

# **Congested $C_2$ -Symmetric Aryliodanes Based on an *anti*- Dimethanoanthracene Backbone**

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**Supporting Information**

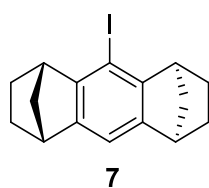
## General Remarks

NMR spectra were recorded on Varian Inova 300 MHz, Varian Inova 400 MHz and Varian 500 MHz FT spectrometers at 30 °C with CDCl<sub>3</sub>, CD<sub>3</sub>OD or DMSO-*d*<sub>6</sub> as the solvent. Chemical shifts are reported in ppm relative to the residual solvent signal. High resolution mass spectra were measured on a Waters/Micromass GCT and Waters 2996 Photodiode Array Detector instrument. Infrared spectra were recorded on a Varian 3100 FT-IR spectrometer at room temperature. Melting points were recorded in open capillaries on a digital Barnsted Electro Thermal 9300 melting point apparatus and are uncorrected.

## Materials

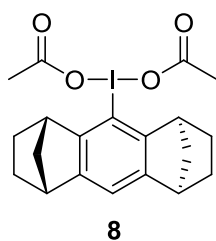
All reagents were obtained from commercial suppliers and used without further purification. Dimethyldioxirane (DMDO)<sup>1</sup> and Koser's reagent<sup>2</sup> were prepared as previously reported. All dry solvents were obtained from a dry solvent purification system with the exception of DMF which was dried by distillation over CaH<sub>2</sub>. Compounds **7**–**12f** were considered light sensitive and were shielded from light by covering with aluminium foil. Thin Layer Chromatography was performed on Merck Aluminium sheets (silica gel 60 F<sub>254</sub>). Detection was carried out by UV and by colouration with ceric ammonium molybdate (CAM). Flash column chromatography was performed using Merck silica gel 60 (230-400 mesh).

### 9-Iodo-1,2,3,4,5,6,7,8-octahydro-1,4;5,8-*anti*-dimethanoanthracene (**7**)



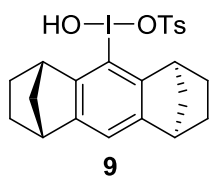
Arene **6** (2.38g, 11.3 mmol, 1.0 eq.) was dissolved in EtOAc (70 mL). To this solution (diacetoxy)iodobenzene (2.18 g, 6.8 mmol, 0.6 eq) and iodine (3.45 g, 13.6 mmol, 1.2 eq.) were added. The purple solution was left stirring at room temperature for 12 hours until TLC analysis (SiO<sub>2</sub>, pentane) showed the starting material had been consumed. A saturated aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (30 mL) was then added and the mixture stirred until the purple colour faded. The organic layer was then washed with H<sub>2</sub>O (2 x 25 mL), dried over MgSO<sub>4</sub> and removed *in vacuo* to yield a yellow solid. The product was isolated as white needles (2.92 g, 74%) after recrystallisation from hot DCM/MeOH. <sup>1</sup>H NMR and <sup>13</sup>C NMR data was consistent with that of literature reports.<sup>1</sup>

### 9-[(Diacetoxy)iodo]-1,2,3,4,5,6,7,8-octahydro-1,4;5,8-*anti*-dimethanoanthracene (8)



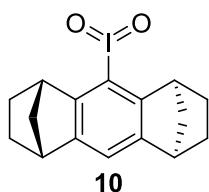
To a stirred solution of iodoarene **7** (1.0 g, 2.96 mmol) in acetic acid (26 mL) at 60 °C, sodium perborate trihydrate (4.56 g, 29.60 mmol) was added portionwise over the course of 20 minutes. After complete addition the reaction mixture was left to stir at this temperature. The reaction was followed by  $^1\text{H}$  NMR through the removal of aliquots at regular intervals. After four hours the starting material had been consumed. The reaction was allowed to cool to room temperature and extracted with DCM (3 x 30 mL). The combined organic extracts were washed with water (3 x 20 mL), dried over  $\text{MgSO}_4$  and the organic solvents removed *in vacuo* to yield the title compound as a white powder (0.99 g, 74%). Mp: 152–155 °C (decomp.); IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3054, 2983, 1651, 1424, 739;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.15–1.22 (m, 2 H,  $\text{CH}_2$ ), 1.24–1.31 (m, 2 H,  $\text{CH}_2$ ), 1.53 (d,  $J = 8.8$  Hz, 2 H,  $\text{CHCHHCH}$ ), 1.87 (d,  $J = 8.8$  Hz, 2 H,  $\text{CHCHHCH}$ ), 1.90–1.95 (m, 4 H,  $\text{CH}_2$ ), 1.97 (s, 6 H,  $\text{CH}_3$ ), 3.47 (brs, 2 H, CH), 3.52 (brs, 2 H, CH), 7.17 (s, 1 H, ArH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  20.5, 26.3, 26.8, 45.4, 47.6, 49.1, 112.4, 117.9, 147.8, 148.1, 176.1; HRMS (EI):  $\text{C}_{20}\text{H}_{23}\text{O}_4\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  calculated: 477.0539, found: 477.0526.

### 9-[Hydroxy(tosyloxy)iodo]-1,2,3,4,5,6,7,8-octahydro-1,4;5,8-*anti*-dimethanoanthracene (9)



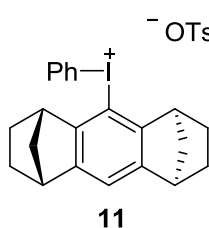
To a solution of **8** (20.0 mg, 0.04 mmol) in  $\text{CDCl}_3$  (1 mL) was added *p*-toluenesulfonic acid monohydrate (7.6 mg, 0.04 mmol). The solution immediately turned a bright yellow colour and was left to stir for 30 min. Examination of this solution by  $^1\text{H}$  NMR revealed signals consistent with the title compound.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.12–1.15 (m, 4 H,  $\text{CH}_2$ ), 1.51 (d,  $J = 8.9$  Hz, 2 H,  $\text{CHCHHCH}$ ), 1.82–1.87 (m, 6 H,  $\text{CH}_2$ ), 2.34 (s, 3 H,  $\text{CH}_3$ ), 3.52 (brs, 4 H, CH), 7.09 (d,  $J = 8.2$  Hz, 2 H, OTs), 7.23 (s, 1 H, ArH), 7.42 (d,  $J = 8.2$  Hz, 2 H, OTs). HRMS (EI):  $\text{C}_{23}\text{H}_{24}\text{O}_3\text{SI}$  [ $\text{M} - \text{OH}$ ] $^+$  calculated: 507.0491, found: 507.0510.

### 9-Iodyl-1,2,3,4,5,6,7,8-octahydro-1,4;5,8-*anti*-dimethanoanthracene (10)



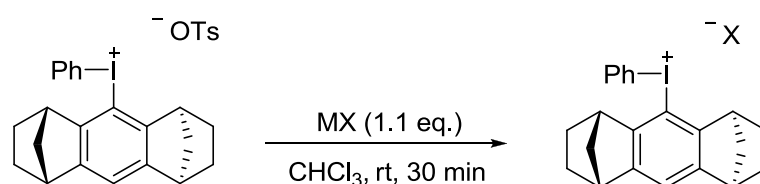
Under an N<sub>2</sub> atmosphere, DMDO (0.1 M in acetone, 35 mL) was added to a solution of iodoarene **7** (336 mg, 1.0 mmol) in dry DCM (5 mL) at 0 °C. A white solid precipitated immediately. The heterogeneous mixture was allowed to reach room temperature and left to stir overnight. The mixture was then filtered, washed with DCM (5 mL) and left to air dry, yielding the title compound as a fine white powder (340 mg, 92%). Mp: 179-182 °C; IR (KBr, cm<sup>-1</sup>): ν 3214, 1634, 1475, 1321, 1251, 1180, 1107, 948, 889, 856, 781; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 1.03 (brs, 2 H, CH<sub>2</sub>), 1.23 (brs, 2 H, CH<sub>2</sub>), 1.54 (brs, 2 H, CHCHHCH), 1.65 (brs, 2 H, CHCHHCH), 1.91 (brs, 4 H, CH<sub>2</sub>), 4.24 (brs, 2 H, CH), 7.29 (s, 1 H, ArH), Two protons are obscured by the residual solvent peak at 3.38 as confirmed by 2D NMR correlation; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 26.7, 27.1, 41.5, 43.1, 49.2, 117.4, 136.4, 144.6, 148.6; HRMS (EI): C<sub>16</sub>H<sub>17</sub>O<sub>2</sub>NaI [M + Na]<sup>+</sup> calculated: 391.0171, found: 391.0152.

### 1,2,3,4,5,6,7,8-Octahydro-1,4;5,8-*anti*-dimethanoanthracene-9-iodonium(phenyl)tosylate (11)



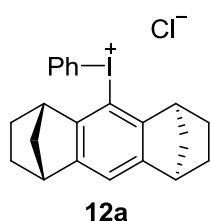
To a stirred solution of arene **6** (210 mg, 1.0 mmol) in TFE/DCM (5 mL, 1:1) was added Koser's reagent (392 mg, 1.0 mmol). The dark purple solution was left to stir at room temperature for a further 4 hours at which point the solution had lightened to a yellow colour. The solvent was removed *in vacuo* to yield a brown oily residue. Upon addition of Et<sub>2</sub>O a white solid precipitated. This was filtered and washed with Et<sub>2</sub>O to yield the title compound as a white solid (571 mg, 98%). Mp: 181-183 °C (decomp.); IR (KBr, cm<sup>-1</sup>): ν 3456, 2967, 2359, 1470, 1208, 1009, 747; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.91-0.95 (m, 2 H, CH<sub>2</sub>), 1.09-1.13 (m, 2 H, CH<sub>2</sub>), 1.54 (d, *J* = 9.1 Hz, 2 H, CHCHHCH), 1.80 (d, *J* = 9.1 Hz, 2 H, CHCHHCH), 1.84-1.98 (m, 4 H, CH<sub>2</sub>), 2.36 (s, 3 H, CH<sub>3</sub>), 3.52 (s, 2 H, CH), 3.56 (s, 2 H, CH), 7.11 (d, *J* = 8.2 Hz, 2 H, Ts), 7.21 (s, 1 H, ArH), 7.39 (t, *J* = 8.4 Hz, PhH), 7.48 (t, *J* = 7.4 Hz, 1 H, PhH), 7.59 (d, *J* = 7.4 Hz, 2 H, PhH), 7.83 (d, *J* = 8.2 Hz, 2 H, Ts); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 21.3, 26.1, 26.5, 45.4, 47.2, 49.3, 104.7, 114.3, 118.5, 126.0, 128.4, 131.3, 131.7, 134.0, 139.3, 142.9, 148.9, 148.3; HRMS (EI): C<sub>22</sub>H<sub>22</sub>I [M - OTs]<sup>+</sup> calculated 413.0766, found 413.0761.

## General procedure for anion exchange



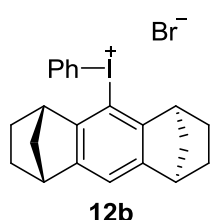
An appropriate metal salt (1.1 eq.) was added in one portion to a stirred solution of **11** (100 mg, 0.17 mmol) in CHCl<sub>3</sub> (5 mL). The heterogeneous mixture was allowed to stir at room temperature for 30 min. The solution was then filtered through a short plug of silica gel and concentrated to yield the product as a white powder.

### 1,2,3,4,5,6,7,8-Octahydro-1,4;5,8-*anti*-dimethanoanthracene-9-iodonium(phenyl) chloride (**12a**)



According to the general procedure, using LiCl (8 mg, 0.19 mmol) the title compound was obtained as a white powder (75 mg, 99%). Mp: 122–123 °C; IR (KBr, cm<sup>-1</sup>):  $\nu$  3508, 3419, 1625, 1212, 1004, 1086, 950; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.99–1.11 (m, 4 H, CH<sub>2</sub>), 1.48–1.50 (m, 2 H, CHCHHCH), 1.79–1.90 (m, 6 H, CHCH<sub>2</sub>), 3.48 (brs, 2 H, CH), 3.54 (brs, 2 H, CH), 7.10 (s, 1 H, ArH), 7.27–7.31 (t,  $J = 7.8$  Hz, 2 H, PhH), 7.40 (m, 1 H, PhH), 7.88 (d,  $J = 7.8$  Hz, 2 H, PhH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  26.1, 26.6, 45.3, 47.0, 49.3, 109.2, 117.7, 119.6, 130.3, 131.1, 133.4, 148.3, 148.7; HRMS (EI): C<sub>22</sub>H<sub>22</sub>I [M – Cl]<sup>+</sup> calculated 413.0766, found 413.0759.

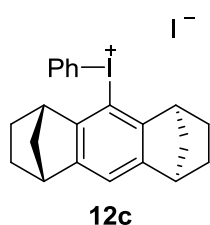
### 1,2,3,4,5,6,7,8-Octahydro-1,4;5,8-*anti*-dimethanoanthracene-9-iodonium(phenyl) bromide (**12b**)



According to the general procedure, using LiBr (16 mg, 0.19 mmol) the title compound was obtained as a white powder (82 mg, 99%). Mp: 162–164 °C; IR (KBr, cm<sup>-1</sup>):  $\nu$  3446, 1636, 1286, 1227, 1174, 1060, 1035, 725; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.09–1.16 (m, 4 H, CH<sub>2</sub>), 1.49 (d,  $J = 8.7$  Hz, 2 H, CHCHHCH), 1.80 (d,  $J = 8.7$  Hz, 2 H, CHCHHCH), 1.83–1.90 (m, 4 H, CH<sub>2</sub>), 3.47 (brs, 2 H, CH), 3.59 (brs, 2 H, CH), 7.09 (s, 1 H, ArH), 7.27–7.31 (m, 2 H, PhH), 7.41 (t,  $J = 7.8$  Hz, 1 H, PhH), 7.88 (d,  $J = 7.8$  Hz, 2 H, PhH); <sup>13</sup>C NMR (100 MHz,

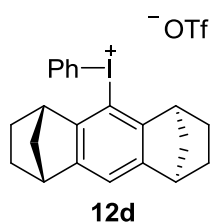
$\text{CDCl}_3$ ):  $\delta$  26.3, 26.8, 45.6, 47.2, 49.4, 110.4, 117.8, 120.5, 130.5, 131.3, 133.7, 148.3, 149.0;  
HRMS (EI):  $\text{C}_{22}\text{H}_{22}\text{I}$   $[\text{M} - \text{Br}]^+$  calculated 413.0766, found 413.0759.

**1,2,3,4,5,6,7,8-Octahydro-1,4;5,8-anti-dimethanoanthracene-9-iodonium(phenyl) iodide (12c)**



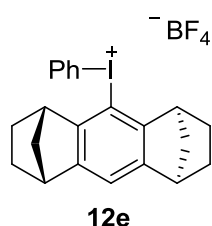
$\text{I}^-$  According to the general procedure, using LiI (25 mg, 0.19 mmol) the title compound was obtained as a white powder (90 mg, 99%). Mp: 135-136 °C; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3437, 2955, 1636, 1262, 1171, 1034, 747;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.05–1.18 (m, 4 H,  $\text{CH}_2$ ), 1.49 (d,  $J = 8.4$ , 2 H,  $\text{CHCHHCH}$ ), 1.80 (d,  $J = 8.4$ , 2 H,  $\text{CHCHHCH}$ ), 1.84–1.91 (m, 4 H,  $\text{CH}_2$ ), 3.47 (s, 2 H, CH), 3.59 (s, 2 H, CH), 7.09 (s, 1 H, ArH), 7.27–7.31 (m, 2 H, PhH), 7.40–7.44 (m, 1 H, PhH) 7.87 (d,  $J = 7.9$  Hz, 2 H, PhH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  26.1, 26.6, 45.4, 47.1, 49.2, 111.2, 117.7, 120.9, 130.5, 131.2, 133.8, 147.8, 148.9; HRMS (EI):  $\text{C}_{22}\text{H}_{22}\text{I}$   $[\text{M} - \text{I}]^+$  calculated 413.0766, found 413.0769.

**1,2,3,4,5,6,7,8-Octahydro-1,4;5,8-anti-dimethanoanthracene-9-iodonium(phenyl) triflate (12d)**



$^-\text{OTf}$  According to the general procedure, using LiOTf (28 mg, 0.19 mmol) the title compound was obtained as a white powder (95 mg, 99%). Mp: 188-189 °C (decomp.); IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  2964, 2871, 2383, 1443, 1256, 1173, 754;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.90–0.94 (m, 2 H,  $\text{CH}_2$ ), 1.08–1.12 (m, 2 H,  $\text{CH}_2$ ), 1.55 (d,  $J = 8.7$  Hz, 2 H,  $\text{CHCHHCH}$ ), 1.91 (d,  $J = 8.7$  Hz, 2 H,  $\text{CHCHHCH}$ ), 1.87–1.94 (m, 4 H,  $\text{CH}_2$ ), 3.47 (brs, 2 H, CH), 3.55 (brs, 2 H, CH), 7.19 (s, 1 H, ArH), 7.43 (t,  $J = 7.8$  Hz, 2 H, PhH), 7.57 (t,  $J = 7.8$  Hz, 1 H, PhH), 7.83 (d,  $J = 7.8$  Hz, 2 H, PhH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  26.1, 26.4, 45.6, 47.4, 49.3, 104.0, 112.9, 119.0, 123.9 (q,  $J = 320$  Hz,  $\text{CF}_3$ ), 132.0, 132.2, 134.2, 149.0, 149.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -78.3; HRMS (EI):  $\text{C}_{22}\text{H}_{22}\text{I}$   $[\text{M} - \text{OTf}]^+$  calculated 413.0766, found 413.0784.

**1,2,3,4,5,6,7,8-Octahydro-1,4;5,8-anti-dimethanoanthracene-9-iodonium(phenyl) tetrafluoroborate (12e)**

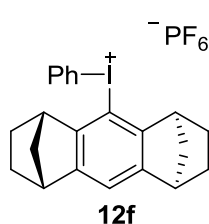


According to the general procedure, using  $\text{AgBF}_4$  (36 mg, 0.19 mmol) the title compound was obtained as a white powder (84 mg, 99%). Mp: 175–176 °C; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  2964, 2871, 1443, 1256, 1033, 754, 644;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.91 (t,  $J = 8.5$  Hz, 2 H,  $\text{CH}_2$ ), 1.11 (t,  $J = 8.5$  Hz, 2 H,  $\text{CH}_2$ ), 1.56 (d,  $J = 9.1$  Hz, 2 H,  $\text{CHCHHCH}$ ), 1.84 (d,  $J = 9.1$  Hz, 2 H,  $\text{CHCHHCH}$ ), 1.93 (m, 4 H,  $\text{CH}_2$ ), 3.48 (brs, 2 H, CH), 3.56 (brs, 2 H, CH), 7.21 (s, 1 H, ArH), 7.45 (t,  $J = 8.2$  Hz, 2 H, PhH), 7.59 (m, 1 H, PhH), 7.85 (d,  $J = 8.2$  Hz, 2 H, PhH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  26.2, 26.3, 45.6, 47.4, 49.3, 102.3, 111.7, 119.4, 132.3, 132.5, 134.1, 149.3, 150.2;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  [-147.7, -147.8]; HRMS (ED):  $\text{C}_{22}\text{H}_{22}\text{I}$   $[\text{M} - \text{BF}_4]^+$  calculated 413.0766, found 413.0780.

**Alternative synthesis of 12e**

*m*CPBA (70% purity, 52 mg, 0.30 mmol) was placed in a pressure tube and dissolved in  $\text{CH}_2\text{Cl}_2$  (1 mL). The aryl iodide **7** (90 mg, 0.27 mmol) was added to this solution and the tube sealed. The reaction mixture was then placed in a preheated oil bath at 80 °C. After 10 min, the reaction mass was cooled to -78 °C.  $\text{BF}_3 \cdot \text{OEt}_2$  (85  $\mu\text{L}$ , 0.68 mmol) and phenylboronic acid (37 mg, 0.30 mmol, dissolved in  $\text{CH}_2\text{Cl}_2$  and chilled to 0 °C) were then added. The mixture turned black and was stirred at -78 °C for a further 30 min. The reaction mixture was then brought to room temperature and applied to a short pad of silica gel. After washing with  $\text{CH}_2\text{Cl}_2$  the product was eluted with  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (20:1). This latter solution was concentrated to yield a black tarry residue. This residue was recrystallised twice from  $\text{CH}_2\text{Cl}_2/\text{pentane}$  to yield the title compound as a white powder (73 mg, 54%). Analytical data was identical to that of **12e** as prepared *via* anion metathesis.

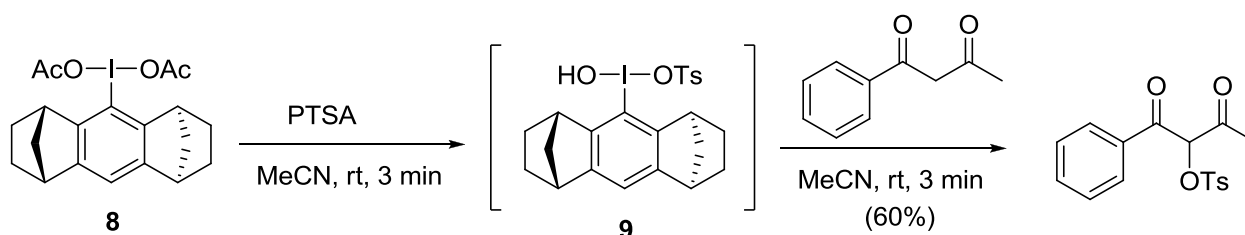
**1,2,3,4,5,6,7,8-Octahydro-1,4;5,8-anti-dimethanoanthracene-9-iodonium(phenyl) hexafluorophosphate (12f)**



According to the general procedure, using  $\text{AgPF}_6$  (48 mg, 0.19 mmol) the title compound was obtained as a white powder (92 mg, 99%). Due to its low solubility the compound was eluted from silica gel using a 2:1  $\text{CHCl}_3/\text{MeOH}$  mixture. Mp: 166–167 °C; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  2934, 2856,

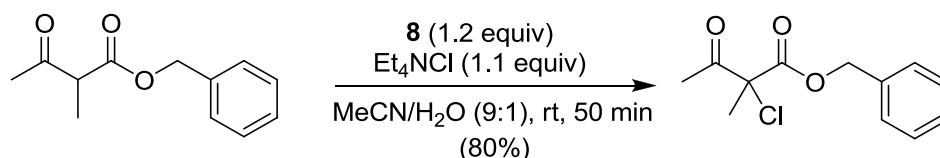
1322, 1249, 1097, 742;  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  0.89-0.93 (m, 2 H,  $\text{CH}_2$ ), 1.04-1.08 (m, 2 H,  $\text{CH}_2$ ), 1.61-1.63 (m, 2 H,  $\text{CHCHHCH}$ ), 1.79-1.82 (m, 2 H,  $\text{CHCHHCH}$ ), 1.96-1.97 (m, 4 H,  $\text{CH}_2$ ), 3.64 (brs, 2 H, CH), 3.67 (brs, 2 H, CH), 7.34 (s, 1 H, ArH), 7.59 (t,  $J = 8.6$  Hz, 2 H, PhH), 7.71-7.73 (m, 1 H, PhH), 8.10 (d,  $J = 8.6$  Hz, 2 H, PhH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  25.7, 26.0, 45.4, 47.1, 48.8, 104.6, 113.3, 118.5, 131.9, 132.0, 134.8, 148.4, 149.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  -70.5 (d,  $J_{\text{P-F}} = 717.0$  Hz); HRMS (EI):  $\text{C}_{22}\text{H}_{22}\text{I}$  [ $\text{M} - \text{PF}_6$ ] $^+$  calculated 413.0766, found 413.0782.

### 1,3-Dioxo-1-phenylbutan-2-yl 4-methylbenzenesulfonate



*p*-Toluenesulfonic acid trihydrate (117 mg, 0.62 mmol) was added to a suspension of **8** (280 mg, 0.62 mmol) in MeCN (5 mL). The mixture immediately became homogenous and turned a bright yellow colour. The solution was left to stir for 3 minutes before benzoylacetone (100 mg, 0.62 mmol) was added in one portion *via* syringe. After stirring the mixture for another 3 minutes a solution of sat. aq.  $\text{NaHCO}_3$  (5 mL) was added. The aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layers were then washed with  $\text{H}_2\text{O}$  (2 x 10 mL), brine (2 x 10 mL) and dried over  $\text{MgSO}_4$  before being concentrated *in vacuo*. The residue was then purified by flash column chromatography ( $\text{SiO}_2$ ; pentane/ $\text{Et}_2\text{O}$  80:20) to yield the product as a white solid (122 mg, 60%).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR data was consistent with that of literature reports.<sup>2</sup>

### $\alpha$ -Chlorination of benzyl-2-methyl-3-oxobutanoate

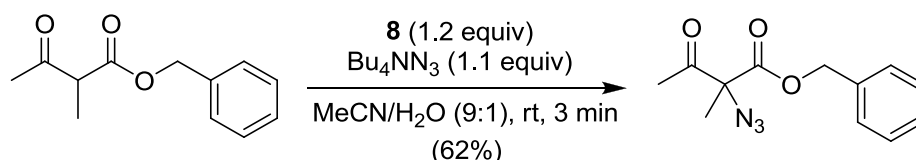


To a solution of benzyl-2-methyl-3-oxobutanoate (103 mg, 0.5 mmol) and  $\text{Et}_4\text{NCl}$  (91 mg, 0.55 mmol) in a MeCN/ $\text{H}_2\text{O}$  mixture (9:1, 1.5 mL) was added in one portion **8** (272 mg, 0.6



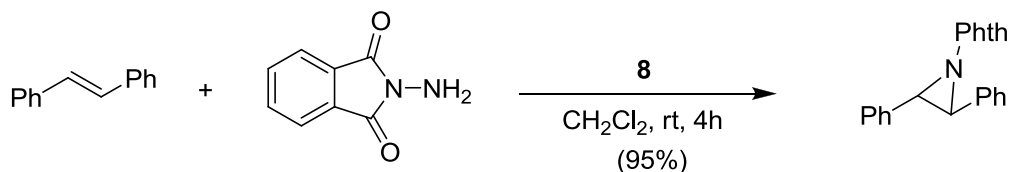
mmol). The reaction mixture was stirred for 50 minutes at which point TLC analysis indicated disappearance of the starting material. The reaction mixture was diluted with Et<sub>2</sub>O (15 mL) and washed with H<sub>2</sub>O (10 mL). The aq. layer was extracted with DCM (10 mL) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvents under reduced pressure gave an oily residue which was purified by flash column chromatography (SiO<sub>2</sub>; pentane/Et<sub>2</sub>O, 90:10) to yield the chlorinated product as a colourless oil (96 mg, 80%). <sup>1</sup>H NMR and <sup>13</sup>C NMR data was consistent with that of literature reports.<sup>3</sup>

### **α-Azidation of benzyl-2-methyl-3-oxobutanoate**



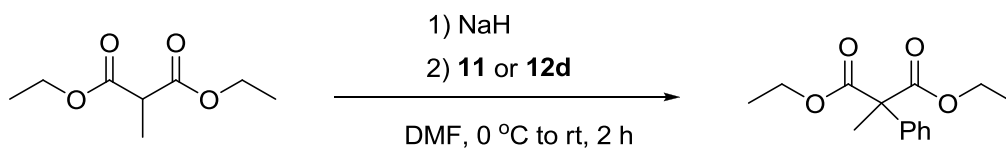
Tetrabutylammonium azide (160 mg, 0.6 mmol, hygroscopic) was placed in a sample vial fitted with a magnetic stirrer bar under a blanket of nitrogen. **8** (308 mg, 0.7 mmol) and a mixture of MeCN/H<sub>2</sub>O (2 mL, 9:1) were added. Stirring was initiated and subsequent addition of benzyl-2-methyl-3-oxobutanoate (105 mg, 0.5 mmol) *via* syringe was carried out immediately, this process being slightly exothermic. Following the addition of the substrate, frothing/bubbling occurred and a colour change to light brown was observed. After disappearance of the starting material as judged by TLC analysis (3 min.), the reaction mixture was diluted with Et<sub>2</sub>O (5 mL) and washed with H<sub>2</sub>O (3 mL). The aqueous layer was extracted with Et<sub>2</sub>O (3 x 5 mL) and the organic layers were combined, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO<sub>2</sub>; pentane/Et<sub>2</sub>O, 98:2→95:5) to afford the title compound as a pale yellow oil (119 mg, 62%). IR (neat, cm<sup>-1</sup>): ν 3036, 2107, 1734, 1456, 1265, 786, 752. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.59 (s, 3 H, COCCH<sub>3</sub>), 2.18 (s, 3 H, CH<sub>3</sub>CO), 5.24 (1 H, d, *J* = 12.3 Hz, CHHPh), 5.27 (1 H, d, *J* = 12.2 Hz, CHHPh), 7.33-7.38 (m, 5 H, ArH). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 24.3, 25.2, 68.5, 70.1, 128.2, 128.7, 128.8, 134.6, 167.8, 198.5. HRMS (CI) calculated for C<sub>12</sub>H<sub>14</sub>N<sub>3</sub>O<sub>3</sub> [M + H]<sup>+</sup> 248.0957, found 248.1040.

### Aziridination of *trans*-stilbene



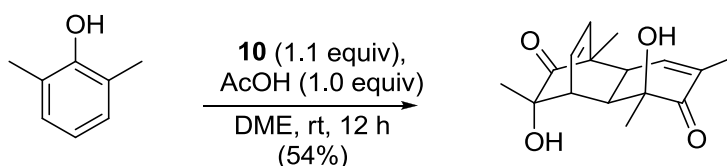
**8** (272 mg, 0.6 mmol) was added in one portion to a stirred mixture of *trans*-stilbene (90 mg, 0.5 mmol) and *N*-aminophthalimide (89 mg, 0.55 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The mixture was stirred at room temperature for 4 hours and was quenched by the addition of sat. aq. Na<sub>2</sub>CO<sub>3</sub> (2 mL) and extracted with EtOAc (3 x 2 mL). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>3</sub> and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO<sub>2</sub>; pentane/EtOAc, 80:20) to yield the product as a white solid (144 mg, 95%). <sup>1</sup>H NMR and <sup>13</sup>C NMR data was consistent with that of literature reports.<sup>4</sup>

### Phenylation of diethyl methylmalonate with **(11)** or **(12d)**



Sodium hydride (60% in paraffin, 20 mg, 0.52 mmol) was added to a solution of diethyl methylmalonate (84 mg, 0.48 mmol) in dry DMF (2.5 mL) at 0 °C. The reaction mixture was left to stir at this temperature for 15 minutes before **11** (365 mg, 0.62 mmol) or **12d** (348 mg, 0.62 mmol) was added in one portion. The yellow solution was then left to stir for two hours at room temperature before the reaction was quenched by the addition of H<sub>2</sub>O (2 mL). The organic layer was separated and washed with brine (3 x 10 mL) before being concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO<sub>2</sub>; pentane/EtOAc, 90:10) to yield the product as a colourless oil (101 mg, 82% using **11** or 95 mg, 79% using **12d**). <sup>1</sup>H NMR and <sup>13</sup>C NMR data was consistent with that of literature reports.<sup>5</sup>

### Oxidative dimerization of 2,6-dimethylphenol



2,6-Xylenol (63 mg, 0.5 mmol) was added to a stirred suspension of **10** (250 mg, 0.55 mmol) in DME (1 mL) at room temperature. Acetic acid (110  $\mu$ L, 0.55 mmol) was then added and the heterogeneous mixture was left to stir for 12 hours. Over time the mixture developed a slight yellow colouration but remained heterogeneous. This mixture was diluted with  $\text{CH}_2\text{Cl}_2$  (2.5 mL) and 1N NaOH (1.5 mL) was added. The organic layer was washed with brine, dried over  $\text{MgSO}_4$  and concentrated *in vacuo*. The product was isolated by preparative TLC ( $\text{SiO}_2$ ; EtOAc/pentane, 1:1) to yield the title compound as a white solid (38 mg, 54%).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR data was consistent with that of literature reports.<sup>6</sup>

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