Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

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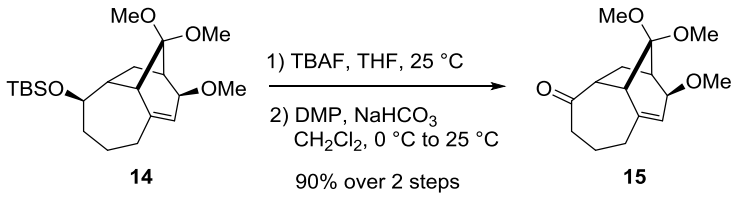
1. General Procedures:

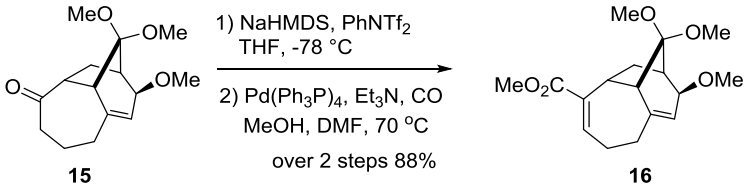
Unless the reaction procedure states otherwise, all reactions were carried out under an atmosphere of argon or nitrogen in oven or flame-dried glassware, which was under positive pressure using balloon of argon or nitrogen. Air- or moisture-sensitive liquids and solutions were transferred via syringe. Reactions were monitored by thin layer chromatography (TLC) using pre-coated silica gel plates GF254 plates. TLC plates were visualized by exposure to ultraviolet light (UV), were stained by submersion in aqueous potassium permanganate solution ($KMnO_4$) or ceric ammonium molybdenate solution (CAM), iodine staining and potassium iodide (Dragondorf). Flash column chromatography was performed on silica gel (200–300 mesh, Qingdao Marine Chemical Factory, China). All chemicals were purchased from commercial vendors, unless otherwise referenced. Reagents obtained from Acros, Aldrich, J&K, TCI, and Aladdin were used without further purification. Anhydrous tetrahydrofuran (THF), diethyl ether (Et_2O) and toluene were freshly distilled from sodium/benzophenone. CH_2Cl_2, Et_3N, DIPA, HMPA and DMPU was dried by distillation over CaH_2. Dess-Martin periodinanewere prepared from known literature procedures[1]. Ozone was generated from oxygen by using ozone generator (PACIFIC). IR spectra were recorded on a Nicolet 200 SXV spectrometer; HRMS were obtained with a Bruker BioTOFQ mass spectrometer; Proton and carbon-13 nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR) spectra were recorded on a Varian INOVA-400/54 spectrometer and Agilent Technologies 600/54 Premium Compact instrument and calibrated by using residual signals ($CDCl_3$: δ 7.26 for ^{1}H NMR, δ 77.00 for ^{13}C NMR; C_6D_6: δ 7.16 for ^{1}H NMR, δ 128.06 for ^{13}C NMR). Data are presented as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, bd = broad doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, dt = doublet of triplets, m = multiplet and/or multiple resonances), integration, and coupling constant reported in Hz. X-ray crystallographic data for compounds **13x** and **10** were obtained at Analytical & Testing Center Sichuan University, P. R. China on Oxford-Xcalibur E.

2. Experimental Procedures and Compound Characterization:



14 15

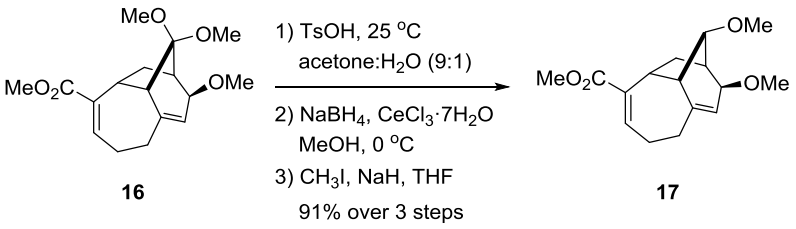
Alcohol 15 To a solution of **14** (9.87 g, 25.82 mmol) in THF (100 mL) was added TBAF (10.13 g, 38.73 mmol) at 25 ºC. After stirring for 5 h, the solvent was evaporated under reduced pressure and the residue was purified by a silica gel pad eluting with petroleum ether/ethyl acetate (1:1) to affordcrude alcohol(6.58 g) as a colorless oil, which was dissolved in CH_2Cl_2 (80 mL). $NaHCO_3$ (6.18 g, 73.59 mmol) and Dess-Martin periodinane (DMP, 15.6 g, 36.80 mmol) was added to the reaction at 0 °C. After stirring for 30 min at 0 °C, the reaction was brought to 25 °C and stirred for another 3 h. The reaction was quenched by addition of *satd. aq*. $Na_2S_2O_3$ (200 mL) and *satd. aq*. $NaHCO_3$ (100 mL). The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (3:1) to give ketone**15** (6.20 g, 23.30mmol, 90% over 2 steps) as colorless yellow oil. **IR** (film, KBr) ν_{max}: 2932, 2857, 1677, 1628, 1457 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.61 – 5.40 (m, 1H), 3.51 (dd, *J* = 3.8, 1.9 Hz, 1H), 3.38 (s, 3H), 3.28 (t, *J* = 9.1 Hz, 1H), 3.21 (s, 3H), 3.17 (s, 3H), 2.48 (dd, *J* = 6.3, 1.7 Hz, 1H), 2.46 – 2.31 (m, 3H), 2.00 – 1.85 (m, 3H), 1.81 – 1.62 (m, 3H), 1.36 (ddt, *J* = 13.9, 8.7, 4.3 Hz, 1H), 0.94 (dd, *J* = 13.2, 4.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.0, 142.2, 121.1, 83.4, 57.4, 54.3, 50.8, 47.7, 45.4, 42.4, 38.3, 37.3, 29.6, 26.4.; **HRMS**: m/z calc'd for $C_{15}H_{23}O_4$ $[M+H]^+$ 267.1591, found 267.1603.



15 16

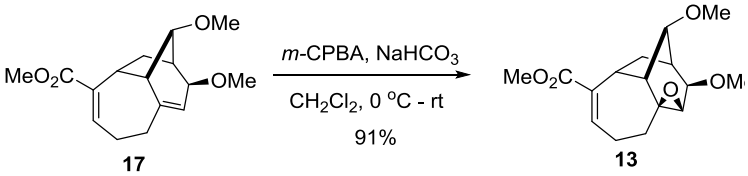
Enoate 16 To a solution of **15** (5.96 g, 22.4 mmol) in THF (120 mL) was added NaHMDS (1.3M in THF, 34.5 mL, 44.8 mmol) dropwise at −78 °C. After stirring for 30 min at this temperature, Tf_2NPh (12 g, 33.6 mmol) was added. Stirring was continued for another 2.5 h,then the reaction was quenched with *satd. aq.* NH_4Cl(200 mL), and extracted with EtOAc (3 × 200 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure to

givepale yellow oil. Without purification, the crude vinyl triflate was dissolved in MeOH (100 mL) and DMF (150 mL), and then Et_3N (9.2 mL, 66 mmol) and $Pd(Ph_3P)_4$ (1.29 g, 1.12 mmol) were added. The resulting mixture was stirred for 10 h under carbon monoxide atmosphere at 70 °C and cooled to 25 °C. The reaction mixture was diluted with H_2O (100 mL) and extracted with EtOAc (3×100 mL). The combined organic phases were washed with brine (200 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (4:1) to give **16** (6.06 g, 19.7 mmol, 88%) as colorless oil. **IR** (film, KBr) ν_{max}: 2923, 2870, 1713, 1645, 1221, 1033cm^{-1}; **^{1}H NMR** (400 MHz, CDCl3) δ 6.83 – 6.75 (m, 1H), 5.54 (d, *J* = 3.0 Hz, 1H), 3.69 (s, 3H), 3.46 (s, 1H), 3.38 (s, 3H), 3.26 (s, 3H), 3.25 (s, 1H), 3.24 (s, 3H), 2.97 (d, *J* = 5.4 Hz, 1H), 2.68 – 2.52 (m, 4H), 2.43 (dd, *J* = 14.8, 7.0 Hz, 2H), 2.23 (dt, *J* = 23.1, 7.6 Hz, 1H), 0.81 (dd, *J* = 13.6, 6.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.59 (s), 140.6, 137.2, 136.7, 120.2, 107.8, 83.56, 57.0, 51.5, 50.8, 47.3, 43.1, 41.1, 37.1, 34.9, 34.8, 22.7; **HRMS**: m/z calc'd for $C_{17}H_{25}O_5$ $[M+H]^+$ 309.1697, found 309.1688.

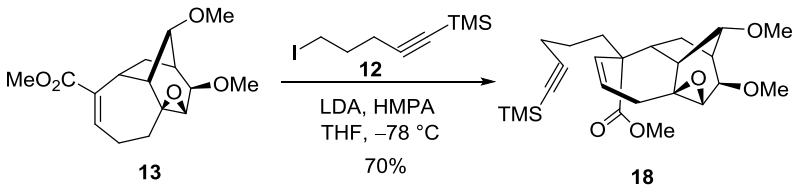


Dimethyl ether17 To a solution of **16** (6 g, 19.5 mmol) in acetone/H_2O (9:1, 120 mL) was added *p*-toluenesulfonic acid (1.68 g, 9.74 mmol) at 25 ºC and stirring was continued for another 6 h. The resulting mixture was diluted with *satd. aq.* $NaHCO_3$ (200 mL) and DCM (150 mL). The layer was separated and the aqueous layer was extracted with DCM (3×150 mL). The combined organic layers were washed with brine (150 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure toaffordcrude ketone(4.9 g). Without further purification, the crude ketone obtained above was dissolved in MeOH (100 mL), and $CeCl_3·7H_2O$ (10.5 g, 28.1 mmol) was added at 25 °C. After stirring for 30 min, $NaBH_4$ (1.7 g, 28.1 mmol) was added at 0 °C. The reaction mixture was stirred for 2 h and quenched by addition ofwater (200 mL). The organic phase was collected and the aqueous layer was extracted with CH_2Cl_2 (3× 150 mL). The combined organic fractions were washed with brine (100 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced

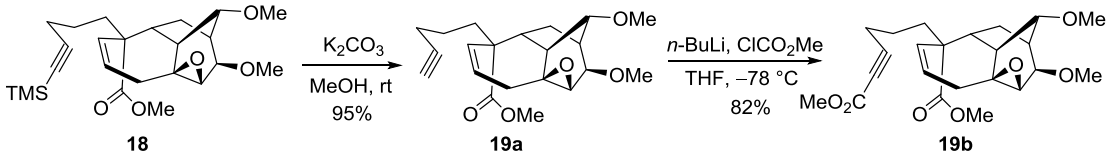
pressure to afford the crude alcohol, which was used directly forsubsequentmethylation without further purification. To a solution of crudealcoholobtained above in THF (50 mL) was added NaH (60%, 2.24 g, 56.1 mmol) and CH_3I (2.32 mL, 37.4 mmol) 0 °C. After stirring for 40 min at 25 °C, the reaction was diluted with ½ *satd. aq.* $Na_2S_2O_3$ (100 mL) and extracted with EtOAc (3 × 100 mL). The combined organic phases were washed with brine (50 mL), dried over anhydrous Na_2SO_4, evaporated under reduced to afforddimethyl ether(4.92 g, 17.7 mmol, 91% over 3 steps). **IR**(film, KBr) ν_{max}: 2987, 2871, 1710, 1459, 1163, 1027 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.87 – 6.79 (m, 1H), 5.65 (d, *J* = 3.4 Hz, 1H), 3.69 (s, 3H), 3.68 – 3.63 (m, 1H), 3.40 (s, 3H), 3.39 (s, 3H), 3.24 (s, 1H), 3.09 (dd, *J* = 8.2, 6.3 Hz, 1H), 3.03 – 2.97 (m, 1H), 2.60 (dd, *J* = 16.4, 8.8 Hz, 4H), 2.54 – 2.32 (m, 3H), 2.32 – 2.19 (m, 1H), 1.19 – 1.06 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 168.3, 139.0, 137.4, 136.6, 119.7, 81.4, 80.8, 57.6, 57.2, 51.5, 41.5, 40.4, 35.1, 34.1, 33.6, 23.1; **HRMS**: m/z calc'd for $C_{16}H_{23}O_4$ $[M+H]^+$ 279.1591, found 279.1613.



Epoxide 13 A solution of **17** (4 g, 14.4 mmol) in CH_2Cl_2 (50 mL) was treated with sodium bicarbonate (3.6 g, 43.2 mmol) and 3-chloroperoxybenzoic acid (85%, 4.39 g, 21.6 mmol) at 0 °C. The reaction was allowed to warm to 25 °C, stirred for additional 2 h, quenched by addition of*satd. aq.* NaS_2O_3 (100 mL), then extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (3:1) to give **13**(3.85 g, 13.1 mol, 91%) as colorless oil. **IR**(film, KBr) ν_{max}: 3381, 2980, 2924, 2890, 2851, 2820, 1439 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (m, 1H), 3.73 (s, 3H), 3.55 (d, *J* = 3.4 Hz, 1H), 3.48 (s, 3H), 3.39 (s, 1H), 3.37 (s, 3H), 3.22 (d, *J* = 3.9 Hz, 1H), 3.17 – 3.06 (m, 1H), 2.67 (t, *J* = 3.6 Hz, 1H), 2.61 – 2.37 (m, 5H), 2.28 – 2.08 (m, 3H), 1.65 – 1.52 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 168.5, 139.6, 135.1, 85.0, 81.9, 60.4, 58.2, 57.1, 53.4, 51.9, 40.6, 35.9, 34.9, 33.0, 25.6; **HRMS**: m/z calc'd for $C_{16}H_{23}O_5$ $[M+H]^+$ 295.1540, found 295.1549.



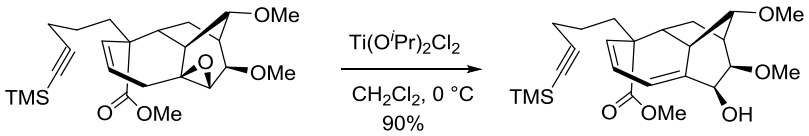
Alkylated Ester 18 To a solution of diisopropylamine (1.7 mL, 12.14 mmol) in THF (30 mL) at 0 °C was added *n*-BuLi (2.4 M, 5.10 mL, 12.24mmol) dropwise. After stirring for 30 min at 0 °C,HMPA (2.49 mL, 14.3 mmol) was added. The resulting mixture was stirred for 30 min, and then **13** (2.1 g, 7.14 mmol) in THF (5 mL) was introduced. After stirring for another 30 min, iodide chain **12** (3.23 g, 12.14 mmol) was added. This reaction mixture was stirred for 2 h, then it was quenched with *satd. aq.* NH_4Cl(50 mL), extracted with EtOAc (3 × 110 mL). The combined organic phases were washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (1:1) to give **18** (2.16 g, 5.0mmol, 70%) as colorless oil. **IR**(film, KBr) ν_{max}: 2950, 2876, 2174, 1721, 1432, 1210 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.12 (d, *J* = 11.6 Hz, 1H), 5.85 (dd, *J* = 14.8, 6.2 Hz, 1H), 3.71 (s, 3H), 3.45 –3.43 (m, 5H), 3.32 – 3.25 (m, 5H), 2.95 (d, *J* = 3.0 Hz, 1H), 2.84 (d, *J* = 12.0 Hz, 2H), 2.36 (s, 1H), 2.25 (dt, *J* = 10.8, 6.4 Hz, 2H), 2.31 –2.14 (m, 3H), 1.83 (td, *J* = 12.4, 4.0 Hz, 1H), 1.78-1.70 (m, 2H), 1.51 – 1.41 (m, 2H), 1.31 –1.24 (m, 3H), 1.02 – 0.92 (m, 1H), 0.82 (d, *J* = 7.4 Hz, 1H), 0.11 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.3, 130.9, 126.6, 106.5, 85.0, 84.9, 81.8, 58.2, 57.9, 57.2, 54.0, 53.0, 52.1, 43.3, 40.6, 37.1, 36.0, 35.0, 27.7, 24.7, 20.0, 0.0; **HRMS**: m/z calc'd for $C_{24}H_{37}O_5Si$ $[M+H]^+$ 433.2405, found 433.2409.



Alkyne19a A solution of **18** (230mg, 0.53 mmol) in MeOH (2 mL) was treated with potassium carbonate (88mg, 0.64 mmol). After stirring for 2 h at room temperature, the reaction mixture was quenched with H_2O (10 mL), extracted with EtOAc (3 ×10 mL). The combined organic phases were washed with brine (8 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure.The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (2/1

to 1:1) to afford **19a** (180 mg, 0.5 mmol, 95%) as colorless oil. **IR** (film, KBr) ν_{max}: 3290, 2949, 2879, 1720, 1431, 1210 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ6.15 (d, *J* = 12.0 Hz, 1H), 5.96 – 5.84 (m, 1H), 3.72 (s, 3H), 3.46 (brs, 4H), 3.36 (brs, 4H), 2.99 (d, *J* = 4.4 Hz, 1H), 2.89 (dd, *J* = 9.6, 5.7 Hz, 2H), 2.39 (brs, 1H), 2.30 (td, *J* = 10.0, 3.8 Hz, 1H), 2.24 – 2.11 (m, 3H), 1.97 (d, *J* = 3.1 Hz, 1H), 1.90 (td, *J* = 12.6, 4.5 Hz, 1H), 1.76 (ddt, *J* = 18.1, 12.4, 7.3 Hz, 2H), 1.55 – 1.48 (m, 1H), 1.30 (dt, *J* = 16.4, 8.2 Hz, 1H), 1.01 (t, *J* = 12.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ173.1, 154.0, 141.8, 137.2, 130.4, 129.8, 88.6, 84.1, 82.5, 73.2, 67.0, 60.3, 58.1, 57.9, 57.5, 52.6, 51.8, 51.6, 42.9, 42.6, 41.5, 30.7, 23.4, 21.0, 19.0, 14.1; **HRMS**: m/z calc'd for $C_{21}H_{29}O_5$ $[M+H]^+$ 361.2010, found 361.2011.

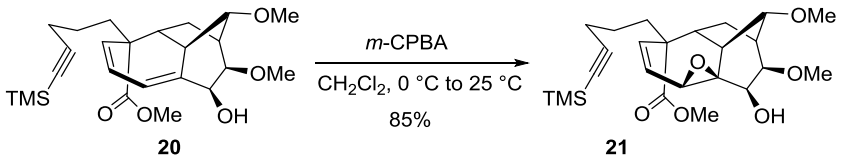
Alkyne Ester 19b To a solution of **19a** (180 mg, 0.50 mmol) in THF (2 mL)*n*-BuLi (2.4M, 0.25 mL)was added dropwise at –78 °C. After stirring for 1 h at this temperature, methyl chloroformate (53μL, 0.69 mmol) was added.Stirring was continued for another 30 min,then the reaction mixture was diluted with s*atd. aq.* $NaHCO_3$ (10 mL) and EtOAc (10 mL), separated, extracted with EtOAc (3× 10 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (2/1 to 1:1) to afford **19b** (171mg, 0.41 mmol, 82%) as a white solid. **IR** (film, KBr) ν_{max}: 2955, 2843, 2235, 1713, 1440 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ6.14 (dd, *J* = 11.7, 2.8 Hz, 1H), 5.91 (td, *J* = 12.2, 11.0, 3.6 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.46 (brs, 4H), 3.37 (brs, 4H), 2.98 (d, *J* = 4.5 Hz, 1H), 2.92 – 2.83 (m, 2H), 2.39 (d, *J* = 7.0 Hz, 1H), 2.36 – 2.24 (m, 3H), 2.18 – 2.09 (td, *J* = 12.5, 4.5 Hz, 1H), 1.91 (td, *J* = 12.5, 4.5 Hz, 1H), 1.75 (dq, *J* = 13.7, 9.5, 9.0 Hz, 2H), 1.36 (dq, *J* = 12.1, 5.7 Hz, 1H), 1.06 – 0.95 (m, 1H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ175.2, 154.0, 130.6, 127.1, 88.6, 85.0, 81.8, 73.2, 58.3, 57.9, 57.3, 54.0, 53.1, 52.6, 52.3, 43.4, 40.6, 37.0, 36.0, 35.0, 27.7, 23.8, 18.9; **HRMS**: m/z calc'd for $C_{23}H_{31}O_7$ $[M+H]^+$419.2064, found 419.2077.



18 **20**

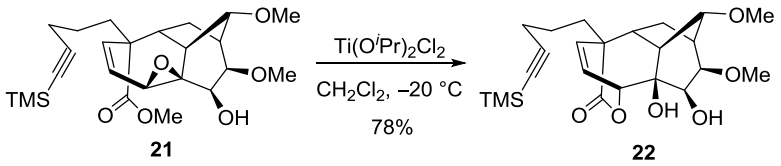
Diene 20a To a solution of **18** (1.8 g, 4.17 mmol) in CH_2Cl_2 (40 mL) at –20 °C was added $Ti(O^iPr)_2Cl_2$ (1.48 g, 6.25 mmol) in several portions. After stirring for 1 h at this temperature, the reaction was quenched with ½ *satd. aq.* $NaHCO_3$ (100 mL) and

extracted with CH_2Cl_2 (3 × 80 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (2:1) to give **20**(1.62 g, 3.75 mmol, 90%) as colorless oil. **IR** (film, KBr) ν_{max}: 2961, 2881, 1723, 1650 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.05 (d, *J* = 13.4 Hz, 2H), 5.89 (d, *J* = 10.6 Hz, 1H), 4.88 (s, 1H), 4.28 (s, 1H), 3.57 (s, 3H), 3.48 (s, 1H), 3.45 (s, 4H), 3.42 (s, 3H), 3.15 (s, 1H), 2.50 (dd, *J* = 11.4, 7.1 Hz, 1H), 2.42 (d, *J* = 5.8 Hz, 1H), 2.20 (t, *J* = 6.8 Hz, 2H), 2.11 – 1.99 (m,1H), 1.89 – 1.78 (m, 1H), 1.77 – 1.62 (m, 1H), 1.53 – 1.42 (m, 3H), 0.14 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.4, 141.8, 137.6, 130.18 129.9, 106.5, 85.0, 84.1, 82.6, 67.1, 58.1, 57.9, 57.5, 51.8, 51.5, 43.0, 42.7, 41.5, 30.7, 24.5, 20.2, 0.1; **HRMS**: m/z calc'd for $C_{24}H_{36}O_5Si$ $[M]^+$432.2327, found 432.2331.

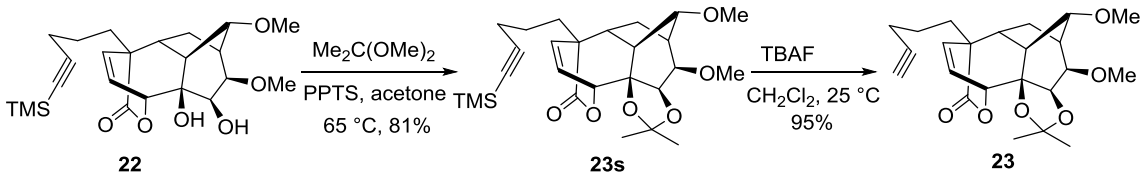


20 **21**

Epoxide 21 A solution of **20** (1.12 g, 2.60 mmol) in CH_2Cl_2 (15 mL) was treated with sodium bicarbonate (874mg, 10.4 mmol) and 3-chloroperoxybenzoic acid (70%, 961mg, 3.9 mmol) at 0 °C. The reaction was allowed to warm to 25 °C, stirred for additional 2 h, quenched by addition of*satd. aq.* NaS_2O_3 (50 mL), then extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (2:1 to 1:1) to afford**21**(990 mg, 2.21 mmol, 85%) as colorless oil. **IR**(film, KBr) ν_{max}: 3341, 2953, 1723, 1658, 1213 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.82 (d, *J* = 10.4 Hz, 1H), 5.52 (d, *J* = 10.4 Hz, 1H), 4.07 (d, *J* = 11.4 Hz, 1H), 3.80 – 3.70 (m, 3H), 3.66 (s, 2H), 3.63 (s, 1H), 3.48 (s, 3H), 3.45 (s, 3H), 3.29 (s, 1H), 2.49 – 2.43 (m, 1H), 2.20 (dd, *J* = 15.4, 8.2 Hz, 4H), 2.04 – 1.96 (m, 2H), 1.83 – 1.76 (m, 1H), 1.76 – 1.69 (m, 2H), 1.55 – 1.47 (m, 1H), 1.43 – 1.36 (m, 1H), 1.28 – 1.23 (m, 2H), 0.14 (s, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.9, 135.6, 128.4, 106.3, 85.1, 81.7, 81.7, 65.9, 61.5, 60.2, 58.0, 57.6, 52.0, 51.7, 46.5, 44.2, 42.5, 41.4, 31.4, 24.7, 20.3, 0.1; **HRMS**: m/z calc'd for $C_{24}H_{37}O_6Si$ $[M+H]^+$ 449.2354, found 449.2363.



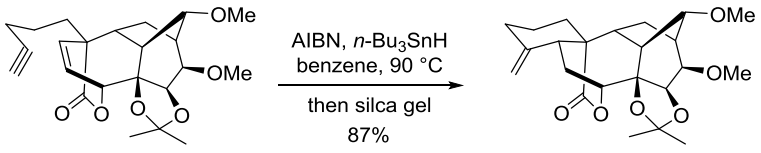
Lactone 22 To a solution of **21** (790mg, 1.76 mmol) in CH_2Cl_2 (15 mL) at –20 °C was added $Ti(O^iPr)_2Cl_2$ (626mg, 2.64 mmol) in several portions. After stirring for 1 h at this temperature, the reaction was quenched with ½ *satd. aq.* $NaHCO_3$ (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (2/1) to give **22**(595mg, 1.37 mmol, 78%) as a white solid. **IR**(film, KBr) ν_{max}: 3653, 3461, 2950, 2875, 1773, 1721, 1641, 1430, 1378, 1203 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.40 (dd, *J* = 8.6, 5.2 Hz, 1H), 6.12 (d, *J* = 8.6 Hz, 1H), 4.52 (d, *J* = 5.2 Hz, 1H), 4.47 – 4.40 (m, 2H), 4.00 (dd, *J* = 11.6, 6.6 Hz, 1H), 3.52 (t, *J* = 4.0 Hz, 1H), 3.44 (d, *J* = 2.4 Hz, 7H), 3.38 (d, *J* = 6.6 Hz, 2H), 2.55 – 2.48 (m, 1H), 2.30 (dd, *J* = 16.6, 6.0 Hz, 2H), 2.20 (dd, *J* = 15.8, 8.6 Hz, 1H), 2.05 – 1.84 (m, 4H), 1.76 – 1.68 (m, 1H), 1.62 (s, 1H), 1.54 – 1.41 (m, 3H), 1.32 – 1.21 (m, 3H), 0.14 (s, 9H); **^{13}C NMR** (100MHz, $CDCl_3$) δ 172.9, 132.5, 127.7, 106.7, 84.9, 83.0, 67.5, 66.2, 58.2, 57.3, 50.2, 45.6, 43.8, 37.3, 34.4, 29.6, 23.7, 20.2, 0.1; **HRMS**: m/z calc'd for $C_{23}H_{35}O_6Si$ $[M+H]^+$ 435.2197, found 435.2191.



Dimethyl acetal 23s To a solution of diol **22** (680 mg, 1.57 mmol) in acetone (30 mL) PPTS (1.18 g, 4.70 mmol) and 2,2-dimethoxypropane (1.93 mL, 15.7 mmol) were added in turn at 25 °C. The reaction was brought to 65 °C and stirred until TLC indicated complete consumption of the starting material (about 4 h). The reaction was quenched by addition of *satd. aq.* $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (1:1) to give **23s** (602 mg, 1.27 mmol, 81%) as a white solid. **IR**(film, KBr) ν_{max}: 2947, 2873, 1770, 1715, 1661, 1443

cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.34 (dd, *J* = 8.6, 5.4 Hz, 1H), 6.15 (d, *J* = 8.6 Hz, 1H), 4.71 (dd, *J* = 11.6, 6.2 Hz, 2H), 3.48 (t, *J* = 4.0 Hz, 1H), 3.45 (s, 3H), 3.36 (s, 1H), 3.34 (s, 3H), 2.47 (dd, *J* = 7.4, 4.0 Hz, 1H), 2.40 – 2.36 (m, 1H), 2.29 (dt, *J* = 16.8, 6.4 Hz, 1H), 2.22 – 2.15 (m, 1H), 1.51 (s, 3H), 1.42 (s, 3H), 1.24 (dd, *J* = 8.6, 5.4 Hz, 3H), 1.09 (dd, *J* = 14.0, 6.0 Hz, 1H), 0.13 (s, 9H); **^{13}C NMR** (100MHz, $CDCl_3$) δ 172.7, 133.5, 126.7, 109.3, 106.7, 84.9, 82.5, 82.0, 81.9, 77.1, 72.7, 58.0, 57.9, 50.3, 43.8, 40.5, 37.7, 34.3, 29.9, 25.9, 25.5, 23.8, 20.2, 0.1; **HRMS**: m/z calc'd for $C_{26}H_{39}O_6Si$ $[M+H]^+$ 475.2510, found 475.2518.

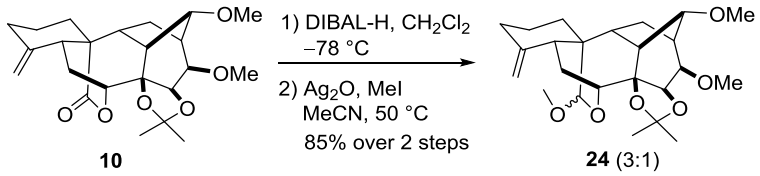
Alkyne 23 To a solution of **23S**(490 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was added TBAF (2 mL, 1 M inTHF) at 25 ºC. After stirring for another 30 min, the reaction was quenched with *satd. aq.* NH_4Cl (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (1/1) to give **23**(324mg, 0.81 mmol, 95%) as a white solid. **IR** (film, KBr) ν_{max}: 3031, 2933, 2782, 1772, 1633, 1461, 1253, 776 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.34 (dd, *J* = 8.6, 5.4 Hz, 1H), 6.15 (d, *J* = 8.6 Hz, 1H), 4.72 (t, *J* = 6.2 Hz, 2H), 3.47 (d, *J* = 4.0 Hz, 1H), 3.45 (s, 3H), 3.36 (s, 1H), 3.34 (s, 3H), 2.49 – 2.44 (m, 1H), 2.40 – 2.36 (m, 1H), 2.32 – 2.23 (m, 1H), 2.21 – 2.11 (m, 1H), 2.10 – 1.92 (m, 3H), 1.88 (dd, *J* = 13.2, 4.8 Hz, 1H), 1.78 – 1.66 (m, 1H), 1.51 (s, 3H), 1.42 (s, 3H), 1.09 (dd, *J* = 13.0, 4.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 133.5, 126.7, 109.3, 83.8, 82.5, 81.9, 77.1, 72.7, 72.6, 68.7, 58.0, 57.9, 50.3, 43.7, 40.4, 37.9, 34.4, 29.9, 25.9, 25.4, 23.6, 18.7; **HRMS**: m/z calc'd for $C_{23}H_{30}O_6$ $[M]^+$402.2037, found 402.2041.



23 **10**

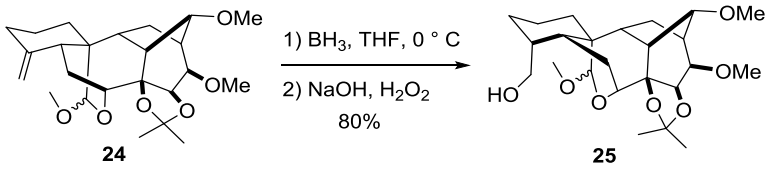
Tetracyclo 10 To a solution of **23**(290 mg, 0.72 mmol) in degassed benzene (20 mL) was added tributyltin hydride (0.77mL, 2.88 mmol) and AIBN (148 mg, 0.29 mmol) at 25ºC. The solution was heated at 90ºCuntil TLC analysis showed complete consumption of the starting material (around 1 h). The reaction was concentrated*in vacuo* and the resulted residue was dissolved in CH_2Cl_2 (10 mL), silica gel (1.45 g, 200–300 mesh) was added at 25ºC to the reaction mixture. After stirring for 10 h, the mixture was filtrated, evaporated and purified by silica gel column chromatography

using petroleum ether/ethyl acetate (3:1) to give **10**(253 mg, 0.63 mmol, 87%) as a white solid. **IR**(film, KBr) ν_{max}: 3480, 3414, 2934, 2861, 1776, 1634, 1462, 1251, 1071, 846, 775 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.91 (s, 1H), 4.82 (s, 1H), 4.67 (d, *J* = 7.0 Hz, 1H), 4.43 (d, *J* = 7.2 Hz, 1H), 3.51 (t, *J* = 4.0 Hz, 1H), 3.43 (s, 3H), 3.37 (s, 3H), 3.27 (d, *J* = 7.0 Hz, 1H), 2.75 (dd, *J* = 9.8, 4.2 Hz, 1H), 2.68 – 2.60 (m, 1H), 2.54 – 2.38 (m, 3H), 2.32 (t, *J* = 14.2 Hz, 2H), 2.13 – 1.97 (m, 2H), 1.92 (td, *J* = 12.0, 5.2 Hz, 1H), 1.78 – 1.56 (m, 3H), 1.51 (s, 3H), 1.37 (s, 3H), 1.14 – 0.96 (m, 2H);**^{13}C NMR** (100MHz, $CDCl_3$) δ 172.9, 148.4, 109.2, 108.8, 82.3, 82.2, 81.2, 71.9, 71.9, 58.0, 57.8, 51.2, 44.5, 42.8, 41.7, 38.5, 35.6, 34.7, 30.1, 26.0, 25.7, 23.7, 23.3; **HRMS**: m/z calc'd for $C_{23}H_{33}O_6$ $[M+H]^+$ 405.2272, found 405.2267.

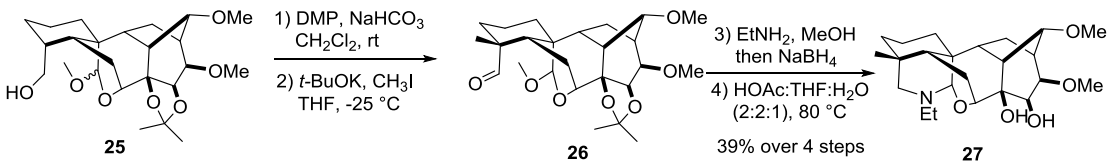


Aldolactol 24 To a solution of **10** (222 mg, 0.55 mmol) in CH_2Cl_2(2 mL) was added DIBAL-H (0.73 mL, 1.5 M in toluene) dropwise over 5 min at –78 °C. After stirring for 1 h at this temperature, the reaction was quenched by addition of EtOAc (15 mL)and *satd. aq.*sodium potassium tartrate (10 mL). Then the resulting mixture was brought to room temperature, andstirring was continued for 1–3 h until the layers could be separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure to afford crude reduction product as colorless oil. Without further purification the crude obtained above was dissolved in MeCN (2 mL), and Ag_2O (509 mg, 2.20 mmol) and MeI (2 mL) were added at 25 °C. The reaction was warmed to 50°Cand stilled for additional 2 h. After being cooled to 25 °C,the reaction mixture was filtrated and evaporated under reduced pressure. The resulting residue was purified by silica gel column chromatography using CH_2Cl_2/acetone (10/1) to give an inseparable mixture of **24** (197.4 mg,0.47 mmol, 85%) as white solid. **IR**(film, KBr) ν_{max}: 2931, 2860, 1460, 1251, 1090, 1034, 841, 776cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.92 (brs, 1.3H), 4.88 (brs, 1.3H), 4.67 (d, *J* = 7.0 Hz, 1H), 4.64 – 4.59 (d, *J* = 7.0 Hz, 0.3H), 4.44 (s, 1H), 4.31 (s, 0.3H), 3.95 (d, *J*= 6.2 Hz, 1H), 3.81 (d, *J* = 6.2 Hz, 0.3H), 3.54 (t, *J* = 4.2 Hz, 1.3H), 3.49 (d, *J* = 4.1 Hz, 0.9H), 3.44 (m, 1.3 H), 3.48 (s, 3H), 3.39 (s, 0.9H), 3.38 (s, 3H), 3.35 (s,

3H), 3.28 (s, 0.9H), 2.47 – 2.31 (m, 5H), 2.21 – 2.05 (m, 2H), 1.98 – 1.80 (m, 3H), 1.66 (s, 2H), 1.51 (s, 3.9H), 1.35 (s, 3.9H), 1.31 – 1.23 (m, 2H), 1.11 (td, *J* = 12.4, 11.1, 3.2 Hz, 1H).;**^{13}C NMR** (100MHz, $CDCl_3$) δ 151.3, 149.1, 108.9, 108.0, 105.0, 104.3, 101.9, 84.7, 84.0, 83.6, 82.9, 78.5, 73.6, 73.1, 58.1, 58.0, 57.9, 56.7, 54.8, 48.1, 46.2, 44.3, 43.8, 43.5, 41.6, 40.9, 39.1, 38.5, 37.6, 35.8, 35.3, 34.7, 33.3, 28.1, 27.2, 26.3, 26.1, 26.0, 25.1, 24.2, 21.4, 21.1; **HRMS**: m/z calc'd for $C_{24}H_{37}O_6$ $[M+H]^+$ 421.2585, found 421.2596.



Alcohol 25 To a solution of **24**(135 mg, 0.32 mmol) in anhydrous THF (4 mL) was added a solution of BH_3•THF (1.28 mL, 1.0 M in THF) dropwise at 0 °C. The resulting solution was stirred at this temperatureuntil TLC analysis showed full conversion. Then, to the reaction solution was added 30% H_2O_2 solution (1 mL) and 3N NaOH aqueous solution (1 mL) slowly in turn at 0 °C. After stirring for 30 min, the reaction was diluted with CH_2Cl_2 (10 mL) and ½ *satd. aq.* NaS_2O_3 (8 mL) and extracted with CH_2Cl_2 (3 × 8 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (1/3) to give **25** a diastereomer mixture (114 mg，0.26 mmol, 80%). For characterization, a small amount pure major isomer **25a** was separated. **IR** (film, KBr) ν_{max}: 3460, 2943, 2856, 1645, 1433, 1232, 1079, 1026 cm^{-1}; **^{1}H NMR** (600 MHz, CD_3OD) δ 4.60 (d, *J* = 6.6 Hz, 2H), 4.33 (s, 1H), 3.81 (d, *J* = 13.8 Hz, 1H), 3.75 (d, *J* = 4.4 Hz, 1H), 3.54 (t, *J* = 3.8 Hz, 1H), 3.51 – 3.46 (m, 1H), 3.44 (d, *J* = 9.6 Hz, 4H), 3.34 (d, *J* = 2.0 Hz, 3H), 3.34 (s, 3H), 2.53 – 2.50 (m, 1H), 2.42 – 2.36 (m, 1H), 2.30 – 2.17 (m, 3H), 2.02 – 1.93 (m, 4H), 1.83 (s, 2H), 1.45 (s, 4H), 1.32 (s, 4H); **^{13}C NMR** (100MHz, CD_3OD) δ 108.2, 102.90, 84.2, 83.9, 82.8, 77.1, 73.6, 63.3, 57.1, 53.6, 48.5, 44.2, 39.9, 39.9, 38.9, 35.0, 33.8, 26.7, 26.5, 25.5, 25.4, 23.1, 17.1; **HRMS**: m/z calc'd for $C_{24}H_{39}O_7$ $[M+H]^+$439.2690,found 439.2698.



***N, O*-acetal 27** A solution of **25** (30 mg, 68.5μmol) in CH_2Cl_2(2 mL) was treated with $NaHCO_3$ (23 mg, 0.274 mmol) and Dess-Martin periodinane (58 mg, 0.137 mmol). The reaction mixture was stirred for 1 h at room temperature, then quenched with *satd. aq.*$Na_2S_2O_3$ (5 mL) and *satd. aq.*$NaHCO_3$ (5 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3×8 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure to give crude aldehyde, which was dissolved in THF (2 mL), then *t*-BuOK (15 mg, 0.137 mmol) and CH_3I (17μL, 0.274 mmol) were added at –20 °C. After stirring for 40 min, the reaction was diluted with ½ *satd. aq.*$Na_2S_2O_3$ (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, evaporated and simply filtrated through a pad of silica gel to afford a labile methylaldehyde **26** as light yellow oil, which was quickly used in the subsequent step without further purification. To a solution of above crude **26** in MeOH (1 mL) was added ethylamine (30% – 35% in methanol, 0.3 mL). The reaction mixture was warm to 50 °C and stirred for 5 h. After evaporation the solution of the reaction mixture, MeOH (1 mL) and $NaBH_4$ (5.2 mg, 0.137 mmol) was added at 25 °C in turn. The reaction was stirred for 30 min before water (5 mL) and CH_2Cl_2 (5 mL) was added and the layers were separated The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtrated and concentrated *in vacuo* to afford crude amine **27s**, which was dissolved in HOAc/H_2O (1:1, 1 mL) and stirred at 100 °C under argon overnight. After being cooled to room temperature, the reaction mixture was diluted with $NH_3{\cdot}H_2O$ (30%, 0.3mL), water (5 mL) and extracted with EtOAc (3×5 mL). The combined organic phases were washed with brine (5 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (3:1) to afford **27** (10.9 mg, 26.7 μmol, 39%) as a white solid. **IR** (film, KBr) ν_{max}: 3460, 3330, 2930, 2871, 1652, 1449 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.33 (s, 1H), 4.29 – 4.23 (m, 1H), 4.13 (s, 1H), 3.99 (s, 1H), 3.57 (s, 2H), 3.47 (s, 1H), 3.46 (s, 3H), 3.45 (s, 3H), 3.43 (d, *J* = 6.4 Hz, 1H), 2.72 (d, *J* = 33.4 Hz, 1H), 2.60 (s, 1H), 2.48 (d, *J* = 22.6 Hz, 2H), 2.40 – 2.29 (m, 3H), 2.23 – 2.15 (m, 2H), 2.03 (s, 2H), 1.83 (s, 3H), 1.25 (s, 4H), 1.07 (s, 3H), 0.84 (d, *J* = 8.2 Hz, 3H); **^{13}C NMR** (100MHz, CD_3Cl_3) δ86.2, 84.3, 84.0, 75.8, 74.3, 66.3, 58.1, 57.5, 53.1, 48.1, 47.4, 44.9, 41.8, 40.5, 39.4, 39.0, 37.8, 34.4, 27.4, 25.9, 22.4, 21.1, 13.1; **HRMS**: m/z calc'd for $C_{23}H_{38}NO_5$ $[M+H]^+$408.2744, found 408.2731.

For a brief characterization of the labile methylaldehyde **26**, a small amount of crude product (10 mg) was purified by silica gel column chromatography using CH_2Cl_2/ acetone (30:1) to give **26** (3mg) as an oil. **^{1}H NMR** (600 MHz, CD_3Cl_3) δ9.65 (s, 1H), 9.61 (s, 0.3H), 4.60 (d, *J* = 7.1 Hz, 1H), 4.57 (d, *J* = 7.2 Hz, 0.3H), 4.29 (s, 1H), 4.27 (s, 0.3H), 3.80 (d, *J* = 6.4 Hz, 1H), 3.76 (s, 1H), 3.75 (d, *J* = 6.6 Hz, 0.3H), 3.48 (s, 3H), 3.49 – 3.47 (m, 2H), 3.4 (s, 3H), 3.49 – 3.41 (m, 2H), 3.27 (s, 3H), 2.65 – 2.53 (m, 2H), 2.49 – 2.41 (m, 4H), 2.23 (dd, *J* = 15.0, 10.7 Hz, 2H), 2.15 – 2.07 (m, 2H), 1.96 – 1.79 (m, 5H), 1.68 – 1.64 (m, 3H), 1.52 – 1.50 (s, 3H), 1.50 (s, 0.9), 1.39 (m, 2H), 1.34 (s, 3H), 1.32 (s, 0.9H), 1.00 (s, 3H); **HRMS**: m/z calc'd for $C_{25}H_{39}O_7[M+H]^+$ 451.2690, found 451.2683.

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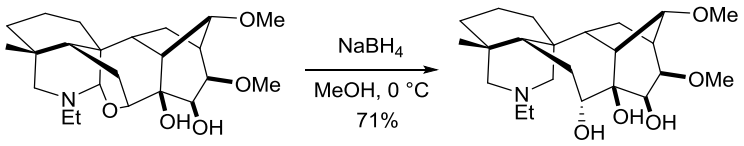
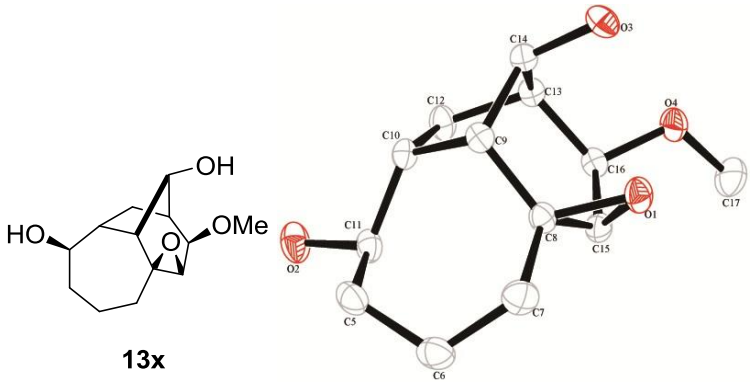


27 **9**

Triol 9 To a solution of**27** (5 mg, 12.3 μmol) in MeOH (0.5 mL) $NaBH_4$ (1.9 mg, 50 μmol) was added in on portion at 0 °C. After stirring for another 30 min, the reaction was quenched by addition of water (3 mL), extracted with CH_2Cl_2 (3 × 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2/MeOH (9:1) to give triol**9** (3.6 mg, 8.8 μmol, 71 %) as a white solid. **IR**(film, KBr) ν_{max}: 3752, 3360, 3920, 2854, 1453, 1351, 1261, 1043, 971 cm^{-1};**^{1}H NMR** (600 MHz, $CDCl_3$) δ5.43 (s, 1H), 4.10 (dd, *J* = 8.4, 5.2 Hz, 1H), 3.86 (d, *J* = 5.0 Hz, 1H), 3.58 (d, *J* = 8.8 Hz, 1H), 3.54 (d, *J* = 4.1 Hz, 1H), 3.50 – 3.46 (m, 3H), 3.44 (s, 3H), 3.41 (s, 3H), 2.83 – 2.76 (m, 1H), 2.74 (dt, *J* = 7.4, 3.8 Hz, 1H), 2.42 (dd, *J* = 10.9, 6.0 Hz, 2H), 2.39 – 2.34 (m, 1H), 2.29 – 2.20 (m, 4H), 2.04 – 1.97 (m, 3H), 1.88 (td, *J* = 10.8, 5.2 Hz, 1H), 1.79 – 1.68 (m, 4H), 1.56 (dd, *J* = 13.4, 5.8 Hz, 2H), 1.45 – 1.30 (m, 4H), 1.23 (d, *J* = 10.9 Hz, 1H), 1.10 (dd, *J* = 13.5, 10.0 Hz, 1H), 1.01 (t, *J* = 7.2 Hz, 3H), 0.89 (s, 3H);**^{13}C NMR** (150MHz, $CDCl_3$) δ86.6, 83.5, 82.5, 78.1, 67.2, 58.9, 58.5, 58.2, 57.1, 52.6, 48.3, 47.8, 47.4, 42.0, 41.6, 36.9, 35.4, 34.4, 29.7, 28.1, 23.3, 23.0, 12.7.; **HRMS**: m/z calc'd for $C_{23}H_{40}NO_5$ $[M+H]^+$410.2901, found 410.2909.

3. X-ray data for compounds 13x and 10

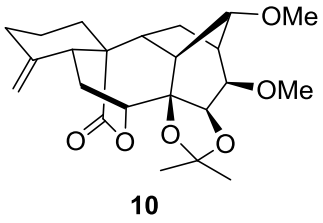


13x

Table 1 Crystal data and structure refinement for 111031_s2_ch

Identification code	111031_s2_ch
Empirical formula	$C_{13}H_{20}O_4$
Formula weight	240.29
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.8545(6)
b/Å	11.1988(4)
c/Å	10.9655(6)
α/°	90.00
β/°	117.846(7)
γ/°	90.00
Volume/Å^3	1178.60(9)
Z	4
ρ_{calc}mg/mm^3	1.354
m/mm^{-1}	0.099
F(000)	520
Crystal size/mm^3	0.38 × 0.35 × 0.12
2Θ range for data collection	7.28 to 50°
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 13$, $-12 \leq l \leq 13$
Reflections collected	4710
Independent reflections	2068[R(int) = 0.0158]
Data/restraints/parameters	2068/0/163
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0402, wR_2 = 0.0916

Final R indexes [all data]	R_1 = 0.0516, wR_2 = 0.1002
Largest diff. peak/hole / e Å^{-3}	0.201/-0.165
Flack Parameter	N/A



10

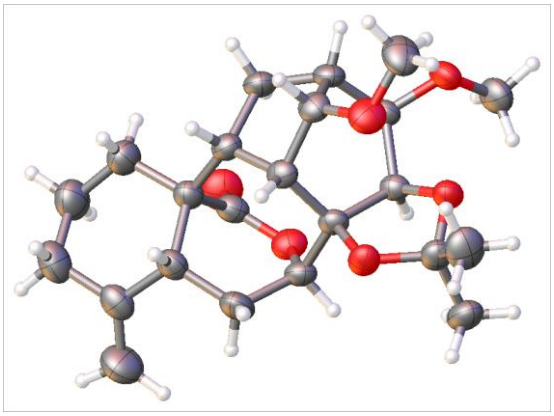
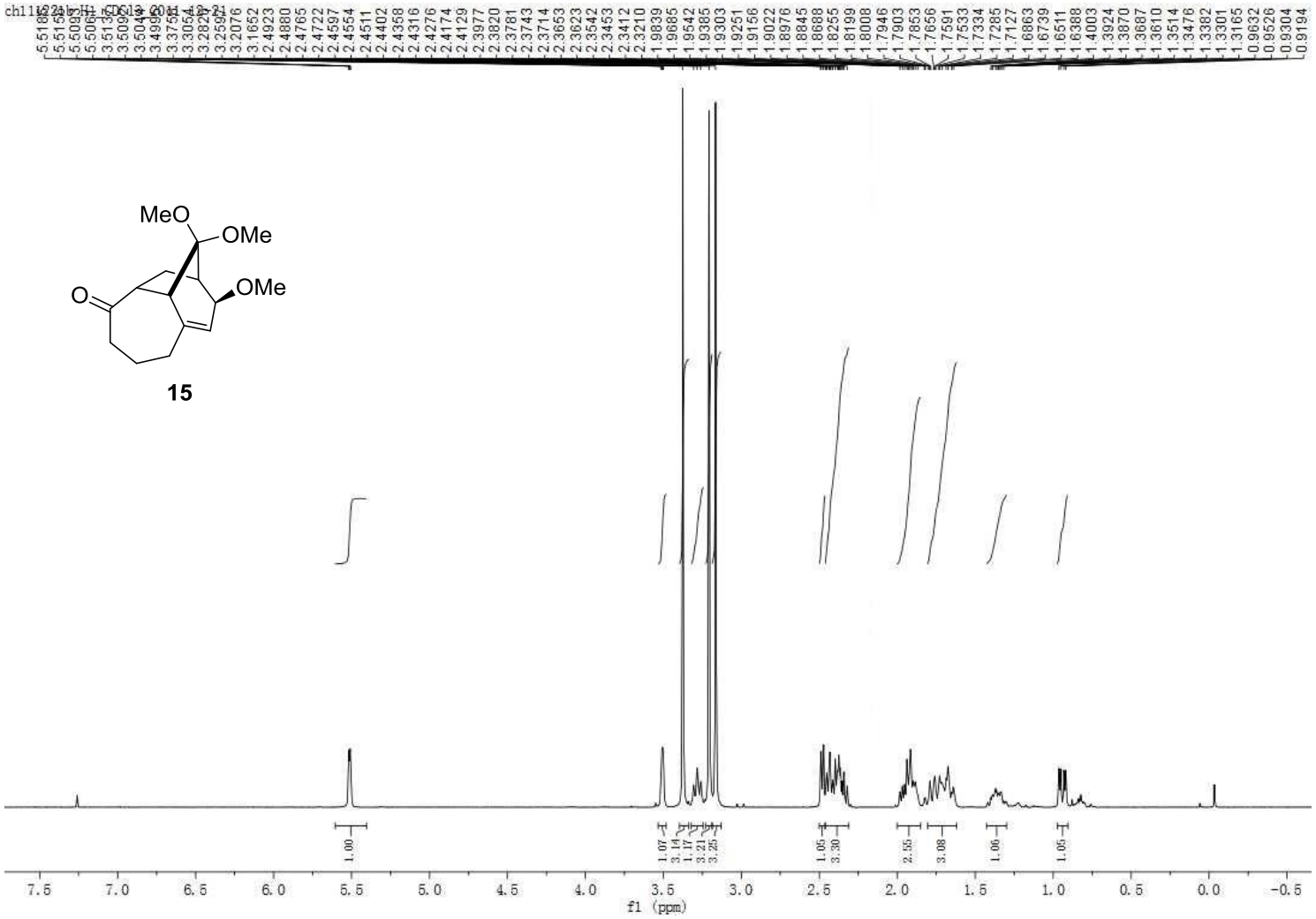


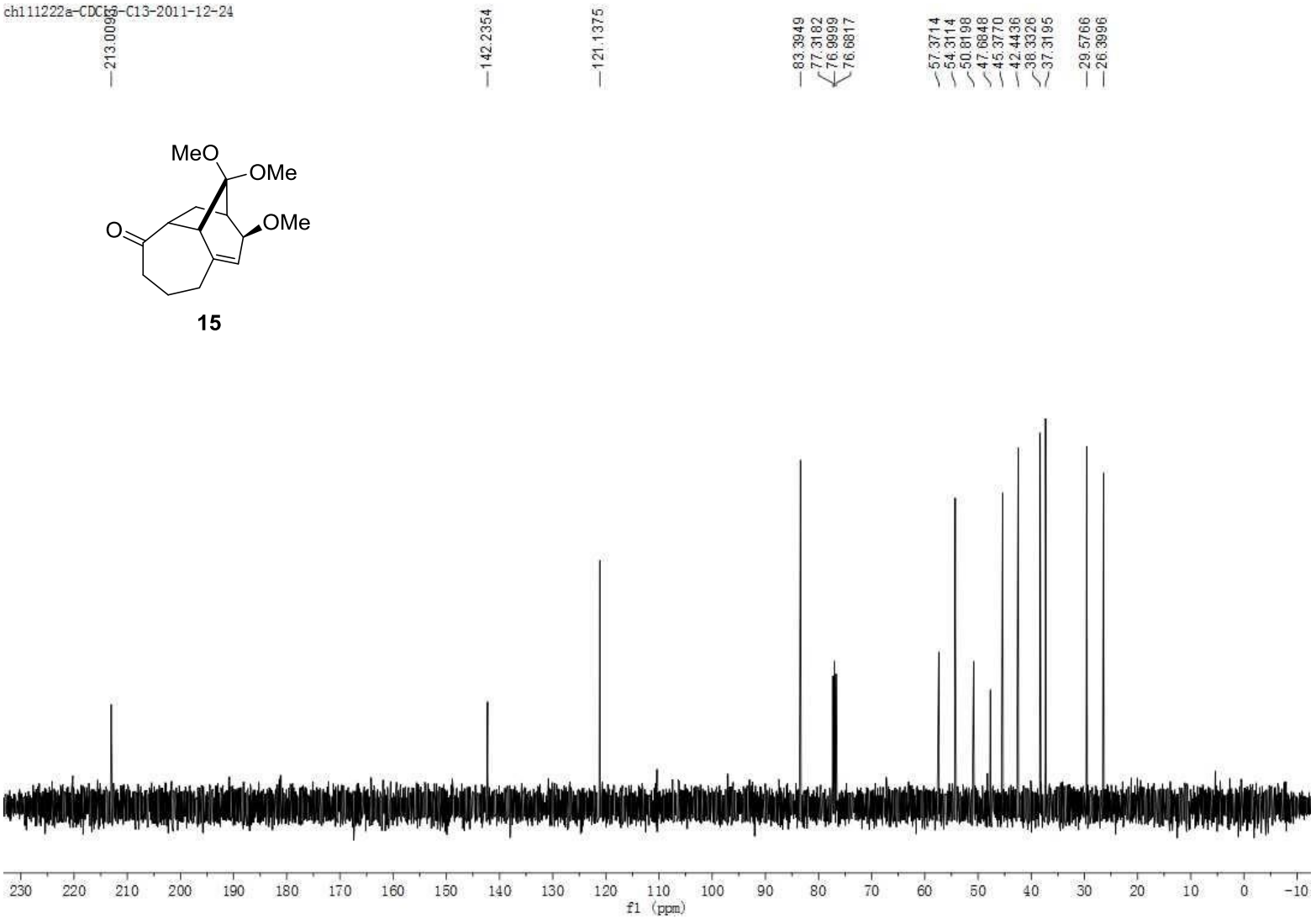
Table 2 Crystal data and structure refinement for 160307_s3_xwy.

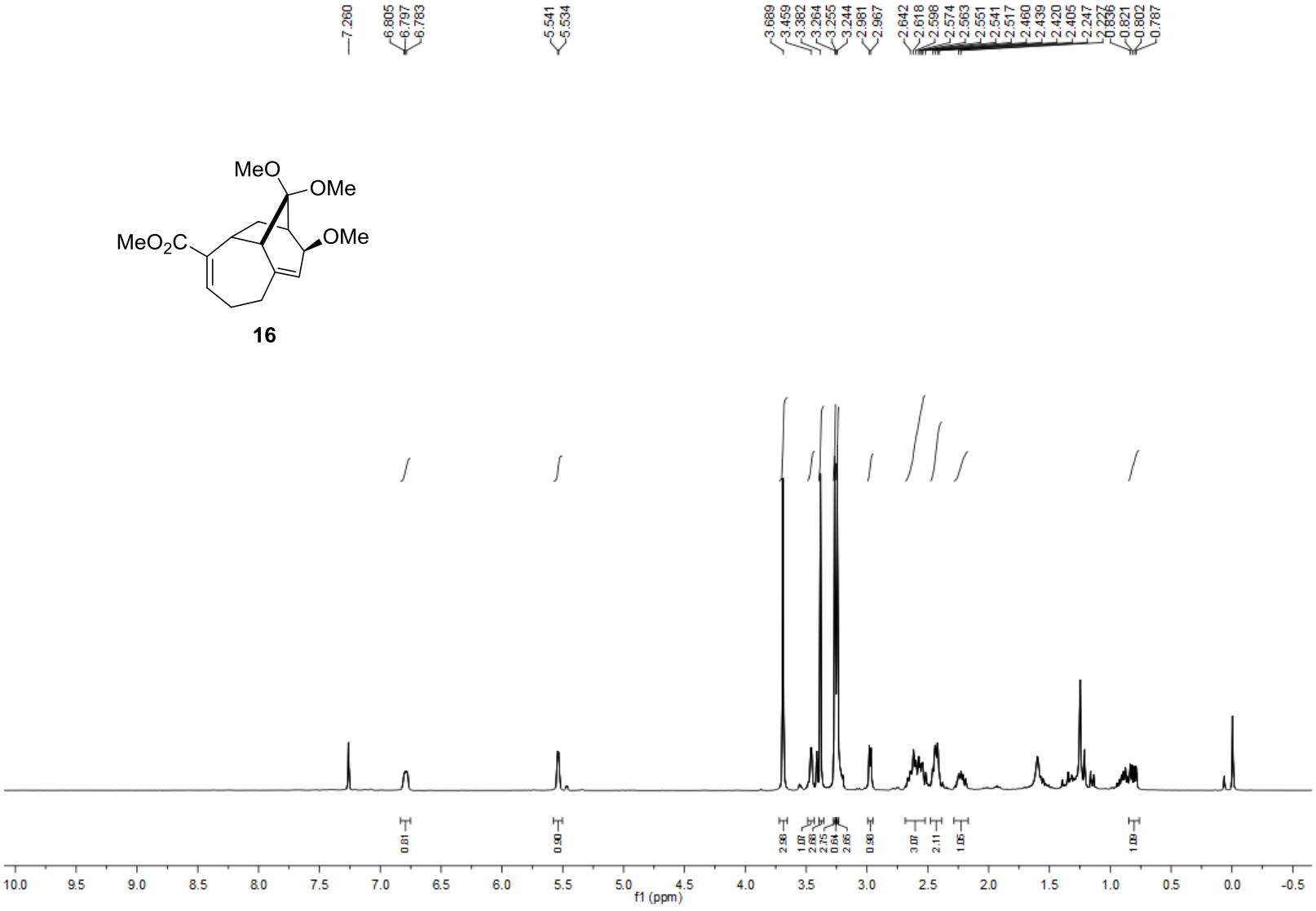
Identification code	160307_s3_xwy
Empirical formula	$C_{23}H_{32}O_6$
Formula weight	404.49
Temperature/K	293.15
Crystal system	triclinic
Space group	P-1
a/Å	8.2403(4)
b/Å	11.2635(5)
c/Å	11.6154(7)
α/°	80.692(4)
β/°	75.701(5)
γ/°	83.849(4)
Volume/Å^3	1028.38(9)
Z	2
ρ_{calc}g/cm^3	1.306
μ/mm^{-1}	0.093
F(000)	436.0
Crystal size/mm^3	0.4 × 0.4 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.08 to 52.74
Index ranges	-10 ≤ h ≤ 9, -14 ≤ k ≤ 13, -14 ≤ l ≤ 14
Reflections collected	8586
Independent reflections	4204 [R_{int} = 0.0184, R_{sigma} = 0.0375]
Data/restraints/parameters	4204/0/275

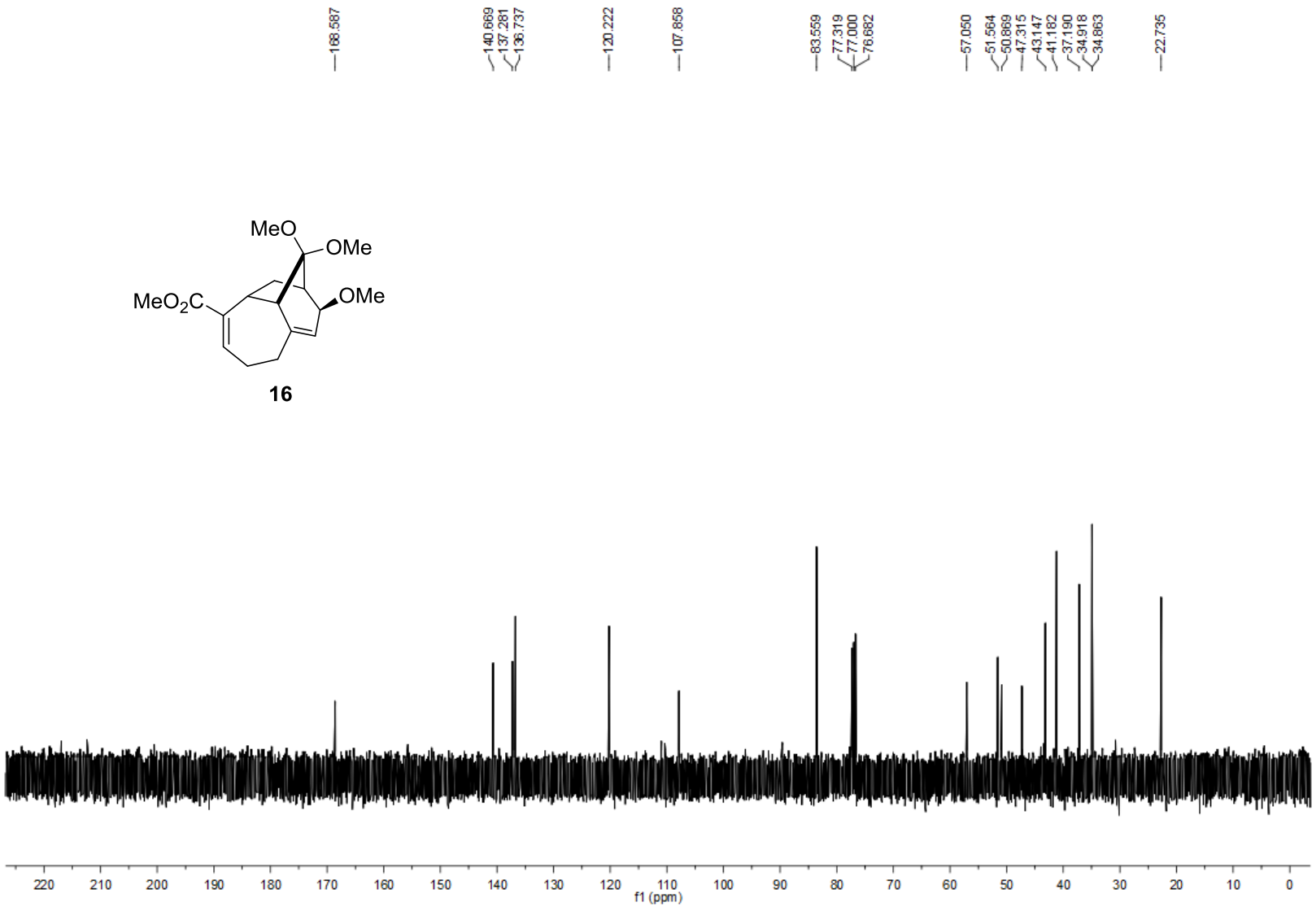
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0474, wR_2 = 0.1041
Final R indexes [all data]	R_1 = 0.0702, wR_2 = 0.1173
Largest diff. peak/hole / e $Å^{-3}$	0.25/-0.15

4. ^{1}H NMR and ^{13}C NMR spectra




ch111222a-CDCl3-C13-2011-12-24
213.0093
142.2354
121.1375
83.3949
77.3182
76.9999
76.6817
57.3714
54.3114
50.8198
47.6848
45.3770
42.4436
38.3326
37.3195
29.5766
26.3996
MeO
OMe
OMe
O
15
f1 (ppm)


7.260
6.805
6.797
6.783
5.541
5.534
3.689
3.459
3.382
3.264
3.255
3.244
2.981
2.967
2.642
2.618
2.598
2.574
2.563
2.551
2.541
2.517
2.460
2.439
2.420
2.405
2.247
0.836
0.821
0.802
0.787
MeO
OMe
OMe
MeO2C
16
0.81
0.90
2.58
1.07
2.68
2.75
0.64
2.65
0.98
3.07
2.11
1.05
1.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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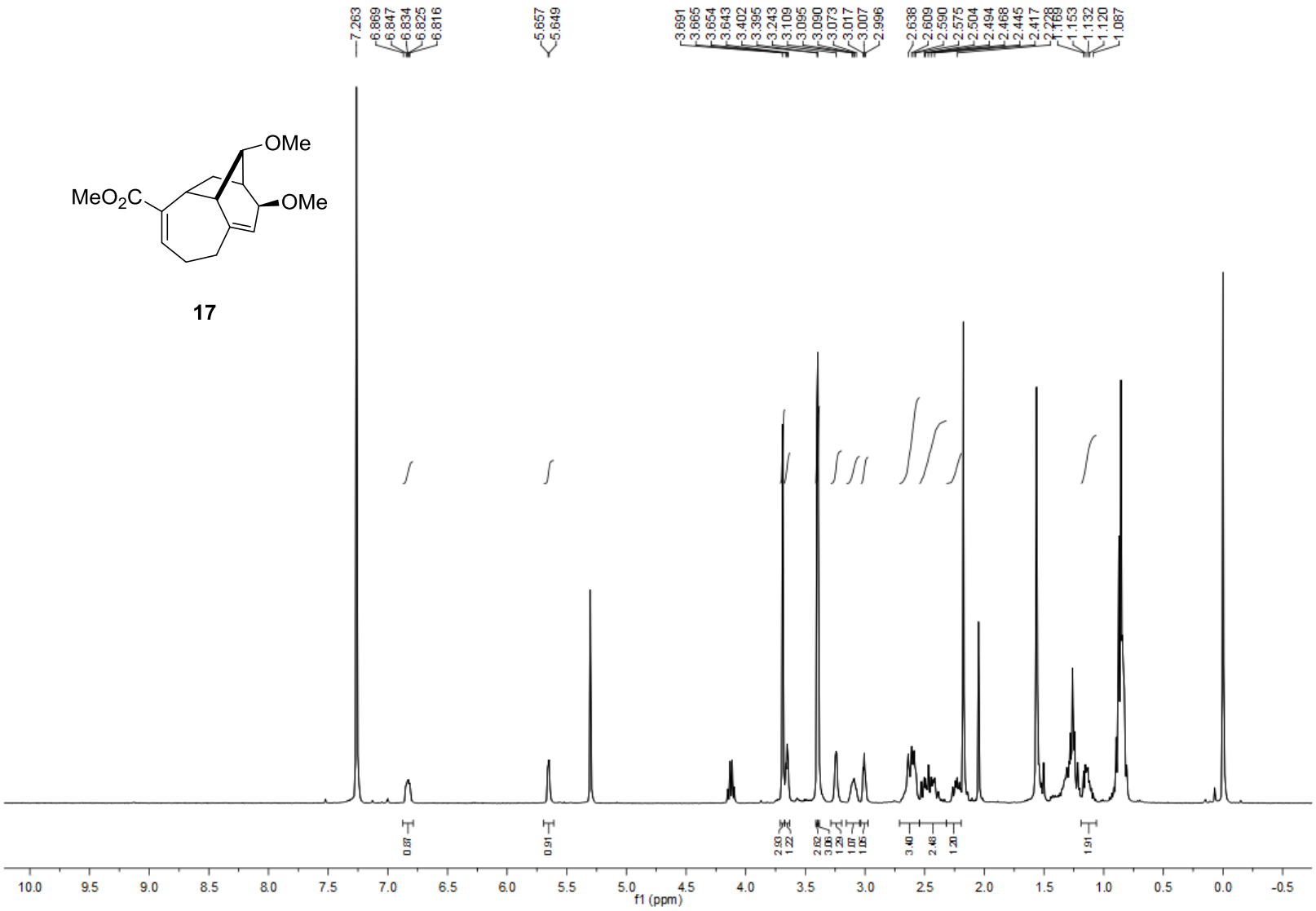
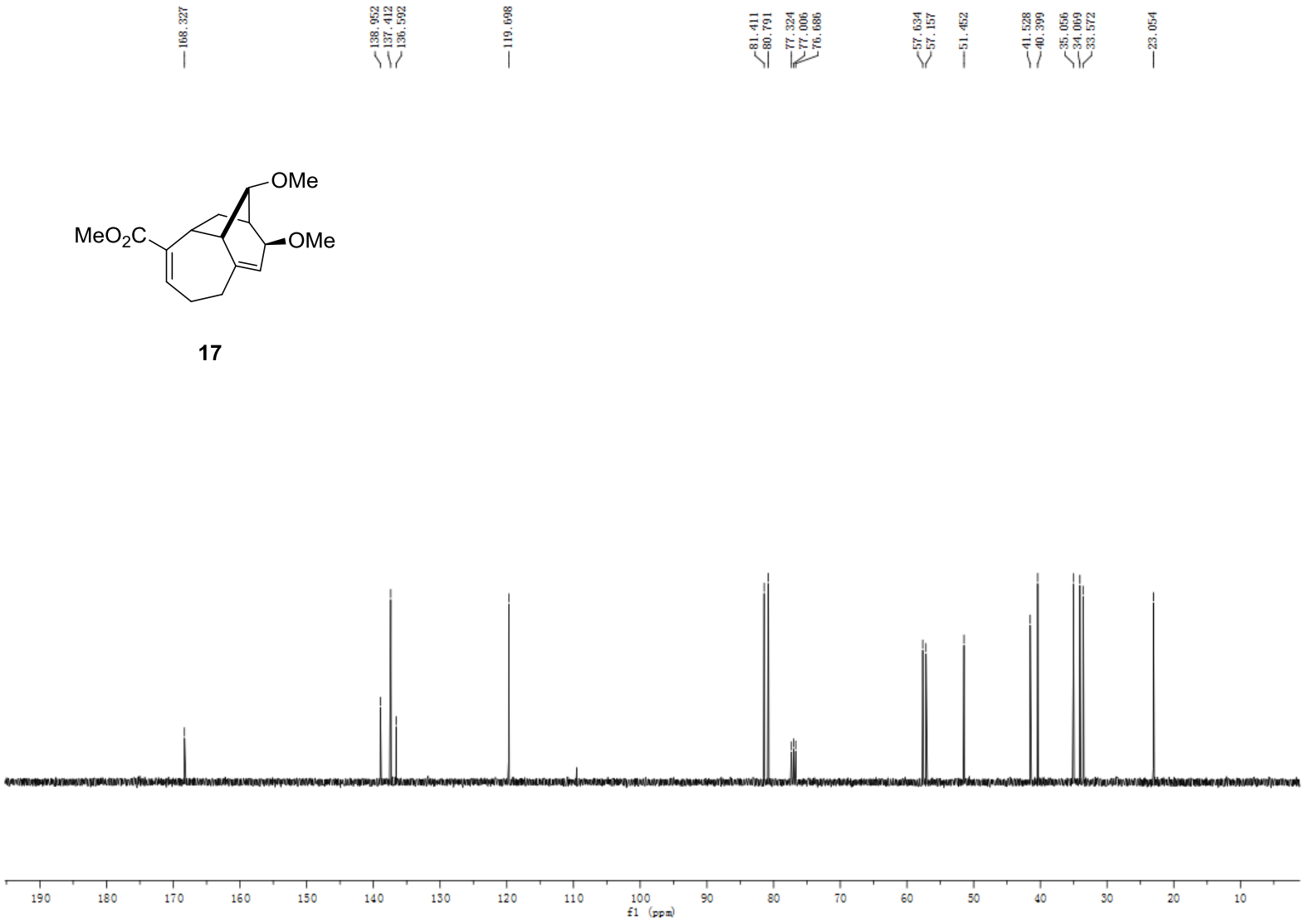
140.669
137.281
136.737
120.222
107.858
83.559
77.319
77.000
76.682
57.050
51.564
50.869
47.315
43.147
41.182
37.190
34.918
34.863
22.735
MeO
OMe
OMe
MeO2C
16
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.263
6.869
6.847
6.834
6.825
6.816
5.657
5.649
3.691
3.665
3.654
3.643
3.402
3.395
3.243
3.109
3.095
3.090
3.073
3.017
3.007
2.996
2.638
2.609
2.590
2.575
2.504
2.494
2.468
2.445
2.417
2.228
1.169
1.153
1.132
1.120
1.087
OMe
MeO2C
OMe
17
f1 (ppm)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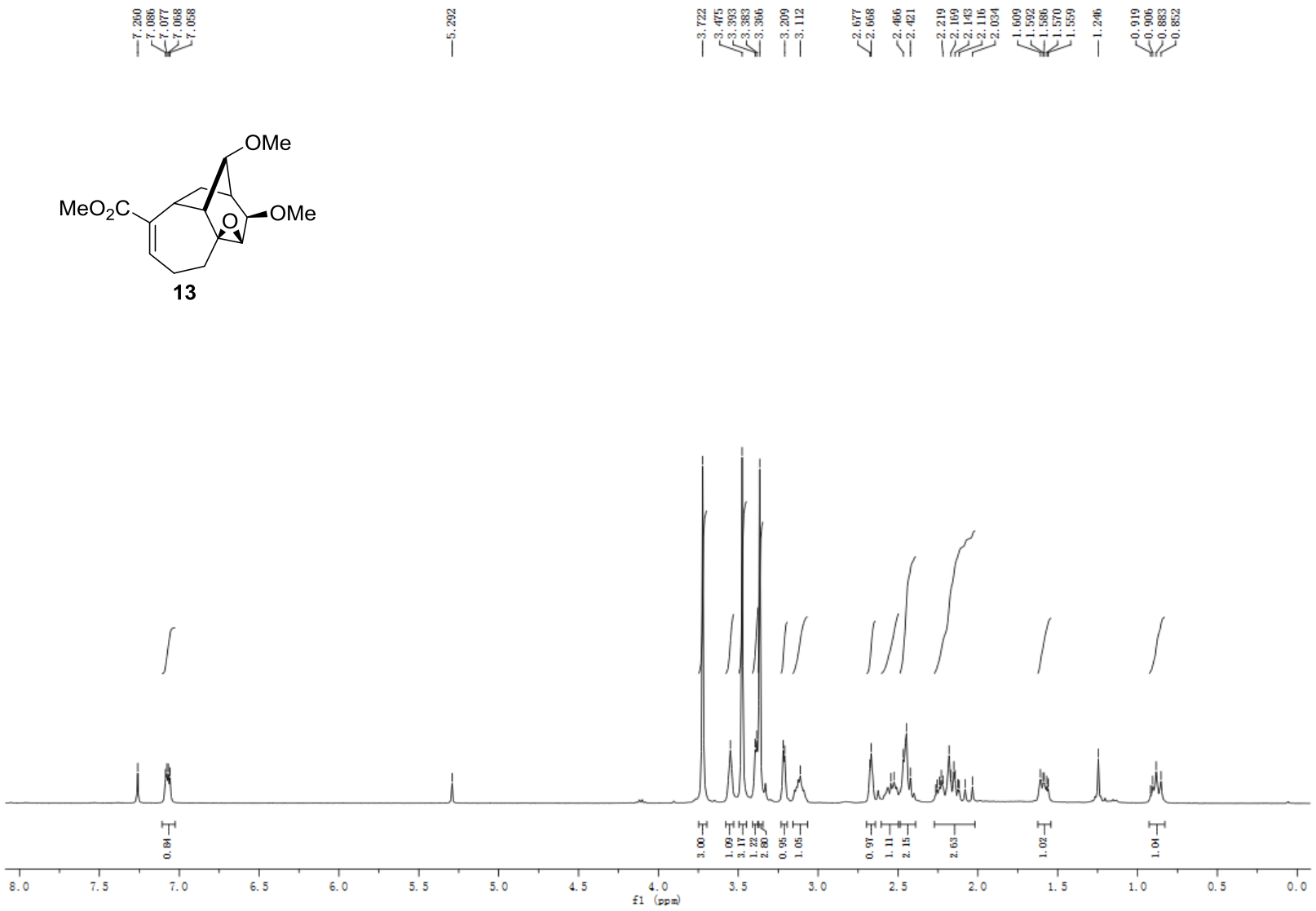
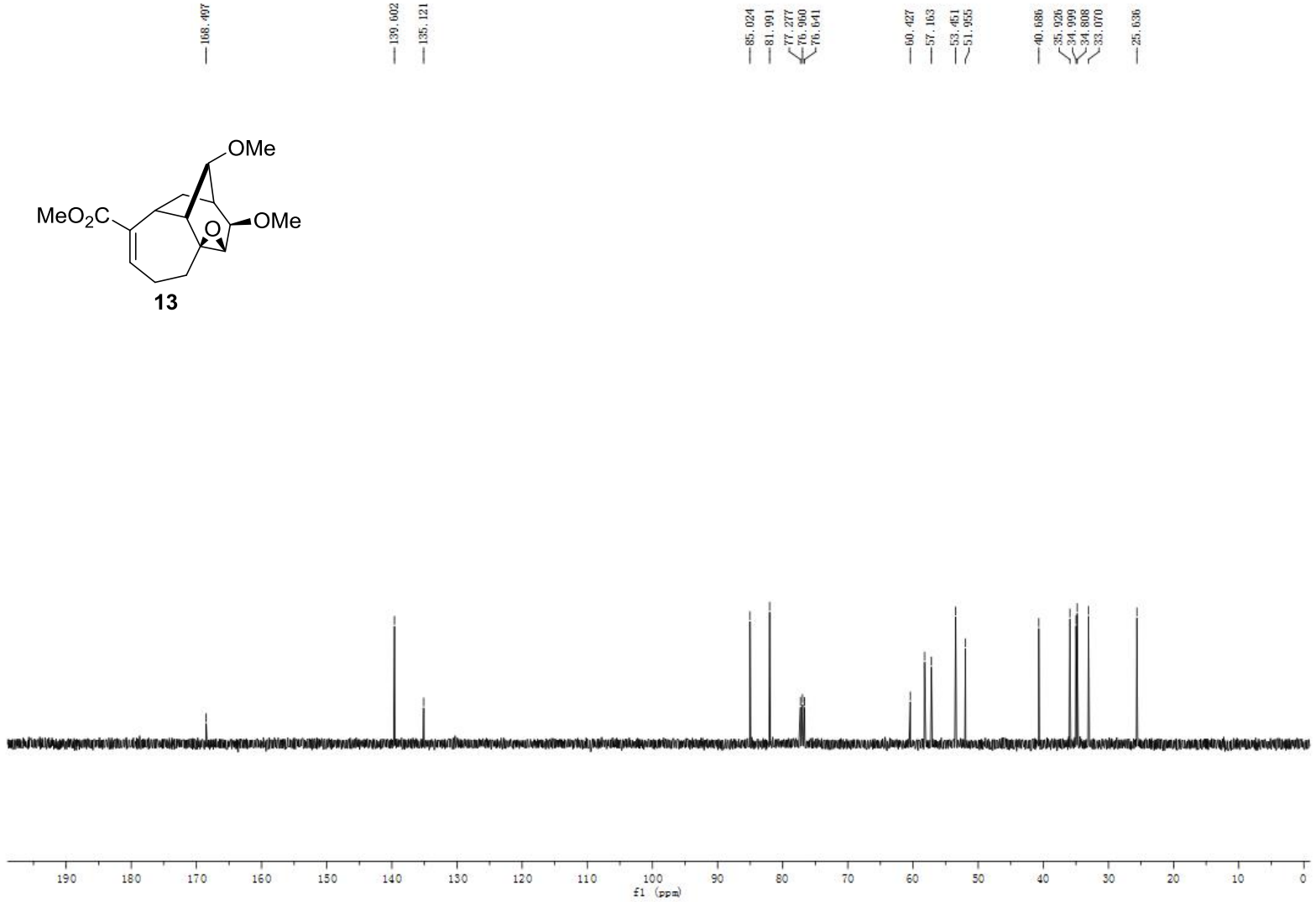
138.952
137.412
136.592
119.698
81.411
80.791
77.324
77.006
76.686
57.634
57.157
51.452
41.528
40.399
35.056
34.069
33.572
23.054
OMe
MeO2C
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

17


7.260
7.086
7.077
7.068
7.058
5.292
3.722
3.475
3.393
3.383
3.366
3.209
3.112
2.677
2.668
2.466
2.421
2.219
2.169
2.143
2.116
2.034
1.609
1.592
1.586
1.570
1.559
1.246
0.919
0.906
0.883
0.852
OMe
MeO2C
O
OMe
13
0.84
3.00
1.09
3.17
1.22
2.80
0.95
1.05
0.97
1.11
2.15
2.63
1.02
1.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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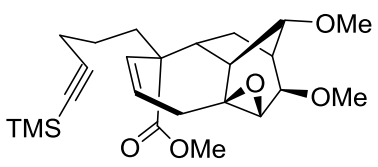
139.602
135.121
85.024
81.991
77.277
76.960
76.641
60.427
57.163
53.451
51.955
40.686
35.926
34.999
34.808
33.070
25.636
OMe
MeO2C
O
OMe
13
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



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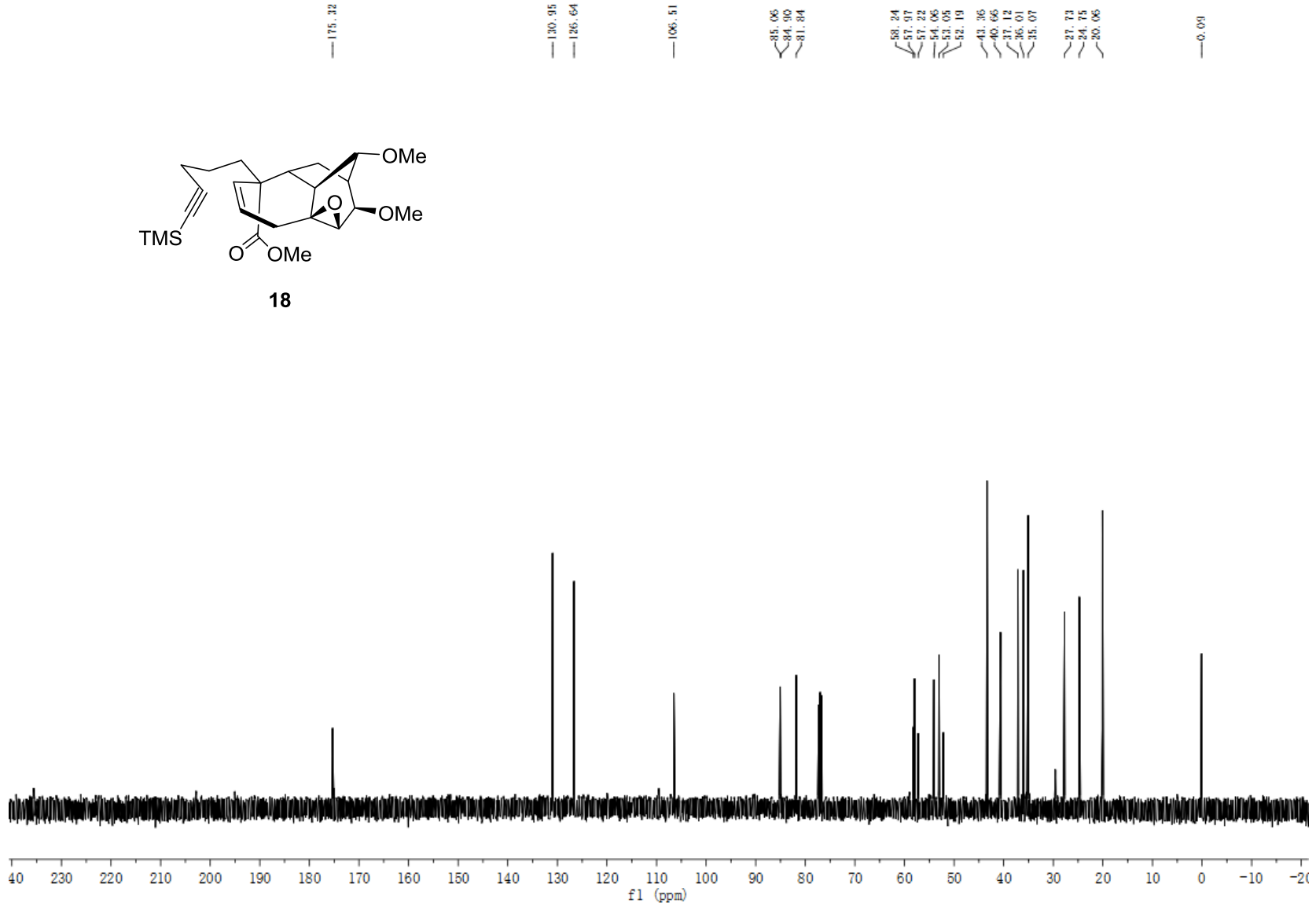
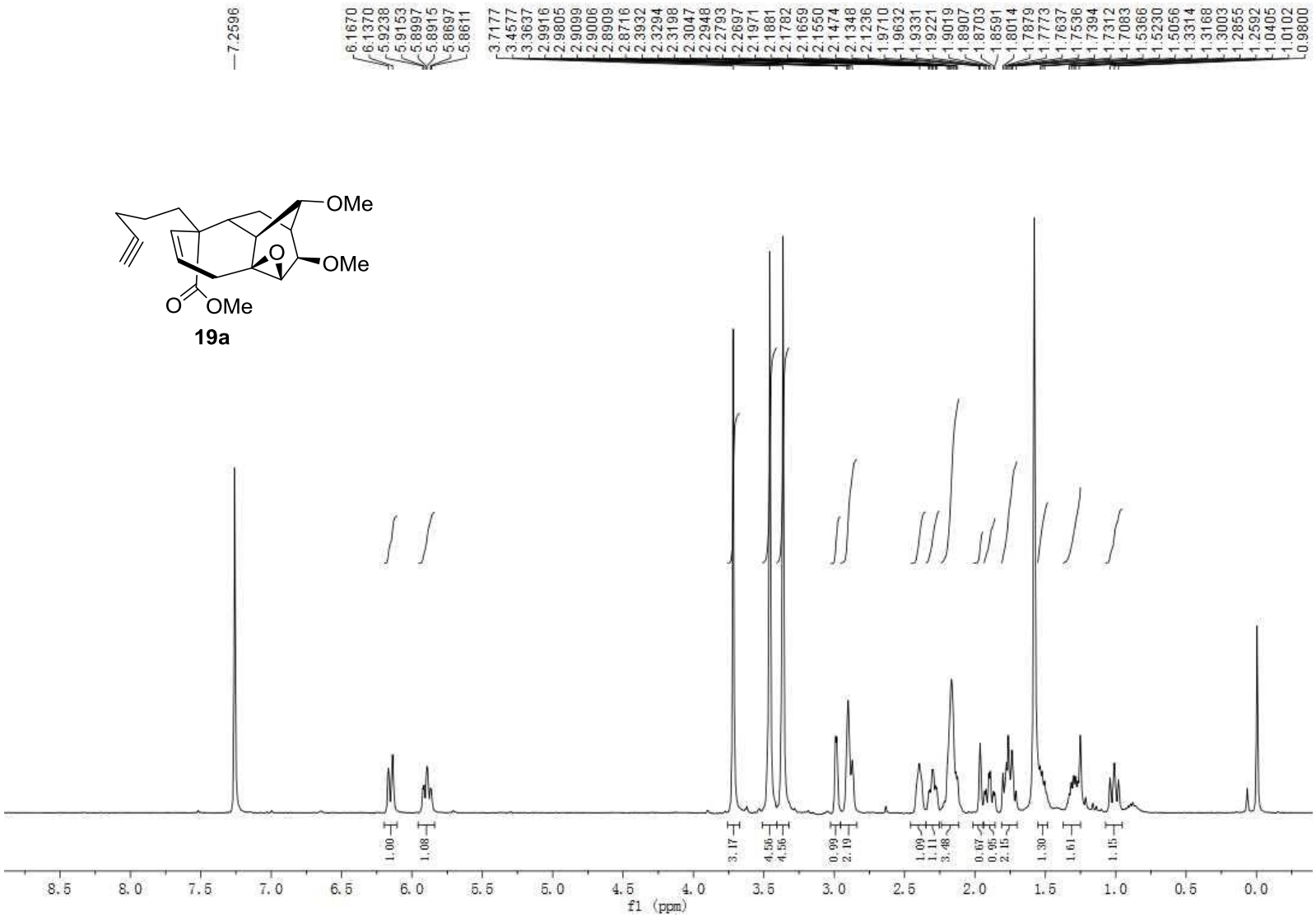

175.32
130.95
126.64
106.51
85.06
84.90
81.84
58.24
57.97
57.22
54.06
53.05
52.19
43.36
40.66
37.12
36.01
35.07
27.73
24.75
20.06
0.00
OMe
OMe
O
TMS
O
OMe
f1 (ppm)

18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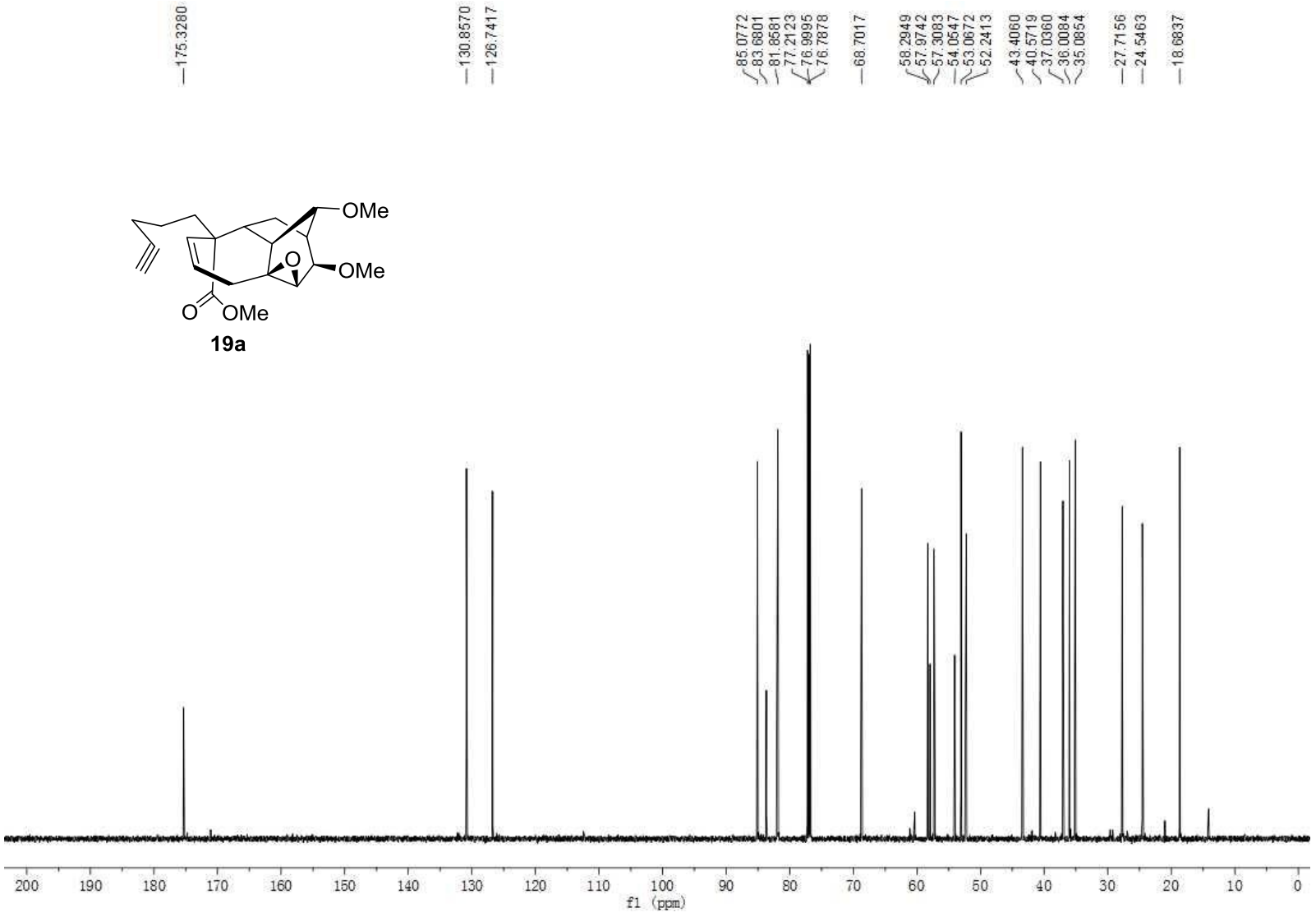
6.1670
6.1370
5.9238
5.9153
5.8997
5.8915
5.8697
5.8611
3.7177
3.4577
3.3637
2.9916
2.9805
2.9099
2.9006
2.8909
2.8716
2.3932
2.3294
2.3198
2.3047
2.2948
2.2793
2.2697
2.1971
2.1881
2.1782
2.1659
2.1550
2.1474
2.1348
2.1236
1.9710
1.9632
1.9331
1.9221
1.9019
1.8907
1.8703
1.8591
1.8014
1.7879
1.7773
1.7637
1.7538
1.7394
1.7312
1.7083
1.5366
1.5230
1.5056
1.3314
1.3168
1.3003
1.2855
1.2592
1.0405
1.0102
0.9800
OMe
OMe
O
O
OMe
19a
1.00
1.08
3.17
4.56
4.56
0.99
2.19
1.09
1.11
3.48
0.67
0.95
2.15
1.30
1.61
1.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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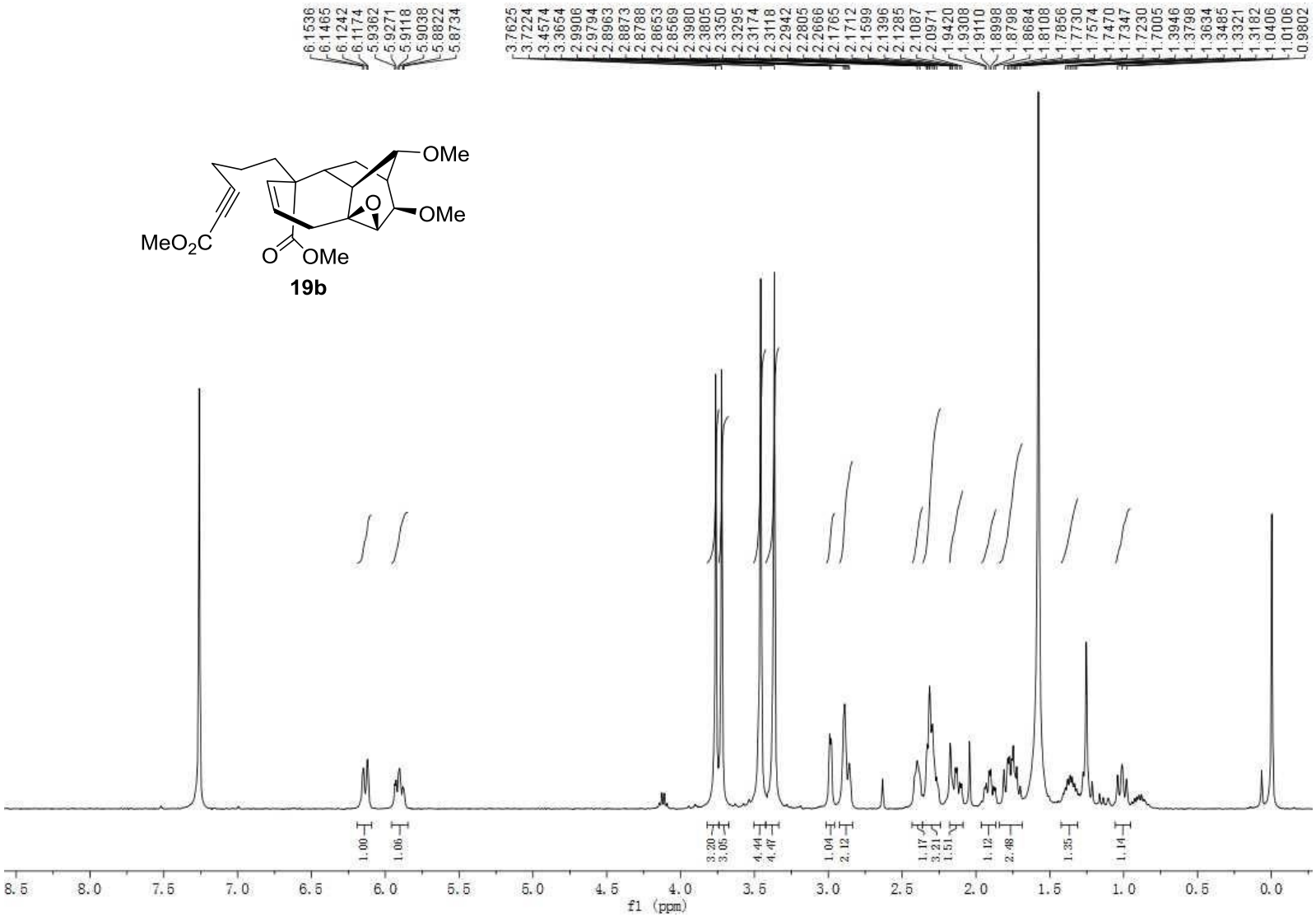
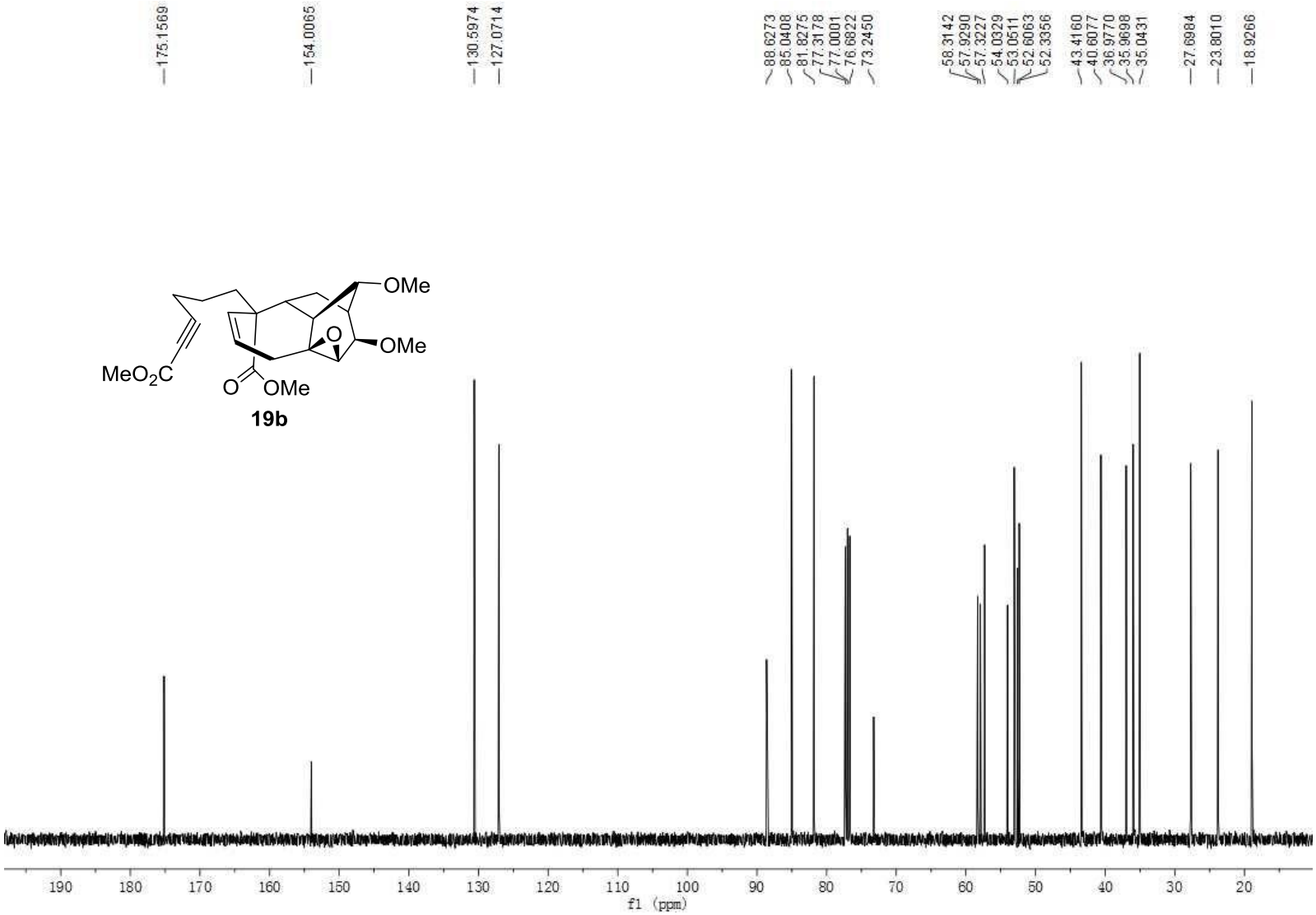
130.8570
126.7417
85.0772
83.6801
81.8581
77.2123
76.9995
76.7878
68.7017
58.2949
57.9742
57.3083
54.0547
53.0672
52.2413
43.4060
40.5719
37.0360
36.0084
35.0854
27.7156
24.5463
18.6837
OMe
OMe
O
O
OMe
19a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OMe
OMe
MeO2C
O
OMe
19b
f1 (ppm)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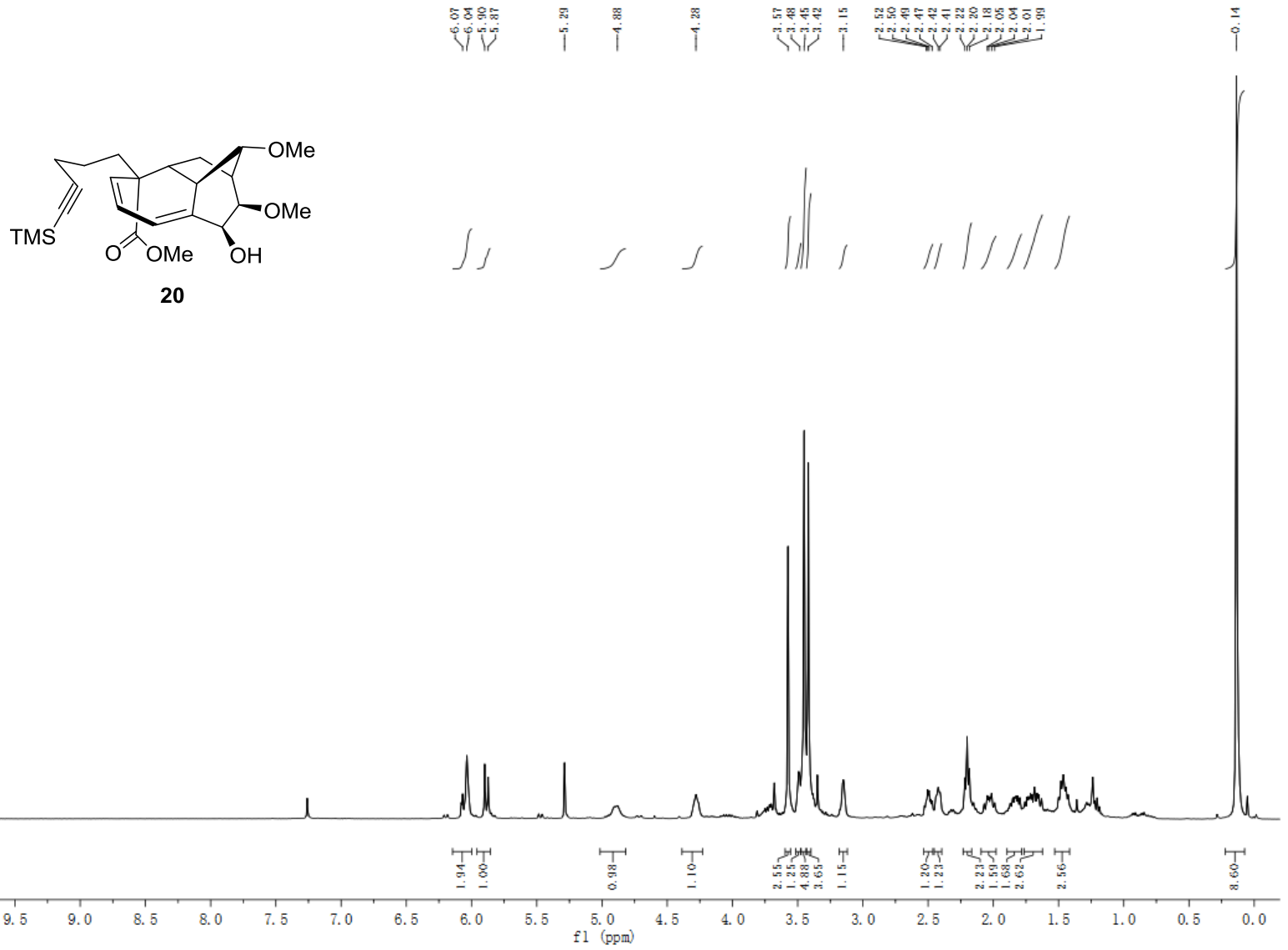
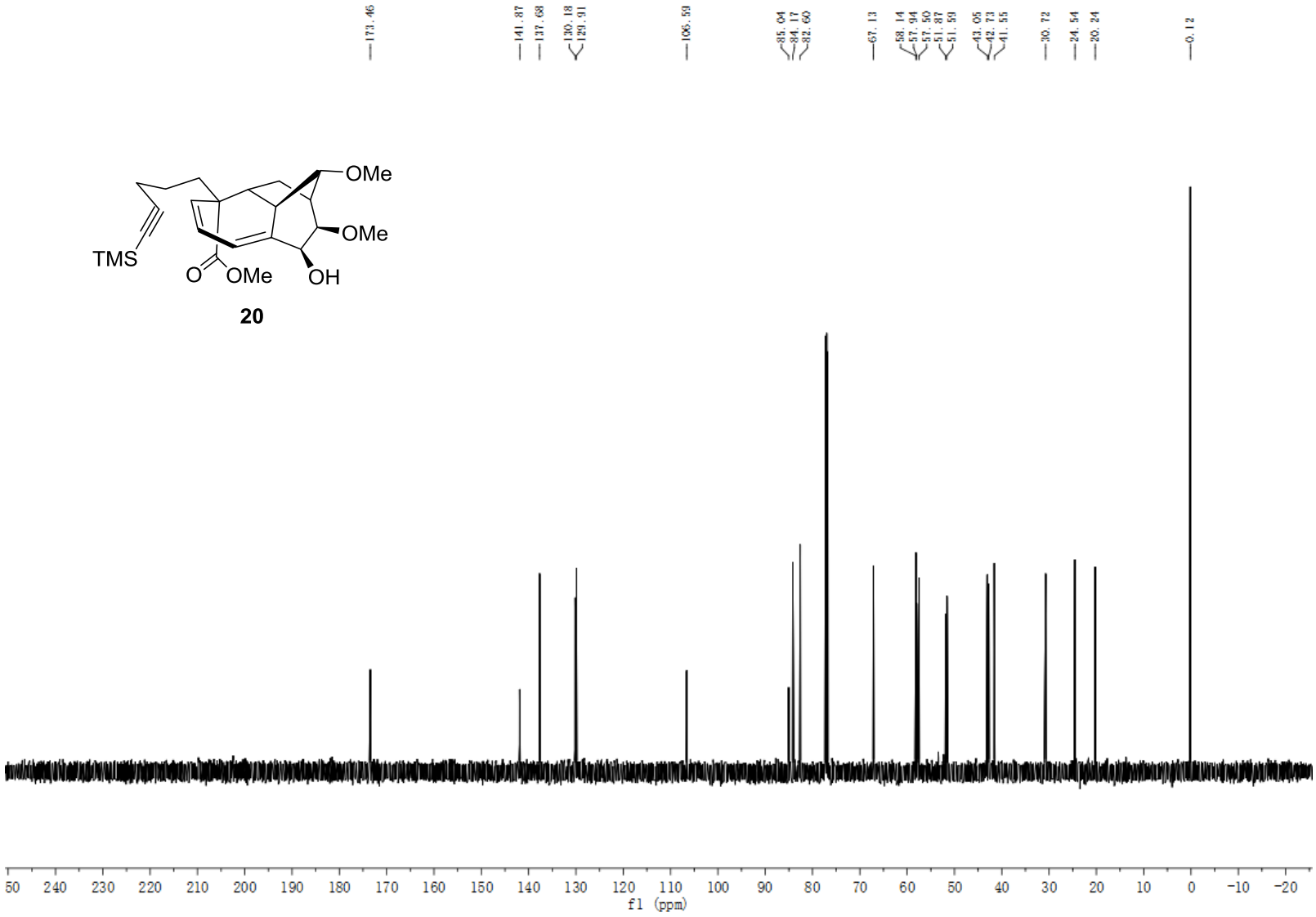
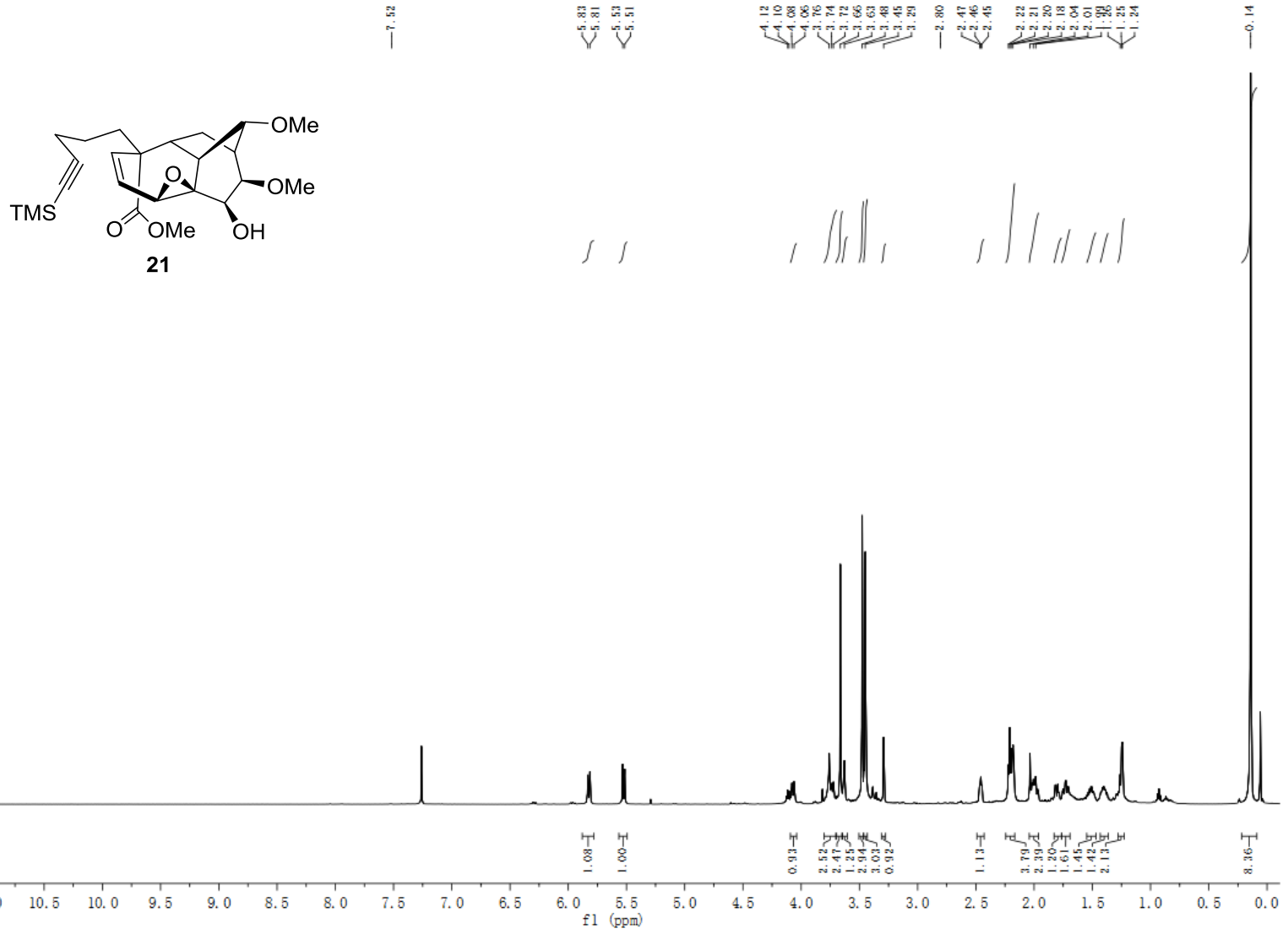
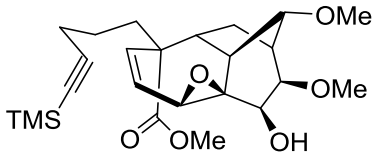
130.5974
127.0714
88.6273
85.0408
81.8275
77.3178
77.0001
76.6822
73.2450
58.3142
57.9290
57.3227
54.0329
53.0511
52.6063
52.3356
43.4160
40.6077
36.9770
35.9698
35.0431
27.6984
23.8010
18.9266
OMe
OMe
O
MeO2C
O
OMe
19b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


OMe
OMe
TMS
O
OMe
OH
6.07
6.04
5.90
5.87
5.29
4.88
4.28
3.57
3.48
3.45
3.42
3.15
2.52
2.50
2.49
2.47
2.42
2.41
2.22
2.20
2.18
2.06
2.04
2.01
1.99
0.14
1.94
1.00
0.98
1.10
2.55
1.25
4.88
3.65
1.15
1.20
1.23
2.23
1.59
1.68
2.62
2.56
8.60
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

20

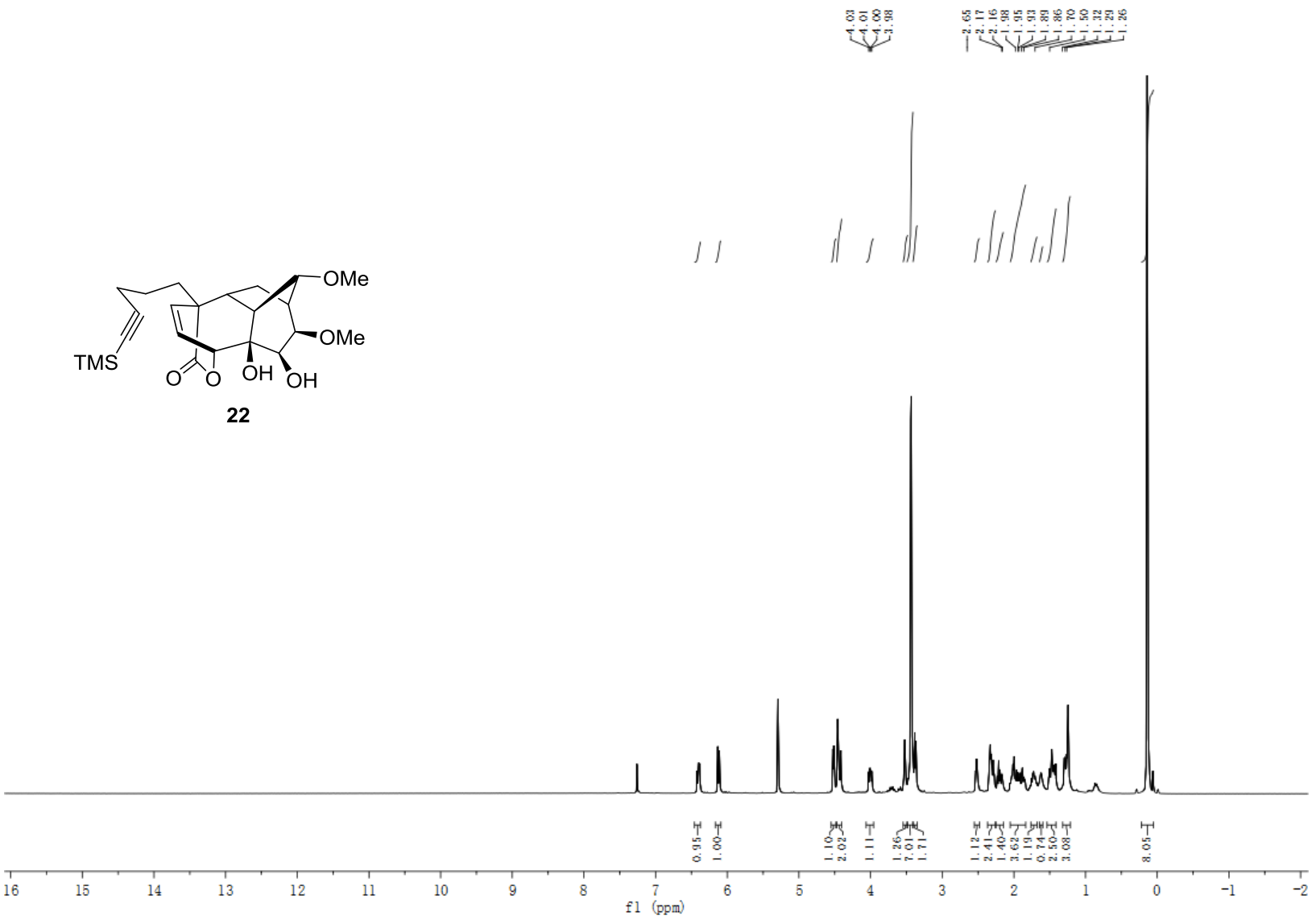

173.46
141.87
137.68
130.18
129.91
106.59
85.04
84.17
82.60
67.13
58.14
57.94
57.50
51.87
51.59
43.05
42.73
41.55
30.72
24.54
20.24
0.12
OMe
OMe
TMS
O
OMe
OH
20
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

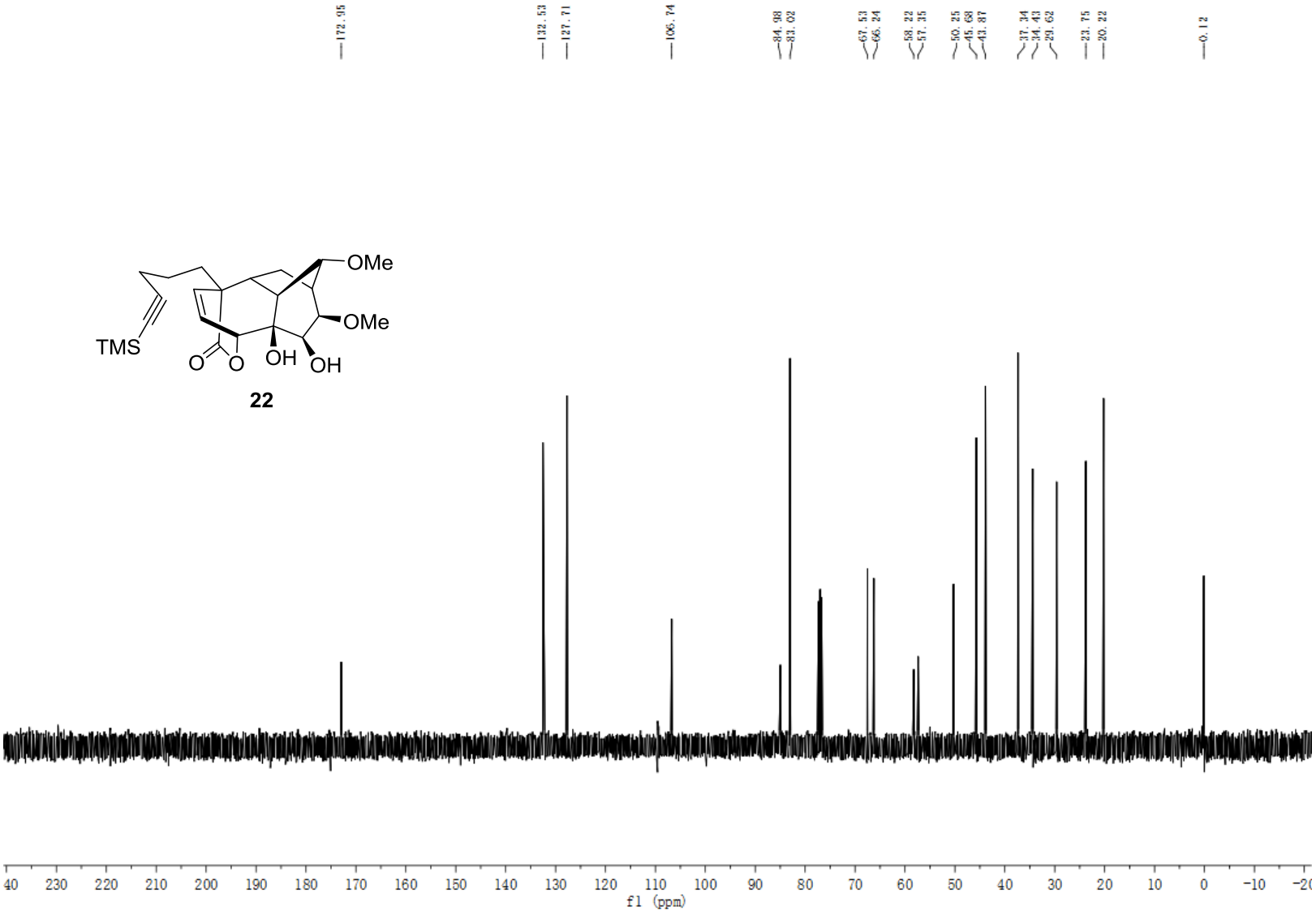

OMe
OMe
OH
O
OMe
TMS
21
f1 (ppm)

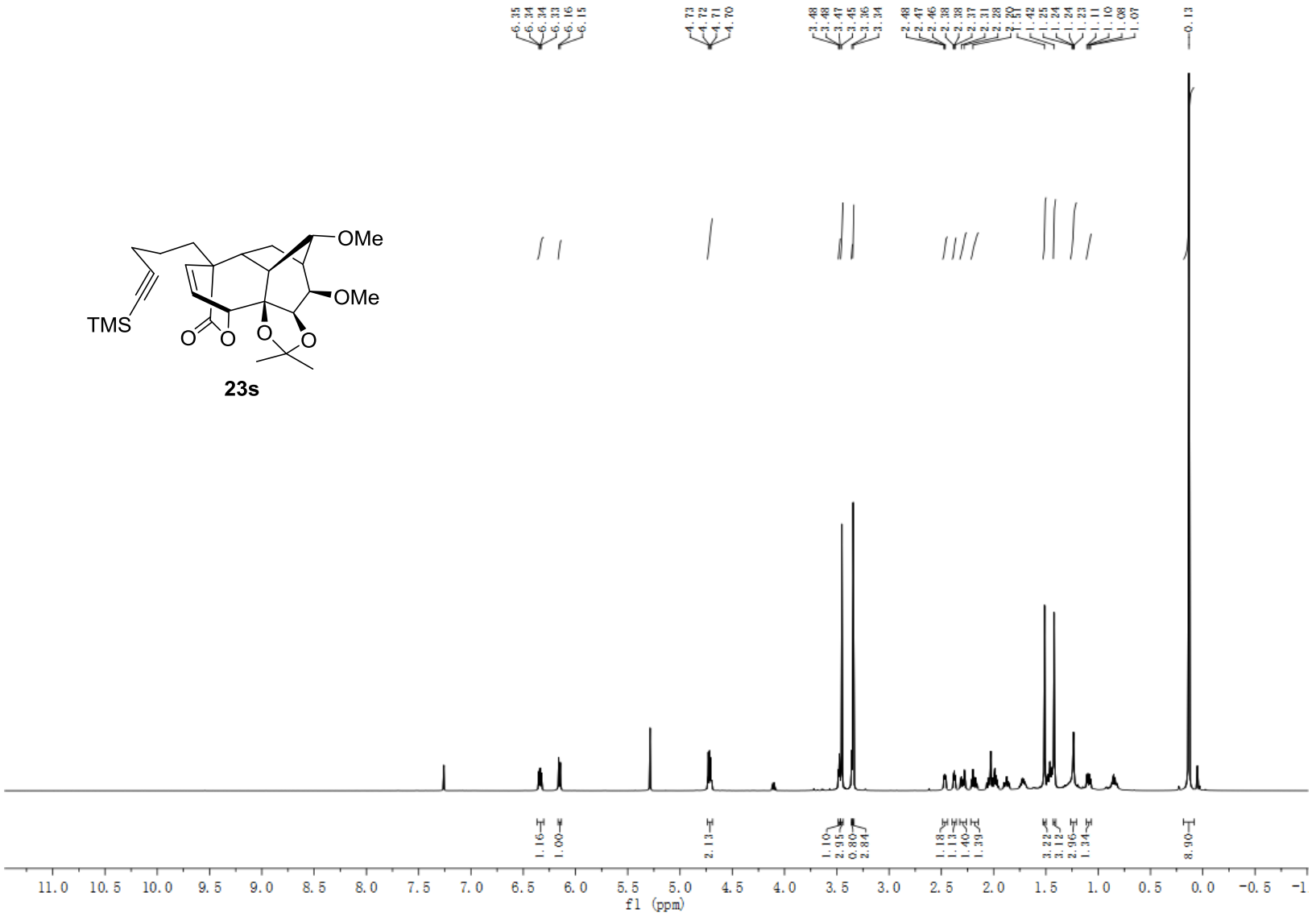

OMe
OMe
O
TMS
O
OMe
OH

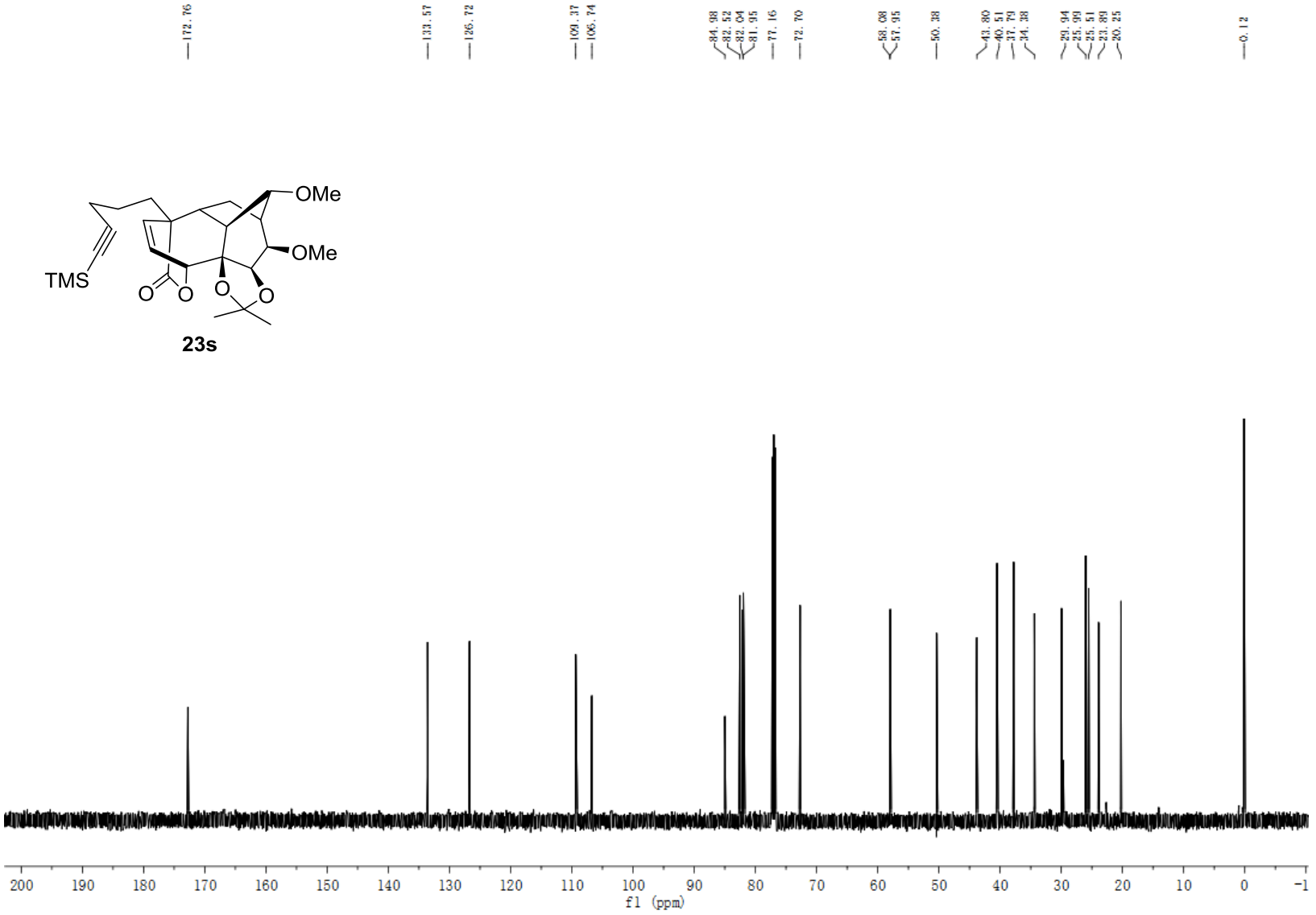
21

173.95
135.64
128.42
106.36
85.13
81.79
81.76
65.95
61.53
60.27
58.01
57.64
52.08
51.74
46.54
44.21
42.57
41.43
31.42
24.71
20.33
0.11
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

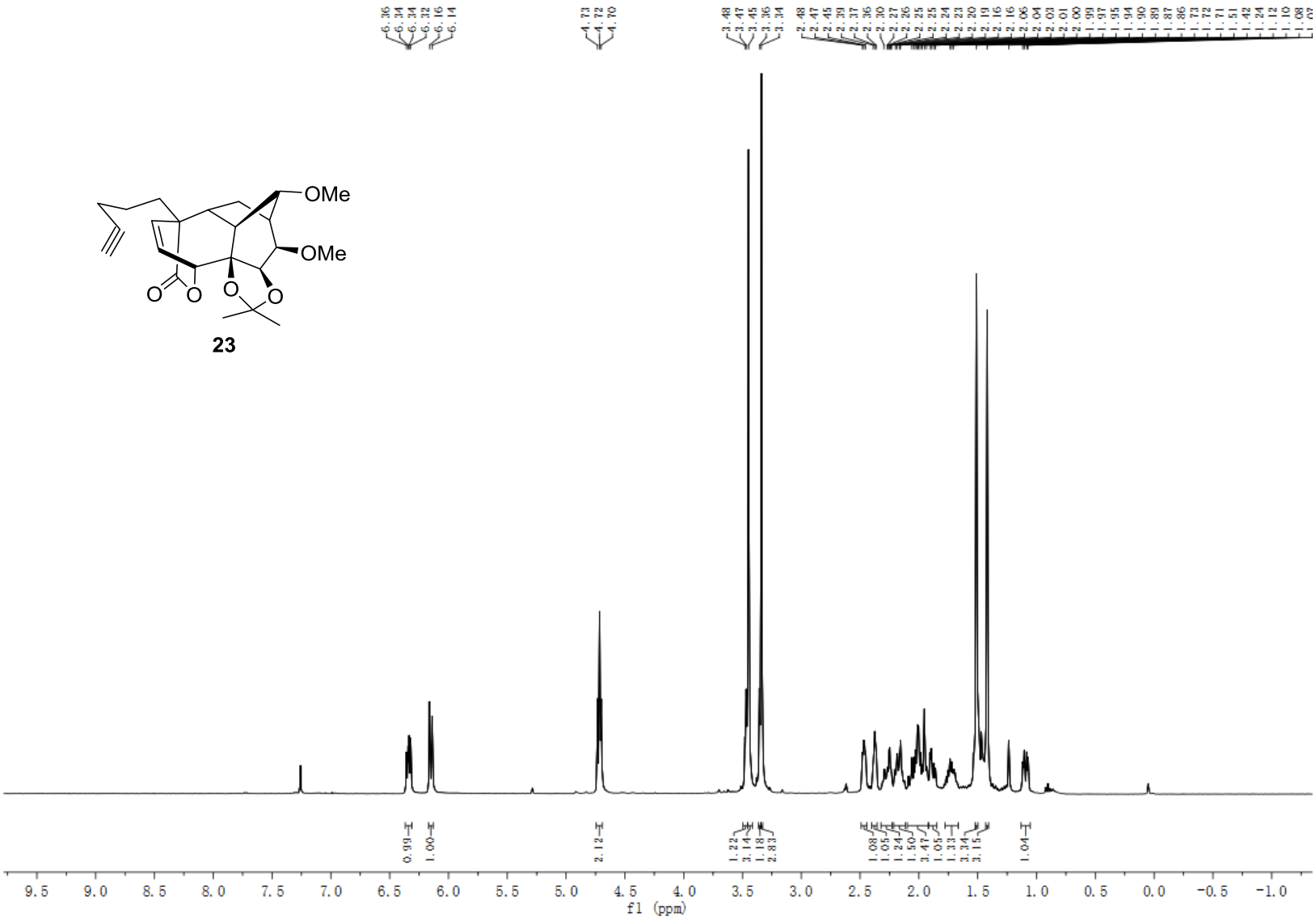

OMe
OMe
TMS
O
O
OH
OH
22
4.03
4.01
4.00
3.98
2.65
2.17
2.16
1.98
1.95
1.93
1.89
1.86
1.70
1.50
1.32
1.29
1.26
0.95
1.00
1.10
2.02
1.11
1.26
7.01
1.71
1.12
2.41
1.40
3.62
1.19
0.74
2.50
3.08
8.05
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
f1 (ppm)

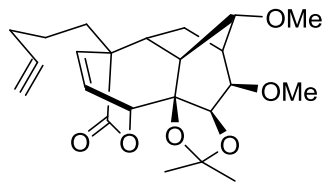

172.95
132.53
127.71
106.74
84.98
83.02
67.53
66.24
58.22
57.35
50.25
45.68
43.87
37.34
34.43
29.62
23.75
20.22
0.12
OMe
OMe
TMS
O
O
OH
OH
22
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OMe
OMe
TMS
O
O
O
O
23s
6.35
6.34
6.34
6.33
6.16
6.15
4.73
4.72
4.71
4.70
3.48
3.48
3.47
3.45
3.36
3.34
2.48
2.47
2.46
2.38
2.38
2.37
2.31
2.28
2.20
1.51
1.42
1.25
1.24
1.24
1.23
1.11
1.10
1.08
1.07
0.13
1.16
1.00
2.13
1.10
2.95
0.80
2.84
1.18
1.13
1.40
1.39
3.22
3.12
2.96
1.34
8.90
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


172.76
133.57
126.72
109.37
106.74
84.98
82.52
82.04
81.95
77.16
72.70
58.08
57.95
50.38
43.80
40.51
37.79
34.38
29.94
25.99
25.51
23.89
20.25
0.12
OMe
OMe
TMS
O
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

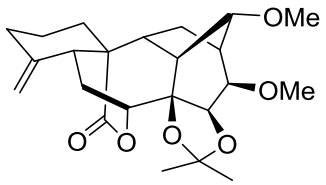
23s


OMe
OMe
O
O
O
O
23
f1 (ppm)


OMe
OMe
O
O
O
O

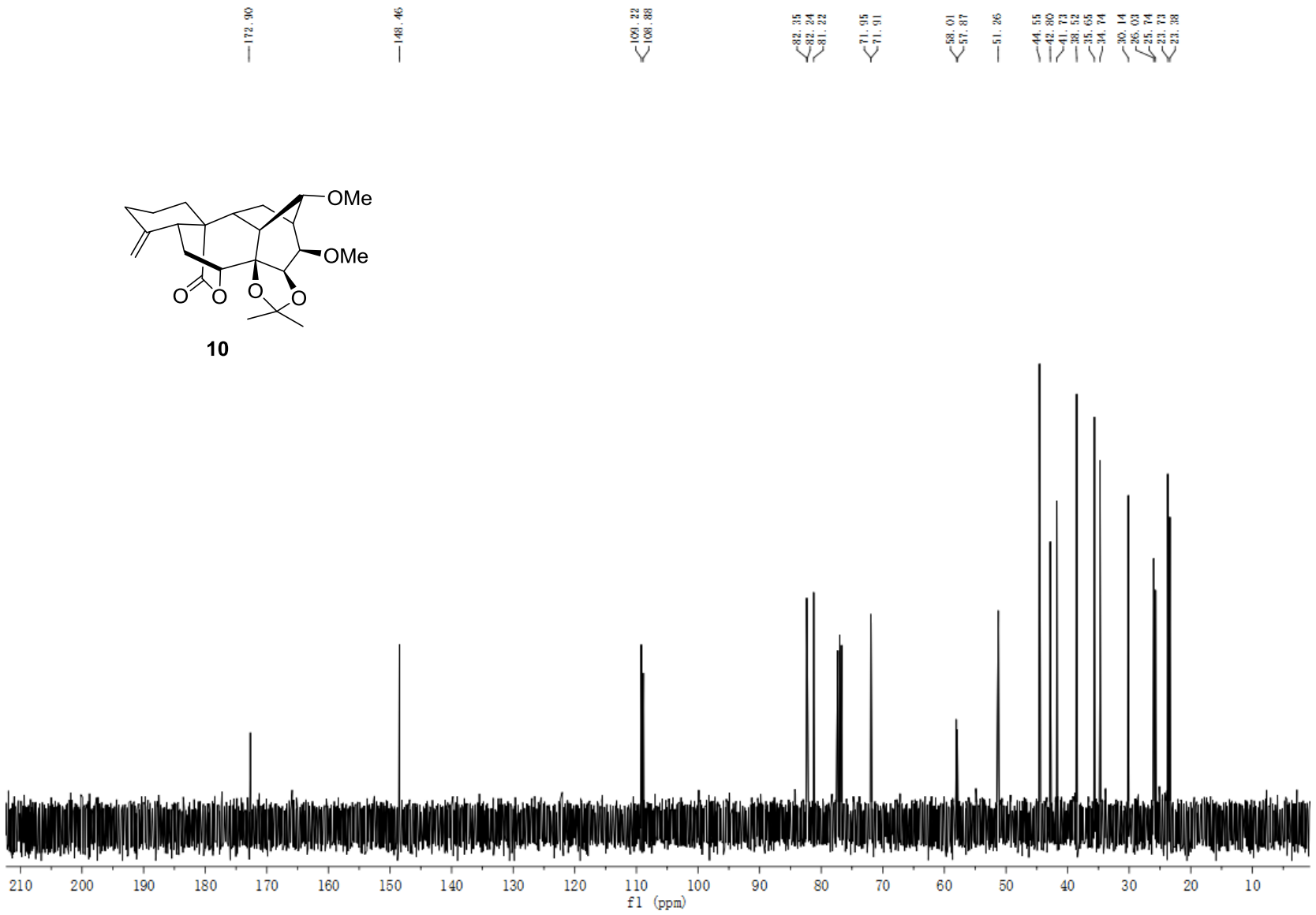
23

172.71
133.51
126.72
109.35
83.86
82.50
81.97
77.13
72.71
72.67
68.78
58.06
57.94
50.32
43.79
40.45
37.94
34.42
29.96
25.97
25.48
23.62
18.76
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

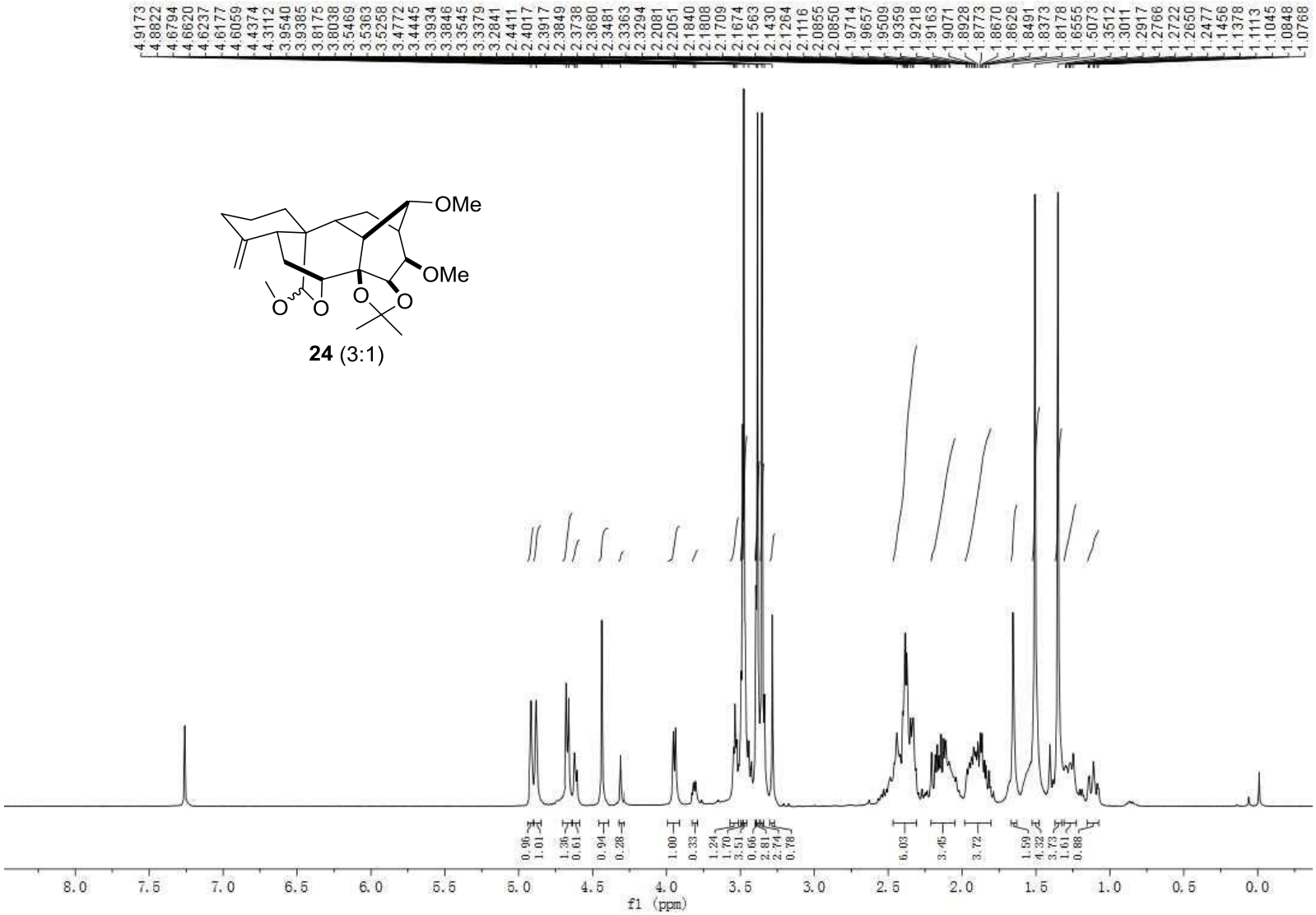

OMe
OMe
O
O
O
O

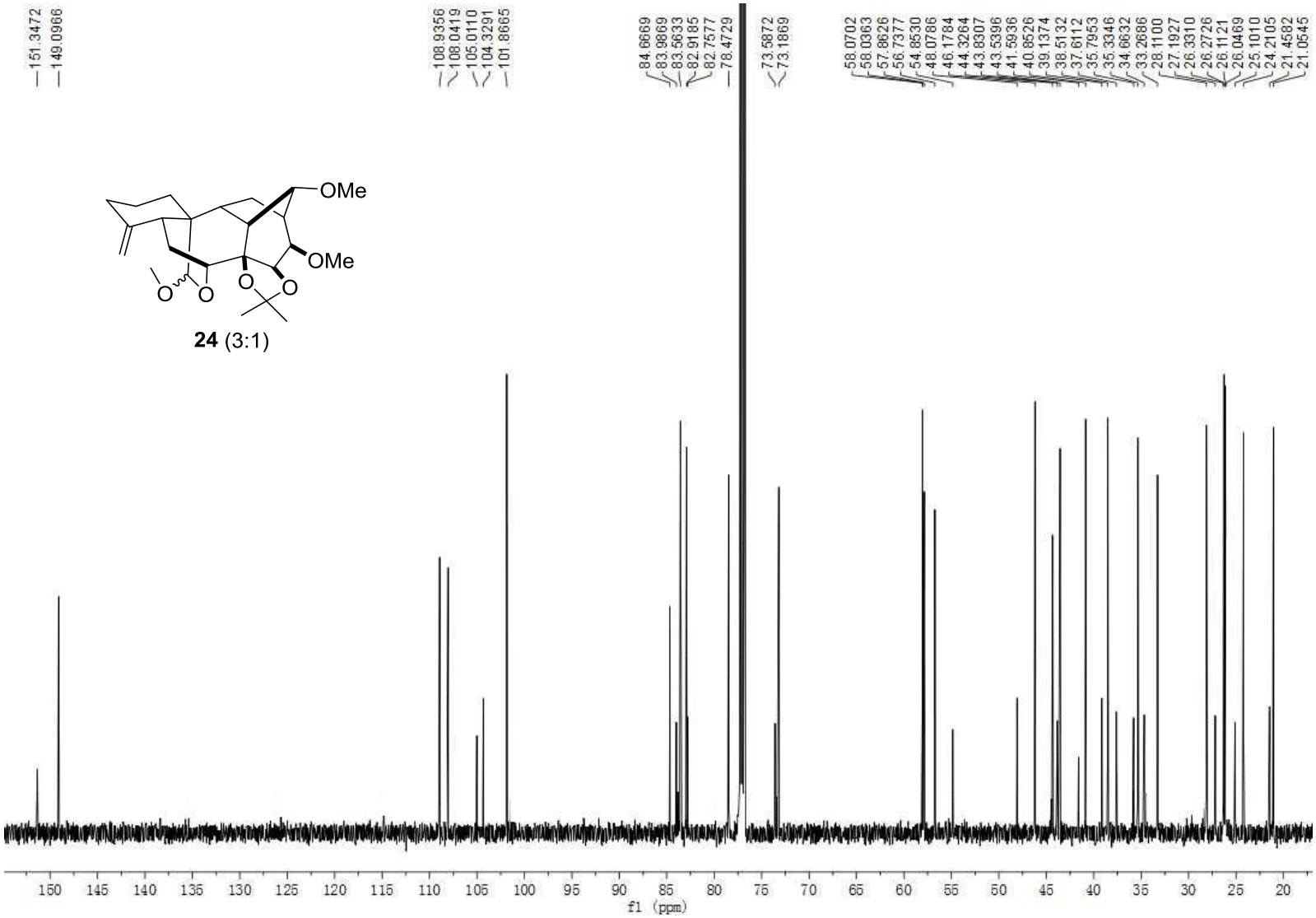
10

4.91
4.82
4.67
4.66
4.44
4.42
3.51
3.43
3.37
3.28
3.26
2.76
2.75
2.73
2.64
2.63
2.62
2.47
2.46
2.45
2.44
2.42
2.41
2.40
2.36
2.32
2.29
2.08
2.06
2.05
2.03
2.03
2.01
1.64
1.51
1.37
1.03
1.01
1.00
1.00
1.01
1.01
0.99
1.03
3.19
3.16
1.13
1.01
1.04
3.17
2.18
2.34
1.15
2.83
3.02
2.06
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
f1 (ppm)

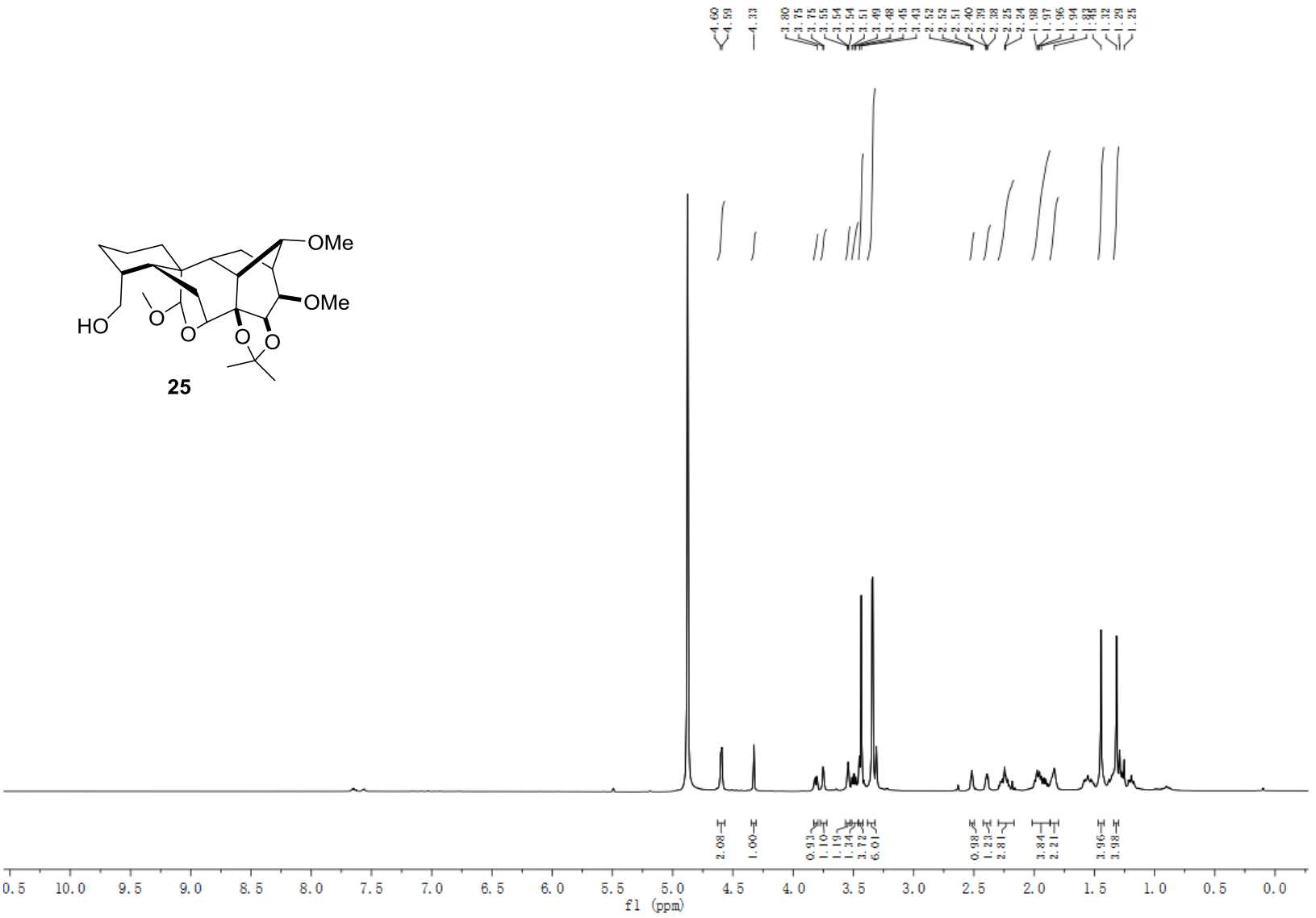

172.90
148.46
109.22
108.88
82.35
82.24
81.22
71.95
71.91
58.01
57.87
51.26
44.55
42.80
41.73
38.52
35.65
34.74
30.14
26.03
25.74
23.73
23.38
OMe
OMe
O
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

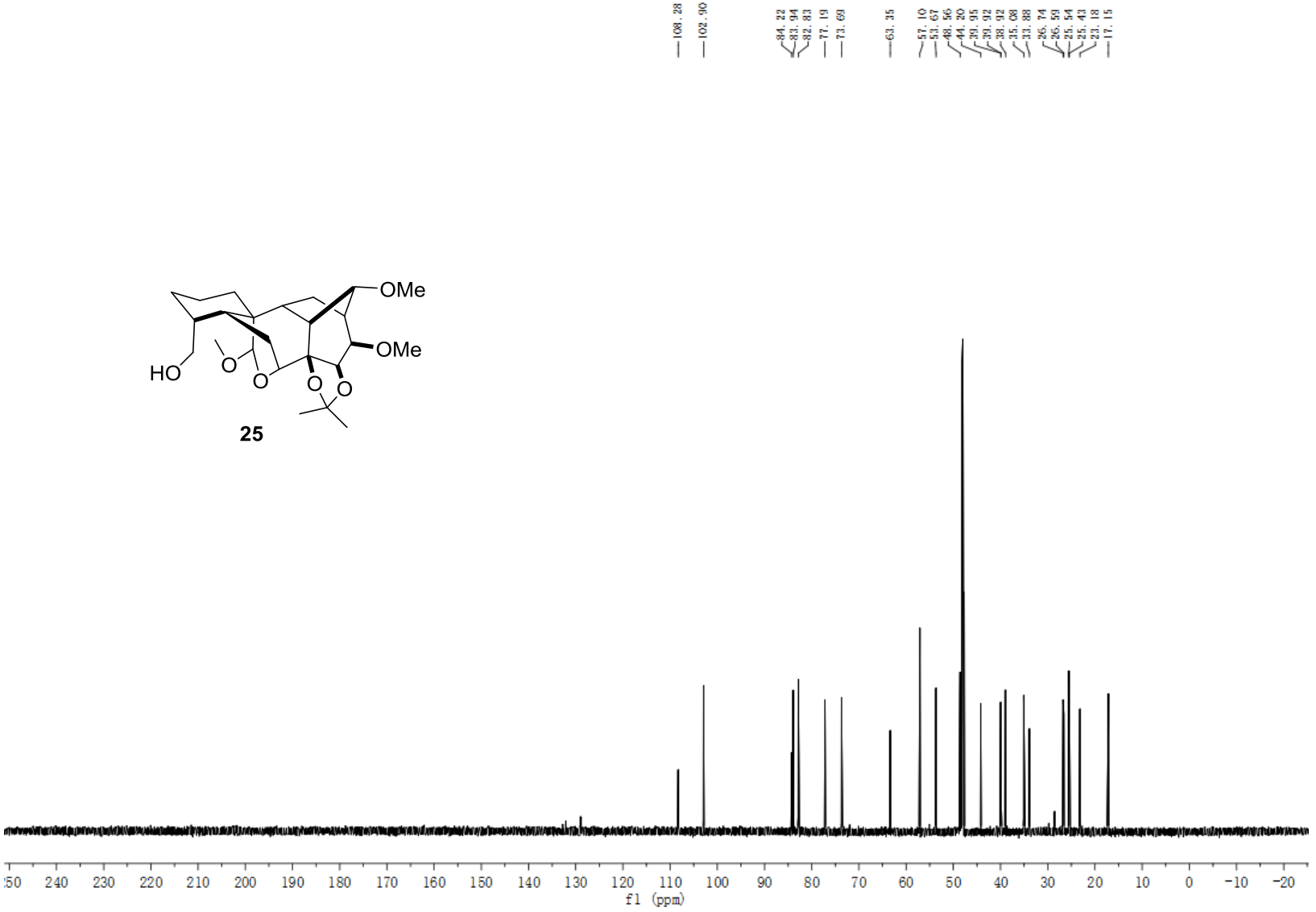
10

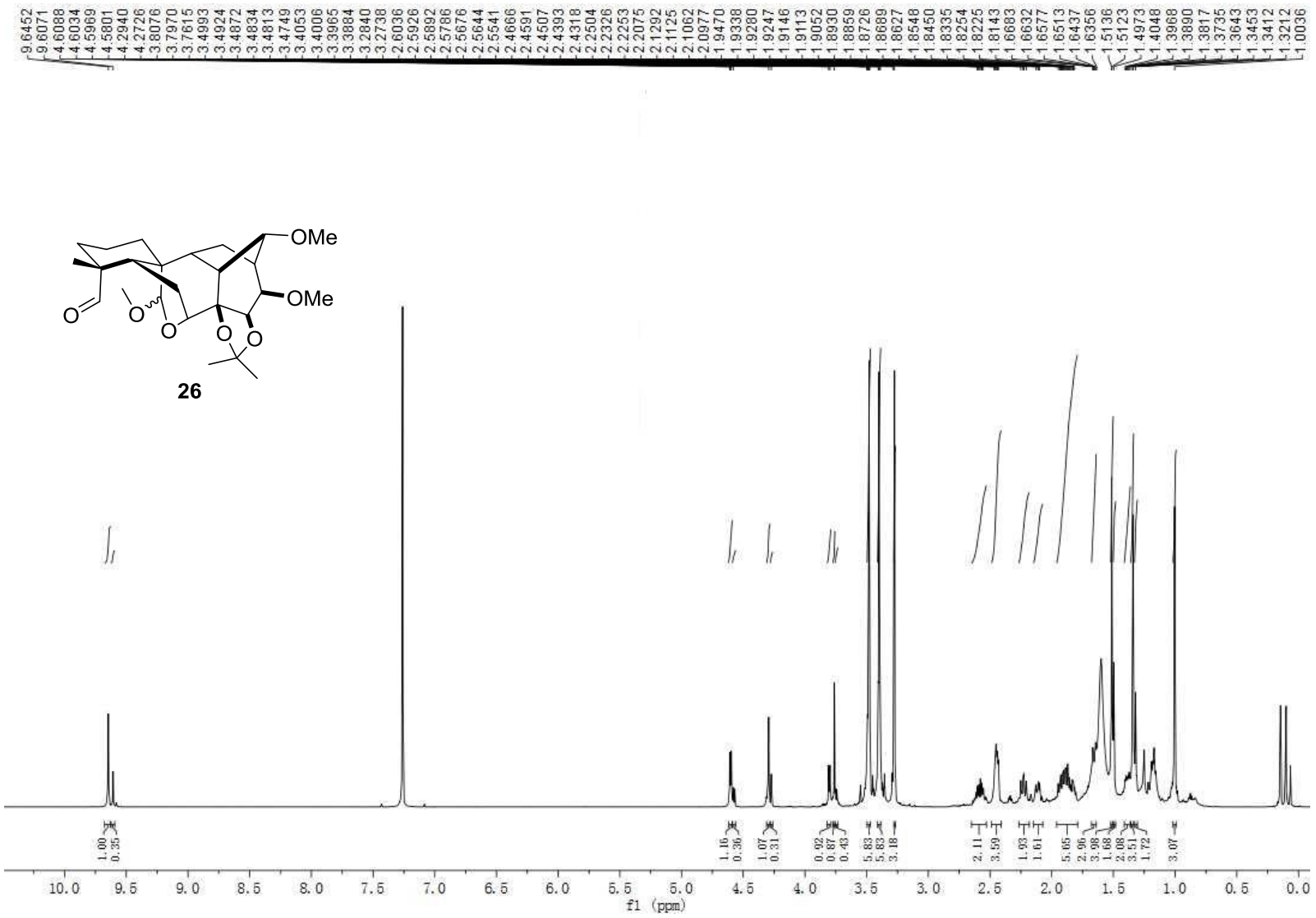

OMe
OMe
O
O
O
O
24 (3:1)
f1 (ppm)

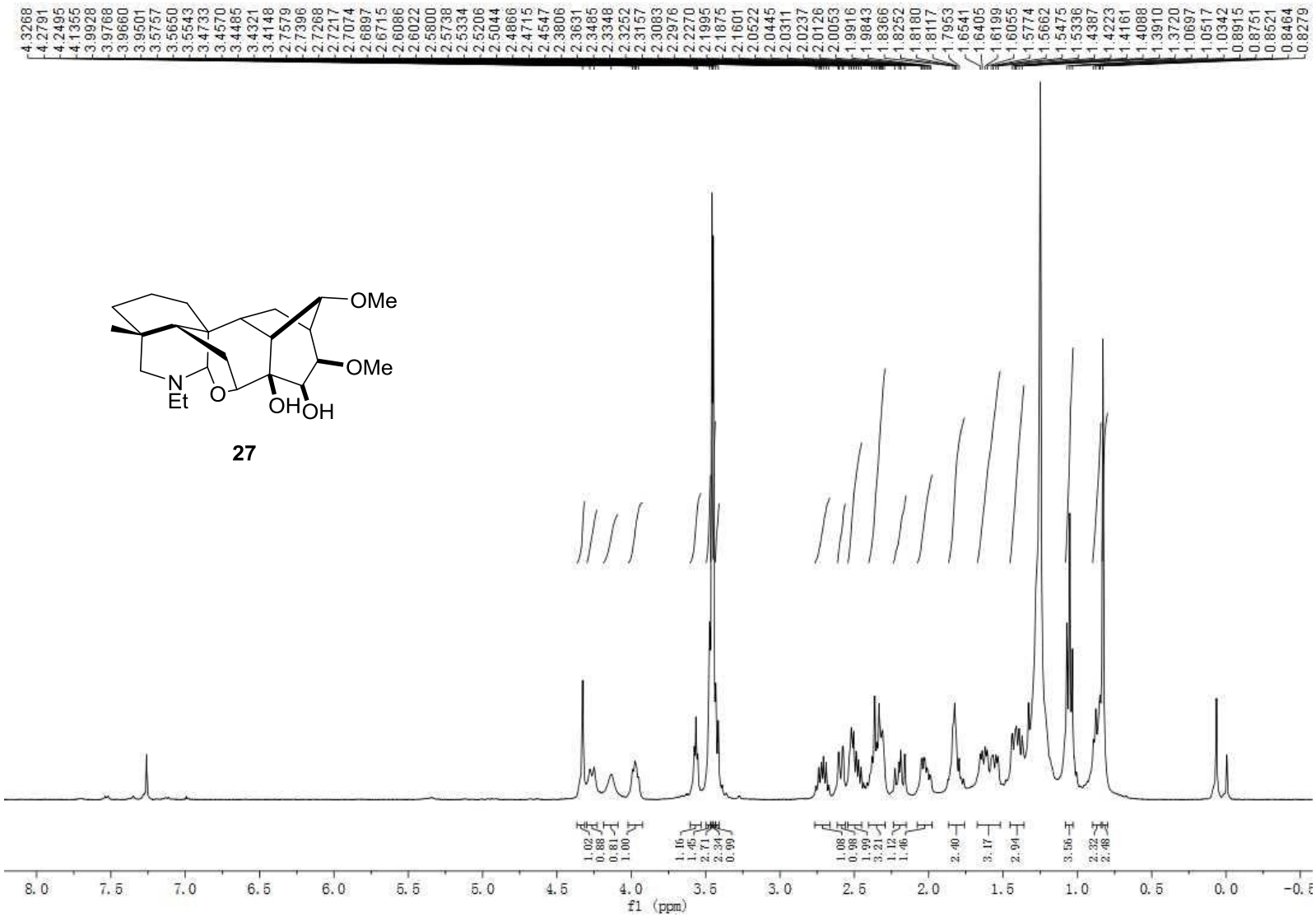

151.3472
149.0966
108.9356
108.0419
105.0110
104.3291
101.8665
84.6669
83.9869
83.5633
82.9185
82.7577
78.4729
73.5872
73.1869
58.0702
58.0363
57.8626
56.7377
54.8530
48.0786
46.1784
44.3264
43.8307
43.5396
41.5936
40.8526
39.1374
38.5132
37.6112
35.7953
35.3346
34.6632
33.2686
28.1100
27.1927
26.3310
26.2726
26.1121
26.0469
25.1010
24.2105
21.4582
21.0545
OMe
OMe
O
O
O
O
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

24 (3:1)

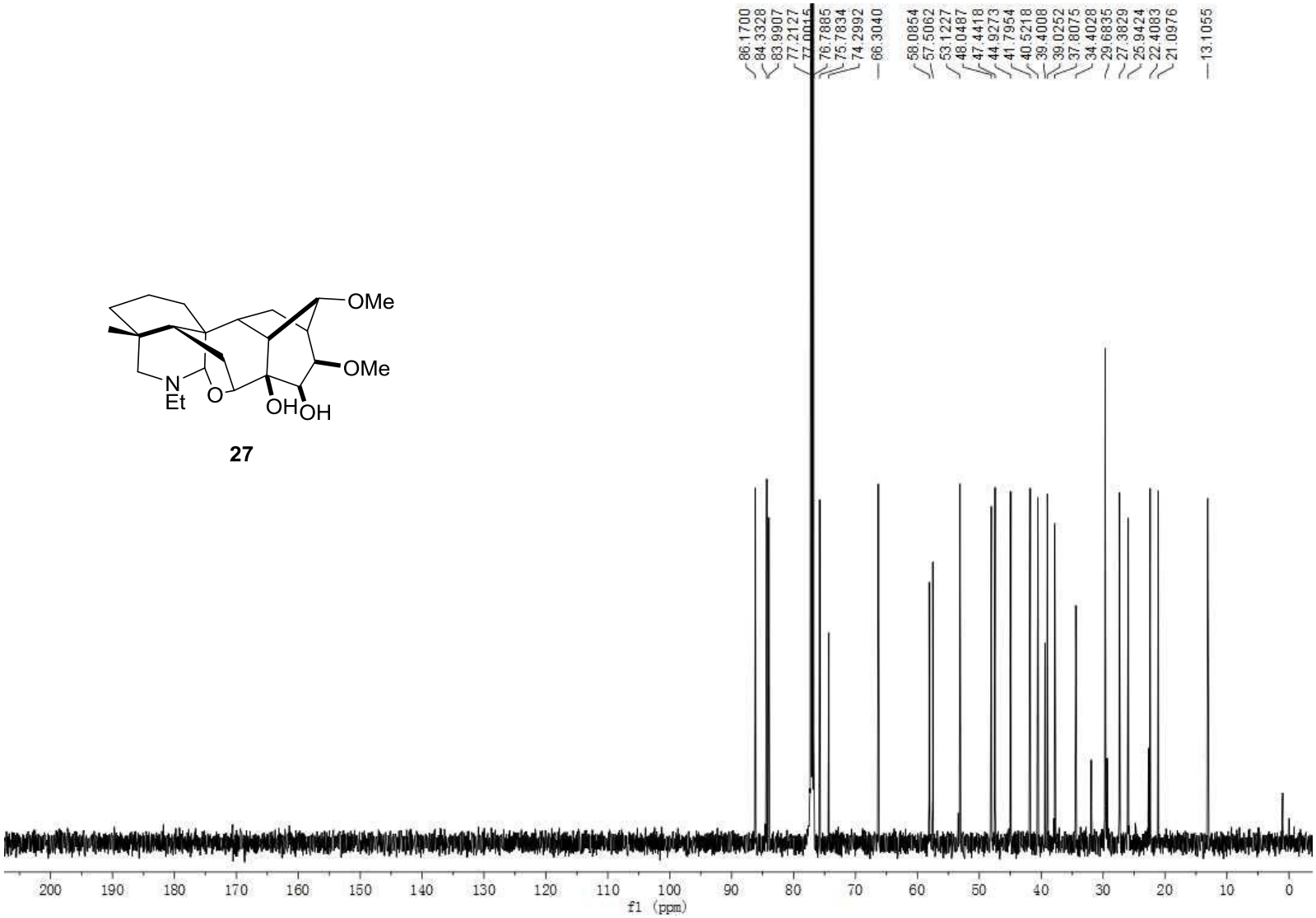

OMe
OMe
HO
O
O
O
O
O
25
4.60
4.59
4.33
3.80
3.75
3.75
3.55
3.54
3.54
3.51
3.49
3.48
3.45
3.43
2.52
2.52
2.51
2.40
2.39
2.38
2.25
2.24
1.98
1.97
1.96
1.94
1.32
1.29
1.25
2.08
1.00
0.93
1.10
1.19
1.34
3.72
6.01
0.98
1.23
2.81
3.84
2.21
3.96
3.98
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


108.28
102.90
84.22
83.94
82.83
77.19
73.69
63.35
57.10
53.67
48.56
44.20
39.95
39.92
38.92
35.08
33.88
26.74
26.59
25.54
25.43
23.18
17.15
OMe
OMe
HO
O
O
O
O
25
f1 (ppm)

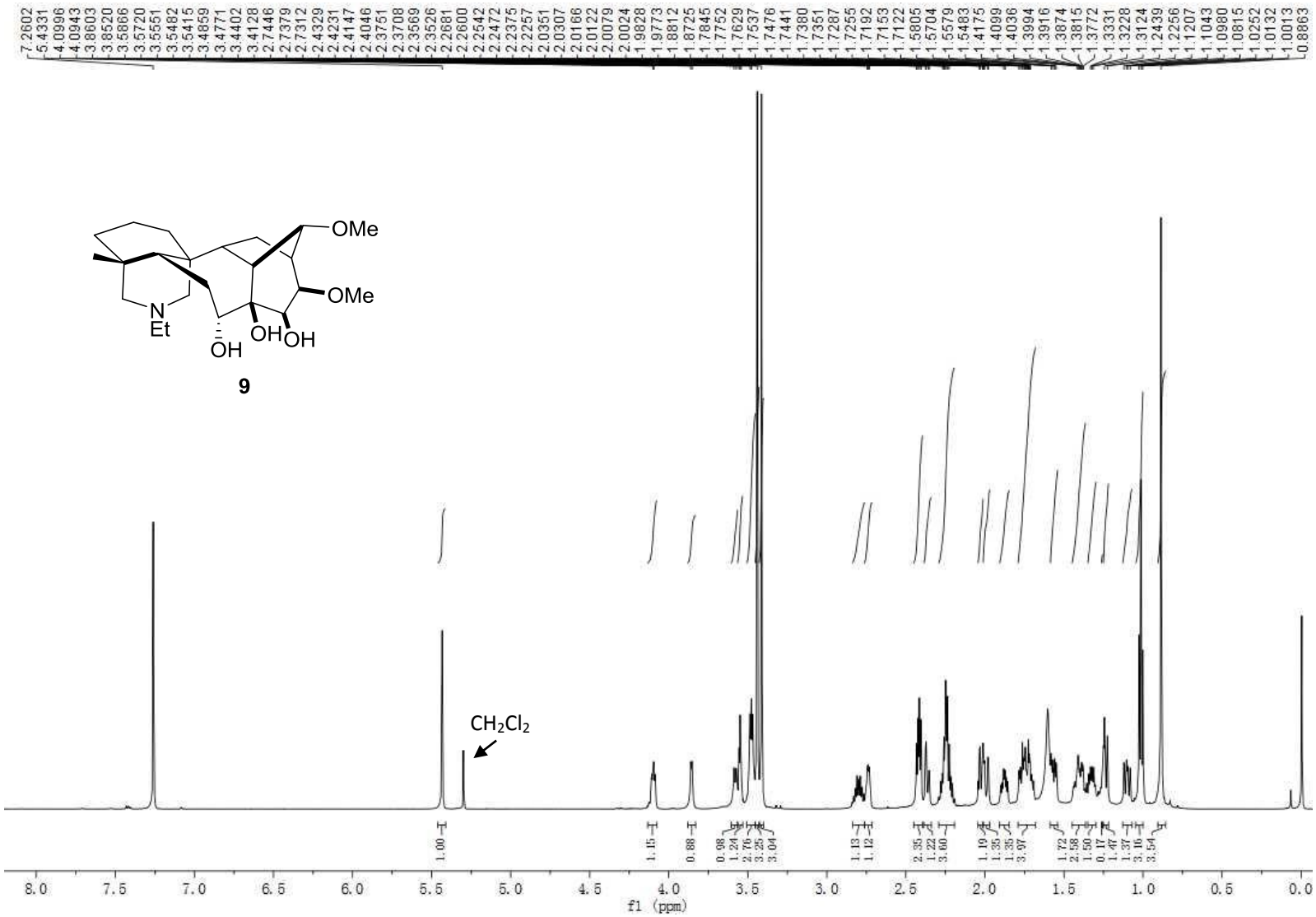

9.6452
9.6071
4.6088
4.6034
4.5969
4.5801
4.2940
4.2726
3.8076
3.7970
3.7615
3.4993
3.4924
3.4872
3.4834
3.4813
3.4749
3.4053
3.4006
3.3965
3.3884
3.2840
3.2738
2.6036
2.5926
2.5892
2.5786
2.5676
2.5644
2.5541
2.4666
2.4591
2.4507
2.4393
2.4318
2.2504
2.2326
2.2253
2.2075
2.1292
2.1125
2.1062
2.0977
1.9470
1.9338
1.9280
1.9247
1.9146
1.9113
1.9052
1.8930
1.8859
1.8726
1.8689
1.8627
1.8548
1.8450
1.8335
1.8254
1.8225
1.8143
1.6683
1.6632
1.6577
1.6513
1.6437
1.6356
1.5136
1.5123
1.4973
1.4048
1.3968
1.3890
1.3817
1.3735
1.3643
1.3453
1.3412
1.3212
1.0036
OMe
OMe
O
O
O
O
O
O
26
1.00
0.35
1.16
0.36
1.07
0.31
0.92
0.87
0.43
5.83
5.83
3.18
2.11
3.59
1.93
1.61
5.65
2.96
3.98
1.68
2.08
3.51
1.72
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



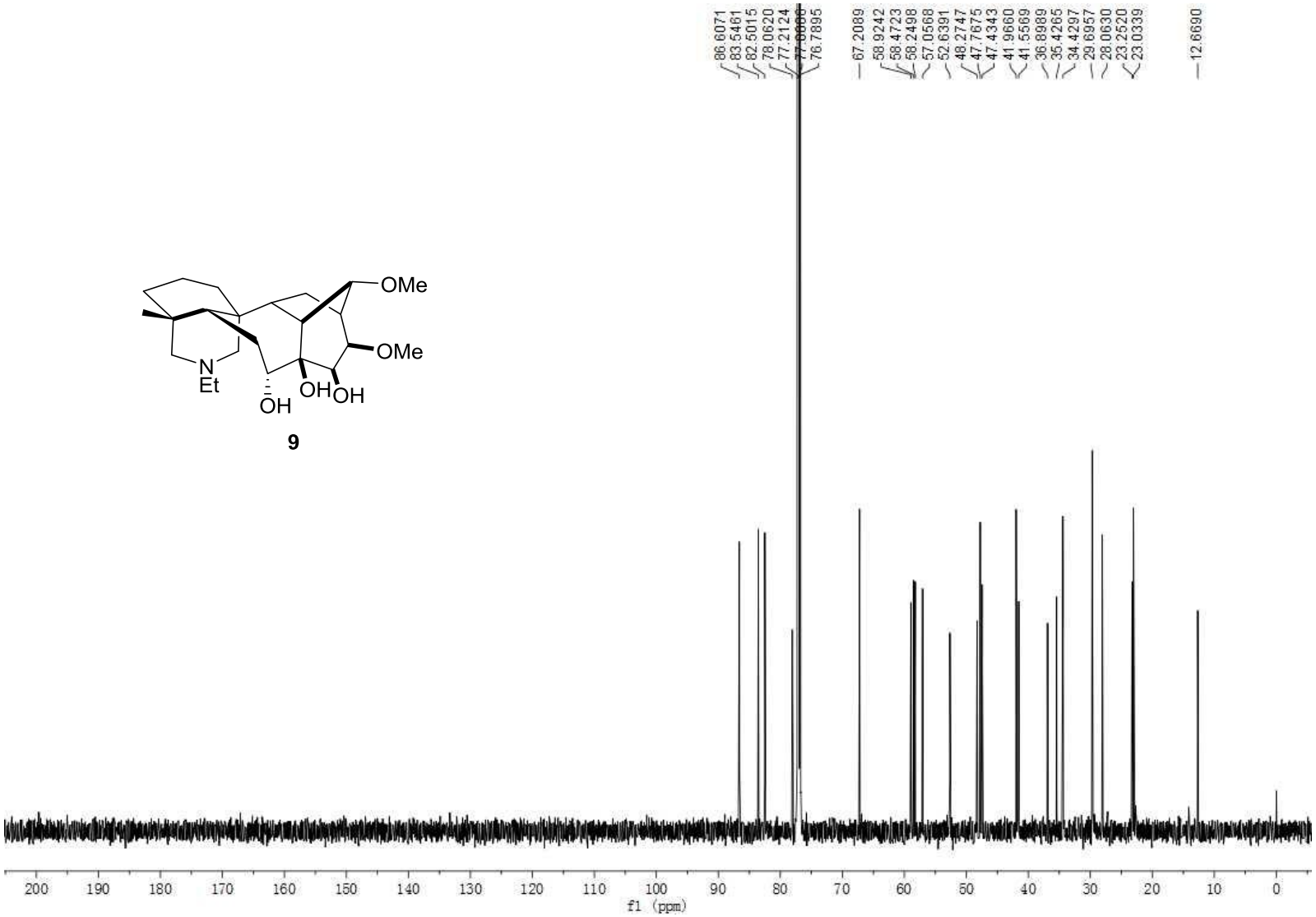
27


OMe
OMe
N
Et
O
OH
OH
86.1700
84.3328
83.9907
77.2127
77.0015
76.7885
75.7834
74.2992
66.3040
58.0854
57.5062
53.1227
48.0487
47.4418
44.9273
41.7954
40.5218
39.4008
39.0252
37.8075
34.4028
29.6835
27.3829
25.9424
22.4083
21.0976
13.1055
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

27



9


OMe
OMe
N
Et
OH
OH
OH
86.6071
83.5461
82.5015
78.0620
77.2124
76.7895
67.2089
58.9242
58.4723
58.2498
57.0568
52.6391
48.2747
47.7675
47.4343
41.9660
41.5569
36.8989
35.4265
34.4297
29.6957
28.0630
23.2520
23.0339
12.6690
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

9