Supporting Information

Total Synthesis of the Reported Structure of Neaumycin B

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1. Materials and Methods

a) Reaction Equipment, Solvents, Reagents and Conditions

All reactions were performed in oven-dried or flame-dried glassware using syringe-septum cap or Schlenk techniques under an inert atmosphere of nitrogen or argon, unless otherwise mentioned. All commercially obtained reagents were used as received. Tetrahydrofuran (THF), dichloromethane (DCM), diethyl ether (Et_2O) and toluene were dried and deoxygenated by passing through a Puresolv™ PS-400 solvent purification system. *N,N'*-dimethylformamide was dried over 4Å molecular sieve beads before use. Hexanes, hexamethylphosphoramide (HMPA) and triethylamine (Et_3N) were distilled over CaH_2 and stored over 4Å molecular sieve beads prior to use.

b) Reaction Monitoring and Purification

Analytical thin layer chromatography was performed on pre-coated silica gel 60 F-254 plates (particle size 40- 55 micron, 230-400 mesh) and visualized by a UV lamp or by staining with *p*-anisaldehyde or $KMnO_4$ stain. Flash Column chromatography was performed using silica gel (Siliacycle Siliaflash®) P60, 40-63 micron particle size, 230-300 mesh) and compressed by air pressure with commercial-grade solvents.

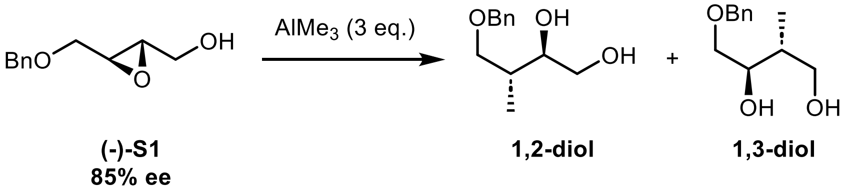
c) Analyses and Compound Characterizations

NMR spectra were recorded at 500 MHz (^{1}H-NMR/^{13}C-NMR) on a Bruker Avance III 500 MHz spectrometer or a Bruker AVANCE NEO600 spectrometer at 300 K. Chemical shifts are reported relative to chloroform-*d* (δ 7.26), acetone-d_6 (δ 2.05), benzene-d_6 (δ 7.16) for ^{1}H-NMR and chloroform-*d* (δ 77.16), acetone-d_6 (δ 206.26), benzene-d_6 (δ 128.06) for ^{13}C-NMR. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared spectra were measured on a Jasco FT/IR 480 plus spectrometer. High-resolution mass spectrometry (HRMS) was obtained on a Waters LC-TOF mass spectrometer (model LCT-XE Premier) or a water GCT Premier spectrometer at the University of Pennsylvania. Single crystal X-ray structures were obtained at the University of Pennsylvania. X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Cu-Kα radiation (λ=1.54178 Å).

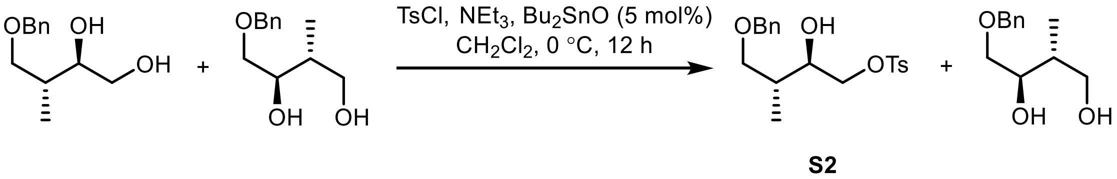
2. Representative Experimental Procedures and Compound Characterizations

(a). Synthesis of the Northwestern Fragment (**5**)

Chiral epoxy alcohol **(-)-S1** was synthesized according to the reported procedure. [1] The optical purity of epoxy alcohol **(-)-S1** was determined to be 85%-88% ee via Mosher ester analysis. (See Fig. S6)

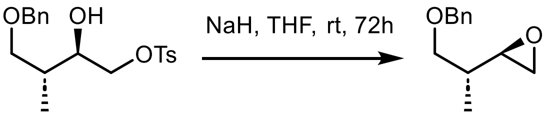


The regioselective ring opening of epoxy alcohol was carried out according to a precedented procedure.[2] To a stirred solution of epoxide **(-)-S1** (16.1 g, 82.9 mmol) in dry CH_2Cl_2 (80mL) at -40^{o}C under argon atmosphere was added $AlMe_3$ (2.0 M in hexanes, 124 mL, 249 mmol, 3.0 eq.) dropwise via addition funnel. The reaction was warmed up to 0^{o}C by transferring the flask to ice water bath and allowed to warmed up to room temperature overnight (ca. 16 hours). The reaction mixture was then cannulated to 2N aqueous HCl (300 mL) pre-cooled to 0^{o}C. The biphasic mixture was stirred until precipitation disappeared. Organic layer was collected and aqueous layer was extracted with CH_2Cl_2 (100mL x 5). The organic layer was combined and dried over Na_2SO_4, filtered, and concentrated *in-vacuo* to afford crude product as a 4:1 mixture of 1,2- and 1,3-diol, which were inseparable on silica gel column and therefore directly used in the next step.



The mixture of 1,2- and 1,3-diol from previous step was dissolved in CH_2Cl_2 (200 mL) under argon atmosphere. NEt_3 (13.6 mL, 98 mmol) and dibutyltin oxide (240 mg, 0.82 mmol) was then added. The solution was cooled to -20^{o}C and TsCl (12.6 g, 66 mmol) was added in one portion. The reaction was allowed to warm up to -10^{o}C and stirred for 16 hours before sat. aq. $NaHCO_3$ (100 mL) was poured into the mixture to quench the reaction. The organic layer was collected, and the aqueous layer was extracted with CH_2Cl_2 (50mL x 3). The organic layer was combined, washed with water (100 mL x 3), brine (50 mL), dried over Na_2SO_4, filtered, and concentrated *in-vacuo* to afford a semi-solid.

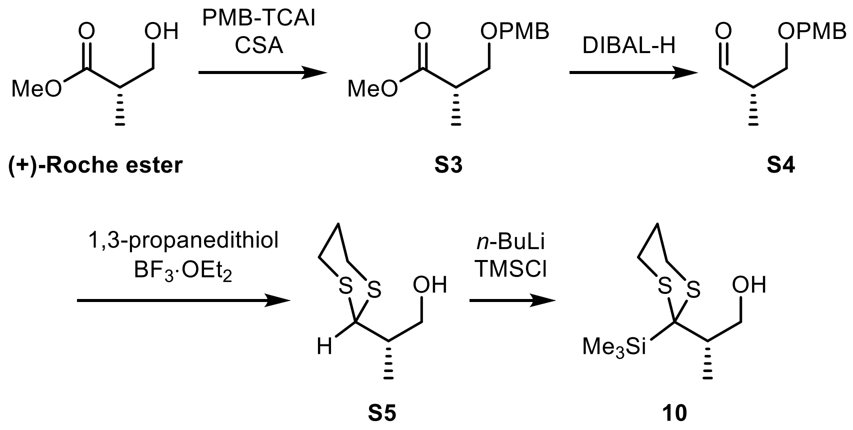
Recrystallization was carried out with hexanes/ethyl acetate at -20°C to afford pure tosyl ester **S2** (18.4 g) as a white crystalline solid. The filtrate from above recrystallization was concentrated and purified on column chromatography (SiO_2, Hexanes/EtOAc *v/v* 4:1 – 3:1) to afford additional **S2** (384 mg), (18.8 g combined, 60% over 2 steps). **^{1}H-NMR** (500 MHz, $CDCl_3$): *δ* 7.79 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.29 (m, 5H), 7.28 (d, *J* = 1.7 Hz, 2H), 4.47 (s, 2H), 4.08 (d, *J* = 4.7 Hz, 2H), 3.76 (q, *J* = 5.3 Hz, 1H), 3.56 (dd, *J* = 9.4, 4.0 Hz, 1H), 3.46 (dd, *J* = 9.3, 7.0 Hz, 1H), 2.44 (s, 3H), 2.01 (tt, *J* = 11.2, 5.4 Hz, 1H), 0.93 (d, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): *δ* 144.98, 137.73, 132.90, 129.98, 128.61, 128.11, 127.96, 127.77, 73.56, 73.51, 73.48, 72.50, 35.36, 21.77, 13.91.



S2

(+)-9
82% ee

Tosyl ester **S2** (11.5 g, 31.2 mmol) was dissolved in THF (300 mL) under argon atmosphere. NaH (2.5 g, 60% dispersion in mineral oil, 62.5 mmol) was washed with hexanes, dried under vacuum, and added into the reaction mixture. The reaction was monitored by TLC. Saturate aq. NH_4Cl (200 mL) was added to quenched the reaction after TLC showed complete conversion (ca. 72 hours). Organic layer was collected and the aqueous layer was extracted with diethyl ether (100 mL x 2). The organic layer was combined and washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 10:1) afforded pure compound **(+)-9** (5.85 g, 97%) as a colorless liquid. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 7.35 (m, *J* = 4.4 Hz, 4H), 7.29 (m, *J* = 6.7, 5.0, 2.2 Hz, 1H), 4.54 (s, 1H), 4.54 (s, 1H), 3.53 (dd, *J* = 9.1, 5.5 Hz, 1H), 3.48 (dd, *J* = 9.1, 6.0 Hz, 1H), 2.91 (ddd, *J* = 6.8, 4.1, 2.7 Hz, 1H), 2.75 (t, *J* = 4.5 Hz, 1H), 2.55 (dd, *J* = 5.0, 2.8 Hz, 1H), 1.71 (tq, *J* = 12.5, 6.3 Hz, 1H), 1.01 (d, *J* = 7.0 Hz, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): *δ* 138.63, 128.50, 127.67, 73.28, 72.87, 54.37, 45.88, 36.75, 13.33. **FT-IR** (film): v_{max} (cm^{-1}) 3031.55, 2965.98, 2917.77, 2857.02, 1578.45, 1540.85, 1495.53, 1482.03, 1454.06, 1414.53, 1361.5, 1257.36, 1203.36, 1100.19, 1027.87, 935.31, 881.31, 832.13, 787.78, 737.64, 698.10. **HRMS** (EI) *m/z* 195.1152 [$(M)^+$; calcd for $C_{12}H_{16}O_2$: 192.1150]. **$[\alpha]^{20}_D$** +5.34 (c 1.40, $CHCl_3$). The optical purity of **(+)-9** prepared was determined to be 82% ee by comparison of the **$[\alpha]^{20}_D$** value of our sample (**$[\alpha]^{20}_D$** +5.34 (c 1.40, $CHCl_3$).) to that of a reported optically pure sample (**(-)-9**, **$[\alpha]^{20}_D$** -6.50 (c 0.5, $CHCl_3$).). [3]

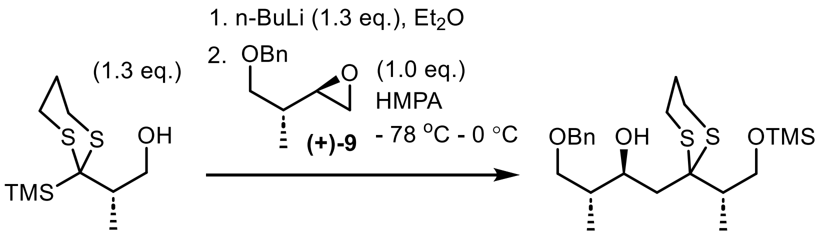


In an oven dried 250 mL round bottom flask equipped with magnetic stir bar, (+)-Roche ester (16.7 g, 141 mmol) was dissolved in dry CH_2Cl_2 (300 mL). PMB trichloroacetimidate (50.0 g, 180 mmol) was added followed by addition of camphor sulfonic acid (327 mg, 1.41 mmol). The mixture was allowed to stir at room temperature for 24 hours, during which white precipitate was formed. After TLC showed complete conversion, the reaction mixture was filtered and concentrated under reduced pressure. Hexanes (300 mL) was then added, and the mixture was filtered again. The filtrate was then concentrated via rotary evaporation and purified via column chromatography (SiO_2, Hexanes/EtOAc *v/v* 20:1) to afford compound **S3** (32.8 g, 97%) as a pale-yellow oil. **^{1}H-NMR** spectra matched the reported value.[4]

To an oven-dried 1L round bottom flask equipped with magnetic stir bar was added compound **S3** (32.8 g, 137 mmol). The flask was evacuated and back-filled with N_2 for 3 times. Dry CH_2Cl_2 (475 mL) was added through addition funnel. The solution was cooled to -78^{o}C and DIBAL-H (1.0 M in toluene, 150 mL, 150 mmol) was added dropwise via addition funnel over 2 hours. The reaction mixture was allowed to stir for another 1 hour at -78^{o}C after the addition was completed. MeOH (190 mL) was added dropwise into the reaction mixture at -78^{o}C to quench the excess DIBAL-H. The mixture was warmed up to rt, and water (125 mL) was added. The mixture was stirred for 15 minutes, during which a white precipitate formed. The crude mixture was passed through a thin pad of celite and concentrated under reduced pressure. The residue was azeotrope 3 times with toluene (50 mL x 3) and placed under high vacuum overnight to remove all water. The product was then directly used in the next step without further purification.

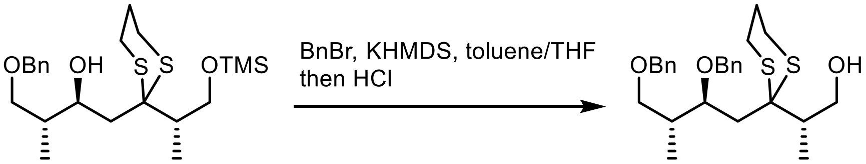
In an oven-dried 1L round bottom flask, crude aldehyde **S4** from previous step was dissolved in dry CH_2Cl_2 (500 mL). The solution was cooled to -78^{o}C. 1,3-propanedithiol (34.3 mL, 342.5 mmol) and $BF_3{\cdot}OEt_2$ (42.3 mL, 342.5 mmol) were added sequentially. The resulting mixture was stirred at -78^{o}C for 2 hours, then at room temperature for another 2 hours. Saturate aq. $NaHCO_3$ (300 mL) was slowly added and the biphasic mixture was stirred overnight. Then the organic layer was collected, and aqueous layer extracted with CH_2Cl_2 (100 ml x 3). The organic layer was combined, dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 4:1) afforded slightly contaminated **S5** as a colorless oil, which was directly used in the next step without further purification.

In an oven-dried, N_2 flushed 1L 3-neck round bottom flask, compound **S5** from previous step was dissolved in dry THF (300 mL). The solution was cooled to 0^{o}C, and n-BuLi (2.47 M in hexane, 125 mL, 308.7 mmol) was added dropwise via addition funnel. The solution turned orange as the deprotonation occurs. The mixture was allowed to stir for 1 hour at 0^{o}C to ensure complete deprotonation. TMSCl (41 mL, 325 mmol) was added dropwise via addition funnel. The reaction mixture was allowed to warm up to room temperature and stirred for another 2 hours, during which a lot of white precipitate formed. 1M HCl (300 mL) was added and the biphasic mixture was stirred at room temperature for 2 hours. The organic layer was collected, and the aqueous layer extracted with ether (100 mL x 3). The organic layers were combined, washed with saturate aq. $NaHCO_3$ (100 mL) and brine (100 mL), dried over Na_2SO_4, filtered and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 7:1 – 5:1) afforded pure compound **10** (21.4 g, 62% over 3 steps) as a white crystalline solid. **^{1}H-NMR** spectra matched the literature value.



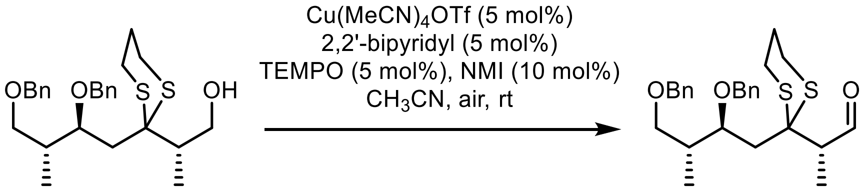
10 **11**

To a stirred solution of alcohol **10** (7.26 g, 29.0 mmol) in ether (100 mL) was added n-BuLi (11.6 mL, 2.5 M in hexanes) at -78^{o}C under argon atmosphere. The solution was stirred at 78^{o}C for 10 min. Then a solution of epoxide **(+)-9** (3.71 g, 19.3 mmol) and HMPA (6.7 mL) in ether (90 mL) was added dropwise at -78^{o}C. The resulting mixture was slowly warmed up to 0^{o}C over 3 hours before sat. aq. NH_4Cl was added. The resulting biphasic mixture was extracted with a mixture of ether/hexanes 3 times (v/v 1:1,100 mL x 3). The organic layers were combined and washed with sat. aq. NH_4Cl (100 mL x 2) and brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 10:1) afforded compound **11** (7.05 g, 82%), which was directly used in the next step without characterization.



11 **S6**

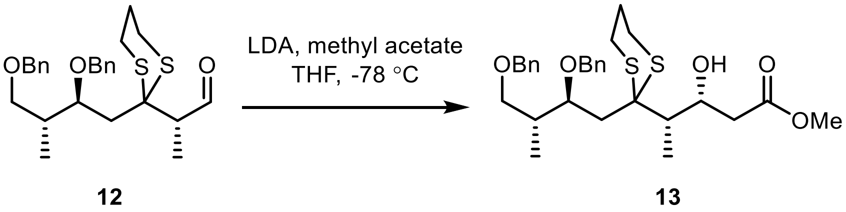
To a stirred solution of compound **11** (7.05 g, 15.8 mmol) in THF (160 mL) was added KHMDS (79 mL, 0.5 M in toluene, 39.5 mmol) at -30^{o}C under argon atmosphere. The resulting solution was stirred at -30^{o}C for 2 minutes before BnBr (11.2 mL, 95 mmol) was added. The resulting mixture was warmed up to 0^{o}C and stirred for 10 mins before 1N HCl (300 mL) was added. The resulting biphasic mixture warmed up to room temperature and stirred for another 1 hour, at which point TLC showed complete hydrolysis of silyl ether. The organic layer was then collected and aqueous layer was extracted with ether (50 mL x 3). The organic layers were combined, washed with sat. aq. $NaHCO_3$ (50 mL) and brine (50 mL), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 4:1) afforded compound **S6** as a colorless liquid, which was directly used in the subsequent oxidation. **^{1}H-NMR** (500 MHz, $CDCl_3$): *δ* 7.39 – 7.27 (m, 10H), 4.63 – 4.47 (m, 4H), 4.04 (ddd, *J* = 8.0, 3.6, 1.8 Hz, 1H), 3.89 (dd, *J* = 11.7, 5.7 Hz, 1H), 3.69 (dd, *J* = 11.6, 4.9 Hz, 1H), 3.54 – 3.42 (m, 2H), 2.86 (ddd, *J* = 14.3, 7.2, 4.0 Hz, 1H), 2.78 (ddd, *J* = 14.5, 7.8, 3.8 Hz, 1H), 2.75 – 2.65 (m, 2H), 2.44 (h, *J* = 6.4 Hz, 1H), 2.35 (qd, *J* = 6.9, 3.5 Hz, 1H), 2.15 (dd, *J* = 15.6, 1.8 Hz, 1H), 2.09 – 2.02 (m, 2H), 1.93 – 1.83 (m, 2H), 1.13 (d, *J* = 6.9 Hz, 3H), 1.00 (d, *J* = 6.9 Hz, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): *δ* 139.12, 138.55, 128.72, 128.50, 128.36, 127.85, 127.74, 127.41, 127.13, 78.42, 73.44, 73.14, 71.07, 65.72, 57.12, 41.70, 36.43, 36.39, 26.43, 25.80, 25.13, 13.45, 11.84. **FT-IR** (film): v_{max} (cm^{-1}) 3435.56 (br), 3086.51, 3062.41, 3029.62, 2932.23, 2903.31, 1604.48, 1585.20, 1496.49, 1454.06, 1421.28, 1365.35, 1308.46, 1275.68, 1240.00, 1208.18, 1089.58, 1066.44, 1027.87, 908.31, 813.81, 736.67, 698.10, 674.00. **HRMS** (ESI) *m/z* 483.1997 [(M+Na)$^+$; calcd for $C_{26}H_{36}O_3NaS_2$: 483.2004]. **[α]^{20}$_D$** -21.9 (c 0.43, $CHCl_3$).



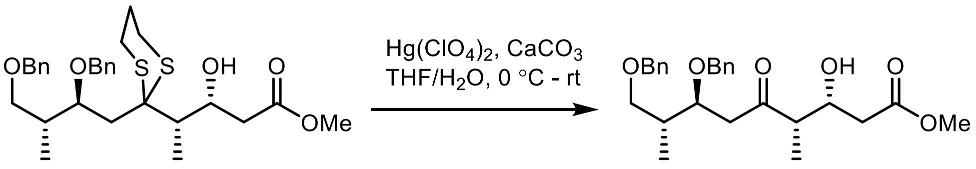
S6 **12**

To a stirred solution of alcohol **S6** obtained above in MeCN (150 mL) was added $Cu(MeCN)_4OTf$

(297 mg, 0.80 mmol), 2,2'-bipyridyl (125 mg, 0.80 mmol), TEMPO (125 mg, 0.80 mmol) and M-methylimidazole (127 µL, 1.60 mmol). The resulting dark brown solution was stirred under open air for 16 h, at which point the color of the solution turned blue. The solution was then concentrated under reduced pressure and diluted with H_2O (400 mL) and ether (100 mL). About 5 g Na_2SO_4 was added and dissolved in aqueous layer to prevent emulsion formation. The organic layer was then separated and the aqueous layer was extracted with ether (100 mL x 4). The organic layers were combined, washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 10:1) afforded compound **12** as a white solid (6.37 g, 87% over 2 steps). Single crystals were obtained by dissolving aldehyde **12** in refluxing hexane followed by slow cooling to 0°C. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 9.97 (d, J = 2.6 Hz, 1H), 7.39 – 7.27 (m, 10H), 4.54 (s, 2H), 4.52 (s, 2H), 4.10 (ddd, J = 8.9, 3.7, 1.6 Hz, 1H), 3.53 – 3.43 (m, 2H), 2.92 (qd, J = 7.0, 2.6 Hz, 1H), 2.82 – 2.70 (m, 3H), 2.61 (ddd, J = 14.4, 6.3, 3.8 Hz, 1H), 2.38 (qd, J = 6.9, 3.7 Hz, 1H), 2.29 (dd, J = 15.5, 1.6 Hz, 1H), 2.10 (dd, J = 15.6, 8.9 Hz, 1H), 1.87 (m, J = 13.1, 9.4, 6.9, 3.9 Hz, 2H), 1.20 (d, J = 7.0 Hz, 3H), 1.01 (d, J = 7.0 Hz, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 202.97, 138.82, 138.44, 128.51, 128.49, 128.41, 127.86, 127.79, 127.74, 127.49, 78.43, 73.53, 73.18, 71.03, 53.74, 52.08, 36.19, 35.87, 26.03, 25.91, 24.92, 11.53, 10.00. **FT-IR** (film): ν_{max} (cm^{-1}) 3407.60, 3087.48, 3062.41, 3029.62, 2934.16, 2903.31, 2854.13, 2733.60, 2360.44, 1952.57, 1714.41, 1604.48, 1585.20, 1496.49, 1454.06, 1421.48, 1365.35, 1308.46, 1277.61, 1255.43, 1207.22, 1087.66, 1067.41, 1027.87, 962.31, 906.38, 868.77, 817.67, 736.67, 698.10. **HRMS** (ESI) *m/z* 481.1847 [(M+Na)$^+$; calcd for $C_{26}H_{34}O_3NaS_2$: 481.1847]. **$[\alpha]^{20}_D$** -52.09 (c 0.96, $CHCl_3$).

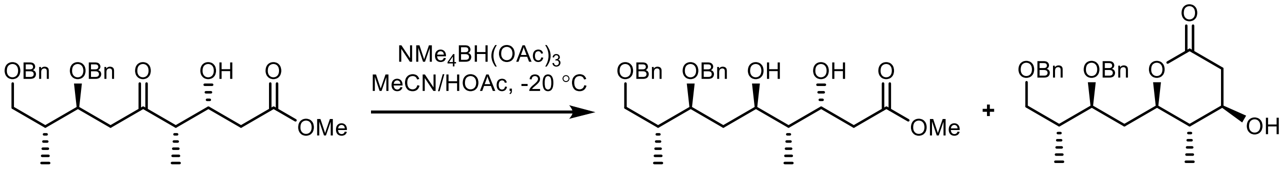


Diisopropylamine (7.3 mL, 52 mmol) was dissolved in THF (150 mL) and cooled to -78°C under argon atmosphere. n-BuLi (21 mL, 2.5 M in hexanes, 52 mmol) was then added dropwise. The resulting yellow solution was stirred at -78°C for 30 min before a solution of methyl acetate (4.2 mL, 52 mmol) in THF (50 mL) was added dropwise. The reaction mixture was stirred at -78°C for 50 min. Aldehyde **12** (11.9 g, 25.9 mmol) was then dissolved in THF (30 mL + 10 mL x 2 rinse) and added dropwise into a stirred solution of ester enolate at -78°C. The reaction mixture was stirred at -78°C for another 20 min before sat. aq. NH_4Cl was added. The organic layer was collected and aqueous layer was extracted with ether (100 mL x 3). The organic layer was washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 4:1) afforded compound **13** as a colorless oil (13.7 g, quant., 15:1 d.r.). ^{1}**H-NMR** (500 MHz, $CDCl_3$): δ 7.40 – 7.27 (m, 10H), 5.02 – 4.95 (m, 1H), 4.55 (d, *J* = 11.2 Hz, 1H), 4.52 (s, 2H), 4.46 (d, *J* = 11.1 Hz, 1H), 4.09 – 4.02 (m, 1H), 3.65 (s, 3H), 3.53 – 3.44 (m, 2H), 2.82 – 2.72 (m, 2H), 2.70 – 2.63 (m, 1H), 2.58 (ddd, *J* = 14.4, 6.2, 3.7 Hz, 1H), 2.48 (dd, *J* = 15.4, 9.1 Hz, 1H), 2.37 (td, *J* = 6.6, 3.7 Hz, 1H), 2.32 (dd, *J* = 15.7, 1.5 Hz, 1H), 2.19 (q, *J* = 7.2 Hz, 1H), 2.14 (ddd, *J* = 15.4, 6.8, 4.6 Hz, 2H), 1.91 – 1.79 (m, 2H), 1.08 (d, *J* = 6.9 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H). ^{13}**C-NMR** (126 MHz, $CDCl_3$): δ 172.61, 138.99, 138.50, 128.49, 128.36, 127.84, 127.75, 127.68, 127.44, 78.97, 73.49, 73.27, 71.13, 68.11, 58.57, 51.76, 43.91, 40.91, 36.40, 36.12, 26.26, 25.85, 25.26, 11.61, 7.72. **FT-IR** (film): ν_{max} (cm^{-1}) 3499.20 (br), 3087.48, 3062.41, 3028.66, 2947.66, 2902.34, 2795.31, 1953.54, 1875.43, 1736.58, 1604.48, 1585.20, 1541.81, 1496.49, 1454.06, 1437.67, 1422.24, 1364.39, 1329.68, 1274.72, 1239.04, 1207.22, 1170.58, 1089.58, 1066.44, 1027.87, 990.27, 908.31, 868.77, 848.53, 817.67, 736.67, 699.07, 606.50. **HRMS** (ESI) *m/z* 555.2224 [$(M+Na)^+$; calcd for $C_{29}H_{40}O_5NaS_2$: 555.2215]. **$[\alpha]^{20}_{D}$** -30.43 (c 1.31, $CHCl_3$).



13 **S7**

To a stirred solution of compound **13** (13.7 g, 25.7 mmol) in THF (250 mL) and H_2O (50 mL) was added $CaCO_3$ (25.7 g, 257 mmol). The resulting mixture was cooled to 0^{o}C and $Hg(ClO_4)_2{\cdot}3H_2O$ (23.3 g, 51.4 mmol) was added portion wise. The resulting mixture was slowly warned up to room temperature over 40 min. Then the reaction mixture was filtered through a pad of celite and Na_2SO_4 and the filter pad was washed with copious amount of diethyl ether. The filtrate was then combined and washed with H_2O (50 mL x 3) and brine (100 mL), dried with Na_2SO_4, filtered, and concentrated *in-vacuo*. The crude β-hydroxyketone **S7** was directly used in the next step without purification.



S7 **14** **S8**

To an oven-dried 500 mL round bottom flask was added freshly prepared $NMe_4BH(OAc)_3$ (47.3 g, 180 mmol). The flask was evacuated and back-filled with argon for 3 times. Then anhydrous MeCN

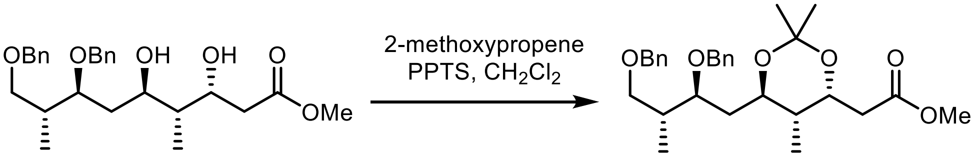
(150 mL) and HOAc (70 mL) were added and the resulting mixture stirred at room temperature for 30 min. Then the solution was cooled to -20°C and the above crude β-hydroxyketone **S7** dissolved in MeCN (30 mL + 10 mL x 2 rinse) was added dropwise. The reaction turned pale-grey due to the presence of residual Hg(II) from previous step. The resulting solution was stirred for 40 h before sat. aq. $NaHCO_3$ was added carefully to neutralize the acetic acid. The mixture was then extracted with ether (150 mL x 5). The organic layers were combined and washed with H_2O (100 mL x 3) and brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. The crude material was repeatedly dissolved in methanol and concentrated by rotary evaporation to remove the residual boron. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 4:1) afforded recovered β-hydroxyketone **S7** (662.7 mg, 8%), *anti*-diol **14** (8.40 g, 73% over 2 steps) and lactone **S8** (754.3 mg, 7%).

β-hydroxyketone **S7**: **^{1}H-NMR** (500 MHz, $CDCl_3$): *δ* 7.37 – 7.25 (m, 10H), 4.54 – 4.43 (m, 4H), 4.34 (dt, *J* = 8.6, 4.3 Hz, 1H), 4.14 (dt, *J* = 8.8, 4.2 Hz, 1H), 3.67 (s, 3H), 3.46 – 3.36 (m, 2H), 2.83 (dd, *J* = 16.3, 8.9 Hz, 1H), 2.65 (td, *J* = 7.2, 4.4 Hz, 1H), 2.55 (dd, *J* = 16.2, 3.6 Hz, 1H), 2.43 (dd, *J* = 16.2, 8.8 Hz, 1H), 2.36 (dd, *J* = 16.1, 4.2 Hz, 1H), 2.21 (dq, *J* = 12.4, 6.6 Hz, 1H), 1.09 (d, *J* = 7.2 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): *δ* 213.20, 172.79, 138.55, 128.51, 128.46, 127.95, 127.90, 127.74, 127.72, 73.27, 72.40, 68.15, 51.91, 51.12, 43.78, 38.47, 36.53, 12.76, 10.55. **FT-IR** (film): ν_{max} (cm^{-1}) 3502.10 (br), 3087.48, 3063.37, 3030.59, 2877.27, 2360.44, 2341.16, 1955.47, 1736.58, 1710.55, 1606.45, 1540.85, 1496.49, 1454.06, 1437.67, 1365.35, 1265.07, 1204.33, 1172.51, 1091.51, 1067.41, 1027.87, 989.30, 910.24, 849.49, 737.64, 699.07, 628.68. **HRMS** (ESI) *m/z* 465.2242 [$(M+Na)^+$; calcd for $C_{26}H_{34}O_6Na$: 465.2253]. **$[\alpha]^{20}_D$** -12.8 (c 0.92, $CHCl_3$).

Diol **14**: **^{1}H-NMR** (500 MHz, $CDCl_3$): *δ* 7.37 – 7.27 (m, 10H), 4.66 (d, *J* = 11.2 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 5.7 Hz, 1H), 4.43 (d, *J* = 4.8 Hz, 1H), 4.37 (ddd, *J* = 9.4, 4.1, 2.1 Hz, 1H), 3.93 (dt, *J* = 10.6, 3.3 Hz, 1H), 3.76 (ddd, *J* = 9.9, 5.4, 1.6 Hz, 1H), 3.69 (s, 3H), 3.41 (dd, *J* = 9.4, 5.6 Hz, 1H), 3.31 (dd, *J* = 9.4, 8.0 Hz, 1H), 2.59 (dd, *J* = 15.3, 9.3 Hz, 1H), 2.42 (tq, *J* = 13.3, 7.4, 6.1 Hz, 1H), 2.33 (dd, *J* = 15.2, 4.1 Hz, 1H), 1.74 (dt, *J* = 14.5, 10.2 Hz, 1H), 1.57 – 1.49 (m, 2H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$): *δ* 173.11, 138.39, 137.72, 128.74, 128.56, 128.11, 128.09, 127.84, 127.76, 81.51, 77.16, 76.67, 73.29, 72.48, 71.05, 69.30, 51.83, 42.21, 39.11, 34.90, 33.88, 11.77, 11.09. **FT-IR** (film): ν_{max} (cm^{-1}) 3451.96 (br), 3063.37, 3030.59, 2959.23, 2916.81, 2878.24, 2360.44, 1736.58, 1604.48, 1496.49, 1455.03, 1436.71, 1364.39, 1265.07, 1204.33, 1170.58, 1091.51, 1065.48, 1027.87, 990.27, 908.31, 847.56, 736.67, 699.07. **HRMS** (ESI) *m/z* 467.2396 [$(M+Na)^+$; calcd for $C_{26}H_{36}O_6Na$: 467.2410]. **$[\alpha]^{20}_D$** -33.2 (c 0.99, $CHCl_3$).

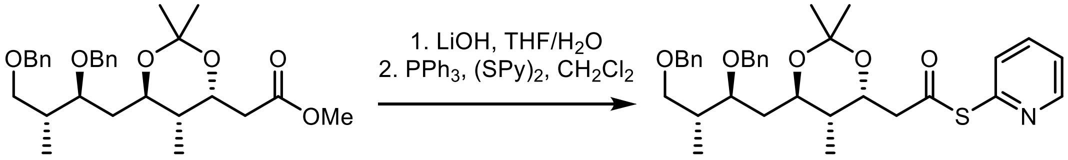
Lactone **S8**: **^{1}H-NMR** (500 MHz, $CDCl_3$): *δ* 7.37 – 7.27 (m, 10H), 4.51 (s, 2H), 4.47 (s, 2H), 3.98

(ddd, *J* = 10.6, 7.7, 3.6 Hz, 1H), 3.76 (q, *J* = 5.6 Hz, 1H), 3.65 (td, *J* = 7.5, 5.6 Hz, 1H), 3.54 (dd, *J* = 9.2, 6.6 Hz, 1H), 3.40 (dd, *J* = 9.2, 5.5 Hz, 1H), 2.82 (dd, *J* = 17.0, 5.6 Hz, 1H), 2.42 (dd, *J* = 17.0, 7.6 Hz, 1H), 2.22 (p, *J* = 6.1 Hz, 1H), 2.05 (ddd, *J* = 14.6, 6.1, 3.5 Hz, 1H), 1.94 – 1.86 (m, 1H), 1.77 (s, 1H), 1.64 (dq, *J* = 9.9, 6.9 Hz, 1H), 1.01 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): *δ* 170.41, 138.80, 138.63, 128.49, 128.47, 128.07, 127.91, 127.71, 127.68, 80.31, 73.37, 72.31, 71.57, 69.97, 41.47, 38.82, 36.04, 34.51, 14.08, 13.75. **FT-IR** (film): ν_{max} (cm^{-1}) 3437.49, 3087.48, 3062.41, 3029.62, 2965.98, 2878.31, 2359.48, 2340.19, 1736.58, 1604.48, 1586.16, 1540.85, 1496.49, 1454.06, 1365.35, 1309.43, 1243.86, 1185.04, 1095.37, 1067.41, 1027.87, 943.02, 919.88, 844.67, 808.99, 738.60, 699.07. **HRMS** (ESI) *m/z* 435.2144 [$(M+Na)^+$; calcd for $C_{25}H_{32}O_5Na$: 435.2147]. **$[\alpha]^{20}_D$** +12.3 (c 0.67, $CHCl_3$).



14 **15**

To a stirred solution of diol **14** (8.4 g, 18.9 mmol) and freshly distilled 2-methoxypropene (3.7 mL, 38.0 mmol) was added PPTS (237 mg, 0.95 mmol). The resulting mixture was stirred at room temperature for 16 hours before NEt_3 was added to quench the reaction. The reaction was concentrated by rotary-evaporation and subjected to chromatography purification (SiO_2, Hexanes/EtOAc *v/v* 10:1) to afford compound **15** (8.8 g, 96%) as a colorless oil. **^{1}H-NMR** (500 MHz, $CDCl_3$): *δ* 7.38 – 7.26 (m, 10H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.48 (s, 2H), 4.45 (d, *J* = 11.5 Hz, 1H), 4.37 (dt, *J* = 9.6, 4.9 Hz, 1H), 3.68 (s, 3H), 3.57 (t, *J* = 5.4 Hz, 1H), 3.54 – 3.51 (m, 1H), 3.39 (qd, *J* = 7.2, 6.5, 3.8 Hz, 2H), 2.47 (dd, *J* = 15.6, 9.4 Hz, 1H), 2.31 (dd, *J* = 15.7, 4.7 Hz, 1H), 2.22 – 2.13 (m, 1H), 1.80 (tdd, *J* = 14.7, 12.2, 5.7 Hz, 2H), 1.71 (td, *J* = 7.2, 5.1 Hz, 1H), 1.34 (s, 3H), 1.29 (s, 3H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): *δ* 172.00, 139.14, 138.82, 128.45, 128.36, 127.87, 127.71, 127.60, 127.49, 100.92, 78.09, 73.23, 72.51, 72.20, 71.18, 65.97, 51.76, 39.81, 36.55, 36.26, 35.87, 25.04, 23.85, 13.84, 12.03. **FT-IR** (film): ν_{max} (cm^{-1}) 3088.44, 3063.37, 3029.62, 2985.27, 2934.16, 2876.31, 1951.61, 1742.37, 1605.45, 1585.20, 1540.85, 1496.49, 1455.03, 1436.71, 1380.78, 1287.25, 1227.47, 1194.69, 1172.51, 1094.40, 1068.37, 1028.84, 1006.66, 956.52, 939.16, 910.24, 849.49, 820.56, 736.67, 698.10. **HRMS** (ESI) *m/z* 507.2723 [$(M+Na)^+$; calcd for $C_{29}H_{40}O_6Na$: 507.2723]. **$[\alpha]^{20}_D$** +1.62 (c 0.39, $CHCl_3$).



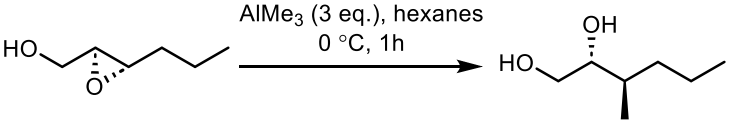
15 **5**

To a stirred solution of compound **15** (8.8 g, 18.0 mmol) in THF (70 mL) was added 1N aqueous LiOH (36 mL, 36 mmol). The resulting biphasic mixture was stirred at room temperature for 16 hours, at which point TLC showed complete hydrolysis of the ester. Sat. aq. NH_4Cl (200 mL) was then added and the mixture was cooled to 0ºC. 1N HCl (40 mL) was carefully added and the organic layer collected. The aqueous layer was extracted with ether (100 mL x 3). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. The crude carboxylic acid was directly used in the next step without purification.

To a stirred solution of carboxylic acid from previous step in CH_2Cl_2 (50 mL) was added PPh_3 (18.9 g, 72 mmol) and $(SPy)_2$ (7.9 g, 36 mmol) under argon atmosphere. The resulting bright yellow solution was stirred for 16 hours. Then the solvent was removed under reduced pressure and the residue was subjected to chromatography purification (SiO_2, Hexanes/EtOAc *v/v* 4:1) to afford crude Northwestern Fragment **5**, which was contaminated with small amount of $(SPy)_2$. To obtain pure compound **5**, contaminated Northwestern Fragment from above was dissolved in CH_2Cl_2 (50 mL) and excess PPh_3 (10 g) was added to consume residual $(SPy)_2$. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 4:1 – 2:1) afforded pure thioester **5** (9.7 g, 95% over 2 steps) as a pale-yellow oil. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 8.62 (dd, *J* = 4.9, 1.8 Hz, 1H), 7.74 (td, *J* = 7.7, 1.9 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.26 (m, 11H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.47 (s, 2H), 4.46 – 4.42 (m, 2H), 3.56 (q, *J* = 5.5 Hz, 1H), 3.52 (dd, *J* = 9.2, 5.8 Hz, 1H), 3.45 – 3.36 (m, 2H), 2.86 (dd, *J* = 15.7, 9.2 Hz, 1H), 2.67 (dd, *J* = 15.7, 4.5 Hz, 1H), 2.17 (p, *J* = 6.3 Hz, 1H), 1.86 – 1.69 (m, 3H), 1.35 (s, 3H), 1.29 (s, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 194.35, 151.69, 150.52, 139.12, 138.81, 137.27, 130.24, 128.46, 128.37, 127.89, 127.74, 127.62, 127.51, 123.63, 101.06, 78.04, 73.24, 72.52, 72.17, 71.19, 65.85, 45.80, 39.92, 36.52, 35.82, 25.15, 23.81, 13.80, 12.18. **FT-IR** (film): ν_{max} (cm^{-1}) 3086.51, 3062.41, 3029.62, 2984.30, 2961.16, 2933.20, 2876.31, 1952.57, 1874.47, 1809.67, 1709.59, 1605.45, 1572.66, 1563.02, 1496.49, 1453.10, 1420.32, 1379.82, 1307.50, 1230.36, 1168.65, 1098.26, 1067.41, 1027.87, 988.34, 935.31, 909.27, 845.63, 820.56, 765.60, 737.64, 698.11, 652.79. **HRMS** (ESI) *m/z* 564.2760 [$(M+H)^+$; calcd for $C_{33}H_{42}NO_5S$: 564.2784]. **$[\alpha]^{20}_D$** +15.4 (c 1.23, $CHCl_3$).

(b). Synthesis of the Northeastern Fragment (**6**)

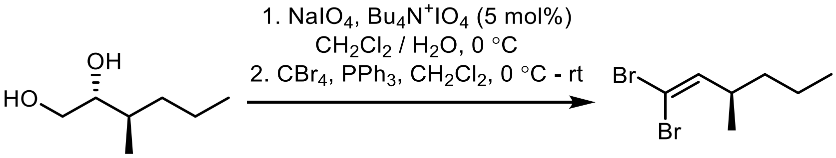
Chiral epoxide **(-)-16** was synthesized following a reported procedure.[5] The optical purity of chiral epoxy alcohol **(-)-16** prepared was determined to be **91%** ee by comparison of the **$[\alpha]^{20}_{D}$** value of our sample (**$[\alpha]^{20}_{D}$** -44.2 (c 1.0, $CHCl_3$).) to the reported optical rotation value (**$[\alpha]^{20}_{D}$** -46.6 (c 1.0, $CHCl_3$).) with a known enantiomeric excess (96.8% ee).[5]



(-)-16
91% ee

17

To a stirred solution of epoxide **(-)-16** (6.91 g, 59.4 mmol, 91% ee) in dry hexanes (80 mL) at -40°C under argon atmosphere was added $AlMe_3$ (2.0 M in hexanes, 79 mL, 158 mmol, 3.0 eq.) dropwise via addition funnel. The reaction was warmed up to 0°C by transferring the flask to ice water bath and allowed the reaction to stirred at 0°C for 1 hour. H_2O (28 mL) was then added dropwise to quench the reaction. CH_2Cl_2 (250 mL) was added to dilute the reaction and NaF (66 g) was added. The mixture was mechanically stirred at room temperature overnight (ca. 16 h). The mixture was then filtered and the solid was washed with CH_2Cl_2. The filtrate was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford crude diol **17** (7.50 g, 95%, >20:1 r.r.), which was directly used in the next step without purification. **^{1}H-NMR** (500 MHz, Chloroform-*d*) δ 3.75 – 3.67 (m, 1H), 3.56 – 3.46 (m, 2H), 2.02 (s, 2H), 1.59 (dtq, *J* = 13.3, 6.6, 3.2 Hz, 1H), 1.54 – 1.46 (m, 1H), 1.42 (dddd, *J* = 17.4, 11.6, 8.6, 4.9 Hz, 1H), 1.29 – 1.19 (m, 1H), 1.19 – 1.10 (m, 1H), 0.91 (t, *J* = 7.1 Hz, 3H), 0.88 (d, *J* = 6.7 Hz, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 77.16, 76.39, 64.81, 36.06, 34.80, 20.19, 15.27, 14.46. ^{13}C NMR (126 MHz, $CDCl_3$) δ 77.16, 76.39, 64.81, 36.06, 34.80, 20.19, 15.27, 14.46.

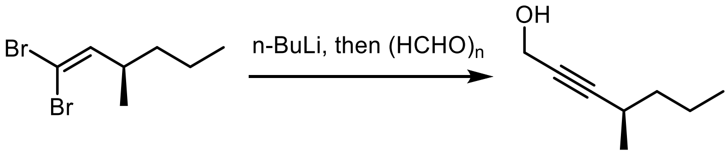


17

18

To a stirred solution of diol **17** (19.7 g) in CH_2Cl_2 (300 mL) and H_2O (600 mL) was added $Bu_4N^+IO_4^-$ (3.23 g, 7.4 mmol) and $NaIO_4$ (63.8 g, 300 mmol) at 20°C. The resulting mixture was stirred at 0°C for 40 min. The organic layer was collected and aqueous layer extracted with CH_2Cl_2 (50 mL x 2). The organic layers were combined and dried over 4Å MS beads. Due to the volatility of the resulting aldehyde (b.p. 118°C), significant loss of mass was observed during the attempt to concentrate the solution under reduced pressure. Therefore, the solution of crude aldehyde in dichloromethane was directly used in the subsequent dibromo olefination without any purification.

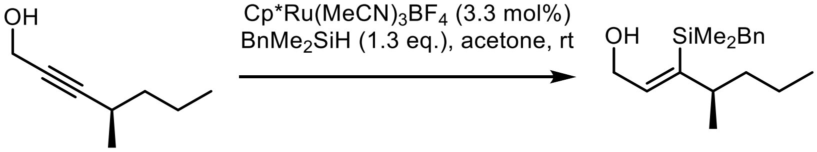
In a separate oven-dried 2L round bottom flask was added PPh_3 (157.3 g, 596 mmol). The flask was evacuated and back-filled with argon for 3 times. Then anhydrous CH_2Cl_2 (300 mL) was added to dissolve the solid. The solution was cooled to 0°C and solid CBr_4 (98.8 g, 298 mmol) was added portion-wise (caution: CBr_4 should be added slowly to avoid rapid heat generation) under a stream of argon. The resulting mixture was stirred at 0°C for 1h, and the crude aldehyde solution was transferred to the above mixture via cannula. The reaction was then warmed-up to room temperature and stirred overnight (ca. 16 h). Pentane (1.4 L) was added and the solid was filtered off. The filtrate was carefully concentrated by distillation through a 20-cm Vigreux column in a 45°C warm water bath. The residue was then purified via column chromatography (SiO_2, pentane) to afford dibromo-olefin **18** (38.05 g, >95% over 2 steps) as a colorless oil. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 6.17 (d, *J* = 9.5 Hz, 1H), 2.47 (qd, *J* = 8.2, 5.4 Hz, 1H), 1.35 – 1.24 (m, 4H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.91 – 0.86 (m, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 144.64, 87.26, 38.48, 38.24, 20.48, 19.36, 14.23. **FT-IR** (film): ν_{max} (cm^{-1}) 2959.23, 2927.41, 2871.49, 2848.35, 1614.13, 1455.03, 1377.89, 1267.97, 1218.79, 1157.08, 1142.62, 952.66, 903.49, 841.78, 782.96, 739.57. **HRMS** (EI) *m/z* 253.9313 [(M)+; calcd for $C_7H_{12}Br_2$: 253.9306]. **$[\alpha]^{20}_D$** -24.3 (c 1.02, $CHCl_3$).



18 **19**

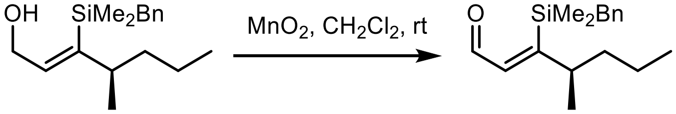
To a stirred solution of dibromo-olefin **18** (38.0 g, 149 mmol) in THF (450 mL) was added *n*-BuLi (130 mL, 2.5 M in hexanes, 328 mmol) at -78°C under argon atmosphere. The solution was stirred at -78°C for 1.5 h and warmed up to 0°C by transferring the flask to an ice water bath. The reaction was stirred at 0°C for another 0.5 h before paraformaldehyde (9.0 g, 300 mmol) was added. The mixture was warmed up to room temperature and stirred for 14 hours. Then sat. aq. NH_4Cl (300 mL) was added and organic layer was collected. The aqueous layer was extracted with ether (100 mL x 3). The organic layers were combined, washed with brine (100 mL x 2), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Vacuum distillation (0.5 torr, 87°C - 91°C) through a 12 cm Vigreux column afforded propargyl alcohol **19** (15.74 g, 84%) as a colorless liquid. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 4.26 (d, *J* = 2.0 Hz, 2H), 2.52 – 2.41 (m, 1H), 1.49 – 1.34 (m, 4H), 1.15 (d, *J* = 6.9 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H). **^{13}C-NMR**

(126 MHz, $CDCl_3$): δ 91.19, 78.51, 51.61, 39.14, 25.79, 21.11, 20.63, 14.02. **FT-IR** (film): ν_{max} (cm^{-1}) 3334.32 (br), 2960.20, 2931.27, 2872.45, 2360.44, 2231.24, 1577.49, 1540.85, 1455.99, 1377.89, 1332.57, 1227.47, 1170.58, 1132.01, 1074.16, 1046.19, 1023.05, 1006.66, 980.63, 919.88. **HRMS** (EI) *m/z* 126.1045 [$(M)^+$; calcd for $C_{18}H_{14}O$: 126.1045]. **$[\alpha]^{20}_D$** -32.1 (c 1.29, $CHCl_3$).



19 **20**

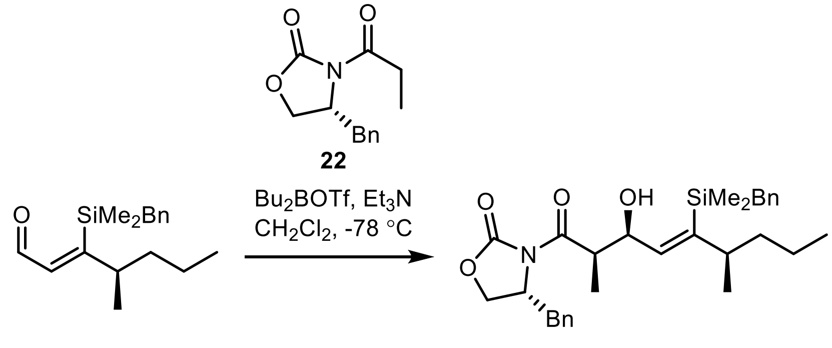
To a stirred solution of alcohol **19** (15.0 g, 119 mmol) and benzyldimethylsilane (25 mL, 155 mmol) in anhydrous acetone (250 mL) under argon atmosphere was added solid $Cp^*Ru(MeCN)_3PF_6$ (2.1 g, 4.16 mmol) under stream of argon flow. The reaction was capped with a rubber septum and stirred for 16 hours under argon overnight (16 h). Then the reaction was concentrated under vacuum and the residue purified by chromatography (SiO_2, Hexanes/EtOAc *v/v* 7:1) to afford alcohol **20** (30.0 g, 91%, >20:1 r.r, >20:1 *Z/E*) as a colorless oil. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 7.21 (t, *J* = 7.7 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.15 (t, *J* = 7.0 Hz, 1H), 4.03 (d, *J* = 7.0 Hz, 2H), 2.20 (s, 3H), 1.34 – 1.14 (m, 4H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 7.0 Hz, 3H), 0.15 (s, 3H), 0.14 (s, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 147.45, 139.99, 138.95, 128.49, 128.31, 124.41, 62.71, 39.68, 37.77, 27.13, 21.16, 21.04, 14.43, -1.00, -1.02. **FT-IR** (film): ν_{max} (cm^{-1}) 3324.68, 3080.73, 3060.48, 3024.80, 2957.30, 2926.45, 2870.52, 2360.44, 2341.16, 1937.15, 1863.86, 1802.15, 1599.66, 1580.38, 1540.85, 1492.63, 1452.14, 1407.78, 1377.89, 1250.61, 1206.26, 1156.12, 1115.62, 1056.80, 1013.41, 970.98, 904.45, 827.31, 790.67, 761.74, 699.07. **HRMS** (ESI) *m/z* 277.1983 [$(M+H)^+$; calcd for $C_{17}H_{29}OSi$: 277.1988]. **$[\alpha]^{20}_D$** -7.28 (c 0.89, $CHCl_3$).



20 **21**

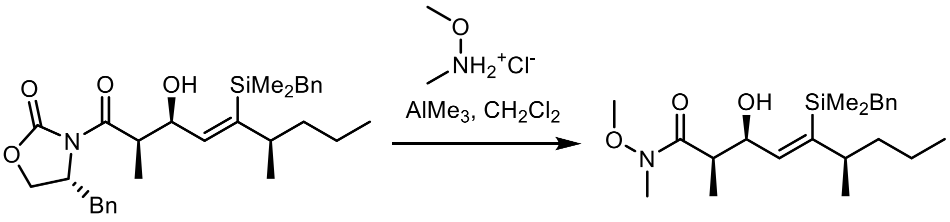
To a stirred solution of alcohol **20** (23.8 g, 86.3 mmol) in anhydrous CH_2Cl_2 (400 mL) was added activated powdery MnO_2 (75 g, 863 mmol). The mixture was stirred at room temperature for 18 hours, at which point TLC showed a complete conversion. Then solid was filtered off through a pad of celite. The solid was washed with copious amount of CH_2Cl_2 until the filtrate showed no UV absorption. The filtrate was concentrated under reduced pressure to give aldehyde **21** as a colorless oil (23.4 g, 98%).

^{1}H-NMR (500 MHz, CDCl$_3$): δ 9.76 (d, *J* = 8.3 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 7.4 Hz, 2H), 6.49 (d, *J* = 8.3 Hz, 1H), 2.48 (q, *J* = 6.6 Hz, 1H), 2.32 (s, 2H), 1.39 (dt, *J* = 13.1, 6.5 Hz, 1H), 1.35 – 1.27 (m, 1H), 1.25 – 1.15 (m, 2H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.86 (t, *J* = 6.9 Hz, 3H), 0.28 (s, 3H), 0.27 (s, 3H). **^{13}C-NMR** (126 MHz, CDCl$_3$): δ 193.20, 176.75, 139.62, 138.52, 128.59, 128.46, 124.88, 39.21, 38.82, 27.29, 20.92, 20.33, 14.31, -0.60, -0.65. **FT-IR** (film): ν_{max} (cm^{-1}) 3329.50, 3081.69, 3060.48, 3024.80, 2959.23, 2929.34, 2871.49, 2733.60, 1941.97, 1868.68, 1675.84, 1599.66, 1563.02, 1493.60, 1453.10, 1408.75, 1376.93, 1253.60, 1205.29, 1159.01, 1141.65, 1111.76, 1057.76, 1029.80, 999.91, 966.16, 905.41, 877.45, 828.28, 793.56, 763.67, 718.35, 700.03, 619.04. **HRMS** (ESI) *m/z* 275.1830 [(M+H)$^+$; calcd for $C_{17}H_{27}OSi$: 275.1831]. **$[\alpha]^{20}_D$** -19.62 (c 1.90, CHCl$_3$).



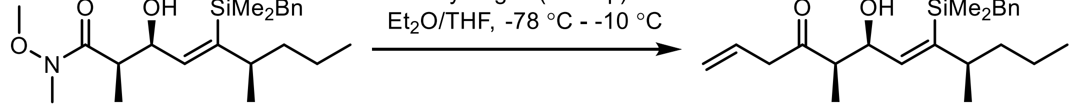
21 **23**

To a stirred solution of **22** (4.85 g, 20.8 mmol) in CH_2Cl_2 (50 mL) under argon atmosphere was added Bu_2BOTf (21.7 mL, 1.0 M in CH_2Cl_2, 21.7 mmol) and NEt_3 (3.2 mL) dropwise at 0°C. The reaction mixture was stirred at 0°C for 1 hour. Then the flask was transferred to a dry ice/acetone bath and aldehyde **21** (4.84 g, 17.5 mmol) in CH_2Cl_2 (3 mL + 1 mL x 2 rinse) was added dropwise. The reaction was stirred at -78°C for 16 hours before sat. aq. $NaHCO_3$ (60 mL), MeOH (24 mL) and 30% aq. H_2O_2 (24 mL) were sequentially added. The resulting mixture was allowed to warm up to room temperature and stirred for 1 hour. The organic layer was separated and aqueous layer extracted with dichloromethane (20 mL x 3). The organic layer was then combined, washed with sat. aq. $Na_2S_2O_3$ (30 mL) and brine (30 mL). Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 8:1) afforded desired adduct **23** and unreacted **22** as an inseparable mixture, which was directly used in next step without further purification.



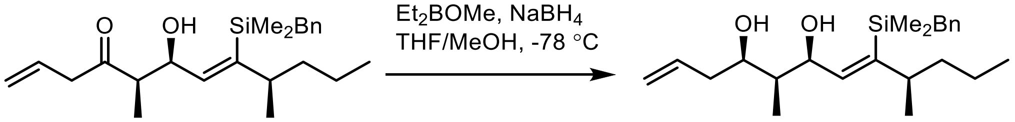
23 **24**

Weinreb amine hydrochloride (3.9 g, 40 mmol) was placed in 500 mL oven-dried round bottom flask. Toluene (30 mL) was added to dissolve the solid and the solution was concentrated under reduced pressure. This process was repeated for 3 times to azeotropically remove water from the salt. Then the flask was evacuated and back-filled with argon for 3 times. CH_2Cl_2 (200 mL) was added and the resulting solution was cooled to 0ºC. $AlMe_3$ (20 mL, 2.0 M in hexanes, 40 mmol) was then added dropwise at 0ºC. The solution was allowed to warm up to room temperature and stirred for 2 hours. Then the solution was cooled to -20ºC and a solution of aldol adduct **23** from previous step in CH_2Cl_2 (5 mL + 2 mL x 2 rinse) was added dropwise. The solution was allowed to warm up to room temperature and stirred for 16 hours. Then sat. aq. Rochelle salt (200 mL) was carefully added and the biphasic mixture was stirred at room temperature for 3 hours until all precipitation disappeared. The organic layer was then collected, and aqueous layer was extracted with ether (150 mL x 4). The organic layer was combined and dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 4:1) afforded pure Weinreb amide **24** (5.68 g, 82% over 2 steps) as a pale-yellow oil. **^{1}H-NMR** (500 MHz, $CDCl_3$): *δ* 7.19 (t, *J* = 7.7 Hz, 2H), 7.09 – 7.04 (m, 1H), 7.02 (d, *J* = 6.8 Hz, 2H), 6.13 (d, *J* = 9.3 Hz, 1H), 4.63 (ddd, *J* = 9.3, 3.4, 1.6 Hz, 1H), 3.68 (s, 3H), 3.20 (s, 3H), 2.94 (s, 1H), 2.27 (d, *J* = 13.7 Hz, 1H), 2.22 (d, *J* = 13.6 Hz, 1H), 2.18 (p, *J* = 6.5 Hz, 1H), 1.41 – 1.33 (m, 1H), 1.33 – 1.27 (m, 1H), 1.25 (d, *J* = 7.1 Hz, 3H), 1.23 – 1.15 (m, 2H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.84 (t, *J* = 6.9 Hz, 3H), 0.13 (s, 3H), 0.11 (s, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): *δ* 148.42, 140.05, 139.29, 128.55, 128.24, 124.25, 70.96, 61.67, 40.36, 39.57, 37.75, 26.87, 21.55, 21.11, 14.43, 11.11, -0.78, -1.24. **FT-IR** (film): ν_{max} (cm^{-1}) 3439.42 (br), 3080.73, 3059.51, 3023.84, 2957.30, 2931.27, 2871.49, 1639.20, 1599.66, 1540.85, 1492.63, 1454.06, 1415.49, 1385.60, 1249.65, 1205.29, 1155.15, 1118.51, 1057.76, 993.16, 904.45, 828.28, 790.67, 762.71, 700.03. **HRMS** (ESI) *m/z* 392.2623 [(M+H)$^+$; calcd for $C_{22}H_{38}NO_3Si$: 392.2621]. **[α]$^{20}_{D}$** +24.7 (c 1.29, $CHCl_3$).

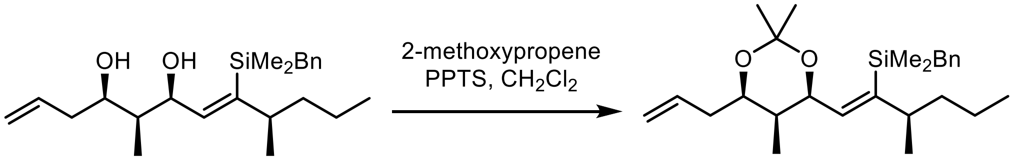


24

To a stirred solution of Weinreb amide **24** (5.29 g, 13.5 mmol) in THF (100 mL) at -78^{o}C under argon atmosphere was added allylmagnesium bromide (40.5 mL, 1.0 M in diethyl ether, 40.5 mmol). The resulting suspension was allowed to warm up to -10^{o}C by transferring the flask to ice/acetone bath. The reaction was allowed to stirred at -10^{o}C for 1 hour before sat. aq. NH_4Cl (200 mL) was added. The organic layer was collected and the aqueous layer was extracted with ether (50 mL x 2). The organic layer was then combined and washed with brine (100 mL x 3), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. The crude β-hydroxyketone was directly used in the next step without further purification.

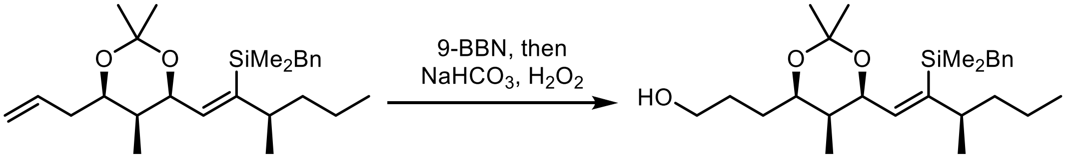


To a stirred solution of crude β-hydroxyketone in dry MeOH (12 mL) and THF (60 mL) at -78^{o}C was added Et_2BOMe (15 mL, 1.0 M in THF, 15 mmol). The resulting solution was stirred at -78^{o}C for 2 hours before solid $NaBH_4$ (1.02 g, 27.0 mmol) was added. The suspension was then stirred at -78^{o}C for 17 hours. Sat. aq. NH_4Cl was added to quench the reaction. The organic layer was collected and aqueous layer extracted with ether (100 mL x 5). The organic layers were combined and washed with brine (100 mL x 3), dried over $Na_2SO_{4,}$ and concentrated *in-vacuo*. The crude product was the dissolved in MeOH (100 mL) and concentrated under reduced pressure. This process was repeated for 5 times to remove boron contaminant. Then hexane (100 mL) was added to the crude product and the resulting mixture was again concentrated to azeotropically remove the residual methanol. Then the crude product was directly used in the next step without further purification.



25

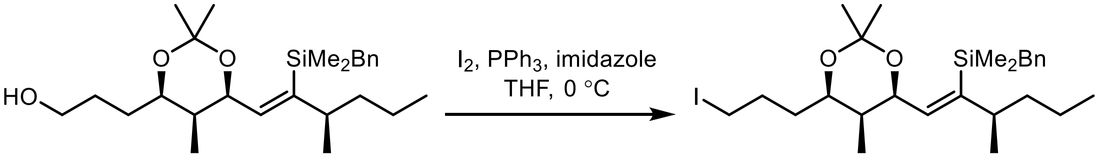
To a stirred solution of crude diol from above in CH_2Cl_2 (150 mL) was added freshly distilled 2-methoxypropene (1.4 mL, 14.6 mmol) and PPTS (340.0 mg, 1.35 mmol). The mixture was stirred at room temperature for 17 hours before NEt_3 (0.5 mL) was added to quench the reaction. The solvent was then removed by rotary evaporation and the residue purified via column chromatography (SiO_2, Hexanes/EtOAc *v/v* 20:1) to afford desired compound **25** (4.02 g, 72% over 3 steps) as a colorless oil. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 7.19 (d, *J* = 7.8 Hz, 2H), 7.11 – 7.04 (m, 1H), 7.00 (d, *J* = 6.8 Hz, 2H), 6.08 (d, *J* = 8.8 Hz, 1H), 5.75 (dddd, *J* = 16.4, 10.3, 7.8, 6.0 Hz, 1H), 5.16 – 5.03 (m, 2H), 4.65 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.90 (td, *J* = 7.0, 2.3 Hz, 1H), 2.29 (ddd, *J* = 13.8, 7.5, 5.8 Hz, 1H), 2.24 (d, *J* = 13.6 Hz, 1H), 2.18 (d, *J* = 13.6 Hz, 2H), 2.10 (dt, *J* = 14.3, 7.0 Hz, 1H), 1.47 (s, 3H), 1.44 (s, 3H), 1.24 (tdd, *J* = 6.8, 4.5, 2.3 Hz, 1H), 1.19 (qq, *J* = 6.4, 2.4 Hz, 2H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.84 (t, *J* = 6.9 Hz, 3H), 0.14 (s, 3H), 0.12 (s, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 146.38, 139.89, 139.82, 134.54, 128.50, 128.31, 124.35, 117.04, 99.13, 73.01, 72.73, 39.58, 38.07, 37.19, 36.57, 30.22, 26.86, 21.38, 21.26, 20.19, 14.41, 5.28, -0.52, -1.28. **FT-IR** (film): ν_{max} (cm^{-1}) 3079.76, 3023.84, 2957.30, 2871.49, 2361.41, 1643.05, 1600.63, 1579.41, 1540.85, 1493.60, 1453.10, 1408.75, 1378.85, 1351.86, 1326.79, 1251.58, 1200.47, 1176.36, 1156.12, 1121.40, 1101.15, 1056.80, 1011.48, 953.63, 934.34, 907.34, 830.21, 789.71, 760.78, 699.07. **HRMS** (ESI) *m/z* 415.3014 [(M+H)$^+$; calcd for $C_{26}H_{43}O_2Si$: 415.3032]. **[α]$^{20}_{D}$** +28.0 (c 1.55, $CHCl_3$).



25 **S9**

To a stirred solution of compound **25** (3.82 g, 9.21 mmol) in THF (60 mL) under argon at 0ºC was added 9-BBN (20 mL, 0.5 M in THF, 10.0 mmol). The reaction was allowed to warm up to room temperature and stirred for 16 hours before sat. $NaHCO_3$ (40 mL) and 30% H_2O_2 (7 mL) were sequentially added. The organic layer was collected and aqueous layer extracted with ether (50 mL x 3). The organic layers were combined and washed with sat. aq. $Na_2S_2O_3$ (40 mL) and brine (40 mL x 3), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 4:1 – 3:1) afforded alcohol **S9** (3.83 g, 96%) as a colorless oil. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 7.20 (t, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 2H), 6.07 (d, *J* = 8.7 Hz, 1H), 4.64 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.85 – 3.81 (m, 1H), 3.64 (dp, *J* = 16.0, 5.4 Hz, 2H), 2.24 (d, *J* = 13.7 Hz, 2H), 2.21 – 2.15 (m, 2H), 1.75 – 1.51 (m, 5H), 1.47 (s, 3H), 1.44 (s, 4H), 1.38 – 1.23 (m, 4H), 1.23 – 1.12 (m, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.84 (t, *J* = 6.8 Hz, 3H), 0.15 (s, 3H), 0.13 (s, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 146.46, 139.86, 139.71, 128.52, 128.31, 124.36, 99.20, 73.59, 72.96, 62.88, 39.59, 38.05, 37.64, 30.17, 30.09, 29.82, 26.87, 21.38, 21.25, 20.15, 14.39, 5.46, -0.52, -1.21. **FT-IR** (film): ν_{max} (cm^{-1}) 3407.60 (br), 3080.73, 3059.51, 3023.84, 2955.38, 2870.52, 2361.41, 1938.11, 1864.83, 1599.66, 1580.38, 1540.85, 1493.60, 1453.10, 1407.78, 1379.82, 1351.86, 1257.36, 1200.47, 1159.01, 1133.94, 1101.15, 1056.80, 1009.55, 976.77, 931.45, 831.17, 789.71, 761.74, 699.07. **HRMS** (ESI) *m/z* 455.2955 [(M+Na)$^+$; calcd for $C_{26}H_{44}O_3NaSi$: 455.2957]. **[α]$^{20}_{D}$** +8.85

(c 0.98, $CHCl_3$).

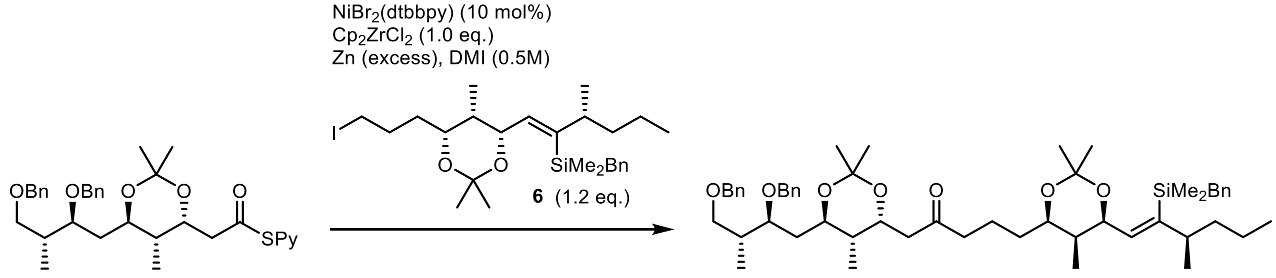


S9

6

To a stirred solution of PPh_3 (2.16 g, 8.23 mmol), imidazole (0.93 g, 13.72 mmol) in THF (40 mL) at 0ºC under argon atmosphere was added I_2 (2.09 g, 8.23 mmol) portion-wise. The resulting suspension was stirred at 0ºC for 1 hour before solution of alcohol **S9** (2.97 g, 6.86 mmol) in THF (10 mL + 5 mL x 2 rinse) was added. The reaction mixture was allowed to warmed up to room temperature and stirred for 1 hour. Then sat. aq. $NaHCO_3$ (100 mL) and sat. aq. $Na_2S_2O_3$ (3 mL) were sequentially added to quench the reaction. The organic layer was collected and aqueous layer extracted with ether (50 mL x 3). The organic layers were combined and washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 30:1) afforded alkyl iodide **6** (3.97 g, 99%) as a colorless oil. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 7.21 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 7.3 Hz, 2H), 6.07 (d, J = 8.7 Hz, 1H), 4.61 (dd, J = 8.8, 2.4 Hz, 1H), 3.80 (ddd, J = 8.6, 4.5, 2.2 Hz, 1H), 3.24 (dt, J = 9.6, 6.7 Hz, 1H), 3.16 (dt, J = 9.5, 7.2 Hz, 1H), 2.24 (d, J = 13.7 Hz, 1H), 2.18 (d, J = 13.6 Hz, 2H), 1.94 (ddt, J = 21.6, 11.6, 5.7 Hz, 1H), 1.84 – 1.72 (m, 1H), 1.60 – 1.52 (m, 1H), 1.44 (s, 3H), 1.42 (s, 3H), 1.39 – 1.25 (m, 3H), 1.23 – 1.14 (m, 2H), 1.12 – 1.06 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H), 0.84 (t, J = 6.9 Hz, 3H), 0.15 (s, 3H), 0.13 (s, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 146.34, 139.85, 128.52, 128.33, 124.41, 99.10, 72.89, 72.23, 39.65, 38.01, 37.30, 33.90, 30.20, 30.01, 26.85, 21.39, 21.27, 20.16, 14.40, 6.89, 5.49, -0.50, -1.17. **FT-IR** (film): ν_{max} (cm^{-1}) 3080.73, 3058.55, 3022.87, 2956.34, 2870.52, 2360.44, 1599.66, 1579.41, 1540.85, 1492.63, 1453.10, 1407.78, 1378.85, 1351.86, 1257.36, 1225.54, 1199.51, 1181.19, 1154.19, 1100.19, 1056.80, 1010.52, 930.49, 830.21, 789.71. 760.78, 699.07. **HRMS** (ESI) *m/z* 543.2144 [(M+H)$^+$; calcd for $C_{26}H_{44}O_2SiI$: 543.2155]. **$[\alpha]^{20}_D$** +12.9 (c 0.67, $CHCl_3$).

(c). Synthesis of the First-Generation Northern Hemisphere (**3a**)

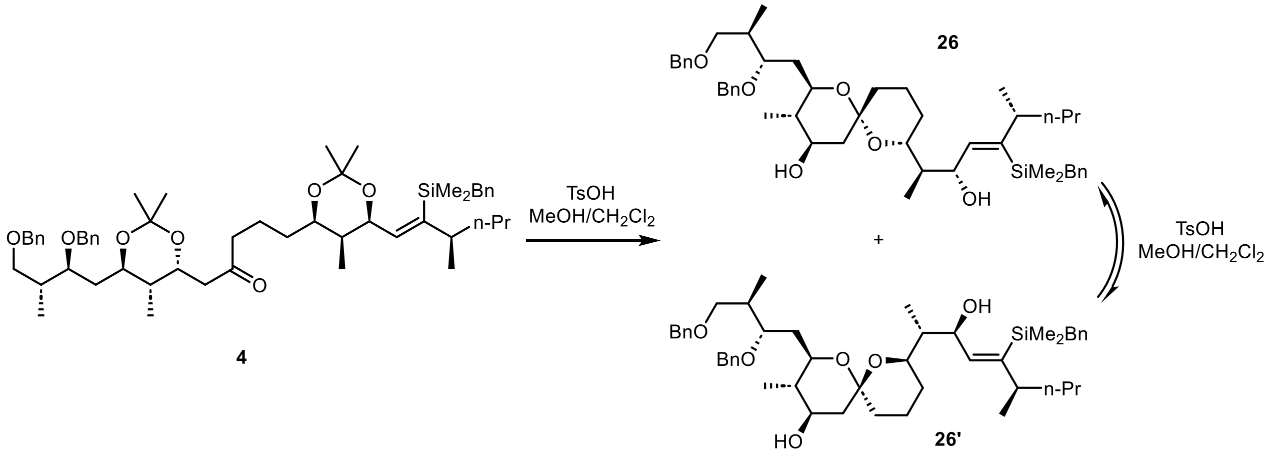


5

4

To an oven-dried 50 mL round bottom flask in a glove box was added thioester **5** (2.42 g, 4.29 mmol), iodide **6** (2.80 g, 5.15 mmol), zinc powder (1.12 g, 17.2 mmol), Cp_2ZrCl_2 (1.26 g, 4.30 mmol), $NiBr_2$(dtbbpy) (209 mg, 0.43 mmol) and DMI (8.5 mL). The flask was sealed with a rubber septum and taken out from the glove box. The reaction was allowed to stir at room temperature under argon for 2.5 hours before sat. aq. $NaHCO_3$ (30 mL) was added. The aqueous layer was extracted with ether (20 mL x 5). The organic layer was combined and washed with sat. NH_4Cl (20 mL x 3). The organic layer was collected and dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 10:1) afforded ketone **4** (2.83 g, 76%) as a colorless oil. **^{1}H-NMR** (500 MHz, acetone-*d6*): δ 7.39 – 7.30 (m, 8H), 7.30 – 7.22 (m, 2H), 7.20 (dd, *J* = 8.3, 7.1 Hz, 2H), 7.06 (d, *J* = 7.2 Hz, 3H), 6.08 (d, *J* = 8.6 Hz, 1H), 4.72 (dd, *J* = 8.7, 2.4 Hz, 1H), 4.58 (d, *J* = 11.7 Hz, 1H), 4.48 (s, 2H), 4.45 (d, *J* = 11.7 Hz, 1H), 4.37 (dt, *J* = 9.4, 4.7 Hz, 1H), 3.94 (ddd, *J* = 7.7, 5.1, 2.3 Hz, 1H), 3.58 (td, *J* = 9.6, 9.1, 5.5 Hz, 2H), 3.42 (td, *J* = 9.1, 8.3, 5.4 Hz, 2H), 2.81 – 2.72 (m, 2H), 2.60 (dd, *J* = 16.1, 9.3 Hz, 1H), 2.50 (t, *J* = 7.2 Hz, 2H), 2.37 – 2.32 (m, 1H), 2.32 – 2.24 (m, 2H), 2.24 – 2.14 (m, 2H), 1.87 (ddd, *J* = 14.6, 6.0, 3.7 Hz, 1H), 1.83 – 1.75 (m, 1H), 1.72 (td, *J* = 7.4, 5.4 Hz, 1H), 1.65 – 1.49 (m, 2H), 1.47 (s, 3H), 1.46 – 1.39 (m, 1H), 1.38 – 1.34 (m, 1H), 1.33 (s, 3H), 1.30 (dt, *J* = 11.6, 4.1 Hz, 4H), 1.28 (s, 3H), 1.23 (s, 3H), 1.18 (ddt, *J* = 17.1, 9.7, 3.9 Hz, 2H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 5.7 Hz, 4H), 0.84 (t, *J* = 6.9 Hz, 3H), 0.78 (d, *J* = 6.9 Hz, 3H), 0.17 (s, 3H), 0.16 (s, 3H). **^{13}C-NMR** (126 MHz, acetone-*d6*): δ 208.78, 206.26, 146.23, 141.26, 140.87, 140.55, 140.21, 129.44, 129.20, 129.11, 129.09, 128.66, 128.49, 128.27, 128.17, 125.17, 101.17, 99.51, 78.99, 73.74, 73.65, 73.60, 73.21, 72.97, 71.67, 66.56, 44.56, 43.79, 40.78, 40.44, 38.47, 37.72, 37.49, 36.46, 34.99, 33.04, 32.46, 27.32, 25.53, 24.31, 23.13, 22.09, 21.82, 20.66, 20.51, 14.70, 14.43, 14.25, 12.63, 5.86, -0.24, -0.99. **FT-IR** (film): v_{max} (cm^{-1}) 3061.44, 3026.73, 2956.34, 2933.20, 2872.45, 2360.44, 2341.16, 1945.82, 1868.68, 1806.97, 1715.37, 1599.66, 1540.85, 1493.60, 1454.06, 1406.82, 1378.85, 1309.43, 1250.61, 1229.40, 1201.43, 1159.97, 1099.23, 1068.37, 1028.84, 1008.59, 932.41, 908.31, 831.17, 789.71, 735.71, 698.10. **HRMS** (ESI) *m/z* 886.6602 [$(M+NH_4)^+$; $C_{54}H_{84}NO_7Si$: 886.6017]. **$[\alpha]^{20}_{D}$** +19.7

(c 0.15, $CHCl_3$).

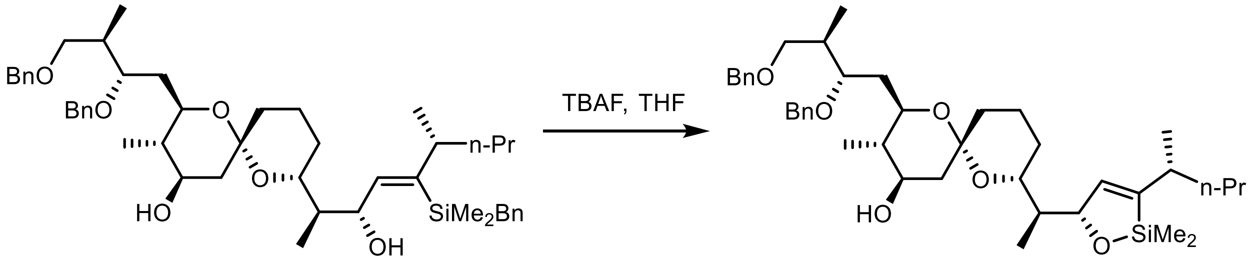


To a stirred solution of ketone **4** (2.83 g, 3.25 mmol) in CH_2Cl_2 (10 mL) and MeOH (20 mL) was added *p*-TsOH·H_2O (114.0 mg, 0.6 mmol). The mixture was allowed to stir at room temperature for 1.5 hours before NEt_3 (0.5 mL) was added to quench the reaction. The solution was concentrated under reduced pressure and purified by flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 5:1) to give desired spiroketal **26** and its epimer **26'**. Epimer **26'** was re-subjected to the same acidic condition to give a mixture **26** and **26'**, which upon chromatography purification (SiO_2, Hexanes/EtOAc *v/v* 6:1) to harvest more **26**. After 3 cycles of equilibration/chromatography purification, desired spiroketal **26** was obtained (1.59 g, 67% after 3 cycles) as a thick, colorless gum.

26: **^{1}H-NMR** ^{1}H NMR (600 MHz, C_6D_6) δ 7.40 – 7.34 (m, 4H), 7.24 – 7.17 (m, 4H), 7.14 – 7.08 (m, 4H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.35 (d, *J* = 8.8 Hz, 1H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.56 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.42 – 4.39 (m, 1H), 4.40 – 4.34 (m, 2H), 3.90 (ddd, *J* = 10.7, 8.4, 2.8 Hz, 1H), 3.84 (dt, *J* = 6.6, 4.7 Hz, 1H), 3.41 (dd, *J* = 9.0, 6.3 Hz, 1H), 2.56 (s, 1H), 2.50 (dd, *J* = 13.1, 4.5 Hz, 1H), 2.40 (qd, *J* = 6.6, 4.6 Hz, 1H), 2.32 (d, *J* = 13.5 Hz, 1H), 2.26 (d, *J* = 13.6 Hz, 1H), 2.25 – 2.20 (m, 1H), 2.00 (ddd, *J* = 14.5, 6.7, 2.7 Hz, 1H), 1.83 (ddd, *J* = 14.0, 8.4, 4.9 Hz, 1H), 1.61 – 1.52 (m, 2H), 1.51 – 1.44 (m, 3H), 1.41 – 1.19 (m, 9H), 1.17 (d, *J* = 7.0 Hz, 3H), 1.14 (d, *J* = 6.9 Hz, 3H), 1.08 (dd, *J* = 13.1, 11.4 Hz, 2H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.99 (d, *J* = 6.4 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 4H), 0.25 (s, 3H), 0.20 (s, 3H). **^{13}C-NMR** *(*151 MHz, C_6D_6) δ 142.43, 128.89, 128.57, 128.51, 128.43, 128.35, 127.98, 127.85, 127.46, 127.40, 124.64, 78.92, 77.66, 73.91, 73.16, 72.63, 72.62, 71.49, 69.66, 44.62, 43.76, 39.97, 38.25, 37.90, 36.94, 36.09, 34.66, 28.44, 27.48, 21.87, 21.37, 20.10, 14.60, 13.22, 7.33. **FT-IR** (film): ν_{max} (cm^{-1}) 3436.53 (br), 3061.44, 3026.73, 2956.34, 2928.38, 2871.45, 2359.48, 1944.86, 1868.68, 1806.01, 1740.44, 1599.66, 1540.85, 1493.60, 1454.06, 1375.00, 1305.57, 1249.65, 1206.26, 1176.36, 1156.12, 1092.48, 1027.87, 985.45, 953.63, 906.38, 829.24, 790.67, 734.75, 698.11. **HRMS** (ESI) *m/z*

793.4839 [(M+Na)$^+$; calcd for $C_{48}H_{70}O_6NaSi$: 793.4839]. **[α]^{20}$_D$** -1.81 (c 0.55, $CHCl_3$).

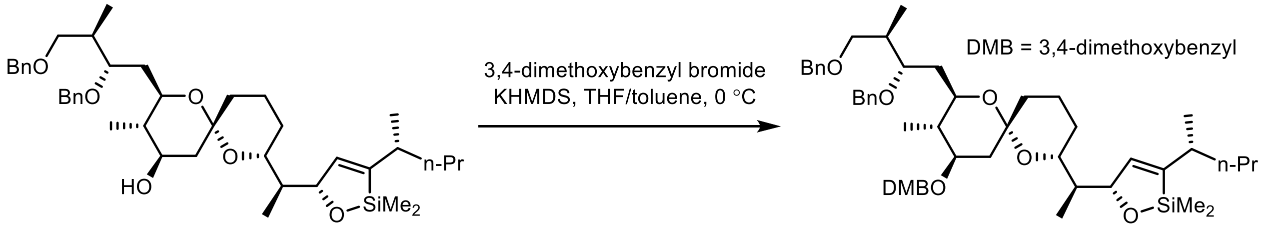
26': **^{1}H-NMR** (600 MHz, C_6D_6): δ 7.42 – 7.36 (m, 2H), 7.31 – 7.27 (m, 2H), 7.24 – 7.19 (m, 3H), 7.13 – 7.07 (m, 4H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.44 (d, *J* = 8.9 Hz, 1H), 4.82 (dd, *J* = 9.0, 2.1 Hz, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.42 – 4.38 (m, 1H), 4.35 (s, 2H), 3.81 (dt, *J* = 8.1, 4.4 Hz, 1H), 3.68 (dd, *J* = 9.0, 5.5 Hz, 1H), 3.48 (dd, *J* = 9.0, 6.1 Hz, 1H), 3.14 – 3.05 (m, 2H), 2.39 (d, *J* = 13.5 Hz, 1H), 2.34 (p, *J* = 6.1 Hz, 1H), 2.27 (d, *J* = 13.4 Hz, 1H), 2.21 (q, *J* = 6.7 Hz, 1H), 2.03 (ddd, *J* = 14.4, 7.6, 2.6 Hz, 1H), 1.88 – 1.81 (m, 2H), 1.68 (dt, *J* = 13.1, 3.9 Hz, 1H), 1.63 (dt, *J* = 13.8, 3.1 Hz, 1H), 1.56 (dq, *J* = 9.8, 3.4 Hz, 1H), 1.51 – 1.24 (m, 11H), 1.23 (d, *J* = 6.9 Hz, 4H), 1.20 (d, *J* = 7.1 Hz, 4H), 1.02 (d, *J* = 6.7 Hz, 3H), 1.00 – 0.94 (m, 2H), 0.90 – 0.86 (m, 6H), 0.22 (s, 6H). **^{13}C-NMR** (150 MHz, C_6D_6): δ 142.91, 128.91, 128.55, 128.54, 128.51, 128.35, 127.98, 127.92, 127.68, 127.60, 124.58, 79.19, 79.17, 74.95, 74.53, 73.39, 73.38, 72.56, 71.84, 70.69, 45.99, 44.70, 43.77, 39.96, 37.91, 37.20, 34.96, 30.22, 29.86, 28.58, 27.37, 21.82, 21.39, 19.06, 15.25, 14.62, 13.63, 7.35, 7.32. **FT-IR** (film): ν_{max} (cm^{-1}) 3434.6, 3026.73, 2955.38, 2926.45, 1599.66, 1493.6, 1454.06, 1376.93, 1248.68, 1205.29, 1095.37, 1057.76, 1027.87, 986.41, 904.45, 829.24, 789.71, 734.75, 698.10. **HRMS** (ESI) *m/z* 793.4854 [(M+Na)$^+$; calcd for $C_{48}H_{70}O_6NaSi$: 793.4839]. **[α]^{20}$_D$** -3.91 (c 2.42, $CHCl_3$).



26 **S10**

To a stirred solution of spiroketal **26** (5.30 g, 6.87 mmol) in THF (50 mL) was added TBAF (1.4 mL, 1.0 M in THF, 1.4 mmol). The reaction mixture was stirred for 15 minutes before sat. aq. NH_4Cl (50 mL) was added. The organic layer was collected and aqueous layer extracted with ether (20 mL x 4). The organic layers were combined and washed with brine (50 mL x 2), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 4:1) afforded siloxane **S10** (4.50 g, 96%) as a colorless gum. **^{1}H-NMR** (500 MHz, C_6D_6): *δ* 7.38 (d, *J* = 7.1 Hz, 2H), 7.34 (d, *J* = 7.1 Hz, 2H), 7.20 (td, *J* = 7.7, 1.7 Hz, 4H), 7.13 – 7.08 (m, 2H), 6.04 (s, 1H), 4.89 (s, 1H), 4.61 (d, *J* = 11.7 Hz, 1H), 4.42 (d, *J* = 11.6 Hz, 1H), 4.38 (s, 2H), 4.09 (ddd, *J* = 10.5, 8.9, 2.6 Hz, 1H), 3.90 (dt, *J* = 7.1, 4.6 Hz, 1H), 3.70 (dd, *J* = 9.0, 5.6 Hz, 1H), 3.61 (ddd, *J* = 10.5, 7.7, 2.3 Hz, 1H), 3.51 (dt, *J* = 10.8, 5.6 Hz, 1H), 3.46 (dd, *J* = 9.0, 6.6 Hz, 1H), 2.48 (dq, *J* = 11.9, 6.3 Hz, 1H), 2.45 – 2.37 (m, 2H), 2.03 (ddd, *J* = 14.3, 7.0, 2.8 Hz, 1H), 1.88 (ddd, *J* = 14.1, 8.8, 4.8 Hz, 1H), 1.81 – 1.74 (m, 1H), 1.67

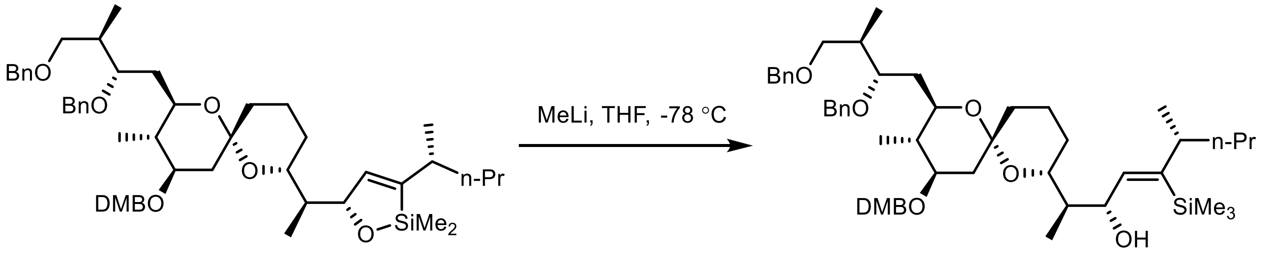
(qd, *J* = 7.1, 2.6 Hz, 1H), 1.64 – 1.57 (m, 2H), 1.53 (d, *J* = 13.3 Hz, 1H), 1.45 – 1.31 (m, 2H), 1.31 – 1.22 (m, 6H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.9 Hz, 3H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.93 – 0.86 (m, 5H), 0.71 (d, *J* = 5.3 Hz, 1H), 0.32 (s, 3H), 0.26 (s, 3H). **^{13}C-NMR** (126 MHz, C_6D_6): δ 148.71, 144.69, 140.17, 139.75, 128.49, 128.42, 127.97, 127.47, 127.38, 98.64, 81.33, 79.11, 75.36, 73.19, 72.75, 71.88, 71.52, 69.84, 44.65, 44.23, 40.30, 38.35, 36.97, 36.92, 36.30, 34.67, 28.77, 22.73, 22.23, 21.11, 20.48, 14.87, 14.32, 14.28, 13.39, 10.35, 1.97, 1.72. **FT-IR** (film): v_{max} (cm^{-1}) 3449.06 (br), 3087.48, 3063.37, 3029.62, 2957.30, 2928.38, 2870.52, 2359.48, 2341.16, 1944.86, 1868.68, 1805.05, 1595.81, 1540.85, 1496.49, 1454.06, 1372.10, 1304.61, 1249.65, 1222.65, 1176.36, 1106.94, 1015.34, 993.16, 971.95, 916.02, 893.84, 863.95, 823.45, 783.92, 734.75, 697.14, 633.50. **HRMS** (ESI) *m/z* 701.4231 [$(M+Na)^+$; calcd for $C_{41}H_{62}O_6NaSi$: 701.4213]. **$[\alpha]^{20}_{D}$** -24.0 (c 1.47, $CHCl_3$).



S10 **S11**

To a stirred solution of siloxane **S10** (4.50 g, 6.63 mmol) in THF (40 mL) at -20°C under argon atmosphere was added KHMDS (25 mL, 0.5 M in toluene, 12.5 mmol). The reaction mixture was stirred for 5 minutes and 3,4-dimethoxybenzyl bromide (1.68 g, 7.29 mmol) was added. The reaction was allowed to warm-up to 0°C and stirred for 15 minutes before sat. aq. NH_4Cl (50 mL) was added. The organic layer was collected and aqueous layer extracted with ether (20 mL x 4). The organic layers were combined and washed with brine (50 mL x 2), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 6:1) afforded compound **S11** (5.20 g, 92%) as a colorless gum. **^{1}H-NMR** (500 MHz, C_6D_6): δ 7.41 – 7.36 (m, 2H), 7.36 – 7.31 (m, 2H), 7.20 (td, *J* = 7.6, 1.6 Hz, 4H), 7.12 (dd, *J* = 7.9, 6.1 Hz, 2H), 7.01 (dd, *J* = 4.2, 2.4 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.05 (s, 1H), 4.90 (s, 1H), 4.66 (d, *J* = 11.4 Hz, 1H), 4.63 (d, *J* = 11.7 Hz, 1H), 4.49 (d, *J* = 11.4 Hz, 1H), 4.42 (d, *J* = 11.6 Hz, 1H), 4.38 (s, 2H), 4.19 (td, *J* = 9.6, 8.9, 2.7 Hz, 1H), 3.92 (dt, *J* = 6.9, 4.5 Hz, 1H), 3.71 (dd, *J* = 9.0, 5.5 Hz, 1H), 3.69 – 3.62 (m, 1H), 3.57 (td, *J* = 10.7, 4.2 Hz, 1H), 3.50 (s, 3H), 3.46 (s, 4H), 2.83 (dd, *J* = 12.9, 4.3 Hz, 1H), 2.49 (p, *J* = 6.0 Hz, 1H), 2.41 (q, *J* = 6.4 Hz, 1H), 2.07 (ddd, *J* = 14.4, 7.1, 2.7 Hz, 1H), 1.94 (ddd, *J* = 14.0, 8.9, 4.8 Hz, 1H), 1.82 – 1.73 (m, 2H), 1.68 (ddd, *J* = 13.8, 7.1, 3.4 Hz, 3H), 1.57 (d, *J* = 13.2 Hz, 1H), 1.46 (d, *J* = 5.4 Hz, 1H), 1.27 (ddd, *J* = 11.7, 6.1, 2.9 Hz, 7H), 1.22 (d, *J* = 6.9 Hz, 3H), 1.13 (d, *J* = 6.4 Hz, 3H), 1.10 (d, *J* = 6.7 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.93 – 0.88 (m, 3H), 0.88 – 0.81 (m, 4H), 0.36 (s, 3H), 0.25 (s, 3H). **^{13}C-NMR** (126 MHz,

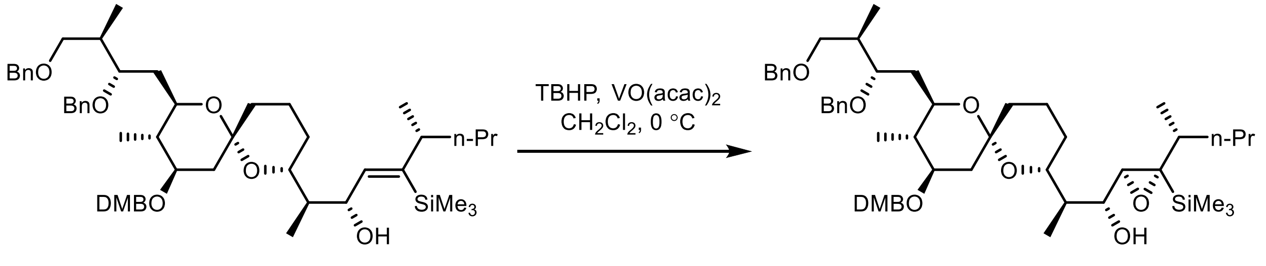
C_6D_6): δ 150.42, 149.89, 148.71, 144.75, 140.16, 139.75, 132.47, 128.49, 128.41, 127.97, 127.47, 127.37, 120.56, 112.60, 112.17, 98.80, 81.37, 79.19, 77.77, 75.63, 73.18, 72.72, 72.26, 71.55, 71.31, 55.71, 55.65, 44.14, 43.03, 40.31, 37.00, 36.92, 36.27, 34.85, 34.54, 28.67, 22.79, 22.73, 22.23, 21.12, 20.50, 19.62, 14.94, 14.32, 13.75, 10.46, 1.97, 1.72. **FT-IR** (film): ν_{max} (cm^{-1}) 3063.37, 3029.62, 2956.34, 2930.31, 2869.56, 1592.91, 1515.78, 1454.06, 1419.35, 1371.14, 1306.54, 1263.15, 1178.29, 1156.12, 1137.80, 1071.26, 1028.84, 1015.34, 971.95, 916.02, 892.88, 862.03, 822.49, 782.96, 765.60, 735.71, 697.14. **HRMS** (ESI) *m/z* 851.4899 [$(M+Na)^+$; calcd for $C_{50}H_{72}O_8NaSi$: 851.4894]. **$[\alpha]^{20}_{D}$** -21.9 (c 0.84, $CHCl_3$).



S11 **27**

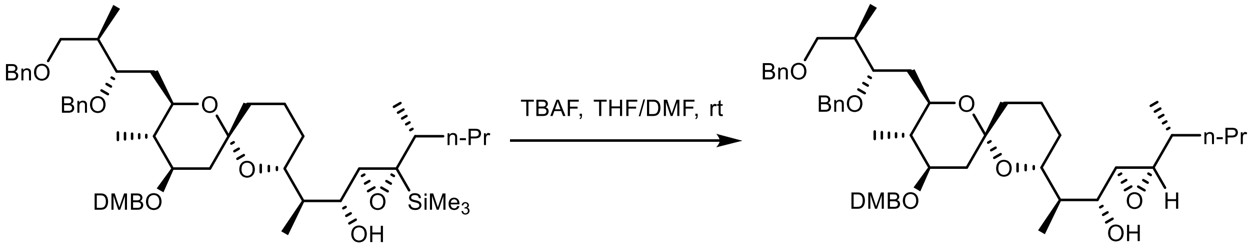
To a stirred solution of compound **S11** (5.20 g, 6.27 mmol) in THF (60 mL) at -78°C under argon atmosphere was added MeLi (4.0 mL, 3.1 M in dimethoxyethane, 12.3 mmol). The resulting mixture was stirred at -78°C for 45 minutes before sat. aq. NH_4Cl (20 mL) was added. The organic layer was collected and aqueous layer extracted with ether (20 mL x 4). The organic layers were combined and washed with brine (20 mL x 2), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 6:1) afforded alcohol **27** (5.40 g, quant.) as a colorless gum. **^{1}H-NMR** (500 MHz, C_6D_6): δ 7.42 – 7.34 (m, 4H), 7.21 (q, *J* = 7.5 Hz, 4H), 7.11 (q, *J* = 7.2 Hz, 2H), 7.06 – 7.01 (m, 2H), 6.70 (d, *J* = 8.6 Hz, 1H), 6.33 (d, *J* = 8.6 Hz, 1H), 4.79 – 4.75 (m, 1H), 4.71 (d, *J* = 11.3 Hz, 1H), 4.61 (d, *J* = 11.7 Hz, 1H), 4.55 (d, *J* = 11.3 Hz, 1H), 4.40 (d, *J* = 11.7 Hz, 1H), 4.38 (d, *J* = 4.1 Hz, 2H), 4.02 (ddd, *J* = 10.8, 8.6, 2.7 Hz, 1H), 3.87 (dt, *J* = 6.6, 4.6 Hz, 1H), 3.76 (dt, *J* = 9.0, 4.5 Hz, 1H), 3.65 (dd, *J* = 9.0, 5.8 Hz, 1H), 3.59 (td, *J* = 10.6, 4.2 Hz, 1H), 3.53 (s, 3H), 3.45 (s, 3H), 3.42 (td, *J* = 6.4, 3.6 Hz, 1H), 2.84 (dd, *J* = 13.0, 4.3 Hz, 1H), 2.51 (d, *J* = 2.1 Hz, 1H), 2.47 – 2.38 (m, 1H), 2.31 (q, *J* = 6.7 Hz, 1H), 2.06 (ddd, *J* = 14.4, 6.9, 2.7 Hz, 1H), 1.89 (ddd, *J* = 14.0, 8.5, 4.9 Hz, 1H), 1.75 (ddt, *J* = 16.5, 10.1, 6.4 Hz, 1H), 1.62 (dq, *J* = 9.1, 5.2, 3.7 Hz, 3H), 1.58 – 1.46 (m, 2H), 1.43 – 1.24 (m, 8H), 1.18 (d, *J* = 7.1 Hz, 3H), 1.17 (s, 3H), 1.15 (d, *J* = 6.0 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.28 (s, 9H). **^{13}C-NMR** (126 MHz, C_6D_6): δ 150.38, 149.94, 147.19, 141.72, 140.07, 139.72, 132.25, 128.50, 128.42, 127.97, 127.46, 127.37, 120.55, 112.69, 112.30, 99.35, 79.04, 77.59, 77.46, 73.64, 73.17, 72.92, 72.65, 71.55, 71.46, 55.78, 55.73, 44.28, 42.95, 39.89, 38.19, 37.01, 36.05, 34.87, 34.57, 28.57, 22.02, 21.32, 20.13, 14.70, 14.57, 13.63, 7.60, 1.39. **FT-IR** (film): ν_{max} (cm^-

^{1}) 3510.77 (br), 3087.48, 3063.37, 3029.62, 2955.38, 2870.52, 2359.48, 2341.16, 1946.19, 1869.65, 1808.90, 1607.38, 1592.91, 1515.78, 1497.45, 1454.06, 1418.39, 1363.43, 1307.50, 1263.15, 1248.68, 1211.08, 1178.29, 1157.08, 1137.80, 1072.23, 1028.84, 988.34, 956.52, 912.16, 838.88, 808.99, 735.71, 698.11. **HRMS** (ESI) *m/z* 867.5194 [(M+Na)$^+$; calcd for $C_{51}H_{76}O_8NaSi$: 867.5207]. **[α]^{20}$_D$** -9.67 (c 1.23, $CHCl_3$).



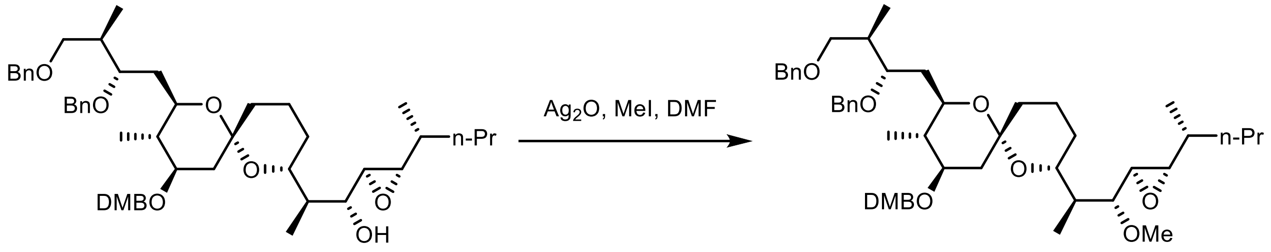
27 **28**

To a stirred solution of compound **27** (5.20 g, 6.15 mmol) and VO(acac)$_2$ (82.2 mg, 0.31 mmol) in CH_2Cl_2 (60 mL) at 0°C under argon atmosphere was added TBHP (2.3 mL, 5.5 M in decane, 12.3 mmol). The reaction was stirred at 0°C for 20 hours before the solvent was removed under reduced pressure. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 5:1) afforded epoxy alcohol **28** (4.60 g, 83%) as a colorless gum. **^{1}H-NMR** (500 MHz, C_6D_6): δ 7.41 – 7.36 (m, 2H), 7.36 – 7.32 (m, 2H), 7.20 (td, *J* = 7.5, 3.3 Hz, 4H), 7.14 – 7.07 (m, 2H), 7.03 – 6.98 (m, 2H), 6.73 (d, *J* = 8.6 Hz, 1H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.48 (d, *J* = 11.5 Hz, 1H), 4.42 (d, *J* = 5.1 Hz, 1H), 4.40 – 4.34 (m, 2H), 4.08 (ddd, *J* = 10.7, 8.3, 2.8 Hz, 1H), 3.89 (dt, *J* = 6.5, 4.8 Hz, 1H), 3.85 (d, *J* = 7.5 Hz, 1H), 3.73 – 3.68 (m, 1H), 3.66 (dd, *J* = 9.0, 5.7 Hz, 1H), 3.56 (dd, *J* = 10.3, 4.2 Hz, 1H), 3.53 (s, 3H), 3.46 (s, 3H), 3.42 (dd, *J* = 9.0, 6.5 Hz, 1H), 3.12 (d, *J* = 7.6 Hz, 1H), 2.82 (dd, *J* = 13.0, 4.2 Hz, 1H), 2.47 – 2.39 (m, 1H), 2.37 (d, *J* = 2.7 Hz, 1H), 2.04 (ddd, *J* = 14.5, 6.6, 2.8 Hz, 1H), 1.91 (ddd, *J* = 14.1, 8.3, 5.0 Hz, 1H), 1.82 – 1.72 (m, 3H), 1.67 – 1.61 (m, 2H), 1.53 (dd, *J* = 10.1, 6.6 Hz, 2H), 1.50 – 1.23 (m, 10H), 1.17 (d, *J* = 6.9 Hz, 3H), 1.13 (d, *J* = 6.5 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 7H), 0.17 (s, 9H). **^{13}C-NMR** (126 MHz, C_6D_6): δ 150.38, 149.95, 140.07, 139.65, 132.14, 128.51, 128.43, 127.98, 127.51, 127.39, 120.80, 112.69, 112.21, 99.24, 78.99, 76.65, 75.91, 73.23, 72.72, 72.67, 71.54, 71.46, 71.03, 63.33, 60.68, 55.74, 55.71, 42.89, 42.33, 37.37, 37.00, 36.11, 34.82, 34.49, 33.05, 28.60, 21.74, 20.24, 18.78, 14.69, 14.57, 14.28, 13.69, 9.25, -0.23. **FT-IR** (film): ν_{max} (cm^{-1}) 3480.88 (br), 3087.48, 3063.37, 3029.62, 2957.30, 2870.52, 2360.44, 1947.75, 1871.58, 1808.90, 1683.55, 1606.41, 1592.91, 1515.78, 1497.45, 1455.03, 1419.35, 1362.46, 1306.54, 1262.18, 1180.22, 1156.12, 1137.80, 1072.23, 1028.84, 955.56, 916.99, 840.81, 808.99, 736.674, 698.11, 642.18. **HRMS** (ESI) *m/z* 861.5345 [(M+H)$^+$; calcd for $C_{51}H_{77}O_9Si$: 861.5337]. **[α]^{20}$_D$** -0.36 (c 1.07, $CHCl_3$).



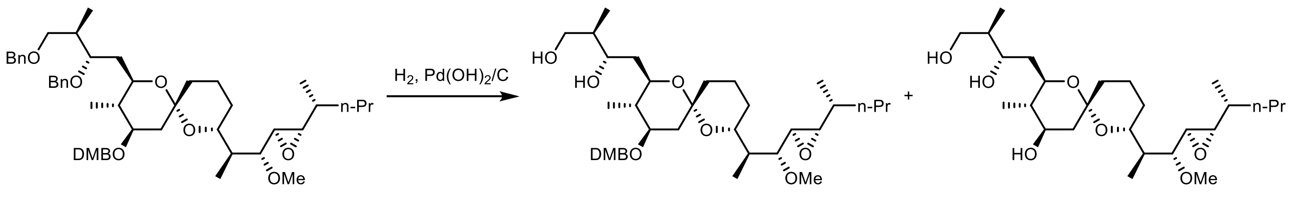
28 **29**

To a stirred solution of epoxy alcohol **28** (4.60 g, 5.34 mmol) in DMF (40 mL) was added TBAF (21 mL, 1,0 M in THF, 21.4 mmol). The reaction was stirred at room temperature for 70 hours before sat. aq. NH_4Cl (200 mL) was added to dilute the reaction mixture. The aqueous layer was extracted with ether (50 mL x 5). The organic layers were combined, diluted with hexanes (100 mL) and washed with sat. aq. NH_4Cl (100 mL x 3). The organic phase was then dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 4:1) afforded compound **29** (4.05 g, 96%) as a colorless gum. **^{1}H-NMR** (500 MHz, C_6D_6): δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 4H), 7.11 (q, *J* = 7.2 Hz, 2H), 6.98 (d, *J* = 6.3 Hz, 2H), 6.72 (d, *J* = 8.6 Hz, 1H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.61 (d, *J* = 11.7 Hz, 1H), 4.47 (d, *J* = 11.7 Hz, 1H), 4.40 (d, *J* = 11.6 Hz, 1H), 4.38 (s, 2H), 4.04 (td, *J* = 9.5, 8.6, 2.5 Hz, 1H), 3.90 – 3.85 (m, 1H), 3.68 (dt, *J* = 8.2, 4.3 Hz, 2H), 3.54 (s, 3H), 3.53 – 3.49 (m, 2H), 3.48 (s, 3H), 3.47 – 3.42 (m, 1H), 2.82 (dd, *J* = 3.8, 2.3 Hz, 1H), 2.76 (dd, *J* = 12.9, 4.3 Hz, 1H), 2.60 (dd, *J* = 7.1, 2.2 Hz, 1H), 2.44 (p, *J* = 6.2 Hz, 1H), 2.25 (d, *J* = 5.7 Hz, 1H), 2.05 (ddd, *J* = 9.9, 7.5, 4.0 Hz, 1H), 1.90 (ddd, *J* = 14.1, 8.8, 4.7 Hz, 1H), 1.75 (dt, *J* = 10.2, 5.0 Hz, 1H), 1.61 (d, *J* = 12.7 Hz, 3H), 1.55 – 1.45 (m, 1H), 1.43 – 1.21 (m, 10H), 1.20 (d, *J* = 6.9 Hz, 4H), 1.15 (d, *J* = 6.9 Hz, 3H), 1.11 (d, *J* = 6.4 Hz, 3H), 0.98 (d, *J* = 6.3 Hz, 3H), 0.82 (t, *J* = 7.0 Hz, 3H). **^{13}C-NMR** (126 MHz, C_6D_6): δ 150.36, 149.97, 140.08, 139.68, 132.05, 128.51, 128.44, 127.97, 127.50, 127.41, 120.81, 112.77, 112.17, 99.03, 79.13, 76.30, 75.40, 73.22, 72.65, 72.47, 71.75, 71.55, 70.88, 60.32, 60.06, 55.78, 55.72, 43.22, 42.99, 36.98, 36.14, 35.62, 34.76, 34.50, 31.96, 28.32, 23.05, 20.65, 20.19, 17.27, 14.92, 14.49, 14.35, 13.66, 9.42. **FT-IR** (film): ν_{max} (cm^{-1}) 3483.78 (br), 3086.51, 3062.41, 3029.62, 2957.30, 2871.49, 2359.48, 1951.61, 1871.58, 1808.90, 1737.55, 1606.41, 1592.91, 1515.78, 1497.45, 1455.03, 1419.35, 1362.46, 1307.50, 1264.11, 1239.04, 1179.26, 1156.12, 1137.80, 1071.26, 1028.84, 957.48, 904.45, 855.28, 808.03, 765.60, 736.67, 699.07. **HRMS** (ESI) *m/z* 811.4745 $[(M+Na)^+]$; calcd for $C_{48}H_{68}O_9Na$: 811.4761]. **$[\alpha]^{20}_D$** -5.59 (c 1.29, $CHCl_3$).



29 **30**

To a stirred solution of epoxy alcohol **29** (670 mg, 0.88 mmol) in DMF (2.0 mL) under argon atmosphere was added Ag_2O (2.38 g, 10.5 mmol) and MeI (0.82 mL, 13.2 mmol). The flask was wrapped with aluminum foil and stirred at room temperature for 72 hours. Ether (10 mL) was added and the mixture was filtered through a thin pad of celite. The filtrate was then washed with sat. aq. NH_4Cl (5 mL x 3), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 7:1) afforded alcohol **30** (599.0 mg, 84%) as a colorless gum. **^{1}H-NMR** (500 MHz, C_6D_6): δ 7.37 (d, *J* = 7.4 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 4H), 7.11 (q, *J* = 7.4 Hz, 2H), 7.04 (d, *J* = 6.0 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 1H), 5.01 (dd, *J* = 6.0, 4.5 Hz, 1H), 4.73 (d, *J* = 11.5 Hz, 1H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.53 (d, *J* = 11.5 Hz, 1H), 4.41 (d, *J* = 11.6 Hz, 1H), 4.38 (s, 2H), 4.07 (ddd, *J* = 10.8, 8.6, 2.6 Hz, 1H), 3.88 (dt, *J* = 6.8, 4.5 Hz, 1H), 3.71 – 3.65 (m, 2H), 3.57 (dt, *J* = 10.4, 5.2 Hz, 1H), 3.53 (s, 3H), 3.50 – 3.44 (m, 5H), 3.34 (s, 3H), 3.16 (dd, *J* = 6.0, 2.1 Hz, 1H), 2.80 (dd, *J* = 12.9, 4.3 Hz, 1H), 2.61 (dd, *J* = 6.9, 2.1 Hz, 1H), 2.46 – 2.37 (m, 1H), 2.06 (ddd, *J* = 14.6, 6.9, 2.7 Hz, 1H), 1.97 – 1.87 (m, 2H), 1.76 (tt, *J* = 10.2, 4.9 Hz, 1H), 1.60 (q, *J* = 4.9 Hz, 2H), 1.54 – 1.45 (m, 2H), 1.45 – 1.31 (m, 2H), 1.31 – 1.22 (m, 6H), 1.20 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 7.0 Hz, 3H), 1.13 (d, *J* = 6.3 Hz, 3H), 1.10 – 1.02 (m, 1H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.82 (t, *J* = 7.0 Hz, 3H). **^{13}C-NMR** (126 MHz, C_6D_6): δ 156.15, 150.45, 149.93, 140.08, 139.68, 132.25, 128.51, 128.43, 127.97, 127.76, 127.51, 127.40, 120.65, 112.48, 112.23, 99.06, 79.12, 78.86, 76.92, 73.23, 73.09, 72.69, 72.52, 71.57, 70.94, 61.49, 58.10, 55.72, 55.67, 54.50, 53.32, 42.78, 41.57, 37.08, 35.94, 35.91, 35.63, 34.84, 34.65, 28.53, 20.47, 20.03, 16.98, 14.88, 14.49, 13.71, 10.70. **FT-IR** (film): ν_{max} (cm^{-1}) 3087.48, 3062.41, 3029.62, 2957.30, 2871.49, 2359.48, 2341.16, 2065.39, 1868.68, 1809.87, 1749.12, 1716.34, 1683.55, 1606.41, 1592.91, 1515.78, 1497.45, 1455.03, 1419.35, 1360.53, 1306.54, 1264.11, 1239.04, 1195.65, 1180.22, 1156.12, 1136.83, 1070.30, 1028.84, 1014.37, 957.48, 904.45, 854.31, 806.10, 765.60, 736.67, 698.11. **HRMS** (ESI) *m/z* 803.5110 [$(M+H)^+$; calcd for $C_{49}H_{71}O_9$: 803.5098]. **$[\alpha]^{20}_D$** -5.68 (c 1.20, $CHCl_3$).

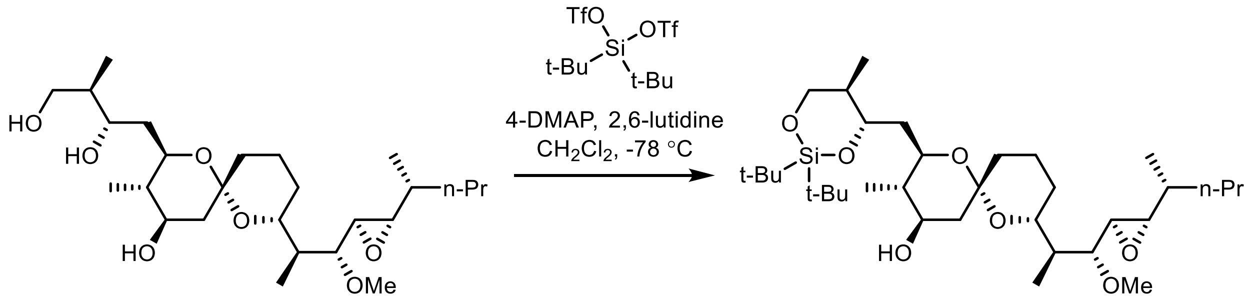


30 **31** **S12**

To a stirred solution of compound **30** (40 mg, 0.052 mmol) in EtOAc (0.5 mL) under argon atmosphere was added $Pd(OH)_2/C$ (9.0 mg). The resulting suspension was evacuated and purged with H_2 for 3 times. The reaction was allowed to stir at room temperature for 45 minutes before the mixture was filtered through a pad of celite. The filter cake was then washed with ether (10 mL x 3) and the filtrate was concentrated under reduced pressure. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 1:1) afforded diol **31** (20.1 mg, 62%) and triol **S12** (7.1 mg, 29%) as colorless gum.

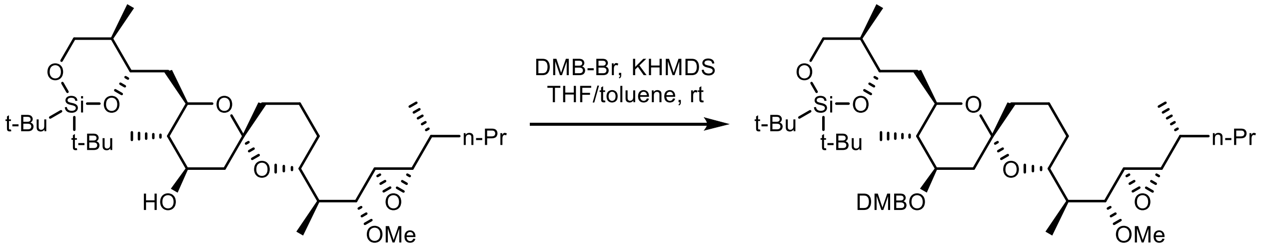
Diol **31**: **^{1}H-NMR** (500 MHz, C_6D_6): δ 6.96 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.94 (d, *J* = 2.0 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 4.59 (d, *J* = 11.6 Hz, 1H), 4.52 (s, 1H), 4.38 (d, *J* = 11.5 Hz, 1H), 4.06 (td, *J* = 10.5, 2.3 Hz, 1H), 3.83 – 3.68 (m, 3H), 3.56 (ddd, *J* = 11.6, 7.5, 1.9 Hz, 1H), 3.53 (s, 3H), 3.46 (s, 6H), 3.43 (ddd, *J* = 9.7, 4.6, 3.3 Hz, 1H), 3.36 – 3.28 (m, 1H), 2.98 (dd, *J* = 7.2, 2.2 Hz, 1H), 2.89 (dd, *J* = 7.2, 3.1 Hz, 1H), 2.73 (dd, *J* = 13.1, 4.3 Hz, 1H), 2.34 (dd, *J* = 6.7, 2.2 Hz, 1H), 1.80 – 1.73 (m, 2H), 1.65 (qd, *J* = 6.9, 3.7 Hz, 1H), 1.62 – 1.52 (m, 2H), 1.52 – 1.38 (m, 4H), 1.38 – 1.23 (m, 6H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.20 – 1.14 (m, 2H), 1.03 (qd, *J* = 10.0, 5.3 Hz, 2H), 0.98 (d, *J* = 6.4 Hz, 3H), 0.95 (d, *J* = 6.4 Hz, 3H), 0.91 – 0.85 (m, 1H), 0.81 (d, *J* = 7.0 Hz, 3H), 0.78 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (126 MHz, C_6D_6): δ 150.39, 149.99, 131.85, 120.82, 112.60, 112.17, 99.23, 82.79, 78.20, 77.12, 75.88, 74.71, 70.92, 67.18, 59.76, 58.77, 57.73, 55.70, 55.67, 42.96, 42.68, 41.18, 38.25, 36.14, 35.73, 35.31, 33.91, 31.96, 28.27, 23.05, 20.42, 20.20, 16.86, 14.40, 14.35, 13.60, 11.44. **FT-IR** (film): ν_{max} (cm^{-1}) 3484.74 (br), 2957.30, 2873.42, 2059.60, 1709.59, 1607.38, 1593.88, 1516.74, 1463.71, 1419.35, 1376.93, 1358.60, 1332.57, 1309.43, 1264.11, 1238.08, 1194.69, 1173.47, 1157.08, 1138.76, 1071.26, 1028.84, 902.52, 853.35, 807.06, 766.57, 736.67, 701.96. **HRMS** (ESI) *m/z* 645.3986 [$(M+Na)^+$; calcd for $C_{35}H_{58}O_9Na$: 645.3979]. **$[\alpha]^{20}_D$** -14.6 (c 1.43, $CHCl_3$).

Triol **S12**: **^{1}H-NMR** (500 MHz, C_6D_6): δ 4.56 (s, 1H), 4.00 (td, *J* = 10.3, 2.3 Hz, 1H), 3.79 (dd, *J* = 10.8, 3.5 Hz, 1H), 3.75 (t, *J* = 7.9 Hz, 1H), 3.71 (dd, *J* = 11.0, 6.9 Hz, 1H), 3.59 – 3.51 (m, 1H), 3.46 (s, 3H), 3.43 (dt, *J* = 7.8, 3.9 Hz, 1H), 2.95 (dd, *J* = 7.1, 2.2 Hz, 1H), 2.90 (dd, *J* = 7.1, 3.1 Hz, 1H), 2.35 (dd, *J* = 6.7, 2.2 Hz, 2H), 1.75 (dt, *J* = 11.1, 3.8 Hz, 2H), 1.64 (qd, *J* = 7.0, 3.6 Hz, 1H), 1.51 (dt, *J* = 14.4, 10.1 Hz, 1H), 1.46 – 1.26 (m, 8H), 1.25 (d, *J* = 6.8 Hz, 4H), 1.24 – 1.09 (m, 4H), 1.03 (dq, *J* = 16.3, 6.2, 5.5 Hz, 3H), 0.96 (dd, *J* = 6.5, 2.8 Hz, 3H), 0.93 – 0.82 (m, 5H), 0.82 – 0.75 (m, 6H). **^{13}C-NMR** (126 MHz, C_6D_6): δ 99.14, 82.68, 78.26, 76.81, 74.60, 68.88, 67.22, 59.81, 58.78, 57.72, 44.63, 42.74, 41.12, 38.13, 37.94, 36.15, 35.75, 35.33, 28.30, 20.44, 20.17, 16.89, 14.39, 14.35, 13.28, 11.38. **FT-IR** (film): ν_{max} (cm^{-1}) 3433.64 (br), 2957.30, 2873.42, 1593.88, 1516.74, 1461.78, 1377.89, 1306.54, 1263.15, 1224.58, 1195.65, 1171.54, 1140.69, 1093.44, 1068.37, 1018.23 993.16, 938.20, 903.49, 844.67, 797.42, 740.53. **HRMS** (ESI) *m/z* 495.3295 [(M+Na)$^+$; calcd for $C_{26}H_{48}O_7Na$: 495.3298]. **[α]$^{20}_D$** +5.94 (c 1.14, $CHCl_3$).

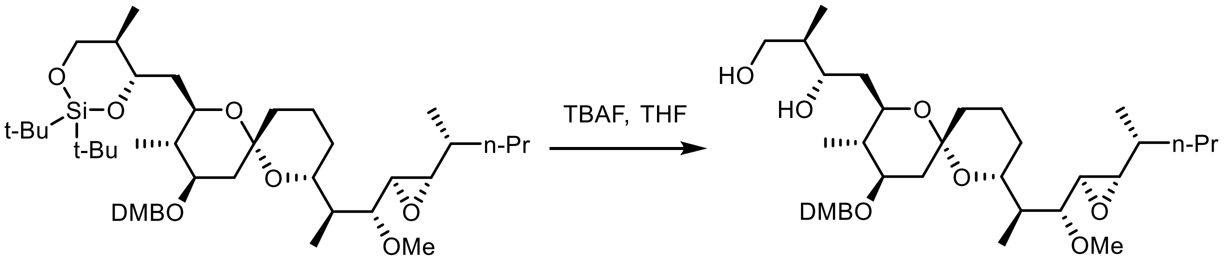


S12

To a solution of triol **S12** (192.7 mg, 0.407 mmol) in CH_2Cl_2 (2.5 mL) at -78^{o}C under argon atmosphere was sequentially added catalytic 4-DMAP (1 chip), 2,6-lutidine (0.19 mL, 1.75 mmol) and di-*t*-butylsilyl-di-trifluoromethanesulfonate (0.15 mL, 0.46 mmol). The reaction was stirred at -78^{o}C for 20 minutes before sat. aq. $NaHCO_3$ (5 mL) was added. The organic layer was collected and aqueous layer was extracted with dichloromethane (10 mL x 3). The organic layers were combined, washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. The crude material was directly used in the next step.

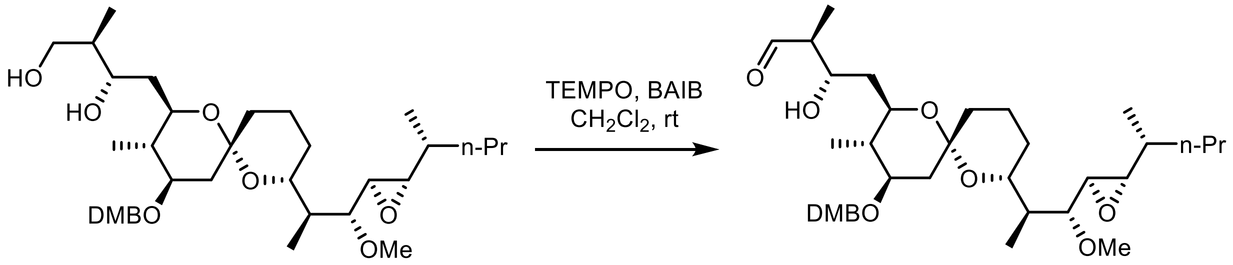


To a stirred solution of crude material from above step in THF (3.3 mL) at -20^{o}C under argon atmosphere was added KHMDS (1.3 mL, 0.5 M in toluene, 0.66 mmol). The mixture was allowed to stir at -20^{o}C for 5 minutes and 3,4-dimethoxybenzyl bromide (91 mg, 0.394 mmol) was added. The mixture was allowed to warm-up to room temperature and stirred for 30 minutes before sat. aq. NH_4Cl (5 mL) was added to quench the reaction. The organic layer was collected and aqueous layer extracted with ether (10 mL x 4). The organic layers were combined and washed with brine (10 mL x 2), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. The crude material was directly subjected to deprotection without purification.



31

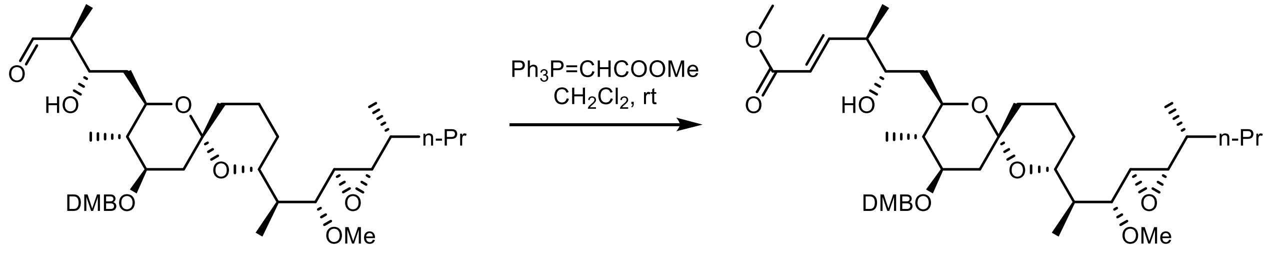
To a stirred solution of crude silyl acetal from above in THF (1.8 mL) was added TBAF (1.2 mL, 1,0 M in THF, 1.2 mmol). The reaction was stirred at room temperature for 72 hours before sat. aq. NH_4Cl (5 mL) was added. The organic layer was collected and aqueous layer extracted with ether (5 mL x 4). The organic layer was combined and washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 1:1) afforded recovered diol **31** (185.2 mg, 73% over 3 steps) as a colorless gum, which solidified upon storage in refrigerator.



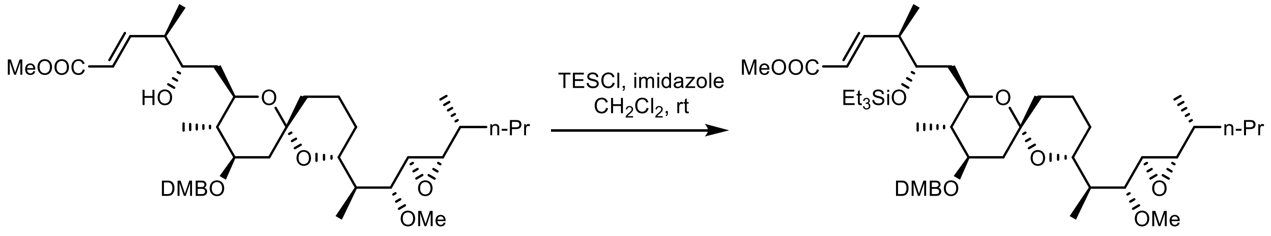
31

32

To a stirred solution of diol **31** (261.9 mg, 0.42 mmol) in dry CH_2Cl_2 (4.2 mL) at 0^{o}C was added TEMPO (12.5 mg, 0.08 mmol) and bis(acetoxy)iodobenzene (161 mg, 0.5 mmol). The solution was allowed to warm-up to room temperature and stirred for 7 hours. The mixture was cooled to 0^{o}C and the solvent was removed under reduced pressure. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 3:1) afforded β-hydroxy aldehyde **32** as a white solid, which was directly used in the next step due to its instability.

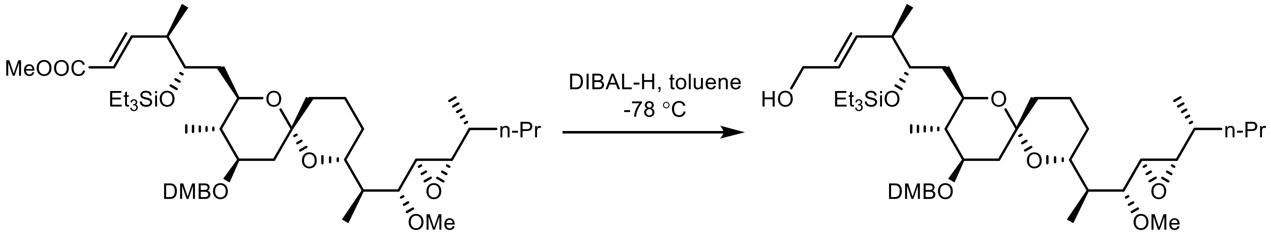


To a stirred solution of aldehyde **32** in CH_2Cl_2 (2 mL) was added solid $Ph_3P{=}CHCO_2Me$ (280 mg, 0.84 mmol). The mixture was stirred at room temperature for 16 hours before solvent was removed under reduced pressure. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 3:1) afforded **33** (281 mg, >95% over 2 steps) as a crystalline solid. **^{1}H-NMR** (600 MHz, C_6D_6): δ 7.41 (dd, *J* = 15.8, 8.2 Hz, 1H), 6.96 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.94 (d, *J* = 1.9 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 5.96 (dd, *J* = 15.8, 1.1 Hz, 1H), 4.58 (d, *J* = 11.6 Hz, 1H), 4.38 (d, *J* = 11.6 Hz, 1H), 4.04 (td, *J* = 10.4, 2.4 Hz, 1H), 4.01 (s, 1H), 3.78 (ddd, *J* = 9.8, 4.0, 1.8 Hz, 1H), 3.56 (ddd, *J* = 11.6, 7.4, 2.1 Hz, 1H), 3.52 (s, 3H), 3.47 (s, 3H), 3.45 (s, 3H), 3.45 – 3.41 (m, 1H), 3.41 (s, 3H), 2.99 (dd, *J* = 7.2, 2.2 Hz, 1H), 2.90 (dd, *J* = 7.2, 3.1 Hz, 1H), 2.71 (dd, *J* = 13.0, 4.3 Hz, 1H), 2.34 (dd, *J* = 6.7, 2.3 Hz, 1H), 2.18 (qd, *J* = 7.2, 5.1 Hz, 1H), 1.76 (pd, *J* = 6.9, 3.0 Hz, 1H), 1.62 (dt, *J* = 14.3, 2.2 Hz, 1H), 1.53 (dtd, *J* = 12.8, 9.6, 9.1, 5.9 Hz, 2H), 1.50 – 1.45 (m, 1H), 1.41 (tq, *J* = 7.5, 3.2 Hz, 2H), 1.38 – 1.25 (m, 5H), 1.24 (d, *J* = 6.9 Hz, 3H), 1.22 – 1.11 (m, 3H), 1.08 – 0.99 (m, 5H), 0.97 (d, *J* = 6.3 Hz, 3H), 0.95 (d, *J* = 6.4 Hz, 3H), 0.92 – 0.83 (m, 1H), 0.79 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR** (151 MHz, C_6D_6): δ 166.62, 151.31, 150.40, 149.96, 131.87, 121.72, 120.76, 112.52, 112.14, 99.17, 82.80, 76.76, 75.87, 74.97, 74.67, 70.83, 59.76, 58.75, 55.64, 50.91, 43.21, 42.85, 42.74, 37.80, 36.08, 35.75, 35.34, 33.91, 28.28, 20.45, 20.17, 16.89, 16.10, 14.35, 13.60, 11.48. **FT-IR** (film): ν_{max} (cm^{-1}) 3496.31, 2956.34, 1723.09, 1654.62, 1516.74, 1463.71, 1358.60, 1266.04, 1157.08, 1072.23, 1011.48. **HRMS** (ESI) *m/z* 699.4079 $[(M+Na)^+$; calcd for $C_{38}H_{60}O_{10}Na$: 699.4089]. **$[\alpha]^{20}_D$** -21.3 (c 0.78, C_6H_6).



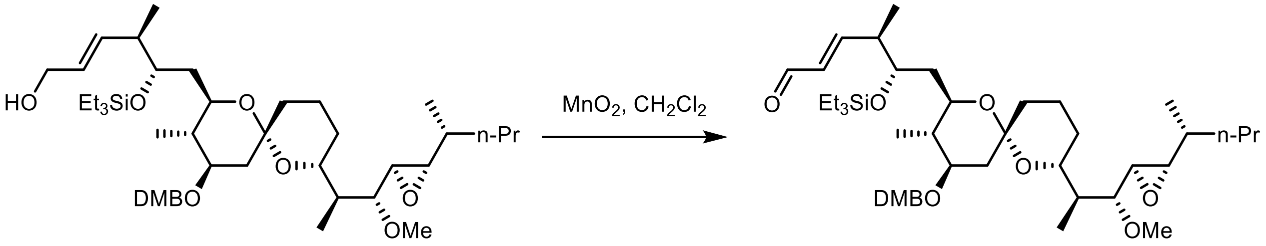
To a stirred solution of compound **33** (160.8 mg, 0.238 mmol) in CH_2Cl_2 (2.3 mL) at room temperature was sequentially added imidazole (32 mg, 0.476 mmol) and triethylsilyl chloride (48 µL, 0.286 mmol). The solution was stirred for 5 hours and additional imidazole (40 mg, 0.587 mmol) and

Et_3SiCl (50 μL, 0.290 mmol) were added. The reaction was allowed to stir overnight (ca. 16h) before sat. aq. $NaHCO_3$ (5 mL) was added. The organic layer was collected and aqueous layer extracted with CH_2Cl_2 (3 mL x 3). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 9:1) afforded **S13** (172.3 mg, 91%) as a colorless gum. **^{1}H-NMR** (500 MHz, C_6D_6): δ 7.46 (dd, *J* = 15.8, 9.2 Hz, 1H), 6.96 – 6.91 (m, 2H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.14 (d, *J* = 15.8 Hz, 1H), 4.57 (dd, *J* = 11.6, 1.5 Hz, 1H), 4.38 (dd, *J* = 11.5, 1.5 Hz, 1H), 4.20 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.05 – 3.96 (m, 1H), 3.58 – 3.52 (m, 1H), 3.51 (s, 3H), 3.48 (d, *J* = 1.3 Hz, 3H), 3.45 (s, 3H), 3.44 (d, *J* = 5.4 Hz, 1H), 3.39 (s, 3H), 3.01 – 2.94 (m, 2H), 2.85 (td, *J* = 8.3, 7.1, 2.7 Hz, 1H), 2.75 (dd, *J* = 13.0, 4.2 Hz, 1H), 2.36 – 2.29 (m, 1H), 2.06 – 1.97 (m, 1H), 1.84 – 1.73 (m, 2H), 1.70 – 1.56 (m, 3H), 1.51 (ddd, *J* = 20.0, 16.2, 9.1 Hz, 2H), 1.44 – 1.31 (m, 2H), 1.31 – 1.18 (m, 8H), 1.16 (dd, *J* = 6.9, 1.7 Hz, 3H), 1.09 (dd, *J* = 6.6, 2.1 Hz, 4H), 1.05 – 0.98 (m, 12H), 0.90 – 0.86 (m, 3H), 0.68 – 0.61 (m, 6H). **^{13}C-NMR** (126 MHz, C_6D_6): δ 166.45, 151.18, 150.34, 149.85, 131.99, 122.29, 120.60, 112.40, 112.13, 98.81, 82.55, 76.61, 74.77, 72.88, 71.47, 70.89, 60.13, 58.73, 57.70, 55.68, 55.61, 50.95, 42.99, 42.97, 40.92, 39.83, 36.15, 35.98, 35.52, 34.16, 28.41, 20.53, 20.33, 17.78, 17.14, 14.46, 13.61, 11.32, 7.30, 5.56. **FT-IR** (film): ν_{max} (cm^{-1}) 3427.85, 2955.38, 2066.35, 1725.98, 1654.62, 1593.88, 1516.74, 1462.74, 1418.39, 1375.00, 1267.97, 1156.12, 1088.62, 14 905.41, 853.35, 803.21, 765.60, 739.57, 687.50. **HRMS** (ESI) *m/z* 813.4962 [(M+Na)$^+$; calcd for $C_{44}H_{74}O_{10}NaSi$: 813.4949]. **[α]$^{20}_D$** +24.71 (c 2.13, C_6H_6).



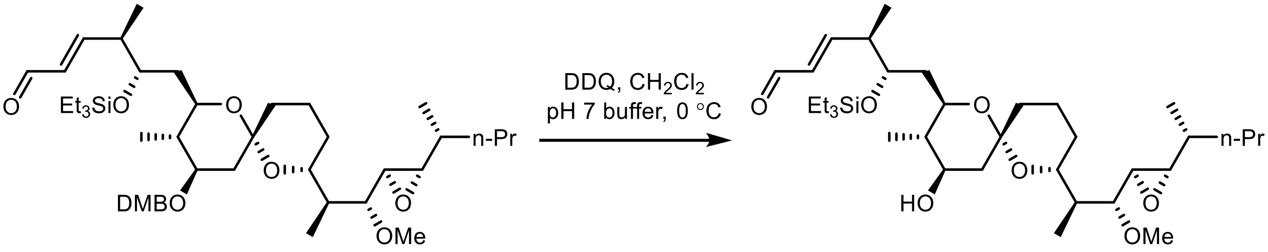
S13

To a stirred solution of compound **S13** (172 mg, 0.217 mmol) in toluene (2.2 mL) at -78°C under argon atmosphere was added DIBAL-H (400 μL, 1.0 M in toluene, 0.4 mmol) dropwise. The solution was stirred at -78°C for 35 min before sat. aq. Rochelle salt (2 mL) was added. The biphasic mixture was stirred at room temperature for 2 hours. The organic phase was collected and aqueous layer extracted with ether (3 mL x 3). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. The crude product was directly used in the next step without purification.



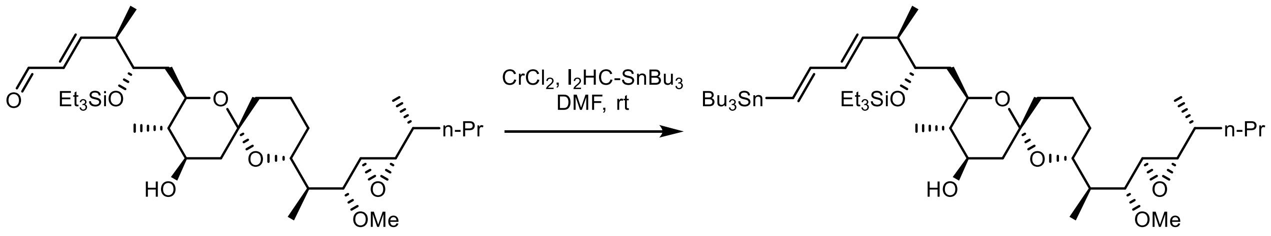
34

The crude product from previous step was dissolved in CH_2Cl_2 (2 mL) and MnO_2 (190 mg, 2.2 mmol) was added. The mixture was stirred for 24 hours and additional MnO_2 (200 mg) was added. The reaction was stirred for another 15 hours. The mixture was filtered through a thin pad of celite. The filter cake was then washed with copious amount of diethyl ether. The filtrate was concentrated under reduced pressure. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 10:1) afforded **34** (140.8 mg, 85% over 2 steps) as a colorless gum. **^{1}H-NMR** (500 MHz, C_6D_6): δ 9.40 (d, *J* = 7.8 Hz, 1H), 6.98 – 6.93 (m, 2H), 6.81 (dd, *J* = 15.8, 8.9 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.26 (dd, *J* = 15.8, 7.8 Hz, 1H), 4.57 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 11.6 Hz, 1H), 4.20 (dt, *J* = 9.6, 3.7 Hz, 1H), 3.93 (td, *J* = 10.3, 2.5 Hz, 1H), 3.52 (s, 4H), 3.47 (s, 3H), 3.45 (s, 4H), 2.96 (qd, *J* = 7.0, 2.3 Hz, 2H), 2.85 (ddt, *J* = 13.1, 9.1, 4.6 Hz, 1H), 2.75 (dd, *J* = 13.0, 4.3 Hz, 1H), 2.33 (dd, *J* = 7.1, 2.0 Hz, 1H), 1.90 (ddd, *J* = 14.1, 9.6, 2.6 Hz, 1H), 1.84 – 1.69 (m, 2H), 1.68 – 1.55 (m, 3H), 1.54 – 1.42 (m, 3H), 1.42 – 1.28 (m, 4H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.26 – 1.11 (m, 4H), 1.09 (d, *J* = 6.9 Hz, 3H), 1.07 (t, *J* = 4.8 Hz, 1H), 1.03 (dd, *J* = 8.8, 7.1 Hz, 12H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 4H), 0.65 (qd, *J* = 7.8, 2.4 Hz, 6H). **^{13}C-NMR** (126 MHz, C_6D_6): δ 192.80, 159.07, 150.39, 149.94, 134.03, 131.93, 120.66, 112.49, 112.16, 98.89, 82.55, 76.50, 74.86, 72.66, 71.33, 71.02, 60.07, 58.74, 57.66, 55.68, 55.65, 43.08, 42.97, 41.32, 39.88, 36.20, 35.97, 35.51, 34.07, 28.49, 20.53, 20.38, 17.39, 17.13, 14.48, 13.62, 11.35, 7.29, 5.56. **FT-IR** (film): ν_{max} (cm^{-1}) 2956.34, 1693.19, 1516.74, 1463.71, 1375, 1264.11, 1157.08, 1080.91, 1011.48, 741.50. **HRMS** (ESI) *m/z* 783.4844 [$(M+Na)^+$; CALCD FOR $C_{43}H_{72}O_9NaSi$: 783.4843]. **$[\alpha]^{20}_D$** +14.2 (c 1.25, C_6H_6).



34 **35**

To a stirred solution of aldehyde **34** (47.9 mg, 0.063 mmol) in CH_2Cl_2 (0.63 mL) and 1M pH 7 phosphate buffer (63 μL) at 0°C was added solid DDQ (17.2 mg, 0.076 mmol). The reaction mixture quickly turned deep green. The mixture was allowed to stir at 0°C for 35 min before sat. aq. $NaHCO_3$ was added. Ether (5 mL x 3) was used to extract the aqueous phase. The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 5:1) afforded **35** (39.0 mg, quant.) as a colorless oil. **^{1}H-NMR** (600 MHz, C_6D_6) δ 9.40 (d, *J* = 7.8 Hz, 1H), 6.80 (dd, *J* = 15.8, 9.0 Hz, 1H), 6.24 (ddd, *J* = 15.8, 7.8, 0.9 Hz, 1H), 4.16 (ddd, *J* = 9.7, 4.1, 2.7 Hz, 1H), 3.82 (td, *J* = 10.3, 2.5 Hz, 1H), 3.52 (ddd, *J* = 11.3, 7.5, 2.2 Hz, 1H), 3.48 (s, 3H), 3.41 – 3.35 (m, 1H), 2.99 – 2.90 (m, 2H), 2.88 – 2.80 (m, 1H), 2.38 – 2.30 (m, 2H), 1.84 (ddd, *J* = 13.9, 9.7, 2.5 Hz, 1H), 1.77 – 1.69 (m, 2H), 1.50 (dddd, *J* = 32.4, 18.9, 11.1, 3.9 Hz, 4H), 1.38 – 1.29 (m, 4H), 1.28 (d, *J* = 6.8 Hz, 4H), 1.27 – 1.20 (m, 3H), 1.16 – 1.10 (m, 1H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.07 – 1.04 (m, 1H), 1.02 (q, *J* = 7.4 Hz, 13H), 0.97 – 0.91 (m, 1H), 0.89 (t, *J* = 6.5 Hz, 6H), 0.64 (qd, *J* = 7.9, 3.2 Hz, 6H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 192.82, 159.11, 134.01, 98.80, 82.48, 74.57, 72.68, 70.98, 69.43, 60.08, 58.77, 57.70, 44.66, 42.97, 41.24, 39.72, 37.97, 36.18, 35.99, 35.54, 28.49, 20.55, 20.34, 17.42, 17.16, 14.48, 13.16, 11.26, 7.28, 7.26, 5.55, 5.53. **FT-IR** (film): ν_{max} (cm^{-1}) 3434.6, 2956.34, 2875.34, 1693.19, 1459.85, 1375.0, 1226.5, 1082.83, 1010.52, 906.38, 726.07. **HRMS** (ESI) *m/z* 633.4155 [$(M+Na)^+$; CALCD FOR $C_{34}H_{62}O_7NaSi$: 633.4163]. **$[\alpha]^{20}_D$** +32.5 (c 1.47, C_6H_6).

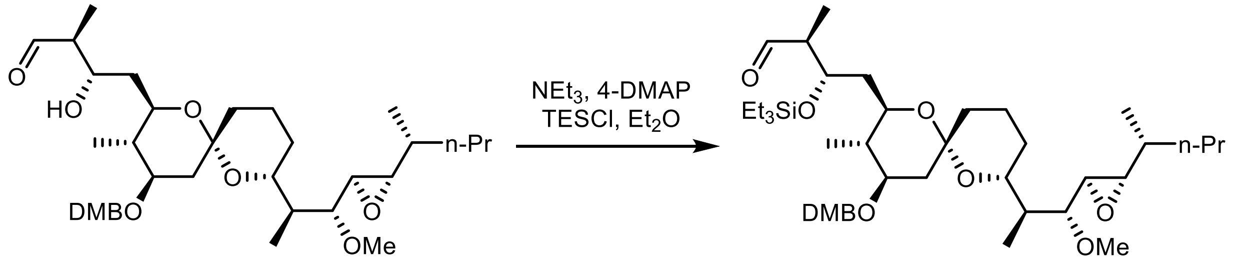


35 **3a**

To an oven-dried 5 mL microwave reaction tube in a glove box was added solid $CrCl_2$ (64.5 mg, 0.525 mmol). The reaction tube was then sealed with a rubber septum and taken out from glove box. The reaction tube was then transferred to an ice-water bath before DMF (0.4 mL, dried over 4Å MS and degassed prior to use) was added via syringe. The resulting blue solution was stirred for 0.5 h at 0°C before a solution of compound **35** (21.4 mg, 0.035 mmol) and Bu_3SnCHI_2 (58.5 mg, 0.105 mmol) in DMF (0.1 mL + 0.1 mL x 2 rinse, dried over 4Å MS and degassed prior to use) was added. The reaction vessel was then covered with aluminum foil and stirred at room temperature under argon atmosphere for 22 hours. The reaction mixture was then transferred to a stirring solution of sat. aq. NH_4Cl (10 mL) and sat. aq. NH_4OH (10 mL) and diethyl ether (10 mL). The mixture was allowed to stir for 1 hour at room temperature until all solid disappeared. Then the aqueous layer was extracted with diethyl ether (10 mL x 3). The organic layers were combined and washed with sat. aq. NH_4Cl (10 mL x

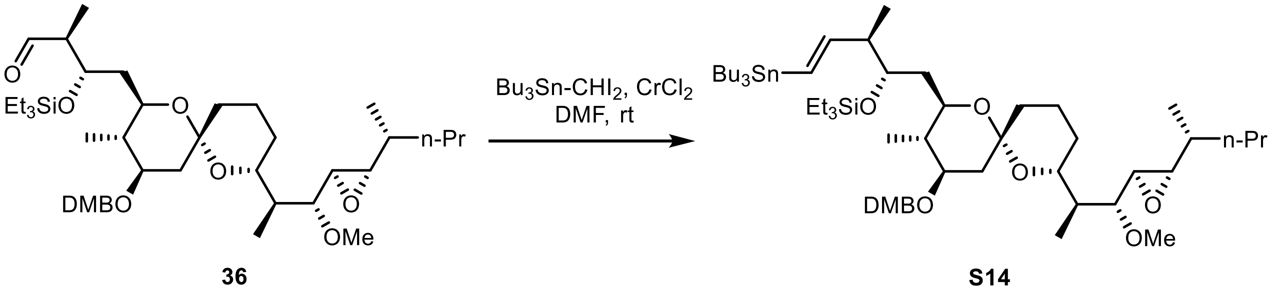
3), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 8:1 buffered with 1% NEt_3) afforded Northern Hemisphere **3a** (25.2 mg, 80%) as a 4:1 mixture of *E/Z* isomers. **^{1}H-NMR** (600 MHz, C_6D_6) δ 6.83 (ddd, *J* = 18.6, 9.8, 1.8 Hz, 1H), 6.44 – 6.25 (m, 2H), 6.08 (ddd, *J* = 15.5, 9.4, 2.0 Hz, 1H), 4.23 (dt, *J* = 7.4, 2.6 Hz, 1H), 4.01 – 3.93 (m, 1H), 3.55 (ddd, *J* = 11.5, 7.3, 2.2 Hz, 1H), 3.48 (d, *J* = 4.7 Hz, 3H), 3.44 (tt, *J* = 10.0, 4.8 Hz, 1H), 3.02 – 2.93 (m, 2H), 2.81 – 2.67 (m, 1H), 2.39 – 2.30 (m, 2H), 2.10 (ddt, *J* = 13.3, 9.6, 1.8 Hz, 1H), 1.84 – 1.73 (m, 2H), 1.72 – 1.39 (m, 14H), 1.39 – 1.28 (m, 21H), 1.28 – 1.23 (m, 5H), 1.17 – 1.10 (m, 3H), 1.07 (t, *J* = 7.9 Hz, 8H), 1.04 – 0.88 (m, 24H), 0.70 (qd, *J* = 7.8, 3.2 Hz, 7H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 148.26, 135.86, 135.18, 130.52, 128.35, 82.59, 82.45, 74.45, 74.28, 73.47, 71.96, 71.30, 69.75, 69.65, 60.18, 59.91, 58.75, 58.63, 57.75, 44.82, 43.05, 41.08, 39.91, 38.30, 36.10, 36.08, 35.60, 30.23, 29.72, 29.67, 29.60, 29.53, 28.38, 27.80, 27.71, 20.62, 20.27, 19.01, 17.24, 14.57, 14.03, 13.97, 13.32, 11.36, 10.87, 9.81, 7.42, 7.38, 5.68. **FT-IR** (film): ν_{max} (cm^{-1}) 3403.74, 2956.34, 2922.59, 1462.74, 1010.52. **HRMS** (ESI) m/z 899.5582 [$(M+H)^+$; CALCD FOR $C_{47}H_{91}O_6SiSn$: 899.5607]. **$[\alpha]^{20}_D$** +38.6 (c 0.55, C_6H_6).

(d). Synthesis of the Second-Generation Northern Hemisphere (**3b**)



32 **36**

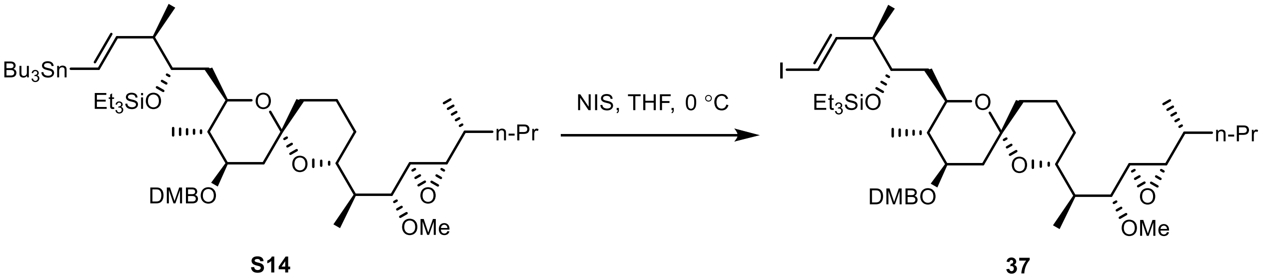
To a stirred solution of aldehyde **32** (463.7 mg, 0.75 mmol) in diethyl ether (7 mL) was added 4-DMAP (270 mg, 2.20 mmol) and NEt_3 (1.3 mL, 9.0 mmol). The mixture was cooled to 0ºC and Et_3SiCl (1.1 mL, 6.7 mmol) was added dropwise. The reaction mixture was then allowed to warm up to room temperature and stirred for another 30 min before water (10 mL) was added to quench the reaction. The organic layer was collected and the aqueous layer was extracted with diethyl ether (5 mL x 3). Then the organic layers were combined and sequentially washed with H_2O (10 mL), sat. aq. $CuSO_4$ (10 mL x 3) and brine (10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 6:1) afforded **36** (463.7 mg, 84%) as a colorless oil. **^{1}H-NMR** (500 MHz, C_6D_6): *δ* 9.92 (d, *J* = 2.3 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.71 (d, *J* = 7.8 Hz, 1H), 4.58 (d, *J* = 11.6 Hz, 1H), 4.44 – 4.35 (m, 2H), 3.99 (td, *J* = 10.3, 2.2 Hz, 1H), 3.51 (s, 4H), 3.48 (s, 3H), 3.46 (s, 4H), 2.98 (d, *J* = 1.5 Hz, 2H), 2.78 – 2.69 (m, 2H), 2.37 (d, *J* = 6.8 Hz, 1H), 2.12 (ddd, J = 14.1, 9.5, 2.3 Hz, 1H), 1.86 – 1.81 (m, 1H), 1.81 – 1.75 (m, 1H), 1.70 – 1.45 (m, 6H), 1.45 – 1.26 (m, 6H), 1.25 (d, J = 6.9 Hz, 3H), 1.19 (d, J = 6.9 Hz, 4H), 1.16 – 1.10 (m, 2H), 1.08 (d, J = 6.4 Hz, 3H), 1.02 – 0.97 (m, 12H), 0.88 (t, J = 7.1 Hz, 4H), 0.66 – 0.58 (m, 7H). **^{13}C-NMR** (126 MHz, C_6D_6): δ 203.91, 150.39, 149.93, 131.98, 120.71, 112.52, 112.16, 98.81, 82.42, 76.47, 74.82, 71.89, 71.30, 70.89, 60.13, 58.80, 57.69, 55.69, 55.64, 50.78, 42.99, 42.87, 39.57, 36.24, 35.99, 35.54, 34.05, 28.44, 22.72, 20.55, 20.41, 17.13, 14.51, 14.28, 13.55, 11.39, 11.25, 7.20, 5.45. **FT-IR** (film): ν_{max} (cm^{-1}) 2956.34, 2875.34, 2727.82, 2280.41, 2066.35, 1723.09, 1607.38, 1592.91, 1516.74, 1463.71, 1418.39, 1375.00, 1357.64, 1332.57, 1306.54, 1264.11, 1239.04, 1194.69, 1179.26, 1156.12, 1137.80, 1071.26, 1030.77, 1012.45, 960.38, 931.45, 904.45, 854.31, 808.03, 764.64, 741.50, 669.18. **HRMS** (ESI) *m/z* 735.4884 [(M+H)$^+$; calcd for $C_{41}H_{71}O_9Si$: 735.4867]. **$[\alpha]^{20}_D$** +9.67 (c 1.34, $CHCl_3$).



36 **S14**

$CrCl_2$ (3.84 g, 31.3 mmol) was weighed and transferred into a 100 mL oven-dried round bottom flask equipped with a magnetic stir bar in a glove box. The flask was sealed with rubber septum and taken out of the glovebox. The flask was wrapped with aluminum foil and cooled to 0°C. *N, N*-dimethylformamide (10 mL, dried over 4Å MS for 48 h and freeze-pump-thaw degassed prior to use) was added. The mixture was stirred at 0°C for 30 mins to form a blue, homogenous solution.

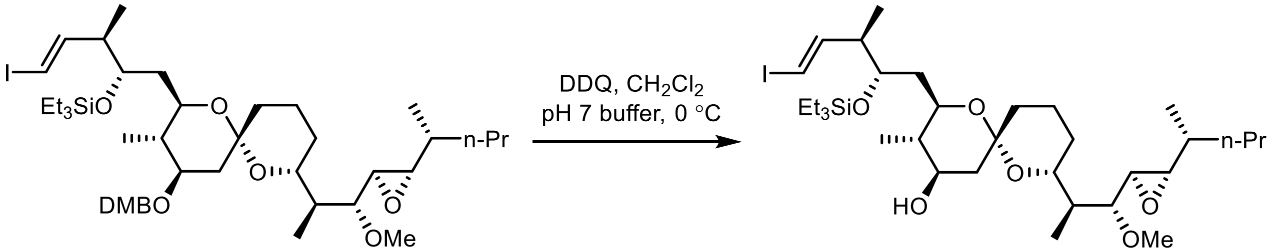
In another round bottom flask charged with compound **36** (1.15 g, 1.57 mmol) was added Bu_3Sn-CHI_2 (3.50 g, 6.28 mmol). The flask was evacuated and back-filled with argon for 3 times. *N, N*-dimethylformamide (2 mL, dried over 4Å MS for 48 h and freeze-pump-thaw degassed prior to use) was added. The solution was transferred into the $CrCl_2$ solution prepared above via syringe. The second flask was rinsed 3 times with dry & degassed DMF (1 mL each), and the reaction mixture was allowed to warm up to rt. The reaction was then stirred at room temperature for 16 hours before ether (30 mL) was added to dilute the reaction. The resulting mixture was transferred into a mixture of sat. aq. NH_4OH (30 mL), sat. aq. NH_4Cl (30 mL) and ethyl acetate (30 mL). The biphasic mixture was vigorously stirred until all solid dissolved. The organic layer was collected and aqueous layer was extracted with ether (20 mL x 3). The organic layers were combined and washed with H_2O (30 mL) and sat. aq. NH_4Cl (30 mL x 2). The organic layer was then dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 8:1-6:1) afforded **S14** (1.21 g, 78%) as a colorless oil. **^{1}H-NMR** (500 MHz, C_6D_6): δ 6.96 (d, J = 7.8 Hz, 2H), 6.71 (d, J = 7.8 Hz, 1H), 6.42 (dd, J = 19.2, 8.4 Hz, 1H), 6.19 (d, J = 19.1 Hz, 1H), 4.61 (d, J = 11.5 Hz, 1H), 4.42 (d, J = 11.6 Hz, 1H), 4.32 – 4.25 (m, 1H), 4.07 (td, J = 10.4, 2.2 Hz, 1H), 3.62 – 3.55 (m, 1H), 3.53 (s, 4H), 3.48 (s, 3H), 3.46 (s, 3H), 3.02 – 2.94 (m, 2H), 2.78 (dd, J = 13.0, 4.5 Hz, 1H), 2.74 (d, J = 7.6 Hz, 1H), 2.34 (dd, J = 6.8, 1.9 Hz, 1H), 2.25 (ddd, J = 12.4, 9.7, 2.2 Hz, 1H), 1.86 (ddd, J = 14.0, 10.6, 3.9 Hz, 1H), 1.81 – 1.70 (m, 3H), 1.66 (tdd, J = 8.1, 6.6, 4.7 Hz, 8H), 1.62 – 1.46 (m, 4H), 1.42 (h, J = 7.2 Hz, 8H), 1.37 – 1.27 (m, 11H), 1.25 (d, J = 6.2 Hz, 5H), 1.16 – 1.13 (m, 1H), 1.10 (t, J = 8.0 Hz, 12H), 1.04 – 0.95 (m, 18H), 0.91 (t, J = 7.0 Hz, 3H), 0.72 (qd, J = 7.9, 1.7 Hz, 6H). **^{13}C-NMR** (126 MHz, C_6D_6): δ 152.09, 150.38, 149.87, 132.11, 120.61, 112.44, 112.17, 98.75, 82.51, 76.82, 74.58, 73.28, 71.72, 70.82, 60.12, 58.71, 57.74, 55.69, 55.61, 46.31, 43.24, 43.10, 40.30, 36.07, 35.48, 34.32, 29.81, 29.76, 29.68, 29.60, 28.40, 28.21, 27.99, 27.89, 27.86, 27.78, 27.56, 27.14, 20.56, 20.28, 19.12, 17.30, 17.17, 14.59, 14.02, 13.97, 13.78, 11.40, 11.24, 11.17, 9.89, 9.80, 8.60, 8.54, 7.53, 7.49, 7.39, 6.00, 5.88, 5.84, 5.77, 5.70. **FT-IR** (film): ν_{max} (cm^{-1}) 2956.34, 2927.41, 2873.42, 1593.88, 1516.74, 1463.71, 1418.39, 1375.00, 1356.68, 1306.54, 1264.11, 1238.08, 1194.69, 1182.15, 1156.12, 1138.76, 1077.05, 1010.52, 959.41, 906.38, 854.31, 804.17, 780.06, 764.64, 740.53, 666.29. **$[\alpha]^{20}_D$** +5.57 (c 0.71, $CHCl_3$)



S14 **37**

To a stirred solution of vinyl stannane **S14** (1.2126 g, 1.20 mmol) in THF (12 mL) at 0°C was added *N*-iodosuccinimide (295 mg, 1.31 mmol). The reaction mixture was stirred at 0°C for 30 min and additional NIS (30 mg) was added. The reaction was stirred at 0°C for another 30 min before sat. aq. $Na_2S_2O_3$ (5 mL) and sat. aq. $NaHCO_3$ (5 mL) were added. The organic layer was collected and aqueous layer was extracted with ether (10 mL x 3). Then the organic layers were combined and washed with brine (20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 8:1-6:1) afforded vinyl iodide **37** (1.0345 g, quant.) as a colorless oil. **^{1}H-NMR** (500 MHz, C_6D_6): δ 6.95 (d, J = 6.8 Hz, 2H), 6.88 (dd, J = 14.5, 9.5 Hz, 1H), 6.71 (d, J = 8.7 Hz, 1H), 6.14 (d, J = 14.5 Hz, 1H), 4.58 (d, J = 11.6 Hz, 1H), 4.39 (d, J = 11.6 Hz, 1H), 4.09 (dt, J = 9.6, 3.5 Hz, 1H), 3.95 (td, J = 10.4, 2.3 Hz, 1H), 3.52 (s, 4H), 3.47 (s, 3H), 3.46 (s, 5H), 2.97 – 2.92 (m, 2H), 2.74 (dd, J = 13.0, 4.3 Hz, 1H), 2.68 (ddd, J = 9.6, 6.8, 2.8 Hz, 1H), 2.31 (dd, J = 7.1, 1.8

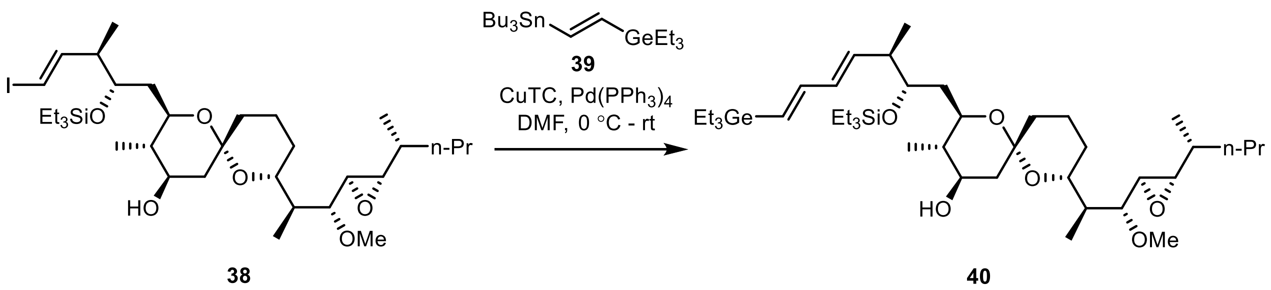
Hz, 1H), 2.02 (ddd, *J* = 13.9, 9.5, 2.4 Hz, 1H), 1.82 – 1.70 (m, 2H), 1.69 – 1.15 (m, 21H), 1.12 (d, *J* = 6.5 Hz, 4H), 1.08 (dd, *J* = 7.5, 3.6 Hz, 5H), 1.05 – 0.97 (m, 13H), 0.91 – 0.85 (m, 6H), 0.64 (qd, *J* = 7.9, 2.0 Hz, 6H). **^{13}C-NMR** (126 MHz, C_6D_6): *δ* 150.40, 149.92, 148.91, 132.03, 120.62, 112.49, 112.20, 98.83, 82.61, 76.59, 75.10, 74.84, 72.49, 71.43, 70.88, 60.16, 58.71, 57.73, 55.70, 55.66, 45.10, 43.04, 42.96, 39.78, 36.13, 36.02, 35.55, 34.45, 34.15, 28.41, 22.73, 20.54, 20.33, 17.69, 17.20, 14.55, 14.28, 13.78, 11.28, 7.31, 5.66, 5.59. **FT-IR** (film): ν_{max} (cm^{-1}) 2956.34, 2874.38, 2361.41, 1594.84, 1516.74, 1462.74, 1418.39, 1374.03, 1357.64, 1306.54, 1266.04, 1238.08, 1195.65, 1181.19, 1156.12, 1138.76, 1084.76, 1011.48, 957.48, 906.38, 854.31, 804.17, 764.64, 740.53, 670.14. **HRMS** (EI) *M/Z* 858.3977 [(M)$^+$; calcd for $C_{42}H_{71}O_8SiI$: 858.3963]. **$[\alpha]^{20}_D$** +22.4 (c 1.00, $CHCl_3$)



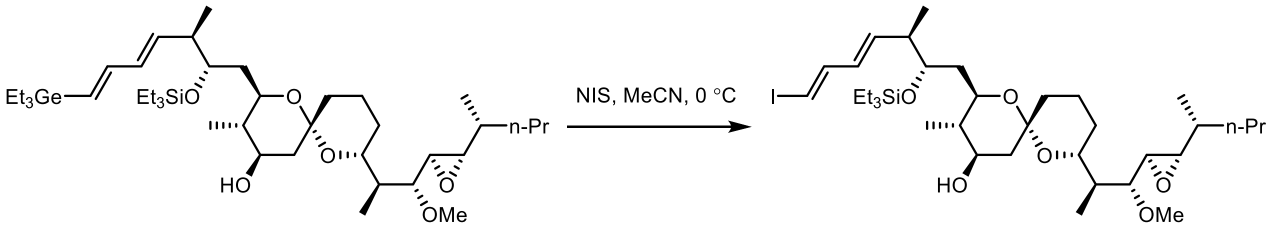
37

38

To a stirred solution of iodide **37** (1.0345 g, 1.20 mmol) in CH_2Cl_2 (12 mL) and pH 7 buffer (1.2 mL) at 0^{o}C was added solid DDQ (545 mg, 2.40 mmol). The reaction mixture quickly turned deep green. The mixture was allowed to stir at 0^{o}C for 30 min before sat. aq. $NaHCO_3$ (30 mL) was added. The organic layer was collected and aqueous layer was extracted with ether (10 mL x 3). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 6:1) afforded **38** (767.7 mg, 90%) as a colorless oil. **^{1}H-NMR** (500 MHz, C_6D_6): *δ* 6.86 (dd, *J* = 14.5, 9.4 Hz, 1H), 6.12 (d, *J* = 14.6 Hz, 1H), 4.05 (dt, *J* = 9.5, 3.5 Hz, 1H), 3.85 (td, *J* = 10.4, 2.3 Hz, 1H), 3.51 (ddd, *J* = 10.8, 7.5, 2.1 Hz, 1H), 3.47 (s, 3H), 3.40 (td, *J* = 10.7, 4.6 Hz, 1H), 2.97 – 2.90 (m, 2H), 2.66 (tt, *J* = 9.1, 6.1 Hz, 1H), 2.34 (dd, *J* = 13.0, 4.6 Hz, 1H), 2.31 (dd, *J* = 6.9, 1.9 Hz, 1H), 1.95 (ddd, *J* = 13.9, 9.6, 2.4 Hz, 1H), 1.77 – 1.67 (m, 2H), 1.56 – 1.49 (m, 2H), 1.49 – 1.41 (m, 2H), 1.39 – 1.17 (m, 13H), 1.11 (ddd, *J* = 12.5, 6.8, 2.9 Hz, 1H), 1.06 (d, *J* = 7.0 Hz, 4H), 1.01 (t, *J* = 8.0 Hz, 14H), 0.96 (d, *J* = 6.5 Hz, 4H), 0.88 (dt, *J* = 11.8, 7.2 Hz, 6H), 0.63 (m, *J* = 7.9, 1.9 Hz, 6H). **^{13}C-NMR** (126 MHz, C_6D_6): *δ* 148.90, 98.74, 82.51, 75.01, 74.54, 72.48, 71.08, 69.62, 60.17, 58.77, 57.76, 45.01, 44.71, 42.95, 39.60, 38.12, 36.11, 36.04, 35.58, 34.45, 28.41, 22.73, 20.57, 20.29, 17.71, 17.24, 14.56, 14.28, 13.32, 11.21, 7.31, 5.59. **FT-IR** (film): ν_{max} (cm^{-1}) 3435.56 (br), 3045.05, 2956.34, 2875.34, 1600.63, 1540.85, 1458.89, 1414.53, 1375.00, 1304.61, 1268.93, 1225.54, 1196.61, 1179.26, 1086.69, 1067.41, 1011.48, 956.52, 905.42, 854.31, 799.35, 761.74, 740.53, 726.07, 671.11, 645.07. **HRMS** (ESI) *M/Z* 709.3367 [(M+H)$^+$; calcd for $C_{33}H_{62}O_6SiI$: 709.3360]. **$[\alpha]^{20}_D$** +37.4 (c 0.62, $CHCl_3$)



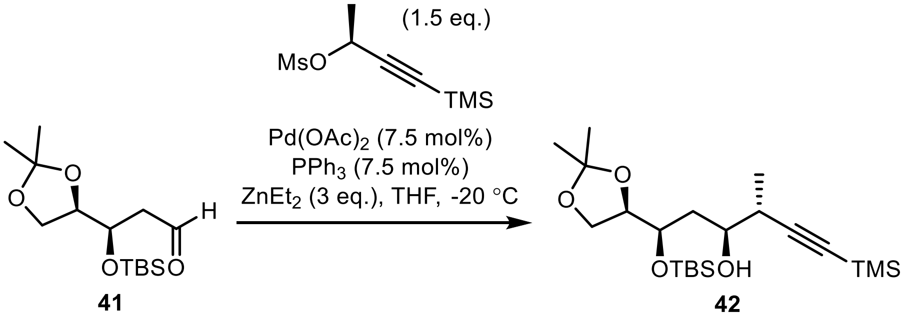
To a mixture of alkenyl iodide **38** (260.0 mg, 0.330 mmol), CuTC (140.2 mg, 0.734 mmol) and $Pd(PPh_3)_4$ (21.2 mg, 0.018 mmol) was added DMF (7 mL, dried over 4Å MS and degassed prior to use) under argon atmosphere. The mixture was cooled to 0°C and stannane **39** (300 µL, 0.734 mmol) was added dropwise. The resulting dark red suspension was stirred at 0°C for 5 hours and additional stannane (100 µL) was added. The resulting solution was warmed up to rt and stirred for another 3 hours. The reaction was quenched with sat. NH_4Cl (20 mL) and sat. $NaHCO_3$ (20 mL). The resulting mixture was stirred under air and extracted with 1:1 mixture of hexanes/ether (10 mL x 3). The organic layers were then combined and washed with sat. $NaHCO_3$ (30 mL). dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 10:1) afforded pure germane **40** (161.5 mg, 63%) as a colorless oil. **^{1}H-NMR** (500 MHz, C_6D_6): δ 6.70 (dd, J = 18.2, 9.9 Hz, 1H), 6.37 (dd, J = 15.3, 9.9 Hz, 1H), 6.12 – 6.06 (m, 1H), 6.06 – 6.01 (m, 1H), 4.23 (dt, J = 9.8, 3.6 Hz, 1H), 3.96 (td, J = 10.3, 2.2 Hz, 1H), 3.55 (ddd, J = 11.3, 7.3, 2.1 Hz, 1H), 3.48 (s, 3H), 3.43 (dq, J = 10.1, 5.1 Hz, 1H), 2.98 (qd, J = 7.0, 2.5 Hz, 2H), 2.76 (ddd, J = 9.4, 6.7, 2.6 Hz, 1H), 2.38 – 2.31 (m, 2H), 2.09 (ddd, J = 13.6, 9.6, 2.3 Hz, 1H), 1.84 – 1.73 (m, 2H), 1.57 (dd, J = 9.8, 4.6 Hz, 3H), 1.49 (dddd, J = 15.2, 12.9, 6.7, 3.1 Hz, 2H), 1.35 (d, J = 7.0 Hz, 5H), 1.30 (ddd, J = 12.2, 5.7, 3.2 Hz, 4H), 1.27 – 1.21 (m, 6H), 1.07 (td, J = 7.9, 4.3 Hz, 20H), 1.00 (d, J = 6.5 Hz, 3H), 0.99 (d, J = 6.4 Hz, 3H), 0.90 (t, J = 5.8 Hz, 4H), 0.80 (q, J = 7.9 Hz, 6H), 0.70 (qd, J = 7.9, 2.4 Hz, 7H). **^{13}C-NMR** (126 MHz, C_6D_6): δ 145.29, 136.34, 134.55, 129.00, 128.06, 98.69, 82.46, 74.46, 73.45, 71.31, 69.77, 60.13, 58.75, 57.74, 44.82, 43.05, 41.17, 39.91, 38.31, 36.11, 36.05, 35.56, 28.38, 20.59, 20.27, 18.92, 17.19, 14.53, 13.28, 11.35, 9.21, 7.38, 5.69, 4.75. **FT-IR** (film): ν_{max} (cm^{-1}) 3435.56, 2955.38, 2873.42, 1576.52, 1460.81, 1375.96, 1225.54, 1083.8, 1010.52, 906.38, 851.42, 798.38, 718.35. **HRMS** (ESI) *m/z* 791.4660 [(M+Na)$^+$; calcd for $C_{41}H_{78}O_6NaSiGe$: 791.4677]. **$[\alpha]^{20}_D$** +49.6 (c 1.57, C_6H_6)



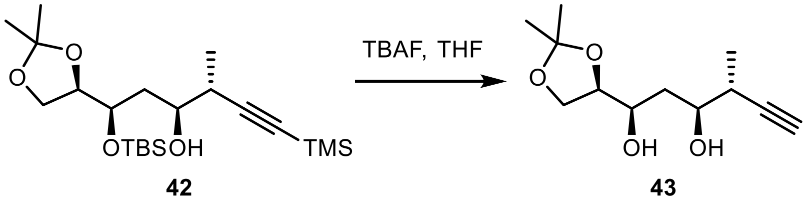
40 **3b**

To a stirred solution of vinylgermane **40** (160.2 mg, 0.208 mmol) in MeCN (1.75 mL) and CH_2Cl_2 (0.5 mL) at 0ºC under argon was added a solution of *N*-iodosuccimide (51.6 mg, 0.230 mmol) in MeCN (1.75 mL) dropwise via syringe pump over 1 hour under dark. TLC showed full conversion upon completion of addition. Sat. $Na_2S_2O_3$ (1 mL) was then added to quench the reaction. The mixture was diluted with water (20 mL) and extracted with 1:1 mixture of hexanes/ether (10 mL x 3). The organic layers were combined and washed with sat. $NaHCO_3$ (20 mL), dried over Na_2SO_4, filtered, and concentrated in-vacuo. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 10:1) afforded pure dienyl iodide **3b** (136.3 mg, 89%) as a colorless oil. **^{1}H-NMR** (500 MHz, C_6D_6): δ 6.92 (dd, *J* = 14.3, 10.3 Hz, 1H), 6.01 (d, *J* = 14.3 Hz, 1H), 5.99 – 5.92 (m, 1H), 5.86 (dd, *J* = 15.4, 8.9 Hz, 1H), 4.15 (dt, *J* = 9.8, 3.3 Hz, 1H), 3.84 (td, *J* = 10.3, 2.4 Hz, 1H), 3.53 (ddd, *J* = 11.5, 7.4, 2.0 Hz, 1H), 3.47 (s, 3H), 3.40 (s, 1H), 2.95 (qd, *J* = 7.0, 2.3 Hz, 2H), 2.59 (tt, *J* = 9.3, 6.6 Hz, 1H), 2.37 – 2.29 (m, 2H), 1.95 (ddd, *J* = 13.9, 9.6, 2.4 Hz, 1H), 1.78 – 1.68 (m, 2H), 1.57 – 1.44 (m, 4H), 1.39 – 1.18 (m, 12H), 1.15 (d, *J* = 6.9 Hz, 3H), 1.07 (t, *J* = 7.9 Hz, 11H), 1.02 – 0.96 (m, 4H), 0.91 (d, *J* = 6.4 Hz, 4H), 0.86 (t, *J* = 7.1 Hz, 3H), 0.69 (qd, *J* = 7.8, 2.4 Hz, 6H). **^{13}C-NMR** (126 MHz, C_6D_6): δ 146.13, 138.22, 131.09, 128.56, 128.35, 128.25, 128.16, 128.06, 127.97, 127.87, 127.52, 98.74, 82.43, 76.47, 74.48, 74.36, 73.04, 71.27, 69.64, 60.14, 58.72, 57.70, 44.79, 43.02, 41.23, 39.77, 38.18, 36.08, 36.04, 35.55, 31.96, 30.22, 28.43, 23.05, 20.54, 20.27, 18.24, 17.17, 14.49, 14.35, 13.30, 11.34, 7.35, 5.65. **FT-IR** (film): ν_{max} (cm^{-1}) 3435.56, 2956.34, 2874.38, 2361.41, 2279.45, 1568.81, 1459.85, 1414.53, 1375, 1279.54, 1225.54, 1196.61, 1179.26, 1084.76, 1010.52, 985.45, 906.38, 856.24, 799.35, 741.5, 668.21. **HRMS** (ESI) *m/z* 757.3331 [(M+Na)$^+$; calcd for $C_{35}H_{63}O_6NaSiI$: 757.3336]. **$[\alpha]^{20}_D$** +58.3 (c 0.47, C_6H_6).

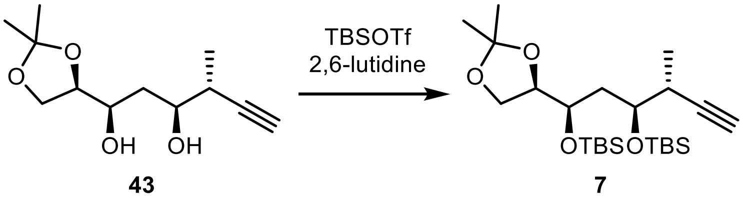
(e). Synthesis of the Southwestern Fragment (**7**)



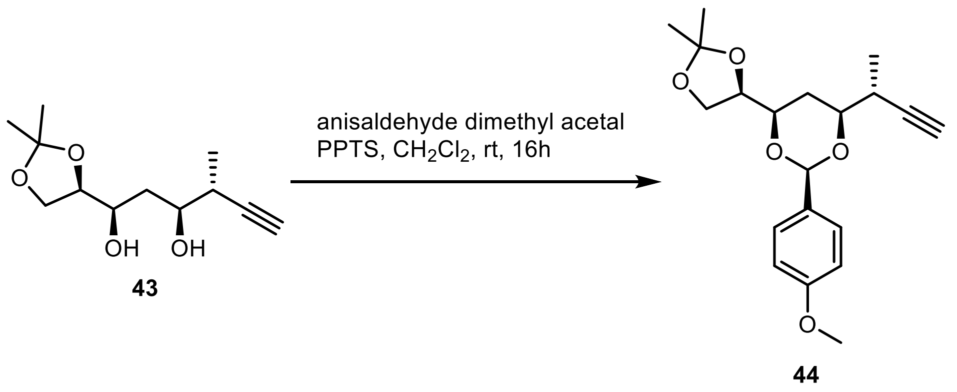
To a flame-dried 250 mL Schlenk flask equipped with magnetic stir bar was added $Pd(OAc)_2$ (71.8 mg, 0.32 mmol). The flask was evacuated and back-filled with N_2 for 3 times. THF (63 mL) was added to dissolve the palladium catalyst, and the solution was cooled to -78°C. Solid PPh_3 (83.9 mg, 0.32 mmol) was then added under a stream of argon, and the mixture was stirred for 0.5 hour. Then aldehyde **41** (1.83 g, 6.35 mmol) and methanesulfonyl ester (2.10 g, 9.53 mmol) were added sequentially followed by dropwise addition of Et_2Zn (19 mL, 1.0 M in hexanes, 19 mmol) via syringe. The reaction mixture was allowed to warm up to -20°C, during which the solution become black. The reaction was allowed to stir at -20°C for 16 hours. Additional $Pd(OAc)_2$ (35 mg, 0.15 mmol) and PPh_3 (41 mg, 0.15 mmol) were dissolved in THF (3 mL) and added via syringe. The mixture was allowed to stir for another 16 hours at same temperature. And the reaction was quenched with saturated aq. NH_4Cl (100 mL) after TLC showed full conversion. Water (100 mL) was added to dissolve inorganic salt and the organic layer was collected. The aqueous layer was extracted with ether (50 mL x 3), and the organic layers were combined, washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in-vacuo* to afford a dark brown oil. The crude material was purified by column chromatography (SiO_2, Hexanes/EtOAc *v/v* 15:1) to give compound **42** and other diastereomers (desired/undesired 4:1) as an inseparable mixture (2.49 g). The mixture was directly subjected to subsequent desilylation.



Compound **42** from above step (2.49 g, 6.01 mmol, mixture of diastereomers) was dissolved in THF (15 mL) followed by addition of tetrabutylammonium fluoride (1.0 M in THF, 15 mL, 15 mmol). The reaction was allowed to stir overnight. The reaction was concentrated by rotary evaporation and the residue purified by column chromatography (SiO_2, Hexanes/EtOAc *v/v* 3:2) to afford diol **43** (>20:1 d.r.) as a viscous, colorless gum (1.03 g, 71% over 2 steps). **^{1}H-NMR** (600 MHz, acetone-*d_6*): δ 4.11 – 4.04 (m, 2H), 3.99 (dd, *J* = 8.1, 6.7 Hz, 1H), 3.85 – 3.81 (m, 1H), 3.81 – 3.78 (m, 1H), 3.76 (dd, *J* = 8.1, 6.8 Hz, 1H), 2.60 (qdd, *J* = 6.9, 3.6, 2.5 Hz, 1H), 2.45 (d, *J* = 2.4 Hz, 1H), 1.76 – 1.64 (m, 2H), 1.35 (s, 3H), 1.29 (s, 3H), 1.18 (d, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (151 MHz, acetone-*d_6*) δ 109.71, 86.58, 79.97, 79.95, 73.48, 73.37, 72.46, 72.34, 72.31, 71.73, 71.72, 66.32, 37.12, 37.04, 33.14, 33.09, 26.96, 25.75, 16.83. **HRMS** (ESI) *m/z* 229.1466 [$(M+H)^+$; calcd for $C_{12}H_{21}O_4$: 229.1440]. **$[\alpha]^{20}_D$** +10.02 (c 1.16, $CHCl_3$).

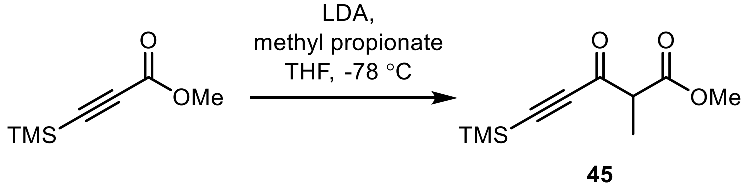


Diol **43** (1.03 g, 4.53 mmol) was dissolved in dry CH_2Cl_2 (25 mL) and the solution was cooled to -78°C. 2,6-lutidine (2.1 mL, 18.0 mmol) was then added followed by dropwise addition of TBSOTf (2.4 mL, 10.8 mmol). The reaction was stirred at -78°C for 1 hour before sat. aq. $NaHCO_3$ (25 mL) was added. The organic layer was collected and aqueous layer was extracted by dichloromethane (10 mL x 3). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 40:1) afforded pure Southwestern Fragment **7** (1.93 g, 93%) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.04 (dt, *J* = 7.6, 6.4 Hz, 1H), 3.99 – 3.92 (m, 2H), 3.78 (ddd, *J* = 8.0, 6.4, 4.3 Hz, 1H), 3.66 (t, *J* = 7.9 Hz, 1H), 2.62 (dtd, *J* = 9.9, 6.9, 2.8 Hz, 1H), 2.03 (d, *J* = 2.5 Hz, 1H), 1.87 (ddd, *J* = 13.7, 7.6, 4.3 Hz, 1H), 1.58 – 1.49 (m, 1H), 1.41 (s, 3H), 1.33 (s, 3H), 1.18 (d, *J* = 7.0 Hz, 3H), 0.89 (s, 18H), 0.10 – 0.04 (s, 12H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 109.34, 85.59, 79.20, 71.05, 70.54, 70.23, 65.99, 38.04, 31.13, 26.63, 26.06, 26.04, 25.53, 18.37, 18.24, 16.43, -3.93, -3.99, -4.47, -4.65. **FT-IR** (film): ν_{max} (cm^{-1}) 3314.07, 2930.31, 2857.99, 1691.27, 1472.38, 1370.18, 1254.47, 1077.05, 956.52, 835.99, 775.24. **HRMS** (ESI) *m/z* 457.3167 [$(M+H)^+$; calcd for $C_{24}H_{49}O_4Si_2$: 457.3169]. **$[\alpha]^{20}_D$** +17.46 (c 2.75, $CHCl_3$).

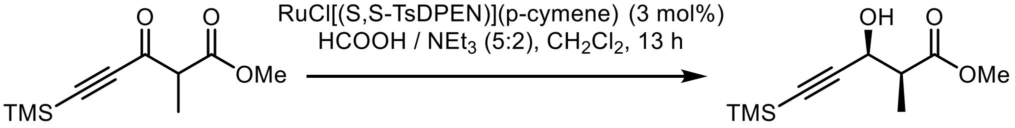


To a stirred solution of diol **43** (220.0 mg, 0.96 mmol) was added anisaldehyde dimethyl acetal (0.26 mL, 1.47 mmol) and PPTS (12.6 mg, 0.05 mmol). The reaction was allowed to stir at room temperature for 16 hours before NEt_3 (0.5 mL) was added to quench the reaction. The reaction mixture was concentrated under reduced pressure and purified by column chromatography (SiO_2, Hexanes/EtOAc *v/v* 7:1) followed by crystallization in a mixture of hexane/ethyl acetate at -20^{o}C to afford titled compound **44** as a crystalline solid (237.2 mg, 71% after recrystallization). **^{1}H-NMR** (600 MHz, acetone-*d$_6$*): *δ* 7.42 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.57 (s, 1H), 4.20 (td, *J* = 6.7, 5.3 Hz, 1H), 4.03 (dd, *J* = 8.3, 6.7 Hz, 1H), 3.99 (ddd, *J* = 11.4, 5.3, 2.4 Hz, 1H), 3.91 – 3.85 (m, 2H), 3.79 (s, 3H), 2.74 (qdd, *J* = 7.1, 4.8, 2.5 Hz, 1H), 2.49 (d, *J* = 2.5 Hz, 1H), 1.72 (dt, *J* = 12.9, 11.4 Hz, 1H), 1.59 (dt, *J* = 12.8, 2.4 Hz, 1H), 1.35 (s, 3H), 1.29 (s, 3H), 1.23 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, acetone-*d$_6$*) δ 161.00, 132.61, 128.61, 114.17, 109.96, 101.46, 86.12, 79.02, 78.39, 77.60, 71.62, 65.80, 31.94, 30.48, 29.37, 26.83, 25.83, 16.67. **FT-IR** (film): ν_{max} (cm^{-1}) 3591.77, 3243.68, 2977.55, 2956.34, 2936.09, 2862.81, 2026.82, 1905.33, 1614.13, 1589.06, 1518.67, 1454.06, 1440.56, 1394.28, 1371.14, 1346.07, 1328.71, 1301.72, 1288.22, 1248.68, 1202.40, 1161.90, 1115.62, 1093.44, 1064.51, 1039.44, 997.98, 961.34, 907.34, 862.99, 843.70, 824.42, 792.60, 778.14, 728.00, 694.25, 645.07, 626.75. **HRMS** (ESI) *m/z* 341.1871 [(M+H)$^+$; calcd for $C_{20}H_{27}O_5$: 347.1858]. **$[\alpha]^{20}_D$** -0.29 (c 0.87, MeOH).

(f). Synthesis of the Southeastern Fragment (**8**)

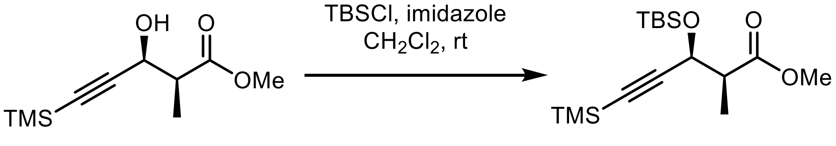


To an oven-dried, N_2 flushed 1L round bottom flask equipped with magnetic stir bar were added diisopropylamine (27.2 mL, 192.6 mmol) and dry THF (400 mL). The solution was cooled to 0^{o}C and n-BuLi (2.5 M in hexane, 77 mL, 192.6 mmol) was added dropwise via syringe. The solution was stirred at 0^{o}C for 0.5 hour, then cooled to -78^{o}C. Methyl propionate (18.5 mL, 192.6 mmol) was then added to the stirring LDA suspension dropwise at -78^{o}C over 15 min, and the resulting mixture was stirred at -78^{o}C for 0.5 hour to allow formation of enolate. Then Methyl (trimethylsilyl)propiolate (10.03 g, 64.2 mmol) was added dropwise via syringe and the reaction mixture was stirred for another 2 hours at -78^{o}C. The reaction is quenched by saturate aq. NH_4Cl (300 mL). The organic layer was separated and the aqueous layer extracted with ether (100 mL x 3). The organic layers were combined and washed with brine (100 mL), dried over Na_2SO_4, filtered and concentrated *in-vacuo*. Column chromatography (SiO_2, CH_2Cl_2) afforded compound **45** (5:1 enol/ketone as indicated by ^{1}H-NMR) as an orange oil (12.01 g, 88%). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 11.93 (s, 3H), 3.79 (s, 16H), 3.76 (s, 3H), 3.59 (q, *J* = 7.3 Hz, 1H), 1.91 (s, 16H), 1.44 (d, *J* = 7.3 Hz, 3H), 0.25 (s, 58H). **^{13}C-NMR** (126 MHz, $CDCl_3$): *δ* 182.81, 173.43, 170.12, 151.38, 105.01, 104.70, 101.39, 100.26, 97.46, 54.68, 52.67, 52.15, 13.25, 12.99, -0.37, -0.72. **FT-IR** (film): v_{max} (cm^{-1}) 2957.30, 1749.12, 1650.77, 1601.59, 1441.53, 1388.50, 1345.11, 1237.11, 1155.15, 1082.83, 908.31, 848.53, 761.74, 702.93, 660.50. **HRMS** (EI) *m/z* 212.0865 [(M)$^+$; calcd for $C_{10}H_{16}O_3Si$: 212.0869].



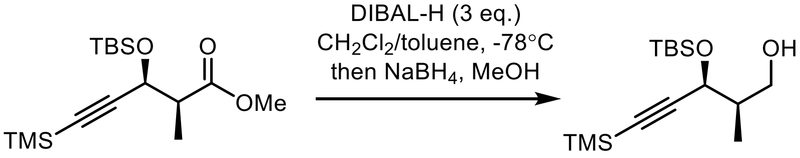
45 **46**

To a flame-dried 1L Schlenk flask equipped with magnetic stir bar was added RuCl[(*S,S*-TsDPEN)](*p*-cymene) (812.8 mg, 1.28 mmol). The flask was evacuated and back-filled with N_2 for 3 times. CH_2Cl_2 (200 mL) was added to dissolve the catalyst. Then 5:2 formic acid / triethylamine azeotrope (33 g) was added via syringe followed by addition of compound **45** (9.04 g, 42.8 mmol). The reaction mixture was stirred under N_2 atmosphere for 13 hours. The reaction was quenched by saturate aqueous $NaHCO_3$ (100 mL) after TLC showed complete conversion of starting material. The organic layer was separated and aqueous layer extracted with CH_2Cl_2 (50 mL x 3). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 7:1-5:1) afforded compound **46** as a colorless oil (7.53 g, 18:1 d.r., 83%). **^{1}H-NMR** (500 MHz, $CDCl_3$): *δ* 4.62 (d, *J* = 4.0 Hz, 1H), 3.73 (s, 3H), 2.87 (brs, 1H), 2.76 (qd, *J* = 7.3, 4.1 Hz, 1H), 1.30 (d, *J* = 7.2 Hz, 3H), 0.16 (s, 10H). **^{13}C-NMR** (126 MHz, $CDCl_3$): *δ* 174.63, 103.78, 90.84, 64.25, 52.15, 45.46, 11.84, -0.07. **FT-IR** (film): v_{max} (cm^{-1}) 3468.35 (br), 2957.30, 2900.41, 2175.31, 1740.44, 1457.92, 1436.71, 1376.93, 1348.00, 1250.61, 1203.36, 1122.37, 1094.40, 1066.44, 1031.43, 966.16, 844.67, 760.78, 701.00, 663.39. **HRMS** (ESI) *m/z* 215.1089 [(M+H)$^+$; calcd for $C_{11}H_{18}O_3Si$: 215.1103]. **$[\alpha]^{20}_D$** -13.15 (c 1.58, $CHCl_3$). The absolute configuration and enantiomeric excess of compound **46** was determined via Mosher ester analysis (See **Figure S109**, **Table S26**).



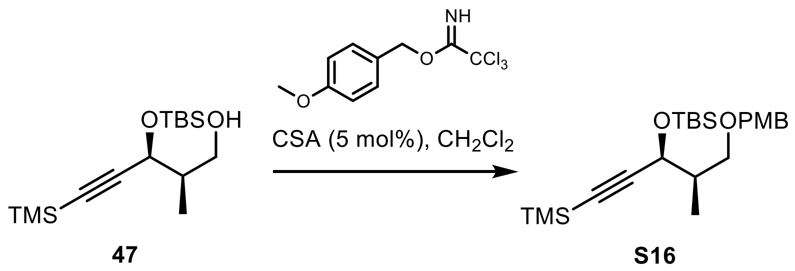
46 **S15**

In an oven dried 1L round bottom flask, compound **46** (7.53 g, 35.1 mmol) was dissolved in dry CH_2Cl_2 (100 mL). Then imidazole (3.58 g, 52.7 mmol) and TBSCl (6.35 g, 42.1 mmol) were added subsequently. The mixture was stirred at room temperature for 16 hours before aqueous $NaHCO_3$ was added to quench the reaction. The organic layer was collected and aqueous layer extracted with CH_2Cl_2 (50 mL x 3). The organic layers were combined and dried over Na_2SO_4, filtered and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 15:1) afforded compound **S15** as a colorless oil (10.33 g, 18:1 d.r., 90%). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 4.73 (d, J = 4.9 Hz, 1H), 3.67 (s, 3H), 2.72 – 2.60 (m, 1H), 1.26 (d, J = 6.9 Hz, 3H), 0.87 (s, 9H), 0.18 – 0.05 (m, 15H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 173.81, 105.61, 90.19, 64.57, 51.80, 46.96, 25.77, 18.26, 11.27, -0.14, -4.43, -5.15. **FT-IR** (film): ν_{max} (cm^{-1}) 2957.30, 2898.49, 2857.99, 2176.27, 1750.08, 1472.38, 1461.78, 1434.78, 1408.75, 1380.78, 1344.14, 1251.58, 1199.51, 1131.05, 1100.19, 1071.26, 1027.87, 983.52, 939.16, 892.88, 841.77, 778.14, 760.78, 690.39, 665.32. **HRMS** (ESI) *m/z* 329.1946 [$(M+H)^{+;}$ calcd for $C_{16}H_{33}O_3Si_2$: 329.1968]. **$[\alpha]^{20}_D$** -100.39 (c 0.99, $CHCl_3$).

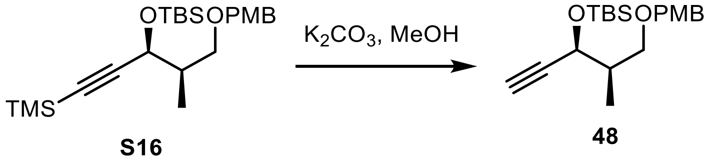


S15 **47**

In a flame dried 100 mL round bottom flask equipped with magnetic stir bar, compound **S15** (328 mg, 1.0 mmol) was dissolved in dry CH_2Cl_2 (10 mL). The mixture was cooled to -78^{o}C and DIBAL-H (1.0 M in toluene, 2.5 mL, 2.5 mmol) was added dropwise via syringe. After the addition was finished, the reaction mixture was allowed to stir for 2 hours at -78^{o}C. The reaction was then quenched by sequential addition of EtOAc (10 mL) and saturate aq. Rochelle salt (20 mL), and the biphasic mixture was stirred at room temperature for 1 hour. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (50 mL x 3). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. The crude product was re-dissolved in MeOH (10mL) and the solution was cooled to 0^{o}C. $NaBH_4$ (50 mg) was added to reduce the aldehyde in the crude mixture. The reaction was then quenched by addition of sat. aq. NH_4Cl (10 mL). The mixture was extracted with diethyl ether (10 mL x 3), dried over Na_2SO_4, filtered, and concentrated *in-vacuo* to afford pure compound **47** (269.5 mg, 89%). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 4.48 (d, *J* = 4.5 Hz, 1H), 3.81 (dd, *J* = 11.0, 8.1 Hz, 1H), 3.56 (dd, *J* = 11.0, 3.8 Hz, 1H), 2.40 (s, 1H), 2.01 (ddq, *J* = 10.9, 7.2, 3.4, 2.9 Hz, 1H), 0.95 – 0.87 (m, 13H), 0.15 (d, *J* = 17.9 Hz, 16H). **^{13}C-NMR** (126 MHz, $CDCl_3$): *δ* 105.22, 91.19, 67.76, 65.83, 41.41, 25.88, 18.27, 12.70, -0.09, -4.39, -5.07. **FT-IR** (film): ν_{max} (cm^{-1}) 3358.43, 2958.27, 2930.31, 2897.52, 2857.99, 2173.38, 1472.38, 1408.75, 1389.46, 1376.93, 1360.53, 1250.61, 1079.94, 1035.59, 983.52, 938.20, 908.31, 841.77, 778.14, 760.78, 698.11, 682.68, 665.32. **HRMS** (ESI) *m/z* 301.1999 [$(M+H)^+$; calcd for $C_{15}H_{33}O_2Si_2$: 301.2019]. **$[\alpha]^{20}_D$** -54.6 (c 1.13, $CHCl_3$).

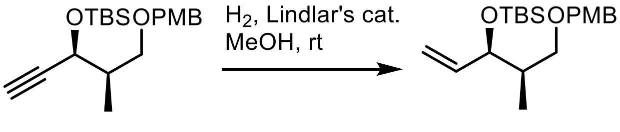


In an oven dried 250 mL round bottom flask equipped with magnetic stir bar, compound **47** (7.54 g, 25.1 mmol) was dissolved in dry CH_2Cl_2 (100 mL). PMB trichloroacetimidate (9.22 g, 32.6 mmol) was added followed by addition of CSA (291 mg, 1.25 mmol). The mixture was allowed to stir at room temperature for 19 hours, during which white precipitate was formed. After TLC showed complete conversion, the reaction mixture was filtered and concentrated under reduced pressure. Hexanes (100 mL) was added, and the resulting trichloroacetimide precipitation was filtered off. The filtrate was then concentrated via rotary evaporation to afford crude **S16** as a yellow oil, which was directly used in next step.



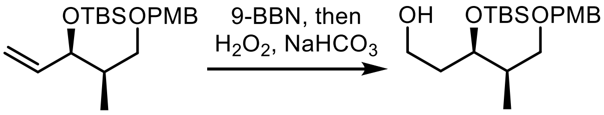
In a 250 mL round bottom flask equipped with magnetic stir bar, crude **S16** from previous step was dissolved in MeOH (50 mL). Powdery K_2CO_3 (3.45 g, 25 mmol) was added and the reaction mixture was stirred at room temperature for 2 hours. Then water was added and the mixture was extracted with ether (50 mL x 4). The organic layers were combined and washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 30:1) afforded compound **48** as a colorless oil (7.40 g, 18:1 d.r., 80% over 2 steps). **^{1}H-NMR** (500 MHz, $CDCl_3$): *δ*

7.25 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.54 (dd, *J* = 3.8, 2.2 Hz, 1H), 4.46 – 4.36 (m, 2H), 3.81 (s, 3H), 3.47 (dd, *J* = 9.1, 7.5 Hz, 1H), 3.34 (dd, *J* = 9.1, 5.9 Hz, 1H), 2.34 (d, *J* = 2.2 Hz, 1H), 2.00 (ddt, *J* = 10.9, 7.1, 4.0 Hz, 1H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.89 (s, 10H), 0.14 (s, 3H), 0.09 (s, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): *δ* 159.25, 130.80, 129.36, 113.89, 85.00, 72.90, 72.58, 71.59, 63.11, 55.42, 40.70, 25.90, 18.33, 11.73, -4.44, -5.13. **FT-IR** (film): v_{max} (cm^{-1}) 3308.29, 2955.38, 2930.31, 2857.02, 1613.16, 1586.16, 1513.85, 1463.71, 1360.53, 1301.72, 1249.65, 1172.51, 1126.22, 1086.69, 1040.41, 1006.66, 939.16, 839.84, 778.14, 672.07, 625.79. **HRMS** (ESI) *m/z* 349.2200 [(M+H)$^+$; calcd for $C_{20}H_{33}O_3Si$: 349.2199]. **[α]$^{20}_D$** -26.48 (c 0.82, $CHCl_3$).



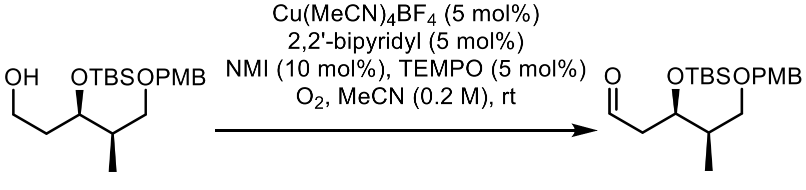
48 **S17**

To an oven-dried 100 mL round bottom flask equipped with magnetic stir bar, compound **48** (5.35 g, 15.3 mmol) and Lindlar's catalyst (5% Pd on $CaCO_3$, 53.5 mg, 1% by weight) was added. The flask was evacuated and back-filled with N_2 for 3 times. MeOH (30 mL) was added via syringe. Then a H_2 balloon was attached to the top of flask and a stream of H_2 was bubbled through the solution for 5 minutes. The reaction mixture was vigorously stirred for another 55 minutes and the progress of conversion was monitored by TLC. After the reaction reached complete conversion, the septum was removed to release the excess H_2, and the mixture was filtered through a pad of celite and concentrated *in-vacuo* to afforded compound **S17** as a colorless oil (5.12 g, 95%). The crude product was directly used in the next step without purification.



S17 **49**

To a flame-dried 250 mL round bottom flask equipped with magnetic stir bar was added compound **S17** (5.12 g, 15.0 mmol). The flask was evacuated and back-filled with N_2 for 3 times. THF (30 mL) was added, and the resulting solution was cooled to 0°C. Then 9-BBN (0.5 M in THF, 33 mL, 16.5 mmol) was added dropwise via syringe. The reaction mixture was warmed up to room temperature and stirred at room temperature for 15 hours. After the completion of hydroboration, the reaction mixture was cooled to 0°C and saturate aq. $NaHCO_3$ (60 mL) was added followed by dropwise addition of 30% aq. H_2O_2 (8.0 mL). The resulting mixture was stirred at 0°C for 0.5 hour and the organic layer was collected via separatory funnel. The aqueous layer was extracted with diethyl ether (50 mL x 3). The organic layers were combined and sequentially washed with saturate aq. $Na_2S_2O_3$ (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 5:1 – 2:1) afforded compound **49** as a colorless oil (4.20 g, 76%). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.44 (d, *J* = 11.5 Hz, 1H), 4.39 (d, *J* = 11.6 Hz, 1H), 3.91 (ddd, *J* = 7.1, 5.1, 4.1 Hz, 1H), 3.80 (s, 3H), 3.74 – 3.65 (m, 2H), 3.47 (dd, *J* = 9.0, 5.9 Hz, 1H), 3.25 (dd, *J* = 9.0, 6.9 Hz, 1H), 1.99 – 1.85 (m, 2H), 1.80 – 1.71 (m, 1H), 1.71 – 1.63 (m, 1H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.88 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): *δ* 159.27, 130.82, 129.36, 113.90, 72.91, 72.30, 71.93, 60.53, 55.42, 38.83, 36.29, 26.03, 18.21, 12.81, -4.26, -4.43. **FT-IR** (film): ν_{max} (cm^{-1}) 3420.14(br), 2954.41, 2929.34, 2856.06. 1613.16, 1586.16, 1513.85, 1462.74, 1361.50, 1301.72, 1249.65, 1173.47, 1085.73, 1039.44, 836.95, 775.24. **HRMS** (ESI) *m/z* 369.2458 [$(M+H)^+$; calcd for $C_{20}H_{37}O_4Si$: 369.2461]. **$[\alpha]^{20}_D$** +16.6 (c 0.85, $CHCl_3$).

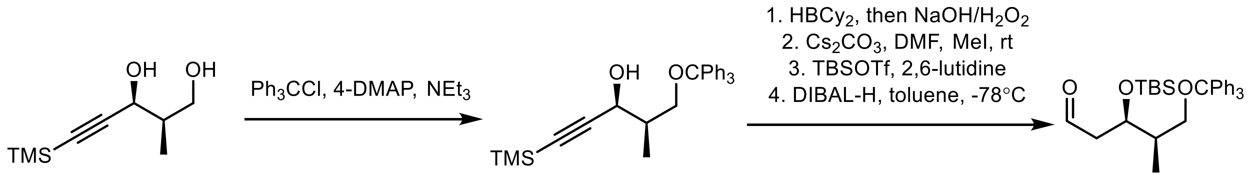


49 **8**

To a 250 mL round bottom flask equipped with magnetic stir bar were added compound **49** (4.20 g, 11.4 mmol), $Cu(MeCN)_4BF_4$ (179.3 mg, 0.57 mmol), 2,2'-bipyridyl (89.0 mg, 0.57 mmol), TEMPO (89.0 mg, 0.57 mmol) and NMI (90 μL, 1.14 mmol). MeCN (50 mL) was added and the mixture was stirred to dissolve all solids. Then a stream of O_2 was bubbled through the solution for 5 minutes and the reaction mixture was vigorously stirred under an O_2 atmosphere for 3 hours, during which the color of the solution turned from dark brown to greenish blue. Then water (300 mL) was added and the mixture was extracted with hexanes (50 mL x 4). The organic layer was dried over Na_2SO_4, filtered and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 15:1) afforded Southeastern Fragment **8** as a colorless oil (3.47 g, 87%). **^{1}H-NMR** (500 MHz, $CDCl_3$): *δ* 9.77 (t, *J* = 2.5 Hz, 1H), 7.26 – 7.22 (m, 2H), 6.90 – 6.84 (m, 2H), 4.42 (d, *J* = 11.4 Hz, 1H), 4.38 (d, *J* = 11.5 Hz, 1H), 4.34 (td, *J* = 5.9, 3.8 Hz, 1H), 3.81 (s, 3H), 3.43 (dd, *J* = 9.1, 6.7 Hz, 1H), 3.28 (dd, *J* = 9.1, 5.9 Hz, 1H), 2.54 (pt, *J* = 5.5, 3.1 Hz, 2H), 1.89 (qd, *J* = 6.7, 3.8 Hz, 1H), 0.91 (d, *J* = 6.9 Hz, 3H), 0.86 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): *δ* 202.17, 159.27, 130.64, 129.37, 113.89, 77.41, 77.36, 76.91, 72.83, 71.81, 68.51, 55.41, 49.17, 39.71, 25.94, 25.90, 18.18, 12.17, -4.29, -4.56. **FT-IR** (film): ν_{max} (cm^{-1}) 2955.38, 2930.31, 2895.59, 2856.06, 2723.00, 1725.98, 1613.16, 1586.16, 1513.85, 1463.71, 1361.50, 1301.72, 1249.65, 1172.51, 1087.66, 1038.48, 836.96, 776.21. **HRMS** (ESI) *m/z*

389.2126 [$(M+Na)^{+;}$ calcd for $C_{20}H_{34}O_4NaSi$: 389.2124]. **[α]$^{20}_{D}$** +8.02 (c 1.23, $CHCl_3$).

Synthesis of Triphenylmethyl Protected Southeastern Fragment (**50**) for Crystallography Analysis



47'

50

To a stirred solution of compound **47’** (780 mg, 4.19 mmol, prepared by exposure of compound **47** to aqueous HCl) in CH_2Cl_2 (15 mL) was added NEt_3 (0.94 mL, 6.70 mmol), 4-DMAP (1 chip) and TrCl (1.28 g, 4.60 mmol). The reaction was allowed to stir for 16 hours before sat. $NaHCO_3$ (10 mL) was added. The reaction mixture was extracted with CH_2Cl_2 (10 mL x 3). The organic layer was combined, dried over Na_2SO_4, filtered, and concentrated *in-vacuo* to afford crude product (1.63 g, 91%), which was directly used in further transformation.

To a flame-dried 100 mL round bottom flask was sequentially added THF (20 mL), cyclohexene (2.3 mL, 22.92 mmol, redistilled) and $BH_3{\cdot}SMe_2$ (0.98 mL, 10.3 mmol). The resulting white suspension was allowed to stir at rt for 3 hours before mono-protected alcohol from above step (1.63 g, 3.82 mmol, dissolved in 4mL THF followed by 4mL x 2 rinse) was added. The reaction mixture was allowed to stir for 20 hours. 1N aq. NaOH (10 mL) and 30% aq. H_2O_2 (10 mL) were then added. The mixture was allowed to stir for another 12 hours to allow complete oxidation of the borane. The pH of the aqueous phase was carefully adjusted to 4 by addition of 1N HCl. The crude mixture was then extracted with EtOAc (10 mL x 3). The organic layers were combined and sequentially washed with sat. aq. $Na_2S_2O_2$ (10 mL x 2) and brine (10 mL), dried over Na_2SO_4, filtered, and concentrated *in-vacuo* to afford the mixture of desired carboxylic acid and cyclohexanol. The crude product was directly subjected to the next step without purification.

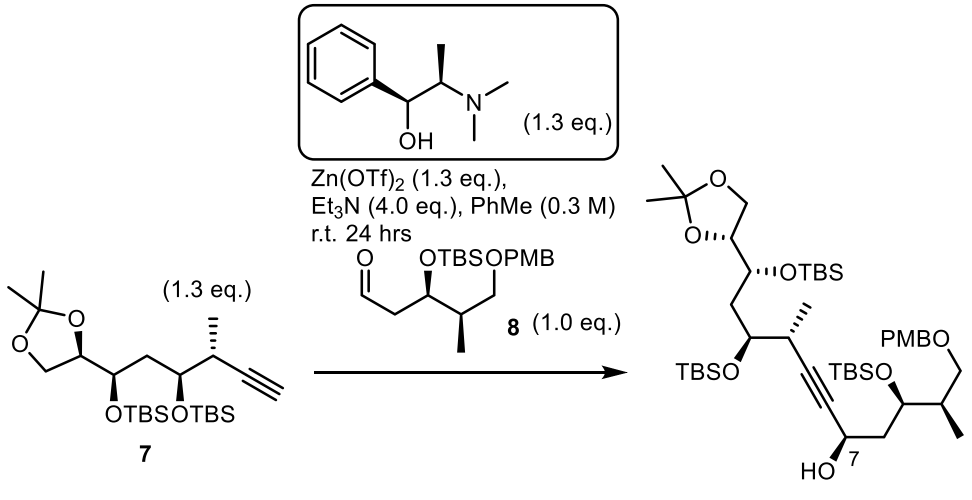
The crude carboxylic acid obtained above was dissolved in DMF (7.6 mL). Cesium carbonate (2.48 g, 7.60 mmol) and methyl iodide (0.47 mL, 7.6 mmol) were sequentially added. The reaction mixture was allowed to stir at room temperature for 16 hours. Water (40 mL) was added to the reaction mixture and the aqueous phase was extracted with ethyl acetate (20 mL x 3). The organic layers were combined and washed with aq. NH_4Cl (20 mL x 3) and brine (20 mL). The organic layer was dried over

Na_2SO_4, filtered, and concentrated *in-vacuo* to afford crude methyl ester, which was directly used in the subsequent step without purification.

In an oven dried 100mL round bottom flask, crude methyl ester from above step was dissolved in dry CH_2Cl_2 (38 mL). Then 2,6-lutidine (2.2 mL, 19.1 mmol) and TBSOTf (3.0 mL, 13.37 mmol) were added subsequently. The mixture was stirred at room temperature for 16 hours before aqueous $NaHCO_3$ was added to quench the reaction. The organic layer was collected and aqueous layer extracted with CH_2Cl_2 (20 mL x 3). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 10:1) afforded the corresponding TBS ether as a colorless oil (1.18 g, 59% over 3 steps).

In a flame dried 100 mL round bottom flask equipped with magnetic stir bar, TBS protected ester from above step (1.1782 g, 2.27 mmol) was dissolved in dry CH_2Cl_2 (22 mL). The mixture was cooled to -78^{o}C and DIBAL-H (1.0 M in toluene, 2.3 mL, 2.3 mmol) was added dropwise via syringe. After the addition was finished, the reaction mixture was allowed to stir for 2 hours at -78^{o}C. The reaction was then quenched by saturate aq. Rochelle salt (20 mL), and the biphasic mixture was stirred at room temperature for 1 hour. The organic layer was then separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL x 3). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 15:1) afforded pure compound **50** as a colorless oil (1.03 g, 92%), which crystallized upon storage in refrigerator. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 9.74 (t, *J* = 2.4 Hz, 1H), 7.46 – 7.40 (m, 6H), 7.33 – 7.19 (m, 8H), 4.28 (td, *J* = 6.0, 3.9 Hz, 1H), 3.13 (dd, *J* = 9.0, 5.7 Hz, 1H), 3.00 (dd, *J* = 9.0, 6.7 Hz, 1H), 2.48 (dd, *J* = 6.0, 2.4 Hz, 2H), 1.89 (tdd, *J* = 6.8, 5.8, 3.9 Hz, 1H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.74 (s, 9H), -0.02 (s, 3H), -0.10 (s, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 202.28, 144.37, 128.85, 127.89, 127.06, 86.71, 69.10, 65.18, 48.87, 40.17, 25.88, 18.08, 12.74, -4.37, -4.55.

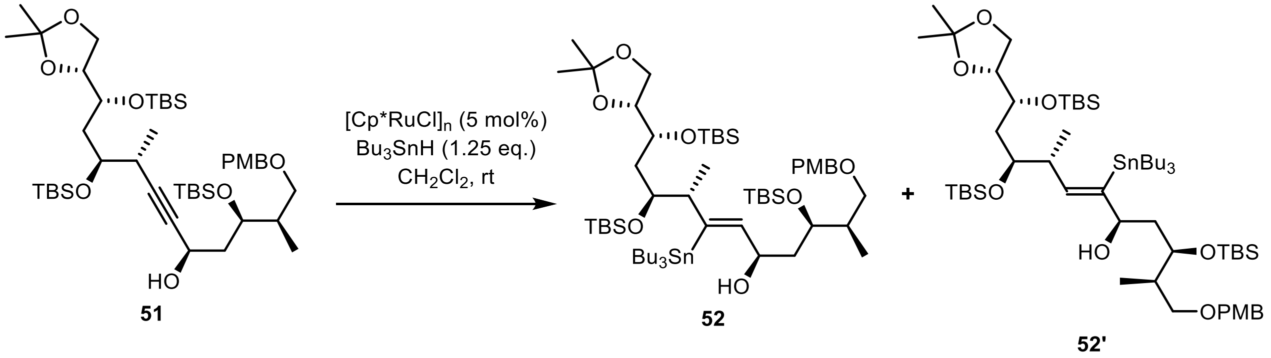
(g). Synthesis of the Southern Hemisphere (**2**)



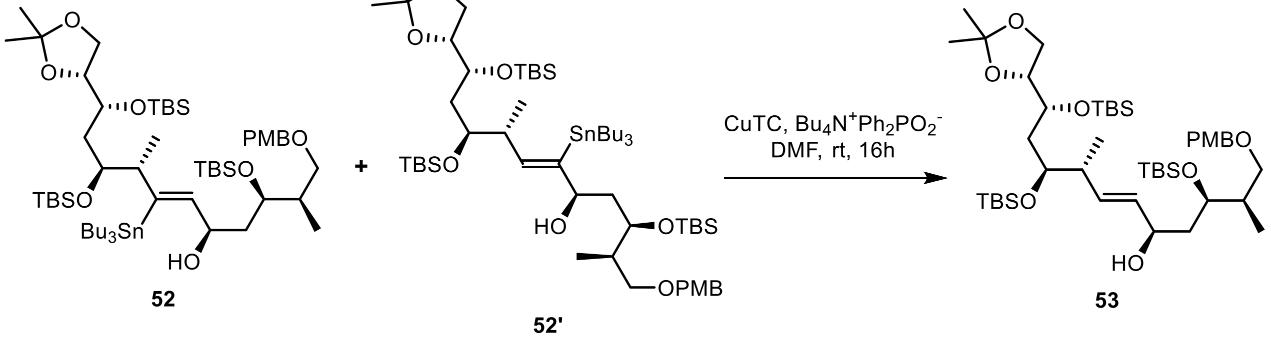
51

To an oven-dried 100 mL round bottom flask equipped with magnetic stir bar were added Zn(OTf)$_2$ (2.30 g, 6.37 mmol, dried at 120^{o}C under vacuum for 2 hours), (+)-N-methylephedrine (1.14 g, 6.37 mmol), NEt$_3$ (2.7 mL, 19.6 mmol) and dry toluene (16 mL). The above mixture was stirred at room temperature for 2 hours. Alkyne **7** (2.90 g, 6.37 mmol) was added via syringe, and the resulting mixture was stirred at room temperature for another 2 hours. Then aldehyde **8** (1.90 g, 5.33 mmol) was added dropwise, and the flask was rinsed with toluene (3 mL). The reaction was allowed to stir for 20 hours. Saturate aq. NH$_4$Cl (30 mL) was added and the organic layer was collected. The aqueous layer was extracted with ethyl acetate (20 mL x 3). The organic layers were combined, dried over MgSO$_4$, filtered, and concentrated *in-vacuo*. Column chromatography (SiO$_2$, Hexanes/EtOAc *v/v* 20:1 – 15:1) afforded compound **51** as a colorless oil (3.91 g, 90%, >20:1 d.r. at C7). **^{1}H-NMR** (500 MHz, CDCl$_3$): δ 7.25 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.44 – 4.38 (m, 3H), 4.11 (td, *J* = 6.8, 5.3 Hz, 1H), 4.03 (dt, *J* = 7.9, 3.8 Hz, 1H), 3.99 (ddd, *J* = 7.2, 5.7, 3.5 Hz, 1H), 3.95 (dd, *J* = 8.3, 6.7 Hz, 1H), 3.83 (q, *J* = 6.0 Hz, 1H), 3.80 (s, 3H), 3.78 (dd, *J* = 8.3, 6.9 Hz, 1H), 3.53 (dd, *J* = 8.9, 5.0 Hz, 1H), 3.22 (t, *J* = 8.4 Hz, 1H), 2.66 – 2.56 (m, 2H), 1.95 (tt, *J* = 16.6, 6.4 Hz, 2H), 1.76 (ddd, *J* = 14.1, 8.6, 4.0 Hz, 1H), 1.73 – 1.66 (m, 1H), 1.50 (dt, *J* = 13.7, 6.8 Hz, 2H), 1.44 (s, 3H), 1.32 (s, 3H), 1.12 (d, *J* = 7.0 Hz, 3H), 0.95 – 0.85 (m, 30H), 0.11 – 0.03 (m, 18H). **^{13}C-NMR** (126 MHz, CDCl$_3$): δ 159.19, 130.95, 129.30, 113.86, 109.40, 86.50, 83.84, 78.59, 72.84, 72.04, 70.67, 70.64, 70.09, 65.56, 59.49, 55.41, 41.53, 39.19, 37.24, 31.61, 26.44, 26.07, 26.02, 26.01, 25.08, 18.27, 18.23, 18.18, 15.25, 12.91, -4.07, -4.21, -4.31, -4.39, -4.46, -4.52. **FT-IR** (film): ν_{max} (cm^{-1}) 3467.38 (br), 2955.38, 2930.31, 2893.66, 2857.02, 1613.16, 1587.13, 1513.85, 1471.42, 1462.74, 1301.72, 1250.61, 1212.04, 1171.54, 1075.72, 1005.70, 955.55, 938.20, 836.96, 776.21, 668.21. **HRMS** (ESI) *m/z* 845.5214 [(M+Na)$^+$; calcd for $C_{44}H_{82}O_8NaSi_3$:

845.5215]. **[α]$^{20}_{D}$** +20.07 (c 0.65, CHCl$_3$).

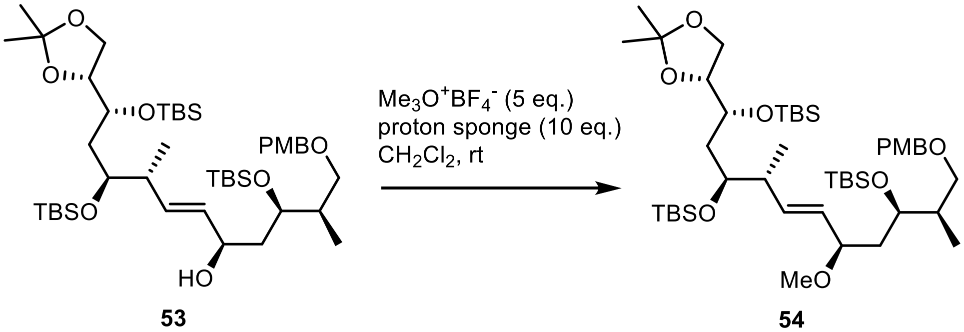


To a flame dried 100 mL round bottom flask equipped with magnetic stir bar was added compound **51** (3.52 g, 4.29 mmol) and [Cp*RuCl]$_4$ (58 mg, 0.214 mmol). The flask was evacuated and back-filled with argon for 3 times and CH$_2$Cl$_2$ (21 mL) was added. The content was stirred at room temperature to give a purple solution. Then the reaction mixture was cooled to -20^{o}C and Bu$_3$SnH (1.4 mL, 5.15 mmol) was slowly added via syringe pump over 1.5 hours, during which the color of the solution turned from purple to brown. The reaction mixture allowed to cool to 0^{o}C during the addition period and was stirred for another 10 minutes after the addition was completed. Then all volatiles are removed under reduced pressure. Column chromatography (SiO$_2$, Hexanes/EtOAc *v/v* 40:1) afforded vinylstannane **52** (distal) and **52'** (proximal) as a separable 1:2 mixture (3.45 g, 72% combined yield) and recovered starting material (806 mg, 23% recovery). Both vinylstannanes were directly subjected to the next step without further separation or characterization.

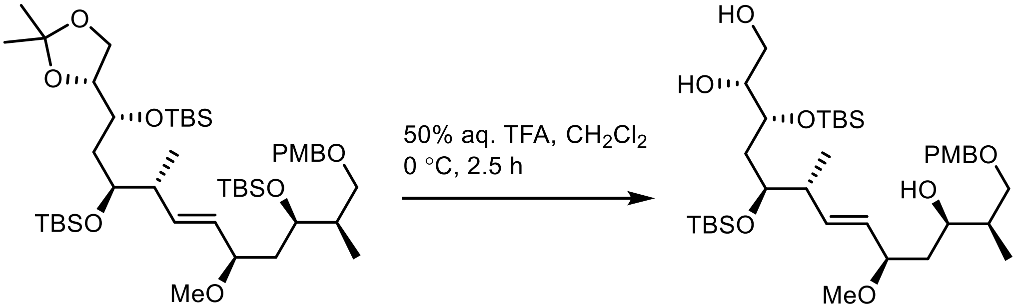


To an oven-dried 250 mL round bottom flask equipped with a stir bar was added the mixture of compound **52** and compound **52'** (3.40 g, 3.06 mmol), copper(I) thiophene-2-carboxylate (1.28 g, 6.73 mmol, pre-washed with MeOH to remove trace Cu(II) and dried under vacuum overnight) and Bu$_4$NPh$_2$PO$_2$ (3.52 g, 7.65 mmol). The flask was evacuated and back-filled with argon for 3 times. Dry & degassed DMF (30 mL) was added. The resulting suspension was stirred at room temperature for

16 hours. Then the reaction mixture was transferred to a stirred saturated aqueous solution of NH_4Cl (100 mL) via cannula. The flask was rinsed with ether (30 mL x 2). The organic layer was collected, and aqueous layer extracted with diethyl ether (30 mL x 3). The organic layer was combined and dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 10:1) afforded compound **53** as a colorless oil (2.52 g, quant.). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.58 (dd, *J* = 15.5, 8.3 Hz, 1H), 5.43 (dd, *J* = 15.6, 6.8 Hz, 1H), 4.42 (d, *J* = 11.7 Hz, 1H), 4.38 (d, *J* = 11.7 Hz, 1H), 4.20 (ddd, *J* = 9.9, 6.9, 3.8 Hz, 1H), 4.02 (q, *J* = 6.6 Hz, 1H), 3.95 (dt, *J* = 7.8, 4.1 Hz, 1H), 3.91 (dd, *J* = 8.3, 6.6 Hz, 1H), 3.85 (td, *J* = 5.4, 2.7 Hz, 1H), 3.80 (s, 3H), 3.75 (ddd, *J* = 9.3, 5.7, 4.0 Hz, 1H), 3.66 (t, *J* = 7.7 Hz, 1H), 3.49 (dd, *J* = 9.0, 5.4 Hz, 1H), 3.22 (dd, *J* = 9.0, 7.3 Hz, 1H), 2.30 (td, *J* = 9.0, 4.6 Hz, 1H), 1.95 (dt, *J* = 11.8, 6.6 Hz, 1H), 1.66 – 1.50 (m, 3H), 1.44 (ddd, *J* = 13.9, 8.6, 5.5 Hz, 1H), 1.39 (s, 3H), 1.32 (s, 3H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.91 – 0.81 (m, 27H), 0.10 – 0.03 (m, 18H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 159.22, 134.45, 132.42, 131.01, 129.27, 113.87, 109.35, 78.77, 72.79, 72.40, 71.90, 70.91, 70.26, 69.80, 65.62, 55.42, 41.11, 40.75, 39.01, 37.43, 26.57, 26.09, 26.04, 25.44, 18.31, 18.27, 18.24, 16.99, 12.86, -3.96, -4.24, -4.40, -4.44, -4.56. **FT-IR** (film): ν_{max} (cm^{-1}) 3483.78 (br), 2929.34, 1742.37, 1613.16, 1587.13, 1513.85, 1462.74, 1369.21, 1250.61, 1075.12, 835.99, 775.24, 666.29. **HRMS** (ESI) *m/z* 847.5379 [$(M+Na)^+$; calcd for $C_{44}H_{84}O_8NaSi_3$: 847.5372]. **$[\alpha]^{20}_D$** +16.83 (c 0.56, $CHCl_3$). The absolute configuration of compound **53** was determined via Mosher ester analysis (See **Table S27**).



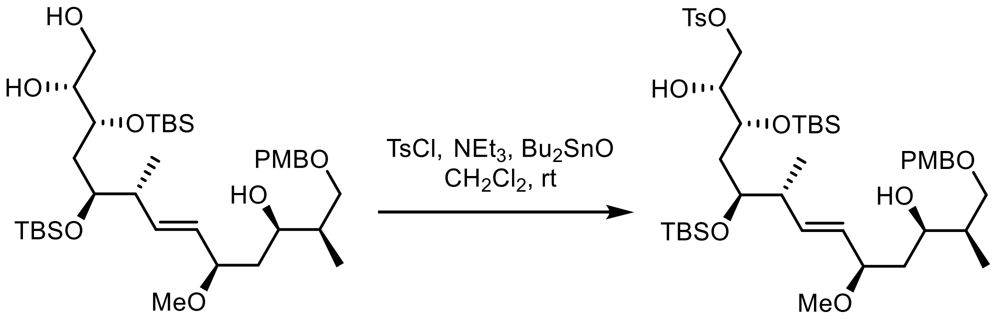
To an oven-dried 100 mL 3-neck round bottom flask equipped with a stir bar was added compound **53** (3.14 g, 3.81 mmol) and proton sponge (4.90 g, 22.9 mmol). The flask was evacuated and back-filled with N_2 for 3 times. Dry CH_2Cl_2 (40 mL) was added to dissolve all solid. $Me_3O^+{\cdot}BF_4^-$ (1.69 g, 11.40 mmol) was quickly weighed and added to the above solution under a stream of N_2. The flask was wrapped with aluminum foil and stirred at room temperature for 5 hours. Additional Me_3OBF_4 (0.7040 g) and proton sponge (2.00 g) were added. Saturate aqueous $NaHCO_3$ (20 mL) was added to quench the reaction. The organic layer was collected and the aqueous layer extracted with CH_2Cl_2 (20 mL x 3). The organic layer was combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was dissolved in a minimal amount of EtOAc and hexanes (30 mL) was added. The white precipitate formed was filtered off, and the filtrate was concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 25:1) afforded compound **54** as a colorless oil (2.67 g, 84%). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 7.24 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 5.58 (dd, J = 15.6, 8.4 Hz, 1H), 5.22 (dd, J = 15.6, 8.3 Hz, 1H), 4.42 (d, J = 11.7 Hz, 1H), 4.38 (d, J = 11.6 Hz, 1H), 4.01 (q, J = 6.6 Hz, 1H), 3.91 (td, J = 7.7, 5.3 Hz, 2H), 3.85 (ddd, J = 7.9, 5.3, 2.1 Hz, 1H), 3.80 (s, 3H), 3.76 – 3.71 (m, 1H), 3.62 (t, J = 7.8 Hz, 1H), 3.57 (td, J = 8.6, 4.0 Hz, 1H), 3.51 (dd, J = 8.9, 5.3 Hz, 1H), 3.21 (s, 3H), 3.18 (d, J = 8.7 Hz, 1H), 2.30 (t, J = 7.4 Hz, 1H), 1.90 (d, J = 6.4 Hz, 1H), 1.67 (ddd, J = 13.7, 8.9, 4.3 Hz, 1H), 1.57 (ddd, J = 12.8, 8.4, 4.2 Hz, 1H), 1.51 – 1.38 (m, 2H), 1.36 (s, 3H), 1.30 (s, 4H), 1.01 (d, J = 6.8 Hz, 3H), 0.92 – 0.85 (m, 33H), 0.12 – 0.01 (m, 18H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 159.15, 135.21, 131.46, 131.13, 129.25, 113.82, 109.27, 79.15, 78.77, 72.71, 72.37, 72.03, 70.39, 69.88, 65.72, 55.78, 55.40, 40.70, 40.42, 39.10, 37.75, 26.57, 26.11, 26.06, 26.04, 25.48, 22.80, 22.49, 18.33, 18.30, 18.21, 17.65, 14.27, 14.21, 12.27, -3.92, -3.94, -4.21, -4.34, -4.47, -4.60. **FT-IR** (film): ν_{max} (cm^{-1}) 2955.38, 2885.95, 2857.02, 1613.16, 1587.13, 1513.85, 1471.42, 1379.82, 1369.21, 1301.72, 1250.61, 1213.01, 1075.12, 1005.70, 976.77, 955.56, 939.16, 913.13, 836.96, 775.24, 669.18. **HRMS** (ESI) *m/z* 861.5546 [(M+Na)$^+$; calcd for $C_{45}H_{86}O_8NaSi_3$: 861.5528]. **$[\alpha]^{20}_D$** +110.55 (c 0.57, $CHCl_3$).



54 **55**

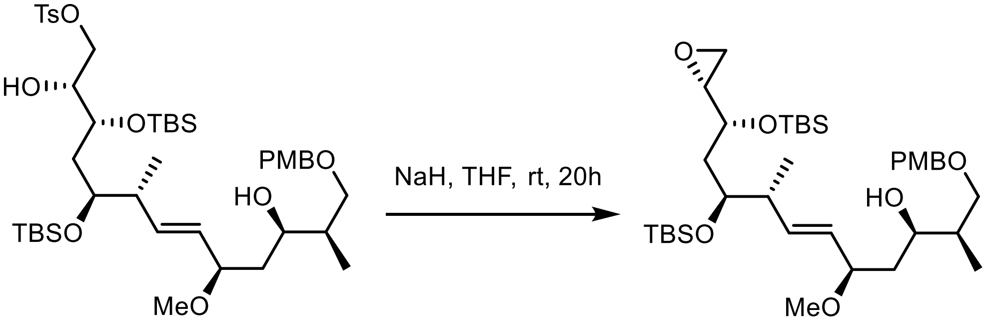
In a 100 mL round bottom flask equipped with magnetic stir bar, compound **54** (2.67 g, 3.19 mmol) was dissolved in CH_2Cl_2 (62 mL). The solution was cooled to 0°C and aqueous TFA (50%, 4.1 mL) was added dropwise. The biphasic mixture was stirred at 0°C for 2 hours. Saturate aq. $NaHCO_3$ (60 mL) was added slowly to quench the reaction. The organic layer was separated, and aqueous layer extracted with CH_2Cl_2 (10 mL x 3). The organic layer was combined, dried over Na_2SO_4, filtered and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 3:1) afforded triol **55**

(1.9361 g, 88%). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 7.24 (d, J = 8.5 Hz, 2H), 6.98 – 6.77 (m, 2H), 5.59 (dd, J = 15.6, 7.3 Hz, 1H), 5.37 (dd, J = 15.6, 7.8 Hz, 1H), 4.43 (s, 2H), 3.97 (dt, J = 9.7, 3.0 Hz, 1H), 3.88 – 3.76 (m, 5H), 3.69 (dt, J = 8.9, 3.4 Hz, 1H), 3.62 – 3.51 (m, 3H), 3.47 (qd, J = 9.1, 5.7 Hz, 2H), 3.27 (s, 3H), 2.40 (td, J = 7.1, 3.2 Hz, 1H), 2.09 (d, J = 44.0 Hz, 4H), 1.82 (ddt, J = 20.1, 12.9, 5.3 Hz, 3H), 1.66 (ddd, J = 13.8, 9.6, 4.0 Hz, 1H), 1.58 (ddd, J = 11.5, 7.9, 4.0 Hz, 1H), 1.48 (ddd, J = 13.5, 9.0, 4.4 Hz, 1H), 1.30 (q, J = 7.2 Hz, 2H), 1.02 (d, J = 6.9 Hz, 3H), 0.91 (dd, J = 13.6, 5.6 Hz, 24H), 0.11 – 0.03 (m, 15H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 159.32, 135.06, 130.91, 130.44, 129.32, 113.93, 80.00, 74.12, 73.07, 72.54, 72.38, 70.28, 69.98, 64.91, 56.37, 55.38, 42.07, 40.19, 38.59, 36.70, 26.01, 25.98, 18.18, 18.12, 14.13, 11.39, -4.02, -4.15, -4.17, -4.59. **FT-IR** (film): ν_{max} (cm^{-1}) 3435.56 (br), 2930.31, 2857.02, 1739.48, 1613.16, 1586.16, 1513.85, 1462.74, 1361.50, 1301.72, 1250.61, 1173.47, 1086.69, 1005.70, 978.70, 938.20, 871.67, 836.96, 775.24, 737.64, 674.96. **HRMS** (ESI) *m/z* 707.4354 [$(M+Na)^{+;}$ calcd for $C_{36}H_{68}O_8NaSi_2$: 707.4351]. **[α]^{20}$_D$** -1.78 (c 1.05, $CHCl_3$).



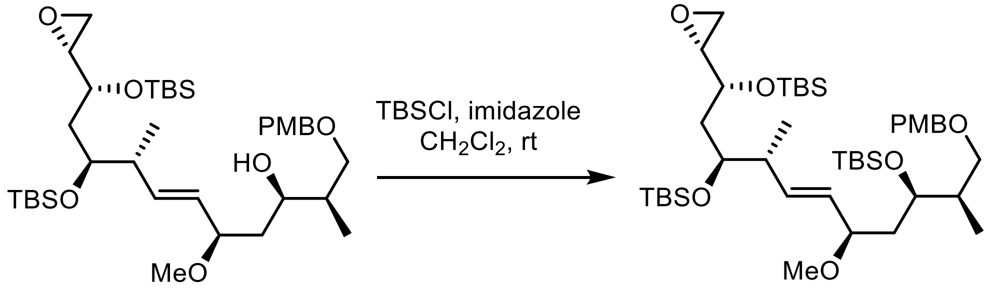
55 **S18**

To an oven-dried 25 mL 3-neck round bottom flask equipped with magnetic stir bar was added triol **55** (1.94 g, 2.83 mmol) and n-Bu_2SnO (140 mg). The flask was evacuated and back-filled with N_2 for 3 times. Dry CH_2Cl_2 (14 mL) and NEt_3 (1.2 mL, 8.49 mmol) were added via syringe. The solution was cooled to 0°C and TsCl (593 mg, 3.11 mmol) was added in one portion. The reaction mixture was stirred at 0°C for 19 hours, before saturate aq. $NaHCO_3$ (30 mL) was added to quench the reaction. The organic layer was separated, and aqueous layer extracted with CH_2Cl_2 (5 mL x 3). The organic layer was combined, dried over Na_2SO_4, filtered, and concentrated *in-vacuo* to afford compound **S18** (2.27 g, 95%) as a colorless oil, which was directly subjected to the next step without further purification.



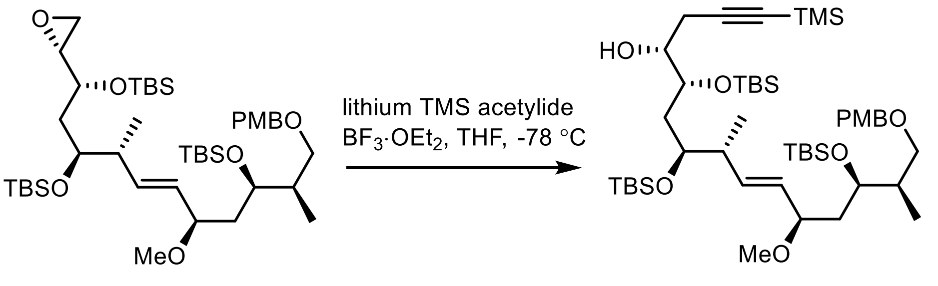
S18 **S19**

In an oven-dried 100 mL round bottom flask equipped with magnetic stir bar, tosylate **S18** (2.27 g, 2.70 mmol) was dissolved in dry THF (90 mL). Sodium hydride (60% dispersion in mineral oil, 162 mg, 4.05 mmol) was washed with pentane and added portion wise into the solution above. The reaction mixture was stirred at room temperature for 20 hours. Saturate aq. $NaHCO_3$ (100 mL) was added, and the organic layer was collected. The aqueous layer was extracted with diethyl ether (10 mL x 3). The organic layer was combined, washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated *in-vacuo* to afford epoxide **S19** (1.78 g, 98%) as a colorless oil. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 7.24 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 5.62 (dd, J = 15.6, 8.5 Hz, 1H), 5.26 (dd, J = 15.6, 8.3 Hz, 1H), 4.43 (s, 1H), 4.43 (s, 1H), 3.99 (d, J = 9.5 Hz, 1H), 3.85 (ddd, J = 8.0, 5.5, 2.3 Hz, 1H), 3.80 (s, 3H), 3.78 (dd, J = 8.4, 3.5 Hz, 1H), 3.48 (d, J = 5.6 Hz, 2H), 3.30 (ddd, J = 8.5, 6.7, 4.8 Hz, 1H), 3.25 (s, 3H), 2.95 (s, 1H), 2.89 (ddd, J = 6.7, 4.1, 2.7 Hz, 1H), 2.74 (t, J = 4.5 Hz, 1H), 2.49 (dd, J = 4.9, 2.7 Hz, 1H), 2.34 – 2.25 (m, 1H), 1.90 – 1.80 (m, 1H), 1.66 (tdd, J = 14.3, 7.2, 4.5 Hz, 3H), 1.55 (ddd, J = 14.2, 8.6, 2.7 Hz, 1H), 1.35 – 1.26 (m, 2H), 1.02 (d, J = 6.8 Hz, 3H), 0.92 (dd, J = 14.4, 7.2 Hz, 24H), 0.14 (s, 3H), 0.07 (s, 3H), 0.06 (s, 6H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 159.36, 135.23, 131.03, 130.43, 129.33, 113.95, 79.92, 77.17, 74.36, 73.17, 72.21, 71.96, 70.45, 56.18, 55.41, 44.92, 40.64, 40.37, 39.62, 38.57, 34.27, 26.03, 25.99, 22.48, 18.25, 18.21, 17.46, 14.19, 11.43, -4.04, -4.08, -4.42, -5.08. **FT-IR** (film): ν_{max} (cm^{-1}) 3512.70 (br), 2955.38, 2929.34, 2895.59, 2857.02, 1740.44, 1613.16, 1586.16, 1513.85, 1462.74, 1411.64, 1381.75, 1361.50, 1301.72, 1250.61, 1172.51, 1103.08, 1031.73, 1005.70, 976.77, 960.38, 928.56, 905.42, 871.67, 837.92, 777.17, 724.14, 670.14. **HRMS** (ESI) *m/z* 689.4249 [$(M+Na)^+$; calcd for $C_{36}H_{66}O_7NaSi_2$: 689.4245]. **$[\alpha]^{20}_D$** +19.91 (c 0.61, $CHCl_3$).



S19 **56**

In an oven dried 1L round bottom flask, compound **S19** (1.71 g, 2.56 mmol) was dissolved in dry CH_2Cl_2 (25 mL). Imidazole (523 mg, 7.69 mmol) were added. The solution was cooled to -78°C and TBSCl (773 mg, 5.13 mmol) was added. The mixture was stirred at rt for 1 hour before aqueous $NaHCO_3$ (10 mL) was added to quench the reaction. The organic layer was collected and aqueous layer extracted with CH_2Cl_2 (10 mL x 3). The organic layers were combined and dried over Na_2SO_4, filtered and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 20 :1) afforded epoxide **56** as a colorless oil (580.4 mg, 99%). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 7.24 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 5.56 (dd, J = 15.6, 8.4 Hz, 1H), 5.17 (dd, J = 15.6, 8.4 Hz, 1H), 4.43 (d, J = 11.6 Hz, 1H), 4.38 (d, J = 11.7 Hz, 1H), 3.91 (ddd, J = 7.8, 4.4, 2.9 Hz, 1H), 3.84 (ddd, J = 7.9, 5.6, 2.3 Hz, 1H), 3.80 (s, 3H), 3.55 (td, J = 8.6, 4.2 Hz, 1H), 3.50 (dd, J = 8.8, 5.4 Hz, 1H), 3.30 (ddd, J = 8.4, 6.6, 4.9 Hz, 1H), 3.22 – 3.17 (m, 4H), 2.89 (ddd, J = 6.7, 4.1, 2.7 Hz, 1H), 2.74 (t, J = 4.5 Hz, 1H), 2.48 (dd, J = 4.9, 2.6 Hz, 1H), 2.29 (p, J = 6.8, 6.3 Hz, 1H), 1.89 (tt, J = 9.6, 5.0 Hz, 1H), 1.73 – 1.60 (m, 3H), 1.45 – 1.37 (m, 1H), 1.35 – 1.27 (m, 1H), 1.01 (d, J = 6.9 Hz, 3H), 0.95 – 0.82 (m, 30H), 0.14 (s, 3H), 0.09 – 0.01 (m, 15H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 159.18, 135.35, 131.41, 131.12, 129.26, 113.85, 79.22, 72.74, 72.36, 72.22, 71.99, 56.17, 55.72, 55.41, 44.93, 40.75, 40.43, 39.57, 39.06, 29.86, 26.11, 26.03, 26.00, 22.48, 18.30, 18.26, 18.21, 17.34, 14.20, 12.18, -4.03, -4.09, -4.20, -4.32, -5.06. **FT-IR** (film): ν_{max} (cm^{-1}) 2955.38, 2929.34, 2857.02, 1613.16, 1587.13, 1513.85, 1471.42, 1407.78, 1384.64, 1360.53, 1301.72, 1250.61, 1171.54, 1103.54, 1041.37, 1005.70, 976.77, 960.38, 928.56, 836.96, 776.21, 726.07, 669.18. **HRMS** (ESI) *m/z* 781.3293 $[(M+H)^+]$; calcd for $C_{42}H_{81}O_7Si_3$: 781.3290]. **$[\alpha]^{20}_D$** +21.8 (c 0.57, $CHCl_3$).



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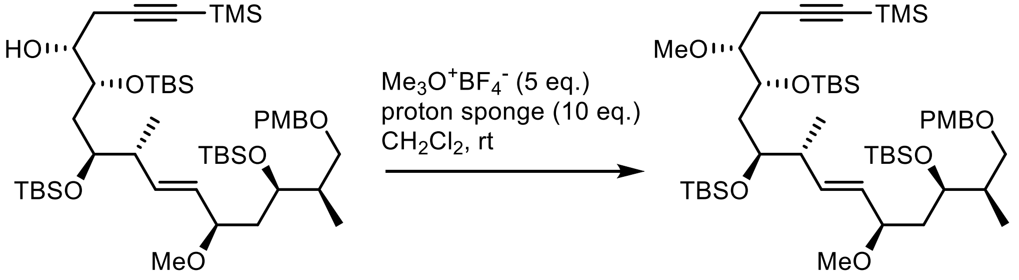
57

To an oven-dried, N_2 flushed 50 mL round bottom flask equipped with magnetic stir bar was added THF (13 mL) followed by TMS acetylene (2.3 mL, 15.7 mmol). The solution was cooled to -78°C and n-BuLi (2.5 M in hexane, 5.8 mL, 14.4 mmol) was added dropwise. The resulting solution was stirred at -78°C for 1 hour to afford lithium TMS acetylide solution.

To an oven-dried 50 mL round bottom flask equipped with magnetic stir bar was added epoxide **56** (2.05 g, 2.63 mmol) and THF (13 mL). The flask was cooled to -78°C and the above lithium TMS acetylide solution was added via cannula. Then $BF_3 \cdot OEt_2$ (1.7 mL, 14.4 mmol) was added dropwise to the above solution. The reaction mixture was stirred at -78°C for 16 hours. Then saturate aq. $NaHCO_3$ (30 mL) was added to quench the reaction. The biphasic mixture was stirred for 3 hours at room temperature, and the organic layer was collected. The aqueous layer was extracted with diethyl ether (10 mL x 3). The organic layers were combined, washed with brine, dried over Na_2SO_4, filtered, and concentrated *in-vacuo* to afford pure compound **57** (2.21 g, 95%) as a colorless oil. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.56 (dd, *J* = 15.6, 7.3 Hz, 1H), 5.25 (ddd, *J* = 15.7, 8.4, 1.2 Hz, 1H), 4.44 (d, *J* = 11.6 Hz, 1H), 4.38 (d, *J* = 11.6 Hz, 1H), 3.95 – 3.90 (m, 1H), 3.88 (td, *J* = 5.7, 4.9, 3.2 Hz, 1H), 3.80 (s, 3H), 3.69 (dt, *J* = 7.8, 3.8 Hz, 1H), 3.61 (t, *J* = 7.0 Hz, 1H), 3.55 (dt, *J* = 8.4, 4.2 Hz, 1H), 3.53 – 3.49 (m, 1H), 3.21 (s, 3H), 3.19 (t, *J* = 8.6 Hz, 1H), 2.44 (dd, *J* = 16.7, 6.5 Hz, 1H), 2.41 – 2.32 (m, 2H), 1.93 – 1.83 (m, 1H), 1.77 (ddd, *J* = 13.1, 8.4, 4.2 Hz, 1H), 1.70 (ddd, *J* = 13.8, 8.5, 5.1 Hz, 1H), 1.51 (ddd, *J* = 13.5, 7.9, 5.0 Hz, 1H), 1.45 – 1.39 (m, 1H), 1.34 – 1.27 (m, 2H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 17.9 Hz, 37H), 0.14 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.05 (s, 3H), 0.02 (s, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 159.18, 135.72, 131.18, 131.05, 129.25, 113.84, 103.81, 86.81, 79.10, 72.76, 72.66, 72.47, 71.09, 70.47, 69.89, 55.80, 55.41, 41.99, 40.39, 38.83, 37.47, 26.10, 25.72, 18.29, 18.23, 18.19, 14.97, 11.98, 0.26, -3.65, -4.01, -4.21, -4.25, -4.29, -4.44. **FT-IR** (film): ν_{max} (cm^{-1}) 3435.56, 2956.34, 2929.34, 2896.56, 2857.02, 2709.50, 2360.44, 2171.35, 1743.33, 1613.16, 1587.13, 1513.85, 1471.42, 1462.74, 1405.85, 1386.57, 1361.50, 1301.72, 1250.61, 1172.50, 1099.23, 1043.30, 1005.70, 975.8, 939.16, 837.92, 775.24, 670.14. **HRMS** (ESI) *m/z* 901.5659 [(M+Na)$^+$; calcd for $C_{47}H_{90}O_7NaSi_4$: 901.5661]. **$[\alpha]^{20}_D$** +10.04 (c

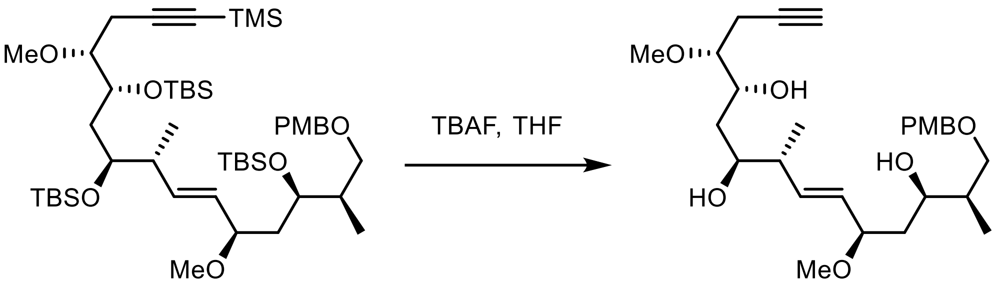
1.03, $CHCl_3$).



57 **58**

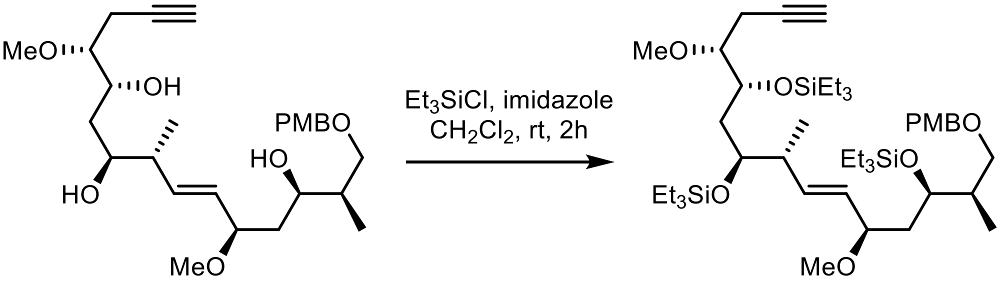
To an oven-dried 25 mL 3-neck round bottom flask equipped with a stir bar was added compound **57** (2.20 g, 2.50 mmol) and proton sponge (4.30 g, 20.0 mmol). The flask was evacuated and back-filled with N_2 for 3 times. Dry CH_2Cl_2 (12 mL) was added to dissolve all solid. $Me_3O^+ \cdot BF_4^-$ (1.84 g, 12.5 mmol) was quickly weighed and added to the above solution under a stream of N_2. The flask was wrapped with aluminum foil and stirred at room temperature for 5 hours. Saturate aqueous $NaHCO_3$ (30 mL) was added to quench the reaction. The organic layer was collected and the aqueous layer extracted with CH_2Cl_2 (10 mL x 3). The organic layer was combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was dissolved in a minimal amount of EtOAc and hexanes (30 mL) was added. The white precipitate formed was filtered off, and the filtrate was concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc *v/v* 30:1) afforded compound **58** (2.02 g, 90%) as a colorless oil. **^{1}H-NMR** (500 MHz, $CDCl_3$): *δ* 7.26 – 7.22 (m, 2H), 6.90 – 6.82 (m, 2H), 5.57 (dd, *J* = 15.6, 8.1 Hz, 1H), 5.23 (dd, *J* = 15.6, 8.3 Hz, 1H), 4.42 (d, *J* = 11.7 Hz, 1H), 4.38 (d, *J* = 11.6 Hz, 1H), 3.92 (dt, *J* = 7.9, 3.7 Hz, 1H), 3.87 (dt, *J* = 7.5, 5.1 Hz, 1H), 3.80 (s, 3H), 3.73 (td, *J* = 6.6, 2.5 Hz, 1H), 3.57 (td, *J* = 8.7, 4.1 Hz, 1H), 3.52 (dd, *J* = 8.9, 5.3 Hz, 1H), 3.40 (s, 3H), 3.30 (dt, *J* = 7.3, 4.8 Hz, 1H), 3.22 (s, 3H), 3.19 (t, *J* = 8.5 Hz, 1H), 2.55 (dd, *J* = 17.0, 5.1 Hz, 1H), 2.37 (dd, *J* = 17.0, 7.0 Hz, 1H), 2.34 – 2.28 (m, 1H), 1.90 (dp, *J* = 14.8, 7.1 Hz, 1H), 1.77 (dt, *J* = 12.8, 6.1 Hz, 1H), 1.67 (ddd, *J* = 13.6, 9.0, 4.3 Hz, 1H), 1.48 – 1.42 (m, 1H), 1.39 (ddd, *J* = 13.3, 8.5, 4.2 Hz, 1H), 1.31 (q, *J* = 7.0 Hz, 1H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.93 – 0.83 (m, 32H), 0.13 (s, 9H), 0.11 (s, 3H), 0.08 (s, 3H), 0.06 (s, 3H), 0.05 (d, *J* = 1.5 Hz, 6H), 0.03 (s, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$): *δ* 13C NMR (126 MHz, CDCl3) δ 159.13, 135.29, 131.48, 131.11, 129.26, 113.81, 105.13, 85.91, 82.09, 79.07, 72.70, 72.32, 69.85, 69.82, 58.61, 55.78, 55.39, 41.47, 40.36, 39.12, 36.49, 29.85, 26.10, 26.09, 22.48, 20.59, 18.29, 18.24, 18.19, 16.55, 14.21, 12.32, 0.20, -3.74, -4.23, -4.27, -4.36, -4.38. **FT-IR** (film): ν_{max} (cm^{-1}) 2956.34, 2929.34, 2895.59, 2857.02, 2708.53, 2176.27, 1613.16, 1587.13, 1513.85, 1471.42, 1462.74, 1406.82, 1386.57, 1361.50, 1301.72, 1249.65, 1182.15, 1171.54, 1099.23, 1041.37, 1005.7, 975.80, 938.20, 921.81, 837.92, 774.28, 669.18. **HRMS** (ESI) *m/z* 915.5825 [(M+Na)$^+$; calcd for

$C_{48}H_{92}O_7NaSi_4$: 915.5818]. **[α]^{20}$_D$** +17.48 (c 0.69, $CHCl_3$).



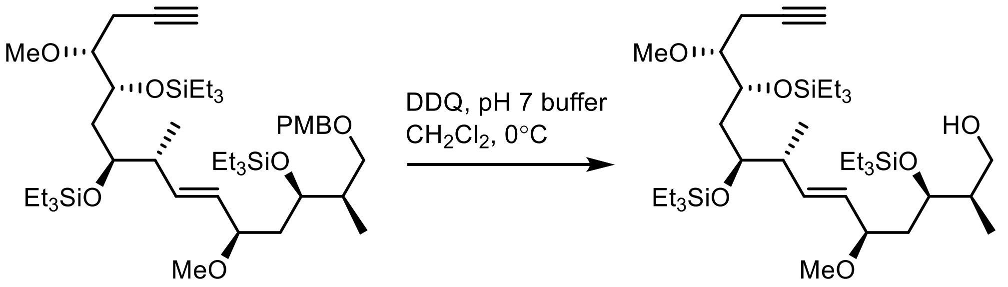
58 **S20**

In a 100 mL round bottom flask equipped with magnetic stir bar, compound **58** (2.02 g, 2.26 mmol) was dissolved in THF (10 mL). Tetrabutylammonium fluoride (13.6 mL, 1M in THF, 13.6 mmol) was then added. The reaction mixture was stirred at room temperature for 16 hours, at which point TLC showed full conversion. The reaction mixture washed with sat. aq. NH_4Cl, extracted with ethers, dried over Na_2SO_4, filtered concentrated under reduced pressure. The crude material was then filtered through a pad of silica gel. (Hexanes/EtOAc = 1:2 as eluent) to afford triol **S20**, which was used directly in the next step without further purification.



S20 **60**

In a 100 mL round bottom flask equipped with magnetic stir bar, crude triol **S20**, imidazole (1.54 g, 22.6 mmol) was dissolved in CH_2Cl_2 (23 mL). Triethylsilyl chloride (2.3 mL, 13.6 mmol) was then added. The reaction mixture was stirred at room temperature for 2 hours, at which point TLC showed full conversion. Saturate $NaHCO_3$ (10 mL) was added to quench the reaction. The organic layer was collected and the aqueous layer extracted with Hexanes (10 mL x 3). The organic layers were combined and washed with H_2O (10 mL x 2), sat. $CuSO_4$ (10 mL) and brine (10 mL), dried over Na_2SO_4, filtered, concentrated under reduced pressure and dried *in-vacuo* overnight to afford pure silyl ether **60** (1.67 g, 90% over 2 steps).



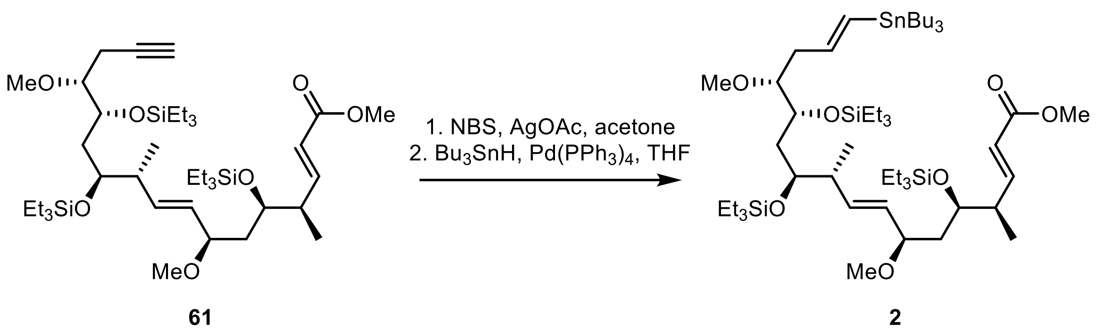
60 **S21**

In a 100 mL round bottom flask equipped with magnetic stir bar, crude silyl ether **60** (1.60 g, 1.95 mmol) was dissolved in CH_2Cl_2 (20 mL). 1M pH 7 phosphate buffer (2 mL) was added and the reaction mixture was cooled to 0°C. DDQ (885.3 mg, 3.90 mmol) was the added in portions. The reaction mixture was stirred at 0°C for 1 hour and additional DDQ (450 mg) and pH 7 buffer (1 mL) were added. The reaction was stirred for another 0.5 hour before the content was poured into a stirred saturated solution of $NaHCO_3$ (100 mL). The organic layer was collected and aqueous layer was extracted with 1:1 Hexanes/Et_2O (20 mL x 3). The organic layers were combined and washed with sat. NH_4Cl (50 mL), dried over Na_2SO_4, filtered and concentrated *in-vacuo*. Column chromatography (SiO_2, Hexanes/EtOAc = 10:1) afforded desired product **S21** (1.24 g, 90%) as a colorless oil. **^{1}H-NMR** (500 MHz, $CDCl_3$): 5.60 (dd, *J* = 15.6, 7.7 Hz, 1H), 5.26 (dd, *J* = 15.6, 8.3 Hz, 1H), 4.02 (dt, *J* = 8.9, 3.4 Hz, 1H), 3.96 (td, *J* = 6.6, 3.6 Hz, 1H), 3.79 (td, *J* = 6.7, 2.9 Hz, 1H), 3.70 – 3.64 (m, 1H), 3.62 (td, *J* = 8.8, 3.6 Hz, 1H), 3.49 (ddd, *J* = 10.8, 7.3, 5.3 Hz, 1H), 3.41 (s, 3H), 3.31 (td, *J* = 6.1, 3.8 Hz, 1H), 3.24 (s, 3H), 2.89 (dd, *J* = 7.3, 3.3 Hz, 1H), 2.53 (ddd, *J* = 16.8, 5.6, 2.7 Hz, 1H), 2.36 (ddt, *J* = 12.4, 6.5, 2.7 Hz, 2H), 1.96 (t, *J* = 2.7 Hz, 2H), 1.76 (dt, *J* = 13.6, 6.1 Hz, 1H), 1.68 (ddd, *J* = 13.4, 9.5, 3.6 Hz, 1H), 1.60 – 1.53 (m, 3H), 1.47 (dt, *J* = 13.9, 7.1 Hz, 1H), 1.04 (d, *J* = 6.9 Hz, 3H), 1.01 – 0.94 (m, 27H), 0.81 (d, *J* = 7.0 Hz, 3H), 0.68 – 0.58 (m, 18H). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ 135.79, 131.06, 82.18, 81.93, 78.82, 77.16, 72.64, 72.48, 69.70, 69.57, 66.06, 58.43, 55.77, 41.78, 40.15, 38.81, 36.34, 19.06, 15.79, 12.48, 7.14, 7.09, 7.06, 5.43, 5.23. **HRMS** (ESI) *m/z* 723.4839 [$(M+Na)^+$; calcd for $C_{37}H_{76}O_6NaSi_3$: 723.4847]. **$[\alpha]^{20}_D$** +13.7 (c 1.06, C_6H_6).

S21 **61**

In a 100 mL round bottom flask equipped with magnetic stir bar, compound **S21** (1.23 g, 1.75 mmol) was dissolved in CH_2Cl_2 (18 mL) and powdery $NaHCO_3$ (442 mg, 5.26 mmol) was added. The reaction mixture was cooled to 0^{o}C followed by addition of DMP (1.12 g, 2.63 mmol). The reaction mixture was warmed up to rt and stirred for 2 hours, at which point TLC showed complete conversion. Saturate aqueous $Na_2S_2O_3$ (10 mL) and saturate aqueous $NaHCO_3$ (10 mL) were then added to quench the reaction. The organic layer was collected and aqueous layer extracted with diethyl ether (10 mL x 3). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated *in-vacuo*. The crude mixture was then passed through a plug of silica gel (Hexanes/EtOAc = 15:1 as eluent) to afford the desired aldehyde, which was directly used in next step without further purification due to its air-sensitivity.

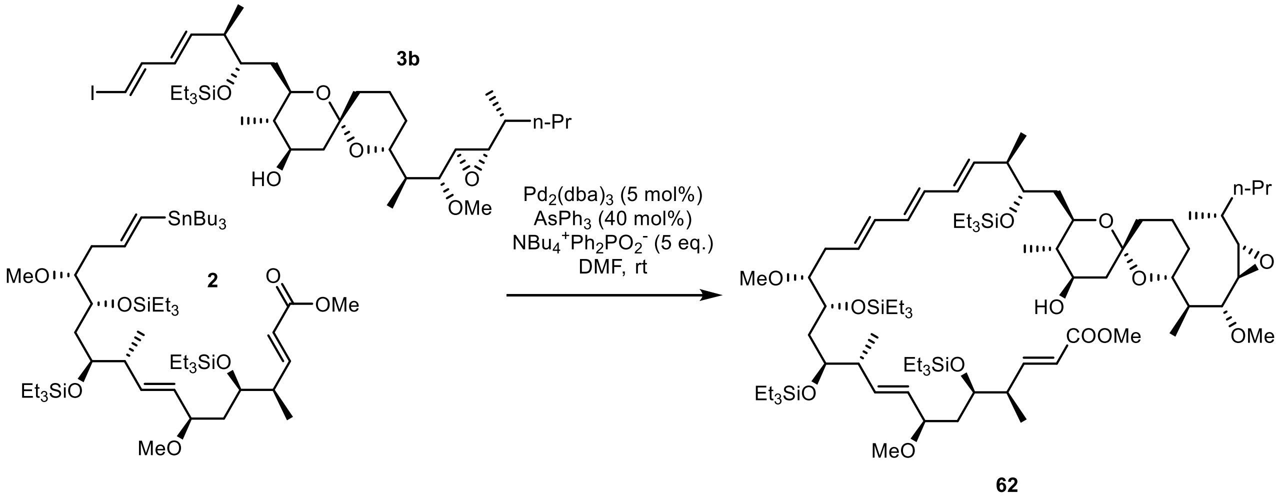
To the crude aldehyde from above was added dry LiCl (148.4 mg, 3.50 mmol). The flask was then evacuated and back-filled with argon for 3 times. CH_3CN (15 mL) was then added followed by sequential addition of phosphonate (0.48 mL, 3.50 mmol) and i-PrNEt$_2$ (0.61 mL, 3.50 mmol). The LiCl particles slowly dissolved and the reaction mixture gradually turned cloudy. The reaction was allowed to stir at room temperature for 24 hours, at which point TLC showed full conversion. Saturate aqueous NH_4Cl (20 mL) and diethyl ether (20 mL) were added. The organic layer was collected and aqueous layer extracted with hexanes (10 mL x 3). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated in-vacuo. Column chromatography (SiO_2, Hexanes/EtOAc = 40:1) afforded desired product **61** (1.044 g, 79% over 2 steps) as a colorless oil. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 7.07 (dd, *J* = 15.9, 6.7 Hz, 1H), 5.80 (dd, *J* = 15.9, 1.5 Hz, 1H), 5.58 (dd, *J* = 15.5, 8.1 Hz, 1H), 5.22 (dd, *J* = 15.6, 8.3 Hz, 1H), 3.95 (tt, *J* = 6.6, 3.4 Hz, 2H), 3.78 (td, *J* = 6.6, 2.7 Hz, 1H), 3.72 (s, 3H), 3.63 (td, *J* = 9.4, 8.2, 2.9 Hz, 1H), 3.40 (s, 3H), 3.30 (ddd, *J* = 6.6, 5.3, 3.8 Hz, 1H), 3.23 (s, 3H), 2.52 (ddd, *J* = 17.1, 5.5, 2.8 Hz, 1H), 2.47 (ddt, *J* = 8.4, 3.7, 2.2 Hz, 1H), 2.36 (dd, *J* = 6.7, 2.8 Hz, 1H), 2.33 (dd, *J* = 6.7, 2.6 Hz, 1H), 1.95 (t, *J* = 2.7 Hz, 1H), 1.77 (dt, *J* = 13.5, 6.2 Hz, 1H), 1.60 – 1.52 (m, 1H), 1.46 (dt, *J* = 13.8, 7.0 Hz, 1H), 1.36 (ddd, *J* = 14.1, 9.6, 3.0 Hz, 1H), 1.02 (dd, *J* = 6.9, 1.4 Hz, 6H), 1.00 – 0.93 (m, 27H), 0.63 (qd, *J* = 7.9, 3.4 Hz, 18H). **^{13}C-NMR** (126 MHz, $CDCl_3$): *δ* 167.21, 151.65, 135.55, 131.20, 120.94, 82.26, 82.07, 78.64, 77.16, 72.56, 71.94, 69.62, 69.58, 58.47, 55.80, 51.52, 42.79, 41.85, 40.29, 36.43, 19.07, 16.26, 14.26, 7.14, 7.09, 5.43, 5.35, 5.24. **HRMS** (ESI) *m/z* 777.4944 [(M+Na)$^+$; calcd for $C_{40}H_{78}O_7NaSi_3$: 777.4953]. **$[\alpha]^{20}_D$** +188.03 (c 1.25, C_6H_6).



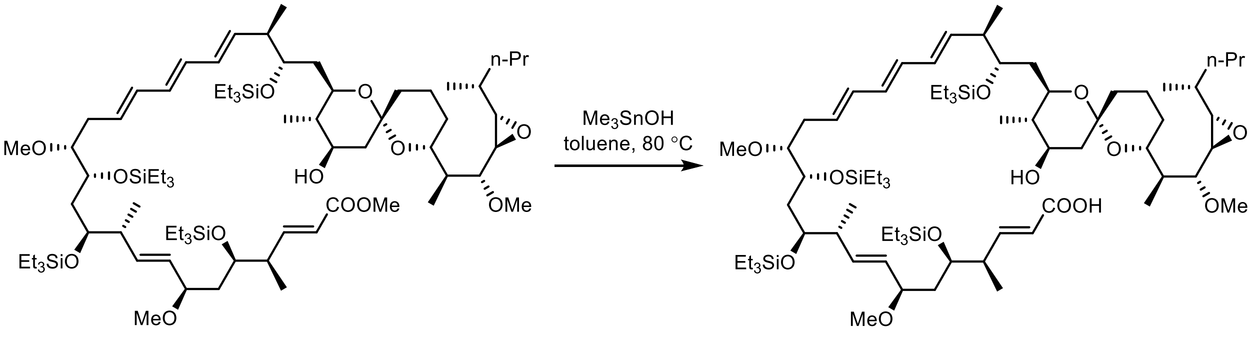
To a 100 mL round bottom flask charged with compound **61** (1.0400 g, 1.38 mmol), AgOAc (23.4 mg, 0.14 mmol) was added acetone (14 mL). The mixture was cooled to 0ºC and solid NBS (294 mg, 1.65 mmol) was added in one portion. The reaction mixture was warmed up to rt and stirred for 2 hours, at which point TLC showed full conversion. Saturate aqueous $Na_2S_2O_3$ (10 mL) and saturate aqueous $NaHCO_3$ (10 mL) were then added to quench the reaction. The aqueous layer was extracted with diethyl ether (20 mL x 3). The organic layers were combined, washed with brine (20 mL) and dried over Na_2SO_4, filtered and concentrated *in-vacuo*. The crude mixture was then passed through a plug of silica gel (Hexanes/EtOAc = 20:1 as eluent) to afford the desired bromo alkyne (1.1051 g, 96% crude yield), which was directly used in next step.

To a 50 mL round bottom flask charged with bromo alkyne from above step was added $Pd(PPh_3)_4$ (150.0 mg, 0.13 mmol). The flask was evacuated and back-filled with argon for 3 times. THF (13 mL) was then added to dissolve the mixture. The solution was cooled to -78ºC and tributyltin hydride (0.77 mL, 2.91mmol) was added dropwise via syringe. The reaction mixture was allowed to warm up to room temperature and stirred for 30 min, at which point TLC showed full conversion. The reaction mixture was then concentrated under reduced pressure and purified by flash chromatography (SiO_2, pre-treated with 1% NEt_3 in hexanes, Hexanes/EtOAc = 60:1) to afford desired product **2** as a colorless oil (1.2628 g, 91% yield). **^{1}H-NMR** (500 MHz, $CDCl_3$): 7.07 (dd, *J* = 15.9, 6.7 Hz, 1H), 6.10 – 5.90 (m, 2H), 5.79 (dd, *J* = 15.9, 1.4 Hz, 1H), 5.62 (dd, *J* = 15.6, 8.4 Hz, 1H), 5.19 (dd, *J* = 15.5, 8.4 Hz, 1H), 3.95 (dt, *J* = 9.7, 3.3 Hz, 1H), 3.85 (dt, *J* = 8.5, 4.3 Hz, 1H), 3.80 (ddd, *J* = 7.9, 5.3, 2.5 Hz, 1H), 3.72 (s, 3H), 3.63 (td, *J* = 9.4, 3.0 Hz, 1H), 3.33 (s, 3H), 3.23 (s, 3H), 3.16 (dt, *J* = 8.0, 3.7 Hz, 1H), 2.47 (ddt, *J* = 10.7, 4.4, 1.5 Hz, 1H), 2.45 – 2.39 (m, 1H), 2.31 (td, *J* = 8.7, 4.3 Hz, 1H), 2.22 (ddd, *J* = 14.5, 8.6, 5.1 Hz, 1H), 1.75 (ddd, *J* = 12.7, 7.9, 4.4 Hz, 1H), 1.57 (dt, *J* = 10.7, 6.2 Hz, 1H), 1.53 – 1.44 (m, 7H), 1.40 – 1.35 (m, 1H), 1.31 (dt, *J* = 14.7, 7.3 Hz, 7H), 1.03 (d, *J* = 5.0 Hz, 3H), 1.02 (d, *J* = 5.1 Hz, 3H), 1.00 – 0.93 (m, 27H), 0.87 (dt, *J* = 10.9, 7.6 Hz, 15H), 0.66 – 0.56 (m, 18H). **^{13}C-NMR** (126 MHz, $CDCl_3$): *δ* 167.21, 151.75, 146.94, 135.72, 131.13, 129.82, 120.89, 83.98, 78.75, 77.16, 72.74, 71.96, 69.46, 58.54, 55.82, 51.50, 42.77, 41.36, 40.36, 37.96, 36.71, 29.28, 27.44, 17.44, 14.18, 13.85, 9.54, 7.13, 7.11, 5.40, 5.35. **HRMS** (ESI) *m/z* 1069.6156 [(M+Na)$^+$; calcd for $C_{52}H_{106}O_7NaSi_3Sn$: 1069.6166]. **$[\alpha]^{20}_{D}$** +39.87 (c 0.90, $CHCl_3$).

(h). Total Synthesis of Reported Structure of Neaumycin B (**1**)



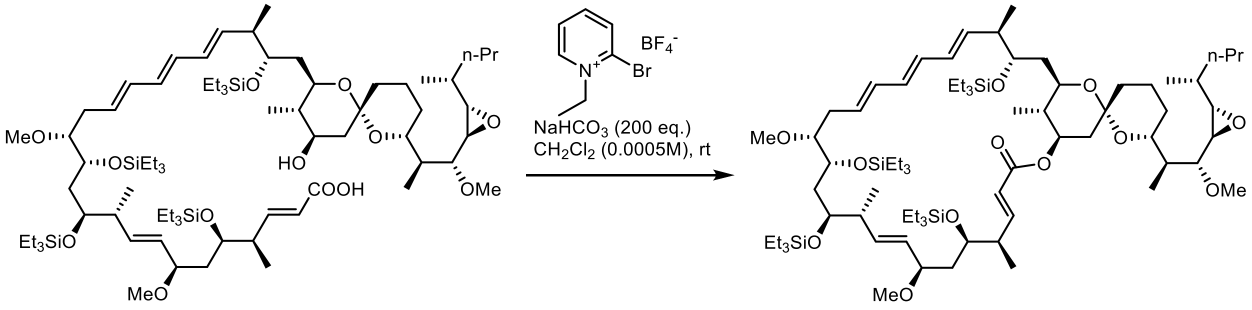
To a stirring solution of Northern Hemisphere **3b** (136.0 mg, 0.185 mmol), Southern Hemisphere **2** (291.1 mg, 0.278 mmol) and $Bu_4N^+Ph_2P(O)O^-$ (425 mg, 0.925 mmol) in DMF (1.8 mL, dried over 4Å MS and degassed prior to use) under argon atmosphere was added a suspension of $Pd_2(dba)_3$ (8.2 mg, 0.009 mmol) and $AsPh_3$ (22.0 mg, 0.072 mmol) in DMF (1.8 mL, dried over 4Å MS and degassed prior to use). The reaction mixture was covered with aluminum foil and stirred at room temperature for 3 hours, at which point TLC showed complete conversion. The reaction mixture was then transferred to a stirring saturate aq. NH_4Cl (50 mL). The aqueous phase was then extracted with 1:1 hexanes/diethyl ether (10 mL x 4). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 8:1 – 5:1) afforded pure triene **62** (226.2 mg, 89 %) as a colorless oil. **^{1}H-NMR** (600 MHz, C_6D_6): δ 7.38 (dd, *J* = 15.8, 6.8 Hz, 1H), 6.34 – 6.27 (m, 2H), 6.27 – 6.20 (m, 2H), 6.01 (dd, *J* = 15.4, 9.2 Hz, 1H), 5.97 (dd, *J* = 16.0, 1.6 Hz, 1H), 5.94 – 5.87 (m, 2H), 5.41 (dd, *J* = 15.6, 8.3 Hz, 1H), 4.22 (ddd, *J* = 9.7, 4.0, 2.5 Hz, 1H), 4.17 (dt, *J* = 9.3, 3.3 Hz, 1H), 4.06 (dq, *J* = 10.0, 3.8, 3.4 Hz, 2H), 3.94 (td, *J* = 10.4, 2.3 Hz, 1H), 3.87 (ddd, *J* = 10.6, 8.5, 2.9 Hz, 1H), 3.55 (ddd, *J* = 11.2, 7.4, 2.0 Hz, 1H), 3.03 – 2.94 (m, 2H), 2.74 (tt, *J* = 7.8, 5.8 Hz, 1H), 2.67 – 2.57 (m, 1H), 2.49 (td, *J* = 8.6, 4.3 Hz, 1H), 2.42 (tdd, *J* = 7.0, 4.0, 1.6 Hz, 1H), 2.40 – 2.32 (m, 3H), 2.15 – 2.10 (m, 1H), 2.10 – 2.05 (m, 1H), 1.84 – 1.72 (m, 4H), 1.66 (ddd, *J* = 13.9, 9.2, 2.9 Hz, 1H), 1.57 (dd, *J* = 10.4, 4.2 Hz, 2H), 1.54 – 1.44 (m, 2H), 1.35 (d, *J* = 6.9 Hz, 4H), 1.33 – 1.25 (m, 7H), 1.24 (dd, *J* = 6.9, 4.2 Hz, 5H), 1.22 – 1.17 (m, 5H), 1.12 – 1.02 (m, 38H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.98 (d, *J* = 6.4 Hz, 3H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 4H), 0.69 (dqd, *J* = 26.0, 7.9, 5.1 Hz, 23H). **^{13}C-NMR** (151 MHz, C_6D_6): δ 166.60, 151.45, 136.49, 135.26, 133.03, 132.30, 132.26, 131.71, 131.21, 128.06, 121.55, 98.71, 84.65, 82.46, 79.09, 74.47, 73.45, 73.22, 72.54, 71.35, 69.74, 69.66, 60.19, 58.74, 58.04, 57.74, 55.83, 50.97, 44.87, 43.08, 42.97, 41.50, 41.39, 41.10, 39.90, 38.27, 37.48, 36.11, 36.07, 35.61, 34.45, 32.83, 28.42, 22.73, 20.59, 20.28, 18.92, 17.95, 17.21, 14.53, 14.28, 14.05, 13.33, 11.39, 7.39, 7.33, 5.72, 5.67. **FT-IR** (film): v_{max} (cm^{-1}) 3477.99, 2956.34, 2876.31, 2359.48, 1727.91, 1655.59, 1540.85, 1458.89, 1414.53, 1377.89, 1238.08, 1176.36, 1101.15, 1008.59, 916.99, 853.35, 799.35, 739.57. **HRMS** (ESI) *m/z* 1385.9458 [(M+Na)$^+$; CALCD FOR $C_{75}H_{142}O_{13}NaSi_4$: 1385.9425]. **$[\alpha]^{20}_{D}$** +64.8 (c 0.51, C_6H_6).



62 **63**

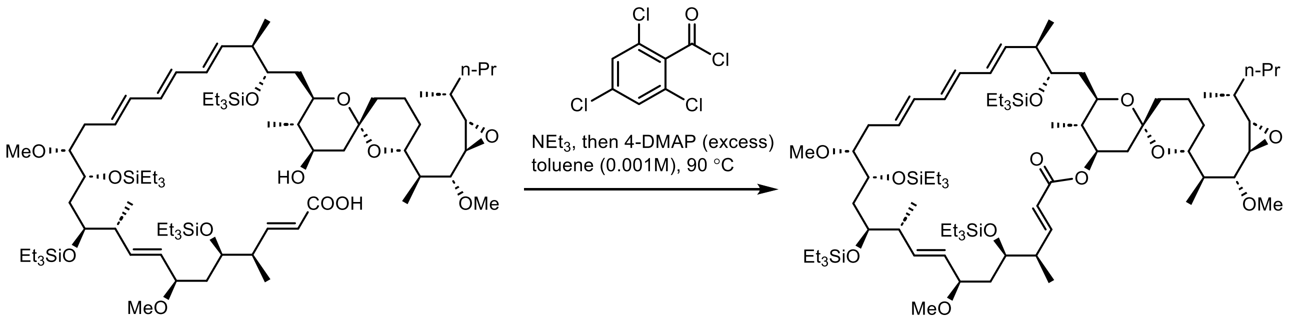
To a stirred solution of triene **62** (249 mg, 0.182 mmol) in toluene (4 mL) under argon was added Me_3SnOH (330 mg, 1.82 mmol). The reaction was heated at 90°C for 24 hours, at which point TLC showed full conversion. The reaction mixture was concentrated *in-vacuo* and directly purified by flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 100:0 – 4:1 – 3:1) to give seco acid **63** (213.4 mg, 86 %) as a white foam. **^{1}H-NMR** (600 MHz, C_6D_6): δ 7.43 (dd, *J* = 15.8, 6.7 Hz, 1H), 6.31 (ddd, *J* = 14.7, 10.7, 3.4 Hz, 2H), 6.23 (qd, *J* = 10.6, 9.9, 5.0 Hz, 2H), 6.01 (dd, *J* = 15.3, 9.2 Hz, 1H), 5.97 – 5.87 (m, 3H), 5.42 (dd, *J* = 15.6, 8.3 Hz, 1H), 4.22 (ddd, *J* = 9.8, 4.0, 2.5 Hz, 1H), 4.15 (dt, *J* = 9.5, 3.3 Hz, 1H), 4.07 (qd, *J* = 8.5, 8.1, 3.3 Hz, 2H), 3.95 (td, *J* = 10.3, 2.3 Hz, 1H), 3.87 (ddd, *J* = 10.4, 8.3, 2.9 Hz, 1H), 3.56 (ddd, *J* = 11.7, 7.4, 2.2 Hz, 1H), 3.49 (s, 3H), 3.49 – 3.45 (m, 1H), 3.35 (s, 3H), 3.27 (s, 4H), 2.99 (t, *J* = 1.9 Hz, 2H), 2.74 (ddq, *J* = 13.7, 6.9, 3.4, 2.4 Hz, 1H), 2.63 (ddd, *J* = 14.9, 6.7, 3.2 Hz, 1H), 2.51 (td, *J* = 8.5, 4.1 Hz, 1H), 2.43 – 2.34 (m, 4H), 2.09 (dddd, *J* = 16.1, 13.7, 9.0, 2.9 Hz, 2H), 1.84 – 1.73 (m, 4H), 1.64 (ddd, *J* = 14.0, 9.2, 3.0 Hz, 1H), 1.58 (dd, *J* = 10.3, 4.2 Hz, 2H), 1.54 – 1.44 (m, 3H), 1.43 – 1.26 (m, 15H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.11 – 1.03 (m, 36H), 1.02 (d, *J* = 6.5 Hz, 3H), 0.99 (d, *J* = 6.4 Hz, 3H), 0.93 – 0.88 (m, 6H), 0.76 – 0.63 (m, 23H). **^{13}C-NMR** (151 MHz, C_6D_6): δ 170.90, 153.74, 136.43, 135.32, 133.04, 132.19, 132.15, 131.78, 131.28, 131.10, 128.06, 121.29, 98.75, 84.57, 82.48, 79.09, 74.46, 73.43, 73.16, 72.43, 71.39, 69.84, 69.81, 60.30, 58.85, 57.98, 57.77, 55.79, 44.81, 43.02, 41.49, 41.44, 41.05, 39.91, 38.20, 37.47, 36.10, 36.07, 35.61, 32.76, 30.23, 28.41, 20.60, 20.28, 18.91, 17.69, 17.22, 14.53, 13.87, 13.35, 11.36, 7.39, 7.35, 7.31, 5.73, 5.69, 5.65. **FT-IR** (film): v_{max} (cm^{-1}) 3454.85, 2916.81, 2849.31, 2359.48, 1697.05, 1651.73, 1576.52, 1540.85, 1463.71, 1416.46, 1375.96, 1237.11, 1101.15. **HRMS** (ESI) *m/z* 1366.9711 [(M+NH$_4$)$^+$;

CALCD FOR $C_{74}H_{144}NO_{13}Si_4$: 1366.9715]. **[α]^{20}$_D$** +58.3 (c 0.43, C_6H_6).



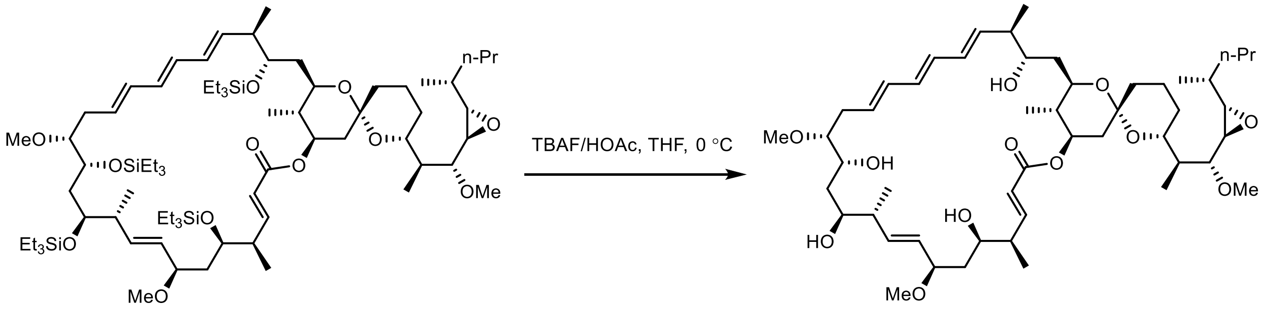
63 **64**

To a stirred solution of seco-acid **63** (213 mg, 0.1577 mmol) in dichloromethane (300 mL) under argon was added solid $NaHCO_3$ (2.646 g, 31.5 mmol) and 2-bromo-N-ethylpyridinium tetrafluoroborate (864 mg, 3.15 mmol). The reaction mixture was allowed to stir at room temperature for 48 hours before water (100 mL) was added. The organic layer was collected and the aqueous layer was extracted with ether (10 mL x 2). The organic layer was then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Flash chromatography (SiO_2, Hexanes/EtOAc *v/v* 20:1) afforded macrocycle **64** (168.9 mg, 80 %) as a pale-yellow foam. **^{1}H-NMR** (600 MHz, C_6D_6): δ 7.51 (dd, *J* = 16.0, 5.6 Hz, 1H), 6.30 (ddd, *J* = 15.3, 10.6, 8.0 Hz, 2H), 6.17 (ddd, *J* = 14.9, 10.8, 4.6 Hz, 2H), 6.03 – 5.87 (m, 4H), 5.39 (ddd, *J* = 15.7, 8.5, 1.5 Hz, 1H), 5.06 (td, *J* = 11.0, 4.3 Hz, 1H), 4.25 (ddd, *J* = 10.4, 3.8, 2.5 Hz, 1H), 4.13 (q, *J* = 4.7, 3.5 Hz, 1H), 4.12 – 4.10 (m, 1H), 4.08 (q, *J* = 6.4, 6.0 Hz, 1H), 4.05 (t, *J* = 5.8 Hz, 1H), 3.94 (ddd, *J* = 10.6, 8.4, 2.4 Hz, 1H), 3.84 (ddd, *J* = 11.7, 6.7, 1.9 Hz, 1H), 3.49 (s, 3H), 3.28 (td, *J* = 5.7, 3.3 Hz, 1H), 3.26 (s, 3H), 3.21 (s, 3H), 3.13 (dd, *J* = 6.7, 2.1 Hz, 1H), 3.10 (dd, *J* = 6.6, 3.3 Hz, 1H), 2.86 (dd, *J* = 12.6, 4.3 Hz, 1H), 2.76 (ddt, *J* = 13.6, 9.5, 4.7 Hz, 1H), 2.67 – 2.61 (m, 1H), 2.52 (dqd, *J* = 8.4, 4.9, 4.3, 1.7 Hz, 2H), 2.50 – 2.43 (m, 2H), 2.11 (ddd, *J* = 13.7, 10.3, 1.5 Hz, 1H), 2.03 (dt, *J* = 13.9, 5.5 Hz, 1H), 1.90 (td, *J* = 6.8, 3.4 Hz, 1H), 1.84 – 1.75 (m, 2H), 1.71 (dt, *J* = 13.5, 6.5 Hz, 1H), 1.68 – 1.63 (m, 1H), 1.61 (dd, *J* = 13.2, 4.8 Hz, 1H), 1.59 – 1.51 (m, 2H), 1.49 (d, *J* = 6.9 Hz, 3H), 1.48 – 1.25 (m, 19H), 1.22 (d, *J* = 6.7 Hz, 5H), 1.14 (q, *J* = 8.0 Hz, 19H), 1.10 (d, *J* = 6.8 Hz, 4H), 1.07 (td, *J* = 7.9, 2.6 Hz, 21H), 0.94 (q, *J* = 6.8 Hz, 10H), 0.77 (p, *J* = 7.6 Hz, 12H), 0.69 (qd, *J* = 8.0, 2.9 Hz, 12H). **^{13}C-NMR** (151 MHz, C_6D_6): δ 165.85, 150.84, 136.26, 135.56, 133.03, 132.79, 131.98, 131.35, 131.32, 130.02, 128.06, 121.67, 98.82, 83.11, 82.64, 78.94, 75.10, 73.12, 73.08, 72.89, 72.59, 71.57, 71.23, 60.10, 59.03, 57.85, 57.04, 55.47, 43.45, 42.89, 41.85, 41.72, 40.43, 40.09, 38.42, 36.24, 35.95, 35.64, 35.05, 32.36, 31.87, 30.23, 30.15, 29.85, 28.39, 23.14, 22.73, 20.65, 20.25, 18.26, 17.31, 15.39, 15.26, 14.62, 14.39, 14.28, 13.67, 11.59, 7.49, 7.46, 7.36, 5.85, 5.66, 5.64, 5.58. **FT-IR** (film): ν_{max} (cm^{-1}) 2956.34, 1718.26, 1457.92, 1174.44, 1085.73, 1007.62, 739.57. **HRMS** (ESI) *m/z* 1331.9333 [$(M+H)^+$; CALCD FOR $C_{74}H_{139}O_{12}Si_4$: 1331.9344]. **[α]^{20}$_D$** +54.3 (c 0.87, C_6H_6).



(63) **(64)**

To a stirred solution of seco-acid **63** (20.9 mg, 0.0156 mmol) in THF (0.3 mL) under argon was added NEt$_3$ (65 μL, 0.468 mmol) and TCBC (36 μL, 0.234 mmol). The reaction mixture was allowed to stir at room temperature for 20 hours to allow the complete formation of mixed anhydride. Then toluene (8 mL) was added and the resulting diluted solution was taken up by syringe. In a separate flask was added DMAP (171 mg, 1.4 mmol) and toluene (16 mL). The solution was heated up to 90^{o}C and the abovementioned solution of mixed anhydride was slowly added to the solution of DMAP in toluene at reflux over 10 hours. White precipitation formed at the bottom of the flask upon addition of mixed anhydride. The reaction was allowed to stir for another 12 hours after the complete addition of mixed anhydride. Then sat. aq. NaHCO$_3$ was added and the organic layer was collected. The aqueous layer was extracted with ether (10 mL x 2). The organic layer was combined and washed with sat. aq. CuSO$_4$ (10 mL x 2) and sat. NaHCO$_3$ (10 mL). The organic layer was then dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Flash chromatography (SiO$_2$, Hexanes/EtOAc *v/v* 15:1) afforded **64** (14.8 mg, 71%) as a pale-yellow foam. The NMR spectra of the macrolactone product synthesized via Yamaguchi protocol was identical to that prepared employing Mukaiyama conditions.



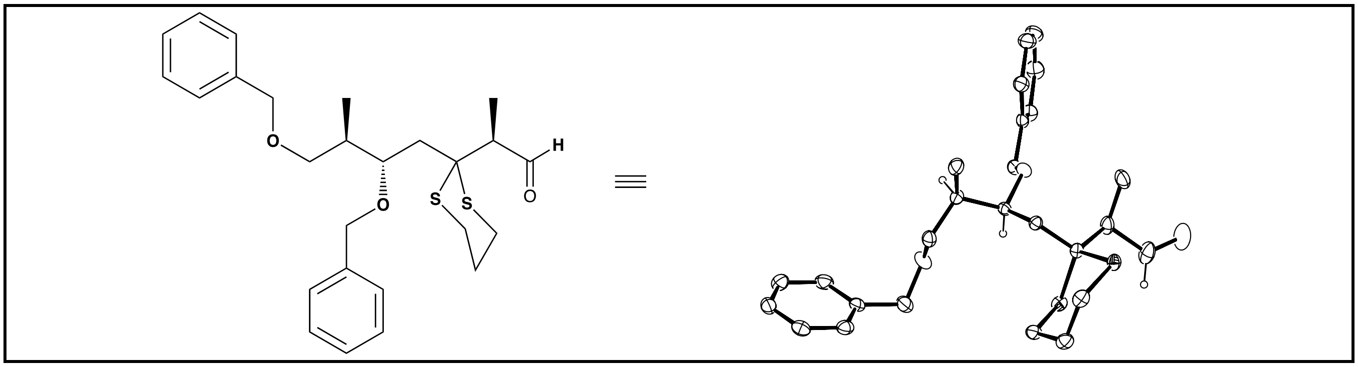
64

Neaumycin B (1)
(proposed structure)

To a stirred solution of silyl ether **64** (168.9 mg, 0.014 mmol) in THF (1.5 mL) under argon was added HOAc (75 μL) and TBAF (1.0 M in THF, 1.5 mL, 1.50 mmol). The reaction mixture was stirred at 0^{o}C for 48h, at which point TLC showed clean conversion. The solvent was then removed under reduced pressure and the residue was purified by normal phase column chromatography (SiO_2, 100% EtOAc) followed by reverse phase column chromatography (C18-SiO_2, MeOH/H_2O *v/v* 10:1) to give synthetic Neaumycin B (**1**) as a white powder (90.3 mg, 80%). **^{1}H-NMR** (600 MHz, $CDCl_3$): *δ* 6.78 (dd, *J* = 15.8, 8.0 Hz, 1H), 6.15 – 6.00 (m, 4H), 5.77 (d, *J* = 15.9 Hz, 1H), 5.72 (dd, *J* = 15.0, 7.4 Hz, 2H), 5.61 (dt, *J* = 13.9, 7.2 Hz, 1H), 5.41 (dd, *J* = 15.5, 8.4 Hz, 1H), 4.71 (td, *J* = 10.8, 4.5 Hz, 1H), 4.00 – 3.93 (m, 1H), 3.89 (d, *J* = 9.6 Hz, 1H), 3.84 (td, *J* = 7.4, 4.0 Hz, 1H), 3.79 (s, 1H), 3.72 (q, *J* = 8.8, 8.2 Hz, 2H), 3.60 (dd, *J* = 11.3, 7.1 Hz, 1H), 3.48 (t, *J* = 9.2 Hz, 1H), 3.15 – 3.02 (m, 3H), 2.98 (dd, *J* = 6.7, 2.3 Hz, 1H), 2.93 (dd, *J* = 6.7, 3.2 Hz, 1H), 2.74 (dd, *J* = 13.0, 4.5 Hz, 1H), 2.47 (dd, *J* = 7.0, 2.4 Hz, 1H), 2.44 (t, *J* = 7.1 Hz, 2H), 2.38 (dt, *J* = 14.5, 7.3 Hz, 2H), 2.18 (h, *J* = 6.9 Hz, 1H), 1.84 (d, *J* = 14.3 Hz, 1H), 1.75 (d, *J* = 14.9 Hz, 1H), 1.71 (dd, *J* = 7.1, 4.0 Hz, 2H), 1.67 (dd, *J* = 13.0, 3.5 Hz, 3H), 1.64 – 1.49 (m, 9H), 1.41 (dddd, *J* = 18.1, 14.4, 10.0, 5.2 Hz, 6H), 1.33 (ddd, *J* = 13.8, 9.9, 3.8 Hz, 2H), 1.31 – 1.17 (m, 6H), 1.15 – 1.09 (m, 9H), 1.02 (d, *J* = 6.3 Hz, 3H), 0.92 (t, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.78 (d, *J* = 6.5 Hz, 3H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 165.56, 150.28, 138.14, 136.34, 133.38, 132.01, 130.71, 130.70, 129.20, 128.36, 122.08, 98.84, 83.95, 82.18, 80.67, 77.16, 76.38, 75.45, 74.95, 74.70, 74.59, 72.11, 71.96, 60.27, 59.31, 58.00, 57.35, 56.19, 43.34, 42.90, 42.40, 42.18, 41.32, 39.64, 36.86, 36.62, 35.70, 35.67, 35.24, 34.18, 32.60, 27.91, 20.28, 20.03, 16.93, 16.53, 15.69, 14.81, 14.42, 13.82, 11.09. **FT-IR** (film): v_{max} (cm^{-1}) 3421.1(br), 2928.38, 1712.48, 1461.78, 1267.97, 1088.62, 1000.87, 909.27, 732.82. **HRMS** (ESI) *m/z* 875.5884 [$(M+H)^+$; calcd for $C_{50}H_{83}O_{12}$: 875.5885]. **$[\alpha]^{20}_D$** +35.2 (c 0.1, $CHCl_3$).

3. Data for Single Crystal X-ray Structures

(a). X-ray Structure Determination of Compound **12**



Compound **12**, $C_{26}H_{34}O_3S_2$, crystallizes in the orthorhombic space group $P2_12_12_1$ (systematic absences h00: h=odd, 0k0: k=odd, and 00l: l=odd) with a=8.07514(5)Å, b=16.05784(8)Å, c=19.04047(10)Å, V=2468.96(2)Å^3, Z=4, and d_{calc}=1.234 g/cm^3. X-ray intensity data were collected on a Rigaku XtaLAB Synergy-S diffractomete[6] equipped with an HPC area detector (HyPix-6000HE) and employing confocal multilayer optic-monochromated Cu-Kα radiation (λ=1.54184 Å) at a temperature of 100K. Preliminary indexing was performed from a series of sixty 0.5° rotation frames with exposures of 0.25 sec. for θ = ±47.20° and 1 sec. for θ = 107.75°. A total of 10262 frames (140 runs) were collected employing ω scans with a crystal to detector distance of 34.0 mm, rotation widths of 0.5° and exposures of 0.15 sec. for θ = ±47.32°, +50.00°, +54.00°, ±58.00°, +62.00°, ±66.00°, +70.00°, +74.00°, and 0.50 sec. for θ = ±47.32°, -70.00°, -74.00°, -78.00°, -82.00°, +86.00°, -86.25°, +90.0°, +94.00°, +106.00°, and +107.75°.

Rotation frames were integrated using CrysAlisPro,[7] producing a listing of unaveraged F^2 and σ(F^2) values. A total of 92147 reflections were measured over the ranges $7.202 \leq 2\theta \leq 149.004°$, $-9 \leq h \leq 10$, $-20 \leq k \leq 20$, $-23 \leq l \leq 23$ yielding 5044 unique reflections (R_{int} = 0.0474). The intensity data were corrected for Lorentz and polarization effects and for absorption using SCALE3 ABSPACK[8] (minimum and maximum transmission 0.6644, 1.0000). The structure was solved by direct methods - SHELXT.[9] Refinement was by full-matrix least squares based on F^2 using SHELXL-2018.[10] All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0308P)^2 + 0.5505P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0220 and wR2=0.0568 for 5005 observed reflections for which F > 4σ(F) and R1=0.0223 and wR2=0.0570 and GOF =1.033 for all 5044 unique, non-zero reflections and 282 variables. The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +0.17 and -0.18 e/Å^3.

Table S1 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in **Table S2** and **Table S3**. Anisotropic thermal parameters are in **Table**

S4. **Table S5** and **Table S6** list bond distances and bond angles. **Figure S1** is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

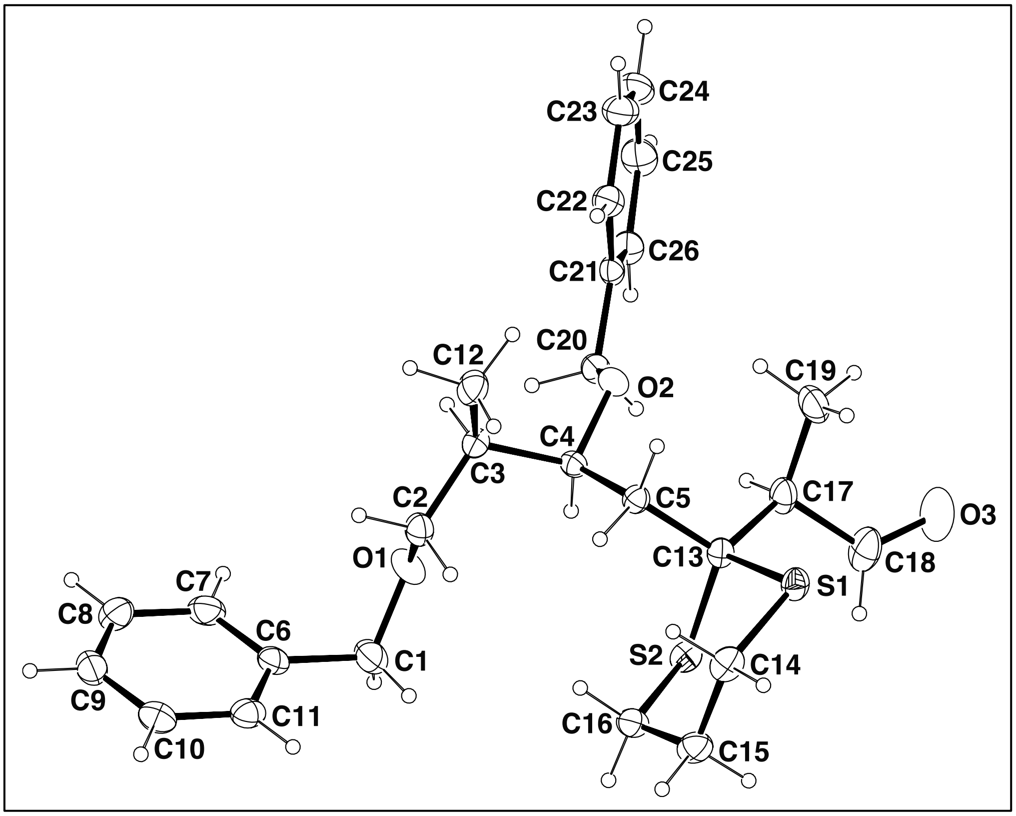


Figure S1. ORTEP drawing of the compound **12** with 50% thermal ellipsoids.

Table S1. Summary of Structure Determination of Compound **12**

Empirical formula	$C_{26}H_{34}O_3S_2$
Formula weight	458.65
Diffractometer	Rigaku XtaLAB Synergy-S
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a	8.07514(5)Å
b	16.05784(8)Å
c	19.04047(10)Å
Volume	2468.96(2)$Å^3$
Z	4
d_{calc}	1.234 g/cm^3
μ	2.140 mm^{-1}
F(000)	984.0
Crystal size, mm	0.21 × 0.08 × 0.08
2θ range for data collection	7.202 - 149.004°
Index ranges	$-9 \le h \le 10$, $-20 \le k \le 20$, $-23 \le l \le 23$
Reflections collected	92147
Independent reflections	5044[R(int) = 0.0474]
Data/restraints/parameters	5044/0/282
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	$R_1 = 0.0220$, $wR_2 = 0.0568$
Final R indexes [all data]	$R_1 = 0.0223$, $wR_2 = 0.0570$
Largest diff. peak/hole	0.17/-0.18 $eÅ^{-3}$
Flack parameter	0.001(3)

Table S2. Refined Positional Parameters for Compound **12**

Atom	***x***	***y***	***z***	**U(eq)**
C1	0.5045(3)	0.65864(12)	0.56419(12)	0.0347(5)
C2	0.5288(2)	0.51332(10)	0.54235(9)	0.0225(3)
C3	0.6515(2)	0.44239(10)	0.54932(8)	0.0200(3)
C4	0.81496(19)	0.46186(10)	0.51085(8)	0.0171(3)
C5	0.8068(2)	0.44778(10)	0.43141(8)	0.0174(3)
C6	0.3305(2)	0.65831(10)	0.59353(10)	0.0244(4)
C7	0.3056(2)	0.64749(11)	0.66530(10)	0.0282(4)
C8	0.1479(3)	0.64837(12)	0.69364(10)	0.0296(4)
C9	0.0116(2)	0.66007(11)	0.65013(10)	0.0266(4)
C10	0.0345(2)	0.67036(10)	0.57871(10)	0.0250(4)
C11	0.1931(2)	0.66904(10)	0.55053(9)	0.0250(4)
C12	0.5741(2)	0.35953(10)	0.52671(10)	0.0275(4)
C13	0.9387(2)	0.49459(9)	0.38806(8)	0.0175(3)
C14	0.7299(2)	0.50872(11)	0.26705(9)	0.0240(4)
C15	0.7078(2)	0.60178(11)	0.27921(9)	0.0258(4)
C16	0.7151(2)	0.62544(10)	0.35633(9)	0.0233(3)
C17	1.1182(2)	0.47098(12)	0.40933(9)	0.0243(4)
C18	1.2468(2)	0.51828(14)	0.36746(10)	0.0333(4)
C19	1.1542(2)	0.37726(13)	0.40667(10)	0.0322(4)
C20	1.0245(2)	0.44287(10)	0.59754(8)	0.0195(3)
C21	1.1148(2)	0.37547(10)	0.63673(8)	0.0182(3)
C22	1.0678(2)	0.29242(10)	0.63108(8)	0.0228(3)
C23	1.1499(3)	0.23174(11)	0.66987(9)	0.0283(4)
C24	1.2782(3)	0.25345(12)	0.71448(10)	0.0307(4)
C25	1.3246(2)	0.33600(13)	0.72067(10)	0.0297(4)
C26	1.2439(2)	0.39696(11)	0.68186(9)	0.0236(3)
S1	0.92818(5)	0.46743(2)	0.29456(2)	0.02087(9)
S2	0.91405(5)	0.60785(2)	0.39830(2)	0.02050(9)
O1	0.59437(16)	0.58397(7)	0.57842(7)	0.0283(3)
O2	0.94264(14)	0.40864(6)	0.53820(5)	0.0190(2)
O3	1.38164(18)	0.49061(12)	0.35415(9)	0.0498(4)

Table S3. Positional Parameters for Hydrogens in Compound **12**

Atom	***x***	***y***	***z***	**U(eq)**
H1a	0.498888	0.666862	0.512718	0.042
H1b	0.565755	0.706398	0.584381	0.042
H2a	0.511227	0.52684	0.492172	0.027
H2b	0.421012	0.497148	0.563044	0.027
H3	0.678731	0.437234	0.600377	0.024
H4	0.84588	0.521168	0.52002	0.021
H5a	0.695893	0.464916	0.414631	0.021
H5b	0.818425	0.387392	0.422144	0.021
H7	0.398331	0.639379	0.695249	0.034
H8	0.132696	0.641007	0.74273	0.035
H9	-0.09687	0.66098	0.669413	0.032
H10	-0.058465	0.678343	0.548858	0.03
H11	0.207837	0.67555	0.501339	0.03
H12a	0.481665	0.345941	0.558027	0.041
H12b	0.657675	0.31538	0.529255	0.041
H12c	0.533434	0.364265	0.478382	0.041
H14a	0.715274	0.497142	0.216356	0.029
H14b	0.641298	0.47871	0.29259	0.029
H15a	0.795616	0.632225	0.253554	0.031
H15b	0.599696	0.619366	0.259704	0.031
H16a	0.629798	0.593206	0.381911	0.028
H16b	0.68661	0.685153	0.360884	0.028
H17	1.132107	0.488404	0.459409	0.029
H18	1.219799	0.572411	0.350904	0.04
H19a	1.081134	0.348132	0.43963	0.048
H19b	1.26988	0.367227	0.419698	0.048
H19c	1.134478	0.35652	0.358993	0.048
H20a	0.942432	0.469544	0.62894	0.023
H20b	1.104128	0.486006	0.582067	0.023
H22	0.979571	0.277122	0.600701	0.027
H23	1.11776	0.175045	0.665718	0.034
H24	1.334187	0.211766	0.740756	0.037
H25	1.411901	0.35108	0.751585	0.036
H26	1.276874	0.453533	0.686065	0.028

Table S4. Refined Thermal Parameters (U's) for Compound **12**

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
C1	0.0289(10)	0.0221(8)	0.0532(12)	0.0037(8)	0.0127(9)	0.0043(7)
C2	0.0179(8)	0.0255(8)	0.0242(8)	-0.0001(7)	0.0020(6)	0.0002(6)
C3	0.0200(8)	0.0219(7)	0.0180(7)	0.0020(6)	0.0027(6)	0.0001(6)
C4	0.0155(7)	0.0181(7)	0.0179(7)	0.0010(6)	-0.0007(6)	0.0029(6)
C5	0.0163(7)	0.0186(7)	0.0171(7)	0.0004(6)	-0.0002(6)	-0.0009(6)
C6	0.0244(9)	0.0157(7)	0.0333(9)	0.0022(7)	0.0045(7)	0.0035(6)
C7	0.0271(10)	0.0265(9)	0.0310(9)	0.0067(7)	-0.0047(8)	0.0047(7)
C8	0.0361(11)	0.0289(9)	0.0237(9)	0.0045(7)	0.0032(8)	0.0014(8)
C9	0.0227(9)	0.0223(8)	0.0347(10)	-0.0016(7)	0.0050(7)	0.0002(7)
C10	0.0265(9)	0.0192(7)	0.0292(9)	-0.0036(6)	-0.0067(7)	0.0007(6)
C11	0.0346(10)	0.0186(7)	0.0219(8)	-0.0004(6)	0.0002(7)	0.0021(7)
C12	0.0260(9)	0.0243(8)	0.0321(9)	0.0006(7)	0.0077(8)	-0.0045(7)
C13	0.0160(8)	0.0212(7)	0.0154(7)	-0.0007(5)	-0.0008(6)	-0.0004(6)
C14	0.0223(9)	0.0312(9)	0.0184(8)	0.0010(6)	-0.0053(6)	-0.0043(7)
C15	0.0222(8)	0.0299(9)	0.0252(9)	0.0072(7)	-0.0046(7)	-0.0005(7)
C16	0.0223(9)	0.0209(8)	0.0267(8)	0.0035(6)	0.0000(7)	0.0025(7)
C17	0.0159(8)	0.0365(9)	0.0203(8)	0.0018(7)	0.0006(6)	0.0022(7)
C18	0.0175(9)	0.0539(12)	0.0284(9)	0.0046(9)	-0.0011(7)	-0.0054(8)
C19	0.0243(9)	0.0417(11)	0.0306(9)	0.0023(8)	0.0032(8)	0.0137(8)
C20	0.0201(8)	0.0213(7)	0.0171(7)	-0.0013(6)	-0.0013(6)	0.0025(6)
C21	0.0175(8)	0.0224(8)	0.0147(7)	-0.0005(6)	0.0021(6)	0.0029(6)
C22	0.0252(9)	0.0233(7)	0.0199(7)	-0.0014(6)	-0.0005(7)	0.0015(7)
C23	0.0382(11)	0.0222(8)	0.0243(8)	0.0011(7)	0.0012(8)	0.0054(7)
C24	0.0349(11)	0.0337(9)	0.0235(8)	0.0046(7)	-0.0012(8)	0.0137(8)
C25	0.0252(10)	0.0396(10)	0.0242(9)	0.0004(7)	-0.0060(7)	0.0049(8)
C26	0.0224(9)	0.0262(8)	0.0223(8)	-0.0006(6)	-0.0008(6)	0.0001(7)
S1	0.0219(2)	0.02504(18)	0.01568(17)	-0.00216(14)	0.00142(15)	0.00028(16)
S2	0.0228(2)	0.01982(17)	0.01885(17)	-0.00096(14)	-0.00124(15)	-0.00440(15)
O1	0.0207(6)	0.0213(6)	0.0429(7)	-0.0050(5)	0.0014(6)	0.0038(5)
O2	0.0198(6)	0.0206(5)	0.0167(5)	-0.0016(4)	-0.0038(4)	0.0047(4)
O3	0.0197(8)	0.0765(12)	0.0533(10)	0.0063(8)	0.0085(6)	-0.0008(7)

Table S5. Bond Distances in Compound **12**, Å

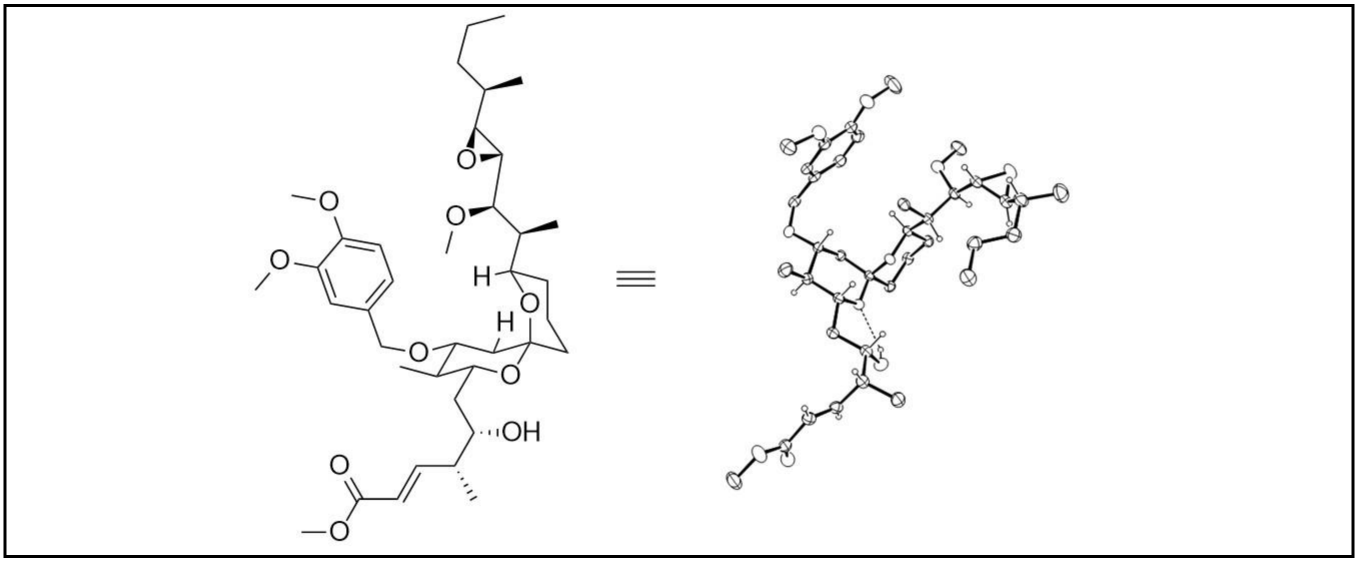
C1-C6	1.512(3)	C1-O1	1.427(2)	C2-C3	1.516(2)
C2-O1	1.428(2)	C3-C4	1.541(2)	C3-C12	1.532(2)
C4-C5	1.531(2)	C4-O2	1.4369(18)	C5-C13	1.543(2)
C6-C7	1.392(3)	C6-C11	1.390(3)	C7-C8	1.384(3)
C8-C9	1.390(3)	C9-C10	1.382(3)	C10-C11	1.389(3)
C13-C17	1.552(2)	C13-S1	1.8349(15)	C13-S2	1.8400(16)
C14-C15	1.523(3)	C14-S1	1.8107(18)	C15-C16	1.518(2)
C16-S2	1.8160(18)	C17-C18	1.514(2)	C17-C19	1.533(3)
C18-O3	1.203(3)	C20-C21	1.503(2)	C20-O2	1.4197(19)
C21-C22	1.391(2)	C21-C26	1.395(2)	C22-C23	1.391(2)
C23-C24	1.384(3)	C24-C25	1.383(3)	C25-C26	1.389(3)

Table S6. Bond Angles in Compound **12**, °

O1-C1-C6	113.53(15)	O1-C2-C3	108.20(13)	C2-C3-C4	111.46(13)
C2-C3-C12	111.16(14)	C12-C3-C4	113.08(14)	C5-C4-C3	113.76(13)
O2-C4-C3	108.75(12)	O2-C4-C5	107.53(12)	C4-C5-C13	115.27(13)
C7-C6-C1	119.81(18)	C11-C6-C1	121.60(17)	C11-C6-C7	118.59(17)
C8-C7-C6	120.97(18)	C7-C8-C9	119.84(17)	C10-C9-C8	119.80(18)
C9-C10-C11	120.08(17)	C10-C11-C6	120.72(16)	C5-C13-C17	112.71(13)
C5-C13-S1	111.78(11)	C5-C13-S2	110.50(11)	C17-C13-S1	103.79(11)
C17-C13-S2	108.36(11)	S1-C13-S2	109.44(8)	C15-C14-S1	114.75(12)
C16-C15-C14	112.84(14)	C15-C16-S2	114.91(13)	C18-C17-C13	112.38(14)
C18-C17-C19	110.20(15)	C19-C17-C13	114.07(15)	O3-C18-C17	123.1(2)
O2-C20-C21	110.01(12)	C22-C21-C20	121.31(15)	C22-C21-C26	119.27(16)
C26-C21-C20	119.36(15)	C21-C22-C23	120.04(17)	C24-C23-C22	120.41(17)
C25-C24-C23	119.76(17)	C24-C25-C26	120.24(18)	C25-C26-C21	120.27(17)
C14-S1-C13	103.57(8)	C16-S2-C13	101.70(8)	C1-O1-C2	112.81(14)
C20-O2-C4	113.10(11)				

This report has been created with Olex2,[11] compiled on 2018.05.29 svn.r3508 for OlexSys.

(b). X-ray Structure Determination of Compound **33**



Compound **33**, $C_{38}H_{60}O_{10}$, crystallizes in the orthorhombic space group $P2_12_12_1$ (systematic absences h00: h=odd, 0k0: k=odd, and 00l: l=odd) with a=9.22500(10)Å, b=19.15890(10)Å, c=21.72220(10)Å, V=3839.20(5)Å^3, Z=4, and d_{calc}=1.171 g/cm^3. X-ray intensity data were collected on a Rigaku XtaLAB Synergy-S diffractometer[6] equipped with an HPC area detector (HyPix-6000HE) and employing confocal multilayer optic-monochromated Cu-Kα radiation (λ=1.54184 Å) at a temperature of 100K. Preliminary indexing was performed from a series of sixty 0.5° rotation frames with exposures of 0.25 sec. for θ = ±47.29° and 1 sec. for θ = 107.75°. A total of 6548 frames (25 runs) were collected employing ω scans with a crystal to detector distance of 32.0 mm, rotation widths of 0.5° and exposures of 1 sec. for θ = ±49.01° and 2.5 sec. for θ = -84.25 and 105.75°.

Rotation frames were integrated using CrysAlisPro[7], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 50504 reflections were measured over the ranges $6.152 \leq 2\theta \leq 149.004°$, $-10 \leq h \leq 11$, $-23 \leq k \leq 23$, $-25 \leq l \leq 27$ yielding 7736 unique reflections (R_{int} = 0.0287). The intensity data were corrected for Lorentz and polarization effects and for absorption using SCALE3 ABSPACK[8] (minimum and maximum transmission 0.6777, 1.0000). The structure was solved by direct methods - ShelXT.[9] Refinement was by full-matrix least squares based on F^2 using SHELXL-2018[10]. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+(0.0376P)^2+0.6825P]$ where $P=(F_o^2+2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0285 and wR2=0.0720 for 7462 observed reflections for which $F > 4\sigma(F)$ and R1=0.0300 and wR2=0.0737 and GOF =1.057 for all 7736 unique, non-zero reflections and 443 variables. The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +0.17 and -0.16 e/Å^3.

Table S7 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in **Table S8** and **Table S9**. Anisotropic thermal parameters are in **Table S10**. **Table S11** and **Table S12**. list bond distances and bond angles. **Figure S2** is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

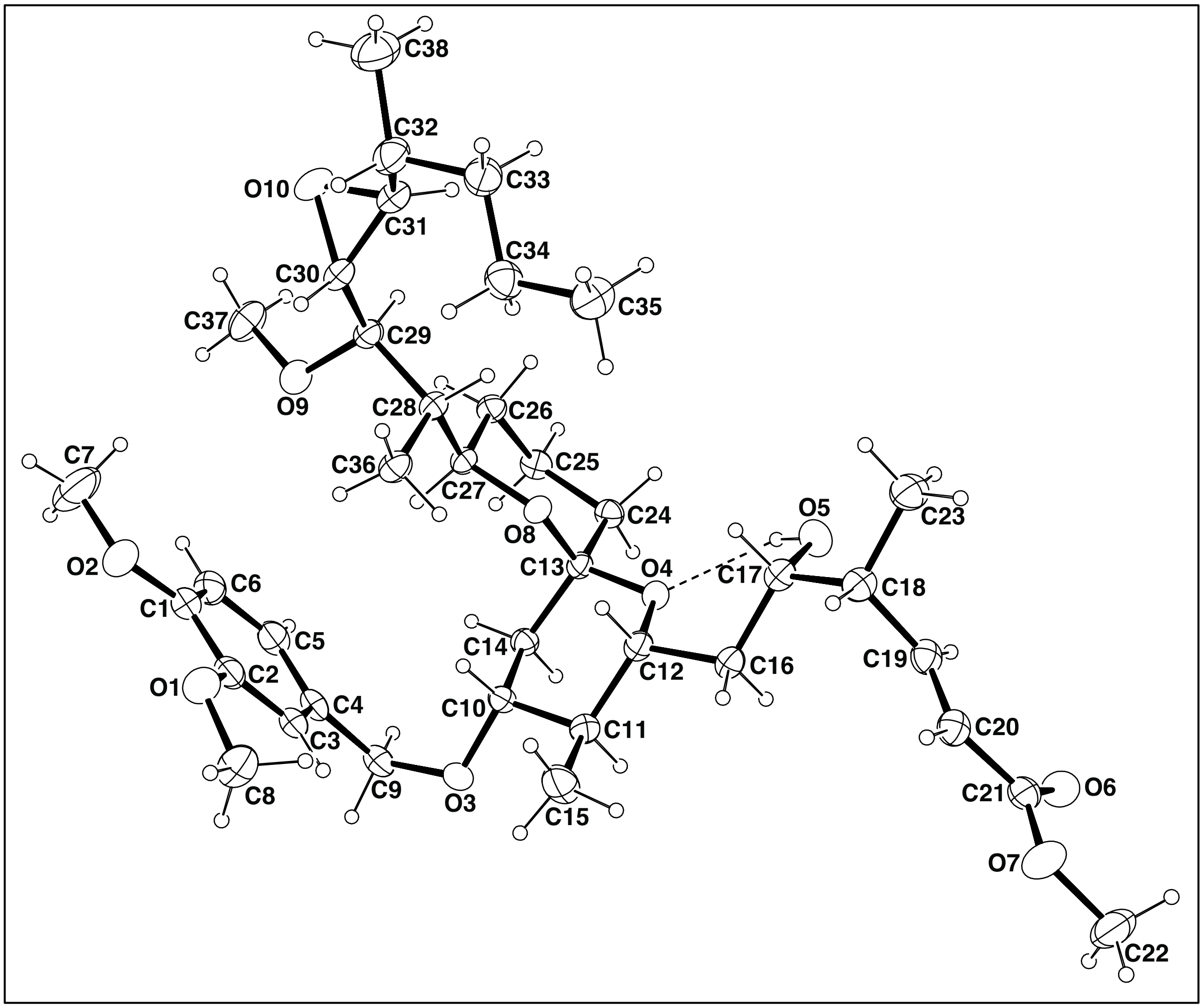


Figure S2. ORTEP drawing of compound **33** with 50% thermal ellipsoids.

Table S7. Summary of Structure Determination of Compound **33**

Empirical formula	$C_{38}H_{60}O_{10}$
Formula weight	676.86
Diffractometer	Rigaku XtaLAB Synergy-S
Temperature/K	100
Crystal system	orthorhombic
Space group	P212121
a	9.22500(10)Å
b	19.15890(10)Å
c	21.72220(10)Å
Volume	3839.20(5)Å^3
Z	4
dcalc	1.171 g/cm^3
μ	0.677 mm^{-1}
F(000)	1472.0
Crystal size, mm	0.24 × 0.08 × 0.06
2θ range for data collection	6.152 - 149.004°
Index ranges	$-10 \le h \le 11$, $-23 \le k \le 23$, $-25 \le l \le 27$
Reflections collected	50504
Independent reflections	7736[R(int) = 0.0287]
Data/restraints/parameters	7736/0/443
Goodness-of-fit on F2	1.057
Final R indexes [I>=2σ (I)]	R1 = 0.0285, wR2 = 0.0720
Final R indexes [all data]	R1 = 0.0300, wR2 = 0.0737
Largest diff. peak/hole	0.17/-0.16 eÅ^{-3}
Flack parameter	0.04(3)

Table S8. Refined Positional Parameters for Compound **33**

Atom	x	y	z	U(eq)
C1	-0.05637(19)	0.45508(9)	0.66387(9)	0.0287(4)
C2	-0.09063(18)	0.52346(9)	0.64425(8)	0.0253(3)
C3	-0.06034(18)	0.57959(9)	0.68193(8)	0.0238(3)
C4	0.00551(18)	0.56959(9)	0.73960(8)	0.0242(3)
C5	0.04172(19)	0.50292(9)	0.75775(8)	0.0284(4)
C6	0.0101(2)	0.44555(10)	0.72012(9)	0.0311(4)
C7	-0.0614(3)	0.33323(11)	0.64307(14)	0.0590(7)
C8	-0.2087(2)	0.59566(10)	0.57158(9)	0.0353(4)
C9	0.03237(19)	0.63167(9)	0.78091(8)	0.0258(3)
C10	0.22964(17)	0.67361(8)	0.71840(7)	0.0200(3)
C11	0.27947(18)	0.74055(9)	0.68689(8)	0.0240(3)
C12	0.42562(18)	0.72623(8)	0.65600(7)	0.0205(3)
C13	0.48938(17)	0.63568(8)	0.72811(7)	0.0180(3)
C14	0.34546(18)	0.64530(8)	0.76144(7)	0.0198(3)
C15	0.1664(2)	0.76521(11)	0.64047(10)	0.0367(4)
C16	0.49735(19)	0.78908(8)	0.62559(7)	0.0223(3)
C17	0.64134(19)	0.77008(9)	0.59523(7)	0.0235(3)
C18	0.6913(2)	0.82312(9)	0.54689(7)	0.0253(4)
C19	0.70049(19)	0.89585(9)	0.57176(7)	0.0243(3)
C20	0.6343(2)	0.95045(9)	0.54711(8)	0.0256(4)
C21	0.65490(19)	1.02146(9)	0.57155(8)	0.0255(3)
C22	0.5923(3)	1.13969(10)	0.55780(11)	0.0444(5)
C23	0.8379(2)	0.80149(10)	0.51963(8)	0.0321(4)
C24	0.61254(18)	0.61405(8)	0.77028(7)	0.0213(3)
C25	0.59411(19)	0.53817(9)	0.79099(7)	0.0227(3)

C26	0.57708(18)	0.48992(8)	0.73526(7)	0.0213(3)
C27	0.45660(17)	0.51513(8)	0.69279(7)	0.0185(3)
C28	0.45223(18)	0.47987(8)	0.62938(7)	0.0196(3)
C29	0.46285(19)	0.40019(8)	0.63441(7)	0.0217(3)
C30	0.4642(2)	0.36567(8)	0.57195(8)	0.0245(3)
C31	0.5981(2)	0.35883(9)	0.53588(8)	0.0278(4)
C32	0.5999(2)	0.35382(10)	0.46629(8)	0.0329(4)
C33	0.6620(2)	0.42075(10)	0.43779(9)	0.0333(4)
C34	0.5770(2)	0.48599(10)	0.45225(8)	0.0322(4)
C35	0.6331(3)	0.54928(10)	0.41720(9)	0.0372(4)
C36	0.31756(19)	0.50312(8)	0.59359(7)	0.0238(3)
C37	0.3630(2)	0.30925(9)	0.69536(9)	0.0355(4)
C38	0.6893(3)	0.29123(12)	0.44552(10)	0.0477(6)
O1	-0.15581(15)	0.52804(7)	0.58799(6)	0.0310(3)
O2	-0.09488(16)	0.40295(7)	0.62407(7)	0.0373(3)
O3	0.09851(12)	0.68987(6)	0.75045(5)	0.0242(2)
O4	0.52999(12)	0.69994(5)	0.70030(5)	0.0193(2)
O5	0.75469(13)	0.76286(7)	0.63950(6)	0.0280(3)
O6	0.72892(15)	1.03712(7)	0.61528(6)	0.0336(3)
O7	0.58039(17)	1.06794(7)	0.53823(6)	0.0362(3)
O8	0.47900(12)	0.58806(5)	0.67772(5)	0.0180(2)
O9	0.34260(14)	0.37728(6)	0.67056(5)	0.0269(3)
O10	0.53846(15)	0.29916(6)	0.56813(6)	0.0329(3)

Table S9. Positional Parameters for Hydrogens in Compound **33**

Atom	x	y	z	U(eq)
H3	-0.084244	0.62545	0.66875	0.029
H5	0.0886	0.495796	0.796176	0.034
H6	0.034609	0.399805	0.733416	0.037
H7a	-0.095509	0.300209	0.611808	0.089
H7b	-0.109472	0.323358	0.682346	0.089
H7c	0.043708	0.328405	0.648054	0.089
H8a	-0.257945	0.593088	0.531671	0.053
H8b	-0.12726	0.628365	0.568811	0.053
H8c	-0.277067	0.611875	0.602995	0.053
H9a	-0.06124	0.646957	0.798659	0.031
H9b	0.095504	0.616919	0.815393	0.031
H10	0.208288	0.637746	0.686211	0.024
H11	0.292821	0.7776	0.718814	0.029
H12	0.410724	0.6896	0.623822	0.025
H14a	0.313298	0.5999	0.778384	0.024
H14b	0.358785	0.677995	0.796274	0.024
H15a	0.193982	0.811213	0.624611	0.055
H15b	0.071631	0.76837	0.660665	0.055
H15cC	0.160966	0.731873	0.606331	0.055
H16a	0.514319	0.825625	0.657002	0.027
H16b	0.431077	0.808542	0.594123	0.027
H17	0.628804	0.724043	0.574207	0.028
H18	0.618522	0.823104	0.512768	0.03
H19	0.757559	0.903335	0.607555	0.029
H20	0.571901	0.943641	0.512828	0.031

H22a	0.538273	1.169648	0.529335	0.067
H22b	0.694556	1.153577	0.558	0.067
H22c	0.552216	1.144562	0.599357	0.067
H23a	0.91127	0.800826	0.552258	0.048
H23b	0.866523	0.834971	0.487764	0.048
H23c	0.829638	0.754841	0.501457	0.048
H24a	0.61444	0.644936	0.806804	0.026
H24b	0.705976	0.619256	0.748333	0.026
H25a	0.507509	0.53423	0.817687	0.027
H25b	0.679769	0.523688	0.815295	0.027
H26a	0.669525	0.488248	0.712157	0.026
H26b	0.554692	0.442066	0.749586	0.026
H27	0.360753	0.509348	0.713683	0.022
H28	0.538983	0.496291	0.60588	0.024
H29	0.554526	0.387973	0.656484	0.026
H30	0.372606	0.369603	0.547593	0.029
H31	0.686545	0.379965	0.554915	0.033
H32	0.498134	0.347624	0.451443	0.039
H33a	0.762622	0.426994	0.452601	0.04
H33b	0.665874	0.414904	0.39254	0.04
H34a	0.58272	0.495408	0.496998	0.039
H34b	0.473882	0.478331	0.44163	0.039
H35a	0.620387	0.541745	0.372903	0.056
H35b	0.736167	0.555999	0.426306	0.056
H35c	0.578708	0.590828	0.429826	0.056
H36a	0.23049	0.484911	0.61384	0.036
H36b	0.322621	0.485119	0.551416	0.036

H36c	0.313399	0.554225	0.592615	0.036
H37a	0.369633	0.275327	0.661714	0.053
H37b	0.280774	0.297366	0.721928	0.053
H37c	0.452693	0.308201	0.71953	0.053
H38a	0.788426	0.295667	0.461265	0.072
H38b	0.691392	0.2895	0.400437	0.072
H38c	0.64557	0.248278	0.461488	0.072
H5a	0.725391	0.738348	0.669047	0.042

Table S10. Refined Thermal Parameters (U's) for Compound **33**

Atom	U11	U22	U33	U23	U13	U12
C1	0.0203(8)	0.0261(9)	0.0396(9)	-0.0031(7)	0.0026(7)	-0.0015(7)
C2	0.0179(8)	0.0302(9)	0.0279(8)	-0.0019(7)	0.0014(6)	-0.0013(7)
C3	0.0164(7)	0.0251(8)	0.0300(8)	0.0005(7)	0.0039(6)	-0.0010(6)
C4	0.0151(7)	0.0299(8)	0.0276(8)	0.0008(7)	0.0045(6)	-0.0024(7)
C5	0.0216(8)	0.0325(9)	0.0311(8)	0.0045(7)	0.0010(7)	-0.0009(7)
C6	0.0247(9)	0.0266(9)	0.0420(10)	0.0059(7)	0.0019(8)	-0.0006(7)
C7	0.0677(17)	0.0246(10)	0.0848(18)	-0.0103(11)	-0.0301(15)	0.0095(11)
C8	0.0432(11)	0.0303(9)	0.0325(9)	0.0021(8)	-0.0094(9)	0.0002(8)
C9	0.0186(8)	0.0324(9)	0.0265(8)	-0.0004(7)	0.0036(7)	-0.0004(7)
C10	0.0165(7)	0.0206(7)	0.0231(7)	-0.0021(6)	0.0003(6)	0.0010(6)
C11	0.0216(8)	0.0203(7)	0.0302(8)	0.0011(6)	-0.0013(7)	0.0012(7)
C12	0.0213(8)	0.0181(7)	0.0223(7)	0.0011(6)	-0.0048(6)	-0.0001(6)
C13	0.0190(8)	0.0166(7)	0.0183(7)	-0.0014(6)	-0.0009(6)	-0.0008(6)
C14	0.0193(8)	0.0203(7)	0.0199(7)	-0.0014(6)	-0.0001(6)	0.0004(6)
C15	0.0257(9)	0.0370(10)	0.0474(11)	0.0178(9)	-0.0013(9)	0.0030(8)
C16	0.0250(8)	0.0184(7)	0.0235(7)	0.0012(6)	-0.0019(6)	-0.0009(6)

C17	0.0256(9)	0.0204(8)	0.0243(8)	0.0000(6)	-0.0013(7)	-0.0001(7)
C18	0.0298(9)	0.0241(8)	0.0219(7)	0.0001(6)	0.0013(7)	0.0005(7)
C19	0.0264(8)	0.0259(8)	0.0206(7)	0.0012(6)	0.0043(7)	-0.0032(7)
C20	0.0284(9)	0.0266(8)	0.0217(7)	0.0007(6)	0.0028(6)	-0.0027(7)
C21	0.0254(8)	0.0269(8)	0.0242(8)	0.0012(7)	0.0080(7)	0.0003(7)
C22	0.0590(14)	0.0232(9)	0.0510(12)	0.0007(8)	0.0101(11)	0.0062(10)
C23	0.0375(10)	0.0306(9)	0.0282(8)	0.0009(7)	0.0078(8)	0.0018(8)
C24	0.0190(8)	0.0239(8)	0.0210(7)	-0.0022(6)	-0.0028(6)	0.0004(6)
C25	0.0228(8)	0.0256(8)	0.0197(7)	0.0024(6)	-0.0032(6)	0.0029(7)
C26	0.0221(8)	0.0198(7)	0.0218(7)	0.0014(6)	-0.0013(6)	0.0021(6)
C27	0.0196(7)	0.0157(6)	0.0201(7)	0.0016(6)	-0.0001(6)	0.0001(6)
C28	0.0230(8)	0.0162(7)	0.0196(7)	0.0004(6)	0.0001(6)	0.0003(6)
C29	0.0237(8)	0.0175(7)	0.0238(7)	-0.0001(6)	-0.0010(7)	0.0011(7)
C30	0.0295(9)	0.0161(7)	0.0280(8)	-0.0022(6)	-0.0009(7)	-0.0007(7)
C31	0.0318(10)	0.0189(7)	0.0327(9)	-0.0028(7)	0.0012(7)	0.0009(7)
C32	0.0390(11)	0.0272(9)	0.0324(9)	-0.0074(7)	0.0043(8)	-0.0038(8)
C33	0.0364(10)	0.0323(10)	0.0313(9)	-0.0032(7)	0.0064(8)	-0.0034(8)
C34	0.0318(10)	0.0350(10)	0.0299(9)	-0.0005(7)	0.0030(7)	-0.0018(8)
C35	0.0474(12)	0.0331(10)	0.0312(9)	0.0017(8)	0.0042(8)	0.0012(9)
C36	0.0278(9)	0.0199(8)	0.0238(7)	0.0003(6)	-0.0038(7)	0.0019(7)
C37	0.0514(12)	0.0205(8)	0.0347(9)	0.0090(7)	-0.0016(9)	-0.0016(8)
C38	0.0627(15)	0.0361(11)	0.0444(11)	-0.0059(9)	0.0184(11)	0.0029(11)
O1	0.0329(7)	0.0284(6)	0.0317(6)	-0.0040(5)	-0.0063(5)	0.0016(5)
O2	0.0367(8)	0.0244(6)	0.0507(8)	-0.0062(6)	-0.0057(6)	-0.0004(6)
O3	0.0186(6)	0.0243(6)	0.0298(6)	-0.0015(5)	0.0028(5)	0.0019(5)
O4	0.0192(5)	0.0180(5)	0.0208(5)	0.0009(4)	-0.0021(4)	-0.0009(4)
O5	0.0252(6)	0.0324(7)	0.0264(6)	0.0077(5)	-0.0003(5)	-0.0015(5)

O6	0.0331(7)	0.0300(6)	0.0376(7)	-0.0084(5)	-0.0002(6)	0.0000(6)
O7	0.0499(8)	0.0243(6)	0.0345(7)	0.0026(5)	0.0010(6)	0.0066(6)
O8	0.0222(5)	0.0153(5)	0.0166(5)	-0.0006(4)	0.0000(4)	-0.0001(4)
O9	0.0320(7)	0.0197(6)	0.0288(6)	0.0079(5)	0.0020(5)	-0.0006(5)
O10	0.0452(8)	0.0167(5)	0.0369(6)	-0.0022(5)	0.0068(6)	0.0030(5)

Table S11. Bond Distances in Compound **33**, Å

C1-C2	1.413(2)	C1-C6	1.379(3)	C1-O2	1.368(2)
C2-C3	1.380(2)	C2-O1	1.365(2)	C3-C4	1.405(2)
C4-C5	1.378(2)	C4-C9	1.510(2)	C5-C6	1.400(3)
C7-O2	1.432(2)	C8-O1	1.429(2)	C9-O3	1.433(2)
C10-C11	1.525(2)	C10-C14	1.520(2)	C10-O3	1.4300(19)
C11-C12	1.531(2)	C11-C15	1.526(2)	C12-C16	1.525(2)
C12-O4	1.4514(18)	C13-C14	1.523(2)	C13-C24	1.517(2)
C13-O4	1.4216(18)	C13-O8	1.4281(17)	C16-C17	1.527(2)
C17-C18	1.532(2)	C17-O5	1.427(2)	C18-C19	1.497(2)
C18-C23	1.534(3)	C19-C20	1.324(2)	C20-C21	1.473(2)
C21-O6	1.208(2)	C21-O7	1.338(2)	C22-O7	1.443(2)
C24-C25	1.531(2)	C25-C26	1.531(2)	C26-C27	1.523(2)
C27-C28	1.535(2)	C27-O8	1.4498(17)	C28-C29	1.533(2)
C28-C36	1.532(2)	C29-C30	1.509(2)	C29-O9	1.428(2)
C30-C31	1.469(3)	C30-O10	1.449(2)	C31-C32	1.515(2)
C31-O10	1.449(2)	C32-C33	1.535(3)	C32-C38	1.524(3)
C33-C34	1.508(3)	C34-C35	1.522(3)	C37-O9	1.423(2)

Table S12. Bond Angles in Compound **33**, °

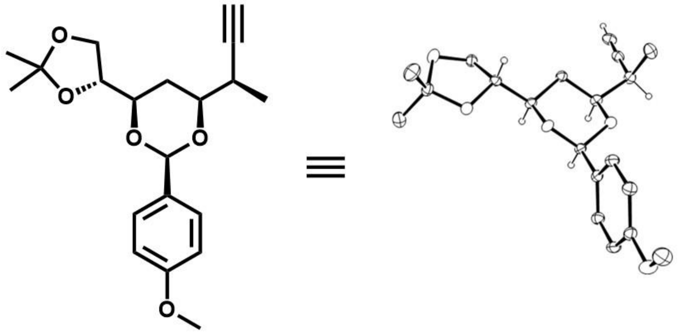
C6-C1-C2	119.29(16)	O2-C1-C2	115.34(16)	O2-C1-C6	125.36(17)
C3-C2-C1	119.88(16)	O1-C2-C1	115.35(15)	O1-C2-C3	124.75(16)
C2-C3-C4	120.66(16)	C3-C4-C9	119.55(15)	C5-C4-C3	119.09(16)
C5-C4-C9	121.35(15)	C4-C5-C6	120.68(17)	C1-C6-C5	120.38(17)
O3-C9-C4	114.09(13)	C14-C10-C11	111.37(13)	O3-C10-C11	106.88(12)
O3-C10-C14	111.91(12)	C10-C11-C12	108.15(13)	C10-C11-C15	110.55(14)
C15-C11-C12	111.60(14)	C16-C12-C11	115.50(13)	O4-C12-C11	110.85(12)
O4-C12-C16	105.87(12)	C24-C13-C14	113.51(12)	O4-C13-C14	109.08(12)
O4-C13-C24	107.20(12)	O4-C13-O8	104.19(11)	O8-C13-C14	112.52(12)
O8-C13-C24	109.78(12)	C10-C14-C13	111.32(12)	C12-C16-C17	112.11(13)
C16-C17-C18	113.55(14)	O5-C17-C16	111.68(13)	O5-C17-C18	107.80(14)
C17-C18-C23	110.52(15)	C19-C18-C17	112.77(13)	C19-C18-C23	109.94(15)
C20-C19-C18	124.28(16)	C19-C20-C21	121.62(16)	O6-C21-C20	125.88(16)
O6-C21-O7	123.41(16)	O7-C21-C20	110.71(15)	C13-C24-C25	110.71(13)
C24-C25-C26	110.62(13)	C27-C26-C25	111.24(13)	C26-C27-C28	115.03(13)
O8-C27-C26	109.78(13)	O8-C27-C28	103.02(11)	C29-C28-C27	111.87(12)
C36-C28-C27	110.41(13)	C36-C28-C29	112.18(13)	C30-C29-C28	111.88(13)
O9-C29-C28	107.19(13)	O9-C29-C30	111.47(14)	C31-C30-C29	121.71(15)
O10-C30-C29	116.16(14)	O10-C30-C31	59.57(11)	C30-C31-C32	123.18(17)
O10-C31-C30	59.54(11)	O10-C31-C32	115.87(15)	C31-C32-C33	110.71(15)
C31-C32-C38	110.57(17)	C38-C32-C33	109.66(17)	C34-C33-C32	114.50(16)
C33-C34-C35	112.30(16)	C2-O1-C8	115.59(14)	C1-O2-C7	116.29(16)
C10-O3-C9	114.55(12)	C13-O4-C12	114.04(11)	C21-O7-C22	115.83(16)
C13-O8-C27	116.88(11)	C37-O9-C29	112.76(14)	C30-O10-C31	60.89(11)

Table S13. Hydrogen Bonds for **33**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O5	H5a	O4	0.84	2.06	2.7376(16)	137.1

This report has been created with Olex2,[11] compiled on 2018.05.29 svn.r3508 for OlexSys.

(c). X-ray Structure Determination of Compound **44**



Compound **44**, $C_{20}H_{26}O_5$, crystallizes in the orthorhombic space group $P2_12_12_1$ (systematic absences h00: h=odd, 0k0: k=odd and 00l: l=odd) with a=6.09706(3)Å, b=9.44713(6)Å, c=32.28758(13)Å, V=1859.758(16)Å^3, Z=4, and d_{calc}=1.237 g/cm^3. X-ray intensity data were collected on a Rigaku XtaLAB Synergy-S diffractometer[6] equipped with an HPC area detector (HyPix-6000HE) and employing confocal multilayer optic-monochromated Cu-Kα radiation (λ=1.54184 Å) at a temperature of 100K. Preliminary indexing was performed from a series of sixty 0.5° rotation frames with exposures of 0.25 seconds for θ = ±47.290° and 1 second for θ = 113.25°. A total of 8902 frames (72 runs) were collected employing ω scans with a crystal to detector distance of 34.0 mm, rotation widths of 0.5° and exposures of 0.5 seconds.

Rotation frames were integrated using CrysAlisPro,[7] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 60677 reflections were measured over the ranges $5.474 \leq 2\theta \leq 148.902°$, $-7 \leq h \leq 7$, $-10 \leq k \leq 11$, $-40 \leq l \leq 40$ yielding 3794 unique reflections (R_{int} = 0.0605). The intensity data were corrected for Lorentz and polarization effects and for absorption using SCALE3 ABSPACK[8] (minimum and maximum transmission 0.3989, 1.0000). The structure was solved by dual space methods - SHELXT.[9] Refinement was by full-matrix least squares based on F^2 using SHELXL.[10] All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0439P)^2 + 0.3819P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0274 and wR2=0.0726 for 3721 observed reflections for which $F > 4\sigma(F)$ and R1=0.0286 and wR2=0.0780 and GOF =1.080 for all 3794 unique, non-zero reflections and 230 variables. The maximum Δ/σ in the final cycle of least squares was 0.000 and the two most prominent peaks in the final difference Fourier were +0.17 and -0.20 e/Å^3.

Table S14 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in **Table S15** and **Table S16**. Anisotropic thermal parameters are in **Table S17**. **Table S18** and **Table S19** list bond distances and bond angles. **Figure S3** is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

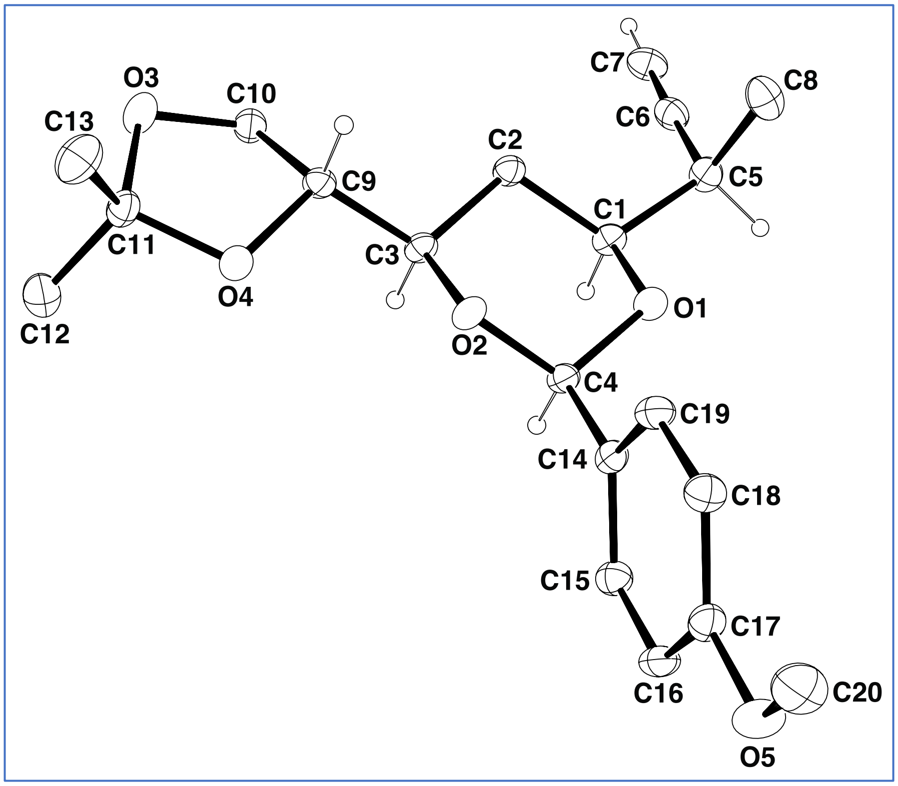


Figure S3. ORTEP drawing of the compound **44** with 50% thermal ellipsoids

Table S14. Summary of Structure Determination of Compound **44**

Empirical formula	$C_{20}H_{26}O_5$
Formula weight	346.41
Diffractometer	Rigaku XtaLAB Synergy-S (HyPix-6000HE)
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a	6.09706(3)Å
b	9.44713(6)Å
c	32.28758(13)Å
Volume	1859.758(16)Å^3
Z	4
d_{calc}	1.237 g/cm^3
μ	0.717 mm^{-1}
F(000)	744.0
Crystal size, mm	0.44 × 0.11 × 0.05
2θ range for data collection	5.474 - 148.902°
Index ranges	$-7 \le h \le 7$, $-10 \le k \le 11$, $-40 \le l \le 40$
Reflections collected	60677
Independent reflections	3794[R(int) = 0.0605]
Data/restraints/parameters	3794/0/230
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	$R_1 = 0.0274$, $wR_2 = 0.0726$
Final R indexes [all data]	$R_1 = 0.0286$, $wR_2 = 0.0780$
Largest diff. peak/hole	0.17/-0.20 eÅ^{-3}
Flack parameter	0.04(5)

Table S15. Refined Positional Parameters for Compound **44**

Atom	***x***	***y***	***z***	**U(eq)**
O1	0.50209(19)	0.80582(12)	0.34048(3)	0.0159(2)
O2	0.32020(18)	0.62888(12)	0.37721(3)	0.0154(2)
O3	-0.1459(2)	0.63361(13)	0.48843(3)	0.0246(3)
O4	0.0173(2)	0.52870(12)	0.43232(3)	0.0185(2)
O5	0.8897(2)	0.25952(14)	0.25659(4)	0.0249(3)
C1	0.3671(3)	0.91625(17)	0.35750(5)	0.0152(3)
C2	0.2846(3)	0.87142(17)	0.40025(4)	0.0156(3)
C3	0.1734(2)	0.72758(17)	0.39648(4)	0.0145(3)
C4	0.3813(3)	0.67693(17)	0.33723(4)	0.0145(3)
C5	0.5049(3)	1.05221(17)	0.35660(5)	0.0180(3)
C6	0.3782(3)	1.17247(18)	0.37297(5)	0.0192(3)
C7	0.2824(3)	1.2713(2)	0.38714(5)	0.0231(4)
C8	0.7253(3)	1.0388(2)	0.37928(6)	0.0245(4)
C9	0.1143(3)	0.66552(17)	0.43815(4)	0.0155(3)
C10	-0.0660(3)	0.74188(18)	0.46144(5)	0.0186(3)
C11	-0.1175(3)	0.50029(18)	0.46776(5)	0.0182(3)
C12	-0.3349(3)	0.4438(2)	0.45247(6)	0.0263(4)
C13	-0.0009(3)	0.4012(2)	0.49723(5)	0.0284(4)
C14	0.5217(3)	0.56684(17)	0.31695(5)	0.0151(3)
C15	0.4561(3)	0.50836(17)	0.27924(5)	0.0174(3)
C16	0.5816(3)	0.40492(18)	0.26016(5)	0.0185(3)
C17	0.7749(3)	0.35893(18)	0.27845(5)	0.0178(3)
C18	0.8429(3)	0.41580(18)	0.31632(5)	0.0190(3)
C19	0.7143(3)	0.51914(19)	0.33516(5)	0.0177(3)
C20	1.0722(3)	0.1933(2)	0.27624(6)	0.0289(4)

Table S16. Positional Parameters for Hydrogens in Compound **44**

Atom	***x***	***y***	***z***	**U(eq)**
H1	0.237415	0.929649	0.338947	0.018
H2a	0.409119	0.865389	0.419859	0.019
H2b	0.17909	0.942204	0.41093	0.019
H3	0.037888	0.73705	0.37926	0.017
H4	0.246723	0.693057	0.320182	0.017
H5	0.538194	1.073367	0.326907	0.022
H7	0.206157	1.350075	0.398426	0.028
H8a	0.698841	1.022228	0.408824	0.037
H8b	0.809406	1.12642	0.375788	0.037
H8c	0.80834	0.959284	0.367715	0.037
H9	0.248155	0.657565	0.455885	0.019
H10a	-0.007313	0.823264	0.47726	0.022
H10b	-0.182144	0.775515	0.442411	0.022
H12a	-0.404181	0.514121	0.43438	0.039
H12b	-0.430859	0.42473	0.47618	0.039
H12c	-0.31074	0.356065	0.436956	0.039
H13a	0.023535	0.309852	0.483582	0.043
H13b	-0.091155	0.387111	0.522009	0.043
H13c	0.140516	0.442269	0.505206	0.043
H15	0.324292	0.539768	0.266529	0.021
H16	0.535273	0.365449	0.234554	0.022
H18	0.974843	0.384405	0.328986	0.023
H19	0.759152	0.557755	0.360978	0.021
H20a	1.137895	0.124276	0.257286	0.043
H20b	1.02273	0.144984	0.301411	0.043
H20c	1.181473	0.265231	0.283516	0.043

Table S17. Refined Thermal Parameters (U's) for Compound **44**

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
O1	0.0204(5)	0.0103(5)	0.0170(5)	-0.0009(4)	0.0030(4)	0.0014(4)
O2	0.0206(5)	0.0129(6)	0.0126(5)	0.0005(4)	0.0033(4)	0.0027(4)
O3	0.0351(7)	0.0168(6)	0.0218(5)	-0.0023(5)	0.0129(5)	-0.0031(5)
O4	0.0260(6)	0.0120(5)	0.0175(5)	-0.0017(4)	0.0056(5)	-0.0022(5)
O5	0.0241(6)	0.0237(7)	0.0271(6)	-0.0108(5)	0.0001(5)	0.0067(5)
C1	0.0183(7)	0.0115(8)	0.0159(7)	-0.0004(6)	0.0006(6)	0.0030(6)
C2	0.0183(7)	0.0135(8)	0.0149(7)	-0.0016(6)	0.0017(5)	0.0003(6)
C3	0.0170(7)	0.0128(8)	0.0135(7)	-0.0016(6)	0.0017(6)	0.0023(6)
C4	0.0196(7)	0.0117(7)	0.0121(6)	0.0000(6)	0.0009(6)	-0.0005(6)
C5	0.0218(8)	0.0128(8)	0.0193(7)	0.0006(6)	0.0027(6)	0.0004(7)
C6	0.0210(7)	0.0156(8)	0.0209(7)	0.0008(6)	-0.0025(6)	-0.0025(7)
C7	0.0263(8)	0.0170(9)	0.0260(8)	-0.0047(7)	-0.0035(7)	0.0011(7)
C8	0.0204(8)	0.0196(9)	0.0336(9)	-0.0004(7)	0.0002(7)	-0.0010(7)
C9	0.0198(7)	0.0119(8)	0.0146(6)	-0.0015(6)	0.0009(6)	-0.0009(6)
C10	0.0216(8)	0.0156(8)	0.0187(7)	-0.0028(6)	0.0045(6)	-0.0023(7)
C11	0.0235(8)	0.0141(8)	0.0169(7)	0.0005(6)	0.0053(6)	0.0000(7)
C12	0.0261(9)	0.0266(10)	0.0263(8)	0.0025(7)	0.0013(7)	-0.0057(8)
C13	0.0312(9)	0.0324(11)	0.0217(8)	0.0067(7)	0.0009(7)	0.0048(8)
C14	0.0207(7)	0.0104(7)	0.0142(6)	0.0010(5)	0.0030(6)	-0.0003(6)
C15	0.0201(7)	0.0162(8)	0.0159(7)	0.0002(6)	-0.0005(6)	0.0001(6)
C16	0.0240(8)	0.0165(8)	0.0151(7)	-0.0038(6)	-0.0004(6)	-0.0005(6)
C17	0.0207(7)	0.0138(8)	0.0189(7)	-0.0018(6)	0.0044(6)	0.0004(6)
C18	0.0190(7)	0.0181(9)	0.0198(7)	-0.0015(6)	-0.0013(6)	0.0017(6)
C19	0.0222(7)	0.0157(8)	0.0151(7)	-0.0020(6)	-0.0006(6)	-0.0001(7)
C20	0.0231(8)	0.0248(10)	0.0389(10)	-0.0092(8)	0.0005(7)	0.0074(7)

Table S18. Bond Distances in Compound **44**, Å

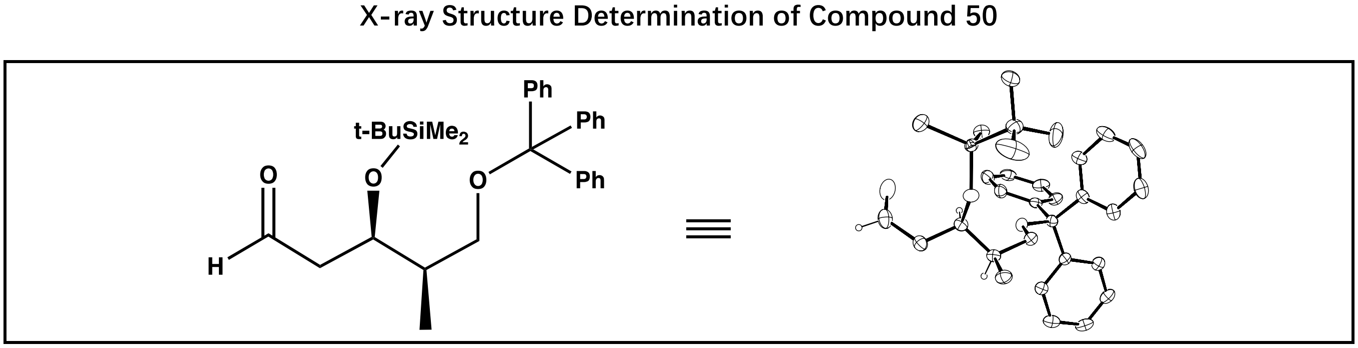
O1-C1	1.4378(18)	O1-C4	1.4267(19)	O2-C3	1.4344(18)
O2-C4	1.4181(17)	O3-C10	1.429(2)	O3-C11	1.436(2)
O4-C9	1.4336(19)	O4-C11	1.4345(18)	O5-C17	1.368(2)
O5-C20	1.425(2)	C1-C2	1.529(2)	C1-C5	1.535(2)
C2-C3	1.523(2)	C3-C9	1.511(2)	C4-C14	1.498(2)
C5-C6	1.472(2)	C5-C8	1.536(2)	C6-C7	1.193(3)
C9-C10	1.514(2)	C11-C12	1.512(2)	C11-C13	1.513(2)
C14-C15	1.396(2)	C14-C19	1.389(2)	C15-C16	1.385(2)
C16-C17	1.388(2)	C17-C18	1.398(2)	C18-C19	1.392(2)

Table S19. Bond Angles in Compound **44**, °

C4-O1-C1	110.61(11)	C4-O2-C3	110.54(11)	C10-O3-C11	107.64(11)
C9-O4-C11	107.46(11)	C17-O5-C20	118.13(13)	O1-C1-C2	109.40(12)
O1-C1-C5	106.65(12)	C2-C1-C5	115.39(13)	C3-C2-C1	108.74(12)
O2-C3-C2	109.68(12)	O2-C3-C9	106.44(12)	C9-C3-C2	112.40(12)
O1-C4-C14	109.27(12)	O2-C4-O1	109.99(12)	O2-C4-C14	109.02(12)
C1-C5-C8	113.65(14)	C6-C5-C1	110.59(13)	C6-C5-C8	110.58(14)
C7-C6-C5	177.46(18)	O4-C9-C3	109.34(12)	O4-C9-C10	101.29(12)
C3-C9-C10	115.49(13)	O3-C10-C9	102.08(13)	O3-C11-C12	110.82(14)
O3-C11-C13	107.89(14)	O4-C11-O3	106.01(12)	O4-C11-C12	107.95(13)
O4-C11-C13	110.39(14)	C12-C11-C13	113.52(15)	C15-C14-C4	119.53(14)
C19-C14-C4	121.55(14)	C19-C14-C15	118.91(14)	C16-C15-C14	120.59(15)
C15-C16-C17	120.04(14)	O5-C17-C16	115.49(14)	O5-C17-C18	124.27(15)
C16-C17-C18	120.22(15)	C19-C18-C17	118.99(15)	C14-C19-C18	121.24(14)

This report has been created with Olex2,[11] compiled on 2021.08.20 svn.r13c46975 for OlexSys.

(d). X-ray Structure Determination of Compound **50**


X-ray Structure Determination of Compound 50

Compound **50**, $C_{31}H_{40}O_3Si$, crystallizes in the monoclinic space group $P2_1$ (systematic absences 0k0: k=odd) with a=8.94406(5)Å, b=35.4322(2)Å, c=9.02579(4)Å, β=91.6565(5)°, V=2859.15(3)$Å^3$, Z=4, and d_{calc}=1.135 g/cm_3 . X-ray intensity data were collected on a Rigaku XtaLAB Synergy-S[6] HPC area detector (HyPix-6000HE), employing confocal multilayer optic-monochromated Mo-Kα radiation (λ=0.71073Å) at a temperature of 100K. Preliminary indexing was performed from a series of thirty 0.5° rotation frames with exposures of 0.5 seconds. A total of 7026 frames (64 runs) were collected employing ω scans with a crystal to detector distance of 34,0 mm, rotation widths of 0.5° and exposures of 0.25 seconds.

Rotation frames were integrated using CrysAlisPro,[7] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 71308 reflections were measured over the ranges $4.988 \leq 2\theta \leq 148.996°$, $-11 \leq h \leq 11$, $-42 \leq k \leq 44$, $-11 \leq l \leq 11$ yielding 11607 unique reflections (R_{int} = 0.0337). The intensity data were corrected for Lorentz and polarization effects and for absorption using SCALE3 ABSPACK[8] (minimum and maximum transmission 0.5395, 1.0000). The structure was solved by direct methods – SHELXT.[9] Refinement was by full-matrix least squares based on F^2 using SHELXL-2018.[10] All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+(0.0465P)^2+0.8017P]$ where $P=(F_o^2+2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0332 and wR2=0.0849 for 11371 observed reflections for which $F > 4\sigma(F)$ and R1=0.0346 and wR2=0.0879 and GOF =1.084 for all 11607 unique, non-zero reflections and 644 variables. The maximum Δ/σ in the final cycle of least squares was 0.000 and the two most prominent peaks in the final difference Fourier were +0.26 and -0.20 e/$Å^3$.

Table S20 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in **Table S21** and **Table S22**. Anisotropic thermal parameters are in **Table S23**. **Table S24** and **Table S25** list bond distances and bond angles. **Figure S4** and **Figure S5** are ORTEP representations of the molecule with 50% probability thermal ellipsoids displayed.

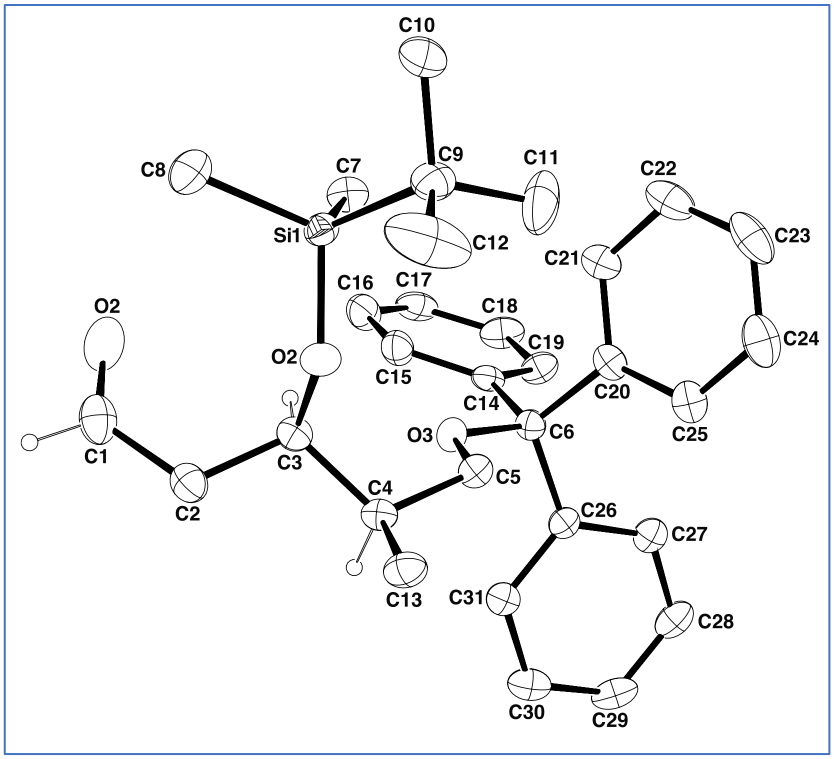


Figure S4-1. ORTEP drawing of molecule no. 1 of the asymmetric unit with 50% thermal ellipsoids

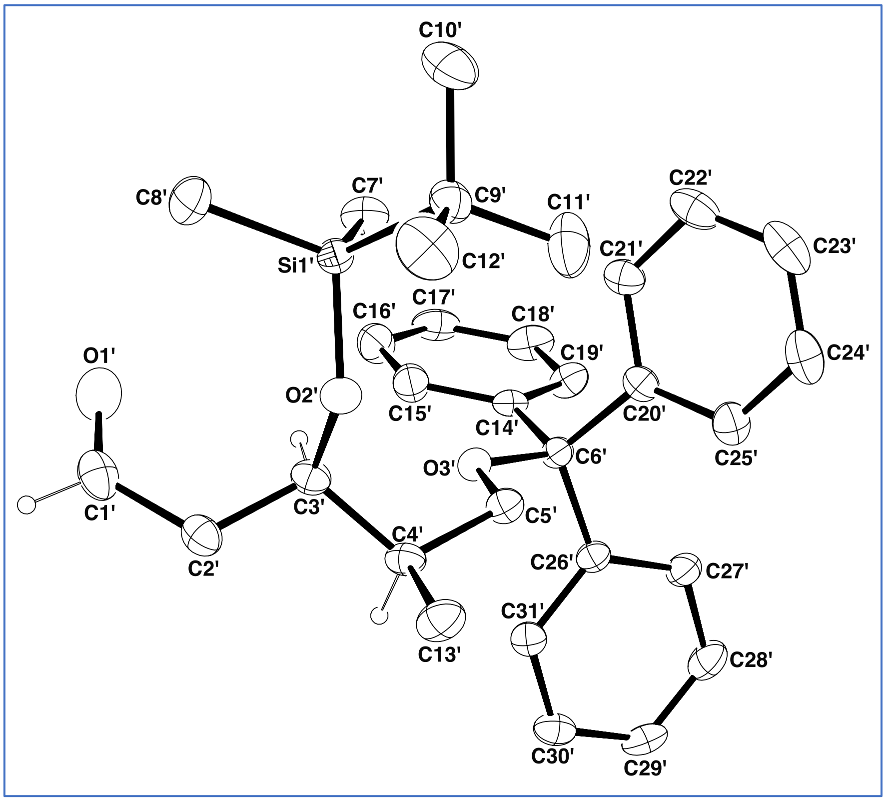


Figure S4-2. ORTEP drawing of molecule no. 2 of the asymmetric unit with 50% thermal ellipsoids

Table S20. Summary of Structure Determination of Compound **50**

Empirical formula	$C_{31}H_{40}O_3Si$
Formula weight	488.72
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a	8.94406(5)Å
b	35.4322(2)Å
c	9.02579(4)Å
β	91.6565(5)°
Volume	2859.15(3)$Å^3$
Z	4
d_{calc}	1.135 g/cm^3
μ	0.937 mm^{-1}
F(000)	1056.0
Crystal size, mm	0.25 × 0.18 × 0.13
2θ range for data collection	4.988 - 148.996°
Index ranges	-11 ≤ h ≤ 11, -42 ≤ k ≤ 44, -11 ≤ l ≤ 11
Reflections collected	71308
Independent reflections	11607[R(int) = 0.0337]
Data/restraints/parameters	11607/1/644
Goodness-of-fit on F^2	1.084

Final R indexes [I>=2σ (I)]	R_1 = 0.0332, wR_2 = 0.0849
Final R indexes [all data]	R_1 = 0.0346, wR_2 = 0.0879
Largest diff. peak/hole	0.26/-0.20 eÅ^{-3}
Flack parameter	-0.008(13)

Table S21. Refined Positional Parameters for Compound **50**

Atom	***x***	***y***	***z***	**U(eq)**
C1	0.6343(3)	0.00516(8)	0.7513(3)	0.0314(6)
C2	0.6016(3)	0.04211(7)	0.8234(3)	0.0252(5)
C3	0.5283(2)	0.07174(7)	0.7223(3)	0.0206(4)
C4	0.5527(3)	0.11166(7)	0.7827(2)	0.0208(4)
C5	0.5062(3)	0.14184(6)	0.6710(2)	0.0206(4)
C6	0.6030(2)	0.17073(6)	0.4486(2)	0.0189(4)
C7	0.3568(3)	0.05968(7)	0.3912(3)	0.0275(5)
C8	0.2512(3)	-0.00497(8)	0.5890(3)	0.0346(6)
C9	0.0792(3)	0.06956(8)	0.5873(3)	0.0287(5)
C10	-0.0382(3)	0.04801(9)	0.4944(3)	0.0364(6)
C11	0.0812(3)	0.11033(9)	0.5335(6)	0.0597(11)
C12	0.0313(4)	0.06794(16)	0.7490(4)	0.0666(13)
C13	0.4708(3)	0.11840(7)	0.9272(3)	0.0262(5)
C14	0.6867(2)	0.15751(7)	0.3115(2)	0.0204(4)
C15	0.7253(3)	0.11978(8)	0.2927(3)	0.0280(5)
C16	0.8062(3)	0.10845(8)	0.1704(3)	0.0334(6)
C17	0.8483(3)	0.13451(9)	0.0655(3)	0.0314(6)
C18	0.8074(3)	0.17179(8)	0.0817(3)	0.0317(6)
C19	0.7269(3)	0.18330(7)	0.2033(3)	0.0264(5)

C20	0.4437(2)	0.18422(7)	0.4066(2)	0.0215(5)
C21	0.3641(3)	0.16651(7)	0.2910(3)	0.0261(5)
C22	0.2149(3)	0.17578(9)	0.2595(3)	0.0348(6)
C23	0.1430(3)	0.20267(9)	0.3435(3)	0.0380(7)
C24	0.2210(3)	0.22016(9)	0.4588(3)	0.0344(6)
C25	0.3697(3)	0.21100(7)	0.4908(3)	0.0262(5)
C26	0.7007(2)	0.20110(6)	0.5266(2)	0.0193(4)
C27	0.6950(3)	0.23895(7)	0.4842(3)	0.0240(5)
C28	0.7926(3)	0.26527(7)	0.5483(3)	0.0282(5)
C29	0.8966(3)	0.25412(8)	0.6565(3)	0.0296(5)
C30	0.9035(3)	0.21669(8)	0.6995(3)	0.0277(5)
C31	0.8065(2)	0.19027(7)	0.6344(2)	0.0217(5)
Si1	0.26995(7)	0.04715(2)	0.56972(7)	0.01990(13)
O1	0.6242(2)	-0.00104(6)	0.6201(2)	0.0402(5)
O2	0.37164(18)	0.06436(5)	0.70919(18)	0.0230(3)
O3	0.59425(18)	0.13795(4)	0.54207(17)	0.0203(3)
C1'	0.2732(3)	0.49083(8)	0.7402(3)	0.0294(5)
C2'	0.2259(3)	0.45374(7)	0.6751(3)	0.0241(5)
C3'	0.1605(2)	0.42575(7)	0.7846(3)	0.0210(4)
C4'	0.1800(3)	0.38486(7)	0.7342(2)	0.0211(5)
C5'	0.1340(3)	0.35643(7)	0.8516(2)	0.0208(4)
C6'	0.2361(2)	0.32905(6)	1.0788(2)	0.0184(4)
C7'	0.0005(3)	0.43941(8)	1.1159(3)	0.0292(5)
C8'	-0.0918(3)	0.50534(7)	0.9126(3)	0.0344(6)
C9'	-0.2837(3)	0.43374(7)	0.9080(3)	0.0264(5)
C10'	-0.3871(3)	0.45162(10)	1.0210(4)	0.0435(7)
C11'	-0.2852(3)	0.39105(9)	0.9254(4)	0.0438(8)

C12'	-0.3441(3)	0.44337(10)	0.7514(3)	0.0418(7)
C13'	0.0931(3)	0.37639(8)	0.5893(3)	0.0293(5)
C14'	0.3256(2)	0.34195(7)	1.2175(2)	0.0195(4)
C15'	0.3863(3)	0.37784(8)	1.2302(3)	0.0284(5)
C16'	0.4699(3)	0.38823(9)	1.3563(3)	0.0349(6)
C17'	0.4943(3)	0.36292(9)	1.4705(3)	0.0322(6)
C18'	0.4331(3)	0.32699(8)	1.4594(3)	0.0317(6)
C19'	0.3490(3)	0.31677(7)	1.3347(3)	0.0264(5)
C20'	0.0773(3)	0.31702(7)	1.1183(2)	0.0209(4)
C21'	0.0012(3)	0.33788(7)	1.2234(3)	0.0245(5)
C22'	-0.1492(3)	0.33095(8)	1.2484(3)	0.0325(6)
C23'	-0.2253(3)	0.30298(9)	1.1696(3)	0.0360(6)
C24'	-0.1503(3)	0.28186(8)	1.0670(3)	0.0341(6)
C25'	-0.0008(3)	0.28876(7)	1.0410(3)	0.0271(5)
C26'	0.3294(2)	0.29817(6)	1.0050(2)	0.0194(4)
C27'	0.3262(3)	0.26046(7)	1.0492(3)	0.0253(5)
C28'	0.4215(3)	0.23417(7)	0.9868(3)	0.0308(5)
C29'	0.5209(3)	0.24493(8)	0.8800(3)	0.0282(5)
C30'	0.5255(3)	0.28239(7)	0.8364(3)	0.0256(5)
C31'	0.4309(3)	0.30858(7)	0.8978(2)	0.0214(5)
Si1'	-0.08735(7)	0.45290(2)	0.93350(7)	0.02023(13)
O1'	0.2734(2)	0.49844(6)	0.8702(2)	0.0375(4)
O2'	0.00430(17)	0.43356(5)	0.79746(18)	0.0220(3)
O3'	0.22575(18)	0.36157(4)	0.98337(16)	0.0192(3)

Table S22. Positional Parameters for Hydrogens in Compound **50**

Atom	*x*	*y*	*z*	U(eq)
H1	0.66554	-0.015071	0.81396	0.038
H2a	0.696528	0.05259	0.864731	0.03
H2b	0.535272	0.037437	0.907392	0.03
H3	0.57229	0.069974	0.621936	0.025
H4	0.662212	0.114777	0.804849	0.025
H5a	0.398764	0.139035	0.643648	0.025
H5b	0.521562	0.167189	0.715038	0.025
H7a	0.386421	0.08631	0.393163	0.041
H7b	0.284459	0.055441	0.309295	0.041
H7c	0.445241	0.043888	0.377281	0.041
H8a	0.348537	-0.016917	0.574427	0.052
H8b	0.178695	-0.014398	0.514451	0.052
H8c	0.216681	-0.011002	0.688294	0.052
H10a	-0.011229	0.048587	0.389967	0.055
H10b	-0.136259	0.05987	0.505287	0.055
H10c	-0.042321	0.021777	0.528405	0.055
H11a	0.147625	0.125284	0.598745	0.09
H11b	-0.020264	0.120761	0.535054	0.09
H11c	0.117419	0.111166	0.432136	0.09
H12a	0.021626	0.041537	0.779595	0.1
H12b	-0.065115	0.080748	0.758109	0.1
H12c	0.106771	0.0805	0.812517	0.1
H13a	0.362662	0.116154	0.908361	0.039
H13b	0.494077	0.143761	0.964549	0.039
H13c	0.503128	0.099607	1.001038	0.039

H15	0.69633	0.101596	0.36373	0.034
H16	0.832435	0.082645	0.159133	0.04
H17	0.904906	0.126843	-0.016734	0.038
H18	0.834342	0.18976	0.009046	0.038
H19	0.699048	0.209048	0.212618	0.032
H21	0.41194	0.147941	0.233102	0.031
H22	0.162275	0.163592	0.180062	0.042
H23	0.041413	0.208987	0.322014	0.046
H24	0.172585	0.238619	0.516761	0.041
H25	0.421436	0.223133	0.570907	0.031
H27	0.623597	0.246863	0.410689	0.029
H28	0.787877	0.290928	0.517959	0.034
H29	0.962838	0.272099	0.70082	0.036
H30	0.974564	0.208949	0.773636	0.033
H31	0.812738	0.164579	0.66402	0.026
H1'	0.305478	0.509802	0.673993	0.035
H2a'	0.313729	0.441897	0.629574	0.029
H2b'	0.150443	0.458481	0.594912	0.029
H3'	0.211594	0.429144	0.883723	0.025
H4'	0.288633	0.380854	0.71601	0.025
H5a'	0.027472	0.360152	0.87475	0.025
H5b'	0.146156	0.330431	0.813625	0.025
H7a'	0.035719	0.413252	1.11143	0.044
H7b'	-0.073375	0.441735	1.1935	0.044
H7c'	0.085322	0.456148	1.138664	0.044
H8a'	0.006447	0.515786	0.940654	0.052
H8b'	-0.167629	0.515907	0.976974	0.052

H8c'	-0.116557	0.511837	0.809253	0.052
H10a'	-0.3526	0.444736	1.121504	0.065
H10b'	-0.489363	0.442405	1.003558	0.065
H10c'	-0.38526	0.479134	1.010312	0.065
H11a'	-0.228315	0.379511	0.845975	0.066
H11b'	-0.388627	0.381936	0.919688	0.066
H11c'	-0.239518	0.384194	1.021656	0.066
H12a'	-0.348012	0.470841	0.739323	0.063
H12b'	-0.44489	0.432862	0.737243	0.063
H12c'	-0.278037	0.432545	0.677829	0.063
H13a'	0.109329	0.350026	0.561117	0.044
H13b'	0.128296	0.393036	0.510902	0.044
H13c'	-0.013781	0.380688	0.603179	0.044
H15'	0.370611	0.395523	1.152165	0.034
H16'	0.510523	0.412955	1.363636	0.042
H17'	0.552365	0.369998	1.555826	0.039
H18'	0.449046	0.309372	1.537599	0.038
H19'	0.306571	0.292225	1.328834	0.032
H21'	0.052549	0.356984	1.278417	0.029
H22'	-0.199993	0.345451	1.319826	0.039
H23'	-0.328203	0.298405	1.186015	0.043
H24'	-0.201529	0.262423	1.013772	0.041
H25'	0.049185	0.274062	0.969643	0.032
H27'	0.258595	0.252663	1.122453	0.03
H28'	0.418225	0.208573	1.017829	0.037
H29'	0.585184	0.226864	0.83721	0.034
H30'	0.594099	0.290116	0.763922	0.031

H31'	0.435138	0.334139	0.866428	0.026

Table S23. Refined Thermal Parameters (U's) for Compound **50**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0243(12)	0.0290(13)	0.0412(15)	0.0073(11)	0.0071(10)	0.0037(10)
C2	0.0223(11)	0.0259(12)	0.0273(11)	0.0054(10)	-0.0003(9)	-0.0018(9)
C3	0.0175(10)	0.0232(11)	0.0213(10)	0.0008(9)	0.0015(8)	-0.0010(8)
C4	0.0208(10)	0.0233(12)	0.0182(10)	-0.0004(8)	-0.0006(8)	-0.0020(8)
C5	0.0216(11)	0.0209(11)	0.0195(10)	-0.0006(8)	0.0032(8)	-0.0013(8)
C6	0.0201(10)	0.0195(11)	0.0172(10)	0.0015(8)	0.0014(8)	-0.0003(8)
C7	0.0276(12)	0.0300(13)	0.0248(12)	-0.0026(9)	-0.0001(9)	-0.0029(10)
C8	0.0396(15)	0.0241(13)	0.0397(14)	-0.0002(11)	-0.0017(12)	-0.0052(11)
C9	0.0189(11)	0.0326(14)	0.0345(13)	-0.0060(11)	0.0001(10)	-0.0015(10)
C10	0.0238(12)	0.0374(15)	0.0474(15)	-0.0010(13)	-0.0098(11)	-0.0018(11)
C11	0.0246(14)	0.0244(15)	0.130(4)	-0.0062(18)	-0.0033(18)	0.0044(11)
C12	0.0252(15)	0.136(4)	0.0389(17)	-0.025(2)	0.0056(13)	0.0118(19)
C13	0.0312(12)	0.0286(13)	0.0189(11)	-0.0020(9)	0.0015(9)	-0.0039(10)
C14	0.0176(10)	0.0275(12)	0.0161(10)	-0.0035(9)	-0.0016(8)	0.0005(9)
C15	0.0341(13)	0.0286(13)	0.0213(11)	-0.0008(10)	-0.0009(10)	0.0076(10)
C16	0.0355(14)	0.0385(15)	0.0260(12)	-0.0073(11)	-0.0017(10)	0.0150(12)
C17	0.0242(12)	0.0504(16)	0.0196(11)	-0.0117(11)	0.0009(9)	0.0033(11)
C18	0.0318(13)	0.0424(16)	0.0211(12)	-0.0037(11)	0.0053(10)	-0.0103(11)
C19	0.0304(12)	0.0279(12)	0.0212(11)	-0.0036(9)	0.0052(9)	-0.0049(10)
C20	0.0195(10)	0.0252(11)	0.020(1)	0.0069(9)	0.0033(9)	-0.0005(9)
C21	0.0232(11)	0.0320(13)	0.0229(11)	0.0047(10)	0.0000(9)	-0.0038(10)
C22	0.0248(13)	0.0477(16)	0.0316(13)	0.0137(12)	-0.0047(10)	-0.0084(11)
C23	0.0182(11)	0.0505(17)	0.0453(16)	0.0222(14)	0.0022(11)	0.0031(11)
C24	0.0265(13)	0.0382(15)	0.0392(15)	0.0119(12)	0.0117(11)	0.0081(11)
C25	0.0257(12)	0.0279(13)	0.0255(12)	0.0054(10)	0.0063(9)	0.0028(10)

C26	0.0195(10)	0.0216(11)	0.017(1)	-0.0021(8)	0.0050(8)	0.0009(8)
C27	0.0276(12)	0.0244(12)	0.0202(10)	0.0002(9)	0.0054(9)	-0.0003(9)
C28	0.0368(13)	0.0239(12)	0.0246(12)	-0.0035(9)	0.0108(10)	-0.0061(10)
C29	0.0308(13)	0.0357(14)	0.0227(11)	-0.0083(10)	0.0078(10)	-0.0144(11)
C30	0.0216(11)	0.0420(15)	0.0196(11)	-0.0027(10)	0.0037(9)	-0.0046(10)
C31	0.0195(10)	0.0260(12)	0.0198(10)	-0.0004(9)	0.0043(8)	0.0004(9)
Si1	0.0191(3)	0.0190(3)	0.0216(3)	-0.0019(2)	0.0004(2)	-0.0015(2)
O1	0.0456(11)	0.0306(10)	0.0451(12)	-0.0025(8)	0.0116(9)	0.0097(9)
O2	0.0184(8)	0.0270(9)	0.0236(8)	-0.0037(7)	0.0006(6)	-0.0028(6)
O3	0.0248(8)	0.0181(8)	0.0182(7)	0.0011(6)	0.0034(6)	0.0013(6)
C1'	0.0197(11)	0.0307(13)	0.0377(14)	0.0089(11)	-0.001(1)	-0.0012(10)
C2'	0.0219(11)	0.0262(12)	0.0242(11)	0.0061(10)	0.0017(8)	0.0026(9)
C3'	0.0175(11)	0.0248(11)	0.0208(10)	0.0008(9)	0.0012(8)	0.0023(9)
C4'	0.0232(11)	0.0239(12)	0.0163(10)	0.0011(9)	0.0022(8)	0.0046(9)
C5'	0.0224(11)	0.0214(11)	0.0185(10)	-0.0003(8)	-0.0013(8)	0.0019(9)
C6'	0.0227(11)	0.0167(10)	0.016(1)	0.0004(8)	0.0004(8)	0.0015(8)
C7'	0.0290(12)	0.0342(14)	0.0243(12)	-0.0017(10)	0.0014(10)	0.0052(10)
C8'	0.0372(14)	0.0211(13)	0.0450(15)	0.0019(11)	0.0067(12)	0.0028(10)
C9'	0.0198(11)	0.0266(13)	0.0331(13)	0.0019(10)	0.0035(9)	0.0004(9)
C10'	0.0273(13)	0.0521(18)	0.0518(17)	-0.0043(15)	0.0143(12)	-0.0034(13)
C11'	0.0298(14)	0.0313(15)	0.070(2)	0.0071(14)	-0.0028(14)	-0.0068(11)
C12'	0.0277(13)	0.055(2)	0.0420(16)	0.0048(14)	-0.0088(12)	-0.0002(13)
C13'	0.0403(14)	0.0282(13)	0.0191(11)	-0.0014(9)	-0.0026(10)	0.0051(11)
C14'	0.0185(10)	0.0232(11)	0.0169(10)	-0.0030(8)	0.0027(8)	0.0030(8)
C15'	0.0339(13)	0.0294(13)	0.0219(11)	-0.0011(10)	0.0005(10)	-0.0064(10)
C16'	0.0379(15)	0.0392(15)	0.0277(13)	-0.0086(11)	0.0017(11)	-0.0145(12)
C17'	0.0240(12)	0.0523(17)	0.0201(11)	-0.0117(11)	-0.0030(9)	0.0026(11)

C18'	0.0353(14)	0.0389(15)	0.0207(11)	-0.0007(10)	-0.0048(10)	0.0116(11)
C19'	0.0328(13)	0.0239(12)	0.0223(11)	-0.0006(9)	-0.0032(9)	0.006(1)
C20'	0.0215(11)	0.0242(11)	0.0168(10)	0.0046(9)	-0.0004(8)	0.0006(9)
C21'	0.0253(11)	0.0285(12)	0.0197(11)	0.0040(9)	0.0015(9)	0.0039(9)
C22'	0.0274(12)	0.0438(16)	0.0265(12)	0.0122(11)	0.0069(10)	0.0062(11)
C23'	0.0227(12)	0.0487(17)	0.0364(14)	0.0191(12)	0.0003(10)	-0.0037(11)
C24'	0.0292(13)	0.0372(15)	0.0354(14)	0.0091(11)	-0.0052(11)	-0.0112(11)
C25'	0.0283(12)	0.0292(13)	0.0234(11)	0.0019(9)	-0.0029(9)	-0.0049(10)
C26'	0.0213(11)	0.0205(11)	0.0161(10)	-0.0014(8)	-0.0016(8)	0.0014(8)
C27'	0.0341(13)	0.0197(11)	0.0222(11)	-0.0005(9)	0.0040(9)	0.0016(10)
C28'	0.0413(15)	0.0199(12)	0.0309(13)	-0.0017(10)	-0.0016(11)	0.0051(10)
C29'	0.0288(12)	0.0304(13)	0.0253(12)	-0.0102(10)	-0.0023(10)	0.0107(10)
C30'	0.0222(11)	0.0353(14)	0.0194(11)	-0.0028(9)	0.0003(9)	0.0027(10)
C31'	0.0224(11)	0.0233(12)	0.0183(10)	0.0010(8)	-0.0014(8)	0.0011(9)
Si1'	0.0192(3)	0.0185(3)	0.0231(3)	0.0003(2)	0.0028(2)	0.0015(2)
O1'	0.0401(11)	0.0347(11)	0.0373(11)	-0.0010(8)	-0.0045(8)	-0.0068(8)
O2'	0.0180(8)	0.0243(9)	0.0238(8)	-0.0019(6)	0.0006(6)	0.0023(6)
O3'	0.0246(8)	0.0175(8)	0.0156(7)	0.0011(6)	0.0000(6)	0.0014(6)

Table S24. Bond Distances in Compound **50**, Å

C1-C2	1.495(4)	C1-O1	1.205(4)	C2-C3	1.526(3)
C3-C4	1.529(3)	C3-O2	1.427(3)	C4-C5	1.520(3)
C4-C13	1.533(3)	C5-O3	1.431(3)	C6-C14	1.538(3)
C6-C20	1.540(3)	C6-C26	1.543(3)	C6-O3	1.439(3)
C7-Si1	1.862(3)	C8-Si1	1.863(3)	C9-C10	1.529(3)
C9-C11	1.525(4)	C9-C12	1.533(4)	C9-Si1	1.893(3)
C14-C15	1.392(4)	C14-C19	1.392(3)	C15-C16	1.397(4)
C16-C17	1.383(4)	C17-C18	1.379(4)	C18-C19	1.391(3)
C20-C21	1.395(3)	C20-C25	1.395(3)	C21-C22	1.395(4)
C22-C23	1.387(5)	C23-C24	1.383(5)	C24-C25	1.391(4)
C26-C27	1.395(3)	C26-C31	1.392(3)	C27-C28	1.392(4)
C28-C29	1.387(4)	C29-C30	1.383(4)	C30-C31	1.395(3)
Si1-O2	1.6485(17)	C1'-C2'	1.495(4)	C1'-O1'	1.204(3)
C2'-C3'	1.529(3)	C3'-C4'	1.530(3)	C3'-O2'	1.432(3)
C4'-C5'	1.527(3)	C4'-C13'	1.532(3)	C5'-O3'	1.437(3)
C6'-C14'	1.536(3)	C6'-C20'	1.534(3)	C6'-C26'	1.540(3)
C6'-O3'	1.440(3)	C7'-Si1'	1.866(3)	C8'-Si1'	1.868(3)
C9'-C10'	1.533(4)	C9'-C11'	1.521(4)	C9'-C12'	1.537(4)
C9'-Si1'	1.891(3)	C14'-C15'	1.386(3)	C14'-C19'	1.395(3)
C15'-C16'	1.394(4)	C16'-C17'	1.379(4)	C17'-C18'	1.388(4)
C18'-C19'	1.383(4)	C20'-C21'	1.395(3)	C20'-C25'	1.396(3)
C21'-C22'	1.393(4)	C22'-C23'	1.387(4)	C23'-C24'	1.379(4)
C24'-C25'	1.386(4)	C26'-C27'	1.395(3)	C26'-C31'	1.395(3)
C27'-C28'	1.393(4)	C28'-C29'	1.383(4)	C29'-C30'	1.385(4)

C30'-C31'	1.382(3)	Si1'-O2'	1.6454(17)

Table S25. Bond Angles in Compound **50**, °

O1-C1-C2	125.3(2)	C1-C2-C3	115.4(2)	C2-C3-C4	111.62(19)
O2-C3-C2	109.11(18)	O2-C3-C4	109.20(18)	C3-C4-C13	112.38(19)
C5-C4-C3	112.38(18)	C5-C4-C13	109.02(19)	O3-C5-C4	108.97(18)
C14-C6-C20	111.37(17)	C14-C6-C26	107.29(17)	C20-C6-C26	113.81(19)
O3-C6-C14	105.20(17)	O3-C6-C20	109.21(17)	O3-C6-C26	109.60(17)
C10-C9-C12	107.3(2)	C10-C9-Si1	110.54(18)	C11-C9-C10	108.2(2)
C11-C9-C12	110.2(3)	C11-C9-Si1	110.59(19)	C12-C9-Si1	110.0(2)
C15-C14-C6	121.2(2)	C19-C14-C6	120.4(2)	C19-C14-C15	118.4(2)
C14-C15-C16	120.5(2)	C17-C16-C15	120.5(3)	C18-C17-C16	119.3(2)
C17-C18-C19	120.6(2)	C18-C19-C14	120.7(2)	C21-C20-C6	119.6(2)
C25-C20-C6	121.8(2)	C25-C20-C21	118.3(2)	C20-C21-C22	120.7(2)
C23-C22-C21	120.4(3)	C24-C23-C22	119.1(2)	C23-C24-C25	120.7(3)
C24-C25-C20	120.8(2)	C27-C26-C6	122.0(2)	C31-C26-C6	119.4(2)
C31-C26-C27	118.4(2)	C28-C27-C26	120.8(2)	C29-C28-C27	120.1(2)
C30-C29-C28	119.6(2)	C29-C30-C31	120.2(2)	C26-C31-C30	120.8(2)
C7-Si1-C8	110.98(13)	C7-Si1-C9	111.86(12)	C8-Si1-C9	108.92(13)
O2-Si1-C7	109.73(10)	O2-Si1-C8	110.14(11)	O2-Si1-C9	105.04(10)
C3-O2-Si1	130.53(14)	C5-O3-C6	116.09(17)	O1'-C1'-C2'	124.9(2)
C1'-C2'-C3'	115.2(2)	C2'-C3'-C4'	111.88(19)	O2'-C3'-C2'	108.65(18)
O2'-C3'-C4'	109.11(18)	C3'-C4'-C13'	112.32(19)	C5'-C4'-C3'	112.51(18)
C5'-C4'-C13'	108.8(2)	O3'-C5'-C4'	109.37(18)	C14'-C6'-C26'	106.71(17)
C20'-C6'-C14'	110.97(17)	C20'-C6'-C26'	114.84(19)	O3'-C6'-C14'	105.80(17)
O3'-C6'-C20'	108.51(17)	O3'-C6'-C26'	109.62(17)	C10'-C9'-C12'	108.5(2)
C10'-C9'-Si1'	110.27(19)	C11'-C9'-C10'	109.6(2)	C11'-C9'-C12'	108.2(2)

Table S25. Bond Angles in Compound **50**, °

C11'-C9'-Si1'	110.82(18)	C12'-C9'-Si1'	109.45(18)	C15'-C14'-C6'	122.3(2)
C15'-C14'-C19'	118.3(2)	C19'-C14'-C6'	119.4(2)	C14'-C15'-C16'	120.6(2)
C17'-C16'-C15'	120.6(3)	C16'-C17'-C18'	119.3(2)	C19'-C18'-C17'	120.2(2)
C18'-C19'-C14'	121.0(3)	C21'-C20'-C6'	118.9(2)	C21'-C20'-C25'	118.2(2)
C25'-C20'-C6'	122.4(2)	C22'-C21'-C20'	120.6(2)	C23'-C22'-C21'	120.3(3)
C24'-C23'-C22'	119.4(2)	C23'-C24'-C25'	120.6(3)	C24'-C25'-C20'	120.9(2)
C27'-C26'-C6'	122.7(2)	C27'-C26'-C31'	118.1(2)	C31'-C26'-C6'	119.0(2)
C28'-C27'-C26'	120.5(2)	C29'-C28'-C27'	120.7(2)	C28'-C29'-C30'	119.1(2)
C31'-C30'-C29'	120.4(2)	C30'-C31'-C26'	121.2(2)	C7'-Si1'-C8'	110.55(13)
C7'-Si1'-C9'	112.42(12)	C8'-Si1'-C9'	109.14(12)	O2'-Si1'-C7'	110.22(10)
O2'-Si1'-C8'	110.40(11)	O2'-Si1'-C9'	103.93(10)	C3'-O2'-Si1'	130.47(14)
C5'-O3'-C6'	114.76(17)				

This report has been created with Olex2, [11] compiled on 2020.11.12 svn.r5f609507 for OlexSys.

4. Cytotoxicity of Synthetic Neaumycin B (**1**) against U87-MG cells

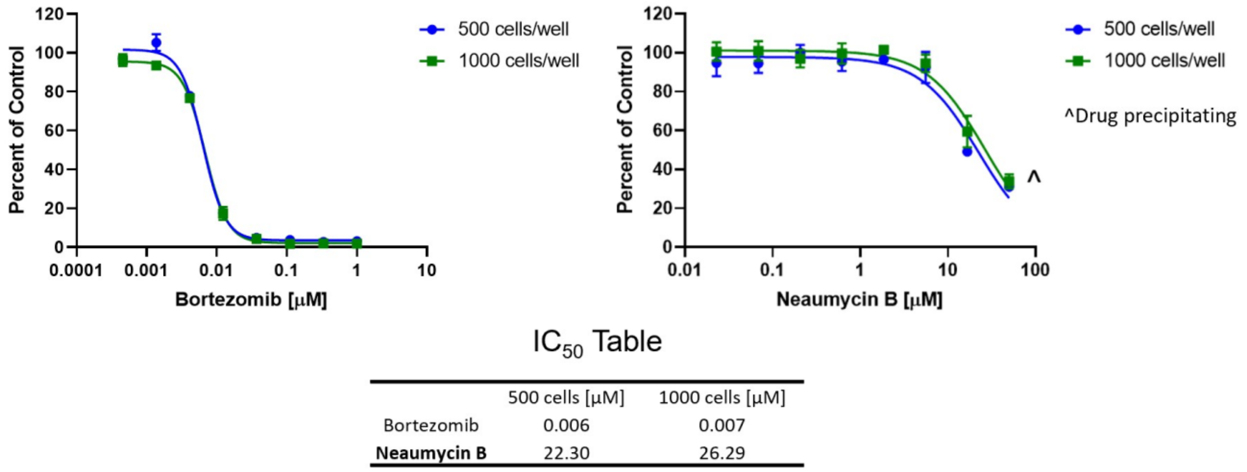
Methods

Cell viability

500 or 1000 U87-MG cells (ATCC, HTB-14) were seeded in 25 µl of growth medium (MEM supplemented with 2mM L-Gln, 1% Penicillin/streptomycin, 1% NEAA, 10% FBS) in 384-well Corning 3750 microplate using a Multidrop Combi Reagent Dispenser (Thermo Scientific). Cells were allowed to attach overnight at 37°C, 5% CO_2, 20% O_2 in a humidified chamber. Fifty nanoliters of Neaumycin B suspended in 100% DMSO was added as an 8-pt dose response with three-fold dilutions between test concentrations in triplicate, starting at 50uM final concentration. The negative control (0.2% DMSO, n=32) and positive control (1uM Bortezomib, n=32) was added to the assay plate. Cells were incubated for 72 hours at 37ºC, 5% CO_2, 20% O_2. Assay plates were removed from the incubator for 1 hour to equilibrate to room temperature prior to adding 20µL of ATPlite (PerkinElmer). Luminescence was measured on an EnVision Xcite Multilabel Plate Reader (PerkinElmer), using the ultrasensitive luminescence measurement technology.

Data Analysis

Raw data values of sample wells were normalized to aggregate Negative control (0.2% DMSO) and expressed as Percent of Control [POC = Test well / $DMSO_{avg}$ x 100]. A non-linear regression curve fit analysis (GraphPad Prism 9) of POC cell viability versus the log10 transformed concentration values was used to determine the IC_{50} values for cell viability.

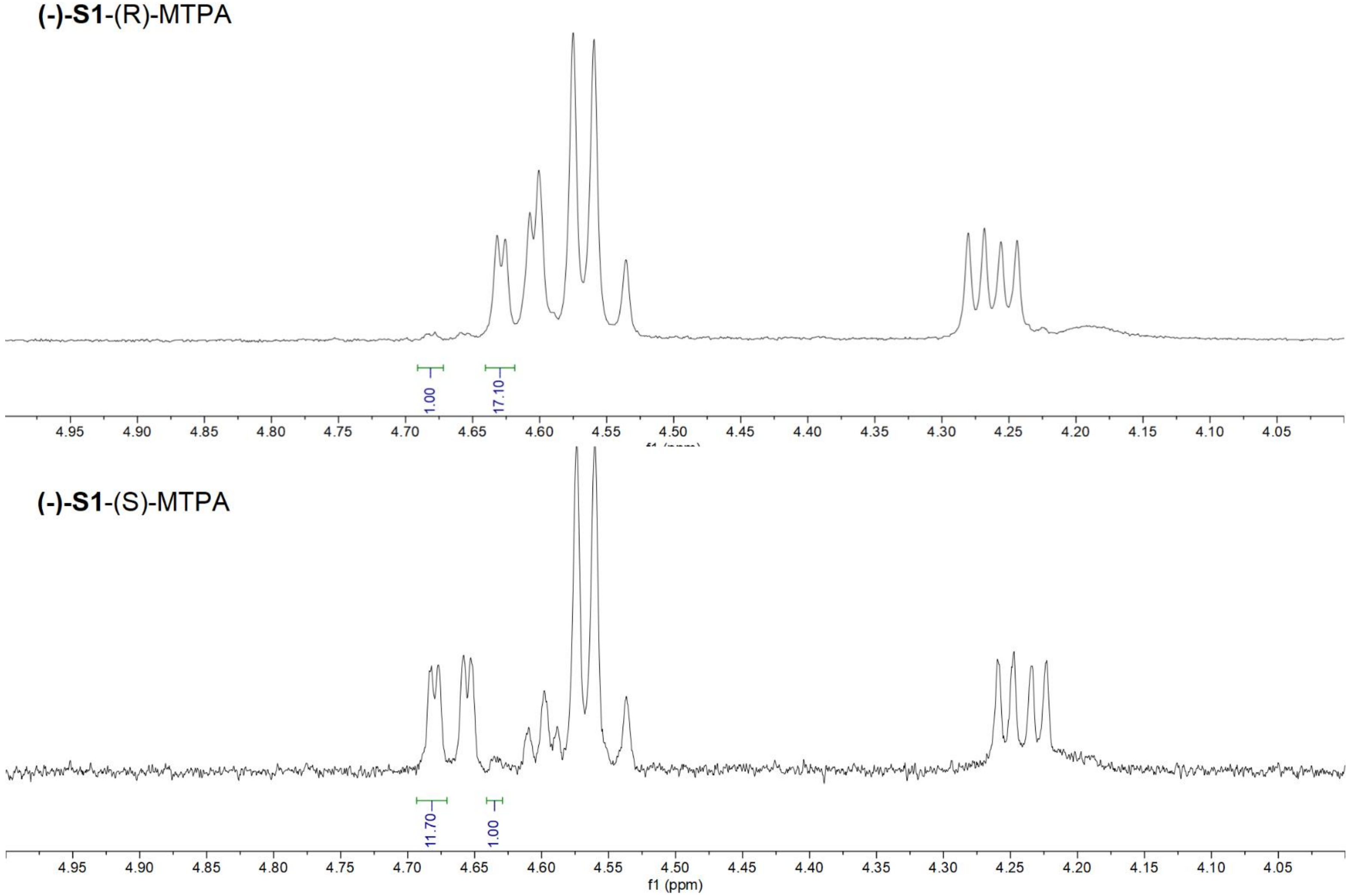


IC_{50} Table

	500 cells [µM]	1000 cells [µM]
Bortezomib	0.006	0.007
Neaumycin B	22.30	26.29

Figure S5. Dose responsive curve for synthetic Neaumycin B (**1**) against U87-MG cells

5. Spectroscopic Data


(-)-S1-(R)-MTPA

(-)-S1-(S)-MTPA

Figure S6. Mosher ester analysis of prepared **(-)-S1**

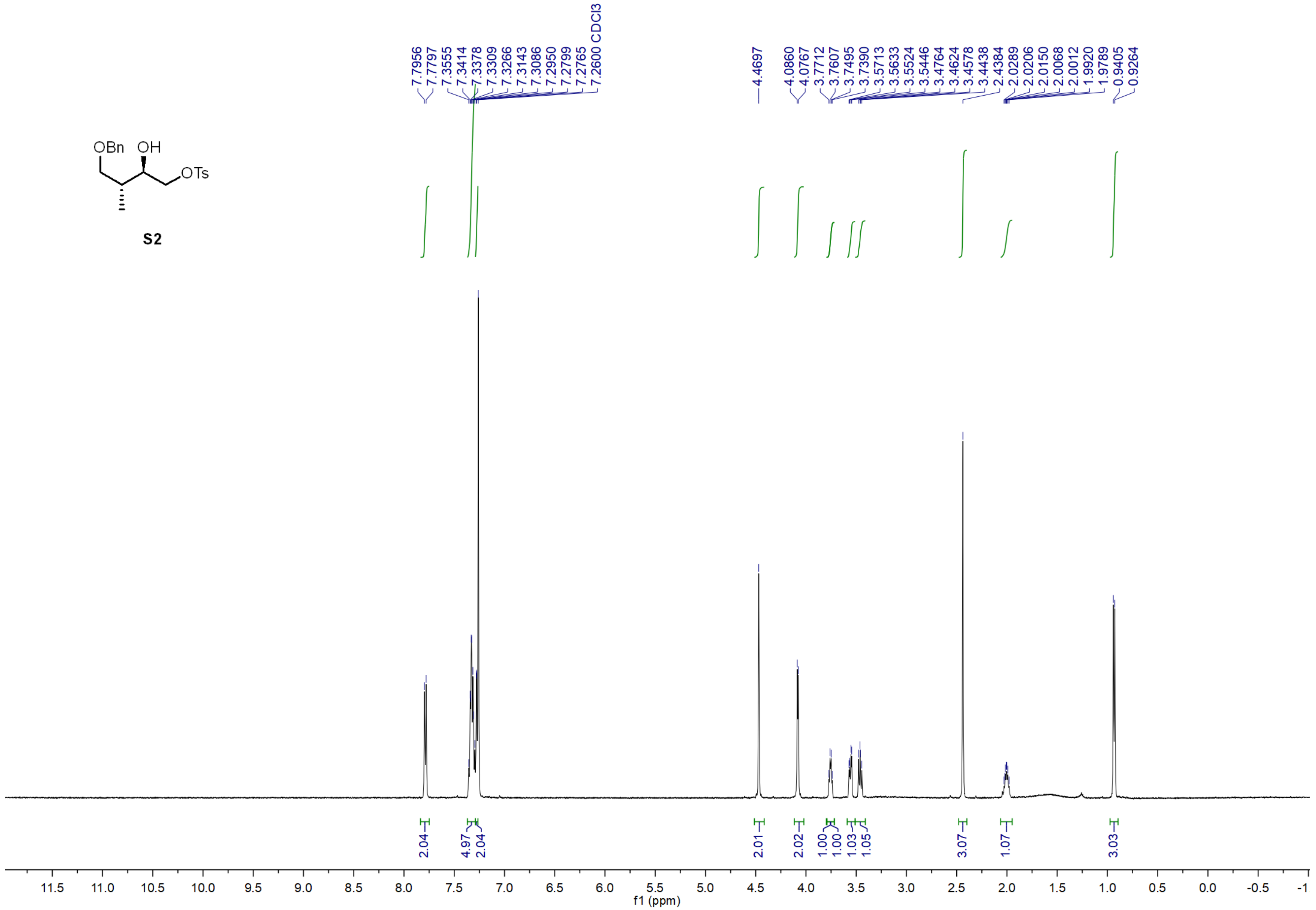


Figure S7. The 500 MHz ^{1}H-NMR of Compound **S2** in Chloroform-*d*

S2

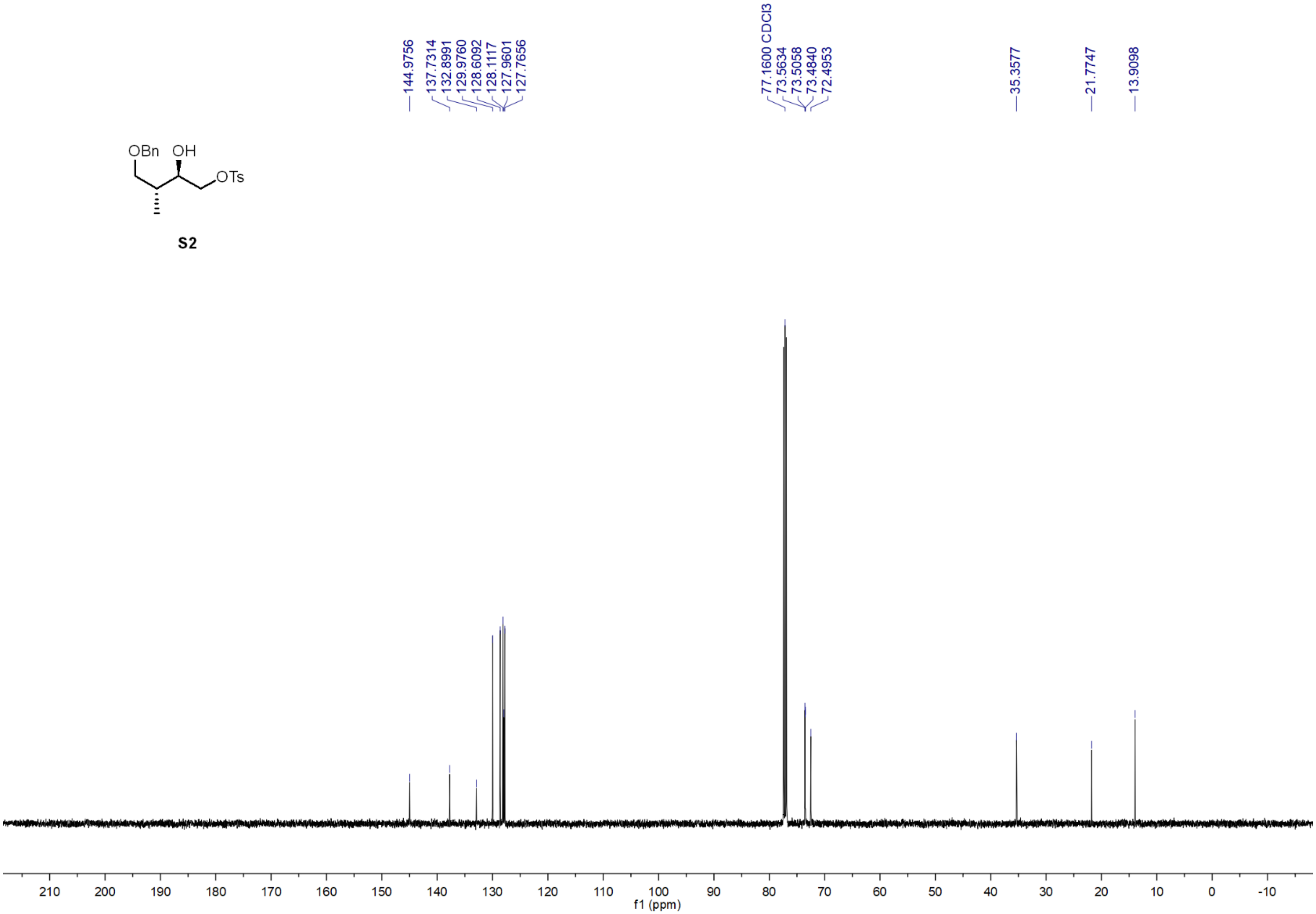


Figure S8. The 125 MHz ^{13}C-NMR of Compound **S2** in Chloroform-*d*

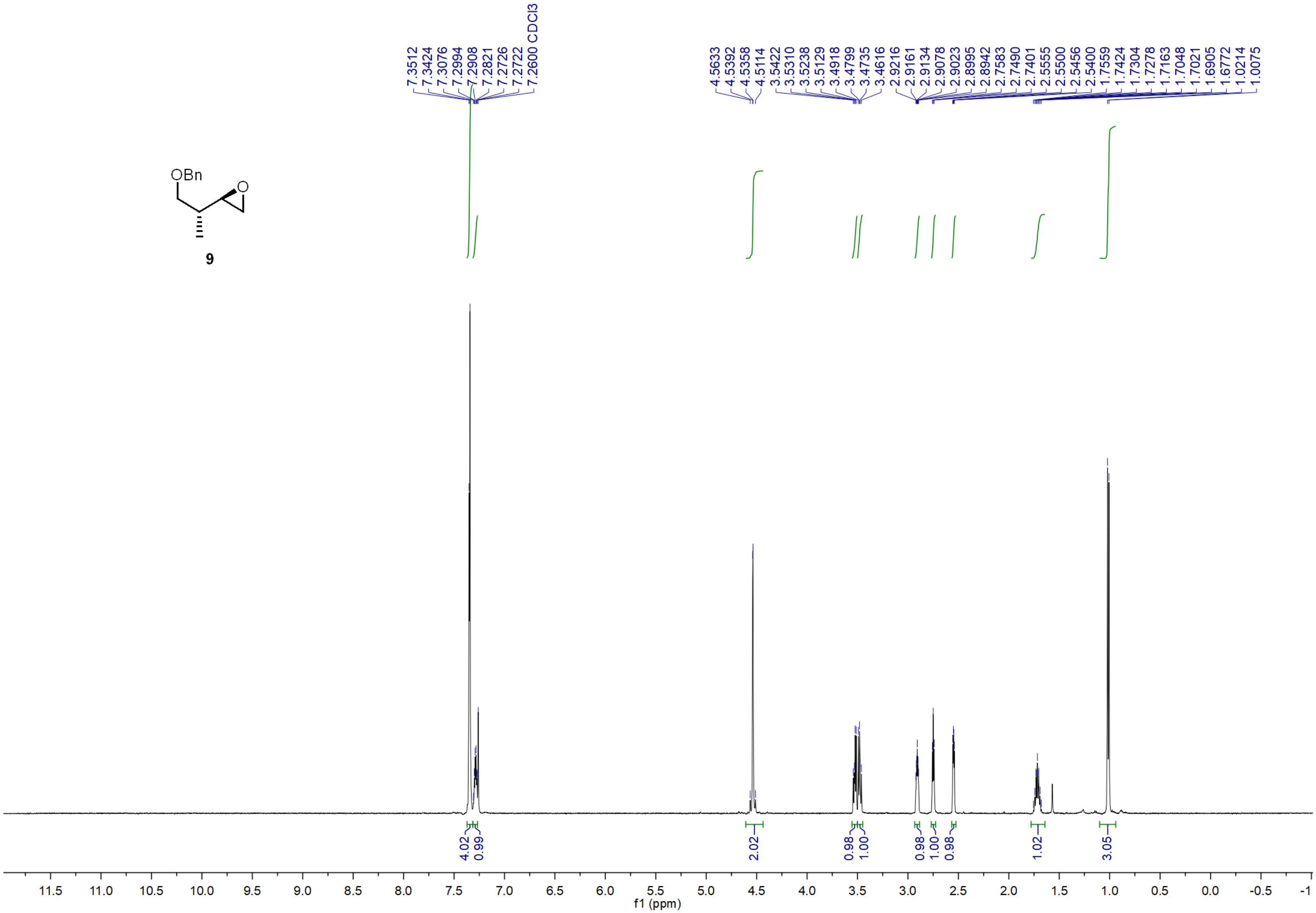


Figure S9. The 500 MHz ^{1}H-NMR of Compound **(-)-9** in Chloroform-*d*

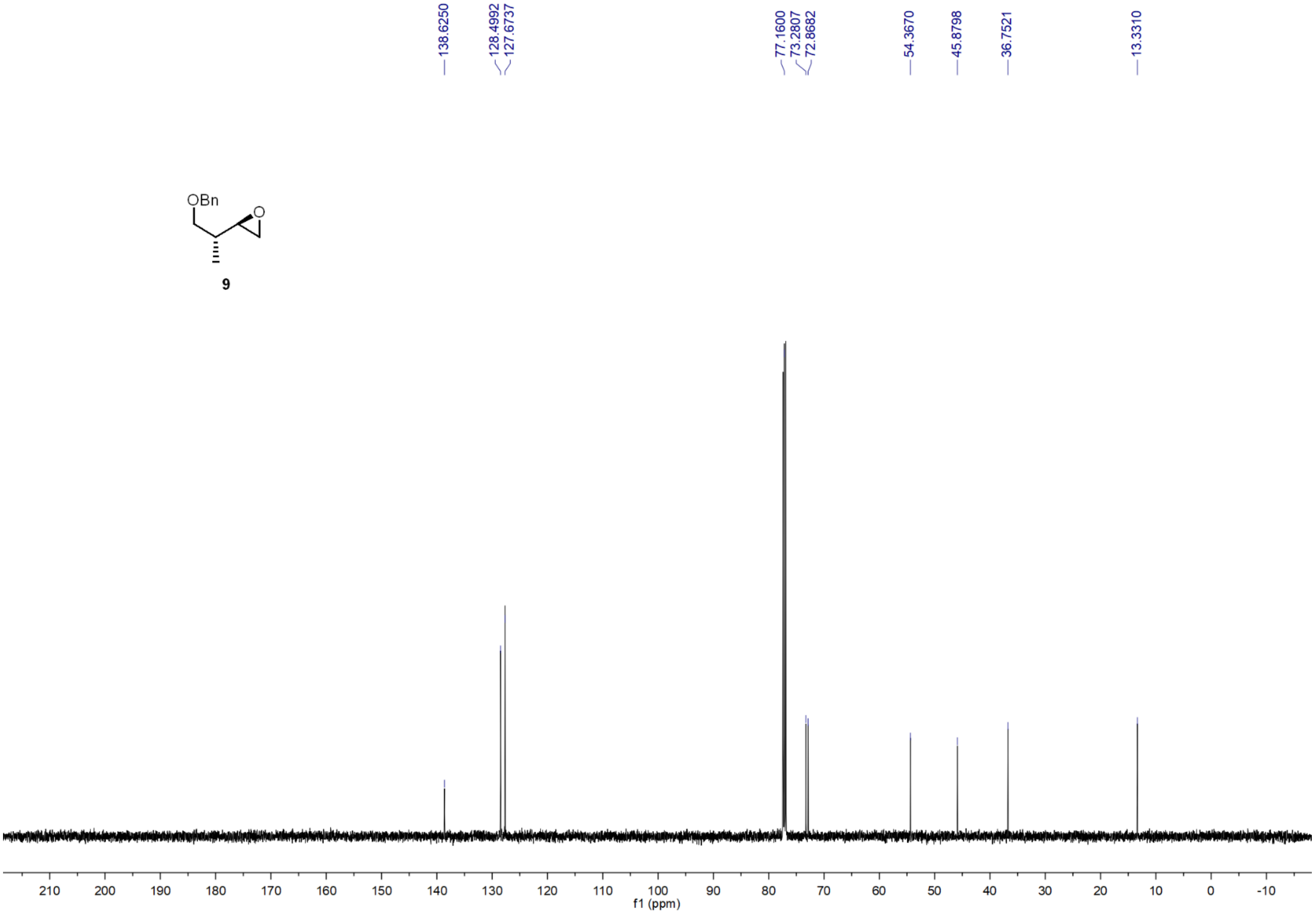


Figure S10. The 125 MHz ^{13}C-NMR of Compound **(-)-9** in Chloroform-*d*

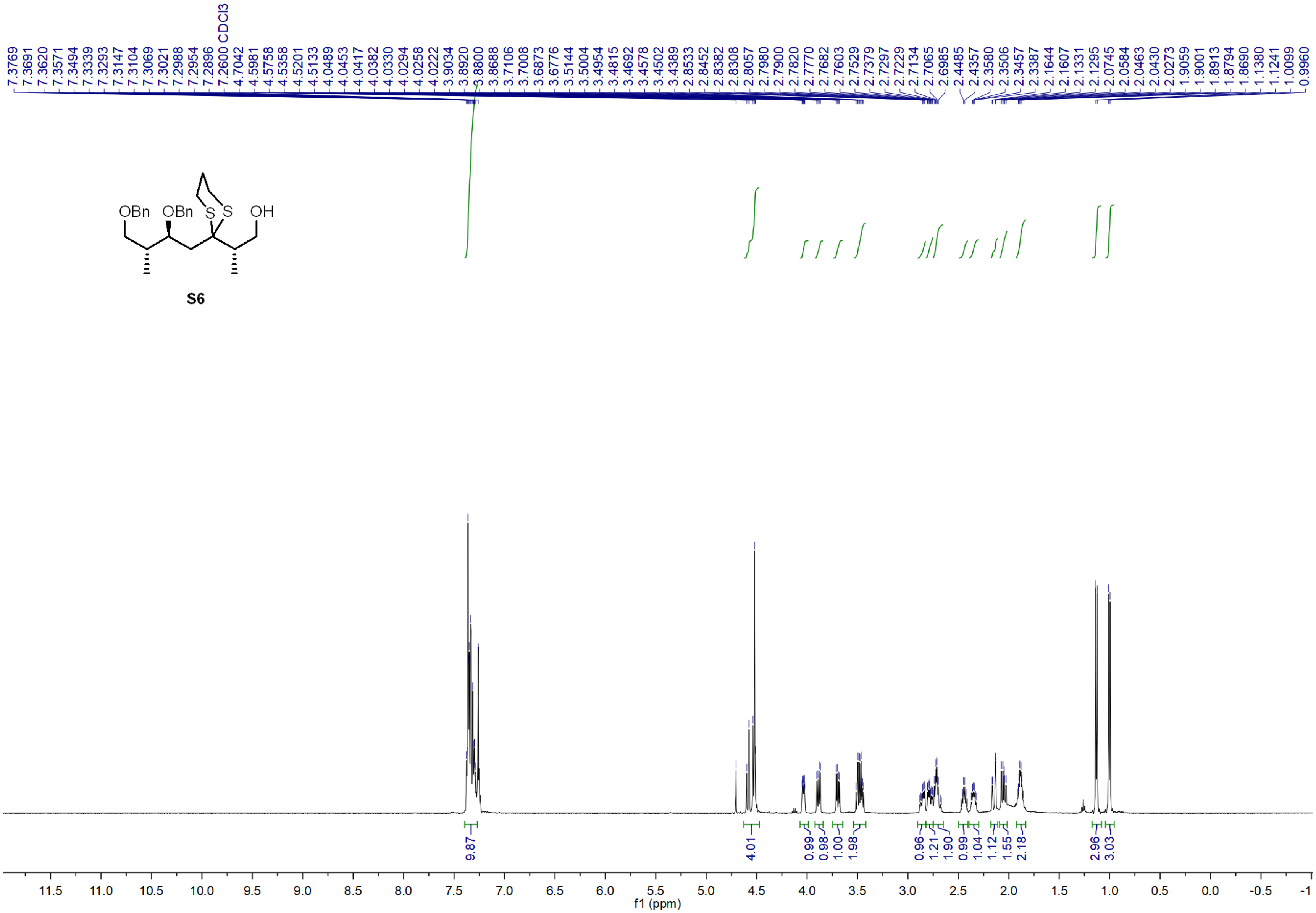


Figure S11. The 500 MHz ^{1}H-NMR of Compound **S6** in Chloroform-*d*

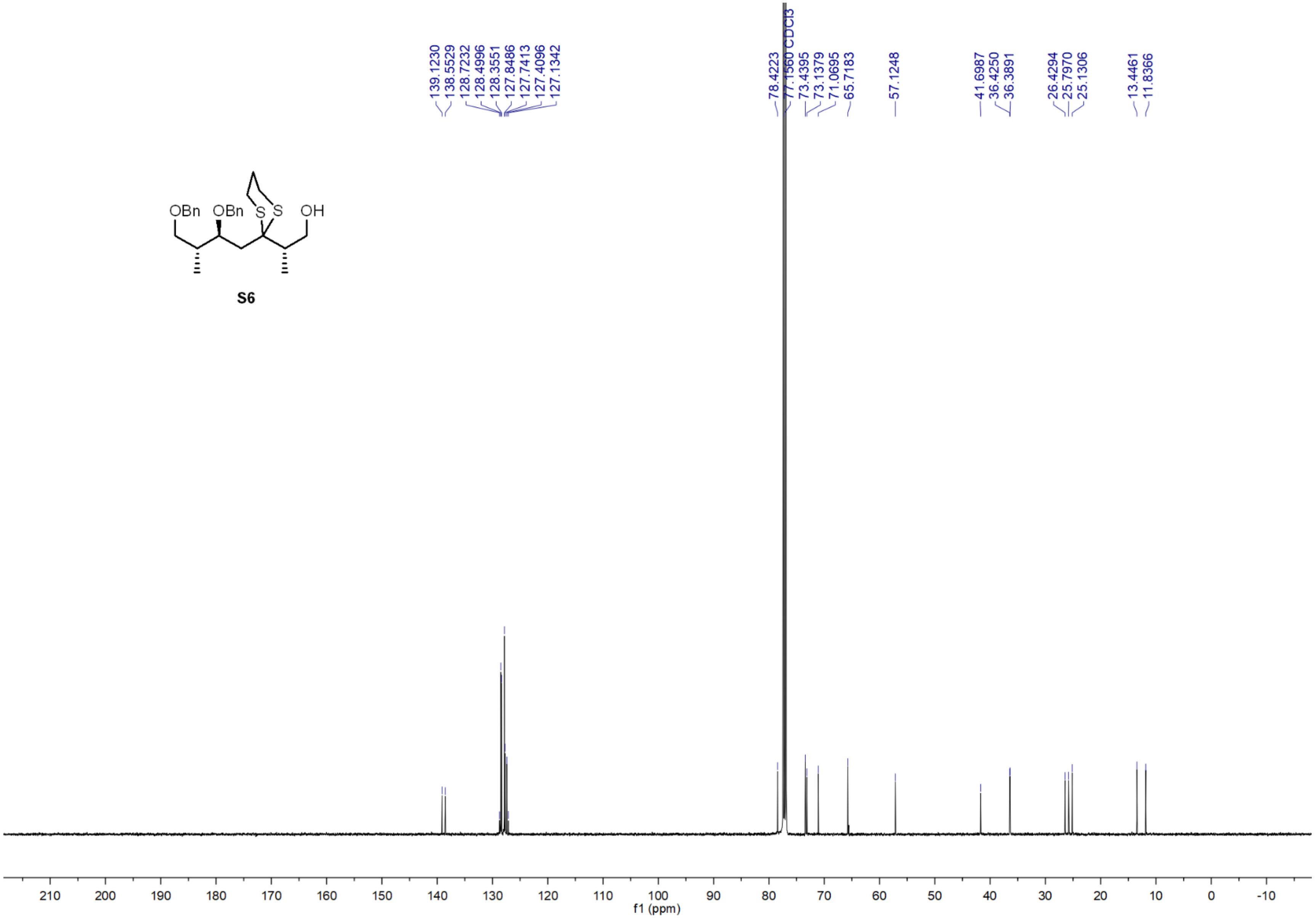


Figure S12 The 125 MHz ^{13}C-NMR of Compound **S6** in Chloroform-*d*

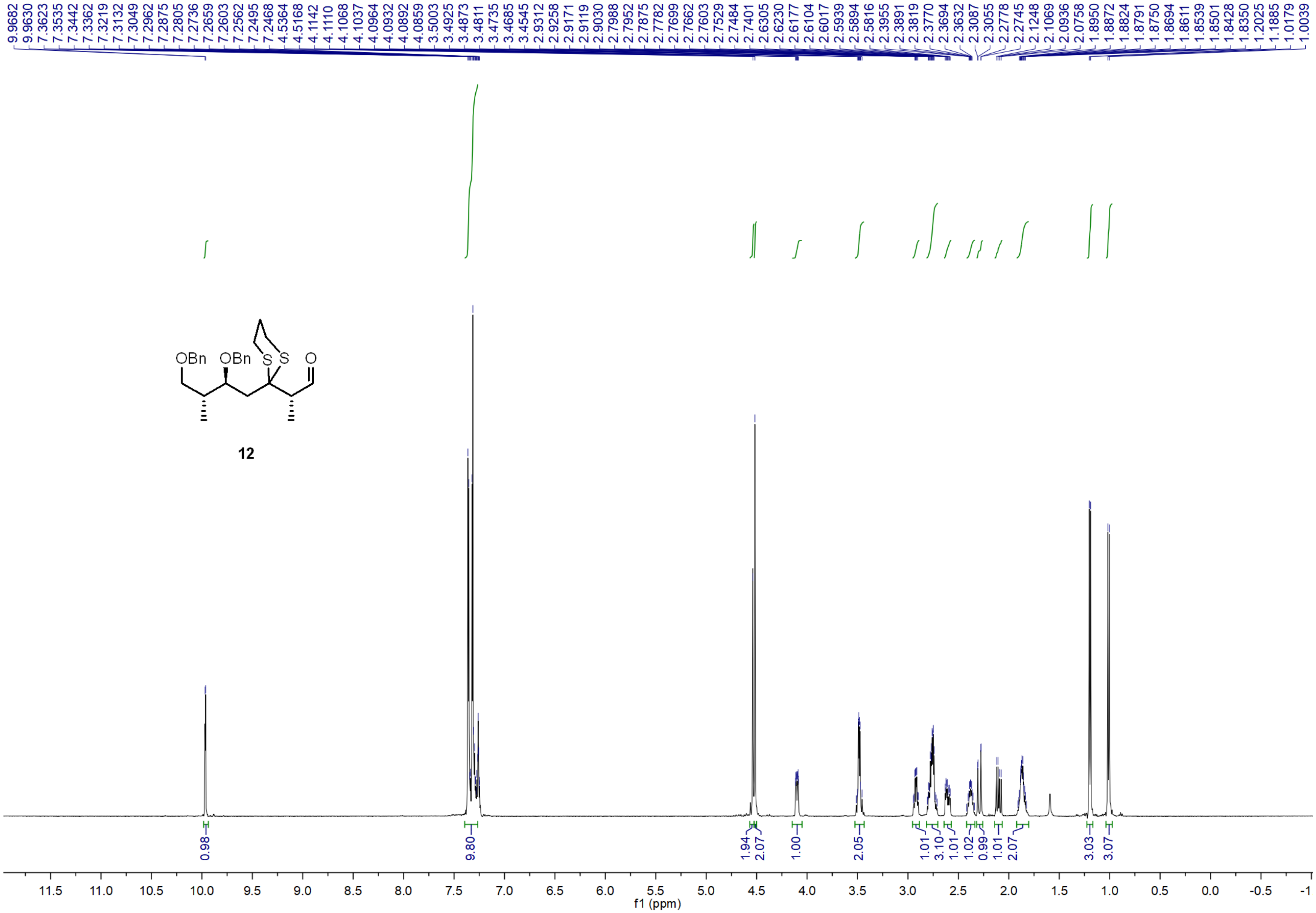


Figure S13. The 500 MHz ^{1}H-NMR of Compound **12** in Chloroform-*d*

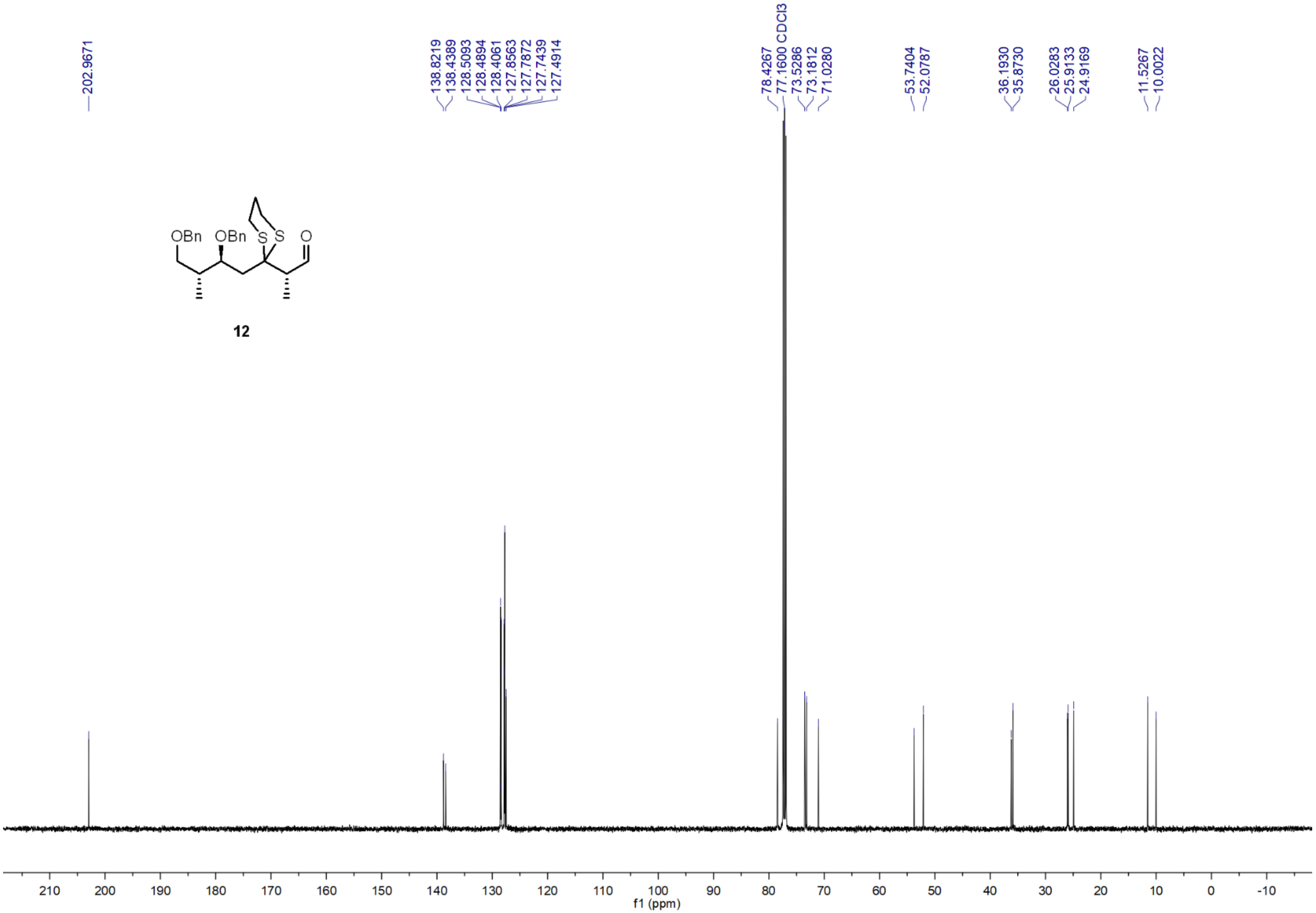


Figure S14. The 125 MHz ^{13}C-NMR of Compound **12** in Chloroform-*d*

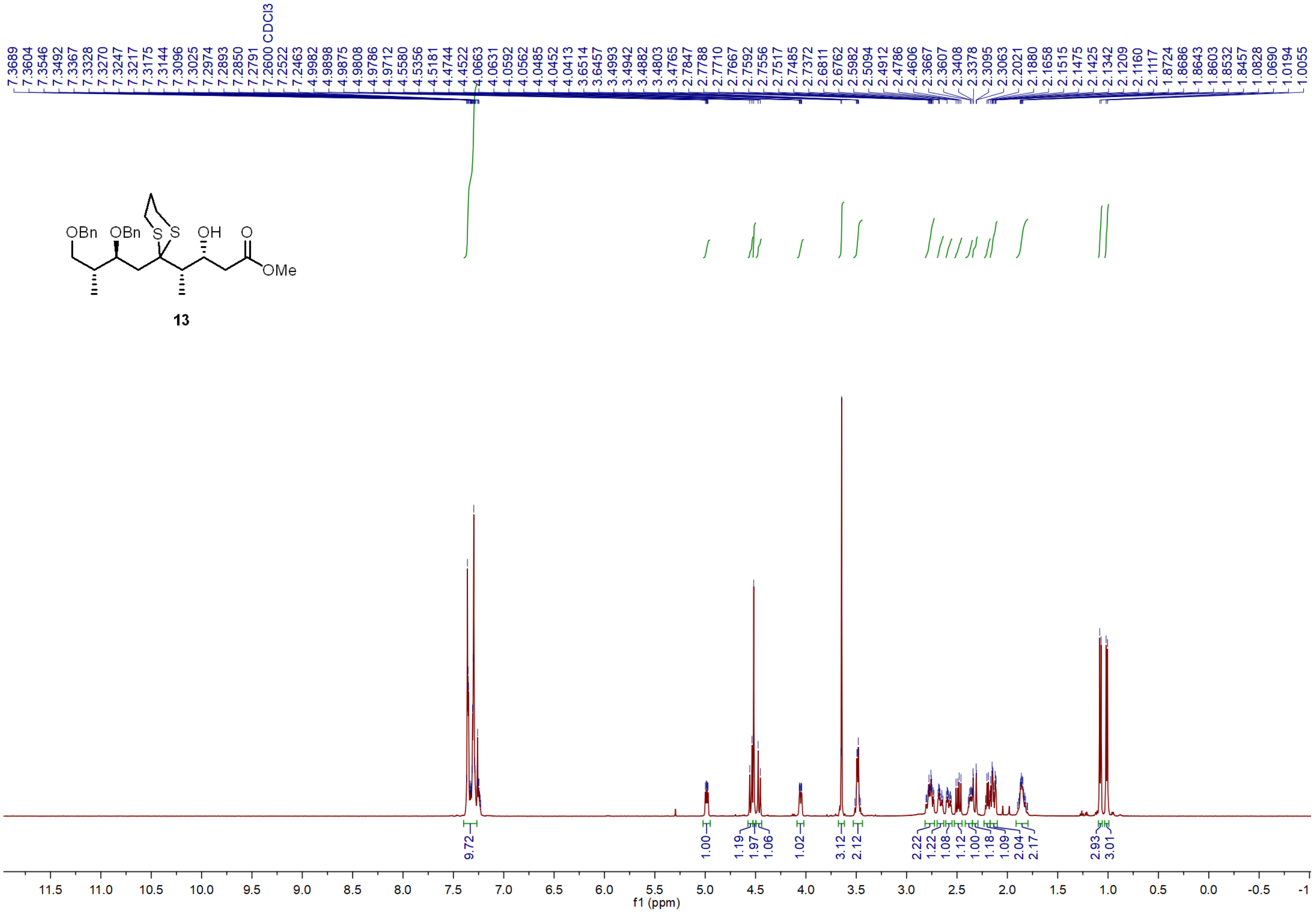


Figure S15. The 500 MHz ^{1}H-NMR of Compound **13** in Chloroform-*d*

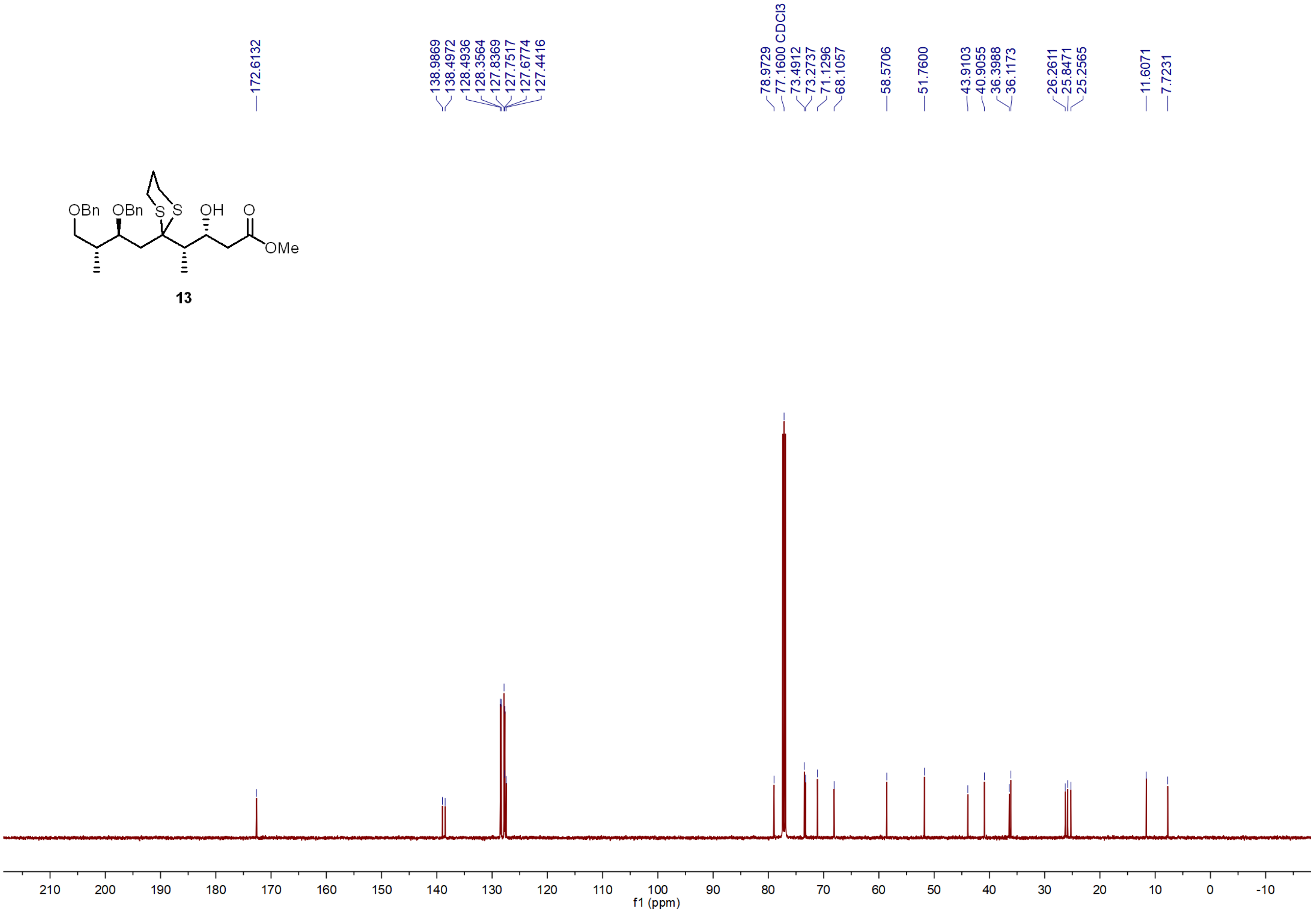
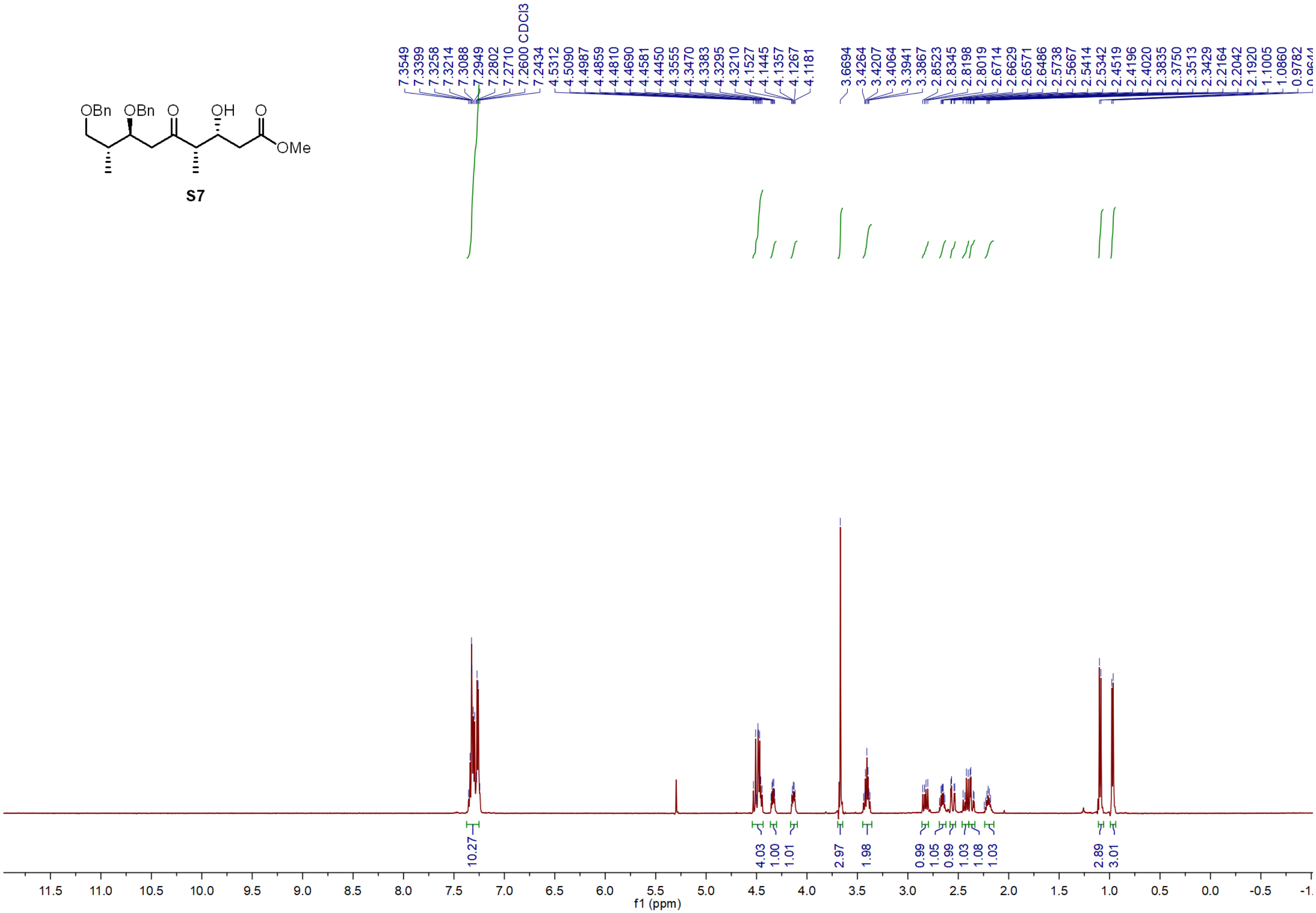


Figure S16. The 125 MHz ^{13}C-NMR of Compound **13** in Chloroform-*d*



S7

Figure S17. The 500 MHz ^{1}H-NMR of Compound **S7** in Chloroform-*d*

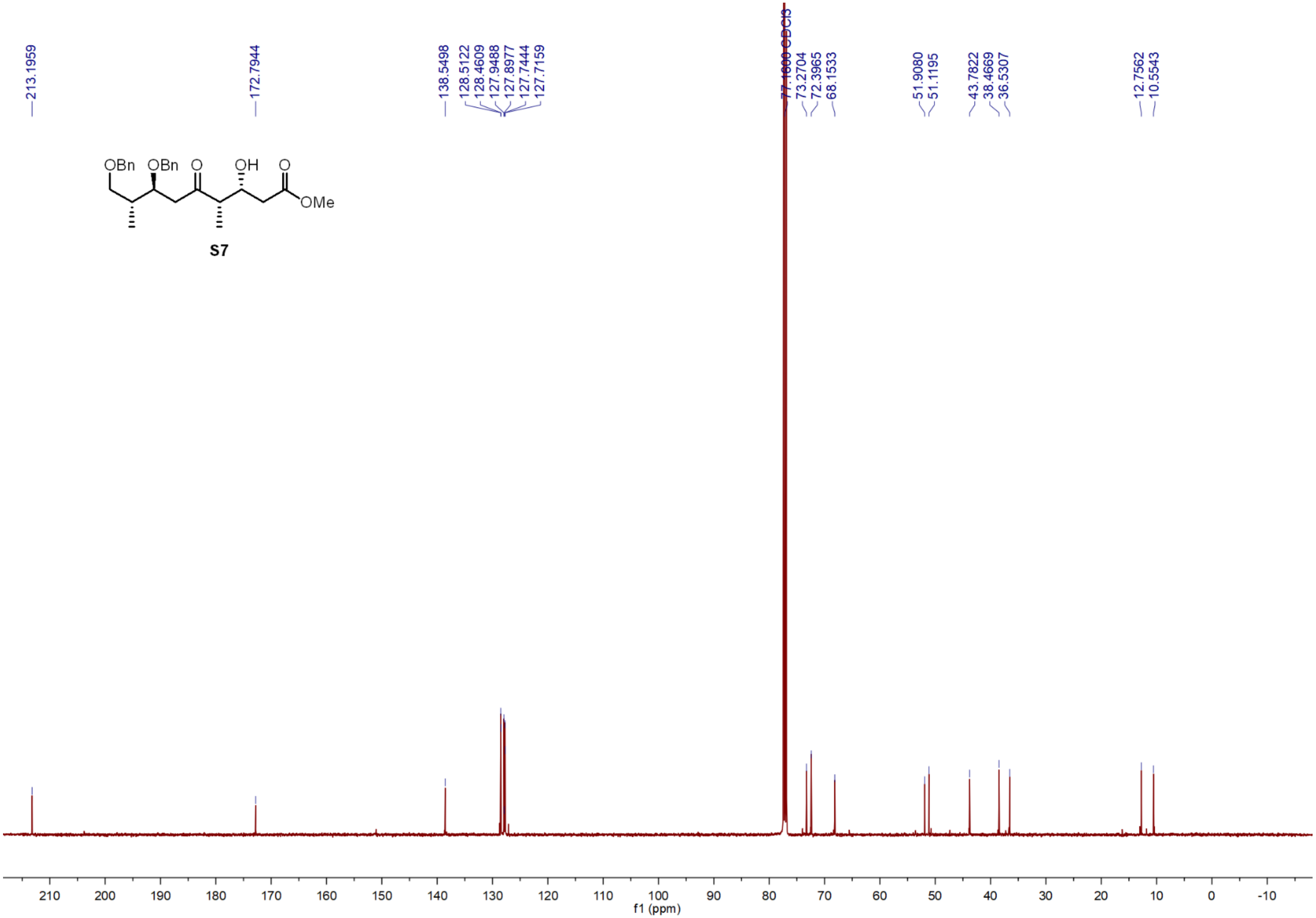


Figure S18. The 125 MHz ^{13}C-NMR of Compound **S7** in Chloroform-*d*

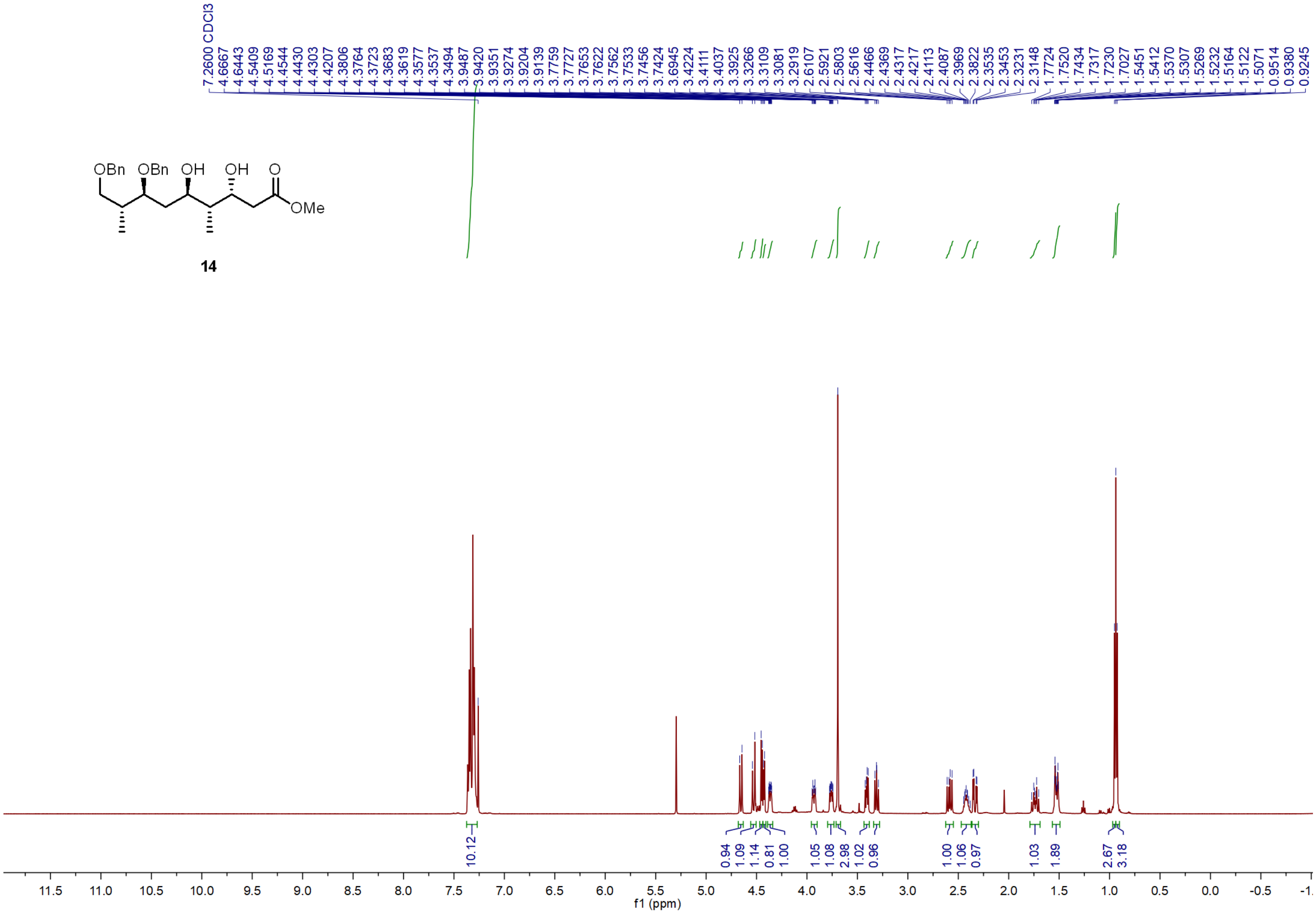


Figure S19. The 500 MHz ^{1}H-NMR of Compound **14** in Chloroform-*d*

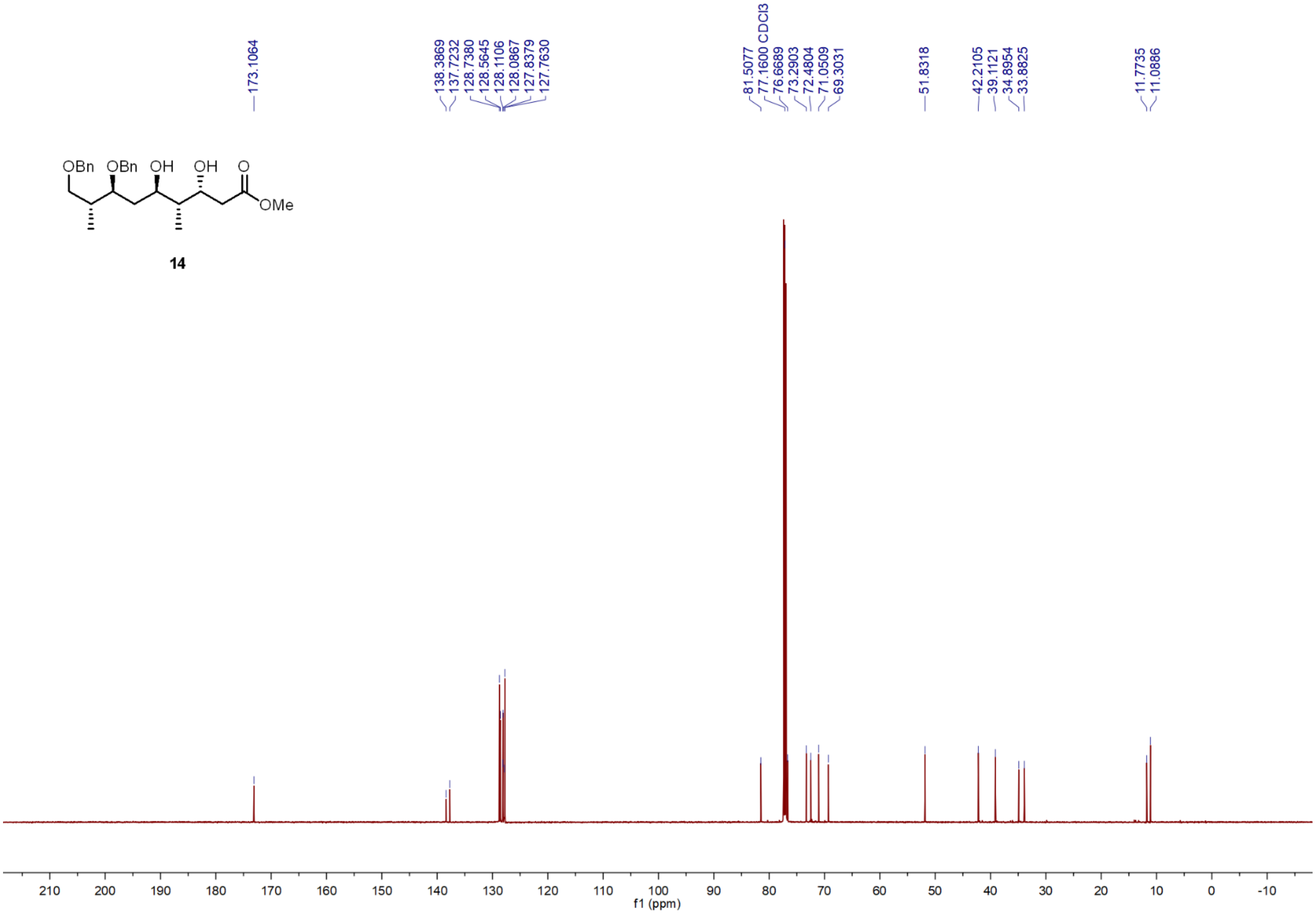


Figure S20. The 150 MHz ^{13}C-NMR of Compound **14** in Chloroform-*d*

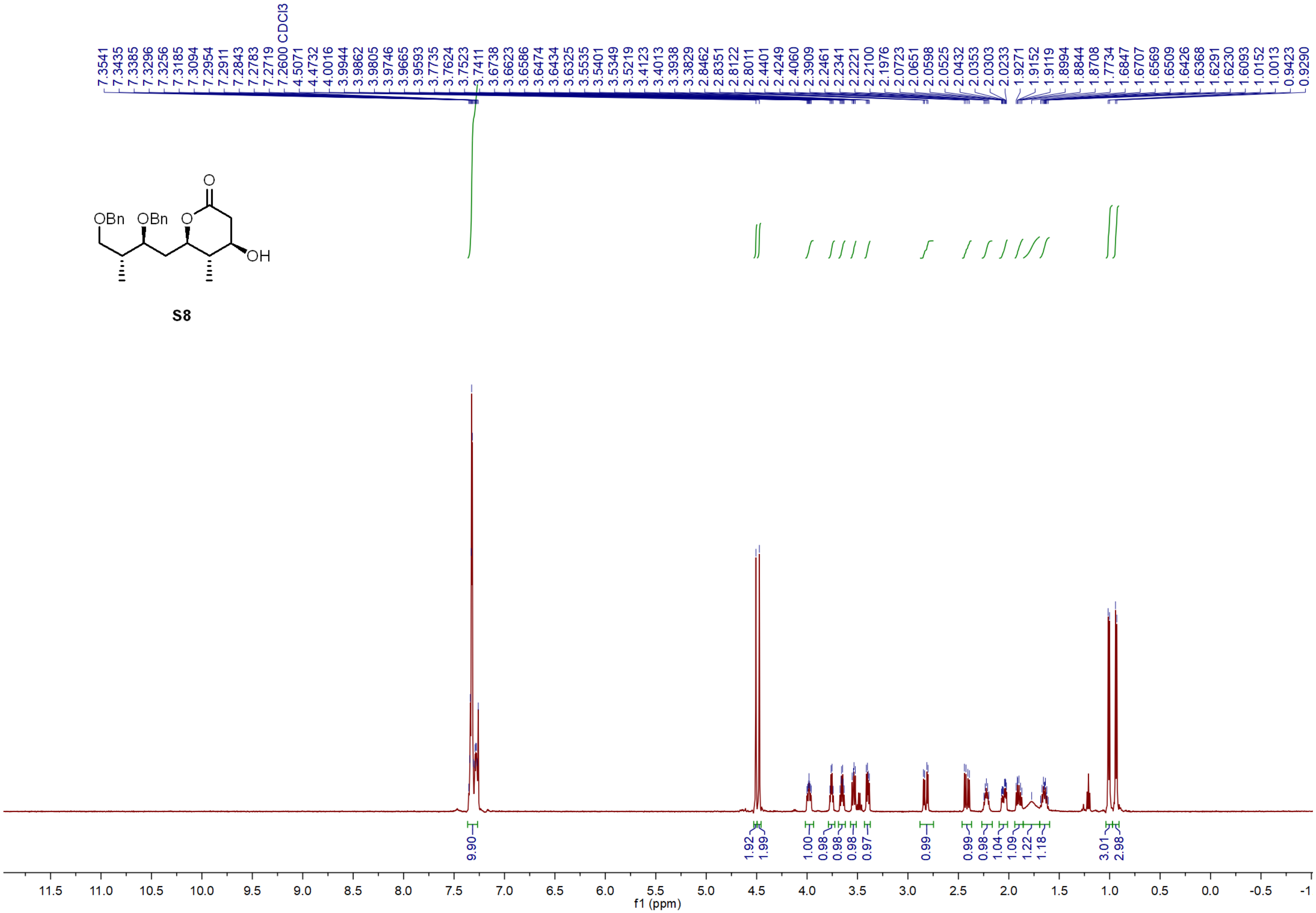


Figure S21. The 500 MHz ^{1}H-NMR of Compound **S8** in Chloroform-*d*

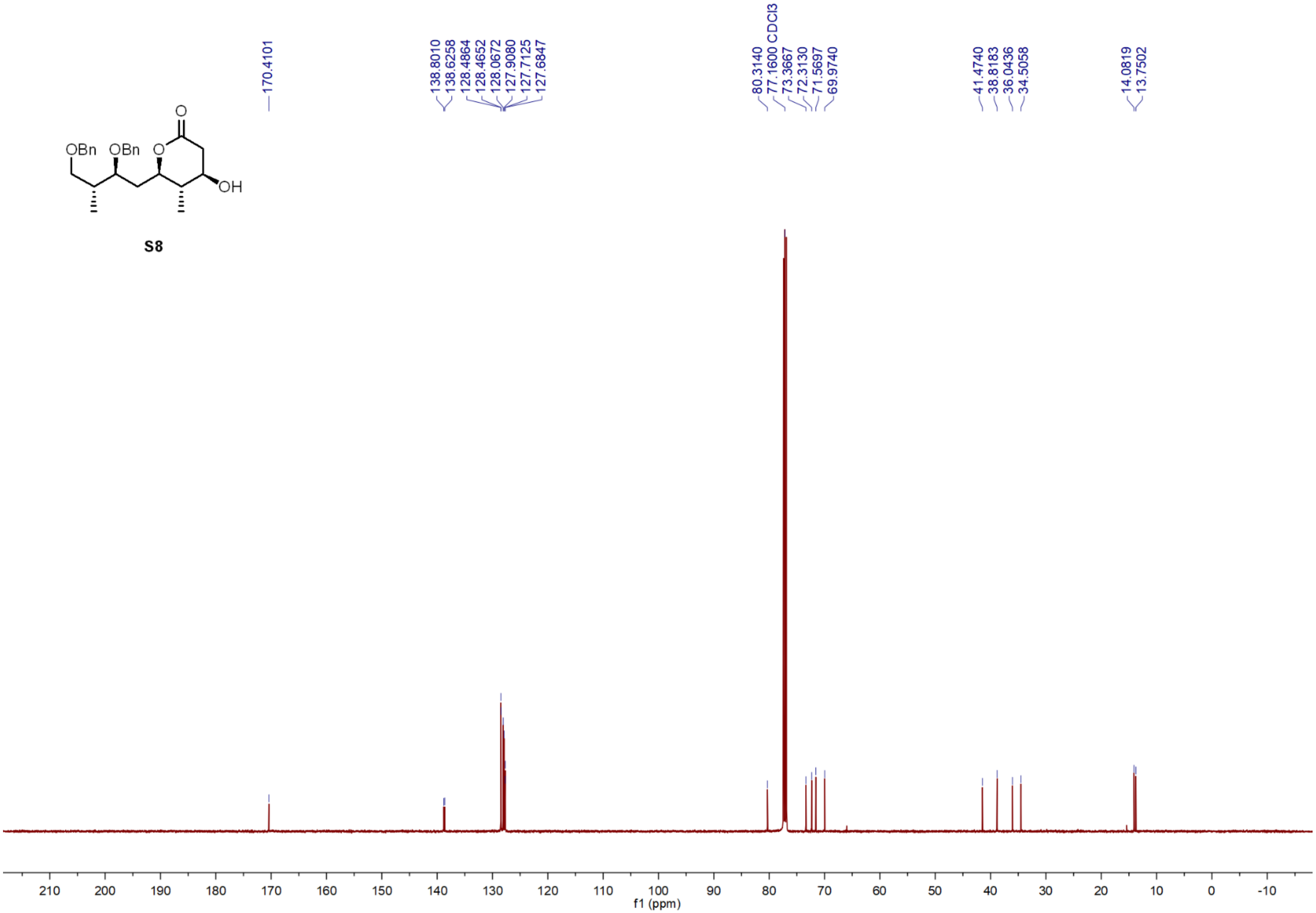


Figure S22. The 125 MHz ^{13}C-NMR of Compound **S8** in Chloroform-*d*

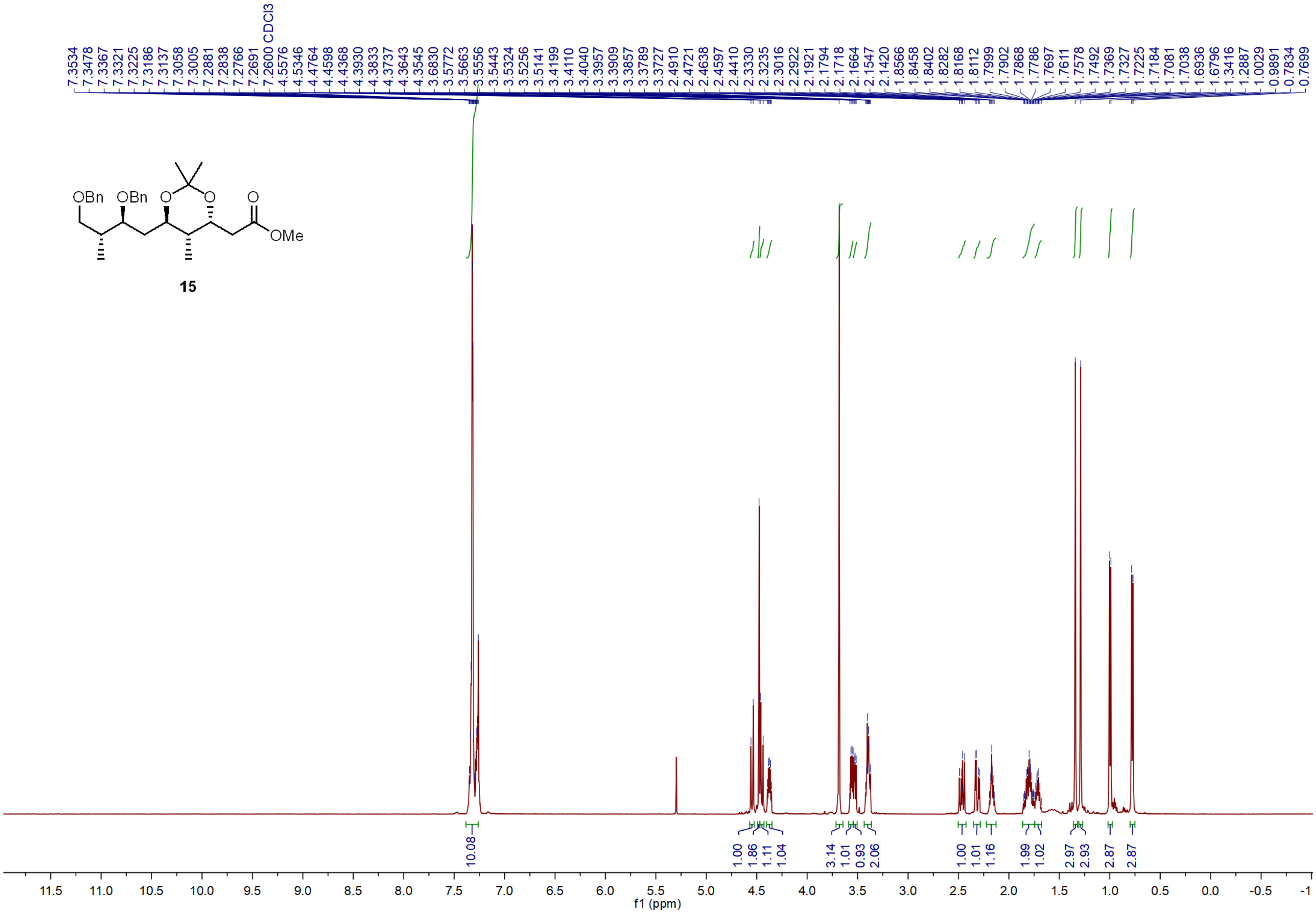


Figure S23. The 500 MHz ^{1}H-NMR of Compound **15** in Chloroform-*d*

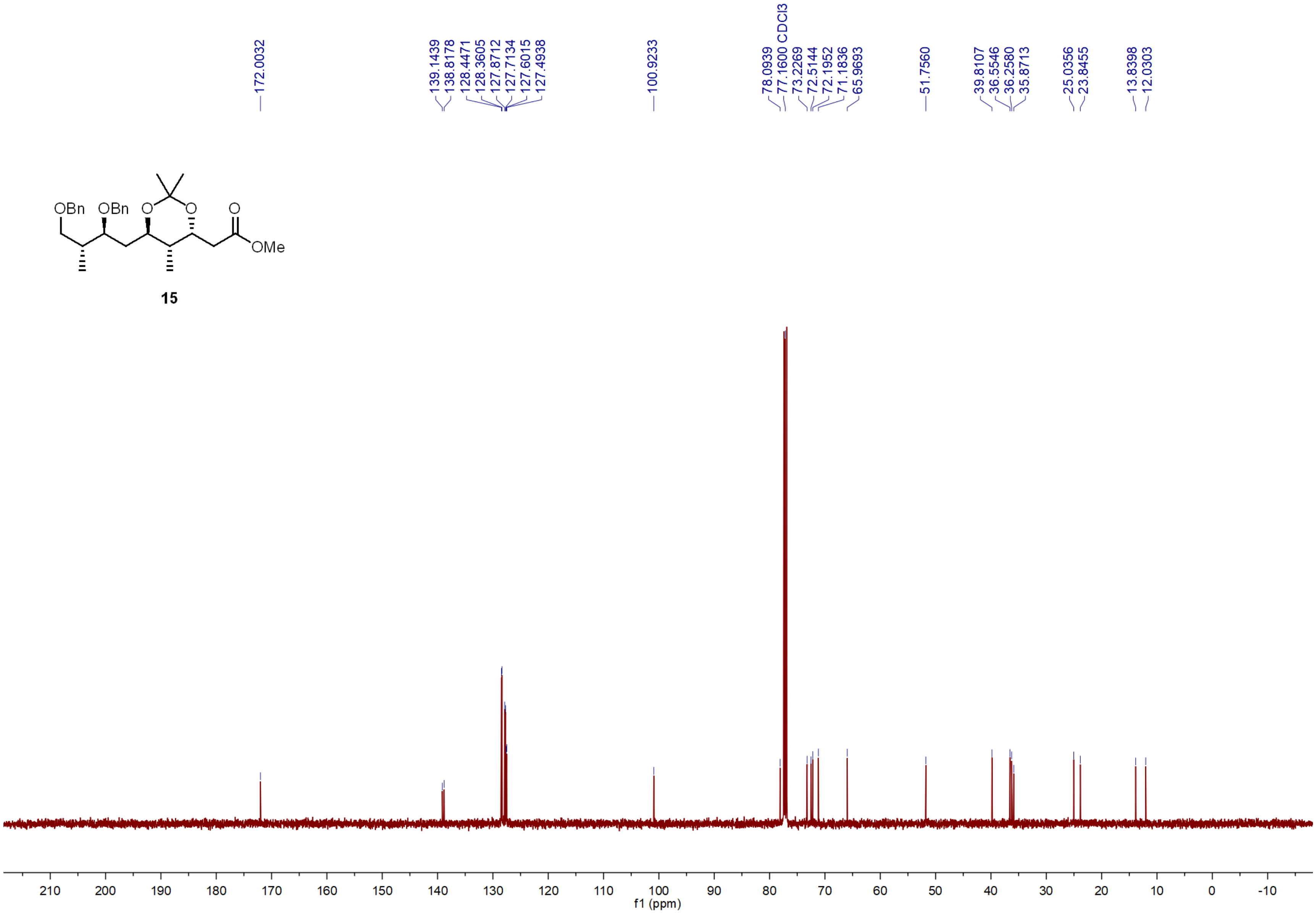


Figure S24. The 125 MHz ^{13}C-NMR of Compound **15** in Chloroform-*d*

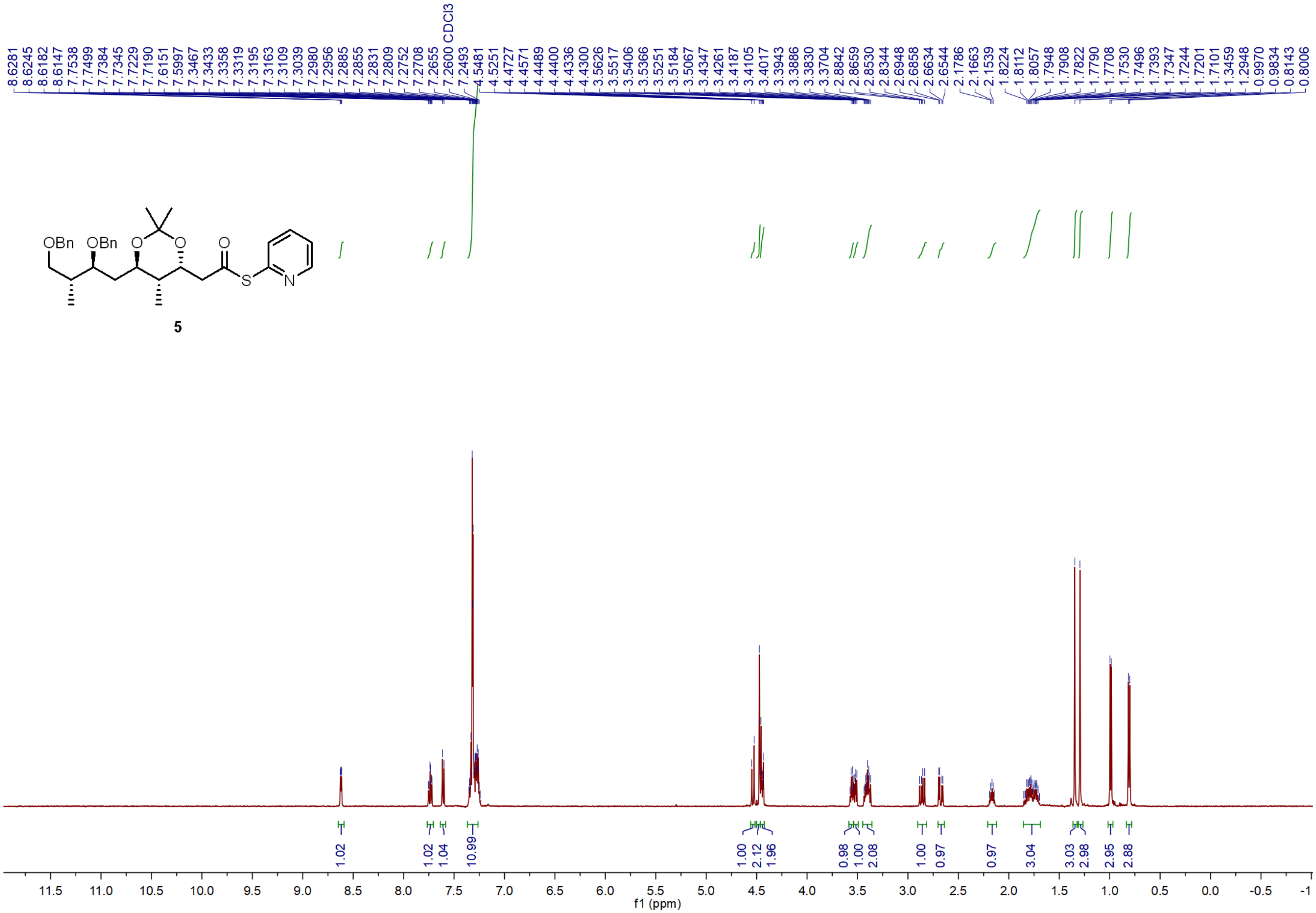


Figure S25. The 500 MHz ^{1}H-NMR of Compound **5** in Chloroform-*d*

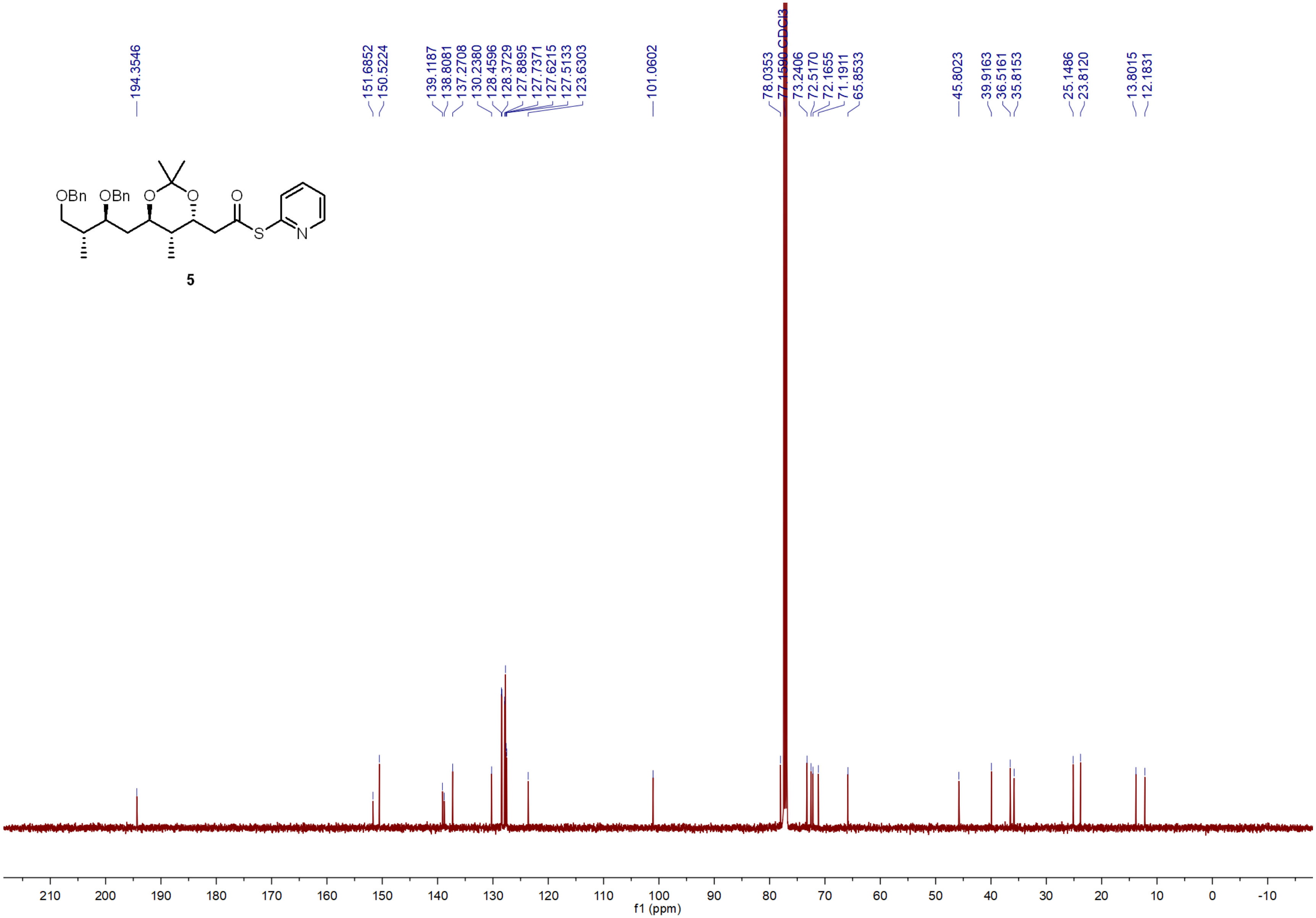


Figure S26. The 125 MHz ^{13}C-NMR of Compound **5** in Chloroform-*d*

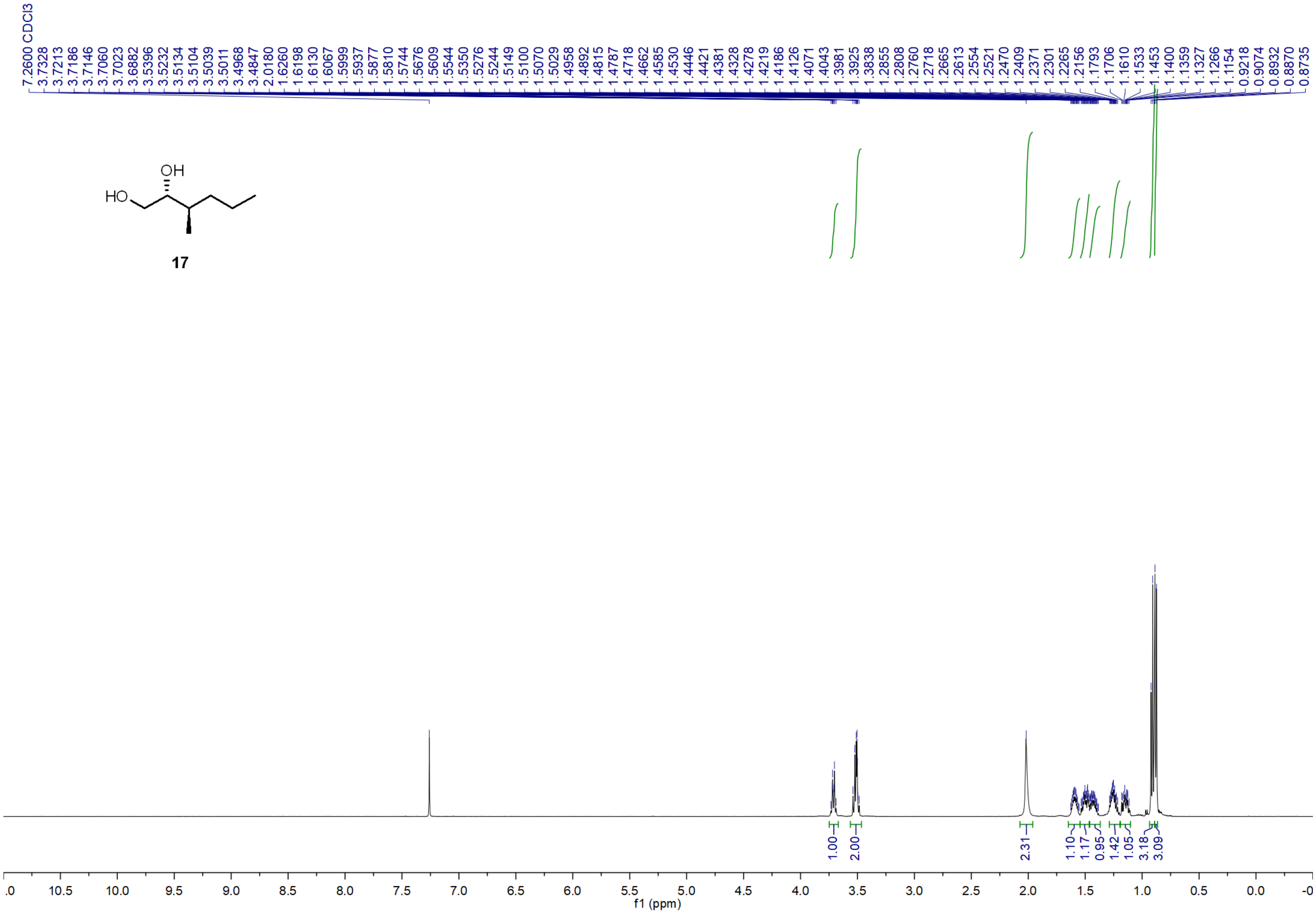
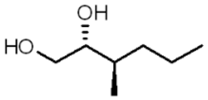


Figure S27. The 500 MHz ^{1}H-NMR of Compound **17** in Chloroform-*d*



17

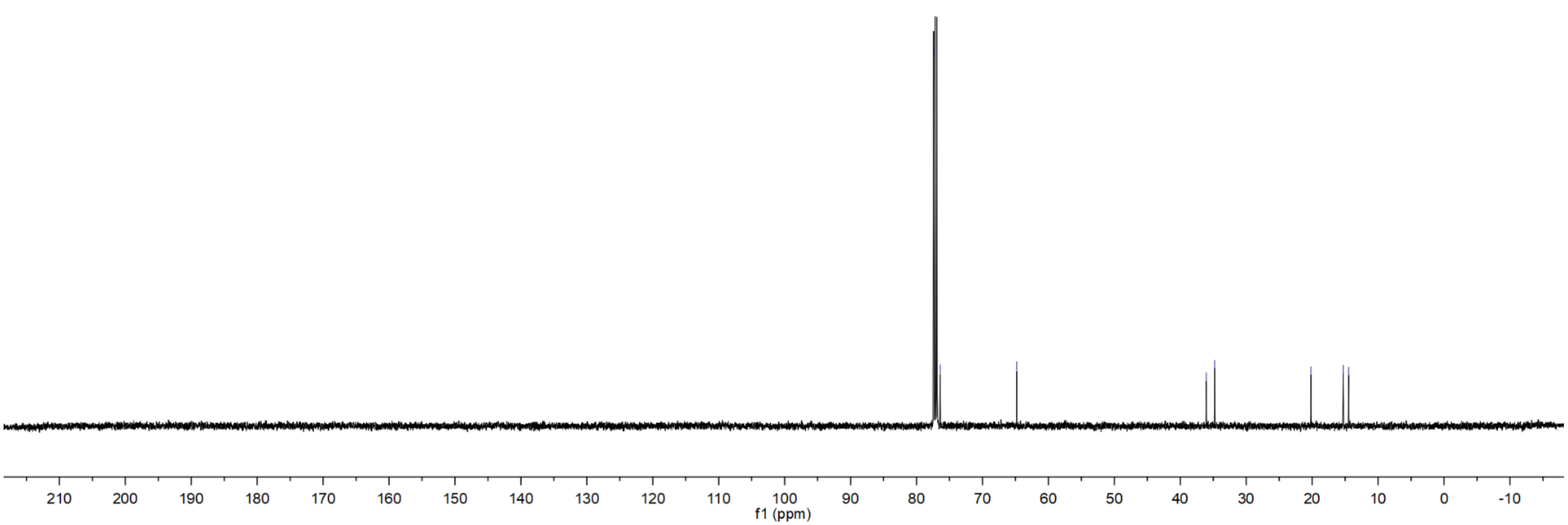


Figure S28. The 125 MHz ^{13}C-NMR of Compound **17** in Chloroform-*d*

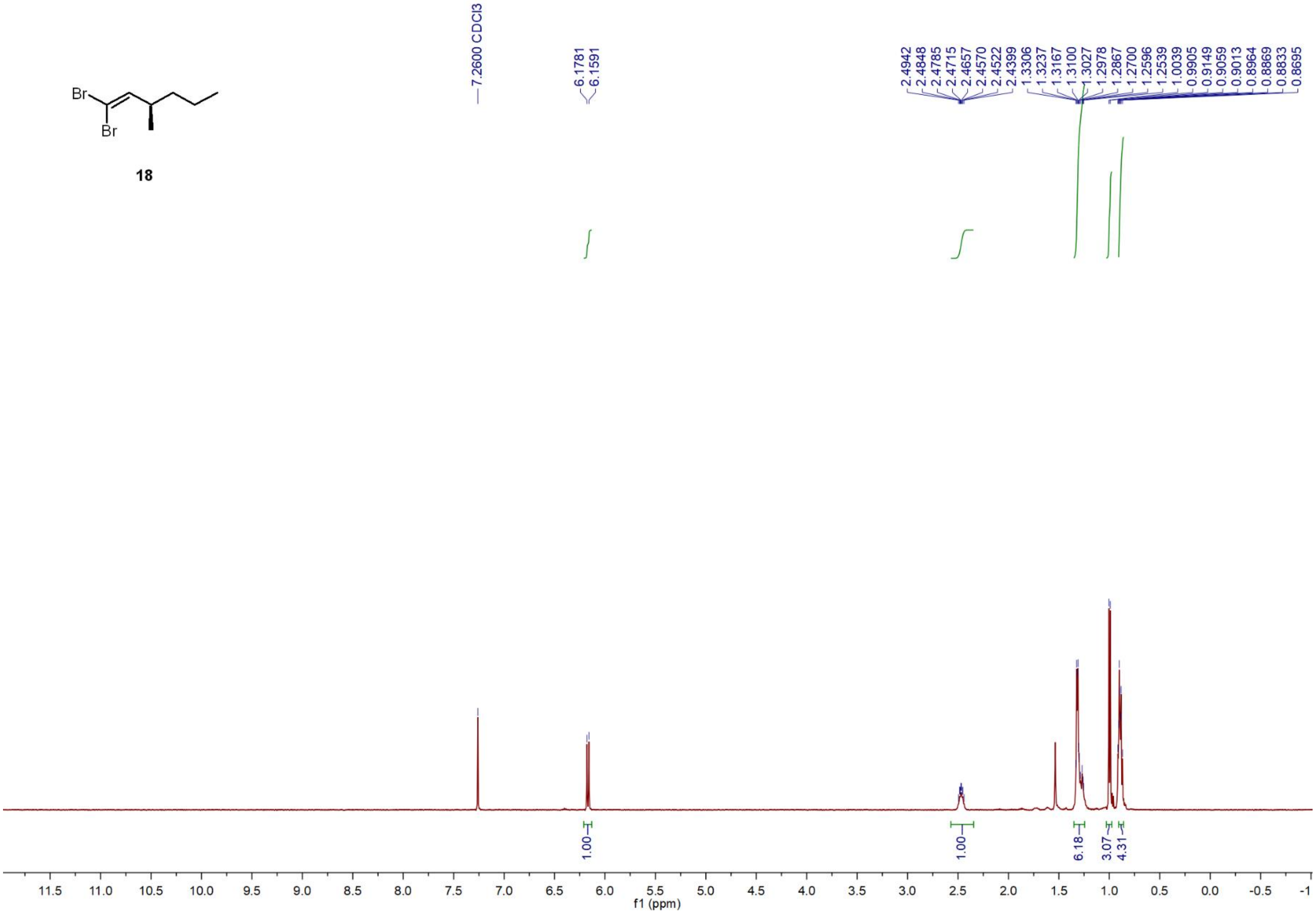


Figure S29. The 500 MHz ^{1}H-NMR of Compound **18** in Chloroform-*d*

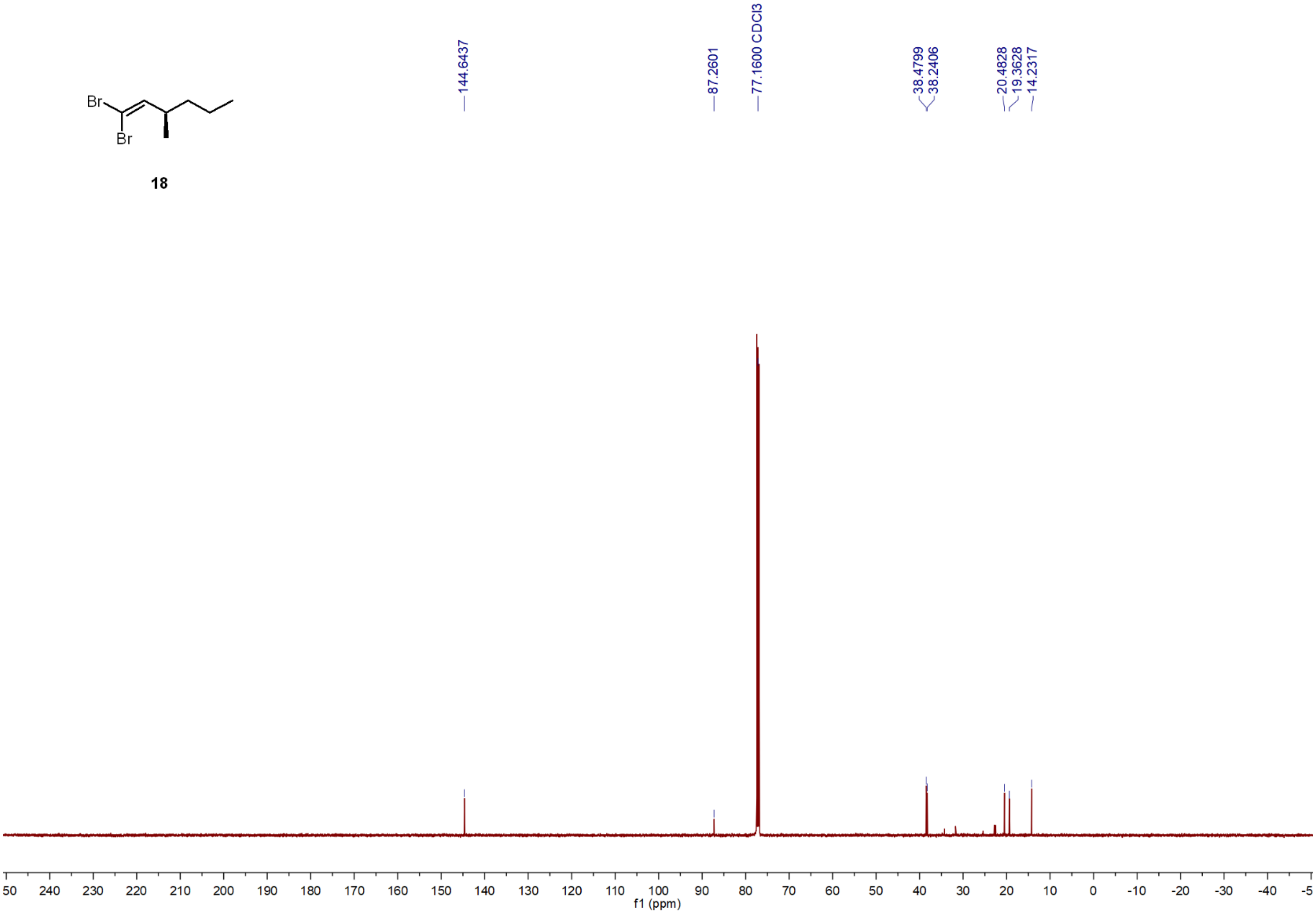


Figure S30. The 125 MHz ^{13}C-NMR of Compound **18** in Chloroform-*d*

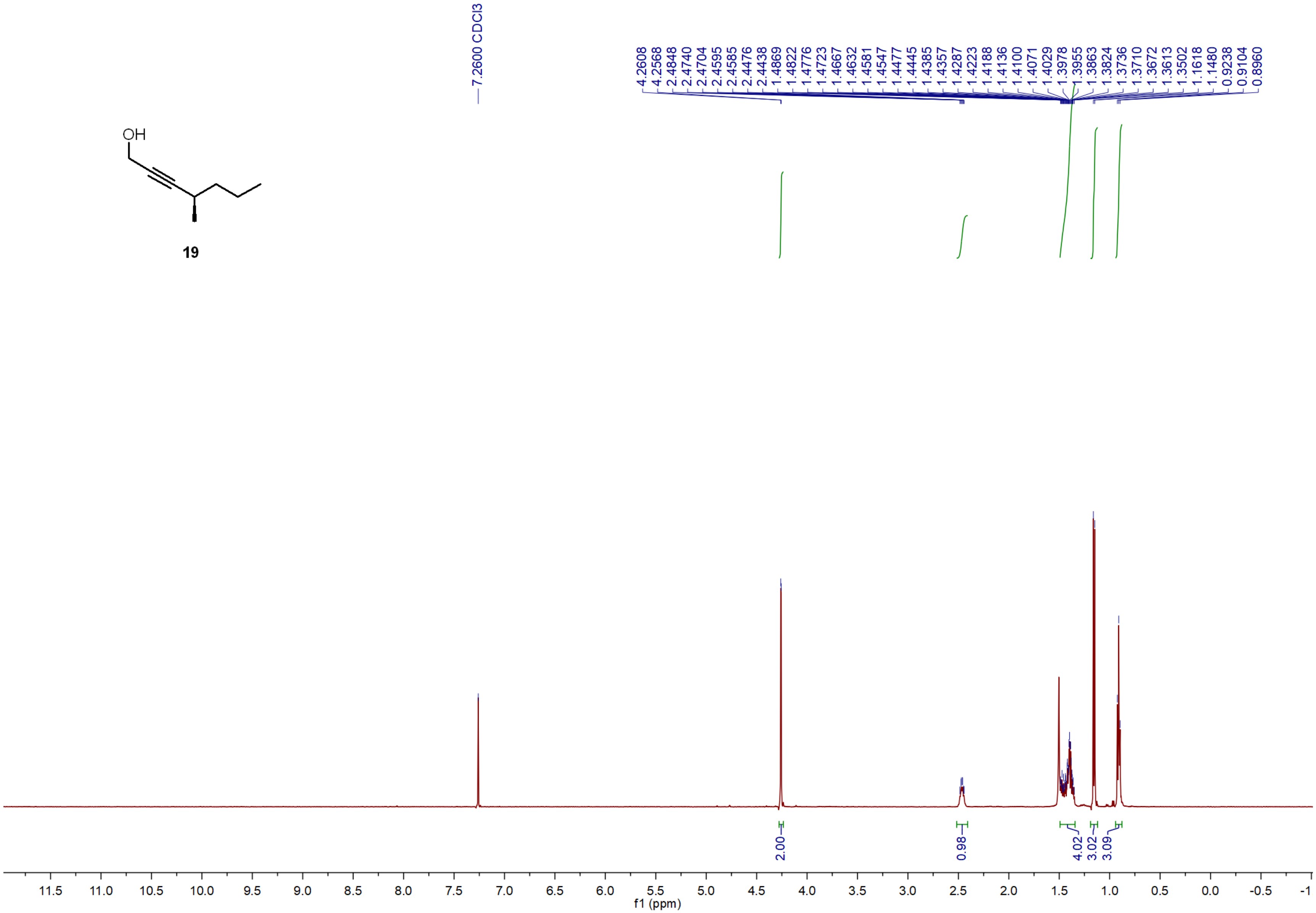


Figure S31. The 500 MHz ^{1}H-NMR of Compound **19** in Chloroform-*d*

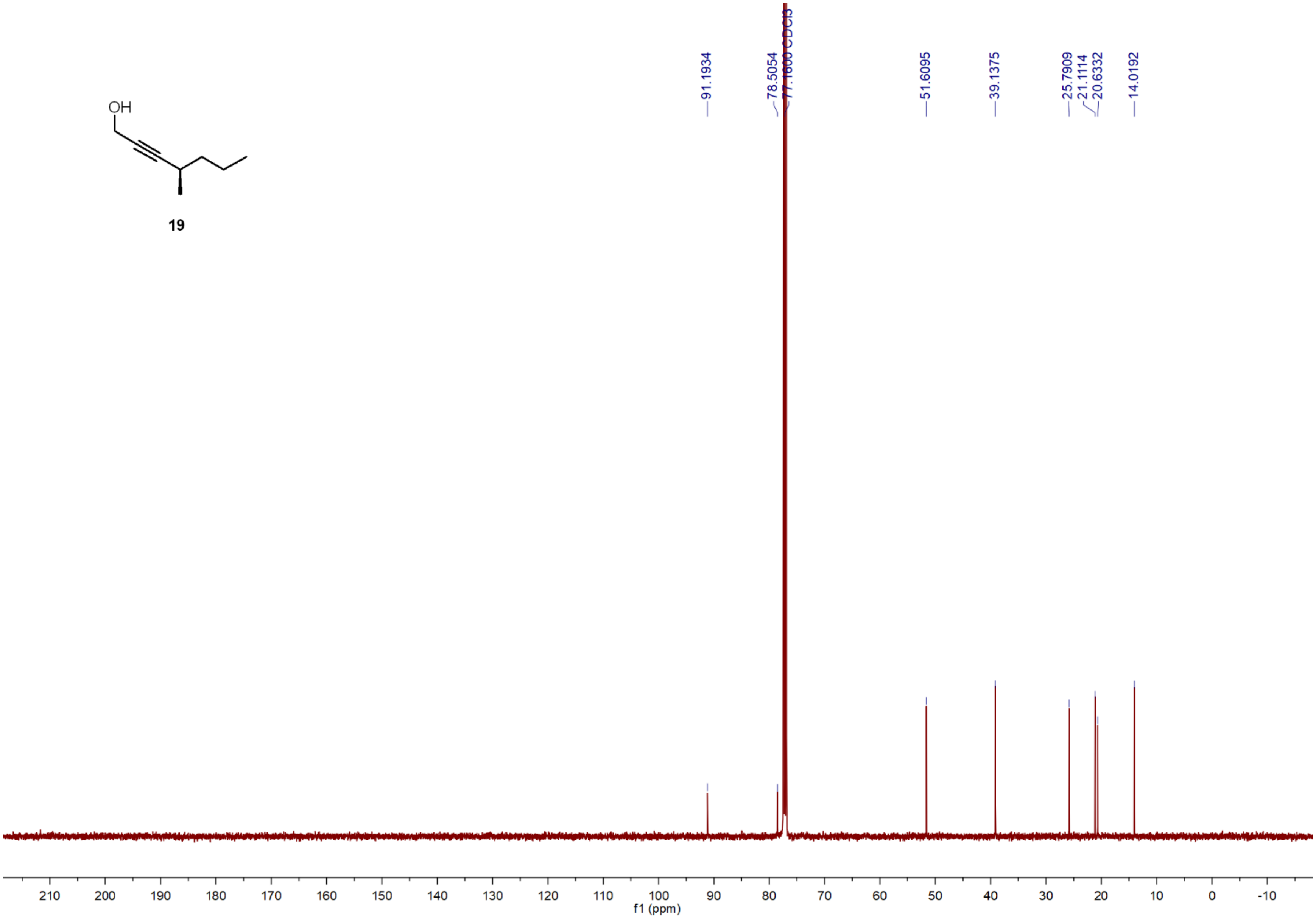
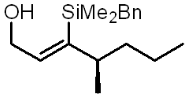


Figure S32. The 125 MHz ^{13}C-NMR of Compound **19** in Chloroform-*d*



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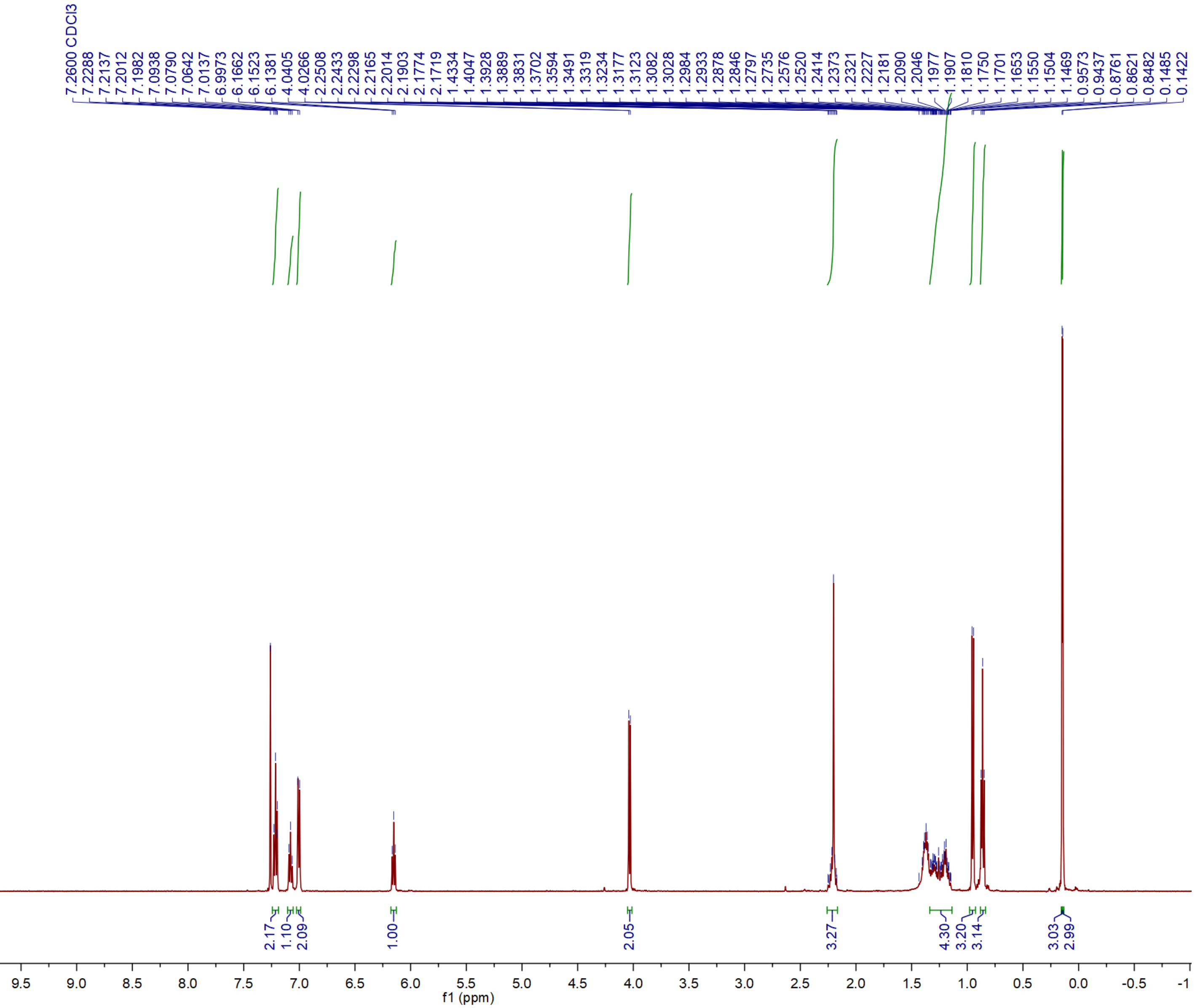


Figure S33. The 500 MHz ^{1}H-NMR of Compound **20** in Chloroform-*d*

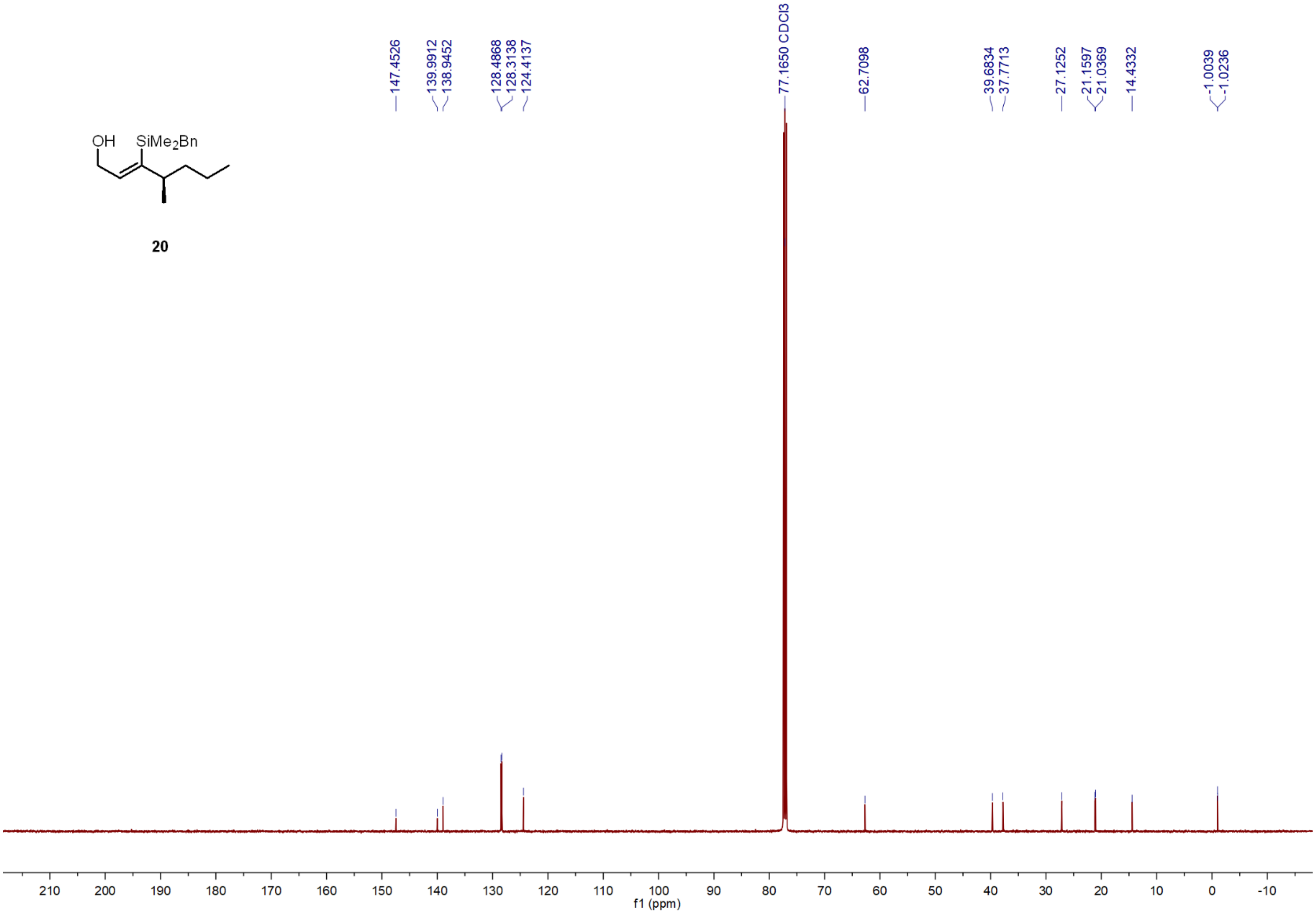


Figure S34. The 125 MHz ^{13}C-NMR of Compound **20** in Chloroform-*d*

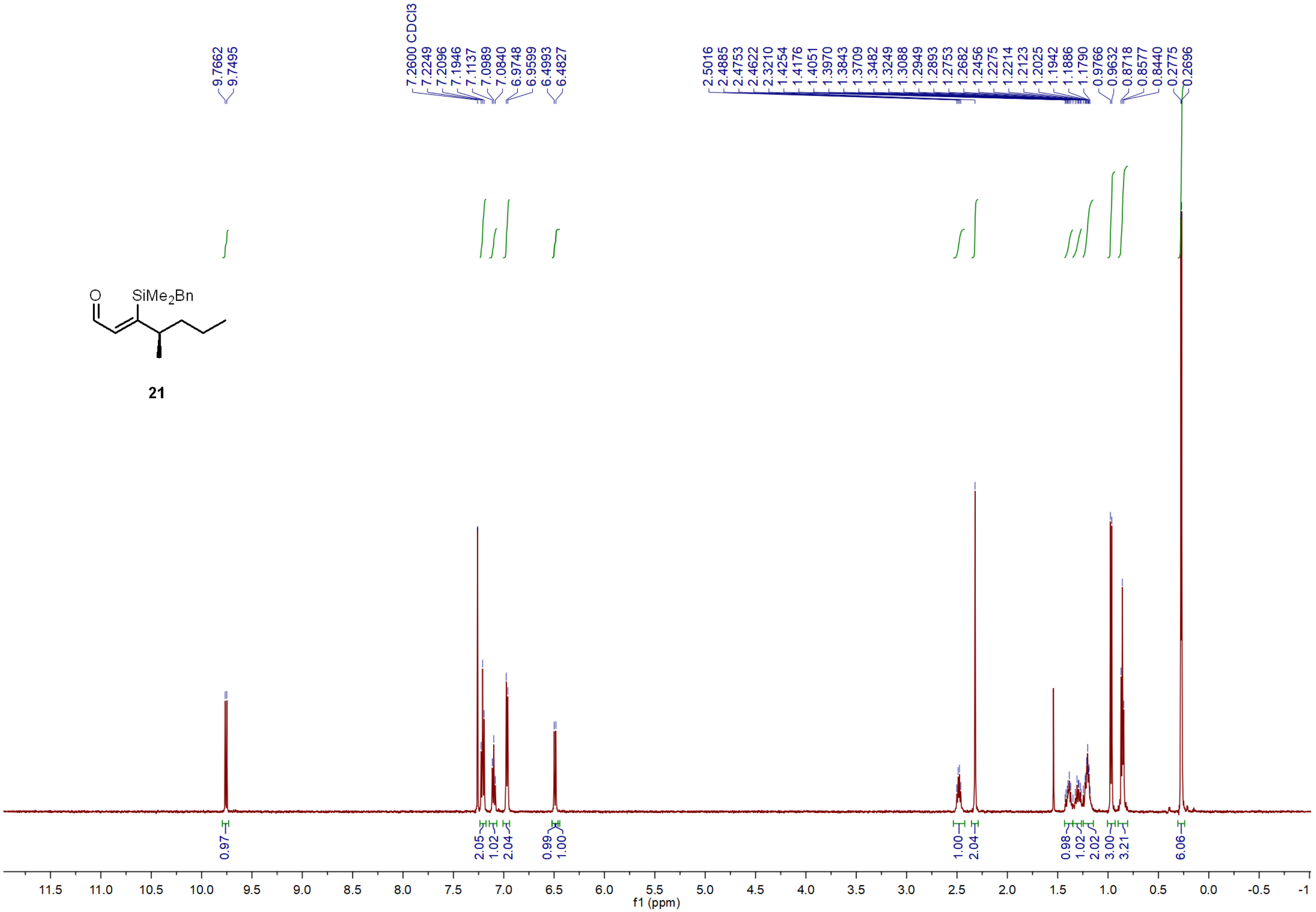


Figure S35. The 500 MHz ^{1}H-NMR of Compound **21** in Chloroform-*d*

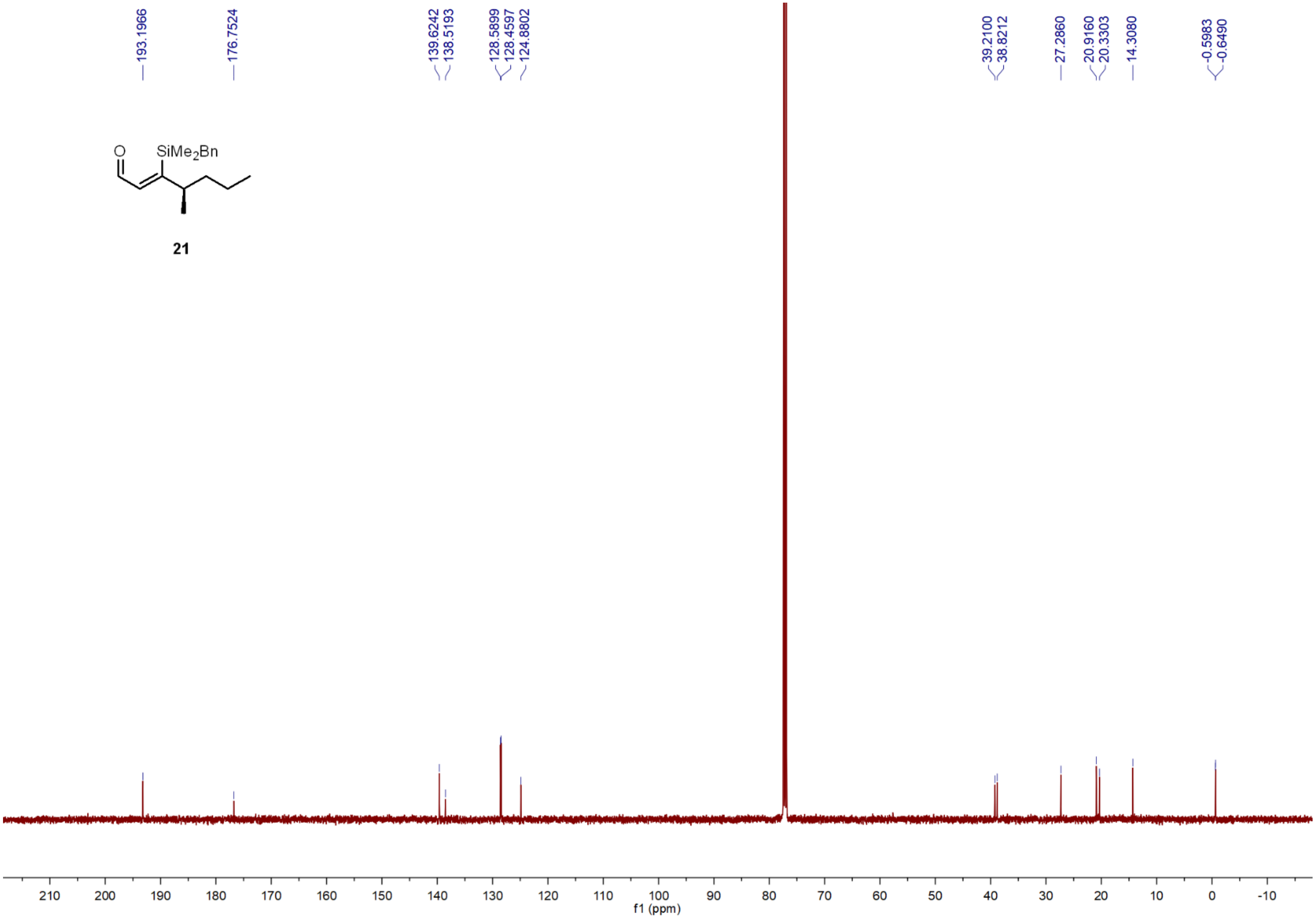


Figure S36. The 125 MHz ^{13}C-NMR of Compound **21** in Chloroform-*d*

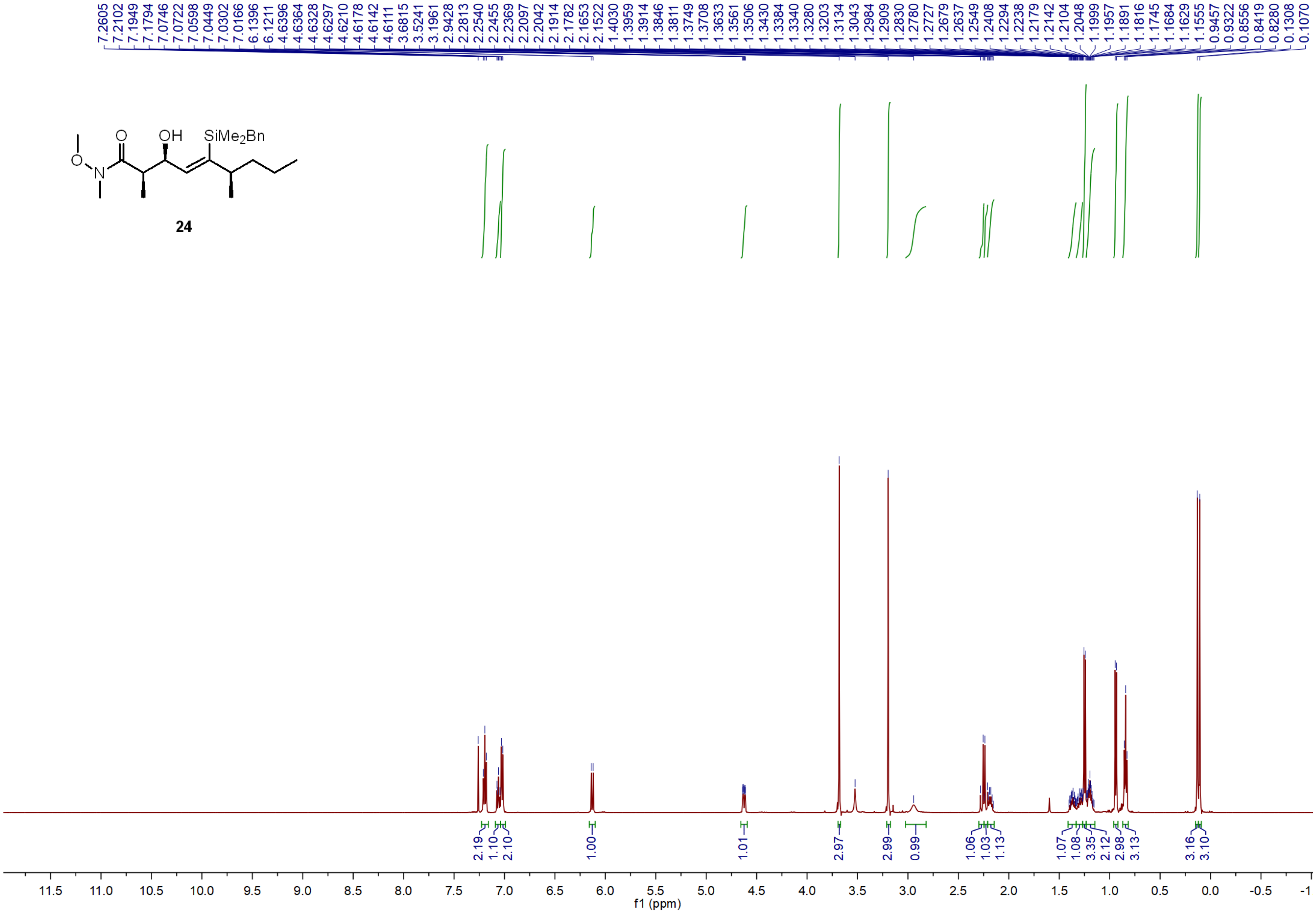


Figure S37. The 500 MHz ^{1}H-NMR of Compound **24** in Chloroform-*d*

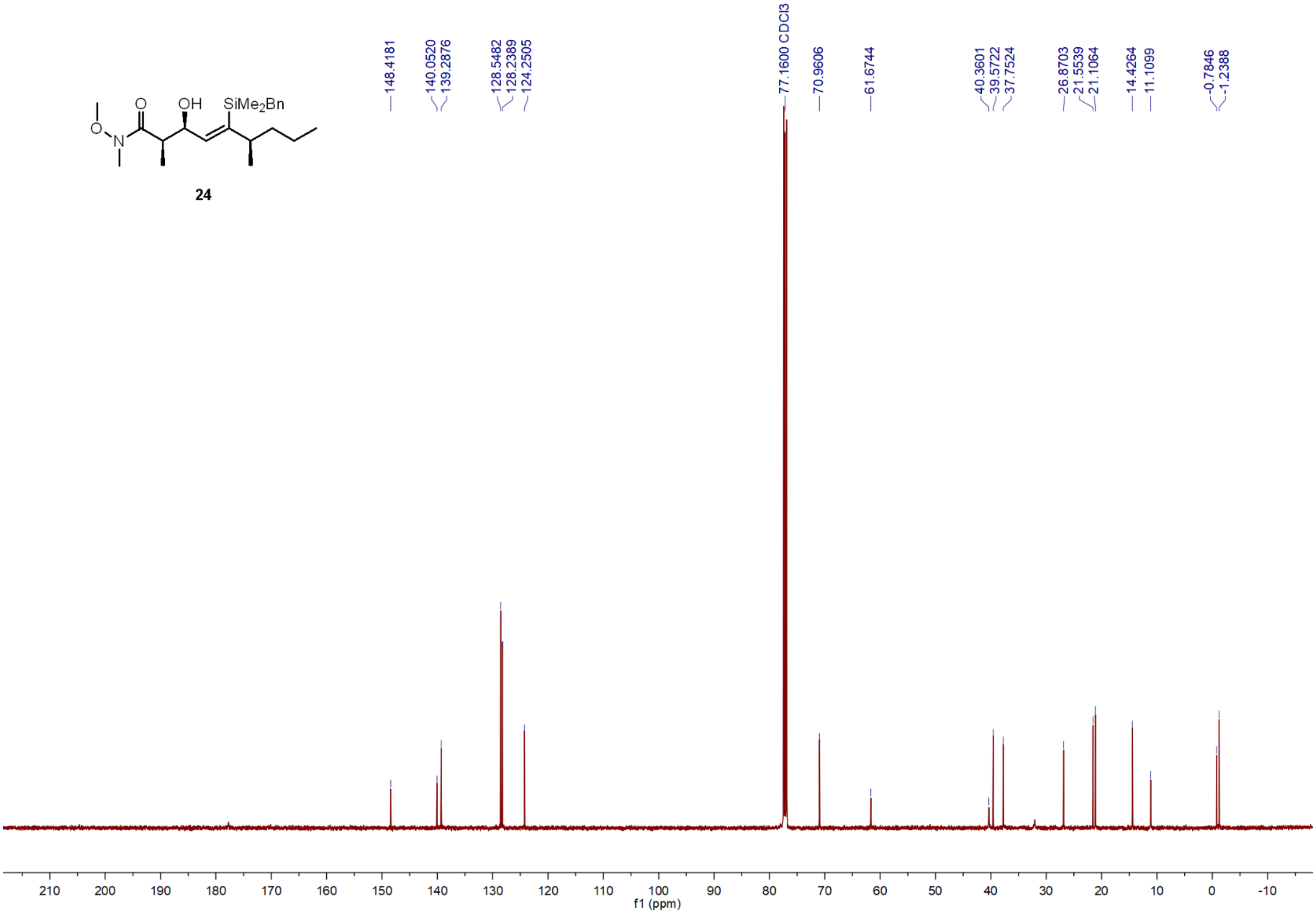


Figure S38. The 125 MHz ^{13}C-NMR of Compound **24** in Chloroform-*d*

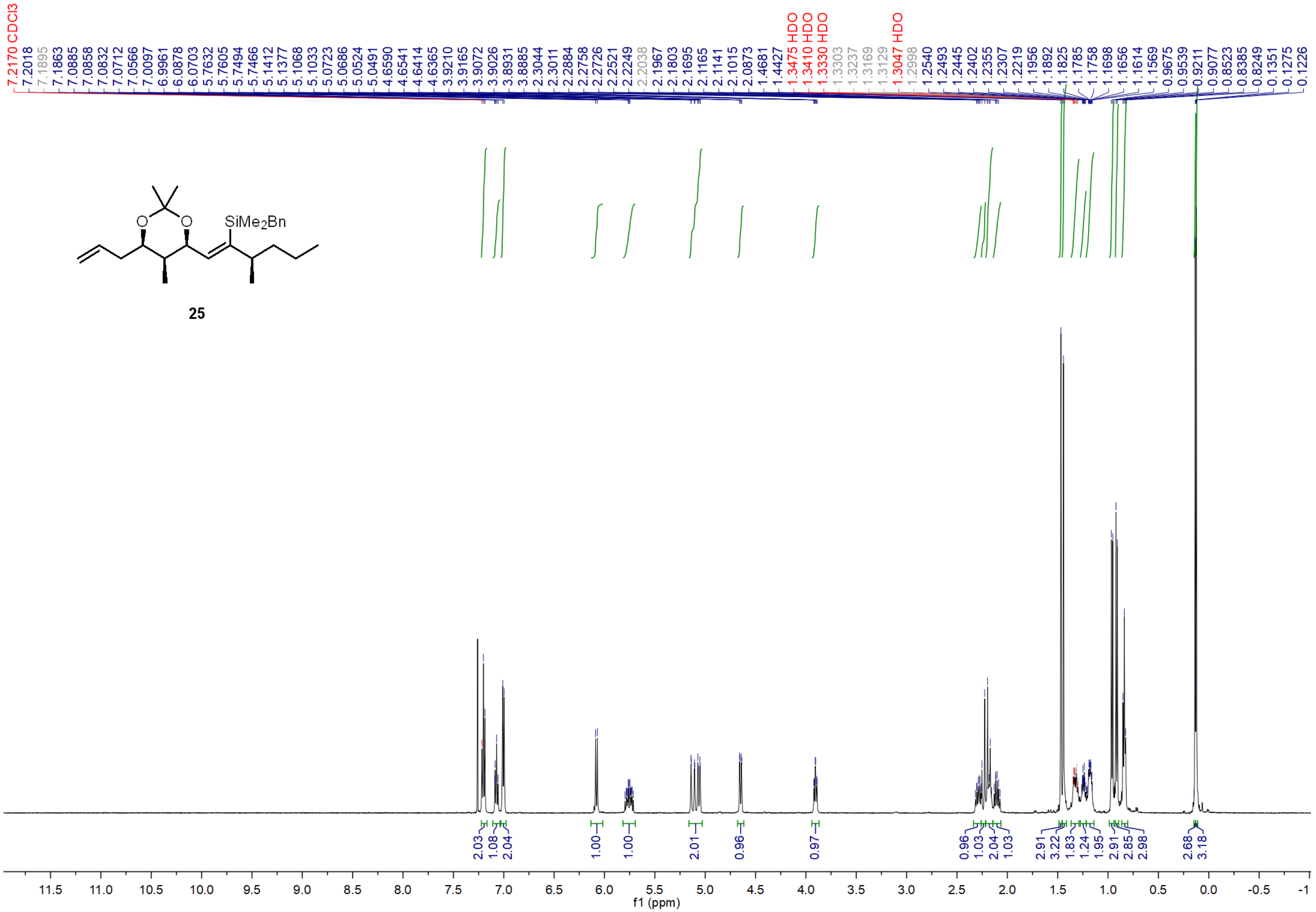


Figure S39. The 500 MHz ^{1}H-NMR of Compound **25** in Chloroform-*d*

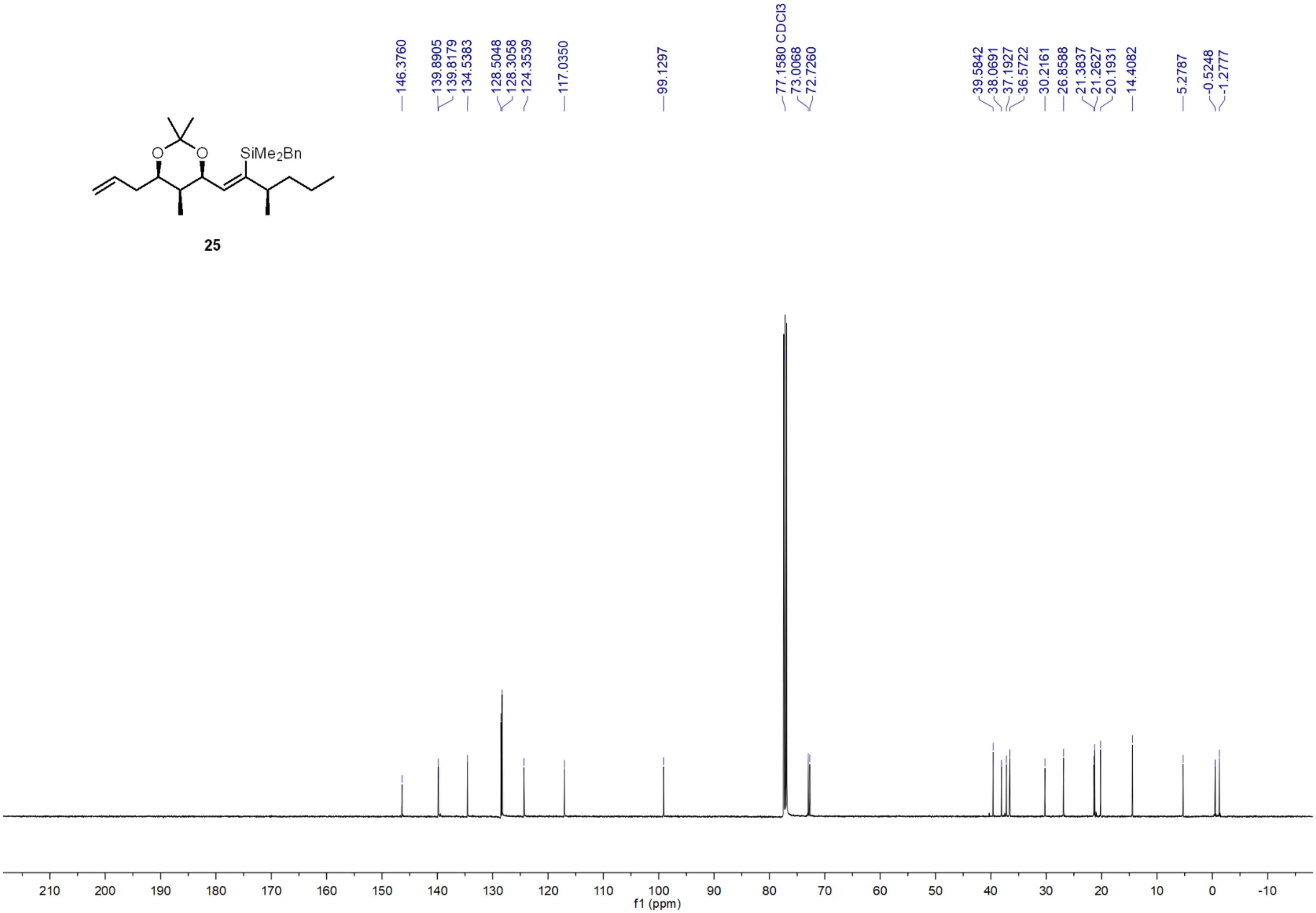


Figure S40. The 125 MHz ^{13}C-NMR of Compound **25** in Chloroform-*d*

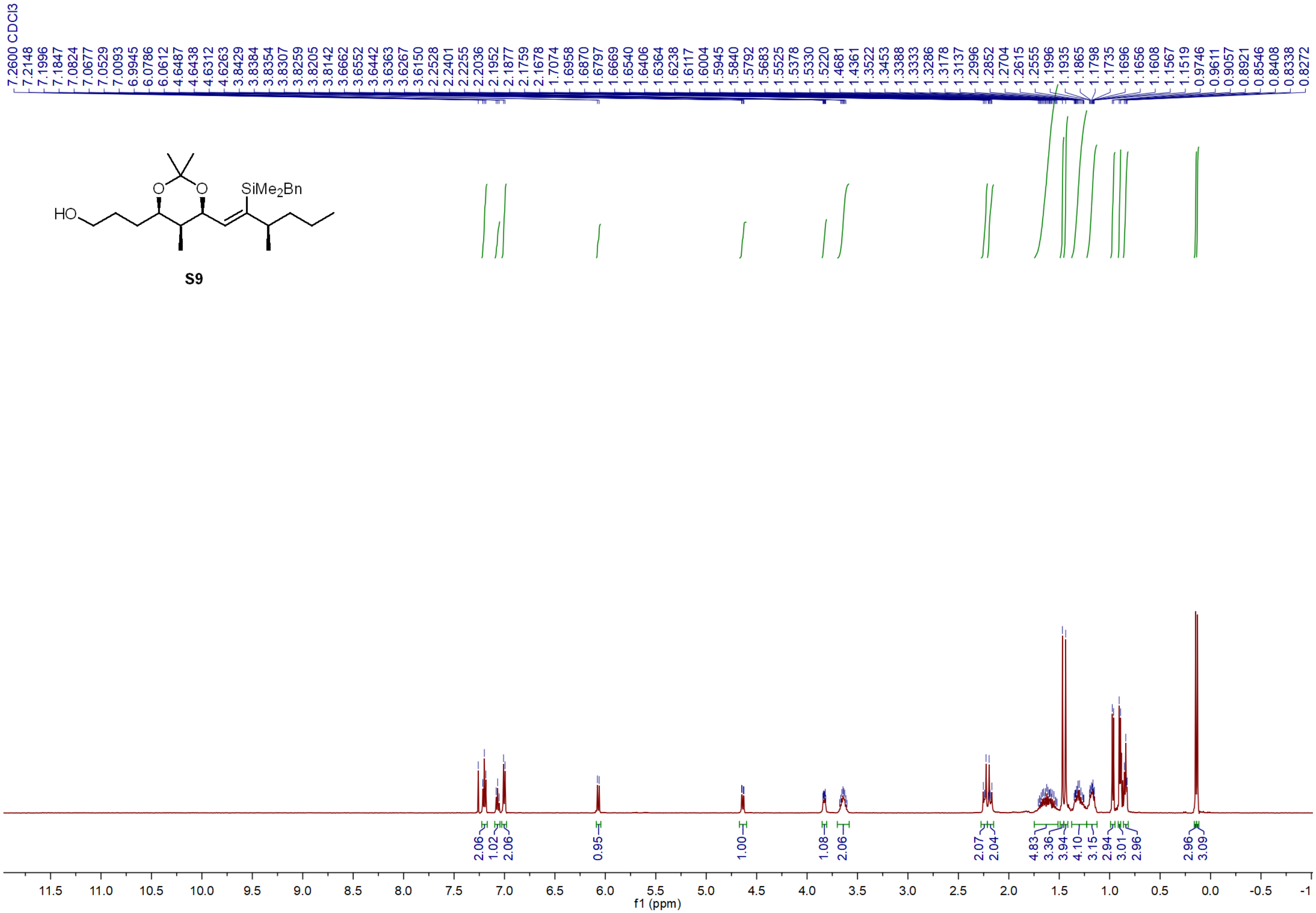


Figure S41. The 500 MHz ^{1}H-NMR of Compound **S9** in Chloroform-*d*

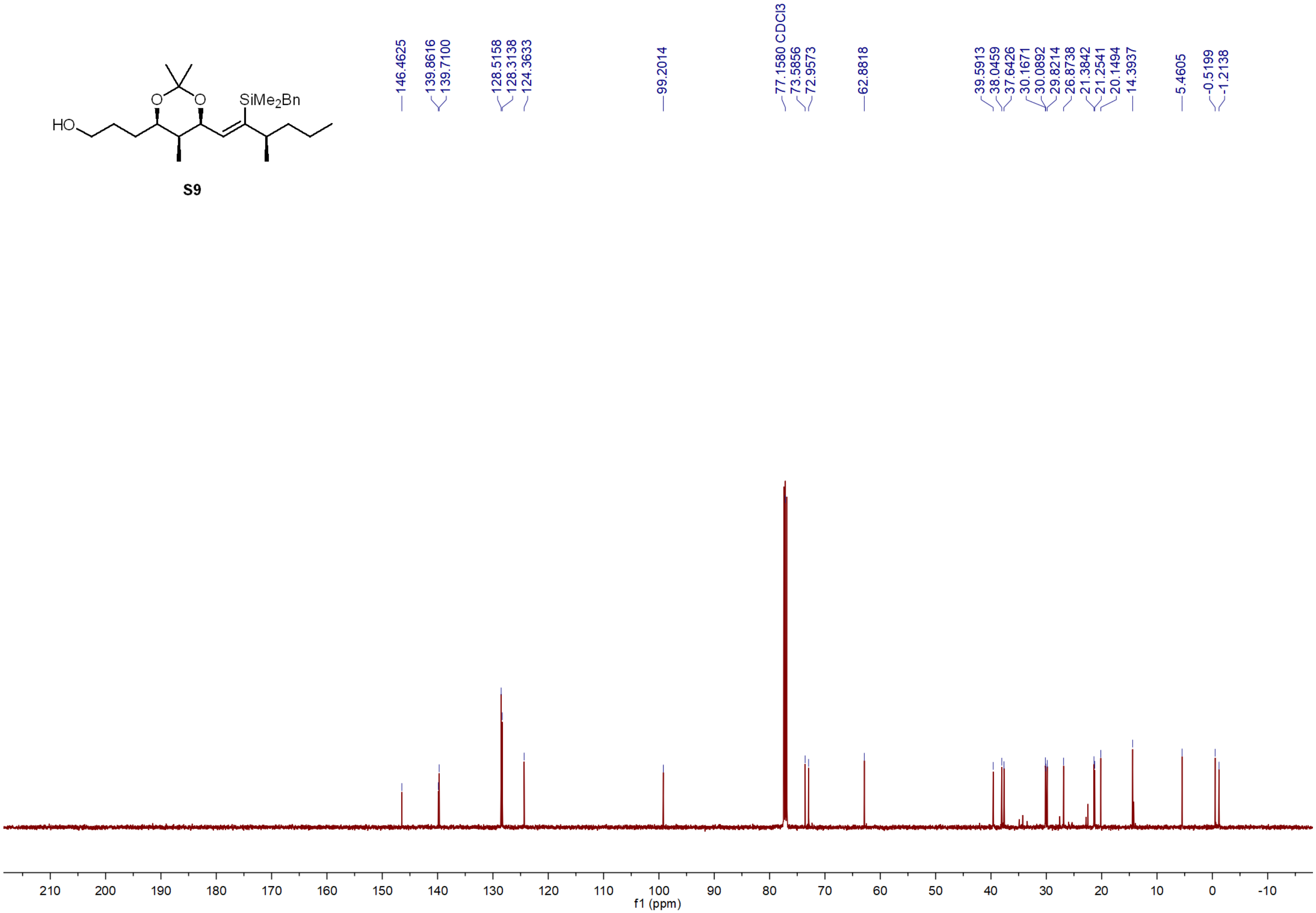


Figure S42. The 125 MHz ^{13}C-NMR of Compound **S9** in Chloroform-*d*

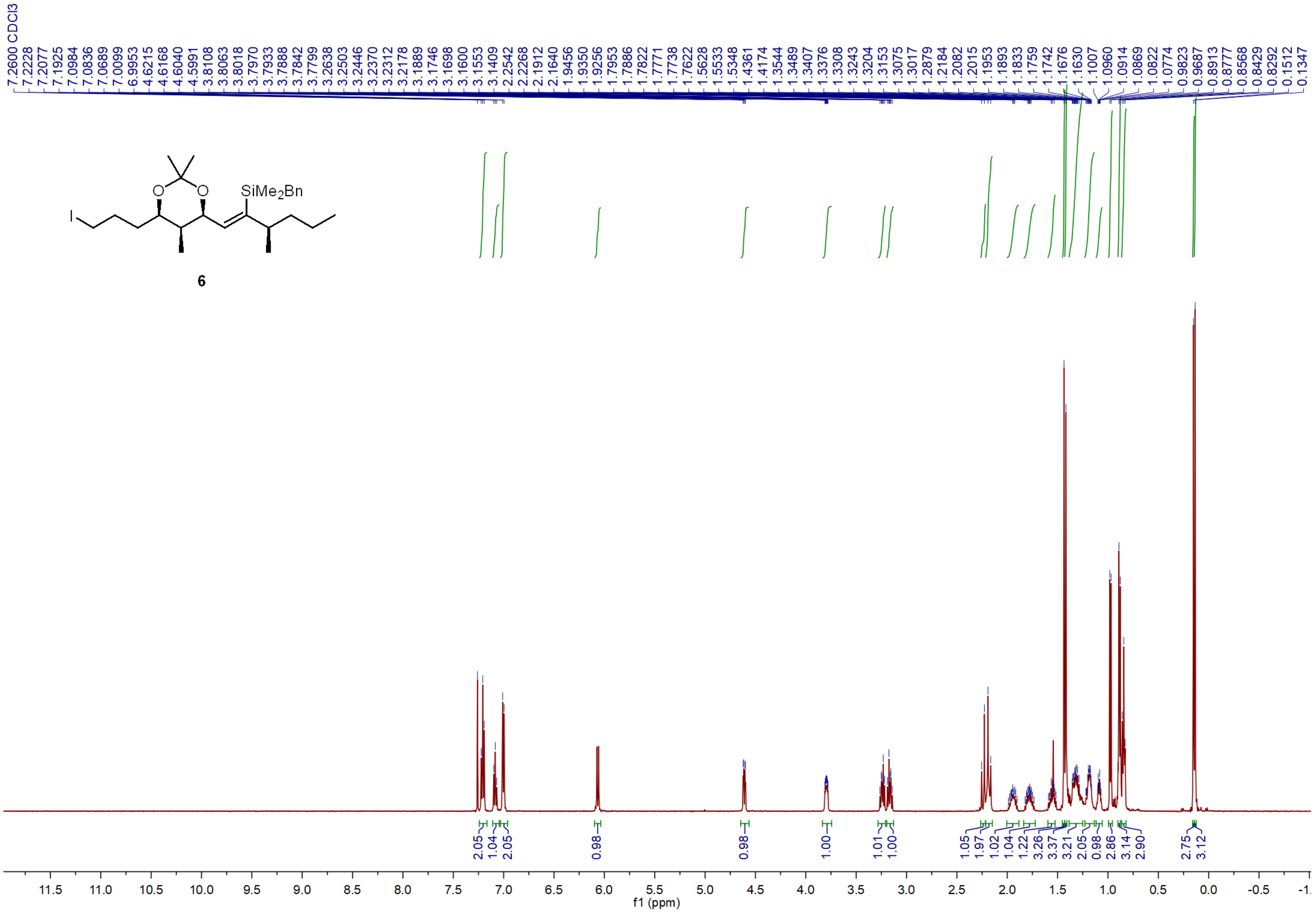


Figure S43. The 500 MHz ^{1}H-NMR of Compound **6** in Chloroform-*d*

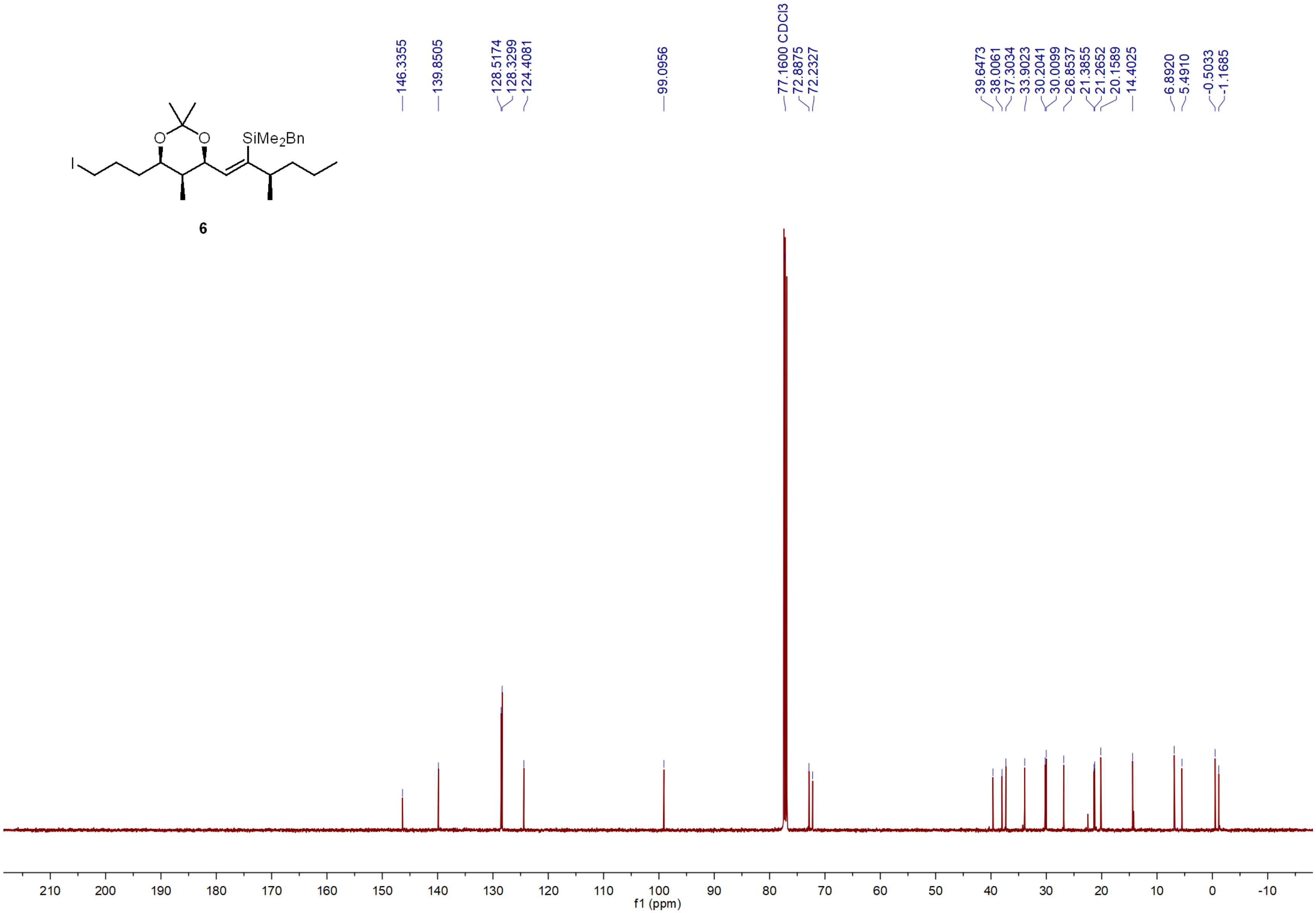


Figure S44. The 125 MHz ^{13}C-NMR of Compound **6** in Chloroform-*d*

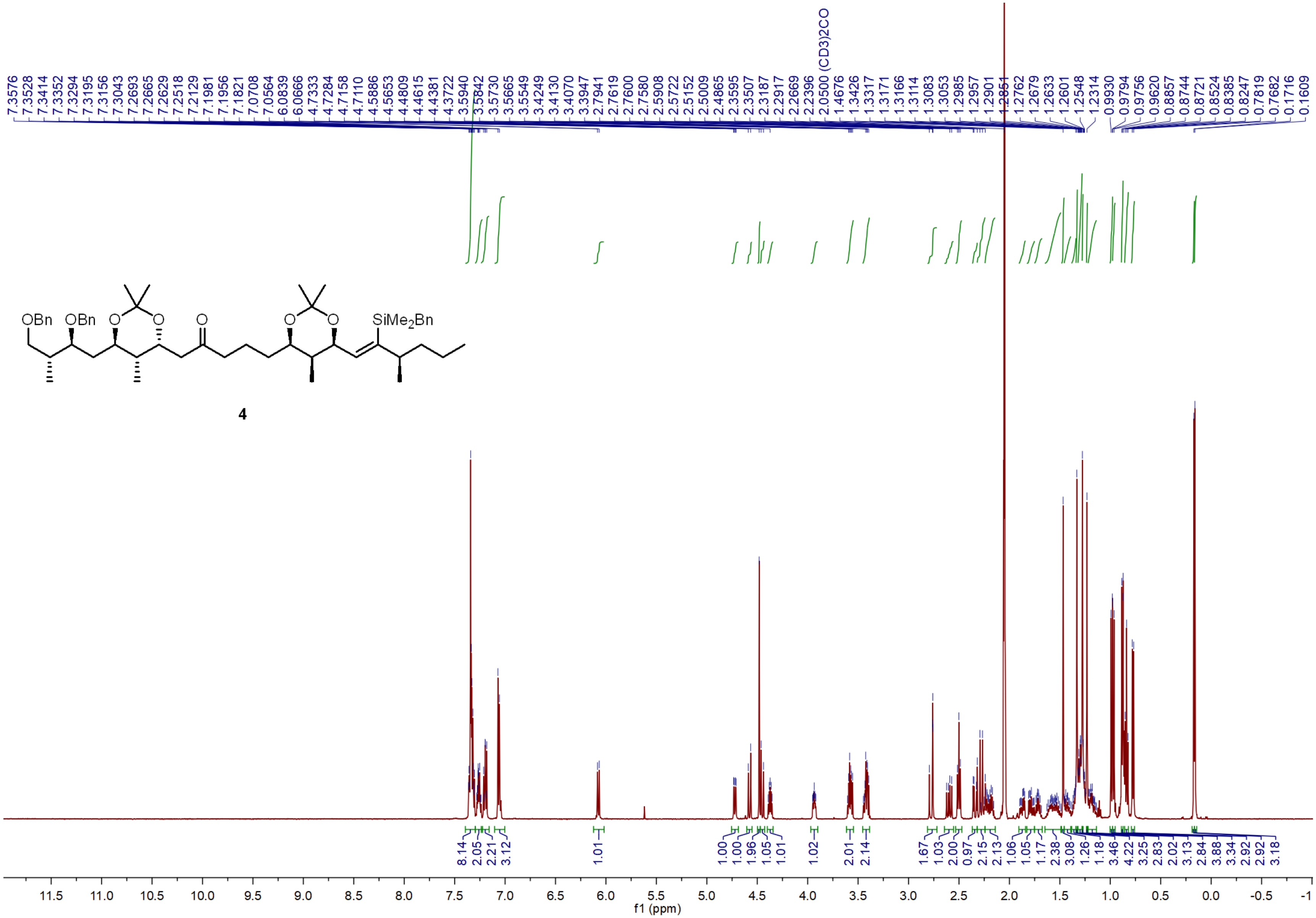


Figure S45. The 500 MHz ^{1}H-NMR of Compound **4** in acetone-*d6*

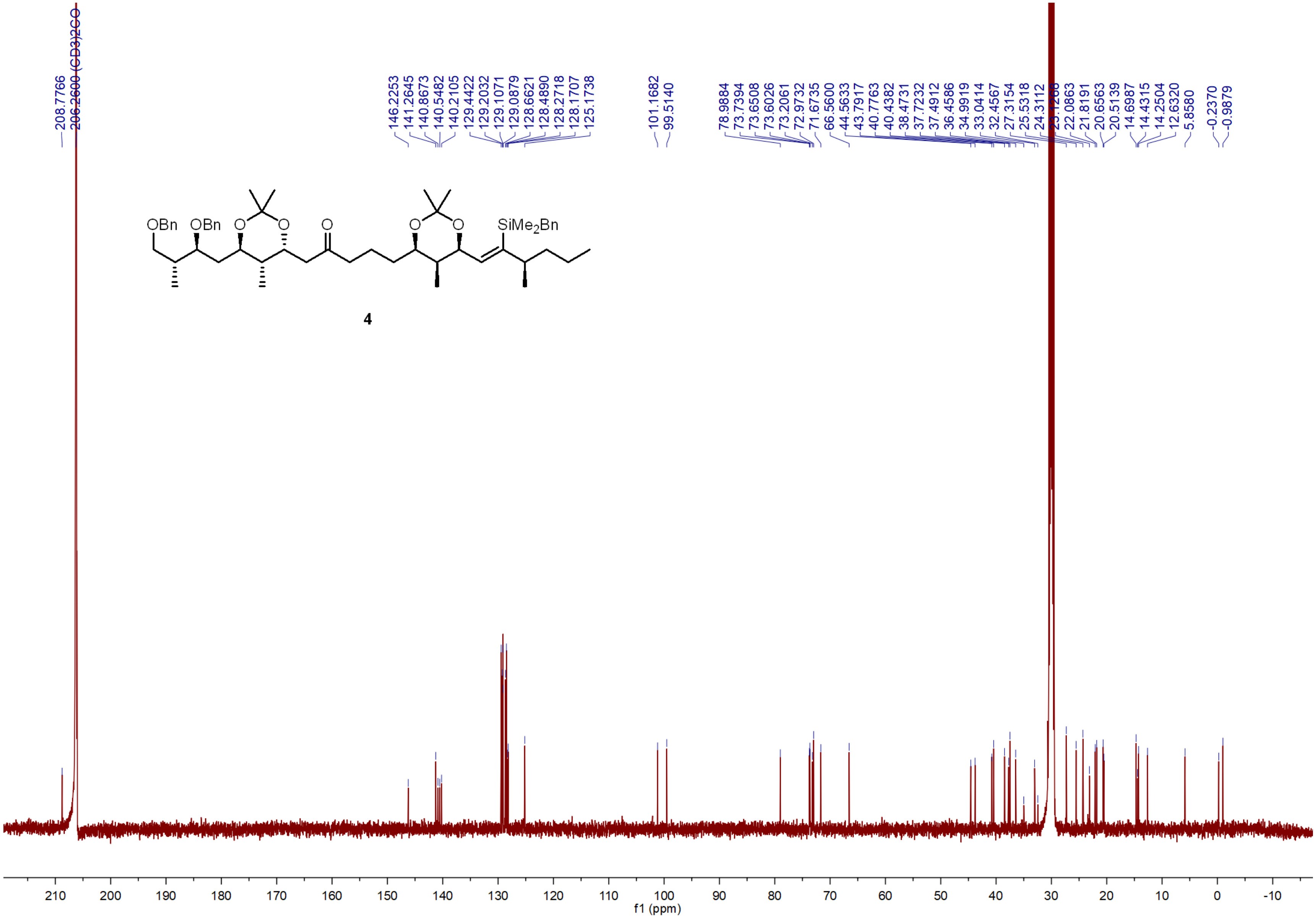


Figure S46. The 125 MHz ^{13}C-NMR of Compound **4** in acetone-*d6*

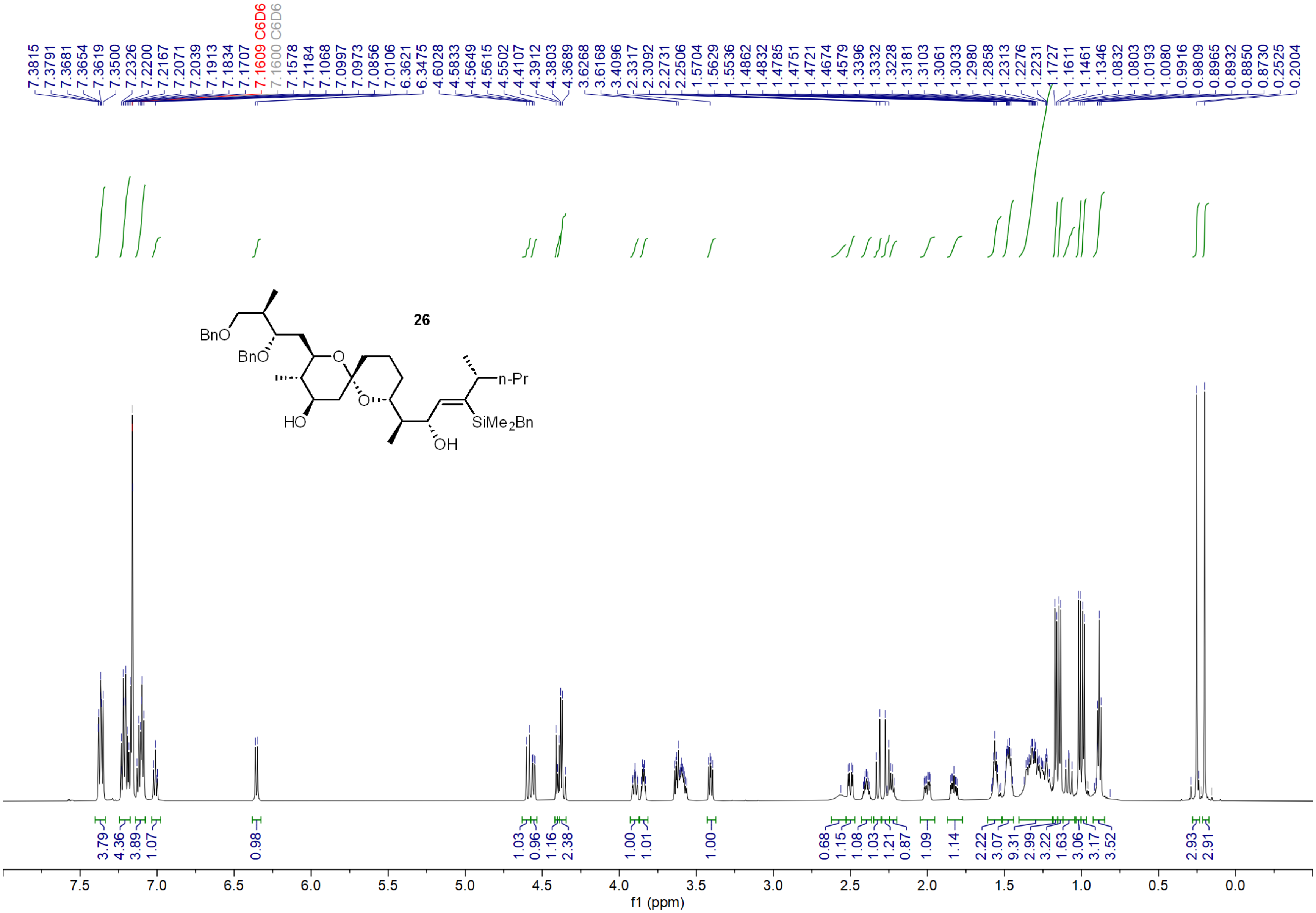


Figure S47. The 600 MHz ^{1}H-NMR of Compound **26** in benzene-*d6*

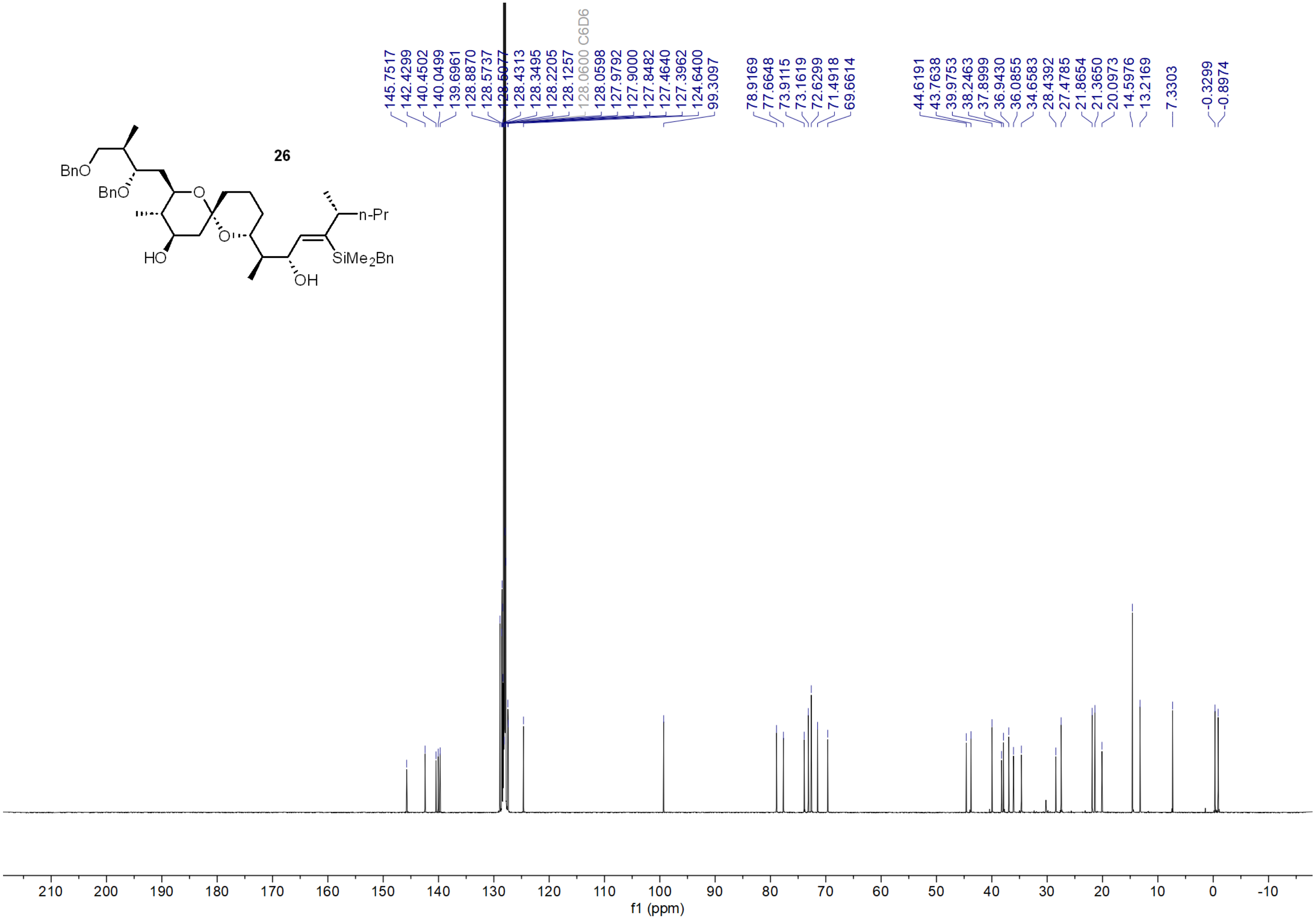


Figure S48. The 150 MHz ^{13}C-NMR of Compound **26** in benzene-*d6*

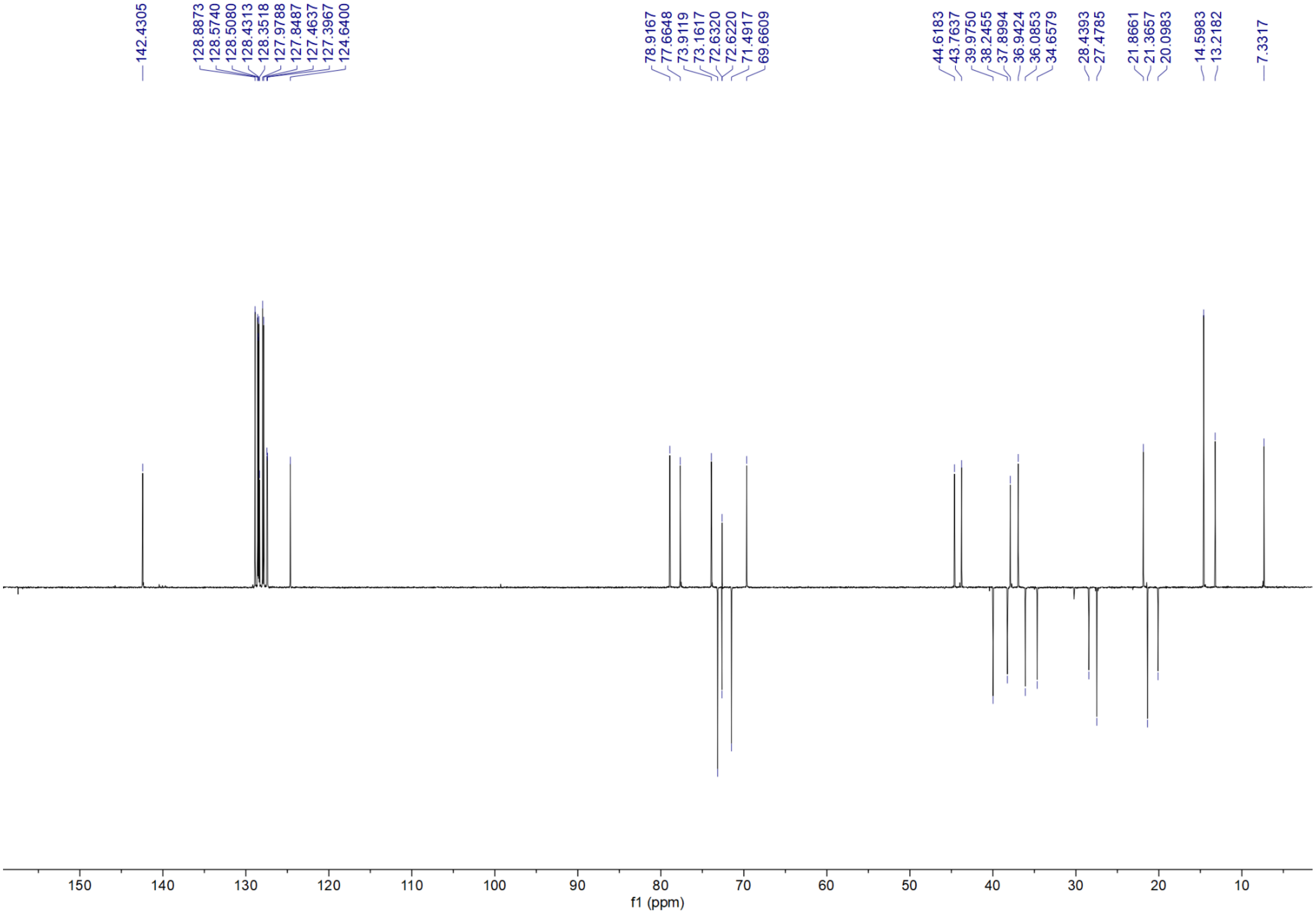


Figure S49. The dept135 150 MHz ^{13}C-NMR of Compound **26** in benzene-*d6*

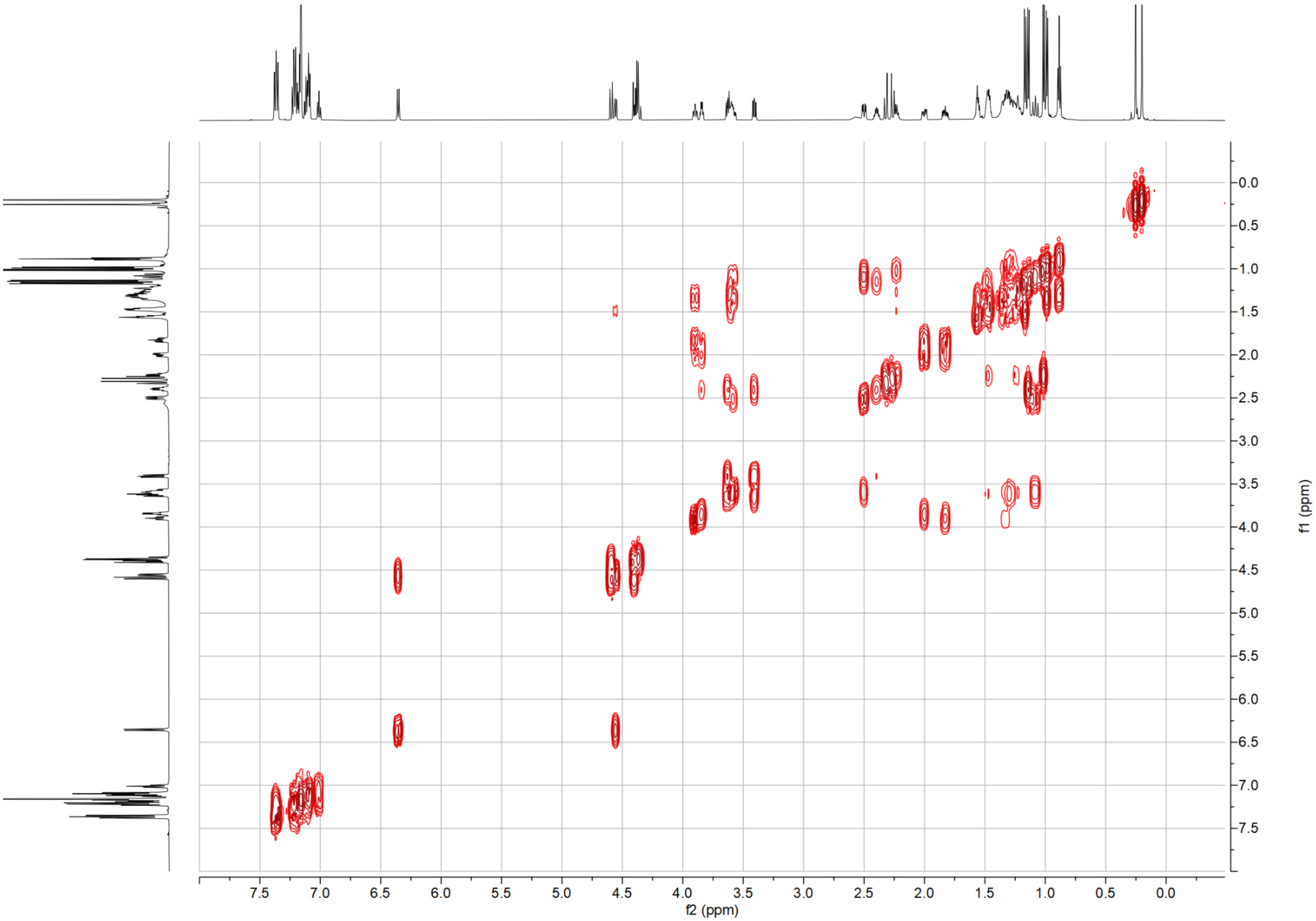


Figure S50. gCOSY NMR of compound **26**, 600 MHz, benzene-*d6*

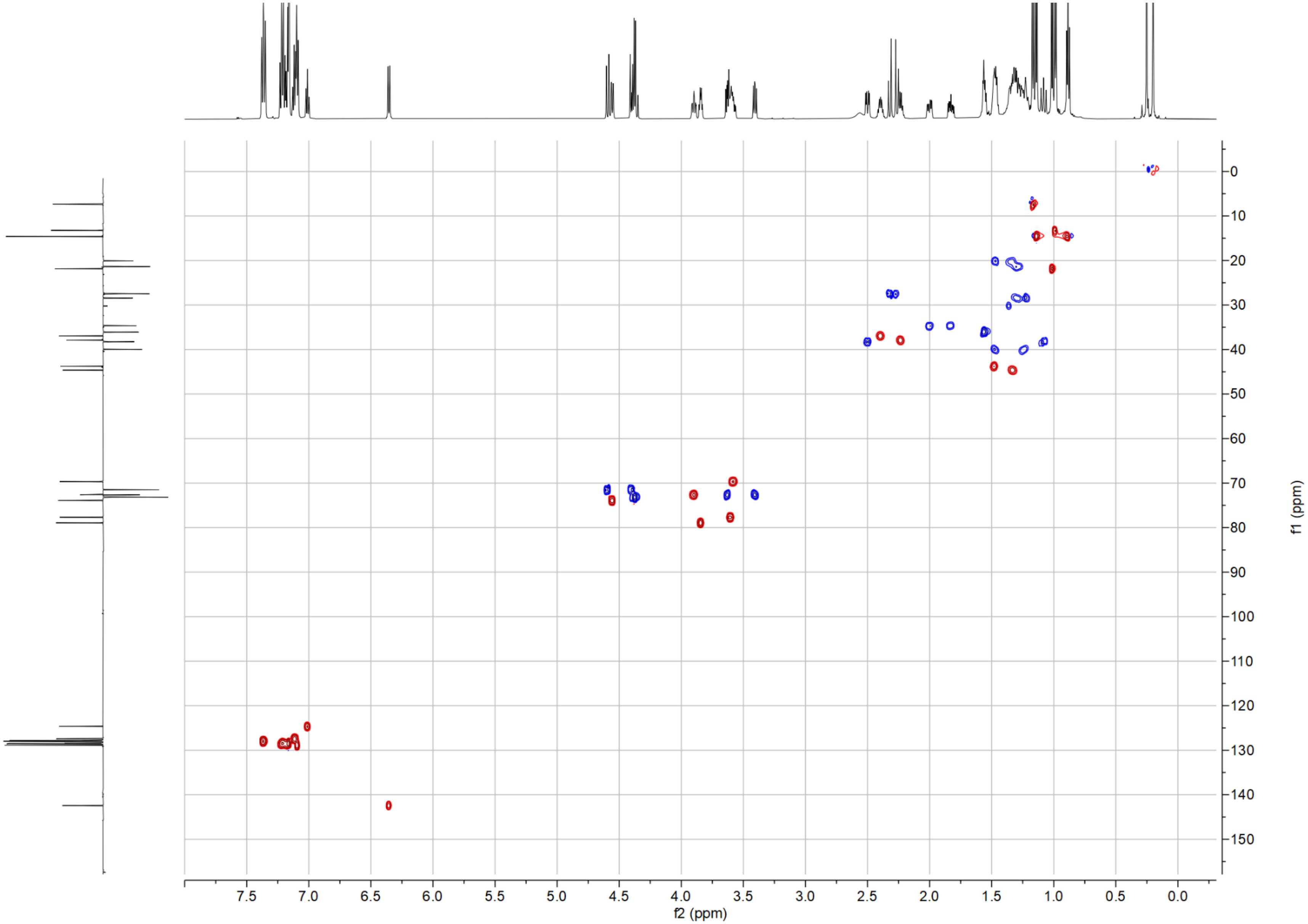


Figure S51. gHSQC NMR of compound **26**, 600 MHz, benzene-*d6*

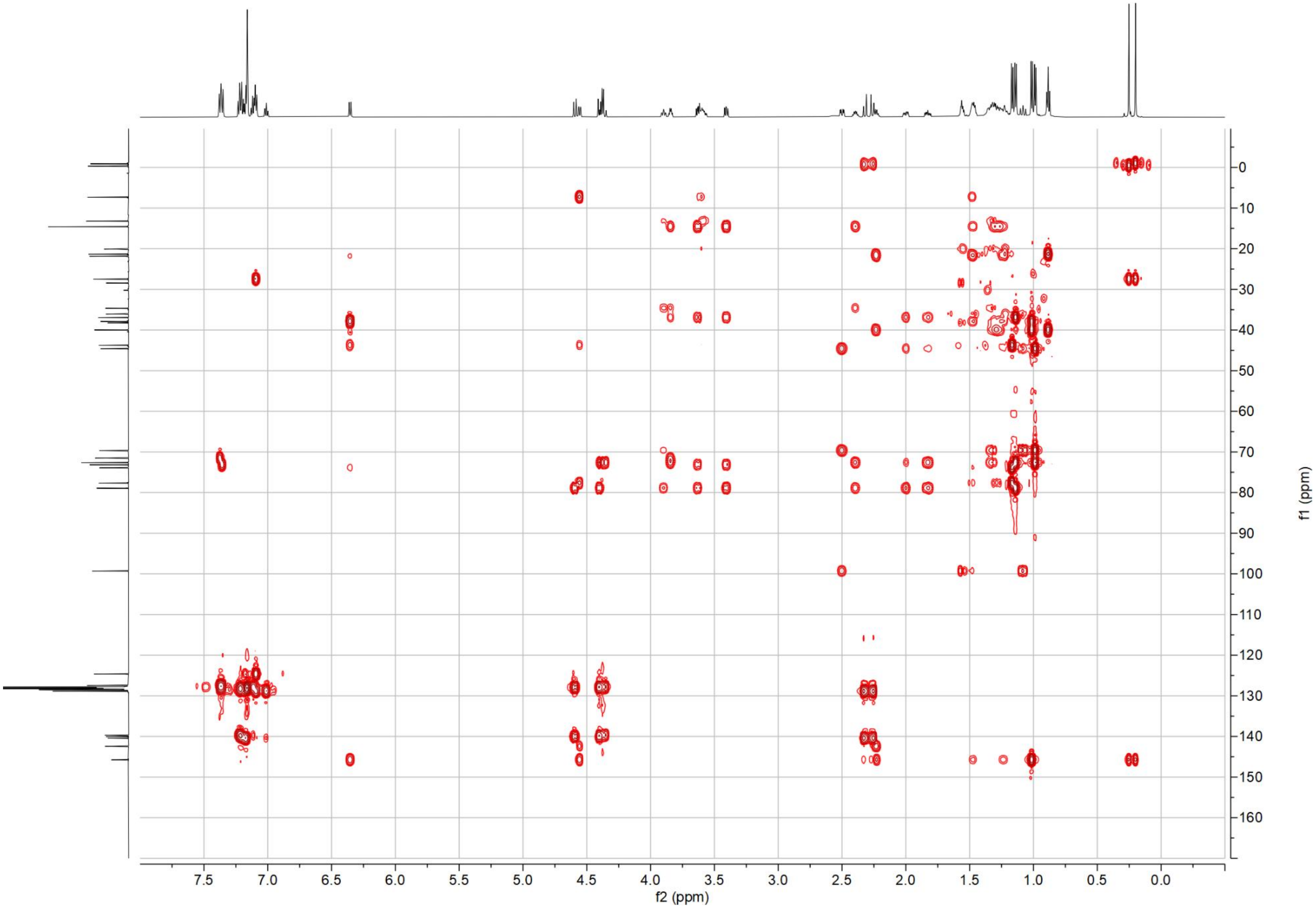


Figure S52. gHMBC NMR of compound **26**, 600 MHz, benzene-*d6*

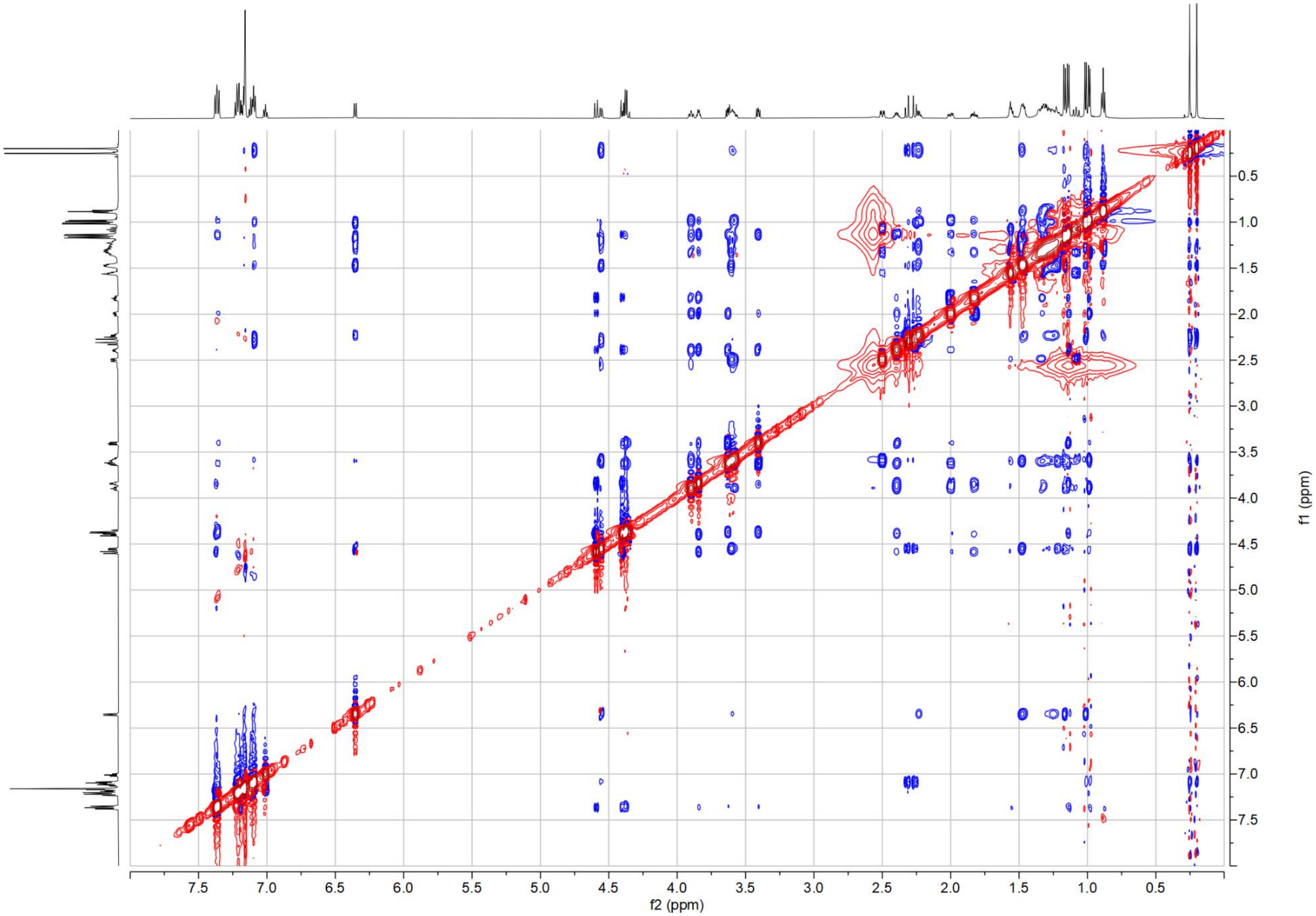


Figure S53. The NOESY NMR spectra of Compound **26**, 600 MHz, benzene-*d6*

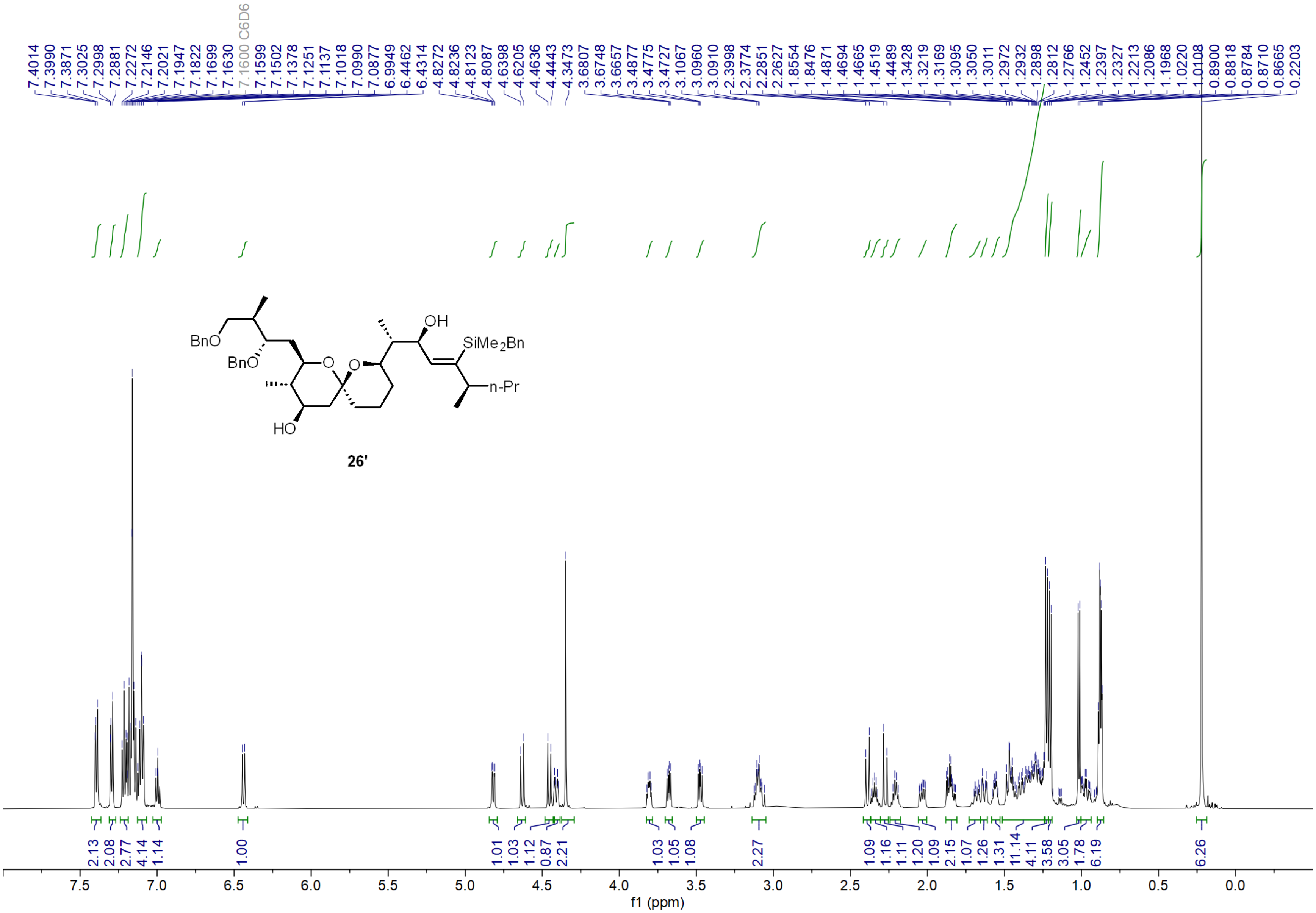


Figure S54. The 600 MHz ^{1}H-NMR of Compound **26’** in benzene-*d6*

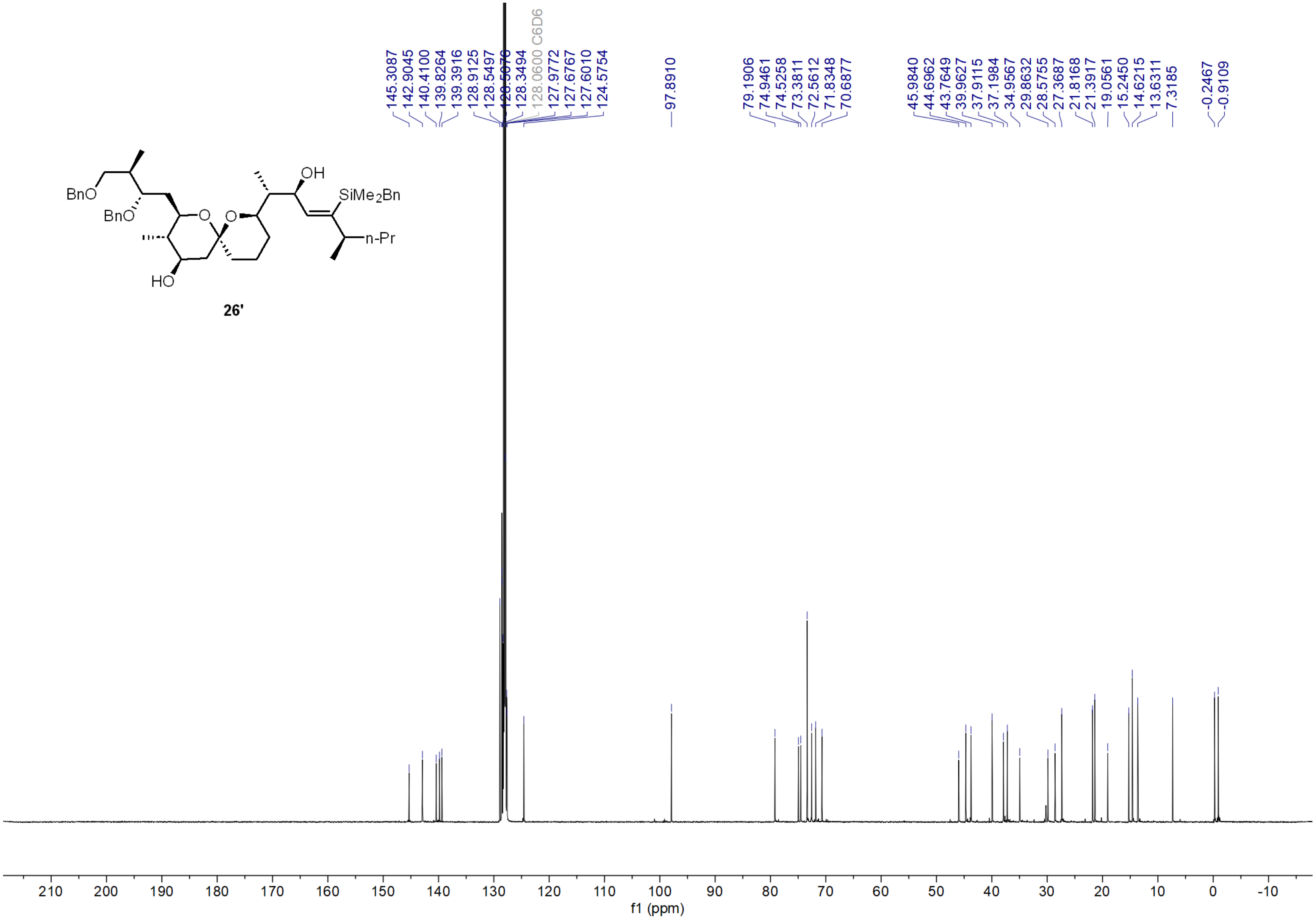


Figure S55. The 150 MHz ^{13}C-NMR of Compound **26’** in benzene-*d6*

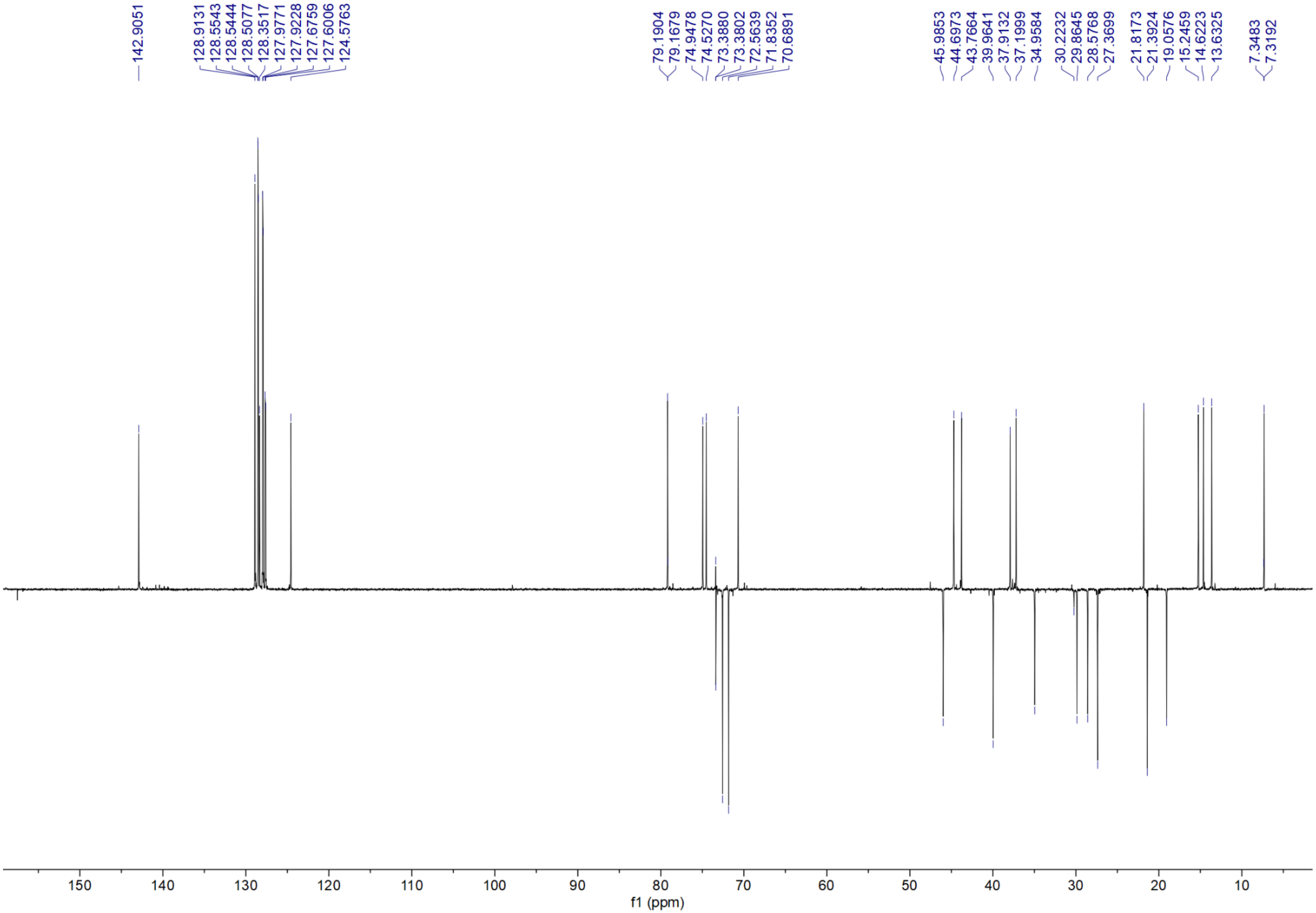


Figure S56. The dept135 150 MHz ^{13}C-NMR of Compound **26’** in benzene-*d6*

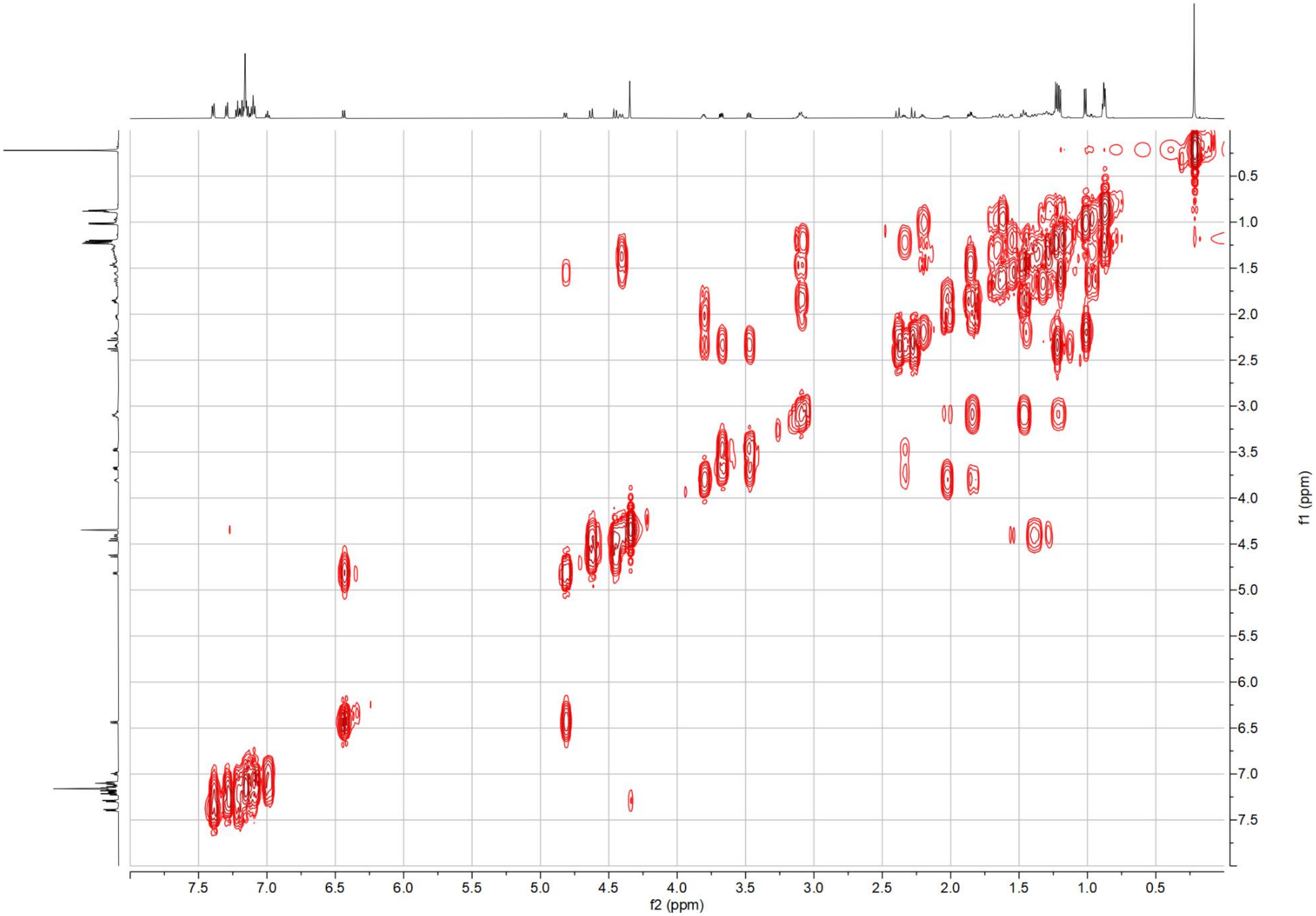


Figure S57. gCOSY NMR of compound **26’**, 600 MHz, benzene-*d6*

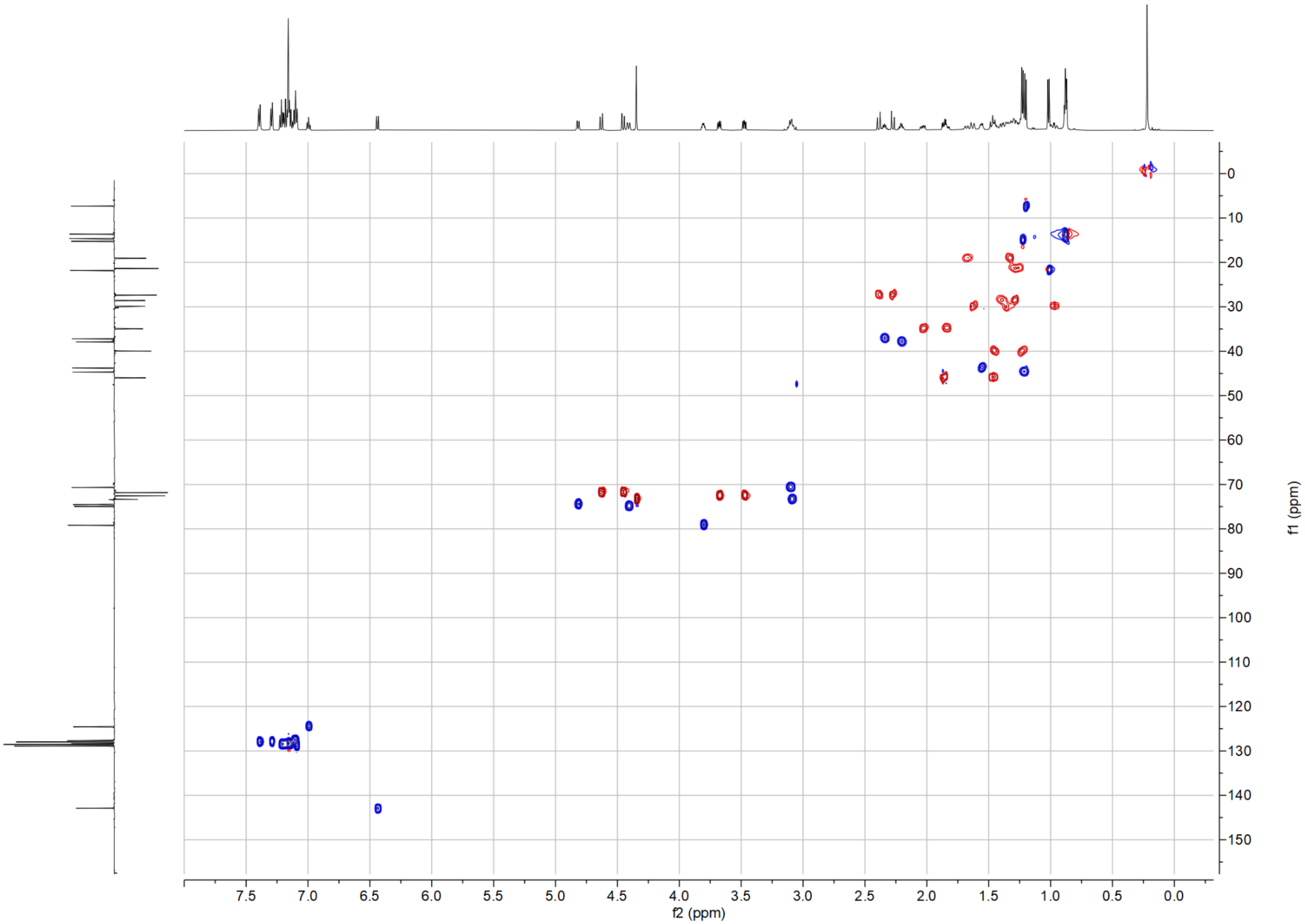


Figure S58. gHSQC NMR of compound **26’**, 600 MHz, benzene-*d6*

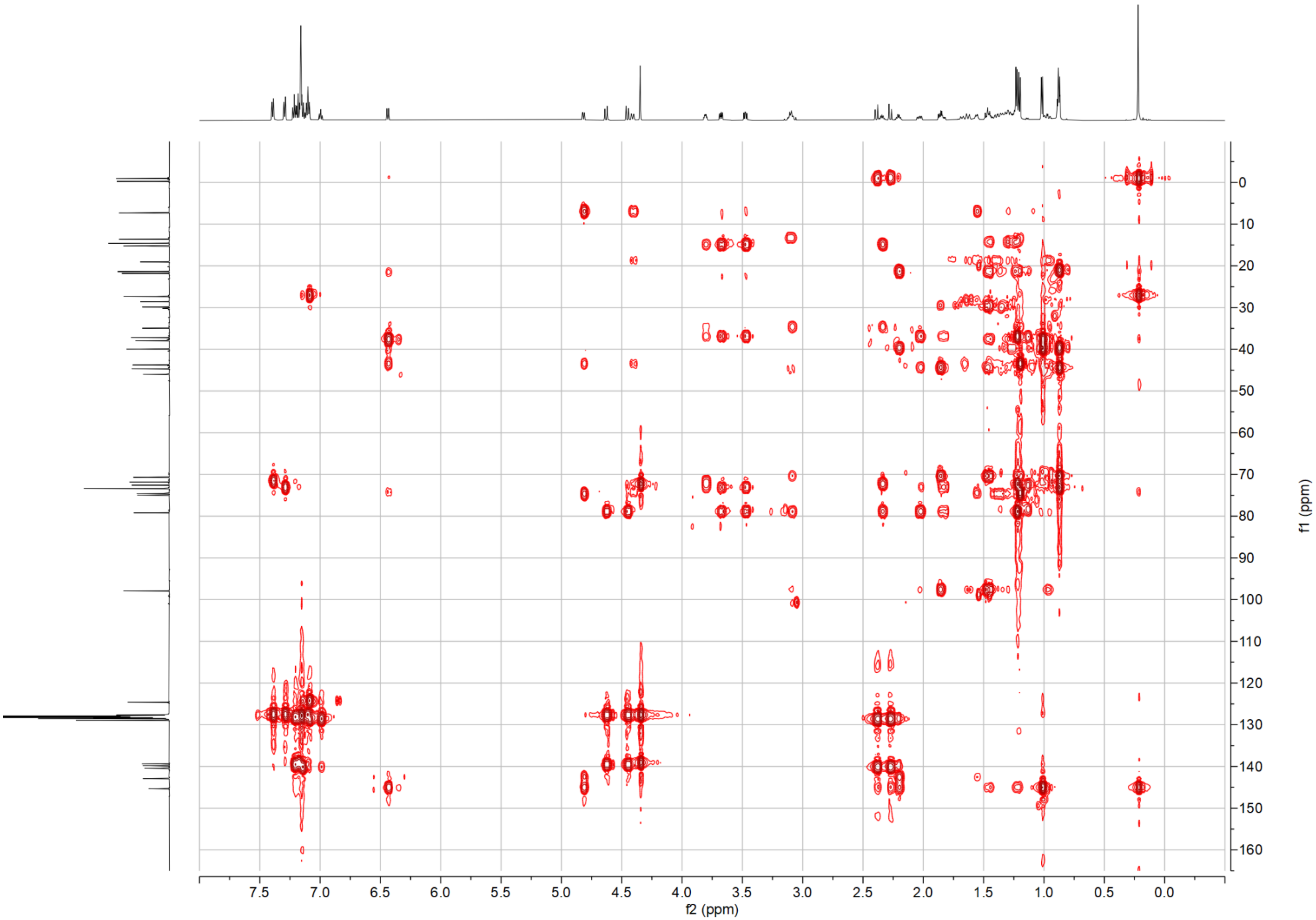


Figure S59. gHMBC NMR of compound **26'**, 600 MHz, benzene-*d6*

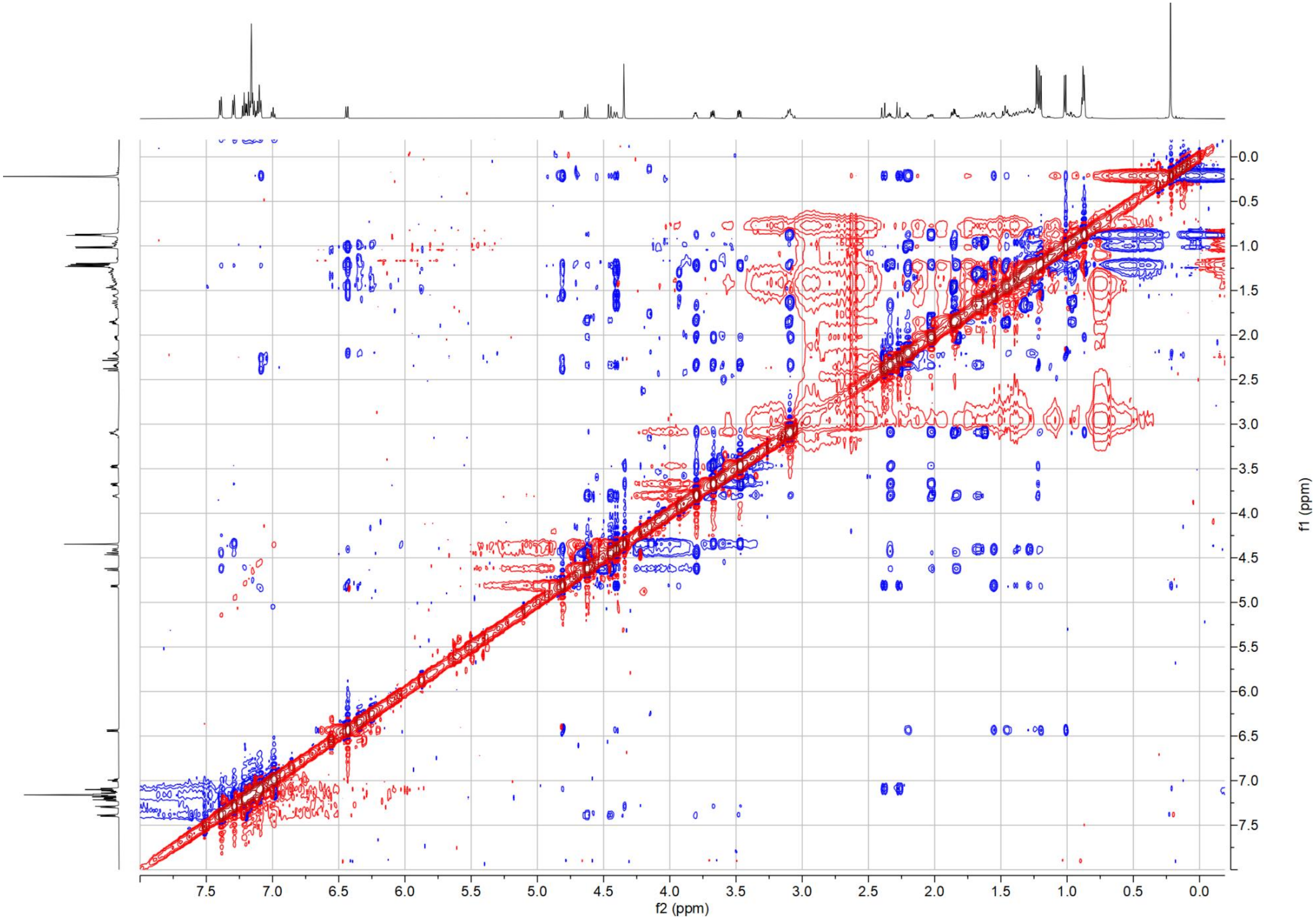


Figure S60. NOESY NMR of compound **26'**, 600 MHz, benzene-*d6*

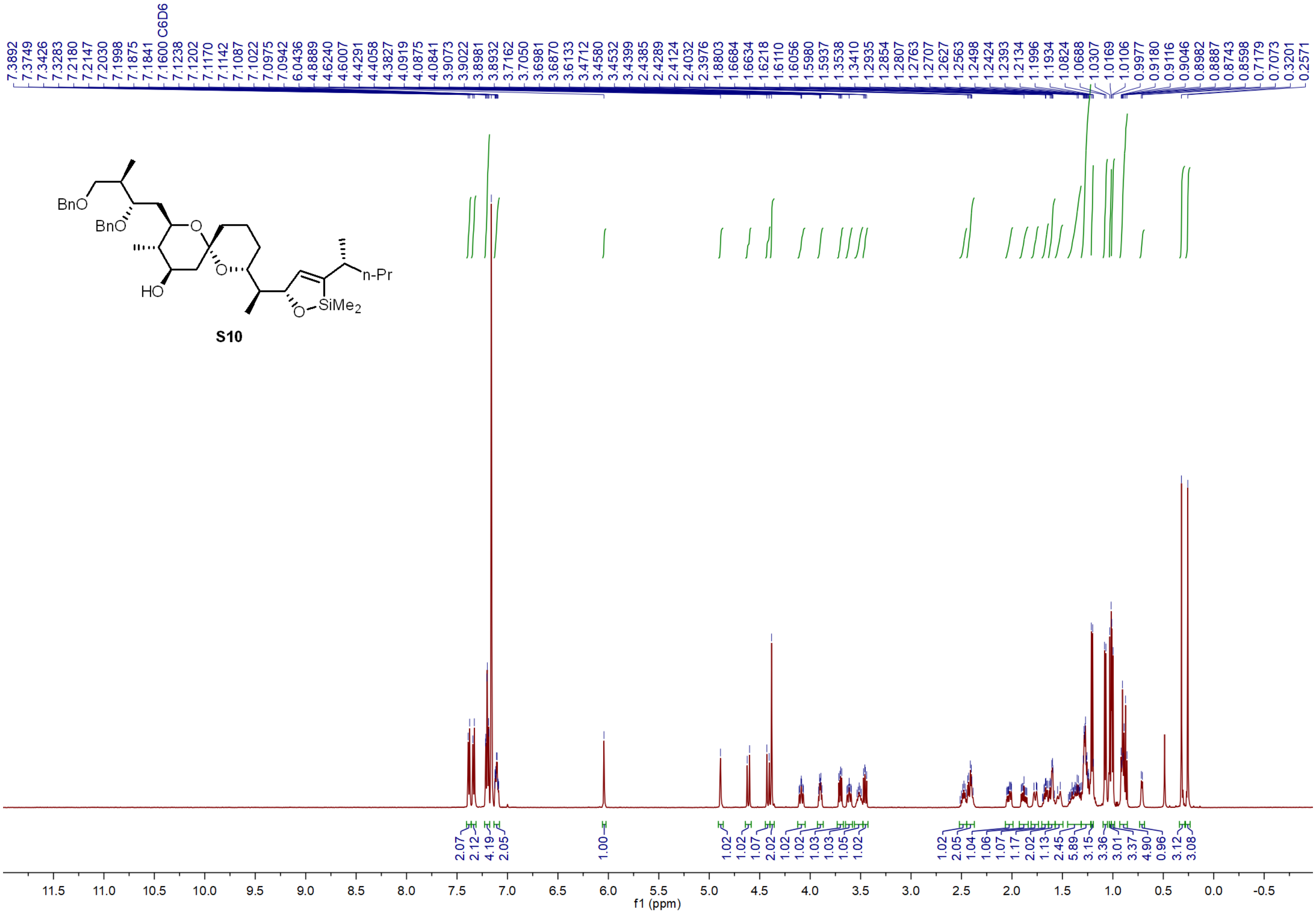


Figure S61. The 500 MHz ^{1}H-NMR of Compound **S10** in benzene-*d6*

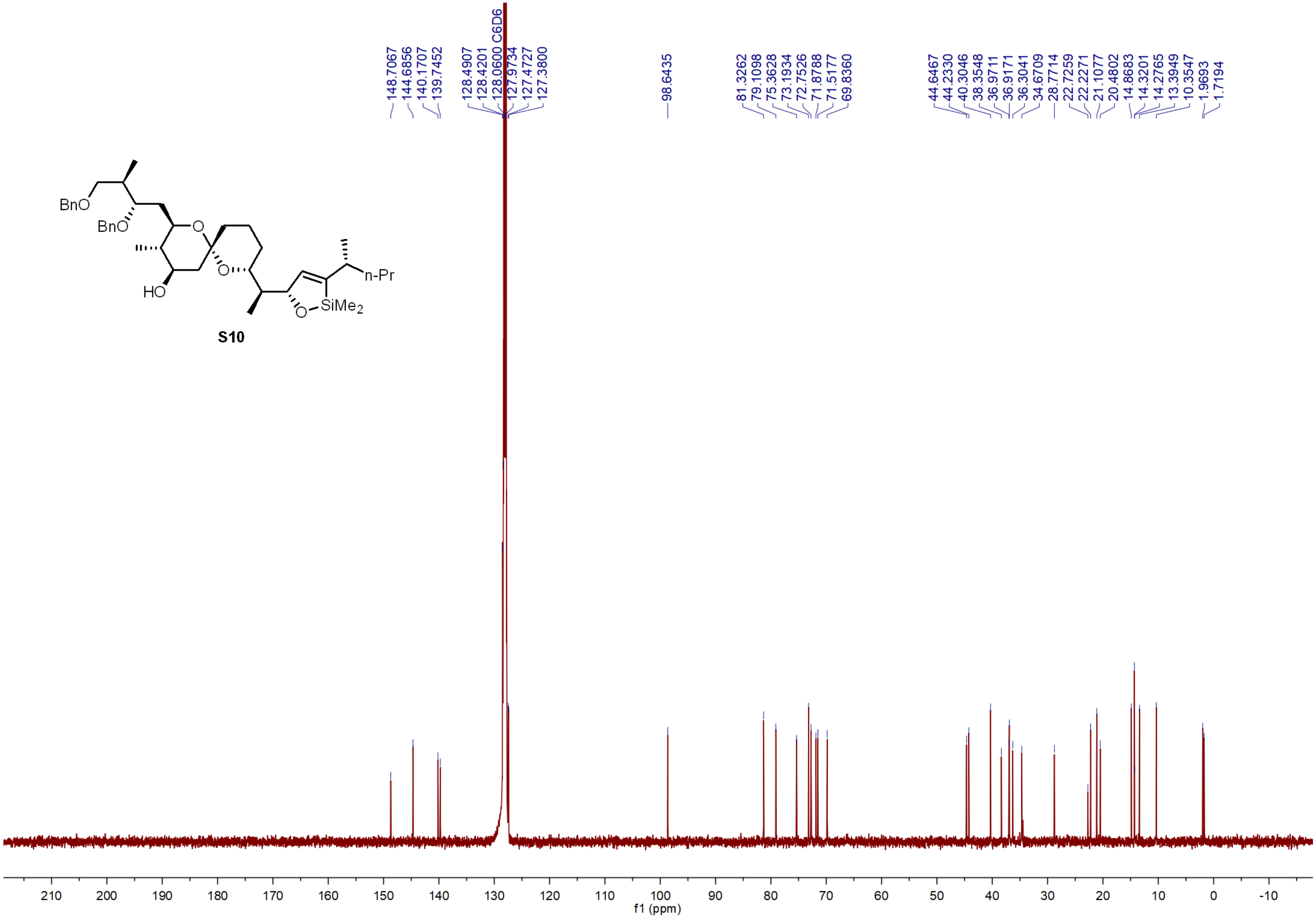


Figure S62. The 125 MHz ^{13}C-NMR of Compound **S10** in benzene-*d6*

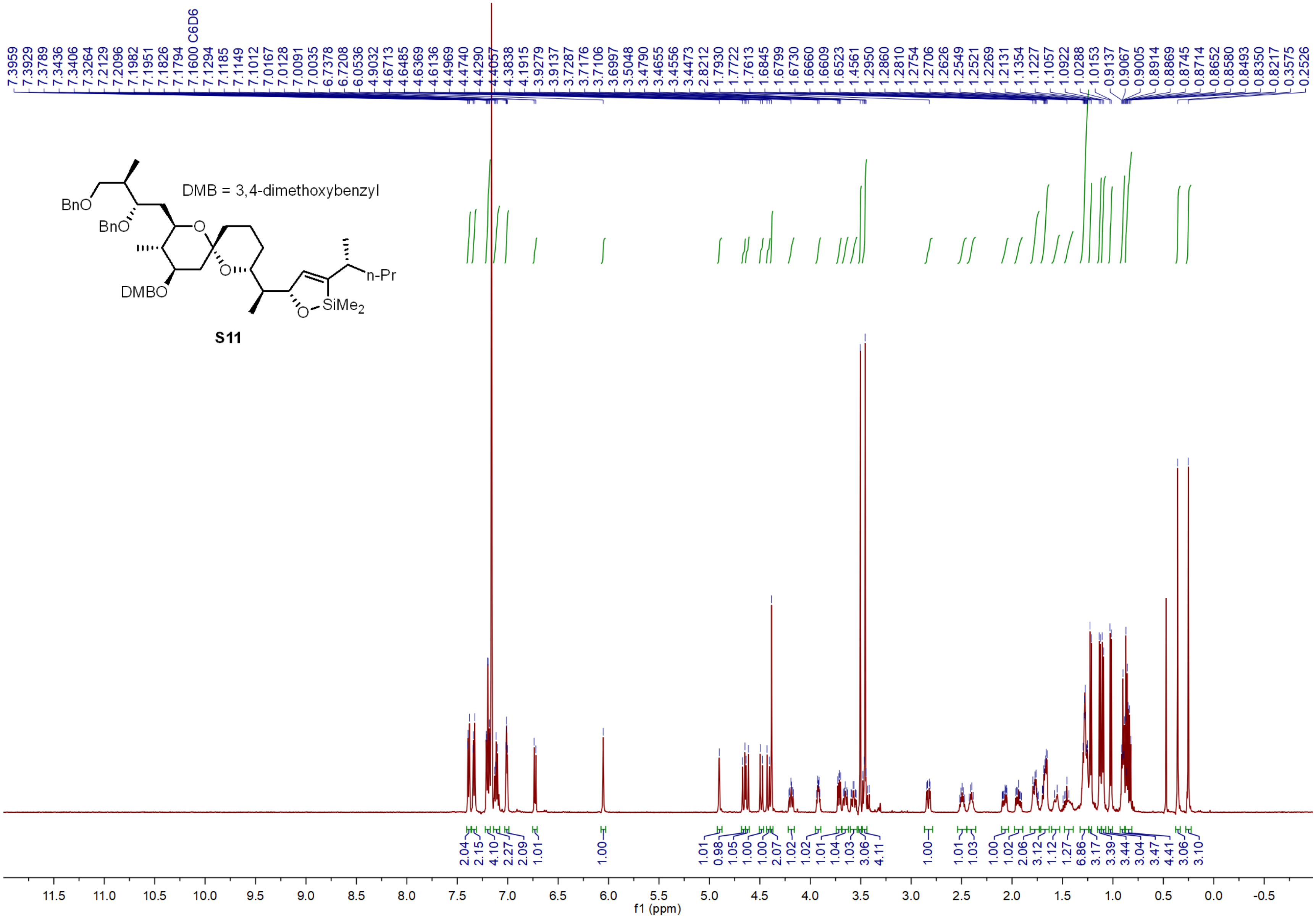


Figure S63. The 500 MHz ^{1}H-NMR of Compound **S11** in benzene-*d6*

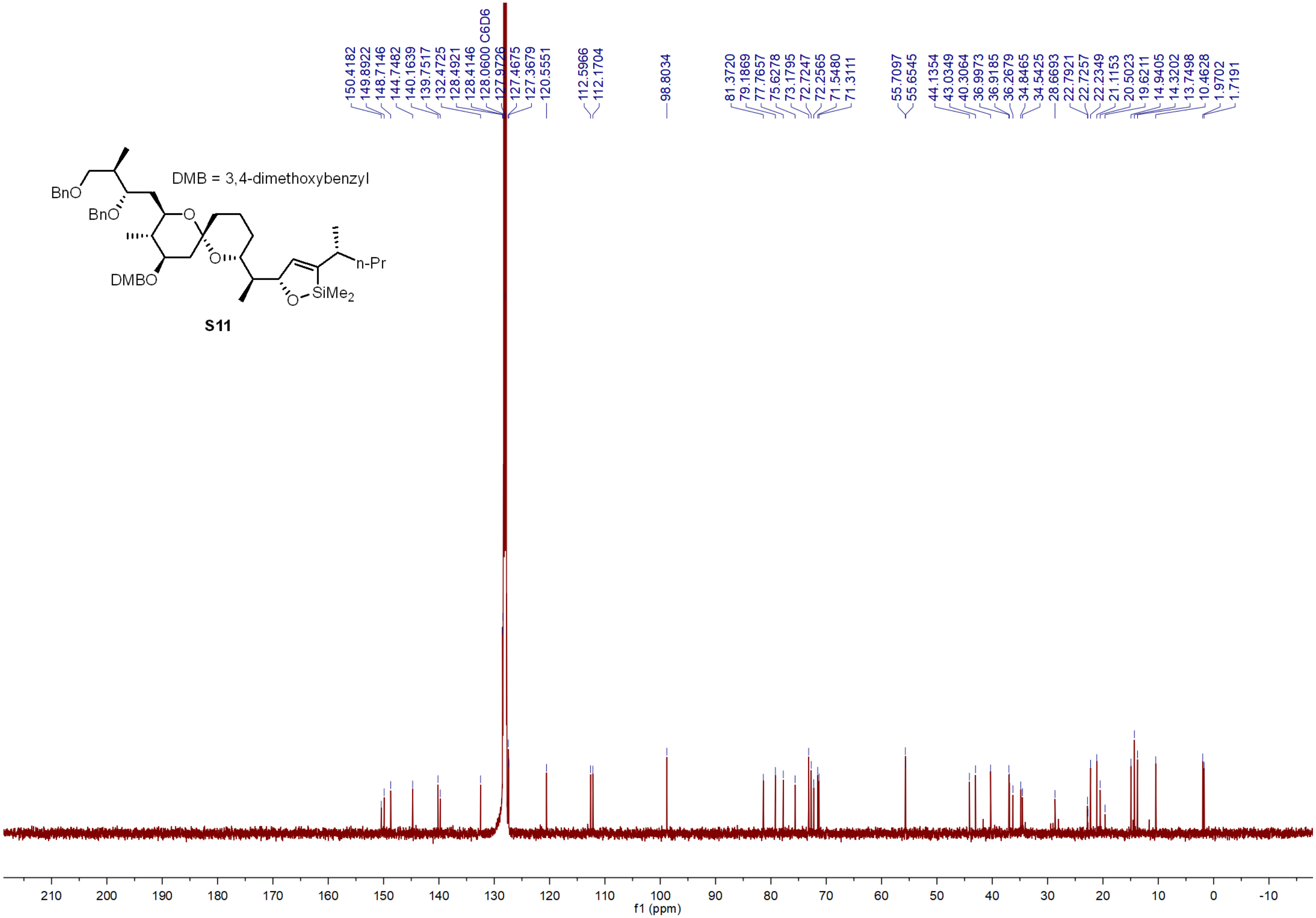


Figure S64. The 125 MHz ^{13}C-NMR of Compound **S11** in benzene-*d6*

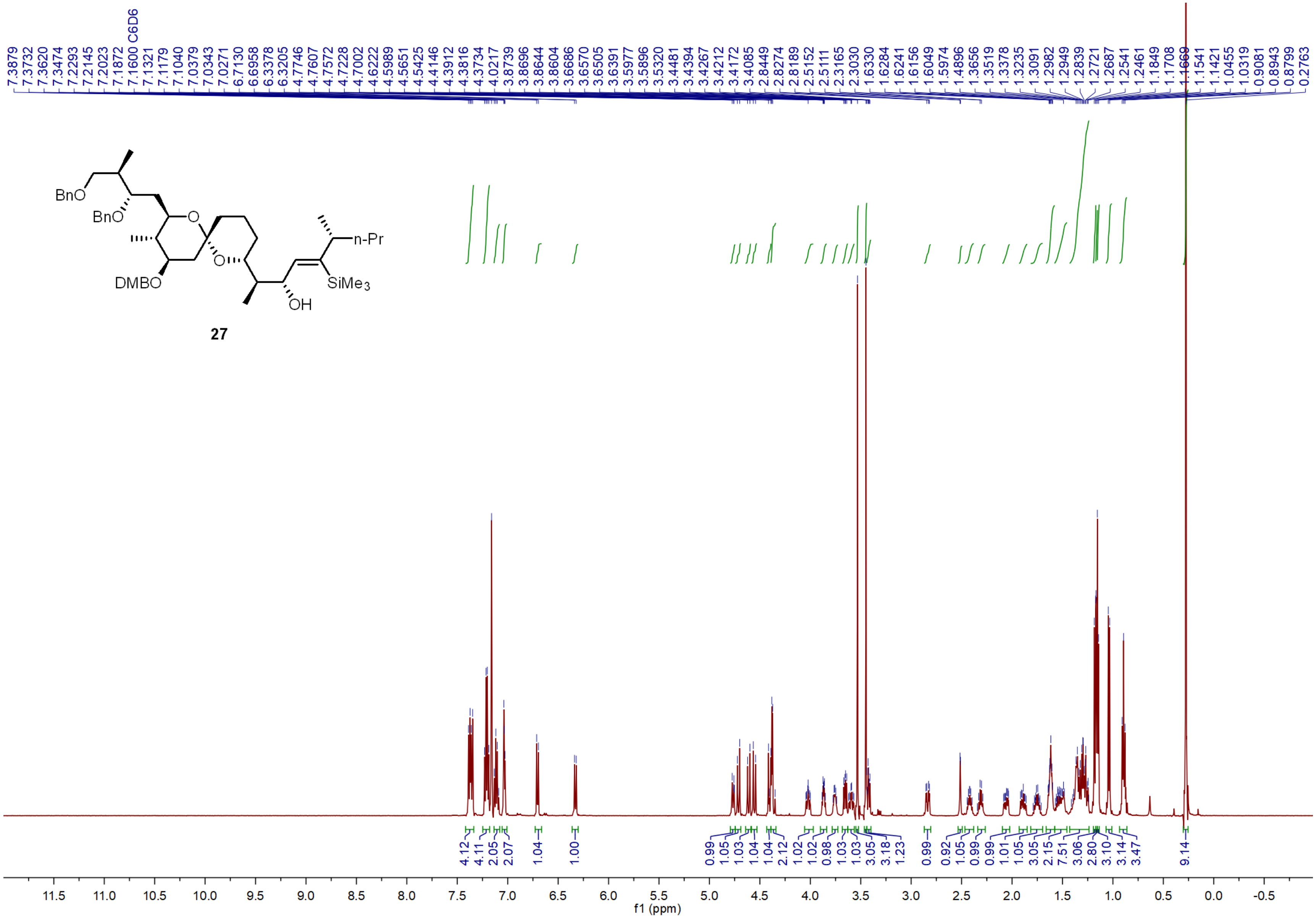


Figure S65. The 500 MHz ^{1}H-NMR of Compound **27** in benzene-*d6*

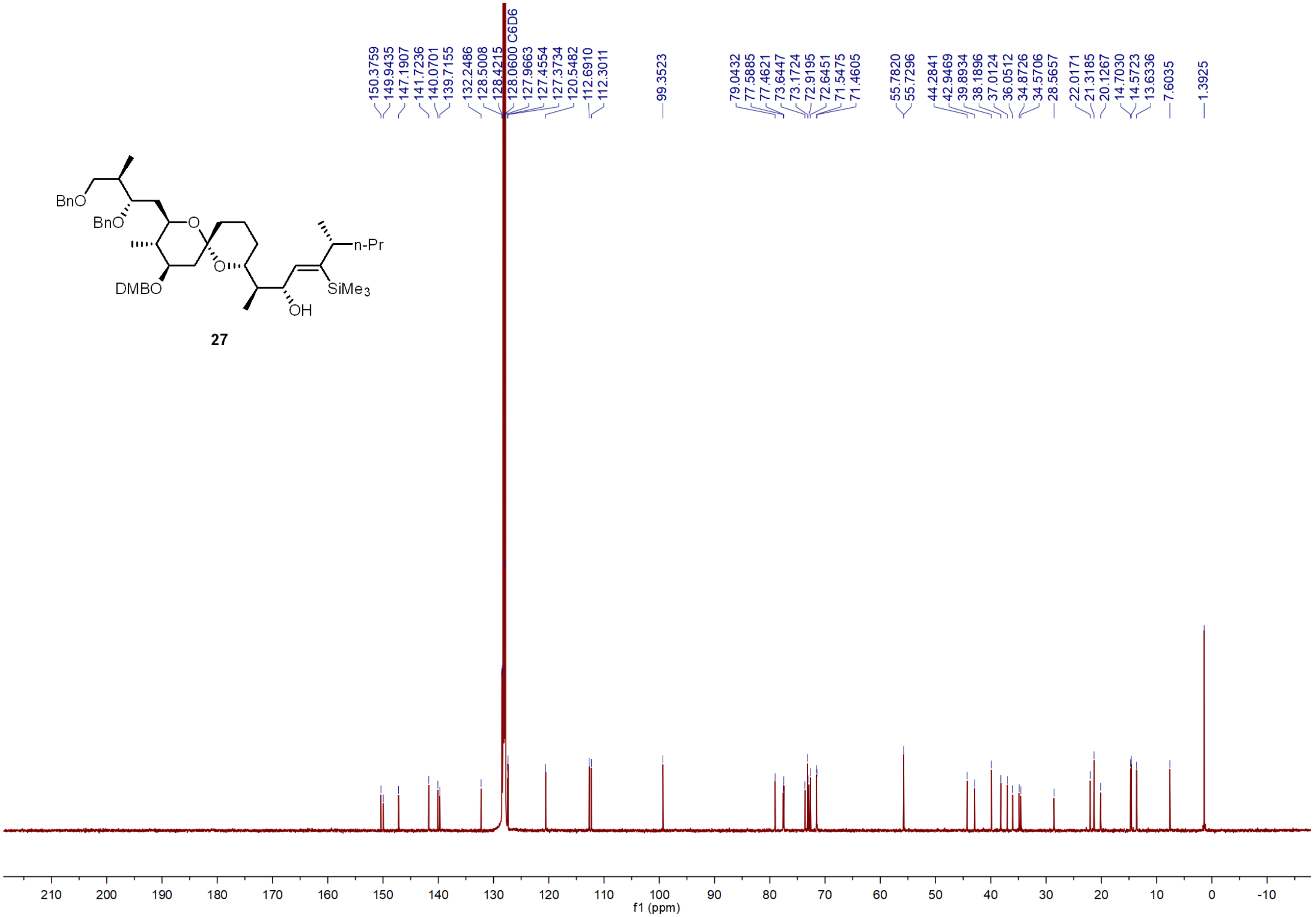


Figure S66. The 125 MHz ^{13}C-NMR of Compound **27** in benzene-*d6*

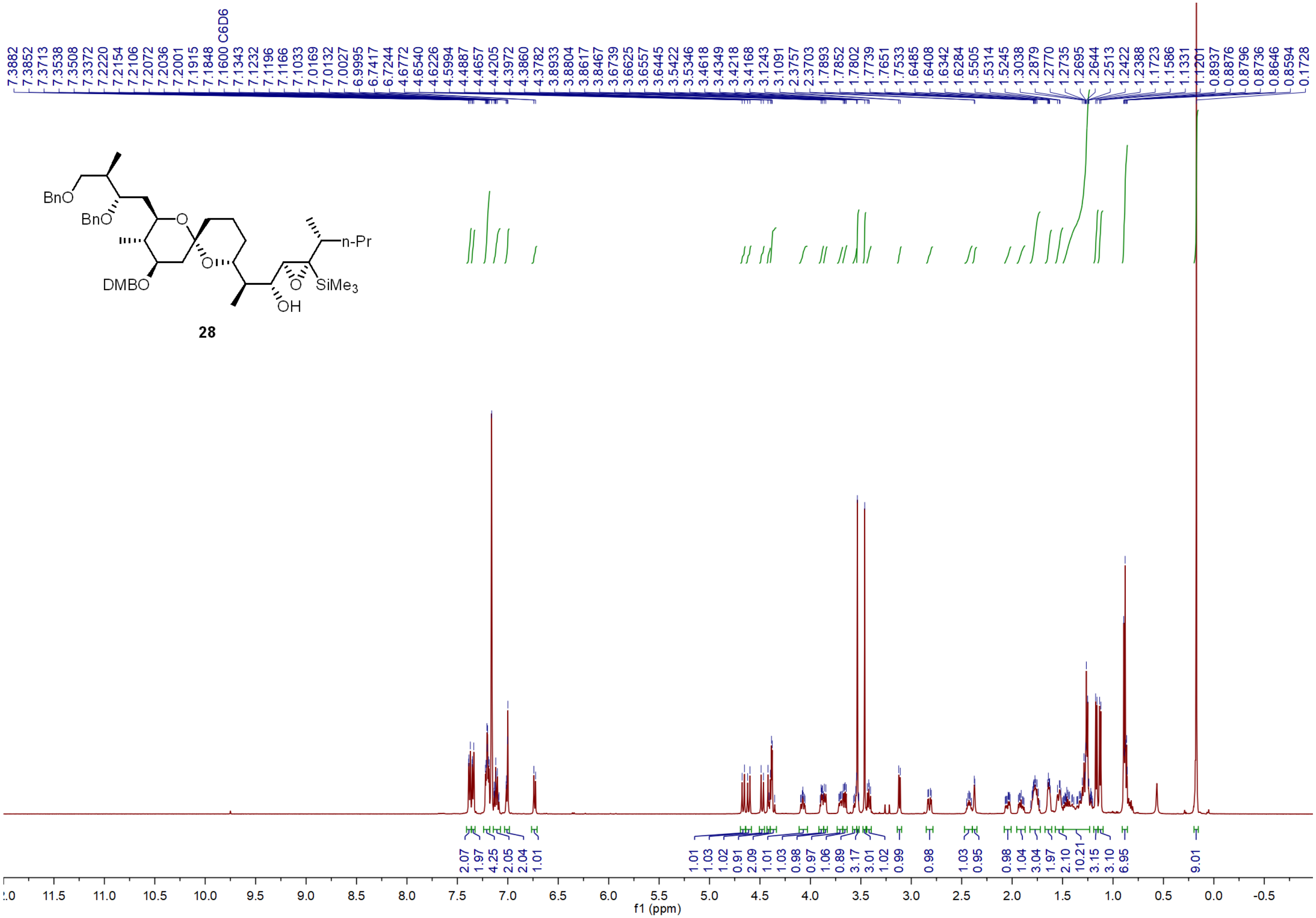


Figure S67. The 500 MHz ^{1}H-NMR of Compound **28** in benzene-*d6*

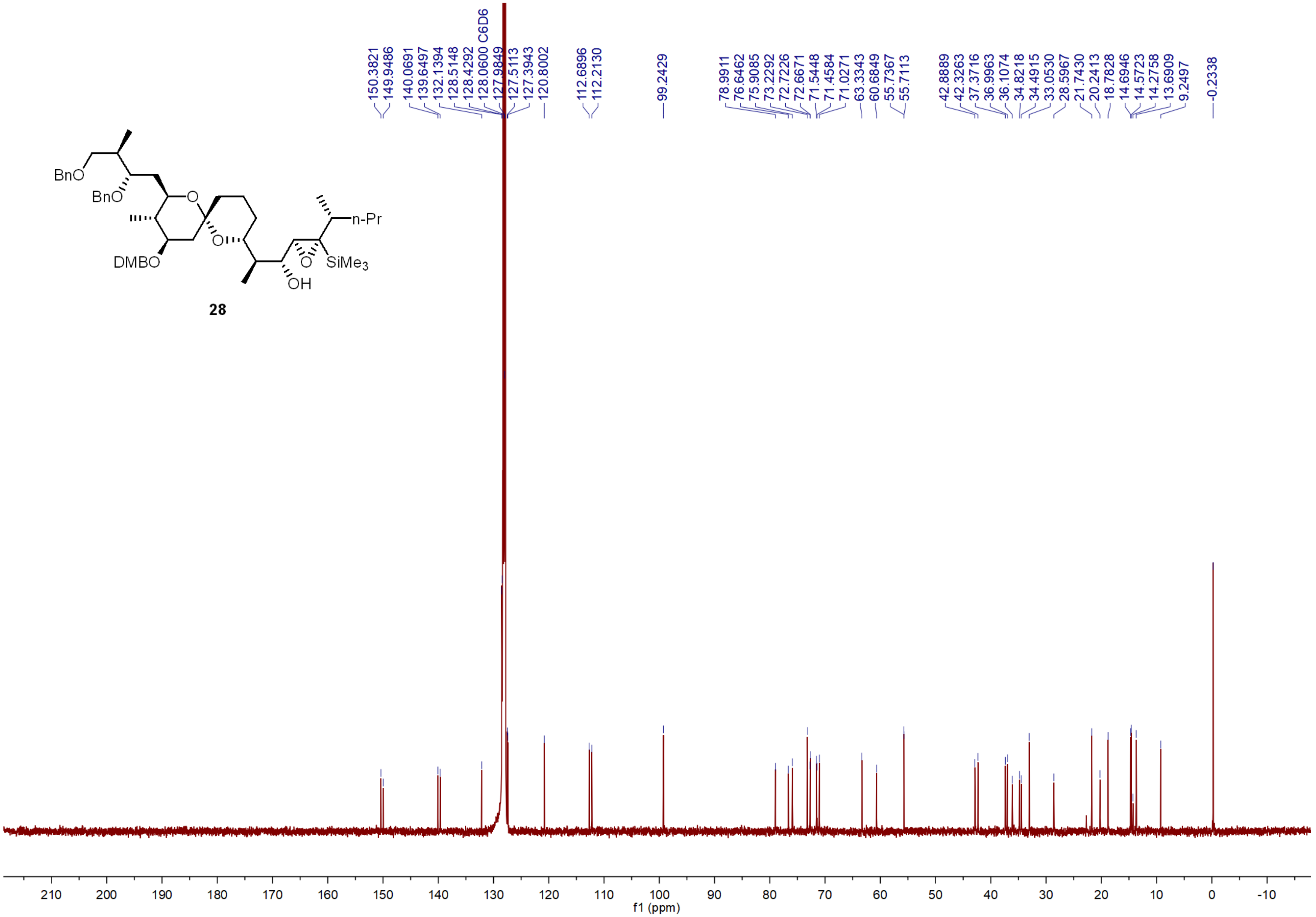


Figure S68. The 125 MHz ^{13}C-NMR of Compound **28** in benzene-*d6*

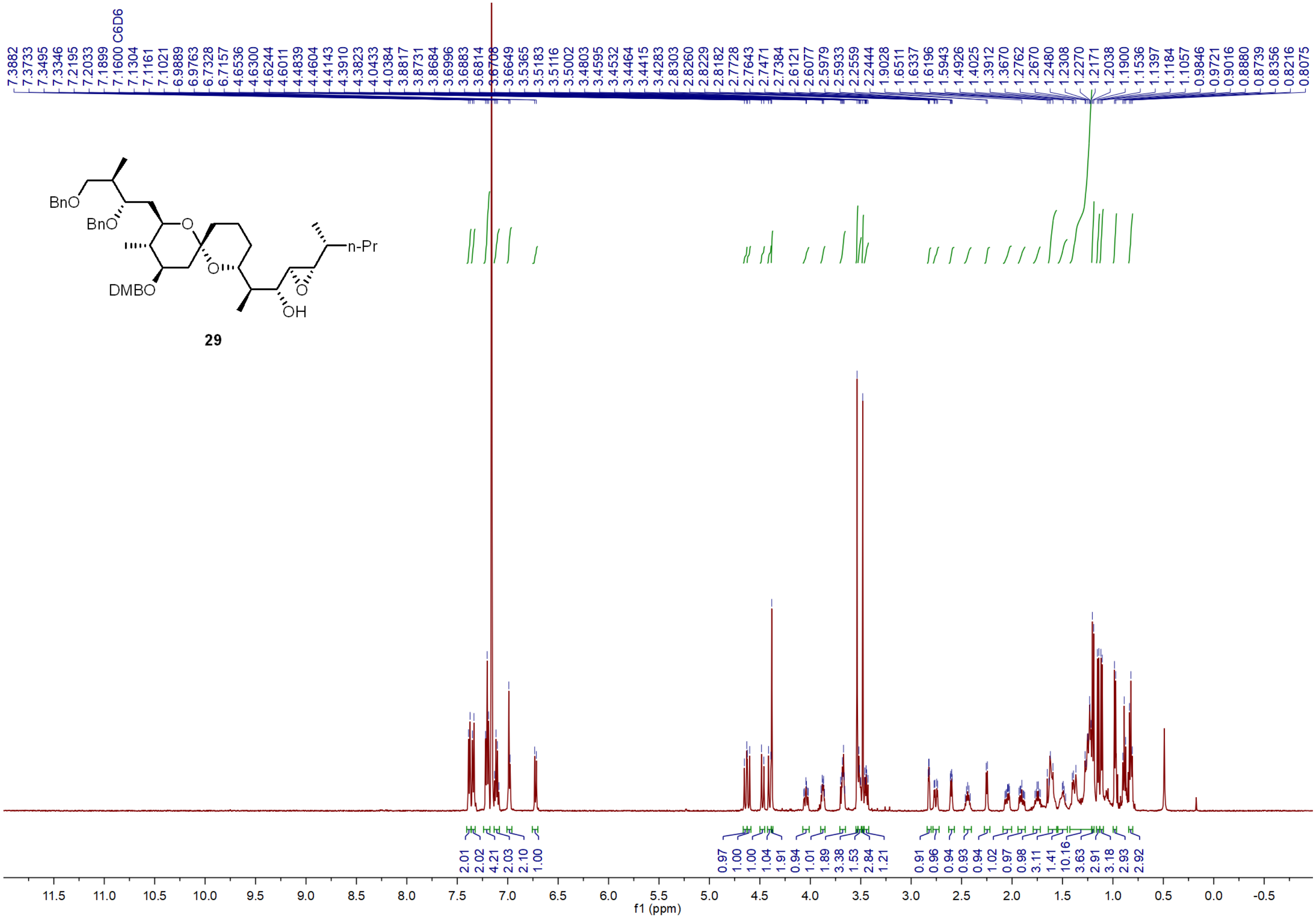


Figure S69. The 500 MHz ^{1}H-NMR of Compound **29** in benzene-*d6*

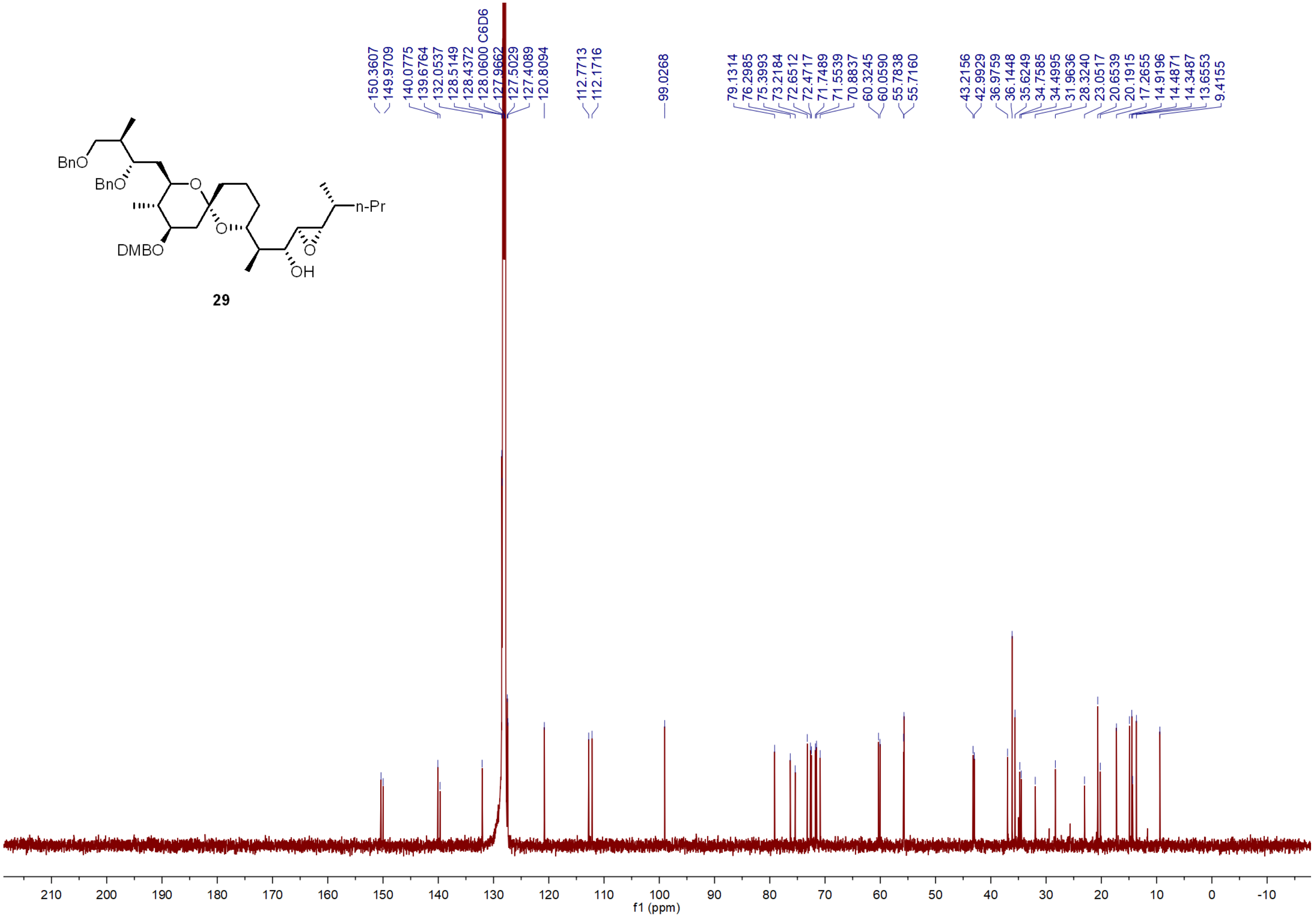


Figure S70. The 125 MHz ^{13}C-NMR of Compound **29** in benzene-*d6*

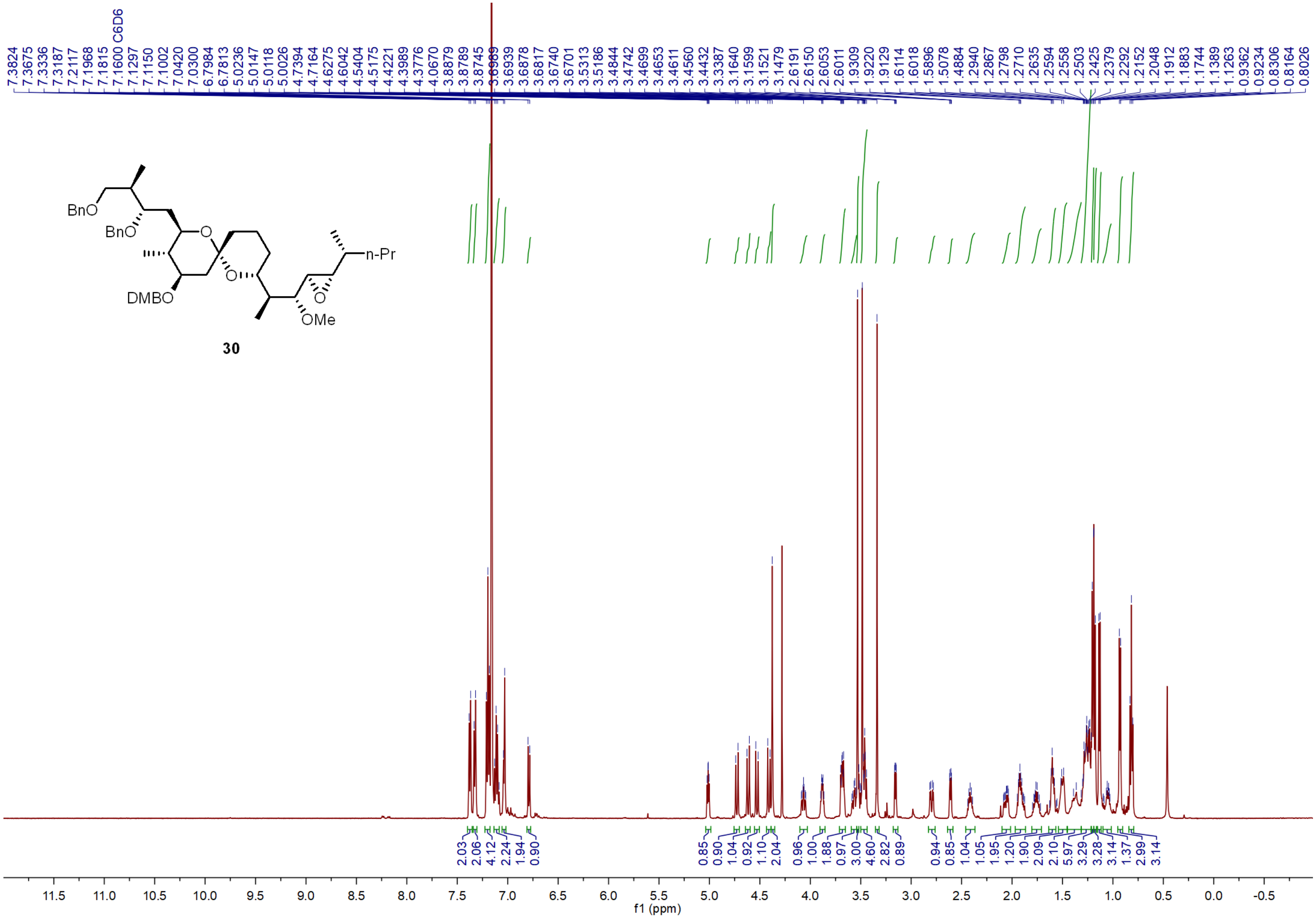
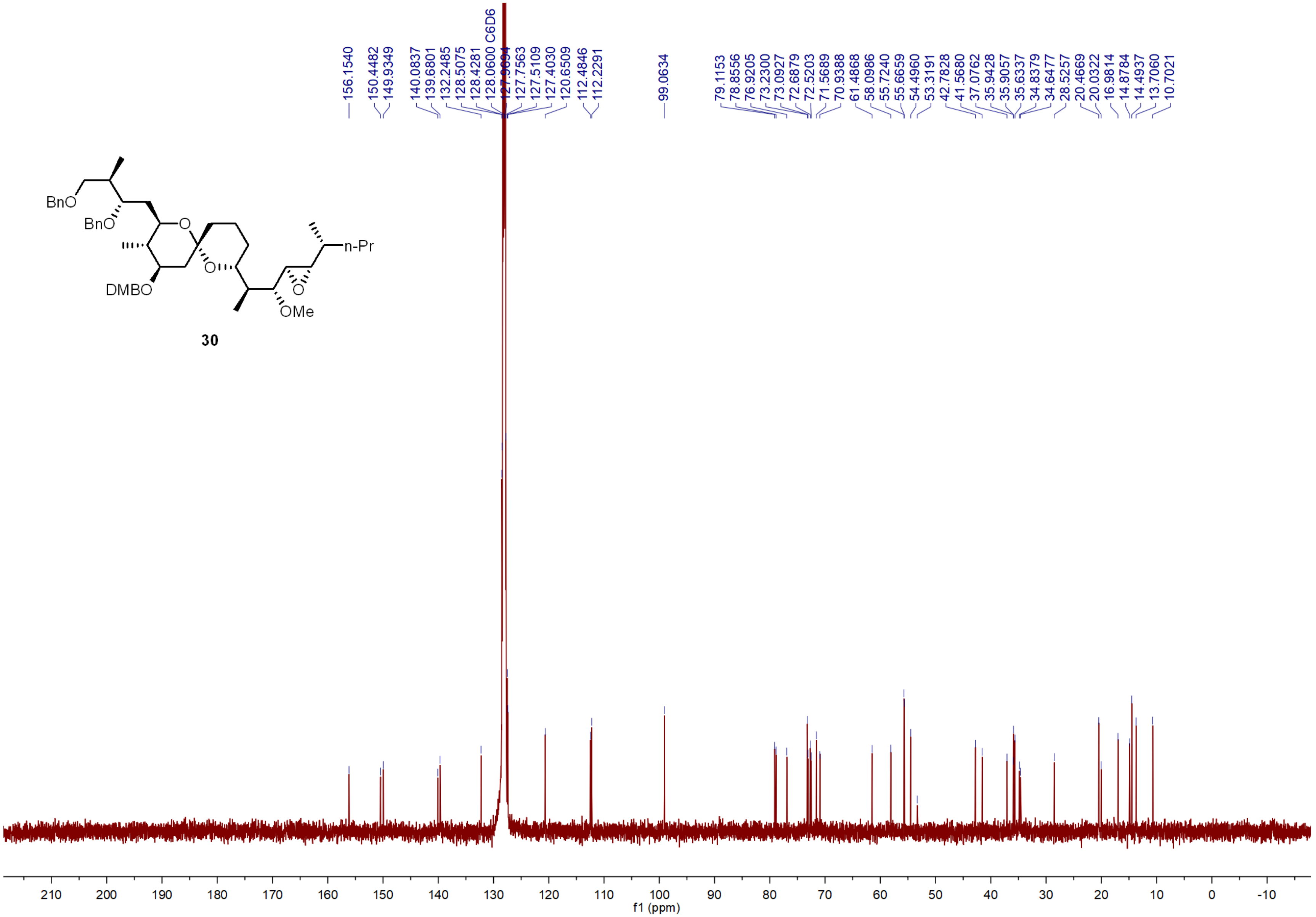
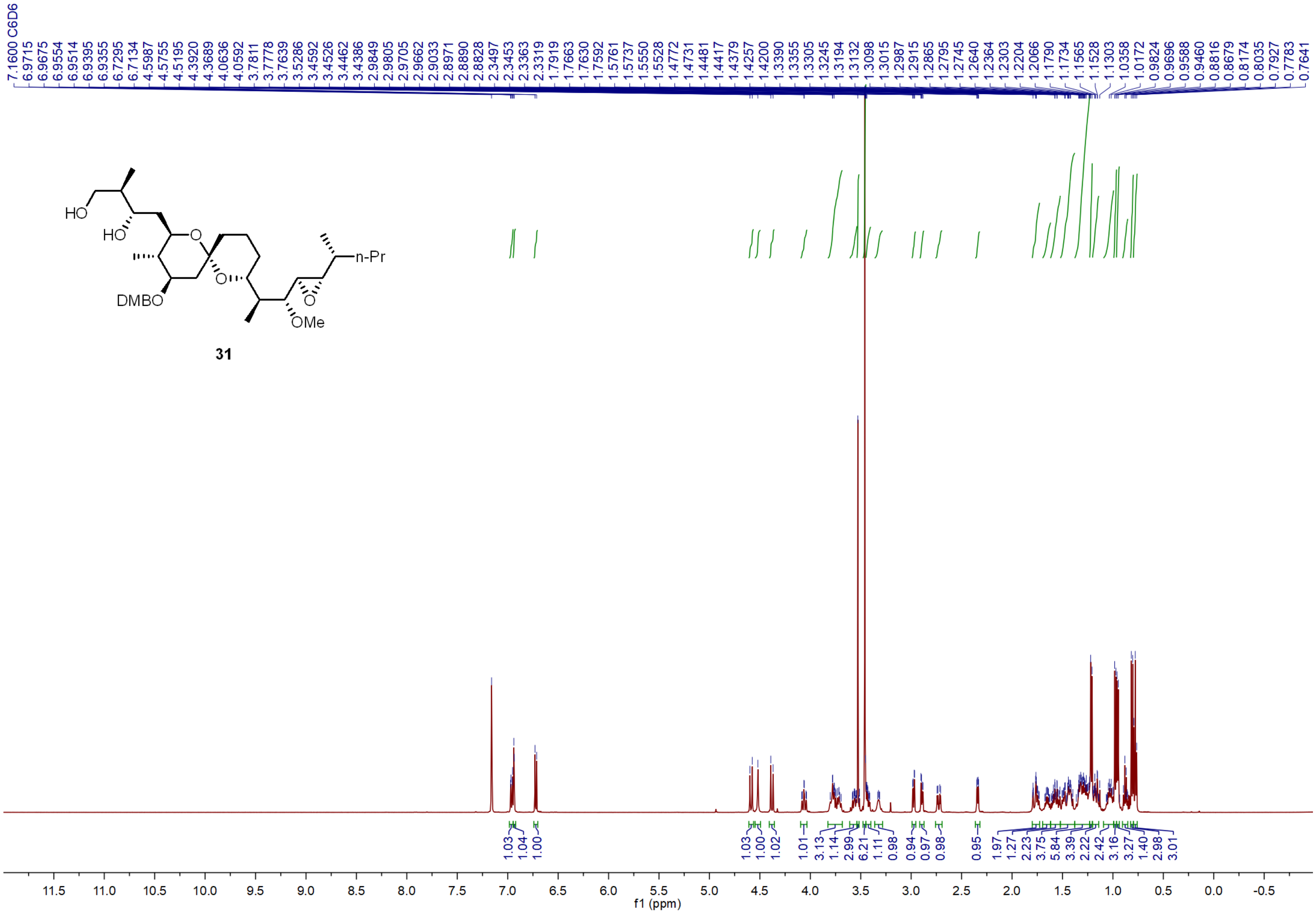


Figure S71. The 500 MHz ^{1}H-NMR of Compound **30** in benzene-*d6*



30

Figure S72. The 125 MHz ^{13}C-NMR of Compound **30** in benzene-*d6*



31

Figure S73. The 500 MHz ^{1}H-NMR of Compound **31** in benzene-*d6*

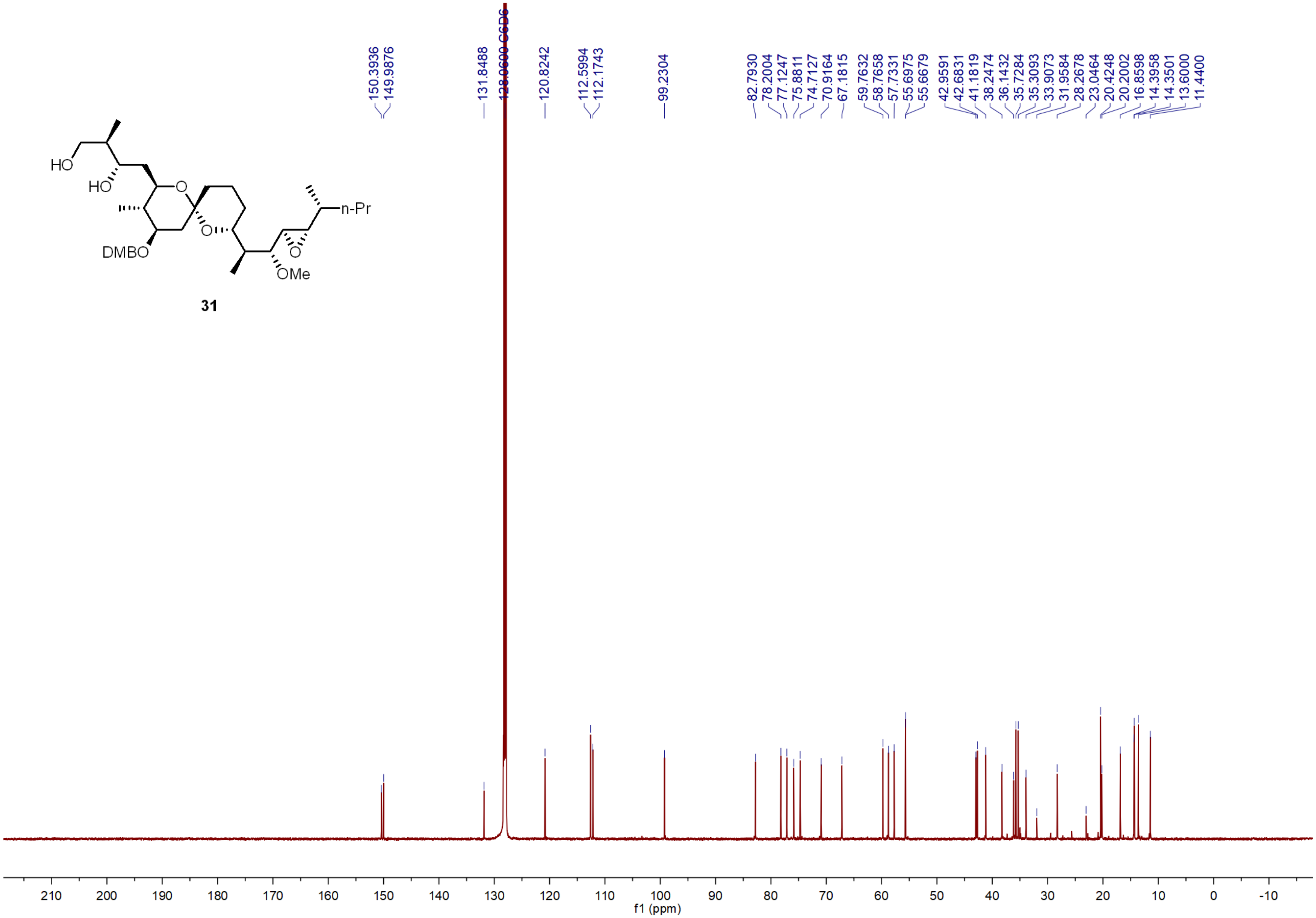
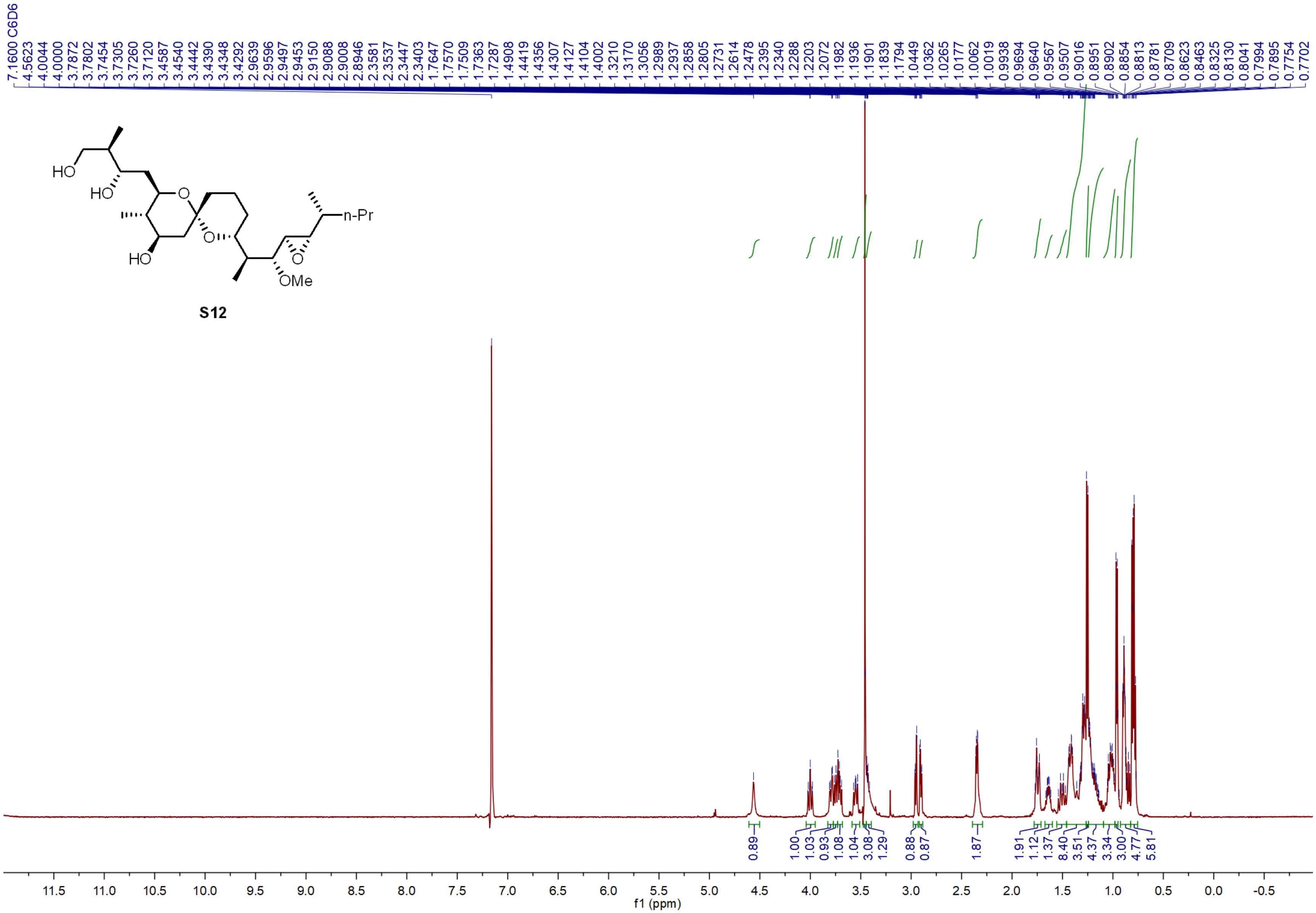
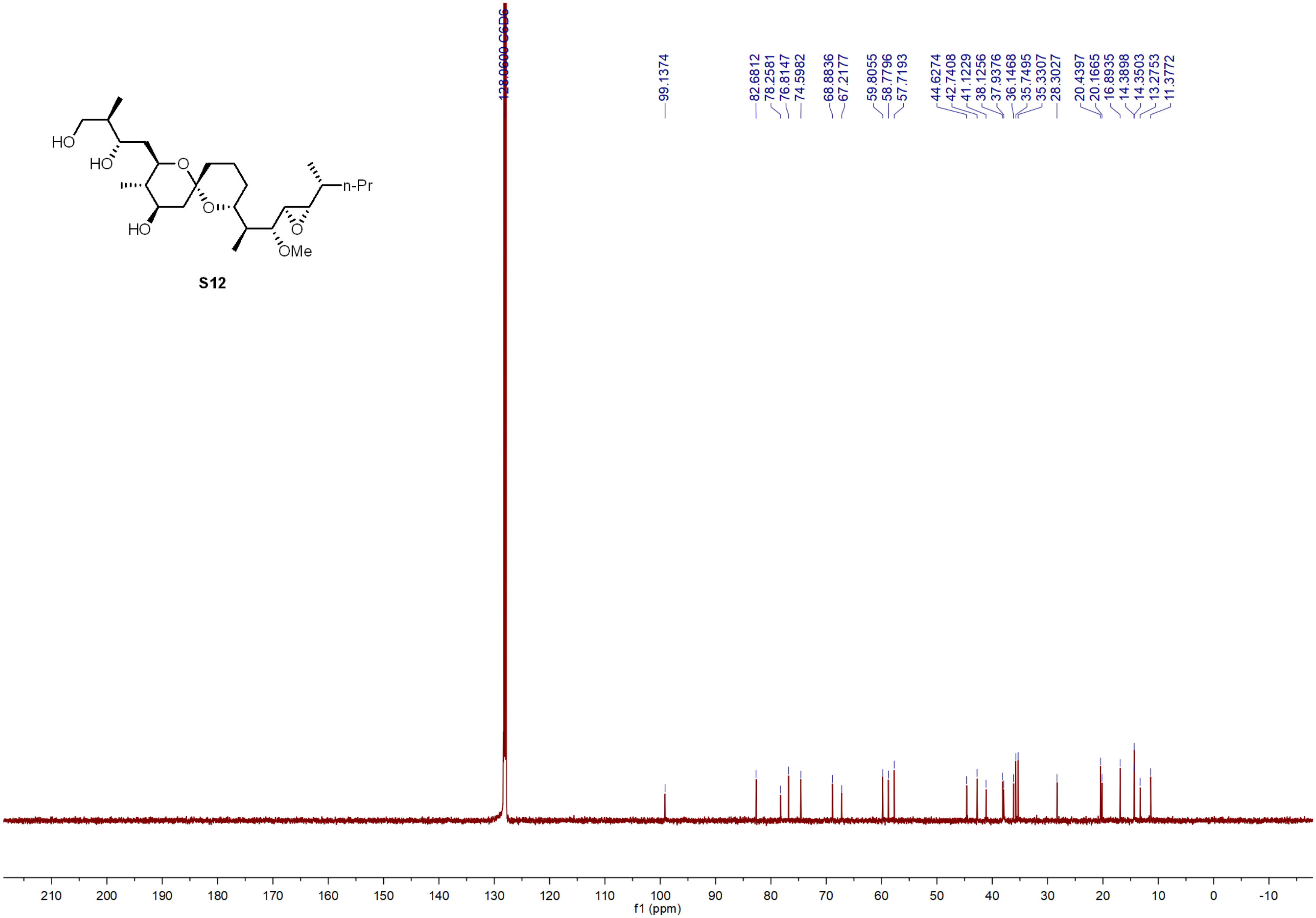


Figure S74. The 125 MHz ^{13}C-NMR of Compound **31** in benzene-*d6*



S12

Figure S75. The 500 MHz ^{1}H-NMR of Compound **S12** in benzene-*d6*



S12

Figure S76. The 125 MHz ^{13}C-NMR of Compound **S12** in benzene-*d6*

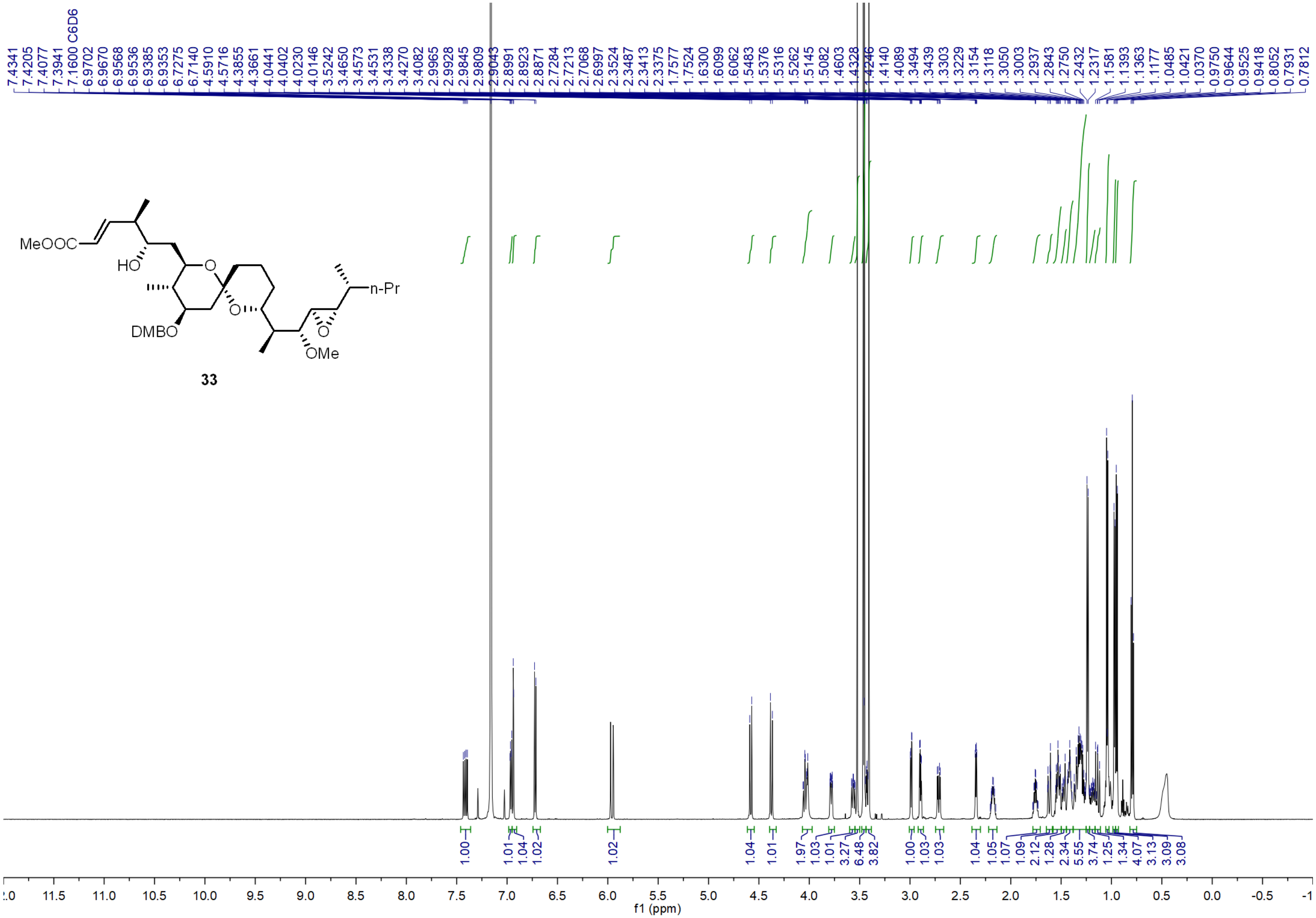


Figure S77. The 600 MHz ^{1}H-NMR of Compound **33** in benzene-*d6*

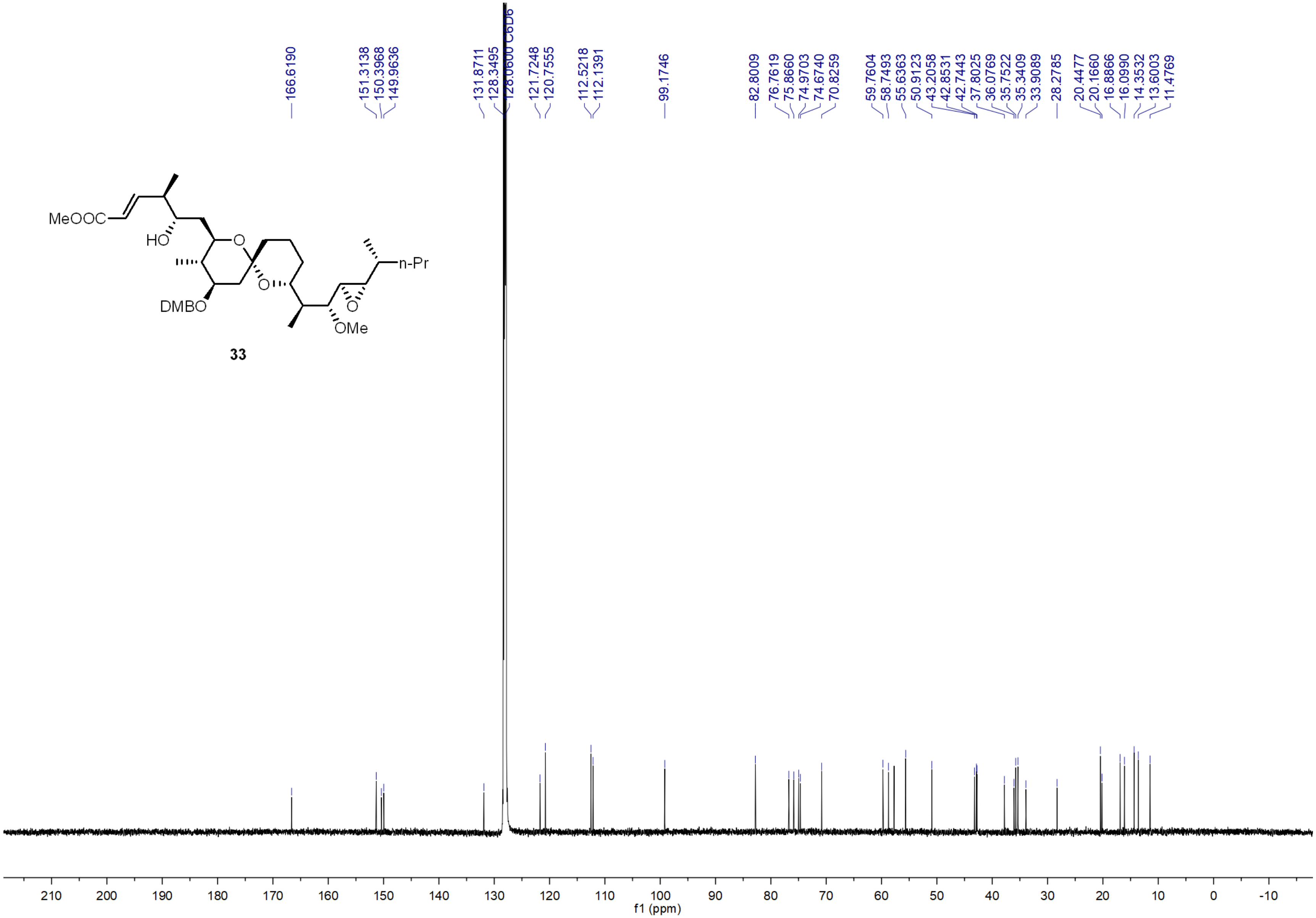


Figure S78. The 150 MHz ^{13}C-NMR of Compound **33** in benzene-*d6*

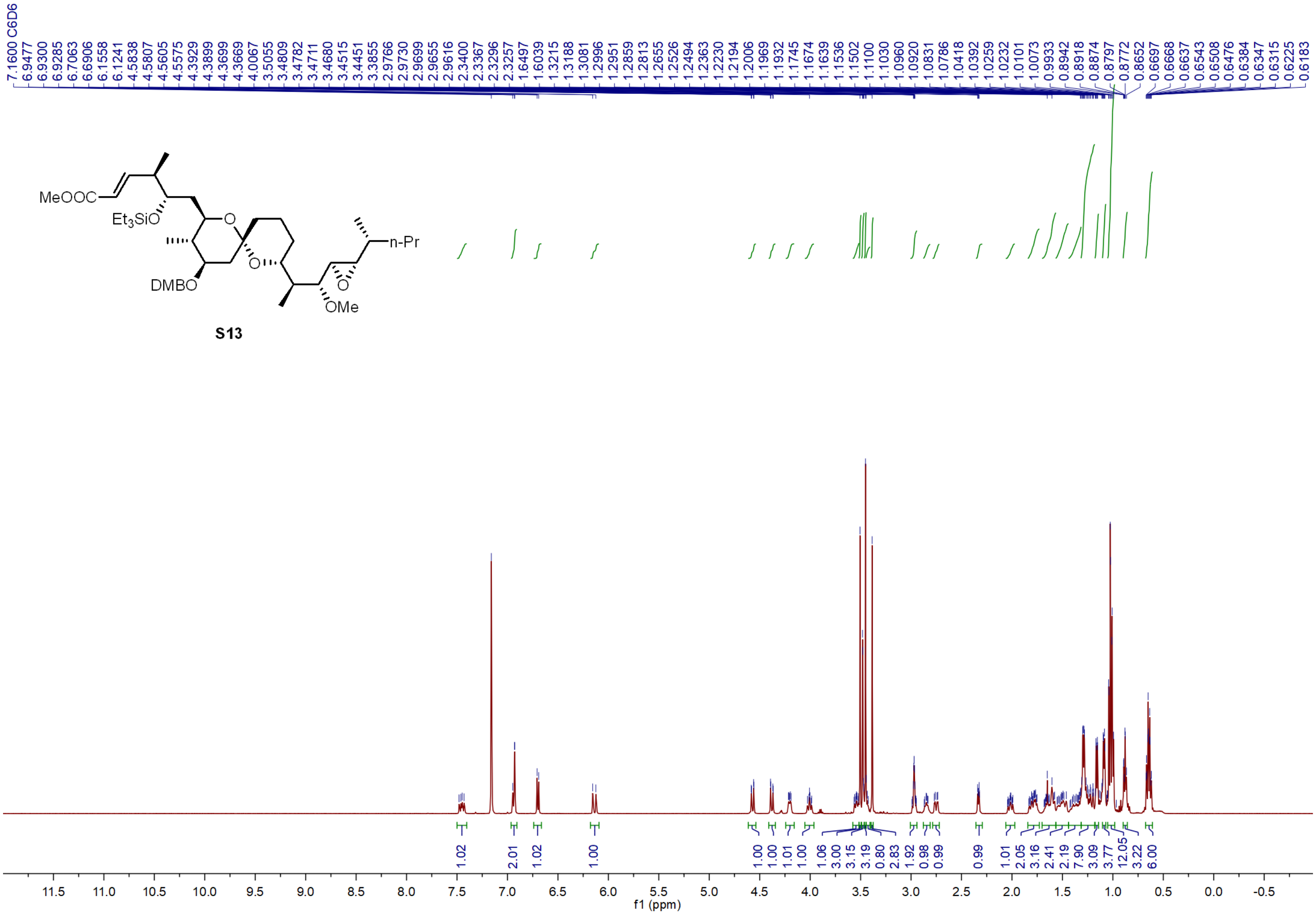


Figure S79. The 500 MHz ^{1}H-NMR of Compound **S13** in benzene-*d6*

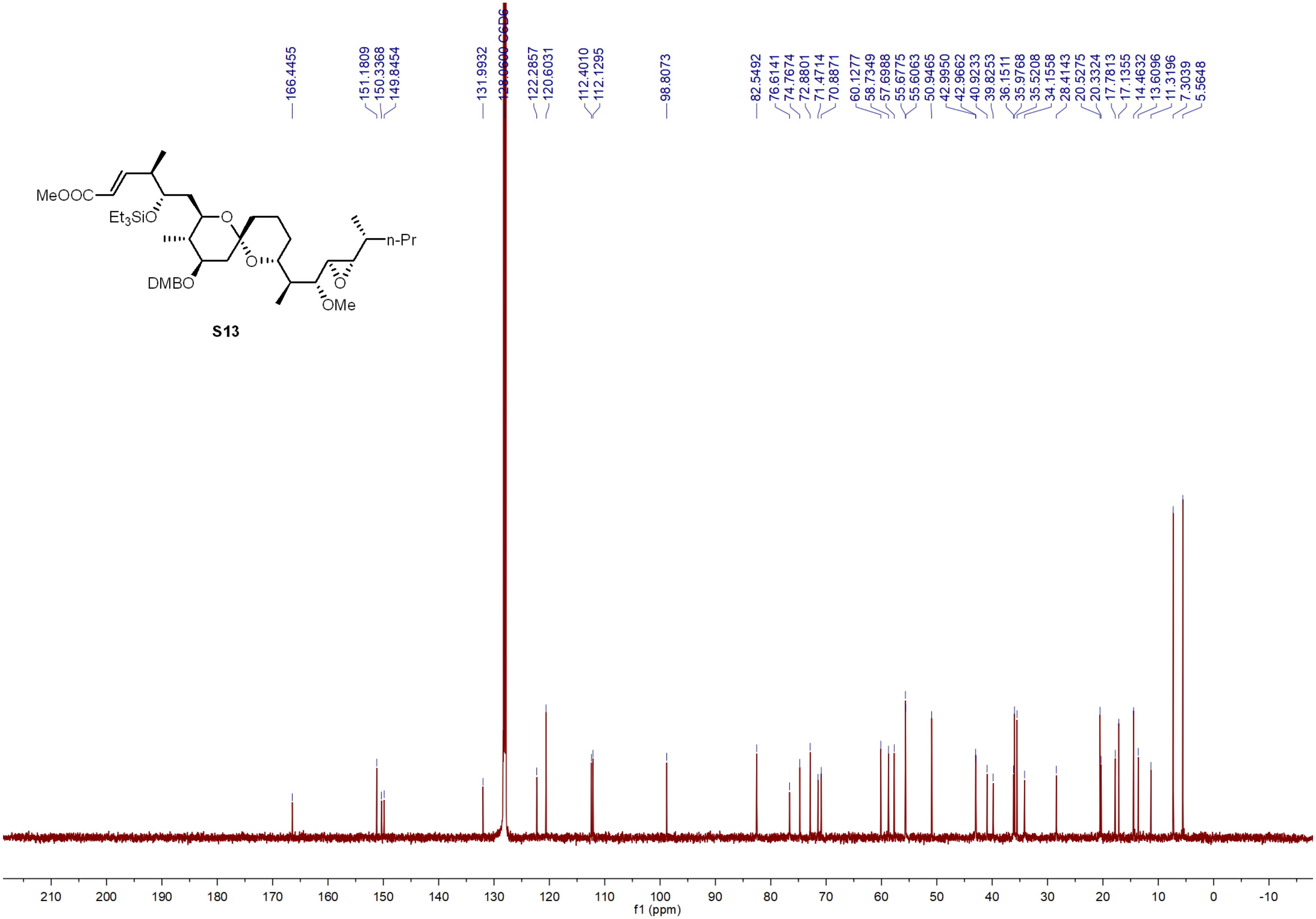


Figure S80. The 125 MHz ^{13}C-NMR of Compound **S13** in benzene-*d6*

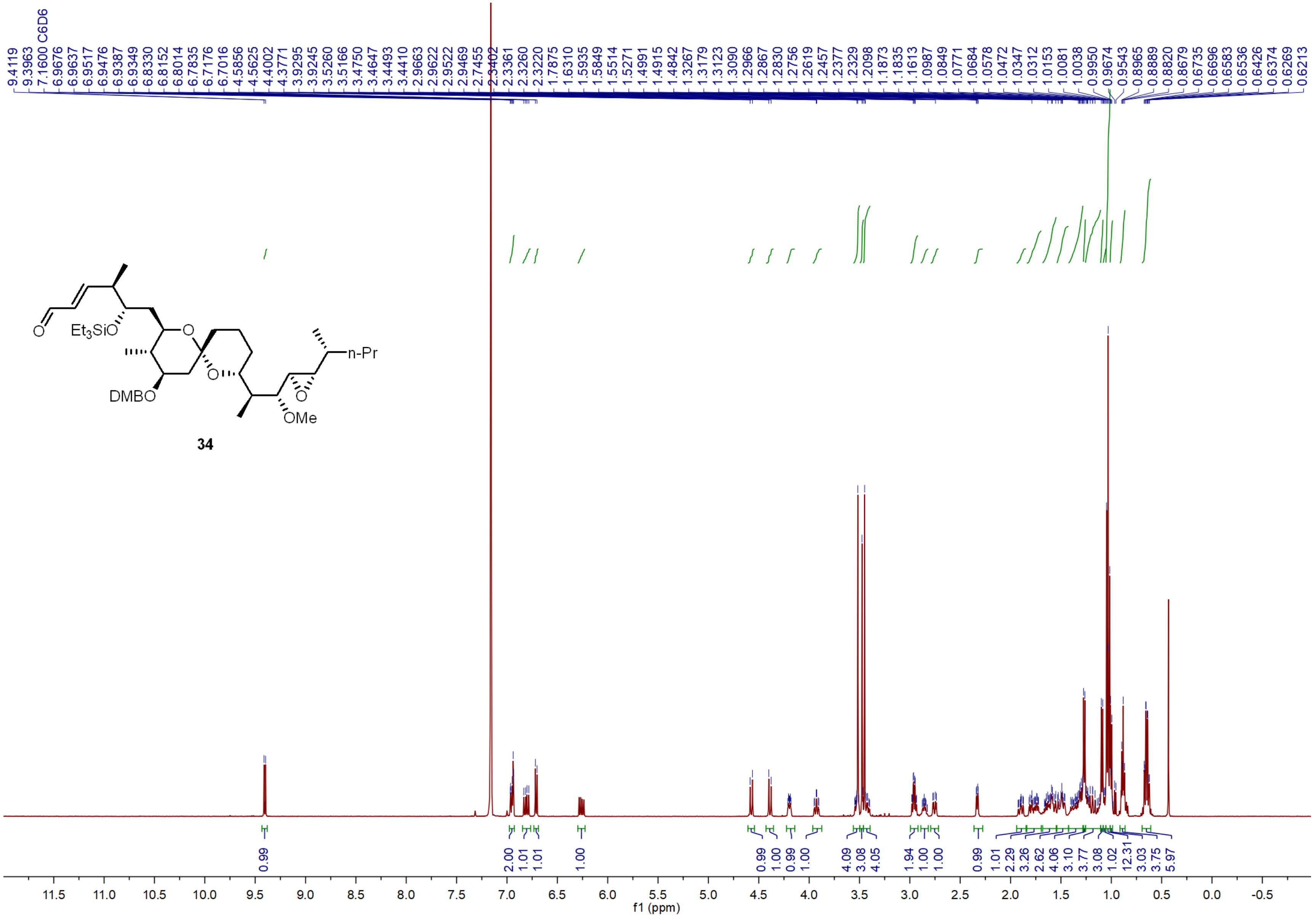


Figure S81. The 500 MHz ^{1}H-NMR of Compound **34** in benzene-*d6*

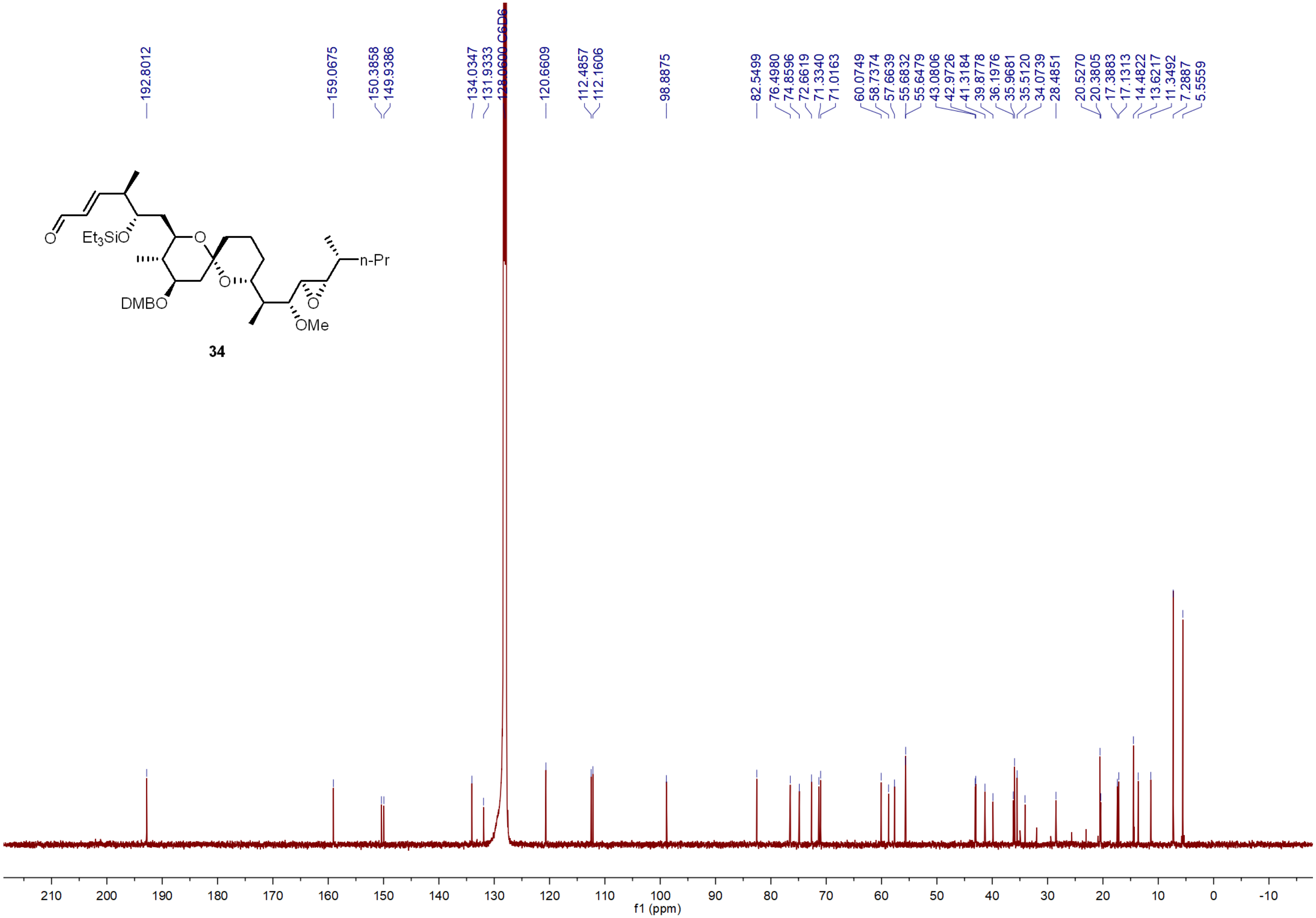


Figure S82. The 125 MHz ^{13}C-NMR of Compound **34** in benzene-*d6*

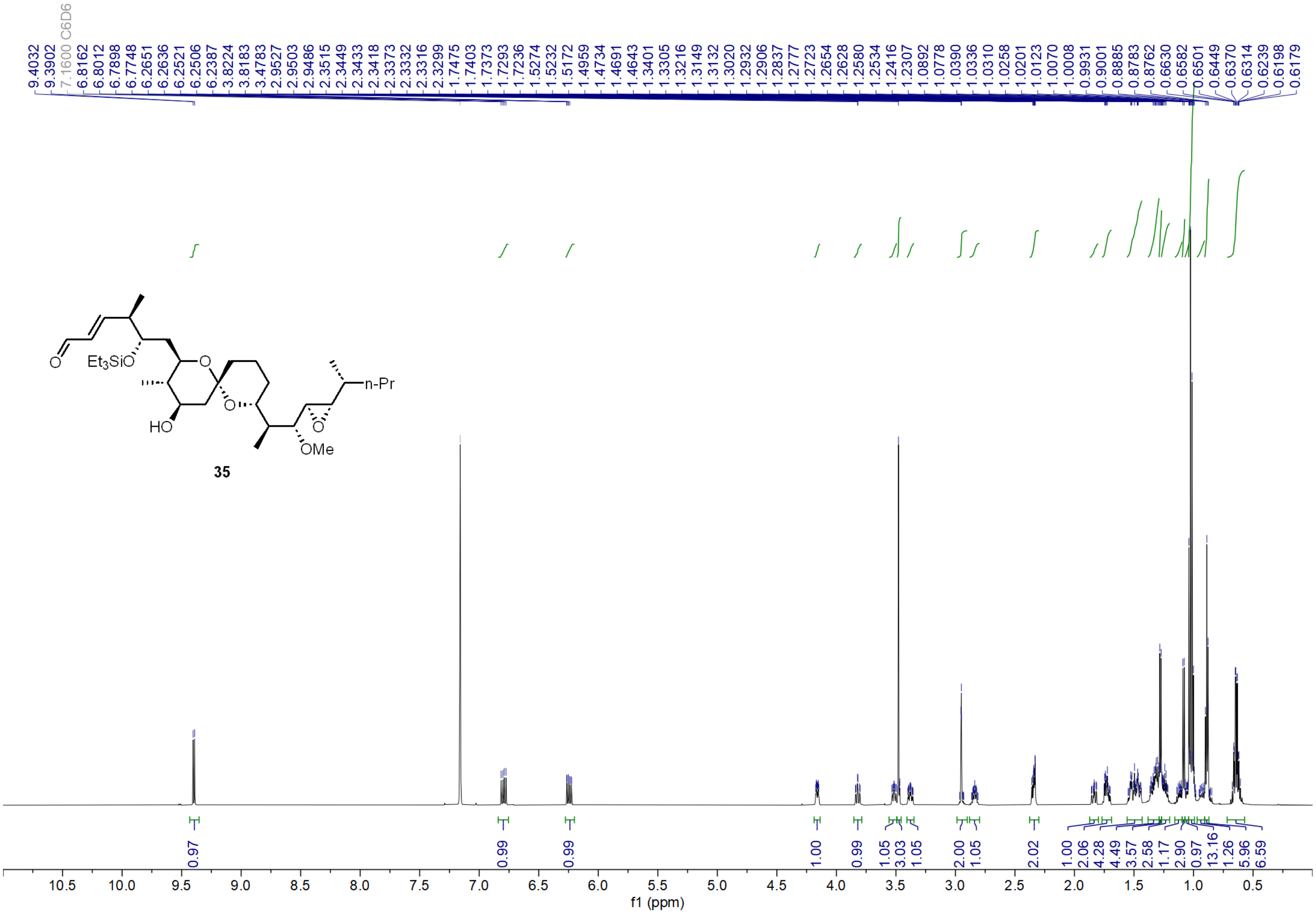


Figure S83. The 600 MHz ^{1}H-NMR of Compound **35** in benzene-*d6*

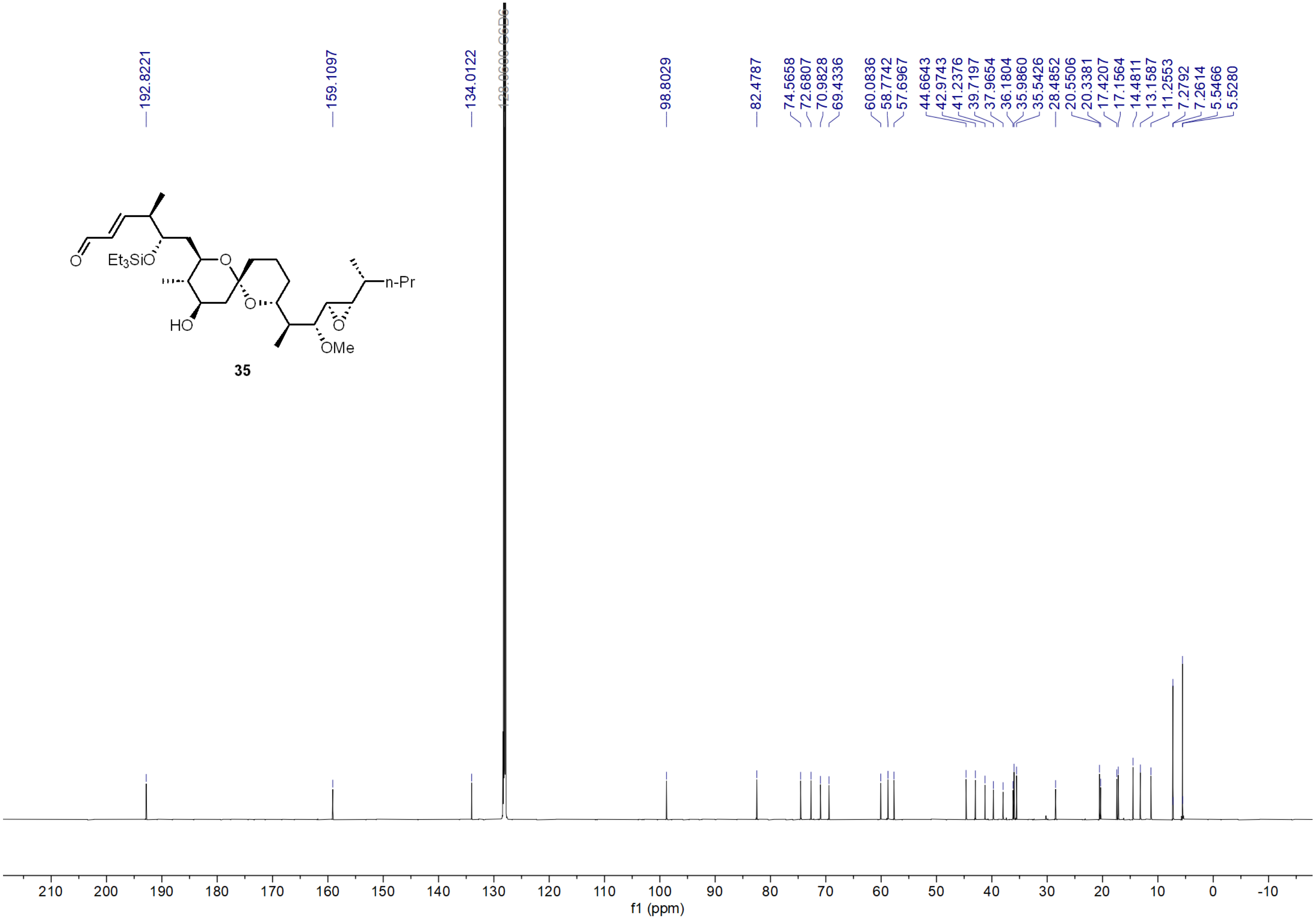
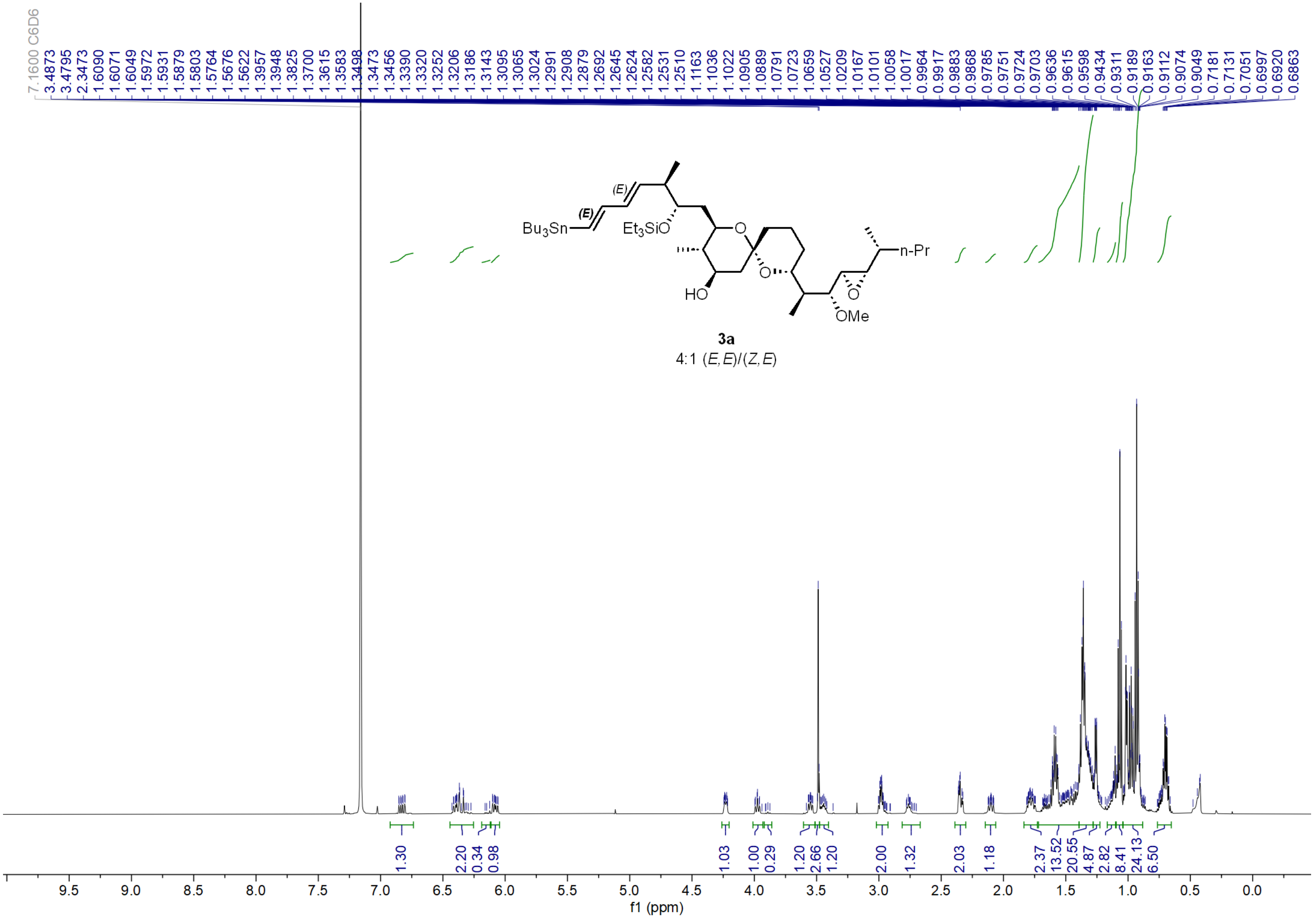


Figure S84. The 150 MHz ^{13}C-NMR of Compound **35** in benzene-*d6*



3a

4:1 (*E*,*E*)/(*Z*,*E*)

Figure S85. The 600 MHz ^{1}H-NMR of Compound **3a** in benzene-*d6*

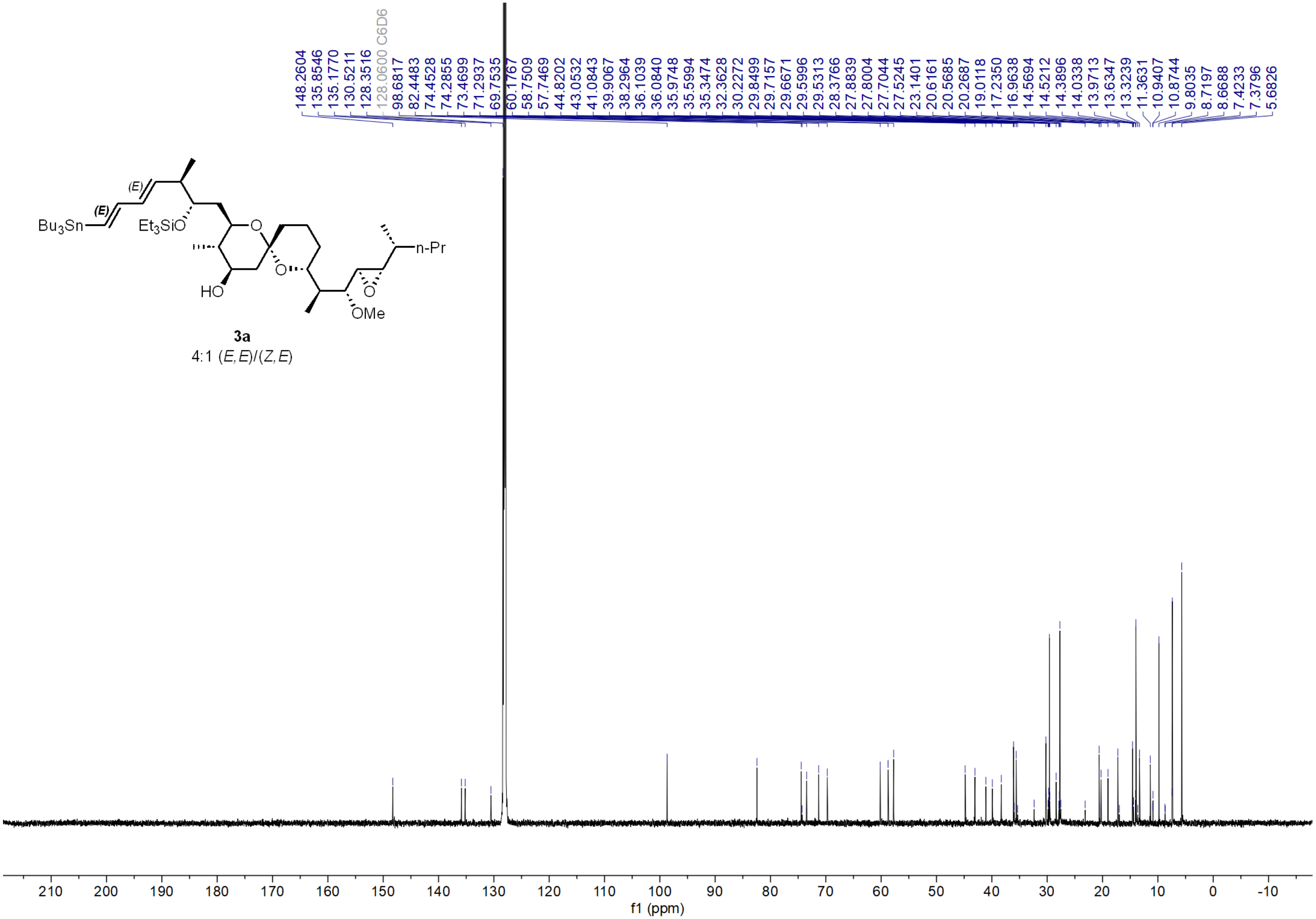
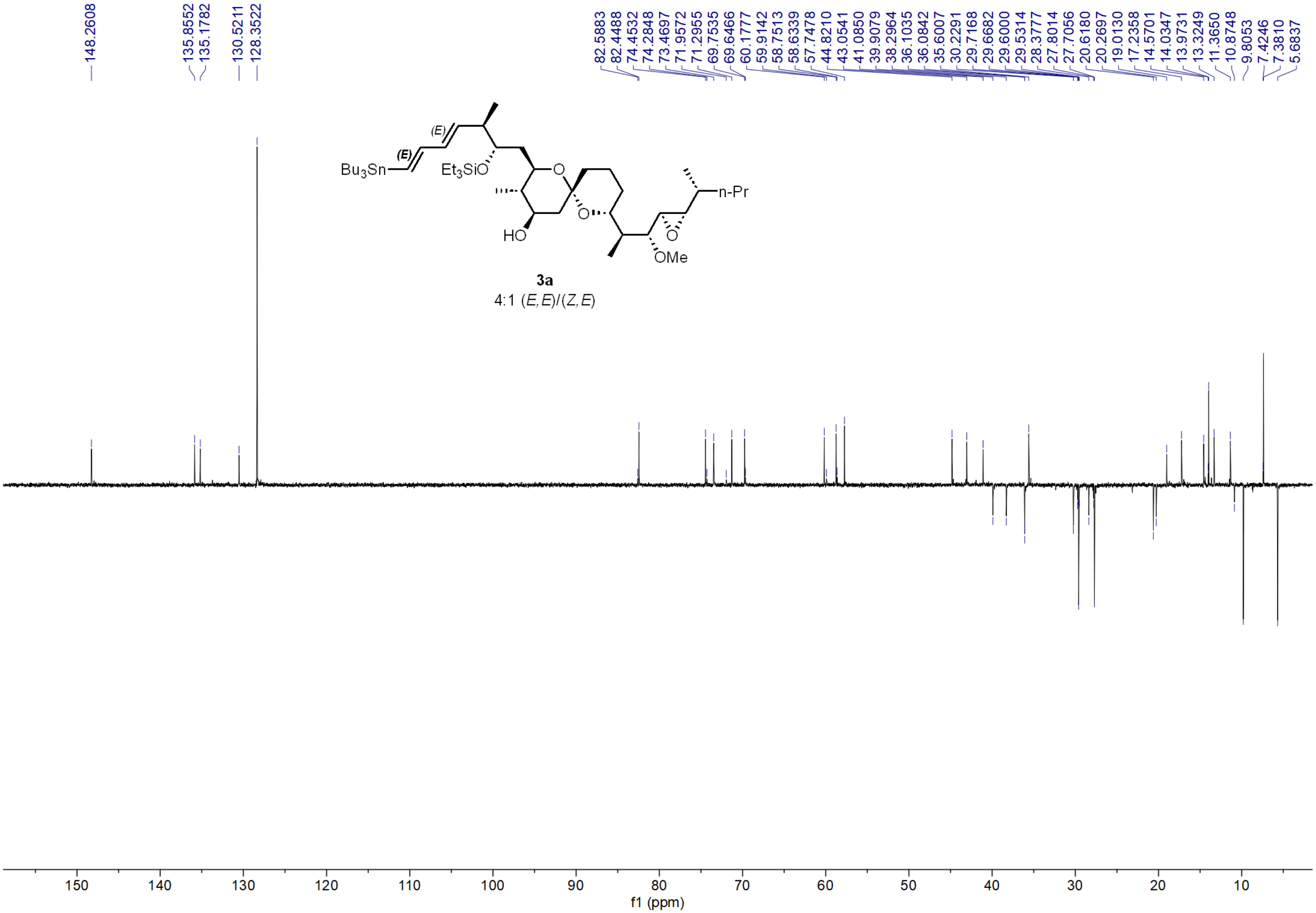


Figure S86. The 150 MHz ^{13}C-NMR of Compound **3a** in benzene-*d6*



3a
4:1 (*E,E*)/(*Z,E*)

Figure S87. The dept 135 ^{13}C-NMR of Compound **3a** in benzene-*d6*, 150 MHz

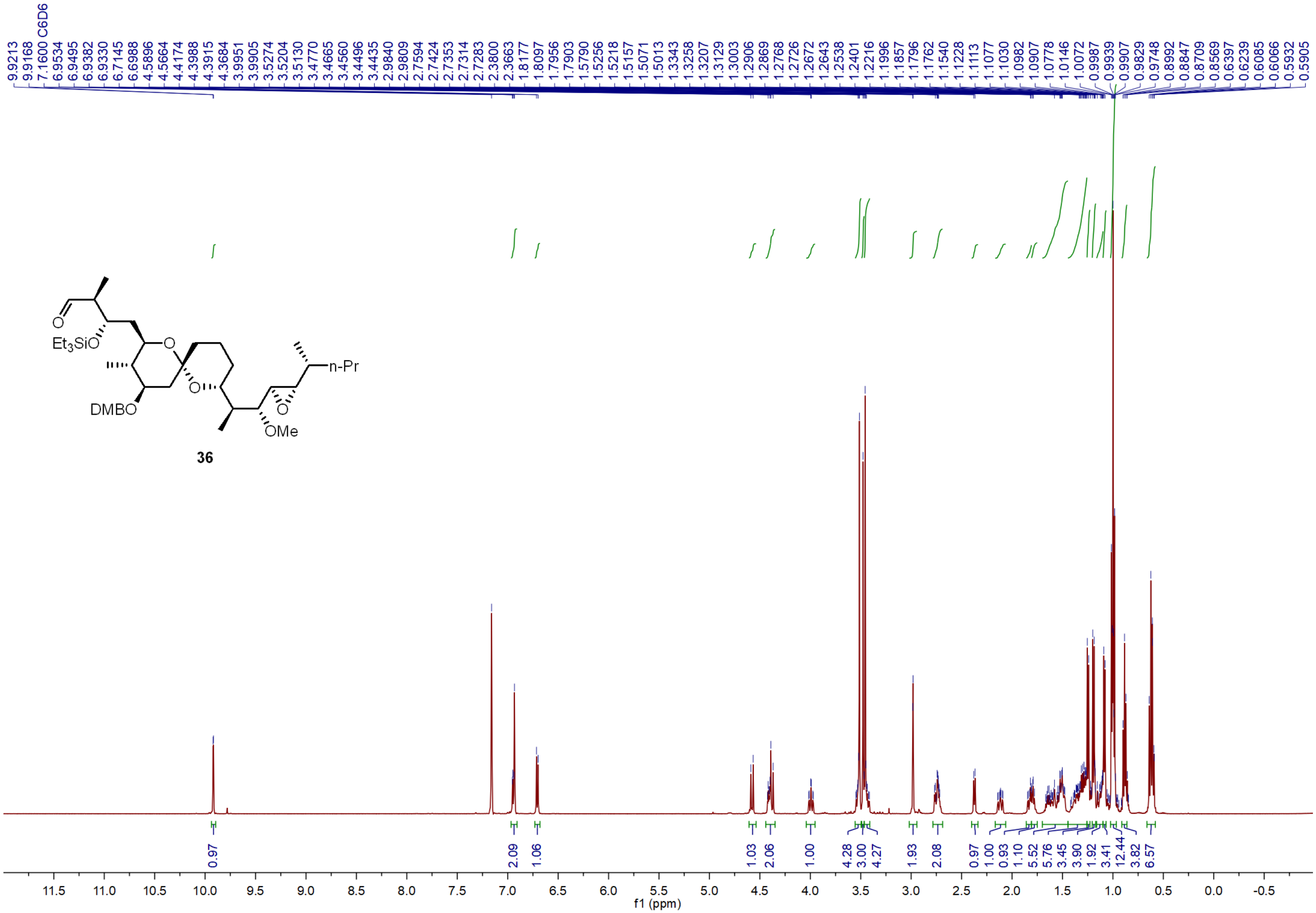


Figure S88. The 500 MHz ^{1}H-NMR of Compound **36** in benzene-*d6*

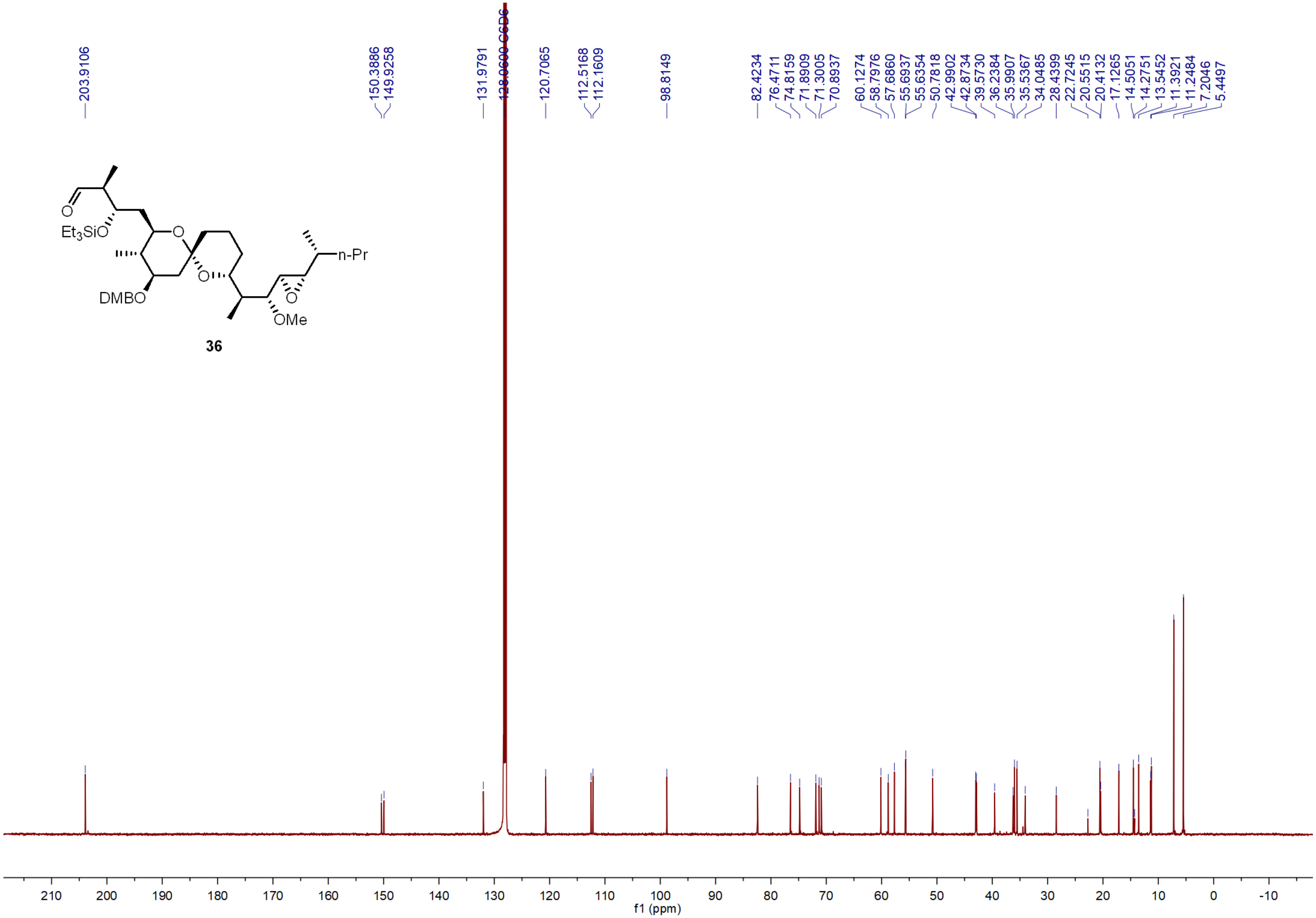


Figure S89. The 125 MHz ^{13}C-NMR of Compound **36** in benzene-*d6*

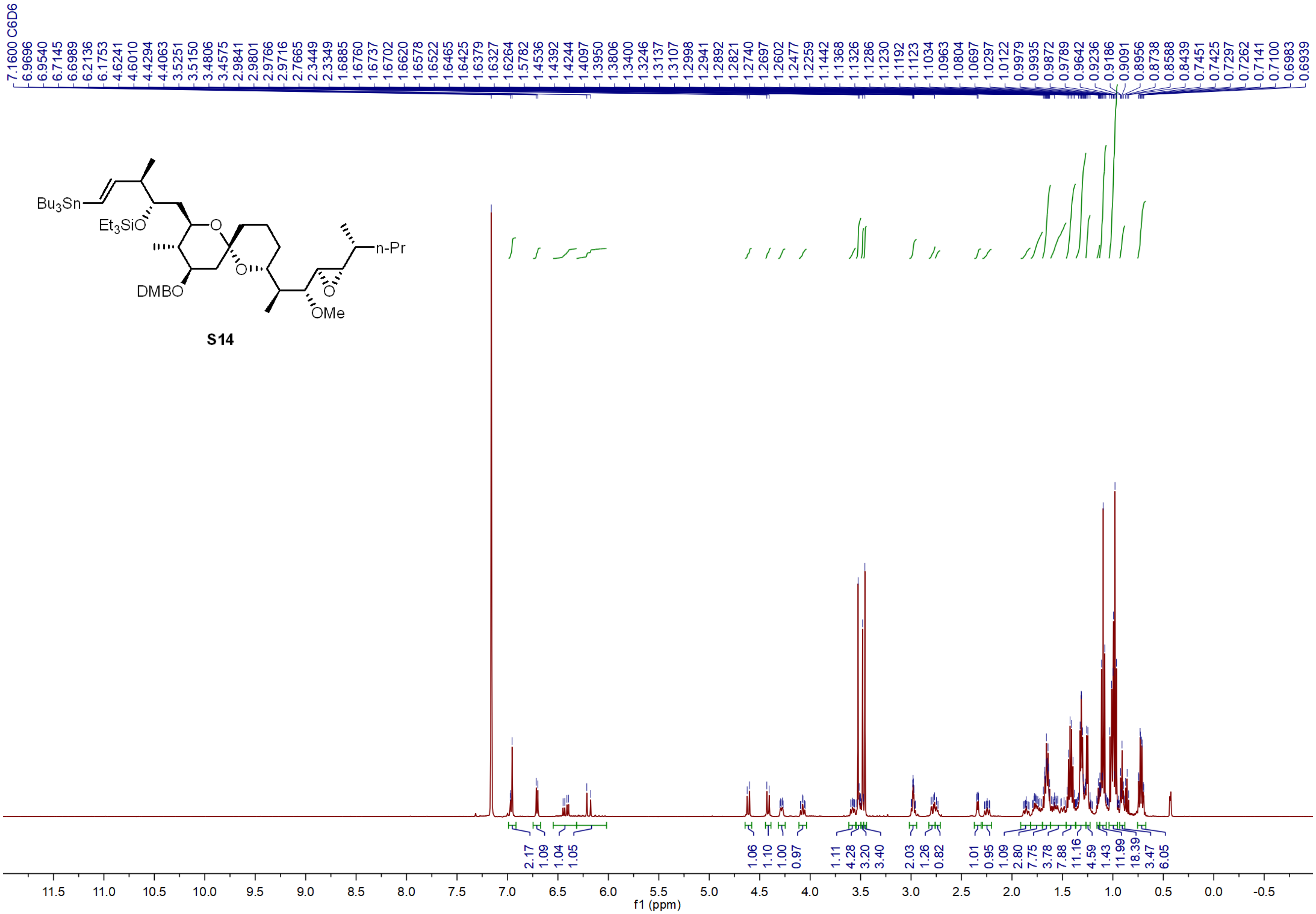


Figure S90. The 500 MHz ^{1}H-NMR of Compound **S14** in benzene-*d6*

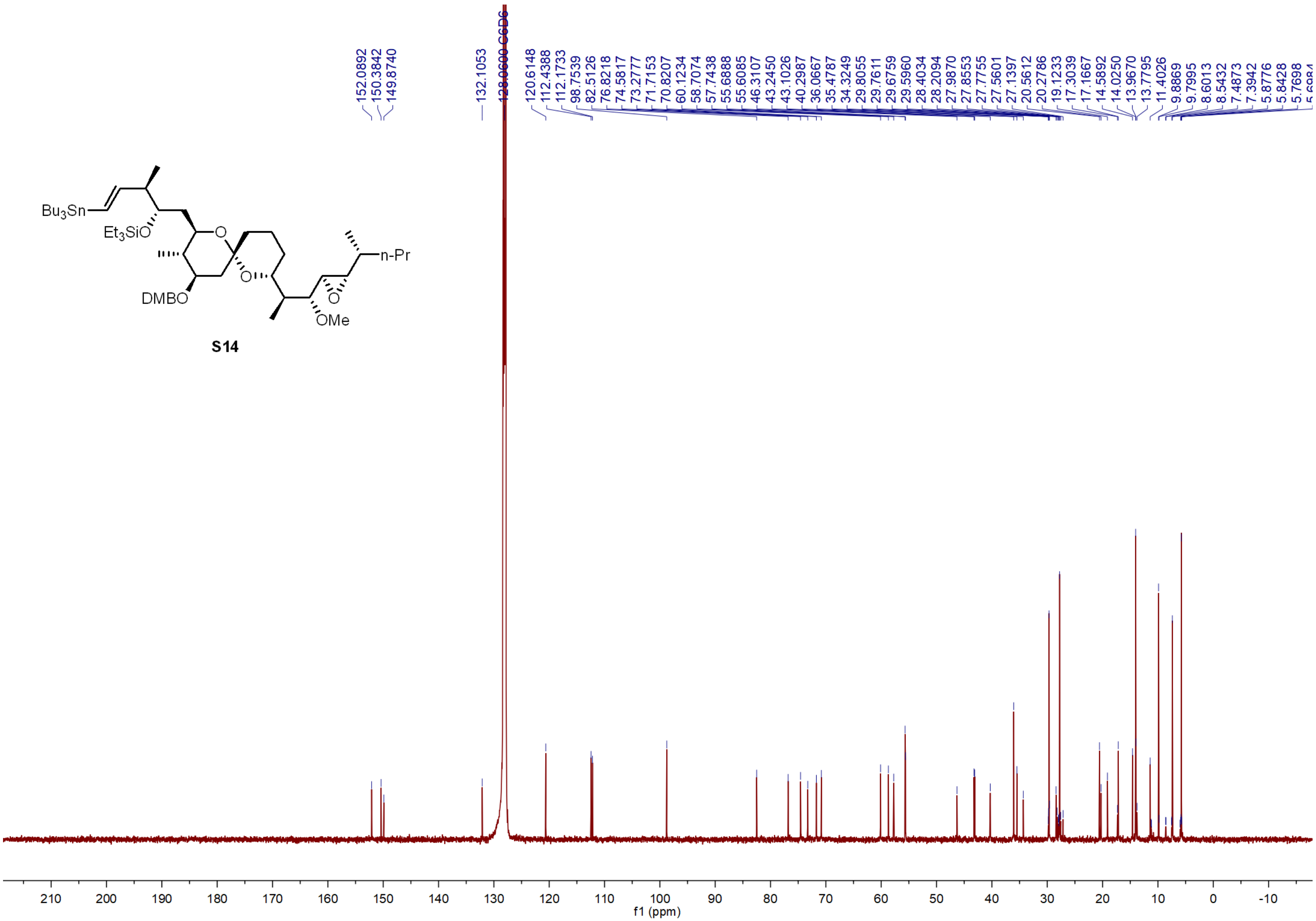


Figure S91. The 125 MHz ^{13}C-NMR of Compound **S14** in benzene-*d6*

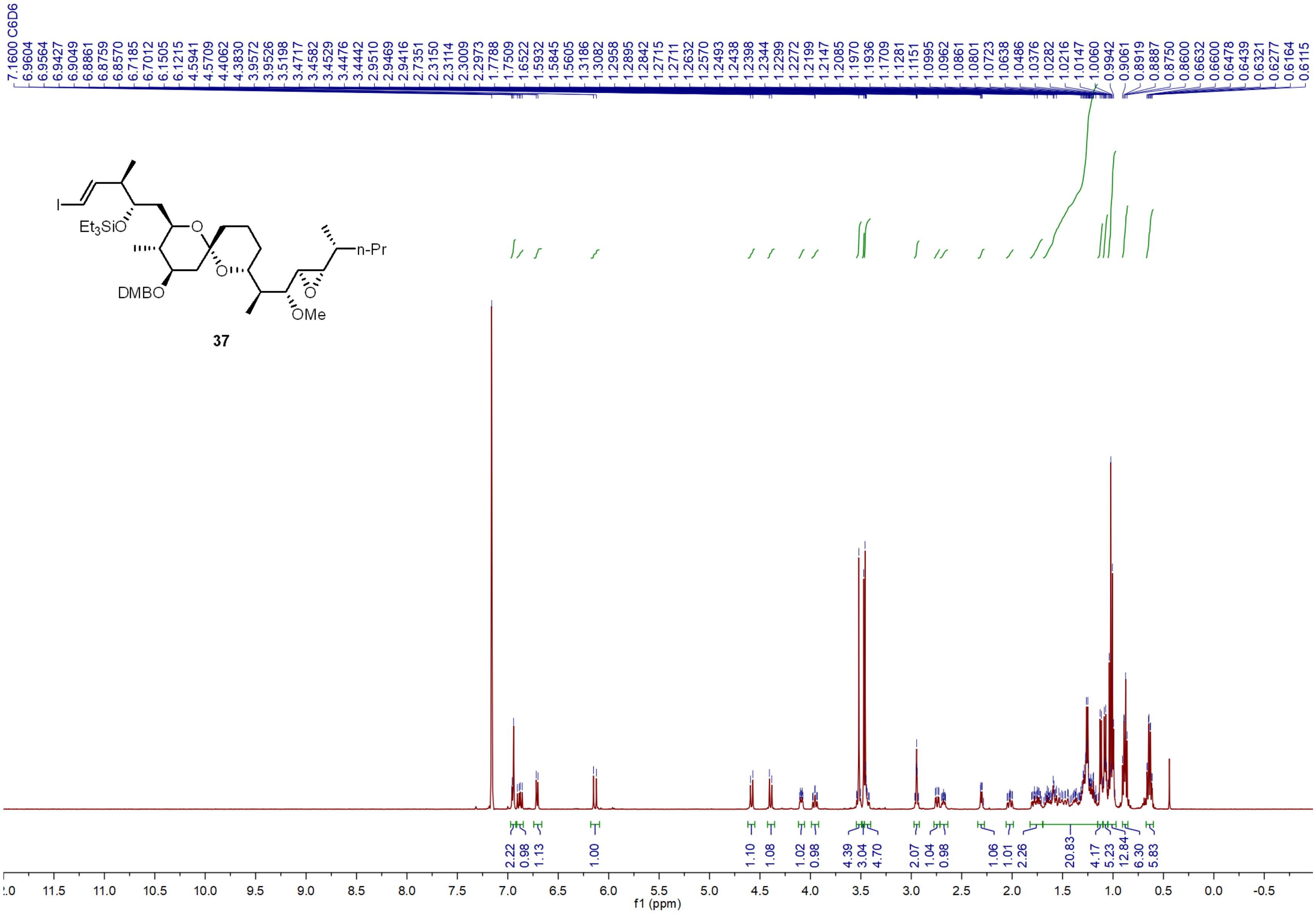


Figure S92. The 500 MHz ^{1}H-NMR of Compound **37** in benzene-*d6*

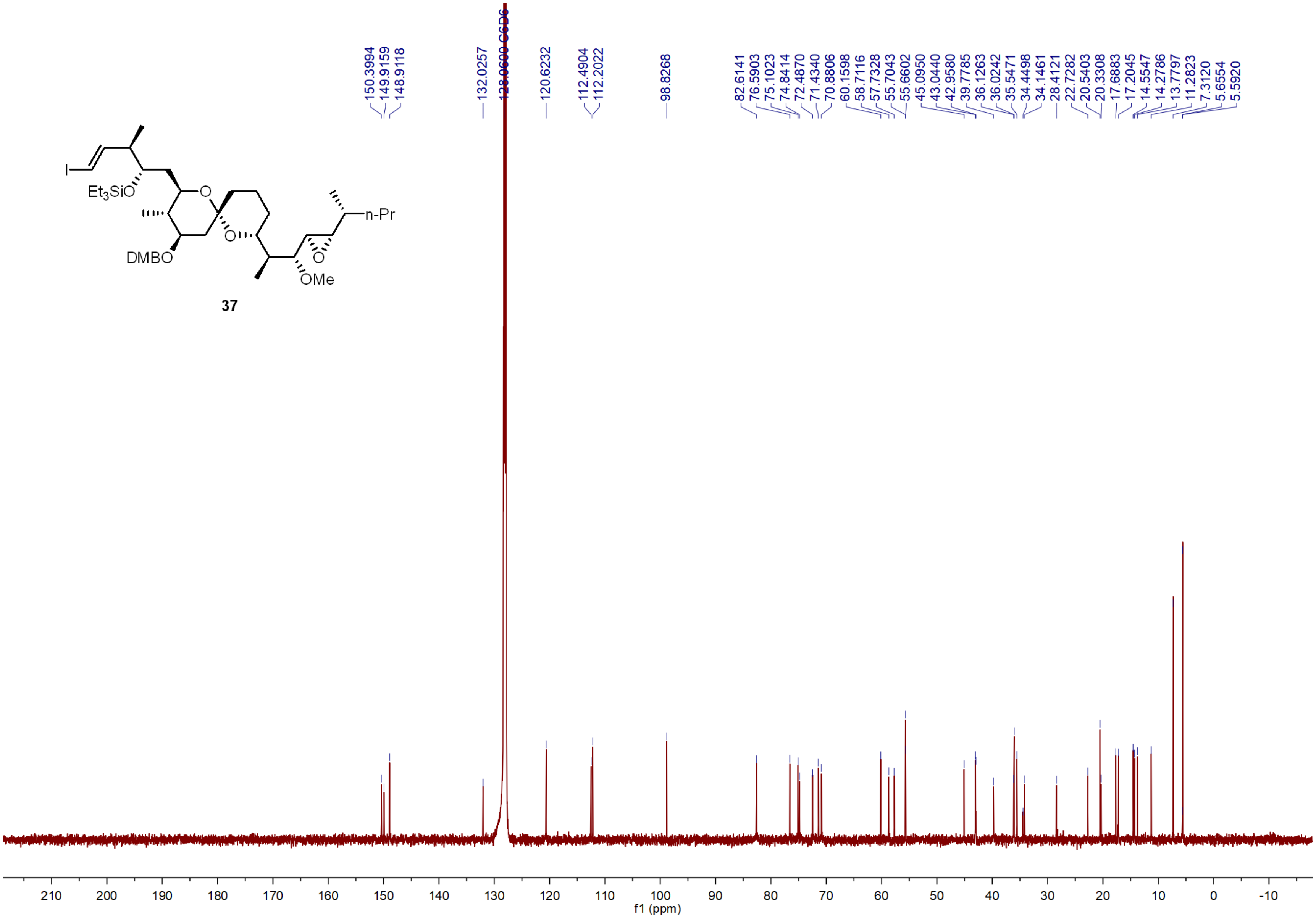


Figure S93. The 125 MHz ^{13}C-NMR of Compound **37** in benzene-*d6*

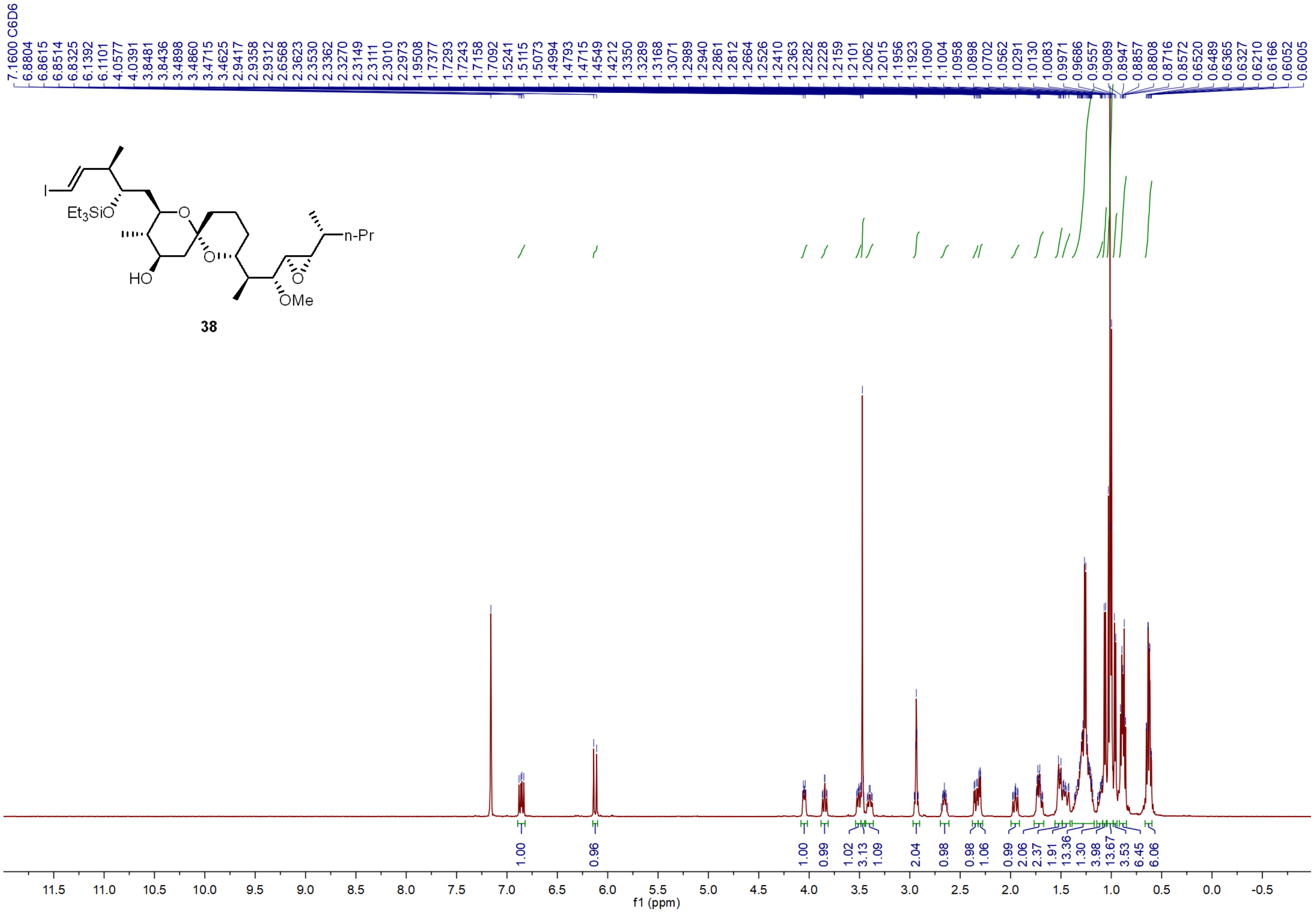


Figure S94. The 500 MHz ^{1}H-NMR of Compound **38** in benzene-*d6*

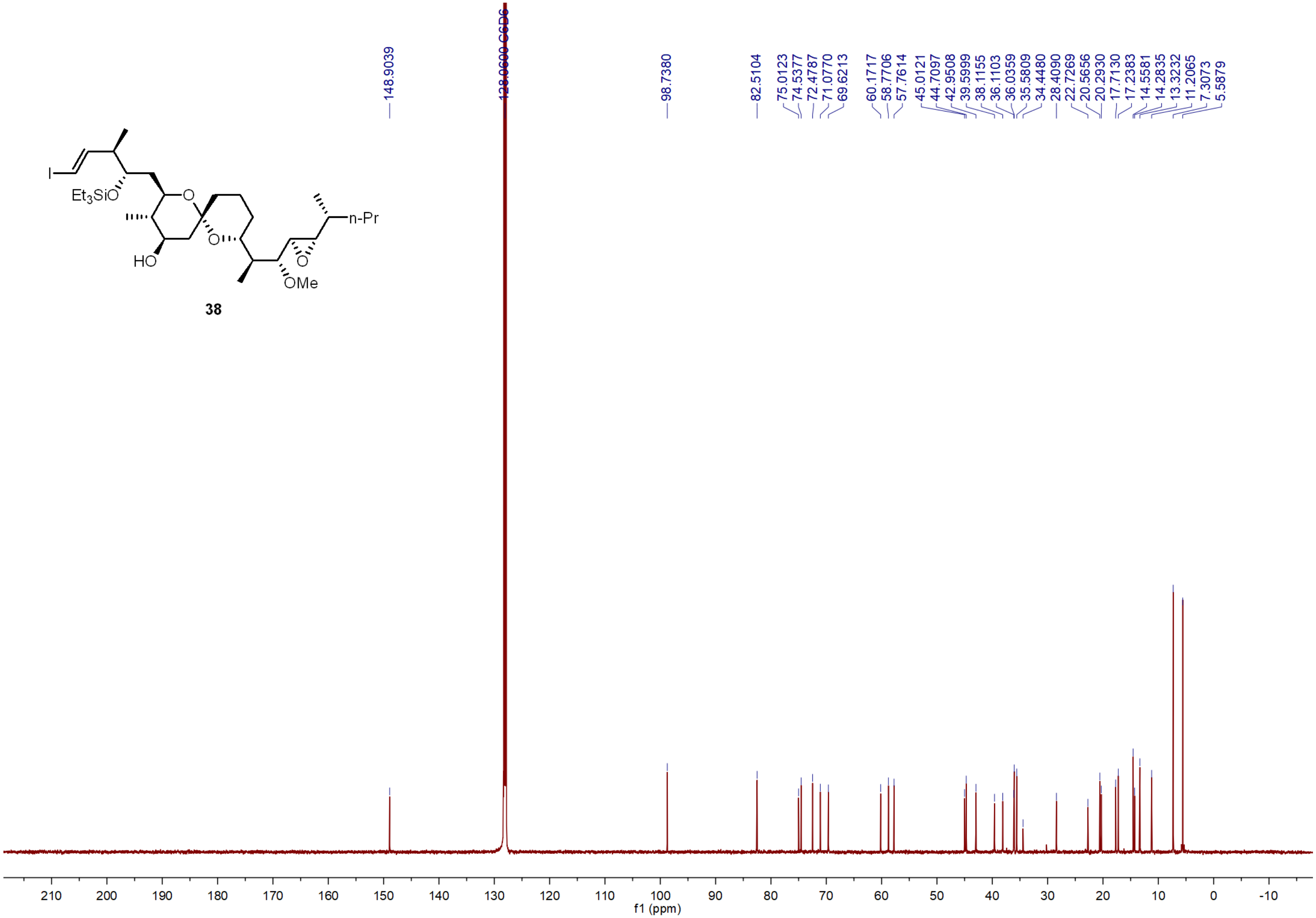


Figure S95. The 125 MHz ^{13}C-NMR of Compound **38** in benzene-*d6*

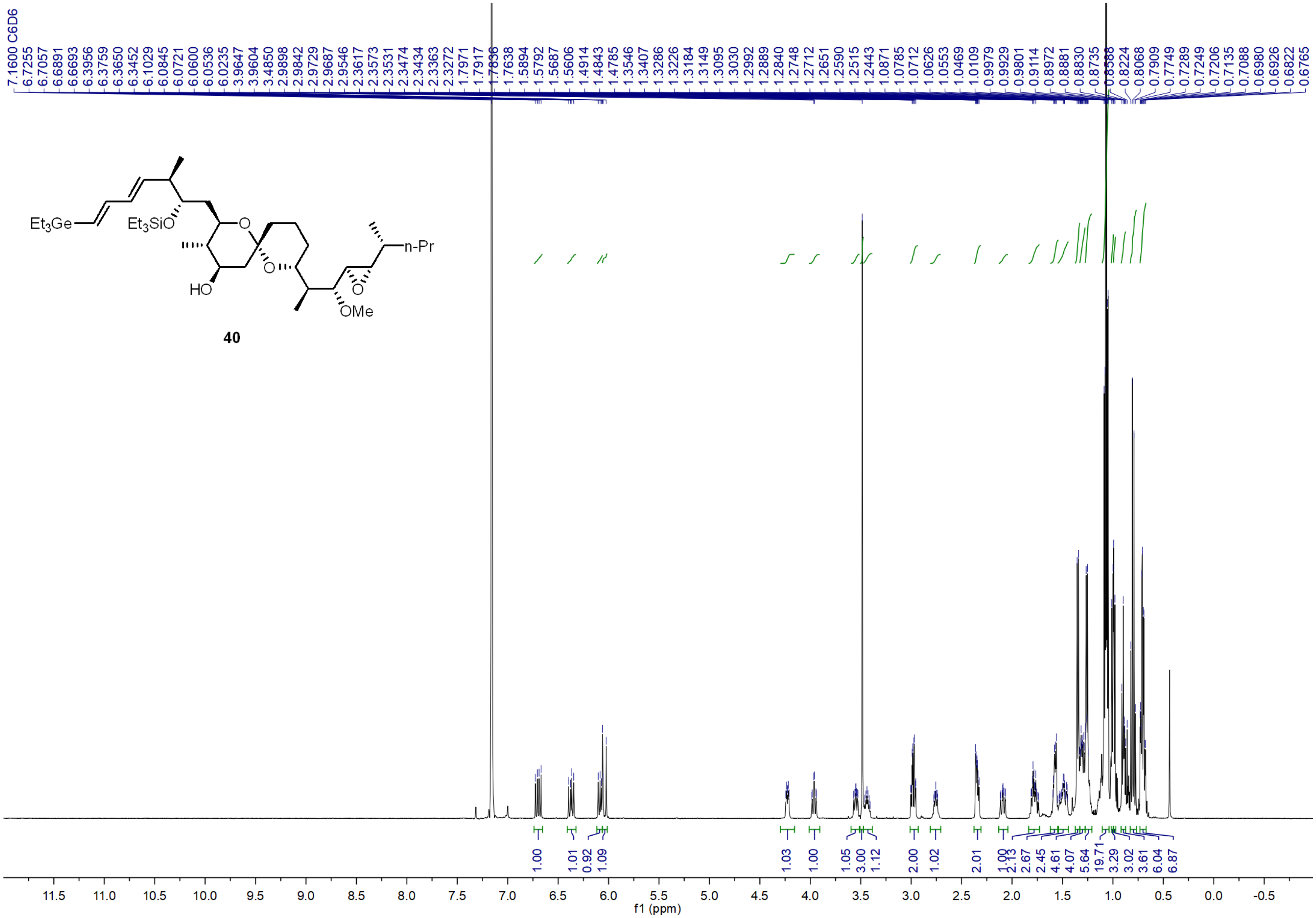


Figure S96. The 500 MHz ^{1}H-NMR of Compound **40** in benzene-*d6*

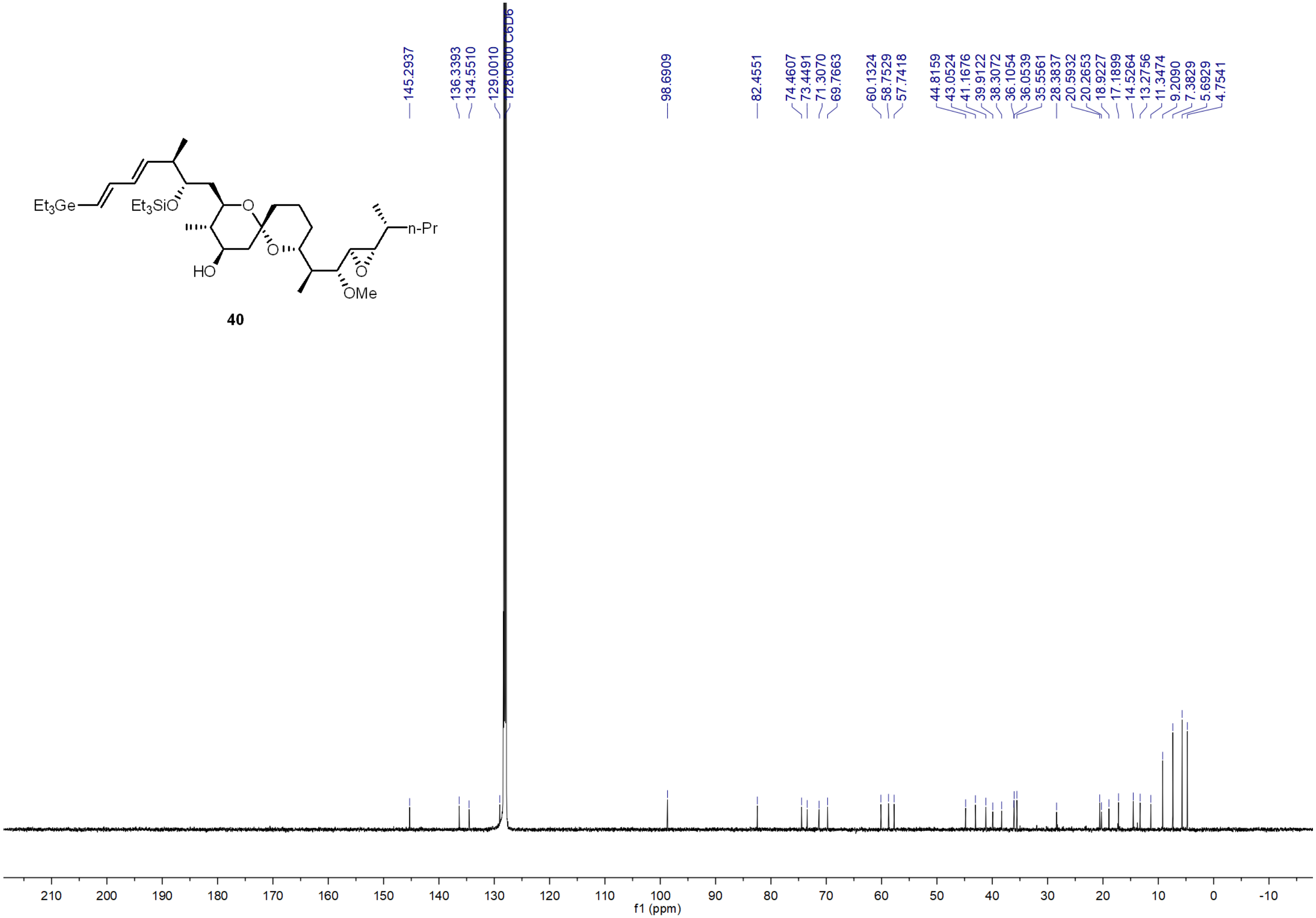


Figure S97. The 125 MHz ^{13}C-NMR of Compound **40** in benzene-*d6*

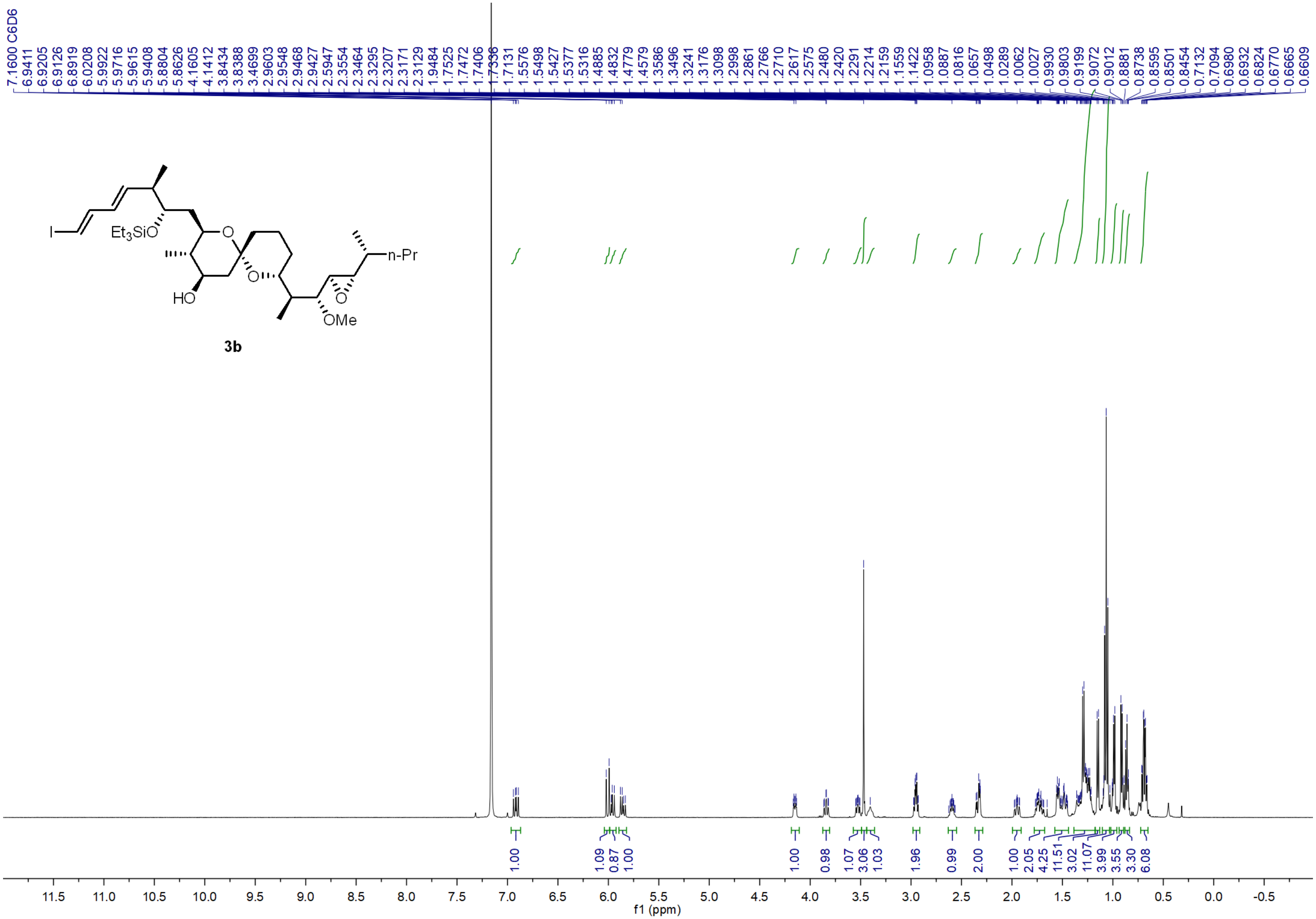


Figure S98. The 500 MHz ^{1}H-NMR of Compound **3b** in benzene-*d6*

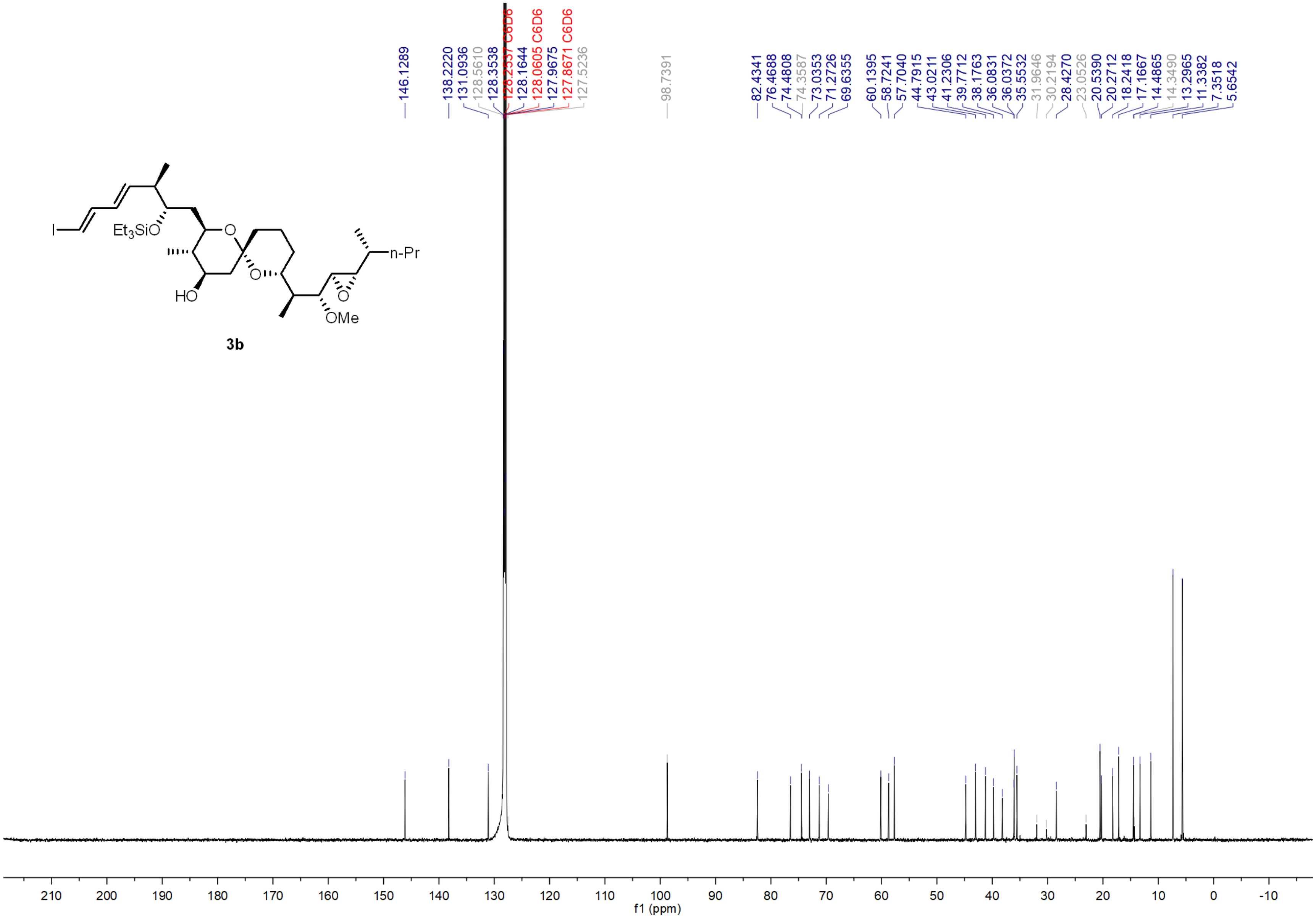


Figure S99. The 125 MHz ^{13}C-NMR of Compound **3b** in benzene-*d6*

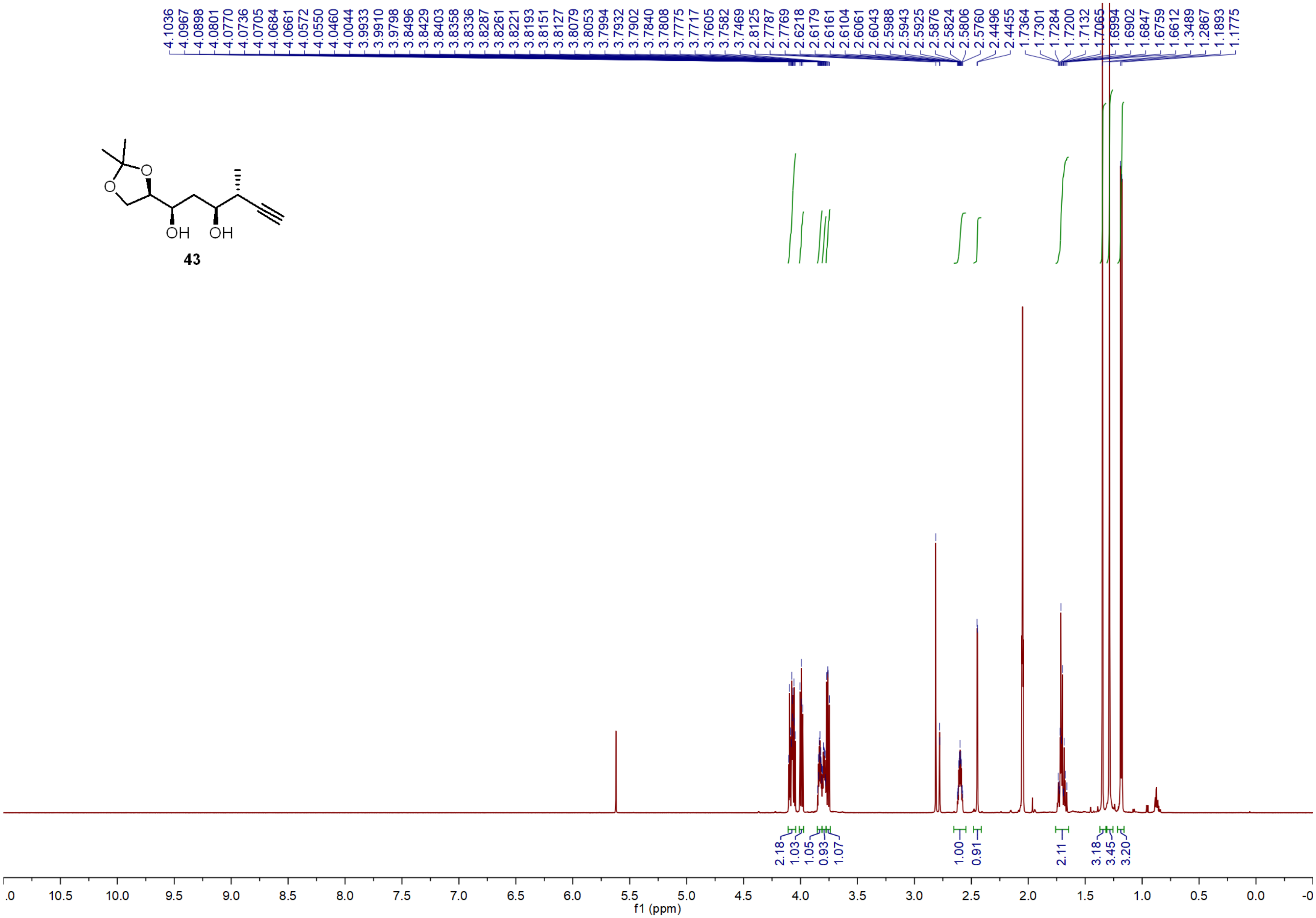


Figure S100. The 600 MHz ^{1}H-NMR of Compound **43** in acetone-*d6*

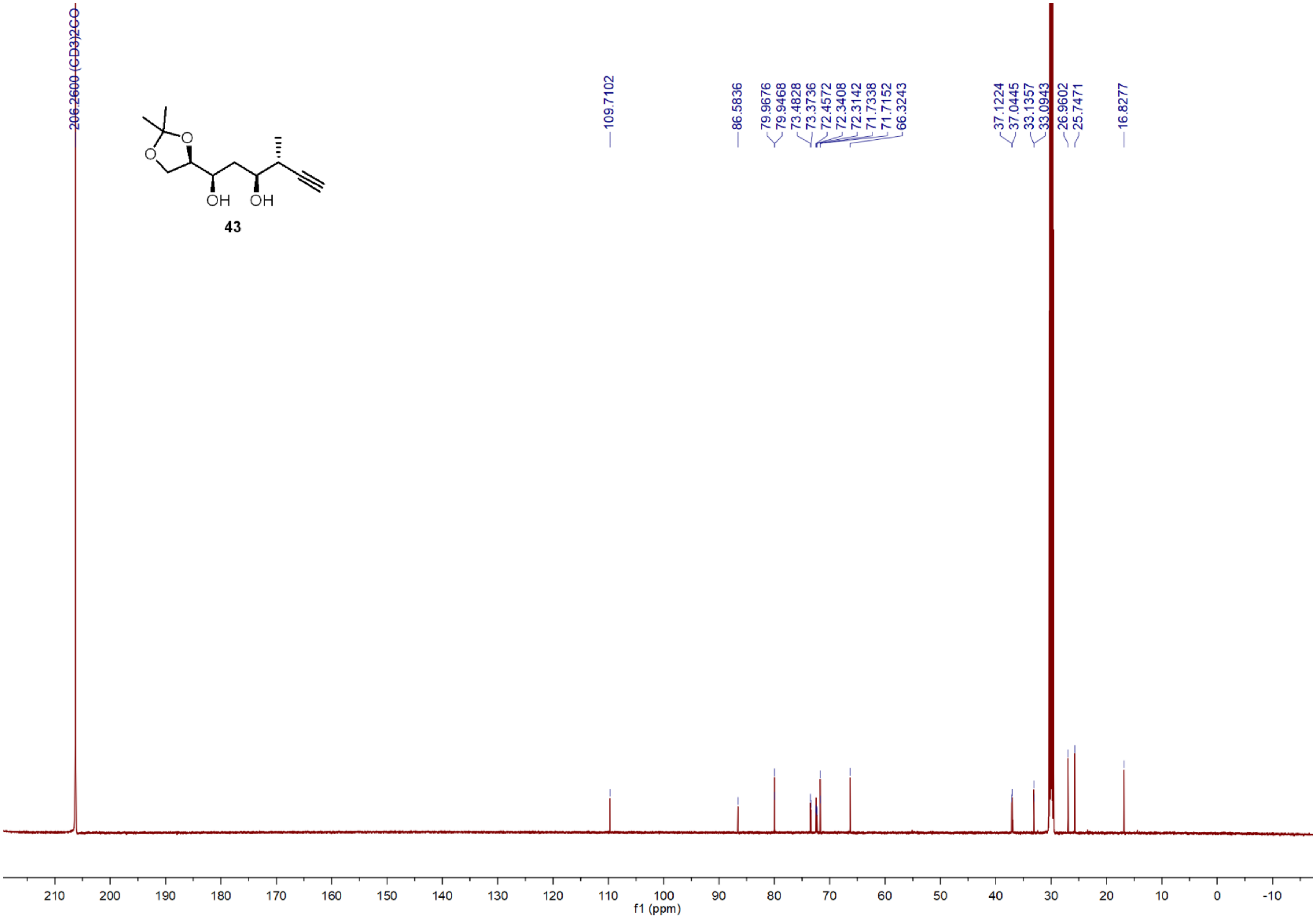


Figure S101. The 150 MHz ^{13}C-NMR of Compound **43** in acetone-*d6*

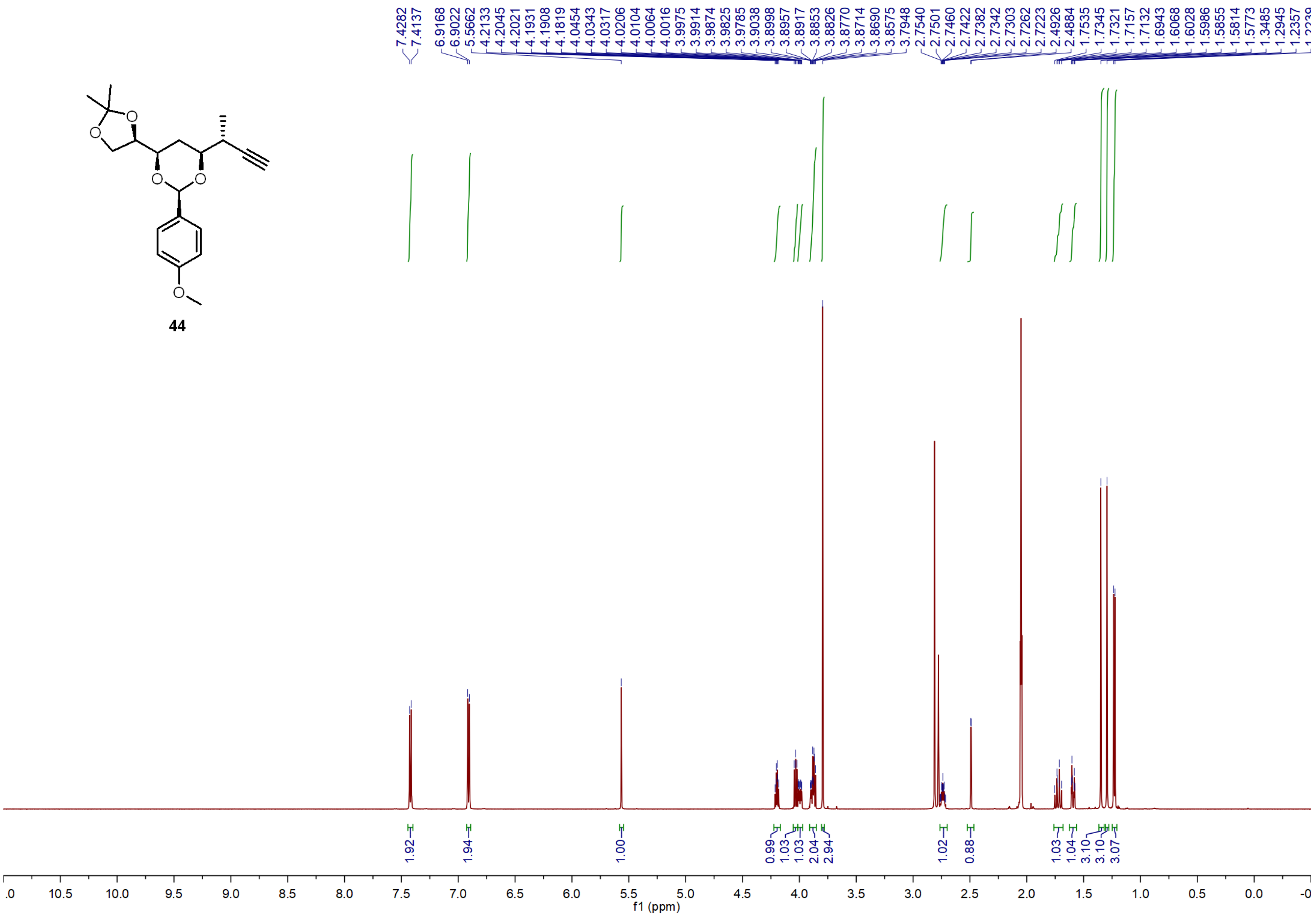


Figure S102. The 600 MHz ^{1}H-NMR of Compound **44** in acetone-*d6*

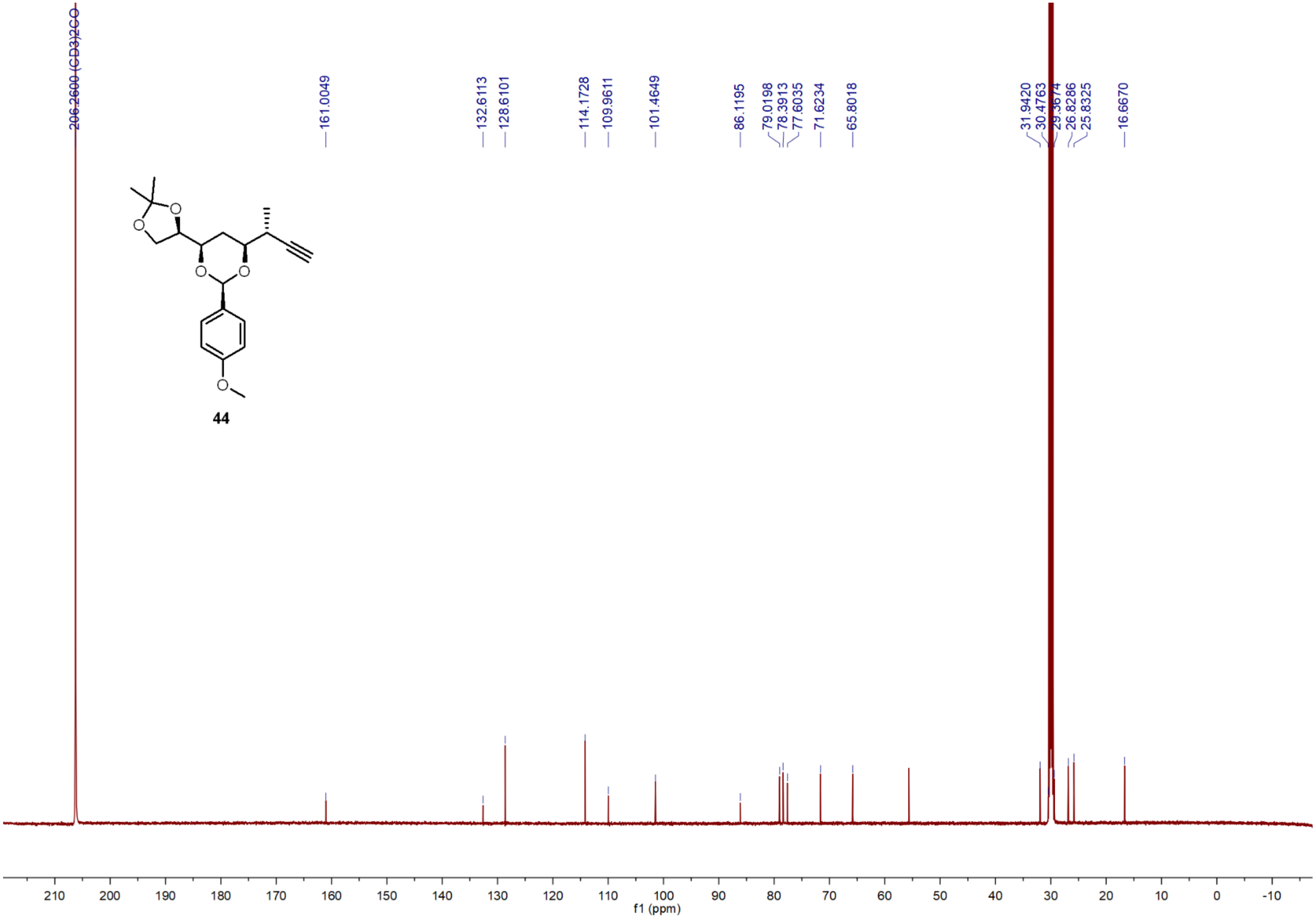


Figure S103. The 150 MHz ^{13}C-NMR of Compound **44** in acetone-*d6*

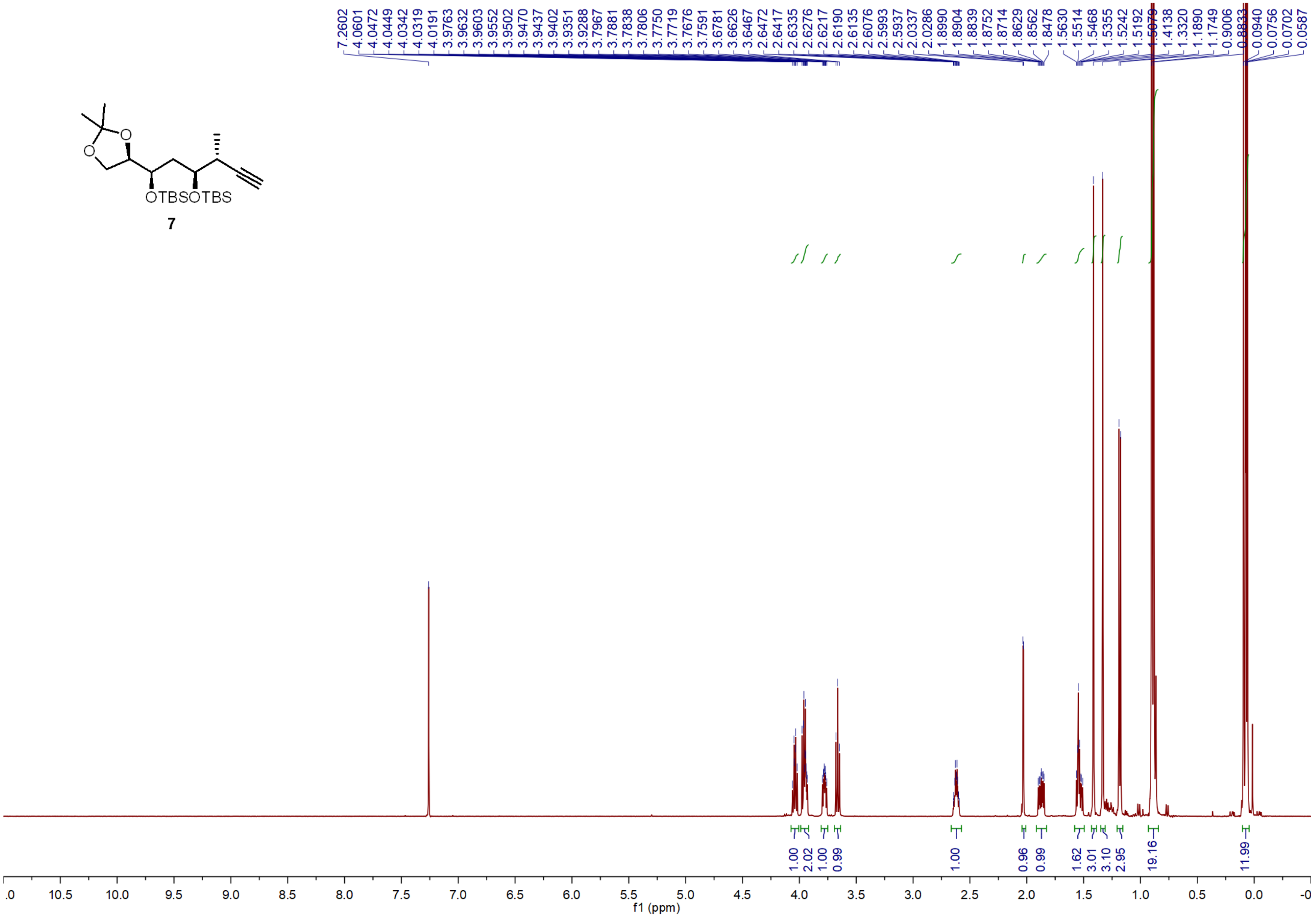


Figure S104. The 500 MHz ^{1}H-NMR of Compound **7** in Chloroform-*d*

7

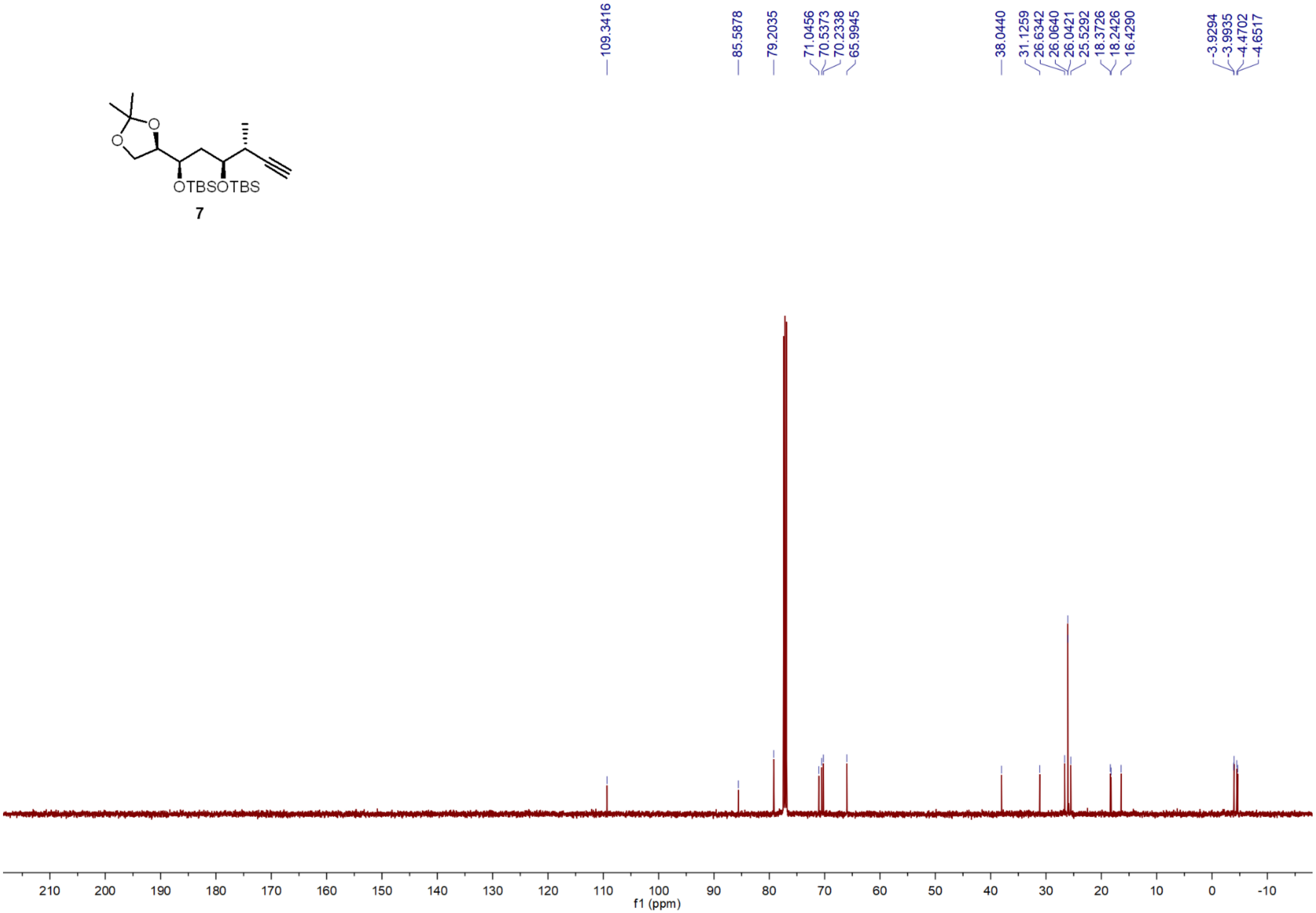


Figure S105. The 125 MHz ^{13}C-NMR of Compound **7** in Chloroform-*d*

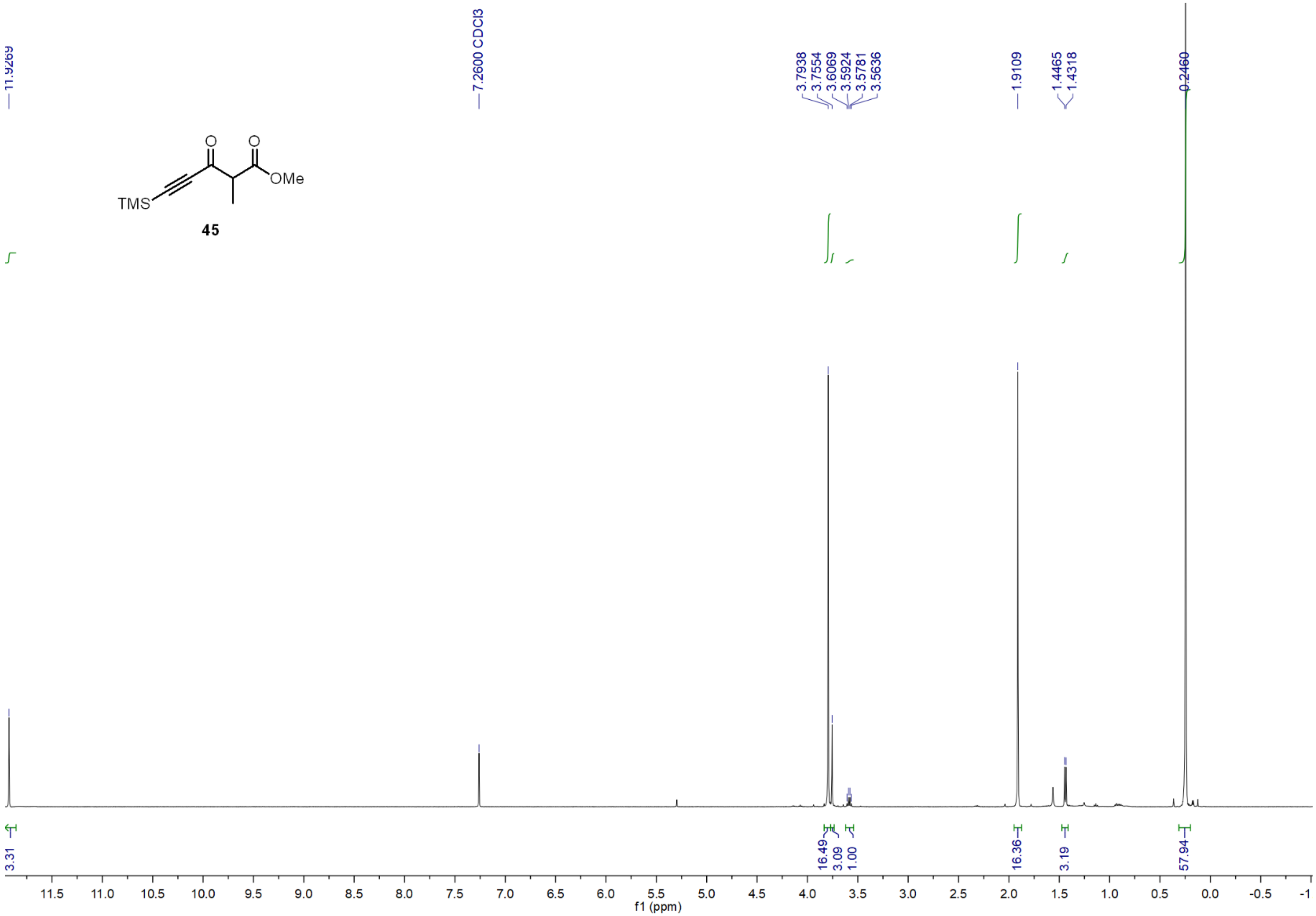


Figure S106. The 500 MHz ^{1}H-NMR of Compound **45** in Chloroform-*d*

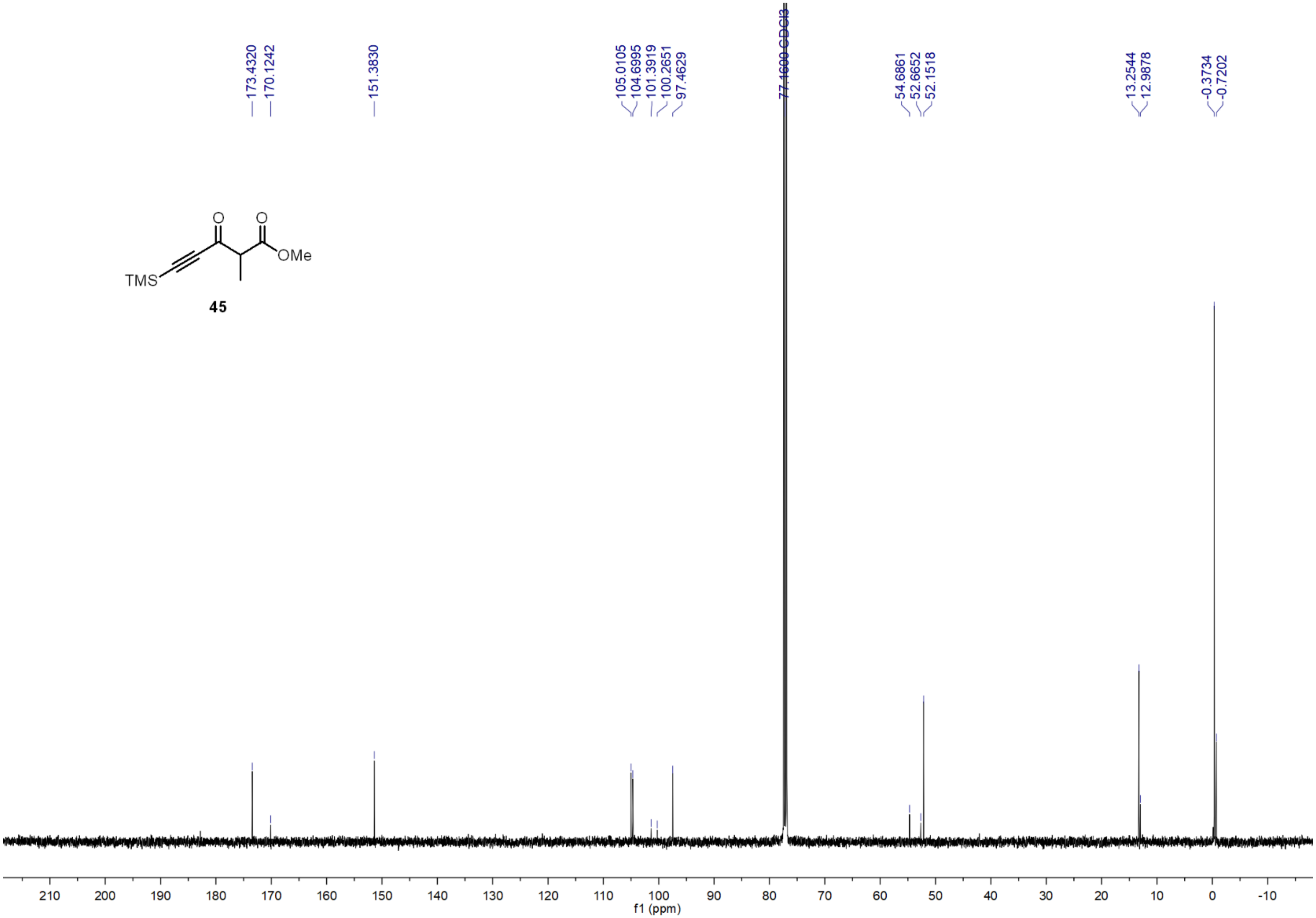


Figure S107. The 125 MHz ^{13}C-NMR of Compound **45** in Chloroform-*d*

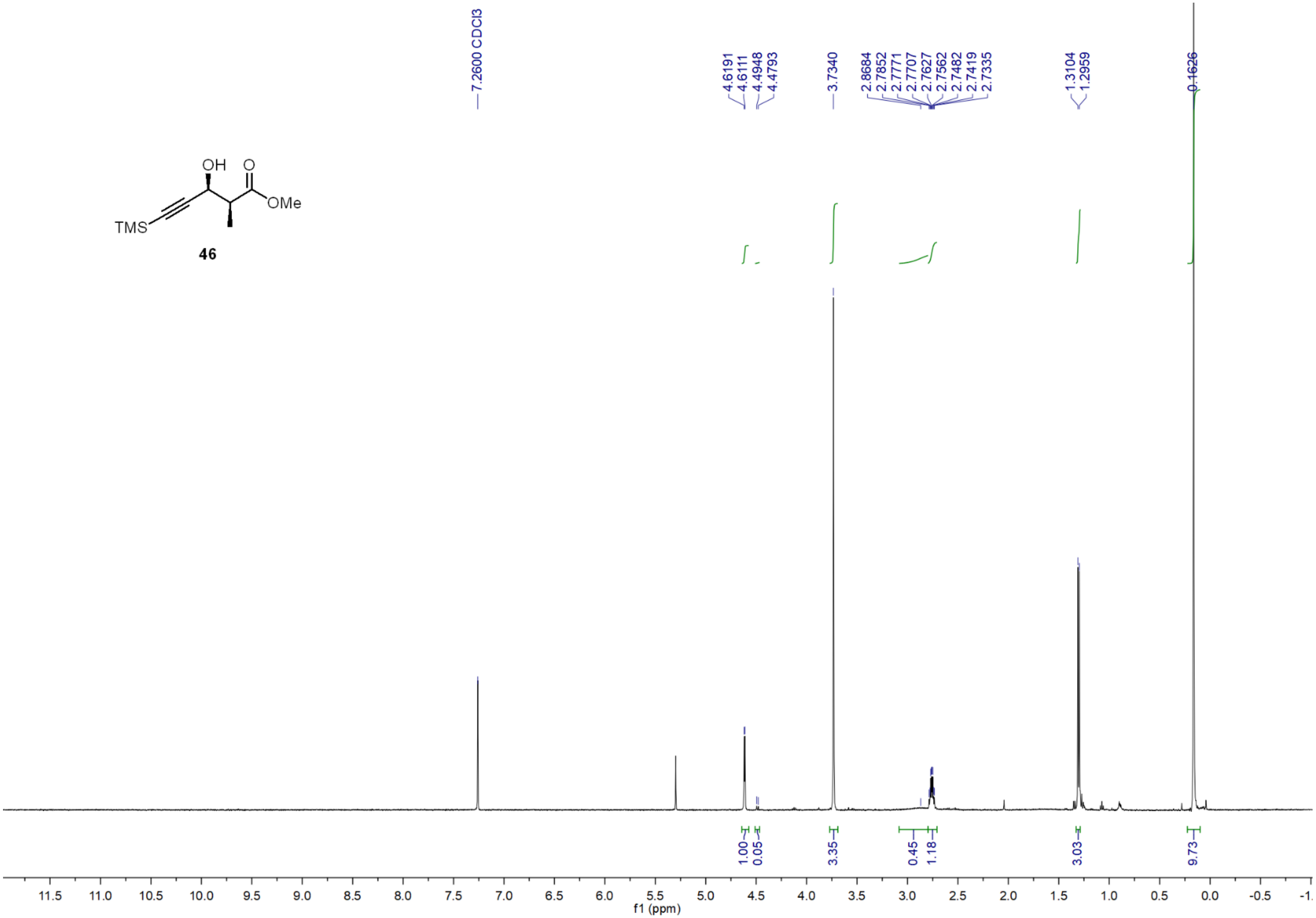


Figure S108. The 500 MHz ^{1}H-NMR of Compound **46** in Chloroform-*d*

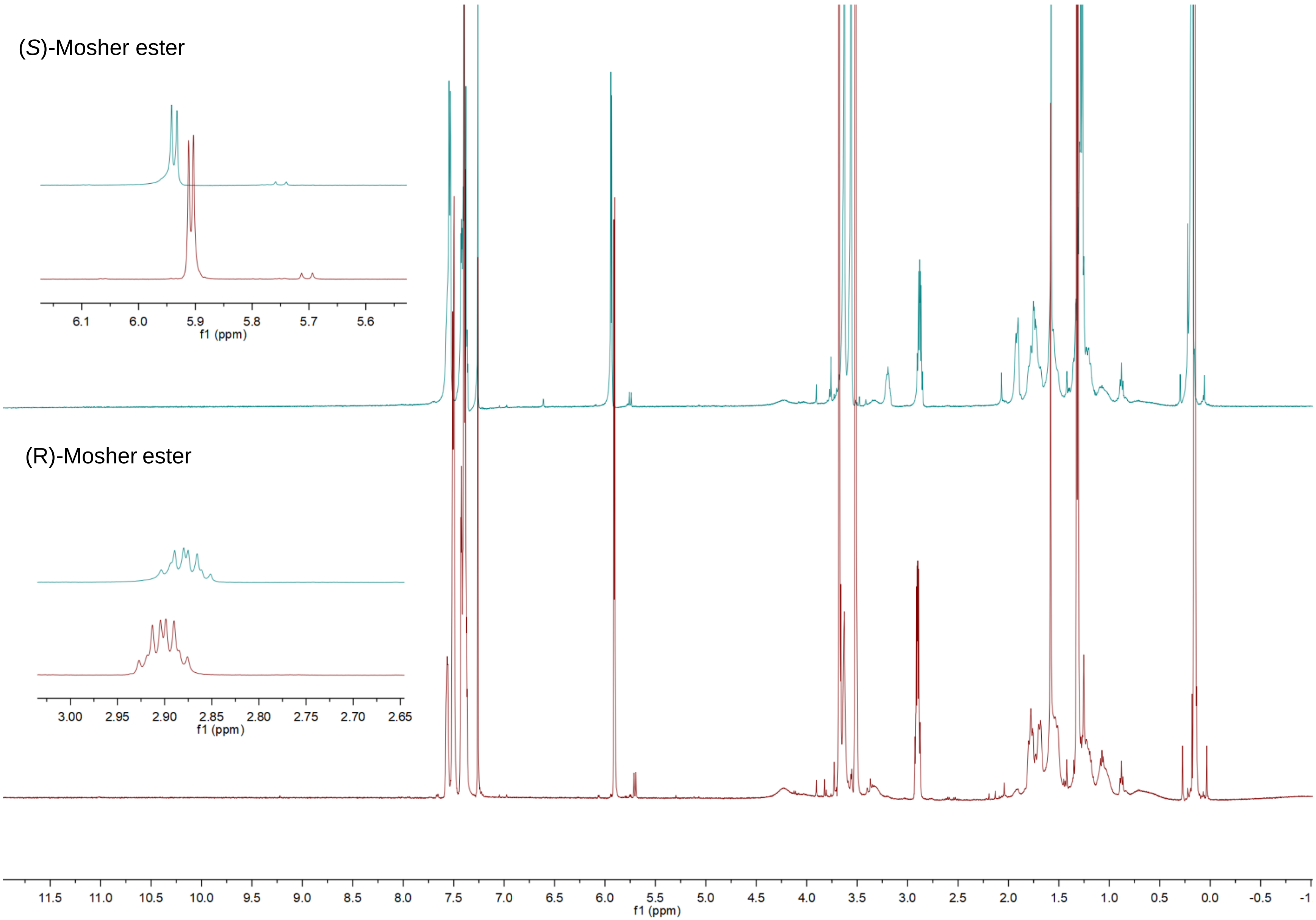
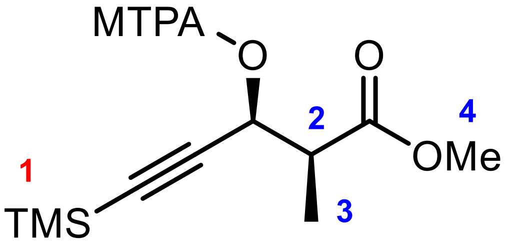


Figure S109. Mosher ester analysis of enantioselectivity of DKR transfer hydrogenation

Table S26. Mosher ester stereochemical confirmation of compound **46**



46

$\Delta\delta = \delta_S - \delta_R$

No.	δ_S	δ_R	$\Delta\delta$
1	0.1786	0.1560	**0.0226**
2	2.8708	2.9014	**-0.0306**
3	1.2733	1.3167	**-0.0434**
4	3.6273	3.6795	**-0.0522**

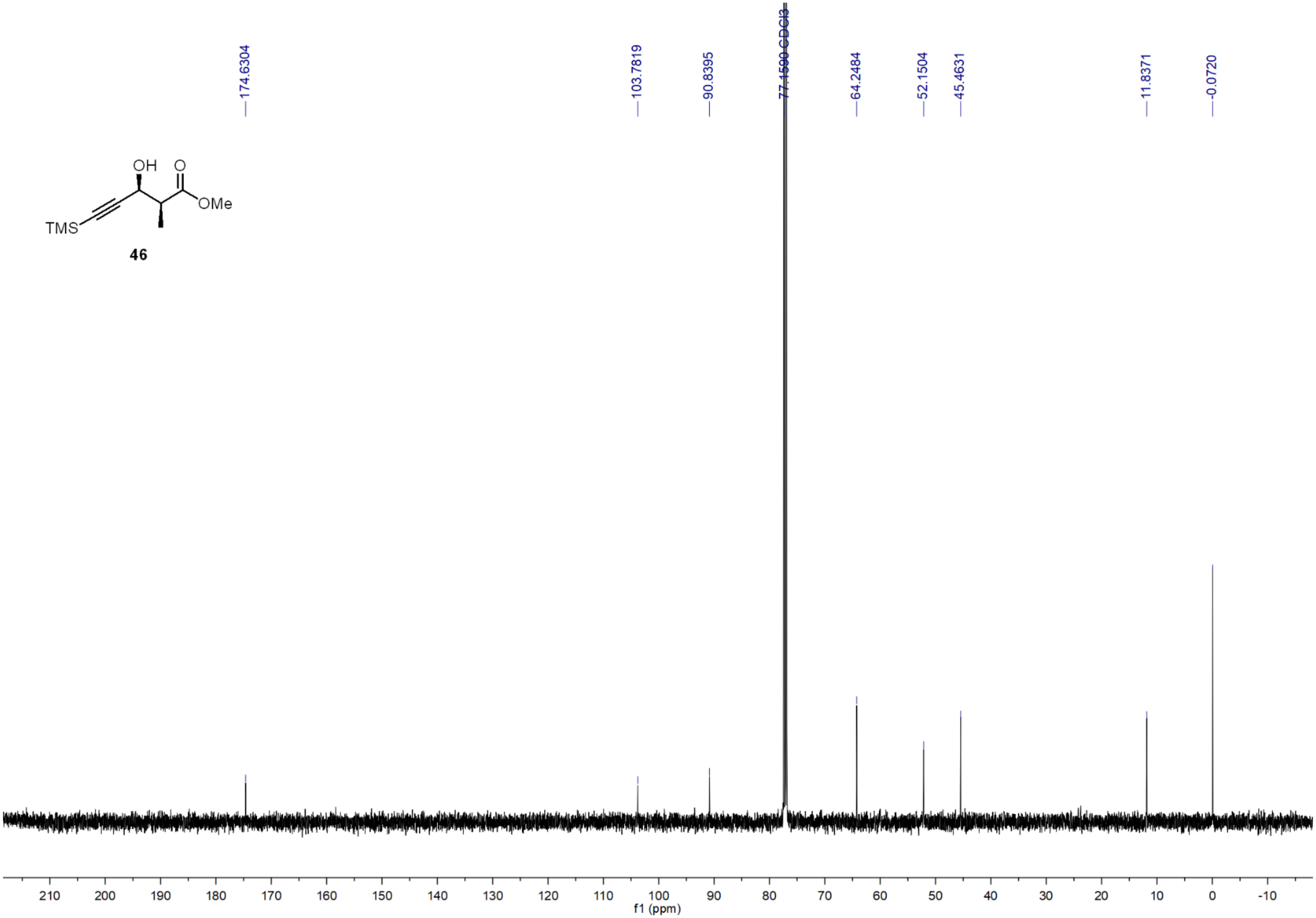


Figure S110. The 125 MHz ^{13}C-NMR of Compound **46** in Chloroform-*d*

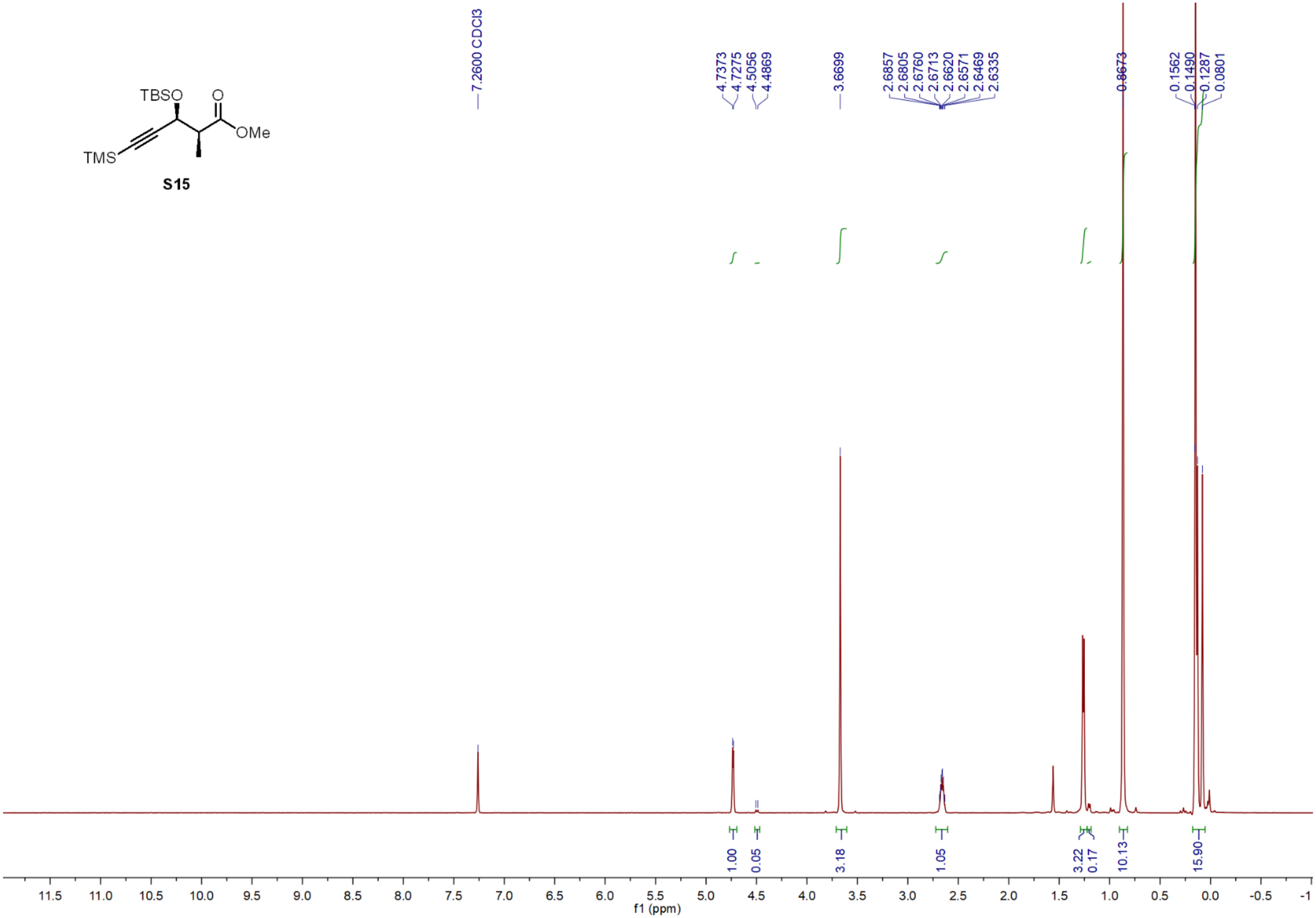


Figure S111. The 500 MHz ^{1}H-NMR of Compound **S15** in Chloroform-*d*

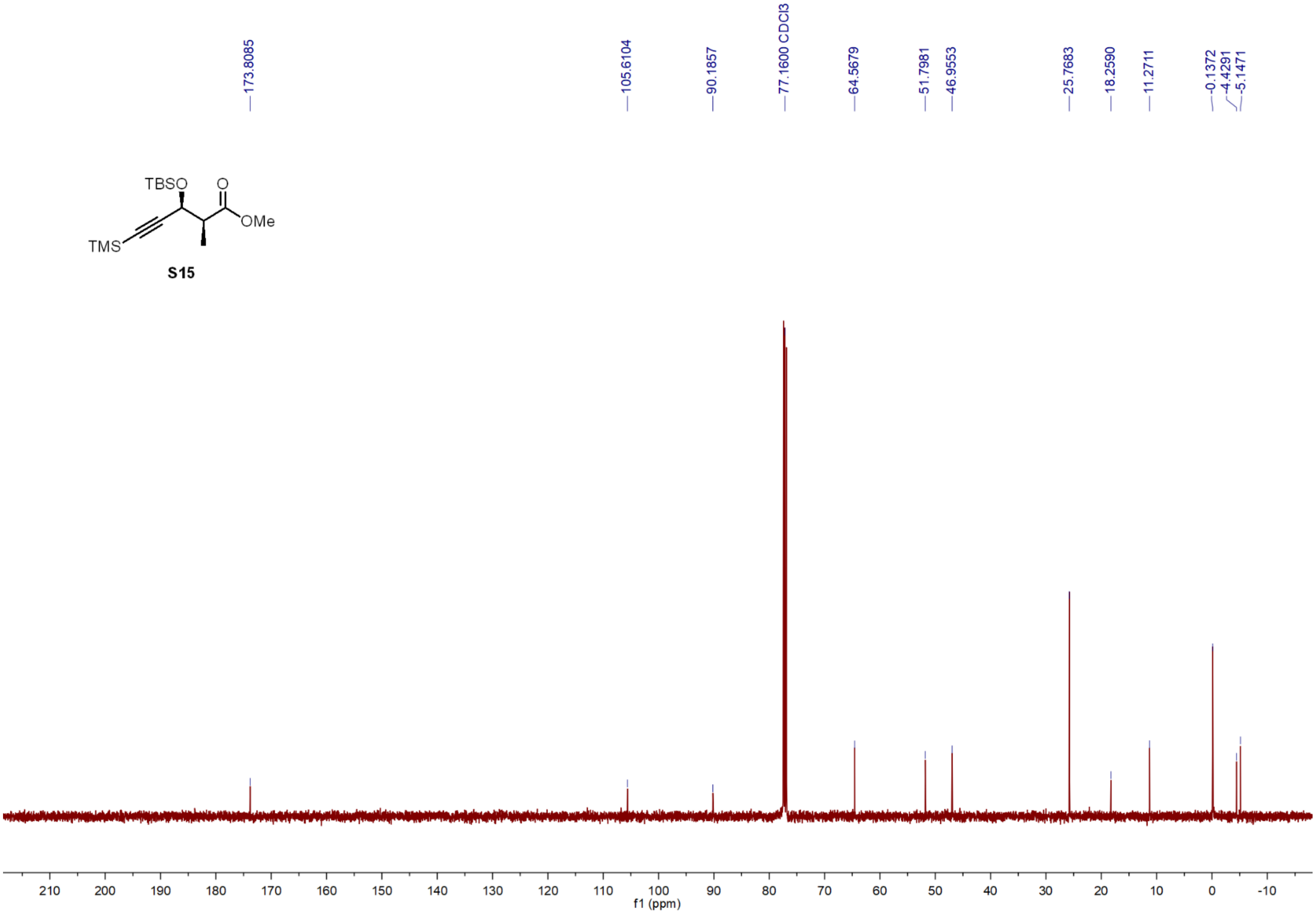


Figure S112. The 125 MHz ^{13}C-NMR of Compound **S15** in Chloroform-*d*

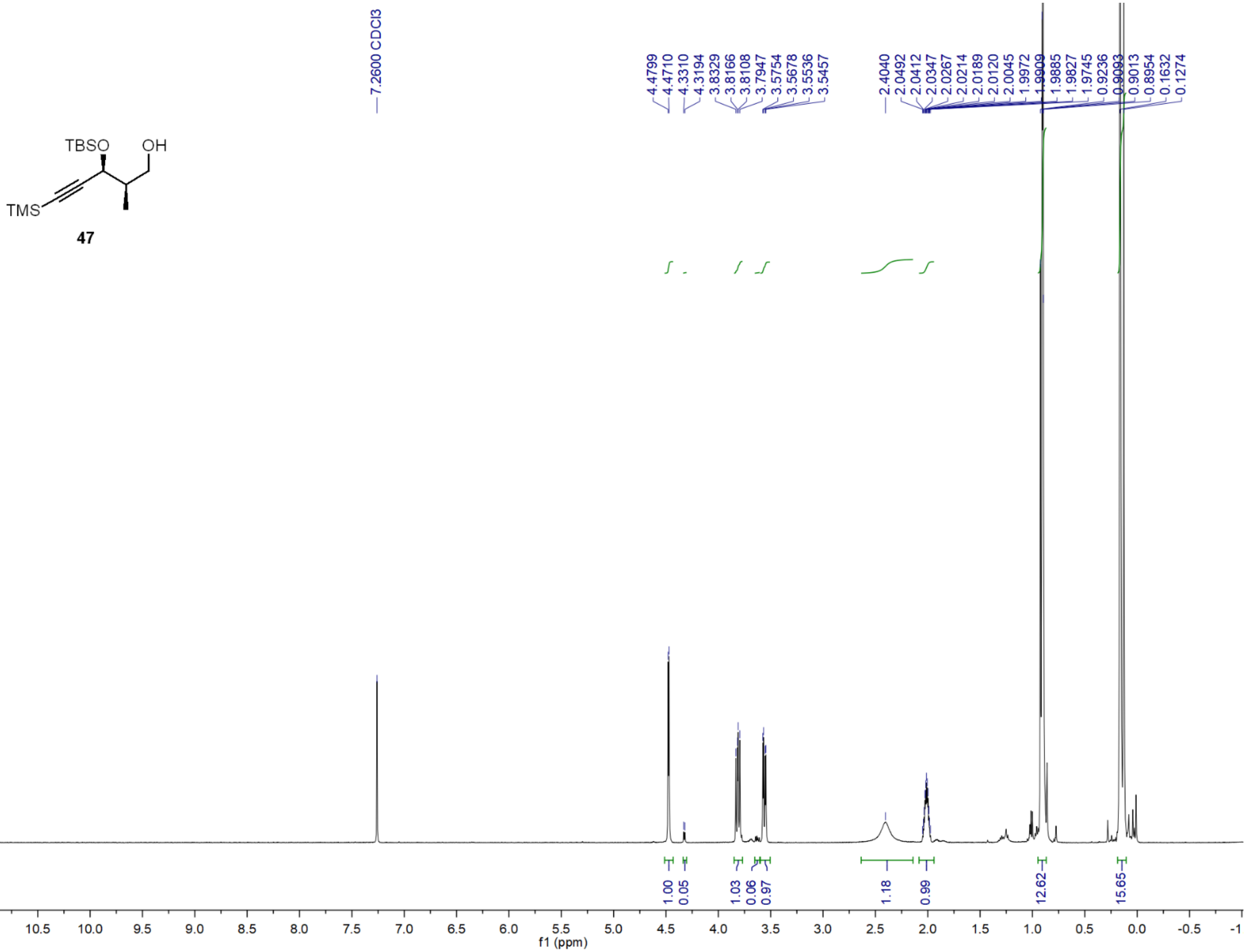


Figure S113. The 500 MHz ^{1}H-NMR of Compound **47** in Chloroform-*d*

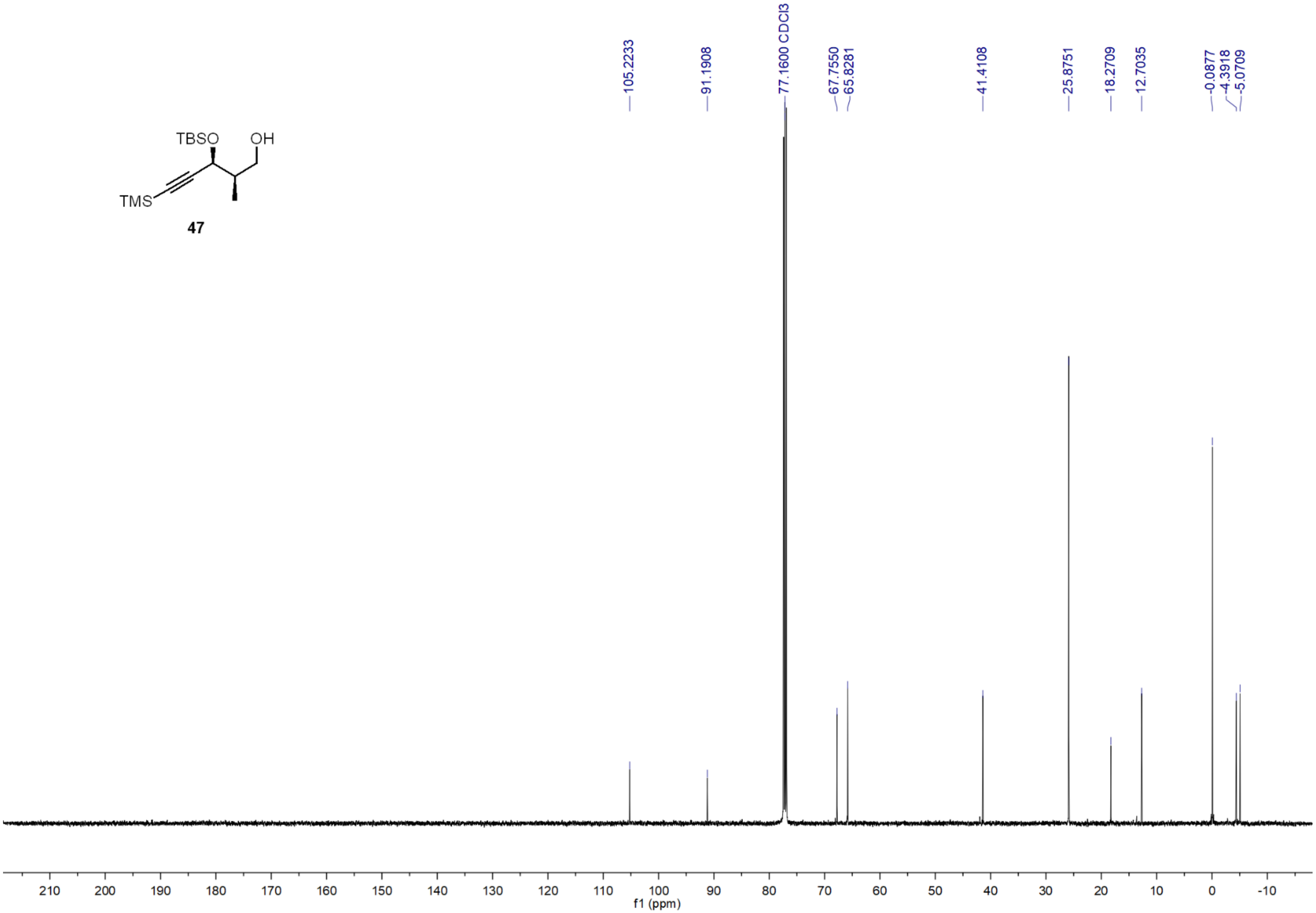


Figure S114. The 125 MHz ^{13}C-NMR of Compound **47** in Chloroform-*d*

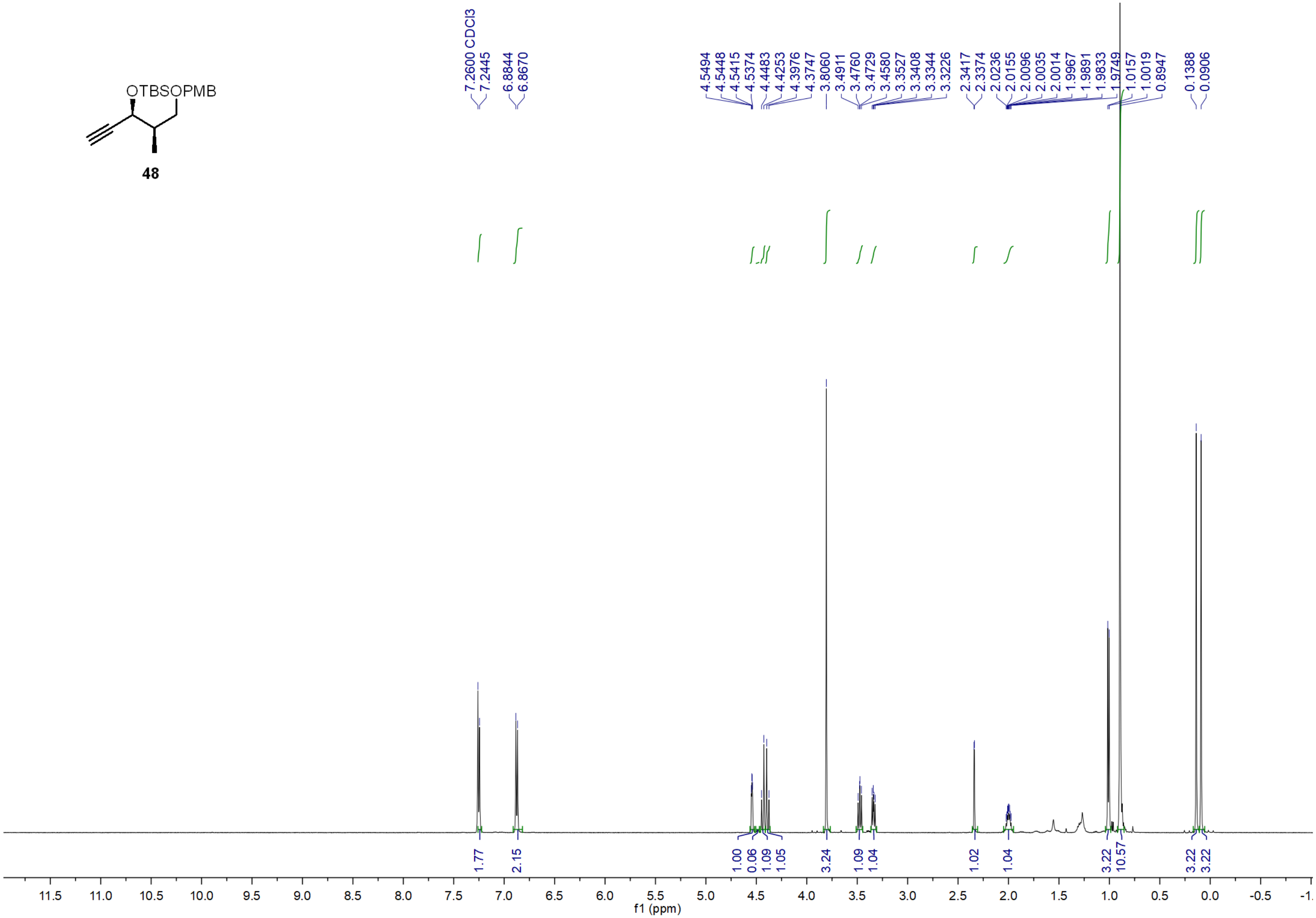
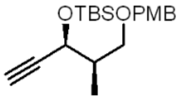


Figure S115. The 500 MHz ^{1}H-NMR of Compound **48** in Chloroform-*d*



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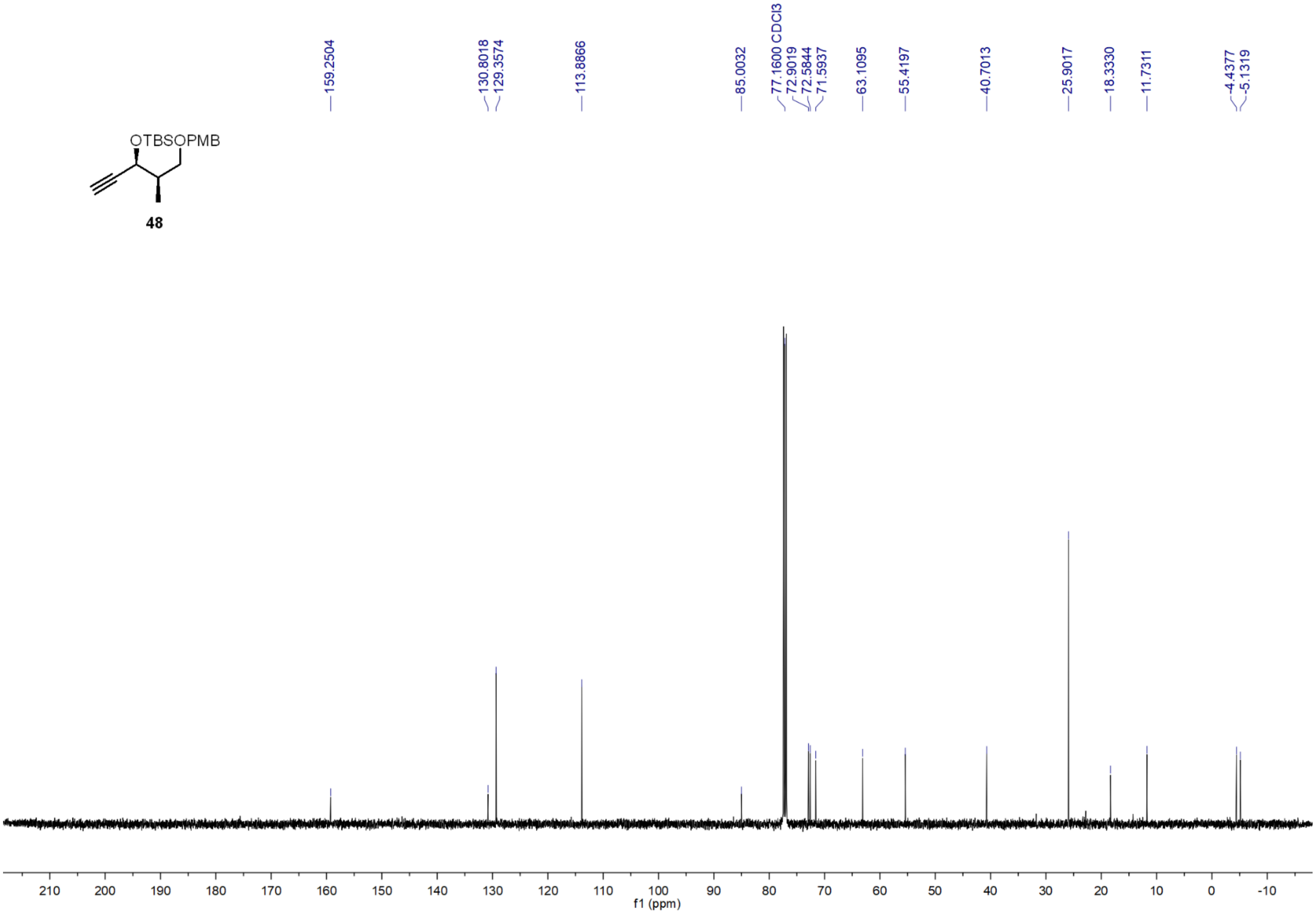


Figure S116. The 125 MHz ^{13}C-NMR of Compound **48** in Chloroform-*d*

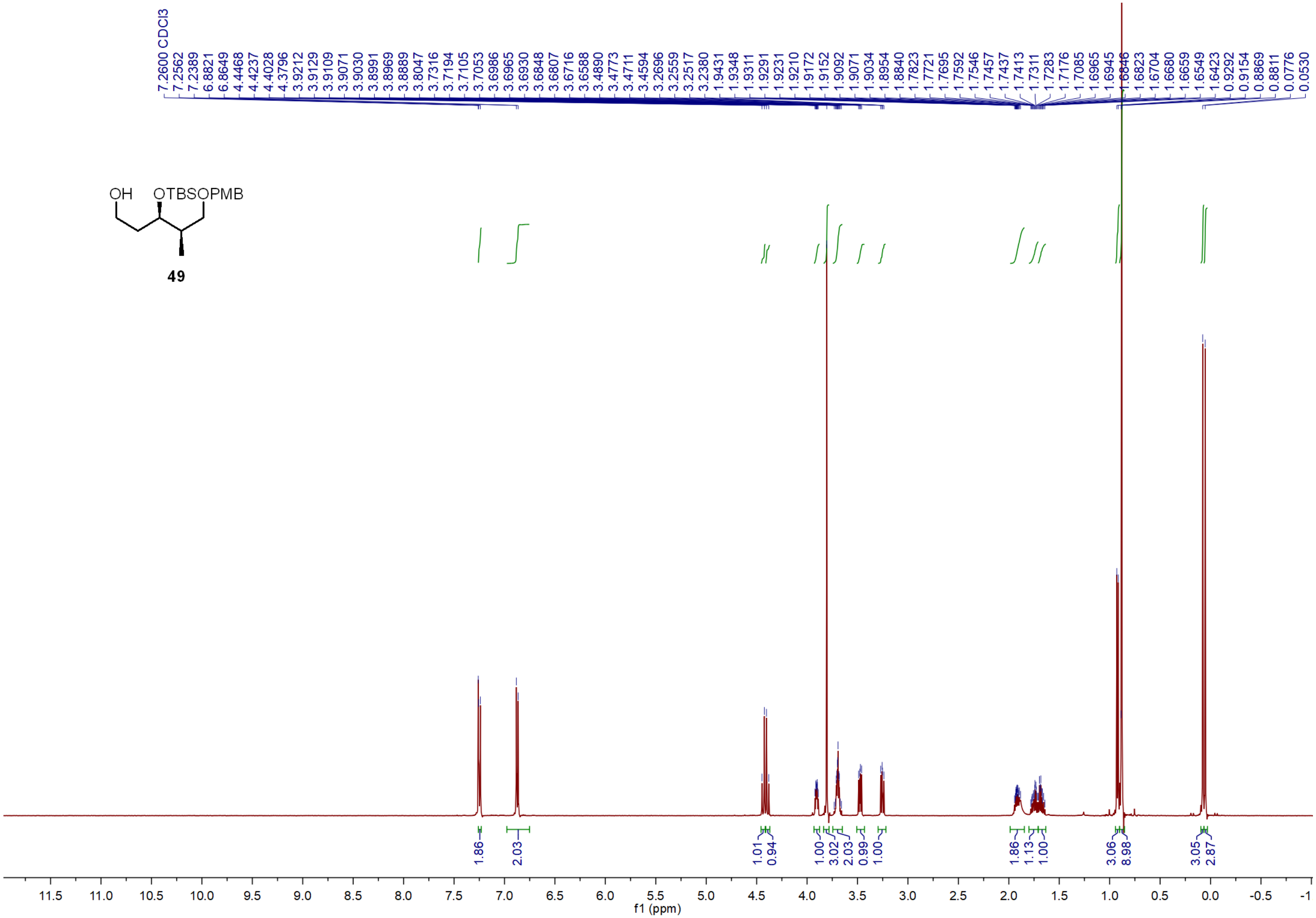


Figure S117. The 500 MHz ^{1}H-NMR of Compound **49** in Chloroform-*d*

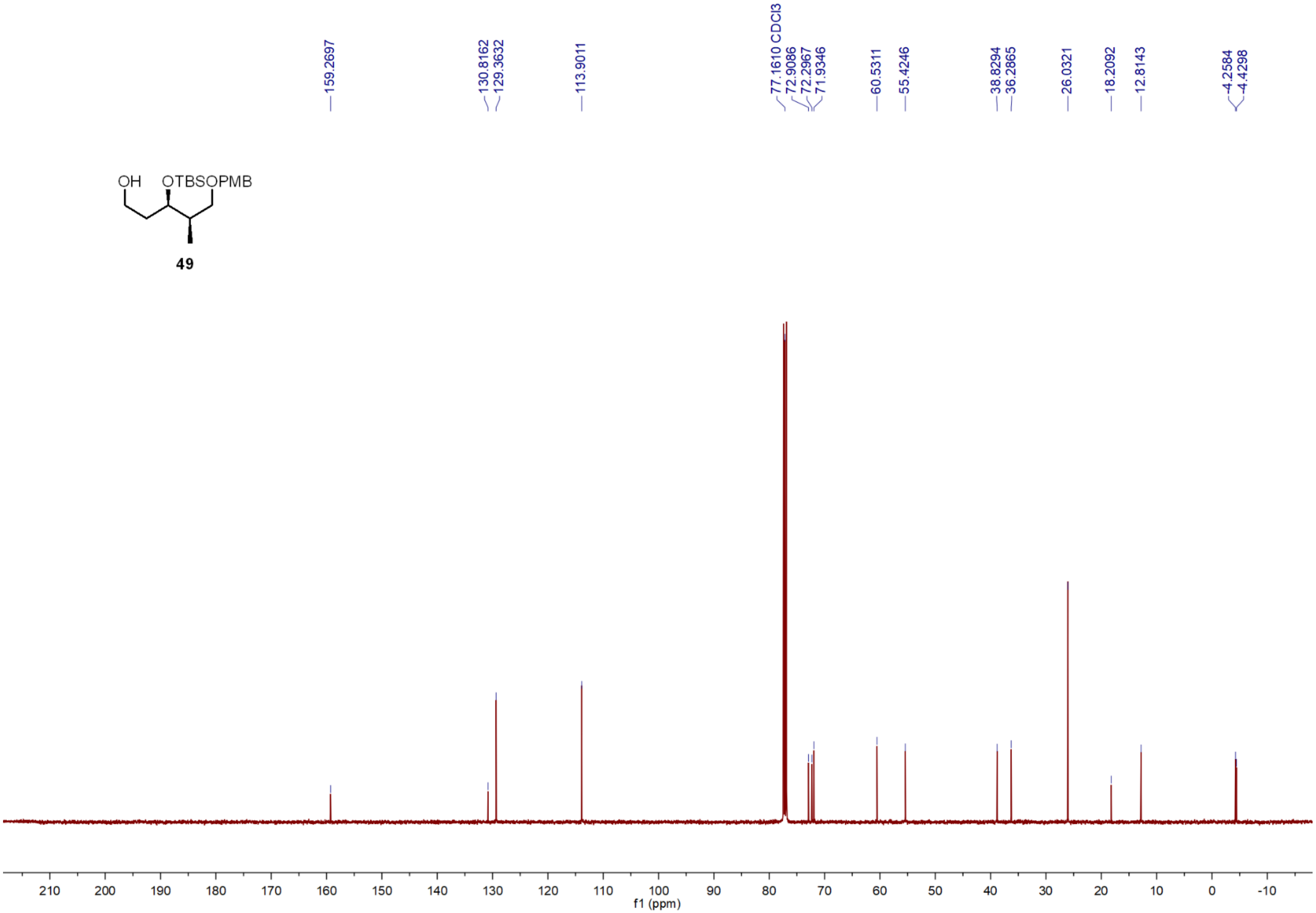


Figure S118. The 125 MHz ^{13}C-NMR of Compound **49** in Chloroform-*d*

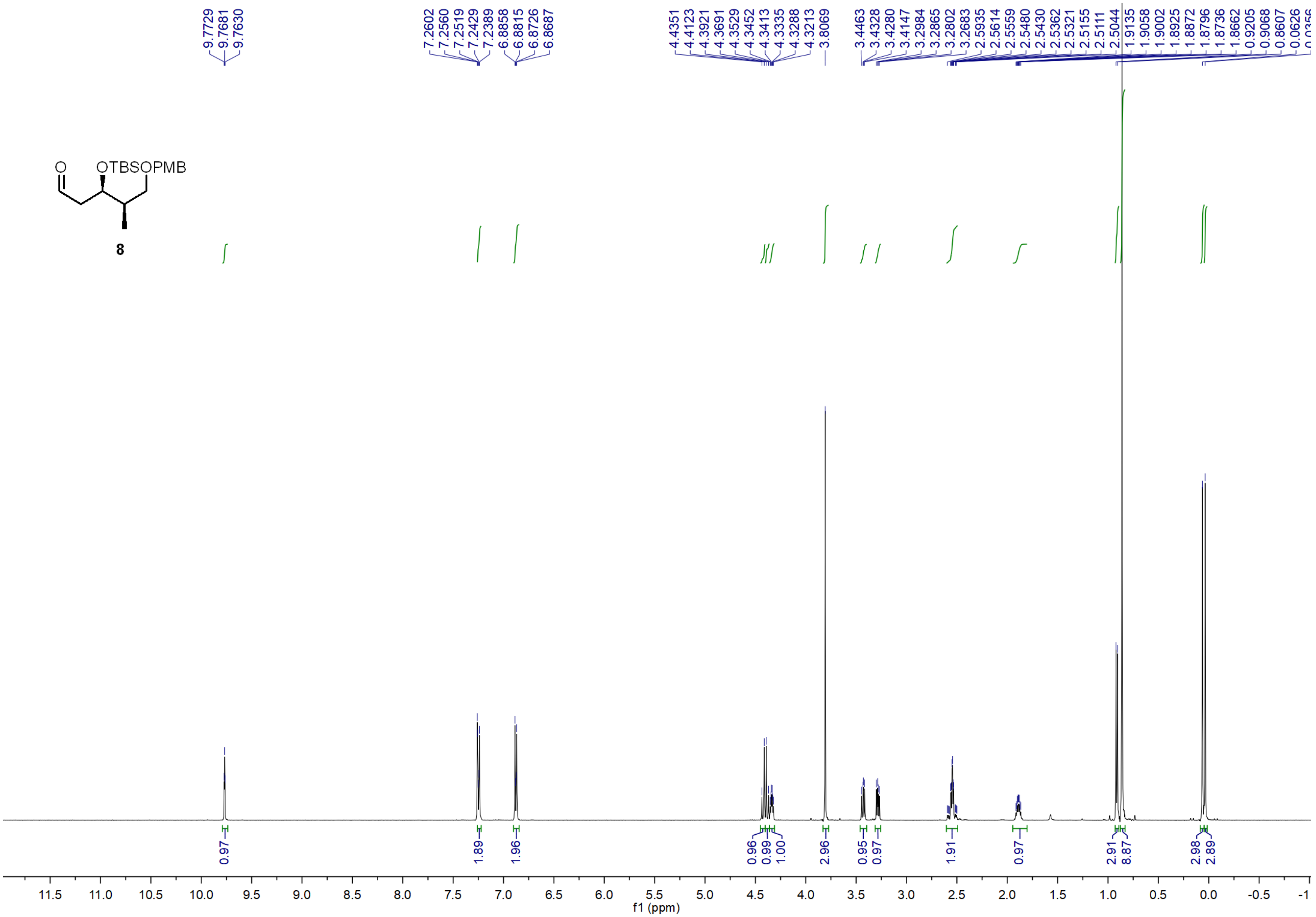


Figure S119. The 500 MHz ^{1}H-NMR of Compound **8** in Chloroform-*d*

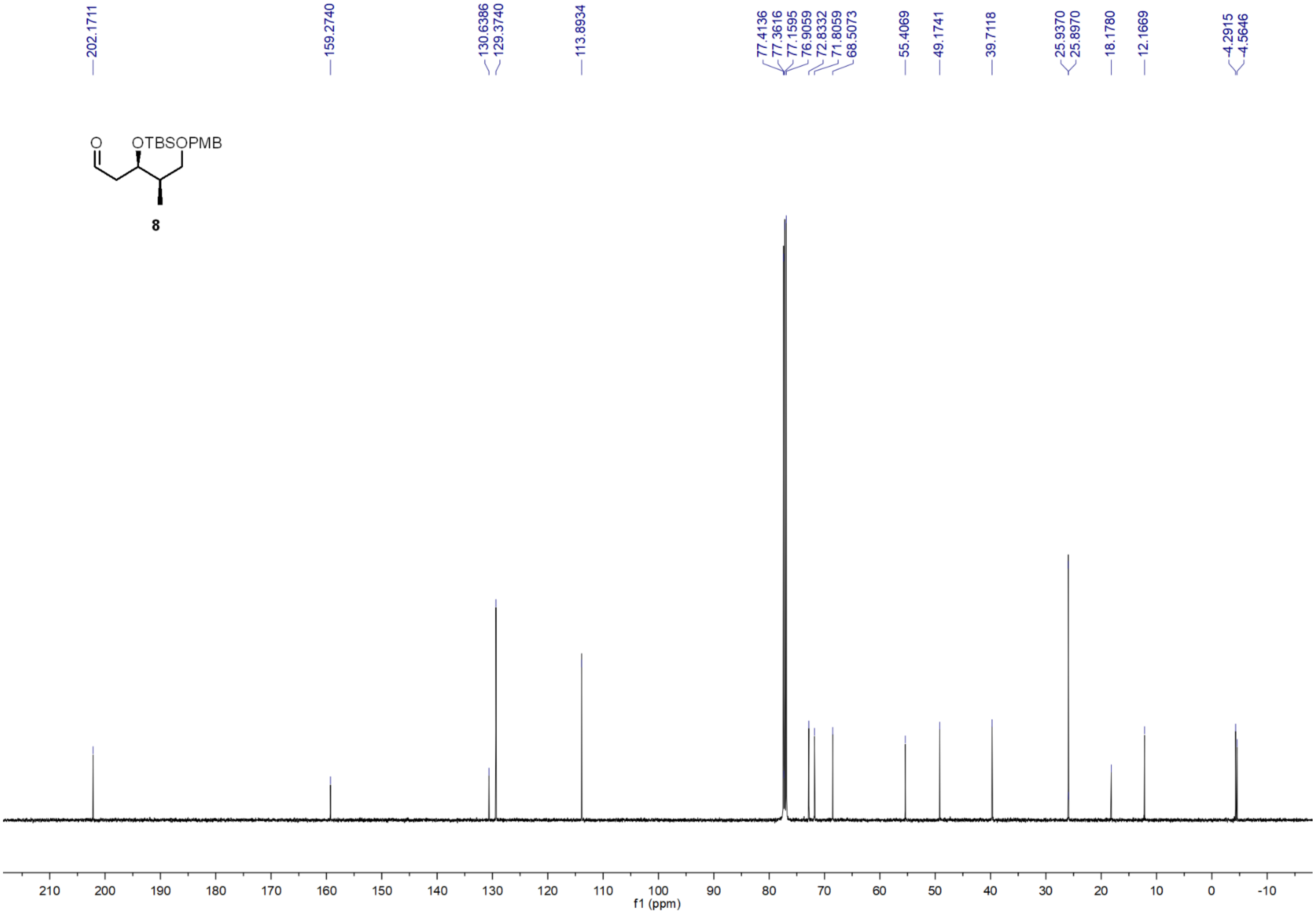


Figure S120. The 125 MHz ^{13}C-NMR of Compound **8** in Chloroform-*d*

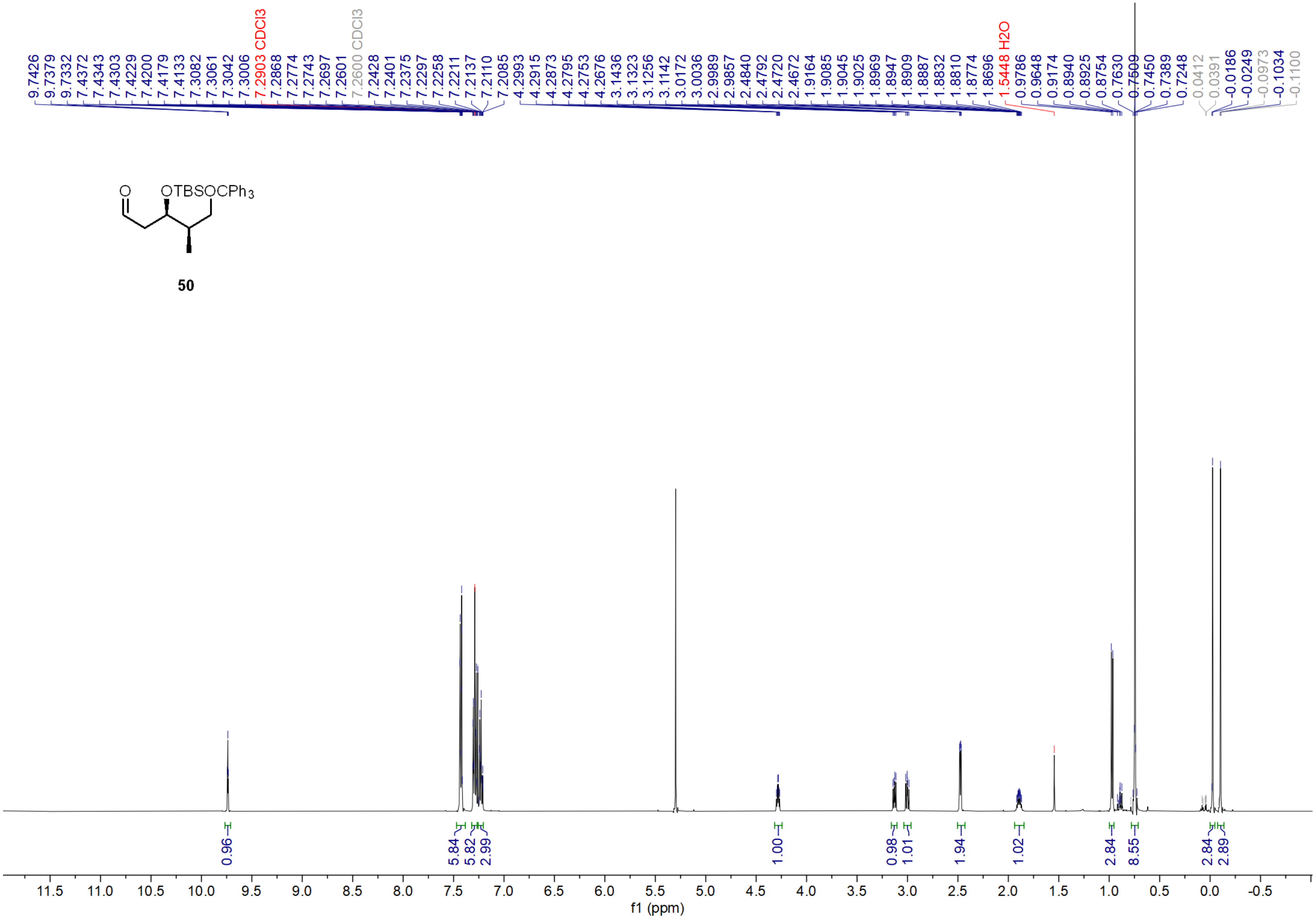


Figure S121. The 500 MHz ^{1}H-NMR of Compound **50** in Chloroform-*d*

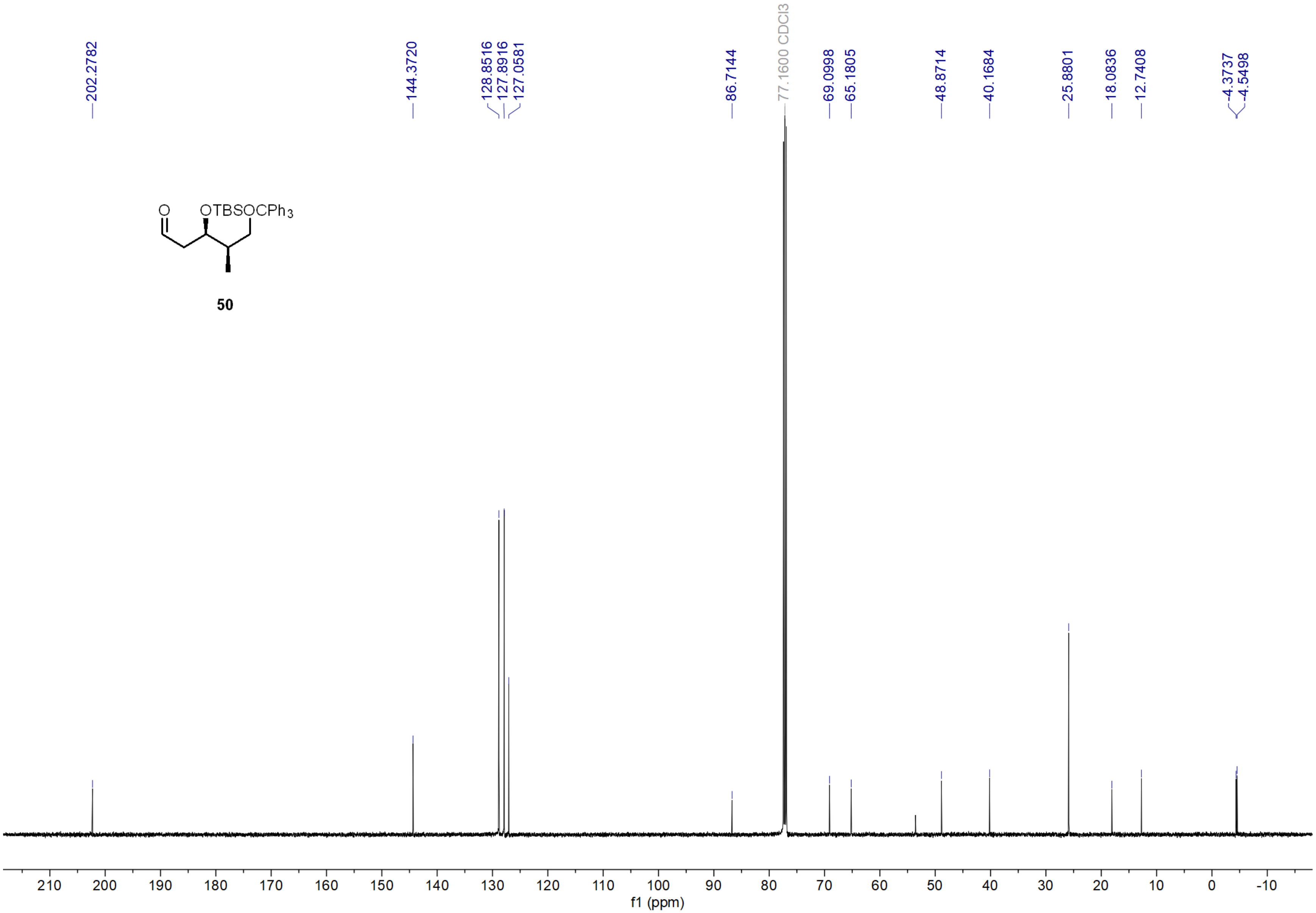


Figure S122. The 125 MHz ^{13}C-NMR of Compound **50** in Chloroform-*d*

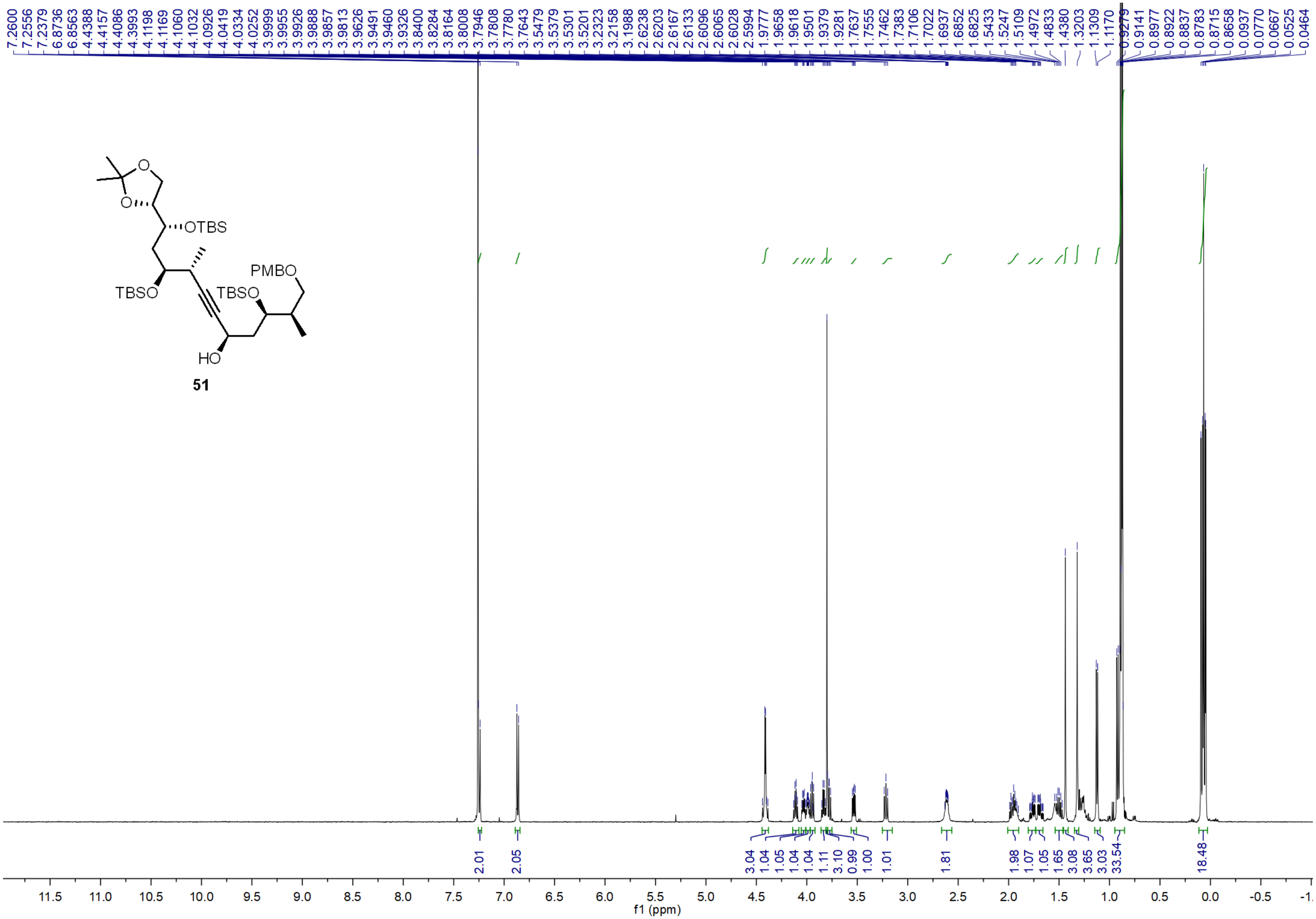


Figure S123. The 500 MHz ^{1}H-NMR of Compound **51** in Chloroform-*d*

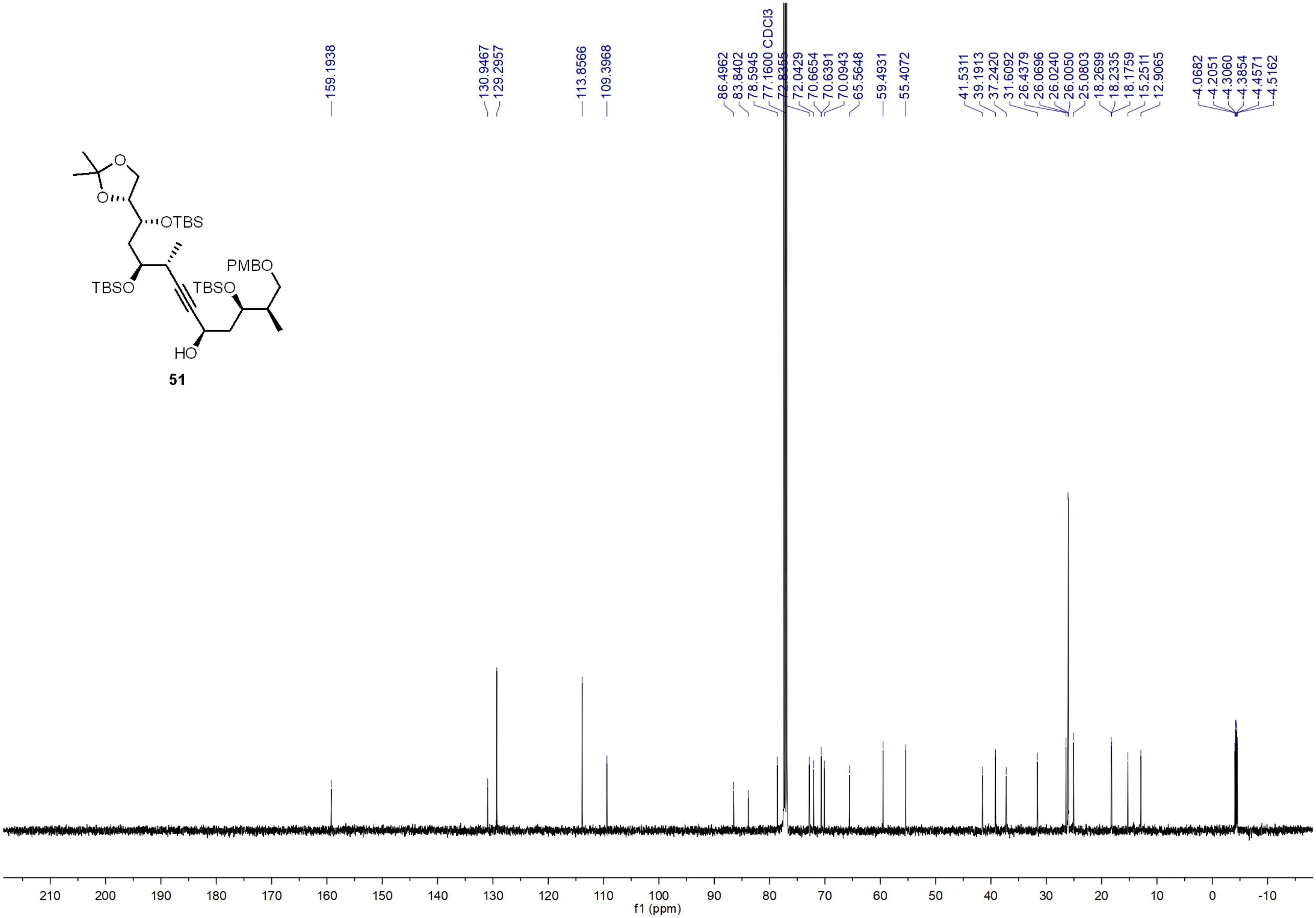


Figure S124. The 125 MHz ^{13}C-NMR of Compound **51** in Chloroform-*d*

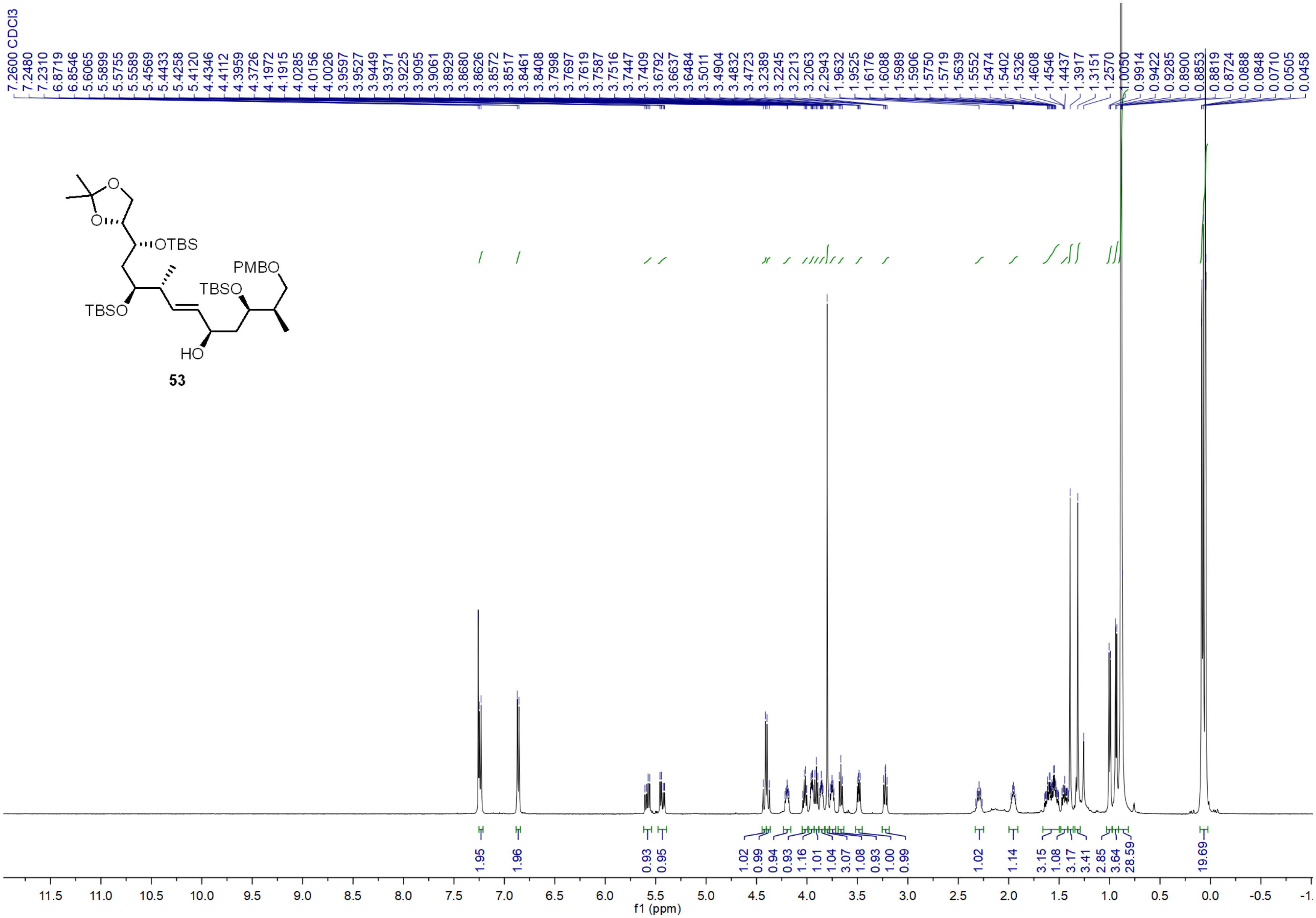
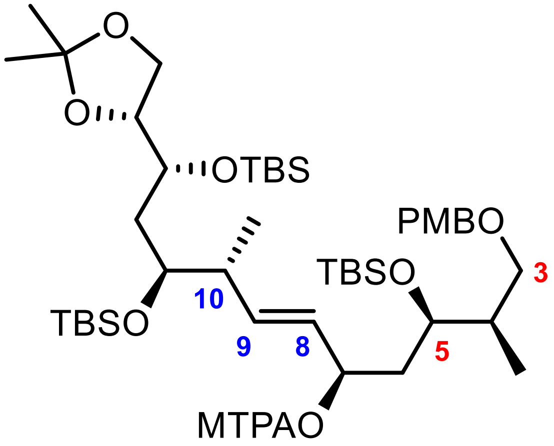


Figure S125. The 500 MHz ^{1}H-NMR of Compound **53** in Chloroform-*d*

Table S27. Mosher ester stereochemical confirmation of compound **53**



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$\Delta\delta = \delta_S - \delta_R$

No.	δ_S	δ_R	$\Delta\delta$
3	3.4915	3.4807	0.0108
5	3.2040	3.1666	0.0374
8	5.4091	5.5273	-0.1182
9	5.7982	5.8748	-0.0766
10	2.3058	2.3393	-0.0335

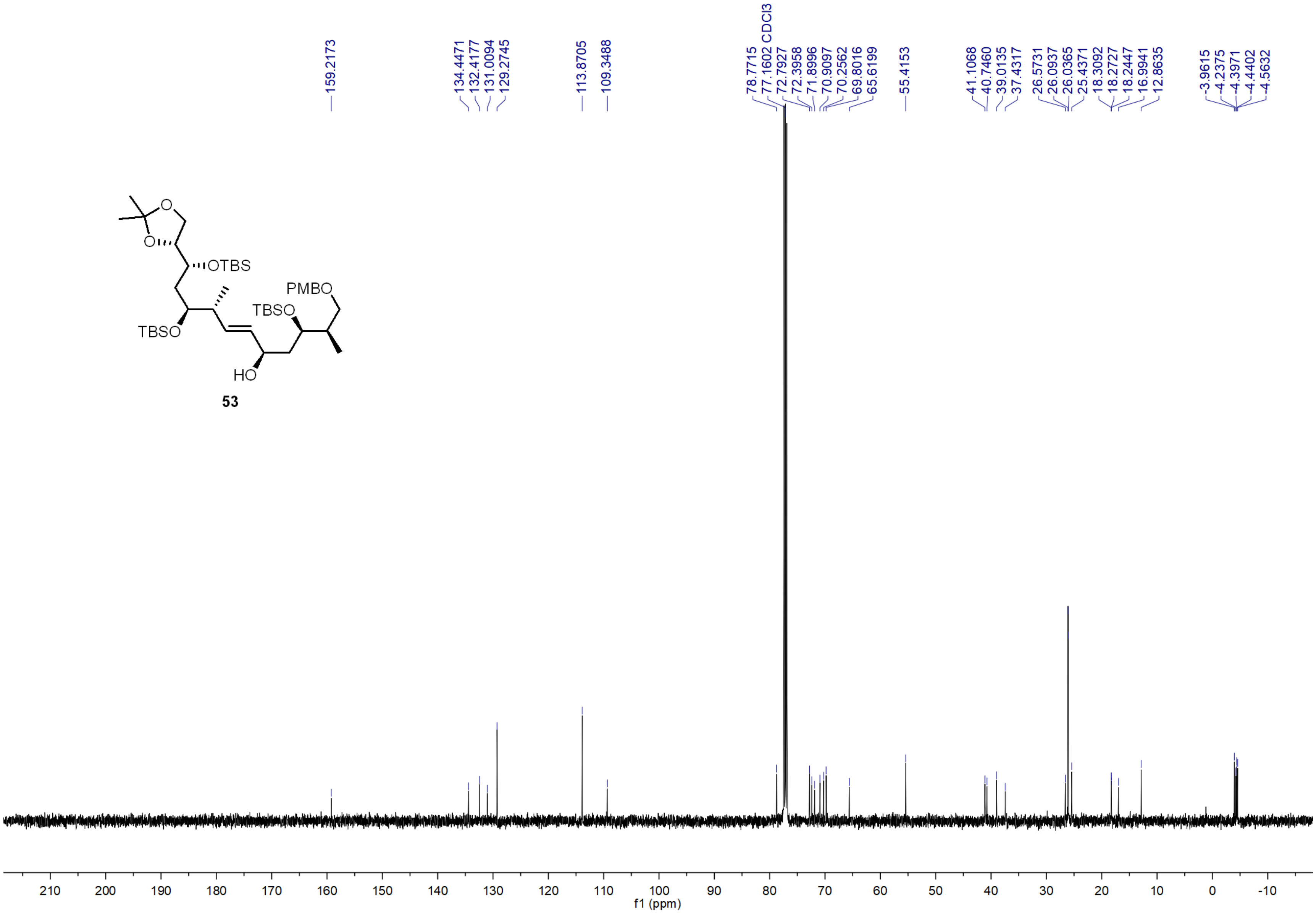
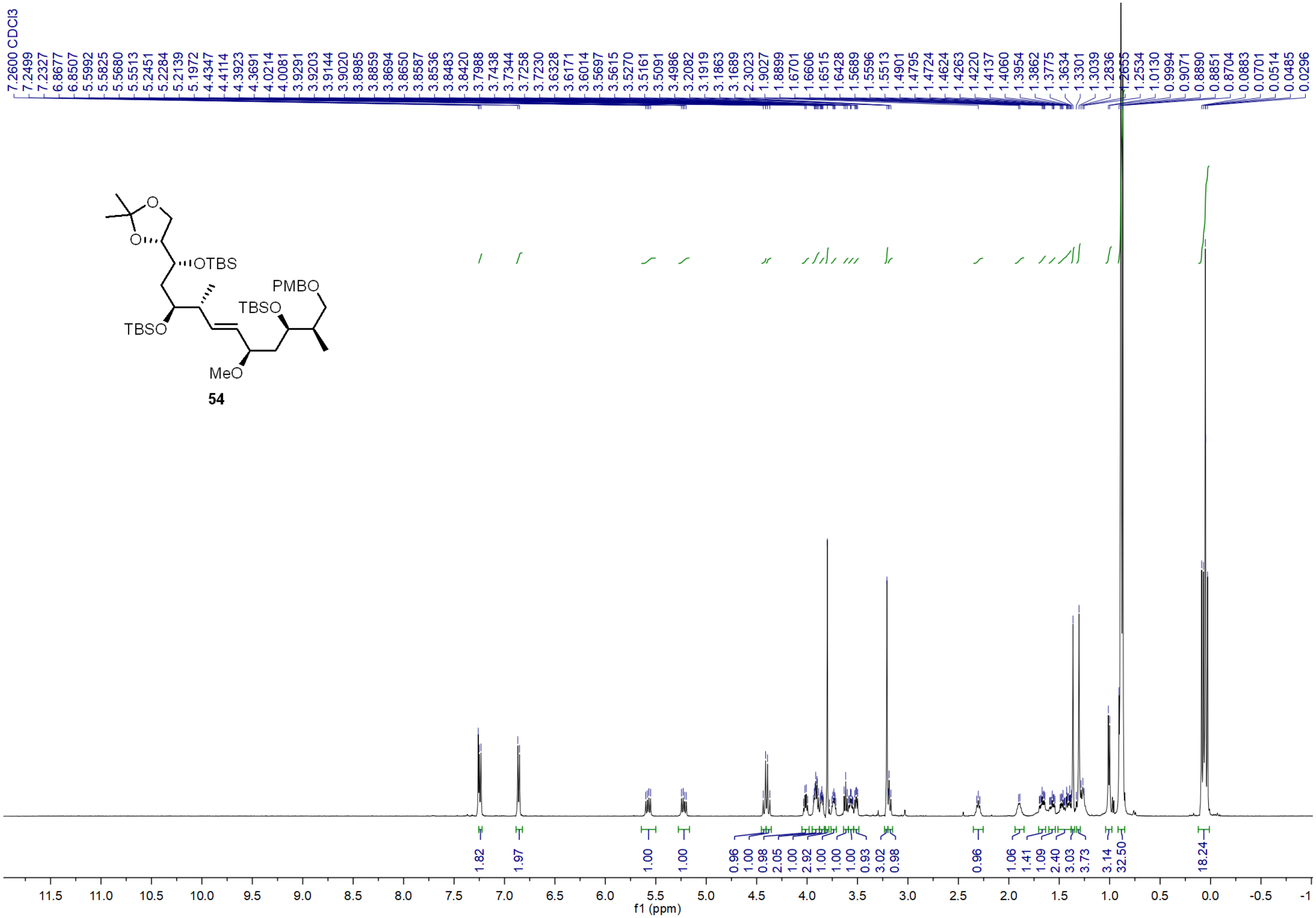


Figure S126. The 125 MHz ^{13}C-NMR of Compound **53** in Chloroform-*d*



54

Figure S127. The 500 MHz ^{1}H-NMR of Compound **54** in Chloroform-*d*

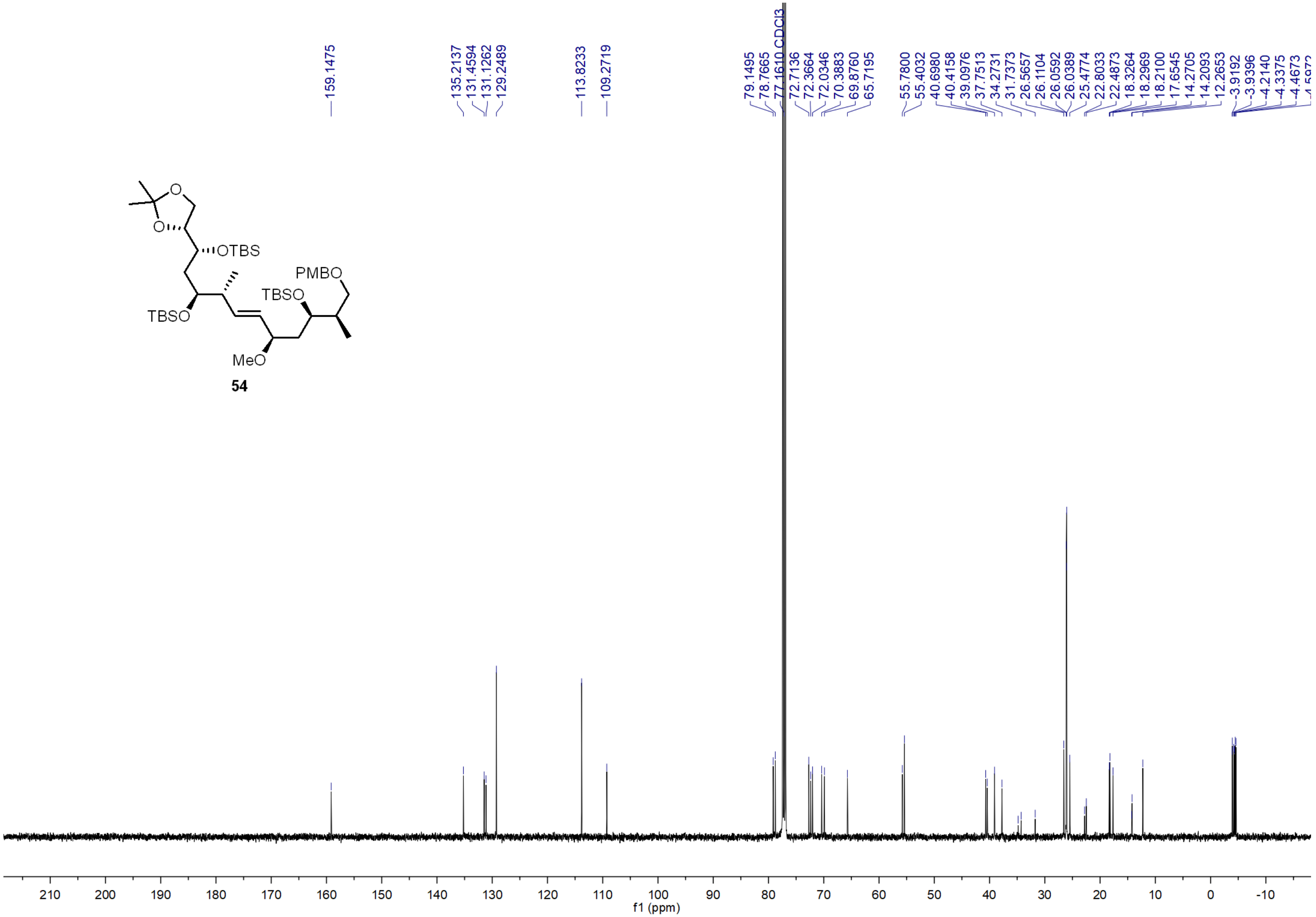


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Figure S128. The 125 MHz ^{13}C-NMR of Compound **54** in Chloroform-*d*

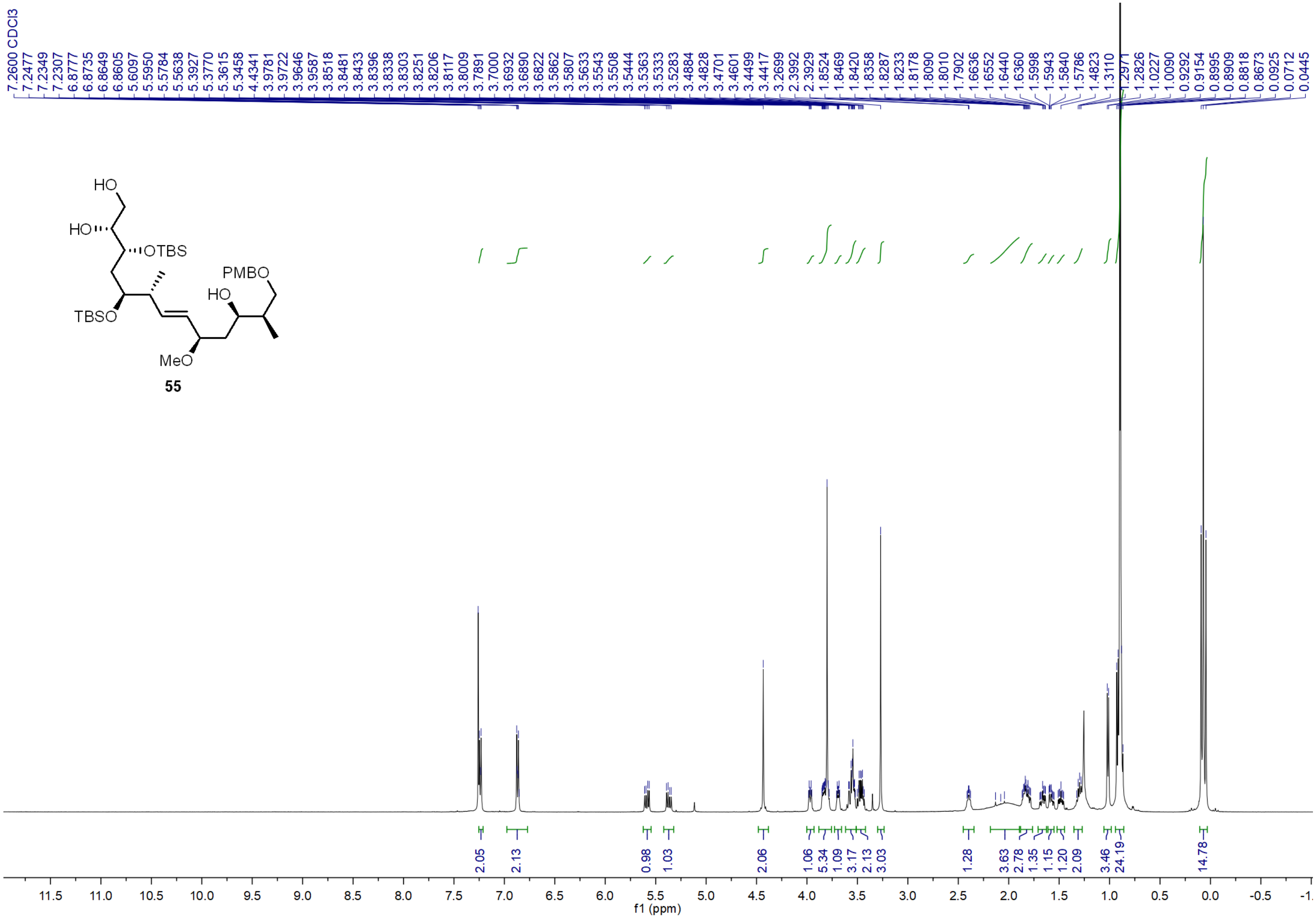

Figure S129. The 125 MHz ^{13}C-NMR of Compound **55** in Chloroform-*d*

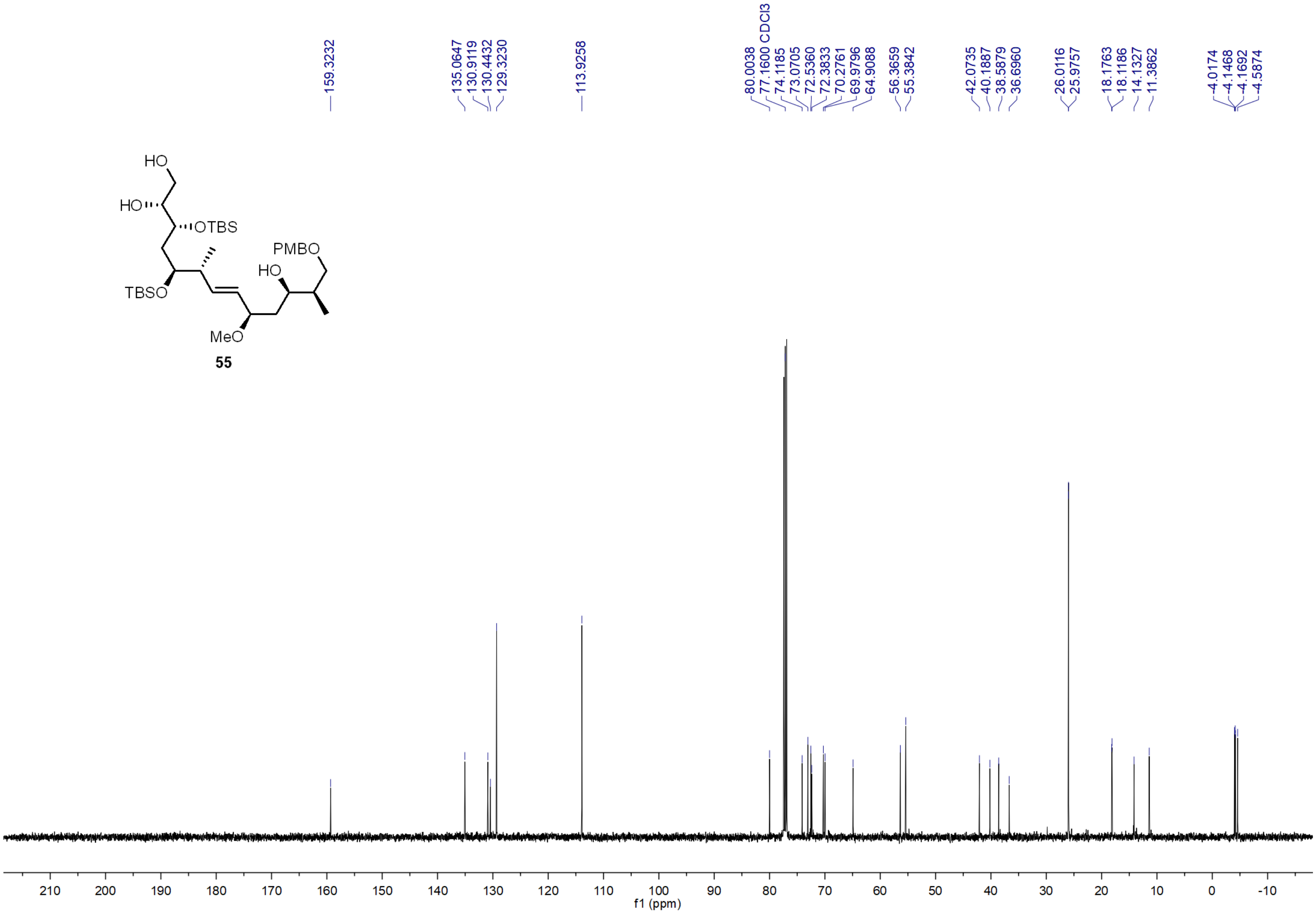

Figure S130. The 125 MHz ^{13}C-NMR of Compound **55** in Chloroform-*d*

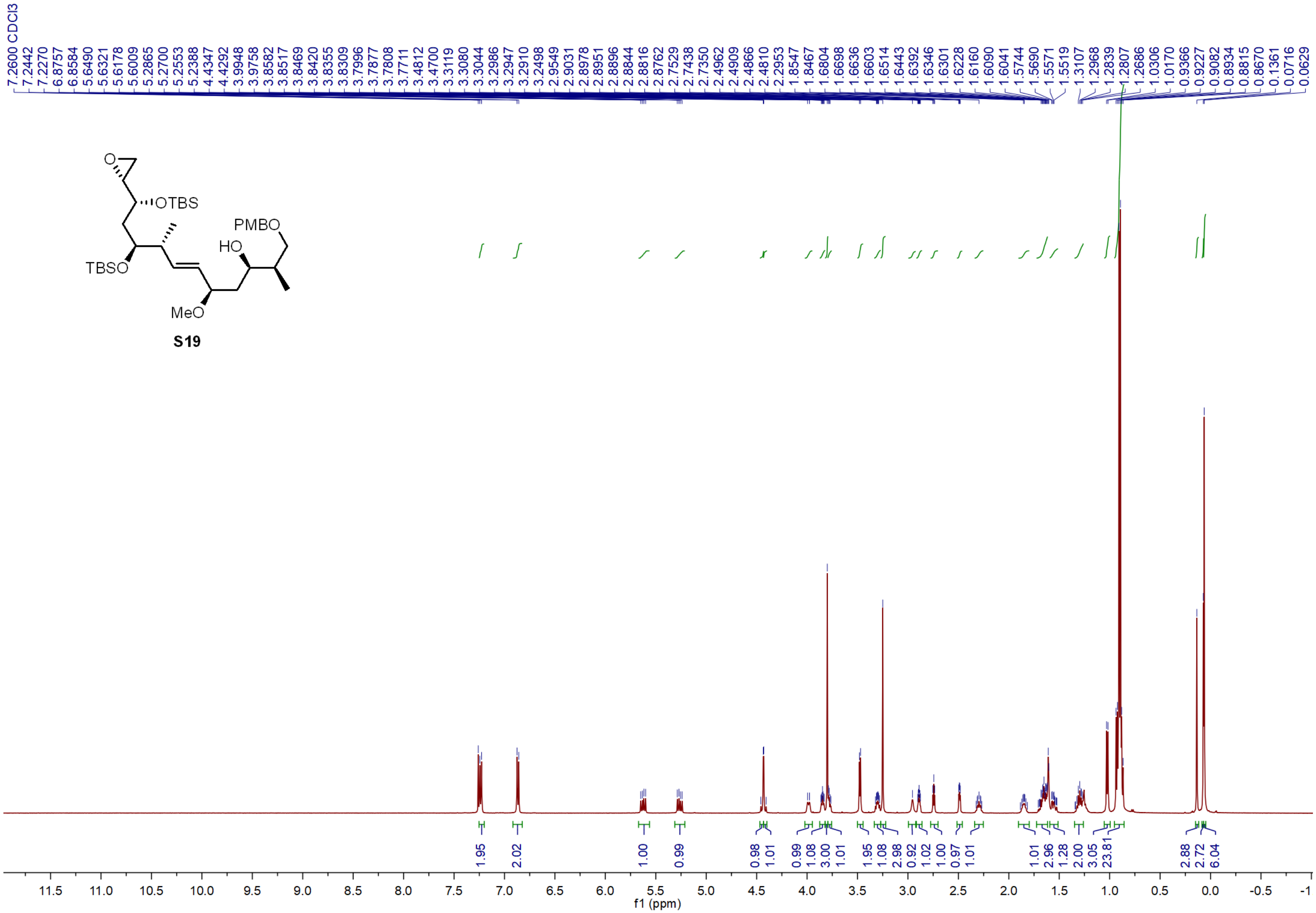

Figure S131. The 500 MHz ^{1}H-NMR of Compound **S19** in Chloroform-*d*

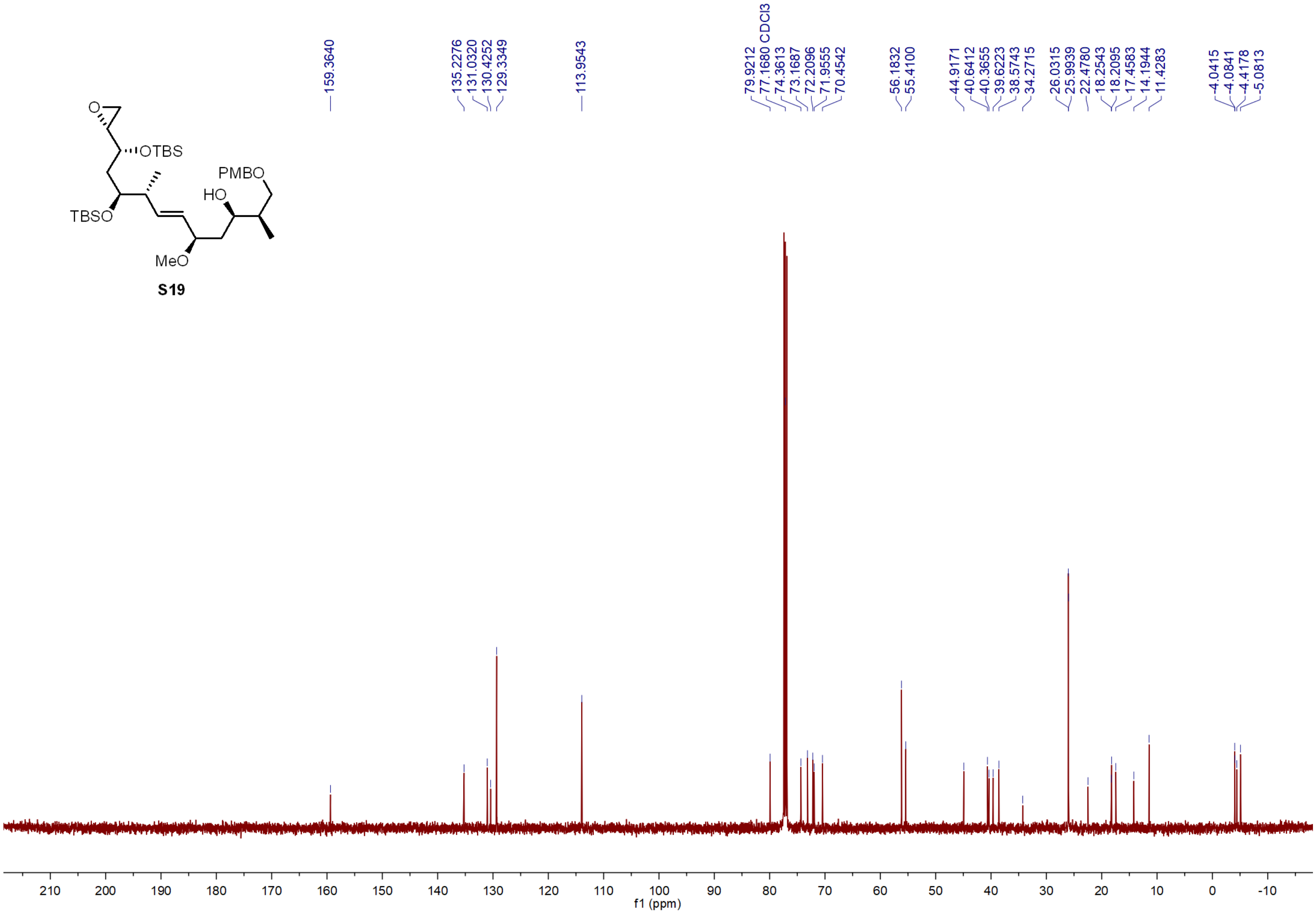

Figure S132. The 125 MHz ^{13}C-NMR of Compound **S19** in Chloroform-*d*

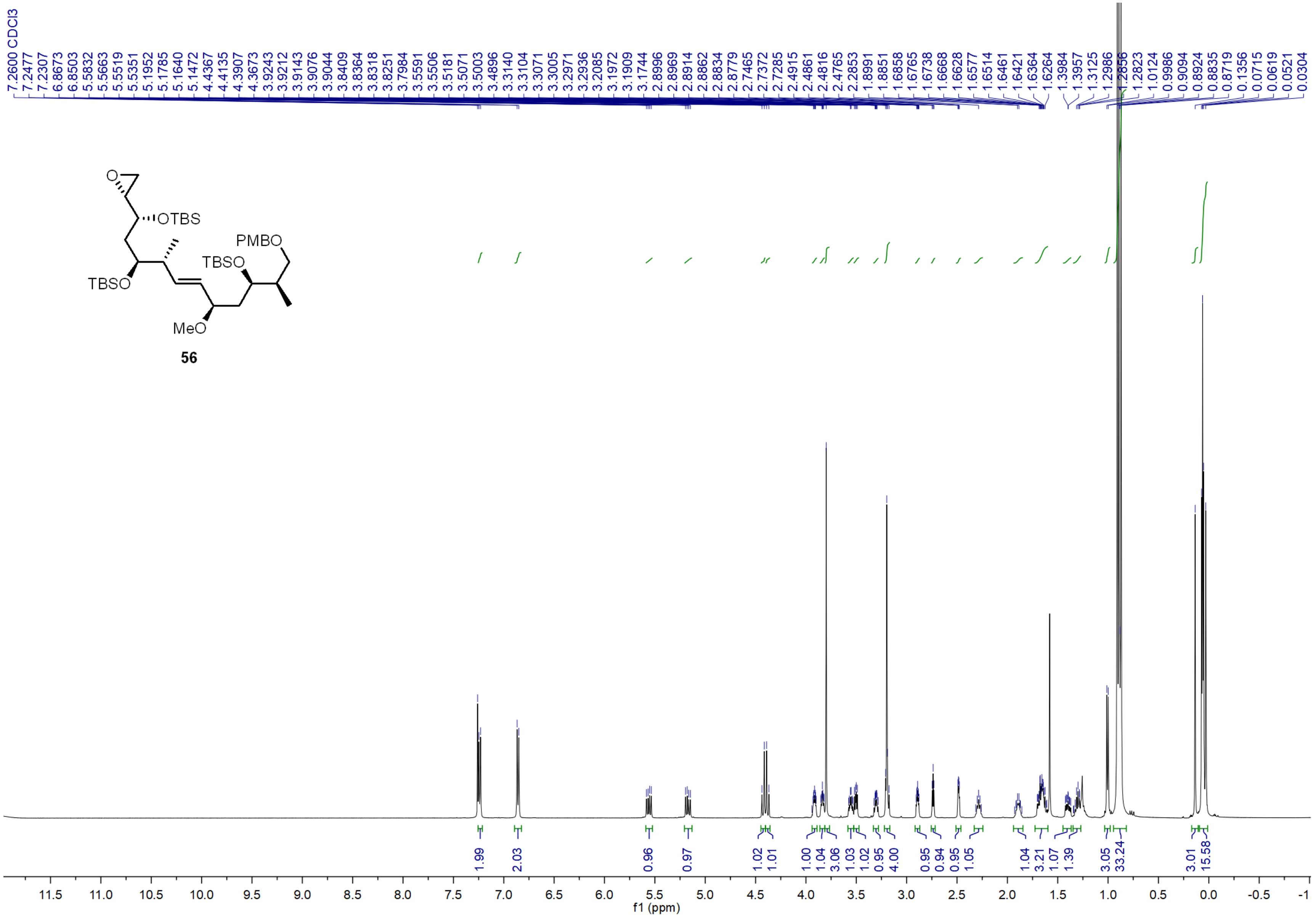

Figure S133. The 500 MHz ^{1}H-NMR of Compound **56** in Chloroform-*d*

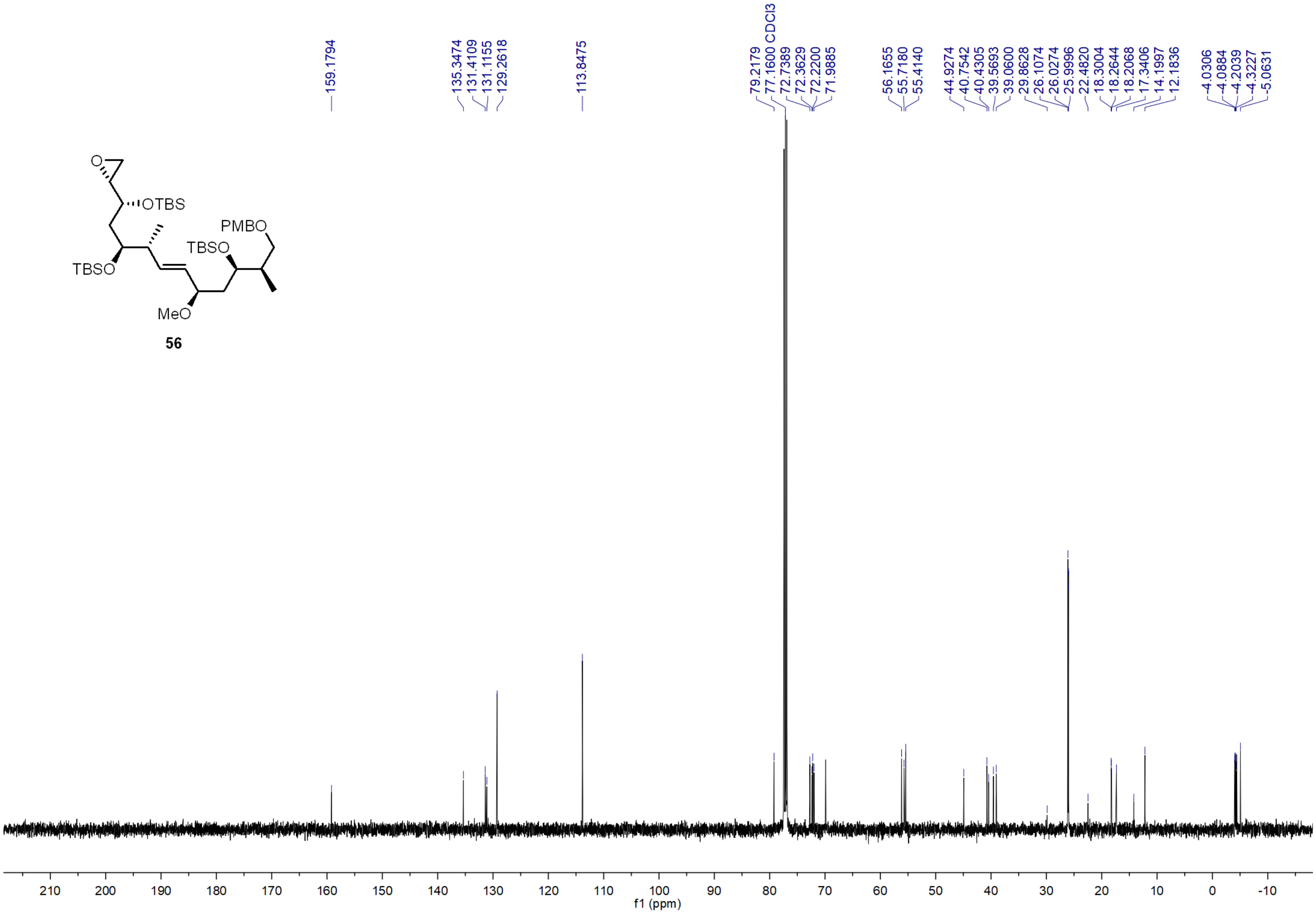

Figure S134. The 125 MHz ^{13}C-NMR of Compound **56** in Chloroform-*d*

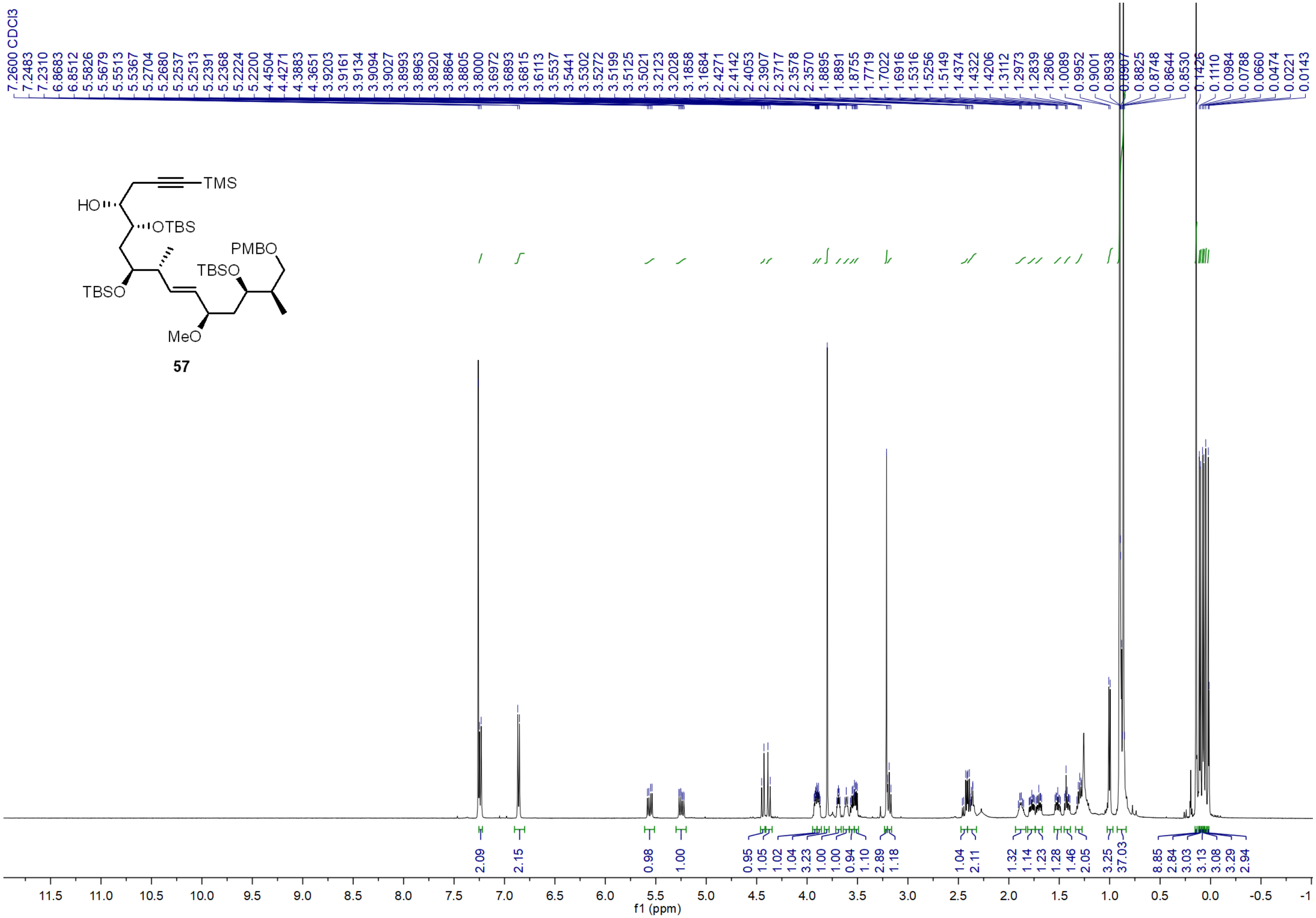

Figure S135. The 500 MHz ^{1}H-NMR of Compound **57** in Chloroform-*d*

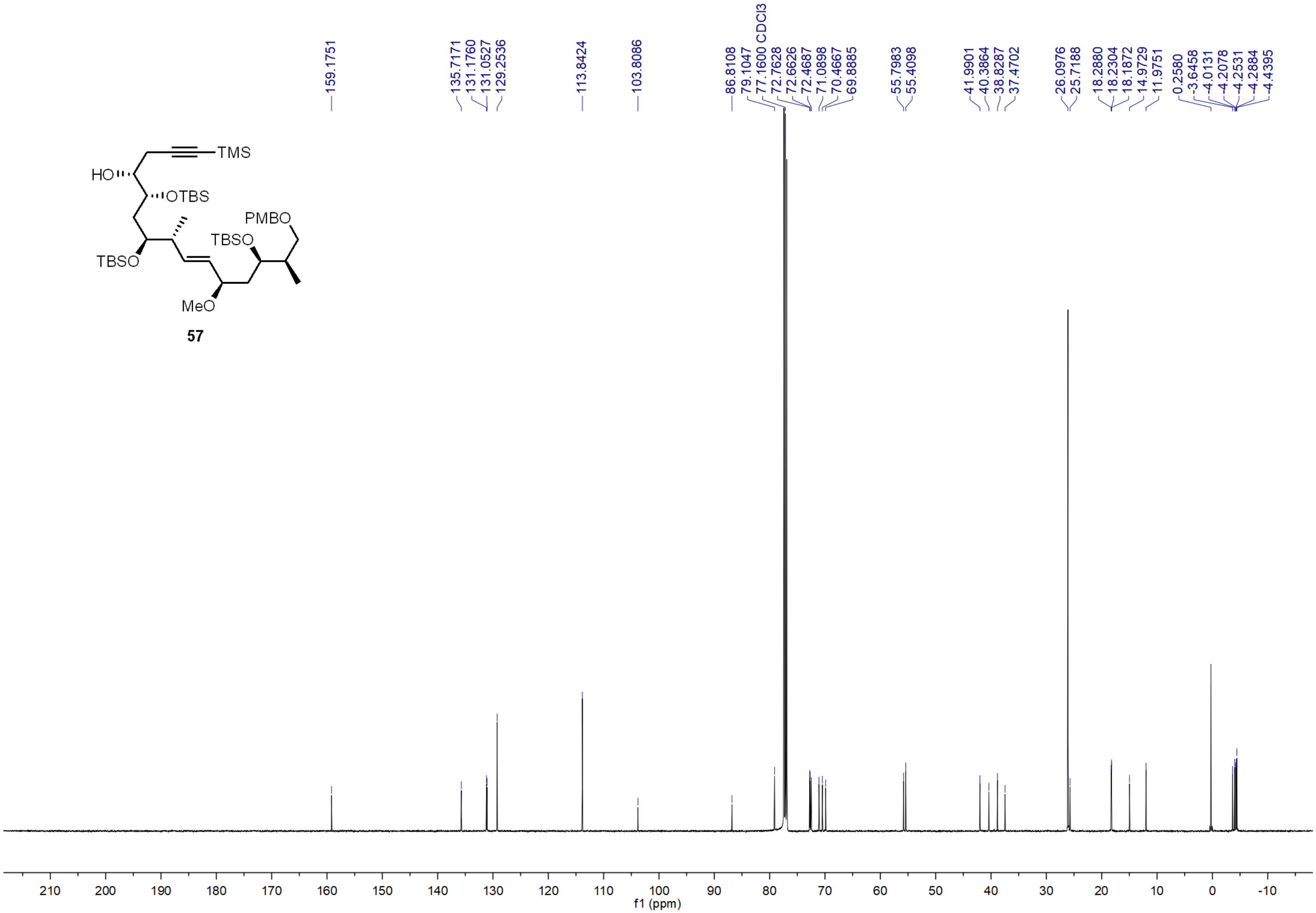

Figure S136. The 125 MHz ^{13}C-NMR of Compound **57** in Chloroform-*d*

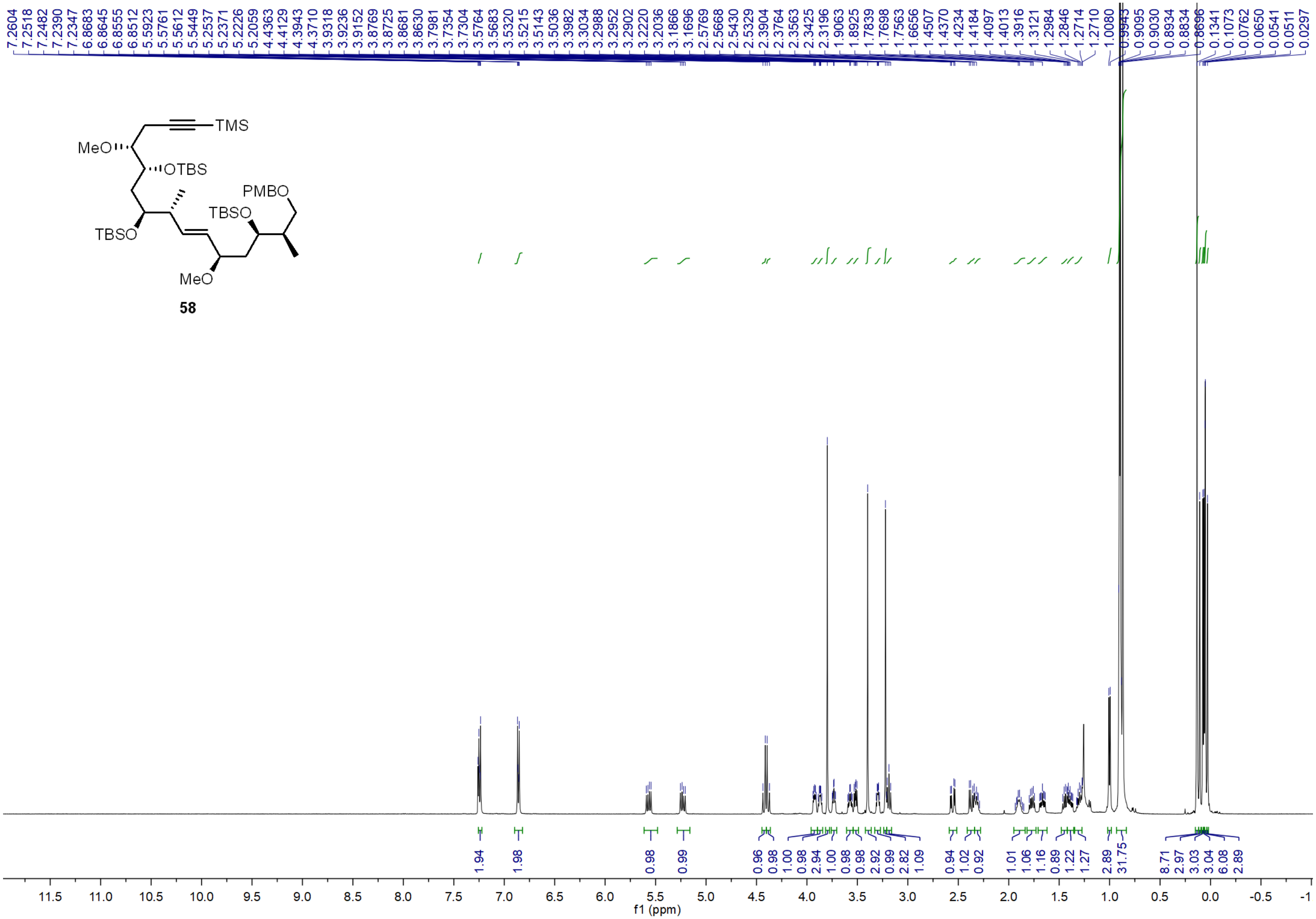

Figure S137. The 500 MHz ^{1}H-NMR of Compound **58** in Chloroform-*d*

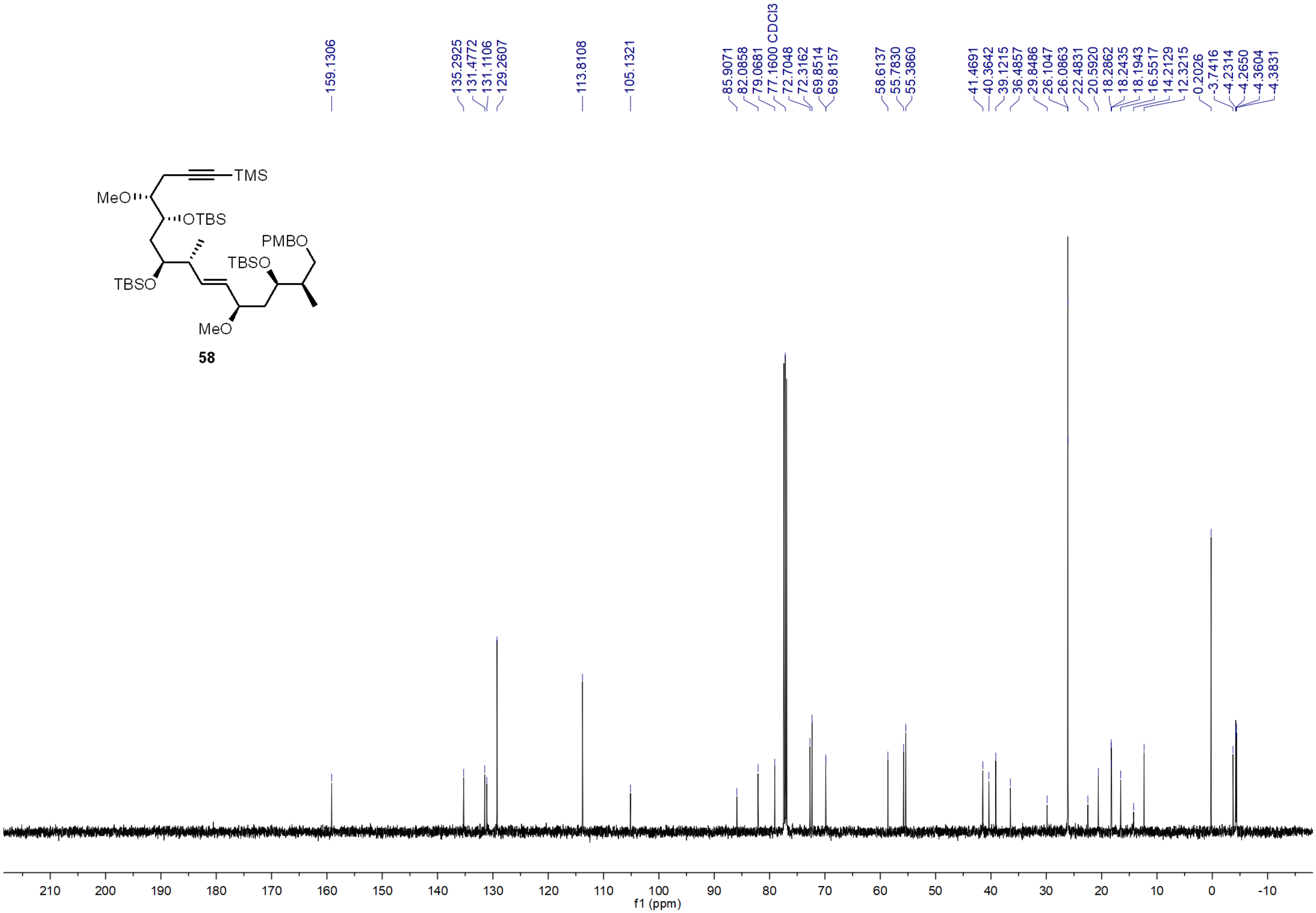

Figure S138. The 125 MHz ^{13}C-NMR of Compound **58** in Chloroform-*d*

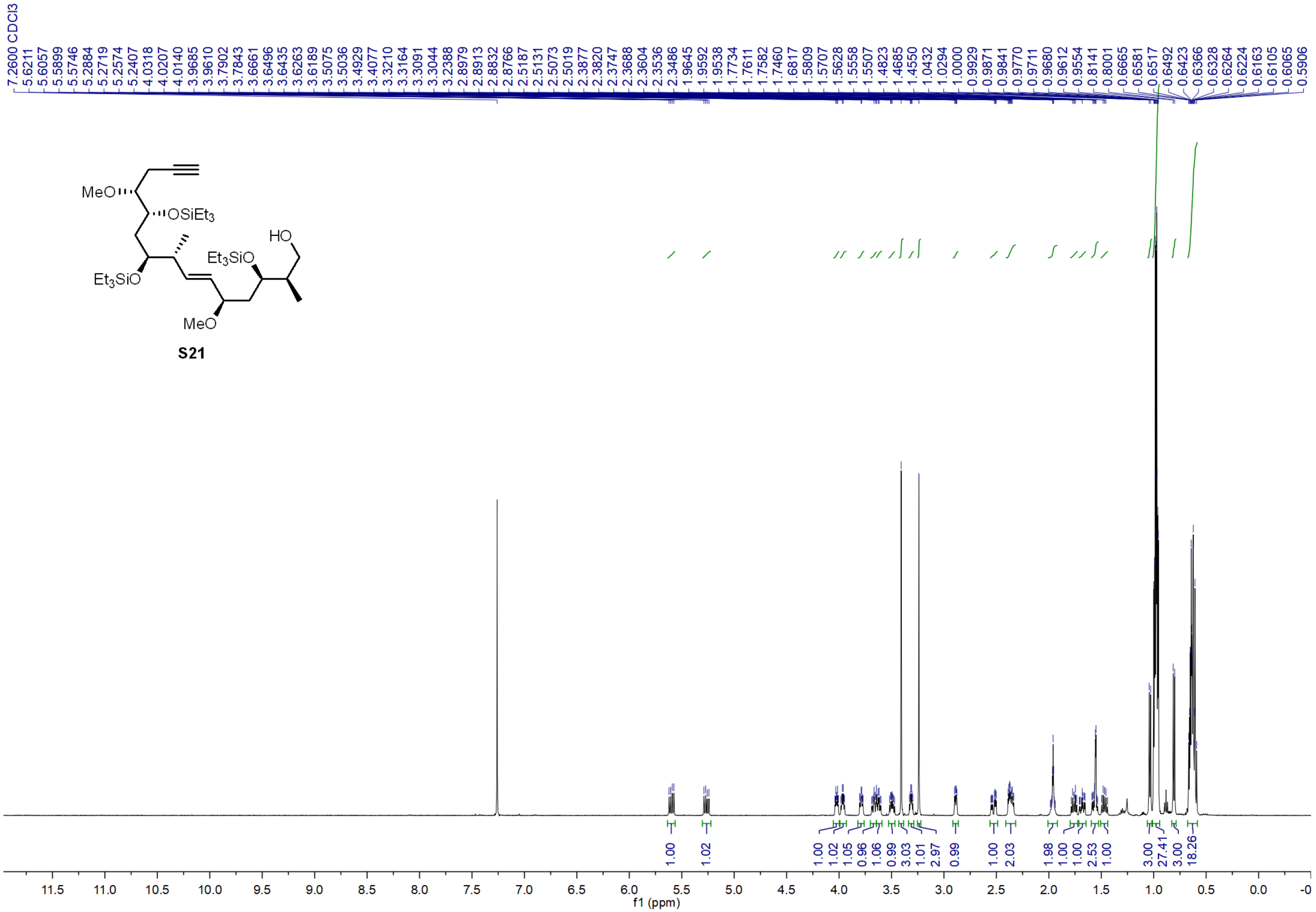

Figure S139. The 500 MHz ^{1}H-NMR of Compound **S21** in Chloroform-*d*

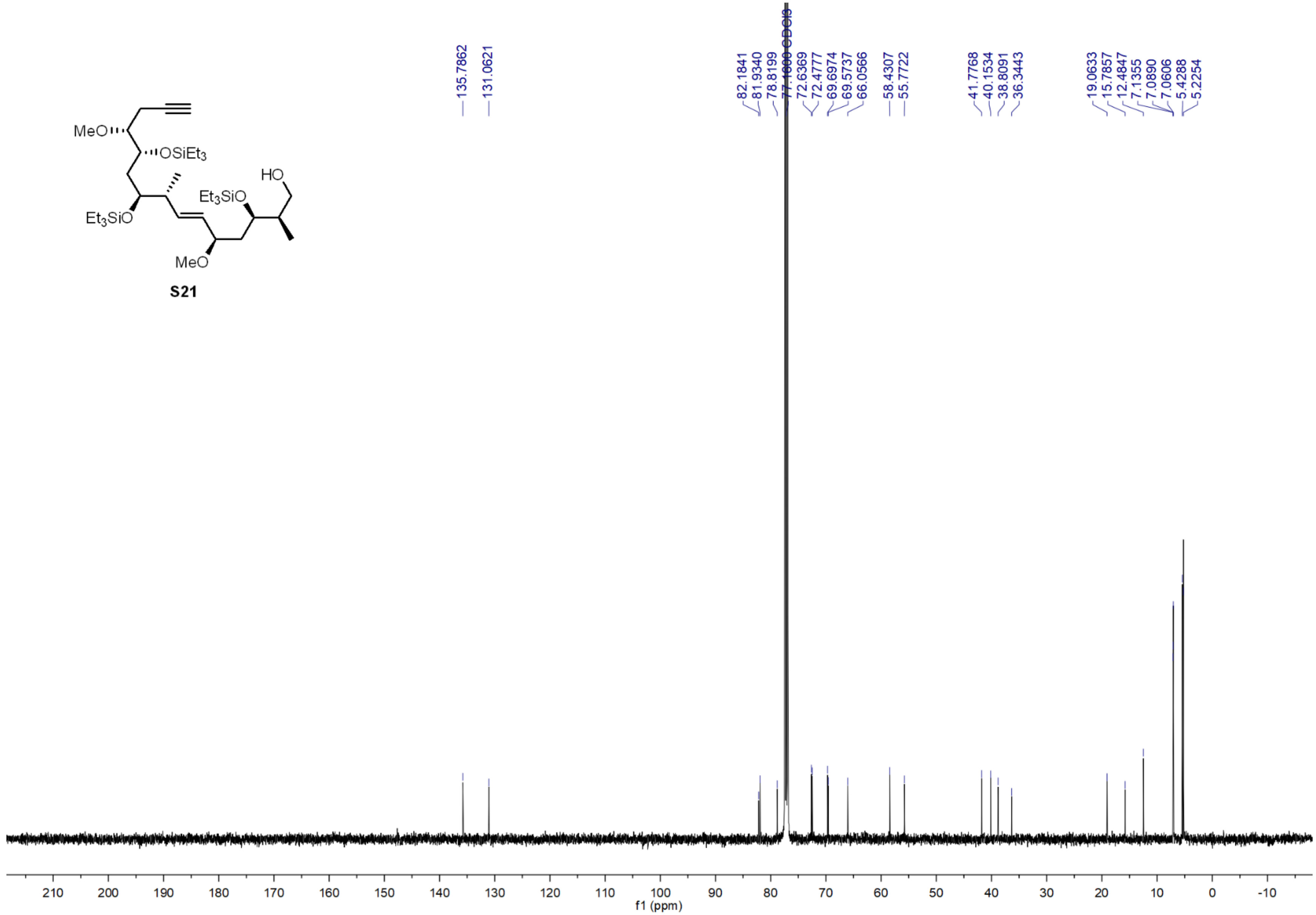

Figure S140. The 125 MHz ^{13}C-NMR of Compound **S21** in Chloroform-*d*

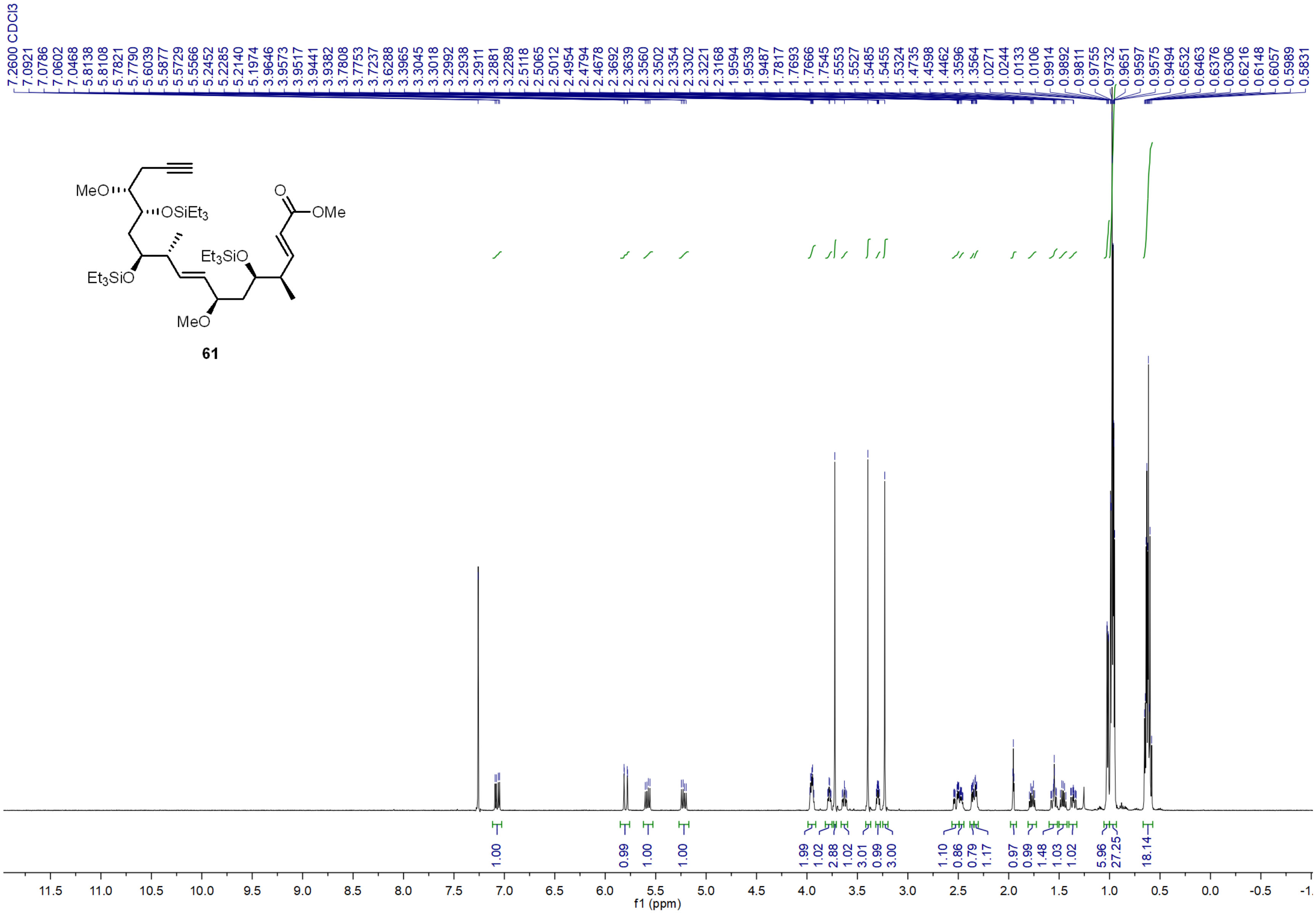

Figure S141. The 500 MHz ^{1}H-NMR of Compound **61** in Chloroform-*d*

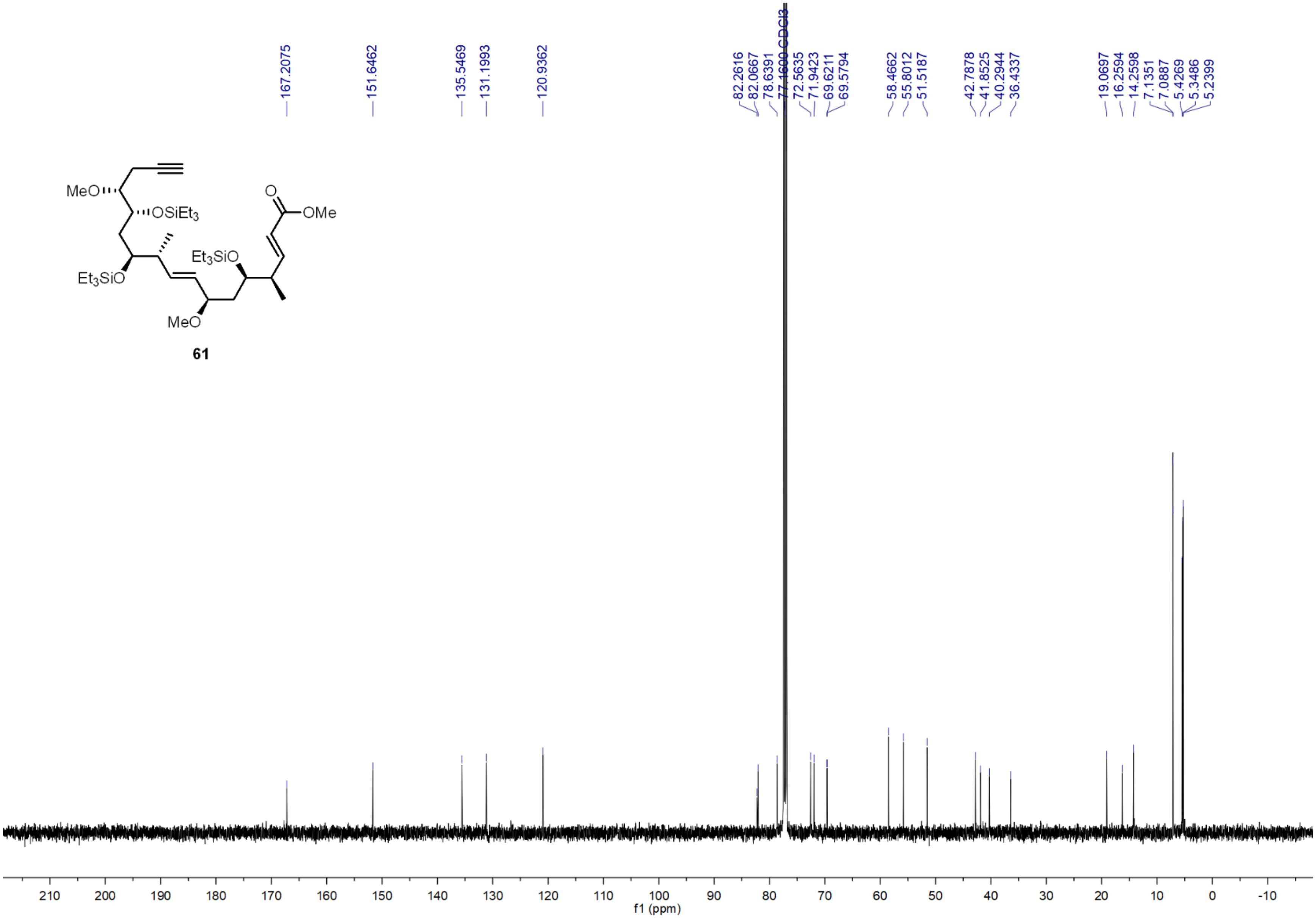

Figure S142. The 125 MHz ^{13}C-NMR of Compound **61** in Chloroform-*d*

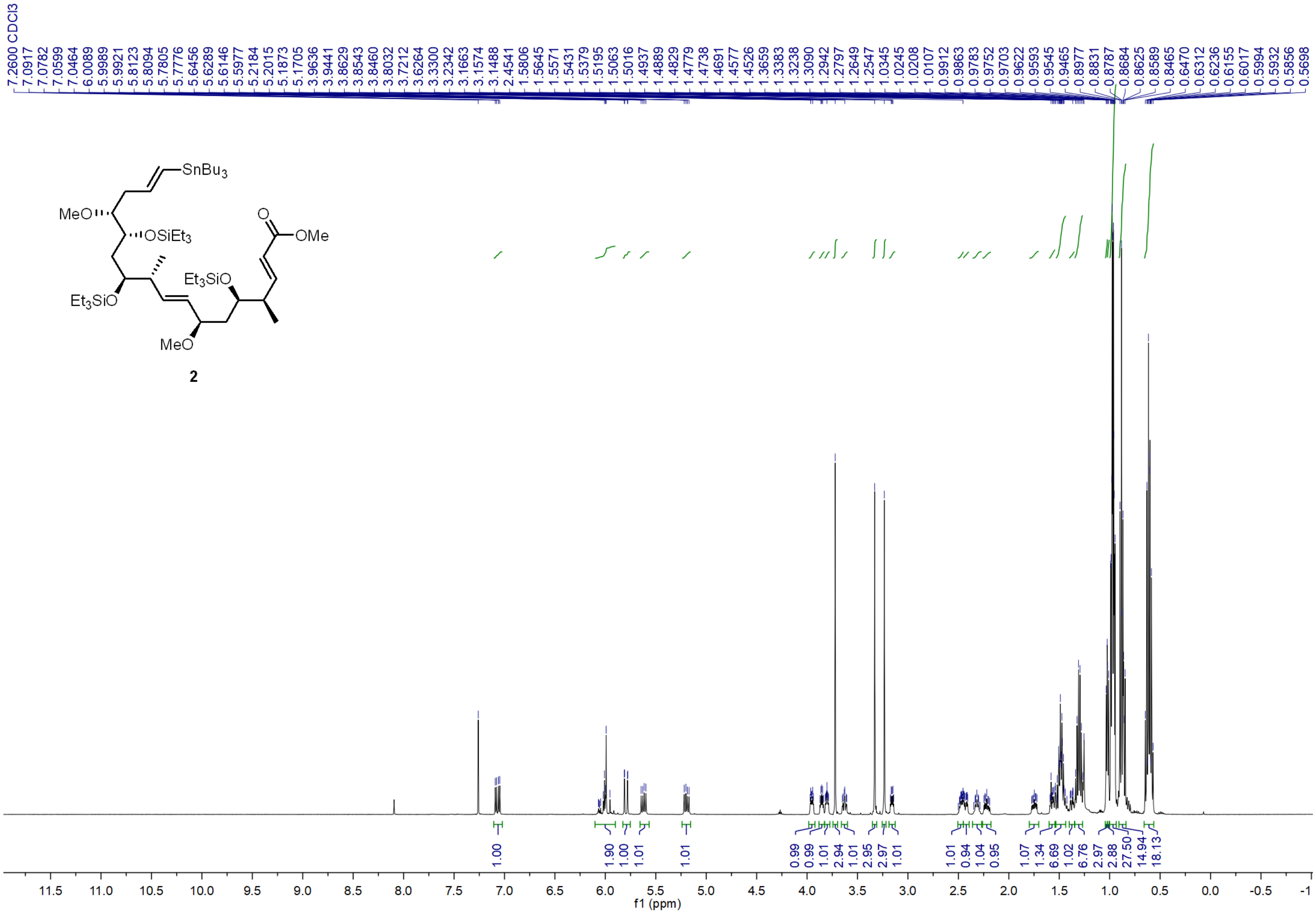

Figure S143. The 500 MHz ^{1}H-NMR of Compound **2** in Chloroform-*d*

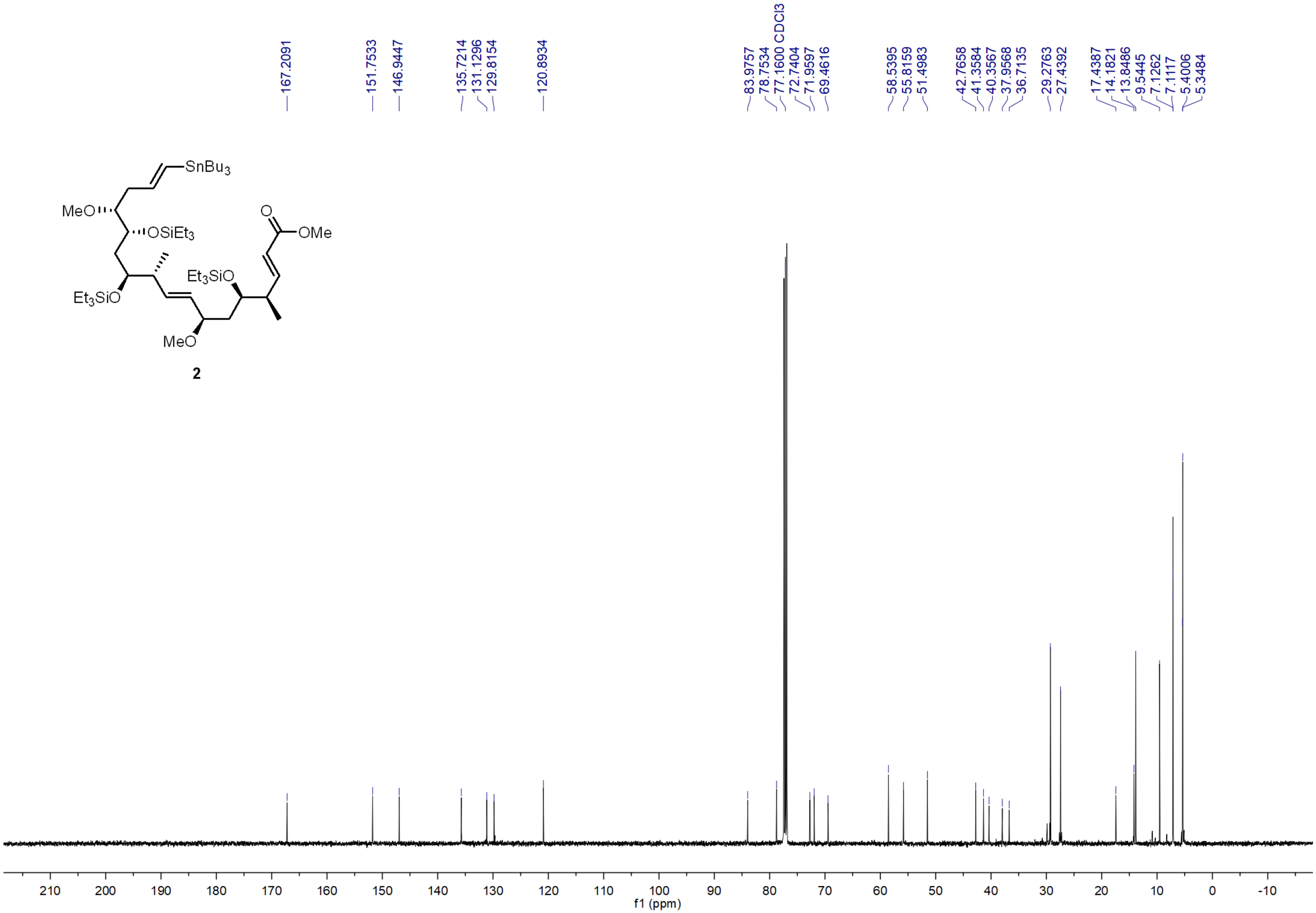

Figure S144. The 125 MHz ^{13}C-NMR of Compound **2** in Chloroform-*d*

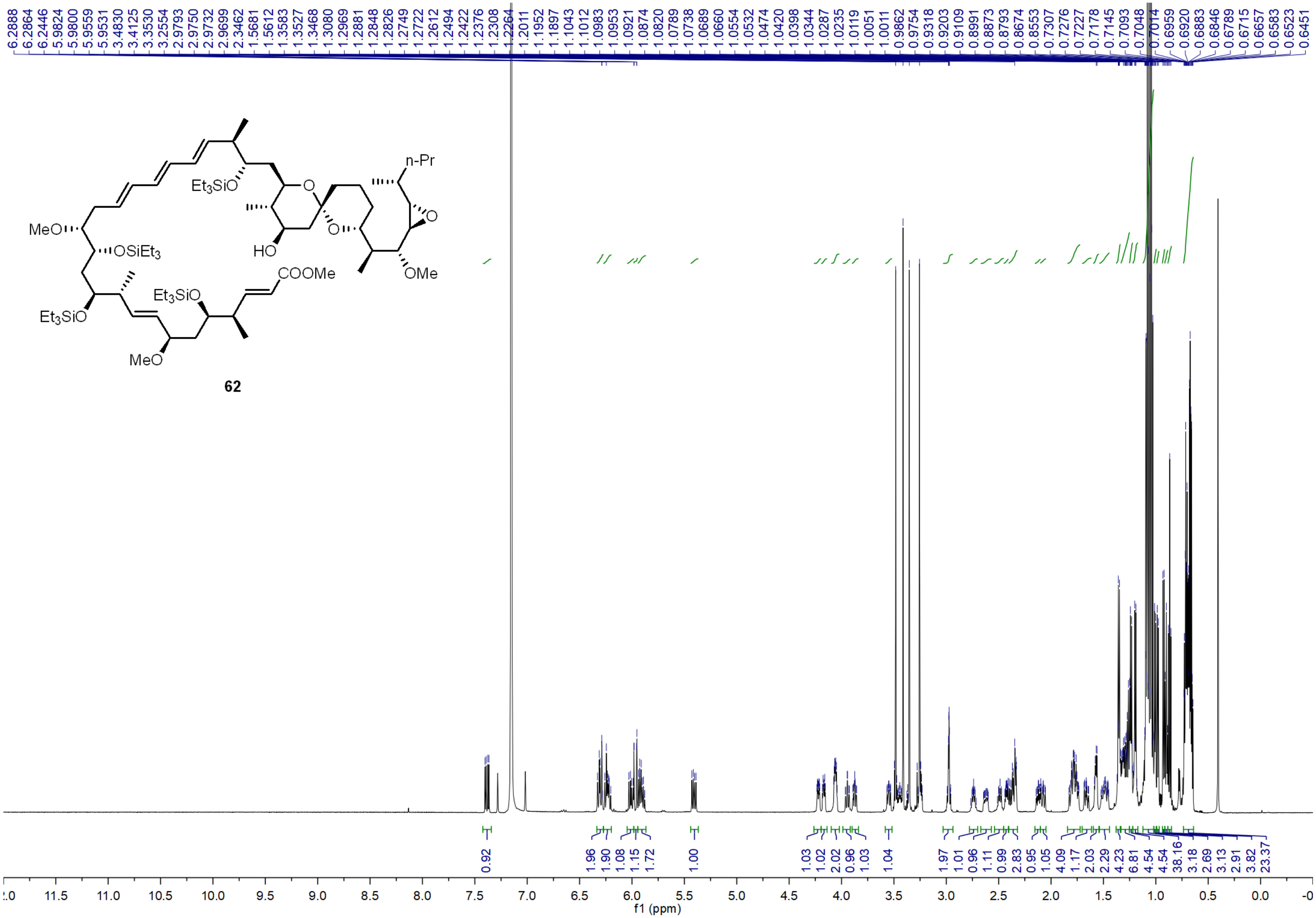

Figure S145. The 600 MHz ^{1}H-NMR of Compound **62** in benzene-*d6*

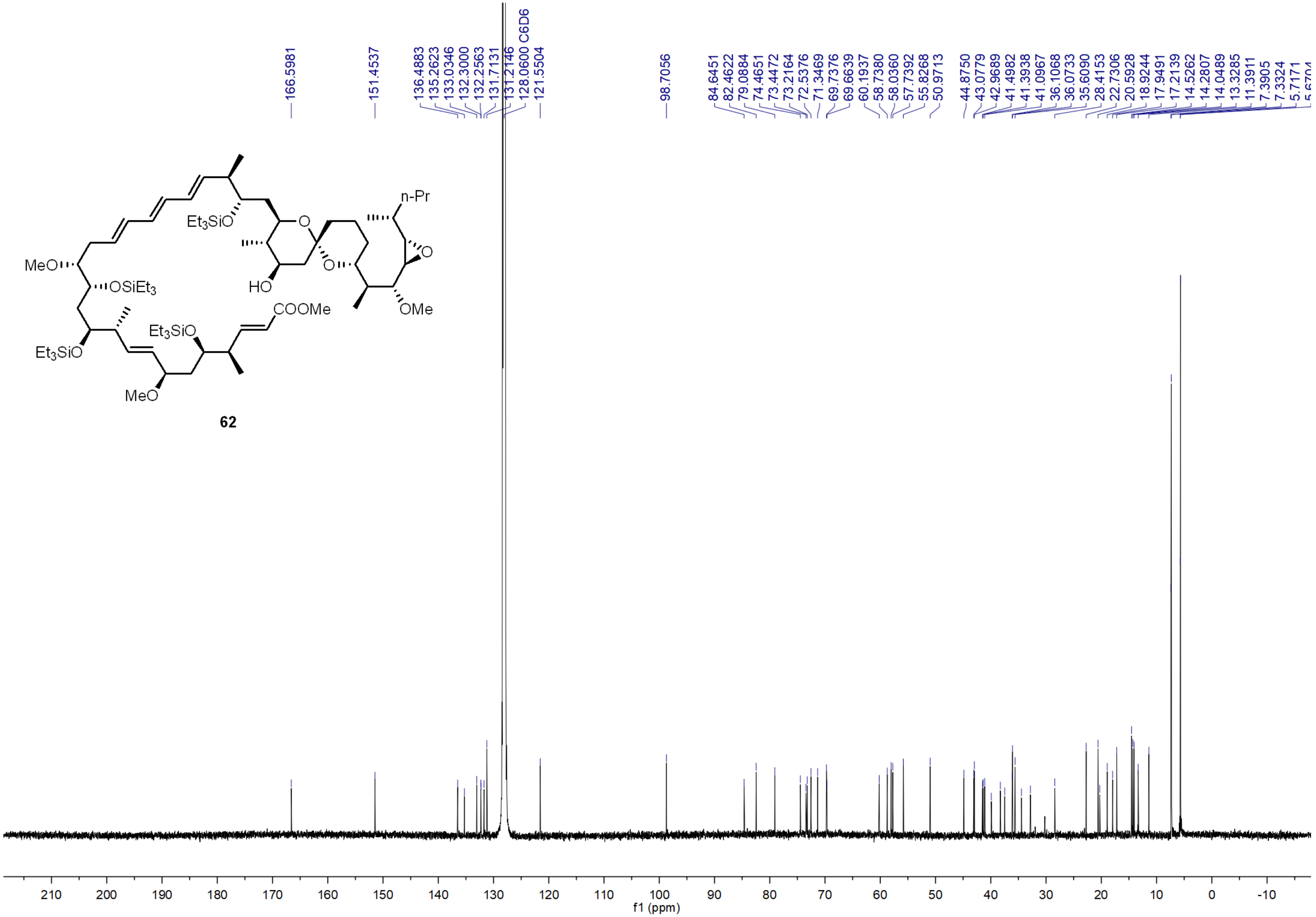

Figure S146. The 150 MHz ^{13}C-NMR of Compound **62** in benzene-*d6*

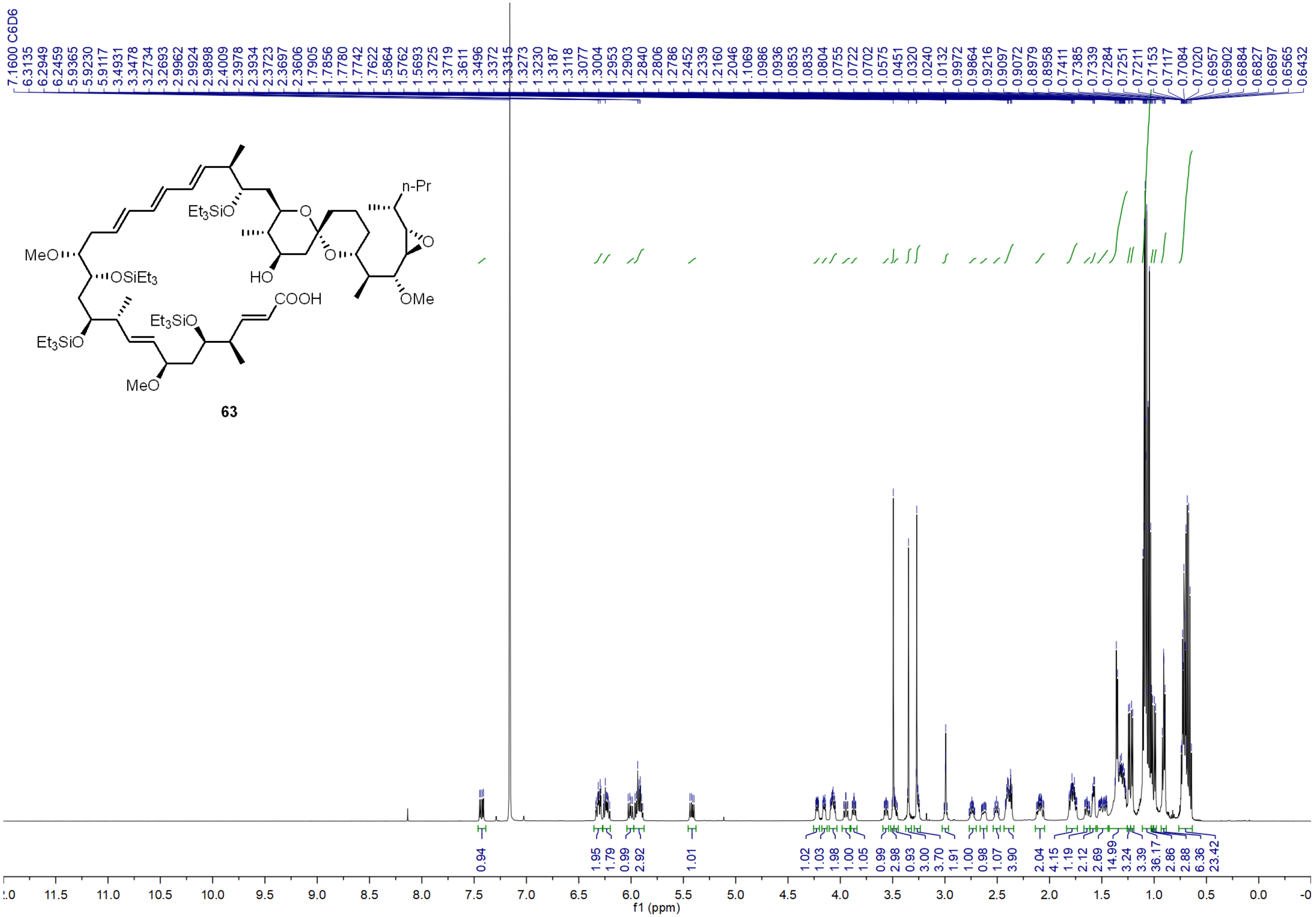

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Figure S147. The 600 MHz ^{1}H-NMR of Compound **63** in benzene-*d6*

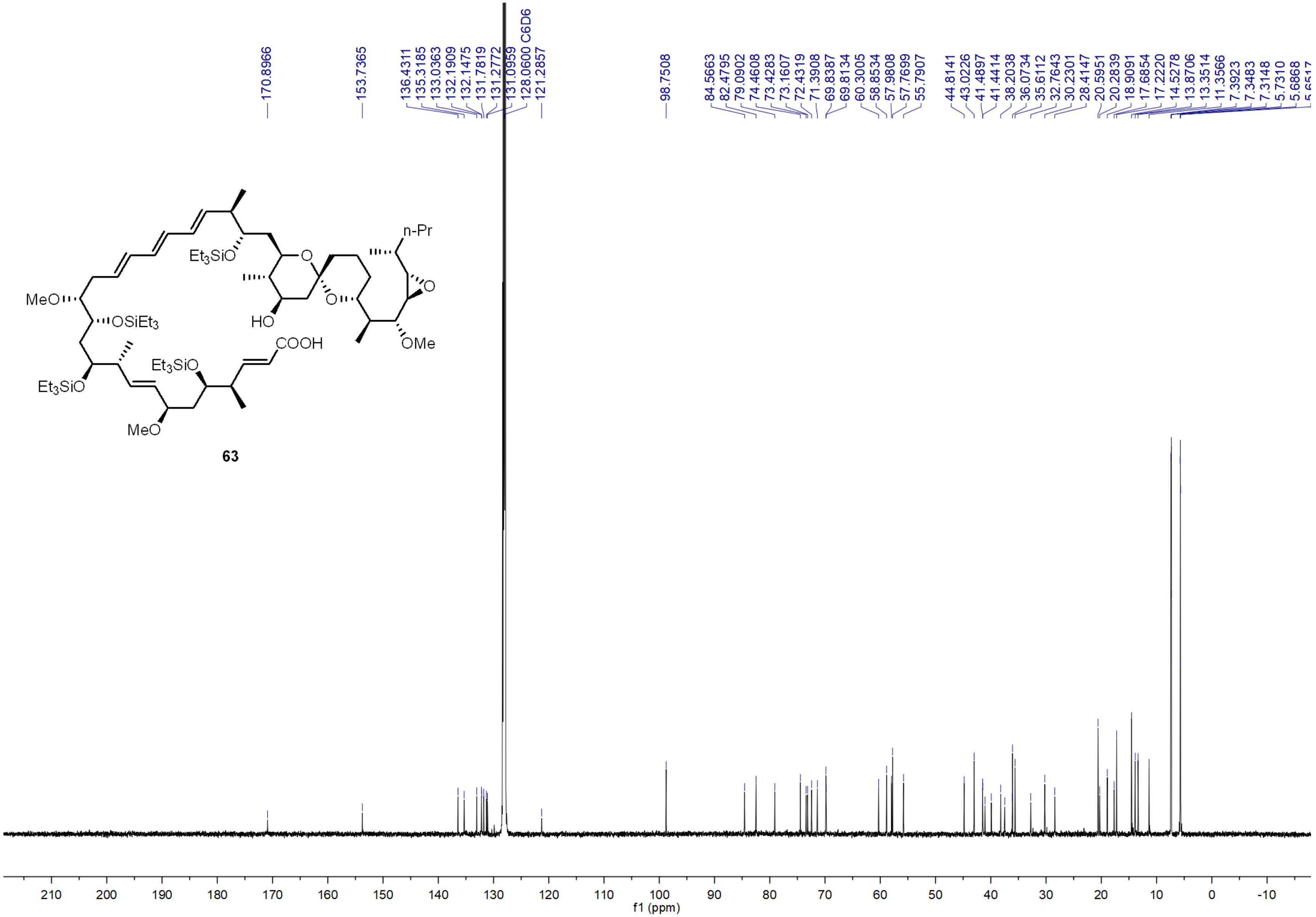

Figure S148. The 150 MHz ^{13}C-NMR of Compound **63** in benzene-*d6*

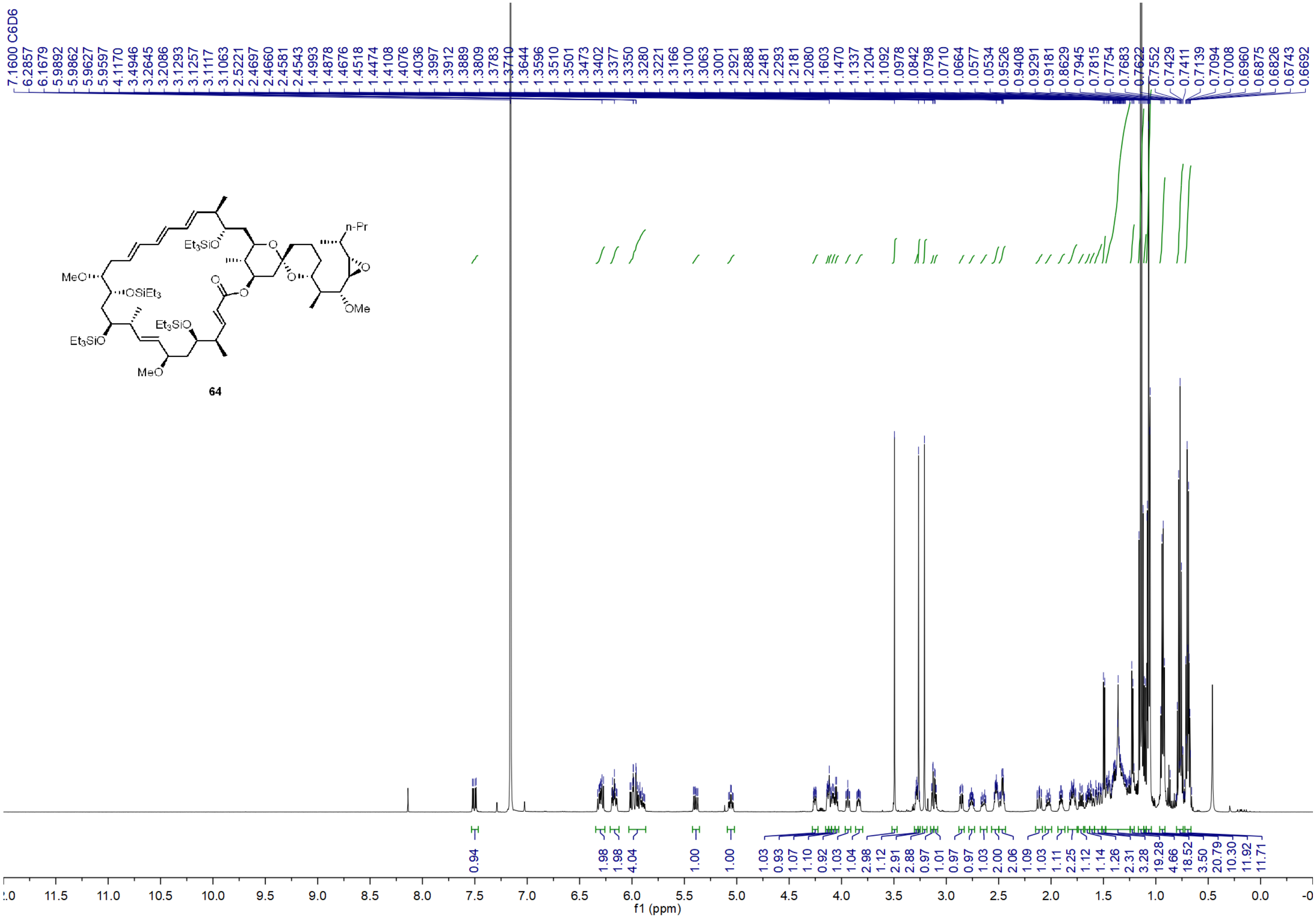

Figure S149. The 600 MHz ^{1}H-NMR of Compound **64** in benzene-*d6*

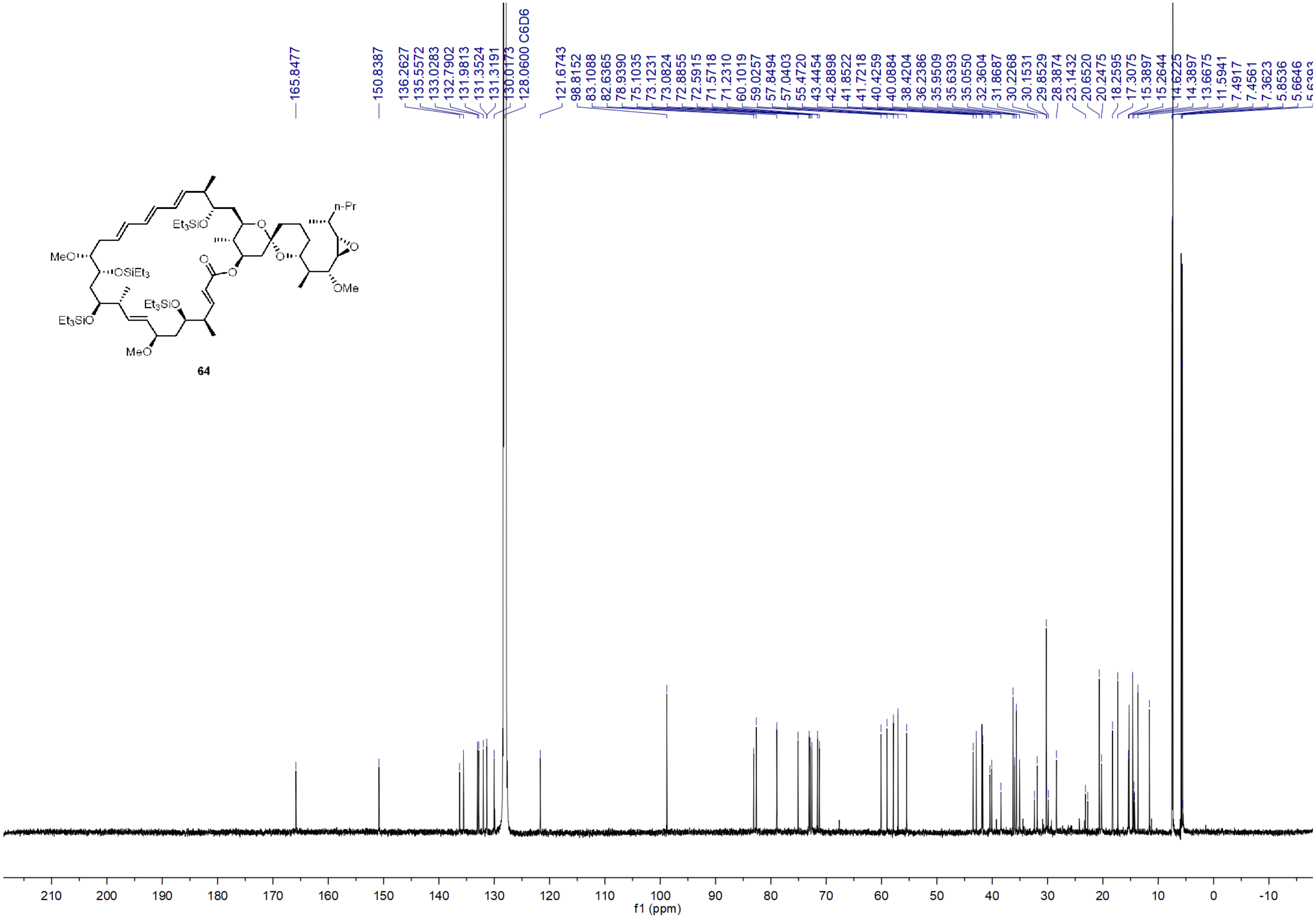

Figure S150. The 150 MHz ^{13}C-NMR of Compound **64** in benzene-*d6*

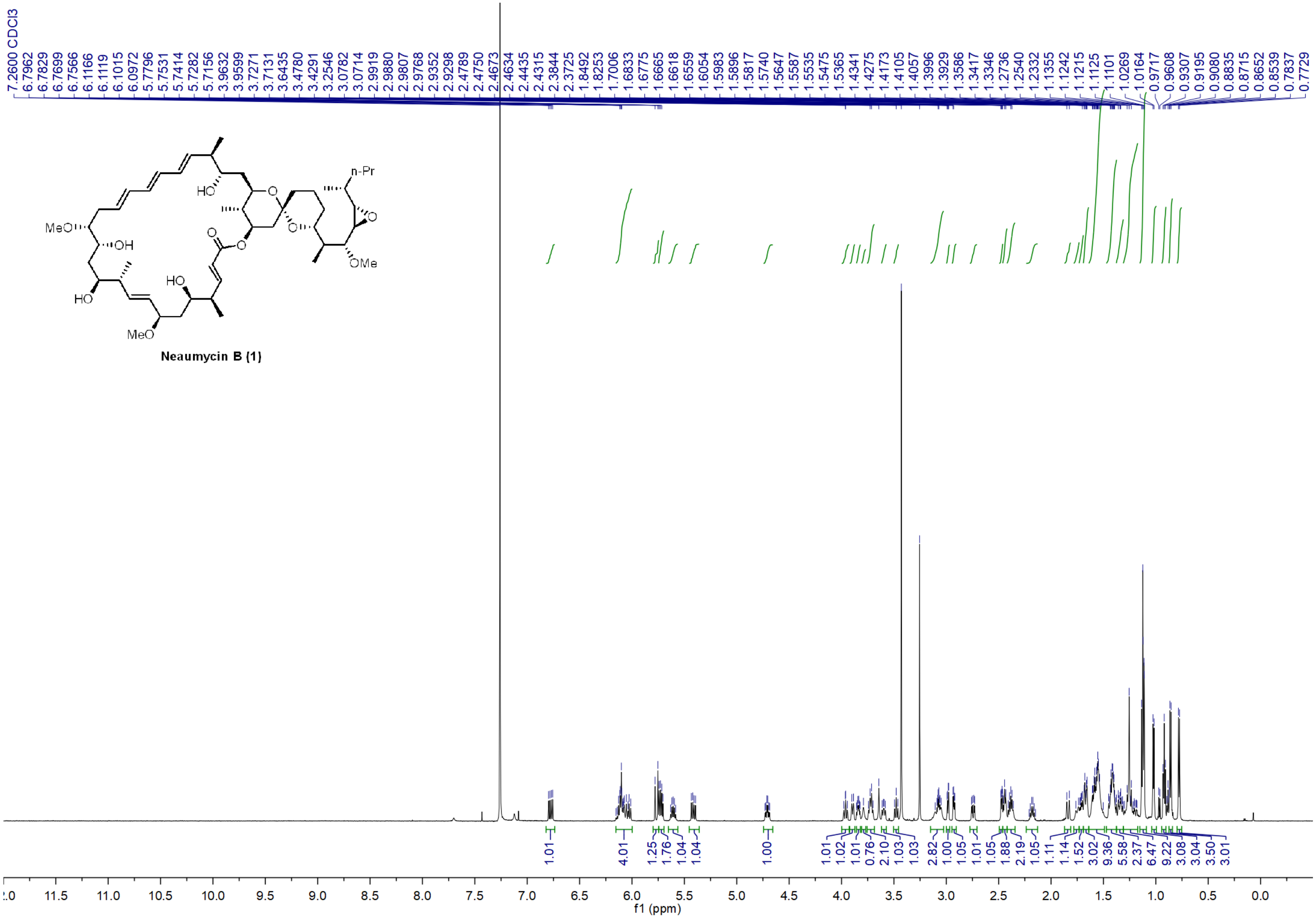

Figure S151. The 600 MHz ^{1}H-NMR of reported Structure of Neaumycin B (**1**) in Chloroform-*d*

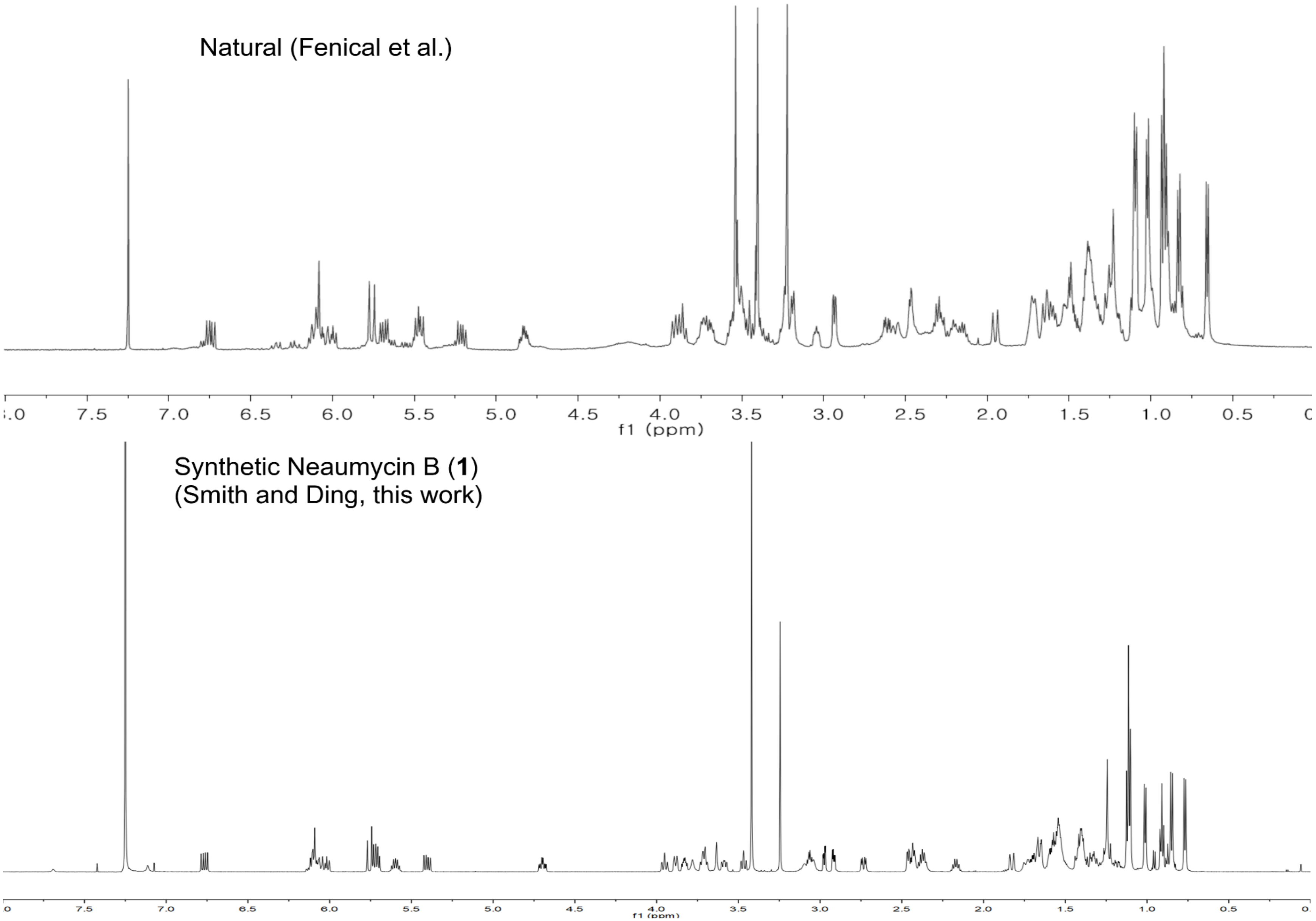

Figure S152. Graphic Comparisons of ^{1}H-NMR spectrum between the synthetic Neaumycin B (**1**) and the reported data[12] in Chloroform-*d*

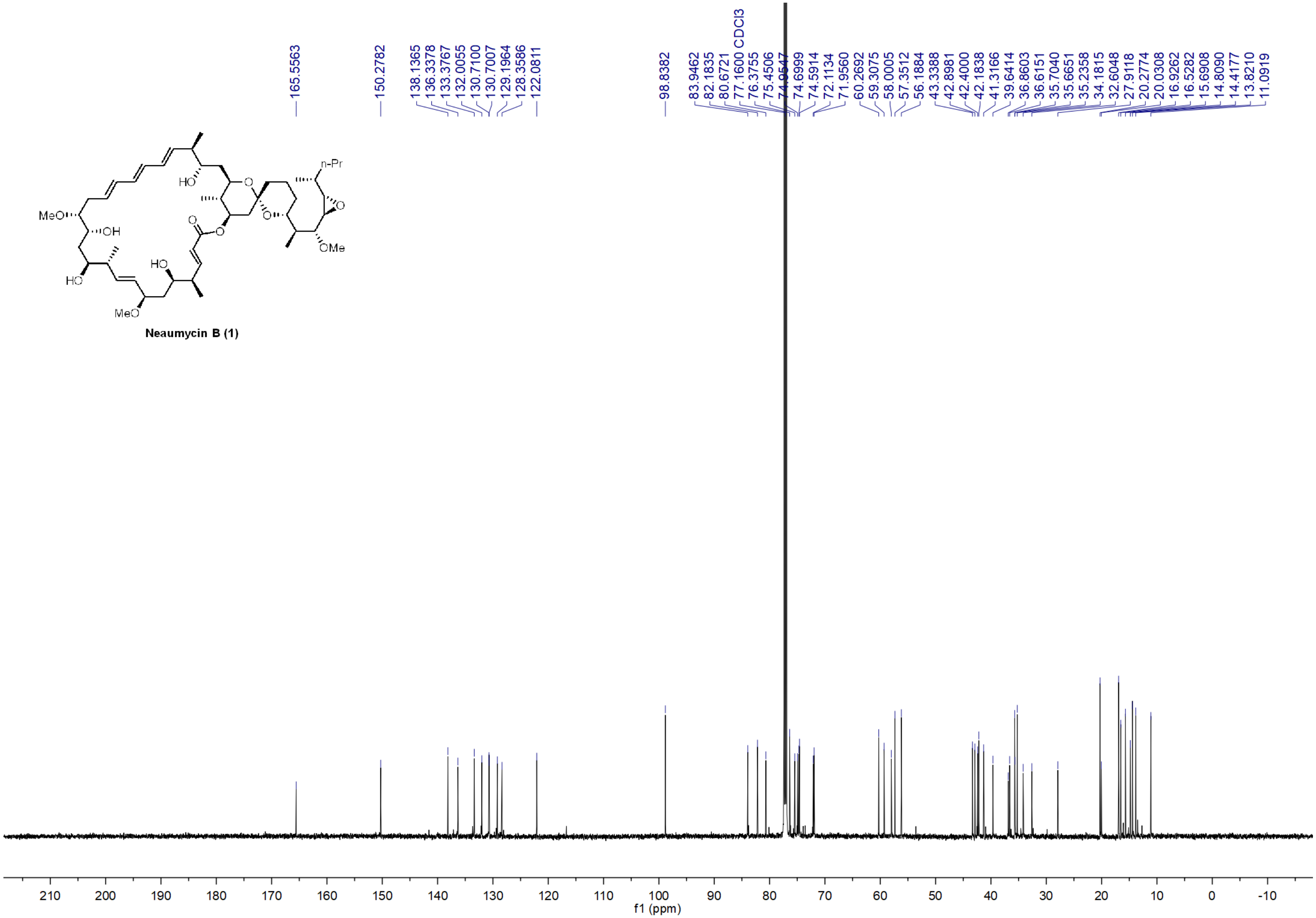

Figure S153. The 150 MHz ^{13}C-NMR of reported Structure of Neaumycin B (**1**) in Chloroform-*d*

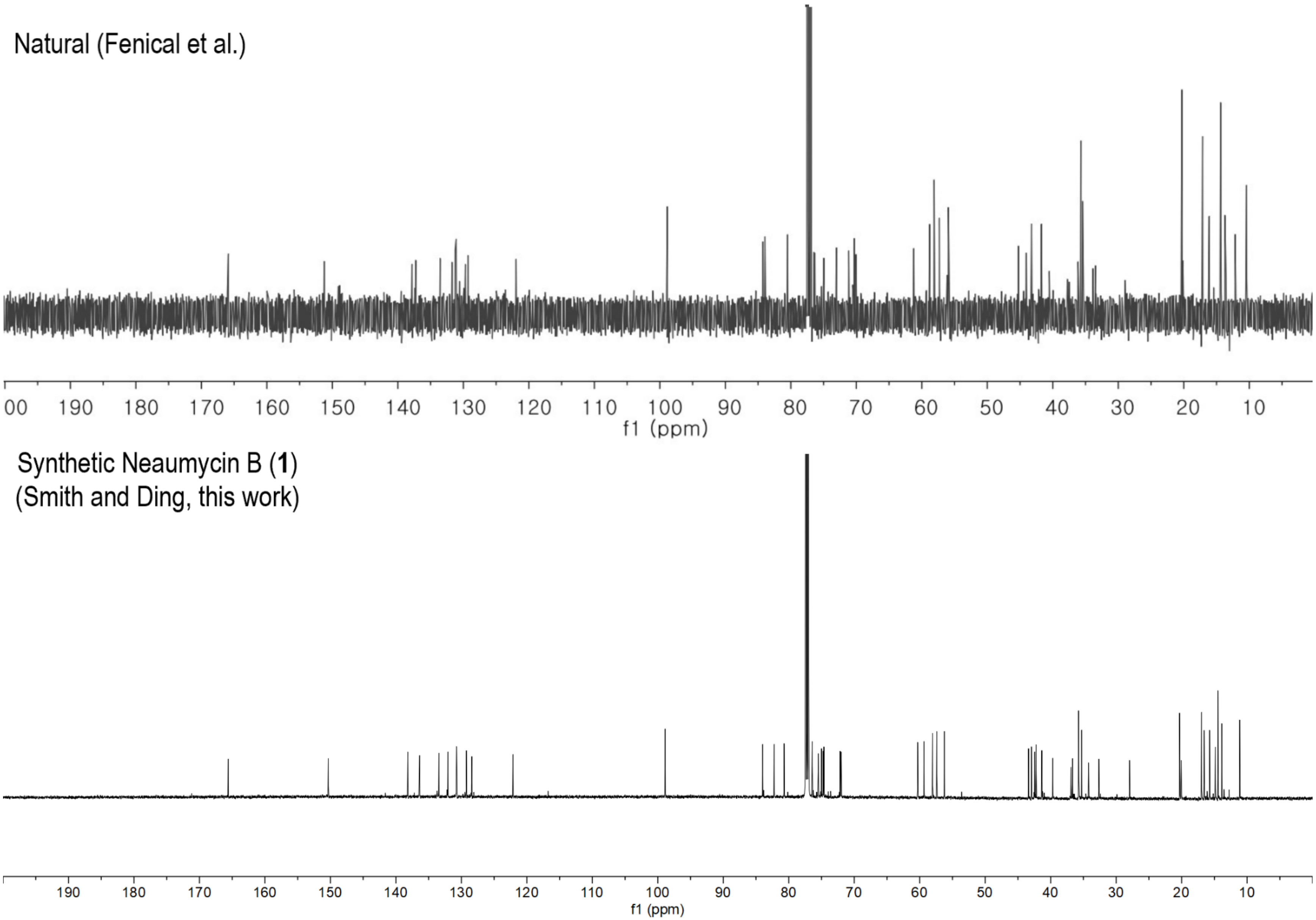

Figure S154. Graphic Comparisons of ^{13}C-NMR spectrum between the synthetic Neaumycin B (**1**) and the reported data[12] in Chloroform-*d*

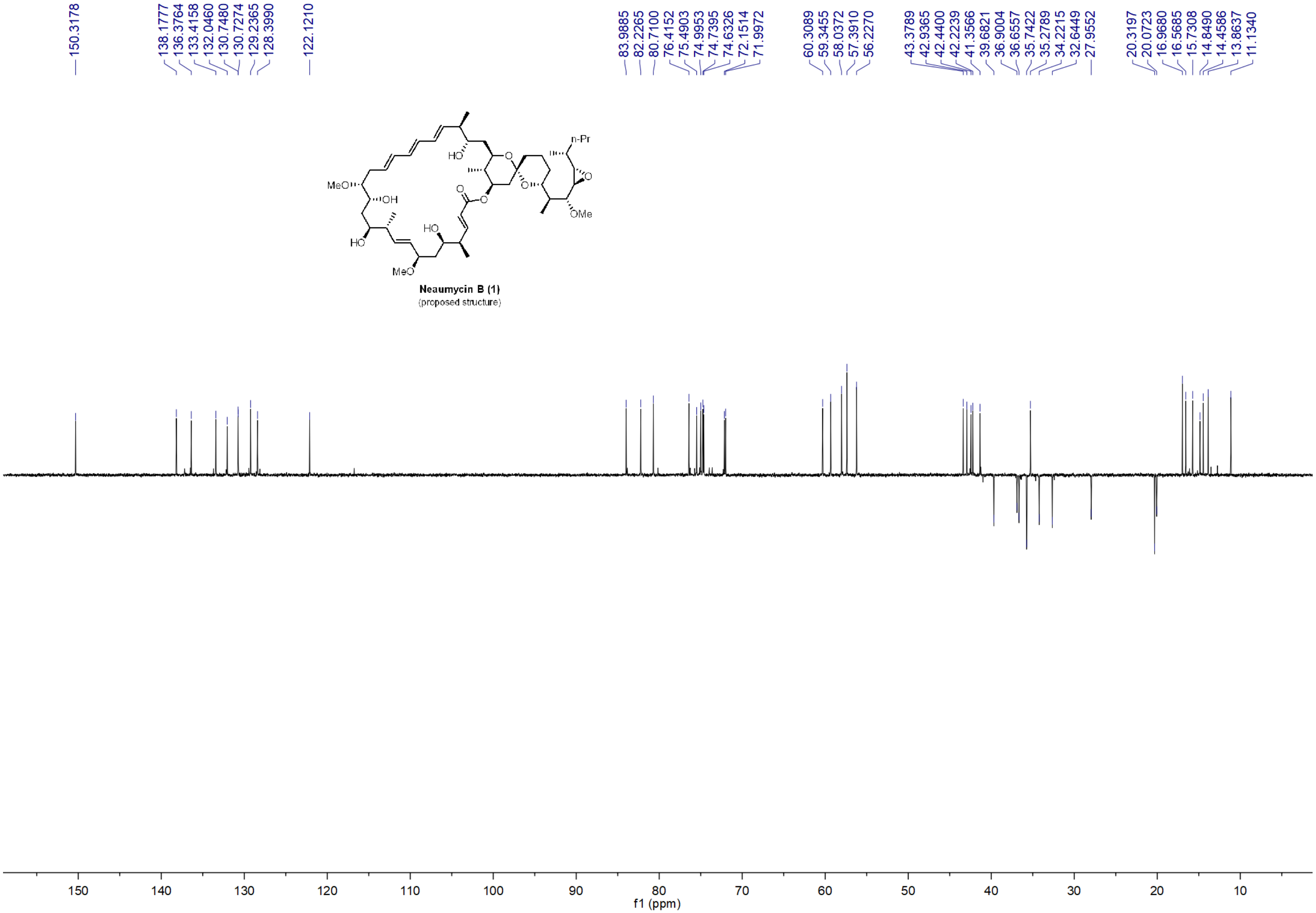

Figure S155. DEPT 135 ^{13}C-NMR of reported Structure of Neaumycin B (**1**), 150 MHz, chloroform-*d*

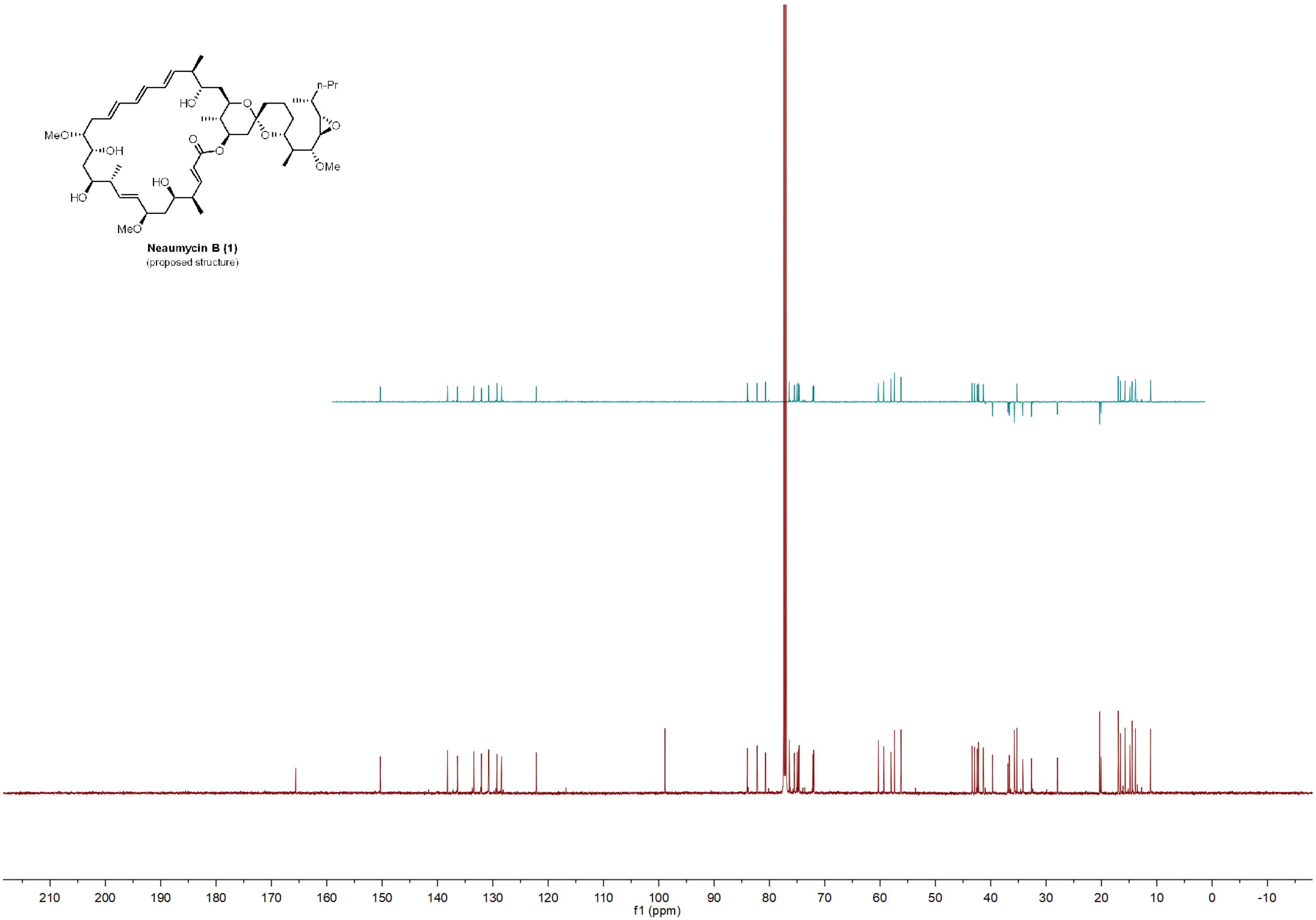

Figure S156. Stacked ^{13}C- and dept 135 ^{13}C-NMR spectra of the reported Structure of Neaumycin B (**1**), 150 MHz, chloroform-*d*

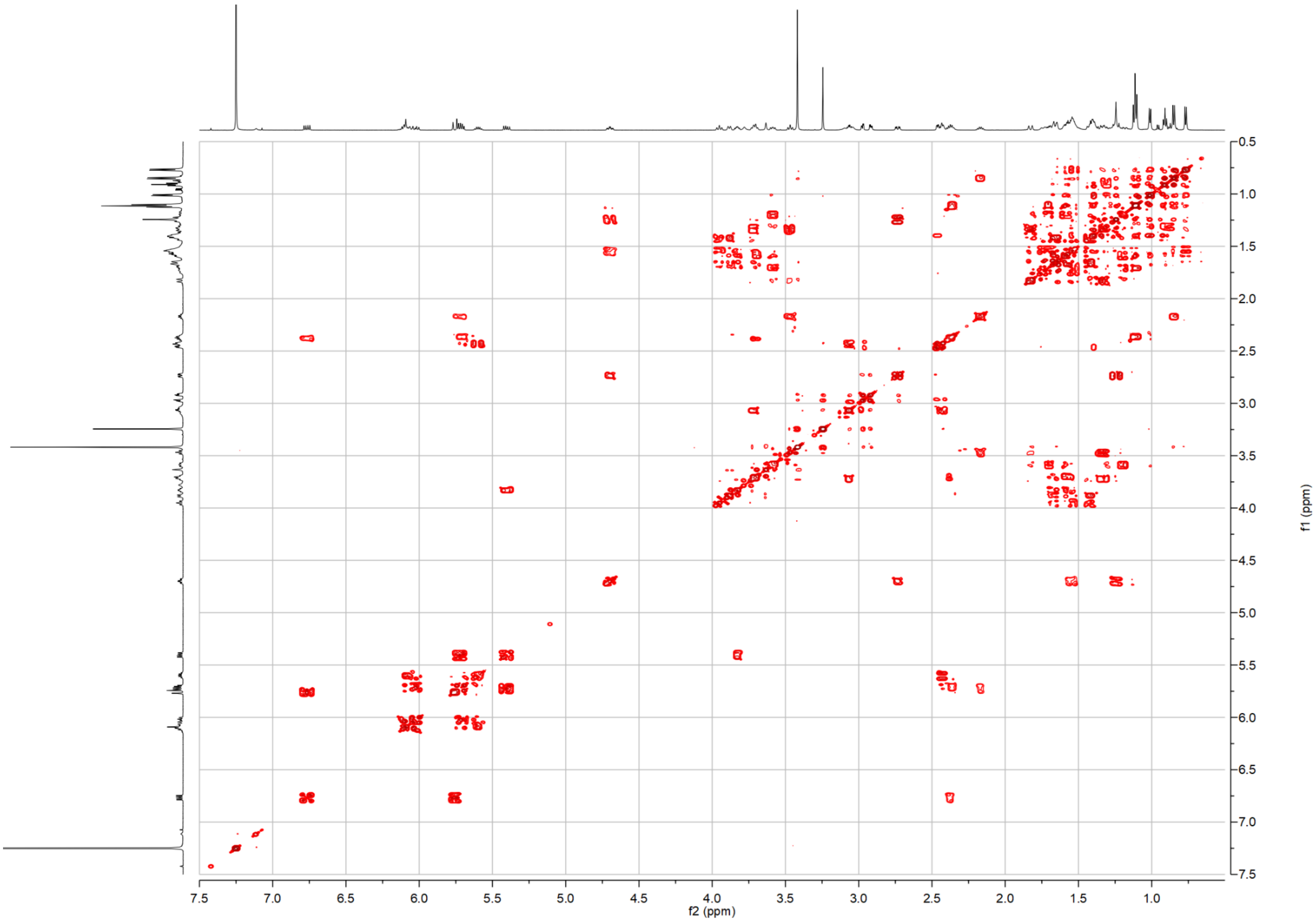

Figure S157. gCOSY NMR of reported Structure of Neaumycin B (**1**), 600 MHz, chloroform-*d*

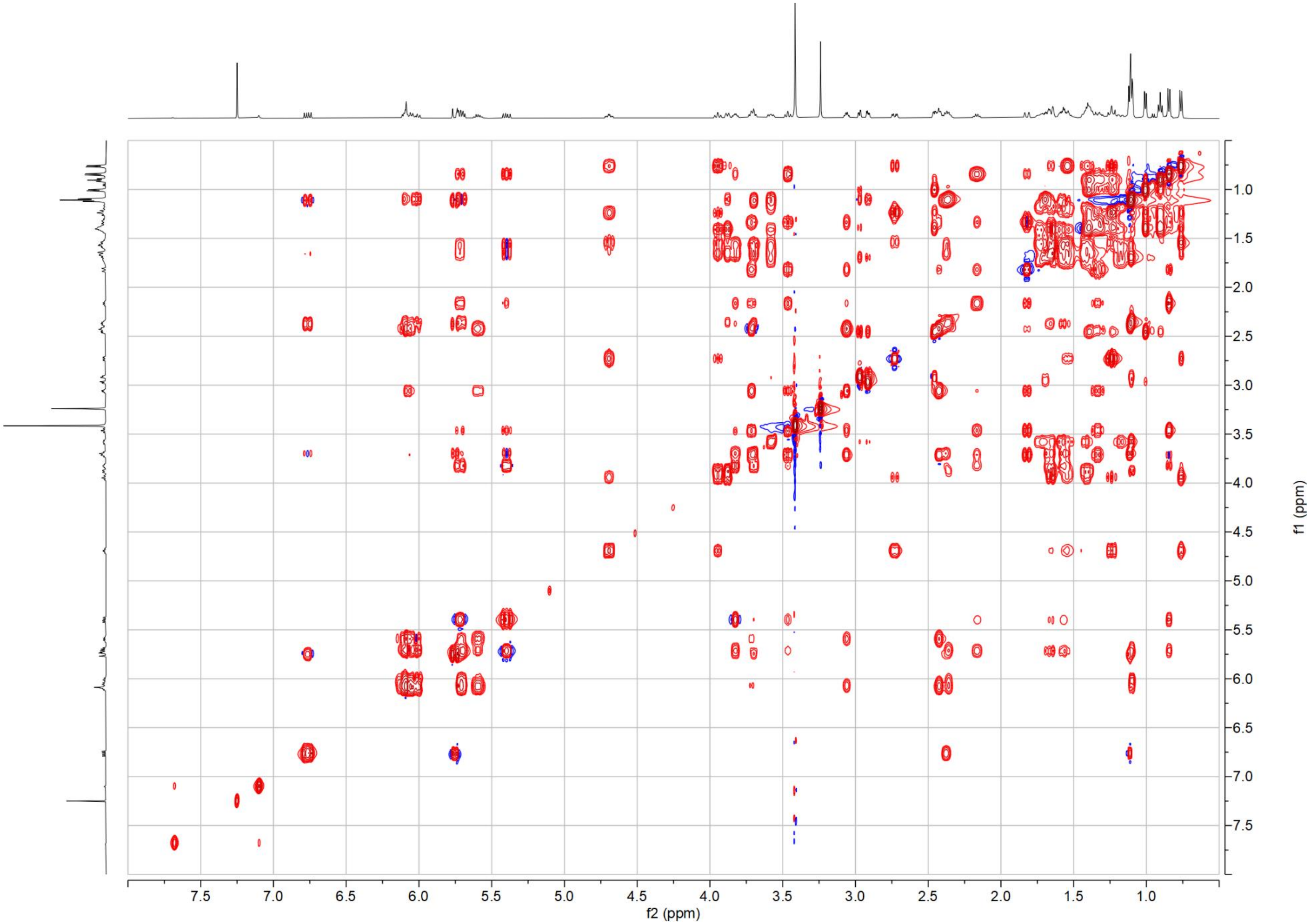

Figure S158. TOCSY NMR of reported Structure of Neaumycin B (**1**), 500 MHz, chloroform-*d*

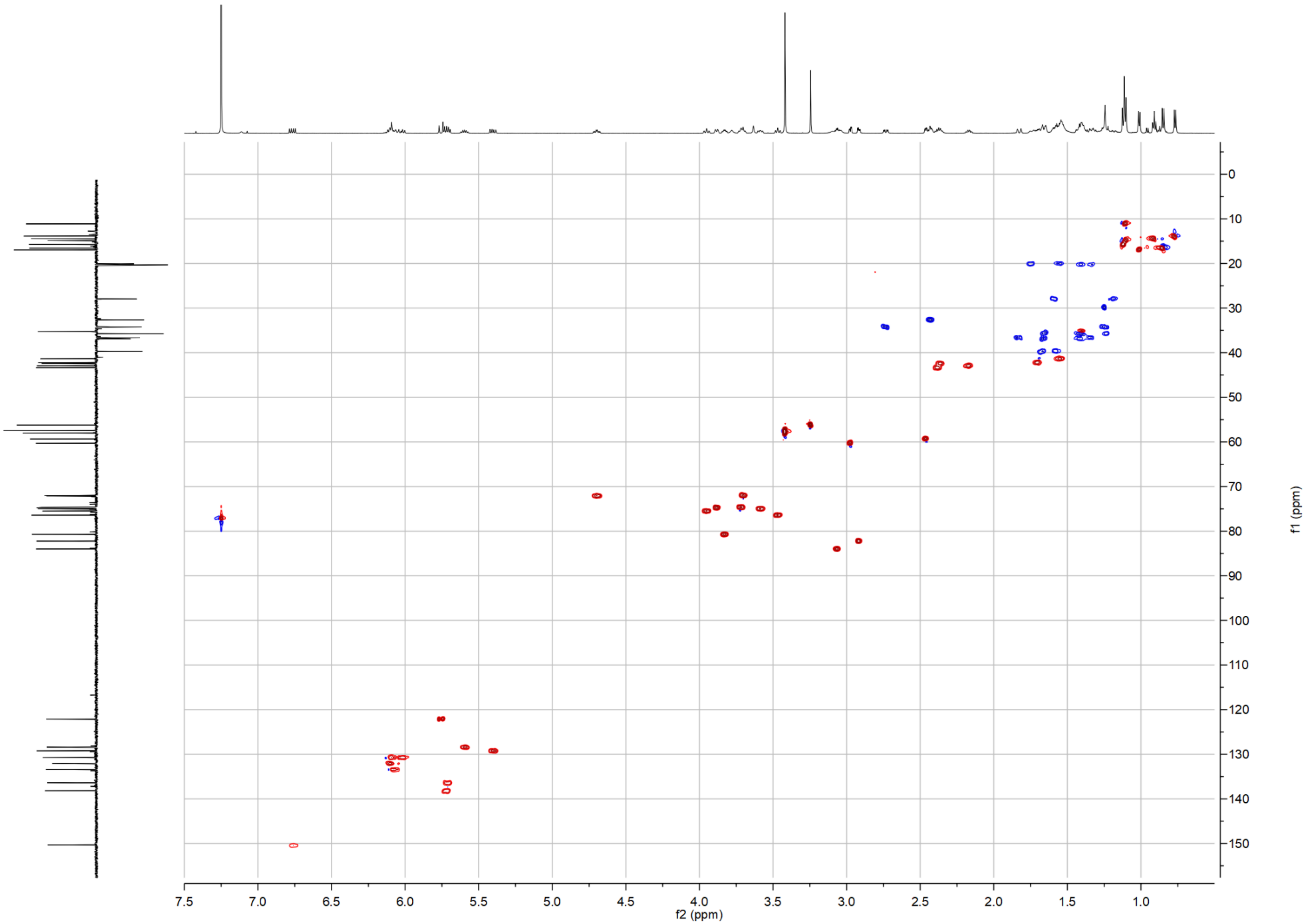

Figure S159. gHSQC NMR of reported Structure of Neaumycin B (**1**), 600 MHz, chloroform-*d*

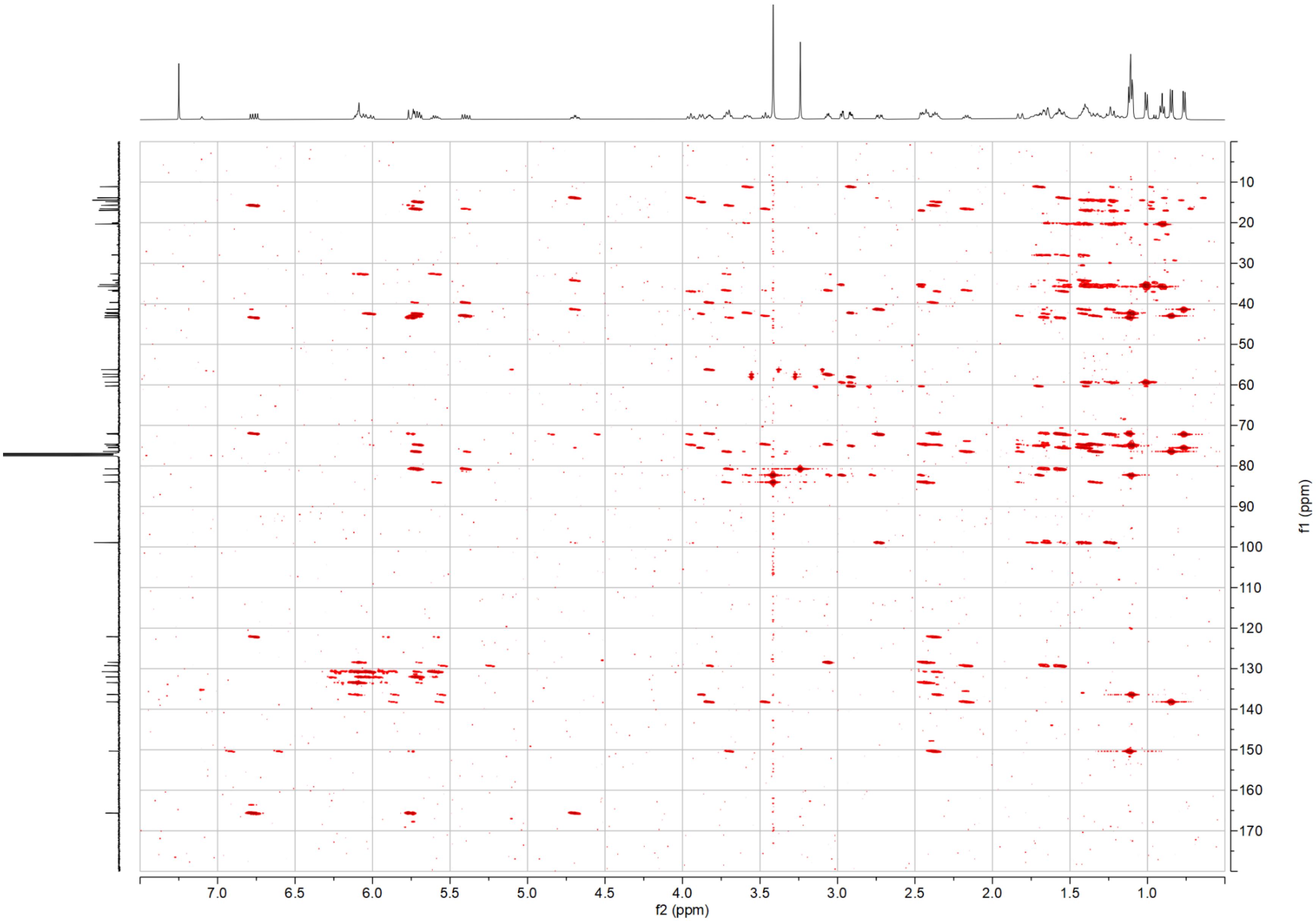

Figure S160. gHMBC NMR of reported Structure of Neaumycin B (**1**), 500 MHz, chloroform-*d*

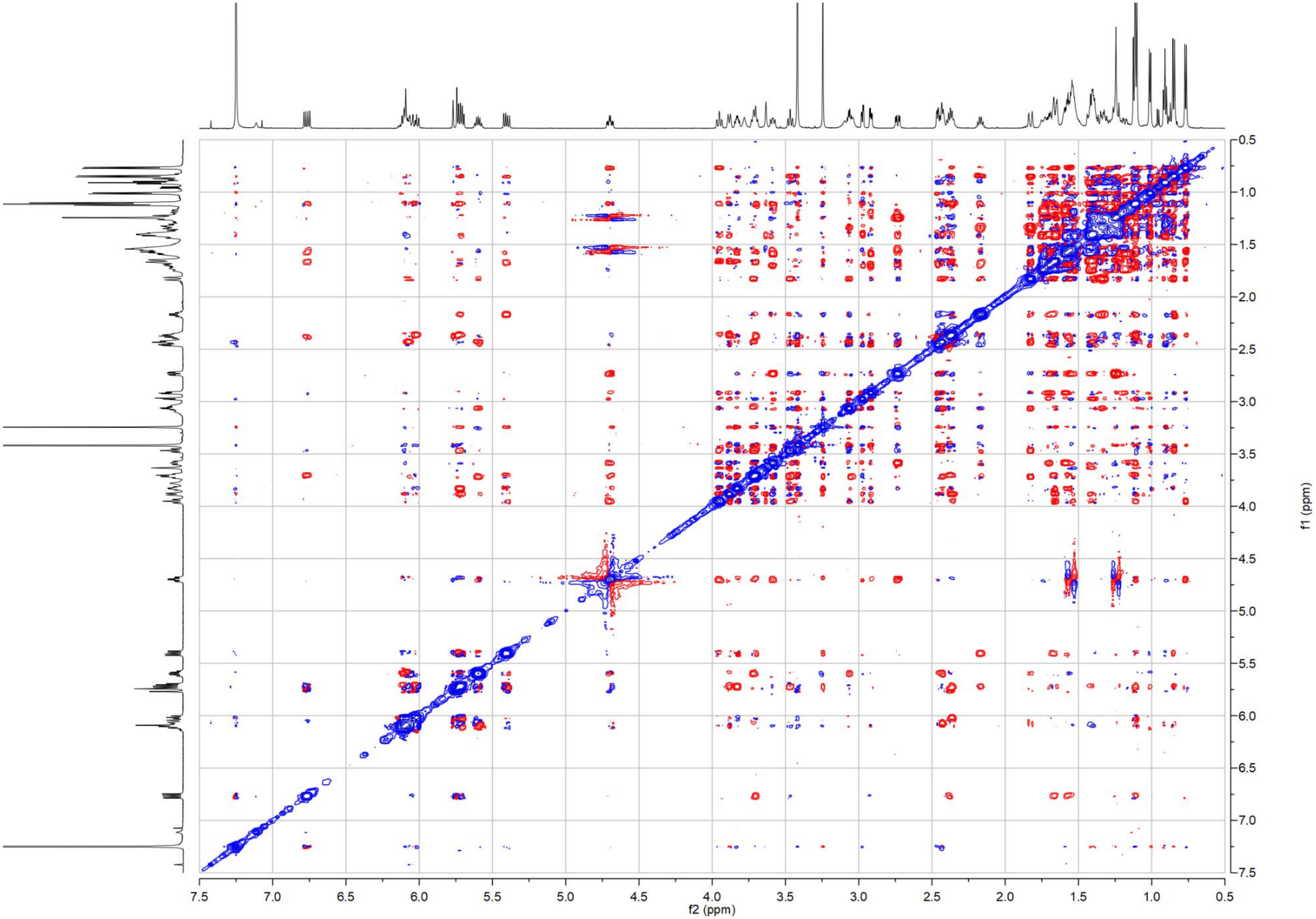

Figure S161. ROESY NMR of reported Structure of Neaumycin B (**1**), 600 MHz, chloroform-*d*

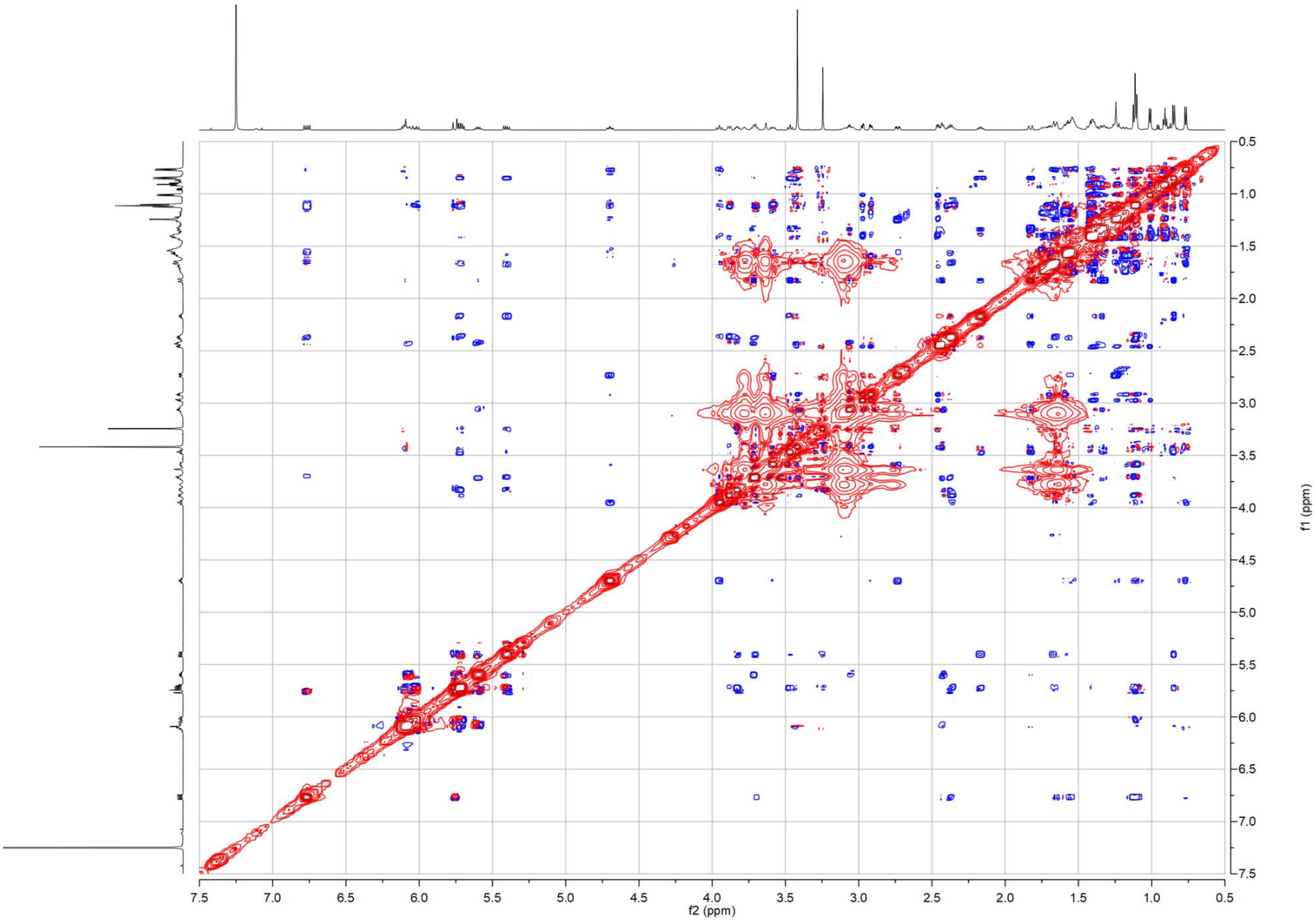

Figure S162. NOESY NMR of reported Structure of Neaumycin B (**1**), 600 MHz, chloroform-*d*

Table S28. Comparison of NMR data (δ in ppm) between synthetic Neaumycin B (1) and the natural product[12] (CDCl$_3$)

[a]. Overlapping signals

No.	Synthetic		Natural		^{1}H-NMR Δδ (ppm)	^{13}C-NMR Δδ (ppm)
	^{1}H-NMR δ (*J* in Hz)	^{13}C-NMR δ	^{1}H-NMR δ (*J* in Hz)	^{13}C-NMR δ		
1		165.6		165.9		-0.3
2	5.75, d (15.9)	122.1	5.76, d (15.6)	122.0	-0.01	0.1
3	6.77, dd (15.8, 8.0)	150.3	6.75, dd (15.6, 9.2)	151.2	0.02	-0.9
4	2.38, m[a]	43.4	2.31, m[a]	44.1	0.07	-0.7
5	3.70, m[a]	72.0	3.56, m[a]	75.0	0.14	-3.0
6a	1.66, m[a]	39.7	1.50, m[a]	40.6	0.16	-0.9
6b	1.57, m[a]		1.50, m[a]		0.07	
7	3.83, dd (7.4, 4.0)	80.7	3.68, dd (8.6, 5.0)	84.3	0.15	-3.6
8	5.40, dd (15.5, 8.4)	129.2	5.22, dd (15.6, 8.5)	129.8	0.18	-0.6
9	5.72, dd (15.0, 7.4)	138.2	5.68, dd (15.6, 7.2)	137.9	0.04	0.3
10	2.17, h (6.9)	43.0	2.22, m[a]	41.7	-0.05	1.3
11	3.47, d (9.2)	76.4	3.89, dd (12.0, 10.3)	70.1	-0.42	6.3
12a	1.83, br d (14.3)	36.7	1.65, m[a]	36.2	0.18	0.5
12b	1.34, m[a]		1.40, m[a]		-0.06	
13	3.72, m[a]	74.6	3.72, ddd (9.7, 6.0, 2.1)	70.3	0.00	4.3
14	3.06, td (6.5, 4.1)	84.0	3.05, ddd (9.5, 5.5, 2.7)	83.9	0.01	0.1
15a	2.43, m	32.6	2.57, br d (15.0)	33.5	-0.14	-0.9
15b	2.43, m		2.28, m[a]		0.15	
16	5.60, dt (13.9, 7.2)	128.4	5.49, m[a]	129.3	0.11	-0.9
17	6.07, m[a]	133.4	6.13, m[a]	133.6	-0.06	-0.2
18	6.09, m[a]	130.7	6.07, m[a]	131.3	0.02	-0.6
19	6.10, m[a]	132.1	6.10, m[a]	131.8	0.00	0.3
20	6.02, m[a]	130.7	6.02, m[a]	131.1	0.00	-0.4
21	5.71, dd (15.0, 7.4)	136.4	5.47, dd (15.0, 9.5)	137.3	0.24	-0.9
22	2.36, m[a]	42.4	2.16, m[a]	45.2	0.20	-2.8
23	3.88, d (9.6)	74.7	3.45, m[a]	76.5	0.43	-1.8
24a	1.66, m[a]	36.9	1.96, br d (14.6)	37.5	-0.30	-0.6
24b	1.41, m[a]		1.23, m[a]		0.18	
25	3.95, dd (12.1, 10.4)	75.5	3.85, dd (11.5, 10.9)	76.3	0.10	-0.8

No.	**Synthetic**		**Natural**		**^{1}H-NMR Δδ (ppm)**	**^{13}C-NMR Δδ (ppm)**
	^{1}H-NMR δ (*J* in Hz)	**^{13}C-NMR δ**	**^{1}H-NMR δ (*J* in Hz)**	**^{13}C-NMR δ**		
26	1.55, m[a]	41.4	1.47, m[a]	41.8	0.08	-0.4
27	4.70, td (10.8, 4.5)	72.1	4.84. ddd (12.8, 11.1, 4.6)	71.2	-0.14	0.9
28a	2.73, dd (13.0, 4.5)	34.2	2.62, dd (12.8, 4.9)	33.9	0.11	0.3
28b	1.24, m[a]		1.27, d (12.8)		-0.03	
29		98.9		98.9		0.0
30a	1.66, m[a]	35.7	1.65, m[a]	37.8	0.01	-2.1
30b	1.40, m[a]		1.39, m[a]		0.01	
31a	1.74, m[a]	20.1	1.73, m[a]	20.2	0.01	-0.1
31b	1.55, m[a]		1.53, m[a]		0.02	
32a	1.58, m[a]	27.9	1.72, m[a]	29.0	-0.14	-1.1
32b	1.18, m[a]		1.01, m[a]		0.17	
33	3.59, dd (11.3, 7.1)	75.0	3.50, m[a]	73.1	0.09	1.9
34	1.70, m[a]	42.2	1.61, m[a]	43.3	0.09	-1.1
35	2.92, dd (6.7, 3.2)	82.2	3.19, dd (7.3, 2.0)	80.5	-0.27	1.7
36	2.98, dd (6.7, 2.3)	60.3	2.94, dd (7.3, 2.3)	61.2	0.04	-0.9
37	2.46, dd (7.0, 2.4)	59.3	2.47, dd (7.0, 2.3)	58.8	-0.01	0.5
38	1.40, m[a]	35.3	1.36, m[a]	35.5	0.04	-0.2
39a	1.39, m[a]	35.7	1.40, m[a]	35.7	-0.01	0.0
39b	1.24, m[a]		1.26, m[a]		-0.02	
40a	1.40, m[a]	20.3	1.39, m[a]	20.3	0.01	0.0
40b	1.33, m[a]		1.34, m[a]		-0.01	
41	0.91, t (6.8)	14.5	0.91, m[a]	14.4	0.00	0.1
42	1.12, m[a]	15.7	1.10, m[a]	16.1	0.02	-0.4
43	0.85, d (6.8)	16.6	0.83, d (6.9)	12.2	0.02	4.4
44	1.10, m[a]	14.9	1.11, m[a]	17.2	-0.01	-2.3
45	0.77, d (6.5)	13.9	0.66, d (6.5)	13.7	0.11	0.2
46	1.10, m[a]	11.1	0.93, m[a]	10.4	0.17	0.7
47	1.01, d (6.3)	17.0	1.02, d (6.4)	17.1	-0.01	-0.1
C7-OMe	3.25, s	56.2	3.23, s	56.0	0.02	0.2
C14-OMe	3.42, s[a]	57.4	3.41, s	57.3	0.01	0.1
C35-OMe	3.42, s[a]	58.0	3.54, s	58.1	-0.12	-0.1

Table S29. 2D COSY and/or TOCSY, HMBC and ROESY NMR data of synthetic Neaumycin B (1), (600 MHz, $CDCl_3$)

No.	^{1}H-NMR δ (ppm)	^{13}C-NMR δ (ppm)	COSY and/or TOCSY	HMBC	ROESY
1	-	165.6	-	-	-
2	5.75	122.1	H42, H4, H5, H3	C1, C3, C4	H4, H42
3	6.77	150.3	H42, H6a, H4, H5, H7	C1, C2, C4, C5, C42	H42, H6a, H6b, H4, H5
4	2.38	43.4	H3, H2, H5, H6a, b	C2, C3, C5, C6, C42	H5, H6a, H42, H2, H3
5	3.70	72.0	H2, H3, H7, H4, H6a, b, H42	C3, C4, C7, C42	H42, H6a, H3, H4, H8
6a	1.66	39.7	H8, H9	C5, C7, C8	H4, H5, H8
6b	1.57	-	H7, H8, H9, H42		H7
7	3.83	80.7	H43, H6a, b, H4, H10, H8, H9, H5	C5, C6, C7-OMe, C9	H6a, H6b, H7-OMe, H9
8	5.40	129.2	H43, H6a, b, H10, H11, H5, H7, H9,	C6, C7, C10	H43, H10, H6a, H7-OMe, H5, H7
9	5.72	138.2	H7, H11, H43, H6a, b, H10, H8	C43, C7, C10, C11	H43, H10, H7-OMe, H7
10	2.17	43.0	H43, H12a, b, H11, H7, H13, H8, H9	C43, C7, C10, C11	H43, H12b, H8
11	3.47	76.4	H43, H12a, b, H10, H14, H13, H7, H8, H9	C8, C9, C11, C12, C43	H43, H12a, H13, H9
12a	1.83	36.7	H43, H12b, H10, H15, H14, H11, H13	C10, C13, C11, C14	H43, H12a, H15, H14, H11, H13
12b	1.34	-	H10, H12a, H13		H10, H14, H12a
13	3.72	74.6	H12a, b, H10, H11, H14, H15, H16, H17	C11, C12, C14, C15	H12a, H15, H14, H11, H16
14	3.06	84.0	H12a, b, H10, H15, H11, H13, H16, H17	C12, C13, C14-OMe, C16	H12b, H12a, H15, H13
15a, b	2.43	32.6	H12a, b, H14, H13, H16, H17	C13, C14, C16, C17	H12a, H14, H14-OMe, H13, H16, H17
16	5.60	128.4	H13, H14, H15, H17-20, H21	C15, C18	H15, H14, H13, H18
17	6.07	133.4	H16	C15	H15
18	6.09	130.7		C16	
19	6.10	132.1	H20	C21	
20	6.02	130.7	H21, H19	C22	H22
21	5.71	136.4	H20, H22	C44, C22, C23, C19	H23, H19, H44

No.	^{1}H-NMR δ (ppm)	^{13}C-NMR δ (ppm)	COSY and/or TOCSY	HMBC	ROESY
22	2.36	42.4	H23, H44, H21, H24	C20, C21, C23, C44	H23, H44
23	3.88	74.7	H44, H24a, b, H22, H25	C21, C22, C25, C44	H21, H22, H24a, b, H25, H45
24a	1.66	36.9	H22, H24b, H23, H25, H45		H23, H25, H24b, H45
24b	1.41	-	H23, H24a, H25		H24a
25	3.95	75.5	H45, H28a, b, H27, H26, H24a, b, H26	C23, C24, C27, C45	H45, H24a, H27, H23
26	1.55	41.4	H45, H28a, b, H25, H27	C45, C24, C27, C25	H45
27	4.70	72.1	H45, H26, H28a, b	C45, C1	H45, H28a, H25, H33
28a	2.74	34.2	H28b, H45, H26, H25	C26, C27, C29	H28b, H31b, H33
28b	1.23	-	H28a, H45, H26, H25	C29	H28a
29	-	98.9	-	-	-
30a	1.66	35.7		C29	
30b	1.40	-	H33	C29	
31a	1.74	20.1		C29	
31b	1.55	-			
32a	1.58	27.9	H32b		
32b	1.18	-	H32a, H33	C31, C33, C34	H32a, H31a
33	3.59	75.0	H34, H32a, b, H30a, b, H46, H31a, b	C46, C31, C34, C35	H46, H32a, H34, H28a, H35-OMe
34	1.70	42.2	H46, H35, H36	C33, C46, C36, C32	H33, H35, H36, H37, H46
35	2.92	82.2	H46, H34, H37, H33, H36	C33, C34, C35-OMe, C36, C37, C46	H35-OMe, H34, H37, H25(w), H27(w), H32a, b
36	2.98	60.3	H38, H46, H47, H34, H37, H33	C35, C37, C38	H33, H34, H38
37	2.46	59.3	H47, H38, H35, H36	C47, C38, C36	H47, H35, H35-OMe, H38
38	1.40	35.3	H37, H47	C47, C37	H36
39a	1.39	35.7	H41		
39b	1.24	-			
40a	1.41	20.3	H41, H37		
40b	1.33	-			
41	0.91	14.5	H39a, b, H40a, b, H37	C40, C39	H40a
42	1.12	15.7	H2, H3, H5, H6a, b	C4, C5, C3	H3, H4, H5

No.	^{1}H-NMR δ (ppm)	^{13}C-NMR δ (ppm)	COSY and/or TOCSY	HMBC	ROESY
43	0.85	16.6	H10, H12a, b, H11, H13, H7	C11, C10, C9	H12a, H10, H11, H8, H9
44	1.10	14.9	H21, H22, H23	C21, C22, C23	H21, H22, H23
45	0.77	13.9	H28a, b, H24a, b, H26, H25, H27	C26, C25, C27	H25, H27, H24a, H26
46	1.10	11.1	H33, H34, H35, H36	C34, C35, C33	H33, H34
47	1.01	17.0	H41, H38, H37	C37, C38, C39	H37
C7-OMe	3.25	56.2		C7	H7
C14-OMe	3.42	57.4		C14	H14
C35-OMe	3.42	58.0		C35	H35

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