## **General Experimental**

## Chemicals

All reagents were purchased from Merck or AlfaAesar and were used as received without further purification unless otherwise stated. All ethers were freshly distilled and degassed before usage in the reactions described below to remove radical inhibitors such as BHT.

## Chromatography

All reactions were monitored by thin-layer chromatography (TLC) on pre-coated silica gel plates. Silica get plates were initially examined under short wave UV light and then developed using aqueous potassium permanganate stain. Flash column chromatography was carried out with pre-loaded GraceResolv<sup>TM</sup> flash cartridges on a Biotage® Isolera Spektra One flash chromatography system.

## Spectroscopy

Quoted yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated. <sup>1</sup>H NMR spectra were recorded at 400, 500 600 or 700 MHz and <sup>13</sup>C NMR at 126, 151 or 176 MHz on a Bruker Avance III 600 or Bruker Avance Neo 700 spectrometer. The chemical shifts ( $\delta$ ) for <sup>1</sup>H and <sup>13</sup>C are quoted relative to residual signals of the solvent on the parts per million (ppm) scale. In the case of multiple rotamers, only the major has been assigned. Coupling constants (*J* values) are reported in Hertz (Hz) and are reported as *J*<sub>H-H</sub>. Signal multiplicities in <sup>13</sup>C NMR were determined using the distortionless enhancement by polarisation transfer (DEPT) spectral editing technique.

## LCMS used for kinetic isotope effect experiments

LCMS was performed using a Waters Acquity uPLC connected to Waters Acquity Single Quad Detector (SQD). All samples were run with the following parameters. Column: Hypersil Gold C4, 1.9  $\mu$ m, 2.1  $\mu$ m × 50  $\mu$ m. Wavelength: 254 nm. Mobile Phase: 50:50 Water (0.1% Formic Acid): MeCN (0.1% Formic Acid) Gradient over 4 min (to 5:95 Water (0.1% Formic Acid): MeCN (0.1% Formic Acid). Flow Rate: 0.6 mL/min. MS Mode: ES+. Scan Range: m/z = 150 – 300. Scan time: 0.25 s. Data obtained in continuum mode. The electrospray source of the MS was operated with a capillary voltage of 3.5 kV and a cone voltage of 50 V. Nitrogen was used

as the nebulizer and desolvation gas at a total flow of 600 L/h. Ion series were generated by integration of the total ion chromatogram (TIC) over the appropriate range.

#### **Preparation of Reagents**

#### (((Trifluoromethyl)sulfonyl)ethynyl)benzene - 6a



To a stirring solution of phenylacetylene (2.41 mL, 22.0 mmol, 1.1 eq.) in dry Et<sub>2</sub>O (100 mL) was added *n*-BuLi (13.8 mL, 1.6 M in hexanes, 1.1 eq.) over 30 min at -78 °C under an argon atmosphere. After being stirred for 0.5 h at -78 °C, the corresponding lithium acetylide was slowly transferred *via* cannula transfer to a solution of triflic anhydride (3.36 mL, 20 mmol, 1.0 eq.) in dry Et<sub>2</sub>O (50 mL) at -78 °C. The reaction was stirred at -78 °C for 30 min before being quenched with water. The aqueous layer was extracted with ether, and the combined organic layers were washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (0-10% EtOAc/cyclohexane) to afford **6a** as a pale yellow oil (3.65g, 16 mmol) in 88% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (d, *J* = 7.5 Hz, 2 H), 7.64 (t, *J* = 7.5, Hz, 1 H), 7.47 (t, *J* = 7.2 Hz, 2 H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  133.9 (CH), 133.5 (CH), 129.2 (CH), 119.1 (C, q, *J* = 323.1 Hz), 115.9 (C), 100.9 (C), 77.4 (C); IR (thin film): 3072, 2852, 2175, 2104, 1596, 1489, 1445 cm<sup>-1</sup>. Known compound.<sup>1</sup> All other alkynyl triflones were prepared in an analogous manner using this procedure.





#### 2-oxo-2-phenylethyl 2-iodobenzoate - 7



Rearranged product observed as a yellow oil from the reaction of THF **1a** with Ph-EBX **5** (Scheme 3 – Major side-product 50%). <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 (dd, *J* = 7.8, 1.7 Hz, 1H), 8.02 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.99 –7.94 (m, 2H), 7.71–7.59 (m, 1H), 7.54–7.48 (m, 2H), 7.45 (td, *J* = 7.6, 1.1 Hz, 1H), 7.19 (td, *J* = 7.7, 1.7 Hz, 1H), 5.60 (s, 2H). <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$  191.9 (C=O), 165.9 (C=O), 141.6 (CH), 134.3 (C), 134.2 (C), 134.1 (CH), 133.2 (CH), 131.8 (CH), 129.1 (CH), 128.2 (CH), 128.0 (CH), 94.6 (C-I), 66.9 (CH<sub>2</sub>). IR (thin film): 2983, 2912, 1754, 1688, 1544 cm<sup>-1</sup>. Known compound.<sup>15</sup>





# General Procedure for aerobic C-H functionalisation of heterocycles – Method A (Alkynylation)

To a solution of heterocycle/ether (1.25 mmol, 5.0 eq.) in HFIP (0.40 mmol) was added (((trifluoromethyl)sulfonyl)ethynyl)benzene **6a** (0.25 mmol, 1.0 eq). The reaction mixture was stirred at 80 °C for 16 h and then poured over sat. aq. NaHCO<sub>3</sub> (5 mL). The organics were extracted with EtOAc (3 x 10 mL), dried over MgSO<sub>4</sub>, filtered and the solvent removed under reduced pressure. The resultant crude residue was purified as described below.

#### 2-(Phenylethynyl)tetrahydrofuran - 8a



Following application of method A, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-(phenylethynyl)tetrahydrofuran **8a** as a clear oil (0.957g, 5.5 mmol, 89%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 700 MHz):  $\delta$  7.43 (dd, 7.0, 3.0 Hz, 2H), 7.34–7.29 (m, 3H), 4.81 (dd, *J* = 7.2 Hz, 5.0 Hz, 1H), 4.08–4.01 (m, 1H), 3.86 (td, *J* = 8.0, 5.5 Hz, 1H), 2.29–2.20 (m, 1H), 2.17–2.07 (m, 2H), 2.00–1.91 (m, 1H); <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$  131.8 (CH), 128.3 (CH), 128.4 (CH), 123.0 (C), 89.2 (C), 84.6 (C), 68.7 (CH), 68.1 (CH<sub>2</sub>), 33.6 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>); IR (thin film): 2929, 2209, 1602, 1558, 1521 cm<sup>-1</sup>. Known compound.<sup>2</sup>





2-Methyl-2-(phenylethynyl)tetrahydrofuran/ 2-methyl-5-(phenylethynyl)tetrahydrofuran – 8b, 8c-a + 8c-b



Following application of method A, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-methyl-2-(phenylethynyl)tetrahydrofuran **8b** and 2-methyl-5-(phenylethynyl)tetrahydrofuran **8c-a** and **8c-b** as a inseparable yellow oil (40 mg, 0.22 mmol, 86%). Assignment for each regioisomer/diastereomer is provided below. Product ratio: **1.7:1:0.5 8b:8c-a:8c-b** respectively. These ratios were calculated using NMR integrations of key protons such as the propargylic C-H.

**8b**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.44–7.39 (m, 2H), 7.30–7.26 (m, 3H), 4.03–3.94 (m, 2H), 2.09–2.18 (m, 3H), 1.86 (dt, *J* = 12.4, 8.4 Hz, 1H), 1.68 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  131.8 (CH), 128.3 (CH), 128.2 (CH), 123.2 (C) 92.5 (C), 82.9 (C), 76.5 (C), 67.8 (CH<sub>2</sub>), 40.3 (CH<sub>2</sub>), 27.8 (CH<sub>3</sub>), 25.8 (CH<sub>2</sub>).

**8c-a**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.44–7.39 (m, 2H), 7.30–7.26 (m, 3H), 4.92 (dd, *J* = 7.2, 5.8 Hz, 1H), 4.33–4.24 (m, 1H), 2.36–2.27 (m, 2H), 2.17–2.13 (m, 1H), 1.51 (m, 1H), 1.28 (d, *J* = 8.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 131.8 (CH), 128.3 (CH), 128.2 (CH), 123.2 (C), 89.7 (C), 84.4 (C), 75.2 (CH), 68.5 (CH), 34.0 (CH<sub>2</sub>), 33.2 (CH<sub>2</sub>), 20.9 (CH<sub>3</sub>).

**8c-b:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.44–7.39 (m, 2H), 7.30–7.26 (m, 3H), 4.73 (dd, *J* = 7.2, 6.1 Hz, 1H), 4.08–4.03 (m, 1H), 2.27–2.23 (m, 2H), 2.17–2.12 (m, 1H), 1.76–1.66 (m, 1H), 1.35 (d, *J* = 6.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 131.8 (CH), 128.3 (CH), 128.2 (CH), 123.2 (C), 89.6 (C), 84.5 (C), 76.4 (CH), 68.7 (CH), 33.9 (CH<sub>2</sub>), 33.1 (CH<sub>2</sub>), 21.6 (CH<sub>3</sub>).

IR (thin film): 3002, 2899, 2199, 1567, 1540, 1521 cm<sup>-1</sup>. HRMS (ESI) calcd for C<sub>14</sub>H<sub>13</sub>O [M+H]<sup>+</sup> 186.1039; observed 186.1032.



51 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 11(ppm)





2,5-Dimethyl-2-(phenylethynyl)tetrahydrofuran (unidentified mixture of 3:1 cis/trans isomers) – 8d



Following application of method A, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2,5-dimethyl-2-(phenylethynyl)tetrahydrofuran **8d** (3:1 mixture of cis/trans isomers) as a yellow liquid (48 mg, 0.24 mmol, 97%). <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>):  $\delta$  7.45–7.37 (m, 2H), 7.31–7.27 (m, 3H), 4.31 (dq, *J* = 12.7, 6.2 Hz, 0.70H), 4.22 (dq, *J* = 8.2, 6.1 Hz, 0.25H), 2.35 (ddd, *J* = 9.4, 6.4, 4.0 Hz, 0.25H), 2.29 (ddd, *J* = 12.2, 8.5, 6.0 Hz, 0.75H), 2.21 (ddt, *J* = 12.7, 8.5, 6.4 Hz, 0.75H), 2.16–2.11 (m, 0.25H), 1.94 (m, 1H), 1.91–1.82 (m, 0.25H), 1.63 (s, 2.25H), 1.61 (s, 0.75H), 1.57–1.52 (m, 0.75H), 1.36 (d, *J* = 6.1 Hz, 0.75H), 1.28 (d, *J* = 6.1 Hz, 2.25H). <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$  131.8 (CH), 131.7 (CH), 128.3 (CH), 128.1 (CH), 123.4 (C), 123.2 (C), 93.8 (C), 93.1 (C), 82.7 (C), 82.5 (C), 76.6 (C), 76.3 (C), 75.3 (CH), 41.5 (CH<sub>2</sub>), 40.4 (CH<sub>2</sub>), 34.3 (CH<sub>2</sub>), 33.1 (CH<sub>2</sub>), 28.7 (CH<sub>3</sub>), 28.4 (CH<sub>3</sub>), 22.4 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>). IR (thin film): 3011, 2921, 2215, 1600, 1540, 1512 cm<sup>-1</sup>. HRMS (ESI) calcd for C<sub>14</sub>H<sub>16</sub>O [M+H]<sup>+</sup> 201.1274; observed 201.1268.





#### 5-(Phenylethynyl)dihydrofuran-3(2H)-one - 8e



Following application of method A, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 5-(phenylethynyl)dihydrofuran-3(2*H*)-one **8e** as a clear oil (40 mg, 0.21 mmol, 84%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.44–7.40 (m, 2H), 7.38–7.29 (m, 3H), 5.30 (dd, *J* = 7.6, 5.2 Hz, 1H), 4.16 (d, *J* = 16.8 Hz, 1H), 3.98 (d, *J* = 16.8 Hz, 1H), 2.85 (dd, *J* = 17.8, 7.7 Hz, 1H), 2.68 (dd, *J* = 17.8, 5.2 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  213.0 (C=O), 132.0 (CH), 129.1 (CH), 128.5 (CH), 121.9 (C), 87.1 (C), 86.2 (C), 69.8 (CH<sub>2</sub>), 67.8 (CH), 43.9 (CH<sub>2</sub>). ); IR (thin film): 2911, 2901, 2206, 1724, 1613, 1558, 1543 cm<sup>-1</sup>. HRMS (ESI) calcd for C<sub>12</sub>H<sub>10</sub>O<sub>2</sub> [M+H]<sup>+</sup> 187.0675; observed 187.0643.





#### 2-Methyl-5-(phenylethynyl)dihydrofuran-3(2H)-one - 8f



Following application of method A, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-(phenylethynyl)-1,4-dioxane **8f** as a yellow oil (39 mg, 0.20 mmol, 78%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.42 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.34–7.31 (m, 3H), 5.35 (dd, *J* = 8.4, 3.0 Hz, 1H), 4.20 (q, *J* = 6.9 Hz, 1H), 2.87 (dd, *J* = 17.9, 8.4 Hz, 1H), 2.70 (dd, *J* = 17.9, 3.0 Hz, 1H), 1.34 (d, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  214.7 (C=O), 131.9 (CH), 129.1 (CH), 128.4 (CH), 121.9 (C), 86.9 (C), 86.4 (C), 73.3 (CH), 65.2 (CH), 43.3 (CH<sub>2</sub>), 15.6 (CH<sub>3</sub>); IR (thin film): 2915, 2899, 2211, 1723, 1613, 1560, 1543 cm<sup>-1</sup>. HRMS (ESI) calcd for C<sub>13</sub>H<sub>12</sub>O<sub>2</sub> [M+H]<sup>+</sup> 201.0910; observed 201.0903.





((2*R*)-4-Oxo-5-(phenylethynyl)tetrahydrofuran-2-yl)methyl acetate and (2-(phenylethynyl)tetrahydrofuran-2-yl)methyl acetate – 8g-a, 8g-b and 8h.



Following application of method A, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded ((2R)-4-oxo-5-(phenylethynyl)tetrahydrofuran-2-yl)methyl acetate **8g-a** + **8g-b** and (2-(phenylethynyl)tetrahydrofuran-2-yl)methyl acetate **8h** as an inseperable yellow oil (39 mg, 0.15 mmol, 61%). Assignment for each regioisomer/diastereomer is provided below. Product ratio is **1:0.35:0.85 8g-a:8g-b:8h** respectively. These ratios were calculated using NMR integrations of key protons such as the propargylic C-H.

**8g-a**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 700 MHz): δ 7.47–7.38 (m, 2H), 7.34–7.27 (m, 3H), 4.95 (t, *J* = 6.2 Hz, 1H), 4.42 (qd, *J* = 7.0, 3.6 Hz, 1H), 4.18 (dd, *J* = 11.6, 3.6 Hz, 1H), 4.01–3.97 (m, 1H), 2.17–2.14 (m, 1H), 2.09 (s, 3H), 2.00-1.91 (m, 2H), 1.75–1.70 (m, 1H). <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>): δ 171.2 (br C=O), 131.9 (CH), 128.5 (CH), 128.4 (CH), 122.8 (C), 85.0 (C), 88.5 (C), 76.6 (CH), 69.4 (CH), 27.9 (CH<sub>2</sub>), 25.8 (CH<sub>2</sub>), 21.06 (CH<sub>3</sub>).

**8g-b:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 700 MHz): δ 7.47–7.38 (m, 2H), 7.34–7.27 (m, 3H), 4.86 (dd, *J* = 7.1, 5.1 Hz, 1H), 4.29 (dd, *J* = 11.4, 3.7 Hz, 1H), 4.12 (dd, *J* = 11.4, 6.8 Hz, 1H), 4.08–4.04 (m, 1H), 2.25–2.00 (m, 3H), 2.08 (s, 3H), 1.91 (dq, *J* = 12.6, 8.2 Hz, 1H). <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>): δ 171.2 (br C=O), 131.8 (CH), 128.6 (CH), 128.4 (CH), 122.8 (C), 88.9 (C), 84.9 (C), 77.7 (CH), 69.4 (CH), 67.0 (CH<sub>2</sub>), 29.8 (CH<sub>2</sub>), 28.1 (CH<sub>2</sub>), 22.8 (CH<sub>3</sub>).

**8h:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 700 MHz): δ 7.47–7.38 (m, 2H), 7.34–7.27 (m, 3H), 4.38 (d, *J* = 11.3 Hz, 1H), 4.22 (d, d, *J* = 11.3 Hz, 1H), 4.08–4.04 (m, 2H), 2.28–2.20 (m, 3H), 2.13 (s, 3H), 2.11–2.05 (m. 1H). <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>): δ 170.9 (C=O), 131.9 (CH), 128.6 (CH), 128.4 (CH), 122.6 (C), 88.8 (C), 84.9 (C), 77.2 (C), 68.2 (C), 66.4 (C), 36.0 (CH<sub>2</sub>), 33.5 (CH<sub>2</sub>), 21.1 (CH<sub>3</sub>).

IR (thin film): 2901, 2211, 1745, 1600, 1565, 1547 cm<sup>-1</sup>. HRMS (ESI) calcd for  $C_{15}H_{16}O_3$  [M+H]<sup>+</sup> 245.1172; observed 245.1161.







#### Ethyl 5-(phenylethynyl)tetrahydrofuran-2-carboxylate - 8i



Following application of method A, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded ethyl 5-(phenylethynyl)tetrahydrofuran-2-carboxylate **8i** as a clear oil (46 mg, 0.18 mmol, 76%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.46–7.38 (m, 2H), 7.37–7.27 (m, 3H), 5.12–5.06 (m, 1H), 4.67 (dd, *J* = 8.3, 5.3 Hz, 1H), 4.23 (dq, *J* = 11.9, 7.1 Hz, 1H), 4.20 (dq, *J* = 11.9, 7.1 Hz, 1H), 2.53–2.41 (m, 1H), 2.38–2.27 (m, 1H), 2.18–2.05 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  172.8 (C=O), 131.9 (CH), 128.5 (CH), 128.4 (CH), 122.7 (C), 88.0 (C), 85.4 (C), 70.2 (CH<sub>2</sub>), 61.2 (CH), 32.9 (CH<sub>2</sub>), 29.9 (CH<sub>2</sub>), 14.3 (CH<sub>3</sub>); IR (thin film): 2921, 2199, 1743, 1575, 1547 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>15</sub>H<sub>16</sub>O<sub>3</sub> [M+H]<sup>+</sup> 245.1172; observed 245.1170.





#### 2,2-Dimethyl-4-(phenylethynyl)-1,3-dioxolane – 8j



Following application of method A, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2,2-dimethyl-4-(phenylethynyl)-1,3-dioxolane **8j** as a clear oil (46 mg, 0.18 mmol, 76%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.48–7.41 (m, 2H), 7.31 (m, 3H), 4.95 (t, *J* = 6.4 Hz, 1H), 4.24 (dd, *J* = 8.0, 6.3 Hz, 1H), 4.02 (dd, *J* = 8.0, 6.3 Hz, 1H), 1.55 (s, 3H), 1.42 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  131.9 (CH), 128.8 (CH), 128.4 (CH), 122.4 (C), 110.5 (C), 86.3 (C), 86.0 (C), 70.2 (CH), 66.2 (CH<sub>2</sub>), 26.4 (CH<sub>3</sub>), 26.2 (CH<sub>3</sub>). IR (thin film): 3001, 2923, 2204, 1601, 1575, 1557 cm<sup>-1</sup>. Known Compound.<sup>4</sup>





#### 2-(Phenylethynyl)tetrahydro-2*H*-pyran – 8k



Following application of method A (<u>10 equivalents of THP</u>), purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-(phenylethynyl)tetrahydro-2*H*-pyran **8k** as a clear oil (30 mg, 0.16 mmol, 64%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  7.45–7.44 (m, 2H), 7.31–7.29 (m, 3H), 4.52 (dd, *J* = 7.9, 2.7 Hz, 1H), 4.06–4.04 (m, 1H), 3.57–3.53 (m, 1H), 1.93–1.90 (m, 2H), 1.79–1.76 (m, 1H), 1.61–1.59 (m, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  131.9 (CH), 128.4 (CH), 128.4 (CH), 122.9 (C), 88.2 (C), 85.3 (C), 67.6 (CH), 66.8 (CH<sub>2</sub>), 32.3 (CH<sub>2</sub>), 25.8 (CH<sub>2</sub>), 22.0 (CH<sub>2</sub>); IR (thin film): 2945, 2901, 2211, 1608, 1562, 1553 cm<sup>-1</sup>. Known compound.<sup>2</sup>





(2*R*,3*S*,4*R*,6*S*)-2-(Acetoxymethyl)-6-(phenylethynyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate and (2*R*,3*S*,4*R*,6*R*)-2-(acetoxymethyl)-6-(phenylethynyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate – 8l-a and 8l-b



Major - 99% (90% as a seperable diastereomer)



Following application of method A, purification by column chromatography (0-25% EtOAc/cyclohexane) afforded single diastereomer (2*R*,3*S*,4*R*,6*S*)-2-(acetoxymethyl)-6-(phenylethynyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate **81-a** as a yellow oil (41 mg, 0.11 mmol, 41%). A inseparable mixture of **81-a** and **81-b** was also isolated, the yield and assignment quoted is of the pure diastereomer **81-a**. Stereochemical assignment is based on J coupling values, in particular of equatorial C-H<sub>1</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.53–7.46 (m, 2H), 7.38–7.29 (m, 3H), 5.43 (ddd, *J* = 11.6, 9.5, 5.0 Hz, 1H, H4), 5.11 (br d, *J* = 4.4 Hz, 1H, H<sub>1</sub>), 5.01 (t, *J* = 9.7 Hz, 1H, H<sub>5</sub>), 4.35 (dd, *J* = 12.3, 4.2 Hz, 1H, H7), 4.23 (ddd, *J* = 9.9, 4.2, 2.1 Hz, 1H, H<sub>6</sub>), 4.10 (dd, *J* = 12.3, 2.1 Hz, 1H, H<sub>8</sub>), 2.34 (ddd, *J* = 12.8, 5.0, 1.5 Hz, 1H, H<sub>2</sub>), 2.10 (s, 3H), 2.07 (m, 1H, H<sub>3</sub>), 2.04 (s, 3H), 2.03 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  171.0 (C=O), 170.4 (C=O), 170.1 (C=O), 132.1 (CH), 129.1 (CH), 128.5 (CH), 121.9 (C), 88.7 (C), 84.6 (C), 71.4 (CH), 70.1 (CH), 69.4 (CH), 64.7 (CH), 62.5 (CH), 35.6 (CH<sub>2</sub>), 21.2 (CH<sub>3</sub>), 21.0 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>). IR (thin film): 2961, 2867, 2214, 1741, 1501, 1440 cm<sup>-1</sup>. HRMS (ESI) calcd for C<sub>20</sub>H<sub>22</sub>O<sub>7</sub> [M+H]<sup>+</sup> 375.1444; observed 375.1436.







f1 (ppm)

#### 2-(Phenylethynyl)-1,4-dioxane - 8m



Following application of method A, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-(phenylethynyl)-1,4-dioxane **8m** as a yellow oil (33 mg, 0.18 mmol, 71%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  7.45 (dd, *J* = 6.2, 1.8 Hz, 2H), 7.31–7.29 (m, 3H), 4.57 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.95–3.92 (m, 2H), 3.77–3.68 (m, 4H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  132.0 (CH), 128.9 (CH), 128.4 (CH), 122.2 (CH<sub>2</sub>), 86.7 (C), 84.4 (C), 70.7 (CH), 66.6 (CH<sub>2</sub>), 66.5 (CH<sub>2</sub>), 66.0 (CH<sub>2</sub>); IR (thin film): 2905, 2892, 2199, 1613, 1560, 1546 cm<sup>-1</sup>. Known compound.<sup>2</sup>





#### 3-(Phenylethynyl)-1,4-oxathiane and 2-(phenylethynyl)-1,4-oxathiane – 8p + 8q



59%, 10:1, **8p:8q** 

Following application of method A, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 3-(phenylethynyl)-1,4-oxathiane and 2-(phenylethynyl)-1,4-oxathian **8p** and **8q** as an inseparable mixture of regioisomers – yellow oil (30 mg, 0.15 mmol, 59%). **8q** (major): <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.51–7.38 (m, 2H), 7.36–7.27 (m, 3H), 4.20 (d, *J* = 8.9 Hz, 1H), 4.05 (ddd, *J* = 11.8, 4.7, 2.9 Hz, 1H), 3.93–3.79 (m, 3H), 2.85 (ddd, *J* = 13.6, 8.9, 2.9 Hz, 1H), 2.72 (ddd, *J* = 13.6, 4.7, 2.2 Hz, 1H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  132.0 (CH), 129.6 (CH), 128.4 (CH), 122.7 (C), 85.4 (C), 84.5 (C), 72.8 (CH<sub>2</sub>), 68.5 (CH<sub>2</sub>), 30.4 (CH), 27.1 (CH<sub>2</sub>); IR (thin film): 2918, 2221, 1619, 1560, 1531 cm<sup>-1</sup>. HRMS (ESI) calcd for C<sub>12</sub>H<sub>12</sub>OS [M+H]<sup>+</sup> 205.0682; observed 205.0680.




# 2-(Phenylethynyl)tetrahydrothiophene - 8r



Following application of method A with the <u>exclusion</u> of HFIP, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-(phenylethynyl)tetrahydrothiophene **8r** as a yellow oil (34 mg, 0.18 mmol, 72%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 (ddd, *J* = 6.0, 2.4, 1.6 Hz, 2H), 7.29–7.26 (m, 3H), 4.27 (t, *J* = 5.8 Hz, 1H), 3.16 –3.09 (m, 1H), 2.93 (dd, *J* = 10.1, 6.6 Hz, 1H), 2.30–2.13 (m, 3H), 2.12–2.04 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  131.8 (CH), 128.3 (CH), 128.1 (CH), 123.4 (C), 90.8 (C), 83.0 (C), 39.1 (CH), 37.1 (CH<sub>2</sub>), 33.0 (CH<sub>2</sub>), 30.6 (CH<sub>2</sub>). IR (thin film): 3002, 2931, 2209, 1602, 1558 cm<sup>-1</sup>. Known compound.<sup>6</sup>





#### (3-Ethoxybut-1-yn-1-yl)benzene - 8s



Following application of method A, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded (3-ethoxybut-1-yn-1-yl)benzene **8s** as a clear oil (25 mg, 0.14 mmol, 57%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.45-7.43 (m, 2H), 7.31–7.29 (m, 3H), 4.39 (q, *J* = 6.6 Hz, 1H), 3.85 (dq, *J* = 14.0 Hz, 7.0, 1H), 3.51 (dq, *J* = 14.0 Hz, 7.0, 1H), 1.53 (d, *J* = 6.6 Hz, 3H), 1.26 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  131.8 (CH), 128.4 (CH), 123.0 (C), 89.6 (C), 84.8 (C), 65.6 (CH), 64.3 (CH<sub>2</sub>), 22.4 (CH<sub>3</sub>), 15.4 (CH<sub>3</sub>); IR (thin film): 2930, 2902, 2185, 1603, 1548, 1521 cm<sup>-1</sup>. Known compound.<sup>8</sup>





110 100 f1 (ppm) ò 

#### (3,4-Dimethoxybut-1-yn-1-yl)benzene – 8t



Following application of method A, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded (3,4-dimethoxybut-1-yn-1-yl)benzene **8t** as a yellow oil (36 mg, 0.19 mmol, 76%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.48–7.42 (m, 2H), 7.38–7.28 (m, 3H), 4.41 (dd, *J* = 7.4, 3.8 Hz, 1H), 3.68 (dd, *J* = 10.5, 7.4 Hz, 1H), 3.64 (dd, *J* = 10.5, 3.8 Hz, 1H), 3.53 (s, 3H), 3.45 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  132.0 (CH), 128.7 (CH), 128.4 (CH), 122.5 (C), 87.0 (C), 85.1 (C), 75.1 (CH), 71.3 (CH<sub>2</sub>), 59.5 (CH<sub>3</sub>), 57.0 (CH<sub>3</sub>); IR (thin film): 2920, 2903, 2197, 1548, 1521 cm<sup>-1</sup>. Known compound.<sup>2</sup>





# (Cyclopent-1-en-1-ylethynyl)benzene – 8u'



Following application of method A, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded (cyclopent-1-en-1-ylethynyl)benzene **8u'** as a clear oil (37 mg, 0.22 mmol, 89%). <sup>1</sup>H NMR (500 MHz, MeOD)  $\delta$  7.43–7.36 (m, 2H), 7.35–7.27 (m, 3H), 6.09 (ddd, *J* = 4.6, 2.6, 2.1 Hz, 1H), 2.50 (m, 4H), 1.96 (m, 2H). <sup>13</sup>C NMR (126 MHz, MeOD)  $\delta$  138.6 (CH), 132.3 (CH), 129.4 (CH), 129.0 (CH), 126.0 (C), 125.0 (C), 91.3 (C), 87.4 (C), 37.3 (CH<sub>2</sub>), 34.1 (CH<sub>2</sub>), 24.3 (CH<sub>2</sub>). IR (thin film): 2944, 2204, 1651, 1550, 1527, 1496 cm<sup>-1</sup>. Known compound.<sup>5</sup>





# General Procedure for aerobic C-H functionalisation of THF – Method B (Alkynylation)

To a solution of THF (1.25 mmol, 5.0 eq.) in HFIP (0.40 mmol) was added the respective acetylenic triflone **6x** (60 mg, 0.25 mmol, 1.0 eq). The reaction mixture was stirred at 80 °C for 16 h and then poured over sat. aq. NaHCO<sub>3</sub> (5 mL). The organics were extracted with EtOAc ( $3 \times 10$  mL), dried over MgSO<sub>4</sub>, filtered and the solvent removed under reduced pressure. The resultant crude residue was purified as described below.

### 2-((4-Methoxyphenyl)ethynyl)tetrahydrofuran - 9a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-((4-methoxyphenyl)ethynyl)tetrahydrofuran **9a** as a yellow oil (35 mg, 0.17 mmol, 69%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41–7.32 (m, 2H), 6.86–6.77 (m, 2H), 4.79 (dd, *J* = 7.1, 5.2 Hz, 1H), 4.06–3.96 (m, 1H), 3.85 (td, *J* = 8.0, 5.5 Hz, 1H), 3.80 (s, 3H), 2.36–2.17 (m, 1H), 2.14–2.00 (m, 2H), 1.99–1.85 (m, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  159.7 (C), 133.3 (CH), 115.1 (C), 114.0 (CH), 87.8 (C), 84.5 (C), 68.8 (CH<sub>2</sub>), 68.0 (CH), 55.4 (CH<sub>3</sub>), 33.6 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>); IR (thin film): 2930, 2903, 2234, 1568, 1501 cm<sup>-1</sup>. Known compound.<sup>2</sup>





### 2-((4-Ethylphenyl)ethynyl)tetrahydrofuran - 10a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-((4-ethylphenyl)ethynyl)tetrahydrofuran **10a** as a yellow oil (39 mg, 0.23 mmol, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41–7.31 (m, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 4.81 (dd, *J* = 7.1, 5.0 Hz, 1H), 4.06–3.96 (m, 1H), 3.90–3.80 (m, 1H), 2.63 (q, *J* = 7.6 Hz, 2H), 2.27–2.17 (m, 1H), 2.14–2.01 (m, 2H), 1.99–1.89 (m, 1H), 1.22 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  144.8 (C), 131.8 (CH), 127.9 (CH), 120.1 (C), 88.4 (C), 84.8 (C), 68.8 (CH), 68.0 (CH<sub>2</sub>), 33.6 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>), 15.5 (CH<sub>3</sub>); IR (thin film): 2942, 2913, 2217, 1558, 1511 cm<sup>-1</sup>. Known compound.<sup>9</sup>





### 2-((4-Pentylphenyl)ethynyl)tetrahydrofuran - 11a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-((4-pentylphenyl)ethynyl)tetrahydrofuran **11a** as a clear oil (51 mg, 0.21 mmol, 84%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 4.80 (dd, *J* = 7.2, 5.1 Hz, 1H), 4.08–3.96 (m, 1H), 3.85 (td, *J* = 8.0, 5.5 Hz, 1H), 2.60–2.54 (m, 2H), 2.28–2.17 (m, 1H), 2.13–2.03 (m, 2H), 1.98–1.87 (m, 1H), 1.58 (tt, *J* = 15.0, 7.4 Hz, 3H), 1.30 (ttd, *J* = 15.4, 8.2, 2.3 Hz, 5H), 0.88 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  143.5 (C), 131.7 (CH), 128.5 (CH), 120.0 (C), 88.4 (C), 84.8 (C), 68.8 (CH), 68.0 (CH<sub>2</sub>), 35.9 (CH<sub>2</sub>), 33.6 (CH<sub>2</sub>), 31.6 (CH<sub>2</sub>), 31.1 (CH<sub>2</sub>), 27.1 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 14.2 (CH<sub>3</sub>); IR (thin film): 2934, 2911, 2902, 2205, 1560, 1512 cm<sup>-1</sup>. Known compound.<sup>10</sup>





# 2-(M-tolylethynyl)tetrahydrofuran – 12a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-(*m*-tolylethynyl)tetrahydrofuran **12a** as a yellow oil (38 mg, 0.20 mmol, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.28–7.22 (m, 3H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 4.81 (dd, *J* = 7.2, 5.0 Hz, 1H), 4.07–3.94 (m, 1H), 3.92–3.79 (m, 1H), 2.31 (s, 3H), 2.27–2.18 (m, 1H), 2.09-2.02 (m, 2H), 2.00–1.90 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  138.0 (C), 132.5 (CH), 129.3 (CH), 128.9 (CH), 128.2 (CH), 122.8 (C), 88.8 (C), 84.8 (C), 68.8 (CH), 68.1 (CH<sub>2</sub>), 33.6 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>), 21.3 (CH<sub>3</sub>). IR (thin film): 2911, 2902, 2213, 1559, 1512 cm<sup>-1</sup>. Known compound.<sup>2</sup>





#### 2-((4-Bromophenyl)ethynyl)tetrahydrofuran - 13a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-((4-bromophenyl)ethynyl)tetrahydrofuran **13a** as a yellow oil (60 mg, 0.24 mmol, 96%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.45–7.38 (m, 2H), 7.33–7.26 (m, 2H), 4.78 (dd, *J* = 7.2, 5.1 Hz, 1H), 4.05–3.94 (m, 1H), 3.85 (ddd, *J* = 8.3, 7.7, 5.5 Hz, 1H), 2.27–2.18 (m, 1H), 2.14–2.01 (m, 2H), 2.00–1.89 (m, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  133.3 (CH), 131.6 (CH), 122.7 (C), 121.9 (C), 90.4 (C), 83.6 (C), 68.7 (CH<sub>2</sub>), 68.2 (CH), 33.5 (CH<sub>2</sub>), 25.7 (CH<sub>2</sub>); IR (thin film): 2929, 2909, 2215, 1540, 1522 cm<sup>-1</sup>. Known compound.<sup>10</sup>





# 2-((3-Fluorophenyl)ethynyl)tetrahydrofuran - 14a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-((3-fluorophenyl)ethynyl)tetrahydrofuran **14a** as a yellow oil (36 mg, 0.19 mmol, 76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29–7.18 (m, 2H), 7.12 (ddd, *J* = 9.5, 2.5, 1.4 Hz, 1H), 7.05–6.96 (m, 1H), 4.80 (dd, *J* = 7.2, 5.0 Hz, 1H), 4.06–3.94 (m, 1H), 3.92–3.81 (m, 1H), 2.31–2.17 (m, 1H), 2.14–2.03 (m, 2H), 2.01–1.89 (m, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  162.4 (d, *J* = 246.4 Hz), 129.9 (d, *J* = 8.6 Hz), 127.7 (d, *J* = 3.0 Hz), 124.8 (d, *J* = 9.4 Hz), 118.6 (d, *J* = 22.8 Hz), 115.7 (d, *J* = 21.2 Hz), 90.3 (C), 83.4 (C), 68.6 (CH<sub>2</sub>), 68.1 (CH), 33.5 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>). IR (thin film): 2930, 2230, 1555, 1512 cm<sup>-1</sup>. Known compound.<sup>2</sup>





# 2-((2-Chlorophenyl)ethynyl)tetrahydrofuran - 15a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-((2-chlorophenyl)ethynyl)tetrahydrofuran **15a** as a yellow oil (37 mg, 0.18 mmol, 73%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 (dd, J = 7.6, 1.8 Hz, 1H), 7.37 (dd, J = 8.0, 1.2 Hz, 1H), 7.22 (td, J = 7.7, 1.8 Hz, 1H), 7.18 (td, J = 7.5, 1.3 Hz, 1H), 4.87 (dd, J = 7.4, 4.5 Hz, 1H), 4.08–3.97 (m, 1H), 3.88 (td, J = 8.2, 5.6 Hz, 1H), 2.28–2.19 (m, 1H), 2.17 –2.08 (m, 2H), 1.99–1.90 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  136.1 (C), 133.5 (CH), 129.5 (CH), 129.3 (CH), 126.5 (CH), 122.8 (C), 94.7 (C), 81.4 (C), 68.7 (CH<sub>2</sub>), 68.1 (CH), 33.5 (CH<sub>2</sub>), 25.5 (CH<sub>2</sub>); IR (thin film): 2929, 2910, 2214, 1543, 1502 cm<sup>-1</sup>. Known compound.<sup>9</sup>







# 2-((4-(Trifluoromethyl)phenyl)ethynyl)tetrahydrofuran - 16a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-((4-(trifluoromethyl)phenyl)ethynyl)tetrahydrofuran **16a** as a yellow oil (52 mg, 0.22 mmol, 88%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.56–7.54 (m, 2H), 7.53–7.51 (m, 2H), 4.81 (dd, *J* = 7.3, 5.0 Hz, 1H), 4.05–3.94 (m, 1H), 3.87 (td, *J* = 7.8, 5.5 Hz, 1H), 2.31–2.17 (m, 1H), 2.15–2.02 (m, 2H), 1.99–1.88 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  132.1 (CH), 130.0 (q, C, *J*<sub>F,C</sub> = 32.7 Hz), 126.8 (C), 125.3 (q, CH, *J*<sub>F,C</sub> = 3.7 Hz), 124.0 (d, CH, *J*<sub>F,C</sub> = 272.2 Hz), 121.3 (CH), 91.8 (C), 83.3 (C), 68.6 (CH<sub>2</sub>), 68.3 (CH), 33.4 (CH<sub>2</sub>), 25.7 (CH<sub>2</sub>); IR (thin film): 2949, 2907, 2222, 1543, 1502 cm<sup>-1</sup>. Known compound.<sup>2</sup>





200 190 180 160 150 f1 (ppm) 

# 2-(Thiophen-2-ylethynyl)tetrahydrofuran - 17a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-(thiophen-2-ylethynyl)tetrahydrofuran **17a** as a brown oil (32 mg, 0.18 mmol, 72%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.29–7.13 (m, 2H), 6.94 (dd, J = 5.1, 3.6 Hz, 1H), 4.82 (dd, J = 7.3, 4.9 Hz, 1H), 4.07–3.94 (m, 1H), 3.85 (td, J = 7.9, 5.5 Hz, 1H), 2.28–2.16 (m, 1H), 2.14–2.04 (m, 2H), 1.99–1.89 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  132.3 (CH), 127.2 (CH), 127.0 (CH), 122.9 (C), 93.1 (C), 77.9 (C), 68.8 (CH<sub>2</sub>), 68.2 (CH), 33.4 (CH<sub>2</sub>), 25.7 (CH<sub>2</sub>); IR (thin film): 3067, 2926, 2209, 1518, 1463 cm<sup>-1</sup>. Known compound.<sup>10</sup>





#### 2-((6-Methoxynaphthalen-2-yl)ethynyl)tetrahydrofuran - 18a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-((6-methoxynaphthalen-2-yl)ethynyl)tetrahydrofuran **18a** as a yellow oil (41 mg, 0.16 mmol, 65%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (s, 1H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.44 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.14 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.09 (d, *J* = 2.5 Hz, 1H), 4.85 (dd, *J* = 7.2, 5.1 Hz, 1H), 4.08–4.00 (m, 1H), 3.91 (s, 3H), 3.96–3.84 (m, 1H), 2.33–2.20 (m, 1H), 2.17–2.07 (m, 2H), 2.01–1.91 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  134.9 (C), 134.3 (C), 131.6 (CH), 129.4 (CH), 129.3 (CH), 128.5 (CH), 126.8 (CH), 119.5 (C), 105.9 (C), 88.8 (C), 68.9 (CH<sub>2</sub>), 68.1 (CH), 55.5 (CH<sub>3</sub>), 33.6 (CH<sub>2</sub>), 27.1 (CH<sub>2</sub>), 25.7 (CH); IR (thin film): 3012, 2930, 2199, 1555, 1503 cm<sup>-1</sup>. HRMS (ESI) calcd for C<sub>17</sub>H<sub>16</sub>O<sub>2</sub> [M+H]<sup>+</sup> 253.1223; observed 253.1199.





### 2-(oct-1-yn-1-yl)tetrahydrofuran - 19a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-(oct-1-yn-1-yl)tetrahydrofuran **19a** as a yellow oil (31 mg, 0.16 mmol, 63%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  4.60-4.53 (m, 1H), 3.98–3.89 (m, 1H), 3.78 (td, *J* = 7.8, 6.1 Hz, 1H), 2.19 (td, *J* = 7.1, 1.8 Hz, 2H), 2.16–2.08 (m, 1H), 2.05–1.97 (m, 1H), 1.96–1.80 (m, 2H), 1.54–1.44 (m, 2H), 1.36-1.25 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  85.4 (C), 80.1 (C), 68.6 (CH<sub>2</sub>), 67.7 (CH), 33.7 (CH<sub>2</sub>), 31.4 (CH<sub>2</sub>), 28.7 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 25.5 (CH<sub>2</sub>), 22.6 (CH<sub>2</sub>), 18.9 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>); IR (thin film): 3022, 2991, 2204. Known compound.<sup>6</sup>





# 2-(3,3-Dimethylbut-1-yn-1-yl)tetrahydrofuran - 20a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) afforded 2-(3,3-dimethylbut-1-yn-1-yl)tetrahydrofuran **20a** as a clear oil (27 mg, 0.18 mmol, 72%). <sup>1</sup>H NMR (500 MHz, CDC13)  $\delta$  4.52 (dd, *J* = 7.0, 5.8 Hz, 1H), 3.98–3.89 (m, 1H), 3.81–3.71 (m, 1H), 2.21–2.04 (m, 1H), 2.05–1.92 (m, 2H), 1.93–1.78 (m, 1H), 1.20 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDC13)  $\delta$  93.5 (C), 78.3 (C), 68.6 (CH), 67.7 (CH<sub>2</sub>), 33.8 (C), 31.1 (CH<sub>3</sub>), 27.0 (CH<sub>2</sub>), 25.4 (CH<sub>2</sub>); IR (thin film): 3002, 2920, 2221 cm<sup>-1</sup>. Known compound.<sup>6</sup>





# General Procedure for aerobic C-H functionalisation of heterocycles – Method C (vinyl triflone)

To a solution of heterocycle (1.25 mmol, 5.0 eq.) in HFIP (0.40 mmol) and glacial acetic acid (0.40 mmol) was added vinyl triflone (0.25 mmol, 1.0 eq.). The reaction mixture was stirred at 80 °C for 16 h and then poured over sat. aq. NaHCO<sub>3</sub> (5 mL). The organics were extracted with EtOAc ( $3 \times 10$  mL), dried over MgSO<sub>4</sub>, filtered and the solvent removed under reduced pressure. The resultant crude residue was purified as described below. Note: the alkenyl triflones were made in accordance with literature procedures.<sup>12,16</sup>

### (Z)-2-(2-Bromo-2-phenylvinyl)tetrahydrofuran – 21a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) gave (*Z*)-2-(2-bromo-2-phenylvinyl)tetrahydrofuran **21a** as a yellow oil (49 mg, 0.20 mmol, 78%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 700 MHz):  $\delta$  7.54–7.50 (m, 2H), 7.37–7.31 (m, 3H), 6.35 (d, *J* = 7.0 Hz, 1H), 4.81 (q, *J* = 7.0 Hz, 1H), 3.96 (dt, *J* = 8.2, 6.9 Hz, 1H), 3.85 (td, *J* = 7.9, 6.2 Hz, 1H), 2.32 (dtd, *J* = 12.5, 7.2, 5.4 Hz, 1H), 2.03–1.93 (m, 2H), 1.70 (dq, *J* = 12.4, 7.9 Hz, 1H); <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$  139.4 (C), 133.0 (CH), 128.9 (CH), 128.4 (CH), 127.7 (C), 125.6 (C), 79.6 (CH), 68.5 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 26.2 (CH<sub>2</sub>); IR (thin film): 2932, 2902, 1623, 1555, 1532 cm<sup>-1</sup>. Known compound.<sup>12</sup>




### (Z)-2-(2-Fluoro-2-phenylvinyl)tetrahydrofuran – 22a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) gave (*Z*)-2-(2-fluoro-2-phenylvinyl)tetrahydrofuran **22a** as a colourless oil (31 mg, 0.16 mmol, 67%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 700 MHz):  $\delta$  7.52 (dd, *J* = 8.4, 1.5 Hz, 2H), 7.39–7.30 (m, 3H), 5.50 (dd, *J* = 36.9, 8.2 Hz, 1H), 4.94–4.88 (m, 1H), 3.98–3.92 (m, 1H), 3.82 (td, *J* = 8.1, 6.0 Hz 1H), 2.24-2.19 (m, 1H), 2.05-1.92 (m, 2H), 1.72-1.64 (m, 1H); <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$  157.7 (CF, d, *J*<sub>F,C</sub> = 250.7 Hz), 132.1 (C, d, *J*<sub>F,C</sub> = 28.2 Hz), 129.2 (CH), 128.6 (CH, d, *J*<sub>F,C</sub> = 1.9Hz), 124.5 (CH, d, *J*<sub>F,C</sub> = 7.2 Hz), 107.6 (C, d, *J*<sub>F,C</sub> = 11.7 Hz), 73.0 (CH), 68.1 (CH<sub>2</sub>), 32.8 (CH<sub>2</sub>), 26.2 (CH<sub>2</sub>); IR (thin film): 3011, 2983, 1625, 1575, 1532 cm<sup>-1</sup>. Known compound.<sup>12</sup>





## (Z)-2-(2-iodo-2-phenylvinyl)tetrahydrofuran – 23a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) gave (*Z*)-2-(2-iodo-2-phenylvinyl)tetrahydrofuran **23a** as a yellow oil (54 mg, 0.18 mmol, 72%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.73–7.48 (m, 2H), 7.45–7.19 (m, 3H), 6.35 (d, *J* = 7.0 Hz, 1H), 4.81 (m, 1H), 3.96 (m, 1H), 3.85 (m, 1H) 2.38–2.18 (m, 1H), 2.07–1.84 (m, 2H), 1.83–1.53 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  139.4 (CH), 133.0 (C), 128.9 (CH), 128.3 (CH), 127.7 (CH), 125.5 (CH), 79.6 (C), 68.5 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 26.2 (CH). 3023, 2981, 2904, 1635, 1550, 1532 cm<sup>-1</sup>. Known Compound.<sup>12</sup>





f1 (ppm)

### (E)-2-styryltetrahydrofuran – 24a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) gave (*E*)-2-styryltetrahydrofuran **24a** as a yellow oil (31 mg, 0.18 mmol, 71%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 15.8 Hz, 1H), 6.20 (dd, *J* = 15.8, 6.6 Hz, 1H), 4.47 (q, *J* = 6.9 Hz, 1H), 3.99–3.93 (m, 1H), 3.88–3.78 (m, 1H), 2.13 (td, *J* = 12.4, 7.2 Hz, 1H), 2.01–1.92 (m, 2H), 1.71 (dq, *J* = 12.4, 7.7 Hz, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  137.0 (C), 130.7 (CH), 130.6 (CH), 128.7 (CH), 127.6 (CH), 126.6 (CH), 79.8 (CH), 68.3 (CH<sub>2</sub>), 32.5 (CH<sub>2</sub>), 26.1 (CH<sub>2</sub>). IR (thin film): 2926, 2900, 1629, 1554, 1515 cm<sup>-1</sup>. Known compound.<sup>16</sup>





200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	
										f1 (ppm)										

## (E)-2-(4-pentylstyryl)tetrahydrofuran-25a



Following application of method B, purification by column chromatography (0-15% EtOAc/cyclohexane) gave (*E*)-2-(4-pentylstyryl)tetrahydrofuran **25a** as a yellow oil (35 mg, 0.15 mmol, 58%).  $\delta^{1}$ H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta^{7.29}$  (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.15 (dd, *J* = 15.8, 6.7 Hz, 1H), 4.46 (q, *J* = 6.9 Hz, 1H), 4.00–3.92 (m, 1H), 3.90–3.79 (m, 1H), 2.61–2.52 (m, 2H), 2.11 (dt, *J* = 12.0, 5.6 Hz, 1H), 1.99–1.87 (m, 2H), 1.70 (dq, *J* = 12.0, 7.6 Hz, 1H), 1.66–1.55 (m, 3H), 1.34–1.30 (m, 5H), 0.95–0.83 (m, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta^{142.6}$  (C), 134.4 (CH), 130.6 (CH), 129.7 (CH), 128.7 (CH), 126.5 (CH), 79.9 (CH), 68.3 (CH<sub>2</sub>), 35.8 (CH<sub>2</sub>), 32.6 (CH<sub>2</sub>), 31.6 (CH<sub>2</sub>), 31.2 (CH<sub>2</sub>), 26.1 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 14.2 (CH<sub>3</sub>). IR (thin film): 2926, 2900, 1629, 1554, 1515 cm<sup>-1</sup>. IR (thin film): 2991, 2926, 2900, 1634, 1540, 1511 cm<sup>-1</sup>. HRMS (ESI) calcd for C<sub>17</sub>H<sub>24</sub>O [M+H]<sup>+</sup> 245.1822; observed 245.1813.





## 2-phenethyltetrahydrofuran – 26



2-(phenylethynyl)tetrahydrofuran **8a** (0.50 mmol, 121mg) in THF (5 mL) was added to a flask containing 10% Pd on C (20 mg) under a N<sub>2</sub> atmosphere. The N<sub>2</sub> was evacuated and H<sub>2</sub> was purged through the flask and bubbled through the solution. The resultant solution was stirred for 16 h under a H<sub>2</sub> atmosphere at room temperature. The resultant solution was filtered through celite and the filter cake was washed with ethyl acetate. The resulting solution was concentrated and gave 2-phenethyltetrahydrofuran **26** as a yellow liquid (43 mg, 0.49 mmol, 97%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.32–7.25 (m, 2H), 7.24–7.15 (m, 3H), 3.94–3.86 (m, 1H), 3.82 (qn, *J* = 7.4 Hz, 1H), 3.73 (td, *J* = 7.9, 6.4 Hz, 1H), 2.81–2.73 (m, 2H), 2.66 (ddd, *J* = 13.8, 10.0, 6.3 Hz, 1H), 2.02-1.95 (m, 1H), 1.93–1.83 (m, 3H), 1.82-1.73 (m, 1H), 1.48 (dq, *J* = 11.8, 7.7 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  142.4 (C), 128.5 (CH), 128.4 (CH), 125.8 (CH), 78.8 (CH), 67.8 (CH<sub>2</sub>), 37.6 (CH<sub>2</sub>), 32.8 (CH<sub>2</sub>), 31.5 (CH<sub>2</sub>), 25.9 (CH<sub>2</sub>). Known compound.<sup>13</sup>





### 2,2-dichloro-1-phenyl-2-(tetrahydrofuran-2-yl)ethan-1-one - 27



Trichloroisocyanuric acid (116 mg, 0.5 mmol) was added to a stirring solution of 2-(phenylethynyl)tetrahydrofuran **8a** (0.5 mmol) in MeCN/H2O (2 mL, 10:1). Once the reaction was complete (TLC), the solvent was removed under reduced pressure before the residue was purified by column chromatography (0-10% EtOAc/cyclohexane) to give the dihalohydroxyketone **27** as a clear liquid (116 mg, 92%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.26 – 8.20 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 4.88 (t, *J* = 7.2 Hz, 1H), 4.06 – 3.93 (m, 2H), 2.33 (dtd, *J* = 12.1, 7.9, 4.3 Hz, 1H), 2.19 (dq, *J* = 13.0, 8.3 Hz, 1H), 2.13 – 2.03 (m, 1H), 1.97 (dqn, *J* = 12.1, 8.3 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  188.6 (C=O), 133.4 (C), 132.8 (CH), 130.8 (CH), 128.2 (CH), 89.0 (C), 83.4 (CH), 70.6 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>); IR (thin film): 2965, 1677, 1600, 1250, 1199 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>12</sub>H<sub>12</sub>Cl<sub>2</sub>O<sub>2</sub> [M<sup>35</sup>Cl+H]<sup>+</sup> 259.0287; observed 259.0282.





### (Z)-2-(2-(3,5-bis(trifluoromethyl)phenyl)-2-phenylvinyl)tetrahydrofuran – 28



In a sealed tube, (Z)-2-(2-iodo-2-phenylvinyl)tetrahydrofuran 9ac (75 mg, 0.25 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mg), K<sub>2</sub>CO<sub>3</sub> (100 mg, 0.75 mmol), 3,5-bis(trifluoromethyl)phenylboronic acid (71 mg, 0.275 mmol) were mixed together in dioxane:water (10:1, 1.5 mL) and heated at 70 °C for 16 h under an argon atmosphere. The resultant mixture was cooled to rt and water (10 mL) was added, the resulting mixture was extracted with diethyl ether (3 x 30 mL). The combined organics were dried over MgSO<sub>4</sub>, filtered and the solvent removed under reduced pressure. The resultant crude residue was purified by column chromatography (0-10%)EtOAc/cyclohexane) to afford (Z)-2-(2-(3,5-bis(trifluoromethyl)phenyl)-2phenylvinyl)tetrahydrofuran 28 as a clear oil (89 mg, 0.23 mmol). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.86 (s, 1H), 7.69 (s, 2H), 7.31 (m, 3H), 7.22–7.15 (m, 2H), 6.19 (d, J = 9.0 Hz, 1H), 4.15– 4.07 (m, 1H), 4.01–3.91 (m, 1H), 3.75 (td, *J* = 8.0, 5.9 Hz, 1H), 2.09-1.99 (m, 2H), 1.94-1.85 (m, 1H), 1.80-1.71 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 141.7 (C), 141.3 (C), 140.6 (C), 132.4 (CH), 131.6 (C, q, J<sub>F,C</sub> = 33.3 Hz), 130.2 (br s, CH), 128.7 (CH), 128.4 (C), 127.7 (C), 123.5 (CF<sub>3</sub>, q, J<sub>F,C</sub> = 272.7 Hz), 121.7–121.5 (m, CH), 76.3 (CH), 68.4 (CH<sub>2</sub>), 33.2 (CH<sub>2</sub>), 26.5 (CH<sub>2</sub>); HRMS (ESI) calcd for  $C_{20}H_{16}F_6O [M+H]^+$  387.1178; observed 387.117.





## **Mechanistic studies**

## <sup>13</sup>C Labelled (((trifluoromethyl)sulfonyl)ethynyl)benzene – <sup>13</sup>C-6a

<sup>1</sup>H NMR 700 MHz, CDCl<sub>3</sub>)  $\delta$  7.71–7.68 (m, 2 H), 7.64–7.61 (m, 1 H), 7.50–7.47 (m, 2 H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  133.9 (CH, d, *J* = 2.9 Hz), 133.5 (br s, CH), 129.2 (CH), 119.2 (C, qd, *J* = 323.1, 25.0 Hz), 115.92 (C, d, *J* = 10.6 Hz), 100.9 (m, C), **77.4** (<sup>13</sup>C).

Synthesis as described above (Page 5)





# <sup>13</sup>C Labelled 2-(phenylethynyl)tetrahydrofuran – <sup>13</sup>C-8a

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 700 MHz):  $\delta$  7.45–7.41 (m, 2H), 7.34–7.29 (m, 3H), 4.81 (dt, *J* = 7.1, 4.9 Hz, 1H), 4.09–3.96 (m, 1H), 3.89–3.84 (m, 1H), 2.29–2.20 (m, 1H), 2.17–2.07 (m, 2H), 2.00–1.91 (m, 1H); <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$  131.9 (CH, d, *J* = 2.6 Hz), 128.4 (CH, br s), 128.3 (CH), 122.9 (C, *J* = 12.5 Hz), **89.2** (<sup>13</sup>C), 86.02 (C, d, *J* = 355.7 Hz), 68.7 (CH, d, *J* = 77.5 Hz), 68.1 (CH<sub>2</sub>, d, *J* = 2.1 Hz), 33.6 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>).





### **Kinetic Isotope Experiments**

### MS data for 2-(Phenylethynyl)tetrahydrofuran, non-deuterated







In a seal tubed containing (0.625 mmol) THF and (0.625 mmol) THF-d8 was added HFIP (0.4 mmol) and (((trifluoromethyl)sulfonyl)ethynyl)benzene (60 mg, 0.25 mmol, 1.0 eq). The reaction was heated at 80 °C for 16 h. After this time, the product ratio was determined *via* LCMS analysis by integrating the peak areas of the extracted ion chromatograms (EICs) for the non-deuterated and deuterated species in a similar manner as described previously.<sup>14</sup>

## **LCMS Total Ion Count**



## EIC at 173.23 Da (THF, non-deuterated H<sup>+</sup> adduct)



Height = 63715984

<u>Area = 6036667.0</u>

## EIC at 180.27 Da (THF-d7 deuterated H<sup>+</sup> adduct)



Height = 19001804

<u>Area = 1705952.125</u>

Adduct with H<sup>+</sup>: d0/d7 = 6036667/1705952 = **3.53 = Kinetic Isotope effect** 

## **Tempo Radical Trapping experiment:**



To a solution of THF (0.1 mL, 1.25 mmol, 5.0 eq.) in HFIP (0.4 mmol) was added (((trifluoromethyl)sulfonyl)ethynyl)benzene **6a** (60 mg, 0.25 mmol, 1.0 eq.) and TEMPO (0.25 mmol, 1.0 eq.). The reaction mixture was stirred at 80 °C for 16 h and then analysed *via* LCMS.

## LCMS Total ion count







Entr	Tem	Solvent (in THF)	Other	Yiel	Triflone
у	р		condition	d (A)	(%)
			S	%	Conversion
1	40	HFIP (0.40 mmol)	Control –		0
			No THF		
2	60	HFIP (0.40 mmol)	Control –		trace
			No THF		
3	80	HFIP (0.40 mmol)	Control –		5
			No THF		
4	80	HFIP (2.0 mmol)		68	100
5	80	HFIP (2.0 mmol)	Control –		18
			No THF		
6	80	HFIP (1.0 mmol)		78	100
7	80	HFIP (0.4 mmol)		93	100
8	66			41	80
9	80	CF <sub>3</sub> CH <sub>2</sub> OH (0.40		49	90
		mmol)			
10	80	<i>Tert</i> -C <sub>4</sub> F <sub>9</sub> OH (0.40		32	100
		mmol)			
11	80	AcOH (0.40 mmol)		42	
12	80	HFIP (0.40 mmol)	Argon	0	5
13	RT	HFIP (0.40 mmol)		0	0
14	40	HFIP (0.40 mmol)		38	44
15	60	HFIP (0.40 mmol)		53	60

**Table S1** – Full optimisation table for radical C-H functionalisation of THF 1a with phenylacetylenic triflone 6a.

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