Supporting Information

Diastereo- and Enantioselective Access to Stereotriads through a Flexible Coupling of Substituted Aldehydes and Alkenes

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1. General Information

Unless otherwise stated, all glassware was flame-dried before use and all reactions were performed under an atmosphere of argon. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise stated. All aldehydes were distilled or purified via flash column chromatography before use. Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminium plates coated with silica gel F$_{254}$ with 0.2 mm thickness. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using potassium permanganate. Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck and co.). Neat infra-red spectra were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Wavenumbers ($\nu_{\text{max}}$) are reported in cm$^{-1}$. Mass spectra were obtained using a Finnigan MAT 8200 or (70 eV) or an Agilent 5973 (70 eV) spectrometer, using electrospray ionization (ESI). All $^1$H NMR and $^{13}$C NMR spectra were recorded using a Bruker AV-400 or AV-600 spectrometer at 300K. Chemical shifts were given in parts per million (ppm, $\delta$), referenced to the solvent peak of CDCl$_3$, defined at $\delta = 7.26$ ppm ($^1$H NMR) and $\delta = 77.16$ ($^{13}$C NMR). Coupling constants are quoted in Hz ($J$). $^1$H NMR splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), pentet (p). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br).
2. Preparation of Starting Materials

2.1 Synthesis of unsaturated alcohol substrates (Method A)

To a flame-dried Schlenk flask containing a suspension of Mg powder (15 mmol, 1.5 equiv.) in dry Et₂O (10.0 mL) were added 5 drops 1, 2-dibromoethane and 5 drops of alkyl bromide at ambient temperature and the mixture was stirred for 5 minutes. Then alkyl bromide (12.0 mmol) was slowly added and the reaction was kept stirring at room temperature for 30 minutes.

The Grignard reagent was added to a suspension of (S)-(−)-Propylene Oxide (10 mmol) and CuCN (10 mol%) in THF (20 mL) at -78° C. The reaction mixture was allowed to warm to room temperature over 3 h. Then sat. NH₄Cl solution was slowly added, extracted with ether and the combined organic phases were dried with anhydrous MgSO₄ and filtered. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (heptane/ethyl acetate 4:1).

(S)-6-methylhept-6-en-2-ol (1f)

1f was prepared according to the general procedure and obtained as colorless oil in 78% yield.

H NMR (400 MHz, CDCl₃) δ 4.70 (s, 1H), 4.68 (s, 1H), 3.89 – 3.73 (m, 1H), 2.03 (t, J = 6.2 Hz, 2H), 1.71 (s, 3H), 1.61 – 1.39 (m, 4H), 1.36 (s, 1H), 1.19 (d, J = 6.2 Hz, 3H).

C NMR (100 MHz, CDCl₃) δ 145.9, 110.1, 68.2, 39.0, 37.8, 23.8, 23.7, 22.5.

HRMS (GC-MS): m/z calcd. for (M-H₂O)⁺ 110.1096; found 110.1094.

[α]D²⁰ = 5.5 (C = 0.66, CHCl₃)

FT-IR (neat): 3360 (br), 2966, 2926, 2875, 2857, 1453, 1122 cm⁻¹
(S)-1-chloro-5-(cyclohex-1-en-1-yl)pentan-2-ol (1k)

1k was prepared according to the general procedure and obtained as colorless oil in 70% yield.

$^1$H NMR (CDCl$_3$ 400 MHz): $\delta$ 5.33 (m, 1H), 3.73-3.74 (m, 1H), 3.57 (dd, $J = 3.2$, 10.8Hz, 1H), 3.41 (dd, $J = 7.2$ Hz, 11.2 Hz, 1H), 2.04, 2.06 (m, 1H), 1.82-1.92 (m, 6H), 1.37-1.57 (m, 8H).

$^{13}$C NMR (CDCl$_3$ 100 MHz): $\delta$ 137.2, 12.4, 71.4, 50.6, 37.8, 33.8, 28.2, 25.2, 23.5, 23.0, 22.6.

HRMS (EI): $m/z$ calcd. for (M -H$_2$O - HCl)$^+$ 148.1252; found: 148.1243.

FT-IR (neat): 3377, 2926, 2862, 1657, 1434, 1327, 1275, 1261, 1194, 1133, 1065, 915, 750, 701 cm$^{-1}$.

[$\alpha$$_d^{20}$$]_D = 2.6$ (C = 1.0, CHCl$_3$)

(S)-5-(cyclohex-1-en-1-yl)pentan-2-ol (1l)

1l was prepared according to the general procedure and obtained as colorless, sticky oil in 78% yield.

$^1$H NMR (CDCl$_3$ 400 MHz): $\delta$ 5.23-5.24 (m, 1H), 3.69-3.73 (m, 1H), 2.17-2.22 (m, 2H), 2.10-2.14 (m, 2H), 1.99 (t, $J = 6.0$ Hz, 2H), 1.71-1.79 (m, 2H), 1.30-1.48 (m, 4H), 1.26 (b s, 1H), 1.09(d, $J= 6.4$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$ 100 MHz): $\delta$ 137.6, 121.0, 68.2, 39.0, 37.9, 28.2, 25.2, 23.8, 23.5, 23.0, 22.6.

HRMS (EI) m/z calcd for C$_{10}$H$_{17}$O (M-CH$_4$)$^+$ 153.1274; found: 153.1275.

FT-IR (neat): 3338, 2923, 2857, 2834, 1439, 1372, 1276, 1262, 1125, 1090, 939, 917, 837, 800, 764, 750 cm$^{-1}$.

[$\alpha$$_d^{20}$$]_D = 6.9$ (C = 1.0, CHCl$_3$)
2.2 Synthesis of unsaturated alcohol substrates (Method B)

(S)-tert-butyl((5-iodopentan-2-yl)oxy)dimethylsilane (S-1)
S-1 was prepared in 55% yield according to a known procedure.[1]

General procedure for the synthesis of trisubstituted alkene-substrates

The required vinyl bromides are commercially available or were synthesized based on a previously reported procedure.[2]
Vinyl bromide (15 mmol, 1.5 equiv.) and dry THF (20.0 mL) were added to a flame dried Schlenk flask. The flask was placed in a -78 °C dry ice-acetone bath, n-BuLi was slowly added and the reaction was kept at the same temperature for 30 minutes. Then CuCN (10 mol%) was added in one portion, the reaction was allowed to warm to r.t. and stirred at this temperature for 1h. S-1 was added in one portion at -78 °C, the reaction was stirred at the same temperature for 2 h and quenched with sat. NH₄Cl solution. The biphasic mixture was extracted with ether, the combined organic phased were dried with anhydrous MgSO4, filtered and the solvent was removed under reduced pressure to afford the crude products. Purification by silica gel chromatography (Heptane/Ethyl acetate = 3/1) gave the desired products.

(S, E)-6-methyloct-6-en-2-ol (1g)
1g was prepared according to the general procedure and obtained as colorless, sticky oil in 85% yield.

1H NMR (CDCl3, 400 MHz): δ 5.13-5.18 (m, 1H), 3.72-3.76 (m, 1H), 1.90-1.98 (m, 2H), 1.53-1.54 (m, 3H), 1.50-1.53 (m, 3H), 1.32-1.48 (m, 4H), 1.14 (d, J = 6.0 Hz, 3H).
\(^{13}\)C NMR (CDCl\(_3\) 150 MHz): \(\delta\) 135.6, 118.5, 68.1, 39.5, 38.9, 24.0, 23.5, 15.5, 13.3.

HRMS (EI): m/z calcd. for (M-CH\(_4\))\(^+\) 127.1117; found: 127.1111.

FT-IR (neat): 3335, 2966, 2928, 2861, 1454, 1375, 1129, 970, 938, 815, 776, 735 cm\(^{-1}\).

\([\alpha]_D^{20}\) = 4.1 (C = 1.0, CHCl\(_3\))

\((S)-5\)-(cyclopent-1-en-1-yl)pentan-2-ol (1h)

1h was prepared according to the general procedure and obtained as colorless, sticky oil in 50% yield.

\(^1\)H NMR (CDCl\(_3\) 400 MHz): \(\delta\) 5.22-5.25 (m, 1H), 3.67-3.75 (m, 1H), 2.17-2.22 (m, 2H), 2.10-2.15 (m, 2H), 1.99 (t, \(J = 6.0\) Hz, 2H), 1.71-1.79 (m, 2H), 1.31-1.48 (m, 4H), 1.25 (m, 1H), 1.09 (d, \(J = 6.4\) Hz, 3H).

\(^{13}\)C NMR (CDCl\(_3\) 100 MHz): \(\delta\) 144.6, 123.4, 68.1, 39.4, 31.1, 23.9, 23.5, 23.4.

HRMS (ESI): m/z calcd. for C\(_{10}\)H\(_{19}\)O (M + H\(^+\)) 155.1430; found: 155.1428.

FT-IR (neat): 3367, 2932, 2846, 1457, 1374, 1123, 1081, 1035, 764, 750 cm\(^{-1}\).

\([\alpha]_D^{20}\) = 3.0 (C = 1.0, CHCl\(_3\))

\((S)-5\)-(cyclohept-1-en-1-yl)pentan-2-ol (1i)

1i was prepared according to the general procedure and obtained as colorless, sticky oil in 85% yield.

\(^1\)H NMR (CDCl\(_3\) 400 MHz): \(\delta\) 5.48-5.51 (m, 1H), 3.74-3.78 (m, 1H), 2.00-2.06 (m, 4H), 1.92-1.95 (m, 2H), 1.05-1.71 (m, 2H), 1.35-1.45 (m, 10H), 1.14 (d, \(J = 6.0\) Hz, 3H).

\(^{13}\)C NMR (CDCl\(_3\) 150 MHz): \(\delta\) 144.5, 126.1, 68.1, 40.1, 38.9, 32.7, 32.6, 28.3, 27.4, 26.8, 24.0, 23.5.

HRMS (EI): m/z calcd. for C\(_{12}\)H\(_{22}\)O (M\(^+\)) 182.1671; found: 182.1662.

FT-IR (neat): 3341, 2917, 2847, 1446, 1373, 1275, 1129, 1092, 1067, 987, 941, 845, 764, 750 cm\(^{-1}\).  

\([\alpha]_D^{20}\) = 5.3 (C = 1.0, CHCl\(_3\))
**(S, E)-5-(cyclooct-1-en-1-yl)pentan-2-ol (1j)**

1j was prepared according to the general procedure and obtained as colorless, sticky oil in 75% yield.

**\(^1\)H NMR** (CDCl\(_3\) 400 MHz): \(\delta\) 5.23-5.29 (m, 1H), 3.72-3.76 (m, 1H), 2.05-2.10 (m, 2H), 1.99-2.04 (m, 2H), 1.90-1.94 (m, 2H), 1.32-1.49 (m, 12H), 1.12 (d, \(J = 6.0\)Hz, 3H).

**\(^13\)C NMR** (CDCl\(_3\) 100 MHz): \(\delta\) 140.6, 123.9, 68.2, 39.2, 37.4, 30.0, 28.8, 28.8, 26.5, 26.3, 26.3, 25.9, 24.2, 23.5.

**HRMS** (EI): \(m/z\) calcd. for (M)\(^+\) 196.1827; found: 196.1817.

**FT-IR** (neat): 3367, 2932, 2846, 1457, 1374, 1123, 1081, 1035, 764 cm\(^{-1}\).

\([\alpha]_D^{20} = 6.5\ (C = 1.0,\ CHCl_3)\)
2.3 Synthesis of heteroatom-bridged substrates

**(S)-4-(dimethyl(prop-1-en-2-yl)silyl)butan-2-ol (1d)**

To a flame-dried Schlenk flask containing a suspension of Mg powder (15 mmol, 1.5 equiv.) in dry Et₂O (10.0 mL) were added 5 drops 1, 2-dibromoethane and 5 drops of (chloromethyl)dimethyl(prop-1-en-2-yl)silane and the mixture was stirred for 5 minutes at ambient temperature. Then (chloromethyl)dimethyl(prop-1-en-2-yl)silane (12.0 mmol) was slowly added and the reaction was kept stirring at room temperature for 30 minutes to give ((dimethyl(prop-1-en-2-yl)silyl)methyl)magnesium chloride (7). Grignard reagent 7 was added to a suspension of (S)-(−)-Propylene Oxide (10 mmol) and CuCN (10 mol%) in Et₂O (20 mL) at -78° C. The reaction mixture was allowed to warm to room temperature over 3 h. Then sat. NH₄Cl solution was slowly added, the mixture was extracted with ether and the combined organic phases were dried with anhydrous MgSO₄ and filtered. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (heptane/ethyl acetate 4:1) to give the product as colorless oil in 90% yield.

**^1H NMR** (CDCl₃ 400 MHz): δ 5.57-5.59 (m, 1H), 5.24-5.25 (m, 1H), 3.68-3.73 (m, 1H), 1.81 (t, J = 1.6 Hz, 3H), 1.18 (d, J = 6.0 Hz, 3H), 1.37-1.45 (m, 2H), 0.64-0.72 (m, 1H), 0.48-0.56 (m, 1H), 0.08 (s, 6H).

**^13C NMR** (CDCl₃ 100 MHz): δ 146.8, 125.2, 70.4, 33.4, 22.8, 22.6, 10.2, -3.9, -4.0.

**HRMS** (EI): m/z calcld. for (M-C₃H₇)⁺ 129.0736; found: 129.0728.

**FT-IR** (neat): 3333, 2957, 2926, 1448, 1275, 1255, 1180, 1119, 1069, 1019, 920, 836, 767, 750 cm⁻¹.

[ [α]D 20] = 4.9 (C = 1.0, CHCl₃)

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(S)-1-((2-methylallyl)oxy)propan-2-ol (1a)

To a flame-dried Schlenk flask containing a suspension of NaH powder (33 mmol, 1.1 equiv.), which was previously washed with pentane (50 mL), DMF (50 mL) was added. Allylic alcohol (30 mmol) was added dropwise. After completion of addition of allyl alcohol, the reaction mixture was further stirred for 30 minutes and HMPA (5 equiv.) was added. Then (S)-(-)-Propylene Oxide (35 mmol) was added in one portion at r.t. and the reaction mixture was stirred at 50 °C for 12 h. Upon completion of the reaction, sat. NH₄Cl solution was added and extracted with pentane. The combined organic phases were dried with anhydrous MgSO₄, filtered and the solvent was removed under reduced pressure to afford the crude product. Purification by silica gel chromatography (Pentane/DCM = 1/1) afforded the clean product as colorless oil in 50% yield.

$^{1}H$ NMR (CDCl₃ 400 MHz): $\delta$ 4.98-4.99 (m, 1H), 4.92-4.93 (m, 1H), 3.96-4.04 (m, 1H), 3.95 (s, 2H), 3.43 (dd, $J = 3.2, 9.4$ Hz, 1H), 3.23 (dd, $J = 8.0, 9.4$ Hz, 1H), 1.77 (s, 3H), 1.80 (d, $J = 6.4$ Hz, 3H).

$^{13}C$ NMR (CDCl₃ 100 MHz): $\delta$ 141.9, 112.3, 75.4, 75.1, 66.4, 19.4, 18.6.

HRMS (EI): $m/z$ calcd. for (M-CH₃)$^+$ 115.0754; found: 115.0748.

FT-IR (neat): 3425, 2972, 2859, 1659, 1451, 1374, 1260, 1091, 984, 898, 750 cm$^{-1}$.

$[\alpha]_{D}$ = 28.9 (C = 1.0, CHCl₃)
(S)-1-((2-phenylallyl)thio)propan-2-ol (1e)

2-phenylallyl carbamimidothioate salt was dissolved in water, solid NaOH (5 equiv.) was slowly added followed by (S)-2-methyloxirane (1.2 equiv.), which was added in one portion. Then the reaction mixture was stirred for 2 h and extracted three times with Et₂O. The organic phase was dried with anhydrous MgSO₄, filtered and the solvent was removed under reduced pressure to afford the crude product. Purification by silica gel chromatography (Heptane: Ethyl acetate = 4:1) afforded the pure product as sticky oil (95% yield).

**¹H NMR** (CDCl₃ 600 MHz): δ 7.48-7.49 (m, 2H), 7.32-7.39 (m, 3H), 5.32 (s, 1H), 5.24 (s, 1H), 3.86-3.89 (m, 1H), 3.65 (s, 2H), 2.70 (dd, J = 3.0, 12 Hz, 1H), 2.42-2.45 (m, 2H), 1.25 (d, J = 5.2 Hz, 3H).

**¹³C NMR** (CDCl₃ 150 MHz): δ 143.5, 139.0, 128.4, 128.0, 126.3, 115.4, 65.3, 40.6, 36.5, 22.0.

**HRMS** (ESI): m/z calcd. for (M)$^{+}$ 208.0922; found: 208.0917.

**FT-IR** (neat): 3366, 2968, 2911, 1623, 1494, 1445, 1407, 1302, 1124, 1069, 1038, 902, 777, 698 cm⁻¹.

[α]$^D_{D}$ = 62.8 (C = 1.0, CHCl₃)
2.4. Synthesis of aldehyde 2f

(R)-3-(benzyloxy)-5-phenylpentanal (2f)

The aldehyde was prepared based on a previously reported procedure in 75% yield as colorless sticky oil.\[3\]

\(^1\)H NMR (CDCl\(_3\) 600 MHz): \(\delta\) 9.8 (t, \(J = 2.0\) Hz, 1H), 7.30-7.30 (m, 7H), 7.19-7.25 (m, 3H), 4.58 (s, 2H), 3.98-4.04 (m, 1H), 2.60-2.82 (m, 4H), 1.89-2.09 (m, 2H).

\(^{13}\)C NMR (CDCl\(_3\) 100 MHz): \(\delta\) 141.5, 138.1, 128.5, 128.5, 128.4, 127.9, 127.8, 126.0, 73.7, 71.4, 48.3, 36.1, 31.4.

\([\alpha]_D^{20}\) = 2.0 (C = 1.0, CHCl\(_3\))
3. **Synthesis and Functionalisation of the Coupling Products**

**GP 1:** Alcohol (0.2 mmol) was diluted with 2 mL 1,2-dichloroethane and brought to the reaction temperature using an oil bath. Aldehyde (0.24 mmol, 1.2 eq.) and FeCl$_3$ (0.01 mmol, 5 mol%) were successively added and the reaction was heated for 5 minutes. Water (0.2 mL) was added and the reaction was allowed to cool to room temperature with stirring. The reaction mixture was filtered over silica, eluted with dichloromethane and the solvent was removed under reduced pressure to obtain crude sticky product. Purification by flash column chromatography afforded the pure products.

**GP 2:** Alcohol (0.2 mmol) was diluted with 2 mL dichloromethane. Aldehyde (0.24 mmol, 1.2 eq.) and FeCl$_3$ (0.04 mmol, 20 mol%) were successively added and the reaction was stirred at r.t. until Alcohol was consumed. Water (0.2 mL) was added and the reaction was allowed to cool to room temperature with stirring. The reaction mixture was filtered over silica, eluted with dichloromethane and the solvent was removed under reduced pressure to obtain crude sticky product. Purification by flash column chromatography afforded the pure products.

**GP 3:** Alcohol (0.2 mmol) was diluted with 2 mL dichloromethane. Aldehyde (0.24 mmol, 1.2 eq.) and BF$_3$·Et$_2$O were successively added and the reaction was stirred at r.t. for 2 h. Water (0.2 mL) was added and the reaction was allowed to cool to room temperature with stirring. The reaction mixture was filtered over silica, eluted with dichloromethane and the solvent was removed under reduced pressure. Purification by flash column chromatography afforded the pure products.

**Caution!** To make stereotriads, the reactions are sensitive to the purity of the aldehydes. In order to obtain the reported results, the aldehyde must always be distilled or purified by column chromatography before use. If an impurity is present in the starting materials, the reaction does not reach full conversion. In this case, another dose of catalyst can be added without dramatically influencing the yield and $ee$-values.
4-(((2S,4R)-4-hydroxy-6-phenylhexan-2-yl)dimethylsilyl)butan-2-one (3d)

Compound 3d was prepared according to the GP3 (50% BF3 Et2O) at room temperature and obtained in 70% yield as colorless oil after column chromatography (2:1 of heptane:EtOAc).

1H NMR spectroscopic analysis of the unpurified reaction mixture indicated >20:1 dr.

HPLC analysis (Column: Chiralcel OD-H 250 × 4.6 mm; Solvent System: n-Heptane + 0.1% IPA: EtOH =95:5; Flow: 0.70 mL/min, 254 nm) indicated > 99% ee (t_minor = 12.5 min, t_major = 14.8 min)

1H NMR (CDCl3 600 MHz): δ 7.27-7.30 (m, 2H), 7.17-7.21 (m, 3H), 3.75 (m, 1H), 2.78-2.83 (m, 1H), 2.66-2.71 (m, 1H), 2.39 (t, J = 5.6 Hz, 2H), 2.15 (s, 3H), 1.71-1.80 (m, 2H), 1.46-1.50 (m, 1H), 0.93 (b s, 3H), 0.92-0.96 (m, 1H), 0.74-0.80 (m, 2H), -0.04 (s, 3H), -0.05 (s, 3H).

13C NMR (CDCl3 150 MHz): δ 209.9, 142.1, 128.4, 125.8, 68.2, 40.0, 39.0, 38.2, 32.3, 29.3, 13.9, 13.3, 6.9, -5.5, -5.5.

HRMS (ESI): m/z calcd. for C18H30NaO2Si (M + Na)+ 329.1907; found: 329.1906.

FT-IR (neat): 2947, 2865, 1712, 1454, 1412, 1358, 1065, 839, 764, 700cm⁻¹.

[α]D = 37.5 (C = 0.8, CHCl3)

Synthesis of (2S,4R)-6-phenylhexane-2,4-diol (4a)

Procedure: To a 25-mL, round-bottomed flask was added 3t (1.0 mmol), Na2HPO4 (2.0 mmol, 2.0 eq.) and dichloromethane (10 mL). The suspension was stirred vigorously at room temperature, then m-CPBA solid was slowly added by several portion. The solution was stirred at r.t. for 12. The reaction was quenched with Na2S2O3 (3.2 mmol, 16 eq.) and concentrated in vacuo. The crude residue was redissolved in THF (5 mL) and 3 mL TBAF was added and reflex for 1h. Then 37% H2O2 (64 equiv.) was added at r.t., which
Further stirred for 8 h at the same temperature. The reaction was quenched with Na$_2$S$_2$O$_3$ (3.2 mmol, 16 eq.) extracted with ether and dried over MgSO$_4$. Purification by flash column chromatography (1:1 heptane/EtOAc) afforded (2S,4R)-6-phenylhexane-2,4-diol as colorless oil in 90% yield.

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated >20:1 dr.

HPLC analysis (Column: Chiralcel OD-H 250 × 4.6 mm; Solvent System: n-Heptane + 0.1% IPA:EtOH = 95:5; Flow: 1.0 mL/min, 210 nm; indicated > 99% ee ($t_{\text{minor}} = 21.7$ min, $t_{\text{major}} = 18.5$ min)

$^1$H NMR (CDCl$_3$ 400 MHz): δ 7.17-7.22 (m, 2H), 7.08-7.12 (m, 3H), 3.91-3.99 (m, 1H), 3.76-3.82 (m, 1H), 3.37 (b s, 2H), 2.55-2.72 (m, 2H), 1.62-1.77 (m, 2H), 1.41-1.54 (m, 2H), 1.12 (d, J = 6.0 Hz, 3H).

$^{13}$C NMR (CDCl$_3$ 100 MHz): δ 142.0, 128.4, 125.9, 72.2, 69.1, 44.6, 39.8, 31.7, 24.3.

HRMS (ESI): m/z calcd. for C$_{12}$H$_{18}$NaO$_2$ (M + Na)$^+$ 217.1199; found: 217.1198.

[$[[\alpha]]$]$_D^20$ = 22.4 (c = 1.0, CHCl$_3$)

FT-IR (neat): 3311, 2931, 2860, 1495, 1453, 1320, 1276, 1132, 1076, 932, 838, 748, 698 cm$^{-1}$.

1-(((2S,4R)-4-hydroxy-2-methyl-6-phenylhexyl)oxy)propan-2-one (3c)

Compound 3c was prepared according to the GP3 at r.t. and obtained in 50% yield as colorless oil after column chromatography (2:1 heptane:EtOAc).

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated > 20:1 dr.

HPLC analysis (AD-H column, 3% iPrOH/hexanes, 0.80 mL/min, 254 nm) indicated > 99% ee ($t_{\text{minor}} = 29.8$ min, $t_{\text{major}} = 34.1$ min).

$^1$H NMR (CDCl$_3$ 600 MHz): δ 7.26-7.29 (m, 2H), 7.16-7.21 (m, 3H), 4.04 (s, 2H), 3.69-3.73 (m, 1H), 3.37 (dd, J = 5.4, 7.2 Hz, 1H), 3.32 (dd, J = 7.2, 7.3 Hz, 1H), 2.78-2.82 (m, 1H), 2.66-2.71 (m, 1H), 2.14 (s, 3H), 1.98-2.03 (m, 1H), 1.72-1.81 (m, 2H), 1.54-1.59 (m, 1H), 1.36-1.40 (m, 1H), 0.93 (d, J = 6.6 Hz).
Synthesis of (2S,4R)-2-methyl-6-phenylhexane-1,4-diol (4b)

**Procedure:** To a 25-mL, round-bottomed flask was added 3c (1.0 mmol), Na$_2$HPO$_4$ (2.0 mmol, 2.0 eq.) and dichloromethane (10 mL). The suspension was stirred vigorously at room temperature, then $m$-CPBA solid was slowly added in several portions. The solution was stirred for 12 h at r.t. °C, by which time $^1$H NMR analysis had indicated consumption of the starting material. The reaction was quenched with Na$_2$S$_2$O$_3$ (3.2 mmol, 16 eq.) and concentrated in vacuo. The crude residue was redissolved in THF : 1M HCl = 1:1 (5 mL). The reaction was stirred at r.t. for 3 h, then extracted with ether and dried over MgSO$_4$. Purification by flash column chromatography (1:1 heptane/EtOAc) afforded (2S,4R)-2-methyl-6-phenylhexane-1,4-diol 4b as off-yellow oil in 91% yield.

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated >20:1 dr.

HPLC analysis (Column: Chiralpak IC 250 × 4.6 mm; Solvent System: n-Heptane + 0.1% iPrOH; iPrOH =95:5); Flow: 1 mL/min, 254 nm) indicated > 99% ee (t$_{minor}$ = 17.3 min, t$_{major}$ = 19.9 min)

$^1$H NMR (CDCl$_3$ 600 MHz): δ 7.19-7.23 (m, 2H), 7.09-7.14 (m, 2H), 3.62-3.68 (m, 1H), 3.51 (dd, $J = 4.4$, 10.8 Hz, 1H), 3.32 (dd, $J = 7.6$ Hz, 10.4 Hz, 1H), 2.58-2.76 (m, 2H), 2.76 (bs, 2H), 1.69-1.80 (m, 3H), 1.36-1.47 (m, 2H), 0.84 (d, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$ 150 MHz): δ 206.6, 142.2, 128.3, 128.3, 125.6, 77.7, 76.3, 69.5, 42.7, 40.0, 32.1, 31.2, 26.2, 17.5.

HRMS (ESI): m/z calcd. for C$_{13}$H$_{20}$NaO$_2$ (M + Na)$^+$ 231.1356; found: 231.1353.
FT-IR (neat): 3319, 2927, 1455, 1276.1261, 1033, 764, 750 cm$^{-1}$.

$[\alpha]_D^20 = -7.0$ (C = 0.7, CHCl$_3$)

1-(((2R,4R)-4-hydroxy-2,6-diphenylhexyl)thio)propan-2-one (3e)

Compound 3e was prepared according to the GP3 at r.t. in diethyl ether and obtained in 51% yield as colorless oil after column chromatography (2:1 heptane:EtOAc).

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated >20:1 dr.

HPLC analysis (Column: Chiralcel OD-H 250 × 4.6 mm; Solvent System: (n-Heptane + 0.1% i-PrOH) : i-PrOH = 8:2; Flow: 1.0 mL/min, 210 nm; indicated > 99% ee ($t_{\text{minor}} = 15.2$ min, $t_{\text{major}} = 13.2$ min)

$^1$H NMR (CDCl$_3$ 600 MHz): $\delta$ 7.33-7.36 (m, 2H), 7.17-7.27 (m, 6H), 7.12-7.13 (m, 2H), 3.37-3.40 (m, 1H), 3.11-3.16 (m, 1H), 3.13 ($d$, $J = 6$Hz, 2H), 2.78 ($d$, $J = 6$Hz, 2H), 2.67-2.72 (m, 1H), 2.55-2.60 (m, 1H), 2.25 (s, 3H), 1.93-1.98 (m, 1H), 1.78-1.83 (m, 1H), 1.71-1.74 (m, 2H), 1.47 ($d$, $J = 1.2$Hz, 1H).

$^{13}$C NMR (CDCl$_3$ 150 MHz): $\delta$ 204.0, 142.9, 141.9, 128.6, 128.3, 128.2, 127.7, 126.8, 125.7, 69.1, 42.7, 42.2, 41.9, 40.0, 39.3, 32.0, 27.7.

HRMS (ESI): $m/z$ calcd. for C$_{21}$H$_{26}$NaO$_2$S (M + Na)$^+$ 365.1546; found: 365.1541.

FT-IR (neat): 3423, 3026, 2929, 2858, 1708, 1494, 1453, 1408, 1360, 1276, 1159, 1030, 750, 700 cm$^{-1}$.

$[\alpha]_D^20 = 5.8$ (C = 1.0, CDCl$_3$)

Synthesis of (3R,5R)-1,5-diphenylhexan-3-ol (4c)

Procedure: To a 25-mL, round-bottomed flask was added 3e (1.0 mmol) in MeOH (10 mL) under H$_2$ balloon. The solution was stirred vigorously at room temperature, then
Raney-Ni (23 equiv.) solid was added by one-portion. The solution was stirred at r.t. until the starting materials was consumed. The reaction was filtered via celite concentrated in vacuo. The crude residue was purified by flash column chromatography (5:1 heptane/EtOAc) afforded (3R,5R)-1,5-diphenylhexan-3-ol 9 as sticky colorless oil in 80% yield.

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated >20:1 dr.

HPLC analysis analysis of the Fmoc-derivatized analog (Column: Chiralcel OD-H 250×4.6 mm; Solvent System: (n-Heptane + 0.1% i-PrOH):i-PrOH = 99:1; Flow: 0.7 mL/min, 210 nm; indicated 97% ee ($t_{\text{minor}} = 9.5$ min, $t_{\text{major}} = 16.8$ min)

$^1$H NMR (CDCl$_3$ 400 MHz): $\delta$ 7.02-7.24 (m, 10H), 3.30-3.36 (m, 1H), 2.88-2.97 (m, 1H), 2.57-2.64 (m, 1H), 2.45-2.52 (m, 1H), 1.60-1.74 (m, 4H), 1.19 (d, $J = 7.0$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$ 100 MHz): $\delta$ 146.7, 142.1, 128.5, 128.4, 128.3, 127.1, 126.1, 126.8, 69.5, 45.8, 39.9, 36.5, 32.0, 23.3.

HRMS (ESI): $m/z$ calcd. for C$_{18}$H$_{22}$NaO (M + Na)$^+$ 277.1563; found: 277.1559.

FT-IR (neat): 3352, 2924, 2866, 1602, 1493, 1452, 1276,910, 762, 749, 697 cm$^{-1}$.

$\left[ \alpha \right]_D^{20} = -3.8$ (C = 1.0, CHCl$_3$)

(6R,8R)-8-hydroxy-6-methyl-10-phenyldecan-2-one ((R, R)-3f)

Compound (R, R)-3f was prepared according to the GP1 at 100°C and obtained in 76% yield as colorless oil after column chromatography (3:1 heptane:EtOAc).

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated > 20:1 dr.

HPLC analysis (Chiralcel OD-H 250×4, 6 mm, (n-Heptane+0.1% i-PrOH):EtOH = 95:5, 0.70 mL/min, 210 nm) indicated > 99% ee ($t_{\text{minor}} = 13.93$ min, $t_{\text{major}} = 15.84$ min).

$^1$H NMR (CDCl$_3$ 400 MHz): $\delta$ 7.28-7.32 (m, 2H), 7.12-7.23 (m, 3H), 3.67-3.82 (m, 1H), 2.77-2.85 (m,1H), 2.65-2.73 (m, 1H), 2.42 (t, $J = 7.2$ Hz, 2H), 2.14 (s, 3H), 1.74-1.80 (m, 2H), 1.48-1.71 (m, 4H),1.14-1.33 (m, 4H), 0.91 (d, $J = 6.4$ Hz, 3H).
HRMS (ESI): m/z calcd. for C_{17}H_{26}NaO_2 (M + Na)^+ 327.2295; Found: 327.2291.

FT-IR (neat): 3423, 2966, 1710, 1495, 1454, 1409, 1361, 1165, 1054, 750, 700 cm\(^{-1}\).

\[ [\alpha]^D = \text{-}5.6 \quad \text{(C = 1.0, CHCl}_3) \]

**Synthesis of (6R,8R,E)-8-hydroxy-6-methyl-10-phenyldec-3-en-2-one**

To a solution of \((R, R)-3f\) (0.3 mmol) in 1 mL THF was added lutidine (1.2 mmol, 4 eq.) at room temperature. After stirring for 10 minutes, tert-butylidimethylsilyl trifluoromethanesulfonate (0.9 mmol, 3 eq.) was added dropwise and the reaction mixture was stirred for 13 hours. The reaction was quenched with saturated aqueous ammonium chloride (3 mL), extracted with ether and dried over Na\(_2\)SO\(_4\). The solvent was removed under reduced pressure giving the product as 2:1 mixture of diastereoisomers. Remaining lutidine was removed using filtration over celite, layered with a small pad of silica. The eluent (heptane + 1% trimethylamine) was cooled to -78°C before using.

Previously obtained silyl enol ether and Pd(OAc)_2 (0.03 mmol, 10 mol\%) were dissolved in 3 mL DMSO, frozen in a bath of liquid nitrogen, evacuated and backfilled with pure oxygen using a balloon. The Schlenk tube was directly taken out of the nitrogen bath, warmed to room temperature and heated at 80°C for 13 h. Upon completion, the reaction mixture was diluted with water and extracted with dichloromethane three times. The combined organic phases were dried over Na\(_2\)SO\(_4\) and the solvent removed under reduced pressure. The crude product was purified using flash column chromatography (20:1-9:1 heptane/EtOAc) to give \((6R,8R,E)-8\text{-hydroxy-6-methyl-10-phenyldec-3-en-2-one}\) in 57% yield over 2 steps.

\(^1\)H NMR spectroscopic analysis of the unpurified reaction mixture indicated \(> 20: 1\) dr.

HPLC analysis (Chiralpak IA, (n-heptane + 0.1% iPrOH) : iPrOH = 98.5:1.5, 0.70 mL/min, 210 nm) indicated \(> 99\% \text{ ee}\) (t\(_{\text{minor}} = 7.9\) min, t\(_{\text{major}} = 7.4\) min).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 – 7.23 (m, 2H), 7.18 (dd, $J = 10.0$, 4.4 Hz, 3H), 6.76 (dt, $J = 15.8$, 7.3 Hz), 6.08 (dt, $J = 15.9$, 1.2 Hz, 1H), 3.79 (td, $J = 9.6$, 5.4 Hz, 1H), 2.63 (dd, $J = 9.7$, 6.9 Hz, 2H), 2.24 (s, 3H, H1), 2.23–2.14 (m, 1H), 2.14–2.06 (m, 1H), 1.91–1.73 (m, 2H), 1.59–1.51 (m, 1H), 1.33–1.20 (m, 2H), 0.93–0.91 (m, 12H), 0.06 (s, 3H), 0.04 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 198.6, 147.0, 142.6, 132.7, 128.5(2C), 128.5 (2C), 125.9, 69.8, 44.1, 40.7, 39.9, 31.5, 29.1, 27.1, 26.1 (3C), 19.9, 18.2, -4.0 (TBS), -4.3 (TBS).

HRMS (ESI): $m/z$ calcd. for [M+Na]$^+$ 397.2533, found 397.2535.

FT-IR (neat): 2954, 2928, 1676, 1628, 1459, 1361, 1253, 1064, 980, 835, 774, 748, 700 cm$^{-1}$.

$\left[ \alpha \right]_D^\text{o} = -12.2$ (C = 1, CHCl$_3$).

**Synthesis of (3R,5R)-5-((tert-butyldimethylsilyl)oxy)-3-methyl-7-phenylheptan-1-ol (4d)**

(6R,8R,E)-8-((tert-butyldimethylsilyl)oxy)-6-methyl-10-phenyldec-3-en-2-one (0.7 mmol) was dissolved in 7 mL dichloromethane and cooled to -78° C. Ozone was bubbled through the solution until a blue color was observed (ca. 5 minutes). The ozone generator was turned off and oxygen was bubbled through until the solution became colorless. Sodium borohydride (10.7 mmol, 15 eq.) in methanol (7 mL) was added, the reaction mixture was slowly warmed up to 0°C and stirred at this temperature for 13 h. The reaction was quenched with saturated aqueous NaHCO$_3$, extracted with ether, dried over Na$_2$SO$_4$ and the solvent removed under reduced pressure. Purification by flash column chromatography (9:1 heptane/EtOAc) afforded (3R,5R)-5-((tert-butyldimethylsilyl)oxy)-3-methyl-7-phenylheptan-1-ol 4d as colorless oil (89% yield).

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated $> 20: 1$ dr. HPLC analysis (Lux-Cellulose1 (Chiralcel OD-H), (n-heptane + 0.1% iPrOH) : /iPrOH = 92:8, 0.70 mL/min, 210 nm) indicated $> 99\%$ ee ($t_{\text{minor}} = 8.0$ min, $t_{\text{major}} = 6.4$ min).
**1H NMR** (400 MHz, CDCl$_3$) δ 7.37 – 7.25 (m, 2H), 7.23 – 7.11 (m, 3H), 3.84 – 3.78 (m, 1H), 3.75 – 3.57 (m, 2H), 2.65 (dd, $J = 10.8, 5.8$ Hz, 2H), 1.93 – 1.69 (m, 3H), 1.64 – 1.16 (m, 5H), 0.93 (s, 3H), 0.91 (s, 9H), 0.15 – -0.02 (m, 6H).

**13C NMR** (100 MHz, CDCl$_3$) δ 142.8, 128.5 (4C), 125.8, 67.0, 61.3, 44.6, 40.6, 39.9, 31.6, 26.2, 26.1 (3C), 20.2, 18.3, -4.0, -4.3.

**HRMS** (ESI): $m/z$ calcd. for [M+Na]$^+$ 359.2377, found 359.2374

**FT-IR** (neat): 3333 (br), 2952, 2928, 2856, 1459, 1377, 1254, 1091, 1056, 1030 cm$^{-1}$.

$\left[ \alpha \right]_D^{20} = -23.1$ (c = 1.17, CHCl$_3$)

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**Synthesis of (4R,6R)-4-methyl-8-phenyloctane-1,6-diol (4e)**

![Diagram](image)

**Procedure:** Compound 4e was prepared with slight modifications according to a reported procedure.$^{[4]}$

An approximately 1M solution of trifluoroperacetic acid was prepared according to the following procedure: to a 25-mL, round-bottomed flask was added urea hydrogen peroxide (5 mmol) and anhydrous 1, 2-dichloroethane (5.0 mL). The suspension was cooled to 0 °C in an ice/water bath and trifluoroacetic anhydride (5.5 mmol) added dropwise by syringe. The solution was stirred at 0°C for 1 h, then the ice bath removed and stirred at room temperature for 1 h, by which time the white suspension had changed into a biphasic mixture. Stirring was stopped to allow the layers to separate. To achieve more reproducible results, the biphasic mixture was placed in a -20°C freezer for 1 h to freeze trifluoroacetic acid before addition.

To a 25-mL, round-bottomed flask was added (R, R)-3f (0.2 mmol), HNa$_2$PO$_4$ (1.2 mmol, 6 eq.) and 1, 2-dichloroethane (10 mL). The suspension was stirred vigorously at room temperature, then trifluoroperacetic acid (1M solution in 1, 2-DCE, as prepared above, ∼4 eq) was added dropwise by syringe. The solution was stirred for 4 h at 20 °C, by which time TLC analysis had indicated consumption of the starting material. The
reaction was quenched with Na₂S₂O₃ (3.2 mmol, 16 eq.) and concentrated in vacuo

[Caution! Trifluoroperacetic acid, like other organic peroxides, is potentially explosive and should be used with caution. Although no incidents involving this peroxide were encountered during these studies, rotary evaporation was conducted behind a blast shield as a precaution].

The crude residue was redissolved in methanol and potassium hydroxide (3 mmol, 15 eq.) was added. The reaction was refluxed for 3 h, quenched with saturated aqueous NaHCO₃, extracted with ether and dried over MgSO₄. Purification by flash column chromatography (1:1 heptane/EtOAc) afforded (4R,6R)-4-methyl-8-phenyloctane-1,6-diol 4e as off-yellow oil in 95% yield.

1H NMR spectroscopic analysis of the unpurified reaction mixture indicated > 20: 1 dr.

HPLC analysis (Lux-Cellulose1( Chiralcel OD-H), (n-heptane + 0.1% i-PrOH) : /i-PrOH = 85:5, 0.70 mL/min, 210 nm) indicated > 99% ee (t_minor = 13.9 min, t_major = 15.3 min).

1H NMR (400 MHz, CDCl₃) δ 7.40 – 7.30 (m, 2H, H9/10), 7.26–7.2 (m, 3H, H9/10+11), 3.85–3.73 (m, 1H), 3.66 (t, J = 6.6 Hz, 2H), 2.92–2.79 (m, 1H), 2.76–2.69 (m, 1H), 2.03 (bs, 2H, OH), 1.89–1.48 (m, 6H), 1.47–1.35 (m, 1H), 1.35–1.17 (m, 2H), 0.95 (d, J = 6.6 Hz, 3H).

13C NMR (100 MHz, CDCl₃) δ 142.3, 128.5, 125.9, 69.3, 63.1, 44.9, 40.2, 33.9, 32.2, 30.1, 29.2, 19.5.

HRMS (ESI): m/z calcd. for [M+Na]⁺ 259.1669, found 259.1673.

FT-IR (neat): 3310 (br), 3026, 2927, 2866, 1495, 1454, 1377, 1114, 1054, 919, 746, 699 cm⁻¹.

[ [α]D] = -5.6 (C = 1.07, CHCl₃)
Synthesis of (5R,7R)-7-hydroxy-5-methyl-9-phenylnonanoic acid (4f)

**Procedure:** (R, R)-3f (0.2 mmol) was dissolved in dioxane (2 mL) at room temperature. This solution was vigorously stirred as a solution of potassium hydroxide (2 mmol, 10 eq.) in H₂O (2.0 mL) and a solution of iodine (0.6 mmol, 3 eq.) and potassium iodide (2.4 mmol, 12 eq.) in H₂O (2.0 mL) were added via syringe at similar rates over 10 min. This mixture was stirred for 2 h and the reaction was quenched with 1M aqueous Na₂SO₃ (2 mL). The pH of the mixture was adjusted to 14 with 1M aqueous potassium hydroxide, diluted with water (5 mL) and washed with dichloromethane. The pH of the aqueous layer was adjusted to 3 with 1M aqueous NaHSO₄ and extracted with ether (2x20 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated. Purification by flash column chromatography (2:1 heptane/EtOAc + 1% acetic acid) afforded (5R,7R)-7-hydroxy-5-methyl-9-phenylnonanoic acid 4f as white solid in 80% yield.

¹H NMR spectroscopic analysis of the unpurified reaction mixture indicated > 20: 1 dr.

HPLC analysis (Chiralpak IA column, Chirapak IA, n-heptane + 1% ethanol + 5% isopropanol + 0.1% trifluoroacetic acid, 0.70 mL/min, 210 nm) indicated > 99% ee (tₘᵢₘᵢᵣ = 35.0 min, tₘᵢₗₐᵢₗᵢᵢᵣ = 30.1 min).

¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.21 (m, 2H), 7.20 – 7.08 (m, 3H), 6.13 (bs, 1H, OH), 3.79 – 3.62 (m, 1H), 2.83–2.70 (m, 1H), 2.68–2.60 (m, 1H), 2.29 (t, J = 7.4 Hz, 2H), 1.83 – 1.54 (m, 5H), 1.47 (ddd, J = 13.7, 9.5, 4.1 Hz), 1.37 – 1.06 (m, 3H), 0.87 (d, J = 6.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 179.4, 142.2, 128.5 (2C), 128.5 (2C), 126.0, 69.4, 44.8, 40.1, 37.2, 34.3, 32.2, 29.1, 22.2, 19.3.

HRMS (ESI): m/z calcd. for [M+Na]⁺ 287.1618, found:287.1617.

FT-IR (neat): 3430 (br), 3028, 2931, 2877, 1709, 1455, 1412, 1377, 1251, 1175, 1107, 1050, 746, 700 cm⁻¹.

[ [α]_D ] = -6.0 (C = 1.0, CHCl₃)
4. Synthesis of Stereotriads

\((6R,7S,8R)-8\text{-}\text{hydroxy-6,7\text{-}dimethyl-10-phenyldecan-2\text{-}one}\ (6a)\)

Compound 6a was prepared according to the GP2 at r.t. and obtained in 71% yield as colorless oil after column chromatography (2:1 heptane:EtOAc).

\(^1\)H NMR spectroscopic analysis of the unpurified reaction mixture indicated \(\text{dr} > 15:1\) dr.

HPLC analysis (Chiralcel OD-H 250 × 4, 6 mm, (n-Heptane+0.1% i-PrOH):i-PrOH = 95:5, 1.00 mL/min, 210 nm) indicated > 99% ee (\(t_{\text{minor}} = 14.1\) min, \(t_{\text{major}} = 17.6\) min).

\(^1\)H NMR (CDCl\(_3\) 400 MHz): \(\delta\) 7.20-7.25 (m, 2H), 7.11-7.17 (m, 3H), 3.40-3.45 (m, 1H), 2.78-2.85 (m, 1H), 2.58-2.68 (m, 1H), 2.34 (t, \(J = 7.6\) Hz, 2H), 2.08 (s, 3H), 1.76-1.88 (m, 2H), 1.40-1.64 (m,5H), 1.27 (m,1H), 1.11-1.19 (m, 2H), 0.73 (d, \(J = 6.8\) Hz, 3H), 0.68 (d, \(J = 6.8\) Hz, 3H).

\(^13\)C NMR (CDCl\(_3\) 100 MHz): \(\delta\) 209.1, 142.4, 128.5, 128.4, 125.8, 73.3, 43.9, 42.5, 36.6, 35.1, 32.2, 32.0, 29.9, 21.7, 14.1, 10.1.

HRMS (ESI): \(m/z\) calcd. for C\(_{18}\)H\(_{28}\)NaO\(_2\) (M + Na)+ 299.1982; found: 299.1979.

FT-IR (neat): 3440, 2955, 1710, 1454, 1361, 1276, 1045, 764, 750, 701 cm\(^{-1}\).

\([\alpha]_D^20\) = -1.4 (C= 1.0, CHCl\(_3\)).

\(5\text{-}((1R,2S)-2\text{-}((R)-1\text{-}\text{hydroxy-3-phenylpropyl)cyclopentyl})\)pentan-2\text{-}one\ (6b)\)

Compound 6b was prepared according to the GP2 at r.t. and obtained in 60% yield as colorless oil after column chromatography (2:1 heptane:EtOAc).

\(^1\)H NMR spectroscopic analysis of the unpurified reaction mixture indicated \(\text{dr} > 15:1\) dr.

HPLC analysis analysis of the Fmoc-derivatized analog (IA column, 0.1% iPrOH + Heptane/hexanes = 92:8, 0.70 mL/min, 254 nm) indicated > 99% ee (\(t_{\text{minor}} = 13.8\) min, \(t_{\text{major}} = 12.5\) min).
Compound 6c was prepared according to the GP2 at r.t. and obtained in 74% yield as colorless oil after column chromatography (2:1 heptane:EtOAc). 

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated > 20: 1 dr.

HPLC analysis (AD-H column, 3% iPrOH/hexanes, 0.80 mL/min, 254 nm) indicated > 99% ee ($t_{\text{minor}} = 25.8 \text{ min}, t_{\text{major}} = 15.0 \text{ min}$).

$^1$H NMR (CDCl$_3$ 400 MHz): $\delta$ 7.28-7.32 (m, 2H), 7.18-7.25 (m, 3H), 3.84 (m, 1H), 2.89-2.96 (m, 1H), 2.62-2.69 (m, 1H), 2.21-2.35 (m, 2H), 2.12 (s, 3H), 1.87 (d, $J = 12.4$ Hz, 1H), 1.56-1.75 (m, 7H), 1.33-1.44 (m, 2H), 1.13-1.24 (m, 4H), 0.95-1.07 (m, 3H).

$^{13}$C NMR (CDCl$_3$ 100 MHz): $\delta$ 209.1, 142.4, 128.6, 128.4, 125.8, 70.6, 48.0, 44.0, 38.4, 33.0, 32.8, 32.1, 31.6, 29.9, 26.2, 26.0, 24.8, 20.2.

HRMS (ESI): m/z calcd. for C$_{20}$H$_{30}$NaO$_2$ (M + Na)$^+$ 325.2138; found: 325.2130

FT-IR (neat): 3424, 2920, 2853, 1709, 1495, 1451, 1359, 1300, 1163, 1035, 924, 947, 700 cm$^{-1}$.

$\left[ \alpha \right]_{D}^{20} = 69.0$ (C = 1.4, CHCl$_3$)
5-((1R,2S)-2-((R)-1-hydroxy-3-phenylpropyl)cycloheptyl)pentan-2-one (6d)

Compound 6d was prepared according to the GP2 at r.t. and obtained in 77% yield as colorless oil after column chromatography (2:1 heptane:EtOAc).

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated > 20: 1 dr.

HPLC analysis (Chiralpak IC 250 × 4 column, (n-Heptane+0.1% i-PrOH):EtOH = 8:2, 0.70 mL/min, 210 nm) indicated > 99% ee ($t_{\text{minor}}$ = 7.4 min, $t_{\text{major}}$ = 8.2 min).

$^1$H NMR (CDCl$_3$ 400 MHz): $\delta$ 7.19-7.23 (m, 2H), 7.08-7.15 (m, 3H), 3.51 (m, 1H), 2.77-2.85 (m, 1H), 2.52-2.60 (m, 1H), 2.18-2.30 (m, 2H), 2.04 (s, 3H), 1.48-1.73 (m, 7H), 1.11-1.45 (m, 13H).

$^{13}$C NMR (CDCl$_3$ 150 MHz): $\delta$ 209.3, 142.3, 128.5, 128.4, 125.8, 74.1, 51.8, 43.8, 39.2, 38.1, 34.9, 34.2, 32.9, 30.7, 29.9, 29.9, 28.7, 26.4, 23.9, 21.7.

HRMS (ESI): $m/z$ calcd. for C$_{21}$H$_{32}$NaO$_2$ (M + Na)$^+$ 339.2295; found 339.2292.

FT-IR (neat): 3423, 2919, 2854, 1709, 1454, 1359, 1276, 1032, 750, 700 cm$^{-1}$.

$\left[\alpha\right]_{D}^{20}$ = 37.5 (C = 0.8, CHCl$_3$)

5-((1R,2S)-2-((R)-1-hydroxy-3-phenylpropyl)cyclooctyl)pentan-2-one (6e)

Compound 6e was prepared according to the GP2 at r.t. and obtained in 50% yield as colorless oil after column chromatography (2:1 heptane:EtOAc).

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated = 10: 1 dr.

HPLC analysis (Chiralpak IC 250 × 4 column, (n-Heptane+0.1% i-PrOH):EtOH = 9:1, 1.00 mL/min, 210 nm) indicated > 99% ee ($t_{\text{minor}}$ = 6.7 min, $t_{\text{major}}$ = 7.8 min).

$^1$H NMR (CDCl$_3$ 400 MHz): $\delta$ 7.28-7.32 (m, 2H), 7.18-7.24 (m, 3H), 3.67-3.72 (m, 1H), 2.7-2.94 (m, 1H), 2.61-2.68 (m, 1H), 2.25-2.38 (m, 2H), 2.14 (s, 3H), 1.75-1.83 (m, 2H), 1.55-1.72 (m, 5H), 1.18-1.45 (m, 13H)
**C NMR** (CDCl$_3$ 150 MHz): 209.2, 142.3, 128.6, 128.4, 125.8, 73.5, 50.0, 43.9, 37.4, 34.9, 32.9, 32.6, 31.6, 29.9, 26.3, 26.2, 24.7, 24.0, 21.7.

**HRMS (ESI):** m/z calcd. for C$_{22}$H$_{34}$NaO$_2$ (M + Na)$^+$ 353.2451; found: 353.2450.

**FT-IR** (neat): 2924, 2856, 1711, 1541, 1276, 1261, 750 cm$^{-1}$.

$[\alpha]_D^{20}$ = 53.6 (C = 0.7, CHCl$_3$)

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**5-((1R,2S)-2-((R)-1-hydroxy-2-methylpropyl)cyclohexyl)pentan-2-one (6f)**

Compound 6f was prepared according to to the GP2 at r.t. and obtained in 77% yield as colorless oil after column chromatography (2:1 heptane:EtOAc).

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated $>20:1$ dr.

HPLC analysis analysis of the Fmoc-derivatized analog (AD-H column, (0.1% iPrOH + hexanes): iPrOH = 9:1, 1.0 mL/min, 254 nm) indicated $>99\%$ ee ($t_{\text{minor}} = 8.8$ min, $t_{\text{major}} = 7.6$ min).

$^1$H NMR (CDCl$_3$ 600 MHz): $\delta$ 3.55-3.57 (m, 1H), 2.38-2.47 (m, 2H), 2.13 (s, 3H), 1.81-1.87 (m, 1H), 1.61-1.72 (m, 4H), 1.19-1.55 (m, 11H), 0.98 (d, $J$ = 6.6Hz, 3H), 0.84 (d, $J$ = 6.6 Hz, 3H).

$^{13}$C NMR (CDCl$_3$ 150 MHz): $\delta$ 209.6, 76.5, 44.0, 43.9, 36.0, 32.6, 29.9, 29.5, 28.2, 25.3, 24.0, 23.3, 21.3, 20.9, 15.3.

**HRMS (ESI):** m/z calcd. for C$_{15}$H$_{28}$NaO$_2$ (M + Na)$^+$ 263.1982; found: 263.1978.

**FT-IR** (neat):3458, 2928, 2858, 1711, 1462, 1364, 1276, 1261, 1166, 990, 750 cm$^{-1}$.

$[\alpha]_D^{20}$ = 8.4 (C = 1.0, CHCl$_3$)

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**(R)-methyl 10-hydroxy-10-((1S,2R)-2-(4-oxopentyl)cyclohexyl)decanoate (6g)**

Compound 6g was prepared according to to the GP2 at r.t. and obtained in 70% yield as colorless oil after column chromatography (2:1 heptane:EtOAc).

$^1$H NMR spectroscopic analysis of the unpurified reaction
mixture indicated > 20: 1 dr.

HPLC analysis of the Fmoc-derivatized analog (Chiralpak IA column, 0.1% \(^i\)PrOH/hexanes : \(^i\)PrOH = 92:8, 0.70 mL/min, 210 nm) indicated > 99% ee (t\(_{\text{minor}}\) = 12.6 min, t\(_{\text{major}}\) = 10.9 min).

\(^1\)H NMR (CDCl\(_3\) 600 MHz): \(\delta\) 3.81-3.83 (m, 1H), 3.66 (s, 3H), 2.34-2.44 (m, 2H), 2.29 (t, \(J = 7.8\) Hz, 2H), 2.13 (s, 3H), 1.59-1.80 (m, 6H), 1.12-1.54 (m, 20H), 0.99-1.05 (m, 2H).

\(^{13}\)C NMR (CDCl\(_3\) 150 MHz): \(\delta\) 209.2, 174.4, 71.7, 51.5, 47.8, 44.1, 38.2, 34.1, 32.2, 31.4, 31.0, 29.8, 29.7, 29.4, 29.2, 29.1, 26.6, 26.1, 25.9, 24.9, 24.7, 20.2.

HRMS (ESI): m/z calcd. for C\(_{22}\)H\(_{40}\)NaO\(_4\) (M + Na)\(^+\) 391.2819; found: 398.2815.

FT-IR (neat): 2924, 2854, 1738, 1716, 1439, 1387, 1197, 1167, 750 cm\(^{-1}\).

\(\left[\alpha\right]_D^{20}\) = 40.3 (C = 1.0, CHCl\(_3\))

5-(((1R,2S)-2-((1R,2S)-1-hydroxy-2-methylbutyl)cyclohexyl)pentan-2-one (6h)

Compound 3g was prepared according to the to the GP2 at r.t. and obtained in 71% yield as colorless oil after column chromatography (2:1 heptane:EtOAc).

\(^1\)H NMR spectroscopic analysis of the unpurified reaction mixture indicated > 20: 1 dr.

\(^1\)H NMR (CDCl\(_3\) 600 MHz): \(\delta\) 3.76-3.77 (m, 1H), 2.41-2.49 (m, 2H), 2.16 (s, 3H), 1.27-1.73 (m, 16H), 1.78-1.79 (m, 1H), 0.95 (t, \(J = 7.8\) Hz, 3H), 0.84 (d, \(J = 6.6\) Hz, 3H).

\(^{13}\)C NMR (CDCl\(_3\) 150 MHz): \(\delta\) 209.6, 73.9, 44.0, 43.1, 36.0, 35.5, 32.5, 29.9, 27.7, 27.4, 24.3, 23.5, 22.7, 21.5, 12.1, 12.0.

HRMS (ESI): m/z calcd. for C\(_{16}\)H\(_{30}\)NaO\(_2\) (M + Na)\(^+\) 277.2138; found: 277.2134.

FT-IR (neat): 3459, 2927, 2858, 1711, 1460, 1361, 1166, 993, 954 cm\(^{-1}\).

\(\left[\alpha\right]_D^{20}\) = 13.6 (C = 1.0, CHCl\(_3\))
5-((1R,2S)-2-((1S,2S)-1-hydroxy-2-phenylpropyl)cyclohexyl)pentan-2-one (6i)

Compound 6i was prepared according to the GP2 at r.t. and obtained in 55% yield as colorless oil after column chromatography (2:1 heptane:EtOAc).

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated $= 10:1$ dr.

$^1$H NMR (CDCl$_3$ 600 MHz): $\delta$ 7.30-7.33 (m, 2H), 7.22-7.27 (m, 3H), 2.94-2.99 (m, 1H), 2.36-2.45 (m, 2H), 2.13 (s, 3H), 1.76-1.78 (m, 1H), 1.58-1.67 (m, 4H), 1.44-1.52 (m, 2H), 1.25-1.34 (m, 6H), 1.32 (d, $J = 7.2$ Hz, 3H), 1.21-1.22 (m, 1H), 1.09-1.14 (m, 1H).

$^{13}$C NMR (CDCl$_3$ 150 MHz): $\delta$ 209.4, 143.8, 128.5, 128.4, 126.6, 76.7, 44.7, 44.0, 42.9, 36.5, 32.8, 29.9, 29.6, 26.7, 24.9, 24.2, 21.0, 19.5.

HRMS (ESI): $m/z$ calcd. for C$_{20}$H$_{30}$NaO$_2$ (M + Na)$^+$ 325.2138; found: 325.2126.

FT-IR (neat): 3483, 2924, 2855, 1711, 1494, 1361, 1276, 764, 750, 703 cm$^{-1}$.

$[\alpha]_D^20 = 32.3$ (C = 0.8, CHCl$_3$)

5-((1R,2S)-2-((1R,3R)-3-(benzyloxy)-1-hydroxy-5-phenylpentyl)cyclohexyl)pentan-2-one (6j)

Compound 6j was prepared according to the GP2 (50% BF$_3$ Et$_2$O) at r.t. for 30 min and obtained in 60% yield as colorless oil after column chromatography (2:1 heptane:EtOAc).

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated $> 15:1$ dr.

$^1$H NMR (CDCl$_3$ 600 MHz): $\delta$ 7.35-7.38 (m, 4H), 7.30-7.33 (m, 3H), 7.20-7.23 (m, 3H), 4.58 (dd, $J = 11.4$, 34.02 Hz, 2H), 4.22-4.24 (m, 1H), 3.76-3.78 (m, 1H), 2.66-2.77 (m, 2H), 2.28-2.33 (m, 2H), 2.08 (s, 3H), 1.84-1.91 (m, 2H), 1.60-1.79 (m, 6H), 1.51-1.55 (m, 1H), 1.36-1.48 (m, 3H), 1.14-1.29 (m, 4H), 0.98-1.09 (m, 2H).

$^{13}$C NMR (CDCl$_3$ 150 MHz): $\delta$ 209.2, 142.0, 138.4, 128.4, 128.4, 128.3, 127.9, 127.7, 125.8, 75.4, 67.6, 47.1, 44.1, 38.1, 35.4, 33.9, 32.1, 31.9, 29.8, 26.1, 25.9, 24.8, 20.1.

HRMS (ESI): $m/z$ calcd. for (M + Na)$^+$ 459.2870; found: 459.2865.

FT-IR (neat): 3465, 2920, 2853, 1710, 1495, 1452, 1354, 1163, 1605, 735, 697 cm$^{-1}$.
$\left[ \alpha \right] = 34.2 \ (C = 1.0, \ CHCl_3)$

1-chloro-5-((1S,2R)-2-((S)-cyclohexyl(hydroxy)methyl)cyclohexyl)pentan-2-one (6k)

Compound 6k was prepared according to the GP2 at r.t. and obtained in 40% yield as colorless oil after column chromatography (2:1 heptane:EtOAc).

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated dr > 20:1 dr. The compound was protected with Fmoc for HPLC analysis (Chiralcel OD-H 250 × 4 column, (n-Heptane+0.1% i-PrOH) : i-PrOH = 95:5, 1 mL/min, 210 nm) indicated > 99% ee ($t_{\text{minor}} = 9.9$ min, $t_{\text{major}} = 9.0$ min).

$^1$H NMR (CDCl$_3$ 600 MHz): $\delta$ 4.08 (s, 2H), 3.50-3.51 (m, 1H), 2.56-2.59 (m, 2H), 1.74-1.76 (m, 2H), 1.50-1.62 (m, 3H), 1.44-1.49 (m, 3H), 1.34-1.41 (m, 2H), 1.24-1.30 (m, 6H), 1.11-1.22 (m, 3H), 1.00-1.07 (m, 1 H).

$^{13}$C NMR (CDCl$_3$ 150 MHz): $\delta$ 202.9, 76.4, 48.3, 43.4, 40.0, 39.9, 36.0, 32.5, 31.1, 28.3, 26.6, 26.5, 26.2, 26.0, 25.6, 24.1, 23.4, 21.1.

HRMS (ESI): $m/z$ calcd. for C$_{18}$H$_{31}$ClNaO (M + Na)$^+$ 337.1905; found: 337.1893.

FT-IR (neat): 3377, 2926, 1710, 1657, 1434, 1275, 1261, 1065, 750, 701 cm$^{-1}$.

$\left[ \alpha \right] = -17.7 \ (C = 1.0, \ CHCl_3)$

After X-ray analysis, we reduced 6k to compare the optical rotation with 6l.

Yield > 95%, white solid.

$\left[ \alpha \right] = -16.7 \ (C = 1.0, \ CHCl_3)$
5-((1R,2S)-2-((R)-cyclohexyl(hydroxy)methyl)cyclohexyl)pentan-2-one (6l)

Compound 4f was prepared according to the GP2 at r.t. and obtained in 70% yield as colorless oil after column chromatography (2:1 heptane:EtOAc).

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated > 20:1 dr.

The compound was protected with Fmoc for HPLC analysis (Chiralcel OD-H 250 × 4 column, (n-Heptane+0.1% i-PrOH) : i-PrOH = 95:5, 1 mL/min, 210 nm) indicated > 99% ee ($t_{\text{minor}} = 9.1 \text{ min}, t_{\text{major}} = 10.0 \text{ min}$).

$^1$H NMR (CDCl$_3$ 600 MHz): $\delta$ 3.50-3.52 (m, 1H), 2.36-2.44 (m, 2H), 2.12 (s, 3H), 1.00-1.76 (m, 25H).

$^{13}$C NMR (CDCl$_3$ 150 MHz): $\delta$ 209.5, 76.3, 44.0, 43.5, 40.0, 36.0, 32.6, 31.1, 29.9, 28.4, 26.7, 25.5, 26.2, 26.1, 25.5, 24.2, 23.4, 21.3.

HRMS (ESI): $m/z$ calcd. for C$_{18}$H$_{32}$NaO$_2$ (M + Na)$^+$ 303.2295; found: 303.2293.

FT-IR (neat): 3454, 2902, 2852, 1711, 1450, 1361, 1262, 1163, 984, 750, 699 cm$^{-1}$.

$\left[ \alpha \right]_D^{\text{580}} = 16.4$ (C = 1.0, CHCl$_3$)
5. Applications

Synthesis of 4-(((2S,4R,6S)-6-(benzyloxy)-4-hydroxy-8-phenyloctan-2-yl)dimethylsilyl)butan-2-one (8)

Procedure: Alcohol (0.2 mmol) was diluted with 2 mL dichloromethane. Then aldehyde (0.24 mmol, 1.2 eq.) and BF$_3$·EtO were successively added and the reaction was stirred at r.t. for 2 h. Water (0.2 mL) was added and the reaction was allowed to cool to room temperature with stirring. The reaction mixture was filtered over silica, eluted with dichloromethane and the solvent was removed under reduced pressure. Purification by flash column chromatography afforded the desired pure product 7 in 50% yield.

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated >20:1 dr.

$^1$H NMR (CDCl$_3$ 600 MHz): $\delta$ 7.28-7.37 (m, 7H), 7.18-7.22 (m, 3H), 4.56 (dd, $J$ = 1.2, 2.4 Hz, 2H), 4.02-4.05 (m, 1H), 3.73-3.77 (m, 1H), 2.65-2.75 (m, 2H), 2.56 (b s, 1H), 2.38-2.41 (m, 2H), 2.14 (s, 3H), 2.02-2.08 (m, 1H), 1.84-1.90 (m, 1H), 1.72-1.77 (m, 1H), 1.59-1.63 (m, 1H), 1.49-1.53 (m, 1H), 1.08-1.13 (m, 1H), 0.96-1.01 (m, 1H), 0.94 (d, $J$ = 6.0 Hz, 3H), 0.76-0.79 (m, 2H), 0.04 (s, 6H).

$^{13}$C NMR (CDCl$_3$ 150 MHz): $\delta$ 210.0, 138.2, 128.4, 128.4, 128.3, 127.9, 127.8, 125.8, 76.3, 65.2, 40.8, 39.0, 38.1, 35.4, 31.6, 29.2, 13.6, 13.2, 6.9, -5.5, -5.6.

HRMS (ESI): m/z calcd. for C$_{27}$H$_{46}$NaO$_3$Si (M + Na)$^+$ 463.2639; found: 463.2634.

FT-IR (neat): 2947, 2865, 1715, 1454, 1412, 1356, 1195, 1065, 1029, 839, 700 cm$^{-1}$.

$[\alpha]_D^{	ext{CHCl}_3} = -2.3$ (C = 1.0, CHCl$_3$)
**Synthesis of (2S,4S,6S)-6-(benzyloxy)-8-phenyloctane-2,4-diol**

**Procedure:** To a 25-mL, round-bottomed flask was added 8 (1.0 mmol), Na₂HPO₄ (2.0 mmol, 2.0 eq.) and dichloromethane (10 mL). The suspension was stirred vigorously at room temperature, then m-CPBA solid was slowly added in several portions. The solution was stirred at r.t. for 12. The reaction was quenched with Na₂S₂O₃ (3.2 mmol, 16 eq.) and concentrated in vacuo. The crude residue was redissolved in THF (5 mL) and 3 mL TBAF was added and reflex for 1h. Then 37% H₂O₂ (64 equiv.) was added at r.t., which further stirred for 8 h at the same temperature. The reaction was quenched with Na₂S₂O₃ (3.2 mmol, 16 eq.) Extracted with ether and dried over MgSO₄, then the solvent was removed to afford crude product. The crude product was directly dissolved in MeOH, 10% Pd/C were added and the reaction was stirred under H₂ atmosphere for 2 h. After that, Pd/C was filtered off and the solvent was removed. Purification by flash column chromatography (1:1 heptane/EtOAc) afforded 8 as colorless oil in 86% yield.

¹H NMR spectroscopic analysis of the unpurified reaction mixture indicated >20:1 dr.

¹H NMR (CDCl₃ 600 MHz): δ 7.26-7.38 (m, 2H), 7.14-7.26 (m, 3H), 4.20-4.33 (m, 1H), 4.14-4.15 (m, 1H), 4.10-4.12 (m, 1H), 4.01-4.02 (m, 1H), 3.05 (br s, 1H), 3.02 (br s, 1H), 2.80-2.85 (m, 1H), 2.67-2.72 (m, 1H), 1.86-1.93 (m, 1H), 1.77-1.80 (m, 1H), 1.64-1.80 (m, 4H), 1.24 (d, J = 6.6 Hz, 3H).

¹³C NMR (CDCl₃ 150 MHz): δ 141.9, 128.4, 128.4, 125.8, 70.8, 69.4, 68.7, 44.2, 42.6, 39.1, 32.1, 24.4.

HRMS (ESI): m/z calcd. for C₁₄H₂₂NaO₃ (M + Na)+ 261.1461; found: 261.1461.

FT-IR (neat): 3331, 2931, 1454, 1375, 1323, 1276, 760, 700 cm⁻¹.

[α]D° = 4.3 (C = 1.0, CDCl₃)
Synthesis of (6R,8S,10S)-10-(benzyloxy)-8-methoxy-6-methyltridecan-2-one (10)

Alcohol (1 mmol) was diluted with 10 mL dichloromethane. Aldehyde (1.2 mmol, 1.2 eq.) and BF$_3$·Et$_2$O (50%) were successively added and the reaction was stirred at r.t. for 2 h. Water (0.2 mL) was added and the reaction was allowed to cool to room temperature with stirring. The reaction mixture was filtered over silica, eluted with dichloromethane and the solvent was removed under reduced pressure. The crude reaction mixture was dissolved in 5 mL dichloromethane and cooled to 0° C. Proton sponge (2.5 mmol, 5 eq.) and trimethyloxonium tetrafluoroborate (2 mmol, 4 eq.) were added successively and stirred at 0° C for 3h. The reaction was quenched with saturated aqueous Na$_2$CO$_3$ and extracted with ether. The combined organic layers were dried over MgSO$_4$, filtered and concentrated. Purification by column chromatography (9:1 heptane/EtOAc) afforded the product 9 as colorless oil (71% yield).

$^1$H NMR spectroscopic analysis of the unpurified reaction mixture indicated >20:1 dr.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 – 7.30 (m, 4H), 7.29 – 7.23 (m, 1H), 4.58 (d, $J = 11.4$ Hz, 1H), 4.46 (d, $J = 11.5$ Hz, 1H), 3.69 – 3.50 (m, 1H), 3.49 – 3.36 (m, 1H), 3.26 (s, 3H), 2.45 – 2.27 (m, 2H), 2.11 (s, 3H), 1.69 – 1.33 (m, 9H), 1.33 – 1.03 (m, 4H), 0.95 – 0.89 (m, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 209.2, 139.2, 128.5 (2C), 127.9 (2C), 127.6, 76.1, 76.1, 71.2, 56.5, 44.1, 42.1, 40.5, 37.0, 36.7, 30.0, 29.4, 21.3, 20.0, 18.5, 14.5.

HRMS (ESI): $m/z$ calcd. for [M+Na]$^+$ 371.2557, found 371.2557

FT-IR (neat): 2953, 2927, 2871, 1715, 1455, 1360, 1186, 1161, 1091, 1068, 1028, 735, 698 cm$^{-1}$.

$\left[ \alpha \right]_D^27.2$ (C = 1, CHCl$_3$)
Synthesis of (6\textit{R},8\textit{S},10\textit{S},\textit{E})-10-(benzyloxy)-8-methoxy-6-methyltridec-3-en-2-one

**Procedure:** To a solution of 10 (0.15 mmol) in 0.5 mL diethyl ether was added lutidine (0.45 mmol, 3 eq.) at room temperature. After stirring for 10 minutes, \textit{tert}-butyldimethylsilyl trifluoromethanesulfonate (0.3 mmol, 2 eq.) was added dropwise and the reaction mixture was stirred for 13 hours. The reaction was quenched with saturated aqueous ammonium chloride (3 mL), extracted with ether and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure giving the product as 2:1 mixture of diastereoisomers which was used directly for the next step.

Previously obtained silyl enol ether and Pd(OAc)$_2$ (0.015 mmol, 10 mol\%) were dissolved in 1.5 mL DMSO, frozen in a bath of liquid nitrogen, evacuated and backfilled with pure oxygen using a balloon. The Schlenk tube was directly taken out of the nitrogen bath, warmed to room temperature and heated at 80° C for 13 h. Upon completion, the reaction mixture was diluted with water and extracted with dichloromethane three times. The combined organic phases were dried over Na$_2$SO$_4$ and the solvent removed under reduced pressure. The crude product was purified using flash column chromatography (20:1-9:1 heptane/EtOAc) to give a colorless oil (35% yield over 2 steps).

\textbf{NMR Data}:

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 – 7.24 (m, 5H), 6.75 (dt, $J = 15.8$, 7.4 Hz, 1H), 6.06 (dt, $J = 15.9$, 1.3 Hz, 1H), 4.59 (d, $J = 11.4$ Hz, 1H), 4.45 (d, $J = 11.4$ Hz, 1H), 3.62 – 3.55 (m, 1H), 3.48-3.42 (m, 1H) 3.26 (s, 3H), 2.35 – 2.14 (m, 4H), 2.10 – 2.03 (m, 1H), 1.86 – 1.79 (m, 1H), 1.70 – 1.09 (m, 8H), 1.00 – 0.86 (m, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.6, 147.0, 139.1, 132.9, 128.5 (2C), 128.0 (2C), 127.7, 76.1, 76.0, 71.2, 56.7, 41.9, 40.5, 40.4, 36.6, 29.3, 27.0, 20.1, 18.4, 14.5.

HRMS (ESI): $m/z$ calcd. for [M+Na]$^+$ 369.2400, found 369.2401.

FT-IR (neat): 2958, 2921, 1699, 1673, 1632, 1457, 1254, 1095, 1069 cm$^{-1}$.

$[\alpha]_D^{20} = 24.7$ (C = 1, CHCl$_3$)
Synthesis of (3S,5S,7S)-7-(benzyloxy)-5-methoxy-3-methyldecanal (11)

Procedure: Unsaturated ketone (0.023 mmol) was dissolved in 1 mL dichloromethane and cooled to -78° C. Ozone was bubbled through the solution until a blue color was observed (ca. 5 minutes). The ozone generator was turned off and oxygen was bubbled through until the solution became colorless. The reaction was quenched with dimethyl sulfide (0.05 mL), slowly warmed up and stirred at room temperature for 5 h. The solvent and excess DMS were removed using a high vacuum pump with a liquid nitrogen cooling trap. The remaining yellow oil was dissolved in 3 mL diethyl ether, 3 mL saturated aqueous Na₂CO₃ was added and the biphasic mixture was vigorously stirred at room temperature for 3 h. The mixture was extracted with ether, dried over Na₂SO₄ and the solvent removed under reduced pressure. Purification by flash column chromatography (20:1 – 9:1 heptane/EtOAc) afforded the product as colorless oil (85% yield).

¹H NMR (700 MHz, CDCl₃) δ 9.72 (s, 1H), 7.37 – 7.22 (m, 5H), 4.58 (d, J = 11.4 Hz, 1H), 4.44 (d, J = 11.4 Hz, 1H), 3.58 (td, J = 9.1, 5.6 Hz, 1H), 3.51 – 3.38 (m, 1H), 3.26 (s, 3H), 2.40 (dd, J = 19.1, 8.5 Hz, 1H), 2.24 (dd, J = 10.7, 2.5 Hz, 2H), 1.70 – 1.48 (m, 5H), 1.43 – 1.36 (m, 2H), 1.32 – 1.36 (m, 1H), 0.99 (d, J = 6.2 Hz, 3H), 0.93 (t, J = 7.3 Hz, 3H).

¹³C NMR (176 MHz, CDCl₃) δ 202.9, 139.0, 128.5 (2C), 128.0 (2C), 127.7, 76.0, 76.0, 71.2, 56.5, 51.5, 41.9, 40.2, 36.6, 25.2, 20.4, 18.4, 14.5.

FT-IR (neat): 2957, 2929, 2873, 1724, 1456, 1379, 1092, 1028, 736, 698
Comparison of $^1$H NMR data with reported values$^{[5]}$

![Chemical Structure](image)

| $^1$H NMR (500 MHz, CDCl$_3$) (lit) ppm | $^1$H NMR (700 MHz, CDCl$_3$) (11) ppm |
|---------------------------------------|---------------------------------------|
| 0.93 ppm (t, $J = 7.2$ Hz, 3 H)       | 0.93 (t, $J = 7.3$ Hz, 3H)            |
| 0.99 (d, $J = 6.0$ Hz, 3 H)           | 0.99 (d, $J = 6.2$ Hz, 3H)            |
| 1.32–1.26 (m, 1 H)                    | 1.32 – 1.36 (m, 1H)                   |
| 1.43–1.37 (m, 2 H)                    | 1.43 – 1.36 (m, 2H)                   |
| 1.67–1.46 (m, 5 H)                    | 1.70 – 1.48 (m, 5H)                   |
| 2.27–2.20 (m, 2 H)                    | 2.24 (dd, $J = 10.7$, 2.5 Hz, 2H)     |
| 2.43–2.37 (m, 1 H)                    | 2.40 (dd, $J = 19.1$, 8.5 Hz, 1H)     |
| 3.26 (s, 3 H)                         | 3.26 (s, 3H)                          |
| 3.47–3.42 (m, 1 H)                    | 3.51–3.38 (m, 1H)                     |
| 3.60–3.55 (m, 1 H)                    | 3.58 (td, $J = 9.1$, 5.6 Hz, 1H)      |
| 4.44 (ABq, $J_{AB} = 11.2$ Hz, 2H)   | 4.44 (d, $J = 11.4$ Hz, 1H)           |
| 4.58 and 4.44 (ABq, $J_{AB} = 11.2$ Hz, 2H) | 4.58 (d, $J = 11.4$ Hz, 1H) |
| 7.34–7.26 (m, 5 H)                    | 7.37–7.22 (m, 5H)                     |
| 9.72 (t, $J = 2.0$ Hz, 1 H)           | 9.72 (s, 1H)                          |
| 13C NMR (126 MHz, CDCl3) (lit) ppm | 13C NMR (176 MHz, CDCl3) (11) ppm |
|-----------------------------------|-----------------------------------|
| 14.6                              | 14.5                              |
| 18.5                              | 18.4                              |
| 20.5                              | 20.4                              |
| 25.3                              | 25.2                              |
| 36.7                              | 36.6                              |
| 40.3                              | 40.2                              |
| 42.0                              | 41.9                              |
| 51.6                              | 51.5                              |
| 56.6                              | 56.5                              |
| 71.3                              | 71.2                              |
| 76.1                              | 76.0                              |
| 76.1                              | 76.0                              |
| 127.7                             | 127.7                             |
| 128.1                             | 128.0                             |
| 128.6                             | 128.5                             |
| 139.1                             | 139.0                             |
| 202.8                             | 202.9                             |

**Literature:** \([\alpha]_D^{27} +22.4\) (C = 1.00, CHCl3)

**Our synthesis of 14:** \([\alpha]_D^{20}\) = +6.0 (C = 0.67, CHCl3)
6. Assignment of Absolute Configuration

Dissolving the sample in pentane, then slowly evaporating the solvent to obtain the crystal is suitable for X-Ray analysis. The X-ray intensity data were measured on Bruker D8 Venture and on a Bruker X8 Apex2 diffractometer equipped each with multilayer monochromator, Mo Kα INCOATEC micro focus sealed tube and Oxford Cryostream respectively Kryoflex cooling systems. The structures were solved by direct methods and refined by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were inserted at calculated positions and refined with riding model and as rotating groups. The following software was used: Bruker SAINT software package\textsuperscript{1} using a narrow-frame algorithm for frame integration, SADABS\textsuperscript{2} for absorption correction, OLEX2\textsuperscript{3} for structure solution, refinement, molecular diagrams and graphical user-interface, Shelxe\textsuperscript{4} for refinement and
graphical user-interface *SHELXS-2013* for structure solution, *SHELXL-2013* for refinement, *Platon* for symmetry check. Experimental data and CCDC-Codes can be found in Table S-3. Crystal data, data collection parameters, and structure refinement details are given in Tables S-4 to S-5. Crystal structures visualized in Figure S-1.

**Table S-3** Experimental parameter and CCDC-Code.

| Sample  | Machine | Source | Temp. | Detector Distance | Time/Frame | #Frames | Frame width | CCDC  |
|---------|---------|--------|-------|------------------|------------|---------|-------------|--------|
| JiLiCy2 | D8      | Mo     | 100   | 40               | 15         | 2445    | 0.5         | 1813941 |

**Table S-4** Sample and crystal data of [JiLiCy2].

| Chemical formula | C18H31ClO2 | Crystal system | monoclinic |
|------------------|-------------|----------------|------------|
| Formula weight [g/mol] | 314.88 | Space group | C2 |
| Temperature [K] | 100 | Z | 8 |
| Measurement method | \(\lambda \text{ and } \omega\) scans | Volume [Å³] | 3514.3(4) |
| Radiation (Wavelength [Å]) | MoKα (\(\lambda = 0.71073\)) | Unit cell dimensions [Å] and [°] | 30.5188(19) | 90 |
| Crystal size / [mm³] | 0.99 × 0.199 × 0.126 | 6.3177(4) | 101.588(2) |
| Crystal habit | clear colourless block | Density (calculated) / [g/cm³] | 1.19 | 0.221 |
| Abs. correction Tmin | 0.6932 | Abs. correction Tmax | 0.746 |
| Abs. correction type | multiscan | F(000) [e⁻] | 1376 |

**Table S-5** Data collection and structure refinement of [JiLiCy2].

| Index ranges | -42 ≤ h ≤ 42, -8 ≤ k ≤ 8, -26 ≤ l ≤ 26 | Theta range for data collection [°] | 4.744 to 60.142 |
| Reflections number | 77713 | Data / restraints / parameters | 10283/1/381 |
| Refinement method | Least squares | Final R indices | all data | R1 = 0.0411, wR2 = 0.0753 |
| Function minimized | \(\Sigma w(F_o^2 - F_c^2)^2\) | 1>2σ(I) | R1 = 0.0292, wR2 = 0.0691 |
| Goodness-of-fit on \(F^2\) | 1.031 | Weighting scheme | where \(P = (F_o^2 + 2F_c^2)/3\) |
| Largest diff. peak and hole [e Å⁻³] | 0.27/-0.23 | | |
7. References

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3. Merschaert, A. et al. Org. Proc. Res. Dev. 10, 776–783 (2006)
4. K. V. Chuang, C. Xu, S. E. Reisman Science 2016, 353, 912-915
5. S. K. Woo, M. S. Kwon, E. Lee, Angew. Chem. Int. Ed. 2008, 47, 3242–3244; Angew. Chem. 2008, 120, 3286–3288
8. NMR- and HPLC Spectra
HPLC

Method Description:
Column: Lux Cellulose1 (Charulcel OD-H) 250x4.6 mm
Solvent System: n-Heptane:0.1% IPA:EtOH 95:5
Flow: 0.7 mL/min

Chromatogram

Detector A Channel 1 210nm

| Peak | Ret. Time | Area   | Area%  |
|------|-----------|--------|--------|
| 1    | 12.639    | 26485892 | 49.523 |
| 2    | 15.081    | 26996573 | 50.477 |
| Total|           | 53482465 | 100.000|

Chromatogram

Detector A Channel 1 210nm

| Peak | Ret. Time | Area   | Area%  |
|------|-----------|--------|--------|
| 1    | 12.529    | 101485 | 0.370  |
| 2    | 14.817    | 27295456 | 99.630 |
| Total|           | 27396941 | 100.000|
Method Description:
Column: Lux-Cellulose1 (Chromat OD-H) 250x4.6mm
Solvent System: n-Heptan+0.1%IPA/IPA 8:2
Flow: 1 ml/min

| Peak | Ret. Time | Area     | Area% |
|------|-----------|----------|-------|
| 1    | 13.228    | 30577577 | 49.906|
| 2    | 15.225    | 30692497 | 50.094|
| Total|           | 61270074 | 100.000|

Detector A Channel 1 210nm

| Peak | Ret. Time | Area     | Area% |
|------|-----------|----------|-------|
| 1    | 13.206    | 24756036 | 99.755|
| 2    | 15.237    | 60870    | 0.245|
| Total|           | 24816906 | 100.000|
Method Description:
Column: Lux-C-Cellulose 1 (Chiralcel OD-H) 250x4.6mm
Solvent System: n-Heptane + 0.1%IPA/EtOH 95:5
Flow: 0.7 ml/min

**Chromatogram**

**Detector A Channel 1 210nm**

| Peak | Ret. Time | Area      | Area%  |
|------|-----------|-----------|--------|
| 1    | 29.164    | 49609429  | 50.239 |
| 2    | 33.632    | 49136513  | 49.761 |
| **Total** |          | **98745942** | **100.000** |

**Chromatogram**

**Detector A Channel 1 210nm**

| Peak | Ret. Time | Area      | Area%  |
|------|-----------|-----------|--------|
| 1    | 29.786    | 133739    | 0.144  |
| 2    | 34.122    | 92650914  | 99.856 |
| **Total** |          | **92784653** | **100.000** |
Method Description:
Column: Chiralcel OD-H 250x4.6mm
Solvent System: n-Heptan+0.1%IPA/ETOH 95:5
Flow: 0.7 ml/min

Chromatogram

Detector A Channel 1 210nm

| Peak | Ret. Time | Area   | Area% |
|------|-----------|--------|-------|
| 1    | 13.856    | 15227375 | 50.300 |
| 2    | 15.582    | 15045760 | 49.700 |
| Total|           | 30273135 | 100.000 |

Chromatogram

Detector A Channel 1 210nm

| Peak | Ret. Time | Area   | Area% |
|------|-----------|--------|-------|
| 1    | 13.932    | 100742 | 0.400 |
| 2    | 15.843    | 25086410 | 99.600 |
| Total|           | 25187153 | 100.000 |
Method Description:
Column: Lux Cellulose (Clarity OD-H) 250x4.6mm
Solvent System: n-Heptane+0.1%IPA/IPA 9:1
Flow: 1 ml/min

Chromatogram

Detector A Channel 1 210nm

| Peak | Ret. Time | Area    | Area%  |
|------|-----------|---------|--------|
| 1    | 18.466    | 30596960| 49.752 |
| 2    | 21.735    | 30889482| 50.238 |
| Total|           | 61486442| 100.000|

Chromatogram

Detector A Channel 1 210nm

| Peak | Ret. Time | Area    | Area%  |
|------|-----------|---------|--------|
| 1    | 18.522    | 42807899| 99.490 |
| 2    | 21.664    | 219420  | 0.510  |
| Total|           | 43027319| 100.000|
Detector A Channel 1 210nm

| Peak | Ret. Time | Area   | Area% |
|------|-----------|--------|-------|
| 1    | 9.358     | 21355893 | 49.451|
| 2    | 15.975    | 21830131  | 50.549|
| Total| 16301402  | 100.000 |

Method Description:
Column: Chiralpak IC 250x4.6mm Particle Size 5 micrometer
Solvent System: n-Heptan/IPA 99:1
Flow: 0.7 ml/min T=25°C
Method Description:
Column: Chiralpak IC 250x4.6mm Particle Size 5 micrometer
Solvent System: n-Heptan+0.1%IPA/IPA 9.5:0.5
Flow: 1 ml/min T=25°C

Detector A Channel 1 210nm
| Peak | Ret. Time | Area     | Area%  |
|------|-----------|----------|--------|
| 1    | 17.194    | 14500596 | 49.833 |
| 2    | 19.784    | 14597535 | 50.167 |
| Total|           | 29098131 | 100.000 |

Detector A Channel 1 210nm
| Peak | Ret. Time | Area     | Area%  |
|------|-----------|----------|--------|
| 1    | 17.311    | 26946    | 0.155  |
| 2    | 19.887    | 17402122 | 99.845 |
| Total|           | 17429067 | 100.000 |
Method Description:
Column: Chiralpak IA 250x4.6mm Particle Size 5 micrometer
Solvent System: n-Heptan + 0.1%IPA/IPA 98.5:1.5
Flow: 0.7 ml/min T=25°C

Chromatogram

Detector A Channel 1 210nm

| Peak | Ret. Time | Area   | Area%  |
|------|-----------|--------|--------|
| 1    | 7.197     | 13230578 | 50.412 |
| 2    | 7.690     | 13014542 | 49.588 |
| Total|           | 26245120 | 100.000|

Chromatogram

Detector A Channel 1 210nm

| Peak | Ret. Time | Area   | Area%  |
|------|-----------|--------|--------|
| 1    | 7.381     | 9125615 | 99.697 |
| 2    | 7.985     | 27769  | 0.303  |
| Total|           | 9153385 | 100.000|
**Method Description:**
Column: Lux-Celulose 1 (Chiralcel OD-H), 250x4.6mm
Solvent System: n-Heptan+0.1%IPA/IPA 92.8
Flow: 0.7 ml/min

### Detector A Channel 1 210nm

| Peak | Ret. Time | Area   | Area% |
|------|-----------|--------|-------|
| 1    | 6.365     | 12765643 | 50.368 |
| 2    | 7.995     | 12578918  | 49.632 |
| **Total** | **25344561** | **100.000** |

### Detector A Channel 1 210nm

| Peak | Ret. Time | Area   | Area% |
|------|-----------|--------|-------|
| 1    | 6.379     | 20878529 | 99.398 |
| 2    | 8.025     | 126432  | 0.602 |
| **Total** | **21004961** | **100.000** |
Method Description:
Column: Lux-Cellulose 1 (Chiralcel OD-H) 250x4.6mm
Solvent System: n-Heptane+0.1%IPA/IPA 85:15
Flow: 0.7 ml/min

Detector A Channel 1 210nm

| Peak | Ret. Time | Area    | Area%  |
|------|-----------|---------|--------|
| 1    | 13.921    | 38563857| 49.881 |
| 2    | 15.341    | 38747412| 50.119 |
| Total|           | 77311268| 100.000|

Detector A Channel 1 210nm

| Peak | Ret. Time | Area    | Area%  |
|------|-----------|---------|--------|
| 1    | 14.224    | 33120   | 0.170  |
| 2    | 15.329    | 19505985| 99.830 |
| Total|           | 19539105| 100.000|
Method Description:
Column: Chiralpak IA 250x4.6mm Particle Size 5 micrometer
Solvent System: n-Heptan+1%EtOH+5%IPA+0.1%TFA
Flow: 0.7 ml/min

Chromatogram

| Peak | Ret. Time | Area     | Area% |
|------|-----------|----------|-------|
| 1    | 30.113    | 12027285 | 50.391|
| 2    | 34.963    | 11840586 | 49.609|
| Total| 65.076    | 23867871 | 100.000|

Chromatogram

| Peak | Ret. Time | Area     | Area% |
|------|-----------|----------|-------|
| 1    | 30.065    | 13902395 | 99.698|
| 2    | 35.033    | 42104    | 0.302 |
| Total| 65.098    | 13944499 | 100.000|
Method Description:
Column: Chiralcel OD-H 250x4.6mm
Solvent System: n-Heptane+0.1%IPA IPA 95:5
Flow: 1 ml/min

Chromatogram

Detector A Channel 1 210nm

| Peak | Ret. Time | Area  | Area%  |
|------|-----------|-------|--------|
| 1    | 14.044    | 10614896 | 50.171 |
| 2    | 17.706    | 10542618 | 49.829 |
| Total|           | 21157513 | 100.000 |

Chromatogram

Detector A Channel 1 210nm

| Peak | Ret. Time | Area  | Area%  |
|------|-----------|-------|--------|
| 1    | 14.069    | 33663 | 0.162  |
| 2    | 17.636    | 20750071 | 99.838 |
| Total|           | 20783734 | 100.000 |
Method Description:
Column: Chiralpak IA 250x4.6mm Particle Size 5 micron
Solvent System: n-Heptan+0.1%IPA/IPA 92:8
Flow: 0.7 ml/min

Detector A Channel 1 210nm
Peak | Ret. Time | Area      | Area%  
-----|-----------|-----------|--------
1    | 12.498    | 22575856  | 50.246 
2    | 13.759    | 22354851  | 49.754 
Total|           | 44930707  | 100.000

Detector A Channel 1 210nm
Peak | Ret. Time | Area      | Area%  
-----|-----------|-----------|--------
1    | 12.501    | 28067987  | 99.553 
2    | 13.783    | 126022    | 0.447  
Total|           | 28194009  | 100.000

91
Method Description:
Column: Chiraltak IB 250x4.6 mm ID
Solvent System: n-Heptane=0.1%IPA/IPA 95:5
Flow: 0.7 ml/min
T=25°C

Chromatogram

Detector A Channel 1 210nm

| Peak | Ret. Time | Area    | Area% |
|------|-----------|---------|-------|
| 1    | 14.569    | 12689608| 50.492|
| 2    | 19.314    | 12442491| 49.508|
| Total|           | 25132099| 100.000|

Method Description:
Column: Chiraltak IB 250x4.6 mm ID
Solvent System: n-Heptane=0.1%IPA/IPA 95:5
Flow: 0.7 ml/min
T=35°C

Chromatogram

Detector A Channel 1 210nm

| Peak | Ret. Time | Area    | Area% |
|------|-----------|---------|-------|
| 1    | 15.236    | 97205   | 0.521 |
| 2    | 19.211    | 18552092| 99.479|
| Total|           | 18649297| 100.000|
Method Description:
Column: Chiralpak IC 250x4.6mm Particle Size 5 micronmer
Solvent System: n-Heptan+0.1%IPA:EtOH 0:2
Flow: 0.7 ml/min T=25°C

Detector A Channel 1 210nm

| Peak # | Ret. Time | Area       | Area% |
|--------|-----------|------------|-------|
| 1      | 7.395     | 32742906   | 49.156|
| 2      | 8.235     | 33867381   | 50.844|
| Total  |           | 66610287   | 100.000|

Detector A Channel 1 210nm

| Peak # | Ret. Time | Area       | Area% |
|--------|-----------|------------|-------|
| 1      | 7.390     | 113588     | 0.472 |
| 2      | 8.234     | 23965433   | 99.528|
| Total  |           | 24079021   | 100.000|
Method Description:
Column: Chiralpak IC 250x4.6 mm Particle Size 5 micrometer
Solvent System: (n-Heptane+0.1%IPA)/EtOH 9:1
Flow=1ml/min Temp=25°C

Detector A Channel 1 210nm

| Peak | Ret. Time | Area      | Area%   |
|------|-----------|-----------|---------|
| 1    | 6.725     | 1539172   | 50.085  |
| 2    | 7.779     | 1533924   | 49.915  |
| Total| 7.779     | 3073096   | 100.000 |

Detector A Channel 1 210nm

| Peak | Ret. Time | Area      | Area%   |
|------|-----------|-----------|---------|
| 1    | 6.721     | 90336     | 0.750   |
| 2    | 7.772     | 11949593  | 99.250  |
| Total|           | 12039929  | 100.000 |
Method Description:
Column: Lux-Celldose 1 (Chiralcel OD-H) 250x4.6mm
Solvent System: n-Hexan+0.1%IPA IPA 95:5
Flow: 1mL/min

Chromatogram

**Detector A Channel 1 210nm**

| Peak | Ret. Time | Area       | Area%  |
|------|-----------|------------|--------|
| 1    | 9.003     | 20564374   | 49.634 |
| 2    | 9.979     | 20867465   | 50.366 |
| Total|           | 41431839   | 100.000|

Chromatogram

**Detector A Channel 1 210nm**

| Peak | Ret. Time | Area       | Area%  |
|------|-----------|------------|--------|
| 1    | 9.061     | 108656     | 0.371  |
| 2    | 9.949     | 29216586   | 99.629 |
| Total|           | 29325241   | 100.000|
Method Description:
Column: Lux Cellulose1 (Chiralcel OD-H) 250x4.6mm
Solute System: n-Heptan+0.1%IPA/IPA 95:5
Flow: 1mL/min

Detector A Channel 1 210nm
| Peak # | Ret. Time | Area     | Area% |
|--------|-----------|----------|-------|
| 1      | 8.936     | 22205019 | 49.986|
| 2      | 9.804     | 22217337 | 50.014|
| Total  |           | 44422356 | 100.000|

Detector A Channel 1 210nm
| Peak # | Ret. Time | Area     | Area% |
|--------|-----------|----------|-------|
| 1      | 8.972     | 18318735 | 99.551|
| 2      | 9.861     | 82637    | 0.449 |
| Total  |           | 18401371 | 100.000|
Detector A Channel 1 210nm

| Peak | Ret. Time | Area    | Area%  |
|------|-----------|---------|--------|
| 1    | 7.457     | 14186911| 50.073 |
| 2    | 8.619     | 14145389| 49.927 |
| Total|           | 28332300| 100.000|

Method Description:
Column: Lux-Celulose1 (Chiralcel OD-H) 250x4.6mm
Solvent System: n-Heptan+0.1%IPA/IPA 9:1
Flow: 1 ml/min

Detector A Channel 1 210nm

| Peak | Ret. Time | Area    | Area%  |
|------|-----------|---------|--------|
| 1    | 7.573     | 20185322| 99.588 |
| 2    | 8.799     | 83449   | 0.412  |
| Total|           | 20268771| 100.000|
Method Description:
Column: Chiralpak IA 250×4.6mm Particle Size 5 micron
Solvent System: n-Heptan+0.1%IPA IPA 92:8
Flow: 0.7 ml/min

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**Chromatogram**

**Detector A Channel 1 210nm**

| Peak | Ret. Time | Area     | Area%  |
|------|-----------|----------|--------|
| 1    | 10.886    | 23197684 | 49.804 |
| 2    | 12.638    | 23380160 | 50.196 |
| Total|           | 46577844 | 100.000|

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**Chromatogram**

**Detector A Channel 1 210nm**

| Peak | Ret. Time | Area     | Area%  |
|------|-----------|----------|--------|
| 1    | 10.823    | 27537174 | 99.018 |
| 2    | 12.622    | 273157   | 0.982  |
| Total|           | 27810331 | 100.000|