

## Total synthesis of a cuticular hydrocarbon from the cane beetle *Antitrogus parvulus*: confirmation of the relative stereochemistry

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### Supplementary data

#### General

Flash column chromatography was performed using Merck silica gel (60H; 40-60m, 230-240 mesh). Petrol refers to light petroleum which was redistilled before use and refers to the fraction boiling between 40 and 60 °C. Tetrahydrofuran was dried over sodium-benzophenone and was distilled prior to use. Dichloromethane was dried over CaH<sub>2</sub> and was distilled before use. Ether refers to diethyl ether. Reactions under non-aqueous conditions were carried out under an atmosphere of nitrogen or argon.

Low resolution mass spectra were recorded using a Micromass Trio 200 spectrometer and high resolution mass spectra on a Kratos Concept IS spectrometer. For high molecular weight compounds, peaks corresponding to the all <sup>12</sup>C compound are given. Infra-red spectra were measured using a Genesis FTIR spectrometer on NaBr plates, either neat or as evaporated films unless otherwise stated. Nuclear magnetic resonance spectra were recorded in deuteriated chloroform unless otherwise indicated on either a Bruker Avance 300 (300 MHz), Bruker Ultrashield 400 (400 MHz) or Bruker Ultrashield 500 (500 MHz) spectrometer. Coupling constants (*J*) are given in Hertz (Hz) and chemical shifts relative to tetramethylsilane.

#### (2*R*,6*S*,8*S*,3*E*)-1-Benzoyloxy-2,4,8-trimethylundec-3-en-6-ol **8**

To a solution of (*S*)-3-methylhexanol (63 mg, 0.54 mmol) in DCM (5 ml) was added NaHCO<sub>3</sub> (212 mg, 2.5 mmol) and Dess-Martin periodinane (261 mg, 0.62 mmol) and the reaction was stirred at RT for 30 min. Saturated aqueous NaHCO<sub>3</sub> (4 ml) and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (4 ml) were added and the mixture was extracted with DCM (2 x 10 ml). The combined organic layer was subsequently washed with brine (15 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to yield the aldehyde **7**. Zinc powder (80 mg, 1.22 mmol) was suspended in a solution of bismuth(III) iodide (637 mg, 1.08 mmol) in THF (4 ml) and the mixture was stirred vigorously at RT for 1 h, during which time the orange/grey suspension turned black. The bromide **3** (102 mg, 0.36 mmol) and a solution of aldehyde **7** in THF (2 ml) were added to the bismuth suspension and the reaction mixture was stirred under reflux for 2 h before cooling down to RT. The reaction mixture was concentrated to give a black slurry. Column chromatography eluting with petrol-ether (7:3) gave the *title compound* **8** (67 mg, 60%) as a colorless oil, *R*<sub>f</sub> 0.5 (7:3 petrol-ether); [ $\alpha$ ]<sub>D</sub><sup>20</sup> -6.7 (*c* 0.2 in CHCl<sub>3</sub>) (Found: *M*<sup>+</sup> + Na, 341.2453. C<sub>21</sub>H<sub>34</sub>O<sub>2</sub>Na requires *M*, 341.2452);  $\nu_{\max}$  3436, 2956, 2926, 2870, 1454, 1378, 1273, 1205, 1089, 1028, 901, 832 and 735 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 0.82 (6 H, m, 8-CH<sub>3</sub> and 11-H<sub>3</sub>), 0.88 (3 H, d, *J* 7, 2-CH<sub>3</sub>), 1.09 (1 H, m, 7-H<sub>a</sub>), 1.19-1.29 (5 H, m, 8-H, 9-H<sub>2</sub> and 10-H<sub>2</sub>), 1.41 (1 H, m, 7-H<sub>b</sub>), 1.60 (3 H, s, 4-CH<sub>3</sub>), 1.75 (1 H, br s, OH), 1.86 (1 H, dd, *J* 13 and 10, 5-H<sub>a</sub>), 2.11 (1 H, dd, *J* 13 and 7, 5-H<sub>b</sub>), 2.69 (1 H, m, 2-H), 3.15 (1 H, dd, *J* 9 and 8, 1-H<sub>a</sub>), 3.23 (1 H, dd, *J* 9 and 7, 1-H<sub>b</sub>), 3.63 (1 H, m, 6-H), 4.40 (1 H, d, *J* 12, OCH<sub>a</sub>Ph), 4.43 (1 H, d, *J* 12, OCH<sub>b</sub>Ph), 4.97 (1 H, d, *J* 9, 3-H) and 7.25 (5 H, m, Ar-H);  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 14.5, 16.5, 17.4, 20.0, 20.3, 29.5, 33.2, 39.1, 44.6, 48.5, 66.0, 73.0, 75.3, 127.5, 127.6, 128.4, 132.1, 132.6 and 138.5; *m/z* (ES<sup>+</sup>) 341 (*M*<sup>+</sup> + 23, 100%).

#### (2*R*,6*S*,8*S*,3*E*)-2,4,8-Trimethylundec-3-ene-1,6-diol **9**

To a solution of naphthalene (290 mg, 2.3 mmol) in THF (3 ml) was added lithium metal (12 mg, 1.7 mmol) in small pieces. The reaction mixture was stirred at RT until the lithium was completely dissolved and the reaction turned into a dark green solution. The resulting mixture dark green solution of lithium naphthalenide was then cooled to -25 °C, followed by the dropwise addition of the benzyl ether **8** (90 mg, 0.28 mmol) in THF (2 ml). The resulting mixture was stirred at -25 °C for 2 h. Saturated aqueous NH<sub>4</sub>Cl (5 ml) and water (5 ml) were added and the solution was extracted with ether. The organic extracts were washed with brine (10 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Chromatography eluting with petrol-ether (20:80) gave the *title compound* **9** (50 mg, 78%) as a colourless gum, *R*<sub>f</sub> 0.3 (3:7 petrol-ether); [ $\alpha$ ]<sub>D</sub><sup>20</sup> +26.7 (*c* 0.4 in CHCl<sub>3</sub>) (Found: *M*<sup>+</sup> + Na, 251.1983. C<sub>14</sub>H<sub>28</sub>O<sub>2</sub>Na requires *M*,

251.1982);  $\nu_{\max}$  3308, 2954, 2925, 2870, 1455, 1378, 1072, 1031, 893, 831, 739 and 610  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 0.81-0.88 (9 H, m, 2- $\text{CH}_3$ , 8- $\text{CH}_3$  and 11- $\text{H}_3$ ), 1.01 (1 H, m, 7- $\text{H}_a$ ), 1.21 (1 H, m, 7- $\text{H}_b$ ), 1.28-1.31 (4 H, m, 9- $\text{H}_2$  and 10- $\text{H}_2$ ), 1.55 (1 H, m, 8-H), 1.57 (3 H, s, 4- $\text{CH}_3$ ), 1.88 (2 H, br s, 2 x OH), 1.90 (1 H, dd,  $J$  13 and 10, 5- $\text{H}_a$ ), 2.09 (1 H, dd,  $J$  13 and 3, 5- $\text{H}_b$ ), 2.60 (1 H, m, 2-H), 3.23 (1 H, dd,  $J$  10 and 9, 1- $\text{H}_a$ ), 3.47 (1 H, dd,  $J$  10 and 6, 1- $\text{H}_b$ ), 3.71 (1 H, m, 6-H) and 4.91 (1 H, d,  $J$  9, 3-H);  $\delta_{\text{C}}$  (125 MHz,  $\text{CDCl}_3$ ) 14.4, 16.6, 16.7, 20.0, 20.3, 29.5, 35.4, 39.1, 45.0, 48.5, 66.4, 67.8, 131.2 and 134.2;  $m/z$  ( $\text{ES}^+$ ) 251 ( $\text{M}^+ + 23$ , 100%).

#### **(2R,6S,8S,3E)-2,4,8-Trimethyl-1-(tri-isopropylsilyloxy)undec-3-en-6-ol 10**

Imidazole (75 mg, 1.1 mmol) was added to a solution of the diol **9** (50 mg, 0.22 mmol) in THF (4 ml). After 10 min, tri-isopropylsilyl chloride (51 mg, 0.24 mmol) was added at 0 °C and the reaction mixture stirred at RT for 16 h then concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (4:1) gave the *title compound 10* (80 mg, 94%) as a colourless oil,  $R_f$  0.7 (4:1 petrol-ether);  $[\alpha]_{\text{D}}^{20} +9.6$  ( $c$  0.2 in  $\text{CHCl}_3$ ) (Found:  $\text{M}^+ + \text{H}$ , 385.3503.  $\text{C}_{23}\text{H}_{49}\text{O}_2\text{Si}$  requires  $M$ , 385.3496);  $\nu_{\max}$  2926, 2865, 1461, 1381, 1248, 1089, 1065, 1013, 995, 918, 881, 785, 680 and 658  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 0.83 (6 H, m, 8- $\text{CH}_3$  and 11- $\text{H}_3$ ), 0.87 (3 H, d,  $J$  7, 2- $\text{CH}_3$ ), 0.98 [21 H, m, 3 x  $\text{CH}(\text{CH}_3)_2$ ], 1.14 (1 H, m, 7- $\text{H}_a$ ), 1.22 (1 H, m, 7- $\text{H}_b$ ), 1.25-1.34 (4 H, m, 9- $\text{H}_2$  and 10- $\text{H}_2$ ), 1.47 (1 H, s, OH), 1.54 (1 H, m, 8-H), 1.61 (3 H, s, 4- $\text{CH}_3$ ), 1.86 (1 H, dd,  $J$  13 and 10, 5- $\text{H}_a$ ), 2.10 (1 H, dd,  $J$  13 and 3, 5- $\text{H}_b$ ), 2.54 (1 H, m, 2-H), 3.37 (1 H, dd,  $J$  7 and 9, 1- $\text{H}_a$ ), 3.42 (1 H, dd,  $J$  9 and 7, 1- $\text{H}_b$ ), 3.63 (1 H, m, 6-H) and 4.96 (1 H, d,  $J$  9, 3-H);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 12.0, 14.4, 16.6, 17.1, 18.0, 20.0, 20.2, 29.5, 35.8, 39.1, 44.4, 48.5, 66.0, 68.4, 132.1 and 132.4;  $m/z$  ( $\text{ES}^+$ ) 407 ( $\text{M}^+ + 23$ , 100%).

#### **(2R,4R,6S,8S)- And (2R,4S,6S,8S)- 2,4,8-trimethyl-1-(tri-isopropylsilyloxy)undecan-6-ol 11 and 12**

To a boiling tube with a stirrer bar was placed alkene **10** (80 mg, 0.21 mmol) followed by the  $[\text{Rh}(\text{NBD})\text{diphos-4}]\text{BF}_4$  catalyst (7.5 mg, 0.01 mmol) and DCM (3 ml). The tube was placed inside a steel screw cap high pressure bomb. The pressure gauge block was attached and the bomb was flushed three times with hydrogen and then filled to 950 psi of hydrogen. The reaction mixture was stirred at RT under 950 psi pressures for 5 h then concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (4:1) gave the *title compound 12* (17 mg, 22%) as a colourless oil,  $R_f$  0.5 (4:1 petrol-ether);  $[\alpha]_{\text{D}}^{20} -4.2$  ( $c$  0.2 in  $\text{CHCl}_3$ );  $\nu_{\max}$  3351, 2955, 2926, 2867, 1462, 1380, 1248, 1100, 1067, 1013, 996, 882, 787, 680 and 658  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 0.81-0.84 (12 H, m, 2- $\text{CH}_3$ , 4- $\text{CH}_3$ , 8- $\text{CH}_3$  and 11- $\text{H}_3$ ), 0.99 [21 H, m, 3 x  $\text{CH}(\text{CH}_3)_2$ ], 1.09 (2 H, m, 3- $\text{H}_2$ ), 1.15-1.33 (8 H, m, 5- $\text{H}_2$ , 7- $\text{H}_2$ , 9- $\text{H}_2$  and 10- $\text{H}_2$ ), 1.52 (1 H, m, 8-H), 1.62-1.72 (2 H, m, 2-H and 4-H), 3.36 (1 H, dd,  $J$  6.3 and 9.5, 1- $\text{H}_a$ ), 3.47 (1 H, dd,  $J$  5.7 and 9.5, 1- $\text{H}_b$ ) and 3.73 (1 H, m, 6-H);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 12.0, 14.4, 17.5, 18.1, 20.0, 20.2, 20.3, 26.6, 29.4, 33.3, 39.1, 42.0, 45.0, 46.2, 67.6 and 68.7;  $m/z$  ( $\text{ES}^+$ ) 409 ( $\text{M}^+ + 23$ , 100%). The second fraction was the *title compound 11* (53 mg, 68%) as a colourless oil,  $R_f$  0.45 (4:1 petrol-ether);  $[\alpha]_{\text{D}}^{20} +7.8$  ( $c$  0.2 in  $\text{CHCl}_3$ ) (Found:  $\text{M}^+ + \text{Na}$ , 409.3486.  $\text{C}_{23}\text{H}_{50}\text{O}_2\text{SiNa}$  requires  $M$ , 409.3473);  $\nu_{\max}$  3325, 2922, 2864, 1461, 1379, 1245, 1100, 1067, 1012, 995, 918, 881, 784, 679 and 658  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 0.81-0.84 (12 H, m, 2- $\text{CH}_3$ , 4- $\text{CH}_3$ , 8- $\text{CH}_3$  and 11- $\text{H}_3$ ), 0.99 [21 H, m, 3 x  $\text{CH}(\text{CH}_3)_2$ ], 1.09 (2 H, m, 3- $\text{H}_2$ ), 1.15-1.33 (8 H, m, 5- $\text{H}_2$ , 7- $\text{H}_2$ , 9- $\text{H}_2$  and 10- $\text{H}_2$ ), 1.40 (1 H, br s, OH), 1.53 (1 H, m, 8-H), 1.61-1.70 (2 H, m, 2-H and 4-H), 3.38 (1 H, dd,  $J$  10 and 6, 1- $\text{H}_a$ ), 3.43 (1 H, dd,  $J$  10 and 6, 1- $\text{H}_b$ ) and 3.73 (1 H, m, 6-H);  $\delta_{\text{C}}$  (125 MHz,  $\text{CDCl}_3$ ) 12.0, 14.4, 16.4, 18.1, 19.2, 20.0, 20.4, 26.8, 29.3, 33.5, 38.9, 40.4, 45.8, 46.6, 67.9 and 69.4;  $m/z$  ( $\text{ES}^+$ ) 409 ( $\text{M}^+ + 23$ , 100%).

#### **(2R,4R,6S,8S)-2,4,8-Trimethyl-1-(tri-isopropylsilyloxy)undecan-6-yl 4-methylbenzenesulfonate 13**

Toluene 4-sulfonyl chloride (205 mg, 1.1 mmol) and 4-(dimethylamino)pyridine (202 mg, 1.65 mmol) were added to a stirred solution of the alcohol **11** (143 mg, 0.37 mmol) in DCM (4 ml) at RT. The reaction mixture was stirred at RT for 16 h then concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (4:1) gave the *title compound 13* (185 mg, 93%) as a colourless oil,  $R_f$  0.8 (4:1 petrol-ether);  $[\alpha]_{\text{D}}^{20} +3.2$  ( $c$  0.2 in  $\text{CHCl}_3$ ) (Found:  $\text{M}^+ + \text{H}$ , 541.3738.  $\text{C}_{30}\text{H}_{57}\text{O}_4\text{SSi}$  requires  $M$ , 541.3741);  $\nu_{\max}$  2954, 2863, 1598, 1462, 1362, 1186, 1175, 1096, 1067, 1012, 920, 880, 813, 760, 679 and 662  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 0.72-0.77 (12 H, m, 2- $\text{CH}_3$ , 4- $\text{CH}_3$ , 8- $\text{CH}_3$  and 11- $\text{H}_3$ ), 0.98 [21 H, m,  $\text{CH}(\text{CH}_3)_2$ ], 1.04-1.21 (5 H, m, 8-H, 9- $\text{H}_2$  and 10- $\text{H}_2$ ), 1.27-1.49 (7 H, m, 3- $\text{H}_2$ , 4-H, 5- $\text{H}_2$  and 7- $\text{H}_2$ ), 1.58 (1 H, m, 2-H), 2.37 (3 H, s, Ar- $\text{CH}_3$ ), 3.37 (2 H, d,  $J$  6, 1- $\text{H}_2$ ), 4.64 (1 H, m, 6-H), 7.25 (2 H, d,  $J$  8, Ar-H) and 7.72 (2 H, d,  $J$  8, Ar-H);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 11.0, 13.2, 15.2, 17.0, 18.5, 18.8, 20.6, 25.6, 27.9, 32.3, 37.7, 39.5, 41.2, 42.3, 68.2, 80.7, 126.7, 128.6, 133.9 and 143.3;  $m/z$  ( $\text{ES}^+$ ) 563 ( $\text{M}^+ + 23$ , 100%).

### [(2*R*,4*S*,6*R*,8*S*)-2,4,6,8-Tetramethylundecyloxy](tri-*isopropyl*)silane **14**

Copper(I) iodide (224 mg, 1.18 mmol) was placed in a round bottom flask and the flask was evacuated and purged with nitrogen three times. THF (2 ml) was added, followed by cooling to 0 °C when methylolithium.lithium iodide complex (2.1 ml, 2.13 mmol) was added dropwise to produce a clear solution. The tosylate **13** (64 mg, 0.12 mmol) in THF (1 ml) was added, and reaction mixture was stirred at 0 °C for 1 h then gradually warmed to RT and stirred for 16 h. Saturated aqueous NH<sub>4</sub>Cl (10 ml) was added and the mixture filtered through a pad of celite then partitioned between water and ether. The organic layer was washed with brine (10 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Chromatography of the residue eluting with petrol (100%) gave the *title compound 14* (10 mg, 21%) as a colourless oil, R<sub>f</sub> 0.7 (100% petrol); [α]<sub>D</sub><sup>20</sup> +14.7 (*c* 0.2 in CHCl<sub>3</sub>) (Found: M<sup>+</sup> - C<sub>3</sub>H<sub>7</sub>, 341.3229. C<sub>21</sub>H<sub>45</sub>OSi requires *M*, 341.3234); ν<sub>max</sub> 2954, 2921, 2864, 1461, 1378, 1245, 1098, 1067, 1012, 994, 918, 881, 783, 679 and 657 cm<sup>-1</sup>; δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>) 0.72-0.82 (15 H, m, 2-CH<sub>3</sub>, 4-CH<sub>3</sub>, 6-CH<sub>3</sub>, 8-CH<sub>3</sub> and 11-H<sub>3</sub>), 0.99 [21 H, m, CH(CH<sub>3</sub>)<sub>2</sub>], 0.95-1.28 (8 H, m, 6-H, 7-H<sub>2</sub>, 8-H, 9-H<sub>2</sub> and 10-H<sub>2</sub>), 1.42 (1 H, m, 4-H), 1.48-1.54 (4 H, m, 3-H<sub>2</sub> and 5-H<sub>2</sub>), 1.64 (1 H, m, 2-H), 3.35 (1 H, dd, *J* 9 and 6, 1-H<sub>a</sub>) and 3.45 (1H, dd, *J* 9 and 6, 1-H<sub>b</sub>); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>) 11.0, 13.4, 15.8, 17.1, 18.5, 18.5, 18.6, 19.1, 26.2, 26.3, 28.7, 32.5, 39.2, 40.4, 44.5, 45.6 and 68.2; *m/z* (EI) 341 (M<sup>+</sup> - 43, 100%).

### (2*R*,4*S*,6*R*,8*S*)-2,4,6,8-Tetramethylundecan-1-ol **15**<sup>2a-c</sup>

The silyl ether **14** (75 mg, 0.19 mmol) was dissolved in THF (2 ml), aqueous hydrogen chloride in dioxane (4 M; 0.24 ml) was added and the reaction mixture stirred at RT for 16 h then concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (7:3) gave the *title compound 15* (40 mg, 91%) as a colourless oil, R<sub>f</sub> 0.5 (60:40 petrol-ether); [α]<sub>D</sub><sup>20</sup> +30 (*c* 0.2 in CHCl<sub>3</sub>) lit.<sup>2c</sup> +23.51 (*c* 1.20, CHCl<sub>3</sub>); (Found: M<sup>+</sup> - H<sub>2</sub>O, 210.2342. C<sub>15</sub>H<sub>30</sub> requires *M*, 210.2342); ν<sub>max</sub> 3223, 2954, 2910, 2868, 2841, 1456, 1377, 1034, 985, 808, 738 and 667 cm<sup>-1</sup>; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 0.72 (15 H, m, 2-CH<sub>3</sub>, 4-CH<sub>3</sub>, 6-CH<sub>3</sub>, 8-CH<sub>3</sub> and 11-H<sub>3</sub>), 0.89-1.28 (10 H, m, 5-H<sub>2</sub>, 6-H, 7-H<sub>2</sub>, 8-H, 9-H<sub>2</sub> and 10-H<sub>2</sub>), 1.41 (1 H, m, 4-H), 1.48-1.56 (2 H, m, 3-H<sub>2</sub>), 1.66 (1 H, m, 2-H), 3.35 (1 H, m, 1-H<sub>a</sub>) and 3.40 (1 H, m, 1-H<sub>b</sub>); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>) 14.4, 16.8, 19.5, 19.5, 19.6, 20.1, 27.3, 27.3, 29.7, 33.5, 40.3, 41.5, 45.6, 46.6 and 69.2.

### (2*R*,4*S*,6*R*,8*S*)-1-Iodo-2,4,6,8-tetramethylundecane **16**

Toluene *p*-sulfonyl chloride (25 mg, 0.13 mmol) and DMAP (19 mg, 0.15 mmol) were added to the alcohol **15** (20 mg, 0.088 mmol) in DCM (2 ml) and the mixture stirred at RT for 16 h then concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (4:1) gave the corresponding toluene *p*-sulfonate (28 mg, 85%) as a colourless oil, R<sub>f</sub> 0.7 (80:20 petrol-ether); [α]<sub>D</sub><sup>20</sup> +9.5 (*c* 0.2 in CHCl<sub>3</sub>) (Found: M<sup>+</sup> + Na, 405.2433. C<sub>22</sub>H<sub>38</sub>O<sub>3</sub>NaS requires *M*, 405.2434); ν<sub>max</sub> 2956, 2915, 2870, 1596, 1458, 1360, 1188, 1174, 1098, 962, 831, 812, 791, 665 and 654 cm<sup>-1</sup>; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 0.66-0.80 (15 H, m, 2-CH<sub>3</sub>, 4-CH<sub>3</sub>, 6-CH<sub>3</sub>, 8-CH<sub>3</sub> and 11-H<sub>3</sub>), 0.86-1.45 (13 H, m, 3-H<sub>2</sub>, 4-H, 5-H<sub>2</sub>, 6-H, 7-H<sub>2</sub>, 8-H, 9-H<sub>2</sub> and 10-H<sub>2</sub>), 1.78 (1 H, m, 2-H), 2.38 (3 H, s, Ar-CH<sub>3</sub>), 3.72 (1 H, dd, *J* 6.8 and 9.3, 1-H<sub>a</sub>), 3.77 (1 H, dd, *J* 5.8 and 9.3 1-H<sub>b</sub>) and 7.25 and 7.72 (each 2 H, d, *J* 7, Ar-H); *m/z* (ES<sup>+</sup>) 405 (M<sup>+</sup> + 23, 100%).

Sodium iodide (22 mg, 0.15 mmol) was added to the toluene *p*-sulfonate (28 mg, 0.07 mmol) in acetone (2 ml) and the mixture was stirred under reflux for 16 h then partitioned between hexane and water. The organic layer was washed with brine (10 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Chromatography of the residue eluting with petrol (100%) gave the *title compound 16* (21 mg, 90%) as a colourless oil, R<sub>f</sub> 0.8 (100% petrol); [α]<sub>D</sub><sup>20</sup> +12 (*c* 0.2 in CHCl<sub>3</sub>); (Found: M<sup>+</sup>, 338.1462. C<sub>15</sub>H<sub>31</sub>I requires *M*, 338.1465); ν<sub>max</sub> 2955, 2912, 2869, 2841, 1457, 1378, 1193, and 739 cm<sup>-1</sup>; δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>) 0.72-0.89 (15 H, m, 2-CH<sub>3</sub>, 4-CH<sub>3</sub>, 6-CH<sub>3</sub>, 8-CH<sub>3</sub> and 11-H<sub>3</sub>), 0.92-1.28 (11 H, m, 4-H, 5-H<sub>2</sub>, 6-H, 7-H<sub>2</sub>, 8-H, 9-H<sub>2</sub> and 10-H<sub>2</sub>), 1.41 (2 H, m, 2-H), 1.49 (2 H, m, 3-H<sub>2</sub>), 3.07 (1 H, dd, *J* 3.2 and 9.5, 1-H<sub>a</sub>) and 3.15 (1 H, dd, *J* 4.7 and 9.5, 1-H<sub>b</sub>); δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>) 14.4, 18.8, 19.5, 19.5, 19.6, 20.1, 20.4, 27.2, 27.5, 29.7, 32.3, 40.2, 44.8, 45.5 and 46.0; *m/z* (EI) 338 (M<sup>+</sup>, 5%).

### (2*R*,6*R*,8*S*,3*E*)-1-Benzyloxy-2,4,8-trimethylundec-3-en-6-ol **18**

DIAD (51 mg, 0.25 mmol) was added to a suspension of alcohol (40 mg, 0.13 mmol), 4-nitrobenzoic acid (32 mg, 0.19 mmol) and Ph<sub>3</sub>P (66 mg, 0.25 mmol) in THF at RT and the reaction mixture was stirred for 16 h. After concentration under reduced pressure, chromatography of the residue eluting with petrol-ether (90:10) gave the 4-

nitrobenzoate **17** (41 mg, 70%) as a colorless oil,  $R_f$  0.8 (4:1 petrol-ether);  $\delta_H$  (400 MHz,  $CDCl_3$ ) 0.60 (3 H, d,  $J$  6.8, 8- $CH_3$ ), 0.79 (3 H, t,  $J$  7.3, 11- $H_3$ ), 0.84 (3 H, d,  $J$  6.6, 2- $CH_3$ ), 1.00-1.60 (6 H, m, 7- $H_2$ , 9- $H_2$  and 10- $H_2$ ), 1.64 (3 H, s, 4- $CH_3$ ), 1.70 (1 H, m, 8-H), 2.22 (2 H, m, 5- $H_2$ ), 2.56 (1 H, m, 2-H), 3.14 (2 H, m, 1- $H_2$ ), 4.39 (2 H, s,  $OCH_2Ph$ ), 4.91 (1 H, d,  $J$  9.3, 3-H), 5.34 (1 H, m, 6-H), 7.16 (5 H, m, Ar-H), 8.10 (2 H, d,  $J$  8.6, Ar-H) and 8.19 (2 H, d,  $J$  9.1, Ar-H).

Ester **17** (41 mg, 0.09 mmol) was dissolved in MeOH/acetone (50 : 50; 1.5 ml). Aqueous sodium hydroxide (2n; 1 ml) was added and the reaction was stirred at 50 °C for 1 h. After concentration under reduced pressure, chromatography of the residue eluting with petrol-ether (80:20) gave the *title compound* **18** (41 mg, 70%) as a colourless oil,  $R_f$  0.5 (7:3 petrol-ether);  $\delta_H$  (400 MHz,  $CDCl_3$ ) 0.80-0.84 (6 H, m, 8- $CH_3$  and 11- $H_3$ ), 0.92 (3 H, d,  $J$  6.6, 2- $CH_3$ ), 1.03-1.30 (6 H, m, 7- $H_2$ , 9- $H_2$  and 10- $H_2$ ), 1.39 (1 H, m, 8-H), 1.61 (3 H, s, 4- $CH_3$ ), 1.94 (1 H, dd,  $J$  9.1 and 13.6, 5- $H_a$ ), 2.08 (1 H, dd,  $J$  4.3 and 13.4, 5- $H_b$ ), 2.68 (1 H, m, 2-H), 3.23 (2 H, m, 1- $H_2$ ), 3.70 (1 H, m, 6-H), 4.44 (2 H, s,  $OCH_2Ph$ ), 5.02 (1 H, d,  $J$  9.1, 3-H) and 7.26 (5 H, m, Ar-H);  $\delta_C$  (125 MHz,  $CDCl_3$ ) 14.38, 16.58, 18.03, 19.31, 20.05, 29.08, 33.15, 40.18, 44.56, 48.78, 66.08, 72.96, 75.20, 127.50, 127.53, 128.36, 131.81, 132.72 and 138.64.

### (*R*)-3,7-Dimethyloct-6-enyl 4-methylbenzenesulfonate (*R*)-20<sup>14</sup>

Toluene p-sulfonyl chloride (1.83 g, 9.6 mmol) and 4-dimethylaminopyridine (1.4 g, 11.5 mmol) were added to a stirred solution of the alcohol (*R*)-19 (1.0 g, 6.4 mmol) in DCM (25 ml) at RT and the mixture was stirred at RT for 16 h then concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (4:1) gave the *title compound* (*R*)-20 (1.92 g, 96%) as a colourless oil,  $R_f$  0.7 (70:30 petrol-ether);  $[\alpha]_D^{20} +1.3$  ( $c$  0.3 in  $CHCl_3$ ), Lit.<sup>14</sup>  $[\alpha]_D^{20} +2.68$  ( $c$  1.0 in EtOH); (Found:  $M^+ + Na$ , 333.1494.  $C_{17}H_{26}O_3NaS$  requires  $M$ , 333.1495);  $\nu_{max}$  2961, 2913, 1597, 1453, 1356, 1187, 1173, 1096, 1019, 940, 887, 813, 761 and 662  $cm^{-1}$ ;  $\delta_H$  (400 MHz,  $CDCl_3$ ) 0.75 (3 H, d,  $J$  6.6, 3- $CH_3$ ), 1.04 (1 H, m, 4- $H_a$ ), 1.17 (1 H, m, 4- $H_b$ ), 1.39 (1 H, m, 5- $H_a$ ), 1.45 (1 H, m, 5- $H_b$ ), 1.50 (3 H, s, 7- $CH_3$  or 8- $H_3$ ), 1.59 (1 H, m, 3-H), 1.60 (3 H, s, 7- $CH_3$  or 8- $H_3$ ), 1.75-1.93 (2 H, m, 2- $H_2$ ), 2.38 (3 H, s, Ar- $CH_3$ ), 4.00 (2 H, m, 1- $H_2$ ), 4.95 (1 H, m, 6-H), 7.28 (2 H, d,  $J$  8.6, Ar-H) and 7.72 (2 H, d,  $J$  8.1, Ar-H);  $\delta_C$  (125 MHz,  $CDCl_3$ ) 17.7, 19.0, 21.7, 25.3, 25.8, 28.9, 35.7, 36.7, 69.1, 124.3, 127.9, 129.8, 131.5, 133.2 and 144.7;  $m/z$  (ES+) 333 ( $M^+ + 23$ ), 100%.

Following this procedure, the alcohol (*S*)-19 (1.5 g, 9.6 mmol) gave the (*S*)-4-methylbenzenesulfonate (*S*)-20 (2.8 g, 93%),  $[\alpha]_D^{20} -1.1$  ( $c$  0.3 in  $CHCl_3$ ).

### (*R*)-8-Iodo-2,6-dimethyloct-2-ene (*R*)-21<sup>13</sup>

Sodium iodide (1.83 g, 12.2 mmol) was added to a solution of tosylate (*R*)-20 (1.90 g, 6.1 mmol) in acetone (15 ml). The mixture was stirred at reflux for 16 h then concentrated and partitioned between hexane (30 ml) and aqueous sodium sulphite (15 ml). The organic layer was washed with brine (20 ml), dried over  $Na_2SO_4$  and concentrated under reduced pressure. Chromatography of the residue eluting with petrol (100%) gave the *title compound* (*R*)-21 (1.44 g, 90%) as a colourless oil,  $R_f$  0.8 (100% petrol);  $[\alpha]_D^{20} -5.2$  ( $c$  1.0 in  $CHCl_3$ ) (Found  $M^+$ , 266.0533;  $C_{10}H_{19}I$ , requires  $M$ , 266.0526);  $\nu_{max}$  2961, 2912, 2851, 1449, 1377, 1178, 826 and 733  $cm^{-1}$ ;  $\delta_H$  (400 MHz,  $CDCl_3$ ) 0.82 (3 H, d,  $J$  6.6, 3- $CH_3$ ), 1.11 (1 H, m, 4- $H_a$ ), 1.27 (1 H, m, 4- $H_b$ ), 1.49 (1 H, m, 5- $H_a$ ), 1.54 (3 H, s, 7- $CH_3$  or 8- $H_3$ ), 1.59 (1 H, m, 5- $H_b$ ), 1.62 (3 H, s, 7- $CH_3$  or 8- $H_3$ ), 1.83 (1 H, m, 3-H), 1.87-1.97 (2 H, m, 2- $H_2$ ), 3.11 (1 H, m, 1- $H_a$ ), 3.19 (1 H, m, 1- $H_b$ ) and 5.02 (1 H, m, 6-H);  $\delta_C$  (100 MHz,  $CDCl_3$ ) 5.3, 17.7, 18.7, 25.4, 25.7, 33.6, 36.3, 40.9, 124.5 and 131.5.

Following this procedure, the (*S*)-4-methylbenzenesulfonate (*S*)-20 (2.9 g) gave the (*S*)-iodide (*S*)-21 (2.21 g, 92%),  $[\alpha]_D^{20} +7.6$  ( $c$  0.6 in  $CHCl_3$ ).

### (4*RS*,7*R*)-7,11-Dimethyldodec-10-en-4-yl(phenyl)sulfone (7*R*)-22

To a stirred solution of *n*-butyl phenyl sulfone (776 mg, 3.91 mmol) in dry THF (14 ml) and DMPU (2 ml) was slowly added  $^nBuLi$  (2.94 ml, 1.6 M in hexane, 4.70 mmol) at -40 °C under nitrogen and the solution stirred for 30 min. The iodide (*R*)-21<sup>13</sup> (1.25 g, 4.7 mmol) in THF (4 ml) was added and the reaction mixture allowed to warm to RT overnight. After 16 h, saturated aqueous  $NH_4Cl$  (10 ml) was added and the mixture partitioned between water (10 ml) and ether (20 ml). The organic layer was washed with brine (20 ml), dried over  $Na_2SO_4$  and concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (4:1) gave the *title compound* (7*R*)-22 (1.23 g, 95%) as a colourless oil, a mixture of two diastereoisomers, ratio 50 : 50,  $R_f$  0.4 (4:1 petrol-ether);  $[\alpha]_D^{20} -1.7$  ( $c$  1.6 in  $CHCl_3$ ) (Found:  $M^+ + H$ , 337.2194.  $C_{20}H_{33}O_2S$  requires  $M$ , 337.2196);  $\nu_{max}$  2959, 2926, 2871, 1446, 1377, 1302, 1143, 1083, 725 and 690  $cm^{-1}$ ;  $\delta_H$  (500 MHz,  $CDCl_3$ ) 0.73 (1.5 H, d,  $J$  6.3, 7- $CH_3$ ), 0.75 (1.5 H, d,  $J$  6.6, 7- $CH_3$ ), 0.81

(3 H, t,  $J$  7.3, 1-H<sub>3</sub>), 0.98-1.54 (9 H, m, 2-H<sub>2</sub>, 3-H<sub>2</sub>, 6-H<sub>2</sub>, 7-H and 8-H<sub>2</sub>), 1.51 (3 H, s, 11-CH<sub>3</sub> or 12-H<sub>3</sub>), 1.61 (3 H, s, 11-CH<sub>3</sub> or 12-H<sub>3</sub>), 1.70-1.93 (4 H, m, 5-H<sub>2</sub> and 9-H<sub>2</sub>), 2.80 (1 H, m, 4-H), 4.98 (1 H, m, 10-H), 7.49 (2 H, t,  $J$  7.8, Ar-H), 7.58 (1 H, t,  $J$  7.3, Ar-H) and 7.82 (2 H, d,  $J$  7.5, Ar-H);  $\delta_C$  (125 MHz, CDCl<sub>3</sub>) 14.0, 17.7, 19.2, 19.4, 20.1, 25.4, 25.4, 25.8, 30.0, 30.0, 32.5, 33.7, 33.9, 38.9, 36.6, 36.9, 64.6, 64.7, 124.6, 124.6, 128.8, 129.1, 131.3, 133.5 and 138.3;  $m/z$  (ES<sup>+</sup>) 359 (M<sup>+</sup> + 23, 100%).

#### (4R,7RS)-4-Methyl-7-phenylsulfonyldecan-1-ol (4R)-23

The alkene (7R)-22 (460 mg, 1.37 mmol) was dissolved in DCM/MeOH (1:1, 20 ml) and solution cooled to -78 °C. Ozone from an ozone generator was bubbled through the stirred solution until it turned blue. O<sub>2</sub> was bubbled through the solution at -78 °C until reaction became colourless. NaBH<sub>4</sub> (250 mg, 6.61 mmol) was added and mixture allowed to warm to RT and stirred overnight. The mixture was partitioned between Et<sub>2</sub>O (20 ml) and brine (20 ml), and the organic layer washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (1:4) gave the *title compound* (4R)-23 (364 mg, 85%) as a colourless oil, a mixture of diastereoisomers, ratio 50 : 50, R<sub>f</sub> 0.4 (4:1 petrol-ether);  $[\alpha]_D^{20}$  -2.9 ( $c$  0.2 in CHCl<sub>3</sub>); (Found: M<sup>+</sup> + H, 313.1833. C<sub>17</sub>H<sub>29</sub>O<sub>3</sub>S requires  $M$ , 313.1832);  $\nu_{\max}$  3394, 2933, 2871, 1447, 1380, 1286, 1141, 1083, 727 and 691 cm<sup>-1</sup>;  $\delta_H$  (500 MHz, CDCl<sub>3</sub>) 0.76 (1.5 H, d,  $J$  6.9, 4-CH<sub>3</sub>), 0.77 (1.5 H, d,  $J$  6.9, 4-CH<sub>3</sub>), 0.80 (3 H, t,  $J$  7.7, 10-H<sub>3</sub>), 1.02-1.58 (11 H, m, 3-H<sub>2</sub>, 4-H, 5-H<sub>2</sub>, 6-H<sub>2</sub>, 8-H<sub>2</sub> and 9-H<sub>2</sub>), 1.71-1.83 (2 H, m, 2-H<sub>2</sub>), 2.81 (1 H, m, 7-H), 3.54 (2 H, t,  $J$  6.6, 1-H<sub>2</sub>), 7.50 (2 H, t,  $J$  7, Ar-H), 7.59 (1 H, t,  $J$  7, Ar-H) and 7.82 (2 H, d,  $J$  7, Ar-H);  $\delta_C$  (125 MHz, CDCl<sub>3</sub>) 14.0, 14.0, 19.3, 19.4, 20.1, 25.4, 29.9, 30.0, 30.1, 32.6, 32.7, 33.8, 33.9, 63.2, 64.6, 64.6, 128.8, 129.1, 133.5 and 138.2;  $m/z$  (ES<sup>+</sup>) 335 (M<sup>+</sup> + 23, 100%).

#### (4S)-4-Methyldecan-1-ol (S)-24<sup>15</sup>

To the sulfone (4R)-23 (360 mg, 1.15 mmol) in methanol (30 ml) was added Na/Hg (10%; 10.0 g, 34.6 mmol). After 16 h at RT, the solution was concentrated under reduced pressure and the residue partitioned between saturated aqueous NH<sub>4</sub>Cl (40 ml) and ether (40 ml). The organic layer was washed with brine (20 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (4:1) gave the *title compound* (S)-24 (143 mg, 73%) as a colourless oil, R<sub>f</sub> 0.6 (1:1 petrol-ether);  $[\alpha]_D^{20}$  -3.9 ( $c$  0.3 in CHCl<sub>3</sub>), Lit.<sup>15</sup>  $[\alpha]_D^{20}$  -1.1 ( $c$  5.33 in CHCl<sub>3</sub>); (Found: M<sup>+</sup> - H<sub>2</sub>O, 154.1723. C<sub>11</sub>H<sub>22</sub>, requires  $M$ , 154.1716);  $\nu_{\max}$  3314, 2923, 2854, 1459, 1377, 1056, 898 and 723 cm<sup>-1</sup>;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 0.81 (6 H, m, 4-CH<sub>3</sub> and 10-H<sub>3</sub>), 1.01-1.31 (11 H, m, 3-H<sub>2</sub>, 4-H, 5-H<sub>2</sub>, 6-H<sub>2</sub>, 7-H<sub>2</sub>, 8-H<sub>2</sub> and 9-H<sub>2</sub>), 1.41-1.59 (2 H, m, 3-H<sub>2</sub>) and 3.59 (2 H, t,  $J$  6.8, 1-H<sub>2</sub>);  $\delta_C$  (125 MHz, CDCl<sub>3</sub>) 14.1, 19.7, 22.7, 27.0, 29.7, 30.4, 32.0, 32.7, 33.0, 37.0 and 63.5;  $m/z$  (EI) 154 (M<sup>+</sup> - 18, 5%) and 91 (100).

#### (4S)-4-Methyldecyl toluene 4-sulfonate (S)-25

Toluene 4-sulfonyl chloride (166 mg, 0.87 mmol) and DMAP (127 mg, 1.04 mmol) were added to the alcohol (S)-24 (100 mg, 0.58 mmol) in DCM (8 ml) at RT and the mixture stirred at RT for 16 h then concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (4:1) gave the *title compound* (S)-25 (187 mg, 99%) as a colourless oil, R<sub>f</sub> 0.7 (7:3 petrol-ether);  $[\alpha]_D^{20}$  +3.1 ( $c$  0.4 in CHCl<sub>3</sub>) (Found: M<sup>+</sup> + Na, 349.1812. C<sub>18</sub>H<sub>30</sub>O<sub>3</sub>NaS requires  $M$ , 349.1808);  $\nu_{\max}$  2954, 2922, 2853, 1598, 1465, 1358, 1187, 1174, 1096, 961, 914, 812, 732 and 661 cm<sup>-1</sup>;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 0.73 (3 H, d,  $J$  6.6, 4-CH<sub>3</sub>), 0.81 (3 H, t,  $J$  7.0, 10-H<sub>3</sub>), 0.97-1.27 (13 H, m, 3-H<sub>2</sub>, 4-H, 5-H<sub>2</sub>, 6-H<sub>2</sub>, 7-H<sub>2</sub>, 8-H<sub>2</sub> and 9-H<sub>2</sub>), 1.51-1.65 (2 H, m, 2-H<sub>2</sub>), 2.38 (3 H, s, Ar-CH<sub>3</sub>), 3.94 (2 H, t,  $J$  6.6, 1-H<sub>2</sub>), 7.28 (2 H, d,  $J$  7, Ar-H) and 7.72 (2 H, d,  $J$  7, Ar-H);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 14.1, 19.4, 21.7, 22.7, 26.5, 26.9, 29.6, 31.9, 32.3, 32.5, 36.8, 71.1, 127.9, 129.8, 133.2 and 144.6;  $m/z$  (ES<sup>+</sup>) 349 (M<sup>+</sup> + 23, 70%).

#### (4S)-1-Iodo-4-methyldecane (S)-26<sup>16</sup>

Sodium iodide (1.06 g, 7.04 mmol) was added to the tosylate (S)-25 (1.15 g, 3.52 mmol) in acetone (15 ml) and the mixture stirred under reflux for 2 h then concentrated and partitioned between hexane (30 ml) and aqueous sodium sulphite (15 ml). The organic layer was washed with brine (10 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give the *title compound* (S)-26 (891 mg, 90%) as a colourless oil, R<sub>f</sub> 0.8 (100% petrol);  $[\alpha]_D^{20}$  +2.6 ( $c$  0.2 in CHCl<sub>3</sub>) (Found: M<sup>+</sup>, 282.0837. C<sub>11</sub>H<sub>23</sub>I requires  $M$ , 282.0839);  $\nu_{\max}$  2955, 2922, 2853, 1460, 1378, 1234, 1173, and 724 cm<sup>-1</sup>;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 0.79-0.83 (6 H, m, 4-CH<sub>3</sub> and 10-H<sub>3</sub>), 1.01-1.36 (13 H, m, 3-H<sub>2</sub>, 4-H, 5-H<sub>2</sub>, 6-H<sub>2</sub>, 7-H<sub>2</sub>,

8-H<sub>2</sub> and 9-H<sub>2</sub>), 1.77 (2 H, m, 2-H<sub>2</sub>) and 3.10 (2 H, m, 1-H<sub>2</sub>);  $\delta_C$  (125 MHz, CDCl<sub>3</sub>) 7.7, 14.2, 19.7, 22.7, 27.0, 29.7, 31.3, 32.0, 32.1, 36.9 and 37.9;  $m/z$  (EI) 282 (M<sup>+</sup>, 5%) and 155 (70).

#### **(5S)-5-Methylundecyl(4-methylphenyl)sulfone (S)-27**

To methyl phenyl sulfone (50 mg, 0.32 mmol) in dry THF (3 ml) and DMPU (1 ml) at -40 °C under nitrogen, was slowly added <sup>n</sup>BuLi (240  $\mu$ l, 1.6 M in hexane, 0.38 mmol). The mixture was stirred for 30 min then the iodide (**S**)-**26** (108 mg, 0.38 mmol) in THF (1 ml) was added and the reaction mixture was allowed to warm to RT and stirred overnight. After 16 h, saturated aqueous NH<sub>4</sub>Cl (5 ml) was added and the mixture partitioned between water (2 ml) and ether (10 ml). The organic layer was washed with brine (10 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (4:1) gave the *title compound* (**S**)-**27** (72 mg, 73%) as a colourless oil, R<sub>f</sub> 0.5 (60:40 petrol-ether);  $[\alpha]_D^{20}$  -6.4 (*c* 0.2 in CHCl<sub>3</sub>) (Found: M<sup>+</sup> + H, 311.2032. C<sub>18</sub>H<sub>31</sub>O<sub>2</sub>S, requires *M*, 311.2040);  $\nu_{\max}$  2923, 2854, 1463, 1446, 1305, 1144, 1086, 794, 745, 727 and 688 cm<sup>-1</sup>;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 0.73 (3 H, d, *J* 6.6, 5-CH<sub>3</sub>), 0.81 (3 H, t, *J* 7.0, 11-H<sub>3</sub>), 0.94-1.32 (15 H, m, 3-H<sub>2</sub>, 4-H<sub>2</sub>, 5-H, 6-H<sub>2</sub>, 7-H<sub>2</sub>, 8-H<sub>2</sub>, 9-H<sub>2</sub> and 10-H<sub>2</sub>), 1.62 (2 H, m, 2-H<sub>2</sub>), 3.02 (2 H, m, 1-H<sub>2</sub>), 7.51 (2 H, m, Ar-H), 7.59 (1 H, m, Ar-H) and 7.84 (2 H, m, Ar-H);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 14.1, 19.5, 22.7, 23.0, 25.8, 27.0, 29.7, 31.9, 32.4, 36.4, 36.9, 56.4, 128.1, 129.3, 133.6 and 139.3;  $m/z$  (ES<sup>+</sup>) 333 (M<sup>+</sup> + 23, 100%).

#### **[(7S,11RS,13R,15S,17R,19S)-7,13,15,17,19-Pentamethyldocosan-11-yl](phenyl)sulfone 28**

To a stirred solution of sulfone (**S**)-**27** (13 mg, 0.044 mmol) in THF (0.5 ml) and DMPU (0.5 ml) at -40 °C under nitrogen was slowly added <sup>n</sup>BuLi (33  $\mu$ l, 1.6 M in hexane, 0.053 mmol). The mixture was stirred for 30 min, the iodide **16** (18 mg, 0.053 mmol) in THF (0.5 ml) was added and the mixture allowed to warm to RT and stirred overnight. After 16 h, saturated NH<sub>4</sub>Cl (3 ml) was added and the mixture partitioned between water (2 ml) and ether (5 ml). The organic layer was washed with brine (10 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (4:1) gave the *title compound* **28** (10 mg, 45%) as a colourless oil, a mixture of epimers, R<sub>f</sub> 0.6 (4:1 petrol-ether);  $[\alpha]_D^{20}$  -3.7 (*c* 0.2 in CHCl<sub>3</sub>) (Found: M<sup>+</sup> + H, 521.4380. C<sub>33</sub>H<sub>61</sub>O<sub>2</sub>S requires *M*, 521.4387);  $\nu_{\max}$  2955, 2923, 2870, 1462, 1379, 1304, 1145, 1086, 727 and 691 cm<sup>-1</sup>;  $\delta_H$  (500 MHz, CDCl<sub>3</sub>) 0.64-0.84 (21 H, m, 1-H<sub>3</sub>, 7-CH<sub>3</sub>, 13-CH<sub>3</sub>, 15-CH<sub>3</sub>, 17-CH<sub>3</sub>, 19-CH<sub>3</sub> and 22-H<sub>3</sub>), 0.86-1.80 (33 H, m), 2.91 (1 H, m, 11-H), 7.49 (2 H, t, *J* 7.5, Ar-H), 7.57 (1 H, t, *J* 6.9, Ar-H) and 7.81 (2 H, d, *J* 7.9, Ar-H);  $m/z$  (ES<sup>+</sup>) 543 (M<sup>+</sup> + 23, 100%).

#### **(4S,6R,8R,10S,16S)-4,6,8,10,16-Pentamethyldocosane (16S)-2**

Sodium amalgam (20%; 85 mg, 0.518 mmol) was added to a stirred solution of the sulfone **28** (9 mg, 0.017 mmol) in MeOH (2 ml) at RT and the mixture was stirred for 6 h. After concentration under reduced pressure, saturated ammonium chloride (4 ml) was added and mixture was partitioned between saturated aqueous ammonium chloride (6 ml) and hexane (6 ml). The organic extracts were washed with brine (10 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Chromatography of the residue eluting with two column volumes of hexane (100%) gave the *title compound* (**16S**)-**2** (5 mg, 83%) as a colourless oil, R<sub>f</sub> 1.0 (100% petrol);  $[\alpha]_D^{20}$  +23.3 (*c* 1.2 in CHCl<sub>3</sub>);  $\nu_{\max}$  2956, 2923, 2854, 1463, 1378, 1260, 1094, 1018, 799, 725, 664 and 622 cm<sup>-1</sup>;  $\delta_H$  (500 MHz, CDCl<sub>3</sub>) 0.72-0.82 (21 H, m, 7 x Me), 0.89-1.07 (10 H, m), 1.13-1.30 (20 H, m), 1.41 (2 H, m) and 1.49 (3 H, m);  $\delta_C$  (125 MHz, CDCl<sub>3</sub>) 14.1212, 14.3854, 19.5518, 19.5682, 19.5882, 19.6502, 19.7286, 20.0803, 22.6990, 27.0508, 27.0672, 27.1128, 27.2933, 27.3003, 29.6987, 29.7169, 30.0012, 30.3457, 31.9639, 32.7567, 37.0948, 37.1003, 37.8848, 40.2229, 45.5496, 45.5660 and 46.5428.

#### **[(4RS,7S)-7,11-Dimethyldodec-10-en-4-yl](phenyl)sulfone (7S)-22**

To methyl phenyl sulfone (1.2 g, 5.9 mmol) in THF (20 ml) and DMPU (3 ml) under nitrogen was slowly added <sup>n</sup>BuLi (4.4 ml, 1.6 M in hexane, 7.1 mmol) at -40 °C and the solution stirred for 30 min. The iodide (**S**)-**21**<sup>14</sup> (1.9 g, 7.1 mmol) in THF (6 ml) was added and the mixture allowed to warm to RT overnight. After 16 h, saturated aqueous NH<sub>4</sub>Cl (15 ml) was added and the mixture was partitioned between water (15 ml) and ether (25 ml). The organic layer was washed with brine (25 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Chromatography of the

residue eluting with petrol-ether (4:1) gave the *title compound* (**7S**)-**22** (1.7 g, 90%) as a colourless oil, a mixture of diastereoisomers, ratio 50 : 50,  $R_f$  0.4 (4:1 petrol-ether);  $[\alpha]_D^{20} +3.0$  ( $c$  1.6 in  $\text{CHCl}_3$ ) (Found:  $M^+ + \text{Na}$ , 359.2025.  $\text{C}_{20}\text{H}_{32}\text{O}_2\text{NaS}$  requires  $M$ , 359.2016);  $\nu_{\max}$  3063, 2958, 2927, 2871, 1446, 1378, 1303, 1144, 1084, 757, 726 and 691  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 0.75 (1.5 H, d,  $J$  6.3, 7- $\text{CH}_3$ ), 0.76 (1.5 H, d,  $J$  6.6, 7- $\text{CH}_3$ ), 0.82 (3 H, t,  $J$  7.3, 1- $\text{H}_3$ ), 1.00-1.55 (9 H, m, 2- $\text{H}_2$ , 3- $\text{H}_2$ , 6- $\text{H}_2$ , 7- $\text{H}$  and 8- $\text{H}_2$ ), 1.52 (3 H, s, 11- $\text{CH}_3$  or 12- $\text{H}_3$ ), 1.64 (3 H, s, 11- $\text{CH}_3$  or 12- $\text{H}_3$ ), 1.72-1.95 (4 H, m, 5- $\text{H}_2$  and 9- $\text{H}_2$ ), 2.81 (1 H, m, 4- $\text{H}$ ), 5.01 (1 H, m, 10- $\text{H}$ ), 7.51 (2 H, t,  $J$  7.8, Ar-H), 7.60 (1 H, t,  $J$  7.3, Ar-H) and 7.85 (2 H, d,  $J$  7.5, Ar-H);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 14.0, 17.7, 19.2, 19.4, 20.1, 25.4, 25.4, 25.5, 25.8, 29.9, 30.0, 32.3, 32.5, 33.8, 33.9, 36.5, 36.9, 64.6, 64.7, 124.6, 124.6, 128.8, 129.1, 133.5 and 138.3;  $m/z$  ( $\text{ES}^+$ ) 359 ( $M^+ + 23$ , 100%).

#### (4S,7RS)-4-Methyl-7-phenylsulfonyldecane-1-ol (**4S**)-**23**

The alkene (**7S**)-**22** (690 mg, 2.1 mmol) was dissolved in DCM/MeOH (1:1, 25 ml) and reaction was cooled to  $-78$  °C. Ozone from an ozone generator was bubbled through the stirred solution until it turned blue then  $\text{O}_2$  was bubbled through the solution at  $-78$  °C until it became colourless.  $\text{NaBH}_4$  (375 mg, 9.9 mmol) was added and the mixture allowed to warm to RT and stirred overnight. After partitioning between  $\text{Et}_2\text{O}$  (40 ml) and brine (40 ml), the organic layer was washed with brine, dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (1:4) gave the *title compound* (**4S**)-**23** (559 mg, 87%) as a colourless oil, a mixture of epimers,  $R_f$  0.4 (4:1 petrol-ether);  $[\alpha]_D^{20} +4.7$  ( $c$  0.2 in  $\text{CHCl}_3$ ) (Found:  $M^+ + \text{H}$ , 313.1831.  $\text{C}_{17}\text{H}_{29}\text{O}_3\text{S}$  requires  $M$ , 313.1832);  $\nu_{\max}$  3490, 2933, 2871, 1725, 1586, 1447, 1380, 1287, 1140, 1084, 1024, 999, 758, 726 and 691  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 0.78 (1.5 H, d,  $J$  6.9, 4- $\text{CH}_3$ ), 0.79 (1.5 H, d,  $J$  6.9, 4- $\text{CH}_3$ ), 0.81 (3 H, t,  $J$  7.6, 10- $\text{H}_3$ ), 1.04-1.61 (11 H, m, 3- $\text{H}_2$ , 4- $\text{H}$ , 5- $\text{H}_2$ , 6- $\text{H}_2$ , 8- $\text{H}_2$  and 9- $\text{H}_2$ ), 1.72-1.84 (2 H, m, 2- $\text{H}_2$ ), 2.82 (1 H, m, 7- $\text{H}$ ), 3.56 (2 H, t,  $J$  6.6, 1- $\text{H}_2$ ), 7.49 (2 H, m, Ar-H), 7.61 (1 H, m, Ar-H) and 7.82 (2 H, m, Ar-H);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 14.0, 14.0, 19.2, 20.1, 25.4, 29.9, 30.1, 30.2, 32.4, 32.8, 33.8, 33.9, 63.2, 64.6, 64.6, 128.8, 129.1, 133.5 and 138.2;  $m/z$  ( $\text{ES}^+$ ) 335 ( $M^+ + 23$ , 100%).

#### (4R)-4-Methyldecane-1-ol (**R**)-**24**<sup>18</sup>

To the sulfone (**4S**)-**23** (540 mg, 1.73 mmol) in dry methanol (40 ml) at RT was added Na/Hg (10%; 15.0 g, 51.9 mmol) and the mixture was concentrated under reduced pressure after 16 h. The residue was partitioned between saturated aqueous  $\text{NH}_4\text{Cl}$  (50 ml) and ether (50 ml). The organic layer was washed with brine (30 ml), dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (4:1) gave the *title compound* (**R**)-**24** (206 mg, 70%) as a colourless oil,  $R_f$  0.6 (1:1 petrol-ether);  $[\alpha]_D^{20} +4.7$  ( $c$  0.3 in  $\text{CHCl}_3$ ), Lit.<sup>18</sup>  $[\alpha]_D^{20} +0.7$  ( $c$  3.5 in  $\text{CHCl}_3$ ); (Found:  $M^+ - \text{H}_2\text{O}$ , 154.1714.  $\text{C}_{11}\text{H}_{22}$  requires  $M$ , 154.1716);  $\nu_{\max}$  3325, 2955, 2924, 2855, 1710, 1459, 1378, 1057, 898 and 724  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 0.82 (6 H, m, 4- $\text{CH}_3$  and 10- $\text{H}_3$ ), 1.02-1.32 (11 H, m, 3- $\text{H}_2$ , 4- $\text{H}$ , 5- $\text{H}_2$ , 6- $\text{H}_2$ , 7- $\text{H}_2$ , 8- $\text{H}_2$  and 9- $\text{H}_2$ ), 1.43-1.60 (2 H, m, 3- $\text{H}_2$ ) and 3.60 (2 H, t,  $J$  6.8, 1- $\text{H}_2$ );  $\delta_{\text{C}}$  (125 MHz,  $\text{CDCl}_3$ ) 14.2, 19.7, 22.7, 27.0, 29.7, 30.4, 32.0, 32.6, 32.9, 37.0 and 63.5.

#### (4R)-4-Methyldecyl 4-methylbenzenesulfonate (**R**)-**25**

Toluene *p*-sulfonyl chloride (249 mg, 1.3 mmol) and DMAP (191 mg, 1.56 mmol) were added to the alcohol (**R**)-**24** (150 mg, 0.87 mmol) in DCM (12 ml) at RT and the mixture was stirred at RT for 16 h then concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (4:1) gave the *title compound* (**R**)-**25** (277 mg, 98%) as a colourless oil,  $R_f$  0.7 (7:3 petrol-ether);  $[\alpha]_D^{20} -3.8$  ( $c$  0.4 in  $\text{CHCl}_3$ ) (Found:  $M^+ + \text{Na}$ , 349.1810.  $\text{C}_{18}\text{H}_{30}\text{O}_3\text{NaS}$  requires  $M$ , 349.1808);  $\nu_{\max}$  2956, 2924, 2855, 1735, 1599, 1465, 1362, 1189, 1176, 1098, 964, 917, 814, 734 and 663  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 0.74 (3 H, d,  $J$  6.6, 4- $\text{CH}_3$ ), 0.83 (3 H, t,  $J$  7.0, 10- $\text{H}_3$ ), 0.98-1.30 (13 H, m, 3- $\text{H}_2$ , 4- $\text{H}$ , 5- $\text{H}_2$ , 6- $\text{H}_2$ , 7- $\text{H}_2$ , 8- $\text{H}_2$  and 9- $\text{H}_2$ ), 1.52-1.66 (2 H, m, 2- $\text{H}_2$ ), 2.39 (3 H, s, Ar- $\text{CH}_3$ ), 3.95 (2 H, t,  $J$  6.6, 1- $\text{H}_2$ ), 7.28 (2 H, d,  $J$  7, Ar-H) and 7.73 (2 H, d,  $J$  7, Ar-H);  $\delta_{\text{C}}$  (125 MHz,  $\text{CDCl}_3$ ) 14.1, 19.4, 21.7, 22.7, 26.5, 27.0, 29.6, 31.9, 32.0, 32.4, 36.8, 71.3, 127.9, 129.9, 133.4 and 144.7;  $m/z$  ( $\text{ES}^+$ ) 349 ( $M^+ + 23$ , 100%).

#### (4R)-1-Iodo-4-methyldecane (**R**)-**26**<sup>16</sup>

Sodium iodide (1.6 g, 10.6 mmol) was added to the tosylate (**R**)-**25** (1.73 g, 5.3 mmol) in acetone (20 ml) and the mixture stirred under reflux for 2 h. The mixture was then concentrated and partitioned between hexane (40 ml) and aqueous sodium sulphite (20 ml). The organic layer was washed with brine (15 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give the *title compound* (**R**)-**26** (1.37 g, 92%) as a colourless oil, R<sub>f</sub> 0.8 (100% petrol); [α]<sub>D</sub><sup>20</sup> -1.7 (c 0.2 in CHCl<sub>3</sub>) (Found: M<sup>+</sup>, 282.0835. C<sub>11</sub>H<sub>23</sub>I requires M, 282.0839); ν<sub>max</sub> 2954, 2921, 2852, 2359, 2341, 1458, 1377, 1233, 1173, 723 and 668 cm<sup>-1</sup>; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 0.80-0.84 (6 H, m, 4-CH<sub>3</sub> and 10-H<sub>3</sub>), 1.02-1.36 (13 H, m, 3-H<sub>2</sub>, 4-H, 5-H<sub>2</sub>, 6-H<sub>2</sub>, 7-H<sub>2</sub>, 8-H<sub>2</sub> and 9-H<sub>2</sub>), 1.78 (2 H, m, 2-H<sub>2</sub>) and 3.11 (2 H, m, 1-H<sub>2</sub>); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>) 7.6, 14.1, 19.6, 22.7, 27.0, 29.6, 31.3, 31.9, 32.1, 36.9 and 37.9; m/z (EI) 282 (M<sup>+</sup>, 5%).

#### [(5*R*)-5-Methylundecyl](phenyl)sulfone (**R**)-**27**

To methyl phenyl sulfone (75 mg, 0.48 mmol) in dry THF (5 ml) and DMPU (1.5 ml) under nitrogen was slowly added <sup>n</sup>BuLi (360 ul, 1.6 M in hexane, 0.57 mmol) at -40 °C. The mixture was stirred for 30 min then the iodide (**R**)-**26** (162 mg, 0.57 mmol) in THF (1.5 ml) was added and the mixture allowed to warm to RT. After 16 h, saturated aqueous NH<sub>4</sub>Cl (8 ml) was added and the mixture was partitioned between water (5 ml) and ether (15 ml). The organic layer was washed with brine (15 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (4:1) gave the *title compound* (**R**)-**27** (110 mg, 75%) as a colourless oil, R<sub>f</sub> 0.5 (60:40 petrol-ether); [α]<sub>D</sub><sup>20</sup> +5.2 (c 0.2 in CHCl<sub>3</sub>) (Found: M<sup>+</sup> + H, 311.2034. C<sub>18</sub>H<sub>31</sub>O<sub>2</sub>S requires M, 311.2040); ν<sub>max</sub> 2922, 2984, 1586, 1465, 1447, 1318, 1305, 1145, 1087, 1024, 999, 794, 746, 727 and 689 cm<sup>-1</sup>; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 0.75 (3 H, d, *J* 6.6, 5-CH<sub>3</sub>), 0.82 (3 H, t, *J* 7.0, 11-H<sub>3</sub>), 0.96-1.33 (15 H, m, 3-H<sub>2</sub>, 4-H<sub>2</sub>, 5-H, 6-H<sub>2</sub>, 7-H<sub>2</sub>, 8-H<sub>2</sub>, 9-H<sub>2</sub> and 10-H<sub>2</sub>), 1.63 (2 H, m, 2-H<sub>2</sub>), 3.03 (2 H, t, *J* 8.1, 1-H<sub>2</sub>), 7.51 (2 H, m, Ar-H), 7.60 (1 H, m, Ar-H) and 7.85 (2 H, m, Ar-H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>) 14.2, 19.6, 22.7, 22.9, 25.8, 27.0, 29.6, 31.9, 32.5, 36.4, 36.9, 56.4, 128.1, 129.3, 133.7 and 139.2; m/z (ES<sup>+</sup>) 333 (M<sup>+</sup> + 23, 100%).

#### [(7*R*,11*RS*,13*R*,15*S*,17*R*,19*S*)-7,13,15,17,19-Pentamethyldocosan-11-yl]phenylsulfone **29**

To the sulfone (**R**)-**27** (20 mg, 0.07 mmol) in dry THF (0.8 ml) and DMPU (0.8 ml) at -40 °C under nitrogen was slowly added <sup>n</sup>BuLi (50 ul, 1.6 M in hexane, 0.08 mmol). The mixture was stirred for 30 min then the iodide **16** (27 mg, 0.8 mmol) in THF (0.8 ml) was added and the reaction mixture was allowed to warm to RT and stirred overnight. After 16 h, saturated aqueous NH<sub>4</sub>Cl (5 ml) was added and the mixture partitioned between water (3 ml) and ether (8 ml). The organic layer was washed with brine (15 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ether (4:1) gave the *title compound* **29** (11 mg, 34%) as a colourless oil, a mixture of epimers, R<sub>f</sub> 0.6 (4:1 petrol-ether); [α]<sub>D</sub><sup>20</sup> +4.0 (c 0.2 in CHCl<sub>3</sub>) (Found: M<sup>+</sup> + H, 521.4371. C<sub>33</sub>H<sub>61</sub>O<sub>2</sub>S requires M, 521.4387); ν<sub>max</sub> 2954, 2922, 2869, 1463, 1378, 1304, 1145, 1086, 727 and 691 cm<sup>-1</sup>; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 0.63-0.83 (21 H, m, 1-H<sub>3</sub>, 7-CH<sub>3</sub>, 13-CH<sub>3</sub>, 15-CH<sub>3</sub>, 17-CH<sub>3</sub>, 19-CH<sub>3</sub> and 22-H<sub>3</sub>), 0.87-1.80 (33 H, m), 2.91 (1 H, m, 11-H), 7.49 (2 H, t, *J* 7.5, Ar-H), 7.58 (1 H, m, Ar-H), 7.82 (2 H, m, Ar-H); m/z (ES<sup>+</sup>) 543 (M<sup>+</sup> + 23, 100%).

#### (4*S*,6*R*,8*R*,10*S*,16*R*)-4,6,8,10,16-Pentamethyldocosane (**16R**)-**2**

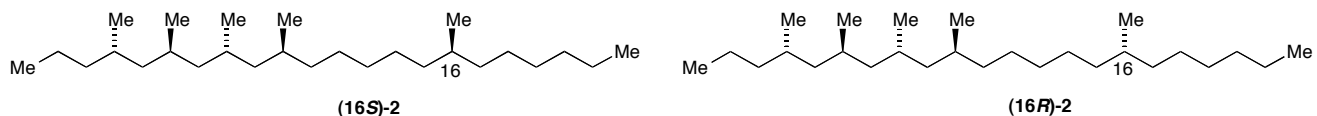
Sodium amalgam (20%; 104 mg, 0.641 mmol) was added to a stirred solution of the sulfone **29** (11 mg, 0.021 mmol) in MeOH (2 ml) at RT and the mixture was stirred for 6 h. After concentration under reduced pressure, saturated aqueous ammonium chloride (4 ml) was added and reaction was partitioned between saturated ammonium chloride (6 ml) and hexane (6 ml). Organic layer was washed with brine (10 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Chromatography of the residue eluting with two column volumes of hexane (100%) gave the *title compound* (**16R**)-**2** (6 mg, 85%) as a colourless oil, R<sub>f</sub> 1.0 (100% petrol); [α]<sub>D</sub><sup>20</sup> -4.8 (c 1.1 in CHCl<sub>3</sub>); ν<sub>max</sub> 2957, 2924, 2854, 1464, 1378, 1260, 1094, 1018, 799, 725 and 664 cm<sup>-1</sup>; δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>) 0.72-0.83 (21 H, m, 7 x Me), 0.89-1.06 (10 H, m), 1.11-1.30 (20 H, m), 1.41 (2 H, m) and 1.49 (3 H, m); δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>) 14.1266, 14.3890, 19.5354, 19.5518, 19.5773, 19.6338, 19.7176, 20.0766, 22.6990, 27.0472, 27.0599, 27.1037, 27.2629, 27.2689, 29.6951, 29.6951, 29.9757, 30.3311, 31.9603, 32.7439, 37.0884, 37.0966, 37.8702, 40.2101, 45.5296, 45.5533 and 46.5191.



### Comparison of the $^{13}\text{C}$ data of the epimers (16*S*)- and (16*R*)-2 with those of the natural product

The  $^{13}\text{C}$  spectra of (16*S*)-2 and (16*R*)-2 were measured on a Bruker AVANCE III 400 MHz spectrometer, using 12288 transients of 32k complex points in a total experiment time of 16 h, and referenced to internal  $\text{CDCl}_3$  solvent at 77.00 ppm. The free induction decay was weighted with a Gaussian function corresponding to a line width of 0.78 Hz and zero filled to 256k complex points before Fourier transformation and peak picking. The positions of poorly resolved lines were refined using mild Lorentz-Gauss resolution enhancement. Shift difference plots were constructed by taking the difference between the chemical shifts of the synthetic material and those reported for the natural material in chemical shift order.

Table of  $^{13}\text{C}$  NMR data of (16*S*)-2, (16*R*)-2 and the natural product



Carbon Numbering	Natural Product	(16 <i>S</i> )-2	(16 <i>R</i> )-2
C1	14.380	14.3854	14.3890
C2	20.074	20.0803	20.0766
C3	40.218	40.2229	40.2101
C4 (CH)	29.712	29.7169	29.6951
C5	45.545	45.5496	45.5296
C6 (CH)	27.295	27.3003	27.2689
C7	46.538	46.5428	46.5191
C8 (CH)	27.291	27.2933	27.2629
C9	45.561	45.5660	45.5533
C10 (CH)	29.996	30.0012	29.9757
C11	37.879	37.8848	37.8702
C12	27.060	27.0672	27.0599
C13	30.339	30.3457	30.3311
C14	27.106	27.1128	27.1037
C15	37.093	37.1003	37.0966
C16 (CH)	32.751	32.7567	32.7439
C17	37.089	37.0948	37.0884
C18	27.044	27.0508	27.0472
C19	29.712(29.697) <sup>19</sup>	29.6987	29.6951
C20	31.957	31.9639	31.9603
C21	22.694	22.6990	22.6990
C22	14.116	14.1212	14.1266
Me-4, 6, 8, 10	19.646	19.6502	19.6338
Me-4, 6, 8, 10	19.585	19.5882	19.5773
Me-4, 6, 8, 10	19.564	19.5682	19.5518
Me-4, 6, 8, 10	19.549	19.5518	19.5354
Me-16	19.724	19.7286	19.7176