**SUPPORTING INFORMATION FOR**

β-Hydroxysulfoxides as Chiral Cyclic Ketone Equivalents: Enantioselective Synthesis of Polysubstituted Cyclohexanones, Cyclohexenones and Cyclohexenediones

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**Experimental Section**

**General:** Melting points were obtained in open capillary tubes and are uncorrected. $^1$H- and $^{13}$C-NMR spectra were recorded in CDCl$_3$ at 300 and 75 MHz, respectively. All reactions were monitored by thin layer chromatography that was performed on precoated sheets of silica gel 60, and flash column chromatography was done with silica gel 60 (230-400 mesh) of Merck. Eluting solvents are indicated in the text. The apparatus for inert atmosphere experiments was dried by flaming in a stream of dry argon. CH$_2$Cl$_2$ was dried over P$_2$O$_5$. Dry THF was distilled from sodium/benzophenone ketyl. CH$_3$CN was dried over 4Å molecular sieves. All other reagent quality solvents were used without purification. For routine workup, hydrolysis was carried out with water, extractions with CH$_2$Cl$_2$, and solvent drying with Na$_2$SO$_4$. The synthesis of derivatives 2a-d and 13 has been previously described.$^1$

**General Procedure for m-CPBA Oxidations. Method A.** m-CPBA (2 equiv) in CH$_2$Cl$_2$ (0.5 M) was added to a solution of sulfoxides 2a-d (1 equiv) in CH$_2$Cl$_2$ (0.5 M) at 0 °C. The mixture was stirred for 1-2 h and washed with saturated aqueous Na$_2$SO$_3$ and NaHCO$_3$. After workup, the residue was purified by crystallization.

General Procedure for Reductions with NaBH₄/CeCl₃. Method B. To a solution of the corresponding carbonyl compound (1 equiv) in MeOH (0.5 M), CeCl₃ (3 equiv) and NaBH₄ (3 equiv) were sequentially added at –78 ºC. The reaction mixture was stirred for 2-3 h and treated with 5% HCl and saturated aqueous NaCl. After several extractions with AcOEt and workup, the residue was purified by flash chromatography.

General Procedure for Reductions with L-Selectride. Method C. To a solution of L-Selectride (1 M in THF, 3 equiv), a solution of the corresponding carbonyl compound (1 equiv) in THF (0.3 M) was added at –78 ºC. After stirring for 1-2 h, the mixture was sequentially treated with H₂O, MeOH, 5% NaOH and H₂O₂. After several extractions with AcOEt and workup, the residue was purified by flash chromatography.

General Procedure for TBDMS Protections. Method D. To a solution of the corresponding alcohols (1 equiv) in CH₂Cl₂ (0.5 M) at 0 ºC under argon, 2,6-lutidine (2.5 equiv) and TBDMSTf (1.5 equiv) were sequentially added. The reaction mixture was stirred for 4-5 h and treated with 5% HCl. After workup, the residue was purified by flash chromatography.

General Procedure for MeSO₂pTol Elimination. Method E. To a solution of the corresponding β-hydroxy sulfone (1 equiv) in CH₃CN (0.1 M), Cs₂CO₃ (2 or 3 equiv) was added at rt. After the time indicated in each case (see Table 1 for reaction conditions), the mixture was filtered through celite and the solvent evaporated to afford a residue which was purified by flash chromatography.

(4S,5S)-4-Hydroxy-5-methyl-4-[(p-tolylsulfonyl)methyl]-2-cyclohexenone (3a).

![3a]

Compound 3a was obtained following method A from 2a¹ (2.0 g, 6.9 mmol), in 90% yield as a white solid: mp 145-146 ºC (EtOAc/hexane); [α]D²⁰ = +21.2 (c 1, acetone); ¹H RMN δ 7.80 and 7.39 (AA’BB’ system, 4H), 7.06 (dd, 1H, J = 0.9 and 10.2 Hz), 5.96 (d, 1H, J = 10.2 Hz), 4.08 (broad s, 1H), 3.50 and 3.45 (AB system, 2H, J = 14.2 Hz), 2.62-2.37 (m, 3H), 2.47 (s, 3H), 1.09 (d, 3H, J = 6.6 Hz); ¹³C RMN δ 197.8, 148.9, 145.6, 137.4, 130.2 (2C), 129.1, 127.6 (2C), 71.7, 62.7, 42.0, 38.3, 21.7, 14.5; FAB-MS m/z (rel ints) 295 ([M + H]⁺, 51), 277 (77), 257 (66), 239 (54), 215 (60), 203 (76), 189 (94), 171 (100); HRMS (FAB) calcd for C₁₅H₁₉O₄S [M + H]⁺ 295.1004, found 295.1007.
(1S,4R,6S)-6-Methyl-1-[(p-tolylsulfonyl)methyl]-2-cyclohexene-1,4-diol (4).

![Structure of compound 4]

To a solution of DIBALH 1 M in hexanes (18.9 mL, 18.9 mmol) in THF (60 mL), a solution of 3a (312 mg, 6.30 mmol) in THF (20 mL) was added dropwise under argon at –78 ºC. After 30 min at the same temperature, the excess of organoaluminum reagent was destroyed with methanol and the mixture was poured into an Erlenmeyer containing ethyl acetate and a saturated solution of potassium sodium tartrate and stirred vigorously for 30 min. The organic layer was washed with brine and dried over MgSO₄. After workup, compound 4 was obtained in 95% yield as a white solid: mp 118-119 ºC (EtOAc/hexane); [α]D²⁰ = +56.0 (c 1, acetone); ¹H RMN (CD₃OD) δ 7.76 and 7.40 (AA’BB’ system, 4H), 5.73 (dd, 1H, J = 2.0 and 10.2 Hz), 5.63 (dt, 1H, J = 10.2 and 1.6 Hz), 4.14 (m, 1H), 3.49 and 3.40 (AB system, 2H, J = 14.5 Hz), 2.43 (s, 3H), 2.13-2.00 (m, 1H), 1.70 (m, 1H), 1.48 (ddd, 1H, J = 10.1, 12.3, 12.6 Hz), 0.94 (d, 3H, J = 6.7 Hz); ¹³C RMN (CD₃OD) δ 146.2, 139.4, 135.5, 132.2, 130.9 (2C), 129.1 (2C), 70.8, 68.1, 63.9, 36.8, 35.6, 21.5, 15.4. Anal. calcd. for C₁₅H₂₀O₄S: C, 60.79; H, 6.80; S, 10.82. Found C, 60.67; H, 6.48; S, 10.68.

(1S,4R,6S)-4-[(tert-Butyldimethylsilyl)oxy]-6-methyl-1-[(p-tolylsulfonyl)methyl]-2-cyclohexene-1-ol (5).

![Structure of compound 5]

Compound 5 was obtained following method D from 4 (152 mg, 0.51 mmol), in 93% yield after flash chromatography (EtOAc/hexane 1:3), as a white solid: mp 145-147 ºC (ethyl ether/hexane); [α]D²⁰ = +47.0 (c 1, acetone); ¹H RMN δ 7.79 and 7.35 (AA’BB’ system, 4H), 5.94 (d, 1H, J = 10.2 Hz), 5.70 (dd, 1H, J = 3.2 and 10.2 Hz), 4.21 (m, 1H), 3.60 (s, 1H), 3.53 and 3.31 (AB system, 2H, J = 14.5 Hz), 2.44 (s, 3H), 2.32 (m, 1H), 1.89 (ddd, 1H, J = 5.4, 8.1, 13.5 Hz), 1.56 (ddd, 1H, J = 3.2, 5.3, 13.5 Hz), 1.00 (d, 3H, J = 7.0 Hz), 0.87 (s, 9H), 0.05 (s, 6H); ¹³C RMN δ 144.9, 138.3, 131.9, 130.8, 129.9 (2C), 127.6 (2C), 71.6, 64.1, 63.8, 36.5, 34.5, 25.9, 25.8 (3C), 21.6, 18.2, 14.3, −4.5 (2C).
(4R,6S)-4-[(tert-Butyldimethylsilyl)oxy]-6-methyl-2-cyclohexenone (6).

Compound 6 was obtained following method E from 5 (80 mg, 0.19 mmol), in 89% yield after flash chromatography (EtOAc/hexane 3:1), as a colorless oil: \([\alpha]_D^{20} = +67.0 \; (c \; 0.4, \; \text{acetone})\); \(^1\)H RMN \(\delta \) 6.77 (dt, 1H, \(J = 10.1 \) and 2.0 Hz), 5.91 (dd, 1H, \(J = 2.4 \) and 10.1 Hz), 4.59 (m, 1H), 2.38 (m, 1H), 2.21 (m, 1H), 1.77 (dt, 1H, \(J = 10.5 \) and 12.5 Hz), 1.14 (d, 3H, \(J = 6.5 \) Hz), 0.91 (s, 9H), 0.12 (s, 6H); \(^{13}\)C RMN \(\delta \) 201.1, 154.1, 128.3, 68.1, 41.9, 40.2, 25.7 (3C), 18.1, 15.0, –3.5, –3.7; MS (EI): \(m/z \) (%) 183 ([M – C\(_4\)H\(_9\)]\(^+\), 99), 165 (7), 139 (13), 113 (11), 85.9 (40), 84 (62), 75 (100); HRMS (EI) calcd for C\(_9\)H\(_{15}\)O\(_2\)Si (M – C\(_4\)H\(_9\))\(^+\) 183.0841, found 183.0844.

(4S)-4-Hydroxy-3,5,5-trimethyl-4-[(\(p\)-tolylsulfonyl)methyl]-2-cyclohexenone (3b).

Compound 3b was obtained following method A from 2b\(^1\) (2.40 g, 7.83 mmol), in 85 % yield as a white solid: mp 145-146 °C (AcOEt/hexane); \([\alpha]_D^{20} = -25.4 \; (c \; 0.5, \; \text{CHCl}_3)\); \(^1\)H RMN \(\delta \) 7.79 and 7.39 (AA’BB’ system, 4H), 5.92 (broad s, 1H), 4.58 (s, 1H), 3.53 and 3.34 (AB system, 2H, \(J = 13.9 \) Hz), 2.47 (s, 3H), 2.26 (d, 3H, \(J = 1.2 \) Hz), 2.25 (s, 2H), 1.07 (s, 6H); \(^{13}\)C RMN \(\delta \) 196.2, 165.1, 145.5, 137.3, 130.1 (2C), 127.5(2C), 126.8, 77.1, 61.7, 48.9, 42.6, 23.6, 22.3, 21.6, 21.1; MS (EI): \(m/z \) (%) 322 (M\(^+\), 0.2), 266 (8), 170 (18), 155 (18), 111 (100), 91 (67), 68 (34); HRMS (EI) calcd for C\(_{17}\)H\(_{22}\)O\(_4\)S (M\(^+\)) 322.1239, found 322.1233.
(1S,4R)-2,6,6-Trimethyl-1-[(p-tolylsulfonyl)methyl]-2-cyclohexene-1,4-diol (7).

![Structural formula of compound 7]

Compound 7 was obtained following method C from 3b (101 g, 0.31 mmol), in 71% yield as a colorless oil: \([\alpha]_D^{20} = +60.0 (c 1, \text{acetone})\); \(^1\)H RMN \(\delta 7.79\) and 7.35 (AA’BB’ system, 4H), 5.54 (broad s, 1H), 4.15 (m, 1H), 4.09 (s, 1H), 3.42 and 3.25 (AB system, 2H, \(J = 14.5\) Hz), 2.44 (s, 3H), 1.94 (t, 3H, \(J = 1.1\) Hz), 1.77 (dd, 1H, \(J = 6.8\) and 14.9 Hz), 1.65 (ddd, 1H, \(J = 1.1, 4.4\) and 14.9 Hz), 1.06 and 0.93 (2s, 6H); \(^{13}\)C RMN \(\delta 144.9, 139.2, 138.1, 129.9\) (2C), 127.6 (2C), 127.2, 76.4, 63.9, 60.9, 42.3, 38.0, 23.7 (2C), 21.6, 19.6; FAB-MS \(m/z\) (rel intens) 323 ([M – H]+, 31), 307 (100), 289 (72); HRMS (FAB) calcd for C\(_{17}\)H\(_{23}\)O\(_4\)S [M – H]\(^+\) 323.1317, found 323.1313.

(4R)-4-Hydroxy-2,6,6-trimethyl-2-cyclohexenone (9).

![Structural formula of compound 9]

Compound (+)-9 was obtained following method E from 7 (100 mg, 0.31 mmol), in 90% yield after flash chromatography (CH\(_2\)Cl\(_2\)/acetone 10:1), as a colorless oil: \([\alpha]_D^{20} = +48.0 (c 2, \text{EtOH})\) \([\text{Lit}^{2} \ [\alpha]_D^{20} = +52.7 (c 0.45, \text{EtOH})]\); \(^1\)H RMN \(\delta 6.61\) (q, 1H, \(J = 1.7\) Hz), 4.58 (m, 1H), 2.13 (ddd, 1H, \(J = 2.0, 5.0, 12.6\) Hz), 1.82 (dd, 1H, \(J = 10.0\) and 12.8 Hz), 1.77 (d, 1H, \(J = 1.7\) Hz), 1.13 and 1.10 (2s, 6H); \(^{13}\)C RMN \(\delta 203.8, 146.1, 133.7, 64.9, 46.7, 41.9, 25.8, 24.4, 16.1\); MS (EI): \(m/z\) (%) 154 (M\(^+\), 5), 111 (14), 98 (87), 84 (100), 70 (45); HRMS (EI) calcd for C\(_9\)H\(_{14}\)O\(_2\) (M\(^+\)) 154.0994, found 154.0987.

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(1S,4S)-2,6,6-Trimethyl-1-[(p-tolylsulfonyl)methyl]-2-cyclohexene-1,4-diol (8).

![Chemical Structure of 8](image)

Compound 8 was obtained following method B from 3b (50 mg, 0.16 mmol), in 64% yield as a colorless oil: $[\alpha]_D^{20} = +17.0$ (c 0.3, acetone); $^1$H RMN $\delta$ 7.79 and 7.33 (AA’BB’ system, 4H), 5.62 (broad s, 1H), 4.09 (m, 1H), 3.40 and 3.24 (AB system, 2H, $J = 14.5$ Hz), 2.42 (s, 3H), 1.83 (broad s, 3H), 1.73-1.39 (m, 2H), 0.98 and 0.95 (2s, 6H); $^{13}$C RMN $\delta$ 145.1, 140.4, 138.3, 130.1 (2C), 127.9 (2C), 127.0, 77.7, 65.4, 62.5, 43.8, 41.6, 24.7, 22.2, 21.8, 18.6.

(4S)-4-Hydroxy-2,6,6-trimethyl-2-cyclohexenone (9).

![Chemical Structure of (-)-9](image)

Compound (-)-9 was obtained following method E from 8 (27 mg, 0.08 mmol), in 93% yield after flash chromatography (CH$_2$Cl$_2$/hexane 12:1), as a colorless oil: $[\alpha]_D^{20} = -44.0$ (c 0.2, EtOH) [Lit$^2$ $[\alpha]_D^{20} = -50.0$ (c 0.1, EtOH)].

2,6,6-Trimethylcyclohexene-1,4-dione (10b).

![Chemical Structure of 10b](image)

Compound 10b$^3$ was obtained following method E from 3b (47 mg, 0.15 mmol), in 54% yield after flash chromatography (eluent EtOAc/hexane 1:15), as a colourless oil: $^1$H-NMR $\delta$ 6.70 (broad s, 1H), 2.71 (s, 2H), 2.01 (s, 3H), 1.21 (s, 6H).

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$^3$ This compound, also named 4-oxoisophorone, is commercially available.
(4R,5S)-4-Hydroxy-5-ethyl-3,5-dimethyl-4-[(p-tolylsulfonyl)methyl]-2-cyclohexenone (3c).

Compound 3c was obtained following method A from 2c\(^1\) (99 mg, 0.31 mmol), in 95% yield as a white solid: mp 107-108 °C (ethyl ether); [α]\(_D\)\(^{20}\) = −36.0 (c 0.9, CHCl\(_3\)); \(^1\)H RMN \(\delta \) 7.79 and 7.38 (AA’BB’ system, 4H), 5.93 (t, 1H, \(J = 1.4 \) Hz), 4.55 (broad s, 1H), 3.58 and 3.38 (AB system, 2H, \(J = 13.7 \) Hz), 2.47 (s, 3H), 2.45 and 2.04 (AB system, 2H, \(J = 18.6 \) Hz) 2.26 (d, 3H, \(J = 1.4 \) Hz), 1.74-1.43 (m, 2H), 0.99 (s, 3H), 0.79 (t, \(J = 7.5 \) Hz, 3H); \(^13\)C RMN \(\delta \) 196.1, 165.7, 145.4, 137.2, 130.0 (2C), 127.5 (2C), 127.1, 78.0, 61.9, 45.6, 44.2, 24.7, 21.5, 21.3, 19.3, 8.5; MS (EI): \(m/z\) (%) 336 (M\(^+\), 0.14), 307 (1.6), 266 (10), 170 (10), 155 (2), 124 (8), 111 (100), 91 (46), 68 (20); HRMS (EI) calcd for C\(_{18}\)H\(_{24}\)O\(_4\)S (M\(^+\)) 336.1395, found 336.1386.

(6S)-6-Ethyl-2,6-dimethyl-2-cyclohexene-1,4-dione (10c).

Compound 10c\(^4\) was obtained following method E from 3c (15 mg, 0.07 mmol), in 70% yield after flash chromatography (eluent EtOAc/hexane 1:10), as a yellowish oil: [α]\(_D\)\(^{20}\) = +0.6 (c 0.6, CHCl\(_3\)); \(^1\)H-NMR \(\delta \) 6.55 (bs, 1H), 2.78 (dd, \(J = 16.4 \) and 0.8 Hz, 1H), 2.65 (d, \(J = 16.4 \) Hz, 1H), 1.99 (d, \(J = 1.6 \) Hz, 3H), 1.79-1.51 (m, 2H), 1.19 (s, 3H), 0.82 (t, \(J = 7.5 \) Hz, 3H); \(^13\)C-NMR \(\delta \) 203.2, 198.1, 149.3, 137.0, 49.6, 48.7, 32.2, 23.2, 16.7; MS (EI): \(m/z\) (%) 166 (M\(^+\), 56), 151 (15), 95 (76), 83 (37), 68 (77) 55 (100); HRMS (EI) calcd for C\(_{10}\)H\(_{14}\)O\(_2\) (M\(^+\)) 166.0994, found 166.0993.

(4R,5S)-5-(1-Hexynyl)-4-hydroxy-3,5-dimethyl-4-[(ρ-tolysulfonyl)methyl]-2-cyclohexenone (3d).

Compound 3d was obtained following method A from 2d\textsuperscript{1} (150 mg, 0.40 mmol), in 99% yield as a white solid: mp 86-87 °C (ethyl ether); [α]\textsubscript{D}\textsuperscript{20} = +15.0 (c 1, CHCl\textsubscript{3}); \textsuperscript{1}H NMR δ 7.78 and 7.34 (AA′BB′ system, 4H), 5.91 (d, 1H, J = 1.4 Hz), 3.74 (broad s, 1H), 3.52 and 3.36 (AB system, 2H, J = 14.1 Hz), 2.71-2.46 (m, 2H), 2.43 (s, 3H), 2.19 (d, 3H, J = 1.4 Hz), 2.08 (t, 2H, J = 6.9 Hz), 1.43-1.22 (m, 4H), 1.32 (s, 3H), 0.84 (t, 3H, J = 7.3 Hz); \textsuperscript{13}C RMN δ 195.2, 145.2, 137.5, 129.9 (2C), 127.8 (2C), 127.6, 85.1, 81.1, 75.8, 60.3, 47.8, 44.8, 30.6, 22.7, 21.6, 21.6, 20.9, 18.1, 13.4. Anal. calcd. for C\textsubscript{22}H\textsubscript{28}O\textsubscript{4}S: C, 68.01; H, 7.26. Found C, 67.78; H, 7.43.

(6R)-6-(1-Hexynyl)-2,6-dimethyl-2-cyclohexene-1,4-dione (10d).

Compound 10d was obtained following method E from 3d (42 mg, 0.108 mmol), in 68% yield after flash chromatography (EtOAc/hexane 1:10), as a yellowish oil: [α]\textsubscript{D}\textsuperscript{20} = −3.0 (c 0.8, CHCl\textsubscript{3}); \textsuperscript{1}H-NMR δ 6.53 (q, J = 1.4 Hz, 1H), 2.97 (dd, J = 15.8 and 1.4 Hz, 1H), 2.76 (d, J = 15.8 Hz, 1H), 2.10 (t, J = 6.9 Hz, 2H), 2.04 (d, J = 1.4 Hz, 3H), 1.45 (s, 3H), 1.43-1.22 (m, 4H), 0.86 (t, J = 7.1 Hz, 3H); \textsuperscript{13}C-NMR δ 196.3, 195.8, 149.4, 136.9, 85.3, 80.1, 51.3, 44.0, 30.5, 23.9, 21.7, 18.3, 17.1, 13.5; MS (EI): m/z (%) 218 (M\textsuperscript{+}, 13), 203 (20), 190 (32), 175 (32), 161 (30), 147 (25), 133 (17), 96 (100), 68 (82); HRMS (EI) calcd for C\textsubscript{14}H\textsubscript{18}O\textsubscript{2} (M\textsuperscript{+}) 218.1307, found 218.1304.
(3R,4S,5S)-3-Ethyl-4-hydroxy-5-methyl-4-[(p-tolylsulfonyl)methyl]-cyclohexanone (14).

Compound 14 was obtained following method A from 13\textsuperscript{1} (235 mg, 0.76 mmol), in 98% yield as a white solid: mp 147-148 °C (ethyl ether); [α]D\textsuperscript{20} = +9.0 (c 1, acetone); \textsuperscript{1}H NMR δ 7.76 and 7.34 (AA′BB′ system, 4H), 3.44 and 3.38 (AB system, 2H, J = 14.4 Hz), 2.49-2.12 (m, 6H), 2.39 (s, 3H), 1.83-1.76 (m, 1H), 1.30-1.22 (m, 1H), 1.04 (d, 3H, J = 6.0 Hz), 0.85 (t, 3H, J = 7.3 Hz); \textsuperscript{13}C RMN δ 210.2, 144.9, 138.0, 130.0 (2C), 127.6 (2C), 74.9, 59.4, 45.5, 44.8, 40.9, 39.3, 22.7, 21.6, 15.8, 11.3. Anal. calcd. for C\textsubscript{17}H\textsubscript{24}O\textsubscript{4}S: C, 62.94; H, 7.46; S, 9.88. Found C, 63.06; H, 7.13; S, 9.71.

(1S,2R,4S,6S)-2-Ethyl-6-methyl-1-[(p-tolylsulfonyl)methyl]-cyclohexane-1,4-diol (15).

Compound 15 was obtained following method C from 14 (130 mg, 0.40 mmol), in 73 % yield after flash chromatography (EtOAc/hexane 1:1), as a white solid: mp 146-147 °C; [α]D\textsuperscript{20} = +3.0 (c 1, acetone); \textsuperscript{1}H-RMN δ 7.80 and 7.33 (AA′BB′ system, 4H), 4.05 (m, 1H), 3.44 and 3.35 (AB system, 2H, J = 15.0 Hz), 2.43 (s, 3H), 2.43-2.32 (m, 1H), 2.09-1.97 (m, 1H), 1.86-1.38 (m, 5H), 1.22-1.05 (m, 1H), 0.90 (d, 3H, J = 7.5 Hz), 0.87 (t, 3H, J = 6.9 Hz); \textsuperscript{13}C-RMN δ 144.6, 138.3, 129.9 (2C), 127.7 (2C), 75.9, 65.5, 60.3, 39.4, 36.8, 32.9, 32.6, 22.0, 21.6, 15.4, 11.9. Anal. calcd. for C\textsubscript{17}H\textsubscript{26}O\textsubscript{4}S: C, 62.55; H, 8.03; S, 9.82; Found: C, 62.33; H, 7.81; S, 10.06.
(1S,2R,4R,6S)-2-Ethyl-6-methyl-1-[p-tolylsulfonyl)methyl]-cyclohexane-1,4-diol (16).

![Structural formula of compound 16](image)

Compound 16 was obtained following method B from 14 (124 mg, 0.38 mmol), in 75% yield after flash chromatography (EtOAc/hexane 1:1), as a white solid: mp 87-88 ºC (EtOAc/hexane); $[\alpha]_D^{20} = +3.8$ (c 1, CHCl₃); $^1$H-NMR δ 7.79 and 7.35 (AA´BB´ system, 4H), 3.77-3.67 (m, 1H), 3.39 and 3.30 (AB system, 2H, $J = 14.5$ Hz), 2.45 (s, 3H), 2.28-2.15 (m, 1H), 2.09-1.97 (m, 1H), 1.95-1.64 (m, 3H), 1.50-1.32 (m, 1H), 1.29-1.08 (m, 2H), 1.01 (d, 3H, $J = 6.5$ Hz), 0.95 (t, $J = 7.3$ Hz, 3H); $^{13}$C-NMR δ 144.9, 138.7, 130.1 (2C), 127.8 (2C), 75.5, 59.5, 43.7, 37.3, 35.1, 22.4, 21.8, 19.8, 15.8, 15.6, 12.0. Anal. calcd. for C₁₇H₂₆O₄S: C, 62.94; H, 7.46; S, 9.88. Found: C, 63.06; H, 7.13; S, 9.71.

(1S,2R,4S,6S)-4-(terc-Butyldimethylsilyloxy)-2-ethyl-6-methyl-1-[p-tolylsulfonyl)methyl]-cyclohexan-1-ol (17).

![Structural formula of compound 17](image)

Compound 17 was obtained following method D from 15 (95 mg, 0.29 mmol), in 81% yield after flash chromatography (EtOAc/hexane 4:1), as a white solid: mp 121-122 ºC (EtOAc/hexane); $[\alpha]_D^{20} = +1.0$ (c 1, acetone). $^1$H-NMR δ 7.78 and 7.32 (AA´BB´ system, 4H), 4.05 (m, 1H), 3.42 and 3.35 (AB system, 2H, $J = 14.5$ Hz), 2.42 (s, 3H), 2.45-2.31 (m, 1H), 2.13-1.94 (m, 1H), 1.82-0.90 (m, 5H), 0.92-0.86 (m, 15H), 0.07 (s, 6H); $^{13}$C-NMR δ 144.4, 138.4, 129.7 (2C), 127.9 (2C), 75.9, 65.9, 60.7, 39.7, 37.0, 33.2 (2C), 25.8 (3C), 21.8, 21.6, 15.9, 15.4, 11.9, −3.4 (2C). Anal. calcd. for C₂₃H₄₀O₄Si: C, 62.68; H, 9.15; S, 7.27; Found: C, 62.57; H, 8.98; S, 7.33.
(1S,2R,4R,6S)-4-(terc-Butyldimethylsilyloxy)-2-ethyl-6-methyl-1-[(p-tolylsulfonyl)methyl]-cyclohexan-1-ol (18).

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\text{OTBDMS} \quad \text{Me} \quad \text{HO} \quad \text{SO}_2\text{p-Tol} \quad 18
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Compound 18 was obtained following method D from 16 (90 mg, -0.27 mmol), in 87% yield after flash chromatography (EtOAc/hexane 1:4), as a white solid: mp 121-122 °C (EtOAc/hexane); \(\alpha\)\textsubscript{D}\textsuperscript{20} = +3.8 (c 0.8, CHCl\textsubscript{3}). \(\text{H-NMR}\ \delta\) 7.75-7.32 (AA′BB′ system, 4H), 3.70-3.60 (m, 1H), 3.36 and 3.27 (AB, J = 14.5 Hz, 2H), 2.41 (s, 3H), 2.25-2.16 (m, 1H), 1.94-1.60 (m, 4H), 1.46-1.33 (m, 2H), 1.28-1.13 (m, 3H), 0.97 (d, J = 6.4 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H), 0.86 (s, 9H), 0.05 (s, 6H); \(\text{C-NMR}\ \delta\) 144.4, 138.4, 129.8 (2C), 127.3 (2C), 75.3, 69.6, 58.8, 43.2, 39.6, 36.8, 25.8 (3C), 25.5, 22.1, 21.5, 18.0, 15.6, 11.7, –3.7 (2C); FAB-MS \(m/z\) (rel int.) 441 ([M + H]+, 100), 423 (47), 383 (32), 291 (74), 267 (62), 231 (41), 213 (43); HRMS (FAB) calcd for C\textsubscript{23}H\textsubscript{41}O\textsubscript{4}Si ([M + H]+) 441.2516, found 441.2495.

\textbf{(2R, 4S, 6S)-2-Ethyl-6-methyl-4-(terc-butyldimethylsilyloxy) -cyclohexanone (11).}

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\text{OTBDMS} \quad \text{Me} \quad \text{Et} \quad 11
\]

Compound 11 was obtained following method E from 17 (50 mg, 0.11 mmol), in 60% yield after flash chromatography (hexane), as a colourless oil: \(\alpha\)\textsubscript{D}\textsuperscript{20} = –1.7 (c 1.1, CHCl\textsubscript{3}); \(\text{H-NMR}\ \delta\) 4.13 (q, 1H, J = 2.8 Hz), 2.91 (sept, 1H, J = 6.5 Hz), 2.71 (sext, 1H, J = 6.1 Hz), 2.08 (m, 2H), 1.79 (sept, 1H, 6.5 Hz), 1.49 (m, 2H), 1.17 (m, 1H), 0.98 (d, 3H, J = 6.5 Hz), 0.92 (s, 9H), 0.87 (t, 3H, J = 7.7 Hz), 0.09 (s, 6H); \(\text{C-NMR}\ \delta\) 214.8, 66.0, 45.9, 44.5, 41.7, 39.5, 25.8 (3C), 21.6, 18.0, 14.1, 11.7, –3.4 (2C); MS (EI): \(m/z\) (%) 213 ([M – C\textsubscript{4}H\textsubscript{9}]\textsuperscript{+}, 70), 171 (100), 157 (82), 143 (9) 129 (32), 101 (11), 86 (46), 75 (92); HRMS (EI) calcd for C\textsubscript{11}H\textsubscript{21}O\textsubscript{2}Si ([M – C\textsubscript{4}H\textsubscript{9}]\textsuperscript{+} 213.1311, found 213.1309.
(2R, 4R, 6S)-2-Ethyl-6-methyl-4-(tert-butyldimethylsilyloxy)-cyclohexanone (12).

Compound 12 was obtained following method E from 18 (80 mg, 0.18 mmol), in 89% yield after flash chromatography (EtOAc/hexane 1:10), as a colourless oil: \([\alpha]_D^{20} = -4.5\) (c 1.1, CHCl₃); \(^1\)H-NMR \(\delta\) 4.15 (m, 1H), 2.42 (m, 1H), 2.17 (m, 1H), 1.78 (m, 1H), 1.51-1.34 (m, 2H), 1.28-1.17 (m, 2H), 0.99 (d, 3H, \(J = 6.5\) Hz), 0.88 (t, 3H, \(J = 7.3\) Hz), 0.89 (s, 9H), 0.09 (s, 6H); \(^1^3\)C-NMR \(\delta\) 212.7, 69.1, 48.4, 44.9, 42.3, 41.9, 25.8 (3C), 21.9, 18.1, 14.3, 11.7, -3.6 (2C); MS (EI): \(m/z\) (%) 213 ([M – C₄H₉]⁺, 65), 171 (100), 157 (85), 129 (27), 75 (67); HRMS (EI) calcd for C₁₃H₂₁O₂Si ([M – C₄H₉]⁺ 213.1279, found 213.1320.