SUPPLEMENTARY INFORMATION (PART 1)

Asymmetric synthesis of carbocycles: use of intramolecular conjugate displacement

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1-((3-Chloro-1-[(4-fluorophenyl)sulfanyl]propyl)sulfanyl)-4-fluorobenzene (3.2)

![Reaction Scheme]

4-Fluorothiophenol (3.6 g, 28.15 mmol) and CF₃CO₂H (2.38 g, 21.11 mmol) were added to a stirred solution of 3.1 (1.17 g, 7.03 mmol) in CH₂Cl₂ (30 mL) at room temperature and stirring was continued for 24 h. The reaction mixture was quenched with water (20 mL) and extracted with CH₂Cl₂ (2 x 30 mL). The combined organic extracts were washed with aqueous NaOH (10w/v) 2 x 10 mL) and brine, dried (MgSO₄) and evaporated. Flash chromatography of the
residue over silica gel (4 x 15 cm), using 8% Et₂O-hexane, gave 3.2 which was used directly for the next step.

**4,4-Bis[(4-fluorophenyl)sulfanyl]butanenitrile (3.3)**

A solution of 3.2 (2.13 g, 6.44 mmol) in DMSO (2.5 mL) was added to a stirred mixture of NaCN (1.58 g, 32.23 mmol) and Bu₄NI (475 mg, 1.28 mmol) in DMSO (25 mL), and the resulting mixture was stirred at 50 °C for 24 h, cooled to room temperature, diluted with water (20 mL) and extracted with Et₂O (2 x 100 mL). The combined organic extracts were washed with brine, dried (Na₂SO₄) and evaporated. Flash chromatography of the residue over silica gel (4 x 15 cm), using 20% Et₂O-hexane, gave 3.3 (1.37 g, 61% over two steps) as an oil: FTIR \( \nu_{\text{max}} \) (CDCl₃, cast)/cm⁻¹ 3094, 3067, 2856, 2248, 1589, 1489, 1443, 1420; \(^1\)H NMR (500 MHz, CDCl₃) \( \delta \) 7.49-7.45 (m, 4 H), 7.07-7.02 (m, 4 H), 4.27 (t, \( J = 7.1 \) Hz, 1 H), 2.68 (t, \( J = 7.1 \) Hz, 2 H), 2.10 (q, \( J = 7.1 \) Hz, 2 H); \(^{13}\)C NMR (125 MHz, CDCl₃) \( \delta \) 163.1 (CF, d, \(^3\)J_CF = 249.9 Hz), 136.1 (CCCF, d, \(^4\)J_CF = 8.4 Hz), 127.5 (CCCCF, d, \(^5\)J_CF = 3.5 Hz), 118.4 (s), 116.4 (CCF, d, \(^2\)J_CF = 21.9 Hz), 58.5 (d), 31.0 (t), 15.2 (t); exact mass (electrospray) \( m/z \) calcd for C₁₆H₁₃F₂NNaS₂ (M + Na) 344.0350, found 344.0358.

**4,4-Bis[(4-fluorophenyl)sulfanyl]butanal (6)**
DIBAL-H (1 M in PhMe, 3.1 mL, 3.11 mmol) was added by syringe pump over 20 min to a stirred and cooled (-78 °C) solution of 3.3 (500 mg, 1.55 mmol) in CH_2Cl_2 (16 mL). After the addition, stirring at -78 °C was continued for 1 h and then the cold bath was replaced by an ice bath. Stirring at 0 °C was continued for 30 min and the mixture was quenched with water (0.56 mL, 31 mmol) and NaF\(^{2+}\) (1.34 g, 31 mmol). The ice bath was removed, the mixture was diluted with Et_2O (50 mL), stirred vigorously for 1 h and then filtered through a pad of Celite (1 x 3 cm diameter) using Et_2O. Evaporation of the filtrate and flash chromatography of the residue over silica gel (2 x 15 cm), using 20% Et_2O-hexane, gave 6 (359 mg, 72%) as an oil: FTIR \(\nu_{\text{max}}\) (CDCl_3, cast)/cm\(^{-1}\) 3067, 2927, 2249, 2726, 1724, 1589, 1490, 1443, 1443; \(^1\)H NMR (500 MHz, CDCl_3) \(\delta\) 9.80 (s, 1 H), 7.49-7.45 (m, 4 H), 7.07-7.02 (m, 4 H), 4.30 (t, \(J = 6.8\) Hz, 1 H), 2.83 (td, \(J = 7.1, 1.0\) Hz, 2 H), 2.14 (q, \(J = 7.0\) Hz, 2 H); \(^{13}\)C NMR (125 MHz, CDCl_3) \(\delta\) 200.6 (s), 162.9 (CF, \(^1J_{CF} = 249.0\) Hz), 135.7 (CCCF, \(^3J_{CF} = 8.3\) Hz), 128.3 (CCCCF, \(^4J_{CF} = 3.5\) Hz), 116.2 (CCF, \(^2J_{CF} = 21.9\) Hz), 59.2 (d), 41.1 (t), 27.9 (t); exact mass (electrospray) \(m/z\) calcd for C_{16}H_{14}F_{2}NaOS_{2} (M + Na) 347.0346, found 347.0346.

1-(Bromomethyl)-2-(dimethoxymethyl)benzene (4.3)
CH(OMe)₃ (2.54 mL, 23.23 mmol) was added to a solution of 4.2¹¹ (925 mg, 4.65 mmol) and TsOH·H₂O (88 mg, 0.46 mmol) in anhydrous MeOH (23 mL), and the mixture was heated at 50 °C for 12 h., cooled, and quenched with Et₃N (3 mL). The MeOH was evaporated under reduced pressure and the residue was diluted with water (20 mL) and extracted with Et₂O. The combined organic extracts were washed with brine, dried (MgSO₄) and evaporated. Flash chromatography of the residue over silica gel (4 x 15 cm), using 6% Et₂O-hexane, gave 4.3 (1.10 g, 100%) as a colorless oil: FTIR νmax (CDCl₃, cast)/cm⁻¹ 3064, 2991, 2953, 2904, 2829, 1488, 1455; ¹H NMR (500 MHz, CDCl₃) δ 7.60-7.56 (m, 1 H), 7.40-7.37 (m, 1 H), 7.34-7.30 (m, 2 H), 5.64 (s, 1 H), 4.69 (s, 2 H), 3.35 (s, 6 H); ¹³C NMR (125 MHz, CDCl₃) δ 136.2 (s), 135.7 (s), 131.1 (d), 129.0 (d), 128.4 (d), 127.4 (d), 101.1 (d), 53.3 (q), 30.7 (t); exact mass (electrospray) m/z calcd for C₁₀H₁₃⁷⁹BrNaO₂ (M + Na) 266.9991, found 266.9989.

2-[2,2-Bis(phenylsulfanyl)ethyl]benzaldehyde (8)

BuLi (2.5 in hexane, 0.63 mL, 1.57 mmol) was added dropwise to a stirred and cooled (0 °C) solution of (PhS)₂CH₂ (335 mg, 1.45 mmol) in THF (4 mL). Stirring at 0 °C was continued for
10 min and the mixture was then cooled to -78 °C. A solution of 4.3 (300 mg, 1.20 mmol) in THF (6 mL) was added rapidly in one portion and stirring at -78 °C was continued for 30 min and then at 0 °C (ice bath) for 10 min. Hydrochloric acid (4 M, 3 mL) was added, the cold bath was removed and stirring was continued for 3 h. The mixture was diluted with water (20 mL) and extracted with Et₂O (50 mL). The combined organic extracts were washed with brine, dried (MgSO₄) and evaporated. Flash chromatography of the residue over silica gel (2 x 15 cm), using 8% Et₂O-hexane, gave 8 (289 mg, 69%) as a colorless oil: FTIR ν max (CDCl₃, cast)/cm⁻¹ 3055, 2861, 2832, 2742, 1699, 1598, 1574, 1480, 1451; ¹H NMR (500 MHz, CDCl₃) δ 10.03 (s, 1 H), 7.76 (dd, J = 7.6, 1.4 Hz, 1 H), 7.51 (td, J = 7.5, 1.5 Hz, 1 H), 7.41 (td, J = 7.5, 1.1 Hz, 1 H), 7.31-7.24 (m, 7 H), 4.71 (t, J = 7.5 Hz, 1 H), 3.60 (d, J = 7.5 Hz, 2 H); ¹³C NMR (125 MHz, CDCl₃) δ 192.4 (d), 139.9 (s), 134.2 (s), 134.1 (d), 133.5 (d), 133.0 (d), 132.9 (d), 128.9 (d), 127.9 (d), 127.6 (d), 59.5 (d), 39.7 (t); exact mass (EI) m/z calcd for C₂₁H₁₈O₃S 350.0799, found 350.0796.

1-(Bromomethyl)-2-(dimethoxymethyl)-4-fluorobenzene (5.4)

CH(OMe)₃ (4.2 mL, 38.35 mmol) was added to a solution of 5.3¹²¹³ (1.67 g, 7.67 mmol) and TsOH.H₂O (146 mg, 0.77 mmol) in anhydrous MeOH (30 mL) and the mixture was heated at 50 °C for 1 h. The reaction mixture quenched with Et₃N (3 mL) and the MeOH was evaporated under reduced pressure. The residue was partitioned between water (20 mL) and Et₂O (50 mL),
and the organic phase was washed with brine, dried (MgSO₄) and evaporated. Flash chromatography of the residue over silica gel (4 x 15 cm), using 5% Et₂O-hexane, gave 5.4 (1.75 g, 86%) as a colorless oil: FTIR ν max (CDCl₃, cast)/cm⁻¹ 3081, 2993, 2956, 2936, 2907, 2831, 1611, 1595, 1495, 1447, 1423; ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.32 (m, 2 H), 7.01 (td, J = 8.2, 2.8 Hz, 1 H), 5.63 (s, 1 H), 4.64 (s, 2 H), 3.35 (s, 6 H); ¹³C NMR (125 MHz, CDCl₃) δ 162.6 (CF, ¹JC_F = 248.5 Hz), 139.0 (CCCF, ³JC_F = 7.3 Hz), 132.8 (CCCF, ³JC_F = 8.3 Hz), 131.6 (CCCCF, ⁴JC_F = 3.6 Hz), 115.8 (CCF, ²JC_F = 21.7 Hz), 114.9 (CCF, ²JC_F = 23.4 Hz), 99.9 (d, J = 1.8 Hz), 53.1 (q), 29.8 (t); exact mass (electrospray) m/z calcd for C₁₀H₁₂BrFNaO₂ (M + Na) 284.9897, found 284.9896.

2-[2,2-Bis(phenylsulfanyl)ethyl]-5-fluorobenzaldehyde (9)

BuLi (2.5 M in hexane, 1.2 mL, 2.84 mmol) was added dropwise to a stirred and cooled (0 °C) solution of (PhS)₂CH₂ (660 mg, 2.84 mmol) in THF (20 mL). Stirring at 0 °C was continued for 10 min and the mixture was then cooled to -78 °C. A solution of 5.4 (630 mg, 2.36 mmol) in THF (6 mL) was added rapidly in one portion and stirring at -78 °C was continued for another 30 min and then at 0 °C (ice bath) for 10 min. Hydrochloric acid (4 M, 3 mL) was added, the cold bath was removed and stirring was continued for 3 h. The mixture was diluted with water (20 mL) and extracted with Et₂O (50 mL). The combined organic extracts were washed with brine,
dried (MgSO₄) and evaporated. Flash chromatography of the residue over silica gel (3 x 15 cm),
using 10% Et₂O-hexane, gave 9 (839 mg, 96%) as a colorless oil: FTIR ν_max (CDCl₃, cast)/cm⁻¹
3059, 3019, 2923, 2866, 2736, 1695, 1609, 1582, 1494, 1479, 1439, 1419; ¹H NMR (500 MHz,
CDCl₃) δ 10.00 (d, J = 1.7 Hz, 1 H), 7.49 (dd, J = 8.7, 2.8 Hz, 1 H), 7.40-7.37 (m, 4 H), 7.32-
7.29 (m, 7 H), 7.23 (td, J = 8.1, 2.8 Hz, 1 H), 4.63 (t, J = 7.4 Hz, 1 H), 3.58 (d, J = 7.4 Hz, 2 H);
¹³C NMR (125 MHz, CDCl₃) δ 190.5 (d), 161.9 (CF, ¹J_CF = 248.7 Hz), 135.8 (s), 135.8 (s),
135.8 (s), 134.6 (CCCF, ²J_CF = 7.3 Hz), 133.9 (s), 133.0 (d), 129.0 (d), 128.0 (d), 120.6 (CCF,
²J_CF = 21.4 Hz), 117.7 (CCF, ²J_CF = 22.0 Hz), 60.0 (s), 38.5 (t); exact mass (electrospray) m/z
calcd for C₂₁H₁₇FNaOS₂ (M + Na) 391.0597, found 391.0590.

5-Butyl-3-(phenylselanyl)oxolan-2-one (2).

(Me₃Si)₂NK (0.5 M in PhMe, 1.29 mL, 0.65 mmol) was added dropwise to a stirred and cooled (-
78 °C) solution 5-butyloxolane-2-one¹²⁵ (4) (92 mg, 0.64 mmol) in THF (4 mL). Stirring at -78
°C was continued for 45 min. Then a solution of PhSeCl (62 mg, 0.324 mmol) in THF (1 mL)
was injected rapidly in ONE PORTION (this mode of addition is important) and stirring at -78
°C was continued for 20 min. Saturated aqueous NH₄Cl (ca 3 mL) was added and the mixture
was extracted with EtOAc. The combined organic extracts were dried (Na₂SO₄) and evaporated.
Flash chromatography of the residue over silica gel (1 x 15 cm), using 14% Et₂O-hexane, gave 2
as a mixture of diastereomers which was separated into three fractions (more polar, 24 mg, 25%; less polar, 28 mg, 29%; mixture, 20.2 mg, 21%).

The more polar selenide had: FTIR $\nu_{\text{max}}$ (CDCl$_3$, cast)/cm$^{-1}$ 3057, 2956, 2933, 2862, 1764, 1578, 1478, 1466, 1438; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.67-7.65 (m, 2 H), 7.38-7.30 (m, 3 H), 4.41-4.35 (m, 1 H), 4.01 (t, $J = 9.6$ Hz, 1 H), 2.71 (ddd, $J = 13.5$, 9.4, 6.5 Hz, 1 H), 1.93 (ddd, $J = 13.5$, 9.8, 8.6 Hz, 1 H), 1.63-1.56 (m, 1 H), 1.49-1.42 (m, 1 H), 1.36-1.21 (m, 4 H), 0.87 (t, $J = 7.0$ Hz, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 175.8 (s), 135.6 (d), 129.3 (d), 128.8 (d), 127.1 (s), 79.3 (d), 37.6 (d), 36.0 (t), 35.1 (t), 27.1 (t), 22.3 (t), 13.8 (q); exact mass (electrospray) calcd for C$_{14}$H$_{18}$NaO$_2$Se (M + Na) 319.0375, found 319.0374.

The less polar selenide had: FTIR $\nu_{\text{max}}$ (CDCl$_3$, cast)/cm$^{-1}$ 3057, 2956, 2932, 2862, 1770, 1578, 1478, 1467, 1438; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.69-7.67 (m, 2 H), 7.40-7.31 (m, 3 H), 4.35-4.29 (m, 1 H), 3.95 (dd, $J = 7.8$, 3.1 Hz, 1 H), 2.37-2.27 (m, 2 H), 1.73-1.66 (m, 1 H), 1.58-1.51 (m, 1 H), 1.42-1.26 (m, 4 H), 0.89 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 175.7 (s), 135.7 (d), 129.4 (d), 129.1 (d), 126.9 (s), 79.5 (d), 37.2 (d), 36.7 (t), 34.9 (t), 27.2 (t), 22.3 (t), 13.9 (q); exact mass (electrospray) m/z calcd for C$_{14}$H$_{18}$NaO$_2$Se (M + Na) 319.0375, found 319.0375.

(2Z)-2-((2-[2,2-Bis(benzenesulfonyl)ethyl]-5-fluorophenyl)methyl)but-2-ene-1,4-diol (9.1)
DIBAL-H (1 M solution in PhMe, 0.61 mL, 0.61 mmol) was added by syringe pump over 20 min to a stirred and cooled (-78 °C) solution of 9g (40 mg, 0.061 mmol) in PhMe. After the addition, stirring at -78 °C was continued for 1 h. The cold bath was replaced by an ice bath and stirring at 0 °C was continued for 1 h. Finally the ice bath was removed and stirring was continued for 2 h. The reaction mixture was quenched with water (1.226 mmol, 0.022 mL) and NaF\textsuperscript{24} (51 mg, 1.2 mmol), diluted with Et\textsubscript{2}O (50 mL), stirred vigorously for 1 h at room temperature, and then filtered through a pad of Celite (1 x 1 cm), using Et\textsubscript{2}O as a rinse. Evaporation of the filtrate and flash chromatography of the residue over silica gel (1 x 15 cm), using 80% EtOAc-hexane, gave 9.1 (21 mg, 68%) as an oil: FTIR ν\textsubscript{max} (CDCl\textsubscript{3}, cast)/cm\textsuperscript{-1} 3524, 3378, 3069, 2926, 2855, 1588, 1498, 1448; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.82 (dd, J = 8.4, 1.1 Hz, 4 H), 7.67-7.64 (m, 2 H), 7.52-7.49 (m, 4 H), 7.23 (dd, J = 8.5, 5.8 Hz, 1 H), 6.84-6.79 (m, 2 H), 5.28 (t, J = 6.8 Hz, 1 H), 5.10 (t, J = 6.3 Hz, 1 H), 4.18 (d, J = 6.7 Hz, 2 H), 4.13 (s, 2 H), 3.59 (d, J = 6.3 Hz, 2 H), 3.51 (s, 2 H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) δ 162.1 (CF, \textsuperscript{1}J\textsubscript{CF} = 246.8 Hz), 141.7 (s), 139.5 (s), 139.4 (s), 138.1 (s), 134.6 (d), 133.0 (d), 129.7 (s), 129.7 (s), 129.4 (d), 129.1 (d), 128.7 (d), 117.4 (CCF, \textsuperscript{2}J\textsubscript{CF} = 21.3 Hz), 113.7 (CCF, \textsuperscript{2}J\textsubscript{CF} = 21.2 Hz), 83.7 (d), 60.5 (t), 58.4 (t), 37.9 (t), 28.4 (t); exact mass (electrospray) m/z calcd for C\textsubscript{25}H\textsubscript{25}FNaO\textsubscript{6}S\textsubscript{2} (M + Na) 527.0969, found 527.0958.

(2Z)-2-((2-[2-(Benzenesulfonyl)ethyl]-5-fluorophenyl)methyl)but-2-ene-1,4-diol (9.2)
6% Na(Hg) (80 mg) was added to a stirred and cooled (0 °C) solution of 9.1 (5 mg, 0.009 mmol) and Na$_2$HPO$_4$ (14 mg, 0.099 mmol) in MeOH (2 mL). Stirring at 0 °C was continued for 30 min. The ice bath was removed and stirring was continued for 2 h. The reaction mixture was quenched with water (2 mL) and the MeOH was evaporated under reduced pressure. The residue was extracted with EtOAc (20 mL) and the combined organic extracts were washed with water and brine, dried (Na$_2$SO$_4$) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 100% EtOAc, gave 9.2 (2.3 mg, 64%) as a solid: FTIR $\nu_{\max}$ (CDCl$_3$, cast)/cm$^{-1}$ 3415, 3064, 2926, 2855, 1611, 1590, 1499, 1477; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.94 (dt, $J$ = 8.3, 1.6 Hz, 2 H), 7.68 (tt, $J$ = 7.5, 1.5 Hz, 1 H), 7.59-7.57 (m, 2 H), 7.04 (dd, $J$ = 8.3, 5.8 Hz, 1 H), 6.89-6.84 (m, 2 H), 5.30 (t, $J$ = 6.8 Hz, 1 H), 4.21 (d, $J$ = 6.9 Hz, 2 H), 4.16 (s, 2 H), 3.48 (s, 2 H), 3.32-3.28 (m, 2 H), 3.03 (dt, $J$ = 7.9, 4.2 Hz, 2 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 161.7 (CF, $^1J_{CF}$ = 246.1 Hz), 141.7 (s), 139.2 (s), 139.1 (s), 138.9 (s), 134.0 (d), 132.0 (s), 132.0 (s), 131.0 (d), 130.9 (d), 129.5 (d), 128.5 (d), 128.0 (d), 117.9 (CCF, $^2J_{CF}$ = 21.2 Hz), 114.0 (CCF, $^2J_{CF}$ = 21.1 Hz), 60.4 (t), 58.4 (t), 56.9 (t), 38.4 (t), 24.5 (t); exact mass (electrospray) $m/z$ calcd for C$_{19}$H$_{21}$FNaO$_4$S (M + Na) 387.1037, found 387.1028.

For X-ray analysis crystals of 9.2 were grown by slow vapor diffusion of hexanes into a solution of the compound in Et$_2$O.
(6R)-8-(Benzenesulfonyl)-13-fluoro-6-[(1R,2S,5R)-5-methyl-2-(propan-2-yl)cyclohexyl]-oxy)-5-oxatricyclo[8.4.0.0^{3,7}]tetradeca-1(14),2,7,10-pentaen-4-one (9.3)

6% Na(Hg) (100 mg) and Na$_2$HPO$_4$ (37 mg, 0.026 mmol) were added to a stirred and cooled (0 °C) solution of 9g (17 mg, 0.026 mmol) in MeOH (1 mL), and stirring at 0 °C was continued for 30 min. The ice bath was removed and stirring was continued for 2 h. The mixture was quenched with water (2 mL) and the MeOH was evaporated under reduced pressure. The residue was extracted with EtOAc (10 mL) and the organic layer was washed with water and brine, dried (Na$_2$SO$_4$) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 80% EtOAc, gave 9.3 (6 mg, 45%) as an oil: FTIR $\nu_{\text{max}}$ (CDCl$_3$, cast)/cm$^{-1}$ 3065, 2955, 2925, 2869, 1776, 1644, 1613, 1571, 1494, 1448; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.05 (s, 1 H), 8.01 (d, $J = 7.2$ Hz, 2 H), 7.61 (t, $J = 7.4$ Hz, 1 H), 7.53 (t, $J = 7.7$ Hz, 2 H), 7.17 (dd, $J = 8.8$, 2.6 Hz, 1 H), 7.07 (td, $J = 8.2$, 2.7 Hz, 1 H), 6.95 (s, 1 H), 6.70 (dd, $J = 8.4$, 5.2 Hz, 1 H), 3.77 (td, $J = 10.7$, 4.2 Hz, 1 H), 3.69 (d, $J = 15.0$ Hz, 1 H), 3.13 (d, $J = 14.8$ Hz, 1 H), 2.47 (d, $J = 13.8$ Hz, 1 H), 2.00-1.94 (m, 1 H), 1.67-1.63 (m, 2 H), 1.41-1.38 (m, 1 H), 1.24-1.20 (m, 1 H), 1.08-0.77 (m, 12 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 168.3 (s), 161.6 (CF, $^1J_{\text{CF}} = 246.3$ Hz), 142.4 (d), 140.1 (s), 140.0 (s), 135.0 (s), 134.9 (s), 134.0 (d), 131.6 (s), 130.4 (d), 130.3 (d), 129.3 (d), 128.9 (s), 128.4 (d), 125.3 (d), 120.6 (CCF, $^2J_{\text{CF}} = 21.8$ Hz), 116.7 (CCF, $^2J_{\text{CF}} = 21.9$ Hz), 96.4 (d), 77.9 (d), 48.0 (d), 38.8 (t), 34.3 (t), 34.1 (t), 31.6 (d), 25.3 (d), 23.3 (t), 22.3 (q), 21.0 (q),...
15.6 (q); exact mass (electrospray) m/z calcd for C_{29}H_{31}NaO_{5}S (M + Na) 533.1768, found 533.1767.

(5R)-3-[1-Hydroxy-4,4-bis(phenylsulfanyl)butyl]-4-methyl-5-(((1R,2S,5R)-5-methyl-2-(propan-2-yl)cyclohexyl)oxy)-2,5-dihydrofuran-2-one (5i, 5i')

BuLi (2.5 M in hexanes, 0.38 mL, 0.95 mmol) was added to a stirred and cooled (-78 °C) solution of i-Pr₂NH (0.15 mL, 1.11 mmol) in THF (3 mL), and stirring was continued for 30 min at -78 °C. A solution of 3<sup>9,26</sup> (200 mg, 0.79 mmol) in THF (2 mL) was then added dropwise and stirring at -78 °C was continued for 50 min. A solution of aldehyde 5<sup>4</sup> (274 mg, 0.95 mmol) in THF (2 mL) was added at a fast dropwise rate and stirring at -78 °C was continued for 30 min. Saturated aqueous NH₄Cl (ca 3 mL) was added and the mixture was extracted with Et₂O. The combined organic extracts were washed with brine (10 mL), dried (Na₂SO₄) and evaporated. Flash chromatography of the residue over silica gel (2 x 15 cm), using 50% Et₂O-hexane, gave an oil, which was separated into three fractions: less polar alcohol 5i' (41 mg, 10 %), more polar alcohol 5i (52 mg, 12 %), and a mixture of both isomers (172 mg, 40 %).

The more polar alcohol 5i had: FTIR ν<sub>max</sub> (CDCl₃, cast)/cm<sup>-1</sup> 3476, 3058, 2954, 2923, 2869, 1756, 1686, 1583, 1480, 1455, 1439; <sup>1</sup>H NMR (500 MHz, CDCl₃) δ 7.48-7.46 (m, 4 H), 7.33-7.26 (m, 6 H), 5.63 (s, 1 H), 4.46-4.41 (m, 2 H), 3.61 (td, J = 10.7, 4.3 Hz, 1 H), 2.84 (d, J =
9.1 Hz, 1 H), 2.15-1.81 (m, 9 H), 1.70-1.64 (m, 2 H), 1.44-1.39 (m, 1 H), 1.27-1.21 (m, 1 H), 1.03-0.78 (m, 12 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 171.3 (s), 155.6 (s), 133.9 (s), 133.9 (s), 132.9 (d), 132.9 (d), 130.2 (s), 129.0 (d), 129.0 (d), 127.9 (d), 127.9 (d), 100.8 (d), 79.6 (d), 66.4 (d), 58.0 (d), 47.8 (d), 40.5 (t), 34.2 (t), 33.8 (t), 31.7 (t), 31.5 (d), 25.2 (d), 23.1 (t), 22.3 (q), 20.9 (q), 15.8 (q), 11.5 (q); exact mass (electrospray) \(m/z\) calcd for C\(_{31}\)H\(_{40}\)NaO\(_4\)S\(_2\) (M + Na) 563.2260, found 563.2251.

The less polar alcohol 5i' had: FTIR \(\nu_{\text{max}}\) (CDCl\(_3\), cast)/cm\(^{-1}\) 3477, 3058, 2954, 2923, 2869, 1755, 1687, 1583, 1480, 1455, 1439; \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.50-7.48 (m, 4 H), 7.36-7.29 (m, 6 H), 5.68 (s, 1 H), 4.49-4.44 (m, 2 H), 3.64 (td, \(J = 10.7, 4.3\) Hz, 1 H), 2.84 (d, \(J = 9.2\) Hz, 1 H), 2.18-1.88 (m, 9 H), 1.73-1.67 (m, 2 H), 1.46-1.41 (m, 1 H), 1.30-1.25 (m, 1 H), 1.08-0.82 (m, 12 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 171.4 (s), 155.6 (s), 133.9 (s), 133.9 (s), 132.9 (d), 132.9 (d), 130.3 (s), 129.0 (d), 129.0 (d), 127.9 (d), 127.9 (d), 101.1 (d), 79.8 (d), 66.6 (d), 58.1 (d), 47.7 (d), 40.6 (t), 34.2 (t), 33.9 (t), 31.8 (t), 31.5 (d), 25.2 (d), 23.1 (t), 22.3 (q), 20.9 (q), 15.8 (q), 11.6 (q); exact mass (electrospray) \(m/z\) calcd for C\(_{31}\)H\(_{40}\)NaO\(_4\)S\(_2\) (M + Na) 563.2260, found 563.2255.

(5R)-3-[4,4-Bis(benzenesulfonyl)-1-hydroxybutyl]-4-methyl-5-\{[(1R,2S,5R)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy\}-2,5-dihydrofuran-2-one (5j, 5j')

\[5i, 5i', X = \text{SPh} \quad 5j, 5j', Z = \text{SO}_2\text{Ph}\]
MCPBA (70%, 1.18 g, 4.77 mmol) was added to a stirred and cooled (0 °C) solution of a mixture of 5i and 5i' (172 mg, 0.318 mmol) in CH₂Cl₂ (4 mL). The ice bath was removed and stirring was continued for 3 h. The mixture was quenched with a mixture of saturated aqueous NaHCO₃ (3 mL) and saturated aqueous Na₂S₂O₃ (3 mL), and extracted with CH₂Cl₂ (2 x 30 mL). The combined organic extracts were washed with water and brine, dried (Na₂SO₄) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 80% Et₂O-hexane, gave a separable mixture of isomers (140 mg, 73%): more polar sulfone alcohol 5j (74 mg, 39%) and the less polar sulfone alcohol 5j' (66 mg, 34%).

The more polar alcohol 5j had: FTIR ν_max (CDCl₃, cast)/cm⁻¹ 3517, 3065, 2955, 2924, 2870, 1753, 1687, 1585, 1448; ¹H NMR (500 MHz, CDCl₃) δ 7.97-7.94 (m, 4 H), 7.70 (t, J = 7.5 Hz, 2 H), 7.58 (t, J = 7.9 Hz, 4 H), 5.69 (s, 1 H), 4.65 (t, J = 5.8 Hz, 1 H), 4.48 (td, J = 8.4, 3.8 Hz, 1 H), 3.61 (td, J = 10.7, 4.3 Hz, 1 H), 2.89 (d, J = 8.2 Hz, 1 H), 2.46-2.25 (m, 2 H), 2.14-1.91 (m, 7 H), 1.70-1.64 (m, 2 H), 1.44-1.38 (m, 1 H), 1.27-1.21 (m, 1 H), 1.06-0.78 (m, 12 H); ¹³C NMR (125 MHz, CDCl₃) δ 171.3 (s), 156.3 (s), 137.9 (s), 137.7 (s), 134.7 (d), 134.7 (d), 129.7 (d), 129.5 (d), 129.2 (d), 129.2 (d), 101.0 (d), 82.8 (d), 79.8 (d), 66.3 (d), 47.8 (d), 40.5 (t), 34.2 (t), 33.8 (t), 31.5 (d), 25.2 (d), 23.1 (t), 22.3 (t), 22.3 (q), 20.9 (q), 15.8 (q), 11.6 (q); exact mass (electrospray) m/z calcd for C₃₁H₄₀NaO₈S₂ (M + Na) 627.2057, found 627.2050.

The less polar alcohol 5j' had: FTIR ν_max (CDCl₃, cast)/cm⁻¹ 3514, 3066, 2955, 2924, 2870, 1754, 1686, 1585, 1448; ¹H NMR (500 MHz, CDCl₃) δ 7.98-7.94 (m, 4 H), 7.72-7.68 (m, 2 H), 7.60-7.56 (m, 4 H), 5.69 (s, 1 H), 4.66 (t, J = 5.8 Hz, 1 H), 4.47 (td, J = 9.0, 3.9 Hz, 1 H), 3.61 (td, J = 10.7, 4.3 Hz, 1 H), 2.85 (d, J = 8.6 Hz, 1 H), 2.39 (ddt, J = 15.2, 9.2, 5.8 Hz, 1 H), 2.29 (ddt, J = 15.3, 9.0, 6.3 Hz, 1 H), 2.14-1.91 (m, 7 H), 1.70-1.64 (m, 2 H), 1.45-1.36 (m, 1 H), 1.28-1.22 (m, 1 H), 1.06-0.76 (m, 12 H); ¹³C NMR (125 MHz, CDCl₃) δ 171.3 (s), 156.3 (s),
137.9 (s), 137.7 (s), 134.7 (d), 134.7 (d), 129.7 (d), 129.2 (d), 129.2 (d), 101.2 (d), 82.8 (d), 79.9 (d), 66.5 (d), 47.7 (d), 40.6 (t), 34.2 (t), 34.1 (t), 31.5 (d), 25.2 (d), 23.1 (t), 22.4 (t), 22.3 (q), 21.0 (q), 15.7 (q), 11.7 (q); exact mass (electrospray) m/z calcd for C\textsubscript{31}H\textsubscript{40}NaO\textsubscript{8}S\textsubscript{2} (M + Na) 627.2057, found 627.2050.

\textbf{4,4-Bis(benzenesulfonyl)-1-[(5R)-4-methyl-5-\{(1R,2S,5R)-5-methyl-2-(propan-2-yl)cyclohexyl\}oxy]-2-oxo-2,5-dihydrofuran-3-yl]butyl acetate (5k, 5k'). Use of 5j'}

![Reaction Diagram]

DMAP (ca 1 mg, 0.01 mmol) was added to a stirred solution of 5j' (12 mg, 0.0198 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (1 mL). The mixture was then cooled to 0 °C, and AcCl (8.5 µL, 0.11 mmol) and pyridine (0.0128 mL, 0.16 mmol) were added sequentially. The ice bath was left in place but not recharged and stirring was continued for 3 h, during which time the cold bath reached room temperature. The reaction mixture was quenched with saturated aqueous CuSO\textsubscript{4} (2 mL) and water (5 mL), and extracted with CH\textsubscript{2}Cl\textsubscript{2} (2 x 10 mL). The combined organic extracts were washed with brine, dried (MgSO\textsubscript{4}) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 80% Et\textsubscript{2}O-hexane, gave 5k' (10.1 mg, 79%) as a colorless foam: 

FTIR ν\textsubscript{max} (CDCl\textsubscript{3}, cast)/cm\textsuperscript{-1} 3065, 3023, 2955, 2925, 2870, 1760, 1670, 1584, 1448; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.99-7.97 (m, 4 H), 7.76-7.73 (m, 2 H), 7.62 (t, J = 7.8 Hz, 4 H), 5.72 (s, 1 H), 5.58 (dd, J = 8.9, 4.5 Hz, 1 H), 4.54 (t, J = 5.8 Hz, 1 H), 3.64 (td, J = 10.6, 4.2 Hz, 1 H),
2.46-2.39 (m, 1 H), 2.29-2.10 (m, 11 H), 1.73-1.69 (m, 2 H), 1.48-1.42 (m, 1 H), 1.32-1.26 (m, 1 H), 1.10-0.84 (m, 12 H); $^1$H NMR (125 MHz, CDCl$_3$) δ 170.2 (s), 169.4 (s), 159.5 (s), 137.8 (s), 137.6 (s), 134.7 (d), 134.7 (d), 129.7 (d), 129.6 (d), 129.2 (d), 129.2 (d), 126.8 (s), 100.6 (d), 82.6 (d), 79.8 (d), 66.6 (d), 47.7 (d), 40.5 (t), 34.2 (t), 31.5 (q), 30.1 (t), 25.1 (d), 23.1 (t), 22.3 (d), 21.6 (t), 20.9 (q), 20.8 (q), 15.7 (q), 12 (q); exact mass (electrospray) $m/z$ calcd for C$_{33}$H$_{42}$NaO$_9$S$_2$ (M + Na) 669.2162, found 669.2156.

Use of 5j.  DMAP (1.2 mg, 0.01 mmol) was added to a stirred solution of 5j (12 mg, 0.0198 mmol) in CH$_2$Cl$_2$ (1 mL). The mixture was then cooled to 0 °C, and AcCl (8.5 µL, 0.11 mmol) and pyridine (0.0128 mL, 0.16 mmol) were added sequentially. The ice bath was left in place but not recharged and stirring was continued for 3 h, during which time the cold bath reached room temperature. The reaction mixture was quenched with saturated aqueous CuSO$_4$ (2 mL) and water (5 mL), and extracted with CH$_2$Cl$_2$ (2 x 10 mL). The combined organic extracts were washed with brine, dried (MgSO$_4$) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 80% Et$_2$O-hexane, gave 5k (10.3 mg, 81%) as a colorless foam: FTIR $\nu_{\text{max}}$ (CDCl$_3$, cast)/cm$^{-1}$ 3067, 3025, 2955, 2925, 2870, 1761, 1690, 1584, 1448; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.95-7.93 (m, 4 H), 7.70 (t, $J = 7.5$ Hz, 2 H), 7.58 (t, $J = 7.6$ Hz, 4 H), 5.66 (s, 1 H), 5.55 (dt, $J = 8.8$, 4.5 Hz, 1 H), 4.53 (t, $J = 5.8$ Hz, 1 H), 3.61 (td, $J = 10.7$, 4.3 Hz, 1 H), 2.34-2.04 (m, 12 H), 1.69-1.65 (m, 2 H), 1.44-1.37 (m, 1 H), 1.29-1.23 (m, 1 H), 1.07-0.80 (m, 12 H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 170.1 (s), 169.4 (s), 158.9 (s), 137.8 (s), 137.6 (s), 134.7 (d), 134.7 (d), 129.7 (d), 129.6 (d), 129.2 (d), 129.2 (d), 127.0 (s), 100.6 (d), 82.5 (d), 80.0 (d), 66.6 (d), 47.7 (d), 40.6 (t), 34.2 (t), 31.5 (q), 30.1 (t), 25.2 (d), 23.1 (t), 22.3 (d), 21.6 (t), 20.9 (q), 20.8 (q), 15.8 (q), 11.8 (q); exact mass (electrospray) $m/z$ calcd for C$_{33}$H$_{42}$NaO$_9$S$_2$ (M + Na) 669.2162, found 669.2150.
BuLi (2.5 M in hexanes, 0.46 mL, 1.14 mmol) was added to a stirred and cooled (-78 °C) solution of \(i\)-Pr\(_2\)NH (0.18 mL, 1.30 mmol) in THF (5 mL), and stirring was continued for 30 min. A solution of 3 (273 mg, 1.08 mmol) in THF (3 mL) was then added dropwise and stirring at -78 °C was continued for 50 min. A solution of aldehyde 9 (200 mg, 0.54 mmol) in THF (2 mL) was added at a fast dropwise rate and stirring at -78 °C was continued for 30 min. Then saturated aqueous NH\(_4\)Cl (ca 5 mL) was added and the mixture was extracted with Et\(_2\)O. The combined organic extracts were washed with brine (20 mL), dried (Na\(_2\)SO\(_4\)) and evaporated. Flash chromatography of the residue over silica gel (2 x 15 cm), using 50% Et\(_2\)O-hexane, gave crude 9d (171 mg, 51%) which could not be purified by flash chromatography and was used directly for next step.
MCPBA (70%, 465 mg, 1.88 mmol) was added to a stirred and cooled (0 °C) solution of crude 9d (117 mg, ca 0.188 mmol) in CH₂Cl₂ (5 mL). The ice bath was removed and stirring was continued for 4 h. The mixture was quenched with a mixture of saturated aqueous NaHCO₃ (3 mL) and saturated aqueous Na₂S₂O₃ (3 mL), and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic extracts were washed with water and brine, dried (Na₂SO₄) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 60% Et₂O-hexane, gave 9e (81 mg, 63%) as an inseparable mixture of diastereomers: FTIR νₓ (CDCl₃, cast)/cm⁻¹ 3502, 3066, 3021, 2956, 2924, 2871, 1749, 1689, 1613, 1592, 1501, 1499, 1479, 1448; ¹H NMR (500 MHz, CDCl₃) δ 7.86-7.83 (m, 2 H), 7.77-7.73 (m, 2 H), 7.66-7.61 (m, 2 H), 7.52-7.46 (m, 4 H), 7.30-7.26 (m, 1 H), 6.96-6.88 (m, 2 H), 5.96 (s, 1 H), 5.80 (s, 1 H), 5.55 (t, J = 6.1 Hz, 1 H), 3.95 (dd, J = 15.8, 6.1 Hz, 1 H), 3.75 (dd, J = 15.8, 6.2 Hz, 1 H), 3.67 (td, J = 10.7, 4.3 Hz, 1 H), 3.61 (s, 1 H), 2.15-2.04 (m, 5 H), 1.73-1.69 (m, 2 H), 1.47-1.26 (m, 2 H), 1.12-0.82 (m, 12 H); ¹³C NMR (125 MHz, CDCl₃) δ 171.6 (s), 162.2 (CF, ¹JC_F = 247.6 Hz), 157.6 (s), 141.6 (s), 141.6 (s), 138.4 (s), 138.2 (s), 134.4 (d), 134.4 (d), 133.5 (d), 133.5 (d), 129.9 (s), 129.9 (d), 129.2 (d), 129.2 (d), 129.0 (d), 128.8 (s), 115.5 (CCF, ²JC_F = 21.3 Hz), 114.6 (CCF, ²JC_F = 22.5 Hz), 101.3 (d), 83.7 (d), 79.8 (d), 66.1 (d), 47.7 (d), 40.4 (t), 34.2 (t), 31.5 (d), 27.7 (t), 25.4 (d), 23.3 (t), 22.3 (q), 20.8 (q), 15.9 (q), 12 (q); exact mass (electrospray) m/z calcd for C₃₆H₆₃FNaO₆S₂ (M + Na) 707.2119, found 707.2111.
DMAP (ca 1 mg, 0.01 mmol) was added to a stirred solution of 9e (13.5 mg, 0.0197 mmol) in CH$_2$Cl$_2$ (1 mL). The mixture was then cooled to 0 °C, and AcCl (0.0084 mL, 0.11 mmol) and pyridine (0.0128 mL, 0.16 mmol) were added sequentially. The ice bath was left in place but not recharged and stirring was continued for 3 h, during time the cold bath reached room temperature. The reaction mixture was quenched with saturated aqueous CuSO$_4$ (2 mL) and water (5 mL), and extracted with CH$_2$Cl$_2$ (2 x 10 mL). The combined organic extracts were washed with brine, dried (MgSO$_4$) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 50% Et$_2$O-hexane, gave 9f (12.7 mg, 89%) as a colorless foam:

FTIR $\nu_{\text{max}}$ (CDCl$_3$, cast)/cm$^{-1}$ 3068, 2956, 2926, 2871, 1759, 1685, 1613, 1592, 1501, 1448; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.92-7.89 (m, 3 H), 7.63-7.35 (m, 7 H), 7.01 (dd, $J = 9.6$, 2.7 Hz, 1 H), 6.91-6.84 (m, 2 H), 6.16-6.11 (m, 1 H), 5.70 (s, 1 H), 3.93 (d, $J = 6.1$ Hz, 2 H), 3.61 (td, $J = 10.7$, 4.3 Hz, 1 H), 2.34-2.01 (m, 9 H), 1.71-1.65 (m, 2 H), 1.43-1.39 (m, 1 H), 1.31-1.24 (m, 1 H), 1.05-0.73 (m, 12 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 169.6 (s), 169.2 (s), 162.2 (CF, $^1J_{\text{CF}} = 247.1$ Hz), 157.4 (s), 138.4 (s), 138.2 (s), 134.8 (d), 134.8 (d), 134.1 (d), 129.6 (d), 128.8 (d),
127.4 (s), 115.7 (CCF, $J_{CF} = 21.3$ Hz), 114.8 (CCF, $J_{CF} = 22.5$ Hz), 101.1 (d), 81.6 (d), 79.9 (d), 68.1 (d), 47.7 (d), 40.5 (t), 34.2 (t), 31.5 (q), 27.8 (t), 25.4 (d), 23.3 (t), 22.3 (d), 20.9 (q), 20.8 (q), 15.9 (q), 12.5 (q); exact mass (electrospray) $m/z$ calcd for C$_{38}$H$_{43}$FNaO$_9$S$_2$ (M + Na) 749.2225, found 749.2218.

(5R)-3-[1-Hydroxy-6,6-bis(phenylsulfanyl)hexyl]-5-[[1R,2S,5R]-5-methyl-2-(propan-2-yl)cyclohexyl]oxy]-3-(phenylselanyl)oxolan-2-one (10a, 10a')

A solution of LDA was prepared as follows: BuLi (2.5 M in hexanes, 0.625 mL, 1.57 mmol) was added to a stirred and cooled (-78 °C) solution of i-Pr$_2$NH (0.25 mL, 1.76 mmol) in THF (5 mL), and stirring was continued for 30 min at -78 °C. A portion (1.18 mL, 0.32 mmol) of this stock solution was then taken up into a syringe and added manually dropwise over ca 10 min, to a stirred and cooled (-78 °C) solution of lactone 2.1 (100 mg, 0.25 mmol) in THF (2 mL). Stirring at -78 °C was continued for 45 min and then HMPA (0.5 mL) was added dropwise. Stirring was continued for 5 min and then a solution of aldehyde 10$^d$ (127 mg, 0.55 mmol) in THF (2 mL) was added at a fast dropwise rate. Stirring at -78 °C was continued for 20-30 min (tlc control, silica, Et$_2$O-hexane, disappearance of aldehyde monitored). Then saturated aqueous NH$_4$Cl (3 mL) was added and the mixture were extracted with Et$_2$O. The combined organic extracts were washed with brine, dried (Na$_2$SO$_4$) and evaporated. Flash chromatography of the
residue over silica gel (2 x 15 cm), using 30% Et₂O-hexane, gave 10a (more polar isomer, 98 mg, 55%) and 10a' (less polar isomer, 40 mg, 22%) as oils.

The more polar alcohol 10a had: FTIR ν\text{max} (CDCl₃, cast)/cm⁻¹ 3452, 3073, 3058, 2949, 2925, 2866, 1764, 1582, 1478, 1455, 1438; ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.62 (m, 2 H), 7.47-7.43 (m, 5 H), 7.40-7.37 (m, 1 H), 7.33-7.26 (m, 7 H), 5.67 (d, J = 5.8 Hz, 1 H), 4.39 (t, J = 6.6 Hz, 1 H), 3.65 (dd, J = 10.1, 3.9 Hz, 1 H), 3.58 (td, J = 10.7, 4.1 Hz, 1 H), 2.88 (dd, J = 14.6, 6.4 Hz, 1 H), 2.54-2.47 (m, 1 H), 2.17-2.10 (m, 2 H), 1.95-1.92 (m, 2 H), 1.87-1.83 (m, 2 H), 1.70-1.56 (m, 5 H), 1.51-1.35 (m, 3 H), 1.30-0.80 (m, 13 H); ¹³C NMR (100 MHz, CDCl₃) δ 177.2 (s), 138.2 (d), 134.6 (s), 134.5 (s), 133.0 (d), 132.9 (d), 130.0 (d), 129.2 (d), 129.2 (d), 129.1 (d), 129.1 (d), 127.9 (s), 127.9 (d), 125.9 (d), 98.1 (d), 71.8 (d), 58.6 (d), 50.5 (s), 48.0 (d), 39.7 (t), 36.0 (t), 35.2 (t), 34.6 (t), 31.7 (d), 30.7 (t), 27.0 (t), 26.0 (t), 25.2 (d), 23.0 (t), 22.5 (d), 21.4 (t), 15.7 (q); exact mass (electrospray) m/z calcd for C₃₈H₄₈NaO₄S₂⁸₀Se (M + Na) 735.2051, found 735.2050.

The less polar alcohol 10a' had: FTIR ν\text{max} (CDCl₃, cast)/cm⁻¹ 3500, 3073, 3058, 2951, 2925, 2867, 1764, 1582, 1477, 1455, 1438; ¹H NMR (500 MHz, CDCl₃) δ 7.65 (dd, J = 8.1, 1.2 Hz, 2 H), 7.43-7.23 (m, 13 H), 5.66 (dd, J = 6.3, 1.2 Hz, 1 H), 4.34 (t, J = 6.7 Hz, 1 H), 3.59-3.54 (m, 2 H), 2.81 (s, 1 H), 2.70 (dd, J = 15.3, 6.5 Hz, 1 H), 2.46-2.39 (m, 1 H), 2.11-2.07 (m, 1 H), 1.98 (dd, J = 15.3, 1.5 Hz, 1 H), 1.82-1.78 (m, 2 H), 1.69-1.65 (m, 2 H), 1.60-1.46 (m, 4 H), 1.43-1.34 (m, 1 H), 1.30-1.21 (m, 3 H), 1.03-0.77 (m, 12 H); ¹³C NMR (100 MHz, CDCl₃) δ 175.1 (s), 138.1 (d), 134.2 (s), 132.7 (d), 129.9 (d), 129.1 (d), 128.8 (d), 127.6 (d), 125.8 (s), 97.7 (d), 77.3 (d), 71.9 (d), 58.2 (d), 53.4 (s), 47.8 (d), 39.5 (t), 36.6 (t), 35.6 (t), 34.3 (t), 31.4 (d), 31.1 (t), 26.9 (t), 26.0 (t), 25.0 (d), 22.8 (t), 22.3 (q), 21.1 (q), 15.6 (q); exact mass (electrospray) m/z calcd for C₃₈H₄₈NaO₄S₂⁸₀Se (M + Na) 735.2051, found 735.2047.
(5R)-3-[6,6-Bis(benzenesulfonyl)-1-hydroxyhexyl]-5-([(1R,2S,5R)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy)-2,5-dihydrofuran-2-one (10b, 10b'). Use of 10a'

MCPBA (70%, 276 mg, 1.12 mmol) was added to a stirred and cooled (0 °C) solution of 10a' (40 mg, 0.056 mmol) in CH₂Cl₂ (4 mL). The ice bath was left in place but not recharged and stirring was continued for 3 h. The reaction mixture was quenched with a mixture of saturated aqueous NaHCO₃ (2 mL) and saturated aqueous Na₂S₂O₃ (2 mL), and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic extracts were washed with water and brine, dried (Na₂SO₄) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 40% EtOAc-hexane, gave 10b' (29.7 mg, 86%) as a colorless oil: FTIR ν_max (CHCl₃, cast)/cm⁻¹ 3525, 3020, 2953, 2925, 2869, 2848, 2869, 2848, 2869, 1761, 1448; ¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, J = 7.7 Hz, 4 H), 7.70 (t, J = 7.5 Hz, 2 H), 7.58 (t, J = 7.9 Hz, 4 H), 6.91 (t, J = 1.3 Hz, 1 H), 6.01 (s, 1 H), 4.46 (dd, J = 8.4, 3.5 Hz, 1 H), 4.39 (t, J = 5.6 Hz, 1 H), 3.64 (td, J = 10.7, 4.2 Hz, 1 H), 2.41 (br s, 1 H), 2.19-2.07 (m, 4 H), 1.76-1.55 (m, 6 H), 1.49-1.32 (m, 3 H), 1.29-1.23 (m, 1 H), 1.07-0.80 (m, 12 H); ¹³C NMR (125 MHz, CDCl₃) δ 170.4 (s), 143.2 (d), 139.9 (s), 137.8 (s), 134.6 (d), 129.6 (d), 129.1 (d), 99.2 (d), 83.5 (d), 79.2 (d), 66.7 (d), 47.7 (d), 40.4 (t), 34.4 (t), 34.2 (t), 31.5 (d), 27.6 (t), 25.4 (t), 25.3 (d), 24.5 (t), 23.1 (t), 22.2 (q), 20.9 (q), 15.8 (q); exact mass (electrospray) m/z calcd for C₃₂H₄₂NaO₈S₂ (M + Na) 641.2213, found 641.2206.
Use of 10a. MCPBA (70%, 678 mg, 2.75 mmol) was added to a stirred and cooled (0 °C) solution of 10a (98 mg, 0.14 mmol) in CH₂Cl₂ (5 mL). The ice bath was left in place but not recharged and stirring was continued for 2 h. The reaction mixture was quenched with a mixture of saturated aqueous NaHCO₃ (2 mL) and saturated aqueous Na₂S₂O₃ (2 mL), and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic extracts were washed with water and brine, dried (Na₂SO₄) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 40% EtOAc-hexane, gave 10b (74 mg, 88%) as a colorless oil: FTIR νmax (CHCl₃, cast)/cm⁻¹ 3526, 3065, 2954, 2920, 2869, 2848, 1761, 1455, 1448, 1438; ¹H NMR (500 MHz, CDCl₃) δ 7.96-7.93 (m, 4 H), 7.71-7.68 (m, 2 H), 7.59-7.55 (m, 4 H), 6.88 (t, J = 1.4 Hz, 1 H), 5.99 (t, J = 1.2 Hz, 1 H), 4.44-4.43 (m, 1 H), 4.39 (t, J = 5.6 Hz, 1 H), 3.63 (td, J = 10.7, 4.3 Hz, 1 H), 2.58 (br s, 1 H), 2.18-2.07 (m, 4 H), 1.74-1.56 (m, 6 H), 1.49-1.34 (m, 3 H), 1.28-1.23 (m, 1 H), 1.06-0.82 (m, 12 H); ¹³C NMR (125 MHz, CDCl₃) δ 170.5 (s), 143.0 (d), 139.7 (s), 137.8 (s), 134.6 (d), 129.6 (d), 129.1 (s), 99.3 (d), 83.5 (d), 79.4 (d), 66.4 (d), 47.7 (d), 40.4 (t), 34.4 (t), 34.2 (t), 31.5 (d), 27.6 (t), 25.4 (t), 25.3 (d), 24.5 (t), 23.2 (t), 22.2 (q), 20.9 (q), 15.8 (q); exact mass (electrospray) m/z calcd for C₃₂H₄₂NaO₈S₂ (M + Na) 641.2213, found 641.2204.

6,6-Bis(benzenesulfonyl)-1-[[5R]-5-[[1R,2S,5R]-5-methyl-2-(propan-2-yl)cyclohexyl]oxy]-2-oxo-2,5-dihydrofuran-3-yl]hexyl acetate (10c, 10c'). Use of 10b'
DMAP (ca 1 mg, 0.01 mmol) was added to a stirred solution of 10b' (27 mg, 0.044 mmol) in CH₂Cl₂ (3 mL). The mixture was then cooled to 0 °C, and AcCl (0.016 mL, 0.22 mmol) and pyridine (0.28 mL, 0.35 mmol) were added sequentially. The ice bath was left in place but not recharged and stirring was continued for 3 h, during which time the cold bath reached room temperature. The reaction mixture was quenched with saturated aqueous CuSO₄ (2 mL) and water (5 mL), and extracted with CH₂Cl₂ (2 x 10 mL). The combined organic extracts were washed with brine, dried (MgSO₄) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 30% EtOAc-hexane, gave 10c' (25.8 mg, 90%) as a colorless foam:

FTIR ν max (CHCl₃, cast)/cm⁻¹ 3065, 2954, 2926, 2870, 1766, 1448; ¹H NMR (500 MHz, CDCl₃) δ 7.95-7.93 (m, 4 H), 7.72-7.69 (m, 2 H), 7.60-7.56 (m, 4 H), 6.91 (t, J = 1.3 Hz, 1 H), 6.01 (s, 1 H), 5.60-5.58 (m, 1 H), 4.35 (t, J = 5.6 Hz, 1 H), 3.62 (td, J = 10.7, 4.3 Hz, 1 H), 2.17-2.09 (m, 7 H), 1.85-1.64 (m, 4 H), 1.62-1.55 (m, 2 H), 1.44-1.37 (m, 1 H), 1.31-1.22 (m, 3 H), 1.06-0.79 (m, 12 H); ¹³C NMR (125 MHz, CDCl₃) δ 169.7 (s), 168.9 (s), 144.5 (d), 137.9 (s), 137.8 (s), 136.8 (s), 134.6 (d), 129.6 (d), 129.6 (d), 129.1 (d), 98.9 (d), 83.6 (d), 79.2 (d), 68.2 (d), 47.7 (d), 40.5 (t), 34.2 (t), 32.0 (t), 31.5 (q), 27.7 (t), 25.4 (t), 25.2 (d), 24.4 (t), 23.1 (t), 22.2 (q), 20.9 (q), 20.9 (q), 15.7 (q); exact mass (electrospray) m/z calcd for C₃₄H₄₄NaO₉S₂ (M + Na) 683.2319, found 683.2312.

Use of 10b. DMAP (ca 1 mg, 0.01 mmol) was added to a stirred solution of 10b (57 mg, 0.092 mmol) in CH₂Cl₂ (3 mL). The mixture was then cooled to 0 °C, and AcCl (0.033 mL, 0.46 mmol) and pyridine (0.060 mL, 0.74 mmol) were added sequentially. The ice bath was left in place but not recharged and stirring was continued for 3 h, during which time the cold bath reached room temperature. The reaction mixture was then quenched with saturated aqueous CuSO₄ (2 mL) and water (5 mL), and extracted with CH₂Cl₂ (2 x 10 mL). The combined organic
extracts were washed with brine, dried (MgSO₄) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 30% EtOAc-hexane, gave 10c (55 mg, 91%) as a colorless foam: FTIR ν<sub>max</sub> (neat)/cm<sup>-1</sup> 3096, 3067, 2954, 2926, 2870, 1767, 1448; <sup>1</sup>H NMR (500 MHz, CDCl₃) δ 7.96-7.94 (m, 4 H), 7.72-7.68 (m, 2 H), 7.59-7.56 (m, 4 H), 6.85 (t, J = 1.4 Hz, 1 H), 5.97 (t, J = 1.4 Hz, 1 H), 5.51 (tdd, J = 5.6, 2.6, 1.5 Hz, 1 H), 4.36 (t, J = 5.6 Hz, 1 H), 3.63 (td, J = 10.7, 4.3 Hz, 1 H), 2.16-2.07 (m, 7 H), 1.84-1.54 (m, 6 H), 1.44-1.22 (m, 4 H), 1.06-0.80 (m, 12 H); <sup>13</sup>C NMR (125 MHz, CDCl₃) δ 169.8 (s), 168.9 (s), 144.0 (d), 137.9 (s), 137.8 (s), 137.0 (s), 134.6 (d), 129.6 (d), 129.6 (d), 129.1 (d), 129.1 (d), 98.9 (d), 83.6 (d), 79.5 (d), 68.2 (d), 47.7 (d), 40.5 (t), 34.2 (t), 32.3 (t), 31.5 (q), 27.7 (t), 25.4 (t), 25.4 (d), 24.6 (t), 23.2 (t), 22.2 (d), 20.9 (q), 20.8 (q), 15.9 (q); exact mass (electrospray) m/z calcd for C₃₄H₄₄NaO₉S₂ (M + Na) 683.2319, found 683.2310.

**Methyl 2-[bis(phenylsulfanyl)methyl]benzoate (6.3)**

![Chemical Structure](image)

NaH (60%, 1.58 g, 39.32 mmol) was added slowly to a stirred and cooled (0 °C) solution of PhSH (3.9 mL, 38.04 mmol) in DMF (60 mL). Stirring was continued for 10 min, a solution of 6.2<sup>14</sup> (4.68 g, 15.21 mmol) in DMF (10 mL) was then added, and stirring was continued for 12 h. The mixture was quenched with hydrochloric acid (1 M, 5 mL) and extracted with Et₂O (2 x 100 mL). The combined organic extracts were washed with aqueous NaOH (10%, 20 mL) to remove
unreacted PhSH, and the organic phase was washed with water and brine, dried (Na$_2$SO$_4$) and evaporated. Flash chromatography of the residue over silica gel (4 x 15 cm), using 5% Et$_2$O-hexane, gave 6.3 (3.5 g, 65%) as an oil: FTIR $\nu_{\text{max}}$ (cast film)/cm$^{-1}$ 3057, 3019, 2948, 2926, 1715, 1598, 1581, 1480, 1438; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.87-7.83 (m, 2 H), 7.47 (dddd, $J$ = 7.9, 7.4, 1.5, 0.4 Hz, 1 H), 7.39-7.36 (m, 4 H), 7.30-7.21 (m, 7 H), 7.06 (s, 1 H), 3.82 (s, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 167.4 (s), 141.2 (s), 134.4 (d), 132.4 (d), 132.3 (d), 130.4 (d), 129.7 (d), 128.8 (d), 128.1 (s), 127.6 (d), 127.6 (d), 54.7 (q), 52.2 (d); exact mass (electrospray) $m/z$ calcd for C$_{21}$H$_{18}$NaO$_2$S$_2$ (M + Na) 389.0640, found 389.0642.

{2-[Bis(phenylsulfanyl)methyl]phenyl}methanol (6.4)

DIBAL-H (1 M solution in PhMe, 24.6 mL, 24.6 mmol) was added by syringe pump over 20 min to a stirred and cooled (-78 °C) solution of 6.3 (3.49 g, 9.85 mmol) in CH$_2$Cl$_2$ (100 mL). After the addition stirring at -78 °C was continued for 1 h and then the cold bath was replaced by an ice bath and stirring was continued for 1 h. The reaction was quenched with water (3.5 mL, 197 mmol) and NaF$^{24}$ (8.27 g, 197 mmol) at 0 °C, diluted with Et$_2$O (100 mL), stirred vigorously for 1 h at room temperature, and filtered through a pad of Celite using Et$_2$O. Evaporation of the filtrate and flash chromatography of the residue over silica gel (4 x 15 cm), using 40% Et$_2$O-hexane, gave 6.4 (3.13 g, 94%) as an oil: FTIR $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 3396, 3059, 3016, 3003, 2922,
2883, 1602, 1480, 1452, 1439; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.71-7.68 (m, 1 H), 7.40-7.22 (m, 13 H), 5.94 (s, 1 H), 4.66 (s, 2 H), 1.70 (br s, 1 H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 138.0 (s), 137.4 (s), 134.2 (s), 132.8 (d), 129.1 (d), 129.0 (d), 128.9 (d), 128.6 (d), 128.3 (d), 128.0 (d), 63.4 (t), 56.8 (d); exact mass (electrospray) \(m/z\) calcd for C\(_{20}\)H\(_{18}\)NaOS\(_2\) (M + Na) 361.0691, found 361.0697.

2-[Bis(phenylsulfanyl)methyl]benzaldehyde (11)

\[ \text{Et}_3\text{N (4.2 mL, 30 mmol) and DMSO (4.2 mL, 60 mmol) were added to a stirred and cooled (0 °C) solution of 6.4 (1.01 g, 3 mmol) in CH}_2\text{Cl}_2 (30 mL). Stirring was continued for 5 min and then SO}_3\text{-py (1.4 g, 9 mmol) was added and stirring was continued for 12 h, the ice bath being left in place but not recharged. The reaction mixture was quenched with water (5 mL) and extracted with CH}_2\text{Cl}_2 (2 x 20 mL). The combined organic extracts were washed with water and brine, dried (Na}_2\text{SO}_4) and evaporated. Flash chromatography of the residue over silica gel (3 x 15 cm), using 20% Et}_2\text{O-hexane, gave 11 (798 mg, 79%) as an oil: FTIR }\nu_{\text{max}} (\text{CHCl}_3, \text{ cast})/\text{cm}^{-1}\]

3057, 3017, 2834, 2745, 1696, 1597, 1581, 1573, 1480, 1449, 1438; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 10.12 (s, 1 H), 7.85 (d, \(J = 7.7 \text{ Hz}, 1 \text{ H}\)), 7.71 (dd, \(J = 7.6, 1.5 \text{ Hz}, 1 \text{ H}\)), 7.55-7.51 (m, 1 H), 7.43 (td, \(J = 7.5, 1.2 \text{ Hz}, 1 \text{ H}\)), 7.39-7.35 (m, 4 H), 7.24-7.21 (m, 6 H), 6.97 (s, 1 H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 192.7 (d), 141.5 (s), 134.1 (d), 134.0 (s), 133.9 (d), 132.6 (d), 132.3 (s),
129.9 (d), 128.9 (d), 128.3 (d), 127.9 (d), 54.1 (d); exact mass (electrospray) \( m/z \) calcd for \( \text{C}_{20}\text{H}_{16}\text{NaOS}_{2} \) (M + Na) 359.0535, found 359.0538.

\[(5R)-3-[(S)-(2-[\text{Bis(phenylsulfanyl)methyl}]\text{phenyl})(\text{hydroxy})\text{methyl}]-5-\{[(1R,2S,5R)-5-\text{methyl}-2-(\text{propan-2-yl})\text{cyclohexyl}]\text{oxy}\}-2,5\text{-dihydrofuran-2-one} \ (11a)\]

BuLi (2.5 M in hexane, 0.52 mL, 1.29 mmol) was added dropwise to a stirred and cooled (-20 
\(^\circ\)C) solution of PhSeSePh (367 mg, 1.17 mmol) in THF (5 mL). After 10 min, the mixture was cooled to -45 °C, a mixture of 1,1 (140 mg, 0.59 mmol) and 11 (198 mg, 0.59 mmol) in THF (4 mL) was added dropwise, and stirring was continued for 8 h at -45 °C. Then BnBr (0.18 mL, 1.47 mmol) and Bu₄NI (217 mg, 0.589 mmol) were added and stirring was continued for 8 h at -45 °C to -20 °C. The mixture was quenched with saturated aqueous NH₄Cl (5 mL) and extracted with Et₂O (2 x 20 mL). The combined organic extracts were washed with brine, dried (MgSO₄) and evaporated. Flash chromatography of the residue over silica gel (2 x 15 cm), using 40% Et₂O-hexanes, gave 11a [183 mg, 55 %, 83% after correction for recovered 1,1 (75 mg)]: FTIR \( \nu_{\text{max}} \) (CHCl₃, cast)/cm \(^{-1}\) 3423, 3060, 3020, 2955, 2925, 2869, 1766, 1582, 1480, 1439; \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.70 (d, \( J = 6.2 \) Hz, 1 H), 7.43-7.22 (m, 13 H), 6.71 (dd, \( J = 1.6, 1.3 \) Hz, 1 H), 5.90 (s, 1 H), 5.88 (t, \( J = 1.2 \) Hz, 1 H), 5.79 (s, 1 H), 3.60 (td, \( J = 10.7, 4.3 \) Hz, 1 H), 2.09-2.04 (m, 2 H), 1.69-1.61 (m, 2 H), 1.34-1.18 (m, 2 H), 1.02-0.75 (m, 13 H); \(^{13}\)C NMR (100
MHz, CDCl$_3$ δ 170.3 (s), 145.2 (d), 138.4 (s), 137.2 (s), 134.1 (s), 133.6 (s), 133.2 (d), 132.8 (d), 129.3 (d), 128.9 (d), 128.9 (d), 128.5 (d), 128.3 (d), 128.0 (d), 99.4 (d), 79.3 (d), 66.1 (d), 47.7 (d), 40.4 (t), 34.2 (t), 31.4 (d), 25.3 (d), 23.1 (t), 22.2 (d), 20.8 (q), 15.8 (q); exact mass (electrospray) m/z calc for C$_{34}$H$_{38}$NaO$_4$S$_2$ (M + Na) 597.2104, found 597.2102.

(S)-(2-[Bis(phenylsulfanyl)methyl]phenyl)[(5R)-5-[(1R,2S,5R)-5-methyl-2-(propan-2-y1)cyclohexyl]oxy]-2-oxo-2,5-dihydrofuran-3-yl]methyl acetate (11b)

DMAP (0.5 mg, 0.005 mmol) was added to a stirred solution of 11a (28 mg, 0.049 mmol) in CH$_2$Cl$_2$ (2 mL). The mixture was then cooled to 0 °C, and AcCl (0.0104 mL, 0.146 mmol) and pyridine (0.0196 mL, 0.24 mmol) were added sequentially. The ice bath was left in place but not recharged and stirring was continued for 3 h, during which time the cold bath reached room temperature. The reaction mixture was then quenched with saturated aqueous CuSO$_4$ (2 mL) and water (2 mL), and extracted with CH$_2$Cl$_2$ (2 x 10 mL). The combined organic extracts were washed with brine, dried (MgSO$_4$) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 40% Et$_2$O-hexane, gave 11b (23 mg, 76%): FTIR ν$_{max}$ (CHCl$_3$, cast)/cm$^{-1}$ 3060, 3022, 2955, 2924, 2869, 1774, 1745, 1582, 1481, 1454, 1439; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.75-7.73 (m, 1 H), 7.38-7.21 (m, 13 H), 6.94 (s, 1 H), 6.65 (t, J = 1.4 Hz, 1 H), 5.96 (s, 1 H), 5.87 (t, J = 1.1 Hz, 1 H), 3.59 (td, J = 10.7, 4.3 Hz, 1 H), 2.07-1.99 (m, 5 H), 1.67-
1.60 (m, 2 H), 1.39-1.33 (m, 1 H), 1.22-1.15 (m, 1 H), 1.01-0.69 (m, 12 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 169.4 (s), 168.4 (s), 146.7 (d), 137.1 (s), 136.3 (s), 134.1 (s), 133.8 (s), 133.4 (s), 132.7 (d), 132.4 (d), 129.6 (d), 129.2 (d), 128.9 (d), 128.9 (d), 128.4 (d), 128.1 (d), 128.0 (d), 127.7 (d), 98.7 (d), 79.0 (d), 66.3 (d), 55.9 (d), 47.7 (d), 40.4 (t), 34.2 (t), 31.4 (q), 25.2 (d), 23.1 (t), 22.2 (d), 20.8 (q), 15.7 (q); exact mass (electrospray) \(m/z\) calcld for C\(_{36}\)H\(_{40}\)NaO\(_5\)S\(_2\) (M + Na) 639.2209, found 639.2214.

\((S)-2-[Bis(benzenesulfonyl)methyl]phenyl][(5R)-5-[[1R,2S,5R]-5-methyl-2-(propan-2-yl)cyclohexyl]oxy]-2-oxo-2,5-dihydrofuran-3-yl]methyl acetate (11c)

\[11b, \text{X} = \text{SPh} \rightarrow 11c, \text{Z} = \text{SO}_2\text{Ph}\]

MCPBA (70%, 58 mg, 0.26 mmol) was added to a stirred and cooled (0 °C) solution of 11b (16 mg, 0.026 mmol) in CH\(_2\)Cl\(_2\) (3 mL). The ice bath was left in place but not recharged and stirring was continued for 6 h. The reaction mixture was quenched with a mixture of saturated aqueous NaHCO\(_3\) (2 mL) and saturated aqueous Na\(_2\)S\(_2\)O\(_3\) (2 mL), and extracted with CH\(_2\)Cl\(_2\) (2 x 10 mL). The combined organic extracts were washed with water and brine, dried (Na\(_2\)SO\(_4\)) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 40% EtOAc-hexane, gave 11c (14 mg, 82%) as a colorless oil: FTIR \(\nu_{\text{max}}\) (CHCl\(_3\), cast)/cm\(^{-1}\) 3067, 3024, 2955, 2926, 2870, 1768, 1584, 1478, 1446; \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.92-7.79 (m, 5 H), 7.65-7.60 (m, 2 H), 7.52-7.44 (m, 6 H), 7.34-7.30 (m, 1 H), 6.86 (t, \(J = 1.4\) Hz, 1 H), 6.68 (s, 1
H), 6.43 (s, 1 H), 6.01 (t, J = 1.2 Hz, 1 H), 3.62 (td, J = 10.7, 4.3 Hz, 1 H), 2.13-2.07 (m, 5 H), 1.67-1.61 (m, 2 H), 1.40-1.35 (m, 1 H), 1.26-1.19 (m, 1 H), 1.00-0.74 (m, 12 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 169.6 (s), 168.4 (s), 146.7 (d), 138.2 (s), 137.6 (s), 137.6 (s), 136.1 (s), 134.6 (d), 134.4 (d), 133.7 (d), 131.6 (d), 130.8 (d), 130.2 (d), 130.1 (d), 130.0 (d), 129.8 (d), 129.1 (d), 128.9 (d), 128.8 (d), 128.8 (d), 128.3 (d), 124.0 (s), 99.1 (d), 82.6 (d), 79.5 (d), 65.7 (d), 47.7 (d), 40.6 (t), 34.1 (t), 31.4 (q), 30.9 (d), 25.2 (d), 23.1 (t), 22.2 (q), 20.9 (q), 15.8 (q); exact mass (electrospray) \(m/z\) calcd for C\(_{36}\)H\(_{40}\)NaO\(_5\)S\(_2\) (M + Na) 703.2006, found 703.2001.

(S)-2-[(benzenesulfonyl)methyl]phenyl][(5R)-5-{{[(1R,2S,5R)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2-oxo-2,5-dihydrofuran-3-yl]methyl acetate (14) (a) 2-[(Phenylsulfanyl)methyl]benzaldehyde (12)

![Chemical structure](image)

Et\(_3\)N (2.16 mL, 15.5 mmol) and DMSO (2.2 mL, 31.04 mmol) were added to a stirred and cooled (0 °C) solution of 7.3\(^{16}\) (388 mg, 1.55 mmol) in CH\(_2\)Cl\(_2\) (11 mL). Stirring was continued for 5 min and then SO\(_3\)-py (988 mg, 6.21 mmol) was added. Stirring was continued for 12 h, the ice bath being left in place but not recharged. The reaction mixture was then quenched with water (5 mL) and extracted with CH\(_2\)Cl\(_2\) (2 x 20 mL), and the combined organic extracts were washed with water and brine, dried (Na\(_2\)SO\(_4\)) and evaporated. Flash chromatography of the residue over silica gel (2 x 15 cm), using 15% Et\(_2\)O-hexane, gave 12 (343 mg, 89%) as an oil: FTIR \(\nu_{\text{max}}\)
(CDCl$_3$, cast)/cm$^{-1}$ 3059, 3019, 2932, 2836, 2744, 1696, 1598, 1575, 1481, 1451, 1439, 1402; $^1$H NMR (400 MHz, CDCl$_3$) δ 10.23 (s, 1 H), 7.85-7.83 (m, 1 H), 7.49-7.41 (m, 2 H), 7.34-7.21 (m, 6 H), 4.53 (s, 2 H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 192.0 (d), 139.8 (s), 135.3 (s), 133.7 (s), 133.6 (d), 132.8 (d), 131.3 (d), 131.2 (d), 128.9 (d), 127.8 (d), 127.1 (d), 36.3 (t); exact mass (EI) $m/z$ calcd for C$_{14}$H$_{12}$OS (M) 228.0608, found 228.0610.

(b) (5R)-3-[(S)-Hydroxy({2-[(phenylsulfanyl)methyl]phenyl})methyl]-5-{{[1R,2S,5R]-5-methyl-2-(propan-2-yl)cyclohexyl}oxy}-2,5-dihydrofuran-2-one (12a)

BuLi (2.5 M in hexane, 80 µL, 0.20 mmol) was added dropwise to a stirred and cooled (-20 °C) solution of PhSeSePh (63 mg, 0.20 mmol) in THF (2 mL). After 10 min, the mixture was cooled to -45 °C, a mixture of 1.1 (78 mg, 0.33 mmol) and 12 (90 mg, 0.39 mmol) in THF (2 mL) was added dropwise, and stirring was continued for 8 h at -45 °C. Then BnBr (44 µL, 0.36 mmol) and Bu$_4$NI (12 mg, 0.036 mmol) were added and stirring was continued for 8 h at -45 °C to -20 °C. The mixture was quenched with saturated aqueous NH$_4$Cl (5 mL) and extracted with Et$_2$O (2 x 20 mL). The combined organic extracts were washed with brine, dried (MgSO$_4$) and evaporated. Flash chromatography of the residue over silica gel (2 x 15 cm), using 40% Et$_2$O-hexanes, gave 12a [78 mg, 56%, 87% after correction for recovered 1.1 (32 mg)]: FTIR $\nu_{\text{max}}$ (microscope)/cm$^{-1}$ 3452, 3060, 2954, 2924, 2869, 1768, 1584, 1481, 1454, 1439; $^1$H NMR (400
MHz, CDCl$_3$ δ 7.41 (dd, $J = 7.7$, 1.2 Hz, 1 H), 7.34-7.17 (m, 8 H), 6.88 (t, $J = 1.5$ Hz, 1 H), 6.02 (t, $J = 1.3$ Hz, 1 H), 5.93 (s, 1 H), 4.36 (d, $J = 12.6$ Hz, 1 H), 4.15 (d, $J = 12.7$ Hz, 1 H), 3.64 (td, $J = 10.7$, 4.3 Hz, 1 H), 3.16 (s, 1 H), 2.14-2.04 (m, 2 H), 1.70-1.63 (m, 2 H), 1.44-1.21 (m, 2 H), 1.07-0.76 (m, 12 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.2 (s), 144.5 (d), 139.2 (s), 138.3 (s), 135.2 (s), 134.7 (s), 130.9 (d), 130.8 (d), 129.0 (d), 128.5 (d), 128.2 (d), 127.6 (d), 127.1 (d), 99.3 (d), 79.2 (d), 65.8 (d), 47.7 (d), 40.4 (t), 37.1 (t), 34.2 (t), 31.5 (d), 25.5 (d), 23.3 (t), 22.2 (q), 20.8 (q), 15.9 (q); exact mass (electrospray) $m/z$ calc'd for C$_{28}$H$_{34}$NaO$_4$S (M + Na) 489.207, found 489.2070.

(c) (S)-(5R)-5-([(1R,2S,5R)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy)-2-oxo-2,5-dihydrofuran-3-yl][(2-[(phenylsulfanyl)methyl]phenyl)methyl acetate (12b)

![Chemical structure](attachment:structure.png)

DMAP (1.2 mg, 0.01 mmol) was added to a stirred solution of 12a (20 mg, 0.043 mmol) in CH$_2$Cl$_2$ (2 mL). The mixture was then cooled to 0 °C, and AcCl (9.1 μL, 0.13 mmol) and pyridine (21 μL, 0.25 mmol) were added sequentially. The ice bath was left in place but not recharged and stirring was continued for 3 h, during which time the cold bath reached room temperature. The reaction mixture was quenched with saturated aqueous CuSO$_4$ (2 mL) and water (5 mL), and extracted with CH$_2$Cl$_2$ (2 x 10 mL). The combined organic extracts were washed with brine, dried (MgSO$_4$) and evaporated. Flash chromatography of the residue over
silica gel (1 x 15 cm), using 40% Et₂O-hexane, gave 12b (21 mg, 96%) as a colorless oil: FTIR ν\(_{\text{max}}\) (CHCl₃, cast)/cm\(^{-1}\) 3060, 2955, 2925, 2869, 1771, 1748, 1659, 1600, 1584, 1481, 1455, 1439; \(^1\)H NMR (500 MHz, CDCl₃) δ 7.41 (dd, \(J = 7.6, 1.1\) Hz, 1 H), 7.36-7.18 (m, 8 H), 6.94 (t, \(J = 1.3\) Hz, 1 H), 6.83 (t, \(J = 1.4\) Hz, 1 H), 6.03 (t, \(J = 1.2\) Hz, 1 H), 4.36 (d, \(J = 13.0\) Hz, 1 H), 4.31 (d, \(J = 13.0\) Hz, 1 H), 3.64 (td, \(J = 10.7, 4.2\) Hz, 1 H), 2.12-2.03 (m, 5 H), 1.69-1.62 (m, 2 H), 1.43-1.36 (m, 1 H), 1.26-1.20 (m, 1 H), 1.02-0.73 (m, 12 H); \(^1^3\)C NMR (125 MHz, CDCl₃) δ 169.5 (s), 168.6 (s), 146.0 (d), 137.0 (s), 135.8 (s), 135.3 (s), 135.0 (s), 130.7 (d), 130.4 (d), 128.9 (d), 128.9 (d), 128.1 (d), 127.9 (d), 126.6 (d), 98.7 (d), 79.0 (d), 66.4 (d), 47.8 (d), 40.4 (t), 36.7 (t), 34.2 (t), 31.5 (q), 25.4 (d), 23.3 (t), 22.2 (d), 20.9 (q), 20.8 (q), 15.9 (q); exact mass (electrospray) \(m/z\) calcd for C\(_{30}\)H\(_{36}\)NaO\(_5\)S (M + Na) 531.2175, found 531.2172.

(d) \(\text{(S)-2-[(benzenesulfonyl)methyl]phenyl][(5R)-5-[[}(1R,2S,5R)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy]-2-oxo-2,5-dihydrofuran-3-yl]methyl acetate (14)\)

\[
\begin{align*}
\text{OAc} & \quad \rightarrow \\
\text{OAc} & \\
\end{align*}
\]

\[12b, \text{ } X = \text{SPh} \quad \rightarrow \quad 14, \text{ } Z = \text{SO}_2\text{Ph}\]

MCPBA (70%, 102 mg, 0.41 mmol) was added to a stirred and cooled (0 °C) solution of 12b (21 mg, 0.041 mmol) in CH\(_2\)Cl\(_2\) (3 mL). The ice bath was left in place but not recharged and stirring was continued for 4 h. The reaction mixture was quenched with a mixture of saturated aqueous NaHCO\(_3\) (2 mL) and saturated aqueous Na\(_2\)S\(_2\)O\(_3\) (2 mL), and extracted with CH\(_2\)Cl\(_2\) (2 x 10 mL). The combined organic extracts were washed with water and brine, dried (Na\(_2\)SO\(_4\)) and...
evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 60% Et₂O-hexane, gave 14 (22 mg, 100%) as a colorless oil: FTIR ν_{max} (CH₂Cl₂, cast)/cm⁻¹ 3065, 2955, 2926, 2870, 1768, 1585, 1496, 1448; ¹H NMR (400 MHz, CDCl₃) δ 7.88-7.85 (m, 2 H), 7.67-7.52 (m, 4 H), 7.41 (td, J = 7.6, 1.4 Hz, 1 H), 7.31 (td, J = 7.5, 1.4 Hz, 1 H), 7.21 (dd, J = 7.8, 1.3 Hz, 1 H), 6.93 (t, J = 1.4 Hz, 1 H), 6.78 (t, J = 1.4 Hz, 1 H), 6.04 (t, J = 1.3 Hz, 1 H), 4.69 (d, J = 14.1 Hz, 1 H), 4.62 (d, J = 14.1 Hz, 1 H), 3.61 (td, J = 10.7, 4.3 Hz, 1 H), 2.12-2.01 (m, 5 H), 1.68-1.60 (m, 2 H), 1.43-1.32 (m, 1 H), 1.26-1.19 (m, 1 H), 1.01-0.70 (m, 12 H); ¹³C NMR (100 MHz, CDCl₃) δ 169.8 (s), 168.8 (s), 145.1 (d), 139.1 (s), 137.0 (s), 136.8 (s), 133.8 (d), 133.0 (d), 129.5 (d), 129.2 (d), 129.1 (d), 129.0 (d), 128.4 (d), 126.4 (s), 99.2 (d), 79.2 (d), 66.7 (d), 59.4 (t), 47.7 (d), 40.6 (t), 34.2 (t), 31.4 (q), 25.3 (d), 23.2 (t), 22.2 (d), 20.9 (q), 20.8 (q), 15.8 (q); exact mass (electrospray) m/z calcld for C₃₀H₃₆NaO₇S (M + Na) 563.2074, found 563.2074.

(1S)-2-{2-[Bis(benzenesulfonyl)methyl]phenyl}-1-[(3R)-3-[(1R,2S,5R)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy]-5-oxocyclopent-1-en-1-yl]ethyl acetaldehyde (15) (a) 2-{2-[Bis(phenyl-sulfanyl)methyl]phenyl}acetaldehyde (13)
(798 mg, 2.38 mmol) was added dropwise over 5 min. The cold bath was left in place but not recharged and stirring was continued for 12 h, during which time the cold bath reached room temperature. The reaction mixture was quenched with saturated aqueous NH$_4$Cl (ca 10 mL) and extracted with Et$_2$O. The combined organic extracts were washed with brine (20 mL), dried (Na$_2$SO$_4$) and evaporated. Flash chromatography of the residue over silica gel (3 x 15 cm), using 5% Et$_2$O-hexane, gave 8.1, which was used for the next step.

Hydrochloric acid (4 M, 4 mL) was added to a solution of 8.1 in THF (15 mL) and the mixture was refluxed at 66 °C for 3 h, cooled, quenched with saturated aqueous NaHCO$_3$ (ca 5 mL), diluted with water (20 mL) and extracted with Et$_2$O (50 mL). The combined organic extracts were washed with brine, dried (MgSO$_4$) and evaporated. Flash chromatography of the residue over silica gel (3 x 15 cm), using 10% Et$_2$O-hexane, gave 13 (464 mg, 56% over two steps) as an oil: FTIR $\nu_{\text{max}}$ (CDCl$_3$, cast)/cm$^{-1}$ 3058, 3019, 2822, 2724, 1721, 1581, 1480, 1448, 1438, 1415; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.53 (t, $J = 2.3$ Hz, 1 H), 7.71 (d, $J = 6.9$ Hz, 1 H), 7.37-7.24 (m, 12 H), 7.15 (dd, $J = 7.2$, 1.8 Hz, 1 H), 5.54 (s, 1 H), 3.71 (d, $J = 1.9$ Hz, 2 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 199.0 (d), 138.5 (s), 133.9 (s), 133.0 (d), 131.2 (d), 129.7 (s), 129.5 (d), 129.0 (d), 128.5 (d), 128.2 (d), 128.2 (d), 57.9 (d), 47.9 (t); exact mass (electrospray) m/z calcd for C$_{21}$H$_{18}$NaOS$_2$ (M + Na) 373.0691, found 373.0695.

(b) (4$R$)-2-(2-[Bis(benzenesulfonyl)methyl]phenyl)-1-hydroxyethyl)-4-[[1(1$R$,2$S$,5$R$)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy]-2-(phenylselanyl)cyclopentan-1-one (13a, 13a')
(Me₃Si)₂NK (0.5 M in PhMe, 0.92 mL, 0.46 mmol) was added dropwise (over ca 10 min) to a stirred and cooled (-78 °C) solution of lactone 2.1 (166 mg, 0.42 mmol) in THF (5 mL). Stirring at -78 °C was continued for 45 min and then a solution of aldehyde 13 (165 mg, 0.47 mmol) in THF (2 mL) was added. Stirring at -78 °C was continued for 20-30 min (tlc control, silica, 40% Et₂O-hexane, disappearance of aldehyde monitored). Then saturated aqueous NH₄Cl (3 mL) was added and the mixture was extracted with Et₂O. The combined organic extracts were dried (Na₂SO₄) and evaporated. Flash chromatography of the residue over silica gel (2 x 15 cm), using 40% Et₂O-hexane gave 13a and 13a' as an oil. This mixture of diastereoisomers was used directly for next step.

(c) \((4R)-2\{2\{-[\text{Bis(benzenesulfonyl)methyl}][\text{phenyl}]\}-1\text{-hydroxyethyl}\}-4\{-[(1R,2S,5R)-\text{5-methyl-2-(propan-2-yl)cyclohexyl}][\text{oxy}]\}\text{cyclopent-2-en-1-one} (13b, 13b')\)

MCPBA (70%, 1.27 g, 5.1 mmol) was added to a stirred and cooled (0 °C) solution of 13a and 13a' (192 mg, 0.26 mmol) in CH₂Cl₂ (5 mL). The ice bath was left in place but not recharged
and stirring was continued for 12 h. The reaction mixture was quenched with a mixture of saturated aqueous NaHCO₃ (2 mL) and saturated aqueous Na₂S₂O₃ (2 mL) and extracted with CH₂Cl₂. The combined organic extracts were washed with water and brine, dried (Na₂SO₄) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 60% Et₂O-hexane, gave a mixture of diastereomers which was separated into three fractions (more polar, 13 mg, 5%; less polar, 10 mg, 4%; mixture, 73 mg, 27%). The more polar alcohol 13b had: FTIR ν max (CDCl₃, cast)/cm⁻¹ 3508, 3067, 2954, 2928, 2871, 1754, 1584, 1493, 1448; ¹H NMR (500 MHz, CDCl₃) δ 7.99 (dd, J = 7.9, 1.3 Hz, 1 H), 7.84-7.78 (m, 4 H), 7.66-7.62 (m, 2 H), 7.47 (t, J = 7.5 Hz, 4 H), 7.38 (td, J = 7.5, 1.4 Hz, 1 H), 7.31 (td, J = 7.6, 1.3 Hz, 1 H), 7.15 (dd, J = 7.6, 1.3 Hz, 1 H), 6.95 (t, J = 1.4 Hz, 1 H), 6.31 (s, 1 H), 6.02 (t, J = 1.4 Hz, 1 H), 4.60-4.58 (m, 1 H), 3.65 (td, J = 10.7, 4.3 Hz, 1 H), 2.77 (dd, J = 14.5, 2.6 Hz, 1 H), 2.42 (dd, J = 14.5, 9.0 Hz, 1 H), 2.16-2.10 (m, 2 H), 1.71-1.66 (m, 2 H), 1.41-1.37 (m, 1 H), 1.30-1.21 (m, 2 H), 1.05-0.82 (m, 12 H); ¹³C NMR (125 MHz, CDCl₃) δ 170.1 (s), 143.8 (s), 139.1 (s), 139.0 (s), 138.5 (s), 138.0 (s), 134.7 (s), 134.5 (s), 131.8 (s), 131.5 (s), 130.9 (s), 130.0 (s), 129.6 (s), 128.9 (s), 128.9 (s), 127.6 (s), 124.6 (s), 99.4 (s), 82.7 (s), 79.3 (s), 68.6 (s), 47.8 (s), 40.4 (s), 39.0 (s), 34.2 (s), 31.6 (s), 25.4 (s), 23.2 (s), 22.3 (s), 21.0 (s), 15.9 (q); exact mass (electrospray) m/z calcd for C₃₅H₆₄NaO₈S₂ (M + Na) 675.2057, found 675.2046.

The less polar alcohol 13b' had: FTIR ν max (CDCl₃, cast)/cm⁻¹ 3503, 3067, 2955, 2928, 2870, 1753, 1599, 1584, 1493, 1448; ¹H NMR (500 MHz, CDCl₃) δ 7.99-7.94 (m, 1 H), 7.85-7.77 (m, 4 H), 7.66-7.57 (m, 3 H), 7.49-7.28 (m, 5 H), 7.14 (dd, J = 7.6, 1.3 Hz, 1 H), 6.96 (t, J = 1.4 Hz, 1 H), 6.39 (s, 1 H), 6.00 (s, 1 H), 4.61-4.59 (m, 1 H), 3.66 (td, J = 10.7, 4.3 Hz, 1 H), 2.84 (dd, J = 14.5, 2.7 Hz, 1 H), 2.43 (dd, J = 14.5, 9.1 Hz, 1 H), 2.16-2.11 (m, 2 H), 1.71-1.66 (m, 2 H), 1.42-1.38 (m, 1 H), 1.29-1.19 (m, 2 H), 1.08-0.81 (m, 12 H); ¹³C NMR (125 MHz,
CDCl$_3$ δ 13C NMR (CDCl$_3$, 126 MHz) δ 170.1 (s), 144.1 (d), 139.1 (s), 139.0 (s), 138.5 (s), 137.9 (s), 135.4 (d), 134.6 (d), 134.5 (d), 133.7 (d), 131.7 (d), 131.5 (d), 130.8 (d), 130.0 (d), 129.6 (d), 128.9 (d), 128.9 (d), 128.8 (d), 128.3 (d), 127.5 (d), 124.6 (s), 99.3 (d), 82.7 (d), 79.2 (d), 68.6 (d), 47.8 (d), 40.3 (d), 38.5 (d), 34.2 (d), 31.5 (d), 25.4 (d), 23.2 (t), 22.2 (q), 20.9 (q), 15.9 (q); exact mass (electrospray) m/z calcd for C$_{35}$H$_{40}$NaO$_8$S$_2$ (M + Na) 675.2057, found 675.2058.

(d) (1S)-2-{2-[Bis(benzenesulfonyl)methyl]phenyl}-1-[(3R)-3-{{(1R,2S,5R)-5-methyl-2-(propan-2-yl)cyclohexyl}oxy}-5-oxocyclopent-1-en-1-yl]ethyl acetate (15)

![Chemical structure](image)

DMAP (ca 1 mg, 0.01 mmol) was added to a stirred solution of 13b and 13b' (73 mg, 0.11 mmol) in CH$_2$Cl$_2$ (3 mL). The mixture was then cooled to 0 °C, and AcCl (0.048 mL, 0.67 mmol) and pyridine (0.072 mL, 0.89 mmol) were added sequentially. The ice bath was left in place but not recharged and stirring was continued for 3 h, during which time the cold bath reached room temperature. The reaction mixture was quenched with saturated aqueous CuSO$_4$ (2 mL) and water (5 mL), and extracted with CH$_2$Cl$_2$ (2 x 10 mL). The combined organic extracts were washed with brine, dried (MgSO$_4$) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 50% EtOAc-hexane, gave 15 as a mixture of diastereomers which was separated into two fractions (less polar, 22 mg, 28%; mixture, 42 mg,
55%). The less polar isomer had: FTIR νmax (CDCl3, cast)/cm⁻¹ 3066, 2954, 2928, 2870, 1758, 1748, 1584, 1491, 1448; ¹H NMR (500 MHz, CDCl₃) δ 8.16 (dd, J = 7.8, 1.3 Hz, 1 H), 7.94 (dd, J = 8.3, 1.0 Hz, 2 H), 7.71-7.64 (m, 3 H), 7.59-7.49 (m, 3 H), 7.40-7.28 (m, 4 H), 6.98 (dd, J = 7.5, 1.3 Hz, 1 H), 6.81 (t, J = 0.9 Hz, 1 H), 6.35 (s, 1 H), 5.86 (s, 1 H), 5.62 (t, J = 7.3 Hz, 1 H), 3.61 (td, J = 10.7, 4.3 Hz, 1 H), 2.87 (dd, J = 14.3, 7.3 Hz, 1 H), 2.50 (dd, J = 14.3, 7.4 Hz, 1 H), 2.12-2.04 (m, 5 H), 1.68-1.64 (m, 2 H), 1.41-1.34 (m, 1 H), 1.25-1.19 (m, 1 H), 1.00-0.75 (m, 12 H); ¹³C NMR (125 MHz, CDCl₃) δ 170.2 (s), 169.2 (s), 147.0 (d), 138.7 (s), 138.1 (s), 137.7 (s), 134.5 (d), 134.4 (d), 134.1 (s), 132.0 (d), 131.2 (d), 130.5 (d), 129.9 (d), 129.6 (d), 128.9 (d), 128.8 (d), 127.7 (d), 124.4 (s), 99.1 (d), 82.0 (d), 79.8 (d), 69.3 (d), 47.7 (d), 40.4 (t), 35.0 (t), 34.1 (t), 31.5 (q), 25.4 (d), 23.1 (t), 22.2 (d), 20.9 (q), 20.9 (q), 15.9 (q); exact mass (electrospray) m/z calcd for C₃₇H₄₂NaO₉S₂ (M + Na) 717.2162, found 717.2162.

The mixture of isomers (containing mainly the more polar) had: FTIR νmax (CDCl₃, cast)/cm⁻¹ 3067, 2955, 2928, 2870, 1807, 1758, 1748, 1584, 1492, 1448; ¹H NMR (500 MHz, CDCl₃) δ 8.15-7.97 (m, 3 H), 7.75-7.64 (m, 3 H), 7.62-7.31 (m, 7 H), 7.03-6.99 (m, 1 H), 6.85-6.83 (m, 1 H), 6.42-6.39 (m, 1 H), 5.99-5.90 (m, 1 H), 5.73-5.65 (m, 1 H), 3.67-3.57 (m, 1 H), 2.91 (dd, J = 14.2, 7.6 Hz, 1 H), 2.64-2.51 (m, 1 H), 2.15-2.04 (m, 5 H), 1.72-1.66 (m, 2 H), 1.45-1.37 (m, 1 H), 1.29-1.20 (m, 1 H), 1.06-0.78 (m, 12 H); ¹³C NMR (125 MHz, CDCl₃) δ 170.2 (s), 169.3 (s), 147.5 (d), 139.0 (s), 138.8 (s), 138.1 (s), 137.8 (s), 137.7 (s), 137.5 (s), 135.4 (d), 134.6 (d), 134.5 (d), 134.5 (d), 134.4 (d), 134.2 (d), 133.9 (s), 132.0 (d), 131.9 (d), 131.3 (d), 131.3 (d), 130.8 (d), 130.5 (d), 130.5 (d), 130.0 (d), 129.9 (d), 129.9 (d), 129.7 (d), 129.7 (d), 129.6 (d), 128.9 (d), 128.9 (d), 128.9 (d), 128.8 (d), 128.8 (d), 128.7 (d), 128.7 (d), 128.7 (d), 127.7 (d), 127.7 (d), 124.4 (s), 124.4 (s), 99.1 (d), 98.7 (d), 82.1 (d), 82.0 (d), 79.8 (d), 78.5 (d), 69.4 (d), 69.4 (d), 47.7 (d), 47.7 (d), 40.5 (t), 40.1 (t), 35.0 (t), 34.9 (t), 34.2 (t), 34.2 (t),
31.5 (q), 31.5 (q), 25.4 (d), 25.3 (d), 23.1 (t), 22.2 (t), 22.2 (d), 21.0 (q), 21.0 (q), 20.9 (q), 20.9 (q), 15.9 (q); exact mass (electrospray) m/z calcd for C_{37}H_{42}NaO_{9}S_{2} (M + Na) 717.2162, found 717.2163.

**Notes and references**


**X-ray Structure Determination** For X-ray analysis, crystals were grown via slow vapor diffusion of a poor solvent into a solution of the compound in a good solvent, as indicated for the individual compounds below. Data were collected using a three-circle (fixed-chi) diffractometer equipped with an CCD-based area detector. All data were collected using Mo Ka radiation (\(l = 0.71073 \ \text{Å}\)) and with the crystal cooled to −100 °C. The data were corrected for absorption through Gaussian integration from indexing of the crystal faces. Structures were solved using direct methods with dual-space recycling (*SHELXd*), and least-squares refinements were completed using the program *SHELXL-97*. Hydrogen atoms attached to carbons were assigned positions based on the \(sp^2\) or \(sp^3\) hybridization geometries of their attached carbons, and were given thermal parameters 20% greater than those of their parent atoms.
Figure 1. ORTEP diagram of 9c. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Crystallization by vapor diffusion of hexanes into a solution of 9c in Et₂O.

Figure 2. ORTEP diagram of 9.2. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Crystallization by vapor diffusion of hexanes into a solution of 9.1 in Et₂O.
**Figure 3.** ORTEP diagram of 9.4. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Crystallization by vapor diffusion of hexanes into a solution of 9.3 in i-Pr₂O.

**Figure 4.** ORTEP diagram of 9g. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Crystallization by vapor diffusion of hexanes into a solution of 9g in Et₂O.
**Figure 5.** ORTEP diagram of 5l. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Crystallization by vapor diffusion of hexanes into a solution of 5l in CH$_2$Cl$_2$. 
2 less polar
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