Versatile Process for the Stereodiverse Construction of 1,3-Polyols: Iterative Chain Elongation with Chiral Building Blocks

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General

All commercial reagents were used as received. Thin-layer chromatography (TLC) was conducted with precoated glass-backed plates and visualized by exposure to UV light (254 nm) or stained with ceric ammonium molybdate or potassium permanganate. Column chromatography was performed with silica gel (43-60 µm); the eluent used is reported in parentheses. $^1$H NMR spectra were recorded on 600 MHz FT-NMR and 400 MHz FT-NMR spectrometers. $^{13}$C NMR spectra were recorded at 151 MHz or 101 MHz. Chemical shifts are reported in ppm relative to solvent signal. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets). Low resolution mass spectra were recorded applying GC-MS. High resolution mass spectra were obtained using ESI on a MicroTOFMS.

Procedure A - Horner-Wittig reaction and subsequent deprotection

Under a nitrogen atmosphere 1.35 eq. n-butyllithium (2.5 M in hexanes) were added to a solution of 1.35 eq. diisopropylamine in tetrahydrofuran (0.1 M) at -78 °C. The reaction mixture was stirred for 15 min at 0 °C. 1.35 eq. of the desired building block enantiomer 1 were added at -78 °C and stirred for 1 h. Aldehyde (1.00 eq.) was added and the reaction was allowed to warm to room temperature over a period of 0.5-1.5 h. 1.00 eq. potassium tert-butoxide was added and the reaction was stirred for 30-60 min. Saturated ammonium chloride solution was added and the mixture was extracted with dichloromethane. The combined organic phases were washed with 1 N aqueous hydrochloric acid solution. The aqueous phase was extracted three times with dichloromethane. The combined organic phases were washed with saturated sodium bicarbonate solution and with saturated aqueous sodium chloride solution, dried over sodium sulphate and concentrated under reduced pressure. The crude product was purified by column chromatography to yield the $\beta$-hydroxy ketone.

Procedure B – anti-selective reduction of $\beta$-hydroxy ketone to 1,3-diol

Under nitrogen atmosphere 5.00 eq. tetrakis(methylammonium triacetoxyborohydride were dissolved in acetonitrile and acetic acid (4:1, 0.5 M) and cooled to -40 °C. $\beta$-Hydroxy ketone (1.00 eq.) dissolved in acetonitrile was added slowly and the reaction was stirred for 18 h. A saturated aqueous solution of sodium potassium tartrate was added and the reaction mixture was stirred for 30 min. before diluting with dichloromethane and washing with saturated
aqueous sodium bicarbonate. The aqueous phase was extracted with dichloromethane. The combined organic phases were washed with saturated aqueous sodium chloride solution, dried over sodium sulphate and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography to yield the 1,3-anti-diol.

**Procedure C – syn-selective reduction of β-hydroxy ketone to 1,3-diol**

Under nitrogen atmosphere the β-hydroxy ketone was dissolved in tetrahydrofuran/methanol (4:1, 0.1 M) and cooled to -78 °C before 1.10 eq. diethylmethoxyborane were added. The reaction was stirred for 15 min and 1.10 eq. sodium borohydride were added. The reaction was stirred for 1-5 h at -78 °C. A 3 N aqueous sodium hydroxide solution and aqueous 30% hydrogen peroxide solution were added and stirring was continued for 1h at rt. The reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic phases were washed with saturated aqueous sodium chloride solution, dried over sodium sulphate and the solvent was removed under reduced pressure. The residue was purified by column chromatography to yield the 1,3-syn-diol.

**Procedure D – Acetonide protection of the 1,3-diol**

To the 1,3-diol 5 mol% p-toluenesulfonic acid monohydrate and an excess of 2,2-dimethoxypropane (8eq.) was added. The reaction was heated to 45 °C on a rotary evaporator and the pressure held at 330 mbar for 30 - 60 min. Saturated aqueous sodium bicarbonate was added and the mixture was extracted with dichloromethane. The combined organic phases were dried with sodium sulphate and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography to yield the acetonide.

**Procedure E – Ozonolysis of the alkene**

The protected 1,3-diol was dissolved in a 2:1 mixture of dichloromethane and methanol (0.1-0.01 M) and 10 eq. sodium bicarbonate were added. The reaction mixture was flushed with oxygen at -78 °C followed by ozone until blue colour appeared, then flushed again with oxygen until the blue colour was removed again. Dimethyl sulfide (2.00 eq.) was added and the reaction was stirred for 16 h at rt. The reaction was quenched with water and extracted three times with dichloromethane. The combined organic layers were washed with saturated aqueous sodium
chloride solution, dried over sodium sulphate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography to yield the aldehyde.

(R)-6-Hydroxy-1-phenyloct-7-en-4-one (3)

Following procedure A, hydrocinnamaldehyde (1.64 g, 12.2 mmol) was converted with building block (R)-1, diisopropylamine, n-butyllithium and potassium tert-butoxide. After column chromatography (PE/EtOAc 85:15 → 70:30) β-hydroxy ketone 3 was obtained (2.22 g, 10.2 mmol, 83%).

TLC: Rf = 0.27 (PE/EtOAc 70:30) [KMnO4] [CAM]. [α]D20 = +14.2 (c = 1.73, CHCl3). 1H NMR (400 MHz, CDCl3): δ [ppm] = 7.32 – 7.25 (m, 2H), 7.22 – 7.14 (m, 3H), 5.85 (ddd, J = 17.2, 10.5, 5.5 Hz, 1H), 5.28 (dt, J = 17.2, 1.5 Hz, 1H), 5.13 (dt, J = 10.5, 1.4 Hz, 1H), 4.59 – 4.52 (m, 1H), 2.96 (d, J = 3.6 Hz, 1H), 2.65 – 2.59 (m, 4H), 2.45 (t, J = 7.3 Hz, 2H), 1.97 – 1.88 (m, 2H). 13C NMR (151 MHz, CDCl3): δ [ppm] = 211.0, 141.5, 139.2, 128.6, 128.5, 126.1, 115.1, 68.8, 48.9, 42.9, 35.1, 25.0. IR (ATR): νmax [cm−1] = 3443 (b) (OH), 3078 (w) (C=O), 3060 (m) (C=O), 2959 (m) (C=O), 2871 (m) (C=O), 1687 (s) (C=O), 1454 (s), 922 (s), 756 (s), 700 (s). LRMS (EI): m/z (%) 200 (2) [M+H2O], 162 (12), 147 (3), 104 (100), 91 (24), 77 (4). HRMS (ESI): m/z [M+Na]+ calcd for C14H18O2Na+ 241.1199; found: 241.1205.

(3R,5S)-8-Phenyloct-1-ene-3,5-diol (4)

Following procedure B, β-hydroxy ketone 3 (225 mg, 1.03 mmol) was converted with tetramethylammonium triacetoxyborohydride. After column chromatography (PE/EtOAc 70:30 → 50:50) diol 4 was obtained (211 mg, 0.958 mmol, 93%, dr = 90:10).

TLC: Rf = 0.15 (PE/EtOAc 70:30) [KMnO4] [CAM]. 1H NMR (400 MHz, CDCl3, major diastereomer): δ [ppm] = 7.31 – 7.24 (m, 2H), 7.21 – 7.16 (m, 3H), 5.92 (ddd, J = 17.2, 10.5, 5.4 Hz, 1H), 5.28 (dt, J = 17.2, 1.5 Hz, 1H), 5.14 (dt, J = 10.5, 1.4 Hz, 1H), 4.49 – 4.41 (m, 1H), 3.99 – 3.92 (m, 1H), 2.64 (t, J = 7.5 Hz, 2H), 2.14 (bs, 2H), 1.84 – 1.44 (m, 6H). 13C NMR
(101 MHz, CDCl₃, major diastereomer): δ [ppm] = 142.4, 140.8, 128.5, 128.5, 125.9, 114.6, 70.9, 69.2, 42.4, 37.3, 35.9, 27.6. IR (ATR): v max [cm⁻¹] = 3339 (b) (OH), 3084 (vw) (C sp²H), 3062 (vw) (C sp²H), 3026 (w) (C sp³H), 2936 (m) (C sp³H), 2859 (m) (C sp³H), 1452 (m), 920 (m), 747 (m), 697 (s). LRMS (EI): m/z (%) 202 (2) [M+H₂O]⁺, 184 (4) [M⁺-2H₂O], 147 (22), 118 (21), 104 (100), 91 (50), 77 (6). HRMS (ESI): m/z [M+Na]⁺ calcd for C₁₄H₂₀O₂Na⁺ 243.1356; found: 243.1356. HPLC analysis indicated an enantiomeric excess of > 99% [Chiralpak IA; 1.0 mL/min; heptane/ethanol, 90:10; 210 220 nm, major enantiomer (R,S)-13, t_R = 7.54 min.; (other enantiomer (S,R)-13 in racemic mixture: t_R = 8.58 min.)].

(3R,5R)-8-Phenyloct-1-ene-3,5-diol (5)

Following procedure C, hydroxy ketone 3 (984 mg, 4.51 mmol) was converted with diethylmethoxy borane and sodium borohydride. After column chromatography (PE/EtOAc 90:10 → 70:30) diol 5 was isolated as a yellow oil (984 mg, 4.47 mmol, 91%, dr = 84:16).

TLC: R_f = 0.27 (PE/EtOAc 75:25) [UV] [CAM]. ¹H NMR (600 MHz, CDCl₃): δ [ppm] = 7.31 – 7.24 (m, 2H), 7.20 – 7.17 (m, 3H), 5.85 (ddd, J = 16.8, 10.4, 5.9 Hz, 1H), 5.24 (dt, J = 17.2, 1.4 Hz, 1H), 5.09 (dt, J = 10.5, 1.3 Hz, 1H), 4.36 – 4.27 (m, 1H), 3.91 – 3.83 (m, 1H), 3.59-3.36 (bm, 2H), 2.66 – 2.62 (m, 2H), 1.81 – 1.73 (m, 1H), 1.70 – 1.44 (m, 5H). ¹³C NMR (151 MHz, CDCl₃): δ [ppm] = 142.4, 140.8, 128.5, 128.4, 125.8, 114.5, 73.8, 72.3, 42.9, 37.6, 35.9, 27.2. IR (ATR): v max [cm⁻¹] = 3356 (b) (OH), 2938 (s) (C sp³H), 2859 (s) (C sp³H), 1603 (vs) (C=O), 1496 - 1320 (m), 991 (s), 924 (vs). HRMS (ESI): m/z [M+Na]⁺ calcd for C₁₄H₂₀O₂Na⁺ 243.1356; found: 243.1356. HPLC analysis indicated an enantiomeric excess of 99% [Chiralpak OJ; 1.0 mL/min; heptane/iso-propylalcohol, 90:10; 220 nm, major enantiomer (R,R)-5, t_R = 8.06 min. (other enantiomer (S,S)-14 in racemic mixture: t_R = 9.14 min)].
(4S,6R)-2,2-Dimethyl-4-(3-phenylpropyl)-6-vinyl-1,3-dioxane (6)

Following procedure D, diol 4 (194 mg, 0.881 mmol) was converted with 2,2-dimethoxypropane and p-toluenesulfonic acid monohydrate. After column chromatography (PE/EtOAc 100:0 → 98:2) acetonide 6 was obtained (218 mg, 0.837 mmol, 95%, dr = 92:8).

**TLC:** \( R_f = 0.47 \) (PE/EtOAc 90:10) [KMnO4]. ¹H NMR (400 MHz, CDCl3, major diastereomer): \( \delta \) [ppm] = 7.31 – 7.25 (m, 2H), 7.21 – 7.15 (m, 3H), 5.88 (ddd, \( J = 17.3, 10.5, 5.8 \) Hz, 1H), 5.21 (dt, \( J = 17.3, 1.5 \) Hz, 1H), 5.11 (dt, \( J = 10.5, 1.4 \) Hz, 1H), 4.36 – 4.28 (m, 1H), 3.89 – 3.79 (m, 1H), 2.67 – 2.58 (m, 2H), 1.81 – 1.44 (m, 6H), 1.38 (s, 3H), 1.38 (s, 3H). ¹³C NMR (101 MHz, CDCl3, major diastereomer): \( \delta \) [ppm] = 142.6, 139.0, 128.6, 128.5, 125.9, 115.1, 100.5, 68.1, 66.4, 37.8, 36.0, 35.7, 27.5, 25.6, 24.9. IR (ATR): \( \nu_{\text{max}} \) [cm⁻¹] = 3084 (vw) (C sp²H), 3063 (vw) (C sp²H), 3026 (w) (C sp²H), 2986 (m) (C sp³H), 2937 (m) (C sp³H), 2861 (m) (C sp³H), 1453 (m), 1378 (m), 1223 (s), 921 (m), 747 (m), 698 (s). LRMS (EI): \( m/z \) (%) 245 (20) [M+CH₃], 202 (10), 184 (12), 147 (64), 131 (77), 118 (33), 104 (100), 91 (88), 77 (8). HRMS (ESI): \( m/z \) [M+Na]^+ calcd for C₁₇H₂₄O₂Na⁺ 283.1669; found: 283.1670.

(4R,6R)-2,2-Dimethyl-4-(3-phenylpropyl)-6-vinyl-1,3-dioxane (7)

Following procedure D, diol 5 (752 mg, 3.41 mmol) was converted with 2,2-dimethoxypropane and p-toluenesulfonic acid monohydrate. After column chromatography (PE/EtOAc 95:5 → 80:20) acetonide 7 was isolated as a yellow oil (947 mg, 3.64 mmol, 92%).

**TLC:** \( R_f = 0.78 \) (PE/EtOAc 80:20) [UV] [CAM]. ¹H NMR (400 MHz, CDCl₃): \( \delta \) [ppm] = 7.31 – 7.26 (m, 2H), 7.20 – 7.15 (m, 3H), 5.81 (ddd, \( J = 17.2, 10.5, 5.9 \) Hz, 1H), 5.24 (dt, \( J = 17.3, 1.4 \) Hz, 1H), 5.11 (dt, \( J = 10.6, 1.4 \) Hz, 1H), 4.37 – 4.29 (m, 1H), 3.91 – 3.82 (m, 1H), 2.62 (t, \( J = 7.6 \) Hz, 2H), 1.80 – 1.40 (m, 5H), 1.46 (s, 3H), 1.42 (s, 3H) 1.31-1.21 (m, 1H). ¹³C NMR (101 MHz, CDCl₃): \( \delta \) [ppm] = 142.6, 139.0, 128.6, 128., 125.9, 115.4, 98.7, 70.4, 68.8, 36.9,
36.1, 36.0, 30.4, 27.1, 20.0. **IR (ATR):** $v_{\text{max}}$ [cm$^{-1}$] = 3084 (b) (C$_{sp2}$H), 3062 (b) (C$_{sp2}$H), 2990 (s) (C$_{sp3}$H), 2941 (s) (C$_{sp3}$H), 2861 (s) (C$_{sp3}$H), 1496-1378 (m), 987 (s), 918 (vs), 742 (m).

**LRMS (EI):** $m/z$ (%): 260 (1), 245 (20) [M$^+$-CH$_3$], 147 (74), 131 (98), 118 (50), 104 (94), 91 (100). **HRMS (ESI):** m/z [M+Na]$^+$ calcd for C$_{17}$H$_{24}$O$_2$Na$^+$ 283.1669; found: 283.1670.

**(4R,6S)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxane-4-carbaldehyde (8)**

Following procedure E, acetonide 6 (331 mg, 1.27 mmol) was converted with ozone in the presence of sodium bicarbonate followed by treatment with dimethyl sulfide. After column chromatography (PE/EtOAc 85:15 → 70:30) 8 was obtained (293 mg, 1.12 mmol, 88%, dr = 92:8).

**TLC:** $R_f$ = 0.41 (PE/EtOAc 70:30) [KMnO$_4$]. [$\alpha$]$_D^{20}$ = +36.7 (c = 0.85, CHCl$_3$). **$^1$H NMR** (400 MHz, CDCl$_3$, major diastereomer): $\delta$ [ppm] = 9.81 (s, 1H), 7.31 – 7.25 (m, 2H), 7.21 – 7.14 (m, 3H), 4.25 (dd, $J$ = 7.1, 6.1 Hz, 1H), 3.81 – 3.72 (m, 1H), 2.65 – 2.59 (m, 2H), 2.02 (ddd, $J$ = 13.2, 6.0, 4.4 Hz, 1H), 1.82 – 1.44 (m, 5H), 1.42 (s, 3H), 1.39 (s, 3H). **$^{13}$C NMR** (101 MHz, CDCl$_3$, major diastereomer): $\delta$ [ppm] = 202.8, 142.4, 128.6, 128.5, 125.9, 100.3, 74.1, 66.1, 35.9, 35.6, 30.7, 27.4, 27.2, 23.9. **IR (ATR):** $v_{\text{max}}$ [cm$^{-1}$] = 3085 (vw) (C$_{sp2}$H), 3062 (vw) (C$_{sp2}$H), 3026 (w) (C$_{sp2}$H), 2988 (m) (C$_{sp3}$H), 2935 (m) (C$_{sp3}$H), 2862 (m) (C$_{sp3}$H), 1733 (m) (C=O), 1453 (m), 1379 (m), 1222 (s), 747 (m), 698 (s). **LRMS (EI):** m/z (%) 262 (14) [M$^+$], 247 (4), 204 (12), 187 (14), 147 (14), 131 (68), 104 (40), 91 (100), 59 (29). **HRMS (ESI):** m/z [M+Na]$^+$ calcd for C$_{16}$H$_{22}$O$_3$Na$^+$ 285.1461; found: 285.1459.

**(4R,6R)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxane-4-carbaldehyde (9)**
Following procedure E, acetonide 7 (660 mg, 2.53 mmol) was converted with ozone in the presence of sodium bicarbonate followed by treatment with dimethyl sulfide. After column chromatography (PE/EtOAc 90:10 → 80:20) 9 was isolated as a yellow oil (607 mg, 2.32 mmol, 91%).

**TLC:** \( R_f = 0.23 \) (PE/EtOAc 65:35) [UV] [CAM]. \([\alpha]D^{20} = +25.7 \) (c = 1.81, CHCl₃). \(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) [ppm] = 9.58 (s, 1H), 7.31 – 7.25 (m, 2H), 7.21 – 7.14 (m, 3H), 4.27 (dd, \( J = 12.4, 2.8 \) Hz, 1H), 3.93 – 3.84 (m, 1H), 2.62 (t, \( J = 7.5 \) Hz, 2H), 1.83 – 1.50 (m, 5H), 1.46 (d, \( J = 4.8 \) Hz, 6H), 1.35 – 1.25 (m, 1H). \(^1\)C NMR (101 MHz, CDCl₃): \( \delta \) [ppm] = 201.5, 142.4, 128.6, 128.5, 125.9, 99.2, 74.2, 68.4, 36.0, 35.9, 31.2, 30.0, 26.9, 19.6. IR (ATR): \( \nu_{\text{max}} [\text{cm}^{-1}] = 3084 \) (b) (C\(_{\text{sp}2}\)H), 2938 (s) (C\(_{\text{sp}3}\)H), 2816 (s) (C\(_{\text{sp}3}\)H), 1737 (vs) (C=O), 1495 (s), 1453 (s), 1380 (s), 1259 – 1004 (m), 967 (s), 940 (s), 747 (s). LRMS (EI): \( m/z \) [%]: 262 (14) [M], 247 (5) [M\(^+\) – CH₃], 204 (10), 187 (15), 147 (14), 131 (65), 104 (41), 91 (100), 59 (29). HRMS (ESI): \( m/z [M+Na]^+ \) calcd for C\(_{16}\)H\(_{22}\)O\(_3\)Na\(^+\) 285.1461; found: 285.1459.

(S)-1-((4R,6S)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)-4-hydroxyhex-5-en-2-one (10a/11a)

Following procedure A, (S)-1 was treated with \( n \)-butyllithium and diiso propylamine before addition of aldehyde 8 (283 mg, 1.08 mmol) and potassium tert-butoxide. Column chromatography (PE/EtOAc 85:15 → 70:30) afforded 10a/11a (227 mg, 0.655 mmol, 61%).

**TLC:** \( R_f = 0.22 \) (PE/EtOAc 70:30) [KMnO₄] [CAM]. \([\alpha]D^{20} = +7.9 \) (c = 2.41, CHCl₃). \(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) [ppm] = 7.30 – 7.24 (m, 2H), 7.21 – 7.15 (m, 3H), 5.86 (ddd, \( J = 17.2, 10.5, 5.5 \) Hz, 1H), 5.29 (dt, \( J = 17.2, 1.5 \) Hz, 1H), 5.13 (dt, \( J = 10.5, 1.4 \) Hz, 1H), 4.63 – 4.55 (m, 1H), 4.32 – 4.23 (m, 1H), 3.82 – 3.74 (m, 1H), 3.06 – 3.00 (m, 1H), 2.75 – 2.58 (m, 5H), 2.45 (dd, \( J = 15.8, 4.5 \) Hz, 1H), 1.81 – 1.43 (m, 6H), 1.34 (s, 3H), 1.31 (s, 3H). \(^1\)C NMR (101 MHz, CDCl₃): \( \delta \) [ppm] = 208.9, 142.3, 139.0, 128.4, 128.3, 125.7, 114.9, 100.5, 68.5, 66.4, 63.2, 50.0, 49.2, 38.1, 35.8, 35.4, 27.3, 24.5, 24.4. IR (ATR): \( \nu_{\text{max}} [\text{cm}^{-1}] = 3457 \) (b) (OH), 3084 (vw) (C\(_{\text{sp}2}\)H), 3062 (vw) (C\(_{\text{sp}2}\)H), 3025 (w) (C\(_{\text{sp}2}\)H), 2986 (m) (C\(_{\text{sp}3}\)H), 2937 (m) (C\(_{\text{sp}3}\)H), 2860 (m) (C\(_{\text{sp}2}\)H), 1710 (m) (C=O), 1454 (m), 1379 (m), 1222 (s), 925 (m), 748 (m), 699 (s). LRMS
Following procedure A, (S)-1 was treated with n-butyllithium and diisopropylamine before addition of aldehyde 8 (250 mg, 0.953 mmol) and potassium tert-butoxide. Column chromatography (PE/EtOAc 85:15 → 70:30) afforded 12a/13a as a yellow oil (136 mg, 0.393 mmol, 41%).

**TLC:** R_f = 0.40 (PE/EtOAc 65:35) [UV] [CAM]. [α]D^20 = -6.2 (c = 3.0, CHCl_3). ¹H NMR (600 MHz, CDCl_3): δ [ppm] = 7.30 – 7.25 (m, 2H), 7.20 – 7.15 (m, 3H), 5.86 (ddd, J = 17.2, 10.5, 5.5 Hz, 1H), 5.29 (dt, J = 17.2, 1.5 Hz, 1H), 5.13 (dt, J = 10.5, 1.4 Hz, 1H), 4.63 – 4.56 (m, 1H), 4.33 (dddd, J = 12.1, 7.5, 4.9, 2.5 Hz, 1H), 3.84 (dddd, J = 11.6, 7.4, 5.2, 2.4 Hz, 1H), 3.00 (bs, 1H), 2.73 – 2.58 (m, 5H), 2.42 (dd, J = 15.7, 4.8 Hz, 1H), 1.79 – 1.69 (m, 1H), 1.68 – 1.57 (m, 1H), 1.56 – 1.51 (m, 2H), 1.46 – 1.40 (m, 1H), 1.42 (s, 3H), 1.35 (s, 3H), 1.19 – 1.10 (m, 1H). ¹³C NMR (101 MHz, CDCl_3): δ [ppm] = 209.3, 142.5, 139.1, 128.5, 128.4, 125.9, 115.1, 98.9, 68.8, 68.6, 66.1, 50.5, 50.0, 36.8, 36.0, 36.0, 30.2, 27.0, 19.8. IR (ATR): ν_{max} [cm⁻¹] = 3446 (b) (OH), 2992 (s) (C_\text{sp}^3H), 2934 (s) (C_\text{sp}^3H), 2863 (s) (C_\text{sp}^3H), 1711 (vs) (C=O), 1496 (s), 1453 (s), 1380 (s), 1264 (s), 1200 (s), 1123 (m), 993 (s), 904 (s), 754 (m), 699 (m). HRMS (ESI): m/z [M+Na]^+ calcd for C_{21}H_{30}O_{4}Na^+ 369.2036; found: 369.2036.
Following procedure A, (R)-1 was treated with n-butyllithium and diisopropylamine before addition of aldehyde 8 (298 mg, 1.14 mmol) and potassium tert-butoxide. Column chromatography (PE/EtOAc 85:15 → 70:30) afforded 14a/15a (220 mg, 0.635 mmol, 56%).

**TLC:** Rf = 0.27 (PE/EtOAc 70:30) [KMnO4] [CAM]. [α]D20 = +35.0 (c = 2.18, CHCl3).

**1H NMR** (400 MHz, CDCl3): δ [ppm] = 7.31 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 5.86 (ddd, J = 17.2, 10.5, 5.5 Hz, 1H), 5.29 (dt, J = 17.2, 1.5 Hz, 1H), 5.13 (dt, J = 10.5, 1.4 Hz, 1H), 4.60 – 4.52 (m, 1H), 4.32 – 4.23 (m, 1H), 3.83 – 3.73 (m, 1H), 3.08 (bs, 1H), 2.74 – 2.65 (m, 3H), 2.65 – 2.58 (m, 2H), 2.47 (dd, J = 15.6, 4.6 Hz, 1H), 1.81 – 1.41 (m, 6H), 1.34 (s, 3H), 1.31 (s, 3H). 13C NMR (101 MHz, CDCl3): δ [ppm] = 209.4, 142.5, 139.2, 128.6, 125.9, 115.1, 100.7, 68.9, 66.5, 63.6, 50.1, 49.5, 38.3, 35.9, 35.5, 27.5, 24.8, 24.7. IR (ATR): νmax [cm⁻¹] = 3453 (b) (OH), 3084 (vw) (C-s-p2H), 3062 (vw) (C-s-p2H), 3026 (w) (C-s-p2H), 2986 (m) (C-s-p3H), 2936 (m) (C-s-p3H), 2860 (m) (C-s-p3H), 1454 (m), 1379 (m), 1222 (s), 925 (m), 748 (m), 699 (s). LRMS (EI): m/z (%) = 275 (3) [M+ - C4H6OH], 197 (4), 157 (10), 131 (13), 104 (100), 91 (57), 77 (7). HRMS (ESI): m/z [M+Na]+ calcd for C21H30O4Na+ 369.2036; found: 369.2036.

(R)-1-((4R,6R)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)-4-hydroxyhex-5-en-2-one (16a/17a)

Following procedure A, (R)-1 was treated with n-butyllithium and diisopropylamine before addition of aldehyde 9 (247 mg, 0.942 mmol) and potassium tert-butoxide. Column chromatography (PE/EtOAc 85:15 → 70:30) afforded 16a/17a as a yellow oil (259 mg, 0.747 mmol, 78%).

**TLC:** Rf = 0.20 (PE/EtOAc 80:20) [UV] [CAM]. [α]D20 = +7.9 (c = 2.02, CHCl3). 1H NMR (400 MHz, CDCl3) δ [ppm] = 7.30 – 7.24 (m, 2H), 7.20 – 7.15 (m, 3H), 5.86 (ddd, J = 17.2, 10.5, 5.5 Hz, 1H), 5.29 (dt, J = 17.2, 1.5 Hz, 1H), 5.13 (dt, J = 10.5, 1.4 Hz, 1H), 4.60 – 4.51 (m, 1H), 4.32 (dddd, J = 11.9, 7.5, 5.1, 2.5 Hz, 1H), 3.89 – 3.78 (m, 1H), 3.00 (d, J = 3.8 Hz, 1H), 2.71 – 2.65 (m, 3H), 2.61 (t, J = 7.5 Hz, 2H), 2.44 (dd, J = 15.6, 5.0 Hz, 1H), 1.81-1.67 (m, 1H), 1.67 – 1.44 (m, 4H), 1.42 (s, 3H), 1.35 (s, 3H), 1.20 – 1.10 (m, 1H). 13C NMR (101
MHz, CDCl₃) δ [ppm] = 209.7, 142.5, 139.2, 128.6, 128.4, 125.9, 115.1, 98.9, 68.9, 68.8, 66.2, 50.3, 50.2, 36.8, 36.0, 35.9, 30.2, 27.0, 19.8. IR (ATR): νmax [cm⁻¹] = 3458 (b) (OH), 2991 (s) (Csp3H), 2940 (s) (Csp3H), 2863 (s) (Csp3H), 1710 (vs) (C=O), 1496 (s), 1453 (s), 1380 (s), 1264 (s), 1200 (s), 1123 (m), 968 (s), 758 (m), 699 (m). HRMS (ESI): m/z [M+Na]+ calcd for C₂₁H₃₀O₄Na⁺ 369.2036; found: 369.2028.

(2S,4S)-1-((4S,6S)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)hex-5-ene-2,4-diol (10b)

Following procedure B, hydroxy ketone 10a/11a (71.5 mg, 0.206 mmol) was treated with tetramethylammonium triacetoxyborohydride. After column chromatography (PE/EtOAc 70:30 → 50:50) diol 10b was obtained (60.9 mg, 0.175 mmol, 85%).

TLC: Rf = 0.22 (PE/EtOAc 50:50) [KMnO₄] [CAM]. ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.31 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 5.91 (ddd, J = 17.2, 10.5, 5.4 Hz, 1H), 5.29 (dt, J = 17.2, 1.5 Hz, 1H), 5.11 (dt, J = 10.5, 1.5 Hz, 1H), 4.47 – 4.39 (m, 1H), 4.18 – 4.02 (m, 2H), 3.89 – 3.76 (m, 2H), 3.19 (bs, 1H), 2.67 – 2.54 (m, 2H), 1.82 – 1.41 (m, 10H), 1.39 (s, 3H), 1.34 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ [ppm] = 142.5, 141.1, 128.6, 128.5, 125.9, 114.2, 100.8, 70.3, 70.0, 68.3, 66.6, 42.9, 42.4, 39.0, 35.9, 35.5, 27.5, 25.2, 24.8. IR (ATR): νmax [cm⁻¹] = 3424 (b) (OH), 3085 (vw) (Csp2H), 3063 (vw) (Csp2H), 3026 (vw) (Csp2H), 2986 (w) (Csp3H), 2939 (m) (Csp3H), 2861 (w) (Csp3H), 1453 (w), 1381 (m), 1223 (m), 907 (m), 728 (s), 698 (m).

LRMS (EI): m/z (%) 333 (6) [M*-CH₃], 183 (21), 157 (22), 131 (67), 104 (95), 91 (100), 59 (24). HRMS (ESI): m/z [M+Na]+ calcd for C₂₁H₃₂O₄Na⁺ 371.2193; found: 371.2179.
(2R,4S)-1-((4S,6S)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)hex-5-ene-2,4-diol (11c’)

Following procedure C, hydroxy ketone 10a/11a (180.0 mg, 0.519 mmol) was treated with diethylmethoxyborane and sodium borohydride. After column chromatography (PE/EtOAc 70:30 → 50:50) diol 11c’ was obtained (112.2 mg, 0.322 mmol, 62%).

**TLC:** Rf = 0.12 (PE/EtOAc 70:30) [CAM].

**1H NMR** (400 MHz, CDCl3): δ [ppm] = 7.32 – 7.25 (m, 2H), 7.22 – 7.18 (m, 3H), 5.85 (ddd, J = 17.3, 10.5, 5.8 Hz, 1H), 5.29 (dt, J = 17.3, 1.4 Hz, 1H), 5.16 (dt, J = 10.5, 1.3 Hz, 1H), 4.43 – 4.37 (m, 1H), 4.31 – 4.24 (m, 2H), 4.01 – 3.94 (m, 1H), 3.86 (bs, 1H), 3.2 (bs, 1H), 2.67 (t, J = 7.5 Hz, 2H), 1.85 – 1.76 (m, 2H), 1.74 – 1.52 (m, 8H), 1.51 (s, 3H), 1.45 (s, 3H).

**13C NMR** (101 MHz, CDCl3): δ [ppm] = 142.5, 138.6, 128.6, 128.4, 125.9, 115.7, 99.1, 70.3, 69.2, 67.3, 66.2, 42.9, 42.0, 37.3, 36.1, 36.0, 30.4, 27.7, 19.8.

**IR (ATR):** v_max [cm⁻¹] = 3386 (b) (OH), 3026 (vw) (Cₛᵖ₂H), 2985 (w) (Cₛᵖ₃H), 2937 (w) (Cₛᵖ₃H), 1453 (w), 1379 (m), 1222 (s), 1165 (w), 990 (w), 748 (m), 698 (s).

**LRMS (ESI):** m/z (%) 371 (51) [M-Na⁺], 719 (43) [2M + Na⁺], 183 (83), 157 (38), 131 (100).

**HRMS (ESI):** m/z [M+Na]⁺ calcd for C₂₁H₃₂O₄Na⁺ 371.2193; found: 371.2193.

(2S,4S)-1-((4S,6R)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)hex-5-ene-2,4-diol (12b)

Following procedure B, hydroxy ketone 12a/13a (66.2 mg, 0.191 mmol) was treated with tetramethylammonium triacetoxyborohydride. After column chromatography (PE/EtOAc 70:30 → 50:50) diol 12b was obtained (63.8 mg, 0.183 mmol, 96%).

**TLC:** Rf = 0.08 (PE/EtOAc 70:30) [KMnO₄] [CAM].

**1H NMR** (400 MHz, CDCl3): δ [ppm] = 7.32 – 7.23 (m, 2H), 7.20 – 7.14 (m, 3H), 5.92 (ddd, J = 17.2, 10.5, 5.4 Hz, 1H), 5.29 (dt, J = 17.2, 1.6 Hz, 1H), 5.11 (dt, J = 10.5, 1.5 Hz, 1H), 4.47 – 4.39 (m, 1H), 4.21 – 4.08 (m, 2H), 4.01 – 3.94 (m, 1H), 3.86 (bs, 1H), 3.2 (bs, 1H), 2.67 (t, J = 7.5 Hz, 2H), 1.85 – 1.76 (m, 2H), 1.74 – 1.52 (m, 8H), 1.51 (s, 3H), 1.45 (s, 3H).
3.89 – 3.79 (m, 2H), 3.14 (bs, 1H), 2.61 (t, \( J = 7.5 \text{ Hz}, 2H \)), 1.79 – 1.40 (m, 9H), 1.46 (s, 3H), 1.38 (s, 3H), 1.27-1.17 (m, 1H). \(^{13}\text{C NMR} (101 \text{ MHz, CDCl}_3)\): \( \delta [\text{ppm}] = 142.5, 141.1, 128.5, 128.4, 125.9, 114.2, 98.8, 70.6, 70.3, 69.6, 68.9, 43.0, 43.0, 37.3, 36.0, 35.9, 30.3, 27.0, 20.1.\)

\textbf{IR (ATR):} \( \nu_{\text{max}} [\text{cm}^{-1}] = 3450 (\text{m}) (\text{OH}), 3387 (\text{m}) (\text{OH}), 3089 (\text{vw}) (\text{C}_{\text{sp2}}\text{H}), 3061 (\text{vw}) (\text{C}_{\text{sp2}}\text{H}), 3021 (\text{w}) (\text{C}_{\text{sp2}}\text{H}), 2992 (\text{w}) (\text{C}_{\text{sp3}}\text{H}), 2932 (\text{w}) (\text{C}_{\text{sp3}}\text{H}), 2904 (\text{m}) (\text{C}_{\text{sp3}}\text{H}), 2868 (\text{m}), 1461 (\text{m}), 1377 (\text{m}), 1229 (\text{m}), 908 (s), 749 (m), 699 (m).\)

\textbf{LRMS (EI):} \( m/z (%) \ 333 (8) [M^+ - \text{CH}_3], 207 (12), 183 (24), 157 (24), 131 (59), 104 (100), 91 (95), 59 (23).\)

\textbf{HRMS (ESI):} \( m/z [\text{M+Na}^+] \text{ calcd for } \text{C}_{21}\text{H}_{32}\text{O}_4\text{Na}^{+} 371.2193; \text{ found: } 371.2192.\)

\textbf{Following procedure C} hydroxy ketone \( 12a/13a \) (60. mg, 0.173 mmol) was treated with diethylmethoxyborane and sodium borohydride. After column chromatography (PE/EtOAc 90:10 \( \rightarrow \) 70:30) \( 13c \) was isolated as a yellow oil (50.9 mg, 0.146 mmol, 85%).

\textbf{TLC:} \( R_f = 0.09 \) (PE/EtOAc 80:20) [UV] [CAM]. \(^{1}\text{H NMR} (400 \text{ MHz, CDCl}_3)\): \( \delta [\text{ppm}] = 7.30 – 7.25 (\text{m, } 2\text{H}), 7.21 – 7.15 (\text{m, } 3\text{H}), 5.87 (\text{ddd, } J = 17.2, 10.5, 5.8 \text{ Hz}, 1\text{H}), 5.26 (\text{dt, } J = 17.2, 1.5 \text{ Hz}, 1\text{H}), 5.09 (\text{dt, } J = 10.4, 1.4 \text{ Hz}, 1\text{H}), 4.43 – 4.36 (\text{m, } 1\text{H}), 4.24 – 4.14 (\text{m, } 2\text{H}), 3.89 – 3.80 (\text{m, } 1\text{H}), 3.75 – 3.38 (\text{m, } 2\text{H}), 2.62 (\text{t, } J = 7.5 \text{ Hz}, 2\text{H}), 1.80 -1.51 (\text{m, } 8\text{H}), 1.48 – 1.40 (\text{m, } 4\text{H}), 1.39 (s, 3\text{H}), 1.37 – 1.30 (\text{m, } 1\text{H}).\)

\(^{13}\text{C NMR} (101 \text{ MHz, CDCl}_3)\): \( \delta [\text{ppm}] = 142.5, 140.9, 128.6, 128.4, 125.9, 98.9, 73.5, 69.6, 69.0, 67.3, 43.4, 42.7, 36.6, 36.1, 36.0, 30.4, 27.1, 19.9.\)

\textbf{IR (ATR):} \( \nu_{\text{max}} [\text{cm}^{-1}] = 3392 (\text{b}) (\text{OH}), 2990 (s) (\text{C}_{\text{sp3}}\text{H}), 2941 (s) (\text{C}_{\text{sp3}}\text{H}), 1496 (s), 1380 (s), 1265 (s), 1200 (s), 1096 (m), 992 (s), 924 (s), 748 (m), 699 (m).\)

\textbf{HRMS (ESI):} \( m/z [\text{M+Na}^+] \text{ calcd for } \text{C}_{21}\text{H}_{32}\text{O}_4\text{Na}^{+} 371.2193; \text{ found: } 371.2193.\)
(2R,4R)-1-((4S,6S)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)hex-5-ene-2,4-diol (14b)

Following procedure B, hydroxy ketone 14a/15a (70.9 mg, 0.205 mmol) was treated with tetramethylammonium triacetoxyborohydride. After column chromatography (PE/EtOAc 70:30 → 50:50) diol 14b was obtained (63.9 mg, 0.183 mmol, 89%, dr = 83:17).

TLC: Rf = 0.12 (PE/EtOAc 70:30) [KMnO4] [CAM]. 1H NMR (400 MHz, CDCl3, major diastereomer): δ [ppm] = 7.31 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 5.93 (ddd, J = 17.2, 10.5, 5.4 Hz, 1H), 5.30 (dt, J = 17.2, 1.6 Hz, 1H), 5.13 (dt, J = 10.5, 1.5 Hz, 1H), 4.49 – 4.42 (m, 1H), 4.25 – 4.11 (m, 2H), 3.86 – 3.76 (m, 1H), 3.32 (bs, 1H), 2.83 (bs, 1H), 2.62 (t, J = 7.2 Hz, 2H), 1.82 – 1.42 (m, 10H), 1.36 (s, 3H), 1.34 (s, 3H). 13C NMR (101 MHz, CDCl3, major diastereomer): δ [ppm] = 142.5, 141.1, 128.6, 128.4, 125.9, 114.4, 100.7, 70.6, 66.9, 66.5, 64.8, 42.6, 41.6, 38.0, 36.0, 35.6, 27.5, 25.0, 24.9. IR (ATR): vmax [cm⁻¹] = 3387 (b) (OH), 3085 (vw) (Csp2H), 3062 (vw) (Csp2H), 3026 (vw) (Csp2H), 2985 (m) (Csp3H), 2936 (m) (Csp3H), 2859 (m) (Csp3H), 1453 (m), 1379 (m), 1222 (s), 923 (m), 748 (m), 698 (m). LRMS (EI): m/z (%) 333 (8) [M+-CH3], 207 (12), 183 (18), 157 (16), 131 (52), 104 (100), 91 (99), 59 (20). HRMS (ESI): m/z [M+Na]+ calcd for C21H32O4Na+ 371.2193; found: 371.2178.

(2R,4R)-1-((4S,6R)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)hex-5-ene-2,4-diol (16b)

Following procedure B, hydroxy ketone 16a717a (70.5 mg, 0.203 mmol) was treated with tetramethylammonium triacetoxyborohydride. After column chromatography (PE/EtOAc 70:30 → 50:50) diol 16b was obtained (54.6 mg, 0.157 mmol, 77%, dr = 84:16).
**TLC:** $R_f = 0.14$ (PE/EtOAc 70:30) [KMnO$_4$] [CAM]. $^1$H NMR (400 MHz, CDCl$_3$, major diastereomer): $\delta$ [ppm] = 7.31 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 5.93 (ddd, $J = 17.2, 10.5, 5.4$ Hz, 1H), 5.30 (dt, $J = 17.2, 1.6$ Hz, 1H), 5.13 (dt, $J = 10.5, 1.5$ Hz, 1H), 4.49 – 4.41 (m, 1H), 4.28 – 4.14 (m, 2H), 3.89 – 3.79 (m, 1H), 3.46 (bs, 1H), 2.98 (bs, 1H), 2.62 (t, $J = 7.5$ Hz, 2H), 1.83 – 1.50 (m, 7H), 1.50 – 1.34 (m, 3H), 1.43 (s, 3H), 1.38 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$, major diastereomer): $\delta$ [ppm] = 142.5, 141.0, 128.6, 128.4, 125.9, 114.4, 98.9, 70.6, 69.1, 67.6, 66.3, 42.6, 42.1, 36.3, 36.1, 36.0, 30.4, 27.1, 19.8. IR (ATR): $v_{\text{max}}$ [cm$^{-1}$] = 3294 (b) (OH), 3089 (vw) (C$_{sp2}$H), 3065 (vw) (C$_{sp2}$H), 3023 (w) (C$_{sp2}$H), 2990 (m) (C$_{sp3}$H), 2935 (m) (C$_{sp3}$H), 2901 (m) (C$_{sp3}$H), 2868 (w) (C$_{sp3}$H), 1452 (w), 1377 (m), 1197 (m), 918 (m), 750 (m), 697 (s).

**LRMS (EI):** $m/z$ (%) 333 (10) [M$^-$CH$_3$], 183 (20), 157 (20), 131 (51), 117 (24), 104 (100), 91 (88), 59 (18). HRMS (ESI): $m/z$ [M+Na]$^+$ calcd for C$_{21}$H$_{32}$O$_4$Na$^+$ 371.2193; found: 371.2200.

(2S,4R)-1-((4S,6R)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)hex-5-ene-2,4-diol (17c)

![Chemical Structure](image)

Following procedure C, hydroxy ketone 16a/17a (80.0 mg, 0.231 mmol) was treated with diethylmethoxyborane and sodium borohydride. After column chromatography (PE/EtOAc 90:10 → 60:40) 17c was isolated as a yellow oil (64.5 mg, 0.185 mmol, 80%, dr: 71:29).

**TLC:** $R_f = 0.06$ (PE/EtOAc 80:20) [UV] [CAM]. $^1$H NMR (600 MHz, CDCl$_3$, major diastereomer) $\delta$ [ppm] = 7.29 – 7.25 (m, 2H), 7.20 – 7.15 (m, 3H), 5.86 (ddd, $J = 17.2, 10.4, 5.8$ Hz, 1H), 5.27 (dt, $J = 17.2, 1.5$ Hz, 1H), 5.08 (dt, $J = 10.4, 1.4$ Hz, 1H), 4.40 – 4.35 (m, 1H), 4.16 – 4.06 (m, 2H), 3.95 (bs, 1H), 3.84 (ddd, $J = 11.7, 7.3, 5.2, 2.4$ Hz, 1H), 3.57 (bs, 1H), 2.61 (t, $J = 7.5$ Hz, 2H), 1.78 – 1.71 (m, 1H), 1.71 – 1.40 (m, 8H), 1.46 (s, 3H), 1.38 (s, 3H), 1.22 (m, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ [ppm] = 142.5, 140.9, 128.6, 128.5, 125.9, 114.3, 98.9, 73.0, 72.5, 70.5, 68.9, 43.9, 43.6, 37.3, 36.0, 36.0, 30.4, 27.0, 20.1. IR (ATR): $v_{\text{max}}$ [cm$^{-1}$] = 3385 (b) (OH), 2991 (s) (C$_{sp2}$H), 2940 (s) (C$_{sp2}$H), 2915 (s) (C$_{sp3}$H), 2862 (s) (C$_{sp3}$H), 1454 (s), 1434 (s), 1380 (s), 1201 (s), 1170 (s), 1123 (s), 1094 (m), 992 (s), 966 (s), 875 (s), 750 (m), 697 (s), 668 (s), 663 (s), 654 (s), 635 (s), 626 (s), 617 (s), 608 (s), 599 (s), 590 (s), 581 (s), 572 (s), 563 (s), 554 (s), 545 (s), 536 (s), 527 (s), 518 (s), 509 (s), 490 (s), 481 (s), 472 (s), 463 (s), 454 (s), 445 (s), 436 (s), 427 (s), 418 (s), 409 (s), 400 (s), 391 (s), 382 (s), 373 (s), 364 (s), 355 (s), 346 (s), 337 (s), 328 (s), 319 (s), 310 (s), 301 (s), 292 (s), 283 (s), 274 (s), 265 (s), 256 (s), 247 (s), 238 (s), 229 (s), 220 (s), 211 (s), 202 (s), 193 (s), 184 (s), 175 (s), 166 (s), 157 (s), 148 (s), 139 (s), 130 (s), 121 (s), 112 (s), 103 (s), 94 (s), 85 (s), 76 (s), 67 (s), 58 (s), 49 (s), 40 (s), 31 (s), 22 (s), 13 (s), 2 (s).
Following procedure D, diol 10b (27.5 mg, 78.9 μmol) was converted with 2,2-dimethoxypropane and p-toluenesulfonic acid monohydrate. Column chromatography (PE/EtOAc 100:0 → 95:5) afforded 10d (22.4 mg, 58.7 μmol, 73%).

**TLC:** Rf = 0.66 (PE/EtOAc 70:30) [KMnO4]. 1H NMR (400 MHz, CDCl3): δ [ppm] = 7.30 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 5.89 (ddd, J = 17.3, 10.5, 5.8 Hz, 1H), 5.22 (dt, J = 17.3, 1.5 Hz, 1H), 5.12 (dt, J = 10.5, 1.4 Hz, 1H), 4.38 – 4.30 (m, 1H), 4.04 – 3.89 (m, 2H), 3.85 – 3.75 (m, 1H), 2.67 – 2.57 (m, 2H), 1.90 – 1.44 (m, 10H), 1.38 (s, 3H), 1.37 (s, 3H), 1.34 (s, 6H). 13C NMR (101 MHz, CDCl3): δ [ppm] = 142.6, 138.9, 128.6, 128.4, 125.9, 115.2, 100.5, 100.4, 68.0, 66.57, 63.3, 63.1, 42.0, 38.8, 37.4, 36.0, 35.6, 27.6, 25.5, 25.0, 24.9, 24.8. IR (ATR): v_max [cm⁻¹] = 3085 (vw) (Csp2H), 3063 (vw) (Csp2H), 3026 (vw) (Csp2H), 2987 (m) (Csp3H), 2937 (m) (Csp3H), 2860 (w) (Csp3H), 1454 (w), 1378 (m), 1222 (m), 909 (m), 730 (s), 698 (m). LRMS (EI): m/z (%) 373 (20) [M⁺-CH₃], 272 (12), 183 (30), 157 (32), 131 (100), 104 (76), 91 (96), 83 (35), 59 (44). HRMS (ESI): m/z [M+Na]^+ calcd for C24H36O4Na^+ 411.2506; found: 411.2506.
Following procedure D, diol 11c’ (123.3 mg, 0.354 mmol) was converted with 2,2-dimethoxypropane and p-toluenesulfonic acid monohydrate. Column chromatography (PE/EtOAc 100:0 → 95:5) afforded 11d (93.5 mg, 0.241 mmol, 68%).

TLC: Rf = 0.88 (PE/EtOAc 80:20) [CAM]. ¹H NMR (600 MHz, CDCl₃): δ [ppm] = 7.30–7.25 (m, 2H), 7.20–7.16 (m, 3H), 5.82 (ddd, J = 17.3, 10.5, 5.8 Hz, 1H), 5.24 (dt, J = 17.3, 1.5 Hz, 1H), 5.11 (dt, J = 10.5, 1.4 Hz, 1H), 4.35 (ddd, J = 11.6, 5.8, 2.6, 1.3 Hz, 1H), 4.11–4.02 (m, 2H), 3.8–3.75 (m, 1H), 2.64–2.60 (m, 2H), 1.79–1.71 (m, 1H), 1.65–1.47 (m, 8H), 1.46 (s, 3H), 1.41 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H), 1.31-1.23 (m, 1H). ¹³C NMR (151 MHz, CDCl₃): δ [ppm] = 142.5, 138.8, 128.4, 128.3, 125.7, 115.2, 100.3, 98.7, 70.4, 66.7, 64.8, 62.3, 42.3, 39.0, 37.2, 35.8, 35.6, 30.3, 27.4, 24.6, 24.6, 19.8. IR (ATR): ʋmax [cm⁻¹] = 3084 (vw) (C(sp²)H), 3063 (vw) (C(sp²)H), 3025 (vw) (C(sp²)H), 2987 (m) (C(sp³)H), 2939 (m) (C(sp³)H), 2862 (w) (C(sp³)H), 1454 (w), 1378 (s), 1223 (m), 1171 (s), 1018 (m), 918 (m), 748 (m), 698 (s). LRMS (EI): m/z (%) 373 (2) [M⁺-CH₃], 183 (9), 157 (13), 131 (44), 104 (45), 91 (100), 59 (77). HRMS (ESI): m/z [M+Na]⁺ calcd for C₂₄H₃₆O₄Na⁺ 411.2506; found: 411.2505.

(4R,6S)-4-(((4R,6R)-2,2-dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-6-vinyl-1,3-dioxane (12d)

Following procedure D, diol 12b (22.3 mg, 64.0 μmol, 1.00 eq.) was converted with 2,2-dimethoxypropane and p-toluenesulfonic acid monohydrate. Column chromatography (PE/EtOAc 100:0 → 95:5) afforded 12d (22.5 mg, 57.9 μmol, 90%).

TLC: Rf = 0.51 (PE/EtOAc 90:10) [KMnO₄]. ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.31–7.25 (m, 2H), 7.20–7.15 (m, 3H), 5.90 (ddd, J = 17.3, 10.5, 5.8 Hz, 1H), 5.22 (dt, J = 17.3, 1.5 Hz, 1H), 5.13 (dt, J = 10.5, 1.4 Hz, 1H), 4.39–4.30 (m, 1H), 4.07–3.92 (m, 2H), 3.86–3.77 (m, 1H), 2.62 (t, J = 7.6 Hz, 2H), 1.92–1.43 (m, 9H), 1.41 (s, 3H), 1.40–1.36 (m, 9H), 1.22–1.11 (m, 1H). ¹³C NMR (101 MHz, CDCl₃): δ [ppm] = 142.6, 138.9, 128.5, 128.4, 125.8, 115.1, 100.4, 98.5, 69.0, 68.0, 65.7, 62.8, 42.4, 37.4, 36.8, 36.2, 36.0, 30.4, 27.1, 25.6, 25.0, 19.9. IR (ATR): ʋmax [cm⁻¹] = 3084 (vw) (C(sp²)H), 3062 (vw) (C(sp²)H), 3025 (vw) (C(sp²)H), 2989 (m) (C(sp³)H), 2939 (m) (C(sp³)H), 2861 (m) (C(sp³)H), 1453 (m), 1377 (s), 1224 (m), 925 (m), 748
Following procedure D, diol 13c (50.0 mg, 0.143 mmol) was converted with 2,2-
dimethoxypropane and p-toluenesulfonic acid monohydrate. Column chromatography (PE →
PE/EtOAc 90:10) afforded 13d as a yellow oil (43.0 mg, 0.111 mmol, 77%).

**TLC:** R_f = 0.86 (PE/EtOAc 90:10) [UV] [CAM]. **^1H NMR** (600 MHz, CDCl_3): δ [ppm] = 7.29
– 7.25 (m, 2H), 7.20 – 7.16 (m, 3H), 5.82 (ddd, J = 17.3, 10.5, 5.8 Hz, 1H), 5.25 (dt, J = 17.3,
1.4 Hz, 1H), 5.11 (dt, J = 10.5, 1.4 Hz 1H), 4.36 (ddddd, J = 11.6, 5.8, 2.7, 1.3 Hz, 1H), 4.12
(dddd, J = 11.9, 6.7, 5.2, 2.3 Hz, 1H), 4.09-4.04 (m, 1H), 3.83 (ddddd, J = 11.7, 7.4, 5.5, 2.4 Hz,
1H), 2.62 (t, J = 7.7 Hz, 2H), 1.77 – 1.69 (m, 1H), 1.67-1.60 (m, 1H), 1.59 – 1.43 (m, 6H), 1.46
(s, 3H), 1.42 (s, 3H), 1.41 (s, 3H), 1.37 (s, 3H), 1.31 – 1.24 (m, 1H), 1.16-1.10 (m, 1H). **^13C NMR**
(151 MHz, CDCl_3): δ [ppm] = 142.6, 139.0, 128.6, 128.4, 125.8, 115.4, 98.8, 98.6, 70.6,
69.2, 65.0, 64.8, 43.3, 37.6, 37.4, 36.2, 36.0, 30.5, 30.5, 27.1, 20.0. **IR** (ATR): ν_{max} [cm^{-1}] =
2990 (s) (C sp^3H), 2941 (s) (C sp^3H), 2914 (s) (C sp^3H), 2862 (s) (C sp^3H), 1454 (s), 1378 (s), 1260
(s), 1200 (m), 1167 (s), 1132 (s), 1026 (m), 922 (m), 874 (s), 749 (m), 700 (m). **LRMS** (EI):
m/z (%): 373 (34) [M^+-CH_3], 341 (12), 281 (16), 207 (47), 183 (36), 157 (44), 131 (88), 91
(100). **HRMS** (ESI): m/z [M+Na]^+ calcd for C_{24}H_{36}O_4Na^+ 411.2506; found: 411.2506.
(4S,6R)-4-(((4R,6S)-2,2-dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-6-vinyl-1,3-dioxane (14d)

Following procedure D, diol 14b (50.0 mg, 0.143 μmol) was converted with 2,2-dimethoxypropane and p-toluenesulfonic acid monohydrate. Column chromatography (PE/EtOAc 100:0 → 95:5) afforded 14d (47.3 mg, 0.122 mmol, 85%, dr = 83:17).

**TLC:** $R_f = 0.70$ (PE/EtOAc 70:30) [KMnO$_4$]. \(^1\)H NMR (400 MHz, CDCl$_3$, major diastereomer): $\delta$ [ppm] = 7.30 – 7.24 (m, 2H), 7.21 – 7.15 (m, 3H), 5.88 (ddd, $J = 17.3, 10.5, 5.9$ Hz, 1H), 5.21 (dt, $J = 17.3, 1.5$ Hz, 1H), 5.11 (dt, $J = 10.5, 1.4$ Hz, 1H), 4.37 – 4.28 (m, 1H), 4.08 – 3.93 (m, 2H), 3.84 – 3.73 (m, 1H), 2.67 – 2.57 (m, 2H), 1.83 – 1.43 (m, 10H), 1.37 (s, 3H), 1.37 (s, 3H), 1.33 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl$_3$, major diastereomer): $\delta$ [ppm] = 142.6, 138.9, 128.6, 128.4, 125.9, 115.2, 100.6, 100.4, 68.2, 66.7, 62.9, 62.8, 42.2, 39.2, 38.0, 36.0, 35.7, 27.6, 25.5, 25.0, 24.8. IR (ATR): $v_{\text{max}}$ [cm$^{-1}$] = 3084 (vw) (C$_{sp2}$H), 3063 (vw) (C$_{sp2}$H), 3026 (vw) (C$_{sp2}$H), 2986 (m) (C$_{sp3}$H), 2937 (m) (C$_{sp3}$H), 2860 (w) (C$_{sp3}$H), 1454 (w), 1379 (m), 1222 (s), 920 (m), 747 (m), 698 (m). LRMS (EI): $m/z$ (%) 373 (30) [M$^+$-CH$_3$], 272 (8), 183 (34), 157 (36), 131 (100), 104 (71), 91 (97), 59 (40). HRMS (ESI): $m/z$ [M+Na]$^+$ calcd for C$_{24}$H$_{36}$O$_4$Na$^+$ 411.2506; found: 411.2509.

(4S,6R)-4-(((4R,6R)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-6-vinyl-1,3-dioxane (16d)

Following procedure D, diol 16b (40.7 mg, 0.117 mmol) was converted with 2,2-dimethoxypropane and p-toluenesulfonic acid monohydrate. Column chromatography (PE/EtOAc 100:0 → 95:5) afforded 16d (38.8 mg, 99.9 μmol, 85%, dr = 95:5).
TLC: $R_f = 0.82$ (PE/EtOAc 70:30) [KMnO₄]. $^1$H NMR (400 MHz, CDCl₃, major diastereomer): $\delta$ [ppm] = 7.30 - 7.24 (m, 2H), 7.20 - 7.14 (m, 3H), 5.88 (ddd, $J = 17.2, 10.5, 6.0$ Hz, 1H), 5.21 (dt, $J = 17.3, 1.5$ Hz, 1H), 5.11 (dt, $J = 10.5, 1.4$ Hz, 1H), 4.37 - 4.27 (m, 1H), 4.15 - 3.97 (m, 2H), 3.88 - 3.77 (m, 1H), 2.61 (t, $J = 7.6$ Hz, 2H), 1.80 - 1.41 (m, 9H), 1.40 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H), 1.36 (s, 3H), 1.18 - 1.08 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl₃, major diastereomer): $\delta$ [ppm] = 142.6, 138.9, 128.6, 128.4, 125.8, 115.5, 108.0, 96.5, 98.5, 98.5, 70.3, 69.0, 65.4, 65.2, 42.9, 37.0, 28.7, 36.2, 36.0, 30.4, 30.4, 27.1, 20.0, 20.0. IR (ATR): $v_{\text{max}}$ [cm$^{-1}$] = 3084 (vw) (Csp²H), 3063 (vw) (Csp²H), 3026 (wv) (Csp²H), 2988 (m) (Csp³H), 2939 (m) (Csp³H), 2861 (m) (Csp³H), 1454 (m), 1378 (s), 1223 (m), 925 (m), 748 (m), 698 (s).

LRMS (EI): m/z (%) 373 (28) [M+CH₃]⁻, 272 (9), 183 (38), 157 (39), 131 (92), 104 (70), 91 (100), 83 (40), 59 (42).


(4R,6R)-4-(((4R,6R)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-6-vinyl-1,3-dioxane (17d)

Following procedure D, diol 17c (67.1 mg, 0.193 mmol) was converted with 2,2-dimethoxypropane and p-toluenesulfonic acid monohydrate. Column chromatography (PE → PE/EtOAc 90:10) afforded 17d as a yellow oil (60.0 mg, 0.154 mmol, 80%).

TLC: $R_f = 0.89$ (PE/EtOAc 90:10) [UV] [CAM]. $^1$H NMR (400 MHz, CDCl₃) $\delta$ [ppm] = 7.31 - 7.25 (m, 2H), 7.21 - 7.15 (m, 3H), 5.82 (ddd, $J = 17.2, 10.5, 5.8$ Hz, 1H), 5.26 (dt, $J = 17.3, 1.4$ Hz, 1H), 5.13 (dt, $J = 10.5, 1.3$ Hz 1H), 4.35 (ddd, $J = 11.3, 5.5, 2.6, 1.3$ Hz, 1H), 4.10 - 3.95 (m, 2H), 3.82 (ddd, $J = 11.8, 7.3, 5.2, 2.4$ Hz, 1H), 2.62 (t, $J = 7.6$ Hz, 2H), 1.86 - 1.70 (m, 2H), 1.68 - 1.42 (m, 6H), 1.47 (s, 3H), 1.41 (s, 6H), 1.37 (s, 3H), 1.35 - 1.24 (m, 1H), 1.22 - 1.10 (m, 1H). $^{13}$C NMR (101 MHz, CDCl₃) $\delta$ [ppm] = 142.6, 139.0, 128.6, 128.4, 125.8, 115.5, 98.7, 98.5, 70.3, 69.0, 65.4, 65.2, 42.9, 37.0, 36.2, 36.0, 30.4, 30.4, 27.1, 20.0, 20.0. IR (ATR): $v_{\text{max}}$ [cm$^{-1}$] = 2990 (s) (Csp²H), 2947 (s) (Csp³H), 2862 (s) (Csp³H), 1496 (s), 1453 (s), 1378 (s), 1200 (s), 1174 (s), 1105 (s), 1016 (m), 989 (s), 967 (s), 924 (s), 824, 769.

LRMS (EI): m/z (%): 373 (42) [M+CH₃], 272 (10), 258 (8), 243 (45), 187 (41), 183 (45), 159
(35), 157 (43), 131 (99), 104 (76), 91 (100). HRMS (ESI): m/z [M+Na]^+ calcd for C_{24}H_{36}O_{4}Na^+ 411.2506; found: 411.2507.

(4S,6R)-6-((4R,6S)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-1,3-dioxane-4-carbaldehyde (10)

Following procedure E, acetonide 10d (17.9 mg, 46.1 μmol) was converted with ozone in the presence of sodium bicarbonate followed by treatment with dimethyl sulfide. After column chromatography (PE/EtOAc 85:15 → 70:30) aldehyde 10 was obtained (16.0 mg, 41.0 μmol, 89%).

**TLC:** R_f = 0.38 (PE/EtOAc 70:30) [KMnO_4]. [α]_{D}^{20} = -4.0 (c = 1.36, CHCl_3). ¹H NMR (400 MHz, CDCl_3): δ [ppm] = 9.82 (s, 1H), 7.31 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 4.30 – 4.22 (m, 1H), 4.00 – 3.87 (m, 2H), 3.83 – 3.74 (m, 1H), 2.65 – 2.58 (m, 2H), 2.01 – 2.00 (m, 1H), 1.89 – 1.71 (m, 3H), 1.68 – 1.44 (m, 6H), 1.42 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H). ¹³C NMR (101 MHz, CDCl_3): δ [ppm] = 202.6, 142.6, 128.6, 128.4, 125.9, 100.5, 100.3, 74.0, 66.6, 63.0, 63.0, 41.8, 38.8, 36.0, 35.6, 30.3, 27.5, 27.4, 24.9, 24.8, 23.9. IR (ATR): v_max [cm⁻¹] = 3085 (vw) (C_sp2H), 3062 (vw) (C_sp2H), 3025 (vw) (C_sp2H), 2986 (m) (C_sp3H), 2935 (m) (C_sp3H), 2859 (w) (C_sp3H), 1734 (m) (C=O), 1454 (m), 1378 (m), 1222 (m), 748 (s), 699 (m). LRMSE (EI): m/z (%) 375 (12) [M^+ - CH_3], 183 (20), 157 (22), 143 (41), 131 (79), 104 (93), 91 (100), 59 (45). HRMS (ESI): m/z [M+Na]^+ calcd for C_{23}H_{34}O_5Na^+ 413.2298; found: 413.2300.

(4S,6S)-6-((4R,6S)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-1,3-dioxane-4-carbaldehyde (11)
Following procedure E, acetonide 11d (75.0 mg, 0.193 mmol) was converted with ozone in the presence of sodium bicarbonate followed by treatment with dimethyl sulfide. After column chromatography (PE/EtOAc 95:5 → 80:20) 11 was isolated as a yellow oil (47.0 mg, 0.120 mmol, 62%).

**TLC:** R$_f$ = 0.32 (PE/EtOAc 70:30) [KMnO$_4$]. [α]$_D^{20}$ = -9.8 (c = 1.25, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$): δ [ppm] = 9.58 (d, $J$ = 0.6 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.20 – 7.14 (m, 3H), 4.29 (dd, $J$ = 12.2, 2.8 Hz, 1H), 4.15 – 3.98 (m, 2H), 3.83 – 3.73 (m, 1H), 2.62 (t, $J$ = 7.1 Hz, 2H), 1.80-1.34 (m, 10H), 1.46 (s, 3H), 1.45 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ [ppm] = 201.3, 142.6, 128.5, 128.4, 125.8, 100.5, 99.3, 74.3, 66.8, 64.7, 62.3, 42.2, 39.0, 36.0, 35.7, 31.5, 30.0, 27.5, 24.8, 24.7, 19.6. IR (ATR): $\nu_{\text{max}}$ [cm$^{-1}$] = 3085 (vw) (C$_{sp2}$H), 3062 (vw) (C$_{sp2}$H), 3026 (vw) (C$_{sp2}$H), 2990 (m) (C$_{sp3}$H), 2939 (m) (C$_{sp3}$H), 2860 (w) (C$_{sp3}$H), 1738 (m) (C=O), 1454 (m), 1379 (s), 1223 (s), 1223 (m), 749 (m), 699 (s). LRMS (EI): m/z (%): 375 (13) [M+CH$_3$]$^-$, 221 (8), 183 (21), 157 (21), 143 (45), 131 (78), 104 (94), 91 (100), 59 (45). HRMS (ESI): m/z [M+Na]$^+$ calcld for C$_{23}$H$_{34}$O$_5$Na$: 413.2298$; found: 413.2297.

(4$S$,6$R$)-6-(((4$R$,6$R$)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-1,3-dioxane-4-carbaldehyde (12)

Following procedure E, acetonide 12d (54.1 mg, 0.139 mmol) was converted with ozone in the presence of sodium bicarbonate followed by treatment with dimethyl sulfide. After column chromatography (PE/EtOAc 85:15 → 70:30) aldehyde 12 was obtained (43.0 mg, 0.110 mmol, 79%).

**TLC:** R$_f$ = 0.29 (PE/EtOAc 70:30) [KMnO$_4$]. [α]$_D^{20}$ = -11.7 (c = 3.55, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$): δ [ppm] = 9.82 (s, 1H), 7.30 – 7.24 (m, 2H), 7.20 – 7.15 (m, 3H), 4.26 (dt, $J$ = 6.4, 0.9 Hz, 1H), 4.03 – 3.90 (m, 2H), 3.85 – 3.75 (m, 1H), 2.62 (t, $J$ = 7.5 Hz, 2H), 2.07 – 1.99 (m, 1H), 1.88 – 1.43 (m, 8H), 1.43 – 1.33 (m, 12H), 1.22-1.11 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ [ppm] = 202.6, 142.6, 128.5, 128.4, 125.8, 100.3, 98.6, 73.9, 69.0, 65.4, 62.7, 42.3, 36.9, 36.2, 36.0, 30.5, 30.4, 27.3, 27.1, 24.0, 19.9. IR (ATR): $\nu_{\text{max}}$ [cm$^{-1}$] = 3085 (vw) (C$_{sp2}$H), 3062 (vw) (C$_{sp2}$H), 3026 (vw) (C$_{sp2}$H), 2990 (m) (C$_{sp3}$H), 2939 (m) (C$_{sp3}$H), 2862 (w) (C$_{sp3}$H),
1735 (m) (C=O), 1454 (m), 1379 (s), 1223 (s), 736 (s), 699 (s). **LRMS (EI):** m/z 375 (17) [M+-CH₃], 221 (8), 183 (22), 157 (22), 143 (44), 131 (73), 104 (86), 91 (100), 59 (45). **HRMS (ESI):** m/z [M+Na]+ calcd for C₂₃H₃₄O₅Na+ 413.2298; found: 413.2298.

(4S,6S)-6-(((4R,6R)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-1,3-dioxane-4-carbaldehyde (13)

Following procedure **E**, acetonide 13d (37.2 mg, 95.7 µmol) was converted with ozone in the presence of sodium bicarbonate followed by treatment with dimethyl sulfide. After column chromatography (PE/EtOAc 97:3 → 80:20) 13 as isolated as a yellow oil (25.9 mg, 66.3 µmol, 69%).

**TLC:** R₇ = 0.26 (PE/EtOAc 90:10) [UV] [CAM]. [α]D²⁰ = -17.6 (c = 2.09, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ [ppm] = 9.58 (d, J = 0.6 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.20 – 7.14 (m, 3H), 4.30 (dd, J = 12.2, 2.8 Hz, 1H), 4.19 – 4.11 (m, 1H), 4.09 – 4.01 (m, 1H), 3.87 – 3.79 (m, 1H), 2.61 (t, J = 7.6 Hz, 2H), 1.75 – 1.49 (m, 8H), 1.46 (s,3H), 1.45 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H), 1.33 – 1.22 (m, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ [ppm] = 201.3, 142.6, 128.6, 128.4, 125.9, 99.3, 98.6, 74.4, 69.2, 64.7, 64.5, 43.0, 37.5, 36.1, 36.0, 31.6, 30.5, 30.0, 27.1, 20.0, 19.7. **IR (ATR):** v max [cm⁻¹] = 2990 (s) (Cₛ₃H₃), 2940 (s) (Cₚ₃H), 2914 (s) (Cₛ₃H), 1738 (vs) (C=O), 1454 (s), 1379 (s), 1260 (s), 1200 (s), 1165 (s), 1124 (s), 1106 (s), 1028 (m), 940 (s), 913 (s), 874 (s), 748 (s), 734 (s), 700 (s). **LRMS (EI):** m/z (%) = 375 (2) [M+-CH₃], 341 (2), 317 (1), 281 (5), 206 (10), 180 (6), 131 (21), 105 (16) 104 (100), 91 (59), 65 (16). **HRMS (ESI):** m/z [M+Na]+ calcd for C₂₃H₃₄O₅Na+ 413.2298; found: 413.2300.
Following procedure E, acetonide 14d (36.9 mg, 95.0 μmol) was converted with ozone in the presence of sodium bicarbonate followed by treatment with dimethyl sulfide. After column chromatography (PE/EtOAc 85:15 → 70:30) aldehyde 14 was obtained (30.5 mg, 78.1 μmol, 82%).

**TLC:** Rf = 0.38 (PE/EtOAc 70:30) [KMnO₄]. [α]D₂₀²⁰ = +42.9 (c = 1.47, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 9.81 (s, 1H), 7.31 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 4.24 (dt, J = 6.5, 0.8 Hz, 1H), 4.04 – 3.92 (m, 2H), 3.82 – 3.72 (m, 1H), 2.62 (t, J = 7.0 Hz, 2H), 2.05 – 1.98 (m, 1H), 1.81 – 1.49 (m, 9H), 1.41 (s, 3H), 1.38 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ [ppm] = 202.6, 142.6, 128.6, 128.4, 125.9, 100.5, 100.5, 73.9, 66.7, 62.5, 62.5, 42.1, 39.1, 36.0, 35.7, 31.1, 27.6, 27.2, 24.9, 24.7, 24.0. IR (ATR): νmax [cm⁻¹] = 3085 (vw) (Csp²H), 3062 (vw) (Csp²H), 3026 (vw) (Csp²H), 2986 (m) (Csp₂H), 2937 (m) (Csp₃H), 2860 (w) (Csp₃H), 1734 (m) (C=O), 1454 (m), 1380 (m), 1223 (s), 748 (m), 699 (s). LRMS (EI): m/z (%) 375 (18) [M⁺-CH₃], 183 (24), 157 (25), 143 (47), 131 (84), 104 (89), 91 (100), 59 (45). HRMS (ESI): m/z [M+Na]⁺ calcd for C₂₃H₃₄O₅Na⁺ 413.2298; found: 413.2289.

Following procedure C, hydroxy ketone 14a/15a (59.8 mg, 0.173 mmol) was converted with sodium borohydride and diethylmethoxyborane. Column chromatography (PE/EtOAc 70:30 → 50:50) gave diol 15c (38.2 mg, 0.110 mmol, 64%). Part of it (28.8 mg, 82.6 μmol) was subsequently converted to acetonide 15d using 2,2-dimethoxypropane and p-toluenesulfonic
acid monohydrate following procedure D (85%). After column chromatography (PE/EtOAc 100:0 → 95:5), acetonide 15d (26.5 mg, 68.2 µmol) was subjected to ozonolysis according to procedure E. Column chromatography (PE/EtOAc 85:15 → 70:30) gave aldehyde 15 (19.1 mg, 48.9 µmol, 72%, 39% over three steps).

**TLC:** $R_f = 0.28$ (PE/EtOAc 70:30) [KMnO$_4$]. $[\alpha]_D^{20} = +34.8$ ($c = 1.45$, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 9.58 (d, $J = 0.6$ Hz, 1H), 7.31 – 7.24 (m, 2H), 7.20 – 7.15 (m, 3H), 4.28 (dd, $J = 12.3$, 2.8 Hz, 1H), 4.10 – 4.02 (m, 1H), 4.01 – 3.91 (m, 1H), 3.85 – 3.75 (m, 1H), 2.66 – 2.59 (m, $J = 14.1$ Hz, 2H), 1.88-1.71 (m, 3H), 1.66-1.35 (m, 7H), 1.46 (s, 6H), 1.33 (s, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ [ppm] = 201.4, 142.5, 128.6, 128.4, 125.9, 100.4, 99.2, 74.2, 66.6, 65.3, 62.8, 42.2, 38.7, 36.0, 35.6, 30.8, 29.9, 27.5, 25.0, 24.8, 19.6. IR (ATR): $\nu_{\text{max}}$ [cm$^{-1}$] = 3085 (vw) (C$_{\text{sp2}}$H), 3061 (vw) (C$_{\text{sp2}}$H), 3026 (vw) (C$_{\text{sp2}}$H), 2988 (m) (C$_{\text{sp3}}$H), 2937 (m) (C$_{\text{sp3}}$H), 2861 (w) (C$_{\text{sp3}}$H), 1738 (m) (C=O), 1454 (m), 1379 (s), 1223 (s), 749 (m), 700 (m).

LRMS (EI): $m/z$ (%) 375 (22) [M$-$CH$_3$], 221 (9), 183 (24), 157 (24), 143 (45), 131 (84), 104 (96), 91 (100), 59 (41). HRMS (ESI): $m/z$ [M+Na]$^+$ calcd for C$_{23}$H$_{34}$O$_5$Na$^+$ 413.2298; found: 413.2298.

(4$R$,6$S$)-6-(((4$R$,6$R$)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-1,3-dioxane-4-carbaldehyde (16)

Following procedure E, acetonide 16d (26.6 mg, 68.5 µmol) was converted with ozone in the presence of sodium bicarbonate followed by treatment with dimethyl sulfide. After column chromatography (PE/EtOAc 85:15→70:30) aldehyde 16 was obtained (24.1 mg, 61.7 µmol, 90%).

**TLC:** $R_f = 0.38$ (PE/EtOAc 70:30) [KMnO$_4$]. $[\alpha]_D^{20} = +13.0$ ($c = 1.77$, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 9.79 (s, 1H), 7.30 – 7.24 (m, 2H), 7.20 – 7.14 (m, 3H), 4.25 (t, $J = 7.0$ Hz, 1H), 4.10 – 3.96 (m, 2H), 3.87 – 3.77 (m, 1H), 2.61 (t, $J = 7.6$ Hz, 2H), 2.00 (ddd, $J = 13.1$, 6.6, 4.5 Hz, 1H), 1.76 – 1.49 (m, 8H), 1.41 (s, 3H), 1.39 (s, 6H), 1.36 (s, 3H), 1.18-1.07 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ [ppm] = 202.3, 142.6, 128.6, 128.4, 125.8, 100.6, 98.6, 73.7, 69.1, 64.9, 62.2, 42.5, 37.5, 36.1, 36.0, 31.4, 30.4, 27.1, 26.8, 23.9, 19.9. IR (ATR): $\nu_{\text{max}}$
[cm⁻¹] = 3085 (vw) (C\textsubscript{sp2}H), 3062 (vw) (C\textsubscript{sp2}H), 3026 (vw) (C\textsubscript{sp2}H), 2990 (m) (C\textsubscript{sp3}H), 2938 (m) (C\textsubscript{sp3}H), 2861 (w) (C\textsubscript{sp3}H), 1735 (m) (C=O), 1454 (m), 1379 (s), 1223 (s), 748 (m), 699 (s). **LRMS (EI):** m/z (%) 375 (22) [M\textsuperscript{+} - CH\textsubscript{3}], 221 (8), 183 (25), 157 (24), 143 (52), 131 (86), 104 (88), 91 (100), 59 (47). **HRMS (ESI):** m/z [M+Na]\textsuperscript{+} calcd for C\textsubscript{23}H\textsubscript{34}O\textsubscript{5}Na\textsuperscript{+} 413.2298; found: 413.2293.

(4\textit{R},6\textit{R})-6-(((4\textit{R},6\textit{R})-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-1,3-dioxane-4-carbaldehyde (17)

Following procedure E, acetonide 17d (46.7 mg, 0.120 mmol) was converted with ozone in the presence of sodium bicarbonate followed by treatment with dimethyl sulfide. After column chromatography (PE/EtOAc 97:3 → 80:20) 17 was isolated as a yellow oil (38.9 mg, 99.6 µmol, 83%).

**TLC:** R\textsubscript{f} = 0.15 (PE/EtOAc 90:10) [UV] [CAM]. [α]D\textsubscript{20} = +22.3 (c = 2.22, CHCl\textsubscript{3}). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ [ppm] = 9.59 (d, J = 0.6 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.20 – 7.15 (m, 3H), 4.30 (dd, J = 12.2, 3.0 Hz, 1H), 4.10 (dtd, J = 11.4, 6.5, 2.4 Hz, 1H), 3.97 (dddd, J = 11.5, 7.7, 5.2, 2.5 Hz, 1H), 3.81 (ddddd, J = 11.7 7.3, 5.2, 2.4 Hz, 1H), 2.62 (t, J = 7.6 Hz, 2H), 1.86 – 1.69 (m, 3H), 1.68 – 1.49 (m, 5H), 1.47 (s, 3H), 1.46 (s, 3H), 1.41 (s, 3H), 1.37 (s, 3H), 1.36–1.11 (m, 2H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ [ppm] = 201.4, 142.6, 128.6, 128.4, 125.9, 99.2, 98.6, 74.1, 69.0, 65.2, 65.0, 42.7, 37.0, 36.2, 36.0, 30.9, 30.4, 30.0, 27.1, 20.0, 19.7. **IR (ATR):** ν\textsubscript{max} [cm⁻¹] = 2991 (m) (C\textsubscript{sp3}H), 2940 (m) (C\textsubscript{sp3}H), 2862 (s) (C\textsubscript{sp3}H), 1737 (vs) (C=O), 1454, 1379, 1259, 1200, 1172, 1108, 1052, 1017, 970, 944, 904, 874, 750, 700. **LRMS (EI):** m/z (%): 375 (16) [M\textsuperscript{+} - CH\textsubscript{3}], 317 (2), 281 (5), 257 (8), 227 (5), 207 (12), 183 (25), 157 (24), 143 (48), 131 (77), 91 (100). **HRMS (ESI):** m/z [M+Na]\textsuperscript{+} calcd for C\textsubscript{23}H\textsubscript{34}O\textsubscript{5}Na\textsuperscript{+} 413.2298; found: 413.2298.
(R)-3-Hydroxyicos-1-en-5-one (C1a)

(R)-1 was dissolved in THF and reacted with pentadecanal (18, 1.05 g, 3.71 mmol) according to general procedure A. The aldehyde was consumed completely after 30 min. During work-up, no ammonium chloride was added, but the reaction mixture was directly treated with 1 N HCl. The crude product was purified by column chromatography (PE/EtOAc 95:5 → 90:10). β-Hydroxyketone C1a was isolated as a colourless powder (0.96 g, 3.09 mmol 83 % yield).

**TLC:** $R_f = 0.63$ (PE/EtOAc 70:30) [KMnO$_4$, [CAM]. $[a]_D^{20} = +13.7$ (c = 1.07, CHCl$_3$).

**$^1$H NMR** (400 MHz, CDCl$_3$): δ [ppm] = 5.86 (ddd, $J = 17.2, 10.5, 5.5$ Hz, 1H), 5.29 (dt, $J = 17.2, 1.5$ Hz, 1H), 5.13 (dt, $J = 10.5, 1.4$ Hz, 1H), 4.57 (dddt, $J = 7.2, 5.8, 4.4, 1.4$ Hz, 1H), 3.05 (s, 1H), 2.73 - 2.55 (m, 2H), 2.43 (t, $J = 7.4$ Hz, 2H), 1.57 (t, $J = 7.2$ Hz, 2H), 1.36 - 1.19 (m, 24H), 0.90 (t, $J = 6.9$ Hz, 3H). **$^{13}$C NMR** (101 MHz, CDCl$_3$): δ [ppm] = 211.7, 139.2, 115.1, 68.8, 48.8, 43.9, 32.1 29.8, 29.8, 29.6, 29.5, 29.5, 29.3, 23.7, 22.8, 14.3. **IR** (ATR): $\nu_{\text{max}}$ [cm$^{-1}$] = 3342, 3255 (b) (OH), 2914 (vs), 2848 (s) (C$_{sp^3}$), 1707 (s) (C=O) 1465 (m) (CH$_2$-def.), 1381 (m) (CH$_3$-def.), 990 (m), 925 (m) (=C-H def.). **LRMS (EI):** $m/z$ (%): 254 (8) [M$^+$-C$_3$H$_6$O], 85 (18), 71 (48), 58 (100). **HRMS (ESI):** $m/z$ [M+Na]$^+$ calcd for C$_{20}$H$_{38}$O$_2$Na$^+$ 333.2764; found: 333.2758.

(3R, 5S)-Icos-1-ene-3,5-diol (C1b)

β-Hydroxyketone (C1a, 100 mg, 0.320 mmol) was reacted analogue to procedure B with tetramethylammonium triacetoxyborohydride at -24°C for 3 days. The reaction was stirred at least 1h at rt after addition of sodium potassium tartrate. The crude product was purified by column chromatography (PE/EtOAc 95:5 → 80:20) yielding the 1,3-anti-diol (C1b) as colourless solid (89.1 mg, 0.285 mmol, 89 % yield, dr = 89:11).

**TLC:** $R_f = 0.3$ (PE/EtOAc 70:30) [CAM]. $[a]_D^{20} = -6.3$ (c = 3.5, dr 83:17, CHCl$_3$).**$^1$H NMR** (600 MHz, CDCl$_3$, major diastereomer): δ [ppm] = 5.93 (ddd, $J = 17.2, 10.5, 5.4$ Hz, 1H), 5.30
(4S,6R)-2,2-Dimethyl-4-pentadecyl-6-vinyl-1,3-dioxane (C1d)

The free 1,3-anti diol (C1b, 0.30 g, 0.96 mmol) was treated according to procedure D. The starting material was dissolved in dichloromethane and first stirred at 45°C at 630 mbar for 15 min, then proceeding on to 360 mbar until full conversion (~15 min). The crude product was directly purified without work-up by column chromatography (PE/EtOAc 100 → 95:5) adding 3% triethylamine to the chromatography solvent. Compound C1d was isolated as a yellowish oil (0.33 g, 0.94 mmol, 98% yield, dr 90:10).

**TLC:** Rf = 0.8 (PE/EtOAc 90:10) [CAM]. [α]D20 = + 32.3 (c = 3.5, dr 90:10, CHCl3). 1H NMR (400 MHz, CDCl3 major diastereomer): δ [ppm]: 5.88 (ddd, J = 17.4, 10.5, 5.8 Hz, 1H), 5.21 (dt, J = 17.3, 1.5 Hz, 1H), 5.10 (dt, J = 10.5, 1.4 Hz, 1H), 4.36 - 4.29 (m, 1H), 3.84 - 3.76 (m, 1H), 1.79 - 1.60 (m, 2H), 1.58 - 1.48 (m, 1H), 1.45 - 1.36 (m, 2H), 1.37 (s, 3H), 1.37 (s, 3H), 1.30 - 1.24 (m, 25H), 0.88 (t, J = 6.8 Hz, 3H). 13C NMR (101 MHz, CDCl3, major diastereomer): δ [ppm] = 139.0, 115.1, 100.4, 68.1, 66.6, 37.9, 36.2, 32.1, 29.9, 29.8, 29.8, 29.8, 29.7, 29.5, 25.6, 25.5, 24.9, 22.8, 14.3. IR (ATR): νmax [cm⁻¹] = 2922 (vs), 2853 (s) (C sp³), 1465 (s) (CH₂-def.), 1378 (m) (CH₃-def.), 1223 (s) (C-O-C), 987 (m), 920 (m) (=C-H def.). LRMS (EI): m/z (%): 377.4 (100) [M⁺-CH₃], 83.1 (73), 59.1 (63). HRMS (ESI): m/z [M+Na]+ calcd for C₂₅H₄₄O₂Na⁺ 375.3234; found: 375.3235.
(4R,6S)-2,2-Dimethyl-6-pentadecyl-1,3-dioxane-4-carbaldehyde (C1)

![Chemical structure of C1]

Ozonolysis of C1d (0.864 g, 2.45 mmol) according to procedure E at -40°C led to the formation of aldehyde C1 as a colourless oil (2.18 mmol, 89% yield, dr = 90:10) after column chromatography (PE/EtOAc 95:5 → 85:15).

TLC: Rf = 0.33 (PE/EtOAc 90:10) [CAM]. [α]D²⁰ = +17.9 (c= 2.52, dr 90:10, CHCl₃).

**1H NMR** (400 MHz, CDCl₃, major diastereomer): δ [ppm] = 9.82 (s, 1H), 4.25 (dd, J = 7.2, 6.1 Hz, 1H), 3.77 - 3.69 (m, 1H), 2.02 (ddd, J = 13.2, 6.1, 4.4 Hz, 1H), 1.70 (ddd, J = 13.2, 10.5, 7.2 Hz, 1H), 1.54 - 1.48 (m, 1H), 1.42 (s, 3H), 1.39 (s, 3H), 1.37 - 1.31 (m, 1H), 1.29 - 1.24 (m, 26H), 0.88 (t, J = 7.1 Hz, 3H).

**13C NMR** (151 MHz, CDCl₃, major diastereomer): δ [ppm] = 202.9, 100.3, 74.1, 66.3, 36.1, 32.1, 30.7, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 27.4, 25.2, 23.9, 22.8, 14.3. **IR (ATR):** νmax [cm⁻¹] = 2922 (vs), 2852 (s) (Csp³), 1736 (s) (C=O), 1465 (m) (CH₂-def.), 1379 (m) (CH₃-def.), 1224 (s) (C-O-C). **LRMS (EI):** m/z (%): 393.2 (22) [M⁺-CH₃], 267.2 (20), 59.0 (100). **HRMS (ESI):** m/z [M+Na]⁺ calcd for C₂₂H₄₂O₃Na⁺ 377.3026; found: 377.3027.

(R)-1-((4R,6S)-2,2-Dimethyl-6-pentadecyl-1,3-dioxane-4-yl)-4-hydroxyhex-5-en-2-one (C2a)

![Chemical structure of C2a]

Aldehyde C1 (0.595 g, 1.68 mmol) was reacted with (R)-1 (1.8 eq.) according to general procedure A. The crude product was purified by column chromatography (PE/EtOAc 95:5 → 85:15). β-Hydroxyketone C2a was isolated as a yellowish oil (1.04 mmol, 62 % yield, dr = 99:1).

TLC: Rf = 0.10 (PE/EtOAc 90:10) [CAM]. [α]D²⁰ = +19.3 (c= 1.32, dr = 99:1, CHCl₃).

**1H NMR** (400 MHz, CDCl₃): δ [ppm] = 5.86 (ddd, J = 17.2, 10.5, 5.5 Hz, 1H), 5.29 (dt, J = 17.2, 1.5 Hz, 1H), 5.13 (dt, J = 10.5, 1.4 Hz, 1H), 4.62 - 4.51 (m, 1H), 4.28 (tdd, J = 8.8, 6.2,
4.6 Hz, 1H), 3.84 - 3.72 (m, 1H), 3.07 (d, J = 3.9 Hz, 1H), 2.74 - 2.66 (m, 3H), 2.47 (dd, J = 15.6, 4.5 Hz, 1H), 1.69 - 1.57 (m, 2H), 1.54 - 1.45 (m, 1H), 1.42 - 1.36 (m, 1H), 1.29 - 1.21 (m, 27H), 1.34 (s, 3H), 1.33 (s, 3H), 0.88 (t, J = 6.8 Hz, 3H). 13C NMR (101 MHz, CDCl3): δ [ppm] = 209.6, 139.2, 115.1, 100.7, 68.9, 66.7, 63.6, 50.1, 49.6, 38.4, 36.0, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 25.5, 24.9, 24.7, 22.8, 14.3. IR (ATR): νmax [cm⁻¹] = 3416 (b) (OH), 2918 (vs), 2851 (s) (Csp³), 1711 (m) (C=O), 1467 (m) (CH₂-def.), 1379 (m) (CH₃-def.), 1223 (s) (C-O-C), 989 (m), 923 (m) (=C-H def.).


(2S,4R)-1-((4S,6S)-2,2-Dimethyl-6-pentadecyl-1,3-dioxane-4-yl)hex-5-ene-2,4-diol (C2c)

β-Hydroxyketone C2a (50 mg, 0.114 mmol) was treated according to procedure C. The reaction was carried out at -35°C. The crude product was purified by column chromatography (PE/EtOAc 80:20 → 60:40) to yield the diol C2c as colourless liquid (0.107 mmol 94% yield, dr = 91:9).

TLC: Rf = 0.24 (PE/EtOAc 70:30) [CAM]. [α]D²⁰ = +16.3 (c = 3.5, dr = 98:2, CHCl₃). ¹H NMR (400 MHz, CDCl₃, major diasteromer): δ [ppm] = 5.86 (ddd, J = 16.7, 10.4, 5.7 Hz, 1H), 5.26 (dt, J = 17.1, 1.5 Hz, 1H), 5.07 (dt, J = 10.4, 1.5 Hz, 1H), 4.40 - 4.34 (m, 1H), 4.15 - 4.03 (m, 2H), 3.98 (s, 1H), 3.84 - 3.74 (m, 1H), 3.68 (s, 3H), 1.74 - 1.54 (m, 6H), 1.39 (s, 3H), 1.34 (s, 3H), 1.32 - 1.18 (m, 28H), 0.88 (t, J = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃, major diastereomer): δ [ppm] = 140.9, 114.2, 100.7, 72.9, 72.7, 68.0, 66.7, 43.8, 43.0, 39.0, 36.0, 32.0, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 25.4, 25.2, 24.8, 22.8, 14.2. IR (ATR): νmax [cm⁻¹] = 3280 (sb) (OH), 2916 (vs), 2849 (s) (Csp³), 1466 (m) (CH₂-def.), 1376 (m) (CH₃-def.), 1223 (m) (C-O-C), 986 (s), 926 (m) (=C-H def.). LRMS (EI): m/z (%): 425.4 (11) [M⁺-C₄H₇], 267.2 (22), 207.0 (18), 109.0 (68) 55.0 (98), 83.0 (100). HRMS (ESI): m/z [M+Na]+ calcd for C₂₇H₅₂O₄Na⁺ 463.3758; found: 463.3758.
(4R,6R)-4-(((4R,6S)-2,2-Dimethyl-6-pentadecyl-1,3-dioxane-4-yl)methyl)-2,2-dimethyl-6-vinyl-1,3-dioxane (C2d)

The free 1,3-anti diol C2c (0.37 g, 0.840 mmol) was treated according to procedure D. The crude product was purified by column chromatography (PE/EtOAc 95:5 → 90:10) and led to compound C2d as a colourless solid. (0.764 mmol, 91% yield, dr = 90:10).

TLC: \( R_f = 0.96 \) (PE/EtOAc 70:30)[CAM]. \([\alpha]_D^{20} = +1.8 \) (c = 1.86, dr = 90:10, CHCl3).

\(^1\)H NMR (400 MHz, CDCl3, major diastereomer): \( \delta \) [ppm] = 5.82 (ddd, \( J = 17.3, 10.5, 5.8 \) Hz, 1H), 5.25 (dt, \( J = 17.3, 1.4 \) Hz, 1H), 5.12 (dt, \( J = 10.5, 1.3 \) Hz, 1H), 4.34 (dddd, \( J = 11.6, 5.9, 2.7, 1.3 \) Hz, 1H), 4.08 - 3.91 (m, 2H), 3.81 - 3.69 (m, 1H), 1.84 (ddd, \( J = 14.5, 8.0, 6.6 \) Hz, 1H), 1.65 - 1.48 (m, 5H), 1.46 (s, 3H), 1.41 (s, 3H), 1.34 (s, 6H), 1.30 - 1.24 (m, 28H), 0.88 (t, \( J = 7.0 \) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl3, major diastereomer): \( \delta \) [ppm] = 139.0, 115.5, 100.3, 98.7, 70.4, 66.8, 65.5, 63.0, 42.4, 38.8, 36.6, 36.1, 32.1, 30.4, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 25.5, 25.1, 24.9, 22.8, 19.9, 14.3. IR (ATR): \( \nu_{\text{max}} \) [cm\(^{-1}\)] = 2922 (vs), 2853 (s) (C sp\(^3\)), 1465 (s) (CH2-def.), 1377 (s) (CH3-def.), 1224 (s), 1199 (s), 1171 (s) (C-O-C), 987 (m), 920 (m) (=C-H def.). LRMS (El): \( m/z \) (%): 465.4 (38) [M+CH3], 329.2 (22), 109.0 (51), 83.0 (100), 59.0 (82). HRMS (ESI): m/z [M+Na]\(^+\) calcd for C\(_{30}\)H\(_{56}\)O\(_4\)Na\(^+\) 503.4071; found: 503.4071.

Ozonolysis of C2d (0.364 g, 0.760 mmol) according to procedure E led to the formation of aldehyde C2 as a colourless oil (0.692 mmol, 91% yield, dr = 92:8) after column chromatography (PE/EtOAc 90:10 → 70:30).

TLC: \( R_f = 0.34 \) (PE/EtOAc 80:20) [CAM]. \([\alpha]_D^{20} = +34.0 \) (c = 1.29, dr = 92:8, CHCl3).

\(^1\)H NMR (400 MHz, CDCl3, major diastereomer): \( \delta \) [ppm] = 9.59 (d, \( J = 0.7 \) Hz, 1H), 4.29 (dd, \( J = 12.2, 3.1 \) Hz, 1H), 4.07 (dt, \( J = 11.4, 6.4, 2.5 \) Hz, 1H), 4.02 - 3.81 (m, 1H), 3.80 - 3.72 (m, 1H), 3.60 - 3.50 (m, 1H), 3.10 - 3.00 (m, 2H), 2.90 - 2.80 (m, 2H), 2.80 - 2.70 (m, 2H), 2.70 - 2.60 (m, 2H), 2.60 - 2.50 (m, 2H), 2.50 - 2.40 (m, 2H), 2.40 - 2.30 (m, 2H), 2.30 - 2.20 (m, 2H), 2.20 - 2.10 (m, 2H), 2.10 - 2.00 (m, 2H), 2.00 - 1.90 (m, 2H), 1.90 - 1.80 (m, 2H), 1.80 - 1.70 (m, 2H), 1.70 - 1.60 (m, 2H), 1.60 - 1.50 (m, 2H), 1.50 - 1.40 (m, 2H), 1.40 - 1.30 (m, 2H), 1.30 - 1.20 (m, 2H), 1.20 - 1.10 (m, 2H), 1.10 - 1.00 (m, 2H), 1.00 - 0.90 (m, 2H), 0.90 - 0.80 (m, 2H), 0.80 - 0.70 (m, 2H), 0.70 - 0.60 (m, 2H), 0.60 - 0.50 (m, 2H), 0.50 - 0.40 (m, 2H), 0.40 - 0.30 (m, 2H), 0.30 - 0.20 (m, 2H), 0.20 - 0.10 (m, 2H), 0.10 - 0.00 (m, 2H).
1H), 1.85 (ddd, J = 14.2, 8.2, 6.2 Hz, 1H), 1.74 (dt, J = 12.9, 2.7 Hz, 1H), 1.65 - 1.48 (m, 4H), 1.46 (s, 3H), 1.45 (s, 3H), 1.44 - 1.35 (m, 2H), 1.34 (s, 6H), 1.31 - 1.22 (m, 28H), 0.88 (t, J = 6.6 Hz, 3H). \( ^{13}C \) NMR (101 MHz, CDCl\(_3\), major diastereomer): δ [ppm] = 201.4, 100.3, 99.2, 74.2, 66.7, 65.4, 62.8, 42.2, 38.8, 36.1, 32.1, 30.8, 30.0, 29.9, 29.8, 29.7, 29.7, 29.5, 25.5, 25.1, 24.9, 22.8, 19.6, 14.3. IR (ATR): \( \nu_{max} \) [cm\(^{-1}\)] = 2922 (vs), 2853 (s) (C\(_{sp}^3\)), 1741 (m) (C=O), 1465 (s) (CH\(_2\)-def.), 1378 (s) (CH\(_3\)-def.), 1224 (s), 1201(s), 1170 (s) (C-O-C). LRMS (EI): m/z (%):467.4 (56) [M+CH\(_3\)]\(^+\), 349.3 (12), 143.1 (100), 85.0 (77), 59.1 (73). HRMS (ESI): m/z [M+Na]\(^+\) calcd for C\(_{29}\)H\(_{54}\)O\(_5\)Na\(^+\) 505.3863; found: 505.3865.

\((S)-1-((4R,6R)-4-(((4R,6S)-2,2-Dimethyl-6-pentadecyl-1,3-dioxane-4-yl)methyl)-2,2-dimethyl-1,3-dioxane)-4-hydroxyhex-5-en-2-one (C3a)\)

Aldehyde C\(_2\) (0.288 g, 0.597 mmol) was reacted with \((S)-1\) (1.8 eq) according to general procedure A. The crude product was purified by column chromatography (PE/EtOAc 90:10 → 70:30). \( \beta \)-Hydroxyketone C\(_3\)a was isolated as a colourless oil (0.213g, 0.376 mmol, 63 % yield).

**TLC:** \( R_f = 0.2 \) (PE/EtOAc 80:20) [CAM]. [\( \alpha \)]\(_{D}^{20}\) = +19.3 (c= 1.32, CHCl\(_3\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ [ppm] = 5.85 (ddd, J = 17.2, 10.5, 5.5 Hz, 1H), 5.28 (dt, J = 17.2, 1.5 Hz, 1H), 5.13 (dt, J = 10.5, 1.5 Hz, 1H), 4.62 - 4.55 (m, 1H), 4.34 (ddddd, J = 11.9, 7.6, 4.7, 2.5 Hz, 1H), 4.06 - 3.89 (m, 2H), 3.81 - 3.72 (m, 1H), 2.99 (bs, 1H), 2.75 - 2.58 (m, 3H), 2.42 (dd, J = 15.7, 4.7 Hz, 1H), 1.86 - 1.75 (m, 1H), 1.64 - 1.36 (m, 8H), 1.43 (s, 3H), 1.34 (s, 3H), 1.33 (s, 6H), 1.29 - 1.23 (m, 26H), 0.87 (t, J = 6.7 Hz, 3H). \(^{13}C\) NMR (101 MHz, CDCl\(_3\)): δ [ppm] = 209.3, 139.1, 115.1, 100.3, 98.9, 68.7, 66.8, 66.1, 65.7, 62.9, 50.5, 50.0, 42.3, 38.8, 36.5, 36.1, 32.1, 30.2, 29.8, 29.5, 25.5, 25.1, 24.9, 22.8, 19.9, 14.3. IR (ATR): \( \nu_{max} \) [cm\(^{-1}\)] =3458 (b), 2922 (vs), 2853 (s) (C\(_{sp}^3\)), 1712 (m) (C=O), 1465 (w) (CH\(_2\)-def.), 1379 (s) (CH\(_3\)-def.), 1224 (m), 1199 (m), 1170 (m) (C-O-C), 992 (w), 939 (m) (=C-H def.). LRMS (EI): m/z (%):495.4 [M+\text{C}_4\text{H}_7\text{O}], 377.2 (8), 207.0 (14), 82.0 (94), 57.1 (100). HRMS (ESI): m/z [M+Na]\(^+\) calcd for C\(_{34}\)H\(_{62}\)O\(_6\)Na\(^+\) 589.4439; found: 589.4437.
(2S,4S)-1-((4S,6S)-6-(((4R,6S)-2,2-Dimethyl-6-pentadecyl-1,3-dioxane-4-yl)methyl)-2,2-dimethyl-1,3-dioxane-4-yl)hex-5-ene-2,4-diol (C3b)

\[ \beta \text{-Hydroxyketone C3a (0.213g, 0.376 mmol) was treated according to procedure B. The crude product was purified by column chromatography (PE/EtOAc 80:20 → 60:40) to yield the diol C3b as colourless liquid (0.155g, 0.273 mmol, 73% yield, } \text{dr} = 98:2). \]

**TLC:** \( R_f = 0.37 \) (PE/EtOAc 60:40) [CAM]. \([\alpha]_D^{20} = + 3.3 \) (c = 0.45, CHCl\(_3\)). \(^1\)H NMR (600 MHz, CDCl\(_3\), major diastereomer): \( \delta \) [ppm] = 5.92 (ddd, \( J = 17.2, 10.5, 5.4 \) Hz, 1H), 5.29 (dt, \( J = 17.2, 1.6 \) Hz, 1H), 5.12 (dt, \( J = 10.5, 1.5 \) Hz, 1H), 4.44 (s, 1H), 4.21 - 4.12 (m, 2H), 4.05 - 4.00 (m, 1H), 3.96 - 3.91 (m, 1H), 3.83 (s, 1H), 3.78 - 3.73 (m, 1H), 3.07 (bs, 1H), 1.85 - 1.69 (m, 3H), 1.66 - 1.50 (m, 2H), 1.47 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H), 1.29 - 1.22 (m, 26H), 0.88 (t, \( J = 7.0 \) Hz, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) [ppm] = 141.1, 114.2, 100.3, 98.9, 70.7, 70.3, 69.8, 66.8, 65.8, 62.9, 43.1, 43.0, 42.3, 38.8, 36.8, 37.1, 36.1, 32.1, 30.3, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 25.5, 25.1, 24.9, 22.8, 20.1, 14.3. IR (ATR): \( \nu_{\text{max}} \) [cm\(^{-1}\)] = 3422 (vb) (OH), 2922 (vs), 2853 (s) (C\(_{\text{sp}^3}\)), 1379 (s) (CH\(_3\)-def.), 1224 (m), 1200 (m), 1104 (m) (C-O-C). HRMS (ESI): m/z [M+Na\(^+\)] calcd for C\(_{34}\)H\(_{64}\)O\(_6\)Na\(^+\) 591.4595; found: 591.4603.

(4S,6R)-4-(((4R,6S)-2,2-Dimethyl-6-pentyl-1,3-dioxan-4-yl)methyl)-6-(((4R,6S)-2,2-dimethyl-6-vinyl-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-1,3-dioxane (19)

13.5 mg (23.7 \( \mu \)mol) of compound C3b was reacted according to procedure D. The crude product was purified by column chromatography (PE/EtOAc 88:12) to yield 14.5 mg (23.7 \( \mu \)mol, quant.) of compound 19 as colourless liquid.

**TLC:** \( R_f = 0.84 \) (PE/EtOAc 80:20) [CAM]. \([\alpha]_D^{20} = - 3.5 \) (c = 1.46, CHCl\(_3\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) [ppm] = 5.89 (ddd, \( J = 16.8, 10.5, 5.7 \) Hz, 1H), 5.24 - 5.18 (m, 1H), 5.14 - 5.10 (m, 1H), 4.39 - 4.28 (m, 1H), 4.07 - 3.90 (m, 3H), 3.81 - 3.71 (m, 1H), 3.24 - 3.18 (m, 1H), 32
1.90 - 169 (m, 9H), 1.63 - 1.45 (m, 7H), 1.42 - 1.35 (m, 9H), 1.33 - 1.23 (m, 24H), 0.87 (t, J = 6.8 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ [ppm] = 138.9, 115.2, 100.4, 100.3, 98.5, 68.0, 66.8, 65.8, 65.7, 63.0, 62.8, 42.6, 38.8, 37.5, 36.5, 36.1, 32.1, 30.4, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 25.6, 25.5, 25.1, 24.9, 22.8, 20.0, 14.3. IR (ATR): νmax [cm⁻¹] = 2990 (w), 2923 (s), 2854 (m) (C sp³), 1464 (w), 1378 (s) (CH₃-def.), 1199 (w), 1172 (m), 1107 (m), 1104 (m) (C-O-C). HRMS (ESI): m/z [M+Na]+ calcd for C_{37}H_{68}O_{6}Na⁺ 631.4908; found: 631.4908.

2-((4R,6S)-6-(((4R,6S)-2,2-Dimethyl-6-pentyl-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-1,3-dioxan-4-yl)ethanol (20)

Under nitrogen atmosphere 59.2 mg (97.2 µmol) of compound 19 was dissolved 0.82 ml THF (0.1M) and cooled to 0°C. Then 0.49 ml (0.246 mmol, 3 eq, 0.5 M in THF) 9-BBN was added dropwise. The reaction was stirred 10 min at 0°C, then 16 h at rt. The reaction was cooled down to 0°C again and was then quenched with 0.08 ml NaOH (3M, 3eq) and the same amount of H₂O₂ (35%). The mixture was stirred another 15 min at 0°C and then 4 h at rt, before it was diluted with water and extracted four times with 2 ml dichloromethane. The organic phase was washed with saturated aqueous sodium chloride solution, dried over sodium sulphate and the solvent was removed. The crude product was purified by column chromatography yielding 51.7 mg (82.5 µmol, 85%) of compound 20.

TLC: Rf = 0.19 (PE/EtOAc 80:20) [CAM]. 1H NMR (400 MHz, CDCl3) δ [ppm] = 4.10 - 4.03 (m, 1H), 4.03 - 3.91 (m, 4H), 3.80 - 3.71 (m, 2H), 2.41 (bs, 1H), 1.88 - 1.43 (m, 14H), 1.42 (s, 3H), 1.37 (s, 3H), 1.36 (s, 3H), 1.33 (s, 6H), 1.33 (s, 3H), 1.31 - 1.23 (m, 26H), 0.88 (t, J = 7.2 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ [ppm] = 100.6, 100.3, 98.5, 67.1, 66.8, 65.8, 65.7, 63.1, 63.0, 61.5, 42.6, 42.5, 38.8, 38.4, 37.8, 36.1, 32.1, 30.4, 29.9, 29.8, 29.8, 29.8, 29.7, 29.5, 25.1, 25.0, 24.9, 22.8, 20.0, 14.3. IR (ATR): νmax [cm⁻¹] = 3484 (br), 2990 (w), 2922 (s), 2853 (m) (C sp³), 1379 (s) (CH₃-def.), 1199 (s), 1170 (s), 1106 (m) (C-O-C). HRMS (ESI): m/z [M+Na]^+ calcd for C_{37}H_{70}O_{7}Na⁺ 649.5014; found: 649.5014.
(Z)-methyl-4-((4R,6S)-6-(((4R,6S)-6-(((4R,6S)-2,2-Dimethyl-6-pentyl-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-1,3-dioxan-4-yl)but-2-enoate (13)

Compound 20 (52.0 mg 82.9 µmol) was dissolved in 0.83 ml (0.1M) dichloromethane under nitrogen atmosphere. Then 27mg of 4 Å molecule sieve, 15 mg (0.124 mmol, 1.5 eq) NMO and 1.4 mg (4 µmol, 0.05 eq) TPAP were added successively. The reaction was stirred for 2h at rt, before the whole reaction mixture was purified by column chromatography with addition of Et3N (PE/EtOAc95/5 → 80/20). The product can be isolated as colourless liquid (33.7 mg 53.9 µmol, 65%, Rf = 0.53 (PE/EtOAc 70:30, [CAM]).

Under nitrogen atmosphere 3.3 mg (0.084 mmol, 1.8 eq) NaH was suspended in 0.06 ml THF and cooled down to 0°C before 21 mg (0.060 mmol, 1.3 eq) of ethyl 2-(di-o-tolylphosphoryl)acetate (Ando-phosphonate) dissolved in 0.06 ml THF was added. The mixture was stirred for 30 min before cooling down to -78°C. Then 29 mg (0.046 mmol) of the aldehyde dissolved in 0.12 ml THF was added. The reaction was stirred for 2 h at -78°C. The reaction was quenched with saturated aqueous ammonium chloride solution and extracted four times with 2 ml dichloromethane. The organic phase was washed with saturated aqueous sodium chloride solution, dried over Na2SO4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (PE/EtOAc 90/10) yielding 0.018 g (0.026 mmol, 57%, 100% Z-alkene) of compound 21 as white solid.

TLC: Rf = 0.46 (PE/EtOAc 70:30) [CAM]. 1H NMR (400 MHz, CDCl3) δ [ppm] = 6.31 (dt, J = 11.6, 7.0 Hz, 1H), 5.84 (dt, J = 11.6, 1.8 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 4.03 - 3.87 (m, 5H), 3.80 - 3.71 (m, 1H), 3.01 - 2.92 (m, 1H), 2.78 - 2.68 (m, 1H), 1.82(ddd, J = 14.2, 8.0, 6.4 Hz, 2H), 1.69 - 1.42 (m, 10H), 1.41 (s, 3H), 1.36 (s, 3H), 1.33 (s, 12H), 1.30 - 1.26 (t, J = 7.1 Hz, 3H), 1.26 - 1.24 (m, 24H), 0.88 (t, J = 6.8 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ [ppm] = 166.5, 146.2, 121.2, 100.5, 100.3, 98.5, 66.8, 66.3, 65.8, 65.7, 63.0, 60.0, 51.19, 36.1, 32.1, 32.1, 30.4, 29.8, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 25.5, 25.2, 25.0, 24.9, 22.8, 19.9, 14.4, 14.3. IR (ATR): νmax [cm⁻¹] = 2990 (w), 2922 (s), 2853 (m) (C sp³), 1724 (s) (C=O), 1378 (s) (CH₃-def.), 1196 (s), 1171 (s), 1109 (m) (C-O-C). HRMS (ESI): m/z [M+Na]⁺ calcd for C₄₁H₇₄O₈Na⁺ 717.5276; found: 717.5278.
(+)-Cryptocaryol A (22)

Compound 21 (17.5 mg, 25.2 µmol) was dissolved in 0.2 ml THF and then added to a 1:1:1 mixture of TFA/H₂O/THF at 0°C. The reaction mixture was stirred for 30 min before quenching with saturated aqueous sodium bicarbonate solution. The aqueous phase was extracted five times with each 2 ml ethylacetate. The organic phase was washed with saturated aqueous sodium chloride solution, dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was dissolved in 3ml dichloromethane and 0.6 mg (0.1 eq) p-toluolsulfonic acid monohydrate were added. The reaction was stirred for 45 min before saturated aqueous sodium bicarbonate solution was added. The aqueous phase was extracted five times with each 3 ml ethylacetate. The organic phase was washed with saturated aqueous sodium chloride solution, dried over sodium sulphate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (CH₂Cl₂/MeOH 99:1 → 97:3) yielding 4 mg (7.6 µmol, 25%) of the desired product 22.

**TLC:** Rₛ = 0.34 (DCM/MeOH 94:6) [CAM]. ¹H NMR (CD₃OD, 600 MHz) δ [ppm] = 7.05 (ddd, J = 9.8, 6.0, 2.5 Hz, 1H), 5.98 (ddd, J = 9.7, 2.6, 1.0 Hz, 1H), 4.75 - 4.69 (m, 1H), 4.13 - 4.06 (m, 1H), 4.06 - 3.96 (m, 3H), 3.84 - 3.78 (m, 1H), 2.46 (ddddd, J = 18.6, 5.8, 4.2, 1.2 Hz, 1H), 2.37 (ddt, J = 18.6, 11.6, 2.5 Hz, 1H), 1.95 (ddddd, J = 14.5, 9.7, 2.6 Hz, 1H), 1.72 - 1.55 (m, 7H), 1.53 - 1.50 (m, 2H), 1.48 - 1.41 (m, 2H), 1.36 - 1.25 (m, 26H), 0.90 (t, J = 7.0 Hz, 3H). ¹³C NMR (151 MHz, CD₃OD) δ [ppm] = 166.9, 148.5, 121.4, 76.6, 70.2, 70.0, 69.2, 68.3, 66.7, 45.9, 45.9, 45.7, 45.3, 43.9, 39.2, 33.1, 30.9, 30.8, 30.7, 30.4, 26.8, 23.7, 14.4. IR (ATR): νₘₐₓ [cm⁻¹] = 3361 (br) (OH), 2916 (s), 2849 (m) (C sp³), 1720 (m) (C=O), 1466 (s), 1324 (s), 1140 (m), 1091 (m), 843 (s). HRMS (ESI): m/z [M+Na]+ calcd for C₃₀H₅₆O₇Na⁺ 551.3918; found: 551.3918.
Comparison of $^1$H-NMR data of *Cryptocaryol A*

![Chemical Structure of Cryptocaryol A](image)

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Comparison of $^{13}$C-NMR data of *Cryptocaryol A*

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1H NMR (CDCl3, 400 MHz) - d.r. 90:10
$^{13}$C NMR (CDCl$_3$, 101 MHz)

![NMR spectrum of a compound](image)

- $142.4$, $140.8$, $128.5$, $128.5$, $123.9$
- $114.6$
- $70.9$, $69.2$
- $42.4$, $37.3$, $35.9$, $27.5$

(ppm)
$^{1}H$ NMR (CDCl$_3$, 400 MHz)
$^1$H NMR (CDCl$_3$, 600 MHz)

12a/13a
13C NMR (CDCl₃, 101 MHz)

![Chemical Structure](image)

**10a**

**Graphical Data**

- **Chemical Shifts**:
  - 142.5, 141.1, 128.5, 128.4, 125.9, -114.2, -100.8, 70.3, 69.0, 68.3, 66.8, 42.9, 36.0, 35.3, 27.4, 24.8

**ppm Range**

- 210 to -10
13C NMR (CDCl3, 101 MHz)

12b

Chemical shifts (ppm): 142.5, 141.1, 128.5, 128.4, 125.9, -114.2, -98.8, 70.3, 69.6, 68.9, 43.0, 43.0, 37.3, 36.0, 35.9, 30.3, 27.0.
1H NMR (CDCl₃, 400 MHz) - d.r. 83.17

14b

CDCl₃

(ppm)
13C NMR (CDCl₃, 151 MHz)

[Diagram of a chemical structure labeled 17b]

(ppm)
1H NMR (CDCl₃, 400 MHz) - d.r. 83:17

![NMR Spectrogram](image)
13C NMR (CDCl₃, 101 MHz) - d.r. 83:17

14d
$^{1}H$ NMR (CDCl$_3$, 400 MHz)
13C NMR (CDCl3, 101 MHz)

17d
$^{13}$C NMR (CDCl$_3$, 101 MHz)

Chemical shifts (ppm):
- 202.6
- 142.6
- 128.6
- 128.4
- 125.9
- 100.5
- 100.3
- 74.0
- 68.6
- 66.6
- 63.0
- 56.6
- 38.8
- 36.0
- 35.6
- 30.3
- 27.4
- 24.8
- 23.9

Compound 10
$^{13}$C NMR (CDCl$_3$, 101 MHz)

[Chemical structure image]

(CDCl$_3$, 101 MHz)
1H NMR (CDCl₃, 400 MHz)

[Chemical structure image]

(CDCl₃)
13C NMR (CDCl₃, 101 MHz)

[Diagram of a molecular structure with labels for chemical shifts]
$1H$ NMR (CDCl$_3$, 400 MHz)

![NMR Spectrum](image)

Chemical shifts are marked with corresponding peaks.
13C NMR (CDCl₃, 101 MHz)

[Graph showing a 13C NMR spectrum with peaks labeled at various ppm values.]
1H-NMR (CDCl3, 600 MHz) - d.r. 89:11

C1b
$^{13}$C NMR (CDCl$_3$, 151 MHz)

![Chemical Structure](image)

(ppm)
1H NMR (CDCl₃, 400 MHz) - d.r. 90:10

![NMR Spectrum](image_url)
$^{13}$C NMR (CDCl$_3$, 101 MHz) - d.r. 90:10
1H NMR (CDCl3, 400 MHz) - d.r. 90:10
$^{13}$C NMR (CDCl$_3$, 151 MHz) - d.r. 90:10
1H-NMR (CDCl₃, 400 MHz) - d.r. 91:9

C₂c
13C-NMR (CDCl₃, 400 MHz) - d.r. 91:9

C₂c
$^{13}$C-NMR (CDCl$_3$, 101 MHz)

C2d

Chemical shifts (ppm):
- 139.0
- 115.5
- 100.3
- 98.7
- 70.4
- 66.8
- 65.5
- 63.0

Field strength:
- 42.4
- 38.8
- 38.6
- 38.4
- 38.1
- 30.4
- 29.8
- 29.7
- 29.5
- 25.5
- 24.9
- 22.8
- 19.9
- 14.3

(ppm)
$^{1}H$-NMR (CDCl$_{3}$, 400 MHz) - d.r. 92:8
$^{13}$C-NMR (CDCl3, 101 MHz) - d.r. 92:8

C2
$^{1}H$-NMR (CDCl$_3$, 600 MHz) - d.r. 98:2
$^{13}$C-NMR (CDCl$_3$, 101 MHz)

166.5, -146.2, -121.2, 100.5 (Ar), 100.3 (Ar), 98.5

CDCl$_3$

21
13C-NMR (CD3OD, 151 MHz)

(+)-Cryptocaryol A

CD3OD

45.9 45.7 45.3 39.9 39.2 33.1 30.9 30.7 30.4 26.8 23.7

166.9 148.5 121.4 76.6 70.2 70.0 69.2 68.3 66.7 14.4

(ppm)
Area Percent Report

Signal 1: MWD1 F, Sig=220,36 Ref=360,100

| Peak RetTime Type Width Area Height Area % |
|------------------------------------------|--------------------------------------|
| 1 | 7.584 | 0.3043 | 2.2548e6 | 1172.6266 | 64.7882 |
| 2 | 8.575 | 0.4339 | 2.7736e5 | 1033.1373 | 55.2118 |

Totals: 5.0341e4 2205.76179

*** End of Report ***
Signal 1: MW11 F, Sig-220,16 Ref-350,100

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Totals: 9664.04297 613.96179
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISIDs

Signal 1: MW01 B, Stg=254.16 Ref=360.100

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Totals : 1068.90228 66.83522