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

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Supporting Information Table of Contents

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. di*iso*propylamine 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 *β*-hydroxy ketone.

Procedure B – *anti*-selective reduction of *β*-hydroxy ketone to 1,3-diol

Under nitrogen atmosphere 5.00 eq. tetramethylammonium triacetoxyborohydride were dissolved in acetonitrile and acetic acid (4:1, 0.5 M) and cooled to -40 °C. *β*-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

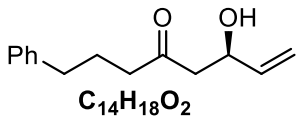
To the 1,3-diol 5 mol% *p*-toluenesulfonic acid monohydrate and an excess of 2,2-dimethoxypropane (8eq.) was added. The reaction was heated to 45 °C on a rotary evaporator and the pressure held at 330 mbar for 30 - 60 min. Saturated aqueous sodium bicarbonate was added and the mixture was extracted with 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)

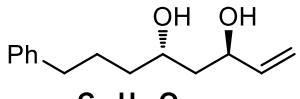


$C_{14}H_{18}O_2$
218.29 g/mol

Following procedure **A**, hydrocinnamaldehyde (1.64 g, 12.2 mmol) was converted with building block (*R*)-**1**, di*iso*propylamine, *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: R_f = 0.27 (PE/EtOAc 70:30) [$KMnO_4$] [CAM]. **$[\alpha]_D^{20}$** = +14.2 (*c* = 1.73, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$): 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). **^{13}C NMR** (151 MHz, $CDCl_3$): 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): ν_{max} [cm^{-1}] = 3443 (b) (OH), 3078 (w) ($C_{sp2}H$), 3060 (w) ($C_{sp2}H$), 3024 (w) ($C_{sp2}H$), 2959 (m) ($C_{sp3}H$), 2871 (m) ($C_{sp3}H$), 1687 (s) (C=O), 1454 (m), 922 (s), 756 (s), 700 (s). **LRMS** (EI): *m/z* (%) 200 (2) [M^+-H_2O], 162 (12), 147 (3), 104 (100), 91 (24), 77 (4). **HRMS** (ESI): *m/z* [M+Na]$^+$ calcd for $C_{14}H_{18}O_2Na^+$ 241.1199; found: 241.1205.

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



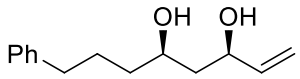
$C_{14}H_{20}O_2$
220.31 g/mol

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: R_f = 0.15 (PE/EtOAc 70:30) [$KMnO_4$] [CAM]. **^{1}H NMR** (400 MHz, $CDCl_3$, 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). **^{13}C NMR**

(101 MHz, $CDCl_3$, 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): ν_{max} [cm^{-1}] = 3339 (b) (OH), 3084 (vw) ($C_{sp2}H$), 3062 (vw) ($C_{sp2}H$), 3026 (w) ($C_{sp2}H$), 2936 (m) ($C_{sp3}H$), 2859 (m) ($C_{sp3}H$), 1452 (m), 920 (m), 747 (m), 697 (s). **LRMS** (EI): *m/z* (%) 202 (2) [M^+-H_2O], 184 (4) [M^+-$2H_2O$], 147 (22), 118 (21), 104 (100), 91 (50), 77 (6). **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{14}H_{20}O_2Na^+$ 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.)].

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

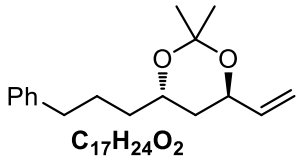


$C_{14}H_{20}O_2$
220.31 g/mol

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]. **^{1}H NMR** (600 MHz, $CDCl_3$): 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). **^{13}C NMR** (151 MHz, $CDCl_3$): 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): ν_{max} [cm^{-1}] = 3356 (b) (OH), 2938 (s) ($C_{sp3}H$), 2859 (s) ($C_{sp3}H$), 1603 (vs) (C=O), 1496 - 1320 (m), 991 (s), 924 (vs). **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{14}H_{20}O_2Na^+$ 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)].

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

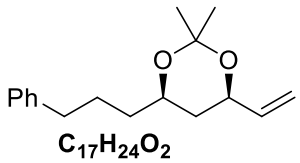


$C_{17}H_{24}O_2$
260.37 g/mol

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) [$KMnO_4$]. **^{1}H NMR** (400 MHz, $CDCl_3$, major diastereomer): δ [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). **^{13}C NMR** (101 MHz, $CDCl_3$, major diastereomer): δ [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): ν_{max} [cm^{-1}] = 3084 (vw) ($C_{sp2}H$), 3063 (vw) ($C_{sp2}H$), 3026 (w) ($C_{sp2}H$), 2986 (m) ($C_{sp3}H$), 2937 (m) ($C_{sp3}H$), 2861 (m) ($C_{sp3}H$), 1453 (m), 1378 (m), 1223 (s), 921 (m), 747 (m), 698 (s). **LRMS** (EI): *m/z* (%) 245 (20) [M^+-CH_3], 202 (10), 184 (12), 147 (64), 131 (77), 118 (33), 104 (100), 91 (88), 77 (8). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{17}H_{24}O_2Na^+$ 283.1669; found: 283.1670.

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



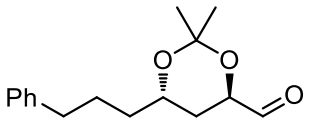
$C_{17}H_{24}O_2$
260.37 g/mol

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]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [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). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [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): ν_{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 $C_{17}H_{24}O_2Na^+$ 283.1669; found: 283.1670.

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

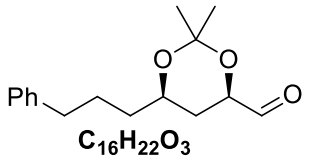


$C_{16}H_{22}O_3$
262.34 g/mol

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) [$KMnO_4$]. **[α]$_D^{20}$** = +36.7 (*c* = 0.85, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$, major diastereomer): δ [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): δ [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): ν_{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 $C_{16}H_{22}O_3Na^+$ 285.1461; found: 285.1459.

(4*R*,6*R*)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxane-4-carbaldehyde (9)

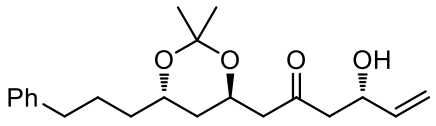


$C_{16}H_{22}O_3$
262.34 g/mol

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]. **[α]$_D^{20}$** = +25.7 (*c* = 1.81, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$): δ [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). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [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): ν_{max} [cm^{-1}] = 3084 (b) ($C_{sp2}H$), 2938 (s) ($C_{sp3}H$), 2816 (s) ($C_{sp3}H$), 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^+-CH_3], 204 (10), 187 (15), 147 (14), 131 (65), 104 (41), 91 (100), 59 (29). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{16}H_{22}O_3Na^+$ 285.1461; found: 285.1459.

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



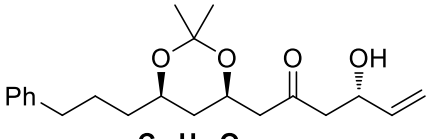
$C_{21}H_{30}O_4$
346.46 g/mol

Following procedure **A,** *(S)*-**1** was treated with *n*-butyllithium and di*iso*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) [$KMnO_4$] [CAM]. **[α]$_D^{20}$** = +7.9 (*c* = 2.41, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$): δ [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). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [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): ν_{max} [cm^{-1}] = 3457 (b) (OH), 3084 (vw) ($C_{sp2}H$), 3062 (vw) ($C_{sp2}H$), 3025 (w) ($C_{sp2}H$), 2986 (m) ($C_{sp3}H$), 2937 (m) ($C_{sp3}H$), 2860 (m) ($C_{sp2}H$), 1710 (m) (C=O), 1454 (m), 1379 (m), 1222 (s), 925 (m), 748 (m), 699 (s). **LRMS**

(EI): *m/z* (%) 275 (6) [M^+-C_4H_6OH], 197 (8), 157 (24), 131 (38), 104 (100), 91 (72). **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{21}H_{30}O_4Na^+$ 369.2036; found: 369.2018.

(*S*)-1-((4*R*,6*R*)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)-4-hydroxyhex-5-en-2-one (12a/13a)

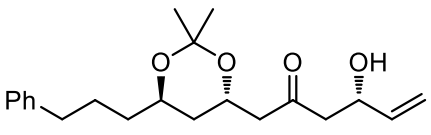


$C_{21}H_{30}O_4$
346.46 g/mol

Following procedure **A,** *(S)*-**1** was treated with *n*-butyllithium and di*iso*propylamine 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]. **$[\alpha]_D^{20}$** = -6.2 (*c* = 3.0, $CHCl_3$). **^{1}H 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). **^{13}C 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) ($C_{sp3}H$), 2934 (s) ($C_{sp3}H$), 2863 (s) ($C_{sp3}H$), 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 $C_{21}H_{30}O_4Na^+$ 369.2036; found: 369.2036.

(*R*)-1-((4*R*,6*S*)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)-4-hydroxyhex-5-en-2-one (14a/15a)

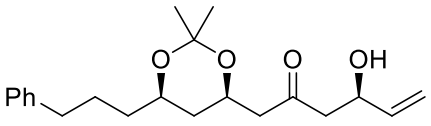


$C_{21}H_{30}O_4$
346.46 g/mol

Following procedure **A,** *(R)*-**1** was treated with *n*-butyllithium and di*iso*propylamine 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: R_f = 0.27 (PE/EtOAc 70:30) [$KMnO_4$] [CAM]. **[α]$_D^{20}$** = +35.0 (*c* = 2.18, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$): 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). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [ppm] = 209.4, 142.5, 139.2, 128.5, 128.4, 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): ν_{max} [cm^{-1}] = 3453 (b) (OH), 3084 (vw) ($C_{sp2}H$), 3062 (vw) ($C_{sp2}H$), 3026 (w) ($C_{sp2}H$), 2986 (m) ($C_{sp3}H$), 2936 (m) ($C_{sp3}H$), 2860 (m) ($C_{sp3}H$), 1709 (m) (C=O), 1454 (m), 1379 (m), 1222 (s), 925 (m), 748 (m), 699 (s). **LRMS** (EI): *m/z* (%) 275 (3) [M^+-C_4H_6OH], 197 (4), 157 (10), 131 (13), 104 (100), 91 (57), 77 (7). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{21}H_{30}O_4Na^+$ 369.2036; found: 369.2036.

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



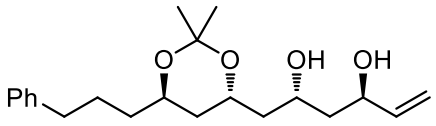
$C_{21}H_{30}O_4$
346.46 g/mol

Following procedure **A,** *(R)*-**1** was treated with *n*-butyllithium and di*iso*propylamine 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: R_f = 0.20 (PE/EtOAc 80:20) [UV] [CAM]. **[α]$_D^{20}$** = +7.9 (*c* = 2.02, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) 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). **^{13}C NMR** (101

MHz, $CDCl_3$) 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): ν_{max} [cm^{-1}] = 3458 (b) (OH), 2991 (s) ($C_{sp3}H$), 2940 (s) ($C_{sp3}H$), 2863 (s) ($C_{sp3}H$), 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 $C_{21}H_{30}O_4Na^+$ 369.2036; found: 369.2028.

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

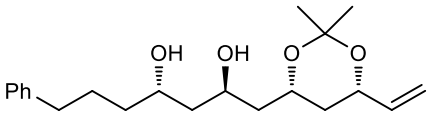


$C_{21}H_{32}O_4$
348.48 g/mol

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: R_f = 0.22 (PE/EtOAc 50:50) [$KMnO_4$] [CAM]. **^{1}H NMR** (400 MHz, $CDCl_3$): 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). **^{13}C NMR** (101 MHz, $CDCl_3$): 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): ν_{max} [cm^{-1}] = 3424 (b) (OH), 3085 (vw) ($C_{sp2}H$), 3063 (vw) ($C_{sp2}H$), 3026 (vw) ($C_{sp2}H$), 2986 (w) ($C_{sp3}H$), 2939 (m) ($C_{sp3}H$), 2861 (w) ($C_{sp3}H$), 1453 (w), 1381 (m), 1223 (m), 907 (m), 728 (s), 698 (m). **LRMS** (EI): *m/z* (%) 333 (6) [M^+-CH_3], 183 (21), 157 (22), 131 (67), 104 (95), 91 (100), 59 (24). **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{21}H_{32}O_4Na^+$ 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')

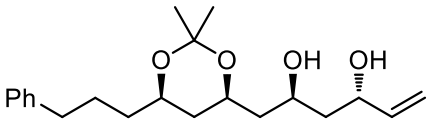


$C_{21}H_{32}O_4$
348.48 g/mol

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: R_f = 0.12 (PE/EtOAc 70:30) [CAM]. **^{1}H NMR** (400 MHz, $CDCl_3$): 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). **^{13}C NMR** (101 MHz, $CDCl_3$): 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): ν_{max} [cm^{-1}] = 3386 (b) (OH), 3026 (vw) ($C_{sp2}H$), 2985 (w) ($C_{sp3}H$), 2937 (w) ($C_{sp3}H$), 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 $C_{21}H_{32}O_4Na^+$ 371.2193; found: 371.2193.

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



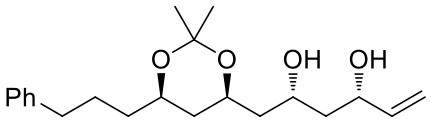
$C_{21}H_{32}O_4$
348.48 g/mol

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: R_f = 0.08 (PE/EtOAc 70:30) [$KMnO_4$] [CAM]. **^{1}H NMR** (400 MHz, $CDCl_3$): 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),

3.89 – 3.79 (m, 2H), 3.14 (bs, 1H), 2.61 (t, *J* = 7.5 Hz, 2H), 1.79 – 1.40 (m, 9H), 1.46 (s, 3H), 1.38 (s, 3H), 1.27-1.17 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [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. **IR** (ATR): ν_{max} [cm^{-1}] = 3450 (m) (OH), 3387 (m) (OH), 3089 (vw) ($C_{sp2}H$), 3061 (vw) ($C_{sp2}H$), 3021 (w) ($C_{sp2}H$), 2992 (w) ($C_{sp3}H$), 2932 (m) ($C_{sp3}H$), 2904 (m) ($C_{sp3}H$), 2868 (m), 1461 (m), 1377 (m), 1229 (m), 908 (s), 749 (m), 699 (m). **LRMS** (EI): *m/z* (%) 333 (8) [M^+-CH_3], 207 (12), 183 (24), 157 (24), 131 (59), 104 (100), 91 (95), 59 (23). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{21}H_{32}O_4Na^+$ 371.2193; found: 371.2192.

(2*R*,4*S*)-1-((4*S*,6*R*)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)hex-5-ene-2,4-diol 13c)

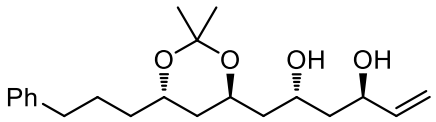


$C_{21}H_{32}O_4$
348.48 g/mol

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 → 70:30) **13c** was isolated as a yellow oil (50.9 mg, 0.146 mmol, 85%).

TLC: R_f = 0.09 (PE/EtOAc 80:20) [UV] [CAM]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.30 – 7.25 (m, 2H), 7.21 – 7.15 (m, 3H), 5.87 (ddd, *J* = 17.2, 10.5, 5.8 Hz, 1H), 5.26 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.09 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.43 – 4.36 (m, 1H), 4.24 – 4.14 (m, 2H), 3.89 – 3.80 (m, 1H), 3.75 – 3.38 (m, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 1.80 -1.51 (m, 8H), 1.48 – 1.40 (m, 4H), 1.39 (s, 3H), 1.37 – 1.30 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ [ppm] = 142.5, 140.9, 128.6, 128.4, 125.9, 114.4, 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. **IR** (ATR): ν_{max} [cm^{-1}] = 3392 (b) (OH), 2990 (s) ($C_{sp3}H$), 2941 (s) ($C_{sp3}H$), 1496 (s), 1380 (s), 1265 (s), 1200 (s), 1096 (m), 992 (s), 924 (s), 748 (m), 699 (m). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{21}H_{32}O_4Na^+$ 371.2193; found: 371.2193.

(2*R*,4*R*)-1-((4*S*,6*S*)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)hex-5-ene-2,4-diol (14b)

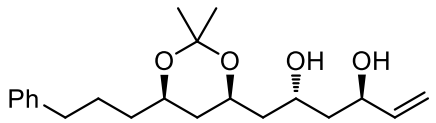


$C_{21}H_{32}O_4$
348.48 g/mol

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: R_f = 0.12 (PE/EtOAc 70:30) [$KMnO_4$] [CAM]. **^{1}H NMR** (400 MHz, $CDCl_3$, 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). **^{13}C NMR** (101 MHz, $CDCl_3$, 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): ν_{max} [cm^{-1}] = 3387 (b) (OH), 3085 (vw) ($C_{sp2}H$), 3062 (vw) ($C_{sp2}H$), 3026 (vw) ($C_{sp2}H$), 2985 (m) ($C_{sp3}H$), 2936 (m) ($C_{sp3}H$), 2859 (m) ($C_{sp3}H$), 1453 (m), 1379 (m), 1222 (s), 923 (m), 748 (m), 698 (m). **LRMS** (EI): *m/z* (%) 333 (8) [M^+-CH_3], 207 (12), 183 (18), 157 (16), 131 (52), 104 (100), 91 (99), 59 (20). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{21}H_{32}O_4Na^+$ 371.2193; found: 371.2178.

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

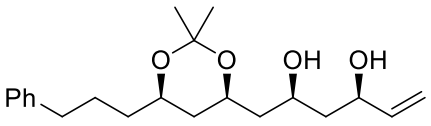


$C_{21}H_{32}O_4$
348.48 g/mol

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): 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 – 4.41 (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): δ [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): ν_{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 $C_{21}H_{32}O_4Na^+$ 371.2193; found: 371.2200.

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



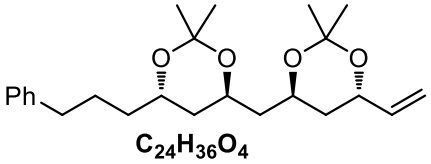
$C_{21}H_{32}O_4$
348.48 g/mol

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) δ [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 (dddd, *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, $CDCl_3$) δ [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): ν_{max} [cm^{-1}] = 3385 (b) (OH), 2991 (s) ($C_{sp3}H$), 2940 (s) ($C_{sp3}H$), 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),

749 (m), 700 (m). **LRMS** (EI): *m/z* (%): 333 (8) [M^+-CH_3], 281 (8), 207 (26), 131 (49), 104 (100), 91 (91). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{21}H_{32}O_4Na^+$ 371.2193; found: 371.2193.

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

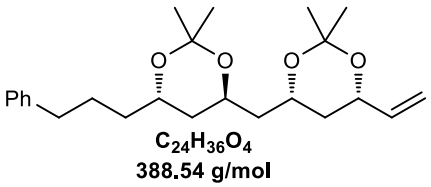


$C_{24}H_{36}O_4$
388.54 g/mol

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: R_f = 0.66 (PE/EtOAc 70:30) [$KMnO_4$]. **^{1}H NMR** (400 MHz, $CDCl_3$): 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). **^{13}C NMR** (101 MHz, $CDCl_3$): 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): ν_{max} [cm^{-1}] = 3085 (vw) ($C_{sp2}H$), 3063 (vw) ($C_{sp2}H$), 3026 (vw) ($C_{sp2}H$), 2987 (m) ($C_{sp3}H$), 2937 (m) ($C_{sp3}H$), 2860 (w) ($C_{sp3}H$), 1454 (w), 1378 (m), 1222 (m), 909 (m), 730 (s), 698 (m). **LRMS** (EI): *m/z* (%) 373 (20) [M^+-CH_3], 272 (12), 183 (30), 157 (32), 131 (100), 104 (76), 91 (96), 83 (35), 59 (44). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{24}H_{36}O_4Na^+$ 411.2506; found: 411.2506.

(4*S*,6*S*)-4-(((4*R*,6*S*)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-6-vinyl-1,3-dioxane (11d)

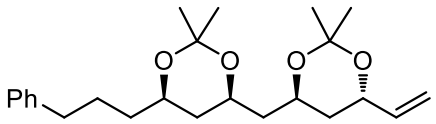


$C_{24}H_{36}O_4$
388.54 g/mol

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: R_f = 0.88 (PE/EtOAc 80:20) [CAM]. **^{1}H NMR** (600 MHz, $CDCl_3$): 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 (dddd, *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). **^{13}C NMR** (151 MHz, $CDCl_3$): 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): ν_{max} [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^+-CH_3], 183 (9), 157 (13), 131 (44), 104 (45), 91 (100), 59 (77). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{24}H_{36}O_4Na^+$ 411.2506; found: 411.2505.

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



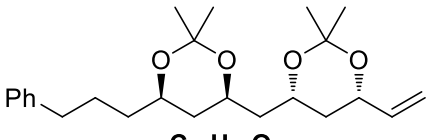
$C_{24}H_{36}O_4$
388.54 g/mol

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: R_f = 0.51 (PE/EtOAc 90:10) [$KMnO_4$]. **^{1}H NMR** (400 MHz, $CDCl_3$): 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). **^{13}C NMR** (101 MHz, $CDCl_3$): 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): ν_{max} [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

(m), 699 (s). **LRMS** (EI): *m/z* (%) 373 (28) [M^+-CH_3], 272 (14), 183 (30), 157 (36), 131 (95), 104 (75), 91 (100), 83 (41), 59 (43). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{24}H_{36}O_4Na^+$ 411.2506; found: 411.2505.

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

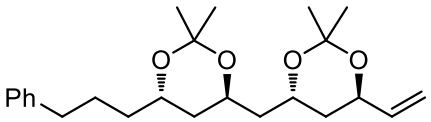


$C_{24}H_{36}O_4$
388.54 g/mol

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]. **^{1}H 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 (dddd, *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 (dddd, *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). **^{13}C 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) ($C_{sp3}H$), 2941 (s) ($C_{sp3}H$), 2914 (s) ($C_{sp3}H$), 2862 (s) ($C_{sp3}H$), 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.

(4*S*,6*R*)-4-(((4*R*,6*S*)-2,2-dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-6-vinyl-1,3-dioxane (14d)

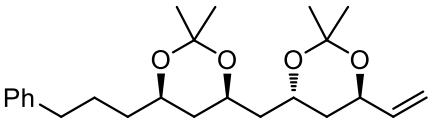


$C_{24}H_{36}O_4$
388.54 g/mol

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): δ [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): δ [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, 25.0, 24.8. **IR** (ATR): ν_{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 $C_{24}H_{36}O_4Na^+$ 411.2506; found: 411.2509.

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

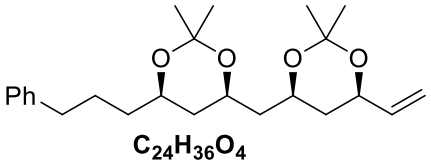


$C_{24}H_{36}O_4$
388.54 g/mol

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) [$KMnO_4$]. **^{1}H NMR** (400 MHz, $CDCl_3$, major diastereomer): δ [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, $CDCl_3$, major diastereomer): δ [ppm] = 142.6, 138.9, 128.6, 128.4, 125.8, 115.2, 100.6, 98.6, 69.2, 68.2, 65.2, 62.4, 42.5, 38.1, 37.6, 36.2, 36.0, 30.5, 27.1, 25.3, 24.7, 20.0. **IR** (ATR): ν_{max} [cm^{-1}] = 3084 (vw) ($C_{sp2}H$), 3063 (vw) ($C_{sp2}H$), 3026 (wv) ($C_{sp2}H$), 2988 (m) ($C_{sp3}H$), 2939 (m) ($C_{sp3}H$), 2861 (m) ($C_{sp3}H$), 1454 (m), 1378 (s), 1223 (m), 925 (m), 748 (m), 698 (s). **LRMS** (EI): *m/z* (%) 373 (28) [M^+-CH_3], 272 (9), 183 (38), 157 (39), 131 (92), 104 (70), 91 (100), 83 (40), 59 (42). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{24}H_{36}O_4Na^+$ 411.2506; found: 411.2502.

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



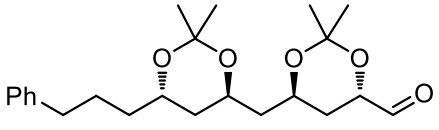
$C_{24}H_{36}O_4$
388.54 g/mol

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, $CDCl_3$) δ [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 (dddd, *J* = 11.3, 5.5, 2.6, 1.3 Hz, 1H), 4.10 – 3.95 (m, 2H), 3.82 (dddd, *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, $CDCl_3$) δ [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, b36.7, 36.2, 36.0, 30.4, 30.4, 27.1, 20.0, 20.0. **IR** (ATR): ν_{max} [cm^{-1}] = 2990 (s) ($C_{sp3}H$), 2947 (s) ($C_{sp3}H$), 2862 (s) ($C_{sp3}H$), 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^+-CH_3], 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 $C_{24}H_{36}O_4Na^+$ 411.2506; found: 411.2507.

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

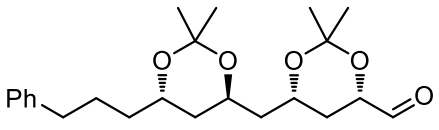


$C_{23}H_{34}O_5$
390.51 g/mol

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) [$KMnO_4$]. **$[\alpha]_D^{20}$** = -4.0 (*c* = 1.36, $CHCl_3$). **^{1}H 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). **^{13}C 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): ν_{max} [cm^{-1}] = 3085 (vw) ($C_{sp2}H$), 3062 (vw) ($C_{sp2}H$), 3025 (vw) ($C_{sp2}H$), 2986 (m) ($C_{sp3}H$), 2935 (m) ($C_{sp3}H$), 2859 (w) ($C_{sp3}H$), 1734 (m) (C=O), 1454 (m), 1378 (m), 1222 (m), 748 (s), 699 (m). **LRMS** (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.

(4*S*,6*S*)-6-(((4*R*,6*S*)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-1,3-dioxane-4-carbaldehyde (11)

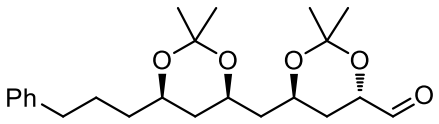


$C_{23}H_{34}O_5$
390.51 g/mol

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): ν_{max} [cm^{-1}] = 3085 (vw) ($C_{sp2}H$), 3062 (vw) ($C_{sp2}H$), 3026 (vw) ($C_{sp2}H$), 2987 (m) ($C_{sp3}H$), 2937 (m) ($C_{sp3}H$), 2860 (w) ($C_{sp3}H$), 1738 (m) (C=O), 1454 (m), 1379 (s), 1223 (s), 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]$^+$ calcd for $C_{23}H_{34}O_5Na^+$ 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)



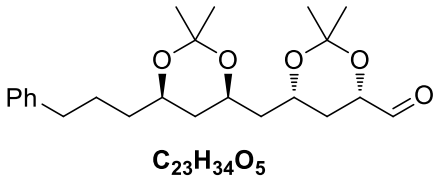
$C_{23}H_{34}O_5$
390.51 g/mol

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): ν_{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^+-CH_3], 221 (8), 183 (22), 157 (22), 143 (44), 131 (73), 104 (86), 91 (100), 59 (45). **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{23}H_{34}O_5Na^+$ 413.2298; found: 413.2298.

(4*S*,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 (13)

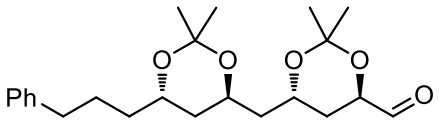


$C_{23}H_{34}O_5$
390.51 g/mol

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: R_f = 0.26 (PE/EtOAc 90:10) [UV] [CAM]. **$[\alpha]_D^{20}$** = -17.6 (*c* = 2.09, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) 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). **^{13}C NMR** (101 MHz, $CDCl_3$) 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): ν_{max} [cm^{-1}] = 2990 (s) ($C_{sp3}H$), 2940 (s) ($C_{sp3}H$), 2914 (s) ($C_{sp3}H$), 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^+-CH_3], 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 $C_{23}H_{34}O_5Na^+$ 413.2298; found: 413.2300.

(4*R*,6*S*)-6-(((4*R*,6*S*)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-1,3-dioxane-4-carbaldehyde (14)

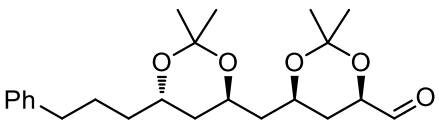


$C_{23}H_{34}O_5$
390.51 g/mol

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: R_f = 0.38 (PE/EtOAc 70:30) [$KMnO_4$]. **[α]$_D^{20}$** = +42.9 (*c* = 1.47, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$): 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). **^{13}C NMR** (101 MHz, $CDCl_3$): 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): ν_{max} [cm^{-1}] = 3085 (vw) ($C_{sp2}H$), 3062 (vw) ($C_{sp2}H$), 3026 (vw) ($C_{sp2}H$), 2986 (m) ($C_{sp3}H$), 2937 (m) ($C_{sp3}H$), 2860 (w) ($C_{sp3}H$), 1734 (m) (C=O), 1454 (m), 1380 (m), 1223 (s), 748 (m), 699 (s). **LRMS** (EI): *m/z* (%) 375 (18) [M^+-CH_3], 183 (24), 157 (25), 143 (47), 131 (84), 104 (89), 91 (100), 59 (45). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{23}H_{34}O_5Na^+$ 413.2298; found: 413.2289.

(4*R*,6*R*)-6-(((4*R*,6*S*)-2,2-Dimethyl-6-(3-phenylpropyl)-1,3-dioxan-4-yl)methyl)-2,2-dimethyl-1,3-dioxane-4-carbaldehyde (15)



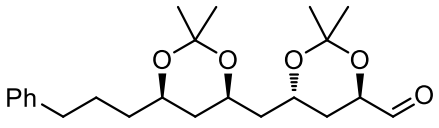
$C_{23}H_{34}O_5$
390.51 g/mol

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, 82.6µmol) 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) [$KMnO_4$]. **[α]$_D^{20}$** = +34.8 (*c* = 1.45, $CHCl_3$). **^{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 – 7.15 (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, $CDCl_3$): δ [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): ν_{max} [cm^{-1}] = 3085 (vw) ($C_{sp2}H$), 3061 (vw) ($C_{sp2}H$), 3026 (vw) ($C_{sp2}H$), 2988 (m) ($C_{sp3}H$), 2937 (m) ($C_{sp3}H$), 2861 (w) ($C_{sp3}H$), 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 $C_{23}H_{34}O_5Na^+$ 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)



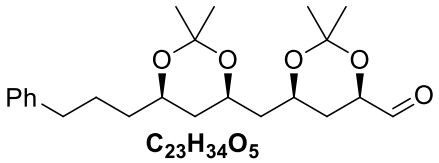
$C_{23}H_{34}O_5$
390.51 g/mol

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) [$KMnO_4$]. **[α]$_D^{20}$** = +13.0 (*c* = 1.77, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$): δ [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, $CDCl_3$): δ [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): ν_{max}

[cm^{-1}] = 3085 (vw) ($C_{sp2}H$), 3062 (vw) ($C_{sp2}H$), 3026 (vw) ($C_{sp2}H$), 2990 (m) ($C_{sp3}H$), 2938 (m) ($C_{sp3}H$), 2861 (w) ($C_{sp3}H$), 1735 (m) (C=O), 1454 (m), 1379 (s), 1223 (s), 748 (m), 699 (s). **LRMS** (EI): *m/z* (%) 375 (22) [M^+-CH_3], 221 (8), 183 (25), 157 (24), 143 (52), 131 (86), 104 (88), 91 (100), 59 (47). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{23}H_{34}O_5Na^+$ 413.2298; found: 413.2293.

(4*R*,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 (17)

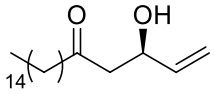


$C_{23}H_{34}O_5$
390.51 g/mol

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_f = 0.15 (PE/EtOAc 90:10) [UV] [CAM]. **$[\alpha]_D^{20}$** = +22.3 (*c* = 2.22, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) 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 (dddd, *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). **^{13}C NMR** (101 MHz, $CDCl_3$) 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_{max} [cm^{-1}] = 2991 (m) ($C_{sp3}H$), 2940 (m) ($C_{sp3}H$), 2862 (s) ($C_{sp3}H$), 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^+-CH_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]$^+$ calcd for $C_{23}H_{34}O_5Na^+$ 413.2298; found: 413.2298.

***(R)*-3-Hydroxyicos-1-en-5-one (C1a)**

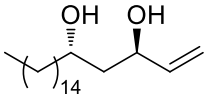


$C_{20}H_{38}O_2$
310.51 g/mol

(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]. **$[\alpha]_D^{20}$** = + 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): ν_{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_3H_6O], 85 (18), 71 (48), 58 (100). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{20}H_{38}O_2Na^+$ 333.2764; found: 333.2758.

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



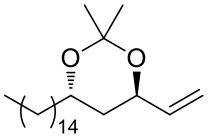
$C_{20}H_{40}O_2$
312.53 g/mol

β-Hydroxyketone (C**1a**, 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]. **$[\alpha]_D^{20}$** = - 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

(dt, *J* = 17.2, 1.5 Hz, 1H), 5.14 (dt, *J* = 10.5, 1.5 Hz, 1H), 4.50 - 4.44 (m, 1H), 3.95 - 3.90 (m, 1H), 2.36 (bs, 2H), 1.75 - 1.64 (m, 2H), 1.57 - 1.39 (m, 4H), 1.33 - 1.22 (m, 24H), 0.88 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, major diastereomer): δ [ppm] = 140.9, 114.5, 70.9, 69.5, 42.4, 37.8, 32.0, 29.8, 29.8, 29.8, 29.8, 29.8, 29.5, 25.8, 22.8, 14.3. **IR** (ATR): ν_{max} [cm^{-1}] = 3340 (sb) (OH), 2915 (vs), 2848 (s) (C sp^3), 1464 (m) (CH_2-def.), 1404 (m) (CH_3-def.), 990 (m), 930 (m) (=C-H def.). **LRMS** (EI): *m/z* (%):311 (1) [M^+-H], 71 (30), 57 (85). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{20}H_{40}O_2Na^+$ 335.2921; found: 335.2921.

(4*S*,6*R*)-2,2-Dimethyl-4-pentadecyl-6-vinyl-1,3-dioxane (C1d)

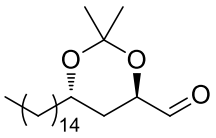


$C_{23}H_{44}O_2$
352.59 g/mol

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: R_f = 0.8 (PE/EtOAc 90:10) [CAM]. **$[\alpha]_D^{20}$ = +** 32.3 (c= 3.5, dr 90:10, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$ 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). **^{13}C NMR** (101 MHz, $CDCl_3$, 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, 29.8, 29.7, 29.5, 25.6, 25.5, 24.9, 22.8, 14.3. **IR** (ATR): ν_{max} [cm^{-1}] = 2922 (vs), 2853 (s) (C sp^3), 1465 (m) (CH_2-def.), 1378 (m) (CH_3-def.), 1223 (s) (C-O-C), 987 (m), 920 (m) (=C-H def.). **LRMS** (EI): *m/z* (%):337.3 (100) [M^+-CH_3], 83.1 (73), 59.1 (63). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{23}H_{44}O_2Na^+$ 375.3234; found: 375.3235.

(4*R*,6*S*)-2,2-Dimethyl-6-pentadecyl-1,3-dioxane-4-carbaldehyde (C1)

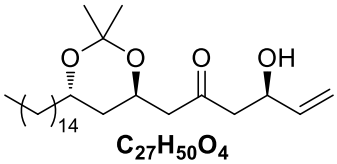


$C_{22}H_{42}O_3$
354.57 g/mol

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: R_f = 0.33 (PE/EtOAc 90:10) [CAM]. **$[\alpha]_D^{20}$ = +** 17.9 (c= 2.52, dr 90:10, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$, 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). **^{13}C NMR** (151 MHz, $CDCl_3$, 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): ν_{max} [cm^{-1}] = 2922 (vs), 2852 (s) (C sp^3), 1736 (s) (C=O), 1465 (m) (CH_2-def.), 1379 (m) (CH_3-def.), 1224 (s) (C-O-C). **LRMS** (EI): *m/z* (%)*:*339.2 (22) [M^+-CH_3], 267.2 (20), 59.0 (100). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{22}H_{42}O_3Na^+$ 377.3026; found: 377.3027.

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



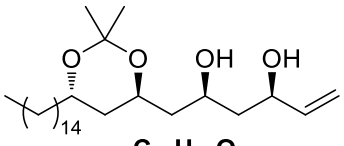
$C_{27}H_{50}O_4$
438.68 g/mol

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: R_f = 0.10 (PE/EtOAc 90:10) [CAM]. **$[\alpha]_D^{20}$ = +** 19.3 (c= 1.32, dr = 99:1, $CHCl_3$). **^{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), 4.62 - 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). **^{13}C NMR** (101 MHz, $CDCl_3$): 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, 29.8, 29.7, 29.7, 29.5, 25.5, 24.9, 24.7, 22.8, 14.3. **IR** (ATR): ν_{max} [cm^{-1}] =3416 (b) (OH), 2918 (vs), 2851 (s) (C sp^3), 1711 (m) (C=O), 1467 (m) (CH_2-def.), 1379 (m) (CH_3-def.), 1223 (s) (C-O-C),989 (m), 923 (m) (=C-H def.). **LRMS** (EI): *m/z* (%):367.3(18) [M^+-C_4H_7O], 307.3 (18), 82.1 (96), 57.1 (100). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{27}H_{50}O_4Na^+$ 461.3601; found: 461.3598.

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

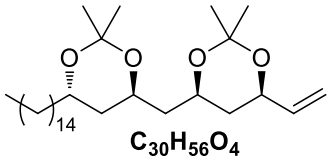


$C_{27}H_{52}O_4$
440.70 g/mol

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: R_f = 0.24 (PE/EtOAc 70:30) [CAM]. **$[\alpha]_D^{20}$ =** +16.3 (c= 3.5, dr= 98:2, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$, 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). **^{13}C NMR** (101 MHz, $CDCl_3$, 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): ν_{max} [cm^{-1}] = 3280 (sb) (OH), 2916 (vs), 2849 (s) (C sp^3), 1466 (m) (CH_2-def.), 1376 (m) (CH_3-def.), 1223 (m) (C-O-C),986 (s), 926 (m) (=C-H def.). **LRMS** (EI): *m/z* (%):425.4 (11) [M^+-CH_3], 267.2 (22), 207.0 (18), 109.0 (68)55.0 (98), 83.0 (100). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{27}H_{52}O_4Na^+$ 463.3758; found: 463.3758.

(4R,6R)-4-(((4*R*,6*S*)-2,2-Dimethyl-6-pentadecyl-1,3-dioxane-4-yl)methyl)-2,2-dimethyl-6-vinyl-1,3-dioxane (C2d)

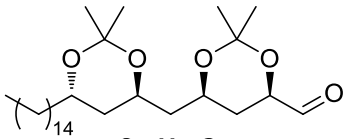


$C_{30}H_{56}O_4$
480.76 g/mol

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, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$, major diastereomer): δ [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, $CDCl_3$, major diastereomer): δ [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, 29.8, 29.7, 29.7, 29.5, 25.5, 25.1, 24.9, 22.8, 19.9, 14.3. **IR** (ATR): ν_{max} [cm^{-1}] =2922 (vs), 2853 (s) (C *sp*^{3}), 1465 (s) (CH_2-def.), 1377 (s) (CH_3-def.), 1224 (s), 1199 (s), 1171 (s) (C-O-C), 987 (m), 920 (m) (=C-H def.). **LRMS** (EI): *m/z* (%)*:*465.4 (38) [M^+-CH_3], 329.2 (22), 109.0 (51), 83.0 (100), 59.0 (82). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{30}H_{56}O_4Na^+$ 503.4071; found: 503.4071.

(4R,6R)-4-(((4*R*,6*S*)-2,2-Dimethyl-6-pentadecyl-1,3-dioxane-4-yl)methyl)-2,2-dimethyl-1,3-dioxane-4-carbaldehyde (C2)



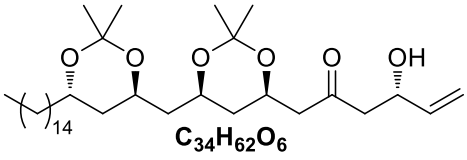
$C_{29}H_{54}O_5$
482.74 g/mol

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, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$, major diastereomer): δ [ppm] = 9.59 (d, *J* = 0.7 Hz, 1H), 4.29 (dd, *J* = 12.2, 3.1 Hz, 1H), 4.07 (dtd, *J* = 11.4, 6.4, 2.5 Hz, 1H), 4.02 - 3.81 (m, 1H), 3.80 - 3.72 (m,

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, 29.8, 29.7, 29.7, 29.5, 25.5, 25.1, 24.9, 22.8, 19.6, 14.3. **IR** (ATR): ν_{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 $C_{29}H_{54}O_5Na^+$ 505.3863; found: 505.3865.

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

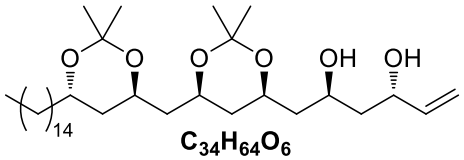


$C_{34}H_{62}O_6$
566.85 g/mol

Aldehyde **C2** (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). *β*-Hydroxyketone **C3a** 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 (dddd, *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): ν_{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^+-C_4H_7O], 377.2 (8), 207.0 (14), 82.0 (94), 57.1 (100). **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{34}H_{62}O_6Na^+$ 589.4439; found: 589.4437.

(2*S*,4*S*)-1-((4*S*,6*S*)-6-(((4*R*,6*S*)-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)

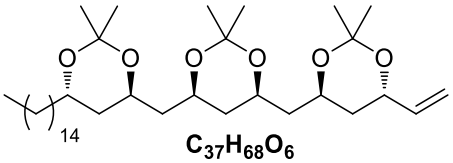


$C_{34}H_{64}O_6$
568.87 g/mol

β-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, 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): δ [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), 1.33 (s, 3H), 1.29 - 1.22 (m, 26H), 0.88 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ [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, 29.8, 29.7, 29.7, 29.5, 25.5, 25.1, 24.9, 22.8, 20.1, 14.3. **IR** (ATR): ν_{max} [cm^{-1}] = 3422 (vb) (OH), 2922 (vs), 2853 (s) (C *sp*^{3}), 1379 (s) (CH_3-def.), 1224 (m), 1200(m), 1104 (m) (C-O-C). **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{34}H_{64}O_6Na^+$ 591.4595; found: 591.4603.

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



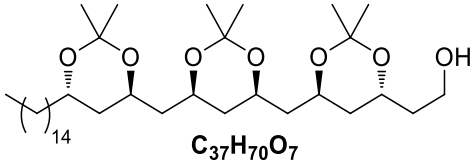
$C_{37}H_{68}O_6$
608.93 g/mol

13.5 mg (23.7 µmol) 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 µmol, 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, $CDCl_3$) δ [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),

1.90 - 169 (m, 9H),1.63 - 1.45 (m, 7H), 1.42 (s, 3H), 1.39 - 1.35 (m, 9H), 1.33 (s, 6H), 1.30 - 1.23 (m, 24H), 0.87 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) 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, 29.8, 29.7, 29.7, 29.5,25.6, 25.5, 25.1, 24.9, 22.8, 20.0, 14.3. **IR** (ATR): ν_{max} [cm^{-1}] =2990 (w), 2923 (s), 2854 (m) (C sp^3), 1464 (w), 1378 (s) (CH_3-def.), 1199 (w), 1172 (m), 1107(m), 1104 (m) (C-O-C). **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{37}H_{68}O_6Na^+$ 631.4908; found: 631.4908.

2-((4*R*,6*S*)-6-(((4*R*,6*S*)-6-(((4*R*,6*S*)-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)

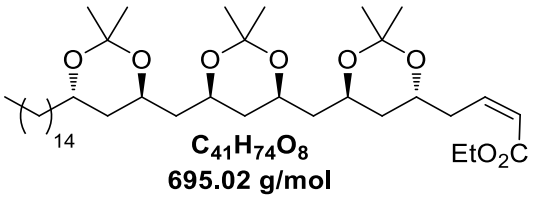


$C_{37}H_{70}O_7$
626.95 g/mol

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 16h 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 H_2O_2 (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: R_f = 0.19 (PE/EtOAc 80:20) [CAM]. **^{1}H NMR** (400 MHz, $CDCl_3$) 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). **^{13}C NMR** (101 MHz, $CDCl_3$) 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, 29.8, 29.7, 29.5, 25.1, 25.0, 24.9, 22.8, 20.0, 14.3. **IR** (ATR): ν_{max} [cm^{-1}] = 3484 (br), 2990 (w), 2922 (s), 2853 (m) (C sp^3), 1379 (s) (CH_3-def.), 1199 (s), 1170 (s), 1106 (m) (C-O-C). **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{37}H_{70}O_7Na^+$ 649.5014; found: 649.5014.

(*Z*)-methyl-4-((4*R*,6*S*)-6-(((4*R*,6*S*)-6-(((4*R*,6*S*)-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)

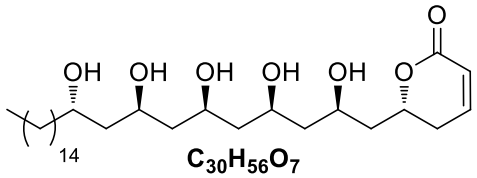


Compound **20** (52.0 mg 82.9 µmol) was dissolved in 0.83 ml (0.1M) dichloromethane under nitrogen atmosphere. Then 27mg of 4 Å moleculare sieve, 15 mg (0.124 mmol, 1.5 eq) NMO and 1.4 mg (4 µmol, 0.05 eq) TPAP were added successively. The reaction was stirred for 2h at rt, before the whole reaction mixture was purified by column chromatography with addition of Et_3N (PE/EtOAc95/5 → 80/20). The product can be isolated as colourless liquid (33.7 mg 53.9 µmol, 65%, R_f = 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 Na_2SO_4 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: R_f = 0.46 (PE/EtOAc 70:30) [CAM]. **^{1}H NMR** (400 MHz, $CDCl_3$) 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). **^{13}C NMR** (101 MHz, $CDCl_3$) 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, 25.1, 25.0, 24.9, 22.8, 19.9, 14.4, 14.3. **IR** (ATR): ν_{max} [cm^{-1}] = 2990 (w), 2922 (s), 2853 (m) (C *sp*^{3}), 1724 (s) (C=O), 1378 (s) (CH_3-def.), 1196 (s), 1171 (s), 1109 (m) (C-O-C). **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{41}H_{74}O_8Na^+$ 717.5276; found: 717.5278.

(+)-Cryptocaryol A (22)

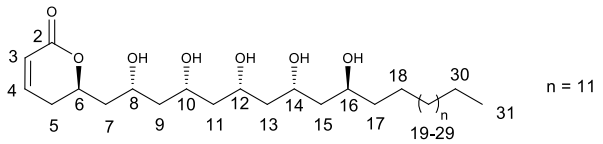


$C_{30}H_{56}O_7$
528.76 g/mol

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/H_2O/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 Na_2SO_4 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 (CH_2Cl_2/MeOH 99:1 → 97:3) yielding 4 mg (7.6 µmol, 25%) of the desired product **22**.

TLC: R_f = 0.34 (DCM/MeOH 94:6) [CAM]. **^{1}H NMR** (CD_3OD, 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 (dddd, *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 (ddd, *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). **^{13}C NMR** (151 MHz, CD_3OD) 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, 30.8, 30.7, 30.4, 26.8, 23.7, 14.4.). **IR** (ATR): ν_{max} [cm^{-1}] = 3361 (br) (OH), 2916 (s), 2849 (m) (C *sp*^{3}), 1720 (m) (C=O), 1466 (s), 1324 (s), 1140 (m), 1091 (m), 843 (s). **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{30}H_{56}O_7Na^+$ 551.3918; found: 551.3918.

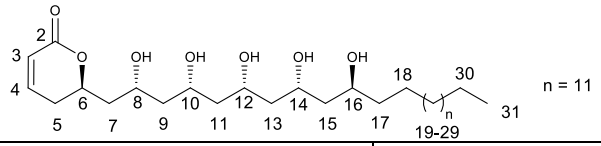
Comparison of ^{1}H-NMR data of *Cryptocaryol A*



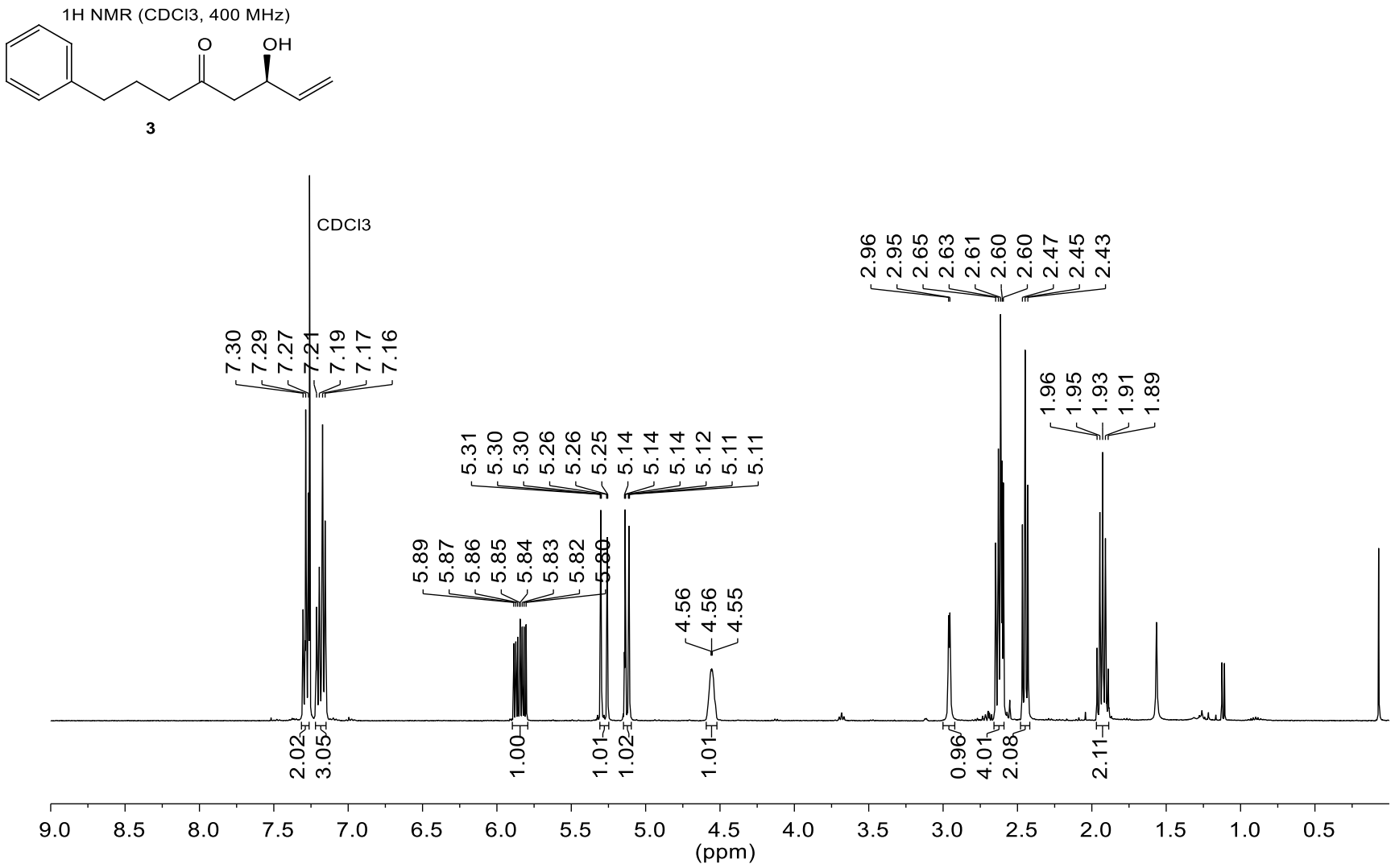
No.	Gustafson *et al.*[1] (600 MHz, CD_3OD)	O'Doherty *et al.*[2] (400 MHz, CD_3OD)	Cossy *et al.*[3] (400 MHz, CD_3OD)	this work (600 MHz, CD_3OD)
3	7.04 ddd (9.8,6.0,2.3)	7.04 ddd (9.6, 6.0, 2.5)	7.05 ddd (9.8, 6.0, 2.7)	7.05 ddd (9.8, 6.0, 2.5)
4	5.97 dd (9.8, 1.9)	5.97 (dd, 9.6, 2.5)	5.98 br d (9.8)	5.98 ddd (9.7, 2.6, 1.0)
6	4.71 m	4.74-4.67 m	4.72 m	4.75-4.69 m
8	4.08 m	4.09 dddd (8.8, 6.4, 6.4, 2.4)	4.09 m	4.13-4.06 m
14	4.02 m	4.04-3.96 m	4.05-3.95 m	4.06-3.96 m
12	4.00 m	4.04-3.96 m	4.05-3.95 m	4.06-3.96 m
10	3.97 m	4.04-3.96 m	4.05-3.95 m	4.06-3.96 m
16	3.79 m	3.82-3.77 m	3.81 m	3.84-3.78 m
5a	2.45 m	2.45 ddd (19.2, 5.2, 5.2)	2.50-2.32 m	2.46 dddd (18.6, 5.8, 4.2, 1.2)
5b	2.36 ddt (18.5, 11.8, 2.6)	2.36 dddd (19.2, 11.6, 2.8, 2.8)	2.50-2.32 m	2.37 ddt (18.6, 11.6, 2.5)
7a	1.94 ddd (14.5, 9.7, 2.3)	1.94 ddd (14.8, 9.6, 2.8)	1.95 ddd (14.4, 9.9, 2.4)	1.95 ddd (14.5, 9.7, 2.6)
9	1.68 m	1.71-1.55 m	1.73-1.54 m	1.72-1.55 m
7b	1.67 m	1.71-1.55 m	1.73-1.54 m	1.72-1.55 m
11	1.63 m	1.71-1.55 m	1.73-1.54 m	1.72-1.55 m
13	1.59 m	1.71-1.55 m	1.73-1.54 m	1.72-1.55 m
15	1.50 m	1.52-1.49 m	1.52 t (6.0)	1.53-1.50 m
17	1.43 m	1.46-1.40 m	1.47-1.41 m	1.48-1.41 m
18	1.32 m	1.32-1.25 m	1.35-1.28 m	1.36-1.25 m
19-28	1.27-1.29 br m	1.32-1.25 m	1.35-1.28 m	1.36-1.25 m
29	1.29 m	1.32-1.25 m	1.35-1.28 m	1.36-1.25 m
30	1.27 m	1.32-1.25 m	1.35-1.28 m	1.36-1.25 m
31	0.89 t (6.9)	0.89 t (6.8)	0.90 t (6.9)	0.90 t (7.0)

[1] T. Grkovic, J. S. Blees, N. H. Colburn, T. Schmid, C. L. Thomas, C. J. Henrich, J. B. McMahon, K. R. Gustafson, *J. Nat. Prod.* **2011**, *5*, 1015–1020. [2] Y. Wang, G. A. O'Doherty, *J. Am. Chem. Soc.* **2013**, *25*, 9334–9337. [3] E. Brun, V. Bellosta, J. Cossy, *J. Org. Chem.* **2015**, *17*, 8668–8676.

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



No.	Gustafson *et al.*[1] (150 MHz, CD_3OD)	O'Doherty *et al.*[2] (400 MHz, CD_3OD)	Cossy *et al.*[3] (100 MHz, CD_3OD)	this work (151 MHz, CD_3OD)
2	167.0	167.0	166.9	166.9
4	148.6	148.6	148.5	148.5
3	121.4	121.4	121.4	121.4
6	76.6	76.6	76.6	76.6
12	70.2	70.2	70.1	70.2
10	69.9	69.9	69.9	70.0
16	69.1	69.1	69.1	69.2
14	68.3	68.2	68.2	68.3
8	66.6	66.6	66.5	66.7
9	46.0	46.0	46.0	45.9
13	45.9	45.9	45.9	45.9
15	45.8	45.8	45.7	45.7
11	45.3	45.3	45.2	45.3
7	43.9	43.9	43.8	43.9
17	39.3	39.3	39.2	39.2
29	33.2	33.1	33.1	33.1
5	31.0	31.0	30.9	30.9
19-28	31.0-30.5	31.0-30.5	30.8-30.5	30.8-30.4
18	26.8	26.8	26.8	26.8
30	23.8	23.8	23.7	23.7
31	14.5	14.5	14.4	14.4


1H NMR (CDCl3, 400 MHz)
O
OH
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CDCl3
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7.27
7.21
7.19
7.17
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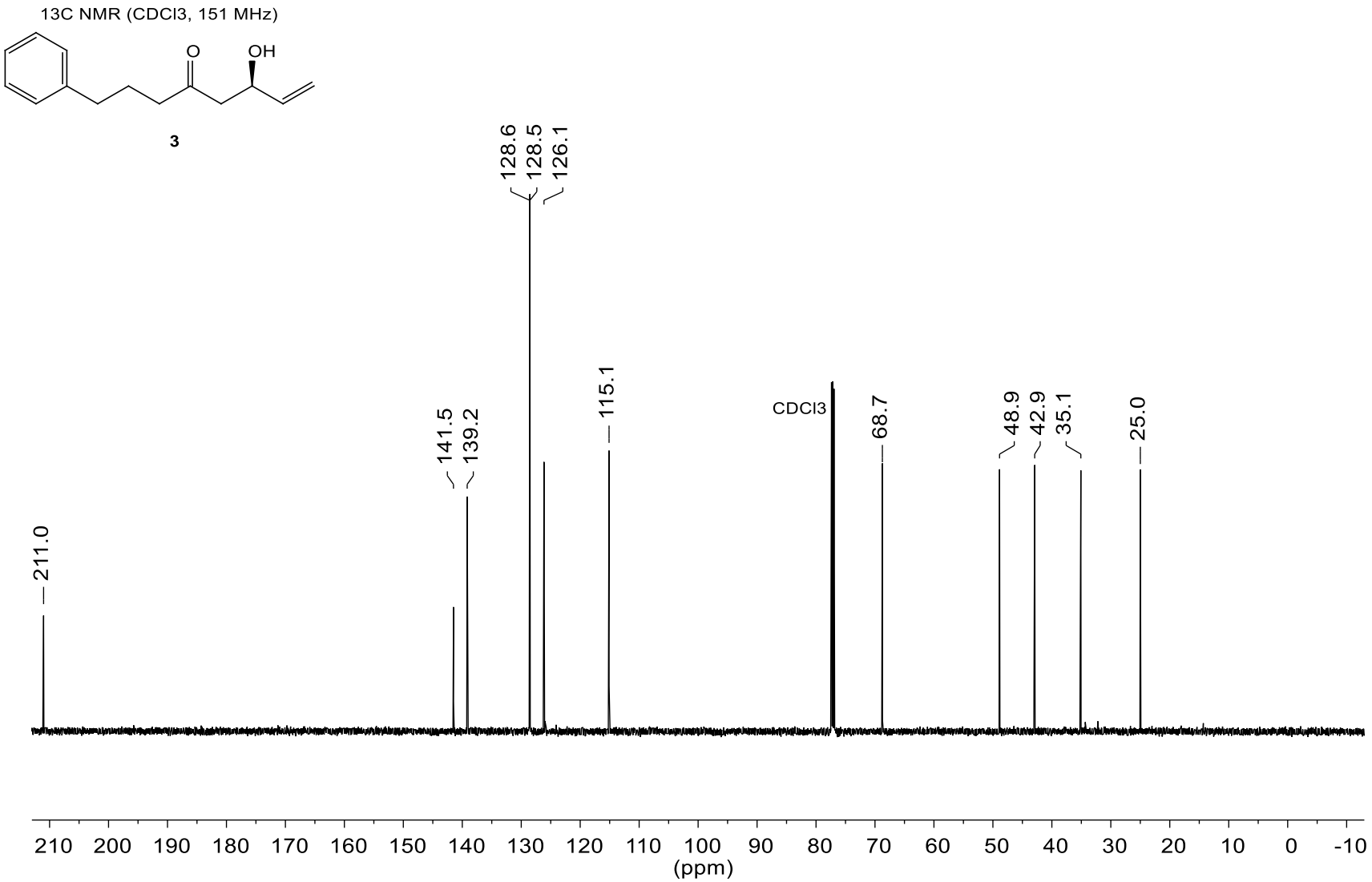
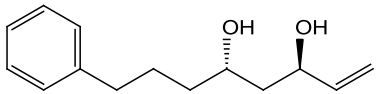
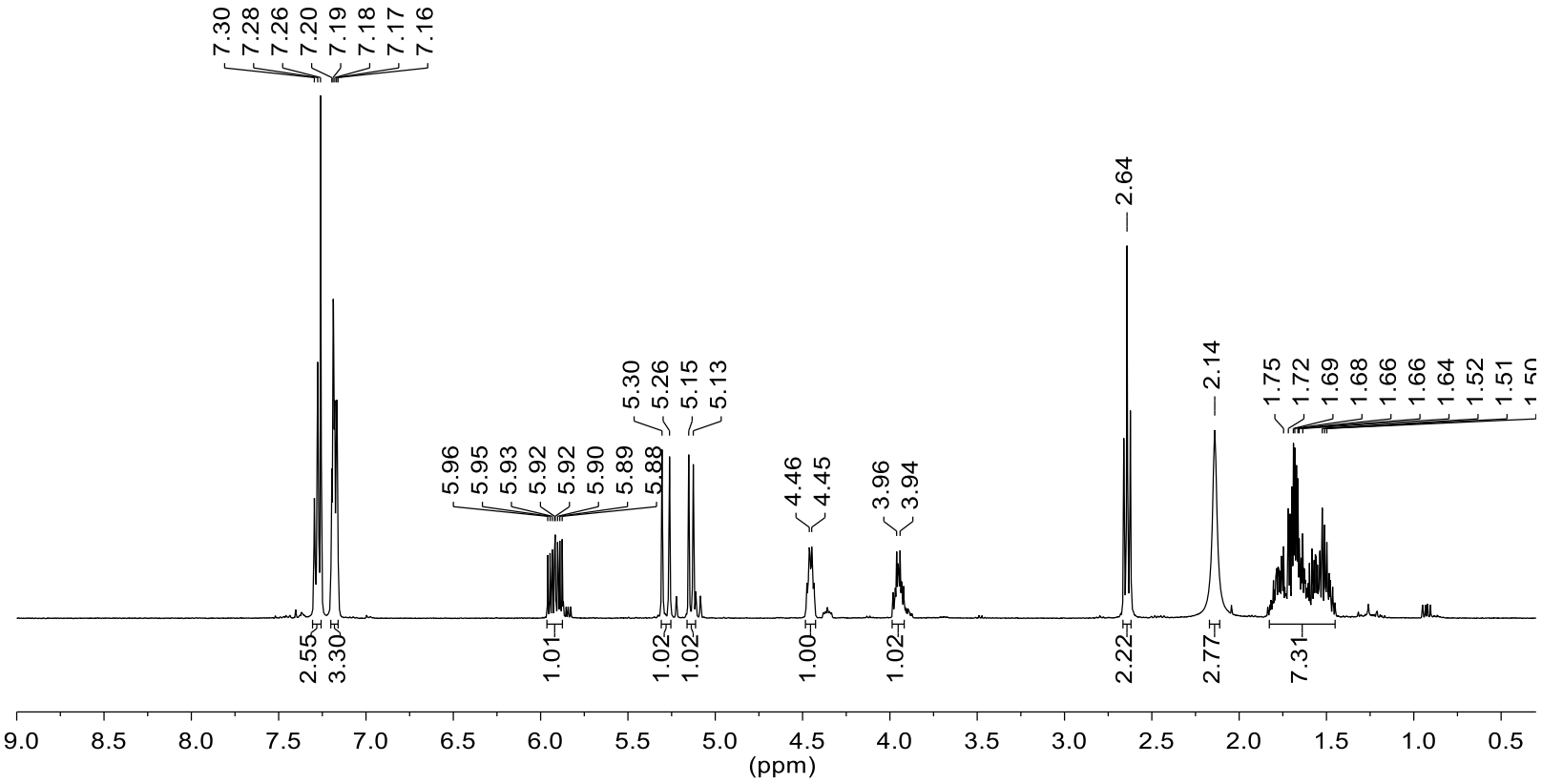
5.30
5.30
5.26
5.26
5.25
5.14
5.14
5.14
5.12
5.11
5.11
5.89
5.87
5.86
5.85
5.84
5.83
5.82
5.80
4.56
4.56
4.55
2.96
2.95
2.65
2.63
2.61
2.60
2.60
2.47
2.45
2.43
1.96
1.95
1.93
1.91
1.89
2.02
3.05
1.00
1.01
1.02
1.01
0.96
4.01
2.08
2.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)


13C NMR (CDCl3, 151 MHz)
O
OH
3
211.0
141.5
139.2
128.6
128.5
126.1
115.1
CDCl3
68.7
48.9
42.9
35.1
25.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

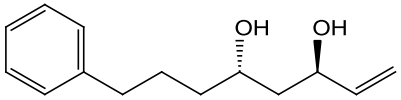
1H NMR (CDCl3, 400 MHz) - d.r. 90:10



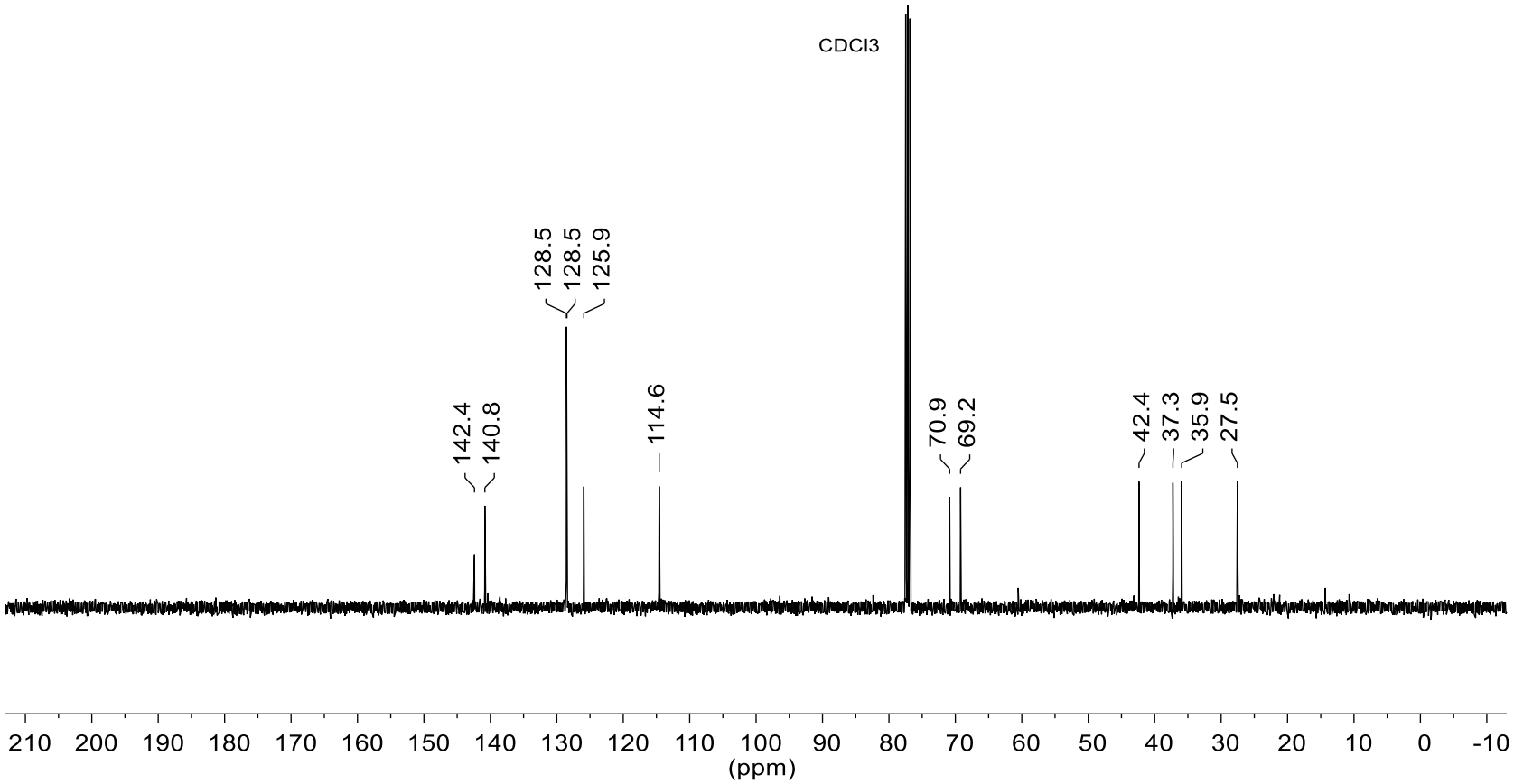
4

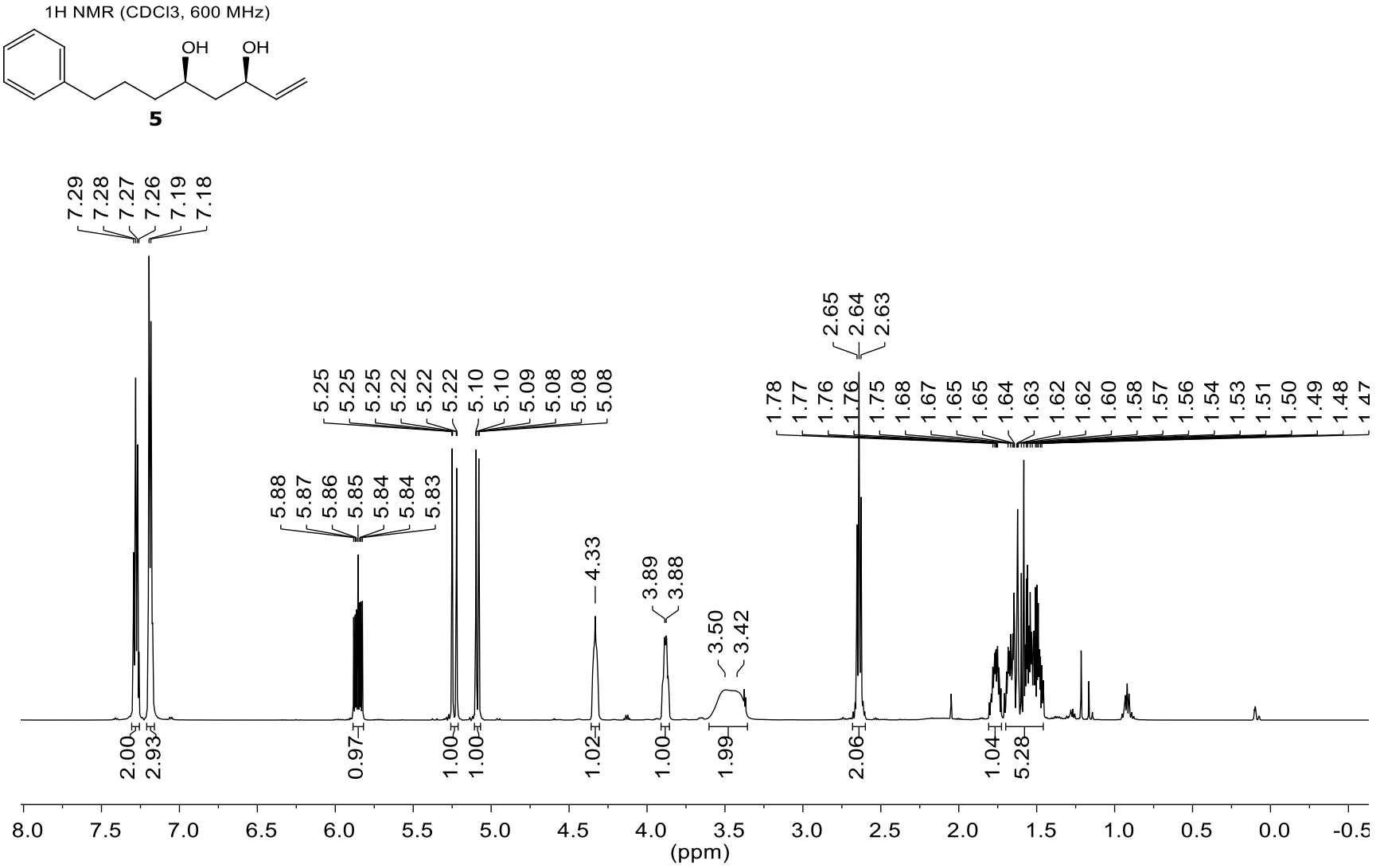


13C NMR (CDCl3, 101 MHz)

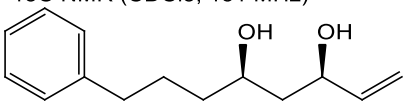


4

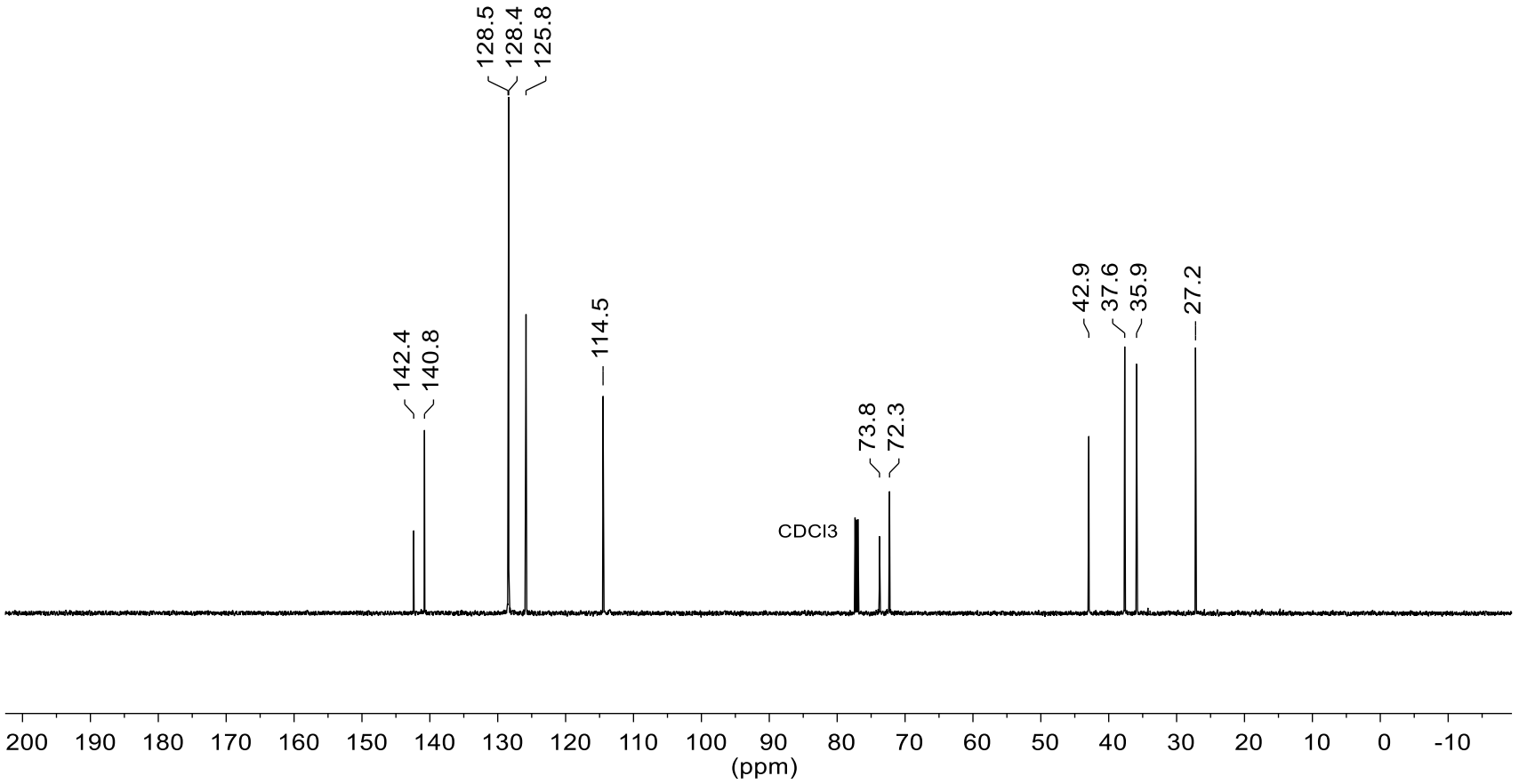


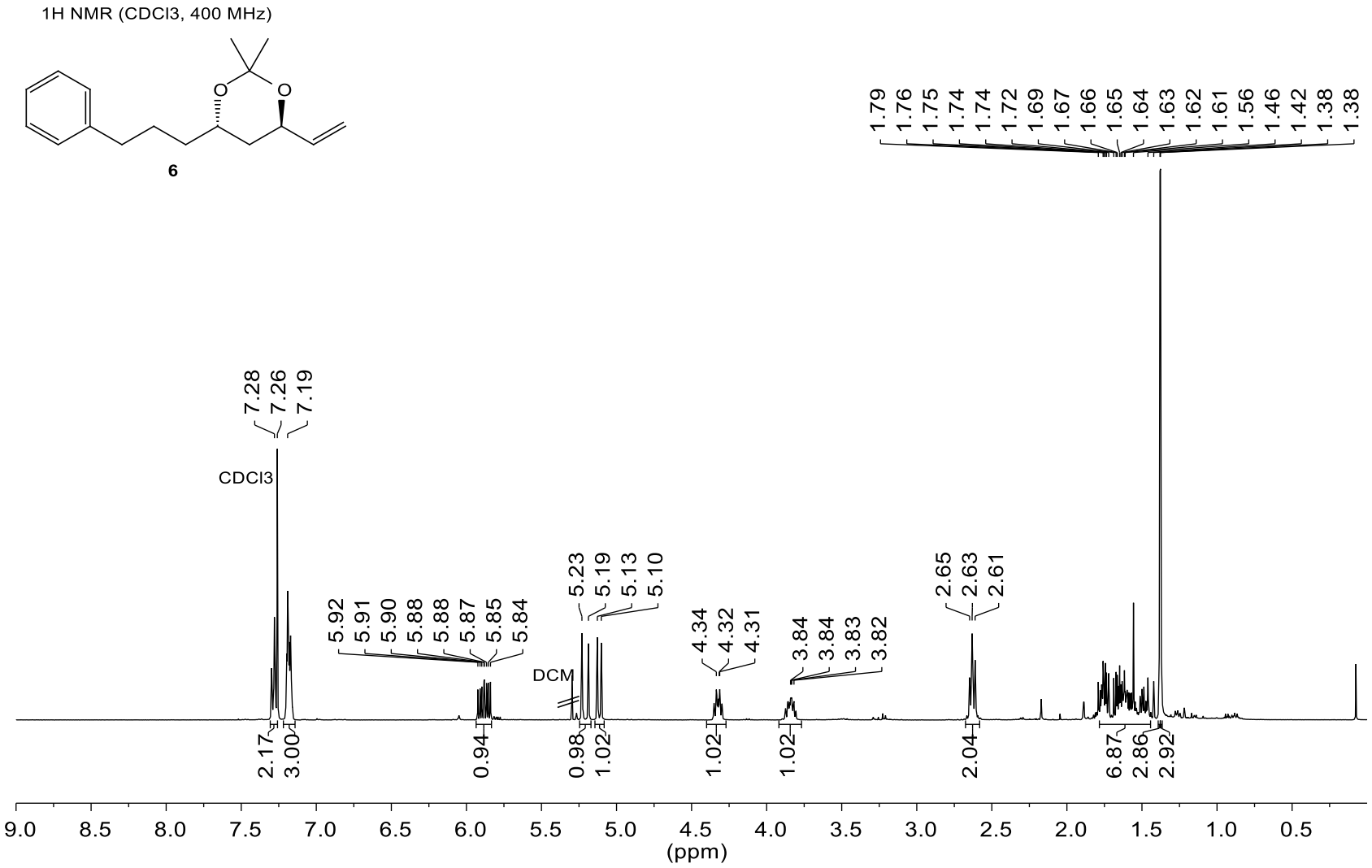

1H NMR (CDCl3, 600 MHz)
OH
OH
5
7.29
7.28
7.27
7.26
7.19
7.18
5.88
5.87
5.86
5.85
5.84
5.84
5.83
5.25
5.25
5.25
5.22
5.22
5.22
5.10
5.10
5.09
5.08
5.08
5.08
4.33
3.89
3.88
3.50
3.42
2.65
2.64
2.63
1.78
1.77
1.76
1.76
1.75
1.68
1.67
1.65
1.65
1.64
1.63
1.62
1.62
1.60
1.58
1.57
1.56
1.54
1.53
1.51
1.50
1.49
1.48
1.47
2.00
2.93
0.97
1.00
1.00
1.02
1.00
1.99
2.06
1.04
5.28
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
(ppm)

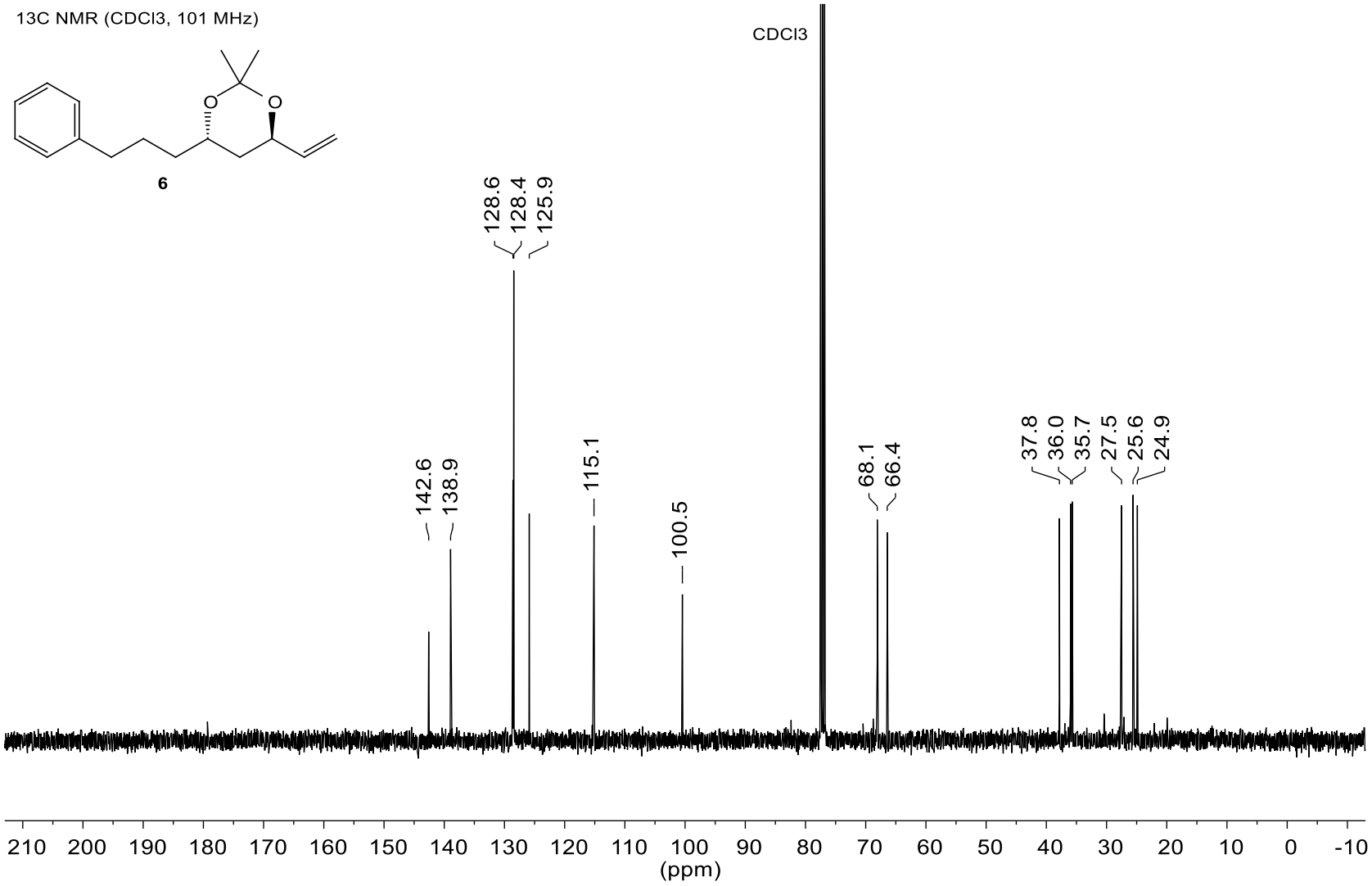
13C NMR (CDCl3, 151 MHz)

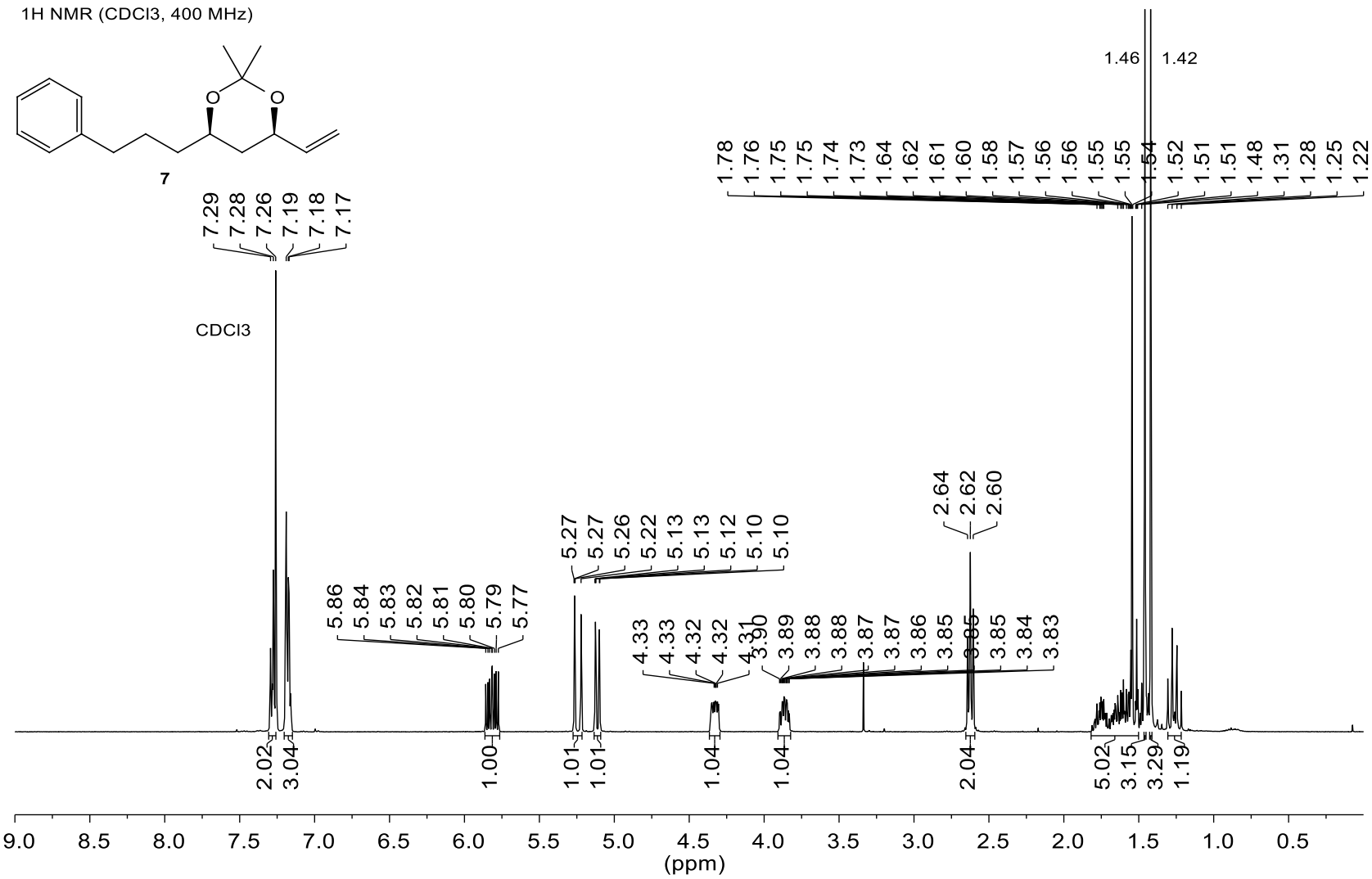


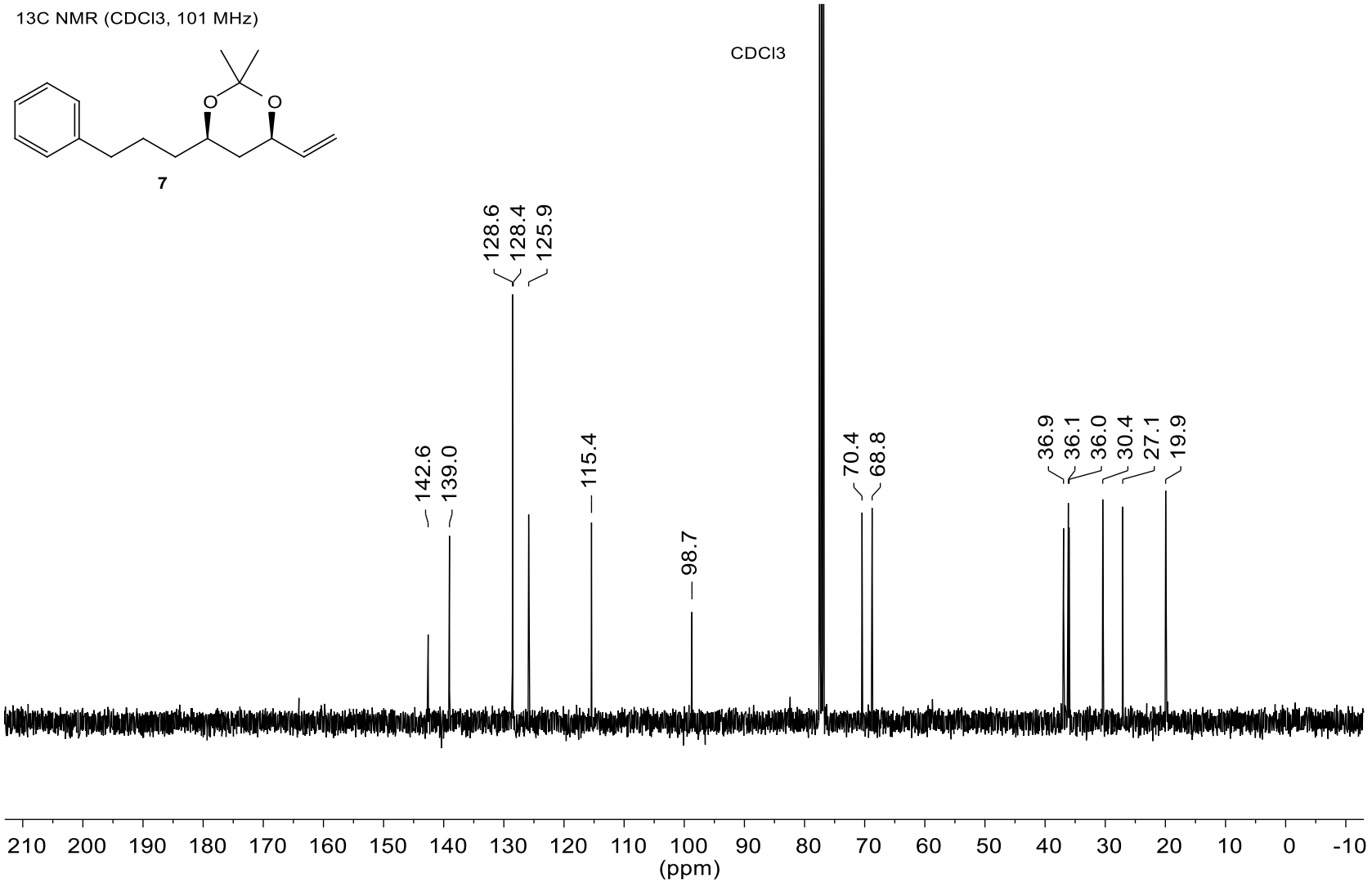
5

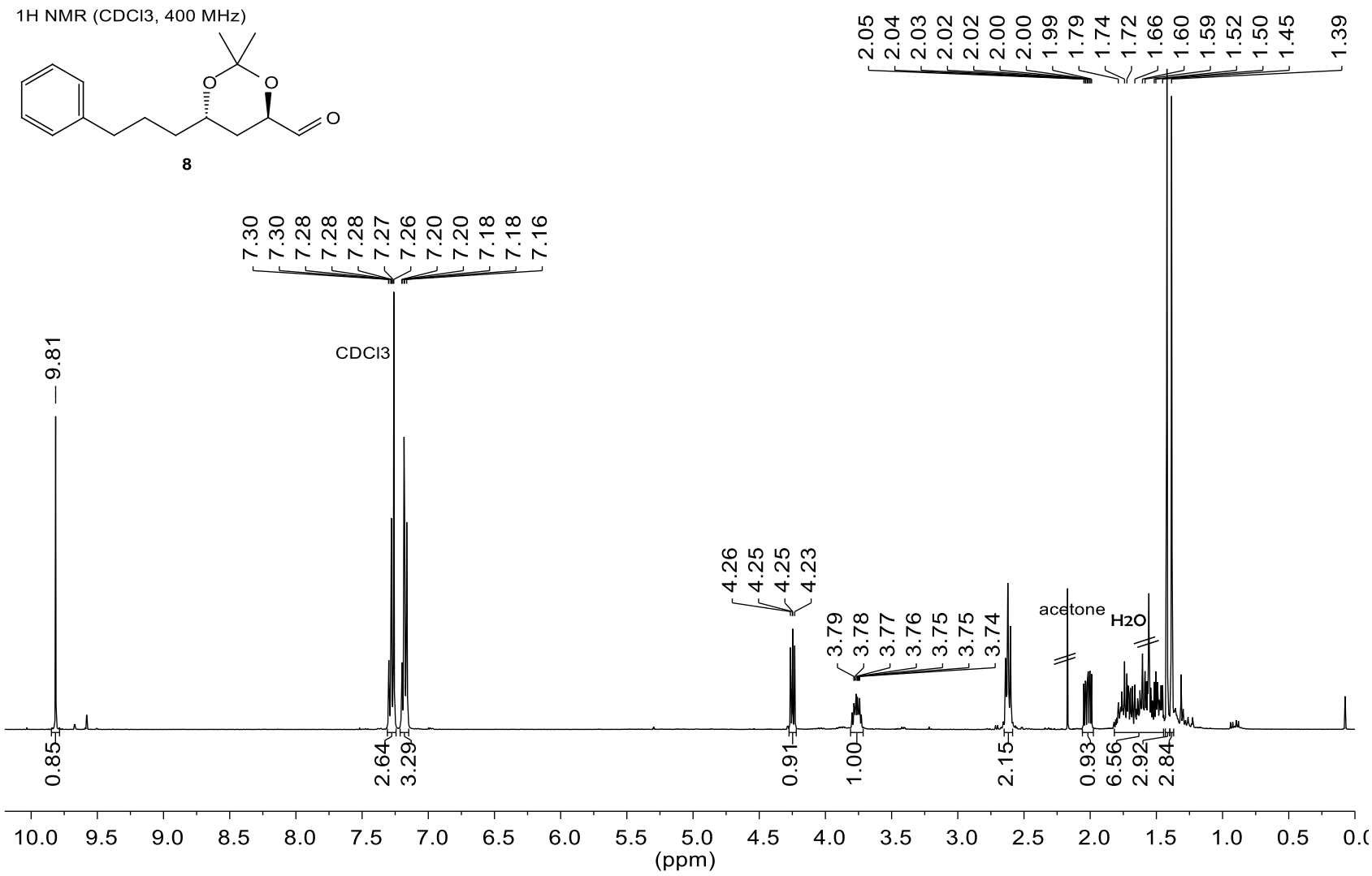


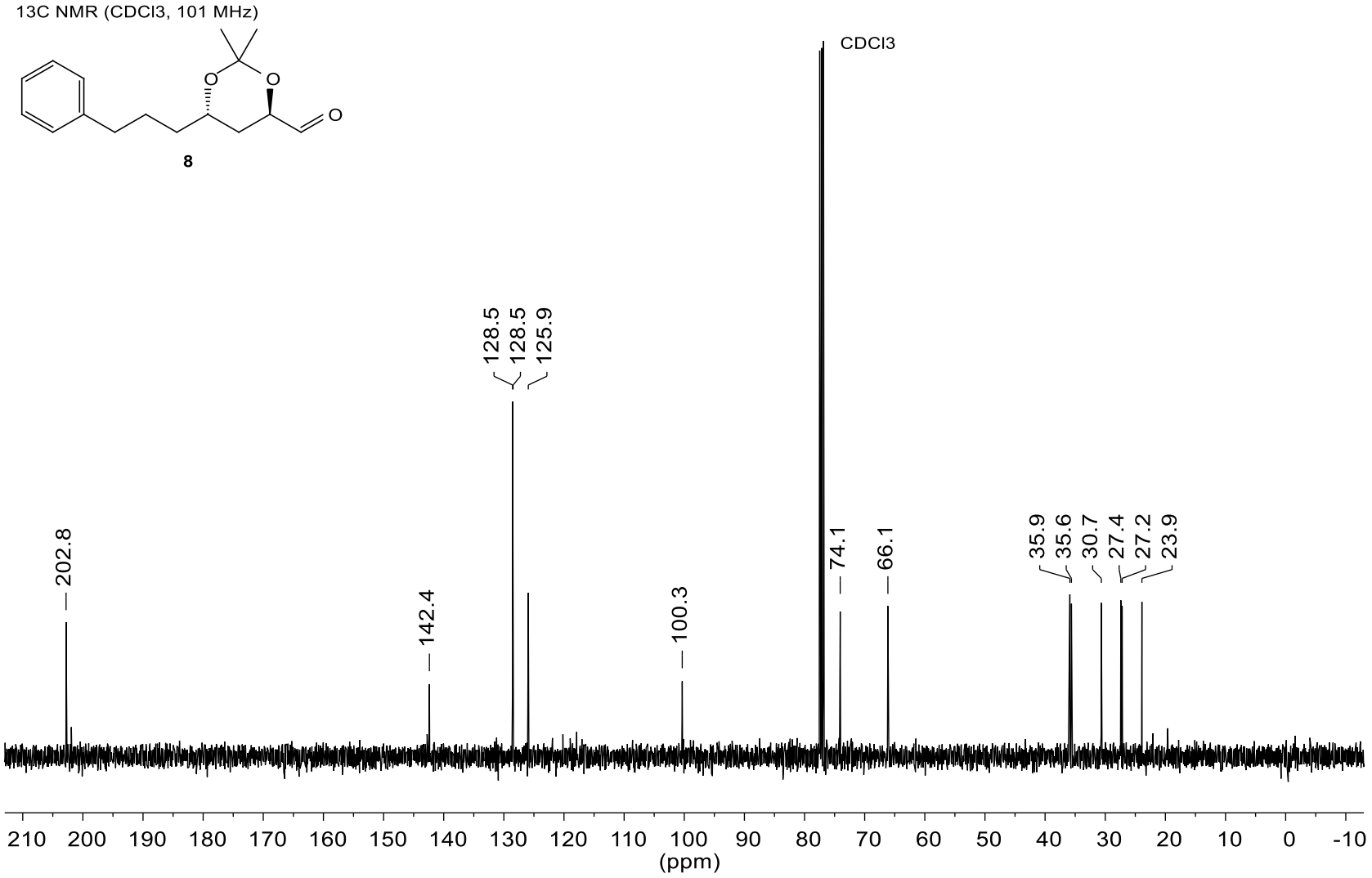

1H NMR (CDCl3, 400 MHz)
6
7.28
7.26
7.19
CDCl3
5.92
5.91
5.90
5.88
5.88
5.87
5.85
5.84
5.23
5.19
5.13
5.10
DCM
4.34
4.32
4.31
3.84
3.84
3.83
3.82
2.65
2.63
2.61
1.79
1.76
1.75
1.74
1.74
1.72
1.69
1.67
1.66
1.65
1.64
1.63
1.62
1.61
1.56
1.46
1.42
1.38
1.38
2.17
3.00
0.94
0.98
1.02
1.02
1.02
2.04
6.87
2.86
2.92
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

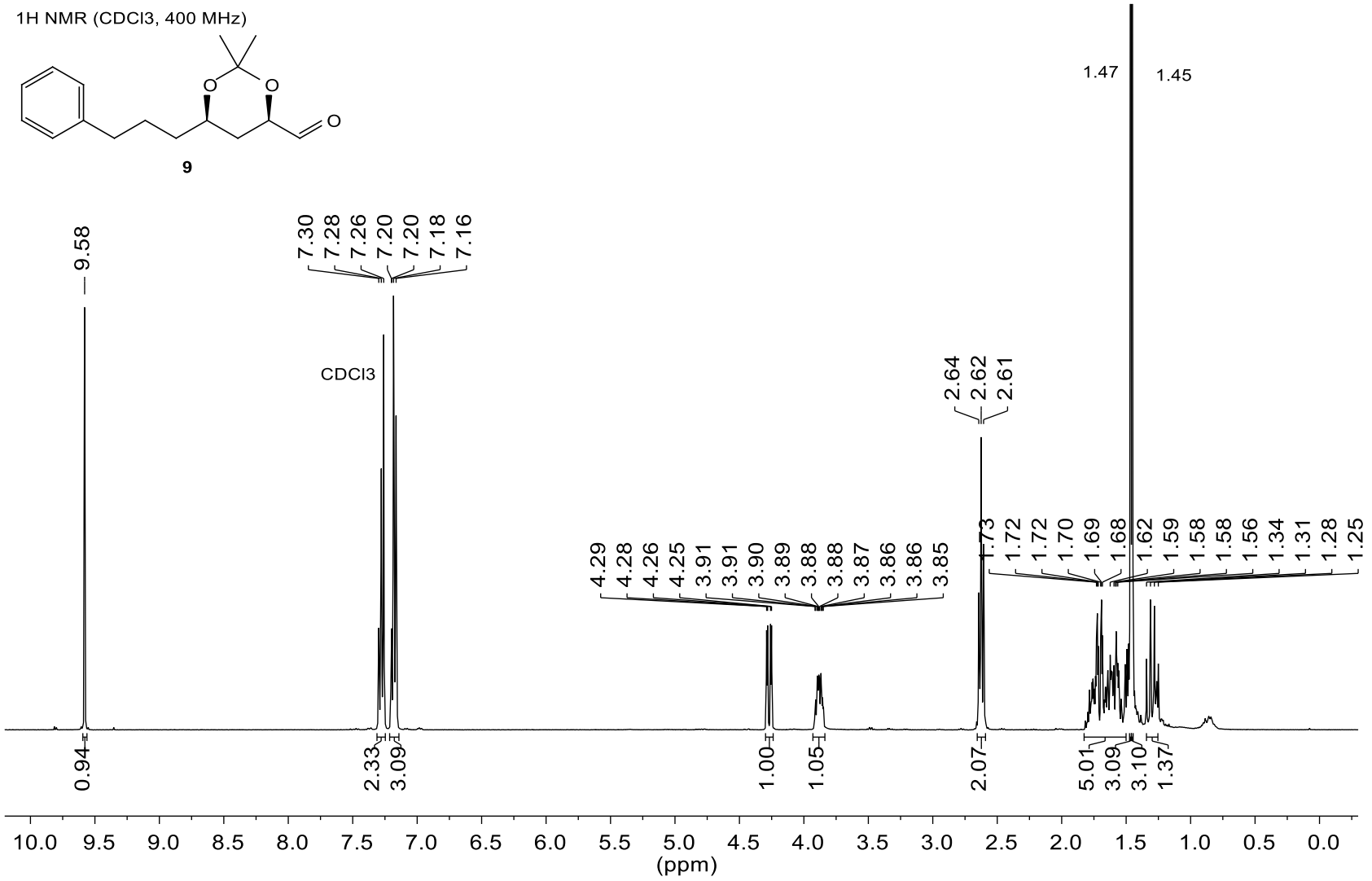

13C NMR (CDCl3, 101 MHz)
6
CDCl3
142.6
138.9
128.6
128.4
125.9
115.1
100.5
68.1
66.4
37.8
36.0
35.7
27.5
25.6
24.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

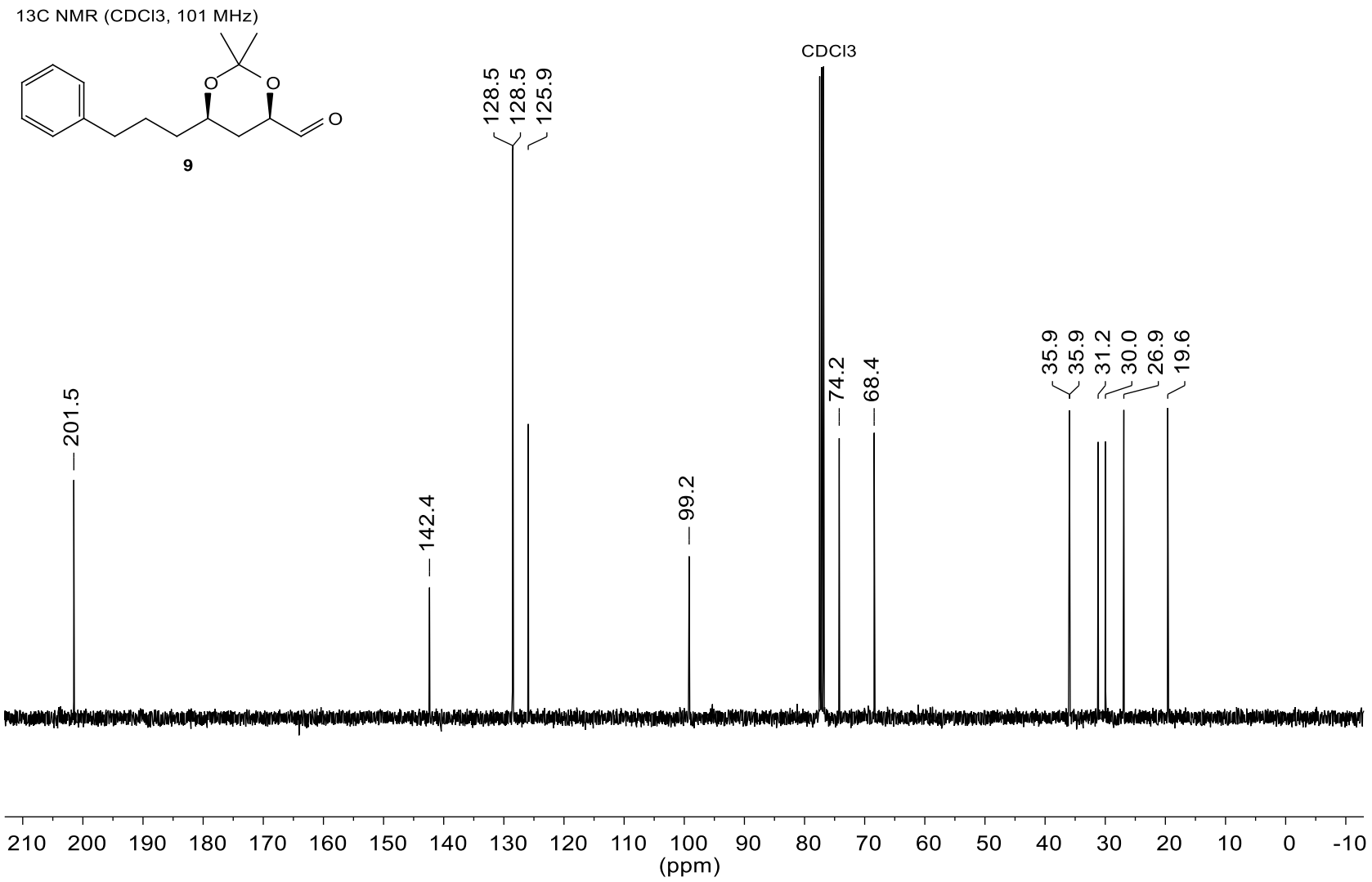

1H NMR (CDCl3, 400 MHz)
7
CDCl3
(ppm)


13C NMR (CDCl3, 101 MHz)
7
CDCl3
142.6
139.0
128.6
128.4
125.9
115.4
98.7
70.4
68.8
36.9
36.1
36.0
30.4
27.1
19.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

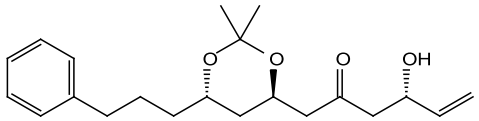

1H NMR (CDCl3, 400 MHz)
8
9.81
CDCl3
7.30
7.30
7.28
7.28
7.28
7.27
7.26
7.20
7.20
7.18
7.18
7.16
4.26
4.25
4.25
4.23
3.79
3.78
3.77
3.76
3.75
3.75
3.74
acetone
H2O
2.05
2.04
2.03
2.02
2.02
2.00
2.00
1.99
1.79
1.74
1.72
1.66
1.60
1.59
1.52
1.50
1.45
1.39
0.85
2.64
3.29
0.91
1.00
2.15
0.93
6.56
2.92
2.84
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


13C NMR (CDCl3, 101 MHz)
O
O
O
8
CDCl3
128.5
128.5
125.9
202.8
142.4
100.3
74.1
66.1
35.9
35.6
30.7
27.4
27.2
23.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)


1H NMR (CDCl3, 400 MHz)
9
9.58
7.30
7.28
7.26
7.20
7.20
7.18
7.16
CDCl3
4.29
4.28
4.26
4.25
3.91
3.91
3.90
3.89
3.88
3.88
3.87
3.86
3.86
3.85
2.64
2.62
2.61
1.73
1.72
1.72
1.70
1.69
1.68
1.62
1.59
1.58
1.58
1.56
1.47
1.45
1.34
1.31
1.28
1.25
0.94
2.33
3.09
1.00
1.05
2.07
5.01
3.09
3.10
1.37
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

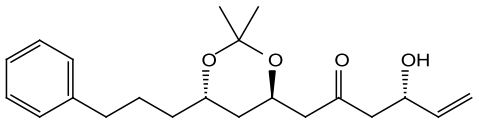

13C NMR (CDCl3, 101 MHz)
9
CDCl3
201.5
142.4
128.5
128.5
125.9
99.2
74.2
68.4
35.9
35.9
31.2
30.0
26.9
19.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

1H NMR (CDCl3, 400 MHz)

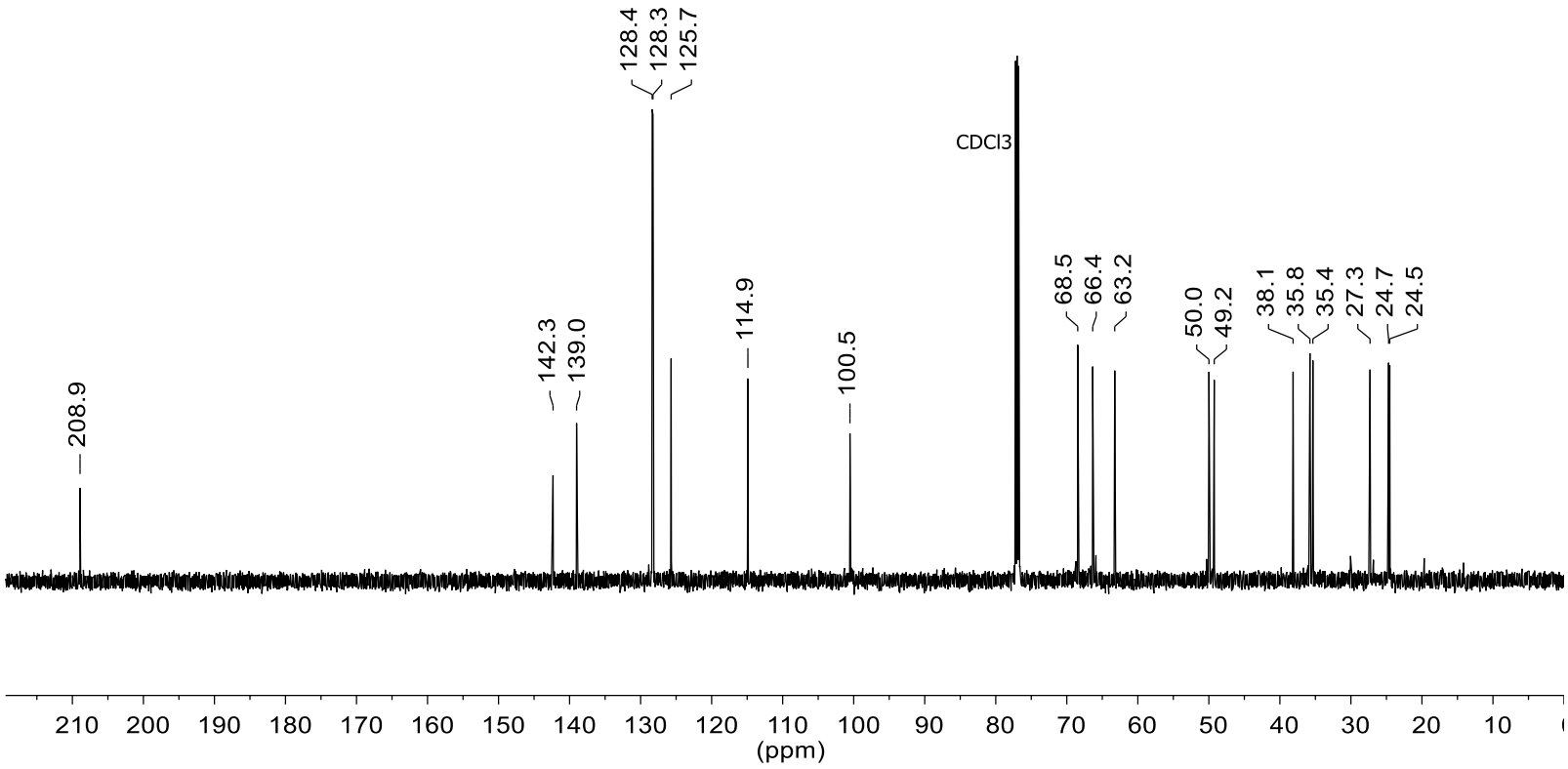


10a/11a

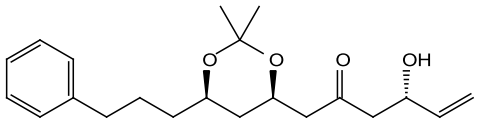
13C NMR (CDCl3, 151 MHz)



10a/11a

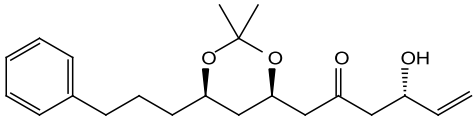


1H NMR (CDCl3, 600 MHz)

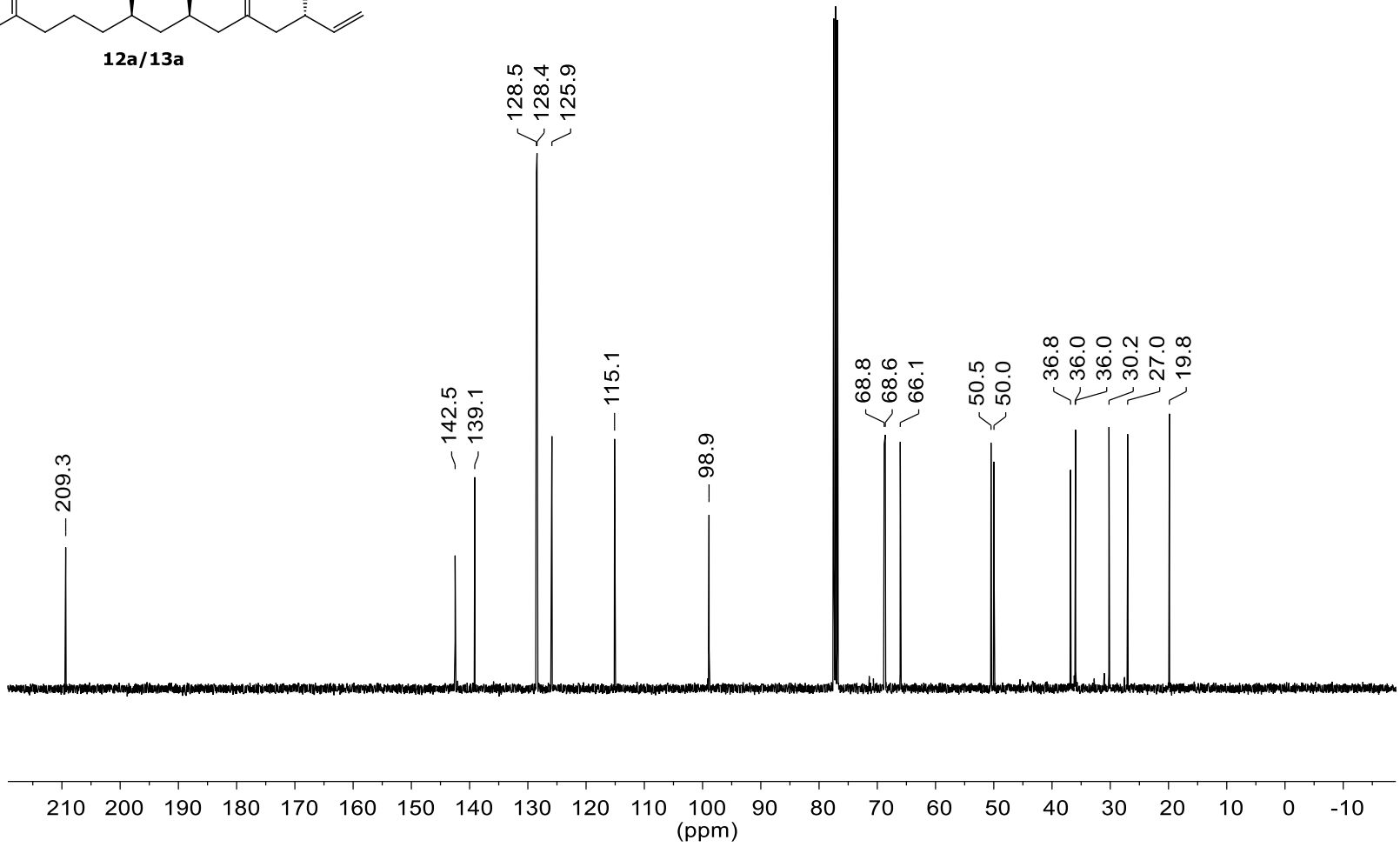


12a/13a

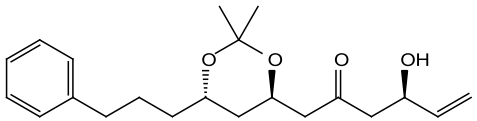
13C NMR (CDCl3, 101 MHz)



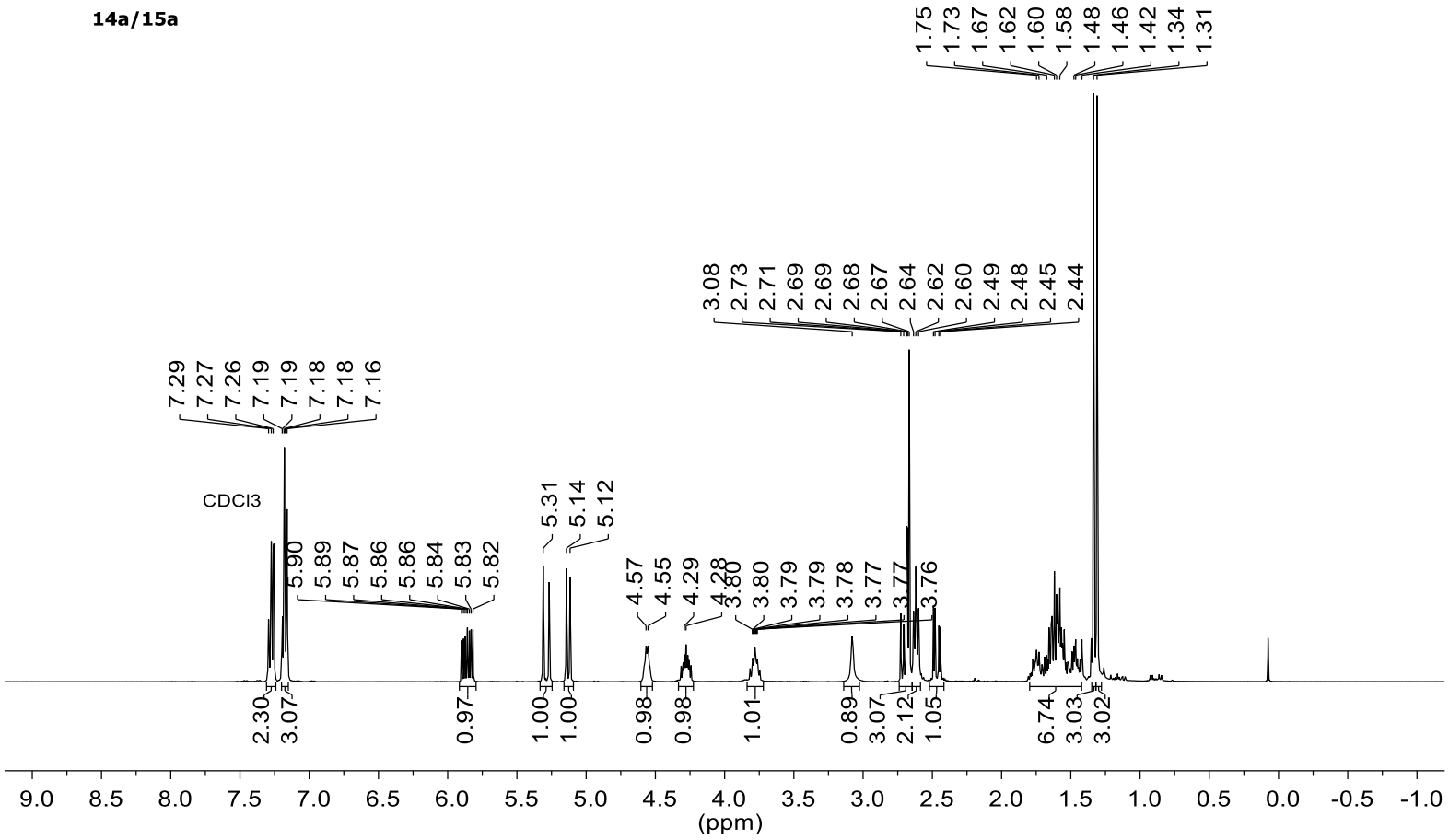
12a/13a

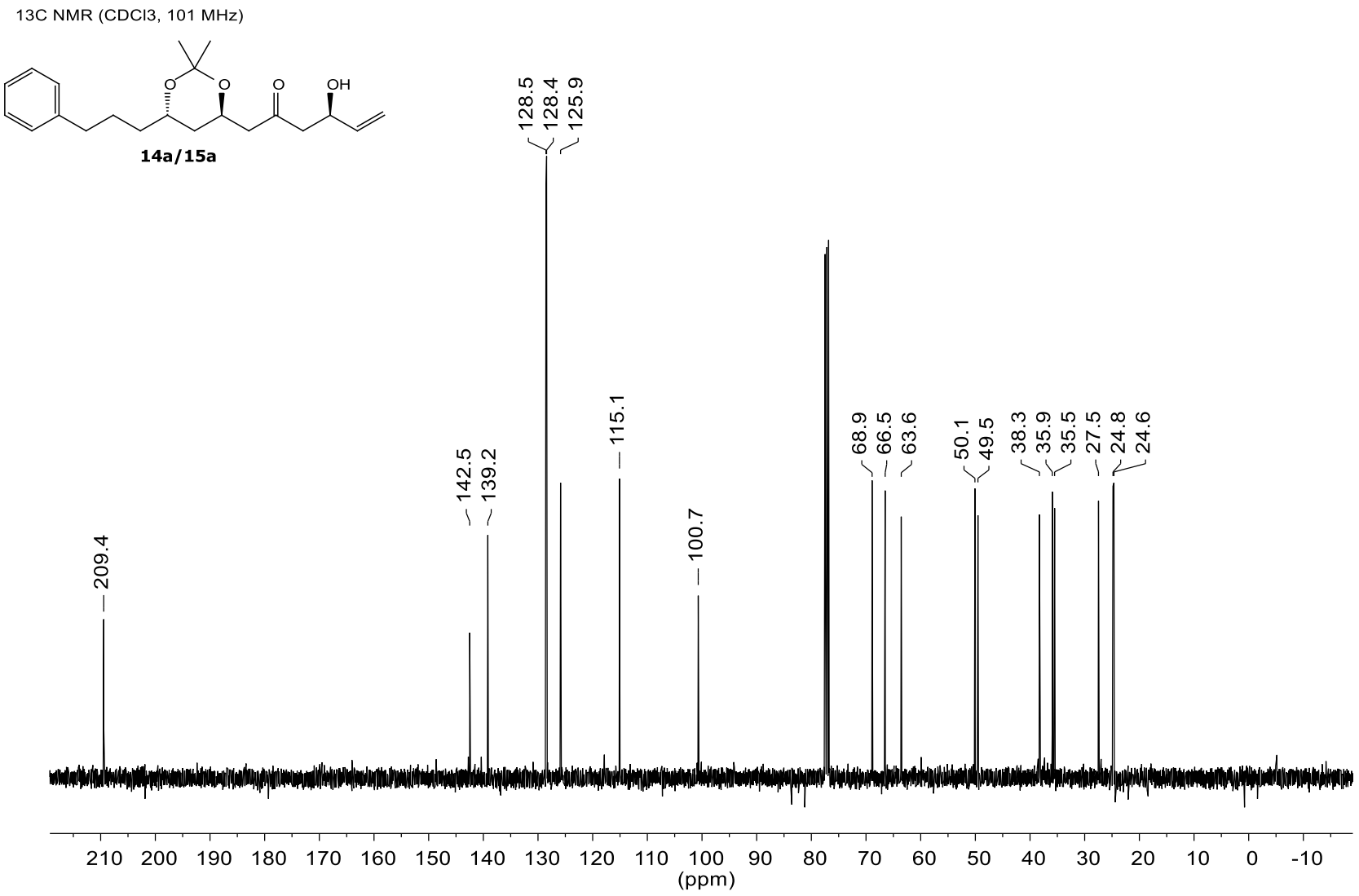


1H NMR (CDCl3, 400 MHz)

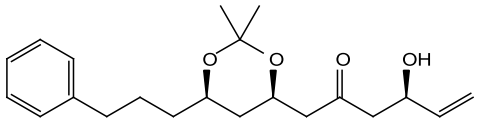


14a/15a

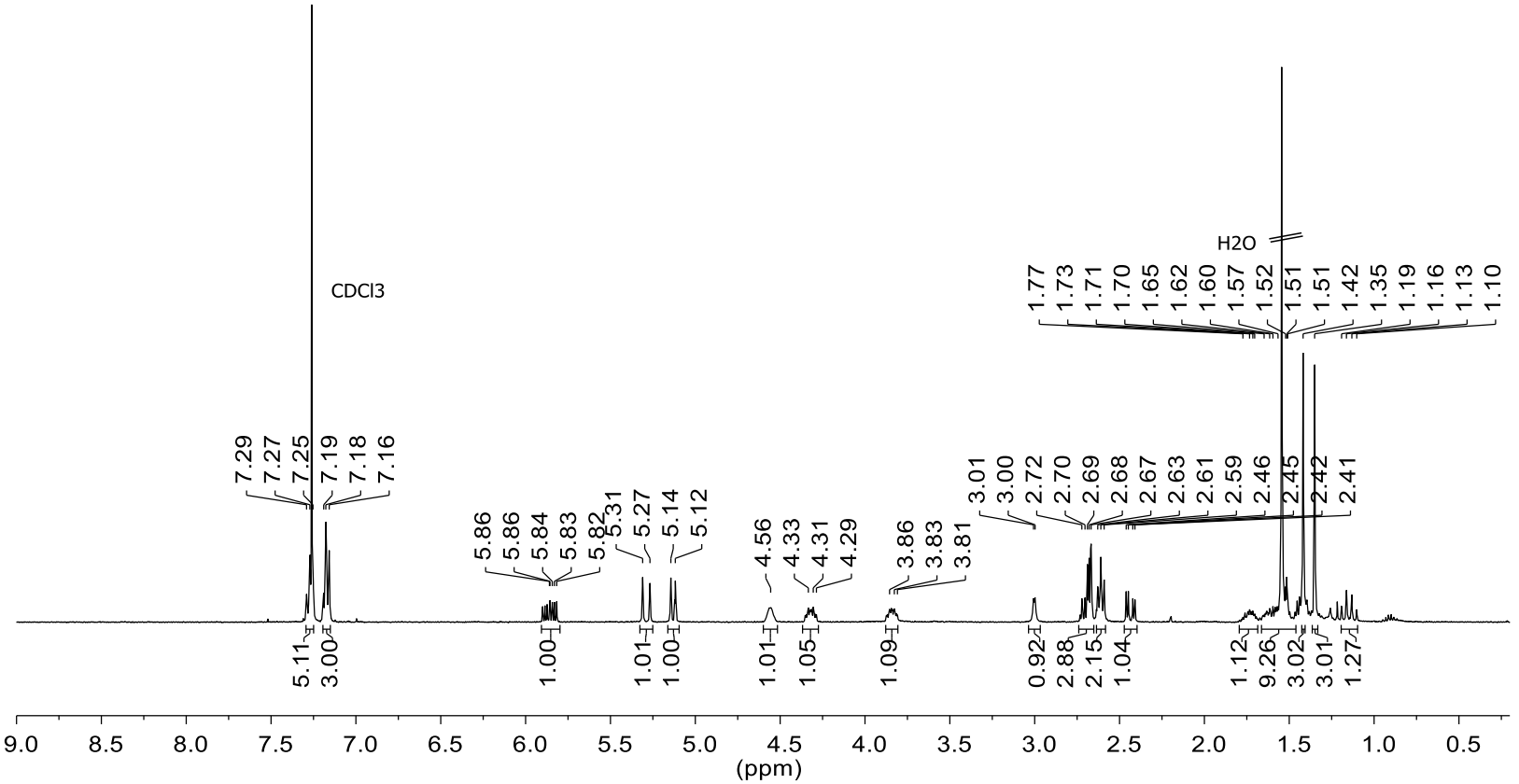



13C NMR (CDCl3, 101 MHz)
O
O
O
OH
14a/15a
209.4
142.5
139.2
128.5
128.4
125.9
115.1
100.7
68.9
66.5
63.6
50.1
49.5
38.3
35.9
35.5
27.5
24.8
24.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

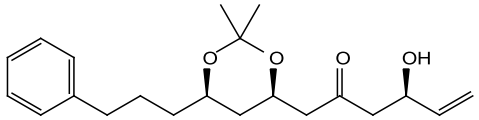
1H NMR (CDCl3, 400 MHz)



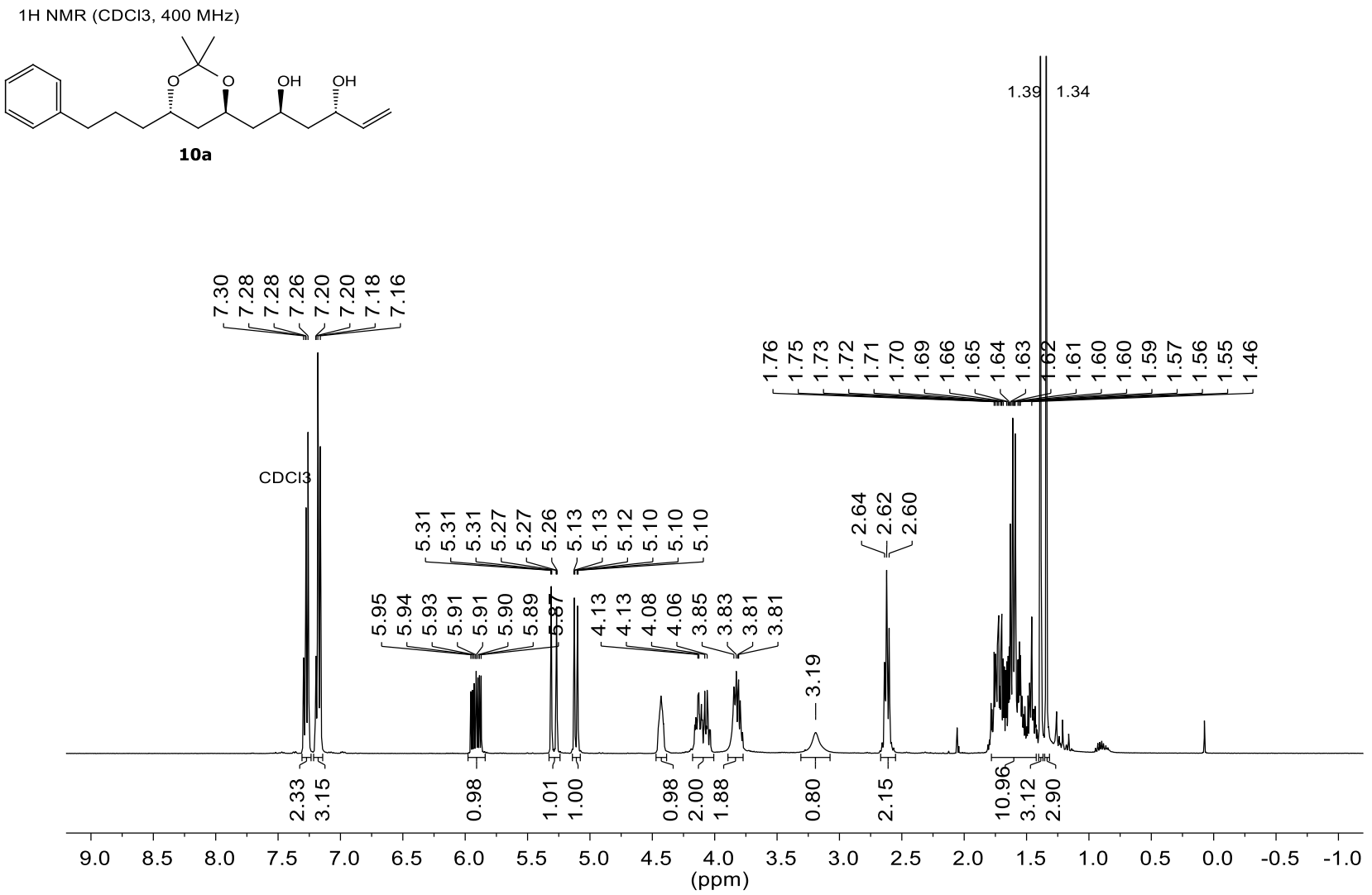
16a/17a



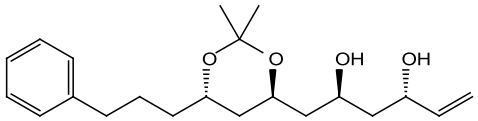
13C NMR (CDCl3, 101 MHz)



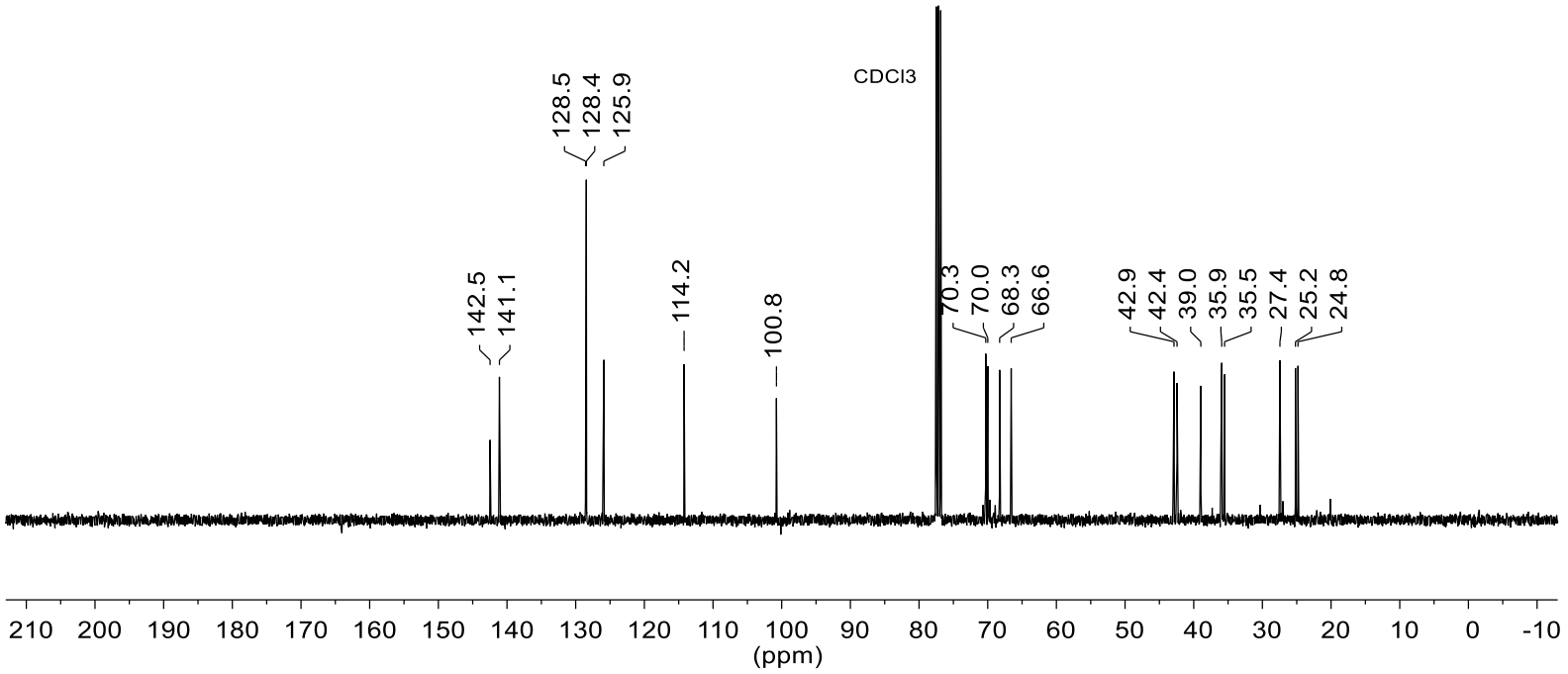
16a/17a


1H NMR (CDCl3, 400 MHz)
O
O
OH
OH
10a
7.30
7.28
7.28
7.26
7.20
7.20
7.18
7.16
CDCl3
5.31
5.31
5.31
5.27
5.27
5.26
5.13
5.13
5.12
5.10
5.10
5.10
5.95
5.94
5.93
5.91
5.91
5.90
5.89
5.87
4.13
4.13
4.08
4.06
3.85
3.83
3.81
3.81
3.19
2.64
2.62
2.60
1.76
1.75
1.73
1.72
1.71
1.70
1.69
1.66
1.65
1.64
1.63
1.62
1.61
1.60
1.60
1.59
1.57
1.56
1.55
1.46
1.39
1.34
2.33
3.15
0.98
1.01
1.00
0.98
2.00
1.88
0.80
2.15
10.96
3.12
2.90
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
(ppm)

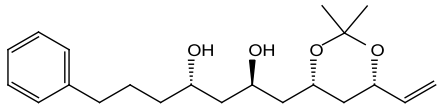
13C NMR (CDCl3, 101 MHz)



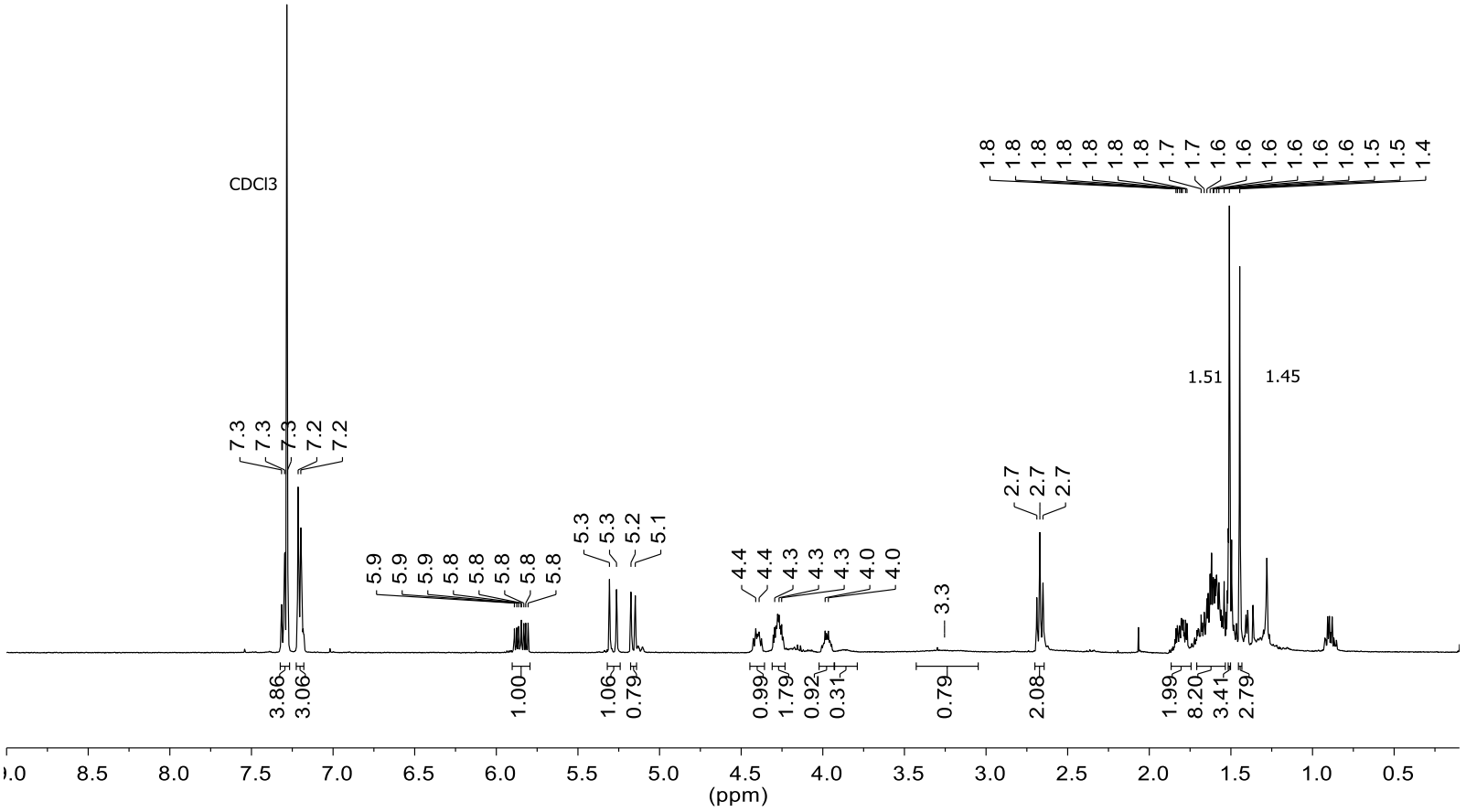
10a

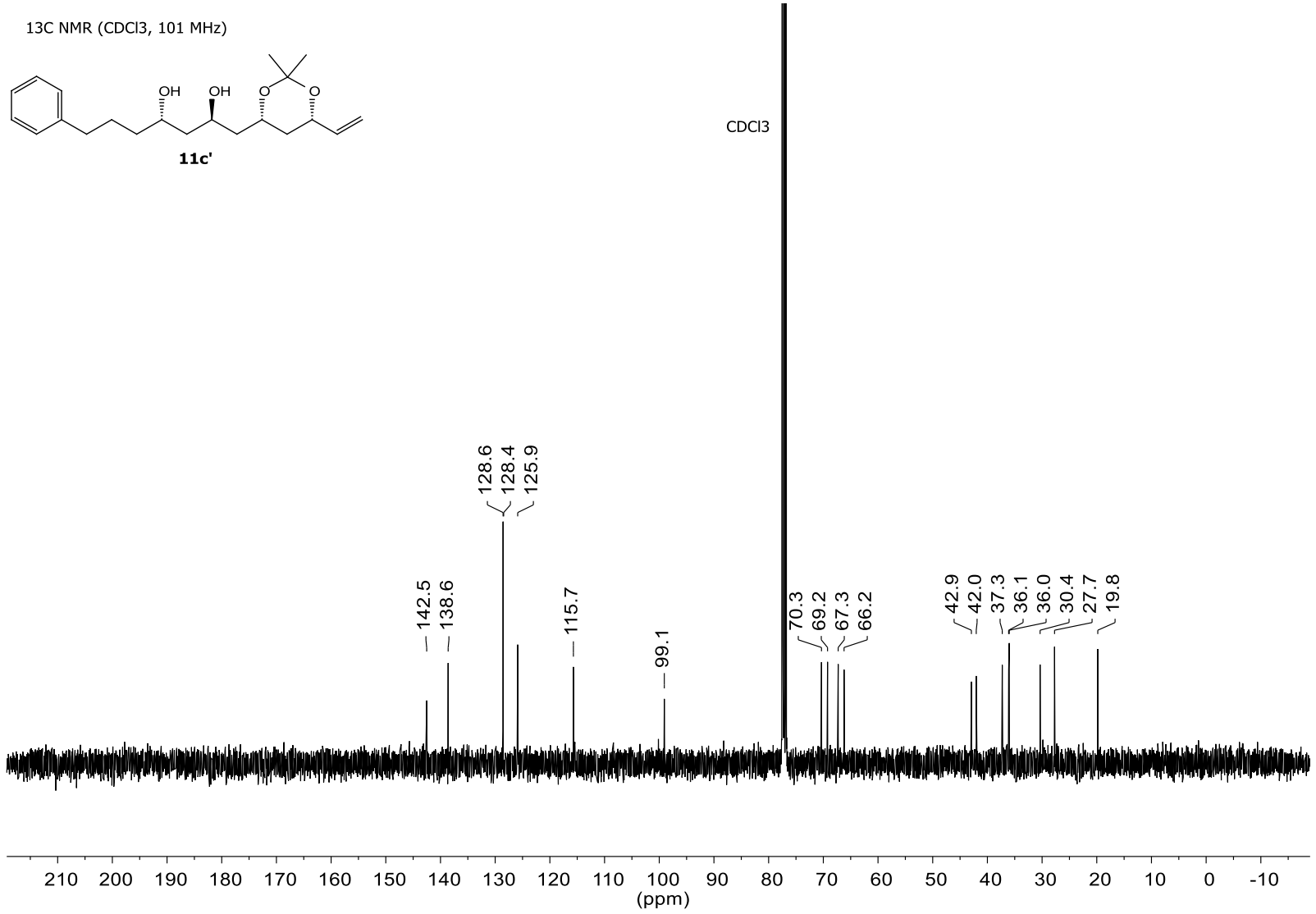


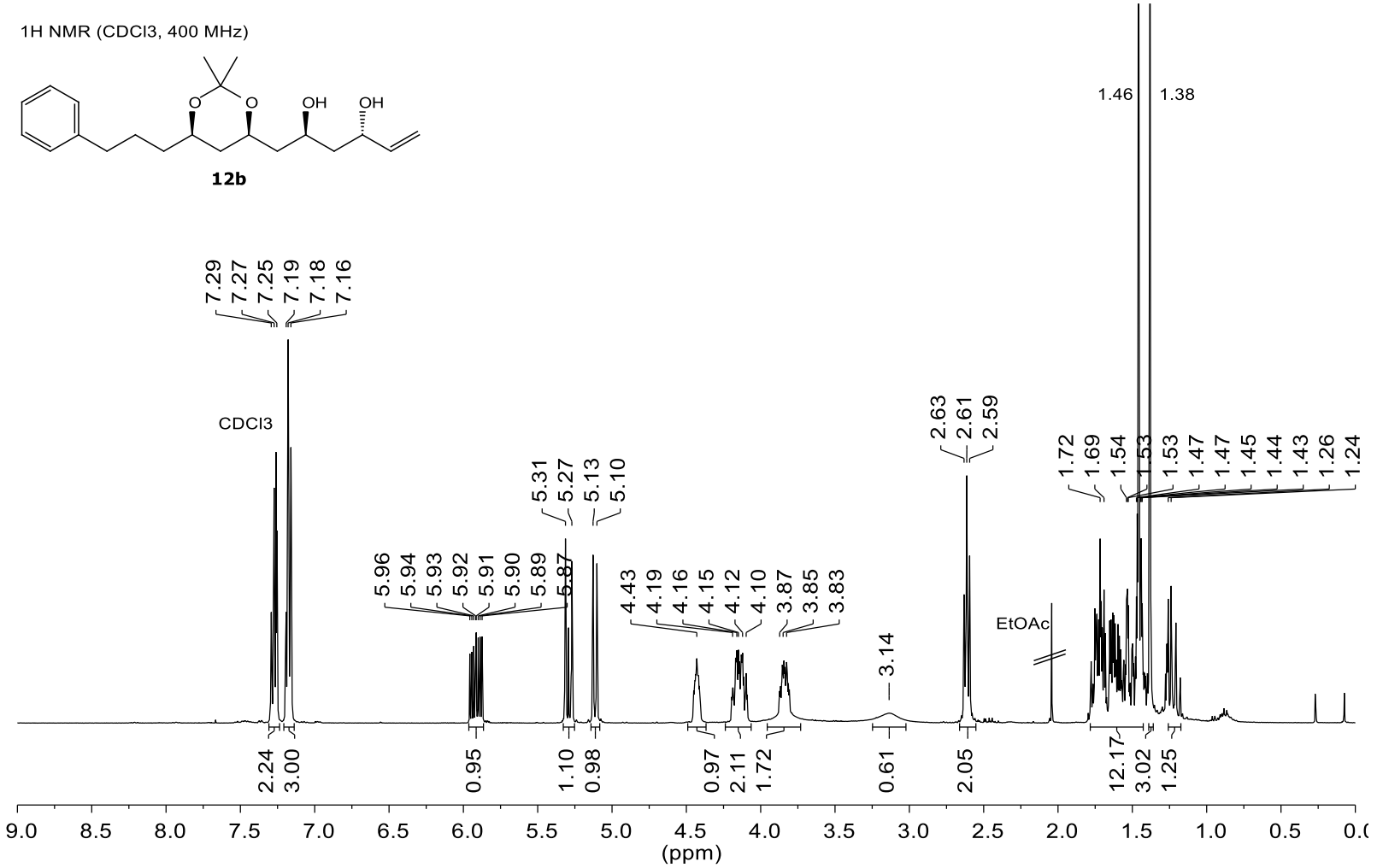
1H-NMR (CDCl3, 400 MHz)

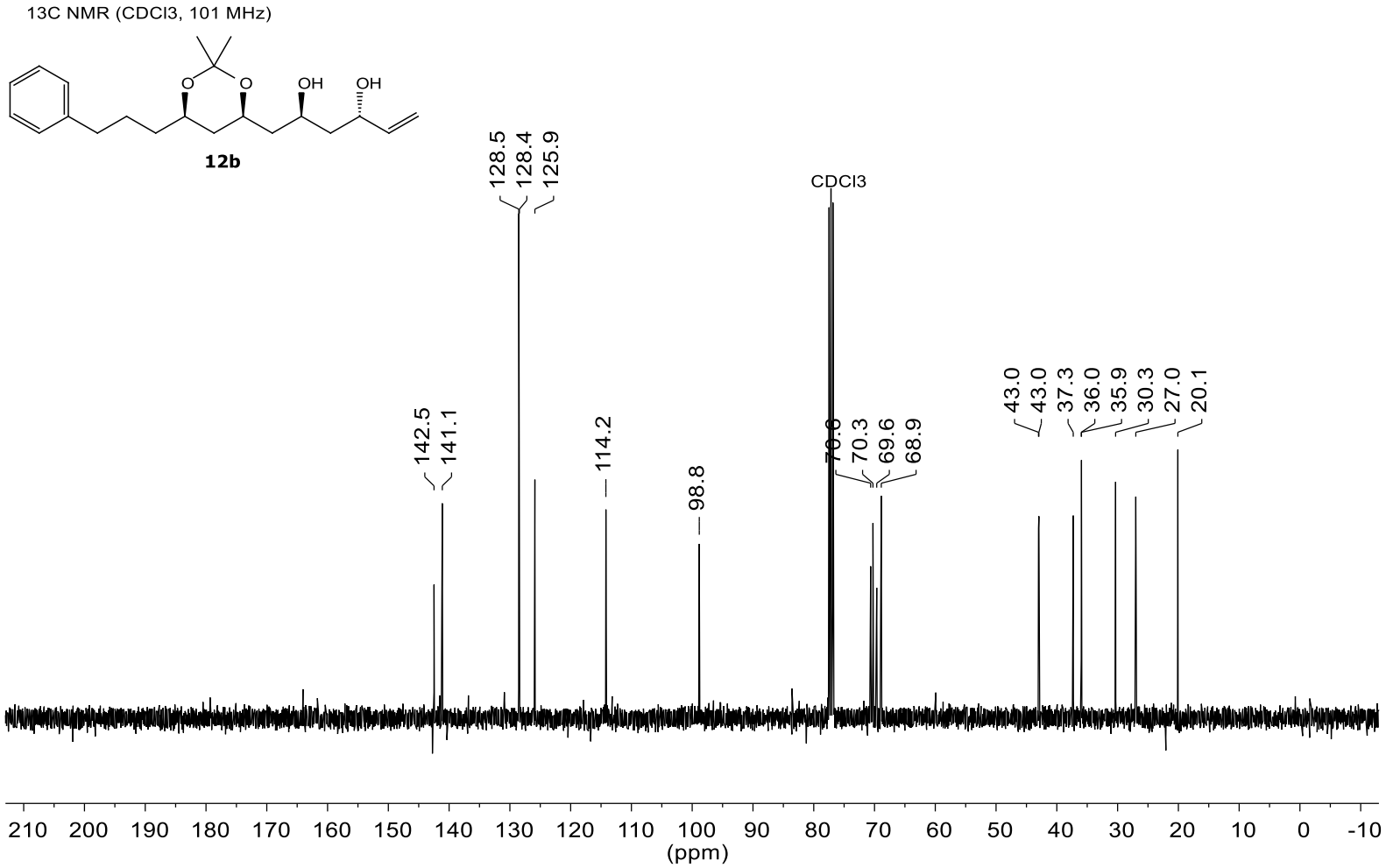


11c'

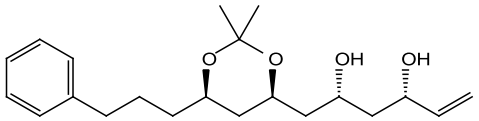



13C NMR (CDCl3, 101 MHz)
OH
OH
O
O
11c'
CDCl3
142.5
138.6
128.6
128.4
125.9
115.7
99.1
70.3
69.2
67.3
66.2
42.9
42.0
37.3
36.1
36.0
30.4
27.7
19.8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

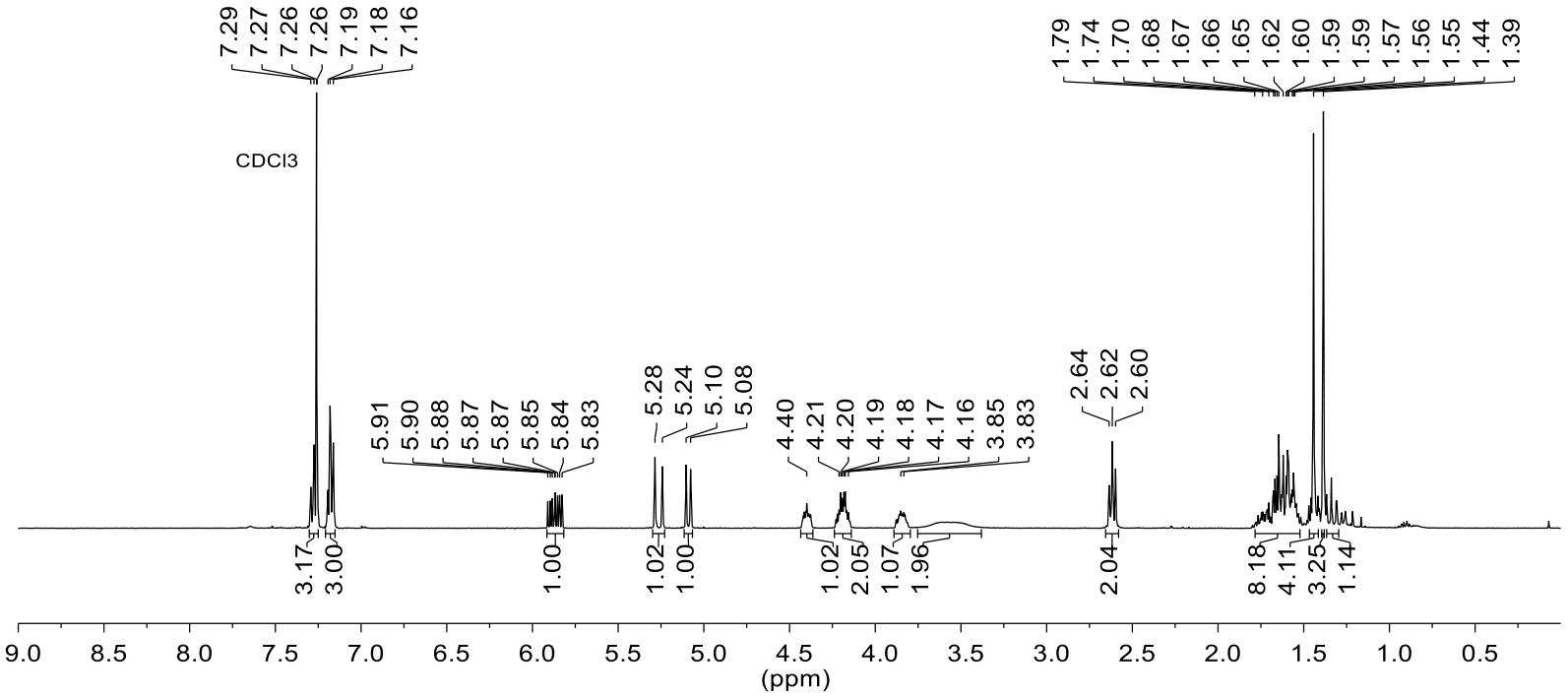

1H NMR (CDCl3, 400 MHz)
O
O
OH
OH
12b
7.29
7.27
7.25
7.19
7.18
7.16
CDCl3
5.96
5.94
5.93
5.92
5.91
5.90
5.89
5.87
5.31
5.27
5.13
5.10
4.43
4.19
4.16
4.15
4.12
4.10
3.87
3.85
3.83
3.14
2.63
2.61
2.59
EtOAc
1.72
1.69
1.54
1.53
1.53
1.47
1.47
1.45
1.44
1.43
1.26
1.24
1.46
1.38
2.24
3.00
0.95
1.10
0.98
0.97
2.11
1.72
0.61
2.05
12.17
3.02
1.25
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

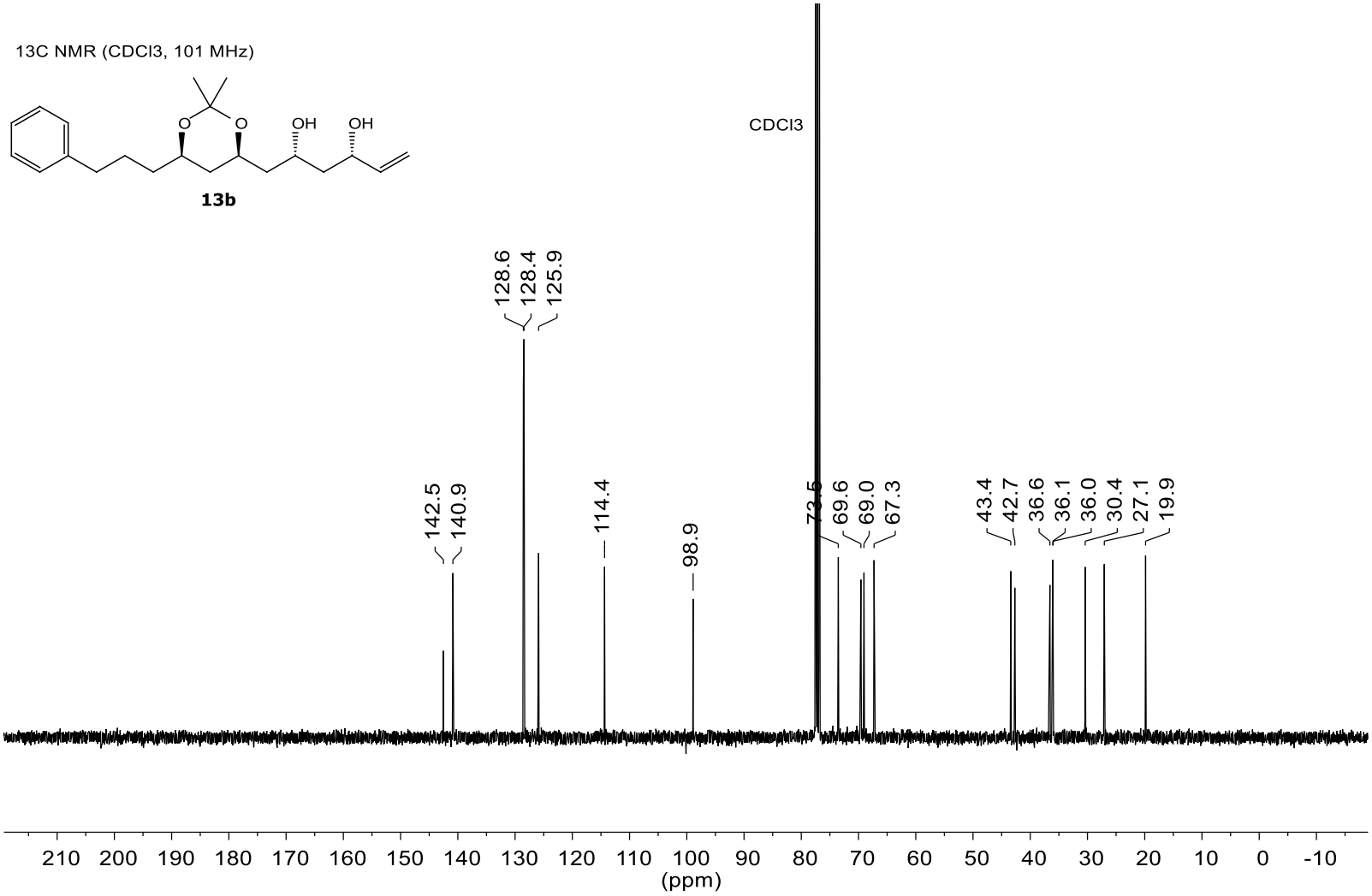

13C NMR (CDCl3, 101 MHz)
O
O
OH
OH
12b
128.5
128.4
125.9
CDCl3
142.5
141.1
114.2
98.8
70.3
69.6
68.9
43.0
43.0
37.3
36.0
35.9
30.3
27.0
20.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

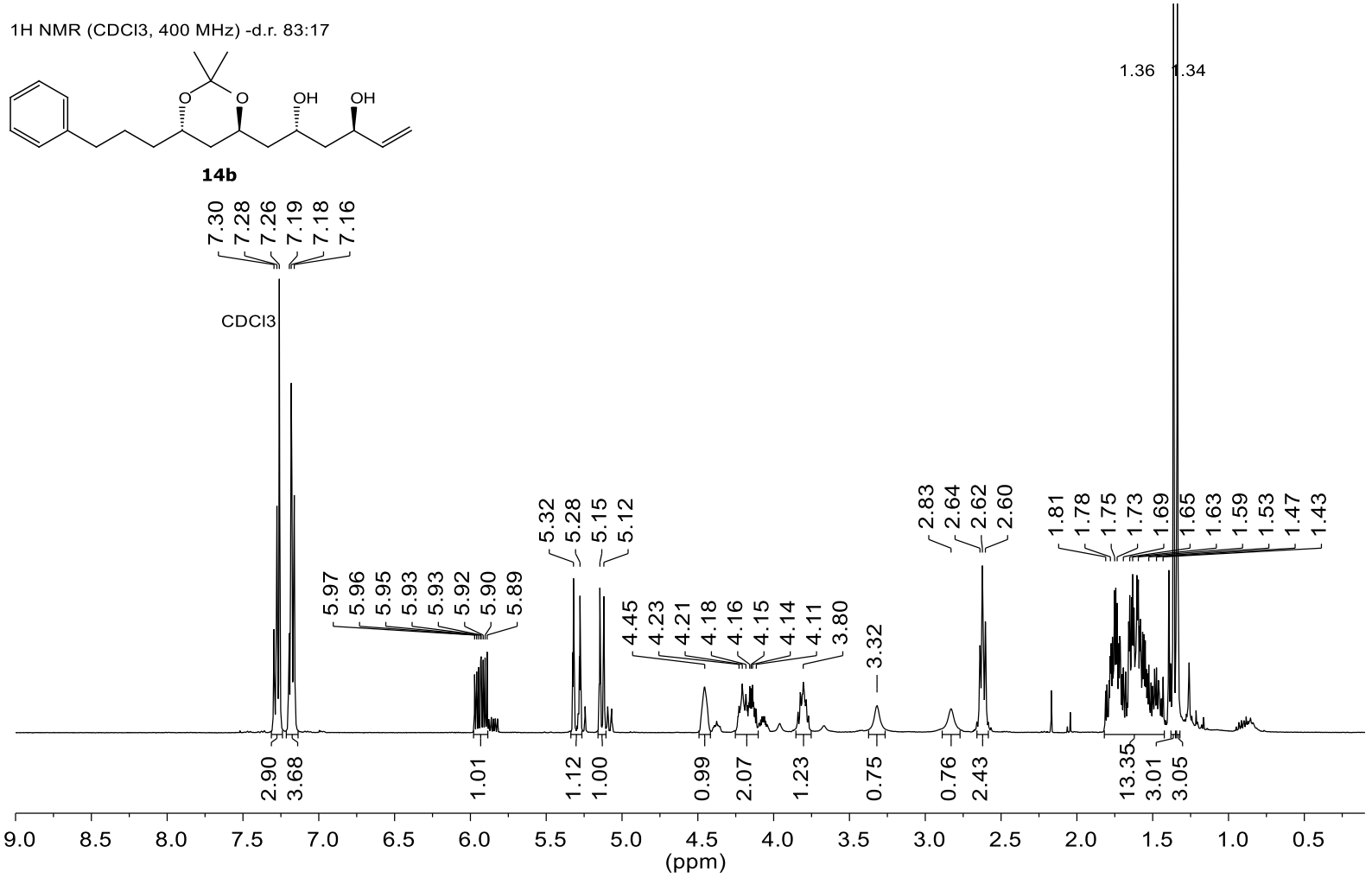
1H NMR (CDCl3, 400 MHz)

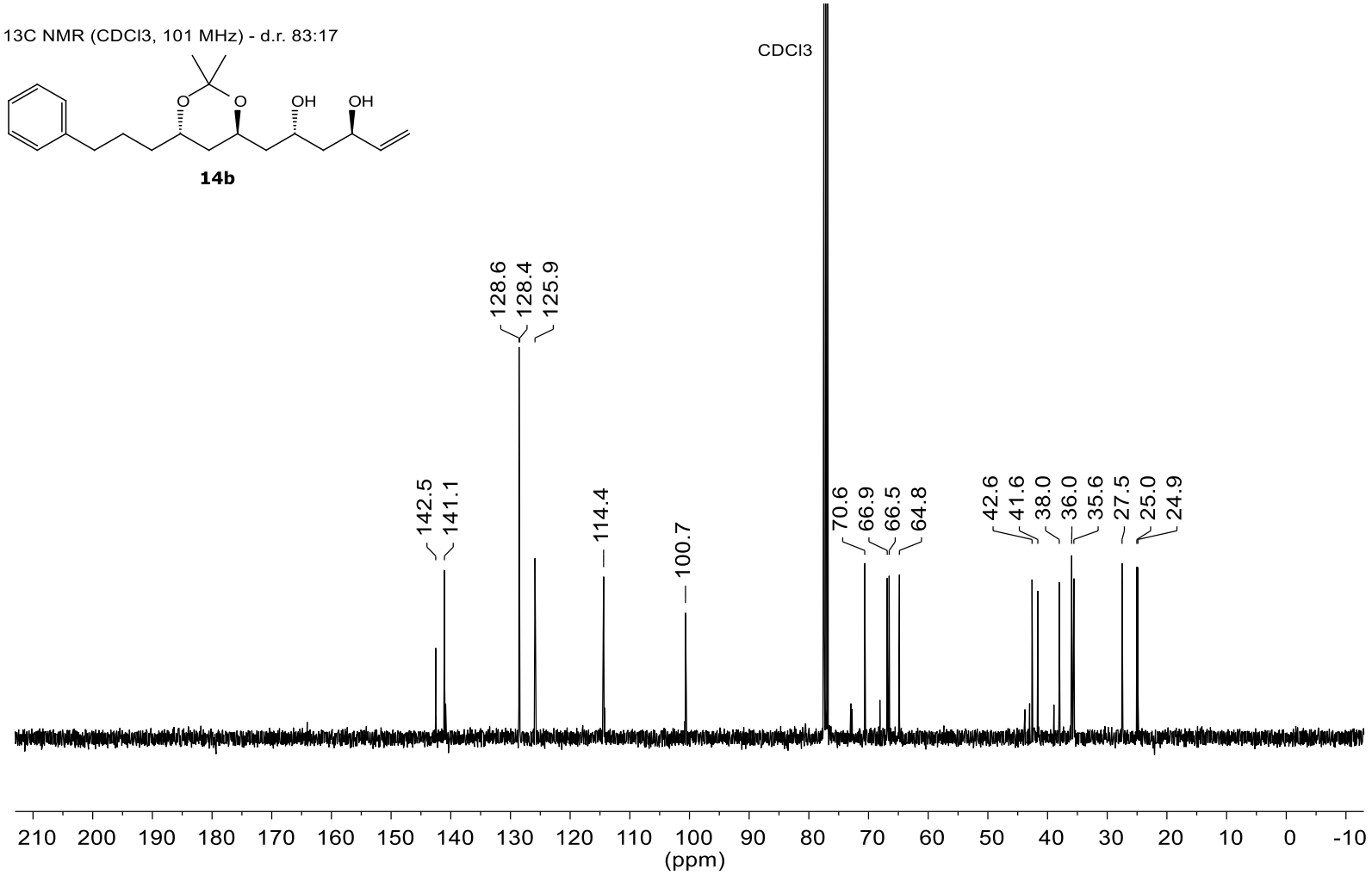


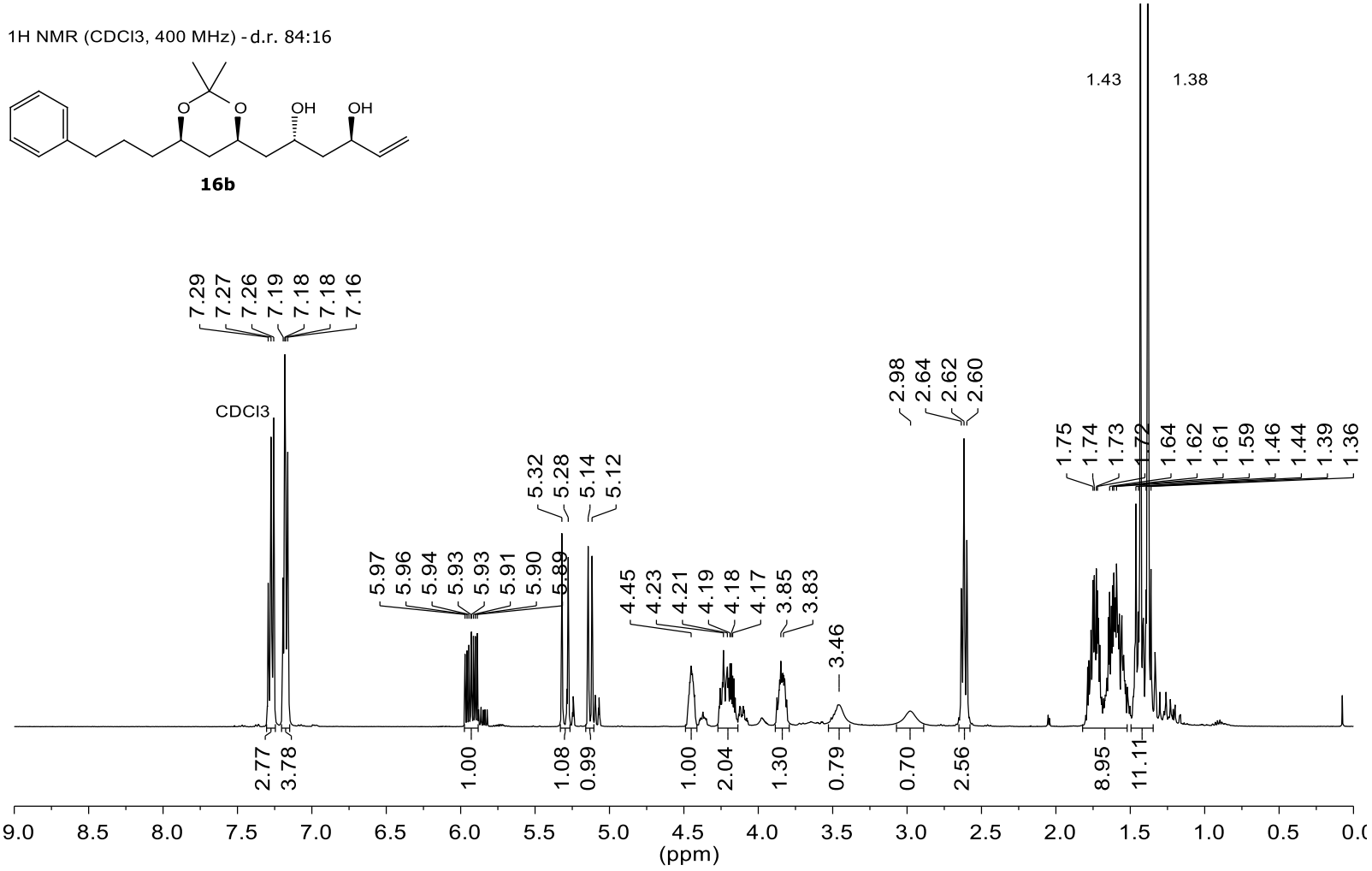
13b

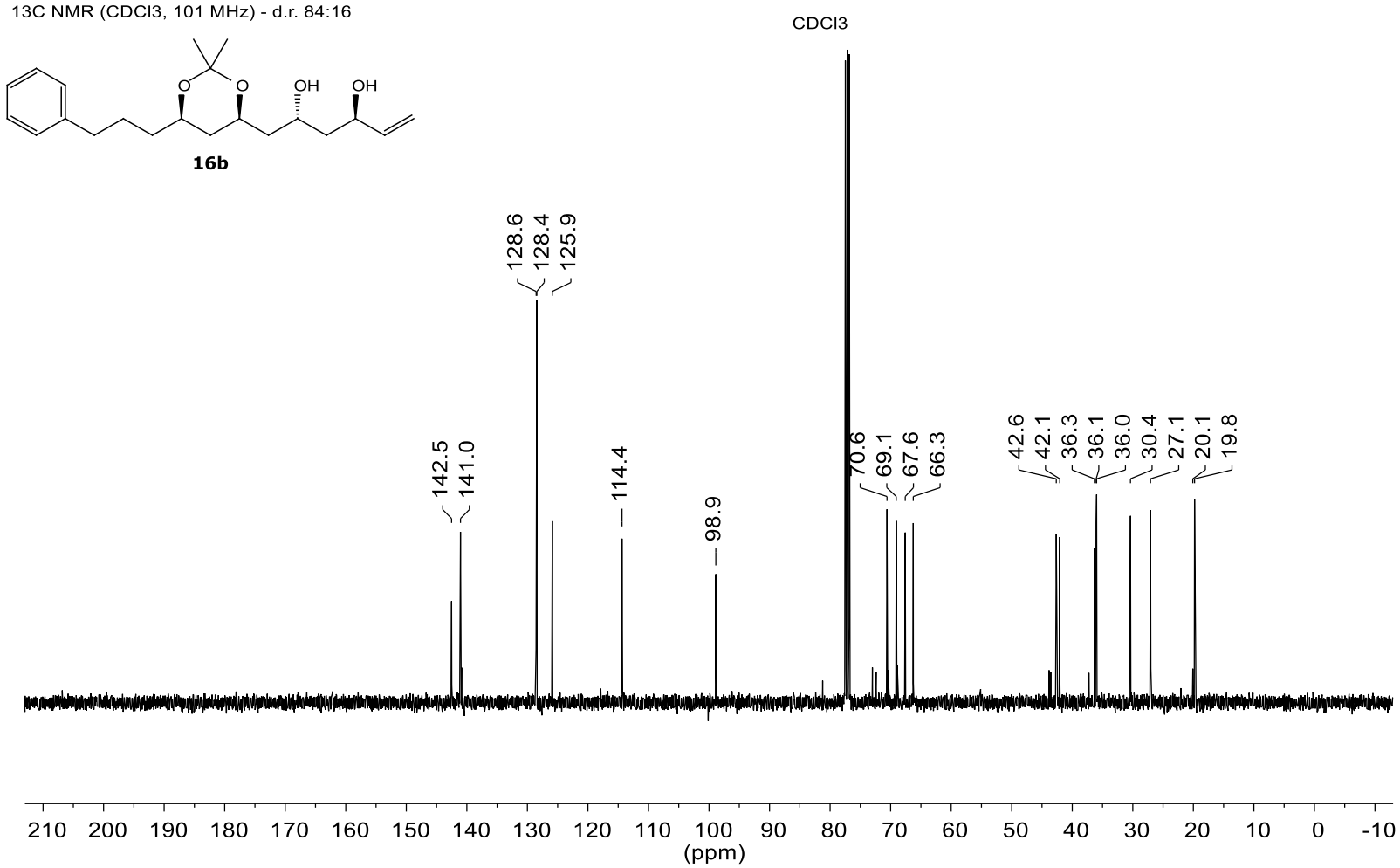


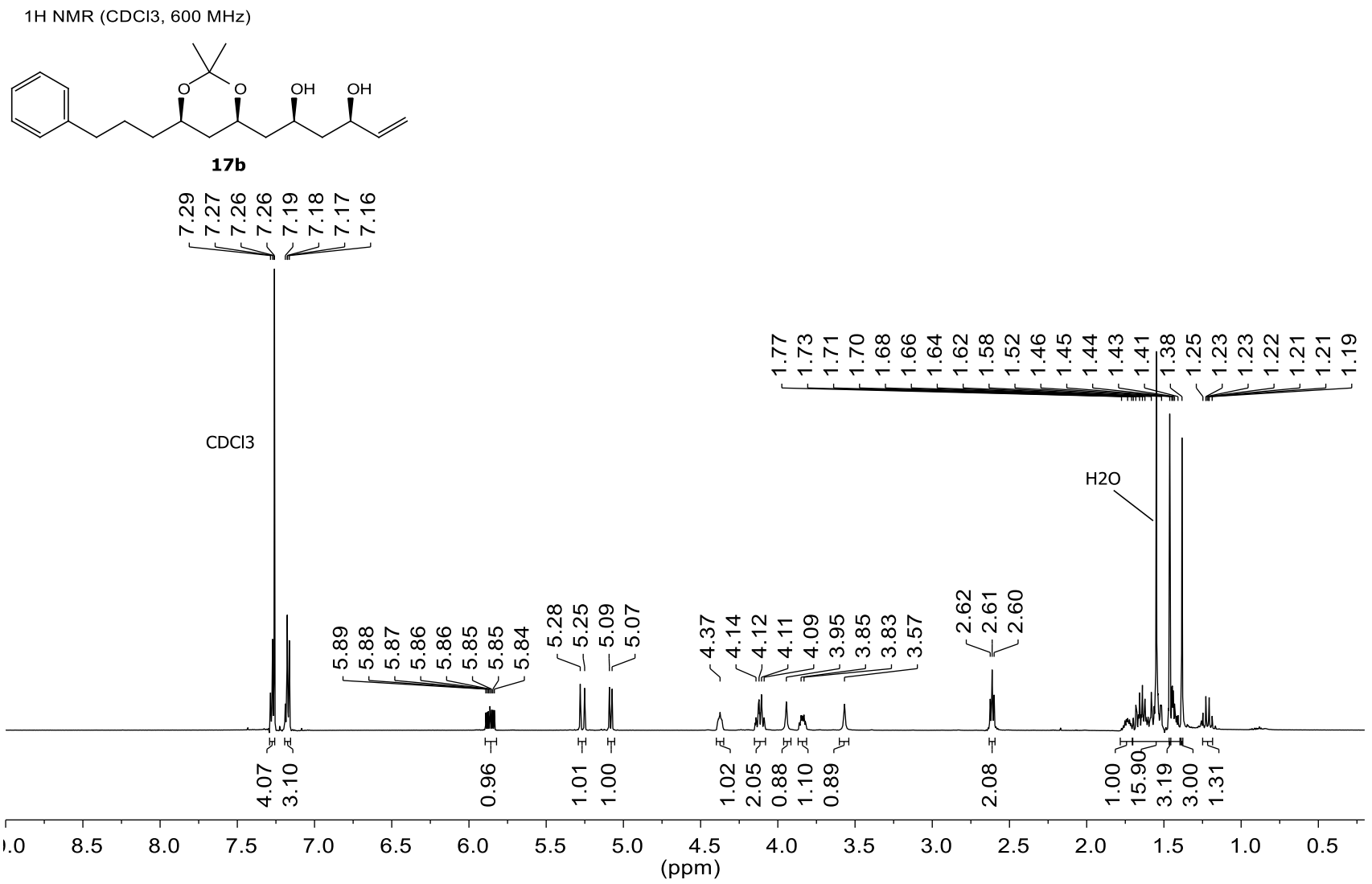

13C NMR (CDCl3, 101 MHz)
O
O
OH
OH
13b
CDCl3
128.6
128.4
125.9
142.5
140.9
114.4
98.9
73.5
69.6
69.0
67.3
43.4
42.7
36.6
36.1
36.0
30.4
27.1
19.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

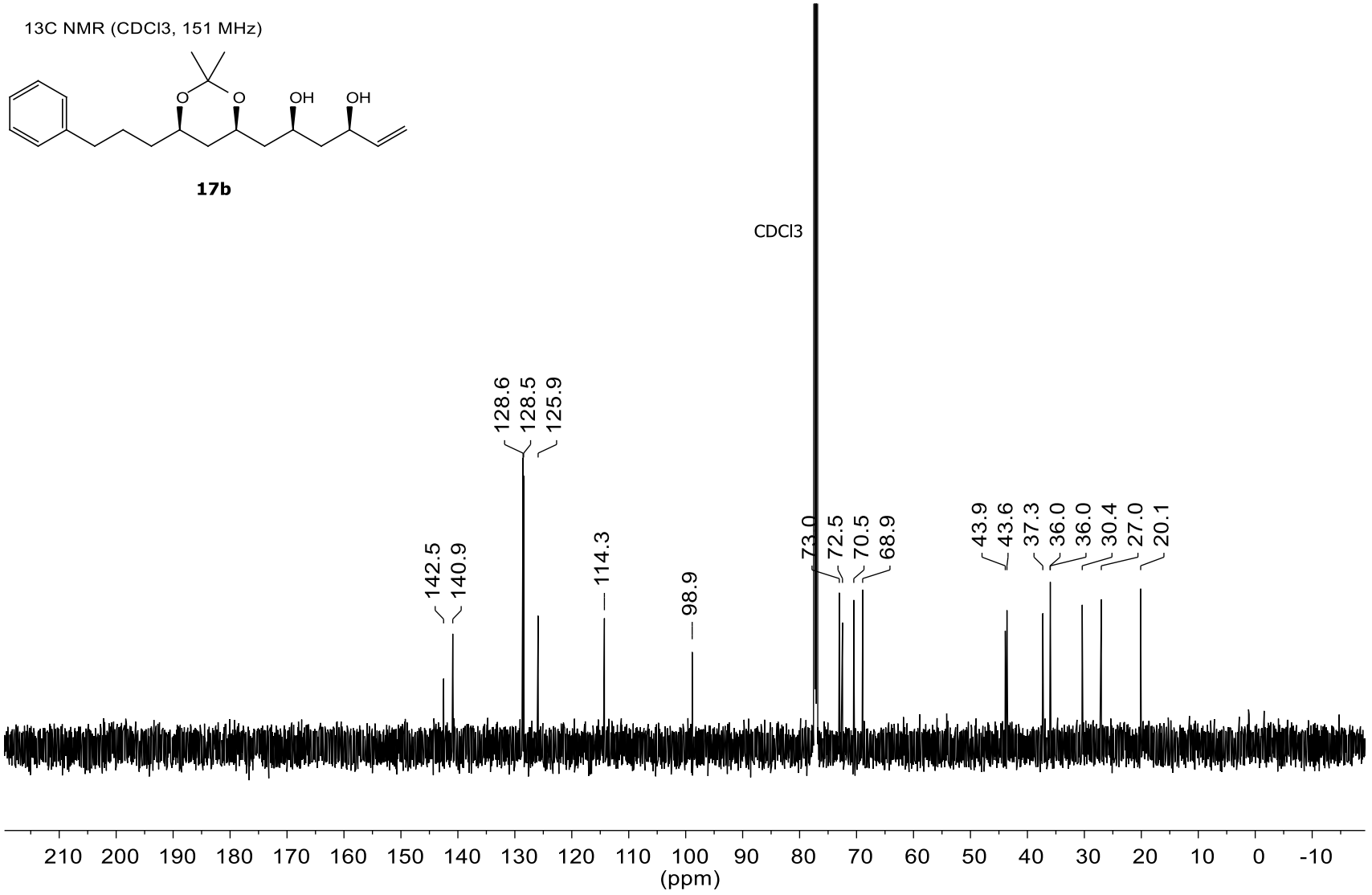

1H NMR (CDCl3, 400 MHz) -d.r. 83:17
O
O
OH
OH
14b
7.30
7.28
7.26
7.19
7.18
7.16
CDCl3
5.97
5.96
5.95
5.93
5.93
5.92
5.90
5.89
5.32
5.28
5.15
5.12
4.45
4.23
4.21
4.18
4.16
4.15
4.14
4.11
3.80
3.32
2.83
2.64
2.62
2.60
1.81
1.78
1.75
1.73
1.69
1.65
1.63
1.59
1.53
1.47
1.43
1.36
1.34
2.90
3.68
1.01
1.12
1.00
0.99
2.07
1.23
0.75
0.76
2.43
13.35
3.01
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

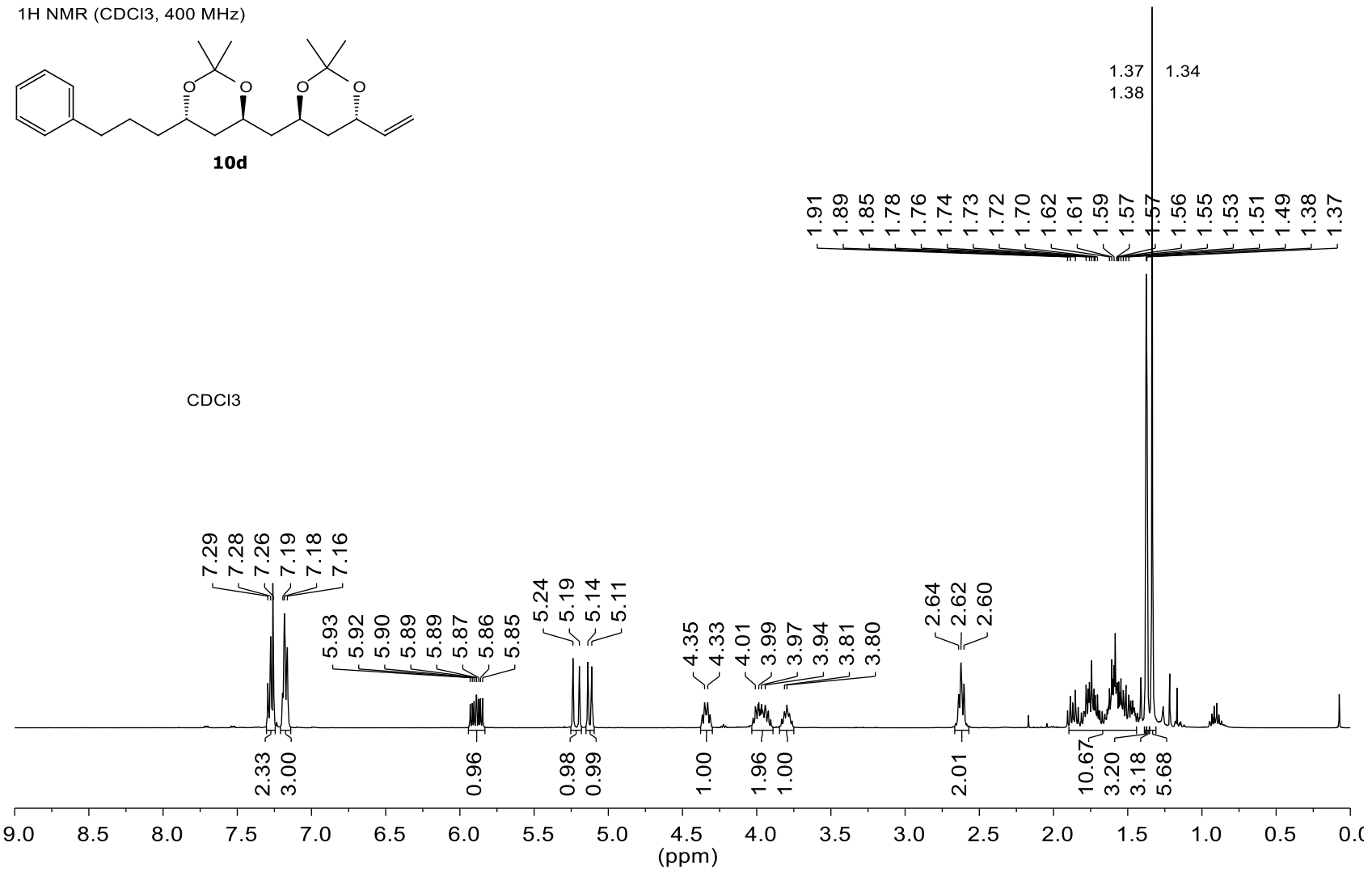

13C NMR (CDCl3, 101 MHz) - d.r. 83:17
O
O
OH
OH
14b
CDCl3
128.6
128.4
125.9
142.5
141.1
114.4
100.7
70.6
66.9
66.5
64.8
42.6
41.6
38.0
36.0
35.6
27.5
25.0
24.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)


1H NMR (CDCl3, 400 MHz) - d.r. 84:16
O
O
OH
OH
16b
7.29
7.27
7.26
7.19
7.18
7.18
7.16
CDCl3
5.97
5.96
5.94
5.93
5.93
5.91
5.90
5.89
5.32
5.28
5.14
5.12
4.45
4.23
4.21
4.19
4.18
4.17
3.85
3.83
3.46
2.98
2.64
2.62
2.60
1.75
1.74
1.73
1.72
1.64
1.62
1.61
1.59
1.46
1.44
1.39
1.36
1.43
1.38
2.77
3.78
1.00
1.08
0.99
1.00
2.04
1.30
0.79
0.70
2.56
8.95
11.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

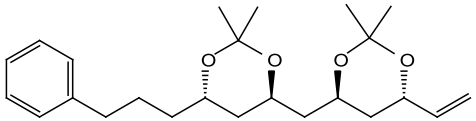

13C NMR (CDCl3, 101 MHz) - d.r. 84:16
O
O
OH
OH
16b
CDCl3
128.6
128.4
125.9
142.5
141.0
114.4
98.9
70.6
69.1
67.6
66.3
42.6
42.1
36.3
36.1
36.0
30.4
27.1
20.1
19.8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)


1H NMR (CDCl3, 600 MHz)
O
O
OH
OH
17b
7.29
7.27
7.26
7.26
7.19
7.18
7.17
7.16
CDCl3
1.77
1.73
1.71
1.70
1.68
1.66
1.64
1.62
1.58
1.52
1.46
1.45
1.44
1.43
1.41
1.38
1.25
1.23
1.23
1.22
1.21
1.21
1.19
H2O
5.89
5.88
5.87
5.86
5.86
5.85
5.85
5.84
5.28
5.25
5.09
5.07
4.37
4.14
4.12
4.11
4.09
3.95
3.85
3.83
3.57
2.62
2.61
2.60
4.07
3.10
0.96
1.01
1.00
1.02
2.05
0.88
1.10
0.89
2.08
1.00
15.90
3.19
3.00
1.31
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

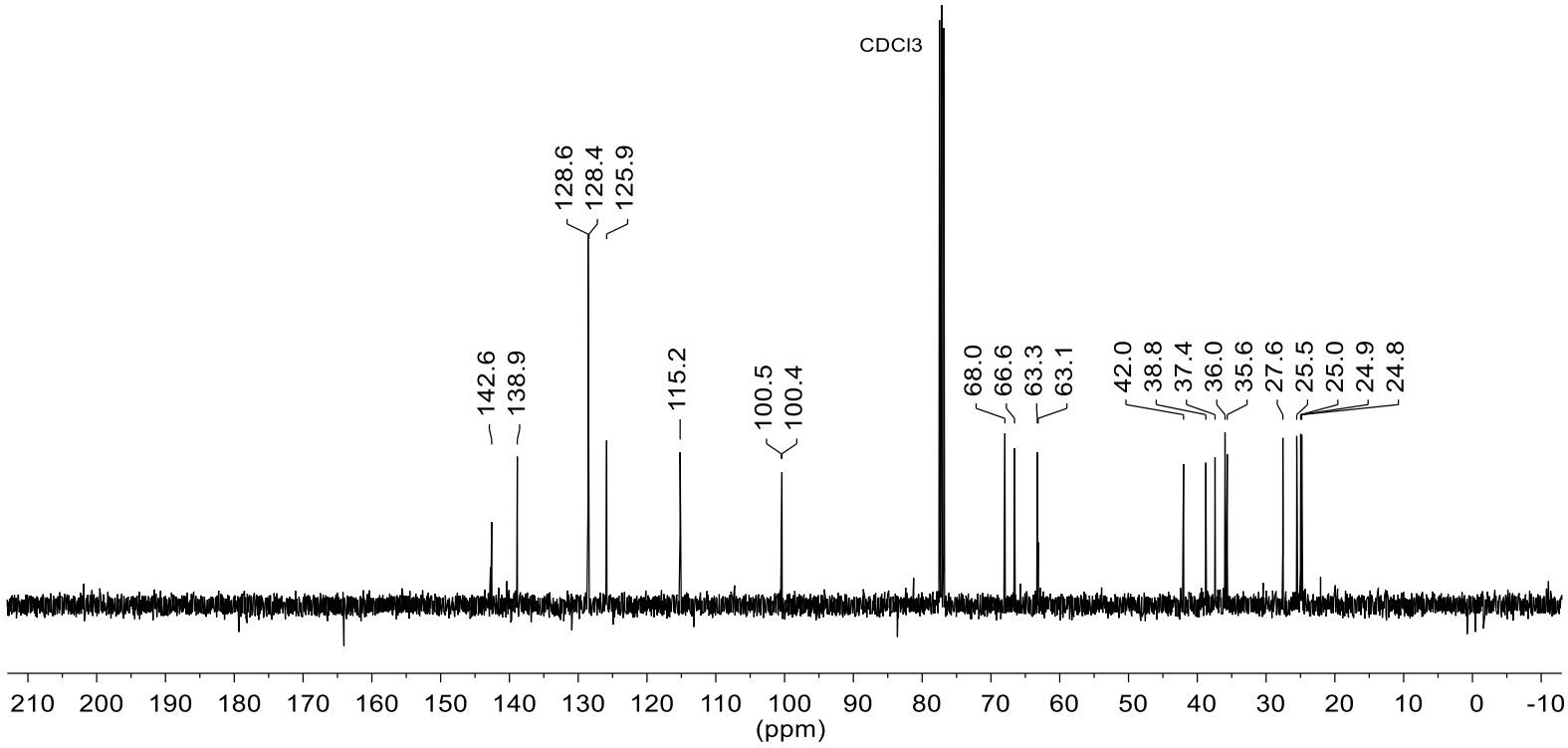

13C NMR (CDCl3, 151 MHz)
O
O
OH
OH
17b
CDCl3
128.6
128.5
125.9
142.5
140.9
114.3
98.9
73.0
72.5
70.5
68.9
43.9
43.6
37.3
36.0
36.0
30.4
27.0
20.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

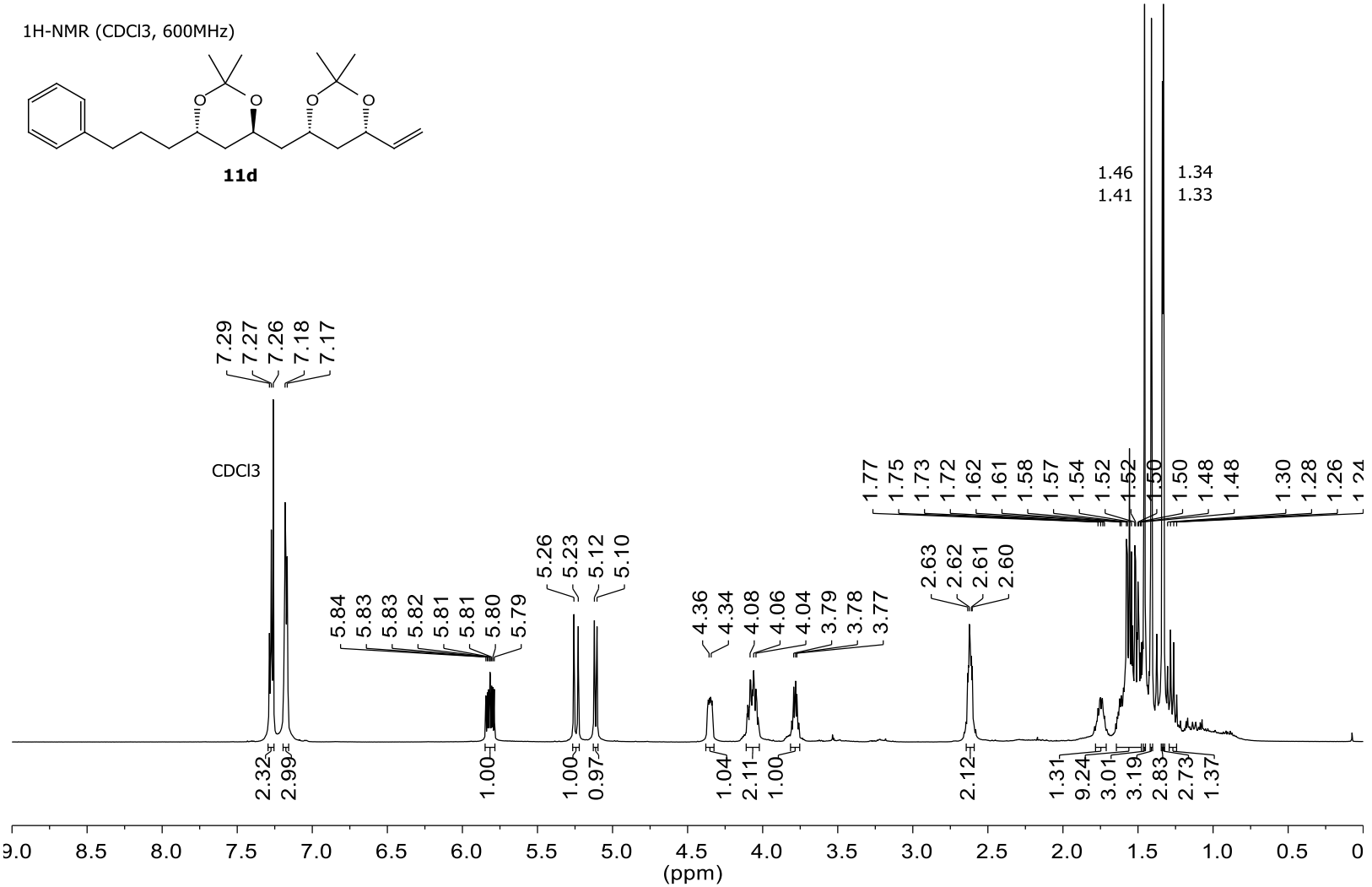

1H NMR (CDCl3, 400 MHz)
10d
CDCl3
1.37
1.38
1.34
1.91
1.89
1.85
1.78
1.76
1.74
1.73
1.72
1.70
1.62
1.61
1.59
1.57
1.57
1.56
1.55
1.53
1.51
1.49
1.38
1.37
7.29
7.28
7.26
7.19
7.18
7.16
5.93
5.92
5.90
5.89
5.89
5.87
5.86
5.85
5.24
5.19
5.14
5.11
4.35
4.33
4.01
3.99
3.97
3.94
3.81
3.80
2.64
2.62
2.60
2.33
3.00
0.96
0.98
0.99
1.00
1.96
1.00
2.01
10.67
3.20
3.18
5.68
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

13C NMR (CDCl3, 101 MHz)

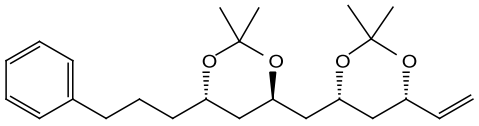


10d

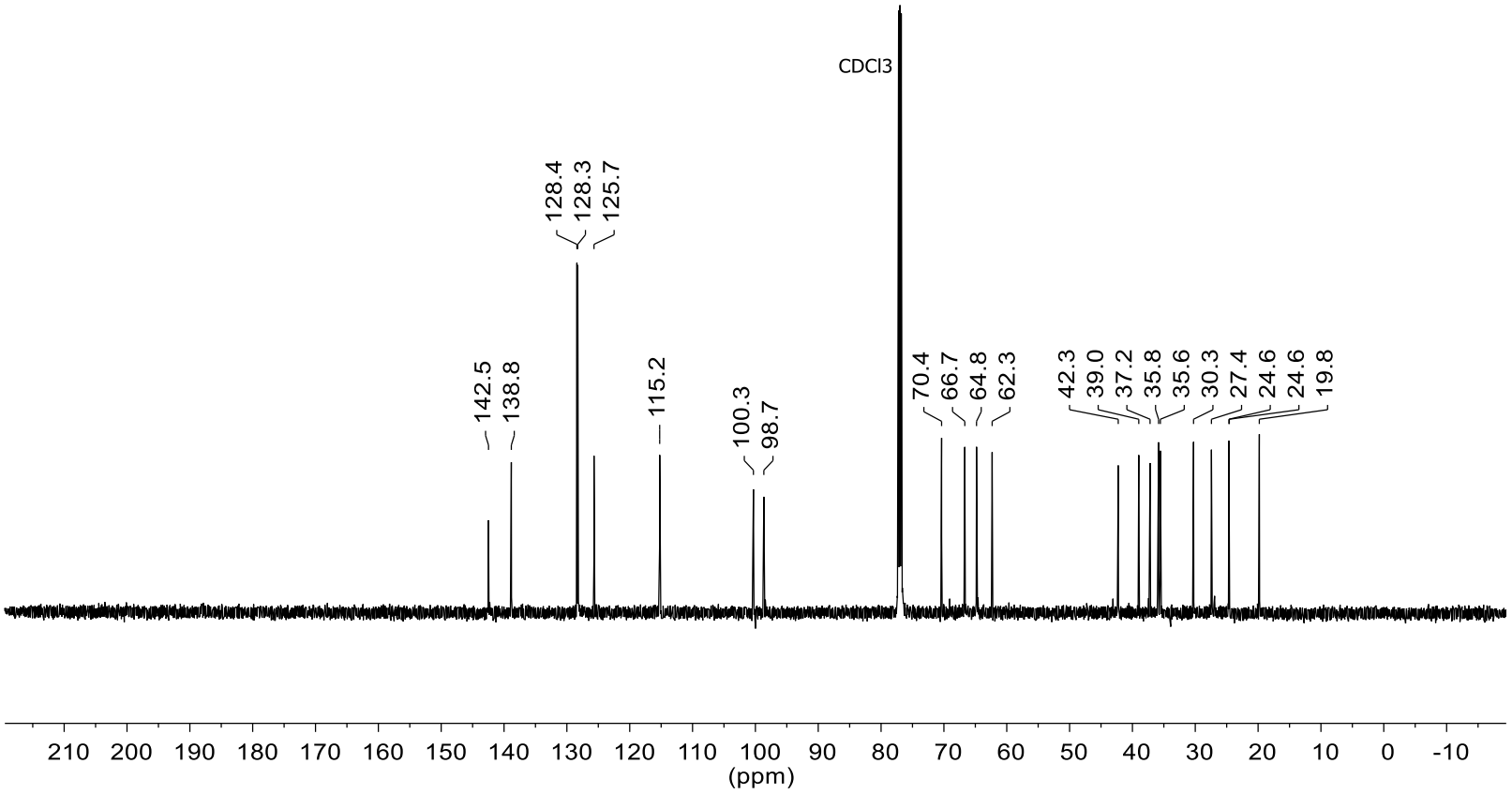


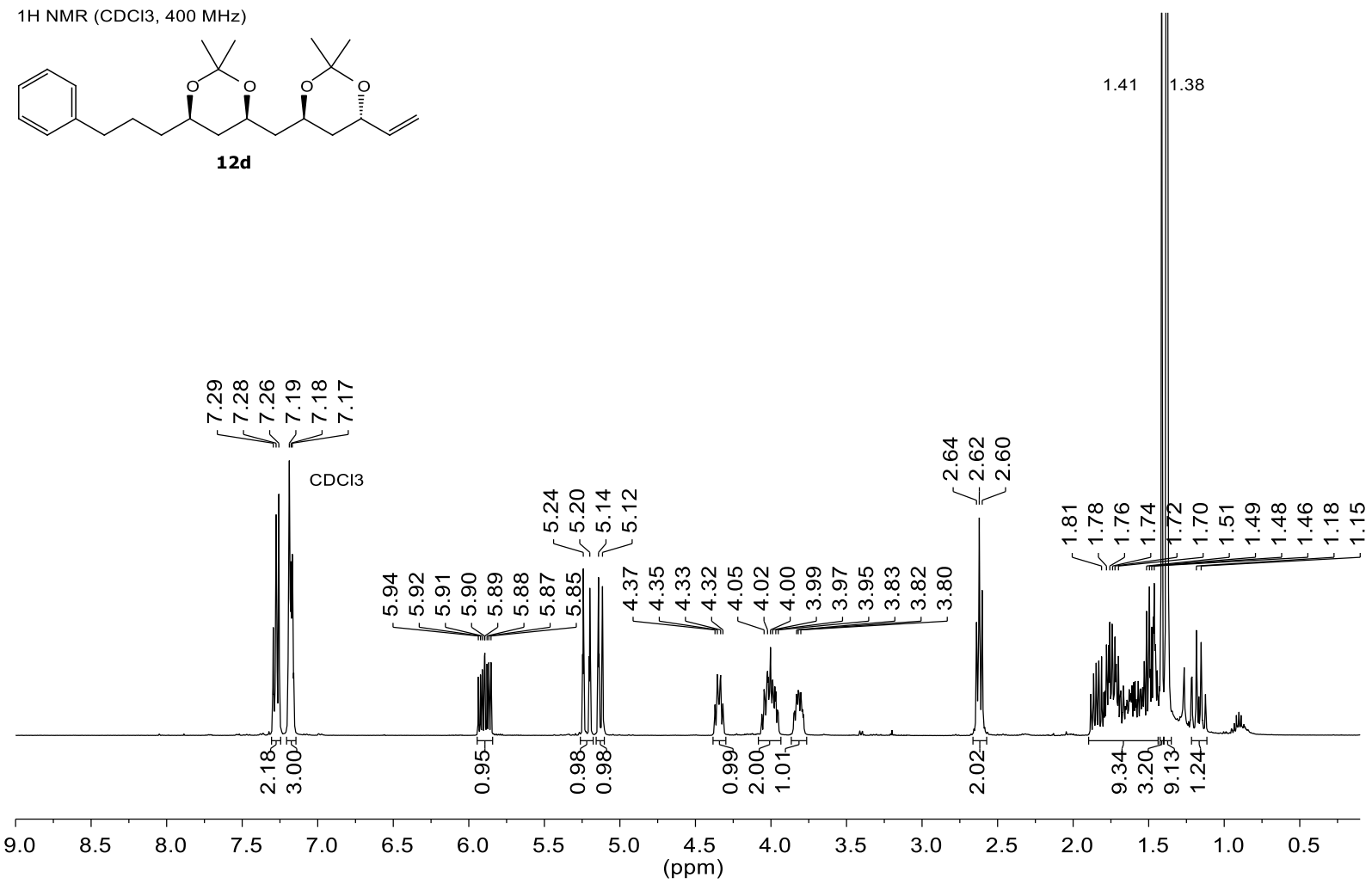

1H-NMR (CDCl3, 600MHz)
11d
CDCl3
7.29
7.27
7.26
7.18
7.17
5.84
5.83
5.83
5.82
5.81
5.81
5.80
5.79
5.26
5.23
5.12
5.10
4.36
4.34
4.08
4.06
4.04
3.79
3.78
3.77
2.63
2.62
2.61
2.60
1.77
1.75
1.73
1.72
1.62
1.61
1.58
1.57
1.54
1.52
1.52
1.50
1.50
1.48
1.48
1.46
1.41
1.34
1.33
1.30
1.28
1.26
2.32
2.99
1.00
1.00
0.97
1.04
2.11
1.00
2.12
1.31
9.24
3.01
3.19
2.83
2.73
1.37
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
(ppm)

13C-NMR (CDCl3, 151 MHz)

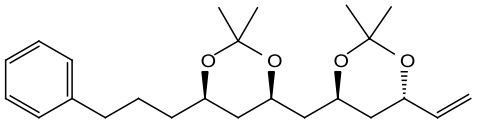


11d

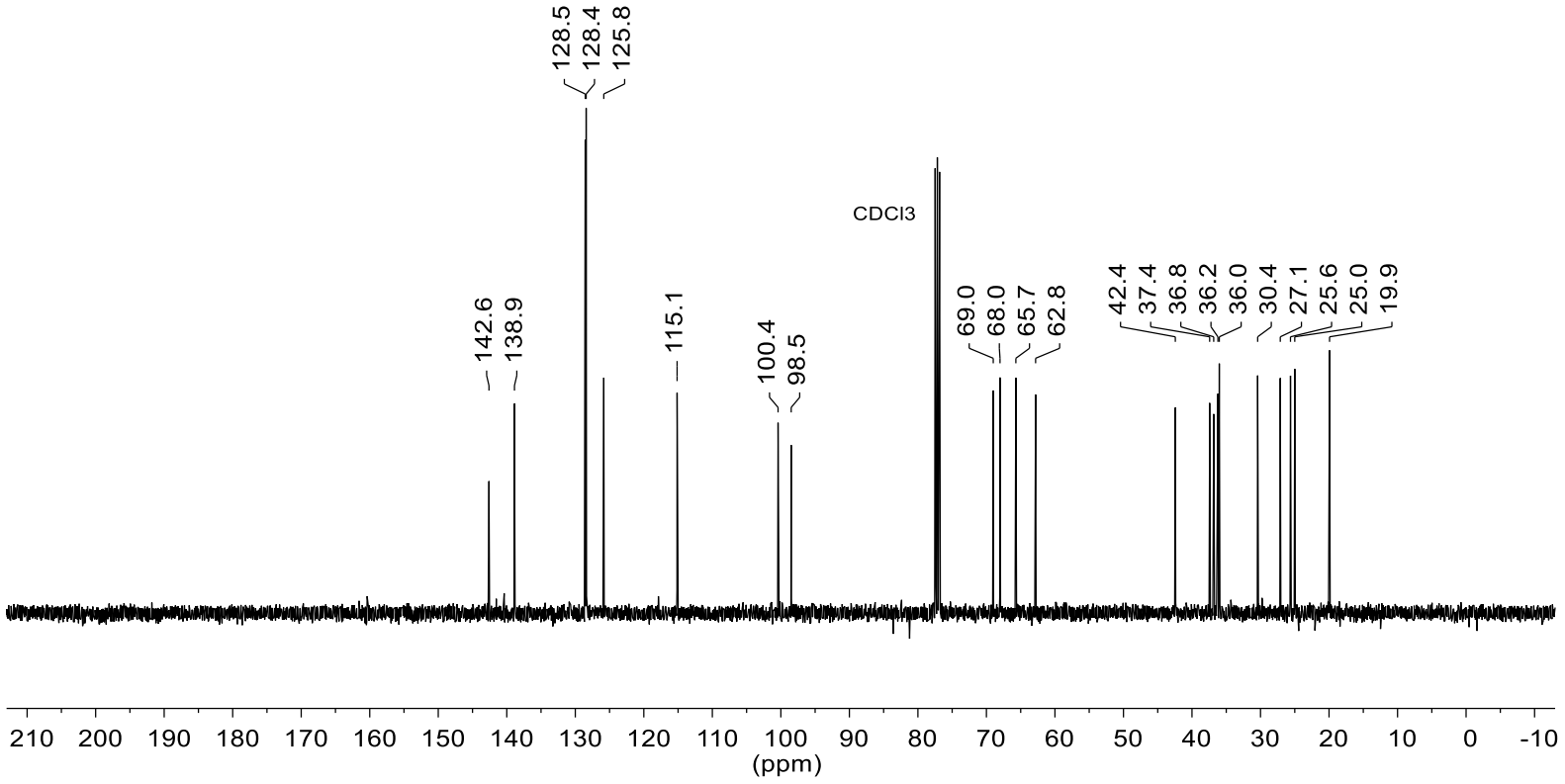



1H NMR (CDCl3, 400 MHz)
12d
CDCl3
7.29
7.28
7.26
7.19
7.18
7.17
5.94
5.92
5.91
5.90
5.89
5.88
5.87
5.85
5.24
5.20
5.14
5.12
4.37
4.35
4.33
4.32
4.05
4.02
4.00
3.99
3.97
3.95
3.83
3.82
3.80
2.64
2.62
2.60
1.81
1.78
1.76
1.74
1.72
1.70
1.51
1.49
1.48
1.46
1.18
1.15
1.41
1.38
2.18
3.00
0.95
0.98
0.98
0.99
2.00
1.01
2.02
9.34
3.20
9.13
1.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

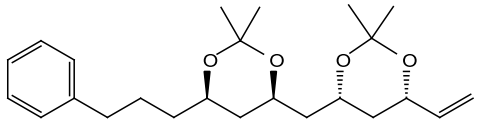
13C NMR (CDCl3, 101 MHz)



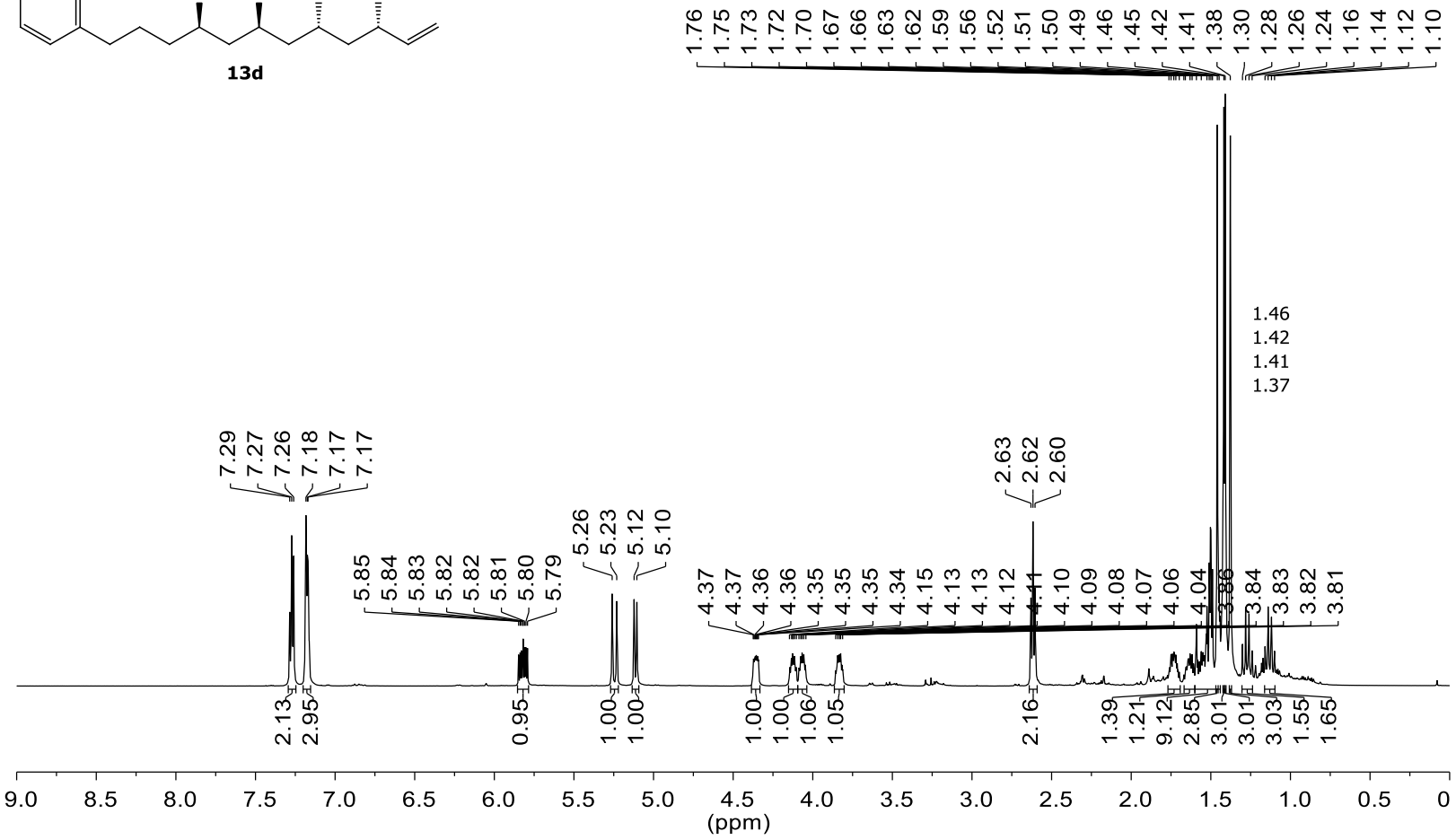
12d

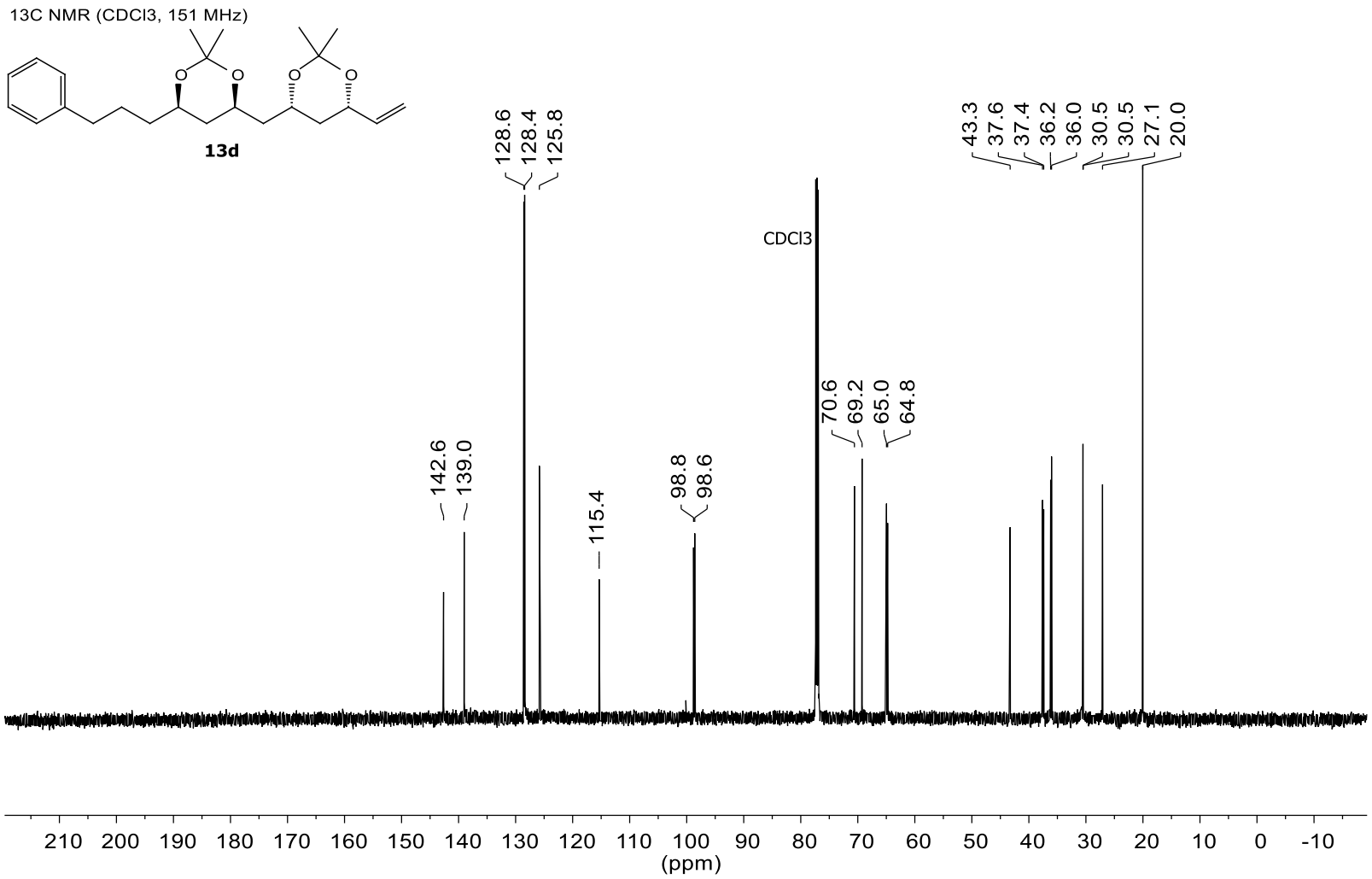


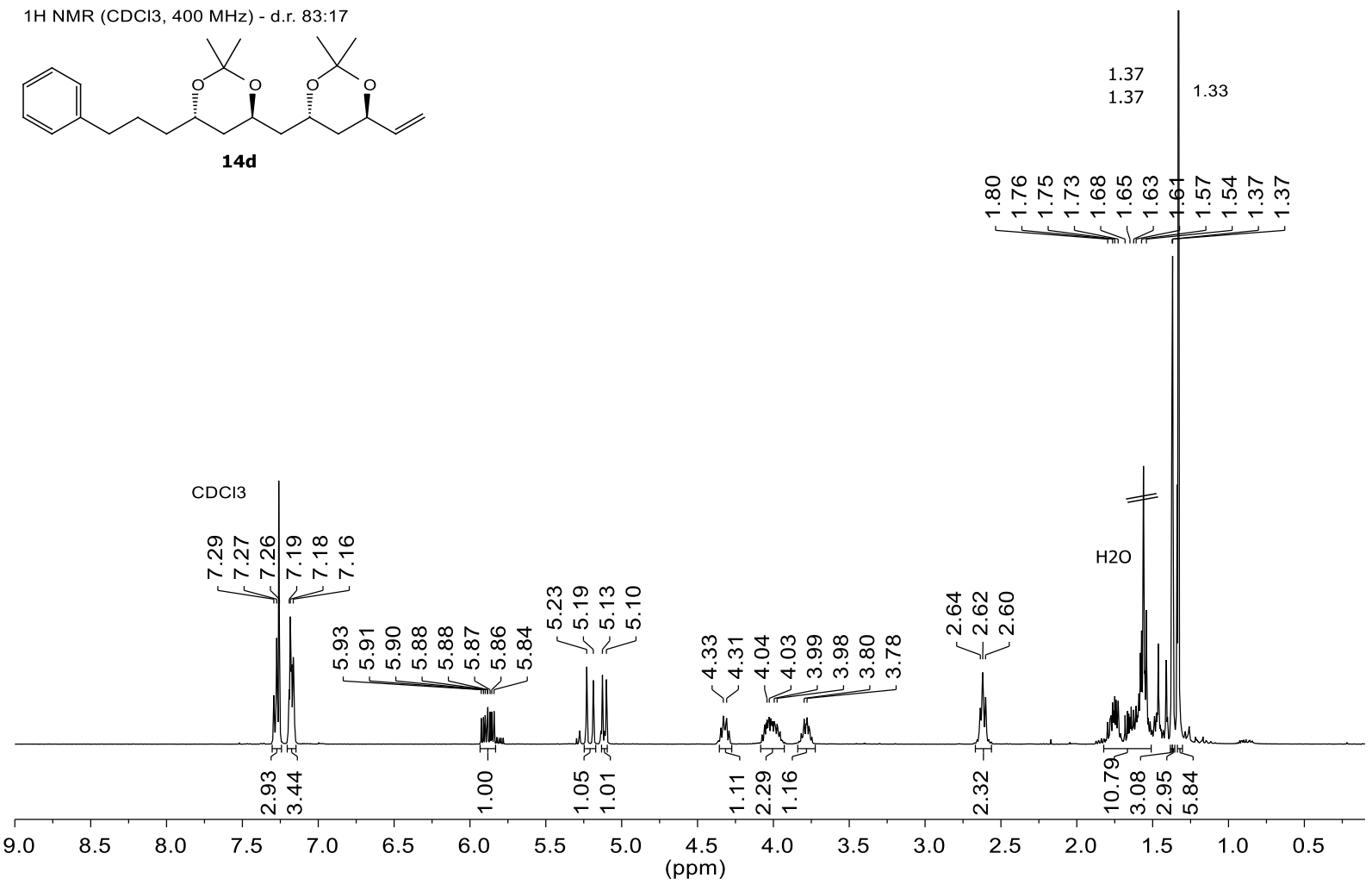
1H NMR (CDCl3, 600 MHz)



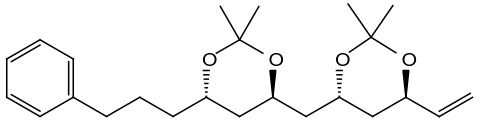
13d



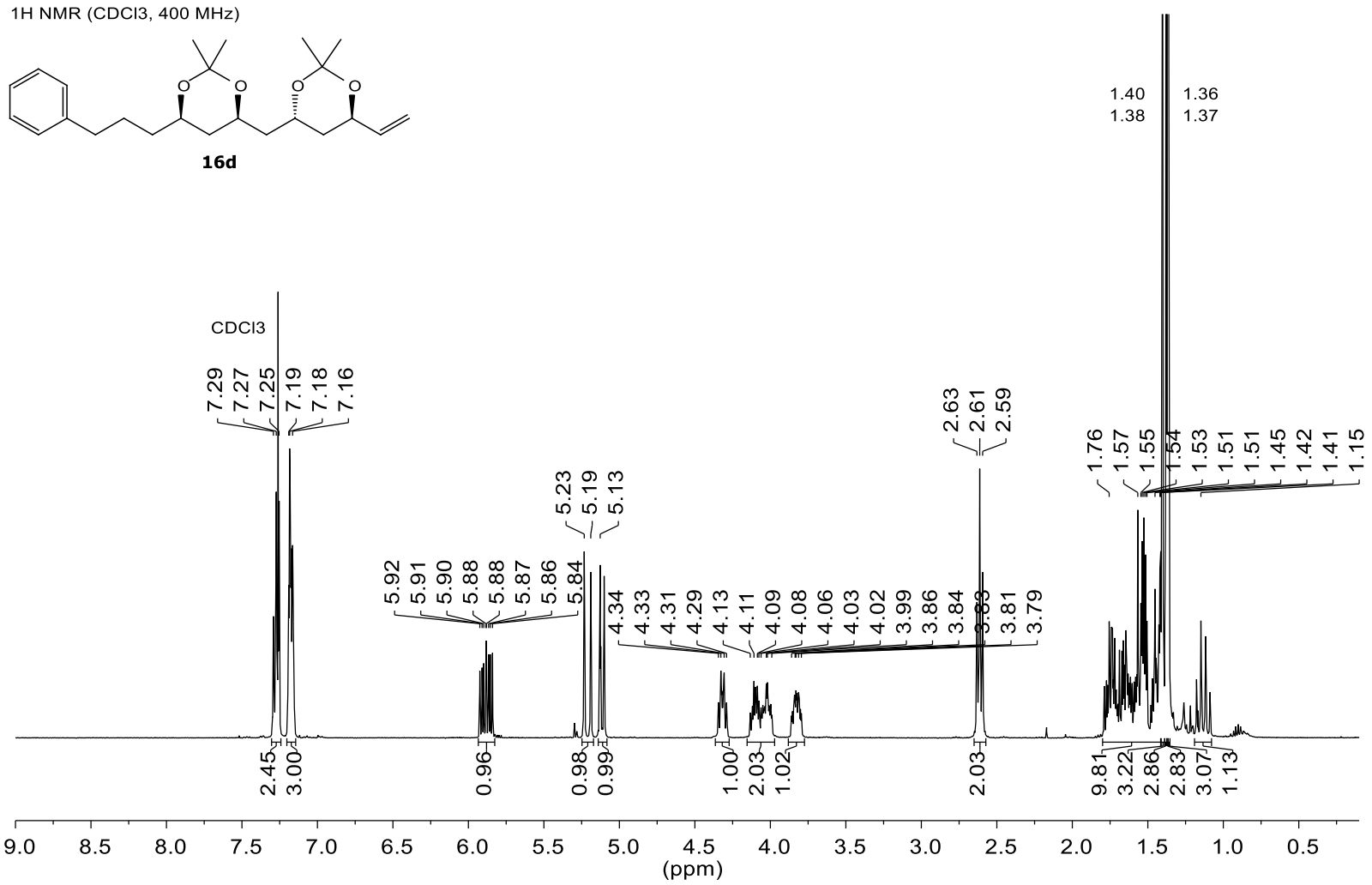

13C NMR (CDCl3, 151 MHz)
13d
128.6
128.4
125.8
43.3
37.6
37.4
36.2
36.0
30.5
30.5
27.1
20.0
CDCl3
142.6
139.0
115.4
98.8
98.6
70.6
69.2
65.0
64.8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

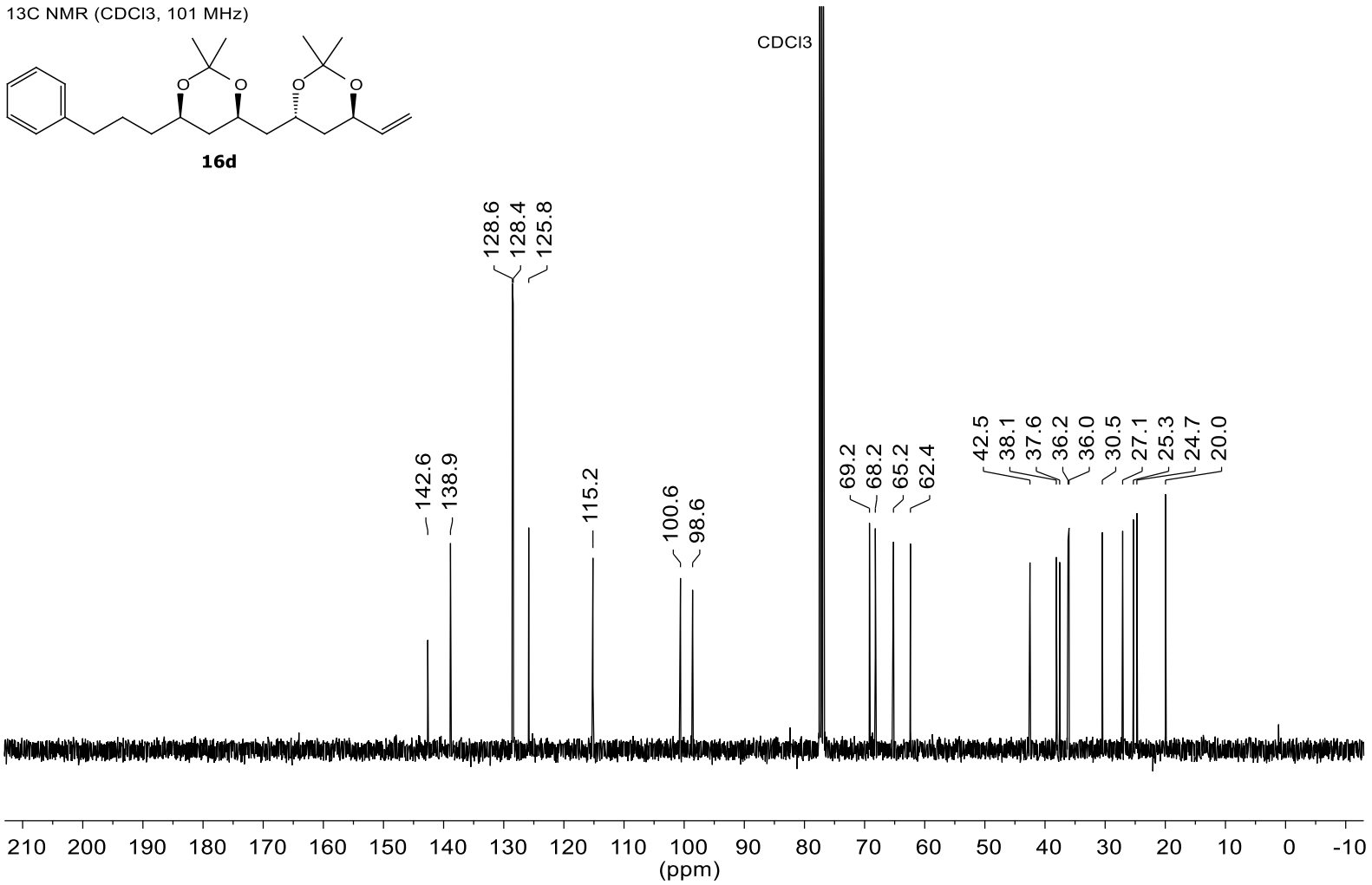

1H NMR (CDCl3, 400 MHz) - d.r. 83:17
14d
CDCl3
H2O
7.29
7.27
7.26
7.19
7.18
7.16
5.93
5.91
5.90
5.88
5.88
5.87
5.86
5.84
5.23
5.19
5.13
5.10
4.33
4.31
4.04
4.03
3.99
3.98
3.80
3.78
2.64
2.62
2.60
1.80
1.76
1.75
1.73
1.68
1.65
1.63
1.61
1.57
1.54
1.37
1.37
1.37
1.37
1.33
2.93
3.44
1.00
1.05
1.01
1.11
2.29
1.16
2.32
10.79
3.08
2.95
5.84
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

13C NMR (CDCl3, 101 MHz) - d.r. 83:17

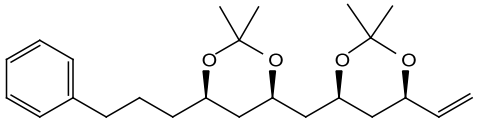


14d


1H NMR (CDCl3, 400 MHz)
16d
CDCl3
7.29
7.27
7.25
7.19
7.18
7.16
5.92
5.91
5.90
5.88
5.88
5.87
5.86
5.84
5.23
5.19
5.13
4.34
4.33
4.31
4.29
4.13
4.11
4.09
4.08
4.06
4.03
4.02
3.99
3.86
3.84
3.81
3.79
2.63
2.61
2.59
1.76
1.57
1.55
1.54
1.53
1.51
1.51
1.45
1.42
1.41
1.15
1.40
1.38
1.36
1.37
2.45
3.00
0.96
0.98
0.99
1.00
2.03
1.02
2.03
9.81
3.22
2.86
2.83
3.07
1.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

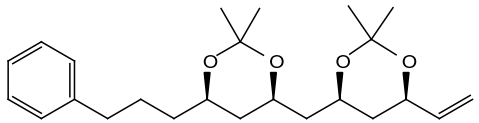

13C NMR (CDCl3, 101 MHz)
16d
CDCl3
128.6
128.4
125.8
142.6
138.9
115.2
100.6
98.6
69.2
68.2
65.2
62.4
42.5
38.1
37.6
36.2
36.0
30.5
27.1
25.3
24.7
20.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

1H NMR (CDCl3, 400 MHz)

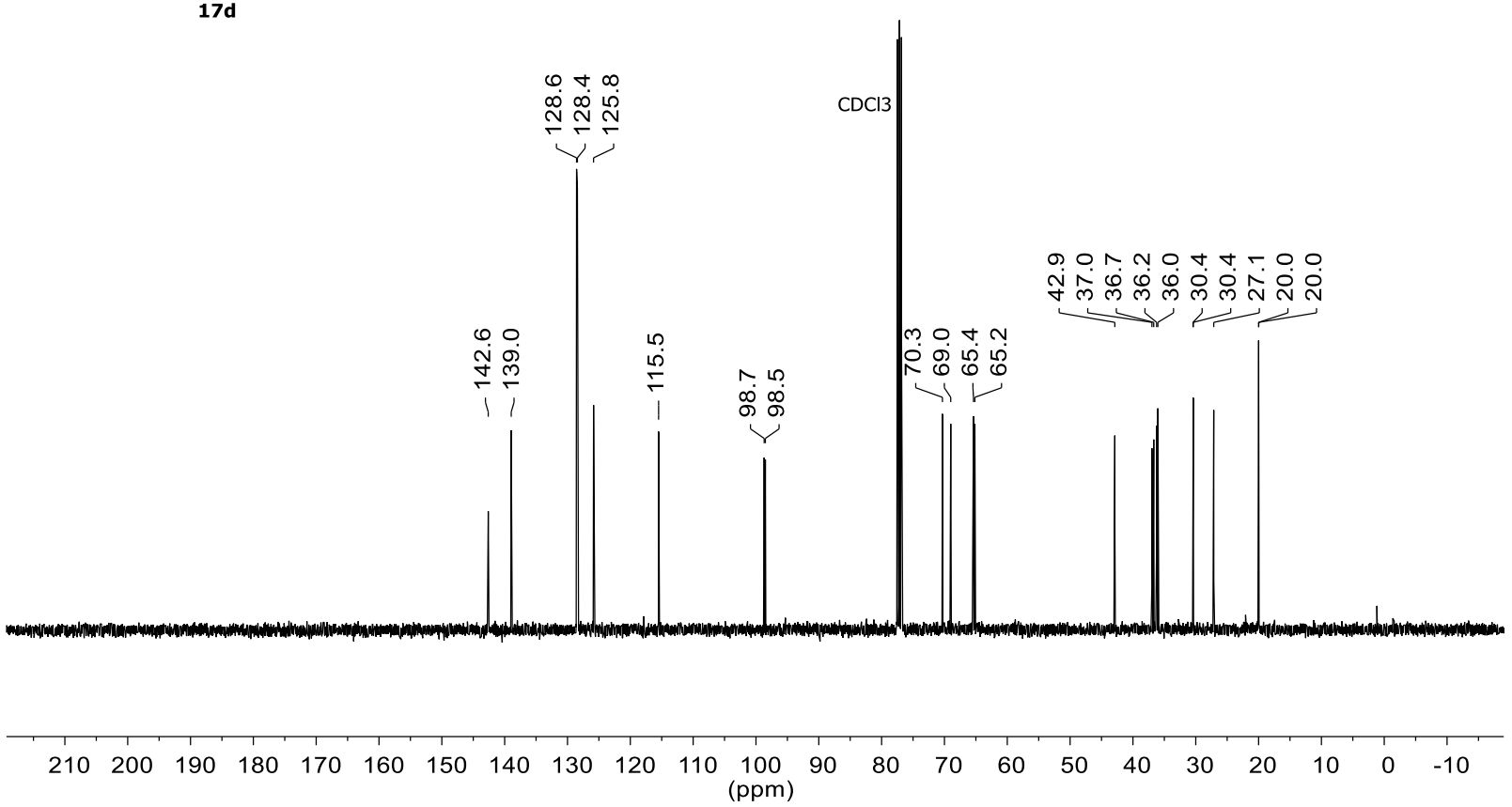


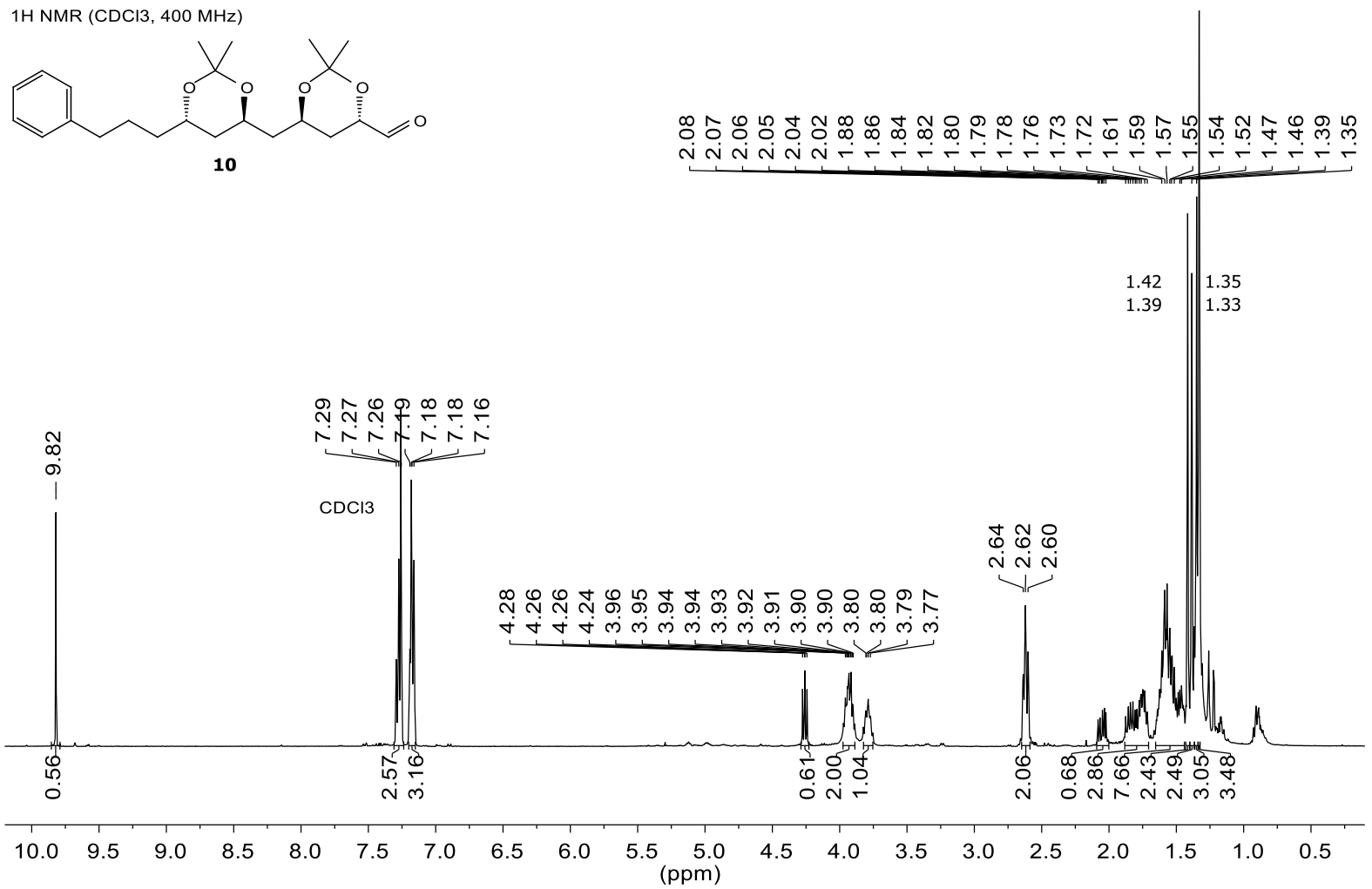
17d

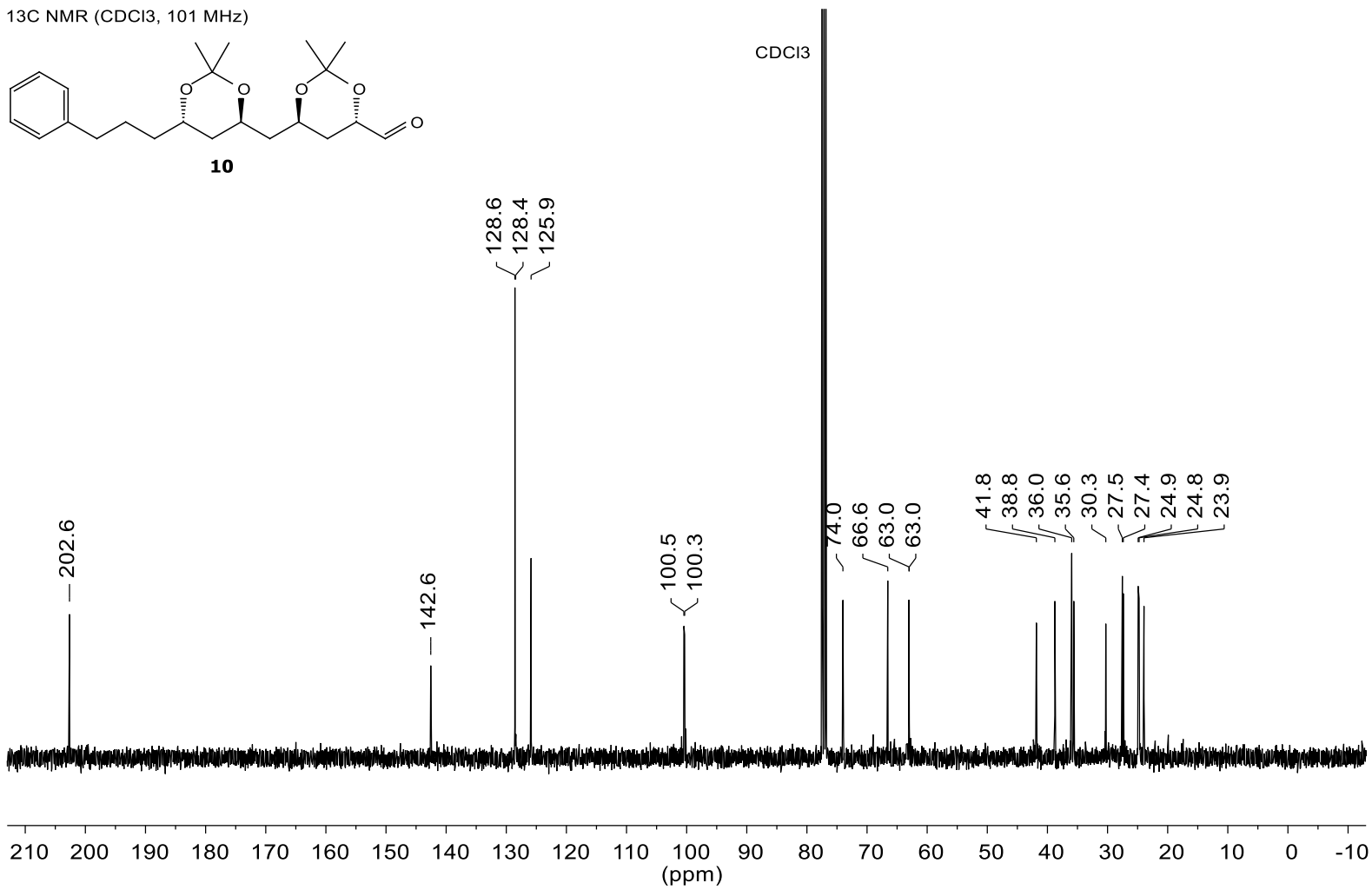
13C NMR (CDCl3, 101 MHz)

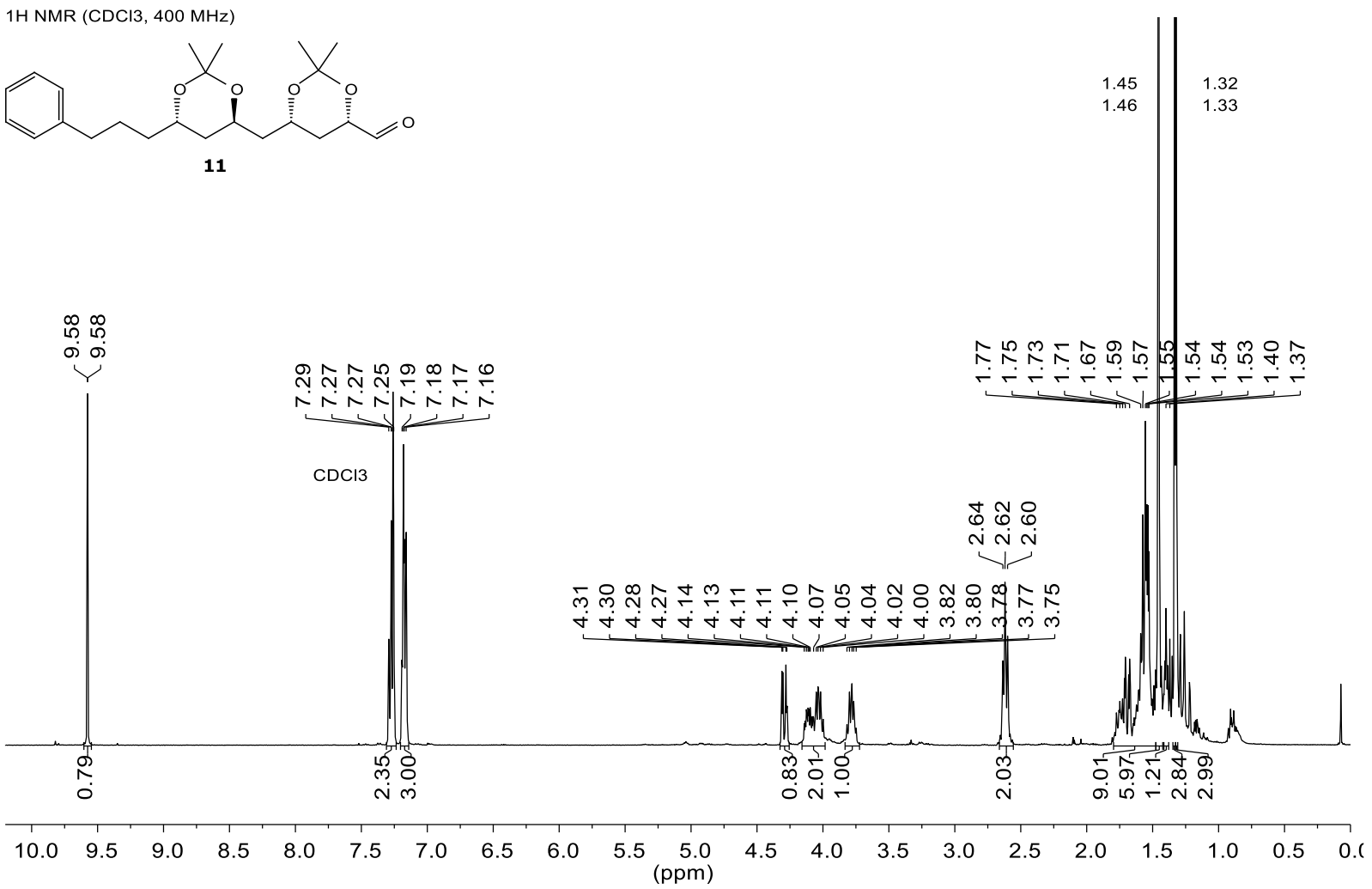


17d

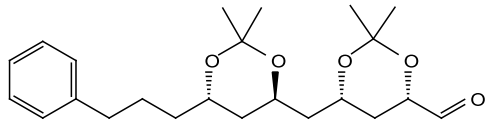



1H NMR (CDCl3, 400 MHz)
10
9.82
7.29
7.27
7.26
7.19
7.18
7.18
7.16
CDCl3
4.28
4.26
4.26
4.24
3.96
3.95
3.94
3.94
3.93
3.92
3.91
3.90
3.90
3.80
3.80
3.79
3.77
2.64
2.62
2.60
2.08
2.07
2.06
2.05
2.04
2.02
1.88
1.86
1.84
1.82
1.80
1.79
1.78
1.76
1.73
1.72
1.61
1.59
1.57
1.55
1.54
1.52
1.47
1.46
1.39
1.35
1.42
1.39
1.35
1.33
0.56
2.57
3.16
0.61
2.00
1.04
2.06
0.68
2.86
7.66
2.43
2.49
3.05
3.48
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

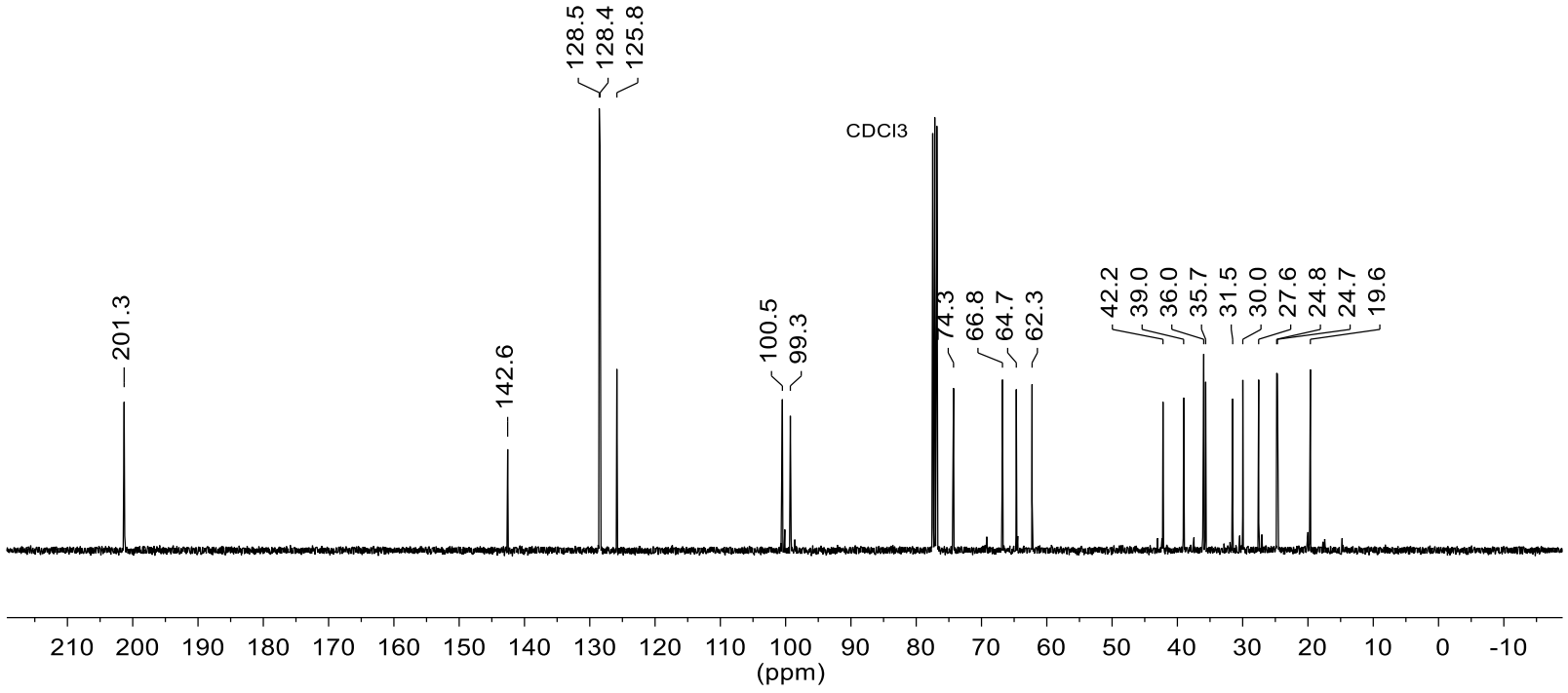

13C NMR (CDCl3, 101 MHz)
10
CDCl3
202.6
142.6
128.6
128.4
125.9
100.5
100.3
74.0
66.6
63.0
63.0
41.8
38.8
36.0
35.6
30.3
27.5
27.4
24.9
24.8
23.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)


1H NMR (CDCl3, 400 MHz)
11
9.58
9.58
7.29
7.27
7.27
7.25
7.19
7.18
7.17
7.16
CDCl3
4.31
4.30
4.28
4.27
4.14
4.13
4.11
4.11
4.10
4.07
4.05
4.04
4.02
4.00
3.82
3.80
3.78
3.77
3.75
2.64
2.62
2.60
1.77
1.75
1.73
1.71
1.67
1.59
1.57
1.55
1.54
1.54
1.53
1.40
1.37
1.45
1.46
1.32
1.33
0.79
2.35
3.00
0.83
2.01
1.00
2.03
9.01
5.97
1.21
2.84
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

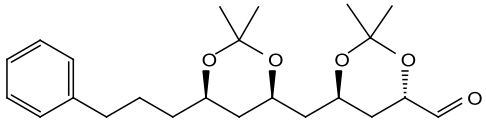
13C NMR (CDCl3, 101 MHz)



11



1H NMR (CDCl3, 400 MHz)



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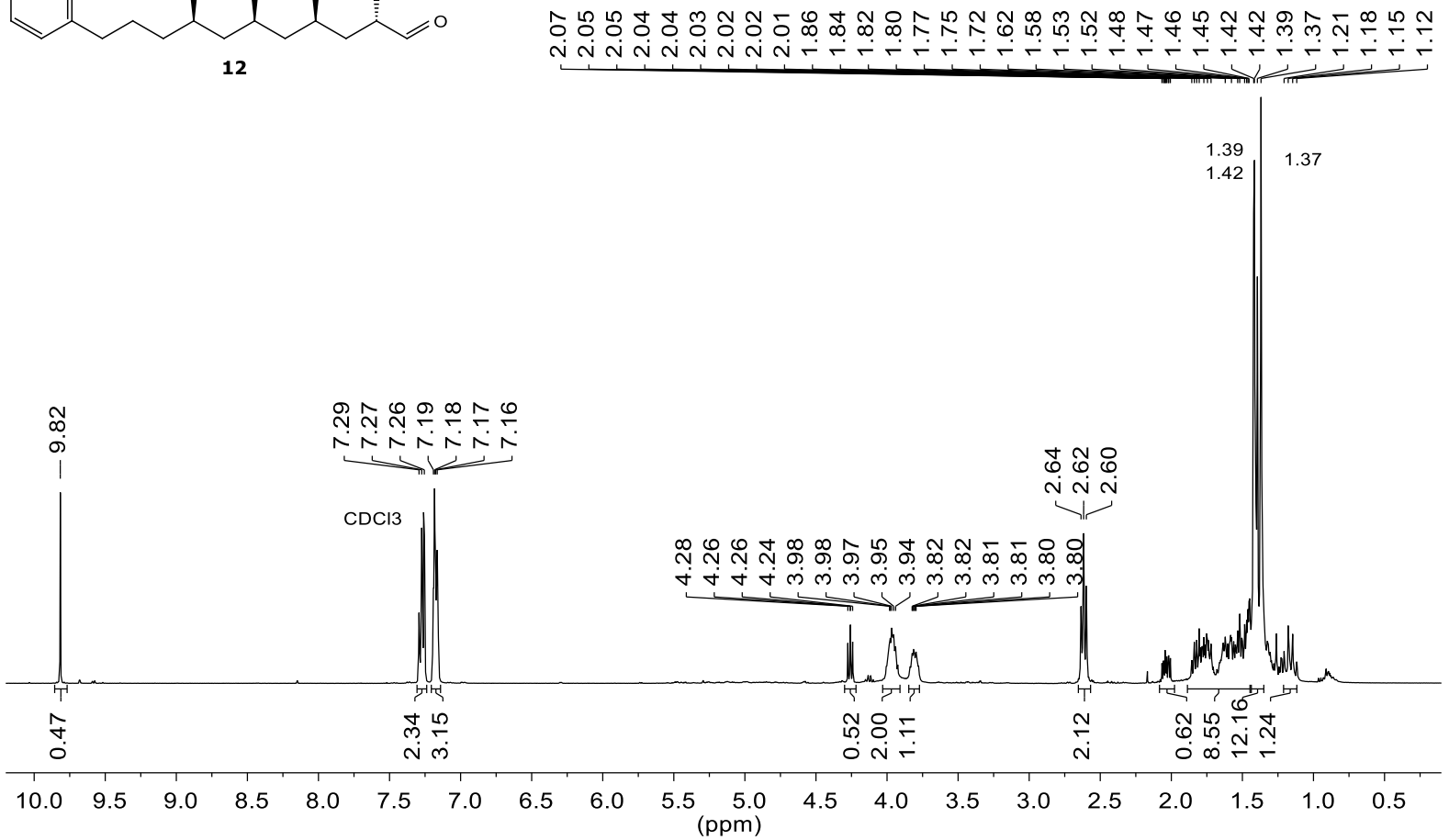
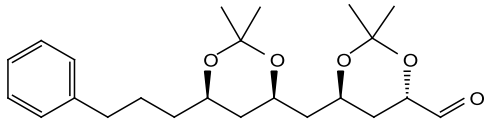
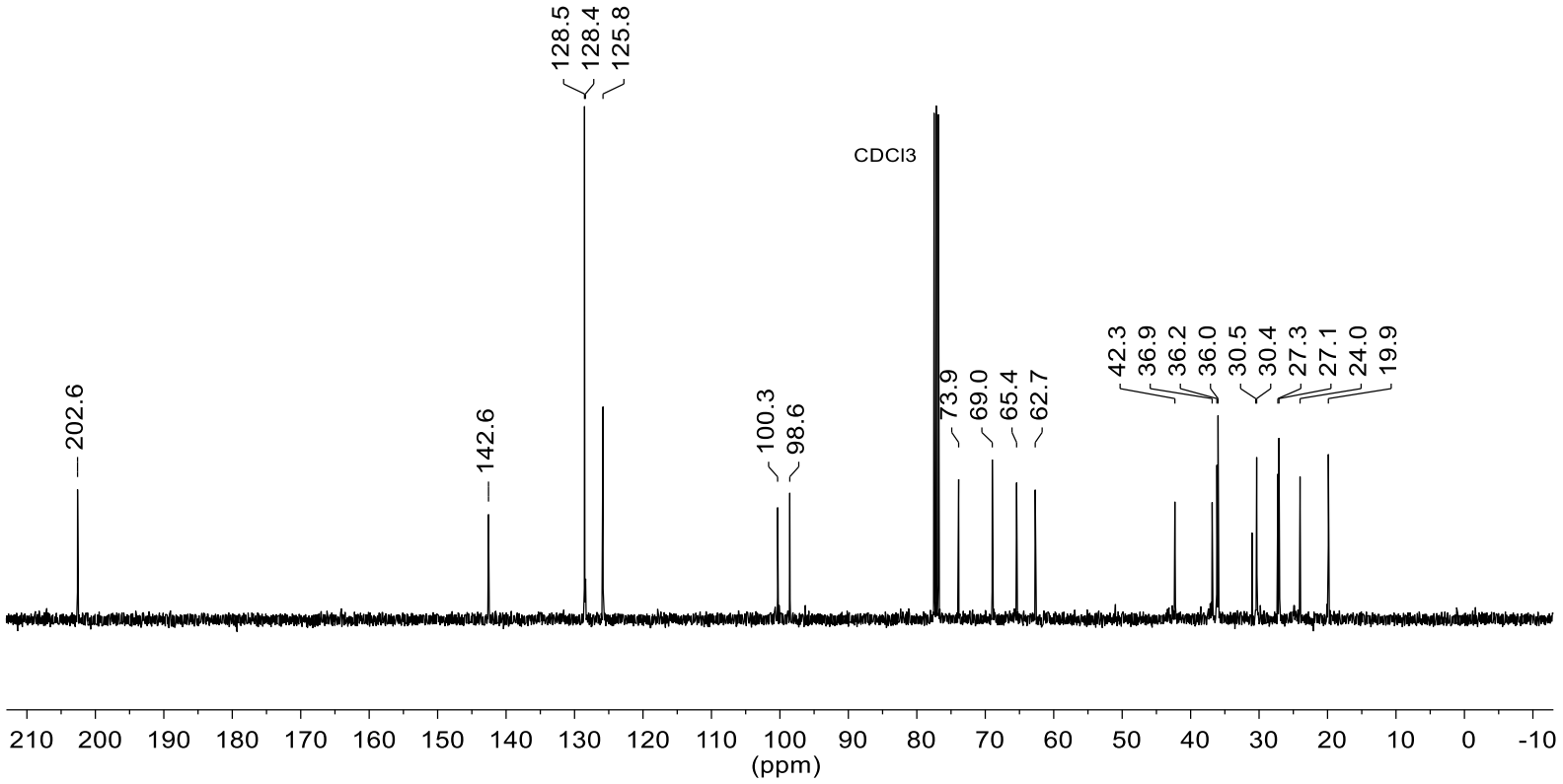
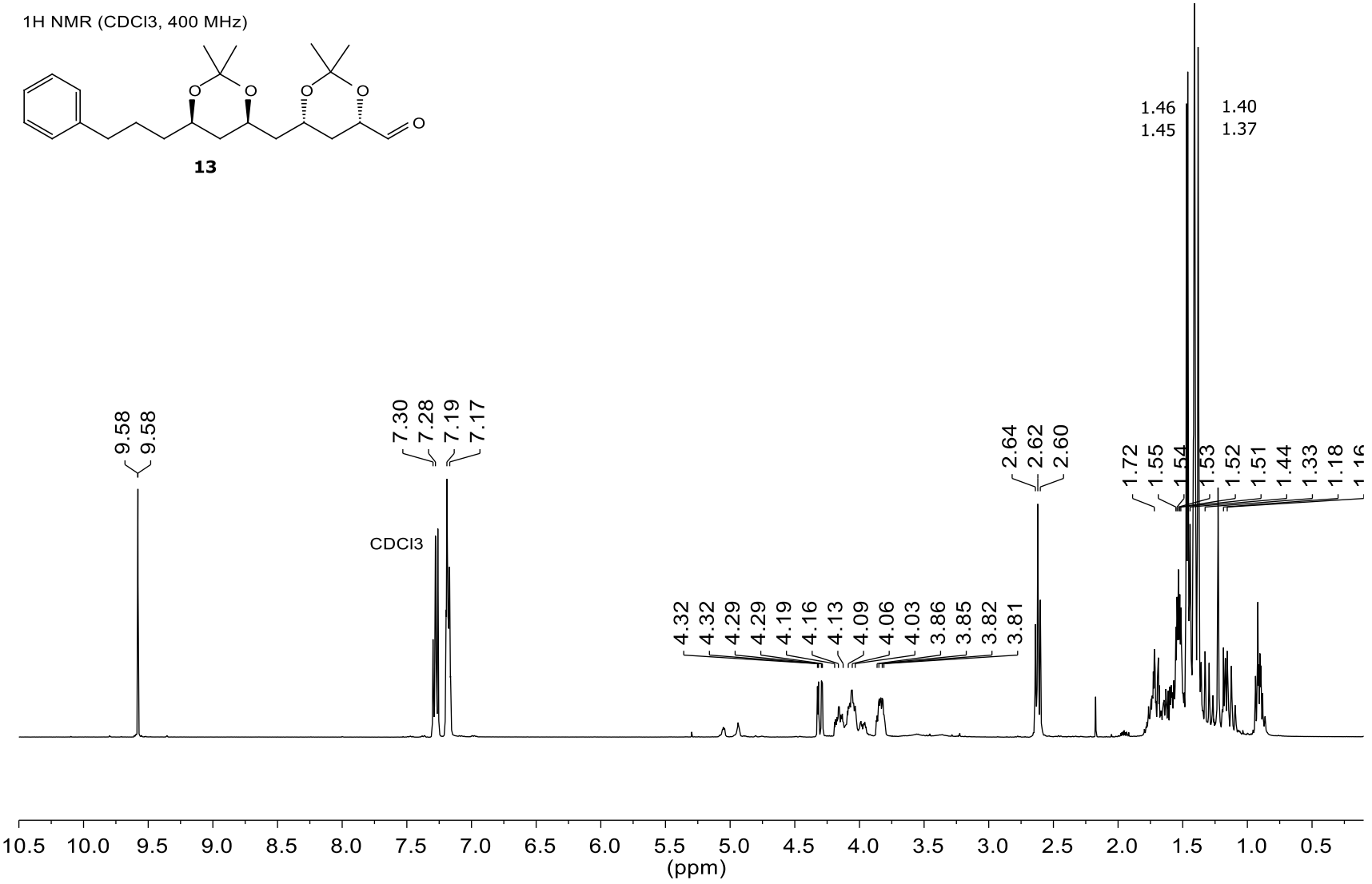


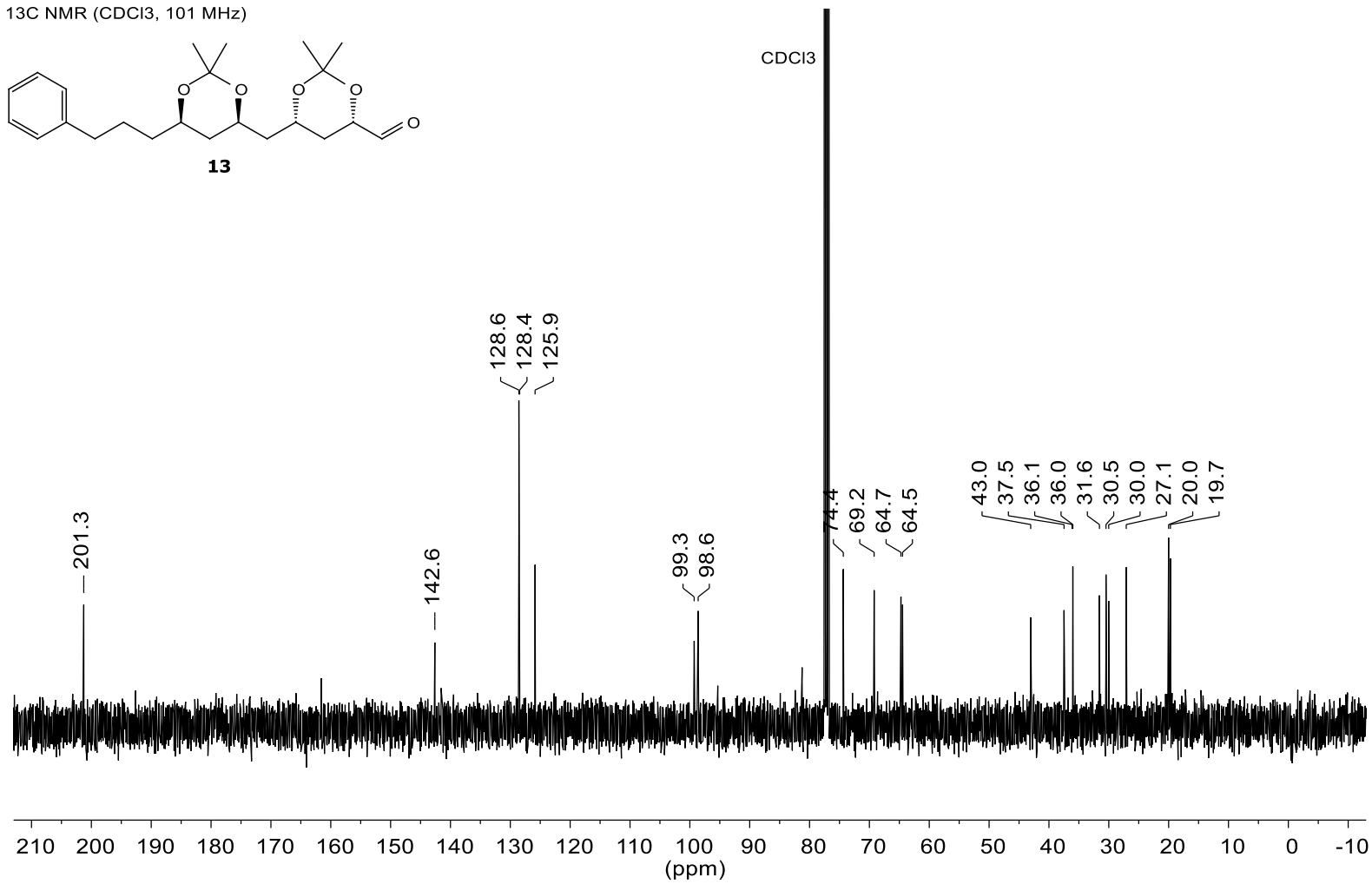
13C NMR (CDCl3, 101 MHz)

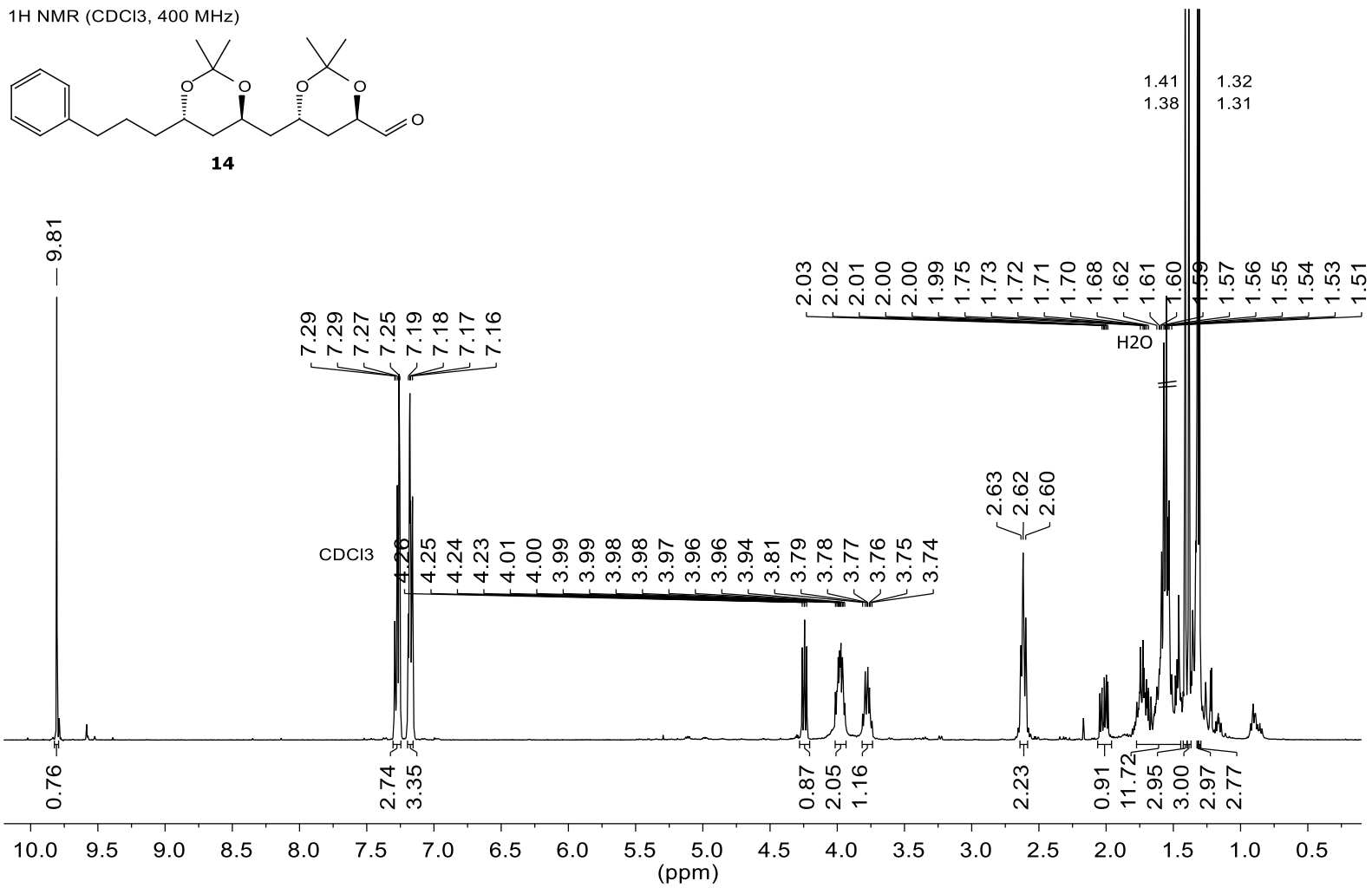


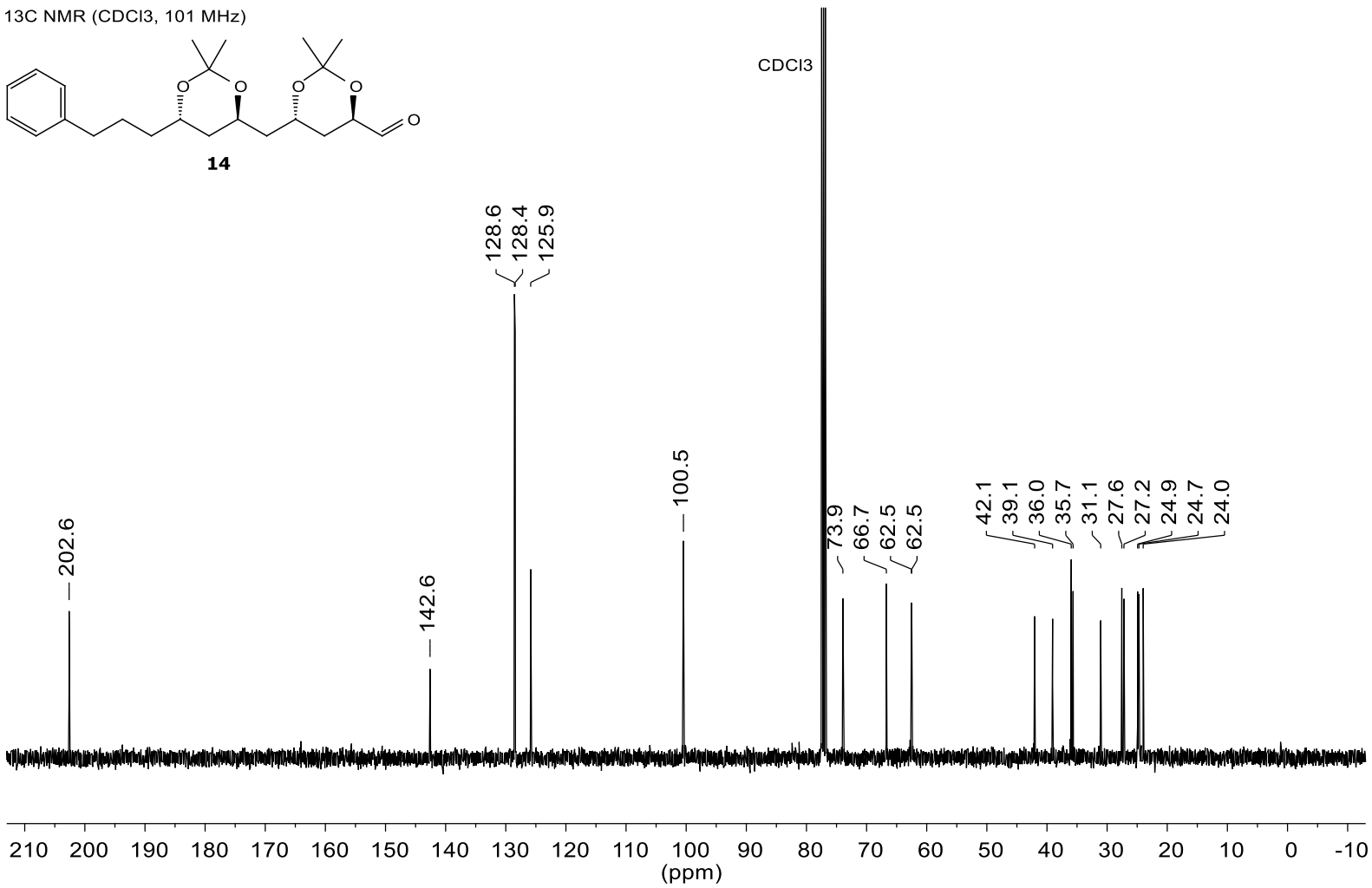
12

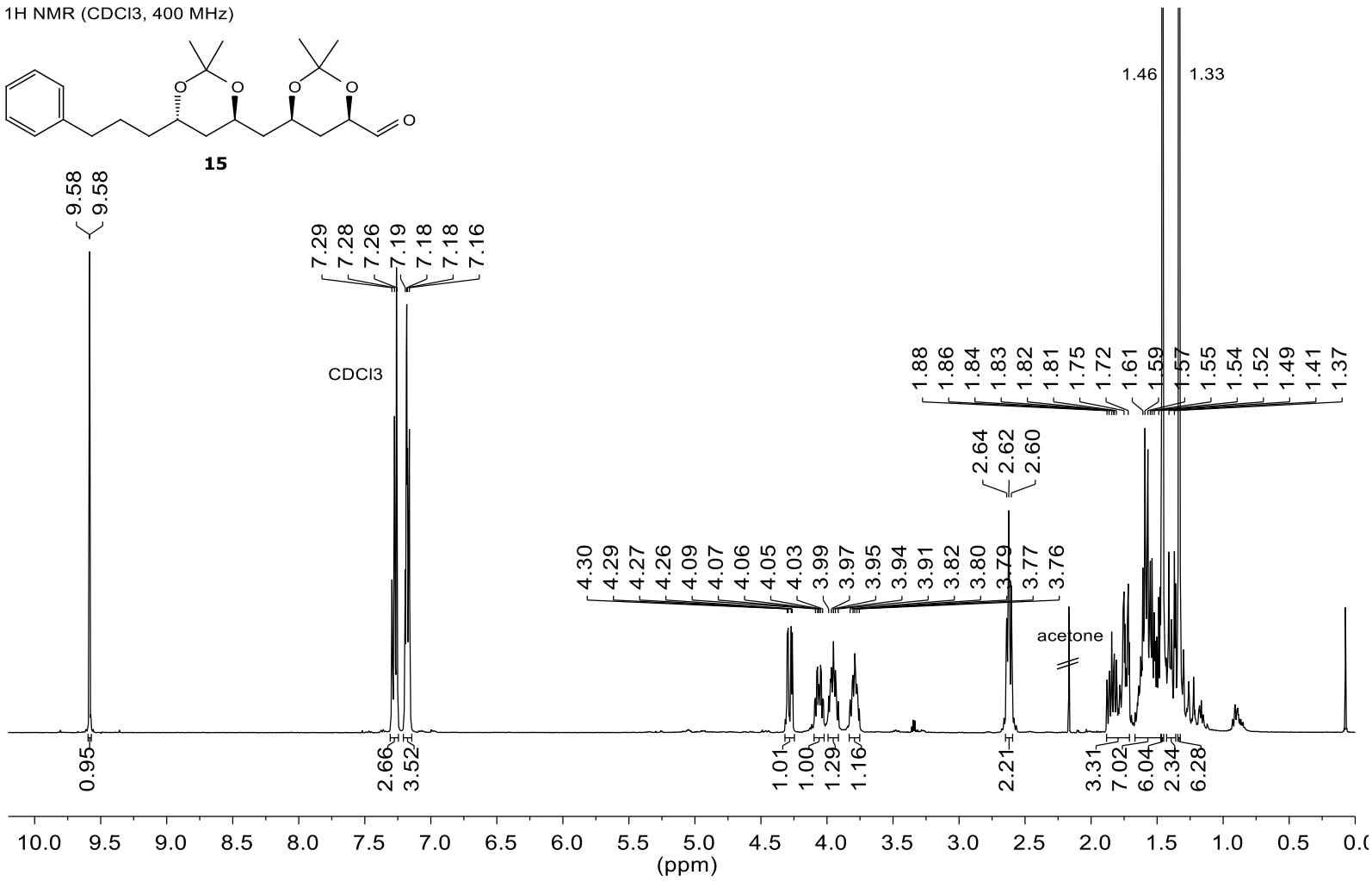



1H NMR (CDCl3, 400 MHz)
13
9.58
9.58
7.30
7.28
7.19
7.17
CDCl3
4.32
4.32
4.29
4.29
4.19
4.16
4.13
4.09
4.06
4.03
3.86
3.85
3.82
3.81
2.64
2.62
2.60
1.72
1.55
1.54
1.53
1.52
1.51
1.46
1.45
1.44
1.40
1.37
1.33
1.18
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

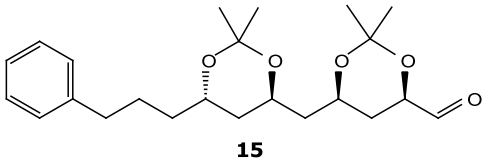

13C NMR (CDCl3, 101 MHz)
13
CDCl3
201.3
142.6
128.6
128.4
125.9
99.3
98.6
74.4
69.2
64.7
64.5
43.0
37.5
36.1
36.0
31.6
30.5
30.0
27.1
20.0
19.7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)


1H NMR (CDCl3, 400 MHz)
14
9.81
7.29
7.29
7.27
7.25
7.19
7.18
7.17
7.16
CDCl3
4.26
4.25
4.24
4.23
4.01
4.00
3.99
3.99
3.98
3.98
3.97
3.96
3.96
3.94
3.81
3.79
3.78
3.77
3.76
3.75
3.74
2.63
2.62
2.60
2.03
2.02
2.01
2.00
2.00
1.99
1.75
1.73
1.72
1.71
1.70
1.68
1.62
1.61
1.60
1.59
1.57
1.56
1.55
1.54
1.53
1.51
H2O
1.41
1.38
1.32
1.31
0.76
2.74
3.35
0.87
2.05
1.16
2.23
0.91
11.72
2.95
3.00
2.97
2.77
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

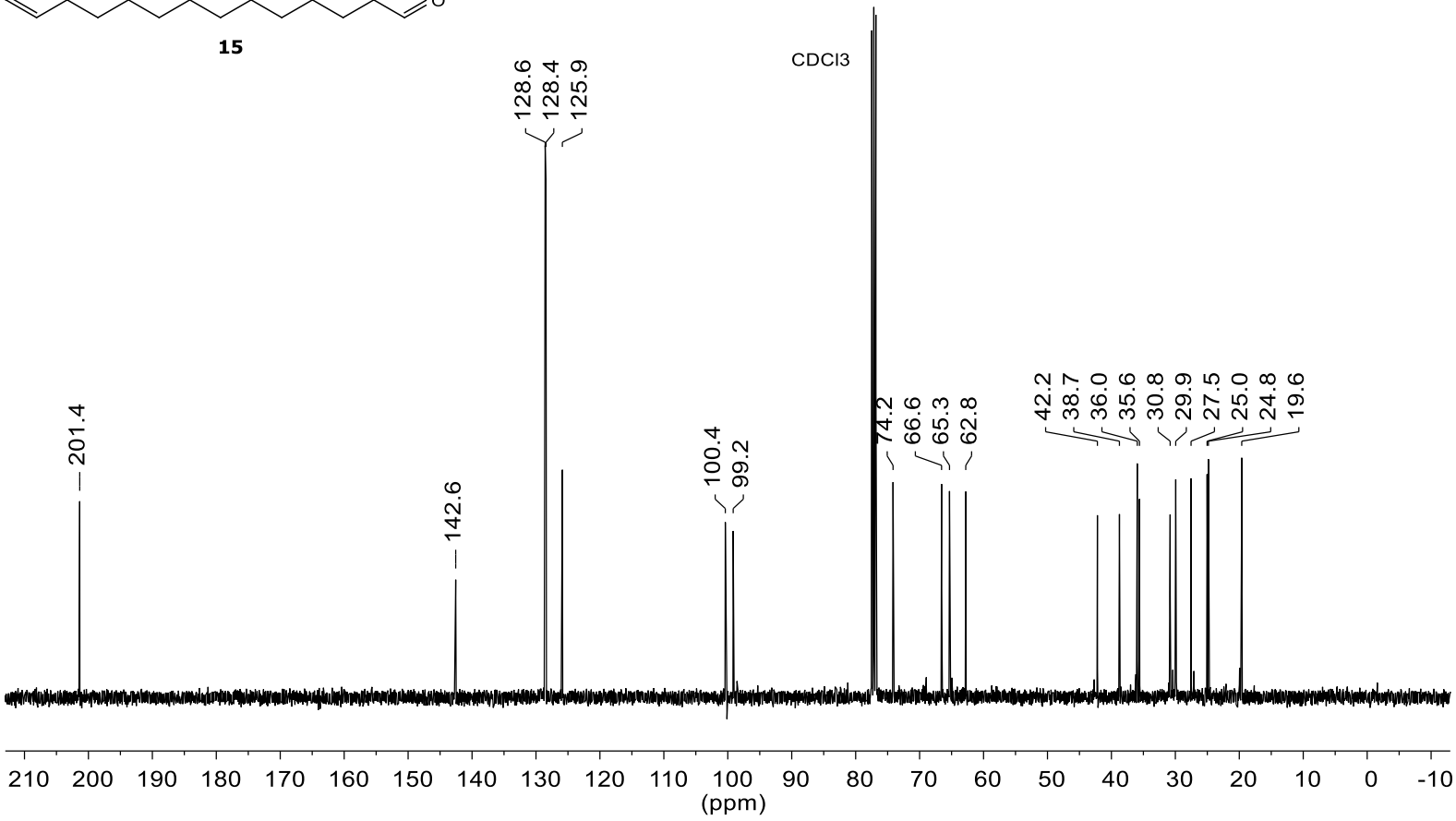

13C NMR (CDCl3, 101 MHz)
14
CDCl3
202.6
142.6
128.6
128.4
125.9
100.5
73.9
66.7
62.5
62.5
42.1
39.1
36.0
35.7
31.1
27.6
27.2
24.9
24.7
24.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

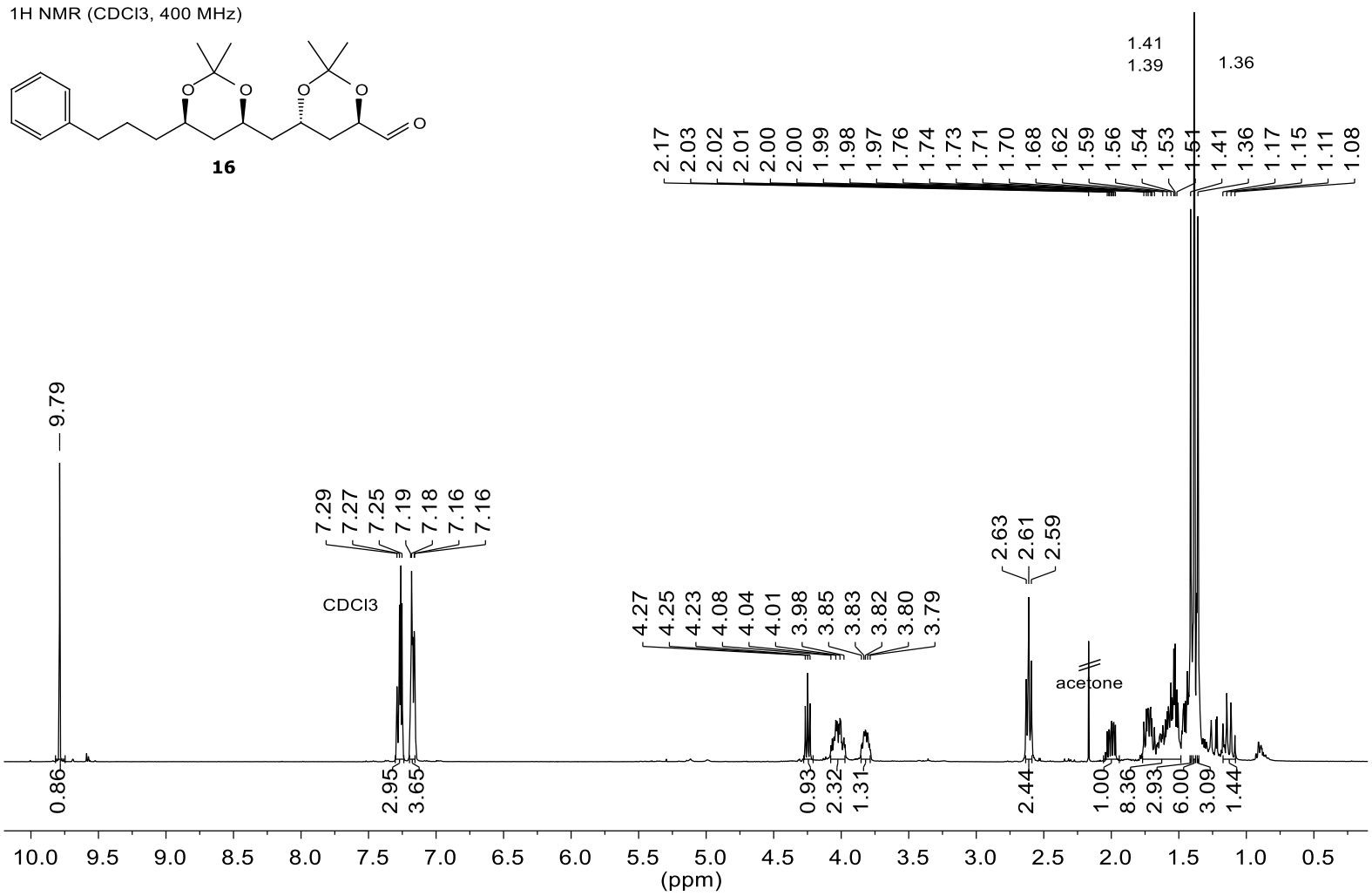

1H NMR (CDCl3, 400 MHz)
15
9.58
9.58
7.29
7.28
7.26
7.19
7.18
7.18
7.16
CDCl3
1.46
1.33
1.88
1.86
1.84
1.83
1.82
1.81
1.75
1.72
1.61
1.59
1.57
1.55
1.54
1.52
1.49
1.41
1.37
2.64
2.62
2.60
4.30
4.29
4.27
4.26
4.09
4.07
4.06
4.05
4.03
3.99
3.97
3.95
3.94
3.91
3.82
3.80
3.79
3.77
3.76
acetone
0.95
2.66
3.52
1.01
1.00
1.29
1.16
2.21
3.31
7.02
6.04
2.34
6.28
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

13C NMR (CDCl3, 101 MHz)

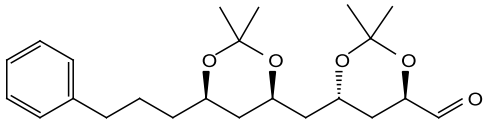


15

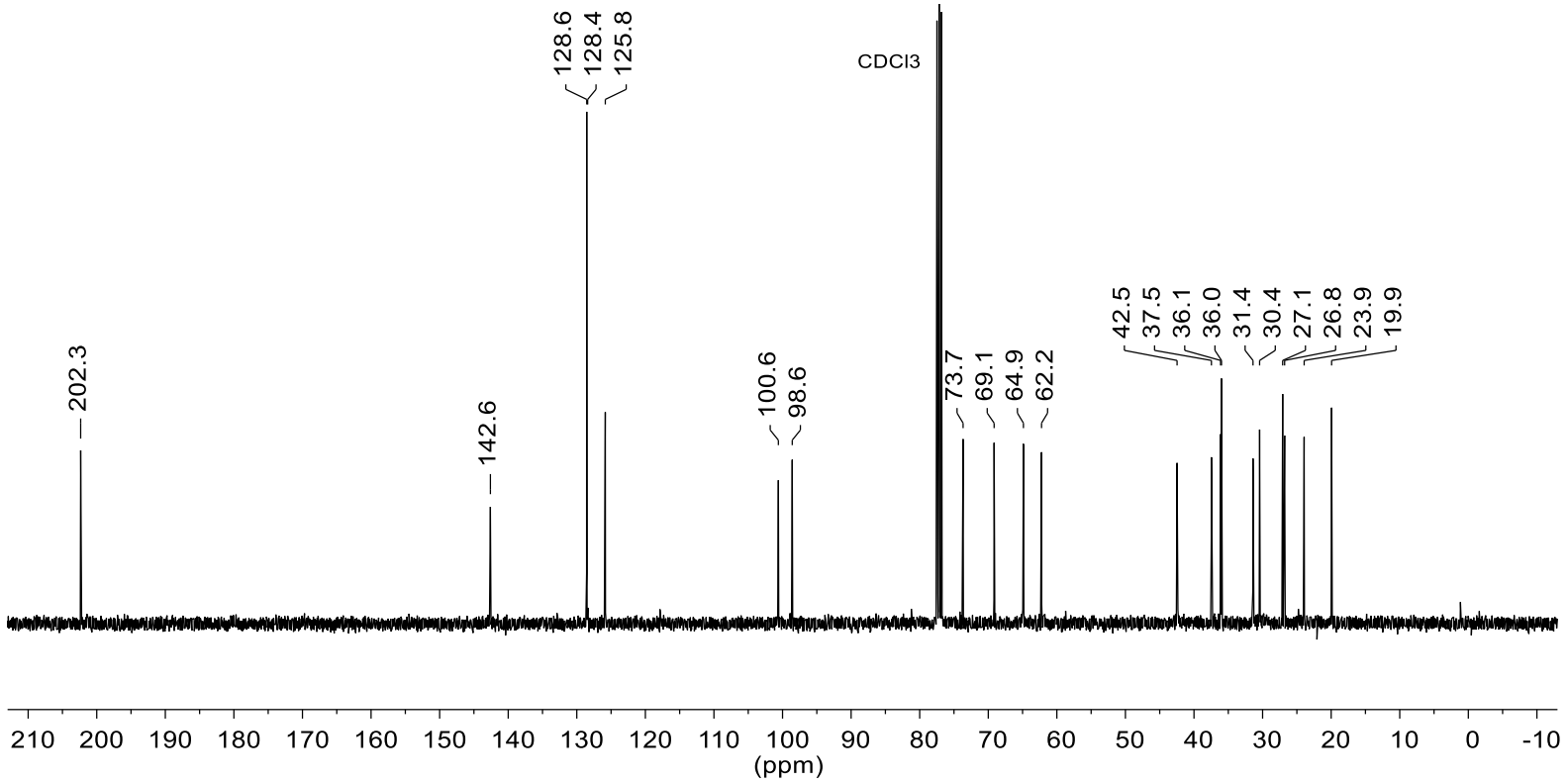


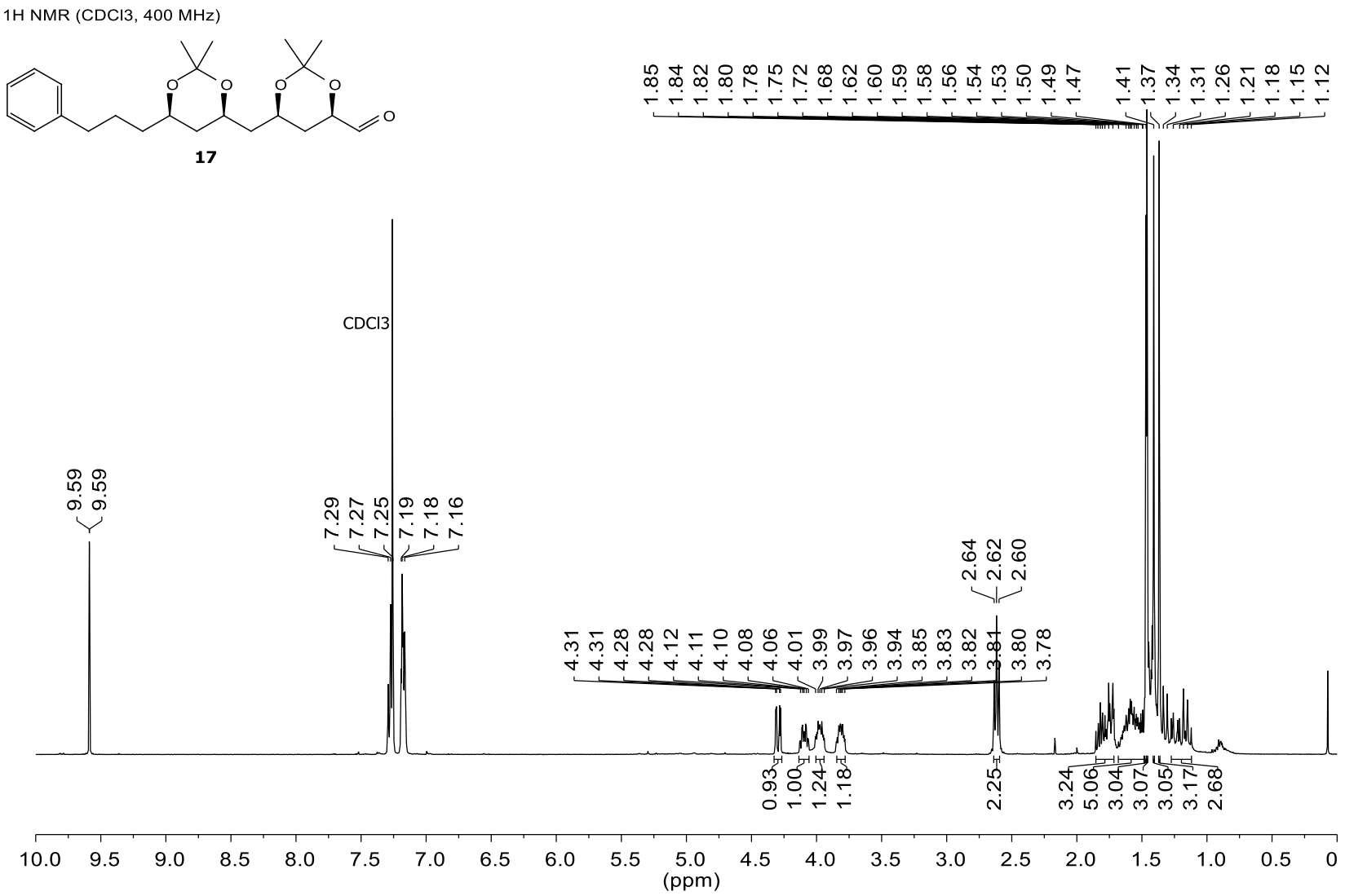

1H NMR (CDCl3, 400 MHz)
16
CDCl3
acetone
(ppm)

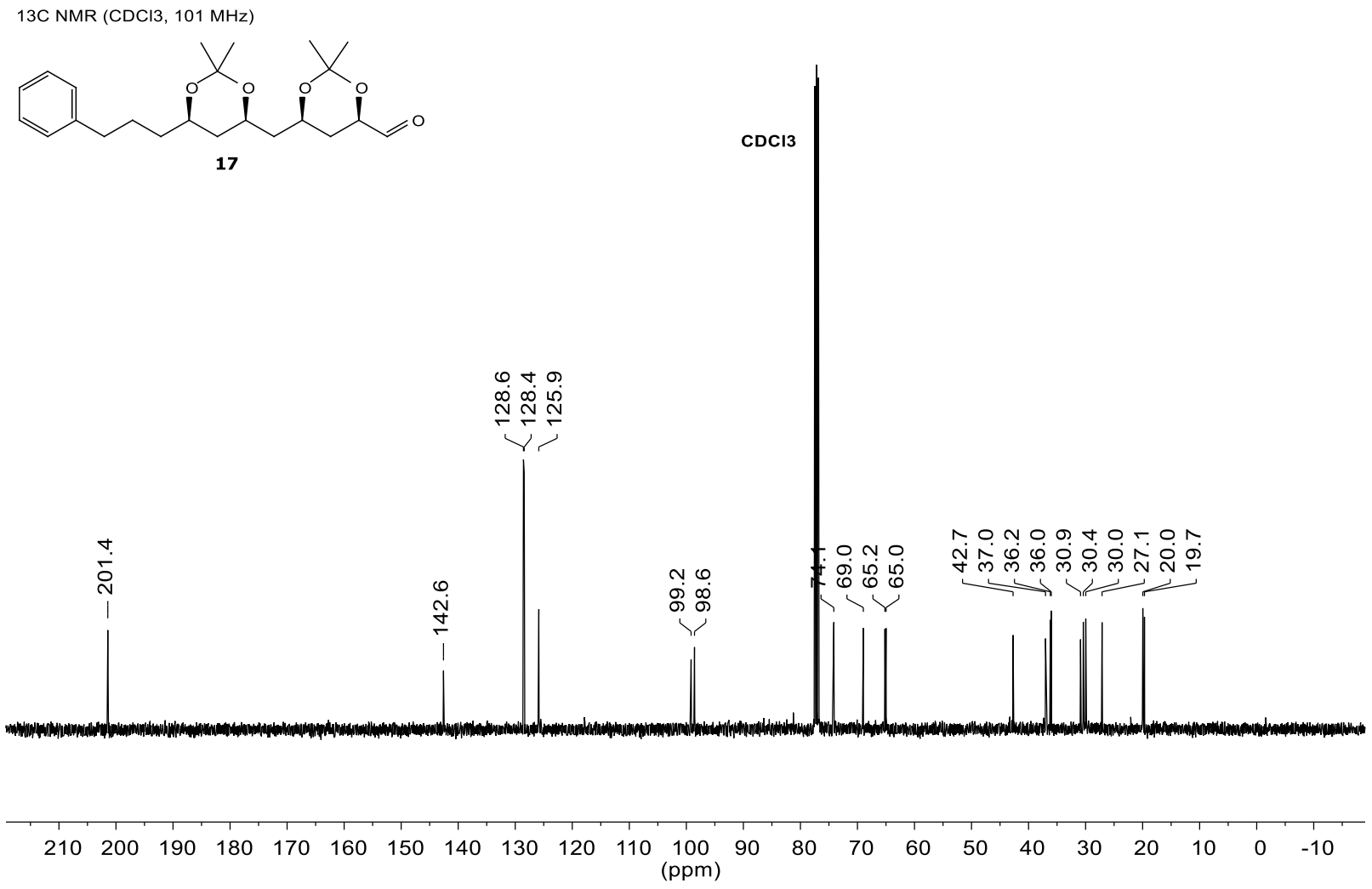
13C NMR (CDCl3, 101 MHz)



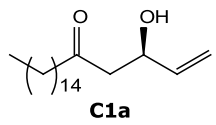
16




1H NMR (CDCl3, 400 MHz)
17
CDCl3
9.59
9.59
7.29
7.27
7.25
7.19
7.18
7.16
4.31
4.31
4.28
4.28
4.12
4.11
4.10
4.08
4.06
4.01
3.99
3.97
3.96
3.94
3.85
3.83
3.82
3.81
3.80
3.78
2.64
2.62
2.60
1.85
1.84
1.82
1.80
1.78
1.75
1.72
1.68
1.62
1.60
1.59
1.58
1.56
1.54
1.53
1.50
1.49
1.47
1.41
1.37
1.34
1.31
1.26
1.21
1.18
1.15
1.12
0.93
1.00
1.24
1.18
2.25
3.24
5.06
3.04
3.07
3.05
3.17
2.68
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
(ppm)

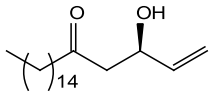

13C NMR (CDCl3, 101 MHz)
17
CDCl3
201.4
142.6
128.6
128.4
125.9
99.2
98.6
74.1
69.0
65.2
65.0
42.7
37.0
36.2
36.0
30.9
30.4
30.0
27.1
20.0
19.7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

1H-NMR (400 MHz, CDCl3)

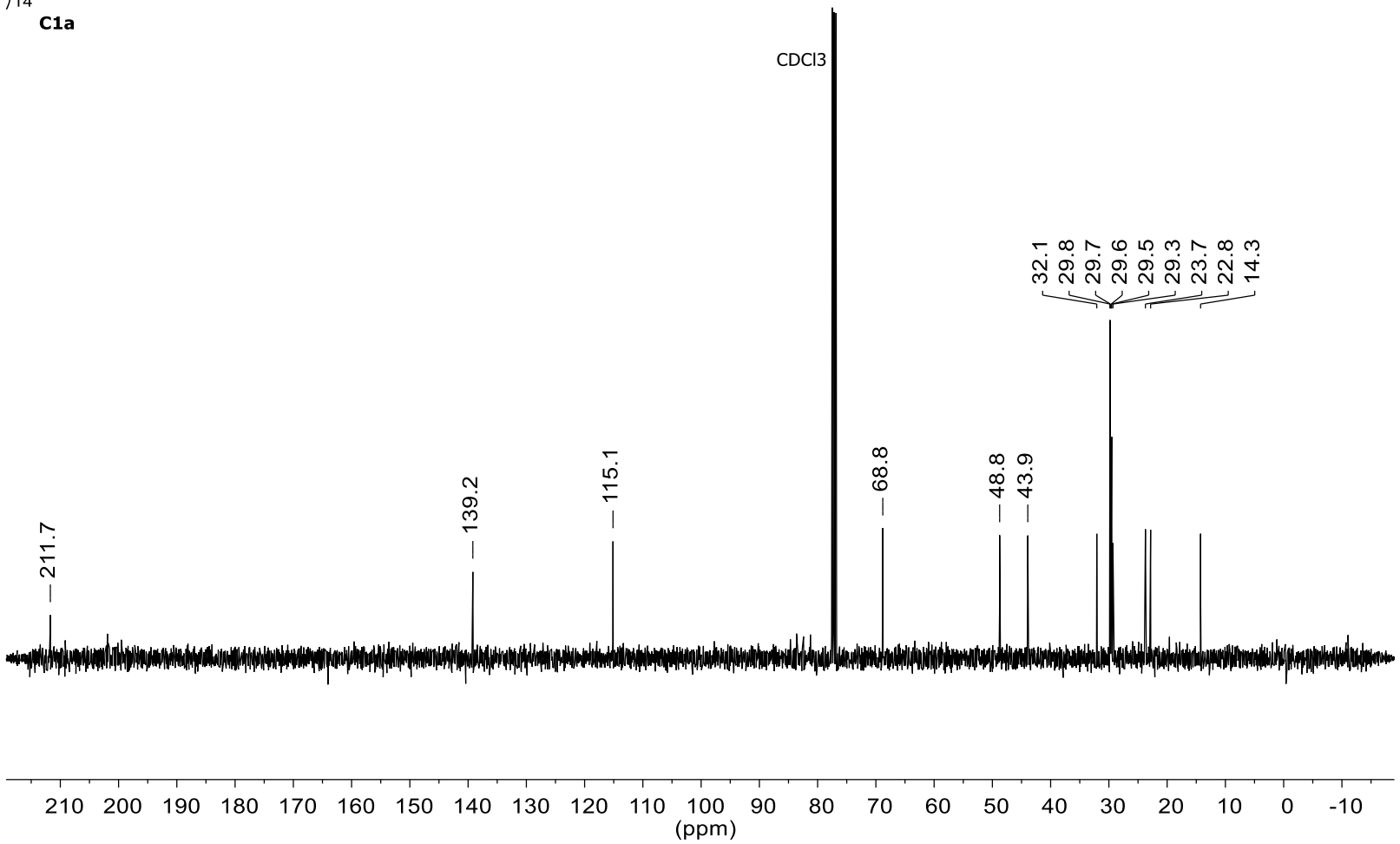


C1a

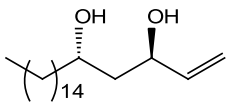
13C-NMR (101 MHz, CDCl3)



C1a

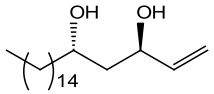


1H-NMR (CDCl3, 600 MHz) - d.r. 89:11



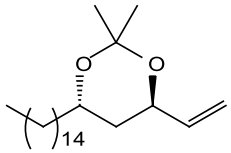
C1b

13C NMR (CDCl3, 151 MHz)



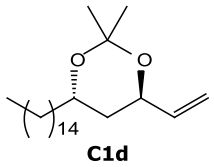
C1b

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



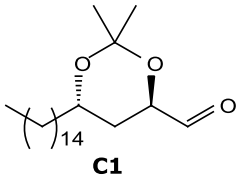
C1d

13C NMR (CDCl3, 101 MHz) - d.r. 90:10



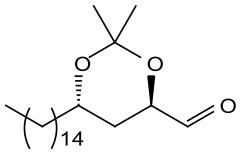
C1d

1H NMR (CDCL3, 400 MHz) - d.r. 90:10



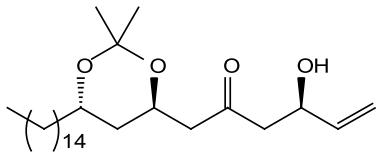
C1

13C NMR (CDCL3, 151 MHz) - d.r. 90:10



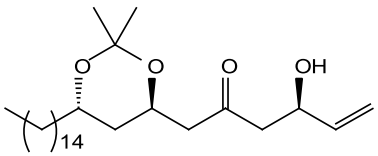
C1

1H-NMR (CDCl3, 400 MHz)



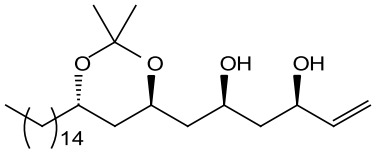
C2a

13C-NMR (CDCl3, 101 MHz)



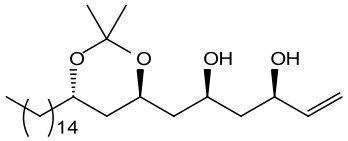
C2a

1H-NMR (CDCl3, 400 MHz) - d.r. 91:9

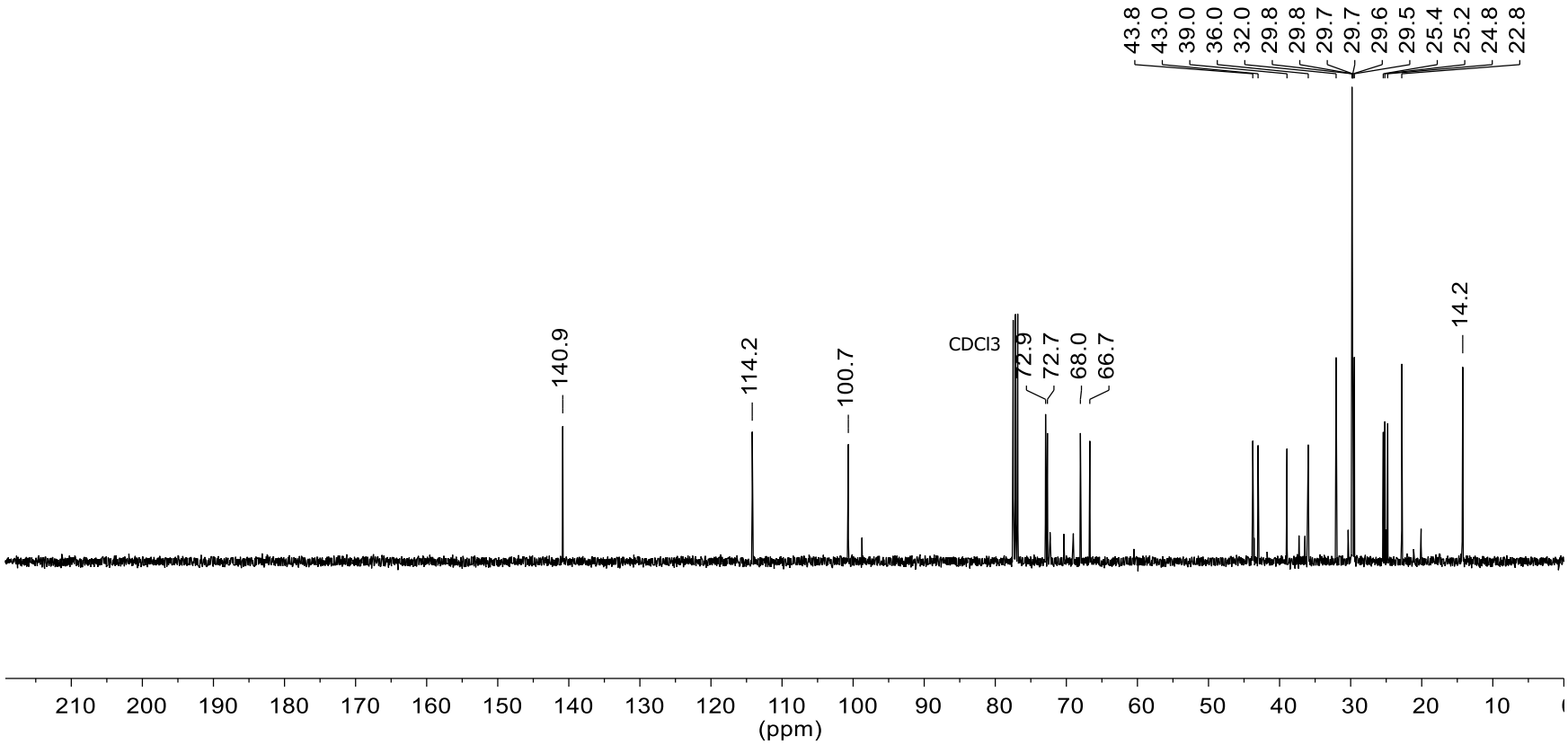


C2c

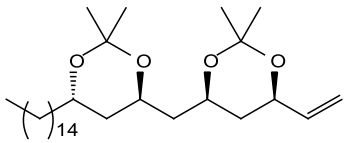
13C-NMR (CDCl3, 400 MHz) - d.r. 91:9



C2c

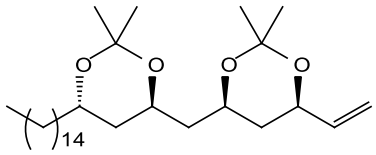


1H-NMR (CDCl3, 400 MHz)

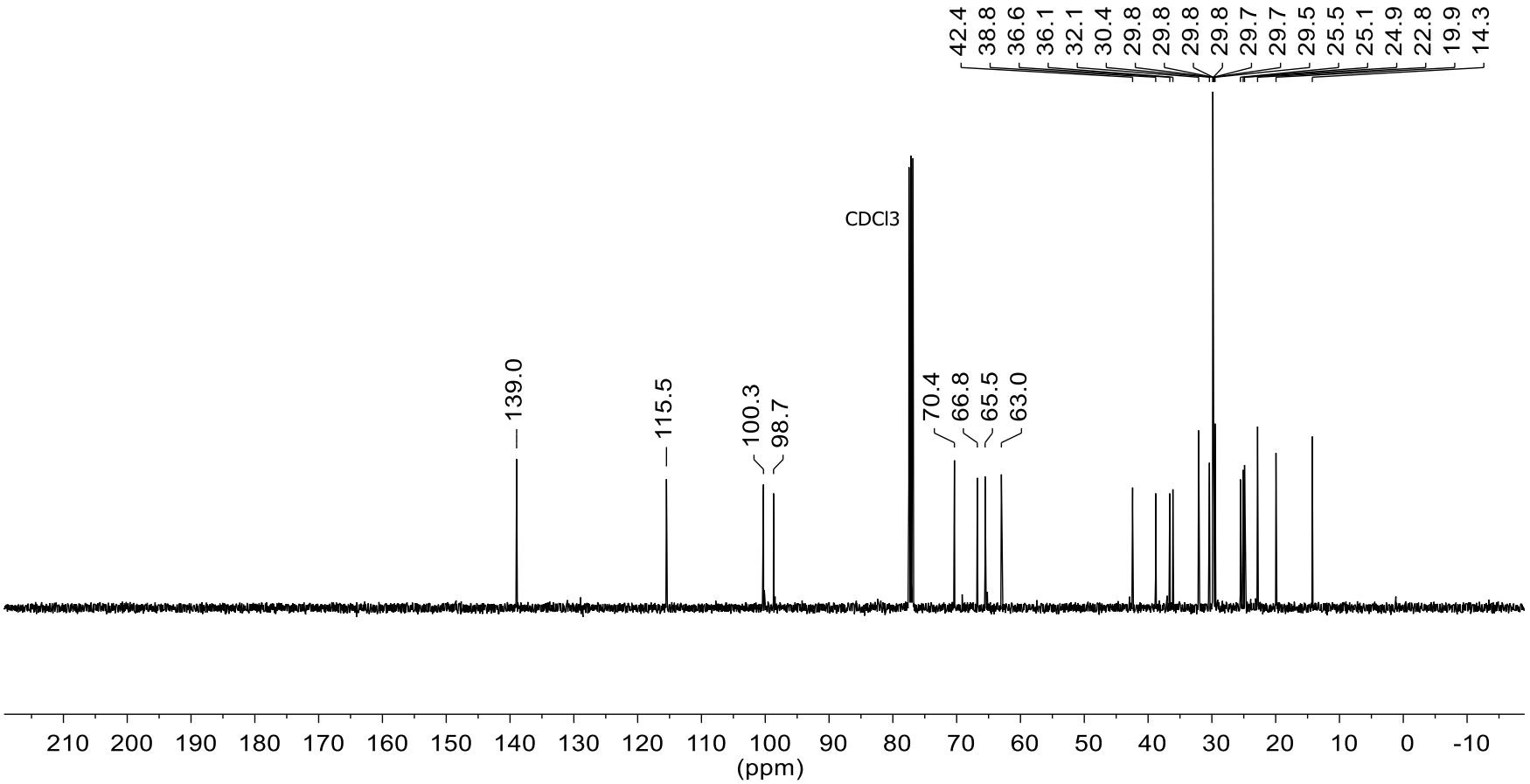


C2d

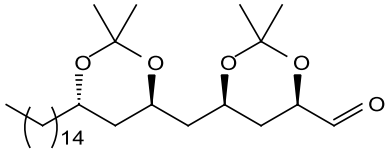
13C-NMR (CDCl3, 101 MHz)



C2d

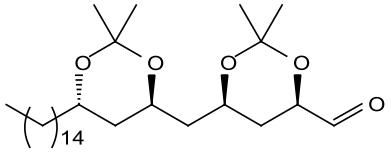


1H-NMR (CDCl3, 400 MHz) - d.r. 92:8

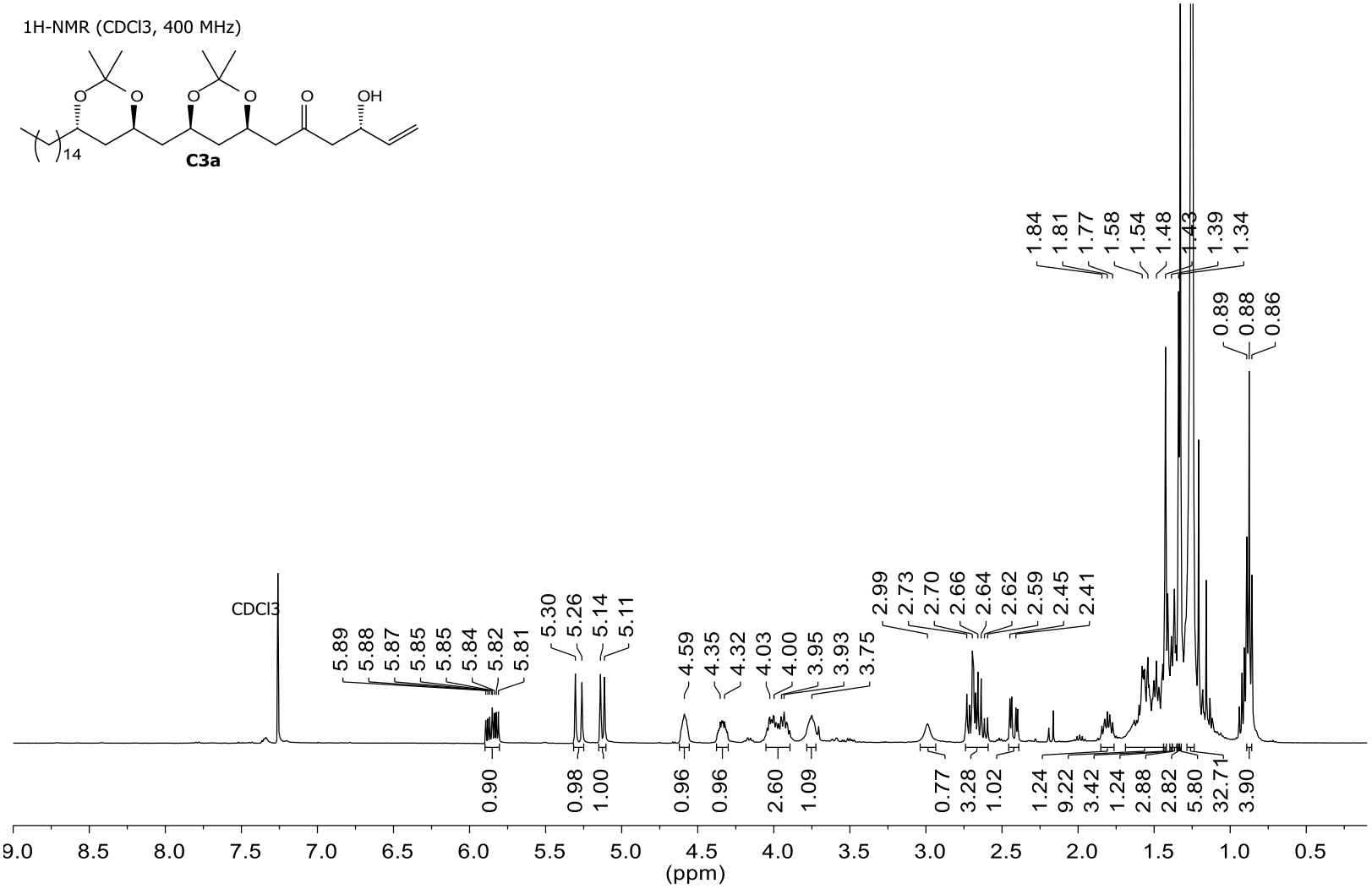


C2

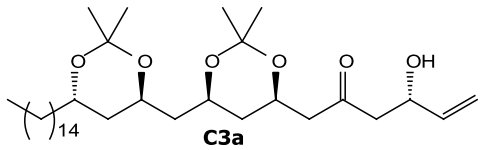
13C-NMR (CDCl3, 101 MHz) - d.r. 92:8



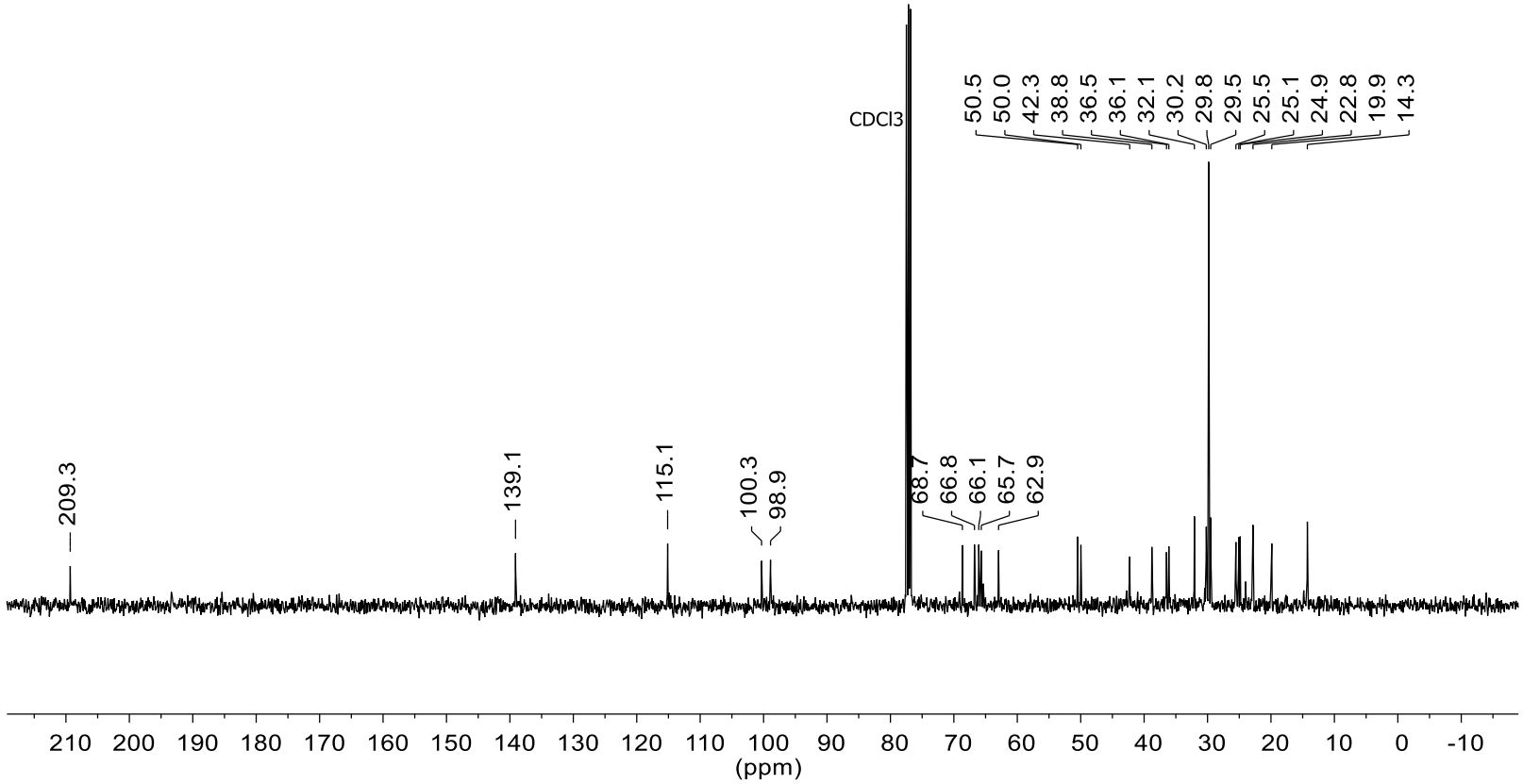
C2


1H-NMR (CDCl3, 400 MHz)
O
O
O
O
O
OH
14
C3a
CDCl3
5.89
5.88
5.87
5.85
5.85
5.84
5.82
5.81
5.30
5.26
5.14
5.11
4.59
4.35
4.32
4.03
4.00
3.95
3.93
3.75
2.99
2.73
2.70
2.66
2.64
2.62
2.59
2.45
2.41
1.84
1.81
1.77
1.58
1.54
1.48
1.43
1.39
1.34
0.89
0.88
0.86
0.90
0.98
1.00
0.96
0.96
2.60
1.09
0.77
3.28
1.02
1.24
9.22
3.42
1.24
2.88
2.82
5.80
32.71
3.90
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

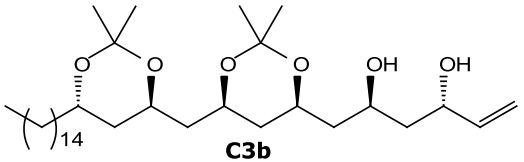
13C-NMR (CDCl3, 101 MHz)



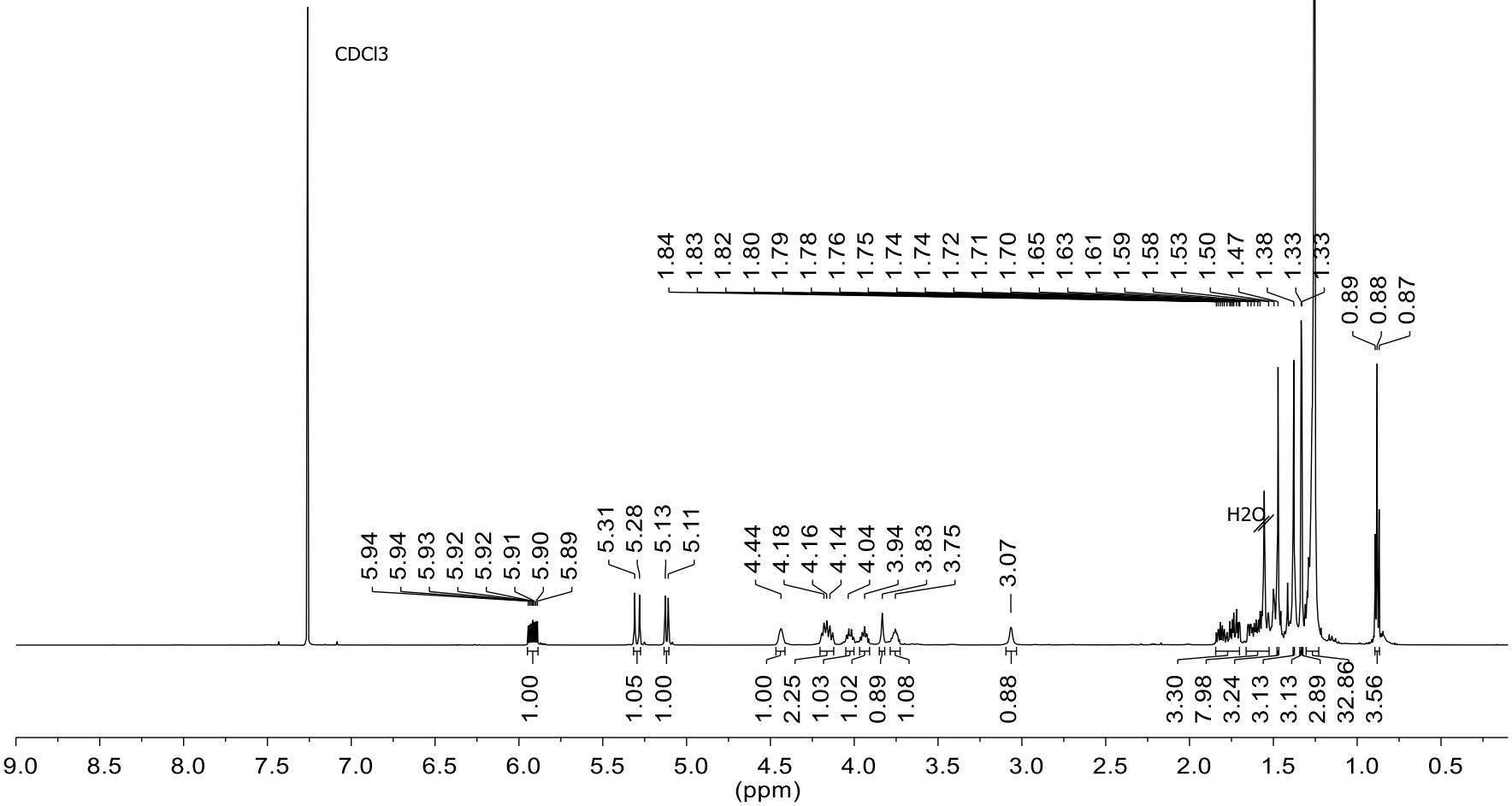
C3a



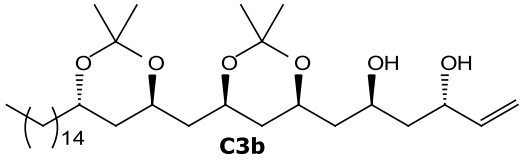
1H-NMR (CDCl3, 600 MHz) -d.r. 98:2



C3b

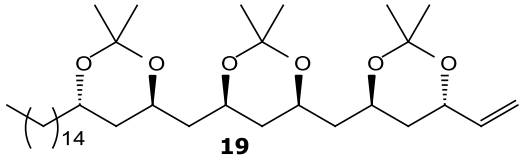


13C-NMR (CDCl3, 151 MHz) - d.r. 98:2



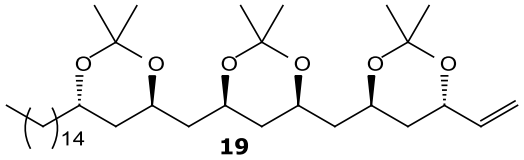
C3b

1H-NMR (CDCl3, 400 MHz)



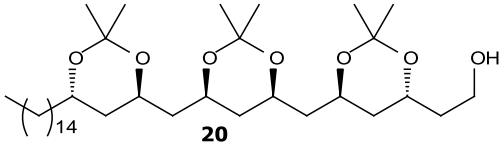
19

13C-NMR (CDCl3, 101 MHz)



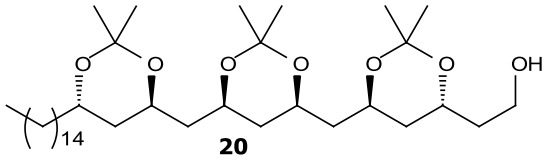
19

1H-NMR (CDCl3, 400MHz)



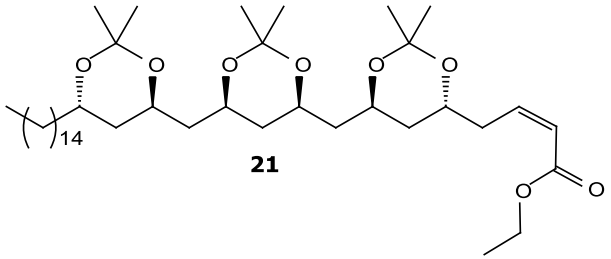
20

13C-NMR (CDCl3, 101MHz)



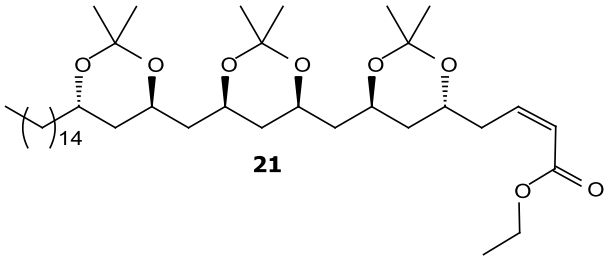
20

1H-NMR (CDCl3, 400 MHz)

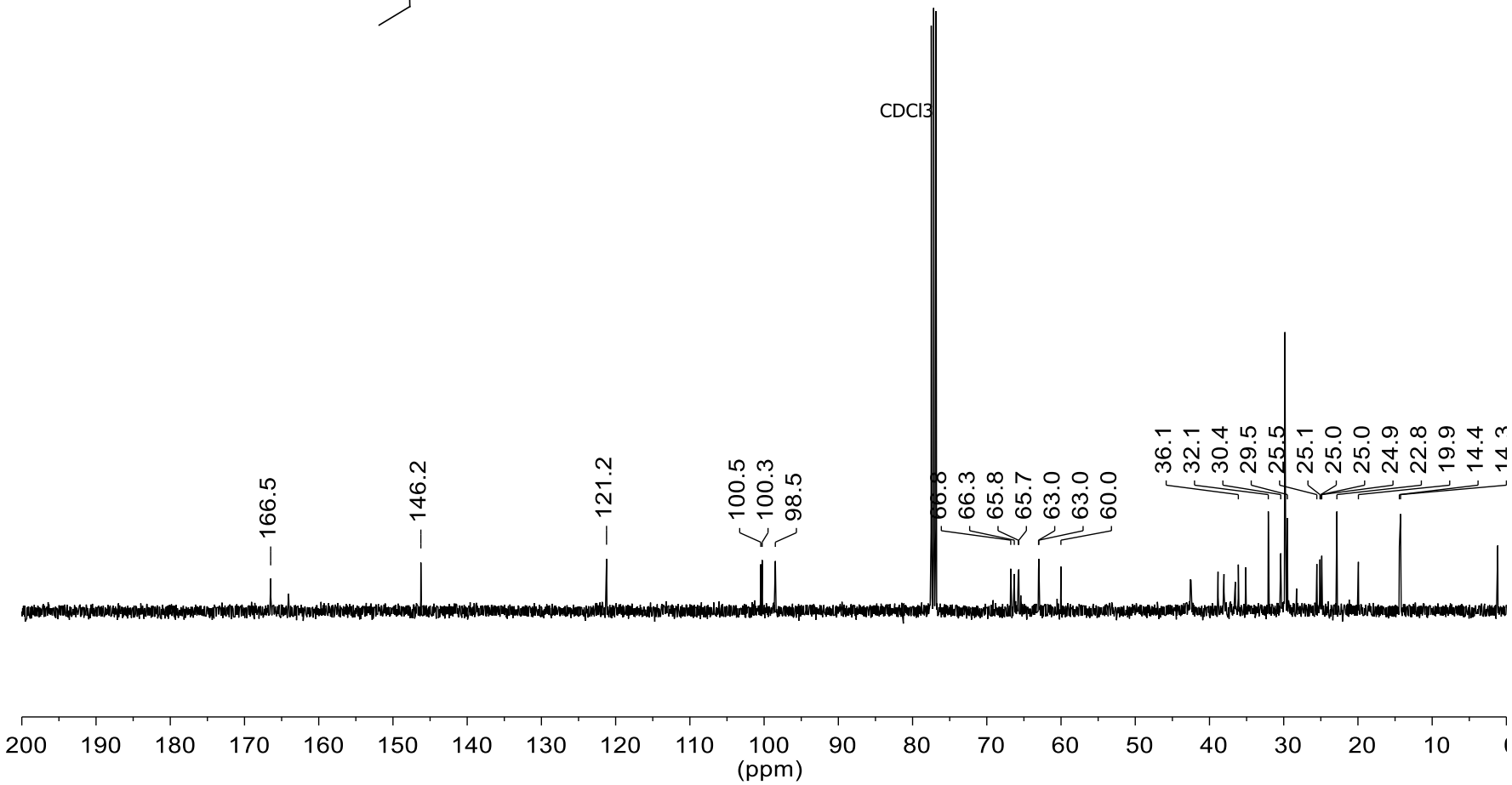


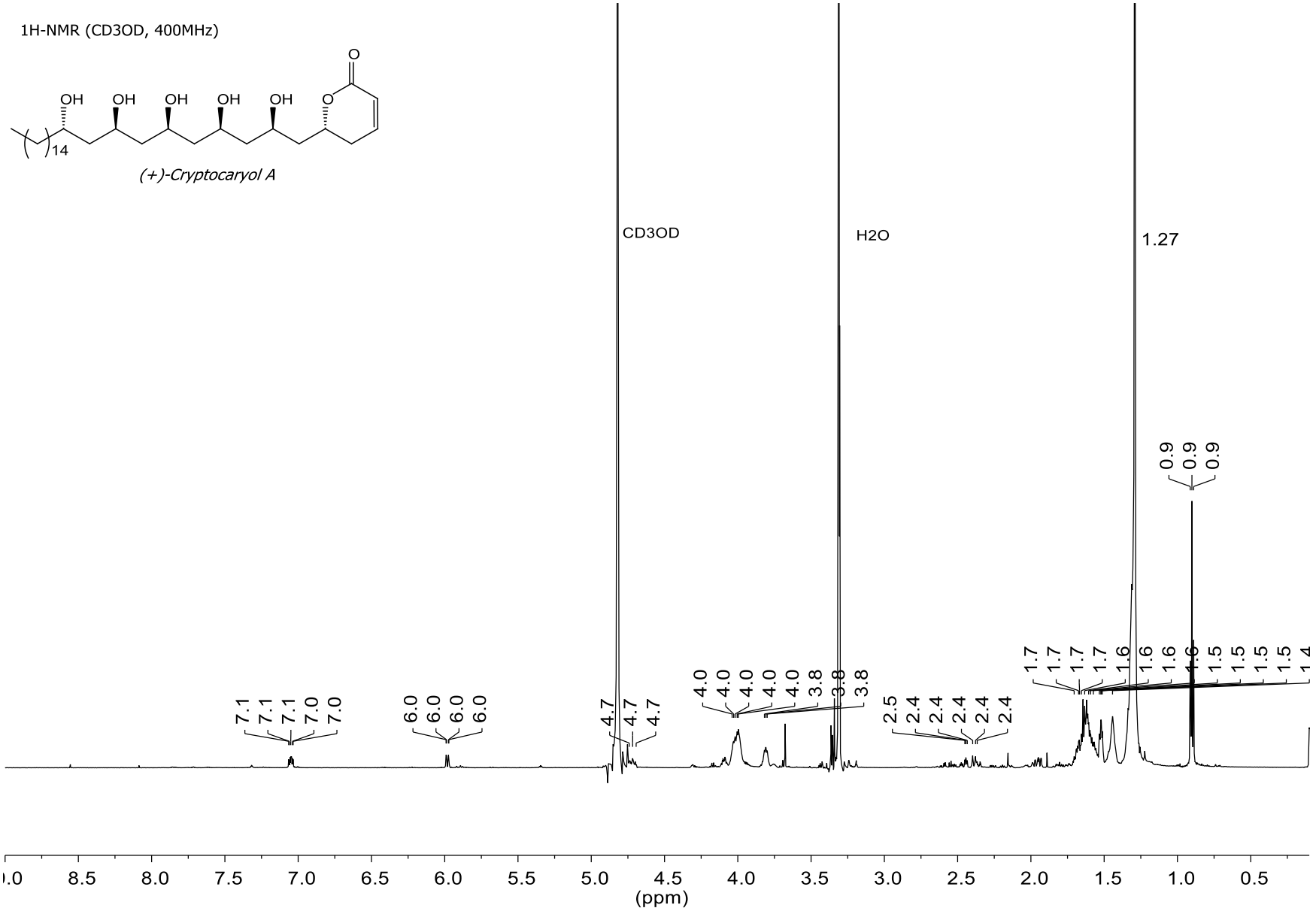
21

13C-NMR (CDCl3, 101 MHz)

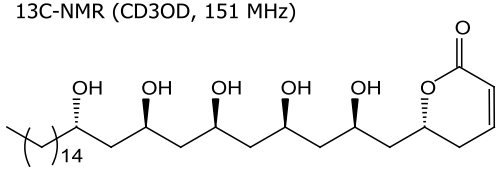


21




1H-NMR (CD3OD, 400MHz)
OH
OH
OH
OH
OH
O
O
14
(+)-Cryptocaryol A
CD3OD
H2O
1.27
0.9
0.9
0.9
7.1
7.1
7.1
7.0
7.0
6.0
6.0
6.0
6.0
4.7
4.7
4.7
4.0
4.0
4.0
4.0
4.0
3.8
3.8
3.8
2.5
2.4
2.4
2.4
2.4
2.4
1.7
1.7
1.7
1.7
1.6
1.6
1.6
1.6
1.5
1.5
1.5
1.5
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

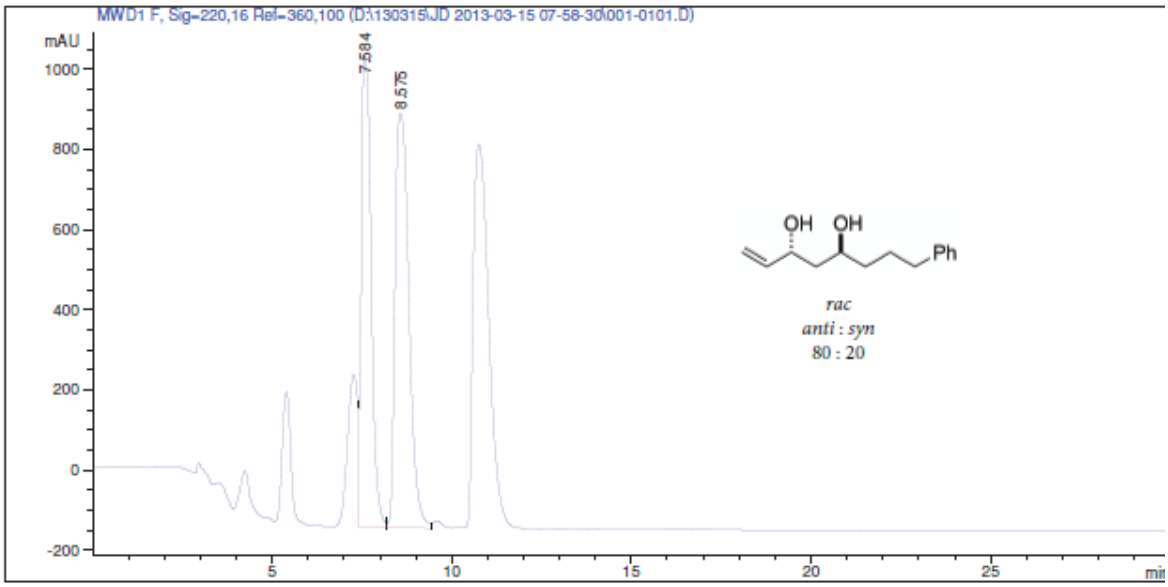
13C-NMR (CD3OD, 151 MHz)



(+)-Cryptocaryol A

Data File D:\130315\JD 2013-03-15 07-58-30\001-0101.D
Sample Name: ocah1049b

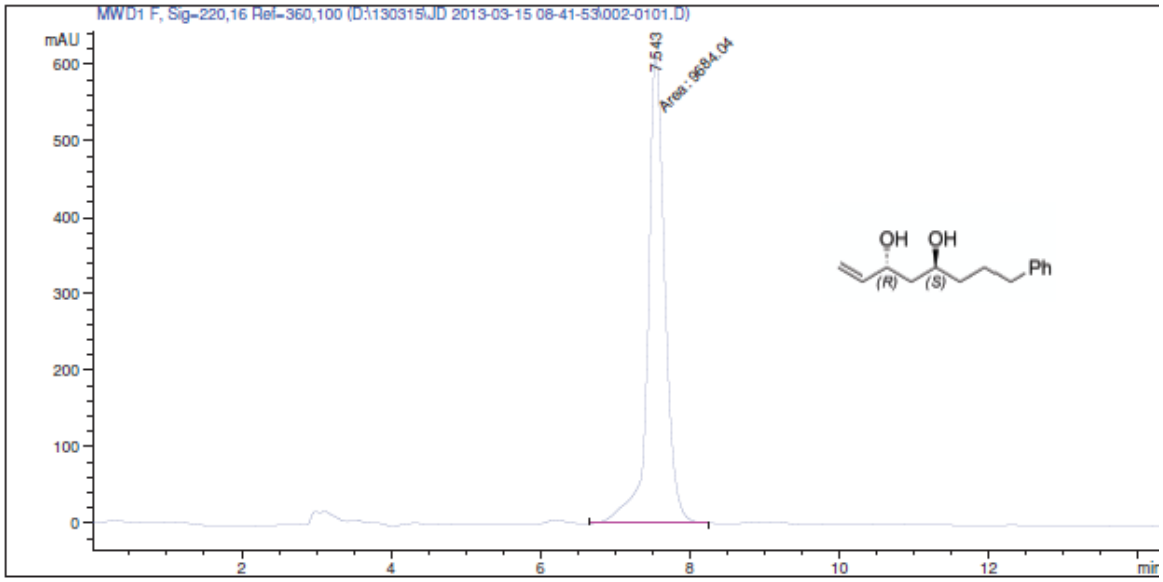
```
==================================================================
Acq. Operator   : I.H.B. - Agilent Installation  Seq. Line :   1
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 3/15/2013 7:58:47 AM                 Inj :   1
                                                 Inj Volume : 20 µl
Method          : D:\130315\JD 2013-03-15 07-58-30\CHIRALPAK IA.M
Last changed    : 3/15/2013 7:45:22 AM by I.H.B. - Agilent Installation
Method Info     : Heptan:Ethanol 90:10 Flow:  1.0 ml/ min    Det: 210 220nm
```




```
==================================================================
                        Area Percent Report
==================================================================

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


Signal 1: MWD1 F, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.584 VV    0.3043 2.25487e4  1172.62646  44.7882
   2   8.575 VV    0.4339 2.77965e4  1033.13733  55.2118

Totals :                  5.03452e4  2205.76379

==================================================================
                        *** End of Report ***
```

Data File D:\130315\JD 2013-03-15 08-41-53\002-0101.D
Sample Name: ocmwiii075

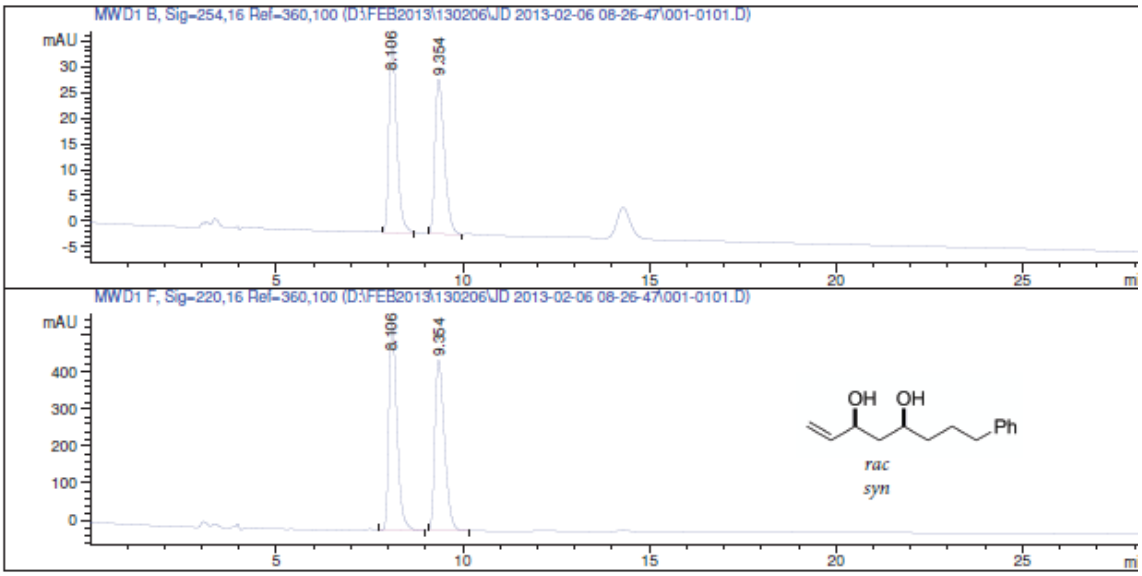
```
==================================================================
Acq. Operator   : I.H.B. - Agilent Installation  Seq. Line :   1
Acq. Instrument : Instrument 1                    Location : Vial 2
Injection Date  : 3/15/2013 8:42:09 AM                 Inj :   1
                                                 Inj Volume : 20 µl
Acq. Method     : D:\130315\JD 2013-03-15 08-41-53\CHIRALPAK IA.M
Last changed    : 3/15/2013 7:45:22 AM by I.H.B. - Agilent Installation
Analysis Method : D:\130315\JD 2013-03-15 08-41-53\CHIRALPAK IA.M
Last changed    : 3/20/2013 2:40:42 PM by I.H.B. - Agilent Installation
Method Info     : Heptan:Ethanol 90:10 Flow:  1.0 ml/ min    Det: 210 220nm
```




```
==================================================================
                        Area Percent Report
==================================================================

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


Signal 1: MWD1 F, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.543 MM    0.2629 9684.04297  613.96179 100.0000

Totals :                  9684.04297  613.96179

==================================================================
                        *** End of Report ***
```

Data File D:\FEB2013\130206\JD 2013-02-06 08-26-47\001-0101.D
Sample Name: ocabdii078

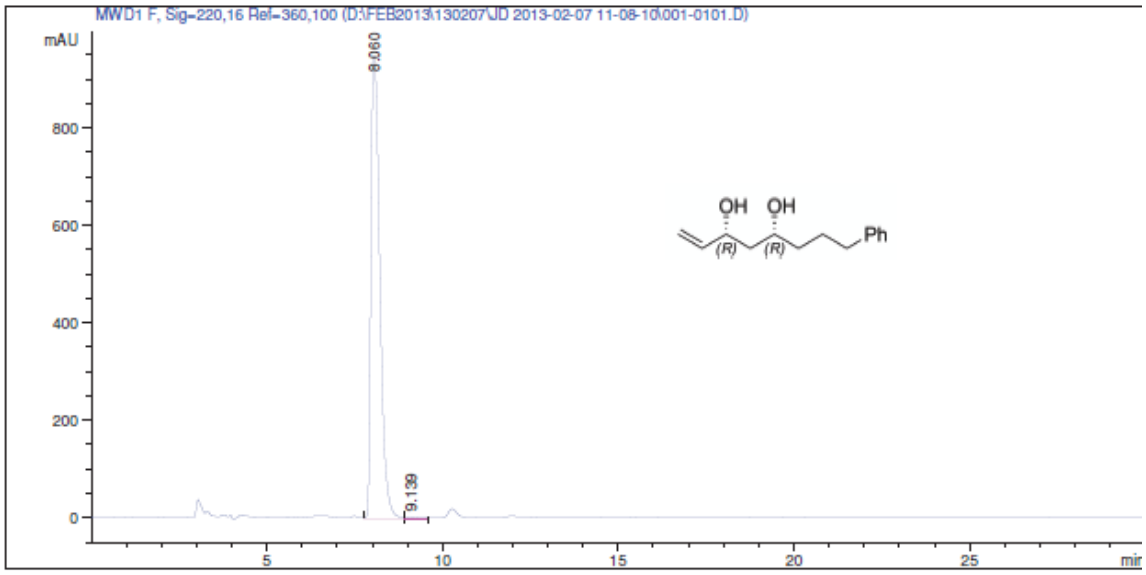
```
==================================================================
Acq. Operator   : I.H.B. - Agilent Installation  Seq. Line :   1
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 2/6/2013 8:27:04 AM                 Inj :   1
                                                 Inj Volume : 2 µl
Acq. Method     : D:\130206\JD 2013-02-06 08-26-47\CHIRAL OJ-H.M
Last changed    : 2/6/2013 7:55:17 AM by I.H.B. - Agilent Installation
Analysis Method : D:\FEB2013\130206\JD 2013-02-06 08-26-47\CHIRAL OJ-H.M
Last changed    : 3/20/2013 2:51:36 PM by I.H.B. - Agilent Installation
Method Info     : Heptan:IPA  90:10 Flow: 1ml/ min Det: 254 220nm 20 Grad
```




```
==================================================================
                        Area Percent Report
==================================================================

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


Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.106 BB    0.2282  544.50885   36.88326  50.9409
   2   9.354 BB    0.2683  524.39343   29.95196  49.0591

Totals :                  1068.90228   66.83522
```

Data File D:\FEB2013\130207\JD 2013-02-07 11-08-10\001-0101.D
Sample Name: ocsh78

```
================================================================
Acq. Operator   : I.H.B. - Agilent Installation  Seq. Line :   1
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 2/7/2013 11:08:25 AM                 Inj :   1
                                                 Inj Volume : 2 µl
Acq. Method     : D:\130207\JD 2013-02-07 11-08-10\CHIRAL OJ-H.M
Last changed    : 2/7/2013 10:21:37 AM by I.H.B. - Agilent Installation
Analysis Method : D:\FEB2013\130207\JD 2013-02-07 11-08-10\CHIRAL OJ-H.M
Last changed    : 2/7/2013 10:21:37 AM by I.H.B. - Agilent Installation
Method Info     : Heptan:IPA  90:10 Flow: 1ml/ min Det: 220 nm 20 Grad
```




```
================================================================
                      Area Percent Report
================================================================

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


Signal 1: MWD1 F, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.060 VV    0.2876 1.68634e4   947.88202  99.4979
   2   9.139 VB    0.3599   85.09708    3.26736   0.5021

Totals :                  1.69485e4   951.14938
```