SUPPORTING INFORMATION

# Isomerization-Allylation Reaction of 1,3-Substituted Propenols.

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#### **General Methods**

All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring. All reactions were monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 sheets, which were visualised with ultraviolet light and then developed with iodine and basic potassium permanganate solution. Flash chromatography was performed on Sigma-Aldrich silica gel 60 as the stationary phase and the solvents employed were of analytical grade. <sup>1</sup>H NMR spectra were recorded on either a Bruker AVX300 (300 MHz) or Bruker 400 MHZ spectrometer at ambient temperature. Data are reported as follows: chemical shift in parts per million ( $\delta$ , ppm) from deuterated chloroform (CDCl<sub>3</sub>) taken as 7.26 ppm, integration, multiplicity (s = singlet; d = doublet; t = triplet; dd = double doublets m = multiplet), and coupling constant (Hz). <sup>13</sup>C NMR spectra were recorded on either a Bruker AVX300 (75 MHz) spectrometer. Chemical shifts are reported in ppm from CDCl<sub>3</sub> taken as 77.0 ppm. Infrared spectra were recorded on a Perkin Elmer RX I FT-IR spectrometer as liquid films or as dilute solutions between two KBr discs. Mass spectra were recorded on either a Micromass GCT Premier or a Waters Micromass LCT Premier spectrometer using electron ionisation (EI) at 70 eV or electrospray (ES) techniques, respectively. Unless stated otherwise, all commercially available reagents were used as received. When necessary, commonly used organic solvents were dried prior to use according to standard laboratory practices.<sup>1</sup>

<sup>&</sup>lt;sup>1</sup> D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals; 3<sup>rd</sup> ed. Pergamon Press, Oxford, 1988* 

#### Synthesis of starting Materials

#### General Procedure A: Formation of Propargylic alcohols

A hexane solution of n-BuLi (2.5 M) (1.1 eq.) was added to a THF (0.5M) solution of phenylacetylene (1.1 eq.) at -78°C. The mixture was stirred at 1hr at that temperature, before the aryl aldehyde was added (1 eq.). The reaction mixture was warmed to room temperature and stirred for 1hr, and quenched with a saturated aqueous NH<sub>4</sub>Cl solution. The aqueous solution was extracted with EtOAc (2 x 15 mL), and the combined organic layers were washed with brine (20 mL). After the organic layer was dried with NaSO<sub>4</sub> and concentrated in vacuo. The crude product was loaded onto a column and chromatographed to afford the requisite propargylic alcohol.

#### General Procedure B: Formation of Propargylic alcohols

The aryl iodide (2 eq.),  $PdCl_2(PPh_3)_2$  (2.5 mol%) and Cul (10 mol%) were weighed into a clean, dry round bottomed flask, purged with argon. Triethylamine was added followed by a solution of 1-phenylprop-2-yn-1-ol (1a), in CH<sub>2</sub>Cl<sub>2</sub> (1M), (to aid the solubility of the aryl iodide in TEA). The reaction was stirred for 3 hours, after which it was filtered through a plug of silicia and washed with CH<sub>2</sub>Cl<sub>2</sub> and EtOAc and concentrated *in vacuo*. The crude mixture was applied directly onto the top of a column and chromatographed to afford the requisite propargylic alcohol.

#### General Procedure C: Formation of Allylic Alcohols

In a clean, oven dried round bottomed flask, purged with argon, and cooled to  $0^{\circ}$ C, Red-Al (65% in PhMe) (2 eq.) was dissolved in diethyl ether (0.5 M) followed by the dropwise addition of a solution of the propargylic alcohol in Et<sub>2</sub>O (0.5 M). The mixture was stirred for 4 hours, maintaining the temperature at 0°C after which the reaction was quenched with several drops of 1 M HCl solution (CAUTION: Rapid evolution of hydrogen gas). The mixture was extracted with 2x25 mL Et<sub>2</sub>O, washed with brine, dried over anhydrous MgSO<sub>4</sub> and concentrated *in vacuo*. The crude mixture was applied directly onto the top of a column and chromatographed to afford the requisite 1,3-diaryl propenol.

#### Procedure D: Isomerisation-Allylation of 1,3-Propenols

Sodium hydride (1.5 equiv.) was added to a clean, dry, argon purged 10 mL roundbottomed flask charged with a THF solution (0.1 M) of the corresponding alcohol. The solution was stirred at 60°C for 30 minutes followed by addition of allyl bromide (1.5 equiv) and the solution was allowed to stir overnight at 60°C. After quenching with distilled water (10 mL) and extraction (2x25 mL EtOAc), the organic layer was washed with distilled water (25 mL) and brine (25 mL), dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The crude mixture was applied directly onto the top of a column and chromatographed to afford the requisite allylated product.

#### 1-phenylprop-2-yn-1-ol

A THF solution of ethynylmagnesium bromide (25.0 mL, 12.5 mmol, 0.5 M) was added dropwise to a solution of benzaldehyde (1.01 mL, 10.0 mmol) in THF (10 mL) and cooled to 0°C. After the addition was complete, the reaction mixture was warmed to room temperature and allowed to stir overnight. The reaction was quenched with saturated aqueous NH<sub>4</sub>Cl (50 mL) and extracted with Et<sub>2</sub>O (3 x 20 mL). The combined organic extracts were rinsed with brine (50ml), dried over MgSO<sub>4</sub> and concentrated. Crude product was applied directly to a column and chromatographed (3:1 hexanes: EtOAc) to afford **1a** (1.28g, 97%) as a brown oil.

Rf (10% EtOAc in hexane) = 0.26; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.53 – 7.51 (2H, m), 7.39 – 7.30 (3H, m), 5.42 (1H, d, *J* = 4.4 Hz), 2.64 (1H, d, *J* = 2.8 Hz <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  140.1, 128.7, 128.6, 126.7, 83.6, 74.9, 64.4. All spectral data were in agreement with those previously reported.<sup>2</sup>

#### 1-(4-fluorophenyl)-3-phenylprop-2-yn-1-ol



The title compound was prepared according to general procedure A, from 4-fluorobenzaldehyde (0.32 mL, 3.30 mmol) using phenylacetylene (0.36 mL, 3.30 mmol) and *n*-butyllithium (2.5 M in hexane) (1.32 mL, 3.30 mmol). The crude product was loaded onto a column and chromatographed (10% EtOAc in hexane) to afford (635 mg, 93%) as a clear oil.

<sup>&</sup>lt;sup>2</sup> C. P. Casey, T. L. Dzwiniel , S. Kraft and I. A. Guzei, *Organometallics* 2003, **22**, 3915.

Rf (10% EtOAc in hexane) = 0.11; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.55 – 7.51 (2H, m), 7.44 – 7.42 (2H, m), 7.32 – 7.25 (3H, m), 7.02 (3H, t, *J* = 8Hz), 5.62 (1H, d, *J* = 4 Hz), 2.99 (1H, m, br <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 162.7 (d, <sup>1</sup>J<sub>C-F</sub> = 246.0 HZ), 136.6 (d, <sup>4</sup>J<sub>C-F</sub> = 3.0 Hz), 131.8, 128.7, 128.7 (d, <sup>3</sup>J<sub>C-F</sub> = 8.0 Hz), 128.4, 122.3, 115.5 (d, <sup>2</sup>J<sub>C-F</sub> = 22.0 Hz), 88.7, 86.9, 64.4 (d, <sup>5</sup>J<sub>C-F</sub> = 1 .0 Hz). All spectral data were in agreement with those previously reported.<sup>3</sup>

#### (E)-1-(3,5-trifluoromethylphenyl)-3-phenylprop-2-en-1-ol



Mg turnings (63.2 mg, 2.60 mmol) and a single crystal of iodine was added to an oven dried round bottomed flask purged with argon. A condenser was fitted and Et<sub>2</sub>O (5.0 mL, 0.5M) added. This mixture was stirred for 10 minutes, after which 1-bromo-3,5-trifluorobenzene (0.41 mL, 2.40 mmol) was added. The reaction mixture was heated to reflux for 20 minutes and then cooled to room temperature until the majority of Mg turnings had disappeared. The formed Grignard was added dropwise to a cooled 0°C solution of cinnamaldehyde (0.25 mL, 2.00 mmol) in THF (5.0 mL, 0.5M). Once the addition was completed the reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched with sat. NH<sub>4</sub>Cl (20 mL) and extracted (2 x 20 mL) EtOAc, the combined organic layers were washed with H<sub>2</sub>O (20 mL) and brine (20 mL), dried over anhydrous MgSO<sub>4</sub> and concentrated. The crude product was applied to a column and chromatographed (15% EtOAc in hexane) to afford **2r** (348 mg, 50%) as a colourless oil.

Rf (10% EtOAc in hexane) = 0.28; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup>; 3323, 1375, 1278, 1172, 1133, 755; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 (2H, s), 7.81(1H, s), 7.42 – 7.23 (5H, m), 6.76 (1H, d, *J* = 16.0 Hz), 6.30 (1H, dd, *J* = 15.2, 7.2 Hz), 5.50 (1H, m, br), 2.23 (1H, d, J = 3.5 Hz<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  145.2, 135.7, 132.8, 131.8 (q, <sup>2</sup>*J*<sub>C-F</sub> = 33.0Hz), 129.8, 128.8, 128.5, 126.8, 126.4 (m), 124.7, 122.0, 121.6 (qn, <sup>3</sup>*J*<sub>C-F</sub> = 4.0 Hz), 74.3; HRMS (ES<sup>+</sup>) Cald for C<sub>17</sub>H<sub>11</sub>F<sub>6</sub>O [M+H]<sup>+</sup> 345.0714. Found 345.0711

<sup>&</sup>lt;sup>3</sup> L. A. Paquette and F. Geng, *J. Am. Chem. Soc.* 2002, **124**, 9199.

#### 1-phenyl-3-(pyridin-3-yl)prop-2-yn-1-ol



The title compound was prepared according to general procedure A, from 3-pyridinecarboxaldehyde (0.62 mL, 6.00 mmol) using phenylacetylene (0.72 mL, 6.60 mmol) and *n*-butyllithium (2.5 M in hexane) (2.64 mL, 6.60 mmol). The crude product was loaded onto a column and chromatographed (40% EtOAc in hexane) to afford **1i** (1.20 g, 96%) as a brown viscous oil.

Rf (40% EtOAc in hexane) = 0.13; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.78 (1H, s), 8.51 (1H, d, *J* = 5.0 Hz), 7.97 (1H, d, *J* = 7.8 Hz), 7.45- 7.42 (2H, m), 7.35 – 7.26 (4H, m) 5.74 (1H, s <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  149.0, 148.1, 136.9, 134.8, 131.8, 128.4, 123.6, 122.1, 88.1, 87.1, 62.6. All spectral data were in agreement with those previously reported.<sup>4</sup>

#### 1-phenyl-3-(4-fluorophenyl)prop-2-yn-1-ol



The title compound was prepared according to general procedure B, from **1a** (200 mg, 1.50 mmol) using 1-fluoro-4-iodibenzene (0.36 mL, 3.00 mmol),  $PdCl_2(PPh_3)_2$  (53.0 mg, 0.075 mmol), Cul (57 mg, 0.30 mmol) and triethylamine (7.5 mL). The crude product was loaded onto a column and chromatographed (10% EtOAc in hexane) to afford **1n** (240 mg, 71%) as a brown oil.

Rf (10% EtOAc in hexane) = 0.35; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.62 – 7.60 (2H, m), 7.47 – 7.34 (5H, m), 7.04 – 6.99 (2H, m), 5.68 (1H, d, *J* = 5.4 Hz), 2.36 (1H, d, *J* = 4.8 Hz <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  162.7 (d, <sup>1</sup>*J*<sub>C-F</sub> = 248.0 Hz), 140.6. 133.7 (d,

<sup>&</sup>lt;sup>4</sup> N. Sakai, R. Kanada, N. Hirasawa and T. Konakahara, *Tetrahedron* 1983, **39**, 9298.

 ${}^{3}J_{C-F} = 9.0$  Hz), 128.7, 128.5, 126.7, 118.5 (d,  ${}^{4}J = 4.0$  Hz), 115.6 (d,  ${}^{2}J_{C-F} = 23.0$  Hz), 88.5 (d,  ${}^{5}J_{C-F} = 1.0$ Hz), 85.6, 65.1. All spectral data were in agreement with those previously reported.<sup>5</sup>

#### 1-phenyl-3-(p-toyl)prop-2-yn-1-ol



The title compound was prepared according to general procedure B, from **1a** (300 mg, 2.28 mmol) using 4-iodotoluene (745 mg, 3.42 mmol),  $PdCl_2(PPh_3)_2$  (84.2 mg, 0.12 mmol), Cul (86.8 mg, 0.46 mmol) and triethylamine (11.4 mL). The crude product was loaded onto a column and chromatographed (5% EtOAc in hexane) to afford **1I** (375 mg, 74%) as a light brown oil.

Rf (30% EtOAc in hexane) = 0.68; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.64 – 7.61 (2H, m), 7.43 – 7.33 (5H, m), 7.14 – 7.12 (2H, m), 5.69 (1H, d, *J* = 5.2 Hz), 2.35 (3H, s), 2.24 (1H, d, *J* = 5.8 Hz <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  140.8, 138.8, 131.7, 129.1, 128.7, 128.4, 16.8, 119.3, 88.0, 86.9, 65.2, 21.5. All spectral data were in agreement with those previously reported.<sup>6</sup>

#### 1-phenyl-3-(4-methylphenyl)prop-2-yn-1-ol



The title compound was prepared according to general procedure B, from **1a** (300 mg, 2.28 mmol) using 4-iodoanisole (1.07 g, 4.56 mmol),  $PdCl_2(PPh_3)_2$  (84.2 mg, 0.12 mmol), Cul (86.8 mg, 0.46 mmol) and triethylamine (11.4 mL). The crude product was loaded onto a column and chromatographed (5% EtOAc in hexane) to afford **1m** (313 mg, 58%) as a brown oil.

<sup>&</sup>lt;sup>5</sup> P. Liu, C. L. Deng, X. Lei and G. Q. Lin, *Eur. J. Org. Chem.* 2011, **36**, 7308.

<sup>&</sup>lt;sup>6</sup> J. Ito, R. Asai and H. Nishiyama, *Org. Lett.* 2010, **12**, 3860.

Rf (10% EtOAc in hexane) = 0.35; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.63 – 7.61 (2H, m), 7.43 – 7.35 (5H, m), 6.86 – 6.83 (2H, m), 5.69 (1H, d, *J* = 6.5 Hz), 3.82 (3H, s), 2.24 (1H, d, *J* = 6.8 Hz <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  142.3, 123.3, 115.7, 111.1, 110.9, 109.2, 96.9, 96.4, 69.7, 69.1, 47.7, 37.7. All spectral data were in agreement with those previously reported.<sup>7</sup>

1-phenyl-3-(pyridin-3-yl)prop-2-yn-1-ol



The title compound was prepared according to general procedure B, from **1a** (151 mg, 1.14 mmol) using 3-iodopyridine (350 mg, 1.71 mmol),  $PdCl_2(PPh_3)_2$  (42.1 mg, 0.06 mmol), Cul (43.4 mg, 0.23 mmol) and triethylamine (5.7 mL). The crude product was loaded onto a column and chromatographed (40% EtOAc in hexane) to afford **1o** (162 mg, 68%) as a viscous brown oil.

Rf (30% EtOAc in hexane) = 0.18; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.76 (1H, s), 8.53 (1H, s), 7.76 (1H, d, *J* = 7.6 Hz), 7.61 (2H, d, *J* = 7.2 Hz), 7.44 – 7.34 (3H, m) 7.28–7.25 (1H, m) 5.72 (1H, d, *J* = 3.1 Hz <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.1, 148.4, 140.6, 139.0, 128.7, 128.4, 126.7, 123.3, 93.4, 82.6, 64.6 ppm. All spectral data were in agreement with those previously reported.<sup>8</sup>

#### 1-phenyl-3-(4-(trifluoromethoxy)phenyl)prop-2-yn-1-ol



The title compound was prepared according to general procedure B, from **1a** (300 mg, 2.28 mmol) using 1-lodo-4-trifluoromethoxybenzene (985mg, 3.42 mmol),  $PdCl_2(PPh_3)_2$  (84.2 mg, 0.12 mmol), Cul (86.8 mg, 0.46 mmol) and triethylamine

<sup>&</sup>lt;sup>7</sup> C. W.Downey, B. D.Mahoney and V. R. Lipari, *J. Org. Chem.* 2009, **74**, 2904.

<sup>&</sup>lt;sup>8</sup> P.N. Rao, J. Uddin and E.E. Knaus, *J. Med. Chem.* 2004, **47**, 3972.

(11.4 mL). The crude product was loaded onto a column and chromatographed (5% EtOAc in hexane) to afford the title compound (499 mg, 75%) as a dark brown oil.

Rf (30% EtOAc in hexane) = 0.23; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3435, 1657, 1640, 1633, 1506, 1259, 1206, 1165, 1019, 698; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.72 (1H, d, *J* = 7.3 Hz), 7.51 (2H, d, *J* = 8.6 Hz), 7.46 – 7.34 (3H, m), 7.18 (2H, d, *J* = 8.3 Hz), 5.70 (1H, d, *J* = 5.5 Hz), 2.25 (1H, d, *J* = 6.0 Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): HRMS (ES<sup>+</sup>) Calcd for C<sub>16</sub>H<sub>12</sub>F<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 292.0789. Found 292.0782

#### 3-(naphthalen-2-yl)-1-phenylprop-2-yn-1-ol



The title compound was prepared according to general procedure B, from **1a** (300 mg, 2.28 mmol) using 2-lodonaphthalene (869 mg, 3.42 mmol),  $PdCl_2(PPh_3)_2$  (84.2 mg, 0.12 mmol), Cul (86.8 mg, 0.46 mmol) and triethylamine (11.4 mL). The crude product was loaded onto a column and chromatographed (5% EtOAc in hexane) to afford the title compound (371 mg, 63%) as a dark brown oil.

Rf (30% EtOAc in hexane) = 0.23; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3409, 1656, 1640, 1587, 1455, 1396, 1098, 1001, 800, 774, 741, 699; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.32 (1H, d, *J* = 8.0 Hz) 7.86 (2H, d, *J* = 9.3 Hz), 7.73 (2H, dd, *J* = 7.3, 1.3 Hz), 7.60 - 7.51 (2H, m), 7.49 - 7.37 (5H, m), 5.87 (1H, d, *J* = 6.3 Hz), 2.37 (1H, d, 6.3 Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  140.7, 133.3, 133.1, 130.7, 129.1, 128.8, 128.5, 128.3, 126.9, 126.8, 126.5, 126.3, 126.1, 125.1, 93.6, 84.9, 65.4 ppm; HRMS (ES<sup>+</sup>) Cald for C<sub>19</sub>H<sub>15</sub>O [M+H]<sup>+</sup> 259.1123. Found 259.1130

#### 1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol



The title compound was prepared according to general procedure B, from **1a** (300 mg, 2.28 mmol) using 4-iodobenzotrifluoride (930 mg, 3.42 mmol),  $PdCI_2(PPh_3)_2$  (84.2 mg, 0.12 mmol), Cul (86.8 mg, 0.46 mmol) and triethylamine (11.4 mL). The crude product was loaded onto a column and chromatographed (5% EtOAc in hexane) to afford the title compound (503 mg, 80%) as a brown oil.

Rf (30% EtOAc in hexane) = 0.15; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 1677, 1639, 1499, 1240, 1035, 670 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.64 – 7.61 (2H, m), 7.59 (4H, s), 7.46 – 7.41 (2H, m), 7.41 – 7.36 (1H, m), 5.73 (1H, d, *J* = 6.0 Hz), 2.29 (1H, d, *J* = 6.2 Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  140.2, 132.0, 130.4 (q, <sup>2</sup>J<sub>C-F</sub> = 32.5 Hz), 128.8, 128.7, 126.7, 126.2 (q, <sup>4</sup>J<sub>C-F</sub> = 1.5 Hz), 125.3 (q, <sup>3</sup>J<sub>C-F</sub> = 3.7 Hz), 121.5 (q, <sup>1</sup>J<sub>C-F</sub> = 204.9 Hz) ppm; 91.1, 85.2, 65.1; HRMS (ES)<sup>+</sup> Cald for C<sub>15</sub>H<sub>12</sub>F<sub>3</sub>O [M+H]<sup>+</sup> 277.0840. Found 277.0840

#### (E)-1-(4-fluorophenyl)-3-phenylprop-2-en-1-ol (4b)



The title compound was prepared according to general procedure C, from the alkyne (579 mg, 2.74 mmol) using Red-Al (65% in PhMe) (1.59 mL, 5.20 mmol). The crude product was applied directly onto the top of a column and chromatographed (10% EtOAc in hexane) to afford **4b** (429 mg, 72%) as a clear oil.

Rf (10% EtOAc in hexane) = 0.12; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.41- 7.26 (7H, m), 7.08 – 7.05 (2H, m), 6.69 (1H, d, *J* = 16.0 Hz), 6.36 (1H, dd, *J* = 16.0, 6.0 Hz), 5.40 (1H, s), 2.01 (1H, s<sup>-13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  162.4 (d, <sup>1</sup>J<sub>C-F</sub> = 244.0 Hz), 138.5 (d, <sup>4</sup>J<sub>C-F</sub> = 4.0 Hz), 136.4, 131.3, 130.8, 128.6, 128.1 128.0 (d, <sup>3</sup>J<sub>C-F</sub> = 8.0 Hz), 126.6, 115.4 (d, <sup>2</sup>J = 21.0 Hz), 74.5 (d, <sup>5</sup>J<sub>C-F</sub> = 1.0 Hz) ppm. All spectral data were in agreement with those previously reported.<sup>9</sup>

<sup>&</sup>lt;sup>9</sup> N. Arai, K.Azuma, N. Nii and T. Ohkuma, *Angew. Chem. Int. Ed.* 2008, **47**, 7457.

#### (E)-1-(3,5-trifluoromethylphenyl)-3-phenylprop-2-en-1-ol (4c)



Mg turnings (63.2 mg, 2.60 mmol) and a single crystal of iodine was added to an oven dried round bottomed flask purged with argon. A condenser was fitted and Et<sub>2</sub>O (5.0 mL, 0.5M) added. This mixture was stirred for 10 minutes, after which 1-bromo-3,5-trifluorobenzene (0.41 mL, 2.40 mmol) was added. The reaction mixture was heated to reflux for 20 minutes and then cooled to room temperature until the majority of Mg turnings had disappeared. The formed Grignard was added dropwise to a cooled 0°C solution of cinnamaldehyde (0.25 mL, 2.00 mmol) in THF (5.0 mL, 0.5M). Once the addition was completed the reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched with sat. NH<sub>4</sub>Cl (20 mL) and extracted (2 x 20 mL) EtOAc, the combined organic layers were washed with H<sub>2</sub>O (20 mL) and brine (20 mL), dried over anhydrous MgSO<sub>4</sub> and concentrated. The crude product was applied to a column and chromatographed (15% EtOAc in hexane) to afford **4c** (348 mg, 50%) as a colourless oil.

Rf (10% EtOAc in hexane) = 0.28; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup>; 3323, 1375, 1278, 1172, 1133, 755; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 (2H, s), 7.81(1H, s), 7.42 – 7.23 (5H, m), 6.76 (1H, d, *J* = 16.0 Hz), 6.30 (1H, dd, *J* = 15.2, 7.2 Hz), 5.50 (1H, m, br), 2.23 (1H, d, J = 3.5 Hz<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  145.2, 135.7, 132.8, 131.8 (q, <sup>2</sup>*J*<sub>C-F</sub> = 33.0Hz), 129.8, 128.8, 128.5, 126.8, 126.4 (m), 124.7, 122.0, 121.6 (qn, <sup>3</sup>*J*<sub>C-F</sub> = 4.0 Hz), 74.3; HRMS (ES<sup>+</sup>) Cald for C<sub>17</sub>H<sub>13</sub>F<sub>6</sub>O [M+H]<sup>+</sup> 347.0871. Found 347.0868

(E)-1-(pyridin-3-yl)-3-phenylprop-2-en-1-ol (4e)



The title compound was prepared according to general procedure C, from the alkyne using Red-AI (0.6 mL, 0.198 mmol) and the crude product was purified by column chromatography (1:1 EtOAc and hexane) to afford the pure product **4e** (200 mg, 72%) as a clear oil.

Rf (10% EtOAc in hexane) = 0.06; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 1579, 1424, 1275, 1027, 967; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.67 (1H, s), 8.55 – 8.53 (1H, m), 7.79 – 7.76 (1H, m), 7.40 – 7.24 (6H, m), 6.72 (1H, d, *J* = 16.0 Hz), 6.35 (1H, dd, *J* = 16.0, 6.8 Hz), 5.45 (1H, d, *J* = 6.4 Hz), 2.42 (1H, s, br <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  149.1, 148.2, 136.1, 134.0, 131.6, 130.6, 128.7, 128.2, 126.7, 123.5, 73.1 HRMS (ES<sup>+</sup>) Cald for C<sub>14</sub>H<sub>14</sub>NO [M+H]<sup>+</sup> 212.1075. Found 212.1077.

#### (E)-3-(naphthalen-2-yl)-1-phenylprop-2-en-1-ol (4f)



The title compound was prepared according to general procedure C, from the alkyne using Red-AI (0.80 mL, 2.54 mmol). The crude mixture was applied directly onto the top of a column and chromatographed (10% EtOAc in hexane) to afford **4f** (244 mg, 74%) as a brown solid.

Rf (9:1 Hexane/EtOAc) =0.11;  $v_{max}$  (thin film) / cm<sup>-1</sup>; 3434, 1656, 1640, 1633, 775, 699; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.18 – 8.14 (1H, m), 7.90 – 7.77 (2H, m), 7.62 – 7.31 (11H, m), 6.46 (1H, dd, *J* = 15.3, 6.2 Hz), 5.53 (1H, d, *J* = 6.04 Hz), 2.15 (1H, s <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.8, 134.7, 134.3, 133.6, 131.2, 128.7, 128.5, 128.1, 127.9, 127.7, 126.4, 126.1, 125.8, 125.6, 124.0, 123.7, 75.3 HRMS (ES+) Calcd. for C<sub>19</sub>H<sub>17</sub>O [M+H]<sup>+</sup> 261.1279. Found. 261.1276.

#### (E)-1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (4g)



The title compound was prepared according to general procedure C, from the alkyne (265 mg, 0.959 mmol) using Red-Al (1.02 mL, 3.28 mmol). The crude mixture was

applied directly onto the top of a column and chromatographed (15% EtOAc in hexane) to afford **4g** (218 mg, 82%) as a colourless oil.

Rf (9:1 Hexane/EtOAc) =0.10;  $v_{max}$  (thin film) / cm<sup>-1</sup>; 3319, 1615, 1493, 1453, 1326, 1163, 1123, 1067, 700; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.59 – 7.47 (4H, m), 7.46 – 7.38 (4H, m), 7.35 – 7.31 (1H, m), 6.75 (1H, dd, *J* = 15.8, 1.0 Hz), 6.49 (1H, dd, *J* = 15.8, 6.0 Hz), 5.34 (1H, m), 2.06 (1H, d, *J* = 3.8 Hz <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.3, 134.1, 128.8, 128.8, 128.1, 126.7, 126.4, 125.5 (q, <sup>4</sup>*J*<sub>C-F</sub> = 3.6 Hz), 74.9 HRMS (ES+) Calcd. for C<sub>16</sub>H<sub>12</sub>OF<sub>3</sub> [M - H]<sup>+</sup> 277.0840. Found 277.0839.

(E)-1-phenyl-3-(4-(trifluoromethoxy)phenyl)prop-2-en-1-ol (4h)



The title compound was prepared according to general procedure C, from the alkyne (250 mg, 0.856 mmol) using Red-Al (0.53 mL, 1.71 mmol). The crude mixture was applied directly onto the top of a column and chromatographed (10% EtOAc in hexane) to afford **4h** (185 mg, 74%) as a brown solid.

Rf (9:1 Hexane/EtOAc) =0.23;  $v_{max}$  (thin film) / cm<sup>-1</sup>; 3339, 1508, 1263, 1219, 1164, 966, 670; <sup>1</sup>H NMR: $\delta$  7.46 – 7.29 (7H, m), 7.22 – 7.11 (2H, m), 6.69 (1H, dd, *J* = 15.8, 1.3 Hz), 6.38 (1H, dd, *J* = 16.0, 6.2 Hz), 5.40 (1H, dd, *J* = 6.4, 2.3 Hz), 2.05 (1H, d, *J* = 3.3 Hz <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  148.6 (q, <sup>3</sup>*J*<sub>C-F</sub> = 1.8 Hz), 142.5, 135.3, 132.5, 128.9, 128.7, 128.0, 127.8, 126.3, 121.1 (q, <sup>4</sup>*J*<sub>C-F</sub> = 0.7 Hz), 74.9 HRMS (ES+) Cald for C<sub>16</sub>H<sub>14</sub>F<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 295.0946. Found 295.0949.





The title compound was prepared according to general procedure C, from the alkyne (307 mg, 1.36 mmol) using Red-AI (0.83 mL, 2.72mmol). The crude product was applied directly onto the top of a column and chromatographed (10% EtOAc in hexane) to afford **4i** (250 mg, 81%) as a clear oil.

Rf (9:1 Hexane/EtOAc) =0.13;  $v_{max}$  (thin film) / cm<sup>-1</sup>; 3415, 1656, 1640, 1505, 1266, 1227, 1158, 834, 741, 701; H NMR: (400 MHz, CDCI<sub>3</sub>)  $\delta$ 7.46 – 7.43 (2H, m), 7.41 – 7.29 (5H, m), 7.04 – 6.97 (2H, m), 6.67 (1H, dd, *J* = 15.8, 1.0 Hz), 6.32 (1H, ddd, *J* = 15.8, 6.5, 0.5 Hz), 5.39 (1H, dd, *J* = 6.04, 3.8 Hz), 2.01 (1H, d, *J* = 3.8 Hz<sup>13</sup>C NMR (100 MHz, CDCI<sub>3</sub>):  $\delta$ = 162.4 (d, <sup>1</sup>*J*<sub>C-F</sub> = 245.4 Hz), 142.7, 132.7 (d, <sup>4</sup>*J*<sub>C-F</sub> = 3.3 Hz), 131.3 (d, <sup>5</sup>*J*<sub>C-F</sub> = 2.2 Hz), 129.4, 128.7, 128.1 (d, <sup>3</sup>*J*<sub>C-F</sub> = 8.0 Hz), 127.9, 126.3, 115.5 (d, <sup>2</sup>*J*<sub>C-F</sub> = 21.5 Hz), 75.1 HRMS (ES+) Calcd. for C<sub>15</sub>H<sub>12</sub>OF [M+H]<sup>+</sup> 227.0872. Found 227.0864.





The title compound was prepared according to general procedure C, from the alkyne (300 mg, 1.35 mmol) using Red-AI (0.84 mL, 2.70 mmol). The crude mixture was applied directly onto the top of a column and chromatographed (15% EtOAc in hexane) to afford **4j** (237 mg, 78%) as a colourless oil.

Rf (9:1 Hexane/EtOAc) =0.20;  $v_{max}$  (thin film) / cm<sup>-1</sup>; 3308, 3022, 2918, 2868, 1513, 1452, 1261, 968, 822, 759, 699; <sup>1</sup>H NMR: (400 MHz, CDCI<sub>3</sub>)  $\delta$  7.48 – 7.43 (2H, m), 7.42 – 7.36 (2H, m), 7.35 – 7.29 (3H, m), 7.16 – 7.11 (2H, m), 6.67 (1H, d, *J* = 15.8 Hz), 6.36 (1H, dd, *J* = 15.8, 6.5 Hz), 5.39 (1H, d, *J* = 6.5 Hz), 2.36 (3H, s), 2.10 (1H, s <sup>13</sup>C NMR (100 MHz, CDCI<sub>3</sub>)  $\delta$ 142.9, 137.6, 133.7, 130.6, 130.5, 129.2, 128.6, 127.7, 126.5, 126.3, 75.2, 21.2 HRMS (ES+) Calcd. for C<sub>16</sub>H<sub>15</sub>O [M-H]<sup>+</sup> 223.1123. Found 223.1121.





The title compound was prepared according to general procedure C, from the alkyne (222 mg, 0.93 mmol) using Red-Al (0.57 mL, 1.86 mmol). The crude product was applied directly onto the top of a column and chromatographed (20% EtOAc in hexane) to afford **2k** (300 mg, 73%) as a colourless oil.

Rf (9:1 Hexane/EtOAc) = 0.08; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.44 – 7.40 (2H, m), 7.39 – 7.34 (2H, m), 7.33 – 7.23 (3H, m), 6.86 – 6.81 (2H, m), 6.61 (1H, d, *J* = 15.9 Hz), 6.24 (1H, dd, *J* = 15.7, 6.6 Hz), 5.34 (1H, d, *J* = 6.9 Hz), 3.78 (3H, s), 2.16 (1H, s <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.3, 142.9, 130.2, 129.3, 129.2, 128.5, 127.8, 127.7, 126.3, 113.9, 75.3, 55.2 ppm. All spectral data were in agreement with those previously reported.<sup>10</sup>

(E)-1-phenyl-3-(pyridin-3-yl)prop-2-en-1-ol (4l)



In an clean, oven-dried round 5ml bottomed flask, purged with argon, a solution of Red-Al (65% in toluene) (0.69 mL, 2.25 mmol) was prepared in toluene (3 ml, 0.5 M) and cooled to 0°C. A THF solution (3 ml, 0.5 M) of the alkyne (304 mg, 1.50 mmol) was added dropwise and the reaction allowed to warm to room temperature and stir for 30 minutes. 2 M  $H_2SO_4$  (3.8 ml, 0.4 M) was then added dropwise (CAUTION: rapid evolution of hydrogen gas) and the resulting acidic solution was allowed to stir at room temperature for a further 2 hours. The biphasic solution was diluted with 10ml of distilled water and washed with 2x25 ml of toluene. The aqueous layer was brought to pH 5-6 by the dropwise addition of 3 M NaOH solution then to pH 8-9 by the dropwise addition of triethylamine. The basic solution was then filtered through a plug of celite and extracted with a further 2x25 ml of toluene. The combined toluene fractions were concentrated in vacuo and the crude product was purified by column chromatography (1:1 EtOAc and hexane) to afford **4l** (214 mg, 68%) as a clear oil.

Rf (3:1 Hexane:EtOAc) =0.09; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3200, 2925, 1416, 1026, 968, 700; <sup>1</sup>H NMR (400 MHz, CDCI<sub>3</sub>):  $\delta$  8.59 (1H, s), 8.46 – 8.44 (1H, m,) 7.71 – 7.68 (1H, m), 7.45- 7.21 (6H, m), 6.69 (1H, d, *J* = 16.0 Hz), 6.46 (1H, dd, *J* = 15.8, 6.0 Hz), 5.42 (1H, d, *J* = 6.0 Hz) <sup>13</sup>C NMR (100 MHz, CDCI<sub>3</sub>):  $\delta$  148.7, 148.5, 142.5, 133.9, 133.0, 132.3, 128.8,128.1, 126.6, 126.4, 123.5, 74.9; HRMS (ES+) Cald for C<sub>14</sub>H<sub>14</sub>NO [M+H]<sup>+</sup> 212.1075. Found 212.1081

<sup>&</sup>lt;sup>10</sup> W. Xu, Y. Zhou, R. Wang, G. Wu and P. Chen, *Org. Biomol. Chem*, 2012, **10**, 367.

#### 2-((dimethyl(phenyl)silyl)methyl)-1-phenylpent-4-en-1-one (3a)



The title compound was prepared according to general procedure C from **1a** (202 mg, 0.753 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (45 mg, 1.13 mmol) and allyl bromide (137 mg, 1.13 mmol) in THF (7.5 mL) which following conversion to the allylated product and column chromatography (4:1 hexane/  $CH_2Cl_2$ ) afforded **3a** as a colourless oil (133 mg, 57%)

Rf (9:1 hexane-ethyl acetate) = 0.68; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3369, 3069, 2954, 1683, 1447, 1227, 1245, 1123, 835; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$ 7.85 – 7.81 (2H, m), 7.58 – 7.50 (3H, m), 7.46 – 7.34 (5H, m), 5.73 (1H, m), 5.02 (1H, m), 4.99 (1H, m), 3.58 (1H, m), 2.56 (1H, m), 2.23 (1H, m), 1.42 (1H, dd, *J* = 15.0, 8.0 Hz), 1.07 (1H, dd, *J* = 14.8, 5.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  203.3, 138.6, 136.7, 135.7, 133.6, 132.8, 129.0, 128.5, 128.2, 127.8, 118.8, 41.6, 39.1, 18.1, -2.0, -2.5; HRMS (EI+) Calcd. for C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>Si [M]<sup>+</sup> 308.1596. Found 308.1617

#### 2-((dimethyl(phenyl)silyl)methyl)-1-(naphthalen-1-yl)pent-4-en-1-one (3b)



The title compound was prepared according to general procedure C from **1b** (53 mg, 0.167 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (10 mg, 0.260 mmol) and allyl bromide (31 mg, 0.254 mmol) in THF (1.9 mL) which following conversion to the allylated product and column chromatography (4:1 hexane/ $CH_2Cl_2$ ) afforded **3b** as a colourless oil (29 mg, 48%).

Rf (9:1 hexane-ethyl acetate) = 0.71; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3447, 1675, 1628, 1250, 1186, 1113, 884, 734, 701; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.21 – 8.20 (1H, m), 7.94 – 7.84 (4H, m), 7.63 – 7.52 (2H, m), 7.52 – 7.47 (2H, m), 7.40 – 7.31 (2H, m),

5.72 (1H, m), 4.98 (1H, m), 3.68 (1H, m), 2.57 (1H, m), 2.25 (1H, m), 1.41 (1H, dd, J = 14.8, 8.0 Hz), 1.07 (1H, dd, J = 14.8, 5.8 Hz), 0.32 (3H, s), 0.26 (3H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  203.4, 138.6, 135.7, 135.5, 134.0, 133.7, 232.5, 129.7, 129.6, 129.1, 128.4, 128.3, 127.9, 127.8, 126.6, 124.3, 116.9, 41.7, 39.4, 18.5, -1.9, -2.5; HRMS (EI+) Calcd. for C<sub>23</sub>H<sub>23</sub>OSi [M-CH<sub>3</sub>]<sup>+</sup> 343.1518. Found 343.1550

#### 2-((dimethyl(phenyl)silyl)methyl)-1-(3-fluorophenyl)pent-4-en-1-one (3c)



The title compound was prepared according to general procedure C from **1c** (55.0 mg, 0.192 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (12 mg, 0.288 mmol) and allyl bromide (35 mg, 0.288 mmol) in THF (1.9 mL) which following conversion to the allylated product and column chromatography (15%  $CH_2Cl_2$  in hexane) afforded **3c** as a colourless oil (12 mg, 23%).

Rf (9:1 hexane-ethyl acetate) = 0.70; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3390, 1687, 1588, 1440, 1253, 1113, 836, 602; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 – 7.40 (4H, m), 7.39 – 7.29 (4H, m), 7.25 – 7.19 (1H, m), 5.65 (1H, m), 4.98 (1H, m), 4.94 (1H, m), 3.43 (1H, m), 2.48 (1H, m), 2.17 (1H, m), 1.33 (1H, dd *J* = 14.8, 7.8Hz), 1.00 (1H, dd, *J* = 14.8, 5.8 Hz), 0.29 (3H, s), 0.26 (3H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  202.1, 162.8 (d, <sup>1</sup>*J*<sub>C-F</sub> = 246.1 Hz), 138.8 (d, <sup>3</sup>*J*<sub>C-F</sub> = 5.8 Hz), 135.3, 133.6, 130.1 (d, <sup>3</sup>*J*<sub>C-F</sub> = 7.7 Hz), 129.1, 127.8, 123.8 (d, <sup>4</sup>*J*<sub>C-F</sub> = 2.9 Hz), 119.7 (d, <sup>2</sup>*J*<sub>C-F</sub> = 21.5 Hz), 117.1, 115.0 (d, <sup>2</sup>*J*<sub>C-F</sub> = 21.9 Hz), 42.0, 39.1, 18.2, -2.0, -2.5; HRMS (EI+) Calcd for C<sub>20</sub>H<sub>23</sub>OFSi [M]<sup>+</sup> 326.1502. Found 326.1510

#### 2-benzyl-1-phenylpent-4-en-1-one (5a)



The title compound was prepared according to general procedure D from commercially available *trans*-1,3-diphenyl-2-propan-1-ol (58 mg, 0.274 mmol),

sodium hydride (60% suspension in mineral oil; unwashed) (16 mg, 0.411 mmol) and allyl bromide (50 mg, 0.411 mmol) in THF (2.7 mL) which following conversion to the allylated product and column chromatography (15%  $CH_2Cl_2$  in hexane) afforded **5a** as a colourless oil (23.9 mg, 35%).

Rf (9:1 hexane-ethyl acetate) = 0.71; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3400, 3027, 1680, 1447, 1235, 918, 741, 699; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 – 7.84 (2H, m), 7.56 – 7.50 (1H, m), 7.46 – 7.39 (2H, m), 7.28 – 7.13 (5H, m), 5.76 (1H, m), 5.03 (2H7, m), 3.82 (1H, ddd, *J* = 13.8, 7.56, 6.3 Hz), 3.13 (1H, dd, *J* = 13.8, 7.8 Hz), 2.83 (1H, dd, *J* = 13.8, 6.5 Hz), 2.56 (1H, dddd, *J* = 14.3, 7.0, 1.2, 1.2 Hz), 2.32 (1H, dddd, *J* = 13.0, 7.3, 2.24, 1.2 Hz) 0.28 (3H, s), 0.25 (3H, s <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  203.0, 140.0, 137.2, 135.2, 132.9, 129.0, 128.5, 128.4, 128.2, 126.2, 117.1, 48.0, 37.6, 36.2; HRMS (ES+) Calcd. for C<sub>18</sub>H<sub>19</sub>O [M+H]<sup>+</sup> 251.1436. Found 251.1444.

#### 2-benzyl-1-(4-fluorophenyl)pent-4-en-1-one (5b)



The title compound was prepared according to general procedure D from **4b** (48 mg, 0.211 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (13 mg, 0.317 mmol) and allyl bromide (38 mg, 0.317 mmol) in THF (2.1 mL) which following conversion to the allylated product and column chromatography (15%  $CH_2Cl_2$  in hexane) afforded **5b** as a colourless oil (25 mg, 44%).

Rf (9:1 hexane-ethyl acetate) = 0.76; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3071, 2923, 2857, 1648, 1588, 1441, 1255, 743, 700; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$ 7.63 – 7.58 (1H, m), 7.53 – 7.49 (1H, m), 7.42 – 7.35 (1H, m), 7.26 – 7.14 (6H, m), 5.73 (1H, m), 5.03 (2H, m), 3.74 (1H, m), 3.09 (1H, dd, J = 13.8, 8.0 Hz), 2.83 (1H, dd, J = 13.8, 6.3 Hz), 2.54 (1H, dddd, J = 14.3, 7.0, 1.3, 1.2 Hz), 2.32 (1H, dddd, J = 13.0, 6.0, 1.4, 1.0 <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ 201.9, 162.8 (d, <sup>1</sup> $J_{C-F} = 246.5$  Hz), 139.3 (d, <sup>3</sup> $J_{C-F} = 5.9$  Hz), 134.9, 130.1 (d, <sup>3</sup> $J_{C-F} = 7.8$  Hz), 129.0, 128.4, 126.3, 123.8 (d, <sup>4</sup> $J_{C-F} = 2.9$  Hz), 119.9 (d, <sup>2</sup> $J_{C-F} = 21.4$  Hz), 117.4, 114.9 (d, <sup>2</sup> $J_{C-F} = 22.2$  Hz), 48.3, 37.7, 38.3 ppm; HRMS (ES+) Calcd. for C<sub>18</sub>H<sub>18</sub>OF [M+H]<sup>+</sup> 269.1342. Found 269.1339.

2-benzyl-1-(3,5-bis(trifluoromethyl)phenyl)pent-4-en-1-one (5c)



The title compound was prepared according to general procedure D from **4c** (48 mg, 0.211 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (13 mg, 0.317 mmol) and allyl bromide (38 mg, 0.317 mmol) in THF (2.1 mL) which following conversion to the epoxide and column chromatography (15%  $CH_2Cl_2$  in hexane) afforded **5c** as a colourless oil (39 mg, 48%).

Rf (9:1 hexane-ethyl acetate) = 0.89; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3399, 1694, 1357, 1279, 1178, 1137, 906, 746, 699, 682; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.10 – 8.08 (2H, m), 7.97 – 7.95 (1H, m), 7.25 – 7.18 (2H, m), 7.17 – 7.11 (3H, m), 5.74 (1H, m), 5.07 (2H, m), 3.76 (1H, m), 3.05 (1H, dd, J = 22.8, 9.3 Hz), 2.95 (1H, dd, J = 13.5, 5.8 Hz), 2.60 (1H, dddd, J = 14.3, 7.3, 1.0, 1.0 Hz), 2.40 (1H, dddd, J = 12.8, 5.8, 1.2, 1.2 Hz <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  201.1, 139.1, 138.7, 134.5, 132.1 (q, <sup>2</sup> $_{J C-F} = 33.9$  Hz), 128.9, 128.7, 128.0 (m), 126.7, 125.9, (q, <sup>3</sup> $_{J C-F} = 3.7$  Hz), 122.8 (q, <sup>1</sup> $_{J C-F} = 270.9$  Hz), 118.0, 49.0, 38.6, 36.6; HRMS (ES+) C<sub>20</sub>H<sub>17</sub>F<sub>6</sub>O [M+H]<sup>+</sup> 387.1184. Found 387.1179.

#### 2-benzyl-1-(furan-2-yl)pent-4-en-1-one (5d)



The title compound was prepared according to general procedure D from previously reported alkene (50 mg, 0.249 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (15 mg, 0.374 mmol) and allyl bromide (45 mg, 0.374 mmol) in THF (2.5 mL) which following conversion to the epoxide and column chromatography (15%  $CH_2Cl_2$  in hexane) afforded **5d** as a colourless oil (20mg, 34%).

Rf (9:1 hexane-ethyl acetate) = 0.57; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3133, 3064, 3028, 2925, 1791, 1761, 1733, 1671, 1566, 1466, 1262, 1163, 1015, 916, 763, 700; <sup>1</sup>H

NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$ 7.56 – 7.53 (1H, m), 7.30 – 7.13 (5H, m), 6.49 – 6.46 (1H, m), 5.75 (1H, m), 5.04 (1H, m), 3.57 (1H, m), 3.07 (1H, dd, *J* = 13.6, 8.0 Hz), 2.81 (1H, dd, *J* = 13.8, 6.5 Hz), 2.54 (1H, dddd, *J* = 14.3, 7.0, 1.3, 1.2 Hz), 2.31 (1H, dddd, *J* = 13.0, 5.8, 1.3, 1.2 Hz<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 191.7, 152.8, 146.5, 139.4, 135.2, 129.0, 128.3, 126.2, 117.6, 117.1, 112.2, 48.9, 37.5, 35.9; HRMS (ES+) Calcd. for C<sub>16</sub>H<sub>17</sub>O<sub>2</sub> [M+H]<sup>+</sup> 241.1229. Found 241.1220.

2-benzyl-1-(pyridin-3-yl)pent-4-en-1-one (5e)



The title compound was prepared according to general procedure C from **4e** (35 mg, 0.166 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (10.0 mg, 0.249 mmol) and allyl bromide (31 mg, 0.249 mmol) in THF (1.7 mL) which following conversion to the allylated product and purification through a plug of silica (eluent 30% EtOAc in hexane) afforded **5e** as a colourless oil (15 mg, 35%).

Rf 0.19; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 2924, 1684, 1584, 1417, 1244, 701; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 9.01 - 8.97$  (1H, m), 8.73 - 8.68 (1H, m), 8.06 - 8.03 (1H, m), 7.36 - 7.12 (6H, m), 5.71 (1H, ddt, J = 17.2, 10.0, 6.8 Hz), 5.00 - 4.97 (2H, m), 3.80 - 3.73 (1H, m), 3.08 (1H, dd, J = 13.6, 8.4 Hz), 2.86 (1H, dd, J = 13.6, 6.0 Hz), 2.59 - 2.52 (1H, m), 2.37 - 2.31 (1H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 202.2$ , 153.2, 149.6, 139.1, 135.5, 134.8, 128.9, 128.5, 127.5, 126.5, 123.5, 117.6, 48.8, 37.9, 36.4; HRMS (ES+) Calcd. for C<sub>17</sub>H<sub>18</sub>NO [M + H]<sup>+</sup> 252.1388. Found 252.11389.





The title compound was prepared according to general procedure D from **4f** (48 mg, 0.184 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (11 mg, 0.276 mmol) and allyl bromide (33 mg, 0.276 mmol) in THF (1.8 mL) which following conversion to the allylated product and column chromatography (15%  $CH_2Cl_2$  in hexane) afforded **5f** as a colourless oil (28 mg, 50%).

Rf (9:1 hexane-ethyl acetate) = 0.69; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3438, 1655, 1640, 1633, 1265, 778, 738, 703; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ 8.10 – 8.05 (1H, m), 7.88 – 7.82 (1H, m), 7.74 – 7.65 (3H, m), 7.59 – 7.43 (3H, m), 7.35 – 7.29 (4H, m), 5.81 (1H, m), 5.07 (2H, m), 4.01 (1H, m), 3.52 (1H, dd. *J* = 14.1, 8.0 Hz), 3.87 (1H, dd, *J* = 14.0, 6.0 Hz), 2.65 (1H, m), 2.40 (1H, m); ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) β 203.4, 137.3, 135.6, 135.1, 133.9, 132.8, 131.8, 128.9, 128.4, 128.0, 127.5, 127.1, 126.0, 125.4, 125.4, 123.5, 117.5, 46.7, 40.0, 34.6; HRMS (ES+) Cald. for C<sub>22</sub>H<sub>21</sub>O [M+H]<sup>+</sup> 301.1592. Found 301.1601

#### 1-phenyl-2-(4-(trifluoromethyl)benzyl)pent-4-en-1-one (5g)



The title compound was prepared according to general procedure D from **4g** (52mg, 0.186 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (12 mg, 0.288 mmol) and allyl bromide (36 mg, 0.288 mmol) in THF (1.9 mL) which following conversion to the allylated product and column chromatography (5% EtOAc in hexane) afforded **5g** as a colourless oil (41 mg, 69%).

Rf (9:1 hexane-ethyl acetate) = 0.64; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 2928, 1682, 1448, 1326, 1265, 1164, 1122, 1067, 739, 701; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) 7.87 – 7.82 (2H, m), 7.57 – 7.51 (1H, m), 7.51 – 7.39 (4H, m), 7.31 – 7.27 (2H, m), 5.76 (1H, m), 5.06 (2H, m), 3.81 (1H, m), 3.19 (1H, dd, J = 13.8, 8.3 Hz), 2.90 (1H, dd, J = 13.8, 5.8 Hz), 2.54 (1H, dddd, J = 14.0, 6.8, 1.3, 1.2 Hz), 2.31 (1H, dddd, J = 13.8, 6.3, 1.2, 1.0 Hz <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 202.2, 143.9 (q, <sup>4</sup> $J_{C-F} = 1.5$  Hz), 136.9, 134.8, 133.1, 129.4, 128.7, 128.6 (q, <sup>2</sup> $J_{C-F} = 32.1$  Hz), 128.2, 125.3 (q <sup>3</sup> $J_{C-F} = 3.7$  Hz) 124.1 (q, <sup>1</sup> $J_{C-F} = 270$  Hz), 117.6, 47.7, 37.0, 36.5; HRMS (ES+) Calcd. for C<sub>15</sub>H<sub>10</sub>OF [M+H]<sup>+</sup> 225.0716. Found 225.0713.

#### 1-phenyl-2-(4-(trifluoromethoxy)benzyl)pent-4-en-1-one (5h)



The title compound was prepared according to general procedure D from **4h** (53 mg, 0.179 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (11 mg, 0.269 mmol) and allyl bromide (32 mg, 0.269 mmol) in THF (1.8 mL) which following conversion to the allylated product and column chromatography (15%  $CH_2Cl_2$  in hexane) afforded **5h** as a colourless oil (32 mg, 51%).

Rf (9:1 hexane-ethyl acetate) = 0.63; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3435, 1679, 1441, 1509, 1449, 1261, 1223, 1164, 1019, 920; <sup>1</sup>H NMR: (300 MHz, CDCl<sub>3</sub>)  $\delta$ 7.99-7.93 (1H, m), 7.85-7.79 (2H, m), 7.61-7.36 (4H, m), 7.19-7.04 (2H, m), 5.82-5.66 (1H, m), 5.09-5.00 (2H, m), 3.83-3.71 (1H, m), 3.16-3.04 (1H, m), 2.83 (1H, dd, *J* = 13.8, 5.8 Hz), 2.59-2.47 (1H, m), 2.32-2.24 (1H, m) <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  203.0, 138.8, 135.3, 133.5, 130.7, 129.0, 128.6, 121.4, 117.9, 98.3, 37.1, 36.9, 11.0 ;HRMS (ES+) Cald. for C<sub>19</sub>H<sub>18</sub>F<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 335.1259. Found 335.1266

#### 2-(4-fluorobenzyl)-1-phenylpent-4-en-1-one (5i)



The title compound was prepared according to general procedure D from **4i** (53 mg, 0.234 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (14 mg, 0.351 mmol) and allyl bromide (42 mg, 0.351 mmol) in THF (2.3 mL) which following conversion to the allylated product and column chromatography (15%  $CH_2Cl_2$  in hexane) afforded **5i** as a colourless oil (31 mg, 49%).

Rf (9:1 hexane-ethyl acetate) = 0.68; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3434, 1657, 1640, 1510, 1222, 703; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$ 7.86 – 7.82 (2H, m), 7.56 – 7.51 (1H, m), 7.45 – 7.39 (2H, m), 7.16 – 7.09 (2H, m), 6.95 – 6.87 (2H, m), 5.75 (1H, m), 5.03 (2H, m), 3.77 (1H, m), 3.09 (1H, dd, J = 13.8, 8.3 Hz), 2.81 (1H, dd, J = 13.8, 6.0

Hz), 2.53 (1H, dddd, J = 14.0, 7.0, 1.3, 1.2 Hz), 2.30 (1H, dddd, J = 13.3, 6.3, 1.0, 1.0 Hz <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  202.8, 161.4 (d, <sup>1</sup> $J_{C-F} = 242$  Hz), 137.2, 135.3 (d, <sup>4</sup> $J_{C-F} = 3.3$  Hz), 133.0, 130.4 (d, <sup>3</sup> $J_{C-F} = 7.7$  Hz), 128.6, 128.1, 117.3, 115.1 (d, <sup>1</sup> $J_{C-F} = 20.8$  Hz), 48.1, 36.7, 36.4; HRMS (ES+) Cald for C<sub>18</sub>H<sub>18</sub>FO [M+H]<sup>+</sup> 269.1342. Found 269.134

#### 2-(4-methylbenzyl)-1-phenylpent-4-en-1-one (5j)



The title compound was prepared according to general procedure D from **4j** (40.0 mg, 0.216 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (13 mg, 0.324 mmol) and allyl bromide (39 mg, 0.324 mmol) in THF (2.1 mL) which following conversion to the allylated product and column chromatography (15%  $CH_2Cl_2$  in hexane) afforded **5j** as a colourless oil (29 mg, 51%).

Rf (9:1 hexane-ethyl acetate) = 0.84; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3059, 3022, 2922, 1681, 1515, 1447, 1236, 1206, 951, 918, 689, 546; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 – 7.85 (2H, m), 7.56 – 7.50 (1H, m), 7.46 – 7.39 (2H, m), 7.09 – 7.02 (4H, m), 5.74 (1H, m), 5.01 (2H, m), 3.79 (1H, ddd, *J* = 13.3, 6.8, 0.7 Hz), 3.08 (1H, dd, *J* = 13.7, 7.3 Hz), 2.78 (1H, dd, *J* = 13.8, 6.8 Hz), 2.53 (1H, dddd, *J* = 14.3, 7.3, 1.2, 1.2 Hz), 2.30 (1H, m), 2.29 (3H, m <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  203.0, 137.2, 136.5, 135.7, 135.3, 132.8, 129.1, 128.9, 128.5, 128.2, 117.0, 48.1, 37.2, 36.1, 21.0; HRMS (ES+) Calcd. for C<sub>19</sub>H<sub>21</sub>O [M+H]<sup>+</sup> 265.1592. Found 265.1577.

#### 2-(4-methoxybenzyl)-1-phenylpent-4-en-1-one (5k)



The title compound was prepared according to general procedure D from **4k** (52 mg, 0.216 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (13 mg, 0.324 mmol) and allyl bromide (39 mg, 0.324 mmol) in THF (2.1 mL) which following

conversion to the allylated product and column chromatography (15%  $CH_2CI_2$  in hexane) afforded **5k** as a colourless oil (22 mg, 37%).

Rf (8% Et<sub>2</sub>O in hexane) = 0.36; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 2921, 1681, 1513, 1247, 1036, 700; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.86 – 7.83 (2H, m), 7.53 – 7.50 (1H, m), 7.43 – 7.39 (2H, m), 7.09 – 7.07 (2H, m), 6.78 – 6.76 (2H, m), 5.73 (1H, ddt, J = 17.2, 10.4, 7.2 Hz), 5.04 – 4.97 (2H, m), 3.74 (3H, s), 3.04 (1H, dd, J = 14.0, 7.6 Hz), 2.75 (1H, dd, J = 14.0, 6.4 Hz), 2.55 – 2.48 (1H, m), 2.32 – 2.25 (1H, m<sup>-13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 203.2, 158.1, 137.3, 135.4, 132.4, 131.7, 130.0, 128.6, 128.2, 117.1, 113.8, 55.2, 48.3, 36.8, 36.2; HRMS (ES+) Calcd. for C<sub>19</sub>H<sub>21</sub>O<sub>2</sub> [M+H]<sup>+</sup> 281.1542. Found 281.1545.

1-phenyl-2-(pyridin-3-ylmethyl)pent-4-en-1-one (5l)



The title compound was prepared according to general procedure C from **4I** (33 mg, 0.154 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (9 mg, 0.231 mmol) and allyl bromide (28 mg, 0.231 mmol) in THF (1.5 mL) which following conversion to the allylated product and purification on silica gel (eluent 30% EtOAc in hexane) afforded **5I** as a colourless oil (16 mg, 42%).

Rf (7:3 hexane-ethyl acetate) = 0.26; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3061, 2925, 2854, 1680, 1576, 1479, 1448, 1424, 1235, 919, 712, 688; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) 8.48 – 8.44 (1H, m), 8.42 – 8.38 (1H, m), 7.87 – 7.82 (2H, m), 7.58 – 7.39 (4H, m), 7.17 – 7.11 (1H, m), 5.75 (1H, m), 5.06 (2H, m), 3.80 (1H, m), 3.12 (1H, dd, *J* = 14.0, 8.5 Hz), 2.85 (1H, dd, *J* = 14.0, 5.8 Hz), 2.55 (1H, m), 2.32 (1H, m) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 202.2, 150.3, 147.7, 136.8, 136.6, 135.1, 134.6, 133.2, 128.7, 128.2, 123.2, 117.7, 47.6, 36.5, 34.3; HRMS (ES+) Calcd. for C<sub>17</sub>H<sub>18</sub>NO [M+H]<sup>+</sup> 252.1388. Found 252.1372.

#### 2-benzyl-1-phenylhex-4-en-1-one (6)



The title compound was prepared according to general procedure C from commercially available *trans*-1,3-diphenyl-2-propan-1-ol (250 mg, 1.19 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (71 mg, 1.78 mmol) and crotyl bromide (301 mg, 1.78 mmol) in THF (12 mL) which following conversion to the allylated product and purification on silica gel (10%  $CH_2Cl_2$  in Hexane) afforded **6** as a colourless oil (138mg, 44%).

Rf (50:50 CH<sub>2</sub>Cl<sub>2</sub>-Hexane) = 0.35; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3401, 3025, 1690, 1447, 1229, 699; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85-7.80 (2H, m), 7.52-7.45 (1H, m), 7.41-7.35 (2H, m), 7.24-7.09 (5H, m), 5.54-5.28 (2H, m), 3.81-3.69 (1H, m), 3.16-3.04 (1H,m), 2.85-2.75 (1H, m), 2.54-2.39 (1H, m), 2.36-2.15 (1H, m), 1.57 (2.55, dd, J = 6.0, 1.2 Hz, major), 1.53 (0.45H, dt, J = 6.8, 0.8 Hz, minor) <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  203.4 (minor), 203.3 (major), 140.0 (major), 139.9 (minor), 137.4 (major), 137.4 (minor), 132.8 (minor), 132.8 (major), 129.1 (major), 129.1 (minor), 128.5, 128.4 (minor), 128.4 (major), 128.2, 127.8 (major), 127.7 (major), 126.9 (minor), 126.3, 126.2 (minor), 126.2 (major), 48.6 (major), 48.5 (minor), 3737 (minor), 37.5 (major), 35.4 (major), 29.7 (minor), 17.9 (major), 12.8; HRMS (ES+) Calcd. for C<sub>19</sub>H<sub>20</sub>O [M]<sup>+</sup> 264.1514. Found 264.1519.

#### (E)-1-bromo-2-methylbut-2-ene

(*E*)-1-bromo-2-methylbut-2-ene was prepared according to the method laid out by Gademann.<sup>11</sup> Tiglic acid (9.01 g, 90.0 mmol) was added portionwise to a slurry of lithium aluminium hydride (10 g, 270 mmol) in diethyl ether (120 ml, 0.75 M) at 0°C and stirred for 2 hours. The solution was carefully quenched with saturated Na<sub>2</sub>SO<sub>4</sub> solution, filtered and the remaining aqueous layer was removed. The ethereal layer

<sup>&</sup>lt;sup>11</sup> S. Bonazzi, S. Güttinger, I. Zemp, U. Kutay and K. Gademann, *Angew. Chem. Int. Ed.* 2007, 46, 8707.

was concentrated on a rotary evaporator at atmospheric pressure (water bath temperature 45°C). The remaining ether and water were distilled off leaving behind the crude alcohol.

The crude alcohol (1.13 g, 13.1 mmol) was then dissolved in diethyl ether (26.2 ml, 0.5 M) and cooled to 0°C followed by dropwise addition of phosphorus tribromide (0.50 ml, 6.55 mmol). The solution was stirred at 0°C for 30 mins then allowed to warm to room temperature and stir for 3 hours. The mixture was quenched with a saturated solution of  $K_2CO_3$  and washed with brine and dried over anhydrous MgSO<sub>4</sub>. The Et<sub>2</sub>O was carefully distilled off under atmospheric pressure followed by distillation under reduced pressure to afford the bromide as a colourless oil (~10% unknown impurity).

IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3429, 2923, 2852, 1440; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.70 (1H, q, *J* = 6.8 Hz), 3.99 (2H, s), 1.76 (3H, s), 1.64 (3H, 6.8 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  132.7, 125.8, 41.8, 14.3, 13.9.<sup>11</sup>

#### (E)-2-benzyl-4-methyl-1-phenylhex-4-en-1-one



The title compound was prepared according to general procedure D from commercially available *trans*-1,3-diphenyl-2-propan-1-ol (100 mg, 0.475 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (27 mg, 0.686 mmol) and bromide **9** (112 mg, 0.686 mmol) in THF (4.8 mL) which following conversion to the epoxide and column chromatography (15%  $CH_2CI_2$  in hexane) afforded **7** as a colourless oil (32 mg, 24%).

Rf (9:1 hexane-ethyl acetate) = 0.75; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3448, 168-, 1641, 1633, 1447, 1232, 945, 750, 699, 500; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$ 7.83 – 7.78 (2H, m), 7.53 – 7.47 (1H, m), 7.43 – 7.36 (2H, m), 7.25 – 7.10 (5H, m), 5.26 (1H, dq, J = 6.5, 1.0 Hz), 3.90 (1H, m), 3.10 (1H, dd, J = 13.8, 8.8 Hz), 2.77 (1H, dd, J = 13.8, 5.5 Hz), 2.50 (1H, dd, J = 13.8, 7.0 Hz), 2.19 (1H, dd, J = 13.6, 7.0 Hz), 1.59 (3H, s), 1.50 (3H, d, J = 6.8 Hz) <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  203.8, 140.1, 137.6, 132.6,

132.5, 129.0, 128.4, 128.3, 128.0, 126.0, 121.7, 46.9, 42.7, 37.7, 15.8, 13.4 ppm; HRMS (ES+) Cald for  $C_{20}H_{23}O [M+H]^+$  279.1749. Found 279.1761

#### 1-deutero-(E)-3-(dimethyl(phenyl)silyl)-1-phenylprop-2-en-1-ol (1-D-1a) (9)



The title compound was prepared according to general procedure A, from 1-deutero-1-phenyl-2-propyn-2-ol (608 mg, 4.57 mmol) and dimethylphenylsilane (920 mg, 6.75 mmol) using  $PtCl_2$  (12 mg, 0.0455 mmol) and XPhos (44 mg, 0.0919 mmol) in THF (1 mL) which the following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **1-D-1a** (920 mg, 75%) as a colourless oil.

Rf (9:1 Hexane/EtOAc) =0.24;  $v_{max}$  (thin film) / cm<sup>-1</sup>; 3401, 1620, 1427, 1248, 1114, 843, 731, 698; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$ 7.55 - 7.51 (2H, m), 7.43 – 7.29 (8H, m), 6.31 (1H, d, *J* = 18.6 Hz), 6.17 (1H, d, *J* = 18.8 Hz), 1.95 (1H, s), 0.38 (3H, s), 0.37 (3H, s <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ 148.8, 142.4, 138.4, 133.8, 129.0, 128.6, 127.8, 127.4, 126.5, 76.3 (t, *J* = 22.2), -2.7; HRMS (ES+) Calcd. for C<sub>17</sub>H<sub>19</sub>DOSi [M]<sup>+</sup> 292.1244. Found 292.1234.

#### 1-deutero-2-((dimethyl(phenyl)silyl)methyl)-1-phenylpent-4-en-1-one (10)



The title compound was prepared according to general procedure D from **9** (43 mg, 0.159 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (8.5 mg, 0.208 mmol) and allyl bromide (21 mg, 0.239 mmol) which following conversion to the allylated product and column chromatography (15%  $CH_2CI_2$  in hexane) afforded **1-D-3a** as a colourless oil (8mg, 13%). 40% deuterium incorporation.

Rf (9:1 hexane-ethyl acetate) = 0.67; IR:  $v_{max}$  (thin film) / cm<sup>-1</sup> 3068, 2954, 2925, 1682, 1447, 1249, 1113, 915, 834, 701; <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.79 – 7.75

(2H, m), 7.56 – 7.51 (1H, m), 7.49 – 7.45 (2H, m), 7.43 – 7.37 (2H, m), 7.37 – 7.30 (3H, m), 5.67 (1H, m), 4.97 (1H, m), 4.93 (1H, m), 3.50 (1H, q, J = 6.8 Hz), 2.49 (1H, dddd, J = 14.0, 7.0, 1.2, 1.2 Hz), 2.17 (1H, m), 1.34 (0.79H, m), 1.00 (0.61H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  203.3, 138.6, 136.7, 135.6, 133.6, 132.8, 129.0, 128.5, 128.2, 127.8, 116.8, 41.6, 39.1, 30.3 (weak) -2.0, -2.5; HRMS (ES+) Calcd for C-<sub>20</sub>H<sub>24</sub>OSi [M]<sup>+</sup> 308.1596. Found 308.1603. Calcd for C<sub>20</sub>H<sub>23</sub>DOSi [M]<sup>+</sup> 309.1675. Found 309.1675. Ratio 3:2.

# Spectral Appendix















Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry This journal is C The Royal Society of Chemistry 2013



































170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 Chemical Shift (ppm)







































