Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Toward the Synthesis of Hypoxia Selective Anticancer Agent BE-43547 A_2

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I. General Information

Unless otherwise noted, all reagents were purchased commercially and used as received. Anhydrous tetrahydrofuran (THF) and toluene (PhMe) were obtained by distillation from sodium/benzophenone ("freshly distilled") or from an AcroSeal bottle ("anhydrous"). Anhydrous acetonitrile (MeCN), dichloromethane (CH2Cl2), diethyl ether (Et2O) were purchased as such from Acros Organics in AcroSeal bottles and were used as received. Air-sensitive reactions were performed under a positive pressure of either nitrogen (N2) or argon (Ar) in reaction vessels sealed with rubber septa.

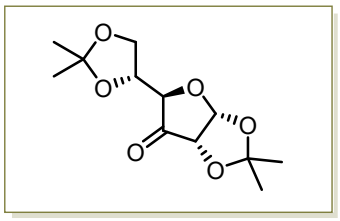
Analytical thin-layer chromatography (TLC) was performed on glass-backed silica-coated plates (Merck TLC Silicagel 60 F254). All reported R_f values were measured using freshly prepared eluent mixtures. Visualization was typically performed using UV light, basic potassium permanganate (KMnO4), or Molisch reagent. Purification by flash column chromatography (FCC) was performed on silica gel (Fisher Scientific, 230 –400 mesh, grade 60) using bulk solvents.

Proton nuclear magnetic resonance (1H NMR) spectra were recorded at Bruker Avance-III 300 spectrometer, at Bruker Avance-III 400 spectrometer, at Bruker Avance 500 spectrometer. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane (0.00 ppm) or the residual solvent peak (7.26 ppm for CDCl3). Multiplets were assigned with the assistance of the multiplet tool in Mestrenova, and are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, app. = apparent. Carbon nuclear magnetic resonance (13C NMR) spectra were recorded at 75 MHz using a Bruker Avance-III 300 spectrometer, at 101 MHz using Bruker Avance-III 400 spectrometer, or at 126 MHz using a Bruker Avance 500 spectrometer. All 13C chemical shifts are reported in ppm relative to the center of the residual solvent peak (77.16 ppm for CDCl3).

Infrared (IR) spectra were measured on Bruker ALPHA FT-IR. Melting points were measured on a Thomas-Hoover Uni-Melt melting point apparatus in open capillary tubes and are uncorrected. HRMS were recorded using ESI-TOF techniques.

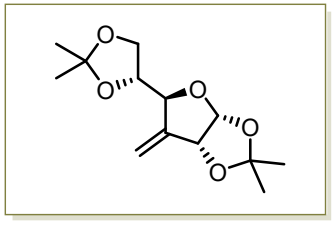
II. Experimental Procedures and Compound Characterization

(3a*R*,5*R*,6a*S*)-5-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyldihydrofuro[2,3-d][1,3]dioxol-6(5H)-one (S1):



1, 2, 5, 6-Di-*O*-isopropylidene-*α*-D-glucofuranose **10** (20.0 g, 76.9 mmol) was dissolved in anhydrous CH_2Cl_2 (200 mL), PDC (20.25 g, 53.8 mmol) and Ac_2O (21.8 mL, 230.7 mmol) were added, and the reaction was heated to reflux and stirred for 3 hours. After completion, the reaction mixture was concentrated in *vacuo* and the residue was applied to a short silica gel column (EtOAc) and the filtrate was washed with aqueous sodium bicarbonate (60 mL), water (60 mL), dried over anhydrous Na_2SO_4, and concentrated to give ketone **S1** as yellow oil in 85% yield (16.9 g) as a pale-yellow oil. **$[\alpha]_D^{20}$** 113.494 (c = 0.455 in $CHCl_3$); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.13 (d, J = 4.5 Hz, 1H), 4.38 (d, J = 4.5 Hz, 1H), 4.36 – 4.32 (m, 2H), 4.04 – 4.00 (m, 2H), 1.45 (s, 3H), 1.43 (s, 3H), 1.33 (s, 6H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 209.0, 114.4, 110.5, 103.2, 79.1, 76.5, 64.4, 27.7, 27.3, 26.1, 25.4; **IR (neat)** υ_{max} 2965, 1732, 1456, 1382,1281, 1116, 1041, 843; **HRMS** calcd for $C_{12}H_{18}NaO_6$ $[M+Na]^+$: 281.1001 ; found: 281.1011

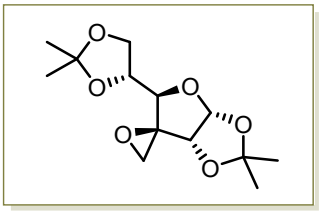
(3a*R*,5*S*,6a*R*)-5-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-methylenetetrahydrofuro [2,3-d][1,3]dioxole (S2):



To a solution of methyl triphenylphosphonium bromide (41.5 g, 116.3 mmol) in dry THF (400 mL), *n*-BuLi (46.5 mL, 116.3 mmol, 2.5 M solution in *n*-Hexane) was added at –78 ^{o}C under nitrogen atmosphere and allowed it to stir for 45 minutes. To the *in situ* generated yellow colored Wittig ylide, a solution of keto compound **S1** (15 g, 58.13 mmol) in dry THF (200 mL) was added drop wise to the reaction mixture at 0 ^{o}C. The reaction mixture was warmed to room temperature and stirred for 4 h. A saturated solution of aqueous NH_4Cl (70 mL) was added and extracted with EtOAc (2 x 100 mL). The

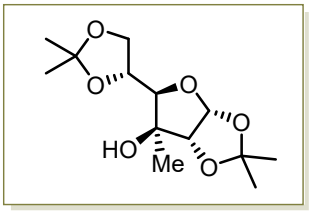
combined organic layer was washed with water (100 mL), brine (75 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography to afford exo-olefin **S2** in 70% yield (10.4 g) as a colorless oil. **$[\alpha]_D^{20}$** 99.714 (*c* = 0.7 in $CHCl_3$); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.79 (d, *J* = 4.0 Hz, 1H), 5.49 (d, *J* = 1.0 Hz, 1H), 5.43 (d, *J* = 1.0 Hz, 1H), 4.89 – 4.86 (m, 1H), 4.66 – 4.62 (m, 1H), 4.08 – 4.02 (m, 2H), 3.95 – 3.90 (m, 1H), 1.50 (s, 3H), 1.42 (s, 3H), 1.35 (d, *J* = 5.9 Hz, 6H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.9, 113.6, 112.7, 109.9, 104.7, 82.3, 79.4, 77.5, 66.9, 27.5, 27.2, 26.7, 25.6; **IR (neat) υ_{max}** 2988, 2940, 1456, 1376, 1215, 1160, 1055, 929, 846; **HRMS** calcd for $C_{13}H_{20}NaO_5$ $[M+Na]^+$: 279.1208 ; found: 279.1199.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyldihydro-5H-spiro[furo[2,3-d][1,3]dioxole-6,2'-oxirane] (S3):



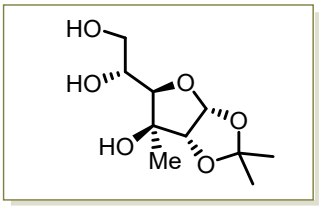
A solution of (3a*R*,5*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-methylenetetrahydrofuro [2,3-d][1,3]dioxole **S2** (10 g, 39.0 mmol) in CH_2Cl_2 (125 mL) was cooled to 0°C, treated with 77% commercial *m*CPBA (aldrich, 8.7 g, 50.8 mmol), warmed to room temperature and allowed to stir for 10 hours. After completion (by TLC analysis), saturated aq. $NaHCO_3$ (40 mL) was added, and the solution was stirred for additional 15 min. and concentrated under reduced pressure. The residue was purified by flash column chromatography to furnish spiro epoxide **S3** in 68% yield (7.2 g) as a colorless oil. **$[\alpha]_D^{20}$** 40.118 (*c* = 0.340 in $CHCl_3$); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.94 (d, *J* = 3.9 Hz, 1H), 4.38 – 4.35 (m, 1H), 4.28 (d, *J* = 3.9 Hz, 1H), 4.07 – 3.99 (m, 3H), 3.16 (d, *J* = 4.8 Hz, 1H), 3.09 (d, *J* = 4.8 Hz, 1H), 1.56 (s, 3H), 1.39 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 112.7, 109.7, 104.3, 84.7, 76.6, 73.1, 67.1, 65.2, 46.4, 27.1, 26.9, 26.6, 25.4; **IR (neat) υ_{max}** 2990, 2942, 1459, 1380, 1220, 1163, 1074, 1023, 855. **HRMS** calcd for $C_{13}H_{20}O_6Na$ $[M+Na]^+$: 295.1158 ; found: 295.1150.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-ol (11):



A solution of the spiro epoxide **S3** (5 g, 18.4 mmol) dissolved in dry THF (60 mL) was added dropwise to a stirring mixture of $LiAlH_4$ (1 g) in dry THF (30 mL) under nitrogen atmosphere and the reaction mixture was heated at reflux for 5 h. After completion, it was cooled and excess $LiAlH_4$ was decomposed by the addition of saturated NH_4Cl solution. The mixture was filtered, and the organic layer was separated. It was washed with brine (25 mL), dried, and evaporated. The crude residue was purified by column chromatography on silica gel using EtOAc–hexanes as eluent to give tertiary alcohol **11** in 87% yield (4.38 g) as a colorless oil. **$[\alpha]_D^{20}$** 24.857 (*c* = 0.140 in $CHCl_3$). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.86 (d, *J* = 3.6 Hz, 1H), 4.32 – 4.25 (m, 1H), 4.23 (d, *J* = 3.6 Hz, 1H), 4.14 (dd, *J* = 8.7, 6.4 Hz, 1H), 3.99 (dd, *J* = 8.7, 5.3 Hz, 1H), 3.81 (d, *J* = 7.6 Hz, 1H), 2.13 (s, 1H), 1.51 (s, 3H), 1.47 (s, 3H), 1.44 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 112.4, 109.7, 104.7, 87.8, 83.2, 80.2, 73.8, 67.9, 27.3, 26.8, 26.6, 25.3, 20.2; **IR (neat) υ_{max}** 3467, 2988, 2938, 1458, 1378, 1218, 1075, 1010, 852. **IR (neat) υ_{max}** 3467, 2988, 2938, 1458, 1378, 1218, 1075, 1010, 852; **HRMS** calcd for $C_{13}H_{22}O_6Na$ $[M+Na]^+$: 297.1314 ; found: 297.1314.

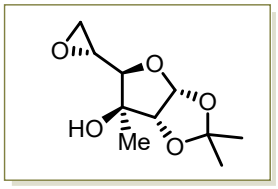
(*R*)-1-((3a*R*,5*R*,6*S*,6a*R*)-6-Hydroxy-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)ethane-1,2-diol (12):



The substrate **11** (5.0 g, 18.2 mmol) was dissolved in 80% AcOH (40 mL) and allowed to stir for 6 h at room temperature. After completion, the solvent was evaporated in rotary evaporator and the last traces of acetic acid by toluene co-evaporation (3×20 mL) to result a white solid **12** which was subjected to recrystallization and then used directly for next reaction. **MP** 124 °C; **$[\alpha]_D^{20}$** 13.714 (*c* = 0.35 in $CHCl_3$); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.89 (d, *J* = 3.6 Hz, 1H), 4.24 (d, *J* = 3.6 Hz, 1H), 4.03 (bs, 1H), 3.88 – 3.77 (m, 3H), 2.83 (s, 1H), 2.71 (d, *J* = 4.5 Hz, 1H), 2.10 (bs, 1H), 1.51 (s, 3H), 1.47 (s, 3H), 1.33 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 112.4, 104.5, 87.9, 82.2, 80.5, 71.2, 64.2, 27.2, 26.5, 20.3; **IR**

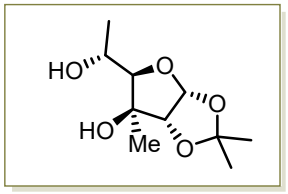
(neat) υ_{max} 3397, 2987, 2931, 1457, 1379, 1218, 1078, 1007, 938, 877, 763 ; **HRMS** calcd for $C_{10}H_{18}O_6Na$ $[M+Na]^+$: 257.0999 ; found: 257.1001.

(3a*R*,5*R*,6*S*,6a*R*)-2,2,6-Trimethyl-5-((*R*)-oxiran-2-yl)tetrahydrofuro[2,3-d][1,3]dioxol-6-ol (13):



Triphenylphosphine (5.04 g, 19.2 mmol) was added to the solution of **12** (3.0 g, 12.8 mmol) in anhydrous toluene (60 mL) and the mixture was stirred at room temperature for 15 min. After addition of activated molecular sieves (3 Å, 2 g), DEAD (3 mL, 19.2 mmol) was added drop wise to the reaction mixture, which was then allowed to stir for 6 h under reflux conditions. After completion (by TLC analysis), the reaction mixture was filtered through a pad of celite and the solvent was evaporated under reduced pressure, the residue was subjected to column purification to give epoxide **13** as white solid in 75% yield over 2 steps (3 g). **MP** 46 °C; **$[\alpha]_D^{20}$** 33.455 (*c* = 0.165 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.92 (d, *J* = 3.6 Hz, 1H), 4.27 (d, *J* = 3.6 Hz, 1H), 3.58 (d, *J* = 6.1 Hz, 1H), 3.27 – 3.22 (m, 1H), 2.88 (dd, *J* = 5.0, 4.1 Hz, 1H), 2.77 (dd, *J* = 5.0, 2.7 Hz, 1H), 2.11 (s, 1H), 1.49 (s, 3H), 1.44 (s, 3H), 1.32 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 112.6, 104.9, 87.3, 82.8, 80.4, 48.9, 45.4, 27.1, 26.5, 18.9; **IR (neat)** υ_{max} 2992, 1459, 1382, 1221, 1171, 1082, 1012, 928, 877 ; **HRMS** calcd for $C_{10}H_{16}O_5Na$ $[M+Na]^+$: 239.0895 ; found: 239.0887.

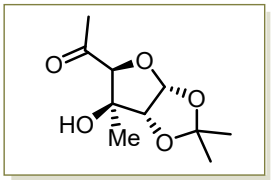
(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-1-Hydroxyethyl)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-ol (14):



A suspension of lithium aluminium hydride (484 mg, 12.7 mmol) in dry THF (10 mL) was added dropwise to a solution of **13** (2.5 g, 11.5 mmol) in dry THF (50 mL) at 0°C over a period of 15 min. After complete addition, the mixture was stirred for 3 h under reflux conditions. Then a mixture of water and THF (1:1) was added dropwise until no further formation of hydrogen could be observed. The inorganic precipitate was filtered off and washed with EtOAc. The combined organic layer was

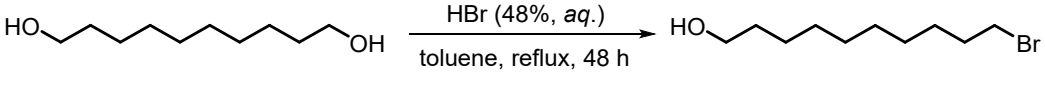
evaporated under reduced pressure and the residue was purified by using flash column chromatography to provide secondary alcohol **14** in 80% yield (2 g) as a white solid. **MP** 49 °C; **$[\alpha]_D^{20}$** 34.40 (*c* = 0.1 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.90 (d, *J* = 3.6 Hz, 1H), 4.32 – 4.24 (m, 1H), 4.22 (d, *J* = 3.6 Hz, 1H), 4.18 (bs, 1H), 3.73 (d, *J* = 4.3 Hz, 1H), 2.68 (bs, 1H), 1.50 (s, 3H), 1.47 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 3H), 1.32 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 112.2, 104.2, 88.8, 84.2, 80.9, 68.3, 27.3, 26.5, 20.8, 19.1; **IR (neat)** υ_{max} 3563, 3424, 2988, 1462, 1383, 1224, 1172, 1084, 1015, 936, 882 ; **HRMS** calcd for $C_{10}H_{18}O_5Na$ $[M+Na]^+$: 241.1052 ; found: 241.1057.

1-((3a*R*,5*S*,6*R*,6a*R*)-6-Hydroxy-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)ethan-1-one (15):



To a solution of alcohol **14** (2.0 g, 9.17 mmol) in anhydrous dichloromethane (50 mL) was added Dess-Martin periodinane (5.8 g, 13.7 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 5 h. TLC showed that no starting material remained. Then the reaction mixture was diluted with additional dichloromethane (60 mL) and the resulting precipitate was filtered off. The filtrate was washed with saturated aqueous sodium hydrogen carbonate (containing 4 g of sodium thiosulfate pentahydrate) (40 mL). The combined organic layer was washed with brine and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the residue was dried under vacuum to give ketone **15** in 70% yield (1.38 g) as a white amorphous solid. **MP** 47 °C; **$[\alpha]_D^{20}$** 12.800 (*c* = 0.050 in $CHCl_3$); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.04 (d, *J* = 3.4 Hz, 1H), 4.25 (d, *J* = 3.5 Hz, 1H), 4.23 (s, 1H), 2.28 (s, 3H), 1.98 (s, 1H), 1.51 (d, *J* = 4.8 Hz, 6H), 1.34 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 209.0, 112.9, 105.2, 87.3, 86.9, 81.7, 29.0, 27.3, 26.6, 19.6; **IR (neat)** υ_{max} 2990, 1721, 1377, 1277, 1225, 1167, 1086, 1027, 770 ; **HRMS** calcd for $C_{10}H_{16}O_5Na$ $[M+Na]^+$: 239.0895 ; found: 239.0882.

10-Bromo-decane-1-ol (17):

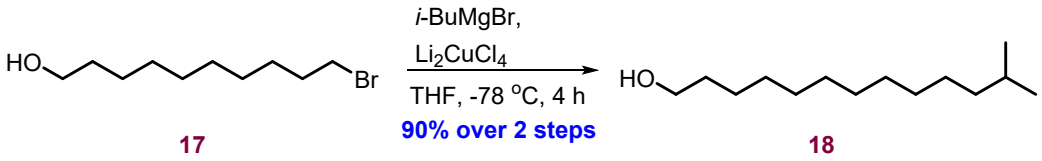


16 **17**

Scheme S1

To a solution of decane-1,10-diol **(16)** (10 g, 57.3 mmol) in toluene (200 mL) was added HBr (8 mL, 68.8 mmol, 9M) and the reaction was stirred at reflux for 24 hours. Additional HBr (2.6 mL, 22.9 mmol) was added. After stirring for 24 hours at reflux the reaction was allowed to cool to room temperature. The phases were separated and the organic phase was diluted with Et_2O (100 mL). The organic phase was washed with NaOH (aq., 2M, 50 mL), brine (50 mL) followed by NaH_2PO_4/Na_2HPO_4 (aq., 50 mL) buffer at pH 7. The organic phase was dried over Na_2SO_4, filtered and concentrated to give bromodecanol **(17)** which was used directly for next reaction.

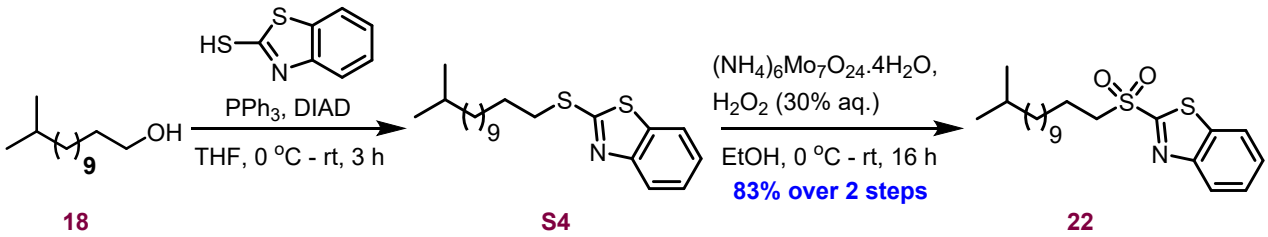
12-Methyl-tridecane-1-ol (18)[1]



Scheme S2

Bromodecanol **(17)** was dissolved in anhydrous THF (9 g, 37.9 mmol) and cooled to -78 °C. THF solution of *i*-BuMgBr (144.1 mL, 1M, 144 mmol) was added dropwise followed by Li_2CuCl_4 (18.9 mL, 0.1M, 1.89 mmol). The reaction was allowed to stir for 10 min at -78 °C and then allowed to warm to room temperature and stirred for overnight. After completion, the reaction was quenched with NH_4Cl, and the precipitate was filtered off. The filtrate was extracted with EtOAc (3×100 mL). The organic phase was washed with water, $NaHCO_3$ and brine then dried over Na_2SO_4 and filtered. Concentration *in vacuo* yielded the product methyl tridecanol **18** in 90% yield (7.3 g).

2-((12-methyltridecyl)sulfonyl)benzo[d]thiazole (22):



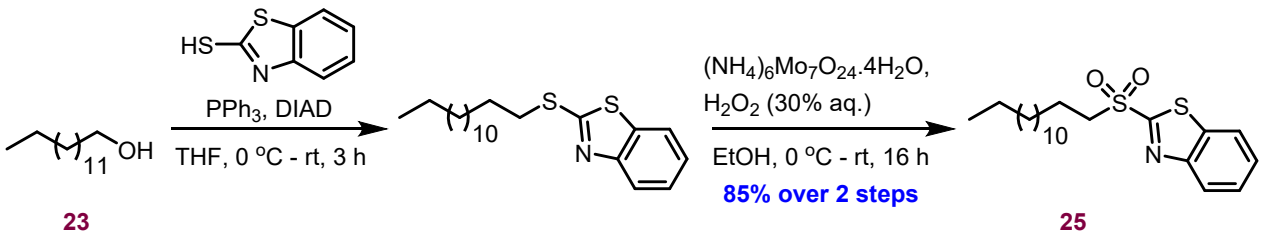
Scheme S3

To a solution of the mixture of alcohol **18** (5 g, 23.36 mmol) and triphenylphosphine (9.2 g, 35 mmol) in anhydrous THF (50 mL) cooled at 0 °C was added 2-mercaptobenzothiazole (5.86 g, 35 mmol) followed by the drop wise addition of DIAD (6.9 mL, 35 mmol). The reaction mixture was stirred gradually allowing it to warm to rt and continue over a period of 3 hours. The reaction mixture was quenched by adding aq saturated $NaHCO_3$ solution (4 mL). The layers were separated, and the aqueous

layer was extracted with EtOAc (50 mL×3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to furnish the crude product. Purification of the crude residue *via* flash chromatography on silica gel afforded sulfide **S4** as a white solid.

2-((12-Methyltridecyl)thio)benzo[d]thiazole **S4** (7.6 g, 20.9 mmol) was dissolved in 100 mL of ethanol. To the solution was added ammonium molybdate tetrahydrate (7.75 g, 6.28 mmol) and 30% H_2O_2 (21.4 mL, 209.3 mmol) slowly at 0 °C. The reaction was allowed to stir for 12 h at room temperature and quenched with 20 mL saturated sodium sulphate solution. The reaction mixture was extracted with EtOAc (3×50 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography to give 2-((12-methyltridecyl)sulfonyl)benzo[d]thiazole **22** as a white crystalline solid in 83% yield over 2 steps (7.6 g). **MP** 72 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.22 (dd, J = 7.6, 1.2 Hz, 1H), 8.05 – 8.00 (m, 1H), 7.62 (dtd, J = 15.0, 7.2, 1.3 Hz, 2H), 3.51 (dd, J = 9.1, 6.9 Hz, 2H), 1.93 – 1.83 (m, 2H), 1.57 – 1.38 (m, 4H), 1.22 (s, 13H), 1.7 – 1.11 (dd, J = 13.4, 6.5 Hz, 2H), 0.86 (d, J = 6.6 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.1, 152.9, 136.9, 128.1, 127.8, 125.6, 122.5, 54.9, 39.2, 30.0, 29.8, 29.7, 29.6, 29.3, 29.0, 28.4, 28.1, 27.5, 22.8, 22.4; **IR (neat)** υ_{max} 2870, 1440, 1215, 795, 698; **HRMS** calcd for $C_{21}H_{34}NO_2S_2$ $[M+H]^+$: 396.2031 ; found: 396.2025.

2-(tetradecylsulfonyl)benzo[d]thiazole (25):

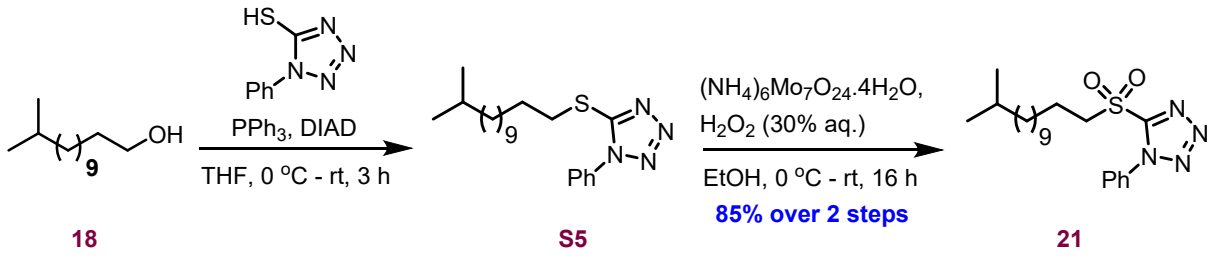


Scheme S4

Compound 25 was prepared using the above-mentioned procedure in 85% Yield. **MP** 63 °C.; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.62 (dt, J = 19.2, 7.3 Hz, 2H), 3.56 – 3.46 (m, 2H), 1.94 – 1.81 (m, 2H), 1.43 (m, 2H), 1.35 – 1.16 (m, 20H), 0.87 (t, J = 6.7 Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 152.9, 136.9, 128.1, 127.8, 125.6, 122.5, 77.5, 77.2, 76.8, 54.9, 32.0, 29.8, 29.7, 29.7, 29.7, 29.6, 29.5, 29.3, 29.0, 28.3, 22.8, 22.4, 14.2.; **IR (neat)** υ_{max} 2915,

2849, 1466, 1326, 1144, 1029, 853, 723, 637. **HRMS** calcd for $C_{21}H_{33}NNaO_2S_2$ $[M+Na]^+$: 418.1850 ; found: 418.1821.

5-((12-Methyltridecyl)sulfonyl)-1-phenyl-1H-tetrazole (21):

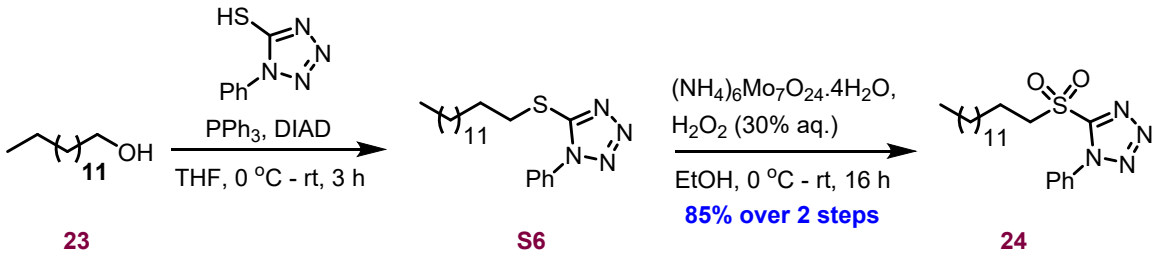


Scheme S5

To a solution of alcohol **18** (4 g, 18.6 mmol) and triphenylphosphine (7.35 g, 28 mmol) in anhydrous THF (50 mL) cooled at 0 °C was added 1-phenyl-1H-tetrazole-5-thiol (5.0 g, 28 mmol) followed by the dropwise addition of DIAD (5.5 mL, 28 mmol). The reaction mixture was stirred gradually allowing it to warm to room temperature and continue over a period of 3 hours. The reaction mixture was quenched by adding aqueous saturated $NaHCO_3$ solution (4 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (50 mL×3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to furnish the crude product. Purification of the crude residue *via* flash chromatography on silica gel afforded sulfide **S5** as a white color solid.

5-((12-Methyltridecyl)thio)-1-phenyl-1H-tetrazole **S5**(6.3 g, 16.8 mmol) was dissolved in 75 mL of ethanol. To the solution was added ammonium molybdate tetrahydrate (6.24 g, 5.50 mmol) and 30% H_2O_2 (17.2 mL, 168 mmol) slowly at 0 °C. The reaction was allowed to stir for 12 h at room temperature and quenched with 20 mL saturated sodium sulphate solution. The reaction mixture was extracted with EtOAc (3×50 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography to give 5-((12-methyltridecyl)sulfonyl)-1-phenyl-1H-tetrazole **21** as a white crystalline solid in 85% yield over 2 steps (6.4 g). **MP** 48 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.8 – 7.5 (m, 5H), 3.73 (t, J = 7.9 Hz, 2H), 1.95 (dt, J = 15.5, 7.7 Hz, 2H), 1.64 – 1.40 (m, 4H), 1.25 (s, 13H), 1.19 – 1.10 (m, 2H), 0.86 (d, J = 6.6 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.6, 133.2, 131.6, 129.8, 125.2, 56.2, 39.2, 30.0, 29.8, 29.7, 29.6, 29.3, 29.0, 28.3, 28.1, 27.5, 22.8, 22.1; **IR (neat)** υ_{max} 2910, 2780, 1320, 1168, 1031, 740, 676; **HRMS** calcd for $C_{21}H_{35}N_4O_2S$ $[M+H]^+$: 407.2481; found: 407.2476.

1-Phenyl-5-(tetradecylsulfonyl)-1H-tetrazole (24):

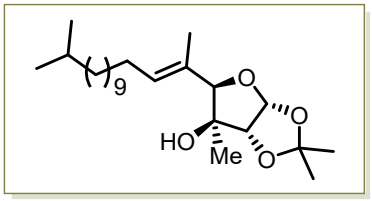


Scheme S6

To a solution of 1-tetradecanol **23** (3 g, 14.0 mmol) and triphenylphosphine (5.5 g, 21 mmol) in anhydrous THF (40 mL) cooled at 0 °C was added 1-phenyl-1H-tetrazole-5-thiol (3.74 g, 21 mmol) followed by the dropwise addition of DIAD (4.13 mL, 21 mmol). The reaction mixture was stirred gradually allowing it to warm to room temperature and continue over a period of 3 hours. The reaction mixture was quenched by adding aqueous saturated $NaHCO_3$ solution (4 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (50 mL×3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to furnish the crude product. Purification of the crude residue *via* flash chromatography on silica gel afforded sulfide **S6** as a white color solid.

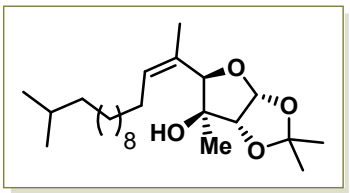
5-((12-Methyltridecyl)thio)-1-phenyl-1H-tetrazole **S6** (6.3 g, 16.8 mmol) was dissolved in 75 mL of ethanol. To the solution was added ammonium molybdate tetrahydrate (6.24 g, 5.50 mmol) and 30% H_2O_2 (17.2 mL, 168 mmol) slowly at 0 °C. The reaction was allowed to stir for 12 h at room temperature and quenched with 20 mL saturated sodium sulphate solution. The reaction mixture was extracted with EtOAc (3×50 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography to give 5-((12-methyltridecyl)sulfonyl)-1-phenyl-1H-tetrazole **24** as white solid in 85% yield over 2 steps (6.4 g). **MP** 52 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 – 7.67 (m, 2H), 7.64 – 7.57 (m, 3H), 3.73 (dd, J = 9.1, 6.9 Hz, 2H), 2.00 – 1.90 (m, 2H), 1.54 – 1.45 (m, 2H), 1.34 – 1.22 (m, 20H), 0.88 (t, J = 6.9 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.6, 133.2, 131.6, 129.9, 125.2, 56.2, 32.1, 29.8, 29.7, 29.6, 29.5, 29.3, 29.0, 28.3, 22.8, 22.1, 14.3; **IR (neat)** υ_{max} 2932, 2861, 1747, 1462, 1381, 1268, 1180, 1127, 1075, 1027, 765, 719; **HRMS** calcd for $C_{21}H_{35}N_4O_2S$ $[M+H]^+$: 407.2481 ; found: 407.2476.

(3a*R*,5*R*,6*S*,6a*R*)-2,2,6-Trimethyl-5-((*E*)-14-methylpentadec-2-en-2-yl)tetrahydrofuro[2,3-d][1,3]dioxol-6-ol (*E*-26):



To a stirred solution of sulfone **21** (2.25 g, 5.55 mmol) in anhydrous THF (25 mL), LiHMDS (6.9 mL, 6.94 mmol, 1 M in THF) was added slowly at -78 °C, the solution becomes yellow colour. After 30 min at -78 °C, the THF (10 mL) solution of ketone **15** (1.0 g, 4.6 mmol) was added dropwise to the reaction mixture. The reaction mixture was slowly warmed to room temperature. After 16 h, the reaction was quenched by the addition of aqueous NH_4Cl (15 mL) solution, and the product was extracted with EtOAc (30 mL x 2). The organic layer was washed with brine, dried over anhydrous sodium sulphate, filtered and concentrated. The residue was purified by silica gel column chromatography to separate the two diastereomers. The combined yield is 82% based on recovery of starting material and observed *E*: *Z* = 3:1 (1.98 g of ***E*-26**, 660 mg of ***Z*-26**). For ***E*-26**, **Appearance** white solid.; **MP** 52 °C; **$[\alpha]_D^{20}$** - 13.607 (*c* = 0.535 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.88 (d, *J* = 3.7 Hz, 1H), 5.68 (t, *J* = 7.2 Hz, 1H), 4.35 (s, 1H), 4.31 (d, *J* = 3.7 Hz, 1H), 2.13 – 2.03 (m, 2H), 1.86 (s, 1H), 1.70 (s, 3H), 1.54 (d, *J* = 12.1 Hz, 6H), 1.33 (d, *J* = 4.5 Hz, 6H), 1.25 (s, 14H), 1.18 – 1.11 (dd, *J* = 13.4, 6.7 Hz, 2H), 0.86 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 130.3, 128.5, 112.1, 104.0, 86.9, 86.3, 78.9, 39.2, 30.1, 29.9, 29.8, 29.7, 29.6, 29.6, 28.1, 27.9, 27.6, 27.2, 26.6, 22.8, 19.6, 15.5; **IR (neat) υ_{max}** 3522, 2929, 2860, 2285, 1988, 1750, 1463, 1378, 1219,1169, 1082, 1019, 881, 768; **HRMS** calcd for $C_{24}H_{44}O_4Na$ $[M+Na]^+$: 419.3137 ; found: 419.3175**.**

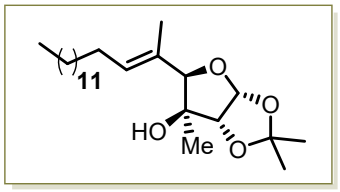
(3a*R*,5*R*,6*S*,6a*R*)-2,2,6-Trimethyl-5-((*Z*)-14-methylpentadec-2-en-2-yl)tetrahydrofuro[2,3-d][1,3]dioxol-6-ol (*Z*-26):



To a stirred solution of sulfone **22** (2.74 g, 6.94 mmol) in anhydrous THF (15 mL), NaHMDS (4.6 mL, 4.6 mmol, 1 M in THF) was added slowly at -78 °C, the solution becomes yellow color. After 30 min at -78 °C, the THF (10 mL) solution of ketone **15** (1.0 g, 4.6 mmol) was added dropwise to the reaction mixture. The reaction mixture was slowly warmed to room temperature. After 16 h, the reaction was quenched by the addition of aqueous NH_4Cl (15 mL) solution, and the product was extracted with EtOAc

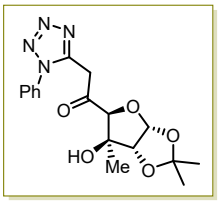
(60 mL x 2). The organic layer was washed with brine, dried over anhydrous sodium sulphate, filtered and concentrated. The residue was purified by silica gel column chromatography to afford exclusively (Z)-olefin ***Z*-26** as a white amorphous solid in 85% yield (1.2 g based on recovery of starting material). **MP** 54 °C; **$[\alpha]_D^{20}$**– 22.783 (*c* = 0.230 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.95 (d, *J* = 3.7 Hz, 1H), 5.51 (t, *J* = 7.3 Hz, 1H), 4.72 (s, 1H), 4.25 (d, *J* = 3.7 Hz, 1H), 2.14 – 1.94 (m, 2H), 1.81 (d, *J* = 1.2 Hz, 3H), 1.54 – 1.47 (m, 4H), 1.32 (d, *J* = 21.0 Hz, 9H), 1.25 (s, 14H), 1.18 – 1.11 (m, 2H), 0.86 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 132.2, 129.1, 112.1, 104.3, 86.6, 82.5, 81.2, 39.2, 30.1, 29.9, 29.8, 29.7, 29.7, 29.5, 28.5, 28.1, 27.6, 27.2, 26.6, 22.8, 21.3, 18.9 **IR (neat)** υ_{max} 3474, 2927, 2858, 1463, 1379, 1217, 1172, 1079, 1013, 883.8, 763 ; **HRMS** calcd for $C_{24}H_{44}O_4Na$ $[M+Na]^+$: 419.3137 ; found: 419.3186.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*E*)-Hexadec-2-en-2-yl)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-ol (*E*-27):



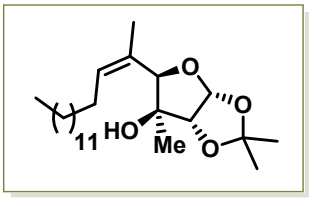
To a stirred solution of sulfone **24** (1.4 g, 3.47 mmol) in anhydrous THF (20 mL), LiHMDS (3.5 mL, 3.46 mmol, 1 M in THF) was added slowly at -78 °C, the solution becomes yellow colour. After 30 min at -78 °C, ketone **15** (500 mg, 2.31 mmol) in THF (5 mL) was added dropwise to the reaction mixture. The reaction mixture was slowly warmed to room temperature. After 16 h, the reaction was quenched by the addition of aqueous NH_4Cl (10 mL) solution, and the product was extracted with EtOAc (30 mL x 2). The organic layer was washed with brine, dried over anhydrous sodium sulphate, filtered and concentrated. The residue was purified by silica gel column chromatography to afford olefin ***E*-27** as a white amorphous solid (combined yield 82% with *E*: *Z* = 3:1**)**. **MP** 53 °C; **$[\alpha]_D^{20}$** – 9.333 (*c* = 0.3 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.87 (d, *J* = 3.7 Hz, 1H), 5.67 (ddd, *J* = 7.2, 6.0, 1.2 Hz, 1H), 4.35 (s, 1H), 4.30 (d, *J* = 3.7 Hz, 1H), 2.09 (q, *J* = 7.3 Hz, 2H), 1.87 (s, 1H), 1.69 (s, 3H), 1.52 (s, 3H), 1.41 – 1.35 (m, 2H), 1.32 (d, *J* = 4.6 Hz, 7H), 1.25 (s, 19H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 130.2, 128.5, 112.1, 104.0, 86.9, 86.3, 78.9, 32.1, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 27.9, 27.2, 26.6, 22.8, 19.6, 15.5, 14.2; **IR (neat)** υ_{max} 3491, 2927, 2857, 1462, 1379, 1217, 1172, 1080, 1017, 881 ; **HRMS** calcd for $C_{24}H_{44}O_4Na$ $[M+Na]^+$: 419.3137 ; found: 419.3175.

1-((3aR,5S,6R,6aR)-6-hydroxy-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-2-(1-phenyl-1H-tetrazol-5-yl)ethan-1-one (28)



To a stirred solution of sulfone **21** (2.74 g, 6.94 mmol) in anhydrous THF (15 mL), NaHMDS (4.6 mL, 4.6 mmol, 1 M in THF) was added slowly at -78 °C, the solution becomes yellow color. After 30 min at -78 °C, the THF (10 mL) solution of ketone **15** (1.0 g, 4.6 mmol) was added dropwise to the reaction mixture. The reaction mixture was slowly warmed to room temperature. After 16 h, the reaction was quenched by the addition of aqueous NH_4Cl (15 mL) solution, and the product was extracted with EtOAc (60 mL x 2). The organic layer was washed with brine, dried over anhydrous sodium sulphate, filtered and concentrated. The residue was purified by silica gel column chromatography to afford tetrazole derived product **28** as a white amorphous solid in 80% yield (1.0 g based on recovery of starting material). The product thus obtained is in keto-enol tautomerism. NMR data is reported for isomer when peaks differ. **MP** 140 °C.; $[\alpha]_D^{20}$ – 80.000 (*c* = 0.2 in $CHCl_3$); ^1H NMR (400 MHz, Benzene-d_6) δ 6.96 – 6.92 (m, 2H), 6.83 (m, 3H), 6.06 (d, J = 3.2 Hz, 1H), 4.67 (d, J = 18.5 Hz,1H), 4.32 (d, J = 3.2 Hz, 1H), 4.29 (s, 1H), 3.98 (bs, 1H), 3.88 (d, J = 18.5 Hz, 1H), 1.48 (s, 3H), 1.26 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 202.7, 150.5, 134.1, 130.1, 129.6, 128.3, 128.1, 127.8, 125.2, 113.0, 106.4, 88.0, 87.2, 82.4, 36.3, 27.4, 26.5, 18.7.; **IR (neat)** υ_{max} 3276. 2986, 2854, 2478, 2318, 1845, 1722, 1595, 1381, 1264, 1081, 921, 765.; **HRMS** calcd for $C_{17}H_{21}N_4O_5$ $[M+H]^+$: 361.1512 ; found: 361.1524

(3a*R*,5*R*,6*S*,6a*R*)-5-((*Z*)-Hexadec-2-en-2-yl)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-ol (*Z*-27):



To a stirred solution of sulfone **25** (5.5 g, 13.8 mmol) in anhydrous THF (30 mL), NaHMDS (13.8 mL, 13.8 mmol, 1 M in THF) was added slowly at -78 °C, the solution becomes yellow color. After 30 min at -78 °C, the THF (20 mL) solution of ketone **15** (2.0 g, 9.2 mmol) was added dropwise to the reaction

mixture. The reaction mixture was slowly warmed to room temperature. After 16 h, the reaction was quenched by the addition of aqueous NH_4Cl (20 mL) solution, and the product was extracted with EtOAc (60 mL x 2). The organic layer was washed with brine, dried over anhydrous sodium sulphate, filtered and concentrated. The residue was purified by silica gel column chromatography to afford olefin ***Z*-27** as a white amorphous solid in 85% yield (2.3 g based on recovery of starting material). **MP** 74 °C; **$[\alpha]_D^{20}$** – 24.000 (*c* = 0.13 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.95 (d, *J* = 3.7 Hz, 1H), 5.51 (t, *J* = 7.3 Hz, 1H), 4.72 (s, 1H), 4.25 (d, *J* = 3.7 Hz, 1H), 2.13 – 1.94 (m, 2H), 1.81 (d, *J* = 1.0 Hz, 3H), 1.54 (s, 3H), 1.34 (s, 4H), 1.27 (d, *J* = 14.9 Hz, 25H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 132.3, 129.1, 112.1, 104.3, 86.6, 82.5, 81.2, 32.1, 30.1, 29.8, 29.7, 29.7, 29.5, 28.5, 27.2, 26.6, 22.8, 21.3, 18.9, 14.3; **IR (neat)** υ_{max} 3426, 2925, 2854, 1464, 1379, 1217, 1170, 1078, 1013, 891 ; **HRMS** calcd for $C_{24}H_{44}O_4Na$ $[M+Na]^+$: 419.3137 ; found: 419.3118.

Procedure for photo-flow under controlled condition for the synthesis of *E*-isomer:

Homemade photo-batch reactor bought from lelesil Mumbai, India and slightly modified for the continuous flow reaction. A 0.20 M solution of *E*-27 was taken in a flask and the solution was passed through perfluoroalkoxy (PFA) coil reactor [inner diameter (ID) 1.0 milimeter (mm)", length 9 meter, volume = 7.8 ml]. The tubing reactor was wrapped within the helical grooves around a cylindrical-shaped frame. The reactor was cooled by circulating chilled water. The cylindrical reactor was irradiated by medium pressure lamp beam of 250W Hg (Xe) arc lamp was placed in between the reactor (Figure S1). The product mixture from the end of capillary reactor as an outlet was collected into a flask.

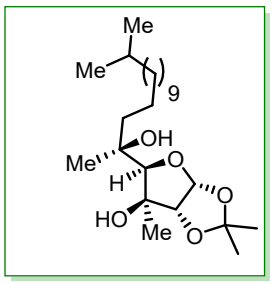
Table S1. Optimization conditions[a]

entry	flow rate (μl/min.)	residence time (min.)	temp. (°C)	*Z*-27 Z-isomer	*E*-27 E-isomer
1	100	15.7	30	44	56
2	50	31.4	30	36	64
3	20	78.5	30	30	70
4	10	157	30	28	72
5	5	304	30	34	66
6	50	31.4	20	47	53
7	20	78.5	20	39	61

[a] Reaction conditions: Stock solution concentration 0.25M in hexane; reactor vol. 1.57 ml; tubing length 2-meter length, light source 250 W Hg lamp; [c] yields are based on the isolated yield.

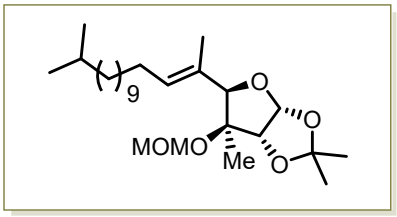
Figure S1

(3aR,5R,6S,6aR)-5-((S)-2-hydroxy-14-methylpentadecan-2-yl)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-ol (30):



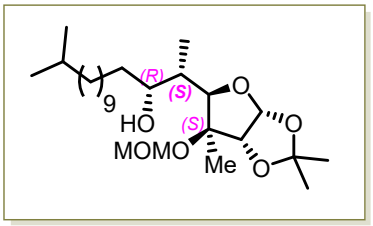
The trisubstituted olefin ***E*-26** (100 mg, 0.252 mmol) was dissolved in anhydrous THF (2 mL) and the solution was cooled to -10 ºC. BH_3-THF (0.5 mL, 1M in THF, 0.505 mmol) was then added slowly and the reaction mixture was allowed to stir at 0 °C for 12 h. After completion, temperature of the reaction mixture was brought to 0 ºC and then treated with NaOH (0.3 mL, 3N) and H_2O_2 (0.3 mL), and stirred vigorously for 2 hours at room temperature. Saturated Na_2SO_3 aqueous solution (1 mL) was then added to quench the reaction. The mixture was extracted with EtOAc (3 X 10 mL), and the combined organic fractions were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography using a gradient of hexanes and ethyl acetate (80:20 to 40:60) to afford the tertiary alcohol **30** in 85% yield (88 mg) as a single diastereomer (white solid). 13C NMR data is reported for a single peak when it splits. **MP** 155 °C; **$[\alpha]_D^{20}$** 2.400 (*c* = 0.3 in $CHCl_3$); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.89 – 5.87 (m, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 4.21 (d, *J* = 3.6 Hz, 1H), 3.71 (d, *J* = 4.0 Hz, 1H), 2.46 (d, *J* = 29.9 Hz, 1H), 1.75 – 1.59 (m, 3H), 1.49 (d, *J* = 3.0 Hz, 3H), 1.45 (d, *J* = 0.6 Hz, 3H), 1.35 – 1.32 (m, 8H), 1.28 –1.24 (m, 16H), 1.17 –1.12 (m, 2H), 0.86 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 112.3, 103.8, 89.6, 84.8, 83.9, 81.0, 76.0, 75.4, 42.5, 39.2, 37.2, 30.2, 30.1, 29.9, 29.8, 29.7, 28.1, 27.6, 27.4, 26.7, 26.6, 23.9, 23.3, 22.8, 21.4, 21.3.; **IR (neat) υ_{max}** 3350, 3059, 1485, 1440, 1308, 1192, 1075, 1002, 759, 724; **HRMS** calcd for $C_{24}H_{46}O_5Na$ $[M+Na]^+$: 437.3243 ; found: 437.3234.

(3a*R*,5*R*,6*S*,6a*R*)-6-(Methoxymethoxy)-2,2,6-trimethyl-5-((*E*)-14-methylpentadec-2-en-2-yl)tetrahydrofuro[2,3-d][1,3]dioxole (31):



To a stirred solution of compound ***E*-26** (900 mg, 2.27 mmol) in CH_2Cl_2 (10 ml) at 0 °C, were added MOMCl (0.21 ml, 2.72 mmol) and DIPEA (0.475 ml, 2.72 mmol). The resulting mixture was slowly warmed to room temperature and vigorously stirred for 12 h. After completion (by TLC analysis), the reaction mixture was diluted with CH_2Cl_2 (30 mL) and water (20 ml) then both the layers were separated. The organic phase was dried over anhydrous Na_2SO_4 and concentrated to give the crude product, which was purified by flash chromatography to give **31** in 93% yield (920 mg) as a brown liquid. **$[\alpha]_D^{20}$** - 5.750 (*c* = 0.480 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.91 (d, *J* = 3.7 Hz, 1H), 5.42 (t, *J* = 7.2 Hz, 1H), 4.77 (d, *J* = 7.5 Hz, 1H), 4.61 (d, *J* = 7.5 Hz, 1H), 4.50 (d, *J* = 3.7 Hz, 1H), 4.19 (s, 1H), 3.33 (s, 3H), 2.06 (q, *J* = 7.2 Hz, 2H), 1.70 (s, 3H), 1.61 (s, 1H), 1.50 (s, 3H), 1.36 – 1.32 (m, 8H), 1.25 (s, 14H), 1.18 – 1.11 (m, 2H), 0.86 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 130.1, 111.8, 104.4, 91.7, 88.8, 86.7, 84.4, 55.4, 39.2, 30.1, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 28.1, 27.8, 27.6, 27.2, 26.6, 22.8, 14.9, 13.6. **IR (neat)** υ_{max} 2927, 2857, 1461, 1377, 1218, 1152, 1077, 927, 880; **HRMS** calcd for $C_{26}H_{48}O_5Na$ $[M+Na]^+$: 463.3399 ; found: 463.3397

(2S,3R)-2-((3aR,5R,6S,6aR)-6-(methoxymethoxy)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-14-methylpentadecan-3-ol (33):



The MOM-protected compound **31** (500 mg, 1.13 mmol) was dissolved in anhydrous THF (5 mL), and cooled to -10 °C. To the solution BH_3.THF (2.2 mL, 2.2 mmol, 1.0 M solution in THF) was added dropwise and stirred at -10 °C for 2 h. The reaction was quenched slowly with H_2O (2 mL). NaOH (2 mL, 20% aqueous solution) was then added dropwise, followed by H_2O_2 (2 mL, 30% aqueous solution). The mixture was allowed to stir for 2 hours, sat. sodium sulphite (5 mL) was then added, and the layers were separated. The organic mixture was extracted with EtOAc (15 mL x 3). The combined organic layers were dried over Na_2SO_4 and the solvent removed in *vacuo* to yield the crude product as clear oil (*d.r.* 10:1). The crude reaction mixture was purified by column chromatography on silica gel (33% EtOAc:hexane) to yield **33** in 80% yield (416 mg) as a colorless oil. **$[\alpha]_D^{20}$** 18.667 (*c* = 0.12 in $CHCl_3$); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.82 (d, *J* = 3.7 Hz, 1H), 4.87 (d, *J* = 7.6 Hz, 1H), 4.75 (d, *J* = 7.6 Hz, 1H), 4.52 (d, *J* = 3.7 Hz, 1H), 3.76 (d, *J* = 8.6 Hz, 1H), 3.75 –3.70 (m, 1H), 3.39 (s, 3H), 3.11 (bs, 1H), 2.11 – 2.03 (m, 1H), 1.62 (s, 3H), 1.49 (s, 3H), 1.44 (s, 3H), 1.31 (s, 4H), 1.25 (s, 15H), 1.17 – 1.13 (m,

2H), 0.93 (d, J = 7.0 Hz, 3H), 0.86 (d, J = 6.6 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 112.0, 103.8, 91.9, 88.2, 85.4, 85.1, 74.1, 55.9, 39.2, 37.8, 33.4, 30.1, 30.0, 29.8, 28.1, 27.6, 27.2, 26.6, 25.6, 22.8, 16.6, 13.4; **IR (neat)** υ_{max} 3421, 2929, 2858, 1465, 1380, 1218, 1070, 1036, 763 ; **HRMS** calcd for $C_{26}H_{50}O_6Na$ $[M+Na]^+$: 481.3505; found: 481.3503.

Mosher ester analysis:

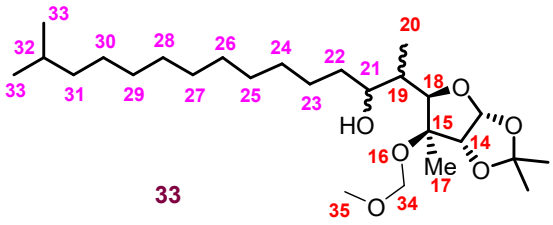
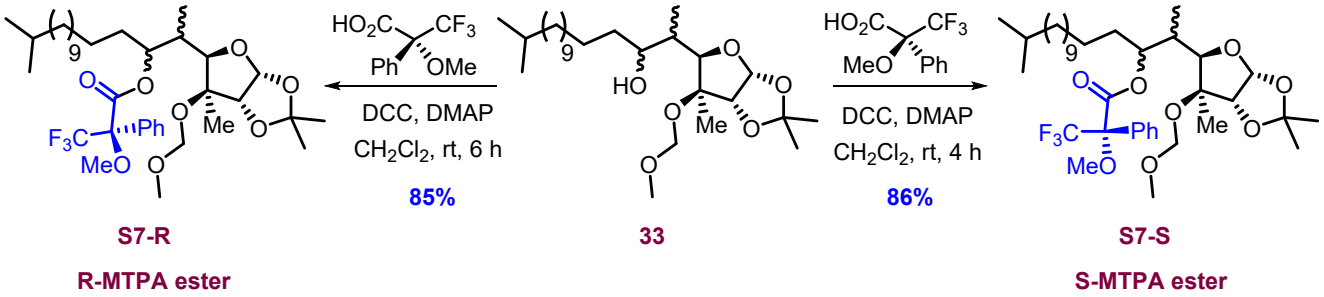


Figure S2



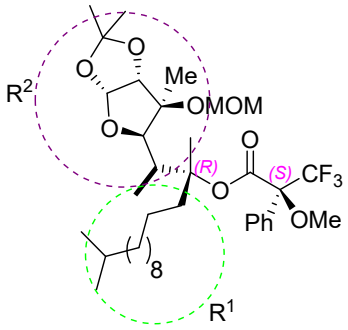
Scheme S7

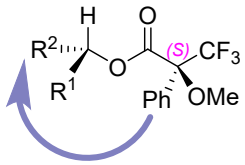
Table S2. $\Delta\delta$ (= δ_S δ_R) data for the S- and R-MTPA- Mosher esters S7-S and S7-R.

	δ *S*-ester S7-S (ppm)	δ *R*-ester S7-R (ppm)	$\Delta\delta^{SR}$ (= $\delta_S - \delta_R$) ppm
14	4.48	4.49	-0.01
34	4.82 & 4.75	4.83 & 4.76	-0.01 & -0.01
35	3.38	3.39	-.01
17	0.88	1.41	-0.53
18	3.65	3.36	-0.01
19	2.40	2.45	-0.05
20	0.80	0.96	-0.16
21	5.42	5.49	-0.07
22	1.61	1.54	+0.07
23	1.30	1.24	+0.06

$\Delta\delta^{SR}$ = δ(*S*-MPTA ester) δ(*R*-MTPA ester) or $\Delta\delta^{SR} = \delta_S$ δ_R

Precisely, protons that have positive $\Delta\delta^{SR}$ values reside within R^1 and the protons with negative values belong to R^2. According to this lipid side chain resides within R^1 (due to its positive $\Delta\delta^{SR}$ values) and the sugar fragment belongs to R^2 *i.e.* on the opposite side of that plane (Figure S3).

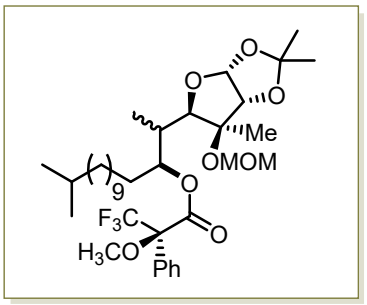




phenyl group shielding effect results upfield chemical shift for the protons belong to R^2

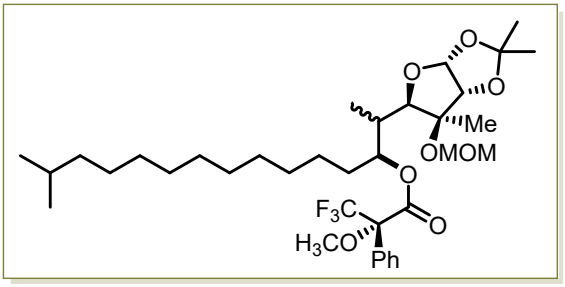
Figure S3

(3*S*)-2-((3a*R*,5*R*,6*S*,6a*R*)-6-(Methoxymethoxy)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-14-methylpentadecan-3-yl (2*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (S7-R):



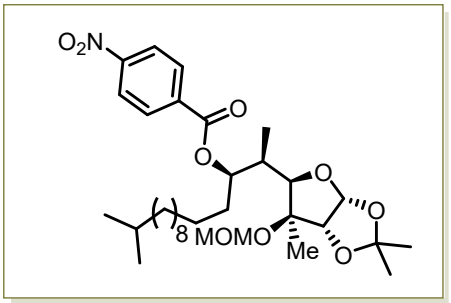
(+) - MTPA ((*R*) - (+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid) (3 mg, 0.013 mmol), DCC (4.5 mg 0.021 mmol) and a catalytic amount of DMAP (0.5 mg) were dissolved in CH_2Cl_2 (1 mL). Compound **59** (5 mg, 0.01 mmol) was added to the solution. The resulting mixture was stirred at room temperature for 16 h. After completion (by TLC analysis) reaction mixture was diluted with additional amount of CH_2Cl_2 and washed with aqueous $NaHCO_3$ solution. The organic layer was separated and concentrated under reduced pressure. The residue was purified by flash column chromatography to give ester **S7-R** in 83% yield (6 mg). **$[\alpha]_D^{20}$** 29.714 (*c* = 0.140 in $CHCl_3$); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.57 – 7.53 (m, 2H), 7.40 – 7.34 (m, 3H), 5.82 (d, *J* = 3.7 Hz, 1H), 5.50 (td, *J* = 6.6, 3.4 Hz, 1H), 4.83 (d, *J* = 7.6 Hz, 1H), 4.76 (d, *J* = 7.6 Hz, 1H), 4.50 (d, *J* = 3.6 Hz, 1H), 3.67 (d, *J* = 9.2 Hz, 1H), 3.55 (s, 3H), 3.38 (s, 3H), 2.50 – 2.40 (m, 1H), 1.46 (s, 3H), 1.41 (s, 3H), 1.31 (s, 4H), 1.27 – 1.23 (m, 9H), 1.21 – 1.11 (m, 11H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.86 (d, *J* = 6.62 Hz,, 6H); **IR (neat)** υ_{max} 2931, 1749, 1463, 1264, 1180, 1074, 1028, 721; **HRMS** calcd for $C_{36}H_{57}O_8F_3Na$ $[M+Na]^+$: 697.3903 ; found: 697.3906.

(3*S*)-2-((3a*R*,5*R*,6*S*,6a*R*)-6-(Methoxymethoxy)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-14-methylpentadecan-3-yl (2*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (S7-S):



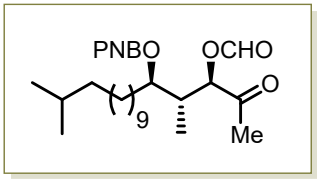
(+) - MTPA ((*S*) - (+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid) (3 mg, 0.013 mmol), DCC (4.5 mg 0.021 mmol) and a catalytic amount of DMAP (0.5 mg) were dissolved in CH_2Cl_2 (1 mL). Compound **59** (5 mg, 0.01 mmol) was added to the solution. The resulting mixture was stirred at room temperature for 16 h. After completion (by TLC analysis) reaction mixture was diluted with additional amount of CH_2Cl_2 and washed with aqueous $NaHCO_3$ solution. The organic layer was separated and concentrated under reduced pressure. The residue was purified by flash column chromatography to give ester **S7-S** in 85% yield (6.2 mg). **$[\alpha]_D^{20}$** 12.500 (*c* = 0.080 in CHCl3); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.58 – 7.53 (m, 2H), 7.40 – 7.36 (m, 3H), 5.82 (d, *J* = 3.7 Hz, 1H), 5.46 – 5.39 (m, 1H), 4.83 (d, *J* = 7.6 Hz, 1H), 4.76 (d, *J* = 7.6 Hz, 1H), 4.48 (d, *J* = 3.7 Hz, 1H), 3.65 (d, *J* = 9.2 Hz, 1H), 3.56 (s, 3H), 3.38 (s, 3H), 2.47 – 2.34 (m, 1H), 1.63 – 1.58 (m, 2H), 1.55 – 1.47 (m, 4H), 1.45 (s, 4H), 1.38 (s, 4H), 1.34 – 1.28 (m, 10H), 1.19 – 1.09 (m, 4H), 0.94 – 0.89 (m, 2H), 0.86 (m, 6H), 0.80 (d, *J* = 7.0 Hz, 3H); **IR (neat) υ_{max}** 2932, 1750, 1463, 1267, 1177, 1077, 1029, 724 ; **HRMS** calcd for $C_{36}H_{57}O_8F_3Na$ $[M+Na]^+$: 697.3903 ; found: 697.3899.

(2*R*,3*R*)-2-((3a*R*,5*R*,6*S*,6a*R*)-6-(Methoxymethoxy)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-14-methylpentadecan-3-yl 4-nitrobenzoate (34):



To a solution of *p*-nitrobenzoic acid (43.7 mg, 0.26 mmol), DCC (90.1 mg, 0.436 mmol) and a catalytic amount of DMAP (2 mg) in anhydrous CH_2Cl_2 (2 mL) was added a solution of alcohol **33** (100 mg, 0.218 mmol) in CH_2Cl_2 (1 mL) and allowed to stir for 4 hours at room temperature. After completion (by TLC analysis), the reaction mixture was diluted with additional CH_2Cl_2 (10 mL) and water (5 mL). The organic layer was separated, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by using short path column chromatography to give PNB-ester **34** in 90% yield (119 mg) as pale-yellow oil. **$[\alpha]_D^{20}$** 37.447 (*c* = 0.235 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 – 8.25 (m, 2H), 8.24 – 8.19 (m, 2H), 5.84 (d, *J* = 3.7 Hz, 1H), 5.55 – 5.49 (m, 1H), 4.85 (d, *J* = 7.6 Hz, 1H), 4.73 (d, *J* = 7.6 Hz, 1H), 4.53 (d, *J* = 3.7 Hz, 1H), 3.74 (d, *J* = 9.4 Hz, 1H), 3.37 (s, 3H), 2.55 – 2.45 (m, 1H), 1.75 – 1.65 (m, 2H), 1.49 (s, 3H), 1.44 (s, 3H), 1.31 (s, 6H), 1.22 (s, 13H), 1.16 – 1.10 (m, 3H), 1.05 (d, *J* = 7.0 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.2, 150.3, 136.6, 130.8, 123.6, 111.7, 103.9, 91.9, 85.5, 85.4, 85.3, 77.9, 55.8, 39.2, 35.9, 30.1, 29.8, 29.8, 29.7, 29.6, 29.0, 28.1, 27.6, 27.3, 26.7, 26.2, 22.8, 16.8, 11.4; **IR (neat) υ_{max}** 2950, 1770, 1540, 1263, 1050, 757 **HRMS** calcd for $C_{33}H_{53}NO_9Na$ $[M+Na]^+$: 630.3618 ; found: 630.3621.

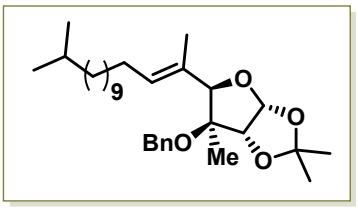
(3R,4R,5R)-3-(formyloxy)-4,16-dimethyl-2-oxoheptadecan-5-yl 4-nitrobenzoate (37):



Solution of **34** (50 mg, 0.082 mmol) in TFA-H_2O (2 mL, 3:2) was stirred at 0 °C for 20 min and at room temperature for 2 h. TFA was co-evaporated with toluene to furnish diol. To the stirred solution of diol in acetone-water (3 mL, 4:1) was added $NaIO_4$ (14 mg, 0.065 mmol) in four portions at 0 °C. The resulting mixture was stirred at 0 °C for 1 h. Acetone was removed on rotary evaporator at 30 °C and the product was extracted with dichloromethane CH_2Cl_2 (3 × 10 mL). The combined organic layer was concentrated, dried over Na_2SO_4 and purified by silica gel column chromatography to afford methyl ketone **37** in 70% yield for two steps (28.3 mg) as a colorless oil. **$[\alpha]_D^{20}$** 18.667 (*c* = 0.075 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 8.33 – 8.28 (m, 2H), 8.20 – 8.15 (m, 2H), 8.07 (s, 1H), 5.38 (ddd, *J* = 8.2, 5.4, 2.4 Hz, 1H), 4.98 (d, *J* = 7.4 Hz, 1H), 2.45 (td, *J* = 7.2, 2.4 Hz, 1H), 2.19 (s, 3H), 1.89 – 1.76 (m, 1H), 1.69 – 1.60 (m, 1H), 1.54 – 1.45 (m, 2H), 1.31 (bs, 4H), 1.23 (s, 11H), 1.17 – 1.10 (m, 5H), 0.85 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 204.7, 160.1, 150.8, 135.7, 130.8, 123.8, 79.4, 74.6, 39.2, 37.6, 32.1, 30.1, 29.8, 29.7, 29.7, 29.6, 29.5, 28.1, 27.6, 25.9, 22.8, 10.6; **IR (neat) υ_{max}** 2930,

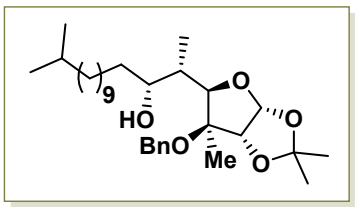
2859, 1730, 1534, 1354, 1279, 1166, 1111, 769, 724 ; **HRMS** calcd for $C_{27}H_{41}NO_7Na$ $[M+Na]^+$: 514.2781 ; found: 514.2776.

(3a*R*,5*R*,6S,6a*R*)-6-(Benzyloxy)-2,2,6-trimethyl-5-((E)-14-methylpentadec-2-en-2-yl)tetrahydrofuro[2,3-d][1,3]dioxole (32):



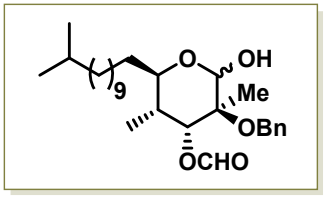
(3a*R*,5*R*,6*S*,6a*R*)-2,2,6-Trimethyl-5-((*E*)-14-methylpentadec-2-en-2-yl)tetrahydrofuro[2,3-d][1,3]dioxol-6-ol ***E*-26** (500 mg, 1.26 mmol) was dissolved in THF (10 mL) and was added sodium hydride (36.3 mg, 1.515 mmol) and benzyl bromide (0.179 mL, 1.515 mmol) at 0 °C for 30 min and the resulting mixture was stirred at 50 °C for 12 h. After completion (by TLC analysis), the reaction was quenched by addition of methanol (1 mL) dropwise, the solvent was removed under reduced pressure, and the residue was dissolved in DCM (25 mL) and washed with 1 M HCl (aq). The aqueous layers were extracted with DCM, and the combined organic layers were washed with saturated $NaHCO_3$ (aq) and brine, dried over Na_2SO_4, filtered, evaporated, and purified by flash column chromatography to give benzyl ether **32** in 90% yield (552 mg). **$[\alpha]_D^{20}$** 27.600 (*c* = 0.1 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33 – 7.27 (m, 4H), 7.25 – 7.21 (m, 1H), 5.94 (d, *J* = 3.8 Hz, 1H), 5.45 (t, *J* = 7.2 Hz, 1H), 4.52 (d, *J* = 5.4 Hz, 2H), 4.46 (d, *J* = 3.8 Hz, 1H), 4.24 (s, 1H), 2.07 (q, *J* = 7.1 Hz, 2H), 1.73 (s, 3H), 1.57 – 1.50 (m, 8H), 1.34 (d, *J* = 10.4 Hz, 7H), 1.25 (s, 11H), 1.18 – 1.11 (m, 2H), 0.86 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.4, 130.4, 130.0, 128.4, 127.3, 126.6, 111.8, 104.5, 89.1, 86.3, 82.9, 65.2, 39.2, 30.1, 29.9, 29.7, 29.6, 29.5, 28.1, 27.9, 27.6, 27.2, 26.6, 22.8, 14.5, 13.9; **IR (neat) υ_{max}** 2948, 2867, 1715, 1425, 1221, 766; **HRMS** calcd for $C_{31}H_{50}NaO_4$ $[M+Na]^+$: 509.3607 ; found: 509.3594.

(2S,3R)-2-((3aR,5R,6S,6aR)-6-(benzyloxy)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-14-methylpentadecan-3-ol (35):



A dry and N_2 -flushed 25 mL round bottomed flask was charged with a solution (3a*R*,5*R*,6*S*,6a*R*)-6-(benzyloxy)-2,2,6-trimethyl-5-((E)-14-methylpentadec-2-en-2-yl)tetrahydrofuro[2,3-d][1,3]dioxole **32** (100 mg, 0.205 mmol) in THF (4 mL) and cooled to 0 °C. BH_3·THF (0.308 mL, 1 M solution in THF, 0.3 mmol) was added and the resulting solution was stirred for 12 h at 0 °C. NaOH (2 mL, 20% aqueous solution) was then added dropwise, followed by H_2O_2 (2 mL, 30% aqueous solution). The mixture was allowed to stir for 2 hours, sat. sodium sulphite (5 mL) was then added, and diluted with ethyl acetate. The layers were separated. The combined organic phase was dried over Na_2SO_4 and the solvent was evaporated in *vacuo*. The crude product (*d.r.* 22:1) was purified by chromatography on silica gel to afford the title compound **35** in 80% yield (82 mg) with. **$[\alpha]_D^{20}$** 5.175 (*c* = 0.05 in $CHCl_3$) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.28 (m, 5H), 5.84 (d, *J* = 3.9 Hz, 1H), 4.60 (q, *J* = 12.0 Hz, 2H), 4.47 (d, *J* = 3.9 Hz, 1H), 3.81 (d, *J* = 8.6 Hz, 1H), 3.74 (bs, 1H), 3.02 (d, *J* = 3.1 Hz, 1H), 2.24 – 2.14 (m, 1H), 1.56 (s, 4H), 1.51 – 1.47 (m, 8H), 1.32 (s, 3H), 1.25 (s, 12H), 1.18 – 1.10 (m, 3H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.8, 128.6, 127.6, 126.8, 111.9, 103.9, 88.5, 85.0, 83.1, 74.2, 65.2, 39.2, 38.0, 33.4, 30.1, 30.0, 29.9, 28.1, 27.6, 27.2, 26.6, 25.6, 22.8, 16.6, 13.4; **IR (neat)** υ_{max} 3420, 2998, 2870, 1398, 1126, 766; **HRMS** calcd for $C_{31}H_{52}O_5Na$ $[M+Na]^+$: 527.3712 ; found: 527.3701.

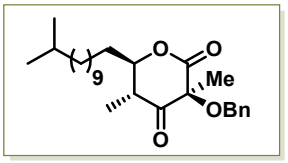
(3S,4R,5R,6R)-3-(benzyloxy)-2-hydroxy-3,5-dimethyl-6-(11-methyldodecyl)tetrahydro-2H-pyran-4-yl formate (38):

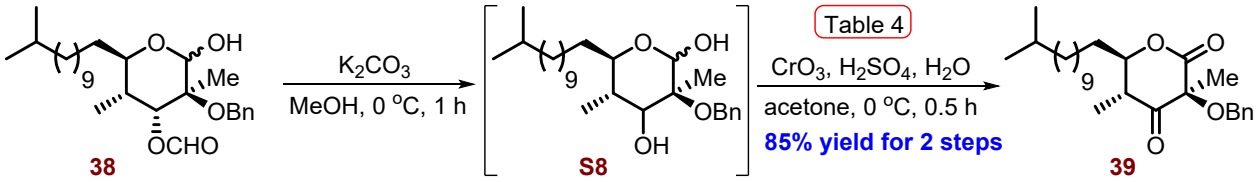


Solution of **35** (50 mg, 0.082 mmol) in 90% TFA (2 mL) was stirred at 0 °C for 20 min and at room temperature for 2 h. TFA was co-evaporated with toluene (3×5 mL) to furnish diol. To the stirred solution of diol in acetone-water (3 mL, 4:1) was added $NaIO_4$ (50.9 mg, 0.238 mmol) in two portions at 0 °C. The resulting mixture was stirred at 0 °C for 1 h. Acetone was removed on rotary evaporator at 30 °C and the product was extracted with dichloromethane CH_2Cl_2 (3 × 10 mL). The combined organic layer was concentrated in *vacuo*, dried over Na_2SO_4, and purified by silica gel column chromatography to afford hemiacetal **38** in 70% yield over two steps (28.3 mg). **$[\alpha]_D^{20}$** 40.00 (*c* = 0.050 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.21 (s, 1H), 7.37 – 7.33 (m, 5H), 5.47 (d, *J* = 2.1 Hz, 1H), 4.71 (d, *J* = 11.8 Hz,

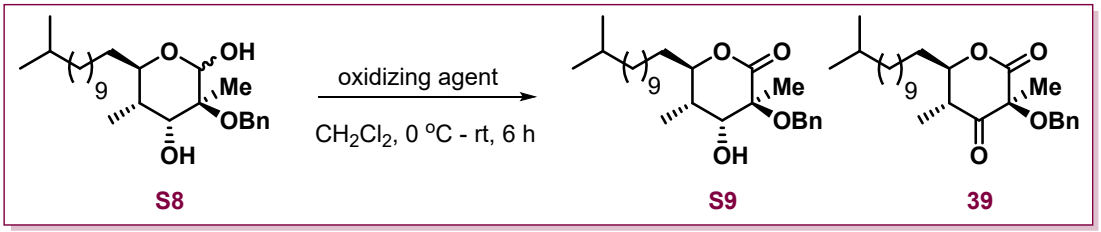
1H), 4.65 – 4.55 (m, 3H), 3.54 – 3.48 (m, 1H), 2.14 – 2.03 (m, 2H), 1.81 – 1.73 (m, 1H), 1.53 – 1.48 (m, 3H), 1.43 – 1.38 (m, 3H), 1.28 (s, 11H), 1.17 – 1.14 (s, 2H), 0.86 (d, J = 6.6 Hz, 9H), 0.77 (d, J = 7.0 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.4, 128.6, 127.9, 127.8, 127.5, 96.2, 75.0, 74.3, 64.9, 39.2, 34.0, 32.7, 30.1, 29.9, 29.9, 29.8, 28.1, 27.6, 25.0, 22.8, 17.1, 12.7; **IR (neat)** υ_{max} 3420, 2930, 2860, 1732, 1463, 1378, 1169, 1088, 802, 754; **HRMS** calcd for $C_{28}H_{46}O_5Na$ $[M+Na]^+$: 485.3243 ; found: 485.3229.

(3S,5R,6R)-3-(benzyloxy)-3,5-dimethyl-6-(11-methyldodecyl)dihydro-2H-pyran-2,4(3H)-dione (39):





Scheme S8



Scheme S9

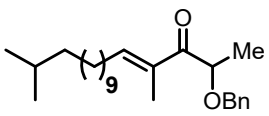
Table S3. Optimization reaction conditions[a]

Entry	Oxidizing agent	Time (h)	S9 (%)[c]	39 (%)[c]
1	DMP	4	82	-
2	PCC	6	85	-
3	PDC	10	80	-
4	**CrO_3, H_2SO_4**	**0.5**	-	**90[d]**
5	SO_3•py	12	81	-

Standard reaction conditions: [a] The reaction was carried out with S8 (1.0 mmol) and oxidizing agent (1.2 mmol) in CH_2Cl_2 (0.2 M) at 0 ˚C for 6 h. [b] Determined after column purification. [c] Isolated yields. [d] Jones conditions, acetone as a solvent medium.

To a stirred solution of hemiacetal **38** (40 mg, 0.086 mmol, 1.0 equiv) in CH_3OH (3 mL) was added K_2CO_3 (18 mg, 0.129 mmol, 1.5 equiv). The reaction mixture was stirred at room temperature for 3 hours and then concentrated under reduced pressure. The residue was extracted with CH_2Cl_2 (3×10 mL). The organic layer was washed with 15 mL water and dried over Na_2SO_4. The filtered organic layer was concentrated. To a stirred solution of the crude lactol S8 in acetone (4 mL) was added dropwise freshly prepared 2M Jones reagent (8.72 mL, 17.44 mmol) at 0 °C and the reaction mixture was gradually allowed to warm to 20 °C and allow it to stir for 30 min. After completion (by TLC analysis), $NaHCO_3$ solution was added to it and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over Na_2SO_4, evaporated under reduced pressure, and subjected to column chromatography to afford **39** in 85% yield (31.6 mg) over 2 steps. **$[\alpha]_D^{20}$** 76.00 (*c* = 0.050 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 – 7.43 (m, 2H), 7.37 – 7.28 (m, 3H), 4.51 (d, *J* = 9.8 Hz, 1H), 4.37 – 4.27 (m, 2H), 2.50 – 2.39 (m, 1H), 1.63 (s, 3H), 1.55 (s, 12H), 1.53 – 1.49 (m, 2H), 1.25 – 1.21 (m, 8H), 1.18 – 1.14 (m, 2H), 0.86 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 205.7, 170.1, 137.1, 128.7, 128.5, 128.2, 82.5, 79.0, 69.1, 47.3, 39.2, 33.3, 30.1, 29.8, 29.8, 29.7, 29.6, 29.5, 28.1, 27.6, 24.1, 22.8, 22.6, 11.2; **IR (neat)** υ_{max} 2925, 2858, 1734, 1460, 1377, 1261, 1099, 1028, 803, 698; **HRMS** calcd for $C_{27}H_{44}O_4Na$ $[M+Na]^+$: 455.3137 ; found: 455.3138.

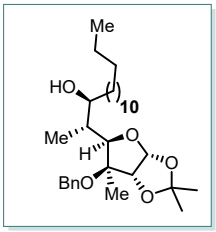
(*E*)-2-(Benzyloxy)-4,16-dimethylheptadec-4-en-3-one (41):



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 6.77 (t, *J* = 7.3, 1H), 4.66 – 4.60 (m, 1H), 4.58 (d, *J* = 11.7 Hz, 1H), 4.35 (d, *J* = 11.6 Hz, 1H), 2.23 (q, *J* = 7.4 Hz, 2H), 1.80 (s, 3H), 1.54 – 1.43 (m, 3H),

1.40 (d, *J* = 6.8 Hz, 3H), 1.26 (s, 13H), 1.89 – 1.10 (m, 3H), 0.86 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR (126 MHz, $CDCl_3$)** *δ* 202.0, 144.5, 138.0, 135.5, 128.5, 128.1, 127.9, 76.7, 71.4, 39.2, 30.1, 29.8, 29.7, 29.6, 29.3, 28.7, 28.1, 27.6, 22.8, 19.5, 11.8, 1.2; **IR (neat)** υ_{max} 2928, 2861, 1716, 1460, 1373, 1270, 1031, 806 cm^{-1}; **HRMS** calcd for $C_{26}H_{42}O_2Na$ $[M+Na]^+$: 409.3083; found: 409.3064.

(2R,3S)-2-((3aR,5R,6S,6aR)-6-(benzyloxy)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)hexadecan-3-ol (42):

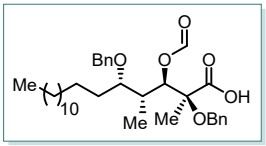


(3a*R*,5*R*,6*S*,6a*R*)-6-(benzyloxy)-2,2,6-trimethyl-5-((*Z*)-14-methylpentadec-2-en-2-yl)tetrahydrofuro[2,3-d][1,3]dioxole (**Z-27**) (500 mg, 1.26 mmol, 1.0 equiv) was dissolved in THF (10 mL) and sodium hydride (36.3 mg, 1.515 mmol) was added at 0 °C followed by benzyl bromide (0.179 mL, 1.515 mmol) and the resulting mixture was stirred at 50 °C for 12 h. After completion (by TLC analysis), the reaction was quenched by addition of methanol (1 mL) dropwise, the solvent was removed under reduced pressure, and the residue was dissolved in DCM (25 mL) and washed with 1 M HCl (aq). The aqueous layers were extracted with DCM, and the combined organic layers were washed with saturated $NaHCO_3$ (aq) and brine, dried over Na_2SO_4, filtered, evaporated, and the crude material was used in the next step without any further purification.

To a stirred solution of the above crude benzyl ether (estimated 0.9 mmol) in THF was added $BH_3 \cdot THF$ (1.08 mL, 1 M solution in THF) at -10 °C and the resulting solution was stirred for 12 hours at same temperature. NaOH (2 mL, 20% aqueous solution) was then added dropwise, followed by H_2O_2 (2 mL, 30% aqueous solution). The mixture was allowed to stir for 2 hours, sat. sodium sulphite (5 mL) was then added, and diluted with ethyl acetate. The layers were separated. The combined organic phase was dried over Na_2SO_4 and the solvent was evaporated in *vacuo*. The crude product was purified by chromatography on silica gel to afford the title compound **42** (440 mg, 72% over 2 steps) with exclusive diastereoselectivity. **$[\alpha]_D^{20}$** 3.333 (*c* = 0.45 in $CHCl_3$); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.36 – 7.27 (m, 5H), 5.86 (d, *J* = 3.9 Hz, 1H), 4.61 (d, *J* = 11.9 Hz, 1H), 4.54 (d, *J* = 11.9 Hz, 1H), 4.49 (d, *J* =

3.8 Hz, 1H), 3.98 – 3.93 (m, 1H), 3.90 (d, *J* = 7.2 Hz, 1H), 2.18 (pd, *J* = 7.2, 1.9 Hz, 1H), 2.02 – 1.98 (bs, 1H), 1.52 (s, 3H), 1.51 – 1.46 (m, 1H), 1.44 (s, 3H), 1.33 (s, 4H), 1.25 (s, 22H), 0.99 (d, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.9, 128.5, 127.5, 126.8, 111.9, 104.1, 87.7, 85.1, 83.0, 77.5, 77.2, 76.8, 73.1, 65.2, 36.6, 33.8, 32.1, 29.9, 29.8, 29.8, 29.8, 29.5, 27.2, 26.7, 26.6, 22.8, 16.0, 14.3, 12.2. **IR (neat)** υ_{max} 3528, 2924, 2853, 2150, 1459, 1378, 1318, 1213, 1166, 1016, 878, 697 cm^{-1}; **HRMS** calcd for C31H53O5 [M+H]+: 505.3888 ; found: 505.3847.

(2S,3R,4R,5S)-2,5-bis(benzyloxy)-3-(formyloxy)-2,4-dimethyloctadecanoic acid (44):



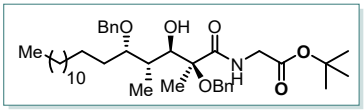
Alcohol **42** (100 mg, 0.2 mmol) was dissolved in THF (10 mL) and sodium hydride (6 mg, 0.238 mmol, 1.2 equiv) was added at 0 °C followed by benzyl bromide (0.03 mL, 0.238 mmol, 1.2 equiv) and the resulting mixture was stirred at 50 °C for 12 hours. After completion (by TLC analysis), the reaction was quenched by addition of methanol (1 mL) dropwise, the solvent was removed under reduced pressure, and the residue was dissolved in DCM (25 mL) and washed with 1 M HCl (aq). The aqueous layers were extracted with DCM, and the combined organic layers were washed with saturated $NaHCO_3$ (aq) and brine, dried over Na_2SO_4, filtered, evaporated, and the crude material was used in the next step without any further purification.

Solution of crude dibenzyl ether (estimated 0.2 mmol) in 90% TFA (2 mL) was stirred at 0 °C for 20 min and at room temperature for 2 h. TFA was co-evaporated with toluene (3×5 mL) to furnish diol and passed through a plug of silica which was used directly for next reaction. To the stirred solution of crude diol in acetone-water (3 mL, 4:1) was added $NaIO_4$ (127.2 mg, 0.58 mmol, 3.0 equiv) in two portions at 0 °C. The resulting mixture was stirred at 0 °C for 1 h. Acetone was removed on rotary evaporator at 30 °C and the product was extracted with dichloromethane CH_2Cl_2 (3 × 10 mL). The combined organic layer was concentrated in *vacuo*, dried over Na_2SO_4 afford formate aldehyde **43**. The crude material was used in the next reaction without further purification.

To a stirred solution of the crude aldehyde **43** (estimated 0.2 mmol) in 3mL of ^{t}BuOH and H_2O (3:1) were added $NaClO_2$ (90 mg, 1.0 mmol, 5.0 equiv), 2-methyl-2-butene (0.21 mL , 2.0 mmol, 10 equiv)

and NaH_2PO_4 (95 mg, 0.8 mmol, 4.0 equiv). The reaction mixture was allowed to stir for 2 h at room temperature. After completion the reaction mixture was diluted with water and EtOAc. The organic layer was separated, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude material was purified by silica gel column chromatography to acid **44** (67 mg, 60% over 4 steps) as colorless oil. **$[\alpha]_D^{20}$** -3.00 (*c* = 0.1 in $CHCl_3$); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.01 (s, 1H), 7.37 – 7.26 (m, 10H), 5.36 (d, *J* = 7.7 Hz, 1H), 4.61 (d, *J* = 10.8 Hz, 1H), 4.54 (d, *J* = 4.1 Hz, 1H), 4.51 (d, *J* = 4.7 Hz, 1H), 4.34 (d, *J* = 11.3 Hz, 1H), 3.53 (ddd, *J* = 7.7, 5.6, 1.7 Hz, 1H), 2.18 – 2.08 (m, 1H), 1.70 – 1.66 (m, 1H), 1.62 – 1.58 (m, 4H), 1.50 – 1.36 (m, 1H), 1.26 (s, 21H), 1.02 (d, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.8, 161.2, 138.9, 137.0, 128.5, 128.3, 128.0, 127.7, 127.4, 127.3, 82.0, 78.3, 77.3, 77.0, 76.7, 71.3, 66.8, 36.9, 31.9, 31.1, 29.8, 29.7, 29.7, 29.6, 29.6, 29.4, 26.1, 22.7, 14.1, 10.8; **IR (neat) υ_{max}** 2925, 2854, 1733, 1459, 1380, 1255, 1167, 1129, 1079, 1027, 737cm^{-1}; **HRMS** calcd for C35H53O6 [M+H]+: 569.3837 ; found: 569.3796.

tert-butyl ((2S,3R,4S,5S)-2,5-bis(benzyloxy)-3-hydroxy-2,4-dimethyloctadecanoyl)glycinate (45):



To a stirred solution of formate acid **44** (20 mg, 0.035 mmol) in CH_3OH (3 mL) was added K_2CO_3 (7.3 mg, 0.053 mmol, 1.5 equiv). The reaction mixture was stirred at room temperature for 3 hours and then concentrated under reduced pressure. The residue was extracted with CH_2Cl_2 (3×10 mL). The organic layer was washed with 15 mL water and dried over Na_2SO_4. The filtered organic layer was concentrated and used for next reaction without any purification.

The crude hydroxy acid (estimated 0.035 mmol) was dissolved in DMF (1 mL) under nitrogen atmosphere. HOBt (5.2 mg, 0.038 mmol, 1.1 eq) and EDC.HCl (8.1 mg, 0.052 mmol, 1.5 eq) were added sequentially at 0 °C. A mixture of amine salt (5.9 mg, crude, 0.035 mmol, 1.0 eq) and DIPEA (0.024 mL, 0.14 mmol, 4.0 eq) was added dropwise to the above reaction mixture at 0 °C and stirred for 30 min. Then reaction mixture was maintained at room temperature for 6 h. After completion of reaction, the reaction mixture was diluted with EtOAc (50 mL) and washed with saturated aqueous NH_4Cl solution (2 x 15 mL). The organic layer was separated and washed with saturated aqueous $NaHCO_3$ solution (2 x 15 mL) followed by brine solution (10 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give α-hydroxy amide **45** (19.5 mg, 86%, over 2 steps) as colorless oil. **$[\alpha]_D^{20}$** 1.67 (*c*

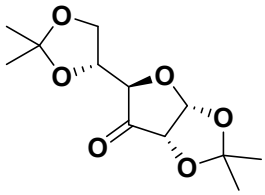
= 0.06 in $CHCl_3$); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.36 – 7.32 (m, 10H), 4.86 (d, *J* = 11.6 Hz, 1H), 4.79 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.52 – 4.43 (m, 2H), 4.32 (d, *J* = 10.7 Hz, 1H), 4.19 (d, *J* = 10.7 Hz, 1H), 3.64 (td, *J* = 7.0, 2.1 Hz, 1H), 3.54 (bs, 1H), 2.57 (bs, 1H), 2.21 (ddd, *J* = 10.7, 6.7, 2.1 Hz, 1H), 1.78 – 1.68 (m, 1H), 1.66 (s, 3H), 1.54 (s, 9H), 1.43 (dd, *J* = 9.8, 5.7 Hz, 2H), 1.25 (s, 22H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.88 (t, *J* = 6.3 Hz, 3H).; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 179.5, 176.0, 128.4, 128.3, 127.8, 127.5, 127.0, 77.6, 77.3, 77.0, 76.7, 72.5, 67.9, 67.8, 31.9, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 22.7, 22.4, 18.9, 14.1.; **IR (neat) υ_{max}** 3218, 3064, 3032, 2926, 2855, 2301, 2249, 2159, 2070, 1985, 1827, 1728, 1594, 1381, 1220, 1026, 981, 738, 699. **HRMS** calcd for $C_{40}H_{64}NO_6$ $[M+H]^+$: 654.4734 ; found: 654.4733.

References:

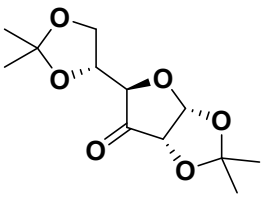
1. Villadsen, N. L.; Jacobsen, K. M.; Keiding, U. B.; Weibel, E. T.; Christiansen, B.; Vosegaard, T.; Bjerring, M.; Jensen, F.; Johannsen, M.; Torring, T.; Poulsen, T. B. *Nat. Chem*. **2017**, *9*, 264.

II. 1H NMR & 13C NMR Spectra

(3a*R*,5*R*,6a*S*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyldihydrofuro[2,3-d][1,3]dioxol-6(5H)-one(S1)

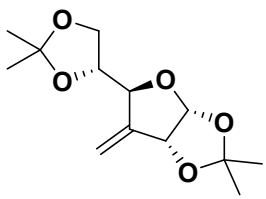


(^{1}H NMR, $CDCl_3$, 500 MHz)

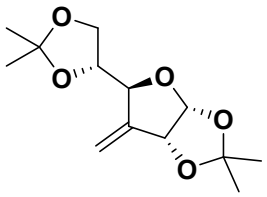


(^{13}C NMR, $CDCl_3$, 125 MHz)

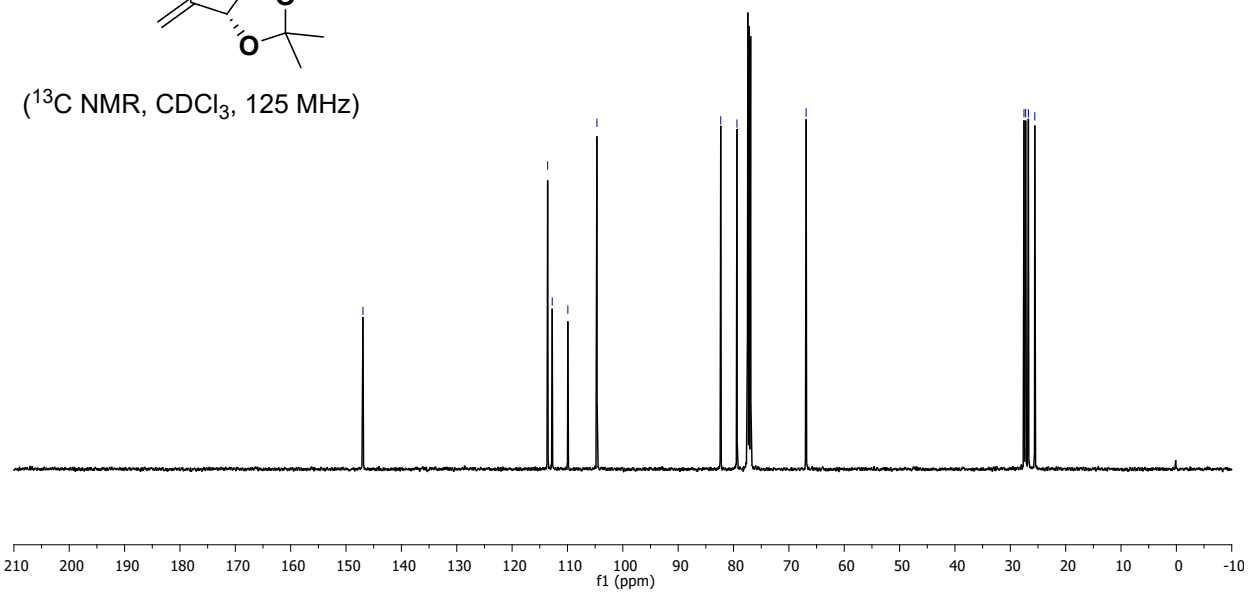
(3a*R*,5*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-methylenetetrahydrofuro[2,3-d][1,3]dioxole(S2)



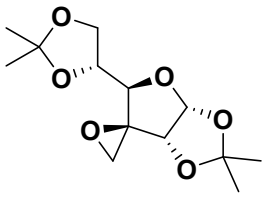
(^{1}H NMR, $CDCl_3$, 500 MHz)



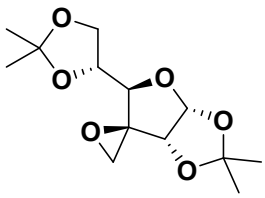
(^{13}C NMR, $CDCl_3$, 125 MHz)



(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyldihydro-5H-spiro[furo[2,3-d][1,3]dioxole-6,2'-oxirane] (S3)

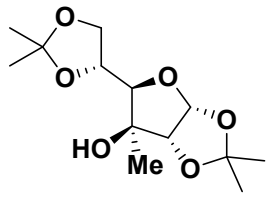


(^{1}H NMR, $CDCl_3$, 500 MHz)

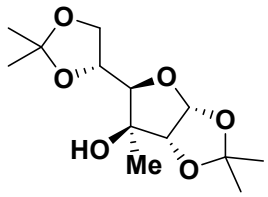


(^{13}C NMR, $CDCl_3$, 125 MHz)

(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-Ol (11)

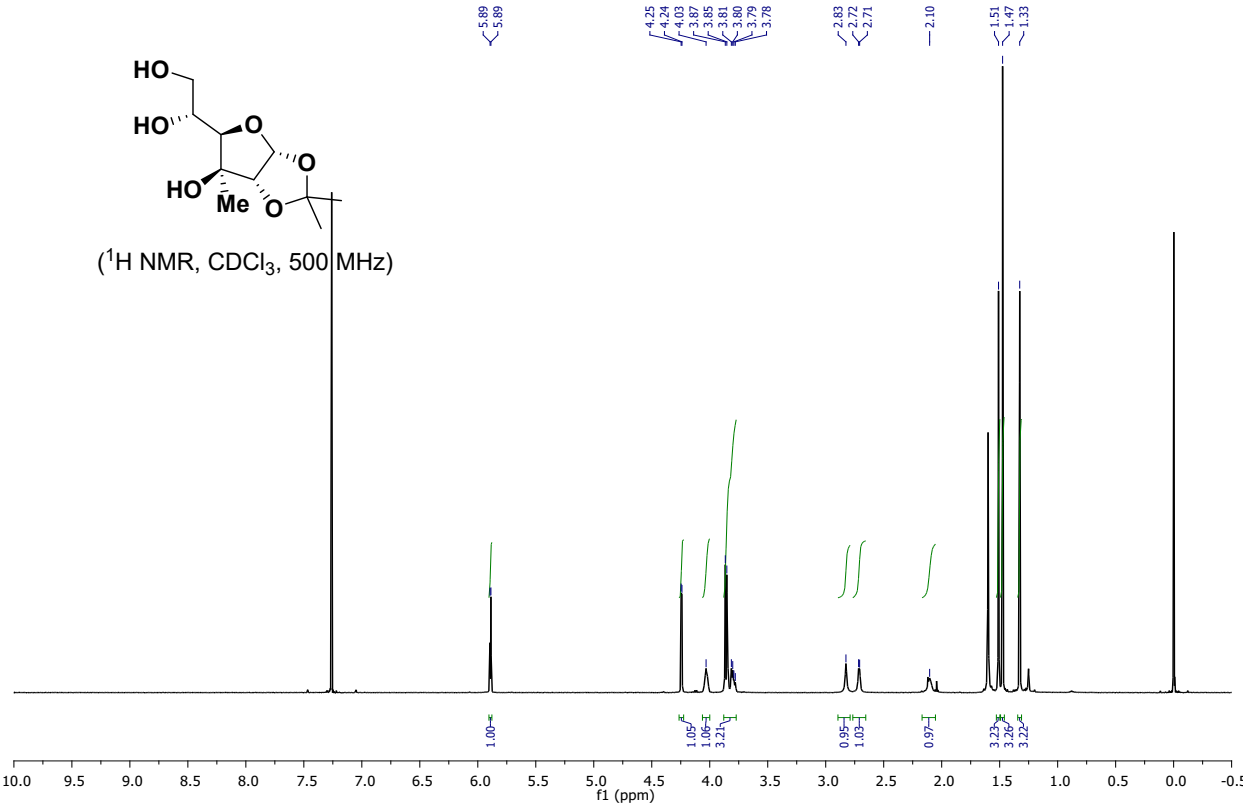


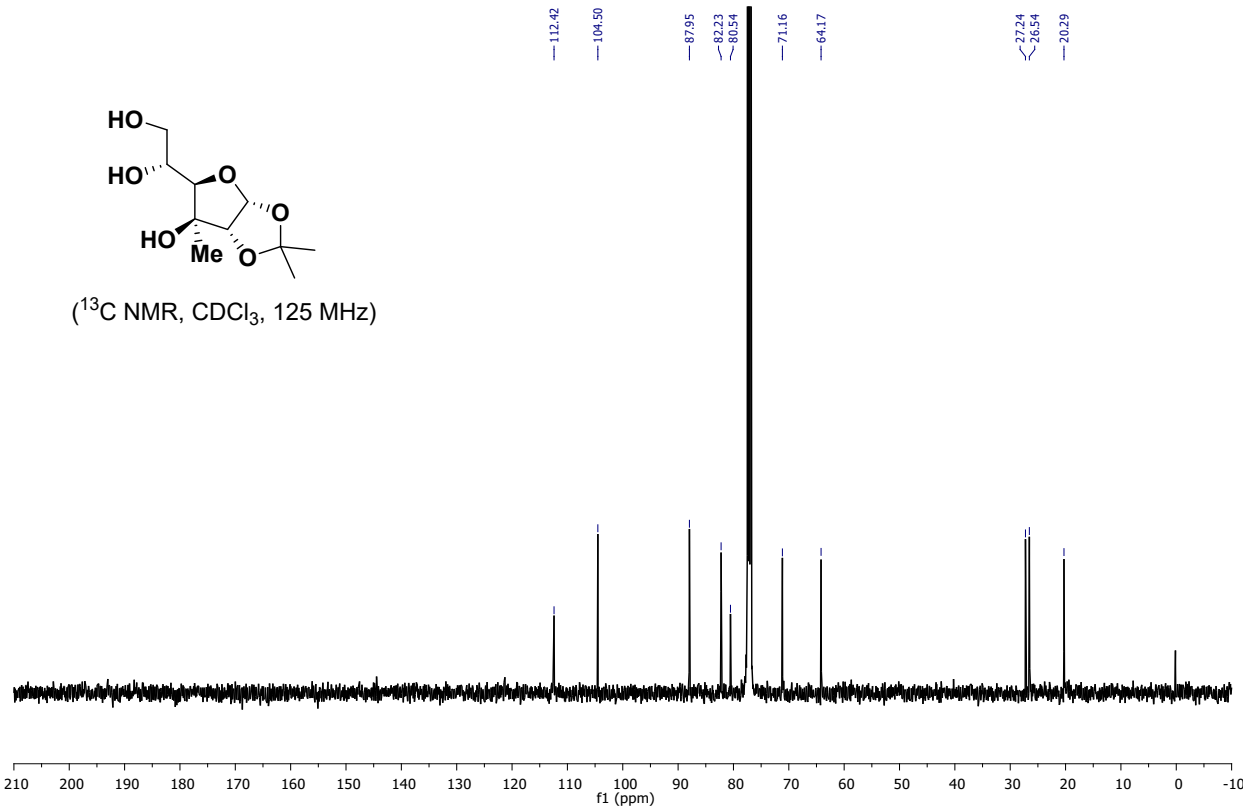
(^{1}H NMR, $CDCl_3$, 400 MHz)



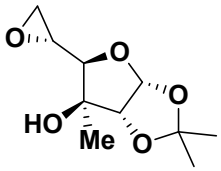
(^{13}C NMR, $CDCl_3$, 100 MHz)

(*R*)-1-((3a*R*,5*R*,6*S*,6a*R*)-6-hydroxy-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)ethane-1,2-diol(12)

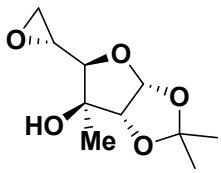




(3a*R*,5*R*,6*S*,6a*R*)-2,2,6-trimethyl-5-((*R*)-oxiran-2-yl)tetrahydrofuro[2,3-d][1,3]dioxol-6-ol (13)

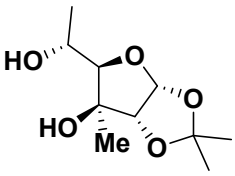


(^{1}H NMR, $CDCl_3$, 400 MHz)

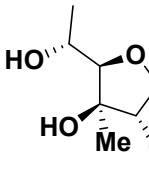


(^{13}C NMR, $CDCl_3$, 100 MHz)

(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-1-hydroxyethyl)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-ol (14)

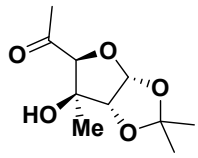


(^{1}H NMR, $CDCl_3$, 400 MHz)

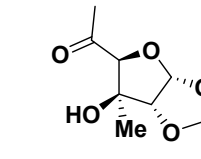


(^{13}C NMR, $CDCl_3$, 125 MHz)

1-((3a*R*,5*S*,6*R*,6a*R*)-6-hydroxy-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)ethan-1-one (15)

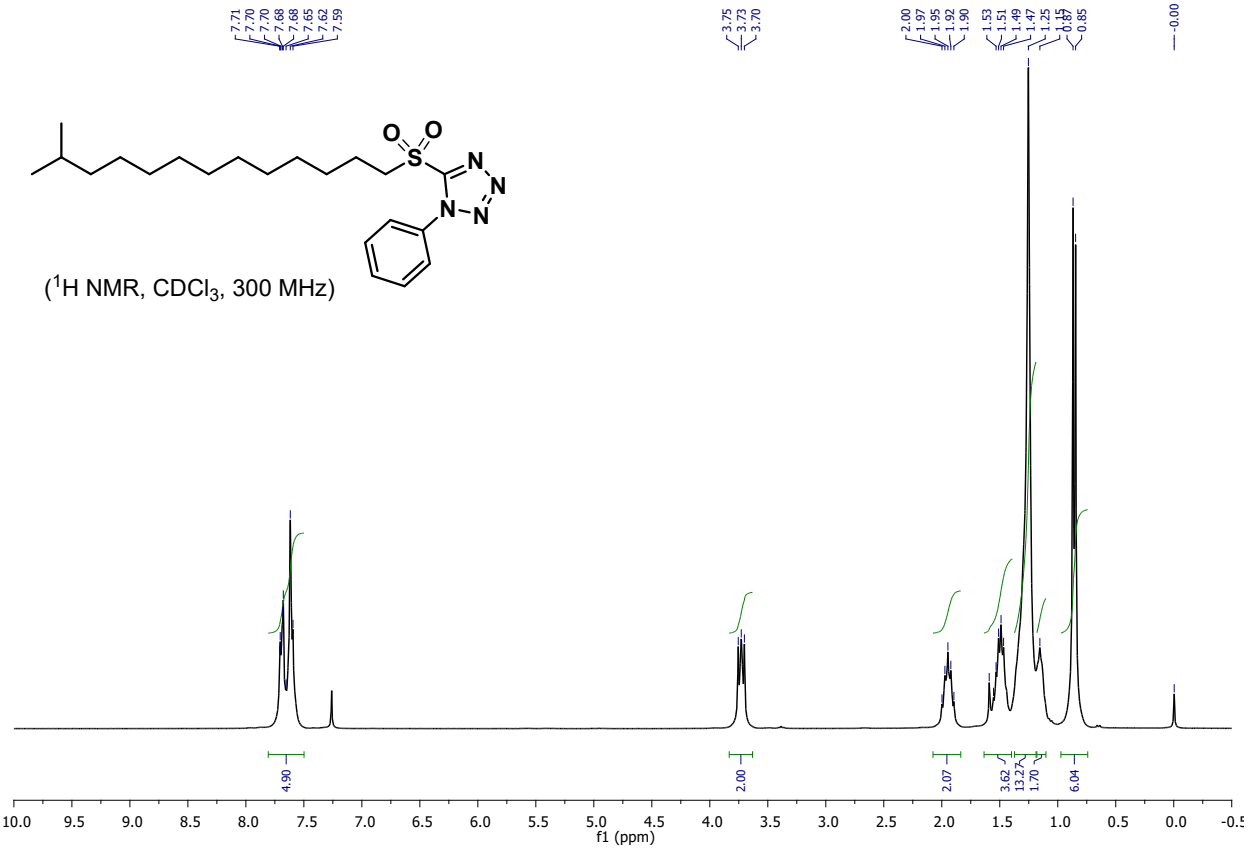


(^{1}H NMR, $CDCl_3$, 500 MHz)

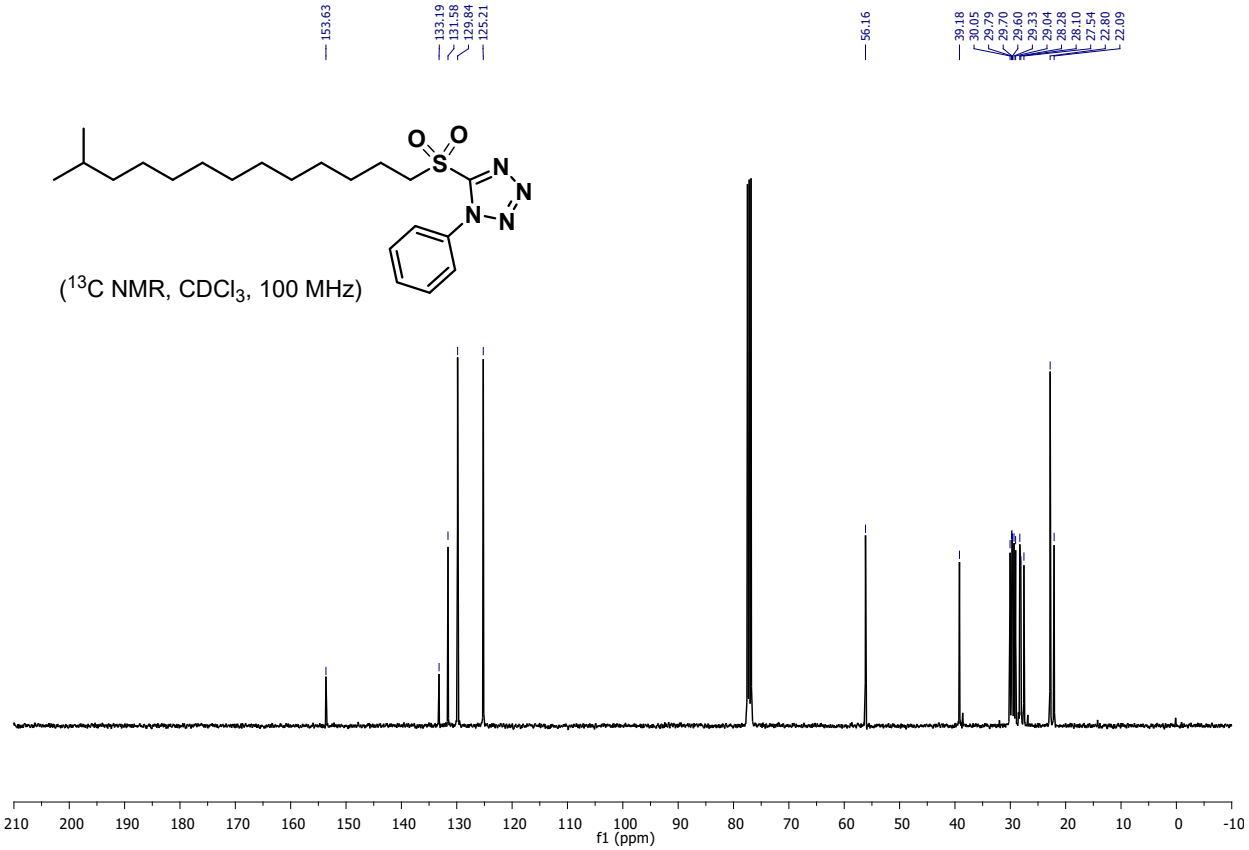


(^{13}C NMR, $CDCl_3$, 100 MHz)

5-((12-methyltridecyl)sulfonyl)-1-phenyl-1H-tetrazole (21)

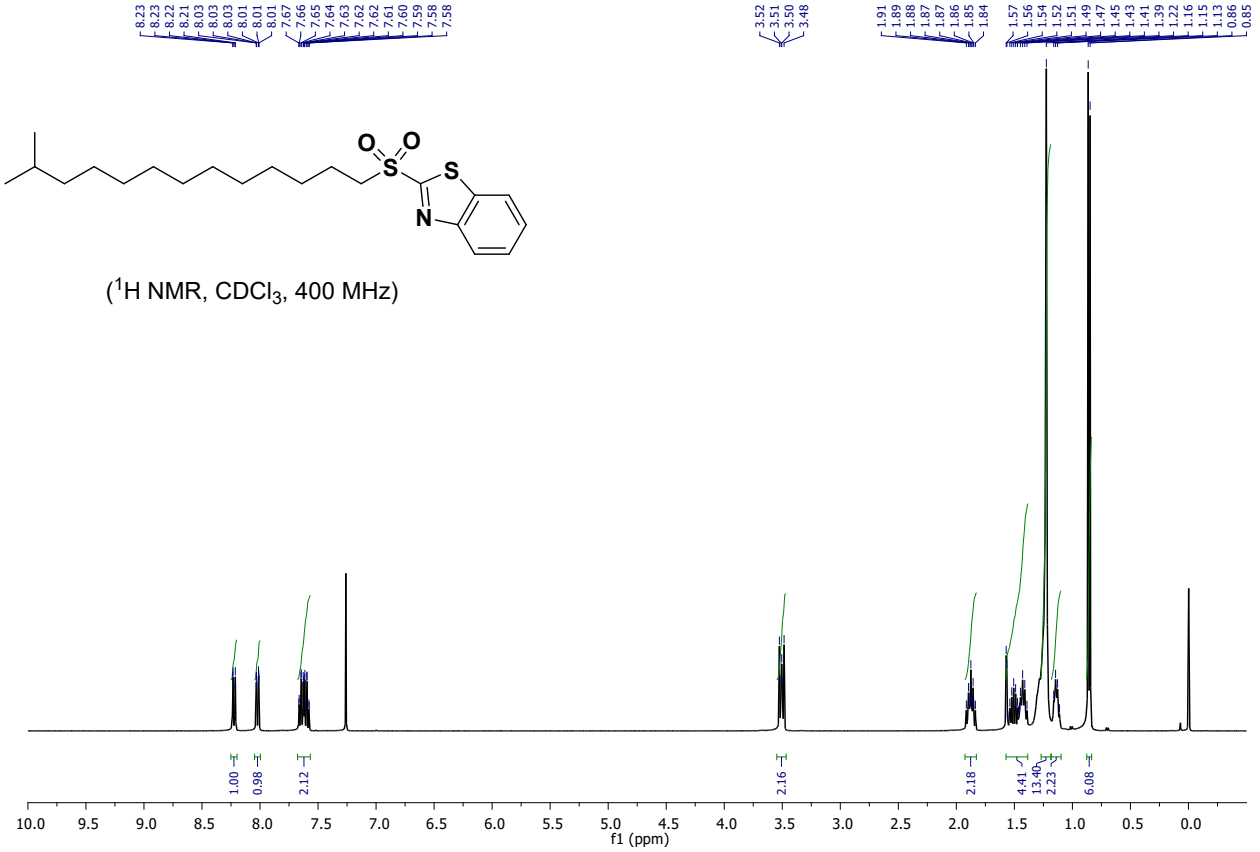


(^{1}H NMR, $CDCl_3$, 300 MHz)

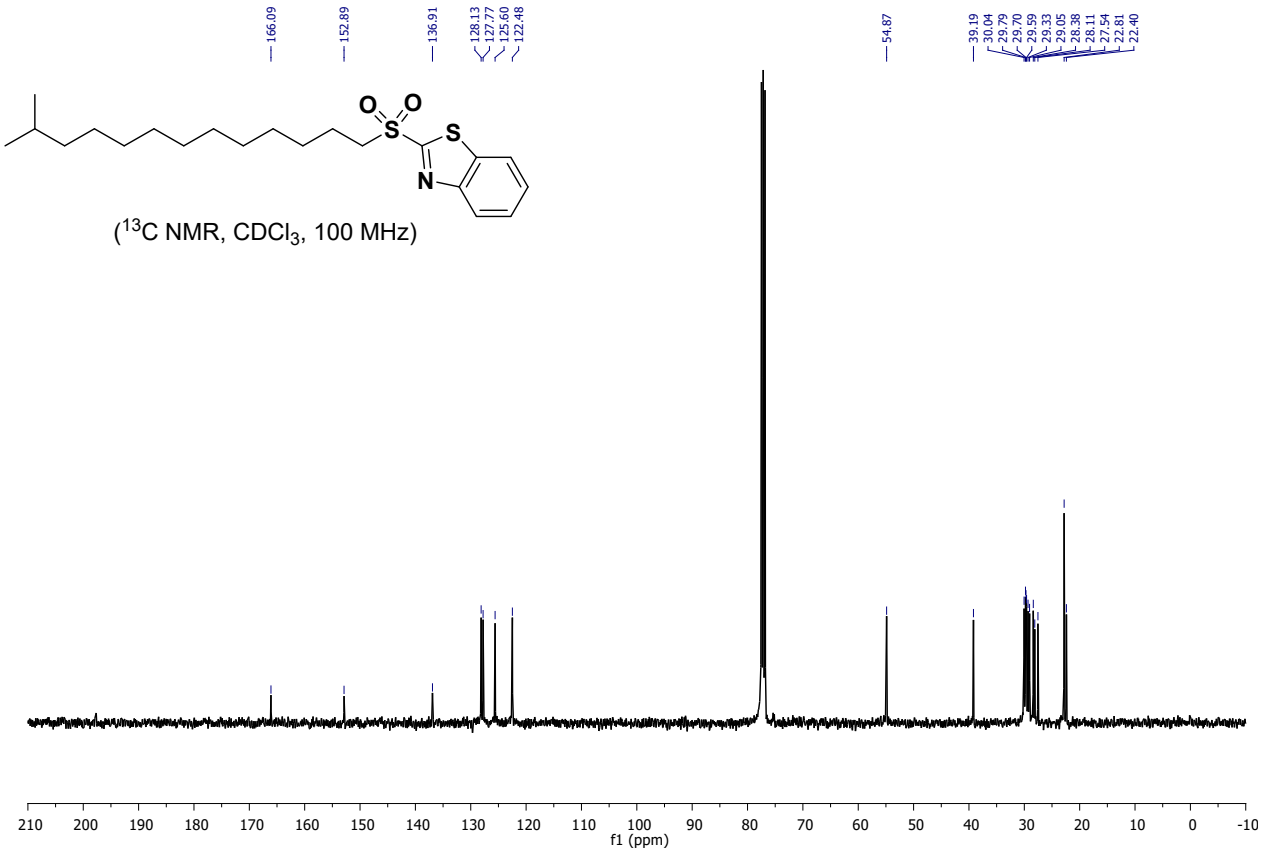


(^{13}C NMR, $CDCl_3$, 100 MHz)

2-((12-methyltridecyl)sulfonyl)benzo[d]thiazole (22)

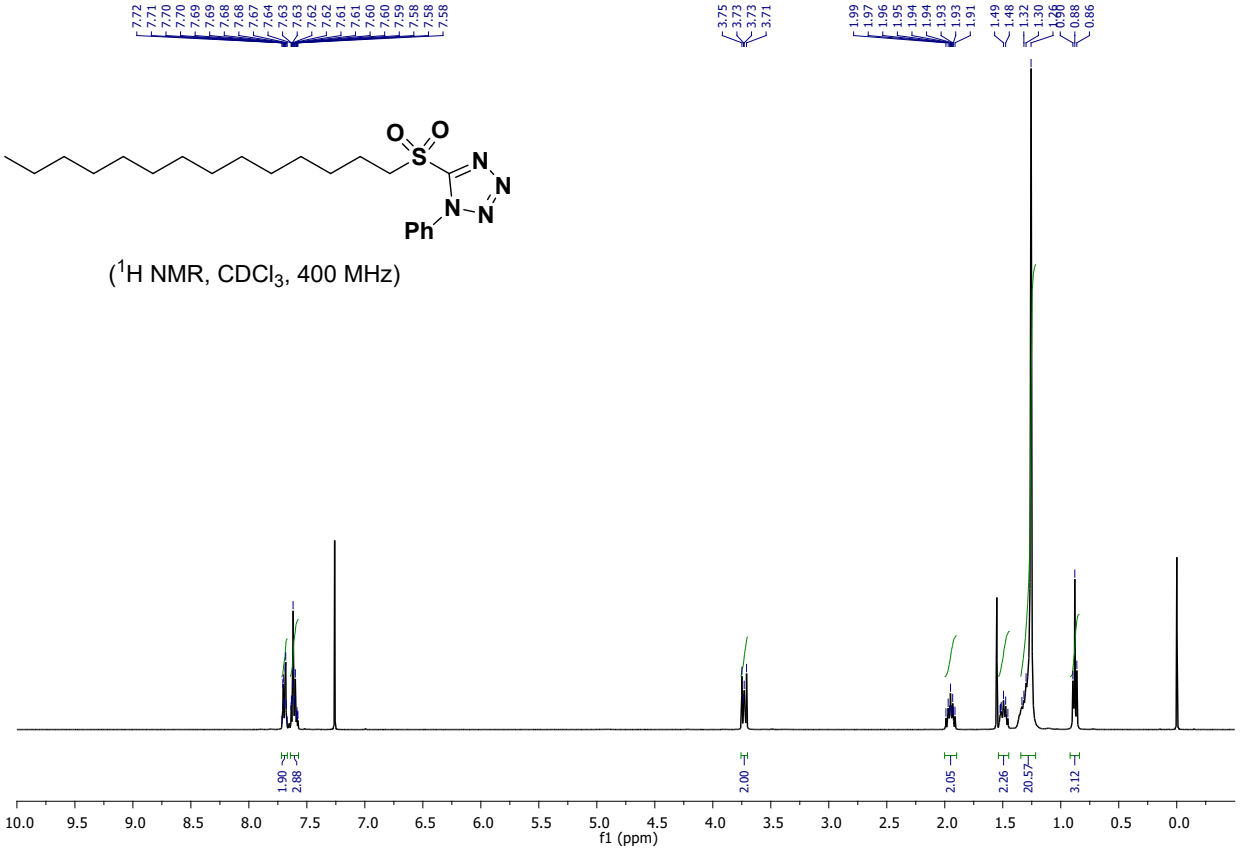


(^{1}H NMR, $CDCl_3$, 400 MHz)

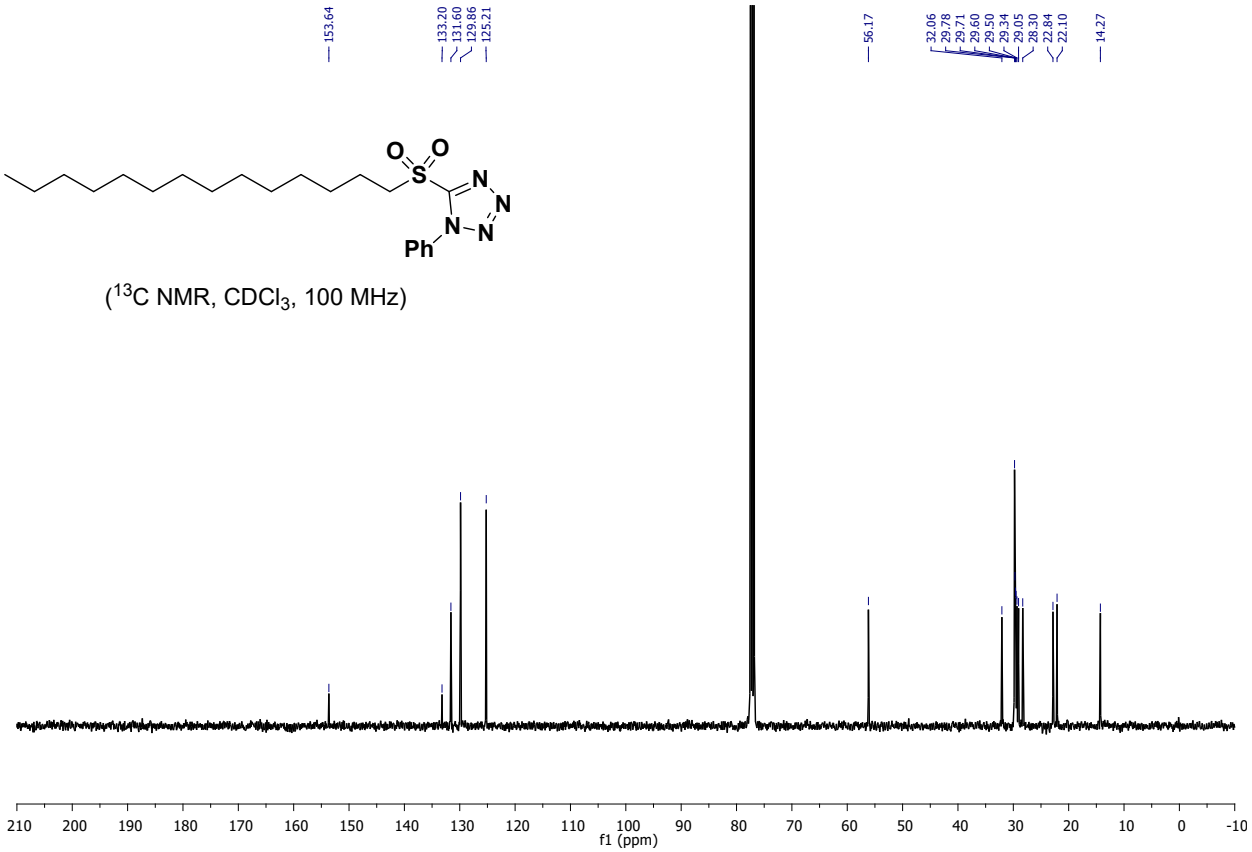


(^{13}C NMR, $CDCl_3$, 100 MHz)

1-phenyl-5-(tetradecylsulfonyl)-1H-tetrazole (24)

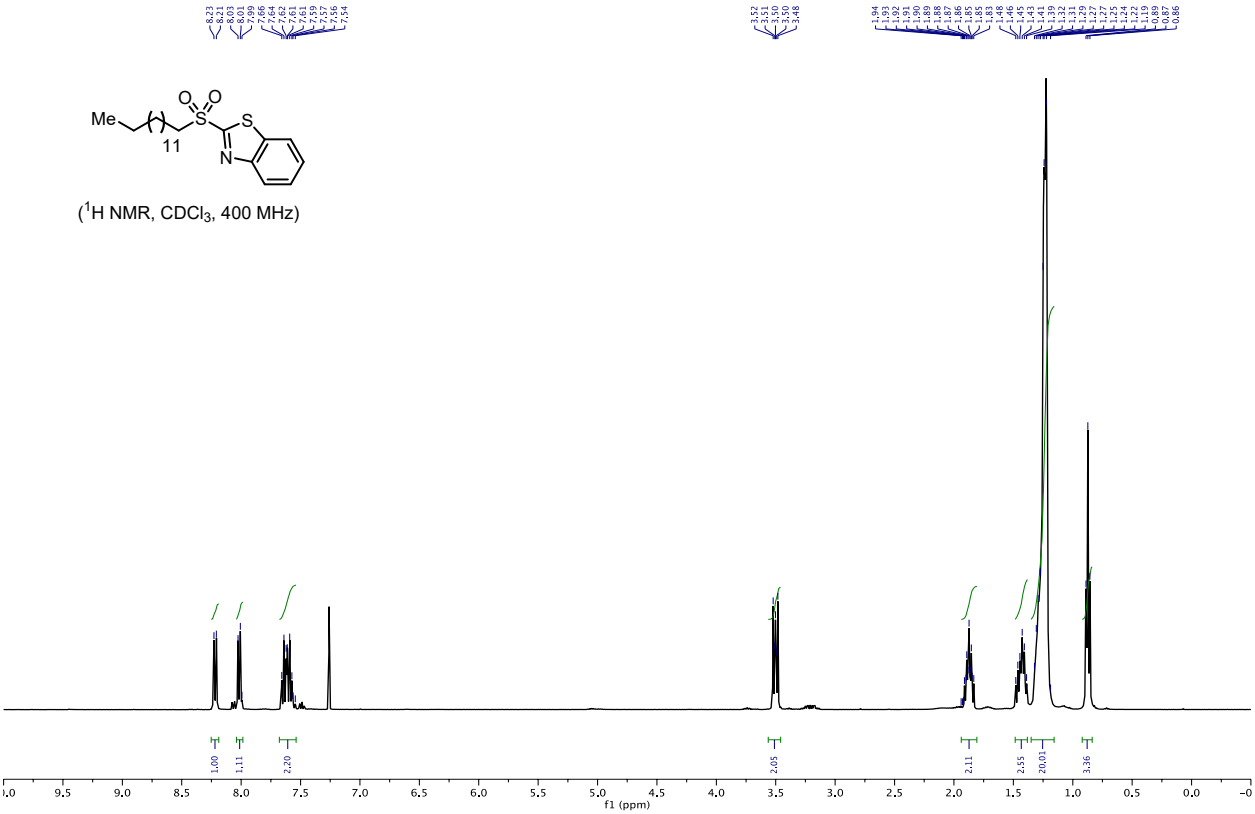


(^{1}H NMR, $CDCl_3$, 400 MHz)

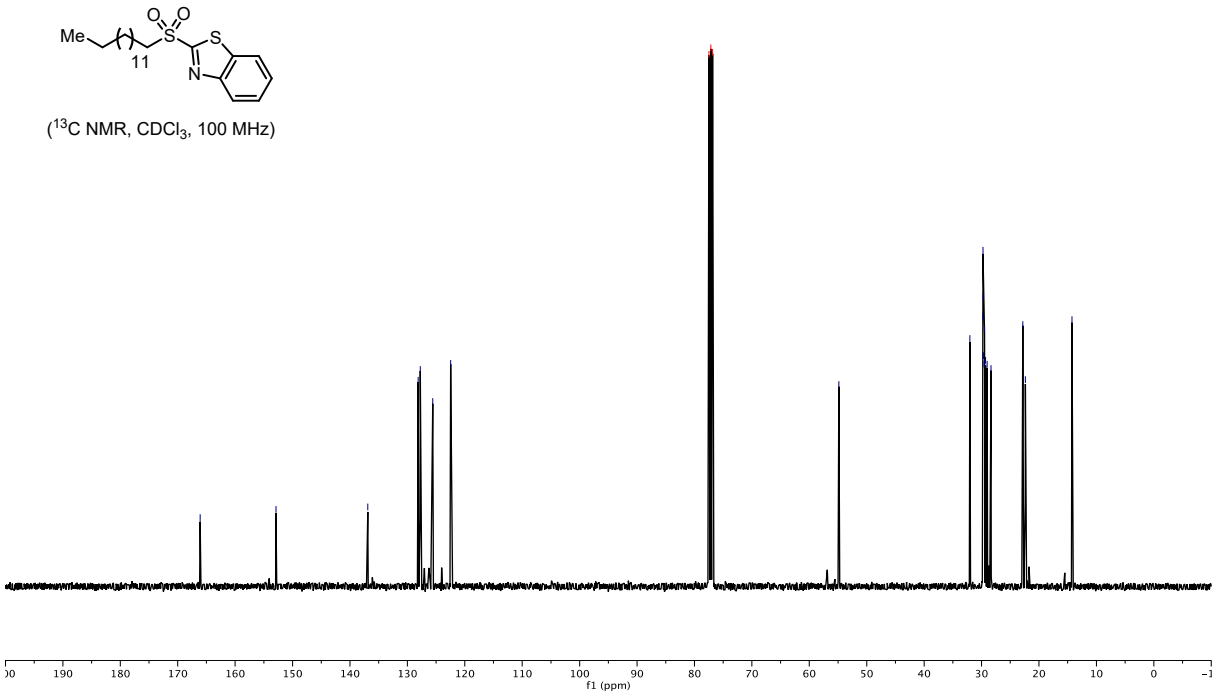


(^{13}C NMR, $CDCl_3$, 100 MHz)

2-(tetradecylsulfonyl)benzo[d]thiazole (25):

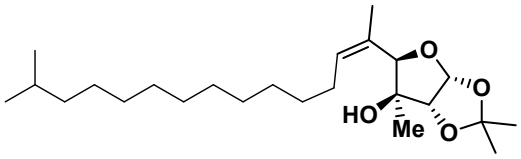


(^{1}H NMR, $CDCl_3$, 400 MHz)

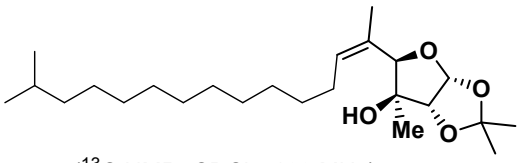


(^{13}C NMR, $CDCl_3$, 100 MHz)

(3a*R*,5*R*,6*S*,6a*R*)-2,2,6-trimethyl-5-((*Z*)-14-methylpentadec-2-en-2-yl)tetrahydrofuro[2,3-d][1,3]dioxol-6-ol (*Z*-26)

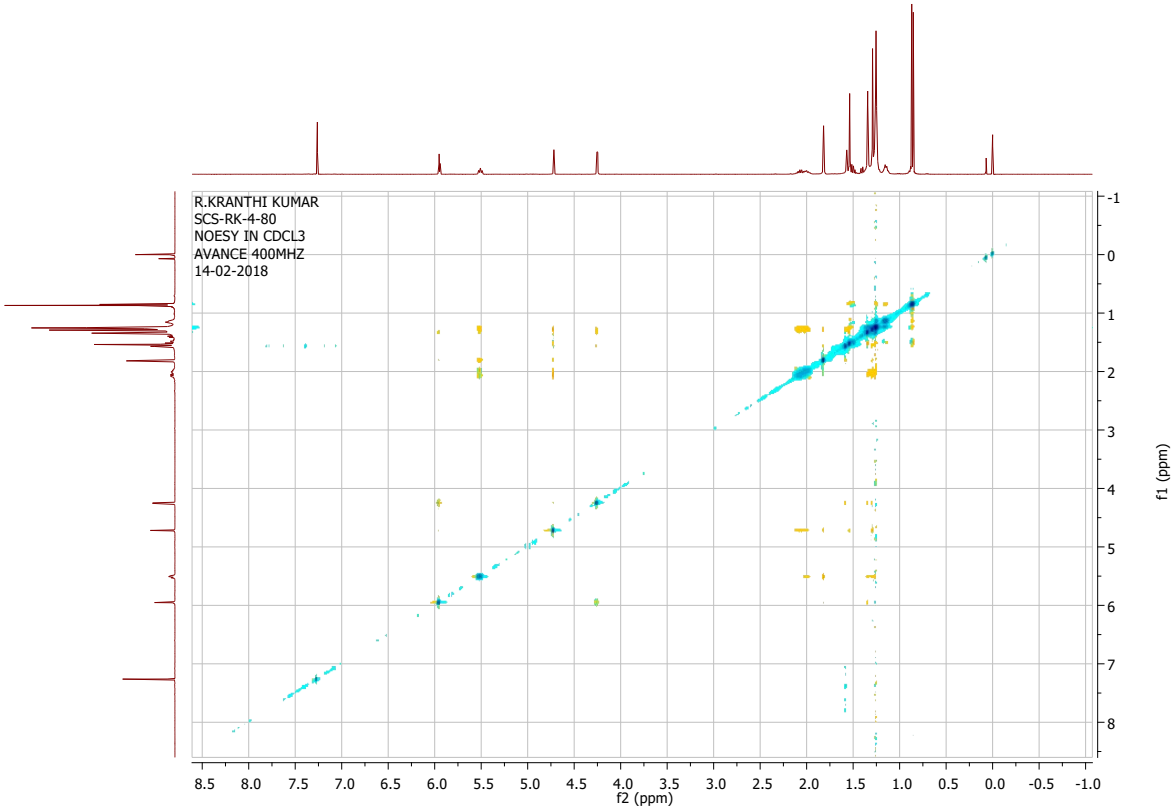


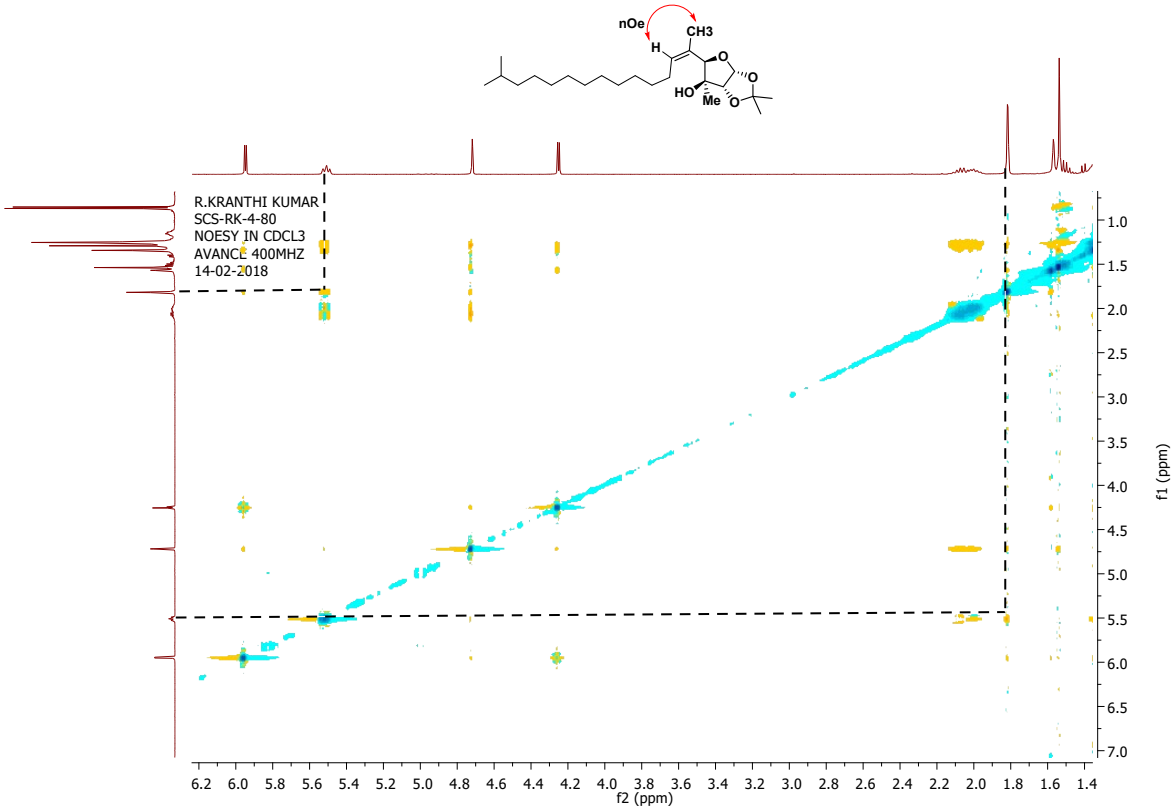
(^{1}H NMR, $CDCl_3$, 400 MHz)



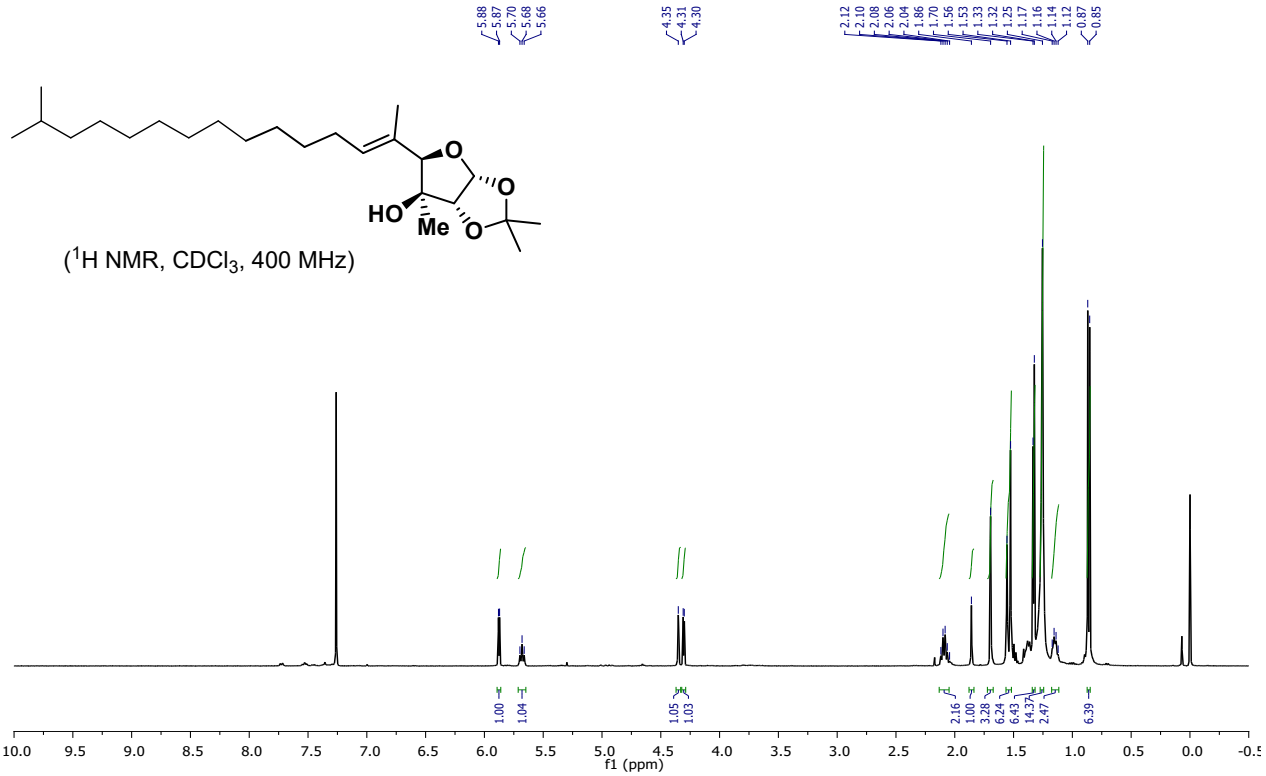
(^{13}C NMR, $CDCl_3$, 100 MHz)

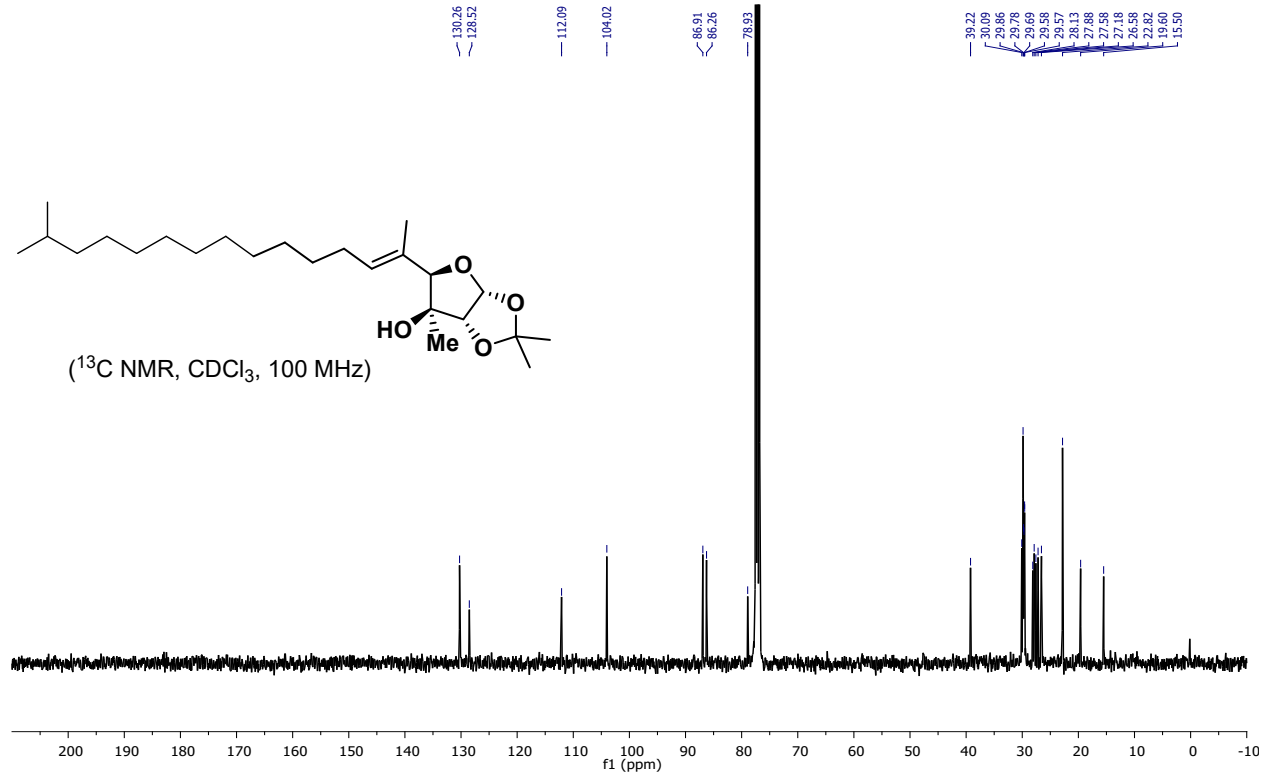
NOESY Spectrum of (3a*R*,5*R*,6*S*,6a*R*)-2,2,6-Trimethyl-5-((*Z*)-14-methylpentadec-2-en-2-yl)tetrahydrofuro[2,3-d][1,3]dioxol-6-ol (*Z*-26):



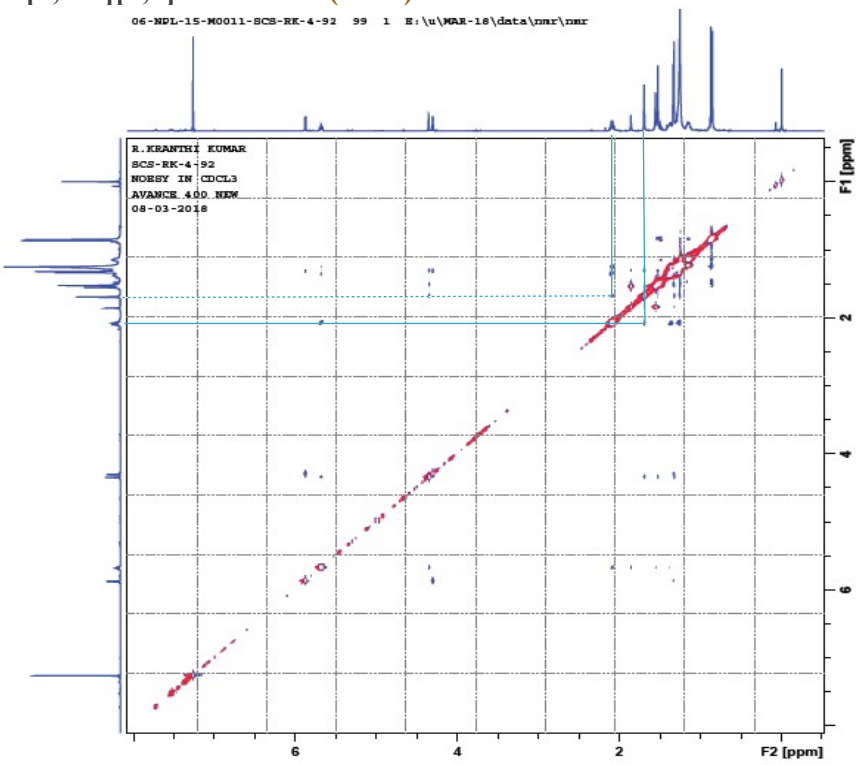


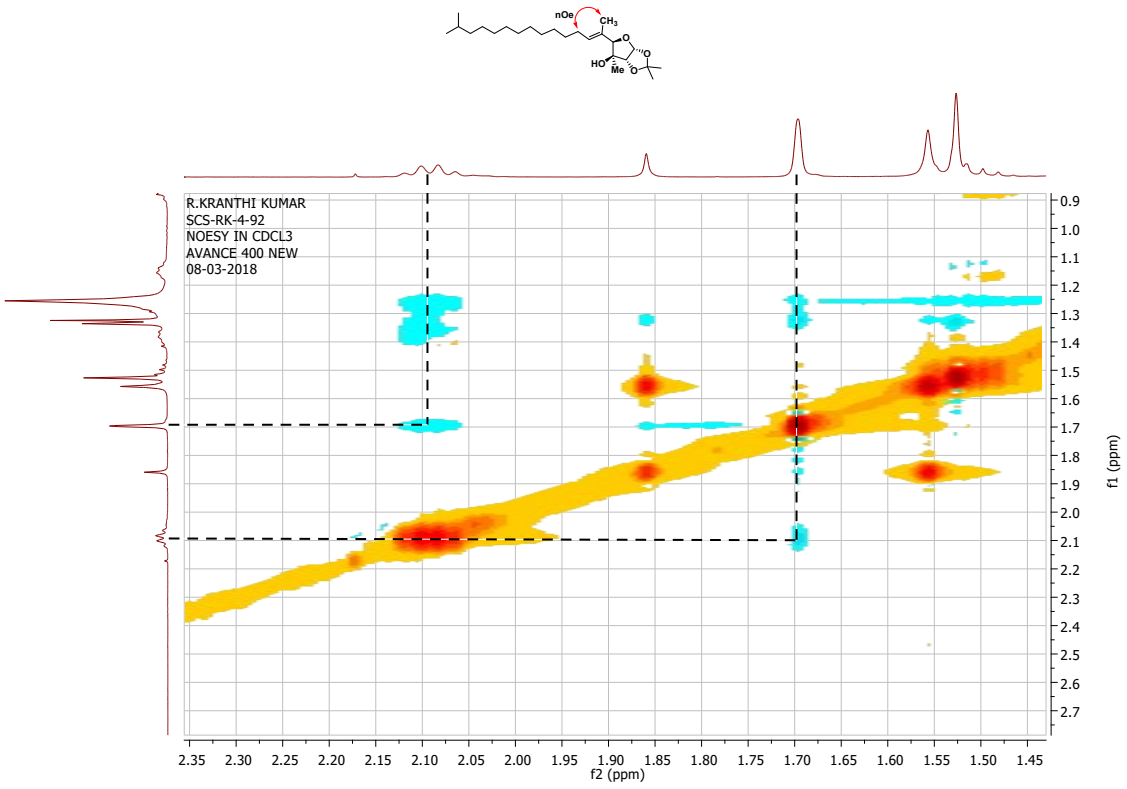
(3a*R*,5*R*,6*S*,6a*R*)-2,2,6-trimethyl-5-((*E*)-14-methylpentadec-2-en-2-yl)tetrahydrofuro[2,3-d][1,3]dioxol-6-ol (*E*-26):



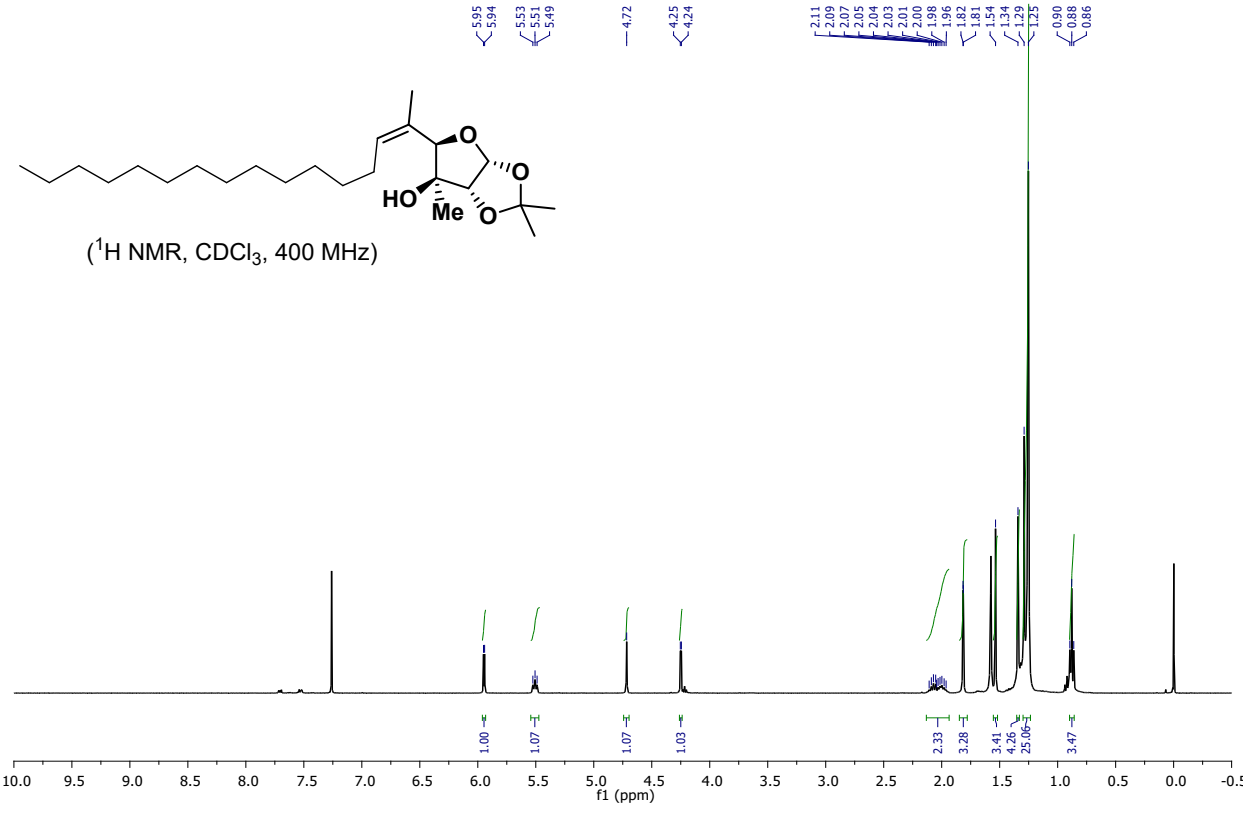


NOESY Spectrum of (3a*R*,5*R*,6*S*,6a*R*)-2,2,6-Trimethyl-5-((*E*)-14-methylpentadec-2-en-2-yl)tetrahydrofuro[2,3-d][1,3]dioxol-6-ol (*E*-26):

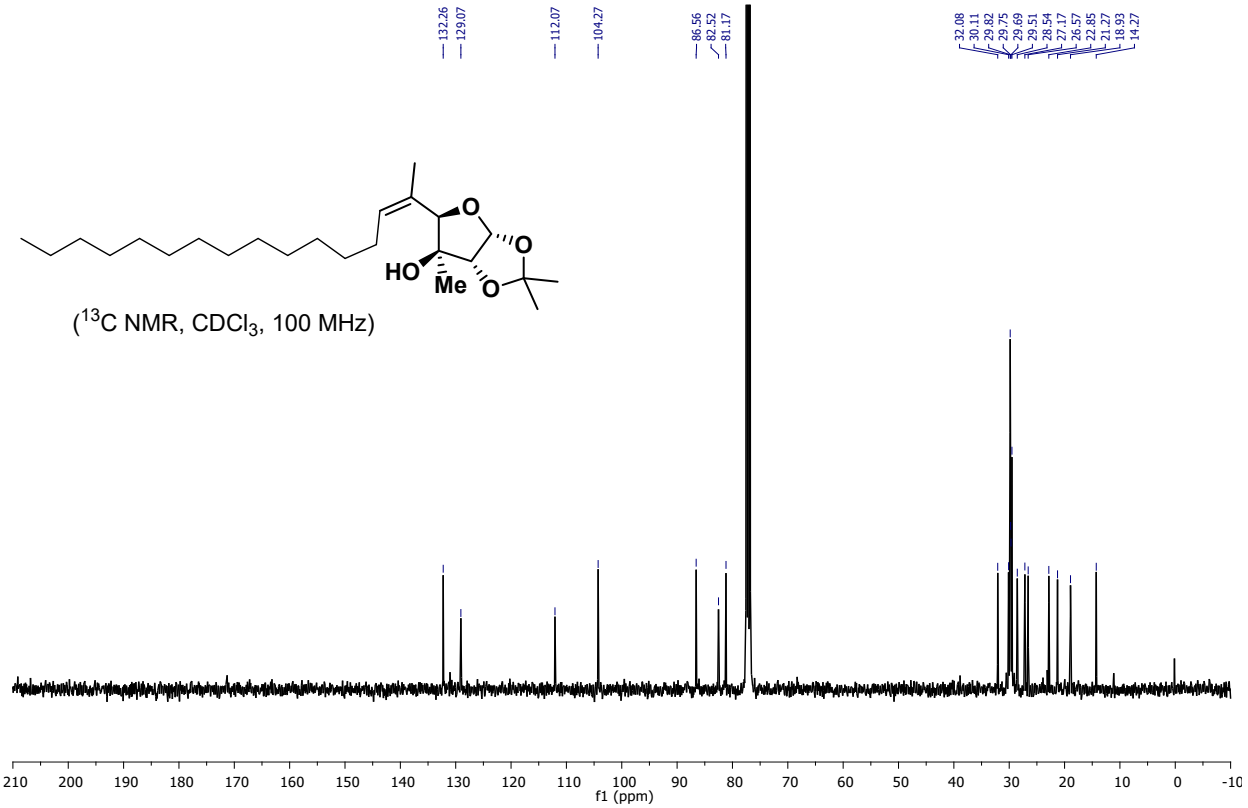




(3a*R*,5*R*,6*S*,6a*R*)-5-((*Z*)-hexadec-2-en-2-yl)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-ol (*Z*-27)

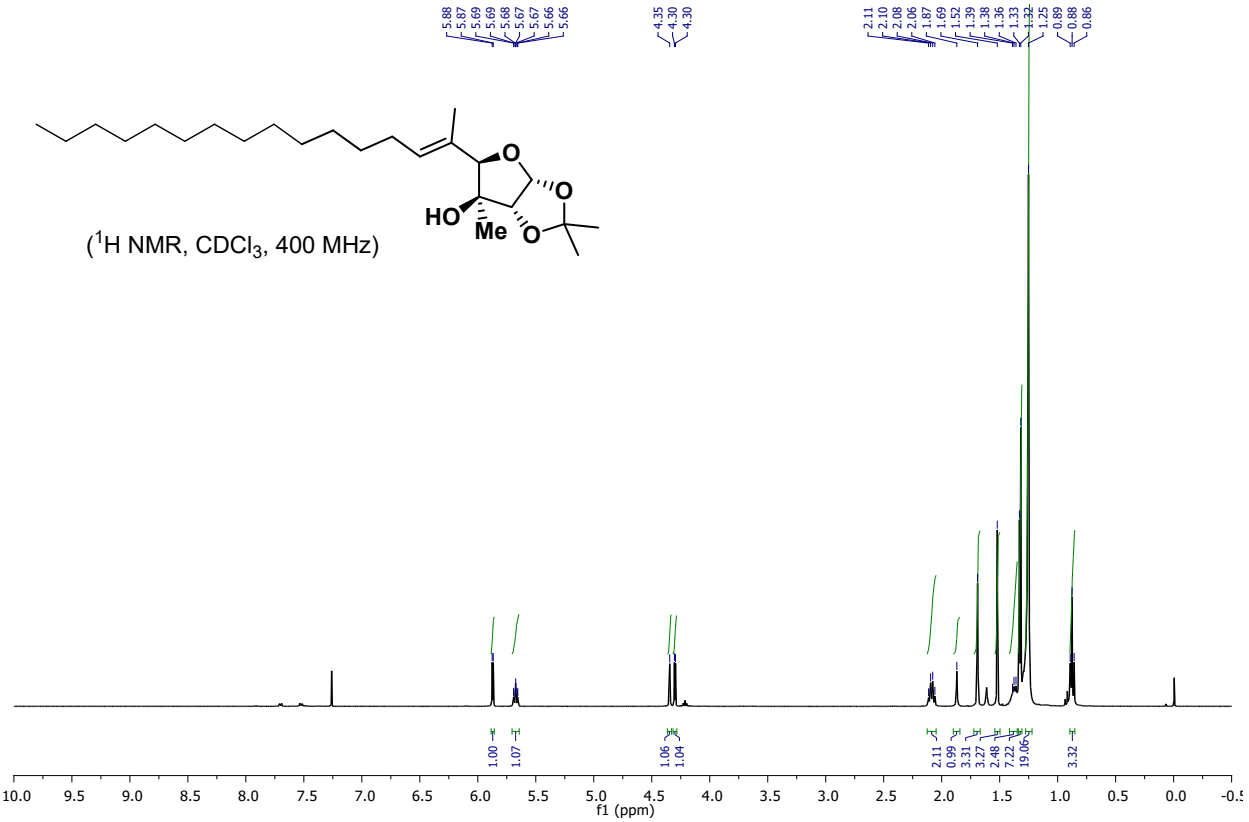


(^{1}H NMR, $CDCl_3$, 400 MHz)

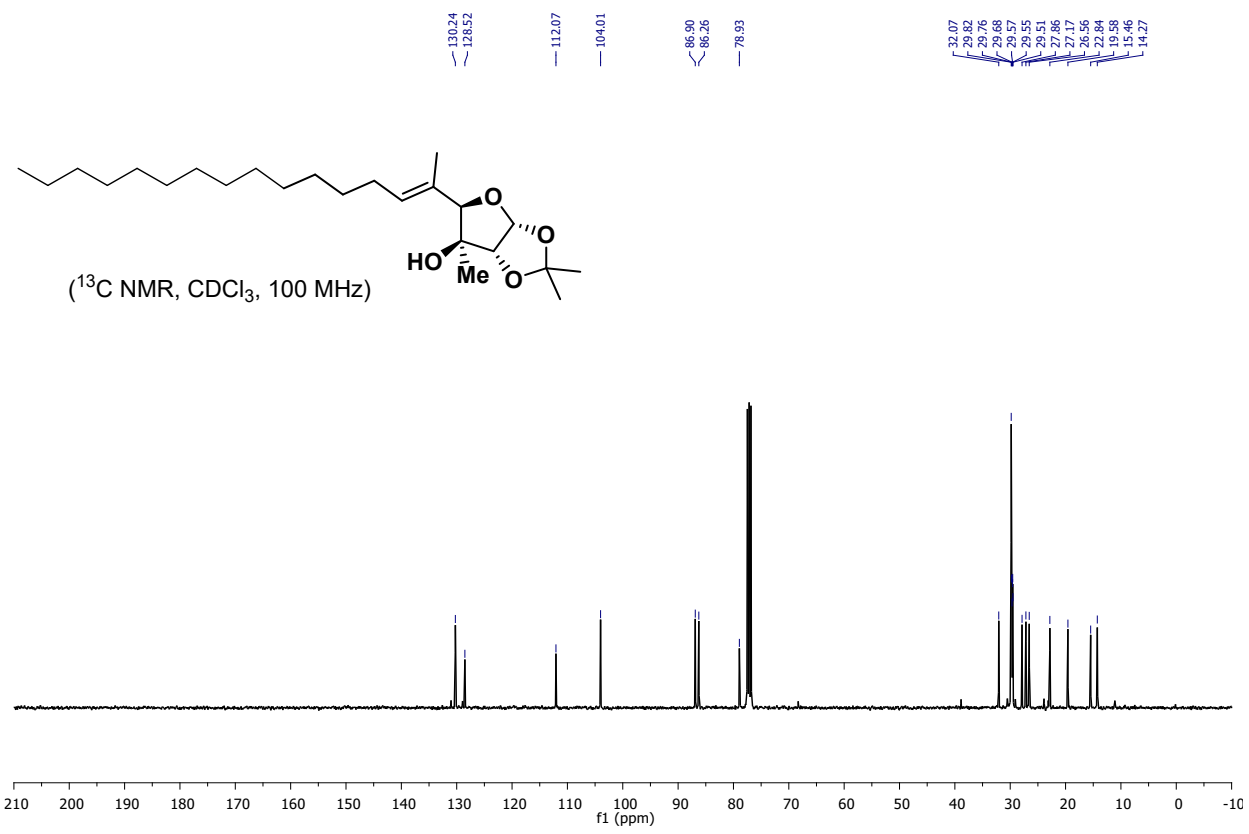


(^{13}C NMR, $CDCl_3$, 100 MHz)

(3a*R*,5*R*,6*S*,6a*R*)-5-((*E*)-hexadec-2-en-2-yl)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-ol (*E*-27)

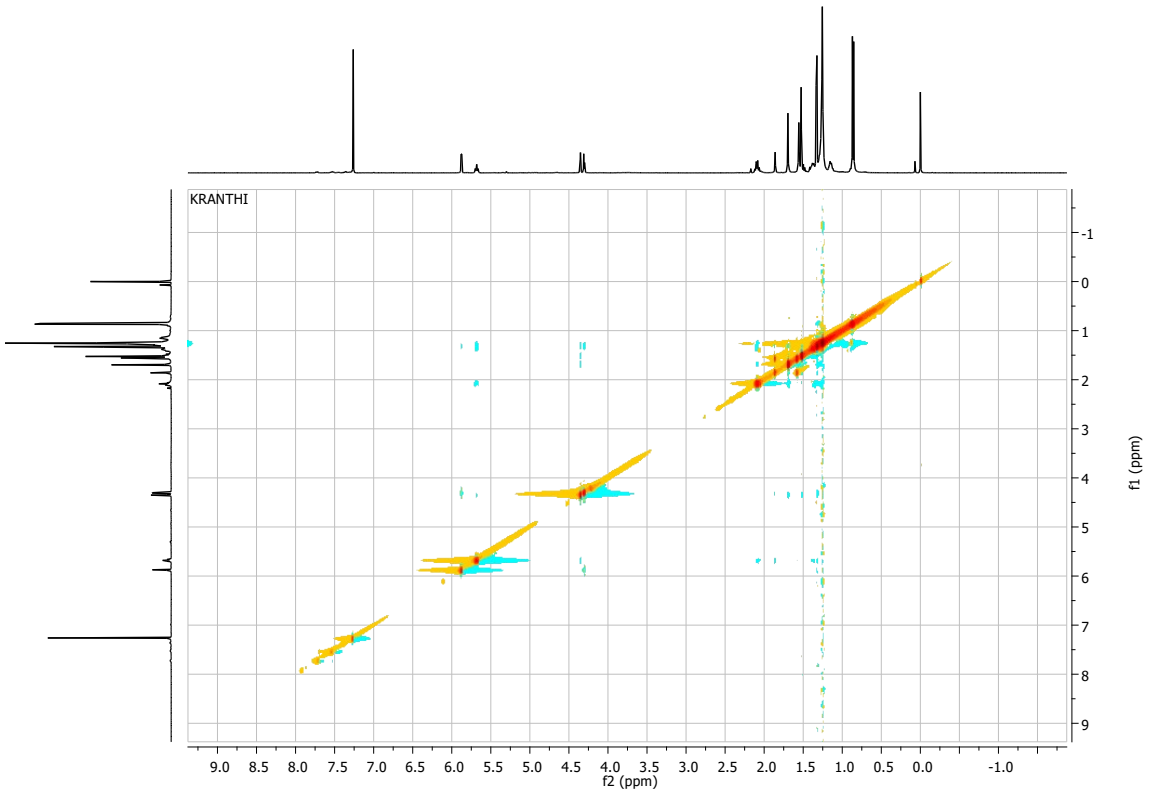


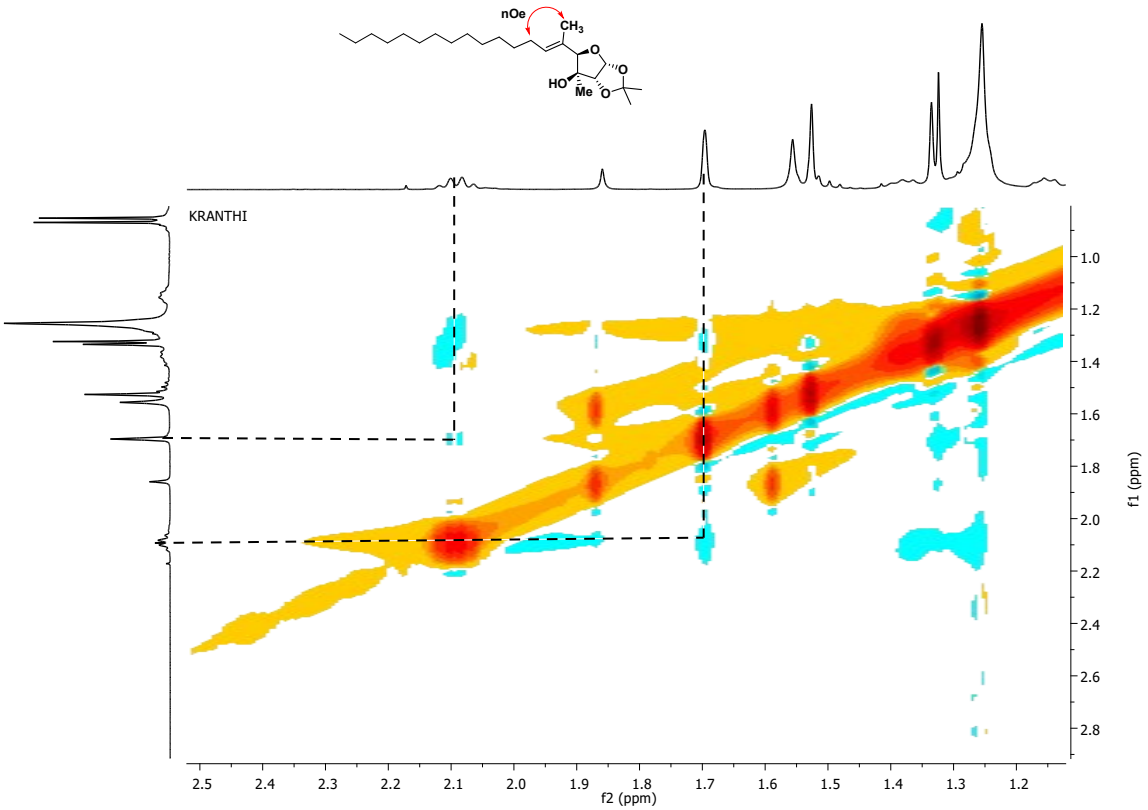
(^{1}H NMR, $CDCl_3$, 400 MHz)



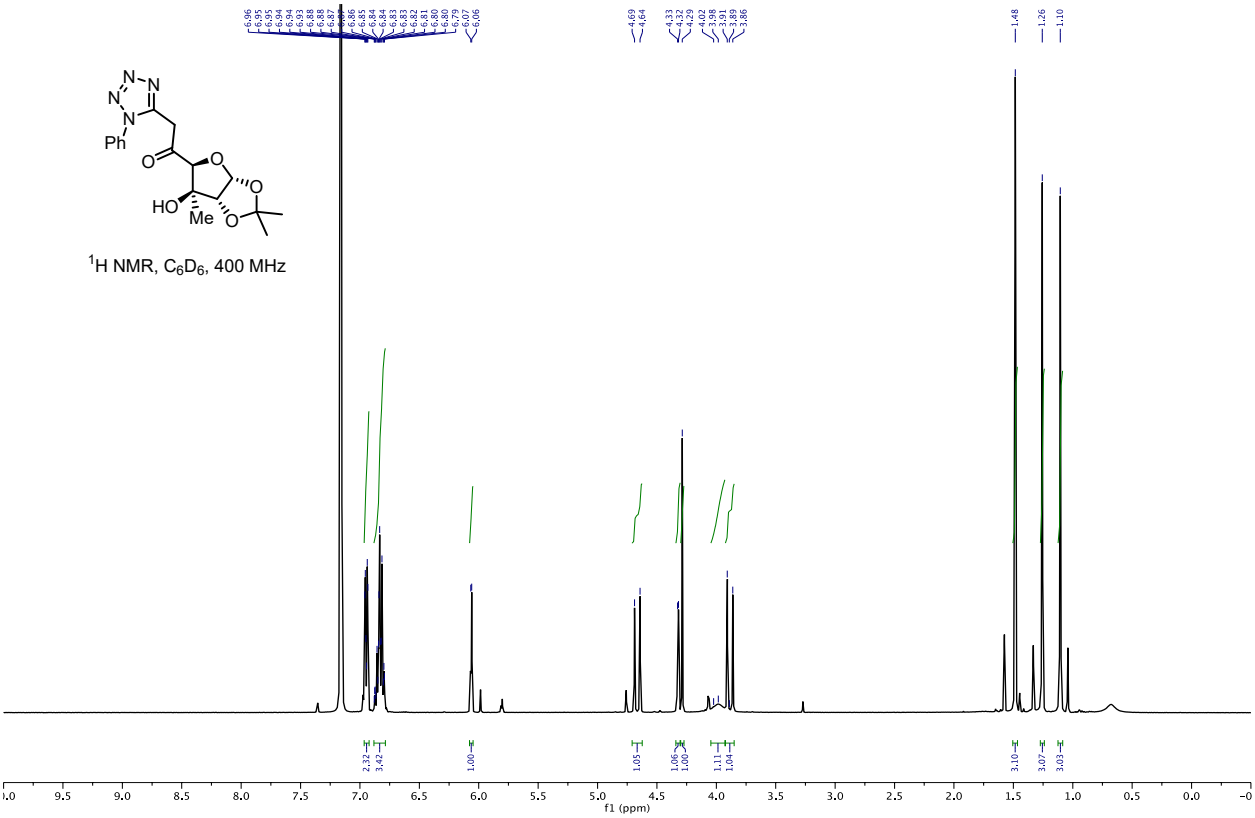
(^{13}C NMR, $CDCl_3$, 100 MHz)

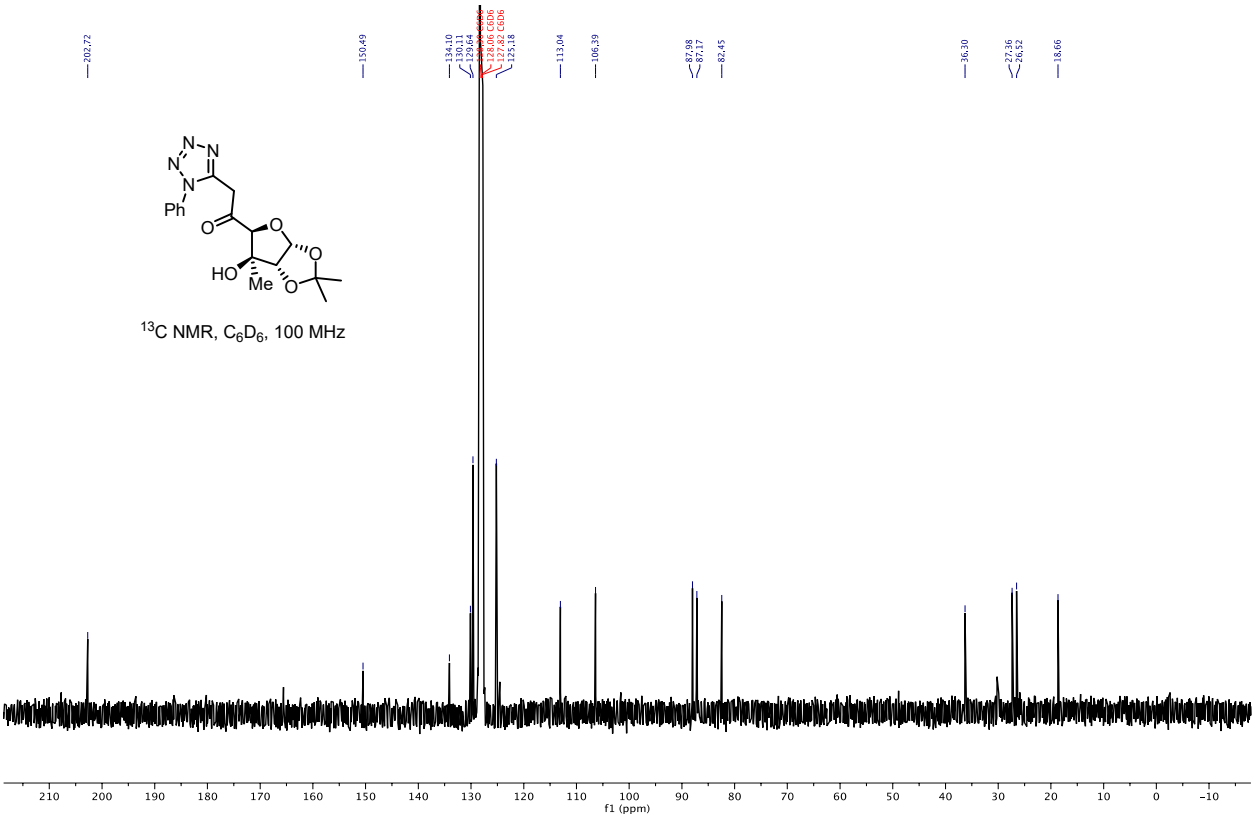
NOESY spectrum of (3a*R*,5*R*,6*S*,6a*R*)-5-((*E*)-Hexadec-2-en-2-yl)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-ol (*E*–27):



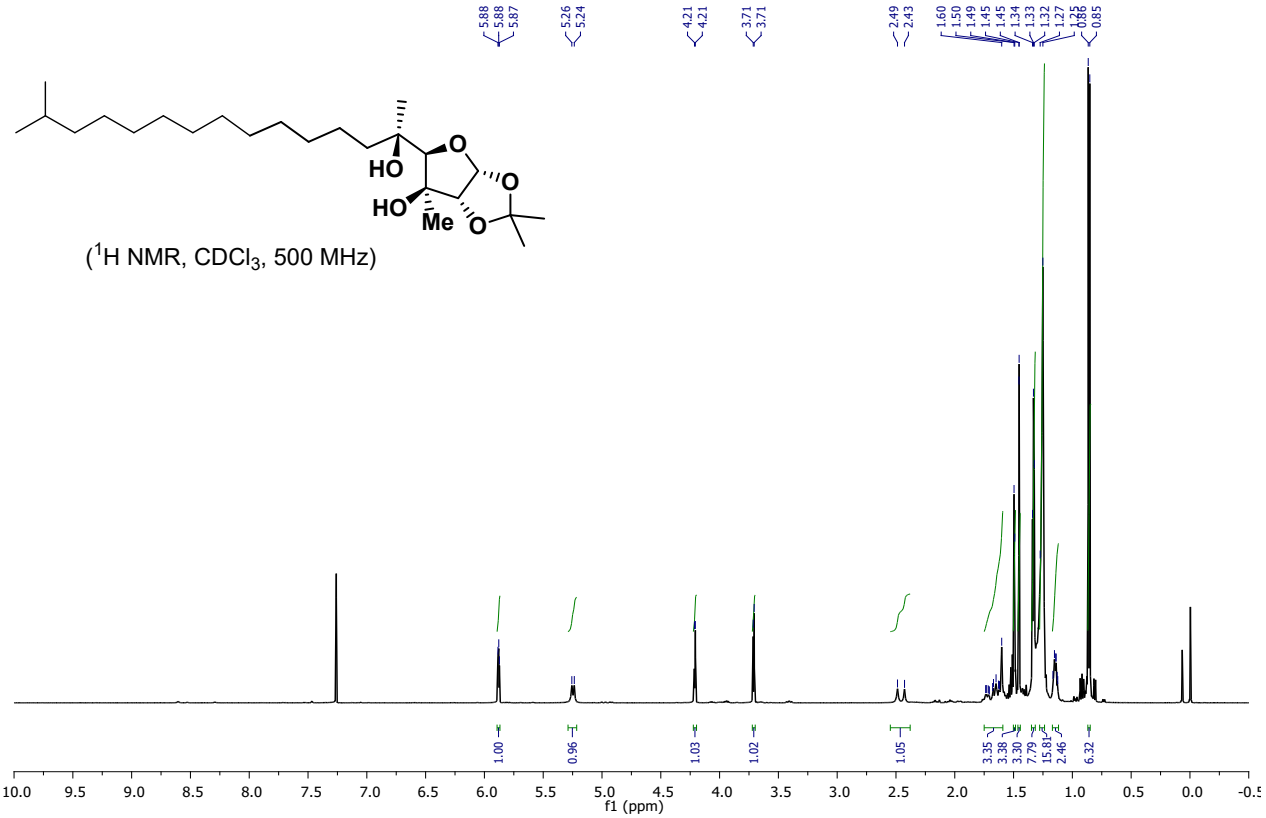


1-((3a*R*,5*S*,6*R*,6a*R*)-6-hydroxy-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-2-(1-phenyl-1H-tetrazol-5-yl)ethan-1-one (28)

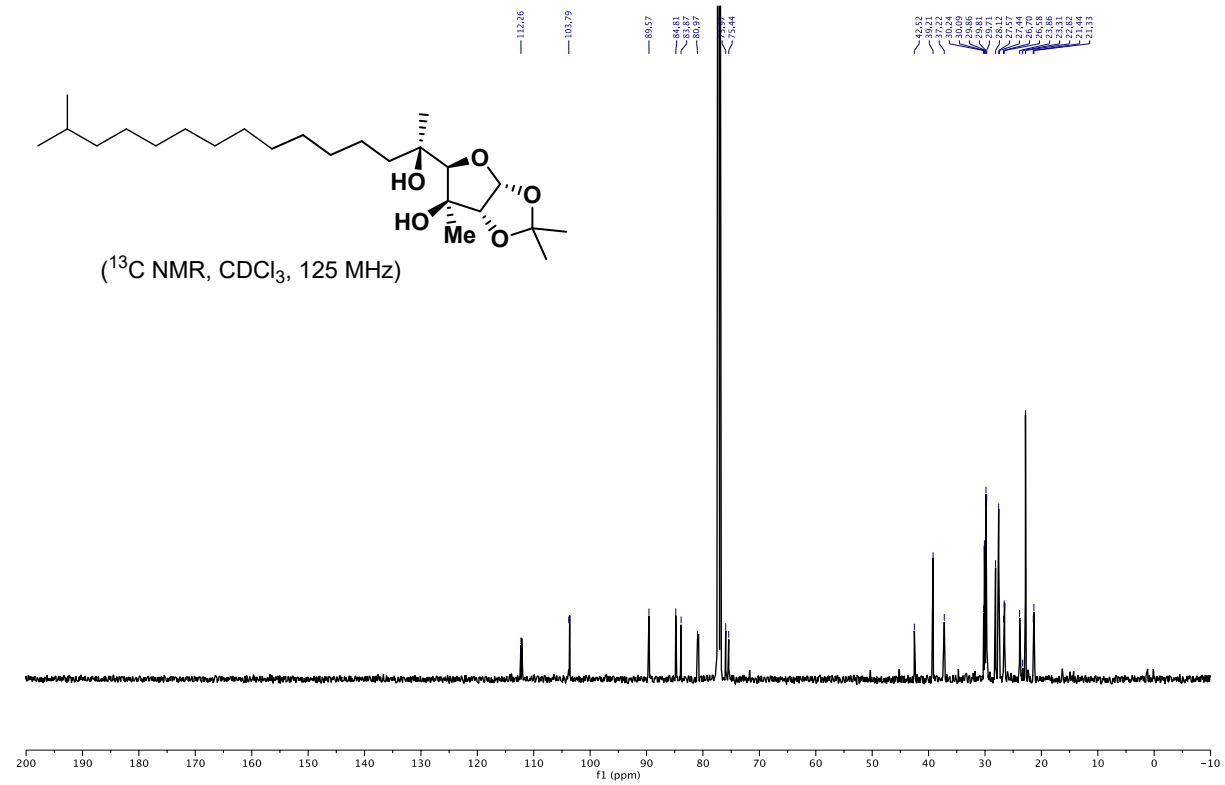




(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2-hydroxy-14-methylpentadecan-2-yl)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-ol (30)

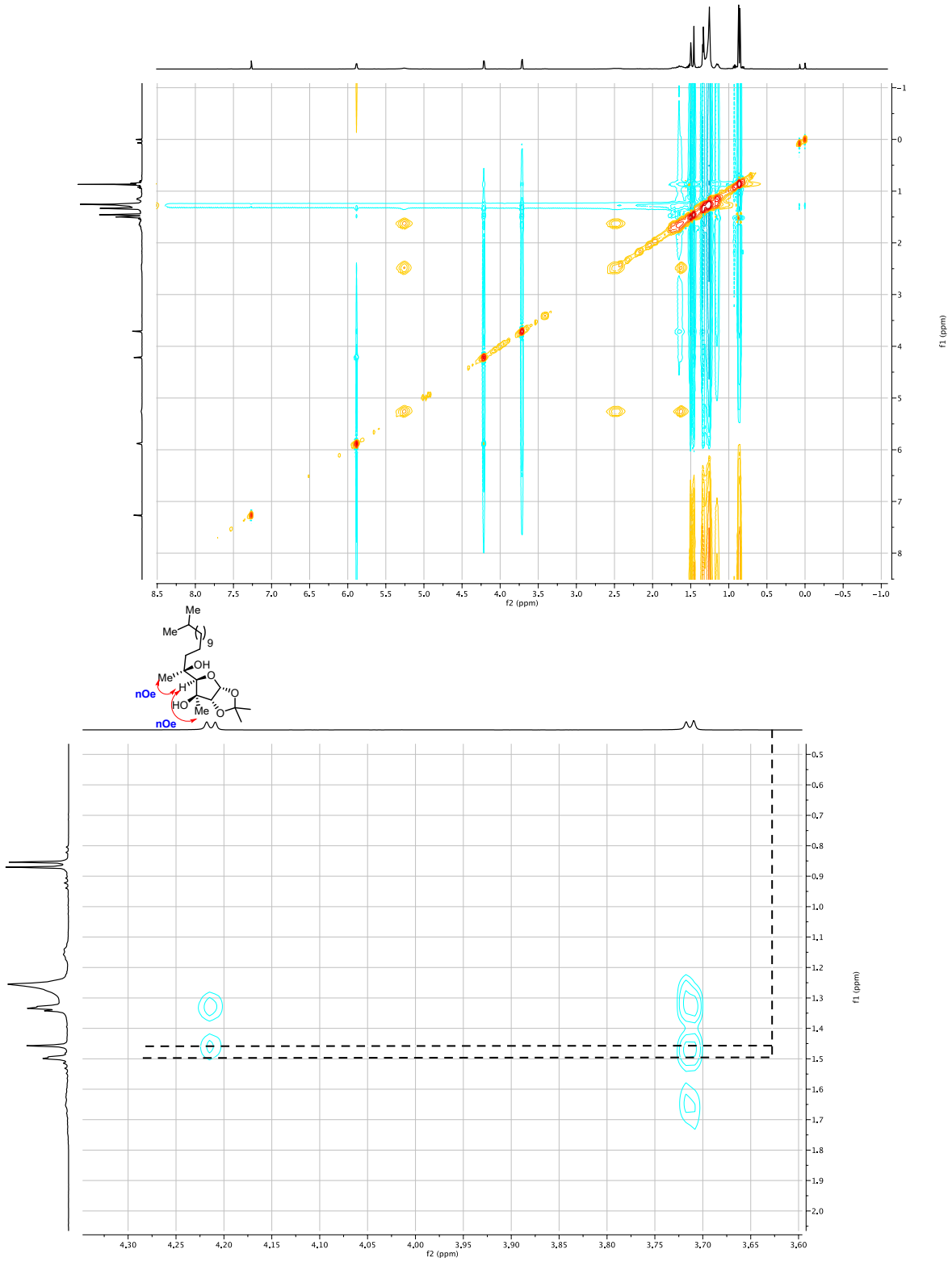


(^{1}H NMR, $CDCl_3$, 500 MHz)

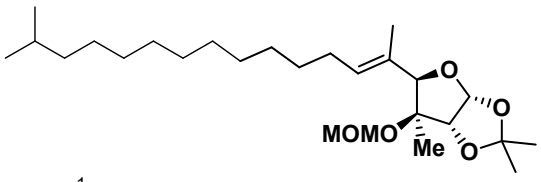


(^{13}C NMR, $CDCl_3$, 125 MHz)

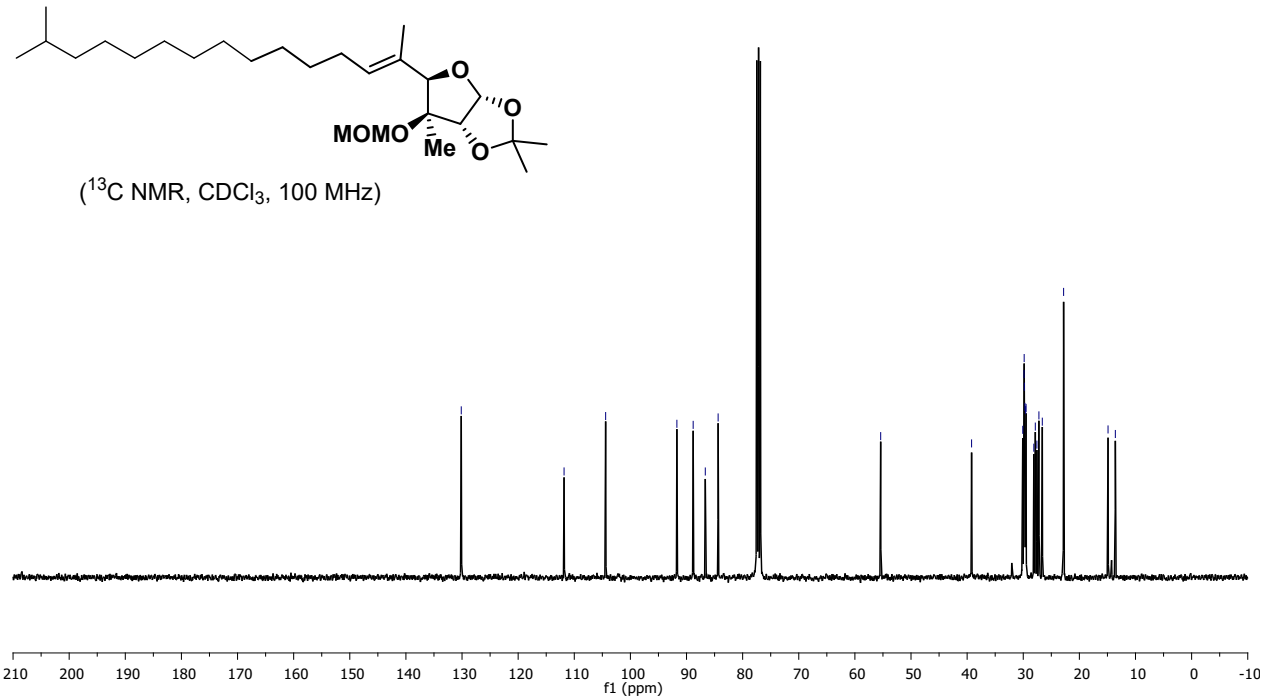
NOESY Spectrum of (3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2-hydroxy-14-methylpentadecan-2-yl)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-ol (30)



(3a*R*,5*R*,6*S*,6a*R*)-6-(methoxymethoxy)-2,2,6-trimethyl-5-((*E*)-14-methylpentadec-2-en-2-yl)tetrahydrofuro[2,3-d][1,3]dioxole (31)

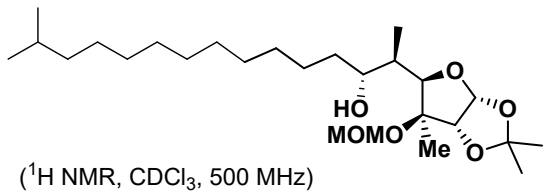


(^{1}H NMR, $CDCl_3$, 400 MHz)

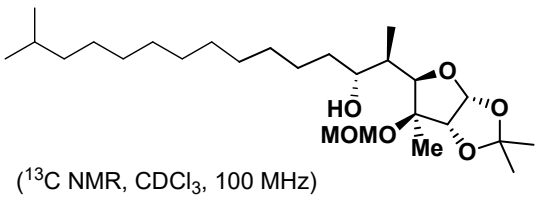


(^{13}C NMR, $CDCl_3$, 100 MHz)

(2*R*,3*R*)-2-((3a*R*,5*R*,6*S*,6a*R*)-6-(methoxymethoxy)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-14-methylpentadecan-3-ol (33)

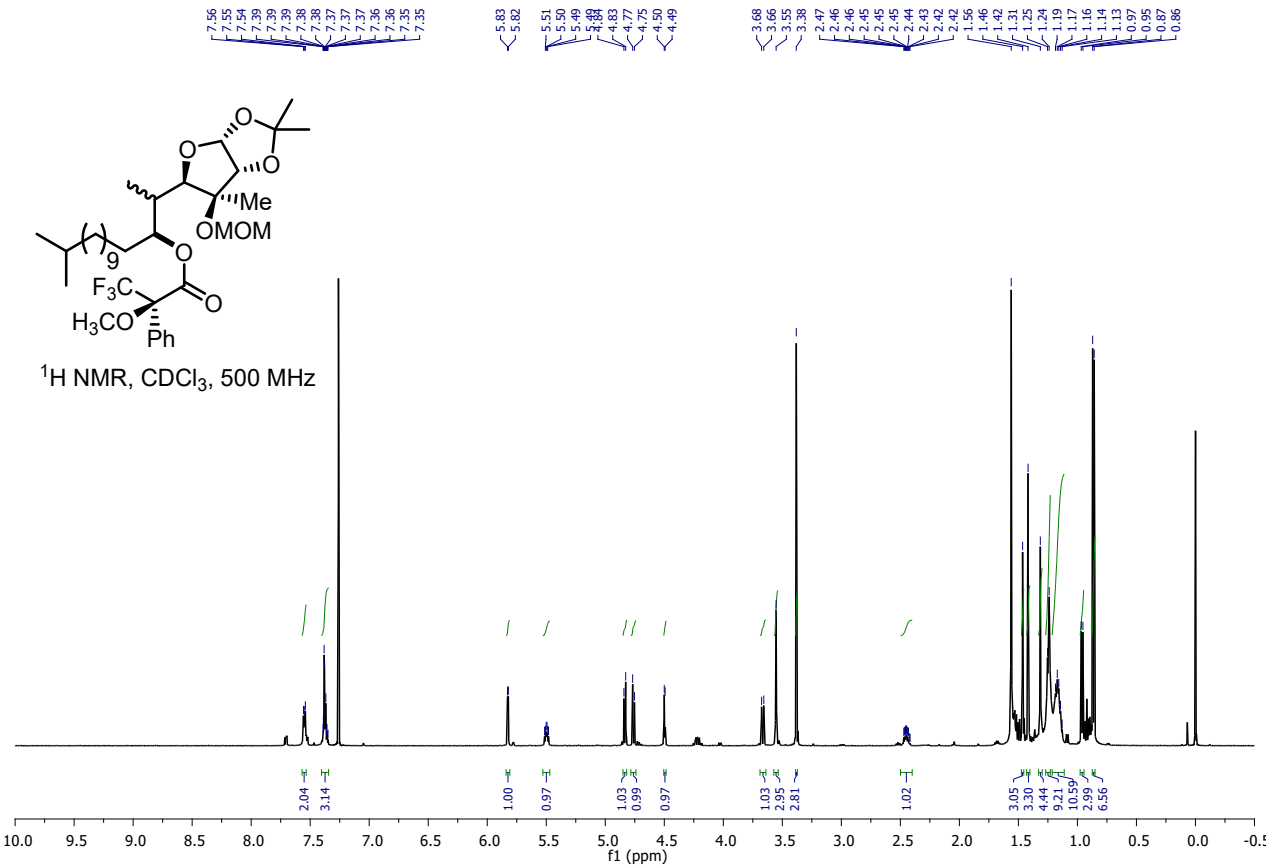


(^{1}H NMR, $CDCl_3$, 500 MHz)

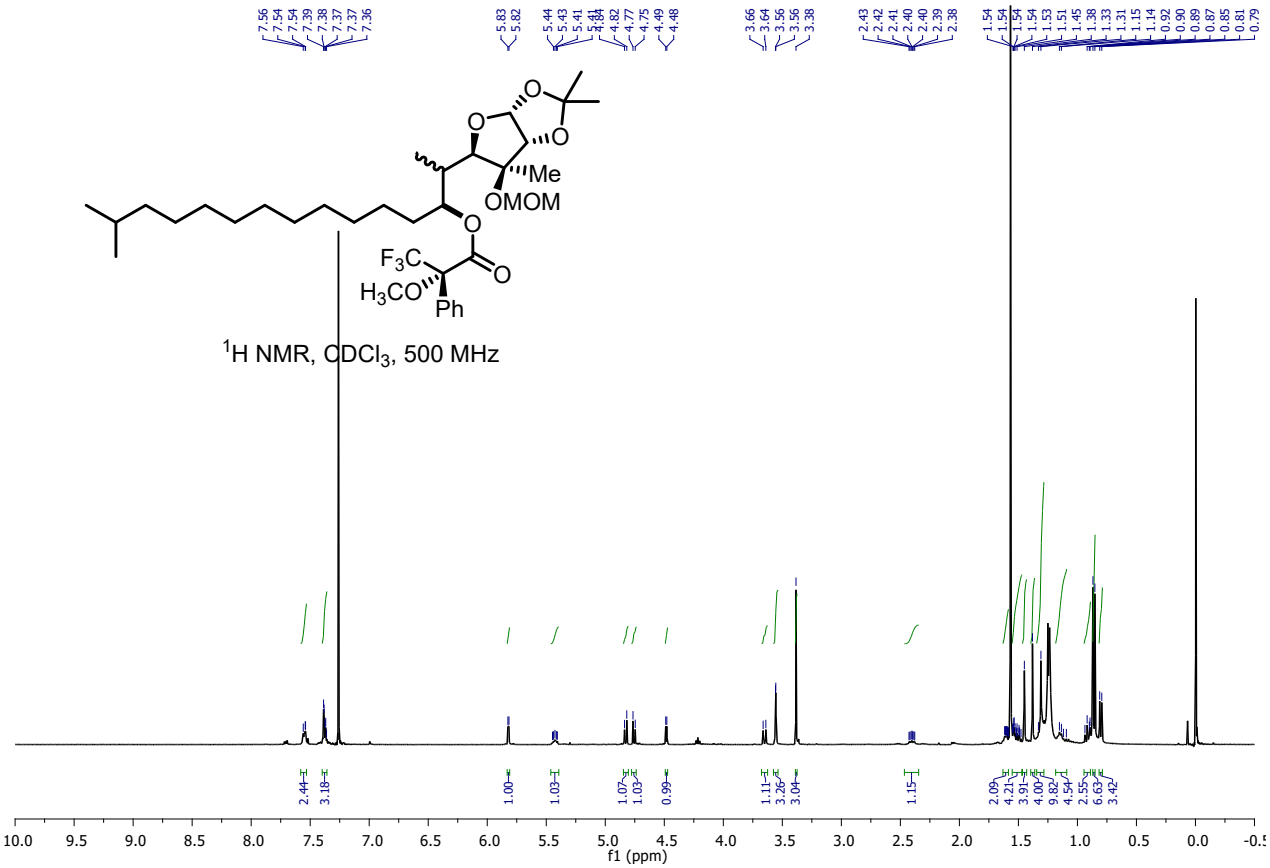


(^{13}C NMR, $CDCl_3$, 100 MHz)

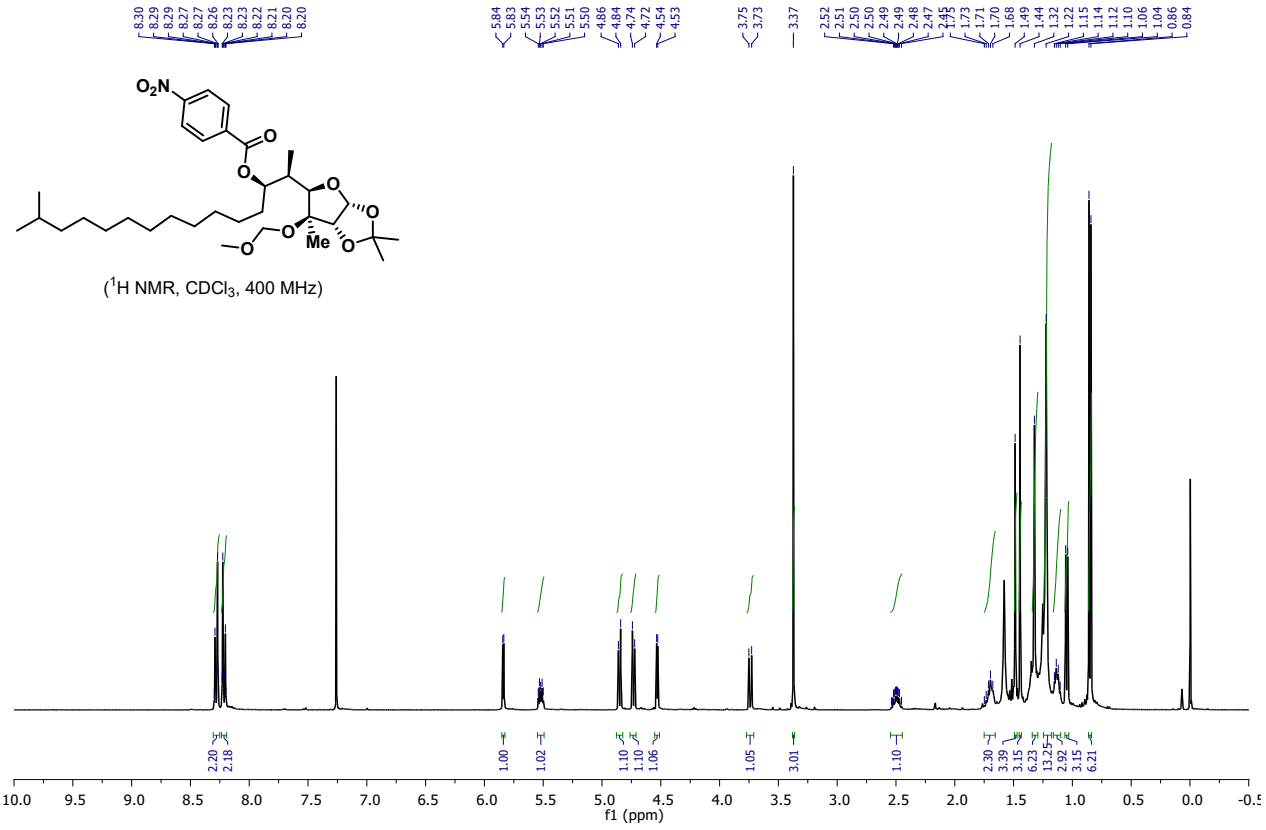
(3*S*)-2-((3a*R*,5*R*,6*S*,6a*R*)-6-(Methoxymethoxy)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-14-methylpentadecan-3-yl (2*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (S7-*R*):

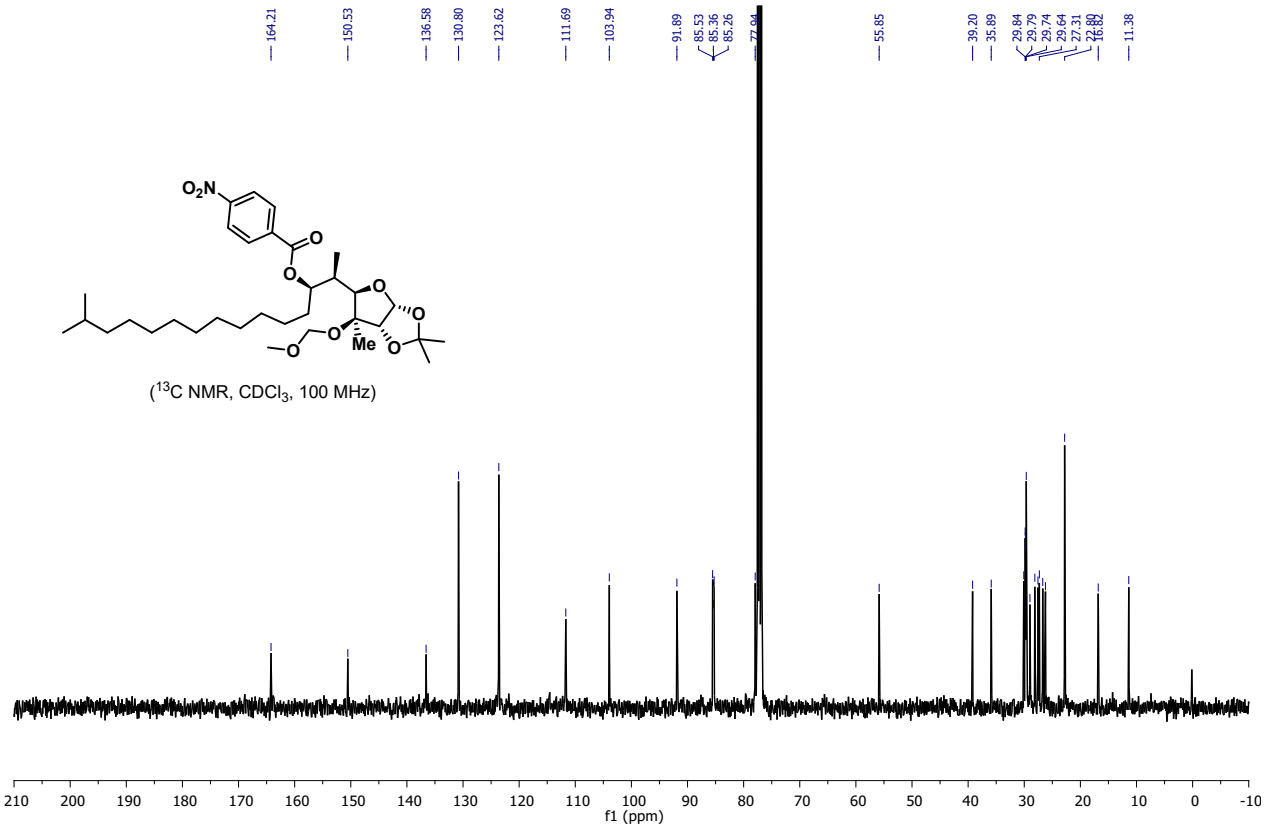


(3*S*)-2-((3a*R*,5*R*,6*S*,6a*R*)-6-(Methoxymethoxy)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-14-methylpentadecan-3-yl (2*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (S7-*S*):

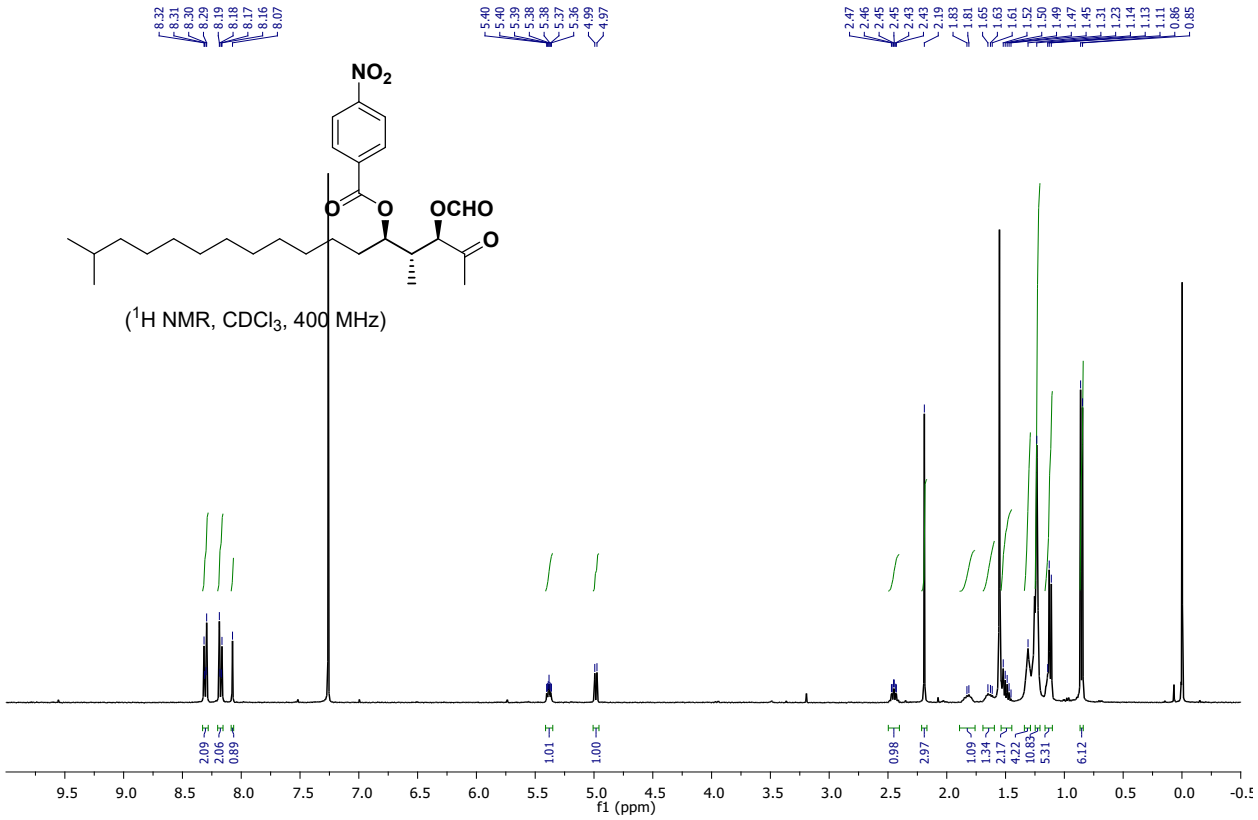


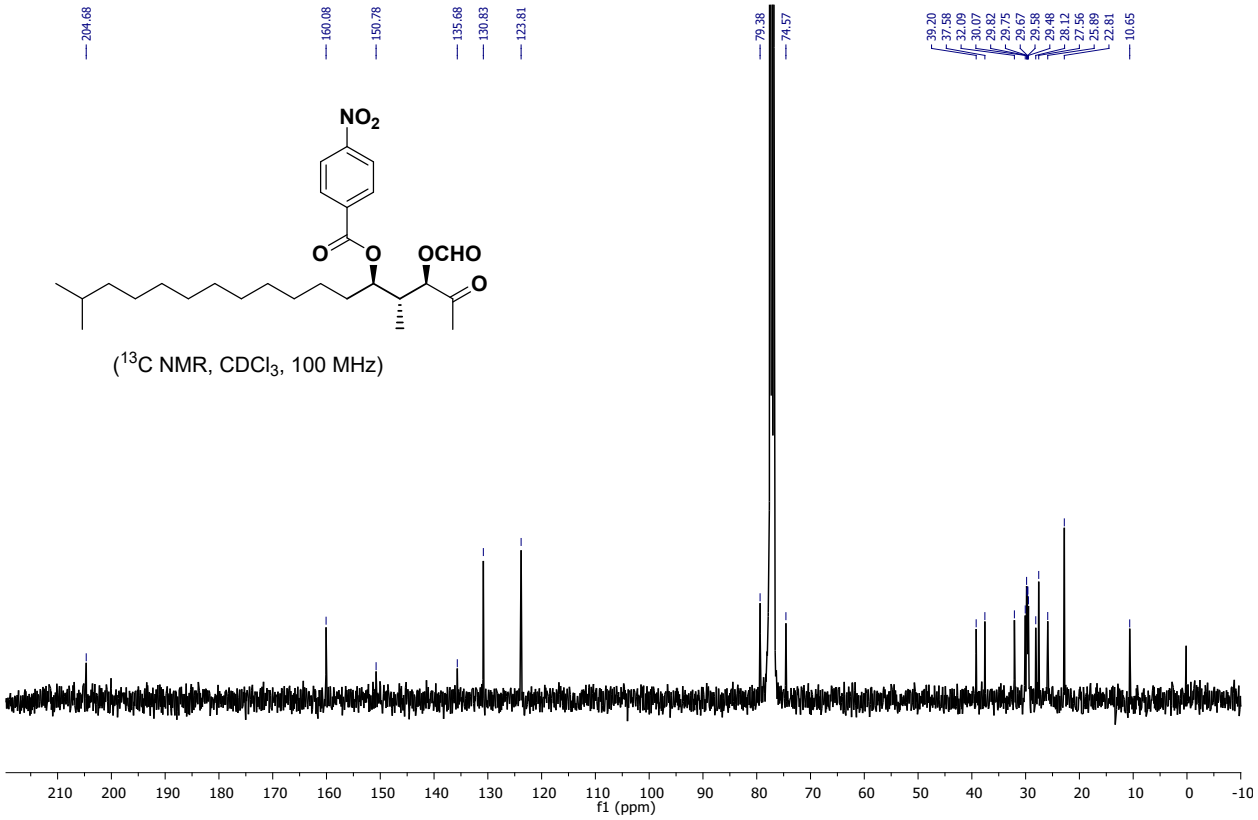
(2*R*,3*R*)-2-((3a*R*,5*R*,6*S*,6a*R*)-6-(methoxymethoxy)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-14-methylpentadecan-3-yl 4-nitrobenzoate (34)



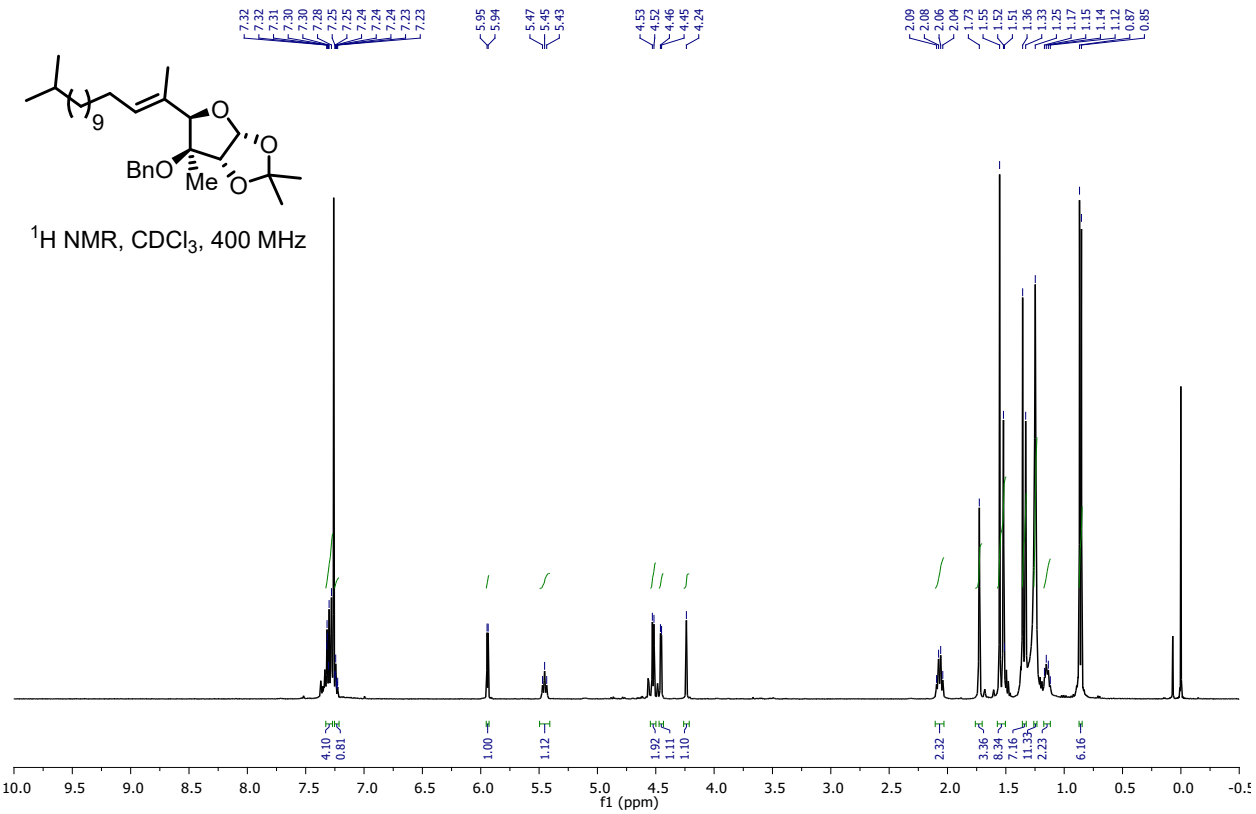


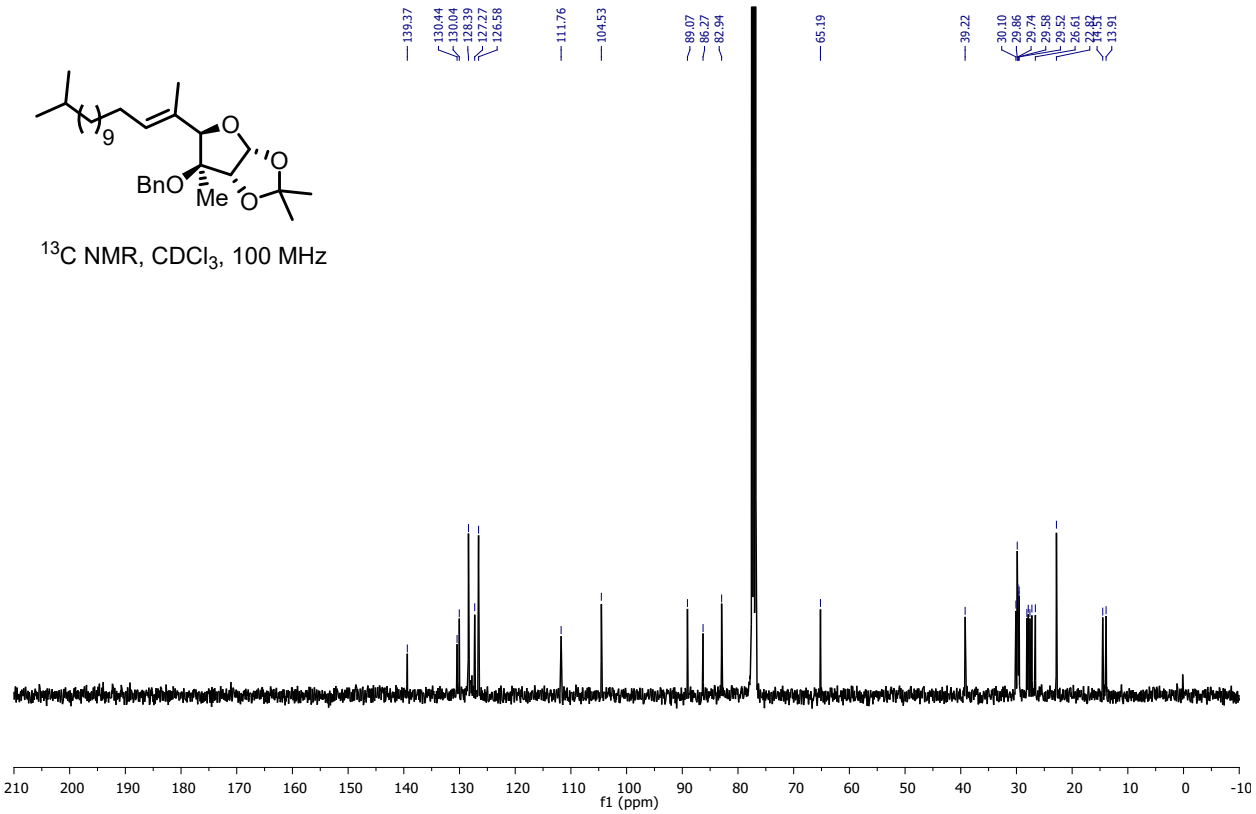
(3*R*,4*R*,5*R*)-3-(formyloxy)-4,16-dimethyl-2-oxoheptadecan-5-yl 4-nitrobenzoate (37)



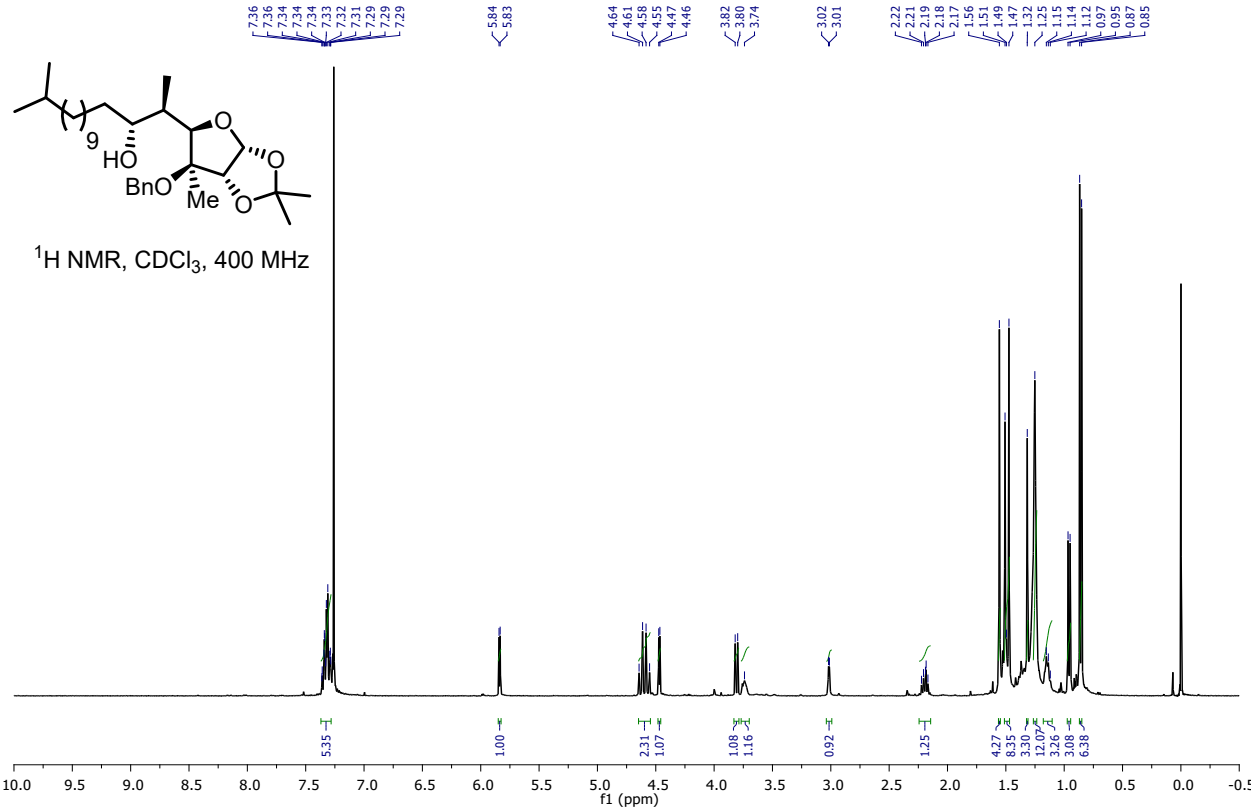


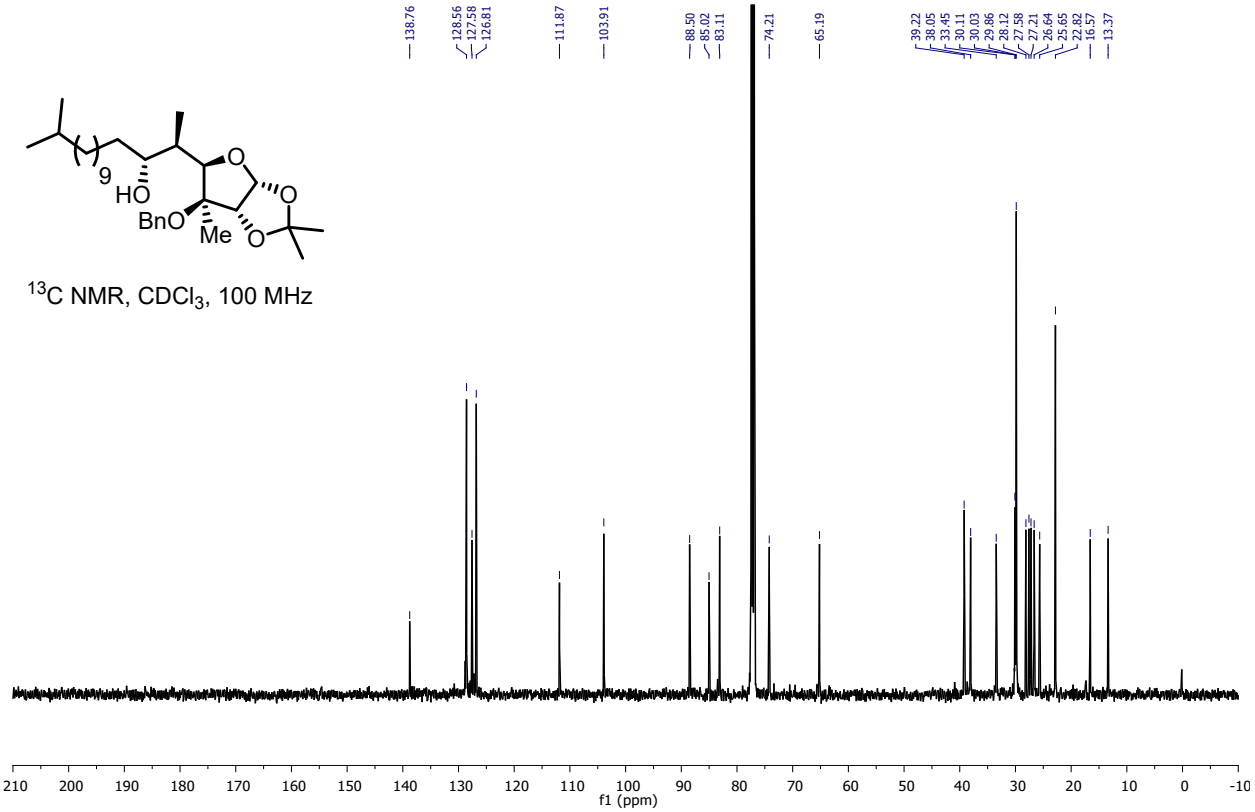
(3a*R*,5*R*,6S,6a*R*)-6-(Benzyloxy)-2,2,6-trimethyl-5-((E)-14-methylpentadec-2-en-2-yl)tetrahydrofuro[2,3-d][1,3]dioxole (32):



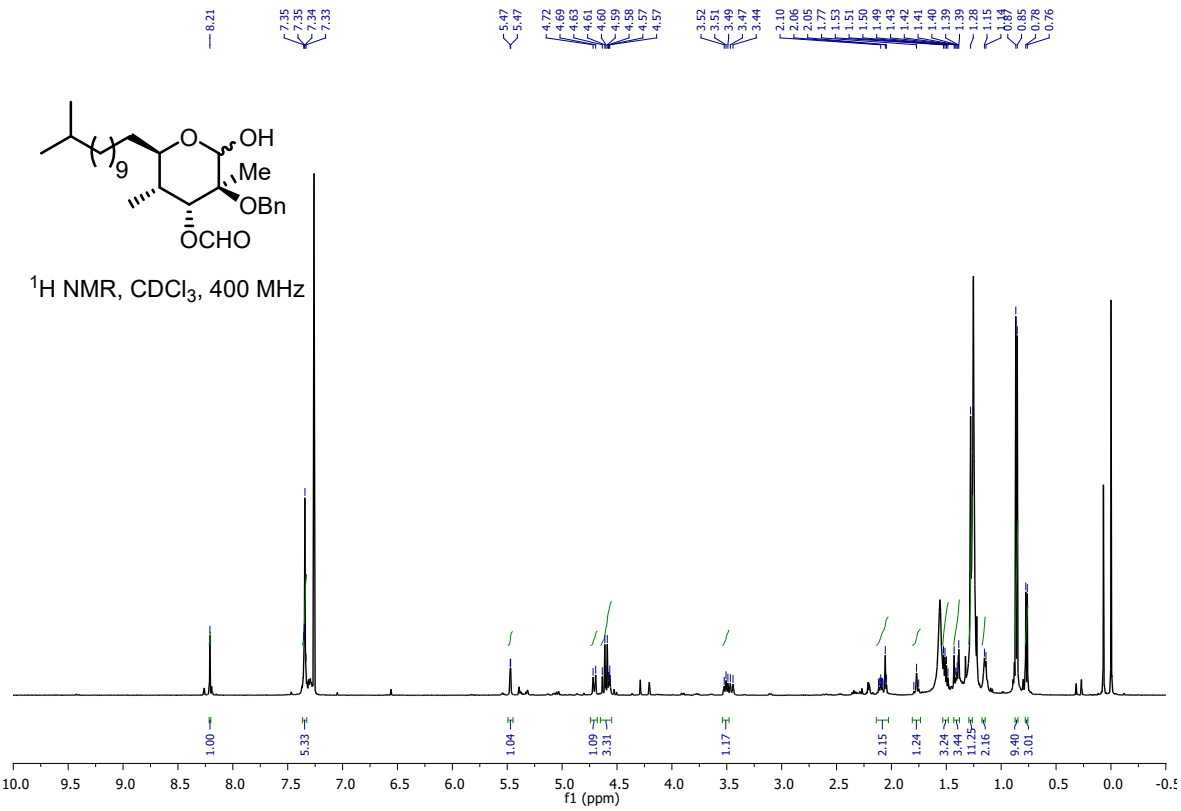


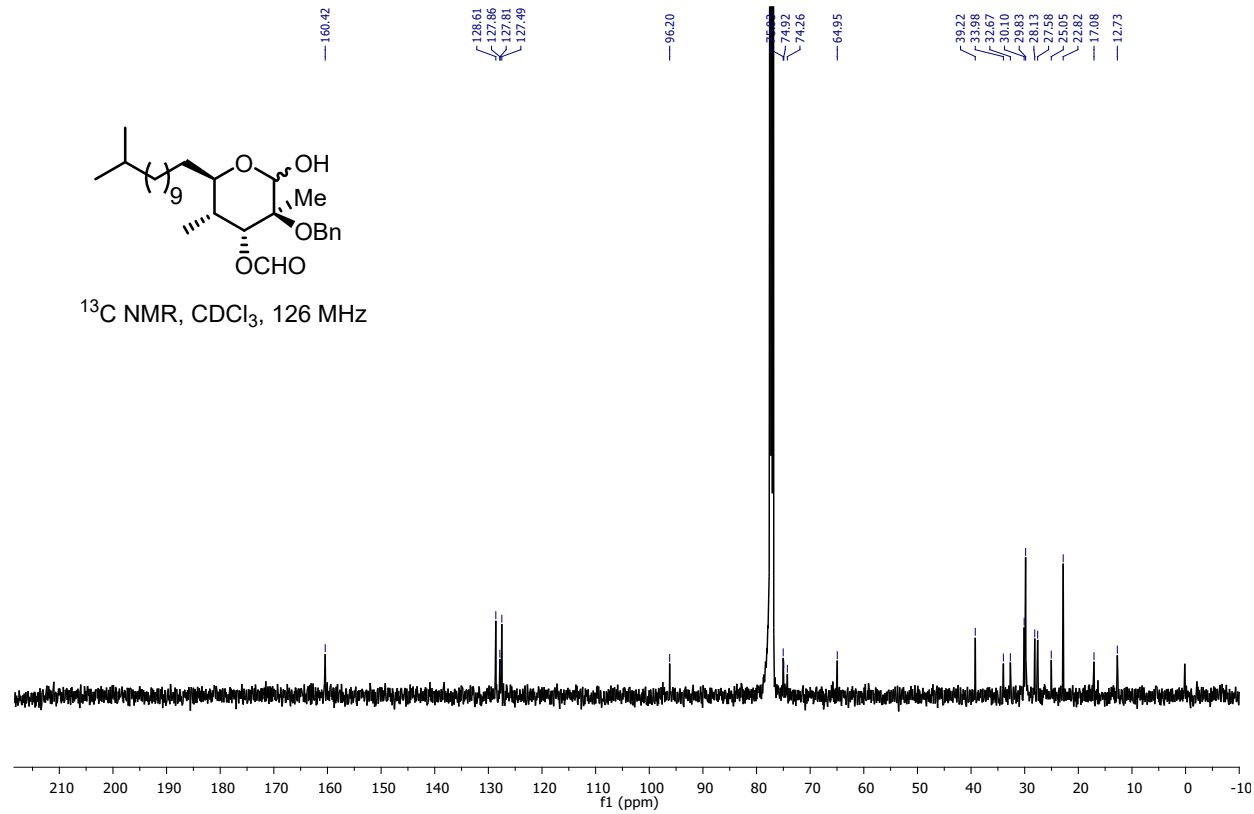
(2*R*,3*R*)-2-((3a*R*,5*R*,6*S*,6a*R*)-6-(Benzyloxy)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-14-methylpentadecan-3-ol (35):



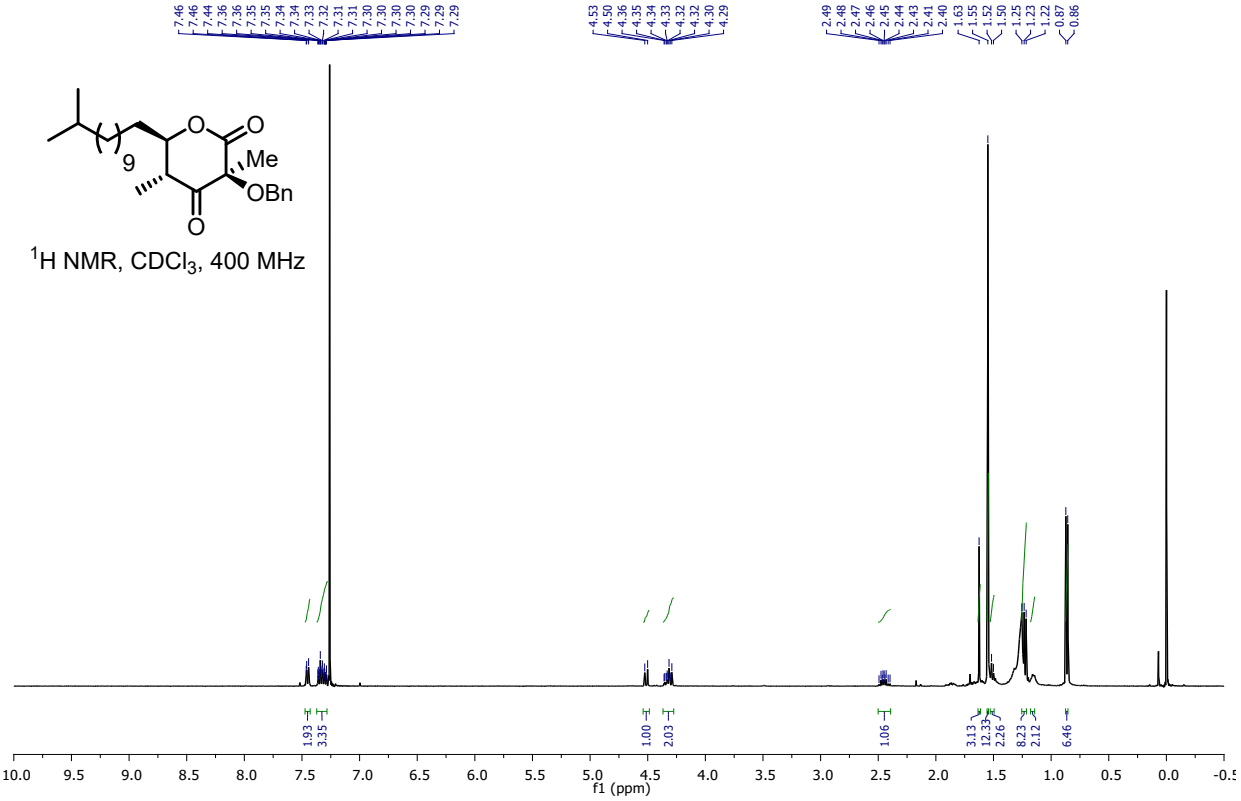


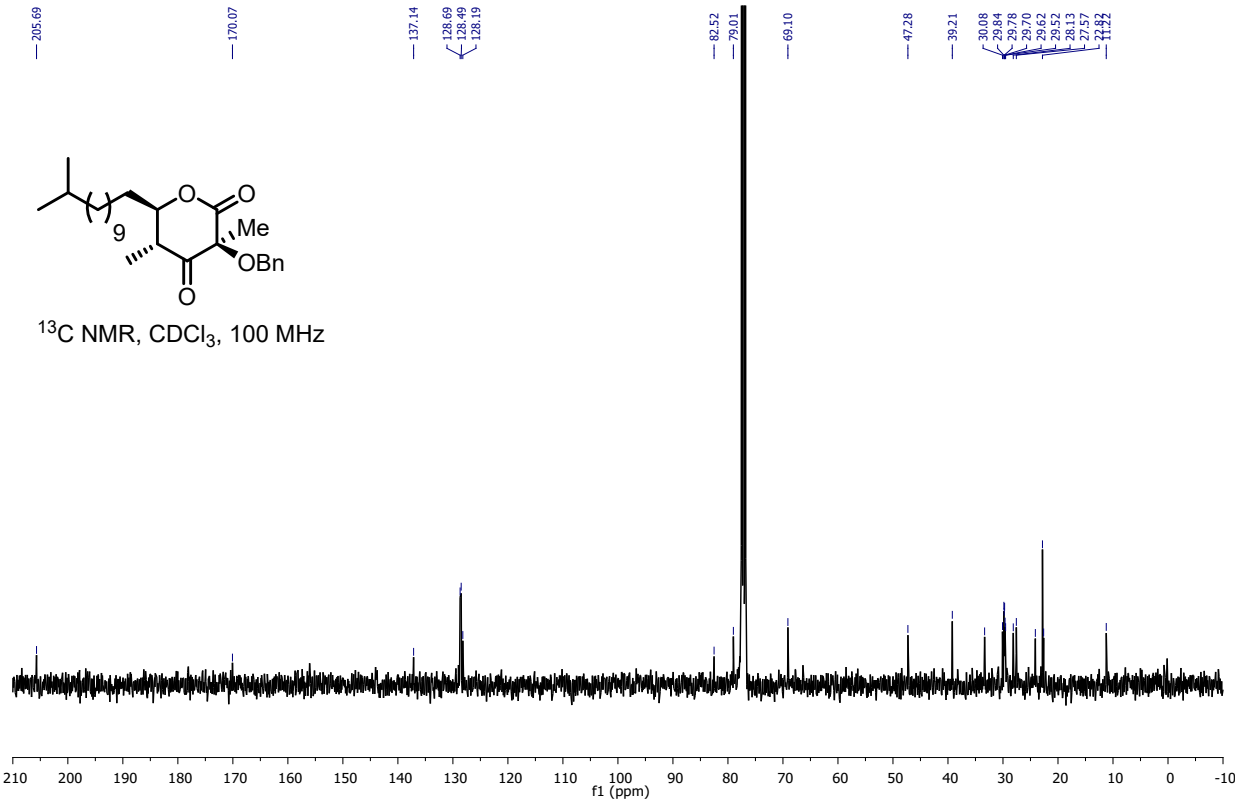
(3*S*,4*R*,5*R*,6*R*)-3-(Benzyloxy)-2-hydroxy-3,5-dimethyl-6-(11-methyldodecyl)tetrahydro-2H-pyran-4-yl formate (38):



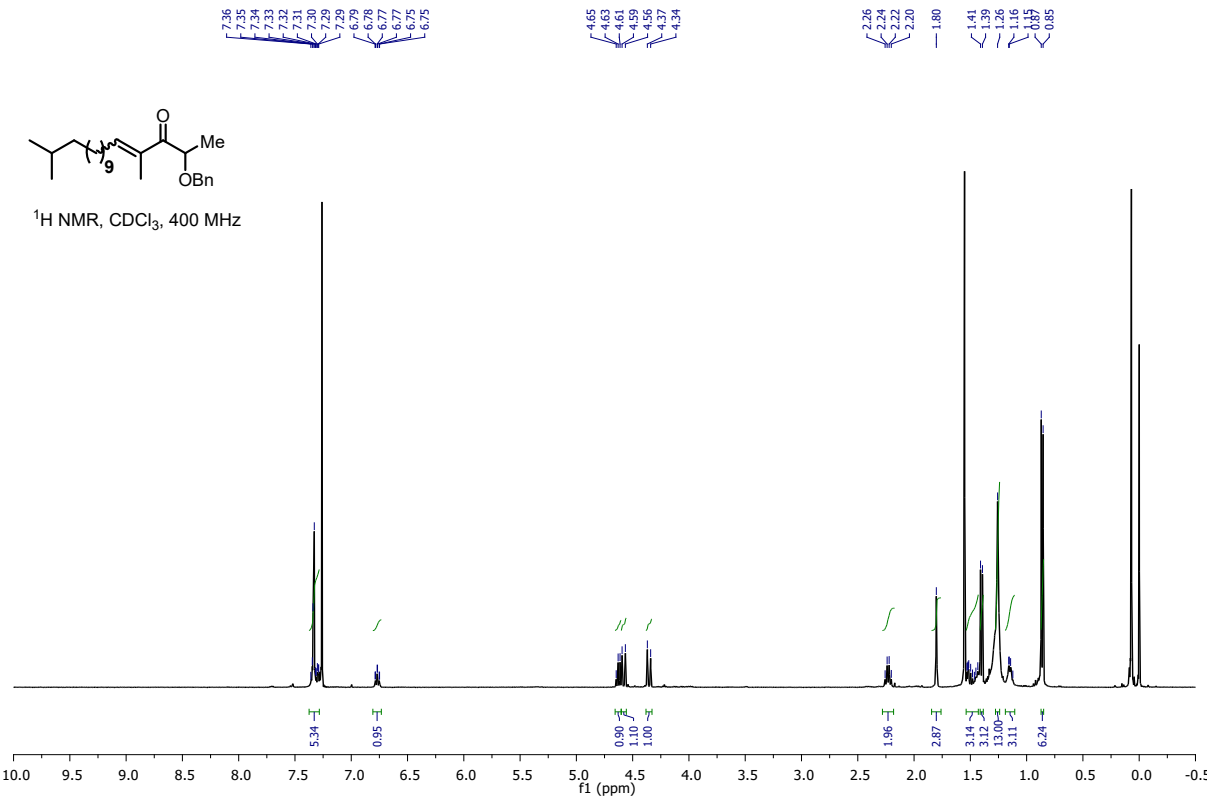


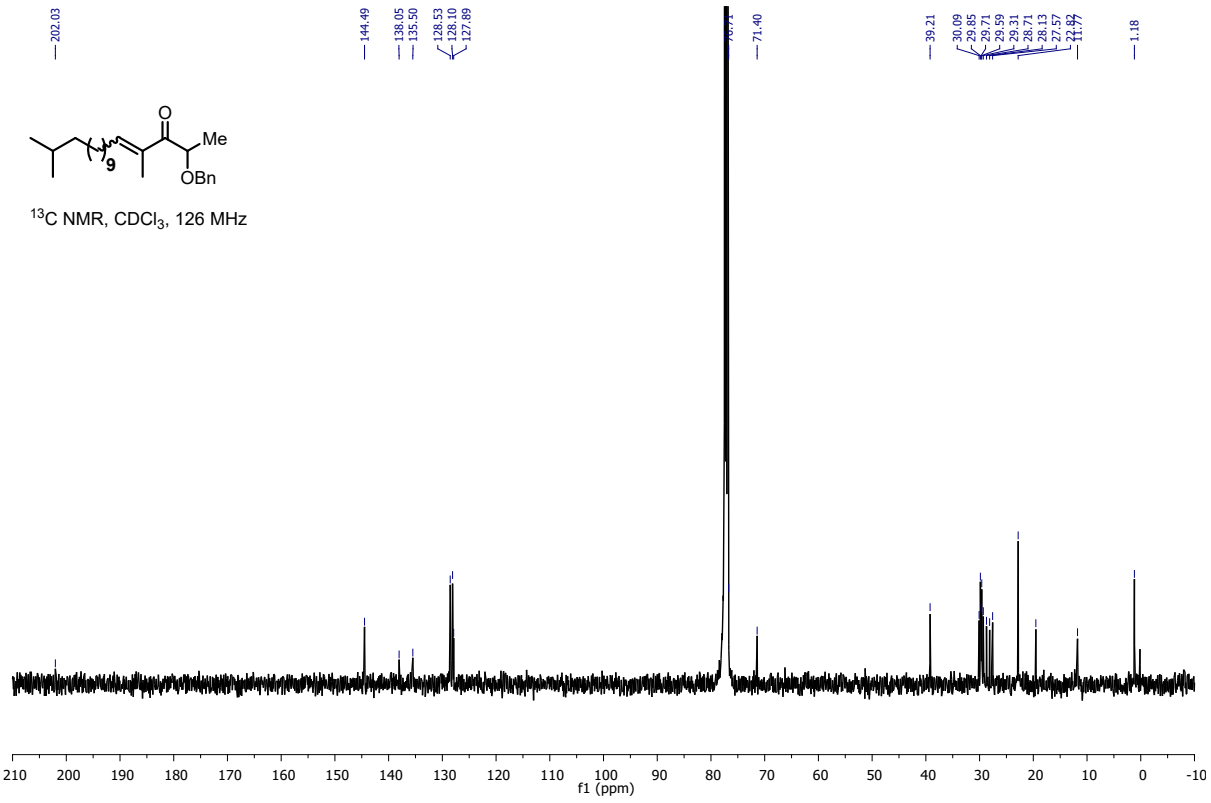
(3*S*,5*R*,6*R*)-3-(Benzyloxy)-3,5-dimethyl-6-(11-methyldodecyl)dihydro-2H-pyran-2,4(3H)-dione (39):



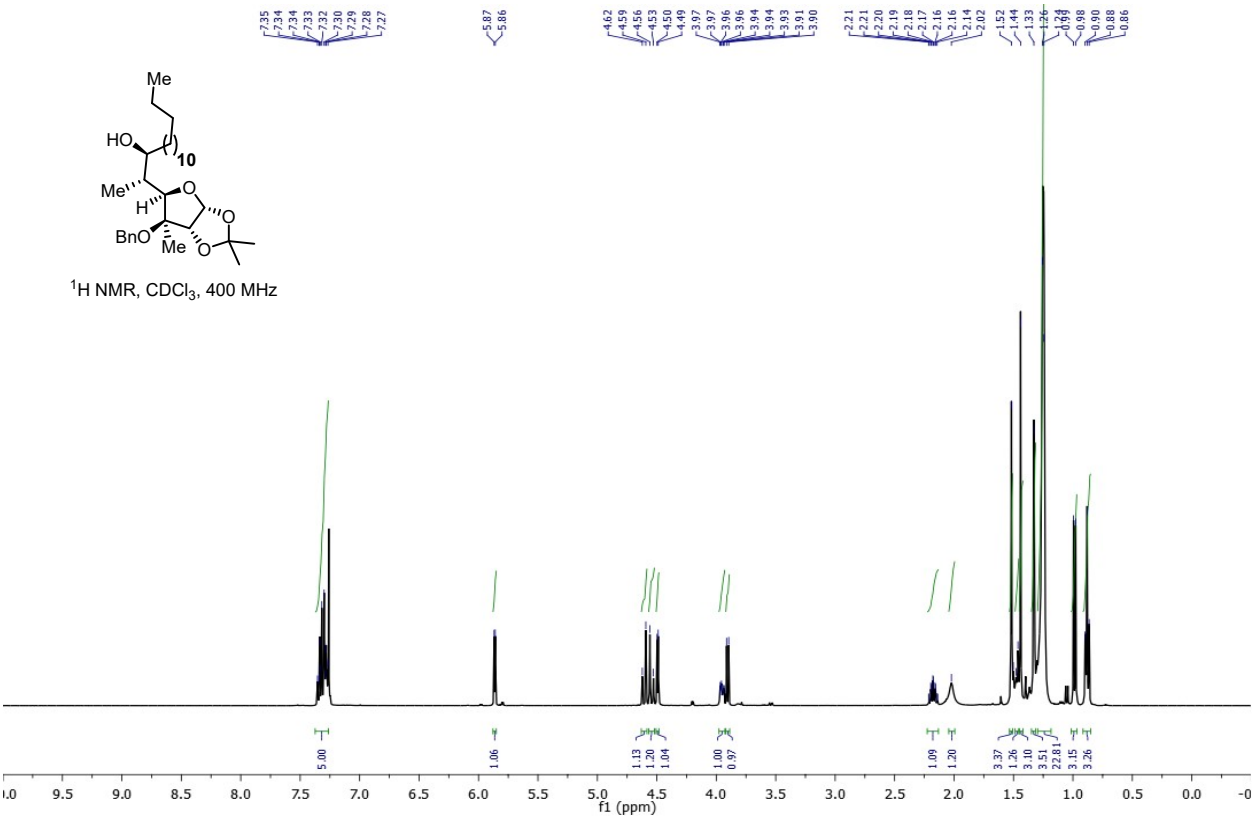


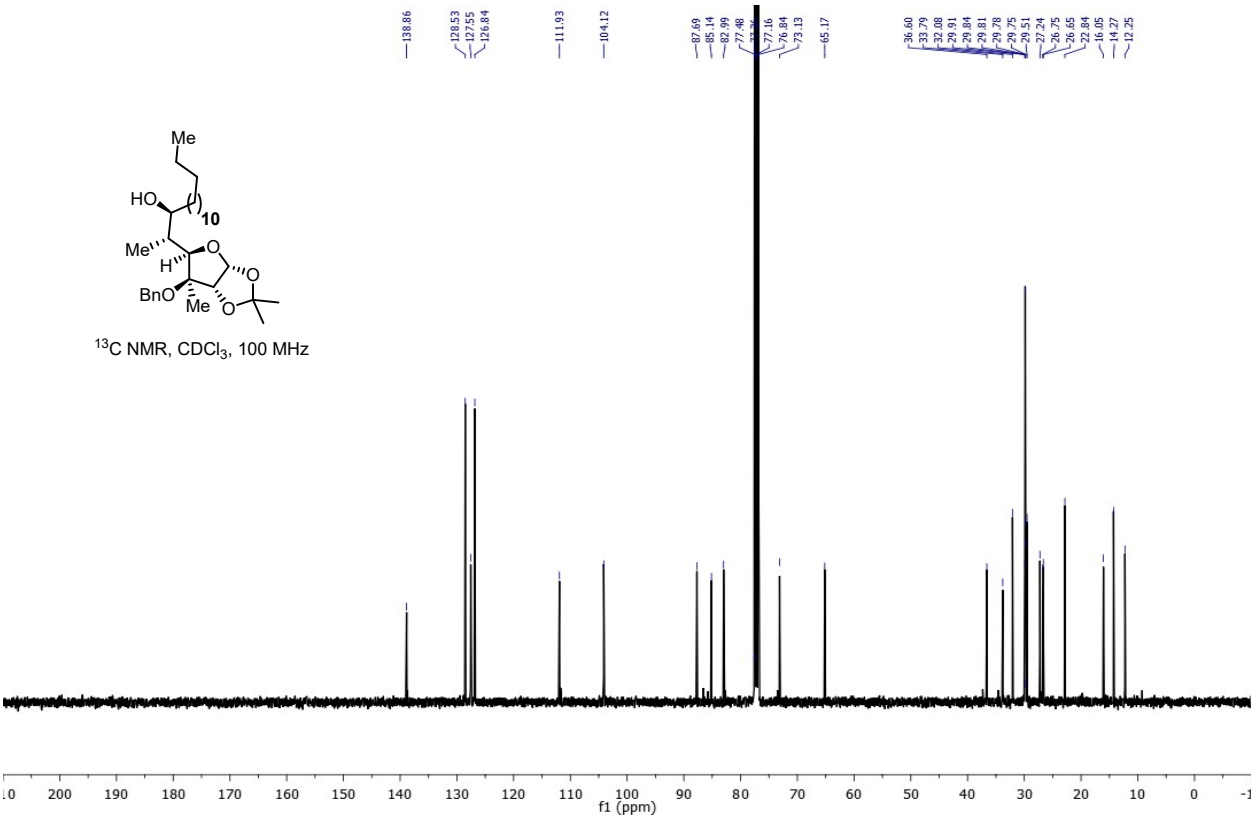
2-(Benzyloxy)-4,16-dimethylheptadec-4-en-3-one (41):



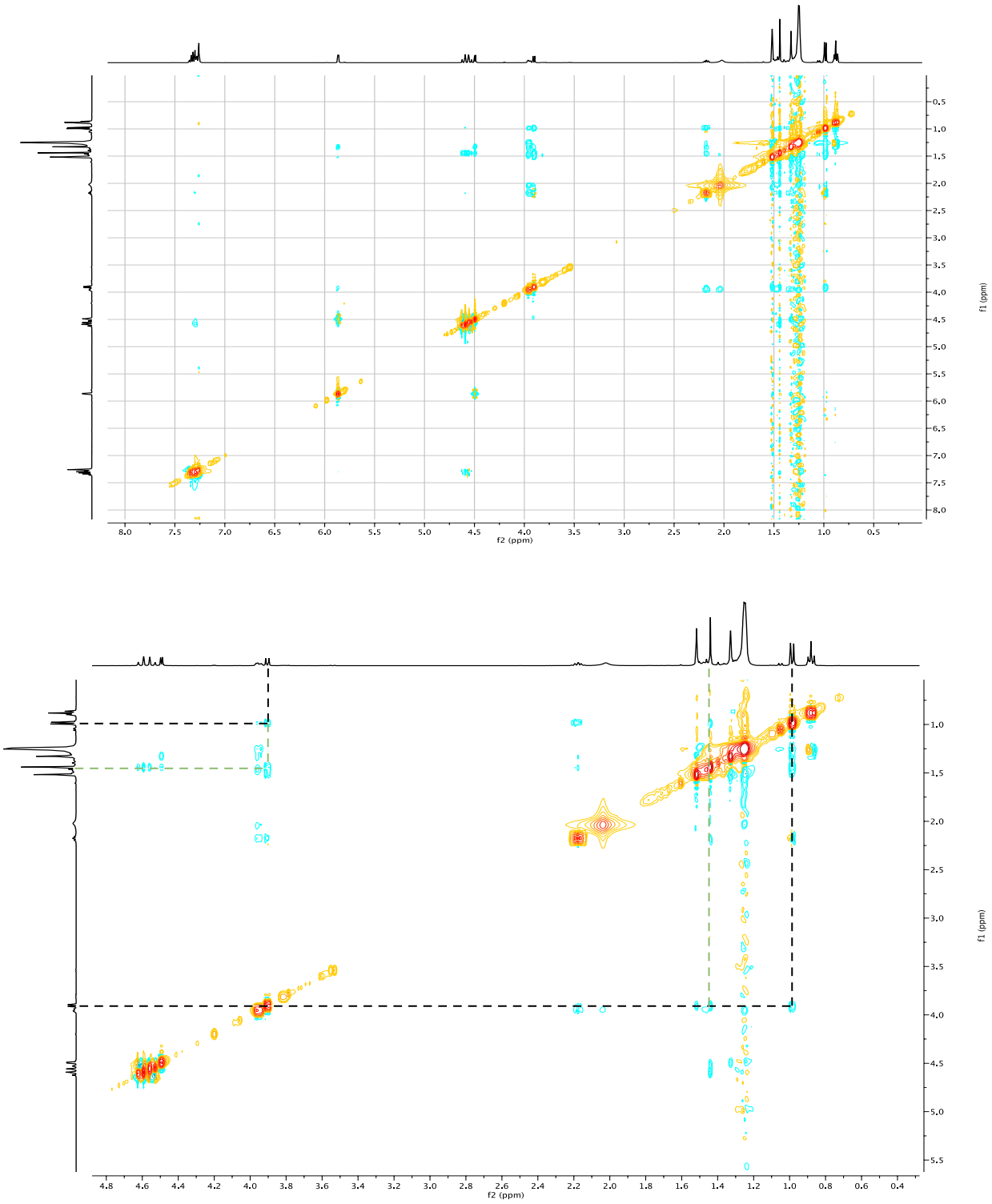


(2R,3S)-2-((3aR,5R,6S,6aR)-6-(benzyloxy)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)hexadecan-3-ol (42)

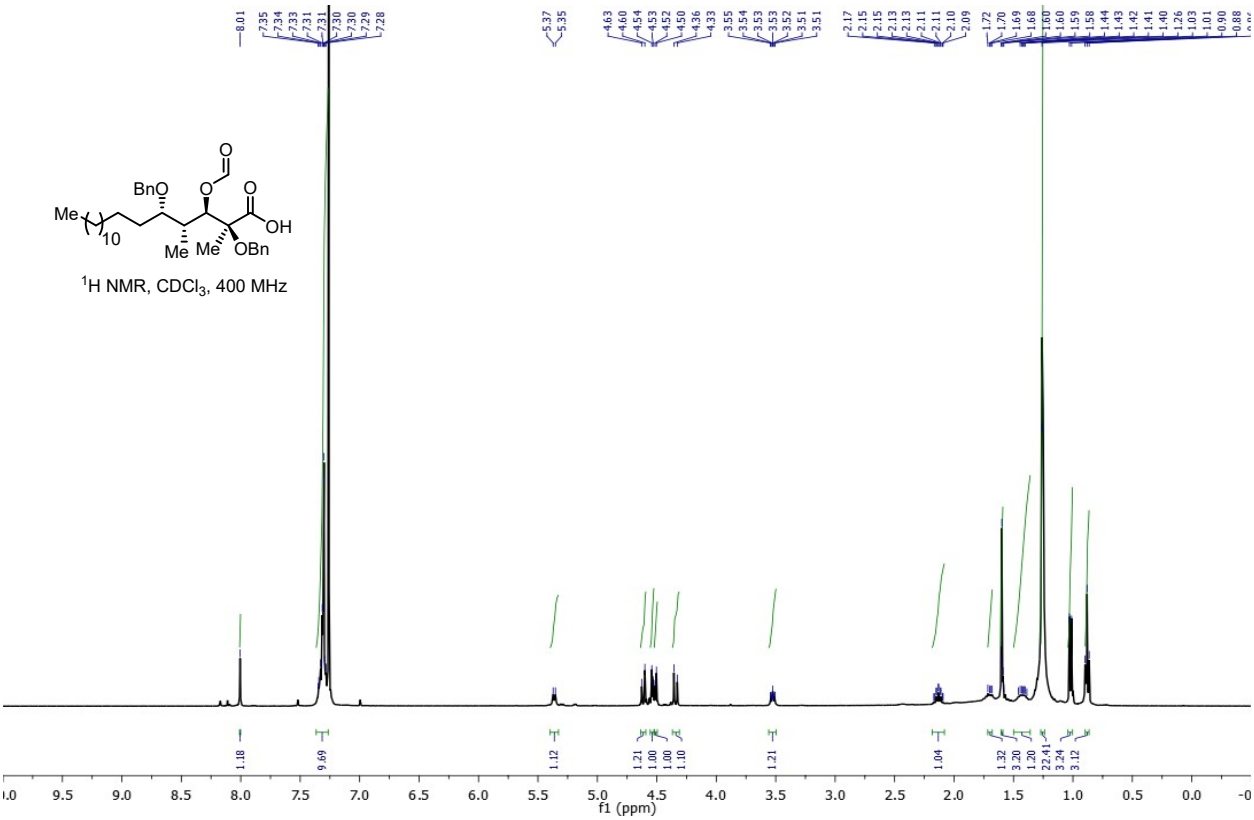


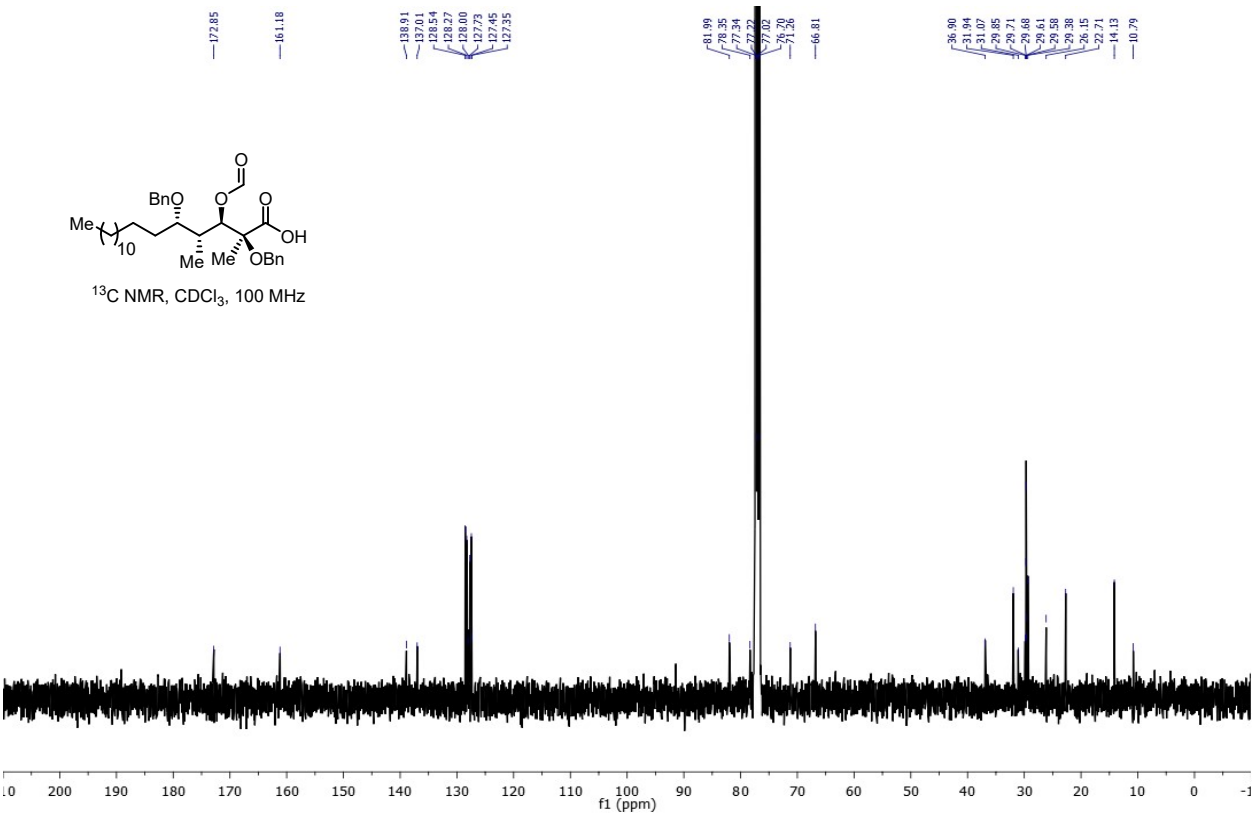


NOESY Spectrum of (2R,3S)-2-((3aR,5R,6S,6aR)-6-(benzyloxy)-2,2,6-trimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)hexadecan-3-ol (42)

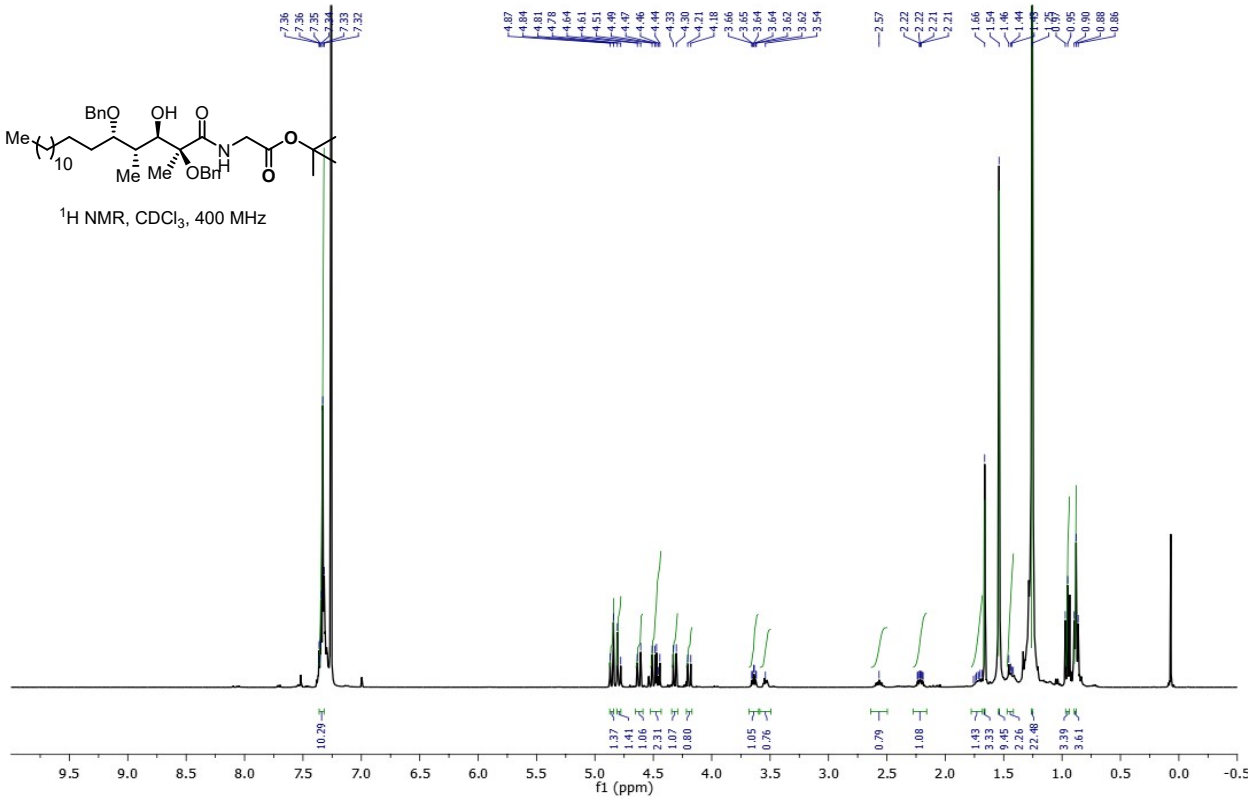


(2S,3R,4R,5S)-2,5-bis(benzyloxy)-3-(formyloxy)-2,4-dimethyloctadecanoic acid (44)

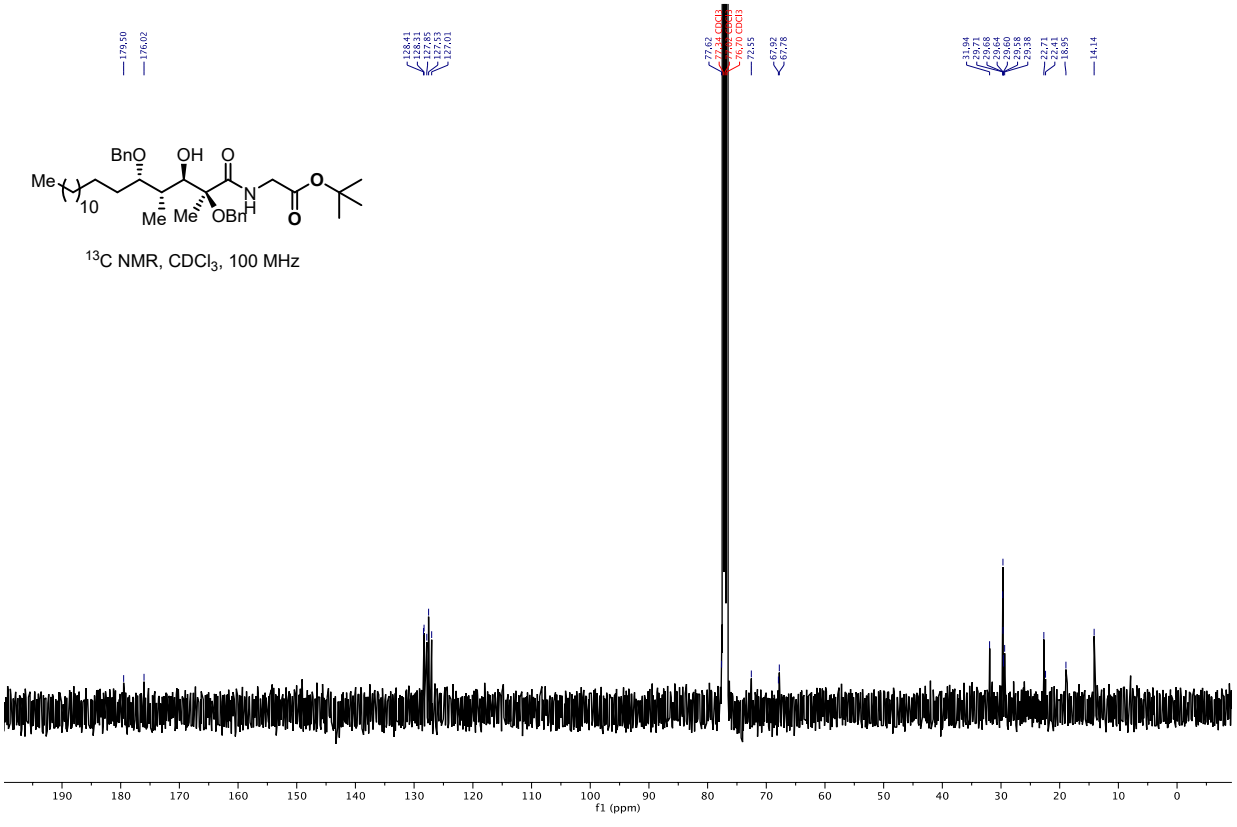




tert-Butyl((2S,3R,4S,5S)-2,5-bis(benzyloxy)-3-hydroxy-2,4-dimethyloctadecanoyl)glycinate (45)



^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 100 MHz