# Enantioselective Desymmetrizing Palladium Catalyzed Carbonylation Reactions: The Catalytic Asymmetric Synthesis of Quaternary Carbon Center Containing 1,3-Dienes

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### **Electronic Supporting Information**

Experiments were conducted at the University of Bath unless otherwise stated.

\* denotes experiments conducted at the University of Oxford.

Reactions were conducted under an inert nitrogen or argon atmosphere with dry solvents unless otherwise stated. Nitrogen and argon were passed through a Drierite<sup>®</sup> filled drying tube before use. Glassware was either oven-dried at >200 °C, and allowed to cool to room temperature under a positive nitrogen pressure or vacuum. Reagents were purchased from Sigma-Aldrich Chemical Co. Ltd., Acros Organics Ltd or Avocado, and used as supplied. The phosphine ligands were purchased from Aldrich chemical company or Strem chemicals, with the exception of those synthesised according to Hayashi<sup>1,2</sup> and Buchwald.<sup>3</sup> The following chemicals were distilled prior to use and stored over 4Å molecular sieves: triethylamine (dist. and stored over KOH), methanol (dist. magnesium), ethanol (dist. magnesium), iso-propanol (dist. Magnesium) *tert*-butanol (dist. magnesium). 'Petrol' refers to petroleum ether fraction in the boiling range 40-60 °C. 4Å molecular sieves were activated by drying in an oven at >150°C. HPLC was performed on either an Agilent 1100 Series or Dionex P680 HPLC with detection at 254 nm, using OD-H and OJ-H columns and with a flow rate of 0.50-1.00 mL/min of hexane/*iso*-propanol (approx 99.8:2) after 30 minutes equilibration time.

#### General Information for Experiments Conducted at the University of Oxford

Tetrahydrofuran, purchased from Rathburn (HPLC grade), was distilled from Na/benzophenone and stored over 4Å molecular sieves prior to use. Diethyl ether, dichloromethane and toluene were collected fresh from an Innovative Technology Inc. PS-400-7 solvent purification system having been passed through anhydrous alumina columns. Thin layer chromatography was performed using aluminium backed silica plates (Merck Kieselgel 60  $F_{254}$ ). Flash column chromatography was carried out using Zeochem ZEOprep hyd. 40-63 micron silica with pre-absorption of the crude product onto silica. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance experiments were carried out using a Bruker AVC-500 MHz NMR spectrometer. Chemical shifts were reported in parts per million from the residual solvent peak. Chemical shifts ( $\delta$ ) are given in parts per million (ppm) and coupling constants (*J*) in Hertz (Hz). Proton multiplicity is assigned using the following abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), septet (sep), multiplet (m), broad (br) and apparent (app.). Where required, proton assignment was achieved using 2D NMR spectroscopy techniques, predominantly COSY and HMQC spectroscopy.

Melting points were determined using a Leica Galen III hot-stage microscope and are reported uncorrected. Infrared measurements were carried out using a Bruker Tensor 27 FT-IR with internal calibration in the range 4000-600 cm<sup>-1</sup>. Accurate mass measurements were carried out on a Bruker MicroTOF mass spectrometer by the internal service at the Department of Organic Chemistry, University of Oxford.

#### General Information for Experiments Conducted at the University of Bath

Anhydrous tetrahydrofuran was collected fresh from an Innovative Technologies 'Grubbs Apparatus' solvent purification system.<sup>4</sup> Thin layer chromatography was performed using Merck or Macherey-Nagel aluminium backed plates coated with a 0.20 mm layer of silica gel 60 with fluorescent indicator  $UV_{254}$ . Flash column chromatography was carried out using Davisil LC 60Å silica gel (35-70 µm) purchased from Fluorochem, and samples were pre-absorbed on silica. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded either a Bruker Avance 400 spectrometer (at 400.1 and 100.6 MHz respectively) or a Bruker Avance AC-300 spectrometer (300.2 and 75.5 MHz respectively) in CDCl<sub>3</sub> with tetramethylsilane

(TMS) ( $\delta_H$  0 ppm) and/or the residual solvent as internal standards. Proton multiplicities were assigned as previously described.

Melting points were determined on a Buchi 535 melting point apparatus and are reported un-corrected. Infra-red spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer with an internal background calibration in the range 4000-600 cm<sup>-1</sup>. Mass spectroscopy, including high resolution spectra, were recorded by the EPSRC National Mass Spectrometry Service Centre, Swansea or at the Mass Spectrometry Service, University of Bath, using either electron impact (EI), chemical ionisation (CI) or electrospray (ES) techniques. Analyses were performed in positive ionisation mode. For low resolution measurements ammonia was used as the CI reagent gas on a Micromass Quantro II triple quadrupole. Elemental analyses were performed by the microanalysis service at the Department of Chemistry at the University of Bath, using an Exeter Analytical Inc CE-440 elemental analyser.

#### General procedure A: The preparation of 2,2-dialkyl-1,3-cyclic diketones

To a stirred solution of 2-methyl-1,3-cyclic diketone (39.7 mmol) and tetrabutyl ammonium hydroxide (40% w/w in water, 27.0 mL, 41.6 mmol) in dioxane (30 mL) was added alkyl bromide (60.3 mmol). The reaction was stirred at room temperature for 24 h, then 1M HCl<sub>(aq)</sub> (200 mL) and ethyl acetate (100 mL) were added. The layers were partitioned and the aqueous layer extracted with ethyl acetate ( $2 \times 100$  mL). The organic portions were combined and washed with water (100 mL) and brine (100 mL), dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure to produce an orange oil which was purified by flash chromatography (solvents as stated).

#### 2-Benzyl-2-methyl-cyclohexane-1,3-dione (ditriflate 10 precursor)



Prepared using general procedure **A** from 2-methyl-1,3-cyclohexanedione (5.0 g, 39.7 mmol) and benzyl bromide (8.39 mL, 60.3 mmol) and purified by flash chromatography (hexane:EtOAc 3:1) to yield the diketone (5.30 g, 62%) as white crystalline needles;  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 7.28-7.16 (3H, m), 7.04-6.99 (2H, m), 3.11 (2H, s), 2.60-2.48 (2H, m), 2.35-2.23 (2H, m), 1.80-1.67 (1H, m), 1.55-1.42 (1H, m), 1.28 (3H, s);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 211.8, 137.1, 130.3, 128.8, 127.4, 65.7, 44.3, 39.7, 22.5, 17.0. Data consistent with literature.<sup>5</sup>

### General procedure B: The preparation of 2,2-dialkyl-1-alkenyltriflate-3cyclohexanones

A stirred solution of 2,2-dialkyl-1,3-cyclohexanedione (0.93 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (418 mg, 2.04 mmol) in anhydrous DCE (5 mL) was cooled to 0°C. To this was added trifluoromethanesulfonic anhydride (0.33 mL, 1.94 mmol), dropwise. The reaction was then heated at 80°C for 18 h, after which it was allowed to cool to room

temperature. Diethyl ether (40 mL) was added, and the white pyridinium triflate salt was removed by filtration, washing with diethyl ether. The filtrate was concentrated under reduced pressure to produce a dark oil which was purified by flash chromatography (solvents as stated).

#### Trifluoro-methanesulfonic acid 6-benzyl-6-methyl-5-oxo-cyclohex-1-enyl ester



Prepared using general procedure **B** from diketone XXX (201 mg, 0.93 mmol) and purified by flash chromatography (hexane:EtOAc 10:1) to yield the mono-alkenyltriflate (188 mg, 58%) as a yellow oil.  $v_{max}$  (film)/cm<sup>-1</sup> 3065 (C-H), 2936 (C-H), 1722 (C=O), 1680 (C=C), 1416 (O-SO<sub>2</sub>), 1142 (SO<sub>2</sub>);  $\delta_{H}$  (400 MHz, CDCl<sub>3</sub>) 7.28-7.20 (3H, m), 7.08-7.02 (2H, m), 5.97 (1H, dd (app. t), *J* 4.7 and 4.7), 3.17 (1H, d, *J* 13.5), 2.83 (1H, d, *J* 13.5), 2.40-2.32 (1H, m), 2.21-2.12 (1H, m), 1.98-1.90 (1H, m), 1.74-1.65 (1H, m), 1.43 (3H, s);  $\delta_{C}$  (100 MHz, CDCl<sub>3</sub>) 209.4, 149.6, 136.3, 130.1, 128.5, 128.2, 117.9, 54.8, 43.1, 37.1, 23.4, 19.6. Data consistent with literature.<sup>6</sup>

# General procedure C: The preparation of 2,2-dialkyl-1,3-cyclohexadienyl *bis*-alkenyltriflates

A stirred solution of 2,2-dialkyl-1-alkenyltriflate-3-cyclohexanone (0.64 mmol) and 2-[N,N-bis(trifluoromethanesulfonyl)amino]-5-chloropyridine (0.30 g, 0.77 mmol) in anhydrous THF (10 ml) was cooled to -78°C. To this was added potassium hexamethyldisilazide (0.5M in toluene, 1.53 mL, 0.77 mmol), dropwise over 15 minutes. The reaction was stirred at -78°C for 2 h, then warmed to room temperature and stirred for a further 4 h. The mixture was then diluted with hexane (30 mL), and washed with water (20 mL), 10% NaOH<sub>(aq)</sub> (20 mL) and brine (20 mL). The organic phase was dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure to produce a dark oil which was purified by flash chromatography (solvents as stated). Trifluoro-methanesulfonic acid 6-benzyl-6-methyl-5-trifluoromethane sulfonyloxycyclohexa-1,4-dienyl ester, 10



Prepared using general procedure **C** from the corresponding mono-alkenyltriflate (223 mg, 0.64 mmol) and purified by flash chromatography (hexane:EtOAc 10:1) to yield *bis*-alkenyltriflate **10** (227 g, 74%) as white needles. mp 89-91°C (hexane)  $v_{max}$  (film)/cm<sup>-1</sup> 3054 (C-H), 2987 (C-H), 1673 (C=C), 1418 (O-SO<sub>2</sub>), 1141 (SO<sub>2</sub>);  $\delta_{H}$  (400 MHz, CDCl<sub>3</sub>) 7.29-7.21 (3H, m), 7.10-7.06 (2H, m), 5.69 (2H, dd (app.t), *J* 3.9 and 3.5), 2.87 (2H, s), 2.76 (1H, dt, *J* 22.8 and 3.9), 2.33 (1H, dt, *J* 22.8 and 3.5), 1.55 (3H, s);  $\delta_{C}$  (100 MHz, CDCl<sub>3</sub>) 147.7, 135.0, 130.1, 128.5, 127.4, 114.2, 45.9, 42.1, 24.5, 23.1. Data consistent with literature.<sup>6</sup>

#### 2-(4-Methoxy-benzyl)-2-methyl-cyclohexane-1,3-dione



Prepared using general procedure **A** from 2-methyl-1,3-cyclohexanedione (5.0 g, 39.7 mmol) and *p*-methoxybenzylchloride (8.39 mL, 60.3 mmol) and purified by flash chromatography (hexane:EtOAc 3:1) to yield the diketone (5.27 g, 54%) as white crystalline needles. mp 87-89°C (EtOAc/hexane)  $v_{max}$  (film)/cm<sup>-1</sup> 2951 (C-H), 2839 (O-CH<sub>3</sub>), 1691, 1610 (Ar), 1511 (Ar), 1457 (Ar), 1247, 1185, 1027, 868 (Ar);  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 6.97-6.92 (2H, m), 6.78-6.73 (2H, m), 3.76 (3H, s), 3.07 (2H, s), 2.59-2.49 (2H, m), 2.39-2.26 (2H, m), 1.82-1.68 (1H, m), 1.60-1.47 (1H, m), 1.27 (3H, s);  $\delta_{C}$  (75 MHz,

CDCl<sub>3</sub>) 211.7, 158.6, 130.9, 128.6, 113.8, 65.4, 55.2, 43.3, 39.4, 22.0, 16.6; *m/z* LRMS (EI<sup>+</sup>) 246.1 ([M]<sup>+</sup>, 100%), 203.1 (30%), 175.0 (90%), 159.1 (45%), 121.1 ([CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>]<sup>+</sup>, 100%); (CI<sup>+</sup>) 264 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for C<sub>15</sub>H<sub>22</sub>NO<sub>3</sub>: 264.1594 [M+NH<sub>4</sub>]<sup>+</sup>; found: 264.1597 [M+NH<sub>4</sub>]<sup>+</sup>; Anal. Calc. for C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>: C, 73.2; H, 7.37; Found: C, 73.2; H, 7.42.

Trifluoro-methanesulfonic acid 6-(4-methoxy-benzyl)-6-methyl-5-oxo-cyclohex-1enyl ester



Prepared using general procedure **B** from the corresponding diketone (250 mg, 1.02 mmol) and purified by flash chromatography (hexane:EtOAc 10:1) to yield the mono-alkenyltriflate (185 mg, 48%) as a yellow oil.  $v_{max}$  (liquid film)/cm<sup>-1</sup> 3424 (C-H), 2938 (C-H), 2838 (C-H), 1716 (C=O), 1614, 1516, 1418 (O-SO<sub>2</sub>), 1246 (SO<sub>2</sub>), 1143, 1015, 937, 874, 812, 756, 679;  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 6.98-6.95 (2H, m), 6.78-6.75 (2H, m), 5.97 (1H, dd (app. t), *J* 4.5 and 4.5), 3.77 (3H, s), 3.10 (1H, d, *J* 13.5), 2.78 (1H, d, *J* 13.5), 2.41-2.32 (1H, m), 2.24-2.12 (1H, m), 2.01-1.92 (1H, m), 1.80-1.68 (1H, m), 1.39 (3H, s);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 209.6, 158.5, 149.6, 130.9, 128.2, 117.7, 113.6, 55.2, 54.5, 41.9, 36.8, 22.8, 19.2; *m/z* LRMS (ES<sup>+</sup>) 149 [M-CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup> (100%), 121 [M-C<sub>8</sub>H<sub>9</sub>O]<sup>+</sup> (100%); (ES<sup>+</sup>) 396 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for C<sub>16</sub>H<sub>21</sub>F<sub>3</sub>NO<sub>5</sub>S: 396.1087 [M+NH<sub>4</sub>]<sup>+</sup>; found: 396.1086 [M+NH<sub>4</sub>]<sup>+</sup>.

Trifluoro-methanesulfonic acid 6-(4-methoxy-benzyl)-6-methyl-5trifluoromethanesulfonyloxy-cyclohexa-1,4-dienyl ester (Table 2, Entry 4 substrate)



Prepared using general procedure **C** from the corresponding mono-alkenyltriflate (274 mg, 0.725 mmol) and purified by flash chromatography (hexane:EtOAc 10:1) to yield the *bis*-alkenyltriflate (240 mg, 65%) as a white powder: mp 57-60°C.  $v_{max}$  (film)/cm<sup>-1</sup> 1514, 1417 (O-SO<sub>2</sub>), 1211 (SO<sub>2</sub>), 1142, 995, 874;  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 7.01-6.99 (2H, m), 6.80-6.77 (2H, m), 5.69 (2H, dd (app.t), *J* 3.8 and 3.8), 3.78 (3H, s), 2.83-2.73 (3H, m), 2.37 (1H, dt, *J* 22.7 and 3.5), 1.52 (3H, s);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 158.6, 147.5, 130.7, 127.7, 113.9, 113.5, 55.2, 45.7, 41.0, 24.2, 22.5; *m/z* LRMS (EI<sup>+</sup>) 388.0 (53%), 255.1 (78%), 241.1 (53%), 211.1 (56%), 199.1 (100%), 121.0 (100%), 77.0 (27%), 69.0 (58%); (CI<sup>+</sup>) 528.2 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for C<sub>17</sub>H<sub>20</sub>F<sub>6</sub>NO<sub>7</sub>S<sub>2</sub>: 528.0580 [M+NH<sub>4</sub>]<sup>+</sup>; found: 528.0587 [M+NH<sub>4</sub>]<sup>+</sup>; Anal. Calc. for C<sub>17</sub>H<sub>16</sub>F<sub>6</sub>O<sub>7</sub>S<sub>2</sub>: C, 40.0; H, 3.16; Found: C, 40.5; H, 3.30.

#### 4-(1-Methyl-2,6-dioxo-cyclohexylmethyl)-benzonitrile



Prepared using general procedure **A** from 2-methyl-1,3-cyclohexanedione (5.0 g, 39.7 mmol) and *p*-cyano benzylbromide (11.8 g, 60.3 mmol) and purified by flash

chromatography (hexane:EtOAc 1:1) to yield the diketone (5.90 g, 61%) as white crystalline needles: mp 94-103°C (DCM/hexane)  $v_{max}$  (film)/cm<sup>-1</sup> 2967 (C-H), 2227 (CN), 1694 (C=O), 1607, 1506, 1418, 1320, 1029, 821 (Ar);  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 7.53-7.50 (2H, m), 7.21-7.18 (2H, m), 3.21 (2H, s), 2.69-2.59 (2H, m), 2.38-2.29 (2H, m), 1.94-1.82 (1H, m), 1.59-1.45 (1H, m), 1.35 (3H, s);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 210.5, 142.9, 132.0, 131.1, 118.7, 110.7, 65.4, 41.3, 38.9, 24.1, 16.6; *m*/z LRMS (El<sup>+</sup>) 241.2 ([M]<sup>+</sup>, 30%), 198.1 (35%), 185.1 ([M-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CN]<sup>+</sup>, 10%), 170.1 (30%), 116.1 (85%), 97.1 (45%), 89.1 (60%), 55.1 (100%); (Cl<sup>+</sup>) 259 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for C<sub>15</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>: 259.1441 [M+NH<sub>4</sub>]<sup>+</sup>; found: 259.1442 [M+NH<sub>4</sub>]<sup>+</sup>; Anal. Calc. for C<sub>15</sub>H<sub>15</sub>NO<sub>2</sub>: C, 74.7; H, 6.27; N, 5.81. Found: C, 74.5; H, 6.30; N, 5.85%.

Trifluoro-methanesulfonic acid 6-(4-cyano-benzyl)-6-methyl-5-oxo-cyclohex-1-enyl ester



Prepared using general procedure **B** from the corresponding diketone (246 mg, 1.02 mmol) and purified by flash chromatography (hexane:EtOAc 5:1) to yield the mono-alkenyltriflate (240 mg, 63%) as a white powder. mp 54-58°C  $v_{max}$  (film)/cm<sup>-1</sup>2981 (C-H), 2939 (C-H), 2230 (CN), 1272 (C=O), 1609, 1415 (O-SO<sub>2</sub>), 1215 (SO<sub>2</sub>), 1142, 1019, 875;  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 7.55-7.52 (2H, m), 7.19-7.16 (2H, m), 6.00 (1H, dd, *J* 3.6 and 2.0), 3.32 (1H, d, *J* 13.3), 2.84 (1H, d, *J* 13.3), 2.53-2.43 (1H, m), 2.32-2.21 (1H, m), 2.15-2.05 (1H, m), 1.80-1.68 (1H, m), 1.44 (3H, s);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 208.5, 148.8, 141.9, 132.1, 130.8, 118.6, 118.2, 111.1, 54.5, 41.7, 36.3, 23.7, 19.3; *m/z* LRMS (El<sup>+</sup>) 373.2 [M]<sup>+</sup> (100%), 116.0 (100%), 107.1 (19%), 89.0 (31%), 79.1 (27%), 69.0 (68%), 55.1 (55%); (Cl<sup>+</sup>) 391 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for C<sub>16</sub>H<sub>14</sub>F<sub>3</sub>NO<sub>4</sub>S: 373.0590 [M]<sup>+</sup>; found: 373.0590 [M]<sup>+</sup>; Anal. Calc. for C<sub>16</sub>H<sub>14</sub>NO<sub>4</sub>SF<sub>3</sub>: C, 51.5; H, 3.78; N, 3.75. Found: C, 57.5; H, 3.83; N, 3.79 %.

Trifluoro-methanesulfonic acid 6-(4-cyano-benzyl)-6-methyl-5-trifluoromethane sulfonyloxy-cyclohexa-1,4-dienyl ester (Table 2, Entry 5 substrate)



Prepared using general procedure **C** from the corresponding mono-alkenyltriflate (270 mg, 0.725 mmol) and purified by flash chromatography (hexane:EtOAc 10:1) to yield the *bis*-alkenyltriflate (55 mg, 15%) as a cream solid: mp 62-65°C.  $\nu_{max}$  (film)/cm<sup>-1</sup> 2991 (C-H), 2944 (C-H), 2230 (CN), 1705, 1410 (O-SO<sub>2</sub>), 1221 (SO<sub>2</sub>), 1140, 1068, 1002, 945, 873, 803, 756, 659;  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 7.59-7.56 (2H, m), 7.21-7.19 (2H, m), 5.73 (2H, dd (app.t), *J* 3.7 and 3.7), 2.94 (2H, s), 2.85 (1H, dt, *J* 23.0 and 4.0), 2.40 (1H, dt, *J* 23.0 and 3.6), 1.57 (3H, s);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 146.7, 141.1, 132.0, 130.4, 116.0, 114.4, 111.2, 45.4, 41.5, 24.2, 22.9; *m*/z LRMS (EI<sup>+</sup>) 506.0 (9%), 389.1 (26%), 255.0 (100%), 239.0 (36%), 206.1 (51%), 117.1 (100%), 89.1 (30%), 69.0 (82%); (CI<sup>+</sup>) 523.1 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for C<sub>17</sub>H<sub>17</sub>F<sub>6</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: 523.0427 [M+NH<sub>4</sub>]<sup>+</sup>; found: 523.0423 [M+NH<sub>4</sub>]<sup>+</sup>.

#### \*2-(4-trifluoromethane-benzyl)-2-methyl-cyclohexane-1,3-dione



Prepared using general procedure **A** from 2-methyl-1,3-cyclohexanedione (3.11 g, 24.63 mmol) and 4-trifluoromethylbenzyl bromide (8.95 g, 37.44 mmol) and purified by flash chromatography (light petroleum:EtOAc 7:1) to yield the diketone (3.70 g, 53%) as a

white crystalline solid: mp. 61-63°C.  $v_{max}$ (film)/cm<sup>-1</sup> 3143, 3050, 2967, 2938, 2891 (CH), 1727, 1697 (CO), 1618, 1510, 1326, 1165, 1121, 1068, 1020;  $\delta_{H}$  (400 MHz, CDCl<sub>3</sub>) 7.45 (2H, d, *J* 8.0), 7.16 (2H, d, *J* 8.0), 3.18 (2H, s), 2.59 (2H, ddd, *J* 16.6, 8.2 and 4.8), 2.31 (2H, ddd, *J* 16.6, 8.2 and 4.8), 1.88-1.77 (1H, m), 1.55-1.45 (1H, m), 1.32 (3H, s);  $\delta_{C}$  (100 MHz, CDCl<sub>3</sub>) 210.7, 141.1, 130.4, 128.9 (q,  ${}^{2}J_{CF}$  32), 125.1, 123.9 (q,  ${}^{1}J_{CF}$  270), 65.1, 41.6, 38.9, 23.4, 16.5; *HRMS* (ESI -ve); C<sub>15</sub>H<sub>14</sub>F<sub>3</sub>O<sub>2</sub>, Requires: 283.0951, Found: 283.0941.

## \*Trifluoro-methanesulfonic acid 6-(4-trifluoromethane-benzyl)-6-methyl-5-oxocyclohex-1-enyl ester



Prepared using general procedure **B** from the corresponding diketone (1.31 g, 4.60 mmol) and purified by flash chromatography (2% Diethyl ether-Hexane) to yield the mono-alkenyltriflate (1.37 g, 72%) as a yellow/orange oil.  $v_{max}$ (film)/cm<sup>-1</sup> 3074 2981, 2940, 2860 (CH), 1723 (CO), 1619 (C=C), 1418, 1326, 1217, 1069 and 1019.  $\delta_{\rm H}$  (200 MHz, CDCl<sub>3</sub>) 7.49 (2H, d, *J* 8.2), 7.16 (2H, d, *J* 8.2), 5.99 (1H, dd, *J* 5.6 and 3.8), 3.29 (1H, d, *J* 13.4), 2.85 (1H, d, *J* 13.4), 2.44 (1H, ddd, *J* 15.0, 8.4 and 6.2), 2.31-1.99 (2H, m), 1.79-1.64 (1H, m), 1.43 (3H, s);  $\delta_{\rm C}$  (125 MHz, CDCl<sub>3</sub>) 208.7, 149.0, 140.3, 130.2, 129.3 (q,  ${}^{2}J_{\rm CF}$  33), 127.3, 125.1 (q,  ${}^{3}J_{\rm CF}$  4), 118.3 (q,  ${}^{1}J_{\rm CF}$  320), 118.0, 54.3, 41.6, 36.3, 33.4 and 19.2.

\*Trifluoro-methanesulfonic acid 6-(4-trifluoromethane-benzyl)-6-methyl-5trifluoromethane sulfonyloxy-cyclohexa-1,4-dienyl ester (Table 2, Entry 6 substrate)



Prepared using general procedure **C** from the corresponding mono-alkenyltriflate (1.63 g, 3.90 mmol) and purified by flash chromatography (2% diethyl ether-hexane) to yield the *bis*-alkenyltriflate (1.21 g, 57%) as a white crystalline solid. m.p. 50-52°C.  $v_{max}$ (film)/cm<sup>-1</sup>; 3083, 3052, 2945, 2893, 2824 (CH), 1619 (C=C), 1417, 1327, 1216, 1068, 1001, 872.  $\delta_{H}$  (200 MHz, CDCl<sub>3</sub>) 7.53 (2H, d, *J* 8.3), 7.19 (2H, d, *J* 8.3), 5.72 (2H, t, *J* 3.7), 2.92 (2H, s), 2.82 (2H, dt, *J* 22.8 and 4.2), 2.36 (2H, dt, *J* 22.8 and 4.2) and 1.56 (3H, s);  $\delta_{C}$  (125 MHz, CDCl<sub>3</sub>) 146.8, 139.6, 130.0, 129.4 (q, <sup>2</sup>*J*<sub>CF</sub> 33), 125.1 (q, <sup>3</sup>*J*<sub>CF</sub> 4), 124.1 (q, <sup>1</sup>*J*<sub>CF</sub> 272), 118.3 (q, <sup>1</sup>*J*<sub>CF</sub> 320), 114.2, 45.4, 41.3, 24.1, 22.8; *HRMS* (ESI - ve); C<sub>17</sub>H<sub>13</sub>F<sub>9</sub>O<sub>6</sub>S<sub>2</sub>+Na, Requires: 570.9902, Found: 570.9902.

#### \*2-(4-fluoro-benzyl)-2-methyl-cyclohexane-1,3-dione



Prepared using general procedure **A** from 2-methyl-1,3-cyclohexanedione (5.00 g, 39.63 mmol) and 4-fluorobenzyl bromide (7.40 mL, 60.24 mmol) and purified by flash chromatography (light petroleum:EtOAc 6:1) to yield the diketone (5.40 g, 58%) as a colourless solid/oil. m.p. <30°C.  $v_{max}$ (film)/cm<sup>-1</sup> 3046, 2964, 2936, 2878 (CH), 1725, 1695

(CO), 1604, 1509, 1222, 1159, 1098, 1025;  $\delta_{H}$  (200 MHz, CDCl<sub>3</sub>) 7.02-6.83 (4H, m), 3.08 (2H, s), 2.55 (2H, ddd, *J* 16.6, 8.0 and 5.2), 2.28 (2H, ddd, *J* 16.6, 8.0 and 5.2), 1.88-1.41 (2H, m), 1.27 (3H, s);  $\delta_{C}$  (125 MHz, CDCl<sub>3</sub>) 211.2, 161.7 (d, <sup>1</sup>*J*<sub>CF</sub> 247), 132.5 (d, <sup>4</sup>*J*<sub>CF</sub> 4), 131.5 (d, <sup>3</sup>*J*<sub>CF</sub> 8), 115.1 (d, <sup>2</sup>*J*<sub>CF</sub> 21), 65.2, 42.1, 39.1, 27.7, 16.5; *HRMS* (ESI+ve); C<sub>14</sub>H<sub>16</sub>FO<sub>2</sub>, Requires: 257.0954, Found: 257.0948.

\*Trifluoro-methanesulfonic acid 6-(4-fluoro-benzyl)-6-methyl-5-trifluoromethane sulfonyloxy-cyclohexa-1,4-dienyl ester (Table 2, Entry 7 substrate) and Trifluoromethanesulfonic acid 6-(4-fluoro-benzyl)-6-methyl-5-oxo-cyclohex-1-enyl ester



Prepared using general procedure **B** from the corresponding diketone (1.50 g, 9.74 mmol) and purified by flash chromatography (2% diethyl ether-hexane) to yield the bisalkenyltriflate (1.85 g, 38%) as a white solid. m.p 60-62°C.  $v_{max}$ (film)/cm<sup>-1</sup> 2987, 2938 (CH), 1509, 1413, 1204, 1140, 1063, 1000, 873; δ<sub>H</sub> (200 MHz, CDCl<sub>3</sub>) 7.09-6.91 (4H, m), 5.71 (2H, t, J 3.6), 2.85 (2H, s), 2.84 (1H, dt, J 22.8 and 3.4), 2.38 (1H, dt, J 22.8 and 3.4), 1.54 (3H, s);  $\delta_{C}$  (125 MHz, CDCl<sub>3</sub>) 161.9 (d, <sup>1</sup>J<sub>CF</sub> 247), 147.1, 131.3 (d, <sup>4</sup>J<sub>CF</sub> 4), 131.1 (d,  ${}^{3}J_{CF}$  8), 118.3 (q,  ${}^{1}J_{CF}$  320), 115.0 (d,  ${}^{2}J_{CF}$  23), 114.0, 45.5 (d,  ${}^{5}J_{CF}$  1), 40.8, 24.1, 22.5; HRMS (ESI+ve); C<sub>16</sub>H<sub>13</sub>F<sub>7</sub>O<sub>6</sub>S<sub>2</sub>+Na, Requires: 520.9939, Found: 520.9934 and the monotriflate (2.24 g, 62%) as an orange oil:  $v_{max}$ (film)/cm<sup>-1</sup>; 3047, 2980, 2938, 2859 (CH), 1721 (CO), 1605 (C=C), 1510, 1416, 1216, 1142, 1056, 874; δ<sub>H</sub> (200 MHz, CDCl<sub>3</sub>); 7.04-7.01 (2H, m), 6.96-6.90 (2H, m), 6.00 (1H, dd, J 5.4 and 3.3), 3.19 (1H, d, J 13.3), 2.80 (1H, d, J 13.3), 2.41 (1H, ddd, J 15.4, 8.5 and 6.5), 2.26-2.17 (1H, m), 2.02 (1H, dt, J 15.4 and 6.5), 1.78-1.71 (1H, m), 1.41 (3H, s);  $\delta_{\rm C}$  (125 MHz, CDCl<sub>3</sub>) 209.1, 161.8 (d,  ${}^{1}J_{CF}$  239), 149.3, 131.9 (d,  ${}^{4}J_{CF}$  4), 131.4 (d,  ${}^{3}J_{CF}$  9), 118.4 (g,  ${}^{1}J_{CF}$  320), 117.8, 115.1 (d,  ${}^{2}J_{CF}$  23), 54.4 (d,  ${}^{5}J_{CF}$  1), 41.4, 36.5, 23.0, 19.1; *HRMS* (ESI+ve); C<sub>15</sub>H<sub>14</sub>F<sub>4</sub>O<sub>4</sub>S, Requires: 389.0441, Found: 389.0428.

#### \*2-(2-methyl-benzyl)-2-methylcyclohexane-1,3-dione



Prepared using general procedure **A** from 2-methyl-1,3-cyclohexanedione (5.00 g, 39.68 mmol) and 2-methylbenzyl bromide (8.05 mL, 60.31 mmol) and purified by flash chromatography (light petroleum:EtOAc 7:1) to yield the diketone (3.97 g, 43%) as a colourless oil:  $v_{max}$ (film)/cm<sup>-1</sup>; 3104, 3062, 3020, 2961, 2939, 2876 (CH), 1724, 1694 (CO), 1541, 1422, 1369, 1283, 909;  $\delta_{H}$  (400 MHz, CDCl<sub>3</sub>) 7.11-7.02 (3H, m), 6.87 (1H, br d, *J* 6.8), 3.15 (2H, s), 2.57 (2H, ddd, *J* 16.4, 8.0 and 5.2), 2.37 (2H, ddd, *J* 16.4, 8.0 and 5.2), 2.23 (3H, s), 1.80-1.64 (2H, m), 1.33 (3H, s);  $\delta_{C}$  (100 MHz, CDCl<sub>3</sub>) 211.6, 136.8, 134.9, 130.8, 129.6, 127.0, 125.8, 65.0, 40.6, 39.3, 21.5, 19.8, 16.8; *HRMS* (ESI +ve); C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>+Na, Requires: 253.1199, Found: 253.1197.

\*Trifluoro-methanesulfonic acid 6-(2-methyl-benzyl)-6-methyl-5-trifluoromethane sulfonyloxy-cyclohexa-1,4-dienyl ester (Table 2, Entry 8 substrate) and Trifluoromethanesulfonic acid 6-(2-methyl-benzyl)-6-methyl-5-oxo-cyclohex-1-enyl ester



Prepared using general procedure **B** from the corresponding diketone (701 mg, 3.04 mmol) and purified by flash chromatography (2% diethyl ether-hexane) to yield the *bis*-alkenyltriflate (701 mg, 20%) as an amber coloured solid. m.p. 47-48°C.  $v_{max}$ (film)/cm<sup>-1</sup>; 3067, 3024, 2990, 2891 (CH), 1605 (C=C), 1457, 1213, 1140, 999, 870;  $\delta_{H}$  (500 MHz, CDCl<sub>3</sub>) 7.15-7.06 (4H, m), 5.74 (2H, dd, *J* 4.1 and 3.2), 2.96 (2H, s), 2.80 (1H, dt, *J* 22.2

and 3.8), 2.38 (1H, dt, *J* 22.2 and 3.8), 2.30 (3H, s), 1.58 (3H, s);  $\delta_{C}$  (125 MHz, CDCl<sub>3</sub>) 147.7, 137.1, 133.8, 130.4, 130.3, 126.9, 125.3, 118.3 (q,  ${}^{1}J_{CF}$  320), 114.4, 45.0, 38.6, 24.2, 22.7, 19.2; *HRMS* (ESI +ve); C<sub>17</sub>H<sub>16</sub>F<sub>6</sub>O<sub>6</sub>S<sub>2</sub>+Na, Requires: 517.0185, Found: 517.0173 and the monotriflate (43 mg, 2%) as an orange oil;  $\nu_{max}$ (film)/cm<sup>-1</sup>; 3066, 3023, 2979, 2939, 2862 (CH), 1718 (CO), 1604 (C=C), 1418, 1378, 1213, 114;  $\delta_{H}$  (500 MHz, CDCl<sub>3</sub>) 7.20-7.12 (3H, m), 7.05 (1H, br d, *J* 7.3), 6.07 (1H, dd, *J* 6.0 and 4.4), 3.22 (1H, d, *J* 14.0), 3.00 (1H, d, *J* 14.0), 2.42-2.36 (1H, m), 2.30 (3H, s), 2.29-2.23 (1H, m), 1.98-1.91 (2H, m), 1.49 (3H, s);  $\delta_{C}$  (125 MHz, CDCl<sub>3</sub>); 209.2, 149.8, 137.0, 134.4, 130.7, 130.3, 127.1, 125.7, 118.3 (q,  ${}^{1}J_{CF}$  320), 117.7, 53.7, 39.5, 36.6, 30.1, 22.3, 19.4; *HRMS* (ESI +ve); C<sub>16</sub>H<sub>17</sub>F<sub>3</sub>O<sub>4</sub>S +Na, Requires: 385.0692, Found: 385.0686

#### 2-Methyl-2-naphthalen-2-ylmethyl-cyclohexane-1,3-dione



Prepared using general procedure **A** from 2-methyl-1,3-cyclohexanedione (5.0 g, 39.7 mmol) and 2-bromomethylnapthalene (13.3 g, 60.3 mmol) and purified by flash chromatography (hexane:EtOAc 3:1) to yield the diketone (8.51 g, 53%) as yellow crystalline needles: mp 86-93°C.  $v_{max}$ (film)/cm<sup>-1</sup>; 2982 (C-H), 2938 (C-H), 1693 (C=O), 1461 (Ar), 1320, 1223, 1028, 827, 769;  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 7.79-7.69 (3H, m), 7.50-7.40 (3H, m), 7.16 (1H, dd, *J* 8.5 and 1.8), 3.30 (2H, s), 2.59-2.49 (2H, m), 2.31-2.20 (2H, m), 1.79-1.65 (1H, m), 1.51-1.38 (1H, m), 1.36 (3H, s);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 211.5, 134.3, 133.3, 132.3, 128.7, 128.1, 128.0, 127.8, 127.6, 126.1, 125.8, 65.3, 43.9, 39.4, 22.7, 16.6; *m*/*z* LRMS (EI<sup>+</sup>) 141.1 ([C<sub>10</sub>H<sub>7</sub>CH<sub>2</sub>]<sup>+</sup>, 100%), 115.0 (20%); (Cl<sup>+</sup>) 284 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for C<sub>18</sub>H<sub>22</sub>NO<sub>2</sub>: 284.1645 [M+NH<sub>4</sub>]<sup>+</sup>; found: 284.1641 [M+NH<sub>4</sub>]<sup>+</sup>.

Trifluoro-methanesulfonic acid 6-methyl-6-naphthalen-2-ylmethyl-5-oxo-cyclohex-1-enyl ester



Prepared using general procedure **B** from the corresponding diketone (271 mg, 1.02 mmol) and purified by flash chromatography (hexane:EtOAc 10:1) to yield mono-the alkenyltriflate (219 mg, 54%) as a yellow oil.  $v_{max}$  (liquid film)/cm<sup>-1</sup> 3057 (C-H), 2979 (C-H), 2936 (C-H), 1722 (C=O), 1682, 1601, 1418 (O-SO<sub>2</sub>), 1216 (SO<sub>2</sub>), 1141, 1017, 871, 817, 754;  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 7.80-7.70 (3H, m), 7.52-7.44 (3H, m), 7.18 (1H, dd, *J* 8.4 and 1.8), 5.94 (1H, dd (app. t), *J* 4.6 and 4.6), 3.36 (1H, d, *J* 13.4), 3.00 (1H, d, *J* 13.4), 2.42-2.32 (1H, m), 2.18-2.06 (1H, m), 1.99-1.90 (1H, m), 1.67-1.54 (1H, m), 1.47 (3H, s);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 209.4, 149.5, 133.8, 133.2, 132.3, 128.8, 127.9 (2 × C), 127.8, 127.6, 125.8, 120.5, 117.7, 54.6, 42.7, 36.7, 23.2, 19.2; *m/z* LRMS (ES<sup>+</sup>) 149.0 [M-F<sub>3</sub>CSO<sub>3</sub>]<sup>+</sup> (100%), 141.1 [M-C<sub>11</sub>H<sub>9</sub>O]<sup>+</sup> (90%), 191.1 (65%), 115.1 (100%) 80.0 (100%); (ES<sup>+</sup>) 416 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for C<sub>19</sub>H<sub>21</sub>F<sub>3</sub>NO<sub>4</sub>S: 416.1138 [M+NH<sub>4</sub>]<sup>+</sup>; found: 416.1139 [M+NH<sub>4</sub>]<sup>+</sup>.

Trifluoro-methanesulfonic acid 6-methyl-6-naphthalen-2-ylmethyl-5trifluoromethanesulfonyloxy-cyclohexa-1,4-dienyl ester (Table 2, Entry 9 substrate)



Prepared using general procedure **C** from the corresponding mono-alkenyltriflate (288 mg, 0.725 mmol) and purified by flash chromatography (hexane:EtOAc 10:1) to yield the

*bis*-alkenyltriflate (227 mg, 59%) as a yellow oil.  $v_{max}$  (film)/cm<sup>-1</sup> 3058 (C-H), 2991 (C-H), 2940 (C-H), 1704, 1602, 1510, 1420 (O-SO<sub>2</sub>), 1216 (SO<sub>2</sub>), 1141, 1001, 946, 892, 743;  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 7.81-7.44 (6H, m), 7.23-7.20 (1H, dd, *J* 8.6 and 1.7), 5.64 (2H, dd (app.t), *J* 3.8 and 3.8), 3.04 (2H, s), 2.62 (1H, dt, *J* 22.8 and 4.0), 2.22 (1H, dt, *J* 22.8 and 3.5), 1.59 (3H, s);  $\delta_{\rm C}$  (75 MHz, CDCl<sub>3</sub>) 147.4, 133.2 (2 × C), 132.4, 128.8, 127.8, 127.7, 127.6, 126.1, 125.9, 120.5, 113.9, 45.7, 41.8, 24.2, 22.9; *m/z* LRMS (EI<sup>+</sup>) 530.1 ([M]<sup>+</sup>, 42%), 397.1 (100%), 388.0 (83%), 142.1 (41%), 140.9 (100%), 115.0 (42%), 69.0 (77%); (CI<sup>+</sup>) 548.1 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for C<sub>20</sub>H<sub>20</sub>F<sub>6</sub>NO<sub>6</sub>S<sub>2</sub>: 548.0631 [M+NH<sub>4</sub>]<sup>+</sup>; found: 548.0631 [M+NH<sub>4</sub>]<sup>+</sup>.

#### 2-Cyclohex-1-enylmethyl-2-methyl-cyclohexane-1,3-dione



Prepared using general procedure **A** from 2-methyl-1,3-cyclohexanedione (5.0 g, 39.7 mmol) and 1-(bromomethyl)cyclohex-1-ene (10.5 g, 60.3 mmol) and purified by flash chromatography (hexane:EtOAc 3:1) to yield the diketone (3.6 g, 41%) as a colourless oil.  $v_{max}$  (liquid film)/cm<sup>-1</sup> 3395 (C-H), 2932 (C-H), 1698 (C=O), 1455, 1318, 1025, 909;  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 5.35-5.30 (1H, m), 2.80-2.70 (2H, m), 2.65-2.56 (2H, m), 2.48 (2H, s), 2.14-1.93 (3H, m), 1.91-1.77 (3H, m), 1.60-1.44 (4H, m), 1.21 (3H, s);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 210.7, 133.0, 126.7, 65.4, 46.7, 38.5, 29.8, 25.3, 21.9, 19.6, 17.7, 14.2; *m*/z LRMS (EI<sup>+</sup>) 220.1 (20%), 177.0 (22%), 164.1 (43%), 149.0 (42%), 127.0 (73%), 91.0 (66%), 78.9 (93%), 67.1 (70%), 54.8 (100%); (CI<sup>+</sup>) 221.1 [M+H]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for C<sub>14</sub>H<sub>21</sub>O<sub>2</sub>: 221.1536 [M+H]<sup>+</sup>; found: 221.1536 [M+H]<sup>+</sup>.

Trifluoro-methanesulfonic acid 6-cyclohex-1-enylmethyl-6-methyl-5-trifluoromethanesulfonyloxy-cyclohexa-1,4-dienyl ester (Table 2, Entry 10 substrate)



Prepared using general procedures **B** and **C** from the corresponding diketone (255 mg, 0.725 mmol) and purified by flash chromatography (hexane:EtOAc 10:1) to yield the *bis*-alkenyltriflate (197 mg, 56%) as white needles: mp 52-54 (hexane).  $v_{max}$  (film)/cm<sup>-1</sup> 2936 (C-H), 1699, 1410 (O-SO<sub>2</sub>), 1246, 1206 (SO<sub>2</sub>), 1139, 1069, 1101, 957, 852, 745;  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 5.81 (2H, dd (app. t), *J* 3.7 and 3.7), 5.46 (1H, br s), 3.10-2.89 (2H, m), 2.24 (2H, s), 1.93 (4H, br d, *J* 20.7), 1.56-1.45 (4H, m), 1.39 (3H, s);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 148.9, 132.5, 127.0, 112.5, 44.1, 43.8, 29.3, 25.4, 24.6, 23.6, 23.1, 22.1 (CF<sub>3</sub> not seen); *m/z* LRMS (El<sup>+</sup>) 484.0 (100%), 443.1 (75%), 419.0 (36%), 401.0 (31%), 95.1 (100%), 69.0 (61%); (Cl<sup>+</sup>) 502.1 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (Cl<sup>+</sup>) calc. for C<sub>16</sub>H<sub>18</sub>O<sub>6</sub>F<sub>6</sub>S<sub>2</sub>: 484.0444 [M+NH<sub>4</sub>]<sup>+</sup>; found: 484.0447 [M+NH<sub>4</sub>]<sup>+</sup>.

#### 2-Allyl-2-methyl-cyclohexane-1,3-dione



Prepared using general procedure **A** from 2-methyl-1,3-cyclohexanedione (5.0 g, 39.7 mmol) and allylbromide (5.15 mL, 60.3 mmol) and purified by flash chromatography (hexane:EtOAc 3:1) to yield the diketone (4.55 g, 69%) as a colourless oil:  $v_{max}$  (liquid film)/cm<sup>-1</sup> 3079 (C-H), 2978 (C-H), 2875 (C-H), 1699 (C=O), 1455, 1427, 1373, 1320, 1026, 921;  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 5.65-5.51 (1H, m), 5.10-5.03 (2H, m), 2.68-2.63 (4H, m), 2.53 (2H, dt, *J* 7.3 and 1.1), 2.08-1.81 (2H, m), 1.24 (3H, s);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 209.9, 132.2, 119.2, 65.2, 41.3, 38.2, 19.5, 17.5; *m/z* LRMS (El<sup>+</sup>) 110.1 (10%), 95.0

(12%), 67.1 (18%), 55.0 (25%); (CI<sup>+</sup>) 184.1 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (EI<sup>+</sup>) calc. for C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>: 166.0988 [M]<sup>+</sup>; found: 166.0986 [M]<sup>+</sup>; Anal. Calc. for C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>: C, 72.3; H, 8.49. Found: C, 70.3; H, 8.41%.

#### 2-Methyl-2-propyl-cyclohexane-1,3-dione



To a stirred solution of palladium on activated carbon (10% wt. loading, 100 mg, 0.094 mmol) in anhydrous ethanol (10 mL) was added 2-methyl-2-propyl-1,3-cyclohexanedione (158 mg, 0.94 mmol) as a solution in anhydrous ethanol (20 mL). The reaction was fitted with a balloon of hydrogen to simulate a pressure of 1 atmosphere, and stirred at room temperature for 24 hours. The reaction was diluted with ethyl acetate and filtered through a celite plug. The filtrate was then concentrated under reduced pressure to yield the aliphatic diketone (158 mg, 100%) as a colourless oil:  $v_{max}$  (liquid film)/cm<sup>-1</sup> 2962 (C-H), 2874 (C-H), 1688 (C=O), 1456, 1426, 1373, 1331, 1131, 1025, 934, 841;  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 2.77-2.56 (4H, m), 2.10-1.97 (1H, m), 1.92-1.80 (1H, m), 1.78-1.73 (2H, m), 1.22-1.09 (5H, m), 0.87 (3H, t, *J* 7.2);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 210.4, 65.9, 40.0, 38.0, 18.7, 18.1, 17.8, 14.4; *m/z* LRMS (EI<sup>+</sup>) 168.1 ([M]<sup>+</sup>, 10%), 139.1 (13%), 126.1 (20%), 111.1 (35%), 69.1 (43%), 55.0 (36%), 41.2 (100%); (CI<sup>+</sup>) 186.2 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for C<sub>10</sub>H<sub>20</sub>NO<sub>2</sub>: 186.1489 [M+NH<sub>4</sub>]<sup>+</sup>; found: 186.1491 [M+NH<sub>4</sub>]<sup>+</sup>; Anal. Calc. for C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>: C, 71.4; H, 9.59. Found: C, 69.5; H, 9.31%.

#### Trifluoro-methanesulfonic acid 6-methyl-5-oxo-6-propyl-cyclohex-1-enyl ester



Prepared according to general procedure **B** using the corresponding diketone (1.71 g, 10.2 mmol) and purified by flash chromatography (hexane:EtOAc 10:1) to yield the

mono-alkenyltriflate (550 mg, 18%) as a yellow oil:  $v_{max}$  (liquid film)/cm<sup>-1</sup> 2964 (C-H), 2938 (C-H), 2877 (C-H), 1723 (C=O), 1679, 1415 (O-SO<sub>2</sub>), 1215 (SO<sub>2</sub>), 1141, 1017, 932, 870, 786, 603;  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 6.07 (1H, dd (app. t), *J* 4.2 and 4.2), 2.65-2.39 (4H, m), 1.94-1.83 (1H, m), 1.55-1.45 (1H, m), 1.28 (3H, s), 1.27-0.99 (2H, m), 0.87 (3H, t, *J* 7.2);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 209.2, 150.9, 116.5, 52.7, 38.5, 36.2, 23.1, 20.0, 18.37, 14.2; *HRMS* (ES<sup>+</sup>) calc. for C<sub>11</sub>H<sub>16</sub>F<sub>3</sub>O<sub>4</sub>S: 301.0716 [M+H]<sup>+</sup>; found: 301.0728 [M+H]<sup>+</sup>.

### Trifluoro-methanesulfonic acid 6-methyl-6-propyl-5-trifluoromethane sulfonyloxycyclohexa-1,4-dienyl ester (Table 2, Entry 11 substrate)



Prepared using general procedure **B** from the corresponding diketone (1.71 g, 10.2 mmol) and purified by flash chromatography (hexane:EtOAc 10:1) to yield the *bis*-alkenyltriflate (2.12 g, 48%) as a yellow oil:  $v_{max}$ (liquid film)/cm<sup>-1</sup> 2966 (C-H), 2941 (C-H), 2879 (C-H), 1705, 1418 (O-SO<sub>2</sub>), 1213 (SO<sub>2</sub>), 1142, 1063, 1000, 912, 862, 809, 612;  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 5.85 (2H, dd (app.t), *J* 3.8 and 3.8), 3.03 (2H, td, *J* 3.8 and 1.1), 1.58-1.53 (2H, m), 1.37 (3H, s), 1.33-1.20 (2H, m), 0.92 (3H, t, *J* 7.2);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 148.7, 113.2, 43.9, 37.3, 24.5, 23.3, 18.0, 13.7; *m/z* LRMS (EI<sup>+</sup>) 432.1 ([M]<sup>+</sup>, 10%), 389.1 ([M-C<sub>3</sub>H<sub>7</sub>]<sup>+</sup>, 100%), 105.0 (40%), 69.0 ([CF<sub>3</sub>]<sup>+</sup>, 100%); *HRMS* (EI) calc. for C<sub>12</sub>H<sub>14</sub>F<sub>6</sub>O<sub>6</sub>S<sub>2</sub>: 432.0131 [M]<sup>+</sup>; found: 432.0127 [M]<sup>+</sup>.

#### 2-Ethyl-2-methyl-cyclohexane-1,3-dione



Prepared using general procedure **A** from 2-methyl-1,3-cyclohexanedione (5.0 g, 39.7 mmol) and ethyl iodide (4.76 mL, 60.3 mmol) and purified by flash chromatography

(hexane:EtOAc 2:1) to yield the diketone (3.24 g, 53%) as a colourless oil:  $v_{max}$  (liquid film)/cm<sup>-1</sup> 2969 (C-H), 2939 (C-H), 2879 (C-H), 1699 (C=O), 1373, 1325, 1265, 1129, 1026, 829;  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 2.77-2.58 (4H, m), 2.10-1.97 (1H, m), 1.92-1.77 (3H, m), 1.21 (3H, s), 0.80 (3H, t, *J* 7.5);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 210.4, 66.2, 38.0, 30.8, 18.1, 17.8, 9.1; *m*/*z* LRMS (EI<sup>+</sup>) 154.1 ([M]+, 42%), 111.1 (61%), 97.1 (45%), 69.0 (53%), 55.0 (58%), 42.2 (100%); (CI<sup>+</sup>) 172.2 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (EI<sup>+</sup>) calc. for C<sub>9</sub>H<sub>14</sub>O<sub>2</sub>: 154.0988 [M]<sup>+</sup>; found: 154.0987 [M]<sup>+</sup>.

#### Trifluoro-methanesulfonic acid 6-ethyl-6-methyl-5-oxo-cyclohex-1-enyl ester



Prepared using general procedure **B** from the corresponding diketone (1.00 g, 6.49 mmol) and purified by flash chromatography (hexane:EtOAC 10:1) to yield the mono-alkenyltriflate (501 mg, 27%) as an orange oil:  $v_{max}$  (liquid film)/cm<sup>-1</sup> 2975 (C-H), 2941 (C-H), 1723 (C=O), 1679, 1460, 1416 (O-SO<sub>2</sub>), 1214 (SO<sub>2</sub>), 1142, 1017, 932, 886, 832, 677, 609;  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 6.11 (1H, dd (app. t), *J* 4.1 and 4.1), 2.66-2.51 (2H, m), 2.48-2.40 (2H, m), 2.02-1.90 (1H, m), 1.64-1.49 (1H, m), 1.28 (3H, s), 0.78 (3H, dd (app. t), *J* 7.4 and 7.4);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 209.15, 150.6, 116.9, 53.2, 36.2, 29.2, 22.7, 20.0, 9.32.

Trifluoro-methanesulfonic acid 6-ethyl-6-methyl-5-trifluoromethane sulfonyloxycyclohexa-1,4-dienyl ester (Table 2, Entry 12 substrate)



Prepared using general procedure **B** from the corresponding diketone (1.00 g, 6.49 mmol) and purified by flash chromatography (hexane:EtOAc 10:1) to yield the *bis*-alkenyltriflate (1.36 g, 51%) as an orange oil:  $v_{max}$  (liquid film)/cm<sup>-1</sup> 2977 (C-H), 2944 (C-H), 2885 (C-H), 1705, 1418 (O-SO<sub>2</sub>), 1213 (SO<sub>2</sub>), 1140, 998, 895, 803, 737, 611;  $\delta_{H}$ 

(300 MHz, CDCl<sub>3</sub>) 5.89 (2H, dd (app. t), *J* 3.7 and 3.7), 3.05 (2H, td, *J* 3.8 and 0.7), 1.63 (2H, q, *J* 7.4), 1.38 (3H, s), 0.87 (3H, t, *J* 7.4);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 148.3, 113.5, 44.4, 28.0, 24.5, 23.0, 8.8.

# General procedure D: The enantioselective methoxycarbonylation of *bis*-alkenyltriflates

An oven dried Schlenk tube was charged with *bis*-alkenyltriflate (0.104 mmol), palladium (II) acetate (2.3 mg, 0.0104 mmol) and cyclohexyl-MOP **15** (5.0 mg, 0.0104 mmol). To this was added anhydrous methanol (0.66 mL) and anhydrous triethylamine (0.33 mL). The Schlenk tube was purged with nitrogen, and then fitted with a balloon of carbon monoxide (previously back-filled with N<sub>2</sub> and purged three times) with a glass tap attachment. The vessel was purged under vacuum, and filled with carbon monoxide using the balloon. This process was repeated three times. The reaction was then left open to the balloon, and heated at 45°C in a pre-heated oil bath for 2 h. The reaction was then cooled to room temperature, diluted with diethyl ether (5 mL) and concentrated under reduced pressure. The crude mixture was then purified by flash chromatography (solvents as stated).

6-Benzyl-6-methyl-5-trifluoromethanesulfonyloxy-cyclohexa-1,4-dienecarboxylic acid methyl ester (11) and 2-benzyl-2-methyl-cyclohexa-3,6-diene-1,3-dicarboxylic acid dimethyl ester (12)



Prepared using general procedure **D** from *bis*-alkenyltriflate **10** (50 mg, 0.104 mmol) to yield in order of elution (hexane:diethyl ether 10:1) monoester **11** (15.4 mg, 38%, 95% *ee*) as a colourless oil. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +5.4 (c. 0.021 in DCM)  $\nu_{max}$  (neat)/cm<sup>-1</sup> 3063, 3030, 2952 (CH sat.), 2884 (CH sat.), 1719 (C=O), 1696 (C=C), 1416 (O-SO<sub>2</sub>), 1213 (O-SO<sub>2</sub>), 1142 (SO<sub>2</sub>);  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 7.20-7.15 (3H, m), 7.02-6.99 (2H, m), 6.76 (1H, dd (app. t),

*J* 3.5 and 3.5), 5.67 (1H, dd (app. t), *J* 3.5 and 3.5), 3.81 (3H, s), 3.51 (1H, d, *J* 13.4), 2.85 (1H, d, *J* 13.4), 2.74 (1H, ddd (app. dt), *J* 24.0, 4.1 and 4.1), 2.28 (1H, ddd (app. dt), *J* 24.0, 3.3 and 3.3), 1.63 (3H, s);  $\delta_{\rm C}$  (75 MHz, CDCl<sub>3</sub>) 166.5, 151.1, 138.0, 137.2, 132.9, 130.2, 128.1, 126.7, 113.5, 52.2, 43.9, 42.2, 26.9, 24.3; *m/z* (FAB<sup>+</sup>) 390.9 ([M+H]<sup>+</sup>, 20%); *HRMS* calc. for C<sub>17</sub>H<sub>18</sub>F<sub>3</sub>O<sub>5</sub>S: 390.0749 [M+H]<sup>+</sup>; found: 390.0732 [M+H]<sup>+</sup> and diester **12** (14 mg, 45%) as a colourless oil.  $v_{\rm max}$  (Nujol)/cm<sup>-1</sup> 3061, 3028, 2988 (CH sat.), 2950 (CH sat.), 1720 (C=O);  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 7.13-7.11 (3H, m), 6.98-6.95 (2H, m), 6.69 (2H, overlapping dd, *J* 4.4 and 3.0), 3.80 (6H, s), 3.50 (2H, s), 2.58 (1H, dt, *J* 24.9 and 4.5), 2.00 (1H, dt, *J* 24.9 and 3.0), 1.68 (3H, s);  $\delta_{\rm C}$  (75 MHz, CDCl<sub>3</sub>) 167.8, 139.8, 136.1, 135.4, 130.6, 127.7, 126.1, 52.0, 43.1, 42.2, 27.5, 25.8; *m/z* (FAB<sup>+</sup>) 301.0 ([M+H]<sup>+</sup>, 25%); *HRMS* calc. for C<sub>18</sub>H<sub>21</sub>O<sub>4</sub>: 301.1440 [M+H]<sup>+</sup>; found: 301.1440 [M+H]<sup>+</sup>.

Enantiomeric excess determined to be 95% ee. Utilising an OD-H Daicel chiral column and a flow rate of 0.8 mLmin<sup>-1</sup> (99.9:0.1 Hexane-*iso*-propylalcohol). Retention times = 16.05 and 27.02 min respectively.

# General procedure E: The enantioselective alkoxycarbonylation of *bis*-alkenyltriflates

An oven dried Schlenk tube was charged with *bis*-alkenyltriflate **10** (50 mg, 0.104 mmol), palladium (II) acetate (2.3 mg, 0.0104 mmol) and PCy<sub>2</sub>-MOP **15** (5.0 mg, 0.0104 mmol). To this was added anhydrous alcohol (0.66 mL) and anhydrous triethylamine (0.33 mL). Where *para*-hydroxyanisole (129 mg, 1.04 mmol) was used as the alcohol the reaction was performed in acetonitrile (1 mL). The Schlenk tube was purged with nitrogen, and then fitted with a balloon of carbon monoxide (previously back-filled with N<sub>2</sub> and purged three times) with a glass tap attachment. The vessel was purged under vacuum, and filled with carbon monoxide using the balloon. This process was repeated three times. The reaction was then left open to the balloon, and heated at 45°C in a pre-heated oil bath for the time stated. The reaction was then cooled to room temperature, diluted with diethyl ether (5 mL) and concentrated under reduced pressure. The crude mixture was then purified by flash chromatography (solvents as stated).

6-Benzyl-6-methyl-5-trifluoromethanesulfonyloxy-cyclohexa-1,4-dienecarboxylic acid ethyl ester and 2-benzyl-2-methyl-cyclohexa-3,6-diene-1,3-dicarboxylic acid diethyl ester (Table 2, Entry 1)



Prepared using general procedure E from *bis*-alkenyltriflate **10** (50 mg, 0.104 mmol) to yield in order of elution (hexane:diethyl ether 10:1) the mono-ester (16.0 mg, 38%) as a colourless oil. δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>) 7.21-7.15 (3H, m), 7.03-7.00 (2H, m), 6.77-6.74 (1H, m), 5.69-5.66 (1H, m), 4.35-4.20 (2H, m), 3.52 (1H, d, J 13.7), 2.85 (1H, d, J 13.7), 2.74 (1H, ddd (app. dt), J 24.0, 4.1 and 4.1), 2.28 (1H, ddd (app. dt), J 24.0, 3.3 and 3.3), 1.63 (3H, s), 1.35 (3H, t, J 7.1); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>) 165.7, 150.9, 137.7, 136.4, 132.8, 129.9, 127.8, 126.4, 113.1, 60.7, 43.6, 41.9, 26.5, 23.9, 14.3 (CF<sub>3</sub> not seen); *m*/z LRMS (EI<sup>+</sup>) 285.0 (30%), 241.1 (30%), 209.1 (35%), 165.0 (40%), 151.0 (40%), 135.1 (50%), 128.1 (60%), 91.1 ( $[C_6H_5CH_2]^+$ , 100%); (Cl<sup>+</sup>) 422  $[M+NH_4]^+$ ; *HRMS* (ES<sup>+</sup>) calc. for  $C_{18}H_{23}F_{3}NO_{5}S$ : 422.1244 [M+NH<sub>4</sub>]<sup>+</sup>; found: 422.1244 [M+NH<sub>4</sub>]<sup>+</sup> and the diester (16.0 mg, 47%) as a colourless oil. δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>) 7.14-7.10 (3H, m), 7.00-6.97 (2H, m), 6.68 (2H, dd, J 4.4 and 3.0), 4.32-4.22 (4H, m), 3.51 (2H, s), 2.58 (1H, dt, J 24.9 and 4.4), 1.99 (1H, dt, J 24.9 and 3.0), 1.69 (3H, s), 1.35 (6H, t, J 7.1); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>) 167.1, 139.6, 135.4, 135.3, 130.3, 127.3, 125.7, 60.4, 42.8, 41.9, 27.1, 25.4, 14.3; m/z LRMS (EI<sup>+</sup>) 237.1 (10%), 92.2 (45%), 91.0 ( $[C_6H_5CH_2]^+$ , 100%), 77.1 ( $[C_6H_5]^+$ , 15%), 65.1 (25%); (Cl<sup>+</sup>) 346 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for C<sub>20</sub>H<sub>28</sub>NO<sub>4</sub>: 346.2013 [M+NH<sub>4</sub>]<sup>+</sup>; found: 346.2016 [M+NH<sub>4</sub>]<sup>+</sup>.

Enantiomeric excess determined to be 94% ee. Utilising an OD-H Daicel chiral column and a flow rate of 0.8 mLmin<sup>-1</sup> (99.8:0.2 Hexane-*iso*-propylalcohol). Retention times = 9.28 and 17.37 min respectively.

6-Benzyl-6-methyl-5-trifluoromethanesulfonyloxy-cyclohexa-1,4-dienecarboxylic acid *iso*-propyl ester and 2-benzyl-2-methyl-cyclohexa-3,6-diene-1,3-dicarboxylic acid di-*iso*-propyl ester (Table 2, Entry 2)



Prepared using general procedure E from bis-alkenyltriflate 10 (50 mg, 0.104 mmol) to yield in order of elution (hexane:diethyl ether 10:1) the iso-propyl mono-ester (21.0 mg, 48%) as a colourless oil.  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 7.20-7.15 (3H, m), 7.04-7.01 (2H, m), 6.74-6.71 (1H, m), 5.70-5.66 (1H, m), 5.16 (1H, septet, J 6.2), 3.52 (1H, d, J 13.5), 2.85 (1H, d, J 13.5), 2.74 (1H, dt, J 24.0 and 4.1), 2.27 (1H, dt, J 24.0 and 3.3), 1.64 (3H, s), 1.34 (3H, d, J 2.1), 1.32 (3H, d, J 2.1); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>) 165.3, 150.9, 137.7, 136.1, 133.1, 129.9, 127.7, 126.3, 113.1, 68.2, 43.6, 41.9, 26.5, 23.9, 21.9 (2 × C) (CF<sub>3</sub> not seen); m/z LRMS (EI<sup>+</sup>) 327.1 ([M-C<sub>6</sub>H<sub>6</sub>CH<sub>2</sub>]<sup>+</sup>, 10%), 285.1 (100%), 151.0 (40%), 135.1 (38%), 91.0 ( $[C_6H_6CH_2]^+$ , 100%); ( $CI^+$ ) 436 (100%)  $[M+NH_4]^+$ ; *HRMS* ( $ES^+$ ) calc. for  $C_{19}H_{22}F_{3}O_{5}S$ : 419.1135 [M+H]<sup>+</sup>; found: 419.1136 [M+H]<sup>+</sup> and the *iso*-propyl diester (6.7) mg, 18%) as a colourless oil.  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 7.14-7.10 (3H, m), 7.02-6.98 (2H, m), 6.65 (2H, overlapping dd, J 4.4 and 3.0), 5.17 (2H, septet, J 6.2), 3.51 (2H, s), 2.57 (1H, dt, J 24.8 and 4.4), 1.98 (1H, dt, J 24.8 and 3.0), 1.69 (3H, s), 1.35 (6H, d, J 2.6), 1.33 (6H, d, J 2.6); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>) 166.7, 139.6, 135.6, 135.1, 130.3, 127.3, 125.6, 67.7, 42.8, 42.0, 27.0, 25.4, 21.9 (2 × C); m/z LRMS (EI<sup>+</sup>) 265.1 ([M-C<sub>6</sub>H<sub>6</sub>CH<sub>2</sub>]<sup>+</sup>, 100%), 255.1 (50%), 91.1 ( $[C_6H_6CH_2]^+$ , 100%), 43.1 ( $[C_3H_7]^+$ , 71%); ( $CI^+$ ) 374  $[M+NH_4]^+$ ; *HRMS* ( $ES^+$ ) calc. for C<sub>22</sub>H<sub>32</sub>NO<sub>4</sub>: 374.2326 [M+NH<sub>4</sub>]<sup>+</sup>; found: 374.2327 [M+NH<sub>4</sub>]<sup>+</sup>.

Enantiomeric excess determined to be 90% ee. Utilising an OD-H Daicel chiral column and a flow rate of 0.8 mLmin<sup>-1</sup> (99.8:0.2 Hexane-*iso*-propylalcohol). Retention times = 15.27 and 23.58 min respectively.

6-(4-Methoxy-benzyl)-6-methyl-5-trifluoromethanesulfonyloxy-cyclohexa-1,4dienecarboxylic acid methyl ester and 2-(4-methoxy-benzyl)-2-methyl-cyclohexa-3,6-diene-1,3-dicarboxylic acid dimethyl ester (Table 1, Entry 4)



Prepared using general procedure **D** from the corresponding *bis*-alkenyltriflate (53 mg, 0.104 mmol) to yield in order of elution (hexane:diethyl ether 10:1) the mono-ester (19 mg, 44%) as a colourless oil.  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 6.95-6.90 (2H, m), 6.77-6.70 (3H, m), 5.69-5.66 (1H, m), 3.81 (3H, s), 3.76 (3H, s), 3.44 (1H, d, *J* 13.9), 2.82 (2H, m), 2.34 (1H, dt, *J* 24.1 and 3.3), 1.60 (3H, s);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 166.1, 158.1, 150.9, 136.7, 132.6, 130.8, 129.8, 116.3, 113.2, 113.0, 55.1, 51.8, 43.6, 41.0, 26.6, 23.8 (CF<sub>3</sub> not seen); *m/z* LRMS (El<sup>+</sup>) 239.2 (30%), 213.1 (30%), 165.0 (55%), 141.1 (55%), 135.1 (100%), 121.1 (100%); (Cl<sup>+</sup>) 438 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for C<sub>18</sub>H<sub>23</sub>F<sub>3</sub>NO<sub>6</sub>S: 438.1193 [M+NH<sub>4</sub>]<sup>+</sup>; found: 438.1194 [M+NH<sub>4</sub>]<sup>+</sup> and the diester (11 mg, 32%) as a colourless oil.  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 6.89-6.87 (2H, m), 6.70-6.66 (4H, m), 3.80 (6H, s), 3.74 (3H, s), 3.43 (2H, s), 2.59 (1H, dt, *J* 24.9 and 4.4), 2.06 (1H, dt, *J* 24.9 and 3.0), 1.65 (3H, s);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 167.5, 157.7, 135.6, 135.2, 131.6, 131.1, 112.7, 55.1, 51.6, 41.9 (2 × C), 27.2, 25.3; *m/z* LRMS (El<sup>+</sup>) 330.2 ([M]<sup>+</sup>, 20%), 300.3 (20%), 299.2 (100%), 121.1 (100%), 91.1 ([C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>]<sup>+</sup>, 30%), 77.1 ([C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>, 20%); (Cl<sup>+</sup>) 348 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for C<sub>19</sub>H<sub>26</sub>NO<sub>5</sub>: 348.1805 [M+NH<sub>4</sub>]<sup>+</sup>; found: 348.1802 [M+NH<sub>4</sub>]<sup>+</sup>.

Enantiomeric excess determined to be 89% ee. Utilising an OD-H Daicel chiral column and a flow rate of 0.8 mLmin<sup>-1</sup> (99.8:0.2 Hexane-*iso*-propylalcohol). Retention times = 14.82 and 23.15 min respectively.

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6-(4-Cyano-benzyl)-6-methyl-5-trifluoromethanesulfonyloxy-cyclohexa-1,4dienecarboxylic acid methyl ester and 2-(4-cyano-benzyl)-2-methyl-cyclohexa-3,6diene-1,3-dicarboxylic acid dimethyl ester (Table 2, Entry 5)



Prepared using general procedure **D** from the corresponding *bis*-alkenyltriflate (53 mg, 0.104 mmol) to yield in order of elution (hexane:diethyl ether 10:1) the mono-ester (16.0 mg, 37%) as a colourless oil.  $\delta_{H}$  (500 MHz, CDCl<sub>3</sub>) 7.47 (2H, d, *J* 8.0), 7.11 (2H, d, *J* 8.0), 6.76 (1H, dd (app. t), *J* 3.0 and 3.0), 5.69 (1H, dd (app. t), *J* 3.0 and 3.0), 3.79 (3H, s), 3.60 (1H, d, *J* 13.0), 2.89 (1H, d, *J* 13.0), 2.79 (1H, dt, *J* 24.0 and 4.0), 2.33 (1H, dt, *J* 24.0 and 3.0), 1.53 (3H, s);  $\delta_{C}$  (125 MHz, CDCl<sub>3</sub>) 165.9, 150.1, 143.4, 136.9, 132.0, 131.6, 130.5, 118.9, 118.4 (q, *J* 319.4, CF<sub>3</sub>), 113.4, 110.4, 52.0, 43.4, 41.7, 26.5, 24.1; *HRMS* (ES<sup>+</sup>) calc. for C<sub>18</sub>H<sub>17</sub>F<sub>3</sub>NO<sub>5</sub>S: 416.0774 [M+H]<sup>+</sup>; found: 416.0773 [M+H]<sup>+</sup> and the diester (14.2 mg, 42%) as a colourless oil.  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 7.45-7.42 (2H, m), 7.10-7.07 (2H, m), 6.71 (2H, dd, J 4.4 and 3.0), 3.81 (6H, s), 3.61 (2H, s), 2.65 (1H, dt, *J* 25.2 and 4.4), 2.06 (1H, dt, *J* 25.2 and 3.0), 1.67 (3H, s);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 167.2, 145.4, 135.8, 134.5, 131.2, 130.9, 115.3, 111.2, 51.8, 42.7, 41.8, 27.1, 25.6; *m/z* LRMS (EI<sup>+</sup>) 209.0 (100%), 177.1 (90%), 117.1 (NCC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>]<sup>+</sup>, 60%), 91.1 ([C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>]<sup>+</sup>, 80%), 59.1 (90%); (Cl<sup>+</sup>) 343.3 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (Cl<sup>+</sup>) calc. for C<sub>19</sub>H<sub>23</sub>N<sub>2</sub>O<sub>4</sub>: 343.1652 [M+NH<sub>4</sub>]<sup>+</sup>; found: 343.1652 [M+NH<sub>4</sub>]<sup>+</sup>.

Enantiomeric excess determined to be 90% ee. Utilising an OD-H Daicel chiral column and a flow rate of 0.8 mLmin<sup>-1</sup> (99.8:0.2 Hexane-*iso*-propylalcohol). Retention times = 16.98 and 22.11 min respectively.

\*6-(4-trifluoromethane-benzyl)-6-methyl-5-trifluoromethanesulfonyloxy-cyclohexa-1,4-dienecarboxylic acid methyl ester and 2-(4-trifluoromethane-benzyl)-2-methylcyclohexa-3,6-diene-1,3-dicarboxylic acid dimethyl ester



Prepared using general procedure **D** from the corresponding *bis*-alkenyltriflate (51 mg. 0.093 mmol) to yield in order of elution (hexane:diethyl ether 20:1) the monoester (17 mg, 40%) as an opaque oil  $v_{max}$ (film)/cm<sup>-1</sup>; 3044, 2984 (CH), 2953, 2887, 1718, 1697 (C=O), 1640 (C=C), 1605, 1511, 1436, 1351, 1159, 965; δ<sub>H</sub> (500 MHz, CDCI<sub>3</sub>) 7.46 (2H, d, J 8.0), 7.13 (2H, d, J 8.0), 6.79-6.78 (1H, m), 5.72-5.71 (1H, m), 3.82 (3H, s), 3.62 (1H, d, J 13.5), 2.92 (1H, d, J 13.5), 2.80 (1H, dt, J 24.2 and 4.1), 2.34 (1H, dt, J 24.2 and 4.1), 1.65 (3H, s); δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>) 165.9, 150.2, 141.7, 136.9, 132.1, 130.0, 128.6 (g,  ${}^{2}J_{CF}$  33), 124.6 (g,  ${}^{3}J_{CF}$  4), 124.2 (g,  ${}^{1}J_{CF}$  272), 118.3 ( ${}^{1}J_{CF}$  320), 113.3, 51.9, 43.4, 41.4, 26.5, 24.0; *HRMS* (ESI +ve); C<sub>18</sub>H<sub>16</sub>F<sub>6</sub>O<sub>5</sub>S+Na, Requires: 481.0515, Found: 481.0516 and the diester (5 mg, 15%) as a colourless oil.  $v_{max}$ (film)/cm<sup>-1</sup>; 2954, 2930. 2854 (CH), 1721 (CO), 1618 (C=C), 1435, 1225, 1163, 1122, 1104, 1034; δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>) 7.39 (2H, d, J 8.2), 7.09 (2H, d, J 8.2), 6.71 (2H, dd, J 4.4 and 3.0), 3.82 (6H, s), 3.60 (2H, s), 2.63 (1H, dt, J 25.2 and 4.4), 2.03 (1H, dt, J 25.2 and 3.0), 1.69 (3H, s); δ<sub>c</sub> (125 MHz, CDCl<sub>3</sub>) 167.2, 143.6, 135.7, 134.6, 130.3, 128.0 (g, <sup>2</sup>J<sub>CE</sub> 33), 124.4 (<sup>1</sup>J<sub>CE</sub> 272), 124.2 (g, <sup>3</sup>J<sub>CF</sub> 4), 51.7, 42.4, 41.7, 27.0, 25.5; *HRMS* (ESI +ve); C<sub>19</sub>H<sub>19</sub>F<sub>3</sub>O<sub>4</sub>+Na, Requires: 391.1128, Found: 391.1126 and the bis-alkenyltriflate starting material (18 mg, 35%).

Enantiomeric excess determined to be 85% ee. Utilising an OD-H Daicel chiral column and a flow rate of 0.8 mLmin<sup>-1</sup> (99.7:0.3 Hexane-*iso*-propylalcohol). Retention times = 8.51 and 9.16 min respectively.

\*6-(4-fluoro-benzyl)-6-methyl-5-trifluoromethanesulfonyloxy-cyclohexa-1,4dienecarboxylic acid methyl ester and 2-(4-fluoro-benzyl)-2-methyl-cyclohexa-3,6diene-1,3-dicarboxylic acid dimethyl ester (Table 2, Entry 7)



Prepared using general procedure **D** from the corresponding *bis*-alkenyltriflate (52 mg, 0.104 mmol) to yield in order of elution (hexane:diethyl ether 20:1) the monoester (15 mg, 35%) as a colourless oil.  $v_{max}$ (film)/cm<sup>-1</sup>; 3044, 2984, 2953, 2887 (CH), 1718, 1697 (CO), 1640 (C=C), 1605, 1511, 1436, 1351, 1159, 965; δ<sub>H</sub> (200 MHz, CDCl<sub>3</sub>) 7.00-6.82 (4H, m), 6.76 (1H, ddd, J 4.4, 3.4 and 1.4), 5.68 (1H, ddd, J 4.4, 3.4 and 1.4), 3.80 (3H, s), 3.50 (1H, d, J 13.9), 2.82 (1H, d, J 13.9), 2.72 (1H, dt, J 24.2 and 4.0), 2.34 (1H, dt, J 23.8 and 3.8), 1.60 (3H, s);  $\delta_{\rm C}$  (125 MHz, CDCl<sub>3</sub>) 166.0, 161.5 (d, <sup>1</sup>J<sub>CF</sub> 244), 150.5, 136.7, 133.3 (d,  ${}^{4}J_{CF}$  3), 132.3, 131.1 (d,  ${}^{3}J_{CF}$  8), 118.3 (g,  ${}^{1}J_{CF}$  320), 114.5 (d,  ${}^{2}J_{CF}$  21), 113.1, 51.8, 43.5, 40.9, 26.5, 23.7; *HRMS* (ESI +ve); C<sub>17</sub>H<sub>16</sub>F<sub>4</sub>O<sub>5</sub>S+Na, Requires: 431.0547, Found: 431.0551 and the diester (12 mg, 36%) as a colourless oil. v<sub>max</sub>(film)/cm<sup>-1</sup>; 3067, 2995, 2980, 2951, 2899 (CH), 1714 (CO), 1507, 1435, 1218, 1034, 828; δ<sub>H</sub> (200 MHz, CDCI<sub>3</sub>) 6.96-6.76 (4H, m), 6.69 (2H, dd, J 4.4 and 3.1), 3.79 (6H, s), 3.47 (2H, s), 2.61 (1H, dt, J 24.9 and 4.4), 2.04 (1H, dt, J 24.9 and 3.1), 1.64 (3H, s); δ<sub>C</sub>  $(125 \text{ MHz}, \text{ CDCI}_3)$  167.3, 161.2 (d,  ${}^{1}J_{CF}$  244), 135.6, 135.1 (d,  ${}^{4}J_{CF}$  3), 134.8, 131.4 (d,  ${}^{3}J_{CF}$  8), 131.4, 114.0 (d,  ${}^{2}J_{CF}$  20), 51.6, 41.8, 27.0, 25.2; *HRMS* (ESI +ve); C<sub>18</sub>H<sub>19</sub>FO<sub>4</sub>+Na, Requires: 341.1160, Found: 341.1154. The *bis*-alkenyltriflate starting material was also recovered (12 mg, 23%).

Enantiomeric excess determined to be >95% ee. Utilising an OD-H Daicel chiral column and a flow rate of 0.8 mLmin<sup>-1</sup> (99.5:0.5 Hexane-*iso*-propylalcohol). Retention times = 7.29 and 7.50 min respectively. \*6-(2-methyl-benzyl)-6-methyl-5-trifluoromethanesulfonyloxy-cyclohexa-1,4dienecarboxylic acid methyl ester and 2-(2-methyl-benzyl)-2-methyl-cyclohexa-3,6diene-1,3-dicarboxylic acid dimethyl ester (Table 2, Entry 8)



Prepared using general procedure **D** from the corresponding *bis*-alkenyltriflate (51 mg. 0.103 mmol) to yield in order of elution (hexane:diethyl ether 20:1) the monoester (15 mg, 36%) as a colourless oil.  $v_{max}$ (film)/cm<sup>-1</sup>; 3022, 2954 (CH), 1719 (CO), 1493, 1461, 1243, 1212, 1141, 1010; δ<sub>H</sub> (200 MHz, CDCl<sub>3</sub>) 7.08-6.97 (4H, m), 6.84 (1H, ddd, J 4.4, 3.0 and 1.4), 5.64 (1H, ddd, J 4.4, 3.0 and 1.3), 3.79 (3H, s), 3.48 (1H, d, J 14.4), 2.95 (1H, d, J 14.4), 2.75 (1H, dt, J 24.0 and 4.4), 2.25 (1H, dt, J 24.0 and 3.0), 2.23 (3H, s), 1.66 (3H, s); δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>) 160.1, 151.1, 137.2, 137.0, 135.7, 133.1, 130.6, 130.1, 124.9, 124.2, 118.3 (g,  ${}^{1}J_{CF}$  320), 113.6, 51.8, 43.2, 39.0, 29.6, 23.9, 19.4; *HRMS* (ESI +ve); C<sub>18</sub>H<sub>19</sub>F<sub>3</sub>O<sub>5</sub>S+Na, Requires: 427.0789, Found: 427.0789 and the diester (9) mg, 28%) as a colourless oil.  $v_{max}$ (film)/cm<sup>-1</sup>; 2990, 2951, 2849 (CH), 1721 (CO), 1434, 1377, 1244, 1222, 1076, 1034; δ<sub>H</sub> (200 MHz, CDCl<sub>3</sub>) 704-6.94 (4H, m), 6.73 (2H, dd, J 4.5 and 2.6), 3.75 (6H, s), 3.49 (2H, s), 2.60 (1H, dt, J 24.6 and 4.5), 2.16 (3H, s), 2.96 (1H, dt, J 24.5 and 3.0), 1.72 (3H, s); δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>) 167.4, 137.5, 137.4, 136.1, 135.7, 129.8, 125.6, 124.6, 52.2, 51.5, 41.6, 39.7, 27.2, 25.6; HRMS (ESI +ve); C<sub>19</sub>H<sub>22</sub>O<sub>4</sub>+Na, Requires: 337.1410, Found: 337.1411. The *bis*-alkenyltriflate starting material was also recovered (11 mg, 22%).

Enantiomeric excess determined to be 80% ee. Utilising an OD-H Daicel chiral column and a flow rate of 0.8 mLmin<sup>-1</sup> (99.7:0.3 Hexane-*iso*-propylalcohol). Retention times = 15.99 and 23.16 min respectively.

6-Methyl-6-naphthalen-2-ylmethyl-5-trifluoromethanesulfonyloxy-cyclohexa-1,4dienecarboxylic acid methyl ester and 2-methyl-2-naphthalen-2-ylmethylcyclohexa-3,6-diene-1,3-dicarboxylic acid dimethyl ester (Table 2, Entry 9)



Prepared using general procedure **D** from the corresponding *bis*-alkenyltriflate (55 mg. 0.104 mmol) to yield in order of elution (hexane:diethyl ether 10:1) the mono-ester (20.0 mg, 44%) as a colourless oil.  $v_{max}$  (liquid film)/cm<sup>-1</sup> 3057 (C-H), 2951 (C-H), 1717 (C=O), 1418 (O-SO<sub>2</sub>), 1244, 1215 (O-SO<sub>2</sub>), 1142, 1011, 892, 867, 761, 608; δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>) 7.78-7.71 (2H, m), 7.67-7.65 (1H, m), 7.48-7.40 (3H, m), 7.16 (1H, dd, J 8.4 and 1.7), 6.73-6.70 (1H, m), 5.67-5.65 (1H, m), 3.84 (3H, s), 3.69 (1H, d, J 13.7), 3.04 (1H, d, J 13.7), 2.70 (1H, ddd (app. dt), J 24.1, 4.1 and 4.1), 2.22 (1H, ddd (app. dt), J 24.1, 3.3 and 3.3), 1.68 (3H, s);  $\delta_C$  (75 MHz, CDCl<sub>3</sub>) 166.1, 150.9, 136.8, 135.4, 133.2, 132.5, 132.1, 128.6, 128.1, 127.7, 127.5, 127.2, 125.7, 125.4, 118.4 (g, J 319.3, CF<sub>3</sub>), 113.0, 51.9, 43.7, 41.9, 26.5, 24.2; *m/z* LRMS (EI<sup>+</sup>) 440.2 (18%), 231.1 (18%), 215.1 (32%), 202.1 (52%), 189.0 (40%), 178.1 (53%), 165.2 (100%), 141.0 (100%), 115.0 (40%), 69.0 (37%); (Cl<sup>+</sup>) 458 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for C<sub>21</sub>H<sub>23</sub>F<sub>3</sub>NO<sub>5</sub>S: 458.1244 [M+NH<sub>4</sub>]<sup>+</sup>; found: 458.1246  $[M+NH_4]^+$  and the diester (11.9 mg, 33%) as a colourless oil.  $\delta_H$  (300 MHz, CDCl<sub>3</sub>) 7.76-7.68 (2H, m), 7.59 (1H, d, J 8.4), 7.41-7.37 (3H, m), 7.15 (1H, d, J 8.4), 6.70 (2H, dd (app.t), J 3.1 and 3.1), 3.83 (6H, s), 3.69 (2H, s), 2.53 (1H, dt, J 25.0 and 4.4), 1.93 (1H, dt, J 25.0 and 3.0), 1.73 (3H, s);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 167.4, 137.0, 135.6, 135.1, 133.1, 131.9, 128.8, 128.6, 127.6, 127.5, 126.6, 125.4, 125.0, 51.6, 42.8, 41.9, 27.2, 25.7; *m/z* LRMS (EI<sup>+</sup>) 350.2 (9%), 319.2 (10%), 259.2 (12%), 215.1 (53%), 177.1 (40%), 142.1 (100%), 115.0 (63%), 91.1 (32%), 59.1 (33%); (Cl<sup>+</sup>) 368.3 [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for  $C_{22}H_{26}NO_4$ : 368.1856 [M+NH<sub>4</sub>]<sup>+</sup>; found: 368.1860 [M+NH<sub>4</sub>]<sup>+</sup>.

Enantiomeric excess determined to be 93% ee. Utilising an OD-H Daicel chiral column and a flow rate of 0.8 mLmin<sup>-1</sup> (99.8:0.2 Hexane-*iso*-propylalcohol). Retention times = 23.18 and 25.92 min respectively.

6-Cyclohex-1-enylmethyl-6-methyl-5-trifluoromethanesulfonyloxy –cyclohexa -1,4dienecarboxylic acid methyl ester and 2-cyclohex-1-enylmethyl-2-methylcyclohexa-3,6-diene-1,3-dicarboxylic acid dimethyl ester (Table 2, Entry 10)



Prepared using general procedure **D** from the corresponding *bis*-alkenyltriflate (53 mg. 0.104 mmol) to yield in order of elution (hexane:diethyl ether 10:1) the mono-ester (16.8 mg, 41%) as a colourless oil.  $v_{max}$  (liquid film)/cm<sup>-1</sup> 3445, 2939 (C-H), 2863 (C-H), 1716 (C=O), 1418 (O-SO<sub>2</sub>), 1219 (SO<sub>2</sub>), 1141, 1037, 1001, 962, 905, 799, 613; δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>) 6.93 (1H, td, J 3.6 and 1.2), 5.75 (1H, td, J 3.6 and 1.2), 5.32 (1H, br s), 3.75 (3H, s), 3.10-2.89 (2H, m), 2.80 (1H, d, J 14.1), 2.27 (1H, d, J 14.0), 1.87 (4H, br d, J 14.0), 1.51-1.43 (7H, m); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>) 166.0, 152.6, 135.4, 134.3, 134.0, 125.8, 111.3, 51.7, 43.9, 42.2, 29.3, 26.9, 25.5, 25.2, 23.2, 22.2 (CF<sub>3</sub> not seen); *m/z* LRMS  $(EI^{\dagger})$  394 (10%), 299.1 ([M-C<sub>6</sub>H<sub>9</sub>CH<sub>2</sub>]<sup>+</sup>, 100%), 107.1 (32%), 95.0 ([C<sub>6</sub>H<sub>9</sub>CH<sub>2</sub>]<sup>+</sup>, 90%), 81.0 ( $[C_6H_9]^+$ , 100%), 69.0 ( $[CF_3]^+$ , 82%), 55.1 (45%); ( $CI^+$ ) 412 (20%)  $[M+NH_4]^+$ ; *HRMS* (EI) calc. for  $C_{17}H_{21}F_{3}O_{5}S$ : 394.1056 [M]<sup>+</sup>; found: 394.1057 [M]<sup>+</sup> and the diester (6.3 mg, 20%) as a colourless oil.  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 6.84 (2H, dd (app.t), J 3.7 and 3.7), 5.21 (1H, br s), 3.73 (6H, s), 2.92 (2H, dd, J 6.9 and 3.7), 2.83 (2H, s), 1.88-1.75 (4H, m), 1.61 (3H, s), 1.48-1.41 (4H, m); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>) 167.2, 136.7, 136.0, 134.1, 124.7, 51.5, 44.6, 40.5, 31.6, 29.4, 27.3, 25.5, 23.2, 22.3; *m/z* LRMS (El<sup>+</sup>) 209.1 (23%), 119.0 (51%), 91.0 (82%), 81.1 ([C<sub>6</sub>H<sub>9</sub>]<sup>+</sup>, 100%), 67.1 (60%), 59.1 ([CH<sub>3</sub>OCO]<sup>+</sup>, 75%); (Cl<sup>+</sup>) 322.3 (10%)  $[M+NH_4]^+$ ; *HRMS* (ES<sup>+</sup>) calc. for  $C_{18}H_{25}O_4$ : 305.1747  $[M+H]^+$ ; found: 305.1751 [M+H]<sup>+</sup>.

Enantiomeric excess determined to be 74% ee. Utilising an OD-H Daicel chiral column and a flow rate of 0.8 mLmin<sup>-1</sup> (100% Hexane). Retention times = 16.68 and 18.10 min respectively.

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6-Methyl-6-propyl-5-trifluoromethanesulfonyloxy-cyclohexa-1,4-diene carboxylic acid methyl ester and 2-Methyl-2-propyl-cyclohexa-3,6-diene-1,3-dicarboxylic acid dimethyl ester (Table 2, Entry 11)



Prepared using general procedure **D** from the corresponding *bis*-alkenyltriflate (47 mg, 0.104 mmol) to yield in order of elution (hexane:diethyl ether 10:1) the mono-ester (11.4 mg, 32%) as a colourless oil.  $\delta_{H}$  (300 MHz, CDCl<sub>3</sub>) 6.95 (1H, td, J 3.6 and 1.1), 5.80 (1H, td, J 3.6 and 1.1), 3.75 (3H, s), 3.03 (2H dd (app. t), J 3.6 and 3.6), 2.13 (1H, overlapping ddd, J 14.0, 12.4 and 4.8), 1.57-1.48 (1H, m), 1.46 (3H, s), 1.28-0.99 (2H, m), 0.87 (3H, t, J 7.2); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>) 165.8, 152.1, 135.6, 133.5, 118.4 (q, J 317.8, CF<sub>3</sub>), 112.0, 51.7, 42.0, 37.7, 26.9, 24.6, 18.7, 14.0; *m/z* LRMS (El<sup>+</sup>) 299.1 (IM-C<sub>3</sub>H<sub>7</sub>)<sup>+</sup>. 73%), 298.1 (100%), 107.0 (40%), 91.1 (50%), 69.0 ( $[CF_3]^+$ , 100%), 40.1 (70%); ( $CI^+$ ) 360 (100%)  $[M+NH_4]^+$ ; *HRMS* (ES<sup>+</sup>) calc. for C<sub>13</sub>H<sub>21</sub>F<sub>3</sub>NO<sub>5</sub>S: 360.1087  $[M+NH_4]^+$ ; found: 360.1087 [M+NH<sub>4</sub>]<sup>+</sup> and the diester (10.0 mg, 38%) as a colourless oil.  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 6.85 (2H, dd (app. t), J 4.6 and 4.6), 3.73 (6H, s), 2.94 (2H, dd (app. t), J 4.6 and 4.6), 2.09-2.04 (2H, m), 1.55 (3H, s), 1.09-0.96 (2H, m), 0.83 (3H, t, J 7.2); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>) 167.2, 136.1, 134.1, 51.5, 40.3, 39.0, 27.6, 26.4, 19.3, 14.4; m/z LRMS (EI<sup>+</sup>) 252.2 ([M]<sup>+</sup>, 100%), 235.1 (85%), 193.1 ([M-CO<sub>2</sub>CH<sub>3</sub>]<sup>+</sup>, 40%), 165.1 (100%), 119.0 (35%), 91.0 (36%), 59.1  $([CH_3OCO]^+, 40\%)$ , 43.2  $([C_3H_7]^+, 43\%)$ ;  $(CI^+)$  270 (100%) $[M+NH_4]^+$ ; *HRMS* (ES<sup>+</sup>) calc. for C<sub>14</sub>H<sub>24</sub>NO<sub>4</sub>: 270.1700  $[M+NH_4]^+$ ; found: 270.1700 [M+NH₄]<sup>+</sup>.

Enantiomeric excess determined to be 87% ee. Utilising an OD-H Daicel chiral column and a flow rate of 0.8 mLmin<sup>-1</sup> (99.8:0.2 Hexane-*iso*-propylalcohol). Retention times = 14.93 and 15.41 min respectively.

6-Ethyl-6-methyl-5-trifluoromethanesulfonyloxy-cyclohexa-1,4-diene carboxylic acid methyl ester and 2-ethyl-2-methyl-cyclohexa-3,6-diene-1,3-dicarboxylic acid dimethyl ester (Table 2, Entry 12)



Prepared using general procedure **D** from the corresponding *bis*-alkenyltriflate (44 mg, 0.104 mmol) to yield in order of elution (hexane:diethyl ether 10:1) the mono-ester (10.6 mg, 31%) as a colourless oil.  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 7.00 (1H, td, *J* 3.6 and 1.2), 5.83 (1H, td, *J* 3.6 and 1.2), 3.75 (3H, s), 3.04 (2H dd (app. t), *J* 3.7 and 3.7), 2.17 (1H, dt (app. septet), *J* 7.4 and 7.0), 1.61 (1H, dt (app. septet), *J* 7.4 and 7.0), 1.47 (3H, s), 0.74 (3H, t, *J* 7.5);  $\delta_{\rm C}$  (75 MHz, CDCl<sub>3</sub>) 165.8, 151.7, 136.1, 133.1, 118.3 (q, *J* 320.1, CF<sub>3</sub>), 112.4, 51.7, 42.5, 28.3, 26.9, 24.3, 9.5; *m/z* LRMS (El<sup>+</sup>) 299.1 ([M-C<sub>2</sub>H<sub>6</sub>]<sup>+</sup>, 45%), 107.0 (50%), 91.1 (50%), 69.1 ([CF<sub>3</sub>]<sup>+</sup>, 100%), 59.1 (40%); (Cl<sup>+</sup>) 346 (15%) [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (El<sup>+</sup>) calc. for C<sub>12</sub>H<sub>15</sub>F<sub>3</sub>O<sub>5</sub>S: 328.0587 [M]<sup>+</sup>; found: 325.0585 [M]<sup>+</sup> and the diester (9.4 mg, 38%) as a colourless oil.  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 6.89 (2H, dd (app. t), *J* 3.6 and 3.6), 3.73 (6H, s), 2.95 (2H, dd (app. t), *J* 3.6 and 3.6), 1.56 (3H, s), 0.65 (3H, t, *J* 7.5);  $\delta_{\rm C}$  (75 MHz, CDCl<sub>3</sub>) 167.2, 135.6, 134.6, 51.5, 40.9, 29.4, 27.6, 26.2, 10.1; *m/z* LRMS (El<sup>+</sup>) 209.2 (20%), 165.1 (25%), 119.0 (30%), 91.1 (100%), 69.1 (25%), 59.1 (45%); (Cl<sup>+</sup>) 256 (100%) [M+NH<sub>4</sub>]<sup>+</sup>; *HRMS* (ES<sup>+</sup>) calc. for C<sub>13</sub>H<sub>22</sub>NO<sub>4</sub>: 256.1543 [M+NH<sub>4</sub>]<sup>+</sup>; found: 256.1543 [M+NH<sub>4</sub>]<sup>+</sup>.

Enantiomeric excess determined to be 61% ee. Utilising an OD-H Daicel chiral column and a flow rate of 0.8 mLmin<sup>-1</sup> (99.8:0.2 Hexane-*iso*-propylalcohol). Retention times = 13.66 and 15.01 min respectively.

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