SUPPORTING INFORMATION

Chemoenzymatic Asymmetric Total Synthesis of Naturally Occurring Resorcylic Acid Lactones Hamigeromycins F-G

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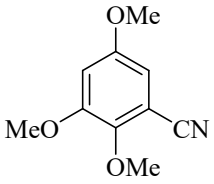
Contents

EXPERIMENTAL DETAILS

GENERAL PROCEDURES

All oxygen and/or moisture-sensitive reactions were carried out under N_2 atmosphere in glassware that had been flame-dried under vacuum (ca. 0.5 Torr) and purged with N_2 prior to use. Unless otherwise stated, materials were obtained from commercial suppliers and used without further purification. THF and diethyl ether were distilled from sodium benzophenone ketyl. Dichloromethane (DCM) and hexane were distilled from calcium hydride. Reactions were stirred magnetically using Teflon-coated magnetic stirring bars. Teflon-coated magnetic stirring bars and syringe needles were dried in an oven at 120 °C for at least 12 h prior to use and then cooled in a desiccator cabinet over Drierite. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel plates with UV light, ethanolic anisaldehyde, and phosphomolybdic acid/heat as developing agents. Silica gel 100–200 mesh was used for column chromatography. Yields refer to chromatographically and spectroscopically homogeneous materials unless otherwise stated. NMR spectra were recorded on 600, 500 and 400 MHz spectrometers at 25 °C in $CDCl_3$ using TMS as the internal standard. Chemical shifts are shown in δ. ^{13}C NMR spectra were recorded with a complete proton-decoupling environment. The chemical shift value is listed as δ_H and δ_C for ^{1}H and ^{13}C, respectively. Coupling constants (*J*) are reported in hertz (Hz), and the resonance multiplicity abbreviations used are s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet; comp, overlapping multiplets of magnetically nonequivalent protons. Optical rotations were measured on Anton Paar digital polarimeter Mass spectrometric analysis was performed in the CRF, IIT-Kharagpur (TOF analyzer). CAL-B (*Candida antarctica* Lipase B), DIPE = Diisopropyl ether.

2,3,5-trimethoxybenzonitrile (8)

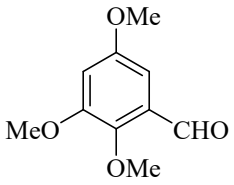


8

1-Bromo-2,3,5-trimethoxybenzene (573 mg, 2.33 mmol) was dissolved in 10 mL dry DMF, CuCN (417 mg, 4.66 mmol) was added to it in one portion and allowed to stir at 135 °C overnight. After completion of the reaction, DMF was evaporated and a saturated solution of Na_2EDTA was poured into it and filtered off. The filtrate was extracted with (2x10 mL) EtOAc and dried over anhydrous Na_2SO_4 and evaporated. The crude extract was purified by column chromatography using 1:4 (EtOAc/Hexane), gave compound 8 (378 mg, 1.96 mmol) as a white solid in 84% yield. R_f = 0.3 (EtOAc/hexane =1:4).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.67 (d, J = 2.8 Hz, 1H), 6.55 (d, J = 2.8 Hz, 1H), 3.92 (s, 3H), 3.85 (s, 3H), 3.77 (s, 3H). **^{13}C{^{1}H}- NMR (126 MHz, $CDCl_3$)** δ 156.08, 153.51, 146.27, 116.23, 106.74, 105.81, 105.67, 61.83, 55.99, 55.81. **HRMS (ESI)** *m/z* for $C_{10}H_{11}NO_3$ [M + H]$^+$, calculated: 193.07, found: 193.073.

2,3,5-trimethoxybenzaldehyde (9)

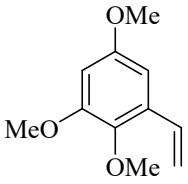


9

Compound **8** (378 mg, 1.96 mmol) was dissolved in 10 mL of dry DCM and stirred at -78 °C. To this solution (2.35 mL, 2.35 mmol, 1M in cyclohexane) DIBAL-H was added dropwise and kept for 1.5h. After completion, the reaction mixture was quenched with a few drops of saturated sodium potassium tartrate (Rochelle salt) and then filtered through elite pad. The filtrate was then evaporated and purified by column chromatography using 1:5 (EtOAc/Hexane) to afford aldehyde **9** (316 mg, 1.61 mmol) as white solid in 82% yield. R_f = 0.4 (EtOAc/hexane =1:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1H), 6.85 (s, 1H), 6.74 (s, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.81 (s, 3H). **13C{1H}- NMR (126 MHz, $CDCl_3$)** δ 189.86, 156.27, 153.99, 147.84, 129.54, 107.40, 99.43, 62.70, 56.04, 55.73. **HRMS (ESI)** *m/z* for $C_{10}H_{12}O_4$ [M + H]$^+$, calculated: 196.07, found: 196.08.

1,2,5-trimethoxy-3-vinylbenzene (10)

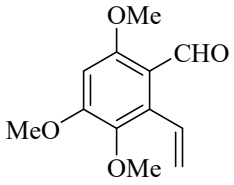


10

Methyl triphenylphosphonium iodide (977 mg, 2.42 mmol) was dried over vaccum and dissolved in 5 mL dry THF and stirred at 0 °C. LiHMDS (2.1 mL, 2.1 mmol, 1M in THF) was added dropwise and stirred at same temperature, after 10 min the aldehyde **9** (316 mg, 1.61 mmol) in 3 mL dry THF was added to it dropwise and allowed to stir at room temperature for 30 min. Finally, the reaction mixture was quenched with saturated NH_4Cl solution and organic part was extracted with (2×10 mL) EtO_2 and 10 mL brine solution, dried over anhydrous Na_2SO_4 and evaporated and purification was done using 1:5 (EtOAc/hexane) to furnish compound **10** (262 mg, 1.35 mmol) as colourless liquid in 84% yield. R_f = 0.5 (EtOAc/hexane = 1:5).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (dd, J = 17.8, 11.1 Hz, 1H), 6.47 (d, J = 2.8 Hz, 1H), 6.31 (d, J = 2.8 Hz, 1H), 5.62 (dd, J = 17.8, 1.1 Hz, 1H), 5.18 (d, J = 11.1 Hz, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 3.62 (s, 3H). **^{13}C{^{1}H}- NMR (126 MHz, $CDCl_3$)** δ 155.92, 153.44, 140.88, 131.27, 131.08, 114.80, 99.92, 99.76, 60.85, 55.53, 55.23. **HRMS (ESI)** *m/z* for $C_{11}H_{14}O_3$ [M + H]$^+$, calculated: 194.09, found: 194.088.

3,4,6-trimethoxy-2-vinylbenzaldehyde (11)



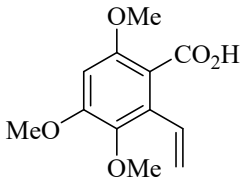
11

To a two-necked round bottom flask, (0.157 mL, 2.02 mmol) dry DMF was added in 3 mL dry DCM under N_2 atmosphere and kept at 0 °C. Then (0.164 mL, 1.75 mmol) $POCl_3$ was added dropwise and the temperature was maintained for 30 min. Compound **10** (262 mg, 1.35 mmol) in 2 mL dry DCM was added to the reaction mixture and stirred at room temperature for 8 h. After the completion of the reaction 10 ml ice cold water was added to it and stirred for 3 h. Finally, the solution was extracted with (2×5 mL) DCM and the organic part was washed with 5 mL of brine solution. The solution was then dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. Purification by column chromatography using 1:5 (EtOAc/Hexane) gave compound **11** (256 mg, 1.15 mmol) as white solid in 80% yield. R_f = 0.3 (EtOAc/hexane = 1.5).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.31 (s, 1H), 7.05 (dd, J = 17.6, 11.7 Hz, 1H), 6.44 (s, 1H), 5.62 (ddd, J = 13.6, 8.7, 1.9 Hz, 2H), 3.95 (s, 3H), 3.90 (s, 3H), 3.67 (s, 3H). **^{13}C{^{1}H}- NMR (126 MHz, $CDCl_3$)** δ 190.20, 159.89, 158.10, 140.70, 135.47, 130.13, 121.98, 116.35, 95.14,

60.28, 56.27, 55.92. **HRMS (ESI)** *m/z* for $C_{12}H_{14}O_4$ [*M* + H]$^+$, calculated: 222.09, found: 222.0934.

3,4,6-trimethoxy-2-vinylbenzoic acid (12)

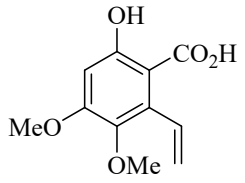


12

Aldehyde **11** (256 mg, 1.15 mmol) was dissolved in 3 mL of DMSO and 2.5 mL 2-methyl-2-butene was added to it and stirred at 10 °C. NaH_2PO_4 (293 mg, 2.44 mmol) in 1.8 mL water was added to the reaction mixture followed by dropwise addition of $NaClO_2$ (213 mg, 2.35 mmol), dissolved in 14 mL water. After completion of the reaction (monitored by TLC analysis) anhydrous Na_2CO_3 was added and the solution was next acidified with concentrated HCl to afford white precipitate, which was next filtered to obtain the acid **12** (226 mg, 1.115 mmol) as white solid in 97% yield. R_f = 0.1 (EtOAc/hexane = 1:1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (dd, *J* = 17.8, 11.6 Hz, 1H), 6.46 (s, 1H), 5.75 (d, *J* = 17.8 Hz, 1H), 5.48 (d, *J* = 11.6 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.70 (s, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 171.74, 154.68, 153.49, 140.84, 131.57, 130.35, 120.45, 113.94, 96.36, 60.41, 56.66, 55.99. **HRMS (ESI)** *m/z* for $C_{12}H_{14}O_5$ [*M* + H]$^+$, calculated: 238.08, found: 238.0850.

6-hydroxy-3,4-dimethoxy-2-vinylbenzoic acid (13)

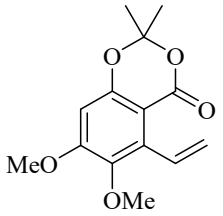


13

The acid **12** (266 mg, 1.115 mmol) was dissolved in 5 mL of dry DCM and stirred under N_2 atmosphere at -78 °C. Then (1.67 mL, 1.67 mmol) BCl_3 solution (1M in DCM) was added to it dropwise. After 1.5h the reaction solution was quenched with ice cubes and allowed to attain room temperature. Then it was extracted with (2×10 mL) DCM, the organic part was washed with 10 mL of brine solution and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure gave crude product. The crude compound was recrystallized using DCM and cyclohexane gave compound **13** (212 mg, 0.945 mmol) as white amorphous solid in 85% yield. R_f = 0.15 (EtOAc/hexane = 1:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.33 (s, 1H), 6.92 (dd, *J* = 17.7, 11.5 Hz, 1H), 6.46 (s, 1H), 5.57 (dd, *J* = 11.5, 1.7 Hz, 1H), 5.51 (dd, *J* = 17.7, 1.7 Hz, 1H), 3.90 (s, 3H), 3.64 (s, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 174.84, 161.78, 159.71, 140.38, 135.19, 131.72, 119.84, 102.08, 99.82, 60.51, 55.99. **HRMS (ESI)** *m/z* for $C_{11}H_{12}O_5$ [*M* + H]$^+$, calculated: 224.07, found: 224.0681.

6,7-dimethoxy-2,2-dimethyl-5-vinyl-4*H*-benzo[d][1,3]dioxin-4-one (14)

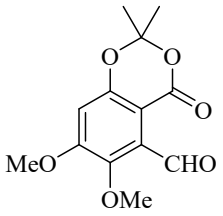


14

Acid compound **13** (212 mg, 0.945 mmol) was dissolved in 1 mL of dry acetone and the solution was stirred at -8 °C under N_2 atmosphere. Acetic anhydride (0.18 mL, 1.87 mmol) was added to it, followed by addition of catalytic amount of conc. H_2SO_4. The reaction mixture was then kept at the same temperature for 12h. After completion of the reaction 10 mL of H_2O was added to it and allowed to attain room temperature and the product was filtered as white amorphous solid **14** (174 mg, 0.66 mmol) in 70% yield. R_f = 0.5 (EtOAc/hexane = 1:3).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (dd, J = 17.7, 11.7 Hz, 1H), 6.38 (s, 1H), 5.83 (dd, J = 17.8, 2.0 Hz, 1H), 5.62 (dd, J = 11.7, 2.0 Hz, 1H), 3.89 (s, 4H), 3.67 (s, 3H), 1.69 (s, 7H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 159.86, 159.35, 154.54, 142.93, 134.68, 130.21, 121.24, 105.00, 103.83, 99.30, 60.11, 56.04, 25.47. **HRMS (ESI)** *m/z* for $C_{14}H_{16}O_5$ [M + H]$^+$, calculated: 264.10, found:264.0999.

6,7-dimethoxy-2,2-dimethyl-4-oxo-4*H*-benzo[d][1,3]dioxine-5-carbaldehyde (29)

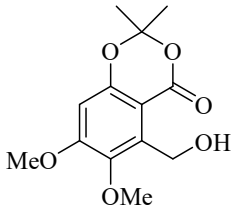


29

The olefin **14** (78 mg, 0.3 mmol) was dissolved in 1.5 mL THF:0.5 mL H_2O. Then OsO_4 (0.035 mL, 0.05 M in toluene), $NaIO_4$ (380 mg, 1.77 mmol) and NMO (208 mg, 1.77 mmol) was added to it and the reaction solution was stirred at room temperature for 6 h. After the complete conversion of the starting material, 10 mL of EtOAc was added and extracted with 2×5 mL of EtOAc. The organic part was then dried over anhydrous Na_2SO_4 and evaporated to afford the crude product. Purification of the crude product by column chromatography using 1:3 (EtOAc/hexane) gave aldehyde **29** (71 mg, 0.27 mmol) as white solid in 90% yield. R_f = 0.3 (EtOAc/hexane = 1:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 6.55 (s, 1H), 3.93 (s, 3H), 3.83 (s, 3H), 1.75 (s, 6H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 191.07, 160.30, 159.51, 154.23, 142.88, 134.53, 106.55, 103.38, 102.18, 62.96, 56.41, 25.57. **HRMS (ESI)** *m/z* for $C_{13}H_{14}O_6$ [M + H]$^+$, calculated: 266.08, found: 266.0783.

5-(hydroxymethyl)-6,7-dimethoxy-2,2-dimethyl-4H-benzo[d][1,3]dioxin-4-one (30)

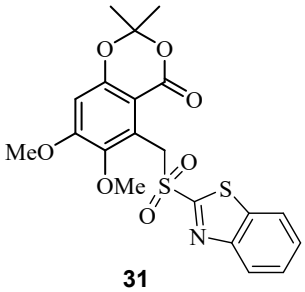


30

$NaBH_4$ (12 mg, 0.31 mmol) was dissolved in 2 mL dry MeOH and kept at 0 °C. Then the aromatic aldehyde **29** (71 mg, 0.27 mmol) was dissolved in 2 mL of dry MeOH and added to it dropwise. After 1.5h the reaction was quenched with saturated NH_4Cl solution and MeOH was evaporated under reduced pressure. Then the residue was extracted with (2×10 mL) Et_2O and the organic part was dried over anhydrous Na_2SO_4 and evaporated and purified with 1:2 (EtOAc/hexane) to furnish aromatic alcohol **30** (70 mg, 0.26 mmol) as white solid in 85% yield. R_f = 0.2 (EtOAc/hexane = 1:2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.44 (s, 1H), 4.88 (s, 2H), 3.91 (s, 3H), 3.82 (s, 3H), 1.72 (s, 6H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 161.72, 159.88, 155.20, 143.29, 137.27, 105.63, 104.28, 100.01, 62.26, 56.15, 25.44. **HRMS (ESI)** *m/z* for $C_{13}H_{16}O_6$ $[M + H]^+$, calculated: 268.09, found: 268.0941.

5-((benzo[d]thiazol-2-ylsulfonyl)methyl)-6,7-dimethoxy-2,2-dimethyl-4*H*-benzo[d][1,3] dioxin-4-one (31)

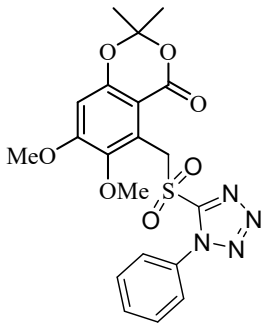


31

To a solution of alcohol **30** (40 mg, 0.15 mmol), PPh_3 (67 mg, 0.26 mmol), BTSH (40 mg, 0.24 mmol) in 2 mL dry THF, DIAD (0.05 ml, 0.24 mmol) was added dropwise and allowed to stir at -10 °C for 6 h. After completion of the reaction, as monitored by TLC, 3 mL of MeOH was added to the reaction mixture. Then mixture of 0.4 mL 30% H_2O_2 solution and ammonium molybdate (64 mg, 0.048 mmol) was added dropwise and stirred at 0 °C overnight. Finally, the reaction was quenched with 10% $Na_2S_2O_3$ solution and evaporated. Then the organic part was washed with 2×10 mL EtO_2 and dried over anhydrous Na_2SO_4 and evaporated and purified with 1:2 (EtOAc/hexane) to furnish aromatic BT sulfone **31** (60 mg, 0.133 mmol) as white solid in 90% yield. R_f = 0.2 (EtOAc/hexane = 1:2)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, J = 8.6 Hz, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.58 (m, 2H), 6.51 (s, 1H), 5.73 (s, 2H), 3.87 (d, J = 15.2 Hz, 6H), 1.71 (s, 6H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 166.47, 160.45, 158.83, 154.57, 152.56, 145.23, 137.21, 127.80, 127.38, 125.44, 122.26, 121.66, 105.82, 105.29, 101.52, 61.63, 56.08, 52.15, 25.40. **HRMS (ESI)** *m/z* for $C_{20}H_{19}NO_7S_2$ $[M + H]^+$, calculated: 449.06, found: 449.059.

6,7-dimethoxy-2,2-dimethyl-5-(((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)methyl)-4*H*benzo[d][1,3]dioxin-4-one (32)

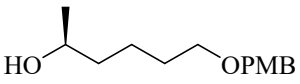


32

To a solution of alcohol **30** (30 mg, 0.11 mmol), PPh_3 (50 mg, 0.19 mmol), PTSH (33 mg, 0.18 mmol) in 2 mL dry THF, DIAD (0.035ml, 0.18 mmol) was added dropwise and allowed to stir at -10 °C for 6 h. After completion of the reaction, as monitored by TLC, 2 mL of MeOH was added to the reaction mixture. Then mixture of 0.3 mL 30% H_2O_2 solution and ammonium molybdate (48 mg, 0.036 mmol) was added dropwise and stirred at 0 °C for overnight. Finally, the reaction mixture was quenched with 10% $Na_2S_2O_3$ solution and evaporated. Then the organic part was washed with (2×5) mL Et_2O and dried over anhydrous Na_2SO_4 and evaporated and purified with 1:2 (EtOAc/hexane) to furnish aromatic PT sulfone **32** (44 mg, 0.095 mmol) as white solid in 85% yield. R_f = 0.2 (EtOAc/hexane = 1:2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 6.4 Hz, 2H), 7.48 (d, J = 7.3 Hz, 2H), 6.41 (s, 1H), 5.11 (s, 2H), 3.87 (s, 3H), 3.78 (s, 3H), 1.67 (s, 6H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 160.06, 159.07, 154.71, 154.32, 143.56, 133.69, 132.29, 129.87, 129.53, 123.98, 105.56, 103.71, 100.40, 61.45, 56.06, 29.65, 25.45. **HRMS (ESI)** *m/z* for $C_{20}H_{20}N_4O_7S$ $[M + H]^+$, calculated: 460.11, found: 460.1098.

***(S)*-6-((4-methoxybenzyl)oxy)hexan-2-ol (*S*-15)**



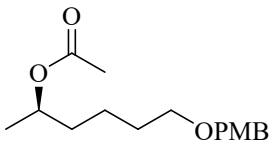
(*S*)-15

Mono PMB protected alcohol from 1,5 pentane diol was oxidized under Swern oxidation condition to produce corresponding aldehyde. A two-necked, round-bottomed flask charged with an excess of Mg (210 mg) and 8 mL of anhydrous Et_2O. To the stirred mixture methyl iodide (0.5 mL, 8.0 mmol) was added dropwise to maintain a gentle reflux. After the addition was complete, the mixture was stirred for 20 min. To this a solution of aldehyde (1.15 g, 5.18 mmol) in dry THF (10 mL) at 0 °C was added dropwise. The resulting mixture was then stirred for 0.5 h at 0 °C, at room temperature. The reaction mixture was quenched by adding cold saturated NH_4Cl solution and the organic part was extracted with (2×15 mL) EtO_2 and 20 mL brine solution, dried over anhydrous Na_2SO_4 and evaporated and purification was done using 1:5 (EtOAc/hexane) to furnish racemic alcohol **15** (986 mg, 4.14 mmol) as colourless liquid in 80% yield in 2 steps. R_f = 0.2 (EtOAc/hexane = 1:3).

The racemic alcohol **15** (986 mg, 4.14 mmol) was dissolved in 6 mL DIPE. Then CAL-B (330 mg) and 4 Å molecular sieves 330 mg and vinyl acetate (0.23 mL, 2.49 mmol) was added and kept in an incubator shaker for 6 h at 28 °C. Finally, it was filtered and the filtrate was evaporated and purified to afford the stereochemically pure alcohol **(*S*)-15** as colourless liquid (493 mg, 2.07 mmol). $[\alpha]_D^{25}$ = -2.4 (c 2.0, MeOH).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 5.0 Hz, 2H) 6.88 (d, *J* = 10.5 Hz, 2H), 4.43 (s, 2H), 3.80 (s, 3H), 3.79 (m, 1H), 3.45 (t, *J* = 8.0 Hz, 2H), 1.48- 1.40 (m, 6H), 1.18 (d, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 159.136, 130.651, 129.285, 113.773, 72.575, 69.965, 68.058, 55.287, 39.03, 30.941, 29.656, 23.461, 22.44. **HRMS (ESI)** *m/z* for $C_{20}H_{19}NO_7S_2$ $[M + H]^+$, calculated: 238.16, found: 238.15.

(*R*)-6-((4-methoxybenzyl)oxy)hexan-2-yl acetate (*R*)-16

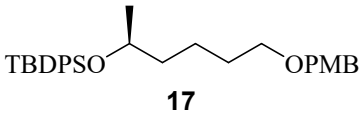


(*R*)-16

$[\alpha]_D^{25}$ = -1.8 (*c* 2.0, MeOH).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 5.0 Hz, 2H) 6.80 (d, *J* = 10.5 Hz,2H), 4.84-4.78 (m, 1H), 4.35 (s, 2H), 3.73 (s, 3H), 3.36 (t, *J* = 8.0 Hz, 2H), 1.95 (s, 3H), 1.55-1.51 (m, 2H), 1.44-1.31 (m, 4H), 1.28 (d, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 170.80, 159.13, 130.69, 129.23, 113.76, 72.54, 70.95, 69.81, 55.27, 35.71, 30.91, 29.56, 22.14, 21.38, 19.93. **HRMS (ESI)** *m/z* for $C_{20}H_{19}NO_7S_2$ $[M + H]^+$, calculated: 280.17, found: 280.16.

(*S*)-*tert*-butyl((6-((4-methoxybenzyl)oxy)hexan-2-yl)oxy)diphenylsilane (17)



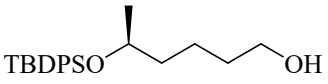
17

Stereochemically pure alcohol **(*S*)-15** (493 mg, 2.07 mmol) [prepared from 1,5 Pentane diol] was dissolved in 5 mL of anhydrous DCM and kept at 0 °C. Imidazole (282 mg, 4.14 mmol) was then added to it and stirred for 10 min followed by TBDPS-Cl (0.6 mL, 2.28 mmol) was added and the reaction mixture was stirred overnight. After completion of the reaction, water was added to the reaction mixture and the organic part was extracted with (2×10 mL) DCM, dried over anhydrous Na_2SO_4 and evaporated and purification was done using 1:30 (EtOAc/hexane) to furnish compound **17** as colourless liquid (848 mg, 1.78 mmol) in 86% yield. R_f = 0.5 (EtOAc/hexane = 1:25). $[\alpha]_D^{25}$ = -6.1 (*c* 2.0, MeOH).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.5 Hz, 4H), 7.80 (m, 6H), 7.24 (d, *J* = 11 Hz, 2H), 6.87 (d, *J* = 11 Hz, 2H), 4.40 (s, 2H), 3.81 (m, 1H), 3.80 (s, 3H), 3.35 (t, *J* = 8.0 Hz, 2H), 1.5-1.49 (m, 6H), 1.04 (s, 9H), 1.04 (d, *J* = 8.1 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 159.12, 135.88, 135.87, 134.98, 134.66, 130.87, 129.42, 129.36, 129.15, 127.45, 127.37,

113.77, 72.48, 70.10, 69.54, 55.27, 39.23, 29.75, 27.06, 23.15, 21.87, 19.26. **HRMS (ESI)** *m/z* for $C_{20}H_{19}NO_7S_2$ [*M* + H]$^+$, calculated: 476.27, found: 476.28.

(*S*)-5-((*tert*-butyldiphenylsilyl)oxy)hexan-1-ol (18)

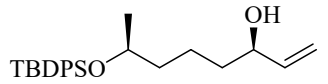


18

Compound **17** (848 mg, 1.78 mmol) was dissolved in 5 mL DCM: pH^7 buffer (20:1) DDQ (647 mg, 2.85 mmol) was added to it at 0 ^{o}C. The reaction mixture was then stirred at room temperature for 1.5h. The reaction mixture was then filtered off, and the filtrate was washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4, evaporated and purification was done by column chromatography (EtOAc/hexane = 1:10) to afford alcohol **18** (538 mg, 1.51 mmol) as colourless liquid in 85% yield. R_f = 0.3 (EtOAc/hexane = 1:10). $[\alpha]_D^{25}$ = -8.4 (*c* 1.5, MeOH).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (m, 4H), 7.43-7.26 (m, 6H), 3.87-3.83 (m, 1H), 3.57-3.53 (m, 2H), 1.44-1.29 (m, 6H), 1.05 (s, 9H), 1.05 (d, *J* = 8.1 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 135.90, 135.89, 134.86, 134.60, 129.49, 129.42, 127.49, 127.41, 69.43, 62.92, 39.09, 32.72, 27.05, 23.19, 21.33, 19.28. **HRMS (ESI)** *m/z* for $C_{20}H_{19}NO_7S_2$ [*M* + H]$^+$, calculated: 356.22, found: 356.19 .

(5*S*)-5-((*tert*-butyldiphenylsilyl)oxy)hex-1-en-3-ol (21)



21

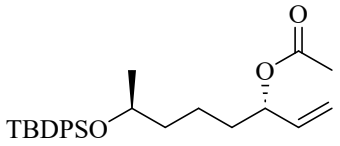
To a solution of aldehyde **19** (484 mg, 1.36 mmol) in 3 mL in dry THF was added (1.9 mL, 1.9 mmol) vinyl magnesium bromide solution (1M in THF) under N_2 atmosphere at 0 ^{o}C. After 1.5h saturated NH_4Cl solution was added dropwise and the organic part was extracted with (2×10 mL) Et_2O and 10 mL brine solution, dried over anhydrous Na_2SO_4 and evaporated and purification was done using 1:10 (EtOAc/hexane) to furnish alcohol **20** (as diastereomeric mixture, 452 mg, 1.18 mmol) as colourless liquid in 87% yield. R_f = 0.2 (EtOAc/hexane = 1:10).

The alcohol **20** (452 mg, 1.18 mmol) was dissolved in 5 mL of DIPE. Then Novozyme- 435 (150 mg) and 4 Å molecular sieves (150 mg) and vinyl acetate (0.07 mL, 0.71 mmol) was added and kept in an incubator shaker for 6h at 36 °C. Finally, it was filtered, and the filtrate was evaporated and purified to afford the stereochemically pure alcohol **21** as a colorless liquid (226 mg, 0.53 mmol). $[\alpha]_D^{25}$ = -6 (*c* 0.1, MeOH).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 4H), 7.39 (ddd, *J* = 14.4, 7.6, 1.4 Hz, 6H), 5.81 (ddd, *J* = 16.9, 10.4, 6.3 Hz, 1H), 5.18 (d, *J* = 17.2 Hz, 1H), 5.08 (d, *J* = 10.4 Hz, 1H), 4.05 – 3.97 (m, 1H), 3.85 (dd, *J* = 11.9, 5.9 Hz, 1H), 1.51 (dd, *J* = 7.7, 5.2 Hz, 2H), 1.43 – 1.39 (m, 2H), 1.36 – 1.30 (m, 2H), 1.06 (s, 9H), 1.06 (d, *J* = 8.1 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 141.11, 135.88, 135.87, 134.85, 134.58, 129.44, 129.38, 127.45, 127.37, 114.58,

73.10, 69.46, 39.25, 36.97, 27.02, 23.21, 21.04, 19.24. **HRMS (ESI)** *m/z* for $C_{24}H_{34}O_2Si$ [*M* + H]$^+$, calculated: 382.23, found: 382.2305.

(3*S*,7*S*)-7-((*tert*-butyldiphenylsilyl)oxy)oct-1-en-3-yl acetate (22)

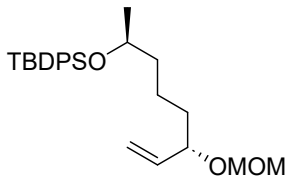


22

$[\alpha]_D^{25}$ = -16 (*c* 0.1, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 4H), 7.40 (dt, *J* = 19.3, 6.9 Hz, 6H), 5.73 (ddd, *J* = 17.1, 10.5, 6.5 Hz, 1H), 5.25 – 5.16 (m, 2H), 5.14 (d, *J* = 10.5 Hz, 1H), 3.83 (dd, *J* = 11.4, 5.7 Hz, 1H), 2.04 (s, 3H), 1.59 – 1.49 (m, 2H), 1.49 – 1.40 (m, 2H), 1.39 – 1.27 (m, 2H), 1.06 (s, 9H), 1.05 (d, *J* = 8.1 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** *δ* 170.30, 136.50, 135.86, 135.83, 134.79, 134.42, 129.46, 129.38, 127.47, 127.37, 116.46, 74.73, 69.32, 39.11, 34.15, 27.00, 23.25, 21.18, 20.86, 19.24. **HRMS (ESI)** *m/z* for $C_{24}H_{34}O_2Si$ [*M* + H]$^+$, calculated: 424.24, found: 424.2039.

(5*S*,9*S*)-9,12,12-trimethyl-11,11-diphenyl-5-vinyl-2,4,10-trioxa-11-silatridecane (24)

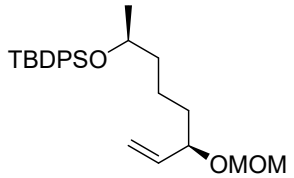


24

Alcohol **23** (218 mg, 0.57 mmol) was dissolved in 5 mL of dry DCM and kept at 0 °C, then DIPEA (0.4 mL, 2.28 mmol) was added dropwise followed by MOMCl (0.112 mL, 1.48 mmol) addition the reaction mixture was allowed to stir for 6 h. After completion of the reaction, 10 mL H_2O was added and the organic part was extracted with (2×10 mL) DCM and dried over anhydrous Na_2SO_4 and evaporated and purified with 1:30 (EtOAc/hexane) to obtain product **24** (209 mg, 0.49 mmol) as colourless liquid in 86% yield. R_f = 0.25 (EtOAc/hexane = 1:50). $[\alpha]_D^{25}$ = -79 (*c* 0.1, MeOH)

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.68 (d, *J* = 7.2 Hz, 4H), 7.39 (dd, *J* = 18.4, 7.3 Hz, 6H), 5.62 (ddd, *J* = 17.6, 9.8, 7.7 Hz, 1H), 5.15 (dd, *J* = 9.3, 6.4 Hz, 2H), 4.68 (d, *J* = 6.7 Hz, 1H), 4.51 (d, *J* = 6.7 Hz, 1H), 3.91 (dd, *J* = 12.8, 6.9 Hz, 1H), 3.85 (dd, *J* = 11.7, 5.8 Hz, 1H), 3.34 (s, 3H), 1.56 – 1.47 (m, 2H), 1.45 – 1.29 (m, 4H), 1.09 (s, 9H), 1.09 (d, *J* = 6.2 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** *δ* 138.36, 135.80, 135.78, 134.84, 134.51, 129.35, 129.29, 127.37, 127.30, 116.88, 93.66, 76.67, 69.42, 55.27, 39.26, 35.33, 26.95, 23.15, 21.09, 19.18. **HRMS (ESI)** *m/z* for $C_{26}H_{38}O_3Si$ [*M* + H]$^+$, calculated: 426.26, found: 426.2598.

(5*R*,9*S*)-9,12,12-trimethyl-11,11-diphenyl-5-vinyl-2,4,10-trioxa-11-silatridecane (39)

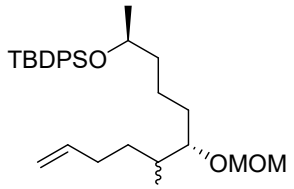


39

Alcohol **21** (226 mg, 0.59 mmol) was dissolved in 5 mL of dry DCM and kept at 0 °C, then DIPEA (0.424 mL, 2.36 mmol) was added dropwise followed by MOMCl (0.112 mL, 1.48 mmol) addition the reaction mixture was allowed to stir for 6 h. After completion of the reaction as indicated by TLC analysis, 50 ml of H_2O was added and the organic part was extracted with (2×10 mL) DCM and dried over anhydrous Na_2SO_4. The organic extract was evaporated and purified with 1:30 (EtOAc/hexane) to obtain product **39** (226 mg, 0.53 mmol) as colourless liquid in 90% yield. R_f = 0.25 (EtOAc/hexane = 1:50). $[\alpha]_D^{25}$ = +11 (*c* 0.1, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 6.8 Hz, 4H), 7.38 (dt, *J* = 14.0, 6.9 Hz, 6H), 5.67 – 5.56 (m, 1H), 5.21 – 5.11 (m, 2H), 4.68 (d, *J* = 6.7 Hz, 1H), 4.51 (d, *J* = 6.7 Hz, 1H), 3.96 – 3.87 (m, 1H), 3.83 (dd, *J* = 11.4, 5.7 Hz, 1H), 3.34 (s, 3H), 1.51 (dd, *J* = 15.6, 9.0 Hz, 2H), 1.44 – 1.33 (m, 4H), 1.04 (s, 9H), 1.04 (d, *J* = 8.1 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 138.48, 135.89, 135.88, 134.96, 134.62, 129.43, 129.37, 127.45, 127.37, 116.96, 93.78, 77.39, 69.58, 55.35, 39.40, 35.47, 29.69, 27.04, 23.24, 21.19, 19.27. **HRMS (ESI)** *m/z* for $C_{26}H_{38}O_3Si[M + H]^+$, calculated: 426.26, found: 426.2597.

(6*S*,10*S*)-10-((*tert*-butyldiphenylsilyl)oxy)-6-(methoxymethoxy)undec-1-en-5-ol (25)



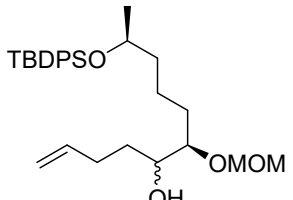
25

The olefin **24** (209 mg, 0.49 mmol) was dissolved in 4 mL of 1,4 dioxane/H_2O (3:1). 2,6 lutidine (0.125 mL, 0.015 mmol) was added followed by OsO_4 (0.246 mL, 0.01 mmol) and $NaIO_4$ (418 mg, 1.96 mmol) addition, the reaction mixture was then stirred for 19h. After completion of the reaction as indicated by TLC analysis, the solvent was evaporated and the organic part was extracted with (2×10 ml) Et_2O and dried over anhydrous Na_2SO_4, evaporated and purified through column chromatography [1:10 (EtOAc/hexane)] to obtain corresponding aldehyde (184 mg, 0.43 mmol) as colourless liquid in 88% yield. R_f = 0.25 (EtOAc/hexane = 1:10).

To a solution of the crude aldehyde (184 mg, 0.43 mmol) in 3 mL dry THF under Ar atmosphere, a freshly prepared homoallyl grignard solution (0.65 mL, 1M in THF) was added dropwise at 0 °C. After 1.5h the reaction mixture was quenched with saturated NH_4Cl solution and organic part was extracted with (2×10 mL) Et_2O and dried over anhydrous Na_2SO_4, evaporated, purified using 1:20 (EtOAc/hexane) to obtain product **25** (177 mg, 0.366 mmol) as colourless liquid in 85% yield (obtained as diastereomeric mixtures). R_f = 0.25 (EtOAc/hexane = 1:10).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 6.5 Hz, 4H), 7.48 – 7.30 (m, 6H), 5.83 (dd, J = 16.0, 9.2 Hz, 1H), 5.01 (dd, J = 29.8, 13.4 Hz, 2H), 4.72 – 4.52 (m, 2H), 3.82 (s, 1H), 3.50 (d, J = 18.9 Hz, 1H), 3.38 (s, 3H), 3.26 (s, 1H), 2.25 (dd, J = 14.8, 7.1 Hz, 1H), 2.18 – 2.07 (m, 1H), 1.66 – 1.11 (m, 10H), 1.05 (d, J = 8.1 Hz, 3H) 1.05 (s, 9H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 138.52, 135.89, 135.87, 134.85, 134.54, 129.47, 129.41, 127.47, 127.40, 114.71, 97.38, 97.09, 83.21, 72.35, 72.15, 69.42, 55.81, 39.53, 32.56, 31.07, 29.89, 27.04, 23.21, 20.88, 19.26. **HRMS (ESI)** *m/z* for $C_{29}H_{44}O_4Si$ $[M + H]^+$, calculated: 484.30, found: 484.3001.

(6*R*,10*S*)-10-((*tert*-butyldiphenylsilyl)oxy)-6-(methoxymethoxy)undec-1-en-5-ol (40)



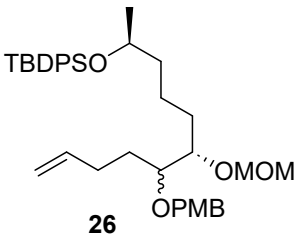
40

The olefin **39** (226 mg, 0.53 mmol) was dissolved in 4 mL of 1,4 dioxane/H_2O (3:1). 2,6 lutidine (0.135 mL, 0.0163 mmol) was added followed by OsO_4 (0.226 mL, 0.011 mmol) and $NaIO_4$ (452 mg, 2.124 mmol) addition, the reaction solution was then stirred for 19h. After completion of the reaction 1,4 dioxane was evaporated and organic part was extracted with (2×10 mL) Et_2O and dried over anhydrous Na_2SO_4, evaporated and purified using 1:10 (EtOAc/hexane) to obtain corresponding aldehyde (206 mg, 0.48 mmol) as colourless liquid in 90% yield (as diastereomeric mixtures). R_f = 0.25 (EtOAc/hexane = 1:10).

To a solution of the crude aldehyde (206 mg, 0.48 mmol) in 3 mL dry THF under Ar atmosphere, a freshly prepared homoallyl Grignard solution (0.7 mL, 1M in THF) was added dropwise at 0 ^{o}C. After 1.5h the reaction mixture was quenched with saturated NH_4Cl solution and organic part was extracted with (2×10 mL) Et_2O and dried over anhydrous Na_2SO_4, evaporated, purified using 1:20 (EtOAc/hexane) to obtain product **40** (200 mg, 0.41 mmol) as colourless liquid in 85% yield (as diastereomeric mixtures). R_f = 0.25 (EtOAc/hexane = 1:10).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 6.7 Hz, 4H), 7.47 – 7.32 (m, 6H), 5.84 (dd, J = 15.6, 8.4 Hz, 1H), 5.01 (m, 2H), 4.72 – 4.54 (m, 2H), 3.82 (s, 1H), 3.50 (d, J = 24.5 Hz, 1H), 3.39 (s, 3H), 3.26 (s, 1H), 2.26 (dd, J = 14.8, 7.0 Hz, 1H), 2.14 (dd, J = 15.6, 7.2 Hz, 1H), 1.62 – 1.11 (m, 9H), 1.05 (d, J = 8.1 Hz, 3H), 1.05 (s, 9H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 137.53, 134.89, 134.86, 133.85, 133.59, 128.48, 128.42, 126.48, 126.40, 113.72, 96.38, 96.12, 96.09, 82.31, 71.19, 68.46, 54.81, 38.59, 31.54, 30.09, 28.89, 26.04, 22.24, 20.03, 18.27. **HRMS (ESI)** *m/z* for $C_{29}H_{44}O_4Si$ $[M + H]^+$, calculated: 484.30, found: 484.3011.

(5*S*,9*S*)-5-(1-((4-methoxybenzyl)oxy)pent-4-en-1-yl)-9,12,12-trimethyl-11,11-diphenyl-2,4,10-trioxa-11-silatridecane (26)

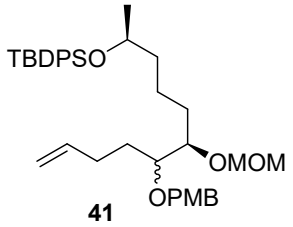


26

To a suspension of vaccum dried NaH (13 mg, 0.55 mmol){60% in mineral oil dispersion} in 3 mL of dry THF was added the alcohol **25** (177 mg, 0.366 mmol) in 3 mL of THF dropwise at 0 °C and stirred for 45 minute. Then, a freshly prepared solution of PMB-Br (74 mg, 0.366 mmol) in 5 mL of THF was added slowly, followed by a catalytic amount of TBAI was added and allowed to stir at room temperature. After completion of the reaction (monitored by TLC), 5 mL of H_2O was added and the organic part was extracted with (2×10 mL) Et_2O and dried over anhydrous Na_2SO_4, evaporated, purified using 1:30 (EtOAc/hexane) to obtain product **26** (184 mg, 0.30 mmol) as colourless liquid in 82% yield (diastereomeric mixtures). R_f = 0.5 (EtOAc/hexane = 1:10).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 5.7 Hz, 4H), 7.38 (dd, J = 13.4, 6.3 Hz, 6H), 7.25 (d, J = 10.9 Hz, 2H), 6.86 (d, J = 6.5 Hz, 2H), 5.79 (dd, J = 16.0, 8.4 Hz, 1H), 4.97 (t, J = 14.6 Hz, 2H), 4.67 – 4.57 (m, 2H), 4.44 (dt, J = 26.7, 11.0 Hz, 2H), 3.84 (d, J = 5.5 Hz, 1H), 3.79 (s, 3H), 3.55 (s, 1H), 3.42 (s, 1H), 3.35 (d, J = 2.0 Hz, 3H), 2.18 (d, J = 2.0 Hz, 1H), 2.05 (s, 1H), 1.63 (s, 1H), 1.57 – 1.28 (m, 7H), 1.05 (s, 9H), 1.05 (d, J = 6.1 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 159.22, 138.67, 135.88, 135.86, 134.95, 134.63, 130.92, 129.51, 129.48, 129.44, 129.41, 129.38, 127.46, 127.39, 114.60, 113.77, 96.85, 79.27, 72.10, 69.51, 55.67, 55.28, 39.59, 30.22, 28.93, 27.05, 23.17, 21.67, 19.26. **HRMS (ESI)** *m/z* for $C_{37}H_{52}O_5Si$ [M + H]+, calculated: 604.36, found: 604.3583.

(5*R*,9*S*)-5-(1-((4-methoxybenzyl)oxy)pent-4-en-1-yl)-9,12,12-trimethyl-11,11-diphenyl-2,4,10-trioxa-11-silatridecane (41)

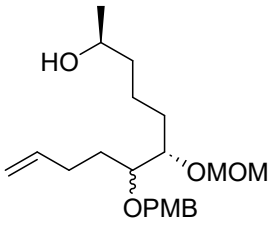


41

To a suspension of vacuum-dried NaH (15 mg, 0.62 mmol){60% in mineral oil dispersion} in 3 mL of dry THF was added the alcohol **40** (200 mg, 0.41 mmol) in 3 mL THF dropwise at 0 °C and stirred for 45 min. Then a freshly prepared solution of PMB-Br (83 mg, 0.41 mmol) in 2 mL of dry THF was added slowly followed by catalytic amount of TBAI was added and allowed to stir at room temperature. After completion of the reaction as monitored by TLC analysis, 5 mL of H_2O was added and the organic part was extracted with (2×10 mL) Et_2O and dried over anhydrous Na_2SO_4, evaporated, purified using 1:30 (EtOAc/hexane) to obtain product **41** (204 mg, 0.34 mmol) in 82% yield (diastereomeric mixtures). R_f = 0.5 (EtOAc/hexane = 1:10).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 6.8 Hz, 4H), 7.46 – 7.29 (m, 6H), 7.23 (s, 2H), 6.85 (d, J = 7.1 Hz, 2H), 5.78 (dd, J = 17.7, 10.4 Hz, 1H), 4.96 (t, J = 14.0 Hz, 2H), 4.62 (dd, J = 15.5, 6.8 Hz, 2H), 4.52 – 4.36 (m, 2H), 3.81 (s, 1H), 3.79 (s, 3H), 3.54 (s, 1H), 3.41 (s, 1H), 3.34 (d, J = 4.9 Hz, 3H), 2.18 (s, 1H), 2.05 (s, 1H), 1.60 (s, 1H), 1.53 – 1.13 (m, 7H), 1.04 (s, 9H), 1.04 (d, J = 6.2 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 159.22, 138.67, 135.89, 135.86, 134.95, 134.63, 130.93, 129.51, 129.44, 129.38, 127.47, 127.39, 114.61, 113.76, 96.85, 79.20, 78.60, 72.07, 69.63, 55.67, 55.27, 39.67, 30.21, 29.99, 28.94, 27.05, 23.19, 21.83, 19.27. **HRMS (ESI)** *m/z* for $C_{37}H_{52}O_5Si$ [M + H]$^+$, calculated: 604.36, found: 604.3576.

(2*S*,6*S*)-7-((4-methoxybenzyl)oxy)-6-(methoxymethoxy)undec-10-en-2-ol (27)

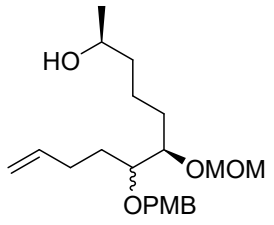


27

To a solution of compound **26** (127 mg, 0.21 mmol) in 5 mL of dry THF, TBAF solution (0.42 mL,1M in THF) was added dropwise at 0 °C and the reaction mixture was allowed to reflux at 70 °C for 6h. After completion of the reaction, the crude reaction mixture was directly subjected to purification by column chromatography using 1:3 (EtOAc/hexane) to obtain product **27** (70 mg, 0.19 mmol) as colourless liquid in 90% yield (diastereomeric mixtures). R_f = 0.2 (EtOAc/hexane = 1:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 2H), 6.87 (d, J = 8.0 Hz, 2H), 5.79 (dd, J = 21.8, 13.0 Hz, 1H), 4.97 (t, J = 14.9 Hz, 2H), 4.66 (d, J = 6.5 Hz, 2H), 4.50 (s, 2H), 3.80 (s, 3H), 3.76 (s, 1H), 3.61 (s, 1H), 3.45 (s, 1H), 3.37 (s, 3H), 2.20 (s, 1H), 2.05 (s, 1H), 1.62 (d, J = 16.4 Hz, 4H), 1.44 (s, 4H), 1.19 (d, J = 6.1 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 159.14, 138.58, 130.78, 129.59, 129.48, 114.73, 113.74, 96.83, 96.26, 79.99, 79.01, 78.45, 78.26, 72.04, 71.74, 67.92, 55.74, 55.26, 39.28, 30.75, 30.13, 29.58, 28.80, 23.46, 22.05. **HRMS (ESI)** *m/z* for $C_{21}H_{34}O_5$ [M + H]$^+$, calculated: 366.24, found: 366.2401.

(2*S*,6*R*)-7-((4-methoxybenzyl)oxy)-6-(methoxymethoxy)undec-10-en-2-ol (27A)

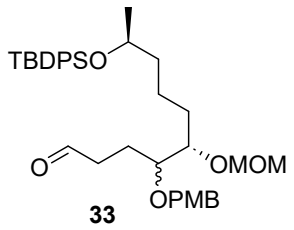


27A

To a solution of compound **41** (145 mg, 0.24 mmol) in 5 mL of dry THF, TBAF solution (0.5 mL, 1M in THF) was added dropwise at 0 °C, the reaction mixture was then allowed to reflux at 70 °C for 6h. After completion of the reaction, the crude reaction mixture was directly subjected to purification by column chromatography using 1:3 (EtOAc/hexane) to obtain product **27A** as colourless liquid (77 mg, 0.21 mmol) in 88% yield (diastereomeric mixtures). R_f = 0.2 (EtOAc /hexane = 1:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 7.8 Hz, 2H), 6.86 (d, J = 8.1 Hz, 2H), 5.86 – 5.71 (m, 1H), 4.96 (t, J = 14.7 Hz, 2H), 4.66 (d, J = 6.1 Hz, 2H), 4.48 (d, J = 7.3 Hz, 2H), 3.79 (s, 3H), 3.78 – 3.74 (m, 1H), 3.61 (s, 1H), 3.44 (d, J = 3.3 Hz, 1H), 3.36 (s, 3H), 2.20 (d, J = 6.1 Hz, 1H), 2.12 – 2.00 (m, 1H), 1.59 (dd, J = 21.4, 6.7 Hz, 4H), 1.47 – 1.38 (m, 4H), 1.16 (d, J = 5.9 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 159.25, 138.60, 130.86, 129.55, 129.44, 114.65, 113.78, 96.91, 79.14, 78.56, 72.08, 67.91, 55.72, 55.27, 39.33, 30.19, 29.67, 28.87, 23.50, 22.15. **HRMS (ESI)** *m/z* for $C_{21}H_{34}O_5$ [M + H]$^+$, calculated : 366.24, found : 366.2410.

(5*S*,9*S*)-9-((*tert*-butyldiphenylsilyl)oxy)-4-((4-methoxybenzyl)oxy)-5-(methoxymethoxy) decanal (33)

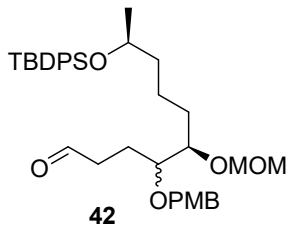


33

The olefin **26** (56 mg, 0.093 mmol) was dissolved in 4 mL of 1,4 dioxane/H_2O (3:1). 2,6-Lutidine (0.1 mL, 1.96 mmol) was added followed by OsO_4 (0.34 mL, 0.017 mmol) and $NaIO_4$ (80 mg, 0.37 mmol) addition, the reaction mixture was stirred for 19h. After completion of the reaction 1,4 dioxane was evaporated and organic part was extracted with (2×10 mL) Et_2O and dried over anhydrous Na_2SO_4, evaporated and purified by column chromatography using EtOAc/Hexane = 1:5 to obtain compound **33** (49 mg, 0.081 mmol) as colourless liquid in 87% yield (as diastereomeric mixtures). R_f = 0.5 (EtOAc/hexane = 1:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, J = 6.7 Hz, 1H), 7.70 (d, J = 7.4 Hz, 4H), 7.39 (d, J = 7.1 Hz, 6H), 7.25 (d, J = 2.0 Hz, 2H), 6.88 (d, J = 8.2 Hz, 2H), 4.67 (m, 2H), 4.60 – 4.29 (m, 2H), 3.91 – 3.85 (m, 1H), 3.82 (s, 3H), 3.71 (s, 1H), 3.47 – 3.40 (m, 1H), 3.38 (s, 3H), 2.64 – 2.36 (m, 2H), 1.93 – 1.72 (m, 2H), 1.49 – 1.40 (m, 2H), 1.39 – 1.27 (m, 4H), 1.08 (d, J = 6.2 Hz, 3H), 1.07 (s, 9H).

(5*R*,9*S*)-9-((*tert*-butyldiphenylsilyl)oxy)-4-((4-methoxybenzyl)oxy)-5-(methoxymethoxy) decanal (42)

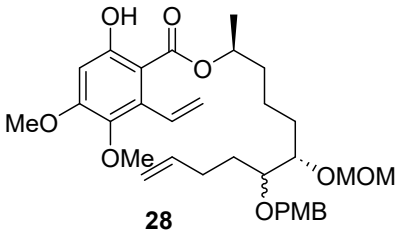


42

The olefin **41** (57 mg, 0.094 mmol) was dissolved in 4 mL of 1,4 dioxane/H_2O (3:1). 2,6-lutidine (0.1 mL, 1.96 mmol) was added followed by OsO_4 (0.34 mL, 0.017 mmol) and $NaIO_4$ (81 mg, 0.38 mmol) addition, the reaction mixture was stirred for 19h. After completion of the reaction 1,4 dioxane was evaporated and organic part was extracted with (2×10 ml) Et_2O and dried over anhydrous Na_2SO_4, evaporated and purified by column chromatography using EtOAc/Hexane (1:5) to obtain aldehyde **42** (51 mg, 0.084 mmol) as colourless liquid in 89% yield (as diastereomeric mixtures). R_f = 0.5 (EtOAc/hexane = 1:5).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.60 (d, J = 6.4 Hz, 4H), 7.31 (dd, J = 17.1, 6.6 Hz, 6H), 7.19 – 7.11 (m, 2H), 6.78 (d, J = 6.6 Hz, 2H), 4.73 – 4.52 (m, 2H), 4.49 – 4.19 (m, 2H), 3.80 – 3.75 (m, 1H), 3.72 (s, 3H), 3.62 (s, 1H), 3.35 – 3.28 (m, 1H), 3.27 (s, 3H), 2.50 – 2.30 (m, 2H), 1.86 – 1.63 (m, 2H), 1.46 – 1.33 (m, 4H), 1.28 – 1.18 (m, 2H), 0.98 (s, 9H), 0.95 (d, J = 6.2 Hz, 3H).

(2*S*,6*S*)-7-((4-methoxybenzyl)oxy)-6-(methoxymethoxy)undec-10-en-2-yl 6-hydroxy-3,4-di-methoxy-2-vinylbenzoate (28)

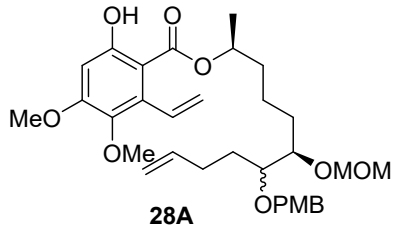


28

To a suspension of vacuum dried NaH (23 mg, 0.95 mmol) 60% (in mineral oil dispersion) in dry THF was added the alcohol **27** (70 mg, 0.19 mmol) in 2 mL dry THF dropwise at 0 °C and stirred for 30 minutes. Then the olefin **14** (46 mg, 0.17 mmol) in 2 mL dry THF was added dropwise to it and allowed to stir at 40 °C for 3h. After completion the reaction mixture was quenched with H_2O and organic part was extracted with (2×10 mL) Et_2O and dried over anhydrous Na_2SO_4, evaporated, purified using 1:5 (EtOAc/hexane) to obtain ester 28 (87 mg, 0.15 mmol) as colourless liquid in 81% yield (as diastereomeric mixtures). R_f = 0.5 (EtOAc / hexane = 1:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.50 (s, 1H), 7.26 (s, 2H), 6.87 (s, 2H), 6.83 (d, J = 12.7 Hz, 1H), 6.43 (s, 1H), 5.78 (d, J = 6.9 Hz, 1H), 5.50 – 5.30 (m, 2H), 5.15 (s, 1H), 4.96 (t, J = 14.5 Hz, 2H), 4.64 (d, J = 13.2 Hz, 2H), 4.48 (d, J = 10.3 Hz, 2H), 3.88 (s, 3H), 3.79 (s, 3H), 3.62 (s, 4H), 3.44 (s, 1H), 3.34 (d, J = 3.0 Hz, 3H), 2.13 (m, 2H), 1.60 (m, 8H), 1.32 (d, J = 6.2 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 170.73, 160.42, 159.24, 158.38, 140.06, 138.56, 134.65, 132.31, 130.80, 129.53, 129.49, 129.41, 118.19, 114.66, 113.76, 104.00, 99.63, 96.82, 79.06, 78.35, 72.82, 72.09, 60.41, 55.81, 55.69, 55.24, 35.94, 30.18, 29.64, 28.85, 21.93, 19.85. **HRMS (ESI)** *m/z* for $C_{32}H_{44}O_9$ $[M + H]^+$, calculated: 572.30, found: 572.2976.

(2*S*,6*R*)-7-((4-methoxybenzyl)oxy)-6-(methoxymethoxy)undec-10-en-2-yl 6-hydroxy-3,4-di-methoxy-2-vinylbenzoate (28A)



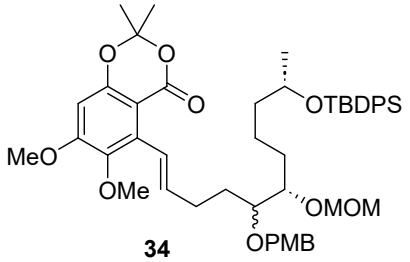
28A

To a suspension of vacuum dried NaH (25 mg, 1.05 mmol) 60% in mineral oil dispersion in dry THF was added the alcohol **16** (77 mg, 0.21 mmol) in 2 mL dry THF dropwise at 0 °C and sitterd for 30 min. Then the olefin **14** (50 mg, 0.19 mmol) in 2 mL dry THF was added dropwise to it and allowed to stir at 40 °C for 3h. After completion the reaction mixture was quenched with H_2O and organic part was extracted with (2×10 mL) Et_2O and dried over anhydrous Na_2SO_4, evaporated, purified using 1:5 (EtOAc/hexane) to obtain ester **28A** (92 mg, 0.16 mmol) as colourless liquid in 85% yield (as diastereomeric mixtures). R_f = 0.6 (EtOAc/hexane = 1:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.49 (s, 1H), 7.24 (s, 4H), 6.86 (d, J = 7.9 Hz, 2H), 6.84 – 6.75 (m, 1H), 6.43 (s, 1H), 5.78 (d, J = 7.0 Hz, 1H), 5.37 (t, J = 15.0 Hz, 2H), 5.21 – 5.09 (m,

1H), 4.96 (t, J = 14.8 Hz, 2H), 4.64 (dd, J = 18.0, 6.5 Hz, 2H), 4.45 (m, 2H), 3.88 (s, 3H), 3.79 (s, 3H), 3.62 (s, 3H), 3.59 (s, 1H), 3.44 (s, 1H), 3.35 (s, 3H), 2.22 (s, 1H), 2.06 (s, 1H), 1.70 (d, J = 7.5 Hz, 4H), 1.48 (m, 6H), 1.31 (d, J = 6.2 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 170.72, 160.43, 159.26, 158.39, 140.07, 138.59, 134.66, 132.35, 130.82, 129.54, 129.51, 129.44, 118.17, 114.71, 113.78, 104.04, 99.66, 96.87, 96.24, 79.14, 78.40, 72.81, 72.13, 60.43, 55.83, 55.71, 55.27, 35.96, 30.20, 29.68, 28.85, 21.87, 19.82. **HRMS (ESI)** *m/z* for $C_{32}H_{44}O_9$ $[M + H]^+$, calculated: 840.43, found: 572.2981.

5-((6*S*,10*S*,*E*)-10-((*tert*-butyldiphenylsilyl)oxy)-5-((4-methoxybenzyl)oxy)-6-(methoxy methoxy)undec-1-en-1-yl)-6,7-dimethoxy-2,2-dimethyl-4*H*-benzo[d][1,3]dioxin-4-one (34)

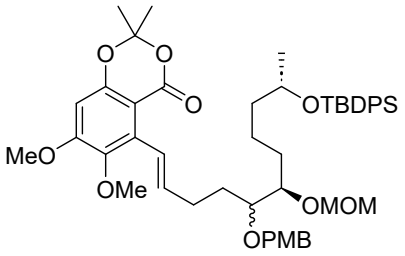


34

To a solution of sulfone **31** (28 mg, 0.0625 mmol) in 3 mL of dry THF kept at -78 ^{o}C (0.1 mL 1M in Hexane) LiHMDS solution was added dropwise and stirred for 45 min. Then aldehyde **33** (49 mg, 0.081 mmol) in 2 mL of dry THF was added and the temperature was slowly allowed to increase at room temperature. After 2.5h the reaction mixture was quenched with saturated NH_4Cl solution and the organic part was extracted with (2×15 mL) Et_2O and dried over anhydrous Na_2SO_4, evaporated, purified using 1:5 (EtOAc/hexane) to obtain *E* olefin **34** (42 mg, 0.05 mmol) as colourless liquid in 80% yield (as diastereomeric mixtures). R_f = 0.3 (EtOAc/hexane = 1:4).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 6.8 Hz, 4H), 7.30 (dd, J = 7.0, 1.8 Hz, 2H), 7.26 (d, J = 7.0 Hz, 4H), 7.18 (dd, J = 12.4, 5.5 Hz, 2H), 6.86 (dd, J = 16.0, 7.1 Hz, 1H), 6.79 – 6.73 (m, 2H), 6.31 – 6.22 (m, 2H), 4.68 (d, J = 6.7 Hz, 1H), 4.55 (t, J = 9.5 Hz, 1H), 4.42 (m, 2H), 3.80 (s, 3H), 3.77 (d, J = 5.8 Hz, 1H), 3.69 (d, J = 1.1 Hz, 3H), 3.59 (d, J = 8.2 Hz, 1H), 3.56 (s, 3H), 3.42 (d, J = 9.4 Hz, 1H), 3.26 (d, J = 9.1 Hz, 3H), 2.44 – 2.33 (m, 1H), 2.28 – 2.17 (m, 1H), 1.72 – 1.64 (m, 1H), 1.61 (s, 6H), 1.56 – 1.50 (m, 1H), 1.46 – 1.40 (m, 2H), 1.33 (d, J = 10.4 Hz, 2H), 1.26 (s, 2H), 0.96 (s, 9H), 0.96 (d, J = 6.2 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 171.15, 159.85, 159.17, 159.01, 154.57, 142.80, 138.14, 135.82, 135.79, 134.95, 134.84, 134.48, 130.93, 129.48, 129.41, 129.32, 127.43, 127.33, 123.03, 113.67, 104.79, 103.80, 98.66, 96.62, 96.15, 80.31, 79.35, 78.39, 78.18, 72.20, 71.81, 69.53, 60.35, 59.88, 55.98, 55.66, 55.19, 39.55, 31.02, 30.55, 30.44, 29.83, 29.69, 29.10, 26.98, 25.54, 25.44, 23.16, 21.88, 21.72, 20.99, 19.20, 14.14. **HRMS (ESI)** *m/z* for $C_{49}H_{64}O_{10}Si$ $[M + H]^+$, calculated: 840.43, found: 840.4272.

5-((6*R*,10*S*,*E*)-10-((*tert*-butyldiphenylsilyl)oxy)-5-((4-methoxybenzyl)oxy)-6-(methoxy methoxy)undec-1-en-1-yl)-6,7-dimethoxy-2,2-dimethyl-4*H*-benzo[d][1,3]dioxin-4-one (43)

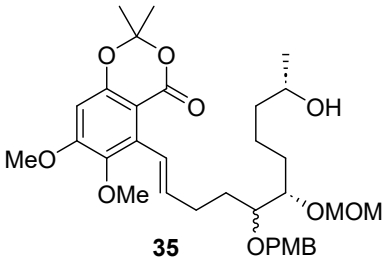


43

To a solution of sulfone **31** (29 mg, 0.063 mmol) in 3 mL of dry THF kept at -78 °C (0.1 mL, 1M in Hexane) LiHMDS solution was added dropwise and stirred for 45 min. Then aldehyde **42** (50 mg, 0.082 mmol) in 2 mL dry THF was added and the temperature was slowly allowed to increase at room temperature. After 2.5h the reaction mixture was quenched with saturated NH_4Cl solution and organic part was extracted with (2×15 mL) Et_2O and dried over anhydrous Na_2SO_4, evaporated, purified using 1:5 (EtOAc/hexane) to obtain *E* olefin **43** (42 mg, 0.05 mmol) as colourless liquid in 79% yield (as diastereomeric mixtures). R_f = 0.3 (EtOAc/hexane = 1:4).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 4H), 7.35 – 7.21 (m, 6H), 7.18 (dd, *J* = 11.8, 6.6 Hz, 2H), 6.85 (dd, *J* = 16.0, 6.9 Hz, 1H), 6.80 – 6.72 (m, 2H), 6.32 – 6.19 (m, 2H), 4.69 (d, *J* = 6.7 Hz, 1H), 4.55 (dd, *J* = 13.2, 8.9 Hz, 1H), 4.41 (m, 2H), 3.78 (d, *J* = 15.9 Hz, 3H), 3.76 – 3.72 (m, 1H), 3.69 (d, *J* = 3.2 Hz, 3H), 3.55 (d, *J* = 1.1 Hz, 3H), 3.48 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.45 – 3.39 (m, 1H), 3.25 (d, *J* = 8.2 Hz, 3H), 2.43 – 2.16 (m, 2H), 1.71 – 1.64 (m, 1H), 1.64 – 1.56 (m, 6H), 1.46 – 1.39 (m, 2H), 1.39 – 1.32 (m, 2H), 1.30 – 1.24 (m, 1H), 1.24 – 1.17 (m, 2H), 0.96 (d, *J* = 6.2 Hz, 3H), 0.95 (s, 9H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 170.59, 159.83, 159.20, 159.07, 154.59, 142.87, 138.19, 135.85, 135.83, 135.00, 134.90, 134.54, 130.97, 129.54, 129.48, 129.44, 129.36, 127.46, 127.36, 123.06, 123.00, 113.73, 104.81, 103.88, 98.69, 96.69, 96.22, 80.38, 79.38, 78.49, 78.25, 72.21, 71.83, 69.63, 69.53, 59.88, 56.01, 55.68, 55.24, 39.60, 31.04, 30.59, 30.49, 29.97, 29.73, 29.18, 27.02, 25.58, 25.50, 23.18, 21.92, 19.24. **HRMS (ESI)** *m/z* for $C_{49}H_{64}O_{10}Si$ $[M + H]^+$, calculated: 840.43, found: 840.4270.

5-((6*S*,10*S*,*E*)-10-hydroxy-5-((4-methoxybenzyl)oxy)-6 (methoxymethoxy) undec-1-en-1-yl)-6,7-dimethoxy-2,2-dimethyl-4*H*-benzo[d][1,3]dioxin-4-one(35)



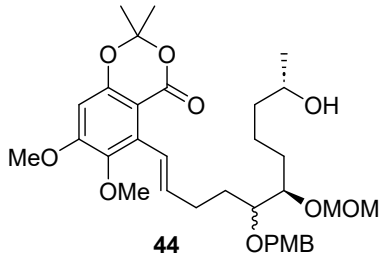
35

To a solution of compound **34** (42 mg, 0.05 mmol) in 10 mL of dry THF, TBAF solution (0.1 mL, 1M in THF) was added dropwise at 0 °C and allowed to refluxed at 70 °C for 8h. After completion (as indicated by TLC analysis), the reaction mixture was directly subjected to purification by column chromatography using 1:1 (EtOAc/hexane) to obtain product **35** (25

mg, 0.042 mmol) as colourless liquid in 84% yield (as diastereomeric mixtures). R_f = 0.1 (EtOAc/hexane = 1:2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, J = 8.0 Hz, 2H), 6.92 (dd, J = 16.0, 9.4 Hz, 1H), 6.85 (dd, J = 8.7, 2.3 Hz, 2H), 6.38 – 6.26 (m, 2H), 4.82 – 4.63 (m, 2H), 4.53 (m, 2H), 3.88 (s, 3H), 3.78 (s, 3H), 3.77 – 3.74 (m, 1H), 3.60 – 3.53 (m, 1H), 3.38 (d, J = 8.7 Hz, 3H), 2.45 (m, 1H), 2.33 (dt, J = 14.4, 7.4 Hz, 1H), 1.80 (ddd, J = 14.3, 8.6, 4.4 Hz, 1H), 1.69 (s, 6H), 1.66 (s, 1H), 1.54 – 1.38 (m, 4H), 1.17 (d, J = 6.2 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 159.90, 159.22, 159.09, 154.62, 142.84, 138.04, 135.01, 130.98, 129.61, 129.53, 123.14, 113.74, 104.85, 103.86, 98.71, 96.71, 96.28, 80.12, 79.18, 78.48, 78.29, 72.24, 71.89, 67.86, 59.96, 56.03, 55.73, 55.25, 39.30, 30.80, 30.33, 29.70, 29.12, 25.58, 25.53, 25.49, 23.42, 22.06. **HRMS (ESI)** *m/z* for $C_{33}H_{46}O_{10}$ [M + H]$^+$, calculated: 602.31, found: 602.3101.

5-((6*R*,10*S*,*E*)-10-hydroxy-5-((4-methoxybenzyl)oxy)-6 (methoxymethoxy) undec-1-en-1-yl)-6,7-dimethoxy-2,2-dimethyl-4H-benzo[d][1,3]dioxin-4-one (44)

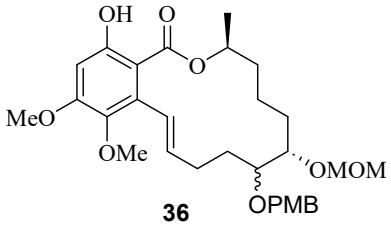


44

A solution of compound **43** (42 mg, 0.05 mmol) in 5 mL of dry THF, TBAF solution (0.1 ml 1M in THF) was added dropwise at 0 °C and allowed to reflux at 70 °C for 8h. After completion (as indicated by TLC analysis), the reaction mixture was directly subjected to purification by column chromatography using 1:1 (EtOAc/hexane) to obtain product **44** (24 mg, 0.04 mmol) as colourless liquid in 80% yield (as diastereomeric mixtures). R_f = 0.1 (EtOAc/hexane = 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, J = 8.5, 6.5 Hz, 2H), 6.92 (dd, J = 16.0, 7.8 Hz, 1H), 6.85 (d, J = 8.4 Hz, 2H), 6.42 – 6.28 (m, 2H), 4.84 – 4.64 (m, 2H), 4.53 (m, 2H), 3.89 (s, 3H), 3.78 (d, J = 1.7 Hz, 3H), 3.75 (s, 1H), 3.57 (d, J = 8.6 Hz, 1H), 3.38 (d, J = 8.0 Hz, 3H), 2.47 (dd, J = 14.6, 7.4 Hz, 1H), 2.39 – 2.28 (m, 1H), 1.74 (s, 2H), 1.69 (s, 6H), 1.67 – 1.60 (m, 2H), 1.46 (d, J = 9.0 Hz, 4H), 1.17 (d, J = 6.2 Hz, 3H).
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$) δ 159.92, 159.18, 159.03, 154.59, 142.74, 138.02, 134.93, 130.87, 129.61, 129.54, 123.10, 113.69, 104.84, 103.77, 98.66, 96.68, 96.24, 80.04, 79.13, 78.46, 78.25, 72.25, 71.87, 67.88, 59.94, 56.02, 55.75, 55.22, 39.31, 30.73, 30.32, 29.63, 29.07, 25.55, 25.45, 23.47, 22.24, 22.03. **HRMS (ESI)** *m/z* for $C_{33}H_{46}O_{10}$ [M + H]$^+$, calculated: 602.31, found: 602.3099.

(3*S*,7*S*,*E*)-16-hydroxy-13,14-dimethoxy-8-((4-methoxybenzyl)oxy)-7-(methoxymethoxy)-3-methyl-3,4,5,6,7,8,9,10-octahydro-1*H*-benzo [c][1]oxacyclotetradecin-1-one (36)



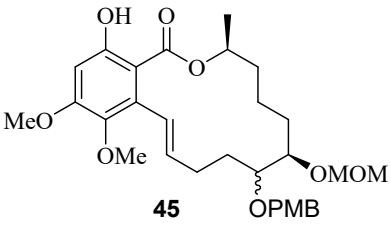
36

NaH (19 mg, 0.8 mmol; 60% dispersion in mineral oil) was dissolved in 5 mL of dry THF and kept at 0 °C. Then alcohol **35** (24 mg, 0.04 mmol) was dissolved in 3 mL of dry THF and added to it dropwise very slowly over 5 min and stirred at room temperature for 24h. After complete conversion (as indicated by TLC analysis), H_2O (3 mL) and EtOAc (5 mL) was added to it. The organic layer was separated and the aqueous part was washed with (2×10 mL) EtOAc. The combined organic part was washed with brine solution (5 mL) and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography (EtOAc/hexane = 1:3) to afford the macrolactone core **36** for Hamigeromycin F (17 mg, 0.031 mmol) as colourless liquid in 77% yield (as diastereomeric mixtures). R_f = 0.50 (EtOAc/ hexane = 1:3).

^{1}H NMR (500 MHz, $CDCl_3$) δ 12.32 (s, 1H), 7.04 (d, J = 8.6 Hz, 2H), 6.60 – 6.56 (m, 2H), 6.53 (d, J = 2.0 Hz, 1H), 6.47 (s, 1H), 5.89 (ddd, J = 15.7, 11.0, 3.3 Hz, 1H), 4.91 – 4.83 (m, 1H), 4.74 (d, J = 7.1 Hz, 1H), 4.63 (d, J = 7.1 Hz, 1H), 4.54 (d, J = 12.0 Hz, 1H), 4.18 (d, J = 12.0 Hz, 1H), 3.92 (s, 3H), 3.72 (s, 3H), 3.63 (d, J = 10.2 Hz, 1H), 3.58 (s, 3H), 3.42 (s, 3H), 3.35 (d, J = 10.8 Hz, 1H), 2.59 – 2.52 (m, 1H), 2.10 (m, 1H), 2.02 – 1.95 (m, 1H), 1.78 – 1.67 (m, 2H), 1.62 (d, J = 11.4 Hz, 2H), 1.46 – 1.31 (m, 3H), 1.28 (d, J = 6.2 Hz, 3H). **^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$)** δ 171.79, 161.74, 159.32, 158.92, 140.37, 136.51, 134.26, 130.71, 130.06, 124.67, 113.42, 103.32, 99.48, 95.51, 73.62, 72.88, 71.65, 69.97, 60.07, 55.89, 55.79, 55.16, 34.13, 29.79, 29.71, 27.36, 26.49, 21.18, 20.37.

HRMS (ESI) *m/z* for $C_{30}H_{40}O_9$ $[M + H]^+$, calculated: 544.27, found: 544.2701.

(3*S*,7*R*,*E*)-16-hydroxy-13,14-dimethoxy-8-((4-methoxybenzyl)oxy)-7-(methoxymethoxy)-3-methyl-3,4,5,6,7,8,9,10-octahydro-1*H*-benzo [c][1]oxacyclotetradecin-1-one (45)



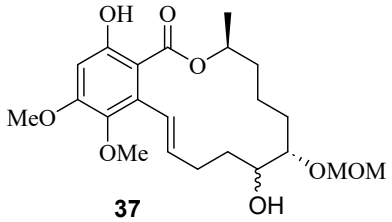
45

The alcohol **44** (23 mg, 0.038 mmol) was dissolved in 10 mL of dry THF and stirred at -10 °C. NaHMDS (0.19 mL, 0.19 mmol) was added to it very slowly over 10 min. After complete conversion saturated solution of NH_4Cl (5 mL) and EtOAc (5 mL) was added to it. The organic layer was separated and the aqueous part was washed with (2×20 mL) EtOAc. The combined organic part was washed with 10 mL brine solution and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography (EtOAc/hexane = 1:5) to afford macrolactone core **45** (16 mg, 0.029 mmol)

for Hamigeromycin G in 78% yield as colorless liquid (as diastereomeric mixtures). R_f = 0.50 (EtOAc/hexane = 1:5).

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.80 (s, 1H), 7.11 (d, J = 8.6 Hz, 2H), 6.69 (d, J = 8.6 Hz, 2H), 6.62 (d, J = 16.0 Hz, 1H), 6.44 (s, 1H), 5.82 (s, 1H), 4.98 (s, 1H), 4.79 (d, J = 6.6 Hz, 1H), 4.69 (d, J = 6.6 Hz, 1H), 4.40 (d, J = 11.7 Hz, 1H), 4.33 (d, J = 11.7 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 1H), 3.73 (s, 3H), 3.57 (s, 3H), 3.50 (d, J = 9.1 Hz, 1H), 3.39 (s, 3H), 2.54 (m, 1H), 2.31 – 2.15 (m, 2H), 1.81 – 1.66 (m, 2H), 1.61 (s, 3H), 1.54 (d, J = 9.3 Hz, 3H), 1.34 (d, J = 6.2 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 171.39, 160.96, 159.11, 158.67, 140.40, 136.15, 134.15, 130.54, 129.44, 125.20, 113.56, 104.13, 99.41, 96.38, 77.95, 75.44, 73.69, 70.23, 60.15, 55.82, 55.42, 55.16, 35.33, 31.53, 30.55, 27.88, 20.97, 20.30. **HRMS (ESI)** *m/z* for $C_{30}H_{40}O_9$ [M + H]$^+$, calculated: 544.27, found: 544.2672.

(3*S*,7*R*,*E*)-16-hydroxy-13,14-dimethoxy-8-((4-methoxybenzyl)oxy)-7-(methoxymethoxy)-3-methyl-3,4,5,6,7,8,9,10-octahydro-1*H*-benzo[c][1]oxacyclotetradecin-1-one (37)

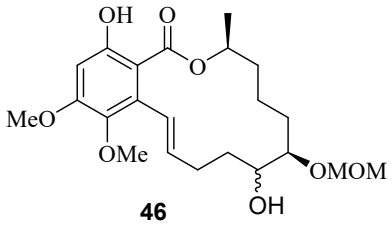


37

To a solution of macrolactone **36** (17 mg, 0.031 mmol) in 5 mL DCM: pH^7 buffer (20:1) at 0 ^{o}C, DDQ (14 mg, 0.062 mmol) was added at once, and he reaction solution was kept for 1.5h. After completion, the reaction mixture was directly subjected to purification through chromatography using (EtOAc–hexane = 1:2) to afford alcohol **37** (11 mg, 0.026 mmol) for Hamigeromycin F in 84% yield (as diastereomeric mixtures) as amorphous white solid. R_f = 0.2 (EtOAc/hexane = 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.49 (s, 1H), 6.63 (d, J = 16.0 Hz, 1H), 6.41 (s, 1H), 6.01 – 5.91 (m, 1H), 5.07 – 4.97 (m, 1H), 4.70 (s, 2H), 3.87 (s, 3H), 3.76 (d, J = 7.0 Hz, 1H), 3.69 (d, J = 8.9 Hz, 1H), 3.58 (d, J = 1.9 Hz, 3H), 3.42 (s, 3H), 3.36 (s, 1H), 2.49 (d, J = 10.8 Hz, 1H), 2.33 (d, J = 9.1 Hz, 1H), 1.74 (s, 2H), 1.72 (s, 2H), 1.67 (d, J = 12.7 Hz, 2H), 1.61 (d, J = 9.6 Hz, 2H), 1.36 (d, J = 6.2 Hz, 3H). **^{13}C{1H}-NMR (101 MHz, $CDCl_3$)** δ 171.27, 160.42, 158.48, 140.32, 135.22, 133.89, 125.13, 104.38, 99.31, 97.01, 83.14, 73.77, 69.13, 60.32, 55.82, 55.70, 36.07, 31.57, 30.82, 29.77, 21.37, 20.53. **HRMS (ESI)** *m/z* for $C_{22}H_{32}O_8$ [M + H]$^+$, calculated: 424.210, found: 424.210.

(3*S*,7*S*,*E*)-16-hydroxy-13,14-dimethoxy-8-((4-methoxybenzyl)oxy)-7-(methoxymethoxy)-3-methyl-3,4,5,6,7,8,9,10-octahydro-1*H*-benzo[c][1]oxacyclotetradecin-1-one (46)

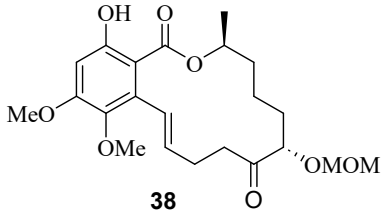


46

To a solution of macrolactone, **45** (16 mg, 0.029 mmol) in 5 mL DCM: pH7 buffer (20:1) at 0 °C, DDQ (13 mg, 0.058 mmol) was added, and the reaction solution was kept for 1.5h. After completion, the reaction mixture was directly subjected to purification through chromatography using (EtOAc/hexane = 1:2) to afford alcohol **46** (11 mg, 0.026 mmol) for Hamigeromycin G in 86% yield (as diastereomeric mixtures) as white amorphous solid. R_f = 0.2 (EtOAc/hexane = 1:2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 12.12 (s, 1H), 6.59 (dd, J = 15.9, 2.0 Hz, 1H), 6.42 (s, 1H), 5.93 – 5.83 (m, 1H), 5.11 – 5.03 (m, 1H), 4.71 (dd, J = 65.1, 6.9 Hz, 2H), 3.87 (s, 3H), 3.68 (d, J = 10.6 Hz, 1H), 3.61 (d, J = 10.4 Hz, 1H), 3.56 (s, 3H), 3.43 (s, 3H), 2.56 (dd, J = 12.5, 2.8 Hz, 1H), 2.20 (m, 1H), 1.94 – 1.67 (m, 6H), 1.49 – 1.41 (m, 2H), 1.37 (d, J = 6.1 Hz, 3H). **^{13}C{1H}-NMR (126 MHz, $CDCl_3$)** δ 171.64, 161.55, 158.85, 140.45, 135.55, 134.15, 124.41, 103.38, 99.50, 95.27, 74.02, 73.38, 68.78, 60.15, 55.83, 35.06, 32.20, 29.55, 28.36, 21.06, 20.83. **HRMS (ESI)** *m/z* for $C_{22}H_{32}O_8$ $[M + H]^+$, calculated: 424.210, found: 424.209.

(3*S*,7*S*,E)-16-hydroxy-13,14-dimethoxy-7-(methoxymethoxy)-3-methyl-4,5,6,7,9,10-hexahydro-1*H*-benzo[c][1]oxacyclotetradecine-1,8(3*H*)-dione (38)

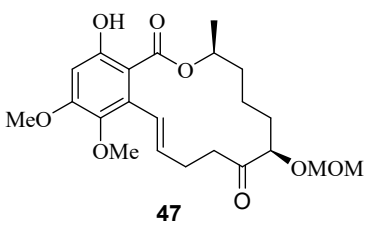


38

To a solution of alcohol **37** (11 mg, 0.026 mmol) in 3 mL of dry DCM at 0 °C was added Dess-Martin periodinane (DMP; 22 mg, 0.052 mmol). After 1h the reaction mixture was quenched with saturated $NaHCO_3$ and the organic part was extracted with DCM, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography (EtOAc/hexane = 1:3) to afford ketone **38** (9 mg, 0.021 mmol) in 81% yield as white amorphous solid. R_f = 0.50 (EtOAc/hexane = 1:3). $[\alpha]_D^{25}$ = +9 (c 0.1, MeOH).

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.01 (s, 1H), 6.53 (d, J = 16.1 Hz, 1H), 6.40 (s, 1H), 5.91 – 5.85 (m, 1H), 5.19 (dd, J = 10.0, 4.3 Hz, 1H), 4.71 (d, J = 6.7 Hz, 1H), 4.65 (d, J = 6.7 Hz, 1H), 4.13 (dd, J = 6.4, 4.1 Hz, 1H), 3.86 (s, 3H), 3.60 (s, 3H), 3.39 (s, 3H), 2.65 (dd, J = 7.4, 3.0 Hz, 1H), 2.53 – 2.47 (m, 1H), 2.06 – 2.01 (m, 1H), 1.77 – 1.73 (m, 2H), 1.65 (ddd, J = 14.0, 8.6, 2.8 Hz, 4H), 1.59 – 1.56 (m, 1H), 1.36 (d, J = 7.2 Hz, 3H). **^{13}C{1H}-NMR (151 MHz, $CDCl_3$)** δ 211.45, 170.15, 159.62, 158.09, 140.44, 133.92, 133.63, 125.26, 104.82, 99.44, 95.96, 82.41, 72.23, 60.33, 55.94, 55.82, 38.76, 35.59, 31.27, 27.82, 20.20, 19.81. **HRMS (ESI)** *m/z* for $C_{20}H_{26}O_7$ $[M + H]^+$, calculated: 422.190, found: 422.1941.

(3*S*,7*R*,*E*)-16-hydroxy-13,14-dimethoxy-7-(methoxymethoxy)-3-methyl-4,5,6,7,9,10-hexahydro-1*H*-benzo[c][1]oxacyclotetradecine-1,8(3*H*)-dione (47)

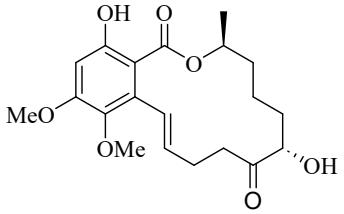


47

To a solution of alcohol **46** (10 mg, 0.0236 mmol) in 3 mL dry DCM at 0 °C was added Dess-Martin periodinane (DMP; 20 mg, 0.047 mmol). After 1 h the reaction mixture was quenched with saturated $NaHCO_3$ and the organic part was extracted with DCM, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography (EtOAc–hexane = 1:3) to afford ketone **47** (8 mg, 0.019 mmol) in 82% yield as white amorphous solid. R_f = 0.50 (EtOAc/hexane = 1:3). $[\alpha]_D^{25}$ = -11 (*c* 0.1, MeOH).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.81 (s, 1H), 6.56 – 6.50 (m, 1H), 6.39 (s, 1H), 5.87 (dt, *J* = 16.0, 6.8 Hz, 1H), 5.17 (ddd, *J* = 9.2, 6.2, 2.9 Hz, 1H), 4.67 (d, *J* = 6.8 Hz, 1H), 4.61 (d, *J* = 6.8 Hz, 1H), 4.15 (dd, *J* = 7.9, 4.1 Hz, 1H), 3.86 (s, 3H), 3.60 (s, 3H), 3.36 (s, 3H), 2.87 – 2.78 (m, 1H), 2.72 – 2.63 (m, 1H), 2.01 (m, 2H), 1.81 – 1.59 (m, 6H), 1.36 (d, *J* = 6.2 Hz, 3H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 210.80, 169.93, 159.33, 158.00, 140.45, 133.94, 133.45, 125.25, 113.40, 104.93, 99.45, 96.04, 81.05, 72.57, 60.33, 55.87, 38.78, 35.69, 31.15, 27.40, 20.55, 20.24. **HRMS (ESI)** *m/z* for $C_{22}H_{30}O_8$ $[M + H]^+$, calculated: 422.190, found: 422.1942.

(3*S*,7*S*,*E*)-7,16-dihydroxy-13,14-dimethoxy-3-methyl-4,5,6,7,9,10-hexahydro-1*H*-benzo[c][1]oxacyclotetradecine-1,8(3*H*)-dione Hamigeromycin F (6)



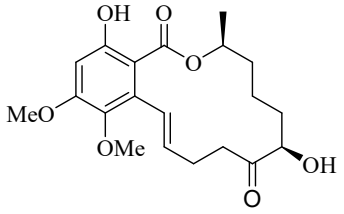
Hamigeromycin F; 6

The ketone **38** (9 mg, 0.0213 mmol) was dissolved in 0.5 mL of MeOH and kept in 0 °C. 1 mL of 4N HCl solution was added to it dropwise. After completion, the reaction mixture was quenched with saturated $NaHCO_3$ solution and neutralised and the organic part was extracted with (2 × 5 mL) DCM, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was then purified by flash column chromatography (EtOAc/hexane = 1:2) to afford the Hamigeromycin F **6** (7 mg, 0.0185 mmol) in 87% yield as white amorphous solid. R_f = 0.20 (EtOAc/hexane = 1:2). $[\alpha]_D^{25}$ = +36 (*c* 0.1, MeOH).

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.69 (s, 1H), 6.62 (d, *J* = 16.2 Hz, 1H), 6.41 (s, 1H), 5.95 (ddd, *J* = 16.1, 8.2, 4.1 Hz, 1H), 4.99 (ddd, *J* = 9.8, 6.2, 2.6 Hz, 1H), 4.36 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.87 (s, 3H), 3.59 (s, 3H), 2.87 – 2.78 (m, 2H), 2.61 – 2.52 (m, 2H), 2.05 (dd, *J* = 10.8, 4.2 Hz, 1H), 1.85 (dd, *J* = 7.2, 4.3 Hz, 1H), 1.70 – 1.64 (m, 2H), 1.52 – 1.47 (m, 1H), 1.36 (d, *J* = 6.1 Hz, 3H), 1.22 (dd, *J* = 8.2, 4.6 Hz, 1H). **^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$)** δ 211.50, 171.13, 160.88, 158.51, 140.23, 133.57, 132.07, 125.63, 103.92, 99.56, 76.61, 73.49, 60.44, 55.82, 45.68, 37.64, 36.07, 32.88, 20.70, 20.09. **HRMS (ESI)** *m/z* for $C_{20}H_{26}O_7$ $[M + H]^+$, calculated: 378.170, found: 378.1679.

IR (KBr) υ_{max}: 3451, 1712, 1644, 1596, 1248, 1021, 754 cm^{-1}.

(3*S*,7*R*,*E*)-7,16-dihydroxy-13,14-dimethoxy-3-methyl-4,5,6,7,9,10-hexahydro-1*H*-benzo[c][1]oxacyclotetradecine-1,8(3*H*)-dione Hamigeromycin G (7)



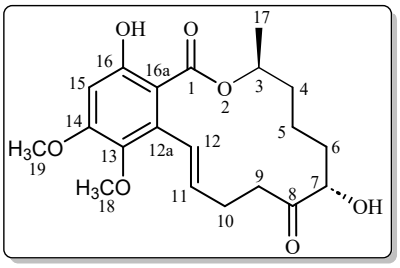
Hamigeromycin G; 7

The ketone **47** (8 mg, 0.019 mmol) was dissolved in 0.5 mL of MeOH and kept in 0 °C. 1 mL of 4N HCl solution was added to it dropwise. After completion, the reaction mixture was quenched with saturated $NaHCO_3$ solution and neutralised and the organic part was extracted with (2× 5mL) DCM, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography (EtOAc–hexane = 1:2) to afford the Hamigeromycin G **7** (6 mg, 0.0159 mmol) in 84% yield as white amorphous solid.

R_f = 0.20 (EtOAc/hexane, 1:2). $[\alpha]_D^{25}$ = +12 (*c* 0.1, MeOH).

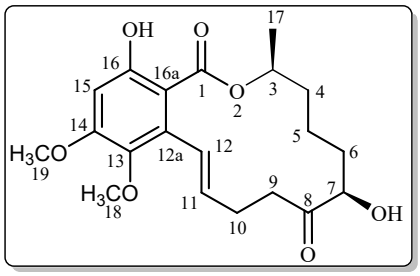
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.06 (s, 1H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.40 (s, 1H), 5.79 – 5.72 (m, 1H), 5.32 – 5.28 (m, 1H), 4.40 (d, *J* = 3.3 Hz, 1H), 3.86 (s, 3H), 3.62 (s, 3H), 3.56 (d, *J* = 4.8 Hz, 1H), 2.81 (dt, *J* = 17.0, 3.8 Hz, 2H), 2.56 – 2.49 (m, 2H), 2.12 (dd, *J* = 16.6, 6.1 Hz, 1H), 1.85 – 1.81 (m, 1H), 1.78 – 1.74 (m, 1H), 1.66 – 1.61 (m, 2H), 1.35 (d, *J* = 6.3 Hz, 3H), 1.03 (dd, *J* = 12.3, 6.5 Hz, 1H). **^{13}C{^{1}H}-NMR (151 MHz, $CDCl_3$)** δ 211.88, 168.69, 158.21, 157.64, 140.53, 133.83, 132.89, 125.87, 105.76, 99.55, 75.98, 71.35, 60.31, 55.85, 37.20, 35.46, 33.00, 27.20, 20.03, 17.93. **HRMS (ESI)** *m/z* for $C_{20}H_{26}O_7$ [*M* + H]$^+$, calculated: 378.170, found: 378.168. **IR** (KBr) υ_{max}: 3453,1710,1641,1592, 1242, 1022, 753 cm^{-1}.

Table 1: NMR comparison table of isolated and synthetic Hamigeromycin F [^{1}H (500 MHz) and ^{13}C (150 MHz) in $CDCl_3$]



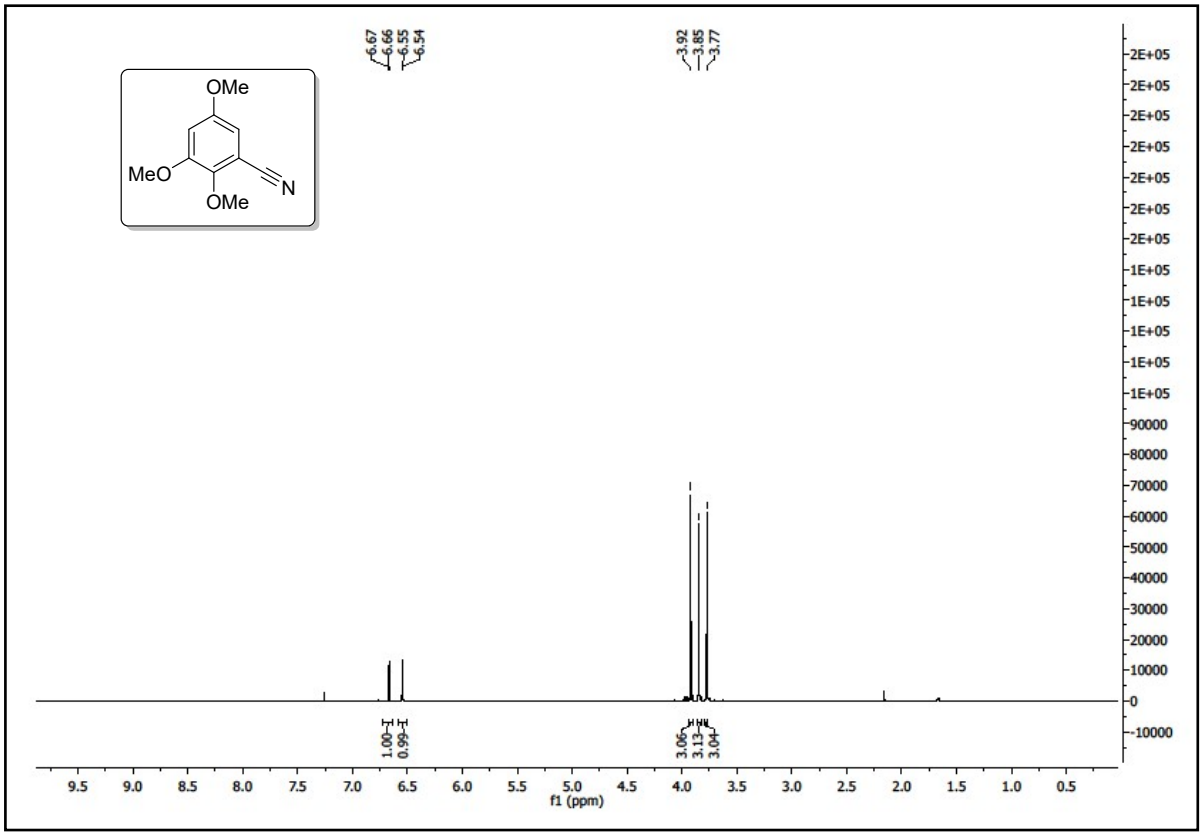
Position	Reported ^{1}H δ (ppm); J (Hz)	Observed ^{1}H δ (ppm); J (Hz)	Δδ (ppm)	Reported ^{13}C δ (ppm)	Observed ^{13}C δ (ppm)	Δδ (ppm)
1				171.1	171.1	0
3	4.99, m	4.99, ddd	0	73.5	73.5	0
4	1.69, m;1.65, m	1.69, m; 1.65, m	0	36.1	36.1	0
5	1.50, m; 1.21, m	1.51, m; 1.22, dd (8.2, 4.6)	0.01, 0.01	20.1	20.1	0
6	2.06, m; 1.84, m	2.05, m; 1.85, m	0.01, 0.01	33	33	0
7	4.36, m	4.36, m	0	76.6	76.6	0
7-OH	3.51, d (4.6)					
8				211.5	211.5	0
9	2.84, m; 2.58, m	2.85, m; 2.58, m	0.01, 0	37.7	37.6	0.1
10	2.81, m; 2.55, m	2.81, m; 2.53, m	0, 0.02	28.4	28.5	0.1
11	5.94, ddd(16.1, 8.2, 4.1)	5.95, ddd (16.1, 8.2, 4.1)	0.01	132.1	132.1	0
12	6.62, d (16.1)	6.62, d (16.2)	0	125.7	125.7	0
12a				133.6	133.6	0
13				140.3	140.2	0.1
14				158.6	158.5	0.1
15	6.41, s	6.41, s	0	99.6	99.6	0
16				160.9	160.9	0
16-OH	11.70, s	11.69, s	0.01			
16a				104	104	0
17	1.36, d (6.2)	1.36, d (6.1)	0	20.7	20.7	0
18	3.59, s	3.59, s	0	60.5	60.4	0.1
19	3.87, s	3.87, s	0	55.8	55.8	0

Table 2 : NMR comparison table of isolated and synthetic Hamigeromycin G [^{1}H (500 MHz) and ^{13}C (150 MHz) in $CDCl_3$]

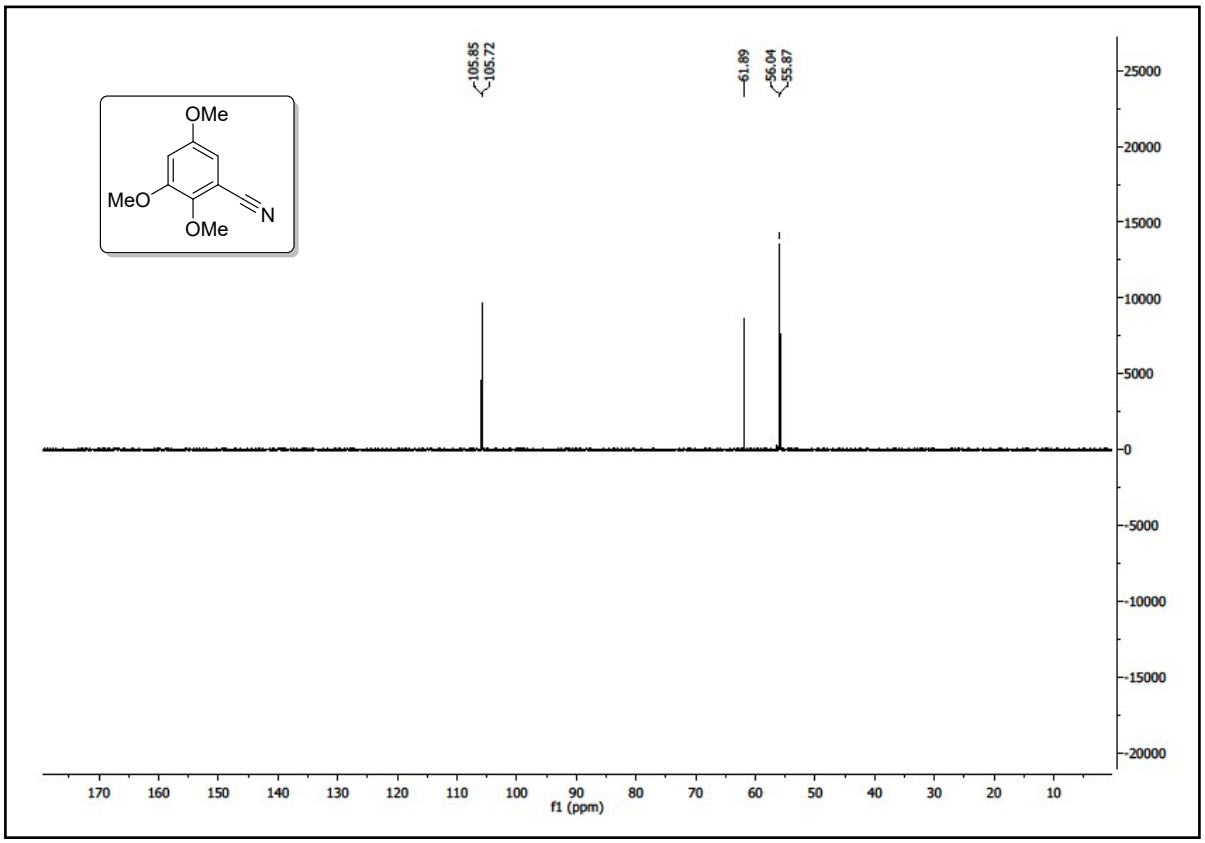


Position	Reported ^{1}H δ (ppm); J (Hz)	Observed ^{1}H δ (ppm); J (Hz)	$\Delta\delta$ (ppm)	Reported ^{13}C δ (ppm)	Observed^{13}C δ (ppm)	$\Delta\delta$ (ppm)
1				168.8	168.7	0.1
3	5.30, m	5.30, m	0	71.4	71.4	0
4	1.77, m; 1.57, m	1.76, m; 1.64, m	0.01, 0.07	35.5	35.5	0
5	1.63, m; 1.04, m	1.64, m; 1.03, dd (12.3, 6.5)	0.01, 0.01	18	18	0
6	2.11, m; 1.81, m	2.11, m; 1.83, m	0, 0.02	33	33	0
7	4.40, m	4.40, d	0	76	76	0
7-OH	3.57, d (4.9)	3.56, d (4.8)	0.01			
8				211.8	211.9	0.1
9	2.80, m; 2.52, m	2.82, m; 2.54, m	0.02, 0.02	37.2	37.2	0
10	2.78, m; 2.50, m	2.78, m; 2.51, m	0, 0.01	27.2	27.2	0
11	5.75, ddd (15.8, 6.8, 6.4)	5.75	0	132.9	132.9	0
12	6.54, br d (15.8)	6.55, d (15.8)	0.01	125.9	125.9	0
12a				133.8	133.8	0
13				140.6	140.5	0.1
14				157.7	157.6	0.1
15	6.40, s	6.40, s	0	99.6	99.6	0
16				158.3	158.2	0.1
16-OH	10.06, s	10.06, s	0			
16a				105.8	105.8	0
17	1.36, d (6.3)	1.35, d (6.3)	0.01	20	20	0
18	3.62, s	3.62, s	0	60.3	60.3	0
19	3.87, s	3.86, s	0.01	55.8	55.9	0.1

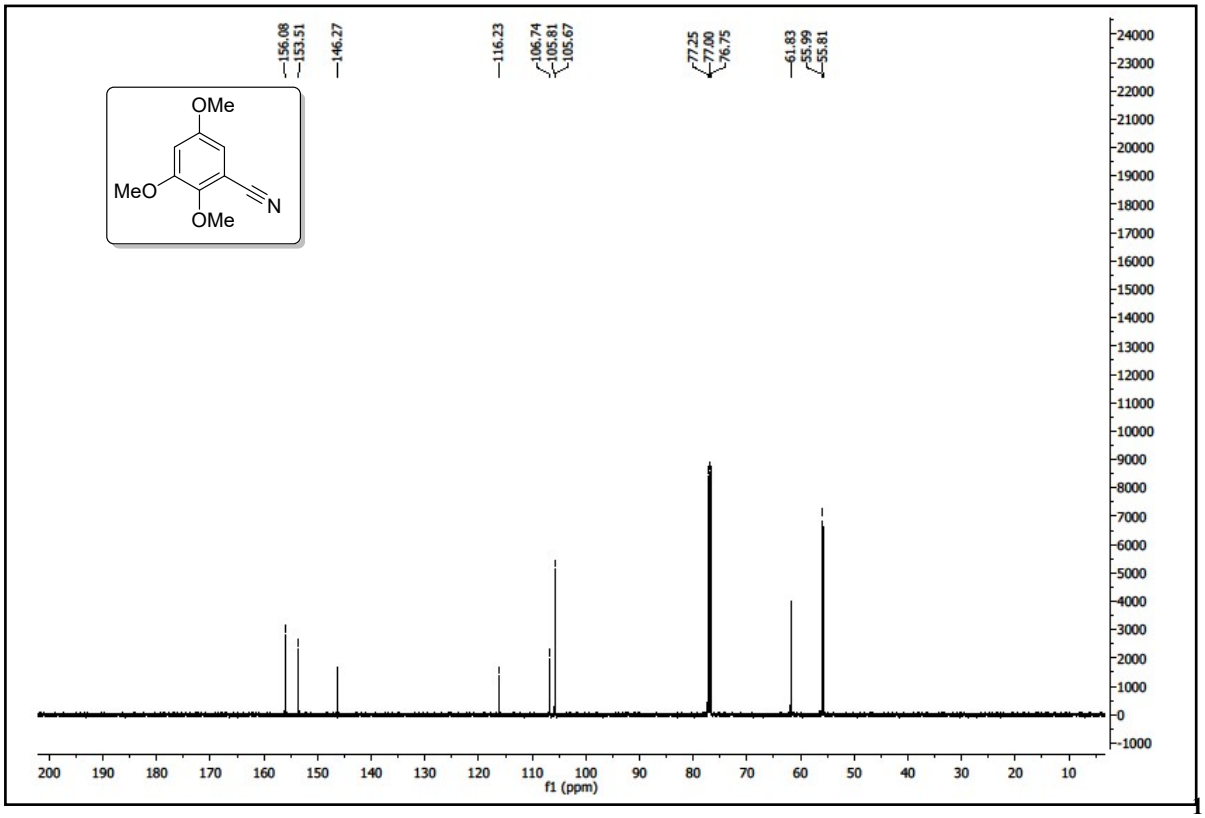
^{1}H NMR of compound 8 (500 MHz, $CDCl_3$)



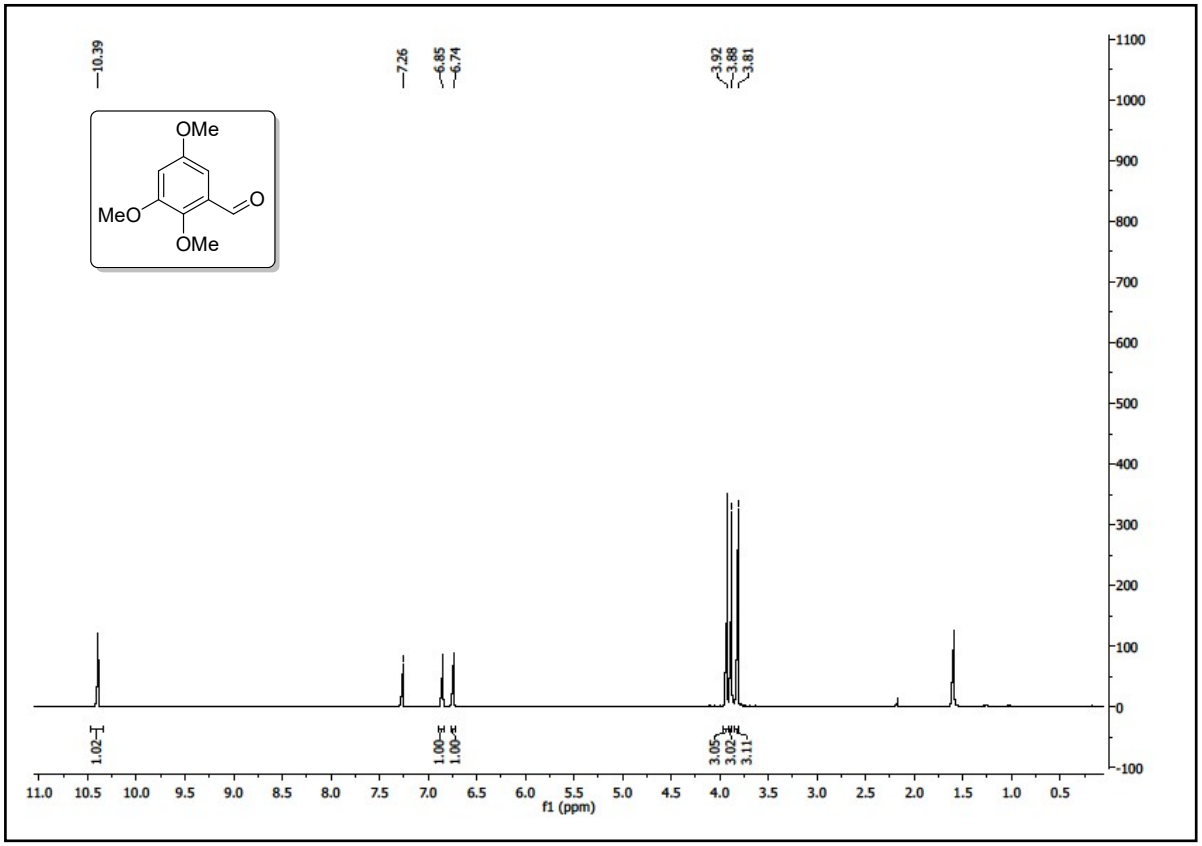
^{13}C DEPT NMR of compound 8 (125 MHz, $CDCl_3$)



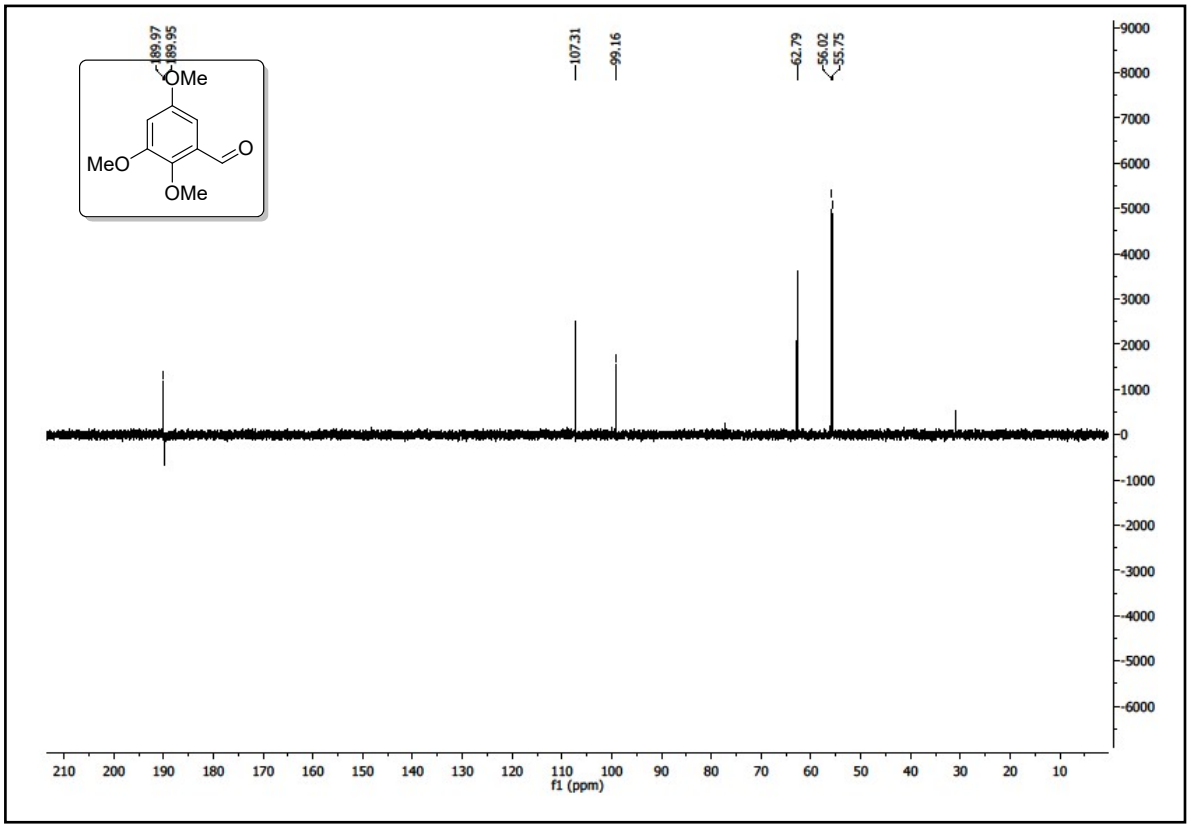
^{13}C NMR of compound 8 (125 MHz, $CDCl_3$)



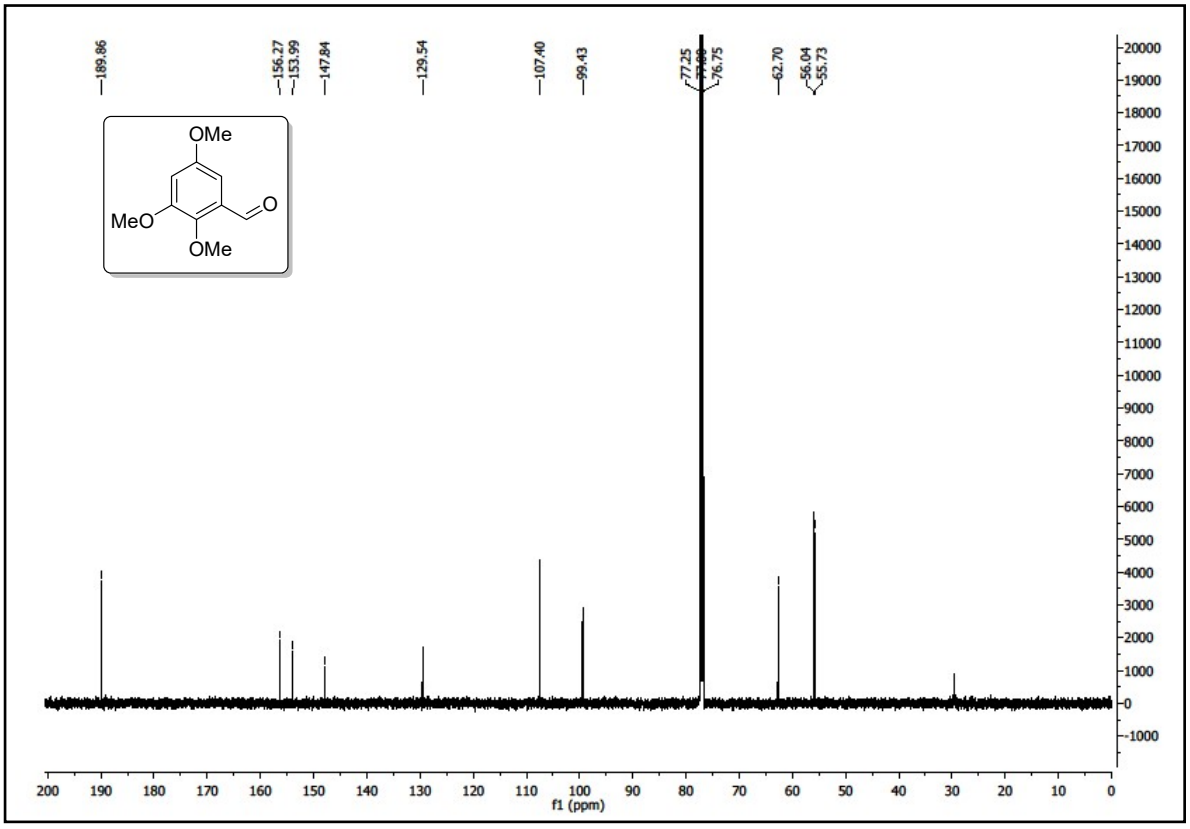
H NMR of compound 9 (400 MHz, $CDCl_3$)



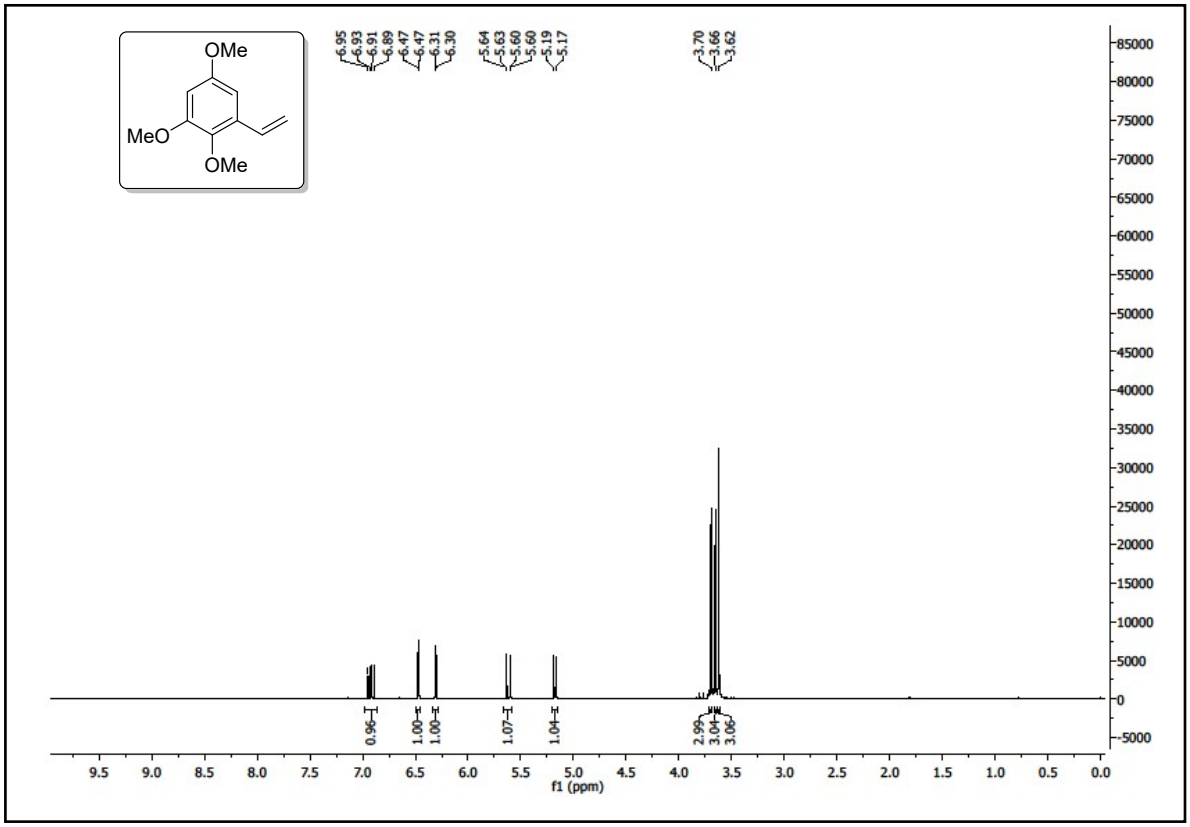
^{13}C DEPT NMR of compound 9 (125 MHz, $CDCl_3$)



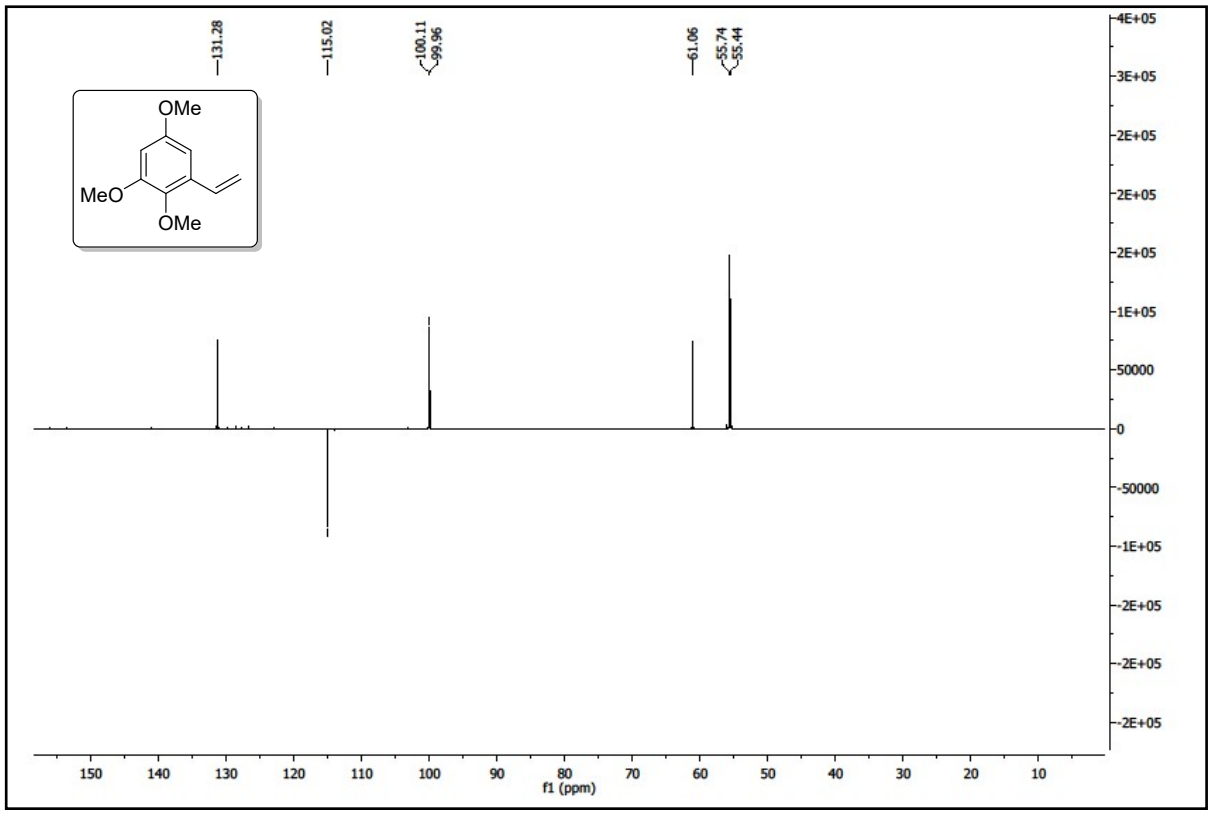
^{13}C NMR of compound 9 (125 MHz, $CDCl_3$)



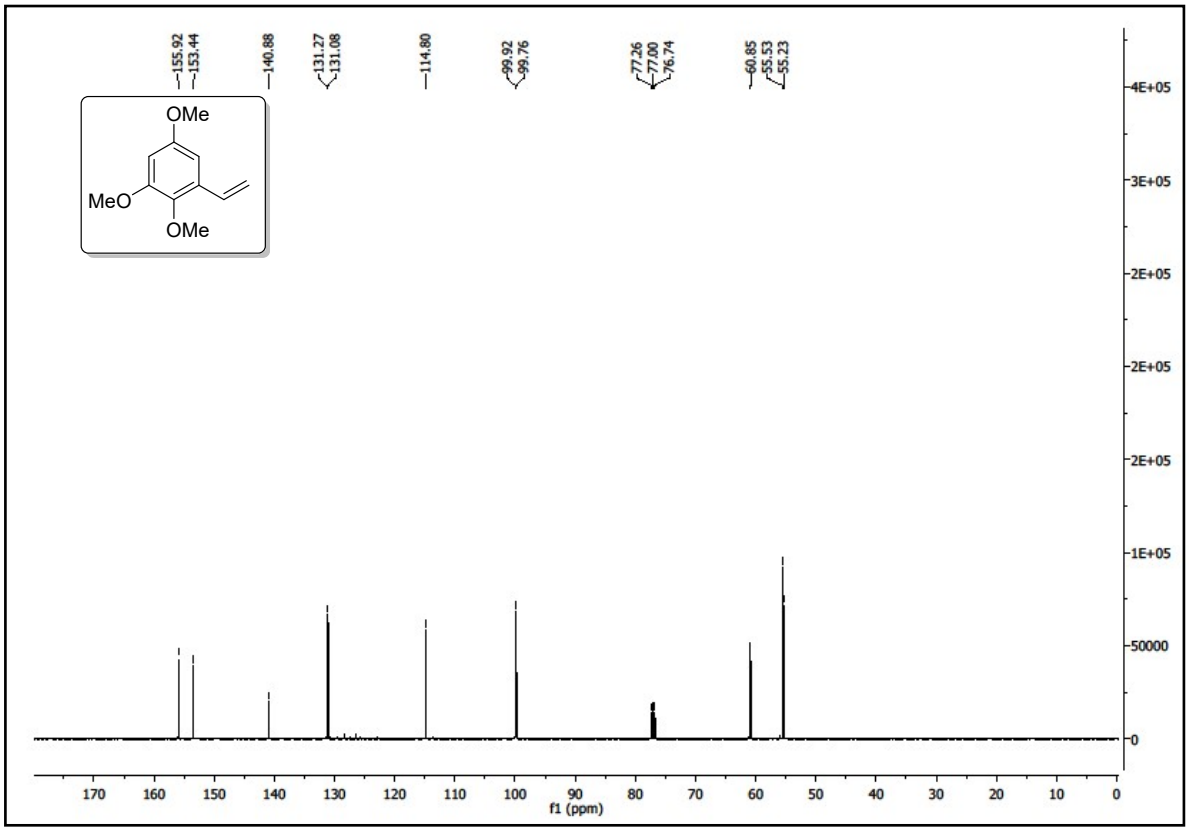
^{1}H NMR of compound 10 (500 MHz, $CDCl_3$)



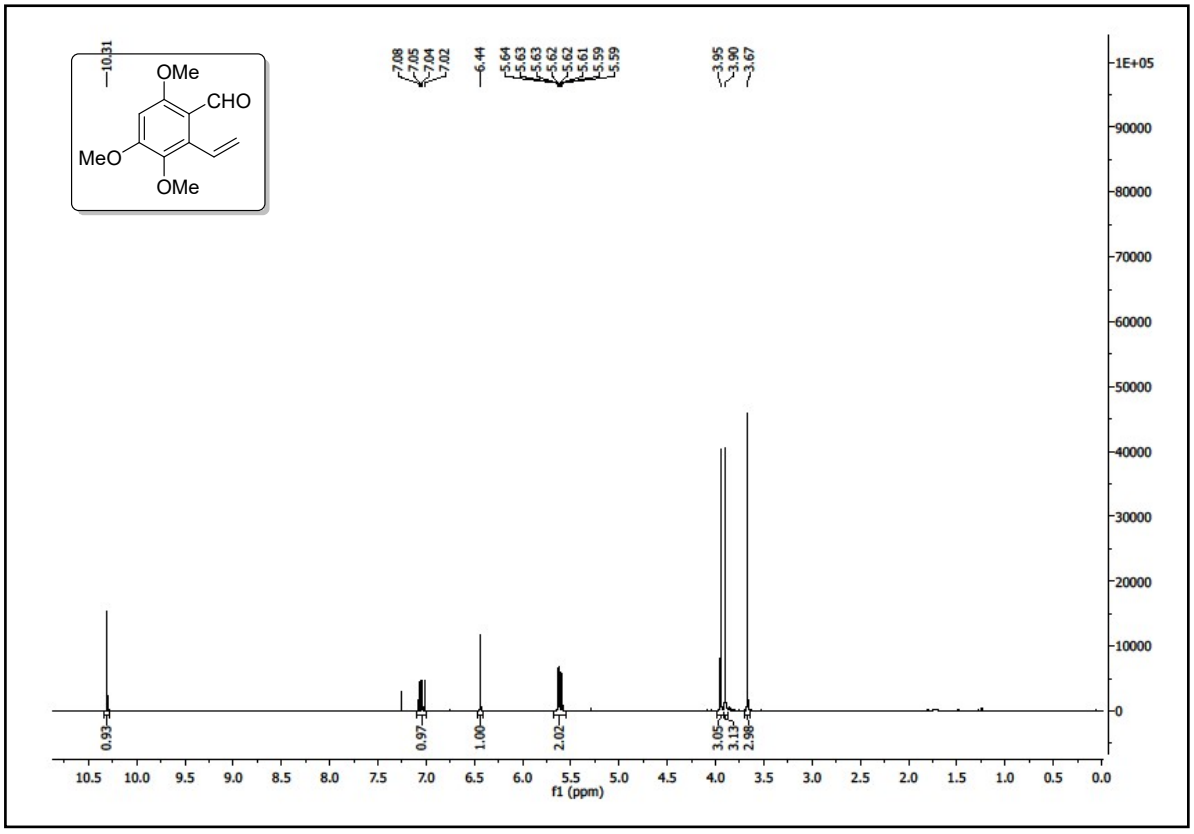
^{13}C DEPT NMR of compound 10 (125 MHz, $CDCl_3$)



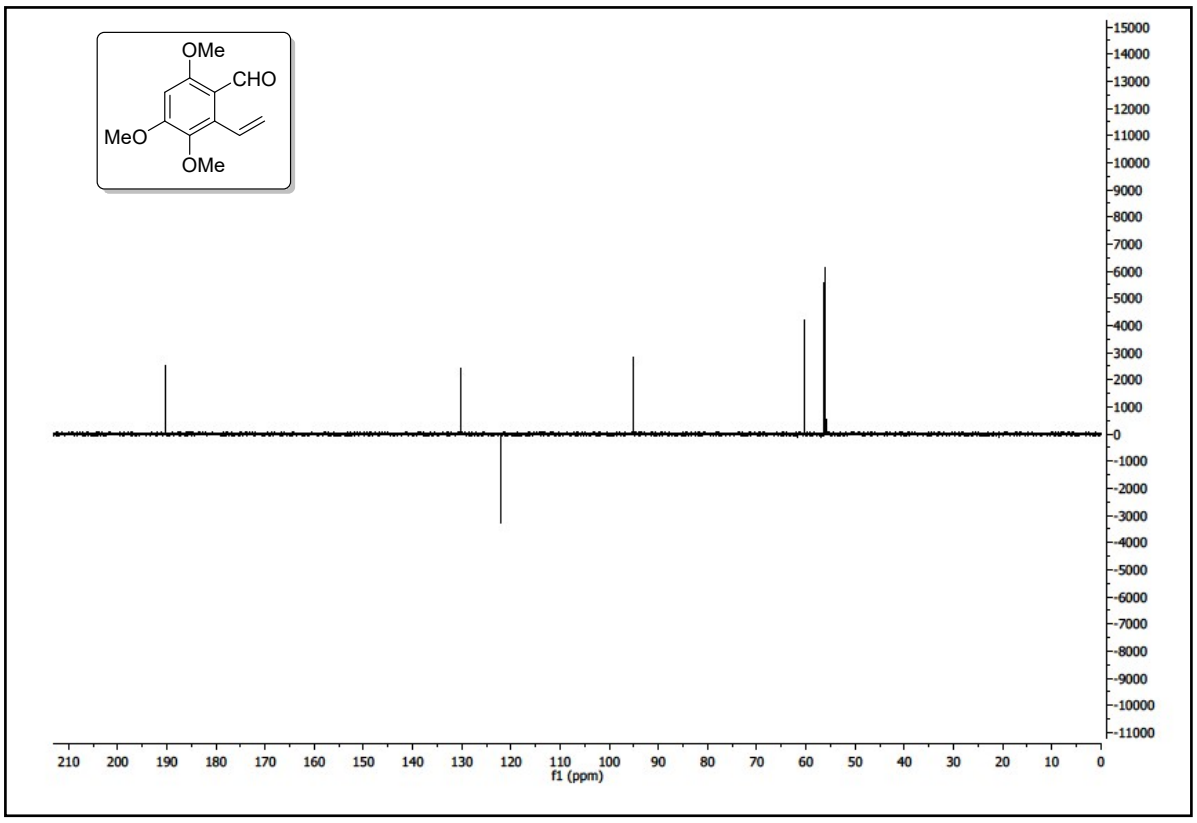
^{13}C NMR of compound 10 (125 MHz, $CDCl_3$)



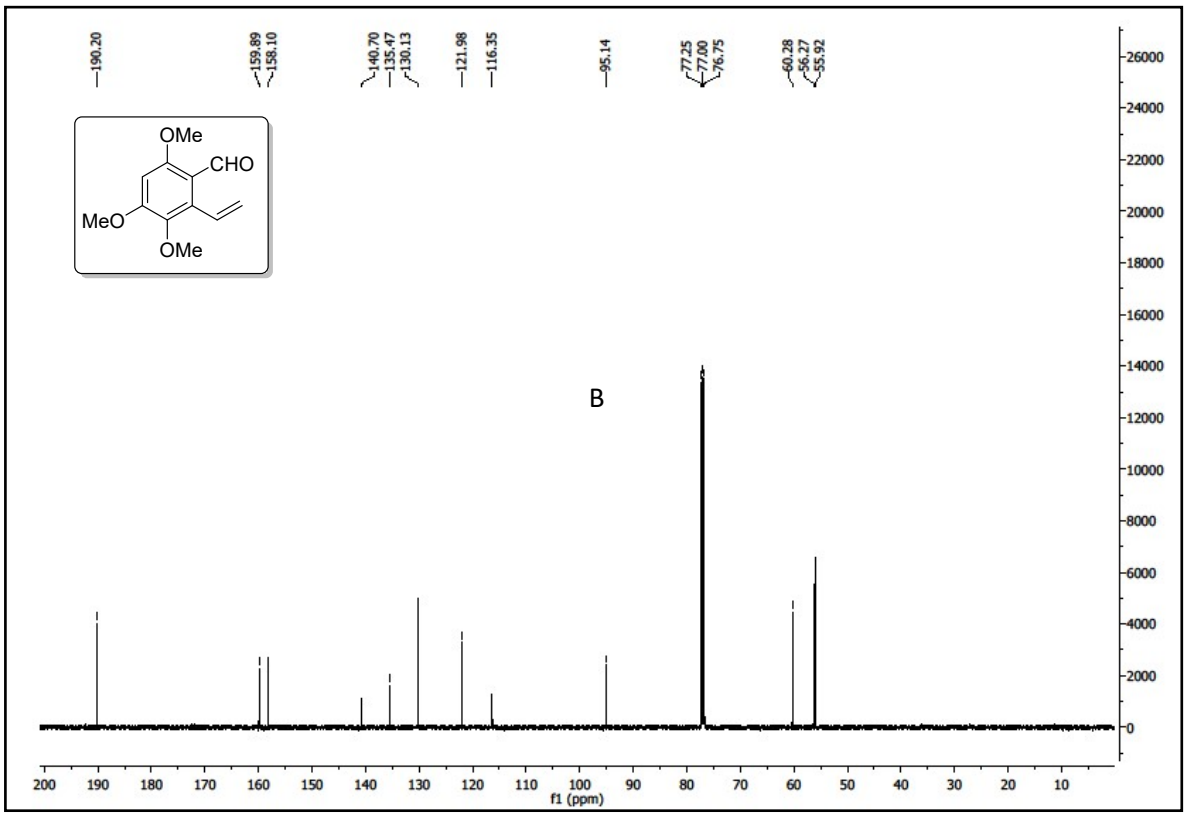
^{1}H NMR of compound 11 (500 MHz, $CDCl_3$)



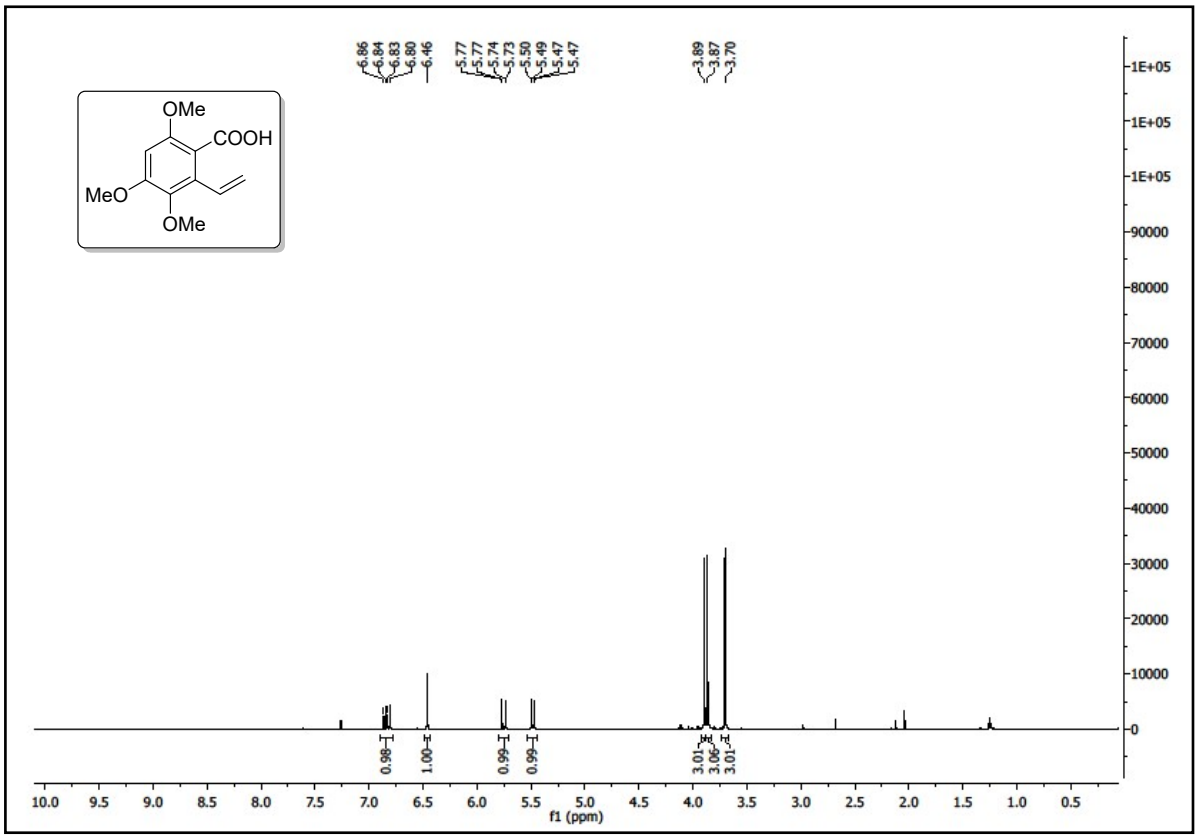
^{13}C DEPT NMR of compound 11 (125 MHz, $CDCl_3$)



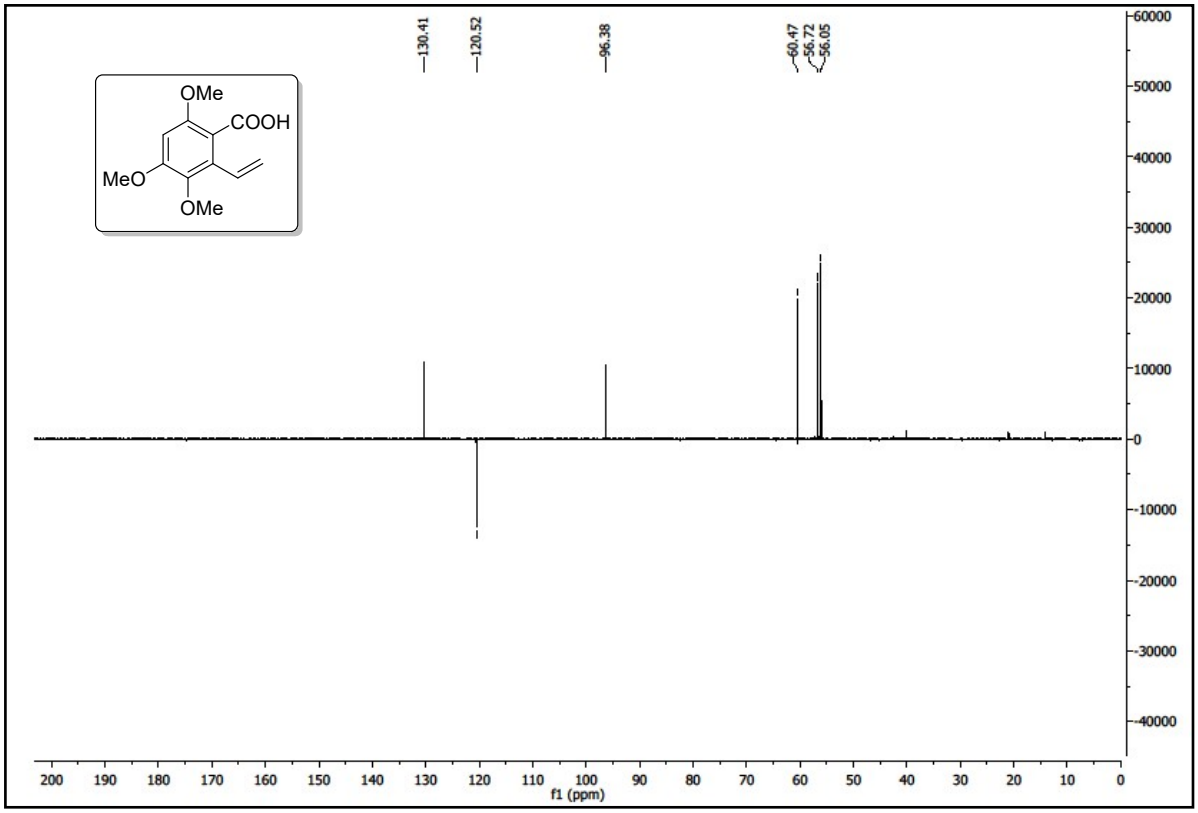
^{13}C NMR of compound 11 (125 MHz, $CDCl_3$)



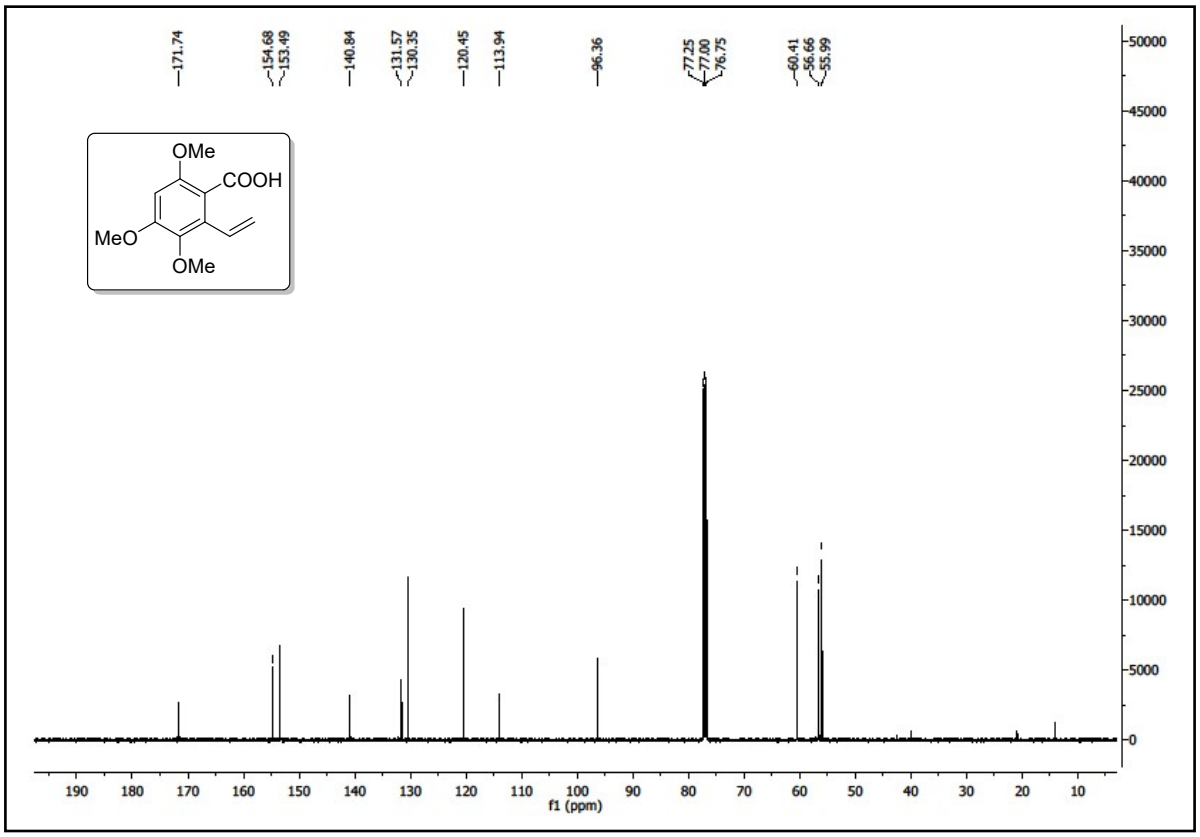
^{1}H NMR of compound 12 (500 MHz, $CDCl_3$)



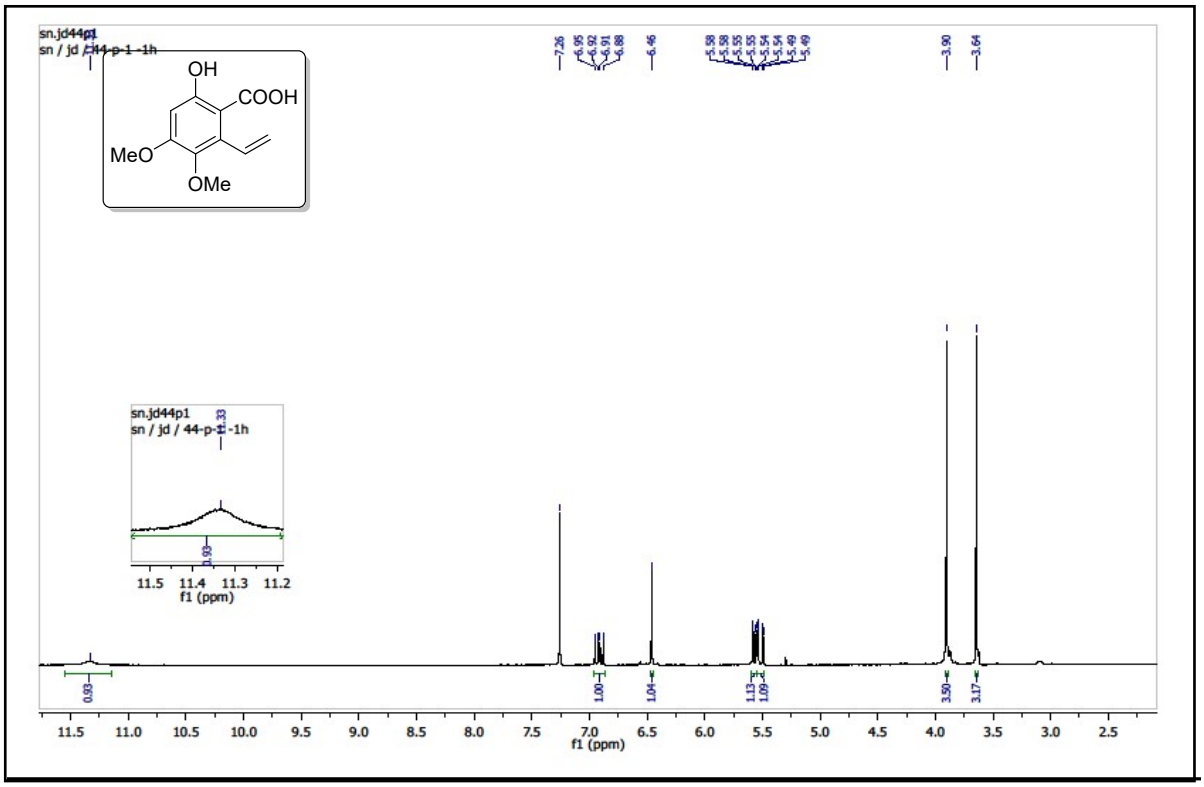
^{13}C DEPT NMR of compound 12 (126 MHz, $CDCl_3$)



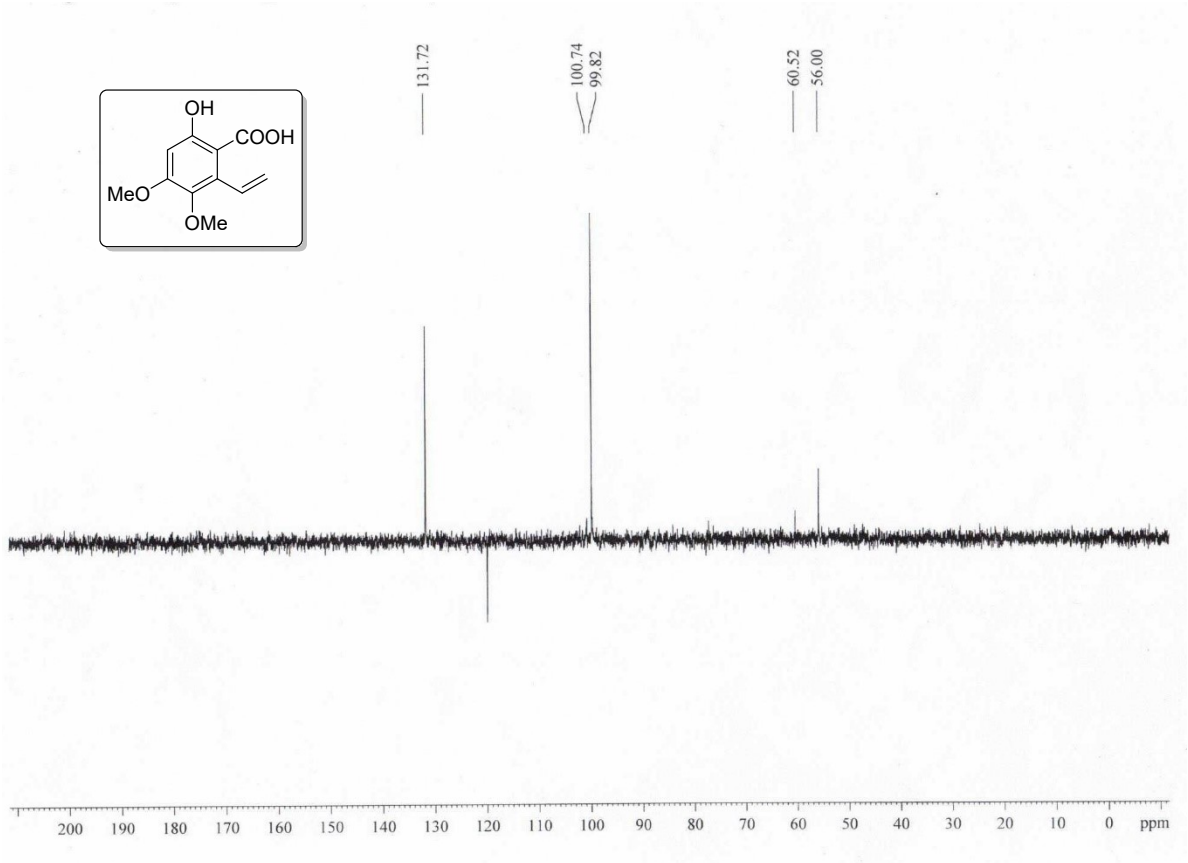
^{13}C NMR of compound 12 (126 MHz, $CDCl_3$)



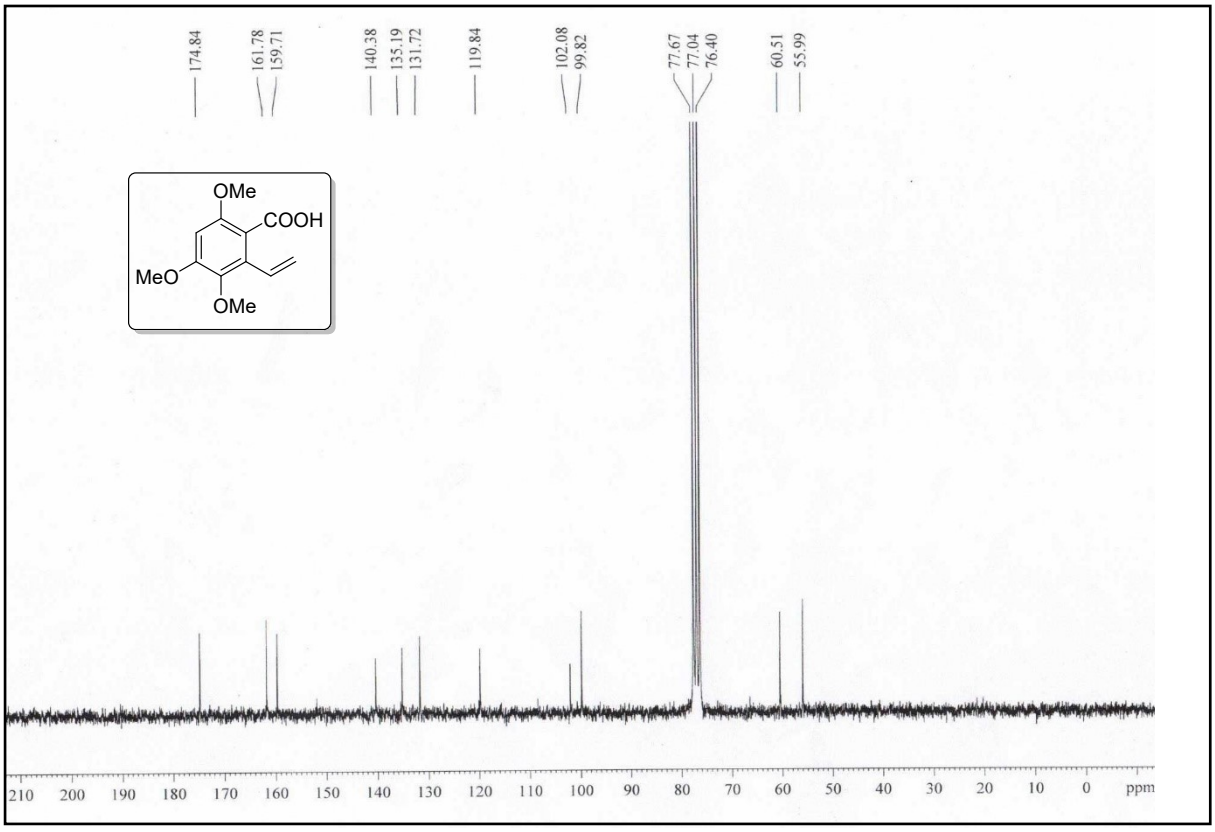
^{1}H NMR of compound 13 (500 MHz, $CDCl_3$)



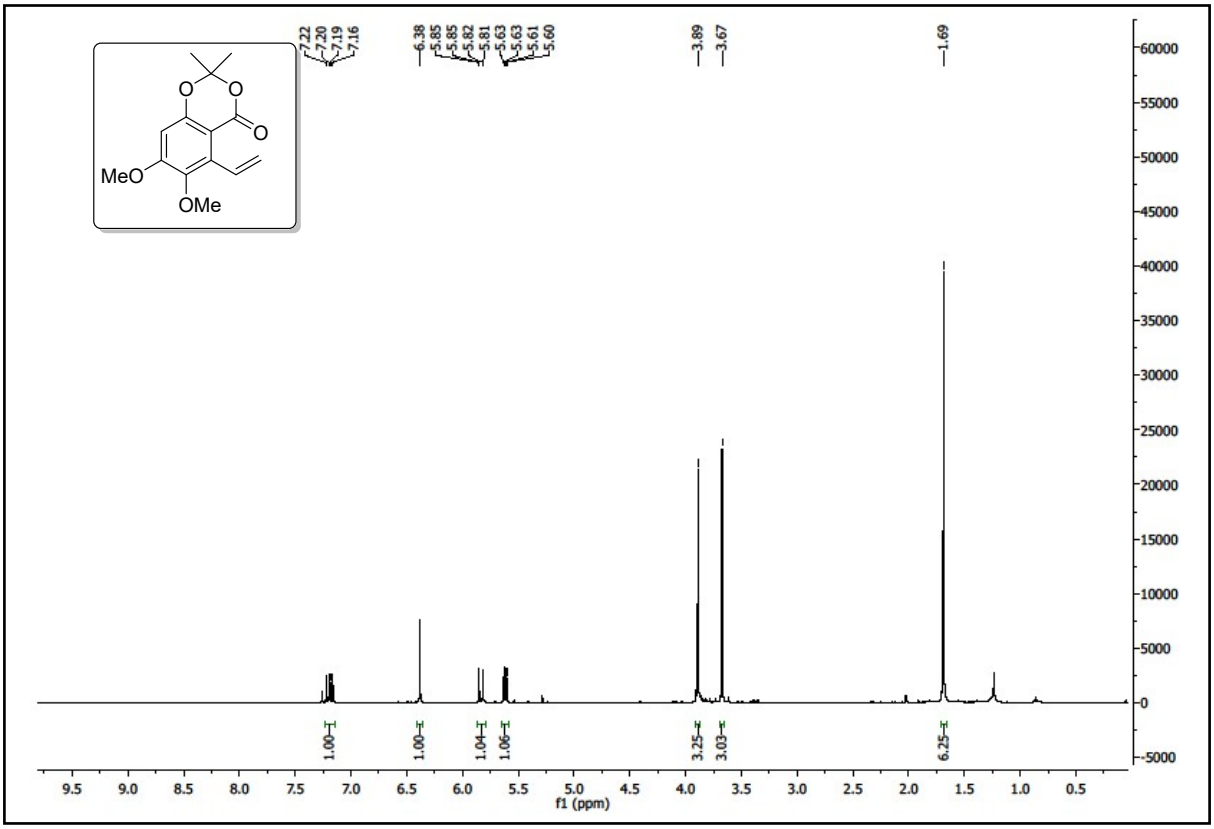
^{13}C DEPT NMR of compound 13 (126 MHz, $CDCl_3$)



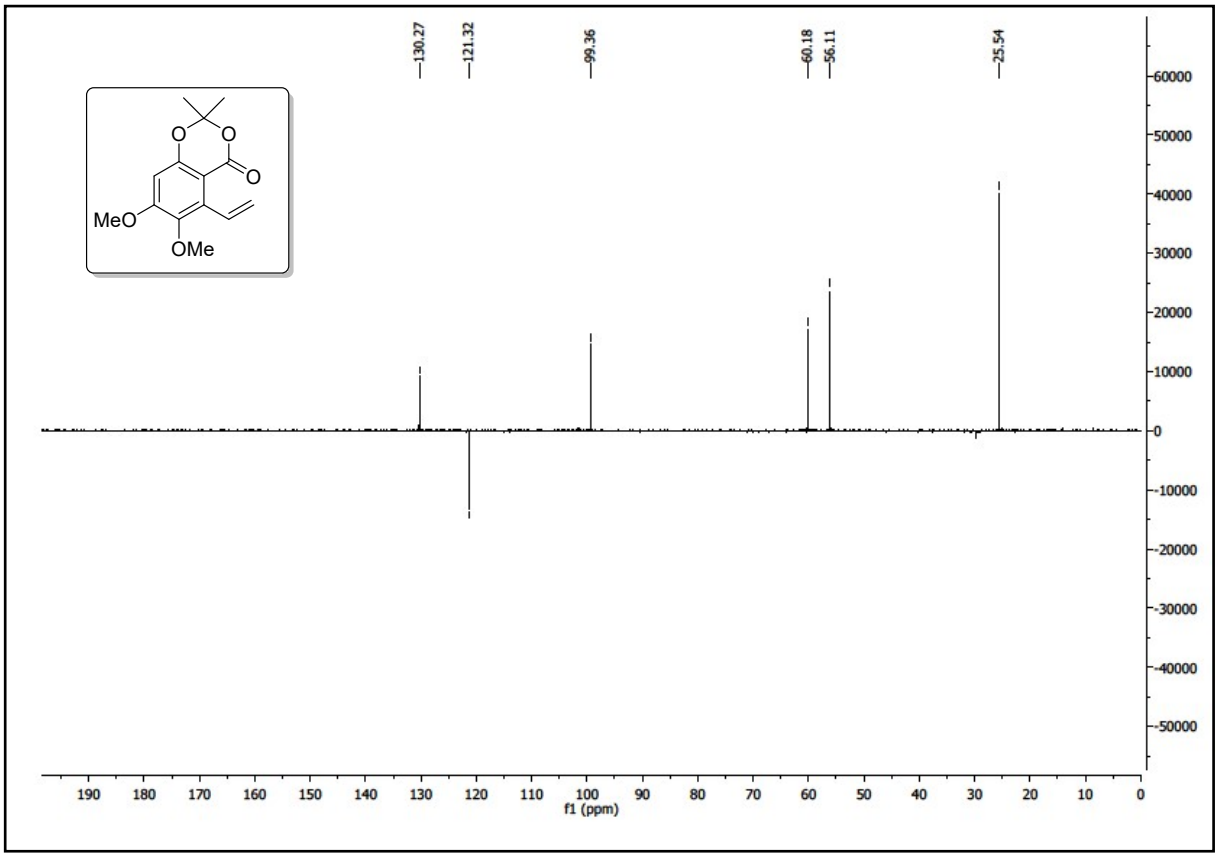
^{13}C NMR of compound 13 (126 MHz, $CDCl_3$)



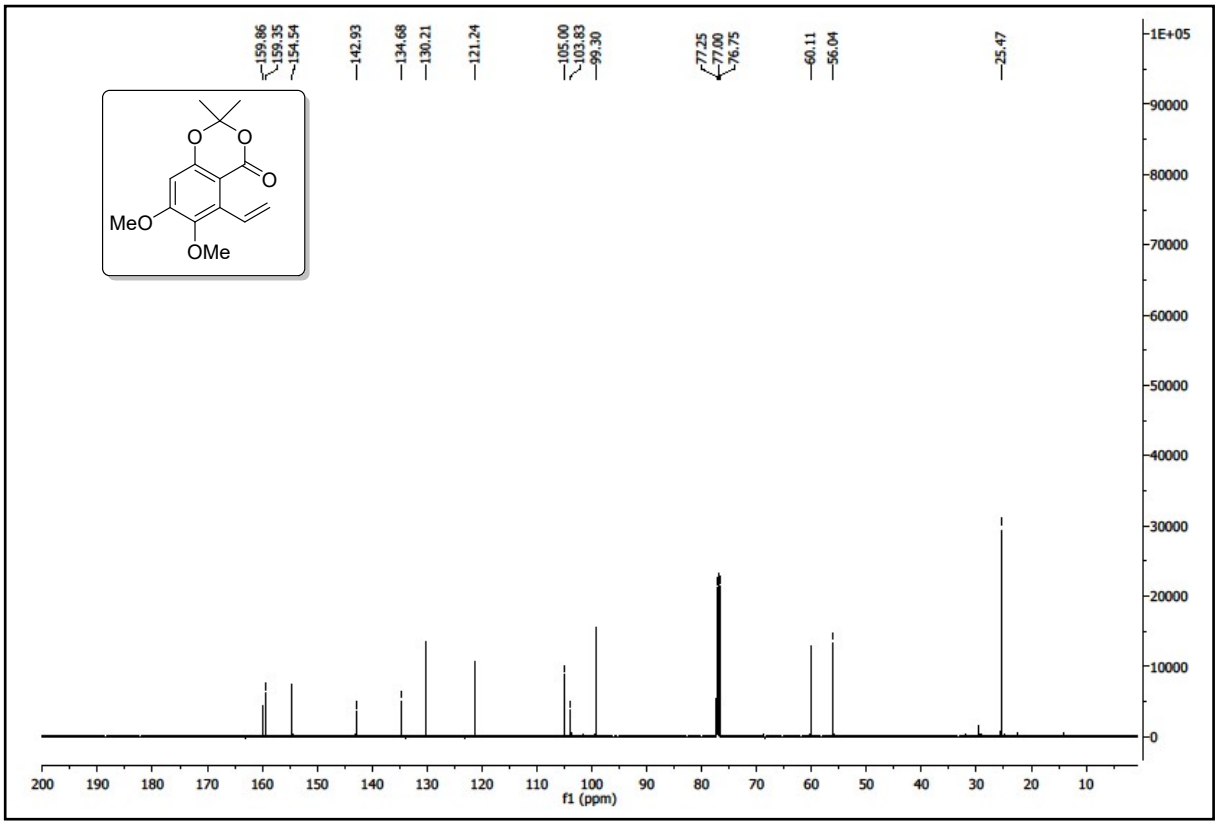
^{1}H NMR of compound 14 (500 MHz, $CDCl_3$)



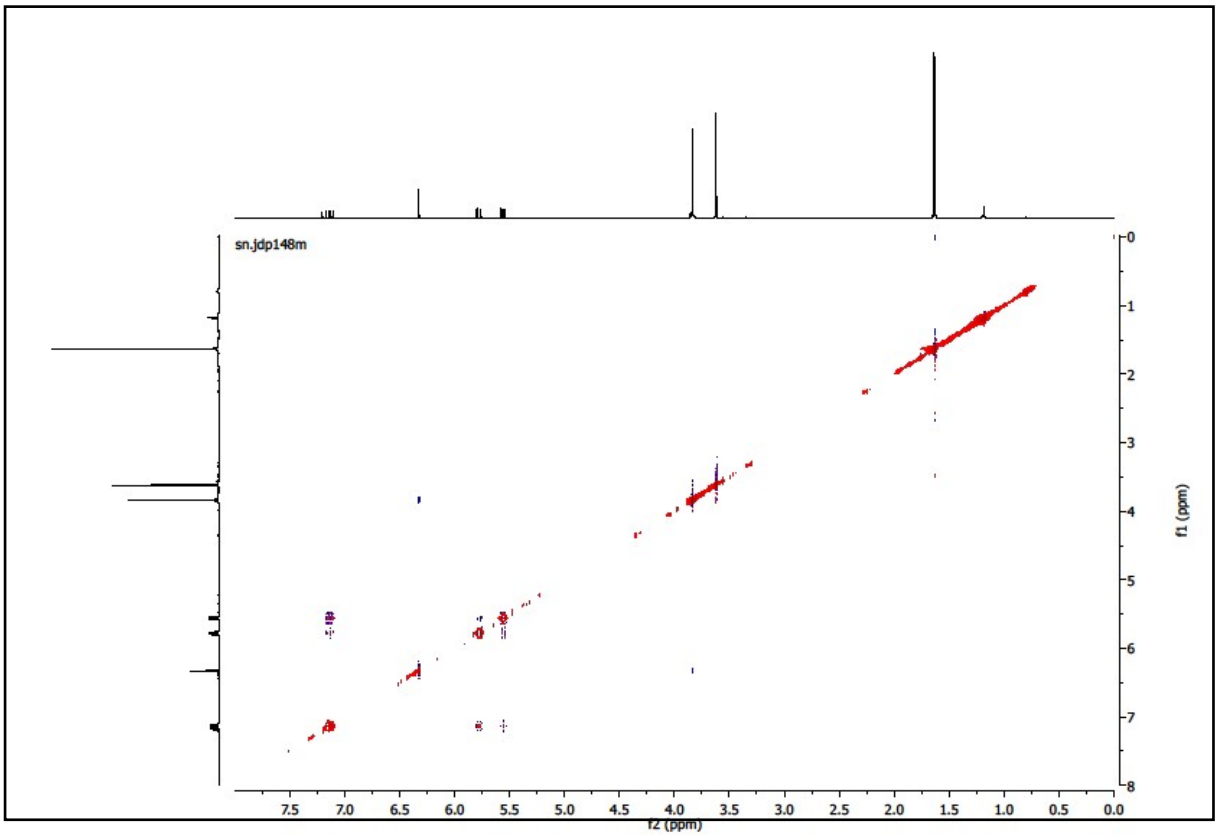
^{13}C DEPT NMR of compound 14 (125 MHz, $CDCl_3$)



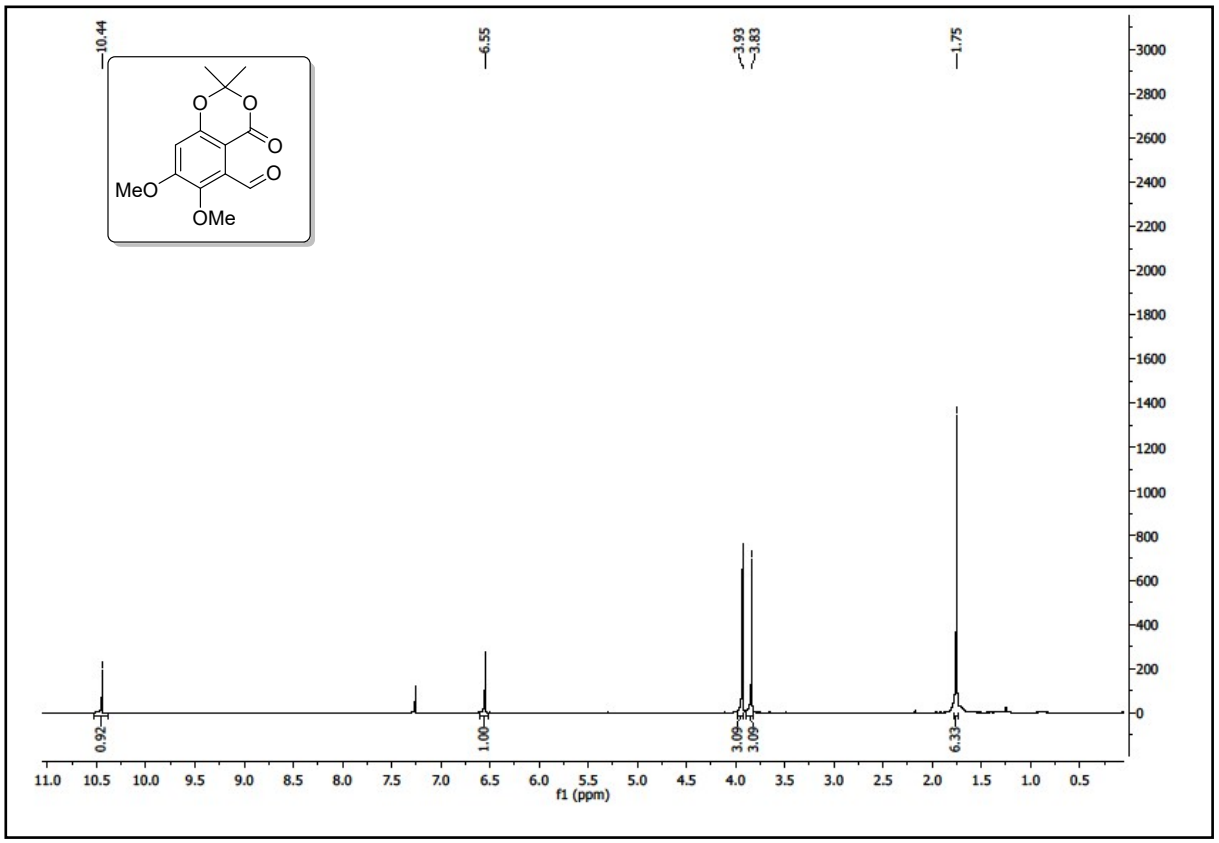
^{13}C NMR of compound 14 (125 MHz, $CDCl_3$)



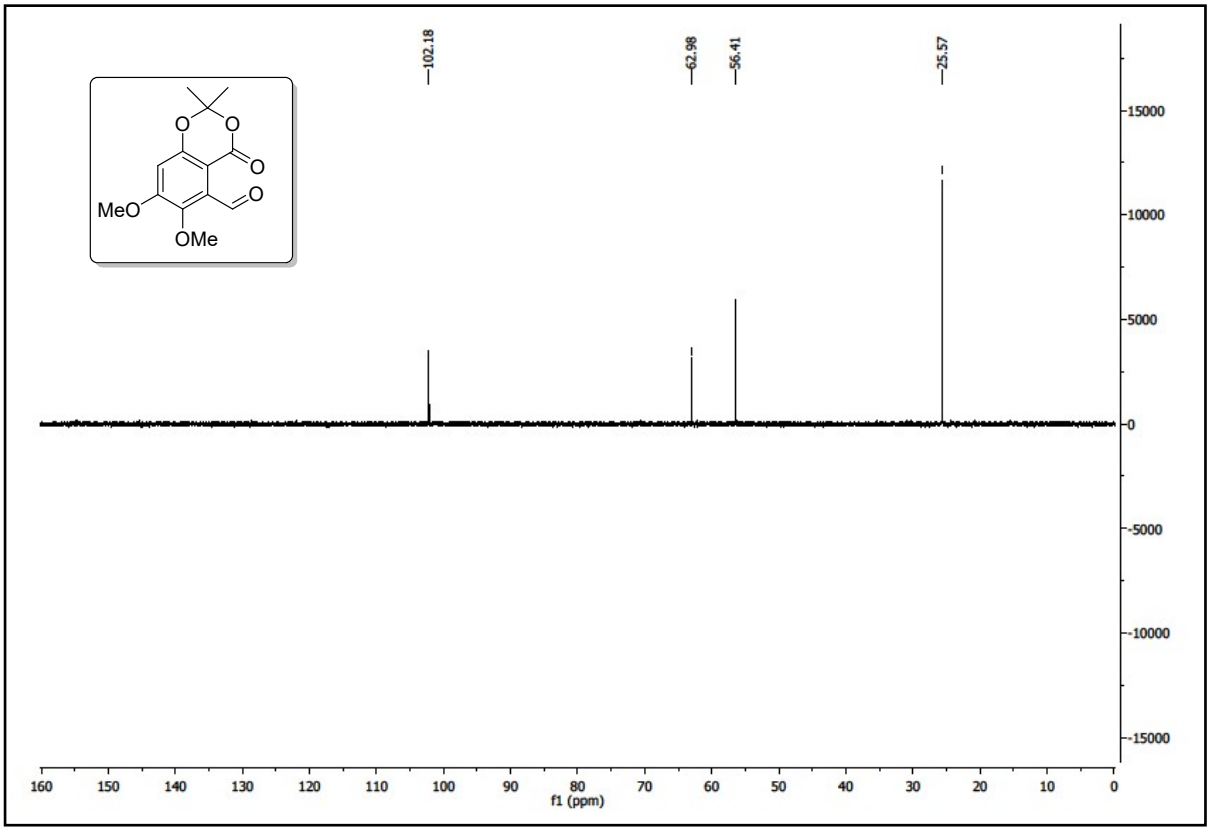
2D NOESY NMR (500 MHz)of compound 14 in $CDCl_3$



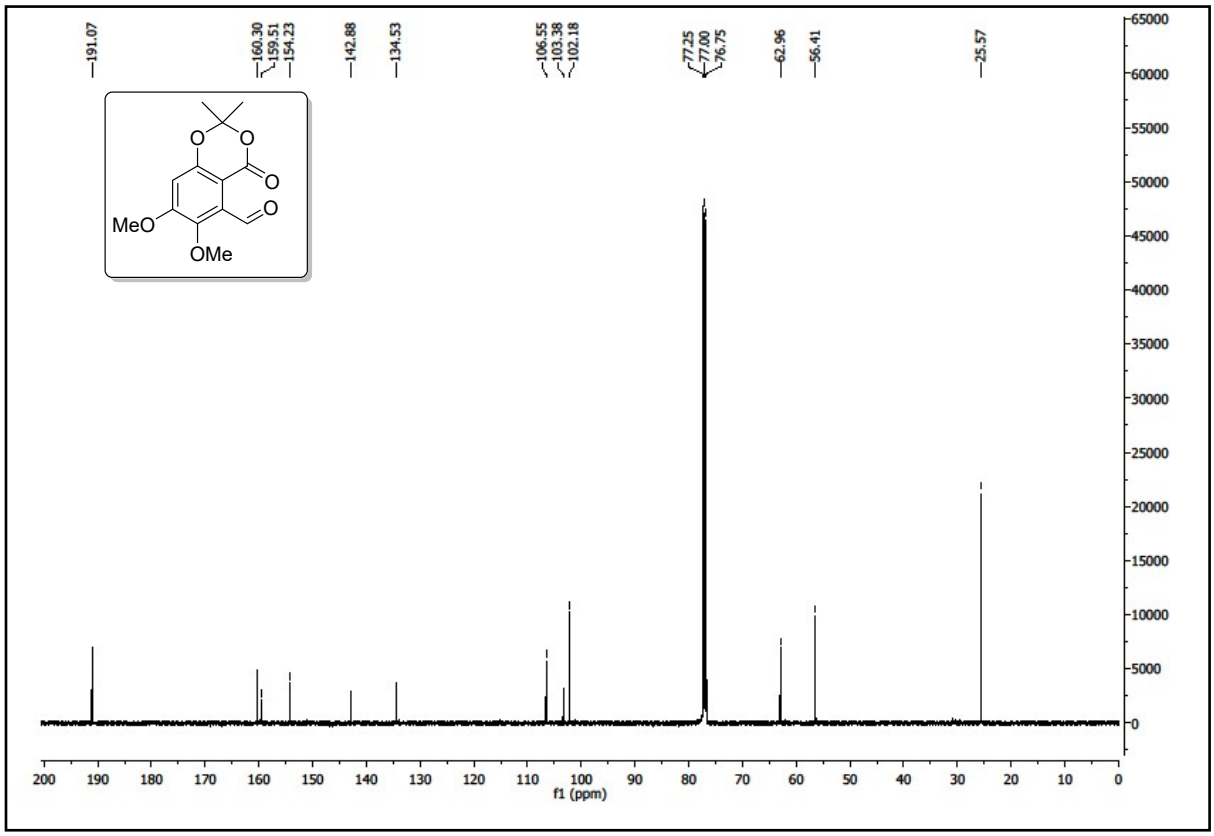
^{1}H NMR of compound 29 (500 MHz, $CDCl_3$)



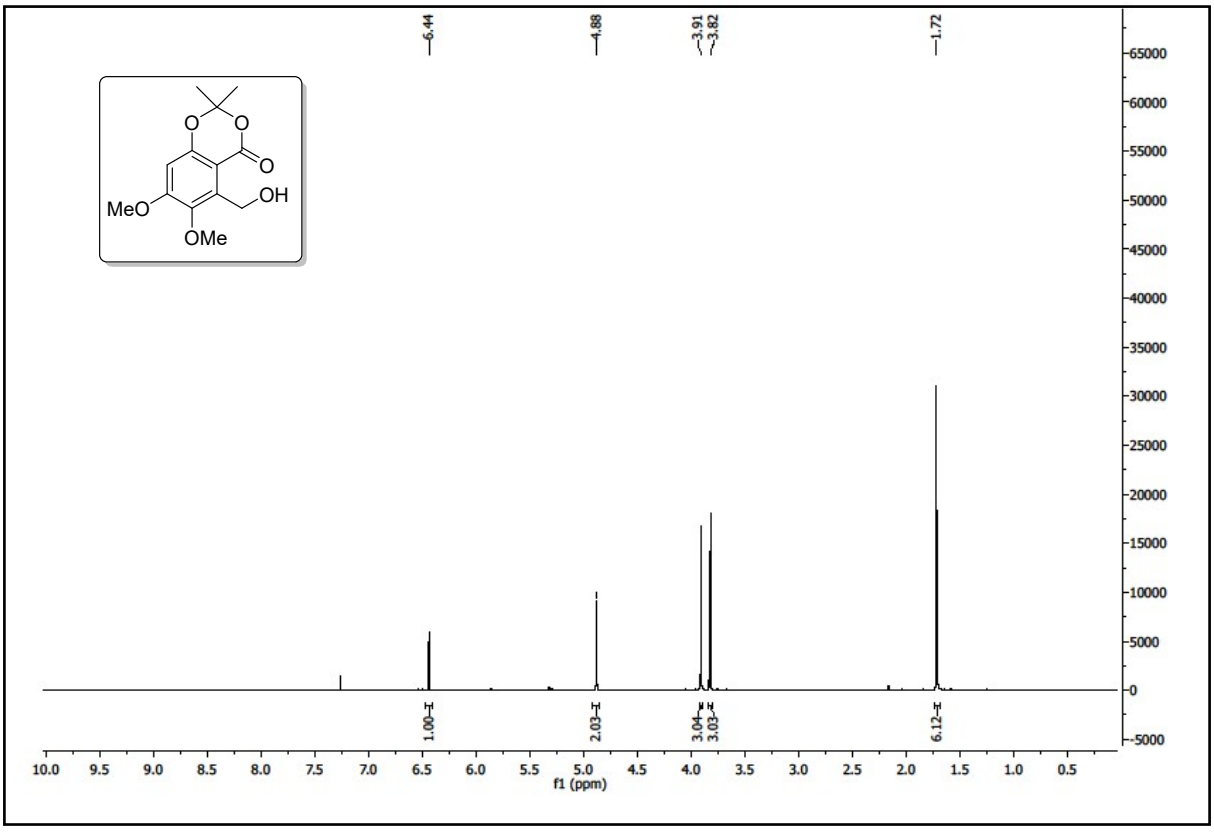
^{13}C DEPT NMR of compound 29 (125 MHz, $CDCl_3$)



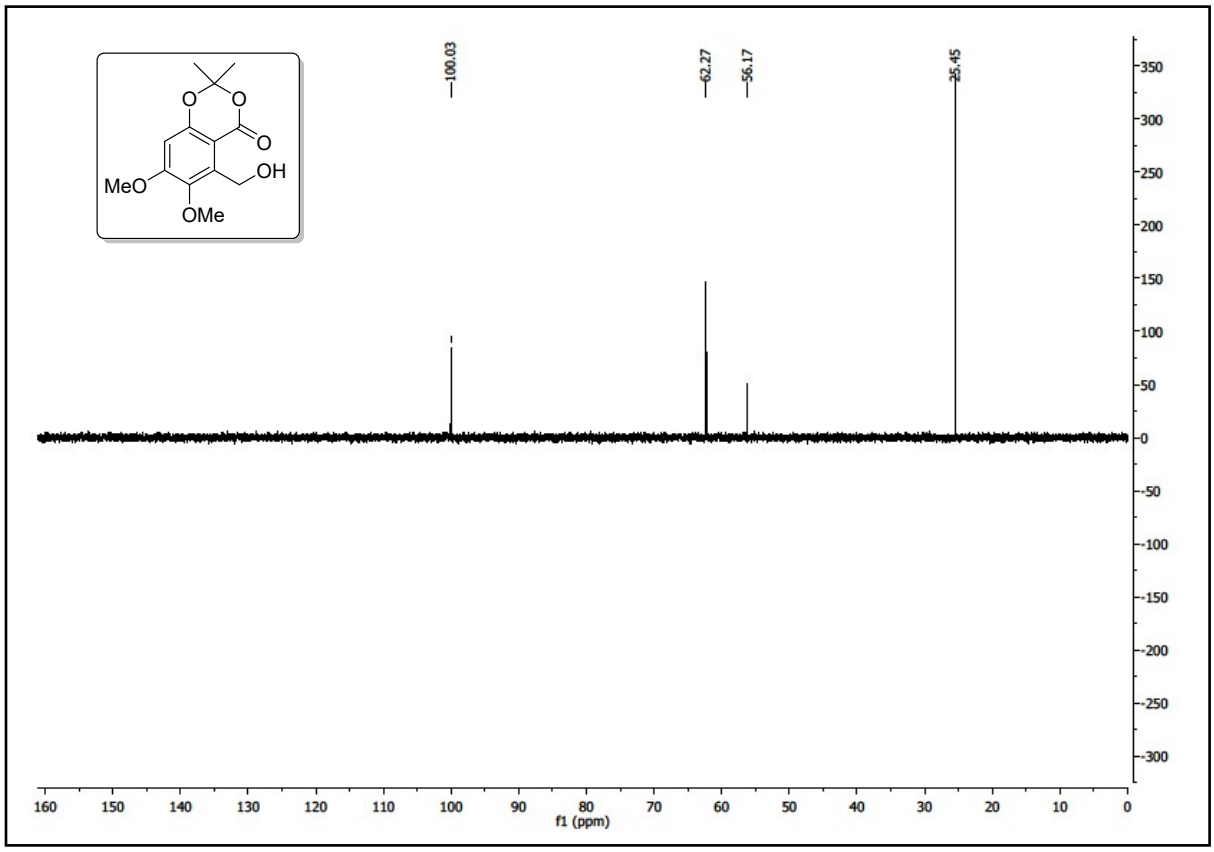
^{13}C NMR of compound 29 (125 MHz, $CDCl_3$)



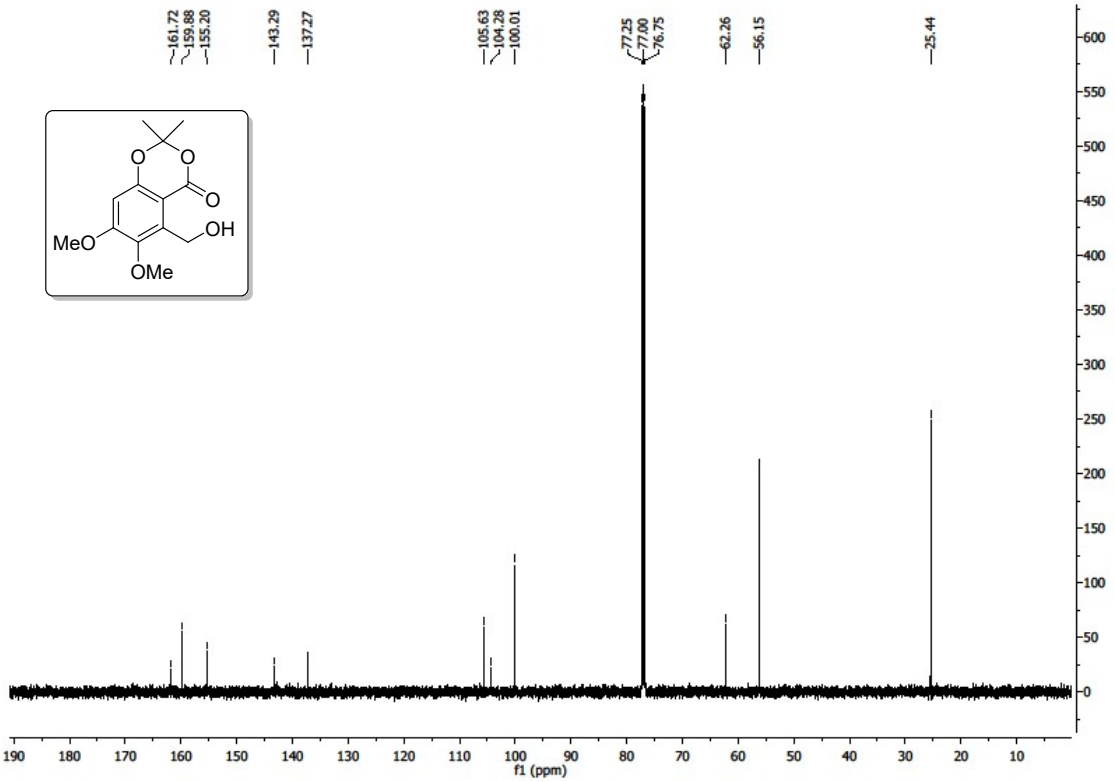
^{1}H NMR of compound 30 (500 MHz, $CDCl_3$)



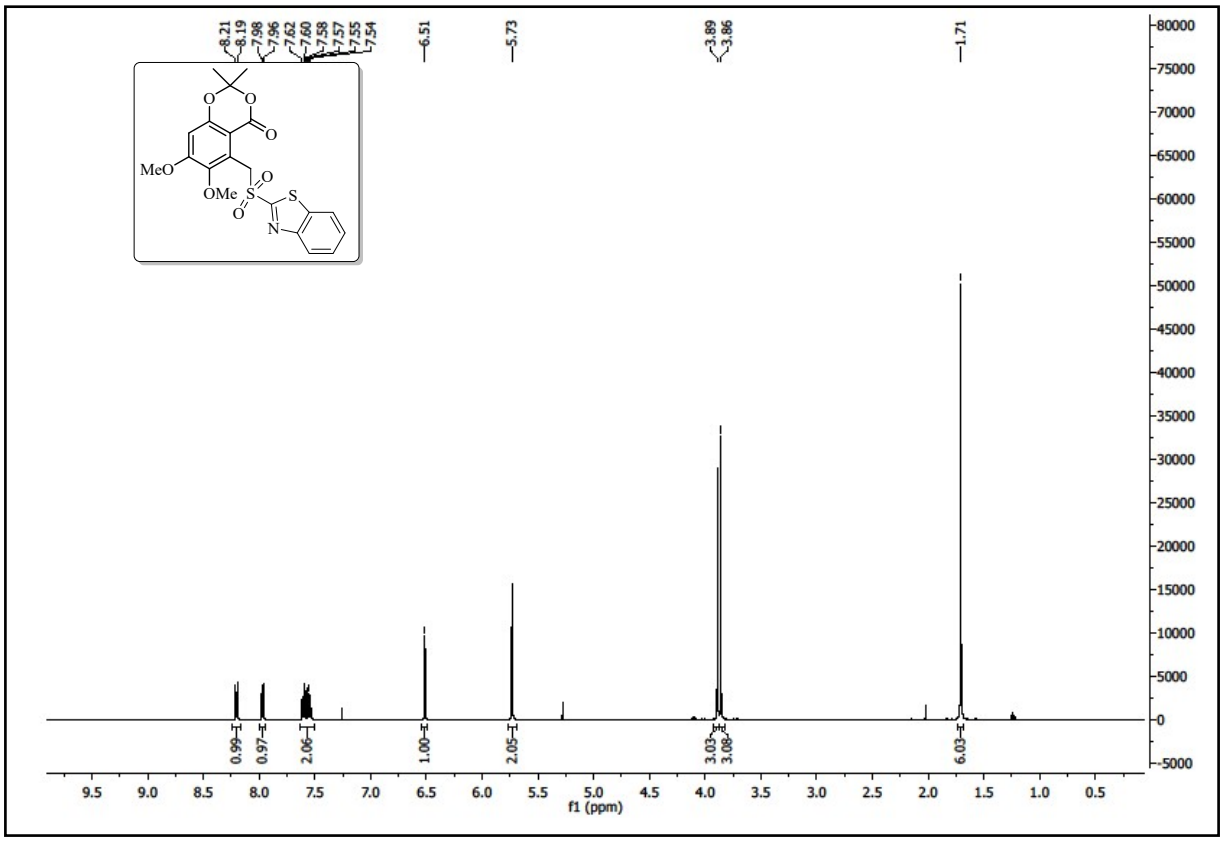
^{13}C DEPT NMR of compound 30 (125 MHz, $CDCl_3$)



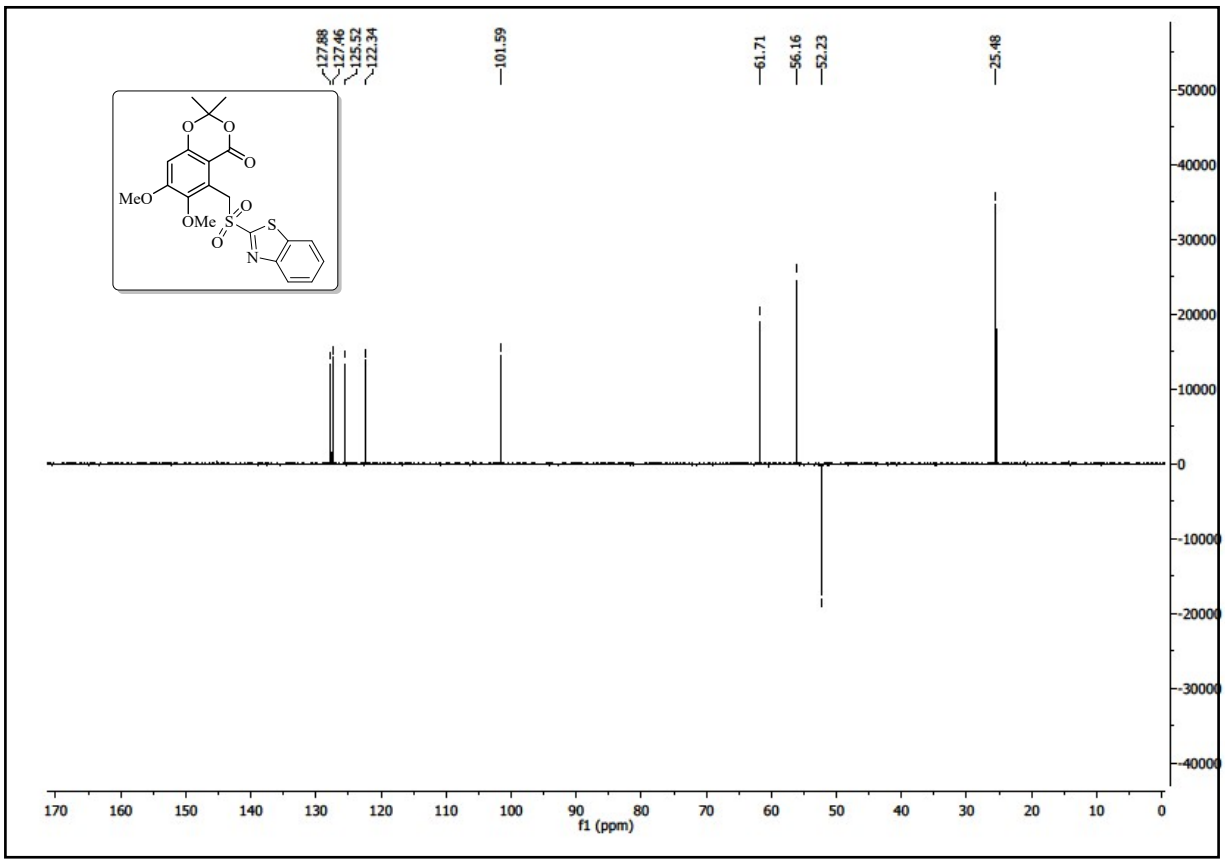
^{13}C NMR of compound 30 (125 MHz, $CDCl_3$)



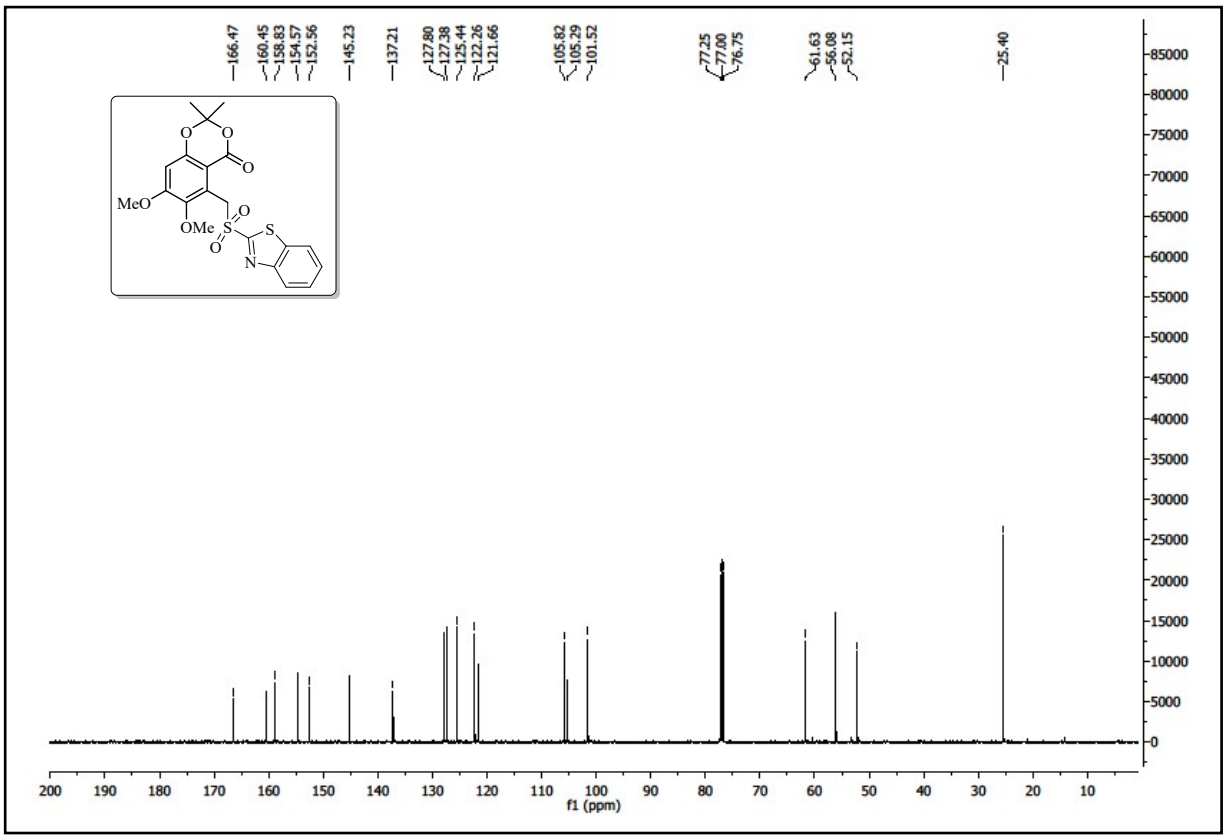
^{1}H NMR of compound 31 (500 MHz, $CDCl_3$)



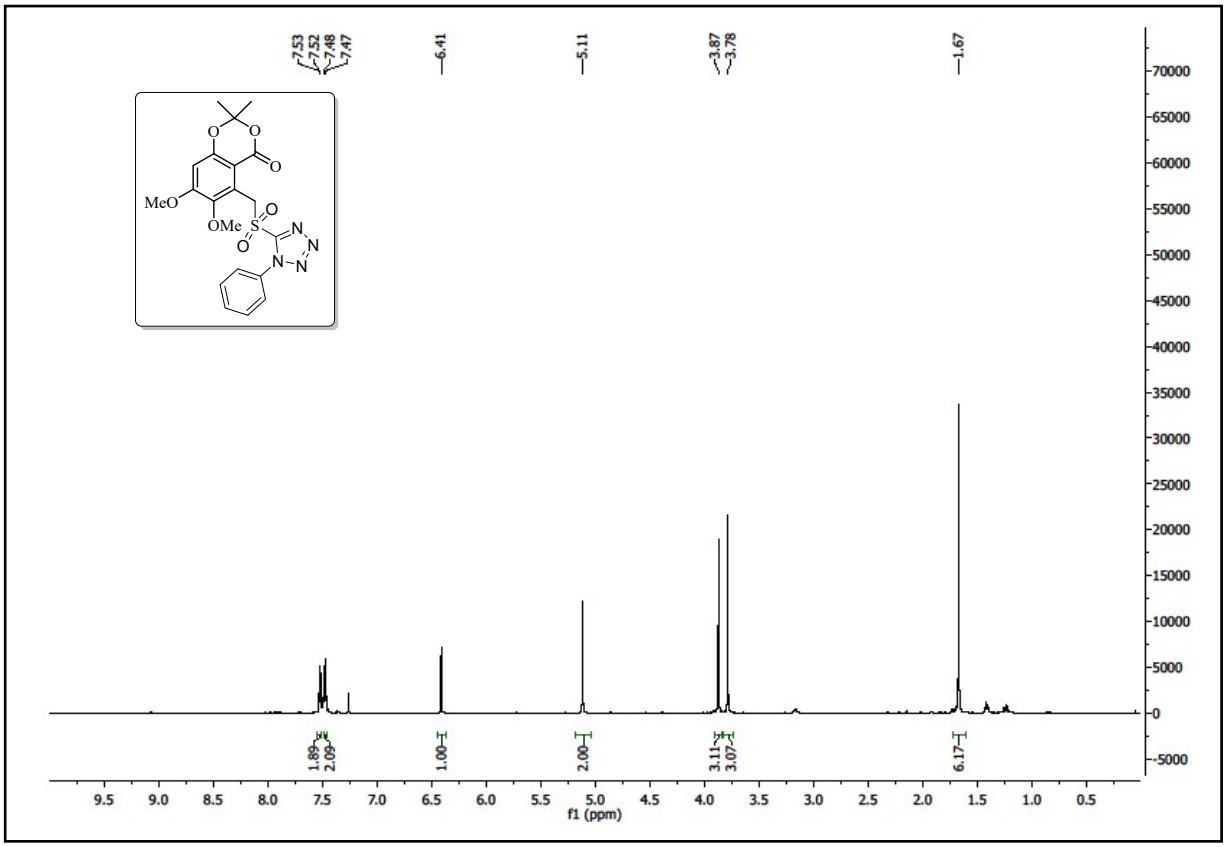
^{13}C DEPT NMR of compound 31 (125 MHz, $CDCl_3$)



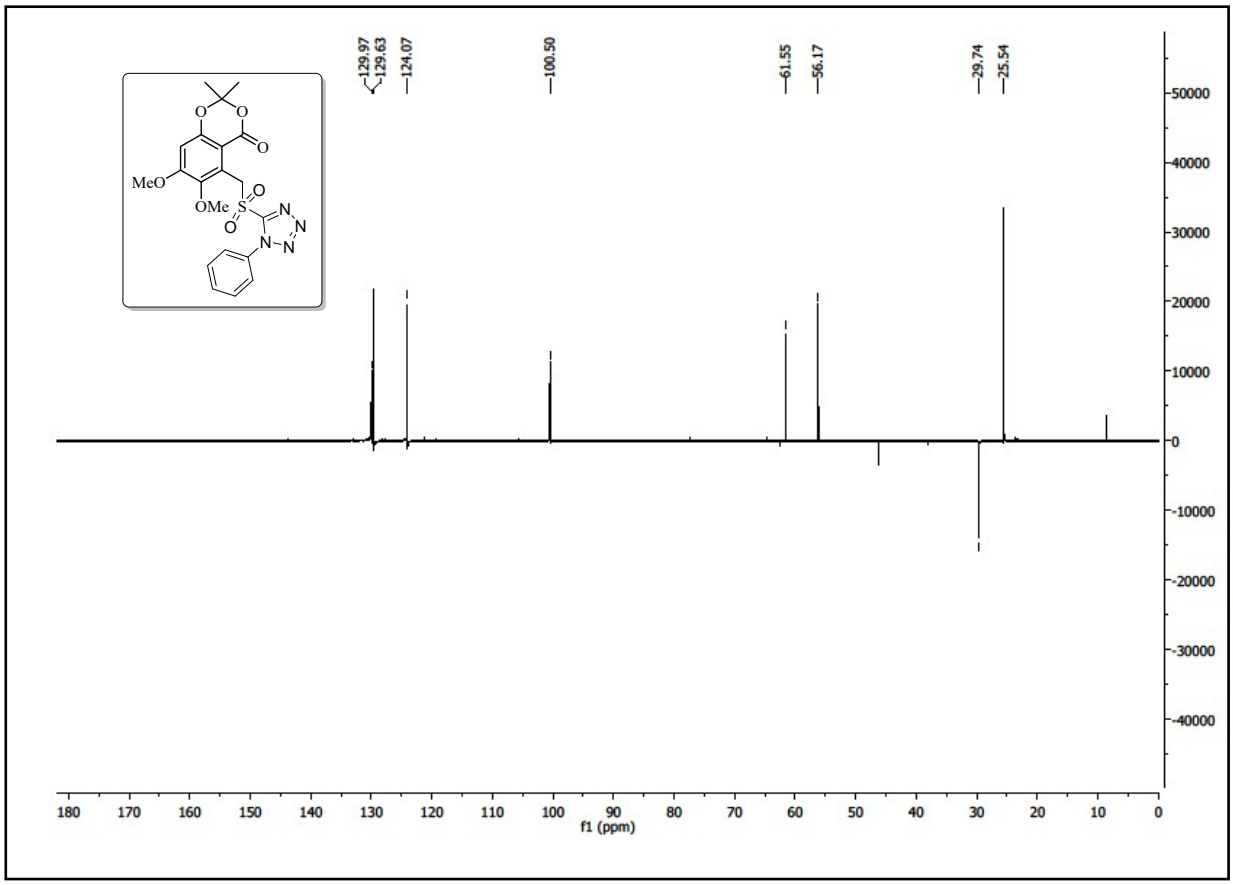
^{13}C NMR of compound 31 (125 MHz, $CDCl_3$)



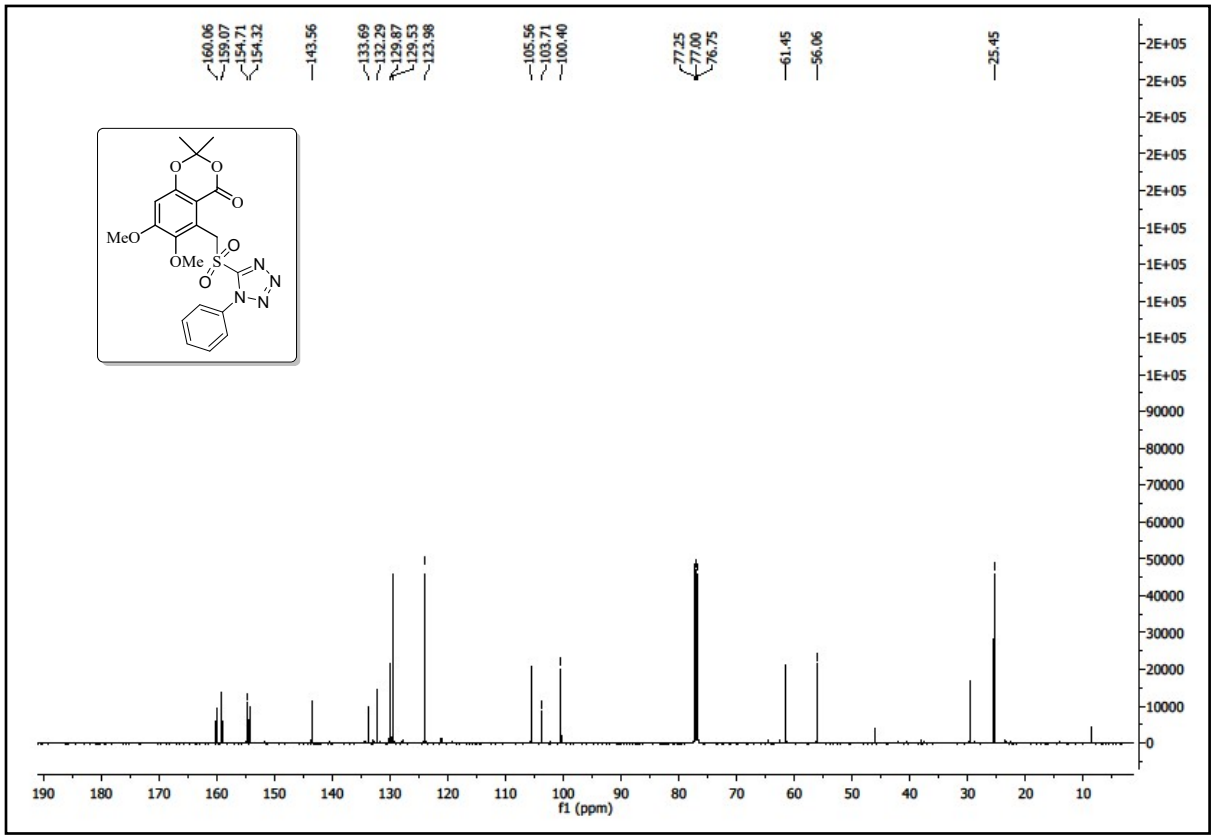
^{1}H NMR of compound 32 (500 MHz, $CDCl_3$)



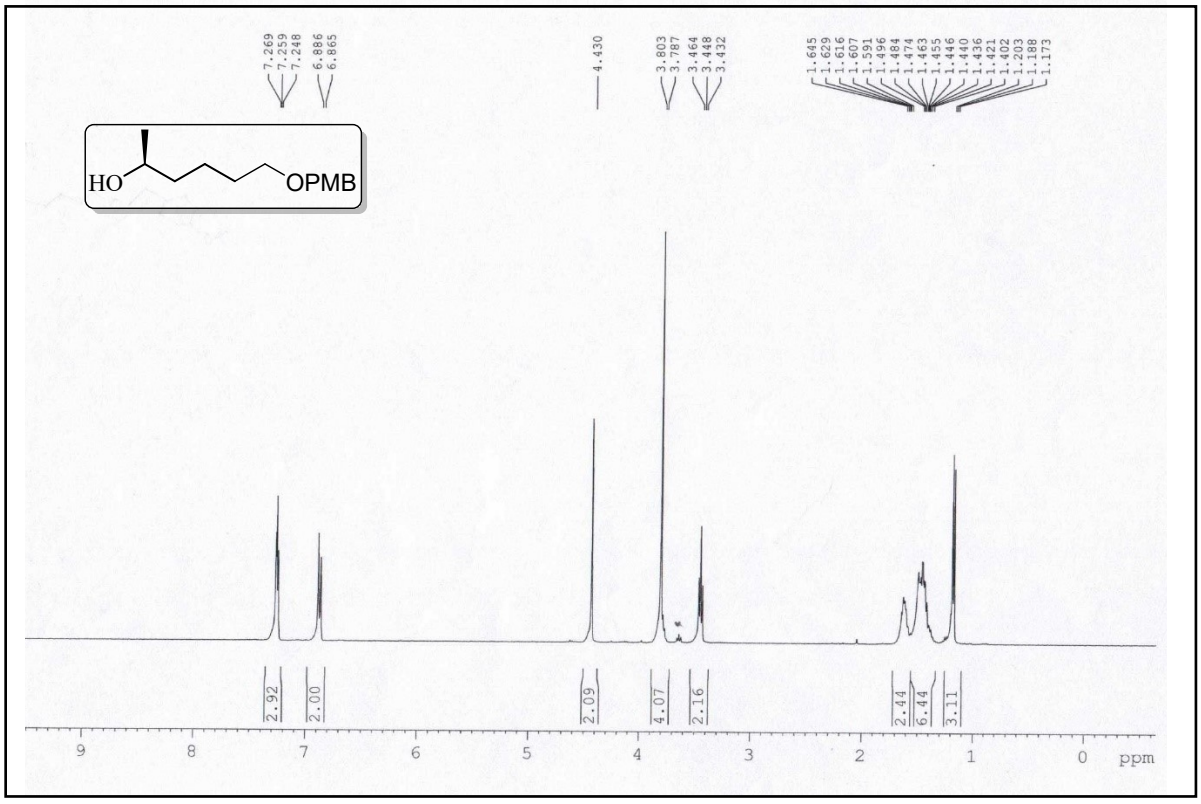
^{13}C DEPT NMR of compound 32 (125 MHz, $CDCl_3$)



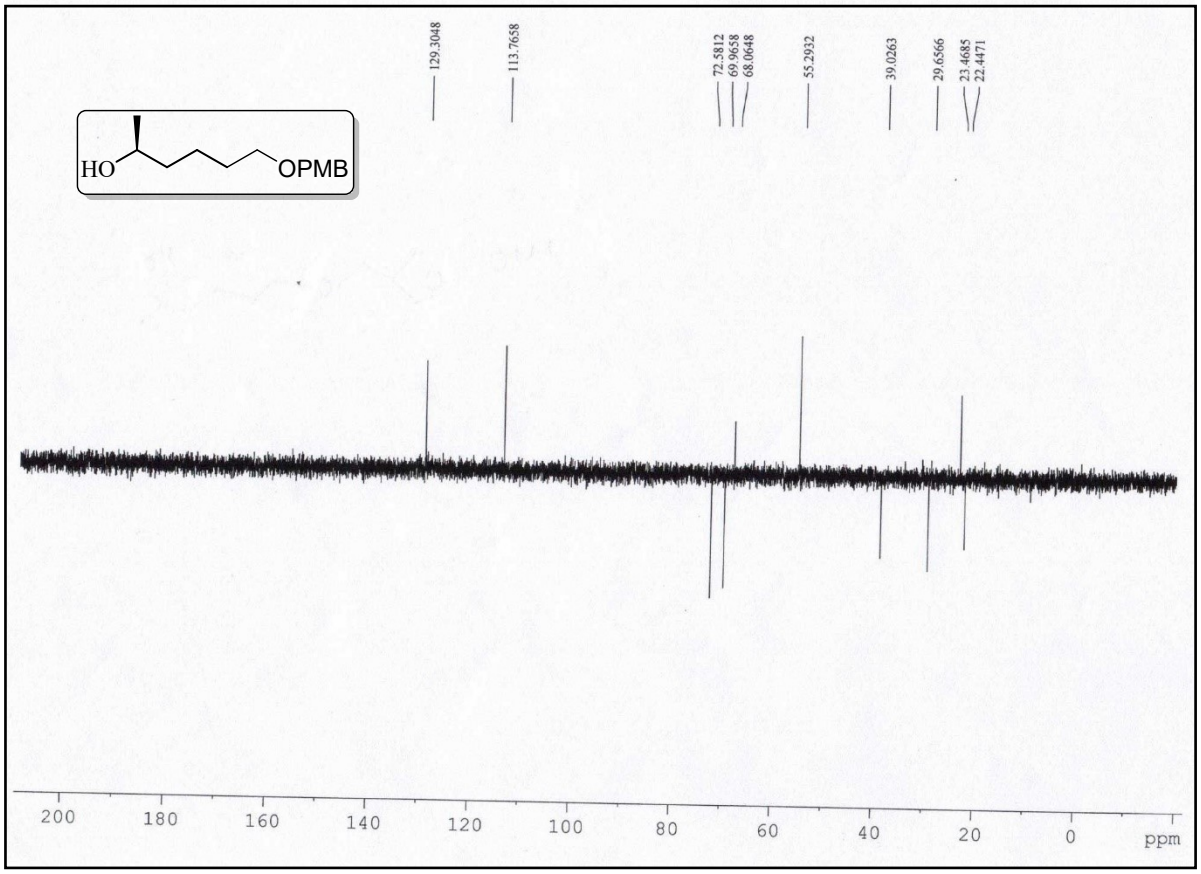
^{13}C NMR of compound 32 (125 MHz, $CDCl_3$)



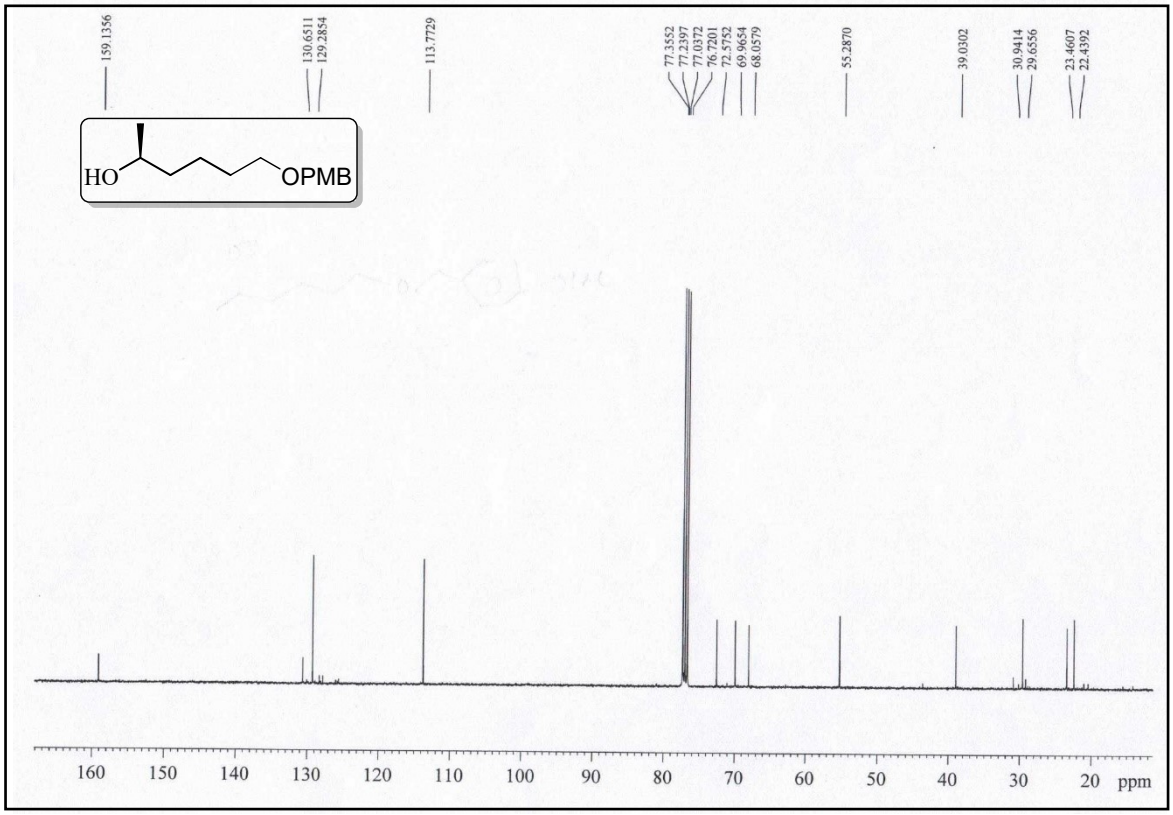
^{1}H NMR of compound (*S*)-15 (500 MHz, $CDCl_3$)



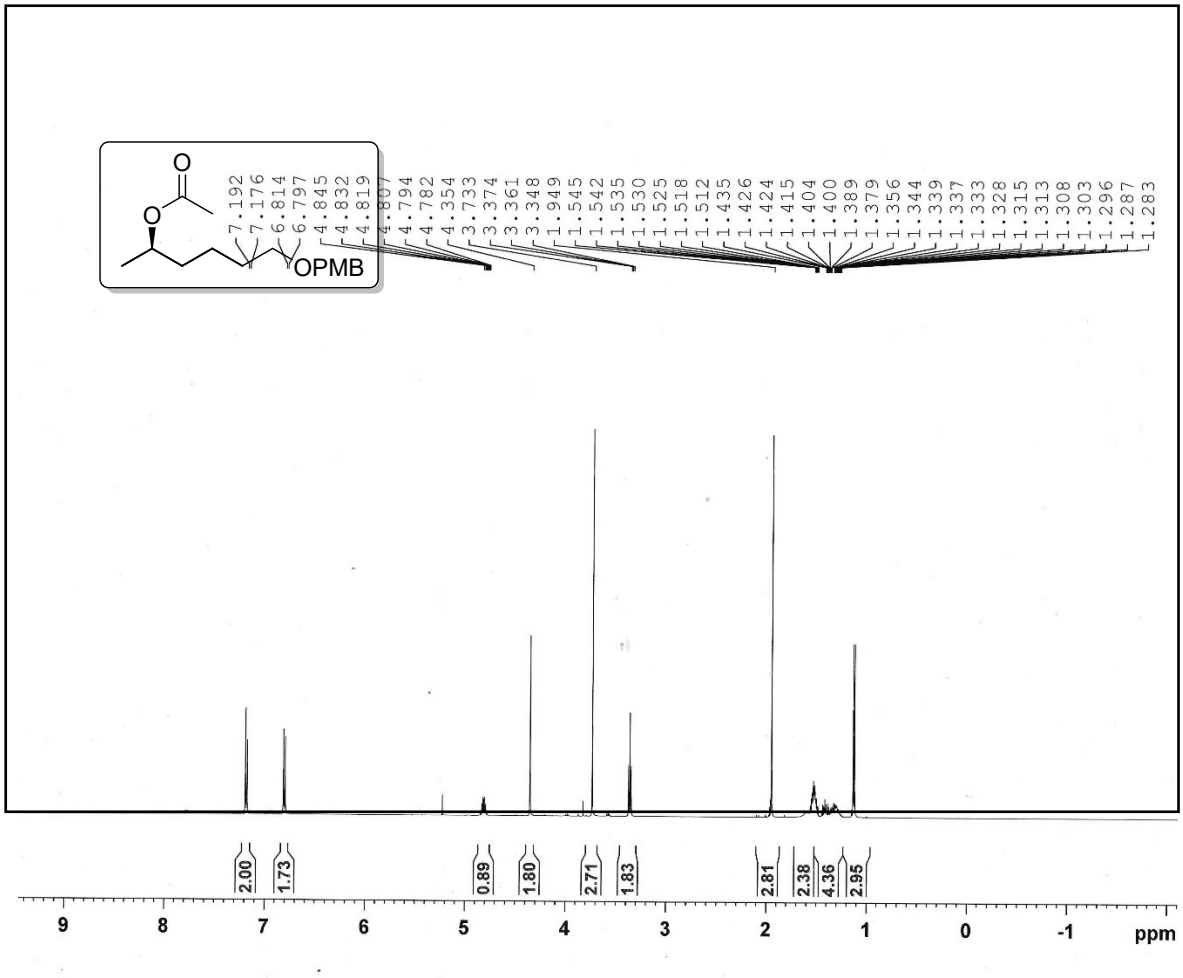
^{13}C DEPT NMR of compound (*S*)-15 (126 MHz, $CDCl_3$)



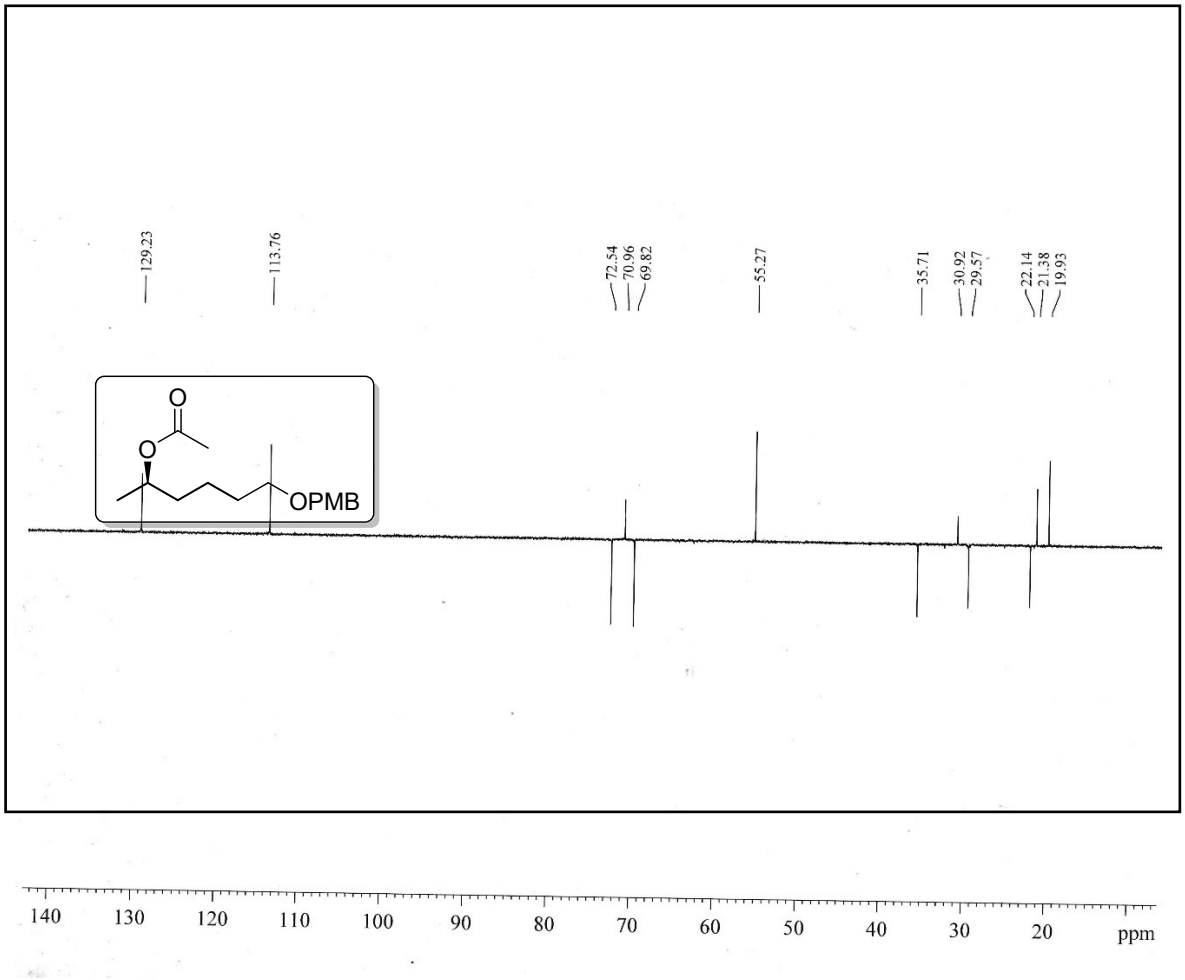
^{13}C NMR of compound (*S*)-15 (126 MHz, $CDCl_3$)



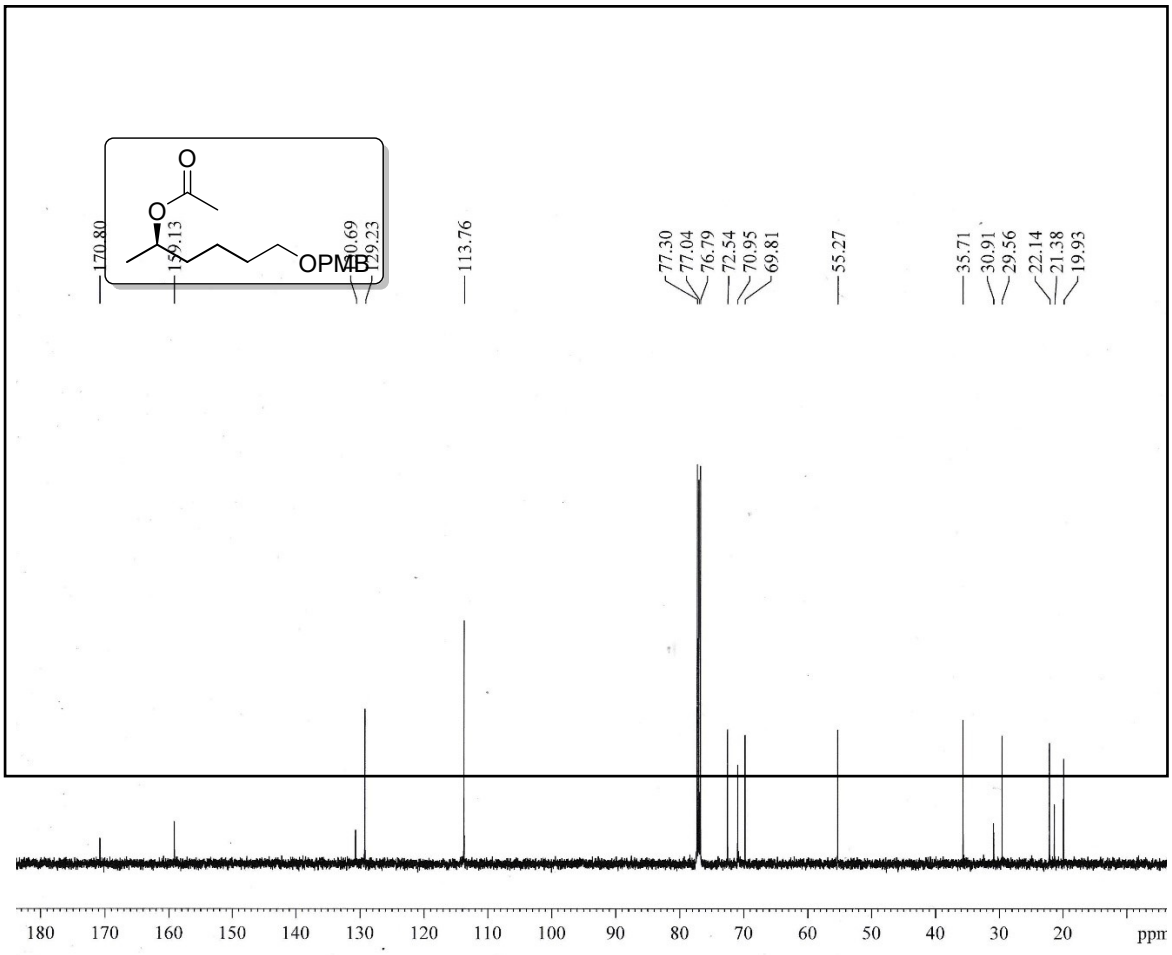
^{1}H NMR of compound (*R*)-16 (500 MHz, $CDCl_3$)



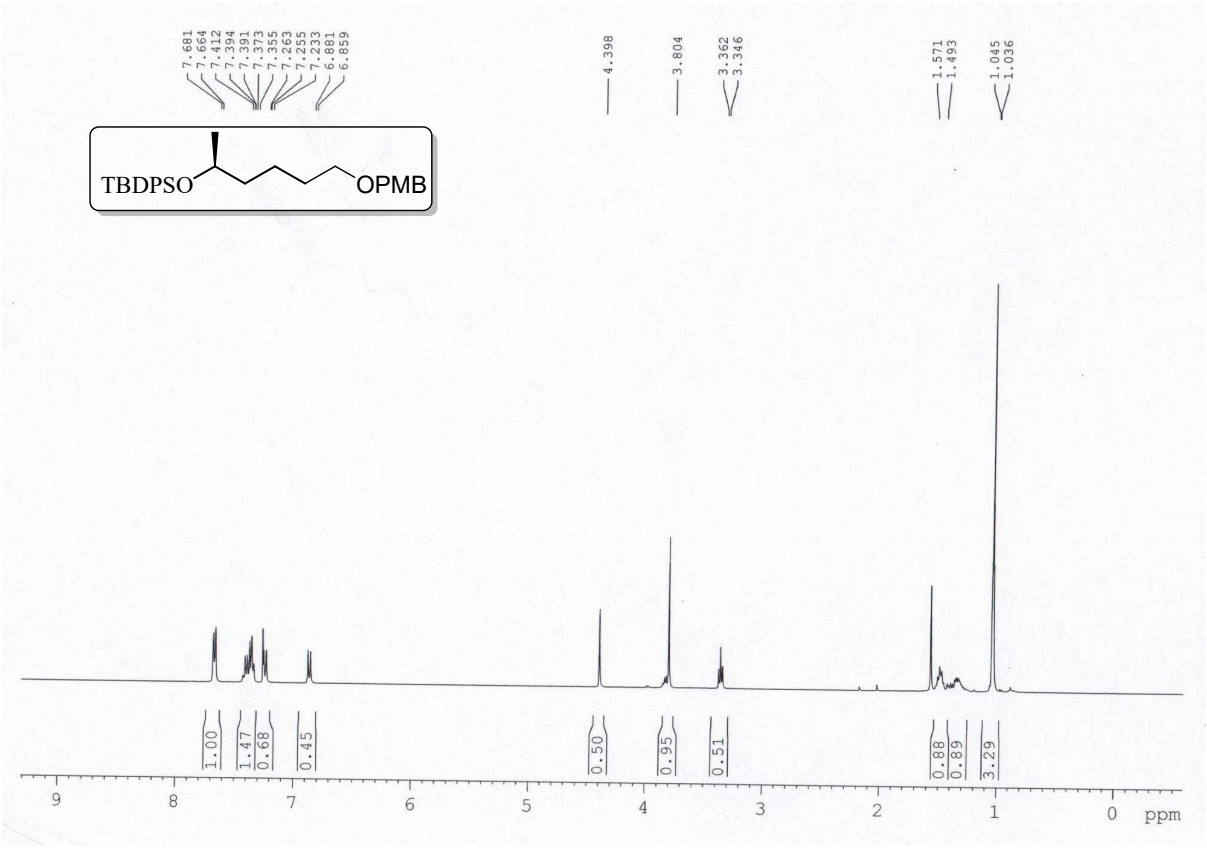
^{13}C DEPT NMR of compound (*R*)-16 (126 MHz, $CDCl_3$)



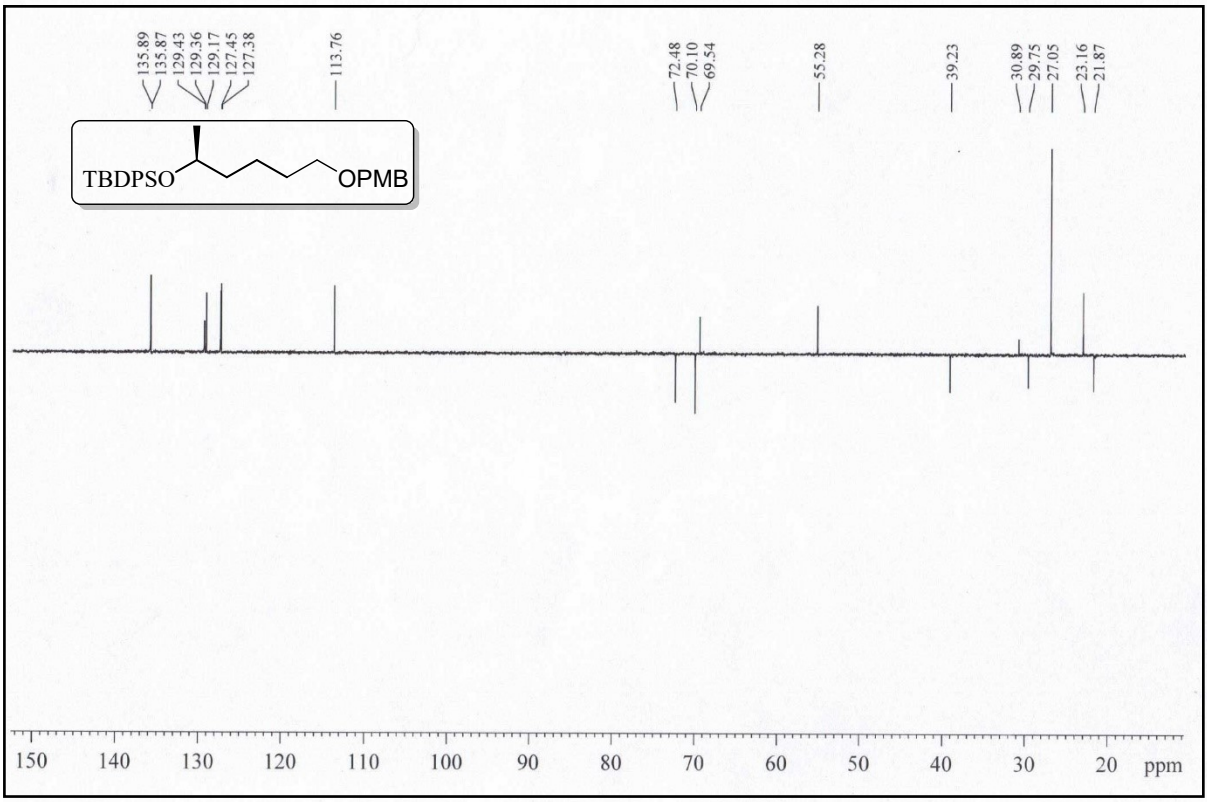
^{13}C NMR of compound (*R*)-16 (126 MHz, $CDCl_3$)



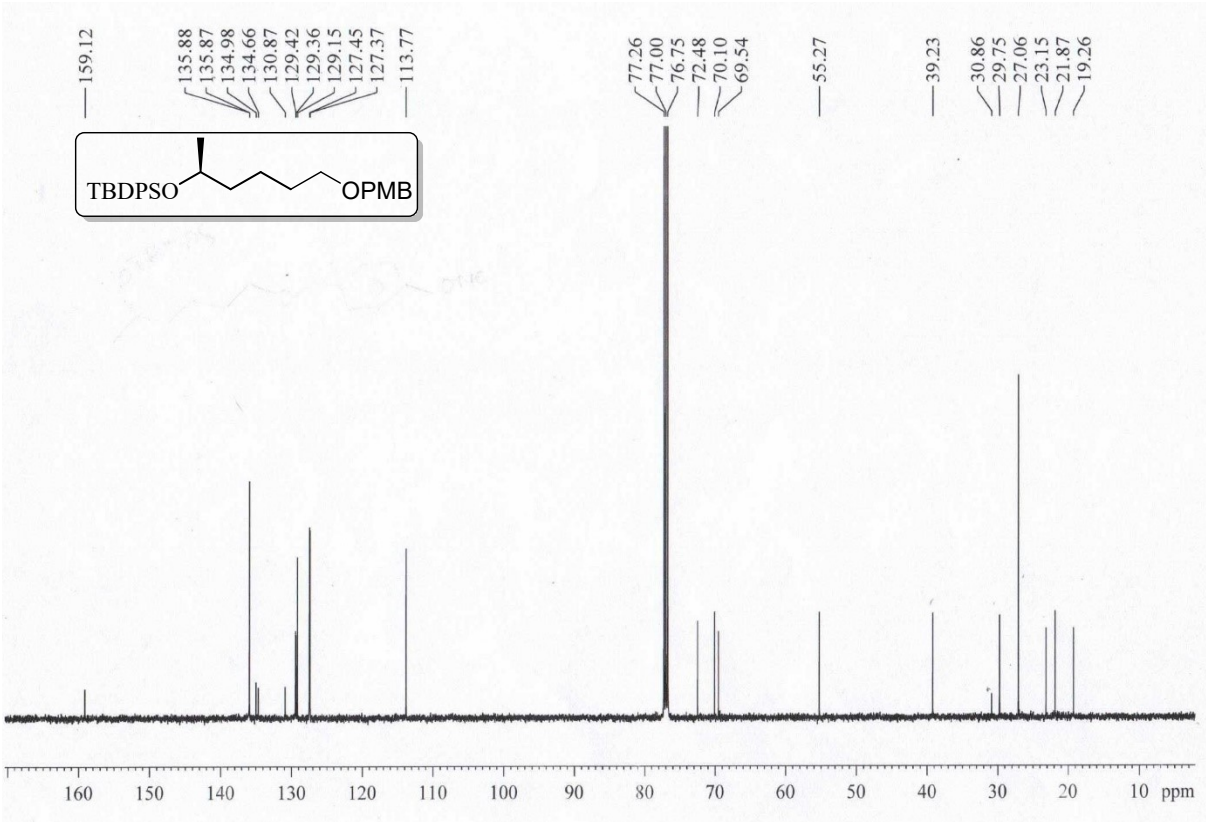
^{1}H NMR of compound 17 (500 MHz, $CDCl_3$)



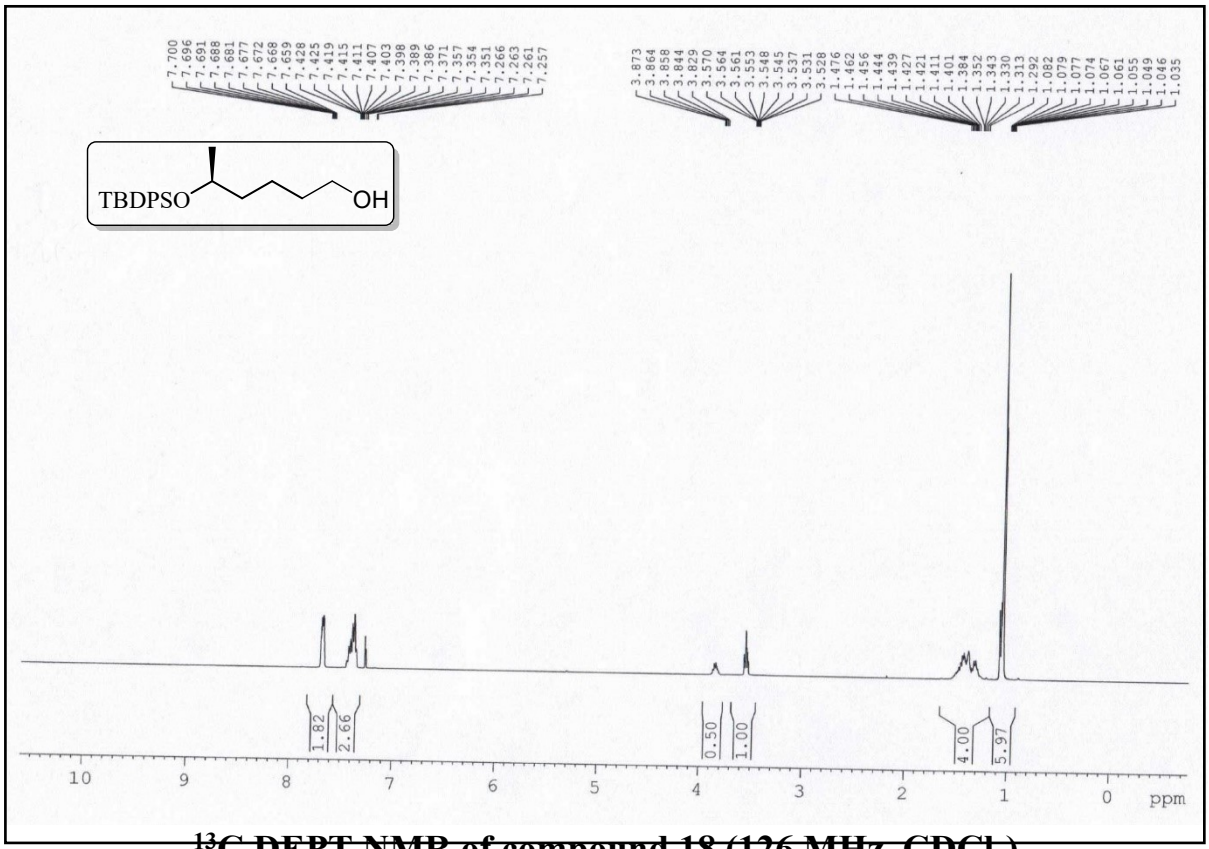
^{13}C DEPT NMR of compound 17 (126 MHz, $CDCl_3$)



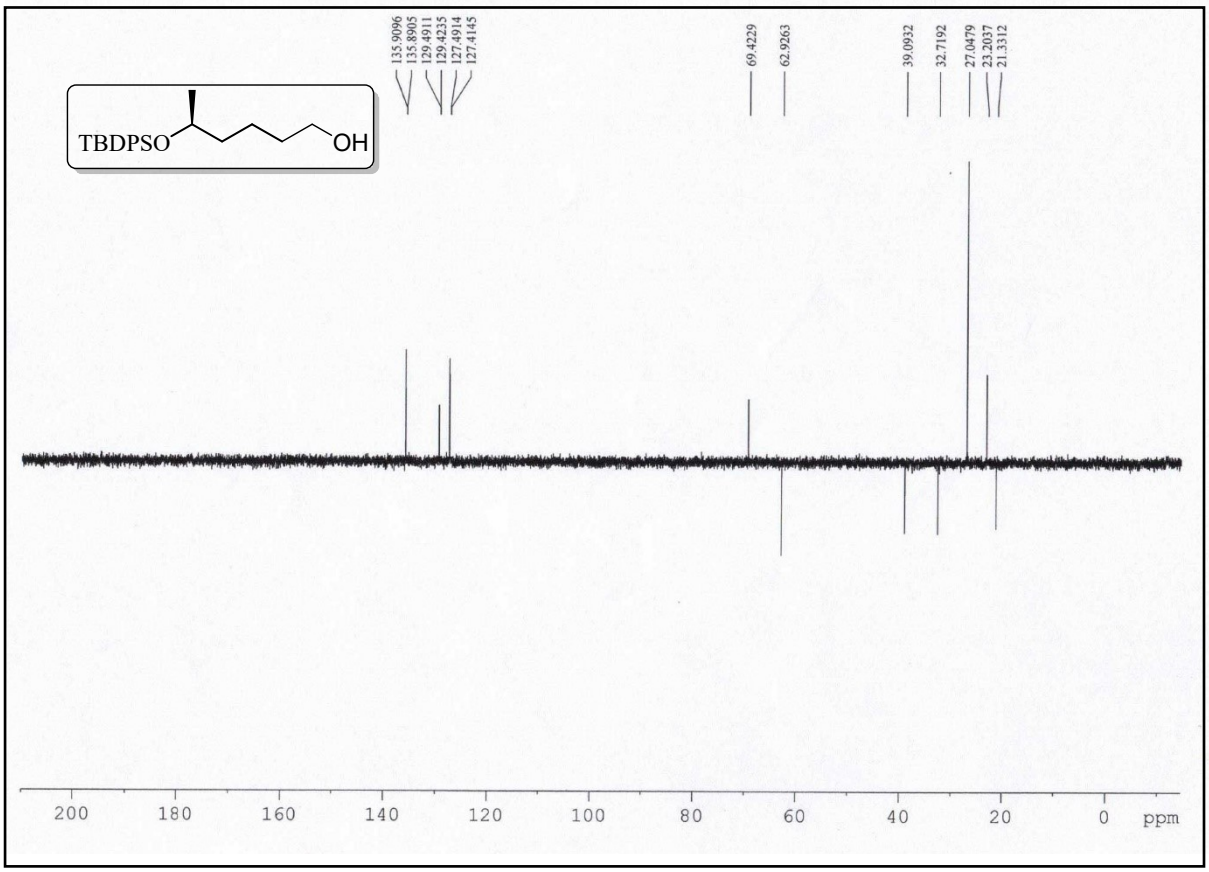
^{13}C NMR of compound 17 (126 MHz, $CDCl_3$)



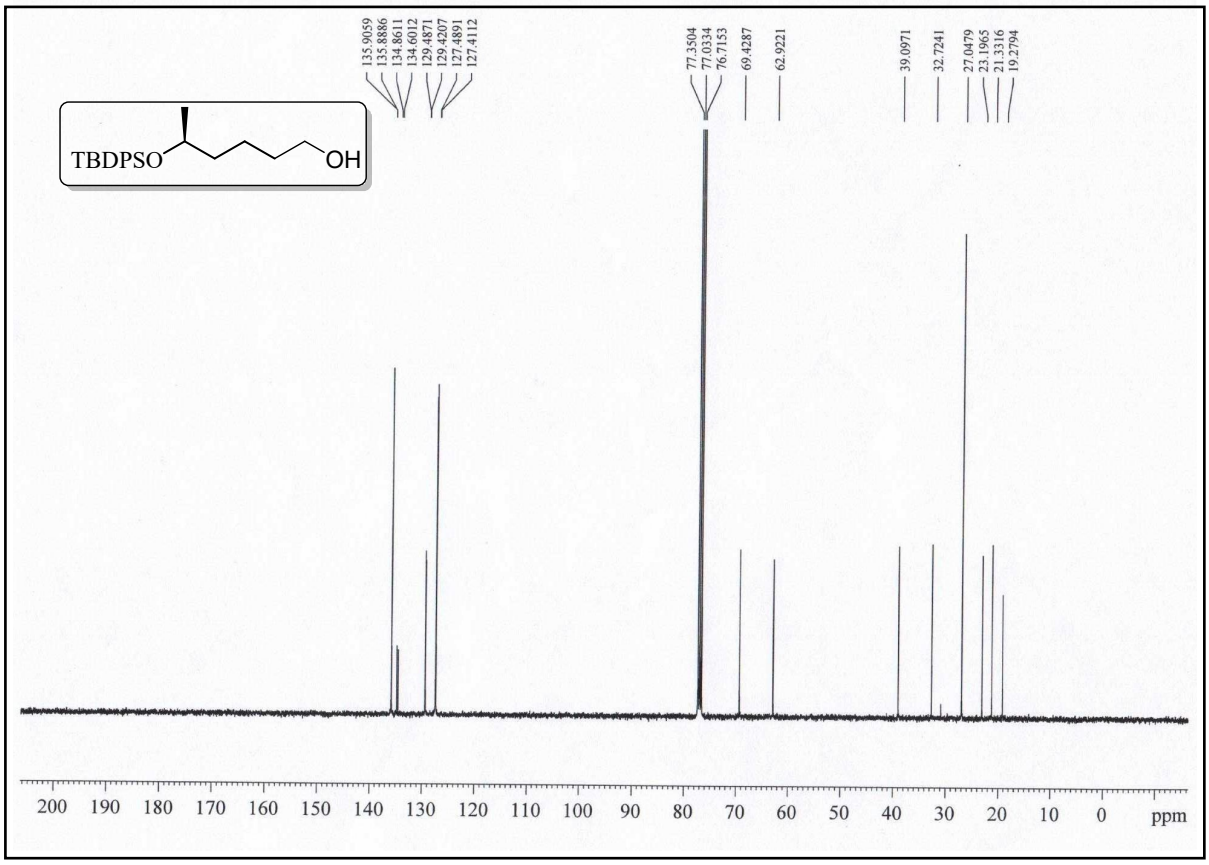
^{1}H NMR of compound 18 (500 MHz, $CDCl_3$)



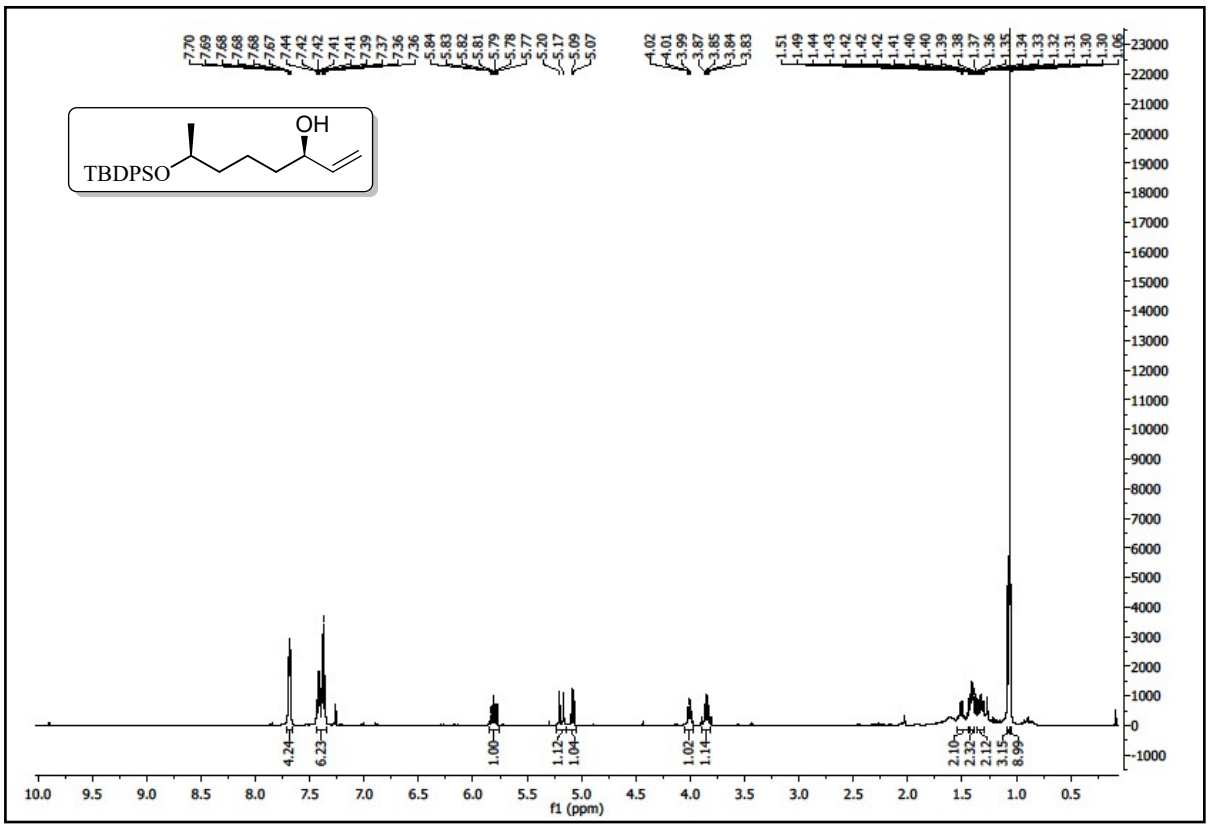
^{13}C DEPT NMR of compound 18 (126 MHz, $CDCl_3$)



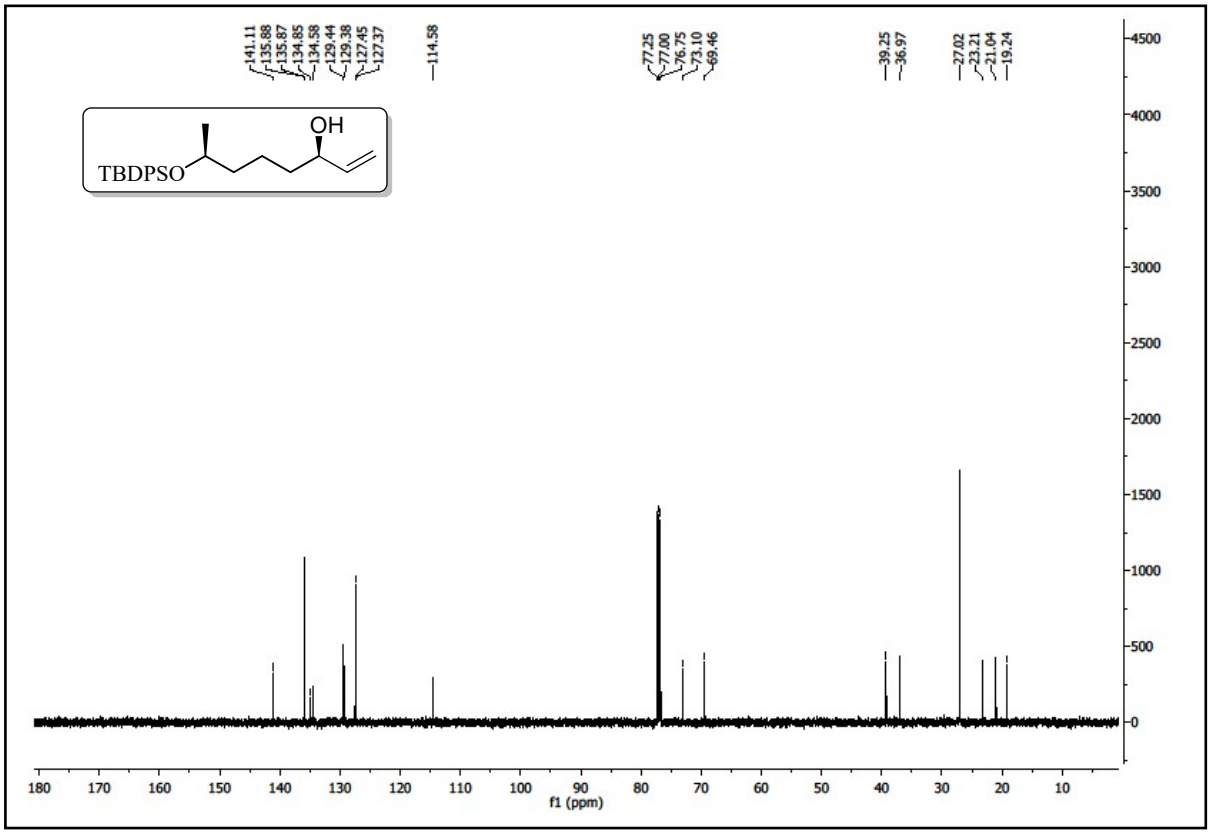
^{13}C NMR of compound 18 (126 MHz, $CDCl_3$)



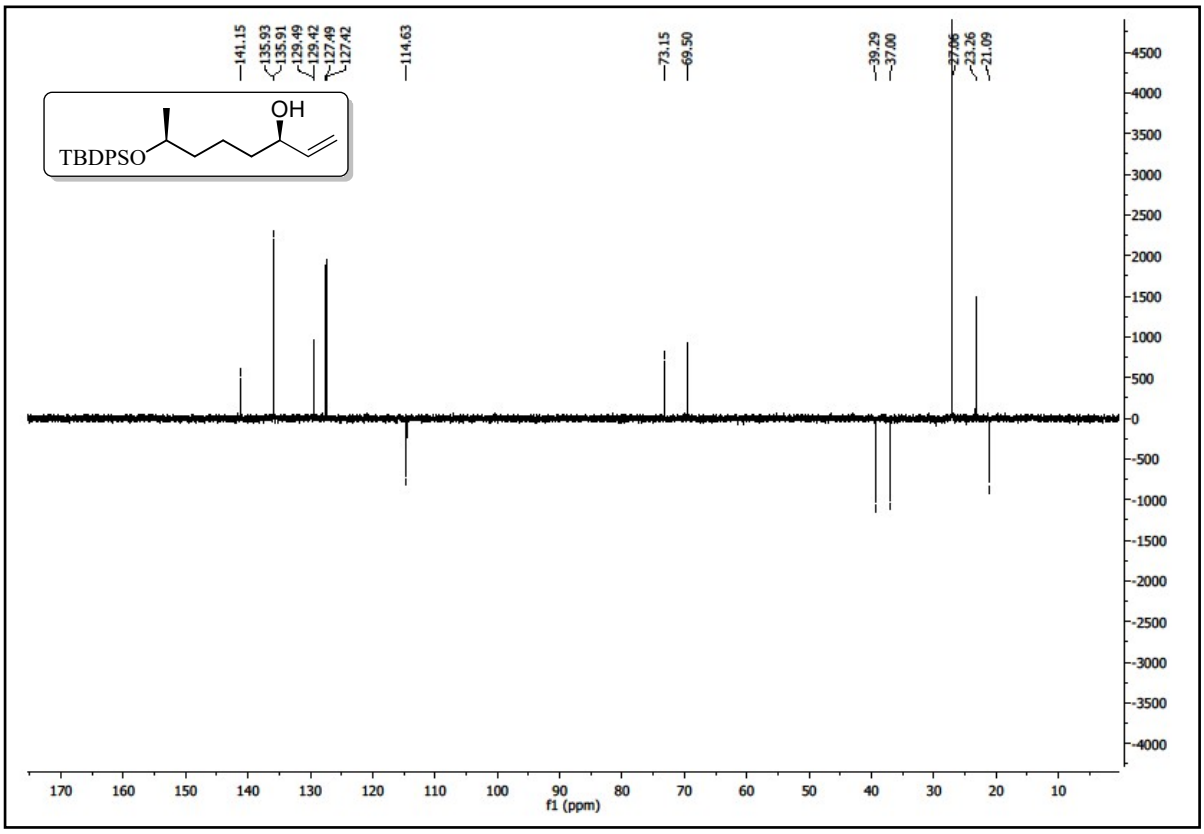
^{1}H NMR of compound 21 (500 MHz, $CDCl_3$)



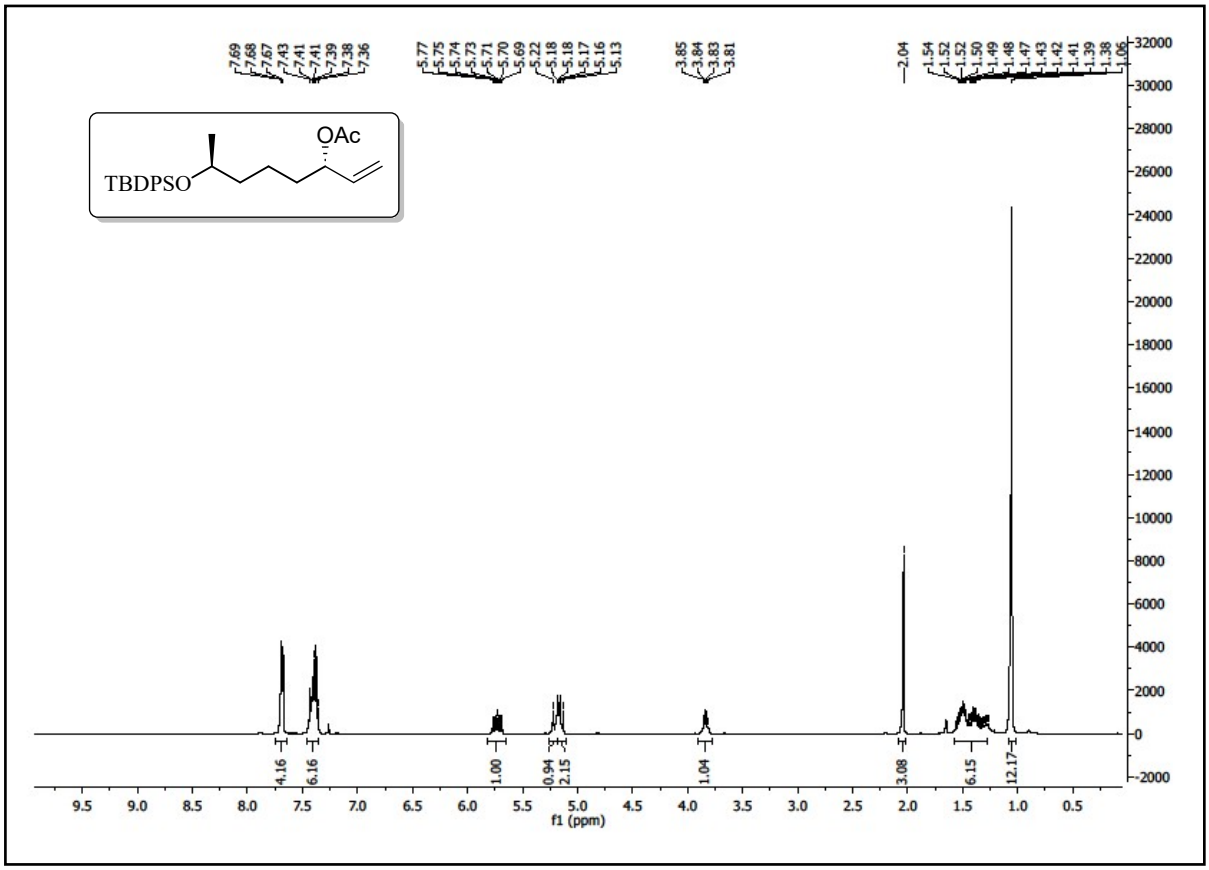
^{13}C NMR of compound 21 (126 MHz, $CDCl_3$)



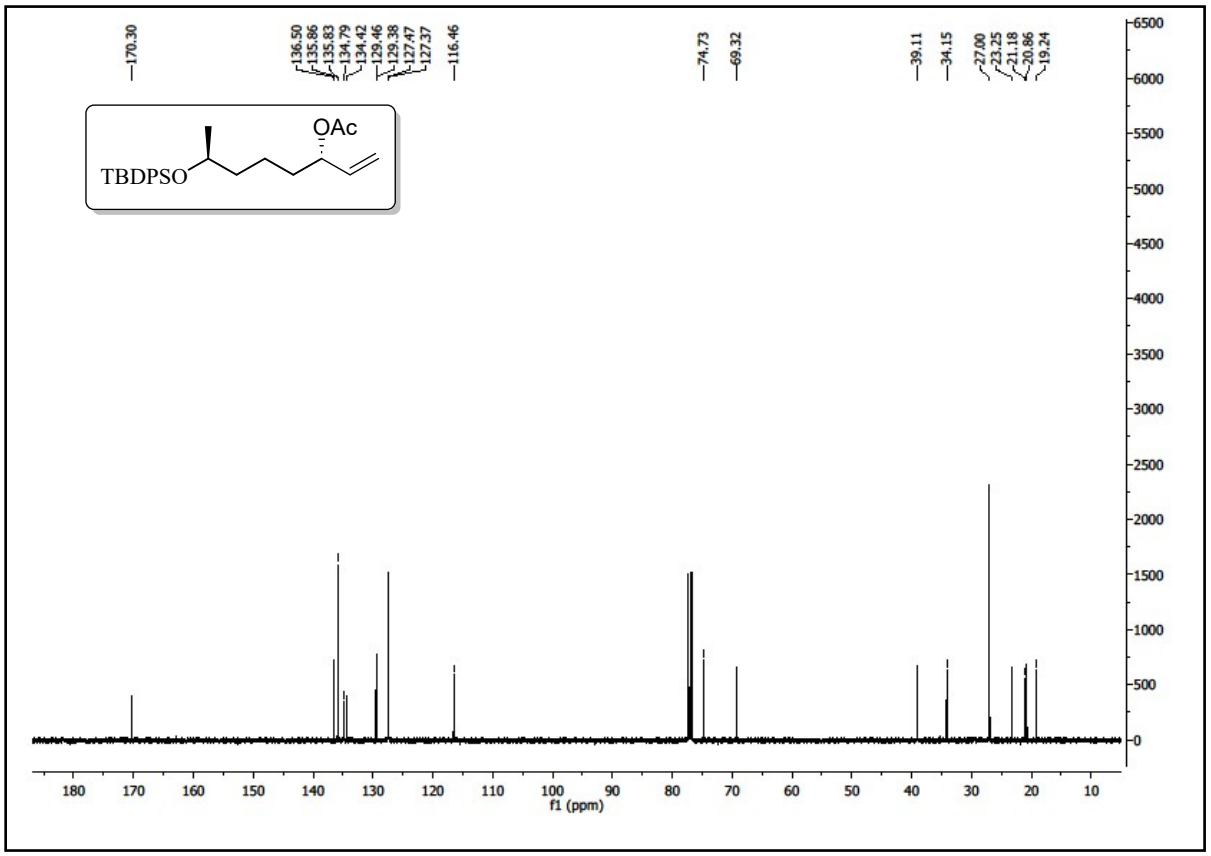
^{13}C DEPT NMR of compound 21 (126 MHz, $CDCl_3$)



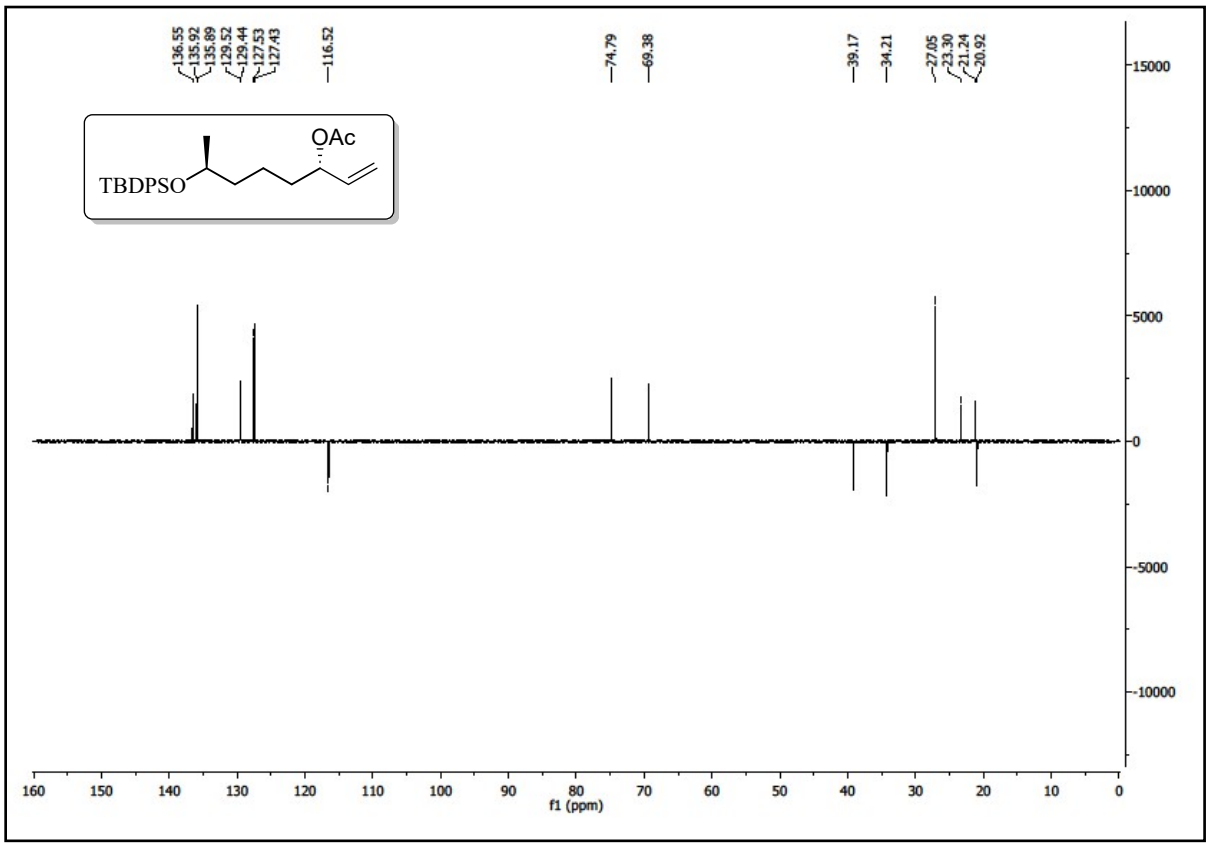
^{1}H NMR of compound 22 (126 MHz, $CDCl_3$)



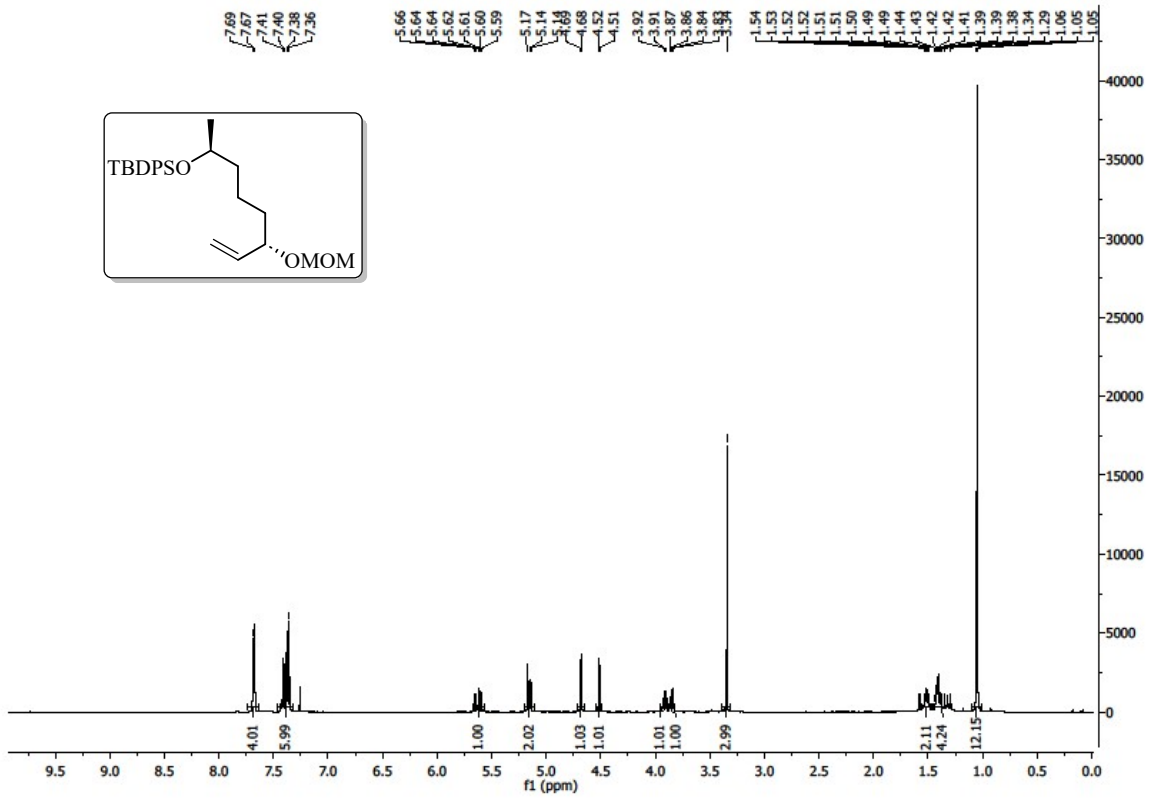
^{13}C NMR of compound 22 (126 MHz, $CDCl_3$)



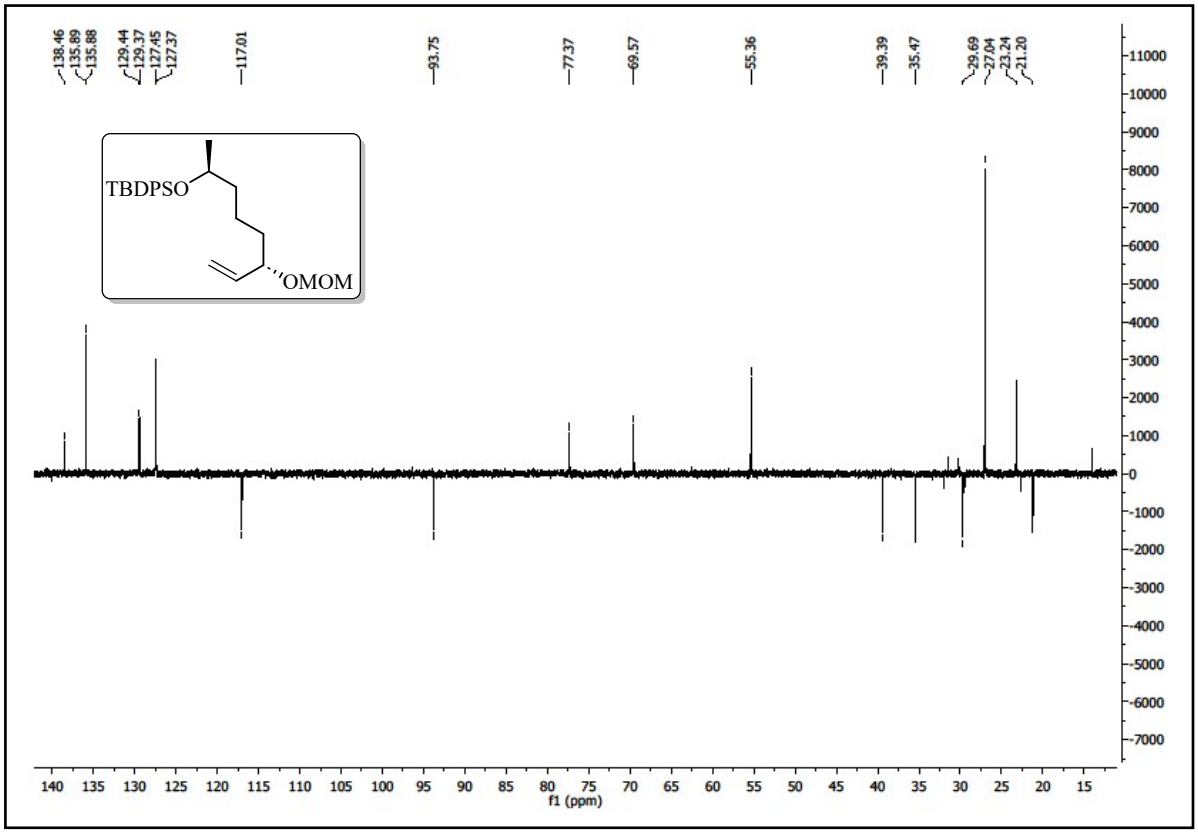
^{13}C DEPT NMR of compound 22 (126 MHz, $CDCl_3$)



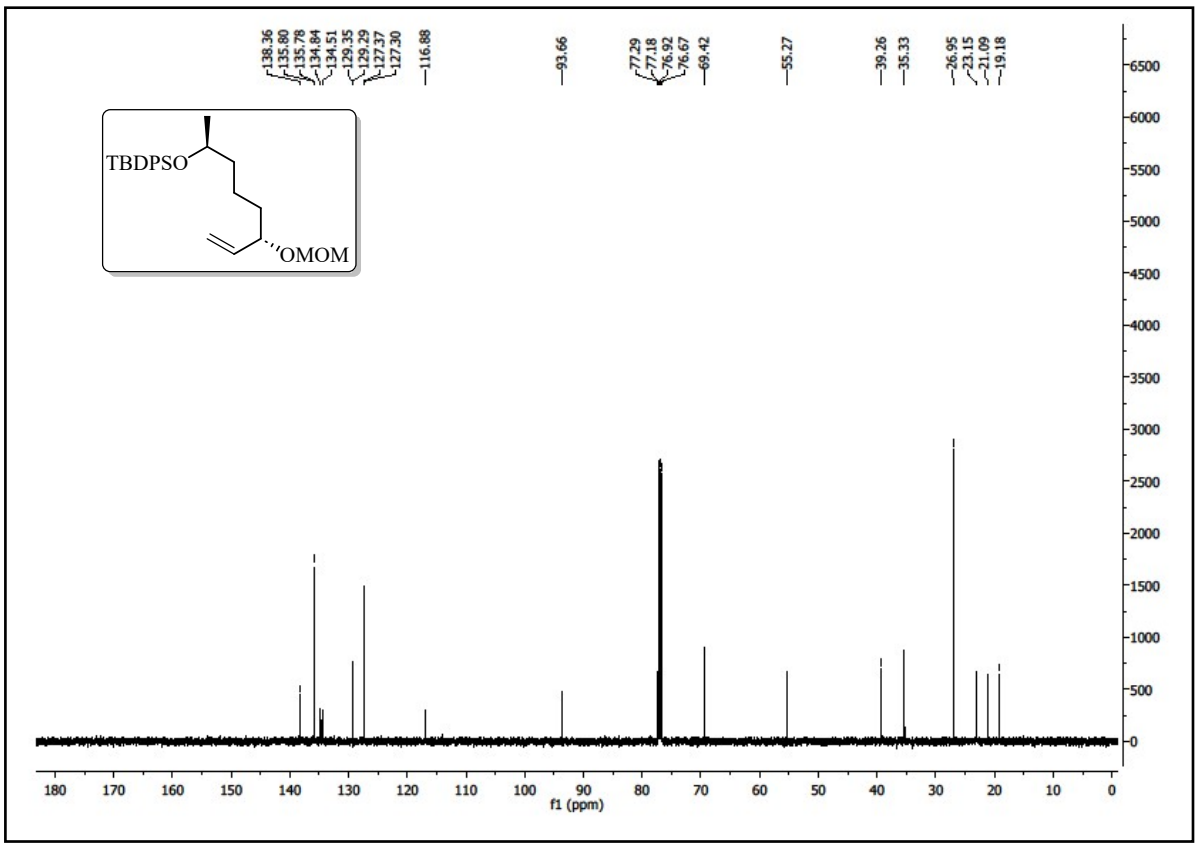
^{1}H NMR of compound 24 (500 MHz, $CDCl_3$)



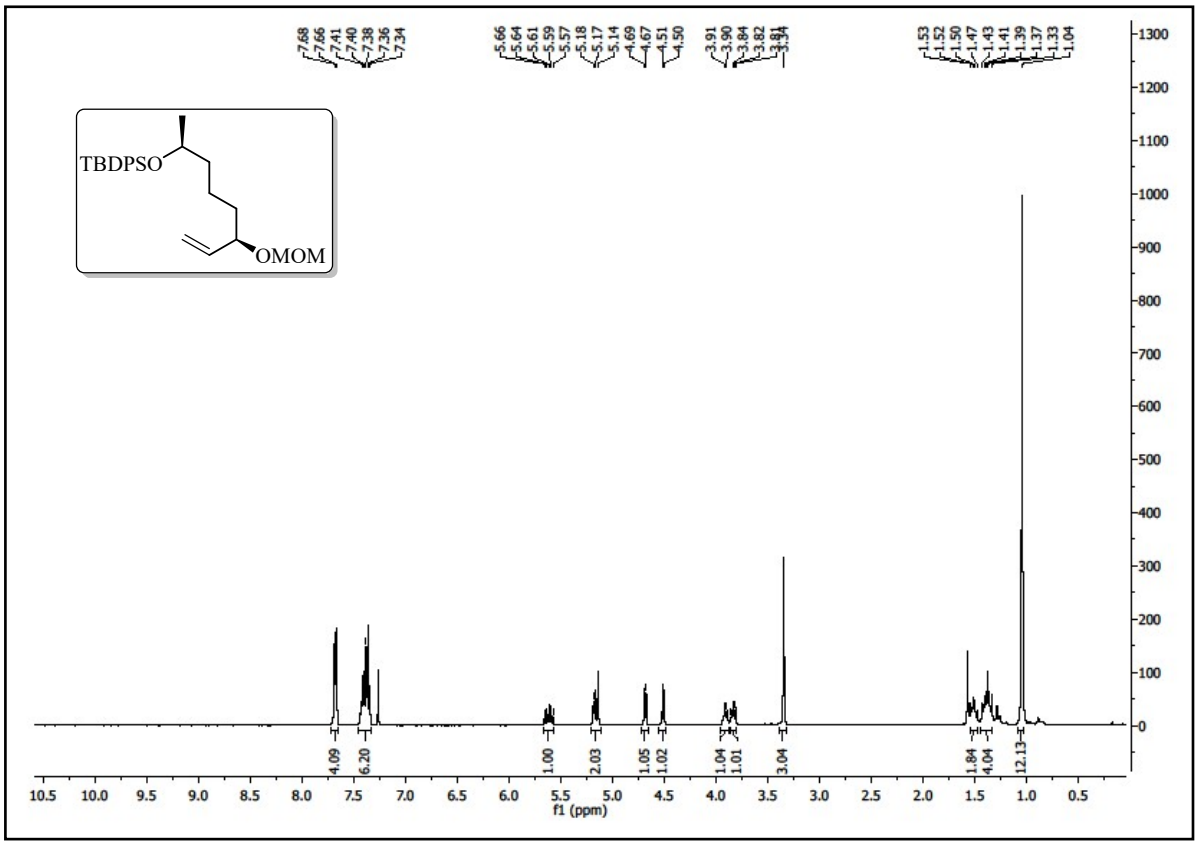
^{13}C DEPT NMR of compound 24 (126 MHz, $CDCl_3$)



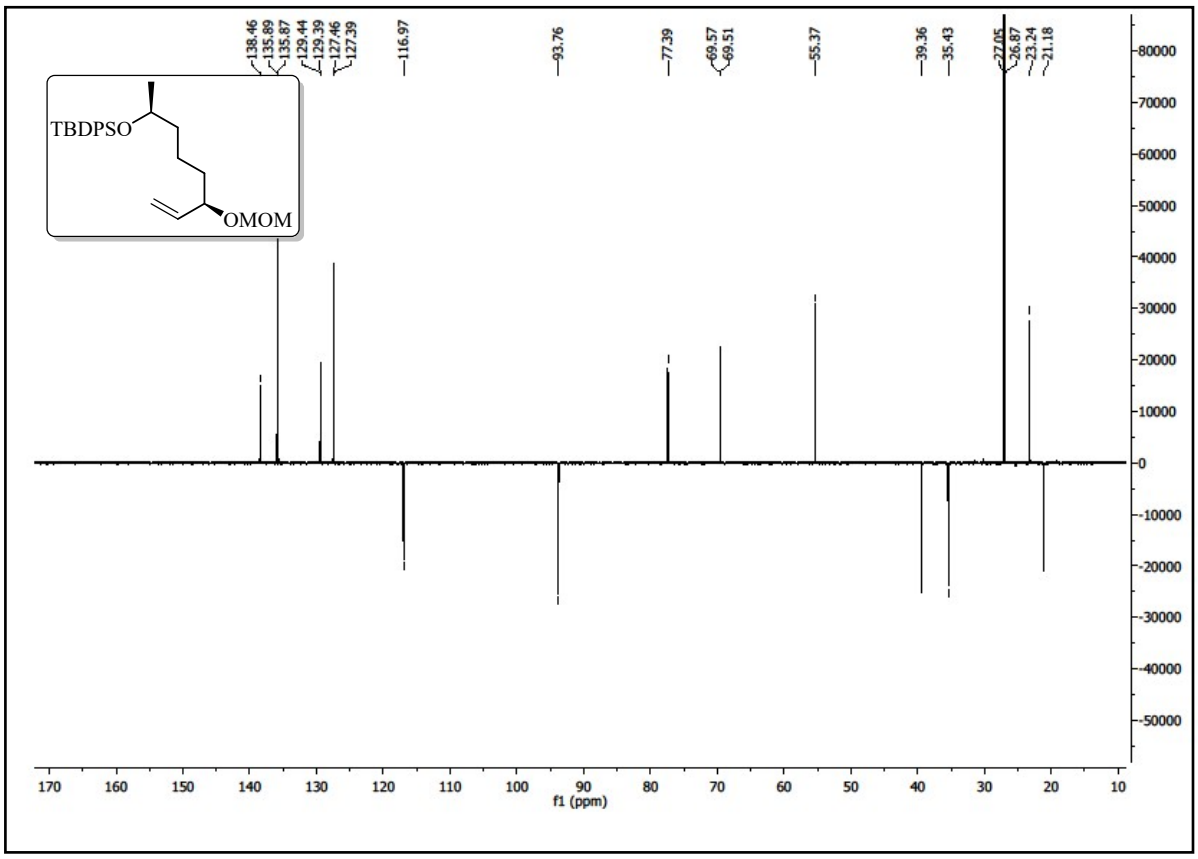
^{13}C NMR of compound 24 (126 MHz, $CDCl_3$)



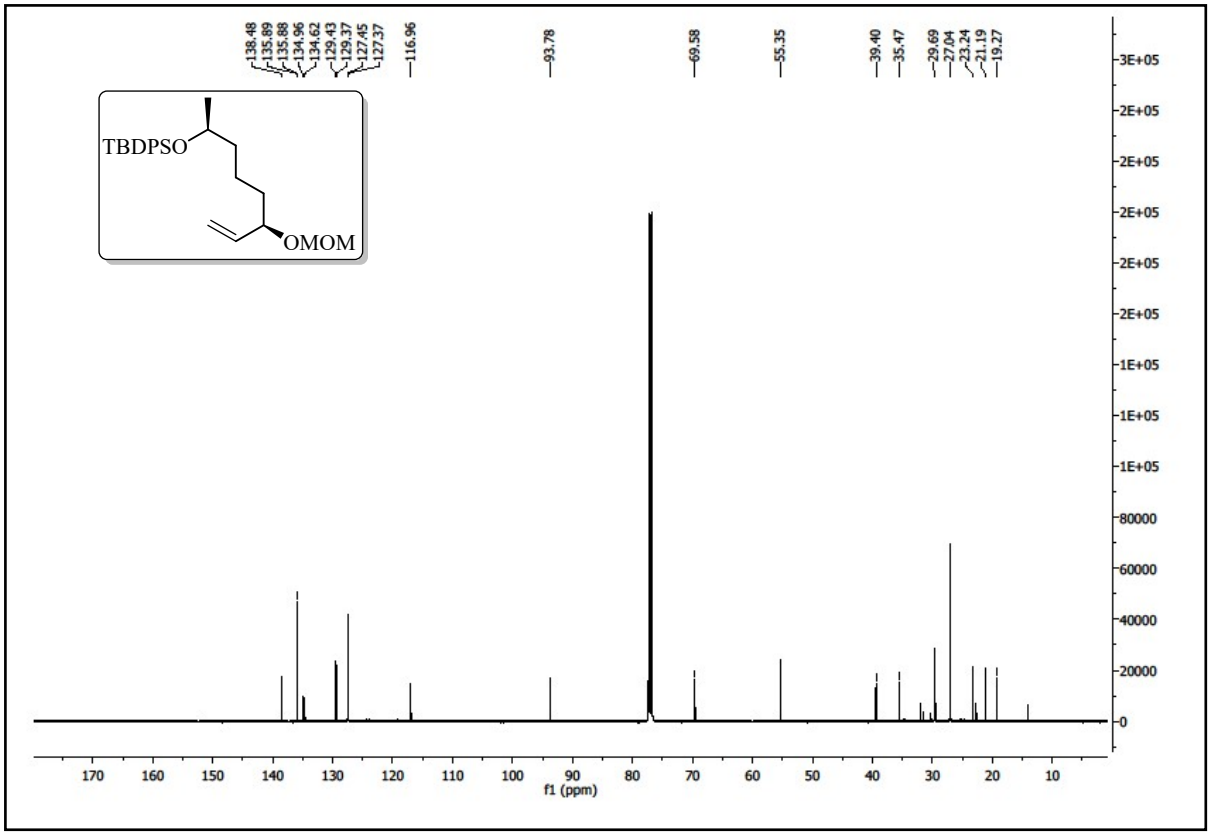
^{1}H NMR of compound 39 (500 MHz, $CDCl_3$)



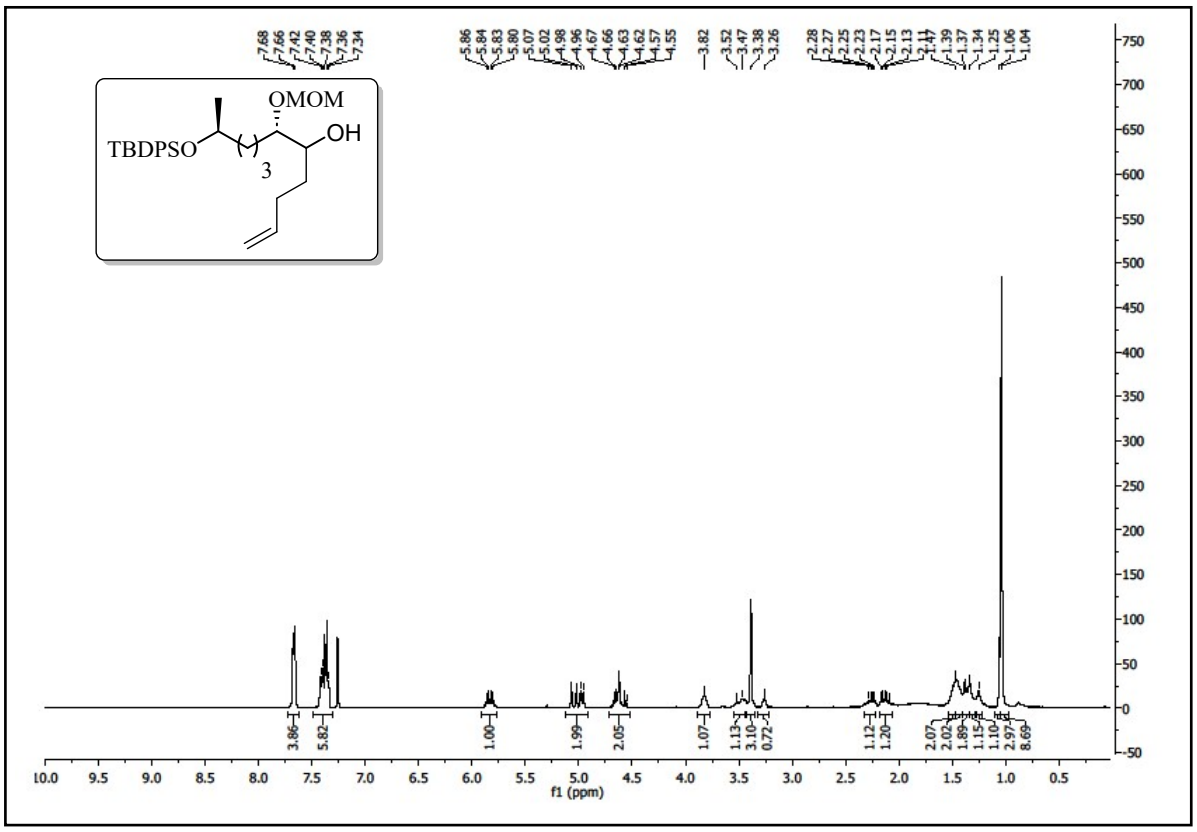
^{13}C DEPT NMR of compound 39 (126 MHz, $CDCl_3$)



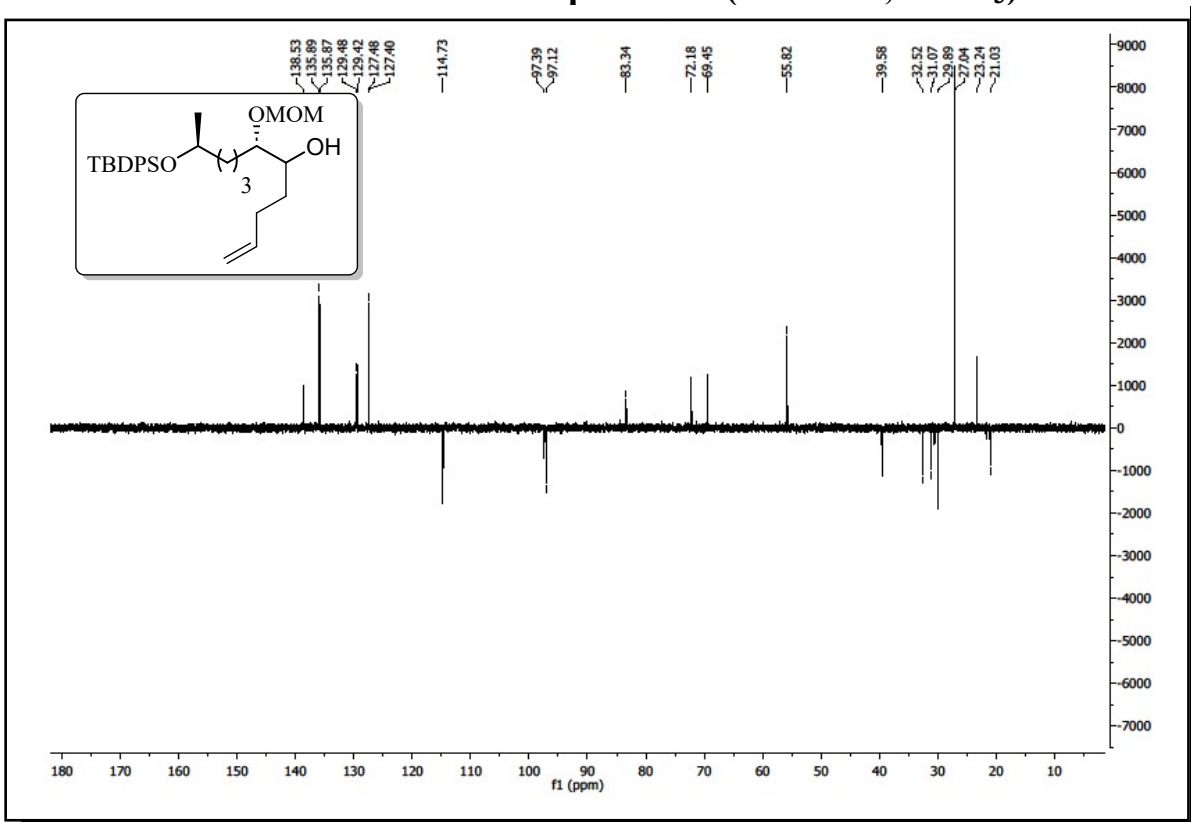
^{13}C NMR of compound 39 (126 MHz, $CDCl_3$)



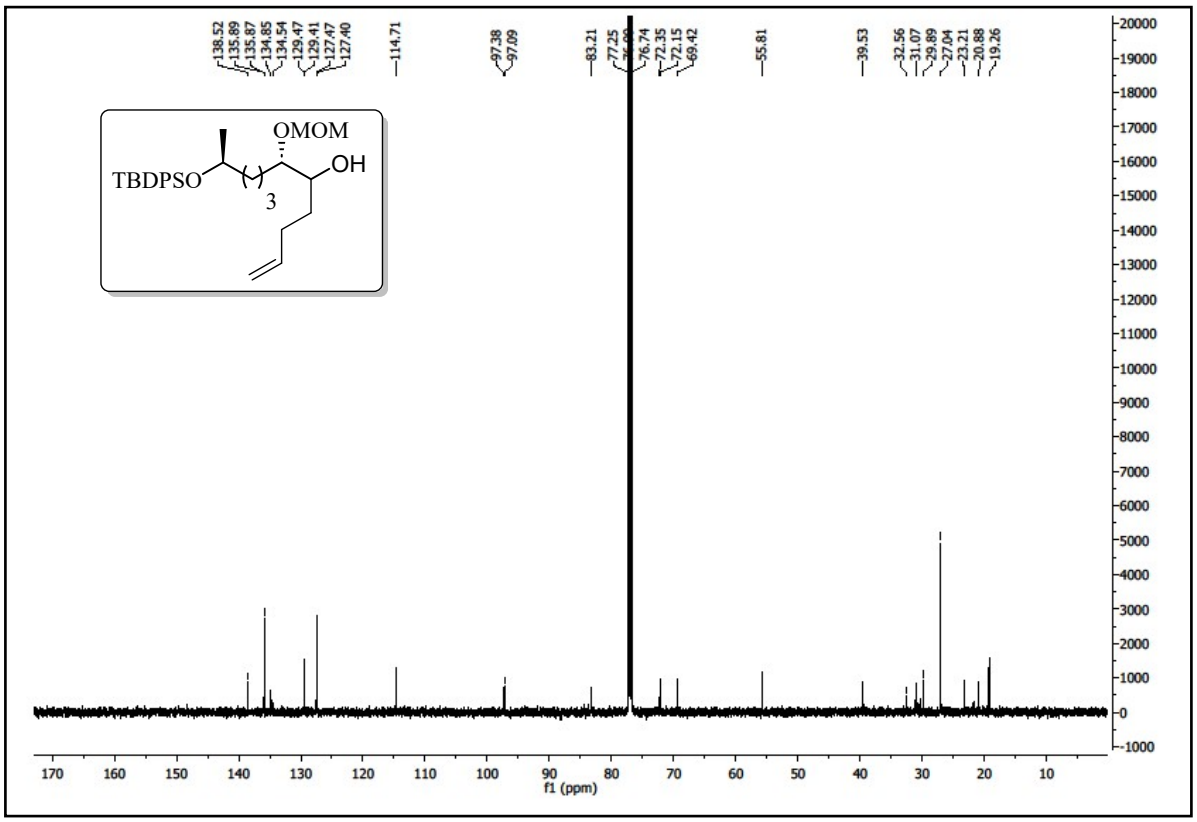
^{1}H NMR of compound 25 (500 MHz, $CDCl_3$)



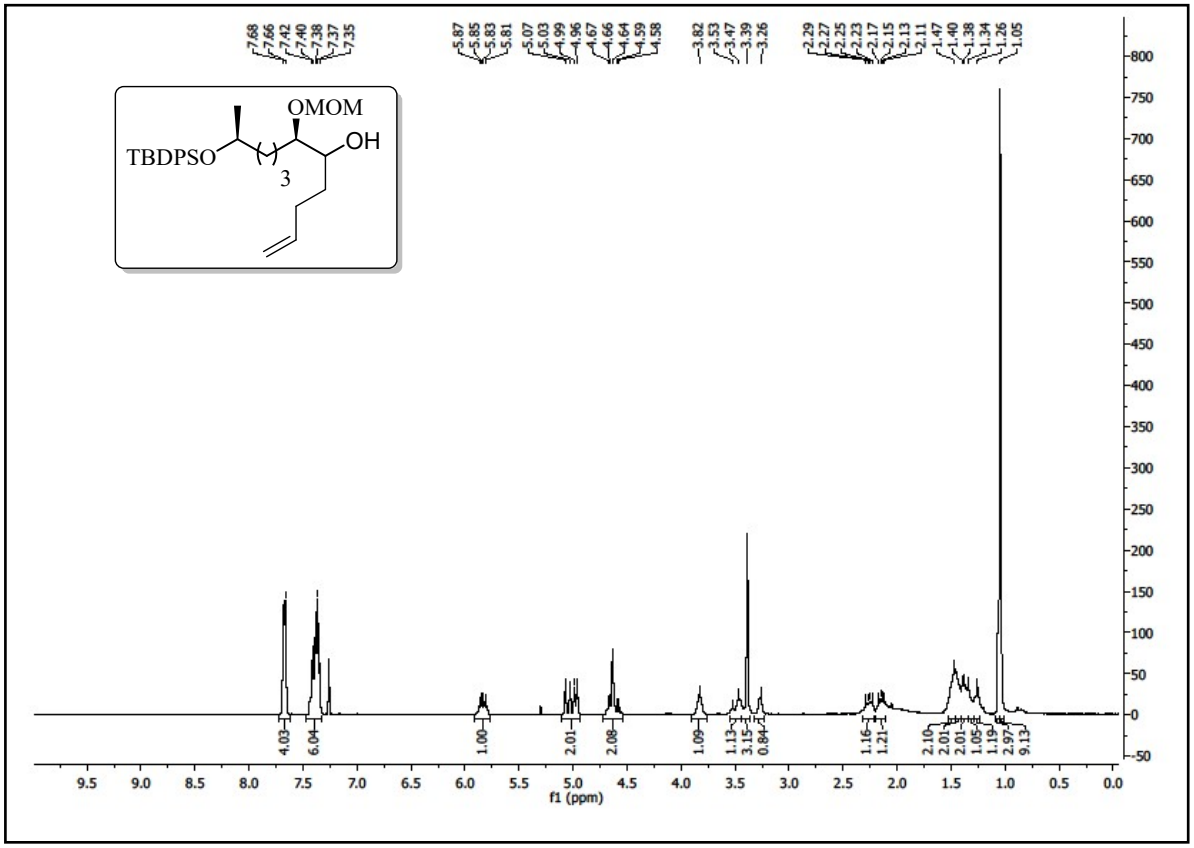
^{13}C DEPT NMR of compound 25 (126 MHz, $CDCl_3$)



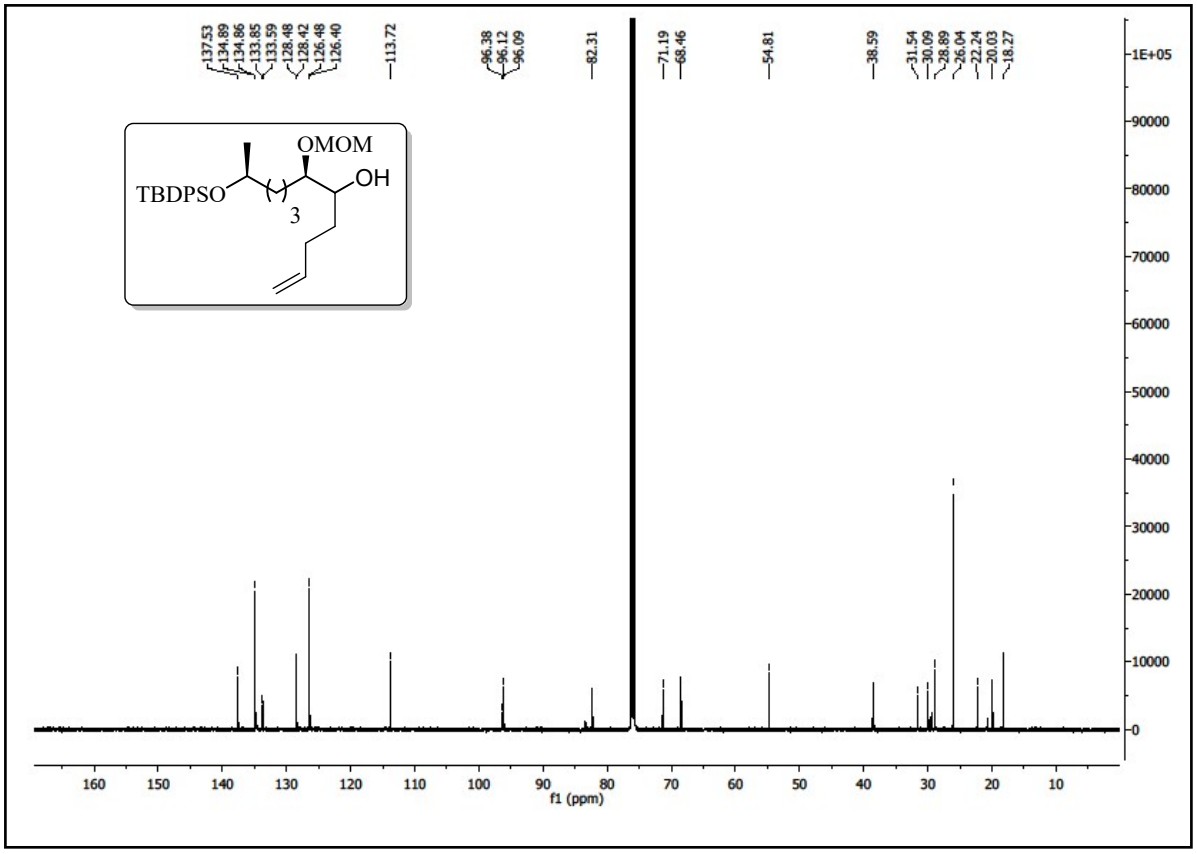
^{13}C NMR of compound 25 (126 MHz, $CDCl_3$)



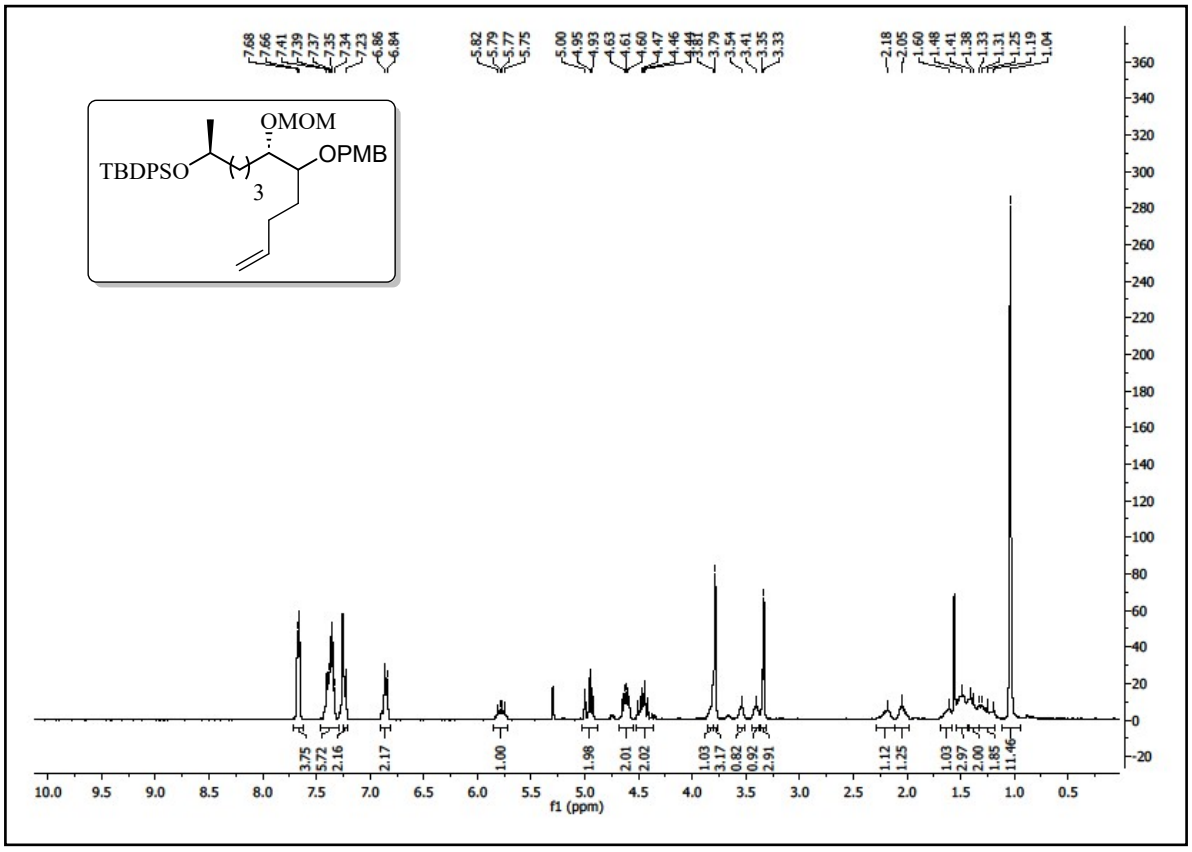
^{1}H NMR of compound 40 (500 MHz, $CDCl_3$)



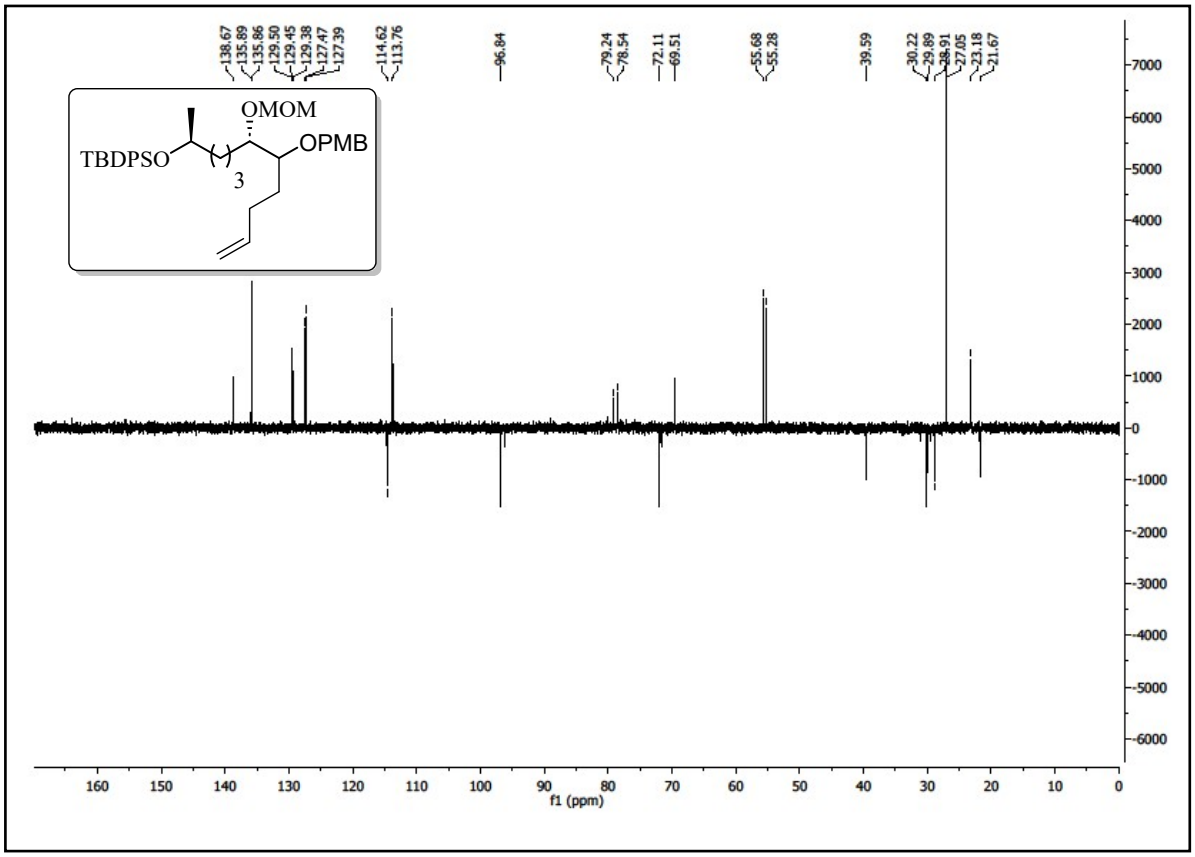
^{13}C NMR of compound 40 (126 MHz, $CDCl_3$)



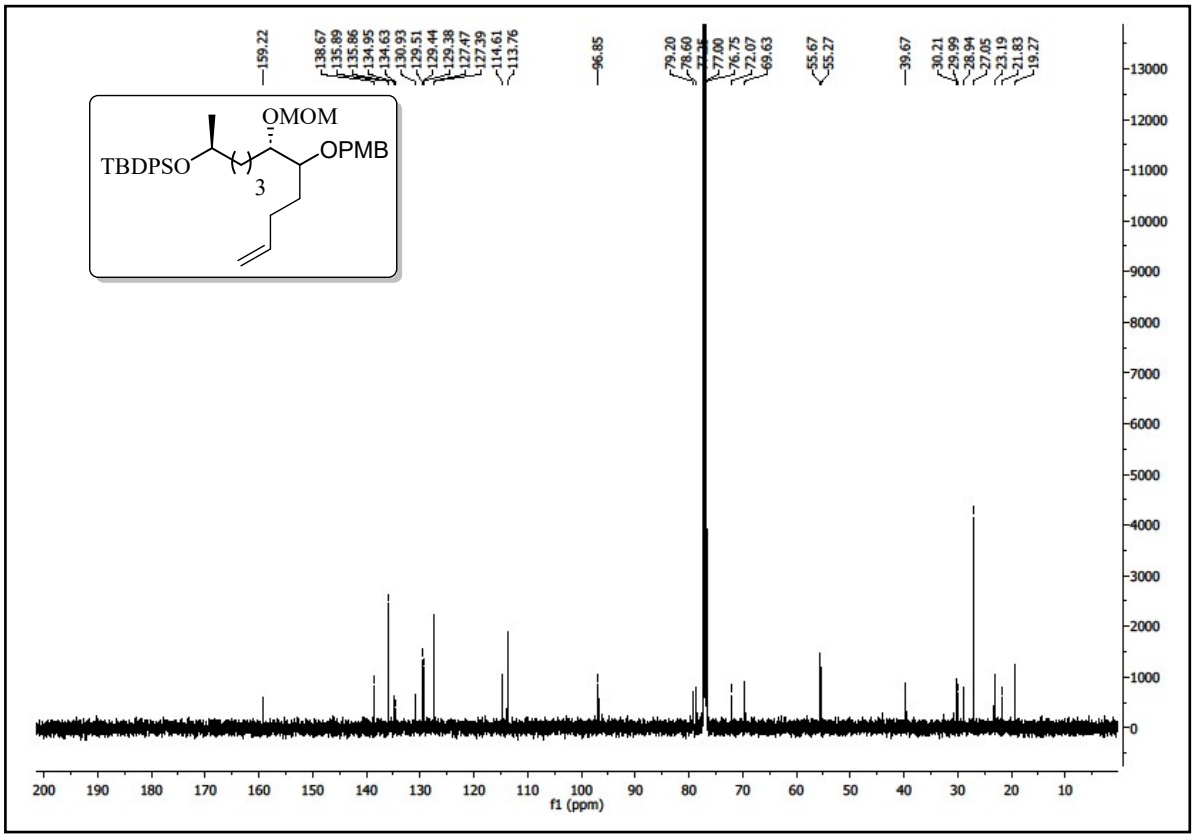
^{1}H NMR of compound 26 (500 MHz, $CDCl_3$)



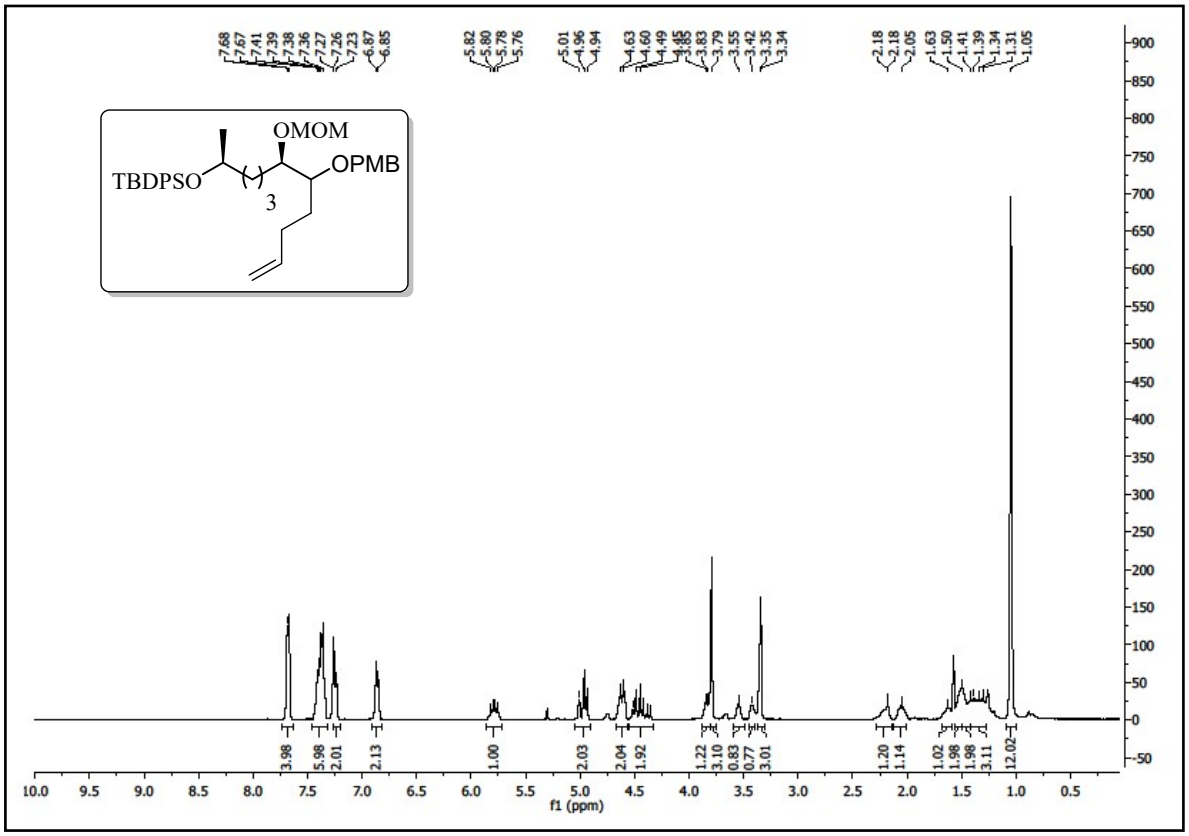
^{13}C DEPT NMR of compound 26 (126 MHz, $CDCl_3$)



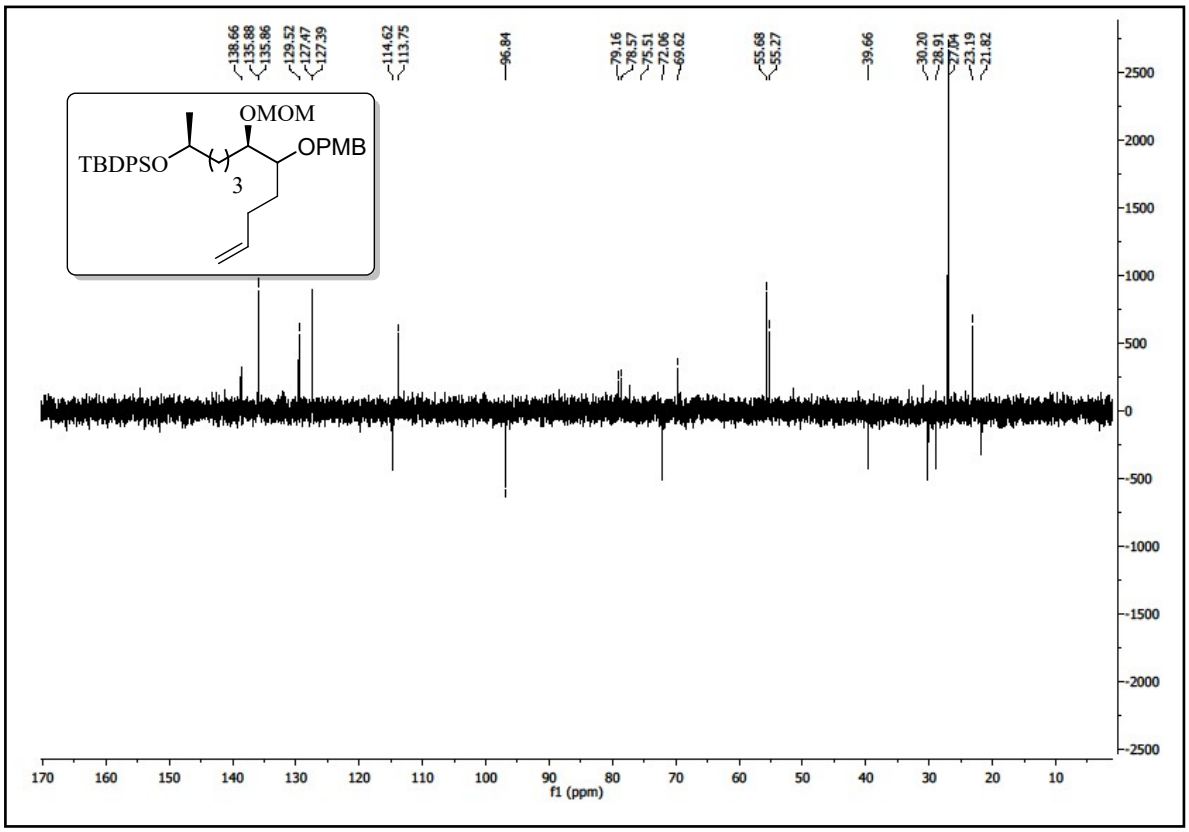
^{13}C NMR of compound 26 (126 MHz, $CDCl_3$)



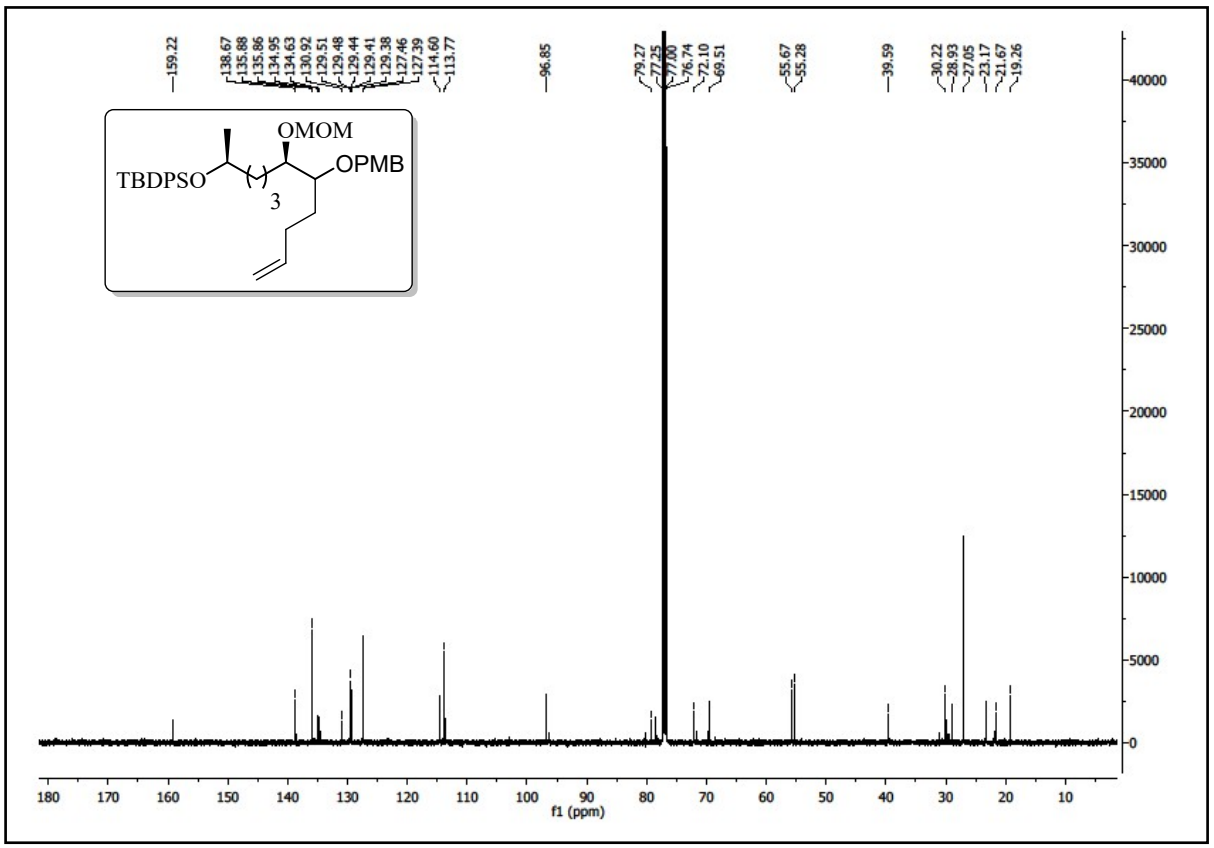
^{1}H NMR of compound 41 (500 MHz, $CDCl_3$)



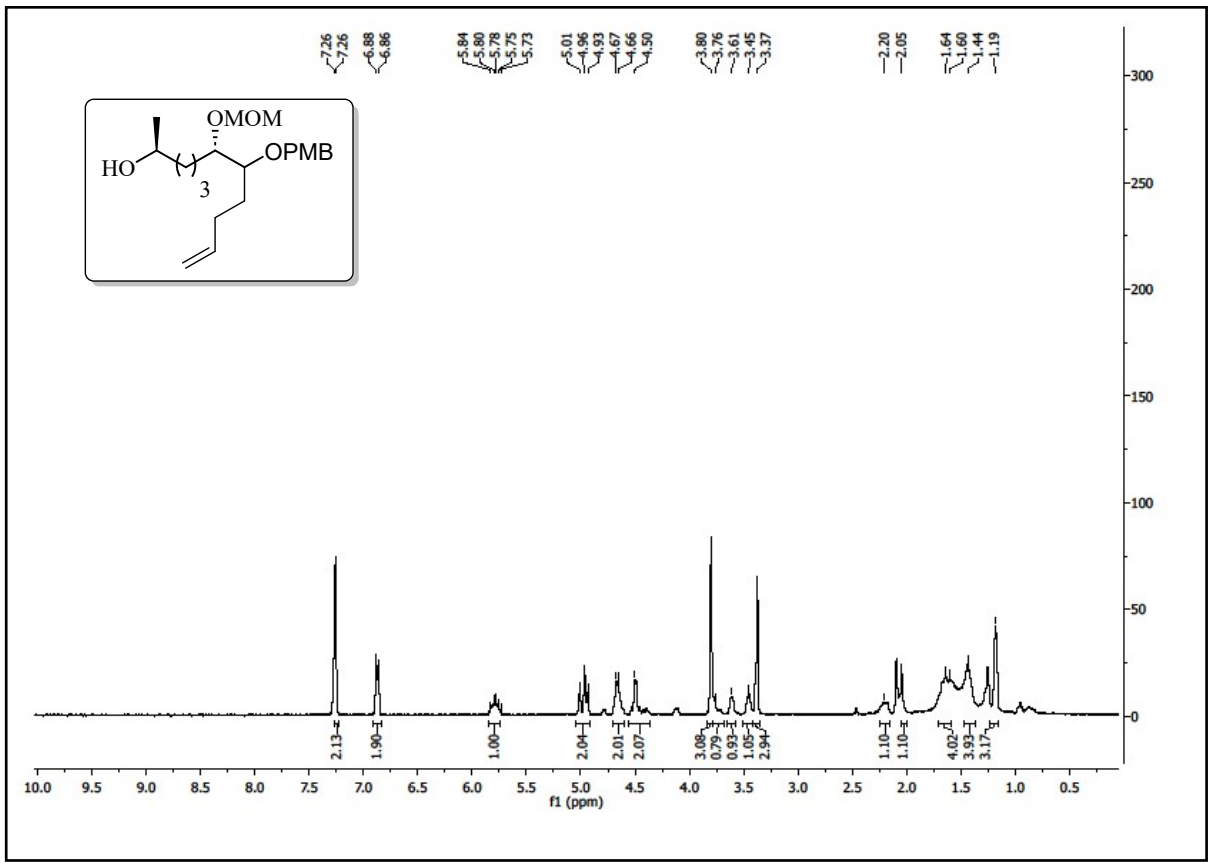
^{13}C DEPT NMR of compound 41 (126 MHz, $CDCl_3$)



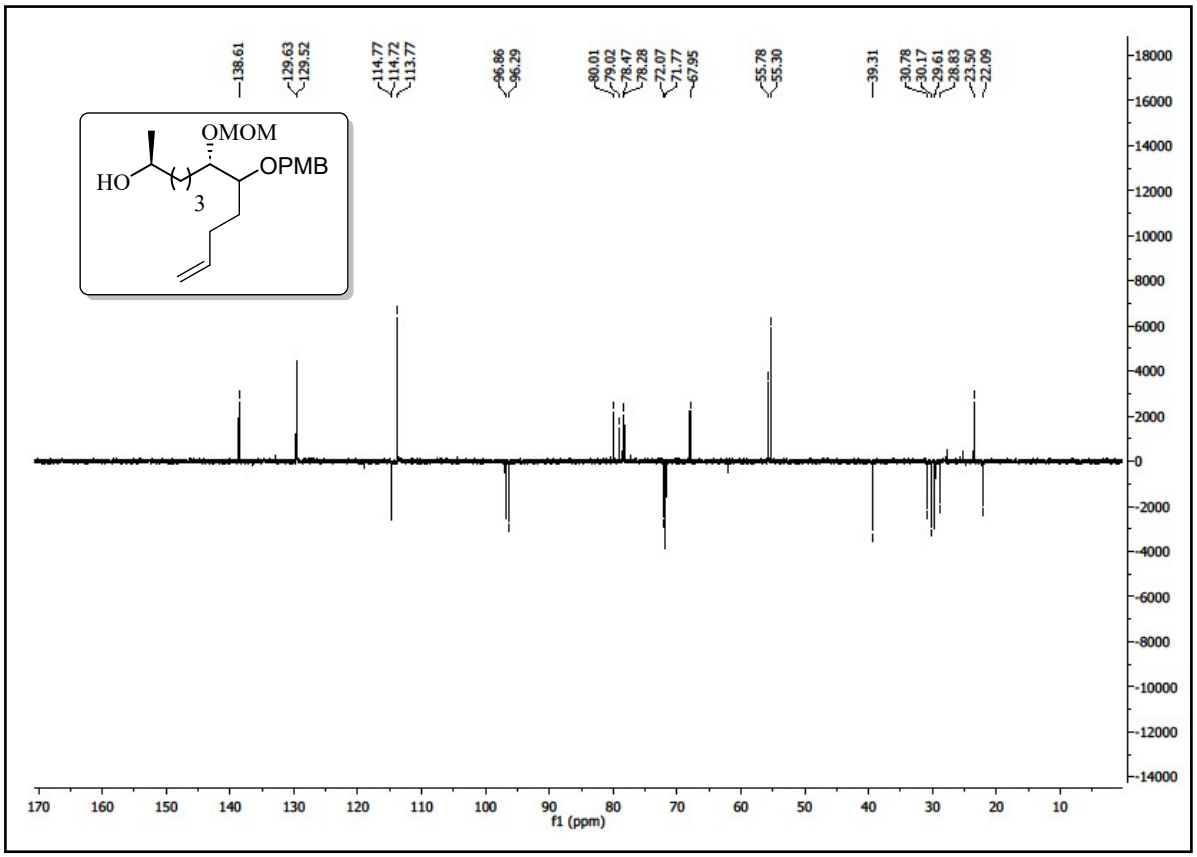
^{13}C NMR of compound 41 (126 MHz, $CDCl_3$)



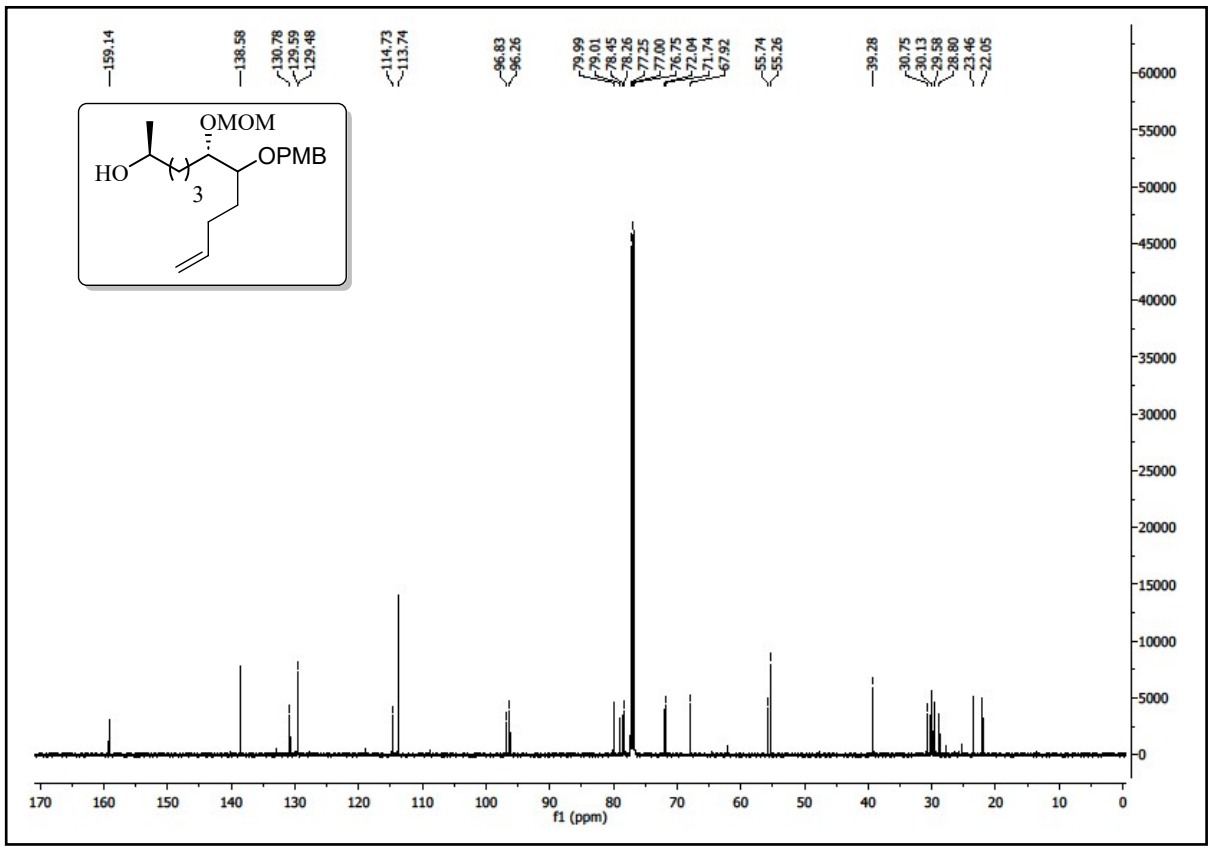
^{1}H NMR of compound 27 (500 MHz, $CDCl_3$)



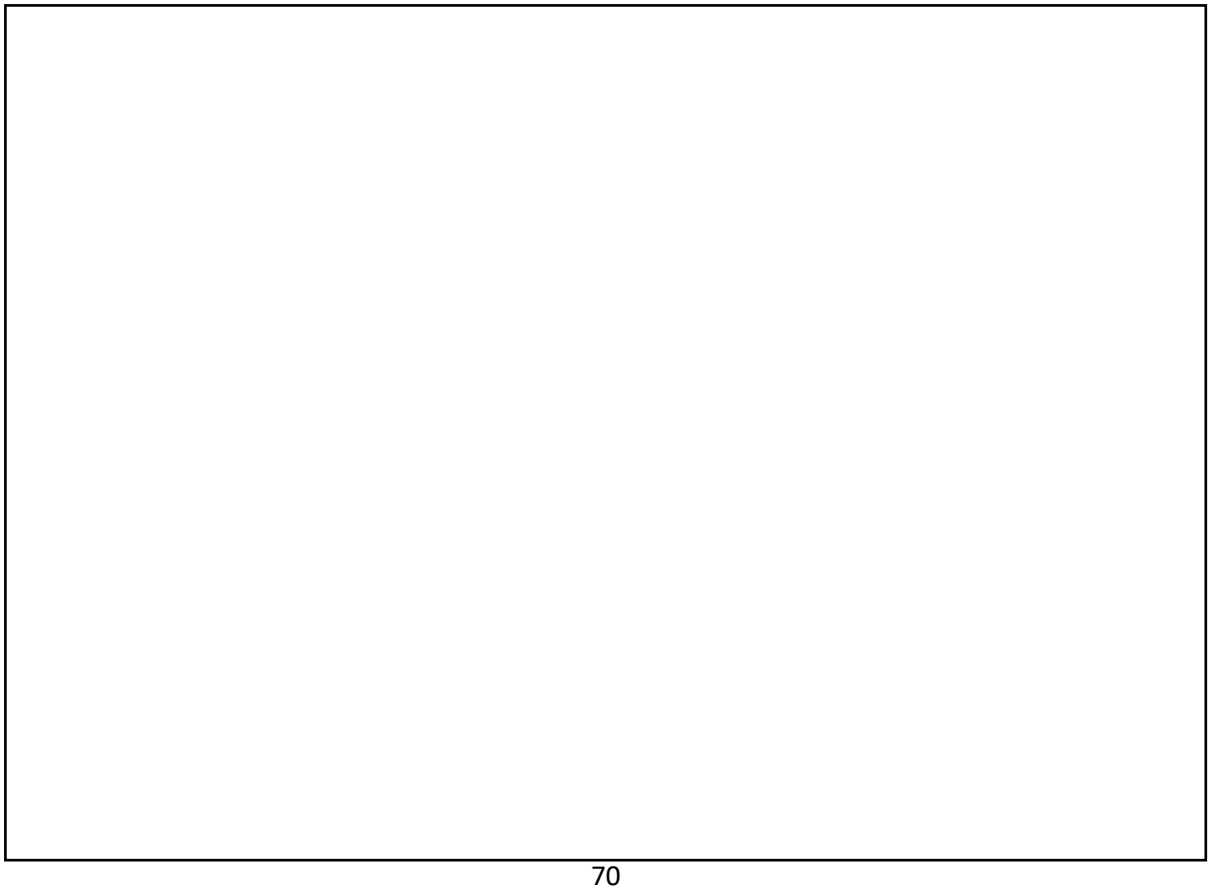
^{13}C DEPT NMR of compound 27 (126 MHz, $CDCl_3$)

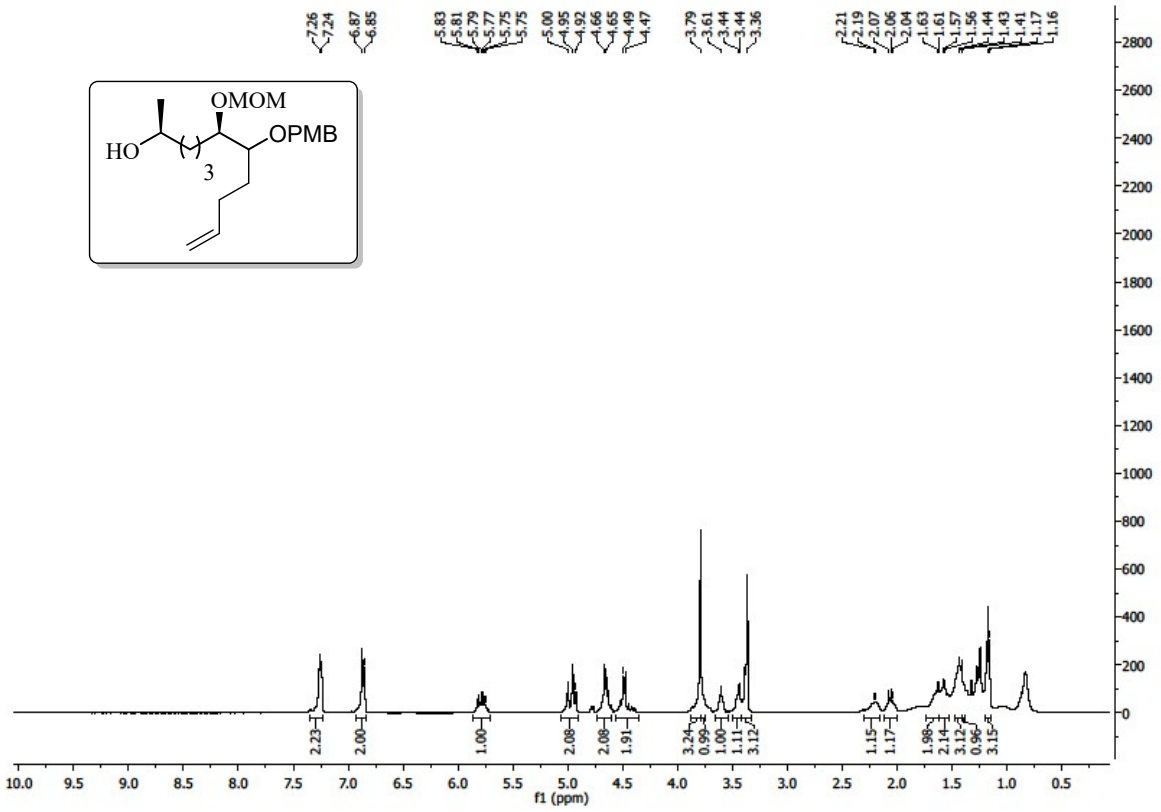


^{13}C NMR of compound 27 (126 MHz, $CDCl_3$)

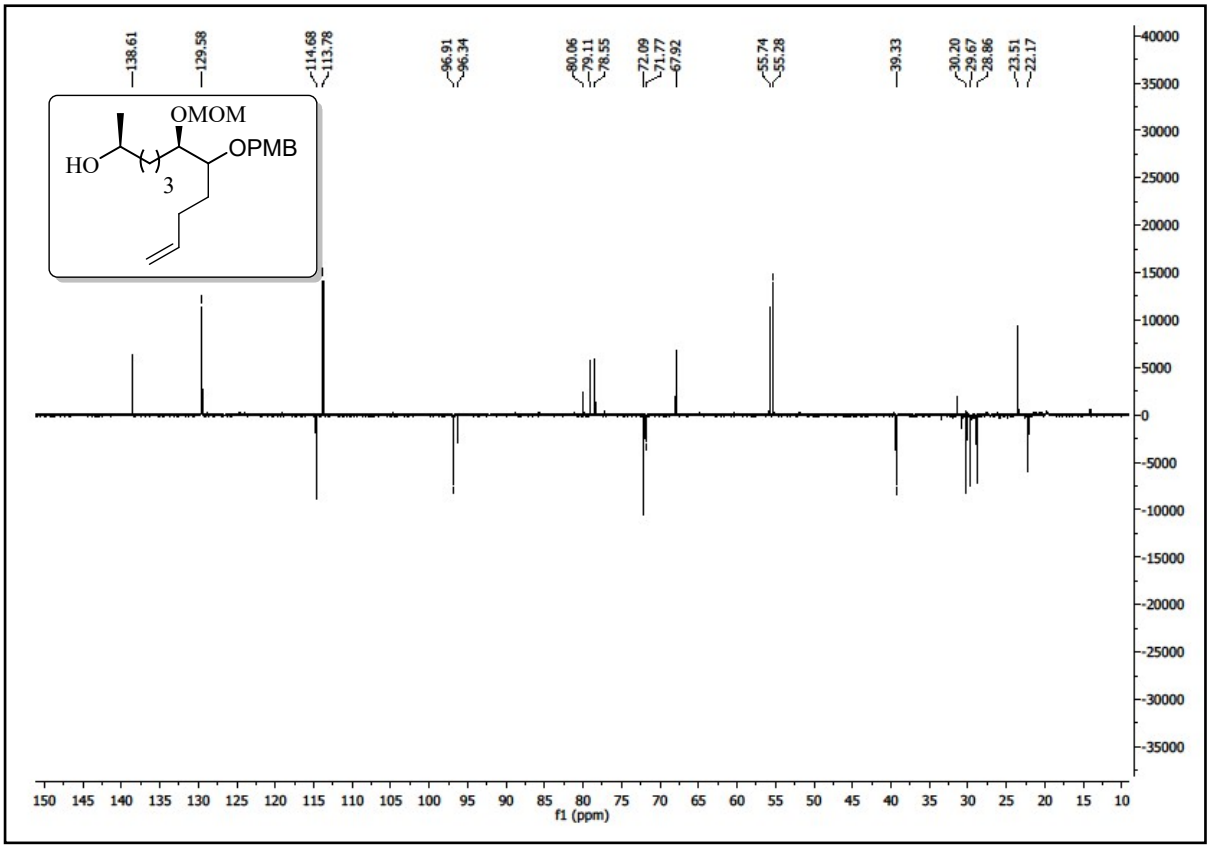


^{1}H NMR of compound 27A (500 MHz, $CDCl_3$)

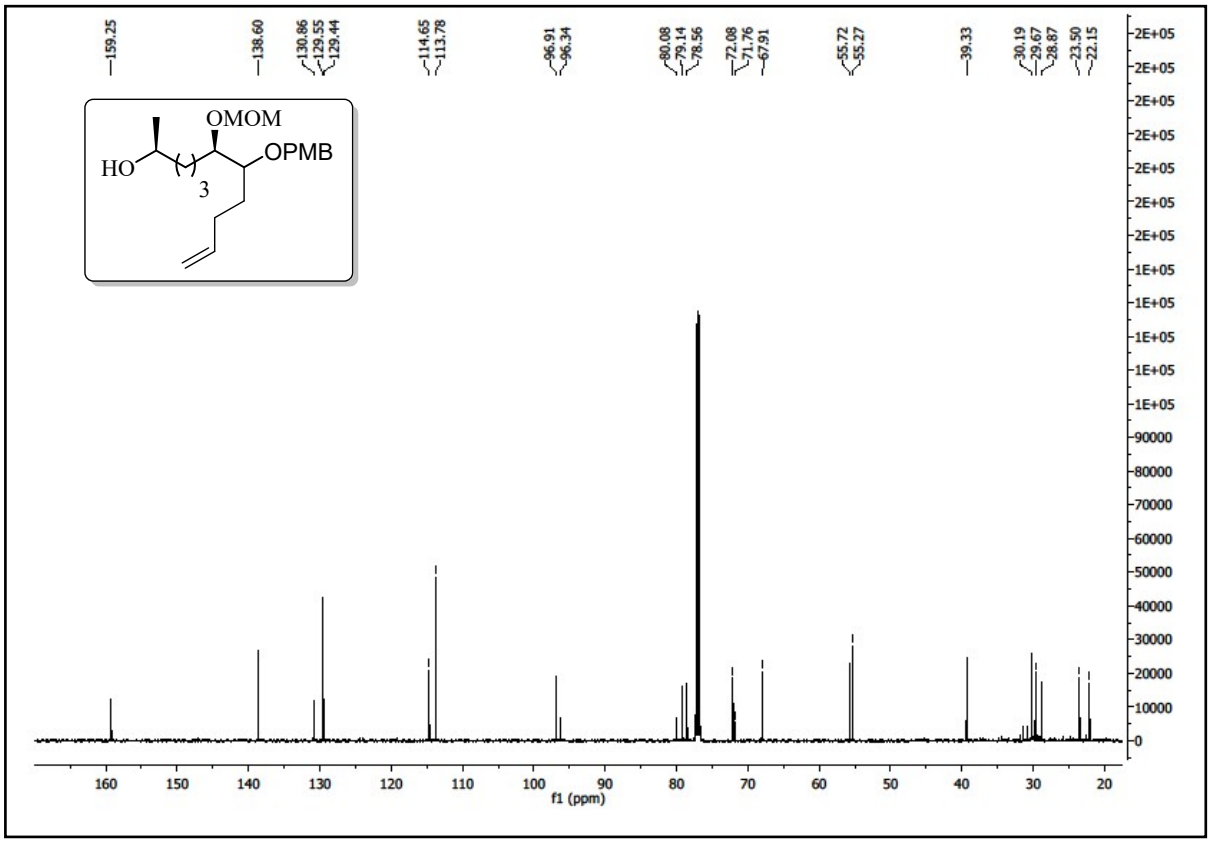




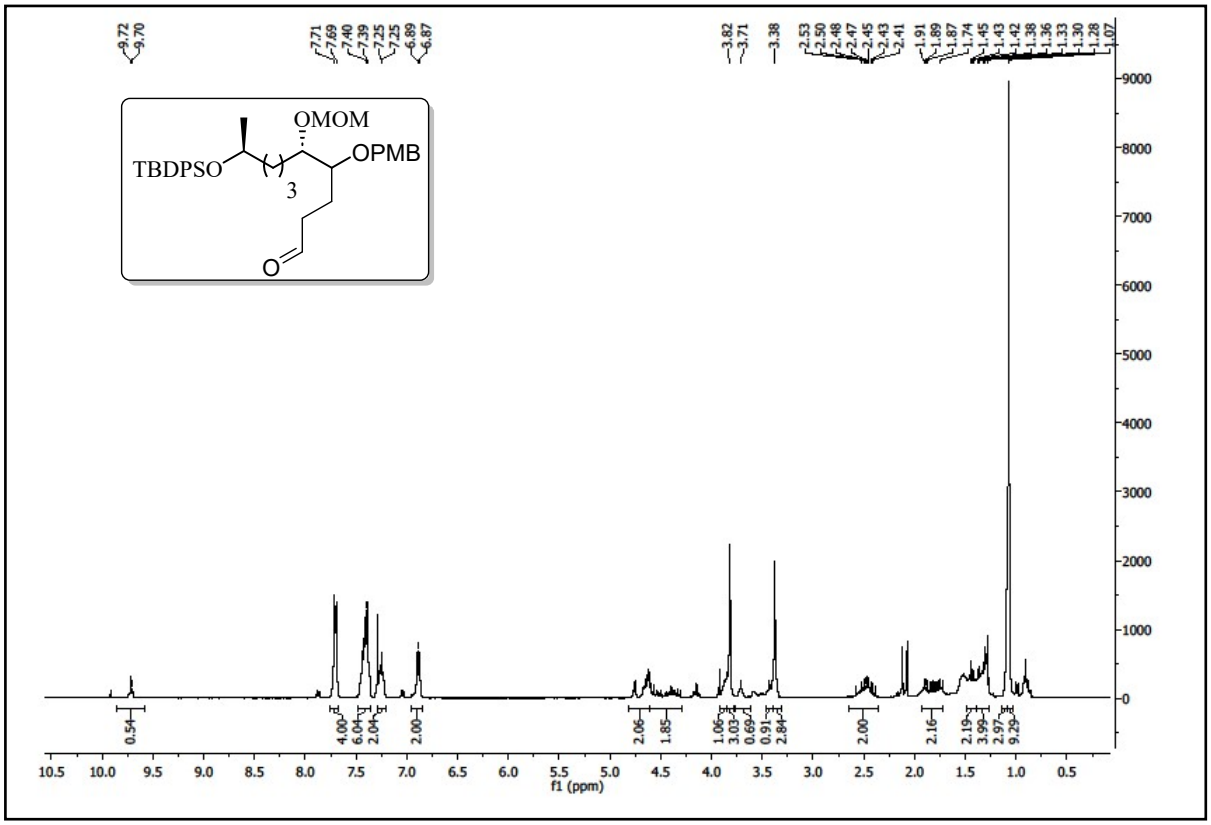
^{13}C DEPT NMR of compound 27A (126 MHz, $CDCl_3$)



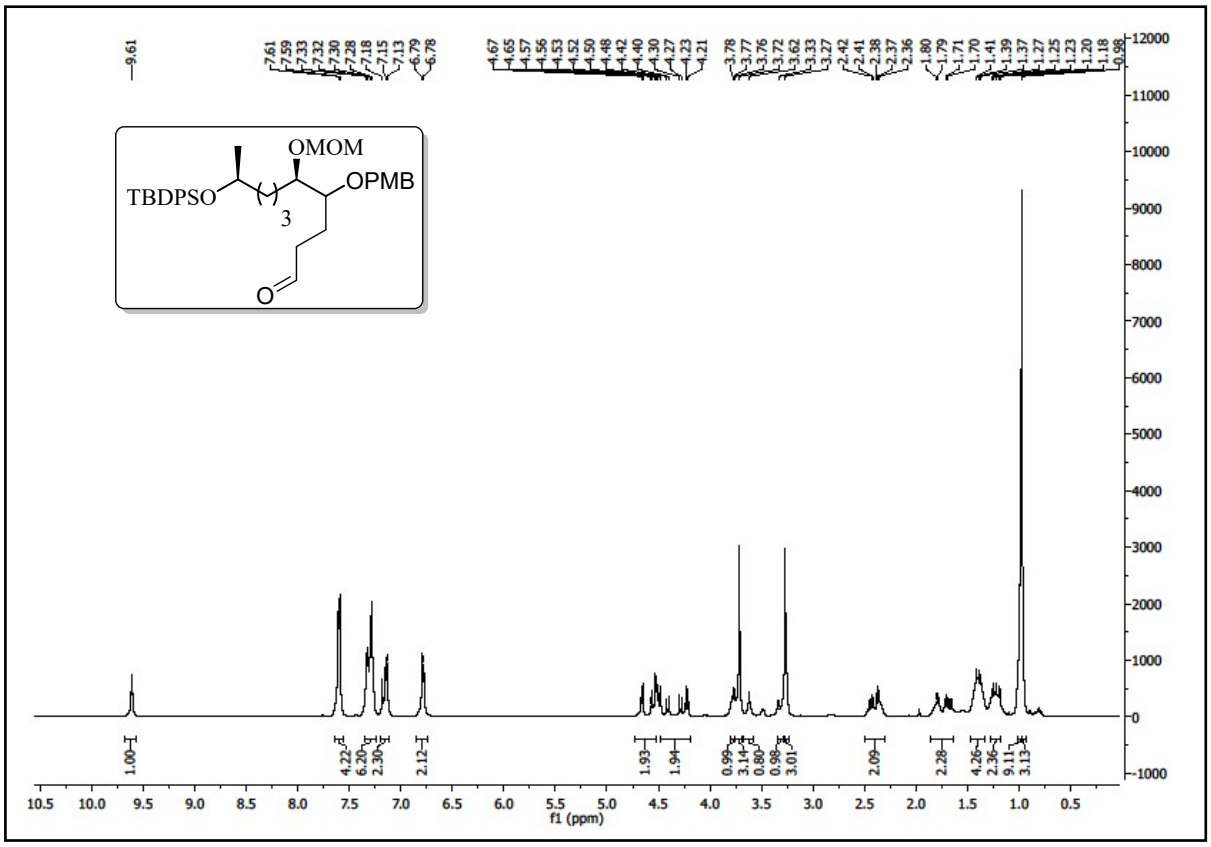
^{13}C NMR of compound 27A (126 MHz, $CDCl_3$)



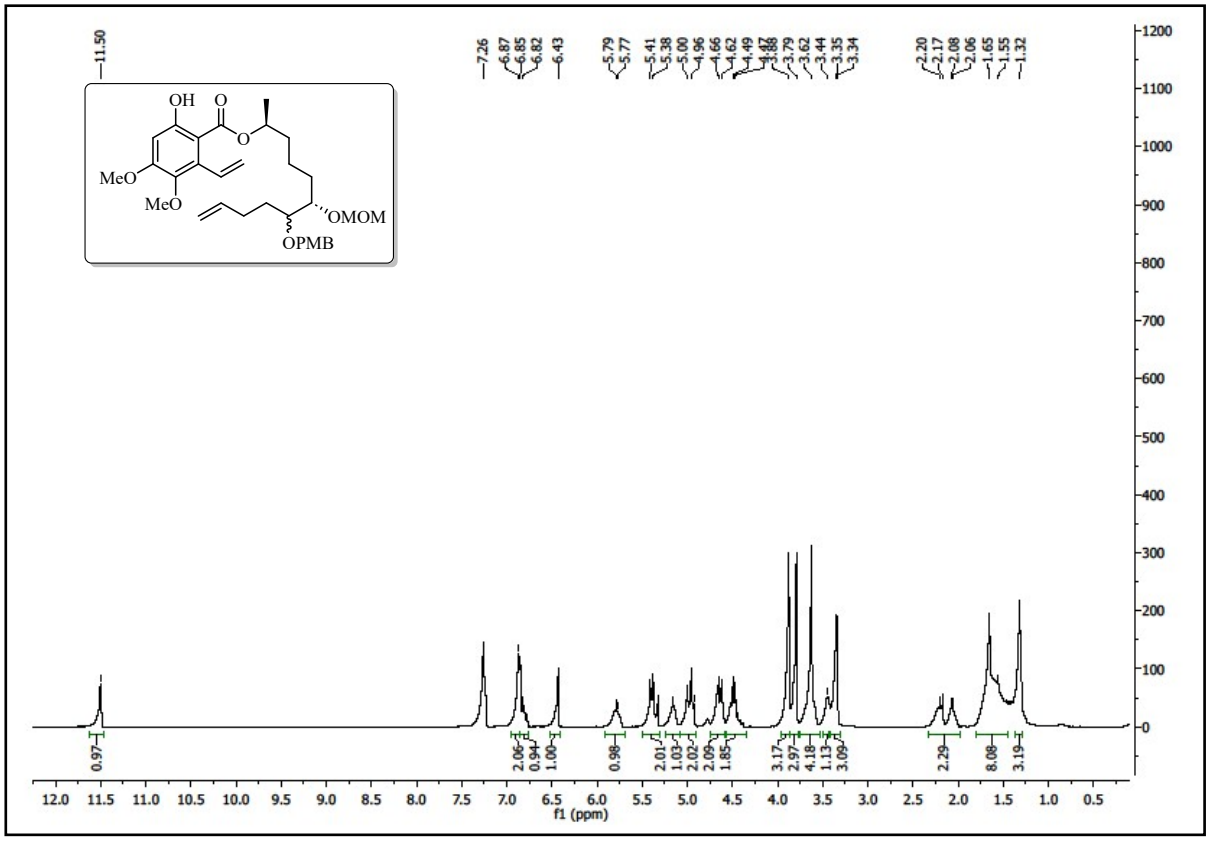
^{1}H NMR of compound 33 (400 MHz, $CDCl_3$)



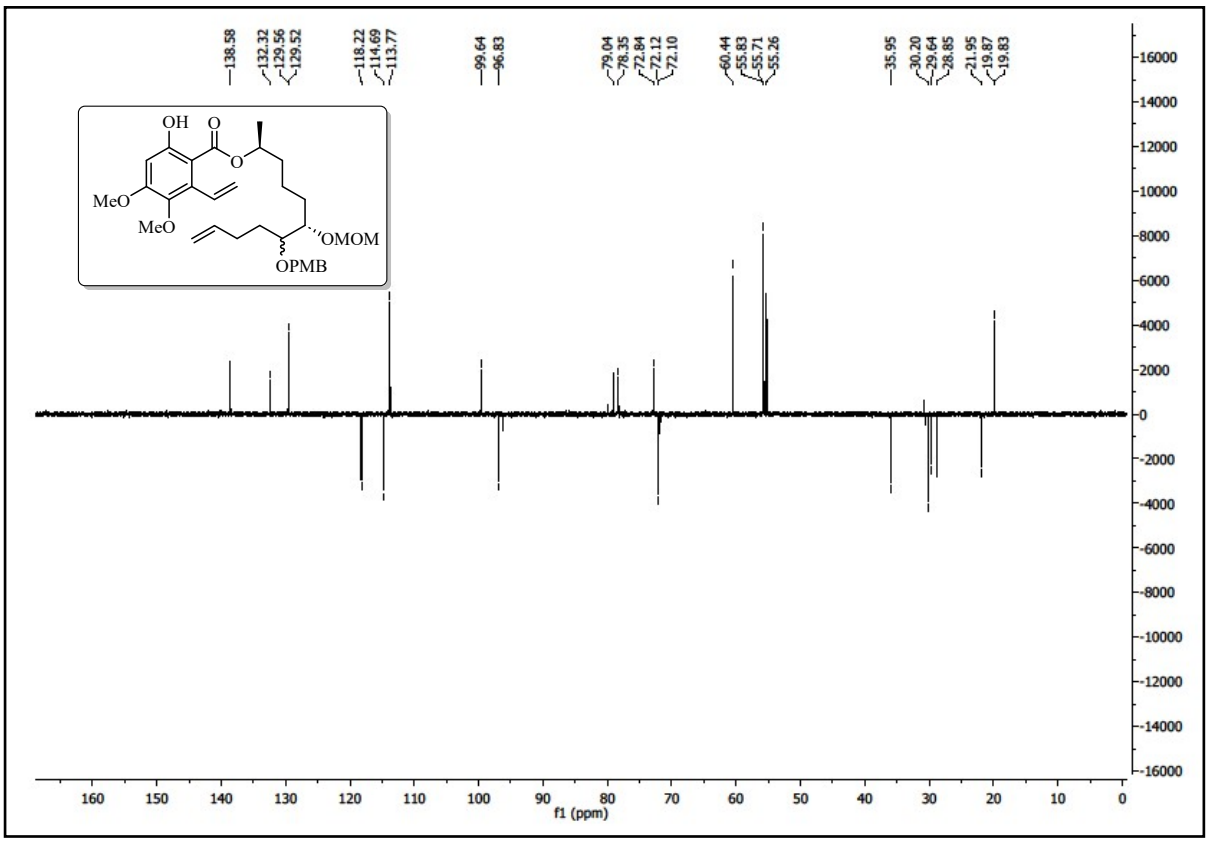
^{1}H NMR of compound 42 (500 MHz, $CDCl_3$)



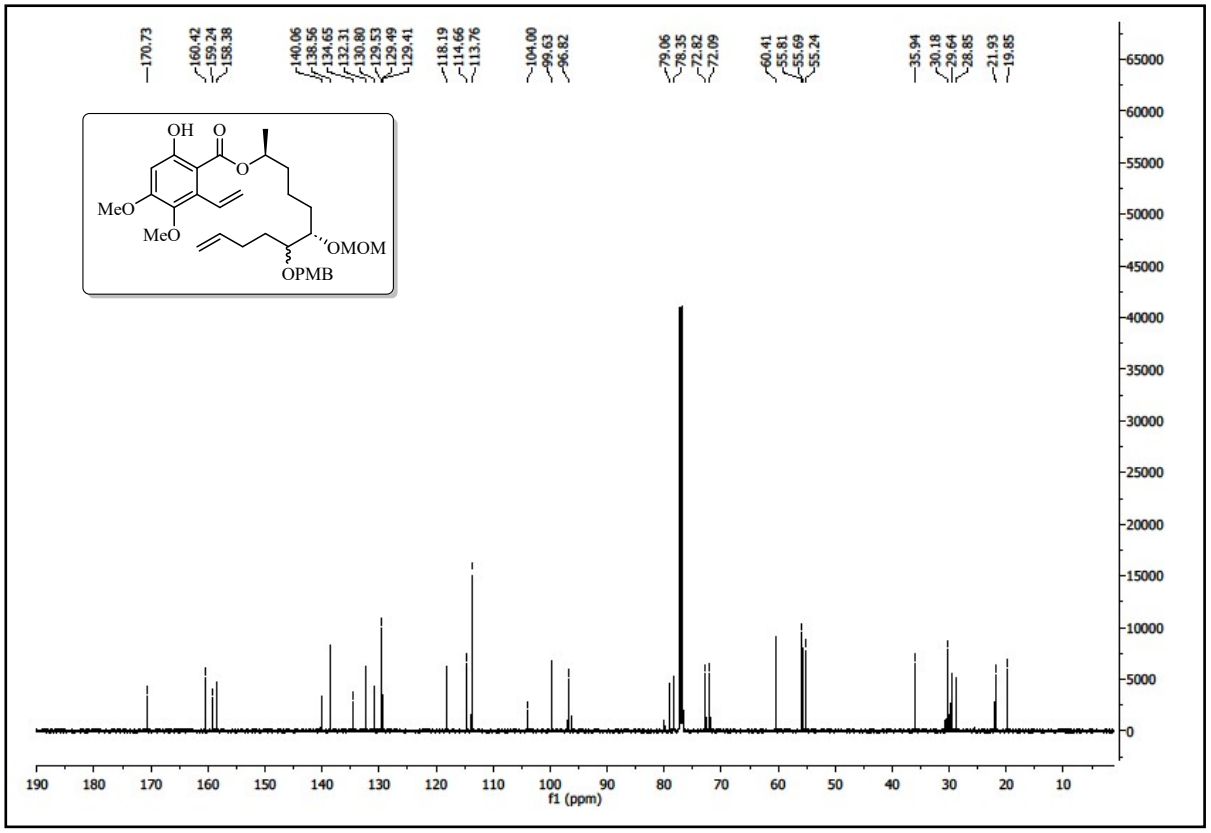
^{1}H NMR of compound 28 (400 MHz, $CDCl_3$)



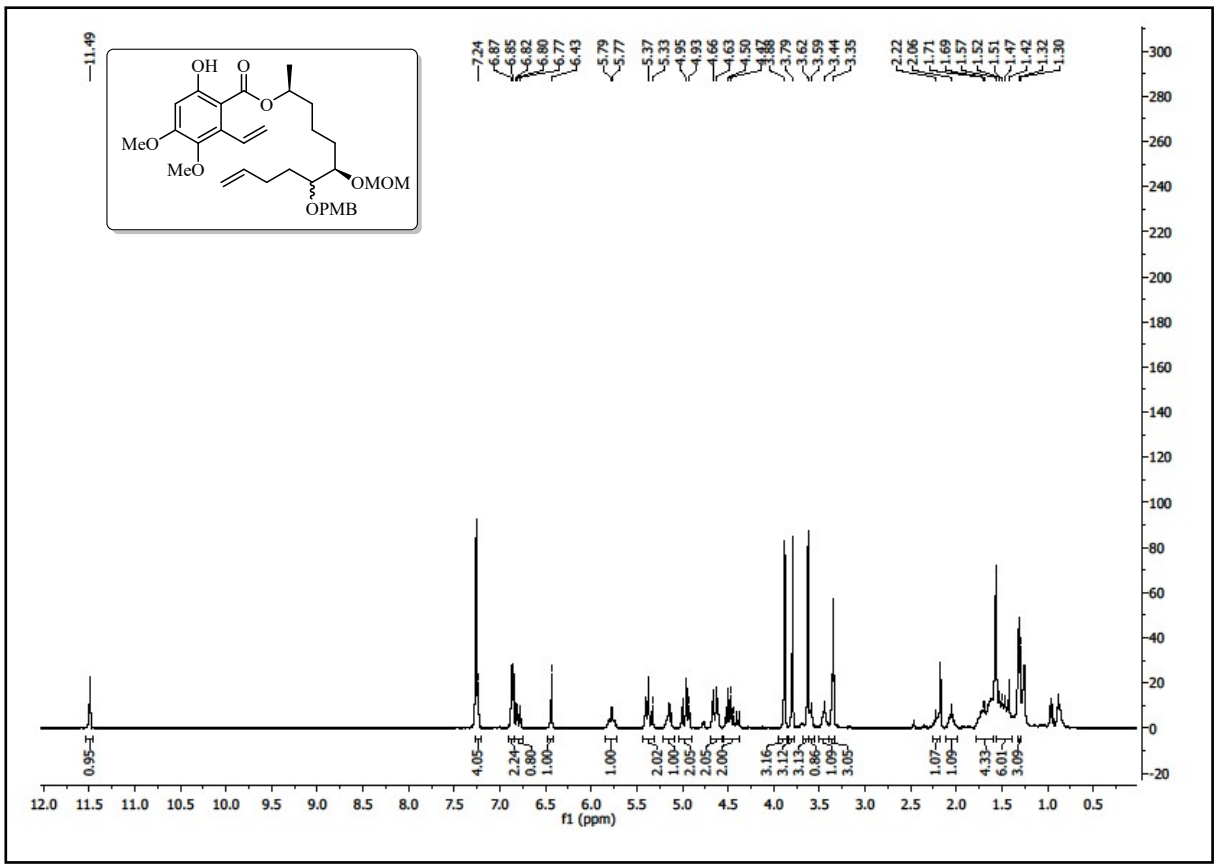
^{13}C DEPT NMR of compound 28 (126 MHz, $CDCl_3$)



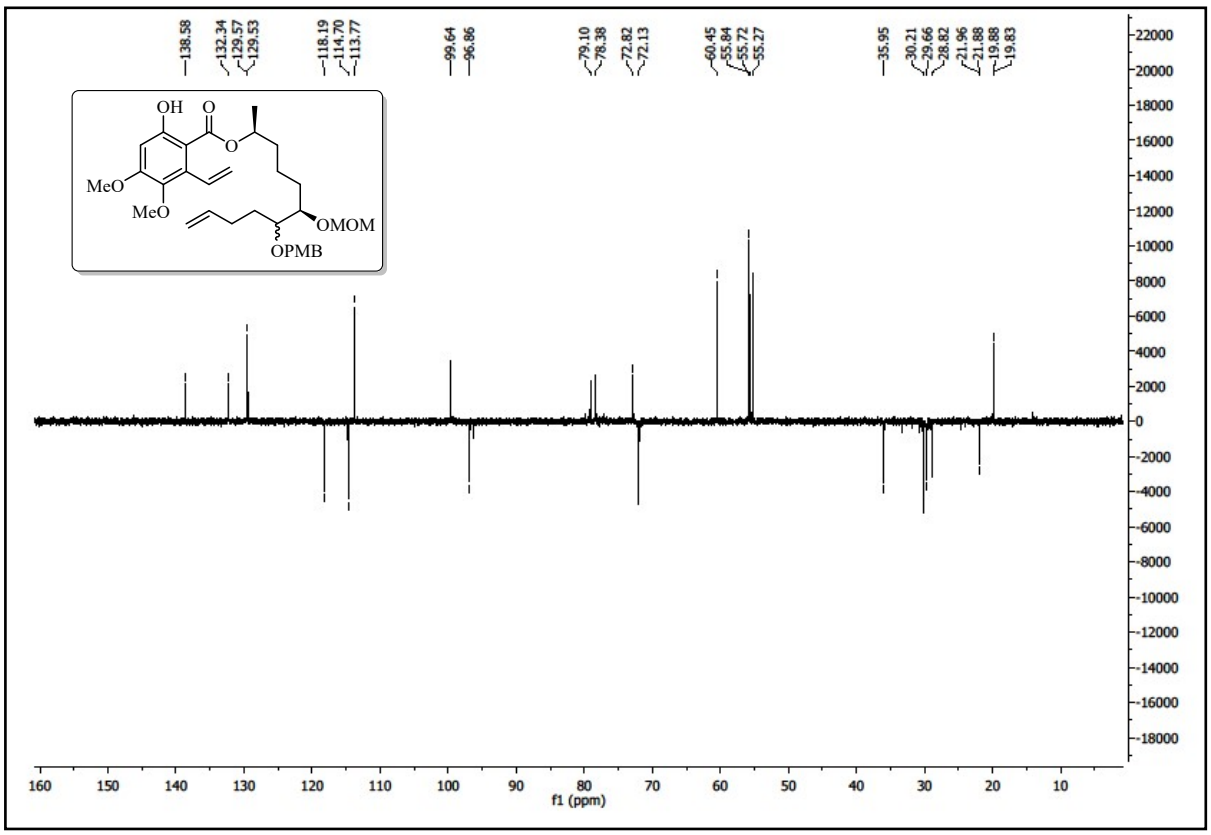
^{13}C NMR of compound 28 (126 MHz, $CDCl_3$)



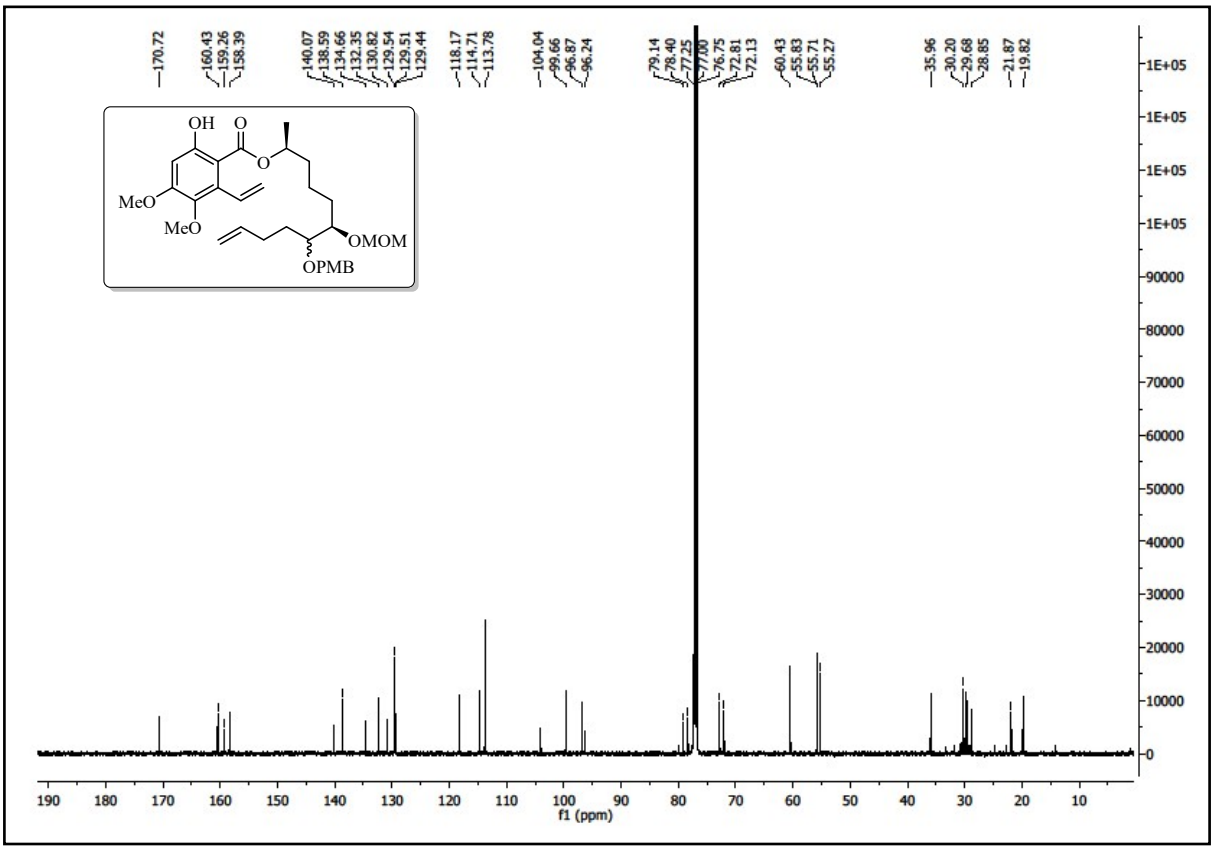
^{1}H NMR of compound 28A (400 MHz, $CDCl_3$)



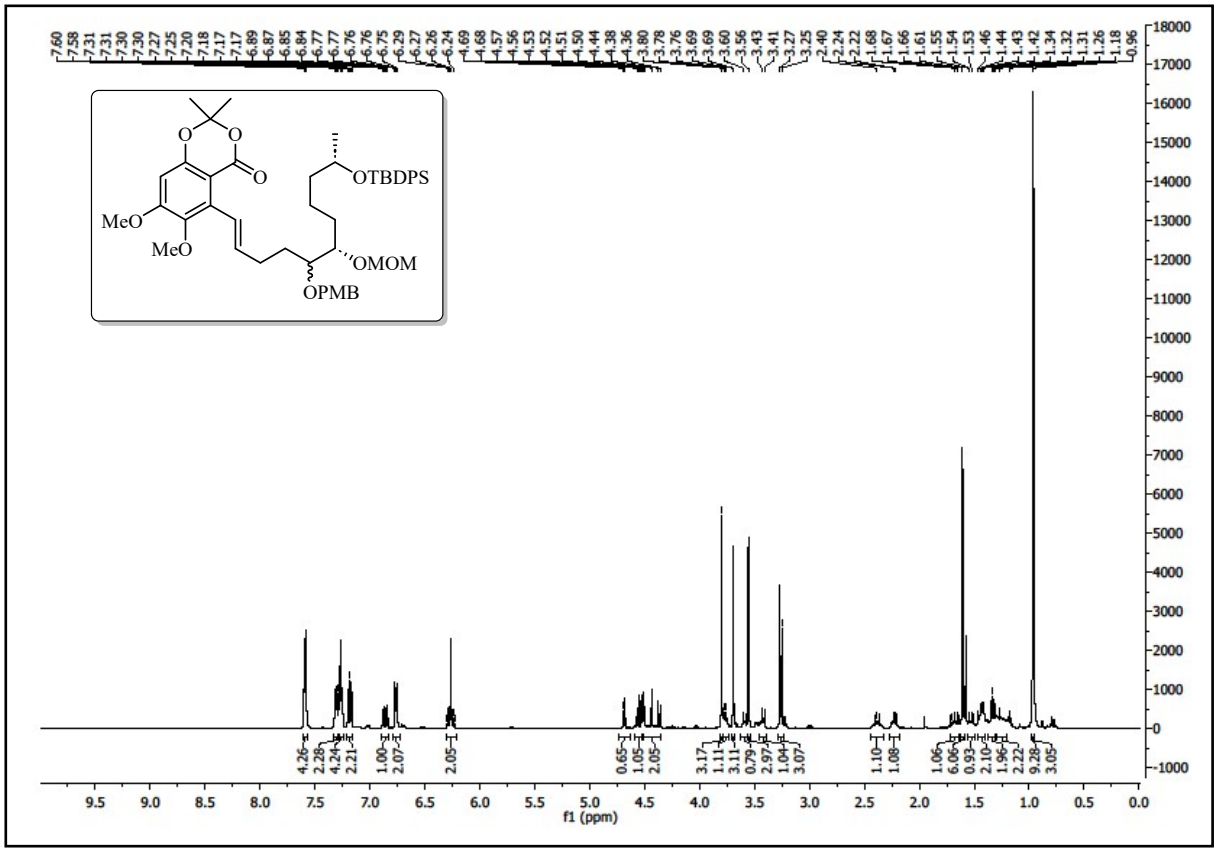
^{13}C DEPT NMR of compound 28A (126 MHz, $CDCl_3$)



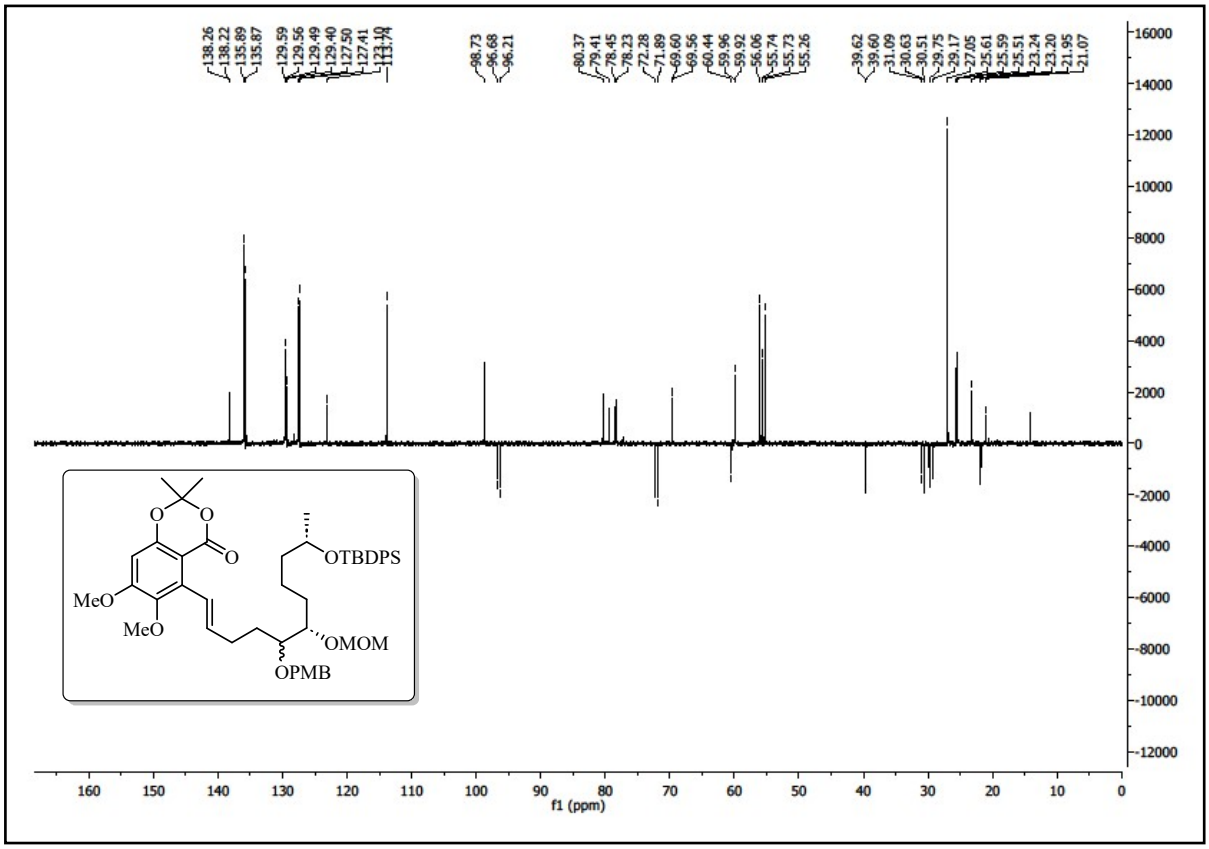
^{13}C DEPT NMR of compound 28A (126 MHz, $CDCl_3$)



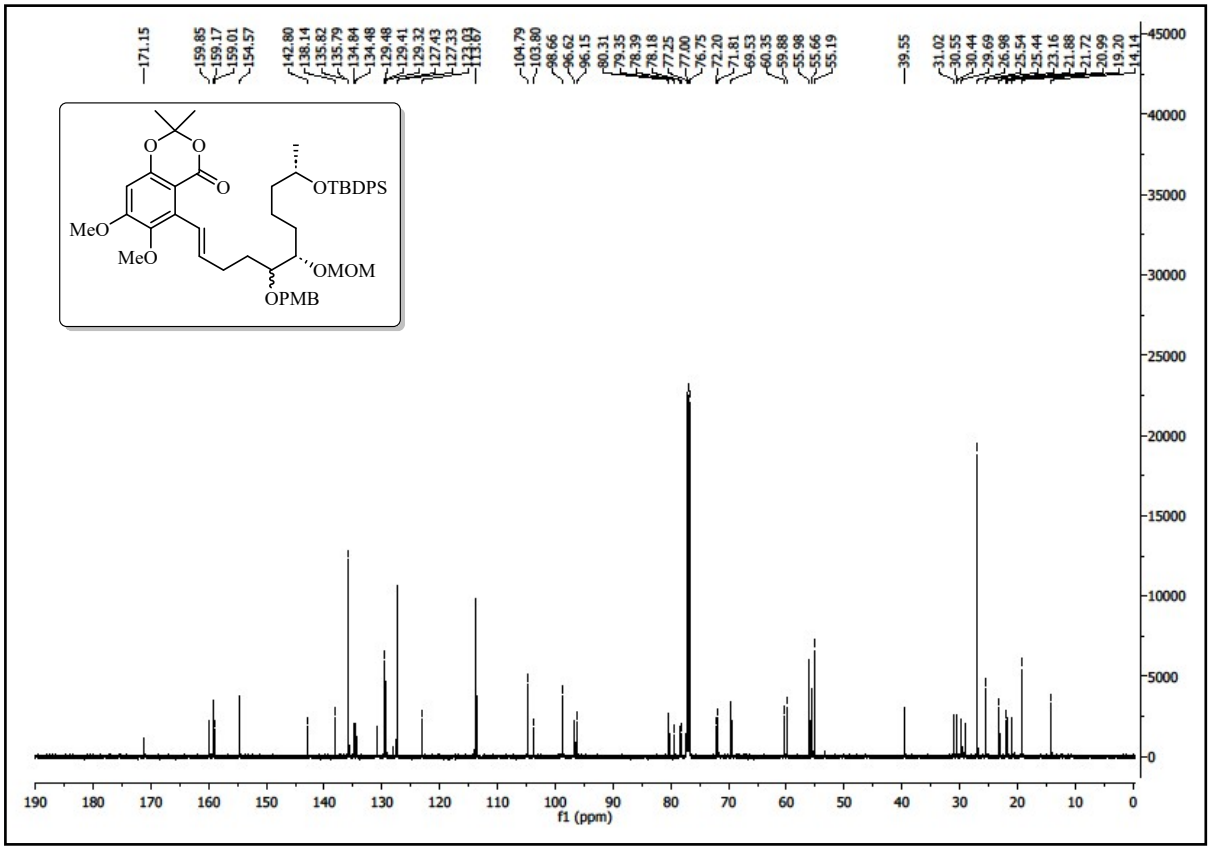
^{1}H NMR of compound 34 (500 MHz, $CDCl_3$)



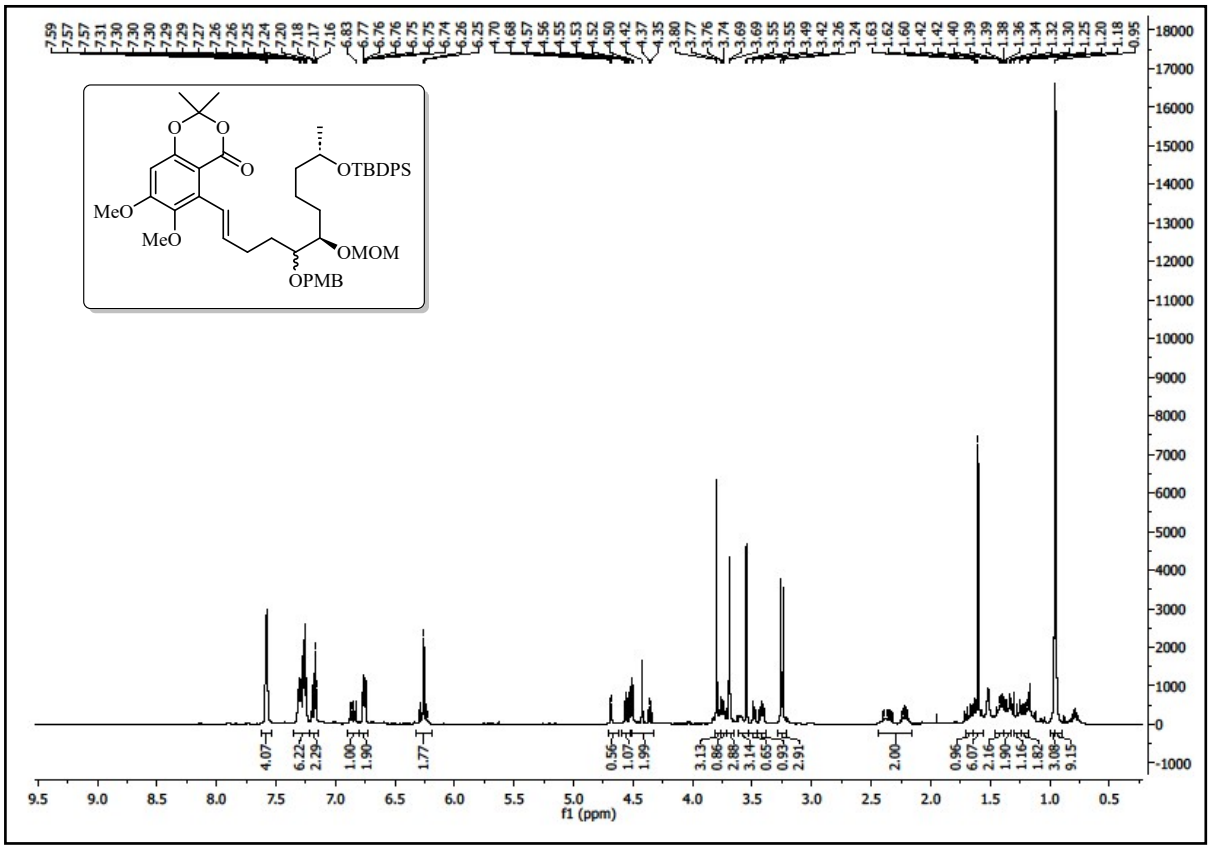
^{13}C DEPT NMR of compound 34 (126 MHz, $CDCl_3$)



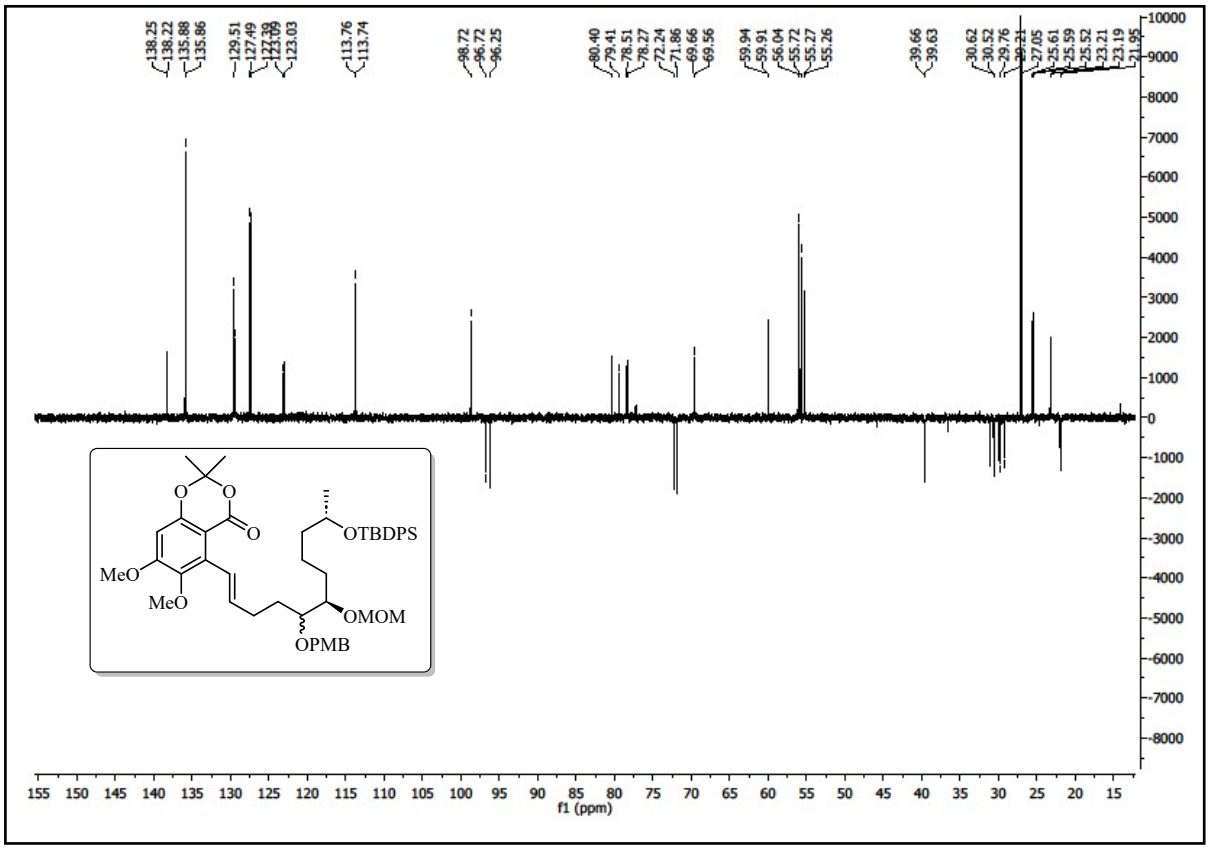
^{13}C NMR of compound 34 (126 MHz, $CDCl_3$)



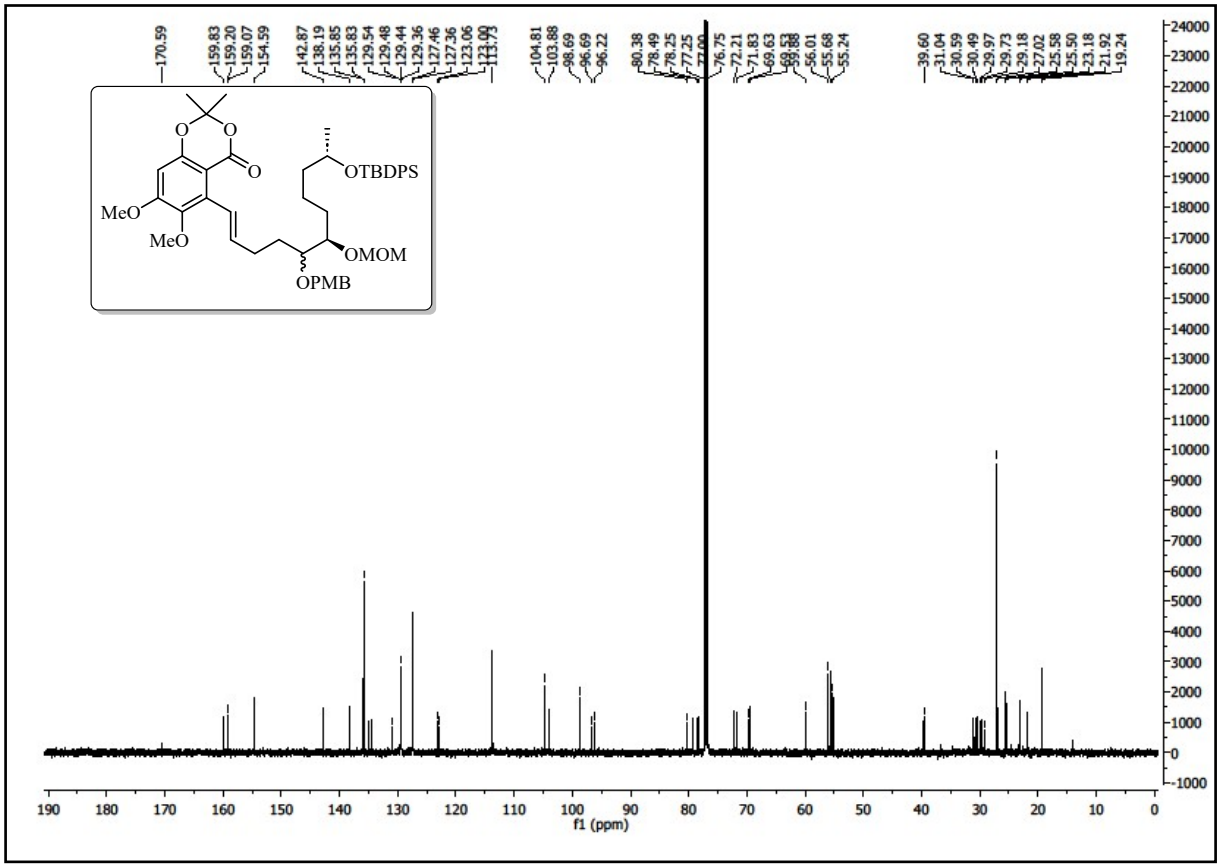
^{1}H NMR of compound 43 (500 MHz, $CDCl_3$)



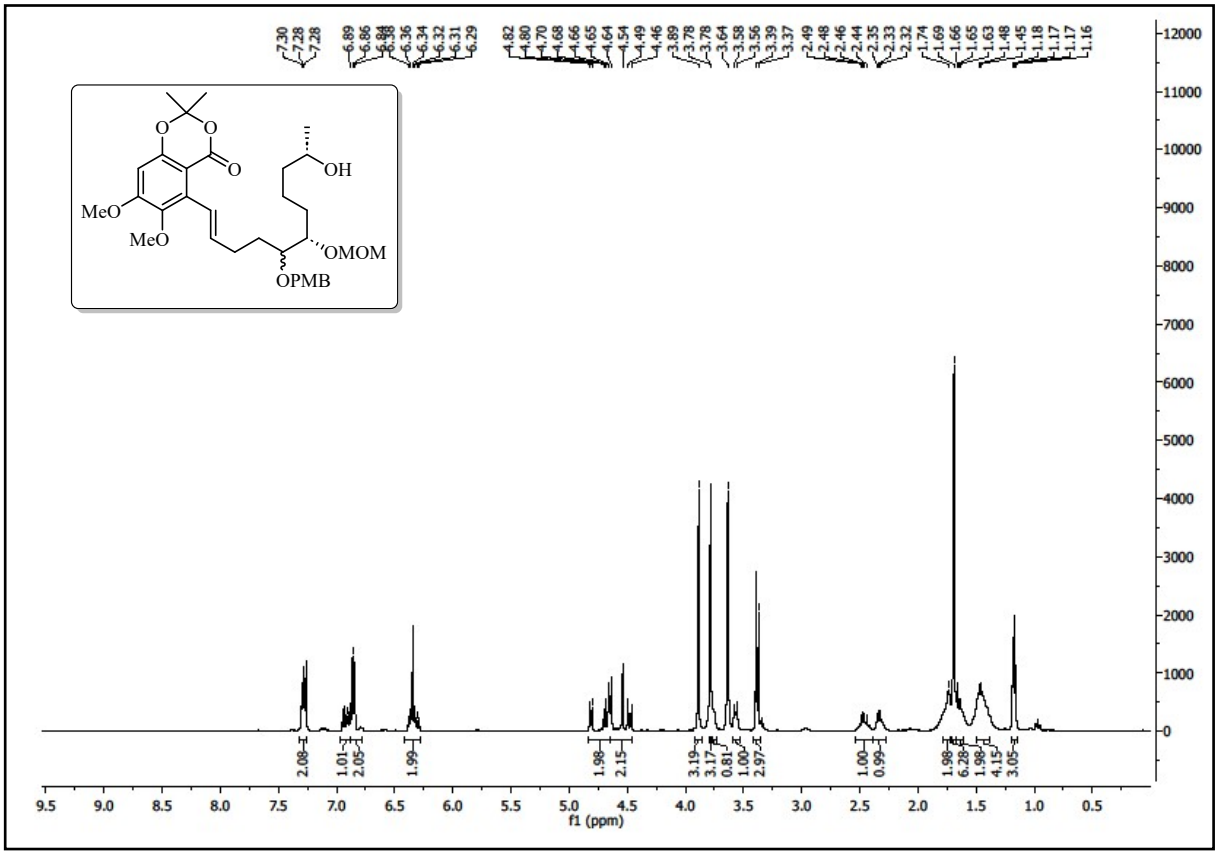
^{13}C DEPT NMR of compound 43 (126 MHz, $CDCl_3$)



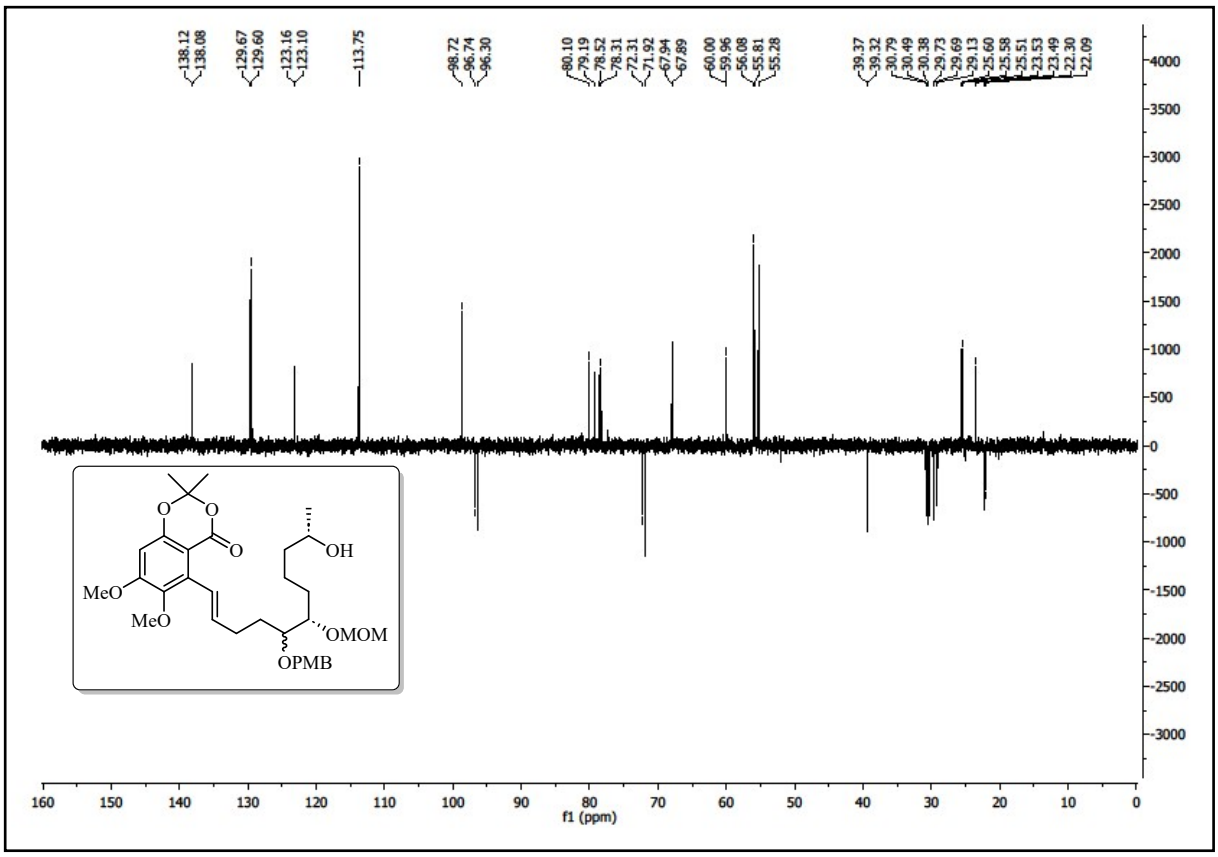
^{13}C NMR of compound 43 (126 MHz, $CDCl_3$)



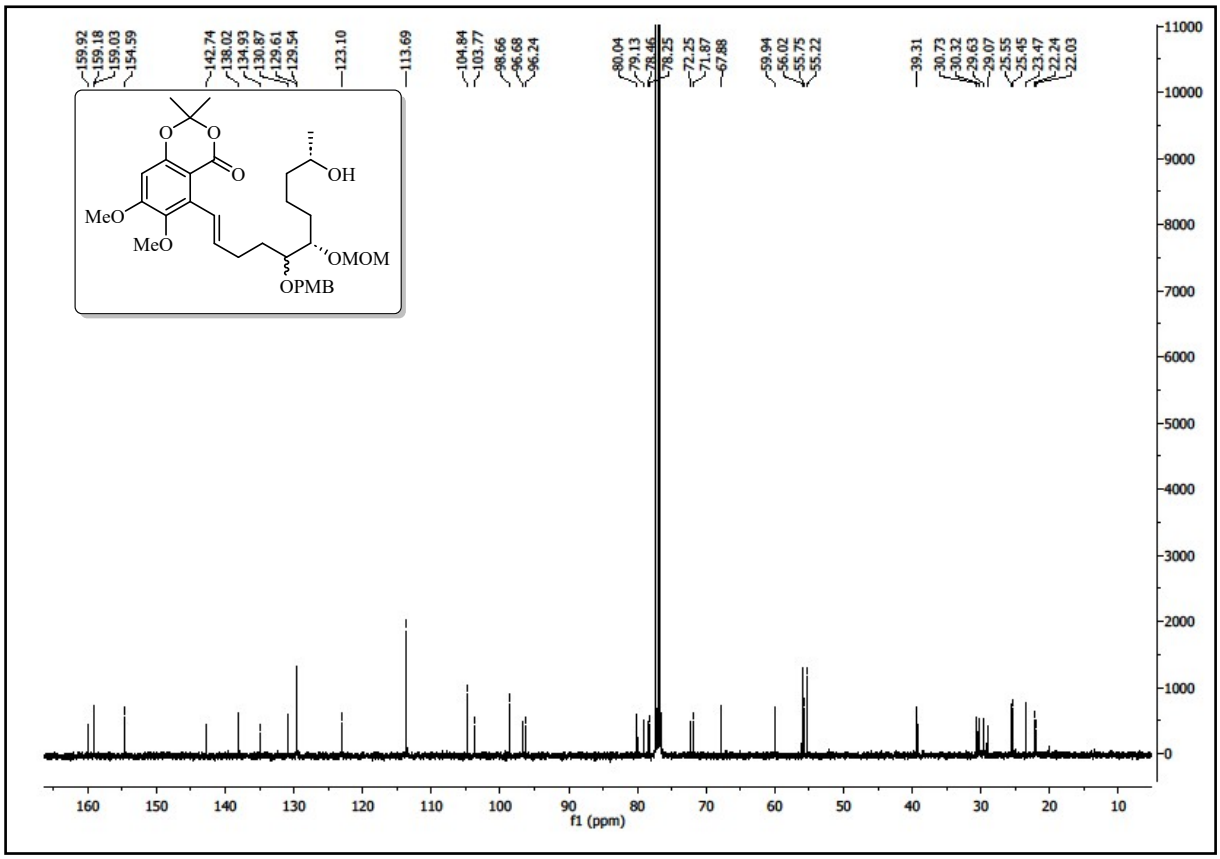
^{1}H NMR of compound 35 (500 MHz, $CDCl_3$)



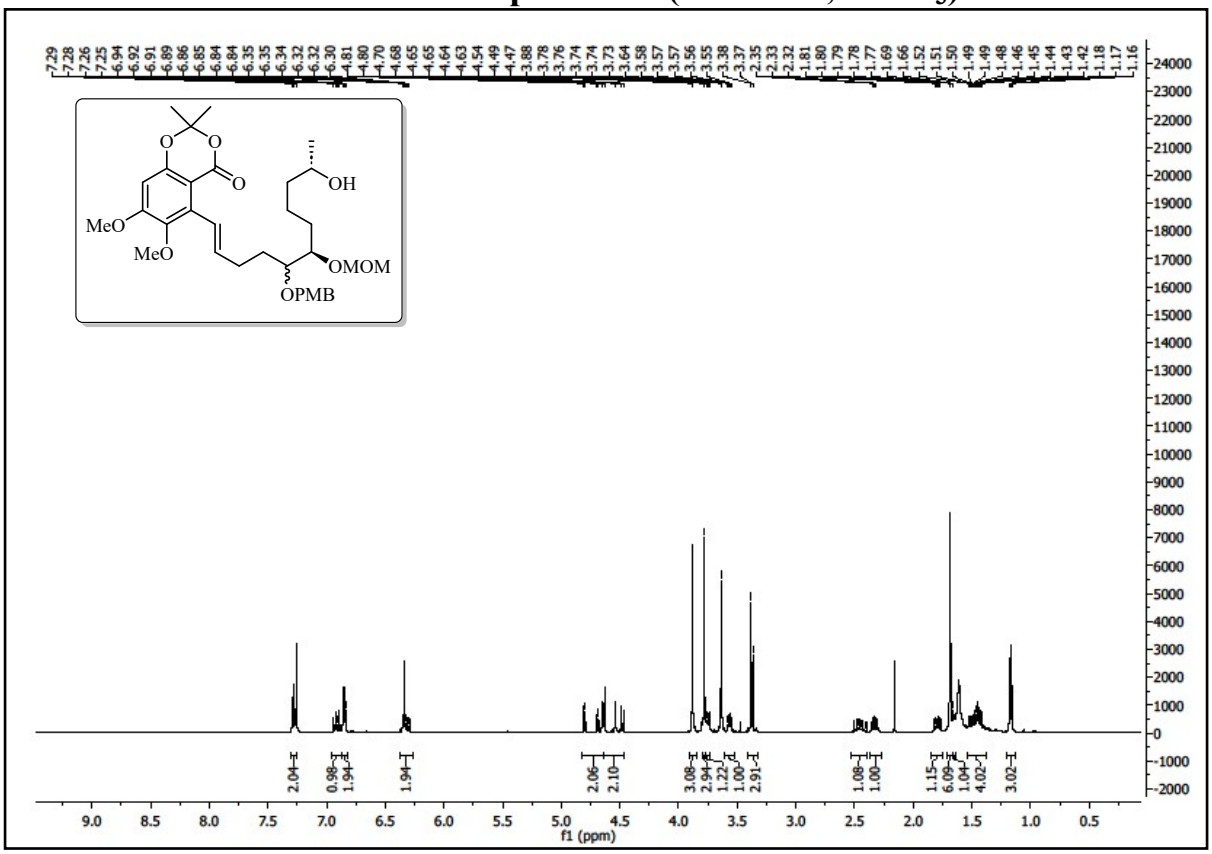
^{13}C DEPT NMR of compound 35 (126 MHz, $CDCl_3$)



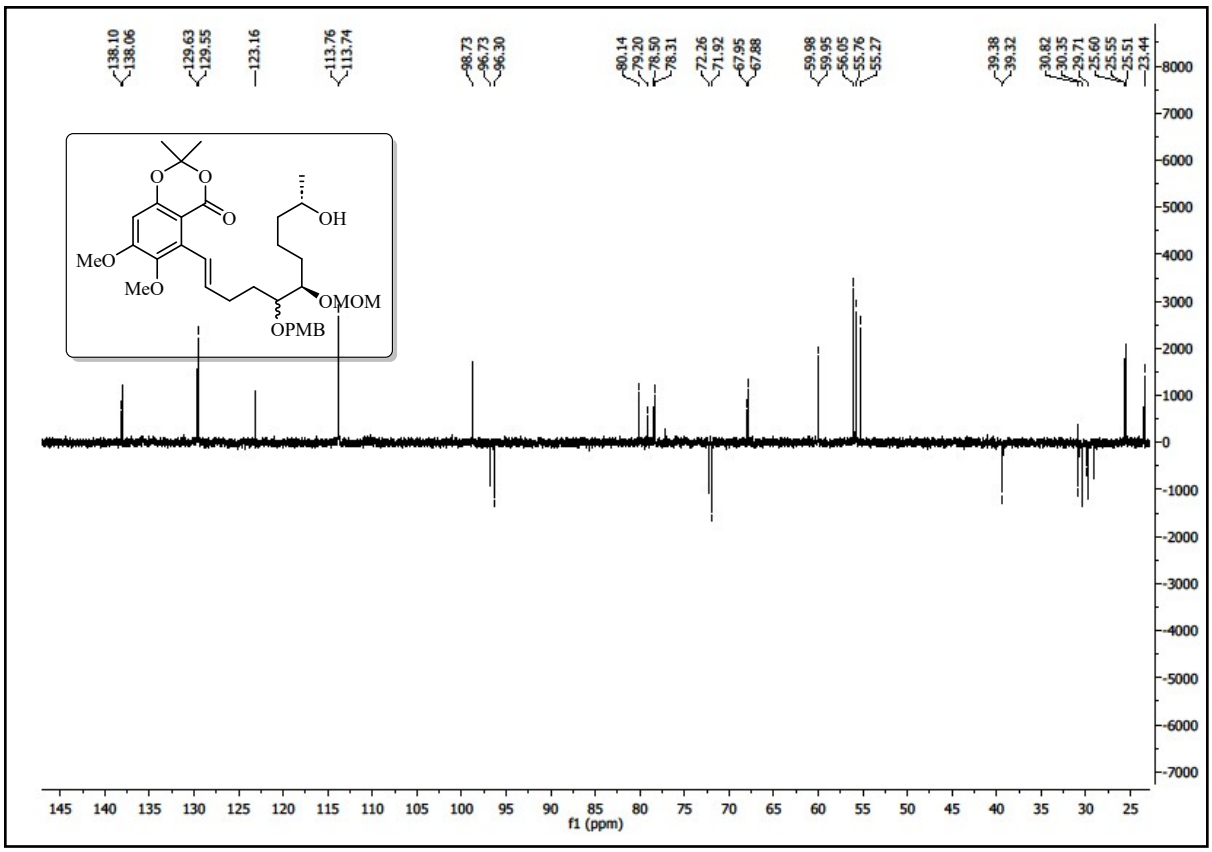
^{13}C NMR of compound 35 (126 MHz, $CDCl_3$)



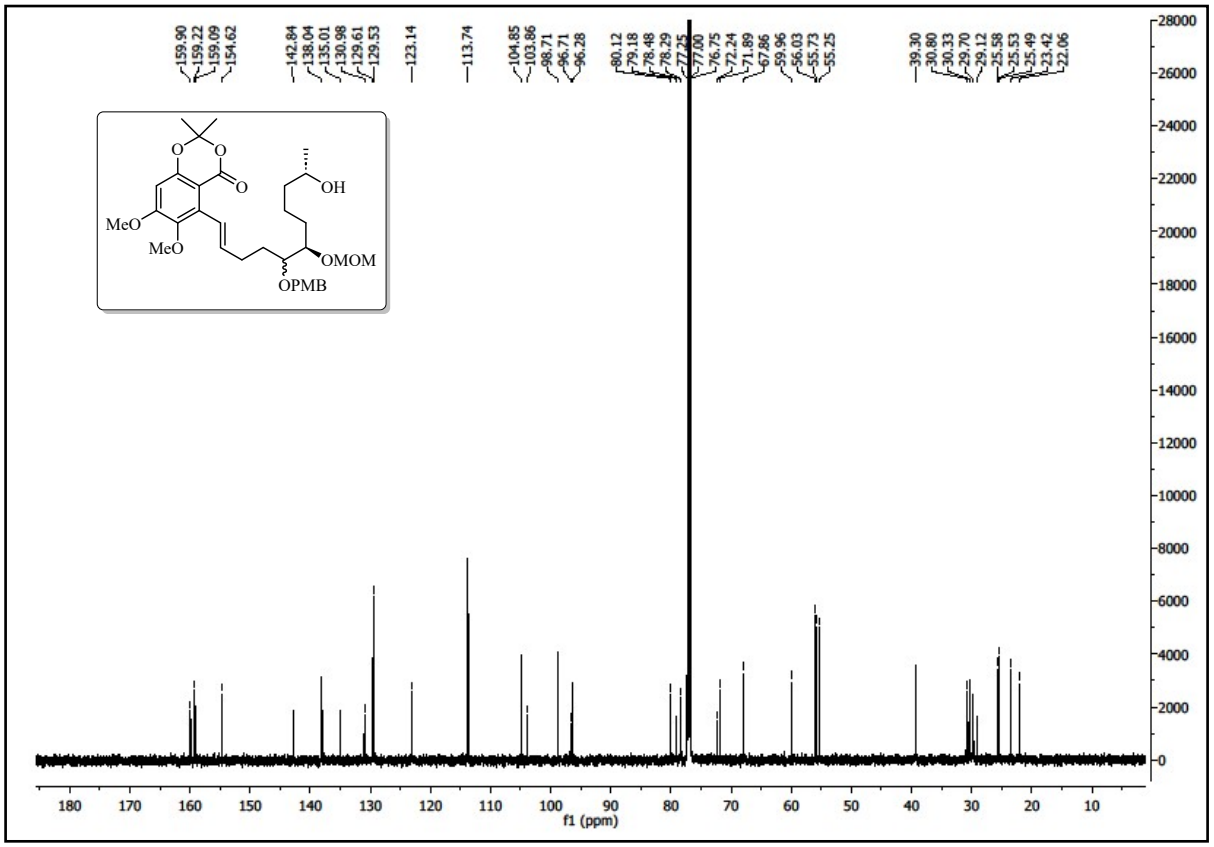
^{1}H NMR of compound 44 (500 MHz, $CDCl_3$)



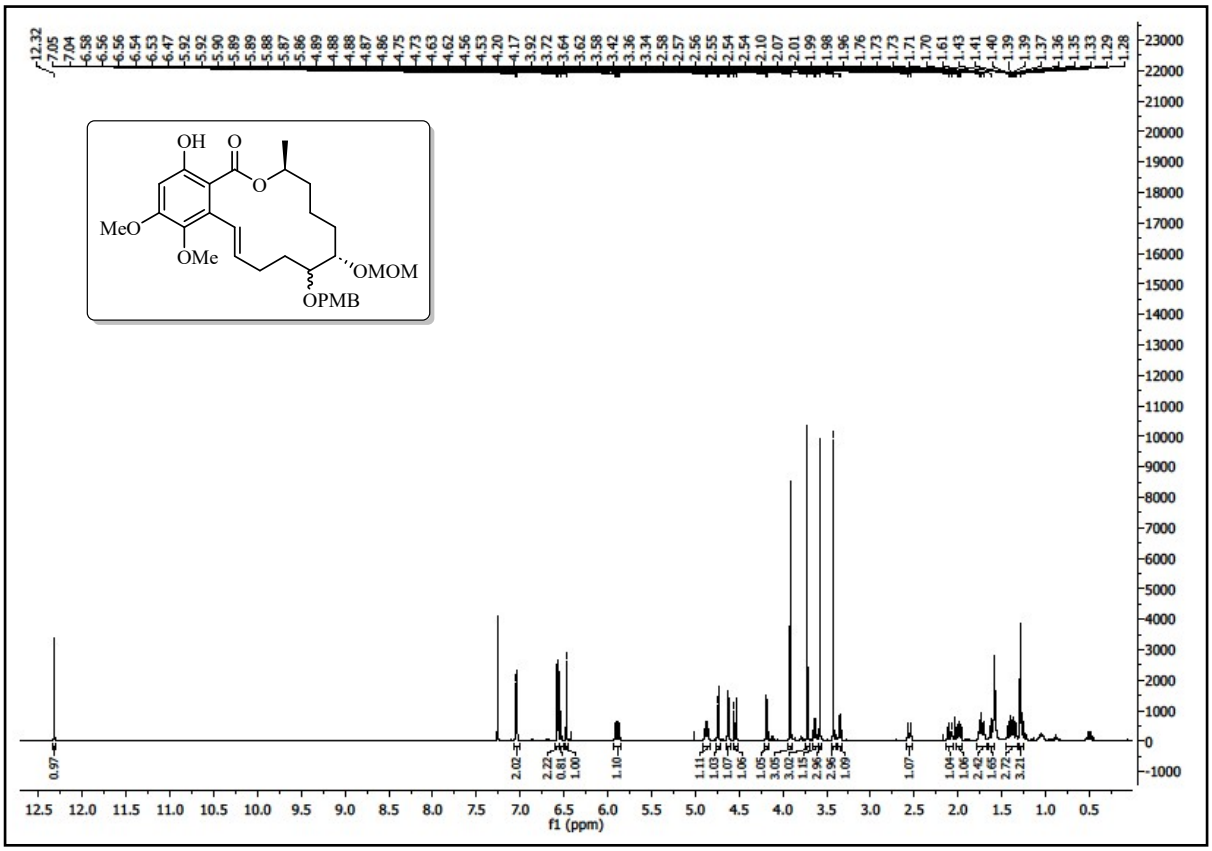
^{13}C DEPT NMR of compound 44 (126 MHz, $CDCl_3$)


138.10
138.06
129.63
129.55
123.16
113.76
113.74
98.73
96.73
96.30
80.14
79.20
78.50
78.31
72.26
71.92
67.95
67.88
59.98
59.95
56.05
55.76
55.27
39.38
39.32
30.82
30.35
29.71
25.60
25.55
25.51
23.44
O
O
O
OH
MeO
MeO
OMOM
OPMB
f1 (ppm)

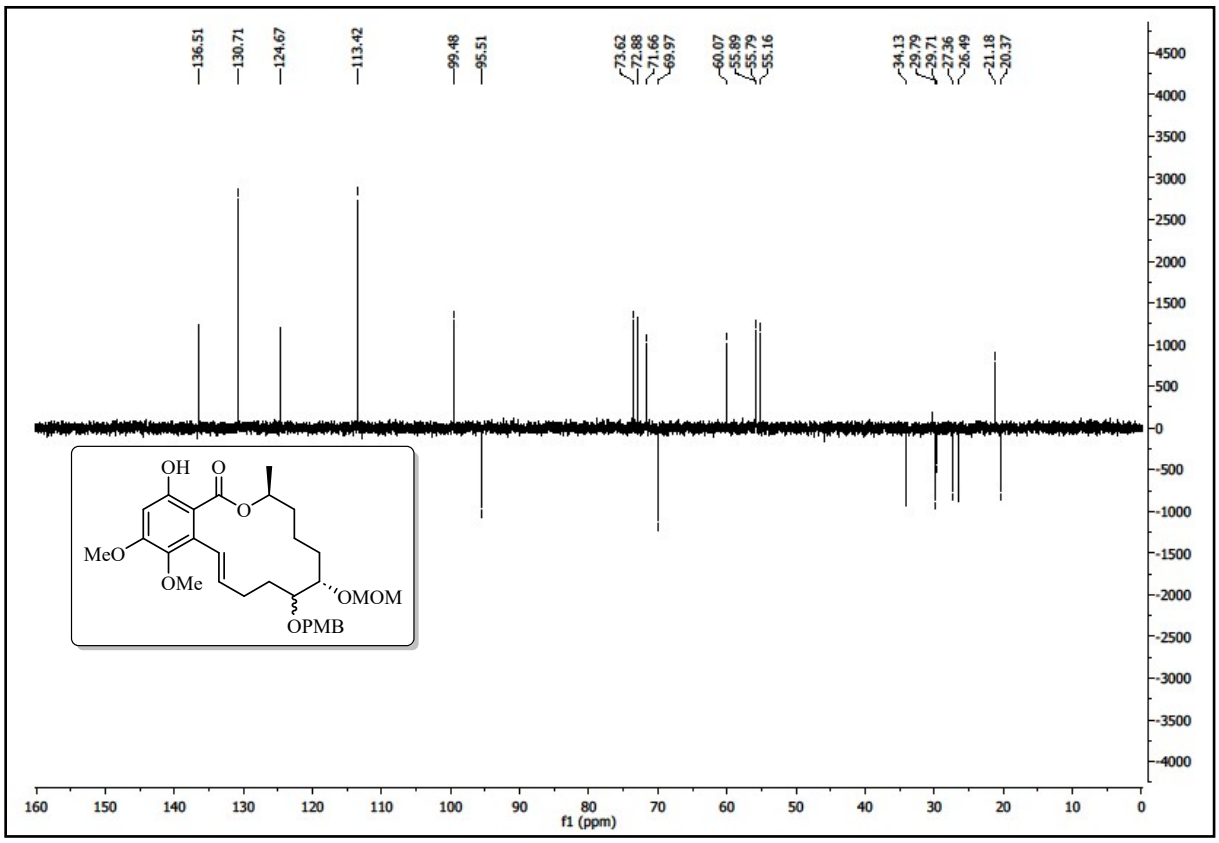
^{13}C DEPT NMR of compound 44 (126 MHz, $CDCl_3$)



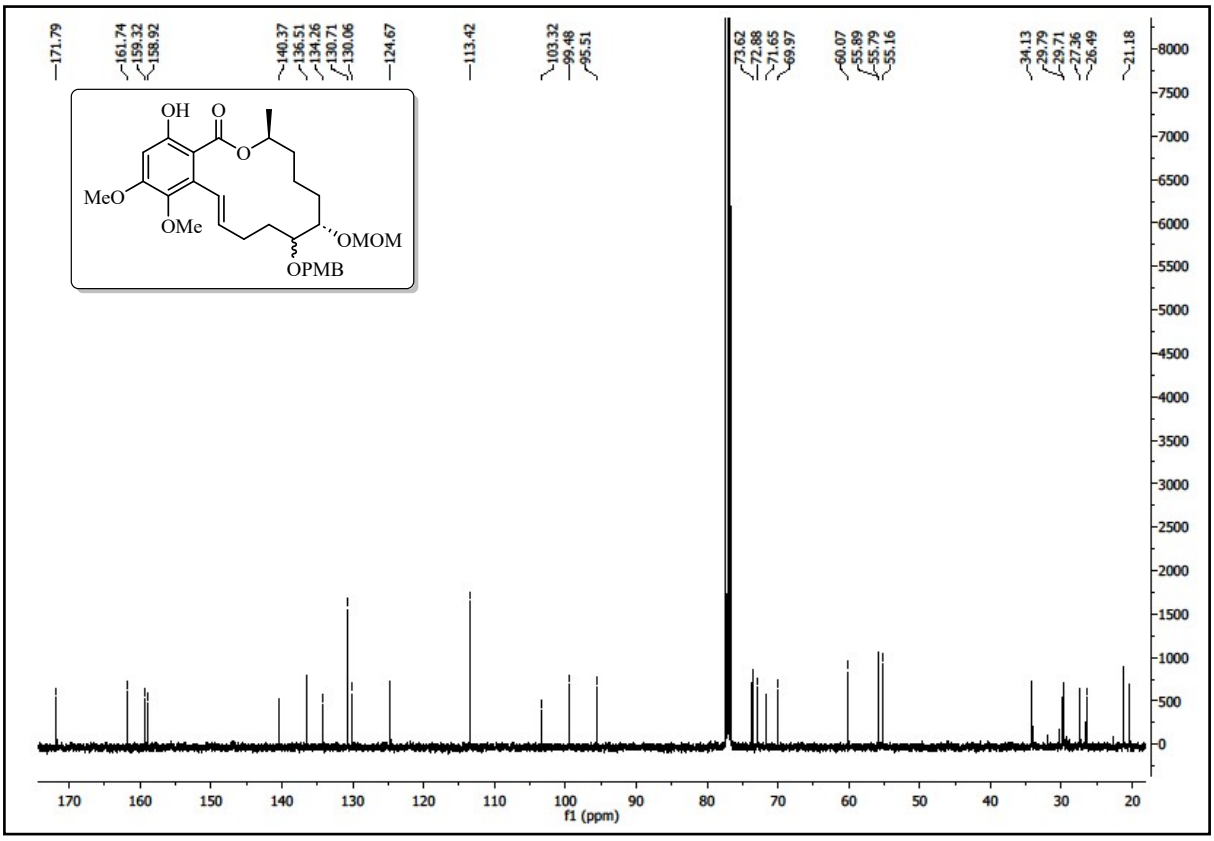
^{1}H NMR of compound 36 (500 MHz, $CDCl_3$)



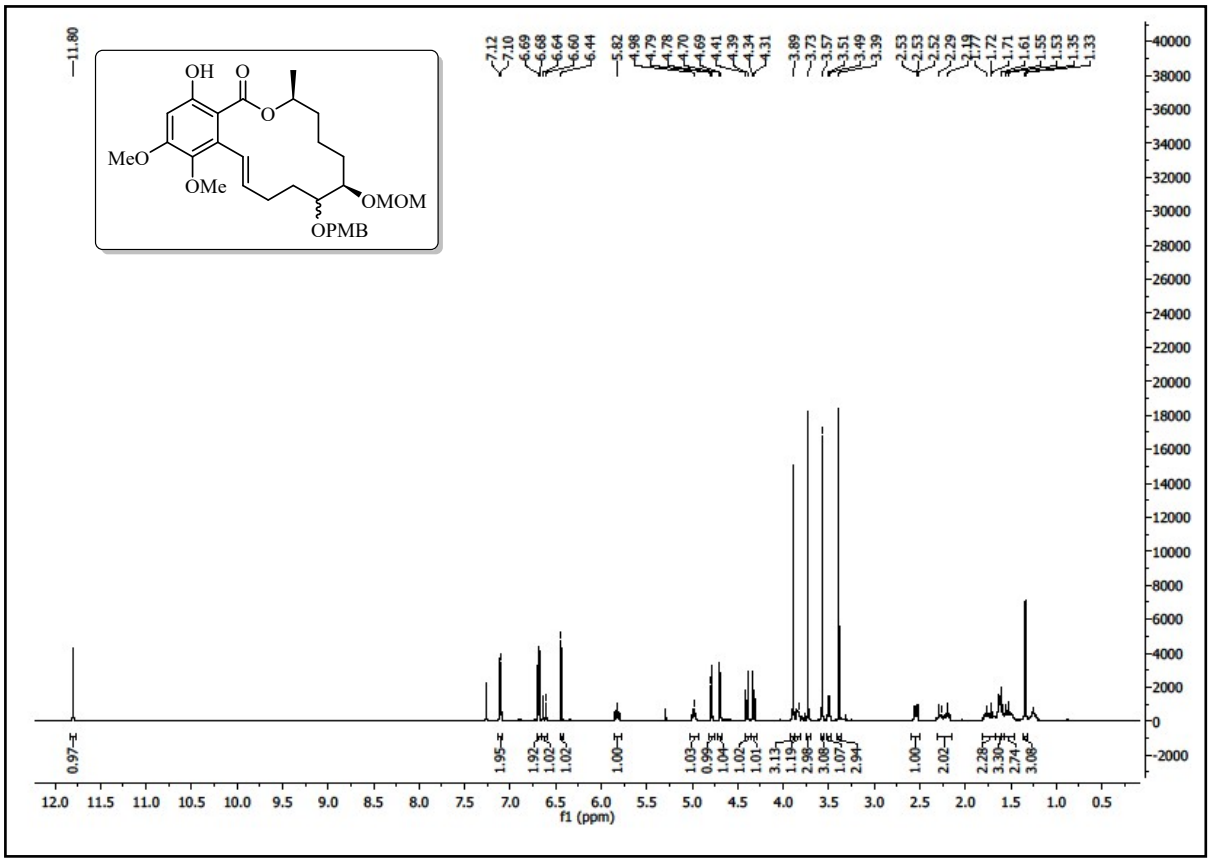
^{13}C DEPT NMR of compound 36 (101 MHz, $CDCl_3$)



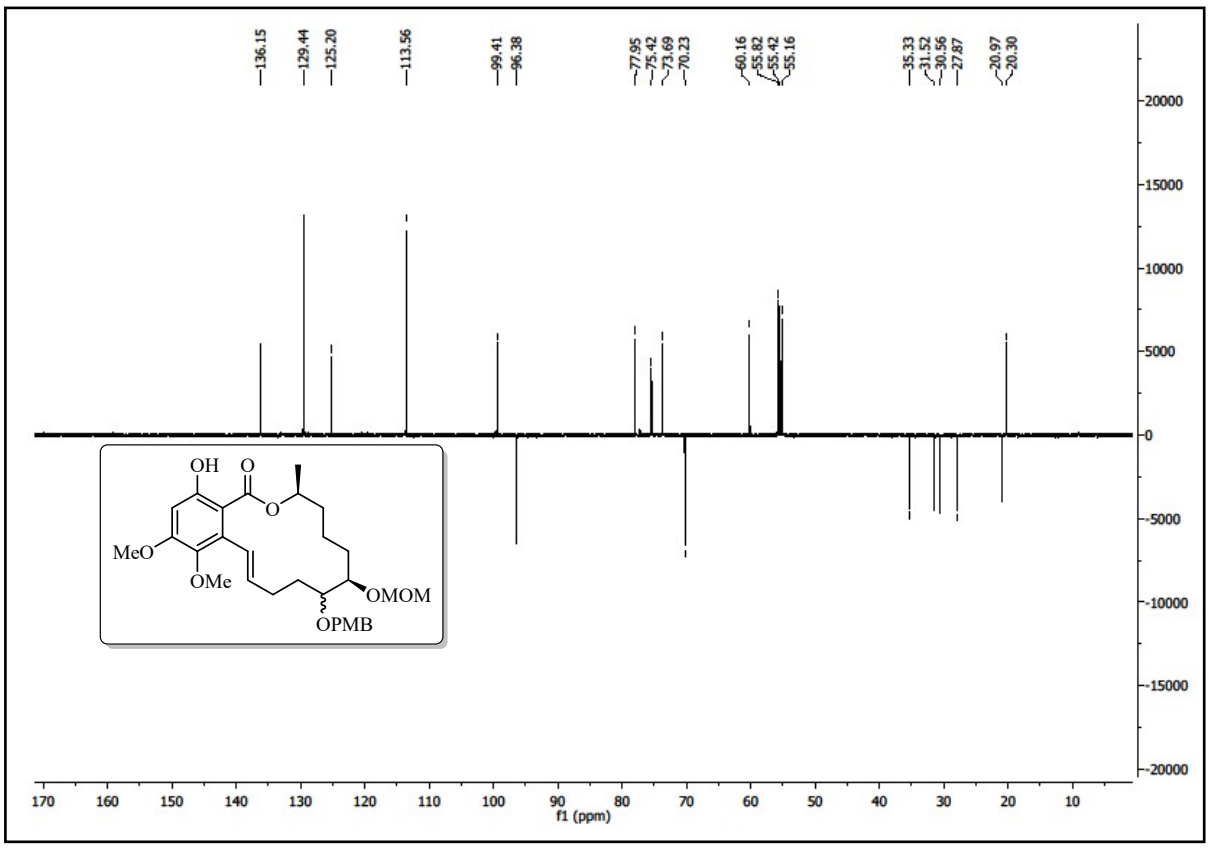
^{13}C NMR of compound 36 (101 MHz, $CDCl_3$)



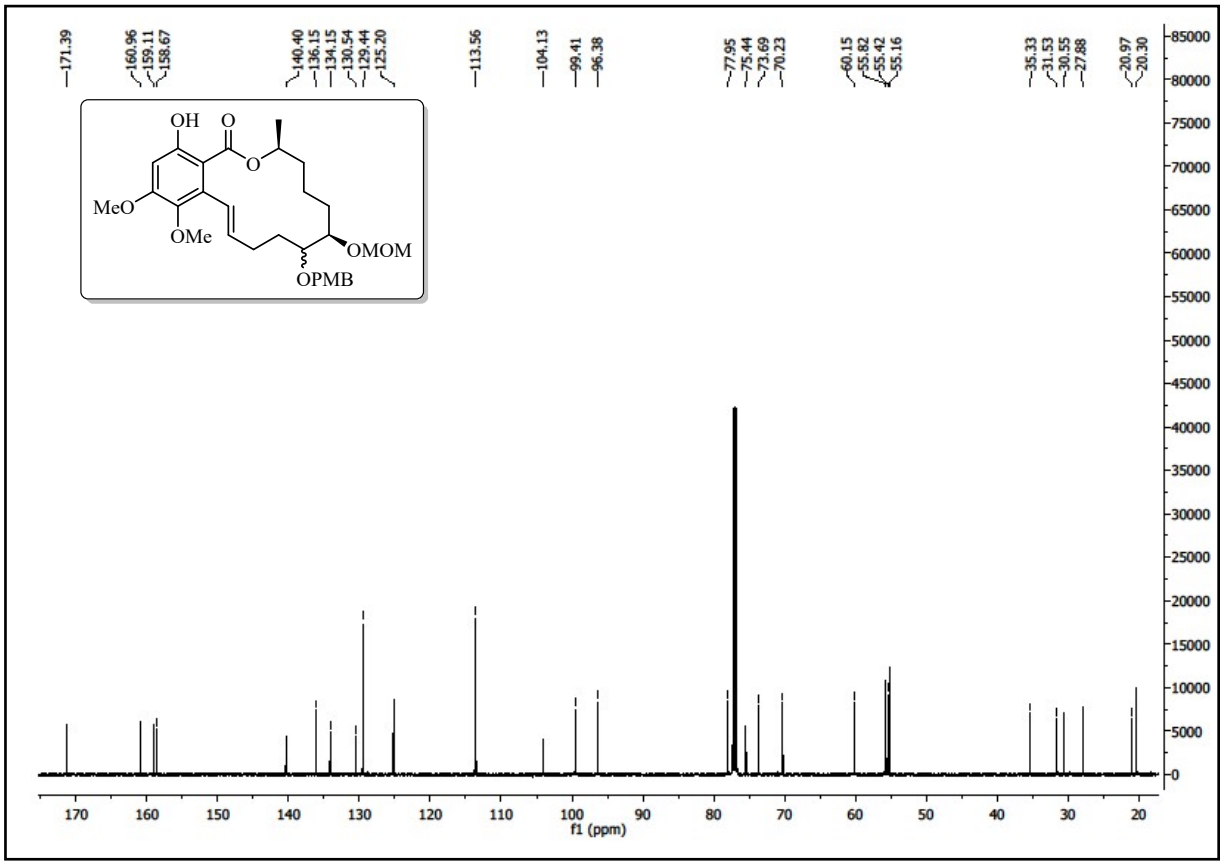
^{1}H NMR of compound 45 (500 MHz, $CDCl_3$)



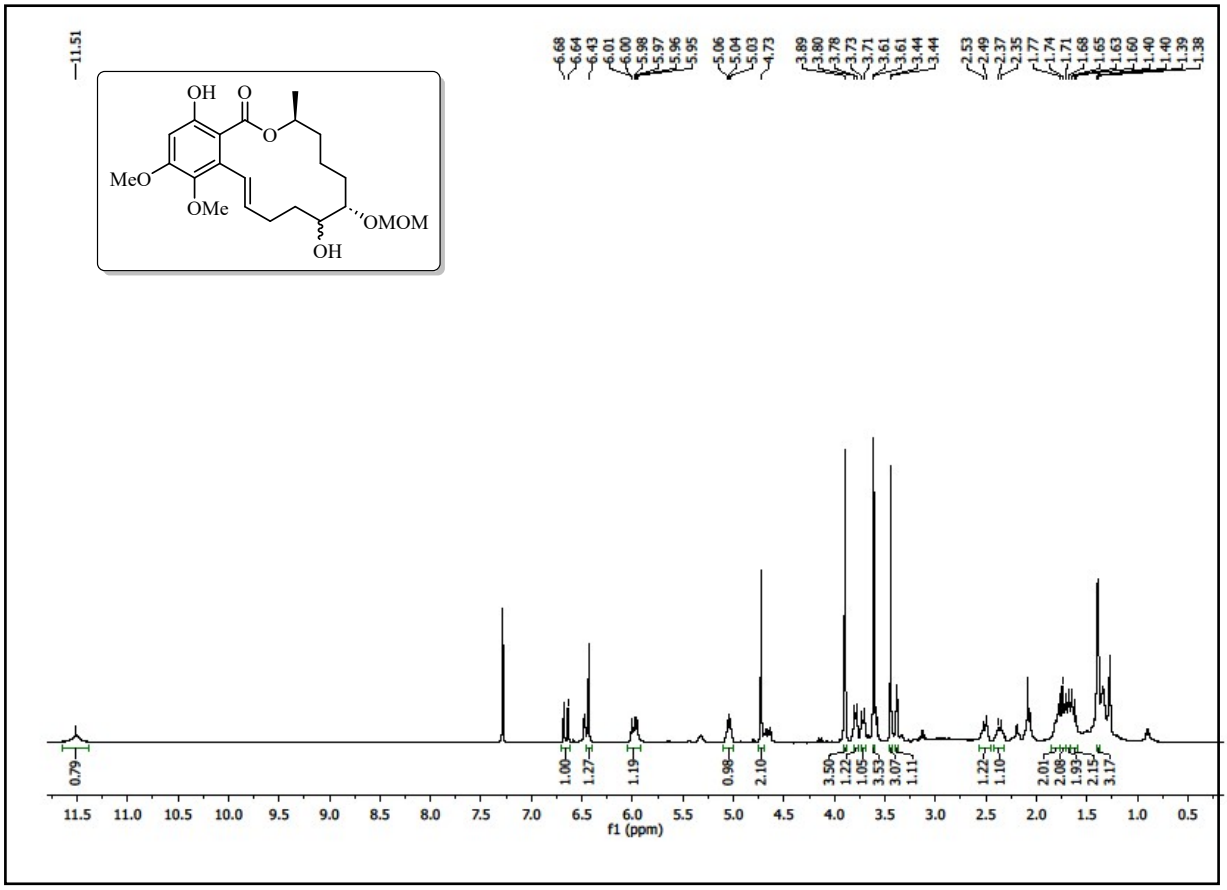
^{13}C DEPT NMR of compound 45 (126 MHz, $CDCl_3$)


136.15
129.44
125.20
113.56
99.41
96.38
77.95
75.42
73.69
70.23
60.16
55.82
55.42
55.16
35.33
31.52
30.56
27.87
20.97
20.30
20000
15000
10000
5000
0
-5000
-10000
-15000
-20000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
OH
O
O
MeO
OMe
OMOM
OPMB

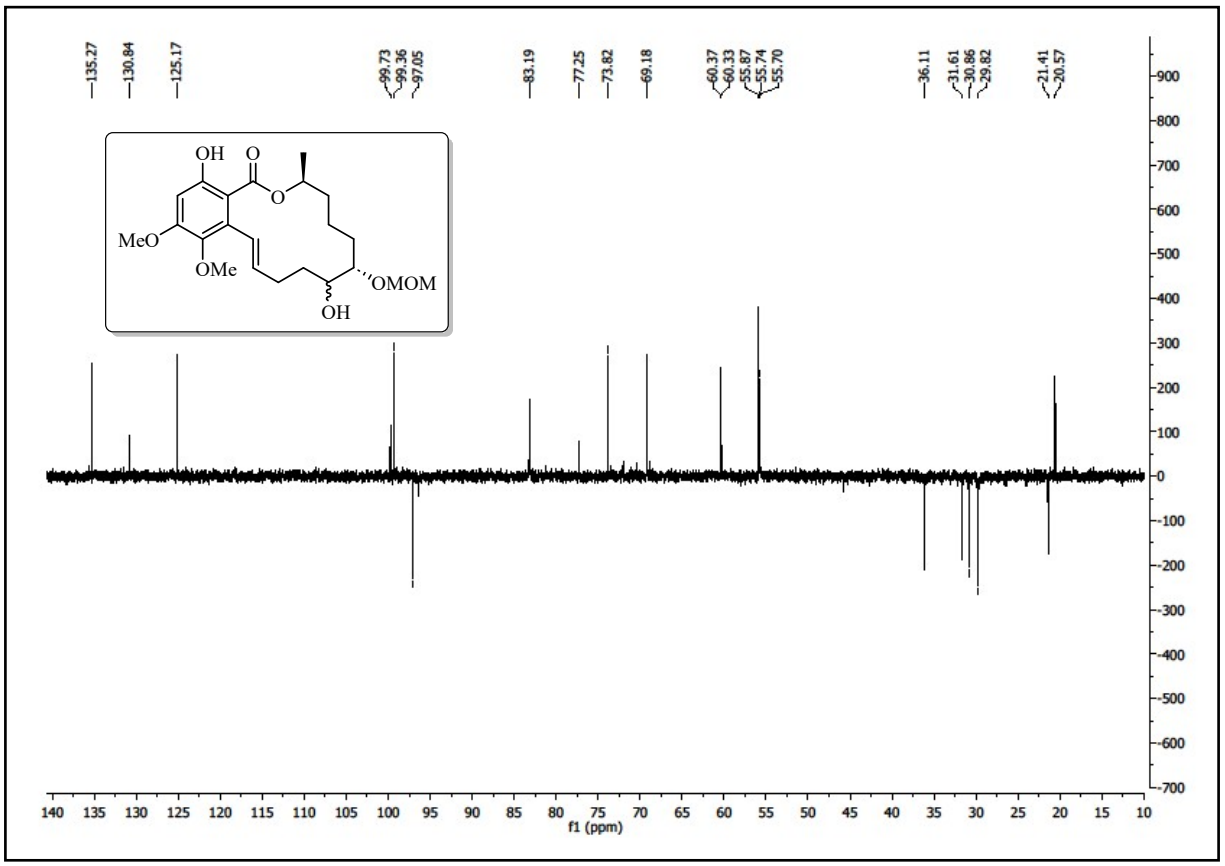
^{13}C NMR of compound 45 (126 MHz, $CDCl_3$)



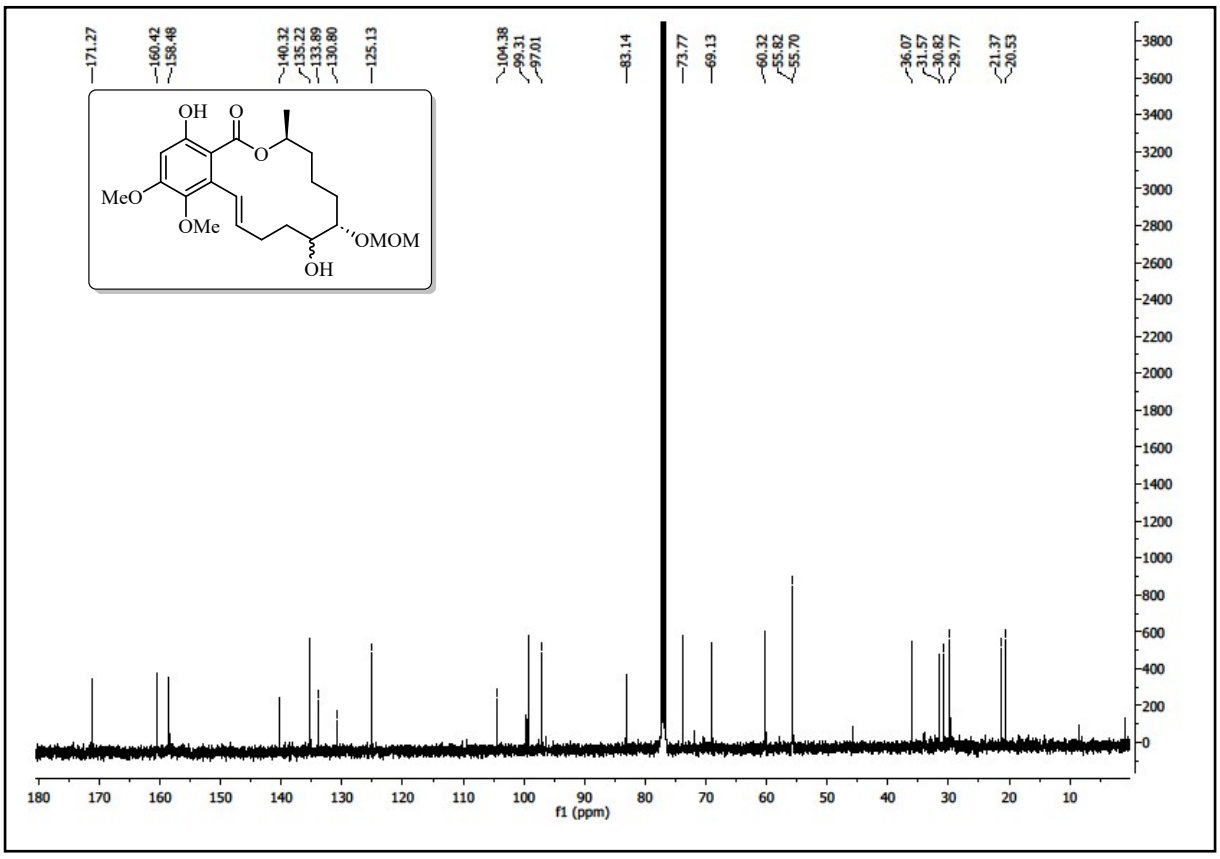
^{1}H NMR of compound 37 (400 MHz, $CDCl_3$)



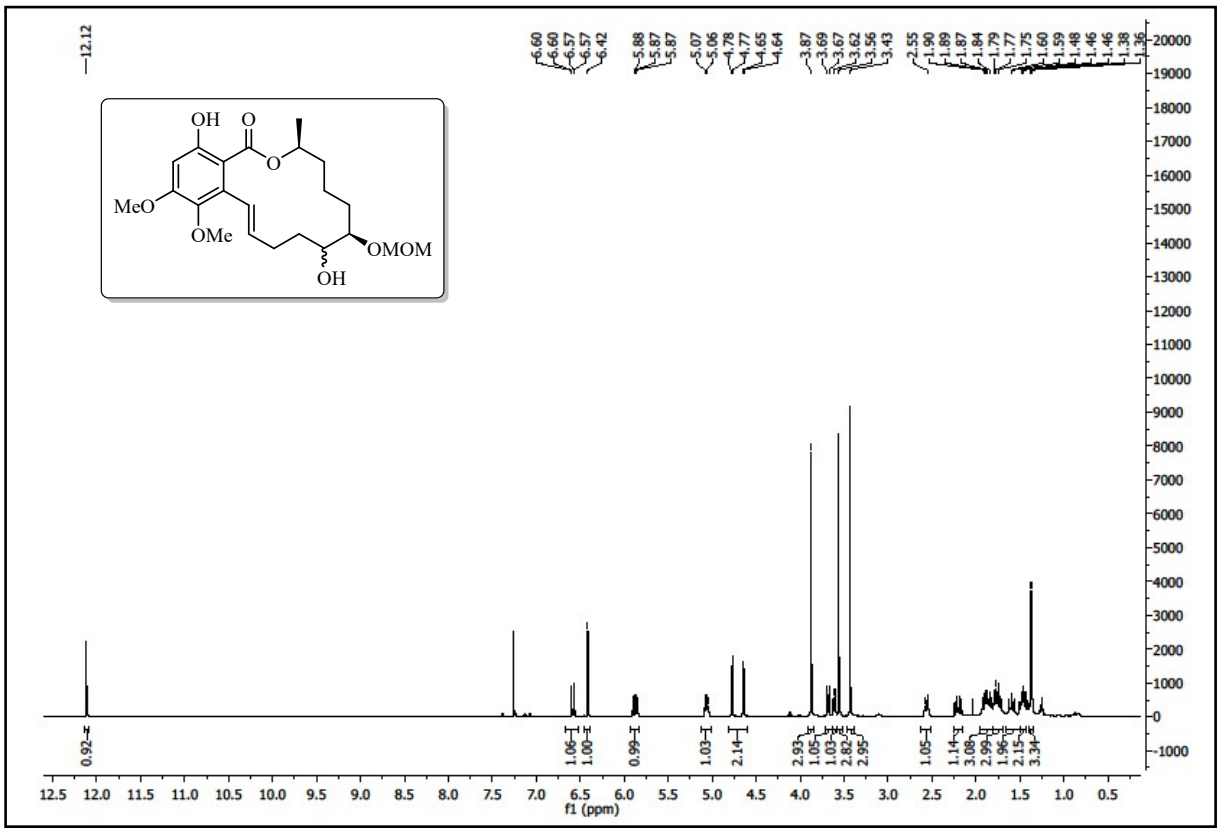
^{13}C DEPT NMR of compound 37 (126 MHz, $CDCl_3$)



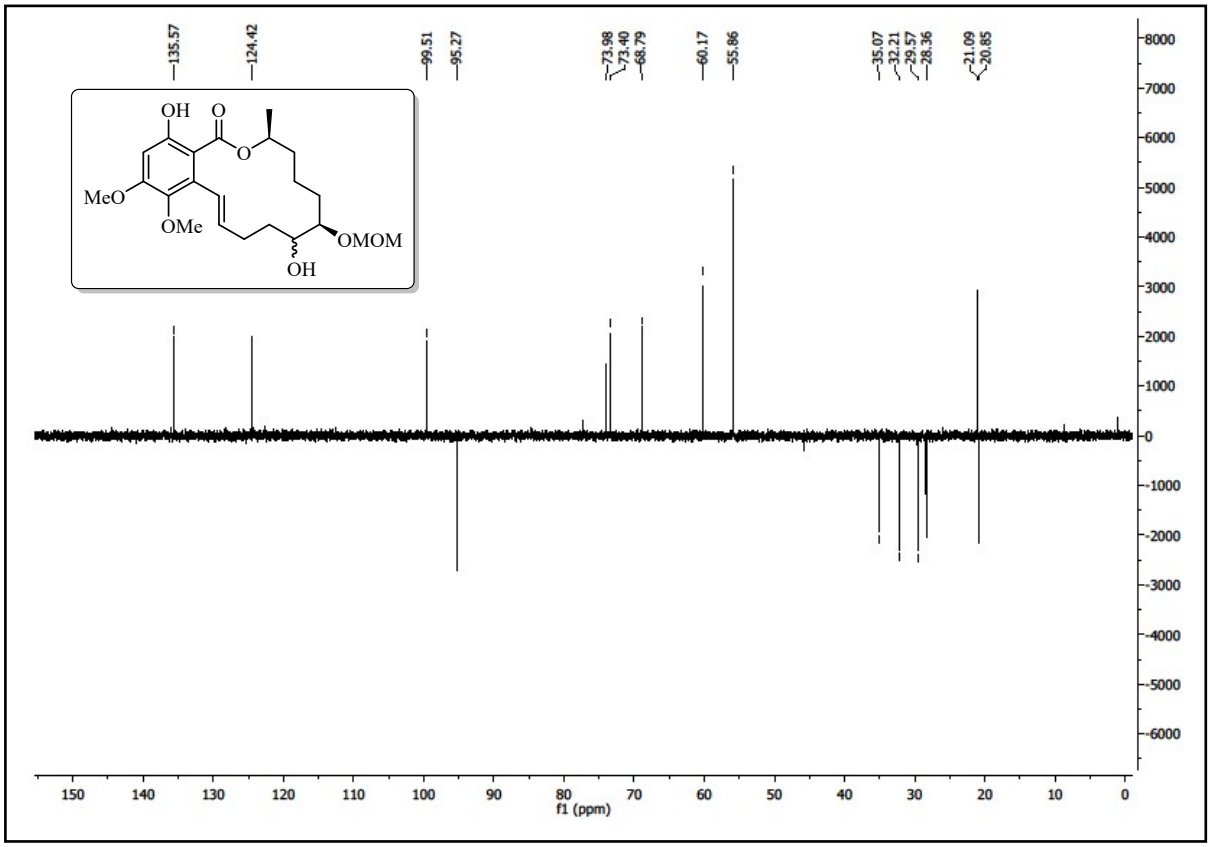
^{13}C NMR of compound 37 (126 MHz, $CDCl_3$)



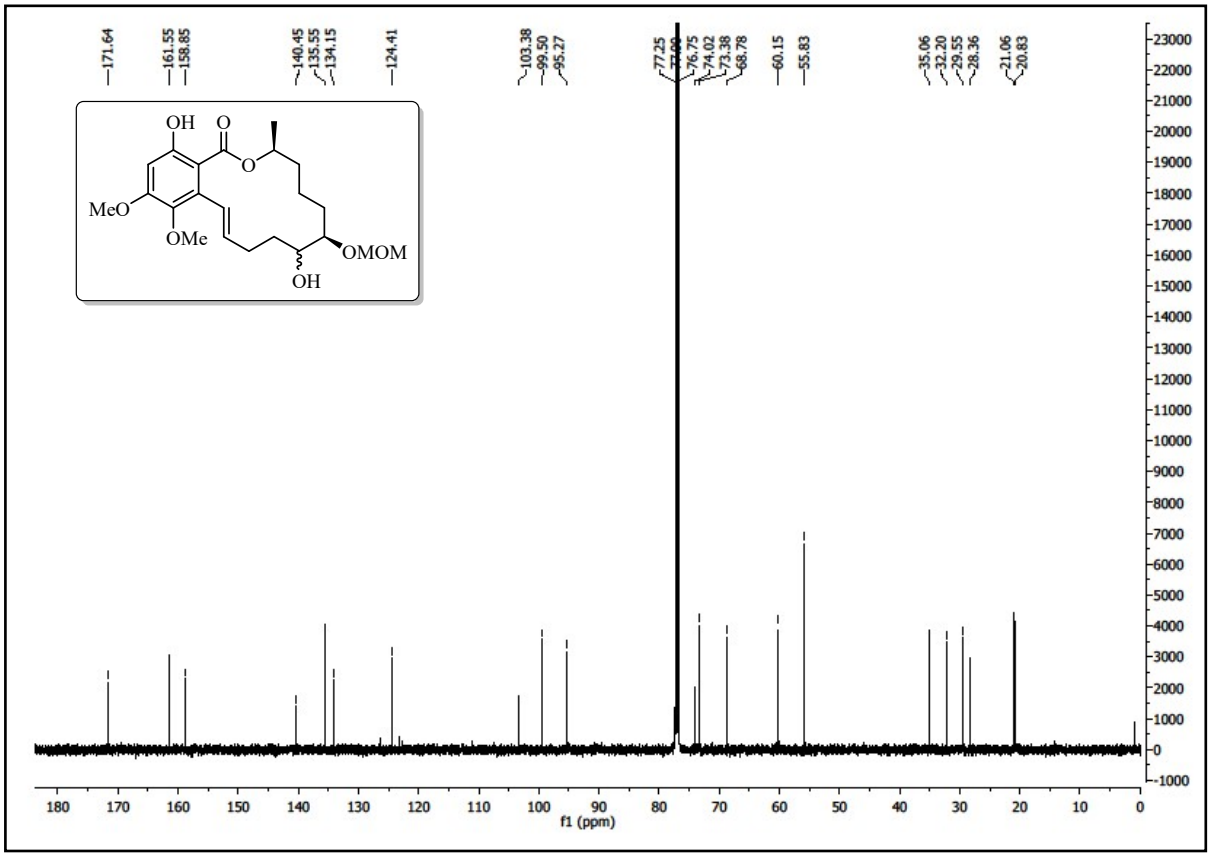
^{1}H NMR of compound 46 (400 MHz, $CDCl_3$)



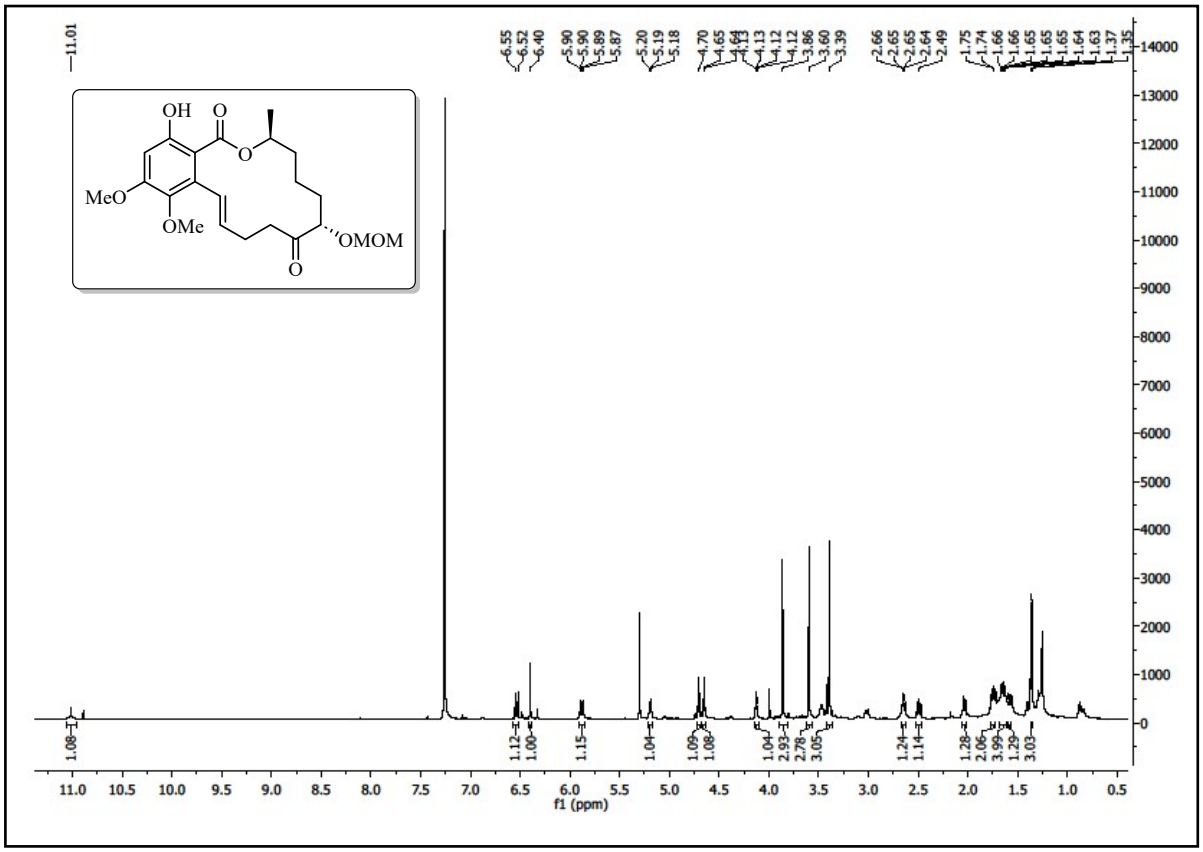
^{13}C DEPT NMR of compound 46 (101 MHz, $CDCl_3$)



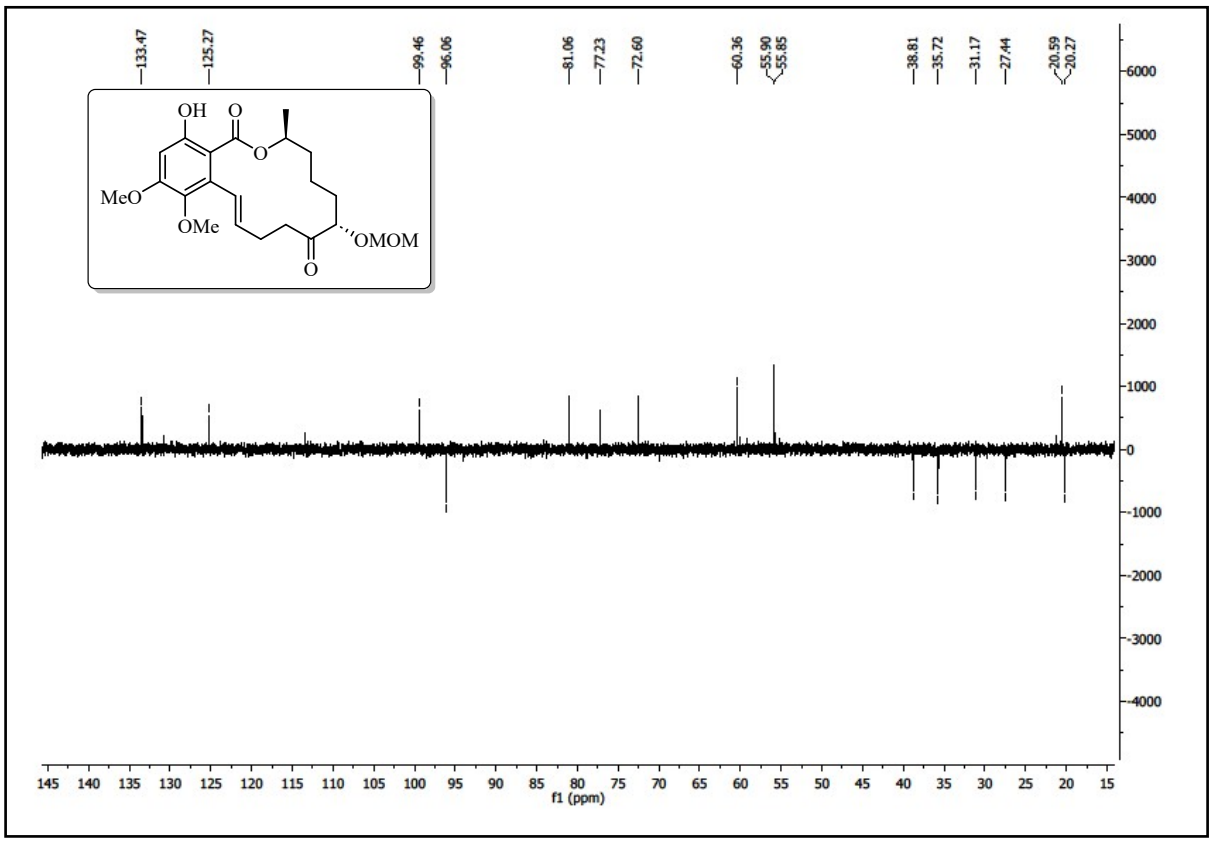
^{13}C NMR of compound 46 (101 MHz, $CDCl_3$)



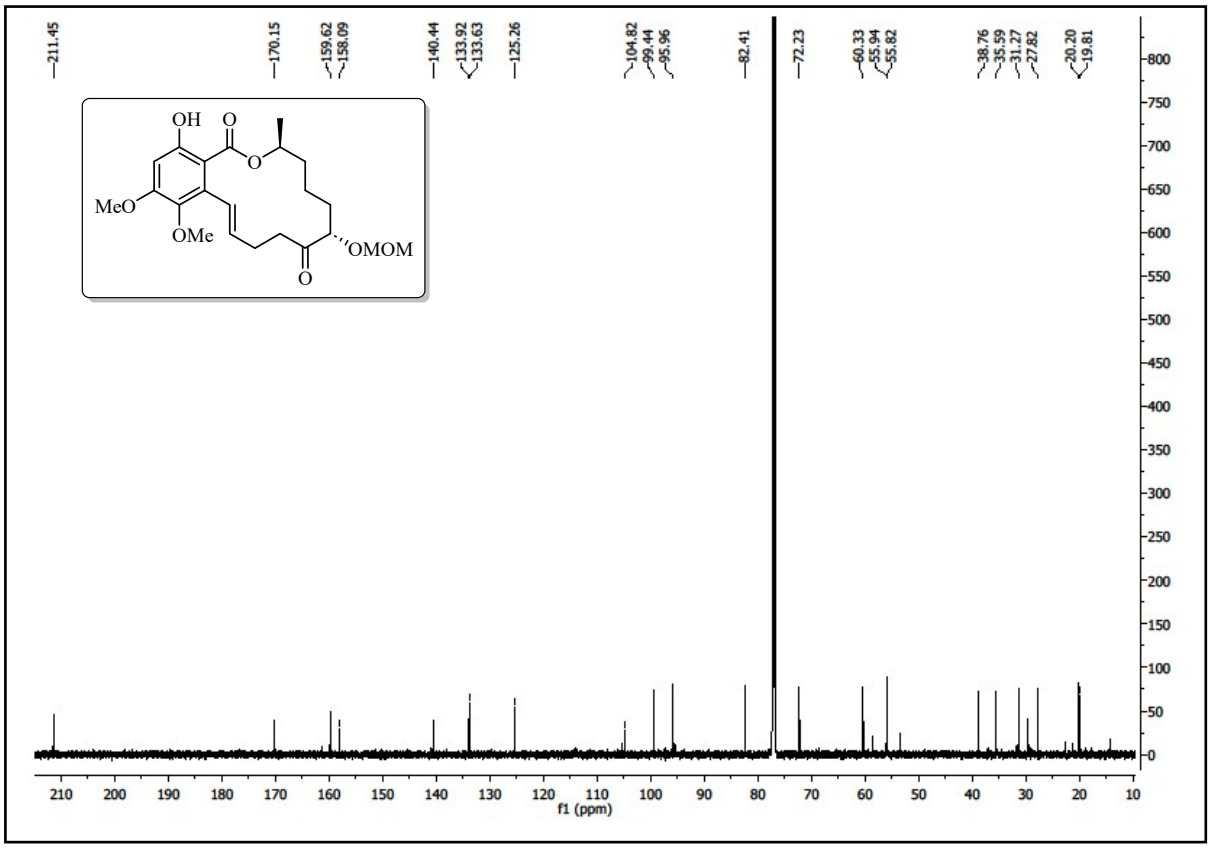
^{1}H NMR of compound 38 (600 MHz, $CDCl_3$)



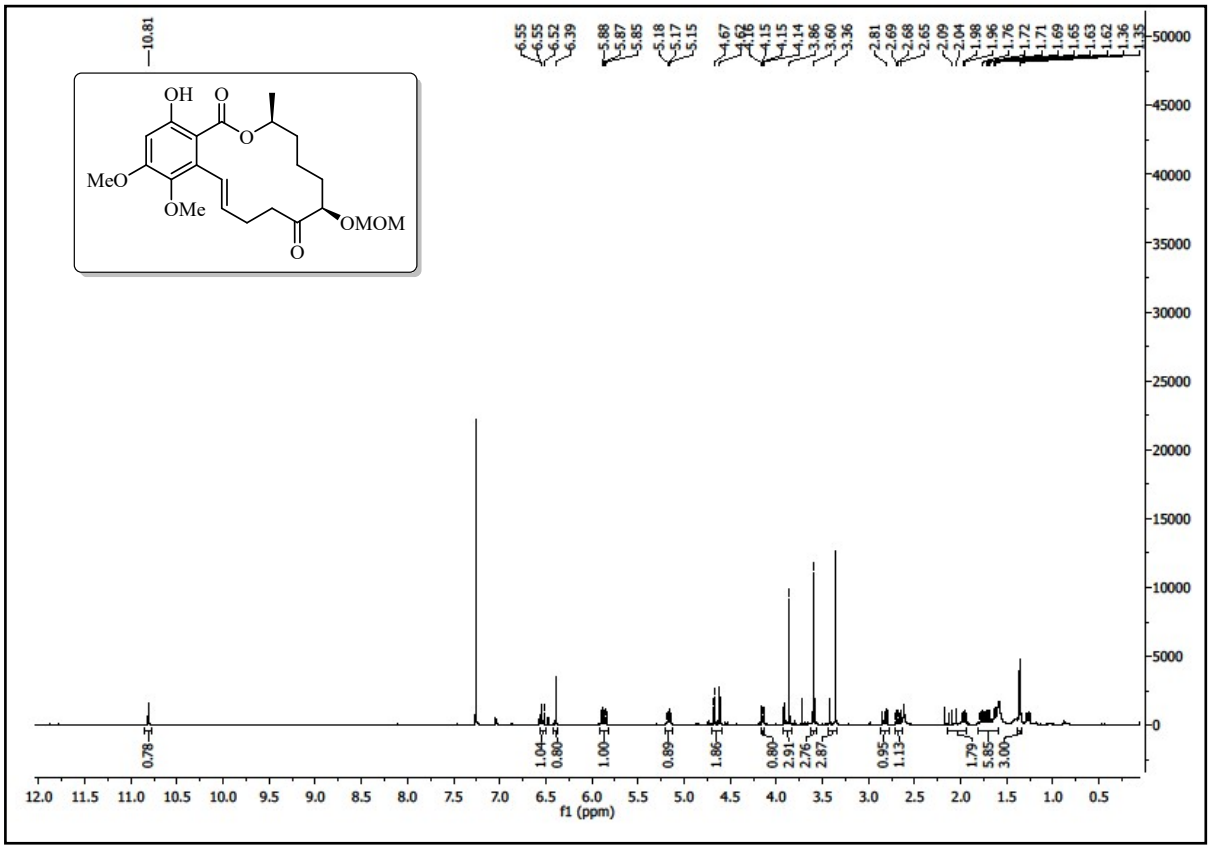
^{13}C DEPT NMR of compound 38 (151 MHz, $CDCl_3$)



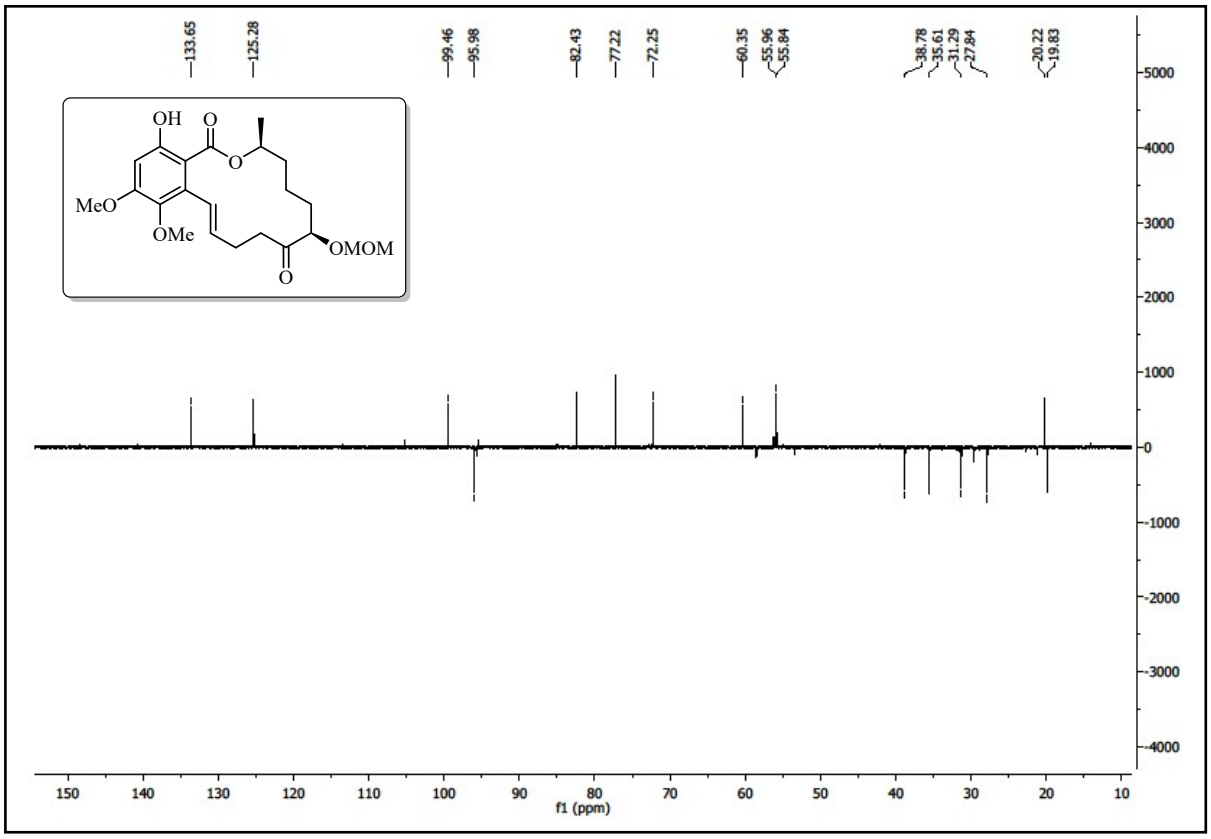
^{13}C NMR of compound 38 (151 MHz, $CDCl_3$)



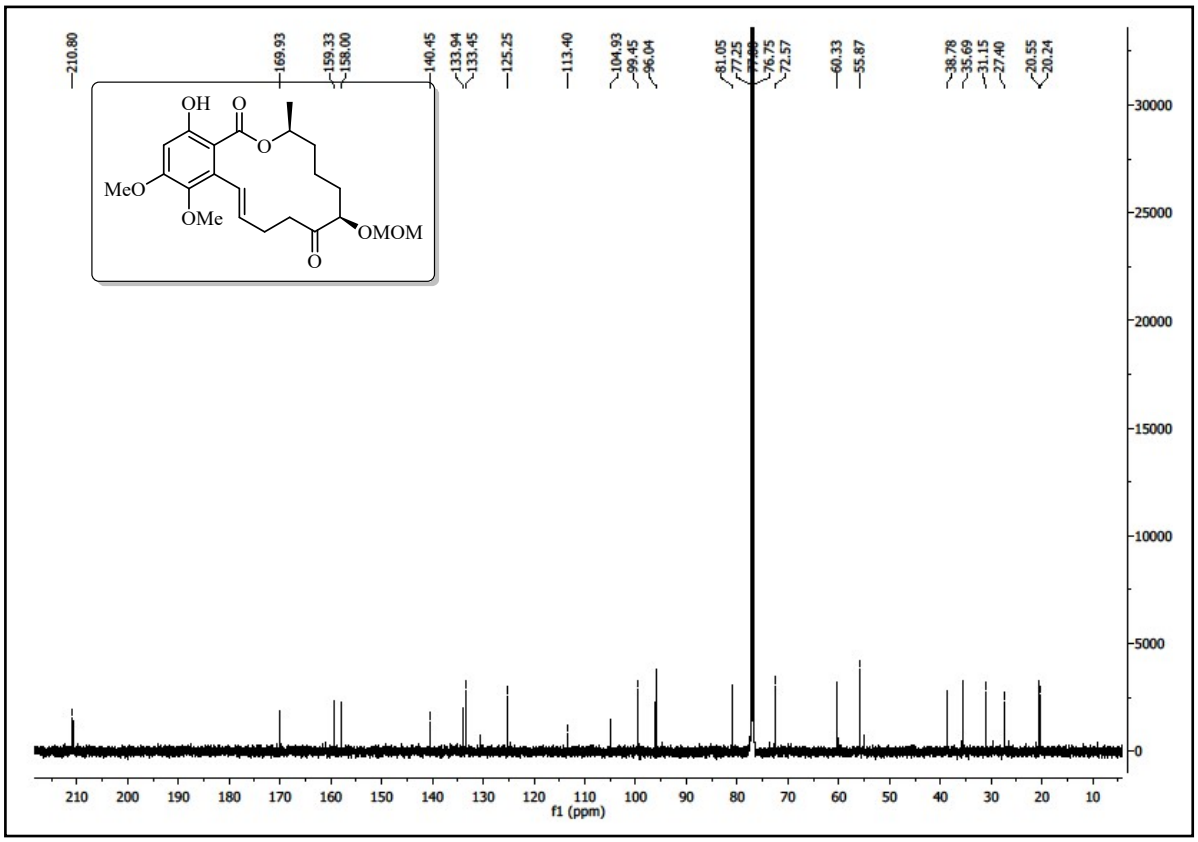
^{1}H NMR of compound 47 (500 MHz, $CDCl_3$)



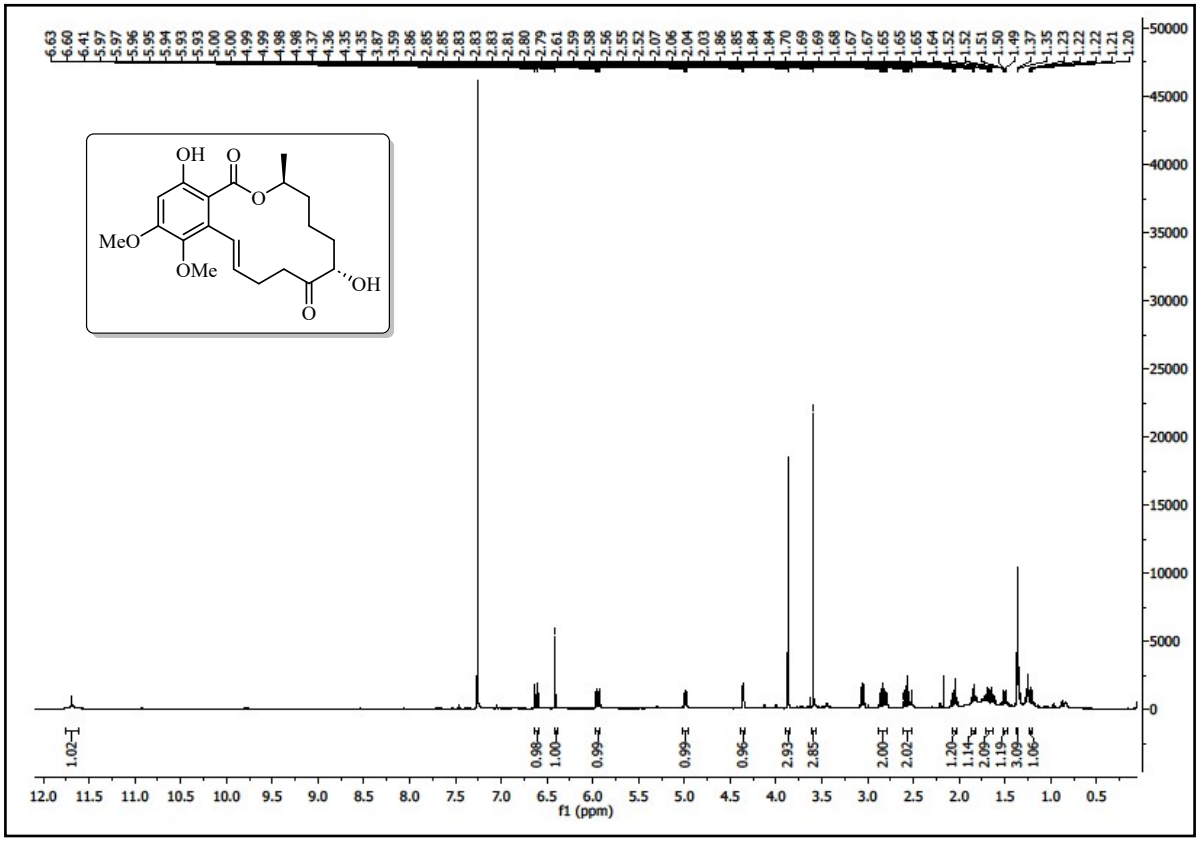
^{13}C DEPT NMR of compound 47 (126 MHz, $CDCl_3$)



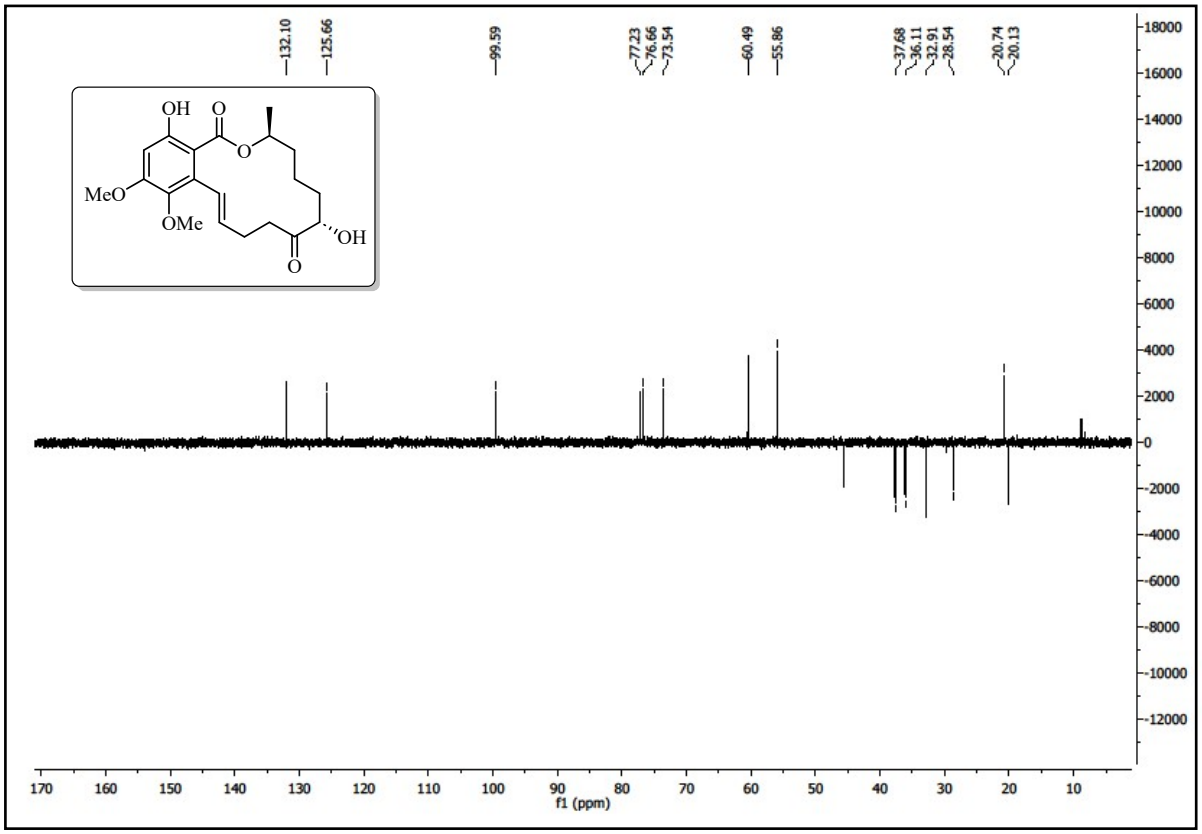
^{13}C NMR of compound 47 (126 MHz, $CDCl_3$)



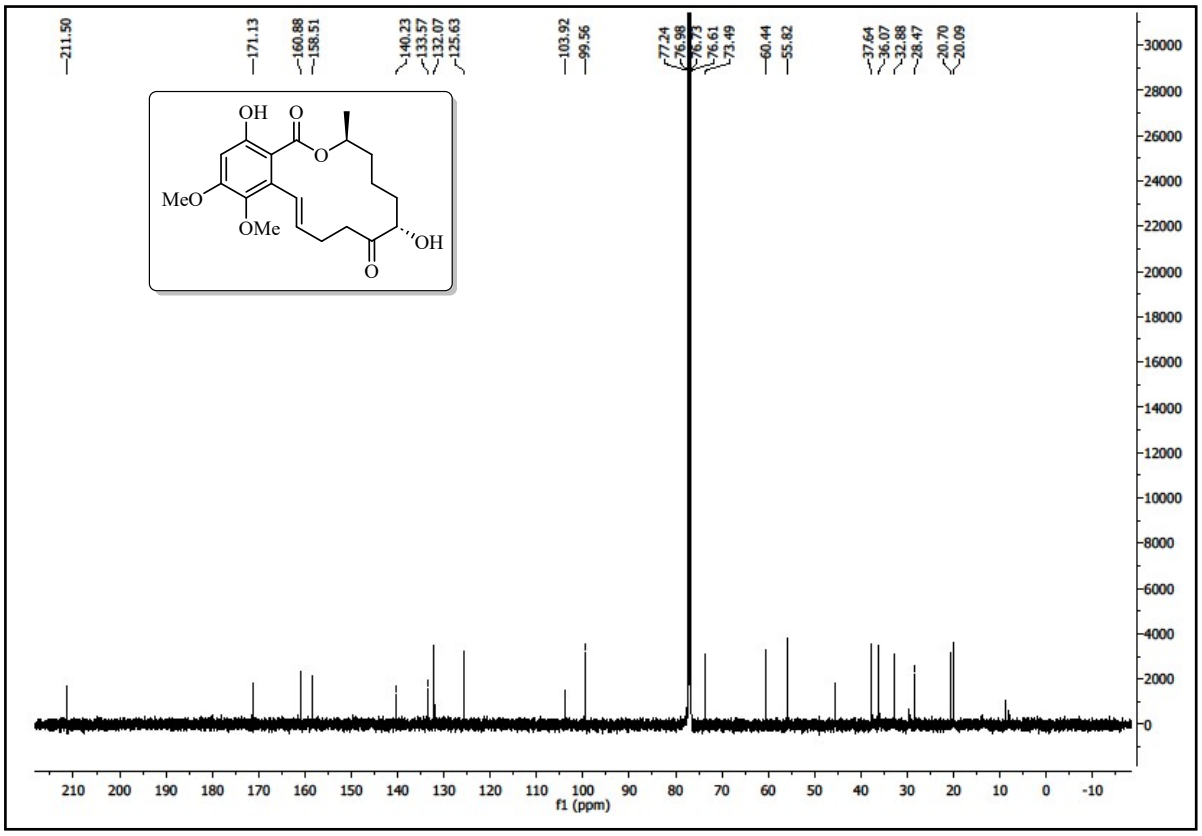
^{1}H NMR of Hamigeromycin F (500 MHz, $CDCl_3$)



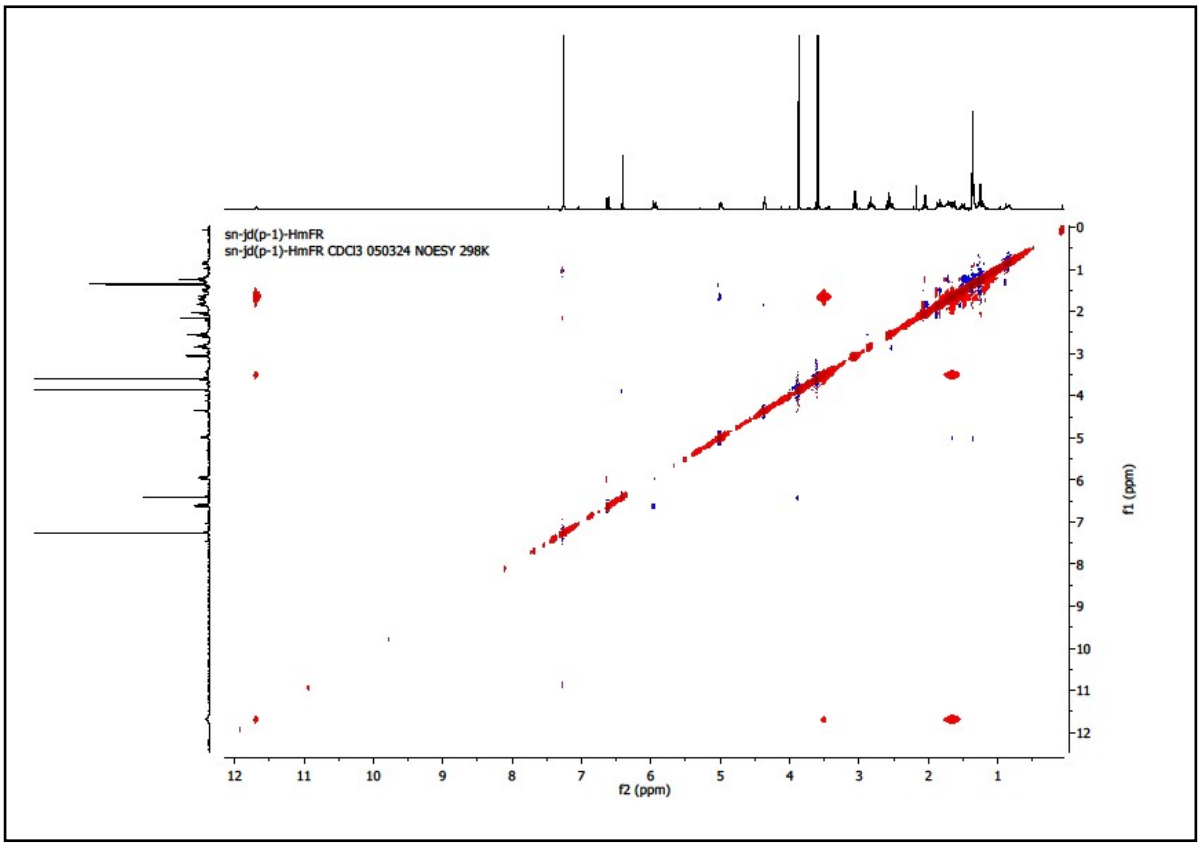
^{13}C DEPT NMR of Hamigeromycin F (125 MHz, $CDCl_3$)



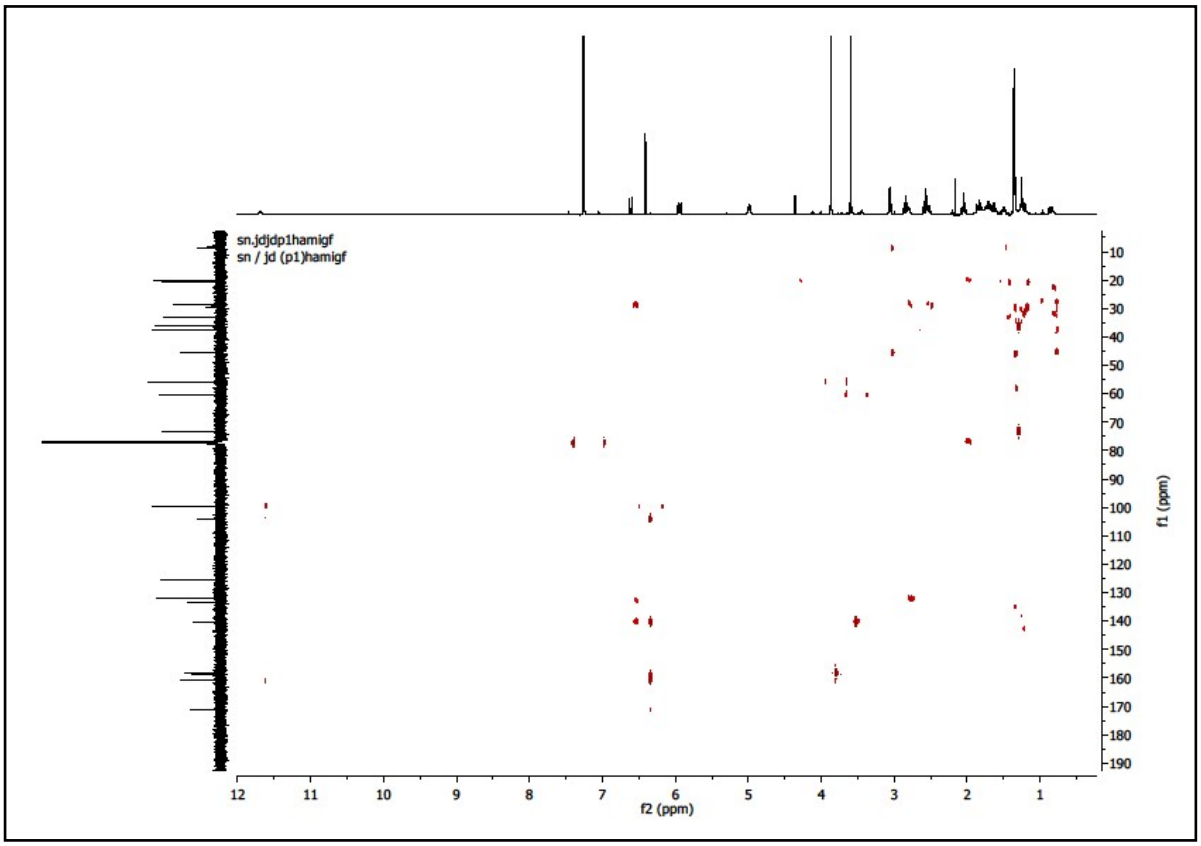
^{13}C NMR of Hamigeromycin F (125 MHz, $CDCl_3$)



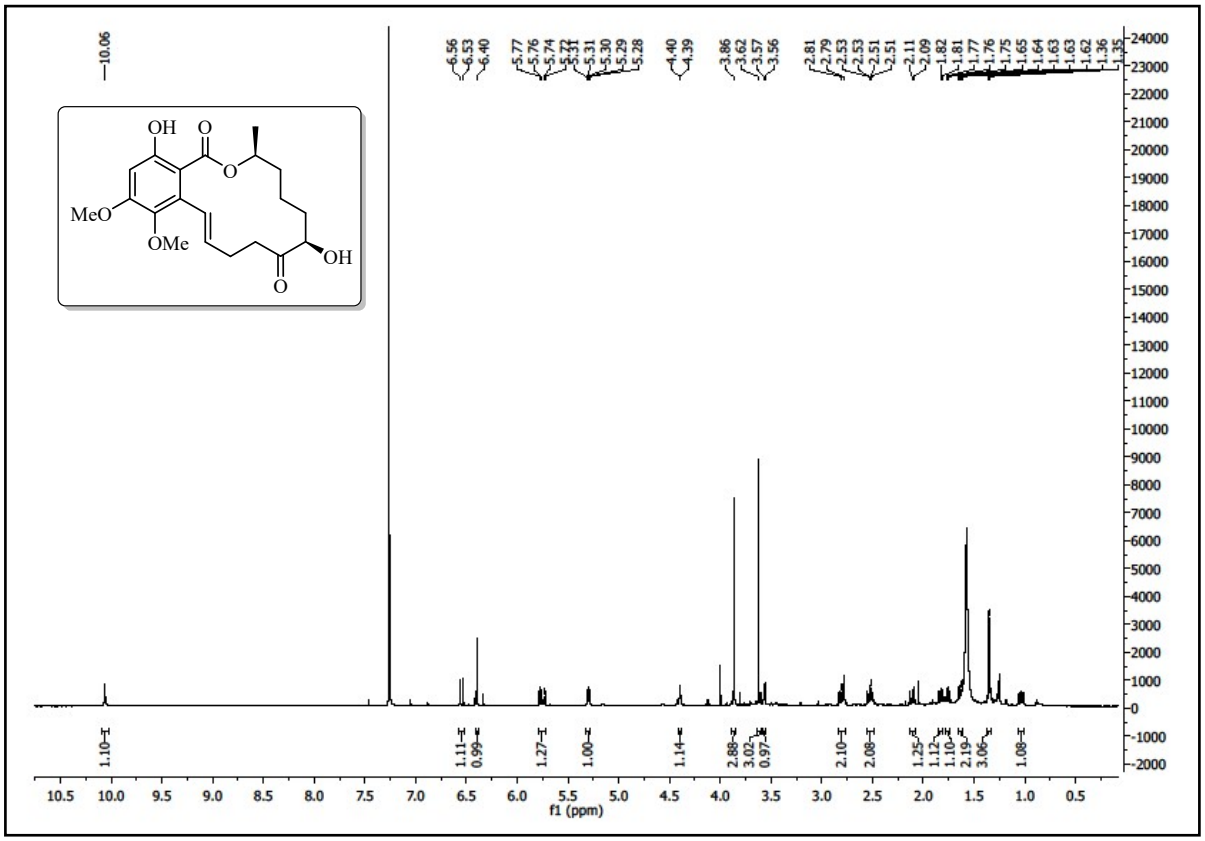
2D NOESY NMR of Hamigeromycin F (6) (600 MHz)



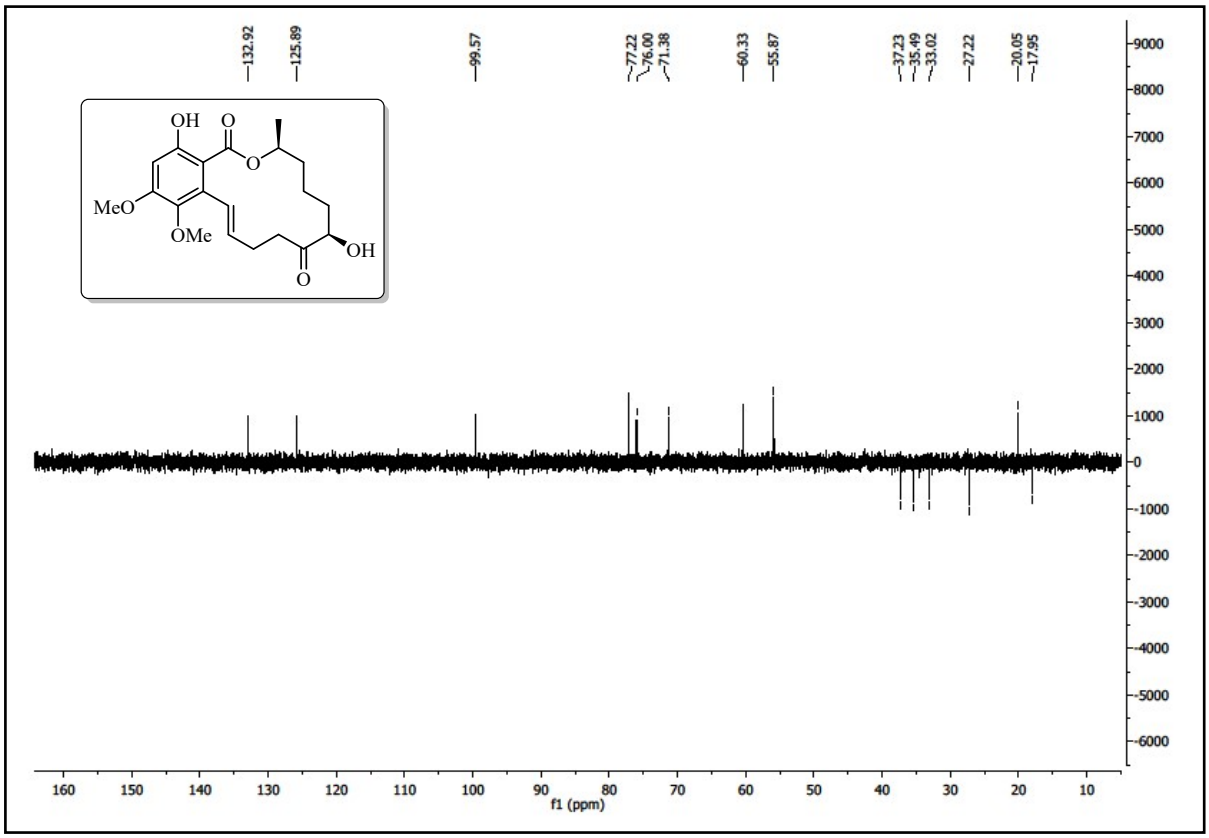
2D HMBC of Hamigeromycin F (6) in $CDCl_3$ (500 MHz)



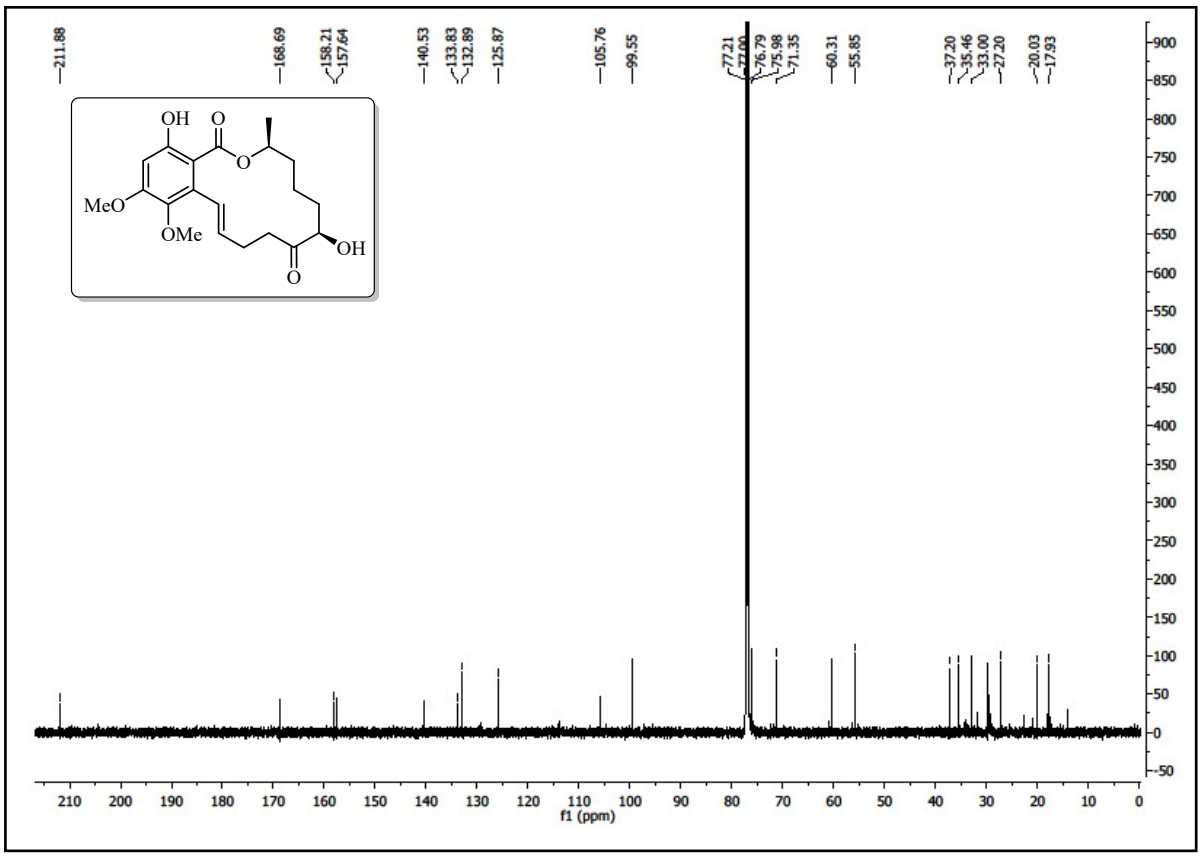
^{1}H NMR of Hamigeromycin G (500 MHz, $CDCl_3$)



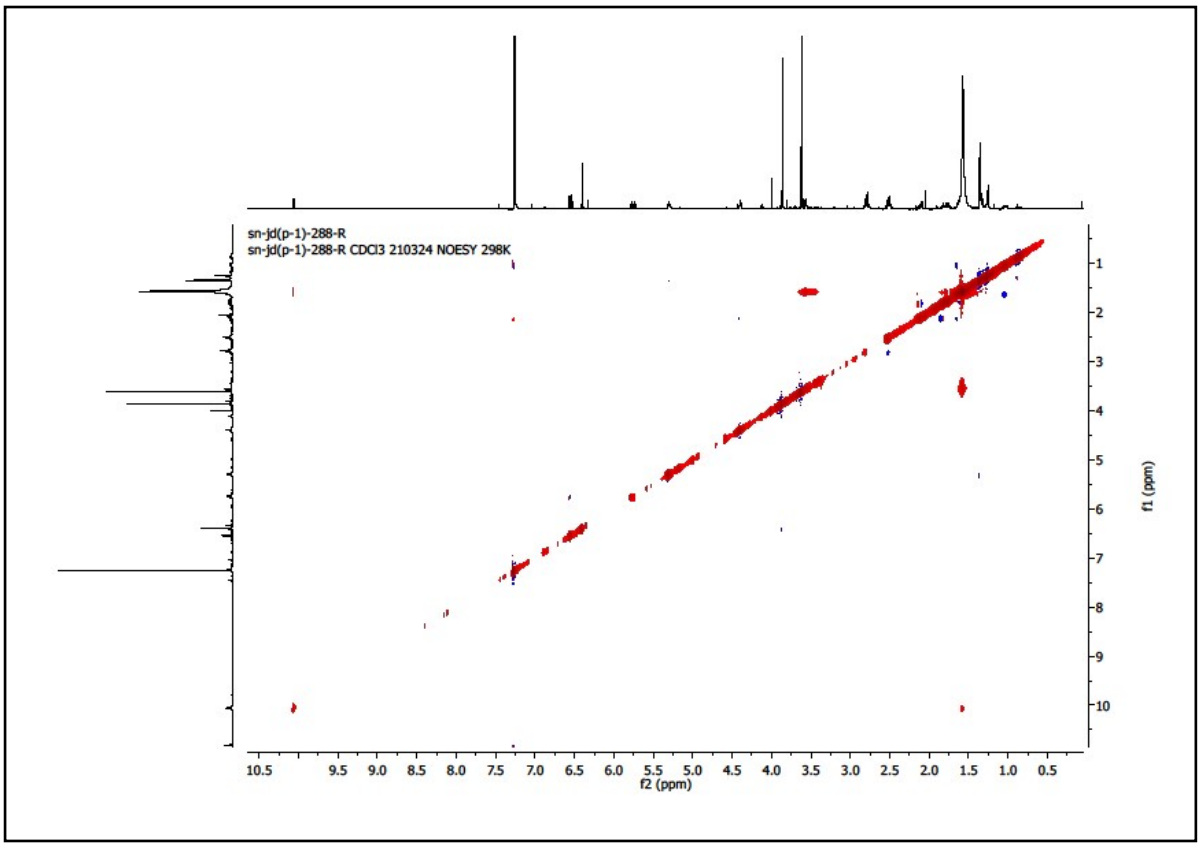
^{13}C DEPT NMR of Hamigeromycin G (125 MHz, $CDCl_3$)



^{13}C NMR of Hamigeromycin G (150 MHz, $CDCl_3$)



2D NOESY NMR of Hamigeromycin G (7) in $CDCl_3$ (600 MHz)



2D HMBC of Hamigeromycin G (7) in $CDCl_3$ (500 MHz)