Novel main group Lewis acids for synthetic and catalytic transformations

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A thesis submitted to Cardiff University in candidature for the degree of Doctor of Philosophy

Department of Chemistry, Cardiff University

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I Acknowledgements

I am very grateful to my supervisor Dr Rebecca Melen for the opportunity to work in her group and for her continued advice and guidance over the past three years. Thanks, must also be given to all the members of the Melen group. To Dr James Lawson as well as Dr Adam Ruddy for helping me to overcome scientific challenges. Also, Jamie Carden must be thanked here for his support in correcting the thesis, as well as all the other current and former members of the Melen group for many happy memories. I would also like to extend my gratitude to Prof. Oestreich for hosting my research stay in Berlin at the TU Berlin. My gratitude is also due to all the professional services staff at Cardiff University; especially Dr Rob Jenkins, Simon Waller, Tom Williams, Evelyn Blake and Jamie Cross. I am also especially grateful to the following people for their collaborative assistance throughout this thesis: Prof Simon Pope, Dr Paul Newman, Jenny Börger, Vladimir Y. Vladimirov, Dale Lyons and Theo A. Gazis. I am specifically appreciative to Dr Lewis C. Wilkins for his assistance in the reactions of alkynyl acids and esters with tris(pentafluorophenyl)borane. Here he did the cyclisation reactions in Scheme 58 and the reactions to give compound **5.16a** and **5.16b** in Scheme 64. He also conducted the catalytic reactions to give **5.17a**, **b**, **f** & **g** in Scheme 65. In Chapter 7 he did the haloboration reaction to give **7.2c** in Scheme 97 and the carboboration reaction to give **7.3c** in Scheme 98. He also collected X-ray data and solved/refined crystal structures of compounds **1h** and **1i** in Figure 2, **1l** in Figure 3, **4.4a** in Figure 10, **5.4c** & **5.16a** in Figure 22, **7.2d** in Figure 31 and **7.3a** in Figure 32. I am also appreciative to Dr Sam J. Adams for the photophysical studies of imine borane adducts in Chapter 4, Dr Emma Richards for the electron paramagnetic resonance spectroscopic measurements in Chapter 6, Prof Qin Yin for guidance in the hydroboration reactions in Chapter 3 and Darren M. C. Ould for solving crystal structures of compound **1n** in Figure 3, **6.2a** in Figure 24 and **6.2b** in Scheme 77.

On a personal note, I am indebted to my family for their unfailing support, to my sister for never failing to cheer me up, and my mother and my father for their continuous believe in me. I want to thank my friends for understanding that a lack of time in some instances does not mean a loss of interest.

II Abstract

The work described herein is concerned with Lewis acidic triarylboranes for synthetic and catalytic transformations where the influence of different substitution pattern and substituents were crucial in determining the resulting reactivity. Chapter 1 will provide a general introduction into acidity and will lay the theoretical foundation for the ensuing chapters. Chapter 2 introduces the boranes utilised in this work and will give literature examples describing reactivities of the currently known boranes. Besides providing several crystal structures, this chapter will discuss the Lewis acidity of these boranes. Chapter 3 explores the hydroboration of imines catalysed by tris[3,5-bis(trifluoromethyl)-phenyl]borane. By testing a variety of various Lewis acids further insight into the mechanism of this hydroboration is gained. Chapter 4 further investigates borane imine adducts and the impact of the adduct formation on the electronic transitions within the imines. The photoactive adducts are then explored as vapochromic materials towards various solvent vapours. Chapter 5 focuses on the formation of pyrones, dihydropyrones and isocoumarins catalysed by tris(pentafluorophenyl)borane. A cross over experiment reveals the nature of this cyclisation reaction. Chapter 6 investigates the radical character of a frustrated Lewis pairs and their resulting reactivity. A novel protocol for a radical Heck-type reaction is provided and the mechanism was investigated. Finally, Chapter 7 will show the ambiguity between 1,1-carboboration and 1,3-haloboration in the reaction of propargyl esters with dichlorophenylborane.

Contents

III List of publications

1) *Divergent Reactivity of FLPs with Diaryl Esters: Carbocation Capture or C-C Coupling by SET,* Y. Soltani, T. A. Gazis, D. M. C. Ould, E. Richards, L. C. Wilkins, V. Y. Vladimirov, R. L. Melen, *manuscript in preparation* (Chapter 6).

2) *Synthesis and photophysical properties of imine borane adducts towards vapochromic materials,* Y. Soltani, S. J. Adams, J. Börger, L. C. Wilkins, P. D. Newman, S. J. A. Pope, R. L. Melen, **Dalton Trans.** (2018), 47, 12656-12660 **DOI:** 10.1039/C8DT03019G (Chapter 4).

3) *Divergent Elementoboration: 1,3-Haloboration versus 1,1-Carboboration of Propargyl Esters*, L. C. Wilkins†, Y. Soltani†, J. Lawson, B. Slater, R. L. Melen, **Chem. Eur. J.** (2018), 24, 7364-7368*,* **DOI:** 10.1002/chem.201801493 (Chapter 7). † Equal contribution.

4) *A Comparative Assessment of Modern Cyclization Methods of Substituted Alkynyl Esters, Ethers, and Acids,* Y. Soltani, L.C. Wilkins, R.L. Melen, **Synlett** (2018), 29(1), 1-7; **DOI:** 10.1055/s-0036-1591862 (Chapter 5).

5) *Stoichiometric and Catalytic C-C and C-H Bond Formation with $B(C_6F_5)_3$ via Cationic Intermediates,* Y. Soltani, L.C. Wilkins, R.L. Melen, **Angew. Chem. Int. Ed.** (2017), 56(39), 11995-11999; **DOI:** 10.1002/anie.201704789, **Angew. Chem.** 2017, 129(39), 12157-12161, **DOI:** 10.1002/ange.201704789 (Chapter 5).

6) *$BArF_3$-Catalyzed Imine Hydroboration with Pinacolborane Not Requiring the Assistance of an Additional Lewis Base,* Q. Yin†, Y. Soltani†, R.L. Melen, M. Oestreich, **Organometallics** (2017), 36(13), 2381-2384; **DOI:** 10.1021/acs.organomet.7b00381 (Chapter 3). † Equal contribution.

IV List of abbreviations

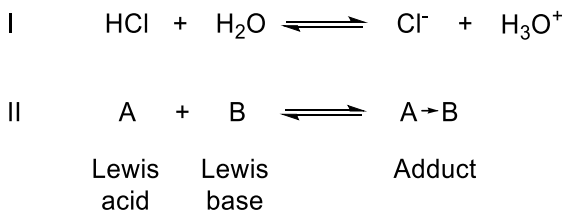
AN	acceptor number
AR	androgen receptor
BCF	tris(pentafluorophenylborane) - $B(C_6F_5)_3$
Bn	benzyl
Cy	cyclohexyl
DCE	1,2-dichloroethane
DCC	Dicyclohexylcarbodiimide
DMAP	4-Dimethylaminopyridine
DMSO	dimethyl sulfoxide
DNA	deoxyribonucleic acid
EPR	electron paramagnetic resonance
FLP	frustrated Lewis Pair
GC	gas chromatography
HMBC	heteronuclear multiple bond correlation
HSAB	hard and soft acids and bases
HSQC	heteronuclear single quantum correlation
HBpin	pinacolborane
HOMO	highest occupied molecular orbital
ICT	intramolecular donor-acceptor charge-transfer
IR	infrared
LA	Lewis acid
LDA	lithium diisopropylamide
LUMO	lowest unoccupied molecular orbital
M	mol/l
nm	nanometre
NMR	nuclear magnetic resonance
PXR	pregnane X receptor
SET	single electron transfer
TEMPO	(2,2,6,6-tetramethylpiperidine-1-yl)oxyl
THF	tetrahydrofuran
TMP	tetramethylpiperidine
TEPO	triethylphosphineoxide

UV	ultra violet
XRD	X-ray diffraction

1 General introduction

1.1 Lewis acids

According to Brønsted and Lowry, acidity concerns the movement of protons and is based on the reaction of a compound with water to form an oxonium-ion (H_3O^+) as shown in Scheme 1 (I).[1]



Scheme 1: (I) Reaction of a Brønsted acid base pair (hydrogen chloride and water) (II) General adduct formation of a Lewis acid with a Lewis base

The ions forming in aqueous hydrogen chloride are not the result of the dissociation of hydrogen chloride into a chloride anion and a proton, rather the result of an acid base reaction between water and hydrogen chloride.

According to Brønsted and Lowry an acid is a substance which can produce hydrogen-ions in solution.[2] In 1923, G. N. Lewis expanded the definition of acids and bases.[3] Similar to the reaction of a proton with water, other electron pair acceptors can show this behaviour. Lewis theory considers the movement of electrons rather than protons where a Lewis acid (electron pair acceptor) and a Lewis base (electron pair donor) can combine to form an adduct (Scheme 1, II).[3]

R. G. Pearson showed that just like Brønsted acids and bases, which are defined by acidity and basicity, Lewis acids and bases can be categorised according to their properties. Therefore he introduced the principle of hard and soft acids and bases (HSAB).[1] He distinguished compounds small in size with a high positive oxidation state as hard Lewis acids and compounds large in size and/or low oxidation states are defined as soft Lewis acids (Table 1).

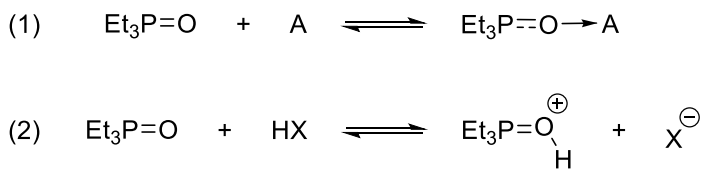
Table 1: Classification of hard and soft Lewis acids[4]

Hard	Borderline	Soft
H^+, Li^+, Be^{2+}, Al^{3+}, BF_3, NC^+	Fe^{2+}, Pb^{2+}, Bi^{3+}, Ni^{2+}, BMe_3, GaH_3	CO, Ag^+, Au^+, Hg^{2+}, BH_3, Br_2

Polarisability is stronger in soft rather than hard Lewis acids. The principle also states that acids show greater affinity for bases of the same class and vice versa. The character of the adduct bond is typically more ionic the harder both Lewis acid and base are.

1.2 The Gutmann Beckett method

Initially to quantitatively describe the electrophilicity of solvents Gutmann and co-workers introduced the acceptor number (AN). In 1975, they used ^{31}P nuclear magnetic resonance (NMR) spectroscopy to measure the shift of triethylphosphineoxide (TEPO) in the presence of various solvents (Table 2).[5]



Scheme 2: Reaction of TEPO with aprotic (1) and protic (2) solvents

Scheme 2 shows that TEPO can interact with both Lewis (1) as well as Brønsted acids (2). In both cases the oxygen atom operates in TEPO as the nucleophile and either donates electron density into the free orbital of the electron accepting Lewis acid (1), or gets protonated and must share one of its valence electron pairs (2). In both cases the adjacent phosphorus atom experiences a reduction in electron density depending of the strength of the (Lewis) acid. The resultant reduced electron density and the resulting deshielding of the phosphorus atom causes a downfield shift in the ^{31}P NMR spectrum. Based on this shift, the AN can now be determined as shown in equation (1).

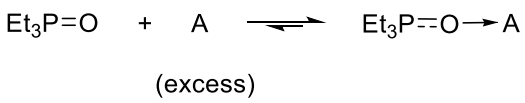
$$(1)\quad AN = \left(\delta_{sample} - 41\right) \cdot \left(\frac{100}{86.14-41}\right)$$

Equation (1) is the difference between the downfield shift of the mixture of acid and TEPO and the value 41 in the equation corresponds to the ^{31}P NMR shift of TEPO in hexane as a weak acid. This difference is multiplied by a constant with the difference of the ^{31}P NMR shift of TEPO in antimony (V) pentachloride (δ = 86.14 ppm) as a very strong Lewis acid and again the shift in hexane (δ = 41 ppm) in the denominator. This creates a scale for Lewis acidity, with an acceptor number of zero corresponding to hexane, and an acceptor number of 100 corresponding to $SbCl_5$ (Table 2).[5] Lewis acids with an acceptor number higher than a 100 are considered super acids.

Table 2: AN of different solvents[5]

Solvent	AN
Hexane	0
Diethyl ether	3.9
Tetrahydrofuran (THF)	8.0
Benzene	8.2
Acetone	12.5
Pyridine	14.2
Dimethylformamide (DMF)	16.0
$SbCl_5$	100.0

In 1996, Beckett and co-workers expanded the Gutmann method to determine the acidity of boranes.[6] They probed the borane catalysed polymerisation of epoxide monomers, and found that the Lewis acidity of these catalysts was a crucial factor in these polymerisation reactions. Beckett *et al.* suggested that an excess of the Lewis acid should be present to make sure the equilibrium is shifted far to the right-hand side (Scheme 3).



Scheme 3: Equilibrium shifted far towards the adduct of TEPO and Lewis acid.

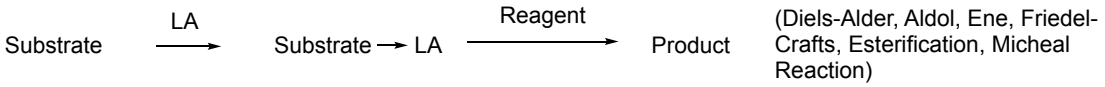
Initially, measurements were in THF at a concentration of 0.7 mol/l. Britovsek and co-workers reduced the concentration to 0.1 mol/l and changed the solvent to benzene-d^6 to prevent polymerisation of the THF in the case of strong Lewis acids.[7] All Lewis acidities measured in this work were carried out after Britovsek's protocol in either $CDCl_3$ or benzene-d^6.

1.3 Reactivity of Lewis acids

Research into Lewis acid catalysed reactions have experienced an uninterrupted expansion in recent decades and researchers are constantly providing new Lewis acid chemistry with more versatile, selective and reactive catalysts, as evidenced by literature.[8] These Lewis acid mediated reactions can be classified into two groups (Scheme 4).

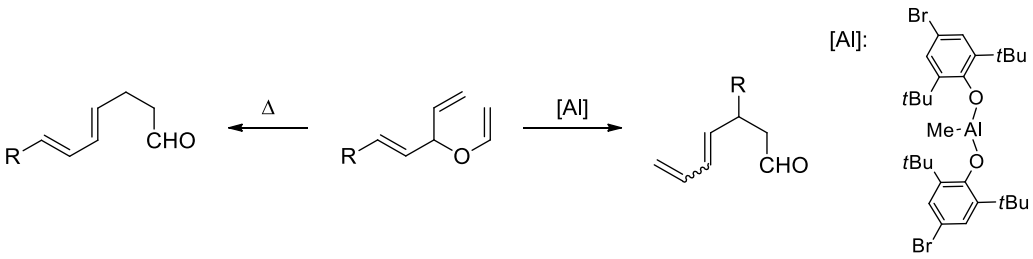
Group A

Group B



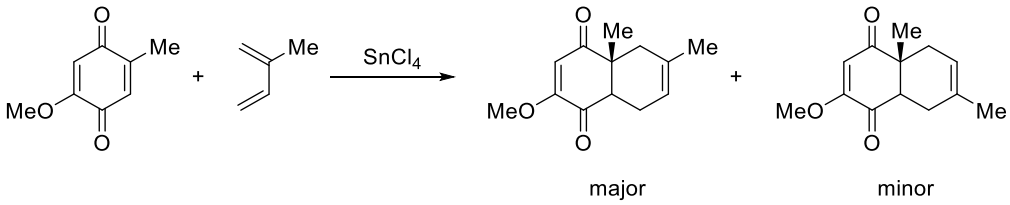
Scheme 4: Different types of Lewis acid mediated reactions. LA: Lewis acid

In group A (Scheme 4), the complex between substrate and Lewis acid leads to the product with the Claisen rearrangement being the most prominent example (Scheme 5).[9]



Scheme 5: Comparison of a Lewis acid and thermally promoted Claisen rearrangement

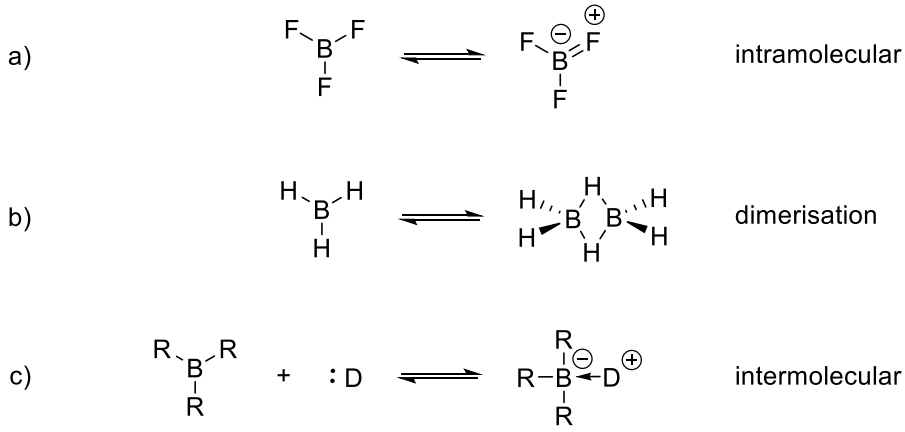
In group B (Scheme 4), the complex formed between substrate and Lewis acid is stable enough to react with a variety of reagents to form the desired product. Here the Lewis acid activates the substrate towards reaction with a second reagent. The Diels-Alder reaction between an unsaturated carbonyl dienophile Lewis acid complex and a diene is a renowned reaction in this class (Scheme 6).[10]



Scheme 6: $SnCl_4$ catalysed Diels-Alder reaction (major:minor 20:1)

1.4 Lewis acidic boron compounds

As with the other group 13 elements, boron atoms possess three valence electrons. Covalently bonded to a monovalent group X its composition is BX_3. The geometrical structure of these compounds is planar with a sp^2-hybridised boron-centre and an XBX-angle of 120°. In this configuration the boron atom only has an electron sextet and seeks one of three possible pathways to saturate its valence shell (Scheme 7).



Scheme 7: Three possible pathways of boranes to achieve neon configuration. D: Electron donor

If the substituents at boron have free electron pairs (Scheme 7, a) a $p_{\pi}p_{\pi}$-bond is formed by back donation of a valence electron pair of the fluorine-atom into the vacant *p*-orbital of the boron-centre. In cases when the substituents do not have any available electron pairs (Scheme 7, b) a dimerisation and a formation of a 2-electron-3-centre bond can occur as in B_2H_6. Apart from these two pathways to gain noble gas configuration, there is also an intermolecular option by adduct formation with a Lewis basic donor molecule (Scheme 7, c). In all cases, there is a transformation of an sp^2-hybridised boron atom to an sp^3-hybridised species. The Lewis acidity of boron halides towards several nitrogen (e.g. triethylamine) and oxygen (e.g. diethyl ether) bases is BF_3<BCl_3<BBr_3. [11] This trend is unexpected when one considers the decrease in electronegativity moving down the periodic table. One generally accepted explanation for this trend is the stronger back donation from fluorine compared to chlorine.[12] This increased back donation reduces the availability of the otherwise empty *p*-orbital on the boron atom to accept an electron pair from a base.[11] However, Politzer and co-workers could show in computational studies that the overlap integral of the boron 2*p* and the fluorine 2*p* orbitals is actually smaller than the corresponding integral for boron 2*p* and a chlorine 3*p* orbital. And when a boron trihalide acts as a Lewis acid it assumes tetrahedral configuration upon adduct formation.[13] As the bond angle between the boron and the halogen atom decreases, the bond lengths increase accordingly. Due to the large charge and the small size of the fluorine atom it gets close enough to the boron atom to form a strong polar bond with good orbital overlap.[14] In BCl_3 the boron-halogen bond is longer and not so strong compared to fluorine (there is a greater mismatch in orbital size). Therefore, more energy is required to distort a BF_3 moiety from planarity compared to a BCl_3 moiety. Surprisingly towards softer Lewis bases the trend is inverted.[15] In these interactions the Lewis acid is barely distorted from its planar geometry, so the strength of the acid-base interaction depends only on the charge of the boron atom which is larger in BF_3 than in BCl_3.[13]

Cationic boron compounds are another uprising field in Lewis acid catalysed chemistry.[16,17] These boron compounds have an oxidation state of (+III) but vary in their coordination number (Figure 1).

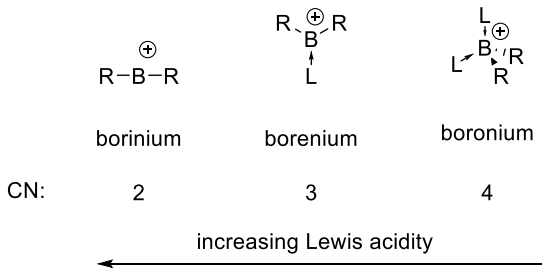
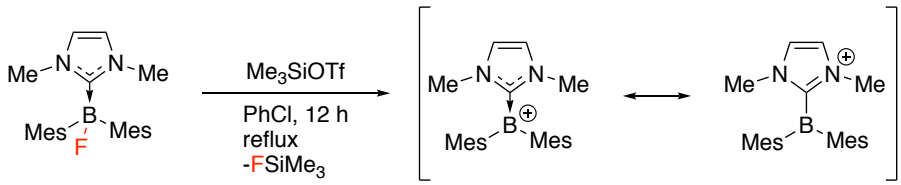


Figure 1: Cationic boron compounds with an oxidation state of +III sorted by Lewis acidity (CN: coordination number)

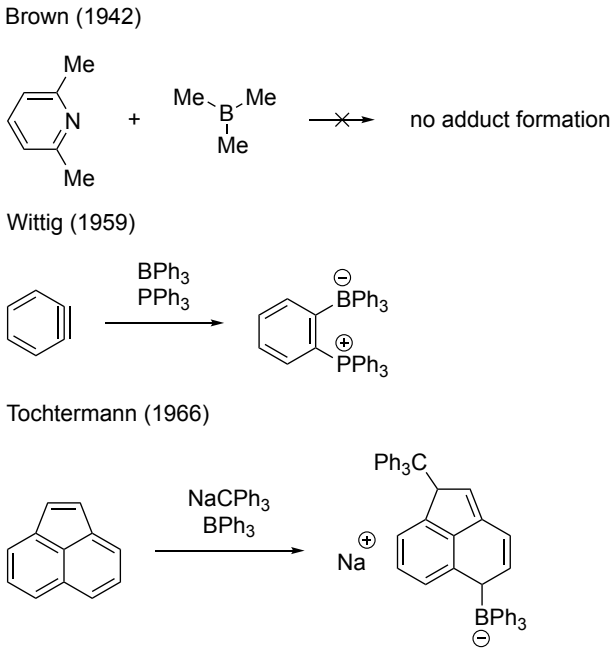
The acidity and therefore the reactivity increases with decreasing coordination number. The boron centre is covalently bonded to two R-groups and is also stabilised with up to two ligands **L** connected *via* a dative bond. The most Lewis acidic borinium ions are *sp*-hybridised with two vacant orbitals, addition of one Lewis base to this species generates the sp^2-hybridised borenium cation of intermediate Lewis acidity. Addition of a second Lewis base then generates the sp^3-hybridised boronium cation which, as a consequence of its neon configuration, is not Lewis acidic. These cations are commonly prepared by removal of anionic ligands (Scheme 8).[18]



Scheme 8: Borenium synthesis by fluoride abstraction

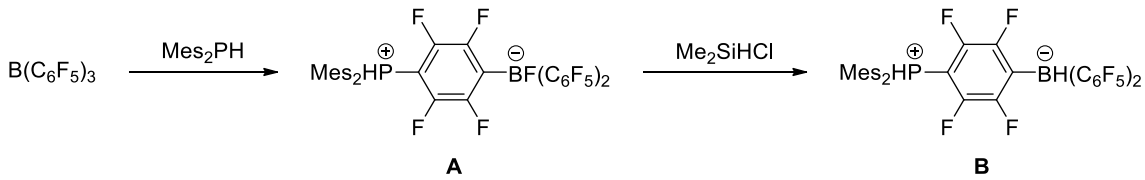
1.5 Frustrated Lewis pairs

In 1942, Brown *et al.* showed that 2,6-lutidine and trimethylborane do not form the expected acid-base complex as would be expected by Lewis' definition of acid base pairs. However, they did not probe further into this unquenched potential between these two compounds (Scheme 9, top).[19] More than a decade later Wittig and Tochtermann showed that these hindered Lewis pairs can add across unsaturated bonds (Scheme 9, bottom).[20,21]



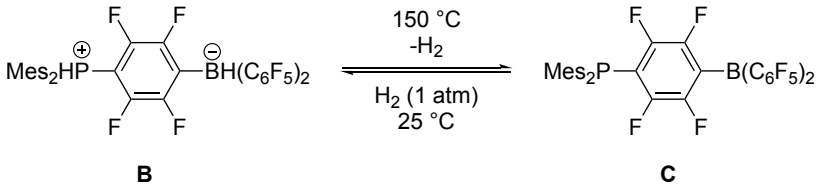
Scheme 9: First literature examples of sterically hindered Lewis pairs and their addition across unsaturated carbon-carbon bonds

In 2006, Stephan and co-workers further investigated this unquenched reactivity.[22] An initial reaction of tris(pentafluorophenyl)borane (BCF) with the sterically demanding disubstituted Mes_2PH yielded the phosphonium-fluoroborate (**A**) through an S_NAr reaction. A subsequent reaction of **A** with chlorodimethylsilane gave the phosphonium-hydridoborate (**B**) (Scheme 10).



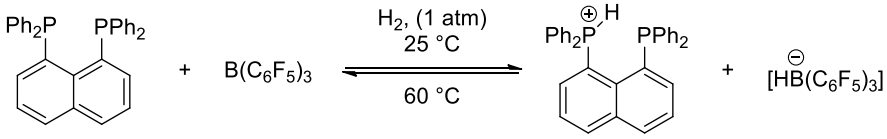
Scheme 10: Reaction of dimesitylphosphine and BCF and a subsequent reaction with chlorodimethylsilane

The resulting colourless compound **B** is stable at room temperature as well as air-stable. Heating the zwitterionic compound **B** to 150 °C leads to dehydrogenation and forms the neutral compound **C** (Scheme 11). The high steric demand around the phosphorus and boron-atom prevents dimerisation or oligomerisation making this intramolecular Lewis acid base pair sterically frustrated. This “frustrated Lewis Pair” (FLP) as defined by Stephan *et al.* readily reacts with H_2 under 1 atmosphere (1 atm) of dihydrogen to give hydridoborate **B** again (Scheme 11).[22]



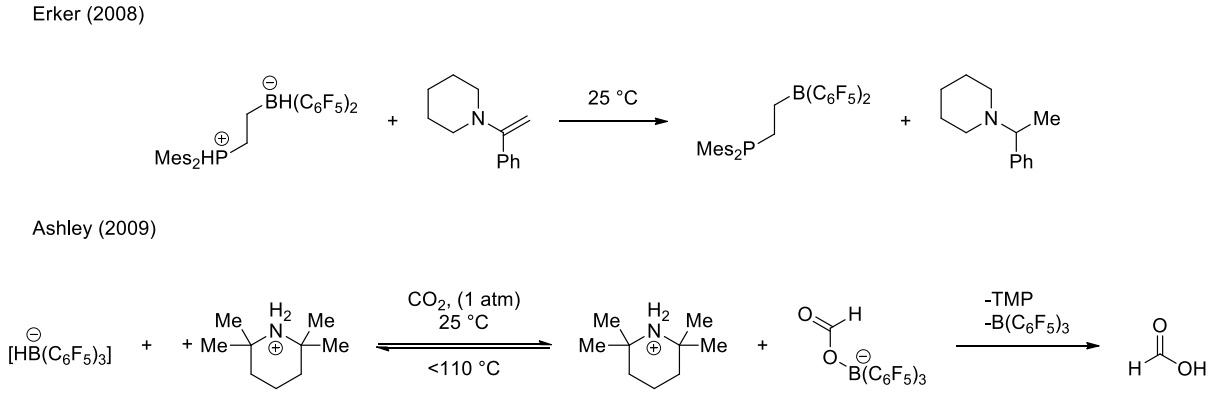
Scheme 11: The first metal-free activation of hydrogen by an FLP

The reaction shown in Scheme 11 was the first example of reversible, hydrogen-activation system using a metal-free compound. Since then a range of FLPs have been developed including intermolecular FLPs (Scheme 12).[23]



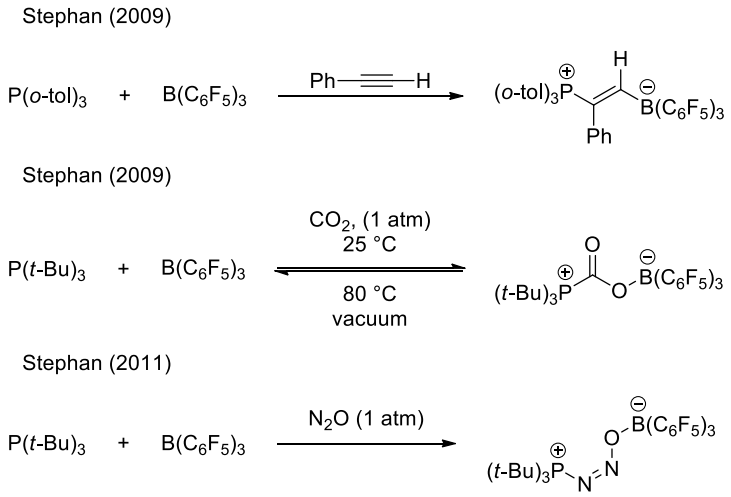
Scheme 12: Reversible binding of H_2 by an intermolecular FLP

The ability of these compounds to activate dihydrogen reversibly led to FLPs being used in metal-free hydrogenation catalysis. Similar to metal catalysed hydrogenations, carbon compounds such as enamines or CO_2 can be reduced to the corresponding amine or formic acid respectively (Scheme 13).[24,25]



Scheme 13: Hydrogenation of an enamine and CO_2 by an activated FLP

The ability to activate small molecules does not stop at dihydrogen but there are plenty of literature examples of other molecules such as C-C π-bonds,[26] CO_2[27] or N_2O[28] that will make use of the unquenched reactivity of the frustrated Lewis pair (Scheme 14).



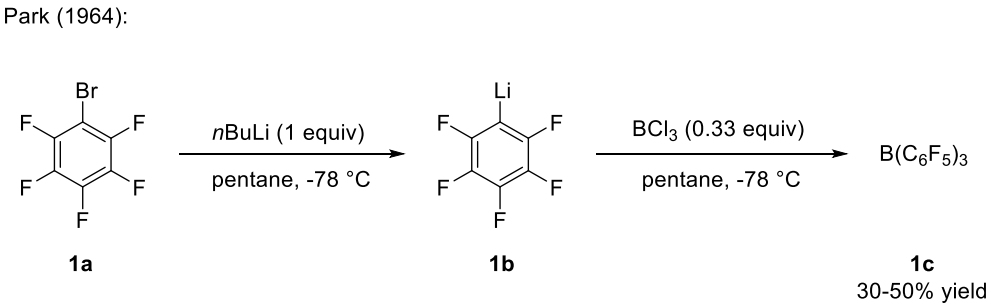
Scheme 14: Activation of various small molecules with intermolecular FLPs

2 Introduction of the boranes synthesised in this work

This chapter will introduce the boranes utilised in this Thesis. Here literature examples for the synthesis and the utilisation of the known boranes tris(pentafluorophenyl)borane, tris[3,5-bis(trifluoromethyl)phenyl]borane and tris(2,4,6-trifluorophenyl)borane are given. Besides these literature known boranes Chapter 2 will describe the synthesis of three novel triarylboranes (Tris(3,4,5-trifluorophenyl)borane, tris(3,4-dichlorophenyl)borane and tris(4-fluorophenyl)borane) and compare their crystal structures with known examples. Finally, a comparison of the acidity determined *via* the Gutmann-Beckett method will try to show a correlation between the substitution patterns of these homoleptic triarylboranes and their acceptor number.

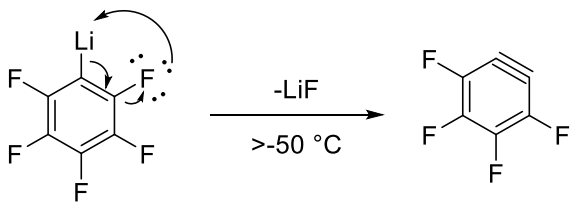
2.1 Tris(pentafluorophenyl)borane

To highlight some of the main points in Chapter 1, boranes have unique features as Lewis acids owing to their vacant *p*-orbital and are very tunable towards their hardness and softness by simply varying the substituents attached to boron. There have been extensive studies by Piers,[29] Stephan,[30] Paradies[31] to name a few to broaden the field of borane Lewis acids and their reactivity. One of the most frequently used boranes is tris(pentafluorophenyl)borane (BCF). This borane was initially synthesized in 1964 by Park and coworkers through lithiation of pentafluorophenylbromide (**1a**) in pentane followed by addition of a boron trichloride solution and two fold sublimation of the crude material to give BCF as a pure white solid (Scheme 15) with an acidity comparable to BF_3 (AN = 76).[32]



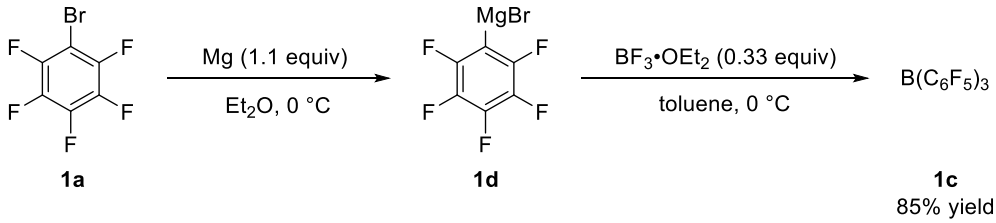
Scheme 15: Initial synthetic route for BCF

The approach used in this thesis circumvents lithiation of **1a** to avoid potential benzyne formation and ensuing risks formed from elimination of LiF (Scheme 16).



Scheme 16: Formation of benzyne derivative through LiF elimination

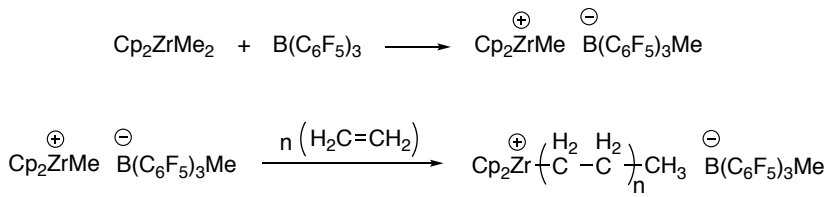
The Grignard reagent **1d** of **1a** is less prone to α-elimination and thereby safer to use (Scheme 17).[33]



1a **1d** **1c**
85% yield

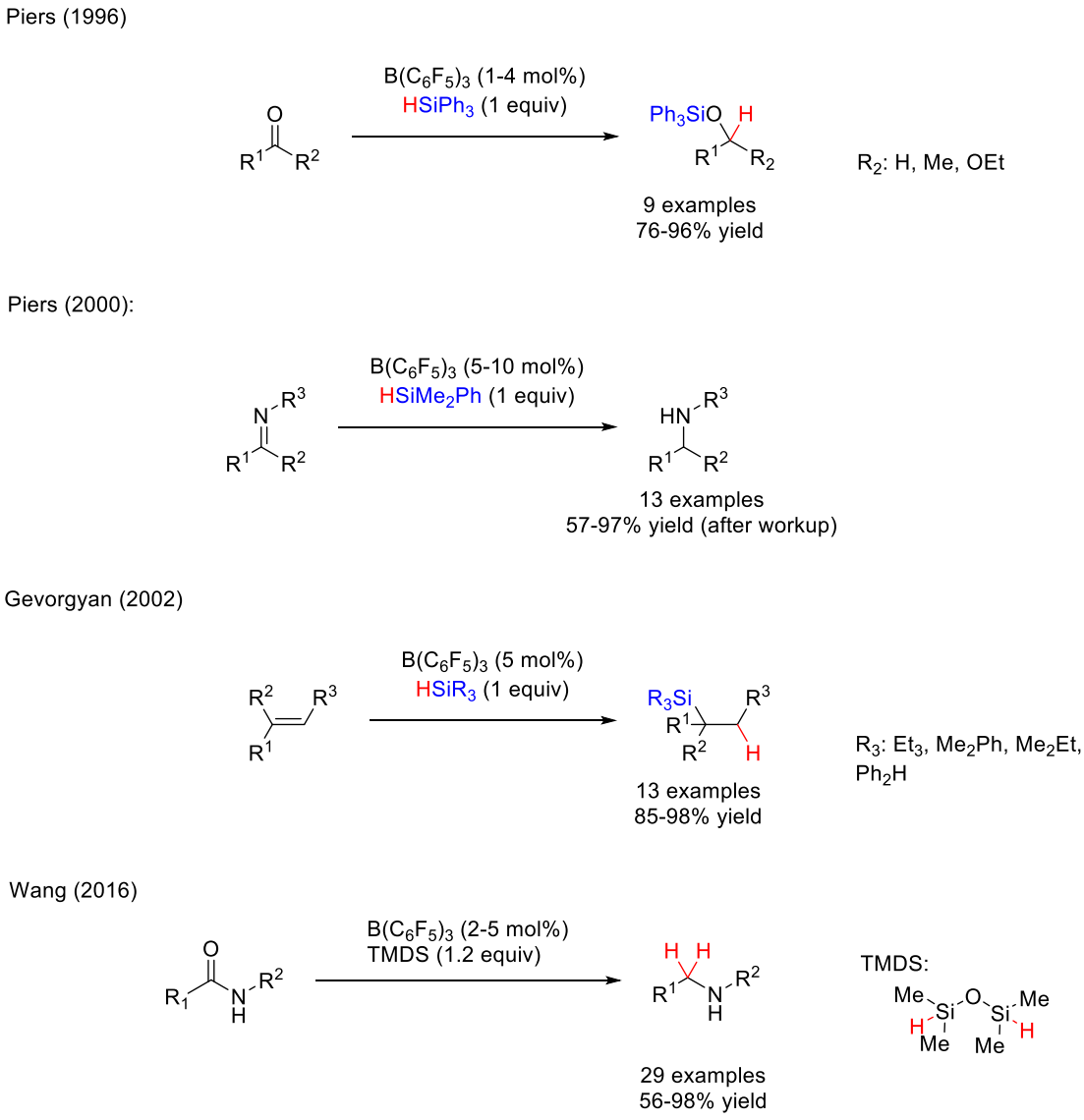
Scheme 17: Alternative synthetic access to BCF

Another advantage of this synthetic approach is that the yields from the Grignard route are improved compared to the lithiation method (85%). It must be mentioned that in order to attain a pure borane, a third sublimation step is required to remove the etherate adduct that forms with BCF. This ether adduct can be clearly distinguished by a signal at around 40 ppm in ^{11}B NMR spectra compared to a broad singulett at 60 ppm for the free BCF. The strong Lewis acid BCF was found by Park to readily form adducts with NH_3, NMe_3, pyridine and PPh_3.[32] It was later used stoichiometrically as an activator component for homogeneous metallocene Ziegler-Natta olefin polymerisation in which the Lewis acid removes a methyl group from the zirconium pre-catalyst to generate the active catalyst $[Cp_2ZrMe]^+$ (Scheme 18).[34]



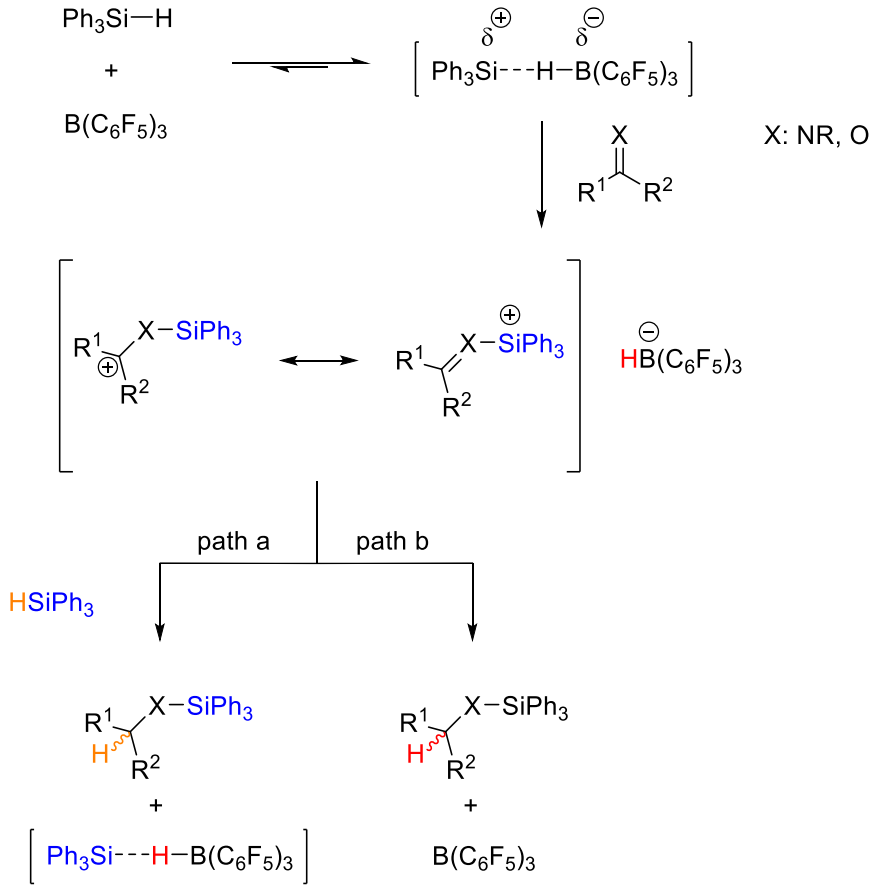
Scheme 18: Homogeneous Ziegler-Natta olefin polymerisation

In more recent literature, BCF has found applications in various other chemical transformations. It catalyses the reduction of unsaturated bonds such as aldehydes,[35] ketones,[35] esters,[35] imines,[36] olefins[37] and amides[38] with the assistance of silanes (Scheme 19).



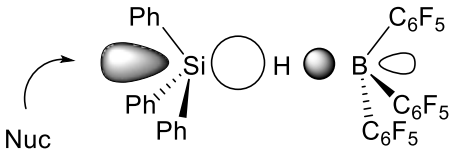
Scheme 19: Hydrosilation of various unsaturated organic compounds

Mechanistic studies by Piers and coworkers showed that initially a borane/silane adduct is formed, thereby increasing the electrophilicity of the silicon-atom. Nucleophilic attack of the Lewis basic substrate at the δ^+ silicon centre aids in the displacement of the hydridoborate yielding the activated substrate. (Scheme 20).[39] Following nucleophilic attack and the formation of the borate anion there are two possible pathways for the formation of the reduced product (Scheme 20, path a or b). Deuterium labelling experiments however pointed towards path b.[39] This pathway shows that the borane is not just needed for the initial formation of the silylium cation but also plays an important role in the transfer of the hydride anion.



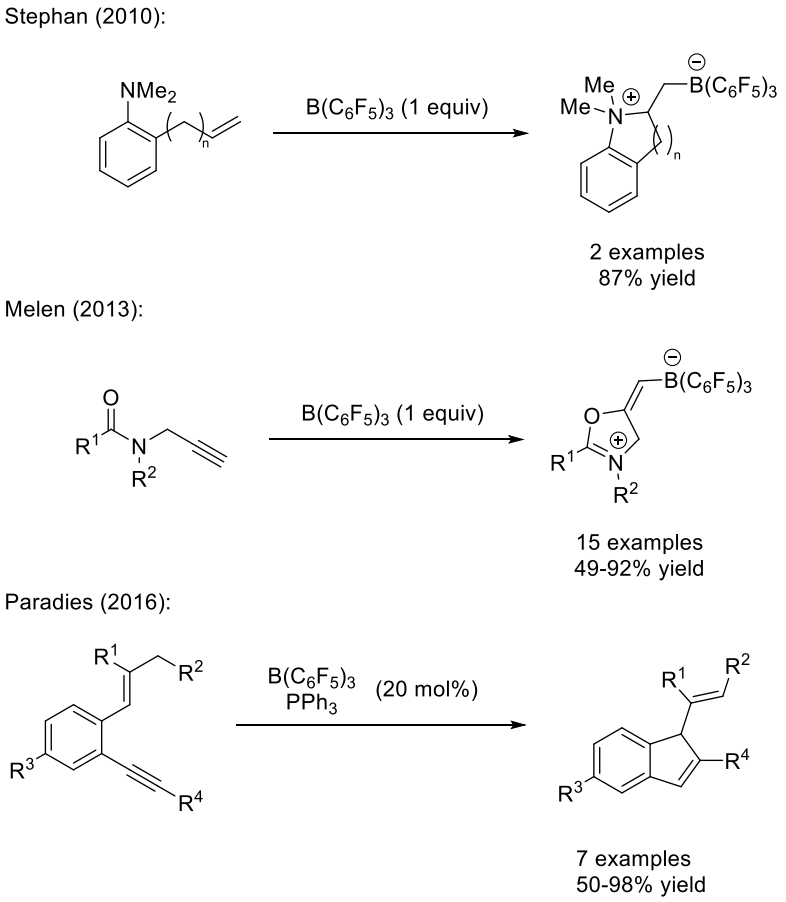
Scheme 20: Mechanism of the hydrosilylation of ketones, aldehydes, esters and imines

Computational studies show that the lowest unoccupied molecular orbital (LUMO) of the borane/silane adduct lies along the Si-H-B axis (Scheme 21).[40] A large orbital lobe *trans* to the Si-H bond is likely the preferred site for nucleophilic attacks and explains the nucleophilic attack from the substrate in the reaction in Scheme 20.



Scheme 21: Nucleophilic attack of the LUMO of the borane/silane adduct

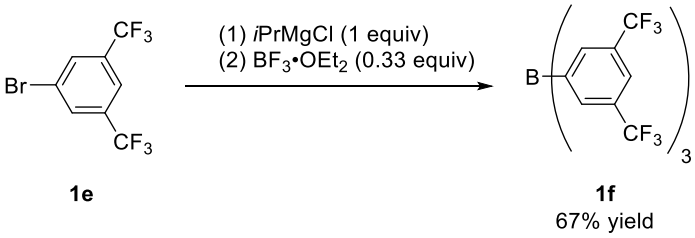
Another important feature of BCF is its steric bulk preventing adduct formation with sterically demanding bases. By increasing the rigidity of the substituents, the tendency to interact with soft Lewis acids is increased. This is observed in several π-bond activations observed in literature and discussed later in this Thesis (Scheme 22).[41–43]



Scheme 22: π-Activation of unsaturated systems by BCF

2.2 Tris[3,5-bis(trifluoromethyl)phenyl]borane

Although there are extensive studies on borane catalysed hydrosilylations,[44] there is little literature evidence of another hydroelementation reaction namely hydroboration. Oestreich and co-workers showed that tris[3,5-bis(trifluoromethyl)phenyl]borane (**1f**) is more suitable for hydroborations than BCF.[45] **1f** was first synthesised by Ashley and co-workers in 2012 using *i*PrMgCl as a transfer Grignard reagent in reaction with boron trifluoride etherate and an ensuing sublimation *in vacuo* (Scheme 23).[46]



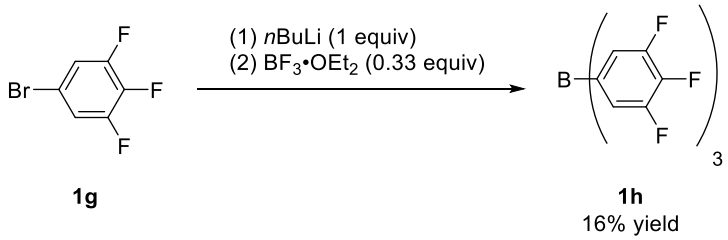
Scheme 23: Synthesis of $BAr^F{}_3$ by Ashley et al.[47]

Oestreich used the same procedure to access triarylborane **1f** with slightly lower yields (62%). The Lewis acidity was found to be slightly higher than BCF (AN = 84 compared to 76) and **1f** was found to be less sterically demanding due to the lack of *ortho*-fluorine-

atoms. Like BCF, **1f** is also able to activate hydrogen in the presence of sterically demanding bases like tetramethylpiperidine (TMP).[48]

2.3 Tris(3,4,5-trifluorophenyl)borane

As part of this thesis, the novel borane tris(3,4,5-trifluorophenyl)borane (**1h**) was synthesised and fully characterised. As with **1f**, it is also devoid of *ortho*-fluorine atoms (Scheme 24).



1g **1h** 16% yield

*Scheme 24: Synthesis of **1h***

As this species lacks *ortho*-fluorine atoms, the lithiation **1g** cannot result in the elimination of LiF to form explosive benzyne species (see Scheme 16) even though the yields could be improved by using a transfer Gringard reagent like *i*PrMgCl. The crystal structure of **1h** shows a similar paddlewheel structure to other triarylboranes (Figure 2).[48]

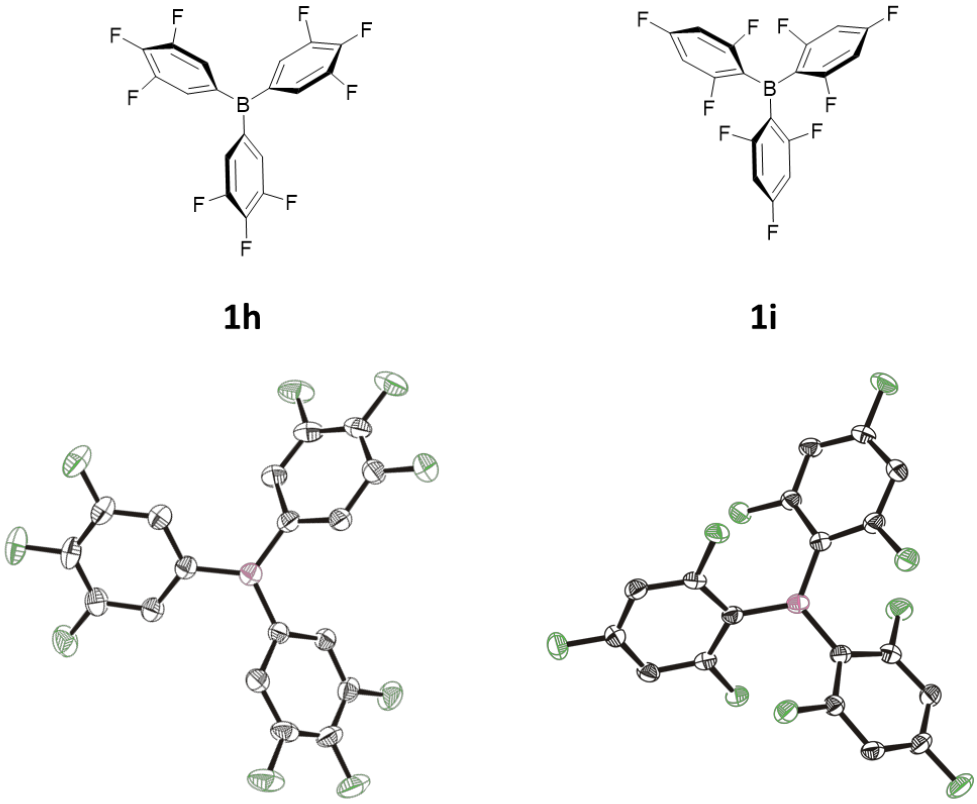
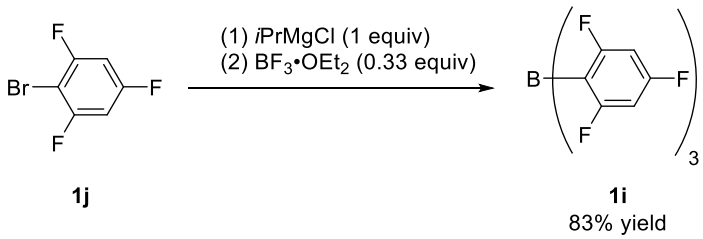


*Figure 2: Comparison of the crystal structures of **1h** and **1i**. Protons omitted for clarity. Thermal ellipsoids set at 50% probability. Carbon: black, fluorine: green, boron: pink*

Interestingly **1h** was found to have a slightly higher Lewis acidity than BCF (AN = 79) even though it bares fewer electron withdrawing fluorine-atoms. As discussed in Chapter 1 the reduction in steric demand in *ortho*-position may allow TEPO, a hard Lewis base, to form an adduct with **1h** and the lack of *ortho*-substituents facilitates the resultant tetrahedral structure.

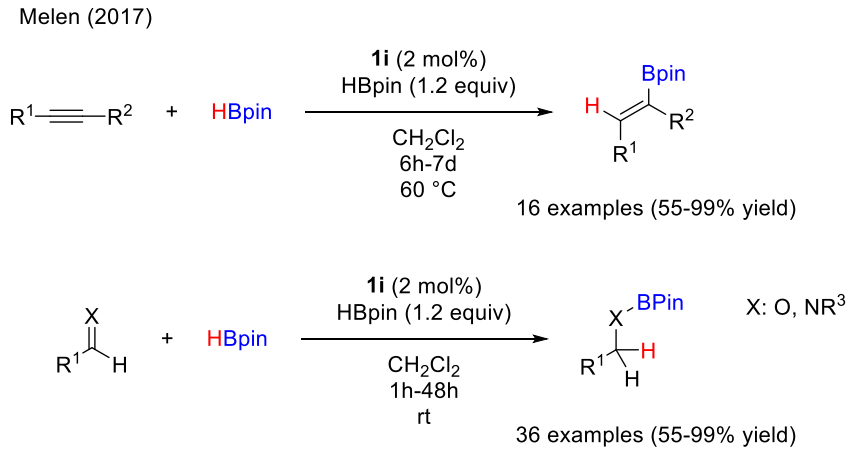
2.4 Tris(2,4,6-trifluorophenyl)borane

Among the homoleptic triarylboranes another borane utilised in this work is tris(2,4,6-trifluorophenyl)borane (**1i**, Figure 2). This represents a Lewis acid with the same steric demand as BCF but with fewer electron withdrawing fluorine atoms, explaining the reduced Lewis acidity (AN = 69). It was first synthesised by Alcazaro *et al.* using again a transfer Gringard reagent in the first step followed by the reaction with boron trifluoride etherate to give **1i** in a very good yield (Scheme 25).[49]



*Scheme 25: Synthesis of **1i***

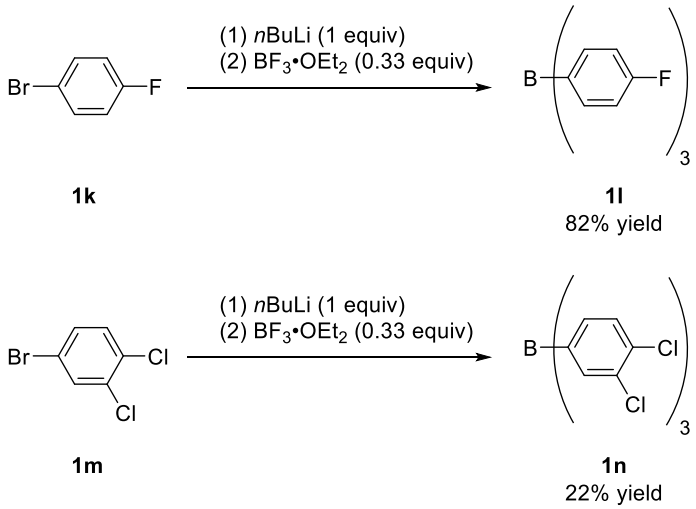
This lower acidity while having the same steric demand as BCF has proven to have some unique catalytic features.[50] Our group could show that **1i** can be used to catalyse the hydroboration of alkynes, aldehydes and secondary aldimines using pinacolborane (HBpin) (Scheme 26).[51]



*Scheme 26: Hydroboration reactions catalysed by **1i***

2.5 Tris(3,4-dichlorophenyl)borane & tris(4-fluorophenyl)borane

As part of this Thesis two more triarylboranes (tris(3,4-dichlorophenyl)borane and tris(4-fluorophenyl)borane) were synthesised and fully characterised (Scheme 27).



*Scheme 27: Synthesis of homoleptic triarylboranes **1l** & **1n***

As expected **1l** has the lowest Lewis acidity of the fluorinated triarylboranes (AN = 66) used in this work having the fewest fluorine substituents. Interestingly, **1n** has a very high acceptor number of 78 even though it bares only two chlorine atom which are less electron withdrawing than fluorine. This is intermediate between BCF (AN = 76) and the 3,4,5-fluorinated borane **1h** (AN = 79). If the only influencing factors were sterics and negative inductivity, we would expect a lower acidity for **1n** but the acceptor number indicates a similar acidity compared to **1c** and **1h**. This indicates that backdonation in the form of a positive mesomeric effect is responsible for the overall acidity of the borane. **1l** and **1n** could both be crystallised by sublimation and their structures determined. The crystal structures of both compounds show the expected paddlewheel structure as found for other boranes (Figure 3).

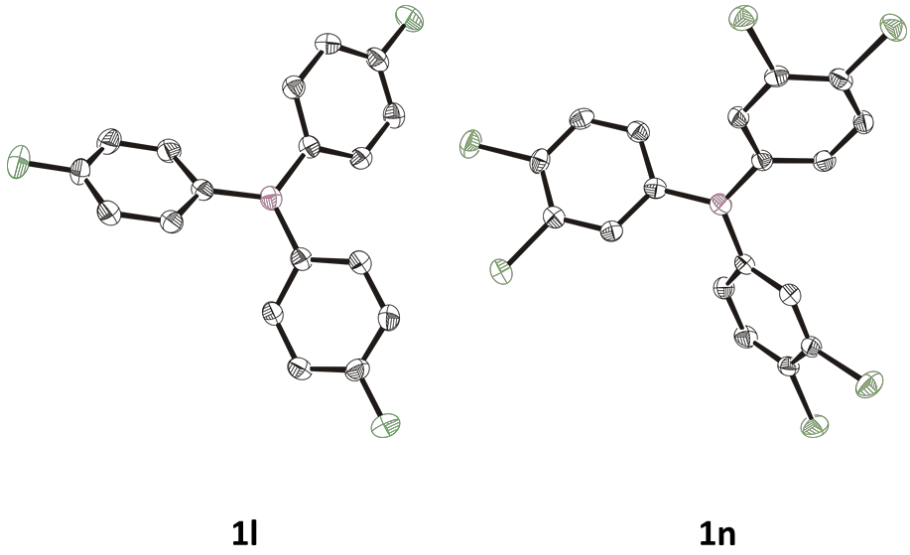


*Figure 3: Crystal structure of **1l** and **1n**. Protons omitted for clarity. Thermal ellipsoids set at 50% probability. Carbon: black, chlorine: light green, fluorine: green, boron: pink*

2.6 Summary

As part of this thesis a range of boranes have been synthesised and their Lewis acidity determined by the Gutmann-Beckett method (Figure 4). However, further investigations are needed to quantify the contributions of inductive and mesomeric effects of the substituents towards the overall acidity.

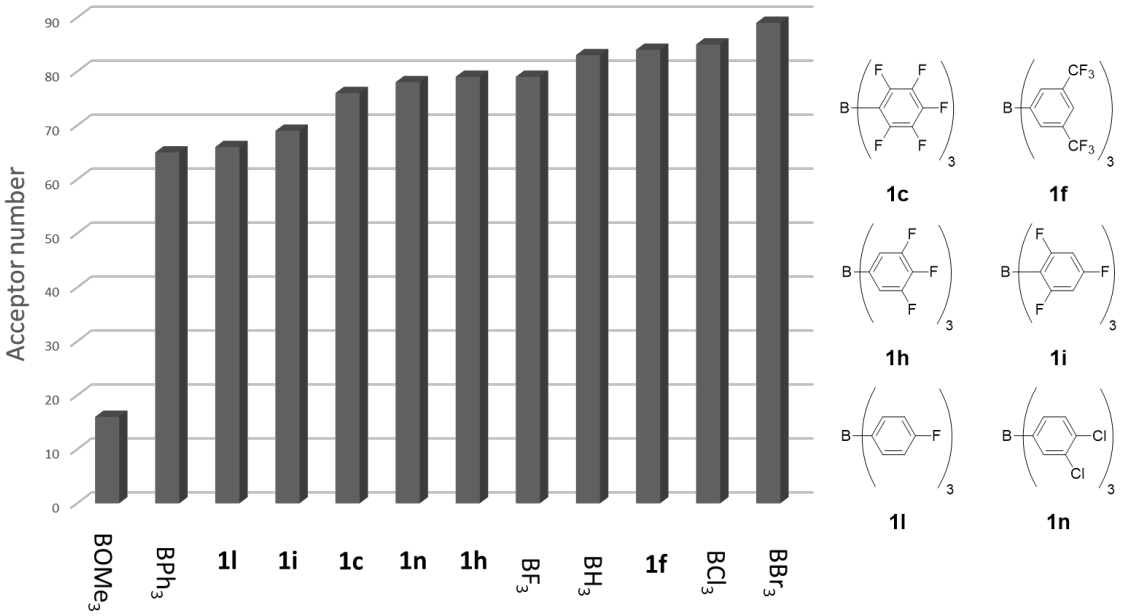


Figure 4: Comparison of the Lewis acidities of various boranes[52]

As Figure 4 shows there is only a slight difference between **1l** (AN = 66) and triphenylborane (BPh_3, AN = 65) it can be concluded that the effect of the fluorine-substituent on the *para* position instead of a proton in terms of acidity is negligible. As already mentioned, **1h** is more Lewis acidic than **1c** towards TEPO. It can be concluded

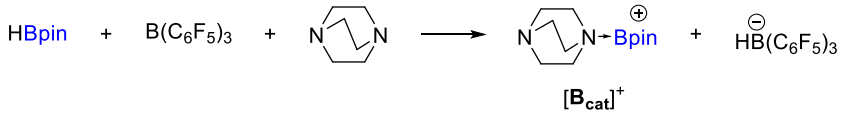
that the increase in steric bulk and the inability to assume a tetrahedral structure has a greater effect on the Lewis acidity, than the additional negative inductive effect added by the two fluorine-atoms in *ortho*-position. By comparing **1n** to **1h** we can show that the positive mesomeric effect of the F-atom must have an influence on the acidity since reducing the number of substituents from 3 (**1h**) to 2 (**1n**) with a lower electronegativity (F = 3.98, Cl = 3.16) equals in almost the same acidity. This argument is supported by the acceptor number of **1f** (AN = 84) since in the case of trifluoromethyl substituents there is no mesomeric stabilisation. Overall, we can see that slight changes in the substitution pattern of these triarylboranes can have big effects towards reactivity and acidity. This will be shown in greater detail in the following chapters of this Thesis.

3 Hydroboration of ketimines

3.1 Introduction

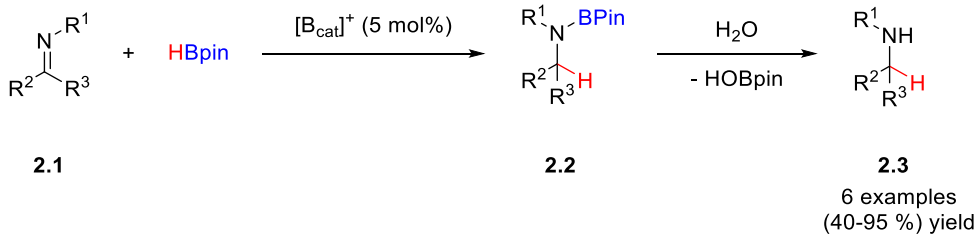
As previously mentioned in Chapter 2, hydroborations are a well-studied hydroelementation reaction with many applications.[53–57] In recent years many groups, besides ourselves, have shown examples of borane catalysed hydroborations.[51,58,59] In this chapter, the metal-free hydroboration of imines to amines is discussed as a straightforward way of preparing amines. Currently the majority of known hydroboration protocols however use metal catalysts.[60–64] This limits the use of the resulting amine products for human consumption (e.g. food products or pharmaceuticals) without costly purification due to regulations by international bodies.[65] The use of non-metal catalysts has the benefit of avoiding an intense purification step.

The hydroboration of aldimines was described in Chapter 2 and can be catalysed by the less Lewis acidic borane tris(2,4,6-trifluorophenyl)borane (**1i**). Unfortunately, this reactivity of **1i** could not be expanded to ketimines.[51] One of the few protocols of boron catalysed ketimine (**2.1**) hydroboration was described by Crudden and co-workers using BCF and 1,4-diazabicyclo[2.2.2]octane (DABCO).[58] The addition of a base is needed to facilitate the hydride abstraction to form the hydridoborate $[HB(C_6F_5)_3]^-$ and to stabilise the formed borenium cation $\mathbf{[B_{cat}]^+}$ (Scheme 28) which represents the actual catalytically active species (Scheme 30).



Scheme 28: Formation of a base-stabilised borenium cation with BCF

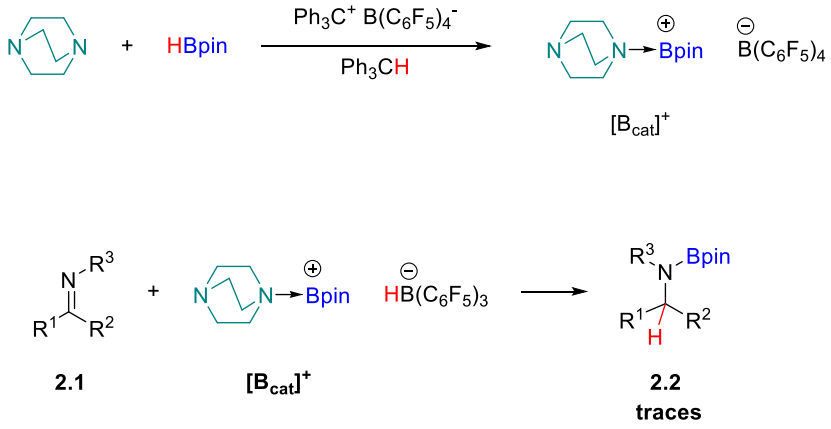
Without the presence of a stabilising base, BCF is known to decompose HBpin to B_2pin_3 and several unidentified compounds by Lewis acid-promoted ring opening.[66] Crudden *et al.* showed that this *in situ* formed borenium cation $\mathbf{[B_{cat}]^+}$ is the actual active species and capable of catalysing the hydroboration of imines (**2.1**) with HBpin (Scheme 29).[58]



Scheme 29: Hydroboration of imines with HBpin catalysed by $[B_{cat}]^+$

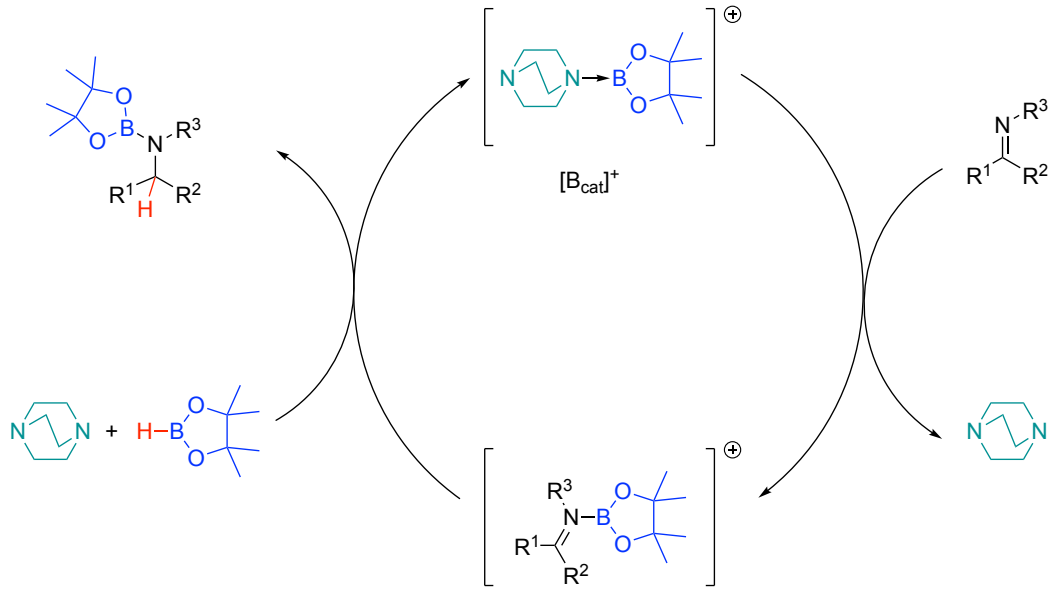
To probe the reactivity of this DABCO-stabilised cation, $\mathbf{[B_{cat}]^+}$ was generated with tetrakis(perfluorophenyl)borate $[B(C_6F_5)_4]^-$ as a more innocent counter anion (Scheme

30, top) and successfully tested as a catalyst (6 examples, 18-96%). To prove that the hydride used to produce the borate anion $[HB(C_6F_5)_3]^-$ cannot participate in side reactions towards ketimines (**2.1**), stoichiometric amounts of the imine were mixed with the hydridoborate salt and only traces of the desired amine could be isolated.



*Scheme 30: (Top) generation of $[B_{cat}]^+[B(C_6F_5)_4]$ (bottom) stoichiometric reaction of $[B_{cat}]^+[HB(C_6F_5)_3]^-$ with imine **2.1** to amine **2.2***

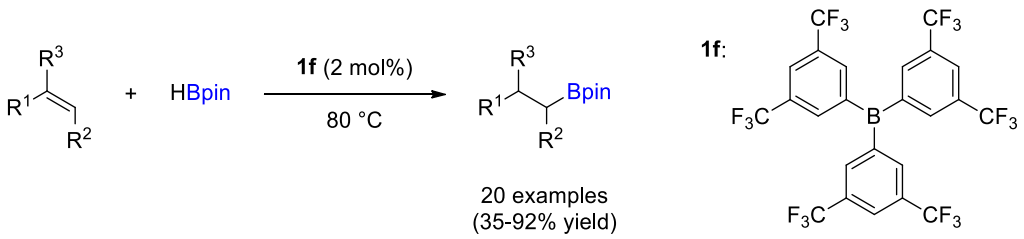
The proposed mechanism of this reaction suggests that the hydridoborate is not the catalyst of the reaction, but rather the generated borenium cation **$[B_{cat}]^+$** (Scheme 31).[58]



Scheme 31: Mechanism of the hydroboration catalysed by $[B_{cat}]^+$

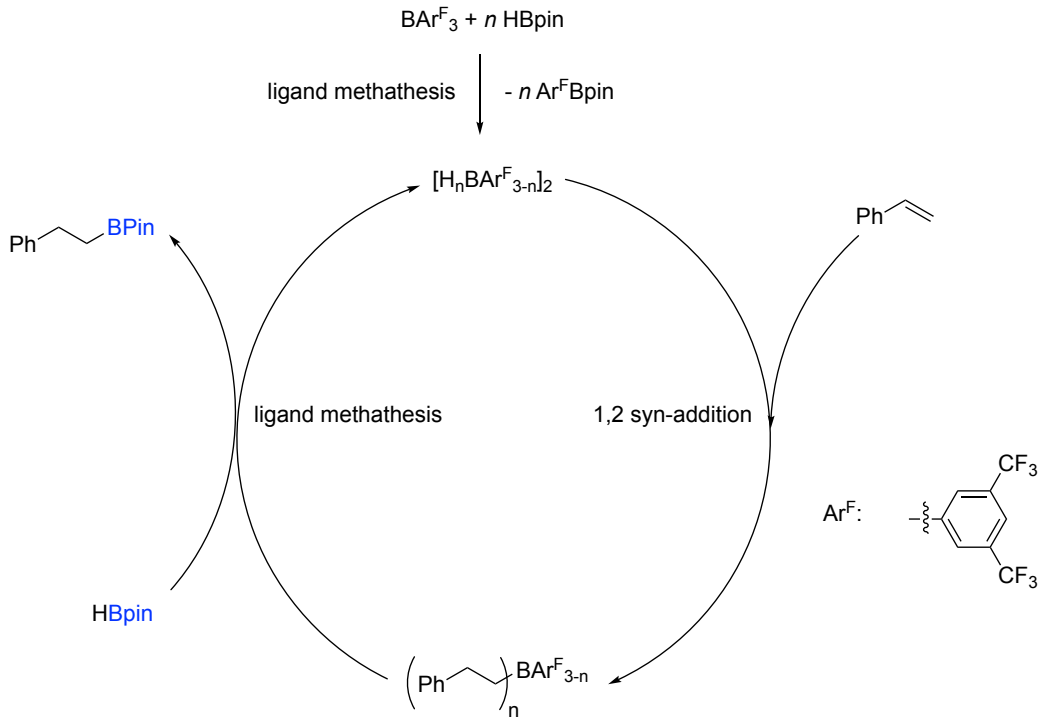
The aforementioned mechanism suggests that the initial heterolysis of the hydridoborane HBpin by BCF is only required to generate the catalytically active cation **$[B_{cat}]^+$**. This indicates that a stronger electrophile is needed to activate ketimines (**2.1**) to make them prone for hydroboration towards pinacolborane.

As recently shown by Oestreich and co-workers **1f** is a very efficient hydroboration catalyst for alkenes without the addition of a base using pinacolborane whereas BCF is not (Scheme 32).[45]



*Scheme 32: Hydroboration of alkenes with HBpin catalysed by **1f***

As Scheme 32 shows, this reaction only works at elevated temperatures and mechanistic studies revealed that the actual catalytic species is not **1f** but rather a borohydride that is formed from a ligand exchange reaction at 80 °C. This forms the catalytically active species **2.4a** and **2.4b** *in situ* (Scheme 33).



Scheme 33: Catalytic cycle of the alkene hydroboration with HBpin

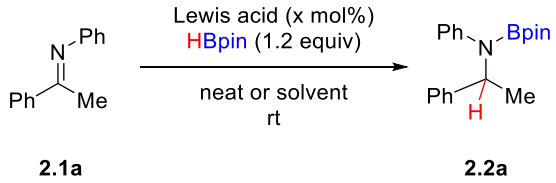
Scheme 33 depicts the catalytic cycle for this hydroboration reaction. An initial ligand metathesis forms the catalytically active mono- or diarylborane **2.4a** and **2.4b**. These species can now undergo a concerted 1,2-*syn*-addition of the B-H-bond across the unsaturated C-C-bond in a highly regioselective manner. A second ligand metathesis replaces the BAr^F_{3-n}-moiety with a Bpin group and the *in situ* generated electron deficient hydroborane **2.4a** or **b** is regenerated to form the desired hydroborated product.

3.2 Aims of this work

The results by Oestreich described above encouraged us (in collaboration with Oestreich) to test if **1f** is also a possible catalyst for the reduction of ketimines without the help of an additional base.

3.3 Results

In this study the model ketimine substrate **2.1a** was tested towards its reactivity with HBpin using various boranes catalysts. In addition, the isoelectronic trityl cation in $[Ph_3C]^+[B(C_6F_5)_4]^-$ was also tested as a potential catalyst (Scheme 34, Table 3).



2.1a **2.2a**

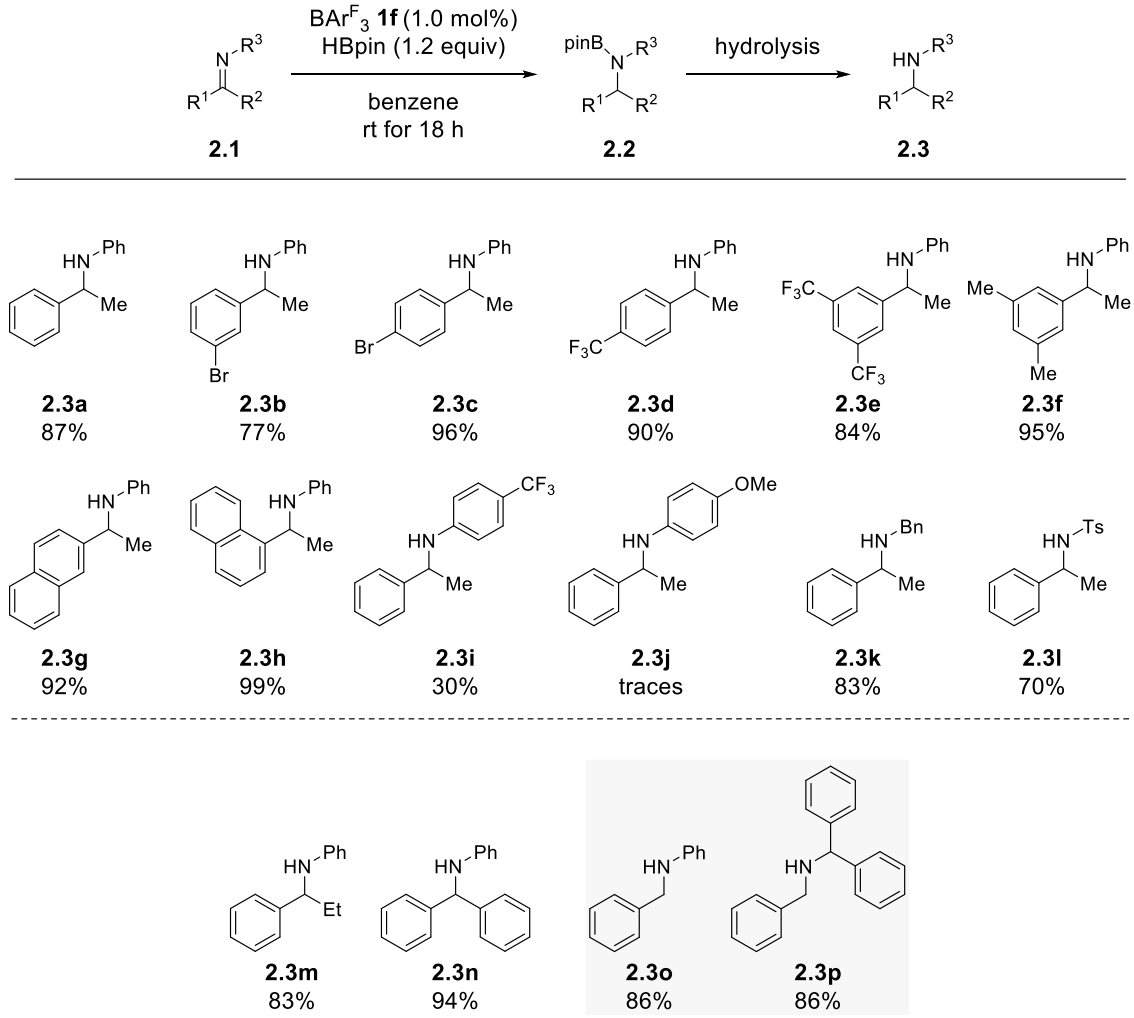
*Scheme 34: Hydroboration of **2.1a** under various conditions*

*Table 3: Optimisation of the Lewis acid catalysed hydroboration of **2.1a** under various conditions*

Entry	Lewis acid	Catalytic loading (mol%)	Time (h)	Solvent	Conversion[a] (%)
1	none	-	18	neat	0
2	BPh_3	2.0	18	neat	0
3	$B(C_6F_5)_3$	2.0	18	neat	36
4	**1f**	2.0	18	neat	100
5	**1f**	0.3	18	neat	100
6	$[Ph_3C]^+[B(C_6F_5)_4]^-$	10.0	18	neat	0
7	$HB(C_6F_5)_2$	3.0	18	neat	5
8	**2.4a**·SMe_2	3.0	18	neat	100
9	**1f**	1.0	1	benzene	58
10	**1f**	1.0	1	toluene	30
11	**1f**	1.0	1	$PhCF_3$	37
12	**1f**	1.0	1	CH_2Cl_2	34
13	**1f**	1.0	1	1,2-$Cl_2C_2H_4$	37
14	**1f**	1.0	1	neat	35
15	**1f**	1.0	18	benzene	100 (87)
16	$B(C_6F_5)_3$	5.0	6	benzene	<5
17	BCl_3	20.0	18	benzene	27
18	BF_3·OEt_2	20.0	18	benzene	99

[a] Conversion determined by gas chromatography (GC) analysis. Number in brackets represents isolated yield of free amine after hydrolysis and purification by flash chromatography on silica gel.

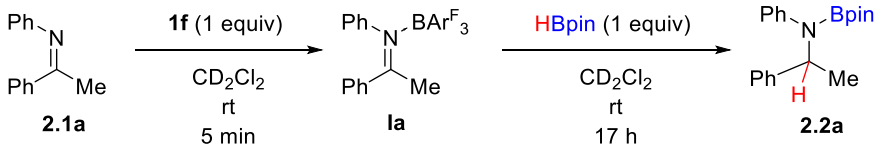
The less Lewis acidic BPh_3 (entry 2, Table 3) shows no activity and to confirm results by Crudden *et al.* BCF was tested (entry 3, 16). Even after 18 h only 36% conversion could be observed. Entry 6 shows that trityl has no observable conversion towards the model system. This is notable as trityl is isoelectronic to the borane (entry 6). $HBAr^{F}_2$ (**2.4a**) was tested as a dimethylsulfide adduct (entry 8) and showed high catalytic (100% GC conversion) activity at a catalyst loading of 3 mol% after 18 h. Interestingly the BCF equivalent of **2.4a** (Piers' borane, $HB(C_6F_5)_2$, entry 7) was found to be appreciably less effective as a catalyst and gives only 5% conversion after 18 h. Boron trihalides were also tested (entry 17 and 18). At low catalyst loadings the conversion using borontrichloride or borontrifluoride is negligible, but raising the catalyst loading to 20 mol% produced the target amine almost quantitatively with boron trifluoride (entry 18). When using the less stable and more Lewis acidic boron trichloride, only 27% conversion could be observed (entry 18). Borane **1f** showed the highest conversion with catalyst loadings as little as 0.3 mol% after 18 h (entry 5). We decided to use 1 mol% as the catalyst loading for further studies since lower catalyst loadings would increase the inaccuracy on the used scale system. The solvent was then varied to determine the most suitable solvent system (entries 9-14) and with 58% conversion after 1 h benzene showed the most promising results (entry 9). This gave us our final optimal conditions of 18 h at room temperature with a catalyst loading of 1 mol%. These conditions gave quantitative conversion determined *via* GC chromatography and after workup 87% of the hydrolysed amine could be isolated (entry 15). With the optimal conditions in hand, a scope of this hydroboration reaction was assessed (Scheme 35).



*Scheme 35: Hydroboration of imines catalysed by **1f** in the presence of HBpin (isolated yields)*

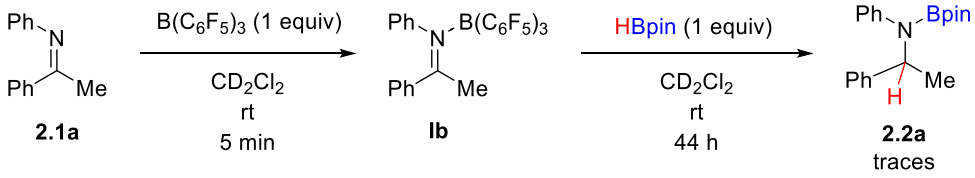
A variety of R^1 groups were tested. Neither electron deficient trifluoromethyl substituted phenyl-rings (**2.3d** and **2.3e**), nor electron rich methyl substituted phenyl rings in R^1 position (**2.3f**) proved to be problematic and gave yields between 84% and 95%. Also, *para*- and *meta*-substituted phenyl bromides (**2.3b** and **2.3c**) showed good yields of 77% and 96% respectively. Replacing the phenyl ring with a 1- or 2-napthyl moiety (**2.3g** and **2.3h**) did not reduce reactivity and excellent yields of 92% and 99% respectively could still be observed. Adding both electron withdrawing trifluoromethyl on the *para*-position of the *N*-phenyl ring (R^3) (**2.3i**) as well as the electron donating methoxy substituent (**2.3j**) reduced the yield to 30% and <5% respectively. When using the sterically less demanding benzyl as an *N*-protecting group (**2.3k**), comparable isolated yield (83%) to the model substrate **2.3a** (87%) was observed. Similar results were observed with **2.3l** which posessed a tosyl-protecting group. Increasing the steric bulk in R^2 position by introducing either an ethyl- (**2.3m**) or a phenyl-moiety (**2.3n**) did not influence the reaction and very good yields (83% and 94% respectively) could be be obtained. The more reactive aldimines showed very good yields as well (86%) even when the steric bulk was increased from a phenyl- (**2.3o**) to a benzhydryl-protecting group (**2.3p**).

To gain a better understanding of this mechanism several stoichiometric reactions were undertaken. Neither the ^{1}H nor the ^{11}B NMR spectrum showed any changes upon mixing with the model substrate **2.1a** with stoichiometric amounts of HBpin. But adding an equivalent of **1f** to a solution of **2.1a** in dichloromethane-d_2 (CD_2Cl_2) revealed a clear downfield shift in the ^{11}B NMR spectrum indicating the formation of an imine-borane adduct (**Ia**, Scheme 36).



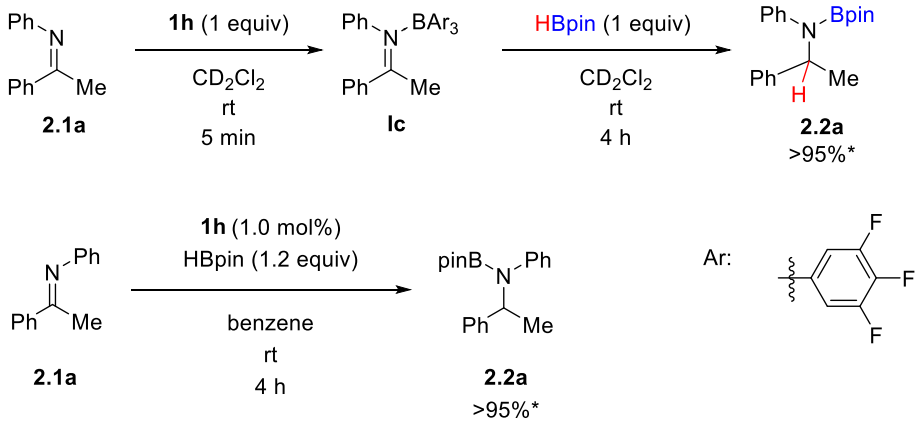
*Scheme 36: Stoichiometric reaction of **2.1a** with **1f** and a subsequent reaction with HBpin*

The addition of an equivalent of HBpin led to a quantitative formation of the desired product **2.2a** after 17 h, with the catalyst crashing out of solution after completion of the reaction. No formation of hydroboranes **2.4a** or **2.4b** or formation of the second product (**2.4c**) of the ligand metathesis could be observed while monitoring this reaction *via* heteronuclear ^{1}H, ^{11}B or ^{19}F NMR spectroscopy. Secondly no hydridoborate anion of **1f** $[HBAr^{F}_{3}]^{-}$, and no borenium cation formed by hydride abstraction of HBpin could be observed in the ^{11}B NMR spectra making a borenium catalysed mechanism highly unlikely, in contrast to Crudden's work.[58] For comparison we repeated the experiment with stoichiometric amounts of BCF as the borane in the first step. (Scheme 37).



*Scheme 37: Stoichiometric reaction of **2.1a** with BCF and 1 equivalent of HBpin*

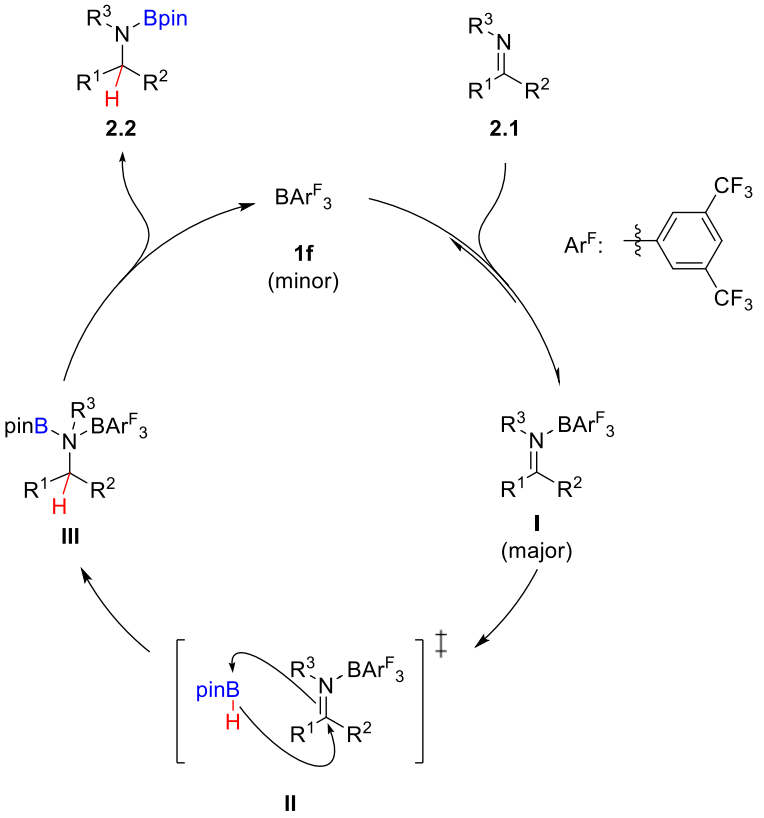
Again, borane imine adduct **Ib** was readily formed after mixing BCF with imine **2.1a** in CD_2Cl_2 as observed in the ^{11}B NMR spectrum. But the addition of an equivalent of HBpin did not lead to the desired product and even after 44 h only traces of amine **2.2a** could be observed *via* ^{1}H-NMR spectroscopy. As discussed in Chapter 1 the *ortho*-fluorine substituents of the triarylborane reduces the ability to assume the resulting tetrahedral structure facilitating the adduct formation between sterically less demanding boranes and Lewis bases. To support this hypothesis borane **1h** was prepared and it was tested catalytically and stoichiometrically in the hydroboration of model substrate **2.1a** (Scheme 38).



*Scheme 38: Stoichiometric (top) and catalytic reaction (bottom) of **2.1a** and tris(3,4,5-trifluorophenyl)borane (**1h**) with HBpin (*NMR-conversion)*

Indeed **1h** showed excellent conversions in the hydroboration of the model substrate **2.1a** to give the desired amine **2.2a**. As seen with **1f** and BCF, **1h** initially forms an adduct with the imine when mixed in CD_2Cl_2 as observed *via* ^{11}B NMR spectroscopy. But only resembles the sterically less demanding borane **1f** in the follow up reaction with HBpin to form amine **2.2a**.

These results of this study can be summarised by the mechanism shown in Scheme 39.



*Scheme 39: Possible catalytic cycle of the hydroboration catalysed by **1f***

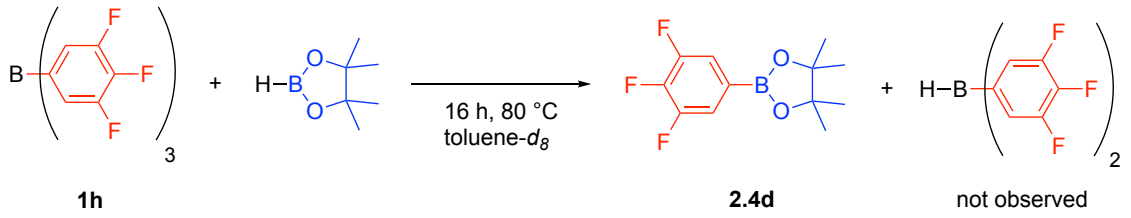
The initial step of the reaction is adduct formation between the borane catalyst and imine substrate to give **I**. This activated imine has a lower energy LUMO compared to the free

imine and a proximate HBpin molecule reduces adduct **I** *via* transition state **II**. The now weakened Lewis adduct **III** is replaced by an unreduced imine (**2.1**) to complete the catalytic cycle.

3.4 Summary & Outlook

To sum up the findings of this chapter, triarylboranes that are less hindered (i.e. lacking substitution in the *ortho* position), such as **1f** and **1h**, show reactivity in the hydroboration of imines where BCF fails. As discussed in Chapter 1, this is a "group B" Lewis acid mediated reaction where a complex is formed first between the Lewis acid and substrate and a second reagent then forms the desired product.

In further studies, it could be shown that heating up a mixture of HBpin and **1h** in toluene-d_8 to 80 °C for 12 h gives one of the products connected to the ligand metathesis described in Scheme 40 to form **2.4d**.



*Scheme 40: Ligand metathesis of **1f** with HBpin to form **2.4d***

This can indicate a further similarity to **1f** making **1h** also a possible pre-catalyst to reduce olefins by formation of the mono and di-substituted hydroboranes *in situ*. Further studies are ongoing in our group to look at using borane **1f** in metal-free catalytic hydroboration reactions.

4 Photophysical studies of $B(C_6F_5)_3$ imine adducts

4.1 Introduction

As discussed in Chapter 2 and 3, borane Lewis acids have been shown to form adducts with a variety of unsaturated moieties, including aldehydes, ketones, aldimines as well as ketimines.[51,67] The electron accepting ability of these trivalent boranes can induce large electronic dipoles, which are able to promote intramolecular donor-acceptor charge-transfer (ICT). There has been several examples showing this photochemical feature (Figure 5). [68–72]

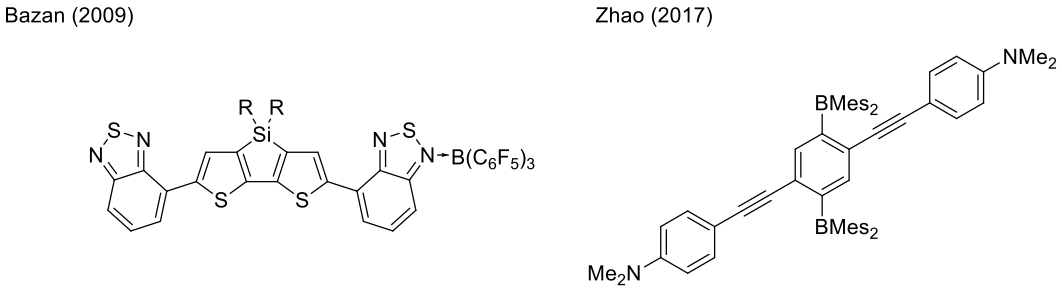
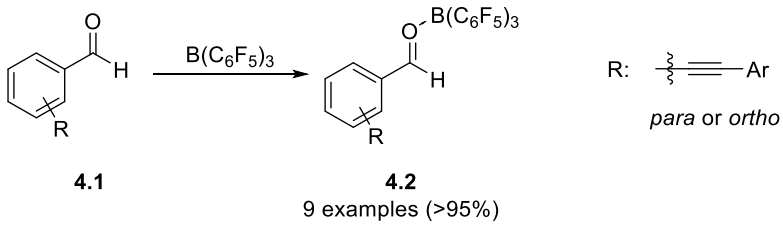


Figure 5: Borane containing compounds experiencing donor-acceptor ICT[68,72]

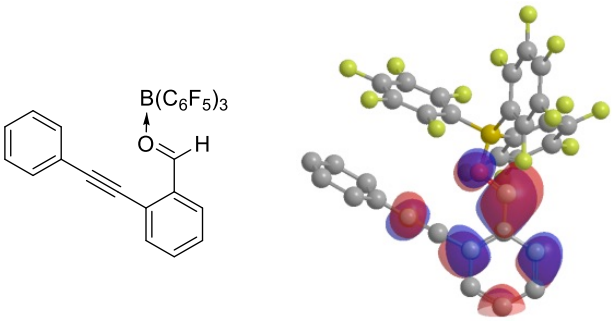
Bazan and co-workers showed that BCF causes modifications in the photoactivity of already photoactive molecules by forming strong Lewis acid/base adducts.[68] Recent findings by Nieto and co-workers showed that the interaction of BCF with tolane derivatives bearing a carbonyl moiety in *ortho*- or *para*- position (Scheme 41) has an effect on the photophysical properties of the aldehyde.[71]



*Scheme 41: Preparation of borane-carbonyl adducts **4.2** by Nieto et al.*

At low concentrations ($c \leq 10^{-5}$mol/l), a solution of these adducts **4.2** displayed the same photophysical features as the initial free aldehydes **4.1**. However, it was found that increasing the concentration would cause a new local maximum to arise in the UV spectrum. Exciting this new maximum revealed the emissive features of these adducts **4.2**. By modifying the Ar-substituent of **4.2** with electron donating and withdrawing moieties, a range of emission maxima from 437 nm to 613 nm could be created. Similar emission maxima were observed in the solid-state of adducts **4.2**. Nieto and co-workers attribute this new absorption band to a lowering in the LUMO level of the aldehyde **4.1** by formation of an adduct with BCF. The spatial distribution of this LUMO is concentrated

around the carbonyl-group showing the direct influence of the carbonyl-borane adduct formation (Figure 6).



4.2a

*Figure 6: Representation of the LUMO orbital of **4.2a** by DFT calculation* [71]

4.2 Aims of this work

These results encouraged us to probe the change of emission of these aldehyde-adducts with boranes (Figure 7) other than BCF to see how the steric and electronic effects of the borane alter the photophysical properties of the aldehyde. We were interested to see if there was an observable trend between the acidity of the borane and the emission maximum of the aldehyde-borane adducts.

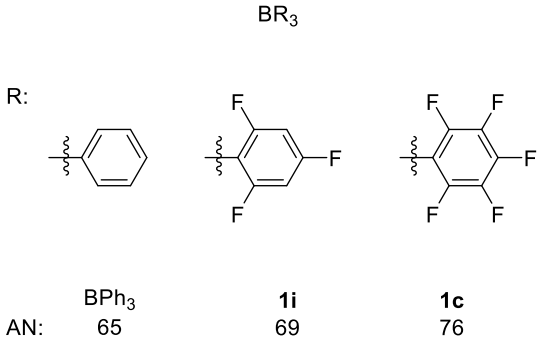


Figure 7: Boranes used to probe the aldehyde-borane adduct formation

4.3 Synthetic results

A variety of literature known aldehydes were synthesised and their ability to form adducts with the boranes in Figure 7 was investigated *via* ^{11}B NMR spectroscopy (Figure 8).

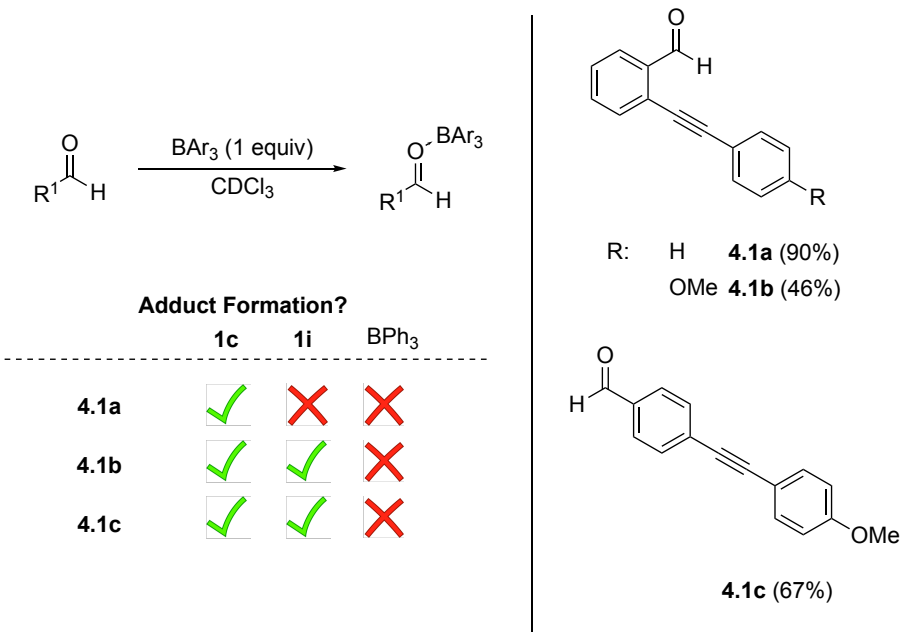
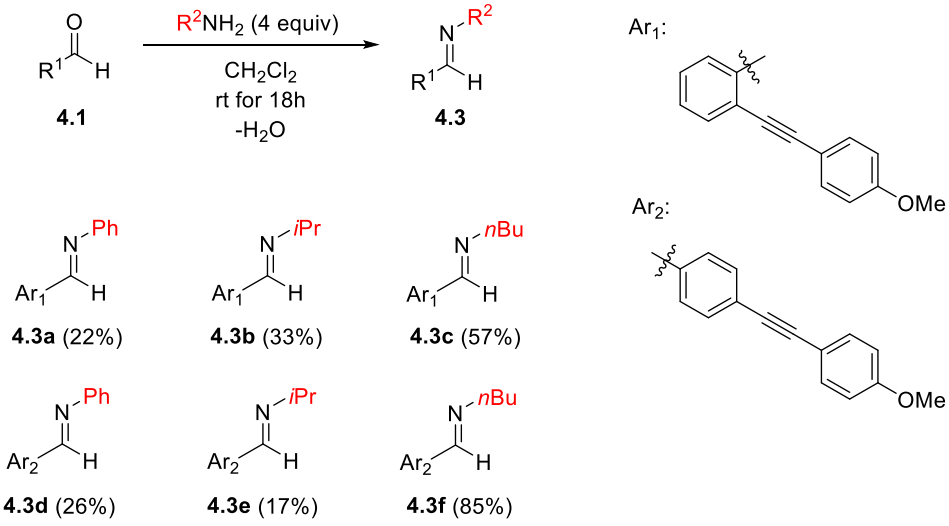


*Figure 8: Adduct formation of aldehydes **4.1** with **1c**, **1i** and BPh_3 (left) and synthesised aldehydes **4.1a-c** isolated yield in brackets (right)*

It was found that compound **4.1a** can only form an adduct with the strongest Lewis acid **1c** and a downfield shift was observed for the borane in the ^{11}B NMR spectrum upon adduct formation. Weaker Lewis acids BPh_3 and **1i** only showed ^{11}B NMR signals of the free acid indicating no adduct formation. The more Lewis basic and electron rich methoxy substituted compounds **4.1b** and **4.1c** could form an adduct with the less acidic borane **1i**, but again BPh_3 showed neither a shift in the ^{11}B NMR spectrum nor a visible change upon mixing aldehyde and borane in $CDCl_3$. To increase the donor ability and hereby facilitate the adduct formation with the weaker Lewis acid BPh_3, the aldehydes **4.1b** and **4.1c** were transformed to their corresponding aldimines with Ph, *i*Pr and *n*Bu-protecting groups (Scheme 42).



*Scheme 42: Synthesis of aldimines **4.2a-4.2f** via a condensation reaction*

All reactions gave the desired imine product. The low yields (17-57%) were attributed to the use of molecular sieves (3Å) in the synthesis, and the resulting difficulties in extraction for the purification. When the drying agent was changed to magnesium sulphate ($MgSO_4$) the isolated yield was increased to 85% (**4.3f**). As with the aldehydes, the imines **4.3** were tested towards their adduct formation with boranes **1c**, **1i** and BPh_3 *via* ^{11}B NMR spectroscopy (Figure 9).

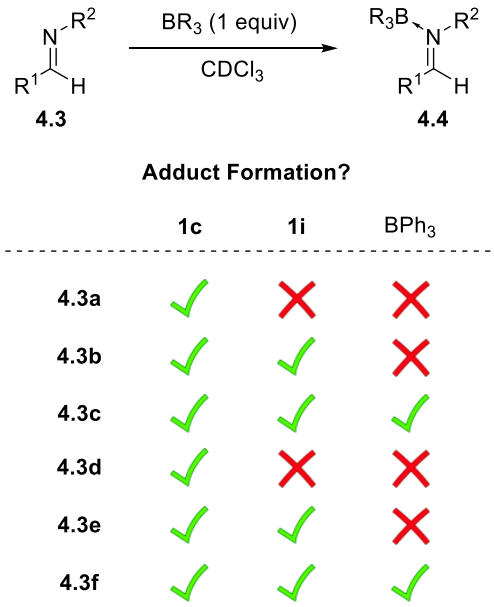
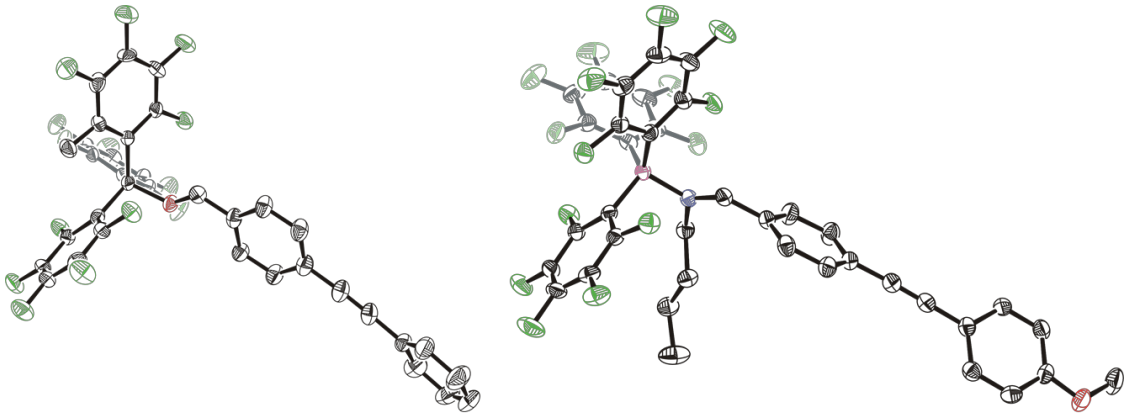


*Figure 9: Adduct formation of imines **4.2***

The *n*Bu-protecting group has the least steric demand of the synthesised imines **4.3**, and forms adducts with all three tested boranes regardless of whether the tolane derivative is *ortho* (**4.3c**) or *para* (**4.3f**) substituted. The sterically more demanding isopropyl group showed no adduct formation with BPh_3, the least acidic of the three boranes.[73] Compounds **4.3b** and **4.3e** shifted the singlet of **1c** and **1i** downfield in the ^{11}B NMR spectra upon mixing in $CDCl_3$, indicating the formation of an adduct in these cases. The sterically most demanding group of the three introduced protecting groups was the phenyl moiety. Here, only **1c** was able to form an adduct with the compounds **4.3a** and **4.3d** whereas both BPh_3 and **1i** showed no shift in the ^{11}B NMR spectra when added to a solution of imine in $CDCl_3$. To study the structural properties of this adduct further, compound **4.4a** was crystallised by slow evaporation of a saturated chloroform/hexane solution. The crystal structure is depicted in Figure 10.



4.2d **4.4a**

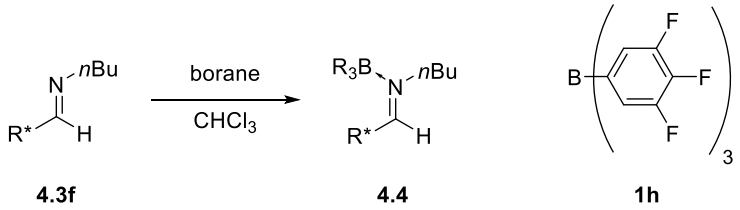
*Figure 10: Solid-state crystal structures of **4.2d** (left) and **4.4a** (right). Thermal ellipsoids set to 50% probability. H atoms omitted for clarity. C: black, N: blue, O: red, B: pink, F: green*

The crystal structure of **4.4a** proved to be the expected adduct. Compared to the initially reported BCF aldehyde adduct **4.2d**, the torsion angle between the two phenyl rings increased from 26.16° to 42.60°. This indicates that, at least in the solid-state, the system is not fully delocalised. The boron nitrogen distance is 1.613(3) Å and *ca.* 0.02 Å lower than similar motifs described in literature.[29] A typical covalent boron nitrogen bond is *ca.* 1.39 Å[74,75], which is much shorter than the observed distance in the crystal structures in Figure 10. The α-carbon of the protecting group has a distance of 3.00 Å to the neighbouring *carbon* atom of the (pentafluoro)phenyl group explaining why the more sterically demanding imines **4.3a** and **4.3d** were less likely to form adducts with the less Lewis acidic boranes **1i** and BPh_3.

4.4 Photophysical results

In preliminary studies, we compared the UV-vis spectra of imines **4.3c** and **4.3f** since both demonstrated promising adduct formation within the range of the tested triarylboranes. Both had two absorption bands around 300 nm. But only the UV-vis spectra of **4.3c** showed an additional peak at 390nm. Based on these results the borane imine adducts of **4.3f** were chosen for further studies to elucidate the solution-state electronic properties of these adducts *via* UV-vis absorption (Table 4, Figure 11), and luminescence spectroscopies (Table 5, Figure 16).

*Table 4: Absorption and molar absorptivity (ε) of imine **4.3f** and various borane adducts*



4.3f **4.4** **1h**

Borane	Compound	Absorption/nm (ε/$dm^3 \cdot mol^{-1} \cdot cm^{-1}$)			
none	**4.3f**	313 (29,800)	329* (24,200)		395 (4,000)
BPh_3	**4.4b**	281 (46,300)	308* (22,300)	329* (17,000)	390 (14,000)
1i	**4.4c**	312 (28,600)	328* (23,000)		387* (10,000)
1c	**4.4a**	312 (24,500)	330* (13,200)		397 (7,400)
1h	**4.4d**	294 (32,800)	317* (19,100)	332* (16,800)	381 (16,800)
$BF_3 \cdot OEt_2$	**4.4e**	317 (21,300)	332* (18,000)		401 (14,000)
BCl_3	**4.4f**	289 (44,300)			399 (23,900)
BBr_3	**4.4g**	289 (54,200)			402 (24,000)

*: Shoulder

An increase in molar absorptivity of the lowest energy band could be observed in all adducts **4.4** compared to the free imine (Figure 11).

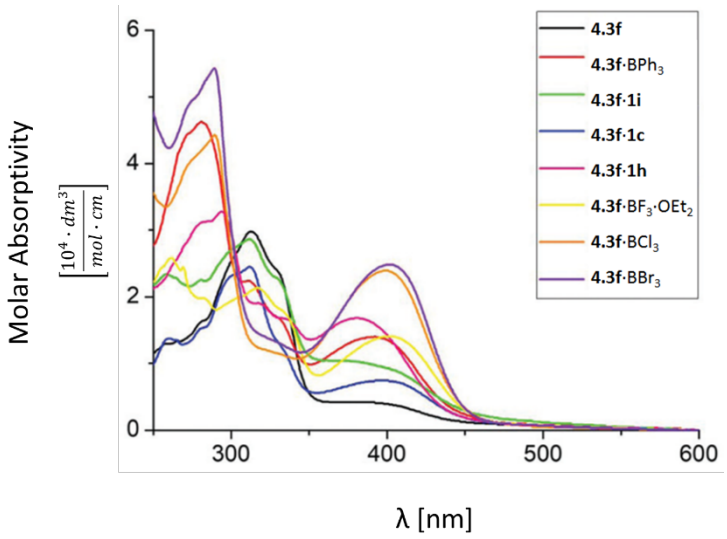


*Figure 11: UV-vis absorption spectra of **4.3f** and its adducts **4.4** in $CHCl_3$ solution*

This increase in molar absorptivity was most pronounced in **4.4g**. In luminescence studies, these solutions were excited at 330 nm and 400 nm correlating with the two absorption bands. While the excitation at 330 nm gave two emission peaks at around 380 nm and 500 nm, excitation at 400 nm only yielded the lower energy emission at around 500 nm. The results of the energetically lower excitation are displayed in Figure 12.

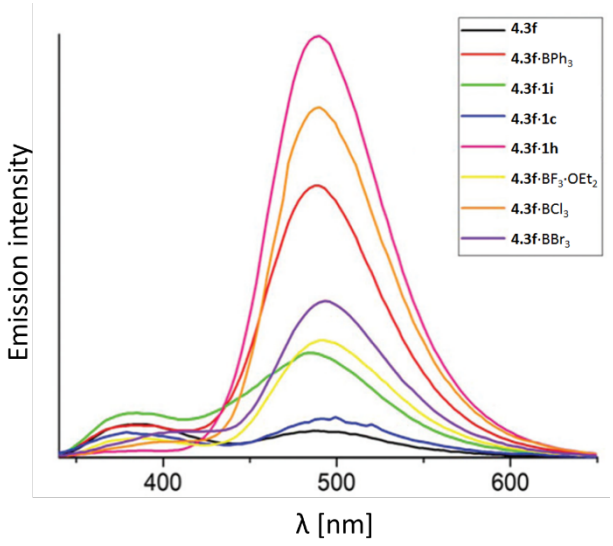


*Figure 12: Steady-state emission spectra of **4.3f** and adducts in $CHCl_3$ solution (λ_{ex}=330 nm, c=10^{-5} M)*

The emission intensity clearly increases upon adduct formation (Figure 12), and the highest intensity is observed with adduct **4.4d**. Here, the boranes that are more sterically hindered or less favourable towards tetrahedral configurations **1i**, **1c** and BF_3, form adducts with lower emission intensities compared to borane imine adducts of **1h**, BCl_3, BBr_3. A reason why the adduct of **1h** and imine **4.3f** has the highest intensity can be explained by the presence of heavier halogens on the boron halides (BBr_3 & BCl_3). These

heavier halogen moieties facilitate intersystem crossing that leads to an excited triplet state. With emission from the triplet state being slow it is highly quenched by other processes.[76] That may also be the reason why the emission intensity of adduct **4.4g** is lower than **4.4f**. In Table 5 the numerical values of the emission maxima are listed.

*Table 5: Steady-state emission maxima of **4.3f** and its adducts **4.4***

Borane	Compound	Emission/nm
none	**4.3f**	490
BPh_3	**4.4b**	491
1i	**4.4c**	493
1c	**4.4a**	501
1h	**4.4d**	490
$BF_3{\cdot}OEt_2$	**4.4e**	496
BCl_3	**4.4f**	493
BBR_3	**4.4g**	495

With both the lowest energy absorption and emission band in hand the direct relation of bathochromic or hypsochromic shift *versus* Lewis acidity determined by the Gutmann-Beckett method could be plotted (Figure 13). With compound **4.3f** the acceptor number of the solvent $CHCl_3$ is visualised instead.[5]

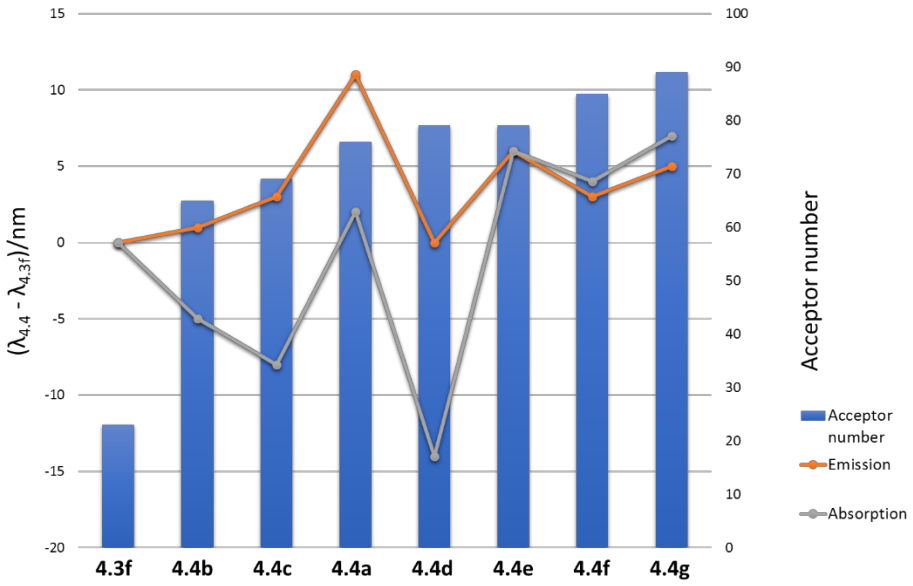


*Figure 13: Difference in the lowest energy absorption and emission band of **4.3f** and adducts **4.4** and the acidity of the respective borane*

To represent these shifts, the difference of the lowest energy absorption and emission band between adduct **4.4** and free imine **4.3f** was formed. These two values are plotted against the acceptor numbers of boranes in adducts **4.4**. In Figure 13, no trivial trend can

be observed, indicating that the change in absorption and emission is dependent upon various factors.

As already mentioned, adducts **4.2** displayed photophysical activities only at concentrations over 10^{-5} mol/l. Literature attributes the concentration dependency with the formation of dimers of **4.2** that are the actual active species.[71] Adducts **4.4** demonstrate activity even below this concentration and it could be argued that even monomers of **4.4** are photophysically active.

Additionally, solvatochromic studies revealed a clear sensitivity of the emission band at 500 nm towards solvent polarity and, among the tested solvents, the least polar hexane displayed the most hypsochromical shift (Figure 14). This sensitivity to the polarity of the solvent can therefore be assigned to a transition with a significant intramolecular charge transfer contribution.

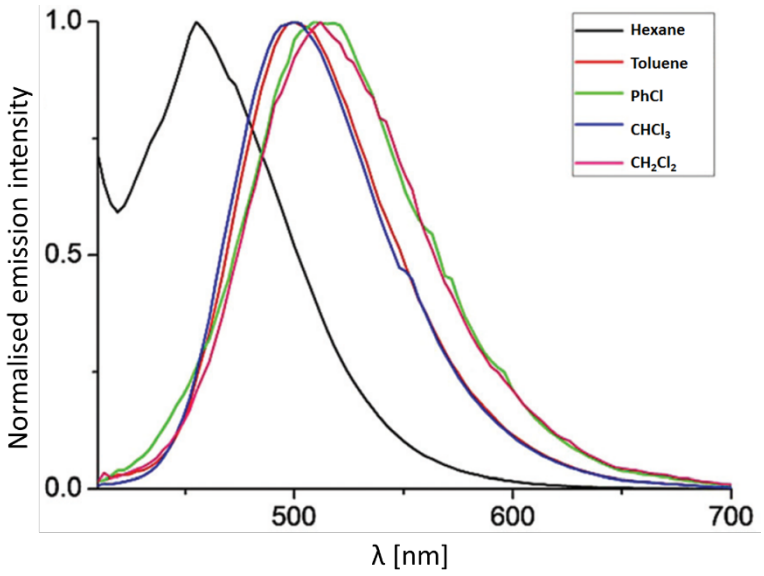


*Figure 14: Solvatochromic fluorescence spectra of **4.4f** (λ_{ex}=400 nm)*

The stability of adduct **4.4a** towards air was further studied and after exposing a solution of **4.4a** in $CHCl_3$ to air for 10 minutes the fluorescence intensity of the charge transfer emission band at 500 nm was observed over time. Interestingly, even after 2 h there was still half of the emission intensity detectable (Figure 15).

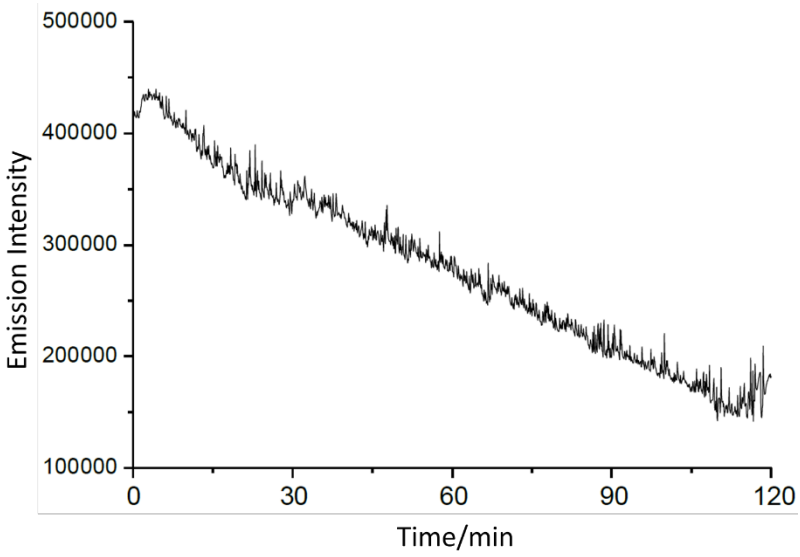


*Figure 15: Time based steady-state emission plot of a 10^{-5} M solution of **4.4a** in $CHCl_3$ (λ_{ex}=400 nm, λ_{em}=500 nm)*

Within these studies the solid-state stability towards light, air and moisture as well as the solvatochromic fluorescence changes encouraged us to further explore the application of this species as a potential vapochromic material. These materials change colour upon exposure to volatile organic compounds, offering a low-cost technology for the detection of analytes.[77] The initial solid-state film fluorescence spectra of both **4.3f** and **4.4a** are clearly distinguished from each other and **4.4a** only shows emission at the lowest energy band even when exited at 330 nm (Figure 16). Both emission maxima experience a bathochromic shift compared to their respective chloroform solutions.

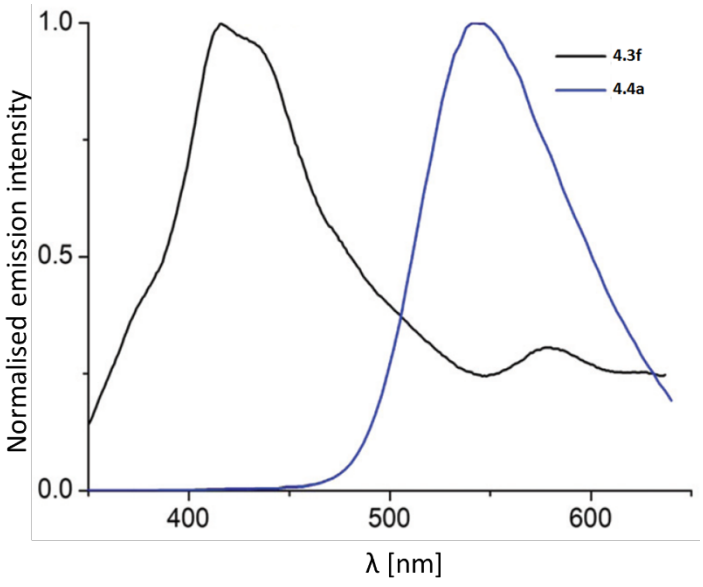


*Figure 16:Solid-state film fluorescence spectra of **4.3f** and **4.4a** (λ_{ex}=330 nm)*

4.5 Vapochromic results

To test the vapochromic potential towards various solvents, a 25 mM solution of **4.4a** was prepared and thin filter strips were impregnated with **4.4a** and dried under vacuum. These strips were suspended in a vial over various undried solvents and the change in fluorescence of these strips was recorded photographically when excited at 365 nm (Figure 17).

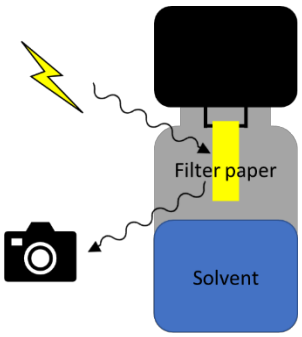


Figure 17: Experimental setup for the vapochromic studies (λ_{ex}=365 nm)

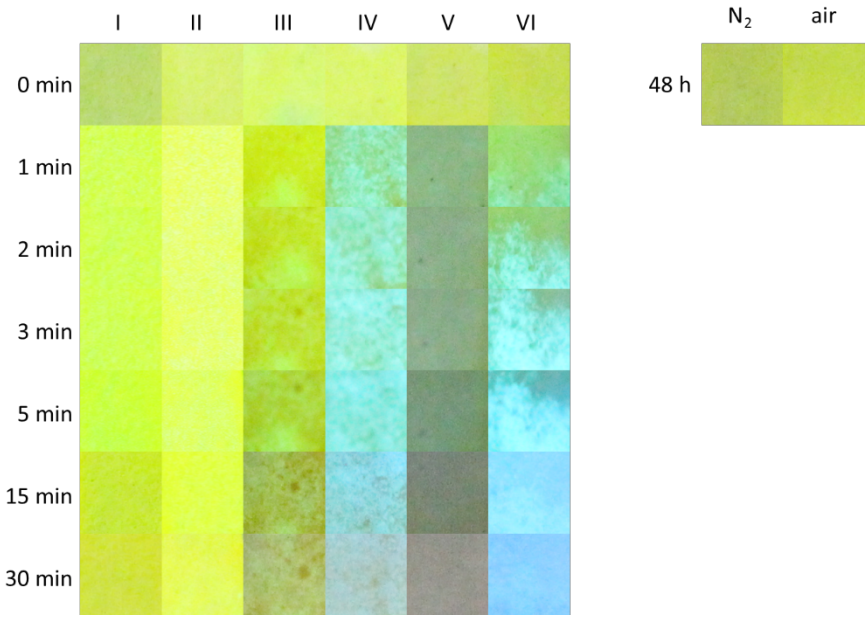


*Figure 18: Photographical results of the setup described in Figure 17 with **4.4a** permeated filter strips excited at 365 nm (I) none (II) hexane (III) toluene (IV) Et_2O (V) THF (VI) methanol (MeOH)*

The blank sample depicted in Figure 18 (**I**, left) is in a closed vial under a nitrogen atmosphere. A second sample was left out to further probe the stability of these adducts towards air and moisture but even after 2 days there is hardly any difference observable between these two samples (Figure 18, right). As expected, hexane (**II**) as the weakest Lewis base alters the colour of the fluorescence the least in the first 30 min. Toluene (**III**) quenches the intensity of the fluorescence, but still the yellow-green colour of the initial adduct is visible after 30 min. Here π-π interaction between the solvent and the imine

could create more non-radiative relaxation pathways, thereby quenching the fluorescence intensity of the filter strips. The more coordinating aprotic solvents (**IV**) and (**V**) have a stronger influence on the filter strips colour. The better donor THF quenches most of the visible fluorescence after 5 min. Et_2O first turns the strips into a blue colour that resembles the emission wavelength of the free imine suggesting **IV** is forming an adduct with **1c** and breaking the adduct **4.4a**. With **VI** the same trend can be observed within the first 5 minutes but after 30 min the colour turns into a slightly darker blue. In an attempt to gain deeper insight into these processes the solvent vial was replaced with a dry vial and the changes were monitored (Figure 19).

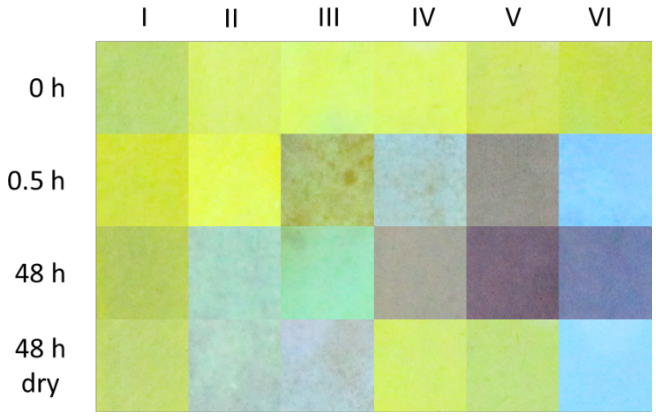
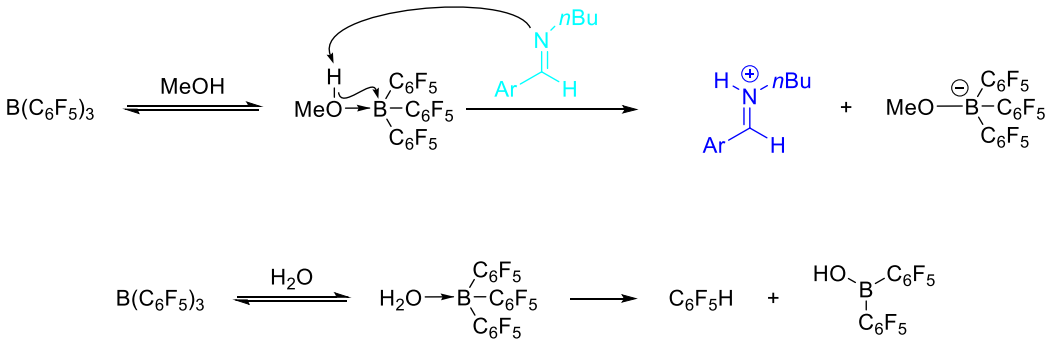


Figure 19: Photographical results of the filter strips over time (λ_{ex}=365 nm) (I) none (II) hexane (III) toluene (IV) Et_2O (V) THF (VI) MeOH

Surprisingly, after being quenched by the solvent vapor the fluorescence of **IV** and **V** were the quickest recover to the original adduct color after drying the strips. This suggests the adduct between **4.3f** and **1c** was reformed after evaporation of the coordinating solvent. With methanol there is observed fluorescence, but the blue colour implies that reformation of the initial imine-borane adduct does not take place.

4.6 Discussion of vapochromic results

Parkin and co-workers could show that an adduct of **1c** and water has the same acidity in acetonitrile (MeCN) as hydrochloric acid making it incompatible with bases which irreversibly deprotonate the adduct to give the corresponding hydroxytriarylborate ($HOBAr_3$).[78] With **VI** being a protic solvent this deprotonation of the adduct of methanol and **1c** by the imine could also be an explanation for the slight change in the blue colour after 30 mins compared to the light blue after 5 mins (Scheme 43).



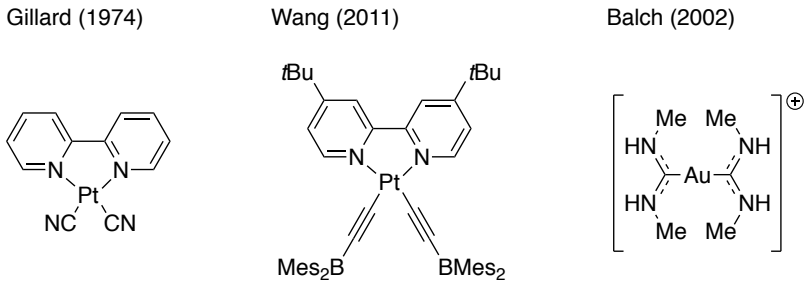
*Scheme 43: Possible decomposition pathways of **4.4a** with methanol (top) and **1c** with water (bottom)*

Compared to the coordinating solvents, the non-coordinating solvents (Figure 19, **II** and **III**) cannot recover the lost fluorescence here. The inability to form an adduct with **1c** makes the unprotected borane more susceptible to attacks from moisture present in the undried solvents (Scheme 43, bottom).

4.7 Summary & Outlook

In conclusion, a number of imines **4.3** could be synthesised, and their borane adducts **4.4** were characterised spectroscopically. The sterically least demanding *n*Bu-protecting group proved to be the most promising in terms of adduct formation. The ICT character of this electronic transition could be identified and the stabilisation by the borane increased the intensity the lowest energy emission and absorption band. The stability of the adduct **4.4a** especially in the solid-state allowed the exploration of the vapochromic properties with a small range of solvents. The results suggest that these adducts indeed could be used to design new vapochromic materials by tuning the charge transfer fluorescence properties.

After understanding this vapor induced phenomenon on a mechanistic level these materials could be utilised to detect volatile organic compounds. Here, an optimised borane-imine adduct could form the base of a sensor to detect and differ between different solvent vapors. This would give an alternative to absorbing the vapors onto an absorbent for later extraction and chromatographic analysis, making this process faster and more cost efficient.



Scheme 44: Gold and platinium based vapochromic materials described in literature.[79–81]

Also most of the literature known vapochromic materials (examples in Scheme 44) have a metal center with the majority being Pt(II) or Au(I) based[77], making this metal-free alternative even more cost effective.

5 $B(C_6F_5)_3$ promoted cyclisation of substituted alkynyl esters, ethers, and acids

5.1 Introduction

Lactones are omnipresent structures in naturally occurring or biologically active compounds. Within this group pyrones, isocoumarins and dihydropyrones are a reoccurring motive (Figure 20).[82,83]

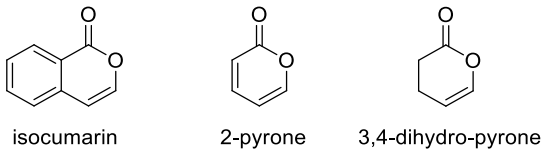


Figure 20: Examples of lactones

They find uses in many pharmaceutical compounds as antiviral[84], anti-inflammatory[85], antibiotic[86], and antispasmoidic[87] drugs. They possess purgative properties[88] and have proven to be effective antimicrobial agents.[89,90] Also, these compounds are considered nonsteroidal antagonists to enzymes and display affinity to enzymes like the androgen receptor[91] (AR), a DNA-binding transcription factor controlling development and maintenance of the male sexual phenotype. Another example is the pregnane X receptor[92] (PXR) a nuclear receptor whose primary function is to sense the presence of foreign toxic substances. Notably, 2-pyrones have proven to be effective inhibitors for enzymes like the HIV-1 protease[93] essential for the viral replication in the HI-virus and serine proteases[94]. Displayed in Figure 21, is thunberginol A, an immunosuppressant isocoumarin derivative, that can be extracted from fermented leaves of *Hydrangea macrophylla* (Figure 21).[95]

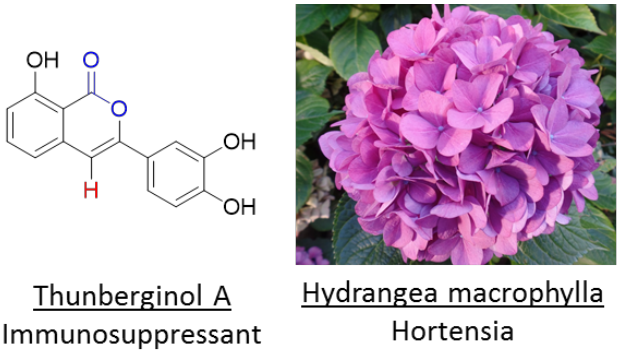
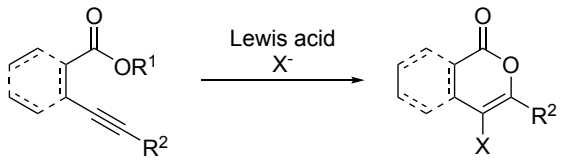


Figure 21: Structure of Thunberginol A (left). Picture of hydrangea macrophylla (right)

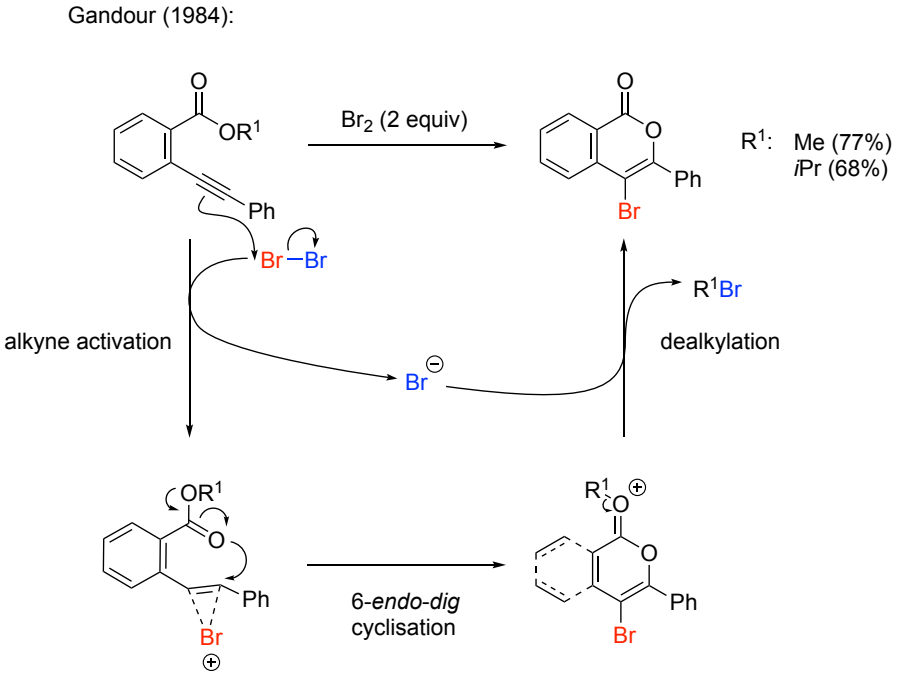
With ubiquitous applications, the synthesis of these heterocycles is of great interest. Literature has provided many intermolecular examples such as the ring expansion of β-lactones or metal catalysed cascade reactions of propiolic acids or esters with alkynes.[96,97] Another well studied approach is an inverse Diels-Alder-type reaction

described by Boger, Mullican and Yamashita.[98,99] Here, we will discuss a Lewis acid promoted intermolecular cyclisation of alkynyl esters (Scheme 45).



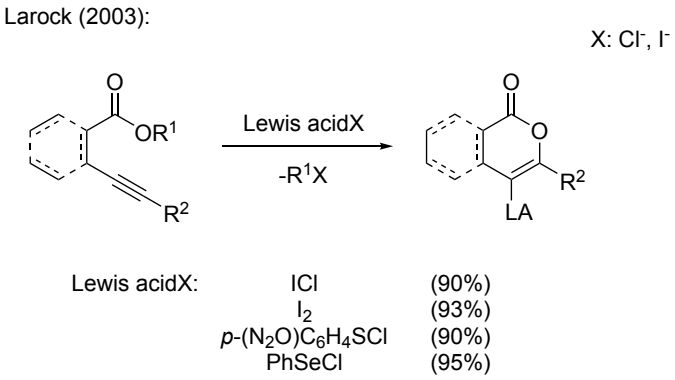
Scheme 45: Intermolecular cyclisation of alkynyl esters promoted by Lewis acids

First reports by Gandour and co-workers in 1984 utilised *in situ* generated bromonium ions to promote this 6-*endo-dig* cyclisation.[100] The Lewis basic bromide anion formed in the generation of the cation promotes the abstraction of the alkyl ester group R^1 (Scheme 46).



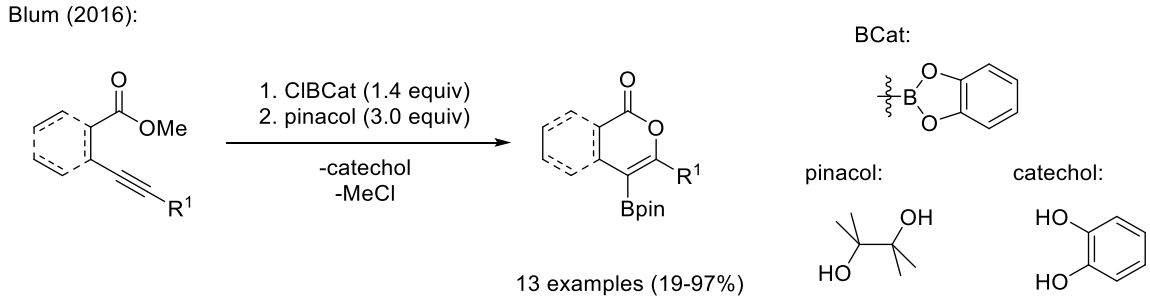
Scheme 46: Bromine promoted cyclisation of alkynyl esters by Gandour and co-workers

Larock *et al.* expanded this scope by utilising various *p*-block Lewis acids in agreement with the mechanism proposed by Gandour (Scheme 47).[101]



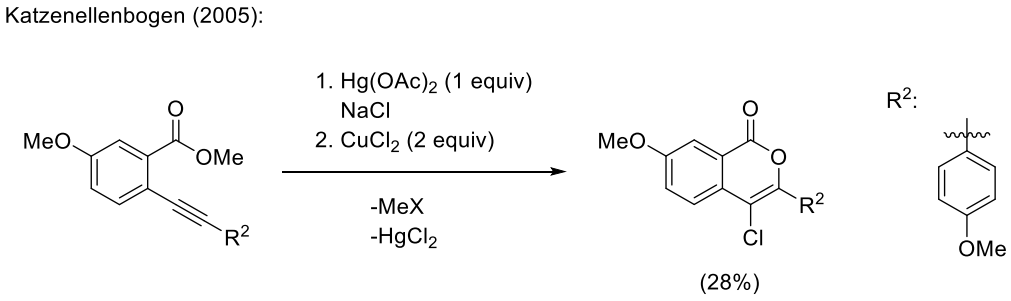
Scheme 47: Chloro-oxycarbonylation by Larock and co-workers

One of the latest examples of this non-metal promoted cyclisation with a consecutive dealkylation by a halide anion was described by Blum and co-workers (Scheme 48).[102]



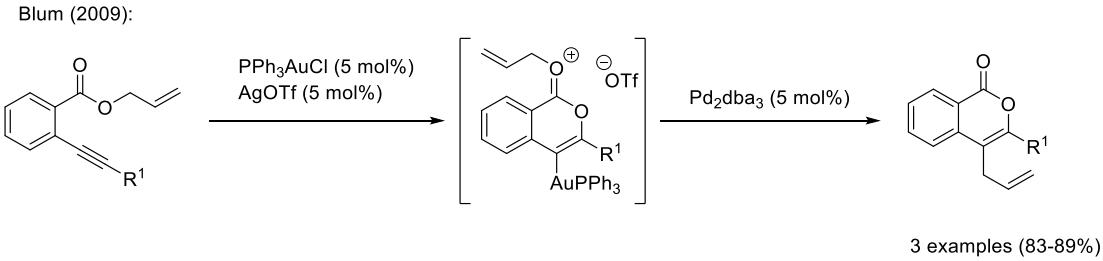
Scheme 48: Stoichiometric reaction of alkynyl esters with B-chlorocatecholborane

Again, this stoichiometric reaction between B-chlorocatechol borane and alkynyl ester is in agreement with the mechanism described by Gandour and Larock. One of the few examples of a stoichiometric transition metal promoted cyclisation was accomplished by Katzenellenbogen and co-workers (Scheme 49).[103]



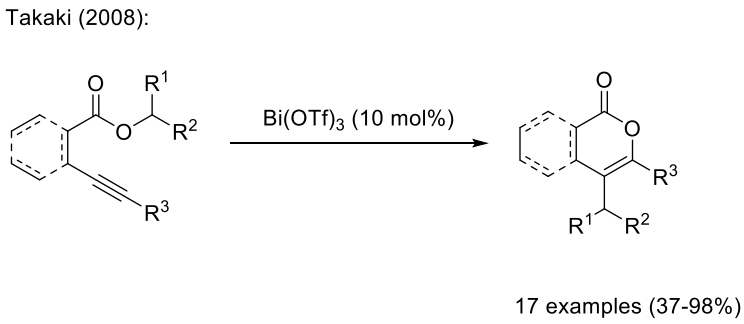
Scheme 49: Mercury(II)acetate promoted cyclisation by Katzenellenbogen et al.

Like the stoichiometric reactions described previously, a soft Lewis acid $HgOAc_2$ is used to promote the 6-*endo-dig* cyclisation, resulting in an isocoumarin derivative with a mercury chloride in the 4-position. Here two equivalents of copper chloride are used in a reaction with the isocoumarin mercurial to give the desired product. Catalytic examples are rare, however the Blum group has described a dual catalytic system (Scheme 50).[104]



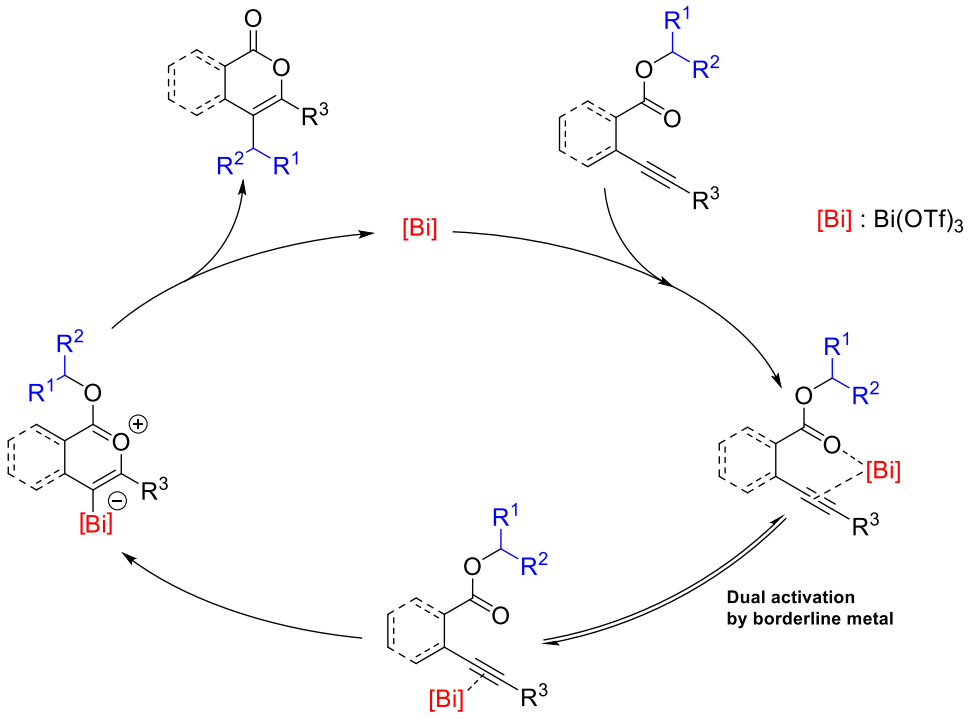
Scheme 50: Catalytic carbo-oxycarbonylation described by Blum et al.

Instead of using a base to dealkylate the cationic intermediate, Blum utilises a secondary palladium catalyst that selectively complexes the allylic ester groups, and a subsequent carbodemetallation forms the final product. Another approach by Takaki and co-workers uses catalytic amounts of bismuth triflate to cyclise the alkynyl ester starting material (Scheme 51).[105]



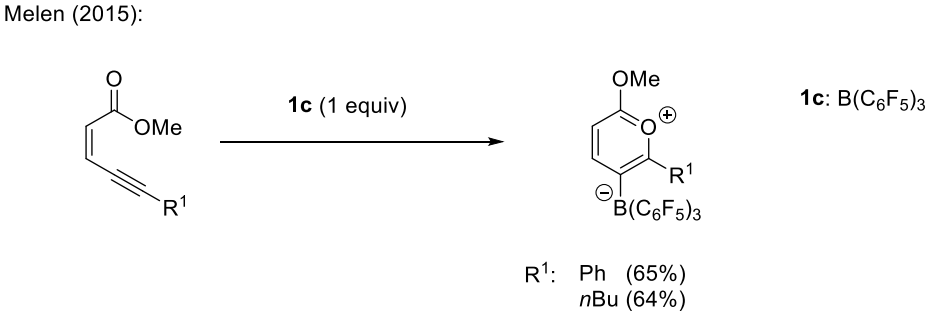
Scheme 51: Bismuth catalysed reaction by Takaki et al.

These α-substituted benzyl esters form a zwitterionic cyclised bismuthate intermediate, which is then replaced by the ester group *via* an intramolecular 1,5-migration (Scheme 52).



Scheme 52: Mechanism postulated by Takaki and co-workers

It should be noted that the uncyclised esters can be activated *via* a σ-activation of the carbonyl group and *via* a π-activation at the unsaturated carbon-carbon bond. The other examples utilised soft Lewis acids to activate the soft Lewis basic centre. In contrast, Takaki describes an initial dual activation of both the carbonyl, as well as the alkyne group, almost using the oxygen-atom as a directing anchor to bring bismuth in the vicinity of the olefinic bond.

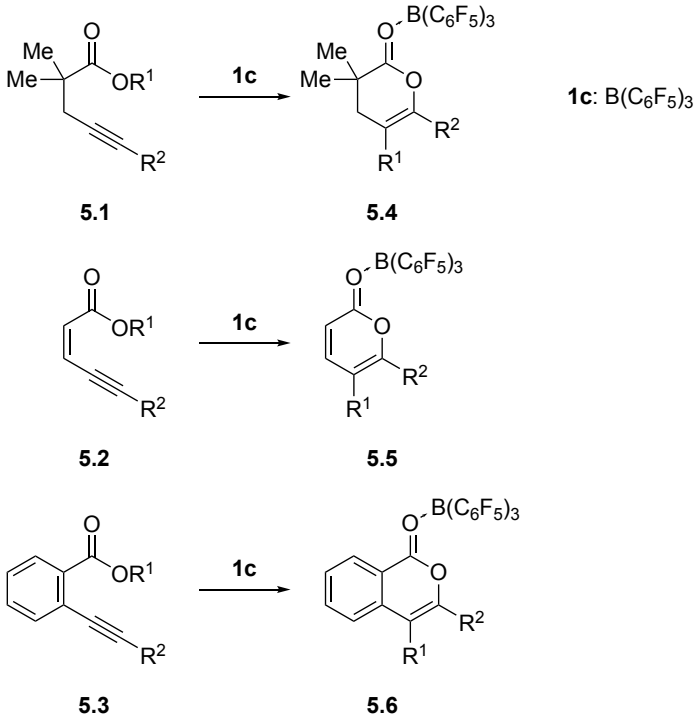


Scheme 53: Reaction by Melen et al. to generate pyrylium borate zwitterions

Initial results within our group showed that BCF is capable of the initial π-activation, but without an additional base to abstract the alkyl-ester group, the product of these cyclisations is a stable zwitterionic pyrylium borate and no catalytic turnover is possible (Scheme 53).[106]

5.2 Aim of this work

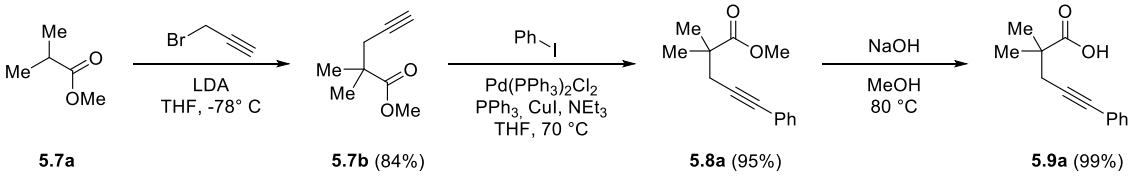
Inspired by the work of Takaki[107] and co-workers the aim of this work was a BCF promoted cyclisation of esters and acids and if possible to reintroduce the liberated borane into the reaction cycle and make this a catalytic reaction (Scheme 54).



*Scheme 54: Cyclisation reactions promoted by **1c** studied in this chapter*

5.3 Synthesis of the starting material and their reaction with $B(C_6F_5)_3$

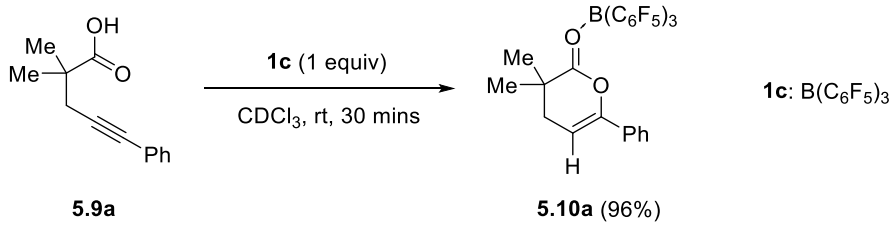
To study the reactivity of BCF towards varying ester groups within these alkynyl esters, access to their free acids was crucial. Here **5.1** was chosen as the model backbone to probe the reactivity described in Scheme 54.



*Scheme 55: Synthetic route to free acid **5.8***

In accordance with a literature procedure,[105] methyl isobutyrate **5.7a** was deprotonated with lithium diisopropylamide (LDA) and an ensuing reaction with 3-bromopropyne yields ester **5.7b** in 84% yield. The terminal alkyne **5.7b** is then cross coupled to an aryl halide *via* a Sonogashira type protocol to give methylester **5.8a** and is then saponificated using sodium hydroxide in methanol to yield the desired product **5.9a** in excellent yields (99%) (Scheme 55). Here, first studies revealed that stoichiometric amounts of BCF are

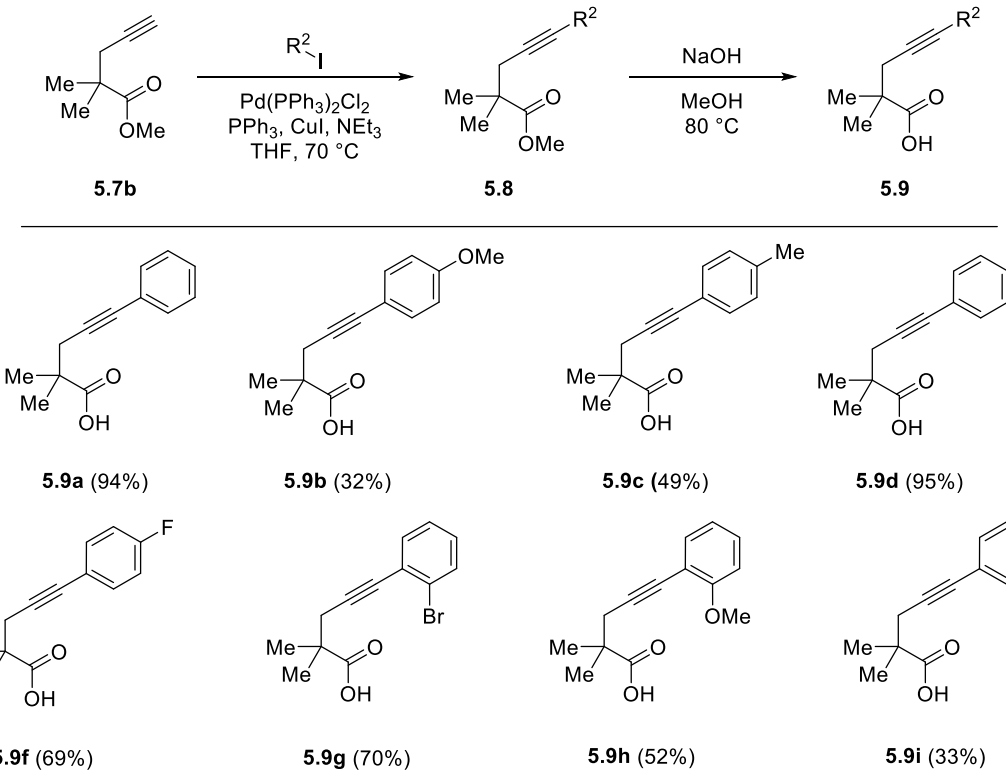
capable to cyclise free acids **5.9** (Scheme 56). This is unusual as typically boranes are unstable with respect to acidic substrates (See Chapter 4).



5.9a **5.10a** (96%)

*Scheme 56: Hydro-oxycarbonylation of **5.9a** promoted by BCF*

This reactivity in Scheme 56 encouraged us to synthesise a scope of free acids **5.9** to see the limitations of this hydro-oxycarbonylation (Scheme 57). Generally, the yield in the saponification step of this reaction was excellent, the electron rich *ortho* (**5.9h**) and *para* (**5.9b**) methoxy substituted acids showed a drop in yield in the first step of the reaction though. This trend could be further observed with compound **5.9c** with an electron donating methyl group in *para* position. 1-Naphtyl substituted acid **5.9i** showed a drop in conversion in the first step yielding 33% of the desired product. Electron neutral (**5.9a**) as well as electron deficient systems **5.9d**, **5.9f** and **5.9g** gave good to excellent yields between 69 and 95% over both steps of the reaction.



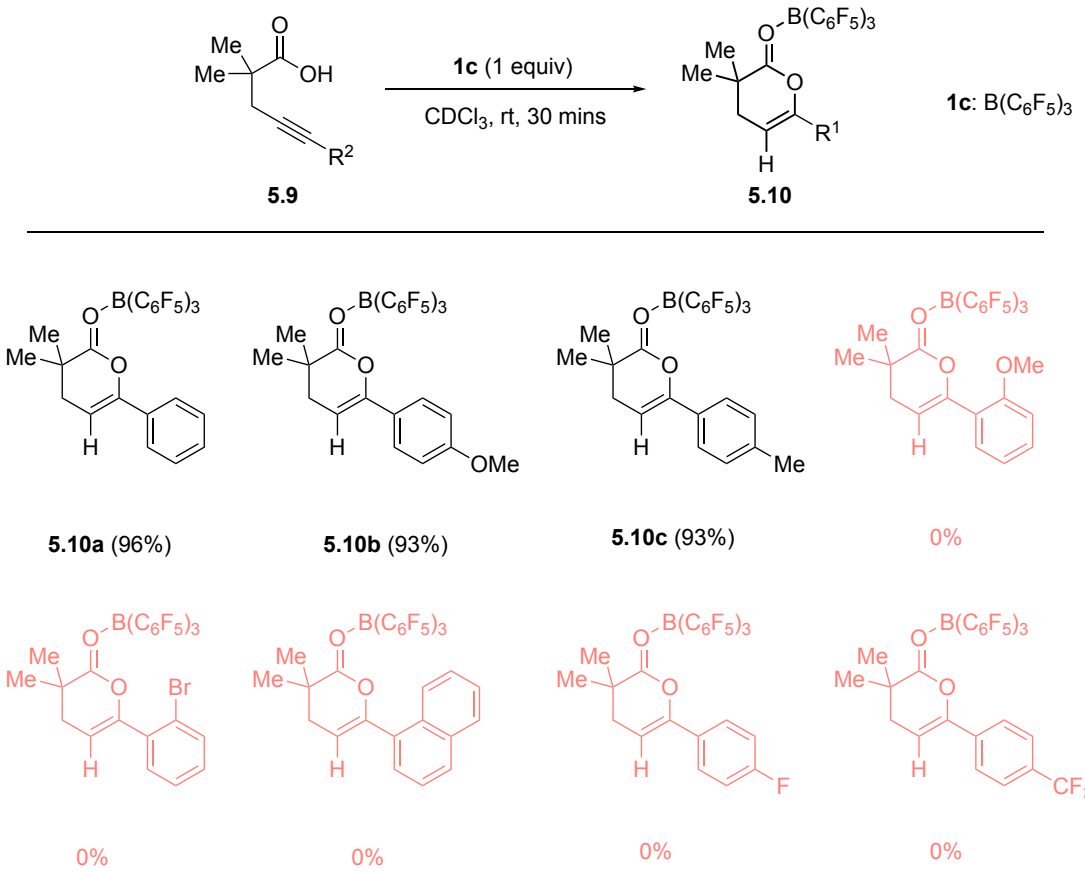
5.7b **5.8** **5.9**

5.9a (94%) **5.9b** (32%) **5.9c** (49%) **5.9d** (95%)

5.9f (69%) **5.9g** (70%) **5.9h** (52%) **5.9i** (33%)

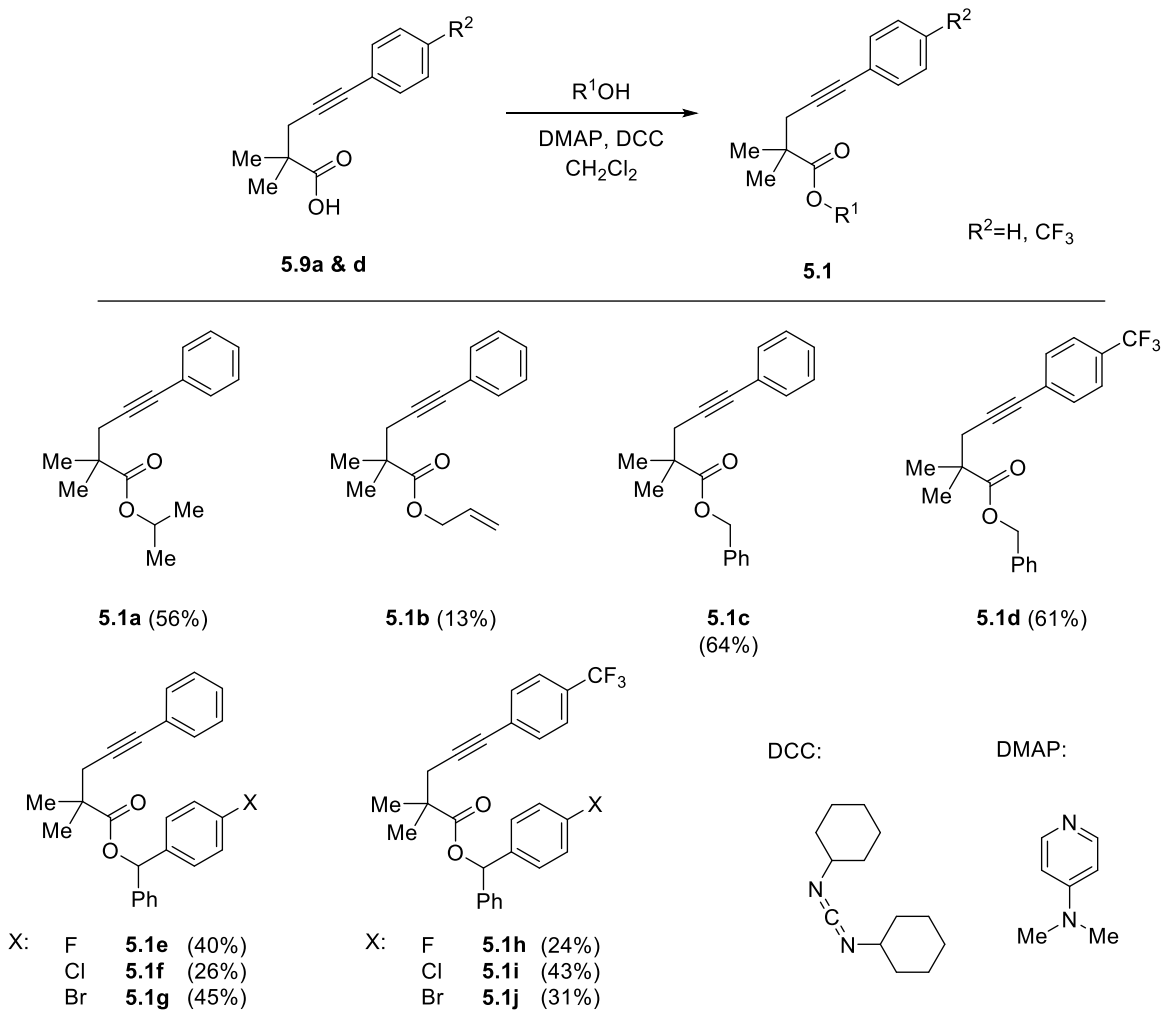
*Scheme 57: Scope of synthesised carboxylic acids **5.9.** Isolated yield after 2 steps in brackets*

With a range of acids to hand, these were reacted with stoichiometric amounts of BCF in $CDCl_3$ at room temperature (Scheme 58).



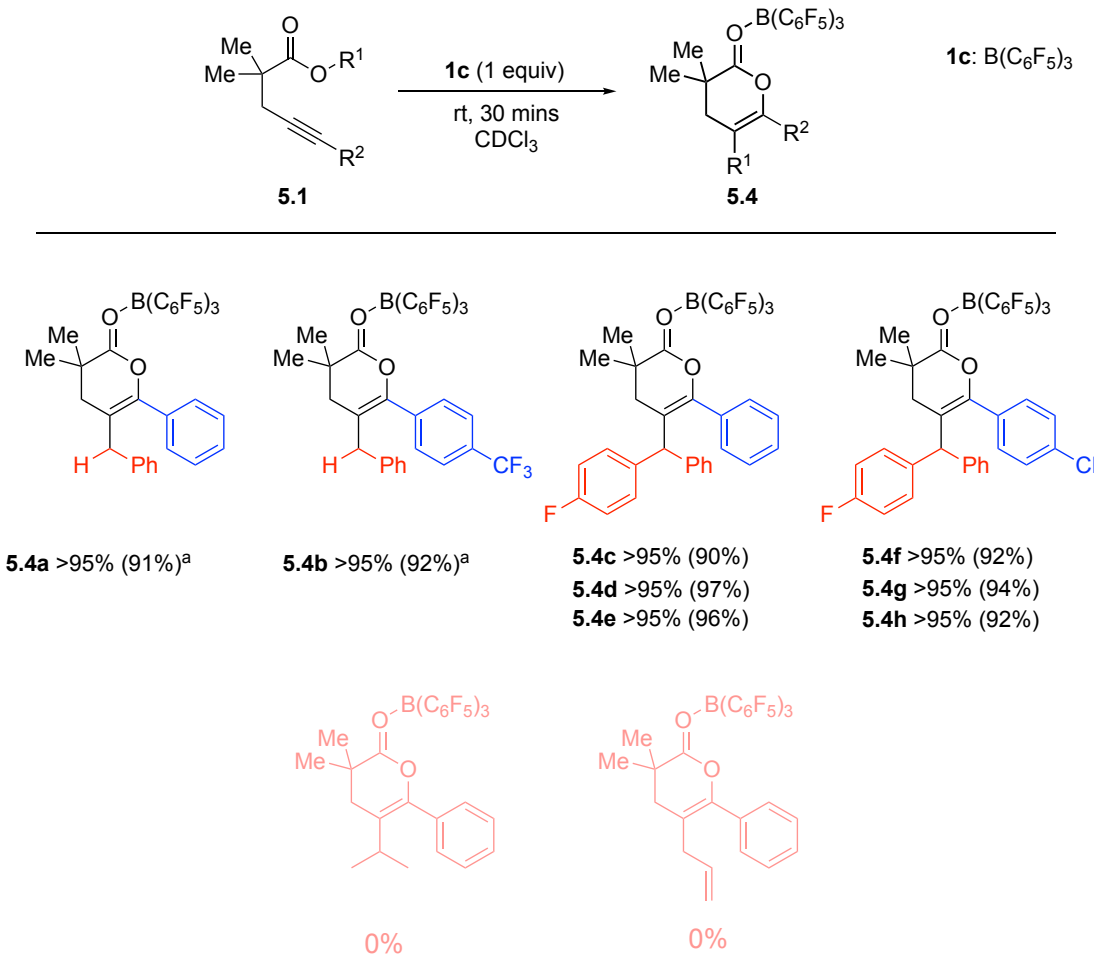
*Scheme 58: Reaction of synthesised acids **5.9** to give dihydropyrone derivatives **5.4**. Isolated yield in brackets.*

In Scheme 58 clear trends are observable. In the *ortho* position substituted carboxylic acids **5.9g**, **5.9h** and **5.9i** do not give the desired product, so a steric demand close to the triple bond is responsible for the hindrance in this borane promoted cyclisation. Also, reducing the electron density in the phenyl ring with a fluoride (**5.9f**) or trifluoromethyl (**5.9d**) substituent in the *para* position quenches the reactivity of the free acid towards this Lewis acid promoted cyclisation. Following this we then turned out attention to ester starting materials. In an esterification step, acids **5.9a** and **5.9d** were reacted with various alcohols. Groups able to stabilise a carbocation were introduced to see if this showed an increase in reactivity, especially for the more deactivated esters of **5.9d**, that did not show any activity towards BCF as a free acid (Scheme 59).



*Scheme 59: Steglich esterification of acids **5.9a** and **5.9b** with various alcohols. Isolated yields in brackets. DMAP: 4-Dimetylaminopyridine, DCC: N,N'-Dicyclohexylcarbodiimide*

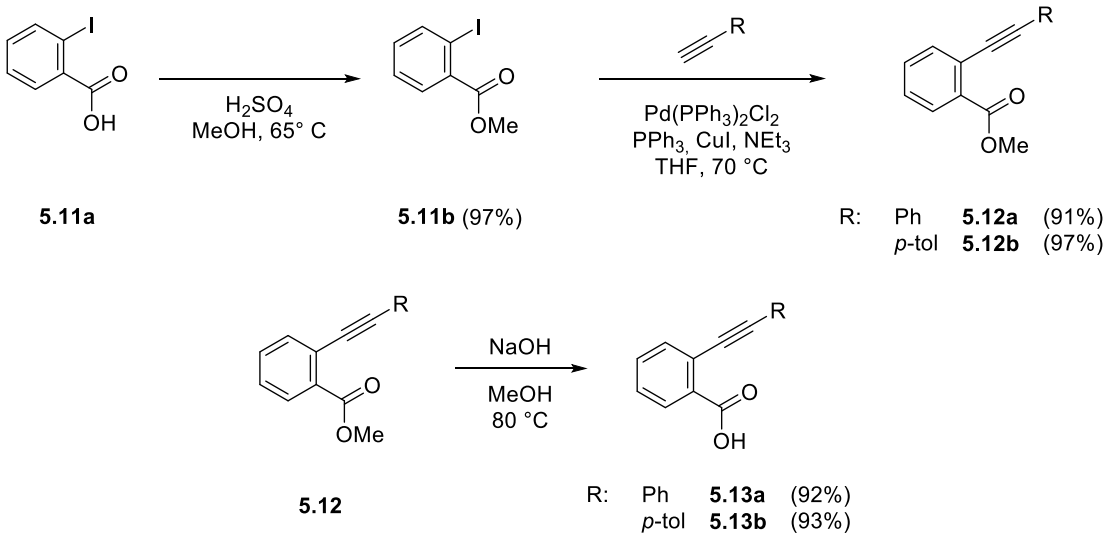
The Steglich[108] esterification was used to introduce alkyl (**5.1a**), allyl (**5.1b**), benzyl (**5.1c** and **5.1d**) and benzhydryl (**5.1e-j**) ester groups. The yield of this esterification step is between 13% and 64% and esters **5.1a-j** could be isolated. Again, in a stoichiometric reaction with BCF the reactivity of these different ester groups was tested (Scheme 60).



*Scheme 60: Stoichiometric cyclisation reaction of esters **5.1** to give dihydropyrones **5.4**. NMR conversion with isolated yields in brackets [a]24h reaction time*

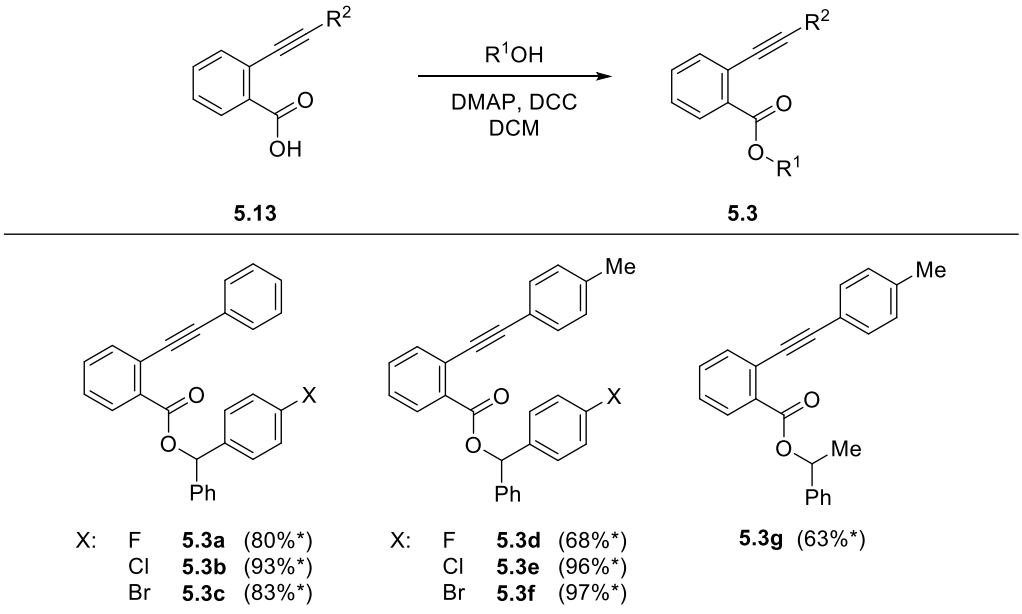
It can be shown that the isopropyl ester **5.1a**, with only a positive inductive effect, does not show any reactivity towards BCF. Also, the allyl group that could stabilise a possible cationic leaving group with only one resonance structure does not yield the desired product. Benzyl esters **5.1c** and **5.1d** did form the desired esters after 24 h reaction time with excellent yields. The best performance was displayed by the benzhydryl derivatives **5.1e-j** with reaction times of 30 mins. Interestingly, trifluoromethyl-substituted esters **5.4b** and **5.4f-h** did give similar results to the less electron deficient esters **5.4a** and **5.4c-e**, indicating that an increase in the stability of the leaving group increases reactivity towards BCF to the otherwise non-reactive carboxylic acid **5.9d**.

Access to these cyclised dihydropyrones encouraged us to widen the scope even further to also access cyclised pyrones **5.5** and isocumarins **5.6**. Therefore esters **5.2** and **5.3** were synthesised *via* their free acids.



*Scheme 61: Synthesis of carboxylic acids **5.12**. Isolated yields in brackets.*

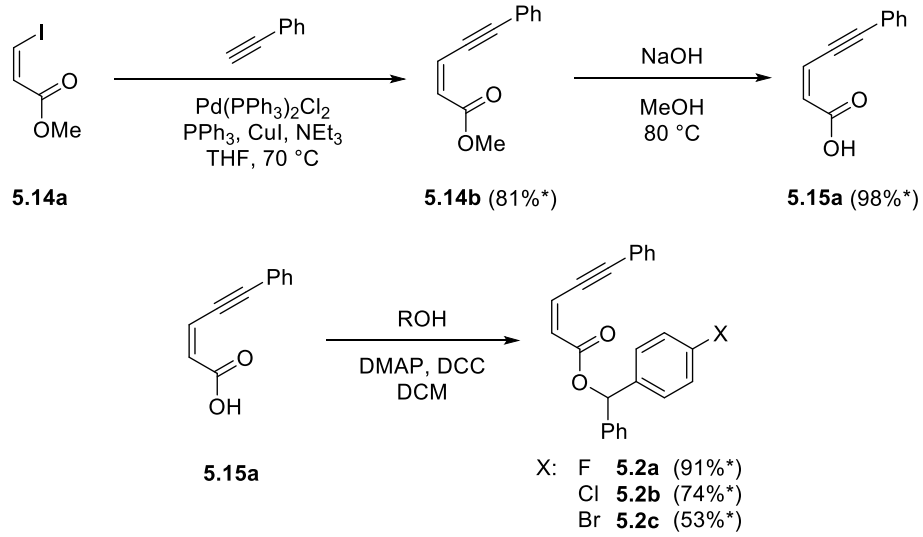
The acid group of iodobenzoic acid **5.11a** was first protected with a methyl substituent and the resulting benzoate **5.11b** reacted with arylacetylenes[109] to give esters **5.12**. After saponification in methanol, carboxylic acids **5.13** could be isolated in very good yields (Scheme 61). Again, Steglich's protocol was used to introduce benzhydryl groups, as well as an ethylphenyl group (**5.3g**) to expand the scope of esters even further (Scheme 62). This esterification step yielded desired products **5.3a-g** in good to excellent yields (68% to 97%).



*Scheme 62: Steglich esterification of acids **5.12**. *isolated yields*

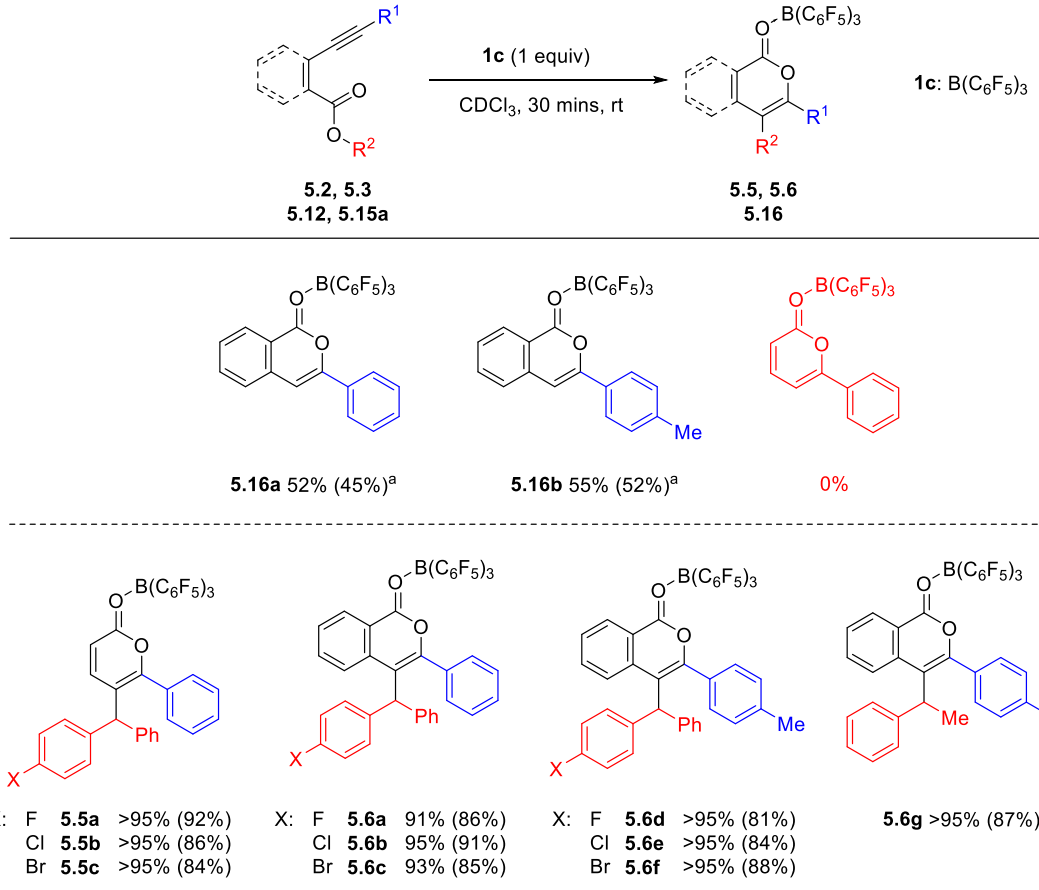
The final group of esters containing and alkene functionality were then also synthesised *via* the free acid of **5.2** (Scheme 63). The benzhydrylic esters showed the fastest reaction in the initial stoichiometric reaction (Scheme 60) so esters **5.2** were synthesised with halide substituted benzhydrols as alcohols. Free acid **5.15a** again was synthesised *via*

a Sonogashira coupling of iodoacrylate with phenylacetylene[110] and a subsequent saponification (Scheme 63).



*Scheme 63: Synthesis of acid **5.15a** and esters **5.2**. *isolated yields*

The esters were then tested in the 1:1 stoichiometric cyclisation reaction with BCF.



*Scheme 64: Reactions of acids **5.12** & **5.15** and **5.2** & **5.3** with stoichiometric amounts of BCF. In situ NMR conversion with isolated yield in brackets. [a] 24 h reaction time*

Even after 24 h free acids **5.12** only showed around 50 percent conversion determined *via in situ* ^{1}H NMR spectroscopy. Compound **5.15a** did not deliver the desired pyrone and as already shown in the first example the reactivity increases when the acid's proton is replaced with benzhydrylic ester groups. All cyclised benzhydryl esters **5.2a-c** and **5.3a-f** show very good isolated yields of the corresponding cyclised lactone (81% to 92%).

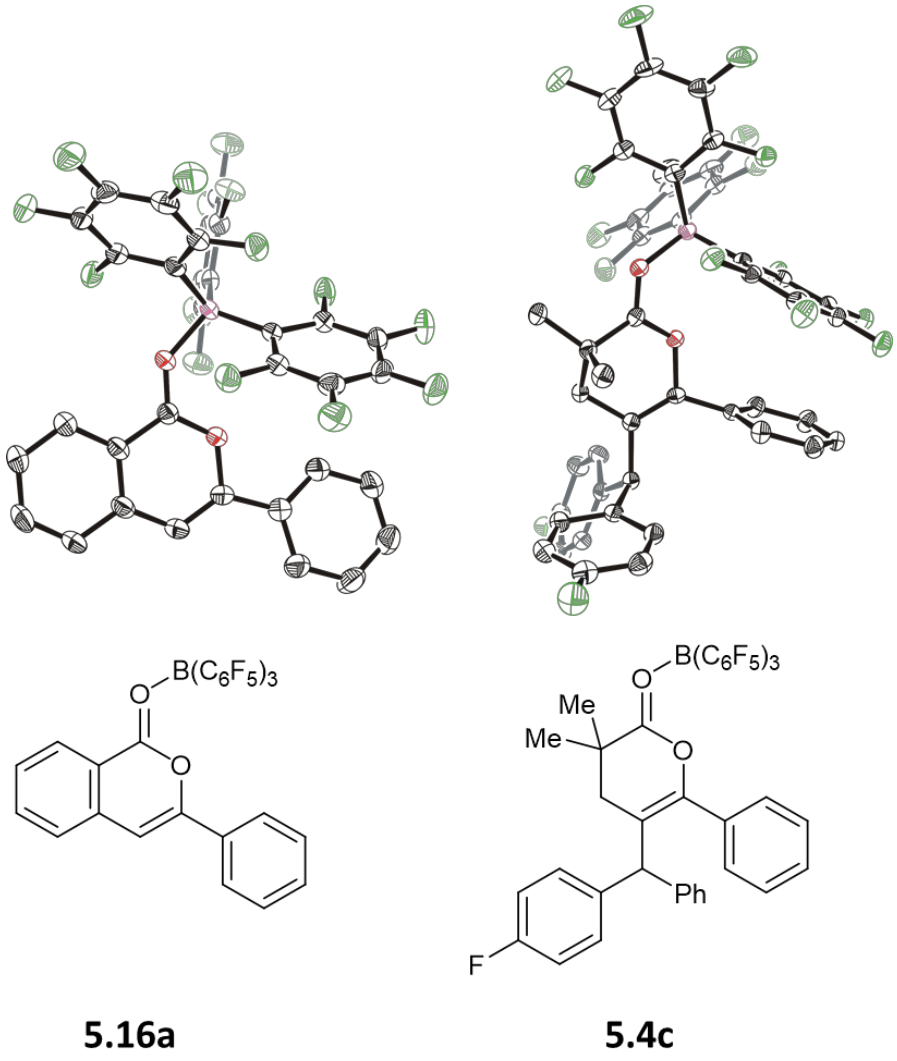


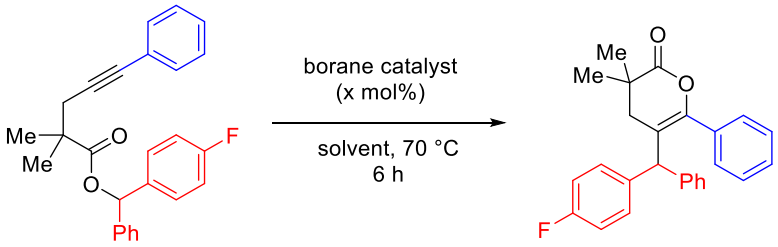
*Figure 22: Crystal structure of isocumarin **5.16a** and dihydropyrone **5.4c**. Protons omitted for clarity. Thermal ellipsoids set at 50% probability. Carbon: black/grey, boron: pink, fluorine: green, oxygen: red*

5.16a and **5.4c** could both be crystallised and structurally characterised. The structures shown in Figure 22 give another proof of connectivity. There are no unexpected features within these structures. The isolated structure could confirm that the final cyclised product does form an adduct through its carbonyl oxygen atom with BCF, which could be of hindrance if this reaction is to be used catalytically.

5.4 Results of the catalytic reaction with $B(C_6F_5)_3$

To probe this system for its catalytic activity, compound **5.1e** was chosen as the model substrate. Indeed, running the reaction with 10 mol% BCF instead of stoichiometric amounts only gave 10% conversion, showing that the final lactone borane adduct is stable at room temperature. Increasing the reaction temperature to 70 °C however gave the desired product quantitively (Table 6, entry 6).

*Table 6: Scope of the catalytic reaction of **5.1e** with various boranes and solvents*



5.1e **5.17a**

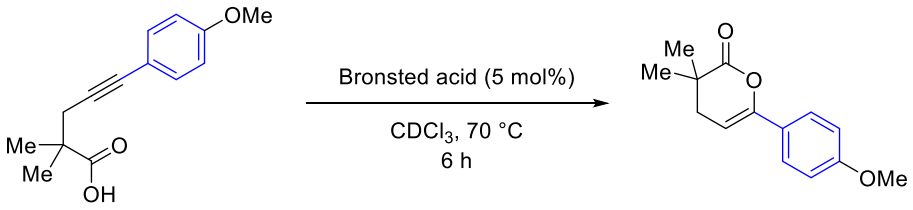
Entry	Catalyst	Solvent	Loading (mol%)	Conv. (%)[a]
1	BPh_3	$CDCl_3$	10	<5
2	$B(2,6\text{-}F_2C_6H_3)_3$	$CDCl_3$	10	<5
3	$B(2,4,6\text{-}F_3C_6H_2)_3$	$CDCl_3$	10	<5
4	$BF_3{\cdot}OEt_2$	$CDCl_3$	10	7
5	$B(C_6F_5)_3$	$CDCl_3$	10	>95
6	$B(C_6F_5)_3$	$CDCl_3$	5	>95
7	$B(C_6F_5)_3$	$CDCl_3$	1	>95
8	$B(C_6F_5)_3$	THF	10	52
9	$B(C_6F_5)_3$	1,4-Dioxane	10	54
10	$B(C_6F_5)_3$	Toluene	10	>95
11	$B(C_6F_5)_3$	Et_2O	10	>95
12	$B(C_6F_5)_3$	CH_2Cl_2	10	>95
13	$B(C_6F_5)_3$	CH_2Cl_2	5	>95

[a] *In situ NMR Conversion determined via ^1H NMR spectroscopy*

Reducing the Lewis acidity quenches the reactivity, and triaryl boranes with fewer fluorine atoms on the aryl rings show no conversion (Table 6, entry 1, 2 and 3). The equally acidic but sterically less demanding boron trifluoride gives only 7% conversion after 6 h (Table 6, entry 4). Reducing the catalyst loading does not affect the reaction and with even as little as 1 mol% BCF quantitative conversion can be observed after 6 h

via ^{1}H NMR spectroscopy (entry 6 & 7). A scope over various solvents revealed that more coordinating solvents such as 1,4-dioxane (entry 9) and THF (entry 10) only convert 50% of the alkynylester **5.1e** to the desired lactone **5.17a**. Diethyl ether (entry 11), dichloromethane (entry 12) and toluene (entry 10) all show similar activity compared to chloroform. Here a complexation of the more coordinating solvents with BCF is suspected to be the reason for the drop in conversion. To ensure that especially the cyclisations of acids **5.9**, **5.13**, **5.15** is not a Brønsted acid promoted reaction, acid **5.9b** was chosen as a model substrate and was reacted with catalytic amounts of two Brønsted acids (Table 7).

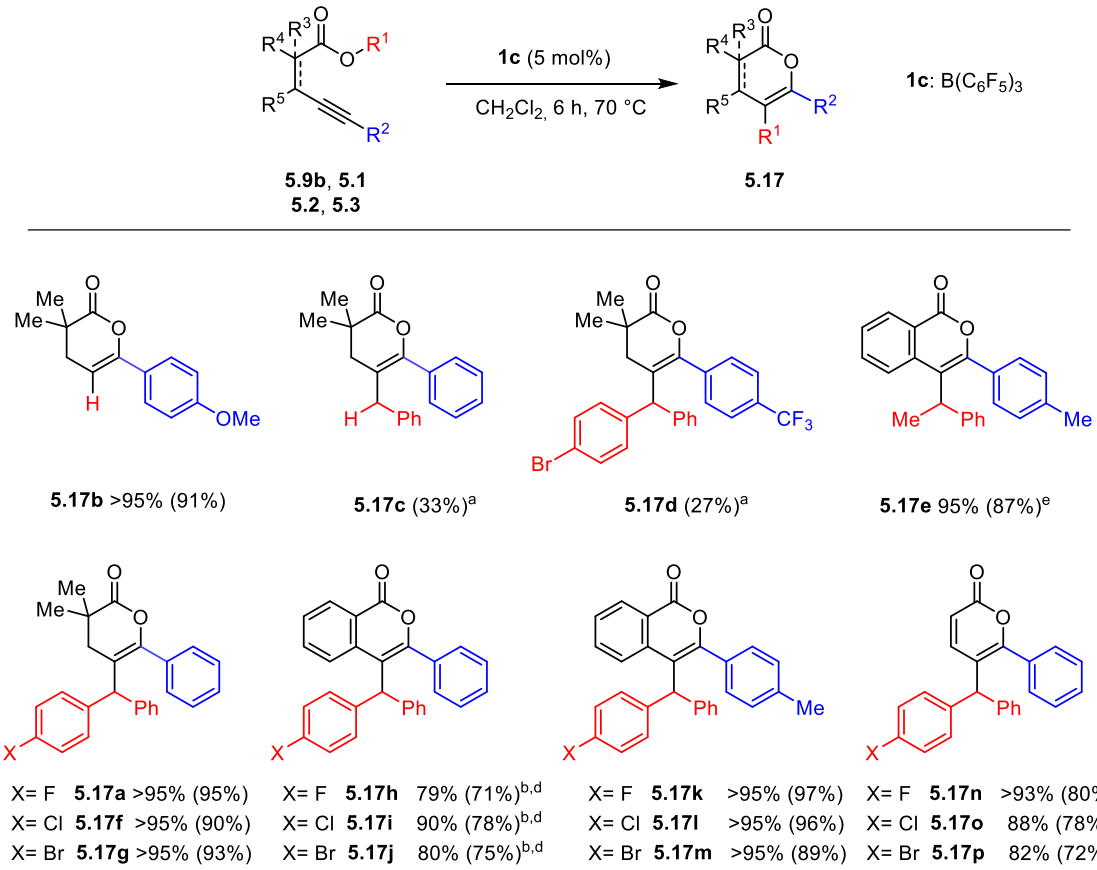
*Table 7: Carboxylic acid **5.9b** in reaction with proton sources*



5.9b **5.17b**

entry	Brønsted acid	Conv. (%)
1	CF_3CO_2H	<5
2	CF_3SO_3H	<5

As shown in Table 7, both triflic acid (Table 7, entry 2) as well as trifluoroacetic acid (entry 1) do not display any reactivity in the tested conditions and hereby making a proton promoted cyclisation more unlikely. The stoichiometric scope (Scheme 64) already showed that not all tested compounds show the same high reactivity as model substrate **5.1e**, which dissuades from using 1 mol% catalyst loading, but instead supports the use of a 5 mol% loading. This catalytic loading is still half of what Takaki and co-workers reported in their bismuth catalysed cyclisation reaction of these alkynylesters.[105] The solvent of choice was CH_2Cl_2, which showed high conversion and facilitated solvent removal after the reaction due to its low boiling point. Entry 13 on Table 6 was chosen as the standard conditions for the catalytic scope. With the optimal conditions determined, the substrate scope was then examined (Scheme 65).



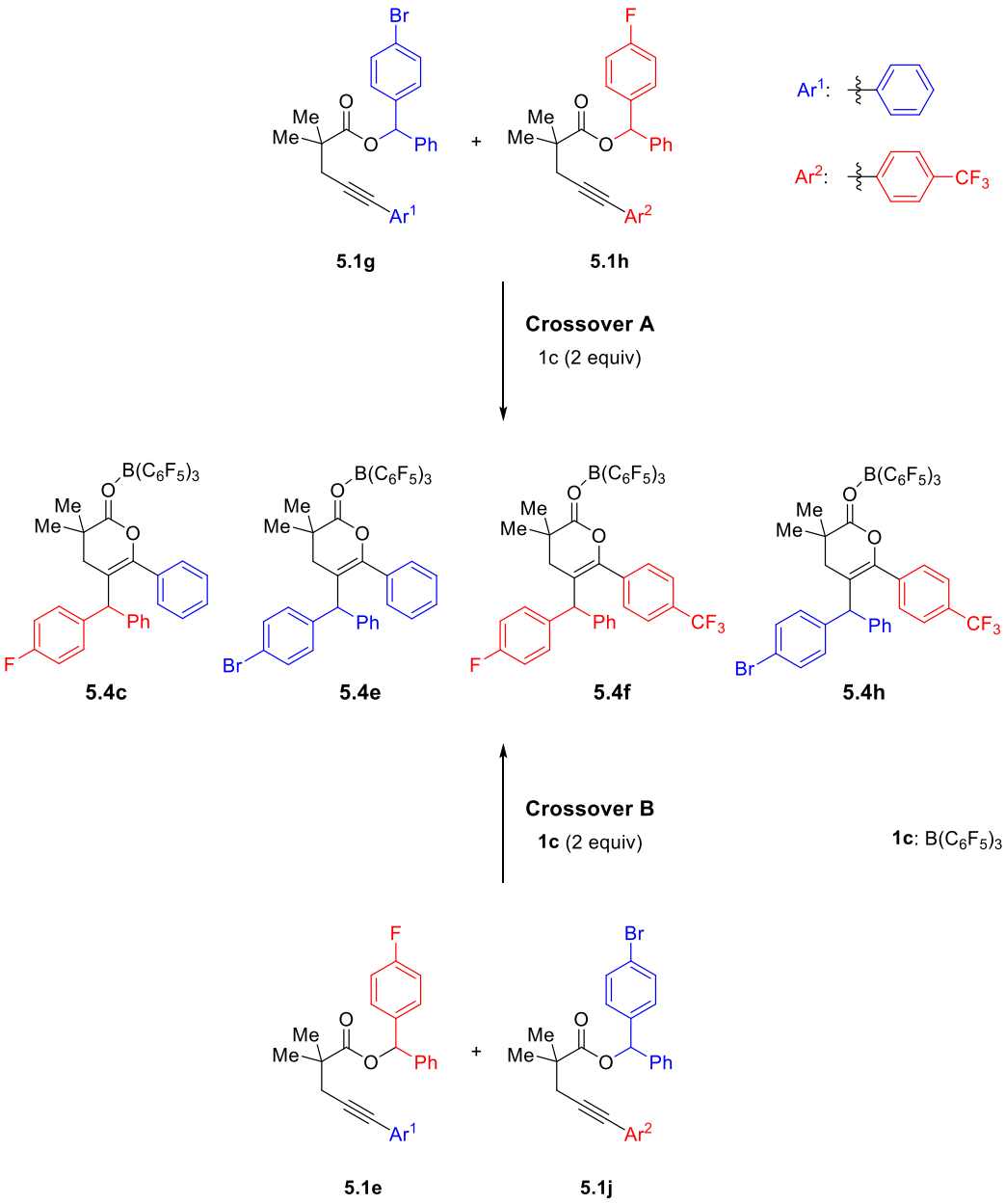
Scheme 65: Catalytic scope with optimised conditions. In situ NMR conversions are given, isolated yields in brackets. [a] 120 h reaction time [b] 10 mol% catalyst loading [c] 16 h reaction time [d] 24 h reaction time [e] 48 h reaction time

Again, electron deficient alkynyl esters and acids are less reactive and only the benzhydryl esters display any reactivity towards the model system and, even after 120 h reaction time, only 27% product **5.17d** could be isolated. Here the conversion stagnates after about 60 h pointing towards an unwanted side reaction of BCF with ester **5.1j**. This trend continues with the less reactive free acids, here only the electron rich methoxy substituted acid **5.9b** shows the desired product in tested conditions. A comparison between cyclised products **5.17h-j** and **5.17k-m** can confirm these findings. The more electron rich methyl substituted esters **5.3d-f** are quantitively converted to the desired product after 6 h. However, the less electron rich esters **5.3a-c** need increased catalyst loading (10 mol%) and reaction time (24 h) to give the cyclised isocumarin derivates **5.17h-j** in very good yields. Another trend that could be observed in the stoichiometric reactions was that benzyl ester **5.1c** is less reactive compared to benzhydrylesters **5.1e-g**. This is again confirmed in the catalytic scope and even after 120 h reaction time only 33% of the cyclised product **5.17c** could be isolated. With ethylphenyl ester **5.3g** quantitative conversion could be achieved, but the reaction time needed to be increased to 48 h. Model substrate **5.1e** and its halide derivatives **5.1f** and **5.1g** gave the products **5.17a** and **5.17f-g** in excellent yields (90-95%). Pyrone formation

is slightly slower and an increase in reaction time (16 or 24 h) is needed to isolate pyrone derivatives **5.17n-p** in good yields.

5.5 Mechanistic studies and discussion

To gain further insight into this cyclisation reaction, a crossover experiment was conducted to see whether this reaction is inter- or intra-molecular. By mixing two differently substituted esters and observing the reaction *via* ^{1}H NMR spectroscopy, should give rise to either four different products in case of an intermolecular reaction, or only two products in the intramolecular case (Scheme 66).



*Scheme 66: Crossover reactions of esters **5.1** to form cyclised dihydropyrones **5.4***

Indeed, both crossover reactions A and B result in a mixture of four products. This speaks for an intermolecular reaction, and the liberation of the ester group as a carbocationic

species. This is in agreement with the reactions carried out in this work. The more stabilised the formed carbocation is, the higher the reactivity of the initial alkynyl ester. These results were confirmed via ^{1}H NMR spectroscopy (Figure 23).

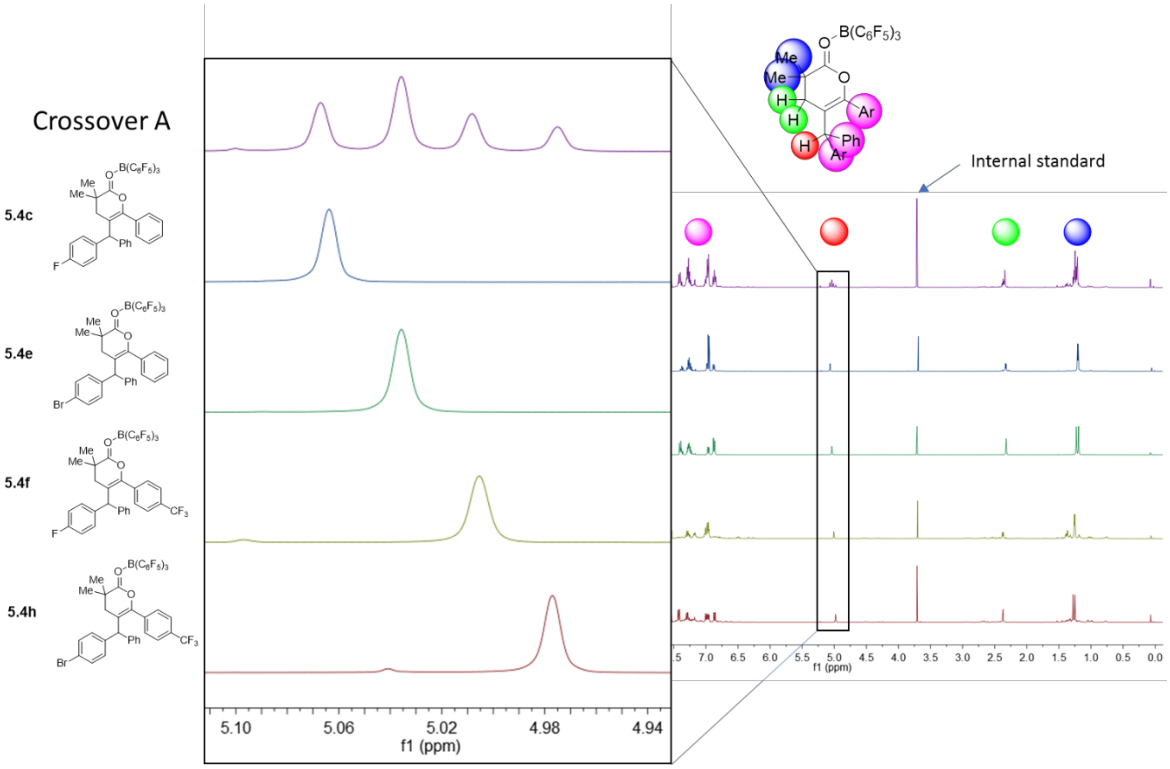
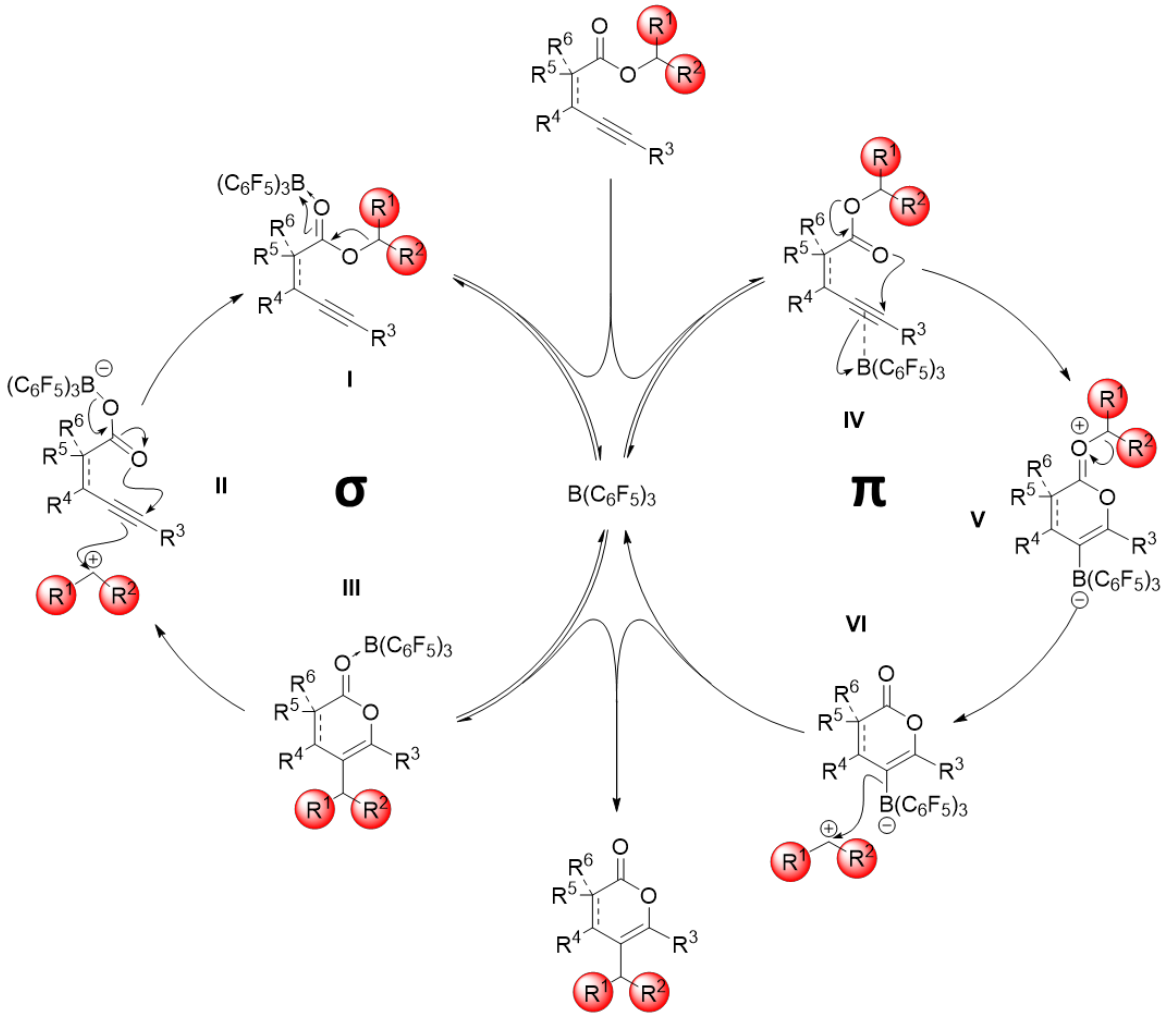


*Figure 23: Stacked ^{1}H NMR spectra of crossover A and single crude reactions to form products **5.4** with 1,4-dioxane as an internal standard in a sealed capillary*

The resulting spectra of both crossover reactions gave 4 signals in the 5 ppm region of the ^{1}H NMR spectrum. Comparing these four signals with the individual peaks resulting from the stoichiometric reaction of esters **5.1** with BCF reveal that each peak represents one of the cyclised products **5.4c**, **5.4e**, **5.4f** and **5.4h**. Here it is noteworthy to mention that the bismuth promoted cyclisation by Takaki and co-workers only gives two products when conducting a crossover experiment.[105] This suggests that there must be differences in the mechanism between these two cyclisation reactions. The collected results allow for two different pathways for the mechanism to take place (Scheme 67).

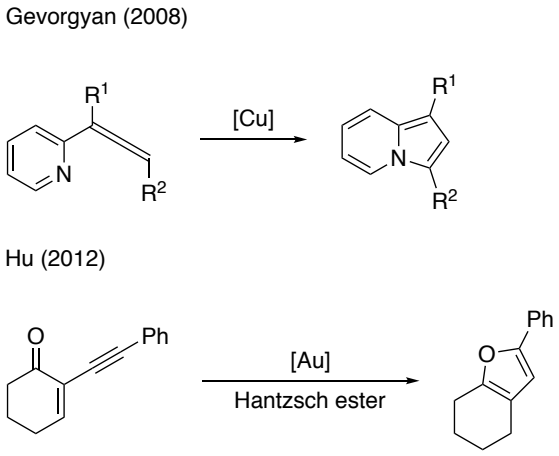


Scheme 67: Possible mechanistic pathways for the cyclisation reaction

As already discussed in Chapter 1, BCF is capable to activate both σ-Lewis basic and π-Lewis basic centres. In Scheme 67, the left catalytic cycle represents the σ-pathway. An initial oxygen-borane adduct (**I**) is formed, facilitating the exit of the ester group as a carbocation. In a second step (**II**), the liberated carbocation can now induce the cyclisation reaction and give the cyclised product as a borane adduct (**III**). A second possible pathway (π-pathway) is the activation of the unsaturated bond (**IV**) and an ensued 6 *endo-dig* cyclisation to give pyrylium borate **V** similar to that observed in the Melen group previously. Now a carbocation is liberated and in a carbodeboronation reaction (**VI**) the final product is formed, and the catalyst is reintroduced into the cycle. Observing the reaction over time shows the presence of a signal in the ^{11}B NMR spectrum at around -16 ppm, characteristic for vinyl borates, [106] that vanishes towards the end of the reaction. This could point towards the π-pathway, but also throughout the reaction a big signal at around 0 ppm is observable in the ^{11}B NMR spectra of this reaction, a region characteristic for boron-oxygen adducts.[106] Thus, the true catalytic cycle is still not fully understood.

5.6 Summary & Outlook

In conclusion, this is the first example of carbo- and hydro-oxycarbonylation promoted by a non-metal catalyst in the literature. Showcasing a highly efficient and fast C-C and C-H-bond formation at relatively mild conditions. Further studies are needed though to determine whether one of the two proposed pathways is correct or a different more complex mechanism is the actual pathway of the studied cyclisation reaction. With this method, biologically active pyrones, dihydropyrones and isocumarins can be synthesised with a very straight forward protocol giving access to potential pharmaceutical compounds without the use of metal catalysts and hereby saving a costly purification step.



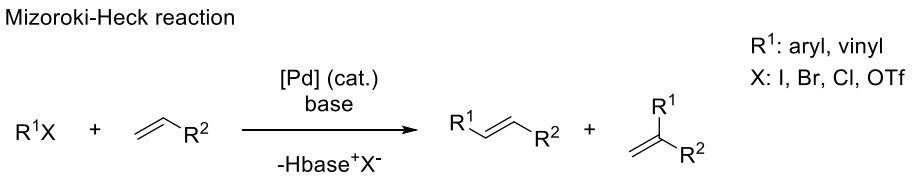
Scheme 68: (top) Copper promoted 5-endo-trig reaction by Gevorgyan et al.[111] (bottom) Gold promoted 5-endo-dig reaction by Hu et al.[112]

Here, other cyclisation reactions promoted by coinage metals shown in Scheme 68 could be of interest as well. Gevorgyan[111] and co-workers could show that allene substituted pyridines can be cyclised by a copper catalyst to give pyrrole derivates and the group around Hu[112] discussed the cyclisation of an unsaturated cyclic ketone system to give a furan derivative. Both reactions are quite similar to the reaction discussed in this chapter and could be promoted by BCF. The reaction of Hu *et al.* needs an additional hydride source in form of an Hantzsch ester, which could quench the reactivity of the borane catalyst. But both systems are promising and could expand the BCF promoted cyclisation reactions and replace precious metals in synthetic transformations.

6 FLP mediated Heck-type reaction

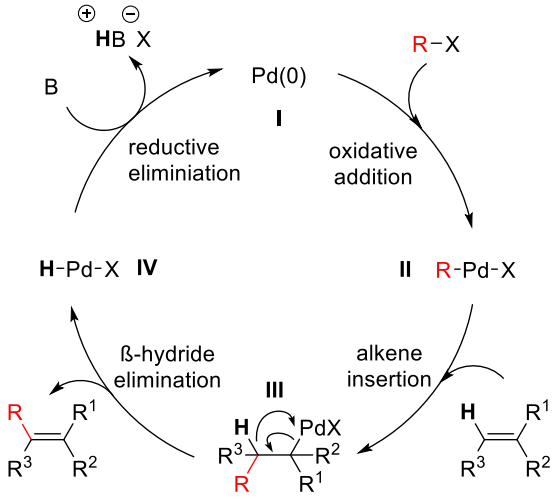
6.1 Introduction

The Mizoroki-Heck reaction is a ubiquitous tool to create important structures in natural products, pharmaceuticals, materials and agrochemicals.[113] It was first described by Mizoroki and colleagues in 1971 (Scheme 69).[114]



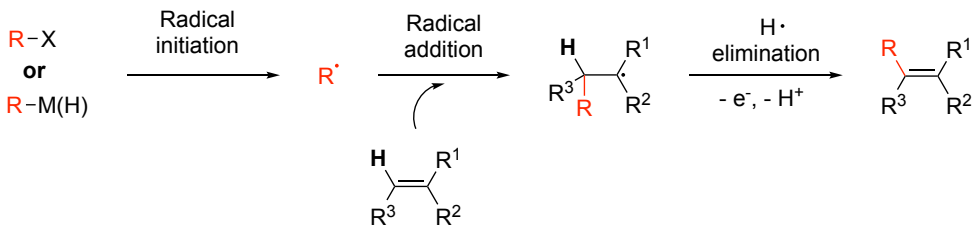
Scheme 69: General reaction of the Mizoroki-Heck reaction

In the following year Heck *et al.* proposed the first full mechanism (Scheme 70).[115]



Scheme 70: Mechanism of the Mizoroki-Heck reaction

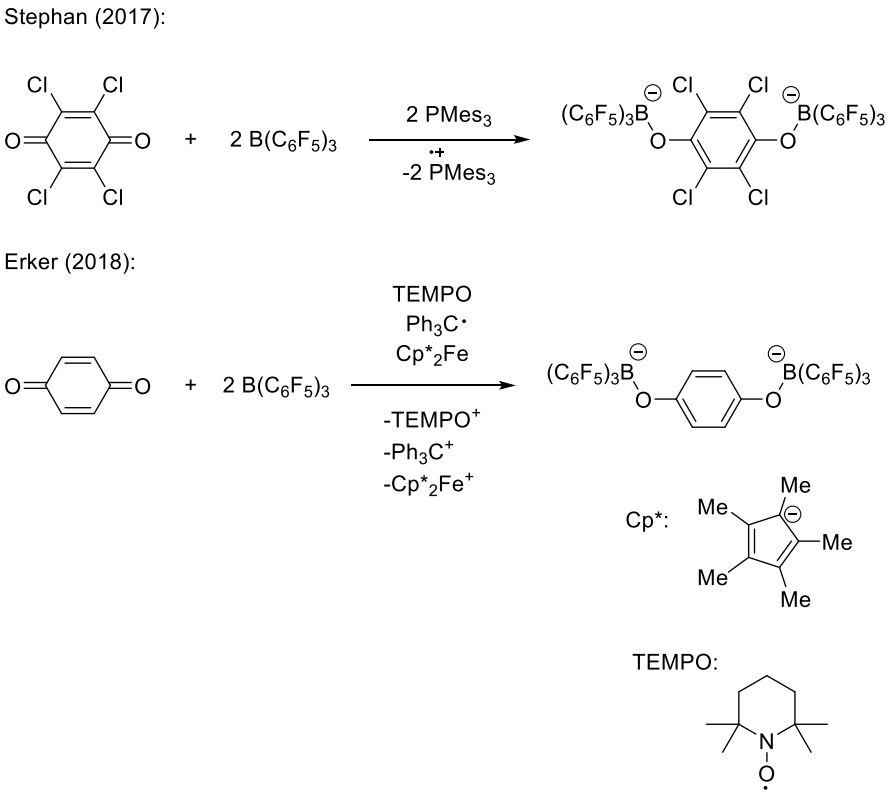
The alkene insertion starts with an oxidative addition of the aryl or vinyl halide on to the palladium catalyst. The now oxidised palladium catalyst reacts with an alkene to form complex **III**. The following β-hydride elimination then gives the arylated alkene and hydridopalladium halide **IV**. Finally, a reductive elimination step promoted by the added base regenerates the Pd(0) catalyst **I** by quenching the hydrogen halide. In recent years, radical processes have been developed performing this Heck-type reaction (Scheme 71).



Scheme 71: General reactivity of radical Heck-type reaction

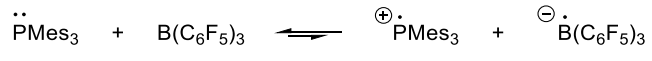
These reactions are mainly, with a few exemptions,[116,117] promoted by transition metals.[118–120] As mentioned earlier, the cost of removing residual catalysts in products for human consumption has a significant impact on total production costs, and is strictly regulated by international bodies.[121] In addition, residual metal catalysts can act as charge carrier traps or photoquenchers strongly affecting the intrinsic properties in products for the modern electronics industry, making metal-free approaches highly desirable.[122]

Recent findings by Stephan[123] and Erker[124] proved that negatively charged BCF radicals can be generated by trapping the resulting anion with benzoquinone (Scheme 72).



Scheme 72: SET BCF reduction of benzochinones by Stephan and Erker. TEMPO: (2,2,6,6-Tetramethylpiperidine-1-yl)oxyl

Erker's example is using oxidative radicals like TEMPO or trityl, whereas Stephan showed that the FLP consisting of BCF and $PMes_3$ has radical character due to a single electron transfer (SET) equilibrium (Scheme 73).



SET equilibrium

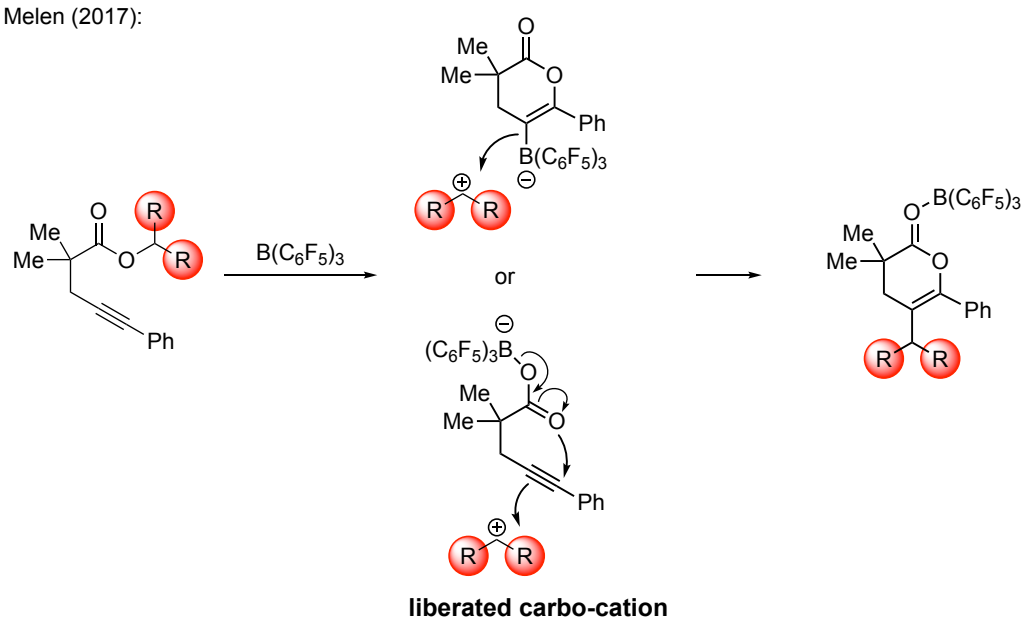
Scheme 73: SET equilibrium of FLP pair BCF/$PMes_3$

This equilibrium is greatly shifted to the left-hand side of the reaction shown in Scheme 73 and the resulting borane radical anion has a very short life time. Therefore, a FLP mixture of BCF and $PMes_3$ shows nearly no activity in electron paramagnetic resonance

(EPR) spectroscopy.[123] Mixing this FLP with a benzoquinone derivative results in a dianion and a phosphine radical cation, which can be clearly detected *via* EPR spectroscopy.

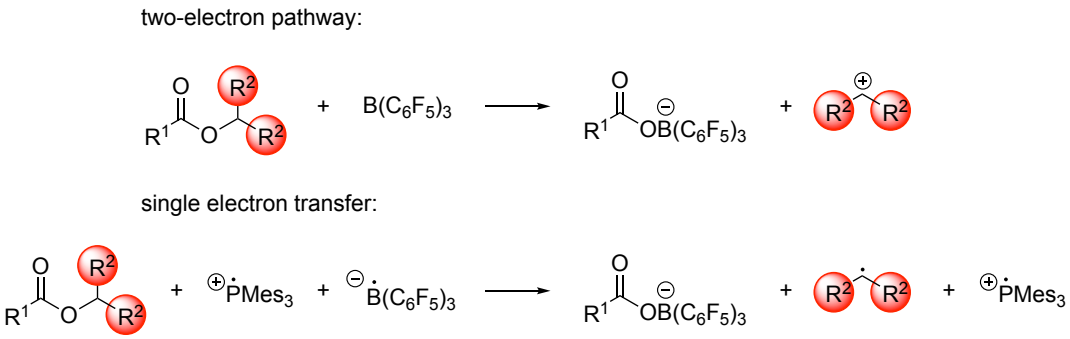
6.2 Aim of this work

As discussed in Chapter 5, BCF can be used in the intramolecular cyclisation of alkynyl carboxylic acids and esters to generate pyrones, dihydropyrones and isocoumarins. In this catalytic reaction BCF is shown to be able to liberate a benzhydryl cation (Scheme 74).



Scheme 74: Cyclisation reaction discussed in Chapter 5

With Stephan's and Erker's recent findings in hand, the possibility to liberate a benzhydryl radical utilizing the BCF radical anion generated *via* SET equilibrium (as shown in Scheme 73), instead of the two-electron diamagnetic pathway (discussed in Chapter 5), is explored (Scheme 75).

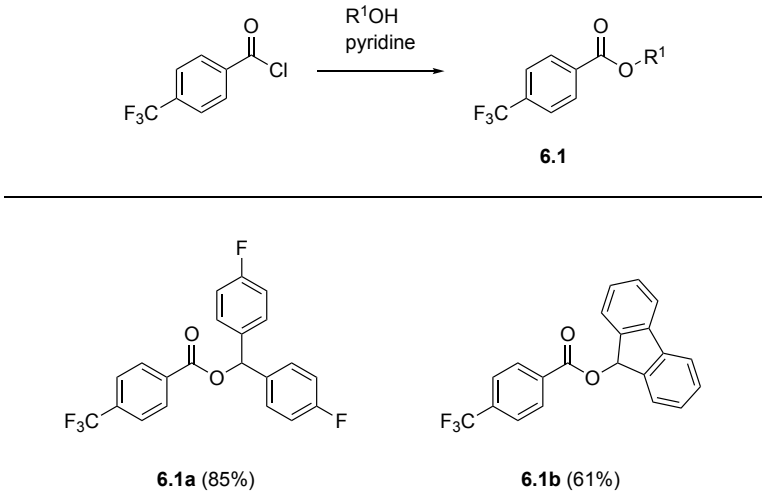


Scheme 75: Reactivity probed in this work

6.3 Results

6.3.1 Synthesis of starting materials

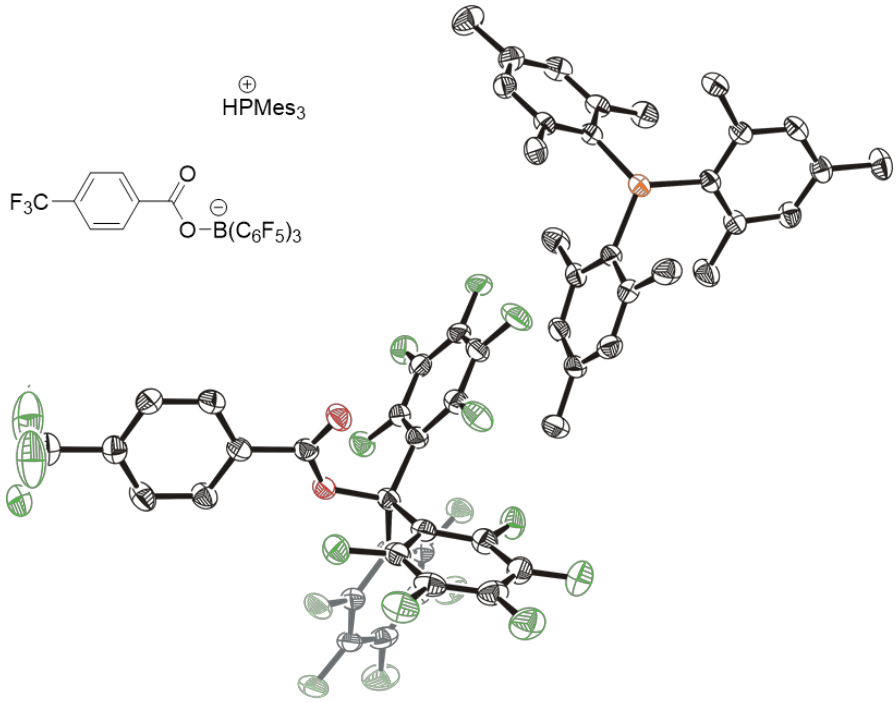
To probe if a carbon radical can be liberated instead of a carbocation, esters **6.1a** and **6.1b** were synthesised in a simple one step esterification from commercially available starting materials to give the products in reasonable yields (Scheme 76).



*Scheme 76: Synthesis of esters **6.1***

6.3.2 Reactivity of Esters **6.1** with (frustrated) Lewis base pairs

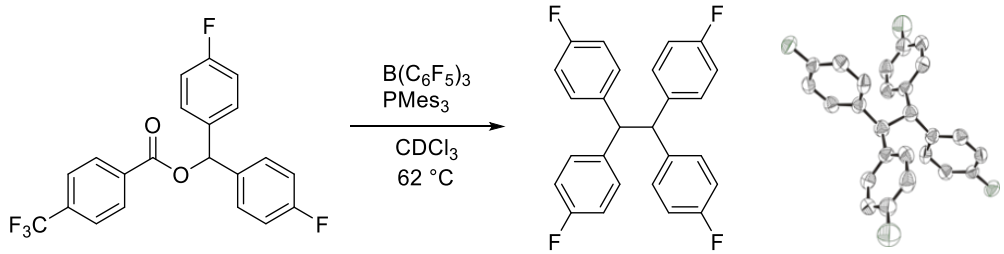
Upon mixing **6.1a** with the FLP $Mes_3P/B(C_6F_5)_3$ in chloroform-*d*[1] a strong purple colouration (Abs_{max} = 571 nm), that is characteristic for the radical cation of Mes_3P, could be observed initially. The deep purple colour turned into a clear orange solution after 12 h at room temperature, or 4 h in a 70 °C oil bath. A doublet ($^1J_{PH}$ = 478 Hz) in the ^{31}P NMR spectrum indicated the presence of a P-H-bond and, after slow evaporation of the reaction mixture, a crop of colourless crystals suitable for X-ray diffraction could be harvested (Figure 24). The product was found to be a phosphonium borate salt $[RCO_2B(C_6F_5)_3][HPMes_3]$. This confirmed the expected reactivity of the borane radical anion with the carbonyl oxygen atom of ester **6.1a** (Scheme 74). However, this raised several questions. 1) Where did the benzhydrol moiety end up and 2) where did the P-H proton come from?



6.2a

*Figure 24: Isolated compound **6.2a** C: black, O: red, B: peach, F: green, P: orange. Thermal ellipsoids set to 50% probability. H atoms omitted for clarity*

Further purification of the solution, following filtration to remove the salt, *via* column chromatography revealed the second product of this reaction to be the homocoupled benzhydryl ester moiety dimer **6.2b** as a white solid. This dimer could be recrystallised in a $CHCl_3$/*n*-hexane mixture to give colourless needles suitable for X-ray diffraction (Scheme 77).



6.1a **6.2b**
34% isolated yield

Scheme 77: Homocoupled product of the liberated carbon radical C: black; F: green. Thermal ellipsoids set to 50% probability. H atoms omitted for clarity

The identification of products **6.2a** and **6.2b** from the reaction mixture, as well as the observation of a deep violet coloured reaction suggested that the generation of a carbon radical was successful. Dimerisation of the radical would then lead to the homocoupled product.

To investigate if this reaction was limited to mesityl phosphine a range of aromatic and aliphatic phosphines were tested in this reaction, but all other phosphines displayed a two-electron diamagnetic reaction pathway. This could be confirmed by monitoring the reactions *in situ* by multinuclear NMR spectroscopy. In the ^{1}H NMR spectra, a doublet of the non-aromatic benzhydrol proton with J~16-20 Hz was observed corresponding to a $^{2}J_{PH}$ coupling (Figure 25). In addition, a $^{6}J_{PF}$ long-range coupling was also observed with $^{6}J_{PF}$~4.0 – 4.5 Hz in the ^{31}P NMR spectra.

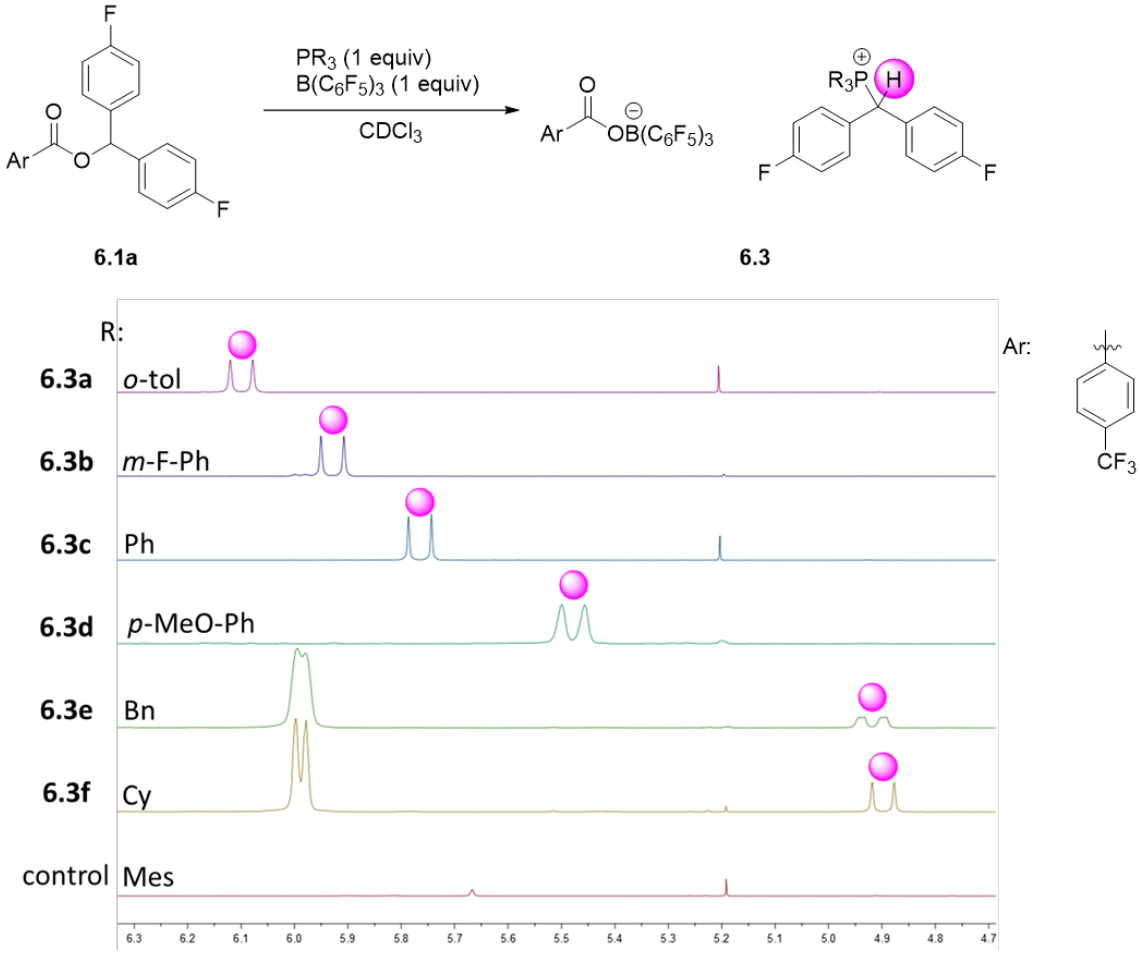


*Figure 25: Reaction of **6.1a** with BCF and various phosphines and stacked zoomed spectra of the reactions in the region of the benzhydrylic proton (pink)*

Stephan and co-workers already showed that tri-*tert*-butylphosphine displays a different reactivity and forms a diamagnetic encounter complex with BCF.[123] With the results in Figure 25, the list of diamagnetic phosphine/BCF encounter complexes was expanded.

6.3.3 EPR results

After confirming that solely mesityl phosphine displays a different reactivity, with a suspected radical intermediate, EPR spectroscopy measurements were undertaken to verify the reactivity proposed in Scheme 75. Stephan and co-workers could observe a very small signal in a solution of BCF/PMes$_3$, which was even more pronounced when the boron atom was replaced with an aluminium atom. The very small signal described

by Stephan *et al.* could not be observed in the EPR spectra upon mixing BCF and $PMes_3$ in $CDCl_3$. In contrast, the reaction mixture of **6.1a** with the $B(C_6F_5)_3/PMes_3$ FLP showed a strong doublet signal in the room temperature EPR spectrum (Figure 26).

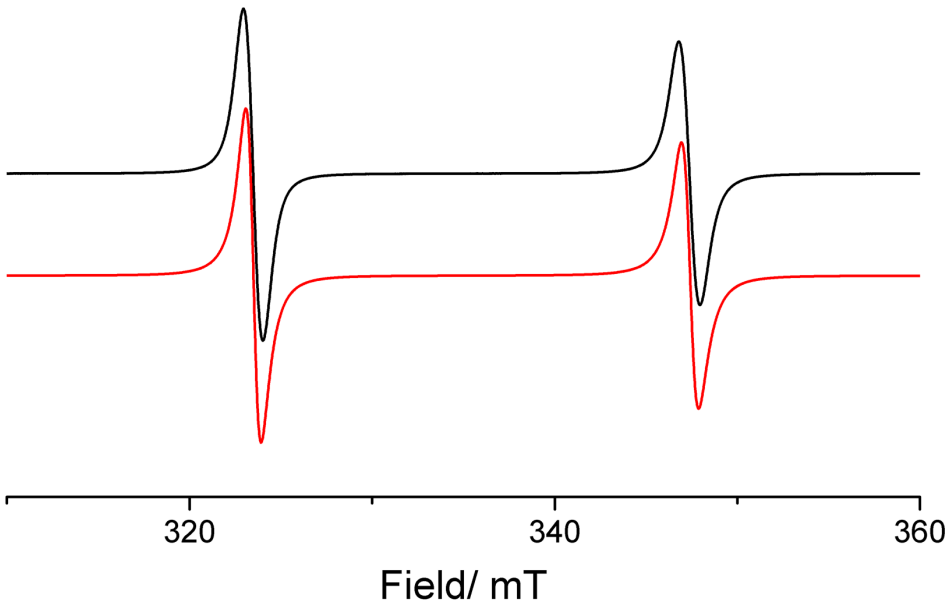


*Figure 26: CW EPR spectrum (T = 298 K) of **6.1a** and $PMes_3$/BCF. Modulation amplitude 2.0 G, microwave power = 2.5 mW. Black (experimental), red (simulated)*

The measured g_{iso} value of 2.0072 and isotropic ^{31}P hyperfine coupling constant of 670 MHz (238.5 G) are comparable with those reported previously for the phosphonium $[Mes_3P]^{+\bullet}$ radical cation.[123] When reacting **6.1b** with the FLP mixture a second smaller signal could be observed due to the carbon based radical (Figure 27). Unfortunately, the poor resolution of the spectrum shown in the inset to Figure 27 arising from a low concentration of radicals precludes accurate determination of the hyperfine coupling, to assign this signal to a fluorenyl radical. However, a preliminary simulation suggests the presence of one large proton coupling ($a_{iso} \approx 63$ MHz) arising from the methylene proton, and a second smaller coupling arising from the two equivalent protons at the 1-position on the aryl rings ($a_{iso} \approx 9$ MHz) (Figure 28). These values are similar to those previously reported on the 9-hydroxyfluorenyl radical.[78]

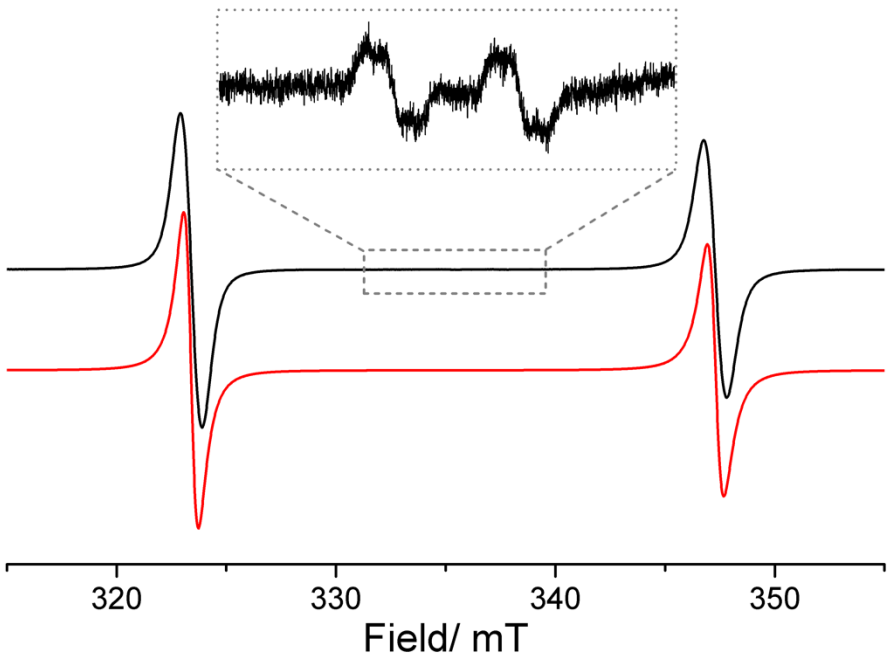


Figure 27: CW EPR spectrum (T = 298 K) of 6.1a and $PMes_3$/BCF. Modulation amplitude 2.0 G, microwave power = 1.6 mW. Black (experimental), red (simulated)

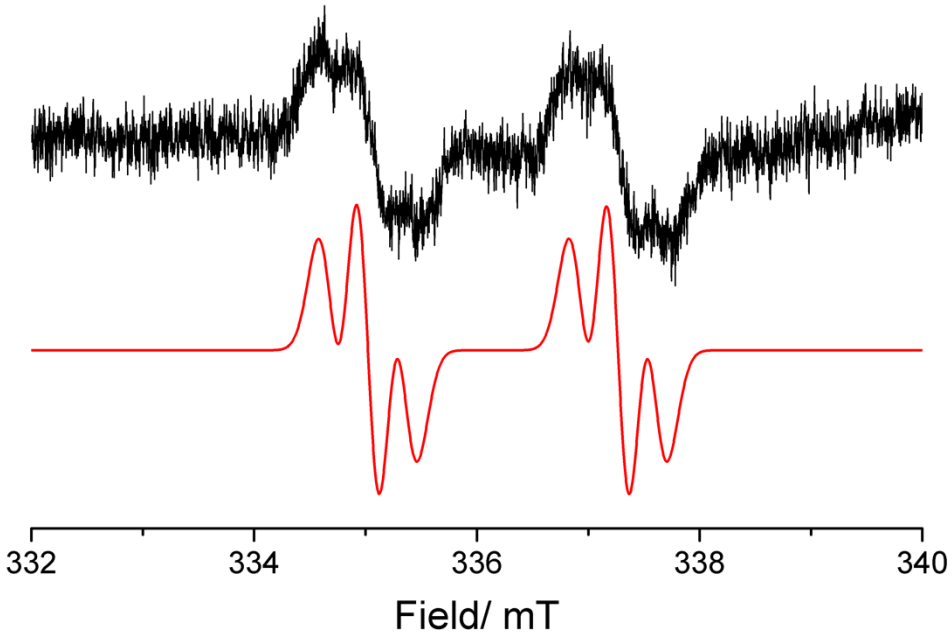


*Figure 28: CW EPR spectrum (T = 298 K) of **6.1a** and $PMes_3$/BCF. Modulation amplitude 2.0 G, microwave power = 1.6 mW. Black (experimental), red (simulated)*

The difference between the two ester moieties suggests that the fluorenyl radical has a longer lifetime than the benzhydryl radical and is therefore also observable in the EPR spectrum. However, in both cases, the presence of radicals could be confirmed.

6.4 Radical Heck-type reaction and mechanism

In a bid to determine the hydrogen source of the protonated phosphonium cation in **6.2a**, the reaction of **6.1b** with the FLP BCF/$PMes_3$ was probed. Indeed, under anhydrous conditions in $CDCl_3$, a doublet was observed in both the ^1H and ^{31}P spectra due to $^1J_{PH}$ coupling. This suggests that the substrate must be acting as the hydrogen source in an unwanted side reaction and not the solvent. Addition of one equivalent of water or D_2O however proved a good ^1H or ^2H source displaying a 1:1 doublet and 1:1:1 triplet in the ^{31}P NMR spectra due to $^1J_{PH}$ (478 Hz) and $^1J_{PD}$ (74 Hz) coupling respectively.[125] Using C_6D_6 as a solvent acted as a poor ^2H source whereas toluene-d_8 acted as a better ^2H source, showing triplet/doublet ratio of 4:1 in the ^{31}P NMR spectrum (Figure 29).

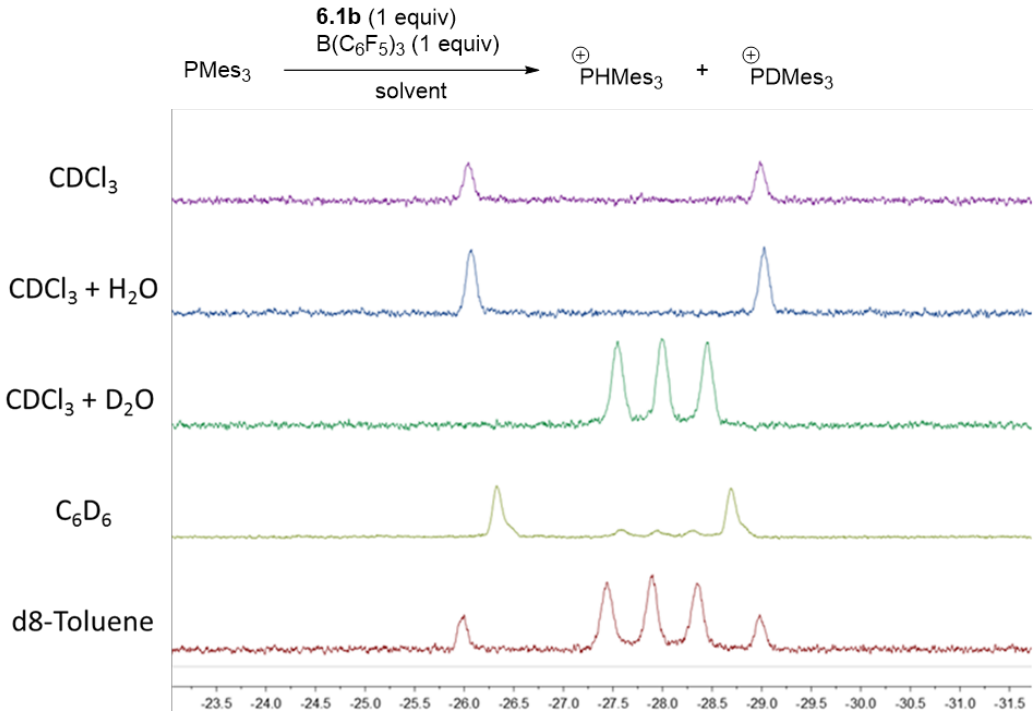
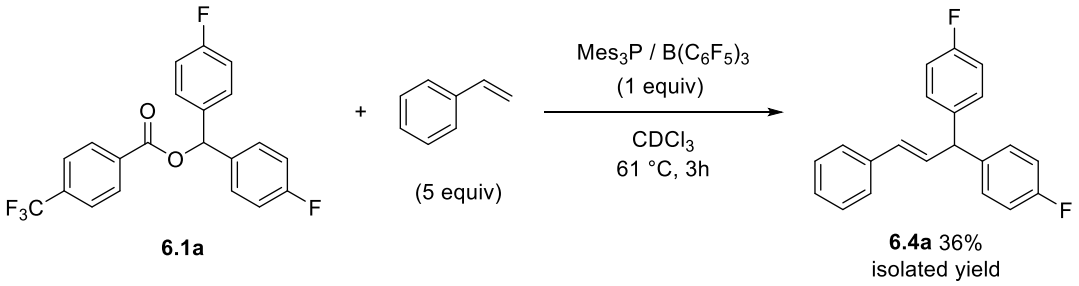


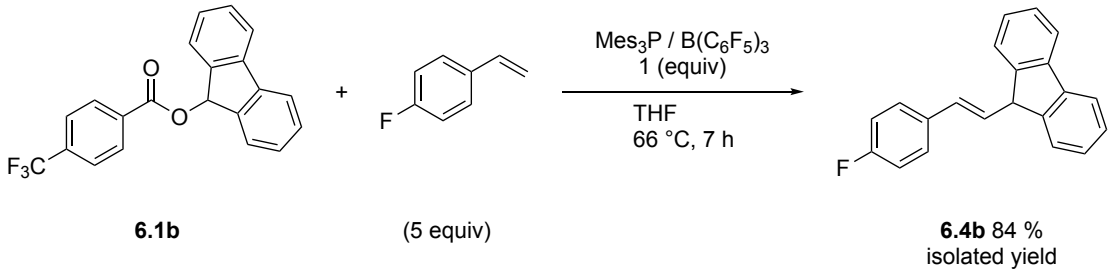
Figure 29: Stacked ^{31}P spectra to determine the quenching source of the phosphonium radical

Using a solvent as a sacrificial hydrogen source showed us that C-H-bond activation is possible but did not significantly increase the yield of homocoupled product **6.2b** (36% in toluene). Instead of using the solvent as a hydrogen source, a more atom efficient way to quench the formed radical cation of Mes_3P was sought. By adding styrene to the reaction, terminal alkenes could be activated in the β-position to give the hetero-coupled product **6.4a** as the *E*-isomer (Scheme 78).



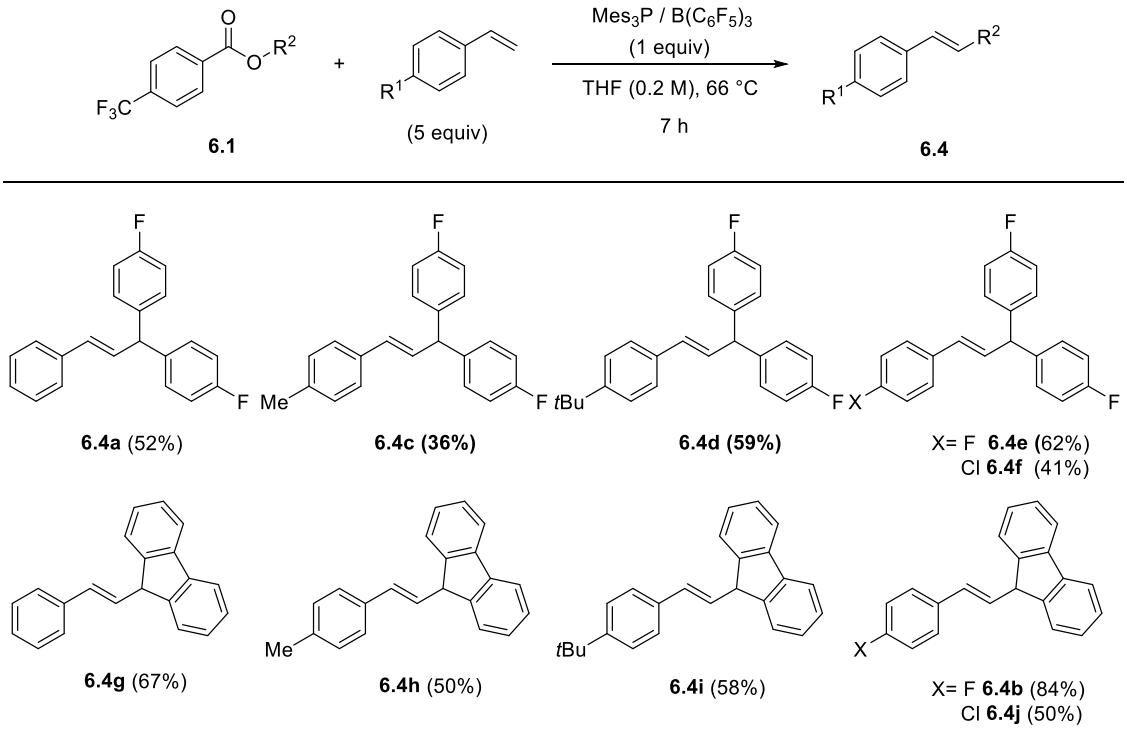
*Scheme 78: Reaction of ester **6.1a** with FLP BCF/PMes$_3$ in the presence of an excess of styrene*

Indeed, the reaction delivered the desired product **6.4a** as the *E*-isomer probably due to the steric demand of the benzhydryl group. An excess of styrene is necessary, as using only one equivalent reduces the yield by about 50% (11% isolated yield). In an attempt to improve the yield of the reaction, a scope of **6.1b** with 4-fluorostyrene over various solvents showed that THF was the most promising and 84% of the expected product **6.4b** was isolated (Scheme 79). Chloro- and bromo-benzene as well as 1,2-dichloroethane (DCE) showed yields similar to chloroform at around 40%. Acetonitrile showed no observable conversion at all.



*Scheme 79: Optimised reaction of **6.1b** with 4-fluorostyrene and FLP BCF/PMes$_3$*

The observed strong purple colouration is much fainter in THF, indicating that there are fewer radical cations of Mes_3P released, leading to an increased reaction time from 3h in $CDCl_3$ to 7h in THF. When following this reaction *via* ^{19}F NMR spectroscopy, fewer side products were observed in THF. The high affinity of THF to form an adduct with $B(C_6F_5)_3$ is likely responsible for the increased reaction time and reduced number of radicals per time unit, as it gives the formed radicals less chance to homocouple or be quenched *via* other undesirable pathways.

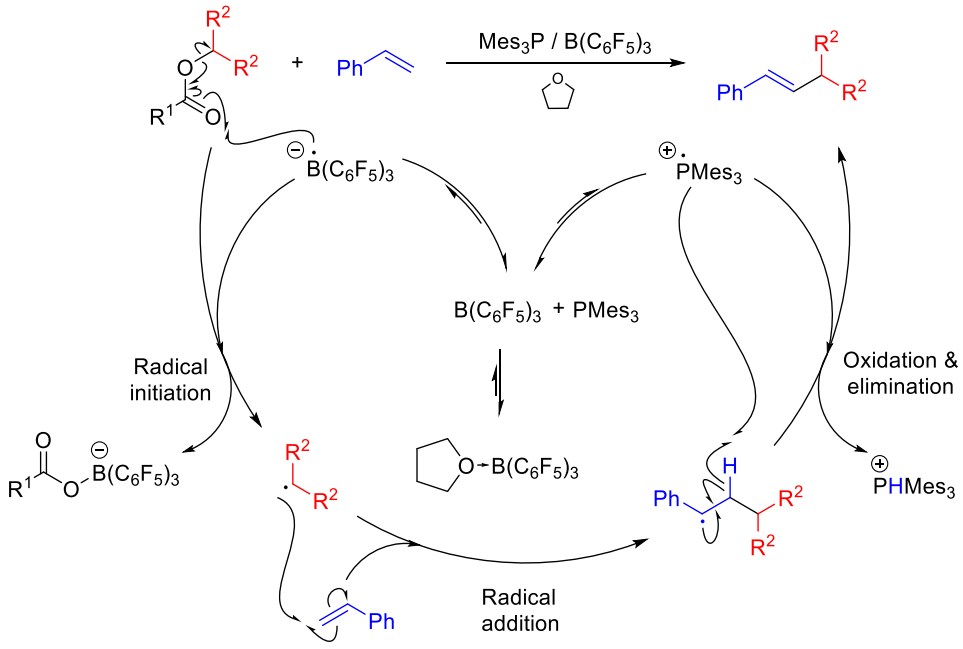


*Scheme 80: Scope over various styrenes in reaction with esters **6.1** and the FLP BCF/PMes3. Isolated yield in brackets*

Scheme 80 displays a range of styrenes in reaction with esters **6.1**, with 4-fluorostyrene showing the best yields with both esters **6.1a** and **6.1b**. Generally, 9-fluorenol ester **6.1b** gave higher conversions than the benzhydryl ester **6.1a**, indicating that longer life times of the formed radical directly translates to higher yields in the coupled product. Chlorine substituted alkenes **6.4f** and **6.4j** experience a drop in yields to 41% and 50% respectively. This can be attributed to unwanted side reactions of radicals with heavier halides. Similar to the products generated from styrene (**6.4a** and **6.4g**), electron rich substituted styrenes yield products **6.4d**, **6.4h** and **6.4i** at around 50%, meanwhile only **6.4c** has a slightly lower yield (36%).

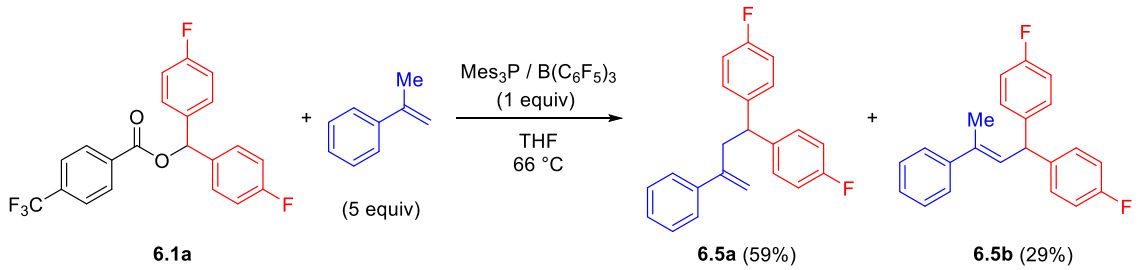
With these results in hand the following mechanism can be postulated (Scheme 81). The reaction can be divided in three steps where the individual steps resemble the general reactivity of radical promoted Heck-type reactions (Scheme 71). The reaction begins with a radical initiation. The created radical is then added onto the unsaturated bond, and a final oxidation and elimination step restores the unsaturated bond. In metal-catalysed radical alkenylations, the formation of the carbon radical is the rate determining step. The high affinity of the formed radical borane anion to the carbonyl oxygen atom of ester **6.1** makes this step very fast. To reduce the amount of free BCF in the reaction mixture, and to slow down the initial radical formation, the coordinating solvent THF was used. After the radical initiation step, the formed carbon radical is added reductively onto the double bond to give the Markovnikov product. Next, the trimesityl phosphonium radial cation can eliminate a hydrogen and reoxidise the radical intermediate to give the final alkenylated

product **6.4**. This also explains why the FLP itself shows no reactivity towards styrene when tested in a control reaction in $CDCl_3$.



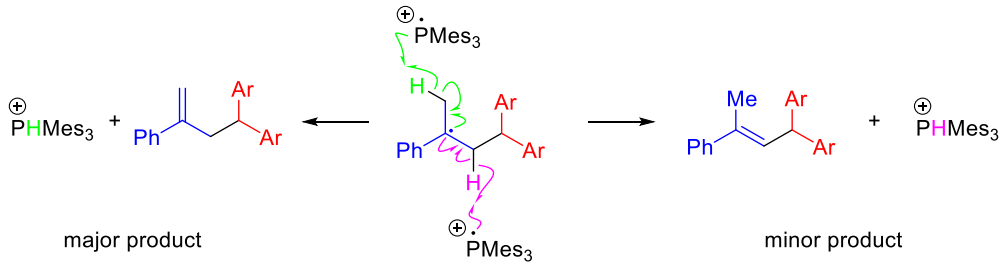
Scheme 81: Possible mechanism of the alkenylation reaction

Interestingly, α-methyl-styrene exhibits an additional alternative reaction pathway generating two products (Scheme 82).



*Scheme 82: Reaction of **6.1a** with α-methyl-styrene. Ratio determined via ^{19}F NMR spectroscopy of the isolated mixture in brackets*

The major product of this reaction is not the expected *E*-isomer **6.5b** but rather compound **6.5a**, indicating that there was an elimination at the α-methyl moiety rather than the β-position. This is plausible looking at the elimination and oxidation steps (Scheme 83).



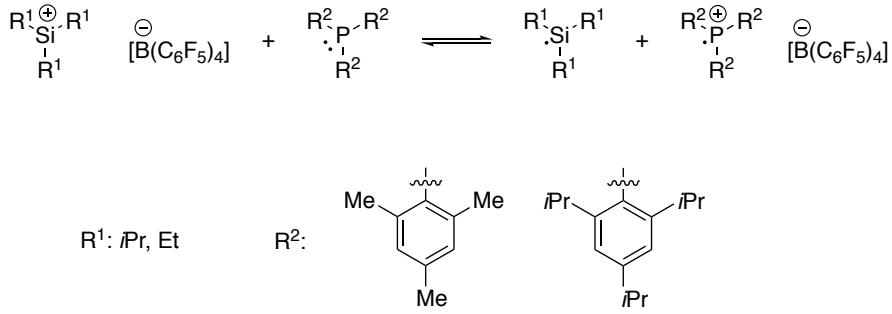
*Scheme 83: Elimination and oxidation step of the reaction of **6.1a** with α-methyl-styrene and the FLP*

Eliminating a hydrogen-atom of the α-methyl group has less steric demand (major product) and with $[Mes_3P]^{+\bullet}$ being quite sterically demanding, eliminating the β-hydrogen atom is the unfavourable process (minor product).

6.5 Summary & Outlook

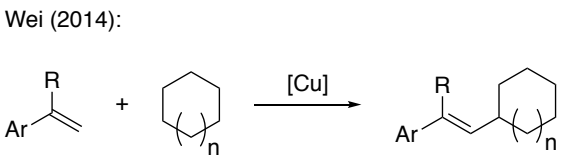
In conclusion, it could be shown that the $Mes_3P/B(C_6F_5)_3$ FLP can be utilised as a powerful metal-free tool for C-C bond formation *via* a radical pathway without using controversial solvents like DCE or CCl_4.[126] The synthesised alkenes show high stereoisomeric purity yielding solely the *E*-isomer. Simple and commercially available starting materials are used, and good functional group tolerance is observed. Further studies into widening the scope as well as mechanistic studies are ongoing in our group.

This novel single electron reactivity of frustrated Lewis pairs is slowly expanding and is in its naissance.[127] Recent findings by Müller[128] and co-workers (anie 2018) have shown that other than BCF also silylium ions $(SiR_3)^+$ display the same single electron transfer equilibrium (Scheme 84).



Scheme 84: SET equilibrium between silylium cations and sterically demanding phosphanes

Here further studies are needed to categorise Lewis acids and explore the ones identified as capable of this SET in their reactivity.



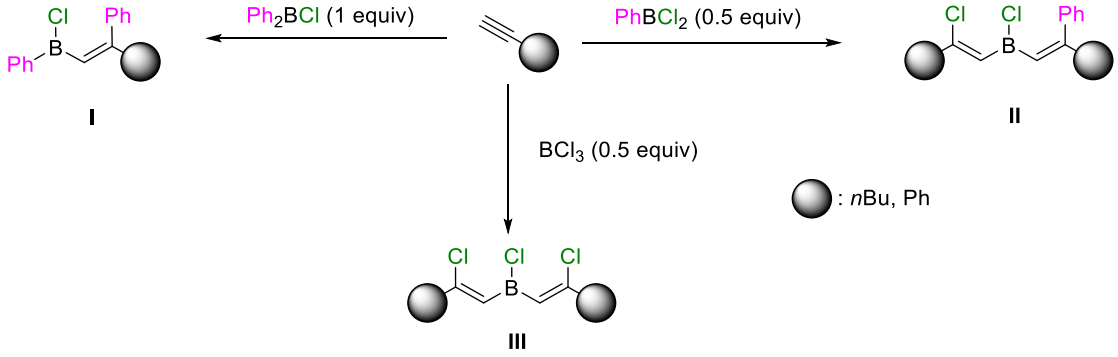
Scheme 85: Direct alkenylation of simple unactivated alkanes with styrenes by Wei et al.[129]

This expanded library of radical anions could be capable of other C-H-activations (e.g. Scheme 85).

7 1,3-Haloboration vs. 1,1-carboboration

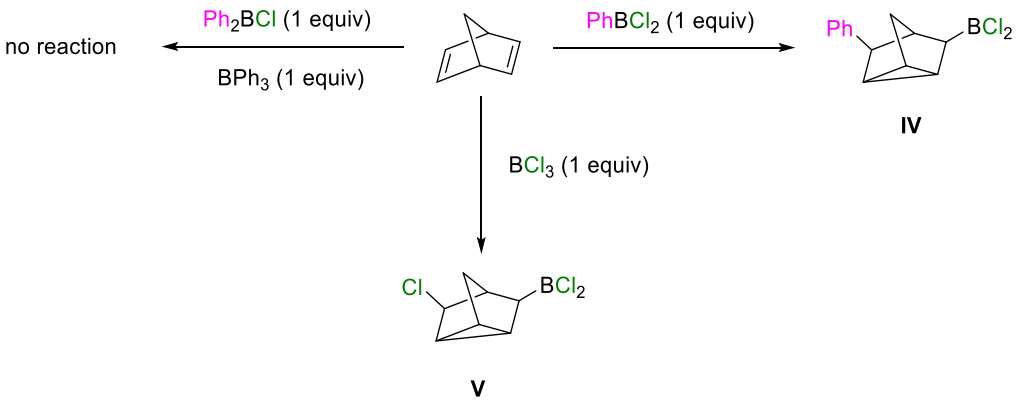
7.1 Introduction

As shown in this work so far, borane Lewis acids exhibit affinity towards unsaturated π-bonds and can activate them. By reacting these electron deficient systems with olefins, a highly desirable boron centre can be introduced into organic compounds, making it available for metal catalysed cross coupling reactions.[130–134] In 1963, Lappert and co-workers first described the addition of boron trichloride and phenyl substituted derivatives across a terminal alkyne (Scheme 86).[135]



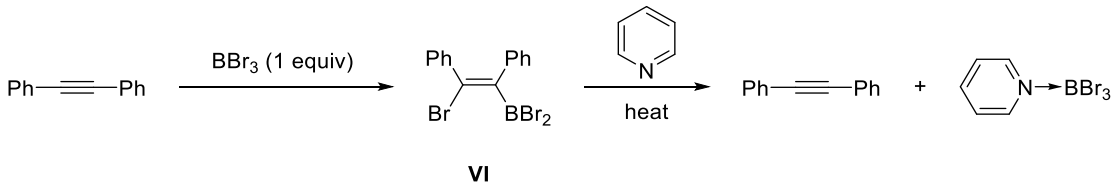
Scheme 86: Reactivity of BCl_3, $PhBCl_2$, Ph_2BCl with terminal alkynes by Lappert and co-workers

Two different reactivities could be observed. Boron trichloride reacts with two equivalents of a terminal alkyne to form alkene **III**. Here, two 1,2-additions across the unsaturated bond take place to form the chloroborated product **III**. When the Lewis acidity of the reacting borane is reduced by the introduction of a phenyl group, a different alkene **II** can be isolated. Again, a 1.2-chloroboration can be observed but instead of a second chloroboration, a 1,2-carboboration takes places, and a B-Ph bond is added across the unsaturated terminal alkyne. Further reduction of the Lewis acidity by introducing another phenyl group into the borane chloride leads to a single carboboration of the terminal alkyne to give product **I**. In later studies, Lappert and colleagues mixed these boranes with norbornadiene yielding similar results (Scheme 87).[136]



Scheme 87: Chloro- and carbo-boration of norbornadiene

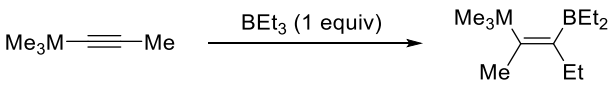
The two weaker Lewis acids, Ph_3B and Ph_2BCl, showed no reactivity towards norbornadiene, but $PhBCl_2$ and BCl_3 result in a 2,6-substituted products (**IV** and **V**). The possible resonance structures make this substitution pattern plausible, with BCl_3 resulting in the chloroborated product **V**, and $PhBCl_2$ yielding the carboborated product **IV** (Scheme 87).



VI

Scheme 88: Reversibility of the haloboration reaction

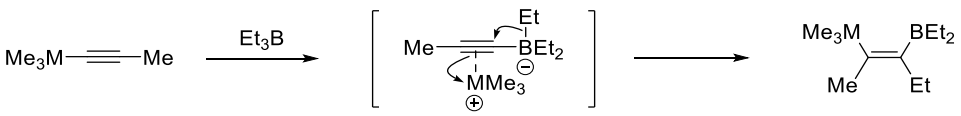
Through the addition of pyridine to 1,2-haloboration product **VI**, Lappert and co-workers could also show that the haloboration reaction can be reversible (Scheme 88).[135] However, this addition reaction is not limited to a 1,2-substitution pattern. Wrackmeyer and co-workers described the first 1,1-carboboration by reacting BEt_3 with activated alkynes (Scheme 89).[137]



M: Si, Ge, Sn, Pb

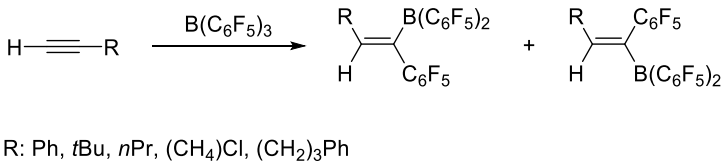
Scheme 89: 1,1-carboboration of activated alkynes

With silyl, germyl, stannyl and plumbyl-groups, activated alkynes undergo a 1,1-carboboration, formally inserting a vinylidene isomer into one of the B-C bonds. Mechanistically, this insertion proceeds differently (Scheme 90).



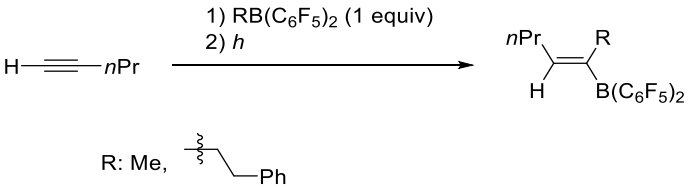
Scheme 90: Mechanism of the 1,1-carboboration in scheme 86

As shown in Scheme 90, the 1,1-carboboration of the activated alkynes is a two-step reaction. First, the borane adds to the substrate, then rearrangement of the zwitterionic intermediate yields the product. However, to migrate the terminal R-group of un-activated alkynes, more electrophilic boranes are required. When reacting BCF with terminal alkynes, Erker and co-workers could observe a migration of a C_6F_5-group (Scheme 91).[138]



Scheme 91: 1,1-carboboration of unactivated alkynes

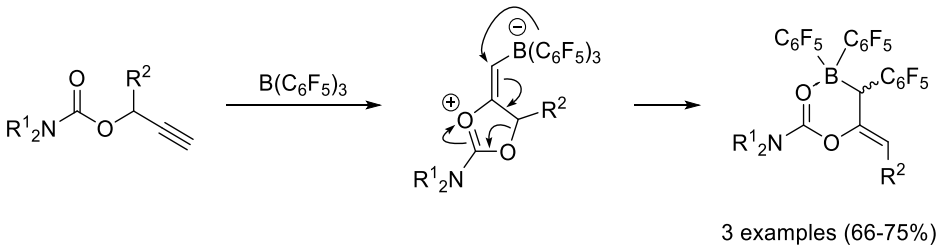
This reaction delivers both the *E* and *Z* isomer as the 1,1-carboborated products. Irradiating the reaction mixture with UV light gives the *Z*-isomer as the main product. This reaction is not limited to transferring the perfluorinated phenyl ring, as other groups have been reported to be transferred (Scheme 92).[139]



Scheme 92: 1,1-Carboboration of 1-pentyne

7.2 Aim of this work

These results encouraged further investigation of electron deficient boranes in reactions with unsaturated system to achieve benzannulations and cyclisations, amongst others.[140] Results within our group gave an insight into the reactivity of propargyl carbamates and other propargyl amides and esters (Scheme 93).[141]

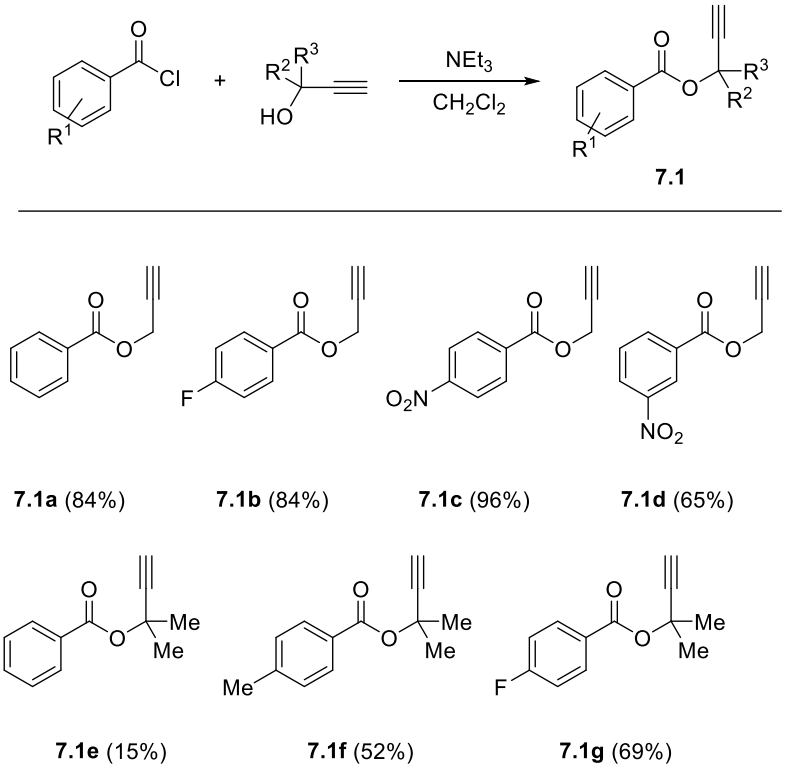


Scheme 93: Reactions of propargyl carbamates with BCF

After the initial work of Lappert and co-workers, the commercially available $PhBCl_2$ did not have the same focus as other Lewis acidic boranes. Based on results within our group, the reactivity of simply accessible propargyl esters with commercially available borane $PhBCl_2$ was probed and was the attention of this study.

7.3 Synthesis of starting materials

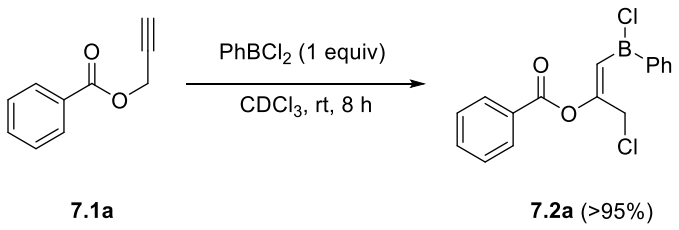
To study this reactivity a scope of esters **7.1** was synthesised (Scheme 94). With the exception of ester **7.1e**, all products **7.1** could be isolated with good yields. Compound **7.1a** was chosen as a model substrate for the unsubstituted propargyl esters **7.1a-d**.



Scheme 94: Esterification of acyl chlorids with propargyl alcohol derivatives. Isolated yields in brackets

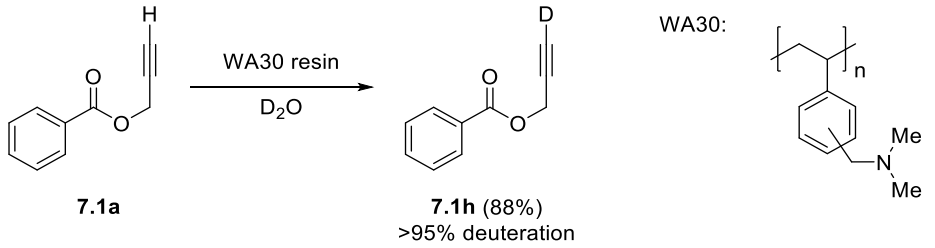
7.4 Reactivity of $PhBCl_2$ and esters **7.1**

The 1:1 stoichiometric reaction of ester **7.1a** with $PhBCl_2$ led to the clean formation of a single product **7.2a** as observed using heteronuclear NMR spectroscopy in $CDCl_3$ after 8 h (Scheme 95).



*Scheme 95: Model substrate **7.1a** in the reaction with stoichiometric amounts of $PhBCl_2$. ^1H NMR conversion in brackets*

Multinuclear NMR spectroscopy (HSQC, HMBC) suggested product **7.2a** from the reaction of **7.1a** with $PhBCl_2$. Varying the solvent did not influence the reaction, and when model substrate **7.1a** and $PhBCl_2$ was mixed in C_6D_6, toluene-d_8, CH_2Cl_2 and PhCl, the same reactivity was displayed, and full conversion could be observed within 8-9 hours. Additionally, trialling other boron reagents such as BCl_3 were unsuccessful with a mixture of products observable in multinuclear NMR spectroscopy. To gain more insight into the formation of 1,3-haloborated product **7.2a**, compound **7.1a** was deuterium labelled with D_2O in the presence of commercially available Lewis basic resin WA30 (Scheme 96).[142]



*Scheme 96: Mild deuteration of terminal alkyne **7.1a**. Isolated yield in brackets*

After successfully labelling compound **7.1a** with a deuterium atom at the terminal alkyne position, the reaction of **7.1h** with $PhBCl_2$ was monitored *via* ^1H and ^2H NMR spectroscopy and compared to the non-deuterated reaction, as depicted in Scheme 95 (Figure 30).

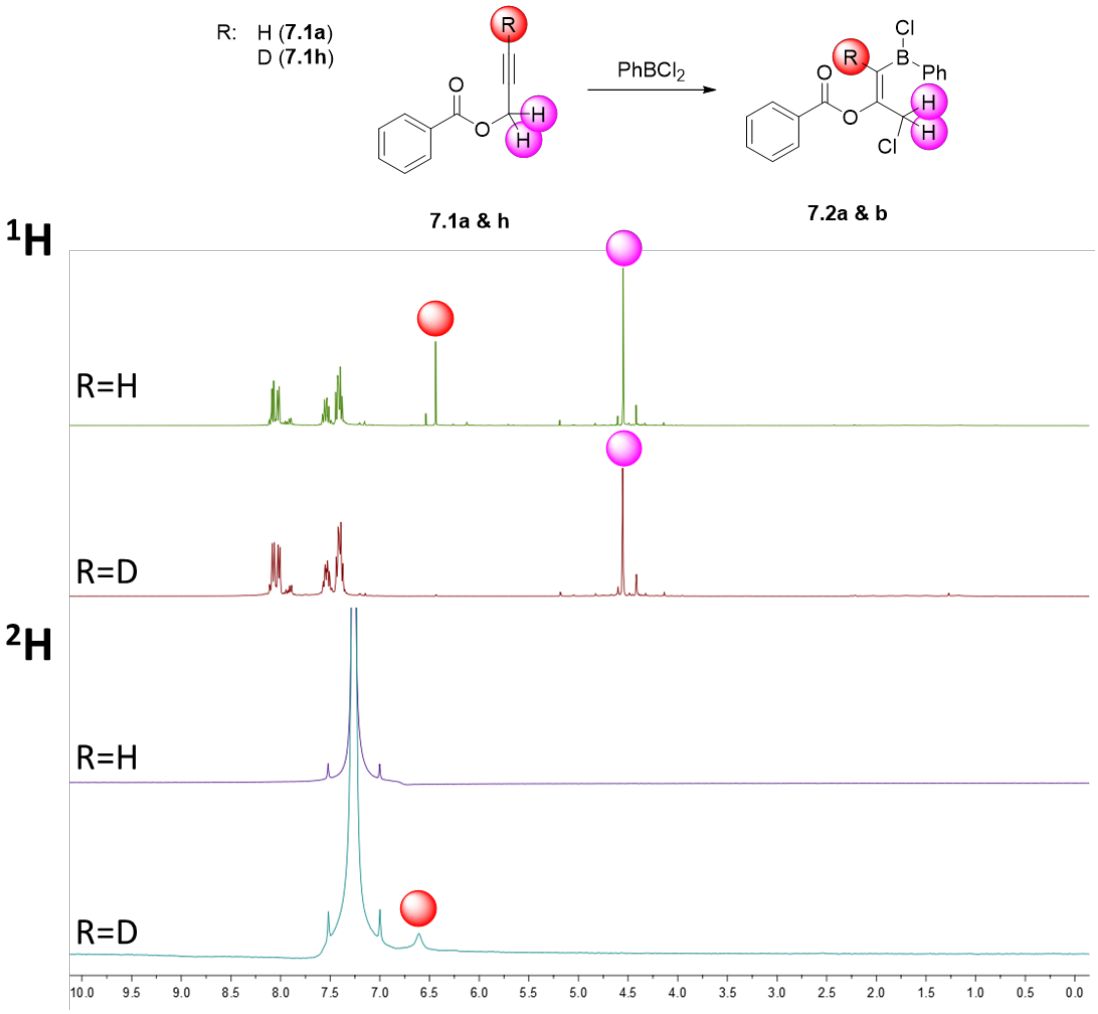
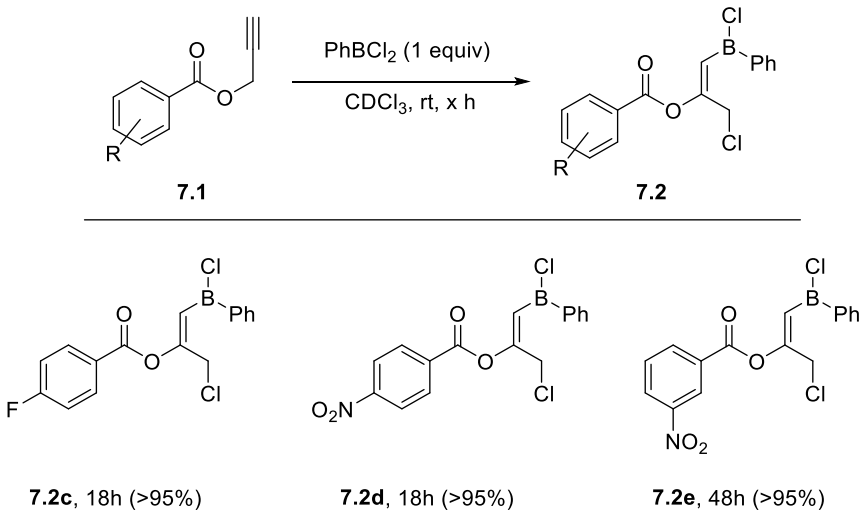


*Figure 30: ^1H and ^2H NMR spectra of haloborated products **7.2a** and **7.2b***

During the course of the reaction, the alkyne signal (δ = 2.3 ppm) of **7.1a** diminishes and a new signal at around δ = 6.5 ppm appears. This signal is absent in the ^1H NMR spectrum of the reaction mixture of **7.1h** and $PhBCl_2$. However, a signal at *ca.* δ =6.5 ppm can be observed in the ^2H NMR spectrum. This clearly identified the fate of the non-

aryl protons in the final product. A scope of other unsubstituted propargyl esters **7.1b-d** gave similar results (Scheme 97).



*Scheme 97: Scope for the 1,3-haloboration reaction of propargyl esters to give producs **7.2***

Electron deficient esters **7.1b-d** display the same reactivity to form the 1,3-haloborated products and slow evaporation of a saturated solution of the reaction mixture of **7.2d** in CH_2Cl_2/hexane produced a crop of crystals suitable for X-ray diffraction. The resolved structure confirmed the spectroscopic data (Figure 31).

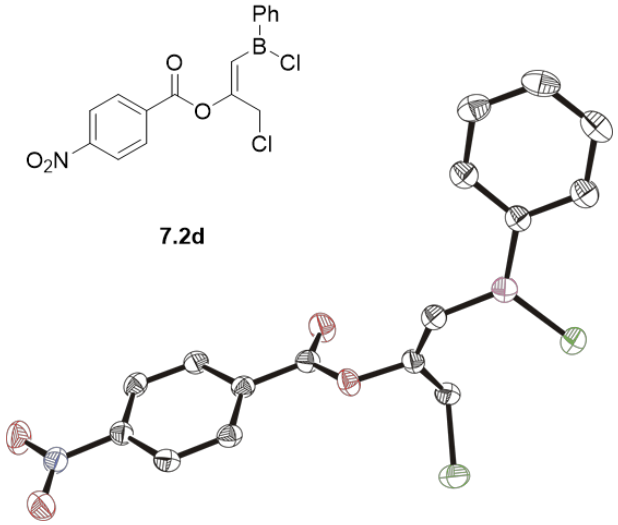
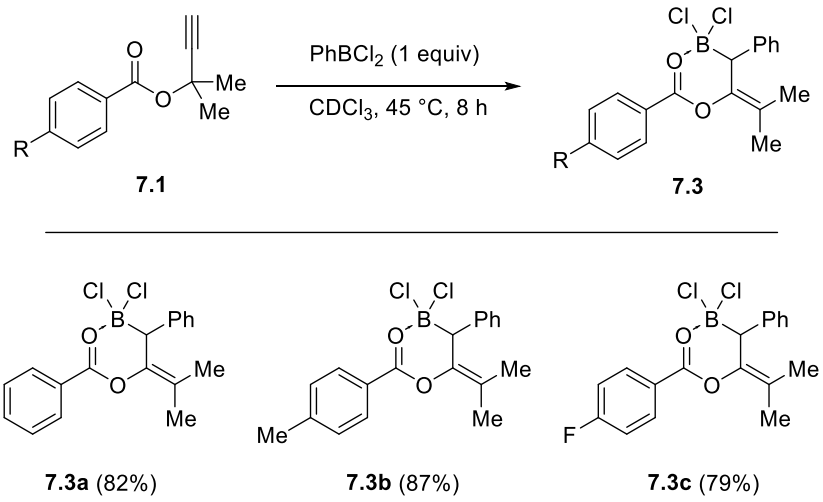


*Figure 31: Solid-state structure of compound **7.2d**. Thermal ellipsoids set to 50% probability. H atoms omitted for clarity. C: black, O: red, B: pink, Cl: green, N: blue*

It is important to mention that the *Z*-isomer was observed in all cases, and there was no adduct formation between the carbonyl oxygen and the vinyl borane visible in the ^{11}B NMR spectrum. When the sterically more demanding dimethyl-substituted esters **7.1e-g** were reacted with $PhBCl_2$, a different reactivity was observed in which a carboboration reaction took place (Scheme 98).



*Scheme 98: 1,1-Carboboration of esters **7.1** to give alkenes **7.3**. Isolated yield in brackets*

Again, slow evaporation of a saturated reaction mixture of **7.3a** in a CH_2Cl_2/hexane solution produced a number of colourless crystals suitable for X-ray diffraction (XRD) (Figure 32).

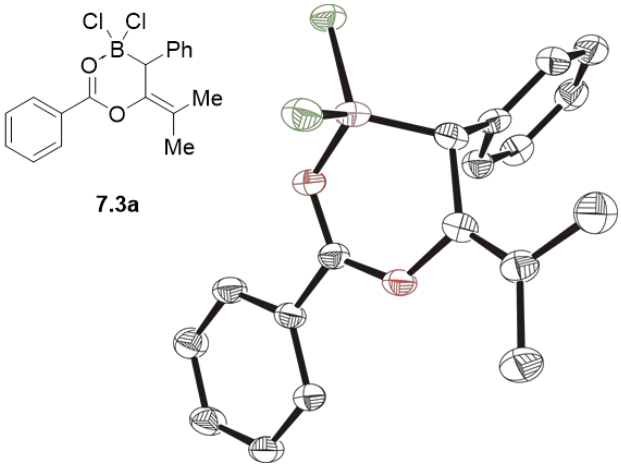
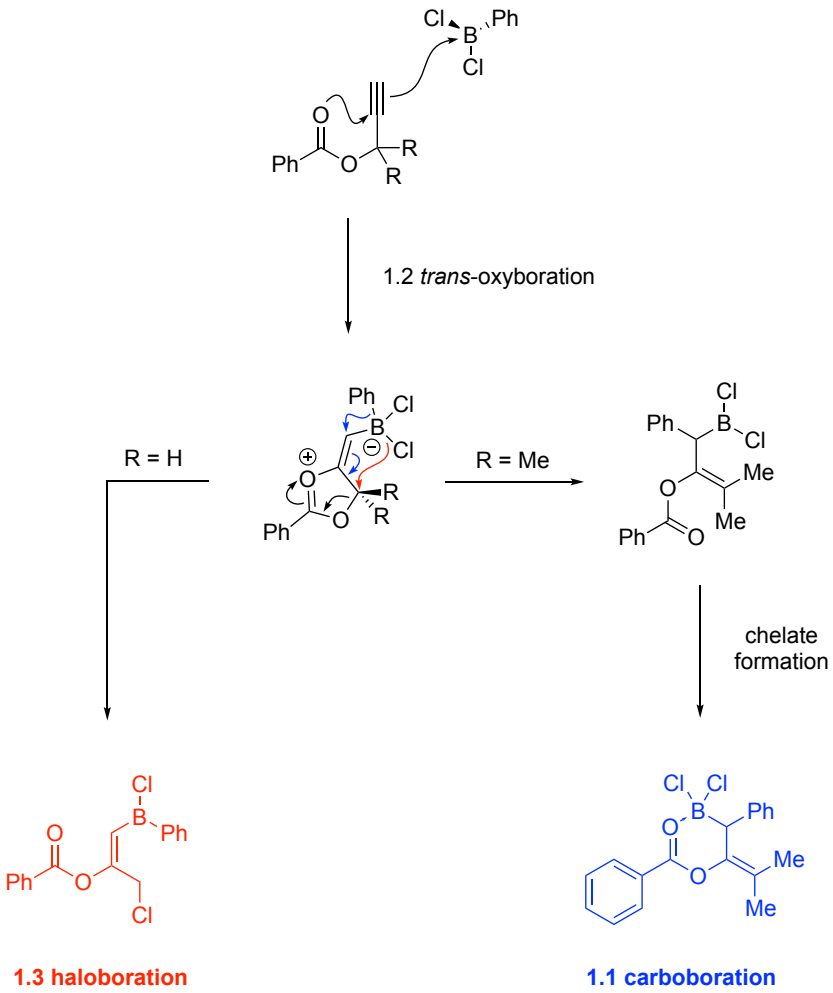


*Figure 32: Solid-state structure of compound **7.2d**. Thermal ellipsoids set to 50% probability. H atoms omitted for clarity. C: black, O: red, B: pink, Cl: green*

The determined structure is in agreement with the results of multidimensional NMR spectroscopy (HSQC, HMBC) of the isolated product **7.3a**. This reactivity resembles the 1,1-carboboration of propargyl carbamates with BCF described in Scheme 93. Here the ^{11}B NMR spectrum gives the expected signal at around 0 ppm, reminiscent of a boron-oxygen adduct (see Chapter 3).

7.5 Mechanism

In contrast to Lappert *et al.* results, it is not the Lewis acidity that influences if a carbo- or halo-boration pathway is chosen, but also the steric demand and electronic effects of the substrate at the α-position of the ester group.



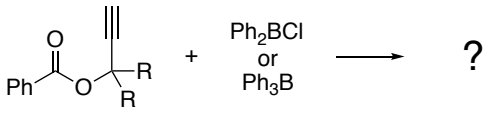
Scheme 99: Possible mechanism for both elementoborations

As with the first step in Scheme 93, a 1,2-*trans*-oxyboration initiates the reaction to form zwitterionic species **A**. Subsequently, ring opening takes places. If the α-position of the ester group is unsubstituted (R = H) a chloride ion is transferred to it, but if there is steric demand present in the α-position (R = Me) this transfer is hindered, promoting a 1,1-carboboration by migrating the phenyl group of the dioxolium borate zwitterion **A**.

7.6 Summary & Outlook

In summary, the ambiguity between these two elementoboration first described by Lappert *et al.* could be confirmed, and as an additional factor other than Lewis acidity the steric demand of the olefin can have an impact of the favoured pathway. This method can provide highly functionalised alkenes with both a boron functionality, as well as a newly formed carbon-carbon bond or halogen suitable for further reactivity.

In future work the isolation of the generated 1,3 haloborated products should be one of the major focuses as well as further reactivity with the generated products to yield compounds interesting for industrial or pharmaceutical purposes.



R = H, Me

Scheme 100: Expanding the reactivity of propargyl esters with borane Lewis acids

Also, in connection with Lapperts[135,136] work the reactivity of these propargyl esters with Ph_2BCl should be probed and the differences in reactivity studied, to see whether the change in substitution pattern und acidity of the Lewis acid also generates a different reactivity.

8 Conclusions

Lewis acids are very versatile reagents and catalysts as shown throughout this Thesis. In particular, triaryl boranes have proven to be capable of many transformations. Chapter 2 emphasised the importance of the substitution pattern of these triaryl boranes and how steric demand can reduce the Lewis acidity of these electron deficient boron centres. As a first result of this chemistry, Chapter 3 showed that triaryl boranes unsubstituted in the *ortho*-position can be used to reduce ketimines catalytically, while triaryl boranes with fluorine atoms in *ortho* position failed to do so.[143] A novel Lewis acid was synthesised for mechanistic studies and showed great activity. Therefore, making further hydroboration studies with this 3,4,5-substituted triaryl borane highly desirable. Here, the scope may be expanded to olefins with initial studies suggesting a ligand metathesis at elevated temperature indicating the presence of a highly reactive hydridoborane species ($H_nBAr^F{}_{2-n}$). The tendency to form imine borane adducts was utilised in Chapter 4 to lower the LUMO of photo physically active aldehydes and imines.[144] Here, the tris(pentafluorophenyl)borane adduct of an *n*Bu protected imine proved to be a viable indicator to differ between coordinating and non-coordinating, as well as protic and aprotic, solvents. These results could be first steps towards photo-physically active borane stabilised indicators for different applications. When increasing the steric demand in *ortho*-position of these triaryl boranes the activation of π-basic centres can be observed. In Chapter 5 this was used to cyclise alkynyl esters to form pyrones, dihydropyrones and isocoumarins.[145,146] A slight variation of the starting material could give a facile metal-free access to biologically active molecules, making this reactivity especially interesting for the pharmaceutical industry. In Chapter 6, a single electron transfer reduction of BCF gave the corresponding radical anion. A similar ester motif as in Chapter 5, in reaction with the formed radical borane anion, liberates a carbon based radical capable of reacting with styrene derivatives to give the formal Heck product. Further expanding this reactivity can be of great interest since the majority of Heck protocols is metal catalysed and, as discussed in this Thesis, metal-free approaches are enticing for various reasons. Finally, Chapter 7 showed the influence of steric hindrance in the reactivity of propargyl esters and the haloborane $PhBCl_2$.[147] An increase in steric demand of the substrates drives the reaction towards a 1,1-carboboration rather than a 1,3-haloboration product. Both reactions give a highly functionalised organic compounds with two functional groups introduced. To summarise these results, this work has showcased various novel reaction pathways and mechanisms and suggests that borane promoted transformations provide an efficient alternative to metal-based reactions.

9 Experimental

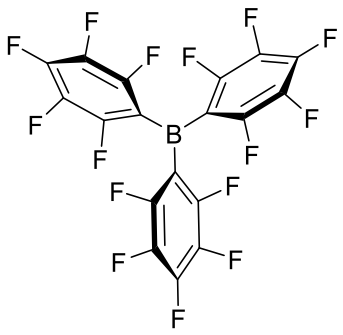
9.1 General procedure

All synthetic procedures and manipulations were performed either in a glove box with a N_2-atmosphere or under N_2 using standard Schlenk like techniques. The solvents were either used straight from the solvent purification system MB SPS-800 (toluene, CH_2Cl_2, MeCN, methanol, DCE, 1,4 dioxane, hexane, pentane) or distilled after stirring over sodium/benzophenone (Et_2O), potassium (THF) or calcium hydride ($CHCl_3$). All solvents were stored over molecular sieves (3 Å). Deuterated solvents were not further purified but also stored over molecular sieves (3 Å). Purchased chemicals were used as received. Imines in Chapter 3 were supplied by Oestreich and co-workers. ^{1}H, ^{11}B, ^{13}C, ^{19}F, ^{31}P NMR spectra were recorded on Bruker Avance 300 or 500 and on Bruker Avance II 400. ^{13}C spectra were recorded as proton uncoupled spectra. NMR spectra are referenced to $BF_3{\cdot}OEt_2$ (^{11}B), $CFCl_3$ (^{19}F), H_3PO_4 (^{31}P) or the respective NMR solvent in the ^{1}H NMR spectrum if not stated differently. Chemical shifts are expressed as parts per million (ppm) downfield shift of the respective NMR solvent. Signals are described as follows: s = singlet, d = doublet, t = triplet, q = quartet, pent. = quintet, sext. = sextet, sept. = septet, m = multiplet and br. = broad. Coupling constants are given in Hertz (Hz). Shimadzu IRaffinity-1 photospectrometer was used to measure IR-spectra. Intensities are described as follows: s = strong (>80%), m = medium (>60%), w = weak (<60%) and br. = broad. Waters LCT Premier/XE and Water GCT Premier was used to do mass spectroscopic measurements. The continuous wave (CW) X-band EPR measurements were performed on a Bruker EMX spectrometer utilizing an ER4119HS resonator, using 100 kHz field modulation, 1.0 mW microwave power and <1G amplitude. Simulations of the EPR spectra were performed using the Easyspin software package running within the Mathworks® MatLab® environment. Melting points were measured using a Gallenkamp apparatus and are reported uncorrected. Quartenary carbons adjecent to a boron atom are omitted due to broadening.

9.2 Lewis acidic boranes utilised in this work

9.2.1 Synthesis and characterisation of boranes **1**

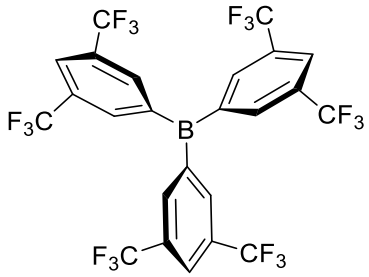
*9.2.1.1 Synthesis of borane **1c***



tris(perfluorophenyl)borane
Chemical Formula: $C_{18}BF_{15}$
Molecular Weight: 511.98 g/mol

1c was synthesised using literature procedure by Lancaster and co-workers.[33] Magnesium turnings (1.18g, 49 mmol, 1 equiv) were suspended in Et_2O (100 ml) and C_6F_5Br **1a** (6.06 ml, 49 mmol, 1 equiv) was added dropwise slowly at 0 °C. The reaction was allowed to stir for 3 h and warmed to room temperature and it turns dark brown. The resulting solution is transferred *via* filter cannula to a stirred solution of $BF_3{\cdot}OEt_2$ (2 ml, 16 mmol, 0.33 equiv) in toluene (100 ml). The excess Et_2O solvent was removed under vacuum leaving the mixture as a toluene solution. The mixture was heated making sure the temperature does not rise over 100 °C overnight. After cooling to room temperature all volatiles were removed under vacuum leaving a bright brown solid residue. The brown cake was subjected to a three-fold sublimation (120 °C, 1 x 10^{-3} bar) giving the desired product **1c** as a white solid. **Yield:** 7.05 g, 13.77 mmol, 85%. The spectroscopic data agrees with literature established values.[33] **^{11}B NMR** (160 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).

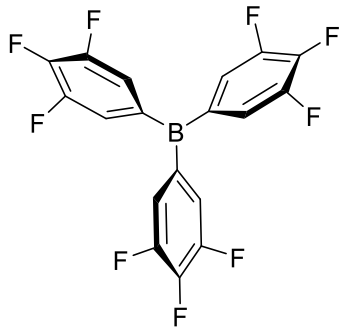
*9.2.1.2 Synthesis of borane **1f***



tris(3,5-bis(trifluoromethyl)phenyl)borane
Chemical Formula: $C_{24}H_9BF_{18}$
Molecular Weight: 650.12 g/mol

1f was synthesised using literature procedures by Ashley and co-workers.[47] *i*PrMgCl (12.15 ml, 24 mmol, 2 M, 1 equiv) was added slowly to a Schlenk flask charged with 1-bromo-3,5-bis(trifluoromethyl)benzene **1e** (3.6 ml, 24 mmol, 1 equiv) in THF (100 ml) at -20 °C. The reaction was allowed to warm to 0 °C for 30 minutes before being cooled to -50 °C. Now $BF_3{\cdot}OEt_2$ (1 ml, 8 mmol, 0.33 equiv) was added dropwise. The mixture was warmed to room temperature and after one hour all volatiles were removed under vacuum. The amber oil was extracted using a toluene/pentane mixture (1:1, 3 x 40 ml). The extract was dried under vacuum. The greyish solid residue was sublimed (100 °C; 1 x 10^{-3} bar) to give **1f** as a white solid. **Yield:** 3.27 g, 5.02 mmol, 62%. The spectroscopic data agrees with literature established values.[47] **^{1}H NMR** (400 MHz, $CDCl_3$, 298K) δ/ppm: 8.22 (s, 3H, *p*-H), δ 7.99 (s, 6H, *o*-H). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 68.8 (s, br). **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: −63.4 (s, CF_3).

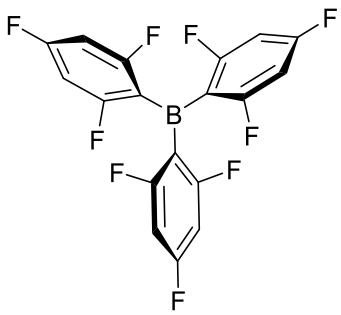
*9.2.1.3 Synthesis of borane **1h***



tris(3,4,5-trifluorophenyl)borane
Chemical Formula: $C_{18}H_6BF_9$
Molecular Weight: 404.04 g/mol

1-Bromo-3,4,5-trifluorobenzene **1g** (3.5 ml, 29.4 mmol, 1 equiv) was dissolved in diethylether (50 ml). The resulting solution was stirred and cooled to –78 °C, and a solution of *n*BuLi (20 ml, 1.47 M, 29.4 mmol, 1 equiv) was added slowly. The resulting yellow solution was stirred for 2 h and turned white. To the still cool mixture, $BF_3{\cdot}OEt_2$ (1.2 ml, 9.8 mmol, 0.33 equiv) was added dropwise and, after stirring for another 2 h, the cooling setup was removed. The reaction was stirred overnight, the solvent was then removed *in vacuo*, and the resulting solid was sublimed at 120 °C under vacuum yielding pale yellow oily crystals that were washed with pentane (3 x 3 ml), dried, and resublimed to afford **1h** (as a pale-yellow crystal. **Yield:** 0.65 g, 16%, 1.56 mmol. **^{1}H NMR** (400 MHz, $CDCl_3$, 298K) δ/ppm: 7.07 (t, $^{3}J_{HF}$ = 7.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 151.3 (ddd, $^{1,2,3}J_{CF}$ = 254.0, 9.6, 2.7 Hz, *m*-C), 143.0 (dt, $^{1,2}J_{CF}$ = 260.9, 15.0 Hz, *p*-C), 136.5–136.0 (m, C-B), 122.0 (dd, $^{2,3}J_{CF}$ = 13.6, 5.4 Hz, *o*-C).[33] **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 64.6 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -133.2 (d, $^{3}J_{FF}$ = 20.1 Hz, *m*-F), -152.4 (t, $^{3}J_{FF}$ = 20.1 Hz, *p*-F). **HRMS** (TOF EI) m/z calculated for $[C_{18}H_6F_9B]^+$: 404.0413, found: 404.0529.

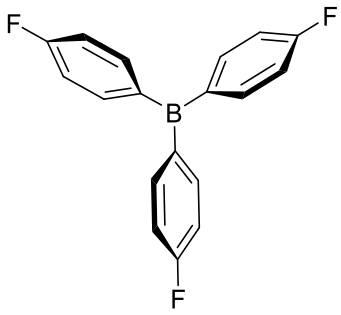
*9.2.1.4 Synthesis of borane **1i***



tris(2,4,6-trifluorophenyl)borane
Chemical Formula: $C_{18}H_6BF_9$
Molecular Weight: 404.04 g/mol

1i was synthesised using literature procedures by Alcazaro and co-workers.[49] 1-Bromo-2,4,6-trifluorobenzene (2.87 ml, 24.3 mmol, 1 equiv) was dissolved in THF (50 ml) and cooled to -20 °C. At this temperature *i*PrMgCl (4.0 ml, 8.1 mmol, 1 equiv, 2M in THF) was added dropwise. The reaction mixture allowed to warm up to 0 °C and after 1 h cooled to -50 °C. At this temperature $BF_3{\cdot}OEt_2$ (1.00 ml, 8.1 mmol, 0.33 equiv) is added dropwise. After stirring for an hour the mixture was allowed to warm to room temperature. All volatiles were removed under vacuum and the resulting solid was subject of a two-fold sublimation (120 °C, 1 x 10^{-3} bar) to give **1i** as a white solid. **Yield:** 3.27 g, 5.02 mmol, 62%. The spectroscopic data agrees with literature established values.[49] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 6.64 (t, $^3J_{HF}$ = 8.3 Hz, 6H, *m*-H). **^{11}B NMR** (160 MHz, $CDCl_3$, 298 K) δ/ppm: 58.4 (br. s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -95.75 (d, $^4J_{FF}$ = 10.4 Hz, 6F, *o*-F), -100.31 (t, $^4J_{FF}$ = 10.4 Hz, 3F, *p*-F).

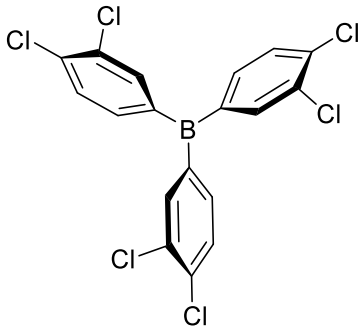
*9.2.1.5 Synthesis of borane **1l***



tris(4-fluorophenyl)borane
Chemical Formula: $C_{18}H_{12}BF_3$
Molecular Weight: 296.10 g/mol

1-bromo-4-fluorobenzene (**46**) (3.72 ml, 34.1 mmol, 1 equiv) was suspended in Et_2O at –78 °C and *n*BuLi (15 ml, 37.5 mmol, 1.1 equiv) was added dropwise and the reaction mixture was allowed to stir at –78 °C for 3h. $BF_3{\cdot}OEt_2$ (1.4 ml, 11.37 mmol, 0.33 equiv) was added to the reaction mixture dropwise and the reaction mixture was allowed to warm to room temperature overnight. Removal of all volatiles *in situ* and a three-fold sublimation of the remaining solid (120 °C, 1 × 10^{-3} mbar) afforded the desired borane **1l** as a white solid. **Yield:** 2.74g, 9.28 mmol, 82%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.64 -7.57 (m, 2H), 7.13 – 7.21 (m, 2H). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 65.2 (s, 1B). **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -107.79 (s, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 165.5 (d, $^{1}J_{CF}$ = 253.0 Hz, 3C, *p*-C), 141.0 (d, $^{3}J_{CF}$ = 8.4 Hz, 6C, o-C), 138.8 (br. s, 3C, B-C), 115.0 (d, $^{2}J_{CF}$ = 20.0 Hz, 6C, m-C). **HRMS** (ESI) *m/z* calculated for $C_{18}H_{12}F_3B$ $[M+H]^+$: 296.0984, found: 296.0996.

*9.2.1.6 Synthesis of borane **1n***



tris(3,4-dichlorophenyl)borane
Chemical Formula: $C_{18}H_9BCl_6$
Molecular Weight: 448.78 g/mol

A solution of 4-bromo-1,2-dichlorobenzene (2.74 g, 12.1 mmol, 1 equiv) in diethylether (50 ml, dry) was cooled to -78° C under nitrogen and *n*BuLi (4.9 ml, 2.5 M, 12.1 mmol, 1 equiv) in hexane was added dropwise. The solution turned yellow and was stirred for an additional 2 h to give a white suspension. $BF_3{\cdot}OEt_2$ (0.5 ml, 4.0 mmol, 0.33 equiv) was added dropwise and the mixture was allowed to warm to room temperature and stirred overnight. The resulting suspension was filtered and the filtrate is concentrated *in vacuo*. The yellow solid was dissolved in $CHCl_3$ (5 ml) and kept at -40 °C over night. The cooled suspension was filtered and pentane (0.1 ml) was added. After storing it at -40 °C for an additional 4 h, a white solid crashed out and was filtered, washed with pentane (3 x 1ml) and dried under reduced pressure yielding **1n** as a white solid. **Yield:** 244 mg, 0.54 mmol, 22%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.60 (s, 1H), 7.60 (d, $^3J_{HH}$ = 9.1 Hz, 1H), 7.37 (dd, $^{3,4}J_{HH}$ = 8.0, 1.6 Hz, 1H). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 65.8 (s). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 139.7, 137.4, 137.3, 133.0, 130.5. **HRMS** (ESI) *m/z* calculated for $C_{18}H_{10}Cl_6B$ $[M+H]^+$: 445.9033, found: 445.9043.

9.2.2 Crystallographic data for **1h**, **1i**, **1l** and **1n**

Compound	**1h**	**1i**	**1l**	**1n**
Empirical Formula	$C_{18}H_6BF_9$	$C_{18}H_6BF_9$	$C_{18}H_{12}BF_3$	$C_{18}H_9BCl_6$
Space Group	P 2_1/n	P 2_1/n	P 2_1/c	P 2_1/n
a/Å	9.6716(3)	10.3269(5)	8.2446(6)	10.9777(7)
b/Å	12.3184(4)	19.3379(11)	17.9887(11)	15.5702(7)
c/Å	13.4558(5)	15.9140(9)	9.8915(6)	11.5678(7)
α/°	90	90	90	90
β/°	100.288(3)	96.824(5)	101.431(6)	111.393(7)
Y/°	90	90	90	90
Volume/Å^3	1577.34(9)	3155.5(3)	1437.91(16)	1841.0(2)
Z	4	8	4	4
T/K	150	150	150	150
D_c/g·cm^{-3}	1.701	1.701	1.368	1.619
R (reflections)	0.0443(2480)	0.0428(5107)	0.0482(2296)	0.0370(3352)
wR2 (reflections)	0.1305(3086)	0.1154(6877)	0.1382(3140)	0.0827(4190)
Theta(max)	73.906	27.103	27.101	27.876

9.2.3 Lewis acidities determined *via* the Gutmann Beckett method[6]

Borane	^{31}P NMR Shift [ppm]	$AN = (\delta - 41.0)\frac{100}{86.14 - 41.0}$
BPh_3	64.94	53
1c	75.98	76
1h	76.92	79
1i	71.90	69
1l	66.73	57
1n	76.24	78

9.2.4 General Procedure A1 for the Gutmann Beckett method

The borane (1.0 equiv) was dissolved in $CDCl_3$ (0.5 ml) and was added to triethylphosphine oxide (0.6 equiv). A capillary containing PPh_3 in $CDCl_3$ was added as a standard and the NMR tube was inverted several times. The ^{31}P NMR chemical shift of the triphenylphosphine (PPh_3) in $CDCl_3$ was calibrated to δ = -5.21 ppm according to Demchuk *et al*.[148] and the acceptor number was calculated according to Beckett *et al*.[6]

9.2.4.1 Triphenylborane (BPh_3)

According to general procedure A1, triphenylborane (15 mg, 0.062 mmol, 1 equiv) and triethylphosphine oxide (5.0 mg, 0.037 mmol, 0.6 equiv). ^{31}P NMR (162 MHz, $CDCl_3$, 298 k) δ/ppm: 64.94 (s).

*9.2.4.2 Tris(pentafluorophenyl)borane (**1c**)*

According to general procedure A1, tris(pentafluorophenyl)borane (20 mg, 0.04 mmol, 1 equiv) and triethylphosphine oxide (3.14 mg, 0.023 mmol, 0.6 equiv). ^{31}P NMR (162 MHz, $CDCl_3$, 298 k) δ/ppm: 75.98 (s).

*9.2.4.3 Tris(3,4,5-trifluorophenyl)borane (**1h**)*

According to general procedure A1, tris(3,4,5-trifluorophenyl)borane (20 mg, 0.050 mmol, 1 equiv) and triethylphosphine oxide (3.98 mg, 0.030 mmol, 0.6 equiv). ^{31}P NMR (162, MHz, $CDCl_3$, 298 k) δ/ppm: 76.92 (s).

*9.2.4.4 Tris(4-fluorophenyl)borane (**1l**)*

According to general procedure A1, tris(4-fluorophenyl)borane (20 mg, 0.068 mmol, 1 equiv) and triethylphosphine oxide (5.5 mg, 0.041 mmol, 0.6 equiv). ^{31}P NMR (162 MHz, $CDCl_3$, 298 k) δ/ppm: 66.73 (s).

*9.2.4.5 Tris(3,4-dichlorophenyl)borane (**1n**)*

According to general procedure A1, tris(3,4-dichlorophenyl)borane (30 mg, 0.067 mmol, 1 equiv) and triethylphosphine oxide (5.38 mg, 0.040 mmol, 0.6 equiv). ^{31}P NMR (162, MHz, $CDCl_3$, 298 k) δ/ppm: 76.24 (s).

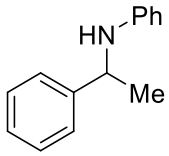
9.3 Hydroboration of imines

9.3.1 General procedure B1:

In a glove box, a 2-ml GLC-vial equipped with a stirring bar is charged with BAr^F_3 (1.0 mol%), imine (1.0 equiv), and HBpin (1.2 equiv). Benzene (1 ml) is added to the reaction, and the resulting mixture is stirred for 18 h at room temperature. The resulting yellow orange solution is then diluted with CH_2Cl_2 (*ca.* 3 ml) and washed with water (3 × 5 ml). The combined organic layers are washed with brine (5.0 ml), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The conversion is determined by GLC-MS analysis of the crude material. The crude mixture is further purified by flash-column chromatography on silica gel using the indicated eluent.

9.3.2 Product characterisation

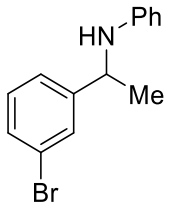
*9.3.2.1 Synthesis of **2.3a***



N-(1-phenylethyl)aniline
Chemical Formula: $C_{14}H_{15}N$
Molecular Weight: 197.28 g/mol

Prepared from (*E*)-*N*,1-diphenylethan-1-imine (0.2 mmol, 39.4 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the general procedure B1. The title compound was purified by flashcolumn chromatography using cyclohexane/TBME (25/1) as eluent to afford **2.3a** as colourless oil. Spectroscopic data agrees with literature values.[149] **Yield:** 34.5 mg, 0.17 mmol, 87% **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.43–7.38 (m, 2H), 7.35 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.30–7.23 (m, 1H), 7.13 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 6.69 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.55 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 4.52 (q, $^3J_{HH}$ = 6.7 Hz, 1H), 4.16 (br. s, 1H), 1.55 (d, $^3J_{HH}$ = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 147.3, 145.2, 129.2, 128.7, 127.0, 125.9, 117.4, 113.4, 53.6, 25.1.

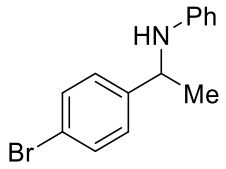
*9.3.2.2 Synthesis of **2.3b***



N-(1-(3-bromophenyl)ethyl)aniline
Chemical Formula: $C_{14}H_{14}BrN$
Molecular Weight: 276.18 g/mol

Prepared from (*E*)-1-(3-bromophenyl)-*N*-phenylethan-1-imine (54.9 mg, 0.2 mmol) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure B1. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **2.3b** as colourless oil. Spectroscopic data agrees with literature values.[149] **Yield:** 42.3 mg, 0.15 mmol, 77% **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.44 (s, 1H), 7.30–7.24 (m, 1H), 7.22 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 7.09 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.02 (t, $^3J_{HH}$ = 8.0 Hz, 2H), 6.59 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.41 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 4.35 (q, $^3J_{HH}$ = 6.7 Hz, 1H), 4.15 (br. s, 1H), 1.42 (d, $^3J_{HH}$ = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 148.0, 146.9, 130.4, 130.2, 129.3, 129.2, 124.7, 123.0, 117.9, 113.6, 53.5, 25.2.

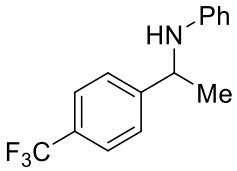
*9.3.2.3 Synthesis of **2.3c***



N-(1-(4-bromophenyl)ethyl)aniline
Chemical Formula: $C_{14}H_{14}BrN$
Molecular Weight: 276.18 g/mol

Prepared from (*E*)-1-(4-bromophenyl)-*N*-phenylethan-1-imine (55.4 mg, 0.2 mmol) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure B1. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **2.3c** as colorless oil. Spectroscopic data agrees with literature values.[149] **Yield:** 53.4 mg, 0.19 mmol, 96% **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.47 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.28 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.17–7.11 (m, 2H), 6.71 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.53 (d, $^3J_{HH}$ = 7.6 Hz, 2H), 4.47 (q, $^3J_{HH}$ = 6.7 Hz, 1H), 4.29 (br. s, 1H), 1.53 (d, $^3J_{HH}$ = 6.8 Hz, 3H).). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 146.8, 144.3, 131.9, 129.3, 127.8, 120.7, 117.9, 113.7, 53.4, 25.1.

*9.3.2.4 Synthesis of **2.3d***

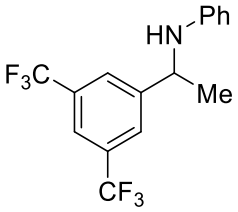


N-(1-(4-(trifluoromethyl)phenyl)ethyl)aniline
Chemical Formula: $C_{15}H_{14}F_3N$
Molecular Weight: 265.28 g/mol

Prepared from (*E*)-*N*-phenyl-1-(4-(trifluoromethyl)phenyl)ethan-1-imine (52.6 mg, 0.2 mmol) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure

B1. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **2.3d** as light-yellow oil. Spectroscopic data agrees with literature values.[149] **Yield:** 47.5 mg, 0.18 mmol, 90%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.48 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 7.40 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.02 (t, $^{3}J_{HH}$ = 8.0 Hz, 2H), 6.60 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 6.40 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H), 4.44 (q, $^{3}J_{HH}$ = 6.8 Hz, 1H), 4.30 (br. s, 1H), 1.44 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 149.4, 146.6, 129.3 (q, $^{2}J_{CF}$ = 32.3 Hz), 129.3, 126.3, 125.7 (q, $^{3}J_{CF}$ = 3.8 Hz), 118.0, 113.6, 53.6, 25.2. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: −64.4 (s, CF_3).

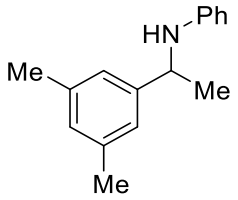
*9.3.2.5 Synthesis of **2.3e***



N-(1-(3,5-bis(trifluoromethyl)phenyl)ethyl)aniline
Chemical Formula: $C_{16}H_{13}F_6N$
Molecular Weight: 333.28 g/mol

Prepared from (*E*)-1-(3,5-bis(trifluoromethyl)phenyl)-*N*-phenylethan-1-imine (0.2 mmol, 66.5 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure B1. The title compound was purified by flash-column chromatography using cyclohexane/TBME (18/1) as eluent to afford **2.3e** as a colourless liquid. Spectroscopic data agrees with literature values.[149] **Yield:** 56.0 mg, 0.17, 84%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.86 (s, 2H), 7.78 (s, 1H), 7.14 (t, $^{3}J_{HH}$ = 8.0 Hz, 2H), 6.74 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 6.50 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H), 4.59 (q, $^{3}J_{HH}$ = 6.7 Hz, 1H), 4.32 (br. s, 1H), 1.57 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 148.3, 146.4, 132.2 (q, $^{2}J_{CF}$ = 33.3 Hz), 129.5, 126.4, 123.5 (q, $^{1}J_{CF}$ = 272.9 Hz), 121.4, 118.6, 113.8, 53.8, 25.1.2 **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: −62.9 (s, CF_3).

*9.3.2.6 Synthesis of **2.3f***

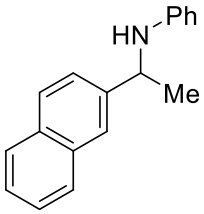


N-(1-(3,5-dimethylphenyl)ethyl)aniline
Chemical Formula: $C_{16}H_{19}N$
Molecular Weight: 225.34 g/mol

Prepared from (*E*)-1-(3,5-dimethylphenyl)-*N*-phenylethan-1-imine (0.2 mmol, 45.2 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure B1. The

title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **2.3f** as a colourless liquid. Spectroscopic data agrees with literature values.[149] **Yield:** 43.1 mg, 0.19 mmol, 95%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.17–7.11 (m, 2H), 7.02 (s, 2H), 6.91 (s, 1H), 6.73–6.67 (m, 1H), 6.61–6.56 (m, 2H), 4.44 (q, $^{3}J_{HH}$ = 6.7 Hz, 1H), 4.28 (br. s, 1H), 2.34 (s, 6H), 1.54 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 147.3, 145.2, 138.2, 129.2, 128.7, 123.8, 117.4, 113.6, 53.8, 25.0, 21.5.

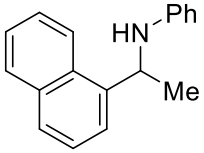
*9.3.2.7 Synthesis of **2.3g***



N-(1-(naphthalen-2-yl)ethyl)aniline
Chemical Formula: $C_{18}H_{17}N$
Molecular Weight: 247.34 g/mol

Prepared from (*E*)-1-(naphthalen-2-yl)-*N*-phenylethan-1-imine (0.2 mmol, 49.6 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure B1. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **2.3g** as a colourless liquid. Spectroscopic data agrees with literature values.[150] **Yield:** 46.0 mg, 0.18 mmol, 92%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.88–7.82 (m, 4H), 7.55 (d, $^{3}J_{HH}$ = 8.6 Hz, 1H), 7.52–7.45 (m, 2H), 7.13 (t, $^{3}J_{HH}$ = 8.0 Hz, 2H), 6.70 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 6.62 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H), 4.68 (q, $^{3}J_{HH}$ = 6.7 Hz, 1H), 4.45 (br. s, 1H), 1.64 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 147.2, 142.7, 133.7, 132.9, 129.3, 128.6, 128.0, 127.8, 126.1, 125.7, 124.6, 124.5, 117.7, 113.7, 54.1, 25.0.

*9.3.2.8 Synthesis of **2.3h***

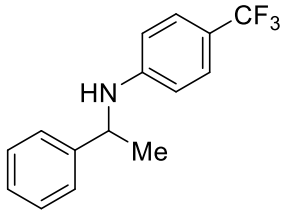


N-(1-(naphthalen-1-yl)ethyl)aniline
Chemical Formula: $C_{18}H_{17}N$
Molecular Weight: 247.34 g/mol

Prepared from (*E*)-1-(naphthalen-1-yl)-*N*-phenylethan-1-imine (0.2 mmol, 49.8 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure B1. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **2.3h** as a colourless liquid. Spectroscopic data agrees with

literature values.[151] **Yield:** 49.9 mg, 0.2 mmol, 99%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.20 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.94 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.79 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.70 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 7.63–7.51 (m, 2H), 7.44 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 7.14–7.07 (m, 2H), 6.72– 6.66 (m, 1H), 6.54 (d, $^3J_{HH}$ = 7.6, 2H), 5.33 (q, $^3J_{HH}$ = 6.4 Hz, 1H), 4.41 (s, 1H), 1.70 (d, $^3J_{HH}$ = 7.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 147.1, 140.0, 134.2, 130.9, 129.3, 127.6, 126.2, 126.0, 125.6, 122.7, 122.5, 117.5, 113.5, 49.7, 23.7.

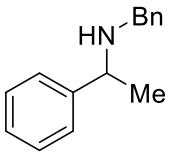
*9.3.2.9 Synthesis of **2.3i***



N-(1-phenylethyl)-4-(trifluoromethyl)aniline
Chemical Formula: $C_{15}H_{14}F_3N$
Molecular Weight: 265.28 g/mol

Prepared from (*E*)-1-phenyl-*N*-(4-(trifluoromethyl)phenyl)ethan-1-imine (0.2 mmol, 51.8 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure B1. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **2.3i** as a colourless liquid. Spectroscopic data agrees with literature values.[149] **Yield:** 15.6 mg, 0.06 mmol, 30%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.34–7.31 (m, 6H), 7.28–7.24 (m, 1H), 6.53 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 4.52 (q, $^3J_{HH}$ = 6.7 Hz, 1H), 1.55 (d, $^3J_{HH}$ = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 149.5, 144.2, 129.0, 127.4, 126.6 (q, $^3J_{CF}$ = 3.7 Hz), 125.9, 125.0 (q, $^1J_{CF}$ = 269.8 Hz), 118.6 (q, $^2J_{CF}$ = 32.0 Hz), 112.8, 53.6, 24.9. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: −65.1 (s, CF_3).

*9.3.2.10 Synthesis of **2.3k***

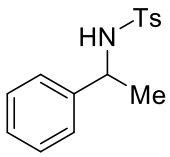


N-benzyl-1-phenylethan-1-amine
Chemical Formula: $C_{15}H_{17}N$
Molecular Weight: 211.31 g/mol

Prepared from (*E*)-*N*-benzyl-1-phenylethan-1-imine (0.2 mmol, 42.9 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure B1. The title compound was purified by flash-column chromatography using cyclohexane/TBME (10/1) as eluent to afford **2.3k** as a colourless liquid. Spectroscopic data agrees with

literature values.[152] **Yield:** 35.9 mg, 0.17 mmol, 83%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.33–7.18 (m, 10H), 3.78 (q, $^3J_{HH}$ = 6.6 Hz, 1H), 3.59 (q, $^3J_{HH}$ = 13.2 Hz, 2H), 2.61 (br. s, 1H), 1.35 (d, $^3J_{HH}$ = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 144.9, 139.9, 128.7, 128.6, 128.4, 127.3, 127.3, 126.9, 57.7, 51.6, 24.3.

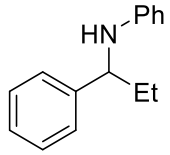
*9.3.2.11 Synthesis of **2.3l***



4-methyl-*N*-(1-phenylethyl)benzenesulfonamide
Chemical Formula: $C_{15}H_{17}NO_2S$
Molecular Weight: 275.37 g/mol

Prepared from 4-methyl-*N*-(1-phenylethylidene)benzenesulfonamide (0.2 mmol, 55.1 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure B1. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **2.3l** as a colourless liquid. Spectroscopic data agrees with literature values.[153] **Yield:** 38.4 mg, 0.14 mmol, 70%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.62 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.19–7.16 (m, 4H), 7.11–7.09 (m, 2H), 5.12 (br. s, 1H), 4.49–4.42 (m, 1H), 2.38 (s, 3H), 1.41 (d, $^3J_{HH}$ = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 143.2, 142.2, 137.7, 129.5, 128.6, 127.5, 127.2, 126.2, 53.7, 23.7, 21.6.

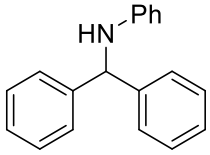
*9.3.2.12 Synthesis of **2.3m***



N-(1-phenylpropyl)aniline
Chemical Formula: $C_{15}H_{17}N$
Molecular Weight: 211.31 g/mol

Prepared from (*E*)-*N*,1-diphenylpropan-1-imine (0.2 mmol, 41.8 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure B1. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **2.3m** as a colourless liquid. Spectroscopic data agrees with literature values.[149] **Yield:** 35.1 mg, 0.17 mmol, 83%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.38–7.30 (m, 4H), 7.26–7.21 (m, 1H), 7.13 – 7.08 (m, 2H), 6.66 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.55 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 4.35 (br. s, 1H), 4.24 (t, $^3J_{HH}$ = 6.7 Hz, 1H), 1.95–1.78 (m, 2H), 0.97 (t, $^3J_{HH}$ = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 147.3, 143.8, 129.2, 128.6, 127.1, 126.7, 117.5, 113.6, 60.1, 31.7, 11.0.

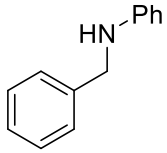
9.3.2.13 Synthesis of ***2.3n***



N-benzhydrylaniline
Chemical Formula: $C_{19}H_{17}N$
Molecular Weight: 259.35 g/mol

Prepared from *N*,1,1-triphenylmethanimine (0.2 mmol, 51.8 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure B1. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **2.3n** as a colourless liquid. Spectroscopic data agrees with literature values.[154] **Yield:** 49.2 mg, 0.19 mmol, 94%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.61–7.45 (m, 10H), 7.37–7.30 (m, 2H), 6.92 (t, $^3J_{HH}$ = 6.6 Hz, 1H), 6.78 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 5.72 (s, 1H), 4.46 (br. s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 147.3, 142.9, 129.2, 128.9, 127.5, 127.4, 117.8, 113.6, 63.2

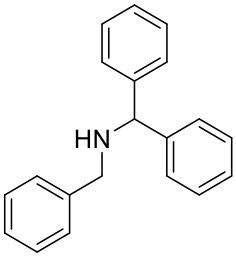
9.3.2.14 Synthesis of ***2.3o***



N-benzylaniline
Chemical Formula: $C_{13}H_{13}N$
Molecular Weight: 183.25 g/mol

Prepared from (*E*)-*N*,1-diphenylmethanimine (0.2 mmol, 36.5 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure B1. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **2.3o** as a colourless liquid. Spectroscopic data agrees with literature values.[155] **Yield:** 31.7 mg, 0.17 mmol, 86% **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.43–7.27 (m, 5H), 7.21 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 6.76 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.68 (d, $^3J_{HH}$ = 7.7 Hz, 2H), 4.36 (br. s, 1H), 4.36 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 148.0, 139.4, 129.4, 128.8, 127.7, 127.4, 117.9, 113.2, 48.6.

*9.3.2.15 Synthesis of **2.3p***



N-benzyl-1,1-diphenylmethanamine
Chemical Formula: $C_{20}H_{19}N$
Molecular Weight: 273.38 g/mol

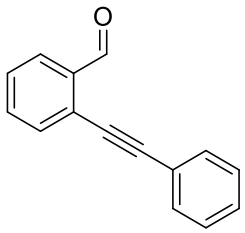
Prepared from (*E*)-*N*-benzhydryl-1-phenylmethanimine (0.2 mmol, 55.1 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure B1. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **2.3p** as a colourless liquid. Spectroscopic data agrees with literature values.[156] **Yield:** 47.9 mg, 0.17 mmol, 86% **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.44–7.42 (m, 4H), 7.33–7.18 (m, 11H), 4.86 (s, 1H), 3.75 (s, 2H), 2.04 (br. s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 143.9, 140.3, 128.6, 128.5, 128.4, 127.5, 127.2, 127.1, 66.5, 51.9.

9.4 Photophysical properties of imines

9.4.1 General procedure C1 for the synthesis of aldehyde reagents **4.1**

In accordance with the literature[71] CuI (1 mol%), $Pd(PPh_3)_2Cl_2$ (2 mol%) and the corresponding aldehyde (1.0 equiv) were stirred in dry NEt_3. The acetylene reagent (1.2 equiv) was added slowly at room temperature. The reaction mixture was heated up to 60 °C for 19 h. After cooling the solution to room temperature, the suspension was filtered using a silica plug and washed with Et_2O (2 x 10 ml). The solvent was removed *in vacuo* and the crude product was purified by column chromatography. The resultant oil was distilled to give the desired product.

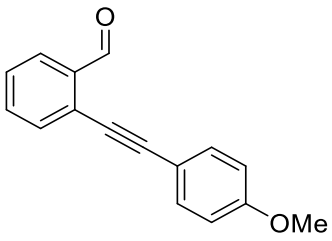
*9.4.1.1 Synthesis of **4.1a***



2-(phenylethynyl)benzaldehyde
Chemical Formula: $C_{15}H_{10}O$
Molecular Weight: 206.24 g/mol

In accordance to General Procedure C1, CuI (20.6 mg, 0.11 mmol, 1 mol%), $Pd(PPh_3)_2Cl_2$ (151 mg, 0.22 mmol, 2 mol%) and 2-bromobenzaldehyde (1.26 ml, 11 mmol, 1.0 equiv) and phenylacetylene (1.42 ml, 13 mmol, 1.2 equiv) in dry NEt_3 (40 ml) were used to synthesise the compound **4.1a**. The crude product was purified by column (SiO_2, hexane/EtOAc, 50:1). The oil was distilled (180 °C, 15 mmHg) to give the desired product as an oil. **Yield:** 2.19 g, 9.70 mmol, 90%. Spectroscopic data agrees with literature known values.[71] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 10.66 (d, $^4J_{HH}$ = 0.8 Hz, 1H), 7.95 (ddd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz, $^4J_{HH}$ = 0.6 Hz, 1H), 7.63 (ddd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz, $^4J_{HH}$ = 0.6 Hz, 1H), 7.59–7.53 (m, 3H), 7.49–7.44 (m, 1H), 7.40–7.35 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 191.8, 135.9, 133.9, 133.3, 131.8, 129.2, 128.7, 128.6, 127.3, 126.9, 122.4, 96.4, 85.0.

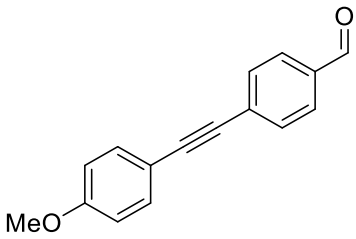
*9.4.1.2 Synthesis of **4.1b***



2-((4-methoxyphenyl)ethynyl)benzaldehyde
Chemical Formula: $C_{16}H_{12}O_2$
Molecular Weight: 236.27 g/mol

In accordance to General Procedure C1, CuI (42 mg, 0.22 mmol, 4 mol%), $Pd(PPh_3)_2Cl_2$ (78 mg, 0.11 mmol, 2 mol%), 2-ethynylbenzaldehyde (0.94 g, 7.22 mmol, 1.3 equiv) and 4-iodoanisol (1.30 g, 11 mmol, 1.0 equiv) in dry NEt_3 (50 ml) were used to synthesise compound **4.1b**. The crude product was purified by column (SiO_2, hexane/EtOAc, 40:1, gradient to 35:1). The resulting orange oil was recrystallised with CH_2Cl_2/Hexane. The product was isolated as a colourless solid. **Yield:** 0.602 g, 2.5 mmol, 46%. Spectroscopic data agrees with literature known values.[71] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 10.65 (d, $^4J_{HH}$ = 0.8 Hz, 1H), 7.94 (ddd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.4 Hz, $^4J_{HH}$ = 0.6 Hz, 1H), 7.65–7.55 (m, 2H), 7.54–7.48 (m, 2H), 7.43 (m, 1H), 6.94–6.88 (m, 2H), 3.85 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 192.0, 160.4, 135.8, 133.9, 133.4, 133.2, 128.4, 127.5, 127.3, 114.5, 114.3, 96.7, 83.9, 55.5.

*9.4.1.3 Synthesis of **4.1c***



4-((4-methoxyphenyl)ethynyl)benzaldehyde
Chemical Formula: $C_{16}H_{12}O_2$
Molecular Weight: 236.27 g/mol

In accordance with General Procedure C1, CuI (15 mg, 0.08 mmol, 1 mol%), $Pd(PPh_3)_2Cl_2$ (114 mg, 0.17 mmol, 2 mol%), 4-ethynylanisole (1.05 ml, 8.1 mmol, 1.0 equiv) and 4-bromobenzaldehyde (1.80 g, 9.7 mmol, 1.2 equiv) in dry NEt_3 (60 ml) were used to synthesise compound **4.1c**. The crude product was purified by column (SiO_2, hexane/EtOAc, 40:1, gradient to 10:1). The product was isolated as a white solid. **Yield:** 1.29 g, 5.5 mmol, 67%. Spectroscopic data agrees with literature known values.[71] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 10.01 (s, 1H), 7.89–7.81 (m, 2H), 7.68–7.62 (m,

2H), 7.53–7.48 (m, 2H), 6.95–6.87 (m, 2H), 3.85 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 191.6, 160.3, 135.2, 133.5, 132.0, 130.2, 129.7, 114.7, 114.3, 93.9, 87.6, 55.5.

9.4.2 General procedure C2 & C3 for the synthesis of imine reagents **4.3**

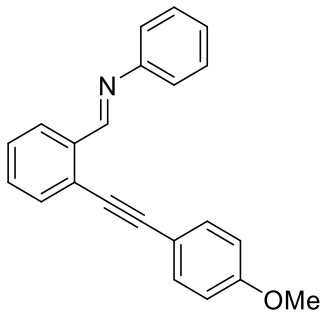
General procedure C2:

The aldehyde (1.0 equiv) was dissolved in dry CH_2Cl_2 with molecular sieves. The amine (4.0 equiv) was added dropwise over a period of 5 minutes. The reaction mixture was stirred for 18 h at room temperature. The solution was filtered and washed with CH_2Cl_2 (2 x 10 ml). The solvent was removed *in vacuo*. The crude product was dried under vacuum to remove the excess amine.

General procedure C3:

The aldehyde (1.0 equiv) was dissolved in dry CH_2Cl_2 with $MgSO_4$. The amine (4.0 equiv) was added added dropwise over a period of 5 minutes. The reaction mixture was stirred for 18 h at room temperature. The solution was filtered through a sinter funnel and washed with CH_2Cl_2. The solvent was removed *in vacuo* with the crude product being dried over $MgSO_4$, and the volatiles removed *in vacuo*.

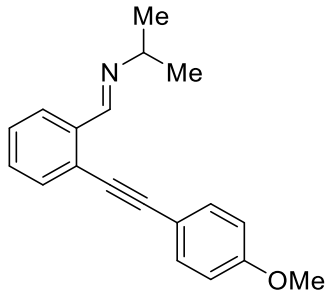
*9.4.2.1 Synthesis of **4.3a***



(*E*)-1-(2-((4-methoxyphenyl)ethynyl)phenyl)-*N*-phenylmethanimine
Chemical Formula: $C_{22}H_{17}NO$
Molecular Weight: 311.38 g/mol

In accordance with General Procedure C2, **4.3a** was synthesised using **4.1b** (100 mg, 0.42 mmol, 1.0 equiv) and aniline (0.15 ml, 1.7 mmol, 4.0 equiv) in CH_2Cl_2 (2.5 ml). The product was isolated as an orange oil. **Yield:** 83 mg, 0.27 mmol, 63 %. **^{1}H NMR** (500 MHz, $CDCl_3$) δ/ppm: 9.10 (s, 1H), 8.30 – 8.24 (m, 1H), 7.61 – 7.57 (m, 1H), 7.50 – 7.46 (m, 2H), 7.44 – 7.40 (m, 2H), 7.18 – 7.13 (m, 2H), 6.91 – 6.87 (m, 2H), 6.76 (tt, $^{3,4}J_{HH}$ = 7.4, 1.0 Hz, 1H), 6.71 – 6.68 (m, 2H), 3.84 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ/ppm: 160.1, 159.2, 152.4, 136.6, 133.2, 132.7, 131.0, 129.4, 129.4, 128.5, 126.7, 126.2, 121.2, 118.7, 115.2, 114.3, 95.7, 85.2, 55.5. **HRMS** (ES^+) *m/z* calculated for $[C_{22}H_{18}NO]^+$ $[M+H]^+$: 312.1388, found: 312.1388.

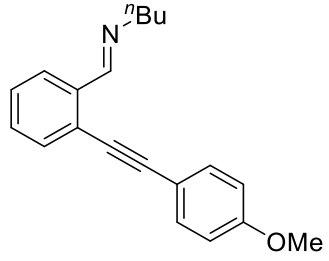
9.4.2.2 Synthesis of ***4.3b***



(*E*)-*N*-isopropyl-1-(2-((4-methoxyphenyl)ethynyl)phenyl)methanimine
Chemical Formula: $C_{19}H_{19}NO$
Molecular Weight: 277.37 g/mol

In accordance with General Procedure C2**, 4.3b** was synthesised using **4.1b** (150 mg, 0.64 mmol, 1.0 equiv) and isopropylamine (0.22 ml, 2.6 mmol, 4.0 equiv) in CH_2Cl_2 (2.5 ml). The product was isolated as a yellow oil. **Yield:** 58 mg, 0.21 mmol, 33%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.90 (d, $^4J_{HH}$ = 0.8 Hz, 1H), 8.09–8.03 (m, 1H), 7.57–7.46 (m, 3H), 7.41–7.29 (m, 2H), 6.94–6.87 (m, 2H), 3.85 (s, 3H), 3.63 (pd, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 0.8 Hz, 1H), 1.29 (d, $^3J_{HH}$ = 6.3 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ/ppm: 160.0, 157.2, 137.0, 133.1, 132.4, 130.1, 128.4, 126.5, 124.3, 115.2, 114.2, 95.0, 85.4, 62.0, 55.5, 24.4. **HRMS** (ES^+) *m/z* calculated for $[C_{19}H_{20}NO]^+$ $[M+H]^+$: 278.1545, found: 278.1552.

9.4.2.3 Synthesis of ***4.3c***

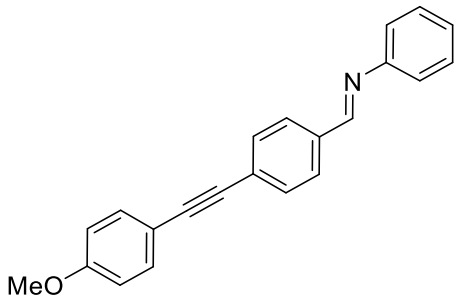


(*E*)-*N*-butyl-1-(2-((4-methoxyphenyl)ethynyl)phenyl)methanimine
Chemical Formula: $C_{20}H_{21}NO$
Molecular Weight: 291.39 g/mol

In accordance with General Procedure C2, **4.3c** was synthesised using **4.1b** (270 mg, 1.1 mmol, 1.0 equiv) and *n*-butylamine (0.45 ml, 4.4 mmol, 4.0 equiv) in CH_2Cl_2 (4 ml). The product was isolated as a yellow solid. **Yield:** 191 mg, 0.65 mmol, 57%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.87 (d, $^4J_{HH}$ = 1.4 Hz, 1H), 8.04 (dd, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.9 Hz, 1H), 7.58–7.46 (m, 3H), 7.42–7.29 (m, 2H), 6.97–6.86 (m, 2H), 3.84 (s, 3H), 3.68 (td, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.4 Hz, 2H), 1.79–1.66 (m, 2H), 1.49–1.34 (m, 2H), 0.96 (t, $^3J_{HH}$ = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 207.2, 160.0, 159.7, 136.8, 133.1, 132.5, 130.1, 128.4, 126.3, 124.4, 115.2, 114.2, 95.0, 85.4, 61.8,

55.5, 33.1, 20.6, 14.1. **HRMS** (ES^+) *m/z* calculated for $[C_{20}H_{22}NO]^+$ $[M+H]^+$: 292.1701, found: 292.1700.

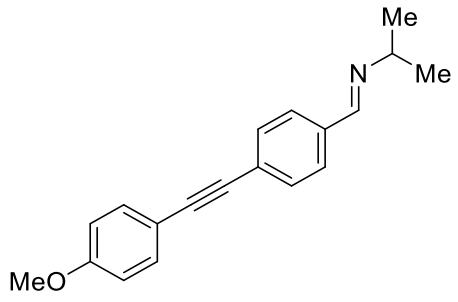
*9.4.2.4 Synthesis of **4.3d***



(*E*)-1-(4-((4-methoxyphenyl)ethynyl)phenyl)-*N*-phenylmethanimine
Chemical Formula: $C_{22}H_{17}NO$
Molecular Weight: 311.38 g/mol

In accordance with General Procedure C2, **4.3d** was synthesised using **4.1c** (150 mg, 0.63 mmol, 1.0 equiv) and aniline (0.23 ml, 2.5 mmol, 4.0 equiv) in CH_2Cl_2 (2 ml). The product was isolated as a light-yellow solid. **Yield:** 52.3 mg, 0.17 mmol, 26%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.46 (s, 1H), 7.92–7.85 (m, 2H), 7.64–7.58 (m, 2H), 7.53–7.47 (m, 2H), 7.44–7.38 (m, 2H), 7.29–7.20 (m, 3H), 6.93–6.87 (m, 2H), 3.84 (d, $^4J_{HH}$ = 0.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ/ppm: 207.2, 160.0, 159.6, 152.0, 135.6, 133.3, 131.9, 129.4, 129.3, 128.8, 126.8, 126.3, 121.0, 115.2, 115.1, 114.2, 92.1, 88.1, 55.5. **HRMS** (ES^+) *m/z* calculated for $[C_{22}H_{18}NO]^+$ $[M+H]^+$: 312.1388, found: 312.1387.

*9.4.2.5 Synthesis of **4.3e***

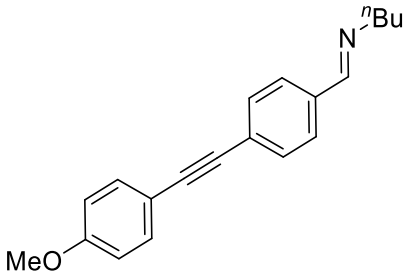


(*E*)-*N*-isopropyl-1-(4-((4-methoxyphenyl)ethynyl)phenyl)methanimine
Chemical Formula: $C_{19}H_{19}NO$
Molecular Weight: 277.37 g/mol

In accordance with General Procedure C2, **4.3e** was synthesised using **4.1c** (250 mg, 1.1 mmol, 1.0 equiv) and isopropylamine (0.36 ml, 4.2 mmol, 4.0 equiv) in CH_2Cl_2 (4 ml). The product was isolated as a yellow solid. **Yield:** 50 mg, 0.18 mmol, 17%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.29 (s, 1H), 7.72–7.68 (m, 2H), 7.56–7.52 (m, 2H), 7.50–7.46 (m, 2H), 6.91–6.86 (m, 2H), 3.83 (s, 3H), 3.61–3.49 (m, 1H), 1.27 (d, $^3J_{HH}$ = 6.3 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 159.9, 157.8, 135.9, 133.3, 131.7, 128.1,

125.7, 115.3, 114.2, 91.3, 88.1, 61.9, 55.5, 24.3. **HRMS** (ES^+) *m/z* calculated for $[C_{19}H_{20}NO]^+$ $[M+H]^+$: 277.1467, found: 277.1469.

*9.4.2.6 Synthesis of **4.3f***



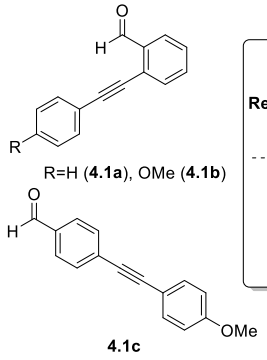
(*E*)-*N*-butyl-1-(4-((4-methoxyphenyl)ethynyl)phenyl)methanimine
Chemical Formula: $C_{20}H_{21}NO$
Molecular Weight: 291.39 g/mol

In accordance with General Procedure C3, **4.3f** was synthesised using **4.1c** (500 mg, 2.1 mmol, 1.0 equiv) and *n*-butylamine (0.84 ml, 8.5 mmol, 4.0 equiv) in CH_2Cl_2 (8 ml). The product was isolated as a yellow solid. **Yield:** 523 mg, 1.8 mmol, 85%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.26 (t, $^4J_{HH}$ = 1.3 Hz, 1H), 7.73–7.65 (m, 2H), 7.58–7.52 (m, 2H), 7.50–7.43 (m, 2H), 6.94–6.84 (m, 2H), 3.83 (s, 3H), 3.62 (td, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.3 Hz, 2H), 1.77–1.63 (m, 2H), 1.47–1.33 (m, 2H), 0.95 (t, $^3J_{HH}$ = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ/ppm: 160.5, 160.2, 136.1, 133.6, 132.1, 128.3, 126.1, 115.6, 114.5, 91.7, 88.4, 62.0, 55.8, 33.5, 21.0, 14.4. **HRMS** (ES^+) *m/z* calculated for $[C_{20}H_{21}NO]^+$ $[M+H]^+$: 292.1701, found: 292.1700.

9.4.3 ^{11}B NMR shifts of the adducts of aldehydes **4.1a-c** and **4.3a-f** with various boranes

9.4.3.1 Definition of adduct formation

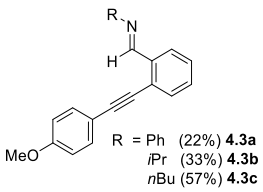
Observing the mixture of aldehydes (**4.1**) and imines (**4.3**) with the boranes in $CDCl_3$ *via* ^{11}B NMR spectroscopy either showed no downfield shift resulting in the initial shift of the used borane or the signal (50 - 60 ppm depending on the borane) vanished and a new down-shifted signal (-10 - 25 ppm depending on the borane and aldehyde or imine) could be observed and adduct formation was assumed.

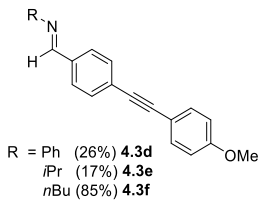


BR_3 R =	C_6F_5	2,4,6-$F_3C_6H_2$	C_6H_5
Relative Lewis acidity	100%	88%	68%
	Adduct Formation?		
4.1a	✓	✗	✗
4.1b	✓	✓	✗
4.1c	✓	✓	✗

*Table 8: ^{11}B-NMR-Shift of the adducts of aldehydes **1a-c** and different boranes*

Compound\Lewis Acid	$B(C_6F_5)_3$	2,4,6-$BArF_9$	BPh_3
4.1a	4.5 ppm	✗	✗
4.1b	4.1 ppm	22.1 ppm	✗
4.1c	4.1 ppm	22.3 ppm	✗





BR_3 R =	C_6F_5	2,4,6-$F_3C_6H_2$	C_6H_5
Relative Lewis acidity	100%	88%	68%
	Adduct Formation?		
4.3a	✓	✗	✗
4.3b	✓	✓	✗
4.3c	✓	✓	✓
4.3d	✓	✗	✗
4.3e	✓	✓	✗
4.4f	✓	✓	✓

Table 2: ^{11}B-NMR-Shift of the adducts of imines **2a-e** with different boranes

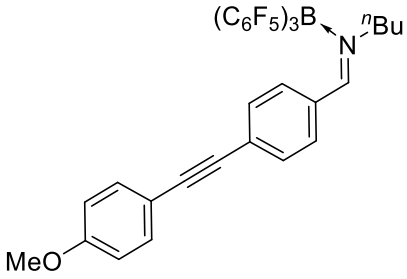
Compound\Lewis Acid	$B(C_6F_5)_3$	2,4,6 $BArF_9$	BPh_3
4.3a	-5.3 ppm	✗	✗

4.3b	-5.0 ppm	-4.7 ppm	✖
4.3c	-3.7 ppm	-3.3 ppm	-1.8 ppm
4.3d	-5.1 ppm	✖	✖
4.3e	-4.0 ppm	-4.4 ppm	✖
4.3f	-3.5 ppm	-3.1 ppm	5.3 ppm

9.4.4 General procedure C4 for the synthesis of the borane imine adducts **4.4**

The imine **4.3** (1.0 equiv) was dissolved in $CDCl_3$ with subsequent addition to the borane (1.0 equiv).

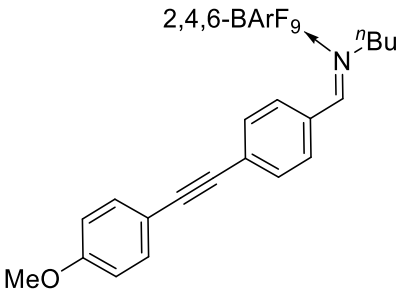
*9.4.4.1 Synthesis of **4.3f-1c** adduct **4.4a**.*



4.4a
Chemical Formula: $C_{38}H_{21}BF_{15}NO$
Molecular Weight: 803.38 g/mol

In accordance with General Procedure C4, the adduct **4.4a** was synthesised using **4.3f** (29.1 mg, 0.10 mmol, 1.0 equiv) and $B(C_6F_5)_3$ (51.2 mg, 0.10 mmol, 1.0 equiv). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.57 (s, 1H), 7.74–7.68 (m, 2H), 7.66–7.60 (m, 2H), 7.54–7.49 (m, 2H), 6.97–6.88 (m, 2H), 4.25–3.96 (m, 2H), 3.85 (s, 3H), 1.07–0.91 (m, 2H), 0.59 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 0.09 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 169.8, 160.7, 148.2 (dm, $^1J_{CF}$ = 247.5 Hz), 140.4 (dm, $^1J_{CF}$ = 248.9 Hz), 137.4 (dm, $^1J_{CF}$ = 255.2 Hz), 133.7, 132.5, 130.1, 129.5, 128.9, 117.2, 114.4, 114.2, 95.4, 87.1, 55.5, 52.9, 30.4, 20.4, 13.1.**11B NMR** (160 MHz, $CDCl_3$, 298 K) δ/ppm: -3.5 (br. s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -127.83 (br. s, 1F), -128.72 (br. s, 1F), -129.23 (br. d, 1F), -130.55 (d, $^2J_{FF}$ = 21.8 Hz, 1F), -131.24 (br. s, 2F), -134.80 (s, 1F), -155.51 (br. d, 1F), -157.18 (t, $^2J_{FF}$ = 20.1 Hz, 1F), -159.94 (br. s, 1F), -162.92 (br. s, 2F), -163.39 (t, $^2J_{FF}$ = 18.8 Hz, 1F), -163.96 (m, 3F)

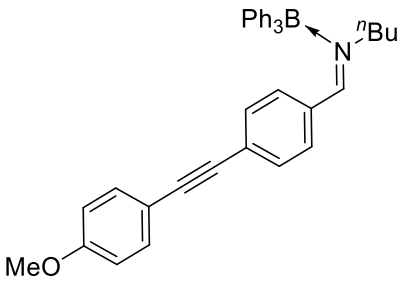
*9.4.4.2 Synthesis of **4.3f-1i** adduct **4.4b**.*



4.4b
Chemical Formula: $C_{38}H_{27}BF_9NO$
Molecular Weight: 695.44 g/mol

In accordance with General Procedure C4, the adduct **4.4b** was synthesised using **4.3f** (29.1 mg, 0.10 mmol, 1.0 equiv) and 2,4,6-Bar$^{F}_{9}$ (**1i**) (40.4 mg, 0.10 mmol, 1.0 equiv). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.61 (s, 1H), 7.71–7.65 (m, 2H), 7.61–7.56 (m, 2H), 7.55–7.49 (m, 2H), 6.96–6.88 (m, 2H), 6.51 (t, $^{3}J_{HH}$ = 9.1 Hz, 6H), 4.08 (t, $^{3}J_{HH}$ = 11.6 Hz, 2H), 3.85 (s, 3H), 0.90 (pent., $^{3}J_{HH}$ = 7.2 Hz, 2H), 0.54 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H), 0.10 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 168.1, 166.1 (dt, $^{2}J_{CF}$ = 29.9 Hz, $^{3}J_{CF}$ = 12.4 Hz), 162.3 (dt, $^{1}J_{CF}$ = 244.9 Hz, $^{3}J_{CF}$ = 15.8 Hz), 160.5, 133.6, 132.3, 130.2, 128.9, 128.7, 117.4, 114.4, 114.4, 100.1–99.1 (m), 94.1, 87.2, 55.5, 52.7, 30.5, 20.6, 13.2.**^{11}B NMR** (160 MHz, $CDCl_3$, 298 K) δ/ppm: -3.1 (br. s). **^{19}F NMR** (376 MHz, $CDCl_3$) δ/ppm: -94.81 – -98.31 (m, 1F), -112.35 (s, 2F).

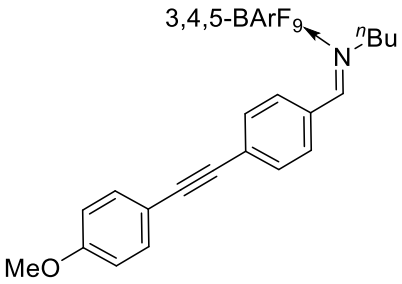
*9.4.4.3 Synthesis of **4.3f**-BPh_3 adduct **4.4c**.*



4.4c
Chemical Formula: $C_{38}H_{36}BNO$
Molecular Weight: 533.52 g/mol

In accordance with General Procedure C4, the adduct **4.4c** was synthesised using **4.3f** (29.1 mg, 0.10 mmol, 1.0 equiv) and BPh_3 (24.2 mg, 0.10 mmol, 1.0 equiv). **^{1}H NMR** (400 MHz, $CDCl_3$) δ/ppm: 8.16 (s, 1H), 7.61–7.36 (m, 17H), 6.82–6.75 (m, 2H), 3.72 (s, 3H), 1.64–1.55 (m, 2H), 1.36–1.25 (m, 2H), 1.17 (s, 2H), 0.86 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H). **^{11}B NMR** (128 MHz, $CDCl_3$) δ/ppm: 4.3 (br. s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ/ppm: 168.6, 160.2, 159.9, 138.7, 135.8, 133.3, 132.2, 131.7, 130.1, 128.1, 127.5, 114.2, 91.4, 88.1, 61.7, 55.4, 33.2, 20.6, 14.1.

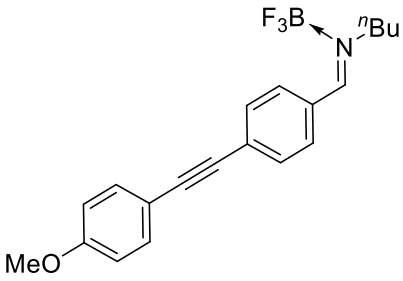
*9.4.4.4 Synthesis of **4.3f**-**1h** adduct **4.4d**.*



4.4d
Chemical Formula: $C_{38}H_{27}BF_9NO$
Molecular Weight: 695.44 g/mol

In accordance with General Procedure C4, the adduct **4.4d** was synthesised using **4.3f** (29.1 mg, 0.10 mmol, 1.0 equiv) and 3,4,5-$BArF_9$ (**1h**) (40.4 mg, 0.10 mmol, 1.0 equiv). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.40 (s, 1H), 7.73 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.58 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.54–7.48 (m, 2H), 6.96–6.89 (m, 2H), 6.81 (dd, $^3J_{HH}$ = 8.9 Hz, $^3J_{HH}$ = 6.8 Hz, 6H), 3.85 (s, 3H), 3.82 (m, 2H), 1.29–1.18 (m, 3H), 1.14 (q, $^3J_{HH}$ = 7.1 Hz, 2H), 0.72 (t, $^3J_{HH}$ = 7.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ/ppm: 170.4, 160.8, 151.0 (ddd, $^1J_{CF}$ = 250.7 Hz, $^3J_{CF}$ = 9.2 Hz, $^4J_{CF}$ = 2.8 Hz), 145.6, 138.3 (dt, $^1J_{CF}$ = 250.5 Hz, $^3J_{CF}$ = 15.5 Hz), 133.7, 132.60, 131.2, 130.8, 127.6, 117.6 (dd, $^3J_{CF}$ = 13.5 Hz, $^4J_{CF}$ = 4.4 Hz), 114.4, 114.1, 96.1, 87.0, 55.5, 52.2, 30.7, 20.0, 13.3. **^{11}B NMR** (160 MHz, $CDCl_3$, 298 K) δ/ppm: 2.9 (br. s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -135.64 (d, $^3J_{FF}$ = 20.3 Hz, 2F), -163.82 (d, $^3J_{FF}$ = 20.3 Hz, 1F).

*9.4.4.5 Synthesis of **4.3f**-BF_3 adduct **4.4e**.*

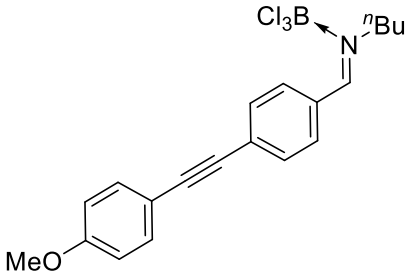


4.4e
Chemical Formula: $C_{20}H_{21}BF_3NO$
Molecular Weight: 359.20 g/mol

In accordance with General Procedure C4, the adduct **4.4e** was synthesised using **4.3f** (29.1 mg, 0.10 mmol, 1.0 equiv) and $BF_3{\cdot}OEt_2$ (12.7 µl, 0.10 mmol, 1.0 equiv). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.29 (br. s, 1H), 7.98–7.92 (m, 2H), 7.61–7.56 (m, 2H), 7.51–7.45 (m, 2H), 6.92–6.83 (m, 2H), 3.82 (s, 3H), 1.84 (pent., $^3J_{HH}$ = 7.5 Hz, 2H), 1.45–1.33 (m, 2H), 0.97 (t, $^3J_{HH}$ = 7.4 Hz, 3H), 0.91–0.81 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 170.4, 160.5, 133.6, 131.5, 130.5, 128.2, 114.4, 114.3, 95.1, 87.6, 61.1,

55.5, 32.3, 32.3, 20.0, 13.7. **^{11}B NMR** (160 MHz, $CDCl_3$, 298 K) δ/ppm: -0.1 (s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -144.19 (s, 3F).

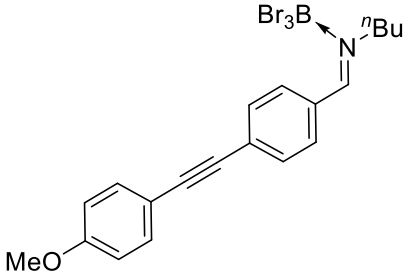
*9.4.4.6 Synthesis of **4.3f**-BCl_3 adduct **4.4f**.*



4.4f
Chemical Formula: $C_{20}H_{21}BCl_3NO$
Molecular Weight: 408.55 g/mol

In accordance with General Procedure C4, the adduct **4.4f** was synthesised using **4.3f** (29.1 mg, 0.10 mmol, 1.0 equiv) and BCl_3 (100 µl, 1 M solution in CH_2Cl_2, 0.10 mmol, 1.0 equiv). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 9.33 (dd, $^3J_{HH}$ = 9.7 Hz, $^4J_{HH}$ = 4.1 Hz, 1H), 8.15 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.63–7.58 (m, 1H), 7.53–7.47 (m, 2H), 6.94–6.87 (m, 2H), 4.32–4.18 (m, 2H), 3.84 (s, $^3J_{HH}$ = 5.1 Hz, 3H), 2.09–1.86 (m, 2H), 1.51–1.39 (m, 2H), 1.04–0.93 (m, $^3J_{HH}$ = 10.6 Hz, $^3J_{HH}$ = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 169.3, 160.8, 133.7, 132.6, 132.5, 131.6, 114.4, 113.9, 96.8, 87.1, 55.5, 51.2, 30.9, 20.3, 13.6. **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 8.1 (s).

*9.4.4.7 Synthesis of **4.3f**-BCl_3 adduct **4.4f**.*



4.4f
Chemical Formula: $C_{20}H_{21}BBr_3NO$
Molecular Weight: 541.92 g/mol

In accordance with General Procedure C4, the adduct **4.4f** was synthesised using **4.3f** (29.1 mg, 0.10 mmol, 1.0 equiv) and BBr_3 (9.5 µl, 0.10 mmol, 1.0 equiv). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 9.61 (s, 1H), 7.82–7.72 (m, 4H), 7.54–7.50 (m, 2H), 6.94–6.90 (m, 2H), 3.85 (s, 3H), 1.54–1.40 (m, 2H), 1.25 (s, 3H), 1.02–0.94 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 170.6, 160.8, 133.8, 132.8, 132.6, 131.6, 130.5, 114.4, 113.9, 97.3, 87.3, 55.5, 52.4, 29.8, 20.3, 13.6. **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: -7.1 (s).

9.4.5 Crystallographic data for **4.4a**

Compound	**4.4a**
Empirical Formula	$C_{38}H_{21}BF_{15}NO$
Space Group	P-1
a/Å	10.8591(5)
b/Å	11.0549(4)
c/Å	15.5476(7)
α/°	75.088(4)
β/°	69.996(4)
Y/°	84.603(4)
Volume/Å^3	1694.73(14)
Z	2
T/K	150
D_c/g·cm^{-3}	1.574
R (reflections)	0.0489(4994)
wR2 (reflections)	0.1380
Theta(max)	27.101

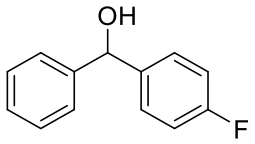
9.5 BCF promoted cyclisation:

9.5.1 Synthesis of the starting materials:

General procedure D1:

According to literature procedure,[157] magnesium turnings (1 equiv) were suspended in THF (15 ml) and activated with 1,2-dibromoethane (*ca.* 0.1 ml) being added at 0 °C. After stirring for 5 minutes halobenzene (0.9 equiv) was added drop wise as a solution in THF (20 ml). The mixture was allowed to warm to room temperature and stirred for an hour. The reaction mixture was cooled with an ice bath and benzaldehyde derivative (0.8 equiv) in THF (20 ml) was added dropwise. After removing the ice bath, the mixture was allowed to stir overnight. The reaction was then quenched with saturated NH_4Cl solution (50 ml). After separating the organic phase, the aqueous phase was extracted with Et_2O. The combined organic layers were dried under vacuum to give desired benzhydrol derivative. The purity (tested via NMR spectroscopy) was satisfiying enough to use in further reaction steps.

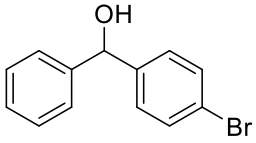
9.5.1.1 Synthesis of 4-fluorobenzhydrol:



(4-fluorophenyl)(phenyl)methanol
Chemical Formula: $C_{13}H_{11}FO$
Molecular Weight: 202.23 g/mol

Synthesised according to General Procedure D1 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.[157] **Yield:** 4.36 g, 21.6 mmol, 83% **^{1}H NMR** (500 MHz, $CDCl_3$, 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)Ar_2), 2.26 (br. s, 1H, OH). **^{19}F NMR** (471 MHz, CDCl3, 298 K) δ/ppm: -115.05 – -115.11 (br. m, 1F, Ar-F).

9.5.1.2 Synthesis of 4-Bromobenzhydrol:

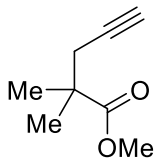


(4-bromophenyl)(phenyl)methanol
Chemical Formula: $C_{13}H_{11}BrO$
Molecular Weight: 263.13 g/mol

Synthesised according to General Procedure D1 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.[157] **Yield:** 3.52 g, 13.4 mmol, 78%. **^{1}H NMR** (300 MHz, $CDCl_3$, 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)Ar_2), 2.23 (br. s, 1H, OH).

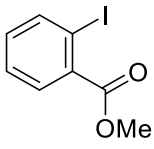
*9.5.1.3 Synthesis of **5.7b**:*



methyl 2,2-dimethylpent-4-ynoate
Chemical Formula: $C_8H_{12}O_2$
Molecular Weight: 140.18 g/mol

A solution of diisopropylamine (20 ml, 0.14 mol) in THF (40 ml) was cooled to -78 °C and *n*-BuLi (1.6 M in hexanes, 79.2 ml, 0.13 mol) was added. The reaction was stirred for 1 h. This mixture was transferred into a dropping funnel and slowly added to a solution of methyl isobutyrate (13.2 ml, 0.12 mol) in THF (30 ml) at 0 °C. The reaction was allowed to warm to room temperature and stirred for 1 h before cooling it down to 0 °C again. A solution of propargyl bromide (80 wt% in toluene, 12.2 ml, 0.12 mmol) in THF (10 ml) was then added dropwise. The reaction mixture was stirred overnight and allowed to warm to room temperature. Water was added and, using a separating funnel, the organic phase was removed, and the aqueous phase is extracted with Et_2O (3 x 20 ml). The combined organic layers were washed with saturated NH_4Cl solution and dried with $MgSO_4$. After filtration all volatiles are removed under vacuum and the residue is distilled (50 °C, 1 x 10^{-3} bar) to give **5.7b** as a colourless oil. The spectroscopic data agrees with literature values.[105] **Yield:** 12.9 g, 42 mol, 84%. **^{1}H NMR** (300 MHz, $CDCl_3$, 298 K) δ/ppm: 3.70 (s, 3H, OCH_3), 2.44 (d, $^4J_{HH}$ = 2.6 Hz, 2H, CH_2), 2.00 (t, $^4J_{HH}$ = 2.6 Hz, 1H, ≡CH), 1.28 (s, 6H, $C(CH_3)_2$).

*9.5.1.4 Synthesis of **5.11b**:*



methyl 2-iodobenzoate
Chemical Formula: $C_8H_7IO_2$
Molecular Weight: 262.05 g/mol

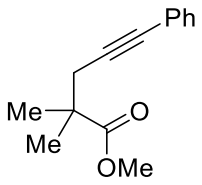
2-Iodo-benzoicacid (15 g, 60.5 mmol, 1 equiv) was stirred in methanol (50 ml) for 10 min to dissolve the acid. The resulting clear solution was cooled with an ice bath and concentrated H_2SO_4 added. After warming the reaction mixture to room temperature, it

was set to reflux overnight. The mixture was allowed to cool down and was neutralised with saturated sodium bicarbonate solution (150 ml). The aqueous was extracted with hexane (3 x 50 ml) and the combined organic layers were filtered through silica and all volatiles were removed under vacuum to give **5.11b** as a yellow oil. The spectroscopic data agrees with literature established values.[158] **Yield:** 15.4 g, 58.7 mmol, 97%. **^{1}H NMR** (300 MHz, $CDCl_3$, 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, OCH_3).

*General Procedure D2 to synthesise esters **5.8**:*

5.7b (0.8 g, 5.7 mmol, 1 equiv) in THF (10 ml) was mixed with NEt_3, iodobenzene derivative (1 equiv), $Pd(PPh_3)_2Cl_2$ (58 mg, 1 mol%), CuI (23 mg, 2 mol%) and PPh_3 (60 mg, 4 mol%) were added according to literature procedure.[105] The resulting mixture was refluxed for 10 h. After cooling to room temperature, the reaction was quenched with water and the organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 20 ml). The combined organic layers were dried with brine and layered over $MgSO_4$. After filtration all volatiles are removed, and the residue is purified via column chromatography (SiO_2) to give desired ester **5.8.**

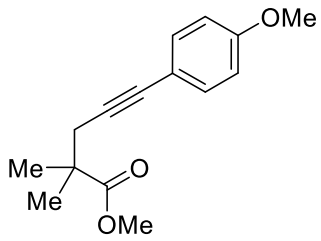
*9.5.1.5 Synthesis of **5.8a**:*



methyl 2,2-dimethyl-5-phenylpent-4-ynoate
Chemical Formula: $C_{14}H_{16}O_2$
Molecular Weight: 216.28 g/mol

Following General Procedure D2, **5.8a** was synthesised using iodobenzene (0.63 ml, 5.7 mmol, 1 equiv) The spectroscopic data agrees with values established in literature established.[105] **R_f** value: 0.11 (2:1 hexane/$CHCl_3$). **Yield** 1.16 g, 5.4 mmol, 95%. **^{1}H NMR** (300 MHz, $CDCl_3$, 298 K) δ/ppm: 7.43–7.23 (m, 5H, Ar-H), 3.71 (s, 3H, OCH_3), 2.66 (s, 2H, CH_2), 1.34 (s, 6H, $C(CH_3)_2$).

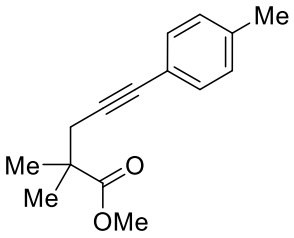
*9.5.1.6 Synthesis of **5.8b**:*



methyl 5-(4-methoxyphenyl)-2,2-dimethylpent-4-ynoate
Chemical Formula: $C_{15}H_{18}O_3$
Molecular Weight: 246.31 g/mol

Following general procedure D2, **5.8b** was synthesised using 4-(methoxy)iodobenzene (1.32 g, 5.7 mmol, 1 equiv). $\mathbf{R_f}$ value: 0.19 (2:1 hexane/$CHCl_3$). **Yield:** 532 mg, 2.17 mmol, 32%. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.32 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar-H), 6.81 (d, $^3J_{HH}$ = 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, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 177.5, 159.3, 133.1, 116.0, 113.9, 85.1, 82.6, 55.4, 52.2, 42.7, 30.7, 24.8. **HRMS** (AP^+) m/z calculated for $[C_{15}H_{19}O_3]^+$ $[M+H]^+$: 247.1334, found: 247.1324.

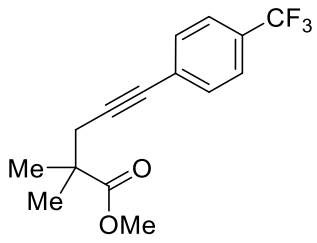
*9.5.1.7 Synthesis of **5.8c**:*



methyl 2,2-dimethyl-5-(*p*-tolyl)pent-4-ynoate
Chemical Formula: $C_{15}H_{18}O_2$
Molecular Weight: 230.31 g/mol

Following General Procedure D2, **5.8c** was synthesised using 4-iodotoluene (1.24 g, 5.7 mmol, 1 equiv). $\mathbf{R_f}$ value: 0.13 (2:1 hexane/$CHCl_3$). **Yield:** 670 mg, 2.91 mmol, 49%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.27 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar-H), 7.08 (d, $^3J_{HH}$ = 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, $C(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 177.5, 137.9, 131.6, 129.1, 120.7, 85.9, 82.9, 52.2, 42.7, 30.7, 24.8, 21.6. **HRMS** (EI^+) m/z calculated for $[C_{15}H_{18}O_2]^+$ $[M]^+$: 230.1307, found: 230.1306.

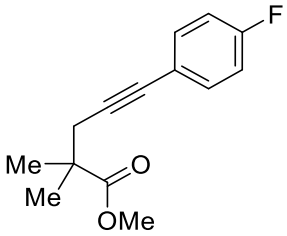
*9.5.1.8 Synthesis of **5.8d**:*



methyl 2,2-dimethyl-5-(4-(trifluoromethyl)phenyl)pent-4-ynoate
Chemical Formula: $C_{15}H_{15}F_3O_2$
Molecular Weight: 284.28 g/mol

Following General Procedure D2, **5.8d** was synthesised using 4-(trifluoromethyl)iodobenzene (1.55 g, 0.84 ml, 5.7 mmol, 1 equiv). **R_f** value: 0.15 (2:1 hexane/$CHCl_3$). **Yield:** 1.59 g, 5.6 mmol, 98%. **^{1}H NMR** (300 MHz, $CDCl_3$, 298 K) δ/ppm: 7.50 (dd, $^3J_{HH}$ = 8.09 Hz, $^3J_{HH}$ = 8.07 Hz, 4H, Ar-H), 3.72 (s, 3H, OCH_3), 2.67 (s, 2H, CH_2), 1.34 (s, 6H, $C(CH_3)_2$). **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -62.79 (s, 3F, CF_3). **HRMS** (AP^+) m/z calculated for $[C_{15}H_{15}O_2F_3]^+$ $[M+H]^+$: 284.1024, found: 284.1021.

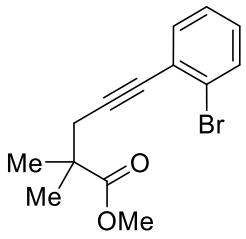
*9.5.1.9 Synthesis of **5.8f**:*



methyl 5-(4-fluorophenyl)-2,2-dimethylpent-4-ynoate
Chemical Formula: $C_{14}H_{15}FO_2$
Molecular Weight: 234.27 g/mol

Following General Procedure D2, **5.8f** was synthesised using 4-fluoroiodobenzene (1.27 g, 5.7 mmol, 1 equiv). **R_f** value: 0.09 (3:1 hexane/$CHCl_3$). **Yield:** 934 mg, 3.99 mmol, 70%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.35 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HF}$ = 5.5 Hz, 2H, Ar-H), 6.97 (t, $^3J_{HH}$ = 8.8 Hz, 2H, Ar-H), 3.71 (s, 3H, OCH_3), 2.64 (s, 2H, CH_2), 1.33 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 177.3, 162.3 (d, $^1J_{CF}$ = 249 Hz, 1C), 133.5 (d, $^3J_{CF}$ = 8.3 Hz, 2C), 119.8, 115.6 (d, $^2J_{CF}$ = 22.0 Hz, 2C), 86.4, 81.8, 52.2, 42.7, 30.7, 24.8. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -111.97 (s, 1F, *p*-F). **HRMS** (AP^+) m/z calculated for $[C_{14}H_{16}O_2F]^+$ $[M+H]^+$: 235.1134, found: 235.1125.

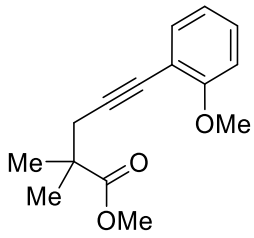
*9.5.1.10 Synthesis of **5.8g**:*



methyl 5-(2-bromophenyl)-2,2-dimethylpent-4-ynoate
Chemical Formula: $C_{14}H_{15}BrO_2$
Molecular Weight: 295.18 g/mol

Following General Procedure D2, **5.8g** was synthesised using 1-bromo-2-iodobenzene (1.61 g, 5.7 mmol, 1 equiv). **R_f** value: 0.18 (2:1 hexane/$CHCl_3$). **Yield:** 1.20 g, 4.07 mmol, 71%. **^{1}H NMR** (400 MHz, $CDCl_3$, 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, OCH_3), 2.72 (s, 2H, CH_2), 1.38 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 177.4, 133.6, 132.4, 129.0, 127.0, 125.9, 125.6, 91.9, 81.5, 52.3, 42.7, 30.8, 24.9. **HRMS** (EI^+) m/z calculated for $[C_{14}H_{15}BrO_2]^+$ $[M]^+$: 294.0255, found: 294.0258.

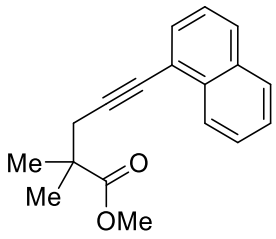
*9.5.1.11 Synthesis of **5.8h**:*



methyl 5-(2-methoxyphenyl)-2,2-dimethylpent-4-ynoate
Chemical Formula: $C_{15}H_{18}O_3$
Molecular Weight: 246.31 g/mol

Following General Procedure D2, **5.8g** was synthesised using 2-(methoxy)iodobenzene (0.74 ml, 5.7 mmol, 1 equiv). **R_f** value: 0.18 (2:1 hexane/$CHCl_3$). **Yield:** 746 mg, 3.03 mmol, 53%. **^{1}H NMR** (400 MHz, $CDCl_3$, 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, OCH_3), 3.71 (s, 3H, OCH_3), 2.72 (s, 2H, CH_2), 1.35 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 177.5, 160.1, 133.7, 129.2, 120.5, 113.0, 110.7, 91.0, 79.0, 55.9, 52.1, 42.7, 31.0, 24.7. **HRMS** (ES^+) m/z calculated for $[C_{15}H_{18}O_3]^+$ $[M]^+$: 246.1256, found: 246.1250.

*9.5.1.12 Synthesis of **5.8i**:*



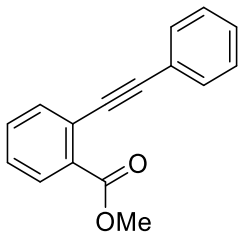
methyl 2,2-dimethyl-5-(naphthalen-1-yl)pent-4-ynoate
Chemical Formula: $C_{18}H_{18}O_2$
Molecular Weight: 266.34 g/mol

Following General Procedure D2, **5.8g** was synthesised using 1-iodonaphthalene (0.83 ml, 5.7 mmol, 1 equiv) $\mathbf{R_f}$ value: 0.14 (2:1 hexane/$CHCl_3$). **Yield:** 505 mg, 1.89 mmol, 33%. **^{1}H NMR** (300 MHz, $CDCl_3$, 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, OCH_3), 2.83 (s, 2H, CH_2), 1.42 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 177.4, 133.6, 133.3, 130.4, 128.3, 128.3, 126.7, 126.4, 126.3, 125.3, 121.5, 91.8, 80.9, 52.3, 42.9, 31.2, 25.0. **HRMS** (EI^+) m/z calculated for $[C_{18}H_{18}O_2]^+$ $[M]^+$: 266.1307, found: 266.1312.

*General Procedure D3 to synthesise esters **5.12**:*

Following literature procedure,[109] methyl 2-iodobenzoate **5.11b** (2.24 ml, 4.00 g, 15.3 mmol, 1 equiv) was dissolved in THF (20 ml) and $Pd(PPh_3)_2Cl_2$ (220 mg, 0.3 mmol, 2 mol%), CuI (120 mg, 0.6 mmol, 4 mol%) and NEt_3 (50 ml) were added. After stirring this mixture for a short time, the terminal alkyne was added (1.2 equiv). The reaction was set to reflux overnight and allowed to cool to room temperature after 16 h. The reaction was quenched with water (100 ml) and CH_2Cl_2 (60 ml) was added. The organic phase is separated and the aqueous phase is extracted with CH_2Cl_2 (2 x 60 ml). The organic layers are combined and all volatiles are removed under vacuum. The residue is purified *via* column chromatography (SiO_2).

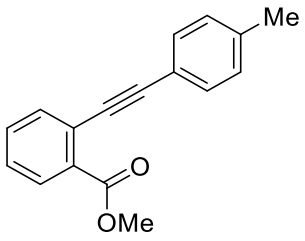
*9.5.1.13 Synthesis of **5.12a**:*



methyl 2-(phenylethynyl)benzoate
Chemical Formula: $C_{16}H_{12}O_2$
Molecular Weight: 236.27 g/mol

Compound **5.12a** was synthesised according to General Procedure D3 with phenylacetylene (1.9 ml, 17.71 mmol, 1.16 equiv). The spectroscopic data agrees with literature established values.[105] **R_f** value: 0.18 (hexane/EtOAc 95:5). **Yield:** 3.27 g, 13.84 mmol, 91%. **^{1}H NMR** (400 MHz, $CDCl_3$, 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, OCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 166.9, 134.1, 132.0, 131.9, 131.9, 130.6, 128.7, 128.5, 128.0, 123.8, 123.4, 94.5, 88.3, 52.4.

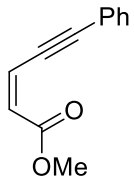
*9.5.1.14 Synthesis of **5.12b**:*



methyl 2-(*p*-tolylethynyl)benzoate
Chemical Formula: $C_{17}H_{14}O_2$
Molecular Weight: 250.30 g/mol

Compound **5.12b** was synthesised according to General Procedure D3 with 4-ethynyltoluene (2.25 ml, 17.71 mmol, 1.16 equiv). **R_f** value: 0.29 (90:10, hexane/EtOAc). **Yield:** 3.78 g, 15.1 mmol, 99%. **^{1}H NMR** (400 MHz, $CDCl_3$, 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, OCH_3), 2.38 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 166.9, 138.8, 134.0, 131.8, 131.7, 131.7, 130.5, 129.2, 127.7, 123.9, 120.2, 94.6, 87.6, 52.2, 21.6. **HRMS** (ES^+) m/z calculated for $[C_{17}H_{14}O_2]^+$ $[M+H]^+$: 250.0994, found: 250.0987.

*9.5.1.15 Synthesis of **5.14b**:*



methyl (*Z*)-5-phenylpent-2-en-4-ynoate
Chemical Formula: $C_{12}H_{10}O_2$
Molecular Weight: 186.21 g/mol

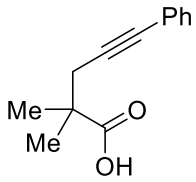
Methyl 3-iodoacrylate **5.14a** (2.24 ml, 4.00 g, 15.3 mmol, 1 equiv) was dissolved in THF (20 ml) and $Pd(PPh_3)_2Cl_2$ (322 mg; 0.45 mmol; 2 mol%), CuI (175 mg, 0.92 mmol, 4 mol%) and NEt_3 (50 ml) were added. After stirring this mixture for a short time,

phenylacetylene (2.96 ml, 26.56 mmol, 1.16 equiv) was added. The reaction was set to stir overnight. The black suspension was quenched with saturated ammonium chloride solution (50 ml) and EtOAc (40 ml) was added. The organic phase was separated, and the aqueous phase is extracted with EtOAc (2 x 40 ml). The organic layers were combined, and all volatiles are removed under vacuum. The residue is purified *via* column chromatography (SiO_2) to give **5.14b** as a yellow-orange oil. The spectroscopic data agrees with literature established values.[110] **R_f** value: 0.07 (50:1, hexane/EtOAc). **Yield:** 4.27 g, 22.93 mmol, 81%. **^{1}H NMR** (400 MHz, $CDCl_3$, 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, OCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 165.3, 132.2, 129.3, 128.4, 127.8, 123.2, 122.6, 101.4, 86.3, 51.5.

*General procedure D4 to synthesise free acids **5.9**, **5.13** and **5.15**:*

Methyl esters are saponified according to literature procedures.[105] A sodium hydroxide (5 equiv) solution in methanol (20 ml) was added to a solution of methyl esters in methanol (20 ml). The mixture was set to reflux overnight and allowed to cool to room temperature afterwards. Water (25 ml) was added and the aqueous mixture was extracted with Et_2O and the organic phase is discarded. After neutralising the aqueous mixture to crash out the protonated acid, the white suspension is extracted with Et_2O (3 x 20 ml). The combined organic layers were dried under vacuum and the residue is purified *via* column chromatography.

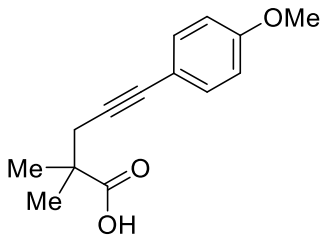
*9.5.1.16 Synthesis of **5.9a**:*



2,2-dimethyl-5-phenylpent-4-ynoic acid
Chemical Formula: $C_{13}H_{14}O_2$
Molecular Weight: 202.25 g/mol

Compound **5.9a** was synthesised according to General Procedure D4 with **5.8a** (670 mg, 2.91 mmol, 1 equiv) as the methyl ester to produce a white solid. **Melting point:** 92–98 °C. **Yield:** 629 mg, 2.91 mmol, 99%. **^{1}H NMR** (400 MHz, $CDCl_3$, 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, CH_2), 2.33 (s, 3H, PhMe), 1.37 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 183.8, 137.9, 131.6, 129.1, 120.7, 85.6, 83.1, 42.5, 30.4, 24.6, 21.6. **HRMS** (ES^+) m/z calculated for $[C_{14}H_{16}O_2]^+$ $[M]^+$: 216.1150, found: 216.1151.

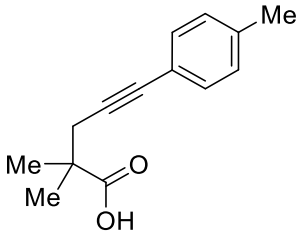
*9.5.1.17 Synthesis of **5.9b**:*



5-(4-methoxyphenyl)-2,2-dimethylpent-4-ynoic acid
Chemical Formula: $C_{14}H_{16}O_3$
Molecular Weight: 232.27 g/mol

Compound **5.9b** was synthesised according to General Procedure D4 with **5.8b** (532 mg, 2.17 mmol, 1 equiv) as the methyl ester to produce a white solid. **Melting point:** 104–108 °C. **Yield:** 501 mg, 2.17 mmol, 99%. **^{1}H NMR** (300 MHz, $CDCl_3$, 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, OCH_3), 2.66 (s, 2H, CH_2), 1.36 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 183.8, 159.3, 133.1, 115.9, 114.0, 84.8, 82.8, 55.4, 42.5, 30.4, 24.6. **HRMS** (ES^-) m/z calculated for $[C_{14}H_{15}O_3]^-$ $[M-H]^-$: 231.1021, found: 231.1015.

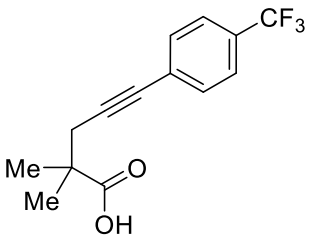
*9.5.1.18 Synthesis of **5.9c**:*



2,2-dimethyl-5-(*p*-tolyl)pent-4-ynoic acid
Chemical Formula: $C_{14}H_{16}O_2$
Molecular Weight: 216.28 g/mol

Compound **5.9c** was synthesised according to General Procedure D4 with **5.8c** (670 mg, 2.91 mmol, 1 equiv) as the methyl ester to produce a white solid. to give an off-white solid. **Melting point:** 92–98 °C. **Yield:** 629 mg, 2.91 mmol, 99%. **^{1}H NMR** (400 MHz, $CDCl_3$, 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, CH_2), 2.33 (s, 3H, PhMe), 1.37 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 183.8, 137.9, 131.6, 129.1, 120.7, 85.6, 83.1, 42.5, 30.4, 24.6, 21.6. **HRMS** (ES^+) m/z calculated for $[C_{14}H_{16}O_2]^+$ $[M]^+$: 216.1150, found: 216.1151

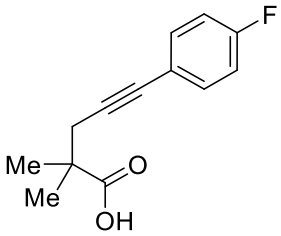
*9.5.1.19 Synthesis of **5.9d**:*



2,2-dimethyl-5-(4-(trifluoromethyl)phenyl)pent-4-ynoic acid
Chemical Formula: $C_{14}H_{13}F_3O_2$
Molecular Weight: 270.25 g/mol

Compound **5.9d** was synthesised according to General Procedure D4 with **5.8d** (1.59 g, 5.6 mmol, 1 equiv) as the methyl ester to produce a white solid. to give an off-white solid. **Melting point:** 80–86 °C. **Yield:** 1.51 g, 5.6 mmol, 97%. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.53–7.48 (m, 4H, Ar-H), 2.70 (s, 2H, CH_2), 1.37 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 183.2, 132.0, 127.5, 125.3 (q, $^3J_{CF}$ = 3.8 Hz, 2C), 123.0, 89.3, 81.9, 42.5, 30.4, 24.7. **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -62.80 (s, 3F, CF_3). **HRMS** (AP^+) m/z calculated for $[C_{14}H_{14}O_2F_3]^+$ $[M+H]^+$: 271.0946, found: 271.0933.

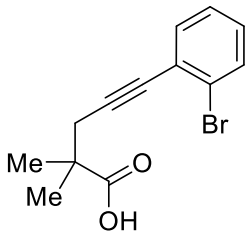
*9.5.1.20 Synthesis of **5.9f**:*



5-(4-fluorophenyl)-2,2-dimethylpent-4-ynoic acid
Chemical Formula: $C_{13}H_{13}FO_2$
Molecular Weight: 220.24 g/mol

Compound **5.9f** was synthesised according to general procedure D4 with **5.8f** (934 mg, 3.99 mmol, 1 equiv) as the methyl ester to produce a white solid. **Melting point:** 77–82 °C. **Yield:** 879 mg, 3.99 mmol, 99%. **^{1}H NMR** (400 MHz, $CDCl_3$, 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, CH_2), 1.37 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 182.7, 162.4 (d, $^1J_{CF}$ = 250 Hz, 1C), 133.6 (d, $^3J_{CF}$ = 8.3 Hz, 2C), 119.7, 115.6 (d, $^2J_{CF}$ = 22.0 Hz, 2C), 86.0, 82.0, 42.5, 30.4, 24.6. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -111.84 (s, 1F, *p*-F). **HRMS** (EI^+) m/z calculated for $[C_{13}H_{13}O_2F]^+$ $[M]^+$: 220.0900, found: 220.0898.

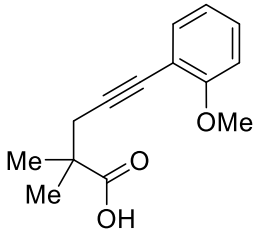
*9.5.1.21 Synthesis of **5.9g**:*



5-(2-bromophenyl)-2,2-dimethylpent-4-ynoic acid
Chemical Formula: $C_{13}H_{13}BrO_2$
Molecular Weight: 281.15 g/mol

Compound **5.9g** was synthesised according to General Procedure D4 with **5.8g** (1.20 g, 4.07 mmol, 1 equiv) as the methyl ester to produce a white solid. **Melting point:** 44–48 °C. **Yield:** 1.13 g, 4.07 mmol, 99%. **^{1}H NMR** (400 MHz, $CDCl_3$, 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, CH_2), 1.42 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 182.6, 133.6, 132.4, 129.1, 127.0, 125.8, 125.6, 91.5, 81.7, 42.5, 30.6, 24.7. **HRMS** (EI^+) m/z calculated for $[C_{13}H_{13}O_2Br]^+$ $[M]^+$: 280.0099, found: 280.0090

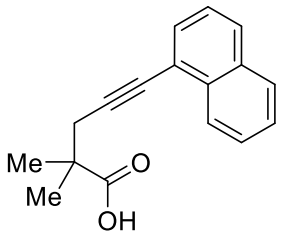
*9.5.1.22 Synthesis of **5.9h**:*



5-(2-methoxyphenyl)-2,2-dimethylpent-4-ynoic acid
Chemical Formula: $C_{14}H_{16}O_3$
Molecular Weight: 232.28 g/mol

Compound **5.9g** was synthesised according to General Procedure D4 with **5.8g** (746 mg, 3.03 mmol, 1 equiv) as the methyl ester to produce a white solid. **Melting point:** 90–94 °C. **Yield:** 696 mg, 42.5 mmol, 99%. **^{1}H NMR** (400 MHz, $CDCl_3$, 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, OCH_3), 2.75 (s, 2H, CH_2), 1.40 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 183.8, 160.2, 133.6, 129.3, 120.5, 112.9, 110.7, 90.7, 79.3, 55.9, 42.6, 30.6, 24.5. **HRMS** (EI^+) m/z calculated for $[C_{14}H_{16}O_3]^+$ $[M]^+$: 232.1099, found: 232.1095.

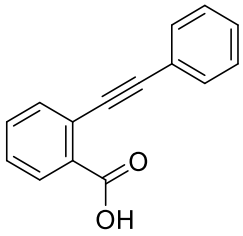
*9.5.1.23 Synthesis of **5.9i**:*



2,2-dimethyl-5-(naphthalen-1-yl)pent-4-ynoic acid
Chemical Formula: $C_{17}H_{16}O_2$
Molecular Weight: 252.31 g/mol

Compound **5.9i** was synthesised according to General Procedure D4 with **5.8i** (505 mg, 1.89 mmol, 1 equiv) as the methyl ester to produce a white solid. **Melting point:** 118–122 °C. **Yield:** 476 mg, 1.89 mmol, 99%. **^{1}H NMR** (400 MHz, $CDCl_3$, 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, CH_2), 1.44 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 183.7, 133.6, 133.3, 130.4, 128.3, 128.3, 126.8, 126.4, 126.4, 125.3, 121.4, 91.5, 81.1, 42.7, 30.8, 24.8. **HRMS** (EI^+) m/z calculated for $[C_{17}H_{16}O_2]^+$ $[M]^+$: 252.1150, found: 252.1149.

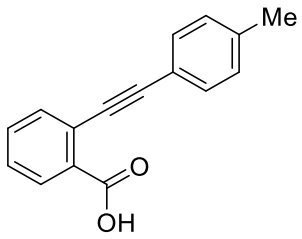
*9.5.1.24 Synthesis of **5.13a**:*



2-(phenylethynyl)benzoic acid
Chemical Formula: $C_{15}H_{10}O_2$
Molecular Weight: 222.24 g/mol

Compound **5.13a** was synthesised according to General Procedure D4 with **5.12a** (3.27 g, 13.84 mmol, 1 equiv) as the methyl ester to produce a white oil. The spectroscopic data agrees with literature established values.[109] **R_f** value: 0.18 (chloroform). **Yield:** 2.84 g, 12.78 mmol, 92%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.15 (dd, $^3J_{HH}$ = 7.9, 1H, Ar-H), 7.70 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Ar-H), 7.61–7.54 (m, 3H, Ar-H), 7.44 (td, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.2 Hz, 1H, Ar-H), 7.36–7.28 (m, 3H, Ar-H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 171.1, 134.2, 132.6, 131.8, 131.4, 130.5, 128.7, 128.4, 128.0, 124.4, 123.1, 95.5, 88.0.

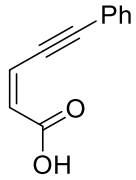
*9.5.1.25 Synthesis of **5.13b**:*



2-(*p*-tolylethynyl)benzoic acid
Chemical Formula: $C_{16}H_{12}O_2$
Molecular Weight: 236.27 g/mol

Compound **5.13b** was synthesised according to General Procedure D4 with **5.12b** (3.78 g, 15.1 mmol, 1 equiv) as the methyl ester to produce a white oil. The spectroscopic data agrees with literature established values.[109] $\mathbf{R_f}$ value: 0.23 (chloroform). **Yield:** 3.47 g, 15.1 mmol, 93%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.14 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Ar-H), 7.68 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ar-H), 7.55 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar-H), 7.47 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Ar-H), 7.42 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar-H), 7.12 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Ar-H), 2.35 (s, $^3J_{HH}$ = 13.8 Hz, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 171.8, 138.9, 134.2, 132.7, 131.8, 131.5, 130.6, 129.3, 127.9, 124.8, 120.2, 95.9, 87.6, 21.7.

*9.5.1.26 Synthesis of **5.15a**:*



(*Z*)-5-phenylpent-2-en-4-ynoic acid
Chemical Formula: $C_{11}H_8O_2$
Molecular Weight: 172.18 g/mol

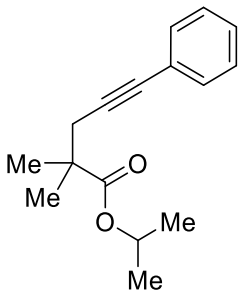
Compound **5.15a** was synthesised according to General Procedure D4 with **5.14b** (3.78 g, 15.1 mmol, 1 equiv) as the methyl ester to produce a bright yellow solid. The spectroscopic data agrees with literature established values.[159] **Yield:** 3.55 g, 20.6 mmol, 98%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.52 (d, $^3J_{HH}$ = 6.9 Hz, 2H, Ar-H), 7.40–7.29 (m, 3H, Ar-H), 6.49 (d, $^3J_{HH}$ = 11.3 Hz, 1H, Ar-H), 6.19 (d, $^3J_{HH}$ = 11.3 Hz, 1H, Ar-H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 169.2, 132.2, 129.5, 128.5, 127.3, 125.2, 122.4, 103.2, 86.2.

*General Procedure D5 to synthesise esters **5.1**, **5.2** and **5.3**:*

According to literature procedure,[108] DMAP (7 mol%) and an alcohol (1–3 equiv) were added to a solution of carboxylic acid in CH_2Cl_2. The solution was cooled to 0 °C and DCC (1.1 equiv) was added. The mixture was allowed to warm to room temperature and stirred overnight. The resulting urea was filtered off. The filtrate was washed twice with

a solution of HCl in water (0.5 M) and once with a saturated sodium bicarbonate solution. The organic phase was separated, dried over $MgSO_4$ and filtered. All volatiles were removed from the filtrate and the residue was purified *via* column chromatography (SiO_2) to give the desired esters **5.1**-**3**

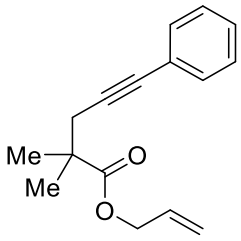
*9.5.1.27 Synthesis of **5.1a**:*



isopropyl 2,2-dimethyl-5-phenylpent-4-ynoate
Chemical Formula: $C_{16}H_{20}O_2$
Molecular Weight: 244.33 g/mol

In accordance with General Procedure D5, **5.1a** was synthesised using **5.9a** (750 mg, 3.7 mmol, 1 equiv) and 2-propanol (11.1 mmol, 1.2 g, 3 equiv) yielding a yellow oil. $\mathbf{R_f}$ value: 0.64. **Yield:** 115 mg, 0.47 mmol, 13%. ^{1}**H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.43–7.21 (m, 5H, Ar-H), 5.01 (hept, $^3J_{HH}$ = 6.2 Hz, 1H, $CH(CH_3)_2$), 2.62 (s, 2H, CH_2), 1.30 (s, 6H, $C(CH_3)_2$), 1.23 (d, $^3J_{HH}$ = 6.3 Hz, 6H, $OC(CH_3)_2$). ^{13}**C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 176.4, 131.7, 128.3, 127.8, 123.9, 87.0, 82.7, 67.9, 42.5, 30.7, 24.7, 21.9. **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 $[C_{16}H_{21}O_2]^+$ $[M+H]^+$: 245.1542, found: 245.1536.

*9.5.1.28 Synthesis of **5.1b**:*

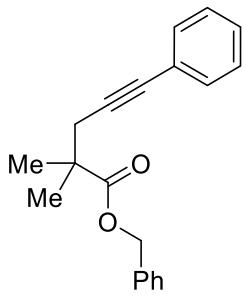


allyl 2,2-dimethyl-5-phenylpent-4-ynoate
Chemical Formula: $C_{16}H_{18}O_2$
Molecular Weight: 24232 g/mol

In accordance with General Procedure D5, **5.1b** was synthesised using **5.9a** (500 mg, 2.5 mmol, 1 equiv) and allylalcohol (0.80 g, 7.4 mmol, 3 equiv) yielding a yellow oil. $\mathbf{R_f}$ value: 0.67. **Yield:** 334 mg, 1.38 mmol, 56%. ^{1}**H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.42–7.24 (m, 5H, Ar-H), 5.97–5.88 (m, 1H, -CH=), 5.37 (d, $^3J_{HH}$ = 16.2 Hz 1H, $=CH_2$,

trans), 5.19 ($^3J_{HH}$ = 10.1 Hz 1H, =CH_2 cis), 4.62 (d, $^3J_{HH}$ = 5.4 Hz 2H, OCH_2–), 2.68 (s, 2H, CH_2), 1.36 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 176.5, 132.4, 131.7, 128.3, 127.9, 123.8, 117.9, 86.8, 82.9, 65.4, 42.8, 30.7, 24.8. **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 $[C_{16}H_{19}O_2]^+$ $[M+H]^+$: 243.1385, found: 243.1380.

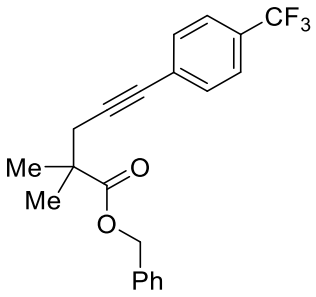
*9.5.1.29 Synthesis of **5.1c**:*



benzyl 2,2-dimethyl-5-phenylpent-4-ynoate
Chemical Formula: $C_{20}H_{20}O_2$
Molecular Weight: 292.38 g/mol

In accordance with General Procedure D5, **5.1c** was synthesised using **5.9a** (2.0 g, 9.89 mmol, 1 equiv) and benzylalcohol (3.2 g, 30 mmol, 3 equiv) yielding a yellow oil. **R_f** value: 0.85. **Yield:** 1.85 g, 6.34 mmol, 64%. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.37–7.23 (m, 10H, Ar-H), 5.15 (s, 2H, OCH_2–), 2.68 (s, 2H, CH_2), 1.35 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 176.6, 136.2, 131.6, 128.5, 128.2, 128.0, 127.8, 127.7, 123.6, 86.6, 82.8, 66.5, 42.7, 30.6 , 24.7. **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 $[C_{20}H_{21}O_2]^+$ $[M+H]^+$: 292.1463, found: 292.1452.

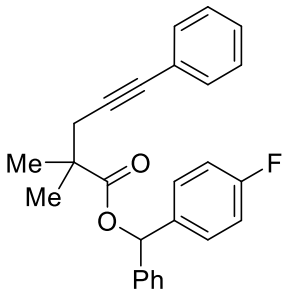
*9.5.1.30 Synthesis of **5.1d**:*



benzyl 2,2-dimethyl-5-(4-(trifluoromethyl)phenyl)pent-4-ynoate
Chemical Formula: $C_{21}H_{19}F_3O_2$
Molecular Weight: 360.38 g/mol

In accordance with General Procedure D5, **5.1d** was synthesised using **5.9d** (1.0 g, 3.7 mmol, 1 equiv) and benzylalcohol (420 mg, 3.89 mmol, 1.05 equiv) yielding a yellow oil. $\mathbf{R_f}$ value: 0.76. **Yield:** 805 mg, 2.23 mmol, 61%. **^{1}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, OCH_2–), 2.70 (s, 2H, CH_2), 1.37 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 176.4, 136.2, 132.0, 129.6 (q, $^2J_{CF}$ = 32.6 Hz, 1C), 128.6, 128.3, 128.2, 128.0, 125.2 (q, $^3J_{CF}$ = 3.8 Hz, 2C), 89.7, 81.8, 66.6 ,42.8, 42.8, 30.8, 24.9. **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -62.77 (s, 3F, CF_3). **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 $[C_{21}H_{20}O_2F_3]^+$ $[M+H]^+$: 361.1415, found: 361.1418.

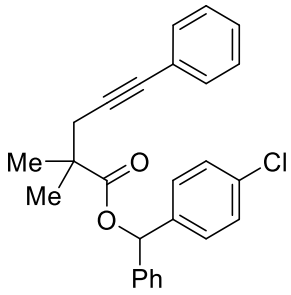
*9.5.1.31 Synthesis of **5.1e**:*



(4-fluorophenyl)(phenyl)methyl 2,2-dimethyl-5-phenylpent-4-ynoate
Chemical Formula: $C_{26}H_{23}FO_2$
Molecular Weight: 386.47 g/mol

In accordance with General Procedure D5, **5.1e** was synthesised using **5.9a** (800 mg, 3.96 mmol, 1 equiv) and 4-fluorobenzhydrol (840 mg, 4.15 mmol, 1.05 equiv) yielding a white solid. $\mathbf{R_f}$ value: 0.72. **Yield:** 605 mg, 1.57 mmol, 40%. **Melting point**: 79–85 °C. **^{1}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, $C(H)Ar_2$), 2.71 (s, 2H, CH_2), 1.37 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 175.7, 162.4 (d, $^1J_{CF}$ = 246 Hz, 1C), 140.2, 136.3, 131.7, 129.1 (d, $^4J_{CF}$ = 8.2 Hz, 2C), 128.5 (d, $^2J_{CF}$ = 50.2 Hz, 2C), 128.0 (d, $^3J_{CF}$ = 16.8 Hz, 2C), 127.0, 123.6, 115.5, 115.3, 86.5, 83.0, 42.9, 31.1, 30.7, 24.9, 24.8. **^{19}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 $[C_{26}H_{24}FO_2]^+$ $[M+H]^+$: 387.1759, found: 387.1760.

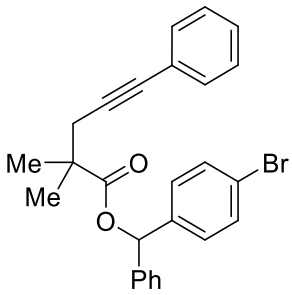
*9.5.1.32 Synthesis of **5.1f**:*



(4-chlorophenyl)(phenyl)methyl 2,2-dimethyl-5-phenylpent-4-ynoate
Chemical Formula: $C_{26}H_{23}ClO_2$
Molecular Weight: 402.92 g/mol

In accordance with General Procedure D5, **5.1f** was synthesised using **5.9a** (900 mg, 4.5 mmol, 1 equiv) and 4-chlorobenzhydrol (1.07 g, 4.89 mmol, 1.1 equiv) yielding a white solid. $\mathbf{R_f}$ value: 0.83. **Yield:** 452 mg, 1.12 mmol, 26%. **Melting point**: 62– 67 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.37–7.27 (m, 14H, Ar-H), 6.85 (s, 1H, $C(H)Ar_2$), 2.73 (s, 2H, CH_2), 1.40 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 175.6, 139.9, 139.0, 133.9, 131.7, 128.8, 128.7, 128.6, 128.3, 128.2, 127.9, 127.0, 123.6, 86.6, 83.1, 76.6, 43.0, 30.7, 24.9, 24.9. **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 $[C_{26}H_{24}O_2Cl]^+$ $[M+H]^+$: 403.1465, found: 403.1452.

*9.5.1.33 Synthesis of **5.1g**:*

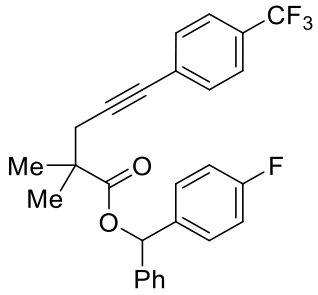


(4-bromophenyl)(phenyl)methyl 2,2-dimethyl-5-phenylpent-4-ynoate
Chemical Formula: $C_{26}H_{23}BrO_2$
Molecular Weight: 447.37 g/mol

In accordance with General Procedure D5, **5.1g** was synthesised using **5.9a** (800 mg, 3.96 mmol, 1 equiv) and 4-bromobenzhydrol (1.1 g, 4.15 mmol, 1.05 equiv) yielding a white solid. $\mathbf{R_f}$ value: 0.72. **Yield:** 795 mg, 1.78 mmol, 45%. **Melting point:** 70–76 °C **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.32 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar-H), 7.27-7.18 (m, 10H, Ar-H), 7.15 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar-H), 6.74 (s, 1H, $C(H)Ar_2$), 2.64 (s, 2H, CH_2), 1.30 (s, 6H, $C(CH_3)_2$) **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 175.6, 139.8, 139.5,

131.8, 131.7, 129.0, 128.7, 128.3, 128.2, 128.0, 127.0, 123.6, 122.0, 86.6, 83.2, 76.6, 43.0, 30.8, 24.9, 24.9. **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 13 (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 $[C_{26}H_{24}O_2Br]^+$ $[M+H]^+$: 447.0960, found: 447.0962.

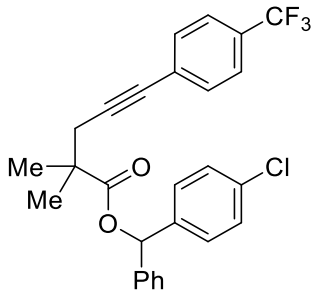
*9.5.1.34 Synthesis of **5.1h**:*



(4-fluorophenyl)(phenyl)methyl 2,2-dimethyl-5-(4-(trifluoromethyl)phenyl)pent-4-ynoate
Chemical Formula: $C_{27}H_{22}F_4O_2$
Molecular Weight: 454.46 g/mol

In accordance with General Procedure D5, **5.1h** was synthesised using **5.9d** (1.0 g, 3.70 mmol, 1 equiv) and 4-fluorobenzhydrol (790 mg, 3.89 mmol, 1.05 equiv) yielding a white solid. $\mathbf{R_f}$ value: 0.78. **Yield:** 405 mg, 1.68 mmol, 24%. **Melting point:** 68– 75 °C. **^{1}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)Ar_2), 2.72 (s, 2H, CH_2), 1.38 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** *partial* (126 MHz, $CDCl_3$, 298 K) δ/ppm: 175.4 (s), 162.3 (d, $^1J_{CF}$ = 246 Hz, 1C), 140.1, 136.2 132.0, 129.1 (d, $^3J_{CF}$ = 8.1 Hz, 1C), 128.7, 128.1, 127.4, 127.0, 125.2 (q, $^3J_{CF}$ = 3.9 Hz), 115.6 (d, $^2J_{CF}$ = 21.6 Hz, 2C), 89.5, 82.0, 76.6, 42.9, 31.1, 30.8, 24.9, 24.9. **^{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). **HRMS** (ES^+) m/z calculated for $[C_{27}H_{22}O_2F_4]^+$ $[M+H]^+$: 454.1556, found: 454.1552.

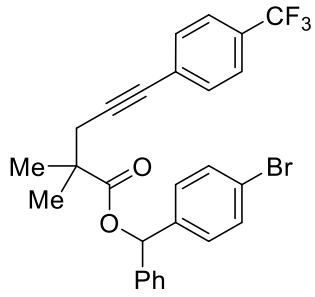
*9.5.1.35 Synthesis of **5.1i**:*



(4-chlorophenyl)(phenyl)methyl 2,2-dimethyl-5-(4-(trifluoromethyl)phenyl)pent-4-ynoate
Chemical Formula: $C_{27}H_{22}ClF_3O_2$
Molecular Weight: 470.92 g/mol

In accordance with General Procedure D5, **5.1i** was synthesised using **5.9d** (1.0 g, 3.7 mmol, 1 equiv) and 4-chlorobenzhydrol (850 mg, 3.9 mmol, 1.05 equiv) yielding a white solid. **R_f** value: 0.74. **Yield:** 750 mg, 1.59 mmol, 43%. **Melting point:** 67–74 °C. **^{1}H 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)Ar_2), 2.74 (s, 2H, CH_2), 1.40 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 175.4, 139.8, 138.9, 134.0, 131.9, 128.9, 128.8, 128.7, 128.2, 127.0, 89.4, 76.6, 42.9, 30.8, 25.0, 24.9. **^{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). **HRMS** (ES^+) m/z calculated for $[C_{27}H_{22}O_2F_4Cl]^+$ $[M+H]^+$: 470.1260, found: 470.1263.

*9.5.1.36 Synthesis of **5.1j**:*

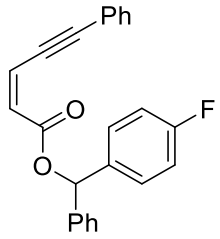


(4-bromophenyl)(phenyl)methyl 2,2-dimethyl-5-(4-(trifluoromethyl)phenyl)pent-4-ynoate
Chemical Formula: $C_{27}H_{22}BrF_3O_2$
Molecular Weight: 515.37 g/mol

In accordance with General Procedure D5, **5.1j** was synthesised using **5.9d** (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. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.51 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar-H), 7.39 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar-H), 7.33–7.27 (m, 7H, Ar-H), 7.39 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar-H), 6.82 (s, 1H, C(H)Ar_2), 2.72 (s, 2H,

CH_2), 1.38 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** *partial* (126 MHz, $CDCl_3$, 298 K) δ/ppm: 175.4, 139.8, 139.4, 131.9, 131.8, 129.0, 128.8, 128.2, 127.0, 125.2 (q, $^3J_{CF}$ = 3.8 Hz, 1C), 122.1, 89.4, 82.0, 76.7, 43.0, 30.8, 25.0, 24.9. **^{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 $[C_{26}H_{23}O_2]^+$ $[M+H]^+$: 515.0834, found: 515.0834.

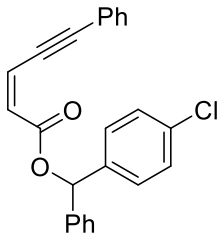
*9.5.1.37 Synthesis of **5.2a**:*



(4-fluorophenyl)(phenyl)methyl (*Z*)-5-phenylpent-2-en-4-ynoate
Chemical Formula: $C_{24}H_{17}FO_2$
Molecular Weight: 356.40 g/mol

In accordance with General Procedure D5, **5.2a** was synthesised using **5.15a** (0.500 g, 2.9 mmol) and 4-fluorobenzhydrol (0.646 g, 3.19 mmol, 1.1 equiv) yielding a yellow oil. **R_f** value: 0.44 (chloroform). **Yield:** 0.946 g, 2.65 mmol, 91%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.46–7.27 (m, 12H, Ar-H), 7.01 (s, 1H, $C(H)Ar_2$), 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). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 163.9, 162.5 (d, $^1J_{CF}$ = 247 Hz), 140.1, 136.2 (d, $^4J_{CF}$ = 3.1 Hz), 132.1, 129.4, 129.3 (d, $^3J_{CF}$ = 8.2 Hz, 2C), 128.7, 128.5, 128.1, 127.9, 127.3, 123.7, 122.6, 115.5 (d, $^2J_{CF}$ = 21.6 Hz, 2C), 102.1, 86.6, 76.6. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -114.30 (s, 1F, *p*-F). **HRMS** (ES^+) m/z calculated for $[C_{24}H_{17}FO_2]^+$ $[M]^+$: 356.1213, found: 356.1210

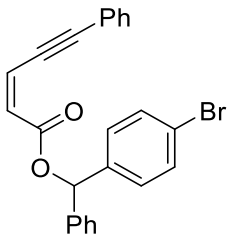
*9.5.1.38 Synthesis of **5.2b**:*



(4-chlorophenyl)(phenyl)methyl (*Z*)-5-phenylpent-2-en-4-ynoate
Chemical Formula: $C_{24}H_{17}ClO_2$
Molecular Weight: 372.85 g/mol

In accordance with General Procedure D5, **5.2b** was synthesised using **5.15a** (0.500 g, 2.9 mmol) and 4-chlorobenzhydrol (0.699 g, 3.19 mmol, 1.1 equiv) yielding a yellow oil. **R_f** value: 0.49 (chloroform). **Yield:** 0.797 g, 2.14 mmol, 74%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.41–7.26 (m, 14H, Ar-H), 6.99 (s, 1H, C(H)Ar_2), 6.45 (d, $^3J_{HH}$ = 11.5 Hz, 1H, =CH), 6.21 (d, $^3J_{HH}$ = 11.6 Hz, 1H, =CH). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 163.9, 139.8, 138.9, 133.9, 132.1, 129.4, 128.8, 128.8, 128.8, 128.5, 128.2, 127.8, 127.3, 123.8, 122.6, 102.1, 86.6, 76.6. **HRMS** (ES^+) m/z calculated for $[C_{24}H_{17}ClO_2]^+$ $[M]^+$: 372.0917, found: 372.0919.

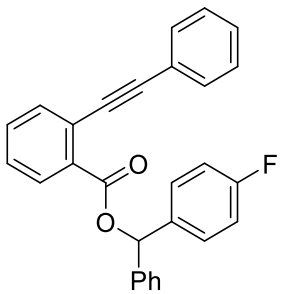
*9.5.1.39 Synthesis of **5.2c**:*



(4-bromophenyl)(phenyl)methyl (*Z*)-5-phenylpent-2-en-4-ynoate
Chemical Formula: $C_{24}H_{17}BrO_2$
Molecular Weight: 417.30 g/mol

In accordance with General Procedure D5, **5.2c** was synthesised using **5.15a** (0.500 g, 2.9 mmol) and 4-bromobenzhydrol (0.841 g, 3.19 mmol, 1.1 equiv) yielding a yellow oil. **R_f** value: 0.53 (chloroform). **Yield:** 0.641 g, 1.54 mmol, 53%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.44–7.27 (m, 14H, Ar-H), 6.97 (s, 1H, C(H)Ar_2), 6.45 (d, $^3J_{HH}$ = 11.5 Hz, 1H, =CH), 6.21 (d, $^3J_{HH}$ = 11.5 Hz, 1H, =CH). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 163.7, 139.6, 139.2, 132.0, 131.7, 129.3, 129.0, 128.6, 128.4, 128.1, 127.6, 127.2, 123.7, 122.4, 121.9, 102.0, 86.4, 76.5. **HRMS** (ES^+) m/z calculated for $[C_{28}H_{17}FO_2]^+$ $[M]^+$: 416.0412, found: 416.0415.

*9.5.1.40 Synthesis of **5.3a**:*

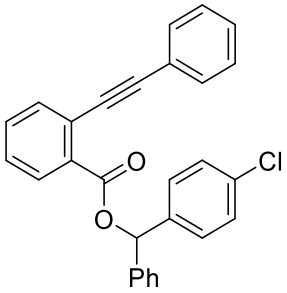


(4-fluorophenyl)(phenyl)methyl 2-(phenylethynyl)benzoate
Chemical Formula: $C_{28}H_{19}FO_2$
Molecular Weight: 406.46 g/mol

In accordance with General Procedure D5, **5.3a** was synthesised using **5.13a** (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 (chloroform). **Yield:** 0.876 g, 2.16 mmol, 80%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.06 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar-H), 7.67 (d, $^3J_{HH}$ = 7.0 Hz, 1H, Ar-H), 7.52 (t, $^3J_{HH}$ = 7.4 Hz, 1H, Ar-H), 7.48–7.27 (m, 13H, Ar-H), 7.16 (s, 1H, C(H)Ar_2), 6.95 (t, $^3J_{HH}$ = 8.1 Hz, 2H, Ar-H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 165.5, 162.5 (d, $^1J_{CF}$ = 247 Hz), 140.1, 136.2 (d, $^4J_{CF}$ = 3.2 Hz), 134.6, 132.1 (s, 15 1C), 131.8, 131.6, 131.0, 129.36 (d, $^3J_{CF}$ = 8.2 Hz, 2C), 128.7, 128.6, 128.4, 128.1, 128.1, 127.3, 124.0, 123.3, 115.5 (d, $^2J_{CF}$ = 21.6 Hz, 2C), 94.8, 88.5, 77.4. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -114.31 (s, 1F, *p*-F). **HRMS** (ES^+) m/z calculated for $[C_{28}H_{20}FO_2]^+$ $[M+H]^+$: 407.1447, found: 407.1441.

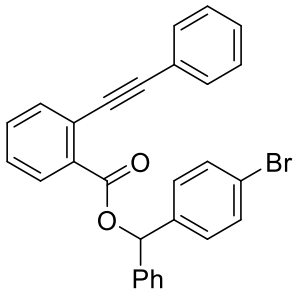
*9.5.1.41 Synthesis of **5.3b**:*



(4-chlorophenyl)(phenyl)methyl 2-(phenylethynyl)benzoate
Chemical Formula: $C_{28}H_{19}ClO_2$
Molecular Weight: 422.91 g/mol

In accordance with General Procedure D5, **5.3b** was synthesised using **5.13a** (0.60 g, 2.7 mmol) and 4-chlorobenzhydrol (0.650 g, 2.97 mmol, 1.1 equiv) yielding a colourless oil. **R_f** value: 0.64 (chloroform). **Yield:** 1.06 g, 2.51 mmol, 93%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.06 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Ar-H), 7.67 (d, $^3J_{HH}$ = 7.6 Hz, 1H, Ar-H), 7.52 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar-H), 7.47–7.21 (m, 16H, Ar-H), 7.13 (s, 1H, C(H)Ar_2). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 165.4, 139.8, 138.9, 134.6, 134.0, 132.1, 131.8, 131.6, 131.0, 128.9, 128.8, 128.8, 128.7, 128.4, 128.2, 128.2, 127.3, 124.0, 123.2, 94.8, 88.5, 77.5. **HRMS** (ES^+) m/z calculated for $[C_{28}H_{20}ClO_2]^+$ $[M+H]^+$: 423.1152, found: 423.1164.

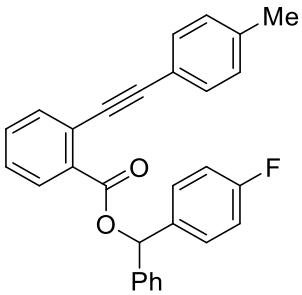
*9.5.1.42 Synthesis of **5.3c**:*



(4-bromophenyl)(phenyl)methyl 2-(phenylethynyl)benzoate
Chemical Formula: $C_{28}H_{19}BrO_2$
Molecular Weight: 467.36 g/mol

In accordance with General Procedure D5, **5.3c** was synthesised using **5.13a** (0.790 g, 2.97 mmol, 1.1 equiv) yielding a colourless oil. $\mathbf{R_f}$ value: 0.65 (chloroform). **Yield:** 1.04 g, 2.23 mmol, 83%. **^{1}H NMR** (400 MHz, $CDCl_3$, 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)Ar_2). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 165.5, 139.7, 139.4, 134.6, 132.1, 131.8, 131.8, 131.5, 131.0, 129.2, 129.2, 128.8, 128.7, 128.4, 128.2, 128.2, 127.3, 124.0, 123.2, 122.1, 94.8, 88.5, 77.5. **HRMS** (ES^+) m/z calculated for $[C_{28}H_{20}BrO_2]^+$ $[M+H]^+$: 467.0647, found: 467.0668.

*9.5.1.43 Synthesis of **5.3d**:*

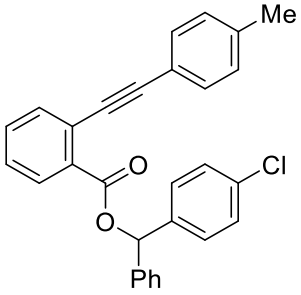


(4-fluorophenyl)(phenyl)methyl 2-(*p*-tolylethynyl)benzoate
Chemical Formula: $C_{29}H_{21}FO_2$
Molecular Weight: 420.48 g/mol

In accordance with General Procedure D5, **5.3d** was synthesised using **5.13b** (0.60 g, 2.54 mmol) and 4-fluorobenzhydrol (0.570 g, 2.79 mmol, 1.1 equiv) yielding a colourless oil. $\mathbf{R_f}$ value: 0.65 (chloroform). **Yield:** 0.725 g, 1.72 mmol, 68%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.98 (d, $^3J_{HH}$ = 7.9 Hz, 1H, Ar-H), 7.59 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Ar-H), 7.43 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Ar-H), 7.41–7.15 (m, 10H, Ar-H), 7.08 (s, 1H, C(H)Ar_2), 7.03 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar-H), 6.88 (t, $^3J_{HH}$ = 8.3 Hz, 2H, ArH), 2.29 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 165.5, 162.5 (d, $^1J_{CF}$ = 247 Hz), 140.1, 138.8, 136.2 (d, $^4J_{CF}$ = 3.2 Hz), 134.5, 132.0, 131.7, 131.5, 131.0, 129.4 (d, $^3J_{CF}$ = 8.2 Hz, 2C), 129.2, 128.7, 128.1, 127.9, 127.3, 124.2, 120.2, 115.5 (d, $^2J_{CF}$ = 21.6 Hz, 2C), 95.1, 88.0,

77.4, 21.7. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -114.36 (s). **HRMS** (ES^+) m/z calculated for $[C_{29}H_{22}FO_2]^+$ $[M+H]^+$: 421.1604, found: 421.1604.

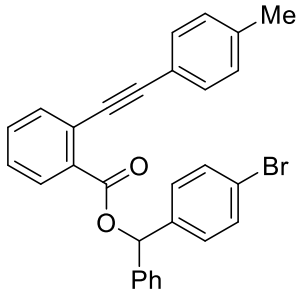
*9.5.1.44 Synthesis of **5.3e**:*



(4-chlorophenyl)(phenyl)methyl 2-(*p*-tolylethynyl)benzoate
Chemical Formula: $C_{29}H_{21}ClO_2$
Molecular Weight: 436,9350

In accordance with General Procedure D5, **5.3e** was synthesised using **5.13b** (0.60 g, 2.54 mmol) and 4-chlorobenzhydrol (0.61 g, 2.79 mmol, 1.1 equiv) yielding a colourless oil. **R_f** value: 0.67 (chloroform). **Yield:** 1.07 g, 2.45 mmol, 96%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.07 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Ar-H), 7.68 (d, $^3J_{HH}$ = 7.6 Hz, 1H, Ar-H), 7.53 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar-H), 7.49–7.22 (m, 12H, Ar-H), 7.14 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar-H), 7.11 (s, 1H, C(H)Ar_2), 2.39 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 165.5, 139.9, 138.9, 138.9, 134.5, 133.9, 132.1, 131.7, 131.5, 131.0, 129.2, 129.0, 128.8, 128.8, 128.2, 128.0, 127.3, 124.2, 120.2, 95.1, 87.9, 77.5, 21.7. **HRMS** (ES^+) m/z calculated for $[C_{29}H_{22}ClO_2]^+$ $[M+H]^+$: 437.1309, found: 437.1308.

*9.5.1.45 Synthesis of **5.3f**:*

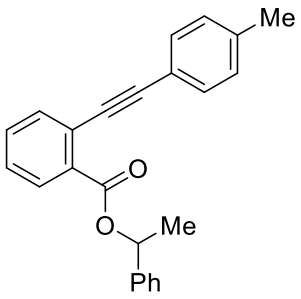


(4-bromophenyl)(phenyl)methyl 2-(*p*-tolylethynyl)benzoate
Chemical Formula: $C_{29}H_{21}BrO_2$
Molecular Weight: 481.39 g/mol

In accordance with General Procedure D5, **5.3f** was synthesised using **5.13b** (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 (chloroform). **Yield:** 1.18 g, 15.1 mmol, 97%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.07 (d, $^3J_{HH}$ = 7.9 Hz, 1H, Ar-H), 7.68 (d, $^3J_{HH}$ = 7.9 Hz, 1H, Ar-H), 7.53 (t, $^3J_{HH}$ = 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)Ar_2), 2.39 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 165.5, 139.8, 139.4, 138.9, 134.5, 132.1, 131.8, 131.7, 131.5, 131.0, 129.2, 128.8, 128.2, 128.0, 127.3, 124.2, 122.1, 120.2, 95.1, 87.9, 77.5, 21.7. **HRMS** (ES^+) m/z calculated for $[C_{29}H_{22}BrO_2]^+$ $[M+H]^+$: 481.0803, found: 481.0825.

*9.5.1.46 Synthesis of **5.3g**:*



1-phenylethyl 2-(*p*-tolylethynyl)benzoate
Chemical Formula: $C_{24}H_{20}O_2$
Molecular Weight: 340.4220 g/mol

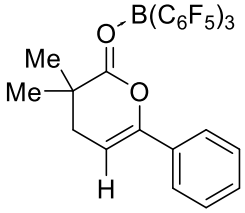
In accordance with General Procedure D5, **5.3g** was synthesised using **5.13b** (0.216 g, 1.07 mmol) and 1-phenylethanol (0.14 ml, 0.143 g, 1.17 mmol, 1.1 equiv) yielding a colourless oil. **R_f** value: 0.26 (1:1, hexane/$CHCl_3$). **Yield:** 82 mg, 0.26 mmol, 24%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.42–7.24 (m, 7H, Ar-H), 7.10 (d, $^3J_{HH}$ = 5.8 Hz, 2H, Ar-H), 5.98–5.89 (m, 1H, C(H)CH_3), 2.70 (s, 2H, CH_2), 2.36 (s, 3H, CH_3), 1.61–1.58 (m, 3H, CH_3), 1.38 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 176.1, 142.0, 137.8, 131.6, 129.1, 128.6, 127.8, 126.0, 120.7, 86.0, 82.9, 72.6, 42.7, 30.7, 24.8, 24.8, 22.5, 21.6. **HRMS** (ES^+) m/z calculated for $[C_{22}H_{24}O_2]^+$ $[M+H]^+$: 321.1855, found 321.1842.

9.5.2 Products of the stoichiometric cyclisation reactions

General procedure D6 to give pyranone borane adducts:

$B(C_6F_5)_3$ (51 mg, 0.1 mmol, 1 equiv) was added to a solution of free acids and esters (0.1 mmol, 1 equiv) in $CDCl_3$ (0.5 ml). The mixture was stirred and when full conversion was observed in ^{1}H NMR spectra the solvent was removed under vacuum and the residue was washed with hexane (2 x 1 ml) to give the desired cyclised heterocyclic borane adduct.

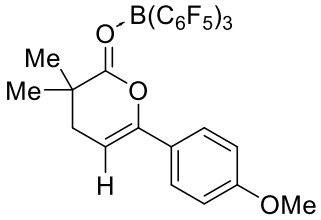
9.5.2.1 Synthesis of ***5.10a***:



3,3-dimethyl-6-phenyl-3,4-dihydro-2*H*-pyran-2-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{31}H_{14}BF_{15}O_2$
Molecular Weight: 714.23 g/mol

In accordance with General Procedure D6, **5.10a** was synthesised using **5.9a** (20 mg, 0.1 mmol) yielding 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. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.38–7.30 (m, 3H, Ar-H), 7.07 (d, $^3J_{HH}$ = 7.2 Hz, 2H, Ar-H), 5.95 (t, $^3J_{HH}$ = 4.0 Hz, 1H, =CH), 2.54 (d, $^3J_{HH}$ = 3.8 Hz, CH_2), 1.46 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 150.5, 147.9 (dm, $^1J_{CF}$ ≈ 240 Hz, 6C), 140.3 (dm, $^1J_{CF}$ ≈ 240 Hz, 3C), 137.3 (dm, $^1J_{CF}$ ≈ 250 Hz, 6C), 130.5, 129.3, 129.0, 124.4, 103.2, 37.6, 32.8, 24.0. **^{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, $^3J_{FF}$ = 15.9 Hz, 6F, *o*-F $B(C_6F_5)_3$), -156.64 (br. s, 3F, *p*-F $B(C_6F_5)_3$), -163.63 (br. s, 6F, *m*-F $B(C_6F_5)_3$). **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 $[C_{14}H_{16}O_2]^+$ $[M+H - (B(C_6F_5)_3)]^+$: 203.1072, found: 203.1079

9.5.2.2 Synthesis of ***5.10b***:

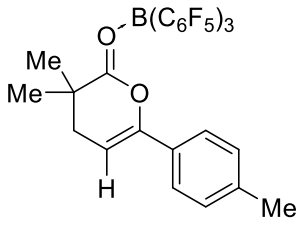


6-(4-methoxyphenyl)-3,3-dimethyl-3,4-dihydro-2*H*-pyran-2-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{32}H_{16}BF_{15}O_3$
Molecular Weight: 744.26 g/mol

In accordance with General Procedure D6, **5.10b** was synthesised using **5.9b** (23 mg, 0.1 mmol) yielding a white solid. **Yield:** 69 mg, 0.09 mmol, 93%. **Melting point:** 80–87 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 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, OCH_3), 2.48 (d, $^3J_{HH}$ = 4.2 Hz, 2H, CH_2), 1.43 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 161.3, 150.4, 148.0 (dm, $^1J_{CF}$ ≈ 240 Hz, 6C), 140.3 (dm, $^1J_{CF}$ ≈ 250 Hz, 3C), 137.2 (dm,

$^{1}J_{CF}$ ≈ 250 Hz, 6C), 126.0, 121.8, 114.3, 101.1, 55.5, 37.6, 32.7, 24.0. **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 1.4 (br. s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -135.03 (d, $^{3}J_{FF}$ = 19.4 Hz, 6F, *o*-F $B(C_6F_5)_3$), - 156.84 (t, $^{3}J_{FF}$ = 20.3 Hz, 3F, *p*-F $B(C_6F_5)_3$), -163.72 (t, $^{3}J_{FF}$ = 18.2 Hz, 6F, *m*-F $B(C_6F_5)_3$). **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 $[C_{14}H_{17}O_3]^+$ $[M+H - (B(C_6F_5)_3)]^+$: 233.1178, found: 233.1183.

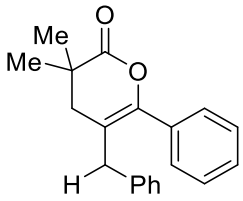
*9.5.2.3 Synthesis of **5.10c**:*



3,3-dimethyl-6-(*p*-tolyl)-3,4-dihydro-2*H*-pyran-2-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{32}H_{16}BF_{15}O_2$
Molecular Weight: 728.26 g/mol

In accordance with General Procedure D6, **5.10c** was synthesised using **5.9c** (22 mg, 0.1 mmol) and yielding a white solid. **Yield:** 68 mg, 0.09 mmol, 93%. **Melting point:** 75–81 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.10 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, Ar-H), 7.01 (d, $^{3}J_{HH}$ = 7.3 Hz, 2H, Ar-H), 5.87 (t, $^{3}J_{HH}$ = 4.5 Hz, 1H, =CH), 2.49 (s, 2H, CH_2), 2.35 (s, 3H, *p*-Me), 1.44 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 150.5, 148.0 (dm, $^{1}J_{CF}$ ≈ 240 Hz, 6C), 140.8, 140.2 (dm, $^{1}J_{CF}$ ≈ 250 Hz, 3C), 137.3 (dm, $^{1}J_{CF}$ ≈ 250 Hz, 6C), 129.6, 126.8, 124.3, 101.9, 37.5, 32.8, 24.1, 21.4. **^{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, $^{3}J_{FF}$ = 18.5 Hz, 6F, *o*-F $B(C_6F_5)_3$), -156.86 (t, $^{3}J_{FF}$ = 19.2 Hz, 3F, *p*-F $B(C_6F_5)_3$), -163.74 (br. s, 6F, *m*-F $B(C_6F_5)_3$). **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 $[C_{14}H_{16}O_2]^+$ $[M-B(C_6F_5)_3]^+$: 216.1150, found 216.1149.

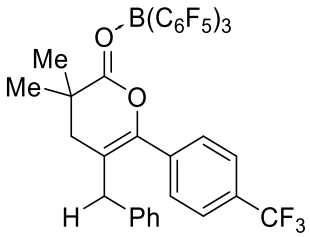
*9.5.2.4 Synthesis of **5.4a**:*



5-benzyl-3,3-dimethyl-6-phenyl-3,4-dihydro-2*H*-pyran-2-one
Chemical Formula: $C_{20}H_{20}O_2$
Molecular Weight: 292.38 g/mol

In accordance with General Procedure D6, **5.4a** was synthesised using **5.1c** (57 mg, 0.2 mmol). However, the adduct could not be isolated by the same work up procedure and was purified *via* column chromatography (SiO_2, chloroform) yielding dihydropyrone **5.4a** as a yellow oil. $\mathbf{R_f}$ value: 0.49. **Yield:** 48 mg, 0.17 mmol, 84%. **^{1}H NMR** (500 MHz, $CDCl_3$, 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, CH_2), 2.18 (s, 2H, CH_2), 1.26 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 174.2, 146.8, 138.7, 133.0, 129.1, 128.8, 128.8 128.7, 128.5, 112.3, 38.7, 37.8, 36.5, 24.9. **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 $[C_{20}H_{20}O_2]^+$ $[M+H]^+$: 292.1463, found: 292.1462.

*9.5.2.5 Synthesis of **5.4b**:*

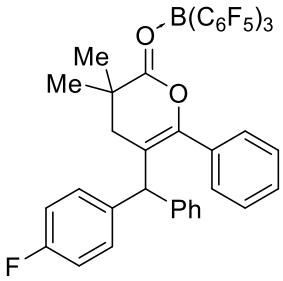


5-benzyl-3,3-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-pyran-2-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{39}H_{19}BF_{18}O_2$
Molecular Weight: 872.36 g/mol

In accordance with General Procedure D6, **5.4b** was synthesised using **5.1d** (45 mg, 0.1 mmol) yielding a white solid. **Yield:** 89 mg, 0.09 mmol, 92%. **Melting point:** 80–86 °C. **^{1}H 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.

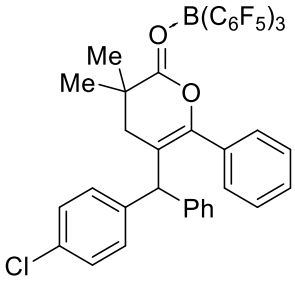
*9.5.2.6 Synthesis of **5.4c**:*



5-((4-fluorophenyl)(phenyl)methyl)-3,3-dimethyl-6-phenyl-3,4-dihydro-2*H*-pyran-2-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{44}H_{23}BF_{16}O_2$
Molecular Weight: 898.45 g/mol

In accordance with General Procedure D6, **5.4c** was synthesised using **5.1e** (39 mg, 0.1 mmol) yielding a white solid. **Yield:** 81 mg, 0.09 mmol 90%. **Melting point:** 168–175 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.45 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ar-H), 7.34 (pent., $^3J_{HH}$ = 6.5 Hz, 5H, Ar-H), 7.06–7.03 (m, 6H, Ar-H), 6.99 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar-H), 5.14 (s, 1H, $CH(Ar)_2$), 2.42–2.32 (m, 2H, CH_2) 1.25 (d, $^4J_{HH}$ = 4.0 Hz, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 162.0 (d, $^1J_{CF}$ = 245 Hz, 1C), 148.0 (dm, $^1J_{CF}$ = 250 Hz, 6C), 140.4, 140.1 (dm, $^1J_{CF}$ = 245 Hz, 3C), 137.1 (dm, $^1J_{CF}$ = 245 Hz, 6C), 136.6, 130.5, 129.01 (s), 129.0 (d, $^3J_{CF}$ = 7.4 Hz, 2C), 128.9, 128.3, 127.6, 50.7, 37.0, 34.6, 23.9, 23.8. **^{11}B NMR** (160 MHz, $CDCl_3$, 298 K) δ/ppm: 1.6 (br. s). **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -114.56 (s, 1F, *p*-F), -135.31 – -135.36 (m, 6F, *o*-F $B(C_6F_5)_3$), -157.08 (t, $^3J_{FF}$ = 20.5 Hz, 3F, *p*-F $B(C_6F_5)_3$), -163.85 (td, 6F, $^3J_{FF}$ = 23.9 Hz, $^4J_{FF}$ = 8.3 Hz, *m*-F $B(C_6F_5)_3$). **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 $[C_{26}H_{24}O_2F]^+$ $[M-B(C_6F_5)_3+H]^+$: 387.1760, found: 387.1752.

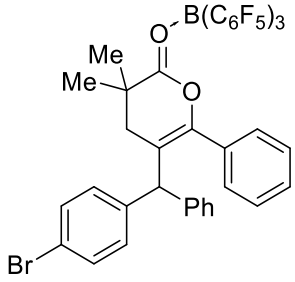
*9.5.2.7 Synthesis of **5.4d**:*



5-((4-chlorophenyl)(phenyl)methyl)-3,3-dimethyl-6-phenyl-3,4-dihydro-2*H*-pyran-2-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{44}H_{23}BClF_{15}O_2$
Molecular Weight: 914.90 g/mol

In accordance with General Procedure D6, **5.4d** was synthesised using **5.1f** (40 mg, 0.1 mmol) and yielding a white solid. **Yield:** 88 mg, 0.09 mmol, 97%. **Melting point:** 149–155 °C. **^{1}H 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)Ar_2), 2.32 (s, 2H, CH_2), 1.22 (s, 3H, CH_3), 1.19 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 186.2, 147.8 (dm, $^1J_{CF}$ ≈ 250 Hz, 6C), 147.5, 140.0 (dm, $^1J_{CF}$ ≈ 250 Hz, 3C), 139.6, 138.6, 137.1 (dm, $^1J_{CF}$ ≈ 250 Hz, 6C), 133.6, 131.0, 130.2, 129.3, 129.2, 129.1, 128.8, 128.2, 127.9, 119.4, 50.7, 37.4, 34.1, 23.6, 23.4. **^{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 $[C_{26}H_{24}O_2Cl]^+$ $[(M\text{-}B(C_6F_5)_3)+H]^+$: 403.1465, found: 403.1455.

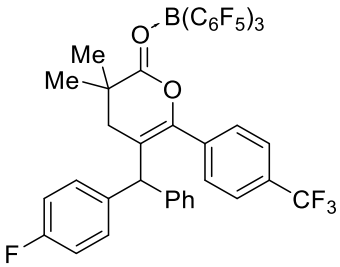
*9.5.2.8 Synthesis of **5.4e**:*



5-((4-bromophenyl)(phenyl)methyl)-3,3-dimethyl-6-phenyl-3,4-dihydro-2*H*-pyran-2-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{44}H_{23}BBrF_{15}O_2$
Molecular Weight: 959.36 g/mol

In accordance with General Procedure D6, **5.4e** was synthesised using **5.1g** (45 mg, 0.1 mmol) yielding a white solid. **Yield:** 92 mg, 0.09 mmol, 96%. **Melting point:** 154–159 °C. **^{1}H 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, $^{3}J_{HH}$ = 7.1 Hz, 2H, Ar-H), 6.87 (d, $^{3}J_{HH}$ = 8.4 Hz, 4H, Ar-H), 5.04 (s, 1H, C(H)Ar_2), 2.32 (s, 2H, CH_2), 1.22 (s, 3H, CH_3), 1.19 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 147.8 (dm, $^{1}J_{CF}$ ≈ 240 Hz, 6C), 147.6, 140.2 (dm, $^{1}J_{CF}$ ≈ 250 Hz, 3C), 140.2 (d, $^{3}J_{CF}$ = 47.6 Hz, 1C), 137.1 (dm, $^{1}J_{CF}$ ≈ 250 Hz, 6C), 132.0, 130.7, 130.26, 129.0, 128.9, 128.9, 128.3, 127.5, 121.3, 51.1, 36.7, 34.9, 24.1, 24.0. **^{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, $^{3}J_{FF}$ = 16.9 Hz, 6F, *o*-F B(C_6F_5)$_3$), -157.02 (t, $^{3}J_{FF}$ = 20.5 Hz, 3F, *p*-F B(C_6F_5)$_3$), -163.79 (td, $^{3}J_{FF}$ = 23.9, $^{4}J_{FF}$ =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 $[C_{26}H_{24}O_2Br]^{+}$ $[(M\text{-}B(C_6F_5)_3)+H]^{+}$: 447.0960, found: 447.0947.

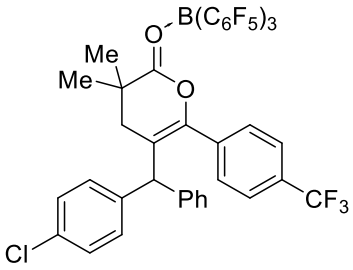
*9.5.2.9 Synthesis of **5.4f**:*



5-((4-fluorophenyl)(phenyl)methyl)-3,3-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-pyran-2-one B(C_6F_5)$_3$ adduct
Chemical Formula: $C_{45}H_{22}BF_{19}O_2$
Molecular Weight: 966.45 g/mol

In accordance with General Procedure D6, **5.4f** was synthesised using **5.1h** (45 mg, 0.1 mmol) yielding a white solid. **Yield:** 89 mg, 0.09 mmol, 92%. **Melting point:** 165–171 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.55 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 7.33–7.27 (m, 3H, Ar-H), 7.19 (d, $^{3}J_{HH}$ = 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, 23 3H, CH_3), 1.28 (s, 3H, CH_3). **^{13}C NMR** *partial* (126 MHz, $CDCl_3$, 298 K) δ/ppm: 148.1 (dm, $^{1}J_{CF}$ = 245 Hz, 6C), 147.9, 140.1, 139.1, 137.3 (dm, $^{1}J_{CF}$ = 250 Hz, 6C), 134.0, 131.3, 130.1, 129.6, 129.6, 129.5, 129.2, 128.6, 128.3, 51.1, 37.7, 34.5, 24.0, 23.92. **^{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, $^{3}J_{FF}$ = 21.7 Hz, $^{4}J_{FF}$ = 8.5 Hz, 6F, *o*-F B(C_6F_5)$_3$), -153.49 (br. s, $^{3}J_{FF}$ = 20.1 Hz, $^{4}J_{FF}$ = 6.9 Hz, 3F, *p*-F B(C_6F_5)$_3$), -161.81 – -161.94 (m, 6F, *m*-F B(C_6F_5)$_3$).

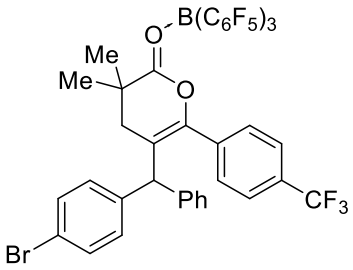
*9.5.2.10 Synthesis of **5.4g**:*



5-((4-chlorophenyl)(phenyl)methyl)-3,3-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-pyran-2-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{45}H_{22}BClF_{18}O_2$
Molecular Weight: 982.90 g/mol

In accordance with General Procedure D6, **5.4g** was synthesised using **5.1i** (47 mg, 0.1 mmol) yielding a white solid. **Yield:** 92 mg, 0.09 mmol, 94%. **Melting point:** 160–168 °C. **^{1}H 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, 146.6 (dm, $^1J_{CF}$ = 240 Hz, 6C), 144.8, 140.6, 138.9 (dm, $^1J_{CF}$ = 245 Hz, 3C), 138.5, 137.4, 136.0 (dm, $^1J_{CF}$ = 245 Hz, 6C), 132.6, 129.0, 128.4, 128.2, 128.1, 128.2, 127.6, 127.6, 126.8, 124.9 (q, $^3J_{CF}$ = 3.5 Hz, 2C), 49.7, 36.0, 33.6, 22.6, 22.6. **^{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 $B(C_6F_5)_3$), -156.46 (s, 3F, *p*-F $B(C_6F_5)_3$), -163.58 (t, $^3J_{FF}$ = 17.7 Hz, 6F, *m*-F $B(C_6F_5)_3$). **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 $[C_{27}H_{23}O_2F_3Cl]+$ $[(M-B(C_6F_5)_3)+H]^+$: 471.1339, found: 471.1330.

*9.5.2.11 Synthesis of **5.4h**:*

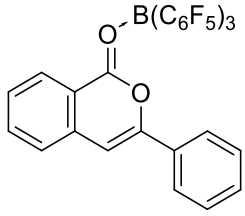


5-((4-bromophenyl)(phenyl)methyl)-3,3-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-pyran-2-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{45}H_{22}BBrF_{18}O_2$
Molecular Weight: 1027.35 g/mol

In accordance with General Procedure D6, **5.4h** was synthesised using **5.1j** (51 mg, 0.1 mmol) yielding a white solid. **Yield:** 93 mg, 0.09 mmol, 92%. **Melting point:** 105–110

°C. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.48 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.35 (d, $^{3}J_{HH}$ = 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, $^{3}J_{HH}$ = 8.3 Hz, 2H, Ar-H), 4.91 (s, 1H, C(H)Ar_2), 2.30 (s, 1H), 1.21 (s, 3H, CH_3), 1.18 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 189.2, 147.9 (dm, $^{1}J_{CF}$ = 245 Hz, 6C), 146.3, 141.3, 140.1 (dm, $^{1}J_{CF}$ = 245 Hz, 3C), 140.0, 136.9 (dm, $^{1}J_{CF}$ = 245 Hz, 6C), 132.1, 130.1, 129.1, 128.9, 128.8, 127.7, 125.8 (q, $^{3}J_{CF}$ = 3.8 Hz, 2C), 121.4, 51.2, 36.7, 35.5, 24.3, 24.2. **^{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, $-CF_3$), -134.97 (br. s, 6F, *o*-F $B(C_6F_5)_3$), -156.09 (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}): 2934 (w), 22361 (w), 1717 (w), 1647 (w), 1618 (w), 24 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 $[C_{27}H_{23}O_2F_3Br]^+$ $[(M-B(C_6F_5)_3)+H]^+$: 515.0834, found: 515.0831.

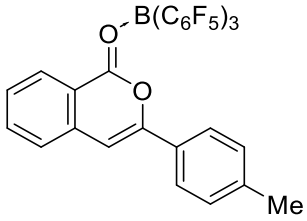
*9.5.2.12 Synthesis of **5.16a**:*



3-phenyl-1*H*-isochromen-1-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{33}H_{10}BF_{15}O_2$
Molecular Weight: 734.23 g/mol

In accordance with General Procedure D6, **5.16a** was synthesised using **5.13a** (22 mg, 0.1 mmol) yielding a pale green solid, that was recrystallised by slow evaporation of a saturated CH_2Cl_2/hexane solution. **Yield:** 33 mg, 0.05 mmol, 45%. **Melting point:** 205–211 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 8.57 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H, Ar-H), 8.09 (t, $^{3}J_{HH}$ = 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). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 154.7, 148.1 (dm, $^{1}J_{CF}$ = 244 Hz, 6C), 140.0 (dm, $^{1}J_{CF}$ = 247 Hz, 3C) 139.3, 139.2, 137.2 (dm, $^{1}J_{CF}$ = 253 Hz, 6C), 131.8, 130.9, 130.6, 129.4, 127.0, 125.6, 117.4, 106.5. **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 0.8 (br. s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -134.77 (d, $^{3}J_{FF}$ = 19.6 Hz, 6F, *o*-F $B(C_6F_5)_3$), -157.14 (t, $^{3}J_{FF}$ = 19.9 Hz, 3F, *p*-F $B(C_6F_5)_3$), -163.79 (t, $^{3}J_{FF}$ = 17.7 Hz, 6F, *m*-F $B(C_6F_5)_3$). **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 $[C_{15}H_{11}O_2]^+$ $[M+H - (B(C_6F_5)_3)]^+$: 223.0759, found: 223.0760.

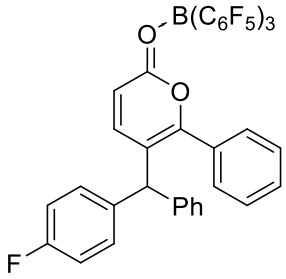
*9.5.2.13 Synthesis of **5.16b**:*



3-(*p*-tolyl)-1*H*-isochromen-1-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{34}H_{12}BF_{15}O_2$
Molecular Weight: 748.25 g/mol

In accordance with General Procedure D6, **5.16a** was synthesised using **5.13b** (24 mg, 0.1 mmol) yielding a pale green solid, that was recrystallised by slow evaporation of a saturated CH_2Cl_2/hexane solution. **Yield:** 39 mg, 0.05 mmol, 52%. **Melting point:** 187–192 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 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, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 154.9, 147.9 (dm, $^1J_{CF}$ = 241 Hz, 6C), 142.5, 140.0 (dm, $^1J_{CF}$ = 246 Hz, 3C), 139.3, 139.2, 137.0 (dm, $^3J_{CF}$ = 253 Hz, 6C), 130.5, 130.4, 130.0, 126.7, 125.3, 117.0, 105.6, 21.5. **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 0.7 (br. s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -134.76 (d, $^3J_{FF}$ = 18.0 Hz, 6F, *o*-F $B(C_6F_5)_3$), - 157.27 (t, $^3J_{FF}$ = 20.3 Hz, 3F, *p*-F $B(C_6F_5)_3$), -163.86 (t, $^3J_{FF}$ = 18.3 Hz, 6F, *m*-F $B(C_6F_5)_3$). **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 $[C_{16}H_{13}O_2]^+$ [M+H - $(B(C_6F_5)_3)]^+$: 237.0916, found: 237.0920.

*9.5.2.14 Synthesis of **5.5a**:*

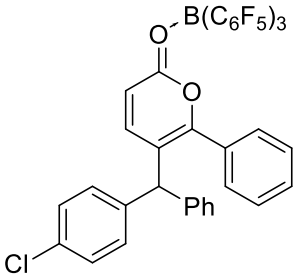


5-((4-fluorophenyl)(phenyl)methyl-6-phenyl-2*H*-pyran-2-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{42}H_{17}BF_{16}O_2$
Molecular Weight: 868.38 g/mol

In accordance with General Procedure D6, **5.5a** was synthesised using **5.2a** (36 mg, 0.1 mmol) yielding a pale green solid that was recrystallised by slow evaporation of a saturated CH_2Cl_2/hexane solution. **Yield:** 80 mg, 0.09 mmol, 92%. **Melting point:** 117–123 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 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)Ar_2). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 162.2 (d, $^1J_{CF}$ = 248 Hz, 1C), 148.0 (dm, $^1J_{CF}$ = 241 Hz, 6C), 140.4, 140.0 (dm, $^1J_{CF}$ = 249 Hz, 3C), 137.1 (dm, $^1J_{CF}$ = 245 Hz, 6C), 136.5, 132.4, 130.5 (d, $^3J_{CF}$ = 8.1 Hz, 2C), 129.6, 129.2, 128.8, 128.5, 128.2, 117.7, 116.5 (d, $^2J_{CF}$ = 21.6 Hz, 2C), 113.6, 49.4. **^{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 $B(C_6F_5)_3$), -157.6 (t, $^3J_{FF}$ = 20.3 Hz, 3F, *p*-F $B(C_6F_5)_3$), -164.2 (t, $^3J_{FF}$ = 18.3 Hz, 6F, *m*-F $B(C_6F_5)_3$). **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 $[C_{24}H_{18}O_2F]^+$ [M+H - $(B(C_6F_5)_3)]^+$: 357.1291, found: 357.1293.

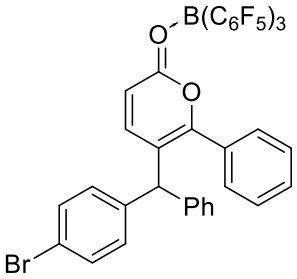
*9.5.2.15 Synthesis of **5.5b**:*



5-((4-chlorophenyl)(phenyl)methyl)-6-phenyl-2*H*-pyran-2-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{42}H_{17}BClF_{15}O_2$
Molecular Weight: 884.83 g/mol

In accordance with General Procedure D6, **5.5b** was synthesised using **5.2b** (37 mg, 0.1 mmol) yielding 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. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.95 (d, $^3J_{HH}$ = 9.4 Hz, 1H, =CH), 7.58 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar-H), 7.44–7.32 (m, 8H, Ar-H), 7.06 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar-H), 6.99–6.86 (m, 6H, Ar-H), 5.49 (s, 1H, C(H)Ar_2). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 168.6, 162.0, 153.9, 148.0 (dm, $^1J_{CF}$ = 238 Hz, 6C), 140.1, 140.0 (dm, $^1J_{CF}$ = 250 Hz, 3C), 139.1, 137.1 (dm, $^1J_{CF}$ = 248 Hz, 6C), 134.2, 132.6, 130.2, 129.7, 129.7, 129.3, 128.8, 128.5, 128.3, 128.1, 124.7, 113.5, 49.6. **^{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 $B(C_6F_5)_3$), -157.6 (t, $^3J_{FF}$ = 20.1 Hz, 3F, *p*-F $B(C_6F_5)_3$), -164.2 (t, $^3J_{FF}$ = 18.3 Hz, 6F, *m*-F $B(C_6F_5)_3$). **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 $[C_{24}H_{18}O_2Cl]^+$ [M+H - $(B(C_6F_5)_3)]^+$: 373.0995, found: 373.1005.

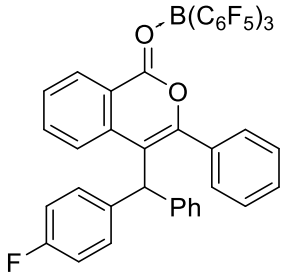
*9.5.2.16 Synthesis of **5.5c**:*



5-((4-bromophenyl)(phenyl)methyl)-6-phenyl-2*H*-pyran-2-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{42}H_{17}BBrF_{15}O_2$
Molecular Weight: 929.29 g/mol

In accordance with General Procedure D6, **5.5c** was synthesised using **5.2c** (42 mg, 0.1 mmol) yielding 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. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.95 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 7.58 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.50 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.45–7.33 (m, 7H), 7.06 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 6.97 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 6.86 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 5.47 (s, 1H, C(H)Ar$_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 161.9, 147.9 (dm, $^1J_{CF}$ = 238 Hz, 6C), 140.1, 140.0 (dm, $^1J_{CF}$ = 254 Hz, 3C), 139.7, 137.0 (dm, $^1J_{CF}$ = 253 Hz, 6C), 132.6, 130.5, 129.6, 129.3, 128.8, 128.5, 128.2, 122.2, 113.5, 49.6. **^{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 $B(C_6F_5)_3$), -157.58 (t, $^3J_{FF}$ = 20.2 Hz, 3F, *p*-F $B(C_6F_5)_3$), -164.14 (t, $^3J_{FF}$ = 18.1 Hz, 6F, *m*-F $B(C_6F_5)_3$). **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 $[C_{24}H_{18}O_2Br]^+$ [M+H - $(B(C_6F_5)_3)$]$^+$: 417.0490, found: 417.0503.

*9.5.2.17 Synthesis of **5.6a**:*

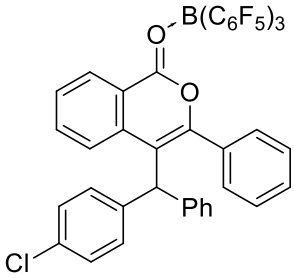


4-((4-fluorophenyl)(phenyl)methyl)-3-phenyl-1*H*-isochromen-1-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{46}H_{19}BF_{16}O_2$
Molecular Weight: 918.44 g/mol

In accordance with General Procedure D6, **5.6a** was synthesised using **5.3a** (41 mg, 0.1 mmol) yielding 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. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 8.62 (d, $^3J_{HH}$ = 7.4 Hz, 1H, Ar-H), 7.79 (t, $^3J_{HH}$ = 7.2 Hz, 1H, Ar-H), 7.73 (t, $^3J_{HH}$ = 7.4 Hz, 1H, Ar-H), 7.67 (d, $^3J_{HH}$ = 8.2 Hz, 1H, Ar-H), 7.48 (t, $^3J_{HH}$ = 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, $^3J_{HH}$ = 8.4 Hz, 4H, Ar-H), 5.81 (s, 1H, C(H)Ar_2). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 169.3, 161.9 (d, $^1J_{CF}$ = 247 Hz, 1C), 154.2 (s, 148.2 (dm, $^1J_{CF}$ = 245 Hz, 6C), 139.8 (dm, $^1J_{CF}$ = 250 Hz, 3C), 139.0, 139.0, 136.9 (dm, $^1J_{CF}$ = 250 Hz, 6C), 135.6 (d, $^3J_{CF}$ = 3.3 Hz, 2C), 131.5, 131.1, 130.6, 129.6, 129.2, 129.1, 128.8, 128.6, 127.8, 127.7, 120.9, 118.3, 116.0 (d, $^2J_{CF}$ = 12.1 Hz, 2C), 49.4. **^{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: - 114.54 (s, 1F, CF), - 134.98 (d, $^3J_{FF}$ = 19.2 Hz, 6F, *o*-F $B(C_6F_5)_3$), -157.48 (t, $^3J_{FF}$ = 18.0 Hz, 3F, *p*-F $B(C_6F_5)_3$), - 164.03 (br. t, $^3J_{FF}$ = 18.2 Hz, 6F, *m*-F $B(C_6F_5)_3$). **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 $[C_{28}H_{20}O_2F]^+$ [M+H - $(B(C_6F_5)_3)]^+$: 407.1447, found: 407.1440.

*9.5.2.18 Synthesis of **5.6b**:*

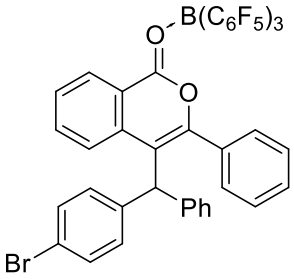


4-((4-chlorophenyl)(phenyl)methyl)-3-phenyl-1*H*-isochromen-1-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{46}H_{19}BClF_{15}O_2$
Molecular Weight: 934.89 g/mol

In accordance with General Procedure D6, **5.6b** was synthesised using **5.3b** (42 mg, 0.1 mmol) yielding a white solid that was recrystallised by slow evaporation of a saturated CH_2Cl_2/hexane solution. **Yield:** 85 mg, 0.09 mmol, 91%. **Melting point:** 194–200 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 8.61 (d, $^3J_{HH}$ = 7.9 Hz, 1H, Ar-H), 7.78 (t, $^3J_{HH}$ = 7.2 Hz, 1H, Ar-H), 7.72 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar-H), 7.64 (d, $^3J_{HH}$ = 8.2 Hz, 1H, Ar-H), 7.47 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar-H), 7.32 (t, $^3J_{HH}$ = 7.8 Hz, 2H, Ar-H), 7.29– 7.17 (m, 4H, Ar-H), 7.05 (d, $^3J_{HH}$ = 7.3 Hz, 2H, Ar-H), 6.99 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar-H), 6.95 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar-H), 5.79 (s, 1H, C(H)Ar_2). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 169.3, 154.3, 148.0 (dm, $^1J_{CF}$ = 238 Hz, 6C), 140.0 (dm, $^1J_{CF}$ = 250 Hz, 3C), 139.4, 138.9, 138.4, 137.07 (dm, $^1J_{CF}$ = 241 Hz, 6C). 133.5, 131.5, 131.1, 130.5, 130.3, 129.5, 129.3, 129.2, 129.1, 128.8, 128.6, 127.8, 127.7, 120.6, 118.3, 49.5. **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 0.6 (br. s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -134.98 (d, $^3J_{FF}$ = 18.5

Hz, *o*-F $B(C_6F_5)_3$), -157.47 (t, $^3J_{FF}$ = 20.0 Hz, *p*-F $B(C_6F_5)_3$), -164.02 (t, $^3J_{FF}$ = 18.3 Hz, *m*-F $B(C_6F_5)_3$). **IR** ν_{max} (cm^{-1}): 3059 (w), 2158 (w), 2027 (w), 1635 (m), 25 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 $[C_{28}H_{20}ClO_2]^+$ [M+H - $(B(C_6F_5)_3)]^+$: 423.1152, found: 423.1151.

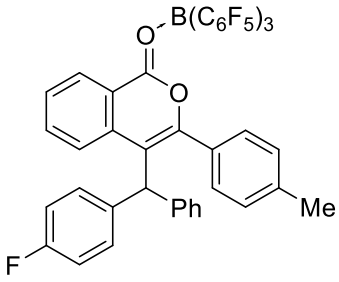
*9.5.2.19 Synthesis of **5.6c**:*



4-((4-bromophenyl)(phenyl)methyl)-3-phenyl-1*H*-isochromen-1-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{46}H_{19}BBrF_{15}O_2$
Molecular Weight: 979.35 g/mol

In accordance with General Procedure D6, **5.6c** was synthesised using **5.3c** (47 mg, 0.1 mmol) yielding 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. **^{1}H 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)Ar_2). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 154.3, 148.0 (dm, $^1J_{CF}$ = 245 Hz, 6C), 140.0 (dm, $^1J_{CF}$ = 250 Hz, 3C), 139.4, 139.0, 138.8, 137.1 (dm, $^1J_{CF}$ = 247 Hz, 6C), 132.2, 131.5, 131.1, 130.6, 130.5, 129.2, 129.1, 128.8, 128.6, 127.7, 127.7, 121.5, 49.5. **^{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.

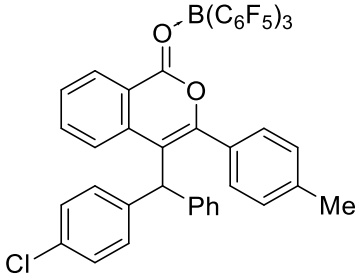
*9.5.2.20 Synthesis of **5.6d**:*



4-((4-fluorophenyl)(phenyl)methyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one
$B(C_6F_5)_3$ adduct
Chemical Formula: $C_{47}H_{21}BF_{16}O_2$
Molecular Weight: 932.47 g/mol

In accordance with General Procedure D6, **5.6d** was synthesised using **5.3d** (42 mg, 0.1 mmol) and yielding a white solid that was recrystallised by slow evaporation of a saturated CH_2Cl_2/hexane solution. **Yield:** 75 mg, 0.08 mmol, 81%. **Melting point:** >230 °C. **^{1}H 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, CH_3). **^{13}C NMR** (126 MHz, DMSO-d_6, 298 K) δ/ppm: 161.7, 160.8 (d, $^1J_{CF}$ = 243 Hz, 1C), 153.9, 147.2 (dm, $^1J_{CF}$ = 239 Hz, 6C), 140.7, 140.1, 139.1 (dm, $^1J_{CF}$ = 251.1 Hz, 3C), 137.2, 136.8, 136.8, 136.2 (dm, $^1J_{CF}$ = 246 Hz), 134.0, 130.6, 130.6, 130.2, 129.2, 129.1, 128.6, 128.0, 126.7 (d, $^3J_{CF}$ = 7.0 Hz, 2C), 121.3, 115.3 (d, $^2J_{CF}$ = 21.3 Hz, 2C), 114.2, 48.5, 20.9. **^{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.

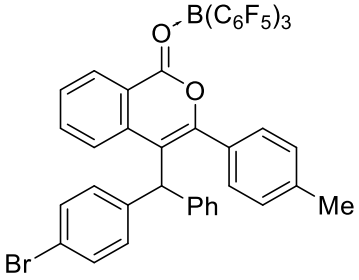
*9.5.2.21 Synthesis of **5.6e**:*



4-((4-chlorophenyl)(phenyl)methyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{47}H_{21}BClF_{15}O_2$
Molecular Weight: 948.92 g/mol

In accordance with General Procedure D6, **5.6e** was synthesised using **5.3e** (44 mg, 0.1 mmol) yielding a white solid that was recrystallised by slow evaporation of a saturated CH_2Cl_2/hexane solution. **Yield:** 79 mg, 0.08 mmol, 84%. **Melting point:** 207–213 °C. **^{1}H 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, ArH), 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)Ar_2), 2.38 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 154.59, 148.03 (dm, $^1J_{CF}$ = 239 Hz, 6C), 142.2, 140.3 (dm, $^1J_{CF}$ = 246 Hz, 3C) 139.6, 139.0, 138.6, 137.1 (dm, $^1J_{CF}$ = 247 Hz, 6C), 133.4, 131.0, 130.3, 129.7, 129.2, 128.8, 128.6, 127.7, 49.5, 21.6. **^{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 $[C_{29}H_{22}ClO_2]^+$ [M+H - $(B(C_6F_5)_3)]^+$: 437.1308, found: 437.1307.

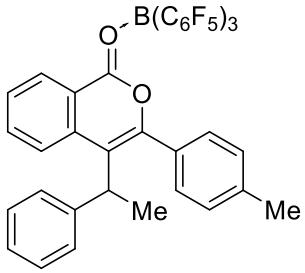
*9.5.2.22 Synthesis of **5.6f**:*



4-((4-bromophenyl)(phenyl)methyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one
$B(C_6F_5)_3$ adduct
Chemical Formula: $C_{47}H_{21}BBrF_{15}O_2$
Molecular Weight: 993:37 g/mol

In accordance with General Procedure D6, **5.6f** was synthesised using **5.3f** (48 mg, 0.1 mmol) yielding a white solid that was recrystallised by slow evaporation of a saturated CH_2Cl_2/hexane solution. **Yield:** 87 mg, 0.09 mmol, 88%. **Melting point:** 220–224 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 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)Ar_2), 2.41 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 169.3, 154.6, 148.0 (dm, $^1J_{CF}$ = 241 Hz, 6C), 142.3, 140.0 (d, $^1J_{CF}$ = 262 Hz, 3C), 139.4, 139.1, 137.1 (d, $^1J_{CF}$ = 249 Hz, 6C), 132.2, 131.1, 130.7, 130.4, 129.7, 129.2, 128.8, 128.5, 127.7, 127.7, 126.6, 121.5, 120.2, 118.2, 49.6, 21.6. **^{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, $^3J_{FF}$ = 18.2 Hz, 6F, *o*-F $B(C_6F_5)_3$), - 157.60 (t, $^3J_{FF}$ = 19.9 Hz, 3F, *p*-F $B(C_6F_5)_3$), -164.10 (t, $^3J_{FF}$ = 18.2 Hz, 6F, *m*-F $B(C_6F_5)_3$). **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 $[C_{29}H_{22}O_2Br]^+$ $[M+H - B(C_6F_5)_3)]^+$: 481.0803, found: 481.0810.

*9.5.2.23 Synthesis of **5.6g**:*



4-(1-phenylethyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one $B(C_6F_5)_3$ adduct
Chemical Formula: $C_{42}H_{20}BF_{15}O_2$
Molecular Weight: 852.41 g/mol

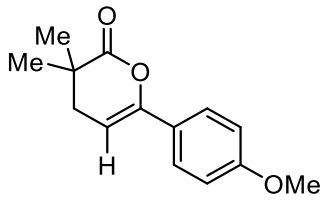
In accordance with General Procedure D6, **5.6g** was synthesised using **5.3g** (68 mg, 0.2 mmol) yielding a yellow solid. **Yield:** 148 mg, 0.17 mmol, 87%. **Melting point:** 72–78 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 8.51 (s, 1H, Ar-H), 7.70 (s, 1H, Ar-H), 7.61 (s, 1H, Ar-H), 7.45 (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, 148.1 (d, $^1J_{CF}$ = 238.1 Hz), 141.9, 141.7, 140.0 (d, $^1J_{CF}$ = 248.4 Hz), 138.4, 138.3, 137.1 (d, $^1J_{CF}$ = 217.8 Hz), 131.1, 130.2, 130.1, 129.8, 129.2, 128.5, 128.4, 127.0, 126.9, 126.6, 125.5, 37.3, 21.5, 18.6. **^{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 $[C_{24}H_{20}O_2]^+$ $[M\text{-}B(C_6F_5)_3]^+$: 340.1463, found: 340.1462.

9.5.3 Products of the catalytic cyclisation reactions

General procedure D7 for the catalytic cyclisation of alkynyl acids and esters.

$B(C_6F_5)_3$ (3 mg, 5 µmol, 5 mol%) was added to a solution of carboxylic acid or ester (0.1 mmol, 1 equiv) in CD_2Cl_2 (0.5 ml) in a sealed tube and the mixture was heated at 70 °C until complete conversion could be observed in the ^{1}H NMR spectrum. The resulting solution was allowed to cool to room temperature and all volatiles were removed under vacuum. The residue was either purified *via* column chromatography (SiO_2) or recrystallisation in a saturated CH_2Cl_2 solution to give the desired free cyclised heterocyclic product.

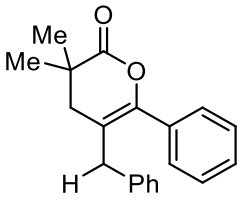
*9.5.3.1 Synthesis of **5.17b**:*



6-(4-methoxyphenyl)-3,3-dimethyl-3,4-dihydro-2*H*-pyran-2-one
Chemical Formula: $C_{14}H_{16}O_3$
Molecular Weight: 232.28 g/mol

In accordance with General Procedure D7, **5.17b** was synthesised using **5.9b** (23 mg, 0.1 mmol) yielding a white solid after recrystallisation. **Yield:** 21 mg, 0.09 mmol 91%. **Melting point:** 68–74 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.53 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 6.88 (d, $^3J_{HH}$ = 8.5 Hz, 2H, Ar-H), 5.60 (t, $^3J_{HH}$ = 4.4 Hz, 1H, =CH), 3.82 (s, 3H, OCH_3), 2.35 (d, $^3J_{HH}$ = 4.4Hz, 2H, CH2), 1.32 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 160.3, 149.8, 126.0, 114.0, 97.4, 55.5, 36.6, 34.5, 25.1. **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 $[C_{14}H_{17}O_3]^+$ $[M+H]^+$: 233.1178, found: 233.1179.

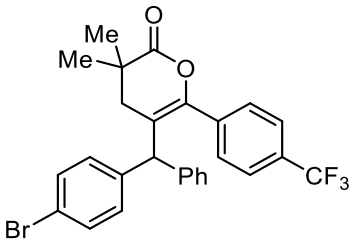
*9.5.3.2 Synthesis of **5.17c**:*



5-benzyl-3,3-dimethyl-6-phenyl-3,4-dihydro-2*H*-pyran-2-one
Chemical Formula: $C_{20}H_{20}O_2$
Molecular Weight: 292.38 g/mol

In accordance with General Procedure D7, **5.17c** was synthesised using **5.9b** (58 mg, 0.2 mmol, 1 equiv). yielding a pale-yellow oil after column chromatography (SiO_2, chloroform). **R_f** value: 0.50. **Yield:** 19 mg, 0.7 mmol, 33%. **^{1}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, $C(CH_3)_2$). Agreeing with values obtained for **5.4a**.

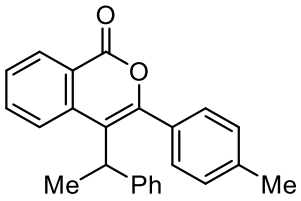
*9.5.3.3 Synthesis of **5.17d**:*



5-((4-bromophenyl)(phenyl)methyl)-3,3-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-pyran-2-one
Chemical Formula: $C_{27}H_{22}BrF_3O_2$
Molecular Weight: 515.37 g/mol

In accordance with General Procedure D7, **5.17d** was synthesised using **5.1j** (500 mg, 0.9 mmol) yielding a white solid after column chromatography (SiO_2, chloroform). $\mathbf{R_f}$ value: 0.64. **Yield:** 138 mg, 0.3 mmol, 27%. **Melting point:** 125–131 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 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 CH_2), 2.16 (d, $^2J_{HH}$ = 17.1 Hz, 1H, diastereotopic CH_2), 1.19 (s, 3H, CH_3), 1.17 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 173.1, 146.7, 140.8 (d, $^2J_{CF}$ = 45.7 Hz, 1C), 136.3, 131.9, 130.8, 129.0, 129.0, 128.9, 127.4, 125.7 (q, $^4J_{CF}$ = 3.8 Hz, 2C) 121.1, 115.5, 51.3, 36.4, 36.2, 29.9, 24.9, 24.8. **^{19}F NMR** (471 MHz, $CDCl_3$, 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 $[C_{27}H_{23}O_2BrF_3]^+$ $[M+H]^+$: 514.0755, found: 514.0761.

*9.5.3.4 Synthesis of **5.17e**:*

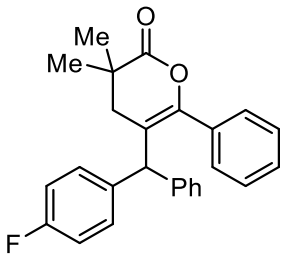


4-(1-phenylethyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one
Chemical Formula: $C_{24}H_{20}O_2$
Molecular Weight: 340.42 g/mol

In accordance with General Procedure D7, **5.17e** was synthesised using **5.3g** (32 mg, 0.1 mmol) yielding a white oil after column chromatography (1:2 hexane/chloroform). $\mathbf{R_f}$ value: 0.23 **Yield:** 17 mg, 0.055 mmol, 55%. **^{1}H NMR** (500 MHz, $CDCl_3$, 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, $^{3}J_{HH}$ = 7.0 Hz, 1H, C(H)(Me)Ar), 2.39 (s, 3H, CH_3), 2.15 (d, $^{2}J_{HH}$ = 16.8 Hz, 1H, CH_2), 1.89 (d, $^{2}J_{HH}$ = 16.8 Hz, 1H, CH_2), 1.45 (d, $^{3}J_{HH}$ = 7.1 Hz, 3H, C(H)(Me)Ar), 1.26 (s, 3H, CH_3), 1.07 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 174.2, 145.9, 142.9, 139.0, 130.4, 129.3, 128.8, 128.4, 127.4, 126.6, 117.5, 38.2, 36.1, 34.3, 24.7, 24.7, 21.5, 17.3. **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 $[C_{29}H_{21}O_2F]^+$ $[M+H]^+$: 320.1855, found: 320.1856.

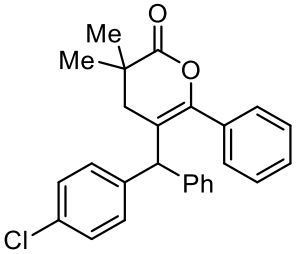
*9.5.3.5 Synthesis of **5.17a**:*



5-((4-fluorophenyl)(phenyl)methyl)-3,3-dimethyl-6-phenyl-3,4-dihydro-2*H*-pyran-2-one
Chemical Formula: $C_{26}H_{23}FO_2$
Molecular Weight: 386.47 g/mol

In accordance with General Procedure D7, **5.17a** was synthesised using **5.1e** (39 mg, 0.1 mmol) gave a white solid after column chromatography (SiO_2, chloroform). **R_f** value: 0.51. **Yield:** 37 mg, 0.95 mmol, 95%. **Melting point:** 139–144 °C. **^{1}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, $^{3}J_{HH}$ = 8.5 Hz, 2H, Ph–H), 5.18 (s, 1H, $C(H)Ar_2$), 2.20–2.10 (m, 2H, CH_2), 1.07 (s, 6H, $C(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 173.8, 161.7 (d, $^{1}J_{CF}$ = 245.8 Hz, 1C), 147.9, 141.7, 137.6 (d, $^{3}J_{CF}$ = 3.3 Hz, 1C), 132.9, 130.6 (d, $^{3}J_{CF}$ = 7.9 Hz, 2C), 129.4, 129.0, 128.6, 128.6, 128.5, 127.0, 115.4 (d, $^{2}J_{CF}$ = 21.2 Hz, 2C), 114.3, 50.9, 36.4, 35.9, 24.8, 24.7. **^{19}F NMR** (376 Hz, $CDCl_3$, 298 K) δ/ppm: –115.82 (s, 1F, *p*-F). **IR** ν_{max} (cm^{-1}): 30 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 $[C_{26}H_{24}O_2F]^+$ $[M+H]^+$: 387.1760, found: 387.1751.

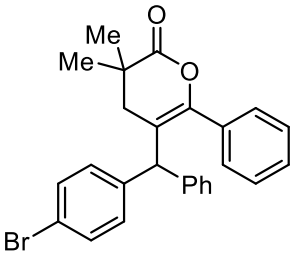
*9.5.3.6 Synthesis of **5.17f**:*



5-((4-chlorophenyl)(phenyl)methyl)-3,3-dimethyl-6-phenyl-3,4-dihydro-2*H*-pyran-2-one
Chemical Formula: $C_{26}H_{23}ClO_2$
Molecular Weight: 402.92 g/mol

In accordance with General Procedure D7, **5.17f** was synthesised using **5.1f** (40 mg, 0.1 mmol) yielding a white solid after column chromatography (SiO_2, chloroform). **R_f** value: 0.49. **Yield:** 36 mg, 0.90 mmol, 90%. **Melting point:** 104–110 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.39–7.26 (m, 10H, Ar-H), 7.07 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar-H), 7.04 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar-H), 5.23 (s, 1H, C(H)Ar_2), 2.23 (s, 2H, CH_2), 1.16 (s, 3H, CH_3), 1.15 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 174.1, 148.0, 141.3, 140.4, 132.8, 132.7, 130.5, 129.5, 129.0, 128.8, 128.7, 128.6, 128.5, 127.2, 114.2, 51.1, 36.4, 35.8, 24.8, 24.7. **IR** ν_{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 $[C_{26}H_{23}O_2Cl]^+$ $[M]^+$: 402.1387, found: 402.1399.

*9.5.3.7 Synthesis of **5.17g**:*

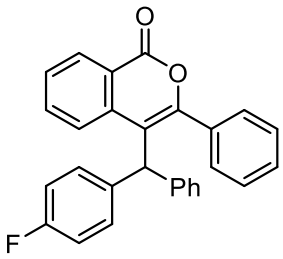


5-((4-bromophenyl)(phenyl)methyl)-3,3-dimethyl-6-phenyl-3,4-dihydro-2*H*-pyran-2-one
Chemical Formula: $C_{26}H_{23}BrO_2$
Molecular Weight: 447.37 g/mol

In accordance with General Procedure D7, **5.17g** was synthesised using **5.1g** (45 mg, 0.1 mmol) yielding a white solid after column chromatography (SiO_2, chloroform). **R_f** value: 0.44. **Yield:** 42 mg, 0.93 mmol, 93%. **Melting point:** 116–121 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, 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)Ar_2), 2.15 (s, 2H, CH_2), 1.09 (s, 3H, CH_3), 1.07 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 174.0, 148.1, 141.3, 140.9, 132.7, 131.7, 130.9, 129.5

(s), 129.1, 128.7, 128.6, 128.5, 127.2, 120.9, 114.0, 51.2, 36.4, 35.8, 24.8, 24.7. **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 $[C_{26}H_{24}O_2Br]^+$ $[M+H]^+$: 447.0960, found: 447.0964

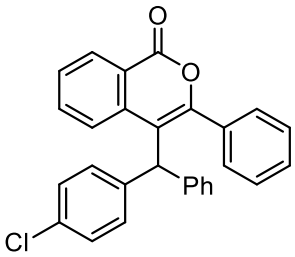
*9.5.3.8 Synthesis of **5.17h**:*



4-((4-fluorophenyl)(phenyl)methyl)-3-phenyl-1*H*-isochromen-1-one
Chemical Formula: $C_{28}H_{19}FO_2$
Molecular Weight: 406.46 g/mol

In accordance with General Procedure D7, **5.17h** was synthesised using $B(C_6F_5)_3$ (5 mg, 10 µmol, 10 mol%) and **5.3a** (41 mg, 0.1 mmol) yielding a white oil after filtration. **Yield:** 29 mg, 0.071 mmol, 71%. **^{1}H NMR** (400 MHz, $CDCl_3$, 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)Ar_2). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 162.2, 161.6 (d, $^1J_{CF}$ = 246 Hz, 1C), 154.4, 141.2, 137.2, 137.1, 137.1, 133.9, 133.3, 130.7 32 (d, $^3J_{CF}$ = 7.9 Hz, 2C), 130.1, 130.1, 129.2, 129.0, 128.8, 128.6, 127.9, 127.2, 127.0, 122.0, 115.5 (d, $^2J_{CF}$ = 21.3 Hz, 2C), 49.3. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) 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 $[C_{28}H_{19}O_2F]^+$ $[M+H]^+$: 406.1369, found: 406.1366.

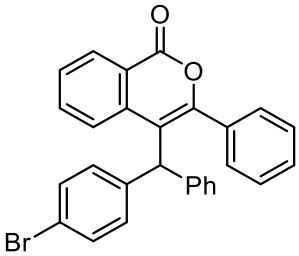
*9.5.3.9 Synthesis of **5.17i**:*



4-((4-chlorophenyl)(phenyl)methyl)-3-phenyl-1*H*-isochromen-1-one
Chemical Formula: $C_{28}H_{19}ClO_2$
Molecular Weight: 422.91 g/mol

In accordance with General Procedure D7, **5.17i** was synthesised using $B(C_6F_5)_3$ (5 mg, 10 µmol, 10 mol%) and **5.3b** (43 mg, 0.1 mmol) yielding a white oil after filtration. **Yield:** 33 mg, 0.078 mmol, 78%. **^{1}H 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)Ar_2). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 162.2., 154.5, 140.9, 139.9, 137.1, 133.9, 133.3, 132.7, 130.5, 130.1, 130.1, 129.2, 129.0, 128.8, 128.8, 128.7, 128.0, 127.1, 127.0, 122.0, 114.9, 49.4. **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.

*9.5.3.10 Synthesis of **5.17j**:*

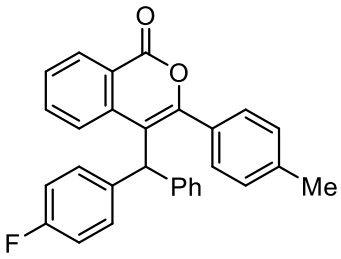


4-((4-bromophenyl)(phenyl)methyl)-3-phenyl-1*H*-isochromen-1-one
Chemical Formula: $C_{28}H_{19}BrO_2$
Molecular Weight: 467.36 g/mol

In accordance with General Procedure D7, **5.17j** was synthesised using $B(C_6F_5)_3$ (5 mg, 10 µmol, 10 mol%) and **5.3c** (47 mg, 0.1 mmol) yielding a white solid after filtration. **Yield:** 35 mg, 0.075 mmol, 75%. **Melting point:** 85–91 °C. **^{1}H 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)Ar_2). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 162.2, 154.5, 140.8, 140.4, 137.1, 133.9, 133.3, 131.7, 130.9, 130.1, 130.1, 129.2, 129.0, 128.8, 128.7, 128.0, 127.1, 127.04, 121.9, 120.8, 114.8, 49.5. **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.

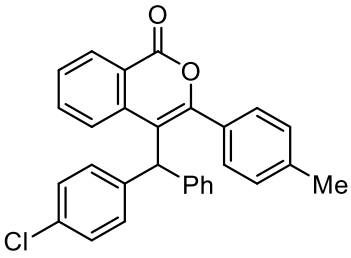
*9.5.3.11 Synthesis of **5.17k**:*



4-((4-fluorophenyl)(phenyl)methyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one
Chemical Formula: $C_{29}H_{21}FO_2$
Molecular Weight: 420.48 g/mol

In accordance with General Procedure D7, **5.17k** was synthesised using **5.3d** (42 mg, 0.1 mmol) yielding a white solid after filtration. **Yield:** 41 mg, 0.097 mmol, 97%. **Melting point:** 142–148 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 8.26–8.23 (m, 1H, Ar-H), 7.31–7.22 (m, 5H, 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)Ar_2), 2.27 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 162.4, 161.6 (d, $^1J_{CF}$ = 246 Hz), 154.6, 141.3, 140.3, 137.3, 137.2, 133.8, 130.7 (d, $^3J_{CF}$ = 7.8 Hz, 2C), 130.4, 130.0, 129.3, 129.0, 129.0, 128.7, 127.8, 127.1, 126.9, 121.9, 115.4 (d, $^2J_{CF}$ = 21.3 Hz, 2C), 114.8, 49.3, 21.5. **^{19}F NMR** (471 MHz, $CDCl_3$, 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 $[C_{29}H_{21}O_2F]^+$ $[M+H]^+$: 420.1526, found: 420.1515.

*9.5.3.12 Synthesis of **5.17l**:*

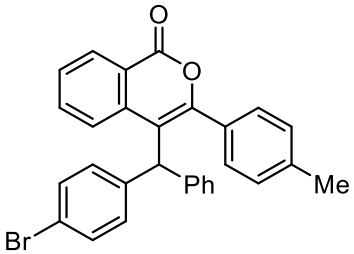


4-((4-chlorophenyl)(phenyl)methyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one
Chemical Formula: $C_{29}H_{21}ClO_2$
Molecular Weight: 436.94 g/mol

In accordance with General Procedure D7, **5.17l** was synthesised using **5.3e** (44 mg, 0.1 mmol) yielding a white solid after filtration. **Yield:** 42 mg, 0.096 mmol, 96%. **Melting**

point: 72–76 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 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, 3H, 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)Ar_2), 2.31 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 162.2, 154.6, 140.8, 140.2, 139.9, 137.1, 133.7, 132.5, 130.4, 130.3, 129.9, 129.2, 128.9, 128.9, 128.6, 128.6, 127.7, 127.0, 126.9, 121.8, 114.5, 49.3, 21.5. **IR** ν_{max} (cm^{-1}): 1730 (w), 1606 (s), 1508 (s), 1487 (m), 34 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 $[C_{29}H_{21}O_2Cl]^+$ $[M+H]^+$: 436.1230, found: 233.1227.

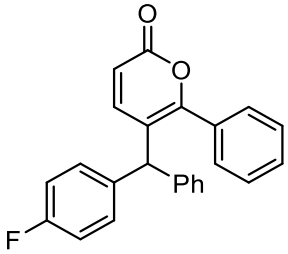
*9.5.3.13 Synthesis of **5.17m**:*



4-((4-bromophenyl)(phenyl)methyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one
Chemical Formula: $C_{29}H_{21}BrO_2$
Molecular Weight: 481.39 g/mol

In accordance with General Procedure D7, **5.17m** was synthesised using **5.3f** (48 mg, 0.1 mmol) yielding a white solid after filtration. **Yield:** 43 mg, 0.089 mmol, 89%. **Melting point:** 56–59 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 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, 4H, Ar-H), 7.08 (d, $^3J_{HH}$ = 7.9 Hz, 4H, ArH), 6.98 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar-H), 5.72 (s, 1H, C(H)Ar_2), 2.28 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 162.3, 154.7, 140.8, 140.5, 140.3, 137.2, 133.8, 131.7, 130.9, 130.4, 130.0, 129.3, 129.0 129.0, 128.7, 127.8, 127.0, 127.0, 121.9, 120.7, 114.5, 49.5, 21.5. **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 $[C_{29}H_{21}O_2Br]^+$ $[M+H]^+$: 480.0725, found: 480.0725.

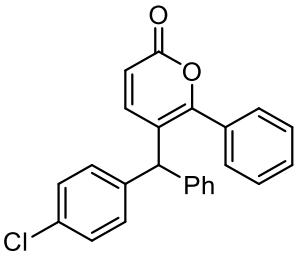
*9.5.3.14 Synthesis of **5.17n**:*



5-((4-fluorophenyl)(phenyl)methyl)-6-phenyl-2*H*-pyran-2-one
Chemical Formula: $C_{24}H_{17}FO_2$
Molecular Weight: 356.40 g/mol

In accordance with General Procedure D7, **5.17n** was synthesised using **5.2a** (36 mg, 0.1 mmol) yielding a yellow oil after filtration. **Yield:** 29 mg, 0.080 mmol, 80%. **^{1}H NMR** (500 MHz, $CDCl_3$, 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)Ar_2). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 161.8 (d, $^1J_{CF}$ = 247 Hz, 1C), 161.7, 159.3, 146.2, 142.1, 138.1 (d, $^3J_{CF}$ = 3.3 Hz, 2C), 132.0, 130.6, 130.6, 130.5, 129.1, 129.0, 128.8, 128.7, 127.4, 117.4, 115.85 (d, $^2J_{CF}$ = 21.4 Hz, 2C), 114.98, 49.21. **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) 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 $[C_{24}H_{17}O_2F]^+$ $[M+H]^+$: 356.1213, found: 356.1209.

*9.5.3.15 Synthesis of **5.17o**:*

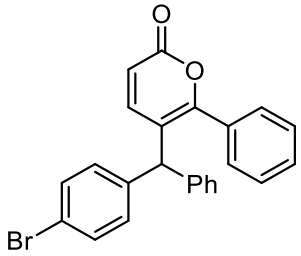


5-((4-chlorophenyl)(phenyl)methyl)-6-phenyl-2*H*-pyran-2-one
Chemical Formula: $C_{24}H_{17}ClO_2$
Molecular Weight: 372.85 g/mol

In accordance with General Procedure D7, **5.17o** was synthesised using **5.2b** (38 mg, 0.1 mmol) yielding a yellow solid after filtration and removal of solvent. **Yield:** 29 mg, 0.078 mmol, 78%. **Melting point:** 45 °C. **^{1}H 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)Ar_2). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 161.6,

159.5, 146.1, 35 141.8, 140.9, 133.2, 132.1, 131.9, 130.6, 130.4, 129.1, 129.1, 129.0, 128.8, 128.7, 117.1, 115.0, 49.4. **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.

*9.5.3.16 Synthesis of **5.17p**:*



5-((4-bromophenyl)(phenyl)methyl)-6-phenyl-2*H*-pyran-2-one
Chemical Formula: $C_{24}H_{17}BrO_2$
Molecular Weight: 417.30 g/mol

In accordance with General Procedure D7, **5.17p** was synthesised using **5.2c** (42 mg, 0.1 mmol) and yielding a yellow oil after filtration. **Yield:** 30 mg, 0.072 mmol, 72%. **^{1}H 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)Ar_2). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 160.5, 158.3, 144.9, 140.6, 140.3, 130.9, 129.6, 129.4 (s), 128.0, 127.8, 127.6, 127.6, 126.3, 126.1, 120.1, 115.9, 113.9, 48.3. **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.

9.5.4 Crystallographic data for **5.16a** and **5.4c**

Compound	**5.16a**	**5.4c**
Empirical Formula	$C_{34}H_{12}BCl_2F_{15}O_2$	$C_{44}H_{23}BClF_{15}O_2$
Space Group	P-1	P 2_1/n
a/Å	10.8906(6)	16.4273(3)
b/Å	11.6131(10)	12.13337(18)
c/Å	12.4826(7)	21.5533(3)
α/°	90.902(6)	90
β/°	95.194(5)	103.2592(15)
Y/°	98. 525(6)	90
Volume/Å^3	1554.20(19)	4181.44(11)

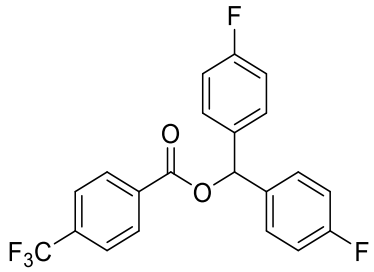
Z	2	4
T/K	150	100
D_c/g·cm^{-3}	1.750	1.426
R (reflections)	0.0413	0.0144
wR2 (reflections)	0.1214	0.1026

9.6 FLP mediated Heck-type reaction

9.6.1 General procedure E1 to synthesise ester **6.1**

Acyl chloride and alcohol were dissolved in pyridine at 0 °C. The mixture was allowed to stir at room temperature overnight. The reaction was quenched with water and extracted with ethyl acetate (3 x 25 ml). The combined organic fractions were washed with saturated NaCl solution (1 x 50 ml) and dried over $MgSO_4$. All volatiles were removed *in vacuo* and the residue was purified *via* column chromatography.

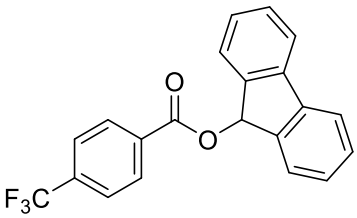
*9.6.1.1 Synthesis of **6.1a**:*



bis(4-fluorophenyl)methyl 4-(trifluoromethyl)benzoate
Chemical Formula: $C_{21}H_{13}F_5O_2$
Molecular Weight: 392.33 g/mol

In accordance to General Procedure E1, 1,4-(trifluoromethyl)benzoyl chloride (3.90 ml, 26.25 mmol, 1.16 equiv), bis(4-fluorophenyl)methanol (5.00 g, 5.01 mmol, 1.00 equiv) and pyridine (18 ml). All volatiles were removed *in vacuo* and the residue was purified *via* column chromatography as a colourless oil (SiO_2, hexane/EtOAc 20:1). $\mathbf{R_f}$ value: 0.54). **Yield:** 7.25 g, 19.37 mmol, 85%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.25 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar-H), 7.74 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.46 – 7.36 (m, 4H, Ar-H), 7.13 (s, 1H), 7.11 – 7.05 (m, 4H, Ar-H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 164.4, 162.7 (d, $^1J_{CF}$ = 247.5 Hz), 135.6 (d, $^5J_{CF}$ = 3.2 Hz), 134.9 (q, $^2J_{CF}$ = 32.7 Hz), 133.3 – 133.2 (m), 130.3, 129.1 (d, $^4J_{CF}$ = 8.3 Hz), 125.7 (q, $^3J_{CF}$ = 3.7 Hz), 123.7 (q, $^1J_{CF}$ = 272.8 Hz), 115.8 (d, $^3J_{CF}$ = 21.7 Hz), 76.9. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -63.12 (s, 3F), -113.38 (s, 2F). **IR** (ATR) ν_{max} (cm^{-1}): 2980, 2970, 1724, 1605, 1508, 1412, 1323, 1261, 1227, 1157, 1128, 1094, 1065, 1017, 966, 860, 829, 758, 772, 762, 702, 565, 540, 500, 482, 419. **HRMS** (EI+) m/z calculated for $C_{21}H_{13}O_2F_5$: 392.0836, found: 392.0828.

*9.6.1.2 Synthesis of **6.1b**:*

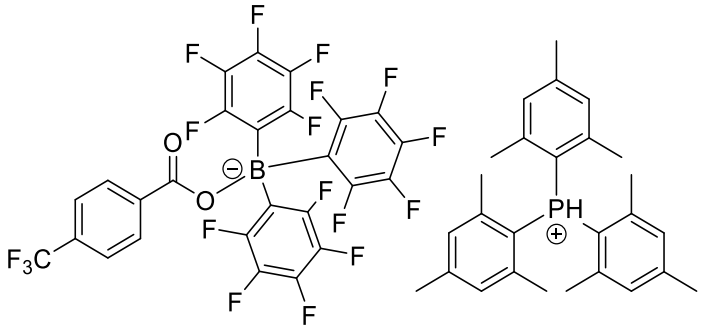


9*H*-fluoren-9-yl 4-(trifluoromethyl)benzoate
Chemical Formula: $C_{21}H_{13}F_3O_2$
Molecular Weight: 354.33 g/mol

In accordance to General Procedure E1, 1,4-(trifluoromethyl)benzoyl chloride (0.5 ml, 4.00 mmol, 1.00 equiv), bis(4-fluorophenyl)methanol (5.00 g, 5.01 mmol, 0.88 equiv) and pyridine (3 ml). All volatiles were removed *in vacuo* and the residue was purified *via* column chromatography as a white solid (SiO_2, Chloroform). **R_f** value: 0.75. **Yield:** 0.865 g, 2.44 mmol, 61% (white solid) **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.24 – 8.18 (m, 2H), 7.71 (dd, $^{3,3}J_{HH}$ = 8.6, 8.0 Hz, 4H), 7.62 (dd, $^{3,4}J_{HH}$ = 7.5, 1.0 Hz, 2H), 7.50 – 7.42 (m, 2H), 7.32 (td, $^{3,4}J_{HH}$ = 7.5, 1.1 Hz, 2H), 7.05 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -63.11 (s). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 166.3, 141.9, 141.3, 134.8 (q, $^2J_{CF}$ = 32.7 Hz), 133.3, 130.5, 129.9, 128.1, 126.2, 125.6 (q, $^3J_{CF}$ = 3.7 Hz), 123.7 (q, $^1J_{CF}$ = 272.8 Hz), 120.3, 76.3. **IR** ν_{max} (cm^{-1}): 420, 493, 586, 621, 653, 700, 727, 738, 759, 773, 860, 916, 933, 954, 1014, 1064, 1097, 1116, 1168, 1257, 1313, 1409, 1454, 1720. **HRMS** (ESI) m/z calculated for $C_{21}H_{13}F_3O_2$ $[M+H]^+$: 354.0868, found: 354.0875.

9.6.2 Synthesis of phosphonium compounds

*9.6.2.1 Synthesis of **6.2a***

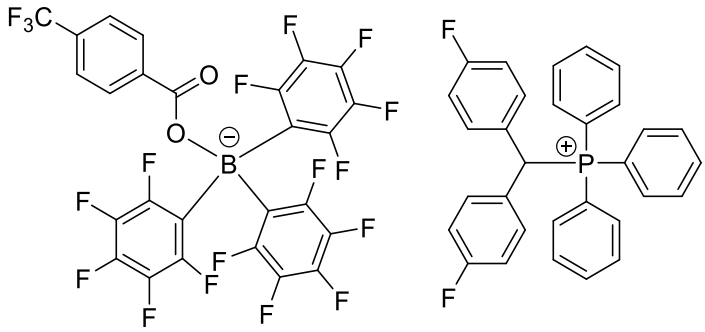


trimesitylphosphonium tris(perfluorophenyl)((4-(trifluoromethyl)benzoyl)oxy)borate
Chemical Formula: $C_{53}H_{38}BF_{18}O_2P$
Molecular Weight: 1090.64 g/mol

Tris(pentafluorophenyl)borane (205 mg, 0.40 mmol, 1 equiv) and trimesitylphosphine (155 mg, 0.40 mmol, 1 equiv) were mixed in $CHCl_3$ (1 ml) to form a bright pink solution. This was then added to a solution of ester **6.1a** (157 mg, 0.40 mmol, 1 equiv) in $CHCl_3$ (1 ml) which gave an intense and deep violet colour. The reaction vessel was sealed and

heated for 4 h at 61 °C which resulted in a gradual change of colour to dark brown initially and ultimately to an amber colour. Recrystallisation was achieved by slow evaporation of the solvent and washing the residue with pentane. Removing the solvent *in vacuo* gave the title compound as a white crystalline solid. Yield: 288 mg, 0.26 mmol, 66%. **Melting Point:** 198 °C. **^{1}H NMR** (500 MHz, CD_3CN, 298 K) δ/ppm: 8.46 (d, $^{1}J_{PH}$ = 492.1 Hz, 1H), 8.12 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H), 7.72 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H), 7.29 – 7.04 (m, 6H), 2.36 (s, 9H), 2.33-1.96 (m, 18H.) **^{13}C NMR** (126 MHz, CD_3CN, 298 K) (partial, without $B(C_6F_5)_3$ signals) δ/ppm: 167.0, 147.7 (d, $^{4}J_{CF}$ = 2.9 Hz), 139.4, 133.2 (q, $^{2}J_{CF}$ = 32.1 Hz), 131.3, 129.9, 129.2, 126.1 (q, $^{3}J_{CF}$ = 3.9 Hz), 125.3 (q, $^{1}J_{CF}$ = 271.6 Hz), 112.8 (d, $^{2}J_{CF}$ = 82.8 Hz), 22.4, 21.6, 21.4 (d, $^{5}J_{CF}$ = 1.2 Hz). **^{19}F NMR** (471 MHz, CD_3CN, 298 K) δ/ppm: -63.32, -135.50 (d, $^{3}J_{FF}$ = 21.4 Hz), -163.00 (t, $^{3}J_{FF}$ = 19.6 Hz), -167.95 (t, $^{3}J_{FF}$ = 17.9 Hz). **^{11}B NMR** (160 MHz, CD_3CN, 298 K) δ/ppm: -4.53 (s). **^{31}P NMR** (202 MHz, CD_3CN, 298 K) δ/ppm: -27.47 (d, $^{1}J_{PH}$ = 492.2 Hz). **IR** (ATR) ν_{max} (cm^{-1}): 1672, 1512, 1464, 1449, 1317, 1306, 1279, 1136, 1084, 1069, 978, 914, 785, 652, 428. **HRMS** (ES^{+}) *m/z* calculated for $[C_{27}H_{34}P]^{+}$: 389.2398, found: 389.2400. **HRMS** (ES^{-}) *m/z* calculated for $[C_{26}H_4O_2F_{18}B]^{-}$: 701.0017, found: 701.0020.

*9.6.2.2 Synthesis of **6.3c***

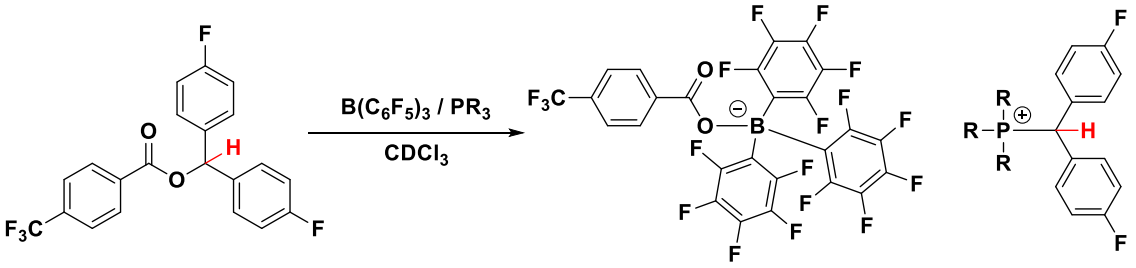


(bis(4-fluorophenyl)methyl)triphenylphosphonium tris(perfluorophenyl)((4-(trifluoromethyl)benzoyl)oxy)borate
Chemical Formula: $C_{57}H_{28}BF_{20}O_2P$
Molecular Weight: 1166.60 g/mol

Bis(4-fluorophenyl)methyl 4-(trifluoromethyl)benzoate (39.2 mg, 0.1 mmol, 1 equiv) and tris(pentafluorophenyl)borane (51 mg, 0.1 mmol, 1 equiv) where mixed in in $CDCl_3$ (0.3 ml). To the resulting red solution triphenylphosphine (26.2 mg, 0.1 mmol, 1 equiv) in $CDCl_3$ (0.3 ml) was added. The resulting mixture was heated to 80 °C in an oil bath for 8 h to give a clear light-yellow solution. *In situ* ^{1}H NMR indicates >95% conversion based on the ester starting material. Removing the solvent quantitatively yields a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.11 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H), 7.83 – 7.77 (m, 3H), 7.61 – 7.55 (m, 6H), 7.50 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H), 7.31 (ddd, $^{3,3,4}J_{HH}$ = 12.2, 8.4, 1.1 Hz, 6H), 7.02 – 6.95 (m, 8H), 5.88 (d, $^{2}J_{PH}$ = 17.2 Hz, 1H). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: -4.23 (s). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) (partial, without $B(C_6F_5)_3$

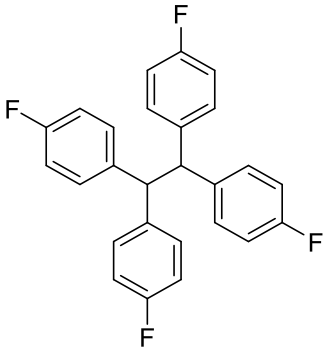
signals) δ/ppm: 167.2, 164.5 (d, $^{4}J_{CF}$ = 2.7 Hz), 162.0 (d, $^{4}J_{CF}$ = 2.7 Hz), 138.5, 136.0 (d, $^{4}J_{CF}$ = 3.0 Hz), 134.5 (d, $^{3}J_{CF}$ = 9.1 Hz), 132.7 (q, $^{2}J_{CF}$ = 32.0 Hz), 130.7 (d, $^{3}J_{CF}$ = 12.3 Hz), 130.1, 127.5 (t, $^{4}J_{CF}$ = 3.7 Hz), 124.9 (q, $^{3}J_{CF}$ = 3.7 Hz), 122.9, 117.0 (d, $^{2}J_{CF}$ = 82.6 Hz), 117.0 (dd, $^{2,4}J_{CF}$ = 21.9, 1.4 Hz), 49.0 (d, $^{1}J_{PH}$ = 44.8 Hz). **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -62.74 (s, 3F), -109.59 (d, $^{6}J_{PF}$ = 4.0 Hz, 2F), -134.35 (d, $^{3}J_{FF}$ = 21.3 Hz, 6F), -161.96 (t, $^{3}J_{FF}$ = 20.6 Hz, 3F), -166.18 (t, $^{3}J_{FF}$ = 19.3 Hz, 6F). **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -62.74 (s), -109.59 (d, $^{3}J_{HF}$ = 4.0 Hz), -134.35 (d, $^{3}J_{FF}$ = 21.3 Hz), -161.96 (t, $^{3}J_{FF}$ = 20.6 Hz), -166.18 (t, $^{3}J_{FF}$ = 19.3 Hz). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 298 K) δ/ppm: 21.69 (t, $^{6}J_{PF}$ = 4.5 Hz).

9.6.3 Reaction of other homoleptic phosphines PR_3



R	H in ^{1}H NMR δ [ppm]	$^{2}J_{PH}$ [Hz]
Ph	5.88	17.20
o-tol	6.10	16.85
m-F-Ph	5.93	17.21
Cy	4.90	16.55
p-MeO-Ph	5.48	17.26
Bn	4.91	16.48

9.6.4 Synthesis of homo-coupled product **6.2b**



1,1,2,2-tetrakis(4-fluorophenyl)ethane
Chemical Formula: $C_{26}H_{18}F_4$
Molecular Weight: 406.42 g/mol

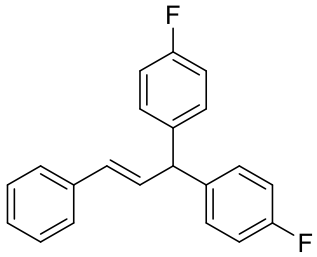
Trismesitylphosphine (0.333 mmol, 130 mg, 1 equiv) and tris(pentafluorophenyl)borane (0.333 mmol, 171 mg, 1 equiv) were dissolved in chloroform (1.0 ml) and ester **1a** (0.333

mmol, 131 mg, 1 equiv) dissolved in chloroform (0.7 ml) was added. The deep purple solution was heated in a sealed vial in an oil bath at 61 °C for 3h. All volatiles were removed *in vacuo* and the residue was purified *via* column chromatography (SiO_2, hexane/EtOAc 20:1) to isolate compound **6.2b** as a white solid. $\mathbf{R_f}$ value: 0.16. **Yield:** 0.024 g, 0.059 mmol, 35%. Spectroscopic analyses agree with literature established values.[160] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 7.09 – 7.00 (m, 8H, Ar-H), 6.88 – 6.77 (m, 8H, Ar-H), 4.63 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 161.3 (d, $^1J_{CF}$ = 245.2 Hz), 138.7 (d, $^4J_{CF}$ = 3.3 Hz), 129.9 (d, $^3J_{CF}$ = 7.9 Hz), 115.4 (d, $^2J_{CF}$ = 21.3 Hz), 55.3. **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: -116.48 (tt, $^3J_{HF}$ = 8.6, $^4J_{HF}$ = 5.3 Hz, 4F). **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$, 296 K) δ/ppm: -116.48 (s, 4F). **HRMS** (TOF MS E-) calculated for [M-HCl] [$C_{26}H_{19}F_4Cl$]: 441.1033, found: 441.1024.

9.6.5 General procedure E2 to synthesise heterocoupled-coupled products **6.4**

Trismesitylphosphine (0.2 mmol, 78 mg, 1 equiv) and tris(pentafluorophenyl)borane (0.2 mmol, 102 mg, 1 equiv) were dissolved in THF (0.5 ml) and alkene (5 equiv) was added. To this faint pink solution, a solution of ester **1** (1 equiv) in THF (0.5 ml) was added. The solution was heated to 66 °C in an oil bath in a sealed NMR-tube. All volatiles were removed *in vacuo* and the residue was purified *via* column chromatography.

*9.6.5.1 Synthesis of **6.4a***

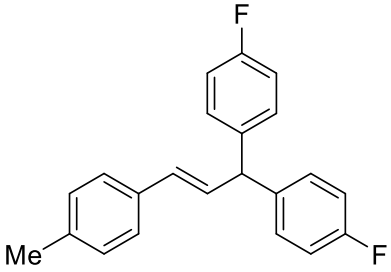


(*E*)-4,4'-(3-phenylprop-2-ene-1,1-diyl)bis(fluorobenzene)
Chemical Formula: $C_{21}H_{16}F_2$
Molecular Weight: 306.36 g/mol

In accordance to General Procedure E2, styrene (104 mg, 1.00 mmol, 5 equiv), ester **6.1a** (79 mg, 0.2 mmol, 1 equiv) were used to synthesise compound **6.4a**. The crude product was purified by column chromatography (SiO_2, hexane) to isolate compound **6.4a** as a colourless oil. $\mathbf{R_f}$ value: 0.14. **Yield:** 0.022 g, 0.072 mmol, 36%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.40 – 7.36 (m, 1H), 7.32 (dd, $^3J_{HF,HH}$ = 10.2, 4.8 Hz, 1H), 7.23 (ddd, $^{3,4}J_{HH,HF}$ = 6.2, 3.8, 1.3 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.05 – 6.98 (m, 2H), 6.60 (dd, $^{3,3}J_{HH}$ = 15.8, 7.4 Hz, 1H), 6.31 (d, $^3J_{HH}$ = 15.9 Hz, 1H), 4.87 (d, $^3J_{HH}$ = 7.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 161.7 (d, $^1J_{CF}$ = 245.1 Hz), 139.1 (d, $^4J_{CF}$ = 3.1 Hz), 137.1, 132.2, 131.9, 130.2 (d, $^3J_{CF}$ = 7.9 Hz), 128.7, 127.7, 126.5, 115.5 (d, $^2J_{CF}$ = 21.2 Hz), 52.7. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -116.40 (s). **IR** ν_{max} (cm^{-1}):

487, 501, 542, 551, 588, 692, 723, 740, 767, 829, 968, 1014, 1097, 1157, 1220, 1448, 1504, 1600, 3026. **HRMS** (ASAP+) calculated for $[M]^+$ $[C_{21}H_{16}F_2]^+$: 366.1220, found: 366.1221.

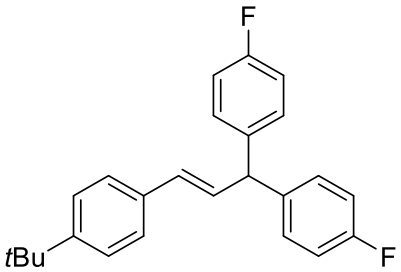
*9.6.5.2 Synthesis of **6.4c***



(*E*)-4,4'-(3-(*p*-tolyl)prop-2-ene-1,1-diyl)bis(fluorobenzene)
Chemical Formula: $C_{22}H_{18}F_2$
Molecular Weight: 320.39 g/mol

In accordance to General Procedure E2, 4-methylstyrene (118 mg, 1.00 mmol, 5 equiv), ester **6.1a** (78 mg, 0.2 mmol, 1 equiv) were used to synthesise compound **6.4c**. The crude product was purified by column chromatography (SiO_2, hexane) to isolate compound **6.4c** as a colourless oil. $\mathbf{R_f}$ value: 0.15. **Yield:** 0.016 g, 0.050 mmol, 25%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.27 (d, $^3J_{HH}$ = 7.4 Hz, 2H), 7.20 – 7.14 (m, 4H), 7.12 (d, $^3J_{HH}$ = 7.9 Hz, 2H), 7.04 – 6.97 (m, 4H), 6.54 (dd, $^{3,3}J_{HH}$ = 15.8, 7.4 Hz, 1H), 6.28 (d, $^3J_{HH}$ = 15.8 Hz, 1H), 4.85 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 161.7 (d, $^1J_{CF}$ = 245.0 Hz), 139.3 (d, $^4J_{CF}$ = 3.1 Hz), 137.5, 134.3, 131.7, 131.2, 130.2 (d, $^3J_{CF}$ = 7.9 Hz), 129.4, 126.4, 115.5 (d, $^2J_{CF}$ = 21.2 Hz), 52.7, 21.3. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -116.53 (s). **IR** ν_{max} (cm^{-1}): 408, 414, 420, 426, 441, 459, 472, 489, 501, 526, 543, 570, 767, 806, 821, 831, 970, 1014, 1037, 1074, 1095, 1157, 1220, 1504, 1600, 2922. **HRMS** (AP-) calculated for $[M-H]^-$ $[C_{22}H_{17}F_2]$: 319.1298, found: 329.1292.

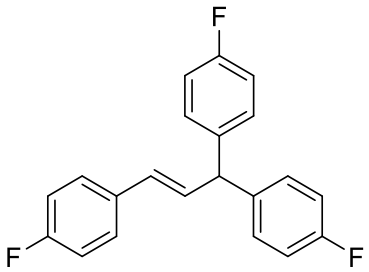
*9.6.5.3 Synthesis of **6.4d***



(*E*)-4,4'-(3-(4-(*tert*-butyl)phenyl)prop-2-ene-1,1-diyl)bis(fluorobenzene)
Chemical Formula: $C_{25}H_{24}F_2$
Molecular Weight: 362.46 g/mol

In accordance to General Procedure E2, 4-*tert*-butylstyrene (160 mg, 1.00 mmol, 5 equiv), ester **6.1a** (71 mg, 0.2 mmol, 1 equiv) were used to synthesise compound **6.4d**. The crude product was purified by column chromatography (SiO_2, hexane) to isolate compound **6.4d** as a colourless oil. $\mathbf{R_f}$ value: 0.18. **Yield:** 0.016 g, 0.044 mmol, 22%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.36 – 7.30 (m, 4H), 7.20 – 7.14 (m, 4H), 7.04 – 6.97 (m, 4H), 6.56 (dd, $^{3,3}J_{HH}$ = 15.8, 7.4 Hz, 1H), 6.29 (dd, $^{3,4}J_{HH}$ = 15.8, 1.2 Hz, 1H), 4.86 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 1.32 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 161.7 (d, $^{1}J_{CF}$ = 245.0 Hz), 150.9, 139.3 (d, $^{4}J_{CF}$ = 3.1 Hz), 134.3, 131.6, 131.5, 130.2 (d, $^{3}J_{CF}$ = 7.9 Hz), 126.2, 125.7, 115.5 (d, $^{2}J_{CF}$ = 21.2 Hz), 52.7, 34.7, 31.4. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -116.53 (s). **IR** ν_{max} (cm^{-1}): 536, 569, 775, 829, 970, 1014, 1097, 1157, 1222, 1363, 1504, 1600, 2958. **HRMS** (AP^-) calculated for $[M-H]^-$ $[C_{25}H_{23}F_2]^-$: 361.1768, found: 361.1765

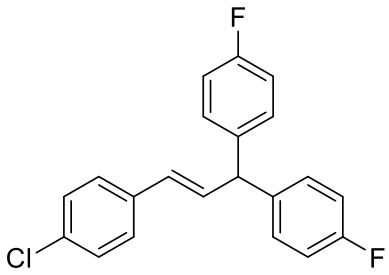
*9.6.5.4 Synthesis of **6.4e***



(*E*)-4,4',4''-(prop-2-ene-1,1,3-triyl)tris(fluorobenzene)
Chemical Formula: $C_{21}H_{15}F_3$
Molecular Weight: 324.35 g/mol

In accordance to General Procedure E2, 4-fluorostyrene (122 mg, 1.00 mmol, 5 equiv), ester **6.1a** (78 mg, 0.2 mmol, 1 equiv) were used to synthesise compound **6.4e**. The crude product was purified by column chromatography (SiO_2, hexane) to isolate compound **6.4e** as a colourless oil. $\mathbf{R_f}$ Value: 0.33. **Yield:** 0.024 g, 0.074 mmol, 37%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.50 – 7.42 (m, 2H), 7.34 – 7.25 (m, 4H), 7.18 – 7.08 (m, 6H), 6.64 (dd, $^{3,3}J_{HH}$ = 15.8, 7.3 Hz, 1H), 6.39 (d, $^{3}J_{HH}$ = 16.4 Hz, 1H), 4.98 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 162.4 (d, $^{1}J_{CF}$ = 246.8 Hz), 161.8 (d, $^{1}J_{CF}$ = 245.3 Hz), 139.0 (d, $^{4}J_{CF}$ = 3.2 Hz), 133.2 (d, $^{4}J_{CF}$ = 3.3 Hz), 132.0, 132.0, 130.1 (d, $^{3}J_{CF}$ = 7.9 Hz), 128.0 (d, $^{3}J_{CF}$ = 8.0 Hz), 115.6 (d, $^{2}J_{CF}$ = 21.6 Hz), 115.5 (d, $^{2}J_{CF}$ = 21.3 Hz), 52.7. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -114.39 (s, 1F), -116.18 (s, 2F). **IR** ν_{max} (cm^{-1}): 433, 459, 507, 524, 543, 570, 771, 798, 819, 846, 968, 1014, 1095, 1155, 1219, 1504, 1600, 3039 **HRMS** (AP-) calculated for $[M-H]^-$ $[C_{21}H_{14}F_3]^-$: 323.1048, found: 323.1048.

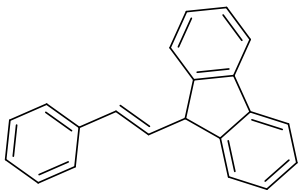
*9.6.5.5 Synthesis of **6.4f***



(*E*)-4,4'-(3-(4-chlorophenyl)prop-2-ene-1,1-diyl)bis(fluorobenzene)
Chemical Formula: $C_{21}H_{15}ClF_2$
Molecular Weight: 340.80 g/mol

In accordance to General Procedure E2, 4-chlorostyrene (139 mg, 1.00 mmol, 5 equiv), ester **6.1a** (78 mg, 0.2 mmol, 1 equiv) were used to synthesise the compound **6.4f**. The crude product was purified by column chromatography (SiO_2, hexane) to isolate compound **6.4f** as a colourless oil. $\mathbf{R_f}$ Value: 0.18. **Yield:** 0.022 g, 0.065 mmol, 32%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.31 – 7.26 (m, 1H), 7.20 – 7.14 (m, 1H), 7.05 – 6.99 (m, 1H), 6.58 (dd, $^3J_{HH}$ = 15.8, 7.3 Hz, 1H), 6.26 (dd, $^{3,4}J_{HH}$ = 15.8, 1.3 Hz, 1H), 4.86 (d, $^3J_{HH}$ = 7.3 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -116.19 (s). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 161.8 (d, $^1J_{CF}$ = 245.3 Hz), 138.9 (d, $^4J_{CF}$ = 3.2 Hz), 135.6, 133.3, 133.0, 130.7, 130.1 (d, $^3J_{CF}$ = 7.9 Hz), 128.9, 127.7, 115.6 (d, $^2J_{CF}$ = 21.3 Hz), 52.7. **IR** ν_{max} (cm^{-1}): 487, 501, 543, 561, 731, 769, 783, 829, 970, 1012, 1091, 1157, 1220, 1404, 1458, 1465, 1490, 1504, 1600, 3032 **HRMS** (EI^+) calculated for [M^+] $[C_{21}H_{15}F_2Cl]^+$: 340.0830, found: 340.0834.

*9.6.5.6 Synthesis of **6.4g***

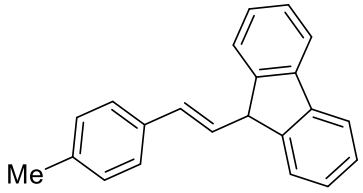


(*E*)-9-styryl-9*H*-fluorene
Chemical Formula: $C_{21}H_{16}$
Molecular Weight: 268.36 g/mol

In accordance to General Procedure E2, styrene (104 mg, 1.00 mmol, 5 equiv), ester **6.1b** (71 mg, 0.2 mmol, 1 equiv) were used to synthesise compound **6.4g**. The crude product was purified by column chromatography (SiO_2, hexane) to isolate compound **6.4g** as a white solid. $\mathbf{R_f}$ value: 0.15. **Yield:** 0.021 g, 0.078 mmol, 39%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.80 (d, $^3J_{HH}$ = 7.6 Hz, 2H), 7.52 (d, $^3J_{HH}$ = 7.4 Hz, 2H), 7.44 – 7.38 (m, 4H), 7.36 – 7.29 (m, 4H), 7.26 – 7.21 (m, 1H), 6.89 (d, $^3J_{HH}$ = 15.6 Hz, 1H), 6.05 (dd, $^3J_{HH}$ = 15.6, 9.1 Hz, 1H), 4.65 (d, $^3J_{HH}$ = 9.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$,

298 K) δ/ppm: 146.2, 141.1, 137.3, 132.7, 129.1, 128.7, 127.7, 127.5, 127.3, 126.4, 125.6, 120.1, 52.5. **IR** ν_{max} (cm^{-1}): 410, 416, 441, 491, 542, 609, 621, 655, 690, 729, 738, 761, 806, 941, 958, 1029, 1101, 1296, 1444, 3016. **HRMS** (ES^-) calculated for $[M-H]^-$ $[C_{21}H_{15}]$: 267.1774, found: 267.1774.

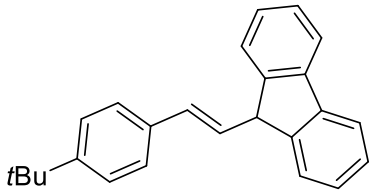
*9.6.5.7 Synthesis of **6.4h***



(*E*)-9-(4-methylstyryl)-9*H*-fluorene
Chemical Formula: $C_{22}H_{18}$
Molecular Weight: 282.39 g/mol

In accordance to General Procedure E2, 4-methylstyrene (118 mg, 1.00 mmol, 5 equiv), ester **6.1b** (71 mg, 0.2 mmol, 1 equiv) were used to synthesise compound **6.4h**. The crude product was purified by column chromatography (SiO_2, hexane) to isolate compound **6.4h** as a white solid. $\mathbf{R_f}$ value: 0.26. **Yield:** 0.016 g, 0.057 mmol, 28%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.79 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 7.55 – 7.49 (m, 2H), 7.43 – 7.38 (m, 2H), 7.33 (dd, $^{3,4}J_{HH}$ = 7.4, 1.2 Hz, 2H), 7.31 – 7.28 (m, 2H), 7.12 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 6.86 (d, $^3J_{HH}$ = 15.6 Hz, 1H), 5.99 (dd, $^{3,3}J_{HH}$ = 15.6, 9.1 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 146.4, 141.1, 137.3, 134.5, 132.5, 129.4, 128.1, 127.6, 127.3, 126.3, 125.6, 120.0, 52.5, 21.3. **IR** ν_{max} (cm^{-1}): 418, 499, 588, 621, 725, 738, 758, 788, 827, 941, 966, 1292, 1298, 1444, 1473, 1510, 2918, 1296. **HRMS** (AP^-) calculated for $[M-H]^-$ $[C_{22}H_{17}]^-$: 281.1330, found: 281.1330.

*9.6.5.8 Synthesis of **6.4i***

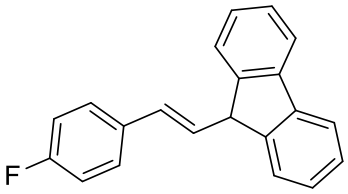


(*E*)-9-(4-(*tert*-butyl)styryl)-9*H*-fluorene
Chemical Formula: $C_{25}H_{24}$
Molecular Weight: 324.47 g/mol

In accordance to General Procedure E2, 4-*tert*-butylstyrene (160 mg, 1.00 mmol, 5 equiv), ester **6.1b** (71 mg, 0.2 mmol, 1 equiv) were used to synthesise compound **6.4i**. The crude product was purified by column chromatography (SiO_2, hexane) to isolate compound **6.4i** as a white solid. $\mathbf{R_f}$ value: 0.21. **Yield:** 0.016 g, 0.049 mmol, 25%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.80 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 7.52 – 7.48 (m, 2H),

7.43 – 7.39 (m, 2H), 7.35 (s, 4H), 7.32 (td, $^{3,4}J_{HH}$ = 7.4, 1.2 Hz, 2H), 6.88 (dd, $^{3,4}J_{HH}$ = 15.6, 0.8 Hz, 1H), 6.01 (dd, $^{3,3}J_{HH}$ = 15.6, 9.2 Hz, 1H), 4.64 (d, $^{3}J_{HH}$ = 9.1 Hz, 1H), 1.32 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 150.7, 146.4, 141.1, 134.5, 132.5, 128.3, 127.6, 127.3, 126.2, 125.7, 125.6, 120.0, 52.6, 34.7, 31.4. **IR** ν_{max} (cm^{-1}): 420, 516, 547, 584, 597, 621, 644, 727, 740, 761, 794, 831, 837, 893, 960, 968, 1018, 1112, 1265, 1361, 1411, 1444, 1473, 1512, 2962. **HRMS** (AP^-) calculated for $[M-H]^-$ $[C_{25}H_{23}]^-$: 323.1800, found: 323.1804.

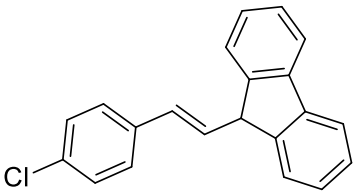
*9.6.5.9 Synthesis of **6.4b***



(*E*)-9-(4-fluorostyryl)-9*H*-fluorene
Chemical Formula: $C_{21}H_{15}F$
Molecular Weight: 286.35 g/mol

In accordance to General Procedure E2, 4-fluorostyrene (122 mg, 1.00 mmol, 5 equiv), ester **6.1b** (71 mg, 0.2 mmol, 1 equiv) were used to synthesise compound **6.4b**. The crude product was purified by column chromatography (SiO_2, hexane) to isolate compound **6.4b** as a white solid. **R_f** Value: 0.15. **Yield:** 0.037 g, 0.073 mmol, 37%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.80 (d, $^{3}J_{HH}$ = 7.5 Hz, 2H), 7.51 (d, $^{3}J_{HH}$ = 7.4 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.37 – 7.30 (m, 4H), 7.03 – 6.96 (m, 2H), 6.84 (d, $^{3}J_{HH}$ = 15.6 Hz, 1H), 5.97 (dd, $^{3,3}J_{HH}$ = 15.6, 9.1 Hz, 1H), 4.63 (d, $^{3}J_{HH}$ = 9.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 162.2 (d, $^{1}J_{CF}$ = 246.5 Hz), 146.0, 141.0, 133.3, 131.3, 128.8 (d, $^{4}J_{CF}$ = 2.3 Hz), 127.8 (d, $^{3}J_{CF}$ = 7.9 Hz), 127.6, 127.2, 125.4, 120.0, 115.5 (d, $^{2}J_{CF}$ = 21.6 Hz), 52.3. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -114.77. **IR** ν_{max} (cm^{-1}): 417, 418, 446, 503, 552, 594, 624, 664, 695, 731, 744, 765, 913, 955, 965, 1037, 1104, 1297, 1449, 3023. **HRMS** (EI^+) calculated for $[M]^+$ $[C_{21}H_{15}F]^+$: calculated 286.1158, found: 286.1158.

*9.6.5.10 Synthesis of **6.4j***



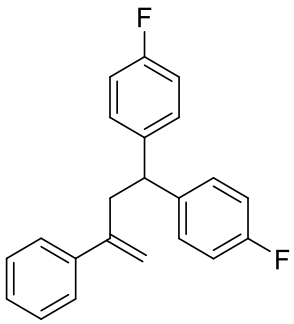
(*E*)-9-(4-chlorostyryl)-9*H*-fluorene
Chemical Formula: $C_{21}H_{15}Cl$
Molecular Weight: 302.80 g/mol

In accordance to General Procedure E2, 4-chlorostyrene (139 mg, 1.00 mmol, 5 equiv), ester **6.1b** (71 mg, 0.2 mmol, 1 equiv) were used to synthesise compound **6.4j**. The crude product was purified by column chromatography (SiO_2, hexane) as a white solid **R_f** value: 0.18. **Yield:** 0.024 g, 0.079 mmol, 40%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.75 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 7.45 (ddd, $^{3,4,4}J_{HH}$ = 7.3, 1.8, 0.9 Hz, 2H), 7.39 – 7.34 (m, 2H), 7.30 – 7.26 (m, 2H), 7.26 – 7.20 (m, 4H), 6.77 (d, $^3J_{HH}$ = 15.6 Hz, 1H), 5.98 (dd, $^{3,3}J_{HH}$ = 15.6, 9.1 Hz, 1H), 4.59 (d, $^3J_{HH}$ = 9.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 146.0, 141.1, 135.8, 133.1, 131.3, 129.9, 128.8, 127.8, 127.6, 127.4, 125.5, 120.1, 52.4. **IR** ν_{max} (cm^{-1}): 401, 408, 414, 422, 459, 497, 514, 576, 621, 642, 682, 727, 740, 756, 792, 821, 833, 889, 937, 943, 958, 1012, 1080, 1093, 1292, 1404, 1444, 1473, 1489, 3018. **HRMS** (AP^-) calculated for $[M-H]^-$ $[C_{21}H_{14}Cl]^-$: 301.0790, found: 301.0788.

9.6.6 Reaction of **6.1a** with α-methylstyrene

In accordance to General Procedure E2, alpha-methylstyrene (118 mg, 1.00 mmol, 5 equiv), ester **6.1a** (79 mg, 0.2 mmol, 1 equiv) were used to synthesise the structural isomers **6.5a** and **6.5b**. The crude product was purified by column chomatography (SiO_2, hexane). **R_f** value: 0.11. **Yield:** 0.057 g, 0.178 mmol, 89%.

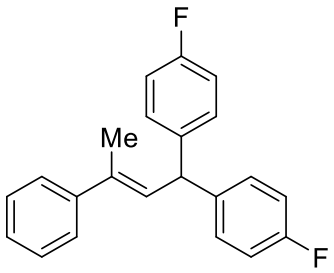
*9.6.6.1 Major product **5a***



4,4'-(3-phenylbut-3-ene-1,1-diyl)bis(fluorobenzene)
Chemical Formula: $C_{22}H_{18}F_2$
Molecular Weight: 320.38 g/mol

Yield (calculated by ^{19}F NMR): 0.118 mmol, 0.038 g, 59% **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.49 – 7.28 (m, 5H), 7.16 – 7.09 (m, 4H), 7.00 – 6.95 (m, 4H), 5.18 (d, $^4J_{HH}$ = 1.0 Hz, 1H), 4.89 – 4.85 (m, 1H), 4.07 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 3.23 (d, $^3J_{HH}$ = 7.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 161.5 (d, $^1J_{CF}$ = 244.5 Hz), 146.1, 141.0, 140.1 (d, $^4J_{CF}$ = 3.1 Hz), 129.5 (d, $^3J_{CF}$ = 7.8 Hz), 128.6, 127.7, 126.5, 115.4, 115.3 (d, $^2J_{CF}$ = 21.3 Hz), 47.8, 42.2. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -116.85 (s). **HRMS** (EI^+) calculated for $[M^+]$ $[C_{22}H_{18}F_2]^+$: 320.1377, found: 320.1381. Retention Time (TOF MS EI^+): 25.269.

*9.6.6.2 Major product **5a***



(*E*)-4,4'-(3-phenylbut-2-ene-1,1-diyl)bis(fluorobenzene)
Chemical Formula: $C_{22}H_{18}F_2$
Molecular Weight: 320.38 g/mol

Yield (calculated by ^{19}F NMR): 0.059 mmol, 0.019 g, 30% **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.48 – 7.28 (m, 5H), 7.24 – 7.18 (m, 4H), 7.06 – 7.00 (m, 4H), 6.22 – 6.13 (m, 1H), 5.07 (d, $^{3}J_{HH}$ = 9.3 Hz, 1H), 2.16 – 2.14 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -116.68 (s). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 161.6 (d, $^{1}J_{CF}$ = 244.8 Hz), 143.4, 140.3 (d, $^{4}J_{CF}$ = 3.2 Hz), 136.2, 130.4, 129.8 (d, $^{3}J_{CF}$ = 7.9 Hz), 128.4, 127.3, 126.0, 115.5 (d, $^{2}J_{CF}$ = 19.8 Hz), 48.6, 16.4. **HRMS** (EI^+) calculated for [M^+] $[C_{22}H_{18}F_2]^+$: 320.1377, found: 320.1381. Retention Time (TOF MS EI^+): 26.103.

9.6.7 Crystallographic data for **6.2a** and **6.2b**

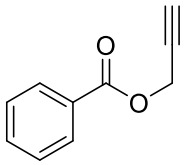
Compound	**5.16a**	**5.4c**
Empirical Formula	$C_{34}H_{12}BCl_2F_{15}O_2$	$C_{44}H_{23}BClF_{15}O_2$
Space Group	P-1	P 2_1/n
a/Å	10.8906(6)	16.4273(3)
b/Å	11.6131(10)	12.13337(18)
c/Å	12.4826(7)	21.5533(3)
α/°	90.902(6)	90
β/°	95.194(5)	103.2592(15)
Y/°	98. 525(6)	90
Volume/Å^3	1554.20(19)	4181.44(11)
Z	2	4
T/K	150	100
D_c/g·cm^{-3}	1.750	1.426
R (reflections)	0.0413	0.0144
wR2 (reflections)	0.1214	0.1026

9.7 Sterics directed halo- and Carbo-boration

9.7.1 General procedure F1 to synthesise propargyl esters **7.1**

Propargyl esters **7.1** were synthesised according to literature procedure.[30] NEt_3 (3.5 ml, 25 mmol, 2 equiv) was added to a solution of acyl chloride (15 mmol, 1.2 equiv) in CH_2Cl_2 (50 ml) and cooled to 0 °C. After adding alkynyl alcohol (1 equiv) dropwise to this solution, the reaction mixture was allowed to warm room temperature and stirred overnight. To quench the reaction water (100 ml) was added and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 50 ml) and the combined organic layers were dried with brine and layered over $MgSO_4$. After filtration all volatiles were removed under vacuum and the residue was purified *via* recrystallisation or column chromatography.

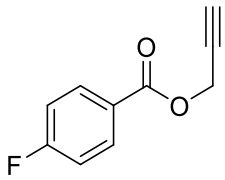
*9.7.1.1 Synthesis of **7.1a***



prop-2-yn-1-yl benzoate
Chemical Formula: $C_{10}H_8O_2$
Molecular Weight: 160.17 g/mol

According to General Procedure F1, ester **7.1a** was synthesised using propargyl alcohol (0.73 ml, 12.5 mmol, 1 equiv.) and benzoyl chloride (1.74 ml, 15 mmol, 1.2 equiv). **Yield:** 1.68 g, 10.5 mmol, 84%. Spectroscopic data agrees with literature values.[141] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.08 (ddd, $^3J_{HH}$ = 6.8, $^4J_{HH}$ = 2.8, $^4J_{HH}$ = 1.5 Hz, 2H, Ar-H), 7.61 – 7.55 (m, 1H, Ar-H), 7.49 – 7.42 (m, 2H, Ar-H), 4.93 (d, $^4J_{HH}$ = 2.5 Hz, 2H, CH_2), 2.52 (t, $^4J_{HH}$ = 2.5 Hz, 1H, ≡CH). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 165.9, 133.5, 129.9, 129.5, 128.6, 77.9, 75.1, 52.6.

*9.7.1.2 Synthesis of **7.1b***

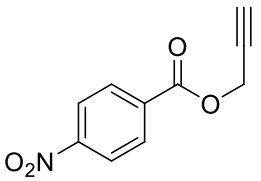


prop-2-yn-1-yl 4-fluorobenzoate
Chemical Formula: $C_{10}H_7FO_2$
Molecular Weight: 178.16 g/mol

According to General Procedure F1, ester **7.1b** was synthesised using propargyl alcohol (0.73 ml, 12.5 mmol, 1 equiv) and 4-fluorobenzoyl chloride (1.77 ml, 15 mmol, 1.2 equiv). **Yield:** 1.87 g, 10.5 mmol, 84%. Spectroscopic data agrees with literature values.[161] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.12 – 8.06 (m, 2H, Ar-H), 7.15 – 7.10 (m, 2H,

Ar-H), 4.92 (d, $^{4}J_{HH}$ = 2.5 Hz, 2H, CH2), 2.52 (t, $^{4}J_{HH}$ = 2.5 Hz, 1H, ≡CH). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 166.1 (d, $^{1}J_{CF}$ = 255.2 Hz), 165.0, 132.6 (d, $^{3}J_{CF}$ = 9.4 Hz), 125.8 (d, $^{4}J_{CF}$ = 3.0 Hz), 115.8 (d, $^{2}J_{CF}$ = 22.1 Hz), 77.7, 75.3, 52.7. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -104.9 (s).

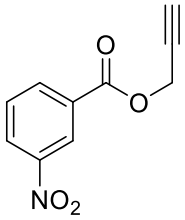
*9.7.1.3 Synthesis of **7.1c***



prop-2-yn-1-yl 4-nitrobenzoate
Chemical Formula: $C_{10}H_7NO_4$
Molecular Weight: 205.17 g/mol

According to General Procedure F1, ester **7.1c** was synthesised using propargyl alcohol (0.73 ml, 12.5 mmol, 1 equiv) and *p*-nitrobenzoylchloride (2.77 g, 15 mmol, 1.2 equiv). **7.1c** was purified via recrystallisation from a saturated of CH_2Cl_2 to give a yellow crystalline solid. **Yield:** 2.36 g, 11.5 mmol, 96%. Spectroscopic data agrees with literature values.[141] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ/ppm: 8.30 (dt, $^{3}J_{HH}$ = 9.0 Hz, $^{4}J_{HH}$ = 2.2 Hz, 2H, Ar-H), 8.23 (dt, $^{3}J_{HH}$ = 9.0 Hz, $^{4}J_{HH}$ = 2.2 Hz, 2H, Ar-H), 4.97 (d, $^{4}J_{HH}$ = 2.5 Hz, 2H, CH2), 2.56 (t, $^{4}J_{HH}$ = 2.5 Hz, 1H, ≡CH). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 164.0, 151.0, 134.9, 131.1, 123.8, 77.1, 75.8, 53.4.

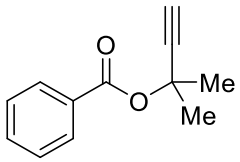
*9.7.1.4 Synthesis of **7.1d***



prop-2-yn-1-yl 3-nitrobenzoate
Chemical Formula: $C_{10}H_7NO_4$
Molecular Weight: 205.17 g/mol

According to General Procedure F1, ester **7.1d** was synthesised using propargyl alcohol (0.73 ml, 12.5 mmol, 1 equiv) *m*-nitrobenzoyl chloride (2.77 g, 15 mmol, 1.2 equiv). **Yield:** 1.67 g, 8.13 mmol, 65%. Spectroscopic analyses agree with literature values.[162] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.90 (dd, $^{4}J_{HH}$ = 2.9, $^{4}J_{HH}$ = 1.1 Hz, 1H, Ar-H), 8.45 (ddd, $^{3}J_{HH}$ = 8.2, $^{4}J_{HH}$ = 2.3, $^{4}J_{HH}$ = 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, $^{4}J_{HH}$ = 2.5 Hz, 2H, CH2), 2.57 (t, $^{4}J_{HH}$ = 2.5 Hz, 1H, ≡CH). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 163.9, 148.4, 135.6, 131.3, 129.9, 127.9, 125.0, 77.1, 75.9, 53.4.

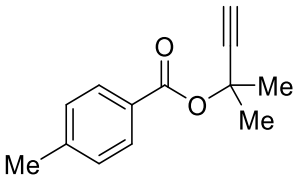
*9.7.1.5 Synthesis of **7.1e***



2-methylbut-3-yn-2-yl benzoate
Chemical Formula: $C_{12}H_{12}O_2$
Molecular Weight: 188.23 g/mol

According to General Procedure F1, ester **7.1e** was synthesised using 2-methylbut-3-yn-2-ol (1.21 ml, 12.5 mmol, 1 equiv) and 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.[163] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.05 – 8.01 (m, 2H, Ar-H), 7.57 – 7.52 (m, 1H, Ar-H), 7.46 – 7.40 (m, 2H, Ar-H), 2.59 (s, 1H, ≡CH), 1.82 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 165.0, 133.1, 130.9, 129.8, 128.4, 84.8, 72.7, 72.4, 29.2.

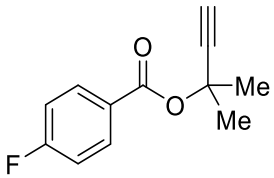
*9.7.1.6 Synthesis of **7.1f***



2-methylbut-3-yn-2-yl 4-methylbenzoate
Chemical Formula: $C_{13}H_{14}O_2$
Molecular Weight: 202.25 g/mol

According to General Procedure F1, ester **7.1f** was synthesised using 2-methylbut-3- yn-2-ol (1.21 ml, 12.5 mmol, 1 equiv) and 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.[30] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.90 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.21 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar-H), 2.57 (s, 1H, ≡CH), 2.38 (s, 3H, Ar-CH_3), 1.80 (s, 6H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 164.0, 142.6, 128.7, 128.0, 127.1, 83.9, 71.5, 71.0, 28.1, 20.7.

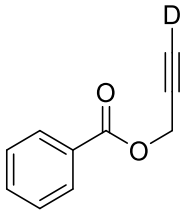
*9.7.1.7 Synthesis of **7.1g***



2-methylbut-3-yn-2-yl 4-fluorobenzoate
Chemical Formula: $C_{12}H_{11}FO_2$
Molecular Weight: 206.22 g/mol

According to General Procedure F1, ester **7.1g** was synthesised using 2-methylbut-3-yn-2-ol (1.21 ml, 12.5 mmol, 1 equiv) and 4-fluorobenzoyl chloride (1.77 ml, 15 mmol, 1.2 equiv). **Yield:** 1.78 g, 8.62 mmol, 69%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.05 – 8.01 (m, 2H, Ar-H), 7.11 – 7.06 (m, 2H, Ar-H), 2.59 (s, 1H, ≡CH), 1.81 (s, 6H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 165.8 (d, $^{1}J_{CF}$ = 253.7 Hz), 164.0, 132.3 (d, $^{3}J_{CF}$ = 9.3 Hz), 127.1 (d, $^{4}J_{CF}$ = 3.0 Hz), 115.5 (d, $^{2}J_{CF}$ = 22.0 Hz), 84.7, 72.8, 72.5, 29.1. **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) δ/ppm: -105.8 (s).

*9.7.1.8 Synthesis of **7.1h***



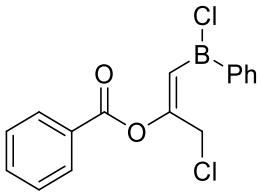
prop-2-yn-1-yl-3-*d* benzoate
Chemical Formula: $C_{10}H_7DO_2$
Molecular Weight: 161.18 g/mol

Deuterated ester **7.1h** was synthesised according to literature procedure. WA30 resin (38 mg) was added to a solution of **7.1a** (0.336 g, 2.1 mmol) in D_2O and stirred for 18 h at room temperature. The suspension was filtered and the filtrate was extracted with Et_2O (4 x 10 ml) and the combined organic layers were concentrated under vacuum to yield desired product **7.1h** as colourless oil. **Yield:** 0.267 g, 1.87 mmol, 88%. Spectroscopic data agrees with literature values.[142] **^{1}H NMR** (400 MHz, $CDCl_3$, 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, CH_2). **^{2}H NMR** (61 MHz, $CDCl_3$, 298 K) δ/ppm: 2.53 (s, ≡CD). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 165.9, 133.5, 130.0, 129.5, 128.6, 77.5, 74.9 (t, $^{1}J_{CD}$ = 39 Hz), 52.6.

9.7.2 General procedure F2 to synthesise 1,3-haloborated products **7.2**

$PhBCl_2$ (32 mg, 0.2 mmol, 26 µl, 1 equiv) was added to a solution of alkyne **7.1** (0.2 mmol, 1 equiv) in $CDCl_3$.

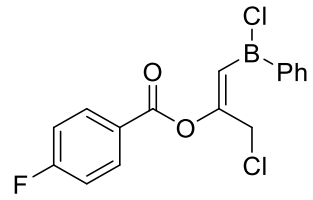
*9.7.2.1 Synthesis of **7.2a***



(*E*)-3-chloro-1-(chloro(phenyl)boraneyl)prop-1-en-2-yl benzoate
Chemical Formula: $C_{16}H_{13}BCl_2O_2$
Molecular Weight: 318.99 g/mol

According to General Procedure F2, ester **7.2a** was synthesised using **7.1a** (32 mg, 0.2 mmol). **^{1}H NMR Conversion:** >95%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.09 – 8.00 (m, 3H, Ar), 7.59 – 7.51 (m, 2H, Ar), 7.46 – 7.36 (m, 5H, Ar), 6.44 (s, 1H, =CH), 4.55 (s, 2H, CH_2). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 164.3, 160.0, 137.2, 136.6, 134.7, 134.1, 130.4, 128.8, 128.4, 128.0, 119.1 (br. s), 41.8. **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 59.5 (br. s).

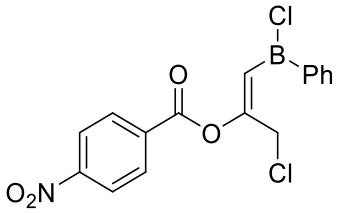
*9.7.2.2 Synthesis of **7.2c***



(*E*)-3-chloro-1-(chloro(phenyl)boraneyl)prop-1-en-2-yl 4-fluorobenzoate
Chemical Formula: $C_{16}H_{12}BCl_2FO_2$
Molecular Weight: 336.98 g/mol

According to General Procedure F2, ester **7.2c** was synthesised using **7.1b** (36 mg, 0.2 mmol). **^{1}H NMR Conversion:** >95%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.11 – 8.06 (m, 2H, Ar), 8.02 – 7.99 (m, 2H, Ar), 7.55 – 7.53 (m, 1H, Ar), 7.41 – 7.36 (m, 2H, Ar), 7.11 – 7.06 (m, 2H, Ar), 6.42 (s, 1H, =CH), 4.53 (s, 2H, CH_2). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 166.5 (d, $^{1}J_{CF}$ = 255.9 Hz, Ar), 163.3, 159.7, 136.9, 136.6, 134.7, 133.1 (d, $^{3}J_{CF}$ = 9.6 Hz, Ar), 128.4, 125.3 (d, $^{4}J_{CF}$ = 3.0 Hz, Ar), 119.1 (br. s), 116.1 (d, $^{2}J_{CF}$ = 22.1 Hz, Ar), 41.8. **^{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: 59.3 (br. s)

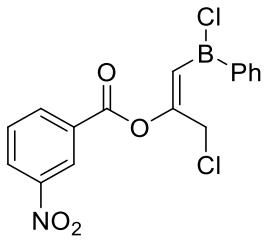
*9.7.2.3 Synthesis of **7.2d***



(*E*)-3-chloro-1-(chloro(phenyl)boraneyl)prop-1-en-2-yl 4-nitrobenzoate
Chemical Formula: $C_{16}H_{12}BCl_2NO_4$
Molecular Weight: 363.99 g/mol

According to General Procedure F2, ester **7.2d** was synthesised using **7.1c** (41 mg, 0.2 mmol). **^{1}H NMR Conversion:** >95%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.27 – 8.25 (m, 4H, Ar), 8.12 – 8.10 (m, Hz, 2H, Ar), 7.67 – 7.63 (m, 1H, Ar), 7.53 – 7.48 (m, 2H, Ar), 6.55 (s, 1H, =C), 4.63 (s, 2H, -CH_2). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 162.4, 158.7, 151.1, 136.6, 134.9, 134.4, 131.5, 128.4, 123.9, 119.6 (br. s), 41.6. **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 59.9 (br. s).

*9.7.2.4 Synthesis of **7.2e***



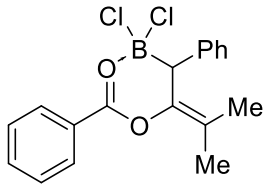
(*E*)-3-chloro-1-(chloro(phenyl)boraneyl)prop-1-en-2-yl 3-nitrobenzoate
Chemical Formula: $C_{16}H_{12}BCl_2NO_4$
Molecular Weight: 363.99 g/mol

According to General Procedure F2, ester **7.2e** was synthesised using **7.1d** (41 mg, 0.2 mmol). **^{1}H NMR Conversion:** >95%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 9.03 – 8.94 (m, 1H, Ar), 8.52 – 8.48 (m, 2H, Ar), 8.14 – 8.10 (m, 2H, Ar), 7.77 – 7.73 (m, 1H, Ar), 7.68 – 7.63 (m, 1H, Ar), 7.54 – 7.49 (m, 2H, Ar), 6.55 (s, 1H, =CH), 4.65 (s, 2H, -CH_2). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 162.2, 158.8, 148.5, 137.0, 136.7, 135.9, 134.9, 130.8, 130.2, 128.5, 128.3, 125.3, 119.7 (br. s), 41.6. **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 60.0 (br. s).

9.7.3 General Procedure F3 to synthesise 1,1-carboborated products **7.3**

$PhBCl_2$ (32 mg, 0.2 mmol, 26 µl, 1 equiv) was added to a solution of methyl substituted alkynes **7.1**. The resulting mixture was heated to 45 °C in a sealed NMR tube. After allowing the reaction mixture to cool to room temperature all volatiles have been removed and the residue was washed with hexane (3 x 1 ml) and recrystallised in a CH_2Cl_2/hexane solution at -40 °C to yield the desired carboborated product **7.3**.

*9.7.3.1 Synthesis of **7.3a***

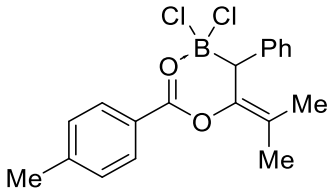


2,2-dichloro-3,6-diphenyl-4-(propan-2-ylidene)-3,4-dihydro-2*H*-1λ^3,5,2λ^4-dioxaborinine
Chemical Formula: $C_{18}H_{17}BCl_2O_2$
Molecular Weight: 347.04 g/mol

According to General Procedure F3, ester **7.3a** was synthesised using **7.1e** (37 mg, 0.2 mmol, 1 equiv). **Yield:** 57 mg, 0.16 mmol, 82%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.22 (d, $^3J_{HH}$ = 7.5 Hz. 2H, Ar), 7.78 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar), 7.55 (t, $^3J_{HH}$ = 7.9 Hz, 2H, Ar), 7.12 (t, $^3J_{HH}$ = 7.5, 2H, Ar), 7.05 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Ar), 6.97 (d, $^3J_{HH}$ = 7.4 Hz, 2H, Ar), 3.82 (s, 1H, B-CH), 1.95 (s, 3H, -CH_3), 1.77 (s, 3H, -CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 171.4, 147.8, 141.1, 138.1, 131.6, 129.8, 128.4, 127.5, 125.9, 124.7, 122.5, 39.51 (br. s,), 18.7, 17.7. **^{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).

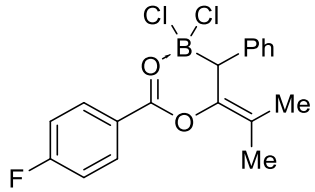
*9.7.3.2 Synthesis of **7.3b***



2,2-dichloro-3-phenyl-4-(propan-2-ylidene)-6-(*p*-tolyl)-3,4-dihydro-2*H*-1λ^3,5,2λ^4-dioxaborinine
Chemical Formula: $C_{19}H_{19}BCl_2O_2$
Molecular Weight: 361.07 g/mol

According to General Procedure F3, ester **7.3b** was synthesised using **7.1f** (40 mg, 0.2 mmol, 1 equiv). **Yield:** 67 mg, 0.17 mmol, 87%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.20 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar), 7.44 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar), 7.21 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Ar), 7.14 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Ar), 7.06 (d, $^3J_{HH}$ = 7.4 Hz, 2H, Ar), 3.90 (s, 1H, B-CH), 2.53 (s, 3H, Ph-CH_3), 2.03 (s, 3H, CH_3), 1.86 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 171.3, 150.4, 147.6, 141.2, 131.7, 130.6, 128.4, 127.5, 125.9, 122.0, 121.8, 39.6 (br. s), 22.5, 18.6 (br. s), 17.7. **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 8.6 (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).

*9.7.3.3 Synthesis of **7.3c***



2,2-dichloro-6-(4-fluorophenyl)-3-phenyl-4-(propan-2-ylidene)-3,4-dihydro-2*H*-1λ^3,5,2λ^4-dioxaborinine
Chemical Formula: $C_{18}H_{16}BCl_2FO_2$
Molecular Weight: 365.03 g/mol

According to General Procedure F3, ester **7.3c** was synthesised using **7.1g** (41 mg, 0.2 mmol, 1 equiv). **Yield:** 58 mg, 16 mmol, 79%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.37 – 8.34 (m, 2H, Ar), 7.33 (t, $^3J_{HF}$ = 8.5 Hz, 2H, Ar), 7.22 (t, $^3J_{HH}$ = 7.4 Hz, 2H, Ar), 7.15 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Ar), 7.05 (d, $^3J_{HH}$ = 7.3 Hz, 2H, Ar), 3.91 (s, 1H, B-CH), 2.03 (s, 3H, CH_3), 1.86 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) δ/ppm: 170.3,, 168.9 (d, $^1J_{CF}$ = 264.1 Hz, Ar), 147.9, 140.9, 134.8 (d, $^3J_{CF}$ = 10.6 Hz, Ar), 128.5, 127.5, 126.0,

122.6, 121.0 (d, $^{4}J_{CF}$ = 2.7 Hz, Ar), 117.6 (d, $^{2}J_{CF}$ = 22.6 Hz, Ar), 39.6 (br. s,), 18.7 (s,), 17.7 (br. s,). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) δ/ppm: 8.8 (s). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ/ppm: - 94.6 – -94.5 (m, 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).

9.7.4 Crystallographic data for **7.2d** and **7.3a**

Compound	**7.2d**	**7.3a**
Empirical Formula	$C_{16}H_{12}BCl_2NO_4$	$C_{18}H_{17}BCl_2O_2$
Space Group	P-1	$P2_1/n$
a/Å	7.1918(4)	13.1814(5)
b/Å	10.3441(6)	8.4219(4)
c/Å	13.0804(7)	15.3446(8)
α/°	96.791(4)	90
β/°	100.323(5)	97.278(4)
Y/°	92.295(4)	90
Volume/$Å^3$	948.75(9)	1689.71(13)
Z	2	4
T/K	150	150
D_c/g·cm^{-3}	1.274	1.364
R (reflections)	0.0401	0.0457
wR2 (reflections)	0.0930	0.1304

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