Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of daphnane and tigliane framework by a tubing-bubbling photo oxidation and an open-chain diastereoselective conjugate addition

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Contents

1. General Information

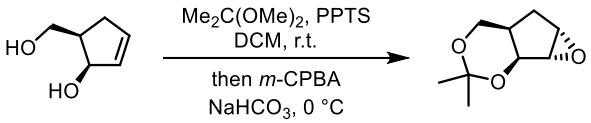
General. Unless otherwise noted, all reactions were carried out in a flame-dried, septum-sealed flask under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Visualization was accomplished by exposure to a UV lamp, and/or treatment with a solution of $KMnO_4$ or a solution of Phosphomolybdic Acid (PMA) followed by brief heating with a heating gun. Most of the products were compatible with standard silica gel chromatography. Column chromatography was performed on silica gel 60N (spherical and neutral, 200–300 mesh) using standard methods.

Structural analysis. NMR spectra were measured on a Bruker Avance-400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^{1}H NMR spectra were recorded at 400 MHz in NMR solvents ($CDCl_3$) and referenced internally to corresponding solvent resonance, and ^{13}C NMR spectra were recorded at 100 MHz, Chemical shift were reported in ppm on the δ scale relative to $CHCl_3$ (δ = 7.26 for ^{1}H NMR, δ = 77.16 for ^{13}C NMR). Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). High resolution mass Spectra (HRMS) were obtained on a Bruker Apex IV FTMS spectrometer or an Agilent 6224 LC/MS TOF spectrometer. Single crystal X-ray diffraction analysis of compound **6'** and **20** were carried out by Dr. You-Song Ding on Bruker apex duo equipment at Center for Applied Chemistry Research, Frontier Institute of Science and Technology, Xi'an Jiaotong University.

Materials. Commercial reagents were purchased from J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, Strem Chemicals or TCI and used as received unless otherwise stated. THF, toluene and benzene were purified by distillation over sodium/benzophenone and stored under N_2, MeCN were purchased from Acros Organics and used directly without further purification.

2. Experimental Details and Spectral Data

Epoxide 10



9 69% **10**

To a stirred solution of diol **9** (11.4 g, 100 mmol, 1.00 equiv) in CH_2Cl_2 (80 mL) and $Me_2C(OMe)_2$ (20 mL), at 0 °C was added PPTs (2.5 g, 9.95 mmol, 0.10 equiv), the reaction mixture was stirred at room temperature for 18 h. After TLC detected starting material consumption, $NaHCO_3$ (42 g, 500 mmol, 5.00 equiv), *m*CPBA (purity 85%, 40.6 g, 200 mmol, 2.00 equiv) were sequentially added at 0 ºC. Then the reaction mixture was stirred at room temperature for 15 h. The resulting mixture was quenched with sat. aq. $Na_2S_2O_3/CH_2Cl_2$ (v/v, 1:2, 500 mL). The organic layer was dried with anhydrous sodium sulfate. The crude product was purified by flash chromatography (petroleum ether/ ethyl acetate 20:1) to give **10** as pale yellow oil (11.81 g, 69%).

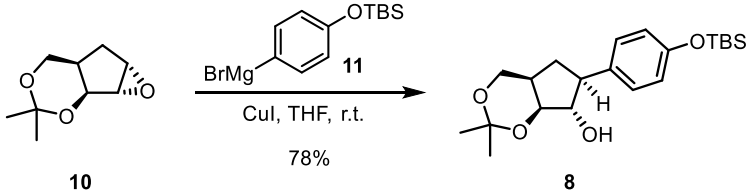
R_f = 0. 45 (Hexanes : EtOAc = 10:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.39 (d, *J* = 4.5 Hz, 1H), 4.13 (dd, *J* = 12.2, 4.5 Hz, 1H), 3.63 (dd, *J* = 12.2, 1.4 Hz, 1H), 3.53 (s, d = 1.9 Hz, 1H), 3.45 (d, *J* = 2.4 Hz, 1H), 2.04 – 1.97 (m, 2H), 1.65 (m, 1H), 1.46 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 97.4z, 70.1, 59.9, 57.6, 56.6, 30.9, 29.1, 29.0, 19.4.

HRMS (ESI, *m/z*) for $C_9H_{14}O_3Na^+$ $[M+Na]^+$: Calcd. 193.0835; Found 193.0847.

Secondary alcohol 8



10 **8**

To a solution of the 4-Siloxyphenylmagnesium bromide **11** (112 mL, 0.5 M in THF, 56 mmol, 1.80 equiv) was added copper (I) iodide (591.9 mg, 3.11 mmol, 0.10 equiv) at 0 °C, stirred for 30 min. To this reaction mixture was then added a solution of cyclopentene oxide **10** (5.3 g, 31.1 mmol, 1.00 equiv) in THF (62 mL) dropwise over a period of 30 min at 0 °C. The reaction mixture was stirred to room temperature for 12 h. The reaction was cooled to 0 °C and quenched with sat. aq. ammonium chloride. Ethyl acetate (5 x 50 mL) was added, and the upper organic layer was separated. The organic layer was dried with anhydrous sodium sulfate, the crude residue was purified by flash

chromatography (petroleum ether/ ethyl acetate 5:1) to give the secondary alcohol **8** (9.16 g, 78%) as yellow oil.

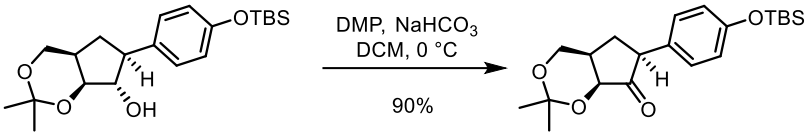
R_f = 0. 25 (Hexanes : EtOAc = 5:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2zH), 4.15 (dd, *J* = 5.8, 2.0 Hz, 1H), 4.05-4.01 (m, 2H), 3.65 (dd, *J* = 11.7, 4.6 Hz, 1H), 2.91-2.84 (m, 1H), 2.26-2.19 (m, 1H), 2.05-2.00 (m, 2H), 1.44 (s, 3H), 1.40 (s, 3H), 0.98 (s, 9H), 0.18 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 135.5, 128.5, 120.1, 98.6, 85.9, 78.5, 61.2, 52.2, 37.0, 34.9, 28.4, 25.8, 20.9, 18.3, -4.3.

HRMS (ESI, *m/z*) for $C_{21}H_{34}O_4SiNa^+$ $[M+Na]^+$: Calcd. 401.2119; Found 401.2111.

Ketone 12



8 **12**

To a mixture of **8** (1.514 g, 4.0 mmol, 1.00 equiv.) and $NaHCO_3$ (2.688 g, 32.0 mmol, 8.00 equiv) in CH_2Cl_2 (40 mL) at 0 °C was added Dess-Martin periodinane (6.786 g, 16.0 mmol, 4.00 equiv), and the reaction mixture was stirred at room temperature for 3 h. The reaction was cooled to 0 °C and quenched with sat. aq. sodium bicarbonate. CH_2Cl_2 (3 x 30 mL) was added, and the upper organic layer was separated. The organic layer was dried with anhydrous sodium sulfate, and filtrated, the crude residue was purified by flash chromatography (petroleum ether/ ethyl acetate 5:1) to give the ketone **12** (1.36 g, 90%) as colorless oil. It's worth noting that the stability of the ketone **12** is poor that will decompose even when store at low temperatures.

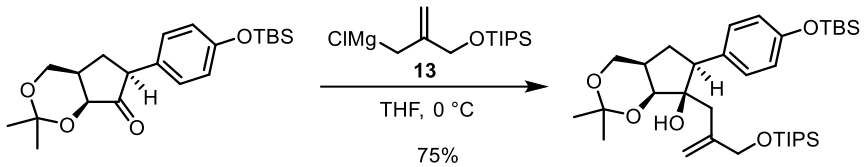
R_f = 0.38 (Hexanes : EtOAc = 4:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11-7.09 (m, 2H), 6.81-6.78 (m, 2H), 4.30 (dd, *J* = 12.1, 3.9 Hz, 1H), 4.22 (d, *J* = 4.6 Hz, 1H), 3.76 (dd, *J* = 12.2, 1.5 Hz, 1H), 3.43-3.37 (m, 1H), 2.67-2.58 (m, 1H), 2.41-2.34 (m, 1H), 2.10-2.04 (m, 1H), 1.52 (s, 3H), 1.45 (s, 3H), 0.97 (s, 9H), 0.19 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.6, 154.8, 131.2, 129.6, 120.3, 98.6, 71.7, 60.0, 54.6, 33.1, 33.0, 29.1, 25.8, 19.3, 18.3, -4.3.

HRMS (ESI, *m/z*) for $C_{21}H_{32}O_4SiNa^+$ $[M+Na]^+$: Calcd. 399.1962; Found 399.1949.

Tertiary alcohol 14



12 **14**

To a solution of **12** (1.33 g, 3.53 mmol, 1.00 equiv) in THF (18 mL) at 0 °C was added allyl magnesium chloride **13** (71 mL, 0.25 M in THF, 5.00 equiv) dropwise over 1 h under nitrogen, and the reaciton mixture was stirred at room temperature for 8 h. The resulting mixture was then quenched with sat. aq. ammonium chloride. Ethyl acetate (3 x 30 mL) was added, the upper organic layer was separated. The organic layer was dried with anhydrous sodium sulfate, and filtrated, the crude residue was purified by flash chromatography (petroleum ether/ ethyl acetate 40:1) to give the the tertiary alcohol **14** (1.6 g, 75%) as colorless oil.

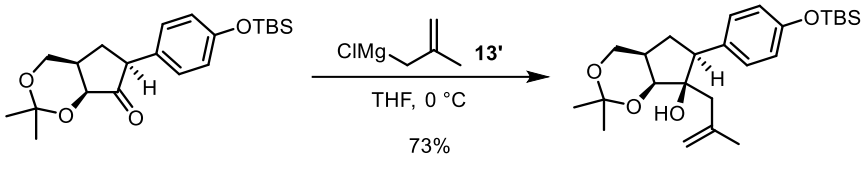
R_f = 0. 55 (Hexanes : EtOAc = 10:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.3 Hz, 2H), 6.76 (d, *J* = 8.3 Hz, 2H), 5.31 (s, 1H), 4.91 (s, 1H), 4.23-4.09 (m, 2H), 4.07 (d, *J* = 5.7 Hz, 1H), 4.03 (dd, *J* = 11.5, 4.7 Hz, 1H), 3.65 (dd, *J* = 11.5, 5.2 Hz, 1H), 2.94-2.89 (m, 1H), 2.84 (s, 1H), 2.28-2.22 (m, 3H), 2.15-2.09 (m, 1H), 2.01-1.95 (m, 1H), 1.44 (s, 3H), 1.43 (s, 3H), 1.09-1.02 (m, 21H), 0.98 (s, 9H), 0.19 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 145.7, 133.1, 130.6, 119.6, 112.2, 99.0, 81.0, 75.2, 66.5, 61.8, 52.4, 44.1, 35.7, 33.7, 28.3, 25.8, 21.5, 18.3, 18.2, 12.2, -4.3.

HRMS (ESI, *m/z*) for $C_{34}H_{60}O_5Si_2Na^+$ $[M+Na]^+$: Calcd. 627.3872; Found 627.3865.

Tertiary alcohol 14'



12 **14'**

To a solution of **12** (1.51 g, 4.00 mmol, 1.00 equiv) in THF (20 mL) at 0 °C was added allyl magnesium chloride **13'** (40 mL, 0.5 M in THF, 5.00 equiv) dropwise over 1 h under nitrogen, and the reaciton mixture was stirred at room temperature for 8 h. The resulting mixture was then quenched with sat. aq. ammonium chloride. Ethyl acetate (3 x 30 mL) was added, the upper organic layer was separated. The organic layer was dried with anhydrous sodium sulfate, and filtrated, the crude residue was purified by flash chromatography (petroleum ether/ ethyl acetate 40:1) to give the the tertiary alcohol **14'** (1.26 g, 73%) as colorless oil.

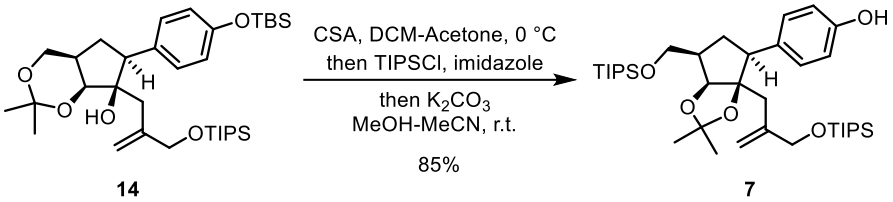
R_f = 0. 48 (Hexanes : EtOAc = 20:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 8.1 Hz, 2H), 4.84 (s, 1H), 4.71 (s, 1H), 4.07 (d, *J* = 5.8 Hz, 1H), 3.99 (dd, *J* = 11.4, 4.7 Hz, 1H), 3.65 (dd, *J* = 11.3, 5.8 Hz, 1H), 2.90 (s, 1H), 2.89-2.86 (m, 1H), 2.28-2.16 (m, 4H), 1.98-1.94 (m, 1H), 1.76 (s, 3H), 1.44 (s, 6H), 0.98 (s, 9H), 0.19 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4, 143.3, 132.9, 130.7, 119.6, 114.6, 99.2, 81.0, 75.3, 62.2, 52.4, 47.9, 36.1, 33.7, 28.1, 25.9, 24.5, 22.1, 18.4, -4.2.

HRMS (ESI, *m/z*) for $C_{25}H_{40}O_4SiNa^+$ $[M+Na]^+$: Calcd. 455.2588; Found 455.2591.

Phenol 7



14 **7**

To a solution of alcohol **14** (1.512 g, 2.5 mmol, 1.00 equiv) in CH_2Cl_2 (20 mL) at 0 °C was added another solution of Camphorsulfonic acid (58 mg, 0.25 mmol, 0.10 equiv) in acetone (5 mL), the reaction mixture was stirred at room temperature for 6 h. Upon complete consumption of starting material (by TLC), the reaction was cooled to 0 °C and imidazole (510.6 mg, 7.5 mmol, 3.00 equiv) was added, then TIPSCl (964 mg, 5.0 mmol, 2.00 equiv) was added dropwise and the mixture was stirred at room temperature for 8 h. The solvent was removed in vacuo, K_2CO_3 (1.728 g, 12.5 mmol, 5.00 equiv), MeOH (12.5 mL) and MeCN (12.5 mL) was added to the bottle successively, the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was concentrated under reduced pressure, then H_2O (20 mL) and Ethyl acetate (3 x 30 mL) was added, the upper organic layer was separated. The organic layer was dried with anhydrous sodium sulfate, and filtrated, the crude residue was purified by flash chromatography (petroleum ether/ ethyl acetate 12:1) to give the the phenol **7** (1.382 g, 85%) as colorless oil.

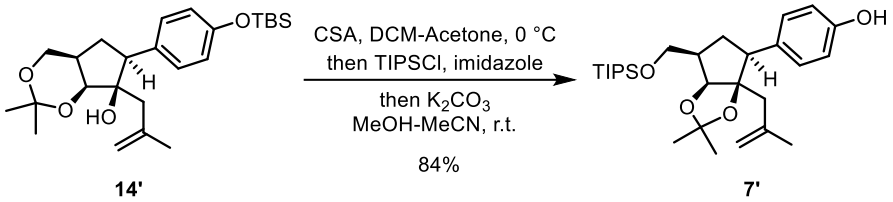
R_f = 0. 22 (Hexanes : EtOAc = 10:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 5.29 (s, 1H), 5.02 (s, 1H), 4.74 (s, 1H), 4.54 (d, *J* = 3.7 Hz, 1H), 4.13-4.03 (m, 2H), 4.00-3.96 (m, 1H), 3.77-3.73 (m, 1H), 2.87 (dd, *J* = 12.5, 6.3 Hz, 1H), 2.52 (s, 2H), 2.03-1.98 (m, 1H), l.92-1.78 (m, 2H), 1.49 (s, 1H), 1.35 (s, 1H), 1.11-1.02 (m, 42H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 145.2, 131.5, 131.3, 114.7, 114.1, 109.7, 91.1, 85.0, 66.8, 63.0, 51.1, 45.9, 42.5, 33.9, 27.1, 26.5, 18.2, 18.1, 12.2, 12.1.

HRMS (ESI, *m/z*) for $C_{37}H_{66}O_5Si_2Na^+$ [M+Na]$^+$: Calcd. 669.4341; Found 669.4341.

Phenol 7'



To a solution of alcohol **14'** (1.08 g, 2.5 mmol, 1.00 equiv) in CH_2Cl_2 (20 mL) at 0 °C was added another solution of Camphorsulfonic acid (58 mg, 0.25 mmol, 0.10 equiv) in acetone (5 mL), the reaction mixture was stirred at room temperature for 6 h. Upon complete consumption of starting material (by TLC), the reaction was cooled to 0 °C and imidazole (510.6 mg, 7.5 mmol, 3.00 equiv) was added, then TIPSCl (964 mg, 5.0 mmol, 2.00 equiv) was added dropwise and the mixture was stirred at room temperature for 8 h. The solvent was removed in vacuo, K_2CO_3 (1.728 g, 12.5 mmol, 5.00 equiv), MeOH (12.5 mL) and MeCN (12.5 mL) was added to the bottle successively, the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was concentrated under reduced pressure, then H_2O (20 mL) and Ethyl acetate (3 x 30 mL) was added, the upper organic layer was separated. The organic layer was dried with anhydrous sodium sulfate, and filtrated, the crude residue was purified by flash chromatography (petroleum ether/ ethyl acetate 20:1) to give the the phenol **7'** (0.99 g, 84%) as colorless foam.

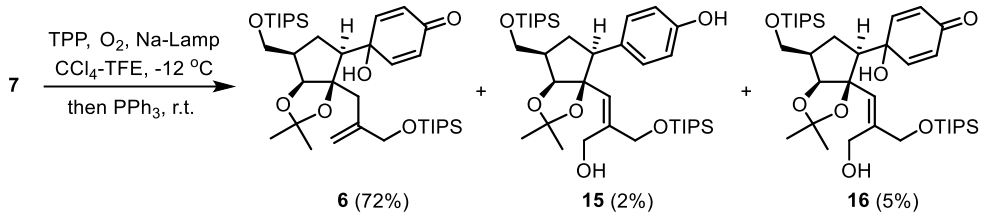
R_f = 0. 67 (Hexanes : EtOAc = 10:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 4.89 (d, *J* = 17.1 Hz, 2H), 4.53 (d, *J* = 3.7 Hz, 1H), 4.01-3.97 (m, 1H), 3.79-3.74 (m, 1H), 2.89 (dd, *J* = 12.4, 6.5 Hz, 1H), 2.53 (d, *J* = 13.8 Hz, 1H), 2.42 (d, *J* = 13.8 Hz, 1H), 2.05-2.00 (m, 1H), l.89-1.81 (m, 2H), 1.67 (s, 3H), 1.51 (s, 3H), 1.35 (s, 3H),1.10-1.06 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 142.6, 131.4, 116.0, 114.6, 109.7, 91.1, 85.1, 63.0, 50.9, 47.6, 45.8, 33.8, 27.1, 26.4, 24.4, 18.2, 18.1, 17.8, 12.4, 12.2.

HRMS (ESI, *m/z*) for $C_{28}H_{46}O_4SiNa^+$ [M+Na]$^+$: Calcd. 497.3058; Found 497.3069.

Dienone 6



A solution of **7** (258.8 mg, 0.4 mmol, 1.00 equiv), TPP (12.3 mg, 0.02 mmol, 0.05 equiv) and TFE (1.6 mL) in CCl_4 (14.4 mL) was injected to the FEP tubing in the tubing bubbling (TB) setup. With continuous circulation of ethanol as a coolant (~ -12 °C) to keep the reaction mixture temperature at 10 °C, a stream of oxygen gas was introduced and bubbled through at a gas flow rate of 0.1 L/min. The solution was irradiated using 150W high pressure sodium lamp (HPSL) for 4 h. The reaction solution was transferred from the FEP tube to a flask by injection syringe. Then to the flask was added triphenylphosphine and stirred at room temperature. After 1 h the reaction mixture was concentrated to dryness and purified directly by flash chromatography (petroleum ether/ ethyl acetate 10:1) to give the desired compound **6** (190 mg, 72%) as colorless oil, and by-products **15** (4.8 mg, 2%) as colorless oil and **16** (14.2 mg, 5%) as colorless oil.

6:

R_f = 0. 49 (Hexanes : EtOAc = 4:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (dd, *J* = 10.4, 3.1 Hz, 1H), 6.92 (dd, *J* = 10.3, 3.0 Hz, 1H), 6.19 (dd, *J* = 10.2, 1.7 Hz, 1H), 6.14 (dd, *J* = 10.3, 1.7 Hz, 1H), 5.26 (s, 1H), 4.88 (s, 1H), 4.53 (d, *J* = 3.7 Hz, 1H), 4.29 (s, 1H), 4.10 (s, 2H), 3.90-3.86 (m, 1H), 3.72-3.68 (m, 1H), 2.77 (d, *J* = 13.9 Hz, 1H), 2.57 (d, *J* = 14.0 Hz, 1H), 2.03-1.82 (m, 3H), 1.75-1.69 (m, 1H), 1.53 (s, 3H), 1.41 (s, 3H), l.11-1.02 (m, 42H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 185.4, 152.5, 150.9, 143.9, 127.5, 126.8, 115.7, 110.4, 93.2, 85.4, 71.2, 66.9, 62.6, 52.1, 44.6, 42.5, 27.9, 26.7, 25.8, 18.2, 18.1, 12.2, 12.1.

HRMS (ESI, *m/z*) for $C_{37}H_{66}O_6Si_2Na^+$ $[M+Na]^+$: Calcd. 685.4290; Found 685.4279.

15:

R_f = 0. 37 (Hexanes : EtOAc = 4:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 5.73 (s, 1H), 4.50 (d, *J* = 4.6 Hz, 1H), 4.27-4.18 (m, 2H), 4.03-3.95 (m, 2H), 3.81-3.76 (m, 1H), 3.59-3.55 (m, 1H), 2.71 (dd, *J* = 12.2, 6.2 Hz, 1H), 2.17-2.10 (m, 2H), 1.92-1.84 (m, 2H), 1.53 (s, 3H), 1.28 (s, 3H), 1.09-1.06 (m, 42H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 138.5, 131.0, 129.4, 129.1, 114.8, 110.4, 91.3, 87.3, 66.6, 62.8, 59.6, 54.6, 46.6, 32.6, 26.5, 25.2, 18.2, 18.1, 12.2, 12.1.

HRMS (ESI, *m/z*) for $C_{37}H_{66}O_6Si_2Na^+$ $[M+Na]^+$: Calcd. 685.4290; Found 685.4298.

16:

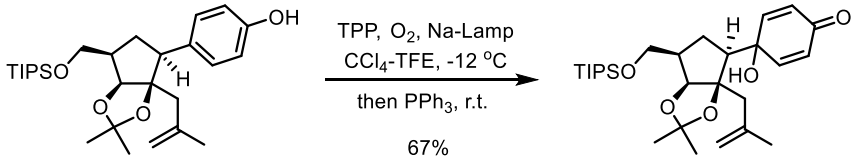
R_f = 0. 36 (Hexanes : EtOAc = 4:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (dd, *J* = 10.2, 3.1 Hz, 1H), 6.99 (dd, *J* = 10.3, 3.1 Hz, 1H), 6.13 (dd, *J* = 10.3, 1.8 Hz, 1H), 6.06 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.63 (s, 1H), 4.53 (d, *J* = 12.4 Hz, 1H), 4.46 (d, *J* = 4.3 Hz, 1H), 4.32-4.20 (m, 3H), 3.92-3.88 (m, 1H), 3.73-3.69 (m, 1H), 2.19-2.13 (m, 1H), 1.90-1.77 (m, 3H), 1.54 (s, 3H), 1.35 (s, 3H), 1.07-1.04 (m, 42H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 185.6, 152.4, 150.6, 136.0, 131.8, 127.7, 126.7, 111.2, 92.9, 88.5, 71.3, 68.2, 62.4, 60.0, 57.8, 45.2, 28.2, 26.2, 24.5, 18.2, 18.1, 12.1, 12.0.

HRMS (ESI, *m/z*) for $C_{37}H_{66}O_7Si_2Na^+$ $[M+Na]^+$: Calcd. 701.4239; Found 701.4252.

Dienone 6'



7' **6'**

A solution of **7'** (189.9 mg, 0.4 mmol, 1.00 equiv), TPP (12.3 mg, 0.02 mmol, 0.05 equiv) and TFE (1.6 mL) in CCl_4 (14.4 mL) was injected to FEP tube by injection syringe. The reaction was kept under oxygen atmosphere by bubbling with an oxygen bottle (0.1 L/min). The solution was irradiated using 150W high pressure sodium lamp (HPSL) for 4 h. The reaction solution was transferred from the FEP tube to flask by injection syringe. Then to the flask was added triphenylphosphine and stirred at room temperature. After 1 h the reaction mixture was concentrated to dryness and purified directly by flash chromatography (petroleum ether/ ethyl acetate 5:1) to give the desired compound **6'** (132 mg, 67%) as yellow foam.

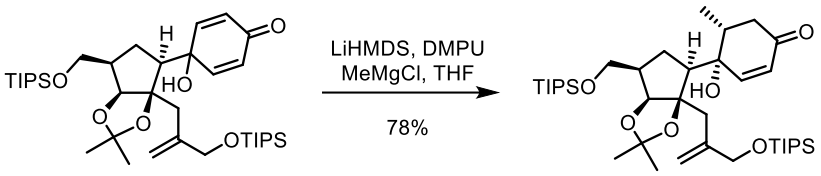
R_f = 0. 66 (Hexanes : EtOAc = 2:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (dd, *J* = 9.9, 3.4 Hz, 1H), 6.92 (dd, *J* = 10.2, 3.1 Hz, 1H), 6.21-6.13 (m, 2H), 4.93 (s, 1H), 4.73 (s, 1H), 4.53 (d, *J* = 3.8 Hz, 1H), 4.27 (s, 1H), 3.89 (dd, *J* = 9.6, 7.5 Hz, 1H), 3.72 (dd, *J* = 9.6, 6.3 Hz, 1H), 2.65 (d, *J* = 13.7 Hz, 1H), 2.57 (d, *J* = 13.7 Hz, 1H), 2.07-1.82 (m, 3H), 1.76 (s, 3H), 1.75-1.69 (m, 1H), 1.54 (s, 3H), 1.41 (s, 3H), l.10-1.04 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 185.5, 152.6, 151.0, 140.9, 127.5, 126.8, 117.7, 110.3, 93.2, 85.1, 71.2, 62.6, 52.4, 48.0, 44.5, 27.7, 26.7, 25.7, 25.1, 18.2, 18.1, 12.1.

HRMS (ESI, *m/z*) for $C_{28}H_{46}O_5SiNa^+$ $[M+Na]^+$: Calcd. 513.3007; Found 513.2997.

Cyclohexenone 5



6 **5**

To a solution of **6** (955 mg, 1.44 mmol, 1.00 equiv) in THF (15 mL) was added lithium hexamethyl disilazide (1.58 mL, 1.0 M in THF, 1.10 equiv) dropwise at -78 °C under argon. After being stirred for 30 min, the reaction mixture was added DMPU (1.04 mL, 8.64 mmol, 6.00 equiv) and sitrred for 30 min, followed by methylmagnesium chloride (1.44 mL, 3.0 M in THF, 3.00 equiv). The mixture was stirred at -78 °C for 1 h and warmed to 0 °C during 6 h. Then the resulting mixture was quenched with sat. aq. ammonium chloride, extracted by ethyl acetate (3 x 20 mL), and the upper organic layer was separated. The organic layer was dried with anhydrous sodium sulfate, and filtrated. The crude product was purified by flash chromatography (petroleum ether/ ethyl acetate 15:1) to give enone **5** (759 mg, 78%) as colorless oil.

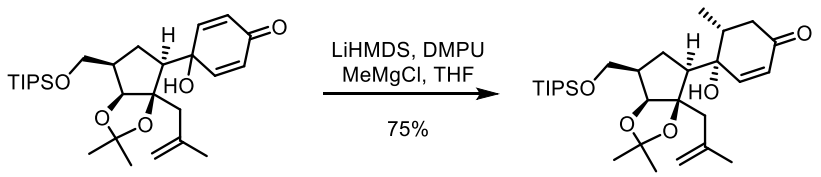
R_f = 0. 58 (Hexanes : EtOAc = 10:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (d, *J* = 10.4 Hz, 1H), 5.88 (d, *J* = 10.4 Hz, 1H), 5.32 (s, 1H), 5.00 (s, 1H), 4.53 (d, *J* = 3.8 Hz, 1H), 4.20 (s, 2H), 3.91-3.86 (m, 1H), 3.80 (s, 1H), 3.72-3.68 (m, 1H), 2.81 (d, *J* = 14.1 Hz, 1H), 2.61-2.55 (m, 3H), 2.48-2.42 (m, 1H), 2.23-2.18 (m, 1H), 1.99-1.94 (m, 1H), 1.86-1.77 (m, 1H), 1.65-1.60 (m, 1H), 1.54 (s, 3H), 1.37 (s, 3H), 1.14-1.03 (m, 45H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1, 153.3, 144.7, 127.4, 115.7, 110.4, 93.2, 84.9, 74.4, 67.2, 62.7, 49.6, 44.7, 43.2, 42.9, 37.7, 28.6, 26.7, 26.0, 18.2, 18.1, 15.7, 12.1.

HRMS (ESI, *m/z*) for $C_{38}H_{70}O_6Si_2Na^+$ $[M+Na]^+$: Calcd. 701.4603; Found 701.4599.

Cyclohexenone 5'



6' **5'**

To a solution of **6'** (834 mg, 1.7 mmol, 1.00 equiv) in THF (17 mL) was added lithium hexamethyl disilazide (1.87 mL, 1.0 M in THF, 1.10 equiv) dropwise at -78 °C under argon. After being stirred for 30 min, the reaction mixture was added DMPU (1.23 mL, 10.2 mmol, 6.00 equiv) and sitrred for 30 min, followed by methylmagnesium chloride (1.7 mL, 3.0 M in THF, 3.00 equiv). The

mixture was stirred at -78 °C for 1 h and warmed to 0 °C during 6 h. Then the resulting mixture was quenched with sat. aq. ammonium chloride, extracted by ethyl acetate (3 x 20 mL), and the upper organic layer was separated. The organic layer was dried with anhydrous sodium sulfate, and filtrated. The crude product was purified by flash chromatography (petroleum ether/ ethyl acetate 10:1) to give enone **5'** (645 mg, 75%) as yellow oil.

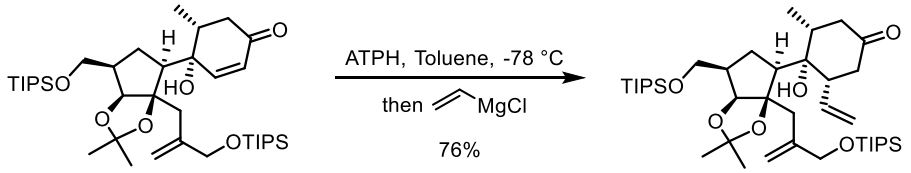
R_f = 0. 55 (Hexanes : EtOAc = 5:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (d, *J* = 10.4 Hz, 1H), 5.88 (d, *J* = 10.4 Hz, 1H), 4.99 (s, 1H), 4.84 (s, 1H), 4.54 (d, *J* = 3.6 Hz, 1H), 3.90 (d, *J* = 8.8 Hz, 1H), 3.87 (s, 1H), 3.71 (dd, *J* = 9.5, 6.4 Hz, 1H), 2.64-2.44 (m, 5H), 2.21 (dd, *J* = 12.3, 6.6 Hz, 1H), 2.00-1.94 (m, 1H), 1.85-1.80 (m, 4H), 1.54 (s, 3H), 1.39 (s, 3H), 1.12 (d, *J* = 6.4 Hz, 3H), 1.10-1.04 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1, 153.3, 141.6, 127.4, 117.3, 110.3, 93.2, 84.9, 74.4, 62.7, 49.5, 48.9, 44.7, 42.9, 37.7, 28.5, 26.6, 25.8, 25.2, 18.2, 18.1, 15.7, 12.2.

HRMS (ESI, *m/z*) for $C_{29}H_{50}O_5SiNa^+$ $[M+Na]^+$: Calcd. 529.3320; Found 529.3323.

Olefin 19



5 **19**

Me_3Al (0.458 mL, 2.0 M in THF, 1.50 equiv) was added in a portion to a solution of 2,6-diphenyl phenol (677.2 mg, 2.75 mmol, 4.50 equiv) in toluene (3.5 mL) at room temperature. The resultant ATPH yellow-orange solution was stirred for 1 h at room temperature.

To a solution of **5** (415 mg, 0.611 mmol, 1.00 equiv) in toluene (2.5 mL) was added ATPH solution prepared above at -78 °C dropwise under argon. The reaction mixture was stirred for 30 min at -78 °C. To the solution was added vinylmagnesium chloride (3.67 mL, 2.0 M in THF, 12.00 equiv) dropwise for 30 min and the reaction mixture was warmed to room temperature during 10 h. Then the resulting mixture was quenched with sat. aq. ammonium chloride, filtered. Ethyl acetate (3 x 20 mL) was added, and the upper organic layer was separated. The organic layer was dried with anhydrous sodium sulfate, and filtrated. The crude product was purified by flash chromatography (petroleum ether/ ethyl acetate 30:1) to give ketone **19** (328 mg, 76%) as pale yellow oil.

R_f = 0. 47 (Hexanes : EtOAc = 20:1), PMA stain.

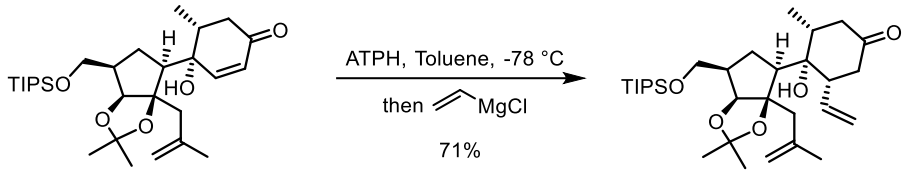
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.20-6.11 (m, 1H), 5.33 (s, 1H), 5.09-5.05 (m, 2H), 5.00 (s, 1H), 4.52 (d, *J* = 3.8 Hz, 1H), 4.20 (s, 2H), 3.93-3.89 (m, 1H), 3.74-3.70 (m, 1H), 3.53 (s, 1H), 3.10-3.07 (m, 1H), (d, *J* = 14.2 Hz, 1H), 2.62 (d, *J* = 14.2 Hz, 1H), 2.54-2.29 (m, 6H), 2.03-1.94 (m, 1H), 1.89-1.70 (m, 2H), 1.52 (s, 3H), 1.36 (s, 3H), 1.13-1.03 (m, 45H).

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

δ 211.7, 144.9, 138.8, 115.6, 115.2, 110.2, 93.1, 85.1, 75.1, 67.3, 62.9, 50.7, 45.4, 44.9, 44.1, 43.5, 41.8, 38.1, 28.6, 26.7, 26.0, 18.2, 18.1, 16.8, 12.2, 12.1.

HRMS (ESI, *m/z*) for $C_{40}H_{74}O_6Si_2Na^+$ $[M+Na]^+$: Calcd. 729.4916; Found 729.4908.

Olefin 19'



5' **19'**

Me_3Al (0.375 mL, 2.0 M in THF, 1.50 equiv) was added in a portion to a solution of 2,6-diphenyl phenol (554.2 mg, 2.25 mmol, 4.50 equiv) in toluene (3.0 mL) at room temperature. The resultant ATPH yellow-orange solution was stirred for 1 h at room temperature.

To a solution of **5'** (253 mg, 0.5 mmol, 1.00 equiv) in toluene (2.5 mL) was added ATPH solution prepared above at -78 °C dropwise under argon. The reaction mixture was stirred for 30 min at -78 °C. To the solution was added vinylmagnesium chloride (3.00 mL, 2.0 M in THF, 12.00 equiv) dropwise for 30 min and the reaction mixture was warmed to room temperature during 10 h. Then the resulting mixture was quenched with sat. aq. ammonium chloride, filtered. Ethyl acetate (3 x 20 mL) was added, and the upper organic layer was separated. The organic layer was dried with anhydrous sodium sulfate, and filtrated. The crude product was purified by flash chromatography (petroleum ether/ ethyl acetate 15:1) to give ketone **19'** (190 mg, 71%) as yellow oil.

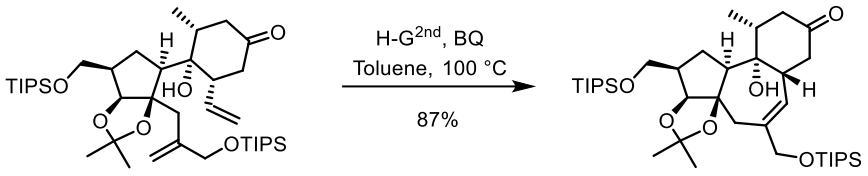
R_f = 0. 55 (Hexanes: EtOAc = 10:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.21-6.13 (m, 1H), 5.09-5.04 (m, 2H), 4.98 (s, 1H), 4.83 (s, 1H), 4.53 (d, *J* = 3.8 Hz, 1H), 3.93-3.89 (m, 1H), 3.75-3.71 (m, 1H), 3.58 (s, 1H), 3.07 (d, *J* = 3.6 Hz, 1H), 2.69-2.61 (m, 2H), 2.55-2.30 (m, 6H), 2.03-1.94 (m, 1H), 1.90-1.81 (m, 4H), 1.75-1.69 (m, 1H), 1.52 (s, 3H), 1.38 (s, 3H), 1.11-1.05 (m, 24H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7, 142.0, 138.8, 116.9, 115.5, 110.2, 93.1, 85.0, 75.2, 62.8, 50.9, 49.1, 45.4, 44.9, 44.1, 41.8, 38.1, 28.5, 26.7, 25.8, 25.3, 18.2, 18.1, 16.8, 12.2.

HRMS (ESI, *m/z*) for $C_{31}H_{54}O_5SiNa^+$ [M+Na]$^+$: Calcd. 557.3633; Found 557.3630.

Tricyclic skeleton 4



19 **4**

To a stirred solution of **19** (362 mg, 0.512 mmol, 1.00 equiv) in toluene (25 mL) was added Grubbs-Hoveyda second-generation catalyst (16.1 mg, 0.026 mmol, 0.05 equiv) and 1,4-benzoquinone (11.1 mg, 0.102 mmol, 0.20 equiv) under argon, and the resultant mixture was stirred at 100 °C for 5 h. Then the mixture was concentrated to dryness and the residue was purified by flash chromatography (petroleum ether/ ethyl acetate 10:1) to give ketone **4** (303 mg, 87%) as colorless oil.

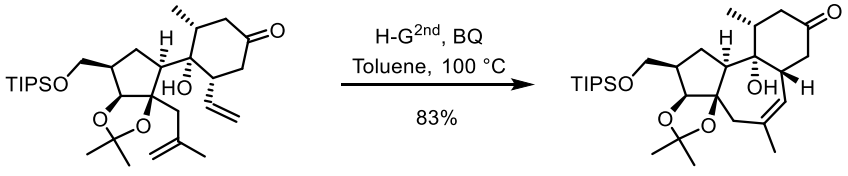
R_f = 0. 33 (Hexanes: EtOAc = 10:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.36 (d, *J* = 4.6 Hz, 1H), 4.18 (d, *J* = 3.7 Hz, 1H), 4.07 (s, 2H), 3.93-3.89 (m, 1H), 3.76-3.72 (m, 1H), 3.63-3.58 (m, 1H), 2.73-2.50 (m, 4H), 2.42 (d, *J* = 18.3 Hz, 1H), 2.28 (dd, *J* = 16.3, 5.2 Hz, 1H), 2.13 (dd, *J* = 14.0, 5.9 Hz, 1H), 1.90-1.78 (m, 3H), 1.69-1.62 (m, 1H), 1.40 (s, 3H), 1.34 (s, 3H), 1.13-1.04 (m, 42H), 1.00 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.8, 140.1, 124.4, 109.8, 88.2, 88.0, 76.6, 67.7, 62.7, 57.7, 46.8, 45.4, 43.3, 41.9, 40.6, 36.4, 28.8, 26.6, 25.7, 18.2, 18.1, 17.7, 12.1.

HRMS (ESI, *m/z*) for $C_{38}H_{70}O_6Si_2Na^+$ [M+Na]$^+$: Calcd. 701.4603; Found 701.4593.

Tricyclic skeleton 4'



19' **4'**

To a stirred solution of **19'** (188 mg, 0.35 mmol, 1.00 equiv) in toluene (17.5 mL) was added Grubbs-Hoveyda second-generation catalyst (11 mg, 0.018 mmol, 0.05 equiv) and 1,4-benzoquinone (7.6 mg, 0.07 mmol, 0.20 equiv) under argon, and the resultant mixture was stirred at 100 °C for 4 h. Then the mixture was concentrated to dryness and the residue was purified by flash chromatography (petroleum ether/ ethyl acetate 5:1) to give ketone **4'** (146 mg, 83%) as yellow

oil.

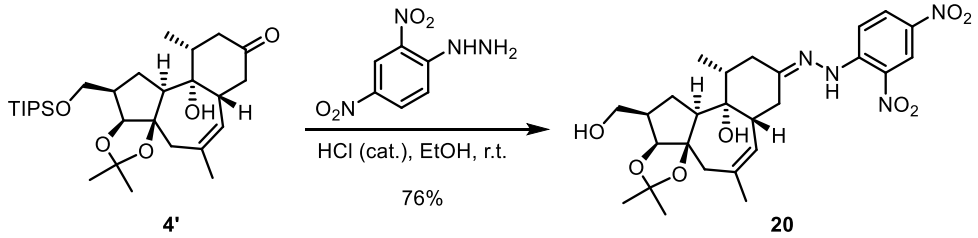
R_f = 0. 56 (Hexanes : EtOAc = 5:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.06 (s, 1H), 4.16 (d, *J* = 2.9 Hz, 1H), 3.94-3.90 (m, 1H), 3.77-3.73 (m, 1H), 3.62-3.59 (m, 1H), 2.75 (d, *J* = 18.7 Hz, 1H), 2.68-2.50 (m, 3H), 2.28-2.20 (m, 2H), 2.10 (dd, *J* = 13.9, 5.4 Hz, 1H), 1.88-1.84 (m, 3H), 1.72-1.61 (m, 4H), 1.40 (s, 3H), 1.35 (s, 3H), 1.10-1.06 (m, 21H), 0.99 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.8, 136.7, 125.0, 109.8, 88.5, 87.8, 76.8 (overlapped with $CDCl_3$), 62.7, 57.8, 48.4, 46.7, 45.3, 42.0, 40.6, 36.2, 28.9, 26.6, 25.7, 25.6, 18.2, 18.1, 17.7, 12.2.

HRMS (ESI, *m/z*) for $C_{29}H_{50}O_5SiNa^+$ $[M+Na]^+$: Calcd. 529.3320; Found 529.3331.

Hydrazone 20



To a stirred solution of **4'** (101.4 mg, 0.2 mmol, 1.00 equiv) and 2,4-dinitrophenylhydrazine (43.6 mg, 0.22 mmol, 1.10 equiv) in EtOH (1 mL) was added a drop of hydrochloric acid, and the resultant mixture was stirred at room temperature for 2 h. Then the resulting mixture was quenched with sat. aq. sodium bicarbonate. Ethyl acetate (3 x 10 mL) was added, and the upper organic layer was separated. The organic layer was dried with anhydrous sodium sulfate, and filtrated. The crude product was purified by flash chromatography (petroleum ether/ ethyl acetate 1:1) to give hydrazone **20** (80.6 mg, 76%) as yellow solid.

R_f = 0. 36 (Hexanes : EtOAc = 1:1), PMA stain.

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.09 (s, 1H), 9.11 (s, 1H), 8.27 (d, *J* = 9.6 Hz, 1H), 7.98 (d, *J* = 9.6 Hz, 1H), 5.21 (s, 1H), 4.28 (d, *J* = 2.2 Hz, 1H), 3.92-3.83 (m, 2H), 3.58-3.55 (m, 1H), 2.80-2.58 (m, 4H), 2.40 (dd, *J* = 17.1, 5.4 Hz, 1H), 2.25-2.10 (m, 3H), 1.91-1.75 (m, 7H), 1.47 (s, 3H), 1.40 (s, 3H), 0.97 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8, 145.3, 137.6, 136.6, 130.0, 129.0, 124.7, 123.7, 116.6, 110.3, 89.0, 88.9, 77.0, 62.0, 57.7, 48.3, 43.7, 38.3, 38.0, 34.2, 29.6, 26.9, 26.5, 25.8, 25.7, 16.7.

HRMS (ESI, *m/z*) for $C_{26}H_{34}N_4O_8Na^+$ $[M+Na]^+$: Calcd. 553.2269; Found 553.2253.

3. The Semi-flow Reactor

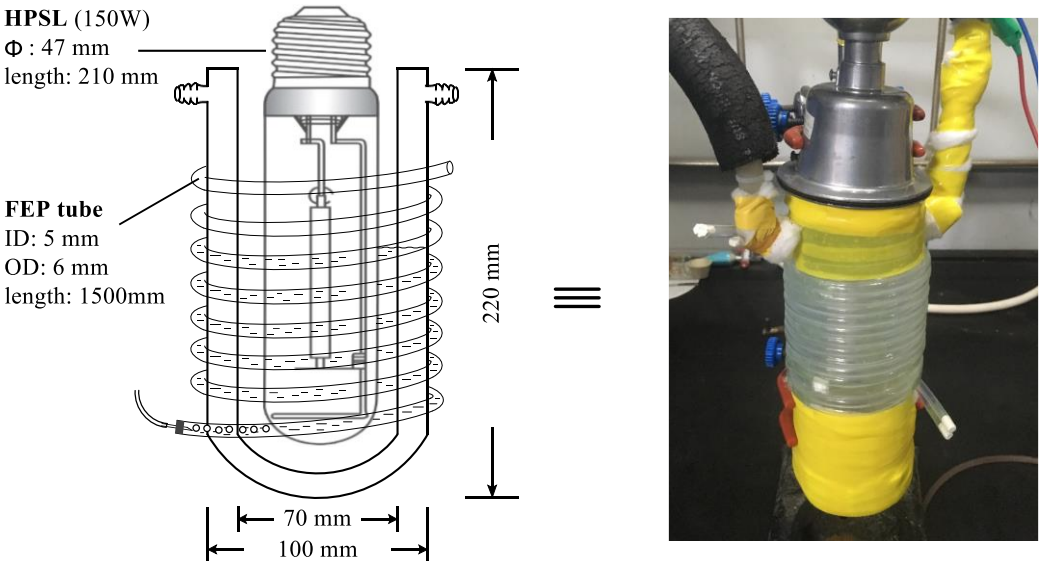


Figure S1. Specific dimensions and photograph of the semi-flow reactor.

4. X-ray Crystallographic Data

1. X-ray crystallographic data for **6'** (CCDC 1850228)

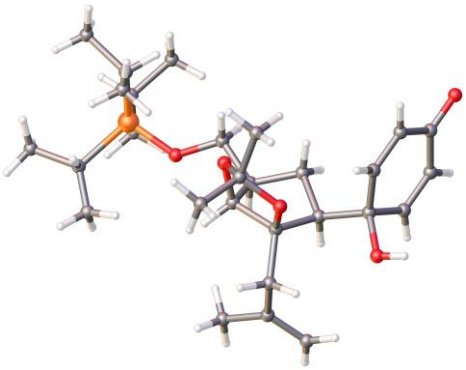


Figure S2. X-ray structure of **6'** with thermal ellipsoids at the 50% probability level.

Table S1. Crystallographic experimental details for **6'**

Identification code	CCDC 1850228
Empirical formula	$C_{28}H_{46}O_5Si$
Formula weight	490.74
Temperature/K	296.15
Crystal system	monoclinic
Space group	C2/c
a/Å	21.082(6)
b/Å	11.132(3)
c/Å	25.377(6)
α/°	90
β/°	93.904(6)
γ/°	90
Volume/Å^3	5942(3)
Z	8
ρ_{calc}g/cm^3	1.097
μ/mm^{-1}	0.111
F(000)	2144.0
Crystal size/mm^3	0.365 × 0.316 × 0.218
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.218 to 49.57
Index ranges	-24 ≤ h ≤ 24, -13 ≤ k ≤ 13, -29 ≤ l ≤ 28
Reflections collected	21762
Independent reflections	5063 [R_{int} = 0.0250, R_{sigma} = 0.0209]
Data/restraints/parameters	5063/16/317
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0720, wR_2 = 0.2074
Final R indexes [all data]	R_1 = 0.0940, wR_2 = 0.2286
Largest diff. peak/hole / e Å^{-3}	0.80/-0.34

2. X-ray crystallographic data for **20** (CCDC 1850229)

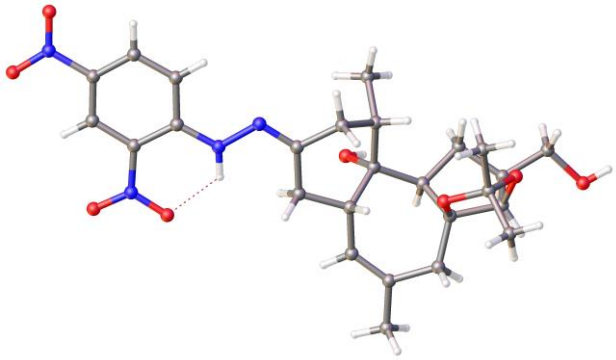
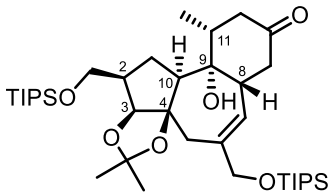


Figure S3. X-ray structure of **20** with thermal ellipsoids at the 50% probability level.

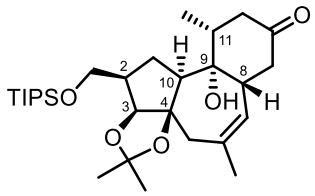
Table S2. Crystallographic experimental details for **20**

Identification code	CCDC 1850229
Empirical formula	$C_{26}H_{34}N_4O_8$
Formula weight	595.62
Temperature/K	296(2)
Crystal system	orthorhombic
Space group	Pnna
a/Å	17.706(9)
b/Å	13.192(7)
c/Å	26.864(14)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	6275(6)
Z	8
ρ_{calc}g/cm^3	1.261
μ/mm^{-1}	0.092
F(000)	2512.0
Crystal size/mm^3	0.34 × 0.167 × 0.149
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.76 to 49.56
Index ranges	-20 ≤ h ≤ 18, -15 ≤ k ≤ 13, -31 ≤ l ≤ 31
Reflections collected	31145
Independent reflections	5374 [R_{int} = 0.0538, R_{sigma} = 0.0478]
Data/restraints/parameters	5374/0/376
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0890, wR_2 = 0.2517
Final R indexes [all data]	R_1 = 0.1827, wR_2 = 0.3179
Largest diff. peak/hole / e Å^{-3}	0.31/-0.21

5. Comparison of NMR Data for Compounds 4 and 4’



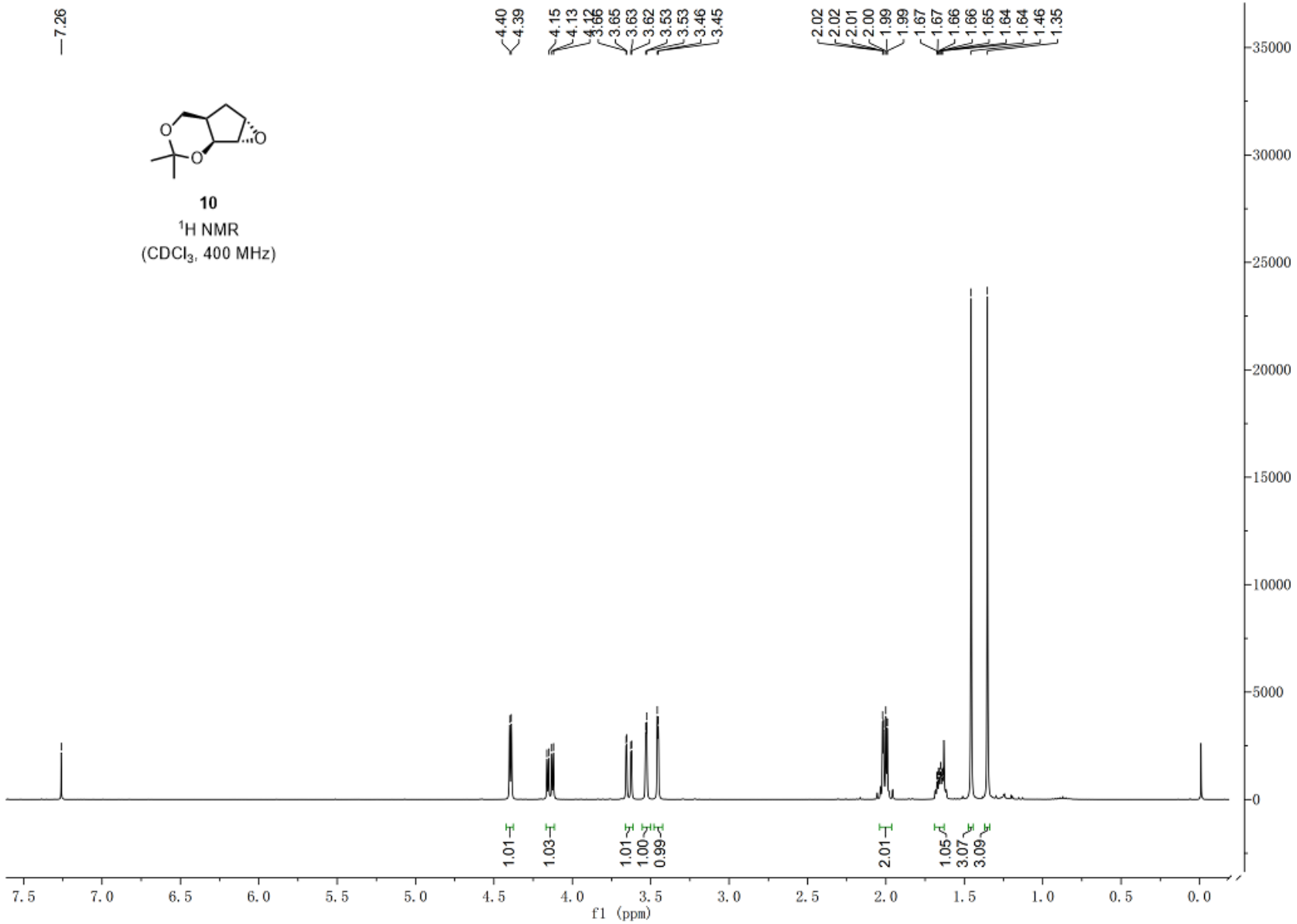
4

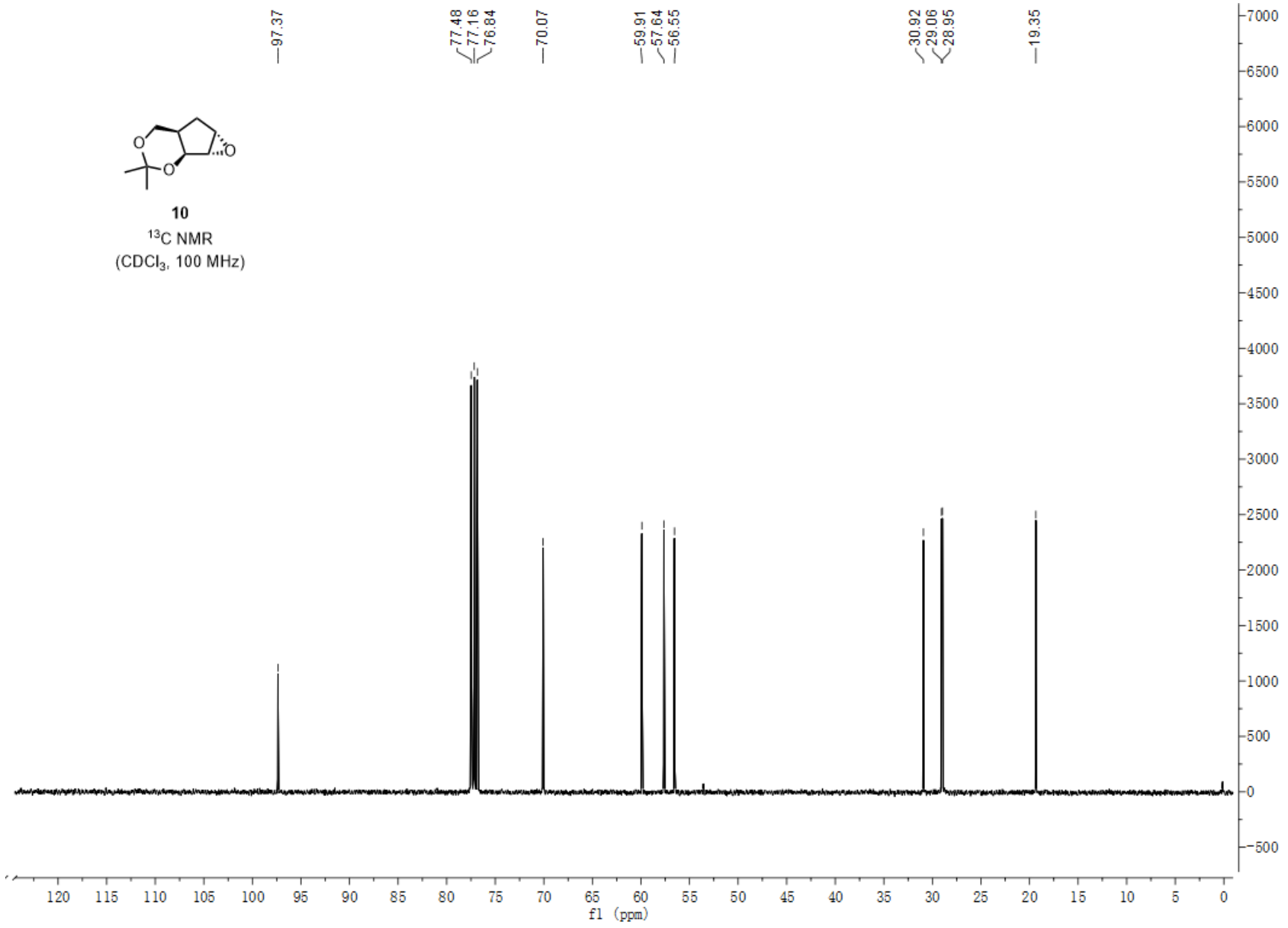


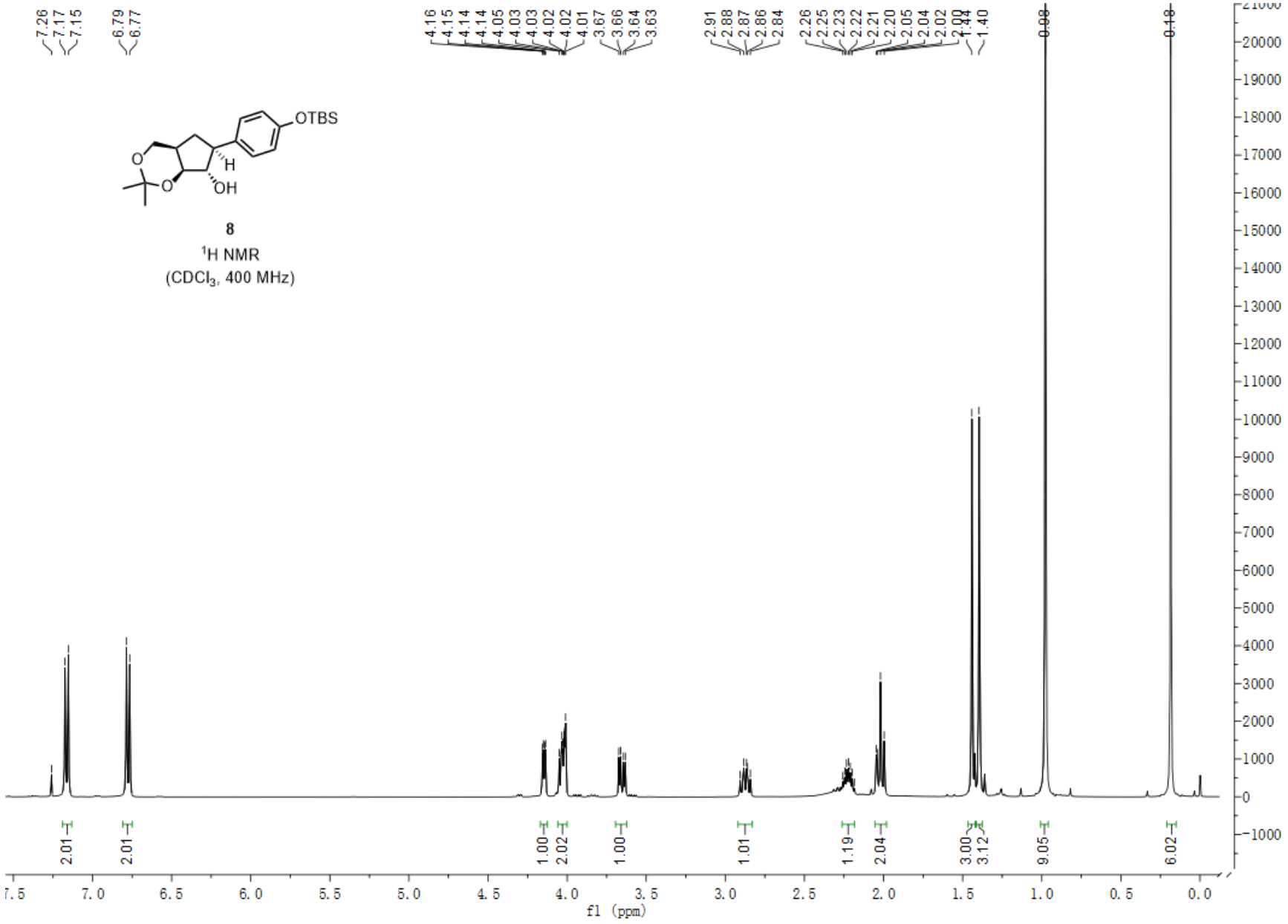
4'

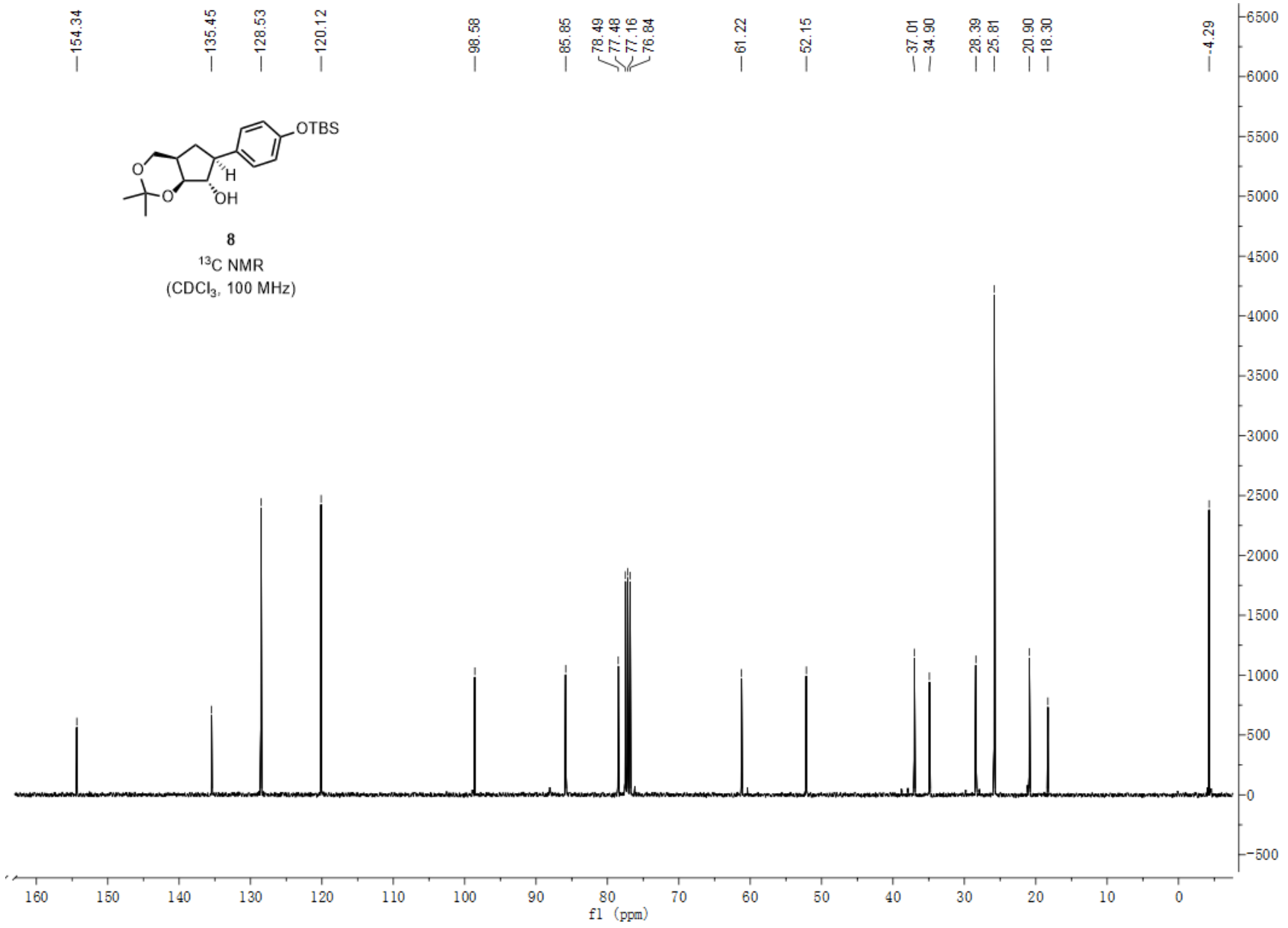
Chiral Carbon	^{1}H NMR ($CDCl_3$)			^{13}C NMR ($CDCl_3$)		
	4(ppm)	**4’**(ppm)	Δδ(ppm)	**4**(ppm)	**4’**(ppm)	Δδ(ppm)
2	1.82	1.84	0.02	45.4	45.3	-0.1
3	4.18	4.16	-0.02	88.0	87.8	-0.2
4	/	/	/	88.2	88.5	0.3
8	3.61	3.61	0.00	40.6	40.6	0.0
9	/	/	/	76.6	76.8	0.2
10	1.83	1.86	0.03	57.7	57.8	0.1
11	2.67	2.65	-0.02	36.4	36.2	-0.2

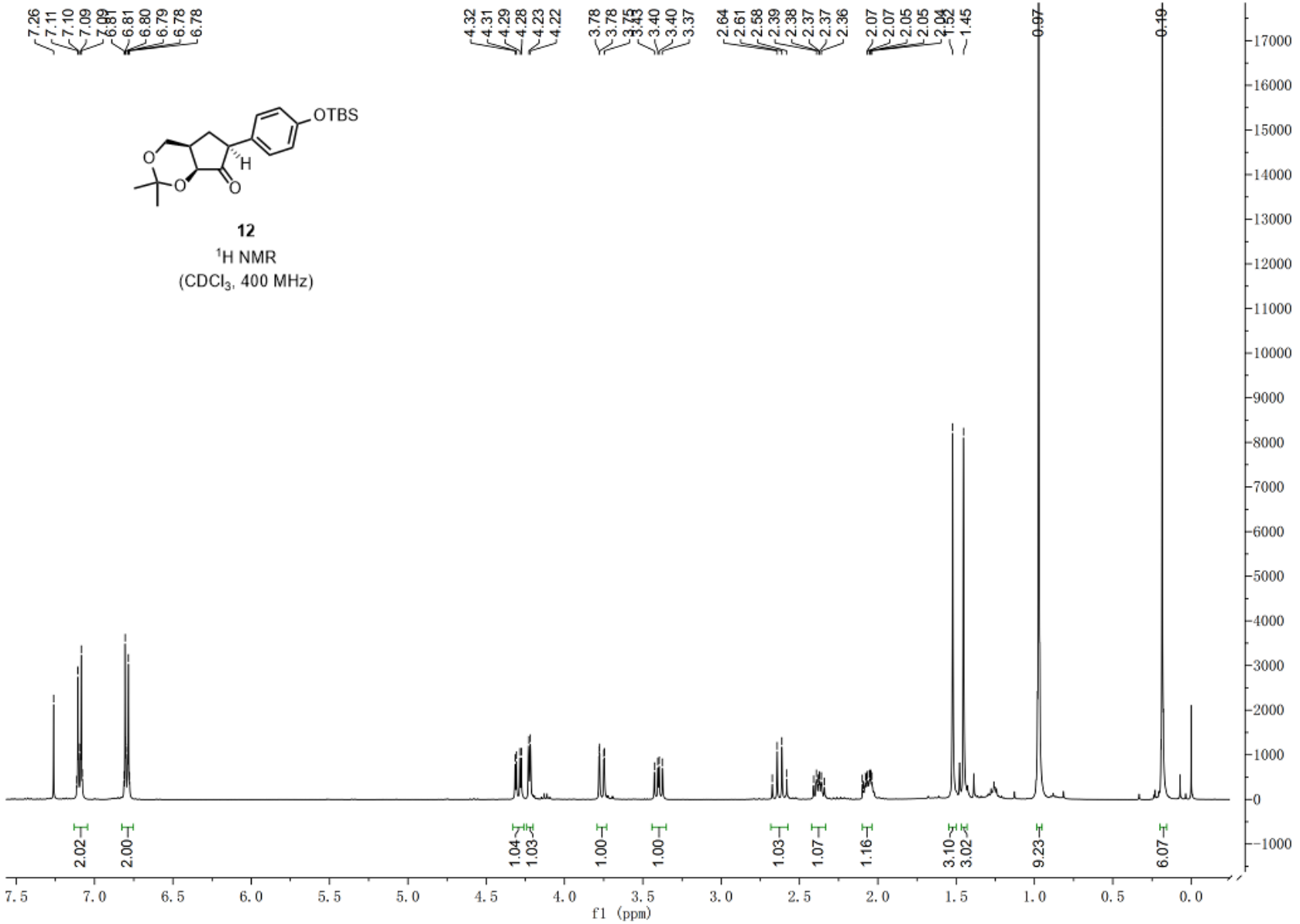
6. ^{1}H and ^{13}C NMR Spectra

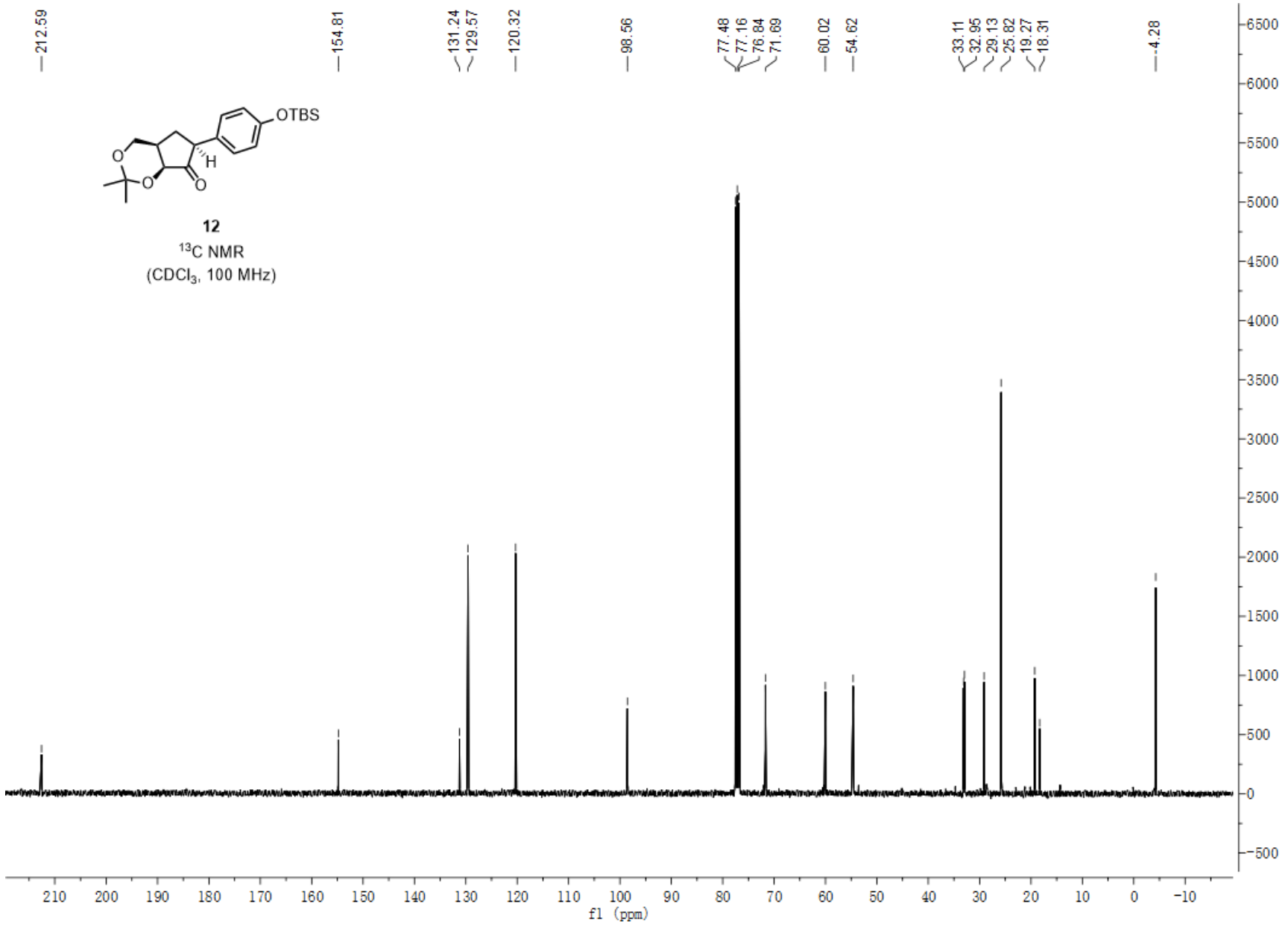


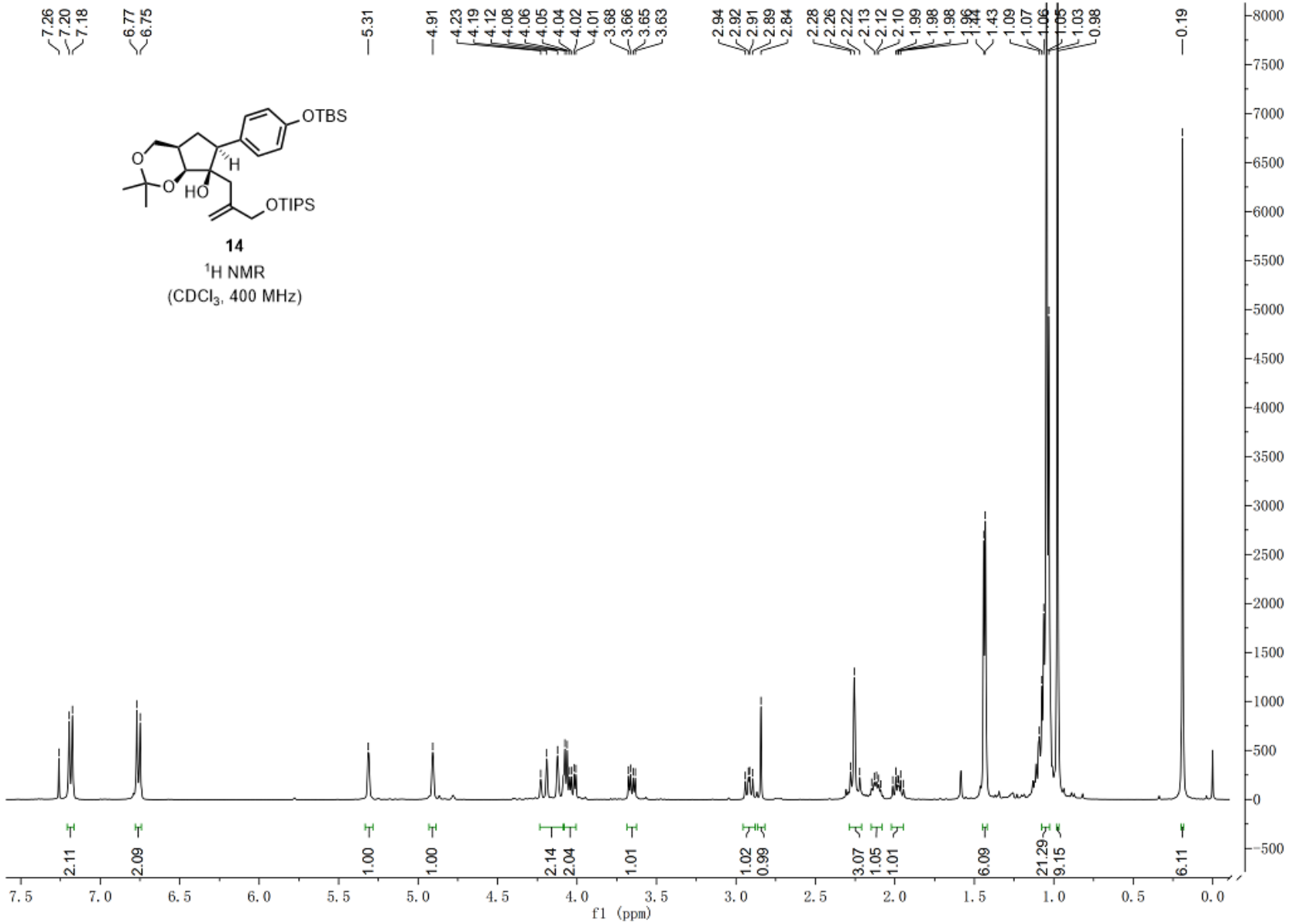

97.37
77.48
77.16
76.84
70.07
59.91
57.64
56.55
30.92
29.06
28.95
19.35
O
O
O
10
13C NMR
(CDCl3, 100 MHz)
f1 (ppm)

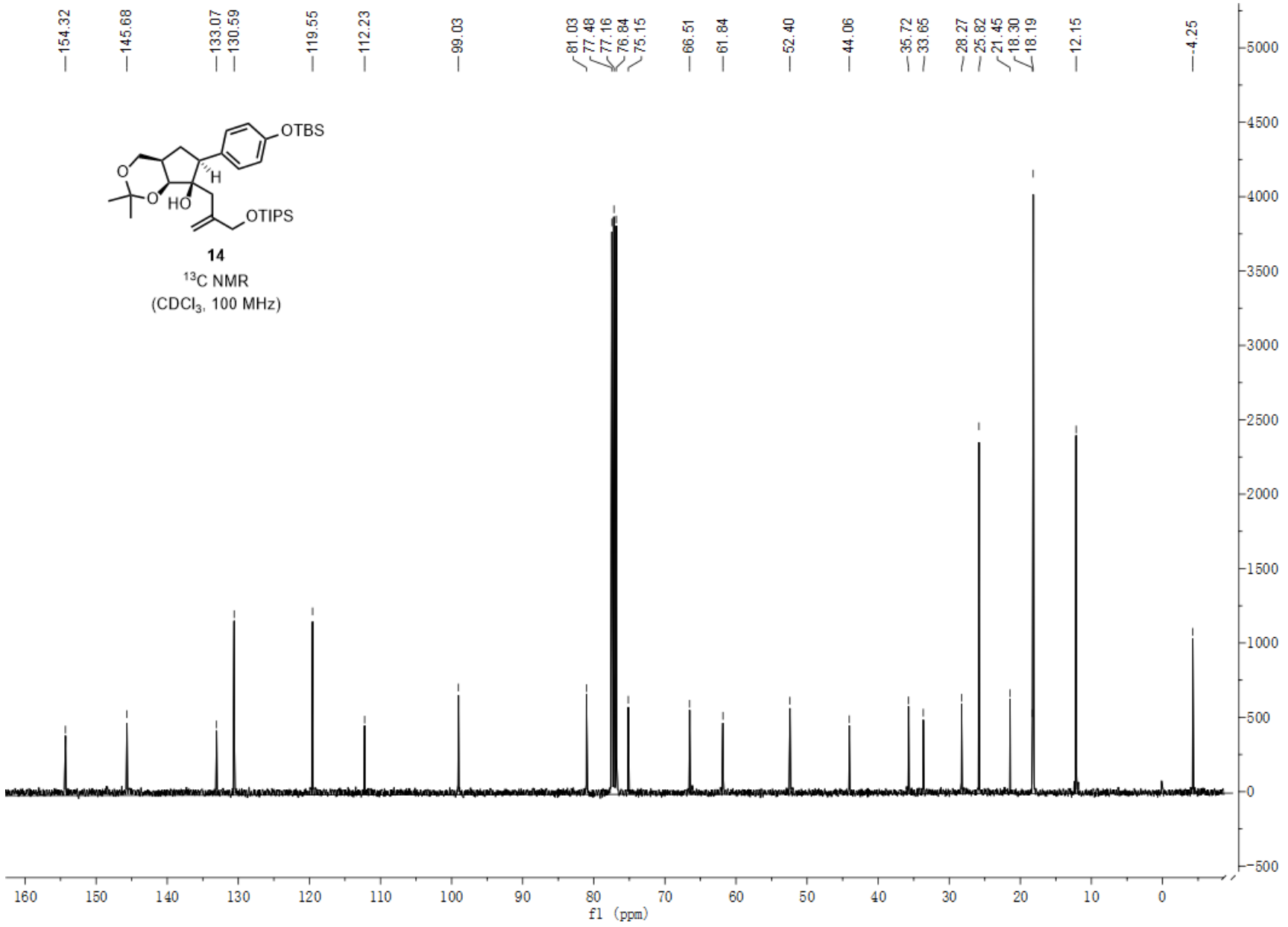

OTBS
H
OH
O
O
8
1H NMR
(CDCl3, 400 MHz)
f1 (ppm)

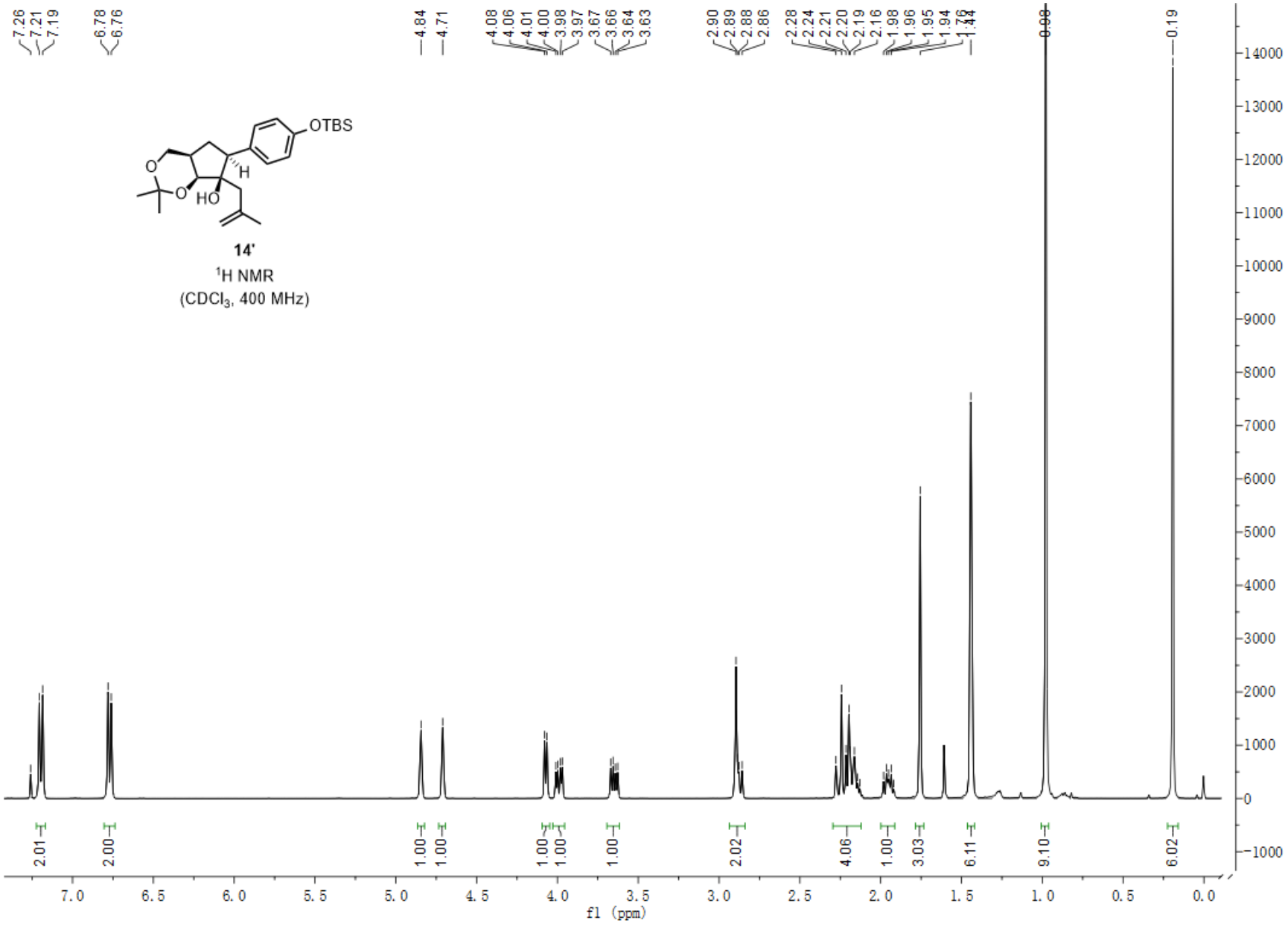

154.34
135.45
128.53
120.12
98.58
85.85
78.49
77.48
77.16
76.84
61.22
52.15
37.01
34.90
28.39
25.81
20.90
18.30
-4.29
OTBS
H
OH
O
O
8
13C NMR
(CDCl3, 100 MHz)
f1 (ppm)

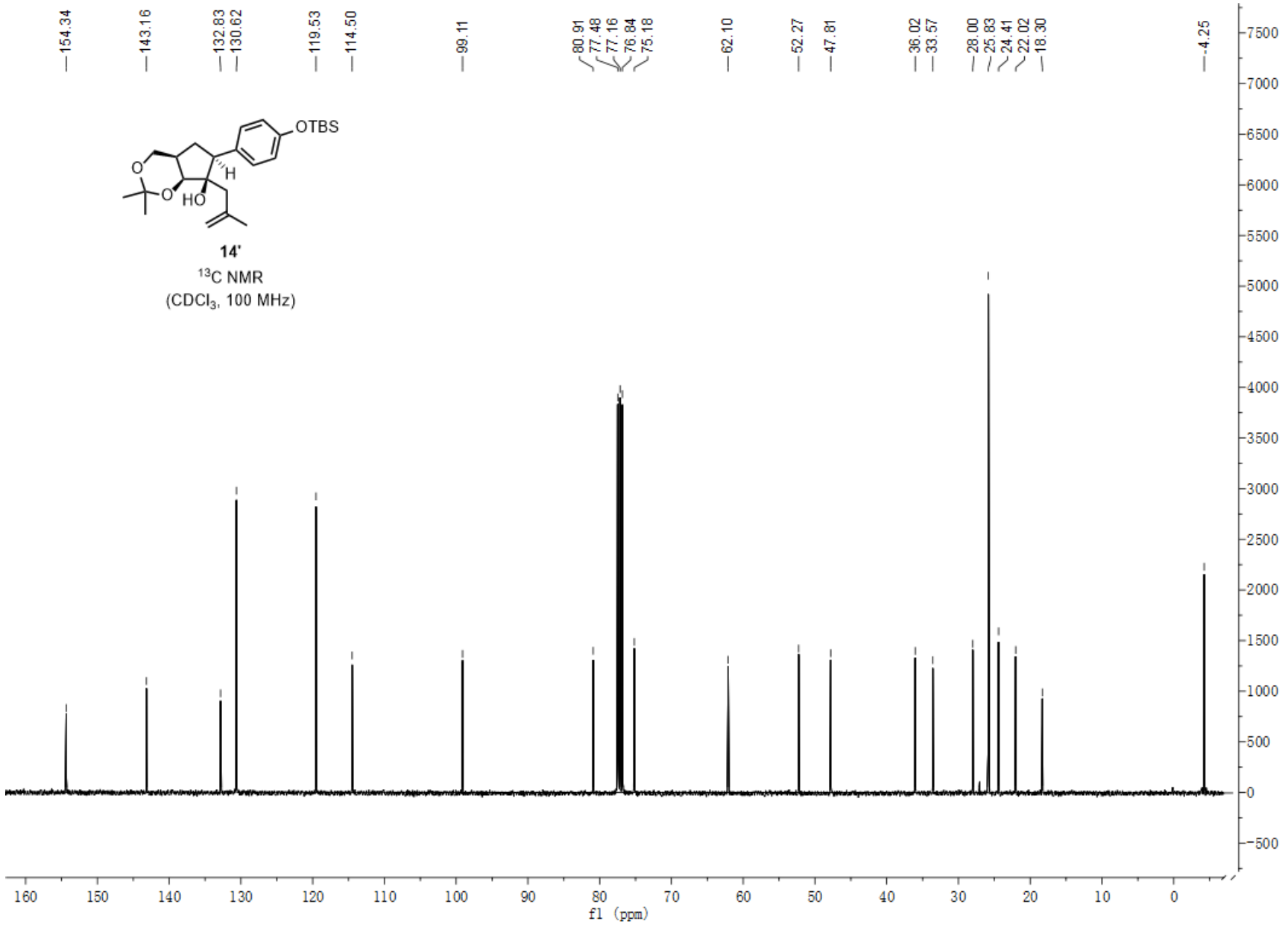

OTBS
H
O
O
O
12
1H NMR
(CDCl3, 400 MHz)
f1 (ppm)

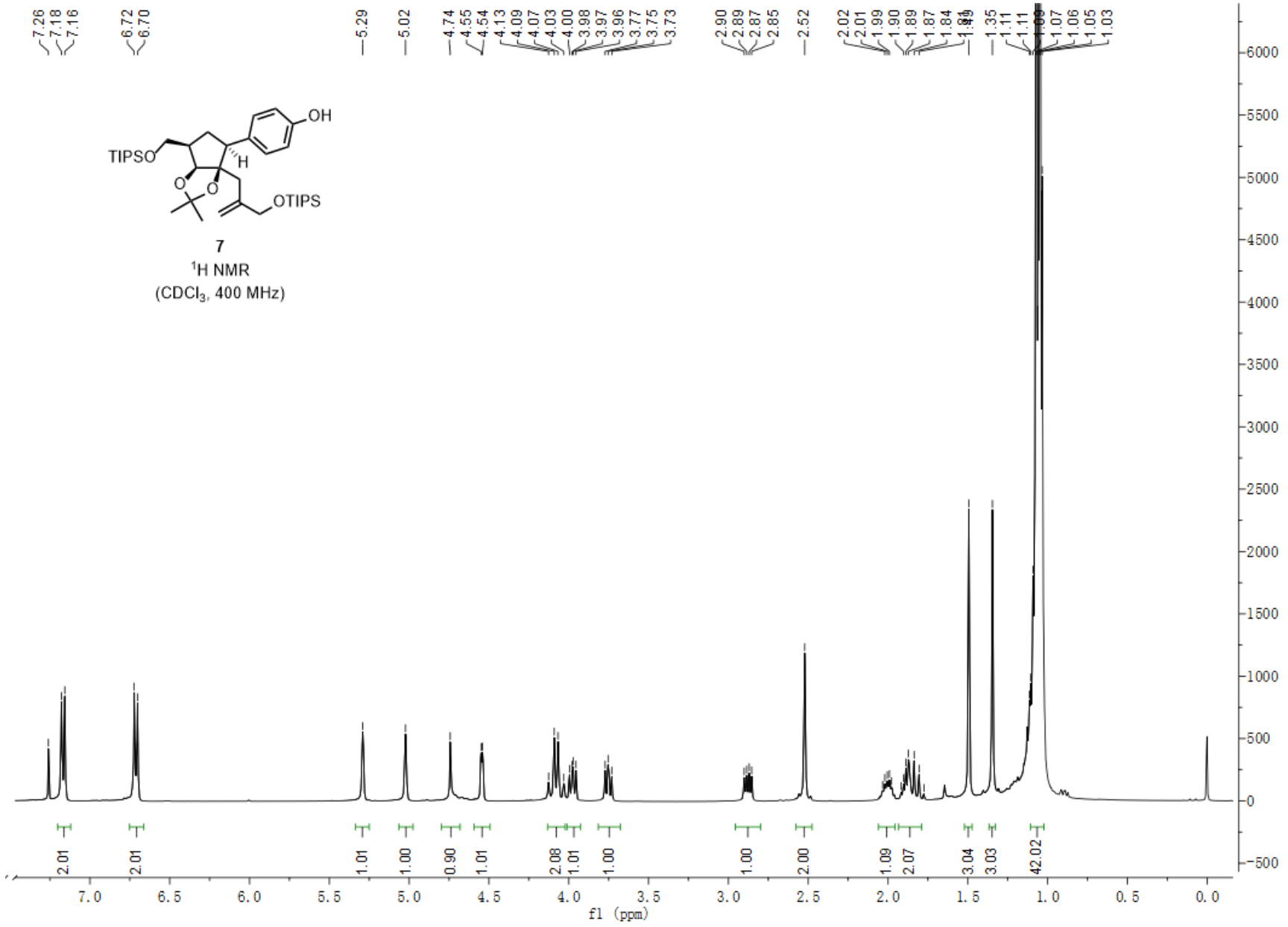

212.59
154.81
131.24
129.57
120.32
98.56
77.48
77.16
76.84
71.69
60.02
54.62
33.11
32.95
29.13
25.82
19.27
18.31
-4.28
OTBS
H
O
O
O
12
13C NMR
(CDCl3, 100 MHz)
f1 (ppm)

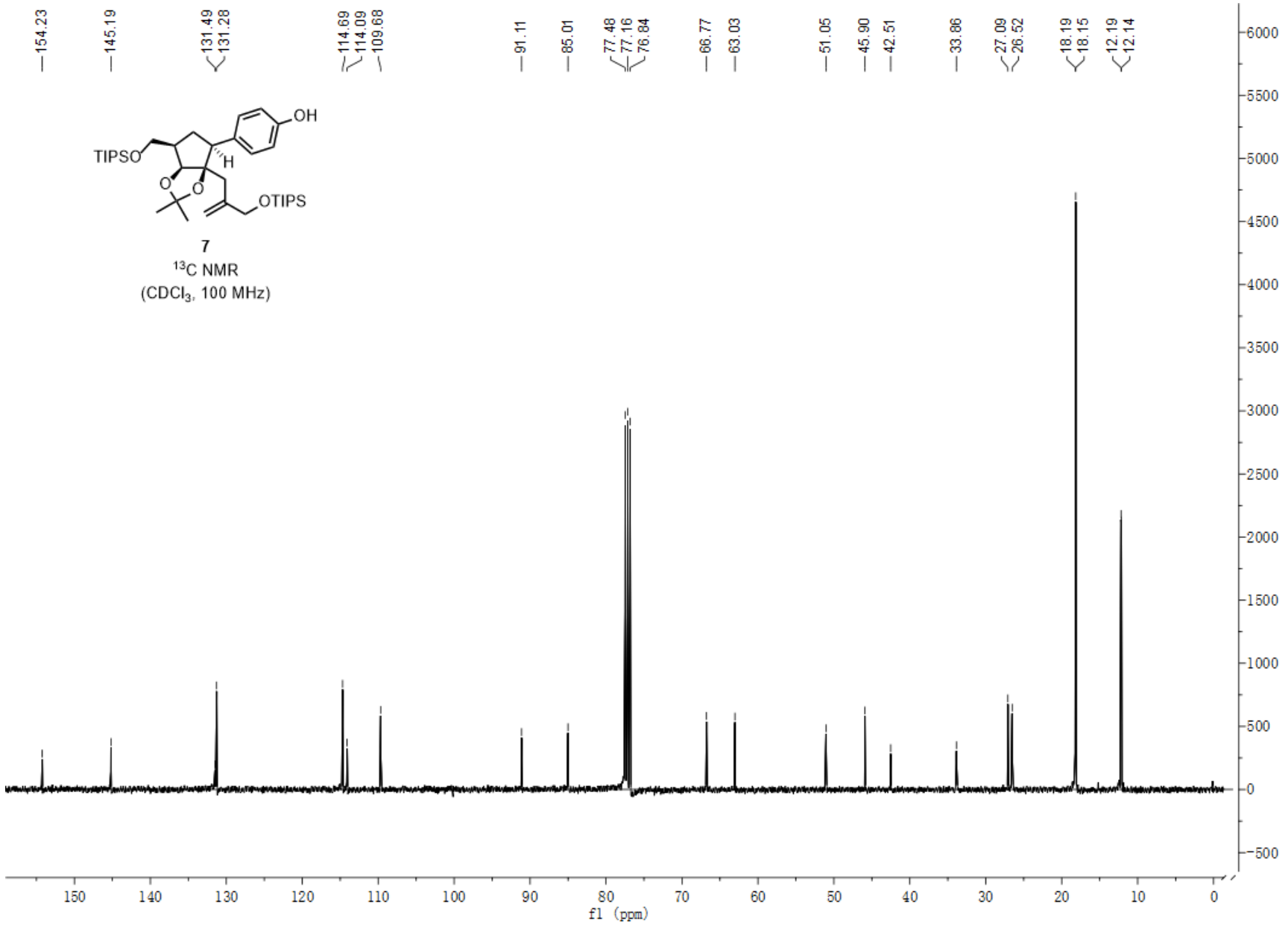

OTBS
H
O
O
HO
OTIPS
14
1H NMR
(CDCl3, 400 MHz)
f1 (ppm)

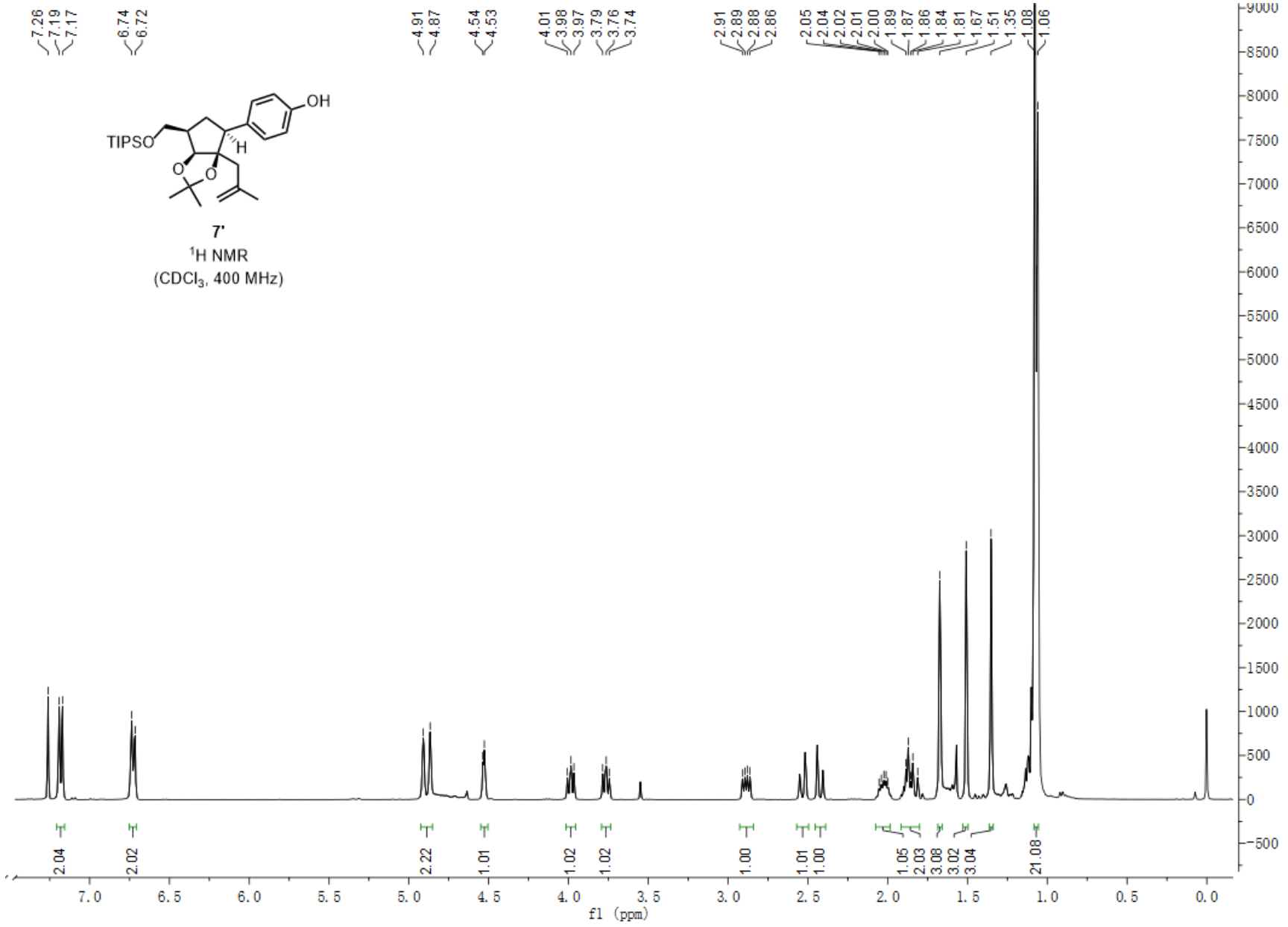

154.32
145.68
133.07
130.59
119.55
112.23
99.03
81.03
77.48
77.16
76.84
75.15
66.51
61.84
52.40
44.06
35.72
33.65
28.27
25.82
21.45
18.30
18.19
12.15
-4.25
OTBS
OTIPS
H
HO
O
O
14
13C NMR
(CDCl3, 100 MHz)
f1 (ppm)


OTBS
O
O
HO
H
14'
1H NMR
(CDCl3, 400 MHz)
7.26
7.21
7.19
6.78
6.76
4.84
4.71
4.08
4.06
4.01
4.00
3.98
3.97
3.67
3.66
3.64
3.63
2.90
2.89
2.88
2.86
2.28
2.24
2.21
2.20
2.19
2.16
1.98
1.96
1.95
1.94
0.98
0.19
2.01
2.00
1.00
1.00
1.00
1.00
1.00
2.02
4.06
1.00
3.03
6.11
9.10
6.02
f1 (ppm)


154.34
143.16
132.83
130.62
119.53
114.50
99.11
80.91
77.48
77.16
76.84
75.18
62.10
52.27
47.81
36.02
33.57
28.00
25.83
24.41
22.02
18.30
-4.25
OTBS
H
HO
O
O
14'
13C NMR
(CDCl3, 100 MHz)
f1 (ppm)


7.26
7.18
7.16
6.72
6.70
5.29
5.02
4.74
4.55
4.54
4.13
4.09
4.07
4.03
4.00
3.98
3.97
3.96
3.77
3.75
3.73
2.90
2.89
2.87
2.85
2.52
2.02
2.01
1.99
1.90
1.89
1.87
1.84
1.35
1.11
1.07
1.06
1.05
1.03
OH
TIPSO
H
O
O
OTIPS
7
1H NMR
(CDCl3, 400 MHz)
2.01
2.01
1.01
1.00
0.90
1.01
2.08
1.01
1.00
1.00
2.00
1.09
2.07
3.04
3.03
42.02
f1 (ppm)

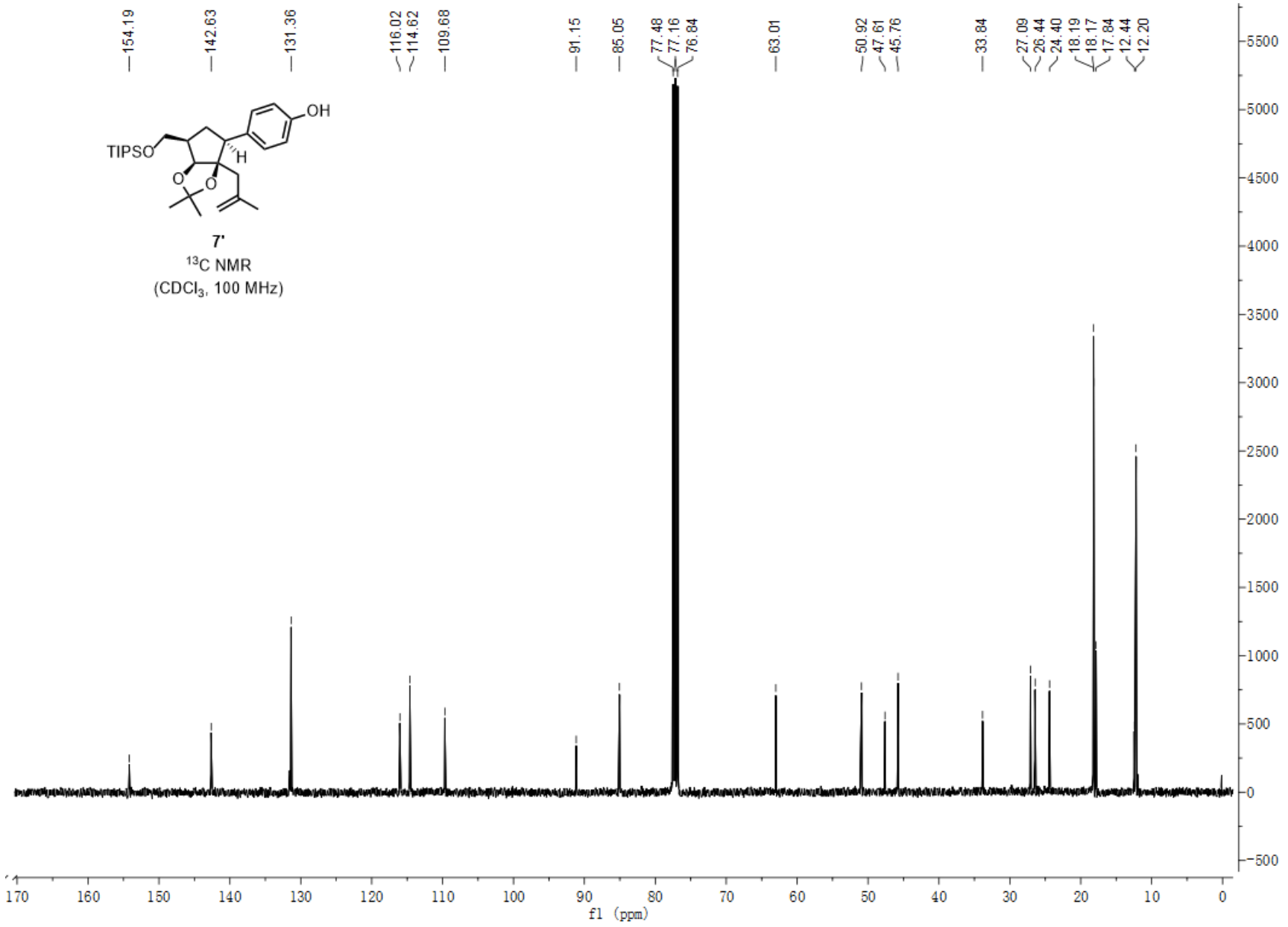

154.23
145.19
131.49
131.28
114.69
114.09
109.68
91.11
85.01
77.48
77.16
76.84
66.77
63.03
51.05
45.90
42.51
33.86
27.09
26.52
18.19
18.15
12.19
12.14
OH
TIPSO
H
O
O
OTIPS
7
13C NMR
(CDCl3, 100 MHz)
f1 (ppm)

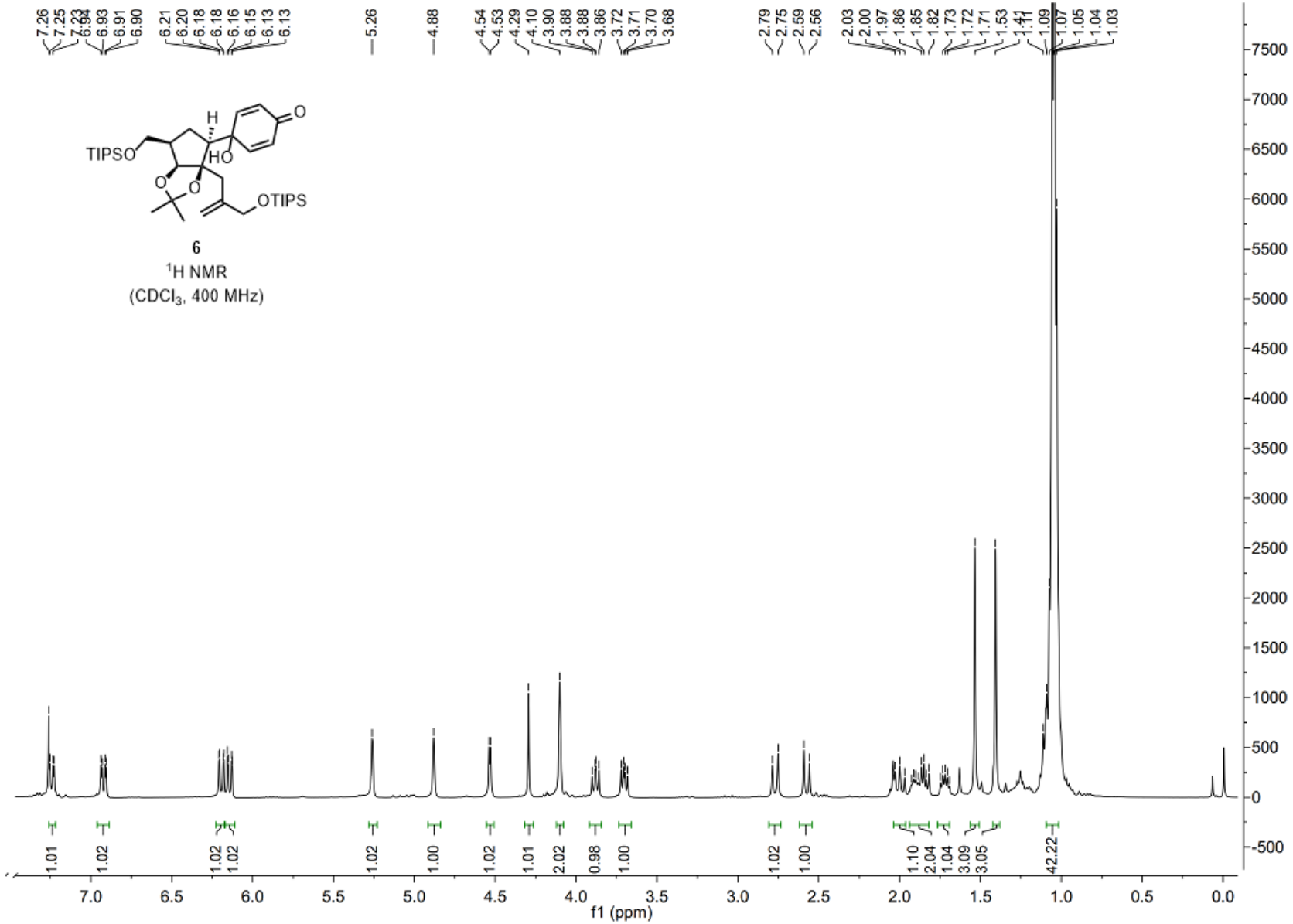


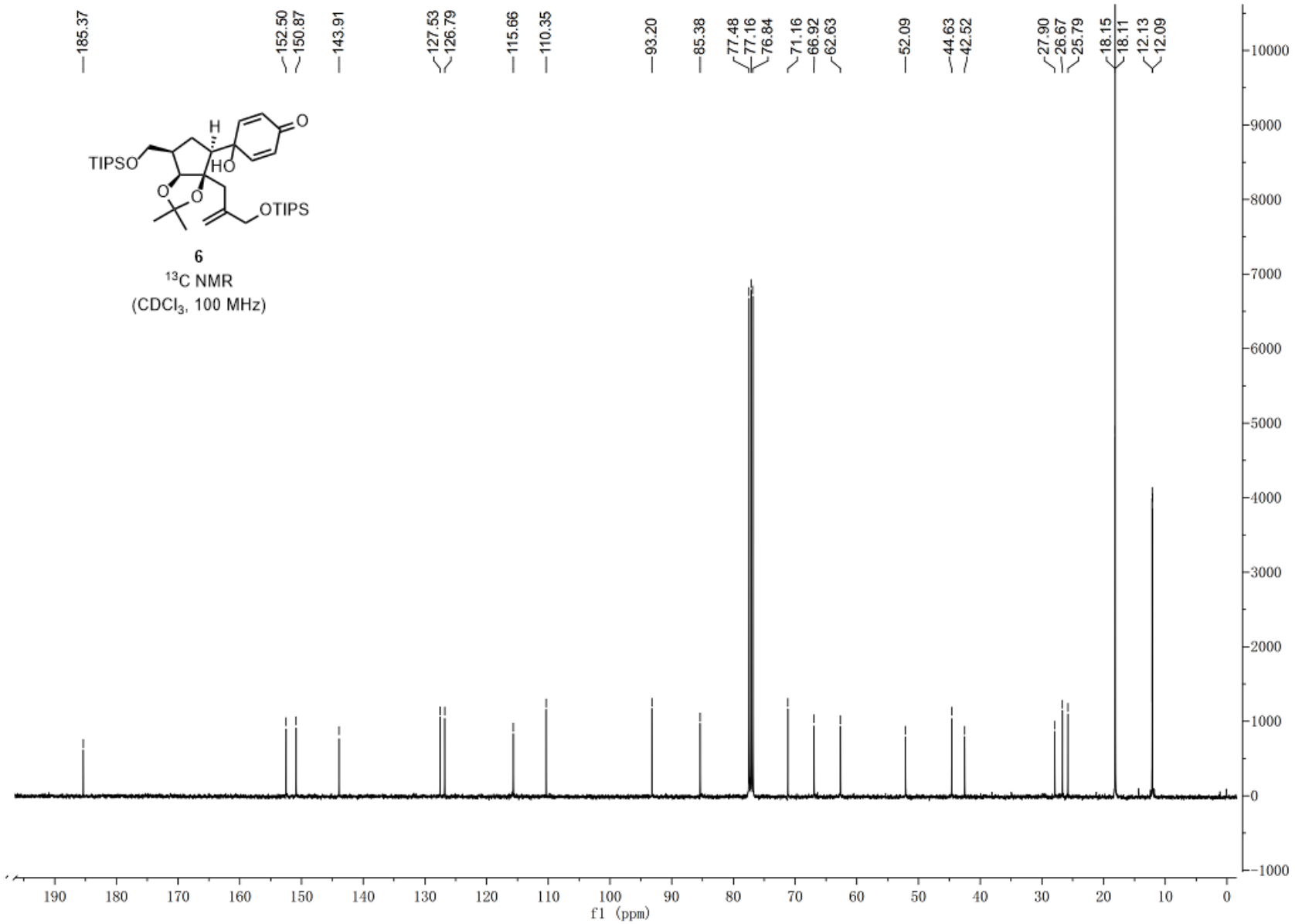
7'

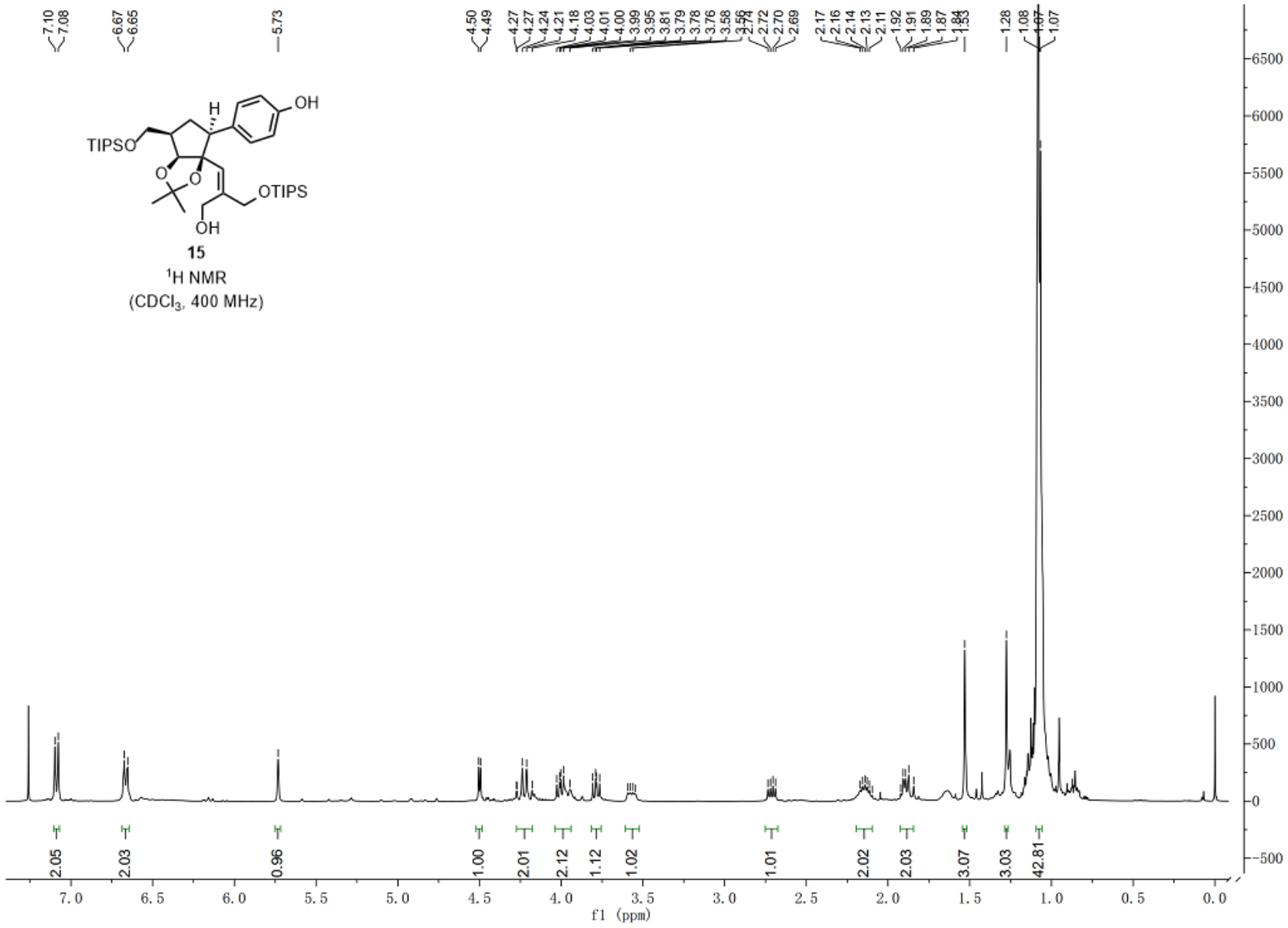
^{1}H NMR

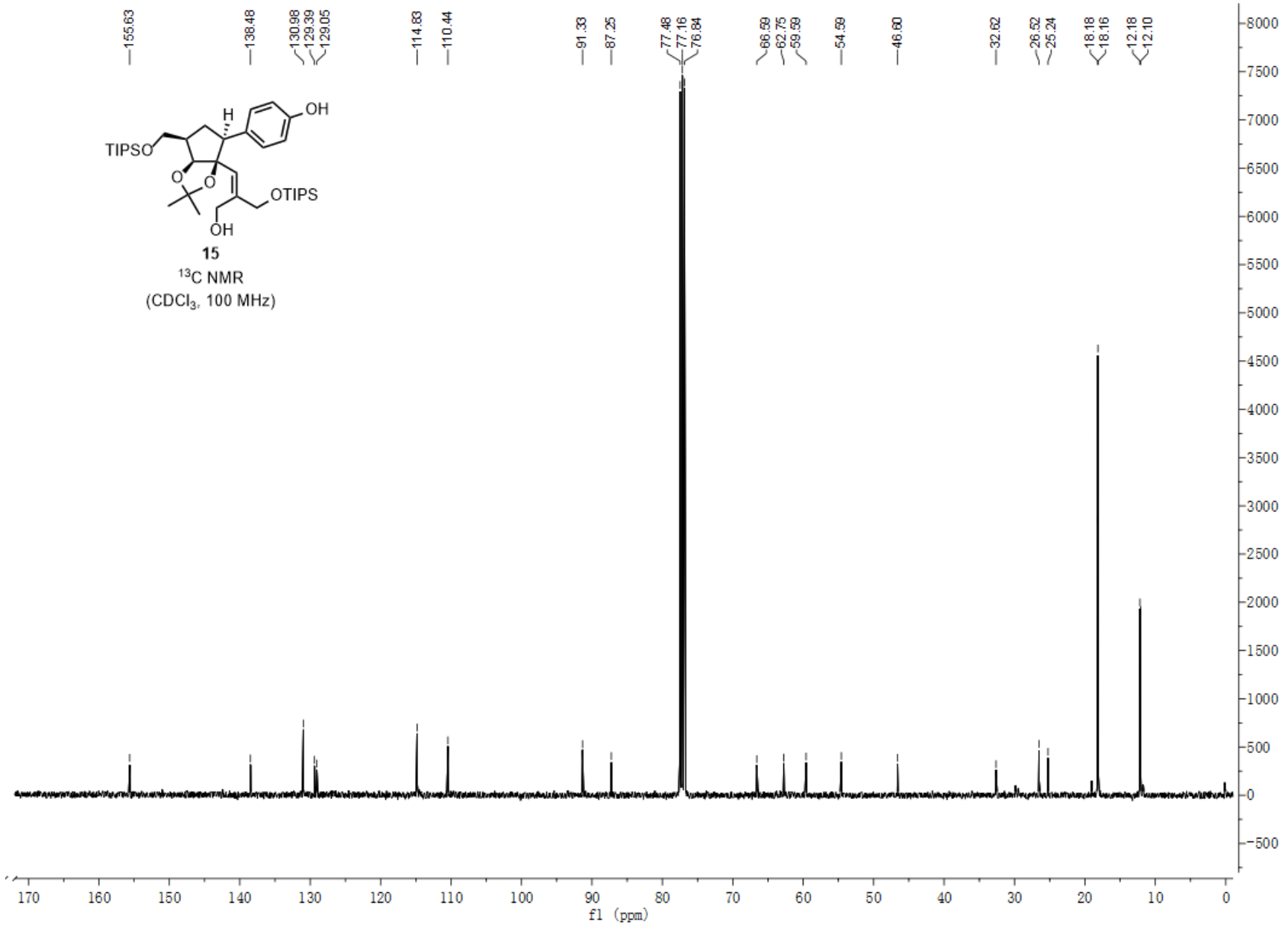
($CDCl_3$, 400 MHz)

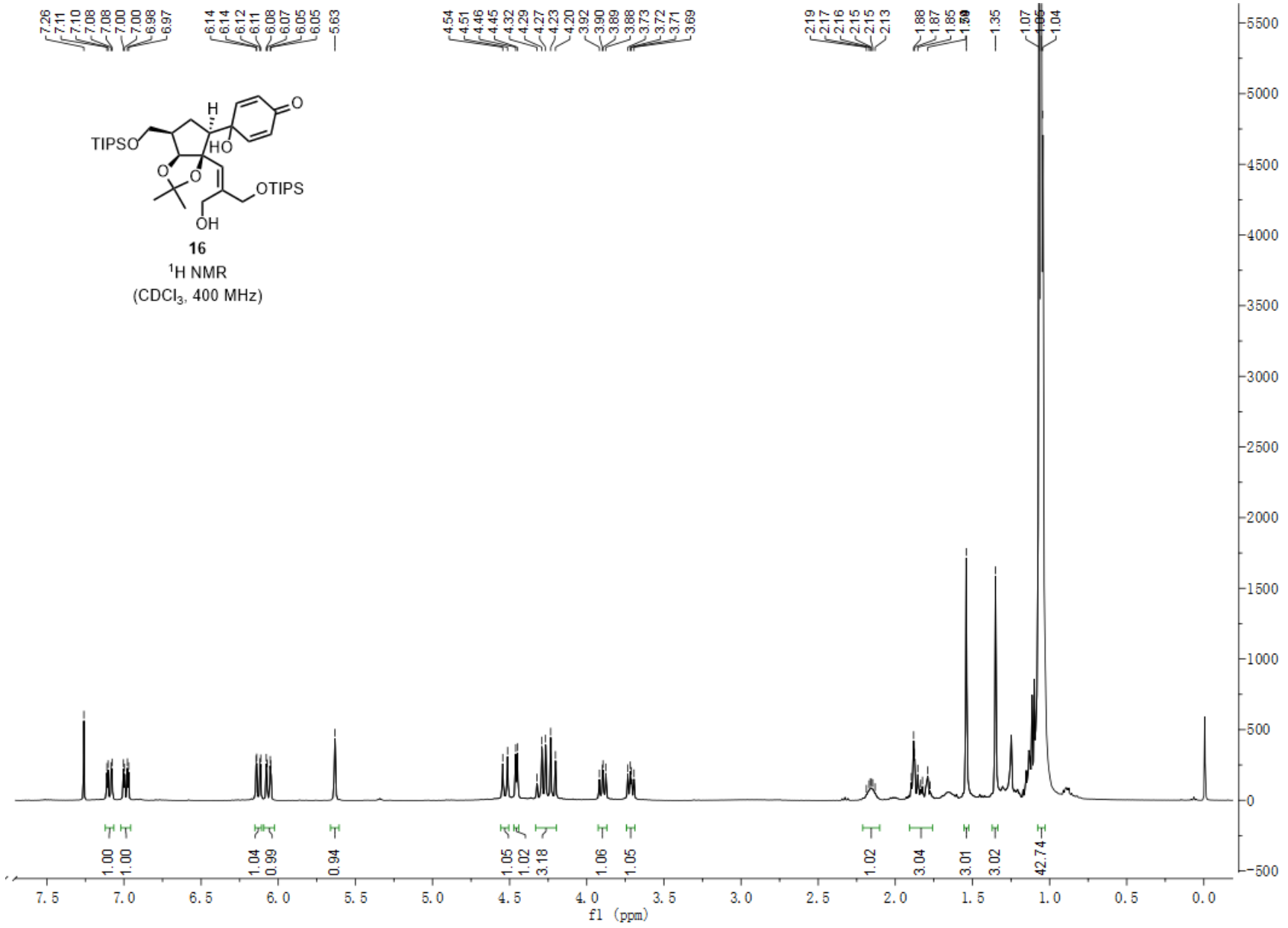

154.19
142.63
131.36
116.02
114.62
109.68
91.15
85.05
77.48
77.16
76.84
63.01
50.92
47.61
45.76
33.84
27.09
26.44
24.40
18.19
18.17
17.84
12.44
12.20
OH
TIPSO
H
O
O
7'
13C NMR
(CDCl3, 100 MHz)
f1 (ppm)

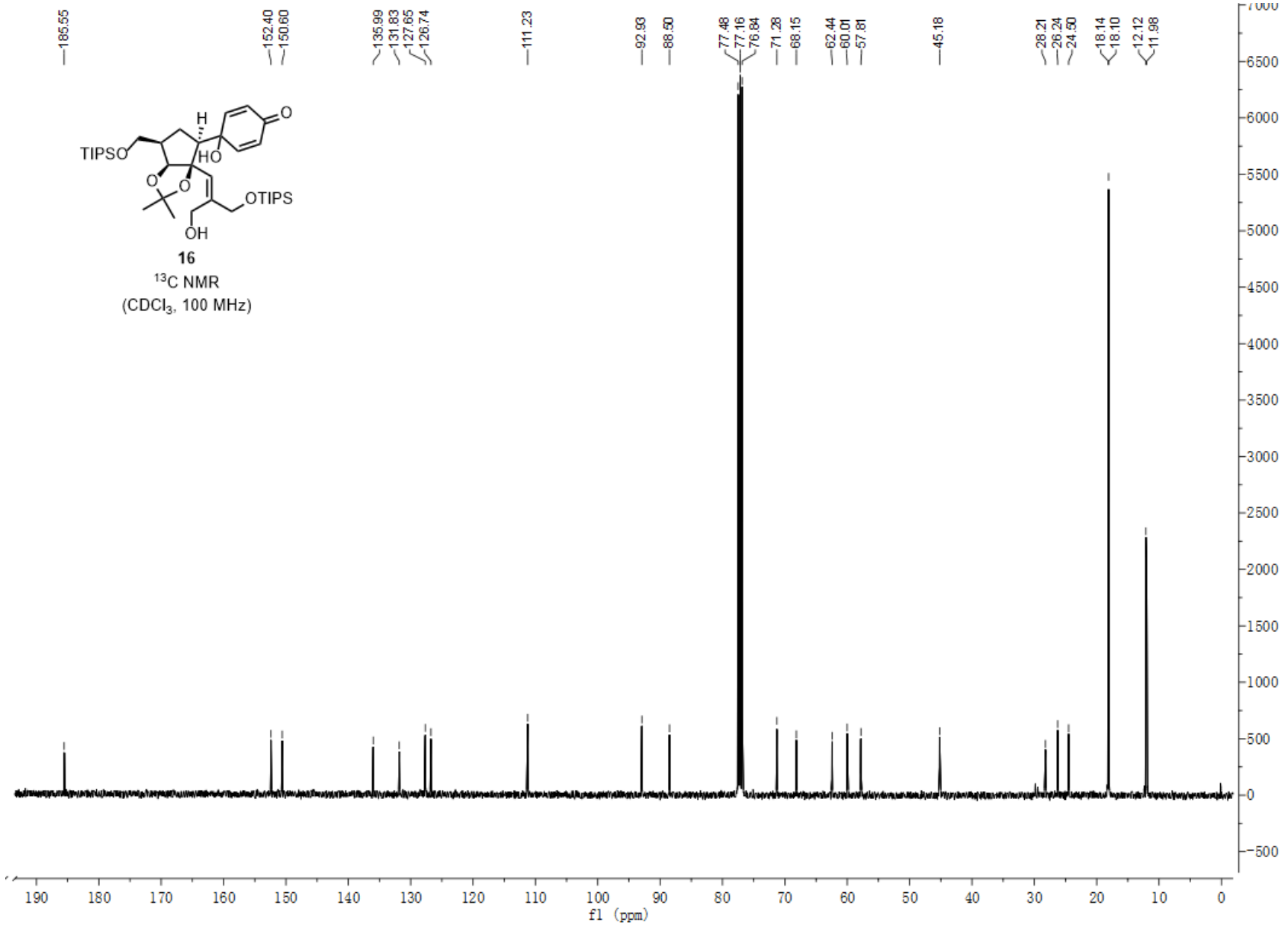

7.26
7.25
7.23
6.94
6.93
6.91
6.90
6.21
6.20
6.18
6.18
6.16
6.15
6.13
6.13
5.26
4.88
4.54
4.53
4.29
4.10
3.90
3.88
3.88
3.86
3.72
3.71
3.70
3.68
2.79
2.75
2.59
2.56
2.03
2.00
1.97
1.86
1.85
1.82
1.73
1.72
1.71
1.53
1.41
1.11
1.09
1.07
1.05
1.04
1.03
TIPSO
H
HO
O
O
O
OTIPS
6
1H NMR
(CDCl3, 400 MHz)
1.01
1.02
1.02
1.02
1.02
1.00
1.02
1.01
2.02
0.98
1.00
1.02
1.00
1.10
2.04
1.04
3.09
3.05
42.22
f1 (ppm)

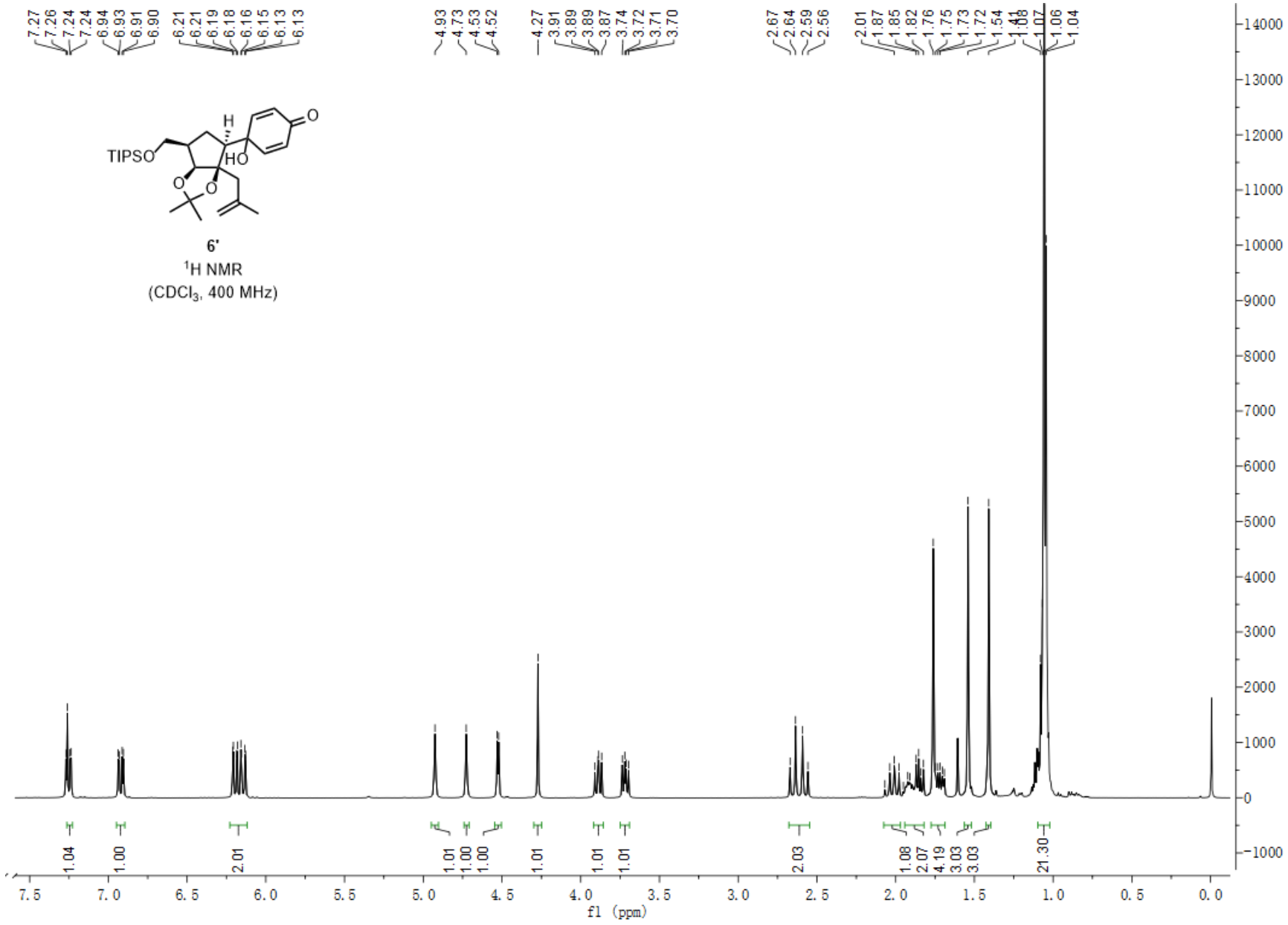

185.37
152.50
150.87
143.91
127.53
126.79
115.66
110.35
93.20
85.38
77.48
77.16
76.84
71.16
66.92
62.63
52.09
44.63
42.52
27.90
26.67
25.79
18.15
18.11
12.13
12.09
TIPSO
H
HO
O
O
O
OTIPS
6
13C NMR
(CDCl3, 100 MHz)
f1 (ppm)

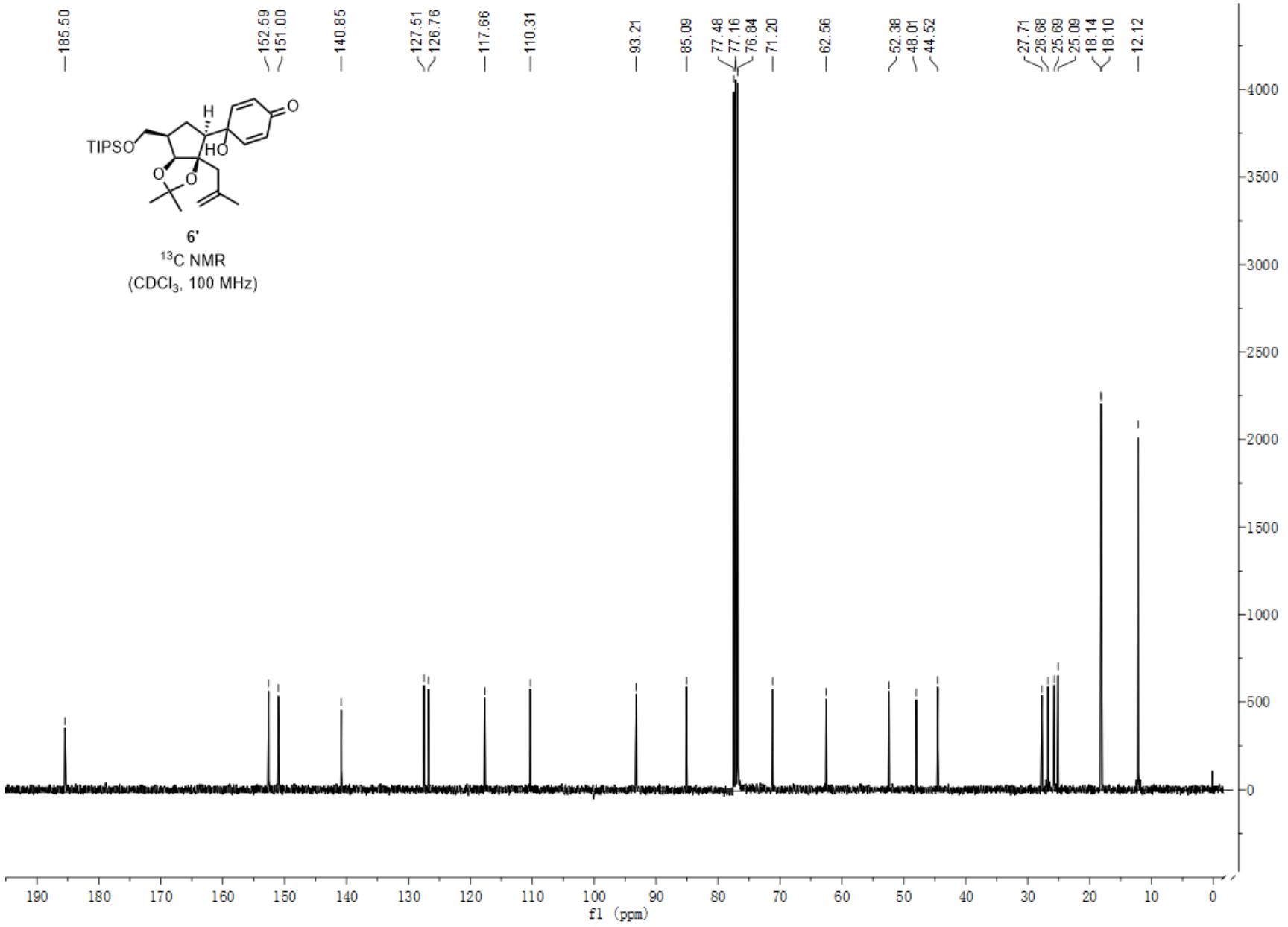

7.10
7.08
6.67
6.65
5.73
4.50
4.49
4.27
4.27
4.24
4.21
4.18
4.03
4.01
4.00
3.99
3.95
3.81
3.79
3.78
3.76
3.58
2.72
2.70
2.69
2.17
2.16
2.14
2.13
2.11
1.92
1.91
1.89
1.87
1.28
1.08
1.07
OH
H
TIPSO
O
O
OTIPS
OH
15
1H NMR
(CDCl3, 400 MHz)
2.05
2.03
0.96
1.00
2.01
2.12
1.12
1.02
1.01
2.02
2.03
3.07
3.03
42.81
f1 (ppm)

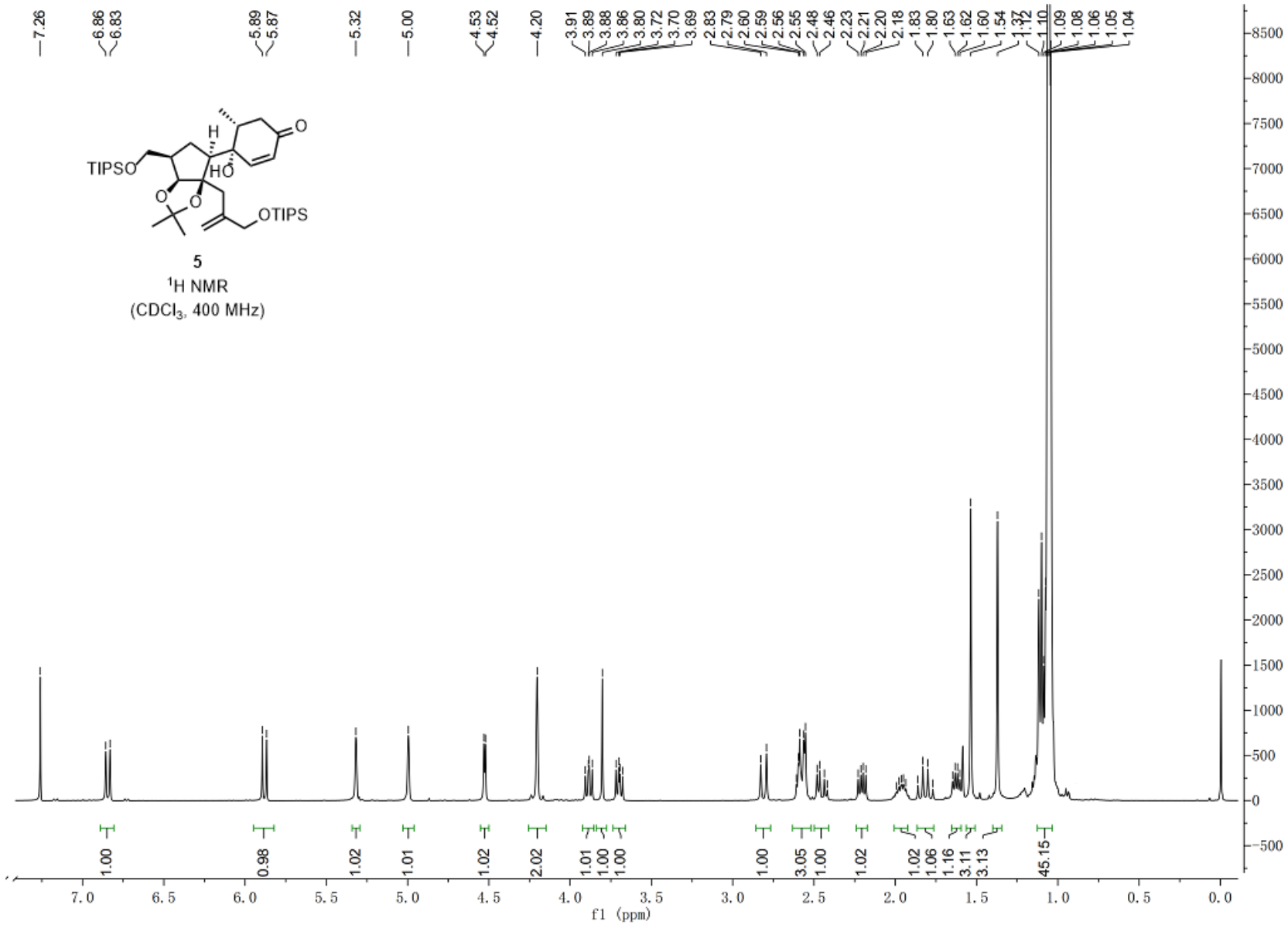

155.63
138.48
130.98
129.39
129.05
114.83
110.44
91.33
87.25
77.48
77.16
76.84
66.59
62.75
59.59
54.59
46.60
32.62
26.52
25.24
18.18
18.16
12.18
12.10
TIPSO
H
OH
O
O
OTIPS
OH
15
13C NMR
(CDCl3, 100 MHz)
f1 (ppm)

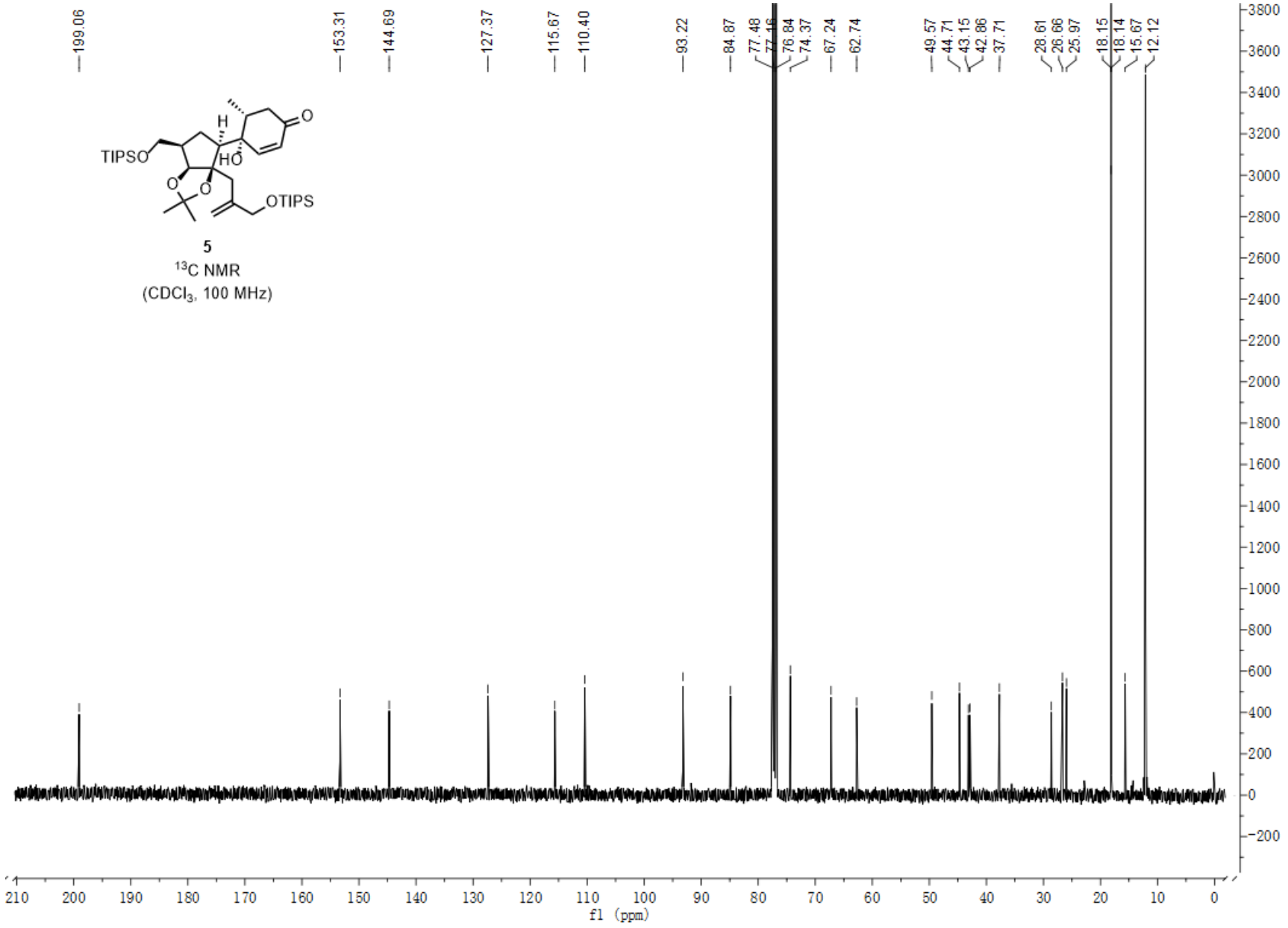

7.26
7.11
7.10
7.08
7.08
7.00
7.00
6.98
6.97
6.14
6.14
6.12
6.11
6.08
6.07
6.05
6.05
5.63
4.54
4.51
4.46
4.45
4.32
4.29
4.27
4.23
4.20
3.92
3.90
3.89
3.88
3.73
3.72
3.71
3.69
2.19
2.17
2.16
2.15
2.15
2.13
1.88
1.87
1.85
1.35
1.07
1.04
TIPSO
H
HO
O
O
O
OTIPS
OH
16
1H NMR
(CDCl3, 400 MHz)
1.00
1.00
1.04
0.99
0.94
1.05
1.02
3.18
1.06
1.05
1.02
3.04
3.01
3.02
42.74
f1 (ppm)


185.55
152.40
150.60
135.99
131.83
127.65
126.74
111.23
92.93
88.50
77.48
77.16
76.84
71.28
68.15
62.44
60.01
57.81
45.18
28.21
26.24
24.50
18.14
18.10
12.12
11.98
TIPSO
H
HO
O
O
O
OTIPS
OH
16
13C NMR
(CDCl3, 100 MHz)
f1 (ppm)


7.27
7.26
7.24
7.24
6.94
6.93
6.91
6.90
6.21
6.21
6.19
6.18
6.16
6.15
6.13
6.13
4.93
4.73
4.53
4.52
4.27
3.91
3.89
3.89
3.87
3.74
3.72
3.71
3.70
2.67
2.64
2.59
2.56
2.01
1.87
1.85
1.82
1.76
1.75
1.73
1.72
1.54
1.41
1.08
1.07
1.06
1.04
TIPSO
H
HO
O
O
O
6'
1H NMR
(CDCl3, 400 MHz)
1.04
1.00
2.01
1.01
1.00
1.00
1.01
1.01
1.01
2.03
1.08
2.07
4.19
3.03
3.03
21.30
f1 (ppm)


185.50
152.59
151.00
140.85
127.51
126.76
117.66
110.31
93.21
85.09
77.48
77.16
76.84
71.20
62.56
52.38
48.01
44.52
27.71
26.68
25.69
25.09
18.14
18.10
12.12
TIPSO
H
HO
O
O
O
6'
13C NMR
(CDCl3, 100 MHz)
4000
3500
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

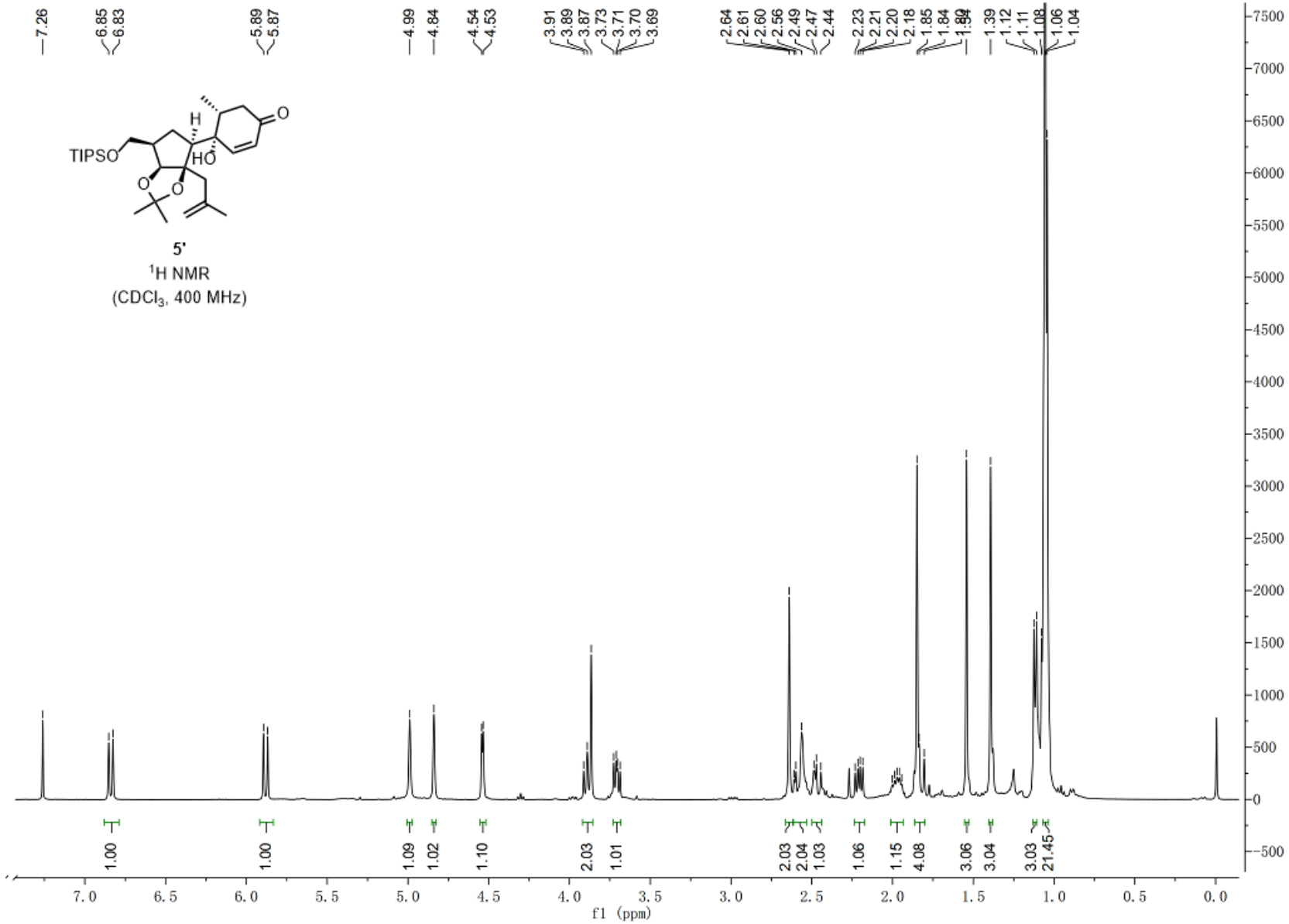

7.26
6.86
6.83
5.89
5.87
5.32
5.00
4.53
4.52
4.20
3.91
3.89
3.88
3.86
3.80
3.72
3.70
3.69
2.83
2.79
2.60
2.59
2.56
2.55
2.48
2.46
2.23
2.21
2.20
2.18
1.83
1.80
1.63
1.62
1.60
1.54
1.37
1.12
1.10
1.09
1.08
1.06
1.05
1.04
TIPSO
H
HO
O
O
O
OTIPS
5
1H NMR
(CDCl3, 400 MHz)
1.00
0.98
1.02
1.01
1.02
2.02
1.01
1.00
1.00
1.00
3.05
1.00
1.02
1.02
1.06
1.16
3.11
3.13
45.15
f1 (ppm)

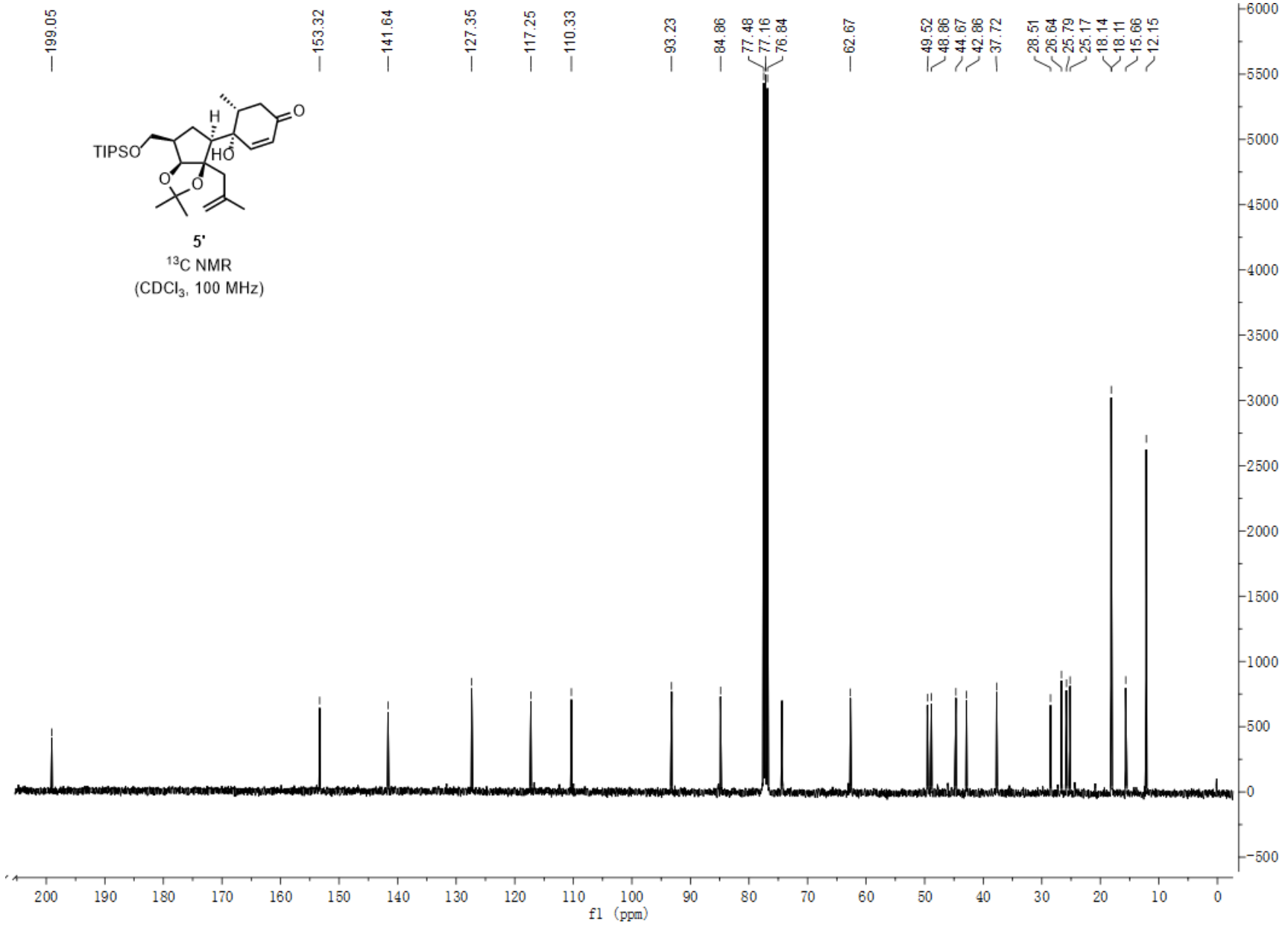


5

^{13}C NMR

($CDCl_3$, 100 MHz)


7.26
6.85
6.83
5.89
5.87
4.99
4.84
4.54
4.53
3.91
3.89
3.87
3.73
3.71
3.70
3.69
2.64
2.61
2.60
2.56
2.49
2.47
2.44
2.23
2.21
2.20
2.18
1.85
1.84
1.39
1.12
1.11
1.08
1.06
1.04
TIPSO
H
HO
O
O
O
5'
1H NMR
(CDCl3, 400 MHz)
1.00
1.00
1.09
1.02
1.10
2.03
1.01
2.03
2.04
1.03
1.06
1.15
4.08
3.06
3.04
3.03
21.45
f1 (ppm)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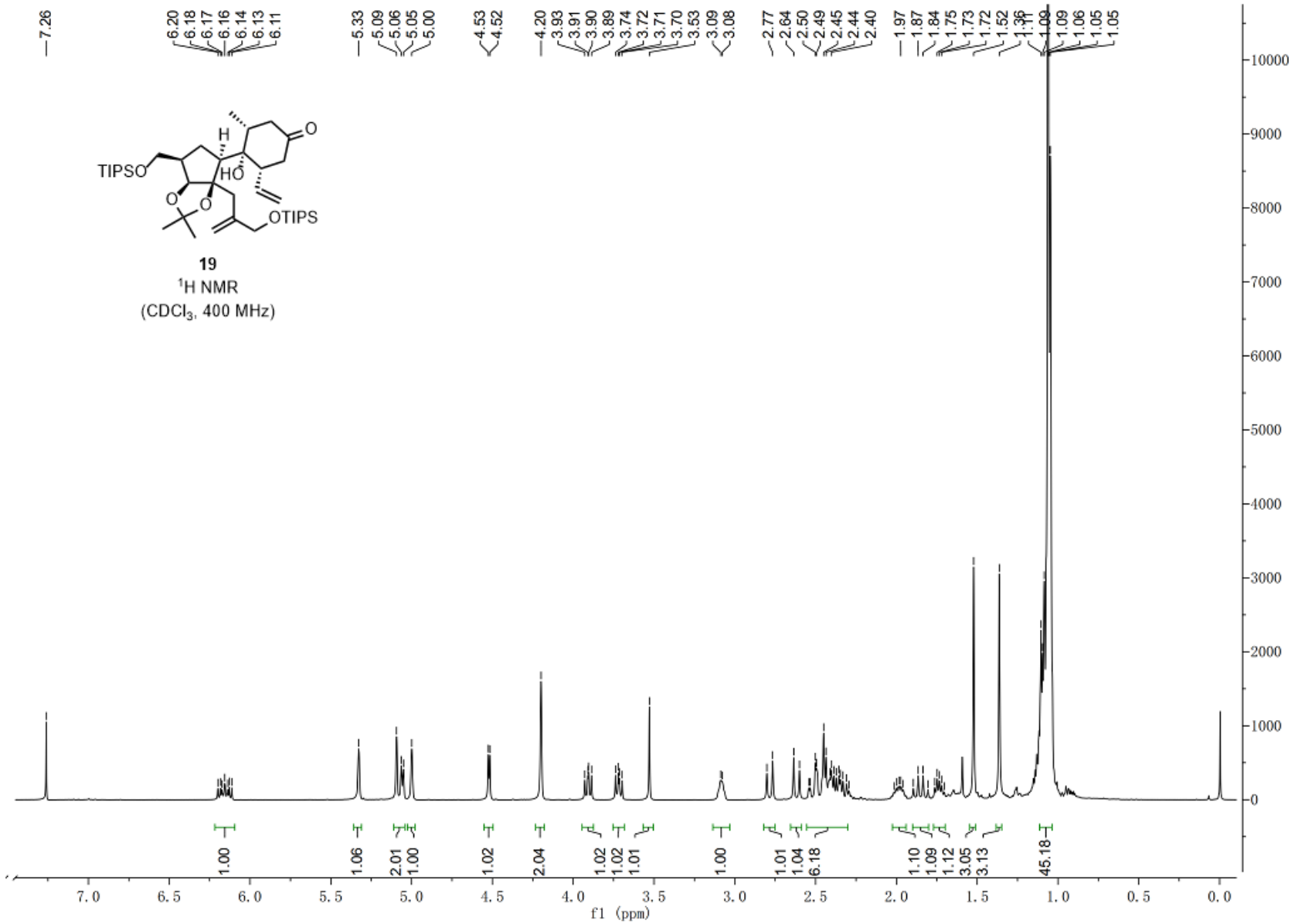
153.32
141.64
127.35
117.25
110.33
93.23
84.86
77.48
77.16
76.84
62.67
49.52
48.86
44.67
42.86
37.72
28.51
26.64
25.79
25.17
18.14
18.11
15.66
12.15
TIPSO
H
HO
O
O
O
5'
13C NMR
(CDCl3, 100 MHz)
f1 (ppm)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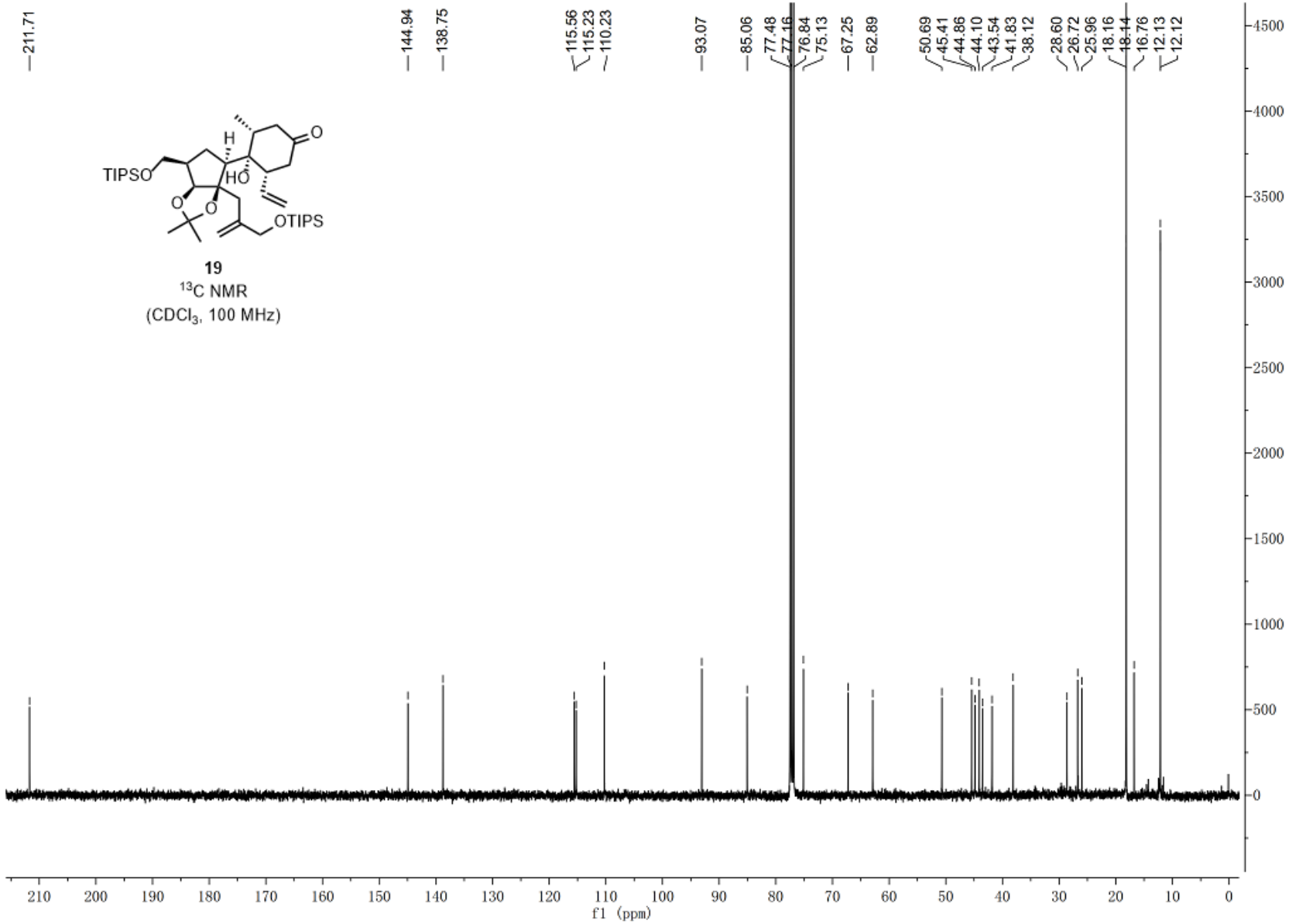
6.20
6.18
6.17
6.16
6.14
6.13
6.11
5.33
5.09
5.06
5.05
5.00
4.53
4.52
4.20
3.93
3.91
3.90
3.89
3.74
3.72
3.71
3.70
3.53
3.09
3.08
2.77
2.64
2.50
2.49
2.45
2.44
2.40
1.97
1.87
1.84
1.75
1.73
1.72
1.52
1.36
1.11
1.09
1.09
1.06
1.05
1.05
TIPSO
H
HO
O
O
O
OTIPS
19
1H NMR
(CDCl3, 400 MHz)
1.00
1.06
2.01
1.00
1.02
2.04
1.02
1.02
1.01
1.00
1.01
1.04
6.18
1.10
1.09
1.12
3.05
3.13
45.18
f1 (ppm)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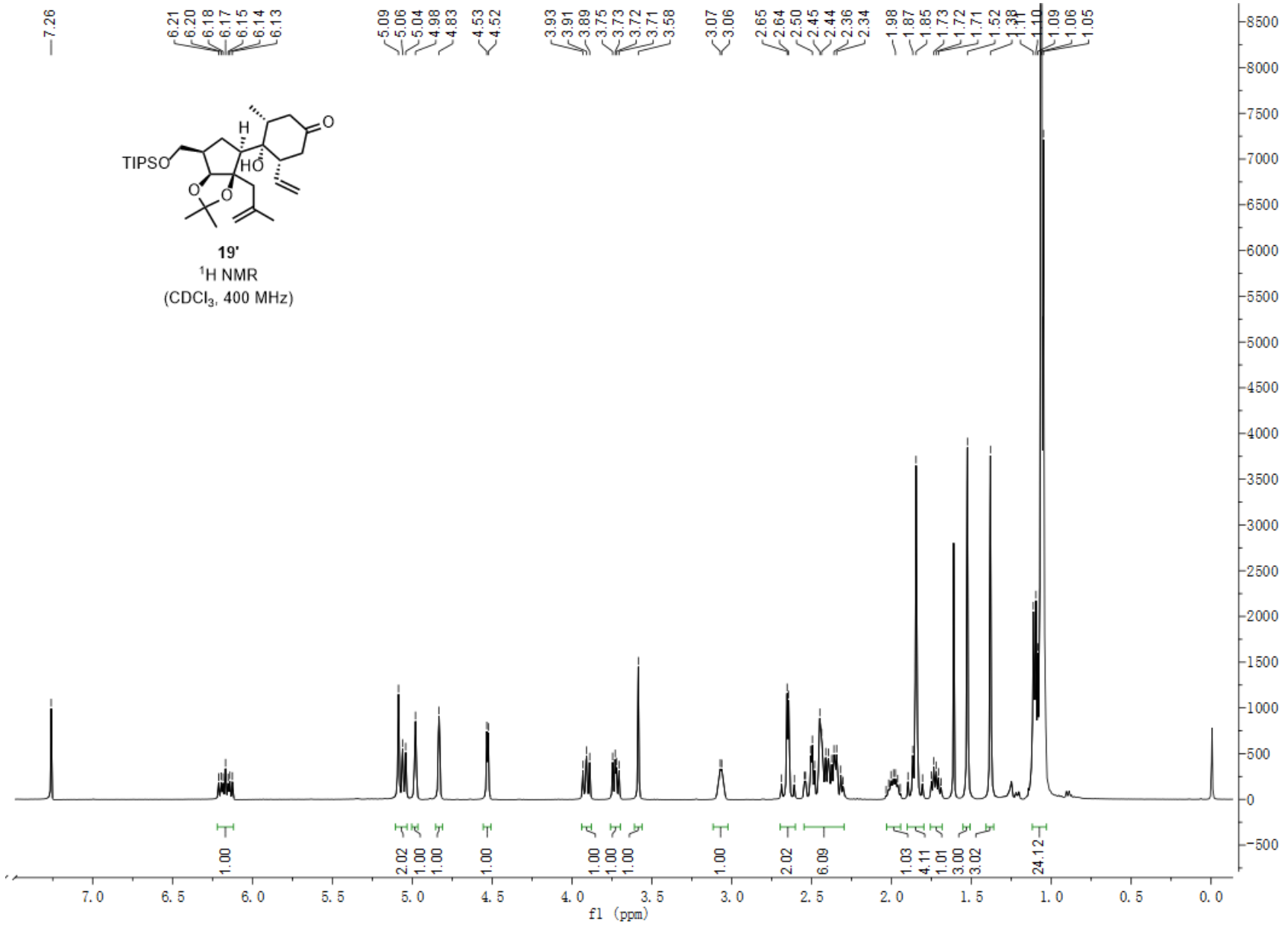
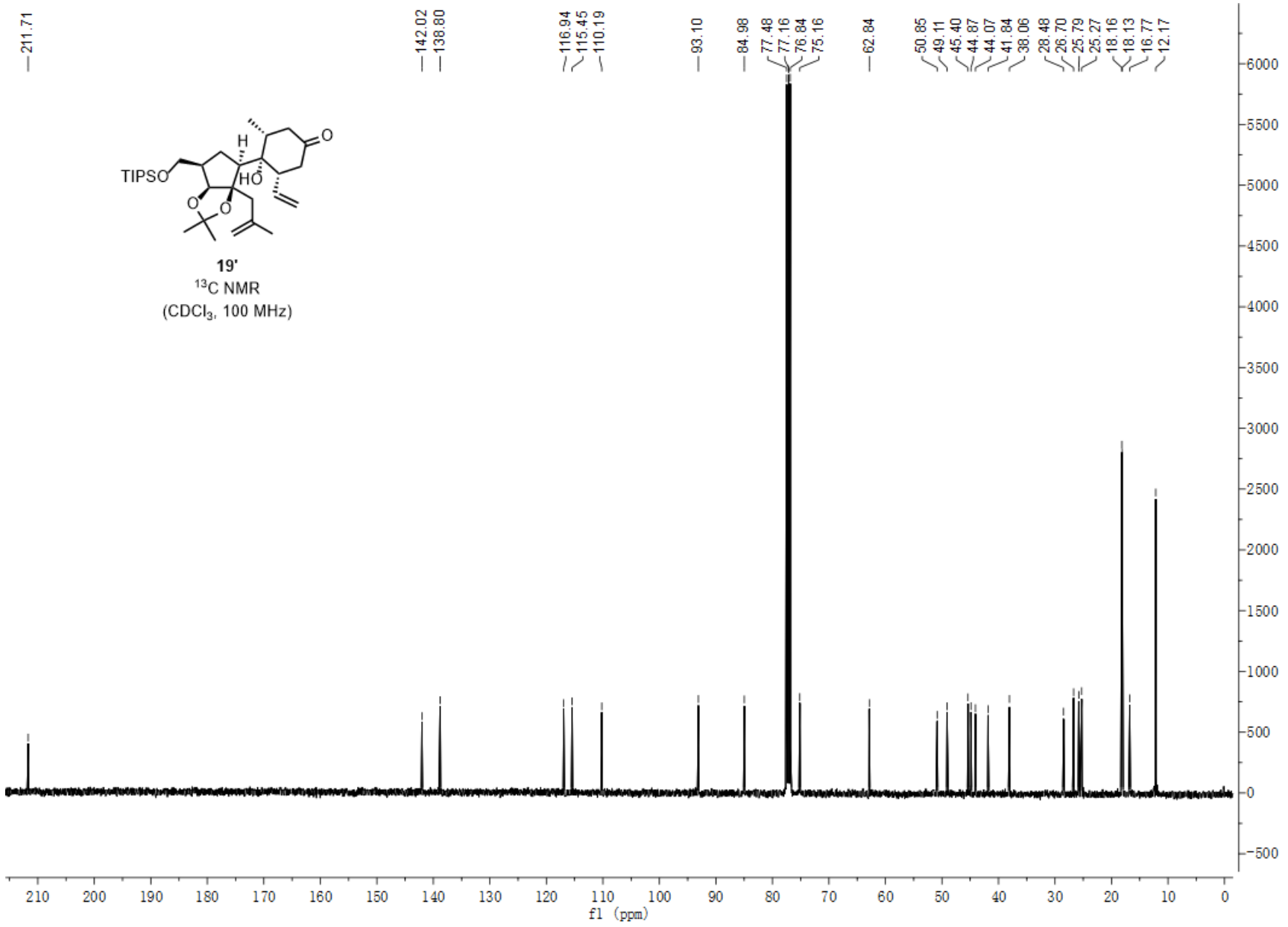
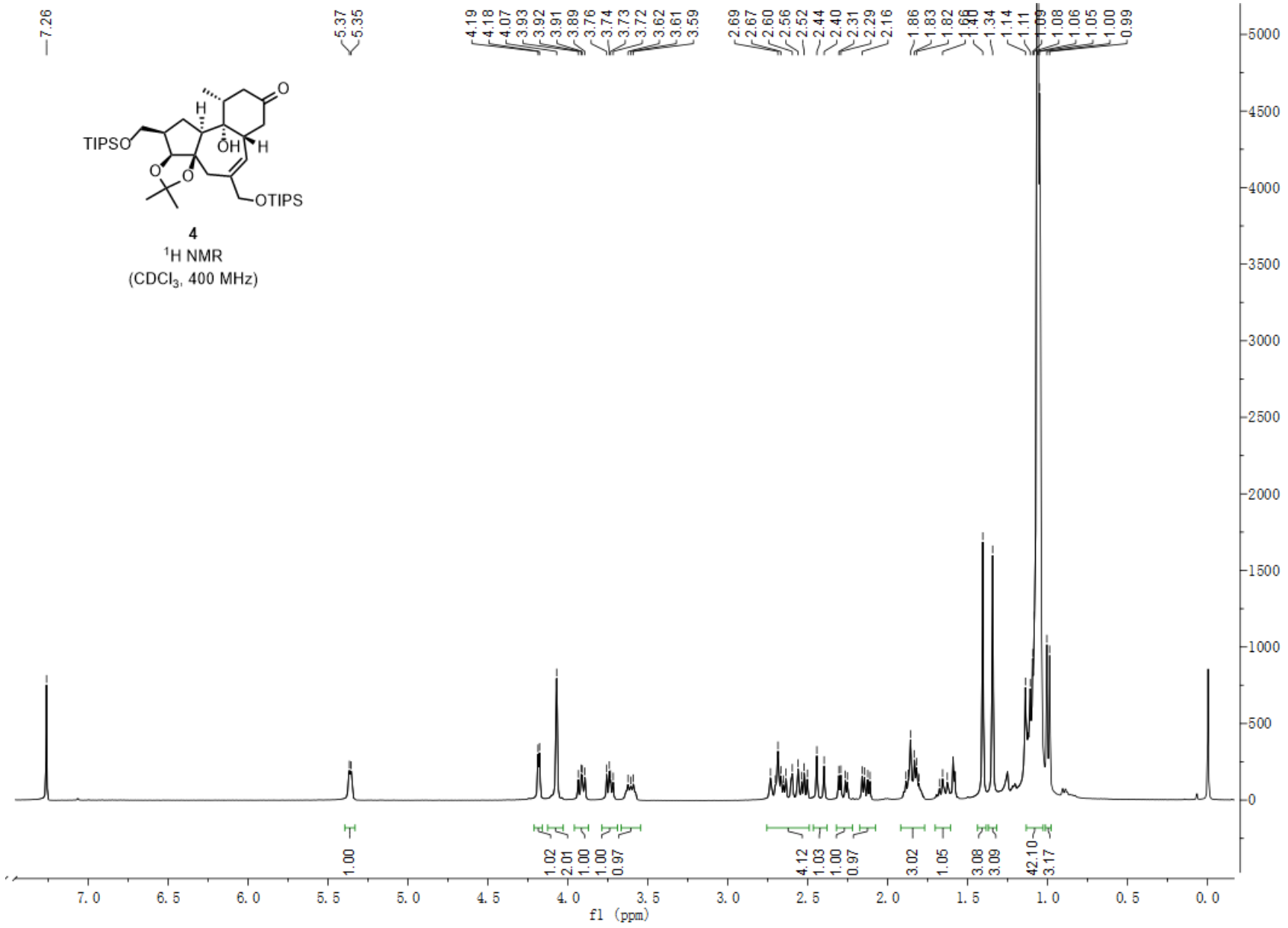
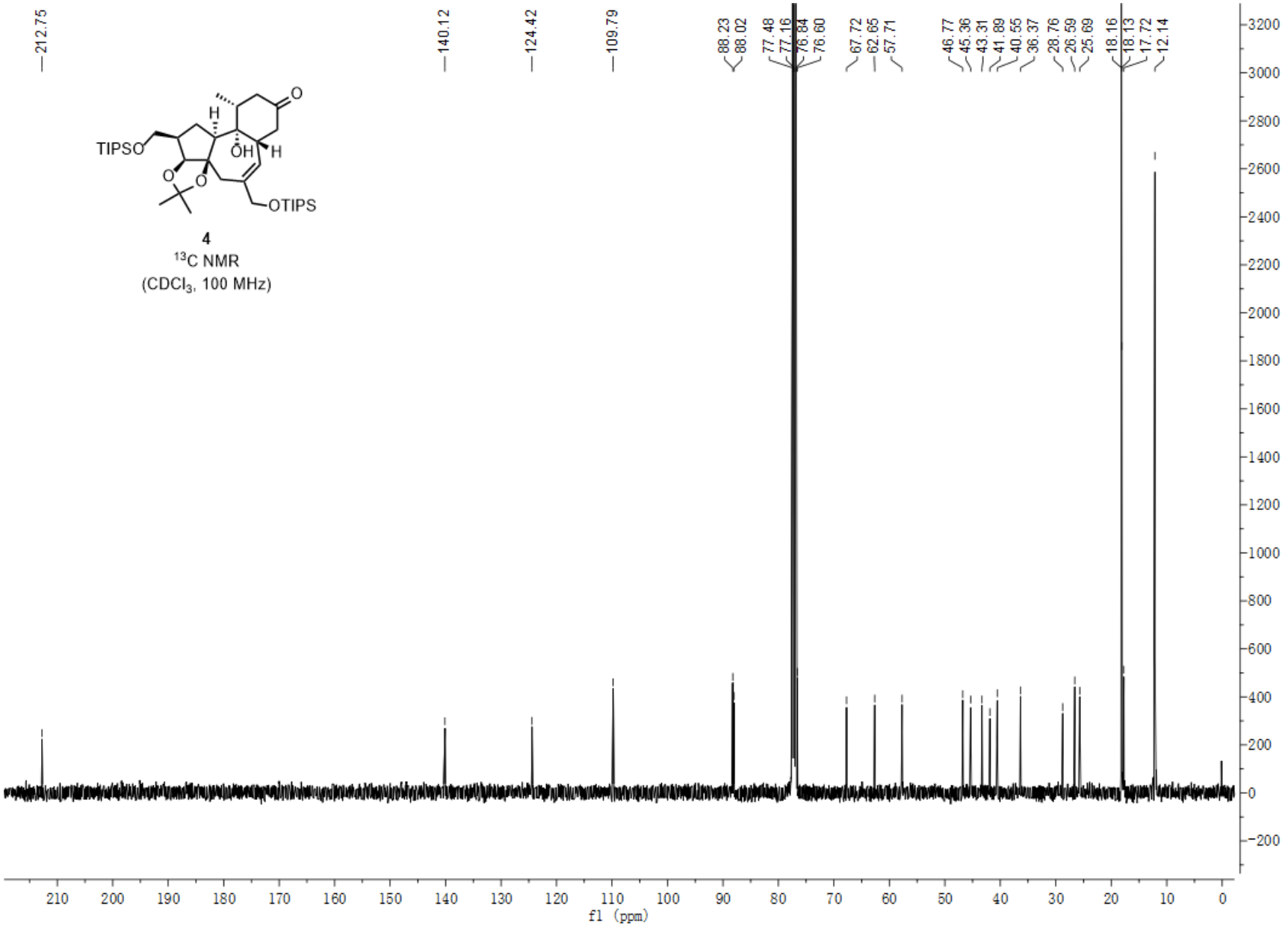
144.94
138.75
115.56
115.23
110.23
93.07
85.06
77.48
77.16
76.84
75.13
67.25
62.89
50.69
45.41
44.86
44.10
43.54
41.83
38.12
28.60
26.72
25.96
18.16
18.14
16.76
12.13
12.12
TIPSO
H
HO
O
O
O
OTIPS
19
13C NMR
(CDCl3, 100 MHz)
f1 (ppm)


7.26
6.21
6.20
6.18
6.17
6.15
6.14
6.13
5.09
5.06
5.04
4.98
4.83
4.53
4.52
3.93
3.91
3.89
3.75
3.73
3.72
3.71
3.58
3.07
3.06
2.65
2.64
2.50
2.45
2.44
2.36
2.34
1.98
1.87
1.85
1.73
1.72
1.71
1.52
1.38
1.11
1.10
1.09
1.06
1.05
TIPSO
H
HO
O
O
O
19'
1H NMR
(CDCl3, 400 MHz)
1.00
2.02
1.00
1.00
1.00
1.00
1.00
1.00
2.02
6.09
1.03
4.11
1.01
3.00
3.02
24.12
f1 (ppm)


211.71
142.02
138.80
116.94
115.45
110.19
93.10
84.98
77.48
77.16
76.84
75.16
62.84
50.85
49.11
45.40
44.87
44.07
41.84
38.06
28.48
26.70
25.79
25.27
18.16
18.13
16.77
12.17
TIPSO
H
HO
O
O
O
19'
13C NMR
(CDCl3, 100 MHz)
f1 (ppm)

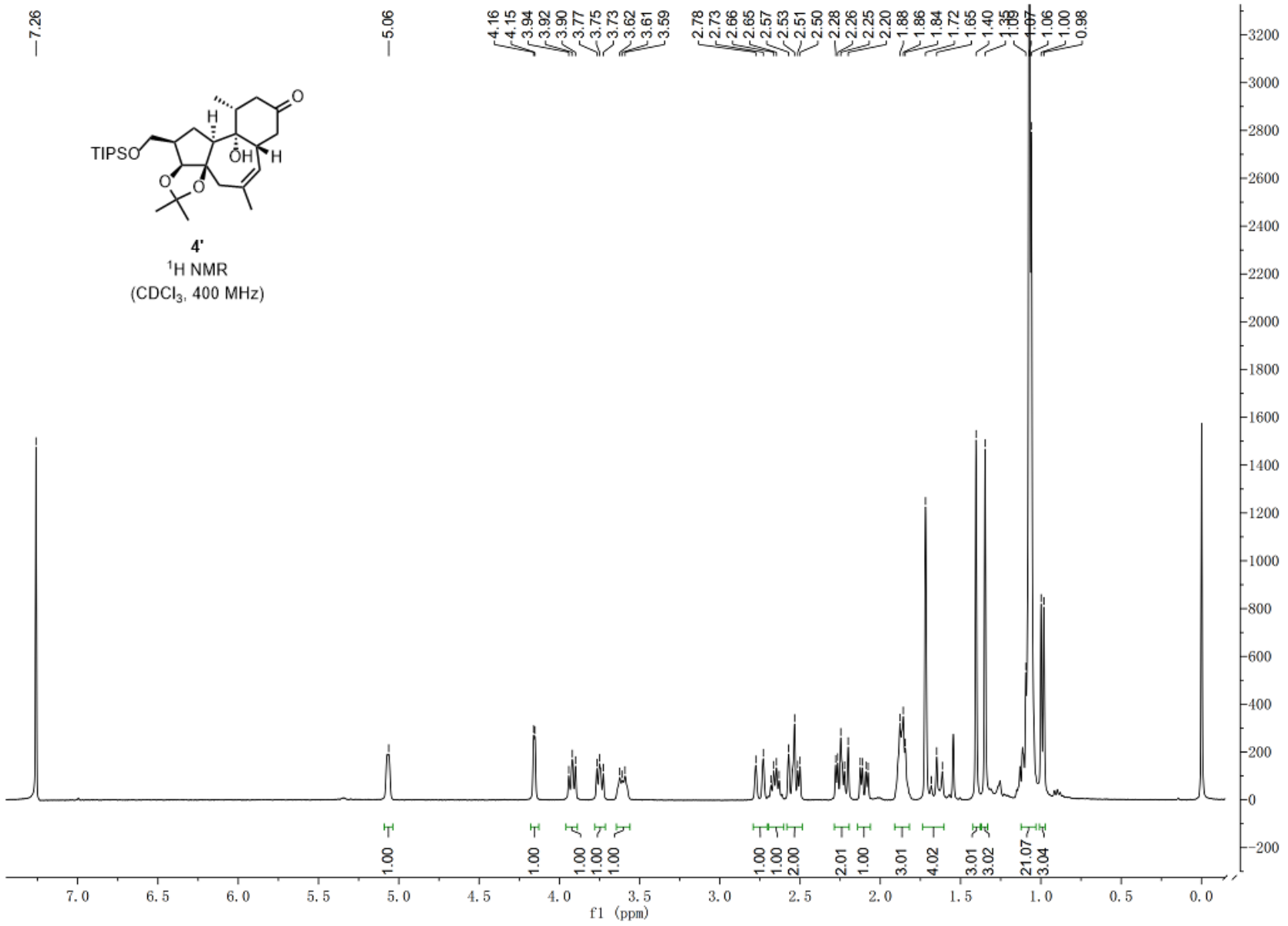

7.26
5.37
5.35
4.19
4.18
4.07
3.93
3.92
3.91
3.89
3.76
3.74
3.73
3.72
3.62
3.61
3.59
2.69
2.67
2.60
2.56
2.52
2.44
2.40
2.31
2.29
2.16
1.86
1.83
1.82
1.34
1.14
1.11
1.09
1.08
1.06
1.05
1.00
0.99
TIPSO
H
OH
H
O
O
O
OTIPS
4
1H NMR
(CDCl3, 400 MHz)
1.00
1.02
2.01
1.00
1.00
0.97
4.12
1.03
1.00
0.97
3.02
1.05
3.08
3.09
42.10
3.17
f1 (ppm)

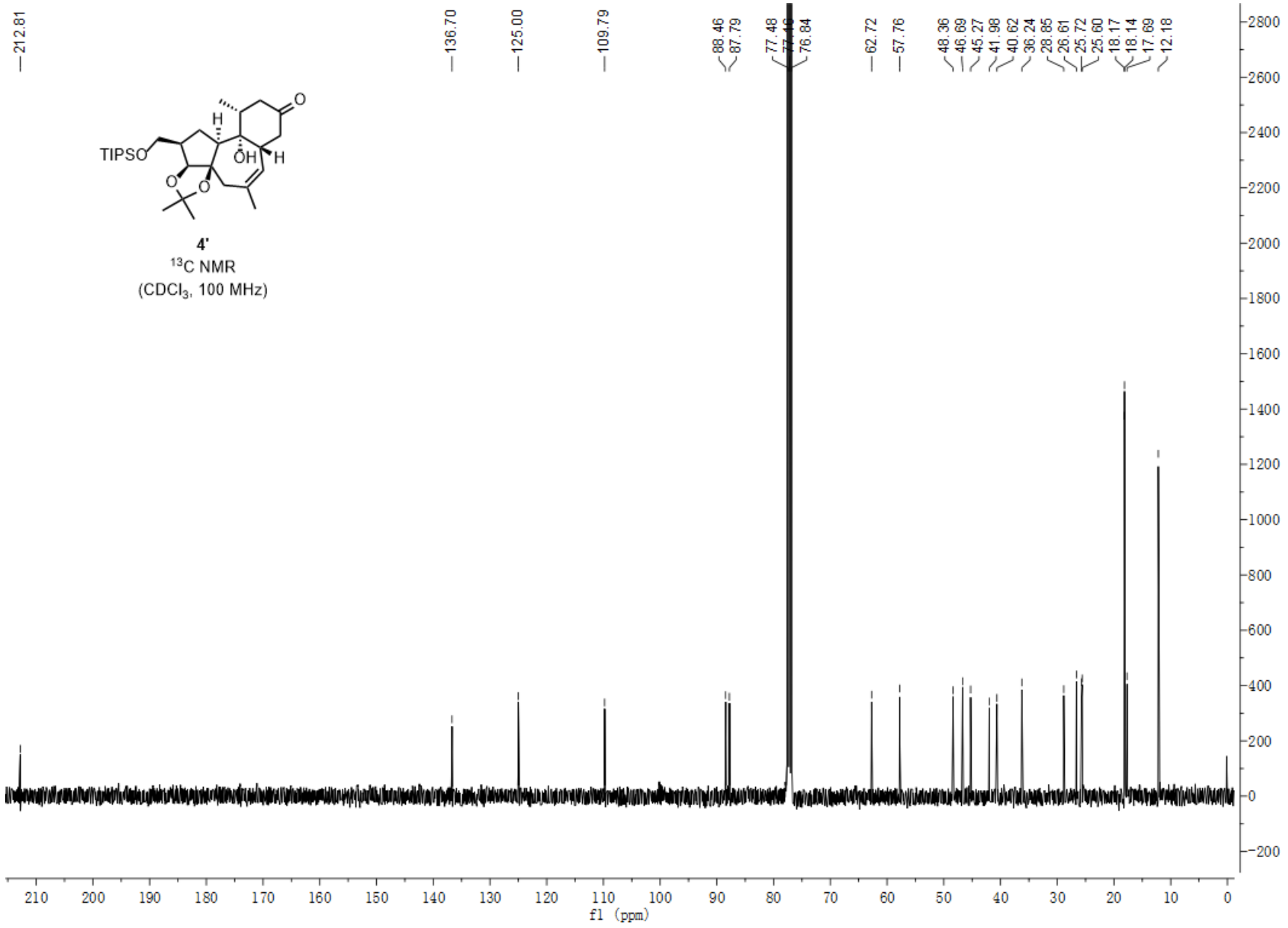


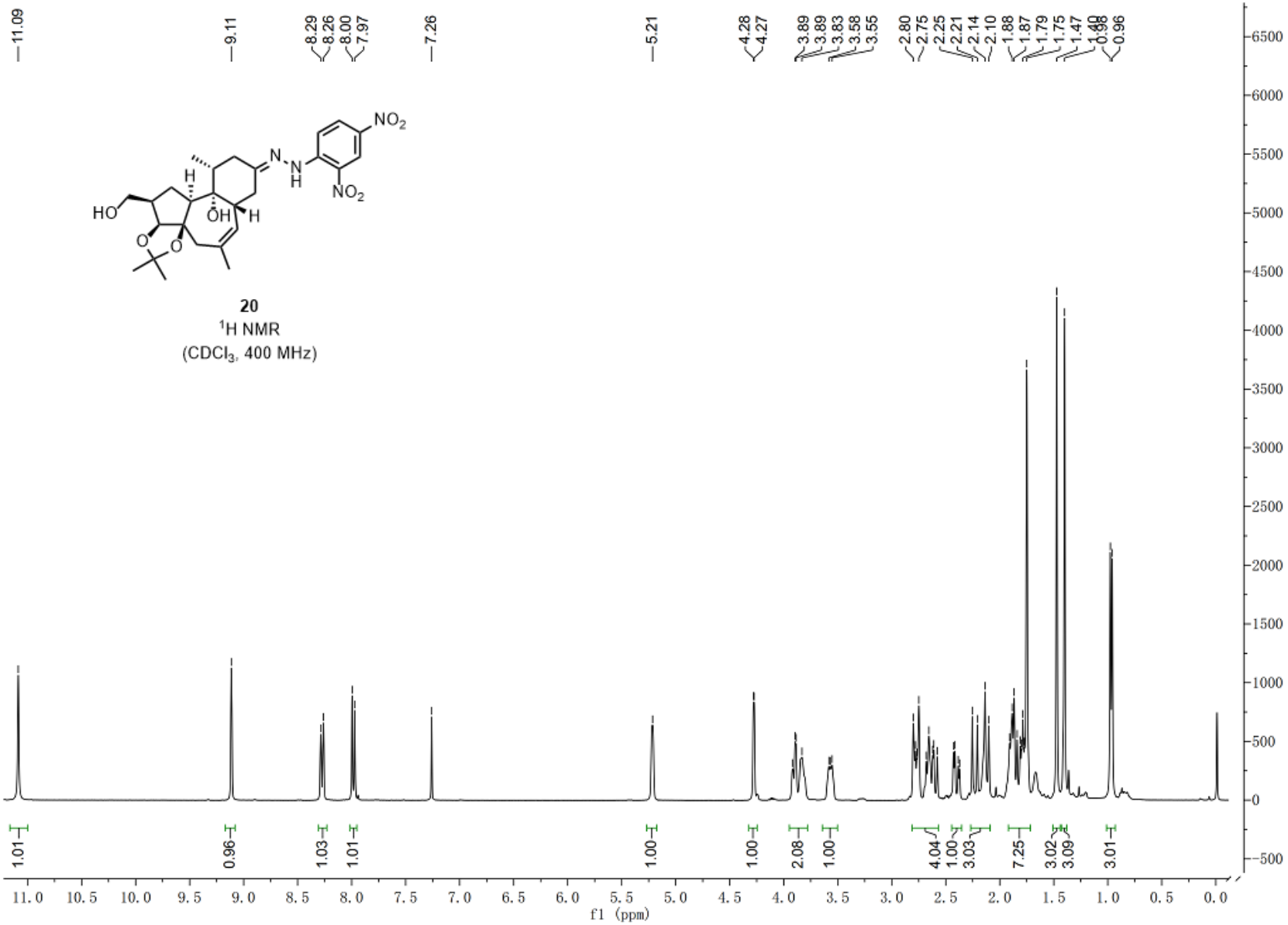
4

^{13}C NMR

($CDCl_3$, 100 MHz)


7.26
5.06
4.16
4.15
3.94
3.92
3.90
3.77
3.75
3.73
3.62
3.61
3.59
2.78
2.73
2.66
2.65
2.57
2.53
2.51
2.50
2.28
2.26
2.25
2.20
1.88
1.86
1.84
1.72
1.65
1.40
1.07
1.06
1.00
0.98
TIPSO
OH
H
O
4'
1H NMR
(CDCl3, 400 MHz)
1.00
1.00
1.00
1.00
1.00
1.00
2.00
2.01
1.00
3.01
4.02
3.01
3.02
21.07
3.04
f1 (ppm)

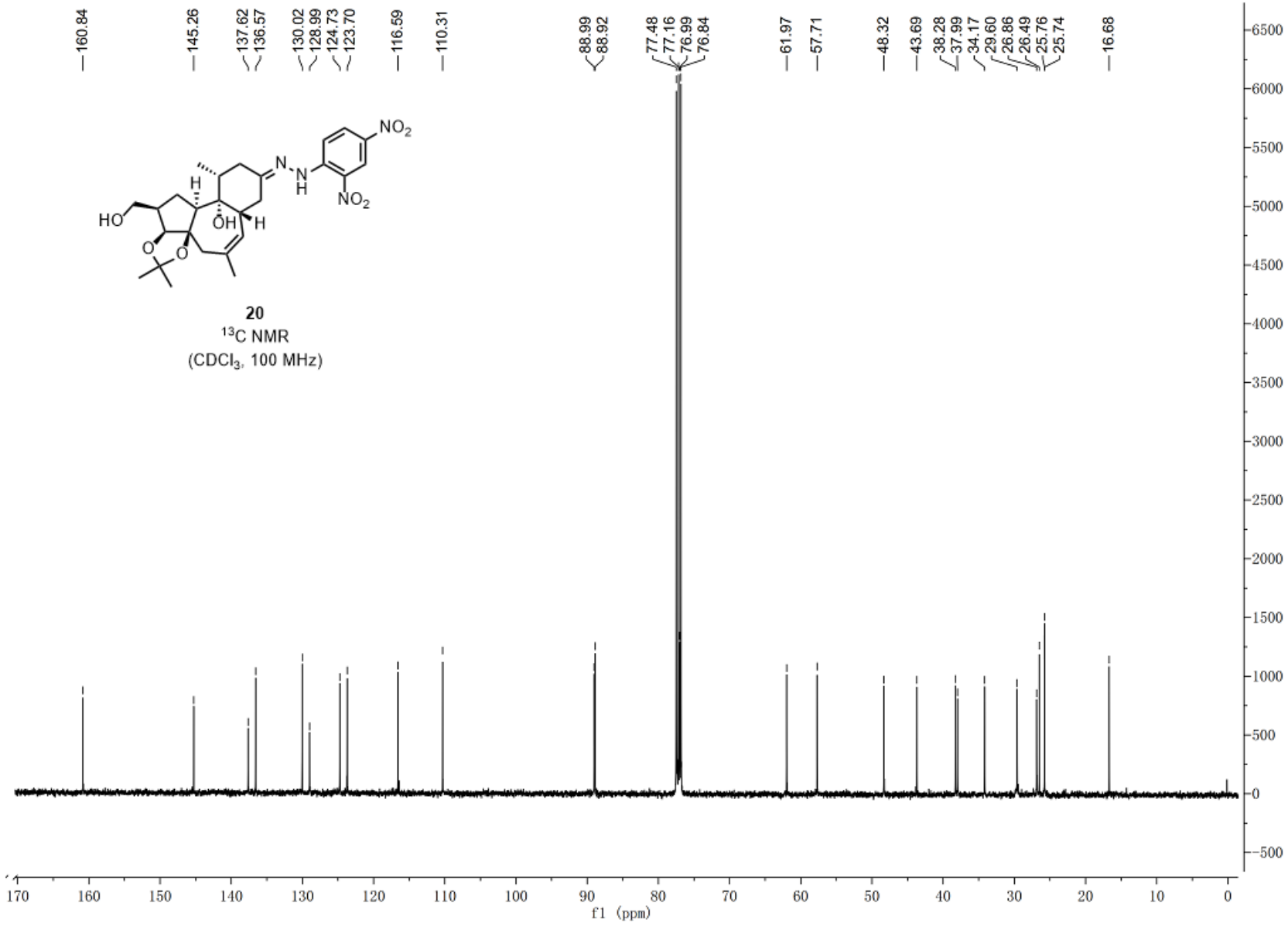

212.81
136.70
125.00
109.79
88.46
87.79
77.48
76.84
62.72
57.76
48.36
46.69
45.27
41.98
40.62
36.24
28.85
26.61
25.72
25.60
18.17
18.14
17.69
12.18
TIPSO
OH
H
O
O
O
4'
13C NMR
(CDCl3, 100 MHz)
f1 (ppm)



20

^{1}H NMR

($CDCl_3$, 400 MHz)


160.84
145.26
137.62
136.57
130.02
128.99
124.73
123.70
116.59
110.31
88.99
88.92
77.48
77.16
76.99
76.84
61.97
57.71
48.32
43.69
38.28
37.99
34.17
29.60
26.86
26.49
25.76
25.74
16.68
NO2
NO2
N
N
H
HO
H
OH
H
O
O
20
13C NMR
(CDCl3, 100 MHz)
f1 (ppm)