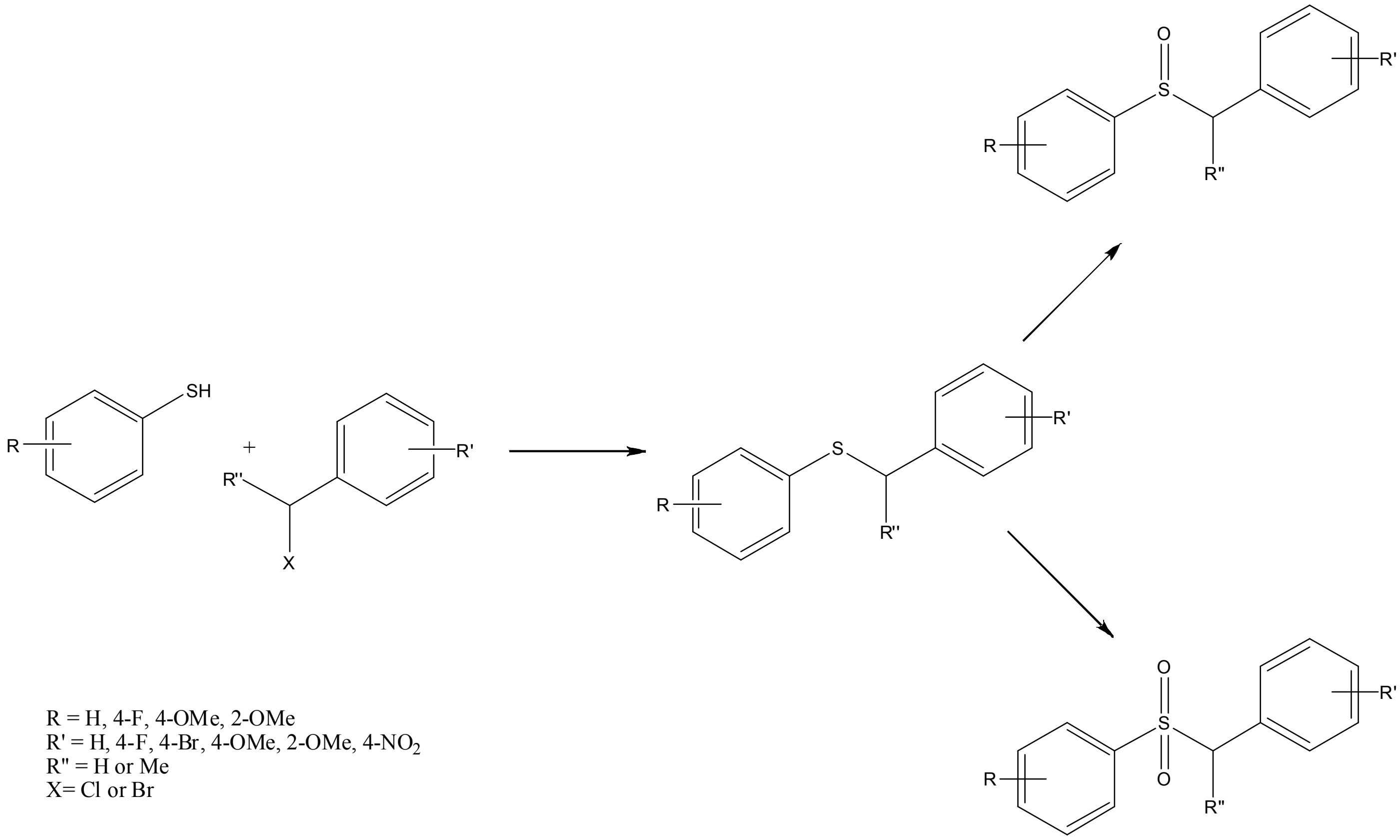
The aryl benzyl sulfides were prepared as summarised in Scheme S1 by benzylation of the aryl thiolate with the appropriate benzyl halide. Selective oxidation to the analogous sulfoxides and sulfones was achieved by appropriate choice of reactions conditions and reagent. In the case of the diastereomeric sulfoxides **23-25**, **28-30** separation of the diastereomers was achieved by selective crystallisation.



R = H, 4-F, 4-OMe, 2-OMe
R' = H, 4-F, 4-Br, 4-OMe, 2-OMe, 4-NO_2
R'' = H or Me
X= Cl or Br

SCHEME S1

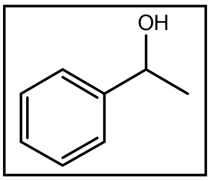
In most cases the α–substituted derivatives were prepared using the secondary benzyl halide for the thiolate alkylation. However, in the case of the sulfone ***R*-16** the α–methyl group was instead introduced by alkylation of the unsubstituted sulfone **E1**.

Procedure A

The ketone (0.30 mol) was added dropwise over 2 min to a suspension of $NaBH_4$ (1.20 mol) in EtOH (100 ml) while stirring at 0 °C under N_2. The reaction mixture was stirred for 1.5 h at 0-10 °C and water (50 ml) added slowly with cooling. The reaction mixture was stirred for an additional 30 min at room temperature and then concentrated at reduced pressure to a milky residue of approximately 30 ml. The residue was stirred at 0 °C for 15 min and extracted with

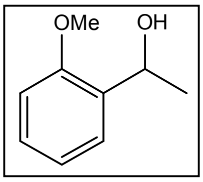
DCM (3 x 20 ml). The organic extracts were combined, dried over $MgSO_4$ and concentrated under reduced pressure to afford the title compound as a clear oil.

α-Methylbenzyl alcohol (A1)[1]



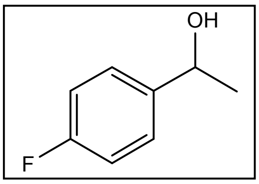
This compound was synthesised following procedure A using $NaBH_4$ (9.10 g, 0.24 mol) in ethanol (150 ml) and acetophenone (7.21 g, 0.06 mol) to give the alcohol as a clear oil (7.18 g, 98%); ν_{max} /cm^{-1} (film) 3360 (OH); δ_H (300 MHz) 1.45 (3H, d, CH_3, *J* 6.5), 2.68 (1H, bs, OH), 4.83 (1H, q, CH, *J* 6.4), 7.22-7.50 (5H, m, ArH).

2-Methoxy-α-methylbenzyl alcohol (A2)[2]



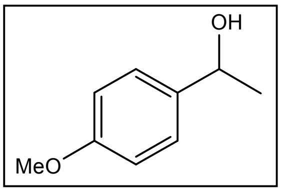
This compound was synthesised following procedure A using $NaBH_4$ (4.96 g, 0.131 mol) in ethanol (100 ml) and 2-methoxyacetophenone (5.00 g, 0.033 mol), to give the alcohol as a clear oil (4.63 g, 93%); ν_{max}/cm^{-1} (KBr) 3419 (OH); δ_H (300 MHz) 1.48 (3H, d, CH_3, *J* 6.5), 2.80 (1H, d, OH, *J* 4.9), 3.83 (3H, s, OCH_3), 5.02-5.15 (1H, m, CH), 6.86 (1H, d, ArH, *J* 8.3), 6.89-7.02 (1H, m, ArH), 7.17-7.27 (1H, m, ArH), 7.28-7.36 (1H, m, ArH).

4-Fluoro-α-methylbenzyl alcohol (A3)[2]



This compound was synthesised following procedure A using $NaBH_4$ (6.76 g, 0.180 mol) in ethanol (100 ml) and 4-fluoroacetophenone (5.00 g, 0.036 mol) to give the alcohol as a clear oil (2.87 g, 58%); ν_{max}/cm^{-1}(film) 3372 (OH); δ_H (MHz) 1.46 (3H, d, CH_3, *J* 6.5), 1.99 (1H, bs, OH), 4.82-4.95 (1H, m, CH), 6.93-7.08 (2H, m, ArH), 7.27-7.38 (2H, m, ArH).

4-Methoxy-α-methylbenzyl alcohol (A4)[3]



This compound was synthesised following procedure A using $NaBH_4$ (12.45 g, 0.330 mol) in ethanol (150 ml) and 4-methoxyaceophenone (10.00 g, 0.066 mol) to give the alcohol as a clear oil (9.16 g, 93%); δ_H (300 MHz) 1.47 (3H, d, CH_3, J 6.4), 1.86 (1H, bs, OH), 3.80 (3H, s, OCH_3), 4.80-4.95 (1H, m, CH), 6.82-6.91 (2H, m, ArH), 7.23-7.32 (2H, m, ArH).

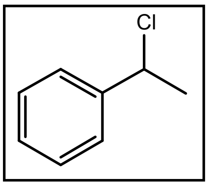
Procedure B

Thionyl chloride (0.12 mol) was added dropwise over 5 min to a solution of alcohol (0.05 mol) in chloroform (30 ml) while stirring at 0 °C under N_2. The reaction vessel was flushed with N_2, covered and the reaction mixture stirred for 16 h at room temperature. Water (20 ml) was added and the reaction mixture stirred for an additional 20 min at 0 °C. The phases were separated and the organic layer was washed with water (3 x 20 ml), dried over $MgSO_4$ and concentrated under reduced pressure to afford the title compound as a brown oil. No purification was undertaken.

Procedure C

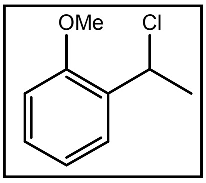
Triethylamine (0.60 mol) and mesyl chloride (0.48 mol) were added to a solution of alcohol (0.40 mol) in DCM (20 ml) while stirring at 0 °C under N_2. The reaction mixture was stirred for 25 h, washed with water (3 x 40 ml), dried over $MgSO_4$ and concentrated under reduced pressure to afford the title compound as a yellow oil.

α-Methylbenzyl chloride (B1)



This compound was synthesised following procedure B using α-methylbenzyl alcohol **A1** (6.00 g, 0.05 mol) in chloroform (30 ml) and thionyl chloride (14.63 g, 0.12 mol) to give the chloride as a yellow oil (5.37 g, 78%); ν_{max}/cm^{-1} (film) 763 (CCl); δ_H (300 MHz) 1.83 (3H, d, CH_3, *J* 6.8), 5.08 (1H, q, CH, *J* 6.8), 7.25-7.48 (5H, m, ArH); δ_c (75.5 MHz) 27.0 (CH_3, CH_3), 59.1 (CH, CH), 126.9, 128.7, 129.1 (3 x CH, aromatic CH), 143.2 (C, quaternary aromatic C).

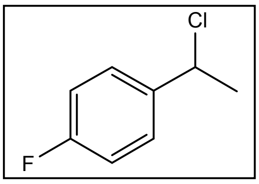
2-Methoxy-α-methylbenzyl chloride (B2)[4]



This compound was synthesised following procedure B using 2-methoxy-α-methylbenzyl alcohol **A2** (2.00g, 13.10 mmol) in chloroform (30 ml) and thionyl chloride (3.91 g, 32.80 mmol) to afford the chloride as a yellow oil which solidified to form a white solid (1.76 g, 79 %); m.p. 35-38 °C (Lit.[4] 37-39 °C) ; ν_{max}/cm^{-1}(film) 1248, 1028 (COC), 754 (CCl); δ_H (300 MHz) 1.79 (3H, d, CH_3, *J* 6.8), 3.83, (3H, s, OCH_3), 5.58 (1H, q, CH, *J* 6.8), 6.80 (1H, d, ArH, *J* 8.3), 6.91 (1H, overlapping dd appears as a triplet, ArH, *J* 7.5), 7.15-7.24 (1H, m, ArH), 7.41-7.49 (1H, m, ArH); δ_c (75.5) 25.8 (CH_3, CH_3), 52.8 (CH_3, OCH_3), 56.0

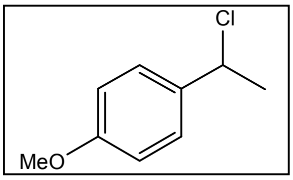
(CH, CH), 111.1, 121.2, 127.5, 129.7 (4 x CH, aromatic CH), 131.4, 156.2 (2 x quaternary C, aromatic C).

4-Fluoro-α-methylbenzyl chloride (C1)[5]



This compound was synthesised following procedure C using 4-fluoro-α-methylbenzyl alcohol **A3** (5.00 g, 35.70 mmol) in DCM (20 ml), triethylamine (5.42 g, 53.60 mmol) and mesyl chloride (4.89 g, 42.8 mmol) to give the chloride as a yellow oil that solidified overnight to a yellow crystalline solid (4.64 g, 82%); m.p. 60-62 °C (Lit. 58-59 °C); ν_{max} /cm^{-1} (film) 836 (C-Cl); δ_H (300 MHz) 1.84 (3H, d, CH_3, *J* 6.8), 5.07 (1H, q, CH, *J* 6.8), 6.99-7.10 (2H, m, ArH), 7.34-7.49 (2H, m, ArH); δ_c (75.5 MHz) 27.0 (CH_3, CH_3), 58.3 (CH, CHCl), 115.9 (CH, d, $^2J_{C\text{-}F}$ 22, aromatic CH), 128.7 (CH, d, $^3J_{C\text{-}F}$ 8, aromatic CH), 139.1 (C, d, $^4J_{C\text{-}F}$ 3, aromatic C), 162.8 (C, d, $^1J_{C\text{-}F}$ 247, C-F)

4-Methoxy-α-methylbenzyl chloride (B3)[5]



This compound was synthesised following procedure B using 4-methoxy-α-methylbenzyl alcohol **A4** (3.50 g, 2.30 mmol) in chloroform (30 ml) and thionyl chloride (7.05 g, 5.80 mmol) to give the chloride as a brown oil (2.56 g, 73%); δ_H (300 MHz) 1.84 (3H, d, CH_3, *J* 6.8), 3.79 (3H, s, OCH_3), 5.09 (1H, q, CH, *J* 6.8), 6.85-6.94 (2H, m, ArH), 7.30-7.40 (2H, m, ArH); δ_c ($CDCl_3$) 26.8 (CH_3, CH_3), 55.7 (CH_3, OCH_3), 59.2 (CH, CH), 114.4, 128.2 (2 x CH, aromatic CH), 135.4, 159.9 (2 x C, quaternary aromatic C).

Procedure D

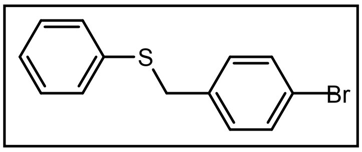
The thiol (0.35 mol) was added dropwise to a suspension of NaH (0.40 mol) in DMF (15 ml) while stirring at 0 °C under N_2. The reaction mixture was stirred for 5 mins and a solution of alkyl halide/tosylate/mesylate (0.38 mol) was added slowly over 15 mins and then stirred for an additional 16 h at room temperature. Water (30 ml) and DCM (30 ml) were added and the phases separated. The organic layer was concentrated under reduced pressure and DCM (5 ml) added. This solution was then washed with aqueous HCl (3 x 10 ml, 2M), dried over $MgSO_4$ and concentrated under reduced pressure to give the crude product. Purification was achieved by either wet flash column chromatography, with hexane/ethyl acetate (100:1) to

(95:5) as eluent, or recrystallisation from a suitable solvent or by a combination of both methods as specified for each compound.

Procedure DA

To aqueous NaOH (30 ml, 1M) at 0°C was added thiol (10 mmol), in one portion, and then a solution of 4-nitrobenzyl chloride (10.2 mmol) in dioxane (20 ml) dropwise over 20 min. The reaction mixture was stirred for 30 min at 0°C and a further 30 min at room temperature to afford a precipitate which was collected by filtration and washed with water (20 ml). The precipitate was dissolved in DCM (30 ml), dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude sulfide as a yellow powdery solid. If no precipitate formed then the solvent was removed at reduced pressure and the residue dissolved in DCM (30 ml), washed with water (3 x 30 ml), dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product. Purification was achieved by either wet flash column chromatography using hexane/ethyl acetate (95:5) as eluent or by recrystallisation from hot MeOH, as specified for each compound, to afford the desired sulfide as a yellow solid.

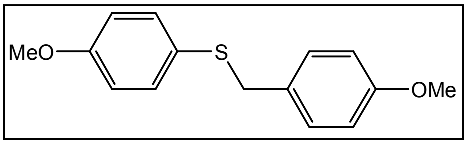
Phenyl-4-bromobenzylsulfide (1)



This compound was synthesised following procedure D using NaH (0.17 g of 67% oil dispersion 4.84 mmol), thiophenol (0.50 g, 4.40 mmol) and 4-bromobenzyl bromide (1.15 g, 4.50 mmol). Purification by column chromatography using hexane (100%) as eluent gave the sulfide as a white crystalline solid (0.98 g, 79%), m.p. 71-72 °C; (Found: C, 55.85; H, 3.97. $C_{13}H_{11}BrS$ requires C, 55.92; H, 3.97%); ν_{max} cm^{-1}(KBr) 687 (C-S); δ_H (300 MHz) 4.04 (2H, s, CH_2), 7.10-7.16 (2H, d, ArH, *J* 8.3), 7.18-7.31 (5H, m, ArH), 7.35-7.42 (2H, d, ArH); δ_C (75.5 MHz) 39.0 (CH_2, CH_2), 121.4 (C, quaternary aromatic C), 127.1, 129.3, 130.7, 130.9, 132.0 (5 x CH, aromatic CH), 136.0, 137.1 (2 x C, quaternary aromatic C).

Single crystals of the sulfide were grown from methanol.

4-Methoxyphenyl-4′-methoxybenzylsulfide (2)[6]

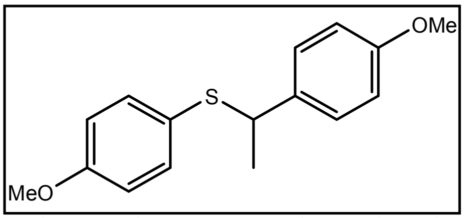


This compound was synthesised following procedure D using NaH (0.19 g, 60% dispersion in mineral oil, 4.66 mmol), 4-methoxybenzenethiol (0.60 g, 4.25 mmol) and 4-methoxybenzyl chloride (0.66 g, 4.21 mmol) to give the sulfide.

Recrystallisation from methanol gave the pure sulfide as a white crystalline solid (0.97 g, 82%), m.p. 90-91 °C (Lit.[6] 89-90 °C); δ_H (300 MHz) 3.78 (6H, s, OCH_3), 3.95 (2H, s, CH_2), 6.74-6.85 (4H, m, ArH), 7.06-7.17 (2H, m, ArH), 7.21-7.30 (2H, m, ArH); δ_C (75.5 MHz) 41.0 (CH_2, CH_2), 55.6, 55.7 (2 x CH_3, OCH_3), 114.1, 114.8 (2 x CH, aromatic CH), 126.6 (C, C-S), 130.4, (CH, aromatic CH), 134.4 (CH, aromatic CH), 130.5 (C, C-C), 159.0, 159.5 (2 x C, C-O).

Single crystals of the sulfide were grown from methanol.

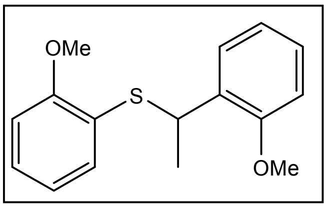
(4-Methoxyphenyl)[1-(4-methoxyphenyl)ethyl]sulfide (3)



This compound was synthesised following procedure D using NaH (1.53 g, 55% dispersion in oil, 0.035 mol), 4-methoxybenzene thiol (4.16 g, 0.029 mol) and 4-methoxy-α-methylbenzyl chloride **B3** (6.12 g, 0.036 mol). Purification by column chromatography using hexane (100%) as eluent followed by recrystallisation from DCM/hexane gave the sulfide as a white solid (5.50 g, 57%), m.p. 73-75 °C; (Found: C, 69.77; H, 6.69; S, 11.47. $C_{16}H_{18}O_2S$ requires C, 70.04; H, 6.61; S, 11.69%); ν_{max} (KBr)/cm^{-1} 1248, 1028 (C-O-C); δ_H ($CDCl_3$) 1.56 (3H, d, CH_3, *J* 7.0), 3.78, 3.77 (6H, 2 x unresolved s, OCH_3), 4.15 (1H, q, CH, *J* 7.0), 6.73-6.87 (4H, m, ArH), 7.11-7.30 (4H, m, ArH); δ_c ($CDCl_3$) 21.9 (CH_3, $CHCH_3$), 48.5 (CH, $CHCH_3$), 55.2 (CH_3, one signal for 2 x OCH_3), 113.6, 114.2 (2 x CH, aromatic CH), 125.2 (C, quaternary aromatic C), 128.4 (CH, aromatic CH), 135.4 (C, quaternary aromatic C), 136.0 (CH, aromatic CH), 158.5, 159.5 (2 x C, quaternary aromatic C); m/z (ESI) 275 [$(M+H^+)$].

Single crystals of the sulfoxide were grown from a DCM/hexane mixture.

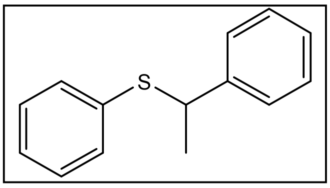
(2-Methoxyphenyl)[1-(2-methoxyphenyl)ethyl]sulfide (4)



This compound was synthesized following procedure D using NaH (0.32 g, 67% dispersion in oil, 9.02 mmol), 2-methoxybenzenethiol (1.09 g, 7.52 mmol) and 2-methoxy-α-methylbenzyl chloride **B2** (1.60 g, 9.40 mmol). Purification by column chromatography using hexane/ethyl acetate (98:2) and recrystallisation from DCM/hexane gave the sulfide as a white crystalline solid (1.74 g, 84%), m.p. 59-61 °C; (Found: C, 69.87; H, 6.58; S, 11.50. $C_{16}H_{18}O_2S$ requires C, 70.04; H, 6.61; S, 11.69%); ν_{max} (KBr)/cm^{-1} 1244, 1025 (C-O-C); δ_H ($CDCl_3$) 1.58 (3H, d, CH_3, *J* 7.1), 3.80 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 4.99 (1H, q, SCH, *J* 7.0), 6.75-6.85 (3H, m, ArH), 6.86-6.94 (1H, m, ArH), 7.07-7.20 (3H, m, ArH), 7.44-7.52 (1H, m, ArH); δ_c ($CDCl_3$) 22.2 (CH_3, $CHCH_3$), 38.1 (CH, $CHCH_3$), 55.9, 56.1 (2 x CH_3, OCH_3), 110.6, 110.8, 121.1, 121.2 (4 x CH, aromatic CH), 124.7 (C, quaternary aromatic C), 127.8, 128.0, 128.3, 131.9 (4 x CH, aromatic CH), 132.0, 156.7, 158.2 (3 x C, quaternary aromatic C); m/z (ESI) 275 [$(M+H)^+$].

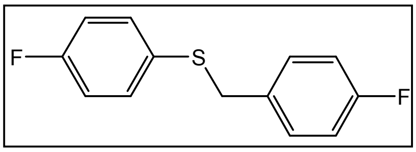
Single crystals of the sulfide were grown from acetonitrile.

Phenyl[(1-phenyl)ethyl]sulfide (D1)[7]



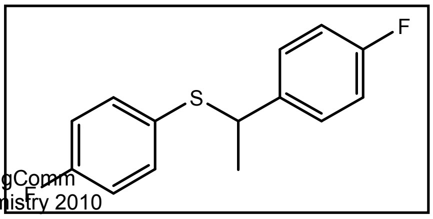
This compound was synthesised following procedure D using NaH (1.28 g, 60% dispersion in oil, 0.03 mol), thiophenol (3.60 g, 0.03 mol) and α-methylbenzyl chloride **B1** (4.37 g, 0.03 mol). Purification by column chromatography using hexane/ethyl acetate (95:5) gave the sulfide as a yellow oil (5.32 g, 78%); ν_{max} (film)/ cm^{-1} 695 (C-S) ; δ_H (300 MHz) 1.62 (3H, d, CH_3, J 7.0), 4.33 (1H, q, CH, J 7.1), 7.09-7.40 (10H, m, ArH); δ_c (75.5 MHz) 22.3 (CH_3, $CHCH_3$), 47.9 (CH, $CHCH_3$), 127.0, 127.1, 127.2, 128.4, 128.7, 132.4 (6 x CH, aromatic CH), 135.2, 143.2 (2 x C, quaternary aromatic C).

4-Fluorophenyl-4′-fluorobenzylsulfide (D2)[8]



This compound was synthesised following procedure D using NaH (0.19 g, 60% dispersion in mineral oil, 4.25 mmol), 4-fluorobenzenethiol (0.54 g, 4.24 mmol) and 4-fluorobenzylchloride (0.61 g, 4.20 mmol). Recrystallisation from hot methanol gave the sulfide as a white solid (0.76 g, 76%), m.p. 84-85 °C (Lit.[8] 84-85 °C); δ_H (300 MHz) 3.97 (2H, s, CH_2), 6.85-7.09 (4H, m, ArH), 7.11-7.20 (2H, m, ArH), 7.21-7.32 (2H, m, ArH); δ_C (75.5 MHz) 40.2 (CH_2, CH_2), 115.7 (CH, d, ${}^2J_{C\text{-}F}$ 21, ArCH), 116.4 (CH, d, ${}^2J_{C\text{-}F}$ 21, ArCH), 130.7 (CH, d, ${}^3J_{C\text{-}F}$ 8, ArCH), 133.7 (C, quaternary aromatic C), 134.2 (CH, d, ${}^3J_{C\text{-}F}$ 8, ArCH), 162.4 (CH, d, ${}^1J_{C\text{-}F}$ 227, ArCH), 162.5 (CH, d, ${}^1J_{C\text{-}F}$ 266, ArCH). One quaternary C not detected.

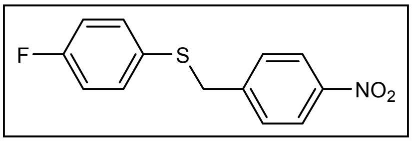
(4-Fluorophenyl)[1-(4-fluorophenyl)ethyl]sulfide (D3)



This compound was synthesised following procedure D using NaH (1.98 g, 50% dispersion in oil, 0.41 mol), 4-

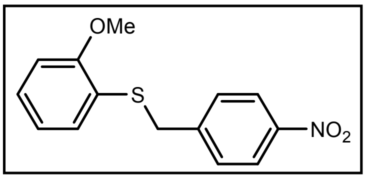
fluorobenzene thiol (4.42 g, 0.35 mol) and 4-fluoro-α-methylbenzyl chloride **C1** (8.20 g, 0.38 mol). Purification by column chromatography using hexane (100%) as eluent gave the sulfide as a low melting point solid (4.70 g, 59%), m.p. 19-25 °C; ν_{max} (film)/cm^{-1} 1225 (aryl-F); δ_H ($CDCl_3$) 1.57 (3H, d, CH_3, *J* 7.0), 4.20 (1H, q, CH, *J* 7.0), 6.87-6.95 (4H, m, ArH), 7.11-7.27 (4H, m, ArH); δ_c ($CDCl_3$) 22.7 (CH_3, $CHCH_3$), 49.0 (CH, $CHCH_3$), 115.9 (CH, d, $^2J_{C-F}$ 22, aromatic CH), 116.7 (CH, d, $^2J_{C-F}$ 22, aromatic CH), 129.6 (CH, d, $^3J_{C-F}$ 8, aromatic CH), 130.2 (C, d, $^4J_{C-F}$ 4, aromatic C), 136.6 (CH, d, $^3J_{C-F}$ 8, aromatic CH), 139.6 (C, d, $^4J_{C-F}$ 3, C-S), 162.6 (C, d, $^1J_{C-F}$ 246, C-F), 163.4 (C, d, $^1J_{C-F}$ 248, C-F); m/z (ESI) 249 [(M-H)$^-$]. HRMS (ESI): Exact mass calculated for $C_{14}H_{11}F_2S$ [M-H]$^-$, 249.0550. Found 249.0547.

4-Fluorophenyl-4′-nitrobenzylsulfide (DA4)



This compound was synthesised following procedure DA using NaOH (75 ml, 1M), 4-fluorobenzenethiol (1.07 ml, 3.27 g, 25.00 mmol) and 4-nitrobenzyl bromide (4.38 g, 25.50 mmol) in dioxane (60 ml). Recrystallisation from hot methanol afforded the pure product as a yellow crystalline solid (6.23 g, 95%), m.p. 55-57 °C; (Found: C, 59.34; H, 3.75; N, 5.27. $C_{13}H_{10}FNO_2S$ requires C, 59.30; H, 3.83; N, 5.32%); ν_{max}/cm^{-1} (KBr) 1505, 1338, (NO_2), 1225, (CF); δ_H (300 MHz) 4.06 (2H, s, CH_2), 6.92-6.98 (2H, m, ArH), 7.22-7.34 (4H, m, ArH), 8.11 (2H, d, ArH, *J* 8.5). δ_c (75.5 MHz) 40.5 (CH_2, CH_2), 116.7 (CH, d, $^2J_{C-F}$ 22, aromatic CH), 124.1 (CH, aromatic CH), 129.5 (C, quaternary aromatic C), 130.0, (CH, aromatic CH), 134.82 (CH, d, $^3J_{C-F}$ 8.2, aromatic CH), 145.9, 147.4 (2 x C, quaternary aromatic C), 162.9 (C, d, $^1J_{C-F}$ 248, aromatic C-F**);** m/z (ESI) 262 [(M-H)$^-$];

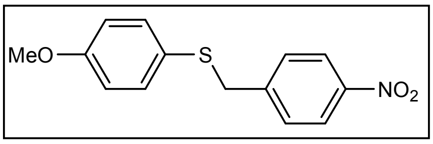
2-Methoxyphenyl-4′-nitrobenzylsulfide (DA5)



This compound was synthesised following procedure DA using aqueous NaOH (75 ml, 1M), 2-methoxybenzene thiol (3.14 ml, 3.61 g, 25.00 mmol) and 4-nitrobenzyl bromide (4.38 g, 25.50 mmol) in dioxane (60 ml). Recrystallisation from hot methanol afforded the pure product as a yellow crystalline solid (5.34 g, 78%), m.p. 61-63 °C. (Found: C, 61.01; H, 4.76; N, 5.05; S, 11.91. $C_{14}H_{13}NO_3S$ requires C, 61.01; H, 4.76; N, 5.09; S, 11.65%); ν_{max}/cm^{-1} (KBr) 1475, 1343 (NO_2), 1294, 1022 (COC). δ_H (300 MHz) 3.88 (6H, s, OCH_3), 4.12 (2H, s, CH_2), 6.79-6.90 (2H, m, ArH), 7.16 (1H, dd, ArH, *J* 7.5, 1.5), 7.20- 7.28 (1H, m, ArH), 7.32- 7.40 (2H, m, ArH), 8.03-8.13 (2H, m, ArH); δ_c (75.5

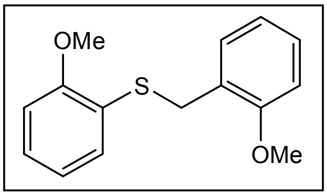
MHz) 37.4 (CH_2, CH_2), 56.2 (CH_3, OCH_3), 111.2, 121.4 (2 x CH, aromatic CH), 122.4 (C, quaternary aromatic C), 123.9 129.4, 130.0, 132.9 (4 x CH, aromatic CH), 146.2, 147.3, 158.7 (3 x C, quaternary aromatic C). m/z (ESI) 276 $[(M+H)^+$.

4-Methoxyphenyl-4′-nitrobenzylsulfide (DA6)[9]



This compound was synthesised following procedure DA using aqueous NaOH (75 ml, 1M), 4-methoxybenzene thiol (3.17 ml, 3.27 g, 25.00 mmol) and 4-nitrobenzyl bromide (4.38 g, 25.50 mmol) in dioxane (60 ml). Recrystallisation from hot methanol afforded the pure product as a yellow crystalline solid (6.47 g, 95%), m.p. 60-62 °C (Lit.[9] 61-62 °C). ν_{max}/cm^{-1}(KBr) 1494, 1342 (NO_2), 1283, 1030 (COC); δ_H (300 MHz) 3.78 (6H, s, OCH_3), 3.99 (2H, s, CH_2), 6.74-6.82 (2H, m, ArH), 7.17-7.30 (4H, m, ArH), 8.04-8.14 (2H, m, ArH).

2-(Methoxyphenyl)-2-(methoxybenzyl)-sulfide (D7)



This compound was synthesised following procedure D using NaH (0.28 g, 67% dispersion in oil, 7.84 mmol), 2-methoxybenzenethiol (0.86 ml, 1.00 g, 7.12 mmol) and 2-methoxybenzyl chloride (1.12 g, 7.12 mmol). Purification by column chromatography using hexane (100%) as eluent gave the sulfide as a white crystalline solid (1.45 g, 78%), m.p. 53-54 °C; δ_H (300 MHz) 3.79 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 4.12 (2H, s, CH_2), 6.78-6.89 (4H, m, ArH), 7.11-7.26 (4H, m, ArH); δ_C (75.5 MHz) 31.71 (CH_2, CH_2), 55.9, 56.1 (2 x CH_3, OCH_3), 110.6, 110.8, 120.8, 121.3 (4 x CH, aromatic CH), 125.5, 126.1 (2 x C, quaternary aromatic C), 127.6, 128.8, 130.4, 130.7 (4 x CH, aromatic CH), 157.75 (C, C-O). One quaternary aromatic C-O not detected.

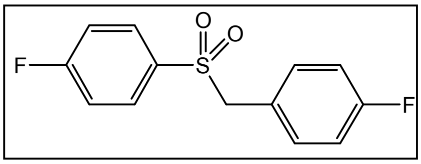
Procedure E

To a stirred solution of sulfide (4.00 mmol) in DCM (20 ml) was added, dropwise over 15 min, a solution of *m*-CPBA* (9.00 mmol) in DCM (15 ml). The reaction mixture was stirred for 16 h, washed with saturated $NaHCO_3$ solution (3 x 30 ml) and water (30 ml), dried with $MgSO_4$ and concentrated under reduced pressure to yield the crude product as a white solid.

The sulfone was purified by either column chromatography, with hexane/ethyl acetate (80:20) as eluent, or by recrystallisation from a suitable solvent or by both methods where stated.

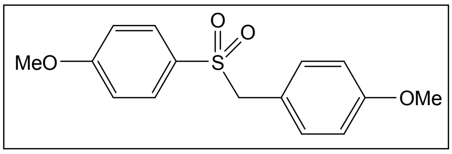
* The percentage purity of *m*-CPBA used is specified for each particular compound.

4-Fluorophenyl-4′-fluorobenzylsulfone (5)[8]



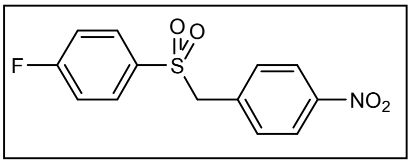
This compound was synthesised following procedure E using sulfide **D2** (0.71 g, 3.00 mmol) and *m*-CPBA (1.48 g, 77%, 6.60 mmol). Recrystallisation from hot methanol gave the sulfone as a white crystalline solid (0.75 g, 97%), m.p. 184-185 °C (Lit.[8] 186-187 °C); ν_{max}/cm^{-1} (KBr) 1050 (SO); δ_H (300 MHz) 4.28 (2H, s, CH_2), 6.93-7.02 (2H, m, ArH), 7.03-7.20 (4H, m, ArH), 7.58-7.68 (2H, m, ArH); δ_C (75.5 MHz) 62.5 (CH_2, CH_2), 116.2 (CH, d, $^2J_{C\text{-}F}$ 22, ArCH), 116.4 (CH, d, $^2J_{C\text{-}F}$ 23, ArCH), 131.9 (CH, d, $^3J_{C\text{-}F}$ 10, ArCH), 132.9 (CH, d, $^3J_{C\text{-}F}$ 8, ArCH), 134.0 (C, quaternary aromatic C), 162.4 (CH, d, $^1J_{C\text{-}F}$ 227, ArCH). Three quaternary aromatic C not detected.

4-Methoxyphenyl-4′-methoxybenzylsulfone (6)



This compound was synthesised following procedure E using sulfide **2** (0.80 g, 3.08 mmol) and *m*-CPBA (1.52 g, 77%, 6.78 mmol). Recrystallisation from hot ethanol gave the sulfone as a white solid (0.81 g, 91%), m.p. 138-139 °C; (Found: C, 61.98; H, 5.47; S, 11.09%. $C_{15}H_{16}O_4S$ requires C, 61.62; H, 5.52; S, 10.97%); ν_{max}/cm^{-1} (KBr) 1312, 1147 (SO_2); δ_H (300 MHz) 3.79 (3H, s, OCH_3), 3.86 (3H, s, OCH_3), 4.22 (2H, s, CH_2), 6.76-6.84 (2H, m, ArH), 6.87-6.92 (2H, m, ArH), 6.96-7.02 (2H, m, ArH), 7.50-7.57 (2H, m, ArH); δ_C (75.5 MHz) 55.7, 56.0 (2 x CH_3, OCH_3), 62.8 (CH_2, CH_2), 114.3, 114.4 (2 x CH, aromatic CH), 120.8, 129.9 (2 x C, quaternary aromatic C), 131.2, 132.4 (2 x CH, aromatic CH), 160.3, 164.4 (2 x C, quaternary aromatic C); m/z (ESI) 293 [$(M+H)^+$].

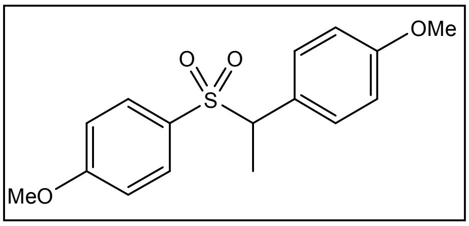
4-Fluorophenyl-4′-nitrobenzylsulfone (7)[10]



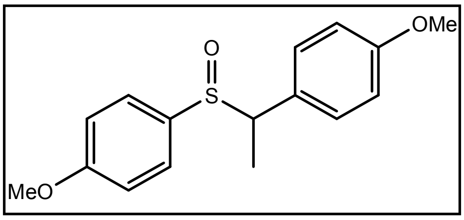
This compound was synthesized following procedure E using 4-fluorophenyl-4′-nitrobenzylsulfide **DA4** (2.00 g, 7.60 mmol) and *m*-CPBA (3.58 g, 15.96 mmol). Recrystallisation from hot ethanol gave the sulfone as a yellow solid (1.58 g, 71%), m.p. 178-180 °C (Lit.[11] 185 °C); δ_H (300 MHz) 4.41 (2H, s, CH_2), 7.14-7.22 (2H, m, ArH), 7.34-7.41 (2H, m, ArH), 7.64-7.73 (2H, m, ArH), 8.14-8.19 (2H, m, ArH); δ_c (75.5) 62.7 (CH_2, CH_2), 117.08 (CH, d, $^2J_{C\text{-}F}$ 23, aromatic CH), 124.2 (CH, aromatic CH), 131.8 (CH, d, $^3J_{C\text{-}F}$ 10, aromatic CH), 132.2 (CH, aromatic CH), 133.9 (C, d, $^4J_{C\text{-}F}$ 3, C-S), 135.5, 148.6 (2 x C, quaternary aromatic C), 166.5 (C, d, $^1J_{C\text{-}F}$ 226, C-F). Single crystals of the sulfone were grown from methanol.

(4-Methoxyphenyl)[1-(4-methoxyphenyl)ethyl]sulfone (9)

(4-Methoxyphenyl)[1-(4-methoxyphenyl)ethyl]sulfoxide (*R*S-25 and *R*R**-30)**



This compound was synthesised following procedure E using (4-methoxyphenyl)[1-(4-methoxyphenyl)ethyl]sulfide **3** (1.46 g, 5.33 mmol) in DCM (20 ml) and a solution of *m*-CPBA (1.90 g, 77%, 8.50 mmol) in DCM (10 ml). Purification by wet flash column chromatography hexane/ethyl acetate 70:30 afforded the less polar compound, the sulfone, as a white solid (0.25 g, 21%), m.p. 131-132 ºC; (Found: C, 62.73; H, 5.96; S, 10.48. $C_{16}H_{18}O_4S$ requires C, 62.72; H, 5.92; S, 10.47%); ν_{max} (KBr)/cm^{-1} 1258, (C-O-C), 1315, 1142 (SO_2); δ_H (300 MHz) 1.72 (3H, d, CH_3, *J* 7.2), 3.80 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 4.16 (1H, q, CH, *J* 7.2), 6.74-6.94 (4H, m, ArH), 7.03-7.11 (2H, m, ArH), 7.40-7.50 (2H, m, ArH); δ_c (75.5**)** 15.0 (CH_3, CH_3), 55.7, 56.0 (2 x CH_3, OCH_3), 65.9 (CH, CH), 114.1, 114.2 (2 x CH, aromatic CH), 126.3, 128.8 (2 x C, quaternary aromatic C), 131.0, 131.8 (2 x CH, aromatic CH), 160.2, 163.9 (2 x C, quaternary aromatic C). Single crystals of the sulfone were grown from a methanol.



The sulfoxide (0.60 g, 45%) was recovered as mixture of diastereomers RR/SS (δ_H 3.99, q) and RS/SR (δ_H 3.76, q) in the ratio 1:7. Successive recrystallisations from DCM/hexane afforded the RS/SR diastereomer as a white crystalline solid (0.49 g, 32%); (Found: C, 66.02; H, 6.36; S, 10.80. $C_{16}H_{18}O_3S$ requires C, 66.18; H, 6.25; S, 11.04%); ν_{max} (KBr)/cm^{-1} 1251 (C-O-C), 1065 (SO); m/z (ESI) 291 [$(M+H)^+$].

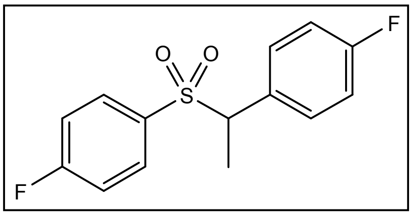
R*S*-25: δ_H ($CDCl_3$) 1.66 (3H, d, CH_3, J 7.2), 3.77 (1H, q, CH, J 7.2), 3.78 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 6.75-6.81 (2H, m, ArH), 6.82-6.92 (4H, m, ArH), 7.12-7.18 (2H, m , ArH); δ_c ($CDCl_3$) 14.6 (CH_3, CH_3), 55.3, 55.4 (2 x CH_3, OCH_3), 66.3 (CH, CH), 113.8, 114.0, 126.9 (3 x CH, aromatic CH), 127.2 (C, quaternary aromatic C), 129.6 (CH, aromatic CH), 132.8 159.5, 161.5 (3 x C, quaternary aromatic C); m.p. 93-94 ºC.

Single crystals of the sulfoxide were grown from a DCM/hexane mixture.

R*R*-30: δ_H ($CDCl_3$) 1.51 (3H, d, CH_3, J 7.2), 3.80 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 3.97 (1H, q, CH, J 7.2), 6.80 (2H, d, ArH, J 8.7), 6.85 (2H, d, ArH, J 9.0), 6.92 (2H, d , ArH, J 8.7), 7.06 (2H, d, ArH, J 9.0); δ_c ($CDCl_3$) 11.9 (CH_3, CH_3), 55.3, 55.4 (2 x CH_3, OCH_3), 63.8 (CH, CH), 113.6, 113.8 (2 x CH, aromatic CH), 126.2 (C, quaternary aromatic C), 127.1, 130.0 (2 x CH, aromatic CH), 131.3, 159.6, 161.9 (3 x C, quaternary aromatic C); m.p. 102-104 ºC.

Single crystals of the sulfoxide were grown from a DCM/hexane mixture.

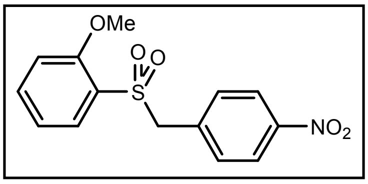
(4-Fluorophenyl)[1-(4-fluorophenyl)ethyl]sulfone (10)



This compound was synthesised following procedure E using (4-fluorophenyl)[1-(4-fluorophenyl)ethyl] sulfide **D3** (1.00 g, 4.23 mmol) in DCM (30 ml) and a solution of *m*-CPBA (2.08 g, 77%, 9.31 mmol) in DCM (20 ml) to give the sulfone as a white crystalline solid (0.87 g, 77%), mp 87-88 ºC; (Found: C, 59.59; H, 4.33; S, 11.70. $C_{14}H_{12}O_2F_2S$ requires C, 59.56; H, 4.28; S, 11.36%); ν_{max} (KBr)/cm^{-1} 1312, 1140 (SO_2); δ_H ($CDCl_3$) 1.76 (3H, d, CH_3, *J* 7.2), 4.22 (1H, q, CH, *J* 7.1), 6.92-7.01 (2H, m, ArH), 7.06-7.17 (4H, m, ArH), 7.50-7.58 (2H, m, ArH); δ_c ($CDCl_3$) 14.4 (CH_3, CH_3), 65.8 (CH, CH), 115.8 (CH, d, $^2J_{C\text{-}F}$ 22, ArCH), 116.5 (CH, d, $^2J_{C\text{-}F}$ 23, ArCH), 129.9 (C, d, $^4J_{C\text{-}F}$ 3, aromatic C), 131.5 (CH, d, $^3J_{C\text{-}F}$ 8., ArCH), 132.4 (CH, d, $^3J_{C\text{-}F}$ 10, ArCH), 133.0 (C, d, $^4J_{C\text{-}F}$ 3, C-S), 163.4 (C, d, $J_{C\text{-}F}$ 247, C-F), 166.2 (C, d, $^1J_{C\text{-}F}$ 254, C-F). m/z (ESI) 283 [$(M+H)^+$].

Single crystals of the sulfone were grown from methanol.

2-Methoxyphenyl-4′-nitrobenzylsulfone (11)

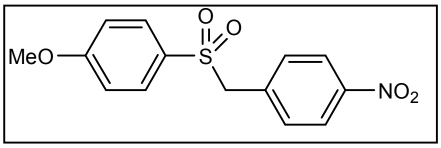


This compound was synthesized following procedure E using 2-methoxyphenyl-4′-nitrobenzylsulfide **DA5** (2.00 g, 7.27 mmol) and *m*-CPBA (3.42 g, 15.26 mmol). Recrystallisation from hot methanol gave the sulfone as a white solid (1.25 g, 57%), m.p. 136-137 °C; (Found: C, 54.65; H, 4.26; N, 4.38; S, 10.50. $C_{14}H_{13}NO_5S$ requires C, 54.71; H, 4.26; N, 4.56; S, 10.43%); ν_{max}/cm^{-1}(KBr) 1519, 1348

(NO_2), 1313, 1154 (SO_2); δ_H (300 MHz) 4.09 (3H, s, OCH_3), 4.69 (2H, s, CH_2), 6.96-7.04 (1H, m, ArH), 7.09 (1H, d, ArH, J 8.3), 7.36-7.43 (2H, m, ArH), 7.54-7.63 (1H, m, ArH), 7.64-7.69 (1H, m, ArH), 8.07-8.16 (2H, m, ArH); δ_c (75.5) 57.0 (CH_3, OCH_3), 60.3 (CH_2, CH_2), 112.8, 121.4, 124.0 (CH, aromatic CH), 126.0 (C, quaternary aromatic C), 131.4, 132.1 (2 x CH, aromatic CH), 136.0 (C, quaternary aromatic C), 136.6 (CH, aromatic CH), 148.4, 157.7 (2 x C, quaternary aromatic C). m/z (ESI) 306 [$(M-H)^-$]; HRMS (ESI): Exact mass calculated for $C_{14}H_{12}NO_5S$ $[M+H]^+$, 306.0449. Found 306.0436.

Single crystals of the sulfone were grown from chloroform.

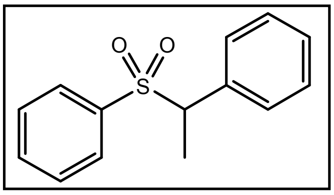
4-Methoxyphenyl-4′-nitrobenzylsulfone (12)



This compound was synthesized following procedure E using 4-methoxyphenyl-4′-nitrobenzylsulfide **DA6** (2.00 g, 7.27 mmol) and *m*-CPBA (3.42 g, 15.26 mmol). Recrystallisation from hot ethanol gave the sulfone as a white solid (1.67 g, 75%), m.p. 153-154 °C.(Found: C, 54.67; H, 4.23; N, 4.52; S, 10.73. $C_{14}H_{13}NO_5S$ requires C, 54.71; H, 4.26; N, 4.56; S, 10.43%) ν_{max}/cm^{-1} (KBr) 1520, 1350 (NO_2), 1314, 1146 (SO_2); δ_H (300 MHz) 3.88 (3H, s, OCH_3), 4.38 (2H, s, CH_2), 6.90-6.97 (2H, m, ArH), 7.26-7.33 (2H, m, ArH), 7.53-7.60 (2H, m, ArH), 8.11-8.17 (2H, m, ArH); δ_c (75.5) 56.1 (CH_3, OCH_3), 62.8 (CH_2, CH_2), 114.8, 124.1 (2 x CH, aromatic CH), 129.3 (C, quaternary aromatic C), 131.1, 132.2 (2 x CH, aromatic CH), 136.1, 148.5, 164.5 (3 x C, quaternary aromatic C). m/z (ESI) 306 [$(M-H)^-$]; HRMS (ESI): Exact mass calculated for $C_{14}H_{12}NO_5S$ $[M+H]^+$, 306.0444. Found 306.0436.

Single crystals of the sulfone were grown from methanol.

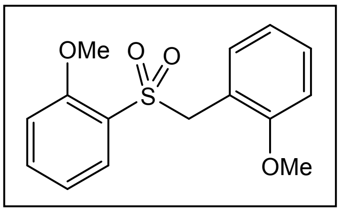
Phenyl[(1-phenyl)ethyl]sulfone (15)[11]



This compound was synthesised following procedure E using phenyl[(1-phenyl)ethyl]sulfide **D1** (0.80 g, 3.74 mmol) in DCM (30 ml) and *m*-CPBA (1.91 g, 71%, 7.85 mmol) in DCM (20 ml). Purification by recrystallisation from hot methanol gave the sulfone as a white crystalline solid (0.73 g, 79%), mp 110-111 ºC; ν_{max} (KBr)/cm^{-1} 1300, 1142 (SO_2); δ_H ($CDCl_3$) 1.78 (3H, d, CH_3, *J* 7.2), 4.24 (1H, q, CH, *J* 7.2), 7.10-7.18 (2H, m, ArH), 7.20-7.28 (3H, m, ArH), 7.36-7.45 (2H, m, ArH), 7.49-7.63 (3H, m, ArH); δ_c ($CDCl_3$) 14.4 (CH_3, CH_3), 66.5 (CH, CH), 128.8, 129.0, 129.2, 129.6, 129.8, 133.9 (6 x CH, aromatic CH), 134.1, 137.2 (2 x C, quaternary aromatic C).

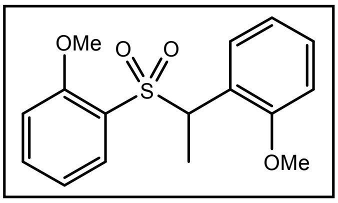
Single crystals of the sulfone were grown from chloroform.

2-(Methoxyphenyl)-2-(methoxybenzyl)-sulfone (E1)



This compound was synthesised following procedure E using *m*-CPBA (0.90 g, 77%, 4.03 mmol) and 2-(methoxyphenyl)-2-(methoxybenzyl)-sulfide **D7** (0.50 g, 1.92 mmol). Recrystallisation from hot methanol gave the sulfone as a white solid (0.44 g, 79%), m.p. 125-126 ºC; ν_{max} (KBr)/cm^{-1} 1047, 1253 (C-O-C), 1148, 1302 (SO_2); δ_H ($CDCl_3$) 3.55 (3H, s, OCH_3), 4.04 (3H, s, OCH_3), 4.71 (2H, s, CH_2), 6.73 (1H, d, ArH, *J* 8.1), 6.88-7.01 (2H, m, ArH), 7.05 (1H, d, ArH, *J* 8.2), 7.22 (2H, d, ArH, *J* 7.5), 7.51-7.60 (1H, m, ArH), 7.63-7.71 (1H, m, ArH); δ_c ($CDCl_3$) 54.9 (CH_2, CH_2), 55.7, 56.7 (2 x CH_3, OCH_3), 111.0, 112.2 (2 x CH, aromatic CH), 117.5 (C, quaternary aromatic C), 120.6, 121.0 (2 x CH, aromatic CH), 127.3 (C, quaternary aromatic C), 130.4, 131.7, 133.0, 135.7 (4 x CH, aromatic CH), 158.1, 158.2 (2 x C, C-O).

1-[1-(2-Methoxyphenyl)ethylsulfonyl]-2-methoxybenzene (*R*-16)



A solution of 2-(methoxyphenyl)-2-(methoxybenzyl)-sulfone **E1** (0.30 g, 1.03 mmol) in DCM (8 ml) was added dropwise over 10 min to a suspension of NaH (0.04 g of 67% oil dispersion 1.08 mmol) in DMF (10 ml) while stirring at 0 °C under N_2. The reaction mixture was stirred for 75 min, the reaction vessel flushed with nitrogen and closed with a rubber bung. Iodomethane (0.07 ml, 0.34 g, 2.40 mmol) was added and the reaction stirred for 16 h at ambient temperature. Water (20 ml) and DCM (20 ml) were then added and the phases separated. The product was extracted from the aqueous layer with DCM (20 ml) which in turn was washed with aqueous HCl (30 ml, 2M), dried over $MgSO_4$ and concentrated under reduced pressure to afford a yellow solid which, after purification by wet flash column chromatography hexane/ethyl acetate (60:40) afforded the α-methylated sulfone as a white solid (0.17 g, 52%), mp 119-121ºC; (Found: C, 62.72; H, 5.88; S, 10.08. $C_{16}H_{18}O_4S$ requires C, 62.72; H, 5.92; S, 10.47%); ν_{max} (KBr)/cm^{-1} 1042, 1258 (C-O-C), 1147, 1304 (SO_2); δ_H (300 MHz) 1.72 (3H, d, CH_3, *J* 7.1), 3.54 (3H, s, OCH_3), 3.99 (3H, s, OCH_3), 5.46 (1H, q, CH, *J* 7.4), 6.60-6.67 (1H, m, ArH), 6.82-6.90 (1H, m, ArH), 6.92–7.01 (2H, m, ArH), 7.14-7.25 (1H, m, ArH), 7.42-7.51 (1H, m, ArH), 7.55-7.64 (2H, m, ArH); δ_c (75.5) 14.1 (CH_3,

CH_3), 55.1 (CH, CH), 55.8, 56.5 (2 x CH_3, OCH_3), 110.5, 112.0, 120.3, 121.1 (4 x CH, aromatic CH), 123.2, 126.5 (2 x C, quaternary aromatic C), 129.9, 130.0, 132.1, 135.4 (4 x CH, aromatic CH), 157.4, 158.4 (2 x C, C-O). m/z (ESI) 307 [$(M+H)^+$]; HRMS (ESI): Exact mass calculated for $C_{16}H_{19}O_4S$ $[M+H]^+$, 307.1007. Found 307.1004.
Single crystals of the sulfone were grown from a DCM/hexane mixture.

Procedure F

A solution of *m*-CPBA* (4.00 mmol) in DCM (15 ml) was added dropwise over 1 h to a stirred solution of sulfide (4.00 mmol) in DCM (20 ml) at 0 °C. The reaction mixture was stirred for an additional 30 min at 0 °C and then washed with saturated $NaHCO_3$ solution (3 x 30 ml) and water (30 ml), dried with $MgSO_4$ and concentrated under reduced pressure to yield the crude product as a white solid. The sulfoxide was purified by either column chromatography, with hexane/ethyl acetate (80:20 to 60:40) as eluent, or by recrystallisation from a suitable solvent or by both methods as specified for each compound.

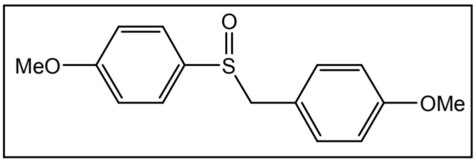
* The percentage purity of *m*-CPBA used is specified for each particular compound.

Procedure G

A solution of sulfide (22 mmol) in MeOH (35 ml) was added dropwise to a solution of sodium periodate (23 mmol) in water (45 ml) while stirring at 0 °C. The reaction mixture was stirred for 16 h and the precipitate that formed was removed by vacuum filtration. The filtrate was concentrated under reduced pressure and DCM (20 ml) was added. DCM (20 ml) was added to the precipitate, the suspension swirled and filtered and the filtrate collected. The combined filtrates were washed with water (2 x 30 ml), dried over $MgSO_4$ and concentrated under reduced pressure to yield a white solid. The sulfoxide was purified by either column chromatography, with hexane/ethyl acetate (80:20 to 60:40) as eluent, or by recrystallisation from a suitable solvent or by both methods as specified for each compound.

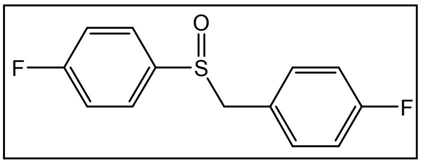
4-Methoxyphenyl-4′-methoxybenzylsulfoxide (17)

A solution of magnesium monoperoxyphthalate (0.69 g, 85%, 1.12 mmol) in DCM (8 ml) was added dropwise over 30 min to a solution of sulfide **2** (0.58 g, 2.24 mmol) in DCM (11 ml) while stirring at 0 °C. The reaction mixture was stirred for additional 16 hours at room temperature. The reaction mixture was then washed with water (3 x 15 ml), dried with $MgSO_4$



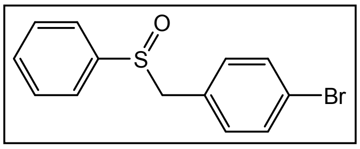
and concentrated under reduced pressure to yield the crude product as a white solid. Purification by column chromatography using hexane/ethyl acetate (40:60) as eluent gave the sulfoxide as a white solid (0.43 g, 75%), m.p. 161-162 °C; (Found: C, 64.97; H, 5.88%. $C_{15}H_{16}O_3S$ requires C, 65.19; H, 5.84%); δ_H (300 MHz) 3.79 (3H, s, OCH_3), 3.84 (3H, s, OCH_3), 3.91 (1H, A of ABq, *J* 12.6, CH_2), 4.05 (1H, B of ABq, *J* 12.6, CH_2), 6.52-7.00 (6H, m, ArH), 7.22-7.29 (2H, m, ArH); δ_C (75.5 MHz) 54.2, 54.5 (2 x CH_3, OCH_3), 61.9 (CH_2, CH_2), 112.8, 113.3, 125.4, 130.6 (4 x CH, aromatic CH), 120.1, 132.6, 158.5, 160.1 (4 x C, quaternary aromatic C).

4-Fluorophenyl-4′-fluorobenzylsulfoxide (18)[8]



This compound was synthesised following procedure F using sulfide **D2** (0.53 g, 2.24 mmol) and magnesium monoperoxyphthalate (0.69 g, 85%, 1.12 mmol) to give the sulfoxide. Purification by column chromatography using hexane/ethyl acetate (40:60) as eluent gave the sulfoxide as a white crystalline solid (0.31 g, 77%), m.p. 162-163 °C (Lit.[8] 160-161 °C); Found: C, 61.80; H, 3.97%. $C_{13}H_{10}F_2OS$ requires C, 61.90; H, 3.96%); ν_{max}/cm^{-1} (KBr) 1050 (SO); δ_H (300 MHz) 4.00 (2H, s, CH_2), 6.90-6.95 (4H, m, ArH), 7.10-7.36 (4H, m, ArH); δ_C (75.5 MHz) 40.2 (CH_2, CH_2), 115.7 (CH, d, $^2J_{C-F}$ 22, ArCH), 116.4 (CH, d, $^2J_{C-F}$ 22, ArCH), 130.7 (C, quaternary aromatic C), 130.8 (CH, d, $^3J_{C-F}$ 8, ArCH), 133.7 (C, d, $^4J_{C-F}$ 3, quaternary aromatic C) 134.2 (CH, d, $^3J_{C-F}$ 8, ArCH), 162.4 (C, d, $^1J_{C-F}$ 246, C-F), 162.6 (C, d, $^1J_{C-F}$ 247, C-F).

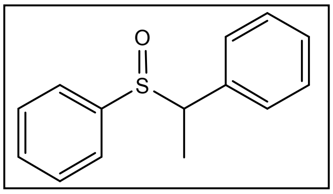
Phenyl-4-bromobenzylsulfoxide (19)



This compound was synthesized following procedure F using phenyl-4-bromobenzylsulfide **1** (1.50 g, 5.40 mmol) and *m*-CPBA (1.21 g, 77%, 5.40 mmol). Purification by column chromatography using hexane/ethyl acetate (60:40) as eluent followed by recrystallisation from hot methanol afforded the sulfoxide as a white solid (0.39 g, 25%), m.p. 157-159°C; (Found: C, 52.78; H, 3.78; Br, 27.46; S, 10.79. $C_{13}H_{11}BrOS$ requires C, 52.89; H, 3.76; Br, 27.07; S, 10.86%); ν_{max}/cm^{-1} (KBr) 1033 (SO), 690 (C-S); δ_H (300 MHz) 3.95 (1H, A of ABq, $SOCH_2$, *J* 12.7), 4.01 (1H, B of ABq, $SOCH_2$, *J* 12.7), 6.75-6.95 (2H, m, ArH), 7.20-7.65 (7H, m, ArH); δ_c (75.5 MHz) 62.4 (CH_2, CH_2), 122.6 (C, quaternary aromatic), 124.4 (CH, aromatic CH), 127.9 (C, quaternary aromatic C), 129.0, 131.3, 131.5, 131.9 (4 x CH, aromatic CH), 142.3 (C, quaternary aromatic C).

Single crystals of the sulfoxide were grown from methanol.

Phenyl[(1-phenyl)ethyl]sulfoxide (*R***R**-23)[12]

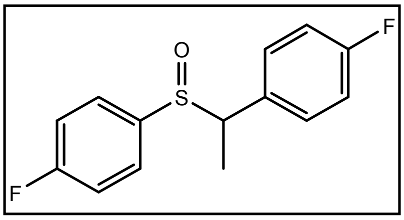


^{t}Butyl-hypochlorite (0.37 g, 4.88 mmol) was added to a solution of phenyl[(1-phenyl)ethyl]sulfide **D1** (1.10 g, 5.14 mmol) in DCM (20 ml) at -78 °C. The reaction mixture was stirred at this temperature for 1 h and then dimethyl sulfide (1.21g, 19.50 mmol) was added. The resulting mixture was removed from the cooling bath and stirred for 30 min at room temperature, then saturated $NaHCO_3$ solution (20 ml) was added. The layers were separated and the organic layer washed with saturated $NaHCO_3$ solution (2 x 30 ml), dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a mixture of the sulfide **D1** (δ_H 4.33, q), RR/SS sulfoxide diastereomer (δ_H 4.04, q) and RS/SR sulfoxide diastereomer (δ_H 3.80, q) in the ratio 9:13:1. Purification by column chromatography using hexane/ethyl acetate (60:40) afforded the sulfoxide diastereomers RR/SS:RS/SR in the ratio 13:1 (0.65 g, 55%). Recrystallisation from acetonitrile afforded only the RR/SS sulfoxide diastereomer as clear crystals (0.57 g, 49%), m.p. 105-106 °C; δ_H ($CDCl_3$) 1.59 (3H, d, CH_3, *J* 7.2), 4.04 (1H, q, CH, *J* 7.2), 6.94-7.03 (2H, m, ArH), 7.07-7.15 (2H, m, ArH), 7.19-7.49 (6H, m, ArH); δ_c ($CDCl_3$) 12.5 (CH_3, CH_3), 64.7 (CH, CH), 125.6, 128.5, 128.6, 128.7, 129.2, 131.3 (6 x CH, aromatic CH), 134.3, 140.8 (2 x C, quaternary aromatic C)

Single crystals of the sulfoxide were grown from acetonitrile.

(4-Fluorophenyl)[1-(4-fluorophenyl)ethyl]sulfoxide (*R***R**-24 and *R***S**-28)

This compound was synthesised following procedure G using (4-fluorophenyl)[1-(4-fluorophenyl)ethyl]sulfide **D3** (1.60 g, 5.67 mmol) in methanol (20 ml) and a solution of sodium periodate (1.21 g, 5.67 mmol) in water (15 ml) to afford the crude product as a mixture of the sulfide **D3** (δ_H 4.20, q), RR/SS sulfoxide diastereomer (δ_H 3.94, q) and RS/SR sulfoxide diastereomer (δ_H 3.81, q) in the ratio 3:1:3. Purification by column chromatography using hexane/ethyl acetate (80:20) afforded the sulfoxide diastereomers RR/SS:RS/SR in the ratio 1:2 (0.80 g, 47%). Successive recrystallisations from DCM/hexane afforded only the RS/SR sulfoxide diastereomer as clear crystals (0.07 g, 4%) while mother liquor of the first recrystallisation afforded ***R*R*-24*** as clear crystals; (Found: C, 63.20; H, 4.54. $C_{14}H_{12}OS$ requires C, 63.14; H, 4.53%); ν_{max} (KBr)/cm^{-1} 1049 (SO); m/z (ESI) 267 [(M+H)$^+$]; HRMS (ESI): Exact mass calculated for $C_{14}H_{13}OF_2S$ [M+H]$^+$, 267.0653. Found 267.0655.



R*R*-24: δ_H ($CDCl_3$) 1.61 (3H, d, CH_3, J 7.2), 3.93 (1H, q, CH, *J* 7.2), 6.92-6.94 (4H, m, ArH), 7.01-7.13 (4H, m, ArH); δ_c ($CDCl_3$) 12.9 (CH_3, CH_3), 63.7 (CH, CH), 115.1 (CH, d, $^2J_{C-F}$ 21, ArCH), 115.8 (CH, d, $^2J_{C-F}$ 22, ArCH), 127.1 (CH, d, $^3J_{C-F}$ 9, ArCH), 129.4 (CH, d, $^4J_{C-F}$ 3, aromatic C), 130.4 (C, d, $^3J_{C-F}$ 8, ArCH), 136.0 (C, d, $^4J_{C-F}$ 3, C-S), 162.7 (C, d, $^1J_{C-F}$ 248, C-F), 164.4 (C, d, $^1J_{C-F}$ 252, C-F), m.p. 93-95 °C.

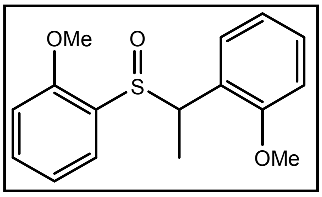
Single crystals of the sulfoxide were grown from a DCM/hexane mixture.

R*S*-28: δ_H ($CDCl_3$) 1.67 (3H, d, CH_3, J 7.2), 3.81 (1H, q, CH, *J* 7.1), 6.92-6.98 (4H, m, ArH), 7.02-7.11 (2H, m, ArH), 7.17-7.25 (2H, m, ArH); δ_c ($CDCl_3$) 16.0 (CH_3, CH_3), 68.0 (CH, CH), 117.3 (CH, d, $^2J_{C-F}$ 21, ArCH), 117.7 (CH, d, $^2J_{C-F}$ 22, ArCH), 129.1 (CH, d, $^3J_{C-F}$ 9, ArCH), 132.1(CH, d, $^3J_{C-F}$ 8, ArCH), 132.5 (C, d, $^4J_{C-F}$ 3, aromatic C), 138.7 (C, d, $^4J_{C-F}$ 3, C-S), 163.1 (C, d, $^1J_{C-F}$ 247, C-F), 164.8 (C, d, $^1J_{C-F}$ 250, C-F); m.p. 95-98 °C.

Single crystals of the sulfoxide were grown from a DCM/hexane mixture.

(2-Methoxyphenyl)[1-(2-methoxyphenyl)ethyl]sulfoxide (R*S*-29)

This compound was synthesised following procedure G using (2-methoxyphenyl)[1-(2-methoxyphenyl)ethyl]sulfide **4** (0.83 g, 3.00 mmol) in methanol (20 ml) and a solution of sodium periodate (0.64 g, 3.00 mmol) in water (15 ml) to afford the



crude product as a mixture of the sulfide **45** (δ_H 4.99, q), RR/SS sulfoxide diastereomer (δ_H 4.89, q) and RS/SR sulfoxide diastereomer (δ_H 4.78, q) in the ratio trace:1:2. Purification by column chromatography using hexane/ethyl acetate (80:20) afforded the sulfoxide diastereomers RR/SS:RS/SR in the ratio 1:2 (0.49 g, 56%). Successive recrystallisations from DCM/hexane afforded only the RS/SR sulfoxide diastereomer as clear crystals (0.04 g, 2%), m.p. 103-105 °C; (Found: C, 66.12; H, 6.23; S, 10.70. $C_{16}H_{18}O_3S$ requires C, 66.18; H, 6.25; S, 11.04%); ν_{max} (KBr)/cm^{-1} 1049 (SO); δ_H ($CDCl_3$) 1.40 (3H, d, CH_3, *J* 7.2), 3.77 (6H, 2 x unresolved s, OCH_3), 4.78 (1H, q, CH, *J* 7.2), 6.80-6.90 (2H, m, ArH), 6.98 (1H, overlapping ddd appears as td, ArH, *J* 7.5, 0.9), 7.16 (1H, overlapping ddd, appears as td, ArH, *J* 7.7, 1.0), 7.22-7.32 (1H, m, ArH), 7.36-7.46 (2H, m, ArH), 7.80 (1H, dd, ArH, *J* 7.7, 1.7); δ_c ($CDCl_3$) 11.1 (CH_3, $CHCH_3$), 54.7 (CH, $CHCH_3$), 55.9, 56.0 (2 x CH_3, OCH_3), 110.6, 110.8, 121.2, 121.5 (4 x CH, aromatic CH), 126.5 (C, quaternary aromatic C), 126.9, 129.4, 129.5 (3 x CH, aromatic CH), 131.2 (C, quaternary aromatic C), 132.2 (CH, aromatic CH), 156.1, 157.4 (2 x C, quaternary aromatic C); m/z (ESI) 291 [$(M+H)^+$]; HRMS (ESI): Exact mass calculated for $C_{16}H_{19}O_3S$ $[M+H]^+$, 291.1055. Found 291.1055.

Single crystals of the sulfoxide were grown from a DCM/hexane mixture.

Crystallographic Data were collected on a variety of instruments, full details are in the CIFs. The structures were solved using SHELXS, refined by full-matrix least-squares using SHELXL-97.[12] Diagrams were generated using PLATON.[13]

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