A Mechanochemical Zinc-Mediated Barbier-Type Allylation Reaction under Ball-Milling Conditions

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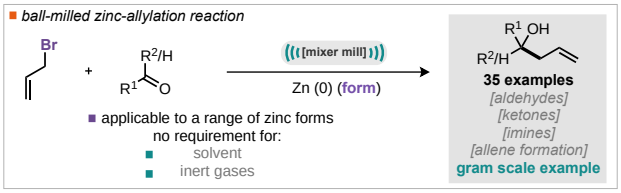
Supporting Information

ABSTRACT: A Ball-milling enabled zinc-mediated Barbier-type allylation reaction is reported. Notably runnning the reaction in this manner renders it effective irrespective of the initial morphology of the zinc metal. The process is operationally simple, does not require inert atmospheres or dry solvents and is reported on a range of aldehyde and ketone substrates, a gram scale process is demonstrated.



INTRODUCTION

The Barbier reaction features the use of base metals, in their zero-valant form, to couple alkyl halides with carbonyl compounds.[1] Since the seminal publication by Barbier in 1899,[2] the use of a variety of metals has been reported, such as, zinc,[3a] magnesium,[3b] samarium,[3c] aluminium,[3d] indium,[3e] cadmium,[3f] antimony,[3g] lead,[3h] tin,[3i] bismuth[3j] and manganese[3k] as well as asymmetric processes[4] and even aqueous media variants.[5] Perhaps the most studied Barbier-type reaction is the allylation of carbonyl groups to deliver versatile homoallylic alcohol products. [1] A common feature of these processes is the requirement of a base metal, whose physical form, solubility and oxide surface layer can lead to variable outcomes. Indeed, the use of chemical additives to circumvent these issues has been well studied (A, Scheme 1).[6]

Recently, we and others have been investigating the use of mechanochemistry[7] to impart impact and shear forces onto reactants *via* ball-milling and thus mechanically activate, rather than chemically activate, zinc metal in a variety of forms.[8] In addition to the ability to mechanically activating metals, ball-milling often requires the use of no or very little solvent (for the reaction portion at least) and can lead to interesting reaction profiles and reduced sensitivity of reactions to oxygen and/or water.[9] To date, we have outcomes, such as; reduced reaction times, alternate selectivity demonstrated, in the context of zinc-mediated transformations, that a ball-milling approach can deliver an improved protocol for the Negishi cross-coupling and Reformatsky reactions (B, Scheme 1). Under these processes it was found that the reactions were operable irrespective of the morphology of the zinc starting material. Thus simply adding the appropriate reagents to the grinding jar under an air atmosphere followed by closing the jar and milling on commercially available equipment led to the desired products in good yields and across a range of substrates.[8ab]

Herein we report the application of ball-milling mechanochemistry for the Barbier-type zinc-mediated coupling of allyl halides to aldehydes and ketones (C, Scheme 1).

RESULTS & DISCUSSION

To begin, our investigations commenced with a model set of substrates, tolualdehyde (**1**) and ally bromide (**2**) with zinc flakes and a variety of stoichiometries, milling times, ball sizes/masses were investigated. We arrived at a molar ratio of regents of 1:1.5 (**1**:**2**) with two equivalents of zinc, and milling in a 10 mL jar for two hours with a single stainless steel ball of 9.25 g mass, which afforded the target allyl alcohol in 81% yield (Table 1, Entry 1). With these conditions in hand we looked to further improve the conversion of starting materials and explored the use of liquid assisted grinding agents (LAG) to refine the reaction outcome. Liquid assisted grinding,[10] a technique more common in mechanochemical crystal engineering,[11] is somewhat counterintuitive and requires the addition of a solvent-type species to reactions which would otherwise be solvent-free.

Scheme 1. Context and Outline of Ball-milling Zinc-Mediated Barbier-Type Reaction

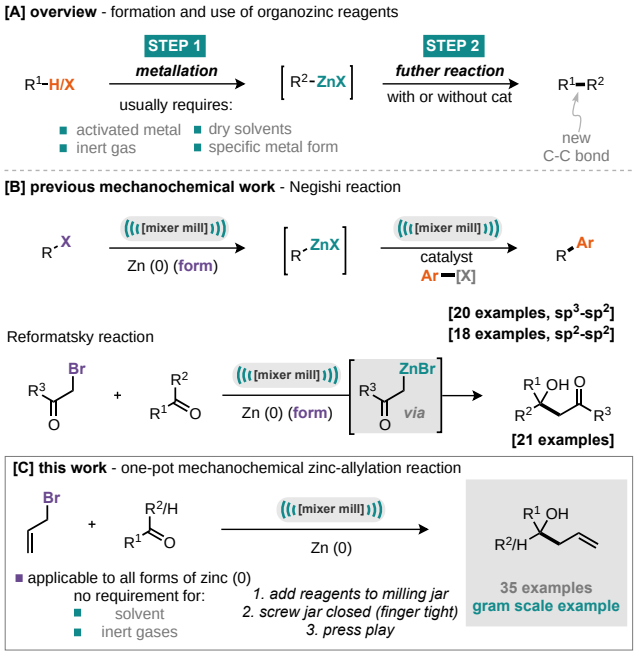
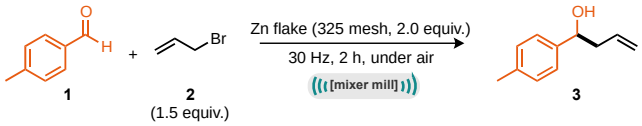


Table 1. Optimization of Model Ball-milled Allylation Reaction



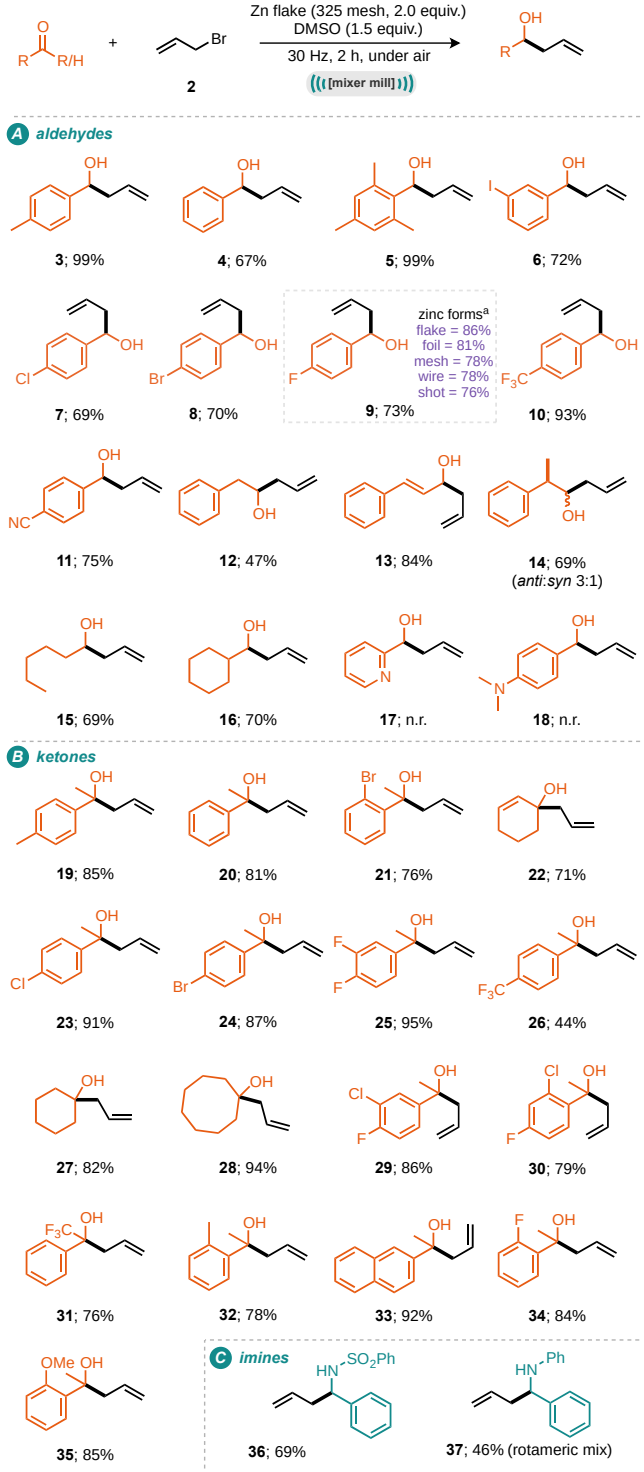
Entry	variation from 'standard conditions'	Yield of 3 [%][a]
1	none	81
2	+ DMA (1.5 equiv.)	85
3	+ DMF (1.5 equiv.)	91
4	+ DMSO (1.5 equiv.)	99
5	+ THF(1.5 equiv.)	85
6	+ DCM (1.5 equiv.)	45
7	+ Hexane (1.5 equiv.)	51
8	+ MeCN (1.5 equiv.)	69
9	**2** (2.0 equiv.)	24
	entries below this line contain DMSO (1.5 equiv.)	
10	30 mins	77
11	1 h	85
12	3 h	99

[a]Isolated yields reported.

Typically, the amount of LAG used is assigned a value; η, which represents a liquid-to-reactant ratio; values between 0.1 and 1 describe reaction regimes within the LAG region as opposed to those that are neat ($\eta < 0.1$) and those that are slurries ($\eta > 1$) or solutions (typically when $\eta > 10$).[10] The precise role of a LAG agent appears to be situation dependent, some have been found to facilitate access to different crystal polymorphic forms,[11] whilst others have led to kinetic versus thermodynamic product outcomes depending on the dielectric constant of the LAG agent.[12] Nonetheless, when screening a small range of LAG agents; representing a range of coordinating abilities and polarities, under the ball-milling Barbier-type reaction it was found that 1.5 equivalents of DMSO ($\eta = 0.44$) afforded the desired product in 99% yield (Table 1, Entry 4). Indeed, there appears to be a general trend that more coordinating liquid additives improve the reaction process, presumably due to the breaking up aggregate organizinc species and ready access to exposed metal surface. Further investigation of the reaction time (Table 1, entires 10-12) with DMSO as LAG identified that two hours was optimal.

Next, our attention turned to exploring the substrate scope of the ball-mill enabled zinc-mediated Barbier-type reaction. Notably the reaction proceeds effectively against a range of aromatic aldehydes with halo substituents; iodo, bromo, chloro and fluoro were all tolerated under these conditions as well as a range of electron withdrawing groups and sterically encumbered mesitylaldehyde (A, Scheme 2). Notably 2-formylpyridine and the electron rich 4-(dimethylamino)benzaldehyde were not competent substrates in this reaction. A range of zinc sources was explored for the reaction of 4-fluorobenzaldehyde with allyl bromide and it was established that as well as zinc flake, zinc foil, zinc mesh, zinc wire and zinc shot are all effective under milling conditions, without any pre-treatment. The ball-milled process is not restricted to aromatic aldehydes with phenacetaldehyde (**12**; 47%), cinnamaldehyde (**13**; 84%), 2-phenylpropanal (**14**; 69%, 3:1 anti:syn), hexanal (**15**; 69%) and cyclohexanecarboxaldehyde (**16**; 70%), all converting to the desired homoallylic alcohol products in moderate to good yields. Notably however crotylbromide and benzyl bromide were not effective substrates under these conditions. A range of 14 acetophenone substrates featuring electron rich, electron poor and sterically encumbered derivatives participated effectively in this process (B, Scheme 2), so to did cyclohexenone (**22**; 71%), cyclohexone (**27**; 82%) and cyclooctone (**28**; 94%). Imine electrophiles also participated in this reaction process to afford homoallylic amines in moderate to good yields (C, Scheme 2).

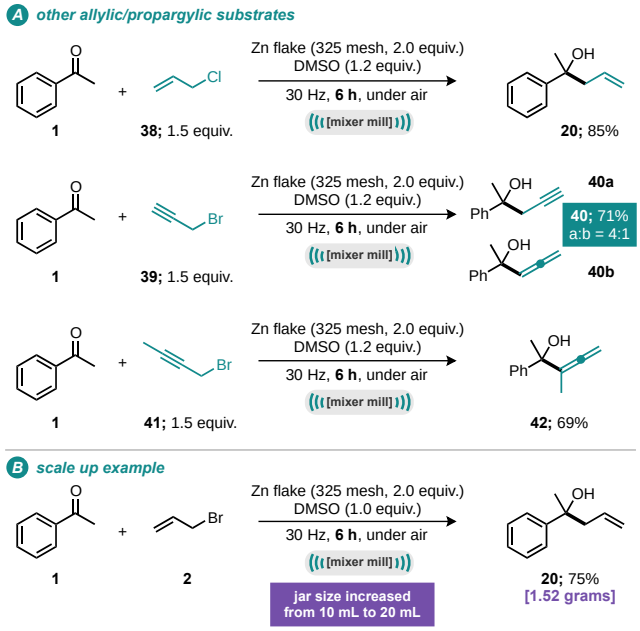
Scheme 2. Scope of the ball-milling enable zinc-mediated Barbier reaction.



a) ^{1}H NMR yield with internal standard.

Alternative allylic and propargylic substrates were also investigated. It was found that allylchloride could effectively be used as pronucleophile in reaction with acetophenone to furnish the corresponding tertiary allylalcohol (**20**) in 85% yield (A, Scheme 3), although this reaction required six hours of milling to go to completion. Propargyl bromide underwent transformation to afford a 4:1 mixture of the homo-propargyl tertiary alcohol (**40a**) and corresponding allenyl derivative (**40b**) in 71% total yield.

Scheme 3. Further investigations



By replacing the terminal alkyne C-H of propargyl bromide with a terminal methyl group through the use of 1-bromo-butyne, 69% of the allenyl tertiary alcohol (**42**) could be isolate. The ball-milling process can also be scaled up, by simply changing to a larger jar (25 mL rather than 10 mL) and increasing the reaction time from two hours to six, we were able to isolate 1.52 grams of Barbier product **20**.

To conclude, an operationally simple Barbier-type zinc-mediated mechanochemical protocol has been developed with good substrate scope and is applicable across a range of different zinc metal morphologies. The developed process, irrespective of the potentially complex behaviour of allyl zinc species,[13] does not require dry solvents or inert atmospheres and can be straightforwardly scaled to deliver gram quantities of material. Furthermore in comparison to earlier work by Suzuki and co-workers using bismuth to mediate this process by ball-milling,[3j] the present method offers improved substrates scope and greatly reduced loading of metal, albeit at increased reaction time.

EXPERIMENTAL SECTION

General Information. Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. DMSO was purchased from Fluorochem (99% purity). Different zinc forms were purchased from different companies as listed below: (1) Zinc granular (20-30 mesh, ACS reagent, ≥98.8%; Sigma-Aldrich). (2) Zinc flake (-325 mesh, 99.9%; Alfa Aesar). (3) Zinc foil (thickness 0.25 mm, 99.9% trace metals basis; Sigma-Aldrich). (4) Zinc shot (10 mm diameter x 2 mm thick, 99.99%, Alfa Aesar). (5) Zinc wire (1.0 mm diameter, 99.95%, Alfa Aesar).

Thin layer chromatography (TLC) was carried out using Merck TLC silica gel 60 sheet, and visualized with ultraviolet light or potassium permanganate stain. Flash column chromatography (FCC) was performed with Sigma Aldrich silica gel 40-60 Å as the stationary phase and solvents employed were analytical grade. ^{1}H NMR spectra were recorded on a Bruker AVX500 (500 MHz) spectrometer at ambient temperature. ^{13}C NMR spectra were recorded on a Bruker AVX500 (125 MHz) spectrometer at ambient temperature. ^{19}F NMR spectra were recorded on a Bruker AVX500 (471 MHz) spectrometer at ambient temperature. Melting points were measured on a Gallenkamp melting point apparatus and are reported corrected by linear calibration to benzophenone (47 - 49 °C) and benzoic acid (121 - 123 °C).

High resolution mass spectroscopy (HRMS) data was obtained on a Thermo Scientific LTQ Orbitrap XL by the EPSRC UK National Mass Spectrometry Facility at Swansea University or on a Waters MALDI-TOF mx in Cardiff University. Spectra were obtained using electron impact ionization (EI), chemical ionization (CI), positive electrospray (ES), pneumatically assisted electrospray (pNSI) or atmospheric solids analysis probe (ASAP+). Infrared spectra were recorded on a Shimadzu IR-Affinity-1S FTIR spectrometer.

The ball mill used was a Retsch MM 400 mixer mill. Unless otherwise stated, mechanochemical reactions were performed in 10 mL stainless steel jars from Retsch with a 12 mm diameter stainless steel ball (~9.25 g). The longest time that this mill can be programmed to run for is 99 minutes. In order to run longer reaction times the mill was started, and then additional time added to the timer in order to ensure that the mill was running continuously for the desired reaction time.

General Procedure A for Reactions of Aldehydes and Allyl Bromide. To a Retsch 10 mL stainless steel milling jar was added the aldehyde (1.0 mmol, 1 equiv.), zinc (typically flake -325 mesh; 2.0 mmol, 131 mg, 2 equiv.), allyl bromide (1.5 mmol, 131 µL, 1.5 equiv.) and DMSO (1.5 mmol, 107 µl, 1.5 equiv.) under air atmosphere. A 12 mm stainless steel ball was added and the mixture was milled at 30 Hz for 2 hours. After the reaction was finished, the resulting black paste was rinsed and transferred with ethyl acetate (50 mL) into a 100 mL conical flask, quenched with 1 M HCl (50 mL) and stirred for 20 minutes. The organic layer was separated and dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was then purified by silica gel flash chromatography.

General Procedure B for Reactions of Ketones and Allyl Bromide. To a Retsch 10 mL stainless steel milling jar was added the ketone (1.0 mmol, 1 equiv.), zinc (typically flake -325 mesh; 2.0 mmol, 131 mg, 2 equiv.), allyl bromide (1.5 mmol, 131 µL. 1.5 equiv.) and DMSO (1.2 mmol, 85 µl, 1.2 equiv.) under air atmosphere. A 12 mm stainless steel ball was added and the mixture was milled at 30 Hz for 2 hours. After the reaction was finished, the resulting black paste was rinsed and transferred with ethyl acetate (50 mL) into a 100 mL conical flask, quenched with distilled water (50 mL) and stirred for at least 30 minutes. The mixture was then filtered through a pad of silica gel (1.5 cm) to remove insoluble materials. The silica gel was then flushed with ethyl acetate (50 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was then purified by silica gel flash chromatography.

1-(p-tolyl)but-3-en-1-ol ***(3)****:* Prepared according to General Procedure A. Purified by column chromatography (Ethyl Acetate/Hexane = 25:75) to give the product (yield: 99%, 160 mg) as a clear oil. Note: 3 is volatile under reduced pressure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 5.81-5.73 (m, 1H), 5.15-5.08 (m, 2H), 4.67 (m, 1H), 2.49-2.45 (m, 2H), 2.31 (s, 3H), 1.96 (s, 1H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 141.1, 137.4, 134.7, 125.9, 118.4, 73.3, 43.9, 21.3. Data is consistent with literature values.[4b,14]

1-phenylbut-3-en-1-ol ***(4)****:* Prepared according to General Procedure A. Purified by column chromatography (Ethyl Acetate/Hexane = 20:80) to give the product (yield: 67%, 99 mg) as a clear oil. Note: 4 is volatile under reduced pressure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.24 (m, 4H), 7.20-7.16 (m, 1H), 5.74-5.66 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.07-5.02 (m 2H), 4.61 (dd, *J* = 7.4, 5.6 Hz, 1H), 2.45-2.36 (m, 2H), 2.18 (app. s, 1H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 144.0, 134.6, 128.5, 127.6, 125.9, 118.4, 73.4, 43.9. Data is consistent with literature values. [4b,14]

1-mesitylbut-3-en-1-ol ***(5)****:* Prepared according to General Procedure A. Purified by column chromatography (Ethyl Acetate/Hexane = 15:85) to give the product (yield: 99%, 188 mg) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (app. s, 3H), 5.91-5.83 (m, 1H), 5.22-5.14 (m, 3H), 2.77-2.70 (m, 1H), 2.54-2.49 (m, 1H), 2.44 (s, 6H), 2.28 (s, 3H), 1.97 (s, 1H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 136.6, 136.1, 135.4, 130.2, 117.8, 70.8, 40.4, 20.9. Data is consistent with literature values.[14]

1-(3-iodophenyl)but-3-en-1-ol ***(6)****:* Prepared according to General Procedure A. Purified by column chromatography (Ethyl Acetate/Hexane = 15:85) to give the product (yield: 72%, 197 mg) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 1H), 6.95 (t, *J* = 7.8 Hz, 1H), 5.68-5.60 (m, 1H), 5.03 (m, 2H), 4.49 (dd, *J* = 7.6, 5.3 Hz, 1H), 2.53 (broad s, 1H), 2.37-2.27 (m, 2H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 146.2, 136.5, 134.8, 133.9, 130.1, 125.1, 118.7, 94.5, 72.4, 43.7. IR (CH_2Cl_2 film): 1639, 1591, 1566, 1472, 1423, 1192, 1061, 995, 918, 781, 696 cm^{-1}. HRMS (TOF-EI+) m/z: [M]+ calcd for $C_{10}H_{11}OI$ 273.9855; found 273.9846.

1-(4-chlorophenyl)but-3-en-1-ol ***(7)****:* Prepared according to General Procedure A. Purified by column chromatography (Ethyl Acetate/Hexane = 15:85→20:80) to give the product (yield: 69%, 126 mg) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.28 (m, 4H), 5.82-5.74 (m, 1H), 5.18-5.15 (m, 2H), 4.74-4.71 (m, 1H), 2.53-2.42 (m, 2H), 2.06 (s, 1H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 142.4, 134.1, 133.3, 128.7, 127.3, 119.0, 72.7, 44.0. Data is consistent with literature values.[4b]

1-(4-bromophenyl)but-3-en-1-ol ***(8)****:* Prepared according to General Procedure A. Purified by column chromatography (Ethyl Acetate/Hexane = 10:90→20:80) to give the product (yield: 70%, 158 mg) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 7.2 Hz, 2H), 7.25 (m, 2H), 5.82-5.74 (m, 1H), 5.18-5.15 (m, 2H), 4.71 (s, 1H), 2.53 (m, 2H), 2.05 (s, 1H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 143.0, 134.1, 131.6, 127.7, 121.4, 119.1, 72.7, 44.0. Data is consistent with literature values.[15]

1-(4-fluorophenyl)but-3-en-1-ol ***(9)****:* Prepared according to General Procedure A. Purified by column chromatography (Ethyl Acetate/Hexane = 15:85→20:80) to give the product (yield: 73%, 121 mg) as a clear oil. Note: 9 is volatile under reduced pressure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.2, 5.7 Hz, 2H), 7.03 (t, *J* = 8.6 Hz, 2H), 5.79 (m, 1H), 5.18-5.14 (m, 2H), 4.73 (dd *J* = 6.8, 6.0 Hz, 1H), 2.54-2.44 (m, 2H), 2.05 (s, 1H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 162.3 (d, *J* = 246 Hz), 139.7 (d, *J* = 2.5 Hz), 134.3, 127.6, 118.9, 115.6 (d, *J* = 21.4 Hz), 72.8, 44.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.2. Data is consistent with literature values.[15]

1-(4-(trifluoromethyl)phenyl)but-3-en-1-ol ***(10)****:* Prepared according to General Procedure A. Purified by column chromatography (Ethyl Acetate/Hexane = 10:90→20:80) to give the product (yield: 91%, 201 mg) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 5.84-5.75 (m, 1H), 5.18 (d, *J* = 12.3 Hz, 2H), 4.82-4.80 (m, 1H), 2.58-2.53 (m, 1H), 2.50-2.44 (m, 1H), 2.13 (s, 1H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 147.9, 133.8, 129.9 (q, *J* = 33 Hz), 126.2, 125.5, 123.2, 119.4, 72.7, 44.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5. Data is consistent with literature values.[14]

4-(1-hydroxybut-3-en-1-yl)benzonitrile ***(11)****:* Prepared according to General Procedure A. Purified by column chromatography (Ethyl Acetate/Hexane = 15:85) to give the product (yield: 75%, 130 mg) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (m, 2H), 7.46 (m, 2H), 5.80-5.71 (m, 1H), 5.16-5.12 (m, 2H), 4.80-4.76 (m, 1H), 2.54-2.48 (m, 2H), 2.46-2.39 (m, 1H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 149.3, 133.5, 132.3, 126.6, 119.4, 119.0, 111.1, 72.5, 43.9. Data is consistent with literature values but the NMR data indicates presence of minor impurities.[4b]

1-phenylpent-4-en-2-ol ***(12)****:* Prepared according to General Procedure A. Purified by column chromatography (Ethyl Acetate/Hexane = 15:85) to give the product (yield: 47%, 76 mg) as a clear oil. Note: 12 is volatile under reduced pressure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.21 (m, 2H), 7.17-7.13 (m, 3H), 5.84-5.73 (m, 1H), 5.10-5.05 (m, 2H), 3.83-3.77 (m, 1H) or 3.80 (tt, 7.7, 4.8 Hz, 1H), 2.74 (dd, *J* = 13.6, 4.9 Hz, 1H), 2.64 (dd, *J* = 13.6, 7.9 Hz, 1H), 2.29-2.18 (m, 1H), 2.16-2.08 (m, 1H), 1.66 (s, 1H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 138.5, 134.8, 129.5, 128.6, 126.6, 118.2, 71.8, 43.4, 41.3. Data is consistent with literature values.[16]

(E)-1-phenylhexa-1,5-dien-3-ol ***(13)****:* Prepared according to General Procedure A. Purified by column chromatography (Ethyl Acetate/Hexane = 15:85) to give the product (yield: 84%, 146 mg) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.22-7.19 (m, 2H), 7.15-7.12 (m, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.14 (dd, *J* = 15.9, 6.4 Hz, 1H), 5.76 (ddt, 17.2, 10.2, 7.1 Hz, 1H), 5.10-5.04 (m, 2H), 4.25 (q, *J* = 5.9 Hz, 1H), 2.31-2.25 (m, 2H), 2.05 (s, 1H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 136.7, 134.2, 131.7, 130.4, 128.6, 127.7, 126.6, 118.4, 71.8, 42.1. Data is consistent with literature values.[14]

2-phenylhex-5-en-3-ol ***(14)****:* Prepared according to General Procedure A. Purified by column chromatography (Ethyl Acetate/Hexane = 20:80) to give the product (yield: 69%, 122 mg) as a clear oil. Note: data was reported here as a mixture of *syn* and *anti* diastereomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.11 (m, 5H, *syn* and *anti*), 5.84-5.77 (m, 1H, *syn*), 5.76-5.67 (m, 1H, *anti*), 5.06-4.98 (m, 2H, *syn* and *anti*),

3.65-3.60 (m, 1H, *syn* and *anti*), 2.75-2.64 (m, 1H, *syn* and *anti*), 2.31-2.27 (m, 1H, *syn*), 2.13-2.07 (m, 1H, *anti*), 2.06-1.97 (m, 1H, *syn*), 1.96-1.91 (m, 1H, *anti*), 1.69 (s, 1H, *anti*), 1.60 (s, 1H, *ant*), 1.26 (d, *J* = 7.0 Hz, 3H, *anti*), 1.21 (d, *J* = 7.1 Hz, *anti*). $^{13}C\{1H\}$ NMR (126 MHz, $CDCl_3$) δ 144.5, 143.4, 135.2, 135.1, 128.6, 128.6, 128.3, 127.9, 126.7, 126.5, 118.0, 117.8, 75.1, 75.1, 45.5, 45.5, 39.6, 39.0, 17.8. 16.5. Data is consistent with literature values.[17,18]

Non-1-en-4-ol ***(15)****:* Prepared according to General Procedure A. Purified by column chromatography (Ethyl Acetate/Hexane = 10:90) to give the product (yield: 69%, 98 mg) as a clear oil. Note: 15 is volatile under reduced pressure. ^1H NMR (500 MHz, $CDCl_3$) δ 5.86-5.78 (m, 1H), 5.13-5.10 (m, 2H), 3.65-3.61 (m, 1H), 2.31-2.26 (m, 1H), 2.16-2.10 (m, 1H), 1.71 (broad s, 1H), 1.45-1.25 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H). $^{13}C\{1H\}$ NMR (126 MHz, $CDCl_3$) δ 135.1, 118.1, 70.8, 42.1, 36.9, 32.0, 25.5, 22.8, 14.2. Data is consistent with literature values but the NMR data indicates presence of minor impurities.[14]

1-cyclohexylbut-3-en-1-ol ***(16)****:* Prepared according to General Procedure A. Purified by column chromatography (Ethyl Acetate/Hexane = 20:80) to give the product (yield: 70%, 108 mg) as a clear oil. Note: 16 is volatile under reduced pressure. ^1H NMR (500 MHz, $CDCl_3$) δ 5.87-5.77 (m, 1H), 5.14-2.09 (m, 2H), 3.39-3.35 (m, 1H), 2.34-2.28 (m, 1H), 2.15-2.07 (m, 1H), 1.86-1.64 (m, 6H), 1.35-0.98 (m, 6H). $^{13}C\{1H\}$ NMR (126 MHz, $CDCl_3$) δ 135.6, 117.9, 74.84, 43.2, 38.9, 29.2, 28.2, 26.6, 26.4, 26.2. Data is consistent with literature values. [4b,14]

2-(p-tolyl)pent-4-en-2-ol ***(19)****:* Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 20:80) to give the product (yield: 85%, 150 mg) as a clear oil. Note: 19 is volatile under reduced pressure. ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 5.69-5.60 (m,1H), 5.17-5.11 (m, 2H), 2.71-2.67 (m, 1H), 2.53-2.48 (m, 1H), 2.35 (s, 3H), 2.08 (s, 1H), 1.54 (s, 3H). $^{13}C\{1H\}$ NMR (126 MHz, $CDCl_3$) δ 144.8, 136.3, 133.9, 129.0, 124.8, 119.4, 73.6, 48.6, 30.1, 21.1. Data is consistent with literature values.[19]

2-phenylpent-4-en-2-ol ***(20)****:* Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 20:80) to give the product (yield: 81%, 131 mg) as a clear oil. Note: 20 is volatile under reduced pressure. 7% unreacted acetophenone was present in the purified NMR. ^1H NMR (500 MHz, $CDCl_3$) δ 7.50-7.47 (m, 2H), 7.41-7.37 (m, 2H), 7.30-7.26 (m, 1H), 5.71-5.63 (m, 1H), 5.20-5.14 (m, 2H), 2.76-2.70 (m, 1H), 2.58-2.52 (m, 1H), 2.26 (broad s, 1H), 1.59 (s, 3H). $^{13}C\{1H\}$ NMR (126 MHz, $CDCl_3$) δ 147.1, 133.8, 128.2,126.7,124.9, 119.4, 73.7, 48.6, 29.9. Data is consistent with literature values. [19]

2-(2-bromophenyl)pent-4-en-2-ol ***(21)****:* Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 15:85) to give the product (yield: 76%, 182 mg) as a clear oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.58 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.30 (dt, *J* = 7.4, 1.3 Hz, 1H), 7.09 (dt, *J* = 7.4, 1.7 Hz, 1H), 5.57 (dddd, *J* = 17.1, 10.1, 8.4, 6.4 Hz, 1H), 5.19 – 5.07 (m, 2H), 3.33 – 3.23 (m, 1H), 2.70 (s, 1H), 2.69 – 2.63 (m, 1H),1.73 (s, 3H). $^{13}C\{1H\}$ NMR (126 MHz, $CDCl_3$) δ 145.1, 135.1, 133.7, 128.6, 128.3, 127.5, 120.0, 119.4, 74.7, 45.1, 27.4. Data is consistent with literature values. [20]

1-allylcyclohex-2-en-1-ol ***(22)****:* Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 15:85) to give the product (yield: 71%, 98 mg) as a clear oil. Note: 22 is volatile under reduced pressure. ^1H NMR (500 MHz, $CDCl_3$) δ 5.93-5.80 (m, 2H), 5.65-5.61 (m, 1H), 5.16-5.13 (m, 2H), 2.31 (m, 2H), 2.11-1.86 (m, 2H), 1.76-1.63 (m, 5H). $^{13}C\{1H\}$ NMR (126 MHz, $CDCl_3$) δ 133.8, 132.3, 130.4, 118.8, 69.3, 46.9, 35.7, 35.7, 19.9, 25.3, 19.1. Data is consistent with literature values.[21]

2-(4-chlorophenyl)pent-4-en-2-ol ***(23)*** Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 20:80) to give the product (yield: 91%, 178 mg) as a clear oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.36 (m, 2H), 7.31-7.29 (m, 2H), 5.60 (dddd, *J* = 20.2, 9.5, 8.2, 6.5 Hz, 1H), 5.13 (dd, *J* = 14.0, 1.3 Hz, 2H), 2.64 (dd, *J* = 13.8, 6.5 Hz, 1H), 2.48 (dd, *J* = 13.8, 8.3 Hz, 1H), 2.13 (s, 1H), 1.52 (s, 3H). $^{13}C\{1H\}$ NMR (126 MHz, $CDCl_3$) δ 146.3, 133.3, 132.5, 128.4, 126.5, 120.0, 73.5, 48.5, 30.0. Data is consistent with literature values.[19]

2-(4-bromophenyl)pent-4-en-2-ol ***(24)****:* Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 20:80) to give the product (yield: 87%, 209 mg) as a clear oil. Note: trace 4'-Bromoacetophenone was observed in the purified NMR. ^1H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (d, *J* = 8.8 Hz, 2H), 7.33-7.31 (d, *J* = 8.8 Hz, 2H), 5.61-5.51 (m, 1H), 5.11 (d, *J* = 12.4 Hz, 2H), 2.63 (dd, *J* = 13.7, 6.5 Hz, 1H), 2.49 (dd, *J* = 13.7, 8.2 Hz, 1H), 2.11 (s, 1H), 1.52 (s, 3H). $^{13}C\{1H\}$ NMR (126 MHz, $CDCl_3$) δ 146.8, 133.3, 131.3, 126.9, 120.7, 120.0, 73.5, 48.4, 30.0. Data is consistent with literature values.[20]

2-(3,4-difluorophenyl)pent-4-en-2-ol ***(25)****:* Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 15:85) to give the product (yield: 95%, 188 mg) as a clear oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.31-7.27 (m, 1H), 7.15-7.09 (m, 2H), 5.62 (m, 1H), 5.16-5.13 (m, 2H), 2.63 (dd, J = 13.8, 6.6 Hz, 1H), 2.49 (dd, J = 13.8, 8.2 Hz, 1H), 2.22 (broad s, 1H), 1.53 (s, 3H). $^{13}C\{1H\}$ NMR (126 MHz, $CDCl_3$) δ 150.1 (dd, *J* = 16.4, 247.0 Hz), 149.1 (dd, *J* = 13.9, 248.2 Hz), 145.0 (t, *J* = 44.0 Hz), 133.1, 120.9 (q, *J* = 33.6 Hz), 120.1, 116.9 (d, *J* = 17.6 Hz), 114.4 (d, *J* = 17.6 Hz), 73.3, 48.5, 29.9. IR (CH_2Cl_2 film): 2984, 1609, 1514, 1418, 1379, 1277, 1153, 1117, 947. 922, 818, 775 cm^{-1}. HRMS (TOF-EI+) m/z: [M-H_2O]+ calcd for $C_{11}H_{10}F_2$ 180.0751; found 180.0747.

2-(4-(trifluoromethyl)phenyl)pent-4-en-2-ol ***(26)****:* Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 15:85) to give the product (yield: 44%, 101 mg) as a clear oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.61-7.55 (m, 4H), 5.64-5.55 (m, 1H), 5.17-5.13 (m, 2H), 2.68 (dd, *J* = 13.8, 6.4 Hz,1H), 2.52 (dd, *J* = 13.8, 8.3 Hz, 1H), 2.24 (s, 1H), 1.56 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.8 (d, *J* = 1.0 Hz), 133.1, 129.0 (q, *J* = 32.4 Hz), 125.4, 125.3 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.8 Hz), 120.2, 73.7, 48.4, 30.0. $^{13}C\{1H\}$ NMR (126 MHz, $CDCl_3$) δ 147.9, 133.8, 129.9 (q, *J* = 32.4 Hz), 126.2, 125.5 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 271.9 Hz), 119.4, 72.7, 44.1. IR (CH_2Cl_2 film): 1379, 1327, 1165, 1125, 1070, 1015, 955, 939, 843 cm^{-1}. HRMS (TOF-EI+) m/z: [M-H_2O]+ calcd for $C_{12}H_9F_3$ 212.0813; found 212.0805.

1-allylcyclohexan-1-ol ***(27)****:* Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 15:85) to give the product (yield: 82%, 115 mg) as a clear oil. ^1H NMR (500 MHz, $CDCl_3$) δ 5.89 (ddt, *J* = 17.7, 10.2, 7.5 Hz), 5.16-5.09 (m, 2H), 2.22 (d, *J* = 7.5 Hz, 2H), 1.64-1.40 (m, 13H), 1.30-1.25 (m, 2H). $^{13}C\{1H\}$ NMR (126 MHz, $CDCl_3$) δ 133.9, 118.8, 71.1, 46.8, 37.5, 25.9, 22.3. Data is consistent with literature values.[19]

1-allylcyclooctan-1-ol ***(28)****:* Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 20:80) to give the product (yield: 94%, 158 mg) as a clear oil. ^1H NMR (500 MHz, $CDCl_3$) δ 5.83 (ddt, 17.7, 10.2, 7.5 Hz, 1H), 5.09-5.02 (m, 2H), 2.15 (d, *J* = 7.5 Hz), 1.59-1.35 (m, 19H). $^{13}C\{1H\}$ NMR (126 MHz, $CDCl_3$) δ 134.2, 118.7, 74.5, 46.1, 36.3, 28.4. 25.1, 22.3. Data is consistent with literature values.

2-(3-chloro-4-fluorophenyl)pent-4-en-2-ol ***(29)****:* Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 20:80) to give the product (yield: 86%, 184 mg) as a clear oil. Note: trace 3'-Chloro-4'-fluoroacetophenone was observed in the purified NMR. ^1H NMR (500 MHz, $CDCl_3$) δ 7.52-7.50 (m, 1H), 7.31-7.27 (m, 1H), 7.10 (t, *J* = 8.7 Hz, 1H), 5.62 (m, 1H), 5.17-5.13 (m, 2H), 2.63 (dd, *J* = 13.8, 6.6 Hz, 1H), 2.49 (dd, *J* = 13.8, 8.1 Hz, 1H), 2.22 (s, 1H), 1.53 (s, 3H). $^{13}C\{1H\}$ NMR (126 MHz, $CDCl_3$) δ 156.8 (d, *J* = 248.2 Hz), 144.8, 132.9, 127.4, 124.8, 120.1, 116.2, 116.2, 73.2, 48.4, 29.9. IR (CH_2Cl_2 film): 1684, 1639, 15.91, 1497, 1391, 1263, 1244, 1076, 1057, 920, 880, 820, 729, 714 cm^{-1} HRMS (TOF-ES+) m/z: [M-H_2O+H]+ calcd for $C_{11}H_{11}ClF$ 197.0533; found 197.0540.

2-(2-chloro-4-fluorophenyl)pent-4-en-2-ol ***(30)****:* Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 20:80) to give the product (yield: 79%, 169 mg) as a clear oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.9, 6.4 Hz, 1H), 7.11 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.97 (ddd, *J* = 8.9, 7.7, 2.7 Hz, 1H), 5.59 – 5.48 (m, 1H), 5.18 – 5.06 (m, 2H), 3.18 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.61 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.46 (s, 1H), 1.68 (s, 3H). $^{13}C\{1H\}$ NMR (126 MHz, $CDCl_3$) δ 161.4 (d, *J* = 312.5 Hz), 139.8 (d, *J* = 5.0 Hz), 133.5, 131.3 (d, *J*= 12.6 Hz), 129.4 (d, *J* = 10.1 Hz), 119.8, 118.5 (d, *J* = 31.5 Hz), 113.8 (d, *J* = 25.2 Hz), 74.1, 45.3, 27.6. IR (CH_2Cl_2 film): 1601, 1578, 1483, 1389, 1377, 1271, 1258, 1215, 1078, 1032, 999, 918, 897, 860, 820 cm^{-1}. HRMS (TOF-ES+) m/z: [M-H_2O+H]+ calcd for $C_{11}H_{11}ClF$ 197.0533; found 197.0540.

*1,1,1-trifluoro-2-phenylpent-4-en-2-ol (**31**):* Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 15:85) to give the product (yield: 76%, 164 mg) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.38 (m, 3H), 5.56 (td, *J* = 17.0, 7.7 Hz, 1H), 5.27 – 5.17 (m, 2H), 2.98 (dd, *J* = 14.3, 6.5 Hz, 1H), 2.85 (dd, *J* = 14.3, 8.0 Hz, 1H), 2.68 (s, 1H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 137.0, 130.5, 128.7, 128.5, 126.6 (d, *J* = 1.3 Hz), 124.3, 122.1, 75.9 (q, *J* = 30.0 Hz), 40.4 (d, *J* = 0.7 Hz). Data is consistent with literature values.[4b,21]

*2-(o-tolyl)pent-4-en-2-ol (**32**):* Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 15:85) to give the product (yield: 78%, 137 mg) as a clear oil. Note: 32 is volatile under reduced pressure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.26 (m, 1H), 6.98 (app. s, 3H), 5.49 (td, *J* = 17.4, 7.3 Hz, 1H), 4.99-4.93 (m, 2H), 2.69 (dd, *J* = 13.9, 6.6 Hz, 1H), 2.42-2.37 (m, 4H), 1.94 (s, 1H), 1.44 (s, 3H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 144.6, 135.4, 134.0, 132.7, 127.1, 126.1, 125.8, 119.4, 74.9, 46.7, 29.0, 22.6. Data is consistent with literature values. [19]

*2-(naphthalen-2-yl)pent-4-en-2-ol (**33**):* Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 15:85) to give the product (yield: 92%, 195 mg) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.86-7.83 (m, 3H), 7.56 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.51-7.46 (m, 2H), 5.64 (m, 1H), 5.15 (dd, *J* = 23.2, 13.6 Hz, 2H), 2.82 (dd, *J* = 13.8, 6.3 Hz, 1H), 2.61 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.23 (s, 1H), 1.65 (s, 3H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 145.1, 133.7, 133.3, 132.4, 128.3, 128.0, 127.6, 126.2, 125.8, 123.7, 123.3, 119.7, 73.9, 48.4, 30.1. Data is consistent with literature values. [19]

*2-(2-fluorophenyl)pent-4-en-2-ol (**34**):* Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 15:85) to give the product (yield: 84%, 151 mg) as a clear oil. Note: 34 is volatile under reduced pressure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (t, *J* = 7.7 Hz, 1H), 7.24 (m, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.04-7.00 (dd, *J* = 12.2, 8.1, 1H), 5.60 (dt, *J* = 16.8, 9.2 Hz), 5.13 (m, 2H), 2.91 (dd, *J* = 13.8, 6.3 Hz, 1H), 2.57 (dd, *J* = 13.8, 8.5 Hz, 1H), 2.42 (s, 1H), 1.63 (s, 3H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 159.5 (d, *J* = 245.7 Hz), 134.1 (d, *J* = 11.3 Hz), 133.7, 128.8 (d, *J* = 8.8 Hz), 127.5 (d, *J* = 5.0 Hz), 124.1 (d, *J* = 2.5 Hz), 119.6, 116.0 (d, *J* = 23.9 Hz), 72.8, 46.7, 28.4. Data is consistent with literature values.[22]

*2-(2-methoxyphenyl)pent-4-en-2-ol (**35**):* Prepared according to General Procedure B. Purified by column chromatography (Ethyl Acetate/Hexane = 30:70) to give the product (yield: 85%, 163 mg) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, 1H), 7.16 (app. s, 3H), 5.68 (m, 1H), 5.15 (m, 2H), 2.88 (dd, *J* = 13.9, 6.5 Hz, 1H), 2.60-2.55 (m, 4H), 2.09 (s, 1H), 1.63 (s, 3H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 144.7, 135.4, 134.1, 132.8, 127.1, 126.2, 125.8, 119.4, 74.9, 46.7, 29.1, 22.6. IR (CH_2Cl_2 film): 2984, 1489, 1458, 1375, 1256, 1152, 1094, 1072, 1055, 997, 932, 914, 760, 727 cm^{-1}. Note: HRMS analysis of 35 was unsuccessful, with unidentifiable fragmentation of the compound

*N-(1-phenylbut-3-en-1-yl)benzenesulfonamide (**36**):* Prepared according to General Procedure A. Purified by column chromatography (Ethyl Acetate/Hexane = 30:70) to give the product (yield: 69%, 129 mg) as white solids. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (m, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.16-7.15 (m, 3H), 7.07-7.05 (m, 2H), 5.57-5.47 (m, 1H), 5.08-4.99 (m, 3H), 4.42 (q, *J* = 6.7 Hz, 1H), 2.52-2.42 (m, 2H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 140.6, 140.3, 133.2, 132.5, 128.8, 128.5, 127.6, 127.2, 126.7, 119.5, 57.3, 42.0. Data is consistent with literature values.[23]

*N-(1-phenylbut-3-en-1-yl)aniline (**37**):* Prepared according to General Procedure A. Purified by column chromatography (Ethyl Acetate/Hexane = 8:92) to give the product (yield: 46%, 103 mg) as white solids. Note: a mixture of rotamers (5.7:1) was observed in the purified NMR. Only the major rotamer is reported here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.19 (m, 4H), 7.15-7.12 (m, 1H), 7.00-6.96 (m, 2H), 6.57-6.52 (m, 1H), 6.41-6.39 (m, 2H), 5.72-5.61 (m, 1H), 5.11-5.03 (m, 2H), 4.29 (dd, *J* = 8.0, 5.1 Hz, 1H), 4.04 (broad s, 1H), 2.54-2.47 (m, 1H), 2.43-2.36 (m, 1H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 147.4, 143.7, 134.8, 129.2, 128.7, 127.1, 126.4, 118.4, 117.5, 113.6, 57.2, 43.4. Data is consistent with literature values.[24]

*2-phenylpent-4-yn-2-ol (**40a**) and 2-phenylpenta-3,4-dien-2-ol (**40b**):* Prepared according to General Procedure B with propargyl bromide (1.0 mmol, 167 µL, 80% wt in PhMe). The reaction mixture was milled for 6 h, and then purified by column chromatography (Ethyl Acetate/Hexane = 15:85) to give an inseparable mixture of 40a and 40b (a:b= 4.2:1, yield: 71%, 114 mg) as a clear oil. Note: Product mixture 40 is volatile under reduced pressure.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.39 (m, 2H, a and b), 7.28-7.24 (m, 1H, a and b), 7.19-7.15 (m, 2H, a and b), 5.47 (t, *J* = 6.6 Hz, 1H, b), 4.90-4.83 (m, 1H, b), 2.64 (dq, *J* = 16.7, 1.8 Hz, 2H, a), 2.41 (s, 1H, a), 2.19 (s, 1H, b), 1.96 (s, 1H, a), 1.57 (s, 3H, b), 1.55 (s, 3H, a). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 206.0, 171.3, 147.2, 146.4, 128.3, 128.3, 127.2, 127.1, 125.0, 124.8, 100.3, 80.5, 79.2, 73.3, 73.1, 71.8, 60.5, 34.7, 30.5, 21.1, 14.3. Data is consistent with literature values.[25,26]

*3-methyl-2-phenyl-4λ^5-penta-3,4-dien-2-ol (**42**):* Prepared according to General Procedure B with 1-bromobut-2-yne (1.0 mmol, 88 µL). The reaction mixture was milled for 6 h, and then purified by column chromatography (Ethyl Acetate/Hexane = 20:80) to give the product 42 (yield: 69%, 120 mg). Note: This product is volatile under reduced pressure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.27-7.24 (m, 1H), 4.91-4.86 (m, 2H), 2.01 (s, 1H), 1.67 (s, 3H), 1.57 (d, *J* = 2.7 Hz, 3H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 205.3, 146.1, 128.2, 127.0, 125.4, 106.0, 77.2, 75.1, 30.3, 14.8. Data is consistent with literature values.[27]

Scale Up Reaction: The reaction was carried out using acetophenone (1.5 g, 1.46 mL, 12.5 mmol, 1.0 equiv.) according to General Procedure B. The reaction mixture was milled for 6 h in a 25 mL jar. Purified by Kugelrohr distillation to give the product (yield: 75%, 1.52 g) as a clear oil. The characterisation data of the product was in accordance with 20.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXX including assessment of different zinc sources and the spectral data (PDF)

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Notes

The authors declare no competing financial interest.
Information about the data that underpins the results presented in this article, including how to access them, can be found in the Cardiff University data catalogue at http://doi.org/XXXX (accessed XXXX).

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