.3 (s), 141.3 (s), 140.1 (dm, $^1J_{CF} = 245$ Hz), 140.0 (s), 136.9 (dm, $^1J_{CF} = 245$ Hz), 132.1 (s), 130.1 (s), 129.1 (s), 128.9 (s), 128.8 (s), 127.7 (s), 125.8 (q, $^3J_{CF} = 3.8$ Hz), 121.4 (s), 51.2 (s), 36.7 (s), 35.5 (s), 24.3 (s), 24.2 (s). **^{11}B NMR** (128 MHz, CDCl_3 , 298 K) δ /ppm: 2.6 (br. s). **^{19}F NMR** (471 MHz, CDCl_3 , 298 K) δ /ppm: -63.26 (s, 3F, $-\text{CF}_3$), -134.97 (br. s, 6F, *o*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -156.09 (br. s, 3F, *p*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -163.44 (br. s, 6F, *m*-F $\text{B}(\text{C}_6\text{F}_5)_3$). **IR** ν_{max} (cm^{-1}): 2934 (w), 22361 (w), 1717 (w), 1647 (w), 1618 (w), 1518 (s), 1462 (s), 1381 (m), 1323 (s), 1288 (m), 1227 (w), 1169 (m), 1126 (s), 1103 (s), 1067 (s), 972 (s), 847 (m), 791 (w), 775 (w), 745 (w), 704 (w), 673 (m), 608 (w), 577 (w), 561 (w). **HRMS** (ES^+) m/z calculated for $[\text{C}_{27}\text{H}_{23}\text{O}_2\text{F}_3\text{Br}]^+ [(\text{M}-\text{B}(\text{C}_6\text{F}_5)_3)+\text{H}]^+$: 515.0834, found: 515.0831.

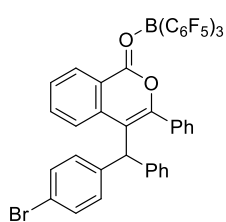


4.11o: Synthesised according to *General Procedure 8* using **4.10i** (41 mg, 0.1 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (51 mg, 0.1 mmol) to give a white solid that was recrystallised by slow evaporation of a saturated CH_2Cl_2 /hexane solution. Yield: 79 mg, 0.09 mmol, 86%. Melting point: 190–195 °C. **^1H NMR** (500 MHz, CDCl_3 , 298 K) δ /ppm: 8.62 (d, $^3J_{\text{HH}} = 7.4$ Hz, 1H, Ar-H), 7.79 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1H, Ar-H), 7.73 (t, $^3J_{\text{HH}} = 7.4$ Hz,

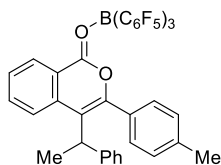
1H, Ar-H), 7.67 (d, $^3J_{\text{HH}} = 8.2$ Hz, 1H, Ar-H), 7.48 (t, $^3J_{\text{HH}} = 7.6$ Hz, 1H, Ar-H), 7.34–7.24 (m, 6H, Ar-H), 7.08–7.00 (m, 4H, Ar-H), 6.97 (t, $^3J_{\text{HH}} = 8.4$ Hz, 4H, Ar-H), 5.81 (s, 1H, C(H)Ar₂). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 169.3 (s), 161.9 (d, $^1J_{\text{CF}} = 247$ Hz), 154.2 (s), 148.2 (dm, $^1J_{\text{CF}} = 245$ Hz), 139.8 (dm, $^1J_{\text{CF}} = 250$ Hz), 139.0 (s), 139.0 (s), 136.9 (dm, $^1J_{\text{CF}} = 250$ Hz), 135.6 (d, $^3J_{\text{CF}} = 3.3$ Hz), 131.5 (s), 131.1 (s), 130.6 (s), 129.6 (s), 129.2 (s), 129.1 (s), 128.8 (s), 128.6 (s), 127.8 (s), 127.7 (s), 120.9 (s), 118.3 (s), 116.0 (d, $^2J_{\text{CF}} = 12.1$ Hz), 49.4 (s). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ /ppm: 0.4 (br. s). **¹⁹F NMR** (471 MHz, CDCl₃, 298 K) δ /ppm: -114.54 (s, 1F, CF), -134.98 (d, $^3J_{\text{FF}} = 19.2$ Hz, 6F, *o*-F B(C₆F₅)₃), -157.48 (t, $^3J_{\text{FF}} = 18.0$ Hz, 3F, *p*-F B(C₆F₅)₃), -164.03 (br. t, $^3J_{\text{FF}} = 18.2$ Hz, 6F, *m*-F B(C₆F₅)₃). **IR** ν_{max} (cm⁻¹): 3032 (w), 2957 (w), 1645 (m), 1603 (m), 1556 (m), 1452 (s), 1377 (m), 1284 (m), 1228 (m), 1161 (w), 1099 (s), 1016 (w), 974 (s), 860 (w), 835 (w), 790 (m), 745 (m), 739 (m), 696 (s), 665 (m), 611 (w), 574 (w). **HRMS** (ES⁺) *m/z* calculated for [C₂₈H₂₀O₂F]⁺ [M+H–(B(C₆F₅)₃)]⁺: 407.1447, found: 407.1440.



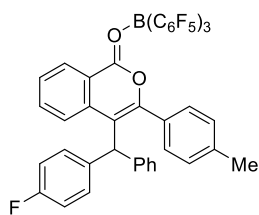
4.11p: Synthesised according to *General Procedure 8* using **4.10m** (42 mg, 0.1 mmol) and B(C₆F₅)₃ (51 mg, 0.1 mmol) to give a white solid that was recrystallised by slow evaporation of a saturated CH₂Cl₂/hexane solution. Yield: 85 mg, 0.09 mmol, 91%. Melting point: 194–200 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 8.61 (d, $^3J_{\text{HH}} = 7.9$ Hz, 1H, Ar-H), 7.78 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1H, Ar-H), 7.72 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H, Ar-H), 7.64 (d, $^3J_{\text{HH}} = 8.2$ Hz, 1H, Ar-H), 7.47 (t, $^3J_{\text{HH}} = 7.6$ Hz, 1H, Ar-H), 7.32 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H, Ar-H), 7.29–7.17 (m, 4H, Ar-H), 7.05 (d, $^3J_{\text{HH}} = 7.3$ Hz, 2H, Ar-H), 6.99 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H, Ar-H), 6.95 (d, $^3J_{\text{HH}} = 7.5$ Hz, 2H, Ar-H), 5.79 (s, 1H, C(H)Ar₂). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 169.3 (s), 154.3 (s), 148.0 (dm, $^1J_{\text{CF}} = 238$ Hz), 140.0 (dm, $^1J_{\text{CF}} = 250$ Hz), 139.4 (s), 138.9 (s), 138.4 (s), 137.07 (dm, $^1J_{\text{CF}} = 241$ Hz), 133.5 (s), 131.5 (s), 131.1 (s), 130.5 (s), 130.3 (s), 129.5 (s), 129.3 (s), 129.2 (s), 129.1 (s), 128.8 (s), 128.6 (s), 127.8 (s), 127.7 (s), 120.6 (s), 118.3 (s), 49.5 (s). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ /ppm: 0.6 (br. s). **¹⁹F NMR** (471 MHz, CDCl₃, 298 K) δ /ppm: -134.98 (d, $^3J_{\text{FF}} = 18.5$ Hz, *o*-F B(C₆F₅)₃), -157.47 (t, $^3J_{\text{FF}} = 20.0$ Hz, *p*-F B(C₆F₅)₃), -164.02 (t, $^3J_{\text{FF}} = 18.3$ Hz, *m*-F B(C₆F₅)₃). **IR** ν_{max} (cm⁻¹): 3059 (w), 2158 (w), 2027 (w), 1635 (m), 1602 (w), 1564 (m), 1517 (m), 1465 (s), 1408 (m), 1377 (m), 1284 (m), 1168 (w), 1097 (m), 970 (m), 908 (m), 858 (w), 829 (w), 800 (m), 790 (m), 767 (m), 696 (s), 611 (w), 513 (w). **HRMS** (ES⁺) *m/z* calculated for [C₂₈H₂₀ClO₂]⁺ [M+H–(B(C₆F₅)₃)]⁺: 423.1152, found: 423.1151.



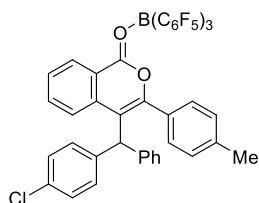
4.11q: Synthesised according to *General Procedure 8* using **4.10n** (47 mg, 0.1 mmol) and $B(C_6F_5)_3$ (51 mg, 0.1 mmol) to give a white solid that was recrystallised by slow evaporation of a saturated CH_2Cl_2 /hexane solution. Yield: 83 mg, 0.08 mmol, 85%. Melting point: 185–189 °C. **1H NMR** (500 MHz, $CDCl_3$, 298 K) δ /ppm: 8.61 (d, $^3J_{HH} = 7.9$ Hz, 1H, Ar-H), 7.83–7.69 (m, 2H, Ar-H), 7.64 (d, $^3J_{HH} = 8.1$ Hz, 1H, Ar-H), 7.48 (t, $^3J_{HH} = 7.6$ Hz, 1H, Ar-H), 7.40 (d, $^3J_{HH} = 8.5$ Hz, 2H, Ar-H), 7.37–7.21 (m, 6H, Ar-H), 7.06 (d, $^3J_{HH} = 7.3$ Hz, 2H, Ar-H), 7.00–6.88 (m, 3H, Ar-H), 5.78 (s, 1H, C(H)Ar₂). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ /ppm: 154.3 (s), 148.0 (dm, $^1J_{CF} = 245$ Hz), 140.0 (dm, $^1J_{CF} = 250$ Hz), 139.4 (s), 139.0 (s), 138.8 (s), 137.1 (dm, $^1J_{CF} = 247$ Hz), 132.2 (s), 131.5 (s), 131.1 (s), 130.6 (s), 130.5 (s), 129.2 (s), 129.1 (s), 128.8 (s), 128.6 (s), 127.7 (s), 127.7 (s), 121.5 (s), 49.5 (s). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ /ppm: 0.4 (br. s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ /ppm: -134.98 (br. s, 6F, *o*-F $B(C_6F_5)_3$), -157.40 (br. s, 3F, *p*-F $B(C_6F_5)_3$), -163.95 (br. s, 6F, *m*-F $B(C_6F_5)_3$). **IR** ν_{max} (cm^{-1}): 3064 (w), 3030 (w), 1645 (m), 1602 (m), 1568 (m), 1518 (m), 1436 (s), 1379 (m), 1286 (m), 1166 (w), 1099 (s), 1010 (w), 974 (s), 906 (m), 792 (m), 765 (m), 729 (m), 694 (s), 617 (w), 609 (w), 576 (w). **HRMS** (ES⁺) m/z calculated for $[C_{28}H_{20}BrO_2]^+$ $[M+H-(B(C_6F_5)_3)]^+$: 467.0647, found: 467.0652.



4.11r: Synthesised according to *General Procedure 8* using **4.10o** (68 mg, 0.2 mmol) and $B(C_6F_5)_3$ (102 mg, 0.2 mmol) to yield compound **3f** as a yellow solid. Yield: 148 mg, 0.17 mmol, 87%. Melting point: 72–78 °C. **1H NMR** (500 MHz, $CDCl_3$, 298 K) δ /ppm: 8.51 (s, 1H, Ar-H), 7.70 (s, 1H, Ar-H), 7.61 (s, 1H, Ar-H), 7.45 (s, 1H, Ar-H), 7.24 (t, $^3J_{HH} = 7.6$ Hz, 2H, Ar-H), 7.14 (d, $^3J_{HH} = 8.0$ Hz, 5H, Ar-H), 6.99 (s, 2H, Ar-H), 4.48 (q, $^3J_{HH} = 7.3$ Hz, 1H, C(H)(Me)Ar), 2.33 (s, 3H, CH_3), 1.72 (d, $^3J_{HH} = 7.3$ Hz, 3H, C(H)(Me)Ar). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ /ppm: 153.1 (s), 148.1 (d, $^1J_{CF} = 238.1$ Hz), 141.9 (s), 141.7 (s), 140.0 (d, $^1J_{CF} = 248.4$ Hz), 138.4 (s), 138.3 (s), 137.1 (d, $^1J_{CF} = 217.8$ Hz), 131.1 (s), 130.2 (s), 130.1 (s), 129.8 (s), 129.2 (s), 128.5 (s), 128.4 (s), 127.0 (s), 126.9 (s), 126.6 (s), 125.5 (s), 37.3 (s), 21.5 (s), 18.6 (s). **^{11}B NMR** (160 MHz, $CDCl_3$, 298 K) δ /ppm: 0.9 (br. s). **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ /ppm: -134.96 (br. s, 6F, *o*-F $B(C_6F_5)_3$), -157.81 (br. s, 3F, *p*-F $B(C_6F_5)_3$), -164.22 (br. s, 6F, *m*-F $B(C_6F_5)_3$). **IR** ν_{max} (cm^{-1}): 2943 (w), 1645 (m), 1608 (w), 1566 (w), 1516 (s), 1495 (s), 1377 (m), 1286 (m), 1184 (w), 1099 (s), 1022 (w), 974 (s), 864 (w), 815 (m), 788 (m), 771 (m), 748 (m), 698 (m), 973 (m). **HRMS** (EI⁺) m/z calculated for $[C_{24}H_{20}O_2]^+$ $[M-B(C_6F_5)_3]^+$: 340.1463, found: 340.1462.

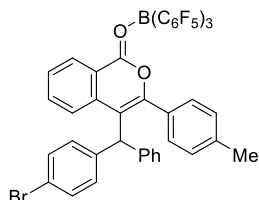


4.11s: Synthesised according to *General Procedure 8* using **4.10p** (42 mg, 0.1 mmol) and $B(C_6F_5)_3$ (51 mg, 0.1 mmol) to give a white solid that was crystallised by slow evaporation of a saturated CH_2Cl_2 /hexane solution. Yield: 75 mg, 0.08 mmol, 81%. Melting point: >230 °C. **1H NMR** (500 MHz, $CDCl_3$, 298 K) δ /ppm: 8.59 (d, $^3J_{HH} = 7.8$ Hz, 1H, Ar-H), 7.79–7.50 (m, 3H, Ar-H), 7.27 (q, $^3J_{HH} = 8.2$ Hz, 3H, Ar-H), 7.12 (d, $^3J_{HH} = 7.4$ Hz, 2H, Ar-H), 7.03–7.01 (m, 4H, Ar-H), 6.95 (t, $^3J_{HH} = 8.1$ Hz, 2H, Ar-H), 6.85 (d, $^3J_{HH} = 7.2$ Hz, 1H, Ar-H), 5.83 (s, 1H, CH(Ar)₂), 2.36 (s, 3H, CH₃). **^{13}C NMR** (126 MHz, $DMSO-d_6$, 298 K) δ /ppm: 161.7 (s), 160.8 (d, $^1J_{CF} = 243$ Hz), 153.9 (s), 147.2 (dm, $^1J_{CF} = 239$ Hz), 140.7 (s), 140.1 (s), 139.1 (dm, $^1J_{CF} = 251.1$ Hz), 137.2 (s), 136.8 (s), 136.8 (s), 136.2 (dm, $^1J_{CF} = 246$ Hz), 134.0 (s), 130.6 (s), 130.6 (s), 130.2 (s), 129.2 (s), 129.1 (s), 128.6 (s), 128.0 (s), 126.7 (d, $^3J_{CF} = 7.0$ Hz), 121.3 (s), 115.3 (d, $^2J_{CF} = 21.3$ Hz), 114.2 (s), 48.5 (s), 20.9 (s). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ /ppm: 0.5 (br. s). **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ /ppm: -114.70 (s, 1F, *p*-F), -134.97 (d, $^3J_{FF} = 19.6$ Hz, 6F, *o*-F $B(C_6F_5)_3$), -157.69 (t, $^3J_{FF} = 19.0$ Hz, 3F, *p*-F $B(C_6F_5)_3$), -164.16 (t, $^3J_{FF} = 18.0$ Hz, 6F, *m*-F $B(C_6F_5)_3$). **IR** ν_{max} (cm^{-1}): 3030 (w), 2158 (w), 1973 (w), 1639 (m), 1606 (w), 1564 (s), 1518 (m), 1506 (m), 1425 (s), 1371 (m), 1282 (m), 1224 (m), 1161 (w), 1099 (m), 985 (m), 974 (s), 858 (w), 788 (m), 771 (m), 746 (m), 715 (m), 690 (s), 675 (m), 613 (m). **HRMS** (ES^+) m/z calculated for $[C_{29}H_{22}FO_2]^+ [M+H-(B(C_6F_5)_3)]^+$: 421.1604, found: 421.1609.

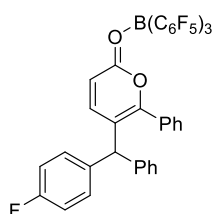


4.11t: Synthesised according to *General Procedure 8* using **4.10q** (44 mg, 0.1 mmol) and $B(C_6F_5)_3$ (51 mg, 0.1 mmol) to give a white solid that was crystallised by slow evaporation of a saturated CH_2Cl_2 /hexane solution. Yield: 79 mg, 0.08 mmol, 84%. Melting point: 207–213 °C. **1H NMR** (500 MHz, $CDCl_3$, 298 K) δ /ppm: 8.58 (d, $^3J_{HH} = 7.7$ Hz, 1H, Ar-H), 7.78–7.66 (m, 2H, Ar-H), 7.62 (d, $^3J_{HH} = 7.7$ Hz, 1H, Ar-H), 7.29 (q, $^3J_{HH} = 6.3, 5.7$ Hz, 3H, Ar-H), 7.25 (d, $^3J_{HH} = 8.6$ Hz, 3H, Ar-H), 7.13 (d, $^3J_{HH} = 7.9$ Hz, 2H, Ar-H), 7.07 (d, $^3J_{HH} = 7.4$ Hz, 2H, Ar-H), 7.01 (d, $^3J_{HH} = 8.4$ Hz, 2H, Ar-H), 6.87 (br. s, 2H, Ar-H), 5.82 (s, 1H, C(H)Ar₂), 2.38 (s, 3H, CH₃). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ /ppm: 154.59 (s), 148.03 (dm, $^1J_{CF} = 239$ Hz), 142.2 (s), 140.3 (dm, $^1J_{CF} = 246$ Hz), 139.6 (s), 139.0 (s), 138.6 (s), 137.1 (dm, $^1J_{CF} = 247$ Hz), 133.4 (s), 131.0 (s), 130.3 (s), 129.7 (s), 129.2 (s), 128.8 (s), 128.6 (s), 127.7 (s), 49.5 (s), 21.6 (s). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ /ppm: 0.5 (br. s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ /ppm: -134.98 (d, $^3J_{FF} = 17.6$ Hz, 6F, *o*-F $B(C_6F_5)_3$), -157.60 (t, $^3J_{FF} = 20.3$ Hz, *p*-F $B(C_6F_5)_3$), -164.11 (t, $^3J_{FF} = 24.2$ Hz, *m*-F $B(C_6F_5)_3$). **IR** ν_{max} (cm^{-1}): 3028 (w), 2158 (w), 1637 (m), 1606 (w), 1564 (s), 1517 (s),

1432 (s), 1375 (w), 1280 (m), 1174 (w), 1097 (s), 1014 (m), 987 (m), 974 (s), 906 (w), 858 (m), 839 (m), 821 (m), 794 (m), 738 (s), 707 (m), 690 (s), 673 (m), 626 (m), 613 (m). **HRMS** (ES⁺) m/z calculated for [C₂₉H₂₂ClO₂]⁺ [M+H-(B(C₆F₅)₃)]⁺: 437.1308, found: 437.1307.

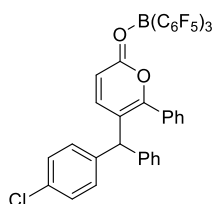


4.11u: Synthesised according to *General Procedure 8* using **4.10r** (48 mg, 0.1 mmol) and B(C₆F₅)₃ (51 mg, 0.1 mmol) to give a white solid that was recrystallised by slow evaporation of a saturated CH₂Cl₂/hexane solution. Yield: 87 mg, 0.09 mmol, 88%. Melting point: 220–224 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.63 (d, ³J_{HH} = 7.5 Hz, 1H, Ar-H), 7.80 (t, ³J_{HH} = 7.3 Hz, 1H, Ar-H), 7.74 (t, ³J_{HH} = 7.5 Hz, 1H, Ar-H), 7.66 (d, ³J_{HH} = 8.2 Hz, 1H, Ar-H), 7.42 (d, ³J_{HH} = 8.5 Hz, 2H, Ar-H), 7.31 (dt, ³J_{HH} = 6.9 Hz, 3H, Ar-H), 7.16 (d, ³J_{HH} = 7.9 Hz, 2H, Ar-H), 7.09 (d, ³J_{HH} = 7.4 Hz, 2H, Ar-H), 6.97 (d, ³J_{HH} = 8.4 Hz, 2H, Ar-H), 6.87 (d, ³J_{HH} = 7.9 Hz, 2H, Ar-H), 5.83 (s, 1H, C(H)Ar₂), 2.41 (s, 3H, CH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 169.3 (s), 154.6 (s), 148.0 (dm, ¹J_{CF} = 241 Hz), 142.3 (s), 140.0 (d, ¹J_{CF} = 262 Hz), 139.4 (s), 139.1 (s), 137.1 (d, ¹J_{CF} = 249 Hz), 132.2 (s), 131.1 (s), 130.7 (s), 130.4 (s), 129.7 (s), 129.2 (s), 128.8 (s), 128.5 (s), 127.7 (s), 127.7 (s), 126.6 (s), 121.5 (s), 120.2 (s), 118.2 (s), 49.6 (s), 21.6 (s). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 0.5 (br. s). **¹⁹F NMR** (471 MHz, CDCl₃, 298 K) δ/ppm: -134.98 (d, ³J_{FF} = 18.2 Hz, 6F, *o*-F B(C₆F₅)₃), -157.60 (t, ³J_{FF} = 19.9 Hz, 3F, *p*-F B(C₆F₅)₃), -164.10 (t, ³J_{FF} = 18.2 Hz, 6F, *m*-F B(C₆F₅)₃). **IR** ν_{max} (cm⁻¹): 3032 (w), 2160 (w), 1638 (m), 1606 (w), 1564 (m), 1518 (m), 1589 (s), 1377 (m), 1321 (w), 1282 (m), 1172 (w), 1097 (s), 1009 (m), 985 (s), 974 (s), 935 (w), 906 (w), 856 (m), 821 (m), 790 (s), 773 (s), 740 (m), 717 (m), 690 (s), 675 (s), 624 (m), 611 (w). **HRMS** (ES⁺) m/z calculated for [C₂₉H₂₂O₂Br]⁺ [M+H-(B(C₆F₅)₃)]⁺: 481.0803, found: 481.0810.

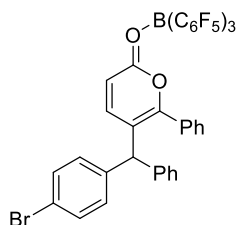


4.11v: Synthesised according to *General Procedure 8* using **4.10s** (36 mg, 0.1 mmol) and B(C₆F₅)₃ (51 mg, 0.1 mmol) to give a pale green solid that was recrystallised by slow evaporation of a saturated CH₂Cl₂/hexane solution. Yield: 80 mg, 0.09 mmol, 92%. Melting point: 117–123 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.92 (br. s, 1H, =CH), 7.57 (t, ³J_{HH} = 7.5 Hz, 1H, Ar-H), 7.45–7.31 (m, 5H, Ar-H), 7.11–7.03 (m, 4H, Ar-H), 7.00–6.94 (m, 4H, Ar-H), 6.91 (br. s, 1H, =CH), 5.49 (s, 1H, C(H)Ar₂). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 162.2 (d, ¹J_{CF} = 248 Hz), 148.0 (dm, ¹J_{CF} = 241 Hz), 140.4 (s), 140.0 (dm, ¹J_{CF} = 249 Hz), 137.1 (dm, ¹J_{CF} = 245 Hz), 136.5 (s), 132.4 (s), 130.5 (d, ³J_{CF} = 8.1 Hz), 129.6 (s), 129.2 (s), 128.8 (s),

128.5 (s), 128.2 (s), 117.7 (s), 116.5 (d, $^2J_{CF} = 21.6$ Hz), 113.6 (s), 49.4 (s). **^{11}B NMR** (128 MHz, CDCl_3 , 298 K) δ/ppm : 0.1 (br. s). **^{19}F NMR** (471 MHz, CDCl_3 , 298 K) δ/ppm : -113.7 (s, 1F, *p*-F), -134.7 (d, $^3J_{FF} = 17.9$ Hz, 6F, *o*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -157.6 (t, $^3J_{FF} = 20.3$ Hz, 3F, *p*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -164.2 (t, $^3J_{FF} = 18.3$ Hz, 6F, *m*-F $\text{B}(\text{C}_6\text{F}_5)_3$). **IR** ν_{max} (cm^{-1}): 3030 (w), 2158 (w), 1973 (w), 1639 (m), 1606 (m), 1564 (s), 1517 (s), 1506 (m), 1435 (s), 137 (m), 1282 (m), 1224 (m), 1161 (w), 1099 (s), 985 (m), 974 (s), 858 (m), 788 (m), 771 (s), 746 (m), 738 (m), 715 (m), 690 (s), 613 (m). **HRMS** (ES^+) m/z calculated for $[\text{C}_{24}\text{H}_{18}\text{O}_2\text{F}]^+ [\text{M}+\text{H}-(\text{B}(\text{C}_6\text{F}_5)_3)]^+$: 357.1291, found: 357.1293.



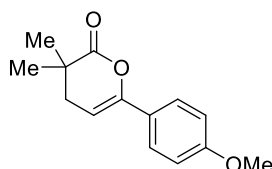
4.11w: Synthesised according to *General Procedure 8* using **4.10t** (37 mg, 0.1 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (51 mg, 0.1 mmol) to give a pale green solid that was recrystallised by slow evaporation of a saturated CH_2Cl_2 /hexane solution. Yield: 76 mg, 0.09 mmol, 86%. Melting point: 120–126 °C. **^1H NMR** (500 MHz, CDCl_3 , 298 K) δ/ppm : 7.95 (d, $^3J_{\text{HH}} = 9.4$ Hz, 1H, =CH), 7.58 (t, $^3J_{\text{HH}} = 7.6$ Hz, 1H, Ar-H), 7.44–7.32 (m, 8H, Ar-H), 7.06 (d, $^3J_{\text{HH}} = 7.5$ Hz, 2H, Ar-H), 6.99–6.86 (m, 6H, Ar-H), 5.49 (s, 1H, C(H)Ar₂). **^{13}C NMR** (126 MHz, CDCl_3 , 298 K) δ/ppm : 168.6 (s), 162.0 (s), 153.9 (s), 148.0 (dm, $^1J_{CF} = 238$ Hz), 140.1 (s), 140.0 (dm, $^1J_{CF} = 250$ Hz), 139.1 (s), 137.1 (dm, $^1J_{CF} = 248$ Hz), 134.2 (s), 132.6 (s), 130.2 (s), 129.7 (s), 129.7 (s), 129.3 (s), 128.8 (s), 128.5 (s), 128.3 (s), 128.1 (s), 124.7 (s), 113.5 (s), 49.6 (s). **^{11}B NMR** (128 MHz, CDCl_3 , 298 K) δ/ppm : 0.1 (br. s). **^{19}F NMR** (471 MHz, CDCl_3 , 298 K) δ/ppm : -134.7 (d, $^3J_{FF} = 18.6$ Hz, 6F, *o*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -157.6 (t, $^3J_{FF} = 20.1$ Hz, 3F, *p*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -164.2 (t, $^3J_{FF} = 18.3$ Hz, 6F, *m*-F $\text{B}(\text{C}_6\text{F}_5)_3$). **IR** ν_{max} (cm^{-1}): 3028 (w), 2158 (w), 1637 (m), 1606 (w), 1564 (m), 1517 (m), 1458 (s), 1375 (m), 1280 (m), 1174 (w), 1097 (m), 1014 (w), 987 (m), 974 (m), 933 (w), 906 (w), 858 (m), 839 (m), 821 (m), 794 (m), 773 (m), 746 (m), 738 (m), 721 (m), 690 (m), 673 (m). **HRMS** (ES^+) m/z calculated for $[\text{C}_{24}\text{H}_{18}\text{O}_2\text{Cl}]^+ [\text{M}+\text{H}-(\text{B}(\text{C}_6\text{F}_5)_3)]^+$: 373.0995, found: 373.1005.



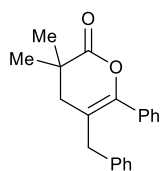
4.11x: Synthesised according to *General Procedure 8* using **4.10u** (42 mg, 0.1 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (51 mg, 0.1 mmol) to give a pale green solid that was recrystallised by slow evaporation of a saturated CH_2Cl_2 /hexane solution. Yield: 78 mg, 0.08 mmol, 84%. Melting point: 92–95 °C. **^1H NMR** (500 MHz, CDCl_3 , 298 K) δ/ppm : 7.95 (d, $^3J_{\text{HH}} = 9.2$ Hz, 1H, =CH), 7.58 (t, $^3J_{\text{HH}} = 7.6$ Hz, 1H, Ar-H), 7.50 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H, Ar-H), 7.45–7.33 (m, 6H, Ar-H), 7.06 (d, $^3J_{\text{HH}} = 7.5$ Hz, 2H, Ar-H), 6.97 (d, $^3J_{\text{HH}} = 6.7$ Hz, 3H, Ar-H, =CH), 6.86 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H, Ar-H), 5.47 (s, 1H, C(H)Ar₂). **^{13}C NMR** (126 MHz, CDCl_3 , 298 K) δ/ppm : 161.9 (s), 147.9 (dm, $^1J_{CF} = 238$

Hz), 140.1 (s), 140.0 (dm, $^1J_{CF} = 254$ Hz), 139.7 (s), 137.0 (dm, $^1J_{CF} = 253$ Hz), 132.6 (s), 130.5 (s), 129.6 (s), 129.3 (s), 128.8 (s), 128.5 (s), 128.2 (s), 122.2 (s), 113.5 (s), 49.6 (s). **^{11}B NMR** (128 MHz, CDCl_3 , 298 K) δ /ppm: 0.0 (br. s). **^{19}F NMR** (471 MHz, CDCl_3 , 298 K) δ /ppm: -134.72 (d, $^3J_{FF} = 17.8$ Hz, 6F, *o*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -157.58 (t, $^3J_{FF} = 20.2$ Hz, 3F, *p*-F $\text{B}(\text{C}_6\text{F}_5)_3$), -164.14 (t, $^3J_{FF} = 18.1$ Hz, 6F, *m*-F $\text{B}(\text{C}_6\text{F}_5)_3$). **IR** ν_{max} (cm^{-1}): 3032 (w), 2160 (w), 1637 (m), 1606 (w), 1564 (m), 1516 (m), 1425 (s), 1377 (m), 1321 (w), 1282 (m), 1172 (w), 1097 (s), 1008 (m), 985 (s), 974 (s), 935 (w), 906 (w), 856 (m), 821 (m), 790 (m), 746 (m), 740 (m), 717 (m), 690 (s), 675 (s), 625 611 (m), 576 (m). **HRMS** (ES^+) m/z calculated for $[\text{C}_{24}\text{H}_{18}\text{O}_2\text{Br}]^+$ $[\text{M}+\text{H}-(\text{B}(\text{C}_6\text{F}_5)_3)]^+$: 417.0490, found: 417.0503.

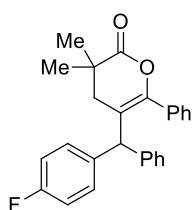
General Procedure 9: Alkynyl carboxylic acids **4.9** or esters **4.10** (0.1 mmol) were dissolved in CDCl_3 (0.2 M), then $\text{B}(\text{C}_6\text{F}_5)_3$ (3 mg, 5 mol%), unless otherwise stated, was added and transferred to a sealable J. Young NMR tube. The resultant solution was heated for 18 h at 70 °C (unless otherwise indicated). Once the reaction was complete as observed by *in situ* NMR spectroscopy, the solvent was removed *in vacuo* and the residue purified by either recrystallisation or column chromatography (SiO_2 , CHCl_3) to obtain the pure product **4.12** after the removal of solvents under reduced pressure.



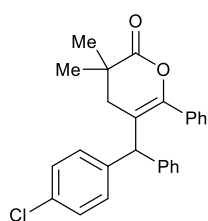
4.12a: Synthesised according to *General Procedure 9* using **4.9c** (23 mg, 0.1 mmol) to give a white solid that was recrystallised from slow evaporation of a saturated CH_2Cl_2 /hexane solution. Yield: 21 mg, 0.09 mmol, 91%. Melting point: 68–74 °C. **^1H NMR** (500 MHz, CDCl_3 , 298 K) δ /ppm: 7.53 (d, $^3J_{\text{HH}} = 8.2$ Hz, 2H, Ar-H), 6.88 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H, Ar-H), 5.60 (t, $^3J_{\text{HH}} = 4.4$ Hz, 1H, =CH), 3.82 (s, 3H, OCH_3), 2.35 (d, $^3J_{\text{HH}} = 4.4$ Hz, 2H, CH_2), 1.32 (s, 6H, $\text{C}(\text{CH}_3)_2$). **^{13}C NMR** (126 MHz, CDCl_3 , 298 K) δ /ppm: 160.3 (s), 149.8 (s), 126.0 (s), 114.0 (s), 97.4 (s), 55.5 (s), 36.6 (s), 34.5 (s), 25.1 (s). **IR** ν_{max} (cm^{-1}): 3067 (w), 2959 (w), 1724 (s), 1676 (s), 1599 (s), 1576 (m), 1508 (m), 1483 (w), 1467 (w), 1427 (s), 1366 (w), 1306 (w), 1253 (m), 1170 (m), 1120 (s), 1093 (s), 1028 (s), 995 (m), 974 (m), 916 (w), 874 (w), 835 (w), 773 (w), 736 (m), 719 (s), 695 (s), 542 (w), 501 (s), 482 (m). **HRMS** (ES^+) m/z calculated for $[\text{C}_{14}\text{H}_{17}\text{O}_3]^+$ $[\text{M}+\text{H}]^+$: 233.1178, found: 233.1179.



4.12b: Synthesised according to *General Procedure 9* using compound **4.10c** (58 mg, 0.2 mmol, 1 equiv.). Once reacted for 5 d, Removal of volatiles after column chromatography gave a pale yellow oil. R_f value: 0.50. Yield: 19 mg, 0.7 mmol, 33%. $^1\text{H NMR}$ (400 MHz, CDCl_3 , 298 K) δ /ppm: 7.52–7.30 (br. m, 7H, Ar-H), 7.18–7.17 (br. s, 3H, Ar-H), 3.55 (s, 2H, CH_2Ph), 2.18 (s, 2H, CH_2), 1.26 (s, 6H, $\text{C}(\text{CH}_3)_2$). Agreeing with values obtained for **4.11f**.

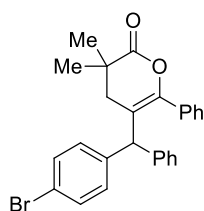


4.12c: Synthesised according to *General Procedure 9* using compound **4.10d** (39 mg, 0.1 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (3 mg, 5 μmol , 5 mol%). Removal of volatiles after column chromatography gave a white solid. A crop of colourless crystals suitable for single crystal X-ray diffraction were obtained by storing a saturated hexane/ CH_2Cl_2 solution at -40°C . R_f value: 0.51 (SiO_2 , hexane/ CHCl_3 1:2). Yield: 37 mg, 0.95 mmol, 95%. Melting point: $139\text{--}144^\circ\text{C}$. $^1\text{H NMR}$ (400 MHz, CDCl_3 , 298 K) δ /ppm: 7.30–7.17 (m, 8H, Ph-H), 7.03–6.97 (m, 4H, Ph-H), 6.92 (t, $^3J_{\text{HH}} = 8.5$ Hz, 2H, Ph-H), 5.18 (s, 1H, $\text{C}(\text{H})\text{Ar}_2$), 2.20–2.10 (m, 2H, CH_2), 1.07 (s, 6H, $\text{C}(\text{CH}_3)_2$). $^{13}\text{C NMR}$ (101 MHz, CDCl_3 , 298 K) δ /ppm: 173.8 (s), 161.7 (d, $^1J_{\text{CF}} = 245.8$ Hz), 147.9 (s), 141.7 (s), 137.6 (d, $^3J_{\text{CF}} = 3.3$ Hz), 132.9 (s), 130.6 (d, $^3J_{\text{CF}} = 7.9$ Hz), 129.4 (s), 129.0 (s), 128.6 (s), 128.6 (s), 128.5 (s), 127.0 (s), 115.4 (d, $^2J_{\text{CF}} = 21.2$ Hz), 114.3 (s), 50.9 (s), 36.4 (s), 35.9 (s), 24.8 (s), 24.7 (s). $^{19}\text{F NMR}$ (376 Hz, CDCl_3 , 298 K) δ /ppm: -115.82 (s, 1F, *p*-F). $\text{IR } \nu_{\text{max}}$ (cm^{-1}): 2988 (w), 1760 (s), 1671 (w), 1603 (m), 1504 (s), 1493 (m), 1466 (w), 1445 (m), 1388 (w), 1367 (w), 1344 (w), 1282 (w), 1219 (s), 1189 (w), 1155 (w), 1132 (w), 1099 (s), 1082 (s), 1070 (s), 1029 (w), 1015 (w), 1003 (w), 926 (w), 876 (w), 835 (m), 807 (w), 773 (m), 731 (w), 700 (s), 635 (w), 624 (w), 618 (w), 598 (w), 570 (w), 549 (m), 533 (m), 506 (m). HRMS (EI^+) m/z calculated for $[\text{C}_{26}\text{H}_{24}\text{O}_2\text{F}]^+$ $[\text{M}+\text{H}]^+$: 387.1760, found: 387.1751.

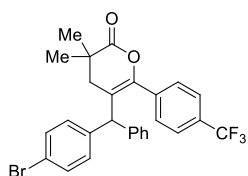


4.12d: Synthesised according to *General Procedure 9* using compound **4.10e** (40 mg, 0.1 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (3 mg, 5 μmol , 5 mol%). R_f value: 0.49 (SiO_2 , hexane/ CHCl_3 1:2). Yield: 36 mg, 0.90 mmol, 90%. Melting point: $104\text{--}110^\circ\text{C}$. $^1\text{H NMR}$ (400 MHz, CDCl_3 , 298 K) δ /ppm: 7.39–7.26 (m, 10H, Ar-H), 7.07 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H, Ar-H), 7.04 (d, $^3J_{\text{HH}} = 8.3$ Hz, 2H, Ar-H), 5.23 (s, 1H, $\text{C}(\text{H})\text{Ar}_2$), 2.23 (s, 2H, CH_2), 1.16 (s, 3H, CH_3), 1.15 (s, 3H, CH_3). $^{13}\text{C NMR}$ (101 MHz, CDCl_3 , 298 K) δ /ppm: 174.1 (s), 148.0 (s), 141.3 (s), 140.4 (s), 132.8 (s), 132.7 (s), 130.5 (s), 129.5 (s), 129.0 (s), 128.8 (s), 128.7 (s), 128.6 (s), 128.5 (s), 127.2 (s), 114.2 (s), 51.1 (s), 36.4 (s), 35.8 (s), 24.8 (s), 24.7 (s). $\text{IR } \nu_{\text{max}}$ (cm^{-1}): 2982 (w), 1759 (s), 1668 (w), 1601 (w), 1515 (w),

1489 (s), 1464 (s), 1389 (w), 1352 (w), 1277 (w), 1225 (w), 1194 (w), 1179 (w), 1157 (w), 1134 (w), 1099 (s), 1069 (s), 1013 (s), 976 (w), 921 (w), 870 (w), 833 (w), 773 (s), 756 (w), 727 (w), 705 (s), 648 (w), 611 (w), 598 (w), 550 (w), 519 (w). **HRMS** (EI⁺) *m/z* calculated for [C₂₆H₂₃O₂Cl]⁺ [M]⁺ 402.1387, found: 402.1399.

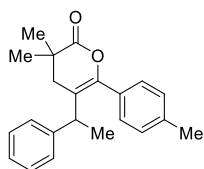


4.12e: Synthesised according to *General Procedure 9* using compound **4.10f** (45 mg, 0.1 mmol) and B(C₆F₅)₃ (3 mg, 5 μmol, 5 mol%). R_f value: 0.44 (SiO₂, hexane/CHCl₃ 1:2). Yield: 42 mg, 0.93 mmol, 93%. Melting point: 116–121 °C. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.37 (d, ³J_{HH} = 8.1 Hz, 2H, Ar-H), 7.30 (s, 5H, Ar-H), 7.25–7.18 (m, 3H, Ar-H), 7.01 (d, ³J_{HH} = 7.6 Hz, 2H, Ar-H), 6.92 (d, ³J_{HH} = 8.2 Hz, 2H, Ar-H), 5.16 (s, 1H, C(H)Ar₂), 2.15 (s, 2H, CH₂), 1.09 (s, 3H, CH₃), 1.07 (s, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 174.0 (s), 148.1 (s), 141.3 (s), 140.9 (s), 132.7 (s), 131.7 (s), 130.9 (s), 129.5 (s), 129.1 (s), 128.7 (s), 128.6 (s), 128.5 (s), 127.2 (s), 120.9 (s), 114.0 (s), 51.2 (s), 36.4 (s), 35.8 (s), 24.8 (s), 24.7 (s). **IR** ν_{max} (cm⁻¹): 3058 (w), 2981 (s), 1767 (m), 1751 (w), 1684 (w), 1667 (w), 1601 (w), 1487 (m), 1446 (m), 1386 (m), 1344 (w), 1285 (w), 1217 (w), 1155 (w), 1107 (s), 1091 (m), 1068 (s), 1029 (w), 1008 (m), 993 (s), 921 (w), 854 (w), 829 (m), 798 (w), 767 (m), 746 (m), 725 (w), 715 (w), 700 (s), 694 (s), 680 (w), 669 (w), 602 (m), 547 (m), 501 (w), 487 (m), 474 (m), 424 (w). **HRMS** (EI⁺) *m/z* calculated for [C₂₆H₂₄O₂Br]⁺ [M+H]⁺: 447.0960, found: 447.0964

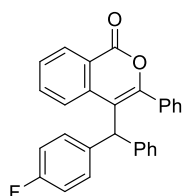


4.12f: Synthesised according to *General Procedure 9* using compound **4.10j** (500 mg, 0.9 mmol) and B(C₆F₅)₃ (3 mg, 5 μmol, 5 mol%) and was heated for 5 d. R_f value: 0.64 (SiO₂, hexane/CHCl₃ 1:2). Yield: 138 mg, 0.3 mmol, 27%. Melting point: 125–131 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.64 (d, ³J_{HH} = 8.3 Hz, 2H, Ar-H), 7.51 (d, ³J_{HH} = 8.2 Hz, 2H, Ar-H), 7.46 (d, ³J_{HH} = 8.4 Hz, 2H, Ar-H), 7.35–7.29 (m, 3H, Ar-H), 7.07 (d, ³J_{HH} = 7.2 Hz, 2H, Ar-H), 6.98 (d, ³J_{HH} = 8.4 Hz, 2H, Ar-H), 5.17 (s, 1H), 2.29 (d, ²J_{HH} = 17.1 Hz, 1H, diastereotopic CH₂), 2.16 (d, ²J_{HH} = 17.1 Hz, 1H, diastereotopic CH₂), 1.19 (s, 3H, CH₃), 1.17 (s, 3H, CH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 173.1 (s), 146.7 (s), 140.8 (d, ²J_{CF} = 45.7 Hz), 136.3 (s), 131.9 (s), 130.8 (s), 129.0 (s), 129.0 (s), 128.9 (s), 127.4 (s), 125.7 (q, ⁴J_{CF} = 3.8 Hz) 121.1 (s), 115.5 (s), 51.3 (s), 36.4 (s), 36.2 (s), 29.9 (s), 24.9 (s), 24.8 (s). **¹⁹F NMR** (471 MHz, CDCl₃, 298 K) δ/ppm: -62.82 (s). **IR** ν_{max} (cm⁻¹): 2981 (w), 2925 (w), 1761 (s), 1668 (w), 1615 (w), 1487 (m), 1465 (w), 1454 (m), 1424 (w), 1410 (w), 1392 (w), 1323 (s), 1228 (m), 1225 (w), 1211 (w), 1194 (w), 1178 (w), 1153 (m), 1129 (s), 1100 (s),

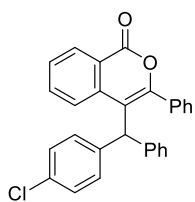
1075 (s), 1065 (s), 1016 (m), 1009 (m), 910 (w), 877 (m), 857 (s), 827 (m), 788 (m), 761 (w), 752 (w), 717 (w), 701 (s), 681 (w), 667 (w), 623 (w), 600 (w), 559 (m), 536 (w), 518 (m), 497 (w), 474 (m), 438 (w). **HRMS** (ES⁺) *m/z* calculated for [C₂₇H₂₃O₂BrF₃]⁺ [M+H]⁺: 514.0755, found: 514.0761.



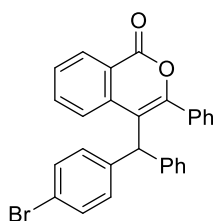
4.12g: Synthesised according to *General Procedure 9* using **4.10k** (32 mg, 0.1 mmol) with B(C₆F₅)₃ (3 mg, 5 mol%) and was heated for 54 h to give a white oil after filtration and removal of solvent. R_f value: 0.23 (SiO₂, hexane/CHCl₃ 1:2). Yield: 17 mg, 0.055 mmol, 55%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.38 (d, ³J_{HH} = 8.0 Hz, 2H, Ar-H), 7.31–7.20 (m, 5H, Ar-H), 7.15 (d, ³J_{HH} = 7.5 Hz, 2H, Ar-H), 4.05 (q, ³J_{HH} = 7.0 Hz, 1H, C(H)(Me)Ar), 2.39 (s, 3H, CH₃), 2.15 (d, ²J_{HH} = 16.8 Hz, 1H, CH₂), 1.89 (d, ²J_{HH} = 16.8 Hz, 1H, CH₂), 1.45 (d, ³J_{HH} = 7.1 Hz, 3H, C(H)(Me)Ar), 1.26 (s, 3H, CH₃), 1.07 (s, 3H, CH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 174.2 (s), 145.9 (s), 142.9 (s), 139.0 (s), 130.4 (s), 129.3 (s), 128.8 (s), 128.4 (s), 127.4 (s), 126.6 (s), 117.5 (s), 38.2 (s), 36.1 (s), 34.3 (s), 24.7 (s), 24.7 (s), 21.5 (s), 17.3 (s). **IR** ν_{max} (cm⁻¹): 1753 (w), 1448 (s), 1386 (s), 1170 (s), 1072 (w), 1024 (m), 910 (s), 827 (s), 777 (s), 732 (m), 700 (w), 410 (s), 401 (m). **HRMS** (ES⁺) *m/z* calculated for [C₂₉H₂₁O₂F]⁺ [M+H]⁺: 320.1855, found: 320.1856.



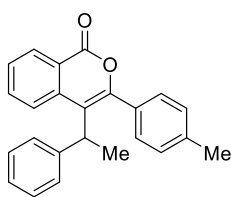
4.12h: Synthesised according to *General Procedure 9* using **4.10l** (41 mg, 0.1 mmol) and B(C₆F₅)₃ (5 mg, 10 μmol, 10 mol%) and was heated for 24 h to give a white oil after filtration and removal of solvent. Yield: 29 mg, 0.071 mmol, 71%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 8.39–8.35 (m, 1H, Ar-H), 7.45–7.37 (m, 7H, Ar-H), 7.32–7.26 (m, 3H, Ar-H), 7.20–7.14 (m, 5H, Ar-H), 6.99–6.94 (m, 2H, Ar-H), 5.82 (s, 1H, C(H)Ar₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 162.2 (s), 161.6 (d, ¹J_{CF} = 246 Hz), 154.4 (s), 141.2 (s), 137.2 (s), 137.1 (s), 137.1 (s), 133.9 (s), 133.3 (s), 130.7 (d, ³J_{CF} = 7.9 Hz), 130.1 (s), 130.1 (s), 129.2 (s), 129.0 (s), 128.8 (s), 128.6 (s), 127.9 (s), 127.2 (s), 127.0 (s), 122.0 (s), 115.5 (d, ²J_{CF} = 21.3 Hz), 49.3 (s). **¹⁹F NMR** (376 MHz, CDCl₃) δ/ppm: -115.92 (s, 1F, *p*-F). **IR** ν_{max} (cm⁻¹): 3059 (w), 1774 (w), 1730 (s), 1624 (w), 1602 (m), 1560 (w), 1504 (m), 1483 (m), 1448 (m), 1305 (w), 1222 (m), 1159 (m), 1136 (w), 1093 (s), 1051 (m), 1029 (m), 1002 (m), 905 (w), 873 (w), 831 (m), 792 (w), 765 (s), 729 (s), 685 (s), 611 (w). **HRMS** (ES⁺) *m/z* calculated for [C₂₈H₁₉O₂F]⁺ [M+H]⁺: 406.1369, found: 406.1366.



4.12i: Synthesised according to *General Procedure 9* using **4.10m** (43 mg, 0.1 mmol) and $B(C_6F_5)_3$ (6 mg, 10 μ mol, 10 mol%) and was heated for 24 h to give a white oil after filtration and removal of solvent. Yield: 33 mg, 0.078 mmol, 78%. **1H NMR** (400 MHz, $CDCl_3$, 298 K) δ /ppm: 8.39–8.34 (m, 1H, Ar-H), 7.46–7.35 (m, 8H, Ar-H), 7.32–7.26 (m, 3H, Ar-H), 7.24 (s, 1H, Ar-H), 7.20–7.11 (m, 5H, Ar-H), 5.81 (s, 1H, C(H)Ar₂). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ /ppm: 162.2 (s), 154.5 (s), 140.9 (s), 139.9 (s), 137.1 (s), 133.9 (s), 133.3 (s), 132.7 (s), 130.5 (s), 130.1 (s), 130.1 (s), 129.2 (s), 129.0 (s), 128.8 (s), 128.8 (s), 128.7 (s), 128.0 (s), 127.1 (s), 127.0 (s), 122.0 (s), 114.9 (s), 49.4 (s). **IR** ν_{max} (cm^{-1}): 3026 (w), 2962 (w), 1778 (w), 1730 (s), 1602 (m), 1560 (w), 1483 (s), 1404 (w), 1305 (m), 1284 (m), 1261 (m), 1224 (m), 1136 (w), 1089 (s), 1051 (m), 1029 (s), 1012 (s), 906 (m), 825 (m), 796 (m), 765 (m), 746 (m), 727 (s), 705 (s), 646 (m), 619 (w), 609 (w). **HRMS** (ES^+) m/z calculated for $[C_{29}H_{21}O_2Br]^+$ $[M+H]^+$: 422.1082, found: 480.1074.

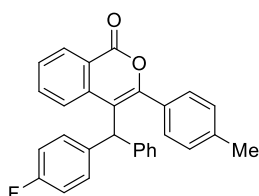


4.12j: Synthesised according to *General Procedure 9* using **4.10n** (47 mg, 0.1 mmol) and $B(C_6F_5)_3$ (6 mg, 10 μ mol, 10 mol%) and was heated for 24 h to give a white solid after filtration and removal of solvent. Yield: 35 mg, 0.075 mmol, 75%. Melting point: 85–91 °C. **1H NMR** (400 MHz, $CDCl_3$, 298 K) δ /ppm: 8.31–8.27 (m, 1H, Ar-H), 7.37–7.27 (m, 10H, Ar-H), 7.24–7.18 (m, 3H, Ar-H), 7.12–7.08 (m, 2H, Ar-H), 7.02–6.98 (m, 2H, Ar-H), 5.71 (s, 1H, C(H)Ar₂). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ /ppm: 162.2 (s), 154.5 (s), 140.8 (s), 140.4 (s), 137.1 (s), 133.9 (s), 133.3 (s), 131.7 (s), 130.9 (s), 130.1 (s), 130.1 (s), 129.2 (s), 129.0 (s), 128.8 (s), 128.7 (s), 128.0 (s), 127.1 (s), 127.04 (s), 121.9 (s), 120.8 (s), 114.8 (s), 49.5 (s). **IR** ν_{max} (cm^{-1}): 2945 (w), 1778 (w), 1732 (s), 1604 (m), 1560 (w), 1483 (s), 1446 (m), 1398 (w), 1305 (m), 1284 (m), 1226 (m), 1182 (m), 1136 (w), 1093 (s), 1074 (s), 1051 (m), 1029 (s), 1008 (s), 908 (w), 825 (m), 792 (w), 765 (m), 744 (m), 695 (s). **HRMS** (ES^+) m/z calculated for $[C_{29}H_{21}O_2Br]^+$ $[M+H]^+$: 466.0568, found: 466.0570.



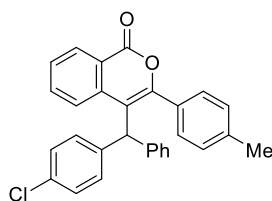
4.12k: Synthesised according to *General Procedure 9* using **4.10o** (34 mg, 0.1 mmol) with $B(C_6F_5)_3$ (6 mg, 10 mol%) and was heated for 43 h to give a white oil after filtration and removal of solvent. R_f value: 0.22 (SiO_2 , hexane/ $CHCl_3$ 1:2). Yield: 25 mg, 0.073 mmol, 73%. **1H NMR** (500 MHz, $CDCl_3$) δ /ppm: 8.33 (d, $^3J_{HH} = 7.5$ Hz, 1H, Ar-H), 7.49–7.36 (m, 4H, Ar-H), 7.33–7.16 (m, 8H, Ar-H), 4.53 (q, $^3J_{HH} = 7.1$ Hz, 1H, C(H)(Me)Ar), 2.36 (s, 3H, CH_3), 1.74 (d, $^3J_{HH} = 7.3$ Hz, 3H,

C(H)(Me)Ar). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 162.6 (s), 153.0 (s), 143.4 (s), 139.9 (s), 136.6 (s), 133.9 (s), 130.2 (s), 129.4 (s), 129.0 (s), 128.8 (s), 127.6 (s), 126.8 (s), 126.3 (s), 126.2 (s), 125.3 (s), 122.2 (s), 117.0 (s), 37.2 (s), 21.5 (s), 18.7 (s). **IR** ν_{\max} (cm⁻¹): 1728 (w), 1105 (m), 1483 (s), 1078 (m), 1062 (m), 1022 (m), 812 (s), 783 (s), 767 (w), 725 (w), 698 (w), 661 (s), 513 (s), 497 (s). **HRMS** (ES⁺) m/z calculated for [C₂₉H₂₁O₂F]⁺ [M+H]⁺: 341.1542, found: 341.1530.



4.12i: Synthesised according to *General Procedure 9* using **4.10p** (42 mg, 0.1 mmol) and B(C₆F₅)₃ (3 mg, 5 μmol, 5 mol%) and was heated for 6 h to give a white solid after filtration and removal of solvent. Yield: 41 mg, 0.097 mmol, 97%. Melting point: 142–148 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm:

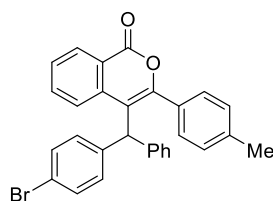
8.26–8.23 (m, 1H, Ar-H), 7.31–7.22 (m, 4H, Ar-H), 7.20–7.11 (m, 4H, Ar-H), 7.10–7.03 (m, 7H, Ar-H), 6.88–6.83 (m, 2H, Ar-H), 5.74 (s, 1H, C(H)Ar₂), 2.27 (s, 3H, CH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 162.4 (s), 161.6 (d, ¹J_{CF} = 246 Hz), 154.6 (s), 141.3 (s), 140.3 (s), 137.3 (s), 137.2 (s), 133.8 (s), 130.7 (d, ³J_{CF} = 7.8 Hz), 130.4 (s), 130.0 (s), 129.3 (s), 129.0 (s), 129.0 (s), 128.7 (s), 127.8 (s), 127.1 (s), 126.9 (s), 121.9 (s), 115.4 (d, ²J_{CF} = 21.3 Hz), 114.8 (s), 49.3 (s), 21.5 (s). **¹⁹F NMR** (471 MHz, CDCl₃, 298 K) δ/ppm: -115.94 – -116.02 (m, 1F, *p*-F). **IR** ν_{\max} (cm⁻¹): 1737 (w), 1625 (s), 1600 (s), 1504 (w), 1483 (m), 1446 (s), 1224 (w), 1161 (s), 1089 (w), 1051 (s), 1024 (m), 837 (m), 825 (s), 808 (s), 765 (w), 752 (m), 727 (m), 698 (w), 677 (m), 609 (s), 526 (w), 509 (s), 497 (s). **HRMS** (ES⁺) m/z calculated for [C₂₉H₂₁O₂F]⁺ [M+H]⁺: 420.1526, found: 420.1515.



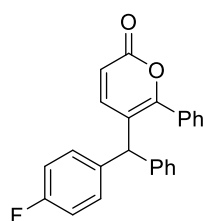
4.12m: Synthesised according to *General Procedure 9* using **4.10q** (44 mg, 0.1 mmol) and B(C₆F₅)₃ (3 mg, 5 μmol, 5 mol%) and was heated for 6 h to give a white solid after filtration and removal of solvent. Yield: 42 mg, 0.096 mmol, 96%. Melting point: 72–76 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm:

8.31–8.27 (m, 1H, Ar-H), 7.36–7.32 (m, 2H, Ar-H), 7.30–7.25 (m, 2H, Ar-H), 7.25–7.14 (m, 6H, Ar-H), 7.12 (d, ³J_{HH} = 8.0 Hz, 4H, Ar-H), 7.07 (d, ³J_{HH} = 8.1 Hz, 2H, Ar-H), 5.77 (s, 1H, C(H)Ar₂), 2.31 (s, 3H, CH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 162.2 (s), 154.6 (s), 140.8 (s), 140.2 (s), 139.9 (s), 137.1 (s), 133.7 (s), 132.5 (s), 130.4 (s), 130.3 (s), 129.9 (s), 129.2 (s), 128.9 (s), 128.9 (s), 128.6 (s), 128.6 (s), 127.7 (s), 127.0 (s), 126.9 (s), 121.8 (s), 114.5 (s), 49.3 (s), 21.5 (s). **IR** ν_{\max} (cm⁻¹): 1730 (w), 1606 (s), 1508 (s), 1487 (m), 1448 (s), 1284 (s), 1089 (m), 1051 (s), 1026

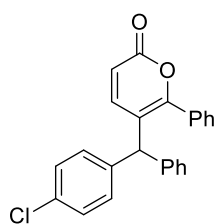
(s), 1014 (s), 831 (s), 769 (m), 748 (m), 729 (s), 698 (m), 547 (s), 518 (s), 499 (s).
HRMS (ES⁺) *m/z* calculated for [C₂₉H₂₁O₂Cl]⁺ [M+H]⁺: 436.1230, found: 233.1227.



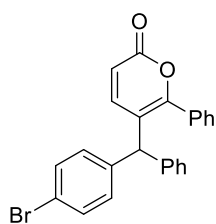
4.12n: Synthesised according to *General Procedure 9* using **4.10r** (48 mg, 0.1 mmol) and was heated for 6 h to give a white solid after filtration and removal of solvent. Yield: 43 mg, 0.089 mmol, 89%. Melting point: 56–59 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.27–8.23 (m, 1H, Ar-H), 7.32–7.27 (m, 4H, Ar-H), 7.27–7.22 (m, 3H, Ar-H), 7.20–7.11 (m, 3H, Ar-H), 7.08 (d, ³J_{HH} = 7.9 Hz, 4H, Ar-H), 6.98 (d, ³J_{HH} = 8.0 Hz, 2H, Ar-H), 5.72 (s, 1H, C(H)Ar₂), 2.28 (s, 3H, CH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 162.3 (s), 154.7 (s), 140.8 (s), 140.5 (s), 140.3 (s), 137.2 (s), 133.8 (s), 131.7 (s), 130.9 (s), 130.4 (s), 130.0 (s), 129.3 (s), 129.0 (s), 129.0 (s), 128.7 (s), 127.8 (s), 127.0 (s), 127.0 (s), 121.9 (s), 120.7 (s), 114.5 (s), 49.5 (s), 21.5 (s). **IR** ν_{max} (cm⁻¹): 2980 (w), 1728 (m), 1483 (m), 1091 (m), 1074 (s), 1026 (s), 1008 (s), 769 (s), 744 (m), 727 (m), 698 (w), 682 (s), 545 (s), 516 (s), 497 (s), 468 (s). **HRMS** (ES⁺) *m/z* calculated for [C₂₉H₂₁O₂Br]⁺ [M+H]⁺: 480.0725, found: 480.0725.



4.12o: Synthesised according to *General Procedure 9* using **4.10s** (36 mg, 0.1 mmol) and B(C₆F₅)₃ (3 mg, 5 μmol, 5 mol%) and was heated for 16 h to give a yellow oil after filtration and removal of solvent. Yield: 29 mg, 0.080 mmol 80%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.41–7.32 (m, 5H, Ar-H), 7.30–7.27 (m, 1H, Ar-H), 7.25–7.16 (m, 3H, Ar-H), 6.99–6.93 (m, 6H, Ar-H), 6.22 (d, ³J_{HH} = 9.6 Hz, 1H, Ar-H), 5.37 (s, 1H, C(H)Ar₂). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 161.8 (d, ¹J_{CF} = 247 Hz), 161.7 (s), 159.3 (s), 146.2 (s), 142.1 (s), 138.1 (d, ³J_{CF} = 3.3 Hz), 132.0 (s), 130.6 (s), 130.6 (s), 130.5 (s), 129.1 (s), 129.0 (s), 128.8 (s), 128.7 (s), 127.4 (s), 117.4 (s), 115.85 (d, ²J_{CF} = 21.4 Hz), 114.98 (s), 49.21 (s). **¹⁹F NMR** (471 MHz, CDCl₃) δ/ppm: -115.24 – -115.32 (m, 1F, *p*-F). **IR** ν_{max} (cm⁻¹): 2980 (s), 1707 (m), 1548 (s), 1504 (w), 1490 (m), 1446 (s), 1226 (m), 1157 (m), 1116 (s), 1097 (m), 1076 (s), 991 (s), 852 (s), 825 (w), 806 (s), 771 (m), 759 (m), 732 (w), 698 (w), 663 (m), 644 (m), 615 (m), 594 (w), 565 (w), 526 (s), 509 (w). **HRMS** (ES⁺) *m/z* calculated for [C₂₄H₁₇O₂F]⁺ [M+H]⁺: 356.1213, found: 356.1209.

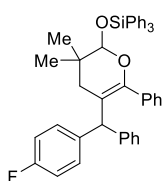


4.12p: Synthesised according to *General Procedure 9* using **4.10t** (38 mg, 0.1 mmol) and $B(C_6F_5)_3$ (3 mg, 5 μ mol, 5 mol%) and was heated for 24 h to give a yellow solid after filtration and removal of solvent. Yield: 29 mg, 0.078 mmol 78%. Melting point: 45 °C. **1H NMR** (500 MHz, $CDCl_3$, 298 K) δ /ppm: 7.41–7.35 (m, 4H, Ar-H), 7.31–7.27 (m, 3H, Ar-H), 7.25–7.20 (m, 3H, Ar-H), 7.19–7.16 (m, 1H, Ar-H), 6.98 (d, $^3J_{HH} = 7.1$ Hz, 2H, Ar-H), 6.95–6.92 (m, 2H, Ar-H), 6.23 (d, $^3J_{HH} = 9.6$ Hz, 1H, Ar-H), 5.37 (s, 1H, C(H)Ar₂). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ /ppm: 161.6 (s), 159.5 (s), 146.1 (s), 141.8 (s), 140.9 (s), 133.2 (s), 132.1 (s), 131.9 (s), 130.6 (s), 130.4 (s), 129.1 (s), 129.1 (s), 129.0 (s), 128.8 (s), 128.7 (s), 117.1 (s), 115.0 (s), 49.4 (s). **IR** ν_{max} (cm^{-1}): 2980 (s), 1720 (w), 1543 (s), 1489 (w), 1446 (m), 1155 (m), 1089 (m), 1014 (s), 1002 (s), 991 (s), 819 (m), 752 (m), 734 (m), 696 (w), 663 (s), 615 (s), 594 (m), 514 (s), 491 (m). **HRMS** (ES^+) m/z calculated for $[C_{24}H_{17}O_2Cl]^+$ $[M+H]^+$: 372.0917, found: 372.0914.

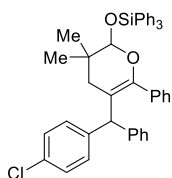


4.12q: Synthesised according to *General Procedure 9* using **4.10u** (42 mg, 0.1 mmol) and $B(C_6F_5)_3$ (3 mg, 5 μ mol, 5 mol%) and was heated for 24 h to give a yellow oil after filtration and removal of solvent. Yield: 30 mg, 0.072 mmol 72%. **1H NMR** (500 MHz, $CDCl_3$, 298 K) δ /ppm: 7.39–7.32 (m, 6H, Ar-H), 7.25–7.17 (m, 4H, Ar-H), 7.16–7.12 (m, 1H, Ar-H), 6.94 (d, $^3J_{HH} = 7.5$ Hz, 2H, Ar-H), 6.86–6.82 (m, 2H, Ar-H), 6.20 (d, $^3J_{HH} = 9.6$ Hz, 1H, Ar-H), 5.32 (s, 1H, C(H)Ar₂). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ /ppm: 160.5 (s), 158.3 (s), 144.9 (s), 140.6 (s), 140.3 (s), 130.9 (s), 129.6 (s), 129.4 (s), 128.0 (s), 127.8 (s), 127.6 (s), 127.6 (s), 126.3 (s), 126.1 (s), 120.1 (s), 115.9 (s), 113.9 (s), 48.3 (s). **IR** ν_{max} (cm^{-1}): 2980 (s), 1720 (m), 1487 (m), 1155 (s), 1097 (s), 1072 (m), 1010 (m), 993 (s), 821 (s), 750 (w), 732 (w), 696 (w), 665 (s), 594 (m), 505 (s), 486 (s). **HRMS** (ES^+) m/z calculated for $[C_{24}H_{17}O_2Br]^+$ $[M+H]^+$: 416.0412, found: 416.0418.

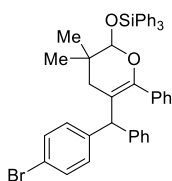
General synthesis 10: Alkynyl ester **4.10** (0.1 mmol, 1 equiv.) was dissolved in CH_2Cl_2 and combined with $B(C_6F_5)_3$ (3 mg, 5 μ mol, 5 mol%) with subsequent heating to 70 °C for 8 h. At this time silane (0.1 mmol, 1 equiv.) was added and the reaction mixture heated again at 70 °C for 8 h. Removal of solvents *in vacuo* yielded the pure cyclic silyl acetal product **6**. Note: NMR spectra show both conformations of cyclic silyl acetals in a ca. 1:1 ratio, however, both diastereomers showed considerable overlap with one another so could not be independently reported.



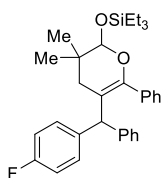
4.13a: Synthesised according to *General Procedure 10* using **4.10d** (39 mg, 0.1 mmol) along with $B(C_6F_5)_3$ (3 mg, 5 μ mol, 5 mol%) and $HSiPh_3$ (26 mg, 0.1 mmol, 1 equiv.) to give a white powdery solid upon removal of volatiles. Yield: 61 mg, 0.09 mmol, 95%. Melting point: 120–127 °C. **1H NMR** (400 MHz, $CDCl_3$, 298 K) δ /ppm: 7.53 (m, 6H, Ar-H), 7.38 (m, 4H, Ar-H), 7.31–7.17 (m, 9H, Ar-H), 7.10–7.02 (m, 5H, Ar-H), 6.92 (m, 2H, Ar-H), 6.78 (m, 2H, Ar-H), 5.03 (m, 1H, C(H)O₂), 4.98 (m, 1H, C(H)Ar₂), 2.08 (d, $^2J_{HH} = 17.4$ Hz, 1H, CH₂), 1.65 (d, $^2J_{HH} = 16.7$ Hz, 1H, CH₂), 0.97–0.95 (m, 6H, C(CH₃)₂). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ /ppm: 161.5 (d, $^1J_{CF} = 254$ Hz), 145.5 (s), 143.4 (s), 139.4 (d, $^3J_{CF} = 13.0$ Hz), 136.0 (s), 136.0 (s), 134.1 (s), 131.0 (s), 130.8 (s), 130.3 (s), 130.1 (s), 129.5 (s), 129.3 (s), 128.9 (s), 128.4 (s), 128.3 (s), 128.1 (s), 128.0 (s), 126.4 (s), 115.1 (d, $^2J_{CF} = 21.2$ Hz), 109.5 (s), 98.6 (s), 51.5 (s), 33.7 (s), 32.0 (s), 25.5 (s), 24.2 (s). **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ /ppm: -116.99 (s, 1F, *p*-F), -117.18 (s, 1F, *p*-F). **^{29}Si NMR** (79 MHz, $CDCl_3$, 298 K) δ /ppm: -11.7 (s, SiPh₃). **IR** ν_{max} (cm⁻¹): 3198 (w), 3009 (m), 2931 (w), 2854 (m), 2439 (m), 2320 (w), 2229 (s), 2094 (s), 2058 (s), 2021 (w), 2000 (w), 1948 (s), 1897 (w), 1751 (m), 1705 (m), 1653 (m), 1625 (w), 1537 (m), 1490 (m), 1395 (s), 1346 (m), 1311 (m), 1274 (m), 1209 (m), 1128 (m), 1051 (s), 1021 (s), 876 (w), 781 (m), 758 (m), 744 (m). **HRMS** (ES⁺) *m/z* calculated for [C₄₄H₄₀FO₂Si]⁺ [M+H]⁺: 647.2782, found: 647.2781.



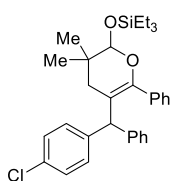
4.13b: Synthesised according to *General Procedure 10* using **4.10e** (40 mg, 0.1 mmol) along with $B(C_6F_5)_3$ (3 mg, 5 μ mol, 5 mol%) and $HSiPh_3$ (26 mg, 0.1 mmol, 1 equiv.) to give a white powdery solid upon removal of volatiles. Yield: 61 mg, 0.09 mmol, 92%. Melting point: 70–75 °C. **1H NMR** (400 MHz, $CDCl_3$, 298 K) δ /ppm: 7.63 (d, $^3J_{HH} = 7.0$ Hz, 6H, Ar-H), 7.48 (m, 4H, Ar-H), 7.41–7.26 (m, 10H, Ar-H), 7.21–7.10 (m, 6H, Ar-H), 6.86 (d, $^3J_{HH} = 7.4$ Hz, 2H, Ar-H), 5.11 (m, 1H, C(H)O₂), 5.07 (m, 1H, C(H)Ar₂), 2.16 (t, $^2J_{HH} = 16.7$ Hz, 1H, CH₂), 1.74 (dd, $^2J_{HH} = 16.6$ Hz, 1H, CH₂), 1.07–1.04 (m, 6H, C(CH₃)₂). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ /ppm: 145.5 (s), 143.1 (s), 142.2 (s), 135.9 (s), 135.9 (s), 135.1 (s), 134.0 (s), 131.9 (s), 130.9 (s), 130.6 (s), 130.3 (s), 129.4 (s), 129.2 (s), 128.7 (s), 128.4 (s), 128.3 (s), 128.2 (s), 128.1 (s), 126.5 (s), 109.0 (s), 98.5 (s), 51.5 (s), 33.6 (s), 31.9 (s), 25.5 (s), 24.1 (s). **^{29}Si NMR** (79 MHz, $CDCl_3$, 298 K) δ /ppm: -11.7 (s, SiPh₃). **IR** ν_{max} (cm⁻¹): 3049 (w), 2972 (w), 2903 (w), 1668 (w), 1599 (w), 1504 (m), 1490 (w), 1427 (m), 1388 (w), 1359 (w), 1334 (w), 1284 (w), 1221 (m), 1159 (w), 1114 (s), 1047 (s), 1029 (m), 974 (m), 949 (w), 902 (m), 875 (m), 852 (s), 827 (m), 813 (w), 727 (s), 695 (s), 603 (m). **HRMS** (ES⁺) *m/z* calculated for [C₄₄H₄₀ClO₂Si]⁺ [M+H]⁺: 663.2486, found: 663.2480.



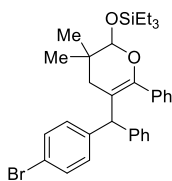
4.13c: Synthesised according to *General Procedure 10* using **4.10f** (45 mg, 0.1 mmol) along with $B(C_6F_5)_3$ (3 mg, 5 μ mol, 5 mol%) and $HSiPh_3$ (26 mg, 0.1 mmol, 1 equiv.) to give a white powdery solid upon removal of volatiles. Yield: 64 mg, 0.09 mmol, 90%. Melting point: 80–86 °C. **1H NMR** (500 MHz, $CDCl_3$, 298 K) δ /ppm: 7.54 (m, 6H, Ar-H), 7.37 (m, 4H, Ar-H), 7.28 (m, 8H, Ar-H), 7.20–7.15 (m, 2H, Ar-H), 7.07 (m, 4H, Ar-H), 7.01–6.96 (m, 2H, Ar-H), 7.01 (m, 2H, Ar-H), 5.00 (m, 2H, $C(H)O_2$, $C(H)Ar_2$), 2.12–2.04 (m, 1H, CH_2), 1.68–1.62 (t, $^2J_{HH} = 16.1$ Hz, 1H, CH_2), 0.97–0.96 (m, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ /ppm: 145.6 (s), 143.0 (s), 142.9 (s), 135.9 (s), 134.0 (s), 131.3 (s), 131.1 (s), 130.3 (s), 129.4 (s), 129.2 (s), 128.7 (s), 128.3 (s), 128.1 (s), 128.0 (s), 126.5 (s), 120.1 (s), 109.0 (s), 98.5 (s), 51.7 (s), 33.6 (s), 31.8 (s), 25.3 (s), 24.1 (s). **^{29}Si NMR** (99 MHz, $CDCl_3$, 298 K) δ /ppm: -11.8 (s, $SiPh_3$). **IR** ν_{max} (cm^{-1}): 3067 (w), 2903 (w), 1647 (w), 1589 (w), 1518 (w), 1485 (w), 1485 (m), 1468 (m), 1427 (m), 1391 (w), 1364 (w), 1335 (w), 1287 (w), 1235 (w), 1188 (w), 1157 (w), 1115 (s), 1047 1115 (s), 1028 1115 (s), 976 1115 (s), 949 (w), 923 (w), 871 (w), 851 (w), 831 (w), 793 (w), 769 (w), 738 (w), 710 (s), 695 (s), 621 (w), 600 (w), 553 (w), 507 (s). **HRMS** (ES^+) m/z calculated for $[C_{44}H_{39}BrO_2SiNa]^+$ $[M+Na]^+$: 729.1800, found: 729.1801.



4.13d: Synthesised according to *General Procedure 10* using **4.10d** (39 mg, 0.1 mmol) along with $B(C_6F_5)_3$ (3 mg, 5 μ mol, 5 mol%) and $HSiEt_3$ (12 mg, 0.1 mmol, 1 equiv.) to give a pale yellow oil upon removal of volatiles. Yield: 47 mg, 0.09 mmol, 93%. **1H NMR** (400 MHz, $CDCl_3$, 298 K) δ /ppm: 7.34–7.24 (m, 8H, Ar-H), 7.18–7.09 (4H, Ar-H), 6.99 (m, 2H, Ar-H), 5.12 (s, 1H, $C(H)O_2$), 4.90 (s, 1H, $C(H)Ar_2$), 2.00 (t, $^2J_{HH} = 17.4$ Hz, 1H, CH_2), 1.57 (m, 1H, CH_2), 1.01–0.98 (m, 15H, 3 x CH_3 ($SiEt_3$), $C(CH_3)_2$), 0.70 (m, 6H, 3 x CH_2). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ /ppm: 161.2 (d, $^1J_{CF} = 255$ Hz) 145.6 (s), 143.3 (s), 139.5 (d, $^2J_{CF} = 28.2$ Hz), 139.2 (s), 136.5 (s), 130.9 (s), 130.8 (s), 129.4 (s), 129.2 (s), 128.7 (s), 128.3 (s), 128.2 (s), 128.1 (s), 126.2 (s), 114.9 (d, $^3J_{CF} = 13.9$ Hz), 109.4 (s), 98.3 (s), 51.3 (s), 33.4 (s), 32.2 (s), 24.5 (s), 24.2 (s), 6.9 (s), 5.0 (s). **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ /ppm: -117.27 (s, $p-F$), -117.56 (s, $p-F$). **^{29}Si NMR** (79 MHz, $CDCl_3$, 298 K) δ /ppm: 19.7 (s, $SiEt_3$). **IR** ν_{max} (cm^{-1}): 3067 (w), 2970 (w), 1962 (w), 1824 (w), 1689 (s), 1599 (w), 1518 (w), 1489 (w), 1468 (m), 1427 (s), 1304 (m), 1257 (w), 1226 (m), 1205 (w), 1158 (w), 1141 (w), 1117 (s), 1094 (s), 1028 (w), 997 (w), 974 (w), 945 (w), 920 (w), 854 (w), 758 (m), 737 (m), 711 (s), 695 (s), 594 (w), 502 (s), 482 (s), 420 (m). **HRMS** (AP^+) m/z calculated for $[C_{32}H_{40}FO_2Si]^+$ $[M+H]^+$: 503.2782, found: 503.2775.



4.13e: Synthesised according to *General Procedure 10* using **4.10e** (40 mg, 0.1 mmol) along with $B(C_6F_5)_3$ (3 mg, 5 μ mol, 5 mol%) and $HSiEt_3$ (12 mg, 0.1 mmol, 1 equiv.) to give a pale yellow oil upon removal of volatiles. Yield: 47 mg, 0.09 mmol, 91%. **1H NMR** (500 MHz, $CDCl_3$, 298 K) δ /ppm: 7.21–7.12 (m, 10H, Ar-H), 7.04–6.95 (m, 4H, Ar-H), 4.98 (s, 1H, C(H)O₂), 4.77 (s, 1H, C(H)Ar₂), 1.87 (m, 1H, CH₂), 1.44 (m, 1H, CH₂), 0.88–0.85 (m, 15H, 3 x CH₃ (SiEt₃), C(CH₃)₂), 0.60–0.55 (m, 6H, 3 x CH₂). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ /ppm: 145.8 (s), 143.2 (s), 142.3 (s), 136.5 (s), 131.9 (s), 130.8 (s), 130.2 (s), 129.4 (s), 129.2 (s), 129.2 (s), 129.1 (s), 128.7 (s), 128.3 (s), 128.2 (s), 128.2 (s), 126.3 (s), 109.1 (s), 98.4 (s), 51.5 (s), 33.4 (s), 32.3 (s), 24.4 (s), 24.2 (s), 6.9 (s), 5.0 (s). **^{29}Si NMR** (99 MHz, $CDCl_3$, 298 K) δ /ppm: 19.7 (s, SiEt₃). **IR** ν_{max} (cm⁻¹): 2955 (w), 2874 (w), 1761 (w), 1728 (w), 1647 (w), 1601 (w), 1518 (w), 1489 (m), 1468 (s), 1408 (w), 1389 (w), 1284 (w), 1238 (m), 1179 (w), 1155 (w), 188 (s), 1059 (s), 1014 (s), 974 (s), 923 (w), 831 (w), 792 (w), 768 (m), 729 (s), 698 (s), 623 (w), 551 (w), 488 (w). **HRMS** (ES⁺) m/z calculated for $[C_{32}H_{40}ClO_2Si]^+$ [M+H]⁺: 519.2486, found: 519.2480.



4.13f: Synthesised according to *General Procedure 10* using **4.10f** (45 mg, 0.1 mmol) along with $B(C_6F_5)_3$ (2 mg, 5 mol%) and $HSiEt_3$ (12 mg, 0.1 mmol, 1 equiv.) to give a clear pale yellow oil upon removal of volatiles. Yield: 53 mg, 0.09 mmol, 95%. **1H NMR** (500 MHz, $CDCl_3$, 298 K) δ /ppm: 7.36 (dd, $^3J_{HH} = 7.9$ Hz, 2H, Ar-H), 7.26–7.18 (m, 8H, Ar-H), 7.08 (dd, $^3J_{HH} = 7.6$ Hz, 2H, Ar-H), 6.98 (dd, $^3J_{HH} = 7.9$ Hz, 2H, Ar-H), 5.03 (s, 1H, C(H)CO₂), 4.84 (s, 1H, C(H)Ar₂), 1.93 (m, 1H, CH₂), 1.50 (m, 1H, CH₂), 0.95–0.90 (m, 15H, 3 x CH₃ (SiEt₃), C(CH₃)₂), 0.66–0.62 (m, 6H, 3 x CH₂). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ /ppm: 145.8 (s), 143.1 (s), 142.8 (s), 136.5 (s), 131.2 (s), 129.4 (s), 129.2 (s), 128.3 (s), 128.2 (s), 128.2 (s), 126.3 (s), 120.0 (s), 109.0 (s), 98.4 (s), 51.5 (s), 33.4 (s), 32.1 (s), 24.5 (s), 24.2 (s), 6.9 (s), 5.1 (s). **^{29}Si NMR** (99 MHz, $CDCl_3$, 298 K) δ /ppm: 19.8 (s, SiEt₃), 19.7 (s, SiEt₃). **IR** ν_{max} (cm⁻¹): 2955 (w), 2908 (w), 2874 (w), 1761 (m), 1724 (m), 1647 (m), 1600 (w), 1518 (m), 1485 (s), 1466 (s), 1391 (m), 1344 (w), 1285 (m), 1238 (m), 1155 (w), 1103 (s), 1070 (s), 1029 (m), 1011 (s), 974 (s), 831 (w), 802 (w), 768 (m), 739 (s), 695 (s), 621 (w), 551 (m), 480 (m). **HRMS** (ES⁺) m/z calculated for $[C_{32}H_{40}BrO_2Si]^+$ [M+H]⁺: 563.1981, found: 563.1982.

6.4.5 Computational Studies

All geometry optimisations were undertaken using the B3LYP functional^[152a] and 6-31G* basis set^[154] within Gaussian09.^[178] Subsequent single point calculations were undertaken using the B3LYP functional and larger 6-311G*+ basis set.

6.4.6 Crystallographic Studies

Crystallographic studies were undertaken on single crystal mounted in paratone and studied on an Agilent SuperNova Dual three-circle diffractometer using Cu-K α or Mo-K α radiation and a CCD detector. Measurements were typically made at 150(1) K with temperatures maintained using an Oxford cryostream. Data were collected and integrated and data corrected for absorption using a numerical absorption correction based on gaussian integration over a multifaceted crystal model within CrysAlisPro.^[156] The structures were solved by direct methods and refined against F^2 within SHELXL-2013.^[170] The structures have been deposited with the Cambridge Structural Database (CCDC deposition numbers 1417004,1417005, 1480722–1480724, 1517858–1517863, 1524192–1524195 and 1545638–1545640).

Table 6.4.1 Crystallographic data for compounds **4.3–4.13**.

Compound	4.3a	4.3b	4.5	4.6
Empirical Formula	C ₃₀ H ₁₀ BF ₁₅ O ₂	C ₂₈ H ₁₄ BF ₁₅ O ₂	C ₄₉ H ₂₄ BF ₁₅ O ₂	C ₅₃ H ₃₂ BF ₁₅ O ₂ Se
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	10.53693(10)	10.9906(3)	15.9561(6)	17.4913(9)
<i>b</i> /Å	13.77283(16)	10.9906(3)	18.8796(7)	12.8840(7)
<i>c</i> /Å	36.3610(4)	14.4145(3)	13.6604(7)	20.4750(10)
α /°	90	90	90	90
β /°	95.1711(10)	91.562(2)	102.743(4)	96.260(4)
γ /°	90	90	90	90
<i>V</i> /Å ³	5255.36(10)	2539.55(10)	4013.8(3)	4586.7(4)
<i>Z</i>	8	4	4	4
<i>T</i> /K	150(2)	150(2)	150(2)	150(2)
<i>D</i> _c /g.cm ⁻³	1.765	1.774	1.556	1.558
Crystal size/mm	0.370 x 0.130 x 0.090	0.170 x 0.060 x 0.040	0.320 x 0.120 x 0.050	0.343 x 0.151 x 0.051
Total data	21738	10428	13686	25867
Unique data	10388	5024	6802	8046
<i>R</i> _{int}	0.0188	0.0415	0.0337	0.0663
<i>R</i> ₁ [<i>F</i> ² >2 σ (<i>F</i> ²)]	0.0343	0.0389	0.0500	0.0558
w <i>R</i> ₂ (all data)	0.0915	0.1235	0.1498	0.1367
GoF	1.041	1.140	1.022	1.054
ρ _{min} / ρ _{max} /eÅ ⁻³	-0.250/0.288	-0.224/0.423	-0.243/0.484	-0.794/0.880
CCDC code	1417004	1417005	1480722	1480723

Compound	4.7	4.11a	4.11d	4.11e
Empirical Formula	C ₄₂ H ₂₉ Cl ₅ O ₂ Se ₃	C ₃₁ H ₁₄ BF ₁₅ O ₂	C ₃₄ H ₁₂ BCl ₂ F ₁₅ O ₂	C ₃₅ H ₁₄ BCl ₂ F ₁₅ O ₂
Crystal System	Triclinic	monoclinic	triclinic	triclinic
Space Group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	9.1231(4)	13.9659(5)	10.8906(6)	10.2165(4)
<i>b</i> /Å	13.3695(6)	11.7430(5)	11.6131(10)	11.5168(6)
<i>c</i> /Å	16.6564(8)	17.0158(7)	12.4826(7)	14.9858(8)
α /°	73.574(4)	90	90.902(6)	95.385(4)
β /°	83.219(4)	98.501(4)	95.194(5)	94.461(4)
γ /°	87.728(4)	90	98.525(6)	111.742(4)
<i>V</i> /Å ³	1934.99(15)	2759.97(19)	1554.20(19)	1618.47(14)
<i>Z</i>	2	4	2	2
<i>T</i> /K	150(2)	150(2)	150(2)	150(2)
<i>D</i> _c /g.cm ⁻³	1.682	1.719	1.750	1.710
Crystal size/mm	0.360 x 0.110 x 0.030	0.497 x 0.425 x 0.303	0.389 x 0.136 x 0.076	0.227 x 0.171 x 0.081
Total data	13349	15097	10405	10489
Unique data	7599	5996	5660	5710
<i>R</i> _{int}	0.0458	0.0399	0.0398	0.0304
<i>R</i> ₁ [<i>F</i> ² >2 σ (<i>F</i> ²)]	0.0357	0.0425	0.0413	0.0368
w <i>R</i> 2 (all data)	0.1002	0.1059	0.1214	0.1009
GoF	1.036	1.026	1.016	1.016
ρ _{min} / ρ _{max} /eÅ ⁻³	-0.601/0.850	-0.218/0.331	-0.525/0.380	-0.689/0.274
CCDC code	1480724	1524194	1545638	1545639

Compound	4.11h	4.11i	4.11m	4.11v
Empirical Formula	C ₄₄ H ₂₃ BF ₁₆ O ₂	C ₄₄ H ₂₃ BClF ₁₅ O ₂	C ₄₅ H ₂₂ BClF ₁₈ O ₂	C ₄₃ H ₁₇ BCl ₃ F ₁₆ O ₂
Crystal System	monoclinic	monoclinic	orthorhombic	Orthorhombic
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>	<i>Pbca</i>
<i>a</i> /Å	16.4273(3)	17.3148(13)	11.6820(3)	16.6460(4)
<i>b</i> /Å	12.13337(18)	11.6132(5)	20.9042(5)	16.9974(5)
<i>c</i> /Å	21.5533(3)	20.9195(13)	33.1030(11)	27.5259(8)
α /°	90	90	90	90
β /°	103.2592(15)	113.426(8)	90	90
γ /°	90	90	90	90
<i>V</i> /Å ³	4181.44(11)	3859.7(5)	8083.8(4)	7788.1(4)
<i>Z</i>	4	4	8	8
<i>T</i> /K	100(2)	173(2)	173(2)	150(2)
<i>D</i> _c /g.cm ⁻³	1.426	1.573	1.614	1.683
Crystal size/mm	0.220 x 0.140 x 0.135	0.070 x 0.030 x 0.020	0.110 x 0.080 x 0.050	0.392 x 0.231 x 0.054
Total data	51694	35904	48324	28641
Unique data	9543	6829	7135	7808
<i>R</i> _{int}	0.0144	0.0680	0.0539	0.0278
<i>R</i> ₁ [<i>F</i> ² >2 σ (<i>F</i> ²)]	0.0386	0.0579	0.0674	0.0521
w <i>R</i> 2 (all data)	0.1026	0.1366	0.1794	0.1540
GoF	1.066	1.046	1.060	1.044
ρ _{min} / ρ _{max} /eÅ ⁻³	-0.210/0.390	-0.276/0.304	-0.339/0.696	-0.889/0.620
CCDC code	1517858	1517859	1517860	1545640

Compound	4.12a	4.12c	4.12f	4.13a
Empirical Formula	C ₁₄ H ₁₆ O ₃	C ₂₆ H ₂₃ FO ₂	C ₂₇ H ₂₂ BrF ₃ O ₂	C ₄₄ H ₃₉ FO ₂ Si
Crystal System	Monoclinic	Triclinic	Monoclinic	Triclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1
<i>a</i> /Å	6.2006(4)	9.8670(7)	10.3127(3)	9.7701(2)
<i>b</i> /Å	7.1664(5)	9.8812(10)	9.3262(3)	18.8537(4)
<i>c</i> /Å	27.3075(16)	11.2904(11)	23.4030(6)	19.9681(4)
α /°	90	69.648(9)	90	87.5026(18)
β /°	94.857(6)	78.120(7)	92.792(2)	83.8723(19)
γ /°	90	86.424(7)	90	81.812(2)
<i>V</i> /Å ³	1209.09(13)	1009.92(17)	2248.20(11)	3618.36(15)
<i>Z</i>	4	2	4	4
<i>T</i> /K	150(2)	100(2)	100(2)	150
<i>D</i> _c /g.cm ⁻³	1.276	1.267	1.520	1.186
Crystal size/mm	0.284 x 0.245 x 0.117	0.180 x 0.160 x 0.120	0.100 x 0.050 x 0.010	0.421 x 0.220 x 0.127
Total data	5630	12495	53772	65007
Unique data	2849	4584	5121	14425
<i>R</i> _{int}	0.0374	0.0185	0.0519	0.0355
<i>R</i> ₁ [<i>F</i> ² >2 σ (<i>F</i> ²)]	0.0478	0.0395	0.0701	0.0439
w <i>R</i> ₂ (all data)	0.1222	0.1033	0.1473	0.1182
GoF	1.043	1.008	1.124	1.014
ρ _{min} / ρ _{max} /eÅ ⁻³	-0.282/0.207	-0.214/0.228	-0.798/0.525	-0.500/0.366
CCDC code	1524195	1517861	1517862	1517863

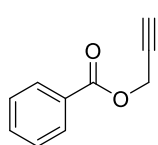
6.5 Boron Mediated and Catalysed Reduction Reactions: Emerging Catalysts, Novel Processing Techniques and Transfer Hydrogenation

6.5.1 Tempering Lewis Acidity of Boranes for General Hydroboration Reactions

6.5.1.1 Synthesis of Starting Materials

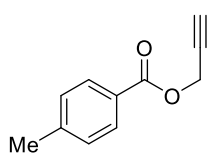
General Procedure 1: Synthesised according to the literature^[164] whereby propargyl alcohol (0.72 ml, 12.5 mmol, 1 equiv.) was dissolved in 100 ml CH₂Cl₂ and cooled to -78 °C. Tetramethylethylenediamine (TMEDA) (1.12 ml, 7.5 mmol, 0.6 equiv.) was added followed by dropwise addition of acyl chloride (13.8 mmol, 1.1 equiv.). After stirring at this temperature for 30 minutes the reaction was warmed to room temperature and quenched with saturated NH₄Cl solution. The aqueous phase was extracted with CH₂Cl₂ (3 x 30 ml) with the combined organic phases being washed with H₂O then dried over K₂CO₃ and Na₂SO₄. Removal of volatiles under reduced pressure gave the crude product as a pale yellow oil. This was purified by either recrystallisation or column chromatography.

General Procedure 2: According to the literature^[20] whereby triethylamine (1.0 equiv.) and 4-dimethylaminopyridine (4-DMAP) (0.02 equiv.) were added to a solution of the propargyl alcohol (1.0 equiv.) in CH₂Cl₂ (ca. 20 ml) and was stirred for 5 min. The solution was cooled to 0 °C and the acyl chloride (1.0 equiv.) added dropwise. The resulting mixture was stirred at this temperature for 30 min and was then allowed to warm to room temperature and was stirred for a further 48 h. The reaction was quenched with water and the aqueous layer extracted twice with CH₂Cl₂. The collective organic phases were washed with brine, dried with MgSO₄, filtered, and the solvent was removed under vacuum and the product purified by column chromatography or recrystallisation.

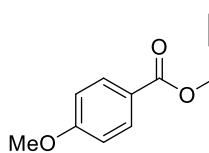


Prop-2-yn-1-yl benzoate: Synthesised according to *General Procedure 1* using benzoyl chloride (1.60 ml, 13.8 mmol, 1.1 equiv.). Purification *via* column chromatography (hexane/ethyl acetate, 20:1) gave the pure product as a colourless oil. Yield: 1.82 g, 11.4 mmol, 91%. Spectroscopic analyses agree with literature established values.^[165] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.09 – 8.07 (m, 2H, Ar-H), 7.58 (tt, ³J_{HH} = 7.5 Hz, ⁴J_{HH} =

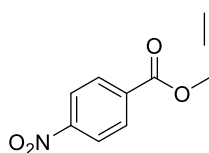
1.3 Hz, 1H, Ar-H), 7.45 (t, $^3J_{\text{HH}} = 7.6$ Hz, 2H, Ar-H), 4.93 (d, $^4J_{\text{HH}} = 2.5$ Hz, 2H, CH₂), 2.52 (t, $^4J_{\text{HH}} = 2.5$ Hz, 1H, $\equiv\text{CH}$).



Prop-2-yn-1-yl-4-methylbenzoate: Synthesised according to *General Procedure 1* using *p*-toluoyl chloride (1.82 ml, 13.8 mmol, 1.1 equiv.). Recrystallisation from hexane by slow evaporation afforded the product as a white crystalline solid. Yield: 2.17 g, 12.5 mmol, 100%. Spectroscopic analyses agree with literature established values.^[20] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 7.96 (d, $^3J_{\text{HH}} = 8.1$ Hz, 2H, Ar-H), 7.25 (d, $^3J_{\text{HH}} = 8.1$ Hz, 2H, Ar-H), 4.91 (d, $^4J_{\text{HH}} = 2.5$ Hz, 2H, CH₂), 2.51 (t, $^4J_{\text{HH}} = 2.5$ Hz, 1H, $\equiv\text{CH}$), 2.41 (s, 3H, CH₃).

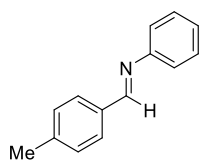


Prop-2-yn-1-yl-4-methoxybenzoate: Synthesised according to *General Procedure 2* using *p*-anisoyl chloride (2.03 ml, 15 mmol, 1.2 equiv.). Purification *via* column chromatography (hexane/ethyl acetate, 5:1) gave the pure product as a colourless oil. Yield: 1.98 g, 10.4 mmol, 83%. Spectroscopic analyses agree with literature established values.^[166] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 8.02 (dt, $^3J_{\text{HH}} = 9.0$ Hz, $^4J_{\text{HH}} = 2.2$ Hz, 2H, Ar-H), 6.92 (dt, $^3J_{\text{HH}} = 9.0$ Hz, $^4J_{\text{HH}} = 2.2$ Hz, 2H, Ar-H), 4.89 (d, $^4J_{\text{HH}} = 2.4$ Hz, 2H, CH₂), 3.86 (s, 3H, OCH₃), 2.50 (t, $^4J_{\text{HH}} = 2.4$ Hz, 1H, $\equiv\text{CH}$).

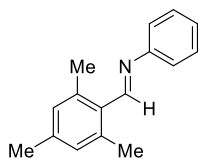


Prop-2-yn-1-yl-4-nitrobenzoate: Synthesised according to *General Procedure 2* using *p*-nitrobenzoylchloride (2.77 g, 15 mmol, 1.2 equiv.). Recrystallisation *via* slow evaporation of CH₂Cl₂ gave the pure product as a yellow crystalline solid. Yield: 2.36 g, 11.5 mmol, 96%. Spectroscopic analyses agree with literature established values.^[167] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 8.30 (dt, $^3J_{\text{HH}} = 9.0$ Hz, $^4J_{\text{HH}} = 2.2$ Hz, 2H, Ar-H), 8.23 (dt, $^3J_{\text{HH}} = 9.0$ Hz, $^4J_{\text{HH}} = 2.2$ Hz, 2H, Ar-H), 4.97 (d, $^4J_{\text{HH}} = 2.5$ Hz, 2H, CH₂), 2.56 (t, $^4J_{\text{HH}} = 2.5$ Hz, 1H, $\equiv\text{CH}$).

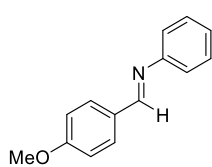
General Procedure 3: In accordance with the literature known procedure^[179] the requisite aldehyde (10 mmol) was dissolved in CH₂Cl₂ (10 ml) along with 3 Å molecular sieves. To this the necessary amine (10 mmol) was added. The reaction was left at ambient temperature for 2 h at which point MgSO₄ was added with subsequent filtration. Volatiles were removed *in vacuo* to leave the pure imine in quantitative yields.



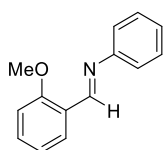
(*E*)-*N*-phenyl-1-(*p*-tolyl)methanimine: Synthesised in accordance with *General Procedure 3* using 4-tolualdehyde (1.18 ml, 10 mmol) and aniline (0.91 ml, 10 mmol). Spectroscopic analyses agree with literature values.^[180] Yield: 1.8 g, 9.2 mmol, 92%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.42 (s, 1H, N=CH), 7.80 (d, ³J_{HH} = 8.0 Hz, 2H, Ar-H), 7.39 (t, ³J_{HH} = 7.8 Hz, 2H, Ar-H), 7.28 (d, ³J_{HH} = 7.9 Hz, 2H, Ar-H), 7.22 (t, ³J_{HH} = 9.1 Hz, 3H, Ar-H), 2.43 (s, 3H, CH₃).



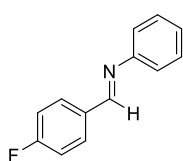
(*E*)-1-mesityl-*N*-phenylmethanimine: Synthesised in accordance with *General Procedure 3* using mesitaldehyde (1.47 ml, 10 mmol) and aniline (0.91 ml, 10 mmol). Spectroscopic analyses agree with literature values.^[181] Yield: 2.0 g, 9.1 mmol, 91%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.80 (s, 1H, N=CH), 7.43 (t, ³J_{HH} = 7.7 Hz, 2H, Ar-H), 7.23–7.06 (m, 3H, Ar-H), 6.95 (s, 2H, Ar-H), 2.56 (s, 6H, CH₃, mesityl), 2.35 (s, 3H, CH₃ mesityl).



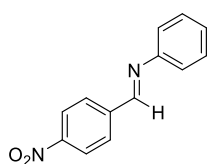
(*E*)-1-(4-methoxyphenyl)-*N*-phenylmethanimine: Synthesised in accordance with *General Procedure 3* using 4-anisaldehyde (1.22 ml, 10 mmol) and aniline (0.91 ml, 10 mmol). Spectroscopic analyses agree with literature values.^[182] Yield: 2.0 mg, 9.4 mmol, 94%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.44 (s, 1H), 7.91 (d, ³J_{HH} = 8.7 Hz, 2H, N=CH), 7.44 (t, ³J_{HH} = 7.7 Hz, 2H, Ar-H), 7.30–7.14 (m, 3H, Ar-H), 7.04 (d, ³J_{HH} = 8.7 Hz, 2H, Ar-H), 3.93 (s, 3H, OCH₃).



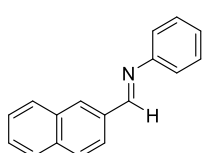
(*E*)-1-(2-methoxyphenyl)-*N*-phenylmethanimine: Synthesised in accordance with *General Procedure 3* using benzaldehyde (1.21 ml, 10 mmol) and aniline (0.91 ml, 10 mmol). Spectroscopic analyses agree with literature values.^[183] Yield: 1.9 g, 9.0 mmol, 90%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.81 (s, 1H, N=CH), 8.05 (d, ³J_{HH} = 5.3 Hz, 1H, Ar-H), 7.26 (s, 3H, Ar-H), 7.17–7.04 (m, 3H, Ar-H), 6.94–6.70 (m, 2H, Ar-H), 3.72 (s, 3H, OCH₃).



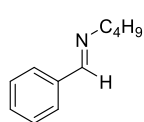
(*E*)-1-(4-fluorophenyl)-*N*-phenylmethanimine: Synthesised in accordance with *General Procedure 3* using benzaldehyde (1.07 ml, 10 mmol) and aniline (0.91 ml, 10 mmol). Spectroscopic analyses agree with literature values.^[183] Yield: 1.8 g, 9.1 mmol, 91%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.43 (s, 1H, N=CH), 7.91 (dd, ³J_{HH} = 8.6, ⁴J_{HH} = 5.6 Hz, 2H, Ar-H), 7.40 (t, ³J_{HH} = 7.7 Hz, 2H, Ar-H), 7.30–7.05 (m, 6H, Ar-H).



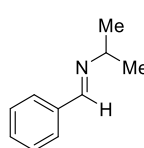
(*E*)-1-(4-nitrophenyl)-*N*-phenylmethanimine: Synthesised in accordance with *General Procedure 3* using benzaldehyde (1.51 g, 10 mmol) and aniline (0.91 ml, 10 mmol). Spectroscopic analyses agree with literature values.^[181] Yield: 2.1 g, 9.4 mmol, 94%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.49 (s, 1H, N=CH), 8.26 (d, ³J_{HH} = 8.7 Hz, 2H, Ar-H), 8.01 (d, ³J_{HH} = 8.7 Hz, 2H, Ar-H), 7.36 (t, ³J_{HH} = 7.7 Hz, 2H, Ar-H), 7.28–7.17 (m, 3H, Ar-H).



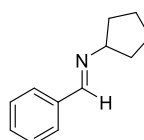
(*E*)-1-(naphthalen-2-yl)-*N*-phenylmethanimine: Synthesised in accordance with *General Procedure 3* using benzaldehyde (1.56 g, 10 mmol) and aniline (0.91 ml, 10 mmol). Spectroscopic analyses agree with literature values.^[181] Yield: 2.1 g, 8.9 mmol, 89%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.52 (s, 1H, N=CH), 8.09 (dd, ³J_{HH} = 10.4, ⁴J_{HH} = 1.6 Hz, 2H, Ar-H), 7.81 (ddd, ³J_{HH} = 8.9, ³J_{HH} = 6.5 Hz, 3H, Ar-H), 7.49–7.41 (m, 2H, Ar-H), 7.38–7.28 (m, 2H, Ar-H), 7.21–7.13 (m, 3H, Ar-H).



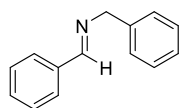
(*E*)-*N*-butyl-1-phenylmethanimine: Synthesised in accordance with *General Procedure 3* using benzaldehyde (1.02 ml, 10 mmol) and ⁿbutylamine (0.99 ml, 10 mmol). Spectroscopic analyses agree with literature values.^[184] Yield: 1.5 g, 9.5 mmol, 95%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.19 (s, 1H, N=CH), 7.66–7.55 (m, 2H, Ar-H), 7.33–7.23 (m, 3H, Ar-H), 3.53 (t, ³J_{HH} = 6.9 Hz, 2H, N–CH₂), 1.61 (pent., ³J_{HH} = 7.1 Hz, 2H, CH₂), 1.31 (h, ³J_{HH} = 7.2 Hz, 2H, CH₂), 0.87 (t, ³J_{HH} = 7.4 Hz, 3H, CH₃).



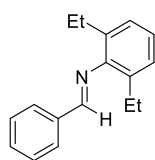
(*E*)-*N*-isopropyl-1-phenylmethanimine: Synthesised in accordance with *General Procedure 3* using benzaldehyde (1.02 ml, 10 mmol) and isopropylamine (0.86 ml, 10 mmol). Spectroscopic analyses agree with literature values.^[184] Yield: 1.3 g, 8.7 mmol, 87%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.31 (s, 1H, N=CH), 7.80–7.69 (m, 2H, Ar-H), 7.54–7.32 (m, 3H, Ar-H), 3.55 (sept, ³J_{HH} = 5.2 Hz, 1H, *i*Pr H), 1.28 (d, ³J_{HH} = 6.3 Hz, 6H, *i*Pr CH₃).



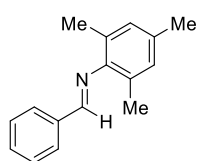
(*E*)-*N*-cyclopentyl-1-phenylmethanimine: Synthesised in accordance with *General Procedure 3* using benzaldehyde (1.02 ml, 10 mmol) and cyclopentylamine (0.99 ml, 10 mmol). Spectroscopic analyses agree with literature values.^[185] Yield: 1.5 g, 8.9 mmol, 89%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.29 (s, 1H, N=CH), 7.78–7.66 (m, 2H, Ar-H), 7.49–7.28 (m, 3H, Ar-H), 4.06–3.39 (m, 1H, N–CH), 1.88 (s, 4H, CH₂), 1.77–1.59 (m, 4H, CH₂).



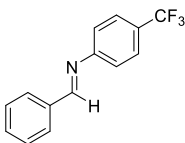
(*E*)-*N*-benzyl-1-phenylmethanimine: Synthesised in accordance with *General Procedure 3* using benzaldehyde (1.02 ml, 10 mmol) and benzylamine (1.09 ml, 10 mmol). Spectroscopic analyses agree with literature values.^[182] Yield: 1.8 g, 9.2 mmol, 92%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.31 (s, 1H, N=CH), 7.77–7.60 (m, 2H, Ar-H), 7.33 (d, ³J_{HH} = 4.9 Hz, 3H, Ar-H), 7.31–7.04 (m, 4H, Ar-H), 4.74 (s, 2H, CH₂Ph).



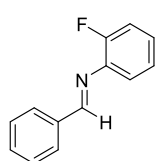
(*E*)-*N*-(2,6-diethylphenyl)-1-phenylmethanimine: Synthesised in accordance with *General Procedure 3* using benzaldehyde (1.02 ml, 10 mmol) and 2,6-diethylaniline (1.65 ml, 10 mmol). Spectroscopic analyses agree with literature values.^[186] Yield: 2.1 g, 8.7 μmol, 87%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.23 (s, 1H, N=CH), 7.92 (d, ³J_{HH} = 6.9 Hz, 2H, Ar-H), 7.52 (d, ³J_{HH} = 6.1 Hz, 3H, Ar-H), 7.11 (d, ³J_{HH} = 7.4 Hz, 2H, Ar-H), 7.07–7.02 (m, 1H, Ar-H), 2.51 (q, ³J_{HH} = 7.4 Hz, 4H, ethyl CH₂), 1.14 (t, ³J_{HH} = 7.5 Hz, 6H, ethyl CH₃).



(*E*)-*N*-mesityl-1-phenylmethanimine: Synthesised in accordance with *General Procedure 3* using benzaldehyde (1.02 ml, 10 mmol) and 2,4,6-trimethylaniline (1.40 ml, 10 mmol). Spectroscopic analyses agree with literature values.^[182] Yield: 2.1 g, 9.4 mmol, 94%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.16 (br. s, 1H, N=CH), 7.86 (br. s, 2H, Ar-H), 7.45 (br. s, 3H, Ar-H), 6.85 (br. s, 2H, Ar-H), 2.24 (s, 3H, *p*-CH₃), 2.08 (s, 6H, *o*-CH₃).



(*E*)-1-phenyl-*N*-(4-(trifluoromethyl)phenyl)methanimine: Synthesised in accordance with *General Procedure 3* using benzaldehyde (1.02 ml, 10 mmol) and 4-trifluoromethylaniline (1.26 ml, 10 mmol). Spectroscopic analyses agree with literature values.^[187] Yield: 2.4 g, 9.1 mmol, 91%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.40 (s, 1H, N=CH), 7.88 (d, ³J_{HH} = 7.4 Hz, 2H, Ar-H), 7.62 (d, ³J_{HH} = 7.9 Hz, 2H, Ar-H), 7.47 (q, ³J_{HH} = 7.8 Hz, 3H, Ar-H), 7.22 (d, ³J_{HH} = 7.0 Hz, 2H, Ar-H).



(*E*)-*N*-(2-fluorophenyl)-1-phenylmethanimine: Synthesised in accordance with *General Procedure 3* using benzaldehyde (1.02 ml, 10 mmol) and 2-fluoroaniline (0.97 ml, 10 mmol). Spectroscopic analyses agree with literature values.^[182] Yield: 1.8 g, 9.0 mmol, 90%. **¹H NMR**

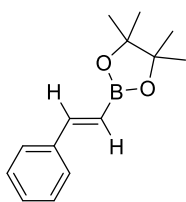
(500 MHz, CDCl₃, 298 K) δ /ppm: 8.53 (s, 1H, N=CH), 7.94 (dd, $^3J_{\text{HH}} = 7.4$, $^4J_{\text{HH}} = 1.9$ Hz, 2H, Ar-H), 7.52–7.45 (m, 3H, Ar-H), 7.19–7.13 (m, 4H, Ar-H).

6.5.1.2 Synthesis of Products

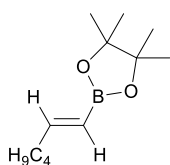
General Procedure 4: In an NMR tube, pinacol borane (31 mg, 0.22 mmol) and the substrate (aldehyde/imine) (0.2 mmol) were combined in CH₂Cl₂ (0.6 ml). To this, *tris*(2,4,6-trifluorophenyl)borane (2 mg, 2 mol%) was added, and the NMR tube sealed. Reactions occurred at 60 °C, while reaction times varied with substrate. Once conversion was complete, as measured by *in situ* ¹H NMR spectroscopy, the reaction mixtures were reduced under vacuum. The alkoxy/amino-pinacol boronates were redissolved in CDCl₃ for NMR spectroscopic analysis. Select examples were subsequently converted to alcohols/amines by hydrolysis as denoted in the text.

General Procedure 5: In an NMR tube, pinacol borane (31 mg, 0.22 mmol) and the substrate alkyne/alkene (0.2 mmol) were combined in CH₂Cl₂ (0.6 ml). To this, *tris*(2,4,6-trifluorophenyl)borane (2 mg, 2 mol%) was added, and the NMR tube sealed. Reactions occurred at 60 °C, while reaction times varied with substrate. Once the reaction was complete, as measured by *in situ* ¹H NMR spectroscopy, the reaction mixtures were concentrated under vacuum and subsequently passed through a short plug of silica in hexane. The pinacol boronates were redissolved in CDCl₃ for NMR spectroscopic analysis.

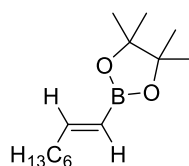
General Procedure 6: As per *General Procedure 5* and *6*, at room temperature.



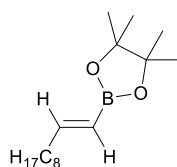
5.2a: Synthesised in accordance with *General Procedure 6* using phenylacetylene (20 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 6 h. Yield: 47 mg, 198 μ mol, 99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 7.42 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2H, Ar-H), 7.33 (d, $^3J_{\text{HH}} = 18.5$ Hz, 1H, =CH), 7.30–7.21 (m, 3H, Ar-H), 6.10 (d, $^3J_{\text{HH}} = 18.5$ Hz, 1H, =CH), 1.24 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: 30.1 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 149.5 (s), 137.5 (s), 128.9 (s), 128.6 (s), 127.1 (s), 83.4 (s), 24.8 (s). **HRMS** (ES)⁺ *m/z* calculated for [C₁₄H₂₀¹⁰BO₂]⁺ [M+H]⁺: 230.1593, found: 230.1600.



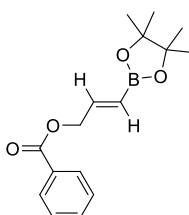
5.2b: Synthesised in accordance with *General Procedure 6* using 1-hexyne (16 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Yield: 30 mg, 142 μmol , 71%. Spectroscopic data agrees with literature values.^[188] **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ/ppm : 6.63 (dt, $^3J_{\text{HH}} = 17.9$ Hz, $^3J_{\text{HH}} = 6.4$ Hz, 1H, =CH), 5.42 (dt, $^3J_{\text{HH}} = 17.9$ Hz, $^4J_{\text{HH}} = 1.5$ Hz, 1H, =CH), 2.17–2.12 (m, 2H, alkyl), 1.42–1.36 (m, 2H, alkyl), 1.35–1.29 (m, 2H, alkyl), 1.26 (s, 12H, pinacol), 0.88 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H, alkyl). **$^{11}\text{B NMR}$** (160 MHz, CDCl_3 , 298 K) δ/ppm : 29.7 (s). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3 , 298 K) δ/ppm : 154.8 (s), 83.0 (s), 35.5 (s), 30.4 (s), 24.8 (s), 22.3 (s), 13.9 (s).



5.2c: Synthesised in accordance with *General Procedure 6* using 1-octyne (22 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 24 h. Yield: 38 mg, 160 μmol , 80%. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ/ppm : 6.63 (dt, $^3J_{\text{HH}} = 18.1$ Hz, $^3J_{\text{HH}} = 6.4$ Hz, 1H, =CH), 5.41 (d, $^3J_{\text{HH}} = 18.1$ Hz, 1H, =CH), 2.14 (q, $^3J_{\text{HH}} = 6.9$ Hz, 2H, CH_2), 1.40 (quintet, $^3J_{\text{HH}} = 7.2$ Hz, 2H, CH_2), 1.32–1.20 (m, 6H, alkyl), 1.26 (s, 12H, pinacol), 0.87 (t, $^3J_{\text{HH}} = 6.6$ Hz, 3H, CH_3). **$^{11}\text{B NMR}$** (160 MHz, CDCl_3 , 298 K) δ/ppm : 29.8 (s). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3 , 298 K) δ/ppm : 154.9 (s), 83.0 (s), 35.9 (s), 31.7 (s), 28.9 (s), 28.2 (s), 24.8 (s), 22.6 (s), 14.1 (s). **HRMS** (AP)⁺ m/z calculated for $[\text{C}_{14}\text{H}_{28}^{10}\text{BO}_2]^+$ $[\text{M}+\text{H}]^+$: 238.2219, found: 238.2226.

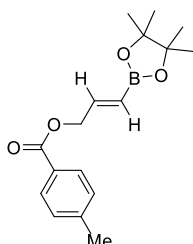


5.2d: Synthesised in accordance with *General Procedure 6* using 1-decyne (28 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Yield: 48 mg, 180 μmol , 90%. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ/ppm : 6.62 (dt, $^3J_{\text{HH}} = 17.9$ Hz, $^3J_{\text{HH}} = 6.4$ Hz, 1H, =CH), 5.41 (dt, $^3J_{\text{HH}} = 17.9$ Hz, $^4J_{\text{HH}} = 1.5$ Hz, 1H, =CH), 2.15–2.11 (m, 2H, alkyl), 1.43–1.36 (m, 2H, alkyl), 1.29–1.22 (m, 10H, alkyl), 1.25 (s, 12H, pinacol), 0.87 (t, $^3J_{\text{HH}} = 7.0$ Hz, 3H, alkyl). **$^{11}\text{B NMR}$** (160 MHz, CDCl_3 , 298 K) δ/ppm : 29.7 (s). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3 , 298 K) δ/ppm : 153.8 (s), 82.0 (s), 34.8 (s), 30.9 (s), 28.4 (s), 28.2 (s), 27.2 (s), 23.8 (s), 21.7 (s), 13.1 (s). **HRMS** (EI)⁺ m/z calculated for $[\text{C}_{16}\text{H}_{31}^{10}\text{BO}_2]^+$ $[\text{M}]^+$: 265.2453, found: 265.2448.

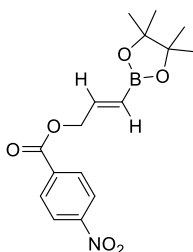


5.2e: Synthesised in accordance with *General Procedure 5* using prop-2-yn-1-yl benzoate (32 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Yield: 33 mg, 114 μmol , 57%. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ/ppm : 8.03–7.96 (m, 2H, Ar-H), 7.48 (t, $^3J_{\text{HH}} = 7.4$ Hz, 1H, Ar-H), 7.36 (q, $^3J_{\text{HH}} = 7.5$ Hz, 2H,

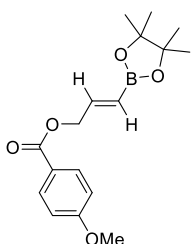
Ar-H), 6.66 (dt, $^3J_{\text{HH}} = 18.1$, $^4J_{\text{HH}} = 4.4$ Hz, 1H, =CH), 5.72 (dt, $^3J_{\text{HH}} = 18.1$, $^4J_{\text{HH}} = 1.8$ Hz, 1H, =CH), 4.87–4.81 (m, 1H, CH₂), 1.20 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: 29.6 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 166.1 (s), 146.0 (s), 133.1 (s), 129.8 (s), 129.7 (s), 128.5 (s), 128.4 (s), 83.5 (s), 75.0 (s), 65.7 (s), 52.5 (s), 24.8 (s). **HRMS** (AP)⁺ m/z calculated for [C₁₆H₂₂¹¹BO₄]⁺ [M+H]⁺: 289.1611, found: 289.1597.



5.2f: Synthesised in accordance with *General Procedure 5* using prop-2-yn-1-yl 4-methylbenzoate (35 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 24 h. Yield: 30 mg, 110 μ mol, 55%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 7.89 (d, $^3J_{\text{HH}} = 8.2$ Hz, 2H, Ar-H), 7.16 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H, Ar-H), 6.66 (dt, $^3J_{\text{HH}} = 4.4$ Hz, $^3J_{\text{HH}} = 18.2$ Hz, 1H, =CH), 5.72 (d, $^3J_{\text{HH}} = 18.2$ Hz, 1H, =CH), 4.83 (d, $^3J_{\text{HH}} = 6.0$ Hz, 2H, CH₂), 2.34 (s, 3H, CH₃), 1.20 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: 29.7 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 166.2 (s), 146.2 (s), 143.8 (s), 129.8 (s), 129.1 (s), 127.2 (s), 83.5 (s), 74.9 (s), 65.6 (s), 52.3 (s), 24.8 (s), 21.7 (s). **HRMS** (AP)⁺ m/z calculated for [C₁₇H₂₄¹⁰BO₄]⁺ [M+H]⁺: 302.1804, found: 302.1792.

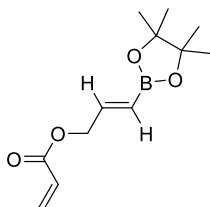


5.2g: Synthesised in accordance with *General Procedure 5* using prop-2-yn-1-yl 4-nitrobenzoate (41 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Yield: 51 mg, 154 μ mol, 77%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 8.26–8.14 (m, 4H, Ar-H), 6.65 (dt, $^3J_{\text{HH}} = 18.1$, $^3J_{\text{HH}} = 4.6$ Hz, 1H, =CH), 5.72 (d, $^3J_{\text{HH}} = 18.2$ Hz, 1H, =CH), 4.90 (dd, $^3J_{\text{HH}} = 8.2$, $^4J_{\text{HH}} = 3.3$ Hz, 2H, CH₂), 1.21 (s, 2H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: 29.6 (br. s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 164.1 (s), 145.1 (s), 134.9 (s), 131.1 (s), 123.8 (s), 83.7 (s), 75.9 (s), 66.8 (s), 53.4 (s), 24.9 (s).

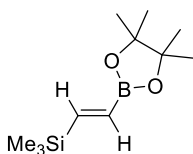


5.2h: Synthesised in accordance with *General Procedure 5* using prop-2-yn-1-yl 4-methoxybenzoate (38 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 24 h. Yield: 44 mg, 138 μ mol, 69%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 7.95 (dd, $^3J_{\text{HH}} = 8.7$, $^4J_{\text{HH}} = 1.8$ Hz, 2H, Ar-H), 6.84 (dd, $^3J_{\text{HH}} = 8.7$, 2H, Ar-H), 6.65 (dt, $^3J_{\text{HH}} = 18.1$, $^3J_{\text{HH}} = 4.3$ Hz, 1H, =CH), 5.71 (d, $^3J_{\text{HH}} = 18.2$ Hz, 1H, =CH), 4.81 (s, 2H, CH₂), 3.78 (s, 3H, OMe), 1.20 (s, 12H, pinacol). **¹¹B NMR** (160

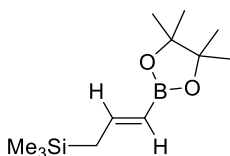
MHz, CDCl₃, 298 K) δ /ppm: 29.6 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 165.9 (s), 163.5 (s), 146.4 (s), 131.8 (s), 122.5 (s), 113.7 (s), 83.5 (s), 74.9 (s), 65.6 (s), 55.5 (s), 52.3 (s), 24.9 (s). **HRMS** (AP)⁺ m/z calculated for [C₁₇H₂₄¹¹BO₅]⁺ [M+H]⁺: 319.1717, found: 319.1704.



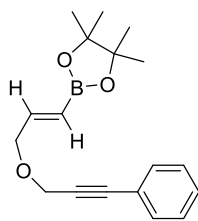
5.2i: Synthesised in accordance with *General Procedure 5* using prop-2-yn-1-yl acrylate (22 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 24 h. Yield: 41 mg, 174 μ mol, 87%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 6.64 (dt, ³J_{HH} = 18.2 Hz, ⁴J_{HH} = 4.6 Hz, 1H, =CH), 6.44 (dd, ³J_{HH} = 17.3 Hz, ⁴J_{HH} = 1.3 Hz, 1H, =CH), 6.14 (dd, ³J_{HH} = 17.3 Hz, ³J_{HH} = 10.4 Hz, 1H, =CH), 5.85 (dd, ³J_{HH} = 10.5 Hz, ⁴J_{HH} = 1.3 Hz, 1H, =CH), 5.70 (dt, ³J_{HH} = 18.1 Hz, ⁴J_{HH} = 1.7 Hz, 1H, =CH), 4.75 (dd, ³J_{HH} = 4.6 Hz, ⁴J_{HH} = 1.8 Hz, 2H, CH₂), 1.26 (s, 12H, pinacol). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ /ppm: 29.6 (s). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 164.6 (s), 144.8 (s), 130.1 (s), 127.2 (s), 82.4 (s), 64.4 (s), 23.8 (s).



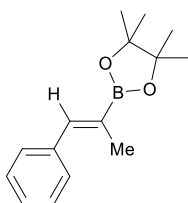
5.2j: Synthesised in accordance with *General Procedure 5* using ethynyltrimethylsilane (20 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 6 h. Yield: 43 mg, 190 μ mol, 95%. Spectroscopic data agrees with literature values.^[126] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 7.11 (d, ³J_{HH} = 21.8 Hz, 2H, =CH), 6.23 (d, ³J_{HH} = 21.8 Hz, 1H, =CH), 1.27 (s, 12H, pinacol), 0.06 (s, 9H, SiMe₃). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: 28.9 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 157.9 (s), 83.3 (s), 24.8 (s), -1.9 (s). **²⁹Si NMR** (80 MHz, CDCl₃, 298 K) δ /ppm: -6.7 (s).



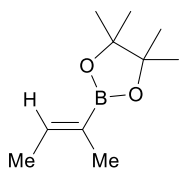
5.2k: Synthesised in accordance with *General Procedure 5* using 3-trimethylsilylpropyne (22 mg, 0.2 mmol) as the substrate gave the product as colourless crystals after 6 h. Yield: 40 mg, 166 μ mol, 83%. Spectroscopic data agrees with literature values.^[189] **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 6.69–6.60 (m, 1H, =CH), 5.22 (d, ³J_{HH} = 17.7 Hz, 1H, =CH), 1.67 (dd, ³J_{HH} = 8.2 Hz, ⁴J_{HH} = 1.0 Hz, 2H, CH₂), 1.24 (s, 12H, pinacol), 0.00 (s, 9H, SiMe₃). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ /ppm: 29.6 (s). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 154.0 (s), 84.6 (s), 30.1 (s), 26.6 (s), 0.00 (s). **²⁹Si NMR** (80 MHz, CDCl₃, 298 K) δ /ppm: 0.8 (s).



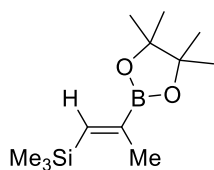
5.2i: Synthesised in accordance with *General Procedure 5* using (3-(prop-2-yn-1-yloxy)prop-1-yn-1-yl)benzene (34 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Yield: 33 mg, 112 μmol , 56%. **$^1\text{H NMR}$** (400 MHz, CDCl_3 , 298 K) δ/ppm : 7.44 (dd, $^3J_{\text{HH}} = 6.6$, $^4J_{\text{HH}} = 3.2$ Hz, 2H), 7.30 (dd, $^3J_{\text{HH}} = 5.1$, $^3J_{\text{HH}} = 1.9$ Hz, 2H), 6.67 (dt, $^3J_{\text{HH}} = 18.1$, $^4J_{\text{HH}} = 4.9$ Hz, 1H), 5.76 (dt, $^3J_{\text{HH}} = 18.1$, $^4J_{\text{HH}} = 1.6$ Hz, 1H), 4.38 (s, 1H), 4.22 (dd, $^3J_{\text{HH}} = 4.9$, $^4J_{\text{HH}} = 1.6$ Hz, 2H), 1.27 (s, 12H, pinacol). **$^{11}\text{B NMR}$** (128 MHz, CDCl_3 , 298 K) δ/ppm : 29.6 (s). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3 , 298 K) δ/ppm : 148.5 (s), 131.9 (s), 128.5 (s), 128.4 (s), 122.8 (s), 86.5 (s), 85.1 (s), 83.4 (s), 71.4 (s), 58.4 (s), 24.9 (s). **HRMS** (AP)⁺ m/z calculated for $[\text{C}_{18}\text{H}_{24}^{10}\text{BO}_3]^+$ $[\text{M}+\text{H}]^+$: 298.1855, found: 298.1849.



5.2m: Synthesised in accordance with *General Procedure 5* using 1-phenyl-1-propyne (23 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Yield: 47 mg, 192 μmol , 96%. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ/ppm : 7.30 (d, $^3J_{\text{HH}} = 7.7$ Hz, 2H, Ar-H), 7.25 (t, $^3J_{\text{HH}} = 7.4$ Hz, 2H, Ar-H), 7.16 (s, 1H, =CH), 7.14 (t, $^3J_{\text{HH}} = 7.4$ Hz, 1H, Ar-H), 1.91 (s, 3H, Me), 1.23 (s, 12H, pinacol). **$^{11}\text{B NMR}$** (160 MHz, CDCl_3 , 298 K) δ/ppm : 30.6 (s). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3 , 298 K) δ/ppm : 141.4 (s), 136.9 (s), 128.4 (s), 127.0 (s), 126.1 (s), 82.5 (s), 23.8 (s), 14.9 (s). **HRMS** (ES)⁺ m/z calculated for $[\text{C}_{15}\text{H}_{22}^{10}\text{BO}_2]^+$ $[\text{M}+\text{H}]^+$: 244.1749, found: 244.1739.

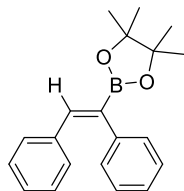


5.2n: Synthesised in accordance with *General Procedure 5* using 2-butyne (11 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 6 h. Yield: 35 mg, 192 μmol , 96%. **$^1\text{H NMR}$** (500 MHz, CDCl_3 , 298 K) δ/ppm : 6.42 (q, $^3J_{\text{HH}} = 6.5$ Hz, 1H, =CH), 1.70 (d, $^3J_{\text{HH}} = 6.8$ Hz, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.25 (s, 12H, pinacol). **$^{11}\text{B NMR}$** (160 MHz, CDCl_3 , 298 K) δ/ppm : 30.2 (s). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3 , 298 K) δ/ppm : 140.8 (s), 83.1 (s), 24.8 (s), 14.3 (s), 13.5 (s). **HRMS** (EI)⁺ m/z calculated for $[\text{C}_{10}\text{H}_{19}^{10}\text{BO}_2]^+$ $[\text{M}]^+$: 181.1514, found: 181.1516.

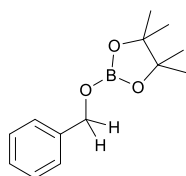


5.2o: Synthesised in accordance with *General Procedure 5* using 1-trimethylsilylpropyne (22 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Yield: 43 mg, 178 μmol , 89%. **$^1\text{H NMR}$** (400 MHz, CDCl_3 , 298 K) δ/ppm : 7.09 (q, $^4J_{\text{HH}} = 6.7$ Hz, 1H, =CH), 1.89 (d, $^4J_{\text{HH}} = 6.7$ Hz, 3H, Me), 1.24 (s, 12H, pinacol), 0.16 (s, 9H,

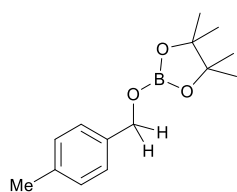
SiMe₃). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 31.4 (s). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 155.9 (s), 82.8 (s), 24.7 (s), 0.8 (s). **²⁹Si NMR** (80 MHz, CDCl₃, 298 K) δ/ppm: -8.44 (s).



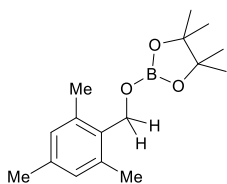
5.2p: Synthesised in accordance with *General Procedure 5* using diphenylacetylene (36 mg, 0.2 mmol) as the substrate gave the product as white crystals after 168 h. Yield: 49 mg, 160 μmol, 80%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.37 (br. s, 1H, Ar-H), 7.29–7.21 (m, 3H, Ar-H), 7.20–7.14 (m, 2H, Ar-H), 7.14–7.07 (m, 3H, Ar-H and =CH), 7.09–7.02 (m, 2H, Ar-H), 1.30 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 30.6 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 143.2 (s), 140.5 (s), 137.0 (s), 131.6 (s), 130.0 (s), 128.9 (s), 128.3 (s), 127.9 (s), 126.3 (s), 83.8 (s), 24.8 (s). **HRMS** (EI)⁺ *m/z* calculated for [C₂₀H₂₃¹⁰BO₂]⁺ [M]⁺: 305.1827, found: 305.1831.



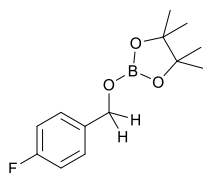
5.3a: Synthesised in accordance with *General Procedure 6* using benzaldehyde (21 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 1 h. Conversion: >99%. Spectroscopic data agrees with literature values.^[190] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.28–7.17 (m, 5H, Ar-H), 4.85 (s, 2H, CH₂), 1.18 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 22.3 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 139.2 (s), 128.3 (s), 127.4 (s), 126.7 (s), 83.0 (s), 66.7 (s), 24.6 (s).



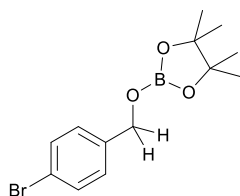
5.3b: Synthesised in accordance with *General Procedure 4* using 4-methylbenzaldehyde (24 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 3 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.16 (d, ³J_{HH} = 8.0 Hz, 2H, Ar-H), 7.06 (d, ³J_{HH} = 8.0 Hz, 2H, Ar-H), 4.81 (s, 2H, CH₂), 2.25 (s, 3H, CH₃), 1.18 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 22.3 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 137.0 (s), 136.3 (s), 129.0 (s), 126.9 (s), 82.9 (s), 66.6 (s), 24.6 (s), 21.2 (s). **HRMS** (EI)⁺ *m/z* calculated for [C₁₄H₂₁¹⁰BO₃]⁺ [M]⁺: 247.1620, found: 247.1614.



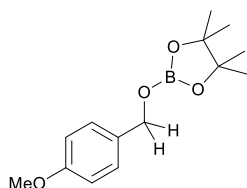
5.3c: Synthesised in accordance with *General Procedure 4* using mesitaldehyde (29 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 3 h. Conversion: >99%. Spectroscopic data agrees with literature values.^[191] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 6.75 (s, 2H, Ar-H), 4.87 (s, 2H, CH₂), 2.30 (s, 6H, *o*-Me), 2.17 (s, 3H, *p*-Me) 1.18 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 22.3 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 137.8 (s), 137.6 (s), 132.2 (s), 128.9 (s), 82.8 (s), 61.2 (s), 22.6 (s), 21.0 (s), 19.5 (s).



5.3d: Synthesised in accordance with *General Procedure 4* using 4-fluorobenzaldehyde (25 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 3 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.26–7.22 (m, 2H, Ar-H), 6.96–6.91 (m, 2H, Ar-H), 4.80 (s, 2H, CH₂), 1.19 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 22.3 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 162.2 (d, ¹J_{CF} = 245 Hz, C-F), 135.0 (d, ⁴J_{CF} = 3.1 Hz), 128.6 (d, ³J_{CF} = 8.1 Hz), 115.1 (d, ²J_{CF} = 21.4 Hz), 83.1 (s), 66.1 (s), 24.6 (s). **¹⁹F NMR** (565 MHz, CDCl₃, 298 K) δ/ppm: -115.3 (s, 1F). **HRMS** (EI)⁺ *m/z* calculated for [C₁₃H₁₈¹⁰BO₃F]⁺ [M]⁺: 251.1369, found: 251.1363.

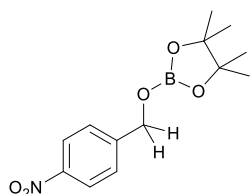


5.3e: Synthesised in accordance with *General Procedure 4* using 4-bromobenzaldehyde (37 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 3 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.38 (d, ³J_{HH} = 7.6 Hz, 2H, Ar-H), 7.14 (d, ³J_{HH} = 7.6 Hz, 2H, Ar-H), 4.79 (s, 2H, CH₂), 1.19 (s, 1H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 22.3 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 138.2 (s), 131.4 (s), 128.4 (s), 121.2 (s), 83.2 (s), 66.0 (s), 24.6 (s). **HRMS** (EI)⁺ *m/z* calculated for [C₁₃H₁₈O₃Br¹⁰B]⁺ [M]⁺: 311.0569, found: 311.0573.

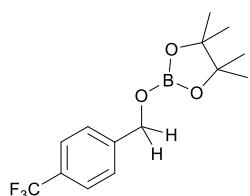


5.3f: Synthesised in accordance with *General Procedure 4* using 4-methoxybenzaldehyde (27 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.20 (d, ³J_{HH} = 8.3 Hz, 2H, Ar-H), 6.79 (d, ³J_{HH} = 8.3 Hz, 2H, Ar-H), 4.77 (s, 2H, CH₂), 3.72 (s, 3H, OMe), 1.18 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 22.3 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 158.0 (s), 127.5 (s), 112.6 (s),

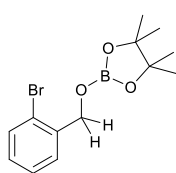
81.9 (s), 65.4 (s), 54.2 (s), 23.6 (s). **HRMS** (EI)⁺ *m/z* calculated for [C₁₄H₂₁¹⁰BO₄]⁺ [M]⁺: 263.1569, found: 263.1565.



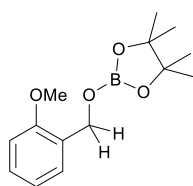
5.3g: Synthesised in accordance with *General Procedure 4* using 4-nitrobenzaldehyde (30 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 48 h. Conversion: >99%. Spectroscopic data agrees with literature values.^[190] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.12 (d, ³J_{HH} = 8.8 Hz, 2H, Ar-H), 7.43 (d, ³J_{HH} = 8.8 Hz, 2H, Ar-H), 4.95 (s, 2H, CH₂), 1.20 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 22.4 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 146.2 (s), 145.6 (s), 125.8 (s), 122.6 (s), 82.4 (s), 64.5 (s), 23.6 (s).



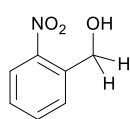
5.3h: Synthesised in accordance with *General Procedure 4* using 4-(trifluoromethyl)benzaldehyde (35 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 3 h. Conversion: >99%. Spectroscopic data agrees with literature values.^[191] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.51 (d, ³J_{HH} = 8.0 Hz, 2H, Ar-H), 7.37 (d, ³J_{HH} = 8.0 Hz, 2H, Ar-H), 4.90 (s, 2H, CH₂), 1.19 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 22.4 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 143.2 (s), 129.6 (q, ²J_{CF} = 32.3 Hz), 126.6 (s), 125.3 (q, ³J_{CF} = 3.7 Hz), 83.2 (s), 65.9 (s), 24.6 (s). **¹⁹F NMR** (471 MHz, CDCl₃, 298 K) δ/ppm: -62.5 (s, 3F, *p*-CF₃).



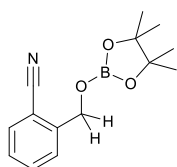
5.3i: Synthesised in accordance with *General Procedure 6* using 2-bromobenzaldehyde (37 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.43 (d, ³J_{HH} = 7.9 Hz, 2H, Ar-H), 7.23 (t, ³J_{HH} = 7.5 Hz, 1H, Ar-H), 7.05 (t, ³J_{HH} = 7.7 Hz, 1H, Ar-H), 4.90 (s, 2H, CH₂), 1.20 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 22.4 (s) **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 138.4 (s), 132.3 (s), 128.6 (s), 127.8 (s), 127.4 (s), 121.6 (s), 83.2 (s), 66.3 (s), 24.6 (s). **HRMS** (EI)⁺ *m/z* calculated for [C₁₃H₁₈O₃Br¹⁰B]⁺ [M]⁺: 311.0569, found: 311.0564.



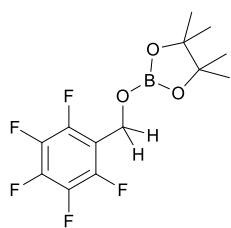
5.3j: Synthesised in accordance with *General Procedure 4* using 2-methoxybenzaldehyde (27 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 24 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.32 (d, ³J_{HH} = 7.5 Hz, 1H, Ar-H), 7.15 (t, ³J_{HH} = 7.9 Hz, 1H, Ar-H), 6.86 (t, ³J_{HH} = 7.4 Hz, 1H, Ar-H), 6.74 (d, ³J_{HH} = 8.2 Hz, 1H, Ar-H), 4.90 (s, 2H, CH₂), 3.71 (s, 3H, OMe), 1.18 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 22.4 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 156.5 (s), 128.3 (s), 127.7 (s), 127.4 (s), 120.4 (s), 109.8 (s), 82.9 (s), 62.3 (s), 55.2 (s), 24.6 (s). **HRMS** (EI)⁺ *m/z* calculated for [C₁₄H₂₁¹⁰BO₄]⁺ [M]⁺: 263.1569, found: 263.1559.



5.3k: Synthesised in accordance with *General Procedure 4* using 2-nitrobenzaldehyde (30 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 48 h. Conversion: >99%. Compound was allowed to hydrolyse, and subsequent filtration through silica afforded a clean NMR spectra of the hydrolysed alcohol product. Spectroscopic data agrees with literature values.^[192] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.01 (d, ³J_{HH} = 8.2 Hz, 1H, Ar-H), 7.68 (d, ³J_{HH} = 7.6 Hz, 1H, Ar-H), 7.58 (t, ³J_{HH} = 7.5 Hz, 1H, Ar-H), 7.39 (t, ³J_{HH} = 7.8 Hz, 1H, Ar-H), 4.91 (d, ³J_{HH} = 5.2 Hz, 1H, CH₂), 2.49 (br. s, 1H, OH). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 136.8 (s), 134.2 (s), 130.0 (s), 128.5 (s), 125.1 (s), 62.6 (s).

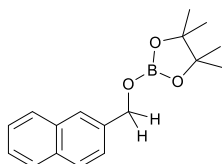


5.3l: Synthesised in accordance with *General Procedure 4* using 2-cyanobenzaldehyde (26 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 4 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.56–7.50 (m, 3H, Ar-H), 7.29 (t, ³J_{HH} = 7.4 Hz, 1H, Ar-H), 5.60 (s, 2H, CH₂), 1.20 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 22.4 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 142.8 (s), 132.9 (s), 132.6 (s), 127.8 (s), 127.4 (s), 117.0 (s), 83.4 (s), 64.4 (s), 24.6 (s). **HRMS** (AP)⁺ *m/z* calculated for [C₈H₈NO]⁺ [M+2H-(C₆H₁₂BO₂)]⁺: 134.0606, found: 134.0600.

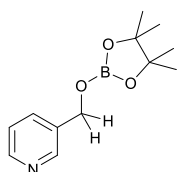


5.3m: Synthesised in accordance with *General Procedure 6* using 2,3,4,5,6-pentafluorobenzaldehyde (39 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 1 h. Conversion: >99%. Spectroscopic data agrees with literature values.^[190] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 5.00 (s, 2H, CH₂), 1.27 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 22.3 (s). **¹³C**

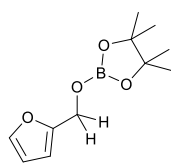
NMR (126 MHz, CDCl₃, 298 K) δ /ppm: 146.6–144.4 (m), 142.4–140.2 (m), 138.5–136.3 (m), 112.1 (td, $^2J_{CF}$ = 17.7 Hz, $^3J_{CF}$ = 3.8 Hz), 83.5 (s), 54.2 (s), 24.5 (s). **¹⁹F NMR** (471 MHz, CDCl₃, 298 K) δ /ppm: -143.1 – -143.2 (m, 2F, *o*-F), -154.1 (t, 1F, *p*-F), -162.3 – -162.4 (m, 2F, *m*-F).



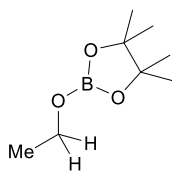
5.3n: Synthesised in accordance with *General Procedure 4* using 2-naphthaldehyde (31 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 7.76–7.69 (m, 4H, Ar-H), 7.40–7.31 (m, 3H, Ar-H), 5.01 (s, 2H, CH₂), 1.19 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: 22.4 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 136.7 (s), 133.4 (s), 132.9 (s), 128.0 (s), 127.9 (s), 127.7 (s), 126.1 (s), 125.8 (s), 125.2 (s), 124.9 (s), 83.1 (s), 66.8 (s), 24.7 (s). **HRMS** (EI)⁺ *m/z* calculated for [C₁₇H₂₁¹⁰BO₃]⁺ [M]⁺: 283.1620, found: 283.1620.



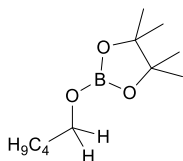
5.3o: Synthesised in accordance with *General Procedure 4* using 3-pyridinecarboxaldehyde (21 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 24 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 8.49 (s, 1H, Ar-H), 8.42 (d, $^3J_{HH}$ = 3.8 Hz, 1H, Ar-H), 7.65 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Ar-H), 7.21 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar-H), 4.85 (s, 2H, CH₂), 1.18 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: 22.3 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 148.5 (s), 148.1 (s), 135.1 (s), 123.5 (s), 83.3 (s), 82.7 (s), 64.3 (s), 24.6 (s). **HRMS** (AP)⁺ *m/z* calculated for [C₆H₈NO]⁺ [M+2H-(C₆H₁₂BO₂)]⁺: 110.0606, found: 110.0602.



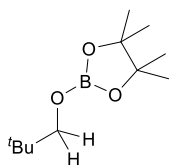
5.3p: Synthesised in accordance with *General Procedure 4* using 2-furaldehyde (19 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Conversion: >99%. Spectroscopic data agrees with literature values.^[193] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 7.30–7.29 (m, 1H, furan), 6.25–6.21 (m, 2H, furan), 4.75 (s, 2H, CH₂), 1.19 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: 22.3 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 152.5 (s), 142.5 (s), 110.2 (s), 108.3 (s), 83.1 (s), 59.2 (s), 24.6 (s).



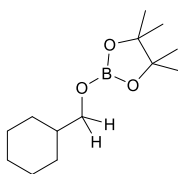
5.3q: Synthesised in accordance with *General Procedure 6* using acetaldehyde (9 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 1 h. Conversion: >99%. Spectroscopic data agrees with literature values.^[194] **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 3.89 (q, ³J_{HH} = 7.0 Hz, 2H, CH₂), 1.24 (s, 12H, pinacol), 1.21 (t, ³J_{HH} = 7.1 Hz, 3H, Me), **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 22.1 (s). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 83.2 (s), 60.7 (s), 24.5 (s), 17.2 (s).



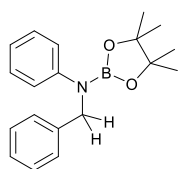
5.3r: Synthesised in accordance with *General Procedure 6* using 1-pentanal (17 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 1 h. Conversion: >99%. Spectroscopic data agrees with literature values.^[195] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 3.76 (t, ³J_{HH} = 6.6 Hz, 2H, CH₂), 1.50 (pent., ³J_{HH} = 6.5 Hz, 2H, CH₂), 1.30–1.23 (m, 4H, CH₂), 1.19 (d, ³J_{HH} = 8.1 Hz, 12H), 0.83 (q, ³J_{HH} = 7.3 Hz, 3H, CH₃). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 22.1 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 82.6 (s), 65.0 (s), 31.1 (s), 27.8 (s), 24.6 (s), 22.4 (s), 14.0 (s).



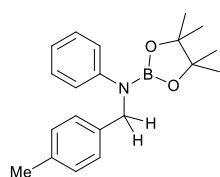
5.3s: Synthesised in accordance with *General Procedure 6* using trimethylacetaldehyde (17 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Conversion: >99%. Spectroscopic data agrees with literature values.^[191] **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 3.51 (s, 2H, CH₂), 1.24 (s, 12H, pinacol), 0.88 (9H, s, ^tBu). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 22.1 (s). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 82.6 (s), 74.9 (s), 32.3 (s), 26.0 (s), 24.6 (s).



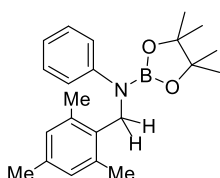
5.3t: Synthesised in accordance with *General Procedure 6* using cyclohexanaldehyde (22 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Conversion: >99%. Spectroscopic data agrees with literature values.^[194] **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 3.63 (d, ³J_{HH} = 6.4 Hz, 2H, CH₂), 1.75–1.62 (m, 5H, alkyl), 1.54–1.45 (m, 1H, alkyl), 1.20 (s, 12H, pinacol), 1.19–1.10 (m, 3H, alkyl), 0.96–0.87 (m, 2H, alkyl). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 22.1 (s). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 82.6 (s), 70.4 (s), 39.3 (s), 29.3 (s), 26.5 (s), 25.8 (s), 24.6 (s).



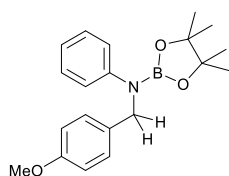
5.4a: Synthesised in accordance with *General Procedure 4* using (*E*)-*N*,1-diphenylmethanimine (36 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 4 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.27–7.23 (m, 4H, Ar-H), 7.18 (t, ³J_{HH} = 6.7 Hz, 1H, Ar-H), 7.08 (t, ³J_{HH} = 7.3 Hz, 2H, Ar-H), 6.65 (t, ³J_{HH} = 7.2 Hz, 1H, Ar-H), 6.56 (d, ³J_{HH} = 8.0 Hz, 2H, Ar-H), 4.24 (s, 2H, CH₂), 1.18 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 21.1 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 129.3 (s), 128.7 (s), 127.6 (s), 127.3 (s), 83.2 (s), 48.7 (s), 24.6 (s). **HRMS** (ES)⁺ *m/z* calculated for [C₁₉H₂₅¹⁰BNO₂]⁺ [M+H]⁺: 309.2015, found: 309.2019.



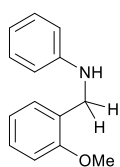
5.4b: Synthesised in accordance with *General Procedure 4* using (*E*)-*N*-phenyl-1-(*p*-tolyl)methanimine (39 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.17 (d, ³J_{HH} = 7.9 Hz, 2H, Ar-H), 7.10–7.04 (m, 4H, Ar-H), 6.62 (t, ³J_{HH} = 7.3 Hz, 1H, Ar-H), 6.54 (d, ³J_{HH} = 7.8 Hz, 2H, Ar-H), 4.18 (s, 2H, CH₂), 2.25 (s, 3H, *o*-Me), 1.18 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 21.1 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 148.3 (s), 136.9 (s), 136.4 (s), 129.4 (s), 129.3 (s), 127.6 (s), 117.5 (s), 112.9 (s), 83.2 (s), 48.1 (s), 24.6 (s), 21.2 (s). **HRMS** (EI)⁺ *m/z* calculated for [C₂₀H₂₆¹⁰BNO₂]⁺ [M]⁺: 322.2093, found: 322.2094; [C₁₄H₁₅N]⁺ [M]⁺ *m/z* calculated: 197.1204, found: 197.1206.



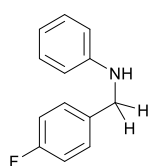
5.4c: Synthesised in accordance with *General Procedure 4* using (*E*)-1-mesityl-*N*-phenylmethanimine (44 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.12 (t, ³J_{HH} = 7.3 Hz, 2H, Ar-H), 6.80 (s, 2H, Ar-H), 6.64 (t, ³J_{HH} = 7.2 Hz, 1H, Ar-H), 6.57 (d, ³J_{HH} = 7.7 Hz, 2H, Ar-H), 4.09 (s, 2H, CH₂), 2.25 (s, 6H, *o*-Me), 2.20 (s, 3H, *p*-Me), 1.18 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 22.3 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 148.6 (s), 137.5 (s), 137.3 (s), 132.2 (s), 129.3 (s), 129.1 (s), 117.4 (s), 112.6 (s), 83.3 (s), 42.5, 24.5, 21.0, 19.5. **HRMS** (EI)⁺ *m/z* calculated for [C₁₆H₁₉N]⁺ [M+2H-(C₆H₁₂BO₂)]⁺: 225.1517, found: 225.1517.



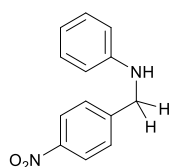
5.4d: Synthesised in accordance with *General Procedure 4* using (*E*)-1-(4-methoxyphenyl)-*N*-phenylmethanimine (42 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Conversion: >99%. Compound was allowed to hydrolyse, and subsequent filtration through silica afforded clean NMR spectra of the secondary amine. Spectroscopic data agrees with literature values.^[149b] **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.30 (d, ³J_{HH} = 8.5 Hz, 2H, Ar-H), 7.20–7.16 (m, 2H, Ar-H), 6.89 (d, ³J_{HH} = 8.6 Hz, 2H, Ar-H), 6.72 (t, ³J_{HH} = 7.3 Hz, 1H, Ar-H), 6.65 (d, ³J_{HH} = 7.7 Hz, 2H, Ar-H), 4.26 (s, 2H, CH₂), 3.95 (br. s, 1H, NH), 3.81 (s, 3H, OMe). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 158.9 (s), 148.2 (s), 131.4 (s), 129.3 (s), 128.8 (s), 117.5 (s), 114.0 (s), 112.9 (s), 55.3 (s), 47.8 (s).



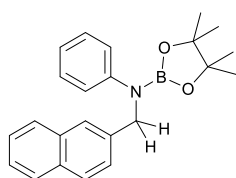
5.4e: Synthesised in accordance with *General Procedure 4* using (*E*)-1-(2-methoxyphenyl)-*N*-phenylmethanimine (42 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 4 h. Conversion: >99%. Compound was allowed to hydrolyse, and subsequent filtration through silica afforded clean NMR spectra of the secondary amine. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.23 (d, ³J_{HH} = 7.2 Hz, 1H, Ar-H), 7.20–7.13 (m, 1H, Ar-H), 7.13–7.05 (m, 2H, Ar-H), 6.87–6.76 (m, 2H, Ar-H), 6.67–6.53 (m, 3H, Ar-H), 4.26 (s, 2H, CH₂), 3.78 (s, 3H, OCH₃). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 157.4 (s), 148.4 (s), 129.2 (s), 128.9 (s), 128.3 (s), 127.3 (s), 120.6 (s), 117.4 (s), 113.1 (s), 110.3 (s), 55.3 (s), 43.5 (s). **HRMS** (ES)⁺ *m/z* calculated for [C₁₄H₁₆NO]⁺ [M+H]⁺: 214.1232, found: 214.1236.



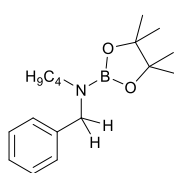
5.4f: Synthesised in accordance with *General Procedure 6* using (*E*)-1-(4-fluorophenyl)-*N*-phenylmethanimine (40 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Conversion: >99%. Compound was allowed to hydrolyse, and subsequent filtration through silica afforded clean NMR spectra of the secondary amine. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.34 (dd, ³J_{HH} = 8.4 Hz, ³J_{HH} = 5.5 Hz, 2H, Ar-H), 7.18 (t, ³J_{HH} = 7.9 Hz, 2H, Ar-H), 7.03 (t, ³J_{HH} = 8.7 Hz, 2H, Ar-H), 6.73 (t, ³J_{HH} = 7.3 Hz, 1H, Ar-H), 6.63 (t, ³J_{HH} = 7.8 Hz, 2H, Ar-H), 4.31 (s, 2H, CH₂), 4.02 (br. s, 1H, NH). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 162.2 (d, ¹J_{CF} = 245 Hz), 148.1 (s), 135.2 (d, ⁴J_{CF} = 3.1 Hz), 129.4 (s), 129.1 (d, ³J_{CF} = 8.0 Hz), 117.9 (s), 115.6 (d, ²J_{CF} = 21.4 Hz), 113.0 (s), 47.8 (s). **¹⁹F NMR** (377 MHz, CDCl₃, 298 K) δ/ppm: -115.7 (s, 1F, *p*-F). **HRMS** (ES)⁺ *m/z* calculated for [C₁₃H₁₃NF]⁺ [M+H]⁺: 202.1032, found: 202.1024.



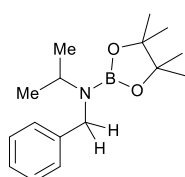
5.4g: Synthesised in accordance with *General Procedure 6* using (*E*)-1-(4-nitrophenyl)-*N*-phenylmethanimine (45 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 24 h. Conversion: >99%. Compound was allowed to hydrolyse, and subsequent filtration through silica afforded clean NMR spectra of the secondary amine. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 8.19 (d, ³J_{HH} = 8.7 Hz, 2H, Ar-H), 7.54 (d, ³J_{HH} = 8.6 Hz, 2H, Ar-H), 7.18 (t, ³J_{HH} = 7.9 Hz, 2H, Ar-H), 6.75 (t, ³J_{HH} = 7.3 Hz, 1H, Ar-H), 6.59 (t, ³J_{HH} = 8.4 Hz, 2H, Ar-H), 4.48 (s, 2H, CH₂), 4.26 (br. s, 1H, NH). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 147.5 (s), 147.3 (s), 129.4 (s), 127.7 (s), 123.9 (s), 121.0 (s), 118.2 (s), 112.9 (s), 47.6 (s). **HRMS** (ES)⁺ *m/z* calculated for [C₁₃H₁₃N₂O₂]⁺ [M+H]⁺: 229.0977, found: 229.0966.



5.4h: Synthesised in accordance with *General Procedure 4* using (*E*)-1-(naphthalen-2-yl)-*N*-phenylmethanimine (46 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 24 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.73–7.68 (m, 4H, Ar-H), 7.37–7.35 (m, 3H, Ar-H), 7.08 (t, ³J_{HH} = 7.9 Hz, 2H, Ar-H), 6.65 (t, ³J_{HH} = 7.3 Hz, 1H, Ar-H), 6.58 (d, ³J_{HH} = 8.0 Hz, 2H, Ar-H), 3.38 (s, 2H, CH₂), 1.17 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 22.3 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 133.5 (s), 132.8 (s), 129.3 (s), 128.4 (s), 127.8 (s), 127.7 (s), 126.2 (s), 125.8 (s), 125.8 (s), 83.2 (s), 48.9 (s), 24.6 (s). **HRMS** (EI)⁺ *m/z* calculated for [C₁₇H₁₅N]⁺ [M+H-(C₆H₁₂BO₂)]⁺: 233.1204, found: 233.1208.

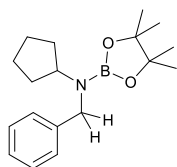


5.4i: Synthesised in accordance with *General Procedure 4* using (*E*)-*N*-butyl-1-phenylmethanimine (32 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.25–7.08 (m, 5H, Ar-H), 4.00 (s, 2H, CH₂), 2.70 (t, ³J_{HH} = 6.9 Hz, 2H, alkyl CH₂), 1.34–1.23 (m, 4H, alkyl CH₂), 1.17 (s, 12H, pinacol), 0.79 (t, ³J_{HH} = 7.3 Hz, 3H, CH₃). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 24.6 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 141.0 (s), 128.3 (s), 127.8 (s), 126.6 (s), 82.2 (s), 49.1 (s), 44.4 (s), 30.8 (s), 24.7 (s), 19.8 (s), 14.1 (s). **HRMS** (ES)⁺ *m/z* calculated for [C₁₁H₁₈N]⁺ [M+2H-(C₆H₁₂BO₂)]⁺: 164.1439, found: 164.1435.

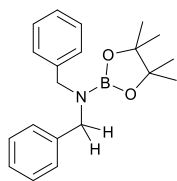


5.4j: Synthesised in accordance with *General Procedure 4* using (*E*)-*N*-isopropyl-1-phenylmethanimine (29 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.19 (br. s, 4H, Ar-

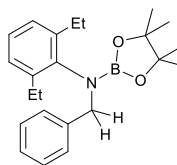
H), 7.10 (br. s, 1H, Ar-H), 4.01 (s, 2H, CH₂), 3.27 (sept, ³J_{HH} = 7.3 Hz, 1H, *i*Pr H), 1.17 (s, 12H, pinacol), 0.93 (d, ³J_{HH} = 6.6 Hz, 6H, *i*Pr CH₃). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 24.6 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 143.2 (s), 128.1 (s), 127.4 (s), 126.3 (s), 81.9 (s), 48.1 (s), 48.0 (s), 24.7 (s), 22.7 (s). **HRMS** (EI)⁺ *m/z* calculated for [C₁₇H₁₆N]⁺ [M+2H-(C₆H₁₂BO₂)⁺]: 150.1283, found: 150.1278.



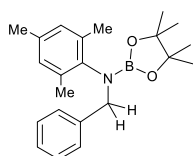
5.4k: Synthesised in accordance with *General Procedure 4* using (*E*)-*N*-cyclopentyl-1-phenylmethanimine (35 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 6 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.29–7.21 (m, 4H, Ar-H), 7.20–7.10 (m, 1H, Ar-H), 4.10 (s, 2H, CH₂), 3.53–3.36 (m, 1H, NCH cyclopentyl), 1.61–1.36 (m, 8H, cyclopentyl), 1.22 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 24.6 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 143.0 (s), 128.1 (s) (s), 127.0 (s), 126.2 (s), 81.9 (s), 58.9 (s), 48.7 (s), 31.2 (s), 24.7 (s), 23.7 (s). **HRMS** (ES)⁺ *m/z* calculated for [C₁₂H₁₈N]⁺ [M+2H-(C₆H₁₂BO₂)⁺]: 176.1439, found: 176.1446.



5.4l: Synthesised in accordance with *General Procedure 4* using (*E*)-*N*-benzyl-1-phenylmethanimine (39 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.22 (dd, ³J_{HH} = 7.9, ³J_{HH} = 6.4 Hz, 4H, Ar-H), 7.14 (td, ³J_{HH} = 8.2, ⁴J_{HH} = 4.1 Hz, 6H), 3.85 (s, 4H, CH₂), 1.22 (s, 12H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 24.9 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 140.2, 128.4, 128.1, 126.8, 82.7, 48.5, 24.8. **HRMS** (ES)⁺ *m/z* calculated for [C₁₄H₁₆N]⁺ [M+2H-(C₆H₁₂BO₂)⁺]: 198.1283, found: 198.1288.

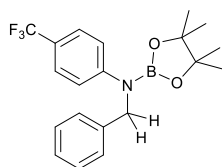


5.4m: Synthesised in accordance with *General Procedure 6* using (*E*)-*N*-(2,6-diethylphenyl)-1-phenylmethanimine (47 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.09 (s, 3H, Ar-H), 7.01–6.92 (m, 5H, Ar-H), 4.15 (s, 2H, CH₂), 2.35–2.31 (m, 2H, CH₂), 2.06–2.01 (m, 2H, CH₂), 1.21 (br. s, 6H, pinacol), 1.07 (br. s, 6H, pinacol), 0.91 (t, ³J_{HH} = 7.1 Hz, 6H, CH₃). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 24.1 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 142.6 (s), 140.8 (s), 140.0 (s), 129.6 (s), 127.9 (s), 126.9 (s), 126.2 (s), 126.1 (s), 82.6 (s), 54.9 (s), 24.6 (s), 23.9 (s), 14.8 (s). **HRMS** (EI)⁺ *m/z* calculated for [C₂₃H₃₂¹⁰BNO₂]⁺ [M]⁺: 364.2562, found: 364.2556.



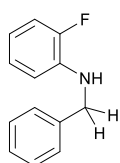
5.4n: Synthesised in accordance with *General Procedure 6* using (*E*)-*N*-mesityl-1-phenylmethanimine (45 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h.

Conversion: >99%. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.11–7.03 (m, 3H, Ar-H), 7.02–7.01 (m, 2H, Ar-H), 6.68 (s, 2H, Ar-H), 4.12 (s, 2H, CH₂), 2.12 (s, 3H, *p*-Me) 1.78 (s, 6H, *o*-Me), 1.23 (br. s, 6H, pinacol), 1.09 (br. s, 6H, pinacol). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ/ppm: 23.8 (s). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 140.6 (s), 139.7 (s), 136.3 (s), 134.9 (s), 129.5 (s), 129.0 (s), 128.0 (s), 126.8 (s), 82.5 (s), 53.7 (s), 24.6 (s), 21.0 (s), 18.2 (s). **HRMS** (ES)⁺ *m/z* calculated for [C₂₂H₃₀¹⁰BNO₂]⁺ [M]⁺: 350.2406, found: 350.2411; **HRMS** (ES)⁺ *m/z* calculated for [C₁₆H₁₉N]⁺ [M+H-(C₆H₁₂BO₂)]⁺: 225.1517, found: 225.1517.



5.4o: Synthesised in accordance with *General Procedure 6* using (*E*)-1-phenyl-*N*-(4-(trifluoromethyl)phenyl)methanimine (50 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 18 h. Conversion: >99%. **¹H NMR** (400 MHz, CDCl₃, 298 K)

δ/ppm: 7.30 (d, 2H, ³J_{HH} = 8.5), 7.27–7.26 (m, 5H, Ar-H), 6.54 (d, ³J_{HH} = 8.5 Hz, 2H, Ar-H), 4.27 (s, 2H, CH₂), 1.19 (s, 12H, pinacol). **¹¹B NMR** (128 MHz, CDCl₃, 298 K) δ/ppm: 22.3 (s). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 150.1 (s), 138.1 (s), 130.2 (s), 128.8 (s), 127.5 (s), 127.4 (s), 126.6 (q, ⁴J_{CF} = 3.8 Hz), 125.1 (q, ¹J_{CF} = 270 Hz), 119.0 (q, ²J_{CF} = 32.6 Hz), 83.3 (s), 47.8 (s), 24.5 (s). **¹⁹F NMR** (377 MHz, CDCl₃, 298 K) δ/ppm: -61.0 (s, 3F, CF₃). **HRMS** (ES)⁺ *m/z* calculated for [C₁₄H₁₃NF₃]⁺ [M+H-(C₆H₁₂BO₂)]⁺: 252.1000, found: 252.1001.



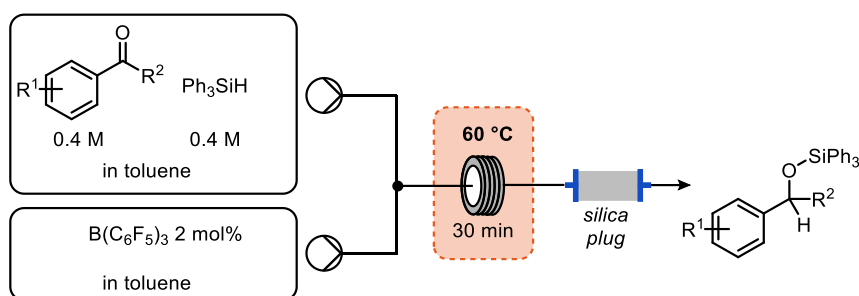
5.4p: Synthesised in accordance with *General Procedure 6* using (*E*)-*N*-(2-fluorophenyl)-1-phenylmethanimine (40 mg, 0.2 mmol) as the substrate gave the product as a colourless oil after 24 h. Conversion: >99%.

Compound was allowed to hydrolyse, and subsequent filtration through silica afforded clean NMR spectra of the secondary amine. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ/ppm: 7.31–7.15 (m, 5H, Ar-H), 6.92–6.85 (m, 2H, Ar-H), 6.61–6.52 (m, 2H, Ar-H), 4.28 (s, 2H, CH₂), 4.24 (br. s, 1H, NH). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 151.6 (d, ¹J_{CF} = 238 Hz), 139.1 (s), 136.7 (d, ³J_{CF} = 11.5 Hz), 128.8 (s), 127.5 (s), 124.7 (d, ⁴J_{CF} = 3.5 Hz), 116.9 (d, ³J_{CF} = 7.0 Hz), 114.5 (d, ²J_{CF} = 18.4 Hz), 112.4 (s), 48.0 (s). **¹⁹F NMR** (377 MHz, CDCl₃, 298 K) δ/ppm: -136.5 (s, 1F). **HRMS** (ES)⁺ *m/z* calculated for [C₁₃H₁₃NF]⁺ [M+H]⁺: 202.1032, found: 202.1026.

6.5.2 Novel Processing Methods in the Hydrosilylation of Aldehydes, Ketones and Imines

6.5.2.1 Synthesis of Products

General Procedure 7: A stock solution of triphenylsilane (1.0 equiv.) and aldehyde or ketone (1.0 equiv.) in toluene (0.4 M) was prepared along with a separate solution of tris(pentafluorophenylborane) (2 mol%) in toluene. 5 ml aliquots of $B(C_6F_5)_3$ and reagent/silane solution were combined using a T-piece adapter *via* syringe pump using a flow rate of 0.083 ml/min. The mixed reaction stream then proceeded to a 5 ml reaction coil where it was heated to 60 °C and left for 30 minutes to reach steady-state before being passed through a short plug of silica gel and collected in a flask for 12 minutes (Scheme 6.5.1). The solvent was removed *in vacuo* followed by characterisation *via* NMR spectroscopy with percent conversion being measured as a ratio between Me (acetophenone) or H (aldehyde) of starting material and product.

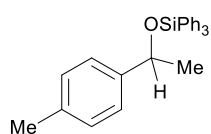


Scheme 6.5.1: General flow schematic for hydrosilylation of ketones and aldehydes.

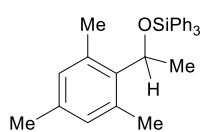
5.5a: Synthesised in accordance with *General Procedure 7* using acetophenone as starting material. Spectroscopic analyses agree with literature known values.^[196] Conversion: 98%. **¹H NMR** (400 MHz, $CDCl_3$, 298 K) δ /ppm: 7.60 (d, $^3J_{HH} = 7.5$ Hz, 6H, Ar-H), 7.40 (d, $^3J_{HH} = 7.0$ Hz, 3H, Ar-H), 7.36–7.24 (m, 11H, Ar-H), 5.04 (q, $^3J_{HH} = 6.3$ Hz, 1H, CH), 1.43 (d, $^3J_{HH} = 6.2$ Hz, 3H, CH_3). **¹³C NMR** (101 MHz, $CDCl_3$, 298 K) δ /ppm: 146.01 (s), 135.6 (s), 134.7 (s), 130.0 (s), 128.2 (s), 127.9 (s), 127.0 (s), 125.6 (s), 72.13 (s), 27.04 (s).

5.5b: Synthesised in accordance with *General Procedure 7* using 4-fluoroacetophenone as starting material. Conversion: 97%. **¹H NMR** (400 MHz, $CDCl_3$, 298 K) δ /ppm: 7.59 (d, $^3J_{HH} = 6.7$ Hz, 6H, Ar-H), 7.44–7.33 (m, 11H, Ar-H), 6.94 (d, $^3J_{HH} = 8.2$ Hz, 2H, Ar-H), 5.02 (q, $^3J_{HH} = 6.3$ Hz, 1H, CH), 1.42 (d, $^3J_{HH} = 6.3$ Hz, 3H, CH_3). **¹³C NMR** (75 MHz, $CDCl_3$, 298 K) δ /ppm: 161.6 (s), 135.5 (s), 134.5 (s), 130.1 (s), 128.7 (d, $^1J_{CF} = 81.2$ Hz), 127.9 (s), 127.1

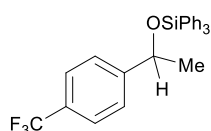
(d, $^3J_{CF} = 8.0$ Hz), 115.0 (d, $^2J_{CF} = 21.3$ Hz), 71.5 (s), 27.1 (s). **^{19}F NMR** (376 MHz, CDCl_3 , 298 K) δ/ppm : -116.2 (s, 1F, CF).



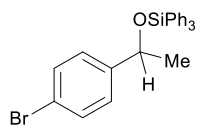
5.5c: Synthesised in accordance with *General Procedure 7* using 4-methylacetophenone as starting material. Conversion: 95%. **^1H NMR** (400 MHz, CDCl_3 , 298 K) δ/ppm : 7.60 (d, $^3J_{\text{HH}} = 6.7$ Hz, 6H, Ar-H), 7.41–7.32 (m, 9H, Ar-H), 7.21 (d, $^3J_{\text{HH}} = 7.8$ Hz, 2H, Ar-H), 7.08 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H, Ar-H), 5.01 (q, $^3J_{\text{HH}} = 6.1$ Hz, 1H, CH), 2.33 (s, 3H, CH_3), 1.41 (d, $^3J_{\text{HH}} = 6.4$ Hz, 3H, CH_3). **^{13}C NMR** (101 MHz, CDCl_3 , 298 K) δ/ppm : 143.0 (s), 136.4 (s), 135.5 (s), 134.7 (s), 129.9 (s), 128.8 (s), 127.8 (s), 125.4 (s), 71.9 (s), 26.9 (s), 21.2 (s).



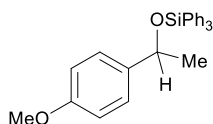
5.5d: Synthesised in accordance with the *General Procedure 7* using 2',4',6'-trimethylacetophenone as starting material. Conversion: measured using mesityl Ar-H C–H of reagent and product. Conversion: 87%. **^1H NMR** (400 MHz, CDCl_3 , 298 K) δ/ppm : 7.54 (d, $^3J_{\text{HH}} = 7.4$ Hz, 6H, Ar-H), 7.38–7.36 (m, 3H, Ar-H), 7.30 (t, $^3J_{\text{HH}} = 7.2$ Hz, 6H, Ar-H), 6.71 (br. s, 2H, Ar-H mes), 5.37 (q, $^3J_{\text{HH}} = 6.5$ Hz, 1H, CH), 2.34–2.15 (br. m, 9H, 3 x CH_3), 1.44 (d, $^3J_{\text{HH}} = 6.6$ Hz, 3H C(CH_3)). **^{13}C NMR** (101 MHz, CDCl_3 , 298 K) δ/ppm : 137.7 (s), 135.4 (s), 135.0 (s), 134.6 (s), 130.2 (s), 129.9 (s), 128.0 (s), 127.8 (s), 69.0 (s), 22.9 (s), 20.8 (s), 20.5 (s).



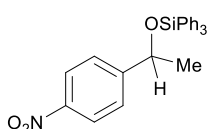
5.5e: Synthesised in accordance with *General Procedure 7* using 4-(trifluoromethyl)acetophenone as starting material. Conversion: 92%. **^1H NMR** (400 MHz, CDCl_3 , 298 K) δ/ppm : 7.49 (d, $^3J_{\text{HH}} = 7.4$ Hz, 6H, Ar-H), 7.51 (d, $^3J_{\text{HH}} = 7.8$ Hz, 2H, Ar-H), 7.42–7.39 (m, 5H, Ar-H), 7.37–7.33 (m, 6H, Ar-H), 5.08 (q, $^3J_{\text{HH}} = 6.3$ Hz, 1H, CH), 1.44 (d, $^3J_{\text{HH}} = 6.3$ Hz, 3H, CH_3). **^{13}C NMR** (101 MHz, CDCl_3 , 298 K) δ/ppm : 150.0 (s), 135.6 (s), 135.5 (s), 134.3 (s), 130.2 (s), 128.0 (s), 125.2 (q, $^3J_{CF} = 3.8$ Hz), 71.6 (s), 26.9 (s). **^{19}F NMR** (283 MHz, CDCl_3 , 298 K) δ/ppm : -62.4 (s, 3F, CF_3).



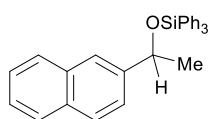
5.5f: Synthesised in accordance with *General Procedure 7* using 4-bromoacetophenone as starting material. Conversion: 77%. **^1H NMR** (400 MHz, CDCl_3 , 298 K) δ/ppm : 7.61 (d, $^3J_{\text{HH}} = 7.4$ Hz, 6H, Ar-H), 7.42–7.35 (m, 11H, Ar-H), 7.18 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H, Ar-H), 5.01 (q, $^3J_{\text{HH}} = 6.4$ Hz, 1H, CH), 1.42 (d, $^3J_{\text{HH}} = 6.3$ Hz, 3H, CH_3). **^{13}C NMR** (101 MHz, CDCl_3 , 298 K) δ/ppm : 145.1 (s), 135.5 (s), 134.4 (s), 131.3 (s), 130.1 (s), 128.0 (s), 127.4 (s), 120.7 (s), 71.5 (s), 26.9 (s).



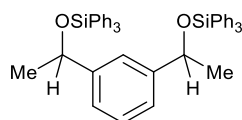
5.5g: Synthesised in accordance with *General Procedure 7* using 4-methoxyacetophenone as starting material. Conversion: 78%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.66–7.63 (m, 2H, Ar-H), 7.61–7.58 (m, 6H, Ar-H), 7.44–7.32 (m, 9H, Ar-H), 6.81 (d, ³J_{HH} = 8.7 Hz, 2H, Ar-H), 5.00 (pent., ³J_{HH} = 6.3 Hz, 1H, CH), 3.78 (s, 3H, OMe), 1.42 (d, ³J_{HH} = 6.3 Hz, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 158.6 (s), 135.6 (s), 135.1 (s), 134.8 (s), 130.0 (s), 129.2 (s), 128.4 (s), 128.2 (s), 127.9 (s), 113.6 (s), 71.7 (s), 55.4 (s), 27.0 (s).



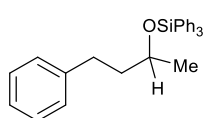
5.5h: Synthesised in accordance with *General Procedure 7* using 4-nitroacetophenone as starting material. Conversion: 92%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 8.12 (d, ³J_{HH} = 8.3 Hz, 2H, Ar-H), 7.62 (d, ³J_{HH} = 7.2 Hz, 6H, Ar-H), 7.47–7.42 (m, 5H, Ar-H), 7.38–7.35 (t, ³J_{HH} = 7.2 Hz, 6H, Ar-H), 5.14 (q, ³J_{HH} = 6.2 Hz, 1H, CH), 1.47 (d, ³J_{HH} = 6.2 Hz, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 153.4 (s), 147.0 (s), 135.4 (s), 134.0 (s), 130.3 (s), 128.0 (s), 126.3 (s), 123.6 (s), 71.3 (s), 26.8 (s).



5.5i: Synthesised in accordance with *General Procedure 7* using 2-acetonaphthone as starting material. Conversion: 93%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.85–7.72 (m, 4H, Ar-H), 7.66 (d, ³J_{HH} = 6.5 Hz, 6H, Ar-H), 7.55 (d, ³J_{HH} = 8.3 Hz, 1H, Ar-H), 7.48–7.42 (m, 6H, Ar-H), 7.39–7.35 (m, 5H, Ar-H), 5.23 (pent., ³J_{HH} = 6.1 Hz, 1H, CH), 1.54 (d, ³J_{HH} = 6.4 Hz, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 143.4 (s), 135.6 (s), 134.6 (s), 133.4 (s), 132.8 (s), 130.1 (s), 129.2 (s), 128.4 (s), 128.1 (s), 128.0 (s), 127.9 (s), 127.7 (s), 126.0 (s), 125.6 (s), 124.2 (s), 124.1 (s), 72.3 (s), 26.9 (s).

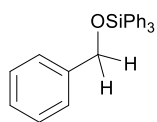


5.5j: Synthesised in accordance with *General Procedure 7* using 1,3-diacetylbenzene as starting material. Conversion: 98%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.58–7.55 (m, 12H, Ar-H), 7.40–7.24 (m, 22H, Ar-H), 4.96 (dd, ³J_{HH} = 6.1 Hz, ⁴J_{HH} = 1.9 Hz, 2H, CH), 1.37 (dd, ³J_{HH} = 6.3 Hz, ⁴J_{HH} = 2.8 Hz, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 145.9 (s), 135.6 (s), 134.7 (s), 130.0 (s), 128.4 (s), 127.9 (s), 124.3 (s), 124.2 (s), 122.9 (s), 122.8 (s), 72.2 (s), 26.9 (s).

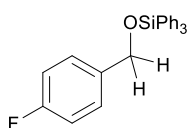


5.5k: Synthesised in accordance with *General Procedure 7* using 4-phenyl-2-butanone as starting material. Spectroscopic analyses agree with literature known values.^[197] Conversion: 99%. **¹H NMR**

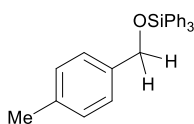
(400 MHz, CDCl₃, 298 K) δ /ppm: 7.67–7.64 (m, 6H, Ar-H), 7.46–7.36 (m, 9H, Ar-H), 7.26–7.14 (m, 3H, Ar-H), 7.04 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H, Ar-H), 4.04 (sext., $^3J_{\text{HH}} = 5.7$ Hz, 1H, CH), 2.73–2.51 (m, 2H, CH₂), 1.94–1.71 (m, 2H, CH₂), 1.22 (dd, $^3J_{\text{HH}} = 6.1$ Hz, $^4J_{\text{HH}} = 0.9$ Hz, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 142.5 (s), 135.6 (s), 135.1 (s), 130.0 (s), 128.5 (s), 128.4 (s), 127.9 (s), 125.7 (s), 69.6 (s), 41.3 (s), 31.9 (s), 23.7 (s).



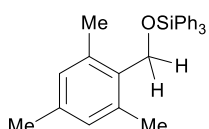
5.6a: Synthesised in accordance with *General Procedure 7* using benzaldehyde as starting material. Spectroscopic analyses agree with literature known values.^[198] Conversion: 98%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 7.66 (d, $^3J_{\text{HH}} = 7.4$ Hz, 6H, Ar-H), 7.46–7.32 (m, 14H, Ar-H), 4.91 (s, 2H, CH₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 140.7 (s), 135.6 (s), 134.1 (s), 130.2 (s), 128.4 (s), 128.1 (s), 127.2 (s), 126.5 (s), 65.7 (s).



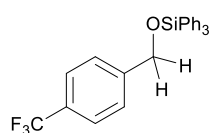
5.6b: Synthesised in accordance with *General Procedure 8* using 4-fluorobenzaldehyde as starting material. Conversion: 95%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 7.65 (d, $^3J_{\text{HH}} = 6.7$ Hz, 6H, Ar-H), 7.47–7.37 (m, 11H, Ar-H), 7.20 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H, Ar-H), 4.84 (s, 2H, CH₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 162.1 (d, $^1J_{\text{CF}} = 245$ Hz), 136.4 (d, $^3J_{\text{CF}} = 3.1$ Hz), 135.5 (s), 134.0 (s), 130.3 (s), 129.2 (s), 128.1 (s), 115.2 (d, $^2J_{\text{CF}} = 21.4$ Hz), 65.2 (s). **¹⁹F NMR** (376 MHz, CDCl₃, 298 K) δ /ppm: -115.8 (s, 1F, CF).



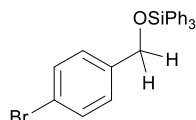
5.6c: Synthesised in accordance with *General Procedure 7* using 4-methylbenzaldehyde as starting material. Spectroscopic analyses agree with literature known values.^[199] Conversion: 94%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 7.60–7.58 (m, 6H, Ar-H), 7.33–7.31 (m, 9H, Ar-H), 7.16 (d, $^3J_{\text{HH}} = 8.0$ Hz, 2H, Ar-H), 7.05 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H, Ar-H), 4.79 (s, 2H, CH₂), 2.26 (s, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 135.9 (s), 135.6 (s), 134.2 (s), 130.2 (s), 129.0 (s), 128.2 (s), 128.0 (s), 126.6 (s), 65.6 (s), 21.3 (s).



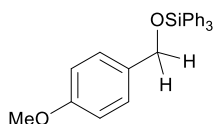
5.6d: Synthesised in accordance with *General Procedure 7* using mesitaldehyde as starting material. Conversion: 62%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 7.49 (d, $^3J_{\text{HH}} = 7.2$ Hz, 8H, Ar-H), 7.33–7.30 (m, 7H, Ar-H), 6.72 (s, 2H, Ar-H), 4.72 (s, 2H, CH₂), 2.16 (s, 3H, *p*-CH₃), 2.12 (s, 6H, *o*-CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 137.6 (s), 135.6 (s), 135.1 (s), 134.4 (s), 133.4 (s), 130.1 (s), 129.0 (s), 127.9 (s), 60.1 (s), 21.1 (s), 19.6 (s).



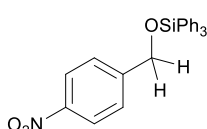
5.6e: Synthesised in accordance with *General Procedure 7* using 4-(trifluoromethyl)benzaldehyde as starting material. Conversion: 97%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.67 (d, ³J_{HH} = 8.4 Hz, 2H, Ar-H), 7.58 (d, ³J_{HH} = 8.1 Hz, 7.47–7.38 (m, 11H, Ar-H), 4.95 (s, 2H, CH₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 144.7 (s), 135.5 (s), 133.8 (s), 130.4 (s), 129.4 (d, ²J_{CF} = 32.3 Hz), 128.2 (s), 126.5 (s), 125.3 (q, ³J_{CF} = 3.8 Hz), 124.4 (d, ¹J_{CF} = 260 Hz), 65.1 (s). **¹⁹F NMR** (376 MHz, CDCl₃, 298 K) δ/ppm: -62.3 (s, 3F, CF₃).



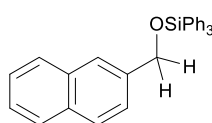
5.6f: Synthesised in accordance with *General Procedure 7* using 4-bromobenzaldehyde as starting material. Conversion: 77%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.66 (d, ³J_{HH} = 6.4 Hz, 6H, Ar-H), 7.45–7.38 (m, 10H, Ar-H), 7.21 (d, ³J_{HH} = 8.3 Hz, 2H, Ar-H), 4.84 (s, 2H, CH₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 139.9 (s), 135.5 (s), 133.9 (s), 132.6 (s), 131.4 (s), 130.3 (s), 128.2 (s), 128.1 (s), 65.1 (s).



5.6g: Synthesised in accordance with *General Procedure 7* using 4-methoxybenzaldehyde as starting material. Conversion: 58%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.67 (d, ³J_{HH} = 8.0 Hz, 6H, Ar-H), 7.41–7.38 (m, 9H, Ar-H), 7.25 (d, ³J_{HH} = 8.5 Hz, 2H, Ar-H), 6.86 (d, ³J_{HH} = 8.6 Hz, 2H, Ar-H), 4.85 (s, 2H, CH₂), 3.78 (s, 3H, OCH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 158.9 (s), 135.5 (s), 134.2 (s), 133.4 (s), 130.2 (s), 128.1 (s), 128.0 (s), 113.8 (s), 65.5 (s), 55.3 (s).



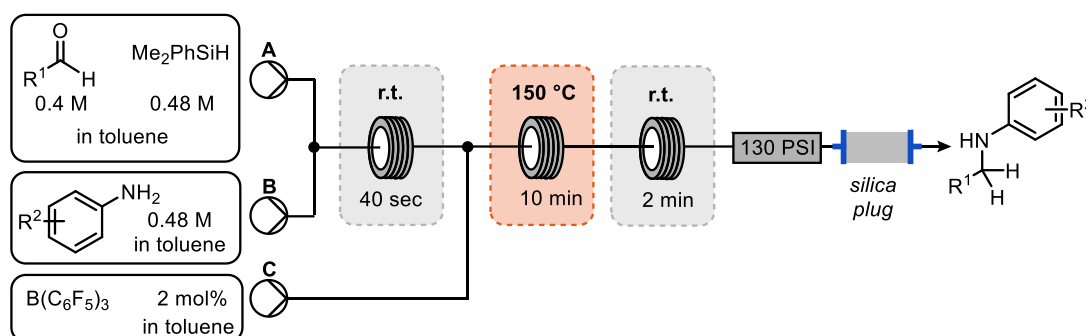
5.6h: Synthesised in accordance with *General Procedure 7* using 4-nitrobenzaldehyde as starting material. Spectroscopic analyses agree with literature values.^[200] Conversion: 95%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 8.18 (d, ³J_{HH} = 8.0 Hz, 2H, Ar-H), 7.66 (d, ³J_{HH} = 7.5 Hz, 6H, Ar-H), 7.51–7.46 (m, 5H, Ar-H), 7.43–7.39 (t, ³J_{HH} = 7.0 Hz, 6H, Ar-H), 4.99 (s, 2H, CH₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 148.2 (s), 147.2 (s), 135.5 (s), 133.4 (s), 130.5 (s), 128.2 (s), 126.7 (s), 123.7 (s), 64.8 (s).



5.6i: Synthesised in accordance with *General Procedure 7* using naphthaldehyde as starting material. Conversion: 97%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.65 (d, ³J_{HH} = 7.3 Hz, 7H, Ar-H), 7.47–7.37 (m, 11H, Ar-H), 7.28 (t, ³J_{HH} = 6.8 Hz, 2H, Ar-H), 6.99 (t, ³J_{HH} = 8.4 Hz, 2H, Ar-H), 4.86 (s, 2H, CH₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 136.3 (s), 136.0

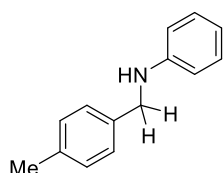
(s), 135.6 (s), 135.1 (s), 134.0 (s), 130.3 (s), 130.0 (s), 129.2 (s), 128.4 (s), 128.3 (s), 128.2 (s), 128.1 (s), 127.9 (s), 65.1 (s).

General Procedure 8: A solution of the aldehyde (0.4 M) and dimethylphenylsilane (0.48 M, 1.2 equiv.) in dry toluene was prepared. This solution was loaded into the sample loop of stream A (Scheme 6.5.2). A solution of the aniline (0.48 M, 1.2 equiv.) in dry toluene was loaded into the sample loop of stream B (Scheme 6.5.2) and a solution of $B(C_6F_5)_3$ (0.008 M, 2 mol%) in dry toluene was loaded into the sample loop of stream C (Scheme 6.5.2). The pumps were set to a flow rate of 0.17 ml min^{-1} and the temperature of the heated coil set to $150 \text{ }^\circ\text{C}$. Streams A and B were set to inject, followed by stream C after 41 s. After waiting for 7 ml (14 min) to be collected as waste (to allow the system to reach steady-state), the output was directed through a plug of silica (to remove the catalyst) and solution collected for 8 min (4 ml). The solvent was removed under reduced pressure and mesitylene ($74 \text{ } \mu\text{l}$, 0.064 g , 0.53 mmol) added as an internal standard. NMR yields were determined by comparing the $-\text{CH}_2$ benzylic peak to the mesitylene CH_3 peak at 2.5 ppm.

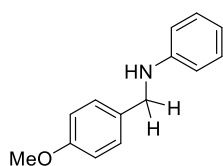


Scheme 6.5.2: General flow schematic for the multistep synthesis of secondary amines.

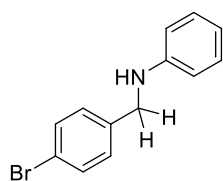
5.7a: Synthesised in accordance with *General Procedure 8* from benzaldehyde and aniline. Spectroscopic analyses agree with literature known values.^[201] Conversion: 69%. **$^1\text{H NMR}$** (400 MHz, CDCl_3 , 298 K) δ /ppm: 7.43 (m, 5H, Ar-H), 7.25 (t, $^3J_{\text{HH}} = 7.9 \text{ Hz}$, 2H, Ar-H), 6.80 (t, $^3J_{\text{HH}} = 7.3 \text{ Hz}$, 1H, Ar-H), 6.71 (d, $^3J_{\text{HH}} = 8.4 \text{ Hz}$, 2H, Ar-H), 4.40 (s, 2H, CH_2), 4.08 (br. s, 1H, NH). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3 , 298 K) δ /ppm: 148.3 (s), 139.5 (s), 129.4 (s), 128.7 (s), 127.6 (s), 127.3 (s), 117.6 (s), 112.9 (s), 48.4 (s). **HRMS** (EI^+) m/z calculated for $[\text{C}_{13}\text{H}_{13}\text{N}]^+ [\text{M}]^+$: 183.1048, found: 183.1043.



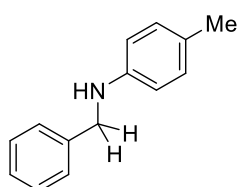
5.7b: Synthesised in accordance with *General Procedure 8* from *p*-tolaldehyde and aniline. Spectroscopic analyses agree with literature known values.^[201] Conversion: 66%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.42–7.35 (m, 6H, Ar-H), 6.94 (t, ³J_{HH} = 7.3 Hz, 1H, Ar-H), 6.83 (d, ³J_{HH} = 7.7 Hz, 2H, Ar-H), 4.45 (s, 2H, CH₂), 3.58 (br. s, 1H, NH), 2.56 (s, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 137.7 (s), 133.1 (s), 129.3 (s), 129.3 (s), 127.5 (s), 127.0 (s), 117.5 (s), 112.9 (s), 48.1 (s), 21.3 (s). **HRMS** (EI⁺) *m/z* calculated for [C₁₄H₁₅N]⁺ [M]⁺: 197.1204, found: 197.1204.



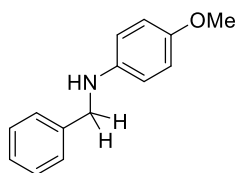
5.7c: Synthesised in accordance with *General Procedure 8* from *p*-anisaldehyde and aniline. Spectroscopic analyses agree with literature known values.^[201] Conversion: 78%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.45 (d, ³J_{HH} = 8.7 Hz, 2H, Ar-H), 7.36 (dd, ³J_{HH} = 8.5, ³J_{HH} = 7.4 Hz, 2H, Ar-H), 7.06 (d, ³J_{HH} = 8.6 Hz, 2H, Ar-H), 6.91 (t, ³J_{HH} = 7.3 Hz, 1H, Ar-H), 6.80 (d, ³J_{HH} = 7.6 Hz, 2H, Ar-H), 4.40 (s, 2H, CH₂), 3.95 (s, 3H, OCH₃), 3.59 (br. s, 1H, NH). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 159.0 (s), 148.3 (s), 129.4 (s), 128.9 (s), 127.0 (s), 117.7 (s), 114.2 (s), 113.0 (s), 55.4 (s), 48.0 (s). **HRMS** (EI⁺) *m/z* calculated for [C₁₄H₁₅NO]⁺ [M]⁺: 213.1154, found 213.1150.



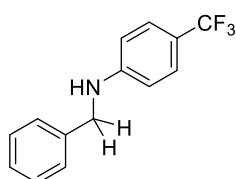
5.7d: Synthesised in accordance with *General Procedure 8* from 4-bromobenzaldehyde and aniline. Spectroscopic analyses agree with literature known values.^[201] Conversion: 89%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.53 (d, ³J_{HH} = 8.3 Hz, 2H, Ar-H), 7.32–7.24 (m, 4H, Ar-H), 6.82 (t, ³J_{HH} = 7.3 Hz, 1H, Ar-H), 6.68 (d, ³J_{HH} = 8.1 Hz, 2H, Ar-H), 4.35 (s, 2H, CH₂), 4.11 (s, 1H, NH). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 147.9 (s), 138.6 (s), 131.7 (s), 129.4 (s), 129.1 (s), 120.9 (s), 117.8 (s), 112.9 (s), 47.7 (s). **HRMS** (EI⁺) *m/z* calculated for [C₁₃H₁₂NBr]⁺ [M]⁺: 261.0153, found: 261.0150.



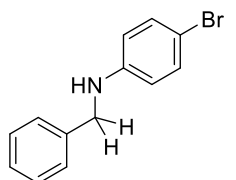
5.7e: Synthesised in accordance with *General Procedure 8* from benzaldehyde and *p*-toluidine. Spectroscopic analyses agree with literature known values.^[201] Conversion: 65%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.58–7.52 (m, 5H, Ar-H), 7.19 (d, ³J_{HH} = 8.4 Hz, 2H, Ar-H), 6.75 (d, ³J_{HH} = 8.4 Hz, 2H, Ar-H), 4.46 (s, 2H, CH₂), 3.53 (br. s, 1H, NH), 2.45 (s, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 145.9 (s), 137.7 (s), 129.8 (s), 128.6 (s), 127.6 (s), 127.0 (s), 113.2 (s), 48.7 (s), 21.3 (s). **HRMS** (EI⁺) *m/z* calculated for [C₁₄H₁₅N]⁺ [M]⁺: 197.1204, found: 197.1204.



5.7f: Synthesised in accordance with *General Procedure 8* from benzaldehyde and 4-methoxyaniline. Spectroscopic analyses agree with literature known values.^[201] Conversion: 45%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.53–7.38 (m, 5H, Ar-H), 6.93 (d, ³J_{HH} = 8.9 Hz, 2H, Ar-H), 6.74 (d, ³J_{HH} = 8.9 Hz, 2H, Ar-H), 4.40 (s, 2H, CH₂), 3.87 (s, 3H, OCH₃), 3.41 (br. s, 1H, NH). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 152.3 (s), 142.4 (s), 139.7 (s), 128.6 (s), 127.9 (s), 127.6 (s), 115.0 (s), 114.3 (s), 55.8 (s), 49.3 (s). **HRMS** (EI⁺) *m/z* calculated for [C₁₄H₁₅NO]⁺ [M]⁺: 213.1154, found: 213.1155.



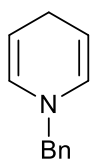
5.7g: Synthesised in accordance with *General Procedure 8* from benzaldehyde and 4-(trifluoromethyl)aniline. Spectroscopic analyses agree with literature known values.^[202] Conversion: 34%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.57–7.48 (m, 7H, Ar-H), 6.76 (d, ³J_{HH} = 7.9 Hz, 2H, Ar-H), 4.46 (s, 2H, CH₂), 3.97 (br. s, 1H, NH). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 150.6 (s), 137.8 (s), 128.9 (s), 127.4 (s), 127.0 (s), 126.7 (q, ³J_{CF} = 3.8 Hz), 119.0 (q, ²J_{CF} = 34 Hz), 112.1 (s), 65.1 (s), 47.8 (s). **¹⁹F NMR** (376 MHz, CDCl₃, 298 K) δ/ppm: -60.7 (s). **HRMS** (EI⁺) *m/z* calculated for [C₁₄H₁₂NF₃]⁺ [M]⁺: 251.0922, found: 251.0920.



5.7h: Synthesised in accordance with *General Procedure 8* from benzaldehyde and 4-bromoaniline. Spectroscopic analyses agree with literature known values.^[203] Conversion: 77%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.58–7.49 (m, 7H, Ar-H), 6.61 (d, ³J_{HH} = 8.8 Hz, 2H, Ar-H), 4.40 (s, 2H, CH₂), 3.59 (br. s, 1H, NH). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 147.1 (s), 137.7 (s), 131.9 (s), 128.7 (s), 127.9 (s), 127.4 (s), 116.8 (s), 114.5 (s), 48.2 (s). **HRMS** (EI⁺) *m/z* calculated for [C₁₃H₁₂NBr]⁺ [M]⁺: 261.0153, found: 261.0142.

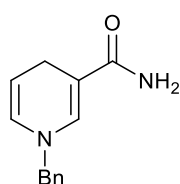
6.5.3 Biologically Inspired Borohydride Sources and Subsequent Transfer Hydrogenation Reactions

6.5.3.1 Synthesis of Starting Materials



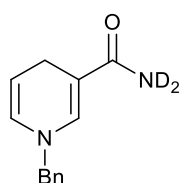
5.8a: Synthesised in accordance with previously outlined procedures.^[204] Pyridine (2.0 ml, 25.3 mmol) was dissolved in acetonitrile (30 ml), then benzyl bromide (3.0 ml, 25.3 mmol) was added. The reaction mixture was stirred under reflux at 80 °C for 12 h. The solution was then cooled and diethyl ether (50 ml) was added to precipitate the crude product. After filtering off the

supernatant and washing the solid with diethyl ether (3 x 10 ml), the bromide salt was obtained as a yellow solid (1.9 g, 7.6 mmol, 30%). A suspension of water (70 ml) and toluene (50 ml) containing sodium dithionite (10.0 g, 60.0 mmol) and sodium carbonate (8.0 g, 70.0 mmol) was stirred vigorously under a nitrogen atmosphere and was heated to 100 °C. 1-Benzyl pyridinium bromide (2.5 g, 10.0 mmol) dissolved in water (100 ml) was then added in small portions over a period of 10 mins. After reflux for 10 minutes, the organic solution was separated and was washed with saturated sodium bicarbonate solution (3 x 10 ml), followed by water (3 x 10 ml) with the organic layer being dried with Na₂SO₄. The solvent was removed under reduced pressure to yield the product as a yellow/red oil. Analytical data agrees with previously reported values.^[204] Yield: 0.63 g, 3.7 mmol, 37%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.33–7.23 (m, 5H, Ar-H), 5.73 (d, ³J_{HH} = 7.9 Hz, 2H, NCH), 4.36–4.33 (m, 2H, =CH), 4.08 (s, 2H, N-CH₂), 2.95 (br. s, 2H, CH₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ/ppm: 139.0 (s), 131.6 (s), 128.7 (s), 127.3 (s), 127.3 (s), 97.9 (s), 56.9 (s), 22.6 (s).

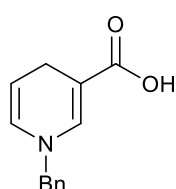


5.8b: Synthesised in accordance with previously outlined procedures.^[205] To a solution of nicotinamide (4.9 g, 40.0 mmol) in a mixture of 1,4-dioxane (100 ml) and methanol (25 ml), benzyl bromide (4.8 ml, 40.0 mmol) was added. The reaction mixture was stirred under reflux at 80 °C for 4 h. The solution was then cooled and 1,4-dioxane (50 ml) was added to precipitate the crude product. After filtering off the supernatant and washing the solid with 1,4-dioxane (3 x 10 ml), the bromide salt was obtained as a white solid (7.5 g, 25.7 mmol, 64%). 1-benzyl-3-carbamoyl pyridinium bromide (0.40 g, 1.4 mmol) was dissolved in water (15 ml) and sodium bicarbonate (0.78 g, 9.4 mmol) was added. Under a nitrogen atmosphere, sodium dithionite (1.63 g, 9.4 mmol) was added in small portions over a period of 10 mins. The reaction mixture was stirred at room temperature for 3 h in the dark, during which time the solution turned from orange to yellow as the yellow product precipitated. The solid was filtered, washed with cold water (2 x 10 ml) and then dissolved in chloroform (20 ml). The organic phase was extracted with water (2 x 10 ml) and was subsequently dried over Na₂SO₄ and evaporated under vacuum to obtain a bright yellow powder. Analytical data agrees with previously reported values.^[205] Yield: 0.21 g, 1.0 mmol, 70%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ/ppm: 7.35 (t, ³J_{HH} = 7.2 Hz, 2H, Ar-H), 7.29 (d, ³J_{HH} = 7.2 Hz, 1H, Ar-H), 7.24 (d, ³J_{HH} = 7.0 Hz, 2H, Ar-H), 7.15 (s, 1H, NCH), 5.73 (dq, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.6 Hz, 1H, NCH), 5.66 (br. s, 2H, NH₂), 4.74 (dt, ³J_{HH} = 3.5 Hz, ⁴J_{HH} = 8.0 Hz, 1H, =CH), 4.28 (s, 2H, N-CH₂), 3.16 (br. s, 2H, CH₂). **¹³C NMR** (101 MHz,

CDCl₃, 298 K) δ /ppm: 170.5 (s), 139.9 (s), 137.4 (s), 129.0 (s), 128.9 (s), 127.8 (s), 127.2 (s), 103.3 (s), 98.9 (s), 57.4 (s), 22.9 (s).

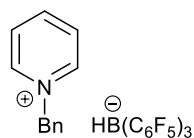


5.8c: A small portion of compound **5.8b** was dissolved twice in methanol-d₄, which was removed under reduced pressure, to yield a bright yellow powder. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 7.36–7.28 (m, 3H, Ar-H), 7.23–7.21 (m, 2H, Ar-H), 7.12 (d, ⁴J_{HH} = 1.4 Hz, 1H, NCH), 5.71 (dq, ³J_{HH} = 8.2 Hz, ⁴J_{HH} = 1.6 Hz, 1H, NCH), 4.72 (dt, ³J_{HH} = 7.9 Hz, ³J_{HH} = 3.4 Hz, =CH), 4.25 (s, 2H, N-CH₂), 3.13 (q, ³J_{HH} = 3.0 Hz, ⁴J_{HH} = 1.4 Hz, 2H, CH₂).

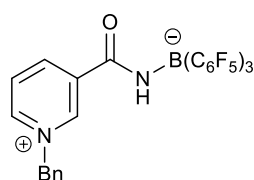


5.8d: Synthesised in accordance with previously outlined procedures.^[205] Nicotinic acid (2.46 g, 20 mmol) was dissolved in a minimal amount of ethanol and diluted with acetonitrile (40 ml). Benzyl bromide (2.4 ml, 20 mmol) was then added and stirred under reflux at 80 °C for 12 h. The solution was cooled and diethyl ether (50 ml) was added to precipitate the crude product. After filtering off the supernatant and washing the solid with diethyl ether (3 x 10 ml), the bromide salt was obtained as a white powder (3.5 g, 11.9 mmol, 60%). A suspension of 1-benzyl-3-carboxypyridinium bromide (2.9 g, 10 mmol) in water (200 ml) and dichloromethane (100 ml) was cooled to 0 °C and stirred under a nitrogen atmosphere. Sodium carbonate (6.4 g, 60 mmol) was added in small portions over a period of 10 minutes. Sodium dithionite (7 g, 40 mmol) was then added slowly over a period of 15 minutes. Stirring was continued over a period of 1 h under a nitrogen stream at 0 °C. The organic layer was washed with water (3 x 100 ml), dried over Na₂SO₄ and the volatiles evaporated under vacuum to afford the yellow product. Analytical data agrees with previously reported values.^[205] Yield: 0.55 g, 2.6 mmol, 26%. **¹H NMR** (400 MHz, CDCl₃, 298 K) δ /ppm: 7.36–7.30 (m, 3H, Ar-H), 7.25–7.23 (m, 3H, Ar-H), 7.22 (d, ³J_{HH} = 1.4 Hz, 1H, NCH), 5.68 (dq, ³J_{HH} = 8.1 Hz, ⁴J_{HH} = 1.7 Hz, 1H, NCH), 4.82 (dt, ³J_{HH} = 8.1 Hz, ⁴J_{HH} = 3.5 Hz, 1H, =CH), 4.29 (s, 2H, N-CH₂), 3.12 (d, ³J_{HH} = 3.2 Hz, 2H, CH₂). **¹³C NMR** (101 MHz, CDCl₃, 298 K) δ /ppm: 173.6 (s), 143.6 (s), 137.1 (s), 129.0 (s), 128.2 (s), 128.0 (s), 127.3 (s), 106.1 (s), 96.7 (s), 57.6 (s), 21.9 (s).

6.5.3.2 Synthesis of Products

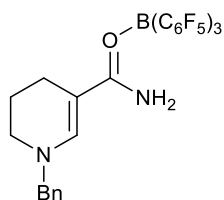


5.9: Compound **5.8a** (17 mg, 0.1 mmol, 1 equiv.) was dissolved in CDCl_3 (0.5 ml) to give a dark red solution to which $\text{B}(\text{C}_6\text{F}_5)_3$ (51 mg, 0.1 mmol, 1 equiv.) was added. This was transferred to an NMR tube to monitor reaction progress. After 30 minutes the reaction showed almost complete conversion to the hydridoborate product **5.9** as observed by *in situ* NMR spectroscopy, at this point removal of solvents *in vacuo* gave a dark red viscous oil. Yield: 63 mg, 92 μmol , 91%. **^1H NMR** (400 MHz, CDCl_3 , 298 K) δ/ppm : 8.64 (t, $^3J_{\text{HH}} = 5.8$ Hz, 2H, *o*-H), 8.43 (t, $^3J_{\text{HH}} = 7.8$ Hz, 1H, *p*-H), 7.97 (t, $^3J_{\text{HH}} = 7.1$ Hz, 2H, *m*-H), 7.46–7.39 (m, 3H, Ar-H), 7.27 (d, $^3J_{\text{HH}} = 7.1$ Hz, 2H, Ar-H), 5.67 (s, 2H, N- CH_2). Note: B-H not observed. **^{13}C NMR** (101 MHz, CDCl_3 , 298 K) δ/ppm : 148.2 (dm, $^1J_{\text{CF}} = 240$ Hz), 146.2 (s), 143.7 (s), 136.7 (dm, $^1J_{\text{CF}} = 250$ Hz), 131.2 (s), 130.4 (s), 130.3 (s), 129.2 (s), 128.9 (s), 66.0 (s). **^{11}B NMR** (128 MHz, CDCl_3 , 298 K) δ/ppm : -25.3 (d, $^1J_{\text{BH}} = 66$ Hz). **^{19}F NMR** (376 MHz, CDCl_3 , 298 K) δ/ppm : -133.82 (br. s, 6F, *o*-F), -162.92 (br. s, 3F, *p*-F), -166.34 (br. s, 6F, *m*-F). **IR** ν_{max} (cm^{-1}): 3091 (w), 2378 (w), 2156 (w), 1641 (m), 1570 (w), 1508 (s), 1487 (w), 1451 (s), 1373 (w), 1273 (m), 1213 (w), 1089 (s), 1028 (w), 974 (s), 910 (m), 787 (w), 760 (m), 743 (m), 700 (m), 679 (m), 617 (w), 601 (w), 567 (w). **HRMS** (ES^-) m/z calculated for $[\text{M}]^- [\text{C}_{18}\text{F}_{15}\text{BH}]^-$: 511.9968, found 511.9984, (ES^+) $[\text{M}]^+ [\text{C}_{12}\text{H}_{12}\text{N}_1]^+$ m/z calculated: 170.0970, found: 170.0963.



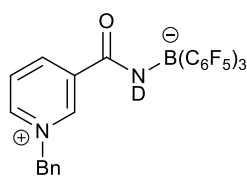
5.10: Compound **5.8b** (42 mg, 0.2 mmol, 1 equiv.) was dissolved in CDCl_3 (0.5 ml) to which $\text{B}(\text{C}_6\text{F}_5)_3$ (102 mg, 0.2 mmol, 1 equiv.) was added, yielding an orange solution. This was transferred to a J-Youngs NMR tube and heated for 12 h at 70 $^\circ\text{C}$. A white crystalline solid precipitated out of solution which was isolated and measured by X-ray diffractometry. The mother liquor was retained for isolation of **5.11** (see below). The remaining solid was washed with cold CH_2Cl_2 (2 x 2 ml) and dried *in vacuo* to garner a white powdery solid. Yield: 63 mg, 87.0 μmol , 44%. Melting point: 124–130 $^\circ\text{C}$. **^1H NMR** (500 MHz, DMSO-d_6 , 298 K) δ/ppm : 9.48 (s, 1H, Ar-H), 9.15 (d, $^3J_{\text{HH}} = 4.9$ Hz, 1H, Ar-H), 8.98 (d, $^3J_{\text{HH}} = 7.5$ Hz, 1H, Ar-H), 8.19 (t, $^3J_{\text{HH}} = 6.5$ Hz, 1H, Ar-H), 7.71 (s, 1H, Ar-H), 7.54 (d, $^3J_{\text{HH}} = 5.3$ Hz, 2H, Ar-H), 7.43 (d, $^3J_{\text{HH}} = 6.1$ Hz, 3H, Ar-H), 5.85 (s, 2H, CH_2), 5.74 (s, 1H, NH). **^{13}C NMR** (126 MHz, DMSO-d_6 , 298 K) δ/ppm : -162.9 (s), 147.8 (dm, $^1J_{\text{CF}} = 240$ Hz), 145.2 (s), 144.5 (s), 143.4 (s), 137.6 (dm, $^1J_{\text{CF}} = 240$ Hz), 136.9 (s), 135.6 (dm, $^1J_{\text{CF}} = 240$ Hz), 134.1 (s), 129.4 (s), 129.3 (s), 129.0 (s), 127.9 (s), 63.4 (s), 54.9 (s). **^{11}B NMR** (160 MHz, DMSO-d_6 , 298 K) δ/ppm : -11.5 (s). **^{19}F NMR** (471 MHz, DMSO-d_6 , 298 K) δ/ppm : -133.31 (d, $^3J_{\text{FF}} = 22.4$

Hz, 6F, *o*-F), -161.93 (d, $^3J_{FF} = 21.4$ Hz, 3F, *p*-F), -166.23 (t, $^3J_{FF} = 20.8$ Hz, 6F, *m*-F). **IR** ν_{\max} (cm⁻¹): 3454 (w), 3071 (w), 1665 (m), 1645 (m), 1625 (w), 1512 (m), 1487 (m), 1458 (s), 1379 (w), 1277 (m), 1180 (w), 1082 (s), 1030 (w), 974 (s), 947 (s), 887 (w), 813 (w), 771 (m), 758 (m), 739 (m), 704 (m), 675 (m), 623 (w), 574 (m), 548 (w). **HRMS** (ES⁻) m/z calculated for [M-H]⁻ [C₃₁H₁₁N₂OBF₁₅]⁻: 722.0761, found: 722.0769.



5.11: The mother liquor from the formation of **5.10** was retained with the solvents being subsequently removed under reduced pressure. The yellow/green solid was then washed with cold pentane (2 x 2 ml) and dried *in vacuo* to yield a yellow/green powdery solid. Yield: 61 mg, 83.4 μ mol, 42%. Melting point: 101–

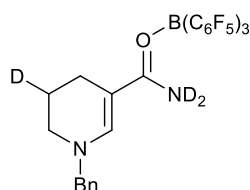
110 °C. **¹H NMR** (500 MHz, CDCl₃, 298 K) δ /ppm: 7.92 (s, 1H, C=CH), 7.39–7.33 (m, 3H, Ar-H), 7.20 (d, $^3J_{HH} = 7.2$ Hz, 2H, Ar-H), 5.52 (br. s, 2H, NH₂), 4.42 (s, 2H, CH₂), 3.15 (t, $^3J_{HH} = 4.9$ Hz, 2H, CH₂), 2.11 (t, $^3J_{HH} = 5.7$ Hz, 2H, CH₂), 1.91 (br. pent., $^3J_{HH} \approx 5$ Hz, 2H, CH₂). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ /ppm: 169.6 (s), 151.5 (s), 147.9 (dm, $^1J_{CF} = 245$ Hz), 139.9 (dm, $^1J_{CF} = 245$ Hz), 137.0 (dm, $^1J_{CF} = 245$ Hz), 134.5 (s), 129.3 (s), 129.2 (s), 128.8 (s), 128.4 (s), 128.0 (s), 125.5 (s), 90.5 (s), 61.3 (s), 45.7 (s), 20.5 (s), 18.9 (s). **¹¹B NMR** (160 MHz, CDCl₃, 298 K) δ /ppm: -2.8 (br. s). **¹⁹F NMR** (471 MHz, CDCl₃, 298 K) δ /ppm: -133.92 (d, $^3J_{FF} = 21.0$ Hz, 6F, *o*-F), -158.14 (t, $^3J_{FF} = 20.2$ Hz, 3F, *p*-F), -163.93 (t, $^3J_{FF} = 19.0$ Hz, 6F, *m*-F). **IR** ν_{\max} (cm⁻¹): 3524 (w), 3420 (w), 1643 (m), 1618 (m), 1558 (w), 1510 (s), 1458 (s), 1418 (m), 1354 (m), 1319 (w), 1279 (m), 1211 (m), 1089 (s), 1028 (w), 976 (s), 877 (m), 806 (m), 773 (m), 764 (m), 750 (m), 734 (m), 696 (m), 675 (m), 625 (w), 609 (w), 574 (w), 556 (w). **HRMS** (ES⁺) m/z calculated for [M+H(-B(C₆F₅)₃)]⁺ [C₁₃H₁₇N₂O]⁺: 217.1341, found: 217.1339.



5.12: Compound **5.8c** (44 mg, 0.2 mmol, 1 equiv.) was dissolved in CDCl₃ (0.5 ml) to which B(C₆F₅)₃ (102 mg, 0.2 mmol, 1 equiv.) was added, yielding an orange solution. This was transferred to a J-Youngs NMR tube and heated for 12 h at 70 °C. A white

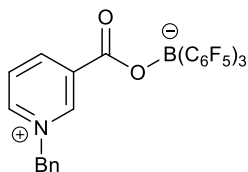
crystalline solid precipitated out of solution which was isolated and washed with cold pentane (2 x 2 ml) and dried *in vacuo* to garner **5.12** as a white powdery solid. The mother liquor was retained for isolation of **5.13** (see below). Yield: 58 mg, 80.0 μ mol, 40%. Melting point: 119–125 °C. **¹H NMR** (500 MHz, DMSO-d₆, 298 K) δ /ppm: 9.47 (br. s, 1H, NCH), 9.15 (s, 1H, NCH), 8.96 (br. s, 1H, =CH), 8.19 (t, $^3J_{HH} = 6.8$ Hz, 1H, =CH), 7.53 (d, $^3J_{HH} = 6.7$ Hz, 2H, Ar-H), 7.43 (d, $^3J_{HH} = 6.2$ Hz, 3H, Ar-H), 5.85 (s, 2H, N-CH₂). **¹³C NMR** (126 MHz, DMSO-d₆, 298 K) δ /ppm: 162.8 (s), 147.8 (dm, $^1J_{CF} =$

240 Hz), 145.2 (s), 144.5 (s), 143.4 (s), 137.5 (dm, $^1J_{CF} = 240$ Hz), 136.9, 135.5 (dm, $^1J_{CF} = 250$ Hz), 134.0 (s), 129.4 (s), 129.3 (s), 128.9 (s), 127.9 (s), 63.4 (s). **^{11}B NMR** (160 MHz, DMSO- d_6 , 298 K) δ /ppm: -11.5 (s). **^{19}F NMR** (471 MHz, DMSO- d_6 , 298 K) δ /ppm: -133.31 (d, $^3J_{CF} = 22.9$ Hz, 6F, *p*-F), -161.9 (t, $^3J_{CF} = 21.4$ Hz, 3F, *p*-F), -166.3 (t, $^3J_{CF} = 20.8$ Hz, 6F, *m*-F). **IR** ν_{max} (cm^{-1}): 3464 (w), 2359 (w), 2164 (w), 1665 (m), 1624 (w), 1514 (m), 1487 (m), 1451 (s), 1379 (m), 1279 (m), 1199 (w), 1178 (w), 1082 (s), 976 (s), 962 (s), 947 (s), 908 (s), 883 (w), 825 (w), 771 (m), 764 (s), 704 (m), 657 (m).



5.13: The mother liquor from the formation of **5.12** was retained with the solvents being subsequently removed under reduced pressure. The orange solid was then washed with cold pentane (2 x 2 ml) and dried *in vacuo* to yield an orange powdery solid.

Yield: 56 mg, 76.6 μmol , 38%. Melting point: 112–116 $^{\circ}\text{C}$. **^1H NMR** (500 MHz, CDCl_3 , 298 K) δ /ppm: 7.91 (s, 1H, =CH), 7.40–7.34 (m, 3H, Ar-H), 7.20 (d, $^3J_{\text{HH}} = 7.0$ Hz, 2H, Ar-H), 4.42 (s, 2H, N- CH_2), 3.14 (d, $^3J_{\text{HH}} = 5.4$ Hz, 2H, CH_2), 2.10 (d, $^3J_{\text{HH}} = 6.1$ Hz, 2H, CH_2), 1.91 (pent., $^3J_{\text{HH}} = 6.1$ Hz, 1H, CHD). **^{13}C NMR** (126 MHz, CDCl_3 , 298 K) δ /ppm: 169.5 (s), 151.5 (s), 147.9 (dm, $^1J_{CF} = 240$ Hz), 139.8 (dm, $^1J_{CF} = 250$ Hz), 137.1 (dm, $^1J_{CF} = 255$ Hz), 134.5 (s), 130.4 (s), 129.3 (s), 128.8 (s), 128.0 (s), 61.3 (s), 45.7 (s), 22.5 (s), 20.5 (s). **^{11}B NMR** (160 MHz, CDCl_3 , 298 K) δ /ppm: -2.78 (br. s). **^{19}F NMR** (471 MHz, CDCl_3 , 298 K) δ /ppm: -133.93 (d, $^3J_{\text{FF}} = 22.1$ Hz, 6F, *o*-F), -158.14 (t, $^3J_{\text{FF}} = 20.4$ Hz, 3F, *p*-F), -163.92 (t, $^3J_{\text{FF}} = 18.7$ Hz, 6F, *m*-F). **IR** ν_{max} (cm^{-1}): 3082 (w), 2160 (w), 2035 (w), 1687 (s), 1647 (m), 1516 (m), 1425 (s), 1386 (m), 1342 (m), 1275 (m), 1198 (w), 1182 (m), 1083 (s), 1033 (w), 975 (s), 934 (m), 906 (m), 881 (m), 812 (m), 773 (m), 758 (s), 724 (s), 706 (s), 677 (s), 665 (s), 650 (m).



5.14: Compound **5.8d** (44 mg, 0.1 mmol, 1 equiv.) was dissolved in CDCl_3 (0.5 ml) to which $\text{B}(\text{C}_6\text{F}_5)_3$ (102 mg, 0.1 mmol, 1 equiv.) was added, yielding an orange solution. This was transferred to a J-Youngs NMR tube and heated for 12 h at 70 $^{\circ}\text{C}$. An orange precipitate formed which was separated

from the supernatant and washed with pentane (2 x 2 ml) then dried *in vacuo* to garner a light orange powdery solid. Yield: 52 mg, 71.7 μmol , 36%. Melting point: 137–144 $^{\circ}\text{C}$. **^1H NMR** (500 MHz, DMSO- d_6 , 298 K) δ /ppm: 9.5 (s, 1H, NCH), 9.31 (d, $^3J_{\text{HH}} = 5.9$ Hz, 1H, NCH), 8.89 (d, $^3J_{\text{HH}} = 7.9$ Hz, 1H, =CH), 8.27 (t, $^3J_{\text{HH}} = 7.0$ Hz, 1H, =CH), 7.55 (br. s, 2H, Ar-H), 7.41 (br. s, 3H, Ar-H), 5.92 (s, 2H, N- CH_2). **^{13}C NMR** (126 MHz, DMSO- d_6 , 298 K) δ /ppm: 147.1 (dm, $^1J_{CF} = 245$ Hz), 146.8 (s), 145.3 (s), 144.9 (s),

117.4 (dm, $^1J_{CF} = 250$ Hz), 135.7 (dm, $^1J_{CF} = 245$ Hz), 133.6 (s), 133.4 (s), 129.4 (s), 129.0 (s), 128.6 (s), 63.5 (s). **^{11}B NMR** (160 MHz, DMSO- d_6 , 298 K) δ /ppm: -4.1 (br. s). **^{19}F NMR** (471 MHz, DMSO- d_6 , 298 K) δ /ppm: -134.10 (d, $^3J_{FF} = 22.0$ Hz, 6F, *o*-F), -160.65 (t, $^3J_{FF} = 21.2$ Hz, 3F, *p*-F), -165.57 (t, $^3J_{FF} = 20.2$ Hz, 6F, *m*-F). **IR** ν_{max} (cm^{-1}): 2978 (w), 2872 (w), 1645 (w), 1514 (m), 1456 (s), 1275 (m), 1182 (m), 1082 (s), 976 (s), 906 (m), 808 (m), 772 (w), 758 (w), 731 (m), 706 (m), 675 (m), 623 (m).

6.5.4 Computational Studies

All geometry optimisations were undertaken using the B3LYP functional^[152a] and 6-31G* basis set^[154] within Gaussian09.^[178] Subsequent single point calculations were undertaken using the B3LYP functional and larger 6-311G*+ basis set.

6.5.5 Crystallographic Studies

Crystallographic studies were undertaken on single crystal mounted in paratone and studied on an Agilent SuperNova Dual three-circle diffractometer using Cu-K α or Mo-K α radiation and a CCD detector. Measurements were typically made at 150(2) K with temperatures maintained using an Oxford cryostream. Data were collected and integrated and data corrected for absorption using a numerical absorption correction based on gaussian integration over a multifaceted crystal model within CrysAlisPro.^[156] The structures were solved by direct methods and refined against F^2 within SHELXL-2013.^[170] The structures have been deposited with the Cambridge Structural Database (CCDC deposition numbers 1556722–1556723, 1532113).

Table 6.5.1 Crystallographic data for compounds **5.2k**, **5.2p** and **5.10**.

Compound	5.2k	5.2p	5.10
Empirical Formula	C ₁₂ H ₂₅ BO ₂ Si	C ₂₁ H ₂₅ BCl ₂ O ₂	C ₃₁ H ₁₂ BF ₁₅ N ₂ O, CHCl ₃
Crystal System	Monoclinic	Monoclinic	Triclinic
Space Group	<i>P21/n</i>	<i>P21/n</i>	<i>P-1</i>
<i>a</i> /Å	6.5494(4)	18.5123(8)	12.5821(9)
<i>b</i> /Å	21.5345(13)	6.02084(19)	12.6326(8)
<i>c</i> /Å	10.8938(7)	19.3786(9)	12.9076(8)
α /°	90	90	88.937(5)
β /°	94.458(6)	107.955(5)	79.854(5)
γ /°	90	90	66.759(6)
<i>V</i> /Å ³	1531.81(17)	2054.75(15)	1852.7(2)
<i>Z</i>	4	4	2
<i>T</i> /K	150(2)	150(2)	150(2)
<i>D_c</i> /g.cm ⁻³	1.042	1.264	1.512
Crystal size/mm	0.236 x 0.182 x 0.095	0.488 x 0.102 x 0.090	0.289 x 0.187 x 0.122
Total data	5536	7867	12937
Unique data	2883	4058	7276
R _{int}	0.0446	0.0460	0.0463
R ₁ [<i>F</i> ² > 2 σ(<i>F</i> ²)]	0.0685	0.0688	0.0478
wR2 (all data)	0.2004	0.1984	0.1409
GoF	1.044	1.050	1.026
ρ_{\min}/ρ_{\max} /eÅ ⁻³	-0.391/0.614	-0.926/0.852	-0.778/0.449
CCDC code	1556722	1556723	1532113

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