Supporting Information

Polysubstituted Oxygen Heterocycles by a Reformatsky-type Reaction/Reductive Cyclization Approach from Enantiopure β-Ketosulfoxides

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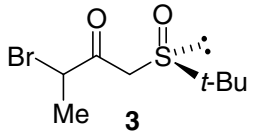
General Experimental Procedures. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ at room temperature on Bruker 300 and 400 MHz spectrometers. All chemical shifts (δ) are quoted in parts par million (ppm). The chemical shifts are referred to the applied NMR solvent (for $CDCl_3$: ^{1}H NMR, 7.27 ppm. and ^{13}C NMR, 77.0 ppm). The coupling constants (J) are given in Hertz (Hz). Resonance patterns are reported with the following notations: br (broad), s (singulet), d (doublet), t (triplet), q (quartet) and m (multiplet). IR spectra were recorded on a Perkin Elmer Spectrum One Spectrophotometer and only the most significant absorption bands are given in cm^{-1}. Mass spectra were recorded by HRMS by electrospray ionisation method obtained with a microTOF LC Bruker Daltonics microTOF LC from Brücker Daltonics apparatus. Microanalyses were obtained by "Service de Microanalyse" at Chemistry Institute of Strasbourg. Specific rotations were determined at room temperature in a Perkin Elmer 241 polarimeter for sodium (λ = 589 nm). X Ray were recorded by a difractometer Kappa CCD Oxford Cryosystem liquid N_2 using monochromatic radiations Mo-Kα =

0.71073 Å. Data of diffraction were corrected by absorption and analysed with OpenMolen Package. Thin-layer chromatography (TLC) was carried on glass plates silica gel 60 F_{254} purchased by Merck. Melting points were obtained on a Büchi 535 apparatus. Column chromatography was carried out on silica gel 60 (40-63 μm, Merck) according to the method of *Still et al.*[1] or on unmetalled silica gel[2].

THF was freshly distilled under argon atmosphere from sodium/benzophenone as well as diethylether; dichloromethane was distilled over CaH_2. MeOH was distilled over Mg. Diisopropylamine was distilled over KOH also under argon atmosphere. All aldehydes were stored under argon atmosphere at low temperature. TMSOTf was freshly distilled before use over a bulb to bulb apparatus. All other reagents and solvents were used as received from commercial sources. All reactions were performed under argon atmosphere unless stated otherwise.

(R(S))-3-Bromo-1-(*tert*-butylsulfinyl)butan-2-one (3)[3] :



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A solution of *n*BuLi (5.0 mmol, 2 eq., 1.6 M in hexane) was added to a solution of diisopropylamine (5.2 mmol, 2.1 eq.) in THF (5 mL) at –78 °C. After 1 h at –78 °C, a solution of (*R)-tert*-butylmethylsulfoxide[4] **2** (5.0 mmol, 2 eq.) in THF (5 mL) was added at –78 °C. The mixture was stirred under these conditions for 1 h. Then methyl 2-bromopropionate **1** (2.5 mmol, 1 eq.) in THF (5 mL) was added at –78 °C to the lithiated sulfoxide anion. The resulting solution was stirred at –78 °C for 30 min. The solution was quenched with a saturated NH_4Cl aqueous solution (10 mL) and additional water. The reaction mixture was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic extracts were dried with $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography over unmetalled silica gel and stored as quickly as possible under argon atmosphere at –20°C. Mixture of two diastereomers. Yellow solid. R_f = 0.40 (EtOAc). Yield 95%. IR (ATR) ν 2991–2865, 1716; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.67 and 4.63 (q, J = 6.6Hz, 1 H), 3.85 and 3.77 (AB, J_{AB} = 13.7 and 12.5 Hz, $\Delta\nu$ = 71 and 81.5 Hz, 2 H), 1.81 and 1.77 (d, J = 6.6 Hz, 3 H), 1.30 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 196.4, 55.1, 55.0, 54.9, 54.3, 48.9, 47.7, 22.8, 22.6, 19.5, 19.0.

Preparation of aldehydes 4 and 6

General procedure. The following description provides a typical experimental protocol for the synthesis of aldehydes **4** and **6**.

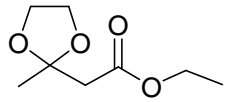
1 Still, W.C; Kahn, M; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

2 Hubbard, J.S; Harris, T.M. *J. Org. Chem.* **1981**, *46*, 2566.

3 Obringer, M.; Colobert, F.; Solladié, G. *Eur. J. Org. Chem.* **2006**, 1455-1467.

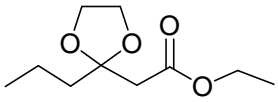
4 Kagan, H.B.; Rebiere.F. *J. Org. Chem.* **1991**, *56*, 5991

Ethyl 2-(2-methyl-1,3-dioxolan-2-yl)acetate[4]:



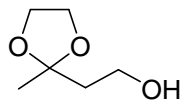
A solution of ethyl-3-oxobutanoate (10 g, 76.8 mmol, 1 eq.) ethylene glycol (5.56 mL, 99.8 mmol, 1.3 eq.) and *p*-TsOH·H_2O (146 mg, 0.77 mmol, 0.01 eq) in benzene (100 mL) was refluxed for one night using Dean-Stark trap, and then cooled to room temperature. After concentration *in vacuo*, to eliminate the benzene, this mixture was dissolved in EtOAc (100 mL). The organic layer was washed subsequentially with an aqueous solution of $NaHCO_3$ 5% (30 mL), brine (30 mL), dried over Na_2SO_4. Filtered and concentrated to afford the ketal ester **SI-1** (12.7 g, 72.9 mmol, 95%) which can be used without any further purification. R_f = 0.26 (CH_2Cl_2/AcOEt 1:4); Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.16 (q, *J* =7.14 Hz, 2 H), 3.98 (s, 4 H), 2.67 (s, 2 H), 1.52 (s, 3 H), 1.27 (t, *J*=7.17 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4, 107.6, 64.7, 60.5, 44.3, 44.3, 26.9, 24.5, 14.2.

Ethyl 2-(2-propyl-1,3-dioxolan-2-yl)acetate:



The product was synthesized using ethyl-3-oxohexanoate (10 g, 63.3 mmol, 1 eq.) utilizing the same method as for ethyl 2-(2-methyl-1,3-dioxolan-2-yl)acetate to afford the ketal ester (11.8 g, 58.4 mmol, 92%). This product can be used without any further purification. Colorless oil; IR (ATR) *v* 2962, 2876, 1733; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.15 (q, *J* = 7.17Hz, 2 H), 4.04-3.95 (m, 4 H), 2.65 (s, 2 H), 1.81-1.76 (m, 2 H), 1.49-1.39 (m, 2 H), 1.27 (t, *J* = 7.17 Hz, 3 H), 0.95 (t, *J* = 7.35 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 169.7, 109.5, 65.2, 60.6, 42.8, 40.13, 17.0, 14.3. HRMS (ESI^+) calcd for $C_{10}H_{18}O_4$ ($M + Na^+$) 225.1097, found 225.1072.

2-(2-methyl-1,3-dioxolan-2-yl)ethanol[4]:

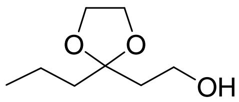


A solution of ethyl 2-(2-methyl-1,3-dioxolan-2-yl)acetate (10 g, 57.5 mmol, 1 eq.) in Et_2O (48 mL) is added dropwise to a suspension of $LiAlH_4$ (1.63 g, 43.1 mmol, 0.75 eq.) in Et_2O (180 mL). Once the addition is finished, the mixture is refluxed for 90 min, then cooled to 0°C and distilled water (3.4 mL) is added slowly. Once the bubbled finished one spatula of Na_2SO_4 is added and the mixture vigorously stirred for 20 min. The flocculent precipitated is filtered over celite. The celite was washed twice with

(4) Tan, J. S.; Ciufolini, M. A. *Org. Lett.* **2006**, *8*, 4771

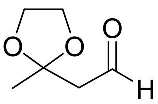
Et_2O (75 mL). The solvent finally eliminated under pressure to afford pure alcohol (6.43 g, 48.7 mmol, 86%). This product can be used without any further purification. R_f = 0.63 (CH_2Cl_2/AcOEt 1:4); Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.00 (s, 4 H) , 3.77 (t, *J* = 6.1 Hz, 2 H), 3.77 (t, *J* = 6.1 Hz, 2 H), 2.80 (br s, 2 H), 1.95 (t, *J* = 6.1 Hz, 2 H), 1.35 (s, 3 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 209.3, 110.5, 64.5, 59.2, 40.3, 23.8.

2-(2-propyl-1,3-dioxolan-2-yl)ethanol:



The [illegible] 2-(2-propyl-1,3-dioxolan-2-yl)acetate (4.3 g, 21.3 mmol, 1 eq.) utilizing the same method as for 2-(2-methyl-1,3-dioxolan-2-yl)ethanol to obtain the corresponding pure alcohol (2.6 g, 19.7 mmol, 98%) which can be used without any further purification. R_f = 0.24 (CH_2Cl_2/AcOEt 1:4); Colorless liquid; IR (ATR) ν 3430, 2960, 2876; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.00-3.97 (m, 4 H), 3.75 (t, *J* = 5.65 Hz, 2 H), 2.81 (br s, 1 H), 1.92 (t, *J* = 5.8 Hz, 2 H), 1.65-1.57 (m, 2 H), 1.46-1.38 (m, 2 H), 0.93 (t, *J* = 7.35 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 112.3, 64.7, 58.9, 39.3, 38.1, 17.1, 14.3. HRMS (ESI$^+$) calcd for $C_8H_{16}O_3$ (M+Li$^+$) 167.1254, found 167.1240.

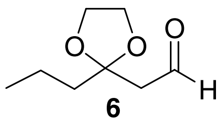
2-(2-methyl-1,3-dioxolan-2-yl)acetaldehyde[4] **(4) :**



4

DMSO (0.77 mL, 10.8 mmol, 1.3 eq.) was added dropwise to a solution of oxalyl chloride (0.93 mL; 10.8 mmol, 1.3 eq.) in dry CH_2Cl_2 (36 mL) at –78°C. A vigorous and exothermic process is observed. The mixture was stirred at –78°C for 15 min, and then a solution of the alcohol **SI-3** (1.1 g, 8.3 mmol, 1 eq.) in dry CH_2Cl_2 (4.5 mL) was added dropwise. The resultant solution was stirred at –78°C for 30 min, and then Et_3N (4.61 mL, 33.3 mmol, 4.0 eq.) was added. The mixture was stirred at –78°C for 5 min then it was slowly warm to room temperature over 40 min, with continued stirring. The reaction mixture was washed with aqueous saturated NH_4Cl (3 x 40 mL), dried Na_2SO_4 and concentrated to give aldehyde **4** (1.0 g, 8.0 mmol, 97%) which was purified by simple filtration over silica gel. R_f = 0.54 (AcOEt/cyclohexane 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.75 (t, *J* = 3.3 Hz, 1 H), 4.01 (br s, 4 H), 2.72 (d, *J* = 3.30 Hz, 2 H), 1.43 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.2, 107.5, 64.7, 52.1, 24.8.

2-(2-propyl-1,3-dioxolan-2-yl)-acetaldehyde (6) :

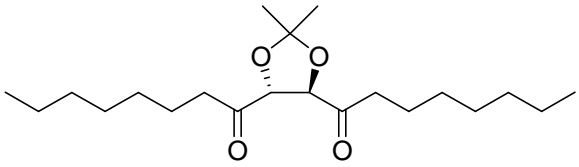


6

The product was synthesized by using alcohol **SI-4** (2.34 g, 14.6 mmol, 1 eq.) to obtain pure aldehyde **6** (2.13 g, 13.4 mmol, 90%) which can be used without any further purification. R_f: 0.6 (CH_2Cl_2/AcOEt 1:4). Yellow pale oil. IR (ATR) ν 2962, 2876, 1724; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 9.75 (t, J = 3.0 Hz, 1 H), 4.00 (s, 4 H), 2.68 (d, J = 3.0 Hz, 2 H), 1.70-1.65 (m, 2 H), 1.46-1.38 (m, 2 H), 0.93 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.5, 109.3, 64.9, 50.5, 40.5, 16.7, 14.0. HRMS (ESI$^+$) calcd for $C_8H_{14}O_3$ (M+Li$^+$) 165.1098, found 165.1080.

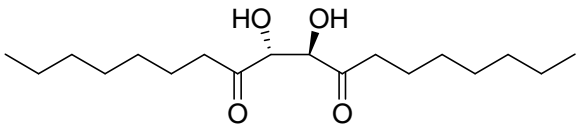
Preparation of aldehyde 18

(+)-(9*R*,10*R*)-9,10-(Isopropylidenedioxy)octadecane-8,11-dione:



A solution of heptyl bromide (4.43 mL, 28.0 mmol, 4.1 eq.) in Et_2O (25 mL) was slowly added to magnesium turnings (669 mg, 27.51 mmol, 4.0 eq.) recovered by Et_2O (2 mL). At the end of the addition, the mixture was refluxed for 30 min and then allowed to cool to room temperature. The mixture was added dropwise to a solution of the bis-Weinreb amide Acide (-)-2,3-*O*-isopropylidène-*L*-tartrique *bis*-(*N*-méthyl-*N*-méthoxyamide)[5] (1.90 g, 6.8 mmol, 1 eq.) in THF (55 mL) cooled to –10 °C. After 15 min at –10 °C, the reaction was quenched with saturated aqueous NH_4Cl and the mixture was acidified with 10% HCl and extracted with EtOAc (3 × 40 mL). The combined organic extracts were washed with brine, dried with magnesium sulfate, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/EtOAc 9:1) to give pure diketone **SI-5** (1.91 g, 5.38 mmol, 78%). R_f = 0.45 (hexane/EtOAc 9:1). Colorless liquid. $[\alpha]_D^{20}$ = +4.7 (c 1, $CHCl_3$); IR (ATR) ν 2990–2857, 1727; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.55 (s, 2 H), 2.73–2.56 (AB part of ABMN, 2nd order, 4 H), 1.67–1.52 (m, 4 H), 1.43 (s, 6 H), 1.34–1.24 (m, 16 H), 0.88 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.7, 112.4, 81.5, 39.1, 31.6, 29.1, 29.0, 26.2, 23.1, 22.6, 14.0; Anal. Calcd. for $C_{21}H_{38}O_4$: C, 71.15; H, 10.80. Found: C, 71.15; H, 10.62.

(–)-(9*R*,10*R*)-9,10-Dihydroxyoctadecane-8,11-dione:

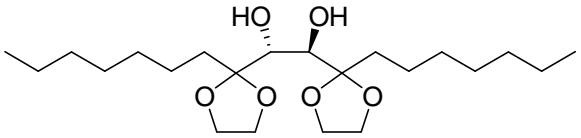


A mixture of trifluoroacetic acid/water (9:1, v/v) (13 mL) was added to the diketone (1 eq., 2.50 g, 7.06 mmol) cooled to 0 °C. After storage of the mixture at this temperature for 2 h, the aqueous acid was removed under reduced pressure and the residue was triturated with Et_2O (5 mL). The supernatant

(5) a) B. M. Kim, S. J. Bae, S. M. So, H. T. Yoo, S. K. Chang, J. H. Lee, J. Kang, *Org. Lett.* **2001**, *3*, 2349–2351; b) D. A. Nugiel, K. Jacobs, T. Worley, M. Patel, R. F. Kaltenbach III, D. T. Meyer, P. K. Jadhav, G. V. De Lucca, T. E. Smyser, R. M. Klabe, L. T. Bacheler, M. M. Rayner, S. P. Seitz, *J. Med. Chem.* **1996**, *39*, 2156–2169.

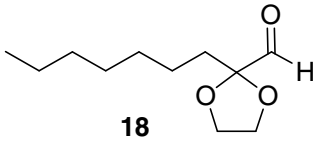
liquid was removed by means of a Pasteur pipette. The remaining solid was washed with diethyl ether (3 × 3 mL), leaving a crystalline solid, and the major portion of the hydrolysis the desired product. The ethereal supernatant liquid and the washings were combined, concentrated under reduced pressure, and the residue thus obtained triturated and washed with diethyl ether in a similar manner to that used for the initial residue to afford a second crystalline portion of the hydrolysis product. The two portions were combined to obtain pure product **SI-6** (1.84 g, 5.85 mmol, 83%). R_f = 0.30 (hexane/EtOAc 8:2). White solid. m.p. 98– 100 °C; $[\alpha]^{D}_{20}$ = –72 (*c* 1, $CHCl_3$); IR (ATR) *v* 3434, 2953–2850, 1717, 1690; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.56 (d, *J* = 6.5 Hz, 2 H), 3.68 (d, *J* = 6.5 Hz, 2 H), 2.73–2.51 (AB part of ABMN, 2nd order, 4 H), 1.75–1.64 (m, 4 H), 1.40–1.25 (m, 16 H), 0.88 (t, *J* = 6.9 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.8, 77.0, 38.0, 31.6, 29.1, 29.0, 23.4, 22.6, 14.0; Anal. Calcd. for $C_{18}H_{34}O_4$ C, 68.75; H, 10.90; Found C, 68.67; H, 10.87.

(–)-(1*R*,2*R*)-1,2-Bis(2-heptyl-1,3-dioxolan-2-yl)ethane-1,2-diol:



A solution of the diketone (1.26 g, 4.02 mmol, 1 eq.), *p*TsOH (77 mg, 0.40 mmol, 0.1 eq.) and ethylene glycol (0.68 mL, 12.06 mmol, 3 eq.) in benzene (40 mL) was refluxed for 16 h in a Dean–Stark trap. Benzene was removed by evaporation and the crude product was diluted in AcOEt (40 mL), washed with saturated $NaHCO_3$ (20 mL) and water (20 mL), dried with magnesium sulfate, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether/EtOAc 1:1) to obtain pure **SI-7** (1.20 g, 2.98 mmol, 74%). R_f = 0.40 (petroleum ether/EtOAc 1:1); White solid; m.p. 47 °C; $[\alpha]^{D}_{20}$ = –3.8 (*c* 1, $CHCl_3$); IR (ATR) *v* 3436, 2956–2853; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.13–3.99 (m, 8 H), 3.86 (s, 2 H), 2.03 (s, 2 H), 1.87–1.57 (m, 4 H), 1.48–1.20 (m, 20 H), 0.90 (t, *J* = 6.6 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 112.4, 71.0, 65.9, 65.7, 34.4, 31.8, 29.8, 29.3, 23.0, 22.6, 14.1.

2-heptyl-[1,3]dioxolane-2-carbaldehyde (18) :



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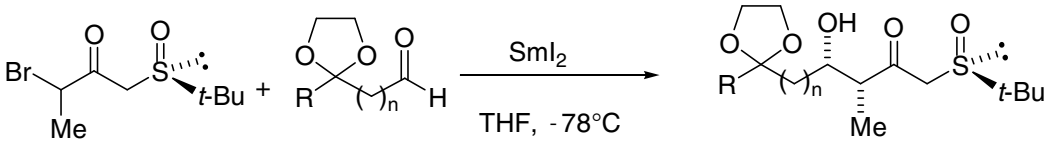
To a solution of diol (0,50 g, 1,24 mmol, 1 eq.) in CH_2Cl_2 (19 mL) plomb tetraacetate (0,66 g, 1,49 mmol, 1,2 eq.) is added at –15°C by littles portions. The mixture is stirred at this temperature for 30 minutes and then warmed up to room temperature and stirred for 30 minutes. After the mixture is filtred over celite and washed with CH_2Cl_2 and concentred under reduced pressure. The residue was purified by silica gel chromatography (cyclohexane / AcOEt 1:1). The product is then used as quickly

as possible for the next step (348 mg, 1,74 mmol, 70%). R_f = 0.50 (cyclohexane / AcOEt, 1:1). Colorless liquid. IR (ATR) ν 3434, 2955-2856, 1744; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.39 (s, 1 H), 4.12-3.96 (m, 4 H), 1.82-1.76 (m, 2 H), 1.48-1.15 (m, 10 H), 0.87 (t, J = 10.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 107.7, 65.9, 32.1, 31.7, 29.7, 29.1, 22.6, 22.1, 14.0.

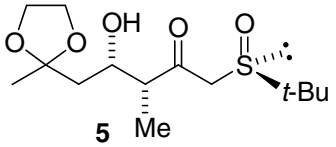
Samarium (II) iodide mediated Reformatsky-type reaction



General procedure. The following description provides a typical experimental protocol for the reformatsky type reaction of chiral γ-bromo-β-ketosulfoxyde with a series of aldehydes.

A solution of SmI_2 was prepared by a rapid addition of diiodomethane (760 µL, 9.4 mmol, 2 eq.) in THF (102 mL) on samarium powder (1.55 g, 10.3 mmol, 2.2 eq.) at 10°C. This mixture was stirring at this temperature for 1h. The solution turned dark blue, and was cooled down to –78°C.A solution of γ-bromo-β-ketosulfoxyde (1.20 g, 4.7 mmol, 1 eq.) in THF (13 mL) was added dropwise. The mixture was stirred under these conditions for 10 minutes. A solution of the aldehyde (6.11 mmol, 1.3 eq.) in THF (13 mL) was added dropwise also at –78°C. The resulting mixture was stirred for 90 min at -78°C. The reaction is quenched by successively addition of a solution of HCl 0.1 M (40 mL) and brine (40 mL). EtOAc (40 mL) was added, and the aqueous phase was extracted with EtOAc (4 x 40 mL). The organic phase was washed with aqueous saturated sodium thiosulphate solution (2 x 40 mL) to remove liberated iodine. Then washed with brine (40 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by unmetalled silica gel chromatography (EtOAc) without pressure.

(+)-[(3*R*,4*S*,(S)*R*)-6-[1,3]dioxolane-4-hydroxy-3-methyl-1-*tert*-butylsulfinyl)-heptan-2-one (5) :

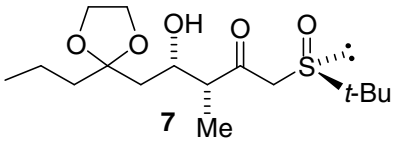


5

The product was obtained by using aldehyde **4** (595mg, 4.57 mmol) to perform the asymmetric Reformatsky reaction to give the Reformatsky adduct **5** (834 mg, 2.72 mmol, 77%); R_f = 0.21 (AcOEt); Orange oil; IR (ATR) ν 3374, 2963, 1708; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.24-4.20 (m, 1 H), 4.05-3.95 (m, 4 H), 3.72 (AB, J_{AB}= 13.56 Hz, $\Delta\nu$ = 25.2 Hz, 2 H), 3.05-2.97 (m, 1 H), 1.88-1.74 (m, 2 H), 1.36 (s, 3 H), 1.28 (s, 9 H), 1.14 (d, J = 6.99 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.8,

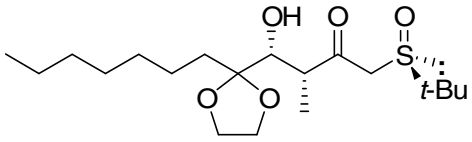
110.1, 69.1, 64.7, 64.3, 58.5, 54.2, 52.2, 41.1, 24.0, 22.8, 10.3. HRMS (ESI^+) calcd for $C_{14}H_{26}O_5S$ (M + Li^+) 306.1656, found 306.1637.

(+)-(3*R*,4*S*,(S)*R*)-8-[1,3]dioxolane-4-hydroxy-3-methyl-1-*tert*-butylsulfinyl)-nona-2-one (7) :



The product was obtained by using aldehyde **6** (965 mg, 6.11 mmol) to perform the asymmetric Reformatsky reaction to give the Reformatsky adduct **7** (1.36 g, 40.7 mmol, 86%); R_f = 0.19 (AcOEt); Orange oil; IR (ATR) *v* 3395, 2961, 2874, 1709; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.20-4.17 (X part of a ABX 2nd order, m, 1 H), 4.01-3.96 (m, 4 H), 3.73 (AB, J_{AB}= 13.56 Hz, Δv= 19.6 Hz, 2 H), 3.04-2.96 (m, 1 H), 1.77 (AB part of a ABX 2nd order, J_{AB}= 15 Hz, J_{AX}= 3 Hz, J_{BX}= 12 Hz, Δv= 36 Hz, 2 H), 1.64-1.60 (m, 2 H), 1.41-1.32 (m, 2 H), 1.28 (s, 9 H), 1.14 (d, *J*= 9.96 Hz, 3 H), 0.92 (t, *J*= 7.35 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.8, 111.8, 69.1, 64.8, 64.6, 58.6, 54.2, 52.2, 39.4, 38.8, 22.8, 17.1, 14.2, 10.8. HRMS (ESI^+) calcd for $C_{16}H_{30}O_5S$ (M+Li) 341.1951, found 341.1933.

(+)-[3*R*,4*S*,(S)*R*]-5-[1,3]dioxolane-4-hydroxy-3-méthyl-1-(*t*-butylsulfinyl)-dodécan-2-one (19) :

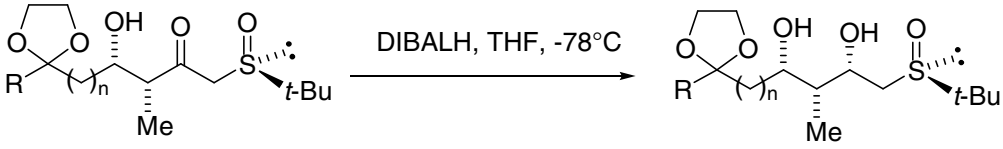


The product was obtained by using aldehyde **18** (1.55 mmol, 310 µl) to perform the asymmetric Reformatsky reaction to give the Reformatsky adduct **19** (357 mg, 0.95 mmol, 73%). R_f = 0.20 (AcOEt); Light yellow solid; IR *v* 3351, 2957-2856, 1706 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.02-3.86 (m, 4H), 3.93 (d, *J* = 10.4 Hz, 1H), 3.58 (AB, J_{AB} = 21.4 Hz, $\Delta\nu$ = 16.3 Hz, 2H), 2.89 (q, *J* = 10.4 Hz, 1H), 2.24 (br s, 1H), 1.87-1.54 (m, 2H), 1.43-1.13 (m, 10H), 1.29 (s, 9H), 1.27 (d, *J* = 10.4 Hz, 3H), 0.88 (t, *J* = 9.9 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm 204.1, 111.5, 74.4, 65.5, 65.3, 57.6, 54.1, 48.7, 33.7, 31.8, 29.8, 29.3, 22.9, 22.6, 22.8, 12.6, 14.1

Diastereoselective reduction of the reformatsky adduct

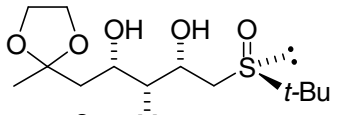
General Procedure. The following description provides a typical experimental procedure for the diastereoselective reduction of the Reformatsky adduct to obtain either 2-methyl-1,3-*syn*-diols or 2-methyl-1-3-*anti*-diols.

Synthesis of 2-methyl-1-3-*syn*-diols:



A solution of Reformatsky adduct (1.87 mmol, 1 eq.) in THF (34.5 mL) was cooled to −78°C and a solution of DIBALH (2.4 eq., 4.5 mmol, 1 M in toluene) was added dropwise. The mixture was stirred under these conditions for 2h. MeOH (1mL), a saturated aqueous solution of sodium and potassium L-tartrate (42mL) and AcOEt (42 mL) were added. The solution was stirring at room temperature until a good separation of the phases was observed. The aqueous phase was extracted with AcOEt (4 x 30mL). The organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified under silica gel chromatography without pressure (CH_2Cl_2/EtOAc/MeOH 6:2:0.3).

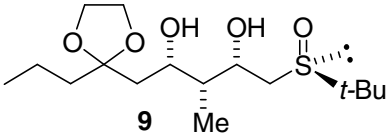
(+)-[2*S*,3*R*,4*S*,(S)*R*]-6-[1,3]dioxolane-4-hydroxy-3-methyl-1-(*tert*-butylsulfinyl)-heptan-2-ol (8):



8

The product was obtained by using ketone **5** (348 mg, 1.13 mmol) to perform the diastereoselective reduction reaction to give of the reduced product **8** (250 mg, 0.81 mmol, 71%); R_f = 0.36 (AcOEt) Colorless wax; $[\alpha]^{20}_D$: + 56.5 (c 0.1; $CHCl_3$) IR (ATR) ν 3362, 2926, 2886; ^{1}H NMR (300 MHz,$CDCl_3$) δ 4.46 (X part of a ABX 2nd order, dt, J_1 = 9.4 Hz, J_2 = 2.4 Hz, 1 H), 4.24 (X part of a ABX 2nd order, br d, J = 10.6 Hz, 1 H), 3.96 (s, 4 H), 3.36 (br s, 2 H), 2.53 (AB part of a ABX 2nd order, J_{AB} = 12.6 Hz, J_{AX} = 9.6 Hz, J_{BX} = 3.0 Hz, $\Delta\nu$ = 90.6 Hz, 2 H), 1.80 (AB part of a ABX 2nd order, J_{AB} = 14.7 Hz, J_{AX} = 10.2 Hz, J_{BX} = 1.0 Hz, $\Delta\nu$ = 72.0 Hz, 2 H), 1.59-1.50 (m, 1H), 1.32 (s, 3H), 1.23 (s, 9H), 0.95 (d, J = 7.05 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 110.4, 72.2, 70.3, 64.8, 64.4, 52.7, 51.3, 43.1, 42.5, 24.3, 22.7, 5.3. HRMS (ESI$^+$) calcd for $C_{14}H_{28}O_5S$ (M + Na^+) 331.1550, found 331.1529.

(+)-[2*S*,3*R*,4*S*,(S)*R*)-6-[1,3]-dioxolane-4-hydroxy-3-methyl-(*tert*-butylsulfinyl)-nonan-2-ol (9):

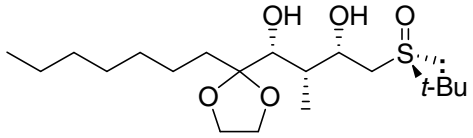


9

The product was obtained by using ketone **7** (145 mg, 0.43 mmol) to perform the diastereoselective reduction reaction to give the reduced product **9** (93 mg, 0.27 mmol, 65%); R_f = 0.5 (EtOAc/MeOH 9:1); Colorless wax. $[\alpha]^{20}_D$: + 94.4 (c 0.5; $CHCl_3$). IR (ATR) ν 3362, 2960, 2926; ^{1}H NMR (300

MHz,$CDCl_3$) δ 4.51 (X part of a ABX 2nd order, dt, J_1 = 24.4 Hz, J_2 = 9.71 Hz, 1 H), 4.25 (X part of a ABX 2nd order, br d, J = 10.39Hz, 1 H), 4.05-3.95 (m, 4 H), 3.50 (br s, 2 H), 2.59 (AB part of a ABX 2nd order, J_{AB} = 12.3 Hz, J_{AX} = 9.6 Hz, J_{BX} = 2.7 Hz, $\Delta\nu$ = 87 Hz, 2 H), 1.83 (AB part of a ABX 2nd order, J_{AB} = 12.7 Hz, J_{AX} = 10.2 Hz, J_{BX} = 1.2 Hz, $\Delta\nu$ = 61.2 Hz, 2 H), 1.65-1.54 (m, 3 H), 1.29 (s, 9 H), 0.99 (d, J = 7.04Hz, 3 H), 0.93 (t, J = 7.28 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 112.4, 72.3, 70.5, 65.2, 64.9, 53.0, 51.6, 42.9, 41.0, 39.8, 23.2, 17.5, 14.6, 6.3. HRMS (ESI^+) calcd for $C_{16}H_{32}O_5S$ ($M + Li^+$) 343.2125, found 343.2108.

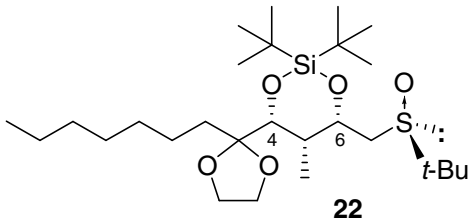
(+)-[2*S*,3*R*,4*S*,(S)*R*]-5-[1,3]dioxolane-4-hydroxy-3-méthyl-1-(*t*-butylsulfinyl)-dodécan-2-ol (20) :



20

The product was obtained by using (+)-[3*R*,4*S*,(S)*R*]-5-[1,3]dioxolane-4-hydroxy-3-méthyl-1-(*t*-butylsulfinyl)-dodécan-2-one **19** (0,28 mmol,104,7 mg) to perform the diastereoselective reduction reaction to give of the reduced product (89 mg ; 0,24 mmol). 85% yield. Light yellow oil. R_f = 0.20 (AcOEt / MeOH : 95 / 5). $[\alpha]^{20}_D$: +79.4 (c 1 ; $CHCl_3$). IR ν 3383, 2955-2854 cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$) δ ppm 4.42 (dt, 1H, J = 12.4 et 2.1 Hz), 4.08-3.92 (m, 4H), 3.88 (d, 1H, J = 2.1 Hz), 3.64 (s large, 1H), 2.62 (s large, 1H), 2.59 (AB part of a ABX 2nd order, J_{AB} = 12.4 Hz, J_{AX} = 10.4 Hz, J_{BX} = 2.1 Hz, $\Delta\nu$ = 83.0 Hz, 2H), 1.91 (m, 1H), 1.77-1.52 (m, 2H), 1.43-1.10 (m, 10H), 1.27 (s, 9H), 1.07 (d, 3H, J = 7.0 Hz); 0.89 (t, 3H, J = 7.0 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 112.1, 77.0, 69.9, 66.2, 65.6, 52.7, 50.6, 38.6, 34.7, 31.8, 29.9, 29.2, 23.0, 22.6, 22.9, 14.1, 7.2.

(+)-[4*R*,5*R*,6*S*]-2,2-di-*t*-butyl-4-(2-heptyl-[1,3]dioxolan-2-yl)-5-méthyl-6-(2-*tert*-butylsulfinylméthyl)-[1,3,2]dioxasilinane (22) :

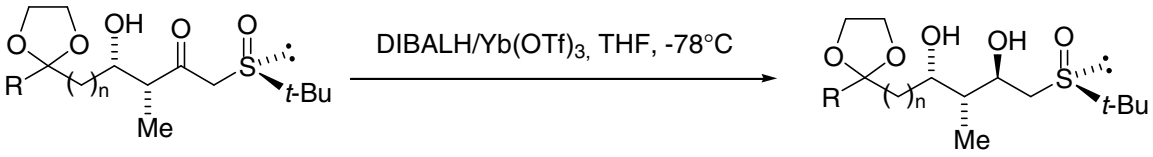


22

To a solution of diol **20** (51,9 mg, 0,137 mmol, 1 eq.) in DMF (0,7 ml) at 0°C are added dropwise 2,6-lutidine (64 µl, 0,548 mmol, 4 eq.) and $(t\text{-Bu})_2Si(OTf)_2$ (55 µl, 0,164 mmol, 1,2 eq.). The mixture is stirring at 0°C for 1h30, then the reaction is hydrolysed by addition of a $NaHCO_3$ aqueous saturated solution (1 ml). The mixture is diluted with Et_2O (10 ml). After separation, the organic layer is washed with an aqueous $NaHCO_3$ saturated solution (10 ml). The aqueous phase is reextracted with Et_2O (3×10 ml). The organic layers are dried over Na_2SO_4, filtered and concentrated under pressure. The residue was purified under silica gel chromatography (cyclohexane / AcOEt 8:2 → 7:3, then CH_2Cl_2 /

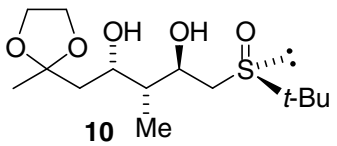
AcOEt, 9:1) to afford product **22** (50 mg, 0,096 mmol, 70%) ; R_f = 0.30 (cyclohexane / AcOEt, 7:3); White solid; mp: 84-85°C; $[\alpha]_D^{20}$ = +77.8 (c 0.45; $CHCl_3$); IR (ATR) ν 2957-2857; ^{1}H NMR (300 MHz,$CDCl_3$) δ 4.82 (X part of a ABX 2nd order, dft, J = 10.7 et 2.2 Hz, 1 H), 4.36 (d, J = 2.2 Hz, 1 H), 4.23-3.90 (m, 4 H), 2.48 (AB part of a ABX 2nd order, J_{BX} = 1.5 Hz, $\Delta\nu$ = 117.8 Hz, J_{AB} = 12.1 Hz, J_{AX} = 10.7 Hz, 2 H), 1.77 (qt, J = 7.1 Hz and 2.2 Hz, 1 H), 1.61-1.48 (m, 2 H), 1.45-1.17 (m, 19 H), 1.11 (s, 9 H), 1.11 (d, J = 7.1 Hz, 3 H), 1.04 (s, 9 H), 0.87 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 111.7, 82.3, 71.7, 67.4, 65.3, 53.0, 52.5, 37.8, 35.2, 31.8, 29.9, 29.3, 22.6, 28.7, 27.6, 23.5, 22.9, 20.6, 14.1, 6.3; Anal. Calcd $C_{27}H_{54}O_5SSi$: C, 62.50; H, 10.49. Found: C, 62.30; H, 10.63.

Synthesis of 2-methyl-1-3-*anti*-diols



A solution of Reformatsky adduct (3.05 mmol, 1 eq.) in THF (37 mL) was added to a solution of $Yb(OTf)_3$ (3.66 mmol, 1.2 eq.) in THF (37 mL) at 0°C. The mixture was stirred 15 min at 0°C and then cooled at –78°C. A solution of DIBALH (7.32 mmol, 7.32 mL, 1M in toluene, 2.4 eq) was added dropwise. The mixture was stirred at –78°C for 3h. Then MeOH (20 mL), a aqueous saturated solution of sodium and potassium L-tartrate (140 mL) and AcOEt (140 mL) were added successively. The solution was stirring until separation of the phases overnight and extracted with AcOEt (3 x 100mL). The organic layers were washed with a saturated aqueous solution of NH_4Cl (100 mL) for 20 min, then a saturated aqueous solution of $NaHCO_3$ (100 mL) and with brine (100 mL). Then, dried over sodium sulphate filtrated and concentrated under reduced pressure to obtain the residue which was purified by silica gel chromatography without pressure (CH_2Cl_2/EtOAc/MeOH 6:2:0.3).

(+)-[2*R*,3*R*,4*S*,(S)*R*]-6-[1,3]dioxolane-4-hydroxy-3-methyl-1-(*tert*-butylsulfinyl)-heptan-2-ol (10) :

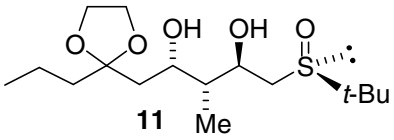


10

The product was obtained by using ketone **5** (145 mg, 0.43 mmol) to perform the diastereoselective reduction reaction to give the reduced product **11** (93 mg, 0.30 mmol, 65%). R_f = 0.36 (AcOEt); White solid; $[\alpha]^{20}_D$: + 63.4 (c 1; $CHCl_3$); mp: 54°C; IR (ATR) ν 3362, 2926; ^{1}H NMR (300 MHz,$CDCl_3$) δ 4.69 (br s, 1 H), 4.32 (X part of a ABX 2nd order, ddd, J_1 = 2.61 Hz, J_2= 6.07 Hz, J_3= 8.68 Hz, 1 H), 4.25 (X part of a ABX 2nd order, br d, J_1= 10.14 Hz, 1 H), 4.00 (s, 4 H), 3.58 (br s, 1 H), 2.75 (AB part of a ABX 2nd order, J_{AB} = 12.8 Hz, J_{AX} = 8.85 Hz, J_{BX} = 2.64 Hz, $\Delta\nu$ = 43 Hz, 2 H), 1.86 (AB part of a ABX 2nd order, J_{AB} = 10.8 Hz, J_{AX} = 7.5 Hz, J_{BX} = 1.0 Hz, $\Delta\nu$ = 74.5 Hz, 2 H), 1.82 (m, 1 H), 1.39 (s,

3 H), 1.28 (s, 9 H), 0.99 (d, *J*= 7.04 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 110.7, 72.6, 68.7, 65.0, 64.7, 54.0, 48.1, 43.4, 42.9, 24.5, 23.0, 10.0. HRMS (ESI^+) calcd for $C_{14}H_{28}O_5S$ ($M + Li^+$) 315.1812, found 315.1811.

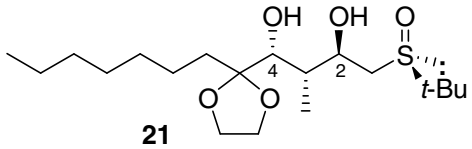
(+)-[2*R*,3*R*,4*S*,(S)*R*)-6-[1,3]-dioxolane-4-hydroxy-3-methyl-(*tert*-butylsulfinyl)-nonan-2-ol (11) :



11

The product was obtained by using ketone **7** (1.02 gr, 3.05 mmol) to perform the diastereoselective reduction reaction to give the reduced product **11** (730 mg, 2.17 mmol, 70%). R_f = 0.36 (AcOEt/MeOH, 9:1). White solid; $[\alpha]^{20}_D$: + 34.7 (c 1; $CHCl_3$); mp: 65°C; IR (ATR) ν 3399, 2961, 2875; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.31 (X part of a ABX 2nd order, ddd, *J* = 8.77, 6.00, 2.88 Hz, 1 H), 4.22 (br d, *J*= 9.96Hz, 1 H), 4.01-3.95 (m, 4 H), 3.20 (br s, 2 H), 2.76 (AB part of a ABX 2nd order, J_{AB} = 12.9 Hz, J_{AX} = 3.0 Hz, J_{BX}= 8.7 Hz, $\Delta\nu$= 54.0 Hz, 2 H), 1.96-1.57 (m, 5 H), 1.42-1.35 (m, 2 H), 1.28 (s, 9 H), 0.99 (d, *J* = 6.96 Hz, 3 H), 0.93 (t, *J* = 7.35 Hz, 3 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 112.0, 72.1, 68.2, 64.8, 64.5, 53.8, 43.0, 40.2, 39.5, 22.6, 17.1, 14.2, 9.5. HRMS (ESI^+) calcd for $C_{16}H_{32}O_5S$ ($M + Li^+$) 343.2125, found 343.2115.

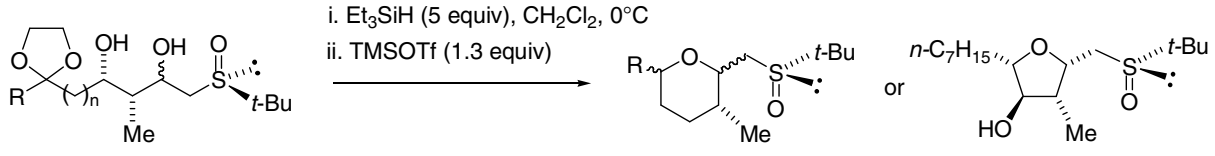
[2*R*,3*R*,4*S*,(S)*R*]-5-[1,3]dioxolane-4-hydroxy-3-méthyl-1-(*t*-butylsulfinyl)-dodécan-2-ol (21) :



21

The product was obtained by using ketone **19** (66 mg, 0,175 mmol) to perform the diastereoselective reduction reaction to give the reduced product (53 mg, 0,140 mmol, 80%); R_f = 0.12 (AcOEt). Light yellow oil. ^{1}H NMR (300 MHz,$CDCl_3$) δ 5.08 (br s, 1 H), 4.30 (X part of a ABX 2nd order, m, 1 H), 4.10-3.92 (m, 4 H), 3.92 (m, 1 H), 3.13 (br s, 1 H), 2.76 (AB part of a ABX 2nd order, J_{AB} = 13.0 Hz, J_{AX} = 10.0 Hz, J_{BX} = 1.9 Hz, $\Delta\nu$ = 57.9 Hz, 2 H), 1.98 (m, 1 H), 1.77-1.50 (m, 2 H), 1.42-1.10 (m, 10 H), 1.27 (s, 9 H), 1.10 (d, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 112.2, 73.3, 73.0, 66.3, 65.5, 54.0, 47.4, 39.2, 34.8, 31.8, 29.9, 29.3, 23.0, 22.6, 22.7, 14.1, 10.0.

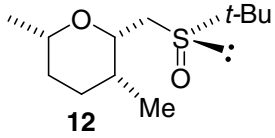
Reductive cyclisation



General procedure. The following description provides a typical experimental procedure for the reductive cyclisation of either 2-methyl-1,3-*syn*-diols or 2-methyl-1,3-*anti*-diols to obtain the THP and THF units.

Et_3SiH (5 eq.; 0.625 mmol) is added dropwise to a solution of 2-methyl-1,3-diol *syn* (1 eq.; 0.125 mmol) in CH_2Cl_2 anhydrous (3.5 mL) at 0°C. After 5 min stirring TMSOTf (1.3 eq.; 0.162 mmol) is added dropwise. The reaction is controlled by TLC (time reactions are between 30 and 90 minutes) and hydrolyzed with distilled water (5mL). After separation of the phases, the organic layer is extracted with CH_2Cl_2 (3x10 mL). The organic layers are dried over Na_2SO_4, filtered and concentrated under reduced pressure.

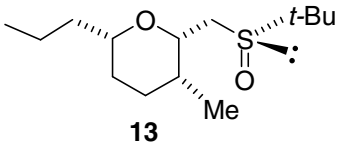
(2*S*,3*R*,6*S*)-2-((*R*)-*tert*-butylsulfinylmethyl)-3,6-dimethyl-tetrahydro-2H-pyran (12) :



12

The product was obtained by using diol **8** (68 mg, 0.22 mmol) to perform the diastereoselective reduction reaction to give a crude mixture which was purified by silica gel chromatography (EtOAc) to obtain pure compound **12** (34 mg, 0.14 mmol, 66%); R_f = 0.27 (AcOEt); White solid; $[\alpha]^{20}_D$: + 154.8 (c 0.33, $CHCl_3$); IR (ATR) ν 3443, 2930; ^{1}H NMR (300 MHz,$CDCl_3$) δ 4.03 (d, J = 10.47 Hz, 1 H), 3.63-3.49 (X part of a ABX 2nd order, m, 1 H), 2.47 (AB part of a ABX 2nd order, J_{AB} = 12.6 Hz, J_{AX} = 10.8 Hz, J_{BX} = 2.1 Hz, $\Delta\nu$ = 84.54 Hz, 2 H), 1.91-1.62 (m, 3 H), 1.48-1.35 (m, 1 H), 1.26 (s, 9 H), 1.19 (d, J = 6.16 Hz, 3 H), 0.99 (d, J = 6.98 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 74.8, 73.4, 52.5, 50.4, 31.1, 27.7, 26.9, 22.9, 21.9, 11.8. HRMS (ESI^+) calcd for $C_{12}H_{24}O_2S$ (M + Li^+) 239.1652, found 239.1645.

(2*S*,3*R*,6*S*)-2-((*R*)-tert-butylsulfinylmethyl)-3-methyl-6-propyl-tetrahydro-2H-pyran (13) :

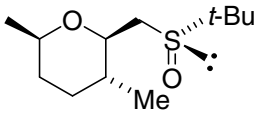


13

The product was obtained by using diol **9** (58 mg, 0.17 mmol) to perform the diastereoselective reduction reaction to give a crude mixture which was purified by silica gel chromatography (EtOAc) to obtain pure compound **13** (35 mg, 0.13 mmol, 74%). R_f = 0.37 (AcOEt/MeOH 96:4). White solid. $[\alpha]^{20}_D$: + 116.8 (c 0.19, $CHCl_3$); IR (ATR) ν 2958, 2931; ^{1}H NMR (300 MHz,$CDCl_3$) δ 4.02 (td, J_1 = 10.64 Hz, J_2 = 2.12 Hz, 1 H), 3.32-3.27 (X part of a ABX 2nd order, m, 1 H), 2.48 (AB part of a ABX 2nd order, J_{AB} = 12.9 Hz, J_{AX} = 10.8 Hz, J_{BX} = 2.1 Hz, $\Delta\nu$ = 87 Hz, 2 H), 1.87-1.36 (m, 9 H), 1.27 (s, 9

H), 0.98 (d, J = 6.87 Hz, 3 H), 0.93 (t, J = 7.03Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 78.6, 73.5, 52.5, 50.6, 38.5, 31.3, 26.1, 22.9, 18.7, 15.3, 14.1, 11.9; Anal. Calcd for $C_{17}H_{34}O_3S$: C, 64.56; H, 10.84. Found: C, 64.21; H, 10.36.

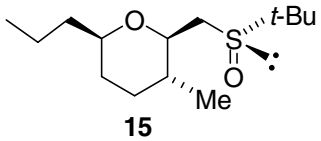
(2*R*,3*R*,6*R*)-2-((*R*)-*tert*-butylsulfinylmethyl)-3,6-dimethyl-tetrahydro-2H-pyran (14) :



14

The product was obtained by using diol **10** (60 mg, 0.19 mmol) to perform the diastereoselective reduction reaction to give 60 mg of crude mixture which was dissolved in MeOH (1.2 mL) containing AcOH (8 µL). Palladium on activated carbon (10%) (one spatula) was added and the mixture was stirred for 48h under H_2 atmosphere. After filtering the solid over SiO_2 and evaporating the solvent, the residue was purified by chromatography (EtOAc) to give the product **14** (39 mg, 0.17 mmol, 90%). R_f = 0.67 (AcOEt/MeOH, 95:5). Colorless wax. $[\alpha]^{20}_D$: + 10.0 (c 0.5, $CHCl_3$).IR (ATR) ν 3443, 2930; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.48-3.38 (m, 2 H), 2.78 (AB part of a ABX 2nd order, J_{AB} = 12 Hz, J_{AX} = 3 Hz, J_{BX} = 3 Hz, $\Delta\nu$ = 95 Hz, 2 H), 1.84-1.58 (m, 5 H), 1.26 (s, 9 H), 1.17 (d, J= 6 Hz, 3 H), 0.94 (d, J =6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 79.0, 74.2, 53.2, 52.1, 34.8, 33.5, 32.8, 22.8, 21.8, 17.7. HRMS (ESI$^+$) calcd for $C_{12}H_{24}O_2S$ (M + Li^+) 239.1652, found 239.1641.

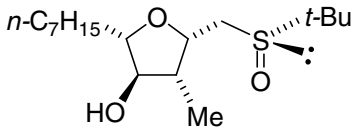
(2*R*,3*R*,6*R*)-2-((*R*)-*tert*-butylsulfinylmethyl)-3-methyl-6-propyl-tetrahydro-2H-pyran (15) :



15

The product was obtained by using diol **11** (46 mg, 0.13 mmol) to perform the diastereoselective reduction reaction to give 30 mg of crude mixture which was dissolved in MeOH (1.2 mL) containing AcOH (8 µL). Palladium on activated carbon (10%) (One spatula) was added and the mixture was stirred for 48h under H_2 atmosphere. After filtering the solid over SiO_2 and evaporating the solvent, the residue was purified by chromatography (EtOAc) to obtain product **15** (26 mg, 0.10 mmol, 77%). R_f = 0.61 (AcOEt/MeOH 95:5). Colorless wax. $[\alpha]^{20}_D$: + 13.5 (c 0.2, $CHCl_3$). IR (ATR) ν 2958, 2931; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.38 (td, J_1 = 4.9 Hz, J_1 = 9.8 Hz, 1 H), 3.32-3.27 (X part of a ABX 2nd order, m, 1 H), 2.79 (AB part of a ABX 2nd order, J_{AB} = 9 Hz, J_{AX} = 3 Hz, J_{BX} = 3 Hz, $\Delta\nu$ = 114 Hz, 2 H), 1.84-1.34 (m, 9 H), 1.26 (s, 9 H), 0.93-0.88 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 79.2, 77.8, 52.4, 38.3, 35.1, 32.8, 31.8, 29.7, 22.9, 18.7, 17.7, 14.1. HRMS (ESI$^+$) calcd for $C_{14}H_{28}O_2S$ (M + Li^+) 267.1965, found 267.1970.

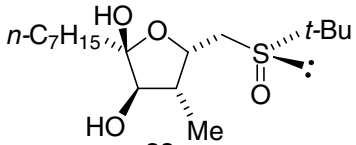
(2*S*,3*R*,4*R*,5*S*)-5-((*R*)-*tert*-butylsulfinylmethyl)-4-methyl-2-heptyl-tetrahydrofuran-3-ol (24) :



24

The product was obtained by using diol **20** (1 eq.; 74 mg; 0.195 mmol). The residue is purified by silica gel chromatography (EtOAc: MeOH; 97:3→96:4) to obtain pure compound **24** (51 mg, 0.16 mmol, 82%). R_f = 0.15 (AcOEt: MeOH, 97:3). White solid. $[\alpha]^{20}_D$: + 88.5 (c=1; $CHCl_3$). mp: 49°C. IR (ATR) *v* 3430; 2957; 2852; ^{1}H NMR (300 MHz,$CDCl_3$) δ 4.52 (dt, J_1 = 8.8 Hz, J_2 = 4.3 Hz, 1 H), 3.64 (td, J_1 = 6.2 Hz, J_2 = 4.5 Hz, 1 H), 3.56 (dd, J_1 = 4.5 Hz, J_2 = 2.6 Hz, 1 H), 3.15 (br s, 1 H), 2.56 (AB part of a ABX 2nd order, J_{AB} = 12.8 Hz, J_{AX} = 9.0 Hz, J_{BX} = 4.3 Hz, Δv =16.0 Hz, 2 H), 2.20 (m, 1 H), 1.55-1.62 (m, 2 H), 1.53-1.12 (m, 19 H), 0.96 (d, J = 7.3 Hz, 3 H), 0.86 (t, J = 6.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 86.3, 83.5, 73.6, 52.9, 47.5, 45.6, 34.3, 31.8, 29.6, 29.2, 26.0, 22.6, 22.8, 14.1, 13.3; Anal. Calcd for $C_{17}H_{34}O_3S$: C, 64.11; H, 10.76. Found: C, 64.03; H, 10.83.

(2S,3R,4R,5S)-5-((R)-*tert*-butylsulfinylmethyl)-2-heptyl-4-methyl-tetrahydrofuran-2,3-diol (23) :



23

Product **23** is a by-product of reaction for the preparation of THF **24**. R_f = 0.06 (EtOAc : MeOH 97:3); ^{1}H NMR (300 MHz,$CDCl_3$) δ 0.86 (t, *J*=7.1 Hz, 3 H), 1.02 (d, *J*= 7.3 Hz, 3 H), 1.15-1.40 (m, 17 H), 1.40-1.56 (m, 2 H), 1.80-2.08 (m, 2 H), 2.52 (m, 1 H), 2.72 (AB part of a ABX 2nd order, J_{AB} = 13.0 Hz, J_{AX} = 6.6 Hz, J_{BX} = 7.5 Hz, Δv =76.5 Hz, 2 H), 3.41 (s, 1 H), 4.92 (dt, J_1 = 7.2 Hz, J_2 = 4.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.9, 14.1, 22.8, 22.5, 22.6, 29.2, 29.7, 31.8, 34.6, 43.6, 47.1, 53.4, 76.1, 83.4, 103.6.