Supporting information:

General experimental remarks: Reagents were purchased from Aldrich, Acros Chimica, Merck or Fluka and were used as received unless otherwise stated. All solvents were reagent grade and were dried and distilled before use according to standard procedures. Chromatography: silica gel, Merck type 9385 230-400 mesh, TLC: silica gel 60, Merck, 0.25 mm. Components were visualized by staining with a) $KMnO_4$, b) a mixture of *p*-methoxybenzaldehyde (2.1 mL), AcOH (1.8 mL), H_2SO_4 (6.3 mL) and EtOH (170 mL) or c) a mixture of Phosphomolybdic acid (25 g), cerium (IV) sulfate (7.5 g), H_2O (500 mL) and H_2SO_4 (25 mL). Mass spectra (HRMS) were recorded on an AEI MS-902. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 (50.32 MHz), a Varian VXR300 (75.48 MHz) or a Varian AMX400 (100.59 MHz) spectrometer in $CDCl_3$. Chemical shift values are denoted in δ values (ppm) relative to residual solvent peaks ($CHCl_3$, ^1H δ=7.26, ^{13}C δ =76.9). Carbon types were determined from APT ^{13}C experiments. Enantio- and diastereoselectivities were determined by capillary GC analysis (Chiraldex B-TA column (30 m x 0.25 mm) or Betadex 120 column (30 m x 0.25 mm)) using a flame ionization detector (in comparison with racemic products). The racemic product **3** was synthesized by 1,4-addition of Me_2CuLi to **1** in Et_2O at 0 ^oC. A racemic mixture of diastereoisomers **5a/5b** was synthesized by 1,4-addition of Me_2CuLi to racemic **3** in Et_2O at 0 ^oC followed by trapping of the enolate with TMSCl in the presence of Et_3N.

(R)-7-Methyl-cyclooct-2-enone (3): $Cu(OTf)_2$ (148 mg, 0.409 mmol, 5 mol%) and R,S,S-L_1 (441 mg, 0.818 mmol, 10 mol%) were dissolved in dry toluene (25 mL) and stirred at rt for 30 minutes under argon. The solution was cooled to -25 ^oC and Me_2Zn (2.0 M in toluene, 20.5 mL, 40.9 mmol, 5.0 eq) was added over 2 minutes. After stirring for 5 minutes, **2** (1.0 g, 8.2 mmol) dissolved in toluene (25 mL) was added *via* a syringe pump over 5 hours. The resulting solution was stirred at -25 ^oC overnight and then quenched with sat. NH_4Cl, extracted with Et_2O (3x), washed with brine and dried (Na_2SO_4). The Et_2O was removed under vacuüm and the product purified by column chromatography (pentane : Et_2O 95:5 to 9:1) to give **3** as a colorless liquid (0.97 g, 7.0 mmol, 85%, ee >99%) and **4** (< 5%) as a colorless oil. ^1H-NMR ($CDCl_3$, 400 MHz) δ = 1.01 (d, *J* = 6.8, 3H), 1.36 (m, 1H), 1.56-1.74 (m, 3H), 2.13 (m, 1H), 2.46 (dd, *J* = 8.4, 13.6, 1H), 2.42-2.62 (m, 2H), 2.70 (dd, *J* = 5.6, 13.6, 1H), 6.04 (d, *J* = 12.0, 1H), 6.35 (dt, *J* = 7.2, 12.4, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 50.3 MHz) δ = 21.5 (t), 21.8 (q), 28.0 (t), 28.8 (d), 32.0 (t), 50.0 (t), 133.3 (d), 141.5 (d), 204.4 (s) ppm. Ee determination: GC Chiraldex B-TA, 30 m x 0.25 mm, He-flow = 1.0 mL/min, T_i = 70 ^oC for 5 min, T_f = 150 ^oC, rate 10 ^oC/min, rt 23.5 (S), 23.8 (R) min. MS(EI) for $C_9H_{14}O$: m/z = 138 [M^+], HRMS calcd for $C_9H_{14}O$: 138.104, found: 138.105.
^1H-NMR **4** ($CDCl_3$, 400 MHz) δ = 1.06 (d, *J* = 6.8, 3H), 1.42-1.82 (m, 8H), 2.11-2.27 (m, 3H), 2.40-2.66 (m, 6H), 5.80 (d, *J* = 12.4, 1H), 5.86 (d, *J* = 12.4, 1H), 6.22 (m, 2H) ppm. ^{13}C-NMR **4** ($CDCl_3$, 50.3 MHz) δ = 18.4 (q), 20.3 (t), 22.6 (t), 28.4 (t), 29.8 (d), 30.0 (t), 30.1 (t), 33.4 (d), 48.7 (t), 61.3 (d), 128.6 (d), 138.7 (d), 140.4 (d), 207.4 (s) ppm. MS(CI) for $C_{17}H_{24}O_2$: m/z = 278 $(M + NH_4)^+$.

[((3R,7R)-3,7-Dimethyl-cyclooct-1-yl)oxy]-trimethylsilane (5a): $Cu(OTf)_2$ (6.6 mg, 18 μmol, 2.5 mol%) and R,S,S-L_1 (20 mg, 37 μmol, 5 mol%) were dissolved in dry DCM

(2.5 mL) and stirred at rt for 30 minutes under argon. Subsequently the solution was cooled to -25 ^{o}C and Me_2Zn (2.0 M in toluene, 0.54 mL, 1.08 mmol, 1.5 eq) was added over 2 minutes. After stirring for 5 minutes, **3** (100 mg, 0.72 mmol) dissolved in DCM (2 mL) was added *via* a syringe pump over 5 hours. The resulting solution was stirred at -25 ^{o}C overnight after which Et_3N (0.30 mL, 2.17 mmol, 3.0 eq), TMEDA (0.55 mL, 3.6 mmol, 5.0 eq) and a pre-stirred (30 min) solution of TMSOTf (0.65 mL, 3.62 mmol, 5.0 eq) and Et_2Zn (1.1 M in toluene, 0.27 mL, 0.30 mmol, 0.42 eq) were added. The mixture was then stirred for 2 hours while slowly warming to ambient temperature. Et_2O (2.5 mL) was added to the solution and the reaction mixture was flashed over a silica-plug (SiO_2 inactivated with Et_3N prior to use). The Et_2O was evaporated under vacuüm and the product purified by column chromatography (pentane; SiO_2 inactivated with Et_3N prior to use) to give **5a** (ee > 99%, de > 98%) as a volatile colorless liquid with still some toluene present. **5a** was immediately used in the next step without further removal of the toluene. For the purpose of analysis the toluene was removed in vacuo from a small sample of the product. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.18 (s, 9H), 0.89 (d, *J* = 6.8, 3H), 0.97 (d, *J* = 6.4, 3H), 0.92-1.16 (m, 3H), 1.36-1.78 (m, 5H), 2.12-2.32 (m, 2H), 4.35 (d, *J* = 8.8, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ = 0.4 (q), 22.5 (q), 23.2 (q), 23.6 (t), 30.8 (d), 33.5 (d), 34.9 (t), 39.7 (t), 40.5 (t), 111.9 (d), 151.0 (s) ppm. MS(EI) for $C_{13}H_{26}OSi$: m/z = 226 [M^+]. Ee determination: Betadex 120, 30 m x 0.25 mm, He-flow = 1.0 mL/min, T = 100 ^{o}C for 30 min, rt. 22.9 (3S,7S), 23.7 (3R,7R) min.

[((3S,7R)-3,7-Dimethyl-cyclooct-1-yl)oxy]-trimethylsilane (5b): $Cu(OTf)_2$ (16 mg, 45 µmol, 2.5 mol%) and S,R,R-L_1 (49 mg, 90 µmol, 5 mol%) were dissolved in dry DCM (6.3 mL) and stirred at rt for 30 minutes under argon. Subsequently the solution was cooled to -25 ^{o}C and Me_2Zn (2.0 M in toluene, 1.36 mL, 2.71 mmol, 1.5 eq) was added over 2 minutes. After stirring for 5 minutes, **3** (250 mg, 1.81 mmol) dissolved in DCM (5 mL) was added *via* a syringe pump over 5 hours. The resulting solution was stirred at -25 ^{o}C overnight after which Et_3N (0.76 mL, 5.5 mmol, 3.0 eq, freshly distilled from CaH_2), HMPA (1.6 mL, 9.0 mmol, 5.0 eq, freshly distilled from CaH_2 under reduced pressure) and a pre-strirred (30 min) solution of TMSCl (1.15 mL, 9.0 mmol, 5.0 eq, freshly distilled from CaH_2) and Et_2Zn (1.1 M in toluene, 0.69 mL, 0.76 mmol, 0.42 eq) were added. The resulting mixture was stirred for 2 hours while slowly warming to ambient temperature. Isolation was performed as for compound **5a** to give **5b** (ee > 99%, de >98%) as a volatile colorless liquid with still some toluene present. **5b** was immediately used in the next step without further removal of the toluene.Complete removal of toluene in vacuo was performed for an analytical sample. NMR data as reported in literature[4b]: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.18 (s, 9H), 0.95 (d, *J* = 4.8, 3H), 0.97 (d, *J* = 4.8, 3H), 1.08-1.18 (m, 1H), 1.21-1.36 (m, 2H), 1.53-1.61 (m, 2H), 1.70-1.79 (m, 2H), 1.87-1.98 (m, 1H), 2.21- 2.32 (m, 1H), 2.60 (dd, *J* = 4.8, 14.0, 1H), 4.44 (d, *J* = 7.6, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ = 0.3 (q), 21.5 (q), 23.5 (q), 24.7 (t), 32.0 (d), 33.7 (d), 34.2 (t), 37.1 (t), 39.7 (t), 113.3 (d) 149.9 (s) ppm. MS(EI) for $C_{13}H_{26}OSi$: m/z = 226 [M^+]. Ee determination: Betadex 120, 30 m x 0.25 mm, He-flow = 1.0 mL/min, T = 100 ^{o}C for 30 min, rt. 23.9 (3R,7S), 25.7 (3S,7R) min.

Methyl 8-hydroxy-(3R,7R)-3,7-dimethyloctanoic acid (1a): 5a (0.72 mmol) was dissolved in MeOH (3.6 mL) and DCM (3.6 mL) and O_3 was bubbled through the

solution at -78 °C until the solution colored green/blue (10-15 min). The solution was then purged with nitrogen, after which $NaBH_4$ (274 mg, 7.2 mmol, 10 eq) was added and the reaction mixture was allowed to slowly warm to ambient temperature. After stirring overnight, the reaction mixture was concentrated and the residue was taken up in Et_2O. Subsequently, 10% HCl (aq) was added and the water layer was extracted with Et_2O (3x). The combined ether extracts were dried ($MgSO_4$) and concentrated. The crude product was used in the next reaction without purification. An analytical sample was purified by column chromatography (pentane-EtOAc 1:2) to give **6a** as a colorless oil. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 0.91 (d, *J* = 6.6, 3H), 0.96 (d, *J* = 6.6, 3H), 1.06-1.45 (m, 7H), 1.61 (m, 1H), 1.97 (m, 1H), 2.11 (dd, *J* = 7.6, 14.8, 1H), 2.33 (dd, *J* = 5.7, 14.8, 1H), 3.46 (m, 2H), 7.04 (s,br, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ = 16.3 (q), 19.5 (q), 24.0 (t), 29.9 (d), 32.9 (t), 35.3 (d), 36.6 (t), 41.5 (t), 67.9 (t), 178.5 (s) ppm. MS(CI) for $C_{10}H_{20}O_3$: m/z = 206 $(M + NH_4)^+$, HRMS calcd for $C_{10}H_{20}O_3$-O: 172.146, found: 172.147. **6a** was dissolved in anhydrous MeOH (11 mL) and TMSCl (0.26 mL, 2.1 mmol, 3.0 eq) was added. The resulting solution was heated under reflux overnight while protected from moisture with a $CaCl_2$-tube, after which TLC (pentane-EtOAc 4:1) showed complete conversion. The mixture was cooled to room temperature and concentrated. $NaHCO_3$ (sat) was added to the residue and the product was extracted with Et_2O (3x). The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated. The product **1a** (65 mg, 0.32 mmol, 45% from **3**) was isolated as a colorless oil after purification by column chromatography (pentane-EtOAc 6:1 to 3:1). $[\alpha]_D^{20}$ (3R,7R)-**1a** = +15.6 (c = 1.27, $CHCl_3$), $[\alpha]_D^{20}$ (3S,7S)-**1a** = -14.4 (c = 0.71, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.90 (d, *J* = 6.8, 3H), 0.92 (d, *J* = 6.8, 3H), 1.05-1.42 (m, 7H), 1.60 (m, 1H), 1.94 (m, 1H), 2.11 (dd, *J* = 8.0, 14.4, 1H), 2.33 (dd, *J* = 6.4, 14.4, 1H), 3.41 (dd, *J* = 6.4, 10.8, 1H), 3.48 (dd, *J* = 6.0, 10.8, 1H), 3.65 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ = 16.4 (q), 19.6 (q), 24.1 (t), 30.1 (d), 33.0 (t), 35.5 (d), 36.7 (t), 41.6 (t), 51.3 (q), 68.2 (t), 173.7 (s) ppm. MS(CI) for $C_{11}H_{22}O_3$: m/z = 220 $(M + NH_4)^+$, HRMS calcd for $C_{11}H_{22}O_3$-O: 186.162, found: 186.162.

Methyl 8-hydroxy-(3R,7R)-3,7-dimethyloctanoic acid (1a) using a one-pot conversion of 3 into 6a: Silyl enol ether **5a** was formed as described earlier starting from 50 mg (0.36 mmol) of **3**. To the reaction mixture was added MeOH (2.0 mL) and O_3 was bubbled through the solution at -78 °C until the solution colored green (5 min). The solution was then purged with nitrogen, after which $NaBH_4$ (137 mg, 3.6 mmol, 10 eq) was added and the reaction mixture was allowed to slowly warm to ambient temperature. After stirring overnight, the reaction mixture was concentrated and the residue was taken up in Et_2O. Subsequently, 10% HCl (aq) was added and the water layer was extracted with Et_2O (3x). The combined ether extracts were dried ($MgSO_4$) and concentrated. The crude carboxylic acid was dissolved in anhydrous MeOH (5.0 mL) and heated under reflux with a $CaCl_2$-tube in the presence of TMSCl (0.14 mL, 1.08 mmol, 3.0 eq). After work-up and purification (see **1a**), the product **1a** (29 mg, 0.14 mmol, 40%) and a side product which proved to be 2,6-Dimethyl-octanedioic acid dimethyl ester (30 mg, 0.13 mmol, 36%) were isolated as colorless oils. ^{1}H-NMR 2,6-Dimethyl-octanedioic acid dimethyl ester ($CDCl_3$, 300 MHz) δ = 0.91 (d, *J* = 6.6, 3H), 1.13 (d, *J* = 6.9, 3H,), 1.12-1.67 (m, 6H), 1.93 (m, 1H), 2.09 (dd, *J* = 7.8, 15.0, 1H), 2.28 (dd, *J* = 5.7, 15.0, 1H), 2.42 (m, 1H), 3.65 (s, 6H) ppm. ^{13}C-NMR ($CDCl_3$, 50.3 MHz) δ = 16.9 (q), 19.5 (q), 24.4 (t),

30.0 (d), 33.6 (t), 36.3 (t), 39.2 (d), 41.4 (t), 51.2 (q), 51.3 (q), 173.5 (s), 171.1 (s) ppm. MS(CI) for $C_{12}H_{22}O_4$: m/z = 248 $(M + NH_4)^+$.

Methyl 8-hydroxy-(3R,7S)-3,7-dimethyloctanoic acid (1b): 5b (1.81 mmol) was dissolved in MeOH (9 mL) and DCM (9 mL) and O_3 was bubbled through the solution at -78 °C until the solution colored green/blue (10-15 min). The solution was then purged with nitrogen, after which $NaBH_4$ (684 mg, 18.1 mmol, 10 eq) was added and the reaction mixture was allowed to slowly warm to ambient temperature. After stirring overnight, the reaction mixture was concentrated and the residue was taken up in Et_2O. Subsequently, 10% HCl (aq) was added and the water layer was extracted with Et_2O (3x). The combined ether extracts were dried ($MgSO_4$) and concentrated. The crude product **6b** (182 mg, 0.97 mmol, 53%) was used in the next reaction without purification. An analytical sample was purified by column chromatography (pentane-EtOAc 1:2) to give **6b** as a colorless oil. NMR data as reported in literature[4b]: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.91 (d, *J* = 6.8, 3H), 0.96 (d, *J* = 6.8, 3H), 1.05-1.46 (m, 7H), 1.59 (m, 1H), 1.95 (m, 1H), 2.14 (dd, *J* = 7.6, 15.2, 1H), 2.33 (dd, *J* = 6.4, 15.2, 1H), 3.42 (dd, *J* = 6.0, 10.4, 1H), 3.50 (dd, *J* = 5.6, 10.4, 1H), 5.8-6.8 (s,br 1H) ppm. ^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ = 16.4 (q), 19.7 (q), 24.0 (t), 30.0 (d), 33.0 (t), 35.4 (d), 36.7 (t), 41.4 (t), 68.0 (t), 178.7 (s) ppm.
6b (182 mg, 0.97 mmol) was dissolved in anhydrous MeOH (15 mL) and TMSCl (0.37 mL, 2.9 mmol, 3.0 eq) was added. The resulting solution was heated under reflux overnight while protected from moisture with a $CaCl_2$-tube, after which TLC (pentane-EtOAc 4:1) showed complete conversion. The mixture was cooled to room temperature and concentrated. $NaHCO_3$ (sat) was added to the residue and the product was extracted with Et_2O (3x). The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated. The product **1b** (163 mg, 0.81 mmol, 45% from **3**) was isolated as a colorless oil after purification by column chromatography (pentane-EtOAc 6:1 to 3:1). $[\alpha]_D^{20}$ (3R,7S)-**1b** = -3.3 (c = 1.22, $CHCl_3$), Lit.[4b,7c] $[\alpha]_D^{25}$ = -3.9, $[\alpha]_D^{20}$ (3S,7R)-**1b** = +3.02 (c = 0.91, $CHCl_3$). ^{1}H-NMR **1b** ($CDCl_3$, 400 MHz) δ = 0.92 (t, *J* = 6.8, 6H), 1.04-1.44 (m, 7H), 1.60 (m, 1H), 1.95 (m, 1H), 2.11 (dd, *J* = 8.0, 14.4, 1H), 2.30 (dd, *J* = 6.0, 14.8, 1H), 3.41 (dd, *J* = 6.4, 10.4, 1H), 3.50 (dd, *J* = 6.0, 10.4, 1H), 3.66 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ = 16.4 (q), 19.6 (q), 24.1 (t), 30.2 (d), 33.0 (t), 35.6 (d), 36.8 (t), 41.5 (t), 51.2 (q), 68.1 (t), 173.7 (s) ppm. MS(CI) for $C_{11}H_{22}O_3$: m/z = 220 $(M + NH_4)^+$, HRMS calcd for $C_{11}H_{22}O_3$-O: 186.162, found: 186.163.

(3R,7R)-3,7-Dimethyl-8-(toluene-4-sulfonyloxy)-octanoic acid methyl ester (7): 1a (116 mg, 0.57 mmol) was dissolved in dry pyridine (1.7 mL) and *p*-TsCl (164 mg, 0.86 mmol, 1.5 eq) was added at 0 °C. The resulting solution was stirred at 4 °C under argon overnight and then quenched with water. The aqueous layer was extracted with Et_2O (3x) and the combined organic layers were washed with sat. $CuSO_4$, sat. $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated to give **7** (194 mg, 0.54 mmol, 95%) as a light yellow oil which was used in the next reaction without purification. An analytical sample was purified by column chromatography (pentane-EtOAc 4:1). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.87 (d, *J* = 6.4, 3H), 0.89 (d, *J* = 6.8, 3H), 1.00-1.36 (m, 6H), 1.77 (m, 1H), 1.89 (m, 1H), 2.09 (dd, *J* = 8.0, 14.4, 1H), 2.25 (dd, *J* = 6.4, 14.4, 1H), 2.44 (s, 3H), 3.65 (s, 3H), 3.80 (dd, *J* = 6.4, 9.2, 1H), 3.86 (dd, *J* = 6.0, 9.2, 1H), 7.34 (d, *J* = 8.0, 2H), 7.78 (d, *J* =

8.0, 2H) ppm. ^{13}C-NMR ($CDCl_3$, 50.3 MHz) δ = 16.2 (q), 19.5 (q), 21.5 (q), 23.8 (t), 30.1 (d), 32.6 (t), 32.7 (d), 36.5 (t), 41.5 (t), 51.2 (q), 74.9 (t), 127.8 (d), 129.7 (d), 173.5 (s) ppm. MS(EI) for $C_{18}H_{28}O_5S$: m/z = 356 [M^+], HRMS calcd for $C_{18}H_{28}O_5S$: 356.166, found: 356.164.

(2R,6R)-2,6-Dimethyl-8-hydroxy-octyl tosylate (8): 7 (193 mg, 0.54 mmol) was dissolved in dry Et_2O and DIBAH (20% wt in toluene, 2.24 mL, 2.71 mmol, 5.0 eq) was added at -78 ^oC. The resulting solution was stirred for 30 minutes under argon and then poured into an aqueous solution of patassium sodium tartrate and stirred until the phases became clear. The aqueous layer was extracted with Et_2O (3x), the combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated. The product **8** (168 mg, 0.51 mmol, 94%) was isolated after column chromatography (pentane-EtOAc 2:1) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.84 (t, *J* = 6.8, 6H), 0.98-1.36 (m, 7H), 1.51 (m, 2H), 1.74 (m, 1H), 1.86 (s, br, 1H), 2.42 (s, 3H), 3.63 (m, 2H), 3.78 (dd, *J* = 6.4, 9.2, 1H), 3.84 (dd, *J* = 6.0, 9.2, 1H), 7.32 (d, *J* = 8.0, 2H), 7.74 (d, *J* = 8.0, 2H) ppm. ^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ = 16.2 (q), 19.3 (q), 21.4 (q), 23.7 (t), 29.1 (d), 32.6 (d), 32.6 (t), 36.8 (t), 39.6 (t), 60.8 (t), 75.0 (t), 127.7 (d), 129.6 (d), 132.8 (s), 144.5 (s) ppm. MS(EI) for $C_{17}H_{28}O_4S$: m/z = 328 [M^+], HRMS calcd for $C_{17}H_{28}O_4S$: 328.171, found: 328.172.

(3R,7S)-3,7-Dimethyl-undecan-1-ol (9): Propyl bromide (0.74 mL, 8.13 mmol) in dry THF (13.6 mL) was added dropwise to Mg (257 mg, 10.6 mmol, 1.3 eq) in an argon-purged flask and then stirred for 1 hour at room temperature. The resulting solution was used immediately. The Grignard reagent (13.1 mL, 7.40 mmol, 16 eq) was added in a dropwise fashion to a solution of **8** (152 mg, 0.46 mmol) and $CuBr{\cdot}SMe_2S$ (95 mg, 0.46 mmol) in dry THF (5.7 mL) at -78 ^oC under argon. After stirring for 1 hour at -78 ^oC, the solution was slowly warmed to 0 ^oC and stirred overnight. The reaction was quenched with sat. NH_4Cl, extracted with Et_2O (3x) and the combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated. **9** (92 mg, 0.46 mmol, 99%) was isolated as a colorless oil after purification by column chromatography (pentane- Et_2O 4:1). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.83 (d, *J* = 6.0, 3H), 0.87 (d, *J* = 6.8, 3H), 0.87 (t, *J* = 6.4, 3H), 1.00-1.40 (m, 14H), 1.48-1.70 (m, 3H), 3.66 (m, 2H) ppm. ^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ = 14.0 (q), 19.5 (q), 19.5 (q), 22.9 (t), 24.2 (t), 29.2 (t), 29.4 (d), 32.6 (d), 36.7 (t), 37.2 (t), 37.3 (t), 39.9 (t), 61.0 (t) ppm. MS(CI) for $C_{13}H_{28}O$: m/z = 218 $(M + NH_4)^+$, HRMS calcd for $C_{13}H_{28}O$-H_2O: 182.203, found: 182.205.

(3R,7S)-3,7-Dimethyl-undecyl tosylate (10): 9 (89 mg, 0.44 mmol) was dissolved in dry pyridine (1.7 mL) and *p*-TsCl (135 mg, 0.71 mmol, 1.6 eq) was added at 0 ^oC. The resulting solution was stirred at 0 ^oC under argon overnight and then quenched with water. The aqueous layer was extracted with Et_2O (3x) and the combined organic layers were washed with sat. $CuSO_4$, sat. $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated to give **10** (148 mg, 0.42 mmol, 94%) as a light yellow oil which was used in the next reaction without purification. An analytical sample was purified by column chromatography (pentane-EtOAc 4:1). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.80 (d, *J* = 6.8, 3H), 0.82 (d, *J* = 6.8, 3H), 0.88 (t, *J* = 6.8, 3H), 0.98-1.70 (m, 16H), 2.45 (s, 3H), 4.06 (m, 2H), 7.34 (d, *J* = 8.4, 2H), 7.79 (d, *J* = 8.0, 2H) ppm. ^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ = 14.1 (q), 19.0

(q), 19.5 (q), 21.5 (q), 22.9 (t), 24.0 (t), 29.1 (d), 29.2 (t), 32.6 (d), 35.6 (t), 36.7 (t), 36.8 (t), 37.1 (t), 69.0 (t), 127.8 (d), 129.7 (d), 133.1 (s), 144.5 (s) ppm. MS(EI) for $C_{20}H_{34}O_3S$: m/z = 354 [M^+], HRMS calcd for $C_{20}H_{34}O_3S$-C_4H_9: 297.152, found: 297.151.

(10S,14S)-10,14-Dimethyl-1-octadecene (11): 6-heptenyl bromide (0.38 mL, 2.49 mmol) in dry THF (6.0 mL) was added dropwise to Mg (91 mg, 3.7 mmol, 1.5 eq) in an argon-purged flask and then stirred for 1 hour at 45 ^oC. The resulting solution was used immediately. The Grignard reagent (2.41 mL, 0.94 mmol, 4.0 eq) was added in a dropwise fashion to a solution of **10** (84 mg, 0.24 mmol) and CuBr·SMe_2 (10.3 mg, 50 µmol, 21 mol%) in dry THF (1.1 mL) at -78 ^oC under argon. After stirring for 1 hour at -78 ^oC, the solution was slowly warmed to 0 ^oC and stirred overnight. The reaction was quenched with sat. NH_4Cl, extracted with Et_2O (3x) and the combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated. **11** (60 mg, 0.21 mmol, 90%) was isolated as a colorless oil after purification by column chromatography (20 g SiO_2, pentane). $[\alpha]_D^{20}$ (10S,14S)-**11** = +2.09 (c = 0.91, $CHCl_3$),), Lit.[16] $[\alpha]_D^{25}$ = +1.78. NMR data as reported in literature[16]: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.835, 0.838 (2d, *J* = 6.4, 6H), 0.89 (t, *J* = 6.8 3H), 1.00-1.42 (m, 26H), 2.04 (m, *J* = 7.6, 2H), 4.93 (m, *J* = 1.6, 10.0, 1H), 4.99 (m, *J* = 1.6, 17.2, 1H), 5.82 (m, *J* = 6.8, 10.0, 17.2, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ = 14.1 (q), 19.6 (q), 22.9 (t), 24.4 (t), 27.0 (t), 28.9 (t), 29.1 (t), 29.3 (t), 29.4 (t), 29.6 (t), 29.8 (t), 32.6 (d), 33.7 (t), 36.7 (t), 37.0 (t), 37.3 (t), 114.0 (t), 139.2 (d) ppm. MS(EI) for $C_{20}H_{40}$: m/z = 280 [M^+], HRMS calcd for $C_{20}H_{40}$: 280.313, found: 280.313.

(5S,9S)-5,9-Dimethylheptadecane (12): hexyl bromide (0.38 mL, 2.69 mmol) in dry THF (6.0 mL) was added dropwise to Mg (91 mg, 3.74 mmol, 1.4 eq) in an argon-purged flask and then stirred for 1 hour at 45 ^oC. The resulting solution was used immediately. The Grignard reagent (2.23 mL, 0.94 mmol, 5.7 eq) was added in a dropwise fashion to a solution of **10** (58 mg, 0.16 mmol) and CuBr·SMe_2 (10.3 mg, 50 µmol, 31 mol%) in dry THF (1.1 mL) at -78 ^oC under argon. After stirring for 1 hour at -78 ^oC, the solution was slowly warmed to 0 ^oC and stirred overnight. Work-up was performed as described for **11**. GC-MS on the crude product showed that only **12** and dodecane were present. After column chromatography (20 g SiO_2, pentane), there was still dodecane present (50 mol% as was estimated by GC) resulting in an estimated isolated yield of 0.11 mmol (70%) of **12**. NMR data as reported in literature[16]: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 0.825, 0.827 (2d, *J* = 6.8, 6H), 0.89 (m, *J* = 6.8, 6H), 1.03-1.40 (m, 28H) ppm. ^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ = 14.0 (q), 14.1 (q), 19.6 (q), 22.6 (t), 23.0 (t), 24.4 (t), 27.0 (t), 29.3 (t), 29.6 (t), 30.0 (t), 31.9 (t), 32.7 (d), 36.7 (t), 37.1 (t), 37.3 (t) ppm. MS(EI) for $C_{19}H_{40}$: m/z = 268 [M^+], HRMS calcd for $C_{19}H_{40}$: 268.313, found: 268.313.