Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Asymmetric Total Synthesis of (+)-Astellatol and (−)-Astellatene

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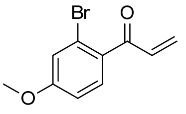
I . Experimental Procedures and Spectroscopic Data of Compounds:

General information:

Unless indicated, all commercially available reagents and anhydrous solvents were purchased at the highest commercial quality and were used as received without further purification. All non-aqueous reactions were carried out under argon atmosphere using dry glassware that had been flame-dried under a stream of argon unless otherwise noted. Flash column chromatography was performed on silica gel (Qingdao Haiyang Chemical Co., Ltd., 200–300 meshes) using petroleum ether/ethyl acetate mixtures of increasing polarity.

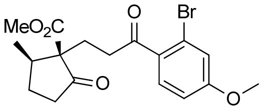
The progress of all the reactions was monitored by thin-layer chromatography (TLC) using UV light as a visualizing agent and aqueous ammonium cerium nitrate/ammonium molybdate or basic aqueous potassium permanganate or 5% phosphomolybdic acid in EtOH as a developing agent. ^{1}H NMR and ^{13}C NMR spectra were recorded on either 400 MHz/500 MHz Bruker instruments. Chemical shifts (δ) are quoted in parts per million (ppm) referenced to the appropriate residual solvent peak ($CDCl_3$), with the abbreviations s, d, dd, ddd, dt, t, td, qd, dq and m denoting singlet, doublet, double doublet, double double doublet, double triplet, triplet, triple doublet, quartet, quadruple doublet, double quartet and multiplet, respectively. J = coupling constants given in Hertz (Hz). High resolution Mass spectra (HRMS) were recorded on a micromass Autospec-Ultima ETOF spectrometer. Optical rotation data were collected on an Autopol automatic polarimeter (Rudolph Research Analytical) using HPLC grade anhydrous MeOH. Melting points (m.p.) were uncorrected and were recorded on a SGW X-4 apparatus. IR spectra were recorded on a Bruker-Alpha spectrometer.



16

To a solution of the compound **15** (0.5 g, 1.82 mmol) in dry THF (20 mL) at 0 ºC under N_2 was added dropwise vinylmagnesium bromide (5.5 mL, 1.0 mol/L). The resulting mixture was stirred for 1 hour at room temperature. The reaction was quenched with 1M HCl at 0 ºC, and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated, and purified by column chromatography (petroleum ether/EtOAc, 30:1) to afford compound **16** (0.36 g, 83%) as a colorless oil.

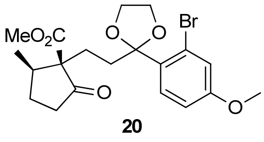
16: R_f = 0.60 (silica gel, petroleum ether/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.6 Hz, 1H), 7.15 (d, J = 2.4 Hz, 1H), 6.89 (dd, J = 8.6, 2.4 Hz, 1H), 6.81 (dd, J = 17.4, 10.5 Hz, 1H), 6.18 (d, J = 17.3 Hz, 1H), 5.99 (d, J = 10.5 Hz, 1H), 3.84 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 161.8, 136.0, 132.4, 131.4, 131.2, 121.3, 119.2, 113.2, 55.8 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_{10}BrO_2^+$ 240.9864; found 240.9857.



17

To a solution of the compound **16** (1.44 g, 6.0 mmol) and compound **14** (0.94 g, 6.0 mmol) in dry EtOH (60 mL) at room temperature was added dropwise DBU (0.22 mL, 1.5 mmol). The resulting mixture was stirred for 1 hour at room temperature and then concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc, 10:1) to afford compound **17** (1.83 g, 77%) as a colorless oil.

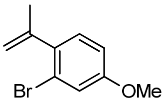
17: R_f = 0.35 (silica gel, petroleum ether/EtOAc = 7:1); $[\alpha]^{25}_D$ = +7.6 (c = 9.3 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.7 Hz, 1H), 7.14 (d, J = 2.5 Hz, 1H), 6.87 (dd, J = 8.7, 2.4 Hz, 1H), 3.83 (s, 3H), 3.69 (s, 3H), 3.39–3.26 (m, 1H), 3.06–2.89 (m, 1H), 2.54 (ddd, J = 19.0, 8.5, 1.8 Hz, 1H), 2.30–2.23 (m, 3H), 2.13–2.00 (m, 2H), 1.84–1.70 (m, 1H), 1.06 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.4, 201.1, 170.8, 161.7, 132.5, 131.1, 120.8, 119.5, 113.0, 61.8, 55.7, 51.9, 41.9, 38.6, 37.0, 28.2, 27.1, 15.9 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{18}H_{22}BrO_5^+$ 397.0651; found 397.0642.



20

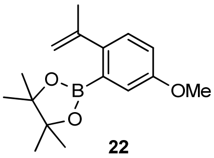
To a solution of the compound **17** (0.75 g, 1.89 mmol) in dry CH_2Cl_2 (3.8 mL) at room temperature was added ethyleneglycol (1.05 mL, 18.9 mmol), trimethyl orthoformate (6.2 mL, 56.7 mmol) and PTSA (72 mg, 0.38 mmol). The resulting mixture was stirred for 12 hours at room temperature. The reaction was quenched with H_2O, and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated, and purified by column chromatography (petroleum ether/EtOAc, 8:1) to afford compound **20** (0.39 g, 47%) as a colorless oil.

20: R_f = 0.36 (silica gel, petroleum ether/EtOAc = 7:1); $[\alpha]^{25}_D = +12.1$ (c = 2.68 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.7 Hz, 1H), 7.14 (d, J = 2.6 Hz, 1H), 6.80 (dd, J = 8.7, 2.6 Hz, 1H), 4.02 (td, J = 5.6, 3.0 Hz, 2H), 3.79 (s, 3H), 3.75 (td, J = 5.8, 5.4, 2.7 Hz, 2H), 3.64 (s, 3H), 2.50 (ddd, J = 18.8, 8.4, 1.5 Hz, 1H), 2.35 (ddd, J = 13.5, 12.2, 4.2 Hz, 1H), 2.29–2.12 (m, 2H), 2.07–1.96 (m, 2H), 1.95–1.87 (m, 1H), 1.84–1.69 (m, 2H), 1.01 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.3, 171.2, 159.7, 132.3, 129.5, 121.0, 120.3, 112.7, 110.0, 64.5, 64.5, 62.4, 55.6, 51.8, 40.1, 38.8, 32.3, 28.3, 25.8, 16.0 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{20}H_{26}BrO_6^+$ 441.0913; found 441.0905.



To a solution of Ph_3PBrMe (9.85 g, 27.5 mmol) and *t*-BuOK (3.09 g, 27.5 mmol) in THF (50 mL) at 0 ºC was added dropwise 2-bromo-4-methoxyacetophenone (4.21 g, 18.4 mmol) in dry THF (15 mL). The resulting mixture was stirred overnight at room temperature. The reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated, and purified by column chromatography (petroleum ether) to afford 2-bromo-4-methoxy-1-(prop-1-en-2-yl)benzene (3.64 g, 87%) as a yellow oil.

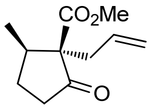
2-bromo-4-methoxy-1-(prop-1-en-2-yl)benzene: R_f = 0.60 (silica gel, petroleum ether/EtOAc = 30:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, J = 2.5 Hz, 1H), 7.11 (d, J = 8.5 Hz, 1H), 6.82 (dd, J = 8.5, 2.5 Hz, 1H), 5.24–5.18 (m, 1H), 4.93 (dt, J = 2.0, 1.0 Hz, 1H), 3.80 (s, 3H), 2.08–2.09 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 145.5, 137.2, 130.3, 121.9, 118.0, 116.2, 113.4, 55.6, 23.9 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_{12}OBr^+$ 227.0066, found 227.0061.



22

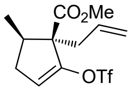
To a solution of 2-bromo-4-methoxy-1-(prop-1-en-2-yl)benzene (5.00 g, 21.8 mmol) in *i*-PrOH (100 mL) was added bis(pinacolato)diboron (13.80 g, 54.5 mmol) and KOAc (5.35g, 54.5 mmol). After the reaction system was vacuumed and backfilled with argon, $PdCl_2$(dppf) (798 mg, 1.09 mmol) was added. Then the solution was stirred at 80 °C for 4 hours. The solution was cooled and filtered. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography (petroleum ether/EtOAc = 50:1) gave the compound **22** (5.25 g, 88%) as bright yellow oil.

22: R_f = 0.42 (silica gel, petroleum ether/EtOAc = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, J = 8.5 Hz, 1H), 7.15 (d, J = 3.0 Hz, 1H), 6.89 (dd, J = 8.5, 2.5 Hz, 1H), 5.03 (s, 1H), 4.86 (s, 1H), 3.82 (s, 3H), 2.12 (s, 3H), 1.33 (s, 12H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 147.1, 142.1, 128.5, 118.9, 115.8, 115.8, 113.9, 83.8, 83.8, 55.4, 24.8, 24.8, 24.8, 24.8, 24.7 ppm; HRMS (m/z): [M+H]$^+$ calcd for $C_{16}H_{24}O_3B^+$ 275.1813, found 275.1809.



To a solution of NaH (0.50 g, 12.5 mmol, 60% suspension in mineral oil) and HMPA (2.2 mL, 12.5 mmol) in THF (10 mL) at room temperature was dropwise added keto ester (1.92 g, 10.4 mmol) in THF (5 mL). After resulting mixture was stirred at room temperature for 1 hour, allyl bromide was added (1.06 mL, 12.5 mmol). The reaction was stirred at room temperature overnight. The reaction was quenched with H_2O and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated, and purified by column chromatography (petroleum ether/EtOAc = 20:1) to afford products (1.53 g, 75%) as colorless oil.

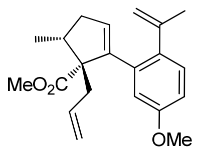
Carboxylate: R_f = 0.64 (silica gel, petroleum ether/EtOAc = 10:1); $[\alpha]^{25}_D$ = +42.9 (c = 0.14 in MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.64–5.49 (m, 1H), 5.06 (d, J = 6.5, 1H), 5.03 (s, 1H), 3.63 (s, 3H), 2.59 (dd, J = 14.0, 6.0 Hz, 1H), 2.52–2.41 (m, 2H), 2.34–2.24 (m, 1H), 2.14–1.96 (m, 2H), 1.80–1.68 (m, 1H), 0.97 (d, J = 6.5, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 216.0, 171.0, 133.1, 119.5, 162.9, 51.9, 38.9, 38.6, 35.7, 28.2, 15.5 ppm; HRMS (m/z): [M+H]$^+$ calcd for $C_{11}H_{17}O_3^+$ 197.1172, found 197.1169.



23

To a solution of the carboxylate (3.2 g, 16.3 mmol) in THF (10 mL) at –78 °C was dropwise added KHMDS (24.5 mL, 24.5 mmol, 1.0 mol/L in THF). The solution was stirred at –78 °C for 1 hour, and a solution of $PhNTf_2$ (8.7 g, 24.5 mmol) in THF (10 mL) was dropwise added. The reaction was stirred at –78 ºC for 1 hour. The reaction was quenched with saturated aqueous NaCl and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated, and purified by column chromatography (petroleum ether) to afford the triflate **23** (4.87 g, 91%) as colorless oil.

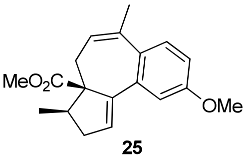
23: R_f = 0.57 (silica gel, petroleum ether/EtOAc = 50:1); $[\alpha]^{25}_D$ = +10.0 (*c* = 0.25 in MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (s, 1H), 5.74–5.65 (m, 1H), 5.13 (d, *J* = 4.5 Hz, 1H), 5.11 (s, 1H), 3.69 (s, 3H), 2.56–2.40 (m, 4H), 2.17–2.04 (m, 1H), 0.95 (d, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.8, 148.1, 132.7, 119.7, 119.7, 118.3, 60.6, 52.0, 39.1, 37.2, 35.0, 15.8 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{12}H_{16}O_5F_3S^+$ 329.0665, found 329.0658.



24

To a solution of pinacol ester **22** (5.04 g, 18.4 mmol) and triflate **23** (5.04 g, 15.4 mmol) in dioxane (280 mL) was added NaOH solution (3N, 55.4 mL). After the reaction system was vacuumed and backfilled with argon, $PdCl_2(dppf)$ (563 mg, 0.77 mmol) was added. The reaction mixture was then stirred at 100 ºC for 3 hours. The solution was cooled and filtered. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography (petroleum ether/EtOAc = 50:1) gave the triene **24** (4.33 g, 86%) as yellow oil.

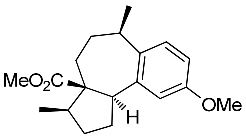
24: R_f = 0.36 (silica gel, petroleum ether/EtOAc = 20:1); $[\alpha]^{25}_D$ = –45.8 (*c* = 0.12 in MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.0 Hz, 1H), 6.71 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.43 (d, *J* = 2.5 Hz, 1H), 6.37 (s, 1H), 5.63 (ddd, *J* = 24.7, 10.4, 7.3 Hz, 1H), 5.05 (s, 1H), 4.95 (s, 1H), 4.93 (s, 1H), 4.92 (d, *J* = 8.0 Hz, 1H), 3.74 (s, 6H), 2.57 (ddt, *J* = 32.1, 16.7, 7.7 Hz, 4H), 2.36–2.25 (m, 1H), 1.98 (s, 3H), 1.00 (d, *J* = 6.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 158.4, 147.8, 142.9, 136.1, 136.0, 135.1, 134.5, 131.4, 118.1, 115.8, 112.1, 111.9, 62.9, 55.3, 51.8, 41.7, 39.8, 37.9, 23.7, 14.8 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{21}H_{27}O_3^+$ 327.1955, found 327.1948.



25

To a solution of compound **24** (3.32 g, 10.2 mmol) in dry CH_2Cl_2 (840 mL) at room temperature was added Grubbs II catalyst (1.73 g, 2.04 mmol). The resulting mixture was stirred for 2 hours reflux. The solution was cooled and filtered. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography (petroleum ether/EtOAc = 50:1) gave the compound **25** (2.78 g, 91.4%) as colorless oil.

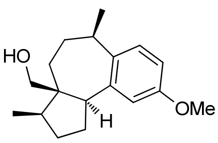
25: R_f = 0.33 (silica gel, petroleum ether/EtOAc = 20:1); $[\alpha]^{25}_D$ = –24.0 (*c* = 0.25 in MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.5 Hz, 1H), 6.83 (dd, *J* = 8.5, 3.0 Hz, 1H), 6.77 (d, *J* = 2.5 Hz, 1H), 5.77–5.72 (m, 2H), 3.81 (s, 3H), 3.64 (s, 3H), 2.64–2.52 (m, 1H), 2.44 (ddd, *J* = 15.4, 7.5, 3.1 Hz, 1H), 2.34–2.14 (m, 3H), 2.02 (s, 3H), 1.01 (d, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 158.3, 147.0, 139.0, 138.6, 132.8, 130.0, 127.5, 122.7, 113.3, 112.9, 74.7, 55.4, 51.6, 42.9, 39.3, 30.1, 24.0, 14.6 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{19}H_{23}O_3^+$ 299.1642, found 299.1635.



26

To a solution of compound **25** (1.52 g, 5.1 mmol) in MeOH (50 mL) at room temperature was added $Pd(OH)_2/C$ (3.04 g). After the reaction system was vacuumed and backfilled with hydrogen (balloon pressure), the solution was stirred at room temperature overnight. The solution was filtered and the filtrate was evaporated under reduced pressure gave the compound **26** (1.54 g, quant.) as colorless oil without further purification.

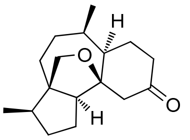
26: R_f = 0.36 (silica gel, petroleum ether/EtOAc = 20:1); $[\alpha]^{25}_D$ = –28.6 (*c* = 0.14 in MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 11.0 Hz, 1H), 7.02 (d, *J* = 3.0 Hz, 1H), 6.68 (dd, *J* = 11.0, 3.5, Hz, 1H), 3.79 (s, 3H), 3.54 (t, *J* = 9.8 Hz, 1H), 3.39 (s, 3H), 2.98–2.92 (m, 1H), 2.77–2.70 (m, 1H), 2.60 (dd, *J* = 13.5, 5.5 Hz, 1H), 2.10–1.99 (m, 2H), 1.94–1.91 (m, 1H), 1.73–1.60 (m, 2H), 1.49–1.44 (m, 2H), 1.35 (d, *J* = 9.0 Hz, 3H), 0.90 (d, *J* = 8.5 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 157.3, 140.8, 139.1, 124.8, 113.7, 110.1, 58.1, 55.4, 50.5, 50.5, 48.8, 40.2, 35.7, 34.2, 31.3, 26.9, 21.9, 16.1 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{19}H_{27}O_3^+$ 303.1955, found 303.1947.



27

To solution of compound **26** (2.7 g, 8.9 mmol) in dry CH_2Cl_2 (50 mL) at 0 °C was dropwise added DIBAL-H (17.8 mL, 26.7 mmol, 1.5 mol/L in THF). The resulting mixture was stirred at 0 °C for 1 hour. The reaction was quenched with 1N HCl and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated. The residue without purified, gave the primary alcohol **27** (2.44 g, quant.) as colorless oil.

27: $R_f = 0.44$ (silica gel, petroleum ether/EtOAc = 10:1); $[\alpha]^{25}_D = -36.0$ ($c = 0.22$ in MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, J = 10.5 Hz, 1H), 6.94 (d, J = 3.0 Hz, 1H), 6.72 (dd, J = 10.5, 3.5 Hz, 1H), 3.79 (s, 3H), 3.40 (dd, J = 14.0, 11.0 Hz, 1H), 3.29 (d, J = 14.0 Hz, 1H), 3.17 (d, J = 14.5 Hz, 1H), 2.97 (q, J = 8.2, 7.1 Hz, 1H), 2.42–2.31 (m, 1H), 2.21–2.12 (m, 1H), 2.00 (dtd, J = 12.1, 10.4, 9.4, 6.4 Hz, 1H), 1.88 (ddt, J = 17.8, 8.4, 4.7 Hz, 3H), 1.58 (dddd, J = 24.1, 17.4, 8.0, 5.0 Hz, 4H), 1.47–1.33 (m, 5H), 1.05 (d, J = 9.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 142.2, 139.0, 125.2, 113.1, 109.4, 63.4, 55.2, 50.1, 47.8, 47.6, 39.8, 36.1, 33.1, 30.9, 26.1, 21.8, 15.5 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{18}H_{27}O_2^+$ 275.2006, found 275.1999.



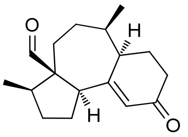
29

To a solution of Na (263 mg, 11.4 mmol) in NH_3 (~10 mL) at –78 °C was dropwise added primary alcohol **27** (157 mg, 0.57 mmol) in THF (2 mL). After the solution was stirred for 20 minutes, *t*-BuOH (4 mL) was added. The solution was stirred for 15 minutes, the reaction was warmed to –45 °C and stirred for another 2 hours. The solution was quenched with MeOH at –45 °C. Saturated NH_4Cl solution (10 mL) was added and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over $NaSO_4$, concentrated.

The crude residue was treated with 1M HCl (2 mL) in dioxane (6 mL) and stirred at room temperature for 1 hour. The reaction was neutralized with saturated aqueous $NaHCO_3$ until PH≈7. The solution was extracted with EtOAc (3 × 10 mL), the combined organic layers were washed with brine, dried over Na_2SO_4, concentrated. The residue was purified by column chromatography (petroleum ether/EtOAc = 20:1) gave the compound **29** (73 mg, 49%) as colorless oil.

29: $R_f = 0.46$ (silica gel, petroleum ether/EtOAc = 10:1); $[\alpha]^{25}_D = +4.3$ ($c = 0.23$ in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (d, J = 10.4 Hz, 1H), 3.29 (d, J = 8.3 Hz, 1H), 2.63–2.46

(m, 3H), 2.31 (d, $J = 14.4$ Hz, 1H), 2.26–2.14 (m, 1H), 2.12–2.01 (m, 1H), 1.93–1.75 (m, 7H), 1.68–1.59 (m, 2H), 1.51–1.40 (m, 1H), 1.28–1.17 (m, 2H), 0.94 (d, $J = 7.2$ Hz, 3H), 0.83 (d, $J = 6.5$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.6, 88.6, 71.5, 58.0, 54.2, 52.0, 48.2, 42.5, 40.8, 39.4, 33.8, 31.5, 27.2, 24.0, 21.7, 19.9, 15.6 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{17}H_{27}O_2^+$ 263.2011, found 263.2004.



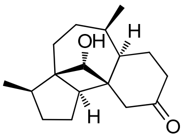
31

To a solution of Na (0.83 g, 36.0 mmol) in NH_3 (~20 mL) at –78 °C was dropwise added primary alcohol **27** (0.5 g, 1.8 mmol) in THF (8 mL). After the solution was stirred for 20 minutes, *t*-BuOH (8 mL) was added. The solution was stirred for 15 minutes, the reaction was warmed to –45 °C and stirred for another 2 hours. The solution was quenched with MeOH at –45 °C. Saturated NH_4Cl solution (20 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated.

The residue was then treated with Dess-Martin periodinane. To a solution of the residue and $NaHCO_3$ (166 mg, 2.0 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added Dess-Martin periodinane (800 mg, 2.0 mmol). The reaction mixture was stirred at 0 °C for 10 minutes. The reaction was quenched with saturated $Na_2S_2O_3$ solution and extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure.

The crude residue was treated with 1M HCl (6 mL) in dioxane (15 mL) and stirred at room temperature for 1 hour. The reaction was neutralized with saturated aqueous $NaHCO_3$ until PH≈7. The solution was extracted with EtOAc (3 × 20 mL), the combined organic layers were washed with brine, dried over Na_2SO_4, concentrated, and purified by column chromatography (petroleum ether/EtOAc = 15:1) gave the aldehyde **31** (160 mg, 34%) as colorless oil.

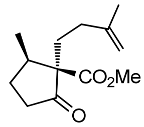
31: $R_f = 0.40$ (silica gel, petroleum ether/EtOAc = 5:1); $[\alpha]^{25}_D = -44.0$ ($c = 0.22$ in MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (d, $J = 1.5$ Hz, 1H), 6.20 (d, $J = 2.5$, 1H), 3.22 (t, $J = 9.5$ Hz, 1H), 2.58–2.48 (m, 2H), 2.46–2.38 (m, 2H), 2.31–2.20 (m, 2H), 2.18–2.10 (m, 1H), 2.08–1.99 (m, 3H), 1.73–1.66 (m, 1H), 1.55–1.47 (m, 1H), 1.37–1.30 (m, 2H), 1.07–1.04 (m, 1H), 1.01 (d, $J = 7.0$ Hz, 3H), 0.90 (d, $J = 7.0$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.5, 199.6, 167.0, 127.0, 62.9, 49.8, 48.6, 45.1, 38.0, 35.2, 34.5, 31.0, 27.9, 26.8, 23.4, 21.3, 15.5 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{17}H_{25}O_2^+$ 261.1849, found 261.1843.



32

To a solution of aldehyde **31** (50 mg, 0.2 mmol), MeOH (0.15 mL) and HMPA (0.8 mL) in dry THF (1.5 mL) at –78 °C was dropwise added SmI_2 (4 mL, 0.1 mol/L in THF). The resulting mixture was stirred at –78 °C for 30 minutes. The reaction was quenched by open the system to air. Then saturated aqueous NH_4Cl (10 mL) was added and the solution was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated, and purified by column chromatography (petroleum ether/EtOAc = 15:1) gave the compound **32** (21.7 mg, 41%) as white solid.

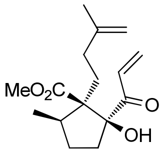
32: R_f = 0.55 (silica gel, petroleum ether/EtOAc = 5:1); $[\alpha]^{25}_{D}$ = +40.2 (*c* = 0.35 in MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92 (s, 1H), 2.49–2.38 (m, 3H), 2.37–2.34 (m, 2H), 2.34–2.27 (m, 2H), 2.19–2.11 (m, 1H), 1.98–1.93 (m, 3H), 1.80–1.75 (m, 2H), 1.57–1.43 (m, 3H), 1.34–1.22 (m, 3H), 1.01 (d, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.1, 73.7, 57.7, 52.1, 51.8, 47.7, 43.2, 42.1, 41.9, 34.5, 32.4, 30.4, 29.3, 23.5, 23.2, 22.0, 13.2 ppm; HRMS (m/z): $[M+H–H_2O]^+$ calcd for $C_{17}H_{25}O^+$ 245.1900, found 245.1896.



38

To a stirred solution of chiral *β*-keto ester **38** (20.0 g, 128.1 mmol) in 1,4-dioxane (256 mL) were added Cs_2CO_3 (83.5 g, 256.3 mmol), 4-iodo-2-methylbut-1-ene (**37**, 50.3 g, 256.6 mmol), and HMPA (27.3 g, 152.3 mmol), and the reaction mixture was heated at 80 °C for 10 hours. After cooling, the mixture was treated with saturated aqueous NH_4Cl and extracted with EtOAc (3 × 200 mL), washed with brine, dried over anhydrous Na_2SO_4, concentrated in reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 100:1) to give the desired product **38** (20.1 g, 70%) as yellow oil.

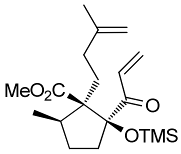
38: R_f= 0.61 (silica gel, petroleum ether/EtOAc = 10:1); $[\alpha]^{25}_{D}$ = +60.0 (*c* = 0.56 in MeOH); IR (film): ν_{max} =1735, 1685, 1250, 1175, 1130, 880, 742 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.67 (s, 2H), 3.65 (s, 3H), 2.51 (dd, *J* = 18.9, 8.4 Hz, 1H), 2.29 (dt, *J* = 11.9, 6.7 Hz, 1H), 2.22–2.08 (m, 2H), 2.08–1.93 (m, 2H), 1.86–1.78 (m, 2H), 1.75 (dd, *J* = 17.0, 6.8 Hz, 1H), 1.70 (s, 3H), 1.02 (d, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 216.4, 171.2, 145.4, 110.1, 62.9, 51.8, 39.7, 38.9, 32.2, 30.0, 28.3, 22.3, 15.9 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{13}H_{21}O_3^+$ 225.1485; found 225.1478.



40

To a solution of methoxypropadiene (**39**, 12.5 g, 178.3 mmol) in dry THF (150 mL) at –78 °C, *n*-BuLi (2.4 M in hexanes, 70.6 mL, 169.5 mmol) was added and the reaction mixture was stirred at –78 °C for 10 minutes. Then a solution of **38** (20.0 g, 89.2 mmol) in dry THF (20 mL) was added within 5 minutes. The reaction was stirred at the same temperature for 1 hour and quenched with H_2O (100 mL). The resulting mixture was allowed to warm to room temperature and extracted with EtOAc (3 × 150 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 10:1) to give the desired product **40** (19.5 g, 78%) as yellow oil.

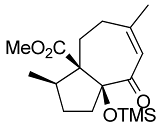
40: R_f= 0.32 (silica gel, petroleum ether/EtOAc= 10:1); $[\alpha]^{25}_D$ = –38.0 (*c* = 1.46 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 17.1, 10.4 Hz, 1H), 6.40 (dd, *J* = 17.1, 2.0 Hz, 1H), 5.74 (dd, *J* = 10.4, 2.0 Hz, 1H), 4.62 (s, 1H), 4.56 (s, 1H), 4.22 (s, 1H), 3.75 (s, 3H), 2.42 (dd, *J* = 16.2, 9.2 Hz, 1H), 2.24–2.13 (m, 1H), 2.11–2.01 (m, 2H), 2.00–1.88 (m, 3H), 1.72–1.65 (m, 1H), 1.64 (s, 3H), 1.49–1.41 (m, 1H), 0.94 (d, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 174.6, 146.0, 131.5, 129.9, 109.7, 90.4, 64.0, 51.5, 43.4, 37.7, 33.4, 31.7, 30.6, 22.5, 17.0 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{16}H_{25}O_4^+$ 281.1753; found 281.1746.



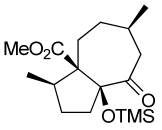
42

The crude compound **40** could be used in this step without further purification. To a stirred solution of the crude product **40** in CH_2Cl_2 (100 mL) were sequentially added Et_3N (50.0 mL, 0.36 mol) and TMSOTf (32.0 mL, 0.18 mol) at 0 ºC. Upon completion, the reaction mixture was quenched with water and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extract was washed with brine and concentrated under reduced pressure. To a solution of the above-obtained crude product in THF (100 mL), was added 1M HCl (135 mL). The reaction mixture was stirred for 10 minutes at room temperature and quenched with water and extracted with EtOAc (3 × 100 mL). The combined organic extract was washed with brine, dried over anhydrous Na_2SO_4, concentrated, and purified by column chromatography (petroleum ether/EtOAc = 100:1) to afford the compound **42** (22.63 g, 92%) as pale-yellow oil.

42: R_f = 0.67 (silica gel, petroleum ether/EtOAc = 20:1); $[\alpha]^{25}_D$ = –41.9 (*c* = 0.53 in MeOH) IR (film): ν_{max} = 2953, 1729, 1694, 1606, 1456, 1398, 1252, 1172, 1135, 887, 842 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.07 (dd, *J* = 17.2, 10.3 Hz, 1H), 6.32 (dd, *J* = 17.2, 2.0 Hz, 1H), 5.67 (dd, *J* = 10.3, 2.0 Hz, 1H), 4.63 (s, 1H), 4.57 (s, 1H), 3.70 (s, 3H), 2.21–1.98 (m, 6H), 1.83–1.67 (m, 2H), 1.65 (d, *J* = 4.3 Hz, 3H), 1.47 (ddd, *J* = 13.4, 11.8, 5.6 Hz, 1H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.08 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 203.6, 172.3, 146.4, 132.7, 128.4, 109.5, 93.8, 65.1, 51.1, 41.0, 35.8, 33.7, 33.0, 32.4, 22.6, 17.3, 1.9 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{19}H_{33}O_4Si^+$ 353.2143; found 353.2132.



5,7-Bicyclic enone



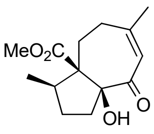
36

A solution of enone **42** (15.0 g, 42.6 mmol) in toluene (1700 mL) was heated to 90 °C. To this solution the Grubbs second-generation catalyst (1.85 g, 2.2 mmol) in toluene (20 mL) was added using a syringe pump over a period of 2 hours. The reaction mixture was stirred at 90 °C for 2 hours and cooled to room temperature. The volatile was removed under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 70:1) to give the corresponding 5,7-bicyclic enone (12.6 g, 91%).

5/7-Bicyclic enone: R_f = 0.52 (silica gel, petroleum ether/EtOAc = 20:1); $[\alpha]^{25}_D$ = +11.5 (*c* = 0.52 in MeOH); IR (film): ν_{max} = 2955, 2344, 2322, 1728, 1676, 1251, 1218, 1178, 1137, 909, 863, 841 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 5.63 (s, 1H), 3.71 (s, 3H), 2.91–2.81 (m, 1H), 2.55–2.45 (m, 2H), 2.16 (dd, *J* = 18.6, 7.3 Hz, 1H), 2.06 (td, *J* = 12.2, 5.2 Hz, 1H), 1.96–1.89 (m, 1H), 1.88 (s, 3H), 1.75–1.63 (m, 2H), 1.18 (dd, *J* = 14.2, 10.8 Hz, 1H), 0.81 (d, *J* = 6.7 Hz, 3H), –0.05 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 205.3, 173.1, 159.6, 124.2, 94.9, 62.9, 51.3, 42.2, 35.6, 34.0, 32.6, 31.4, 26.0, 15.3, 1.3 ppm; HRMS (m/z): $[M+Na]^+$ calcd for $C_{17}H_{28}O_4NaSi^+$ 347.1649; found 347.1643.

5/7-Bicyclic ketone 36: The above-obtained 5,7-Bicyclic enone (20.0 g, 61.6 mmol) and Pd/C (2.0 g) were mixed in MeOH (100 mL) in a Parr high-pressure reactor under hydrogen (730 psi). The reaction mixture was stirred at room temperature for 8 hours, filtered and washed with ethyl acetate. The filtrate was concentrated and purified by column chromatography (petroleum ether/EtOAc = 80:1) to give the compound **36** (19.7 g, 60.4 mmol, 98%).

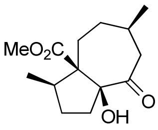
36: R_f = 0.61 (silica gel, petroleum ether/EtOAc = 20:1); $[\alpha]^{25}_D$ = +1.4 (*c* = 0.69 in MeOH); IR (film): ν_{max} = 2335, 2320, 1725, 1256, 1220, 1170, 1124, 841 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.70 (s, 3H), 3.09–3.01 (m, 1H), 2.54 (dd, *J* = 15.1, 9.2 Hz, 1H), 2.39 (ddd, *J* = 12.8, 9.0, 6.4 Hz, 1H), 2.14 (ddd, *J* = 10.1, 5.5, 1.3 Hz, 1H), 2.09–2.01 (m, 1H), 1.98–1.73 (m, 4H), 1.73–1.52 (m, 3H), 1.00 (d, *J* = 6.4 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.10 (s, 9H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 216.2, 173.5, 94.5, 62.7, 51.3, 46.0, 43.2, 35.4, 35.3, 34.7, 31.9, 30.8, 23.2, 14.9, 1.8 ppm; HRMS (m/z): [M+H]$^+$ calcd for $C_{17}H_{31}O_4Si^+$ 327.1986; found 327.1979; [M+Na]$^+$ calcd for $C_{17}H_{30}O_4NaSi^+$ 349.1806; found 349.1797.



41

To a solution of compound **5/7-Bicyclic enone** (120 mg, 0.37 mmol) in THF (5 mL) at room temperature was added 10% HCl water solution (2 mL) dropwise. The reaction mixture was allowed to stir overnight. Water (10 mL) was added and the solution was extracted with EtOAc (3 × 10 mL). The extract was washed with saturated aqueous NaHCO$_3$ solution, washed with brine, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 20:1) to give the compound **41** (78 mg, 84%).

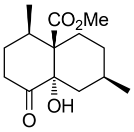
41: R_f= 0.35 (silica gel, petroleum ether/EtOAc = 8:1); $[\alpha]^{25}_D$ = +17.8 (*c* = 0.37 in MeOH); ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.84 (s, 1H), 3.91 (s, 1H), 3.71 (s, 3H), 2.54–2.20 (m, 4H), 2.01–1.95 (m, 1H), 1.90 (s, 3H), 1.88–1.63 (m, 4H), 0.98 (d, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl$_3$) δ 203.1, 173.3, 156.0, 124.4, 91.7, 62.8, 51.7, 42.6, 37.2, 32.9, 32.8, 31.1, 26.1, 16.1 ppm; HRMS (m/z): [M+H]$^+$ calcd for $C_{14}H_{21}O_4^+$ 253.1440; found 253.1432.



43

Tertiary alcohol **43**: To a solution of compound **36** (13.1 g, 40.0 mmol) in THF (250 mL) at room temperature was added 10% HCl water solution (200 mL) dropwise. The reaction mixture was allowed to stir overnight. Water (100 mL) was added and the solution was extracted with EtOAc (3 × 200 mL). The extract was washed with saturated aqueous NaHCO$_3$ solution, washed with brine, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by recrystallization (petroleum ether/EtOAc = 50:1) to give the compound **43** (8.20 g, 81%) as white solid.

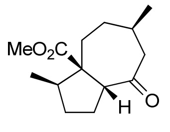
43: $R_f = 0.53$ (silica gel, petroleum ether/EtOAc = 10:1); $[\alpha]^{25}_{D} = -17.9$ ($c = 0.56$ in MeOH); IR (film): $\nu_{max} = 2953, 1722, 1699, 1457, 1205, 734\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$) δ 4.26 (s, 1H), 3.74 (s, 3H), 3.09 (t, $J = 10.8$ Hz, 1H), 2.63−2.57 (m, 1H), 2.44 (dd, $J = 15.5, 8.5$ Hz, 1H), 2.18 (ddd, $J = 10.5, 5.0, 1.5$ Hz, 1H), 1.90−1.86 (m, 1H), 1.78−1.62 (m, 5H), 1.40−1.32 (m, 1H), 0.99−0.94 (m, 4H), 0.83 (d, $J = 7.0$ Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.4, 175.0, 90.9, 61.9, 51.9, 45.7, 45.1, 36.4, 35.3, 34.2, 32.3, 30.8, 23.0, 16.0 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{23}O_4^+$ 255.1591; found 255.1583; $[M+Na]^+$ calcd for $C_{14}H_{22}O_4Na^+$ 277.1410; found 277.1402; CCDC 1589760 contains the supplementary crystallographic data for **43** (m.p. 112−114 °C) and is available free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



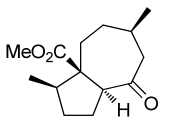
44

6/6-Bicyclic byproduct 44: To a stirred solution of compound **36** (200 mg, 0.61 mmol) in THF (10 ml) was added TBAF (0.92 ml, 0.92 mmol, 1.0 mol/L in THF) at 0 °C. The reaction mixture was stirred for 30 minutes at 0 °C and was then quenched with saturated aqueous NH_4Cl and extracted with EtOAc (3 × 10 mL). The organic extract was washed with brine (3 × 10 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude oil was purified by column chromatography (petroleum ether/EtOAc = 8:1) to give **44** (131 mg, 84%) as white solid.

44: $R_f = 0.27$ (silica gel, petroleum ether/EtOAc = 8:1); $[\alpha]^{25}_{D} = +66.7$ ($c = 1.2$ in MeOH); IR (film): $\nu_{max} = 2958, 2910, 2850, 1731, 1693, 1457, 1260, 1185, 1146, 1076, 1015, 990, 790\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$) δ 3.64 (s, 3H), 2.85 (ddd, $J = 16.0, 12.5, 8.0$ Hz, 1H), 2.48 (s, 1H), 2.41 (ddd, $J = 13.0, 7.0, 4.5$ Hz, 1H), 2.24 (ddd, $J = 16.0, 5.5, 1.0$ Hz, 1H), 2.14 (dt, $J = 7.0, 3.0$ Hz, 1H), 1.89 (ddd, $J = 14.5, 3.5, 1.5$ Hz, 1H), 1.78−1.72 (m, 2H), 1.66−1.59 (m, 2H), 1.37 (ddd, $J = 26.0, 13.0, 5.5$ Hz, 1H), 1.11 (dd, $J = 14.5, 12.5$ Hz, 1H), 0.88−0.82 (m, 7H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.1, 173.2, 75.0, 58.1, 51.4, 37.5, 35.7, 32.7, 31.7, 30.5, 27.4, 26.3, 22.3, 15.8 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{23}O_4^+$ 255.1591; found 255.1585; CCDC 1589761 contains the supplementary crystallographic data for **44** (m.p. 122−124 °C) and is available free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



***epi*-45**



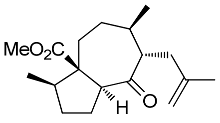
45

Ketone 45 and *epi*-45: To a vigorously degassed solution of compound **43** (4.0 g, 15.7 mmol) in THF (150 mL) and MeOH (25 mL), a freshly prepared SmI_2 solution (314 mL, 0.1 M in THF) was added dropwise at −78 ºC. The reaction mixture was allowed to stir for 1 hour at the same temperature. The reaction was quenched with saturated aqueous $Na_2S_2O_3$ (50 mL) and the solution was extracted with EtOAc (3 × 150 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 40:1) to give the compound **45** (1.89 g, 51%) as colorless crystals and compound ***epi*-45** (1.62 g, 43%) as colorless oil.

From *epi*-45 to 45: To a solution of compound ***epi*-45** (6.0 g, 25.2 mmol) in toluene (150 mL) was added NaOMe (1.36 g, 25.2 mmol) at room temperature. The reaction mixture was stirred overnight at room temperature. Then water (100 mL) was added and the solution was extracted with EtOAc (3 × 100 mL) and washed with brine. The extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 40:1) to give the compound **45** (1.28 g, 21%) as colorless crystals and compound ***epi*-45** (3.74 g, 62%) was recovered as colorless oil.

45: R_f = 0.47 (silica gel, petroleum ether/EtOAc = 10:1); $[\alpha]^{25}_D$ = +114.4 (*c* = 0.90 in MeOH); IR (film): ν_{max} = 1721, 1697, 1457, 1201, 713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.53 (s, 3H), 2.70 (t, *J* = 9.6 Hz, 1H), 2.48−2.45 (m, 1H), 2.33 (d, *J* = 17.6 Hz, 1H), 2.24 (dd, *J* = 10.8, 18.8 Hz, 1H), 1.91 (dd, *J* = 11.6, 17.6 Hz, 1H), 1.84−1.63 (m, 5H), 1.36−1.12 (m, 3H), 0.84 (d, *J* = 6.4 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.4, 173.5, 60.8, 58.3, 52.4, 51.1, 48.1, 37.9, 36.4, 30.3, 29.8, 24.5, 23.7, 15.1 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{23}O_3^+$ 239.1642; found 239.1636; $[M+Na]^+$ calcd for $C_{14}H_{22}O_3Na^+$ 261.1461; found 261.1455.

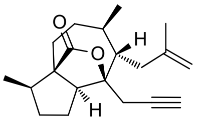
***epi*-45**: R_f = 0.64 (silica gel, petroleum ether/EtOAc = 10:1); $[\alpha]^{25}_D$ = −64.3 (*c* = 0.56 in MeOH); IR (film): ν_{max} = 1725, 1696, 1458, 1201, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.72 (t, *J* = 8.0 Hz, 1H), 3.66 (s, 3H), 2.26−2.13 (m, 3H), 2.05−1.95 (m, 1H), 1.70−1.66 (m, 4H), 1.53 (br, 1H), 1.22−1.15 (m, 1H), 1.11−1.00 (m, 2H), 0.85 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.5, 175.8, 57.6, 57.6, 52.3, 51.6, 48.1, 35.3, 35.2, 34.0, 32.4, 24.5, 23.2, 15.7 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{23}O_3^+$ 239.1642; found 239.1639; $[M+Na]^+$ calcd for $C_{14}H_{22}O_3Na^+$ 261.1461; found 261.1457.



47

To a solution of compound **45** (5.20 g, 21.8 mmol) in THF (100 mL), a freshly prepared LDA solution in THF (21.8 mL, 2.0 mol/L) was added at −78 ºC. The reaction mixture was allowed to stir for 1 hour at the same temperature. Then methallyl bromide (4.42 mL, 43.6 mmol) was added and the reaction mixture was allowed to stir for 2 hours while the reaction temperature was gradiently raised to room temperature. The reaction was quenched with saturated aqueous NH_4Cl (50 mL) and the solution was extracted with EtOAc (3 × 100 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 40:1) to give the compound **47** (5.30 g, 83%) as colorless oil.

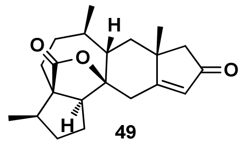
47: $R_f = 0.37$ (silica gel, petroleum ether/EtOAc = 20:1); $[\alpha]^{25}_D = +16.3$ ($c = 0.49$ in MeOH); IR (film): ν_{max} = 2953, 2873, 1722, 1699, 1457, 1205, 1167, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.67 (s, 1H), 4.49 (s, 1H), 3.60 (s, 3H), 3.11 (t, J = 9.5 Hz, 1H), 2.49−2.36 (m, 3H), 2.15−2.04 (m, 2H), 1.90−1.86 (m, 2H), 1.74−1.49 (m, 9H), 0.99 (d, J = 6.0 Hz, 3H), 0.85 (d, J = 5.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.4, 173.4, 143.2, 112.6, 60.7, 59.5, 57.4, 51.1, 48.6, 40.8, 38.3, 35.8, 34.9, 31.6, 24.7, 22.2, 22.0, 14.9 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{29}O_3^+$ 293.2111; found 293.2100; $[M+Na]^+$ calcd for $C_{18}H_{28}O_3Na^+$ 315.1931; found 215.1920.

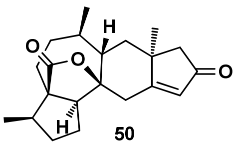


48

Under argon atmosphere, a flame-dried round-bottom flask was charged with magnesium (5.23 g, 218 mmol), $HgCl_2$ (2.96 g, 10.9 mmol) and THF (150 mL). The suspension was cooled to 0 ºC, propargyl bromide (16.4 mL, 218 mmol) was then added dropwise, allowing the reaction mixture to reflux gently. Upon completion, the mixture was stirred at 50 °C for 1 hour then was cooled to room temperature. To this freshly prepared Grignard reagent, a solution of compound **47** (3.20 g, 10.9 mmol) in THF (50 mL) was added dropwise and the reaction mixture was stirred at room temperature for 2 hours. The mixture was then poured into ice-water (100 mL) and saturated aqueous NaCl (50 mL) and extracted with EtOAc (3 × 50 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 60:1) to give the corresponding propargyl-substituted lactone **48** (2.74 g, 84%) as white solid.

48: R_f = 0.40 (silica gel, petroleum ether/EtOAc = 20:1); $[\alpha]^{25}_{D} = -51.8$ (c = 0.56 in MeOH); IR (film): ν_{max} = 2957, 2933, 2361, 1758, 1264, 734, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.80 (s, 1H), 4.76 (s, 1H), 2.63 (d, J = 1.6 Hz, 2H), 2.56 (dd, J =10.8, 4.0 Hz, 1H), 2.18−2.08 (m, 4H), 1.99−1.93 (m, 2H), 1.86−1.74 (m, 5H), 1.71−1.65 (m, 3H), 1.57−1.48 (m, 1H), 1.46−1.39 (m, 1H), 1.32−1.27 (m, 1H), 1.24 (d, J = 6.8 Hz, 3H), 1.03 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.2, 144.4, 112.7, 89.0, 79.8, 72.1, 59.6, 48.5, 48.2, 44.9, 40.5, 36.6, 34.3, 34.1, 30.0, 28.8, 25.3, 22.5, 22.3, 13.3 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{20}H_{29}O_2^+$ 301.2162; found 301.2154.

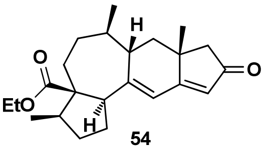

49


50

To a solution of the propargyl-substituted lactone **48** (280 mg, 0.93 mmol) in anhydrous toluene (10 mL), $Co_2(CO)_8$ (350 mg, 1.02 mmol) was added. Then reaction mixture was stirred at 70 °C for 12 hours. The reaction mixture was then concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 7:1) to give the lactone **49** (128 mg, 42%) as white solid and C-7 epimer **50** (64 mg, 21%) as white solid.

49: R_f = 0.37 (silica gel, petroleum ether/EtOAc = 3:1); $[\alpha]^{25}_{D} = +5.9$ (c = 1.1 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (d, J = 1.6 Hz, 1H), 2.99 (d, J = 13.6 Hz, 1H), 2.82 (d, J = 14.9 Hz, 1H), 2.36−2.25 (m, 2H), 2.20−2.08 (m, 3H), 1.85−1.74 (m, 4H), 1.70−1.56 (m, 2H), 1.56−1.47 (m, 1H), 1.35−1.27 (m, 6H), 1.21 (d, J = 6.7 Hz, 3H), 1.14 (m, 1H), 1.04 (d, J = 6.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 182.2, 178.1, 128.2, 89.3, 60.4, 51.3, 48.8, 47.9, 44.7, 42.7, 42.7, 38.2, 36.2, 36.0, 33.6, 31.8, 25.1, 24.6, 23.4, 13.9 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{21}H_{29}O_3^+$ 329.2117; found 329.2107.

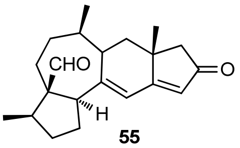
C-7 epimer 50: R_f = 0.39 (silica gel, petroleum ether/EtOAc = 3:1); $[\alpha]^{25}_{D} = -10.6$ (c = 1.3 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (s, 1H), 2.81 (d, J = 13.5 Hz, 1H), 2.71−2.60 (m, 2H), 2.29 (d, J = 7.0 Hz, 2H), 2.16−2.08 (m, 1H), 1.93−1.80 (m, 5H), 1.66−1.59 (m, 1H), 1.41−1.31 (m, 3H), 1.31−1.26 (m, 1H), 1.20−1.19 (m, 6H), 1.15−1.02 (m, 2H), 0.95 (d, J = 5.8 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.6, 183.5, 178.3, 128.6, 90.4, 60.2, 50.5, 50.4, 49.8, 44.3, 44.0, 37.3, 36.8, 35.5, 35.3, 33.1, 32.7, 28.3, 25.6, 23.2, 14.1 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{21}H_{29}O_3^+$ 329.2117; found 329.2107.



54

To a solution of compound **49** (120 mg, 0.37 mmol) in HMPA (5 mL) was added DBU (0.27 mL, 1.83 mmol). The solution was stirred at room temperature for 30 minutes. CH_2Cl_2 (5 mL) and DIPEA (0.13 mL, 0.73 mmol) was then added. To this mixture a solution of $Et_3O^+BF_4^-$ in CH_2Cl_2 (0.73 mL, 0.73 mmol, 1.0 mol/L) was added dropwise. The reaction was allowed to stirred at room temperature for 1 hour. To the reaction mixture water (10 mL) was added and the mixture was extracted with EtOAc (3 × 10 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 30:1) to give the compound **54** (111 mg, 85%) as colorless oil.

54: $R_f = 0.45$ (silica gel, petroleum ether/EtOAc = 3:1); $[\alpha]^{25}_D = -18.3$ ($c = 0.03$ in MeOH); ^1H NMR (400 MHz, $CDCl_3$) δ 6.38 (t, $J = 2.3$ Hz, 1H), 5.65 (s, 1H), 4.19 (dq, $J = 10.8, 7.1$ Hz, 1H), 3.94 (dq, $J = 10.9, 7.1$ Hz, 1H), 2.85 (t, $J = 9.2$ Hz, 1H), 2.48 (dt, $J = 14.1, 3.5$ Hz, 1H), 2.31−2.14 (m, 3H), 2.14−2.05 (m, 1H), 2.05−1.97 (m, 1H), 1.95−1.87 (m, 3H), 1.85−1.77 (m, 1H), 1.67−1.61 (m, 2H), 1.44−1.36 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 4H), 1.05 (s, 3H), 0.93 (d, $J = 6.3$ Hz, 3H), 0.89 (d, $J = 6.5$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.0, 179.4, 173.7, 159.6, 121.8, 118.6, 77.4, 77.1, 76.8, 60.1, 59.1, 54.1, 51.7, 48.4, 44.1, 40.6, 40.5, 39.1, 38.5, 35.8, 30.7, 30.0, 24.9, 21.2, 15.3, 14.3 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{23}H_{33}O_3^+$ 357.2430; found 357.2420.

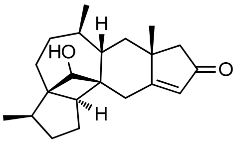


55

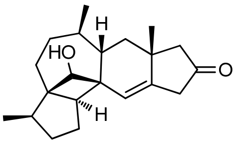
To a solution of compound **54** (111 mg, 0.31 mmol) in CH_2Cl_2 (5 mL), a solution of DIBAL-H (1.6 mL, 1.56 mmol, 1.0 mol/L) was added dropwise at 0 °C. The reaction mixture was allowed to stirred at the same temperature for 1 hour. The reaction was quenched with 3N NaOH solution (3 mL) and was extracted with CH_2Cl_2 (3 × 10 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude diol was used in the next step directly.

The above-obtained crude diol was dissolved in CH_2Cl_2, TPAP (18 mg, 0.05 mmol) and NMO (146 mg, 1.24 mmol) was added at room temperature. The resultant reaction mixture was stirred at room temperature for 1 hour. The solution was filtered and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 30:1) to give the aldehyde **55** (68 mg, 70%) as yellow oil.

55: R_f = 0.62 (silica gel, petroleum ether/EtOAc = 3:1); $[\alpha]^{27}_{D}$ = −29.8 (c = 0.1 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 6.43 (t, J = 2.4 Hz, 1H), 5.67 (s, 1H), 2.88 (t, J = 9.3 Hz, 1H), 2.57 (dt, J = 14.1, 3.9 Hz, 1H), 2.34−2.13 (m, 4H), 2.08−1.83 (m, 5H), 1.73−1.61 (m, 1H), 1.53−1.25 (m, 4H), 1.08 (s, 3H), 1.00 (d, J = 6.8 Hz, 3H), 0.94 (d, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.0, 207.3, 179.0, 158.0, 122.3, 119.4, 62.1, 52.7, 51.9, 48.4, 44.3, 40.7, 40.7, 38.5, 35.8, 35.5, 30.6, 29.5, 25.4, 21.5, 15.6 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{21}H_{29}O_2^+$ 313.2168; found 313.2157.



56

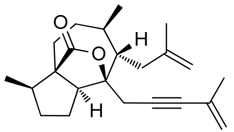


regioisomer of 56

To a vigorously degassed solution of aldehyde **55** (50 mg, 0.16 mmol) in THF (3 mL), MeOH (0.3 mL) and HMPA (1.6 mL), freshly prepared SmI_2 (3.2 mL, 0.32 mmol, 0.1 M in THF) was added dropwise at –78 ºC and stirred for 1 hour. The reaction was quenched with saturated aqueous NH_4Cl (5 mL), extracted with EtOAc (3 × 10 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 15:1) to give regioisomer of **56** (21 mg, 42%) as white solid and **56** (10 mg, 20%) as colorless oil.

Regioisomer of 56: R_f = 0.53 (silica gel, petroleum ether/EtOAc = 5:1); $[\alpha]^{25}_{D}$ = −27.1 (c = 0.35 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33−5.29 (m, 2H), 3.92 (d, J = 4.7 Hz, 1H), 3.03 (d, J = 20.1 Hz, 1H), 2.80 (d, J = 21.5 Hz, 1H), 2.31 (d, J = 17.5 Hz, 1H), 2.17 (dd, J = 9.1, 2.7 Hz, 1H), 2.10−2.06 (m, 1H), 2.03−1.96 (m, 3H), 1.83−1.76 (m, 1H), 1.71−1.63 (m, 3H), 1.58−1.52 (m, 2H), 1.51−1.46 (m, 1H), 1.36−1.31 (m, 1H), 1.28−1.23 (m, 1H), 1.20−1.17 (m, 1H), 1.15 (s, 3H), 1.07 (d, J = 5.8 Hz, 3H), 0.95 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.7, 141.4, 127.3, 74.2, 57.2, 56.5, 49.4, 44.1, 42.6, 42.5, 40.8, 39.1, 38.3, 34.9, 34.8, 34.6, 30.6, 25.2, 24.6, 22.9, 13.0 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{21}H_{31}O_2^+$ 315.2324; found 315.2316.

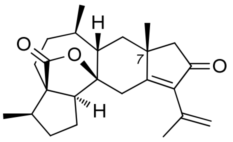
56: R_f = 0.49 (silica gel, petroleum ether/EtOAc = 3:1); $[\alpha]^{25}_{D}$ = +70.5 (c = 0.22 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (s, 1H), 3.71 (s, 1H), 2.54 (d, J = 2.6 Hz, 2H), 2.26 (d, J = 18.6 Hz, 1H), 2.18−2.10 (m, 3H), 2.00−1.91 (m, 2H), 1.82−1.67 (m, 2H), 1.59−1.38 (m, 5H), 1.31−1.18 (m, 6H), 1.04 (d, J = 6.3 Hz, 3H), 0.91 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.5, 187.3, 126.7, 74.5, 57.6, 52.0, 51.5, 43.8, 43.2, 41.7, 41.4, 39.8, 36.5, 34.9, 34.3, 34.0, 30.6, 24.3, 23.9, 23.3, 12.8 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{31}O_2^+$ 315.2324; found 315.2316.



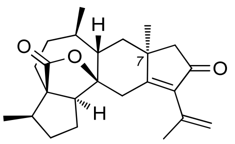
35

To a solution of $PdCl_2(PPh_3)_2$ (0.70 g, 1.0 mmol), CuI (1.58 g, 8.3 mmol) in THF (100 mL, degassed), 2-bromopropene (18.5 mL, 208 mmol) and Et_3N (4.6 mL, 33.2 mmol) was added. Upon completion of the addition, a solution of propargyl-substituted lactone **48** (2.5 g, 8.3 mmol) in THF (50 mL) was added dropwise. The resulted reaction mixture was then stirred for 4 hours at room temperature. The reaction mixture was poured into saturated aqueous NH_4Cl (100 mL) and EtOAc (100 mL), and extracted with EtOAc (3 × 100 mL). The extract was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 60:1) to give the PKR precursor **35** (2.25 g, 80%) as yellow oil.

35: $R_f = 0.26$ (silica gel, petroleum ether/EtOAc = 40:1); $[\alpha]^{25}_D = -56.6$ ($c = 0.53$ in MeOH); IR (film): ν_{max} = 2932, 2872, 1758, 1264, 731, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.19 (s, 1H), 5.14 (s, 1H), 4.79 (s, 1H), 4.75 (s, 1H), 2.74 (s, 2H), 2.57 (dd, J = 4.0, 10.8 Hz, 1H), 2.18−2.08 (m, 3H), 2.02−1.93 (m, 2H), 1.84−1.74 (m, 8H), 1.71−1.64 (m, 3H), 1.56−1.40 (m, 2H), 1.31−1.27 (m, 1H), 1.23 (d, J = 6.8 Hz, 3H), 1.02 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.4, 144.4, 127.0, 121.2, 112.4, 89.4, 85.1, 84.5, 59.6, 48.7, 48.2, 45.0, 40.4, 36.5, 34.3, 33.9, 29.9, 29.6, 25.4, 23.7, 22.5, 22.3, 13.3 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{23}H_{33}O_2^+$ 341.2475; found 341.2475.



59



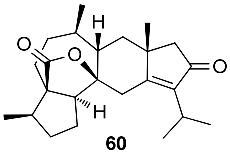
***epi*-59**

To a solution of compound **35** (1.80 g, 5.3 mmol) in anhydrous toluene (10 mL), $Co_2(CO)_8$ (1.99 g, 5.8 mmol) was added. The reaction mixture was stirred at 70 ºC for 12 hours. The reaction mixture was then concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 10:1) to give the lactone **59** (1.33 g, 68%) as white solid and **C-7 epimer of 59** (0.31 g, 16%) as colorless oil.

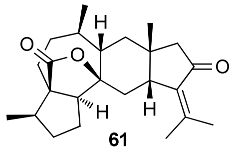
59: $R_f = 0.37$ (silica gel, petroleum ether/EtOAc = 5:1); $[\alpha]^{25}_D = +31.7$ ($c = 0.41$ in MeOH); IR (film): ν_{max} = 2957, 2931, 2872, 1760, 1699, 1457, 1242, 1189, 1145, 734, 703 cm^{-1}; ^1H

NMR (400 MHz, $CDCl_3$) δ 5.19 (s, 1H), 4.79 (s, 1H), 3.19 (d, J = 14.3 Hz, 1H), 2.71 (d, J = 14.4 Hz, 1H), 2.36–2.22 (m, 2H), 2.19–2.05 (m, 3H), 1.91 (s, 3H), 1.85–1.70 (m, 3H), 1.61–1.45 (m, 4H), 1.31–1.13 (m, 9H), 1.03 (d, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.9, 178.1, 173.9, 140.6, 136.5, 118.0, 90.0, 60.4, 51.2, 48.7, 47.6, 44.0, 42.9, 40.7, 38.2, 35.8, 34.4, 33.7, 31.8, 25.6, 25.1, 23.2, 21.3, 13.6 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{33}O_3^+$ 369.2424; found 369.2414.

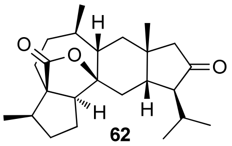
C-7 epimer of 59: R_f = 0.38 (silica gel, petroleum ether/EtOAc = 5:1); $[\alpha]^{25}_D$ = –93.3 (c = 0.60 in MeOH); IR (film): ν_{max} = 2956, 2936, 2870, 1760, 1698, 1455, 1240, 1189, 733, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.14–5.13 (m, 1H), 5.02 (s, 1H), 3.02 (d, J = 13.7 Hz, 1H), 2.65 (dd, J = 9.4, 6.0 Hz, 1H), 2.58 (d, J = 13.8 Hz, 1H), 2.38–2.27 (m, 2H), 2.14 (dd, J = 10.0, 4.3 Hz, 1H), 1.96–1.78 (m, 8H), 1.67–1.63 (m, 1H), 1.41–1.30 (m, 5H), 1.22 (d, J = 6.9 Hz, 3H), 1.18 (s, 3H), 1.13–1.08 (m, 1H), 0.98 (d, J = 5.7 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.1, 178.3, 175.4, 141.5, 136.5, 117.3, 90.6, 60.1, 50.6, 50.0, 49.8, 44.1, 42.4, 37.0, 35.7, 35.6, 35.5, 33.2, 32.6, 28.7, 25.6, 23.2, 22.3, 14.2 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{33}O_3^+$ 369.2424; found 369.2414.



60



61



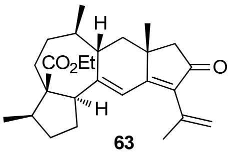
62

To a solution of compound **59** (22 mg, 0.06 mmol) in EtOAc (10 mL) was added Pd/C (10 mg). The reaction flask was vacuumed and backfilled with hydrogen (balloon pressure), the reaction mixture was stirred at room temperature for 10 minutes. The solution was filtered and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 10:1) to give the lactone **60** (8 mg, 36%) as white solid, lactone **61** (3 mg, 14%) as colorless oil and lactone **62** (6 mg, 27%) as white solid.

60: R_f = 0.45 (silica gel, petroleum ether/EtOAc = 5:1); $[\alpha]^{25}_D$ = –10.0 (c = 0.10 in MeOH); IR (film): ν_{max} = 2956, 2925, 2865, 1710, 1454, 1354, 1267, 1203, 1147, 993, 803, 768 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.02 (d, J = 14.4 Hz, 1H), 2.70 (d, J = 14.5 Hz, 1H), 2.67–2.63 (m, 1H), 2.32 (dd, J = 10.0, 5.8 Hz, 1H), 2.26 (d, J = 18.2 Hz, 1H), 2.17–2.04 (m, 3H), 1.88–1.83 (m, 3H), 1.79–1.73 (m, 1H), 1.68–1.58 (m, 4H), 1.56–1.50 (m, 1H), 1.25–1.21 (m, 11H), 1.15 (d, J = 6.9 Hz, 3H), 1.06 (d, J = 6.5 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.5, 178.3, 171.5, 142.4, 89.9, 60.6, 51.8, 48.9, 47.9, 43.8, 43.0, 40.3, 38.3, 36.2, 33.8, 33.6, 31.9, 25.9, 25.8, 25.4, 23.4, 21.1, 19.4, 13.9 ppm; HRMS (m/z): $[M + H]^+$ calcd for $C_{24}H_{35}O_3^+$ 371.2581; found 371.2574. CCDC 1589762 contains the supplementary crystallographic data for **60** (m.p. 110–112 °C) and is available free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Lactone 61: R_f = 0.48 (silica gel, petroleum ether/EtOAc = 5:1); $[\alpha]^{25}_D$ = –25.0 (*c* = 0.43 in MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.70 (d, *J* = 13.5 Hz, 1H), 2.53 (dd, *J* = 10.2, 5.4 Hz, 1H), 2.28–2.15 (m, 6H), 2.03-1.93 (m, 1H), 1.91–1.79 (m, 7H), 1.77–1.70 (m, 3H), 1.67–1.60 (m, 2H), 1.55–1.47 (m, 1H), 1.45–1.38 (m, 3H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.06–1.02 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6, 179.6, 151.4, 133.8, 88.8, 60.3, 53.8, 50.2, 48.7, 44.18, 43.9, 38.8, 38.7, 35.8, 35.5, 35.1, 33.4, 33.4, 27.0, 24.8, 24.4, 23.1, 21.0, 14.2 ppm; HRMS (m/z): $[M + H]^+$ calcd for $C_{24}H_{35}O_3^+$ 371.2581; found 371.2579.

Lactone 62: R_f = 0.52 (silica gel, petroleum ether/EtOAc = 5:1); $[\alpha]^{25}_D$ = +7.5 (*c* = 0.20 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (dd, *J* = 10.4, 5.0 Hz, 1H), 2.23–2.12 (m, 2H), 2.06 (d, *J* = 17.1 Hz, 1H), 2.01–1.81 (m, 7H), 1.80–1.62 (m, 3H), 1.62–1.59 (m, 1H), 1.58–1.52 (m, 1H), 1.51–1.42 (m, 1H), 1.37–1.26 (m, 3H), 1.23 (d, *J* = 6.6 Hz, 3H), 1.17 (s, 3H), 1.10–0.97 (m, 7H), 0.92 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 219.0, 178.9, 88.8, 60.7, 56.4, 54.5, 49.7, 48.2, 43.7, 39.3, 37.3, 36.1, 35.5, 33.3, 33.3, 32.6, 28.7, 25.8, 25.2, 23.2, 23.2, 20.8, 18.7, 13.6 ppm; HRMS (m/z): $[M + H]^+$ calcd for $C_{24}H_{37}O_3^+$ 373.2743; found 373.2737. CCDC 1903613 contains the supplementary crystallographic data for **62** (m.p. 108–110 °C) and is available free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

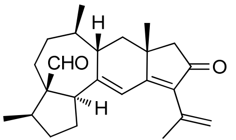


63

To a solution of **59** (1.25 g, 3.4 mmol) in HMPA (30 mL) was added DBU (2.54 mL, 17.0 mmol). The solution was stirred at room temperature for 30 minutes. CH_2Cl_2 (50 mL) and DIPEA (1.18 mL, 6.8 mmol) was then added. To this mixture a solution of $Et_3O^+BF_4^-$ in CH_2Cl_2 (6.8 mL, 6.8 mmol, 1.0 mol/L) was added dropwise. The reaction was allowed to stirred at room temperature for 1 hour. To the reaction mixture water (30 mL) was added and the mixture was extracted with EtOAc (3 × 50 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 30:1) to give the compound **63** (1.18 g, 88%) as colorless oil.

63: R_f = 0.41 (silica gel, petroleum ether/EtOAc = 10:1); $[\alpha]^{25}_D$ = –103.8 (*c* = 0.52 in MeOH); IR (film): ν_{max} = 2957, 2931, 2870, 1763, 1692, 1450, 1240, 733, 710 cm^{-1}; ^{1}H NMR (400

MHz, $CDCl_3$) δ 6.51 (s, 1H), 5.14 (t, J = 1.6 Hz, 1H), 4.92 (s, 1H), 4.18 (dq, J = 10.9, 7.1 Hz, 1H), 3.94 (dq, J = 10.9, 7.1 Hz, 1H), 2.86 (t, J = 9.2 Hz, 1H), 2.47 (d, J = 13.5 Hz, 1H), 2.31–2.08 (m, 4H), 1.95–1.74 (m, 7H), 1.80 (dt, J = 12.5, 4.6 Hz, 1H), 1.67–1.61 (m, 2H), 1.40–1.34 (m, 2H), 1.20 (t, J = 7.1 Hz, 4H), 1.03 (s, 3H), 0.93 (d, J = 6.1 Hz, 3H), 0.89 (d, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.2, 173.8, 171.6, 158.7, 137.1, 134.1, 118.1, 116.8, 60.1, 59.2, 54.4, 51.5, 48.5, 44.1, 40.7, 39.2, 38.6, 38.6, 35.8, 30.7, 30.2, 25.1, 22.4, 21.3, 16.0, 14.4 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{37}O_3^+$ 397.2737; found 397.2724.

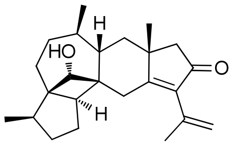


34

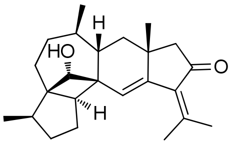
To a solution of compound **63** (1.19 g, 3.0 mmol) in CH_2Cl_2 (50 mL), a solution of DIBAL-H (15.0 mL, 15.0 mmol, 1.0 mol/L) was added dropwise at 0 °C. The reaction mixture was allowed to stirred at the same temperature for 1 hour. The reaction was quenched with 3N NaOH solution (30 mL) and was extracted with CH_2Cl_2 (3 × 30 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude diol was used in the next step directly.

The above-obtained crude diol was dissolved in CH_2Cl_2, TPAP (158 mg, 0.45 mmol) and NMO (1.41 g, 12.0 mmol) was added at room temperature. The resultant reaction mixture was stirred at room temperature for 1 hour. The solution was filtered and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 30:1) to give the aldehyde **34** (784 mg, 74%) as yellow oil.

34: R_f = 0.40 (silica gel, petroleum ether/EtOAc = 10:1); $[\alpha]^{25}_D$ = –78.0 (c = 0.41 in MeOH); IR (film): ν_{max} = 2857, 2831, 1763, 1741, 1450, 1431, 1244, 1220, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 6.55 (t, J = 2.4 Hz, 1H), 5.14 (s, 1H), 4.91 (s, 1H), 2.88 (t, J = 9.3 Hz, 1H), 2.55 (dt, J = 14.0, 3.8 Hz, 1H), 2.29 (d, J = 17.5 Hz, 1H), 2.25–2.18 (m, 2H), 2.14 (d, J = 17.5 Hz, 1H), 2.03–1.92 (m, 6H), 1.90–1.82 (m, 2H), 1.68–1.62 (m, 1H), 1.53–1.42 (m, 1H), 1.39–1.28 (m, 3H), 1.04 (s, 3H), 0.98 (d, J = 6.7 Hz, 3H), 0.92 (d, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.3, 206.1, 171.0, 157.1, 137.0, 134.5, 118.7, 116.9, 61.9, 52.9, 51.5, 48.3, 44.1, 40.7, 38.7, 38.4, 35.7, 35.4, 30.5, 29.5, 25.4, 22.3, 21.4, 15.5 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{33}O_2^+$ 353.2475; found 353.2472.



64

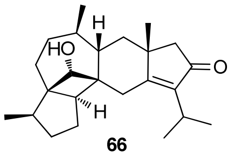


65

To a vigorously degassed solution of aldehyde **34** (550 mg, 1.56 mmol) in THF (26 mL), MeOH (1.5 mL) and HMPA (7.7 mL), freshly prepared SmI_2 (31 mL, 3.12 mmol, 0.1 M in THF) was added dropwise at –78 ºC and stirred for 1 hour. The reaction was quenched with saturated aqueous NH_4Cl (10 mL), extracted with EtOAc (3 × 30 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 15:1) to give **64** (123 mg, 22%) as white solid and **65** (232 mg, 42%) as yellow oil. The stereochemical assignment of the C-18 hydroxyl group was based on our previous studies of a similar substrate[2].

64: $R_f = 0.26$ (silica gel, petroleum ether/EtOAc = 10:1); $[\alpha]^{25}_D = +122.2$ ($c = 0.18$ in MeOH); IR (film): ν_{max} = 2952, 2877, 2362, 2322, 1690, 1684, 1507, 1263, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.17 (s, 1H), 4.77 (s, 1H), 3.69 (s, 1H), 2.74 (d, J = 14.6 Hz, 1H), 2.44 (d, J = 14.6 Hz, 1H), 2.28 (d, J = 18.4 Hz, 1H), 2.18–2.12 (m, 2H), 2.10–2.05 (m, 1H), 1.97–1.93 (m, 5H), 1.78–1.70 (m, 3H), 1.58–1.54 (m, 1H), 1.48–1.40 (m, 2H), 1.32–1.27 (m, 2H), 1.24 (s, 3H), 1.21–1.14 (m, 1H), 1.05 (d, J = 6.3 Hz, 3H), 0.99–0.94 (m, 1H), 0.91 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6, 178.8, 139.4, 137.3, 117.2, 74.7, 57.6, 52.2, 51.9, 43.1, 41.9, 41.5, 41.3, 39.6, 36.5, 35.0, 34.1, 32.5, 30.7, 25.3, 24.2, 23.2, 21.8, 12.9 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{24}H_{35}O_2^+$ 355.2632; found 355.2622.

65: $R_f = 0.49$ (silica gel, petroleum ether/EtOAc = 10:1); $[\alpha]^{25}_D = +4.4$ ($c = 0.49$ in MeOH); IR (film): ν_{max} = 2950, 2355, 2300, 1678, 1638, 1480, 1255, 764 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.42 (s, 1H), 3.97 (d, J = 4.5 Hz, 1H), 2.31 (s, 3H), 2.24 (s, 1H), 2.17 (dd, J = 9.1, 1.7 Hz, 1H), 2.09–2.05 (m, 4H), 1.97 (d, J = 9.6 Hz, 2H), 1.82–1.76 (m, 1H), 1.69–1.66 (m, 1H), 1.54–1.46 (m, 3H), 1.41 (s, 3H), 1.33–1.25 (m, 3H), 1.07–1.04 (m, 6H), 0.97–0.92 (m, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.3, 149.4, 145.7, 130.8, 129.0, 74.4, 57.2, 56.1, 49.9, 44.4, 42.5, 38.7, 38.5, 37.9, 34.9, 34.8, 34.7, 30.6, 26.5, 25.5, 24.6, 22.8, 21.9, 13.0 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{24}H_{35}O_2^+$ 355.2632; found 355.2623. The stereochemical assignment of the C-18 hydroxyl group was based on our previous studies of a similar substrate[2].

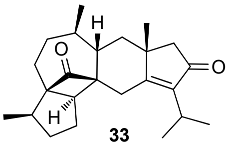


66

From 64 to enone 66: A flame-dried flask was charged with compound **64** (120 mg, 0.34 mmol) and Crabtree's catalyst (24 mg) in CH_2Cl_2 (5 mL). The flask was vacuumed and backfilled with hydrogen (balloon pressure) and the reaction mixture was stirred at room temperature for 1 hour. The solution was evaporated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 20:1) to give **66** (118 mg, 98%) as white solid.

From 65 to enone 66: To a solution of compound **65** (230 mg, 0.65 mmol) in ethyl acetate (20 mL) was added Pd/C (115 mg). The flask was vacuumed and backfilled with hydrogen (balloon pressure), the reaction mixture was stirred at room temperature for 1 hour. The solution was filtered and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 20:1) to give **66** (192 mg, 83%) as white solid.

66: $R_f = 0.28$ (silica gel, petroleum ether/EtOAc = 10:1); $[\alpha]^{25}_D = +56.3$ ($c = 0.16$ in MeOH); IR (film): ν_{max} = 3750, 3745, 2957, 2361, 2322, 1698, 1558, 1507, 1275, 764 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 1H), 2.65 (dt, J = 13.9, 6.9 Hz, 1H), 2.55 (d, J = 14.6 Hz, 1H), 2.38 (d, J = 14.6 Hz, 1H), 2.18 (d, J = 18.2 Hz, 1H), 2.16–2.07 (m, 4H), 2.03–1.93 (m, 2H), 1.82–1.76 (m, 1H), 1.72–1.66 (m, 1H), 1.57–1.38 (m, 5H), 1.32–1.23 (m, 2H), 1.19–1.17 (m, 6H), 1.13 (d, J = 6.9 Hz, 3H), 1.04 (d, J = 6.3 Hz, 3H), 0.93 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.2, 176.2, 140.8, 74.8, 57.6, 52.3, 51.5, 42.6, 41.9, 41.5, 40.7, 39.5, 36.4, 35.0, 34.1, 31.4, 30.7, 25.7, 25.4, 24.2, 23.2, 21.1, 19.7, 12.9 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{24}H_{37}O_2^+$ 357.2788; found 357.2777.

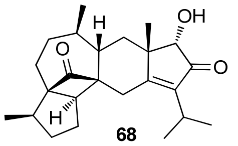


33

Under argon atmosphere, compound **66** (250 mg, 0.70 mmol) was dissolved in CH_2Cl_2 (25 mL), NMO (328 mg, 2.8 mmol) and TPAP (37 mg, 0.105 mmol) was added at room temperature. The resulting reaction mixture was stirred at room temperature for 1 hour. The mixture was then filtered and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 20:1) to give the diketone **33** (244 mg, 98%) as colorless oil.

33: $R_f = 0.44$ (silica gel, petroleum ether/EtOAc = 10:1); $[\alpha]^{25}_D = +148.8$ ($c = 0.43$ in MeOH); IR (film): ν_{max} = 3870, 3745, 3724, 2985, 2931, 2874, 2361, 2329, 1759, 1671, 1457, 764 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.66–2.59 (m, 2H), 2.43 (d, J = 15.0 Hz, 1H), 2.35 (d, J

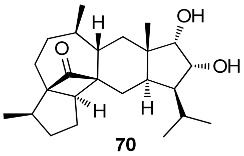
= 9.1 Hz, 1H), 2.21 (d, *J* = 18.1 Hz, 1H), 2.10–2.05 (m, 2H), 1.92–1.83 (m, 2H), 1.73–1.44 (m, 6H), 1.33–1.27 (m, 2H), 1.25–1.12 (m, 14H), 1.00 (d, *J* = 6.0 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 220.0, 207.3, 173.4, 142.1, 77.4, 67.5, 52.3, 43.2, 42.3, 42.1, 41.1, 40.7, 36.4, 35.1, 34.4, 26.9, 25.8, 25.7, 25.3, 23.6, 22.5, 21.2, 19.6, 13.6 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{35}O_2^+$ 355.2632; found 355.2625.



68

To a solution of compound **33** (244 mg, 0.69 mmol) in THF (25 mL), a solution of NaHMDS (2.61 mL, 2.61 mmol, 1.0 mol/L in THF) was added dropwise at –78 °C. The reaction mixture was stirred at the same temperature for 6 minutes. To this mixture a solution of (±)-3-phenyl-2-(phenylsulfonyl)-1,2-oxaziridine (721 mg, 2.76 mmol) in THF (3.0 mL) was added and the resulting mixture was stirred at –78 °C for 30 minutes. The reaction was quenched with saturated aqueous NH_4Cl (10 mL) and the mixture was extracted with EtOAc (3 × 20 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 15:1) to give the compound **68** (251 mg, 99%) as white solid.

68: *R*$_f$ = 0.68 (silica gel, petroleum ether/EtOAc = 6:1); $[\alpha]^{25}_D$ = +103.8 (*c* = 0.26 in MeOH); IR (film): ν_{max} = 3750, 3735, 2361, 2322, 1699, 1558, 1262, 764 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 3.61 (d, *J* = 2.6 Hz, 1H), 3.22 (d, *J* = 2.7 Hz, 1H), 2.69–2.60 (m, 2H), 2.49 (d, *J* = 15.0 Hz, 1H), 2.38 (d, *J* = 9.0 Hz, 1H), 1.96 (dd, *J* = 2.6, 13.7 Hz, 1H), 1.93–1.82 (m, 2H), 1.73–1.68 (m, 2H), 1.66–1.53 (m, 4H), 1.45 (d, *J* = 13.3 Hz, 1H), 1.40 (s, 1H), 1.33–1.27 (m, 2H), 1.25–1.23 (m, 6H), 1.15–1.11 (m, 6H), 1.01 (d, *J* = 6.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 220.0, 208.0, 174.8, 139.6, 79.0, 77.5, 68.2, 43.9, 42.7, 42.4, 41.2, 36.3, 35.3, 35.1, 34.6, 26.9, 25.7, 25.4, 25.3, 24.0, 22.7, 21.2, 19.7, 13.6 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{35}O_3^+$ 371.2581; found 371.2575.

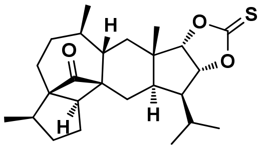


70

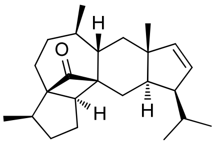
To a solution of compound **68** (150 mg, 0.40 mmol) in MeOH (15 mL) was added $CeCl_3$•$7H_2O$ (166 mg, 0.45 mmol) and $NaBH_4$ (30 mg, 0.80 mmol) at 0 °C,. The reaction mixture was stirred at room temperature for 1 hour. The reaction was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with EtOAc (3 × 10 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude compound **69** was used in next step directly.

The crude compound **69** and Crabtree's catalyst (30 mg) in CH_2Cl_2 (5 mL) was stirred at room temperature for 1 hour under pressured hydrogen (500 psi) in a Parr apparatus. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 6:1) to give the **70** (118 mg, 79%) as white solid.

70: R_f = 0.31 (silica gel, petroleum ether/EtOAc = 4:1); $[\alpha]^{25}_D$ = –11.8 (c = 0.17 in MeOH); IR (film): ν_{max} = 3758, 3755, 2362, 2322, 1717, 1558, 1507, 1276, 1261, 764, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.23 (s, 1H), 3.56 (d, J = 4.5 Hz, 1H), 2.84 (s, 1H), 2.52 (s, 1H), 2.45 (d, J = 8.8 Hz, 1H), 2.12–2.05 (m, 1H), 1.87–1.80 (m, 2H), 1.74 (dd, J = 8.1, 13.4 Hz, 1H), 1.67–1.54 (m, 8H), 1.49–1.39 (m, 2H), 1.35–1.23 (m, 4H), 1.12 (d, J = 6.8 Hz, 3H), 0.98–0.92 (m, 9H), 0.78 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 223.2, 78.9, 77.2, 75.9, 66.8, 54.6, 45.4, 42.2, 42.0, 40.5, 39.1, 36.5, 36.2, 35.3, 34.7, 29.4, 27.0, 25.4, 24.4, 22.6, 22.0, 21.9, 18.9, 13.5 ppm; HRMS (m/z): $[M+H]^+$ calcd for $C_{24}H_{39}O_3^+$ 375.2894; found 375.2888. CCDC 1589763 contains the supplementary crystallographic data for **70** (m.p. 128–130 °C) and is available free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



The cyclic thionocarbonate



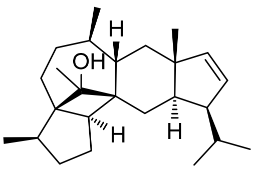
71

To a solution of compound **70** (80 mg, 0.21 mmol) in toluene (20 mL), was added thiocarbonyl diimidazole (374 mg, 2.1 mmol) at rt. The reaction mixture was refluxed and stirred for 48 hours and then cooled to room temperature. 1M HCl solution (10 mL) and EtOAc (10 mL) was added to the reaction mixture and it was extracted with EtOAc (3 × 10 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 20:1) to give the corresponding cyclic thionocarbonate (70 mg, 80%) as white solid.

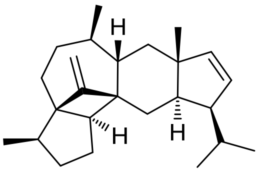
The cyclic thionocarbonate: R_f = 0.39 (silica, petroleum ether/EtOAc = 10:1); $[\alpha]^{25}_D$ = +15.4 (c = 0.13 in MeOH); IR (film): ν_{max} = 3750, 3735, 2362, 2322, 1558, 1507, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.29 (d, J = 6.5 Hz, 1H), 4.76 (d, J = 6.5 Hz, 1H), 2.45 (d, J = 9.0 Hz, 1H), 1.89–1.82 (m, 4H), 1.74–1.53 (m, 9H), 1.37–1.16 (m, 5H), 1.12 (d, J = 6.8 Hz, 3H), 0.99–0.95 (m, 9H), 0.89 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.7, 192.0, 92.6, 90.1, 76.5, 66.0, 55.3, 45.9, 42.3, 42.0, 40.3, 36.8, 36.2, 35.3, 34.5, 27.9, 26.9, 25.2, 24.2, 22.5, 22.2, 22.1, 18.9, 13.5 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{37}O_3^+$ 417.2458; found 417.2449.

A solution of the cyclic thionocarbonate (70 mg, 0.17 mmol) and $P(OCH_3)_3$ (10 mL) was refluxed and stirred for 48 hours. The reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography (petroleum ether/EtOAc = 100:1) to give the alkene **71** (53 mg, 93%) as white solid.

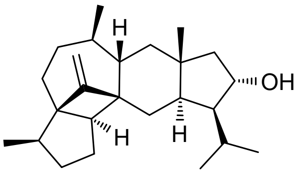
71: R_f = 0.29 (silica gel, petroleum ether/EtOAc = 50:1); $[\alpha]^{25}_D$ = –66.7 (*c* = 0.18 in MeOH); IR (film): ν_{max} = 3750, 3735, 2956, 2931, 2869, 2362, 2329, 1759, 1507, 1457, 1262, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (d, *J* = 6.0 Hz, 1H), 5.81 (dd, *J* = 2.8, 5.9 Hz, 1H), 2.42 (d, *J* = 8.5 Hz, 1H), 2.05–1.99 (m, 1H), 1.94 (dd, *J* = 3.5, 12.6 Hz, 1H), 1.90–1.80 (m, 2H), 1.77–1.59 (m, 8H), 1.57–1.50 (m, 1H), 1.48–1.41 (m, 1H), 1.34–1.19 (m, 4H), 1.15 (d, *J* = 6.8 Hz, 3H), 0.98–0.95 (m, 6H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 223.0, 142.6, 133.9, 75.4, 67.7, 54.5, 46.8, 46.4, 43.9, 42.0, 41.3, 40.6, 36.4, 35.4, 34.9, 29.9, 27.1, 25.3, 23.7, 22.8, 22.7, 22.6, 22.5, 13.5 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{37}O^+$ 341.2839; found 341.2833.



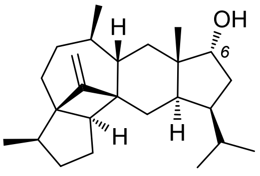
The tertiary alcohol



The diene



Astellatol, 1



The C-6 regioisomer

To a solution of alkene **71** (50 mg, 0.15 mmol) in THF (10 mL), MeLi (0.75 mL, 0.75 mmol, 1.0 mol/L in Et_2O) was added dropwise at room temperature. The reaction mixture was then stirred at 50 ºC for 1 hour, and then re-cooled to 0 ºC before it was quenched with saturated aqueous NH_4Cl (5 mL). The mixture was extracted with ethyl acetate (3 × 10 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 40:1) to give the corresponding tertiary alcohol (46 mg, 88%) as colorless oil.

The tertiary alcohol: R_f = 0.44 (silica gel, petroleum ether/EtOAc = 20:1); $[\alpha]^{25}_D$ = –100.0 (*c* = 0.14 in MeOH); IR (film): ν_{max} = 3750, 3745, 2953, 2870, 2361, 2322, 1699, 1569, 1521, 1276, 1262, 764, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (d, *J* = 5.9 Hz, 1H), 5.80 (dd, *J* = 5.8, 2.8 Hz, 1H), 2.19–2.08 (m, 3H), 2.04–1.98 (m, 2H), 1.90 (t, *J* = 10.0 Hz, 2H), 1.75–1.64 (m, 5H), 1.56–1.49 (m, 3H), 1.40 (s, 3H), 1.29–1.24 (m, 1H), 1.20–1.14 (m, 1H), 1.10 (d, *J* = 6.7 Hz, 3H), 1.02 (d, *J* = 5.8 Hz, 4H), 0.97 (d, *J* = 6.4 Hz, 3H), 0.93 (s, 3H), 0.84 (d, *J* =

6.7 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 143.0, 134.0, 79.5, 59.5, 54.9, 50.2, 46.9, 46.0, 45.9, 42.8, 42.1, 40.7, 36.5, 35.9, 35.6, 35.2, 30.0, 25.9, 24.7, 23.9, 23.8, 23.6, 22.7, 22.6, 14.6 ppm; HRMS (*m/z*): $[M–H_2O+H]^+$ calcd for $C_{25}H_{39}^+$ 339.3046; found 339.3039.

To a solution of the above-obtained tertiary alcohol (25 mg, 0.07 mmol) in CH_2Cl_2 (6 mL) was added pyridine (0.03 mL, 0.35 mmol) and $SOCl_2$ (0.015 mL, 0.21 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 1 hour and quenched with saturated aqueous $NaHCO_3$ (2 mL). The mixture was extracted with CH_2Cl_2 (3 × 10 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether) to give the corresponding diene (17 mg, 71%) as colorless oil.

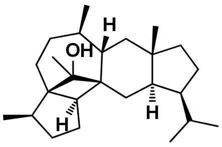
The diene: R_f = 1.0 (silica gel, petroleum ether); $[\alpha]^{25}_D$ = –70.6 (*c* = 0.17 in MeOH); IR (film): ν_{max} = 1275, 1262, 760, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 5.85 (d, *J* = 6.0 Hz, 1H), 5.80 (dd, *J* = 2.7, 5.8 Hz, 1H), 4.86 (s, 1H), 4.66 (s, 1H), 2.15–2.13 (m, 1H), 2.03–2.00 (m, 1H), 1.86 (dd, *J* = 3.6, 12.5 Hz, 1H), 1.77–1.75 (m, 1H), 1.73–1.69 (m, 2H), 1.67–1.62 (m, 3H), 1.60–1.58 (m, 1H), 1.54–1.52 (m, 2H), 1.51–1.46 (m, 2H), 1.44–1.36 (m, 3H), 1.22–1.14 (m, 2H), 1.02 (d, *J* = 6.5 Hz, 3H), 0.98 (s, 3H), 0.96 (d, *J* = 2.7 Hz, 3H), 0.94 (d, *J* = 2.6 Hz, 3H), 0.84 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 161.5, 143.0, 133.9, 102.6, 59.4, 54.5, 50.5, 47.6, 47.2, 46.5, 44.8, 42.8, 41.6, 37.2, 35.2, 34.4, 31.3, 30.1, 27.1, 25.0, 23.8, 23.4, 22.8, 22.6, 13.5 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{39}^+$ 339.3046; found 339.3033.

Astellatol 1: To a solution of the above-obtained diene (15 mg, 0.044 mmol) in THF (2 mL) at 0 °C was added BH_3•Me_2S (0.07 mL, 0.066 mmol, 1.0 mol/L in THF) dropwise. The reaction mixture was stirred at room temperature for 30 minutes and then cooled to 0 °C. To this mixture MeOH (0.1 mL), aqueous NaOH (3N, 1 mL) and aqueous H_2O_2 (30 wt%, 1 mL) were added dropwise. The reaction mixture was stirred at 55 °C for 30 min and was cooled to room temperature. The reaction was quenched with saturated aqueous NH_4Cl (5 mL). The mixture was extracted with EtOAc (3 × 10 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 15:1) to give **astellatol 1** (8.7 mg, 56%) as colorless oil and the **C-6 regioisomer** (2.4 mg, 15%) as colorless oil.

Astellatol 1: R_f = 0.43 (silica gel, petroleum ether/EtOAc = 10:1); $[\alpha]^{25}_D$ = +7.9 (*c* = 0.63 in MeOH); IR (film): ν_{max} = 3750, 3735, 2928, 2856, 2362, 2329, 1558, 1541, 1507, 1276, 1261, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 4.80 (s, 1H), 4.64 (s, 1H), 4.29 (ddd, *J* = 4.2, 7.4, 8.6 Hz, 1H), 2.10 (d, *J* = 8.7 Hz, 1H), 1.97 (dd, *J* = 11.5, 7.1 Hz, 1H), 1.77 (dd, *J* = 12.9, 3.2 Hz, 2H), 1.71–1.58 (m, 5H), 1.56–1.46 (m, 4H), 1.44–1.32 (m, 4H), 1.20–1.10 (m, 2H), 1.08–1.03

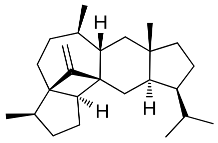
(m, 1H), 1.00 (d, *J* = 6.4, 3H), 0.98 (d, *J* = 8.0 Hz, 3H), 0.98 (d, *J* = 8.0 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.84 (t, *J* = 12.0 Hz, 1H), 0.83 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 102.1, 77.4, 59.5, 57.1, 50.7, 49.8, 46.0, 45.2, 44.5, 43.5, 42.6, 41.7, 36.9, 35.0, 33.9, 31.0, 29.7, 27.0, 24.9, 24.0, 23.0, 21.9, 20.1, 13.2 ppm; HRMS (*m/z*): $[M–H_2O+H]^+$ calcd for $C_{25}H_{39}^+$ 339.3046; found 339.3043.

The C-6 regioisomer: R_f = 0.50 (silica gel, petroleum ether/EtOAc = 10:1); $[\alpha]^{25}_{D}$ = –50.0 (*c* = 0.1 in MeOH); IR (film): ν_{max} = 3745, 3724, 2950, 2928, 2871, 2363, 2322, 1558, 1541, 1507, 1457, 1275, 1261, 764, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.84 (s, 1H), 4.66 (s, 1H), 3.73 (d, *J* = 5.0 Hz, 1H), 2.15–2.13 (m, 1H), 1.97–1.91 (m, 1H), 1.80–1.66 (m, 6H), 1.64–1.63 (m, 1H), 1.59–1.54 (m, 4H), 1.53–1.47 (m, 3H), 1.46–1.38 (m, 3H), 1.19–1.14 (m, 2H), 1.02 (d, *J* = 6.5 Hz, 3H), 0.96–0.94 (m, 6H), 0.83–0.80 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 102.4, 80.0, 59.8, 49.8, 46.6, 46.1, 45.2, 44.8, 42.8, 40.6, 38.0, 37.4, 36.5, 35.2, 34.2, 31.3, 30.8, 27.3, 25.2, 24.3, 23.3, 22.5, 19.5, 13.5 ppm; HRMS (*m/z*): $[M–H_2O+H]^+$ calcd for $C_{25}H_{39}^+$ 339.3046; found 339.3041.



To a solution of the tertiary alcohol (6.1 mg, 0.017 mmol) in MeOH (1 mL) was added PtO_2 (1 mg). The flask was vacuumed and backfilled with hydrogen (balloon pressure), the reaction mixture was stirred at room temperature for 1 hour. The solution was filtered and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 10:1) to give the product (5.7 mg, 94%) as colorless oil.

R_f = 0.44 (silica gel, petroleum ether/EtOAc = 20:1); $[\alpha]^{25}_{D}$ = –65.0 (*c* = 0.12 in MeOH); ^1H NMR (400 MHz, $CDCl_3$) δ 2.27–2.17 (m, 1H), 2.16–2.06 (m, 3H), 2.06–1.86 (m, 4H), 1.80–1.67 (m, 3H), 1.49–1.43 (m, 3H), 1.38 (s, 3H), 1.34–1.25 (m, 7H), 1.19–1.15 (m, 1H), 1.10 (d, *J* = 6.5 Hz, 3H), 1.01 (d, *J* = 5.4 Hz, 3H), 0.95 (d, *J* = 5.6 Hz, 3H), 0.93–0.87 (m, 2H), 0.82 (d, *J* = 5.8 Hz, 3H), 0.78 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 79.6, 59.9, 49.9, 47.3, 46.7, 46.0, 45.4, 42.1, 41.2, 41.0, 40.2, 36.5, 36.0, 35.4, 35.4, 31.5, 28.4, 26.8, 24.7, 24.1, 23.8, 23.7, 22.7, 19.1, 14.6 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{43}O_3^+$ 359.3314; found 359.3303.



Astellatene, 2

To a solution of the above-obtained tertiary alcohol (5 mg, 0.014 mmol) in CH_2Cl_2 (2 mL) was added pyridine (6 μL, 0.07 mmol) and $SOCl_2$ (3 μL, 0.042 mmol) at 0 ºC. The reaction mixture was stirred at 0 ºC for 1 hour and quenched with saturated aqueous $NaHCO_3$ (1 mL). The mixture was extracted with CH_2Cl_2 (3 × 5 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether) to give the **astellatene 2** (2.9 mg, 62%) as colorless oil.

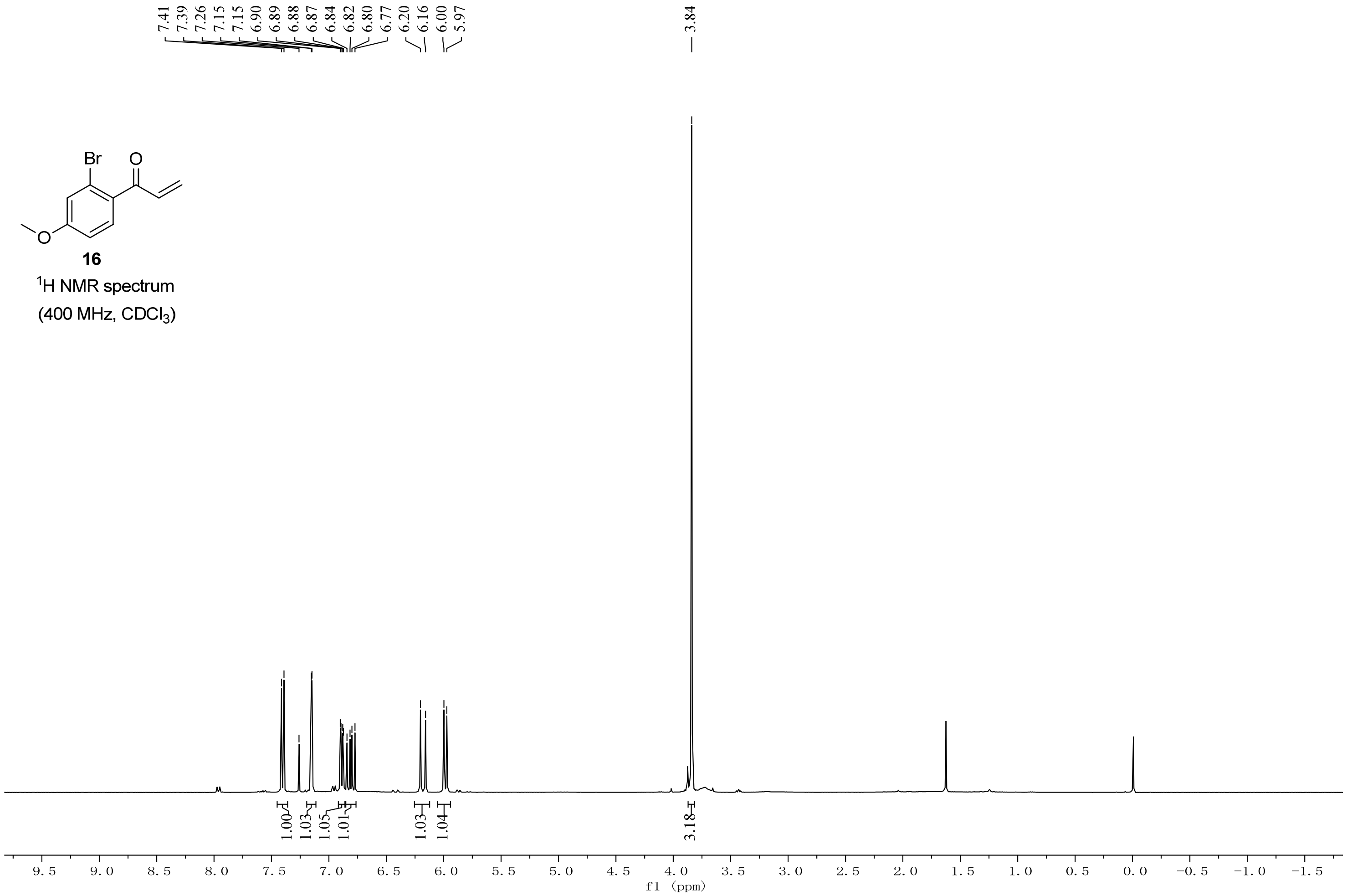
astellatene 2: R_f = 1.0 (silica, petroleum ether); $[\alpha]^{25}_D = -2.0$ (*c* = 0.1 in benzene); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.83 (s, 1H), 4.64 (s, 1H), 2.09 (d, *J* = 7.4 Hz, 1H), 1.84–1.74 (m, 3H), 1.73–1.56 (m, 5H), 1.54–1.40 (m, 7H), 1.40–1.36 (m, 1H), 1.35–1.31 (m, 1H), 1.22–1.16 (m, 2H), 1.09–1.06 (m, 1H), 1.05–0.99 (m, 4H), 0.94 (d, J = 4.3 Hz, 6H), 0.82 (s, 6H), 0.77–0.72 (m, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.7, 102.1, 59.5, 50.0, 46.8, 46.7, 46.6, 44.7, 44.1, 42.7, 41.5, 41.1, 37.1, 35.1, 34.1, 31.3, 31.2, 29.7, 28.0, 27.8, 24.9, 24.1, 23.1, 19.0, 13.4 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{41}^+$ 341.3208; found 341.3200.

II. References

1. Marx, J. N. & Norman, L. R. Synthesis of (–)-acorone and related spirocyclic sesquiterpenes. *J. Org. Chem.* **40,** 1602–1606 (1975).
2. Zhao, N., Xie, S., Chen, G. & Xu, J. Concise synthesis of astellatol core skeleton. *Chem. Eur. J.* **22,** 12634–12636 (2016).

The above references have also been cited in the manuscript main text.

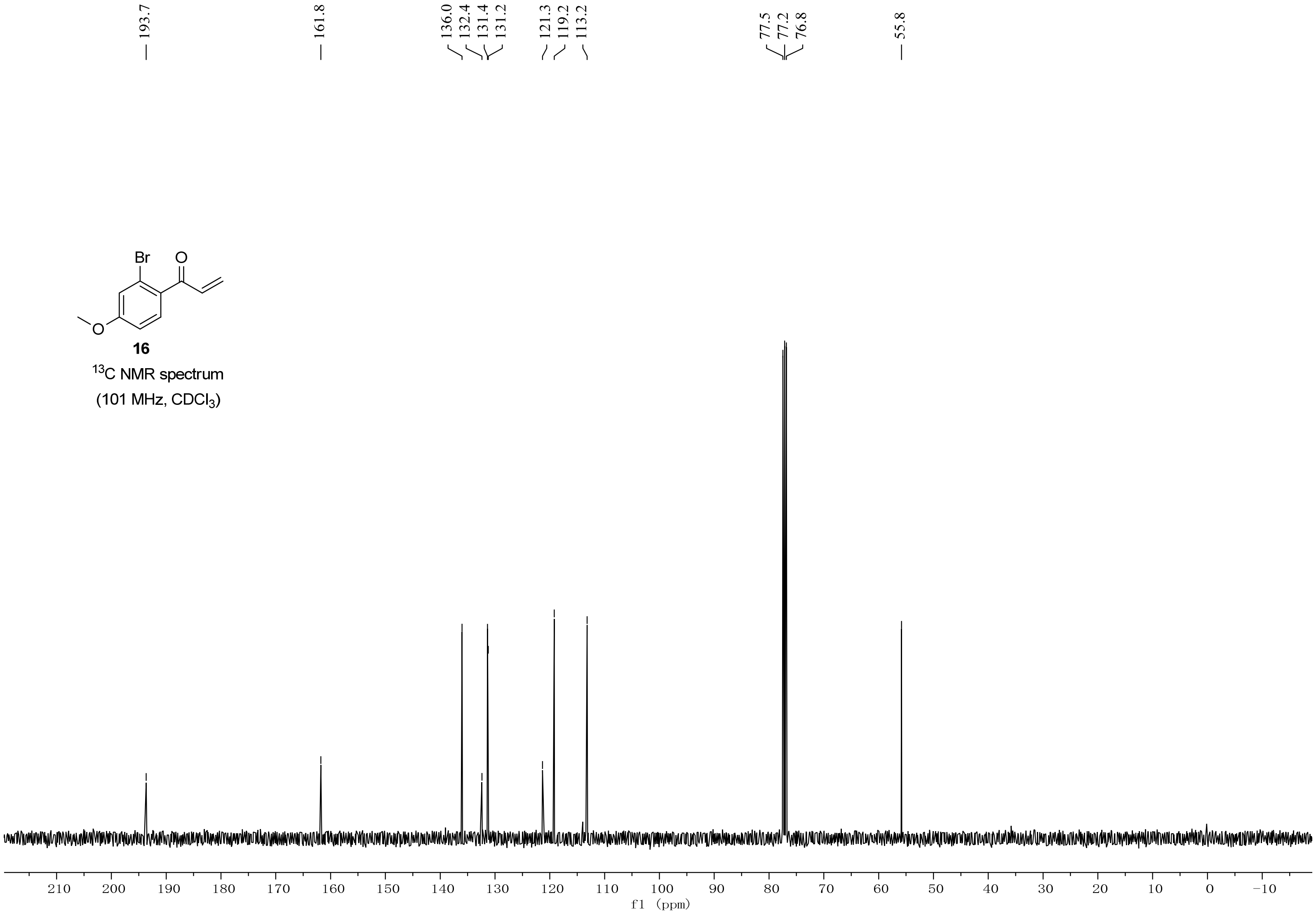
III. ^{1}H and ^{13}C NMR Spectra of compounds



16

^{1}H NMR spectrum

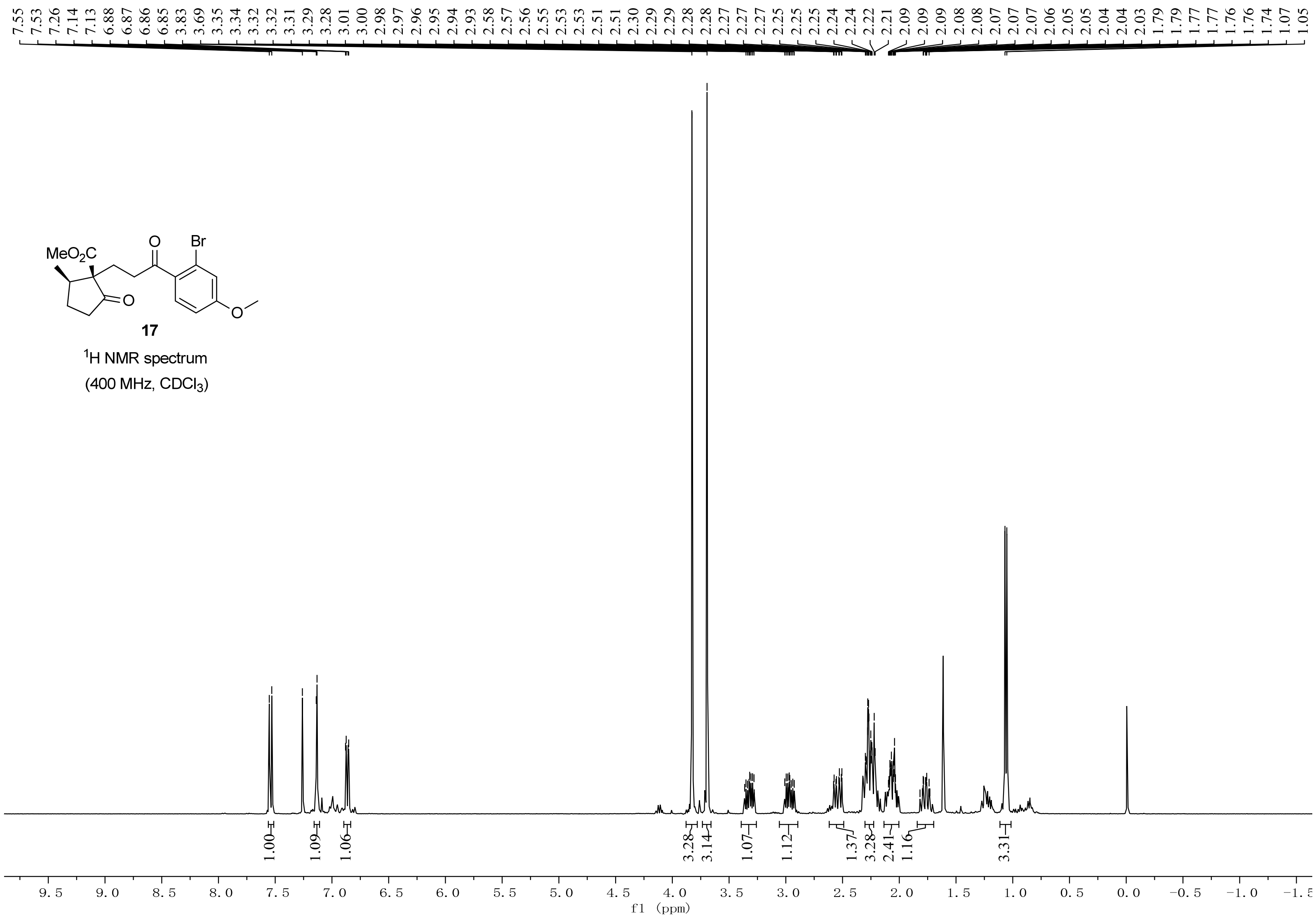
(400 MHz, $CDCl_3$)



16

^{13}C NMR spectrum

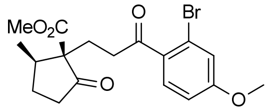
(101 MHz, $CDCl_3$)



17

^{1}H NMR spectrum

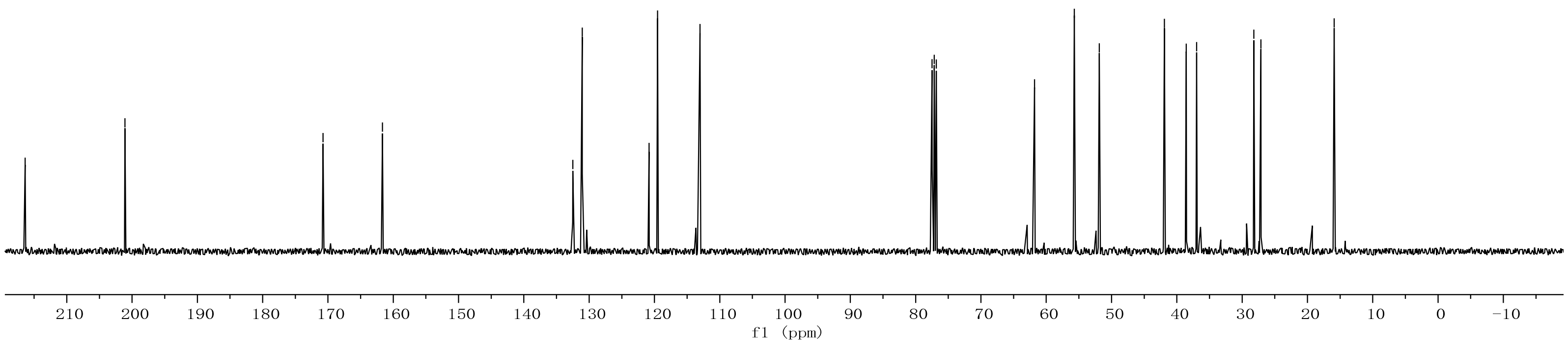
(400 MHz, $CDCl_3$)

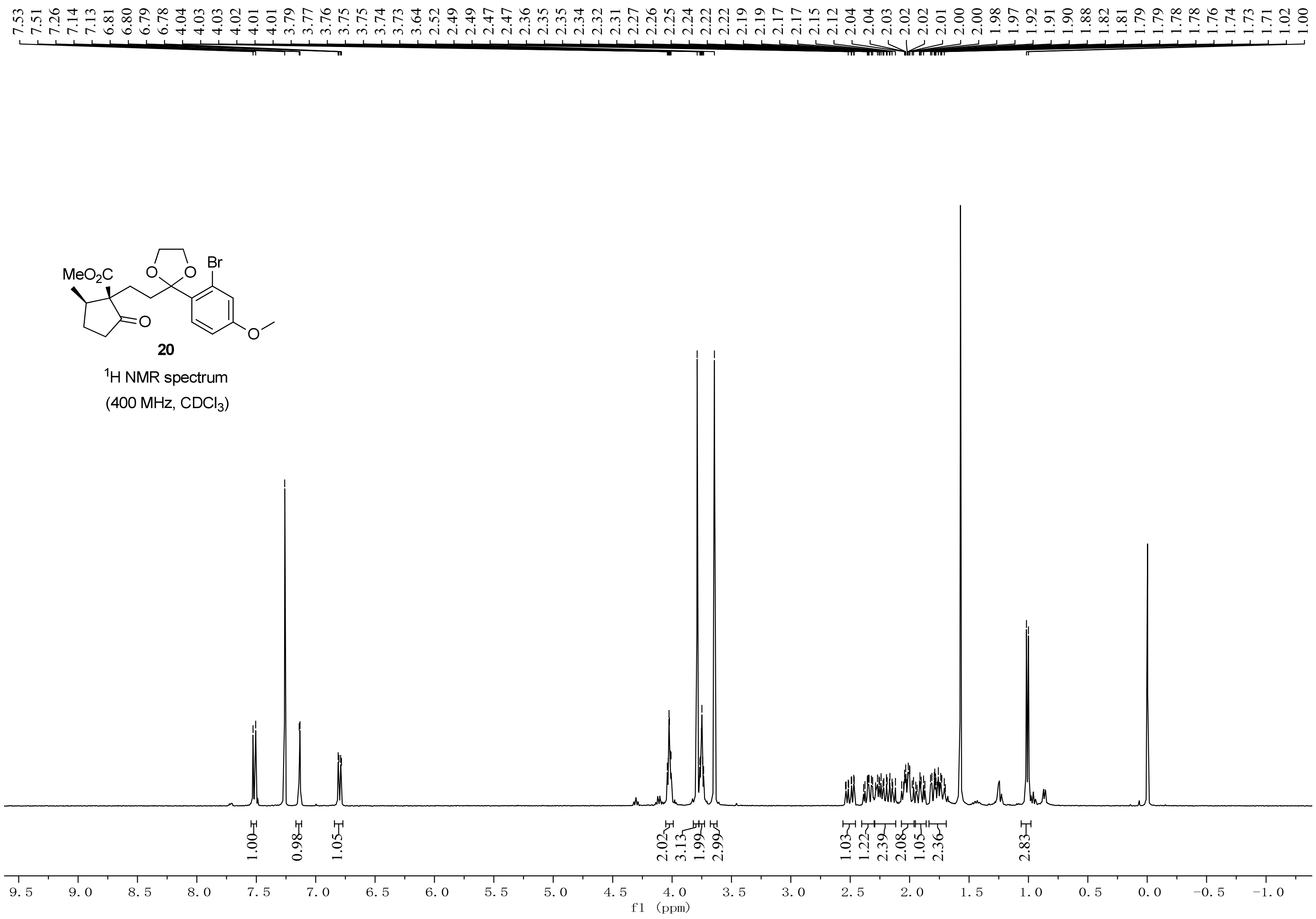


17

^{13}C NMR spectrum

(101 MHz, $CDCl_3$)

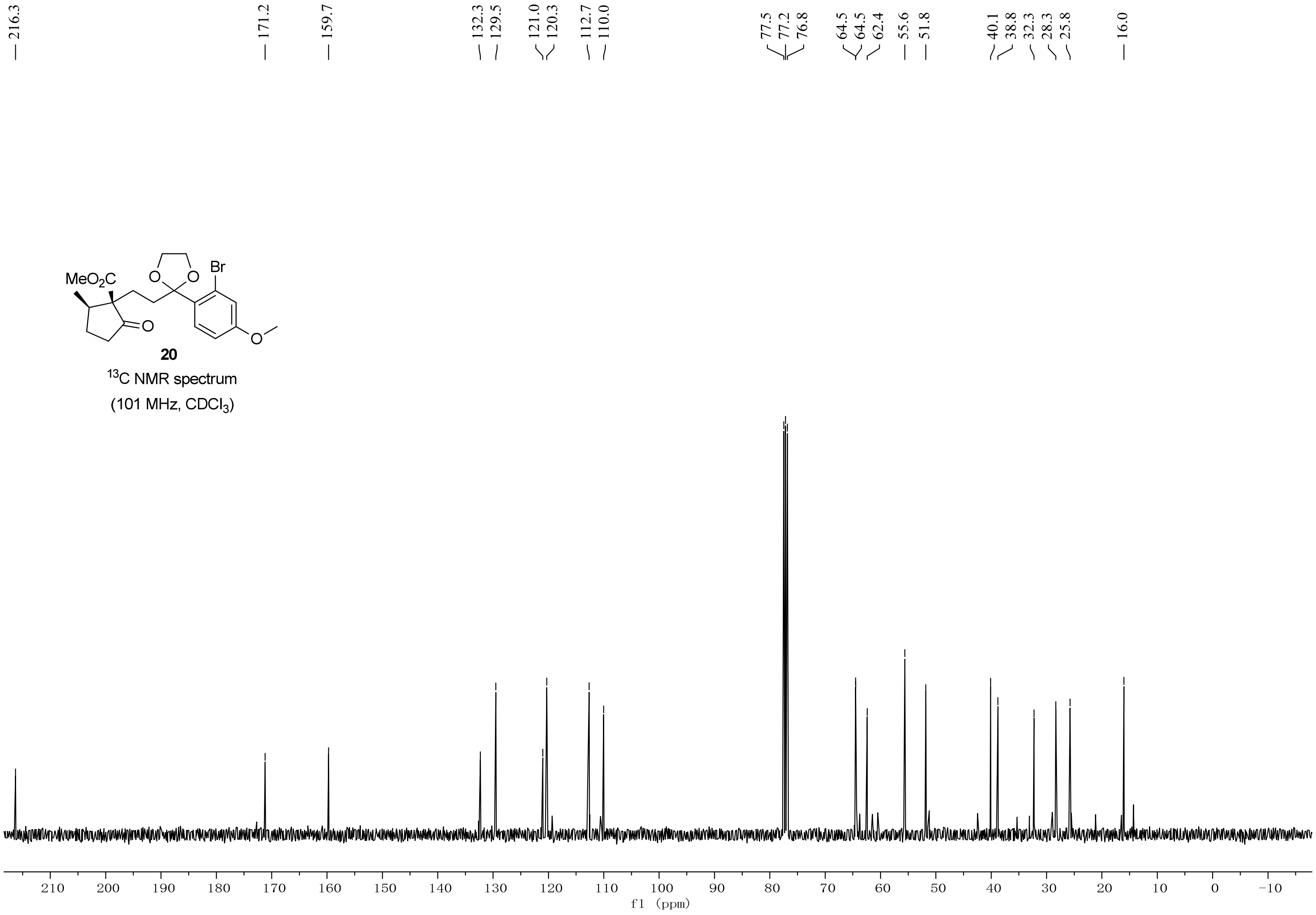




20

^{1}H NMR spectrum

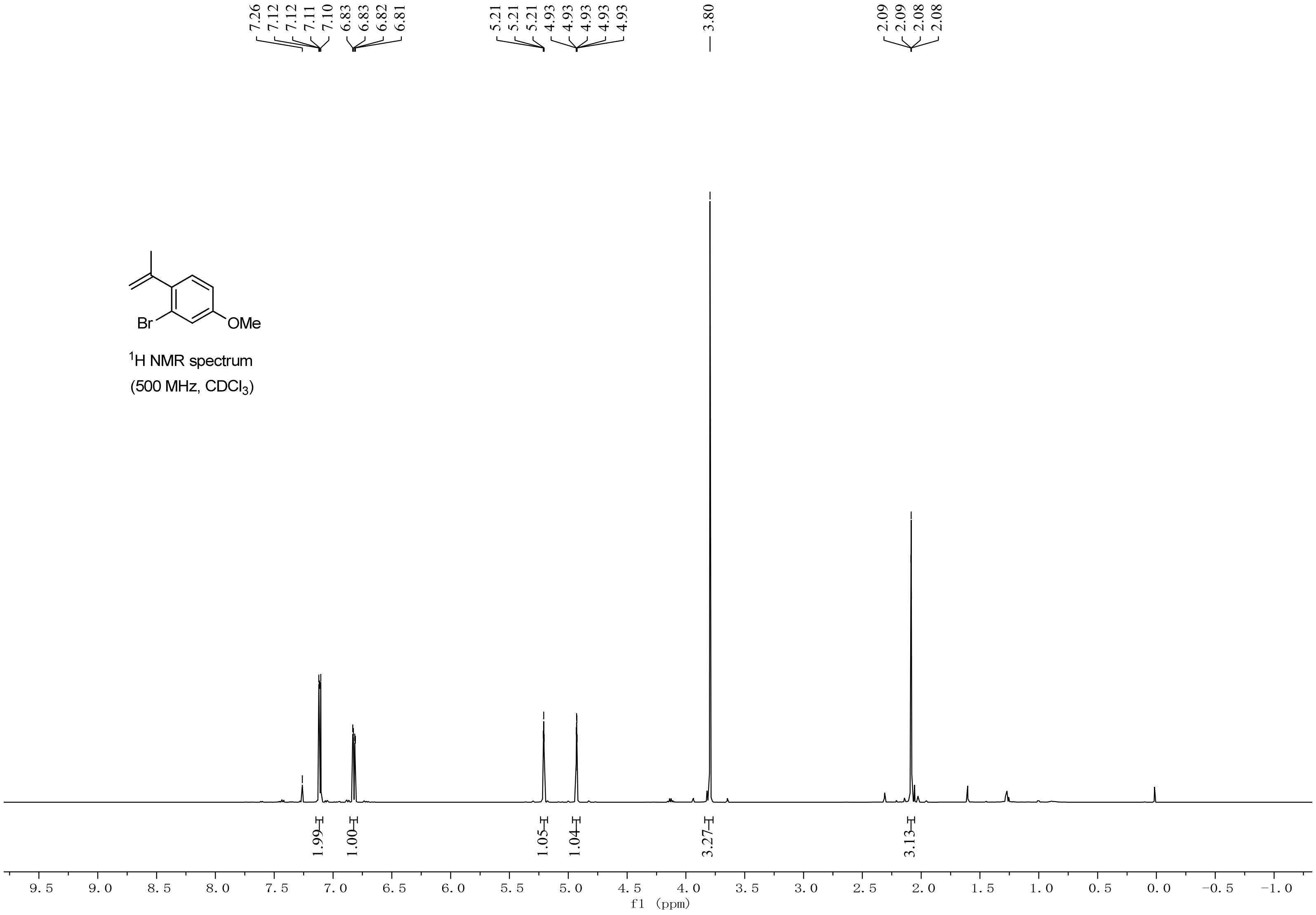
(400 MHz, $CDCl_3$)



20

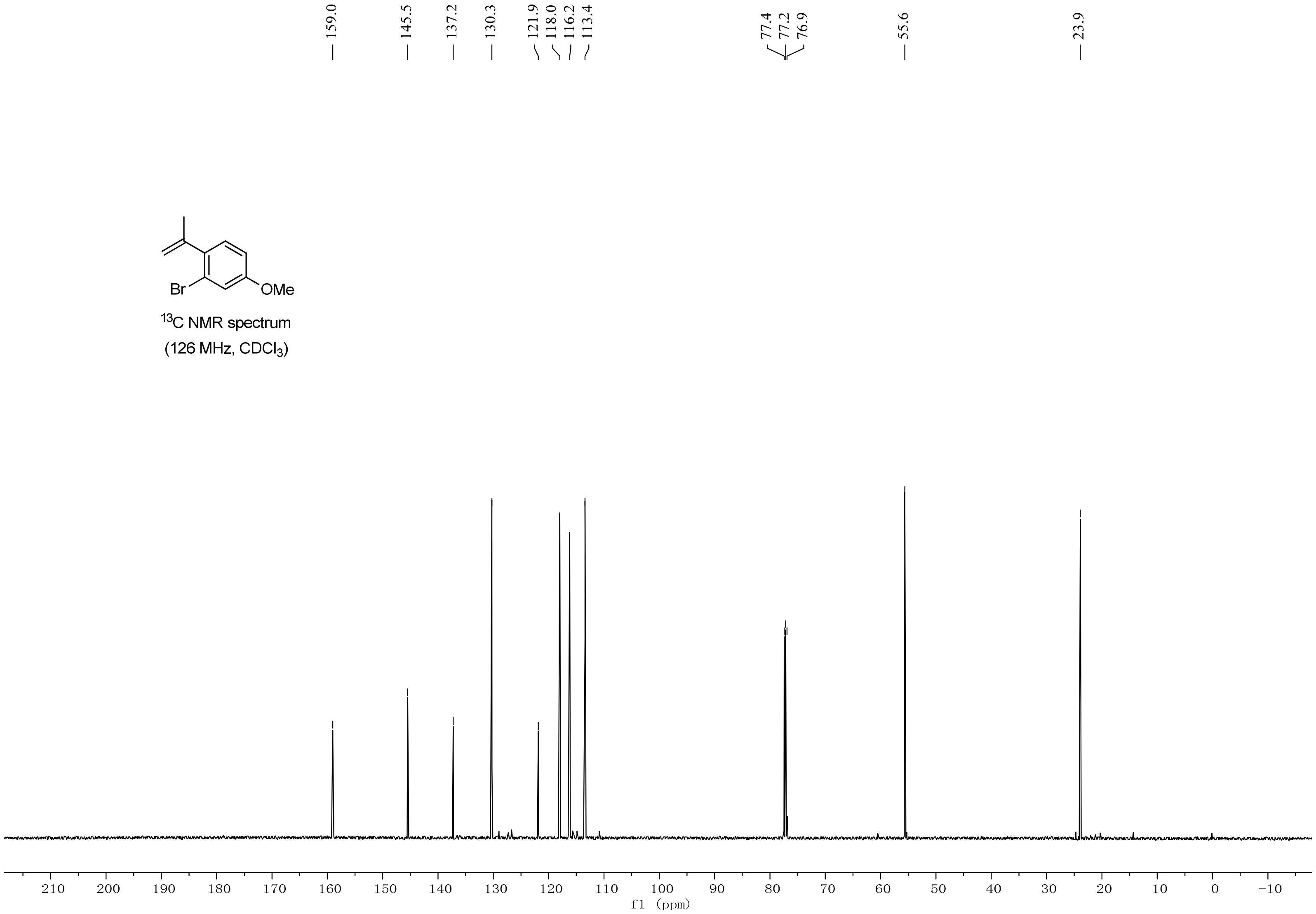
^{13}C NMR spectrum

(101 MHz, $CDCl_3$)

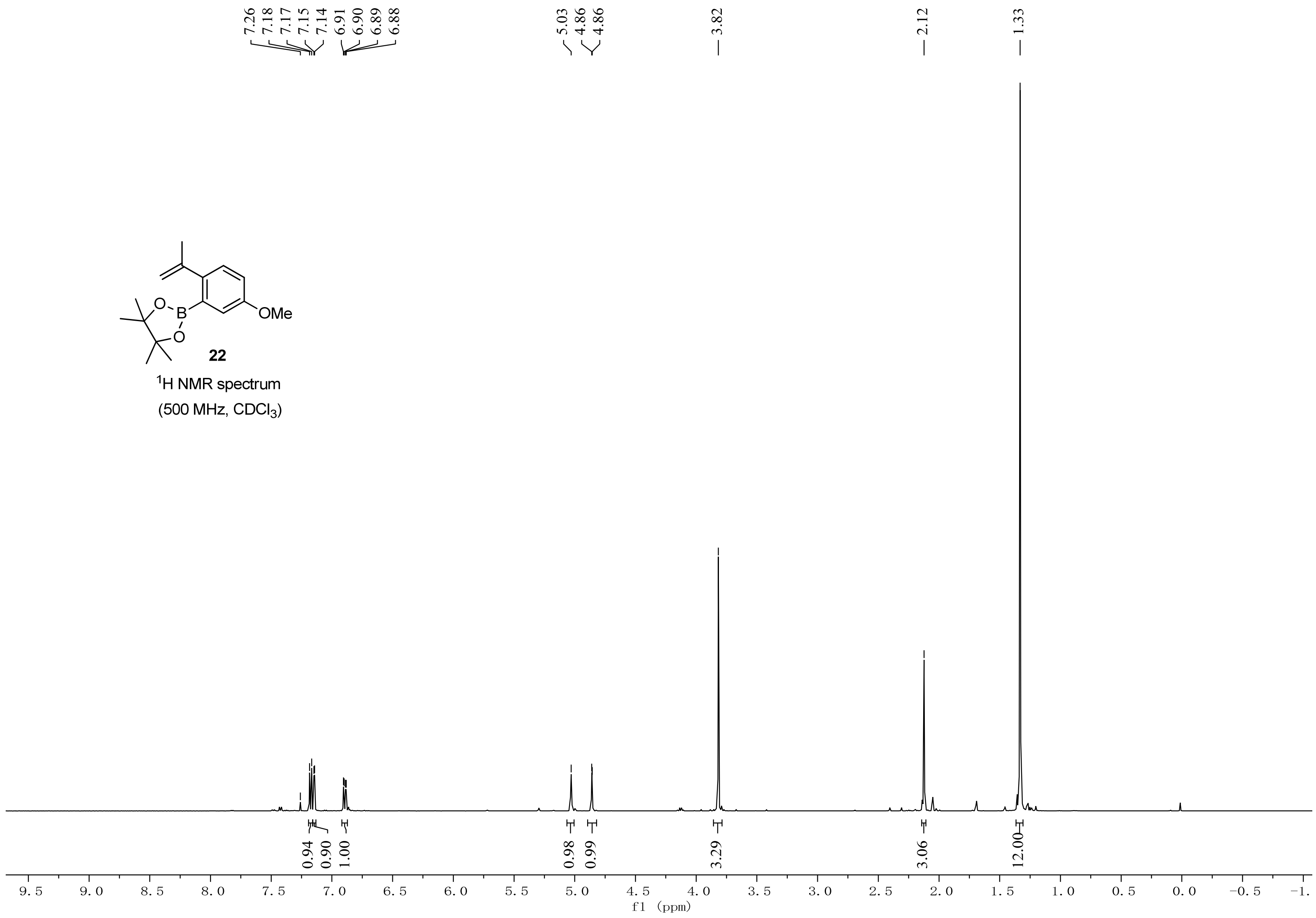


^{1}H NMR spectrum

(500 MHz, $CDCl_3$)



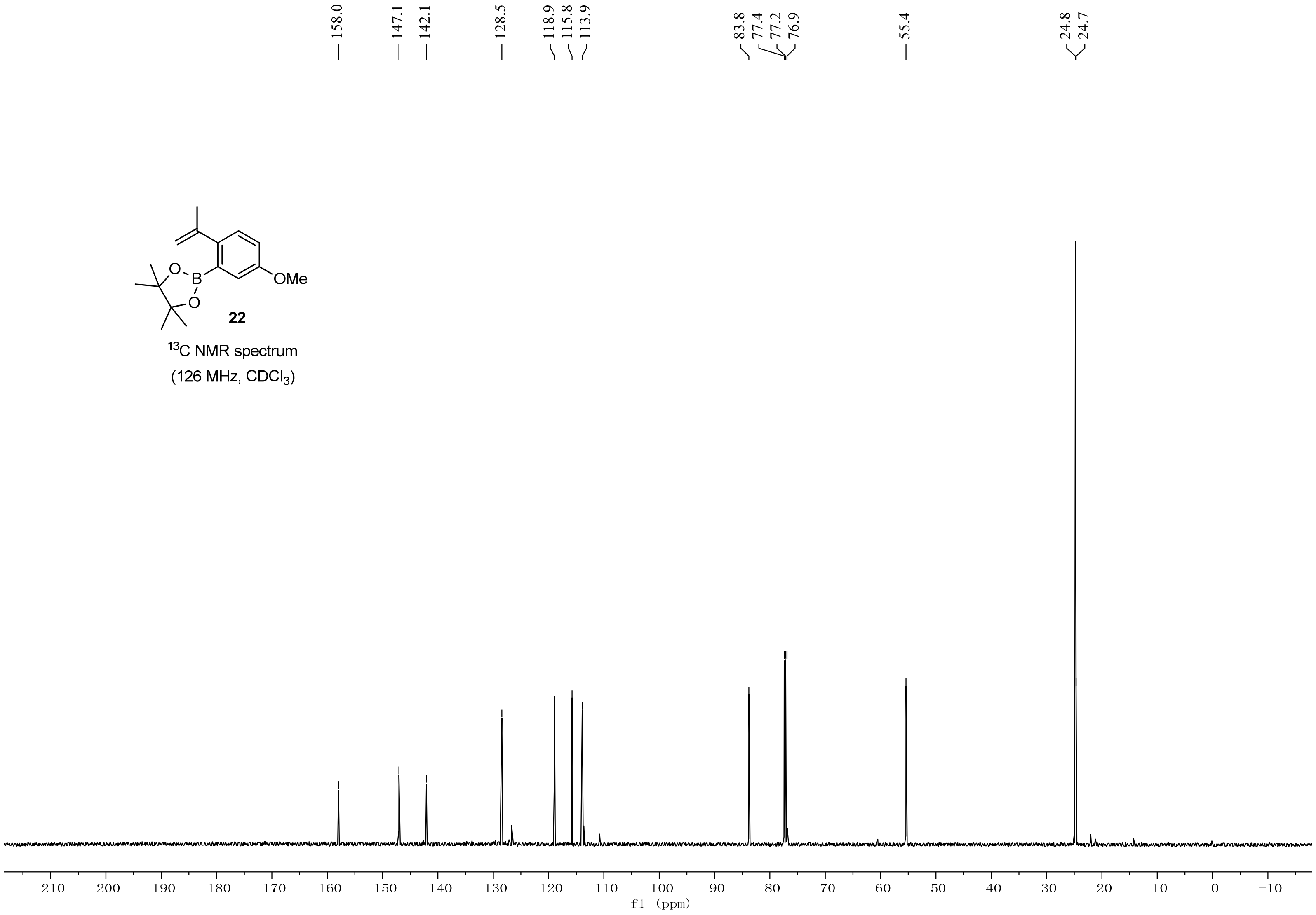
^{13}C NMR spectrum
(126 MHz, $CDCl_3$)



22

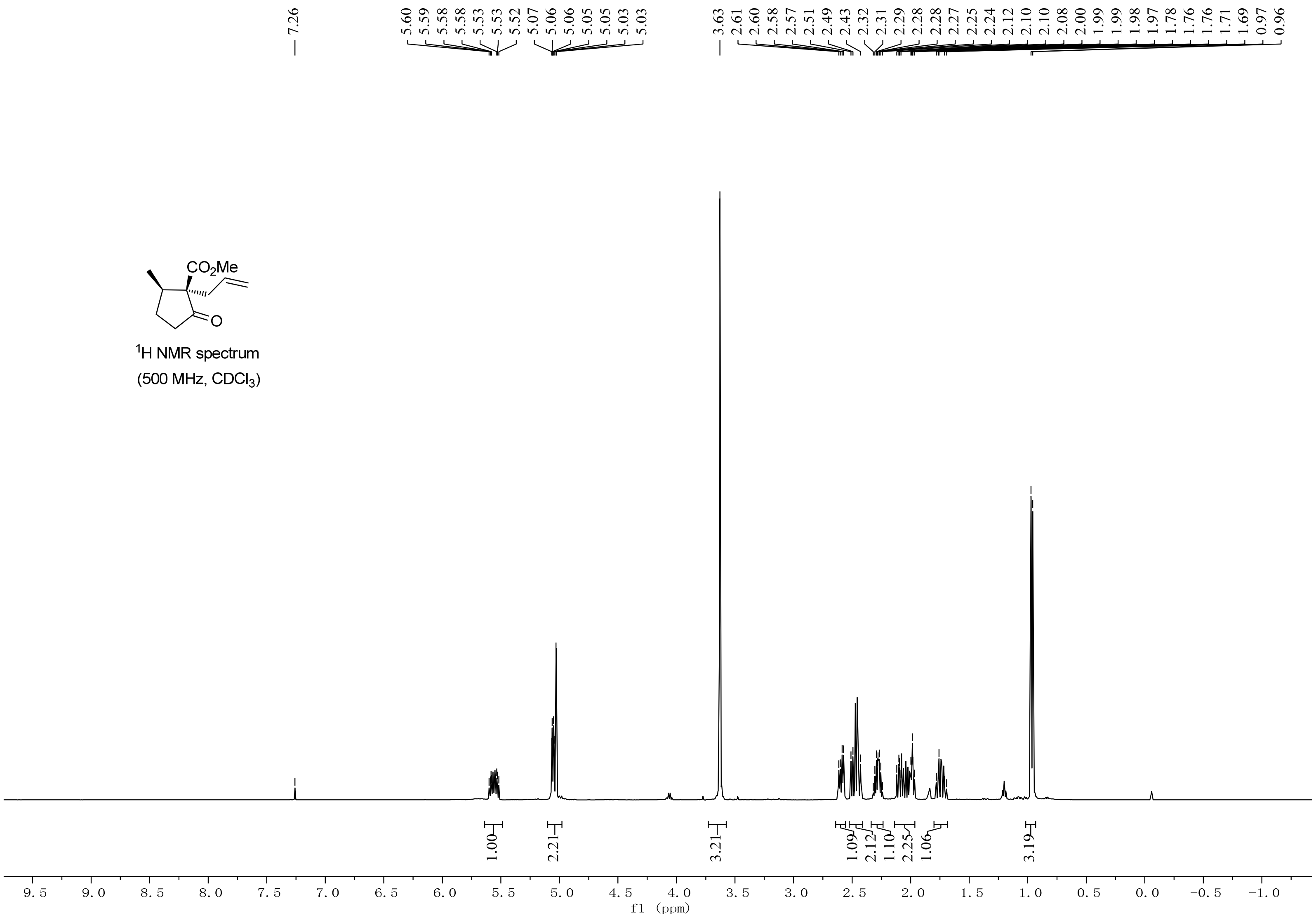
^{1}H NMR spectrum

(500 MHz, $CDCl_3$)



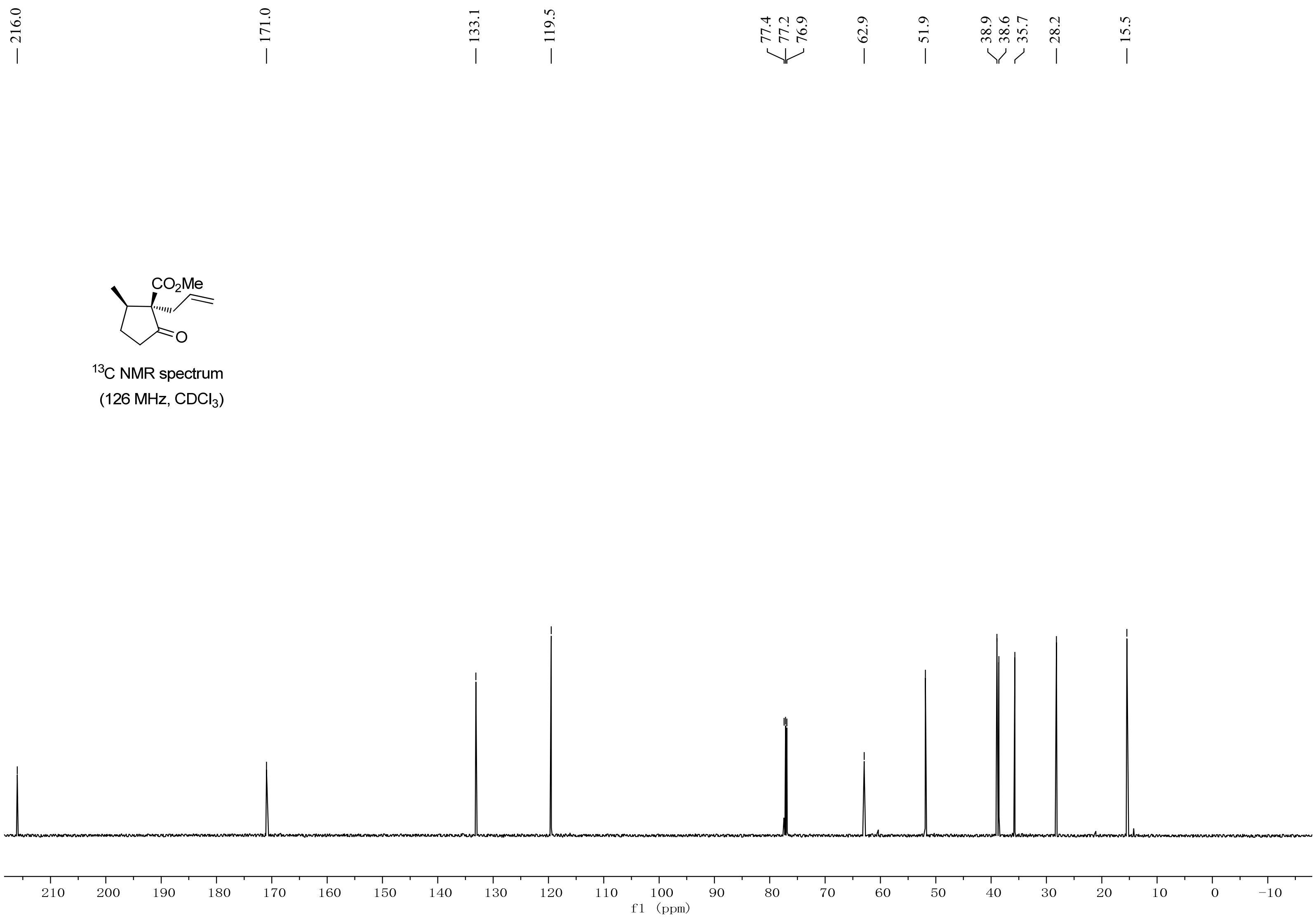
22

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

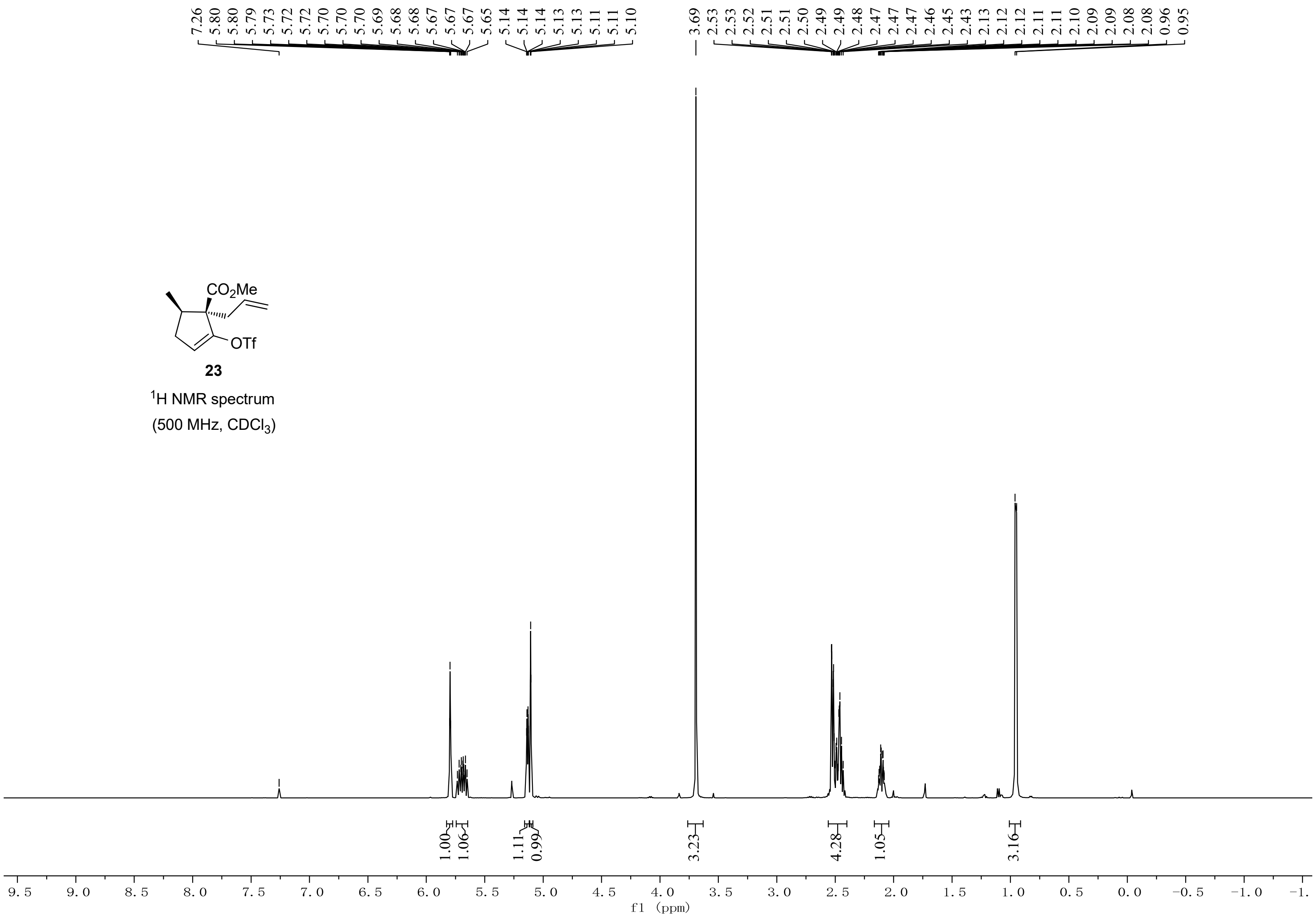


^{1}H NMR spectrum

(500 MHz, $CDCl_3$)

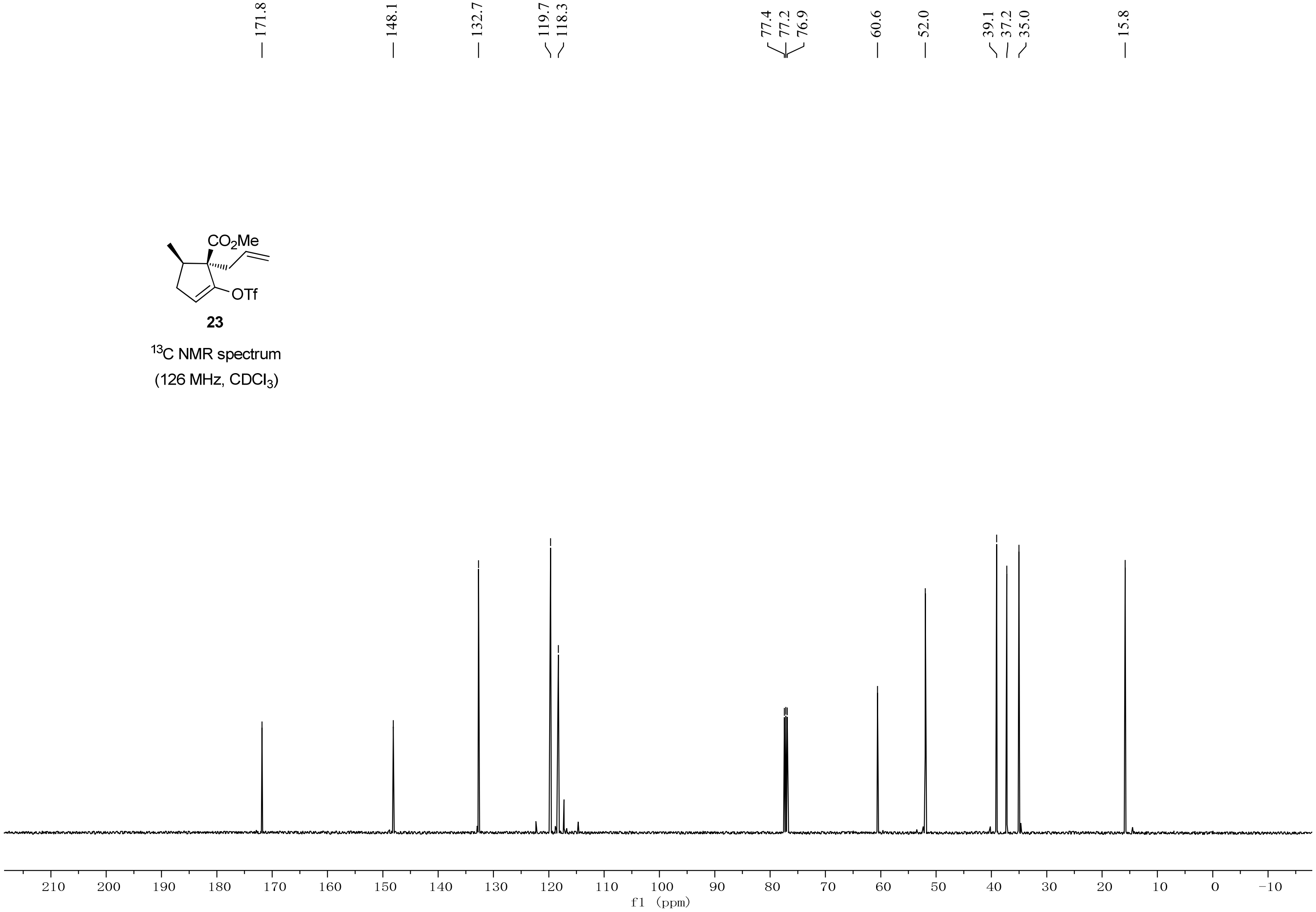


^{13}C NMR spectrum
(126 MHz, CDCl$_3$)



23

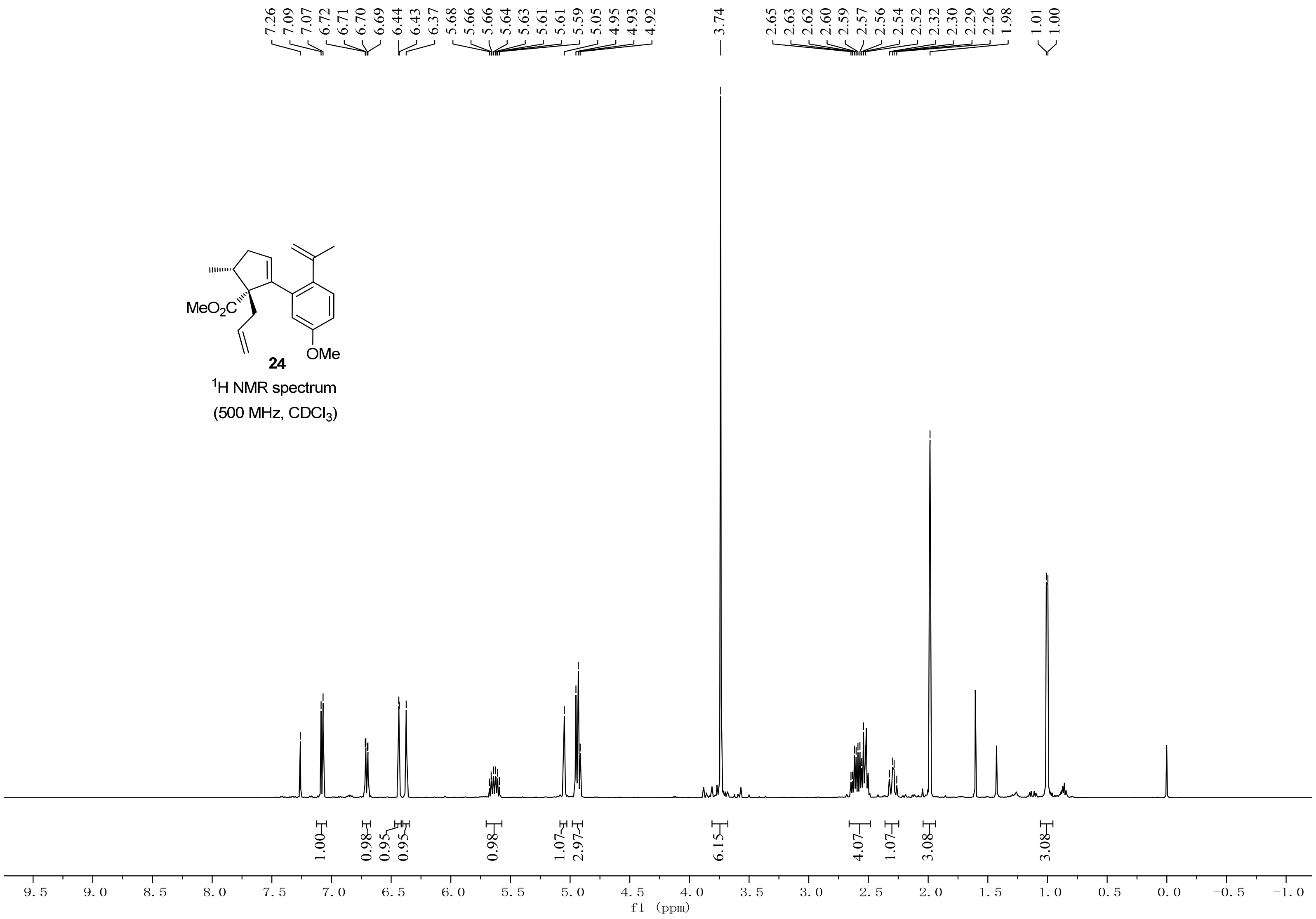
^1H NMR spectrum
(500 MHz, $CDCl_3$)



23

^{13}C NMR spectrum

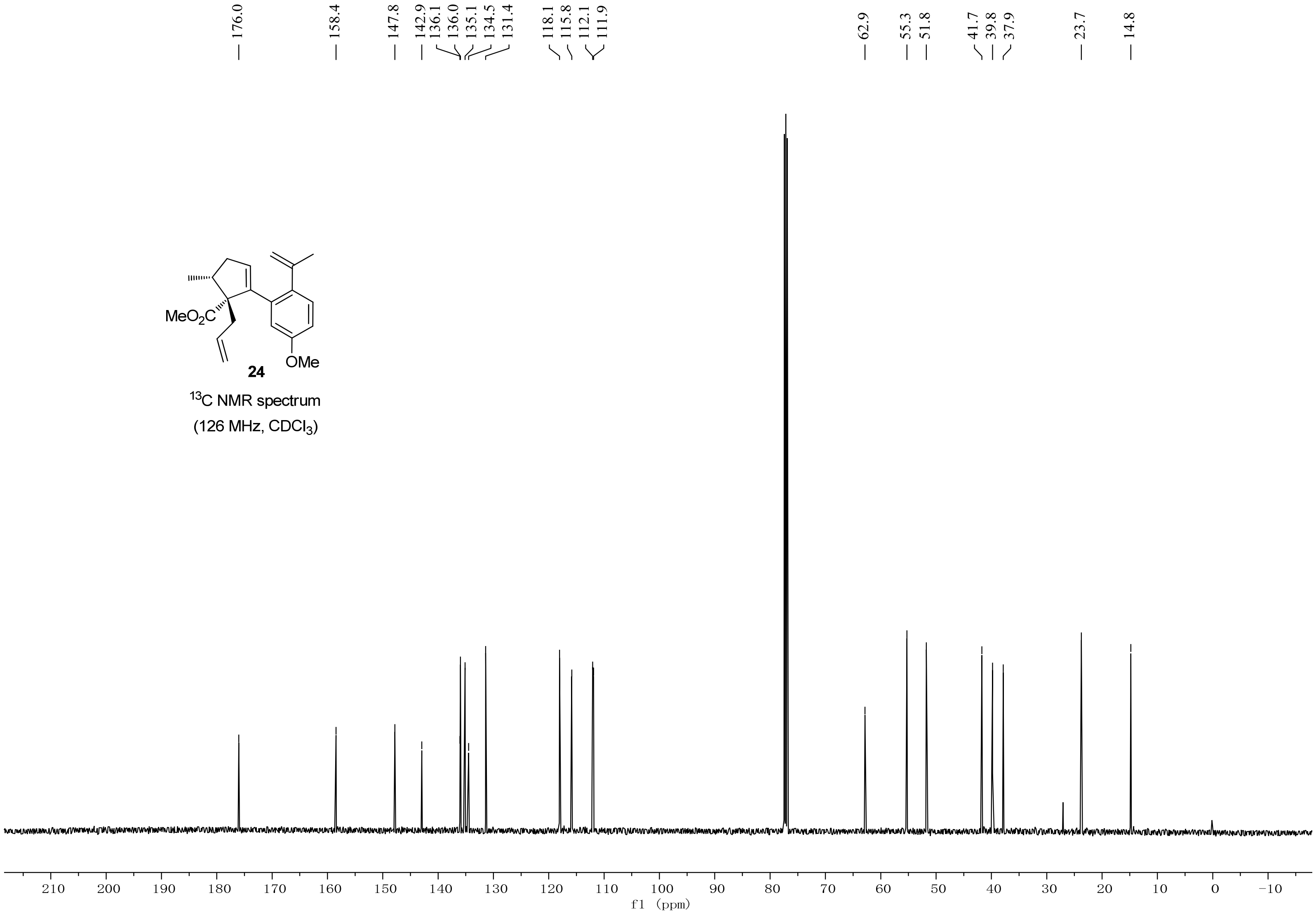
(126 MHz, $CDCl_3$)



24

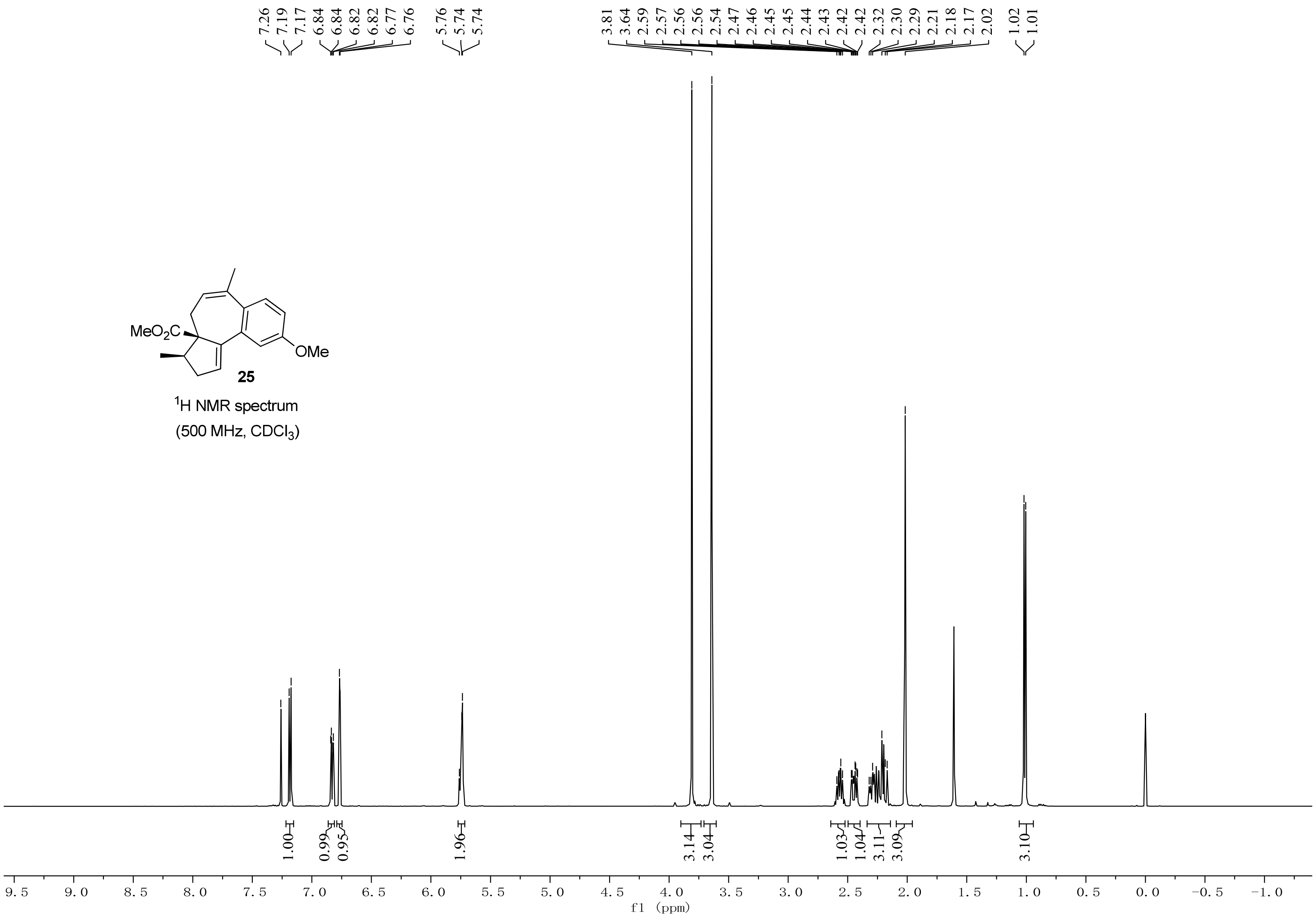
^{1}H NMR spectrum

(500 MHz, $CDCl_3$)



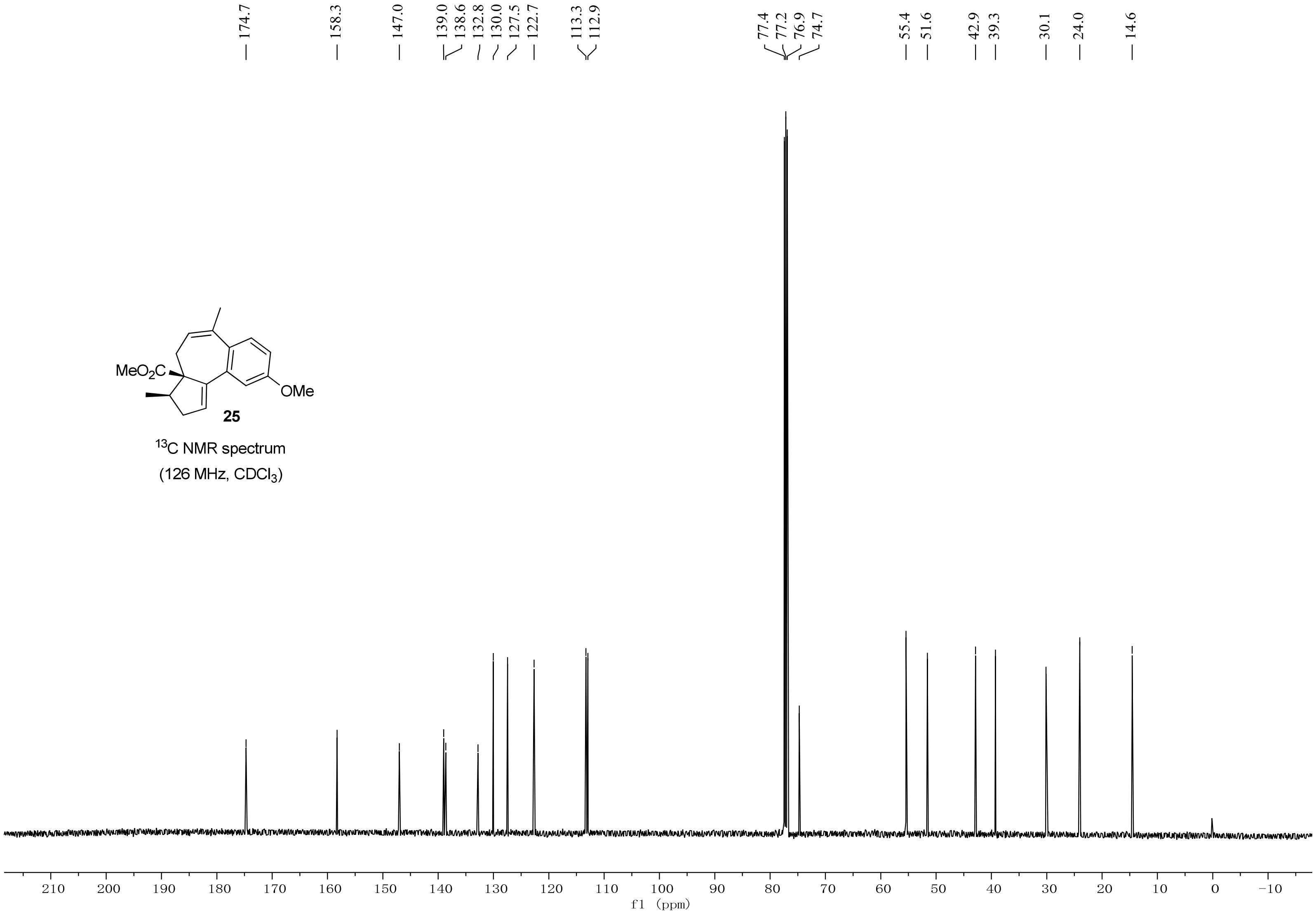
24

^{13}C NMR spectrum
(126 MHz, CDCl$_3$)


25

^{1}H NMR spectrum

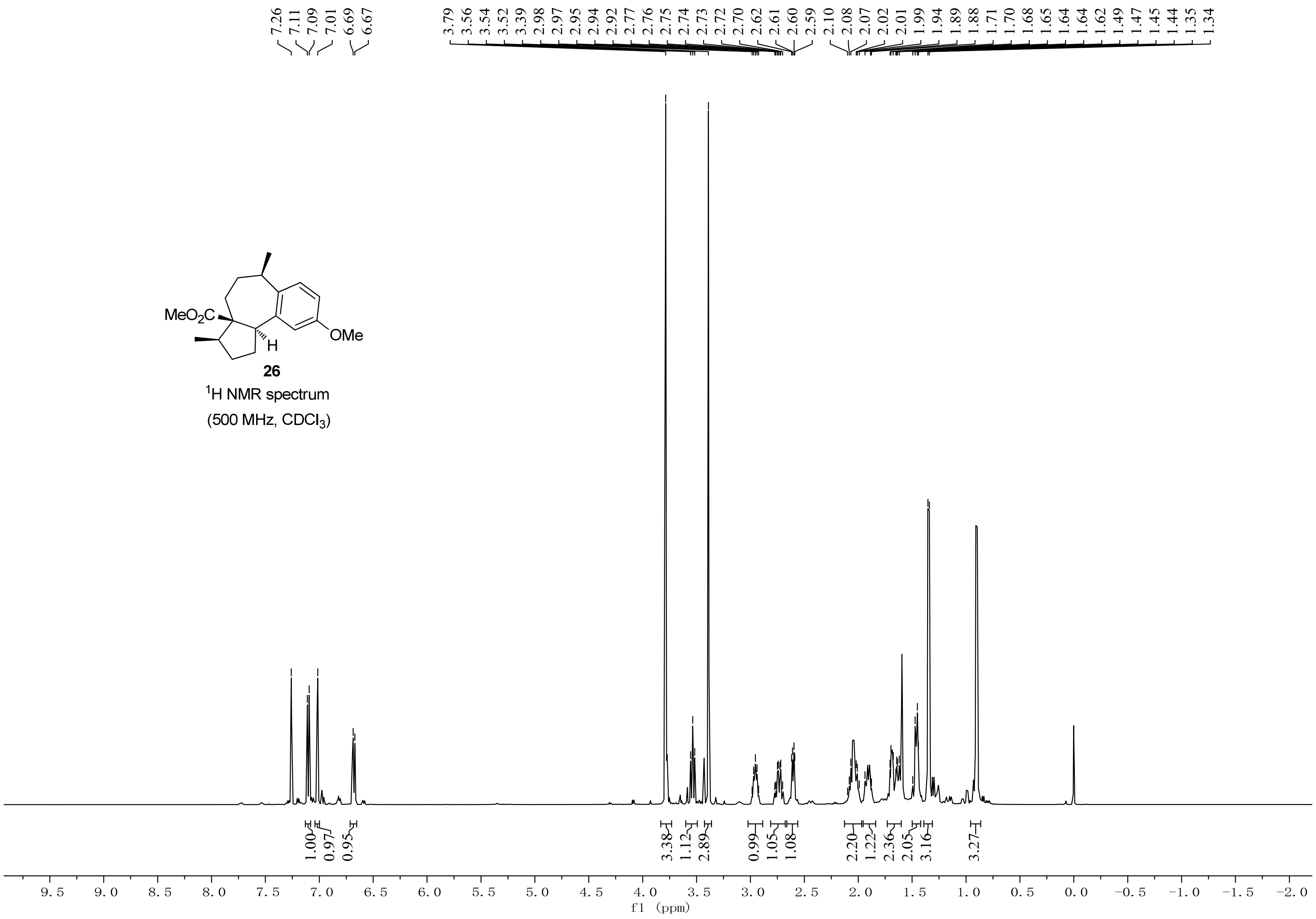
(500 MHz, $CDCl_3$)



25

^{13}C NMR spectrum

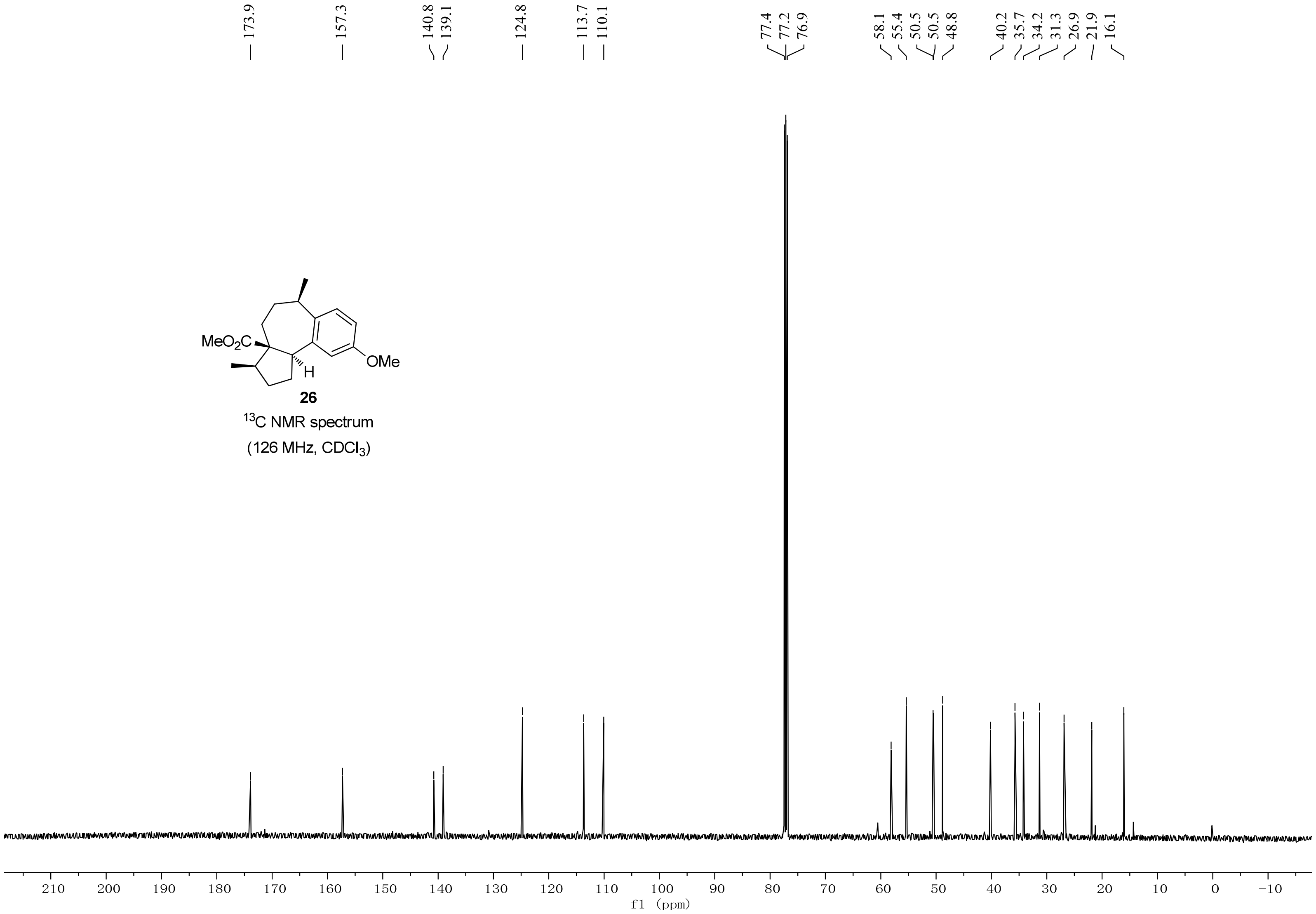
(126 MHz, $CDCl_3$)



26

^{1}H NMR spectrum

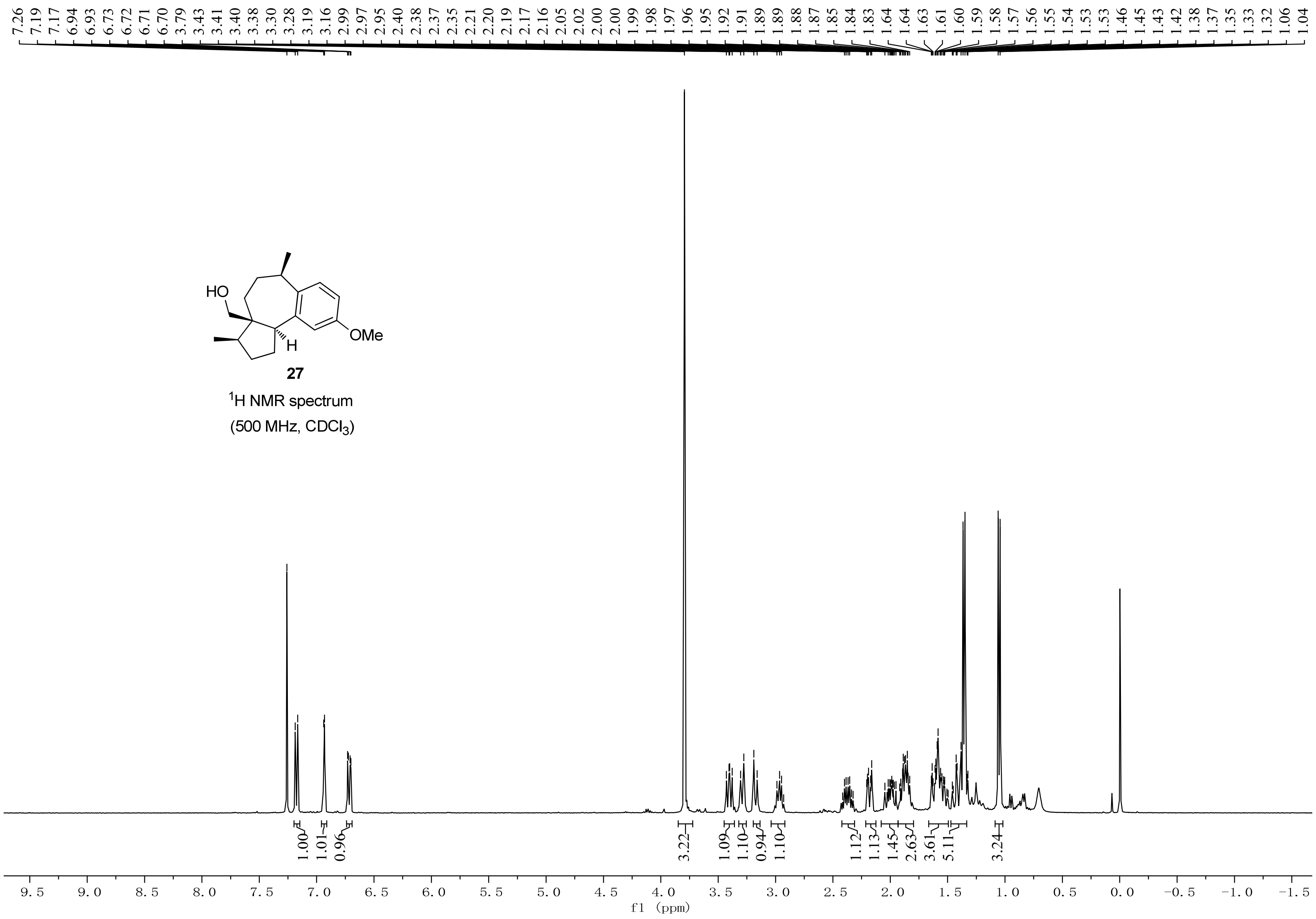
(500 MHz, $CDCl_3$)



26

^{13}C NMR spectrum

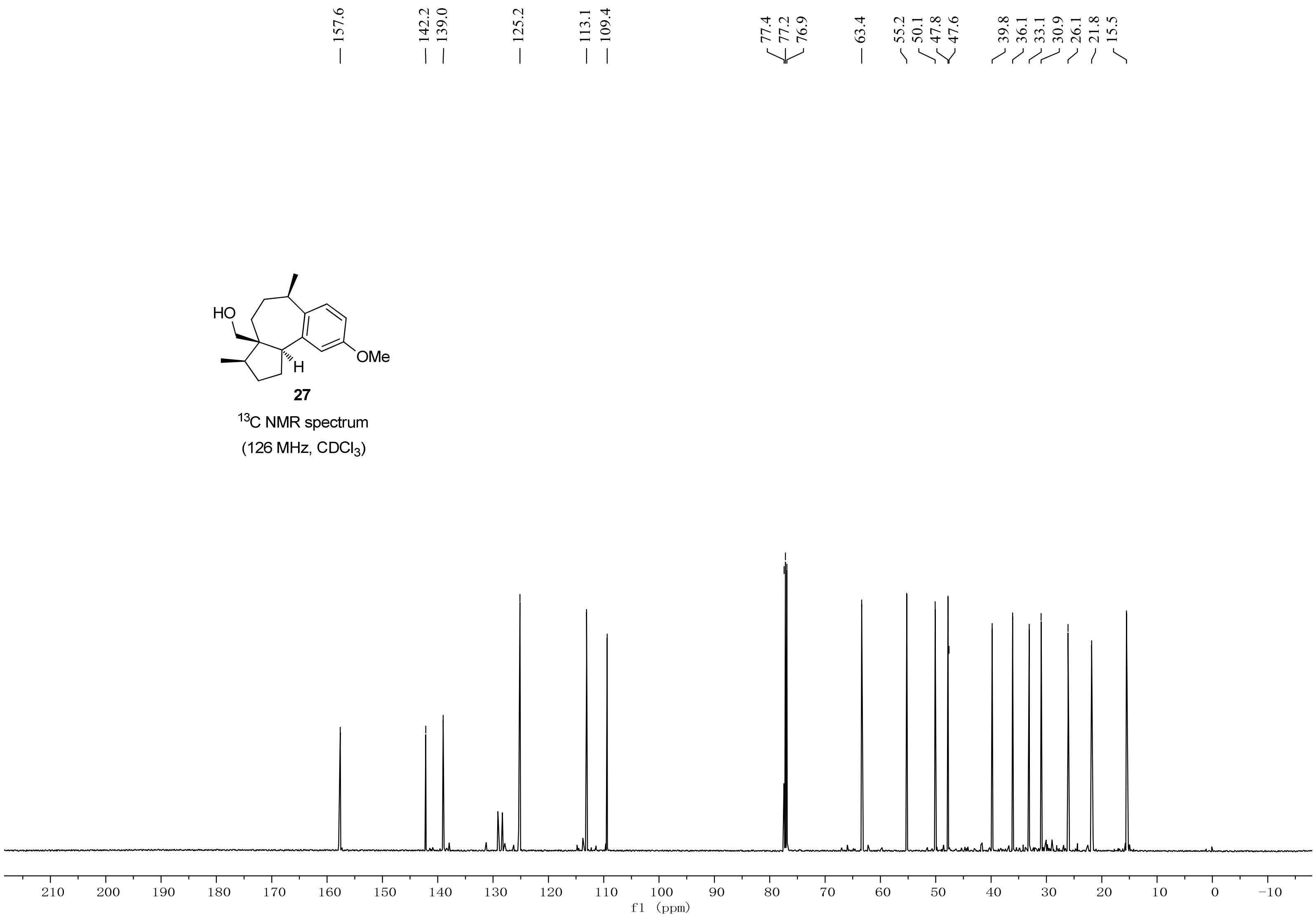
(126 MHz, CDCl$_3$)



27

^{1}H NMR spectrum

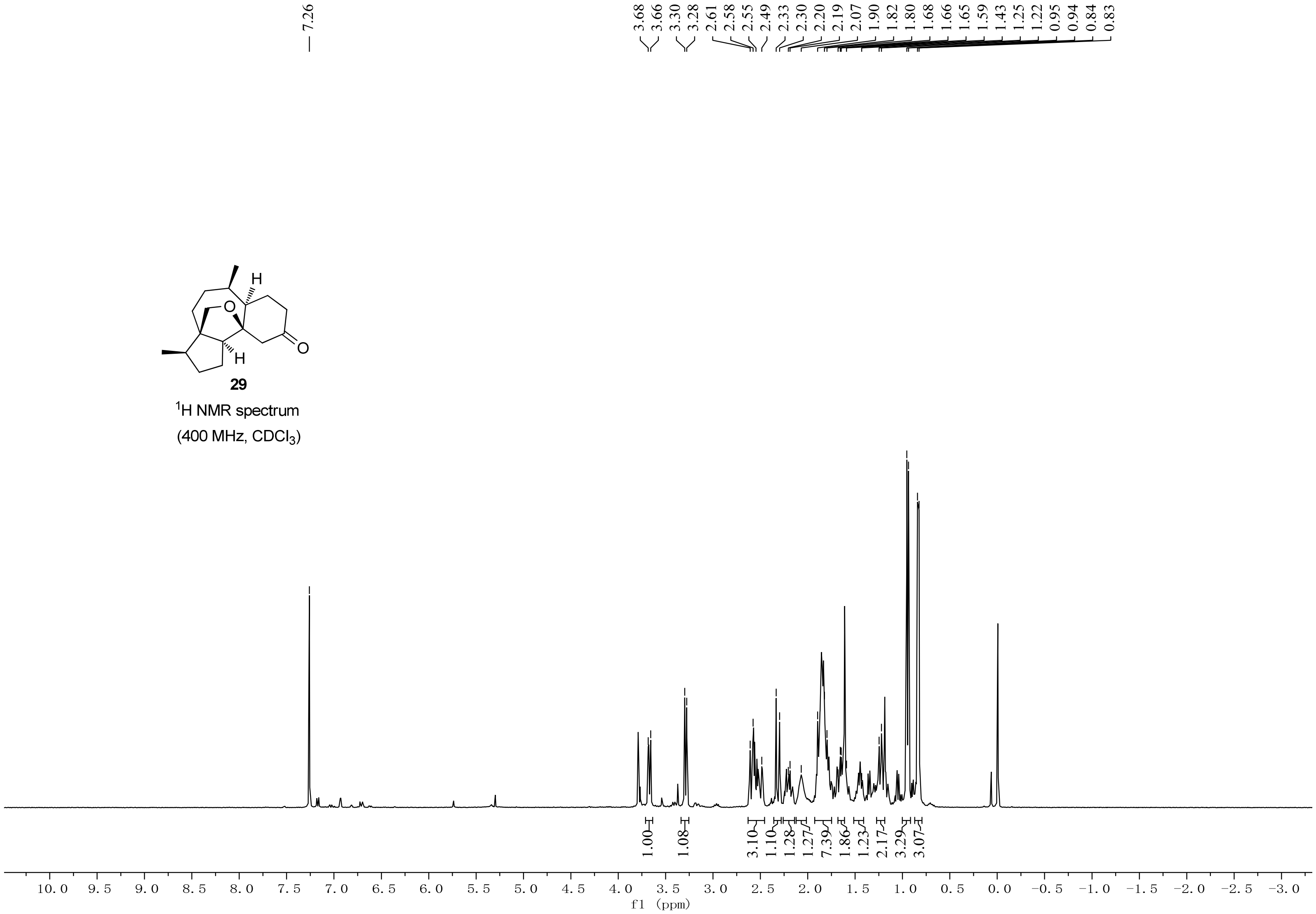
(500 MHz, CDCl$_3$)



27

^{13}C NMR spectrum

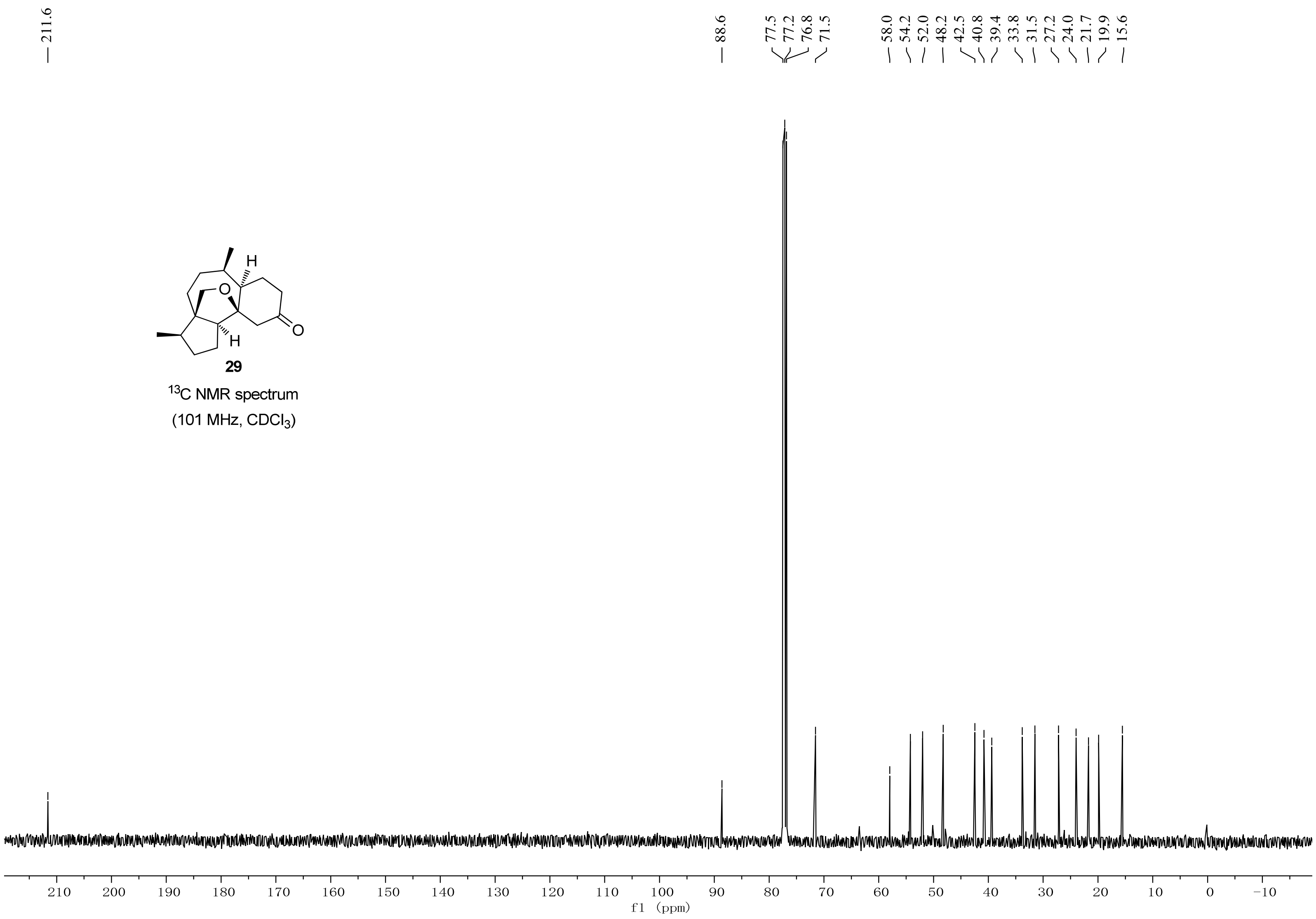
(126 MHz, $CDCl_3$)

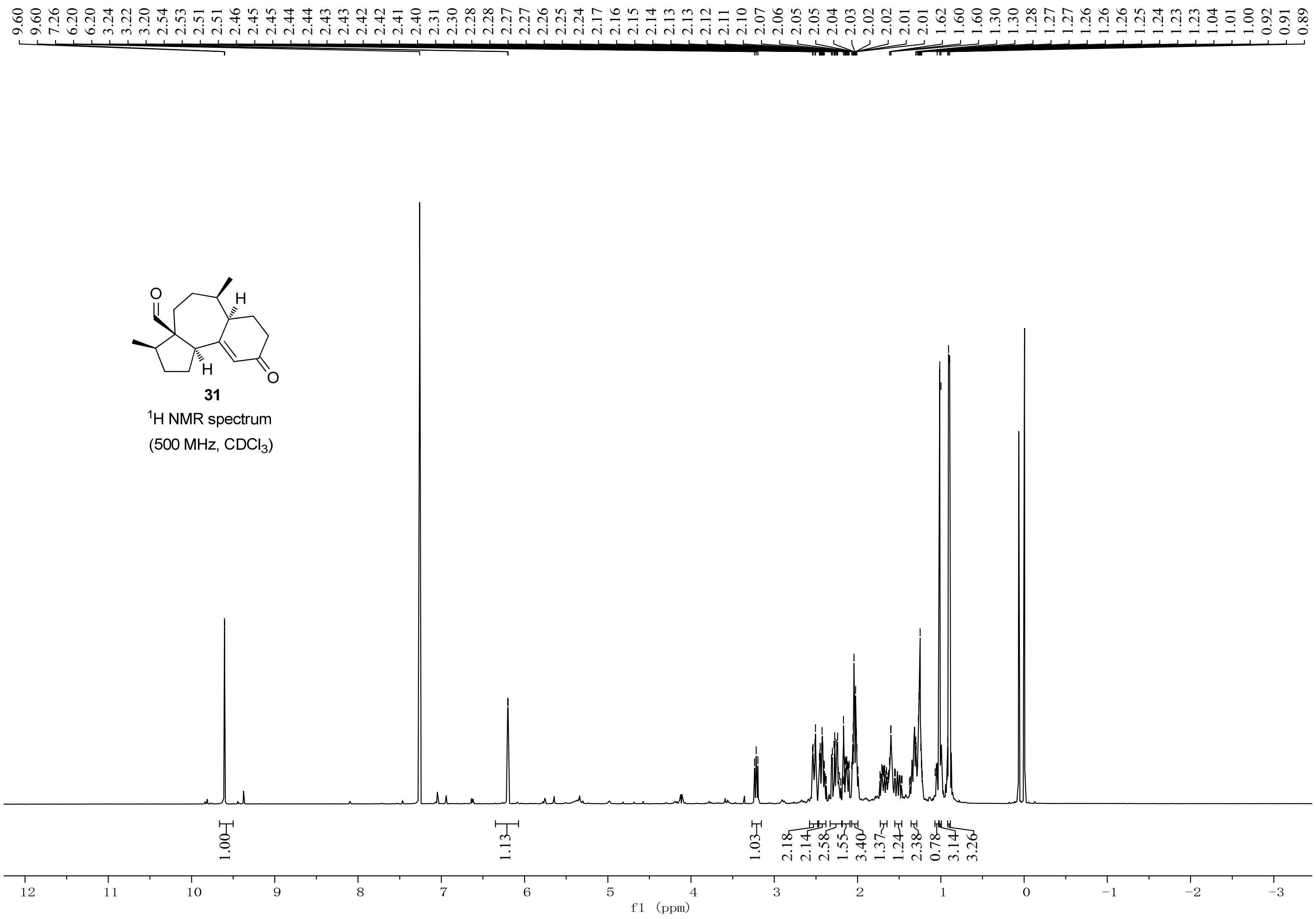


29

^{1}H NMR spectrum

(400 MHz, $CDCl_3$)

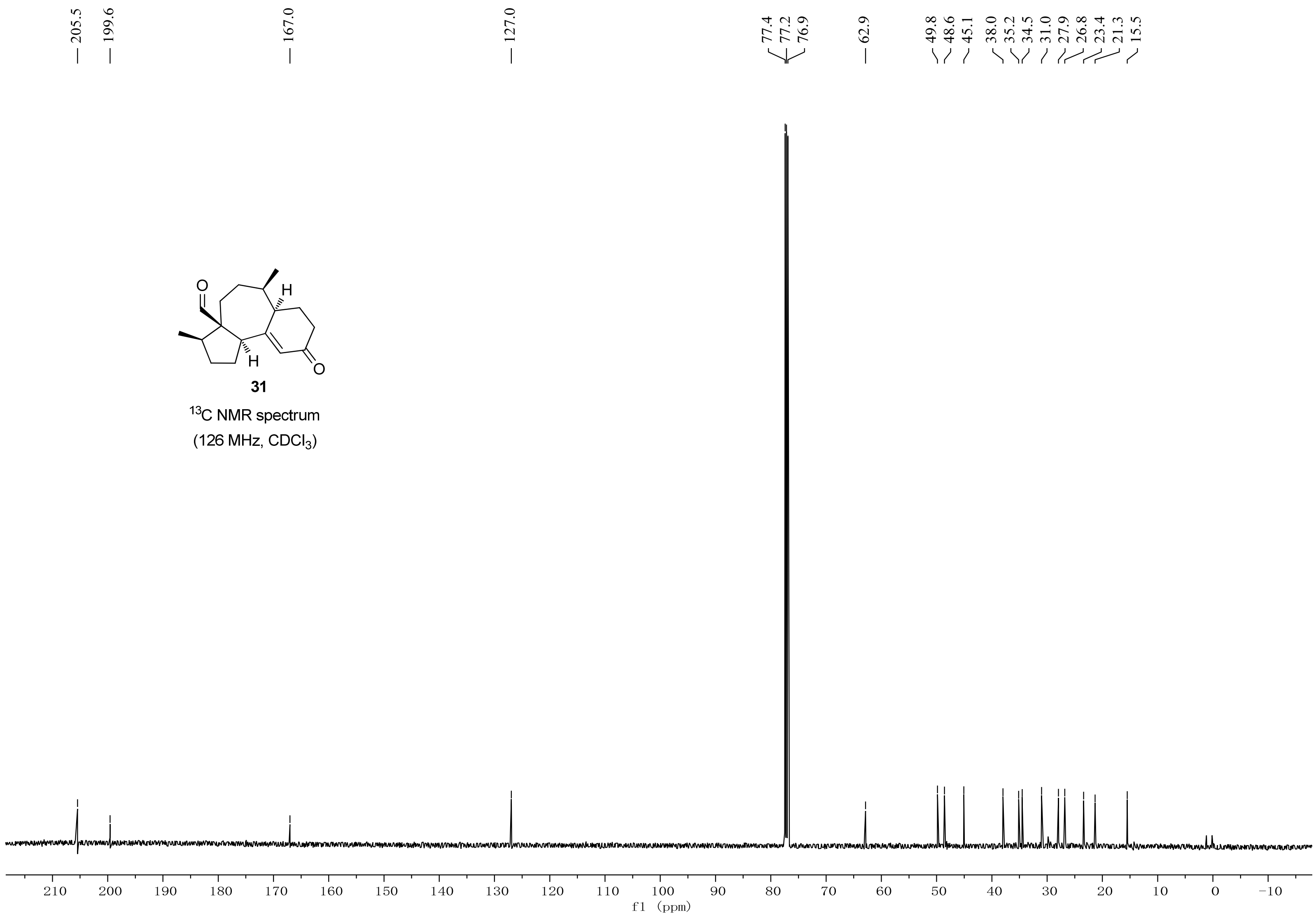

211.6
88.6
77.5
77.2
76.8
71.5
58.0
54.2
52.0
48.2
42.5
40.8
39.4
33.8
31.5
27.2
24.0
21.7
19.9
15.6
H
O
H
O
29
^{13}C NMR spectrum
(101 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



31

^{1}H NMR spectrum

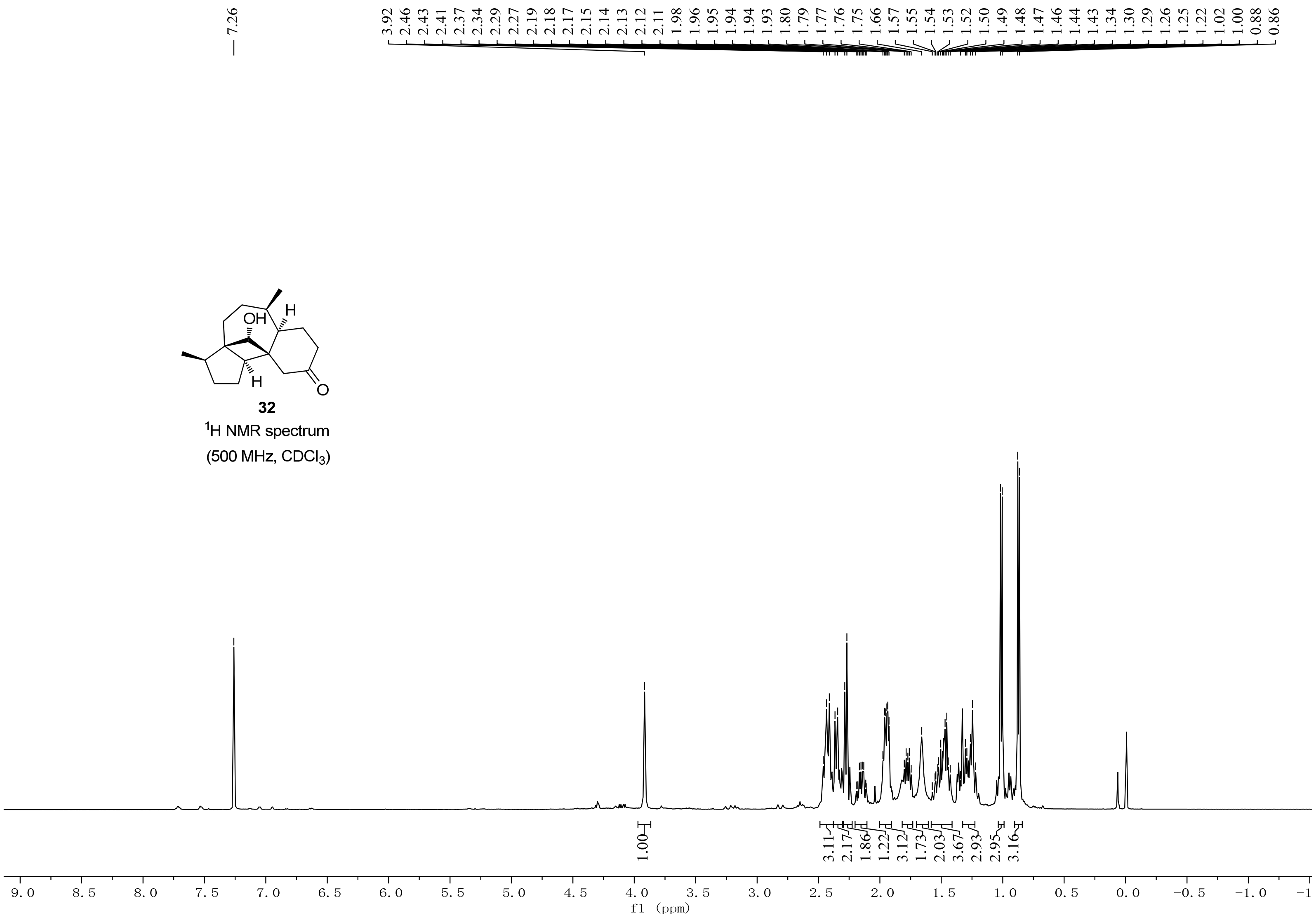
(500 MHz, $CDCl_3$)



31

^{13}C NMR spectrum

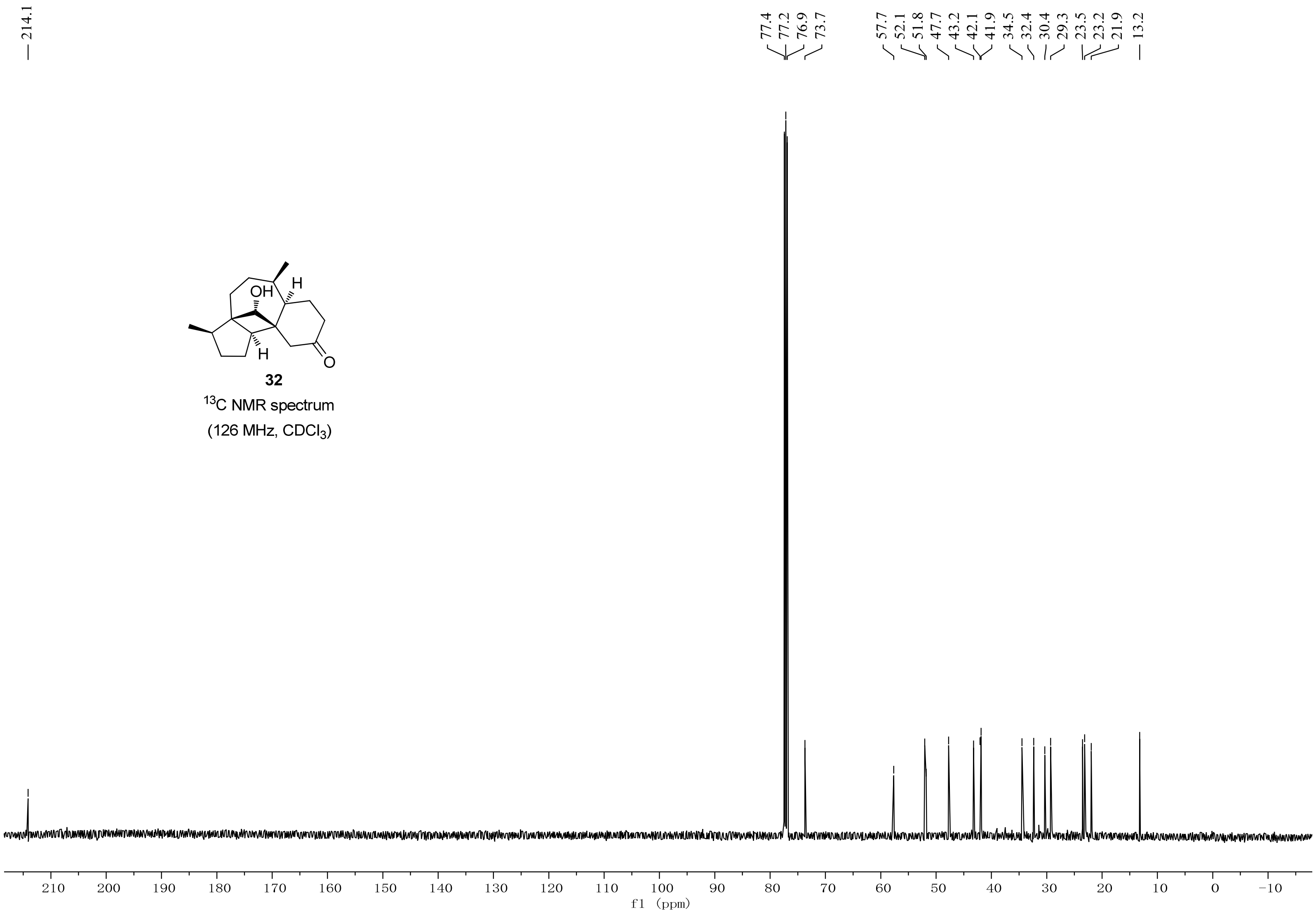
(126 MHz, $CDCl_3$)



32

^{1}H NMR spectrum

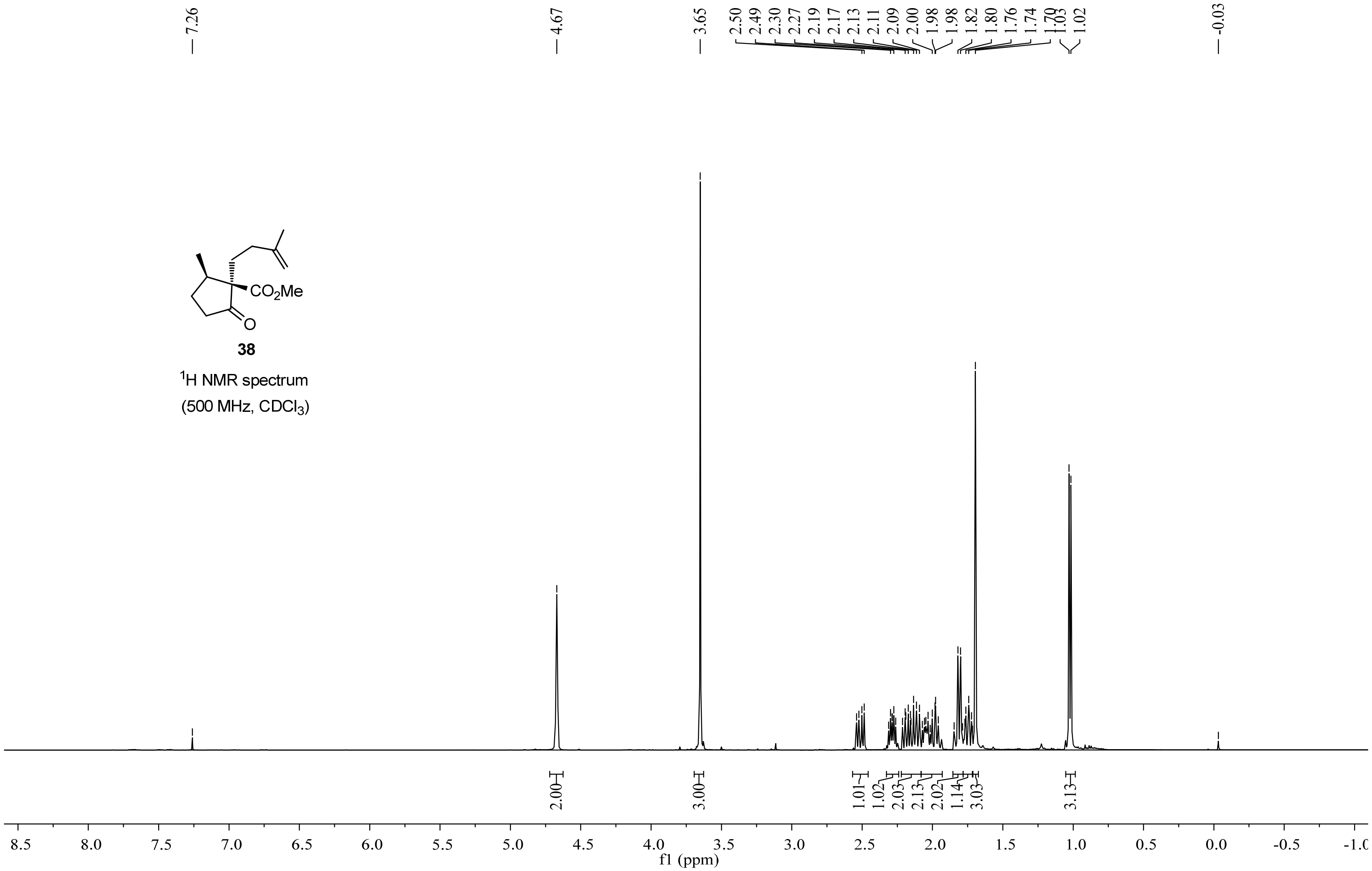
(500 MHz, $CDCl_3$)



32

^{13}C NMR spectrum

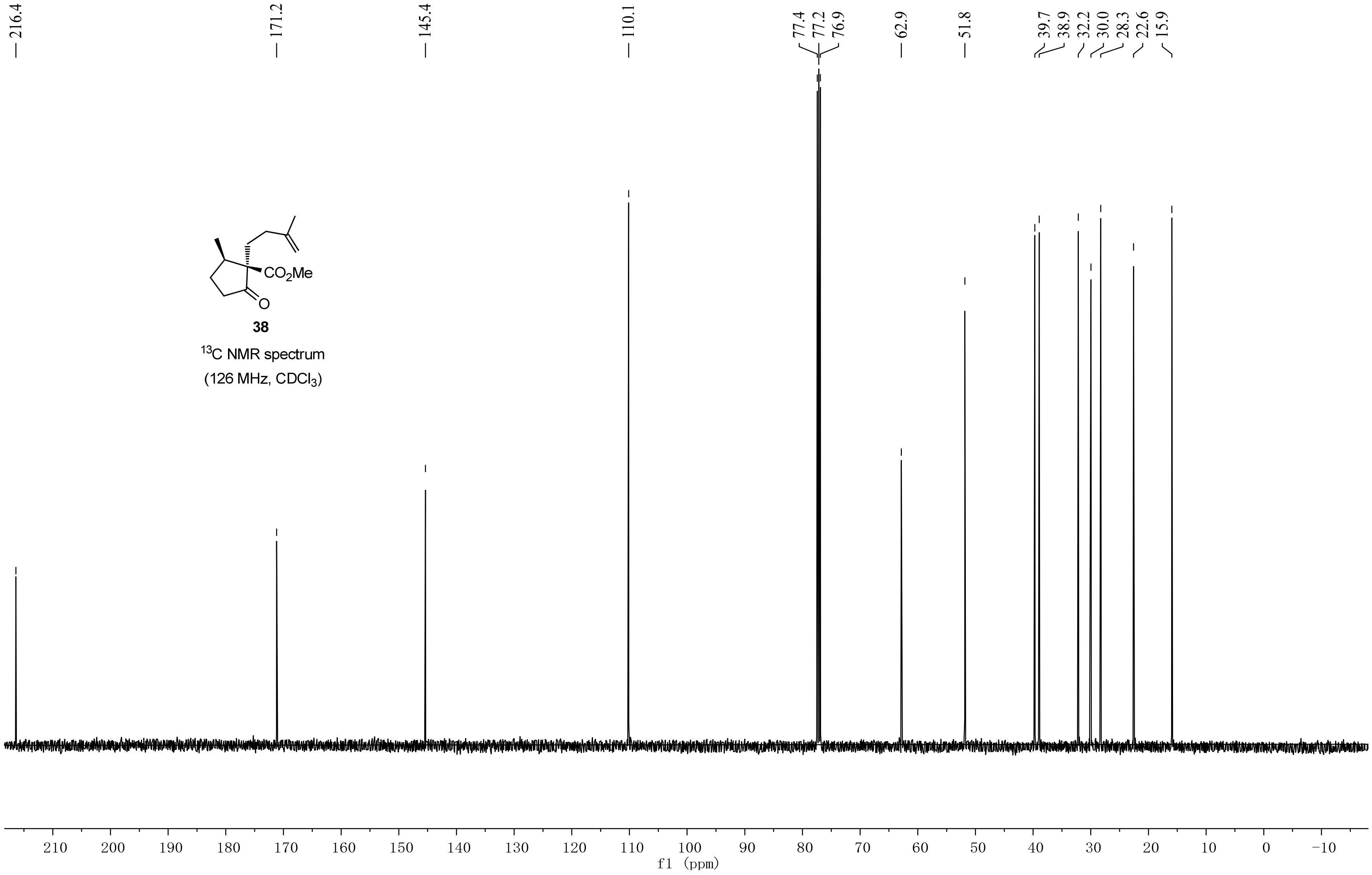
(126 MHz, CDCl$_3$)



38

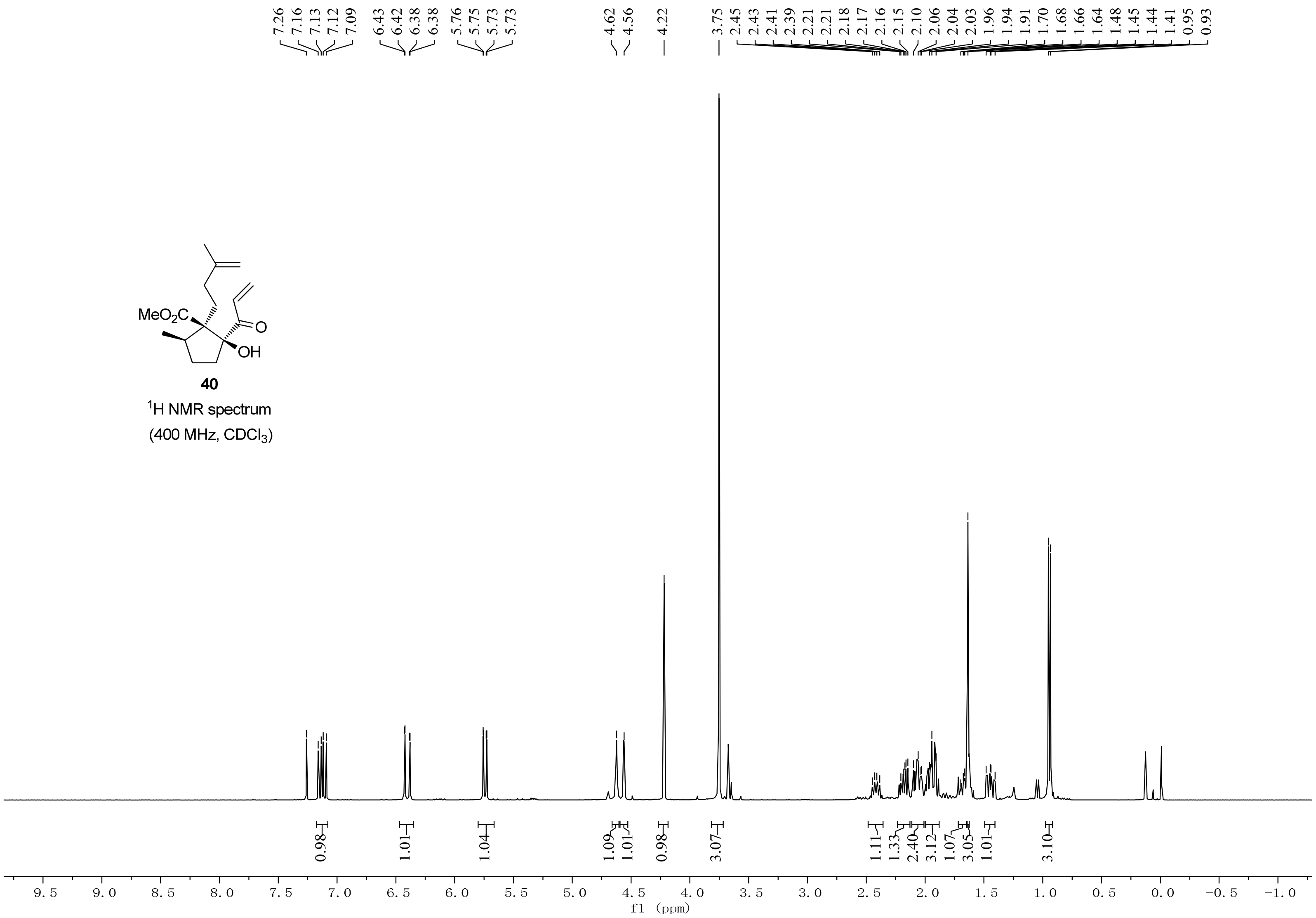
^1H NMR spectrum

(500 MHz, $CDCl_3$)



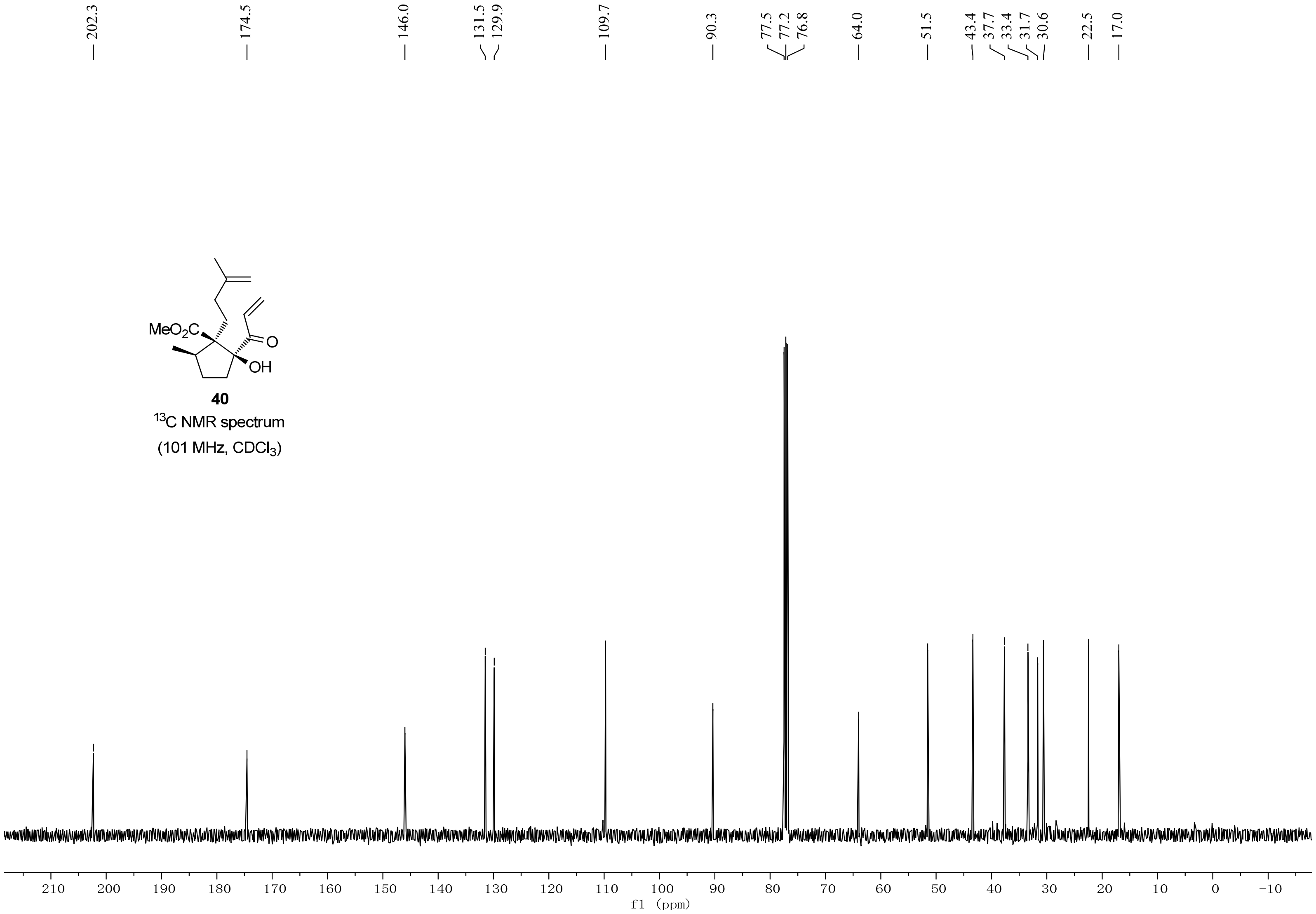
38

^{13}C NMR spectrum
(126 MHz, CDCl$_3$)



40

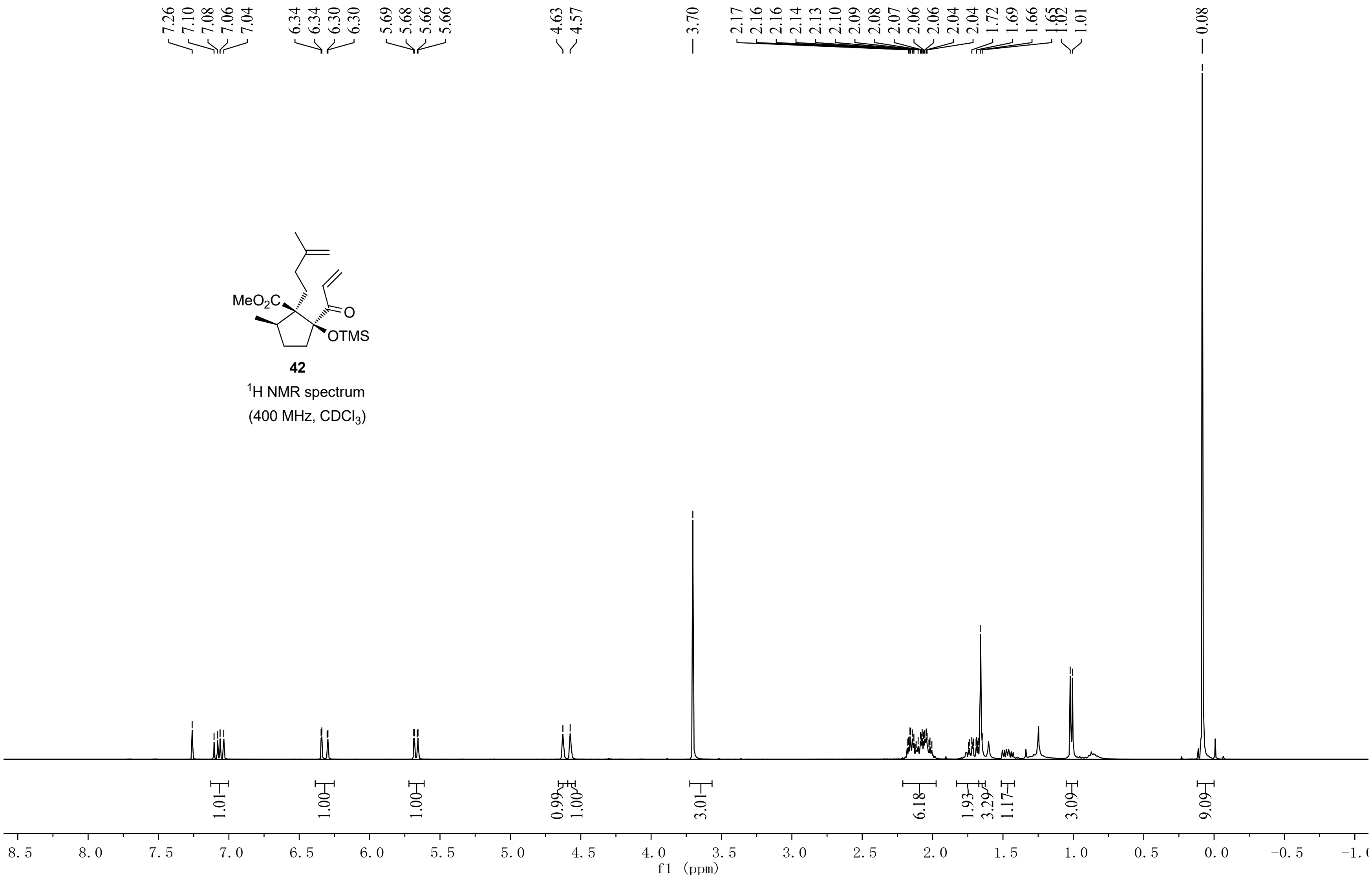
^{1}H NMR spectrum
(400 MHz, CDCl$_3$)



40

^{13}C NMR spectrum

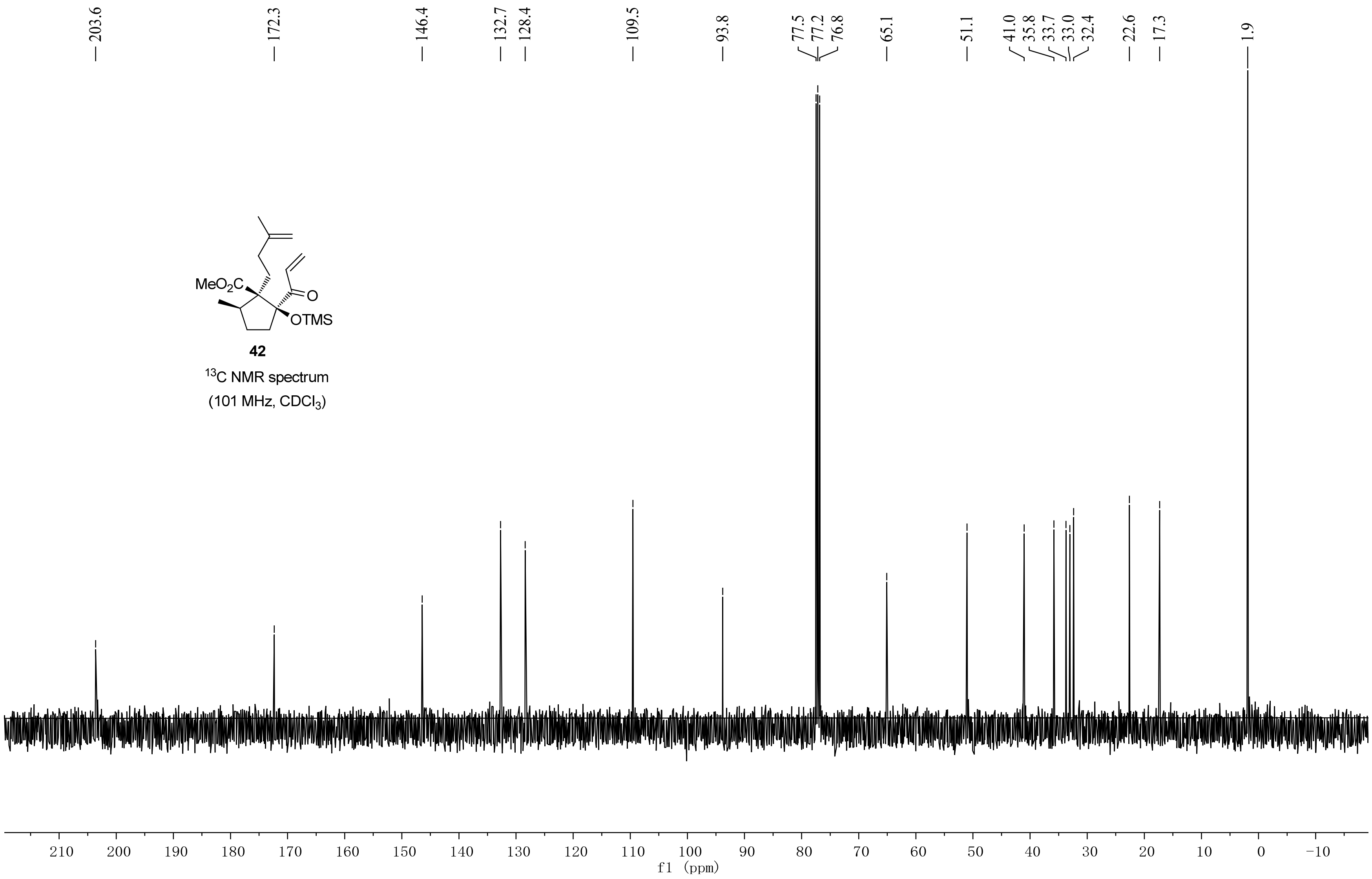
(101 MHz, $CDCl_3$)



42

^{1}H NMR spectrum

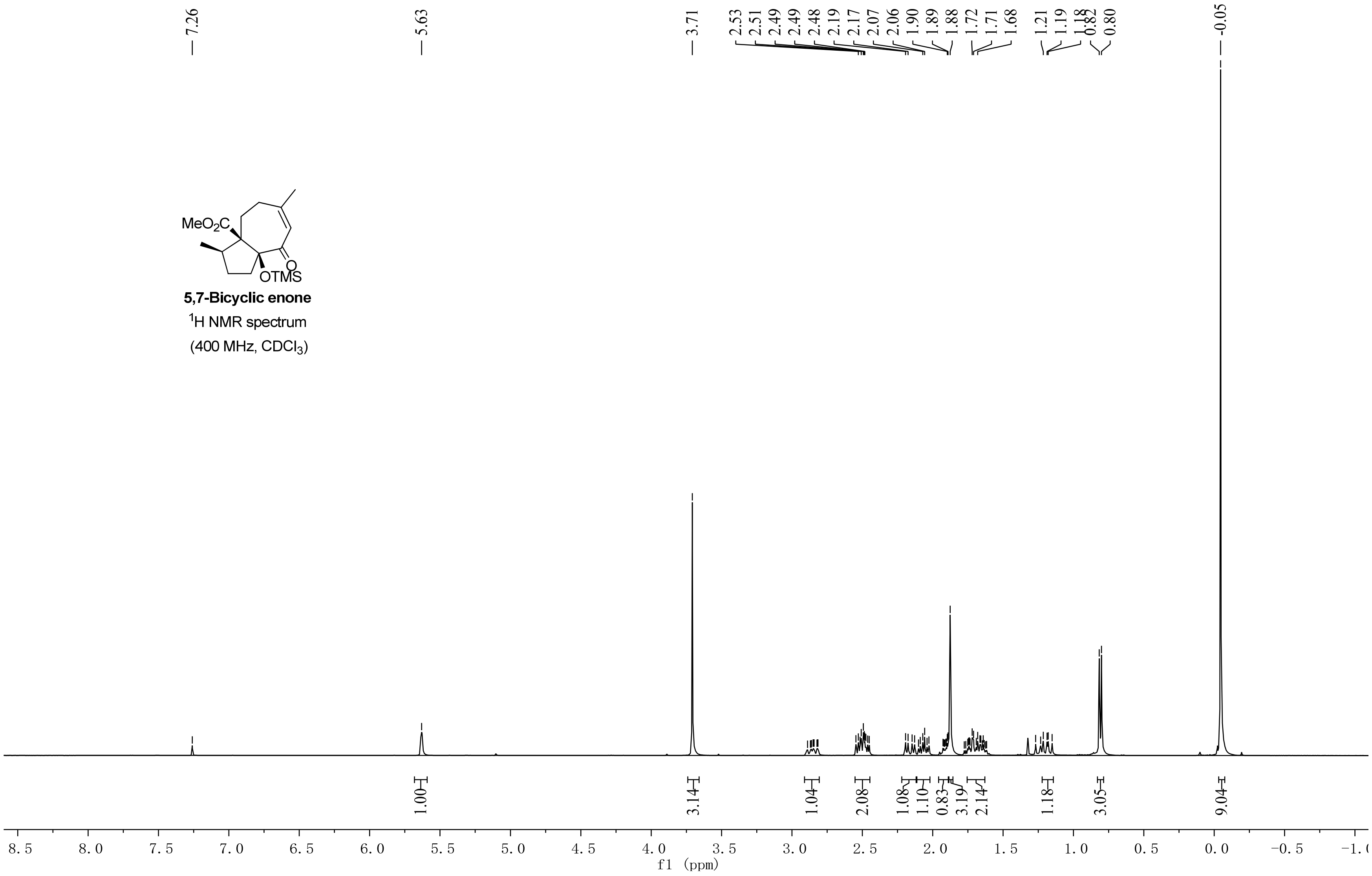
(400 MHz, $CDCl_3$)



42

^{13}C NMR spectrum

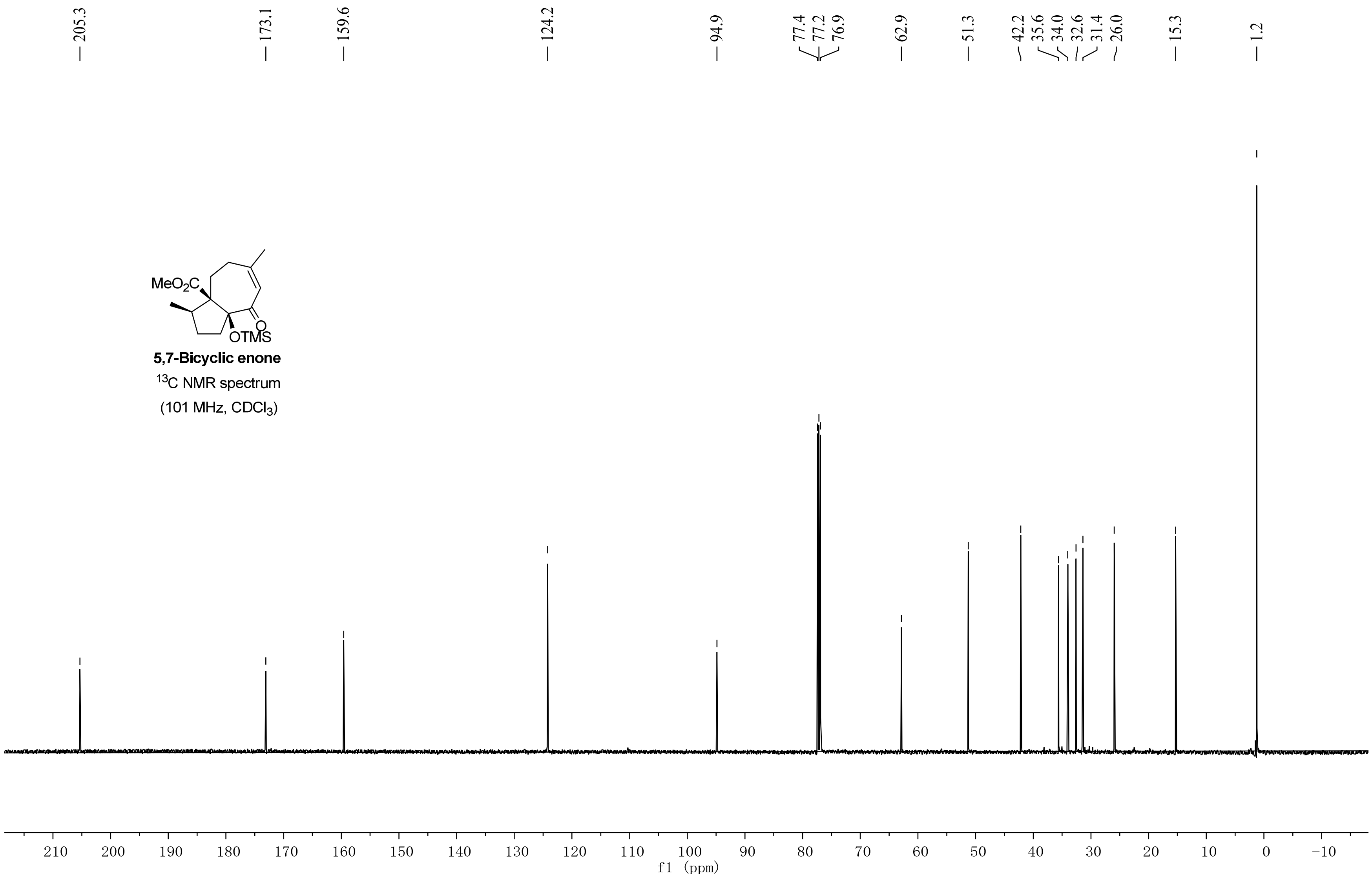
(101 MHz, $CDCl_3$)



5,7-Bicyclic enone

^{1}H NMR spectrum

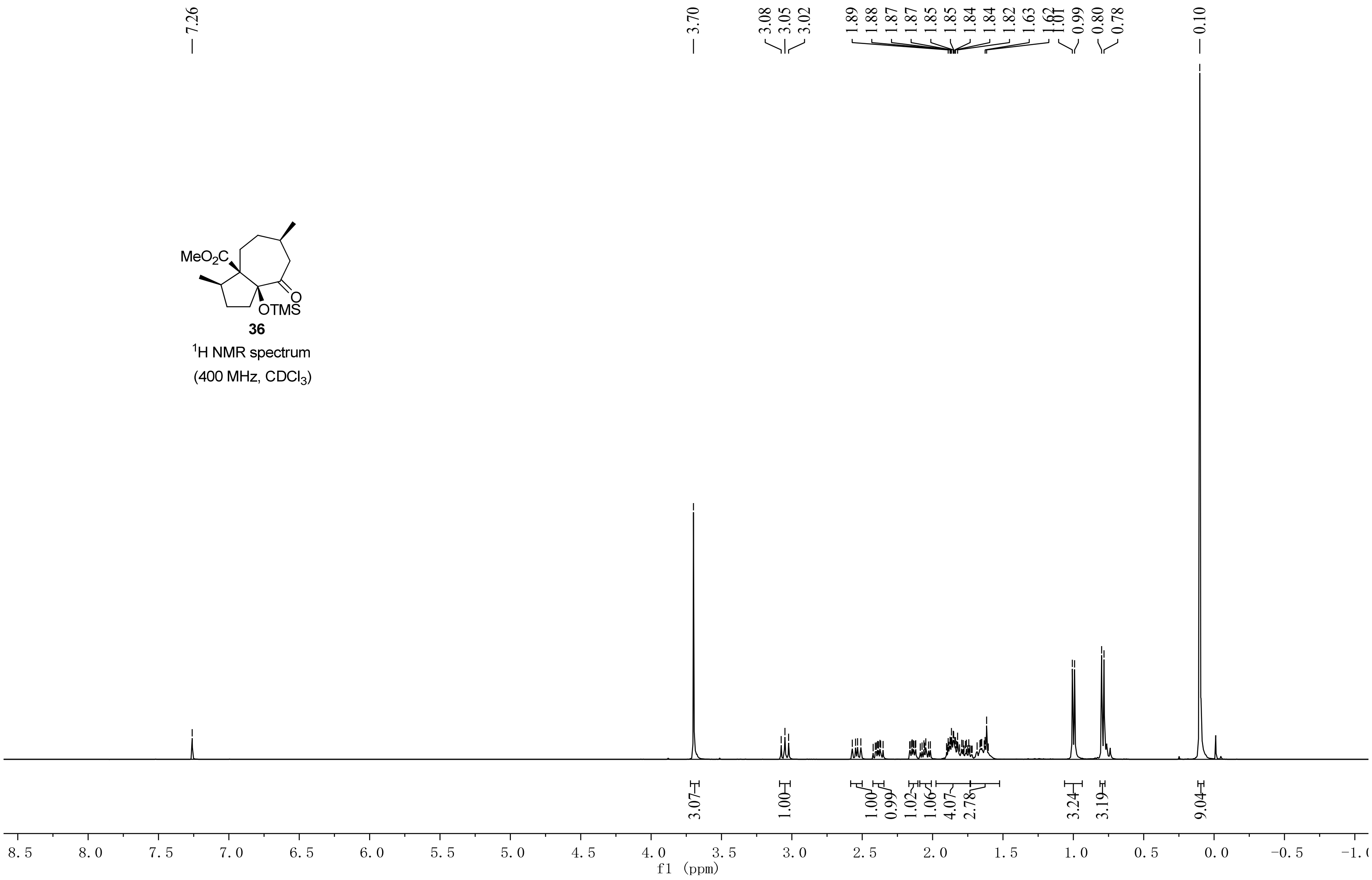
(400 MHz, $CDCl_3$)



5,7-Bicyclic enone

^{13}C NMR spectrum

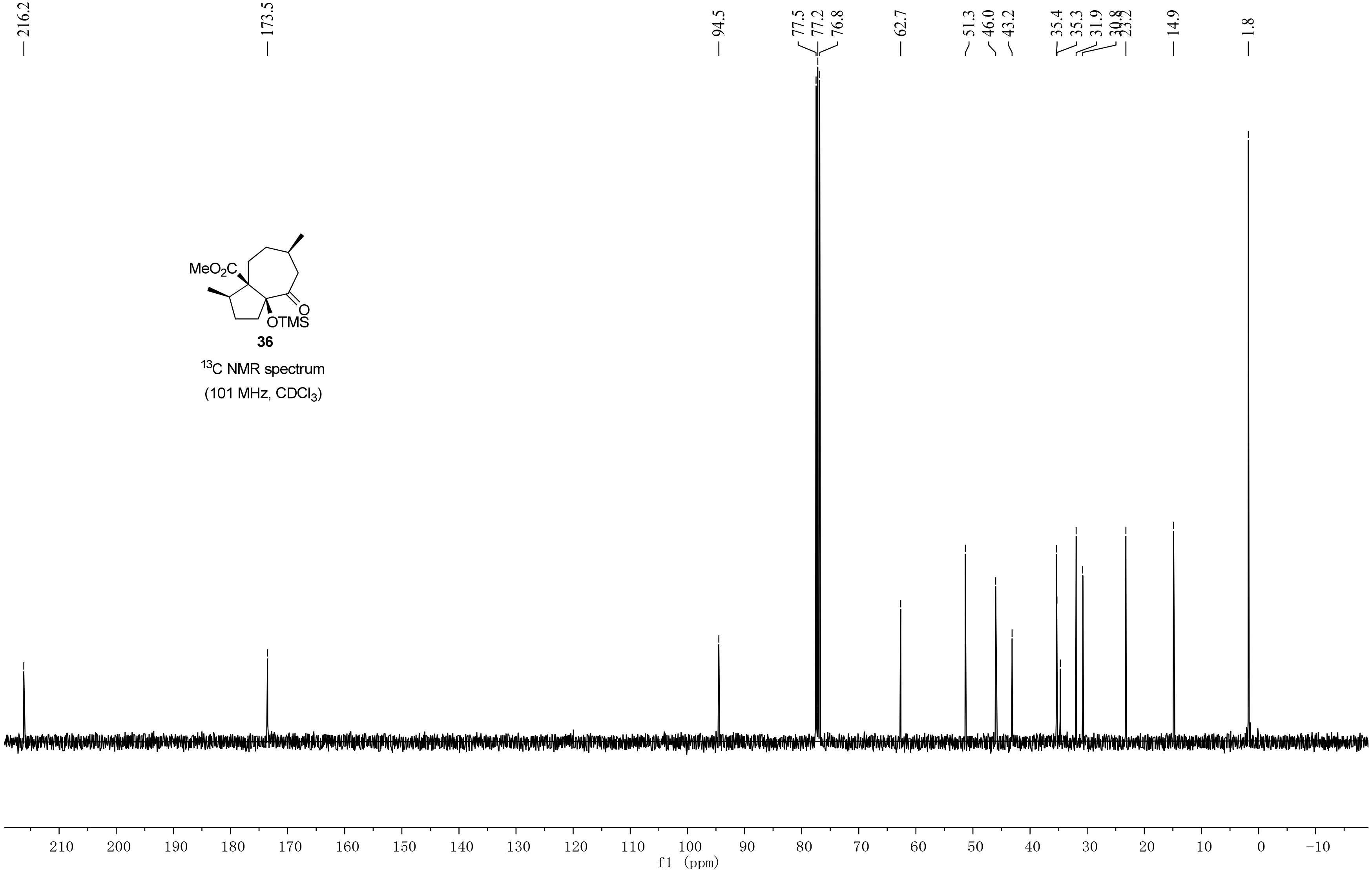
(101 MHz, $CDCl_3$)



36

^{1}H NMR spectrum

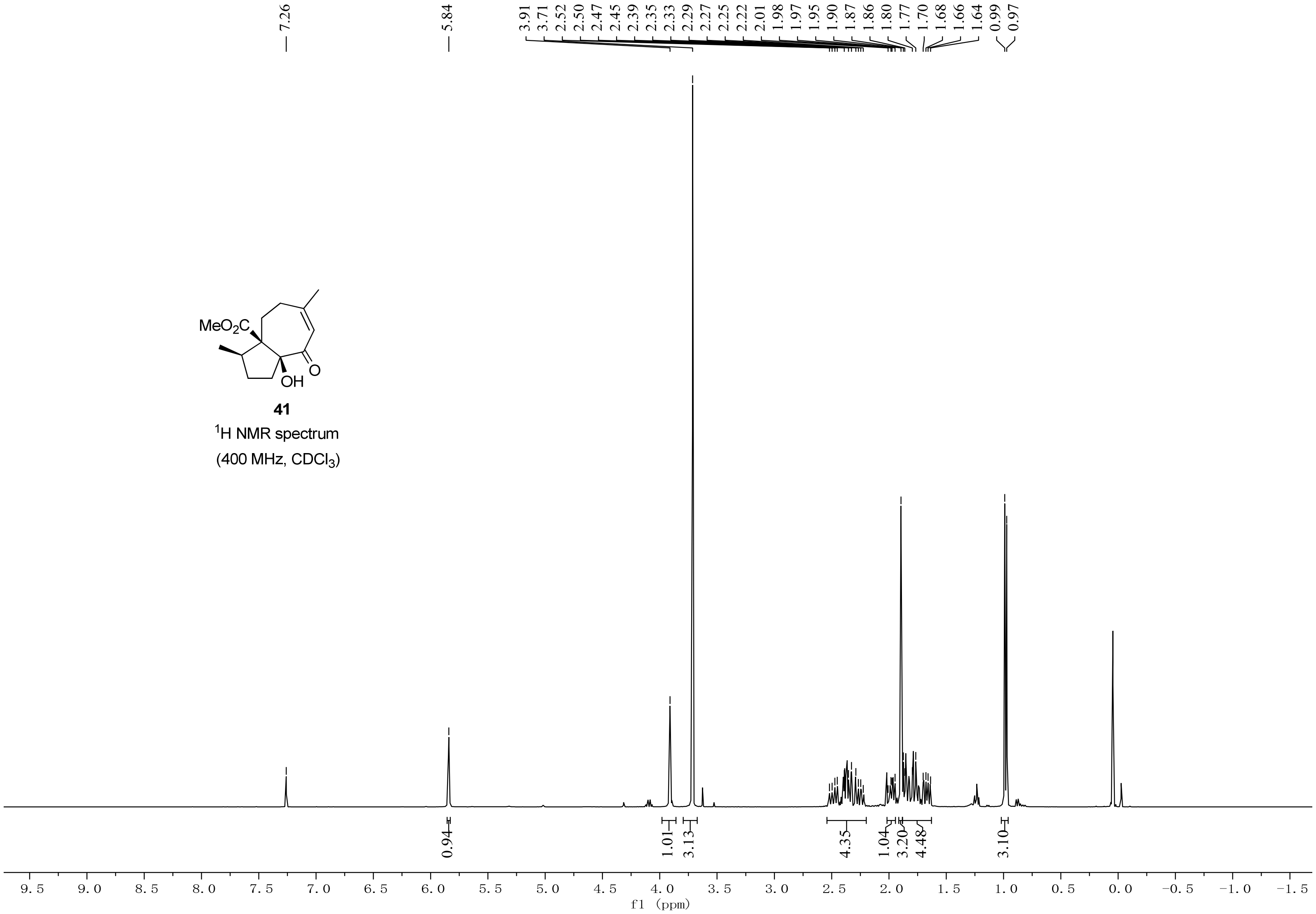
(400 MHz, $CDCl_3$)



36

^{13}C NMR spectrum

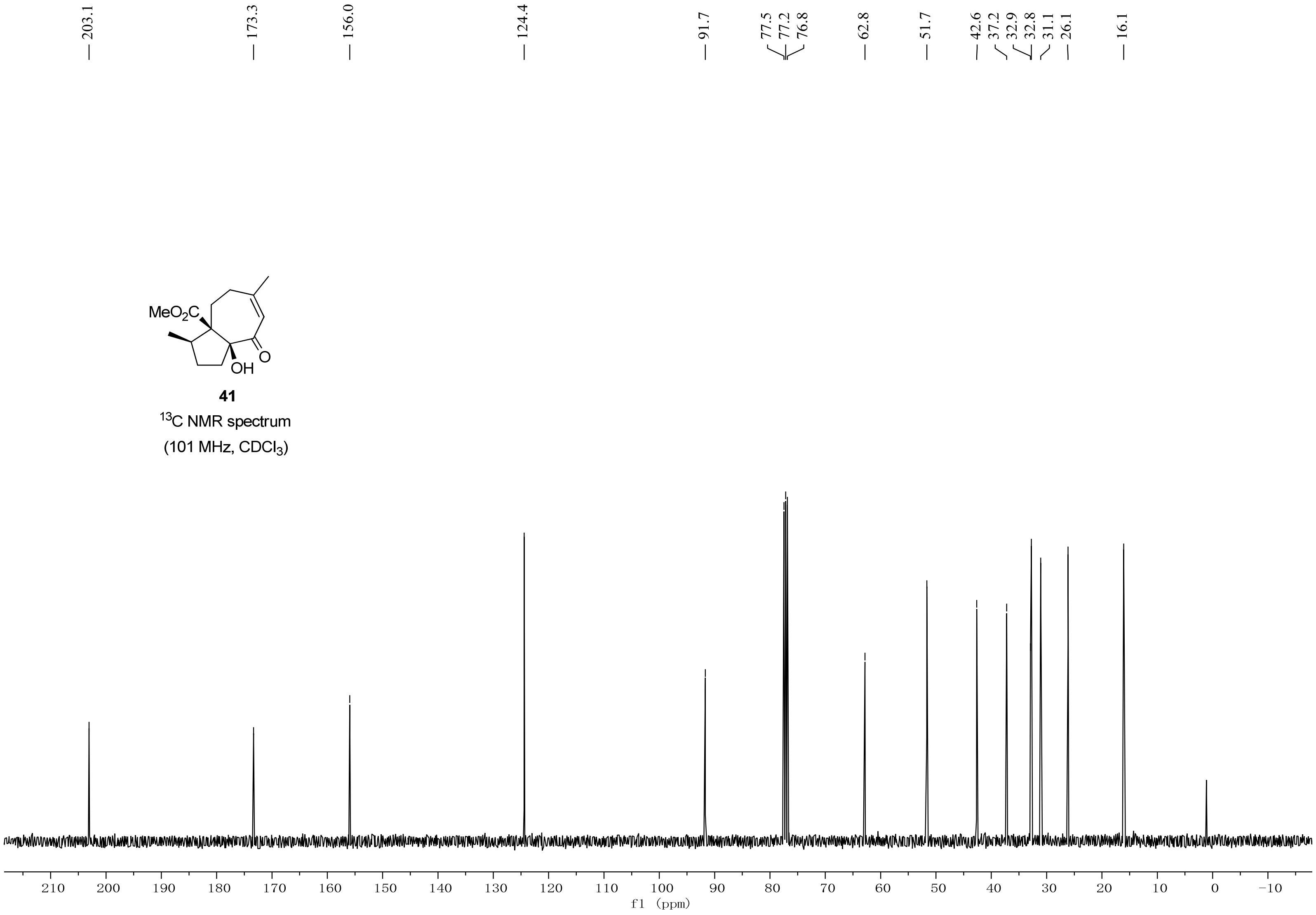
(101 MHz, $CDCl_3$)



41

^{1}H NMR spectrum

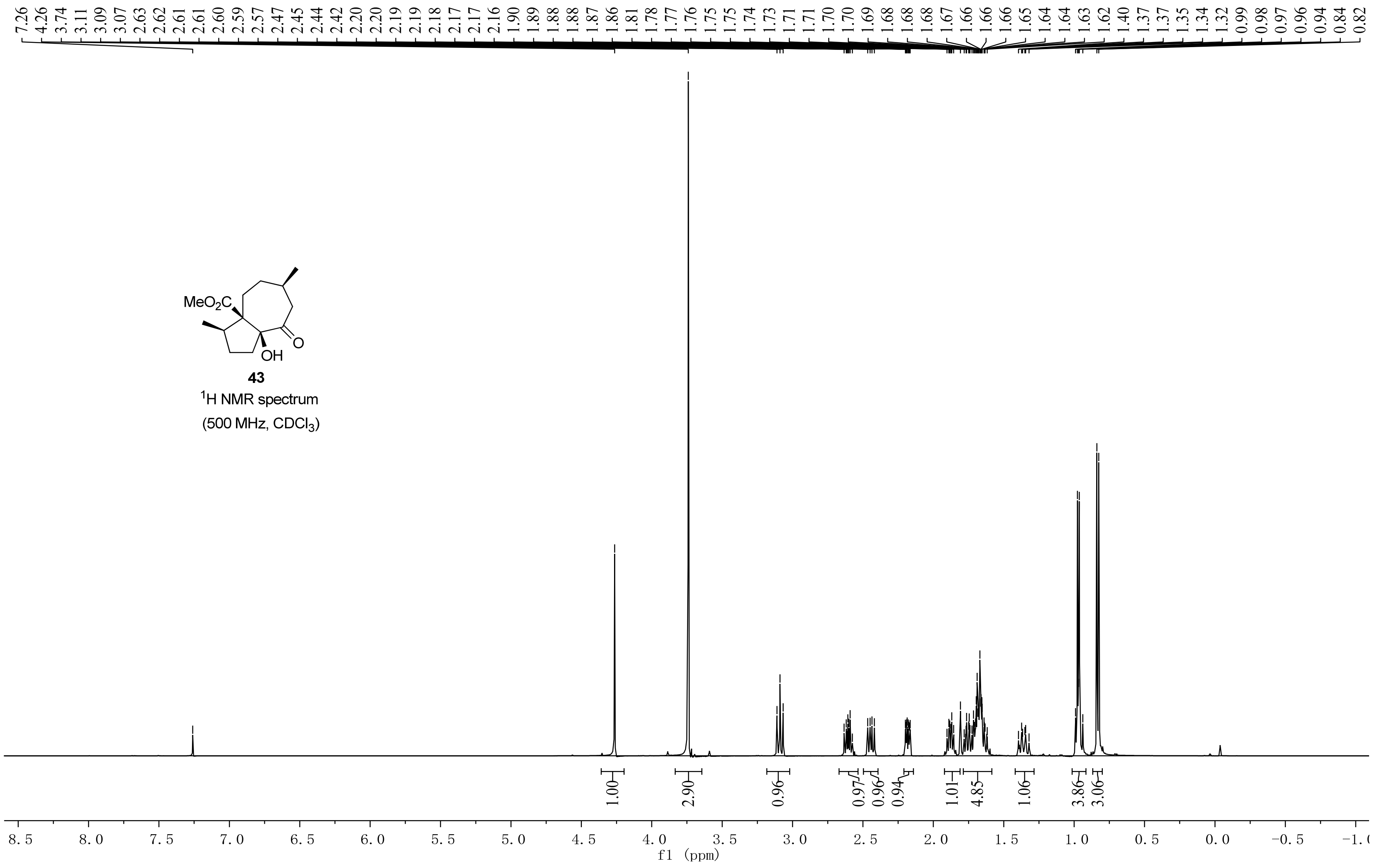
(400 MHz, $CDCl_3$)



41

^{13}C NMR spectrum

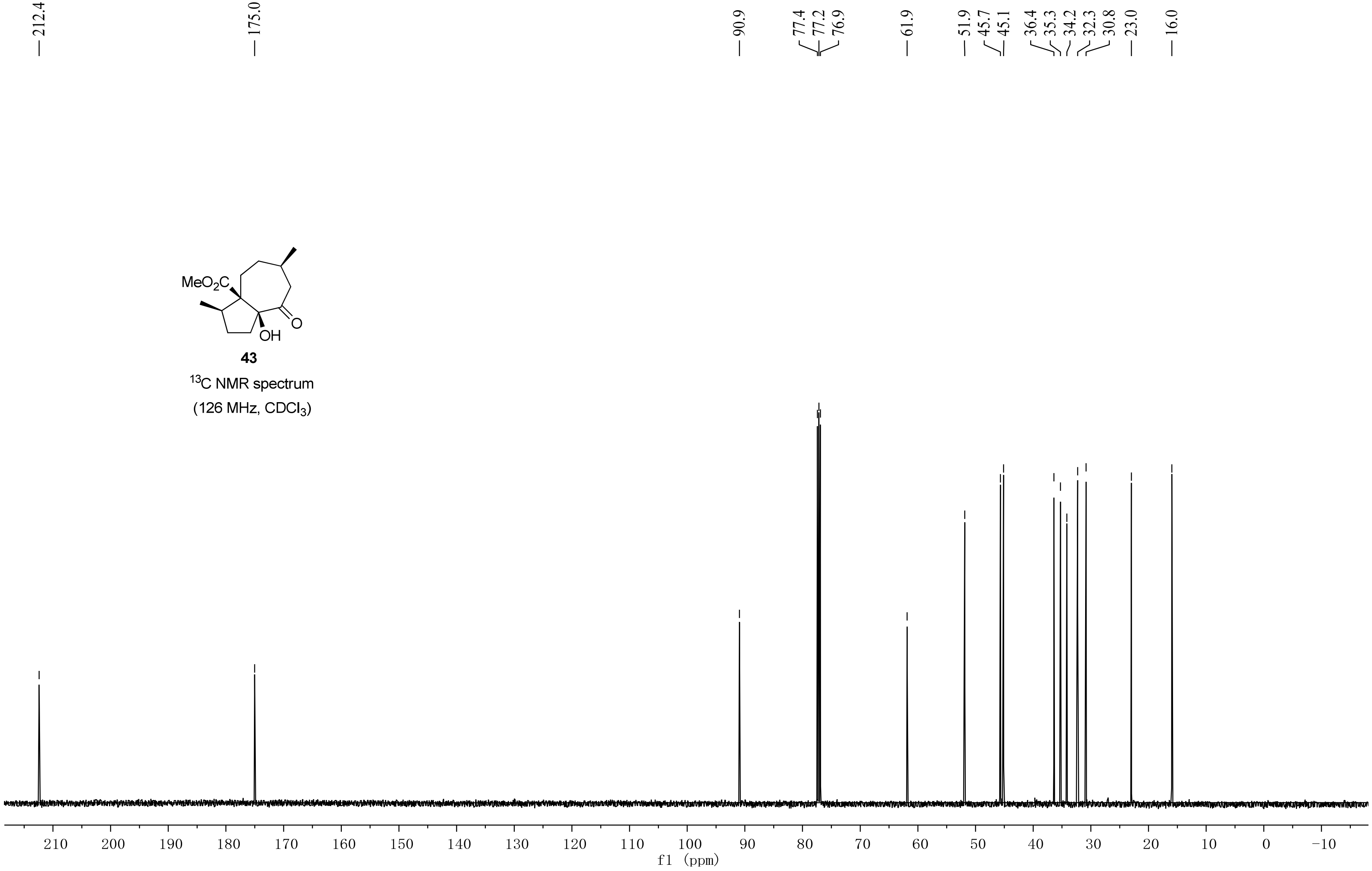
(101 MHz, $CDCl_3$)



43

^{1}H NMR spectrum

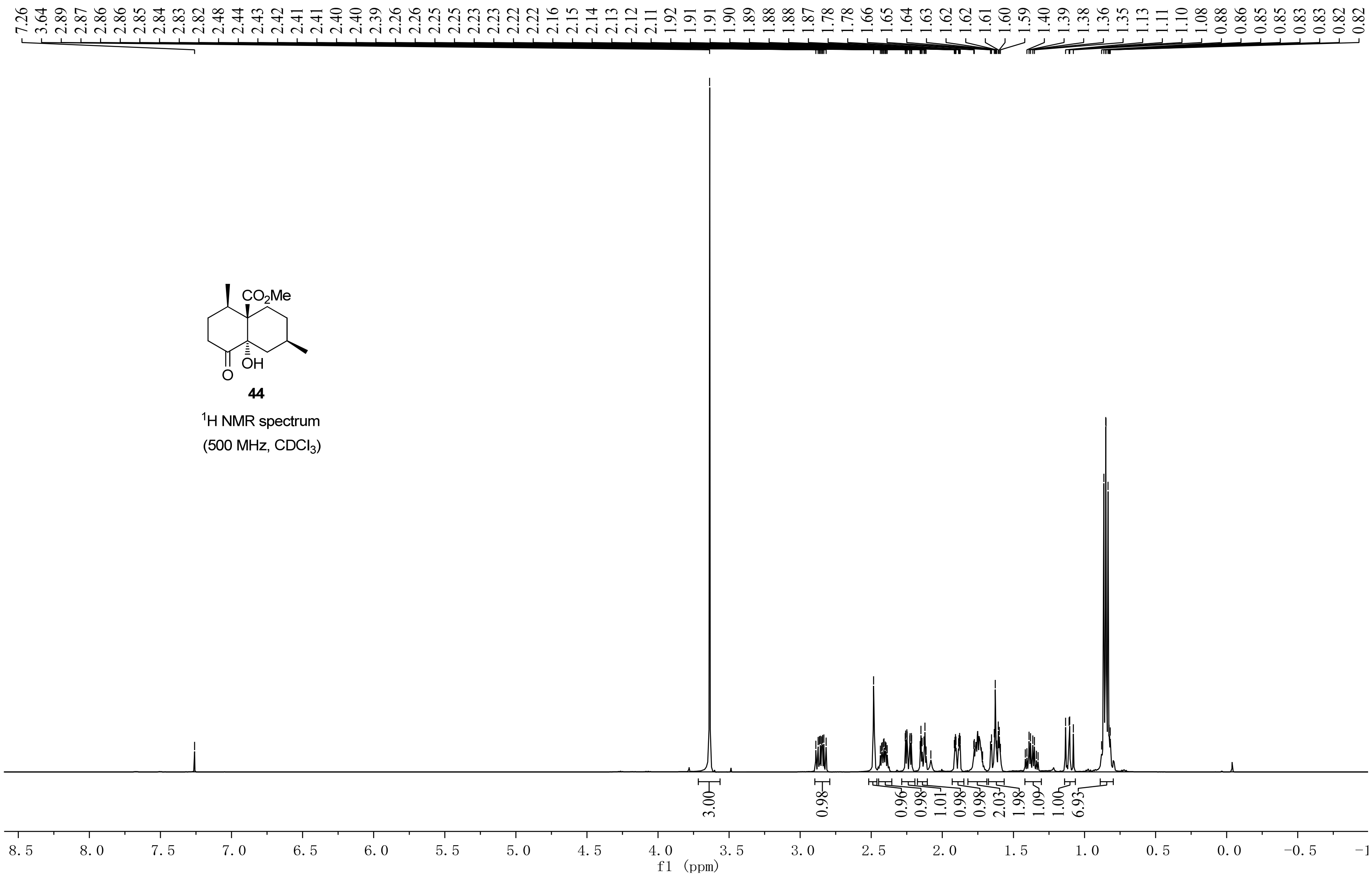
(500 MHz, $CDCl_3$)



43

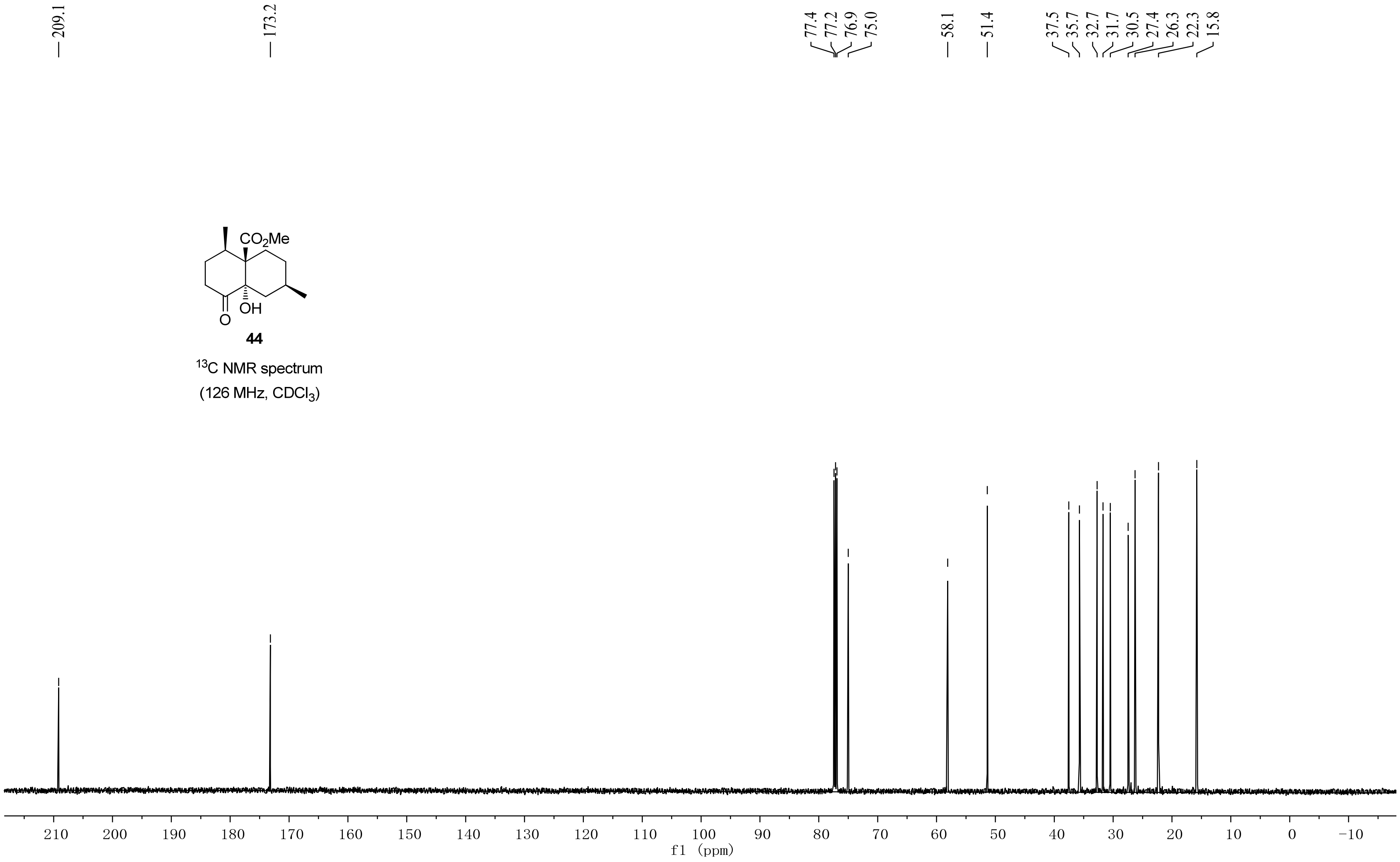
^{13}C NMR spectrum

(126 MHz, $CDCl_3$)



44

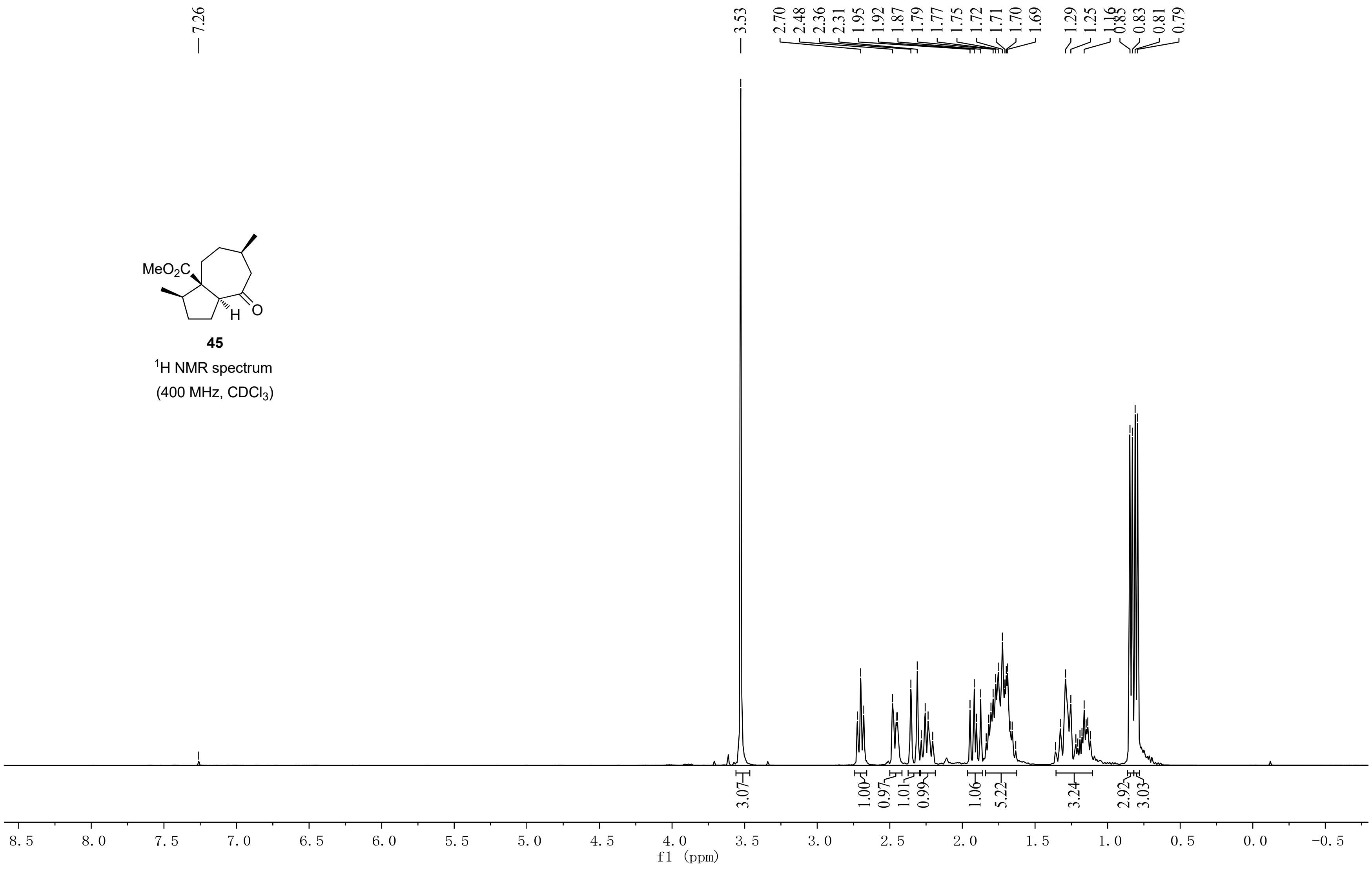
^{1}H NMR spectrum
(500 MHz, $CDCl_3$)



44

^{13}C NMR spectrum

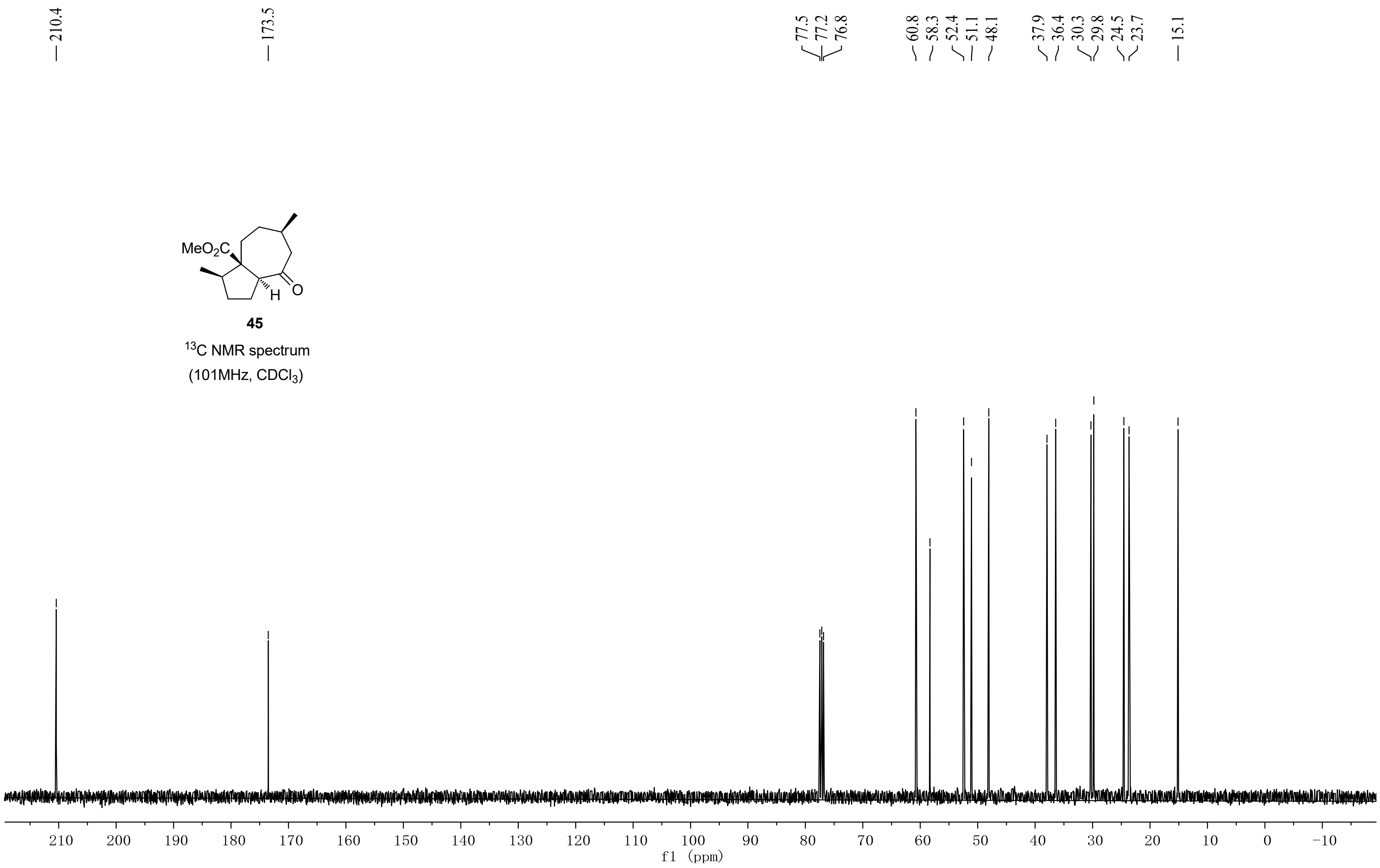
(126 MHz, CDCl$_3$)



45

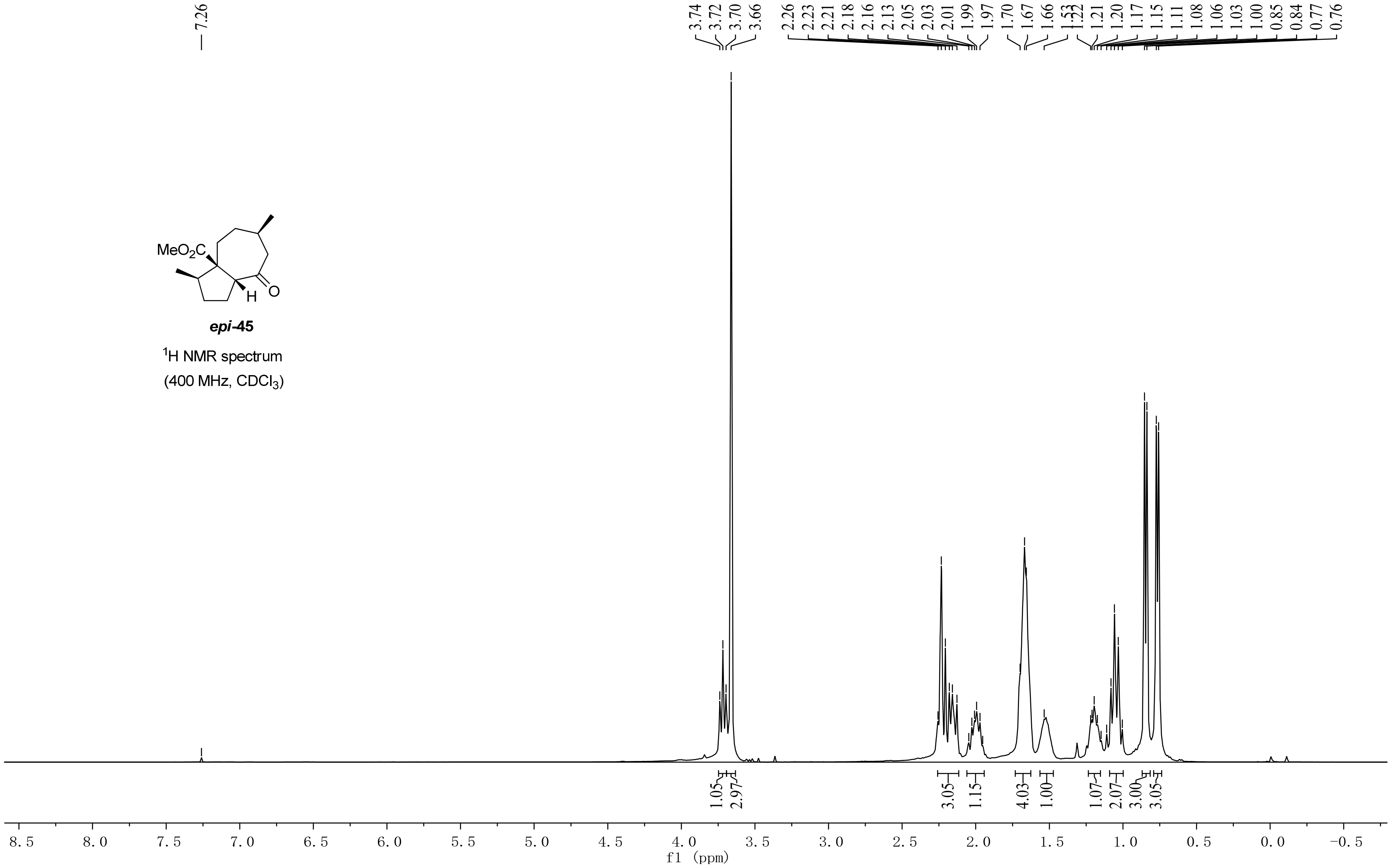
^{1}H NMR spectrum

(400 MHz, CDCl$_3$)



45

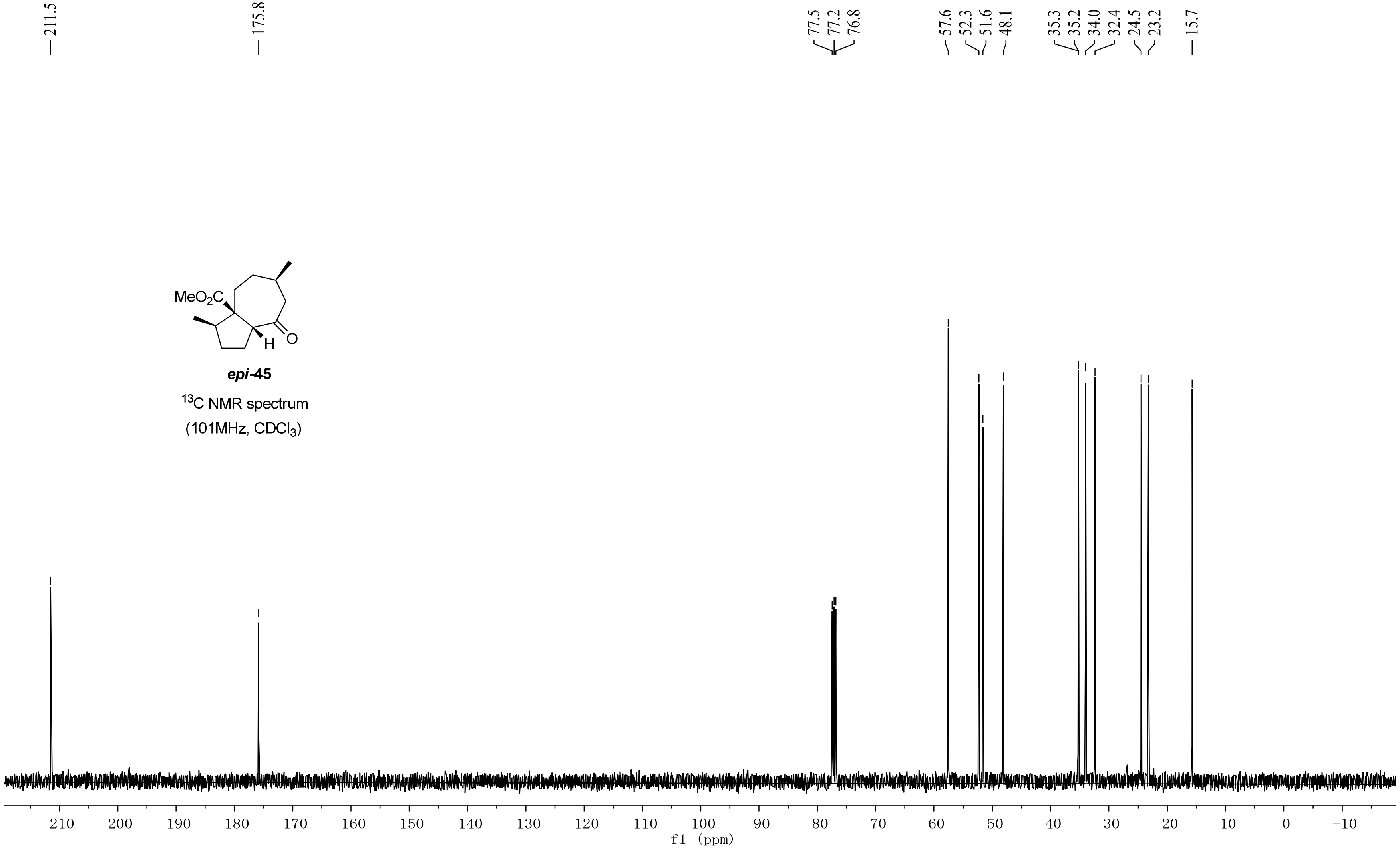
^{13}C NMR spectrum
(101MHz, CDCl$_3$)



***epi*-45**

^{1}H NMR spectrum

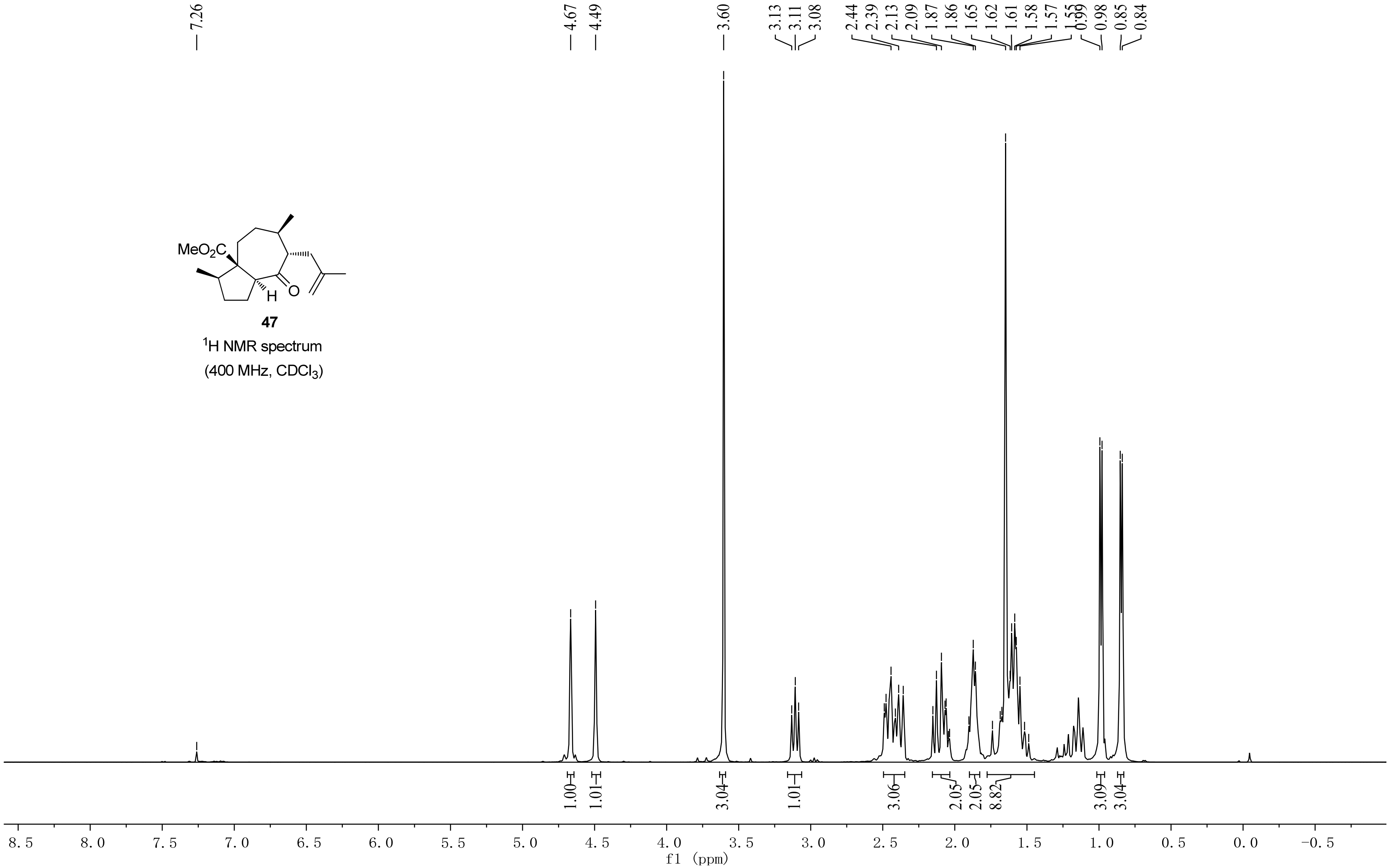
(400 MHz, CDCl$_3$)



***epi*-45**

^{13}C NMR spectrum

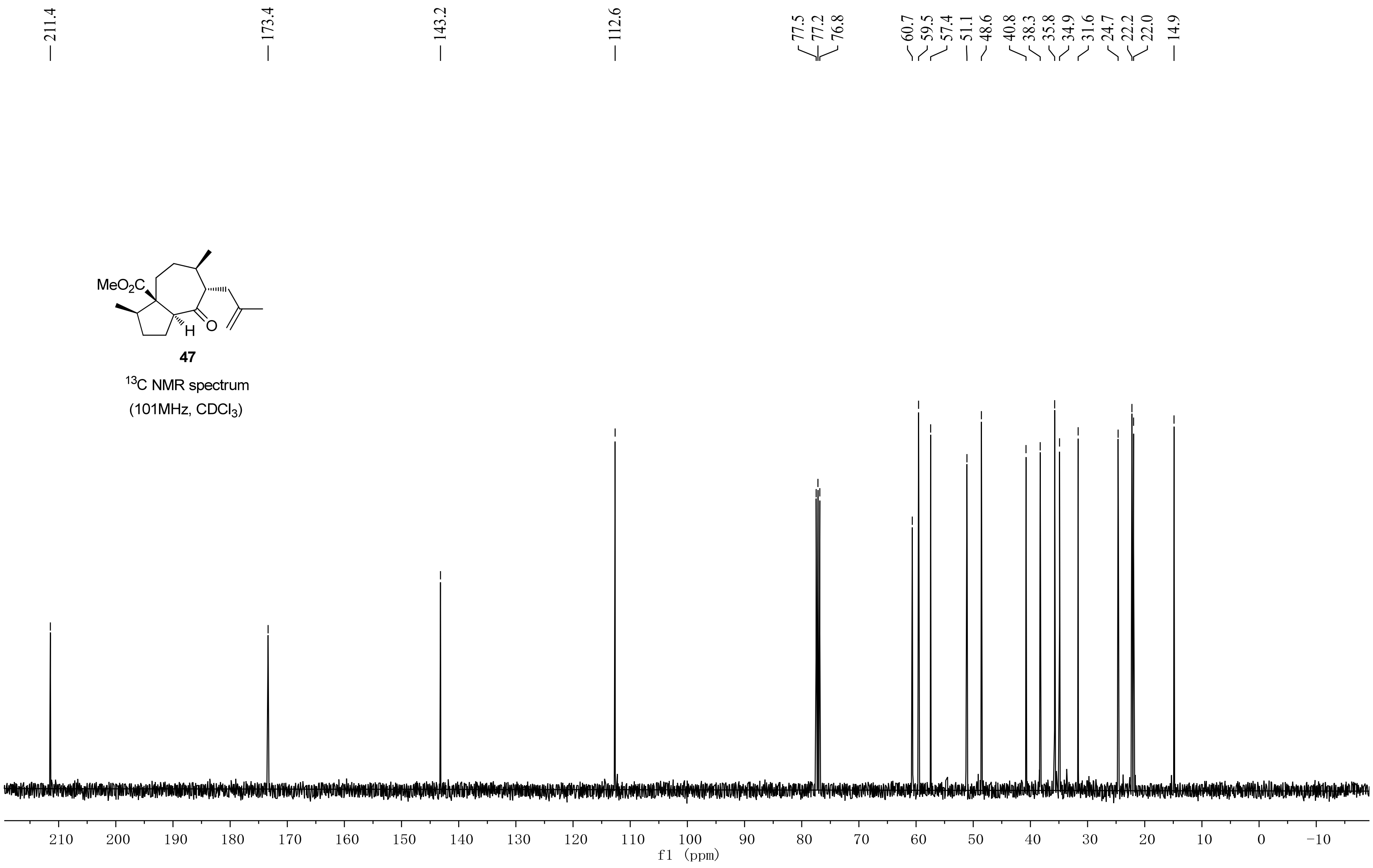
(101MHz, $CDCl_3$)



47

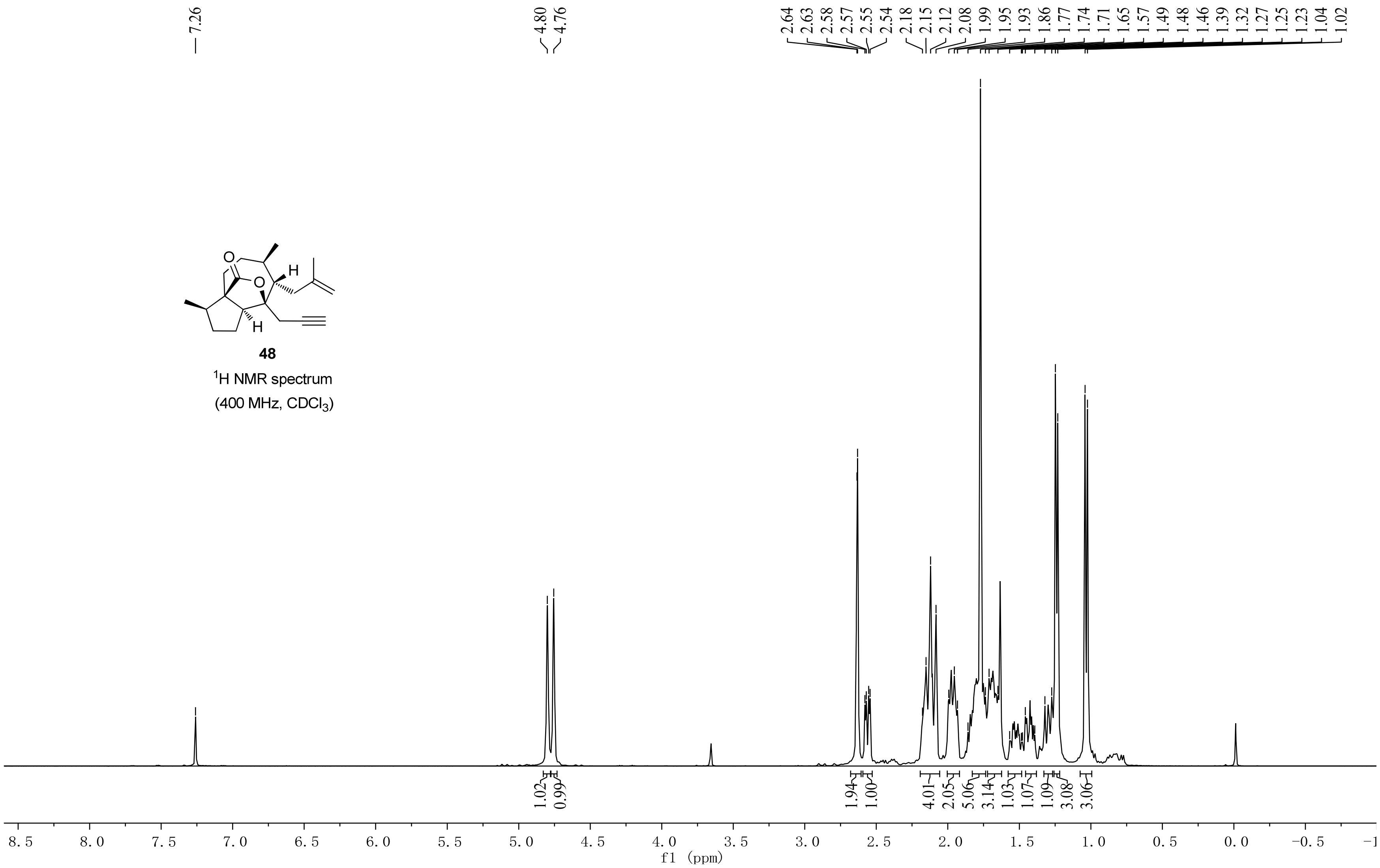
^{1}H NMR spectrum

(400 MHz, $CDCl_3$)



47

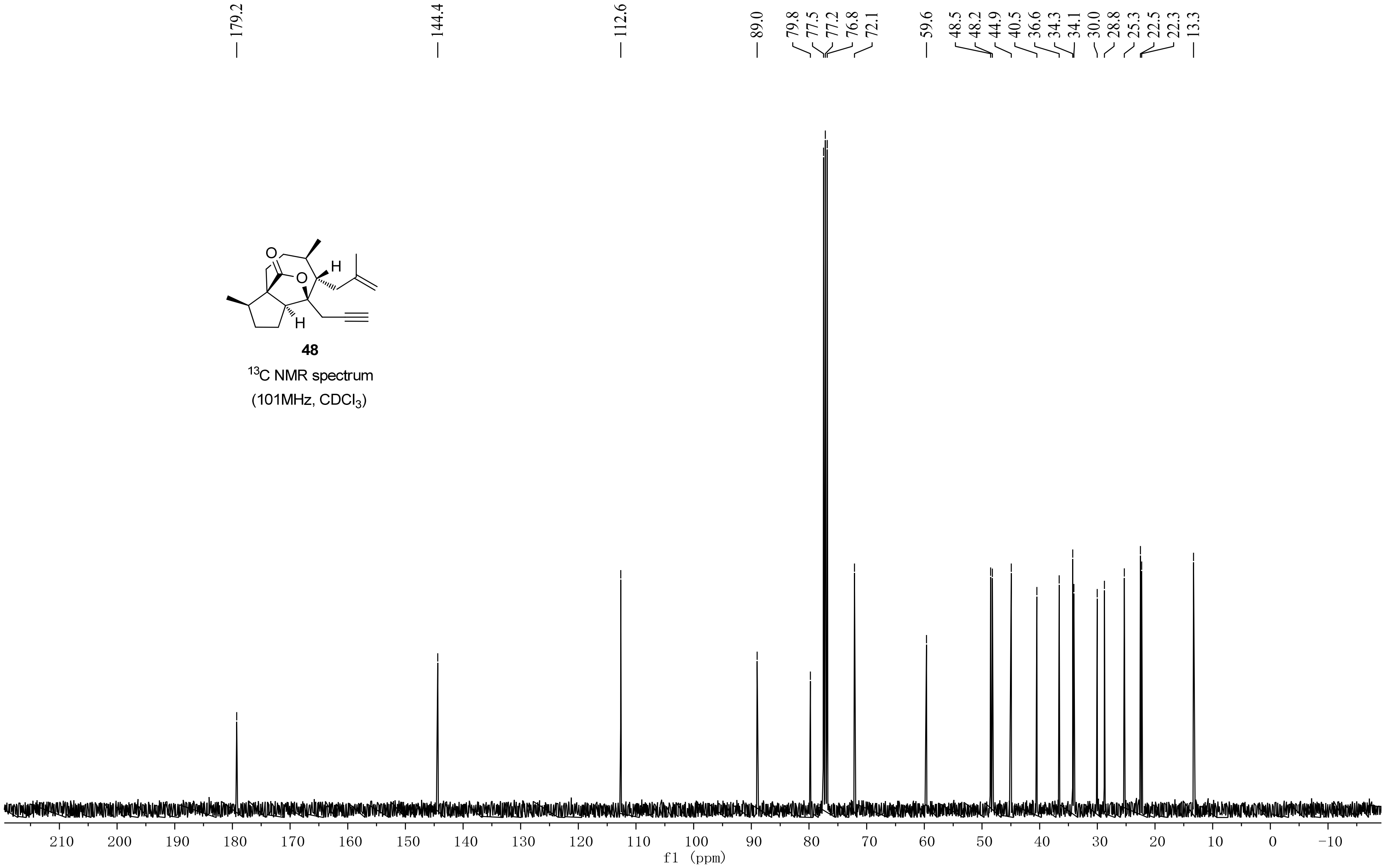
^{13}C NMR spectrum
(101MHz, $CDCl_3$)



48

^{1}H NMR spectrum

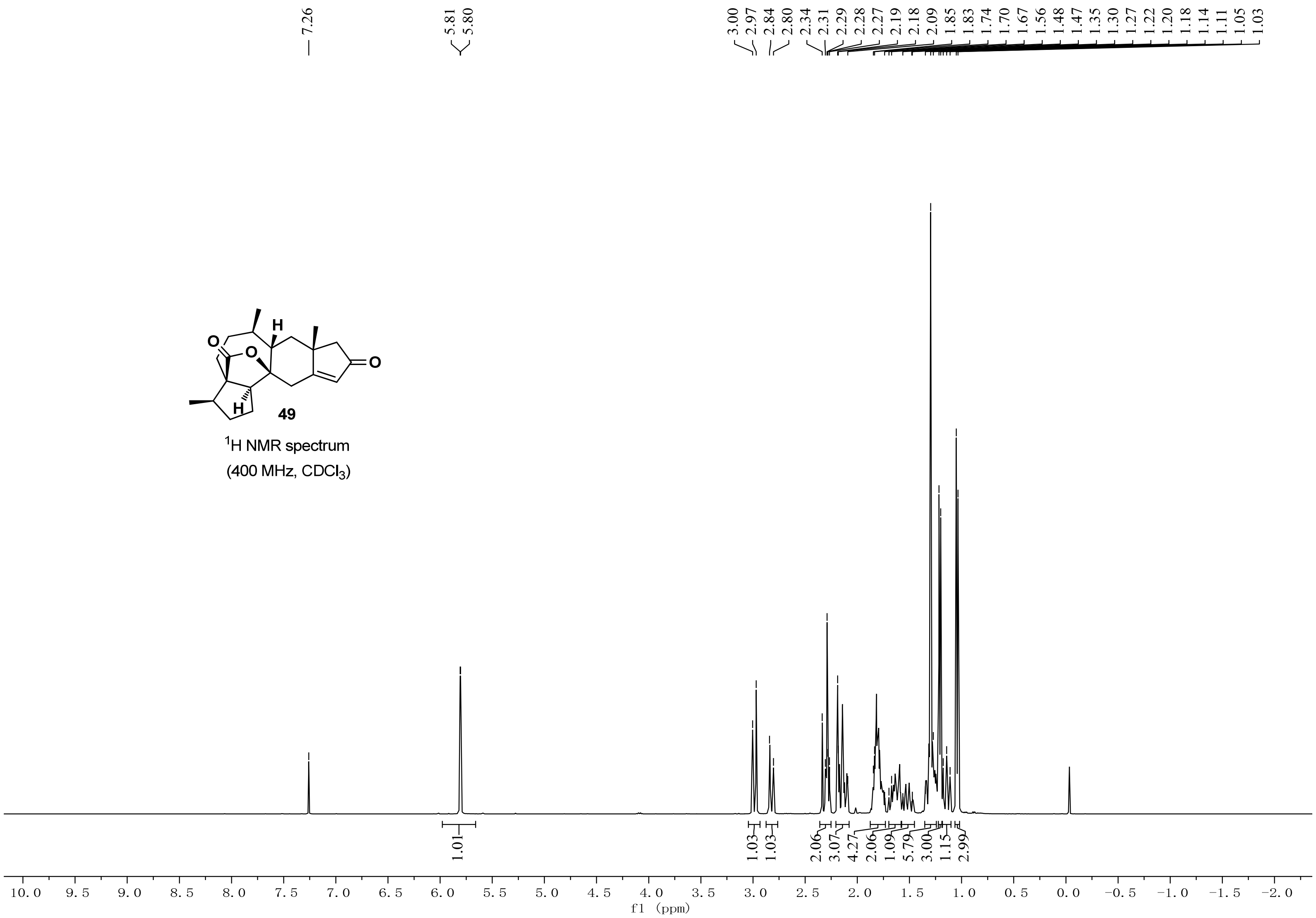
(400 MHz, $CDCl_3$)



48

^{13}C NMR spectrum

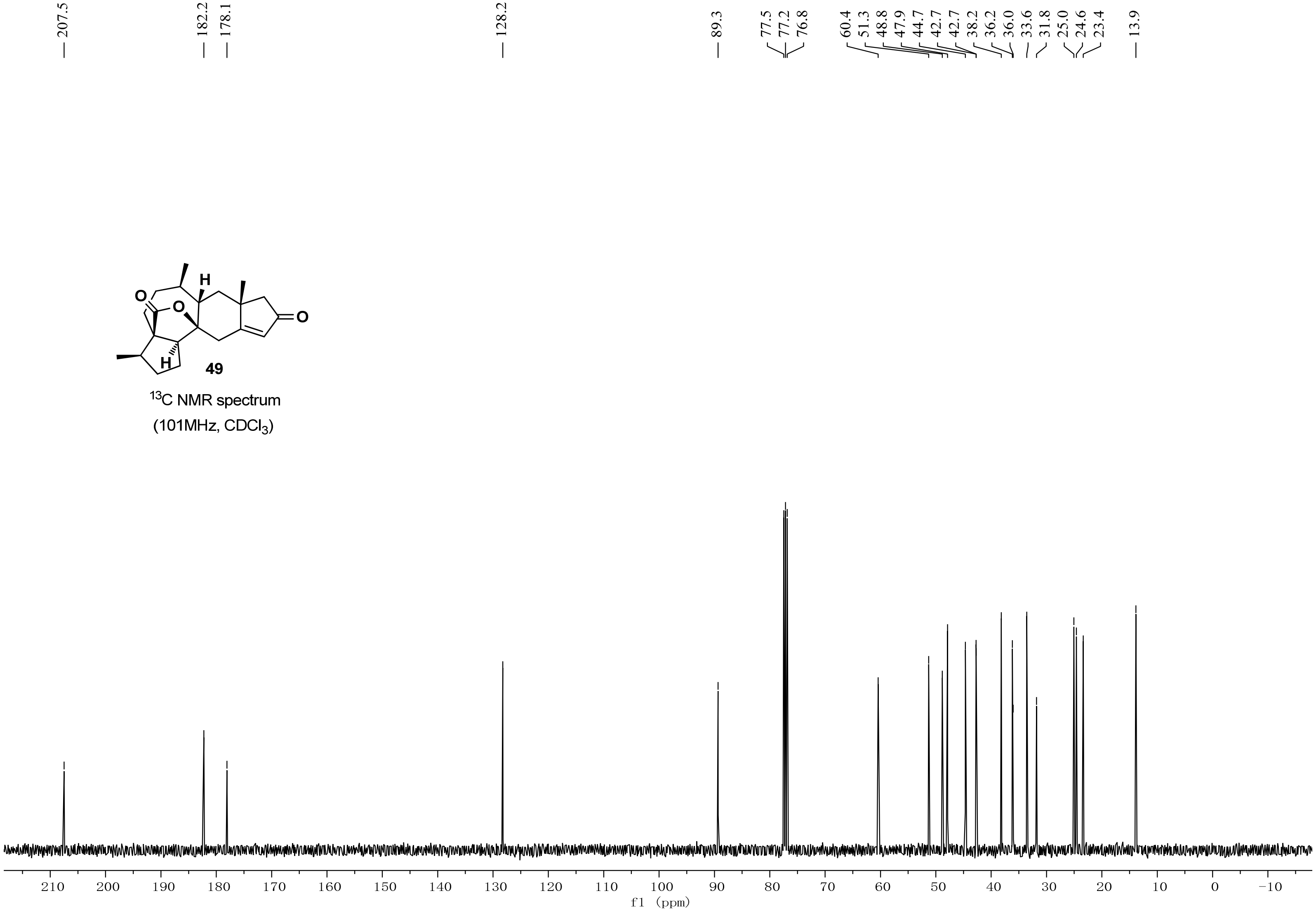
(101MHz, $CDCl_3$)



49

^{1}H NMR spectrum

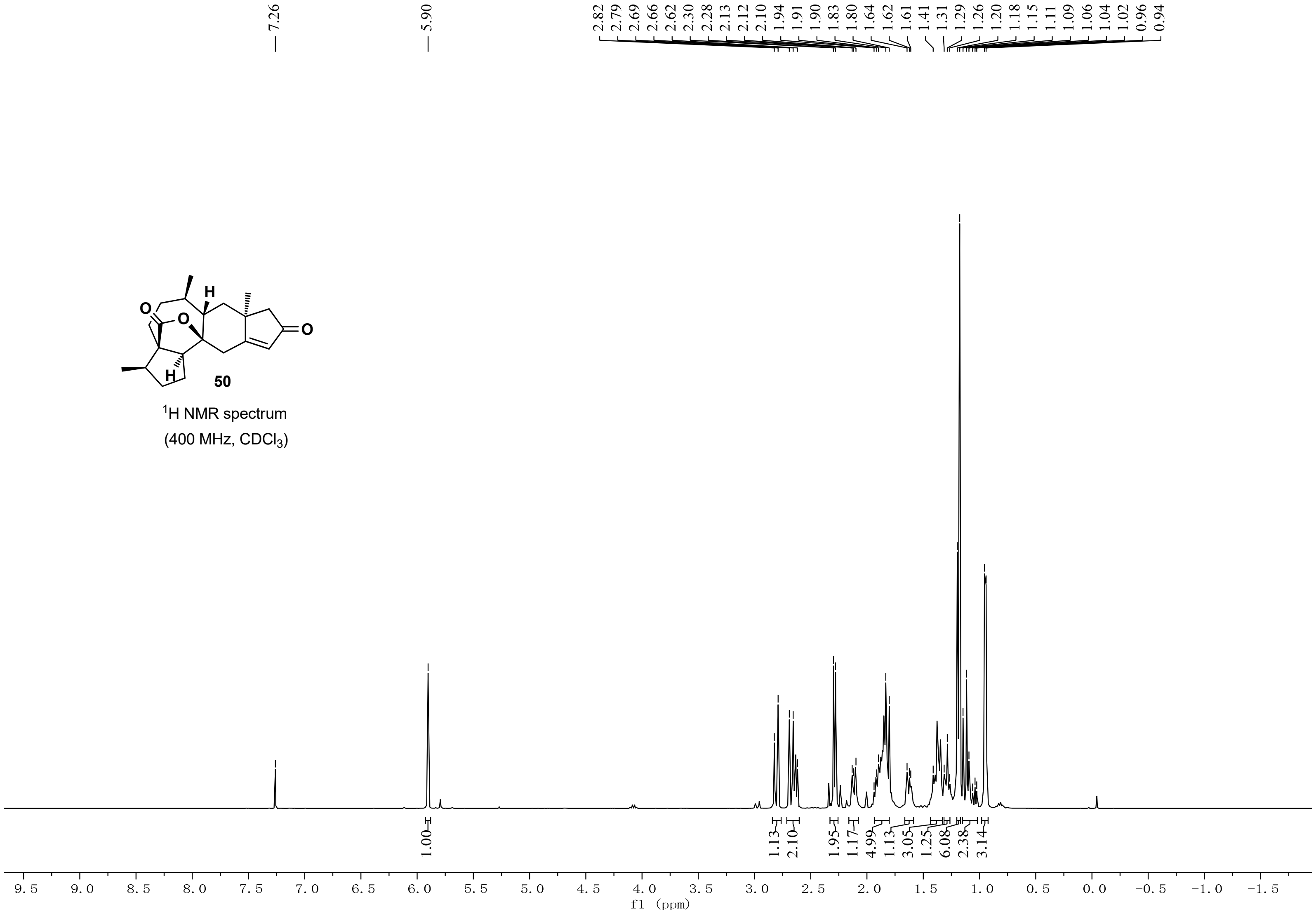
(400 MHz, $CDCl_3$)



49

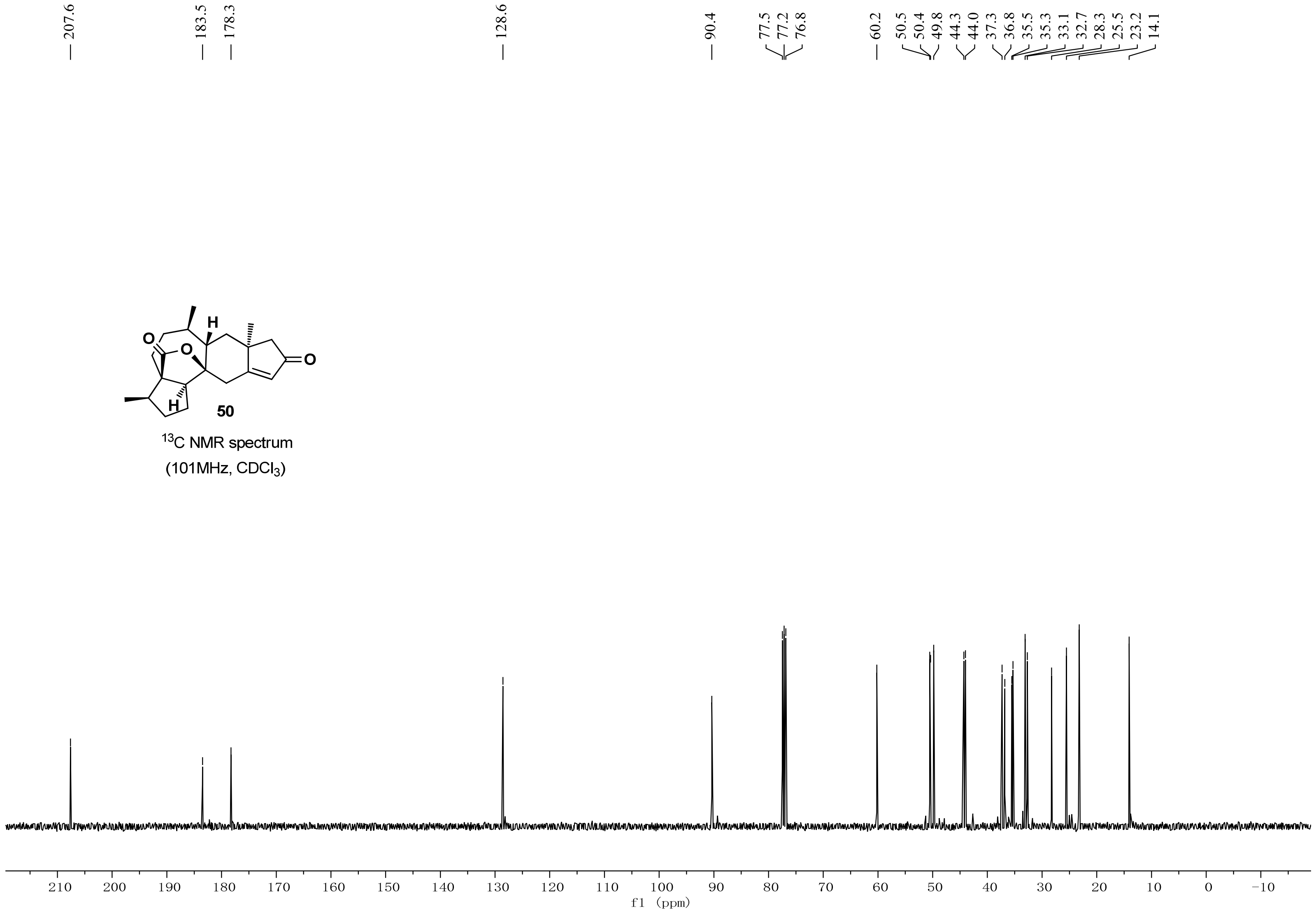
^{13}C NMR spectrum

(101MHz, $CDCl_3$)



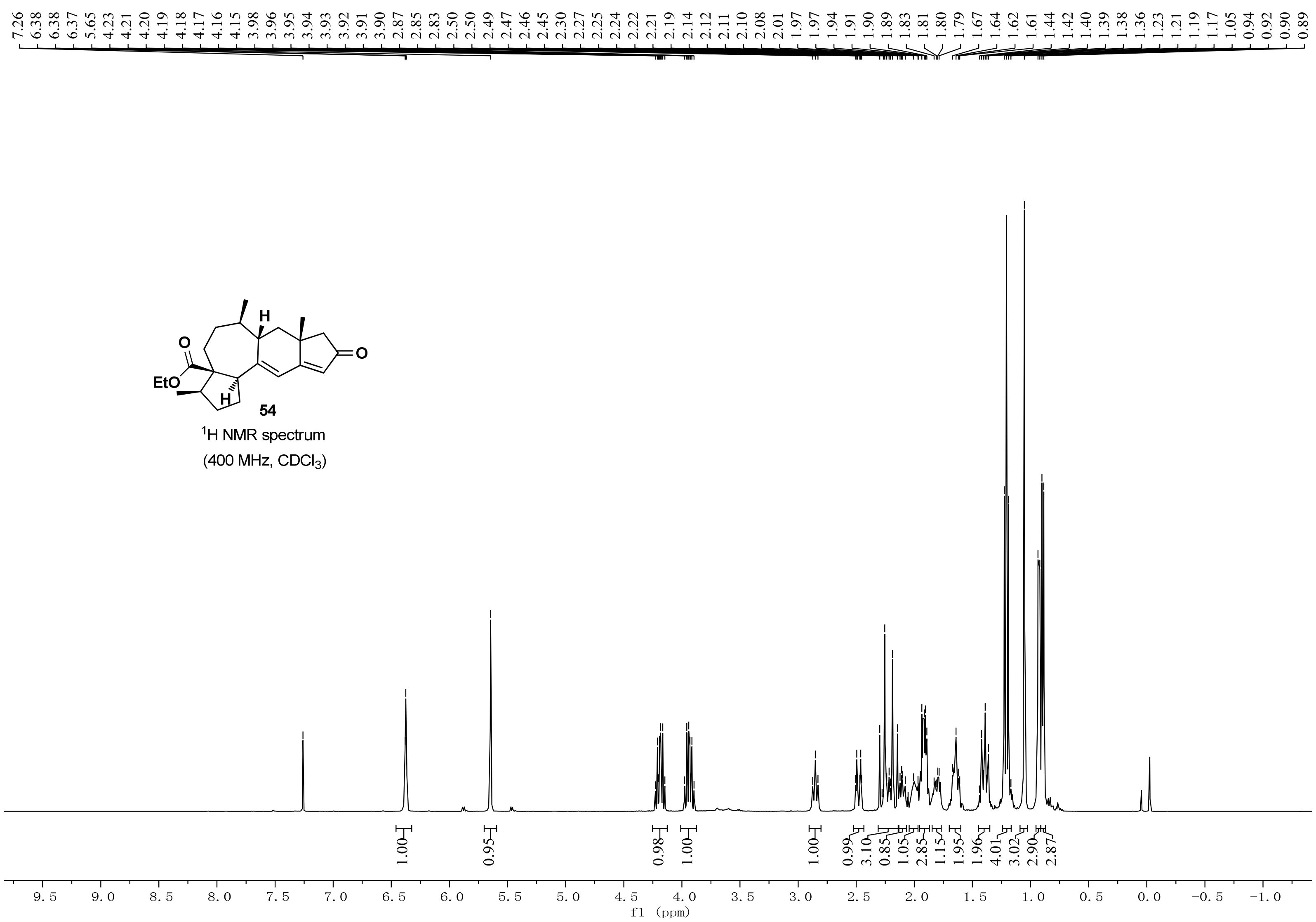
50

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



50

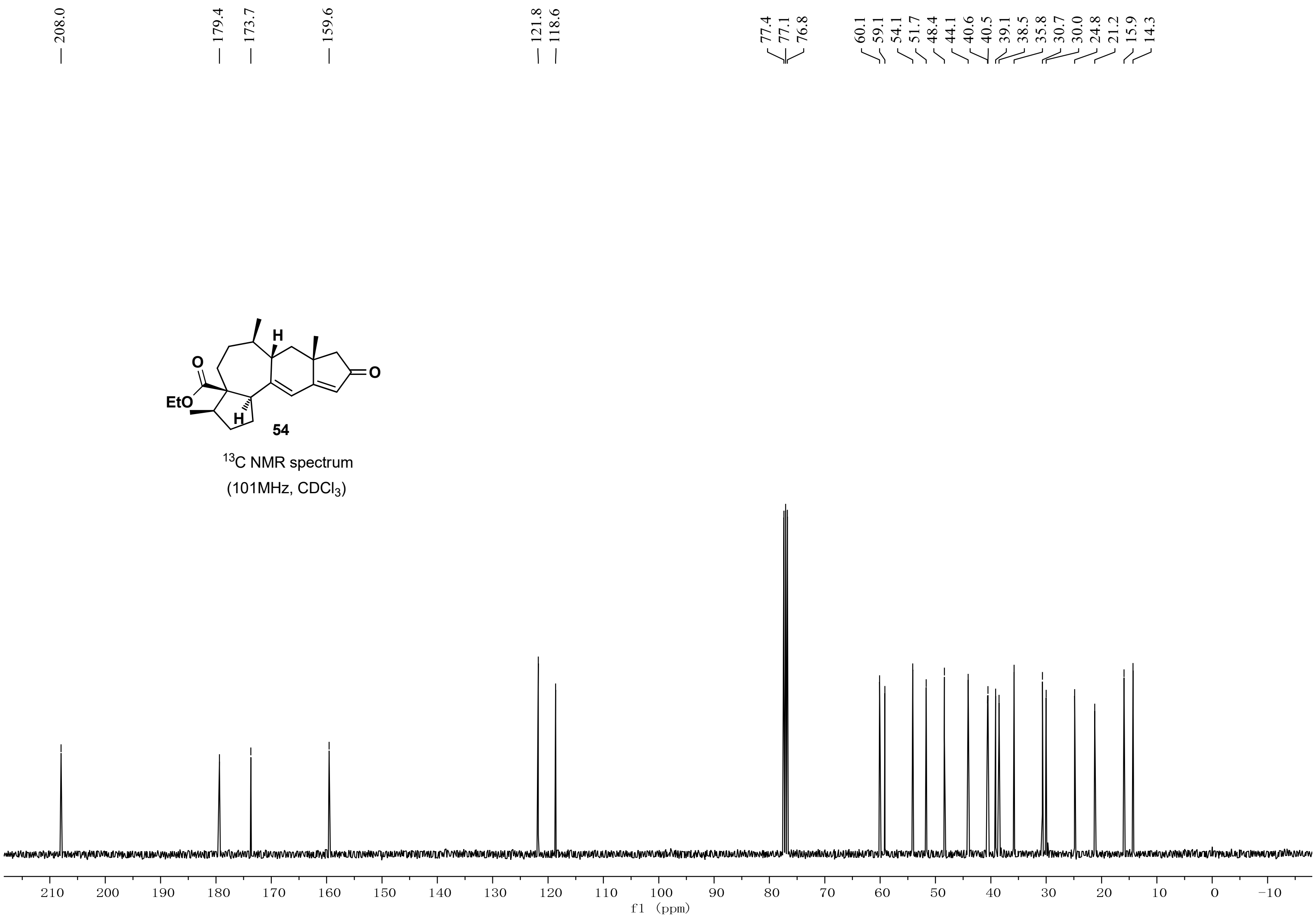
^{13}C NMR spectrum
(101MHz, $CDCl_3$)



54

^{1}H NMR spectrum

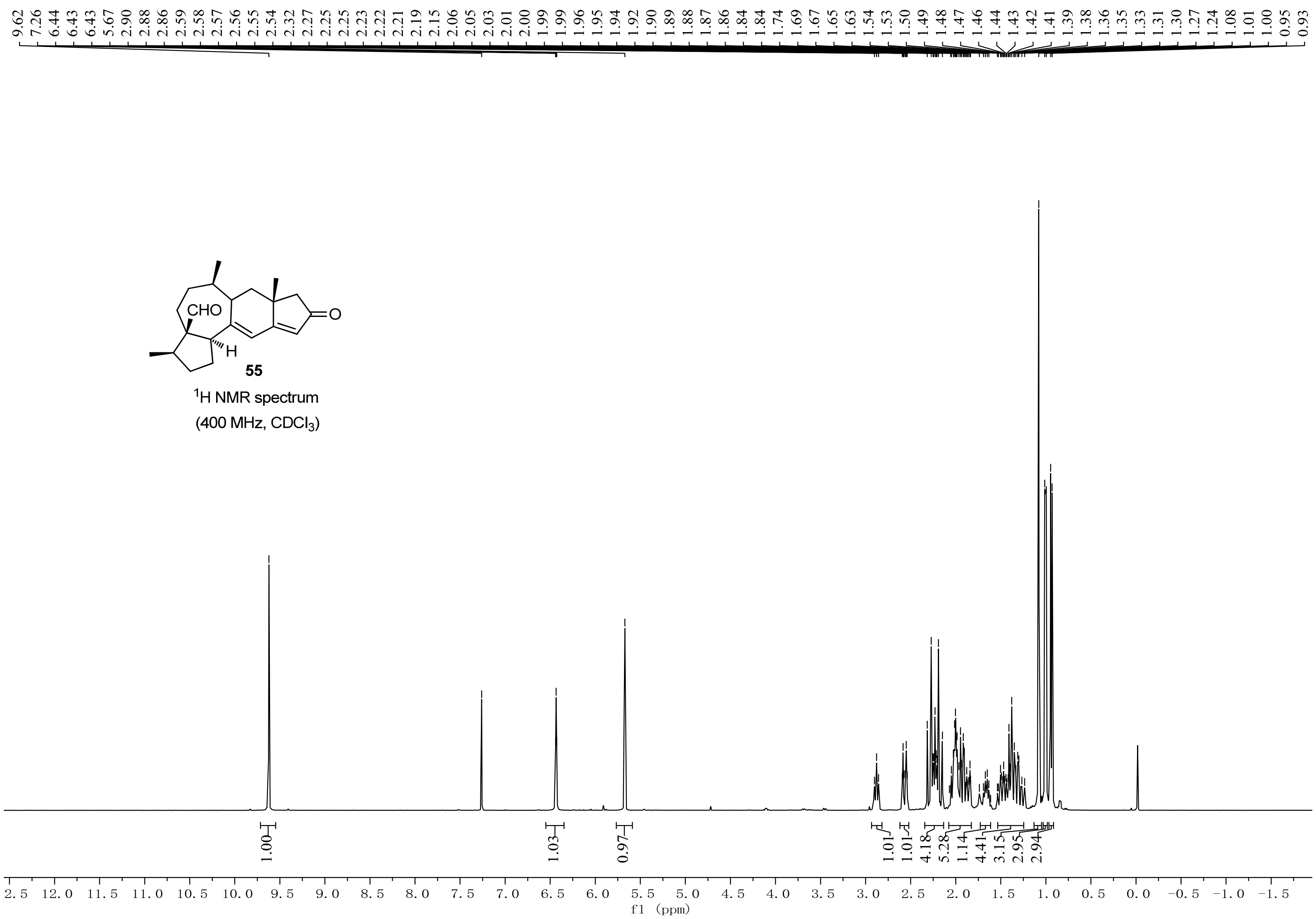
(400 MHz, CDCl$_3$)



54

^{13}C NMR spectrum

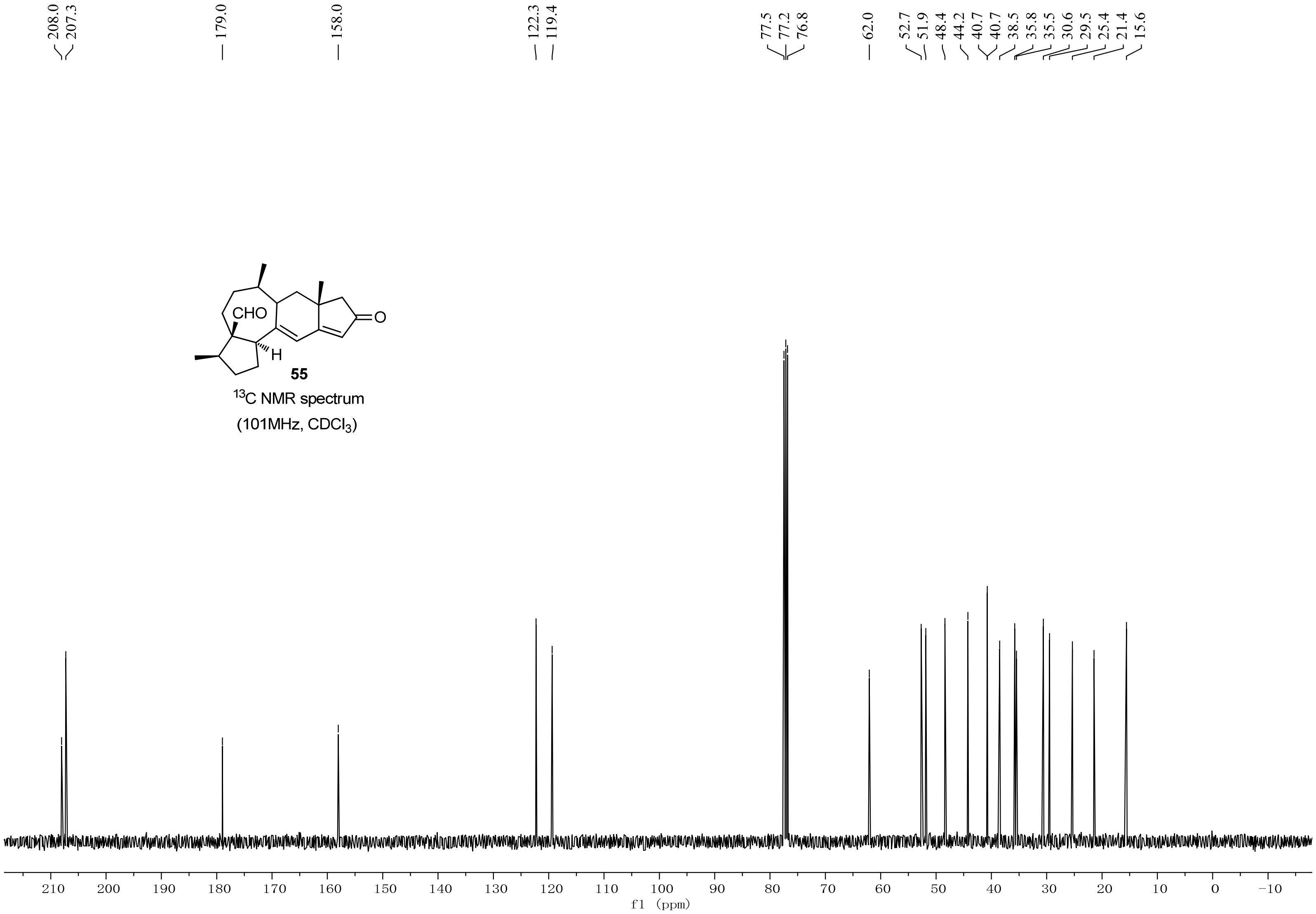
(101MHz, $CDCl_3$)



55

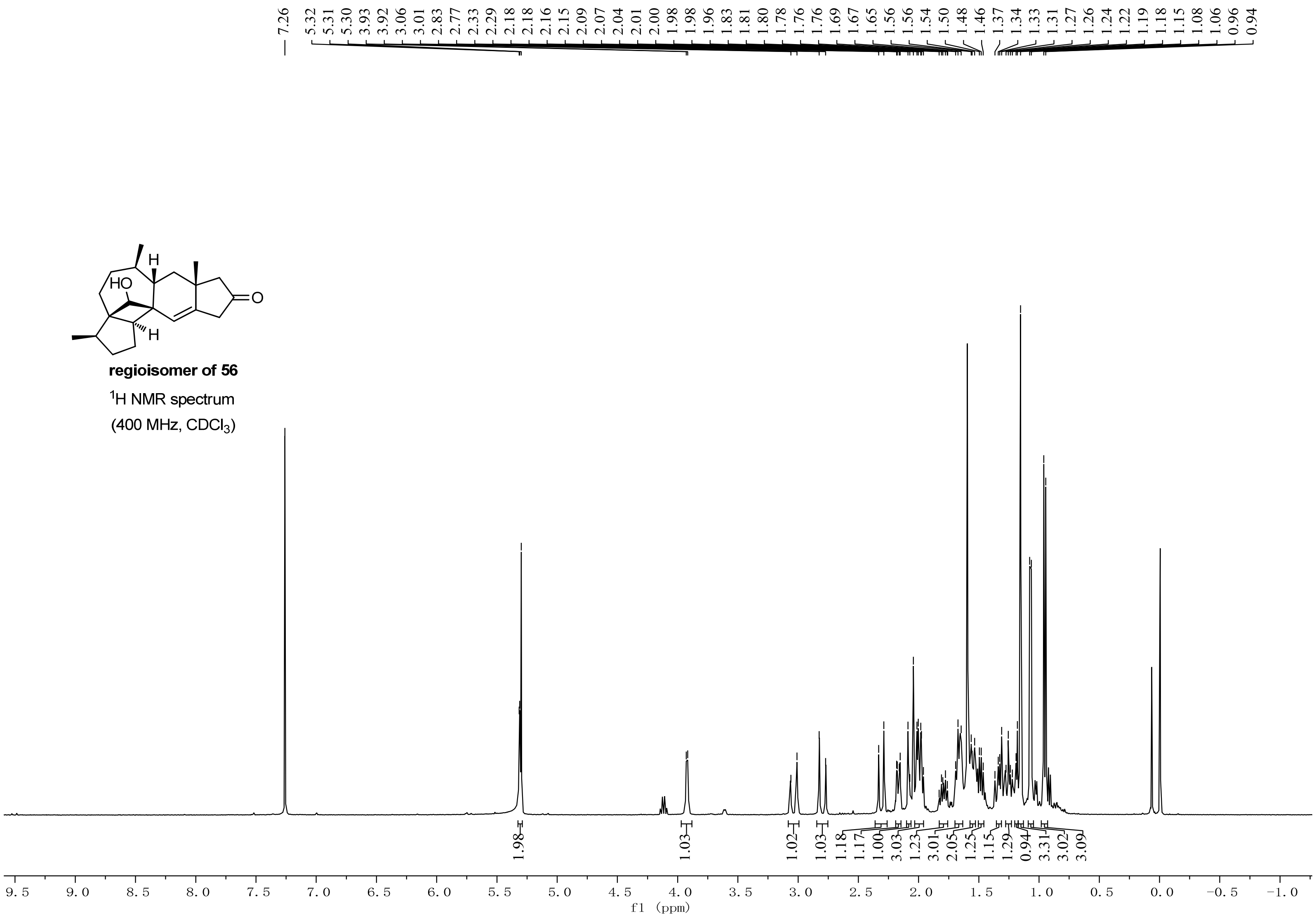
^{1}H NMR spectrum

(400 MHz, $CDCl_3$)


55

^{13}C NMR spectrum

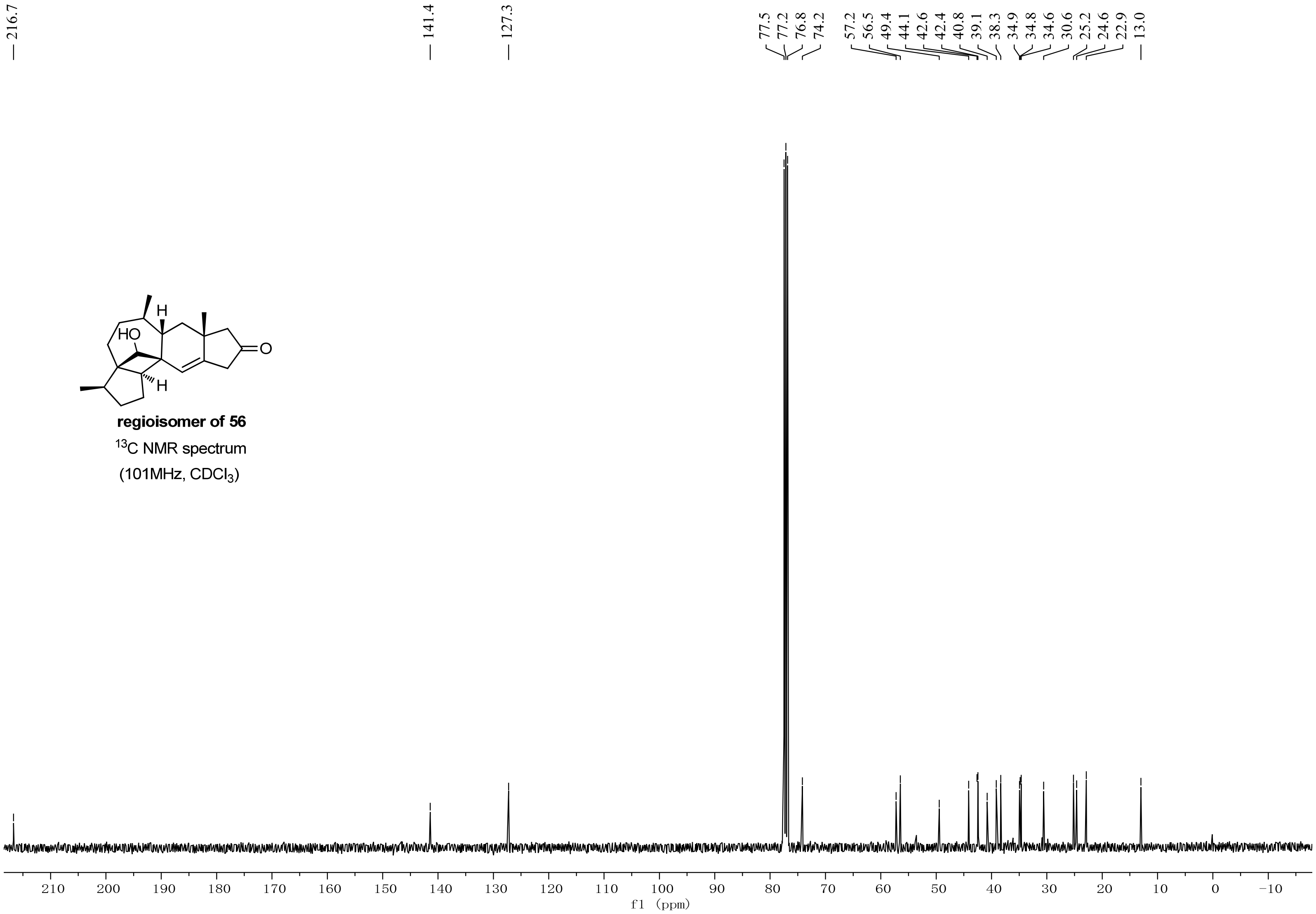
(101MHz, $CDCl_3$)



regioisomer of 56

^{1}H NMR spectrum

(400 MHz, CDCl$_3$)



regioisomer of 56

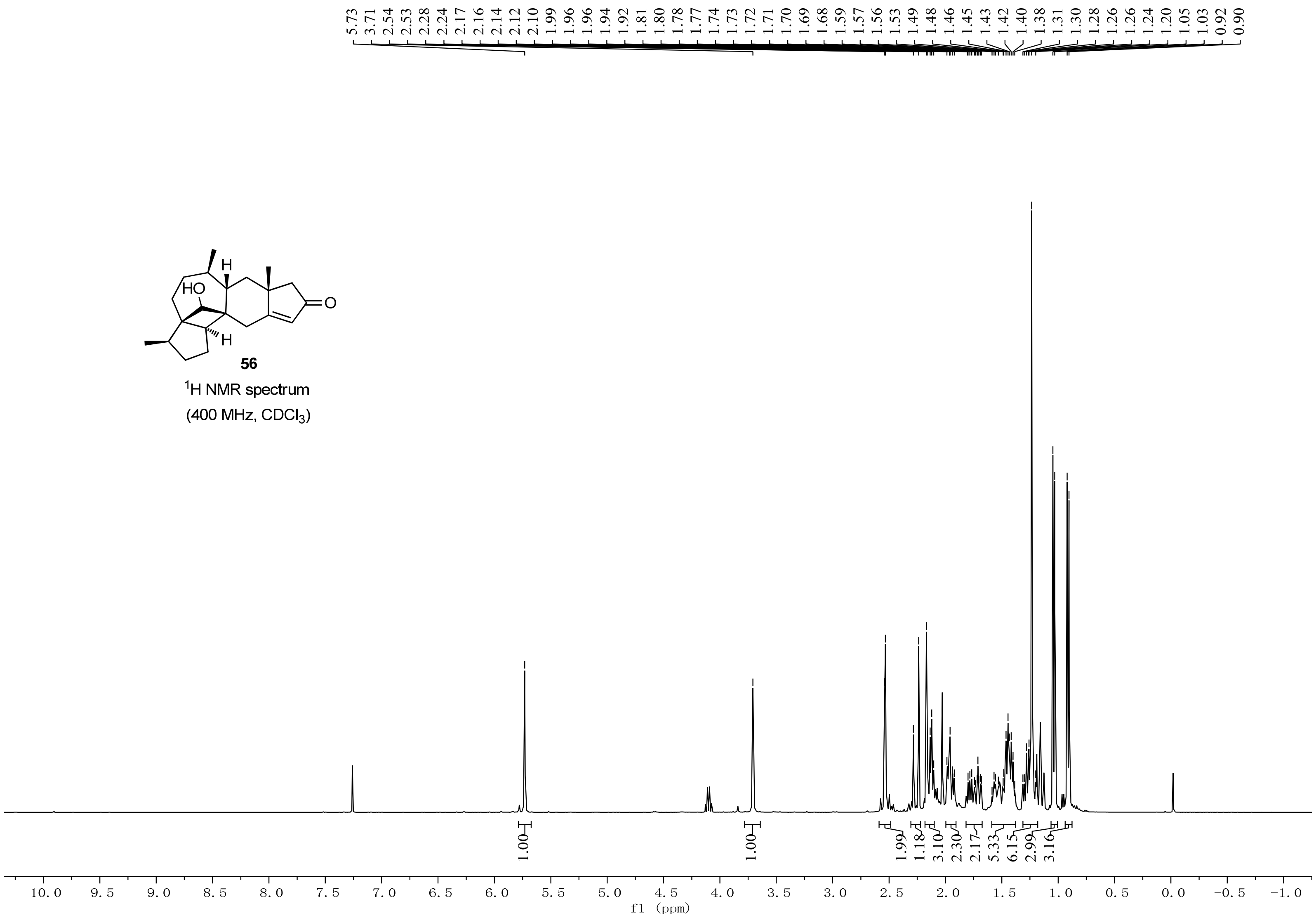
^{13}C NMR spectrum

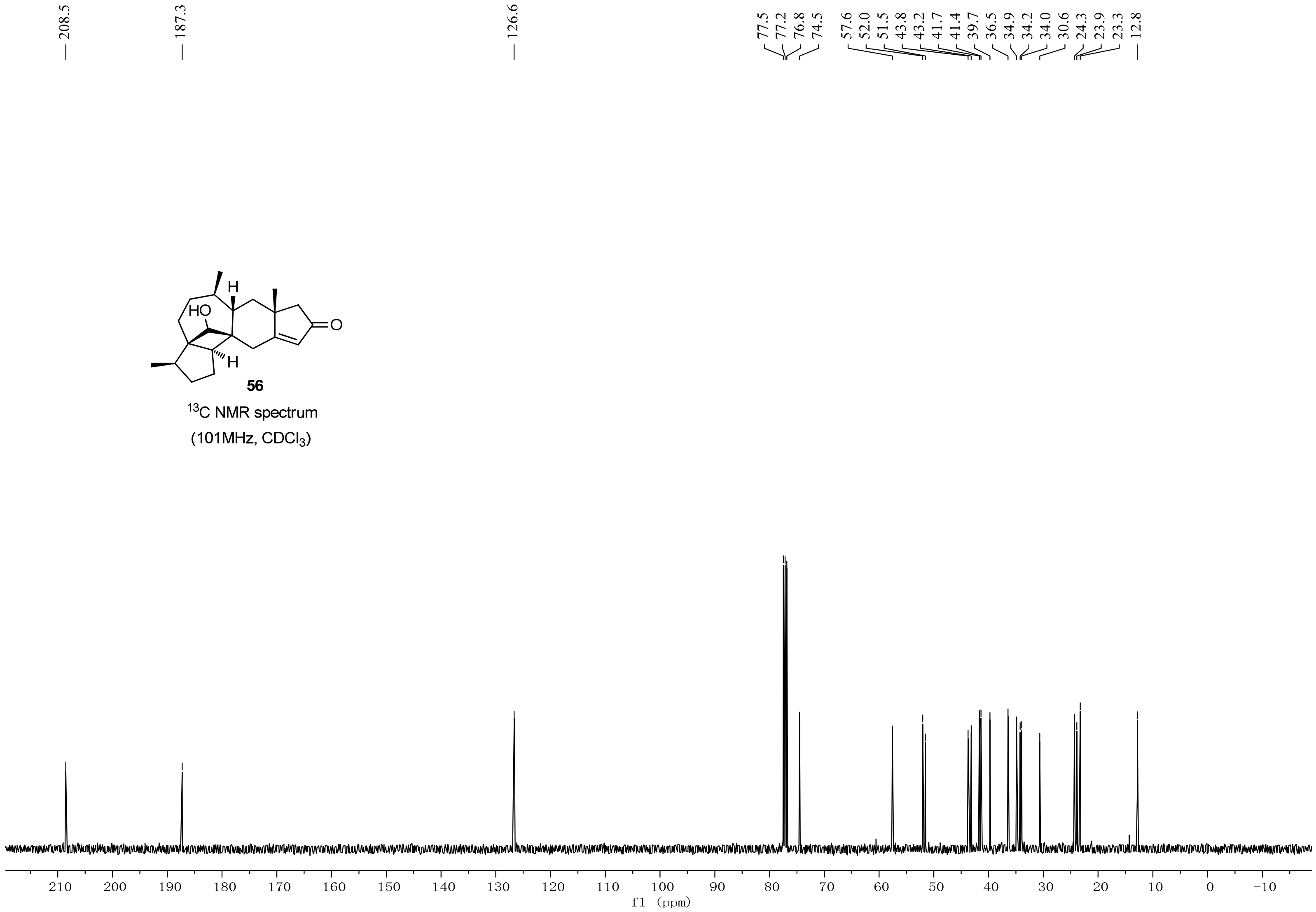
(101MHz, $CDCl_3$)

56

^{1}H NMR spectrum

(400 MHz, $CDCl_3$)

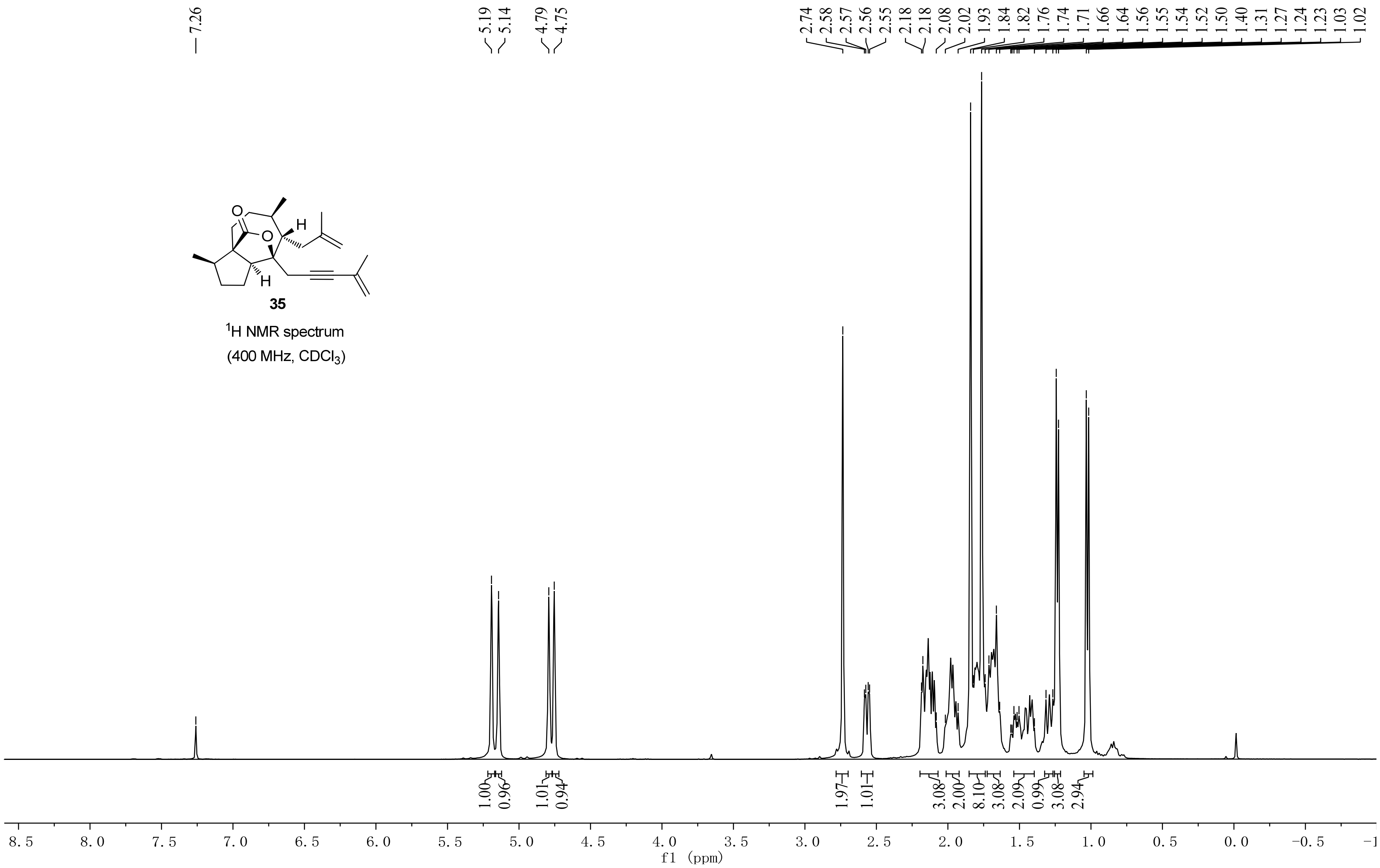




56

^{13}C NMR spectrum

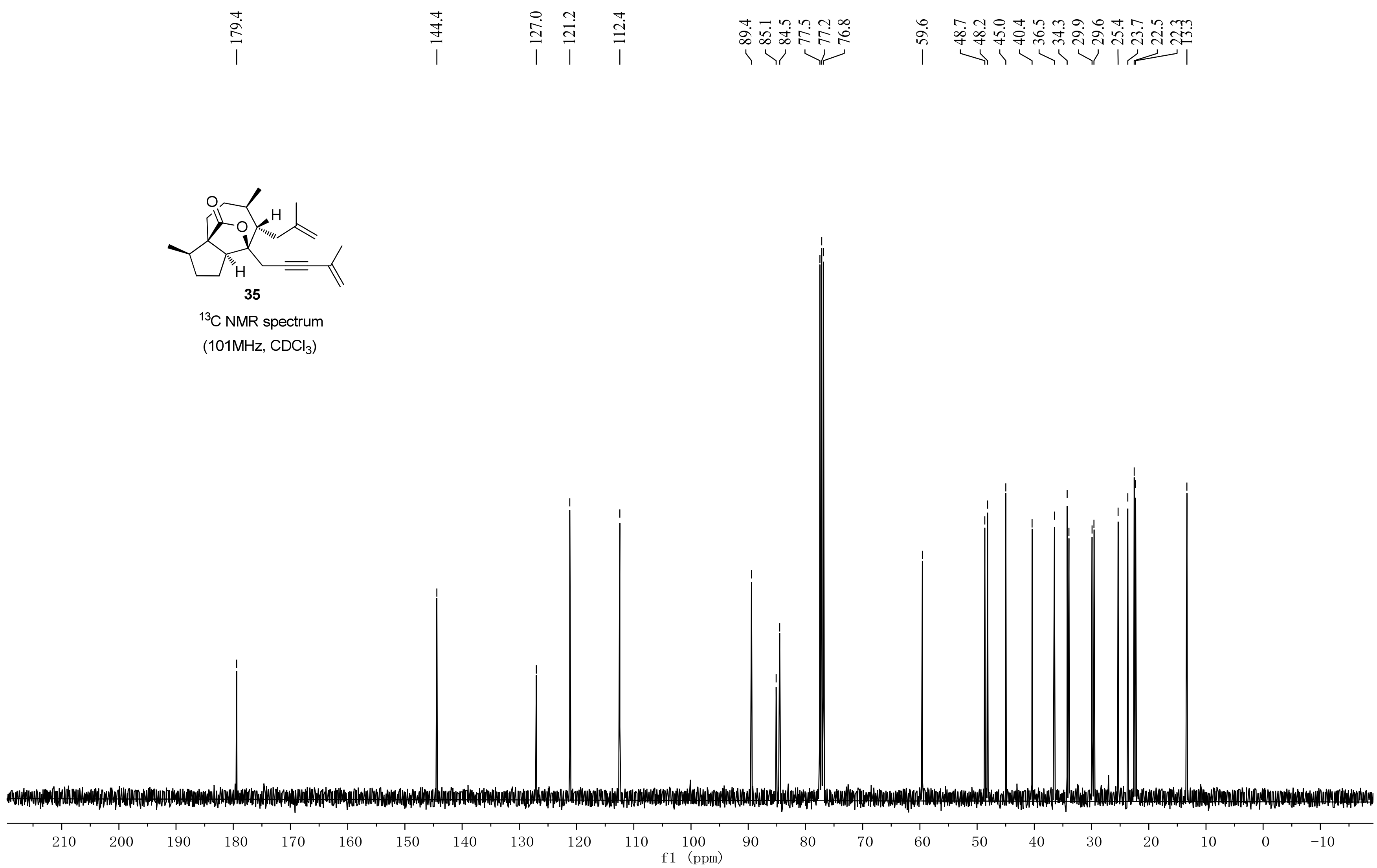
(101MHz, $CDCl_3$)



35

^{1}H NMR spectrum

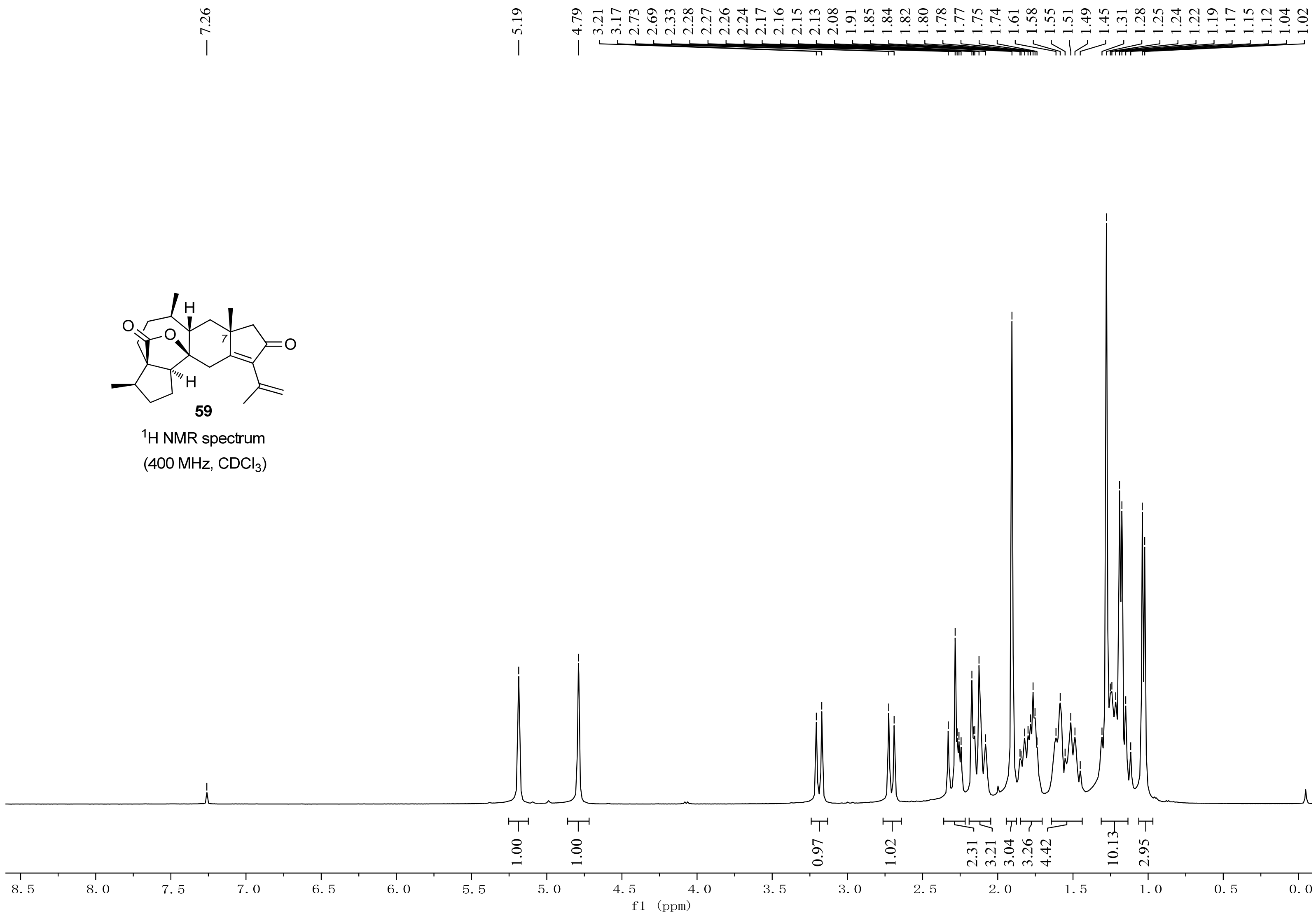
(400 MHz, $CDCl_3$)



35

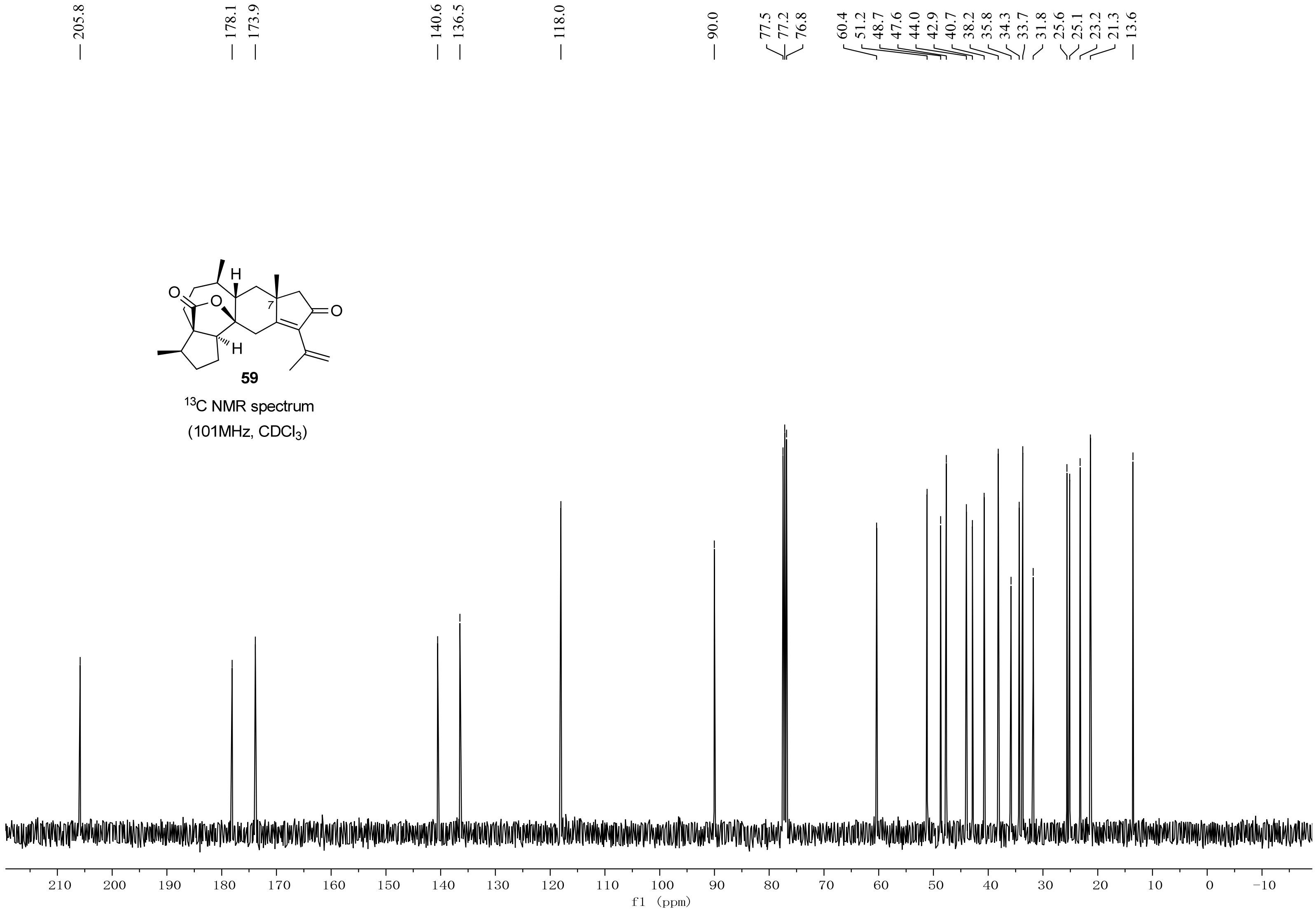
^{13}C NMR spectrum

(101MHz, CDCl$_3$)



59

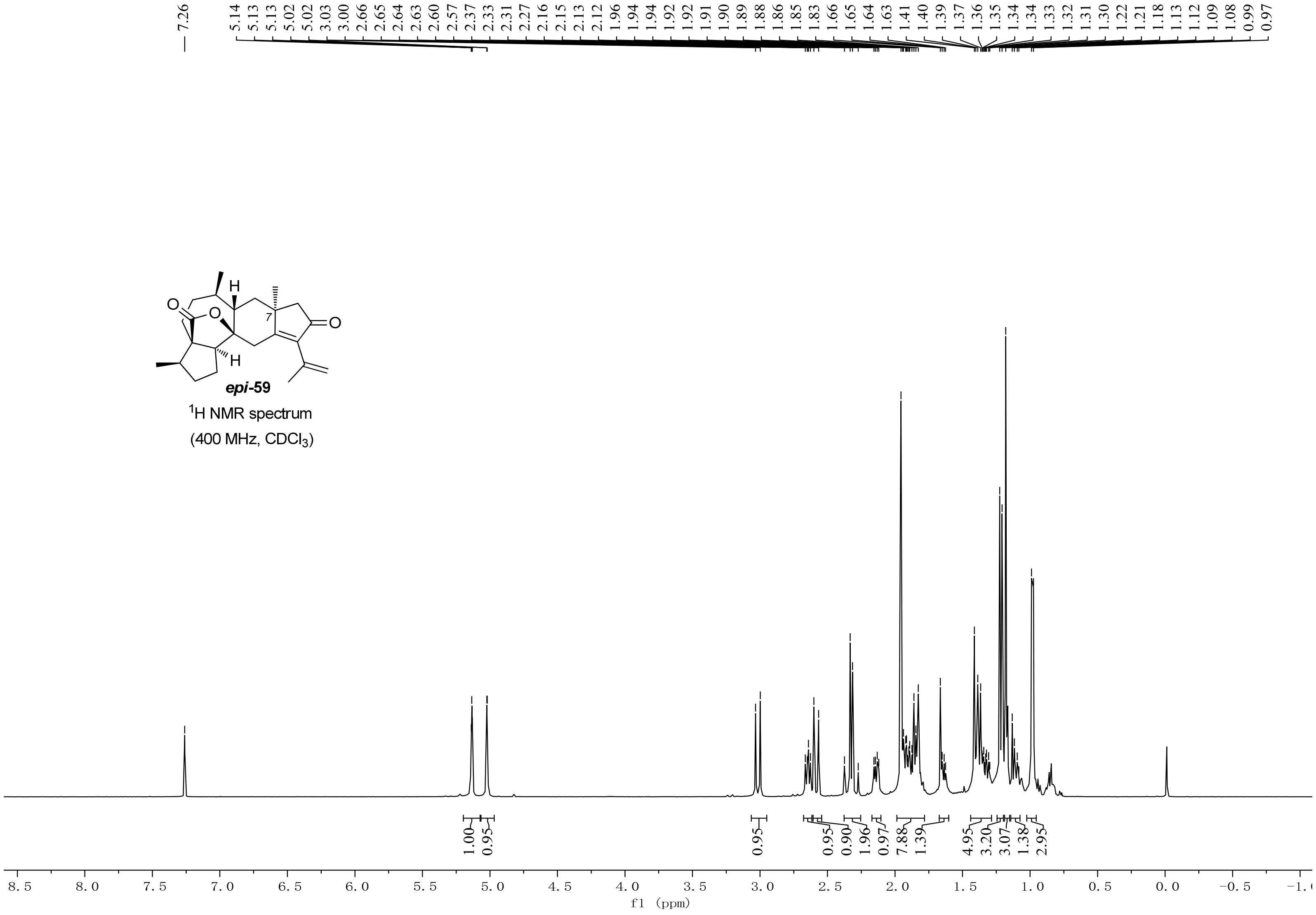
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)



59

^{13}C NMR spectrum

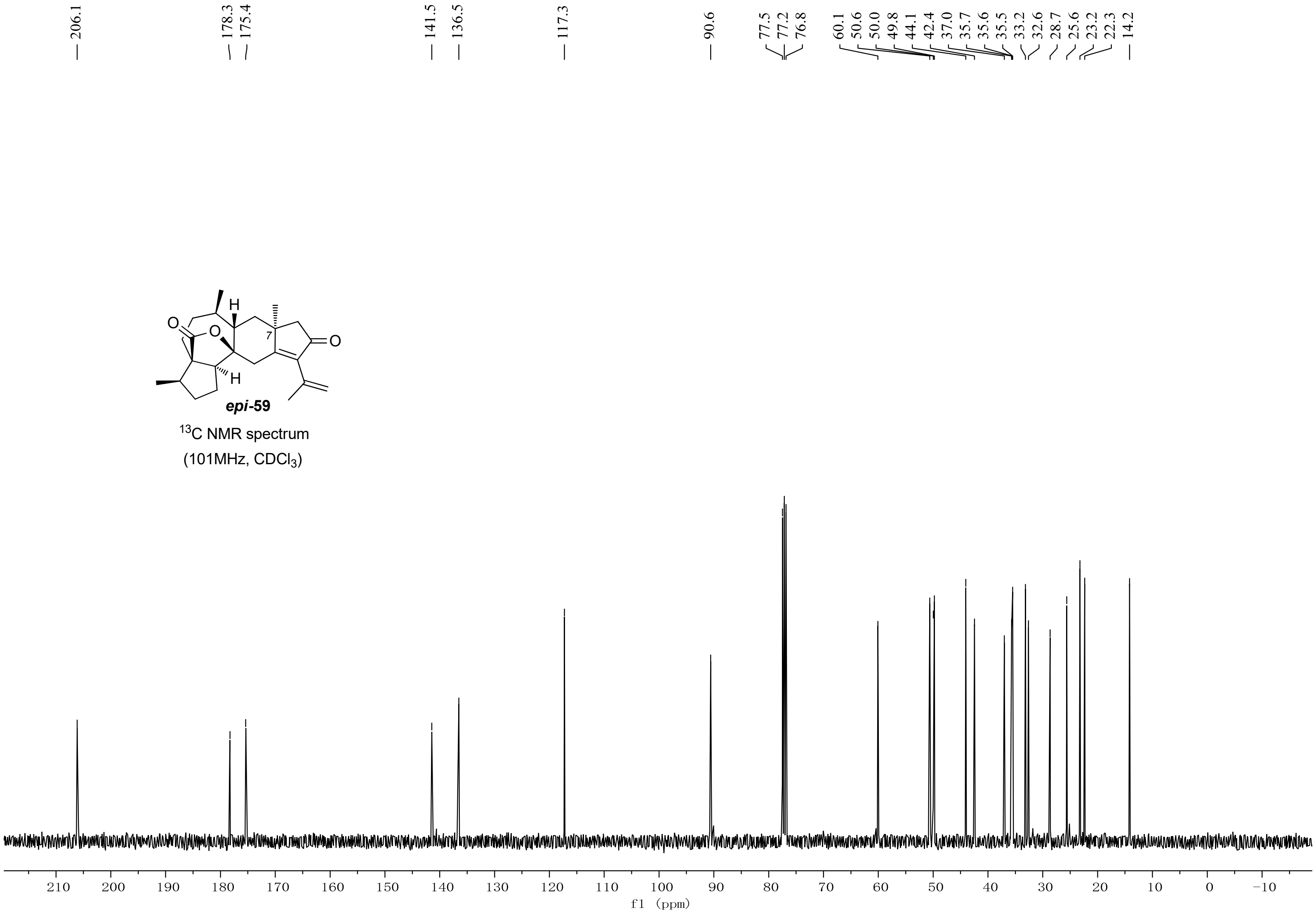
(101MHz, $CDCl_3$)



***epi*-59**

^{1}H NMR spectrum

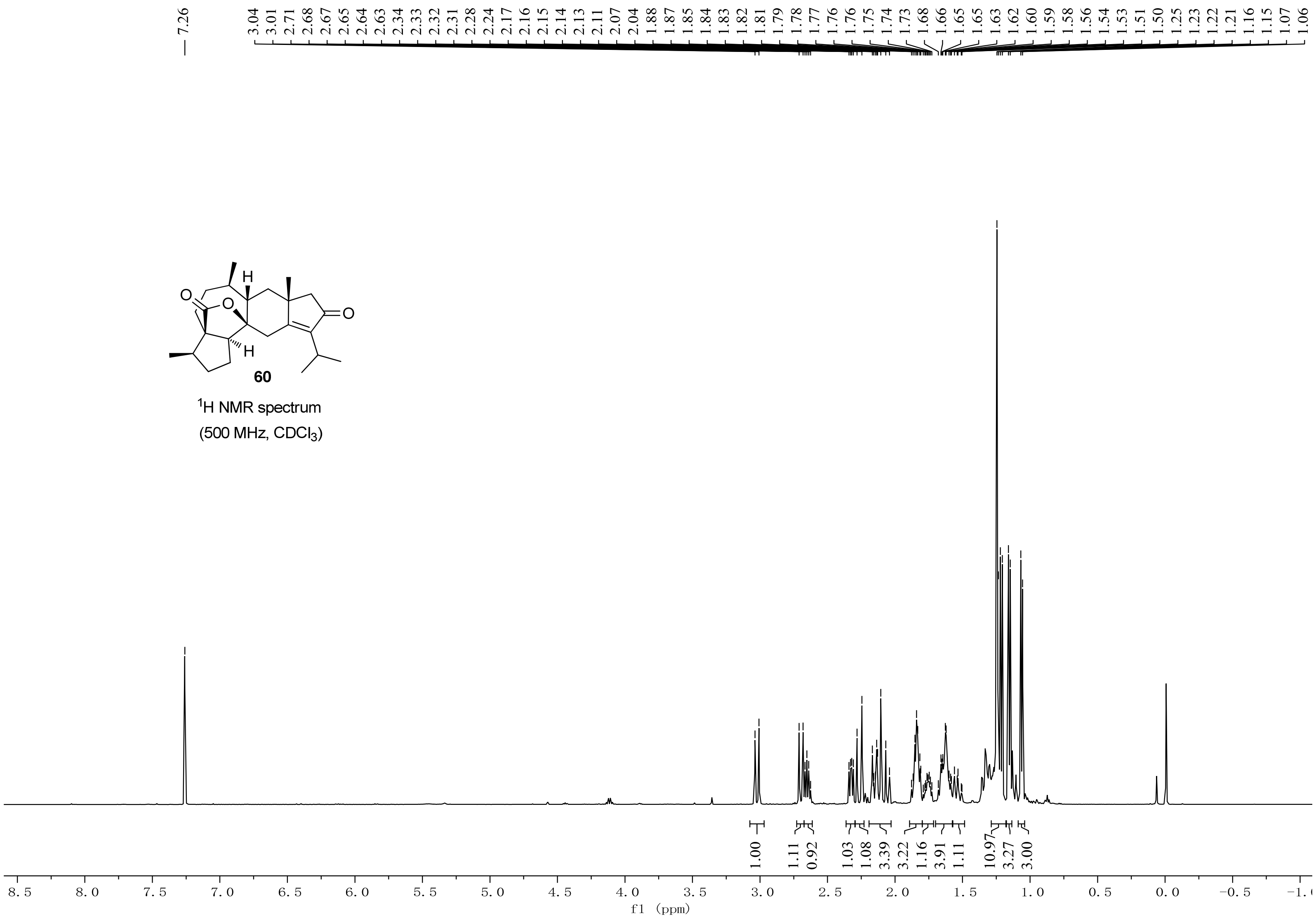
(400 MHz, $CDCl_3$)



***epi*-59**

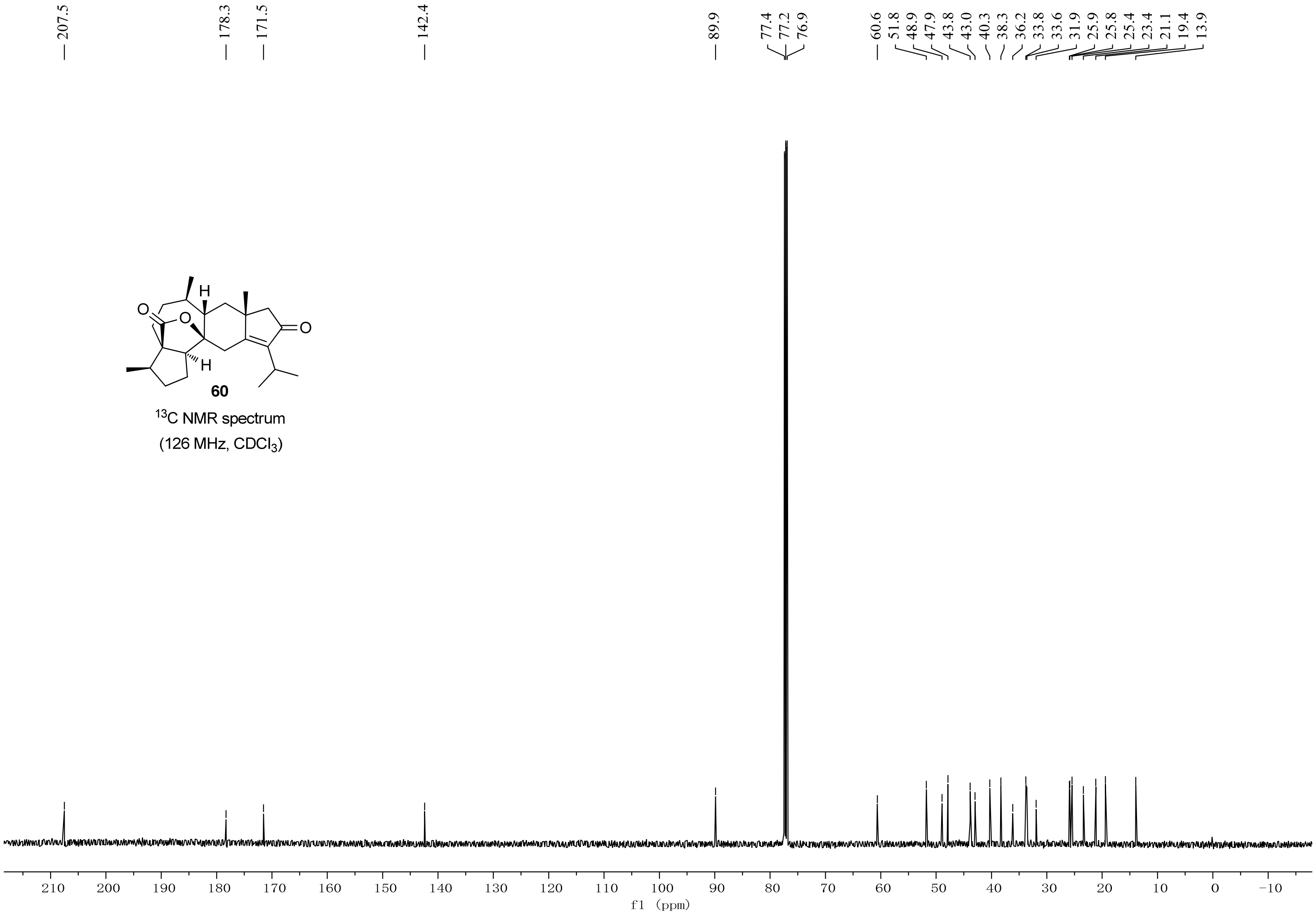
^{13}C NMR spectrum

(101MHz, CDCl$_3$)



60

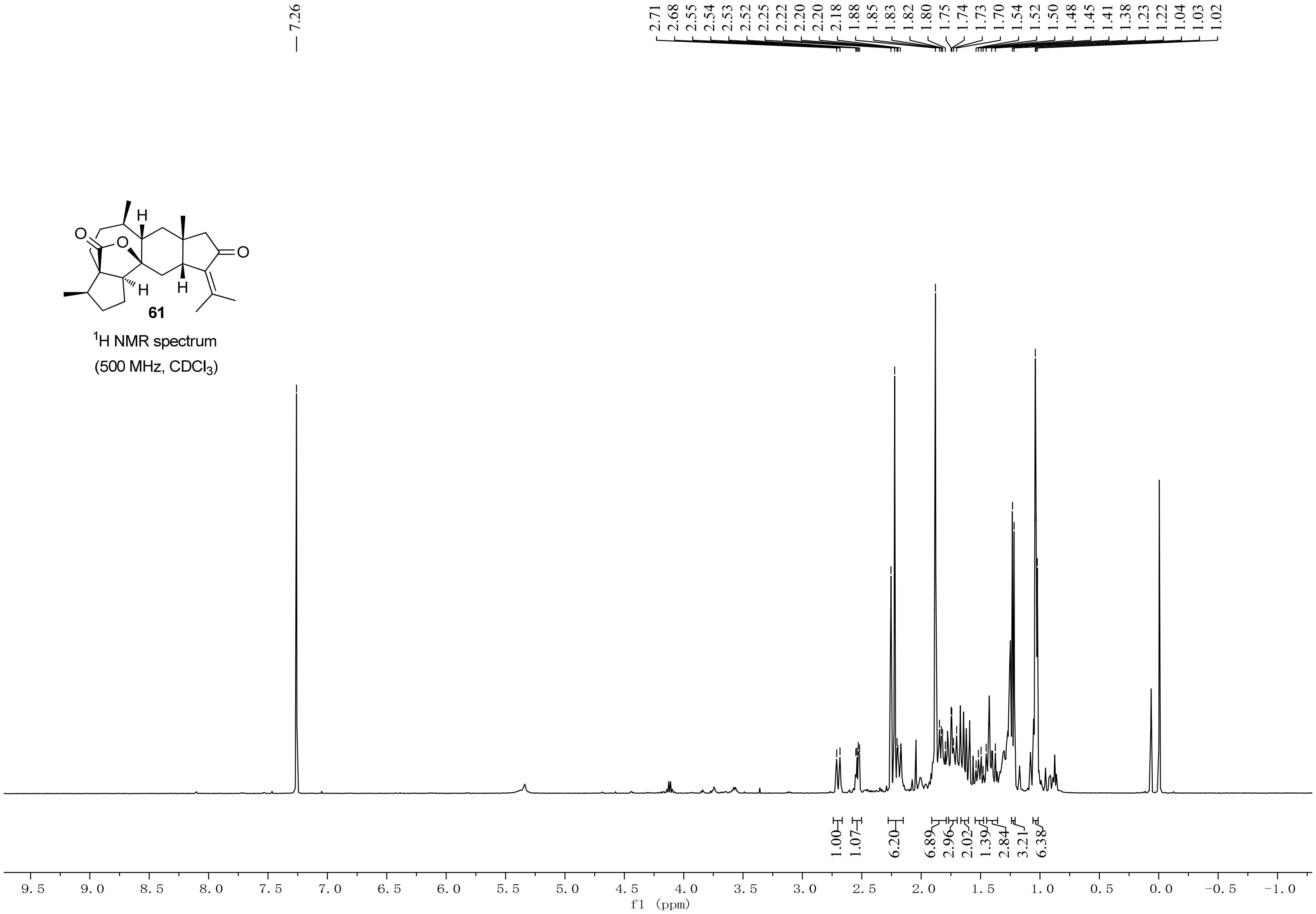
^{1}H NMR spectrum
(500 MHz, $CDCl_3$)



60

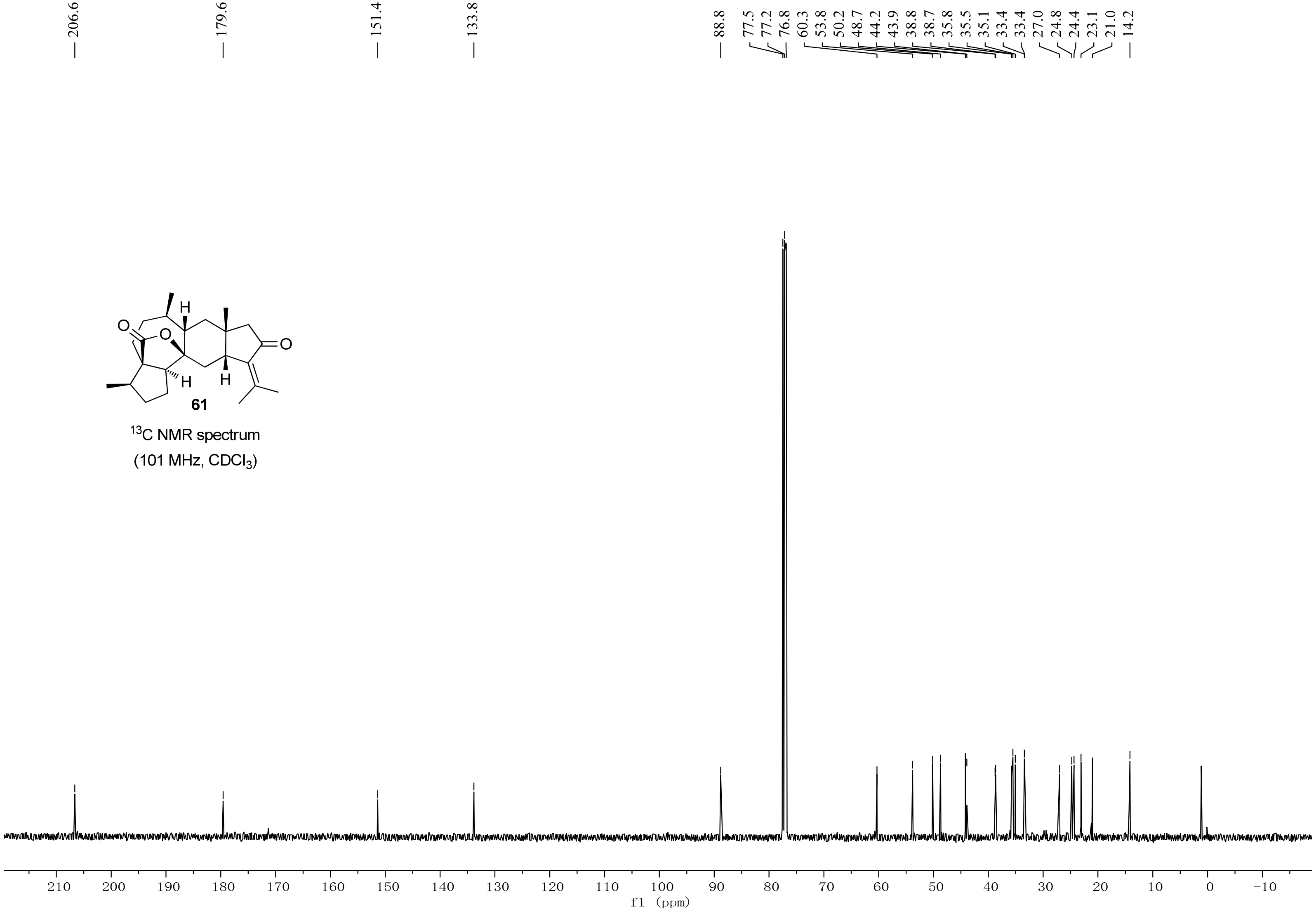
^{13}C NMR spectrum

(126 MHz, $CDCl_3$)



61

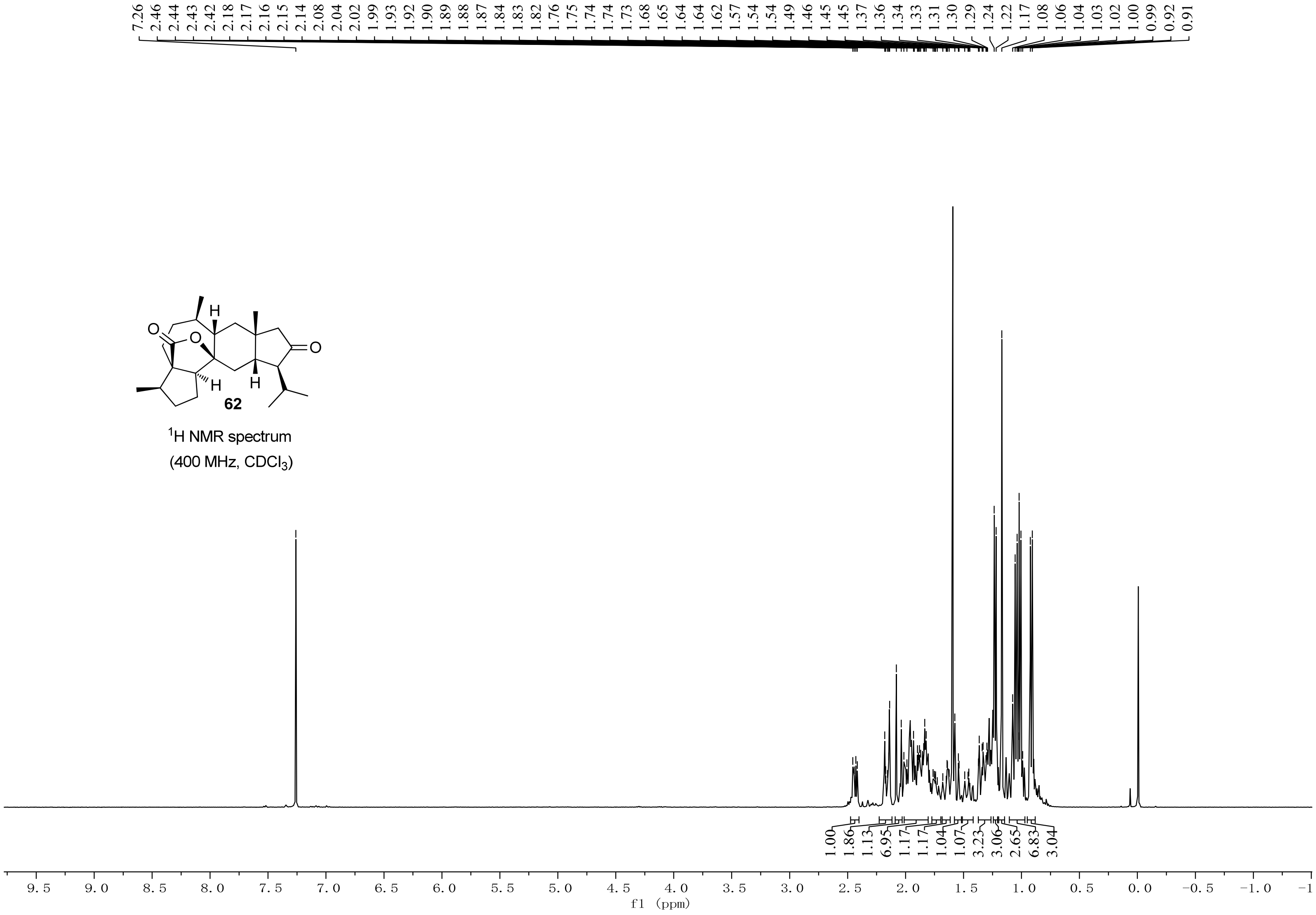
^{1}H NMR spectrum
(500 MHz, CDCl$_3$)



61

^{13}C NMR spectrum

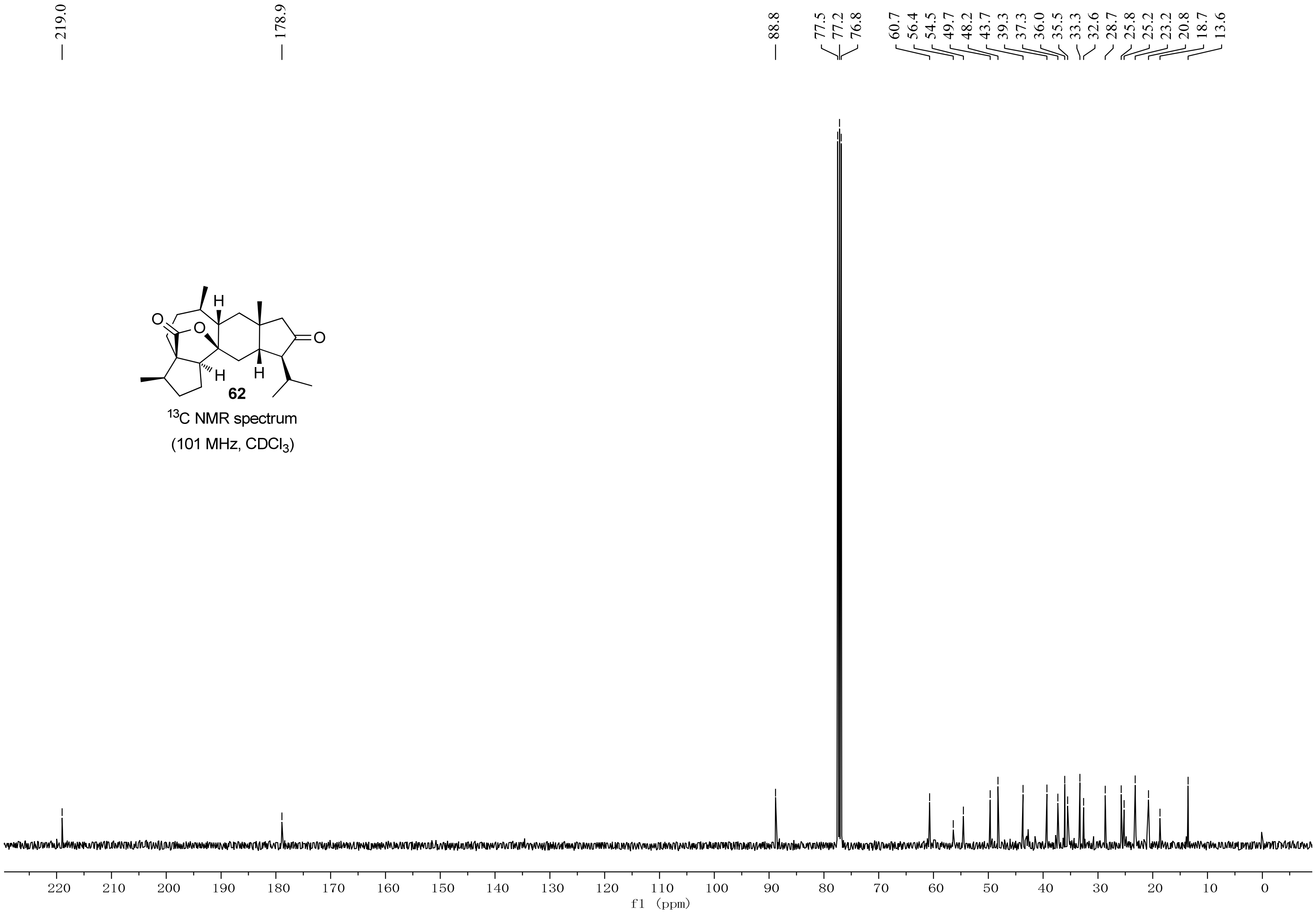
(101 MHz, $CDCl_3$)



62

^{1}H NMR spectrum

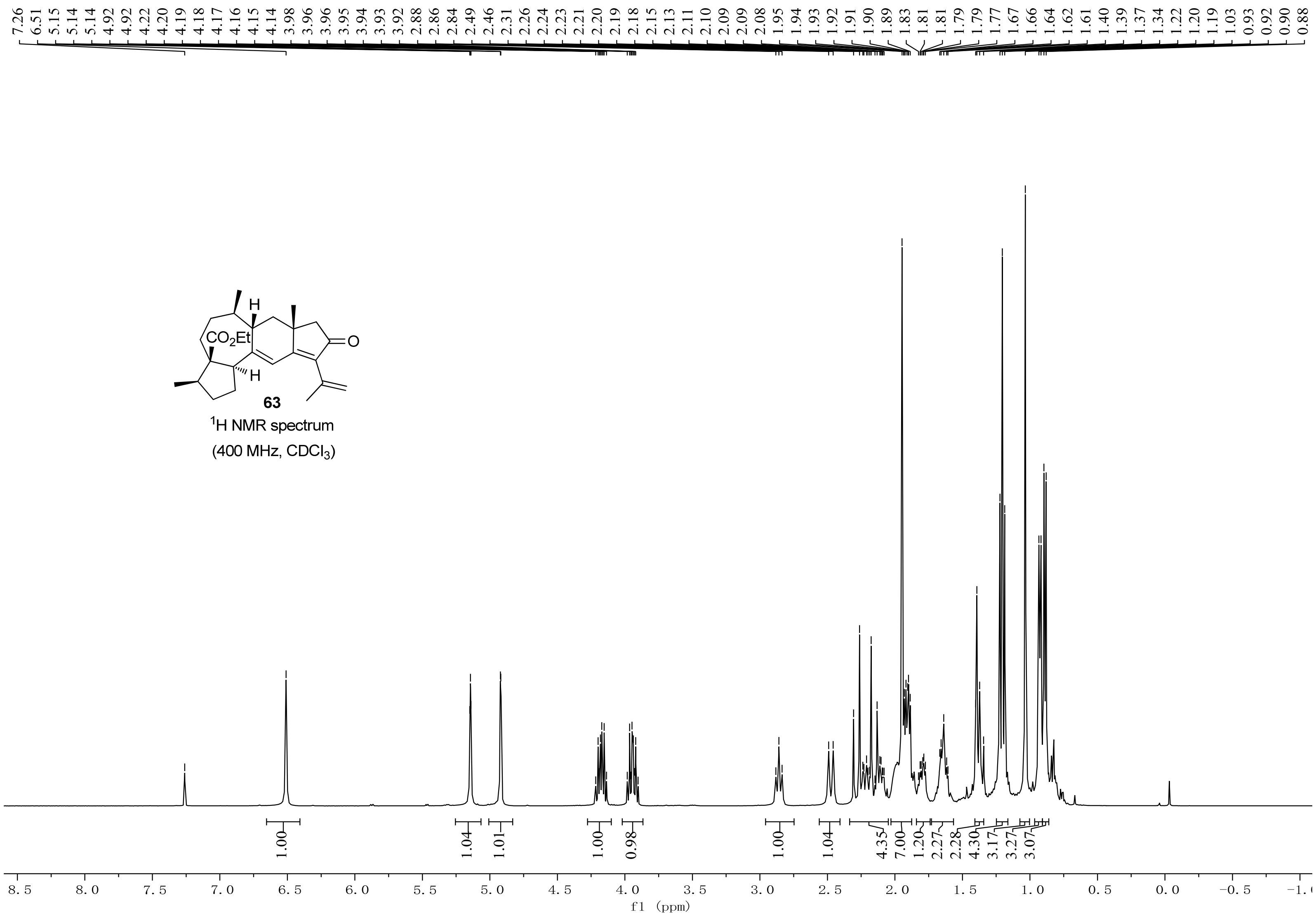
(400 MHz, $CDCl_3$)



62

^{13}C NMR spectrum

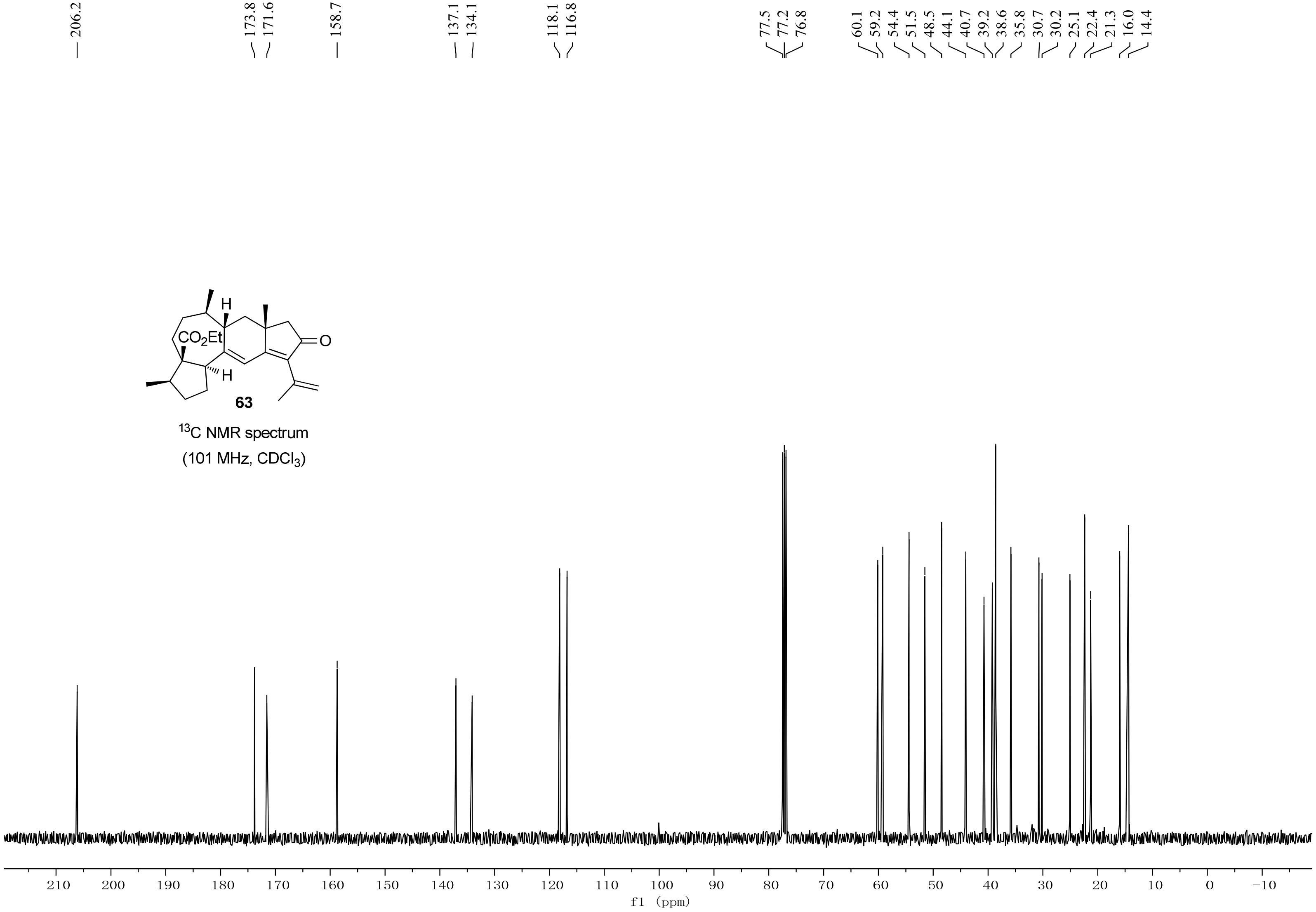
(101 MHz, $CDCl_3$)



63

^{1}H NMR spectrum

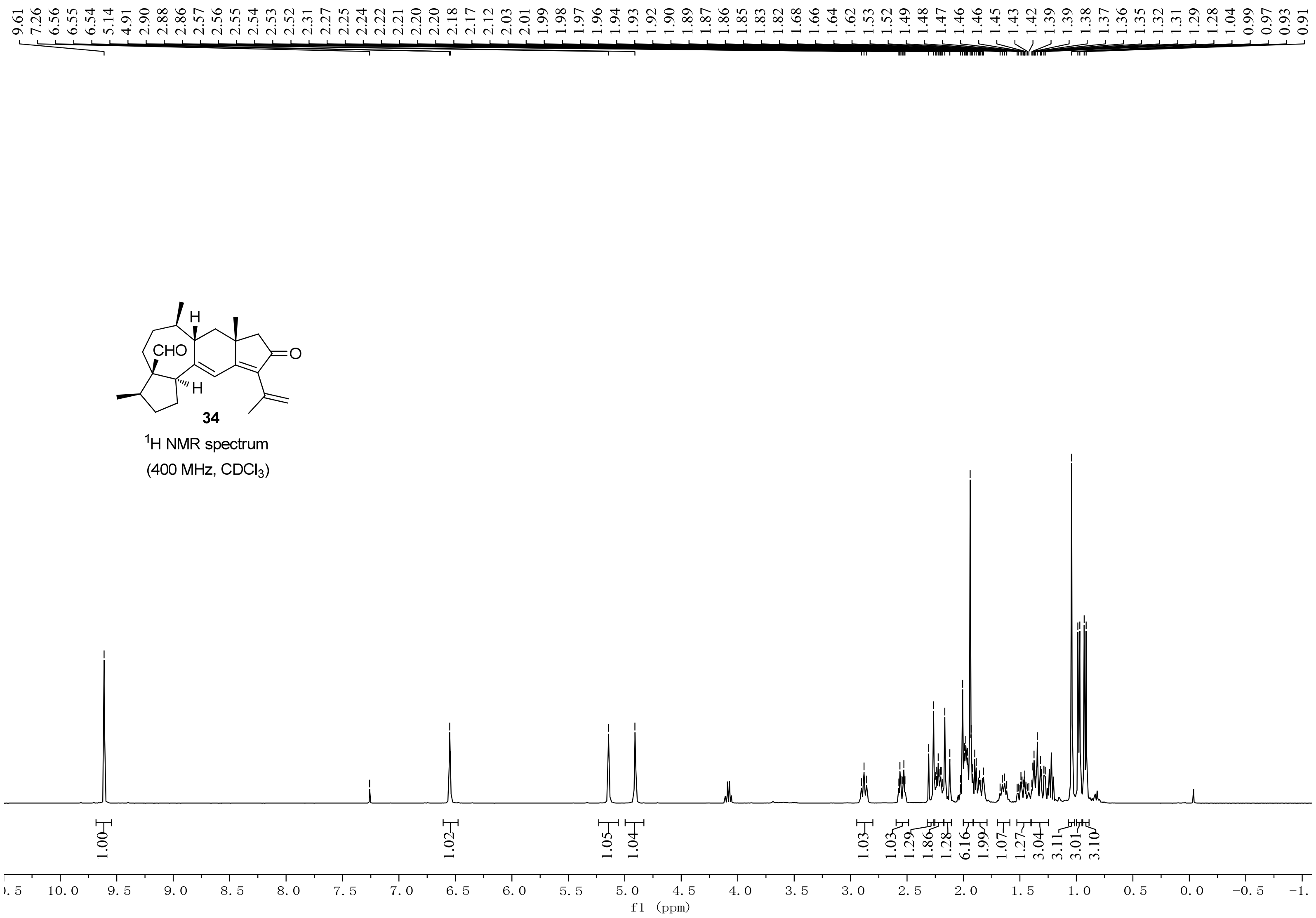
(400 MHz, $CDCl_3$)



63

^{13}C NMR spectrum

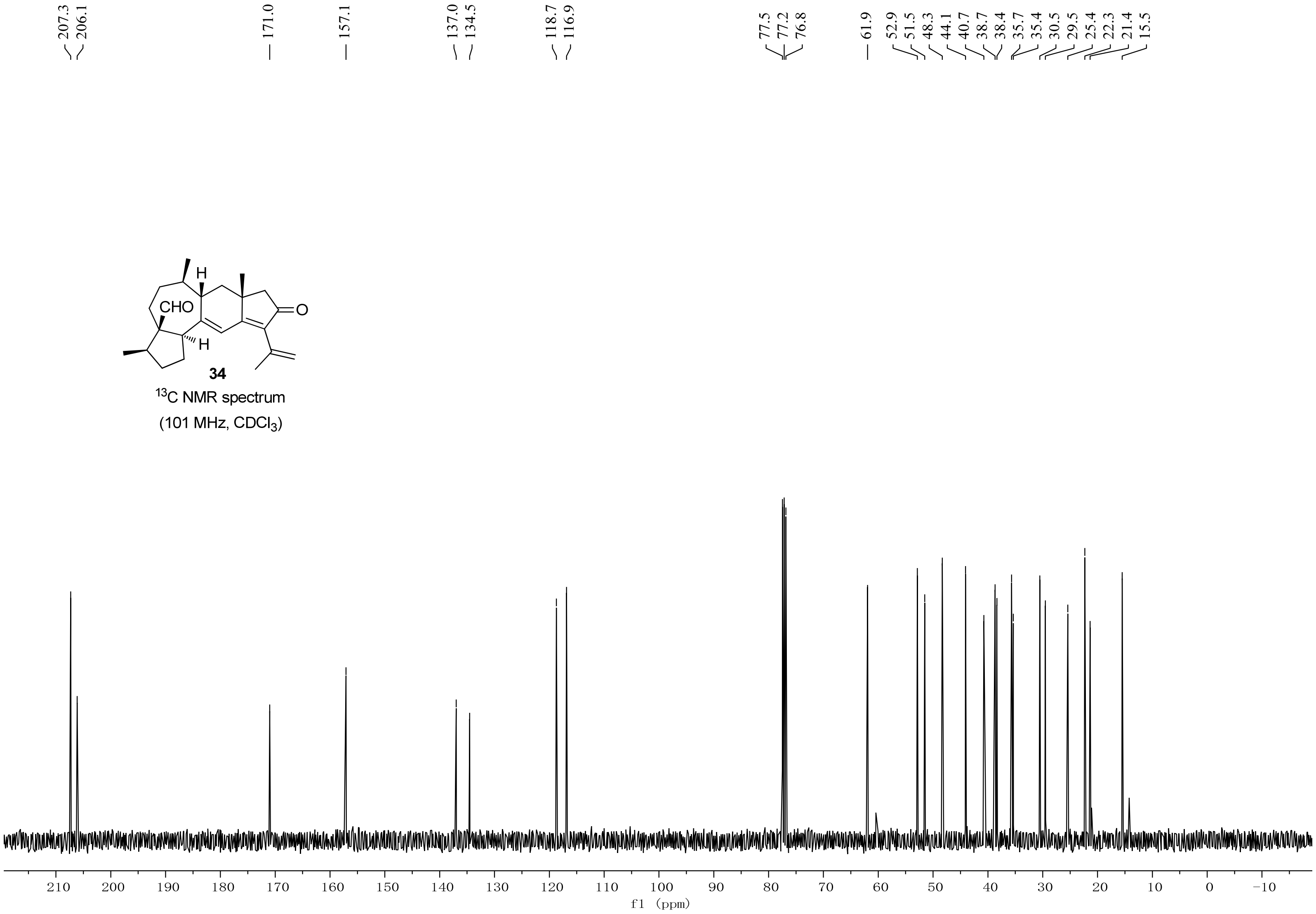
(101 MHz, $CDCl_3$)



34

^{1}H NMR spectrum

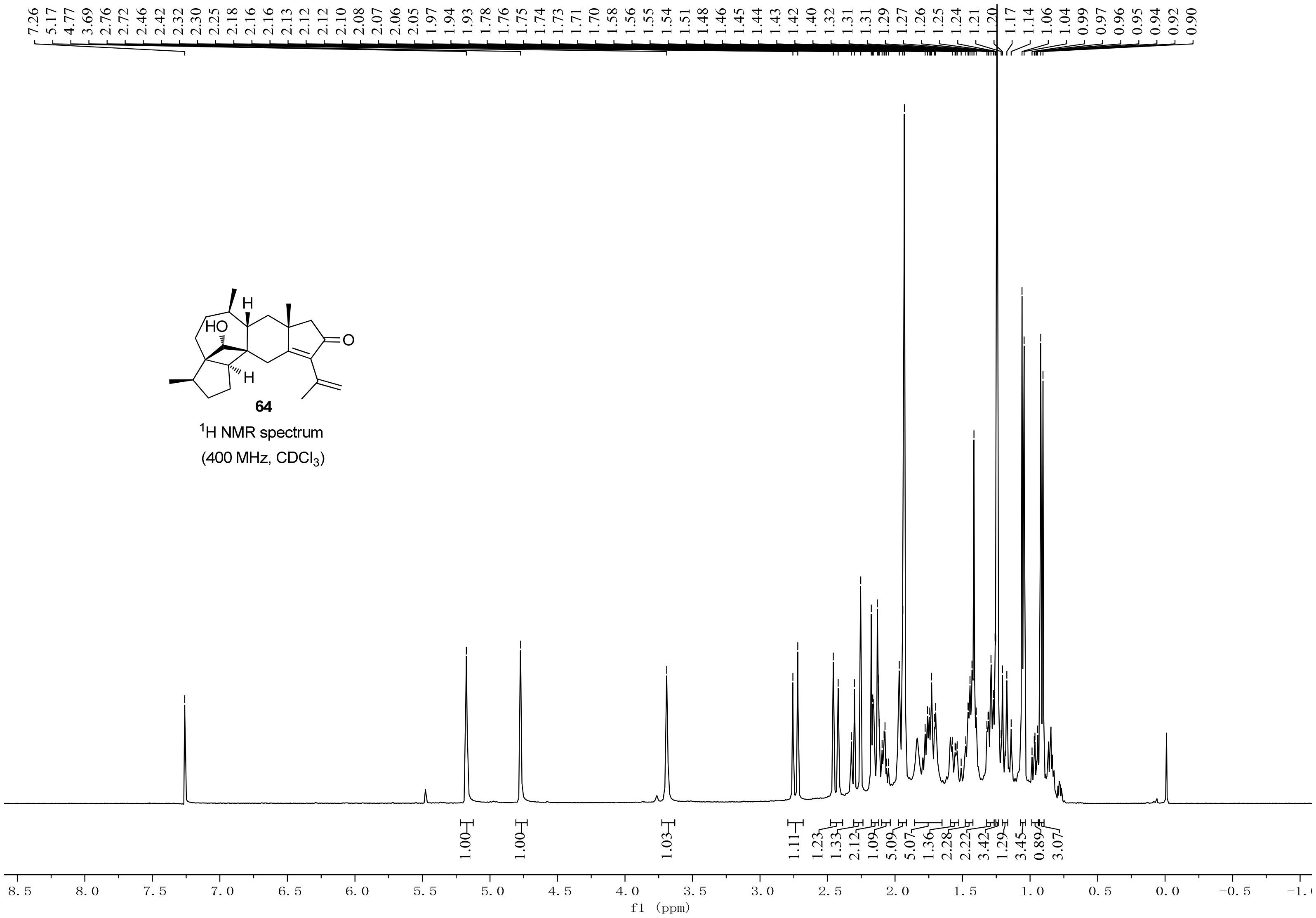
(400 MHz, CDCl$_3$)



34

^{13}C NMR spectrum

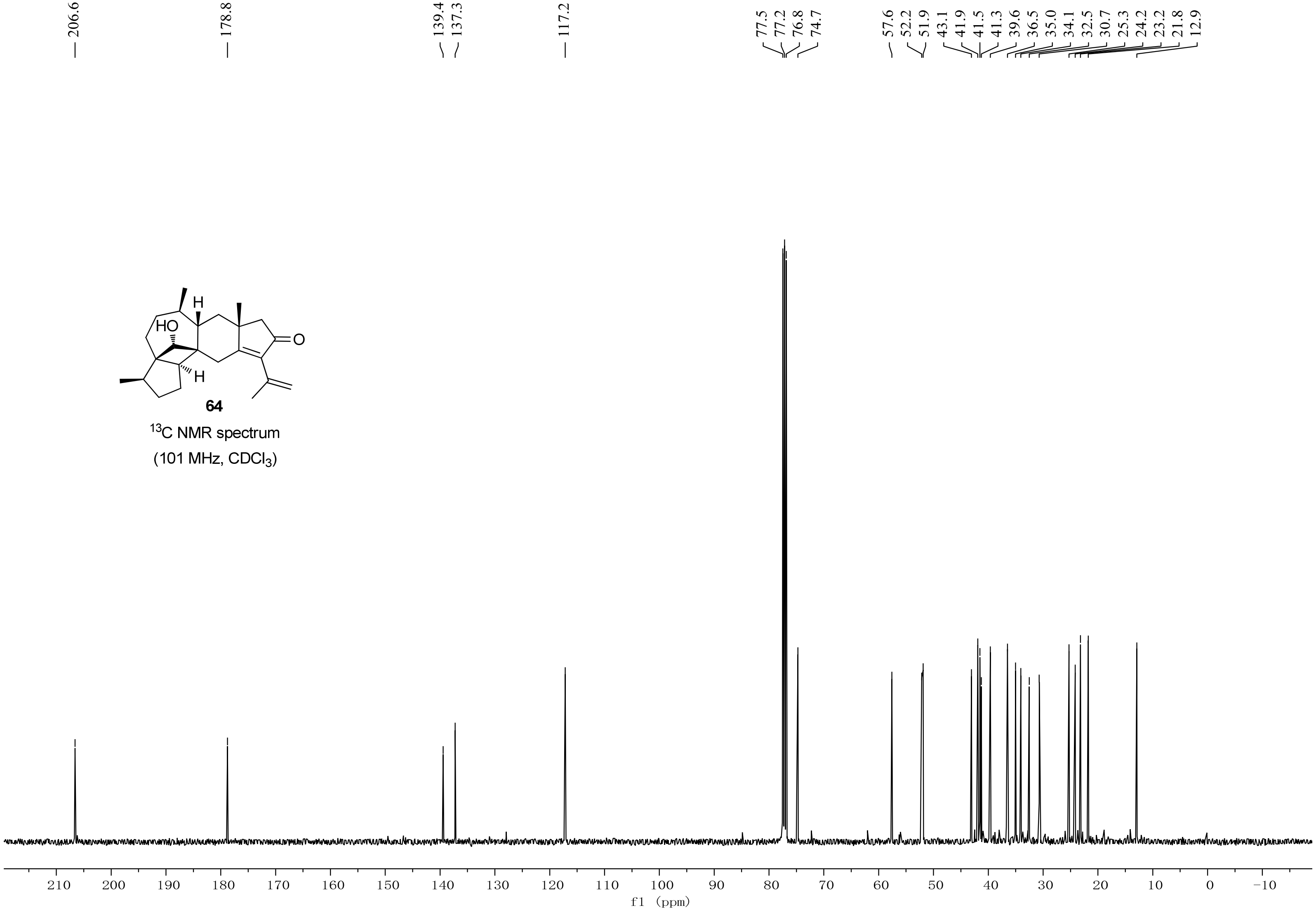
(101 MHz, $CDCl_3$)



64

^{1}H NMR spectrum

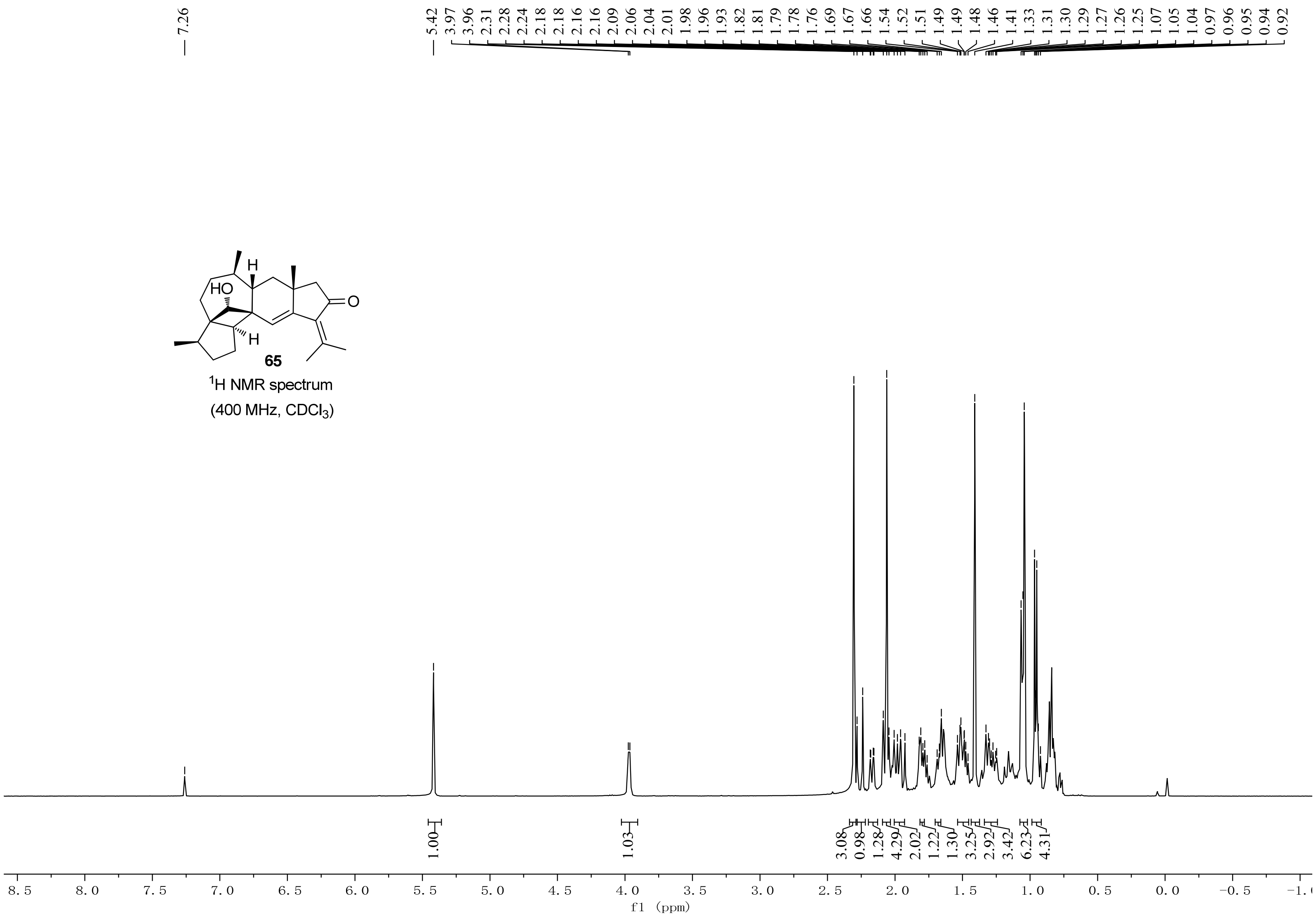
(400 MHz, $CDCl_3$)



64

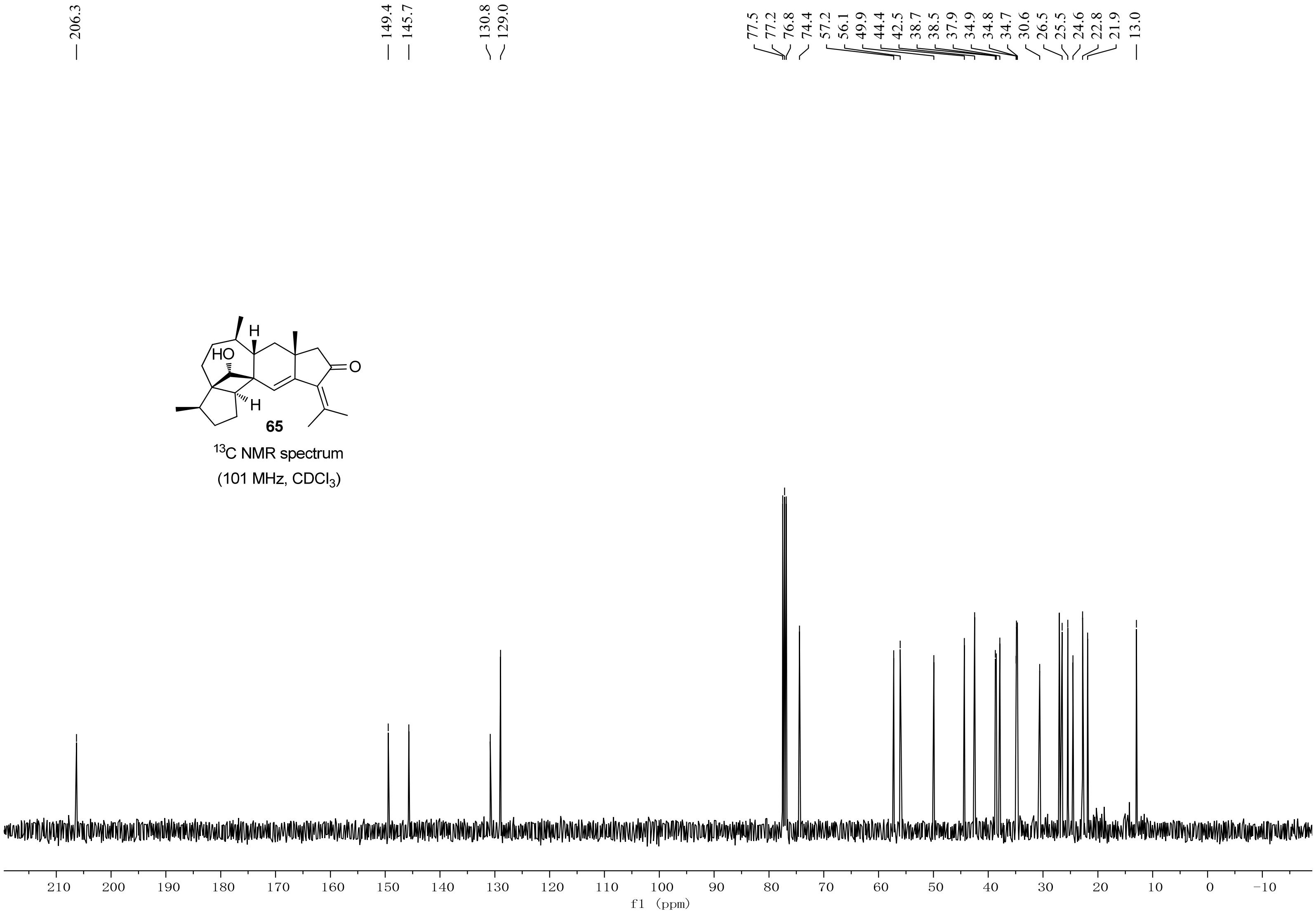
^{13}C NMR spectrum

(101 MHz, $CDCl_3$)



65

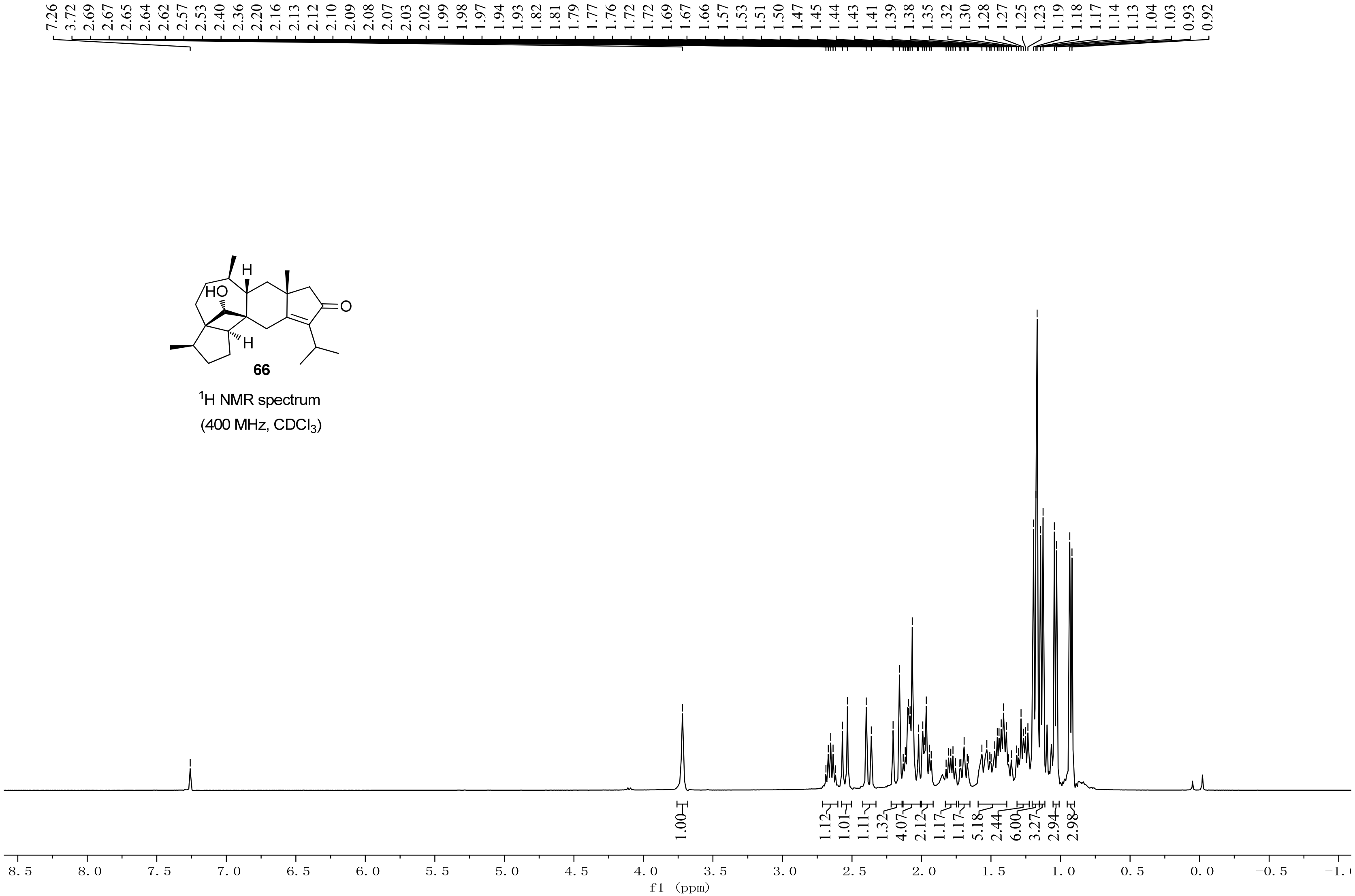
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)



65

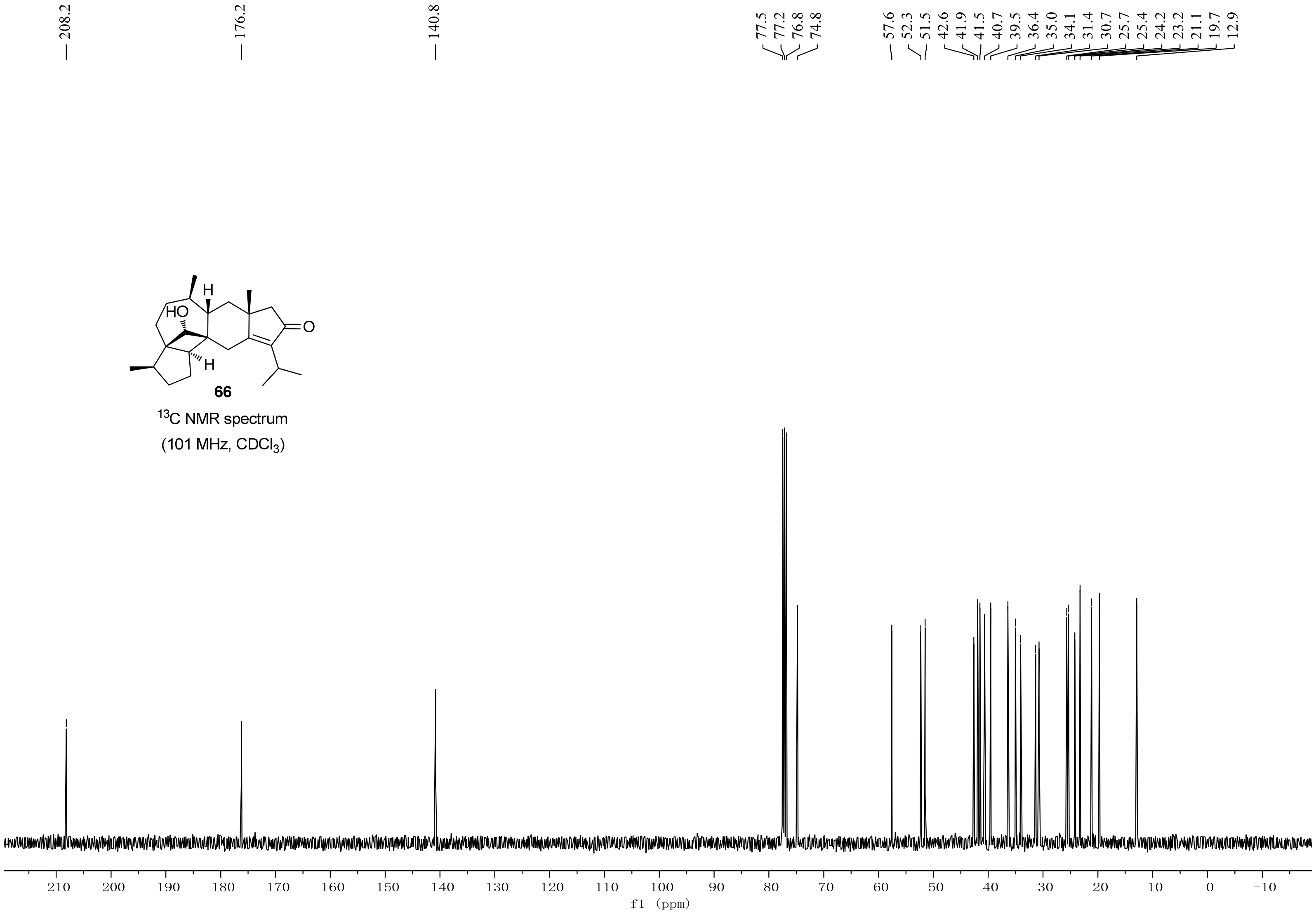
^{13}C NMR spectrum

(101 MHz, $CDCl_3$)



66

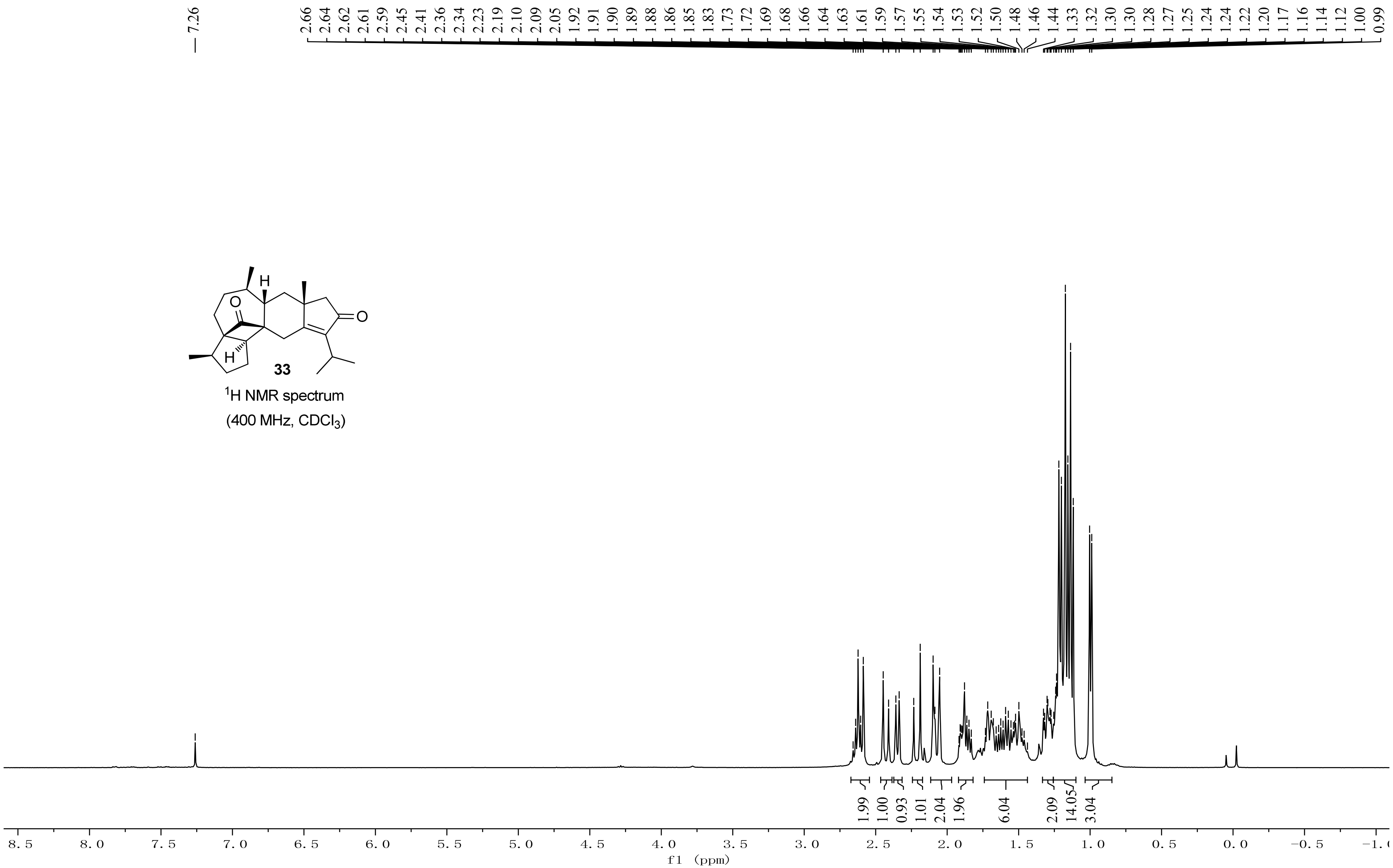
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)



66

^{13}C NMR spectrum

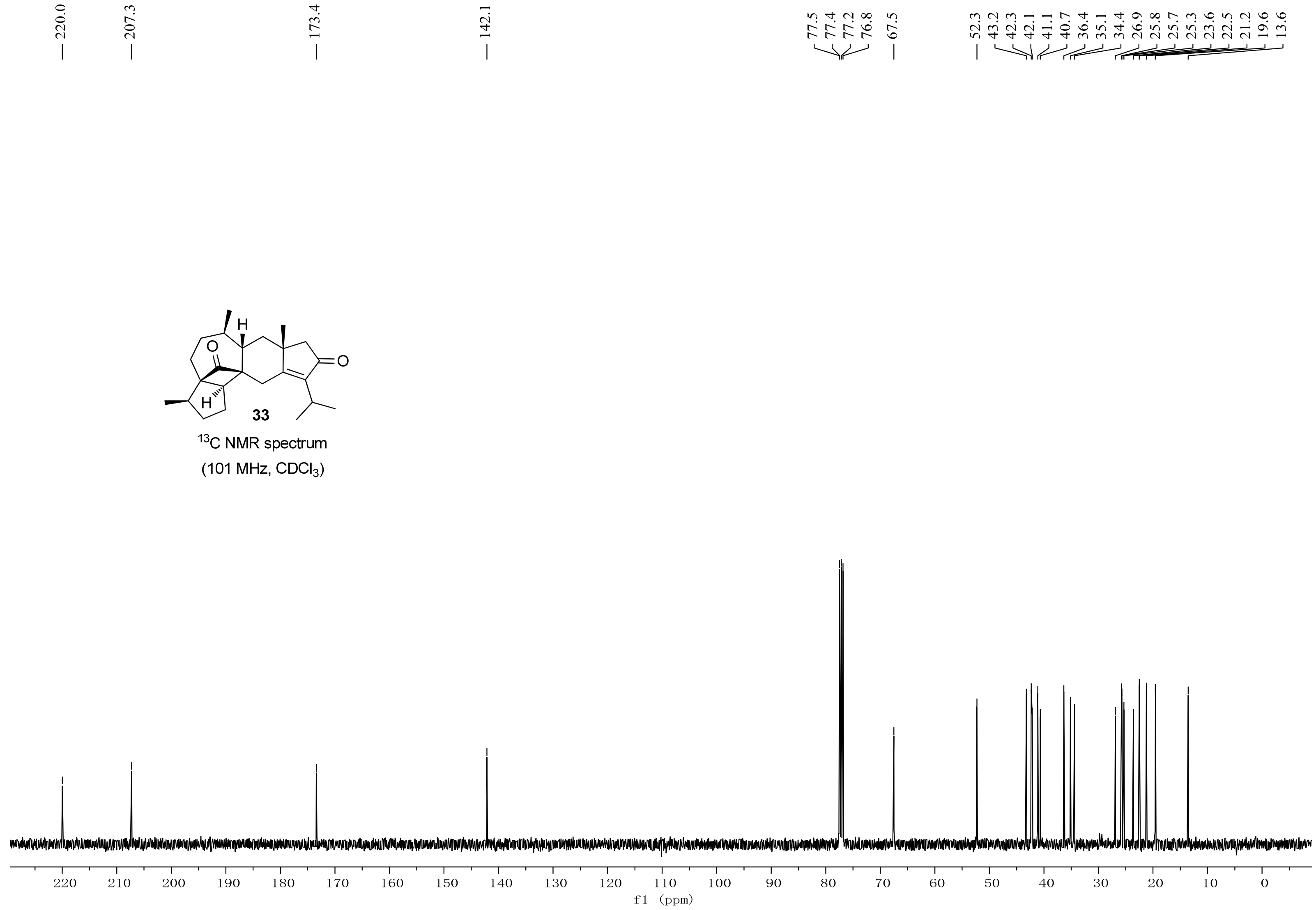
(101 MHz, $CDCl_3$)



33

^{1}H NMR spectrum

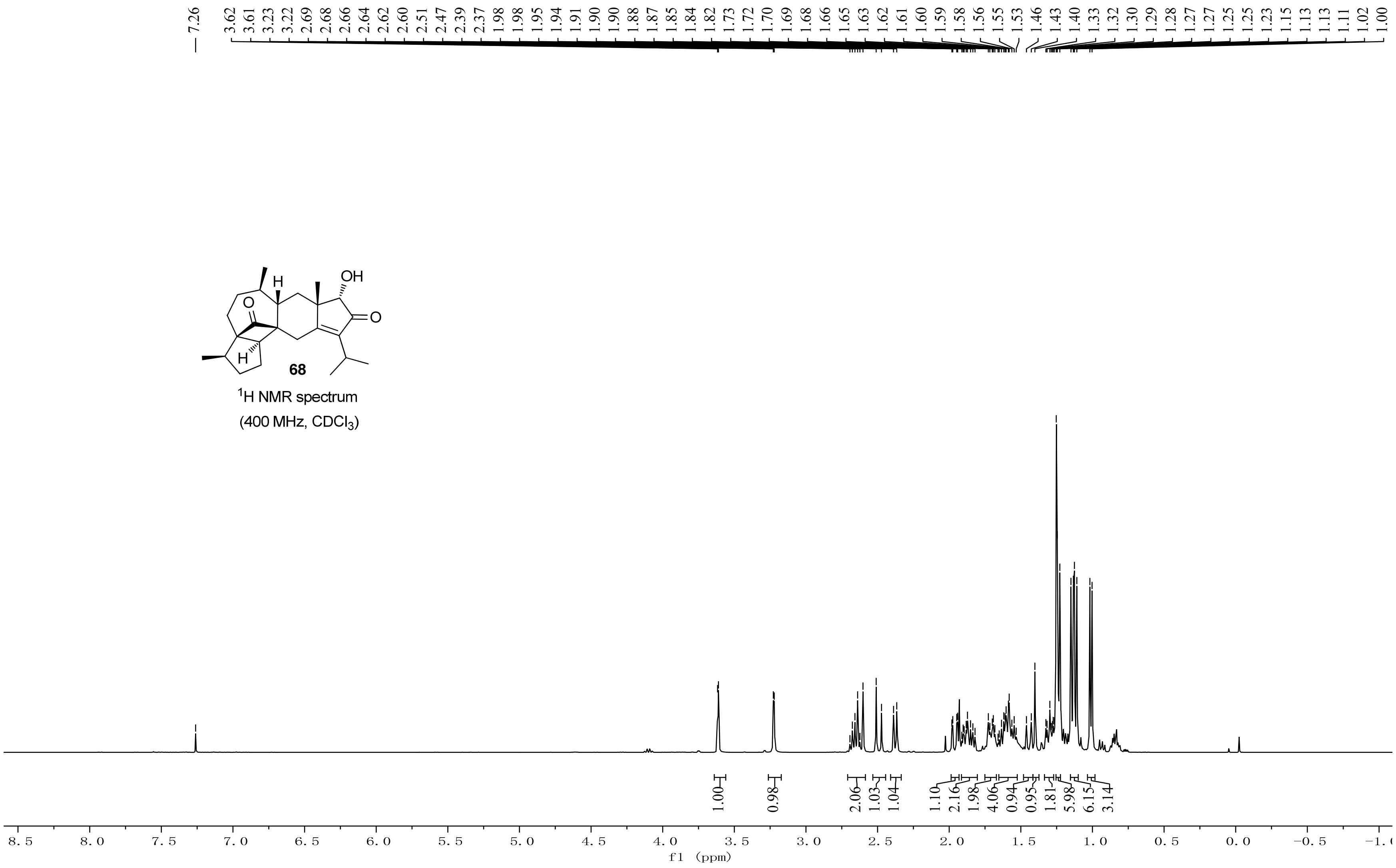
(400 MHz, $CDCl_3$)



33

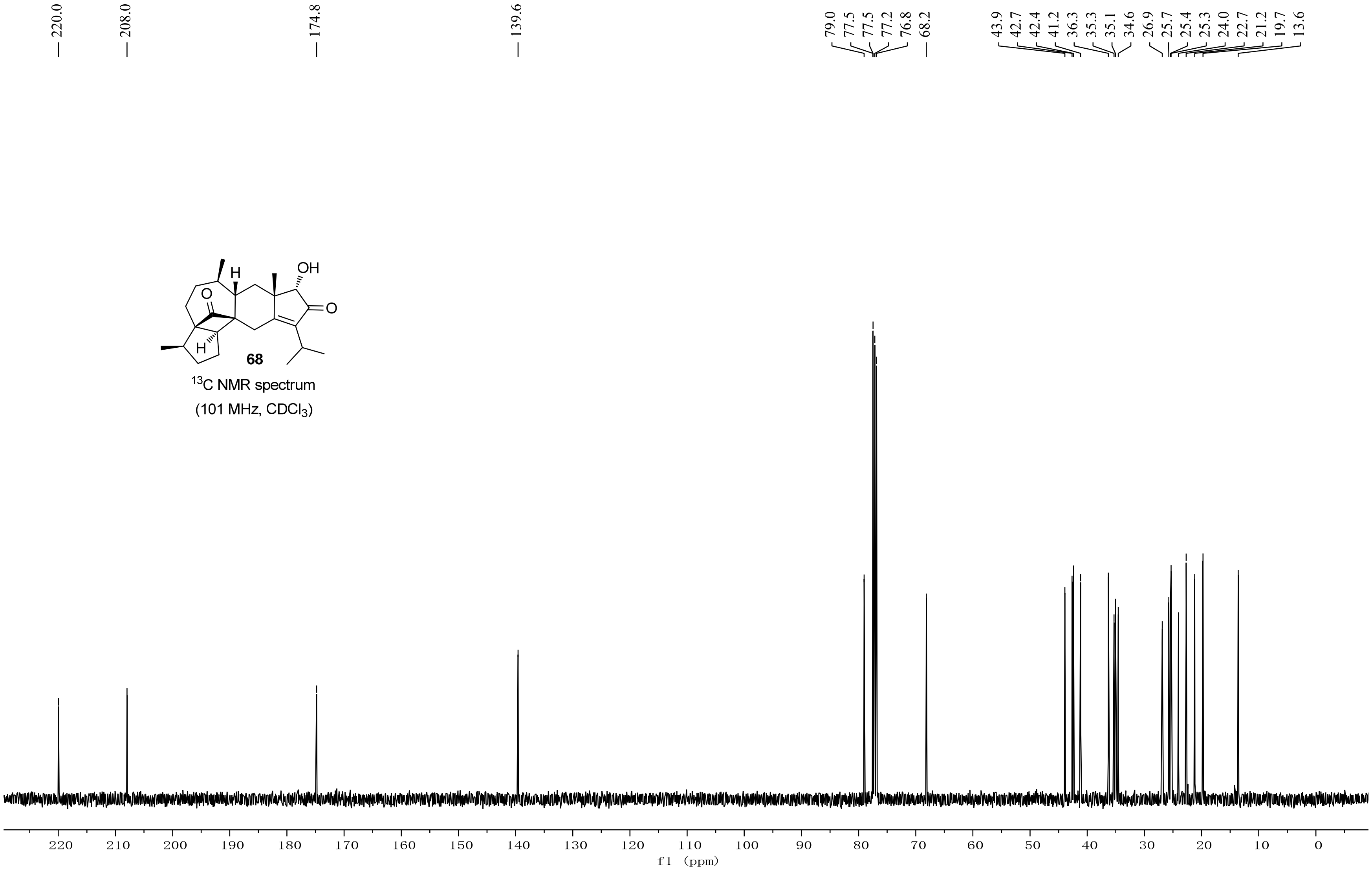
^{13}C NMR spectrum

(101 MHz, $CDCl_3$)



68

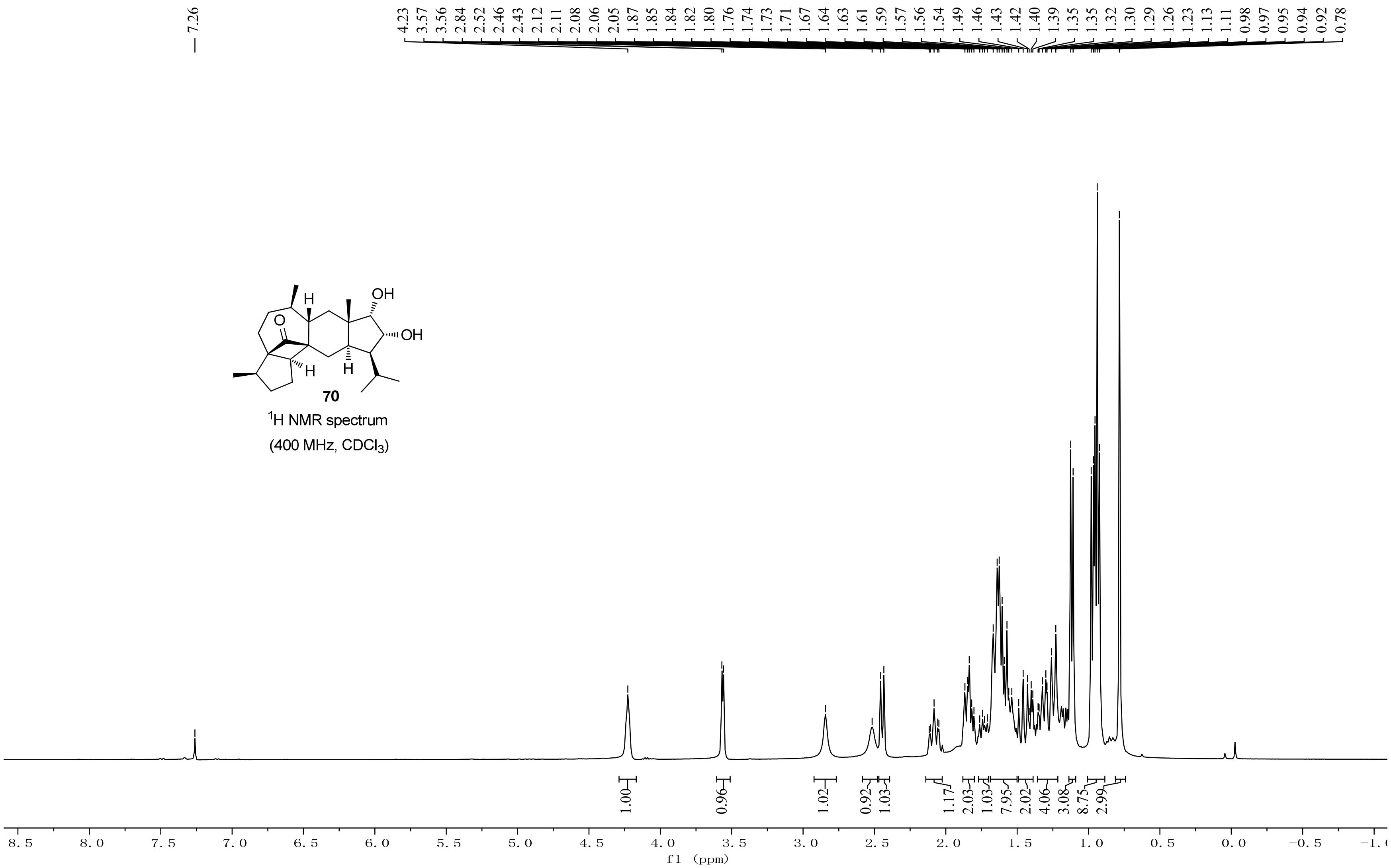
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)

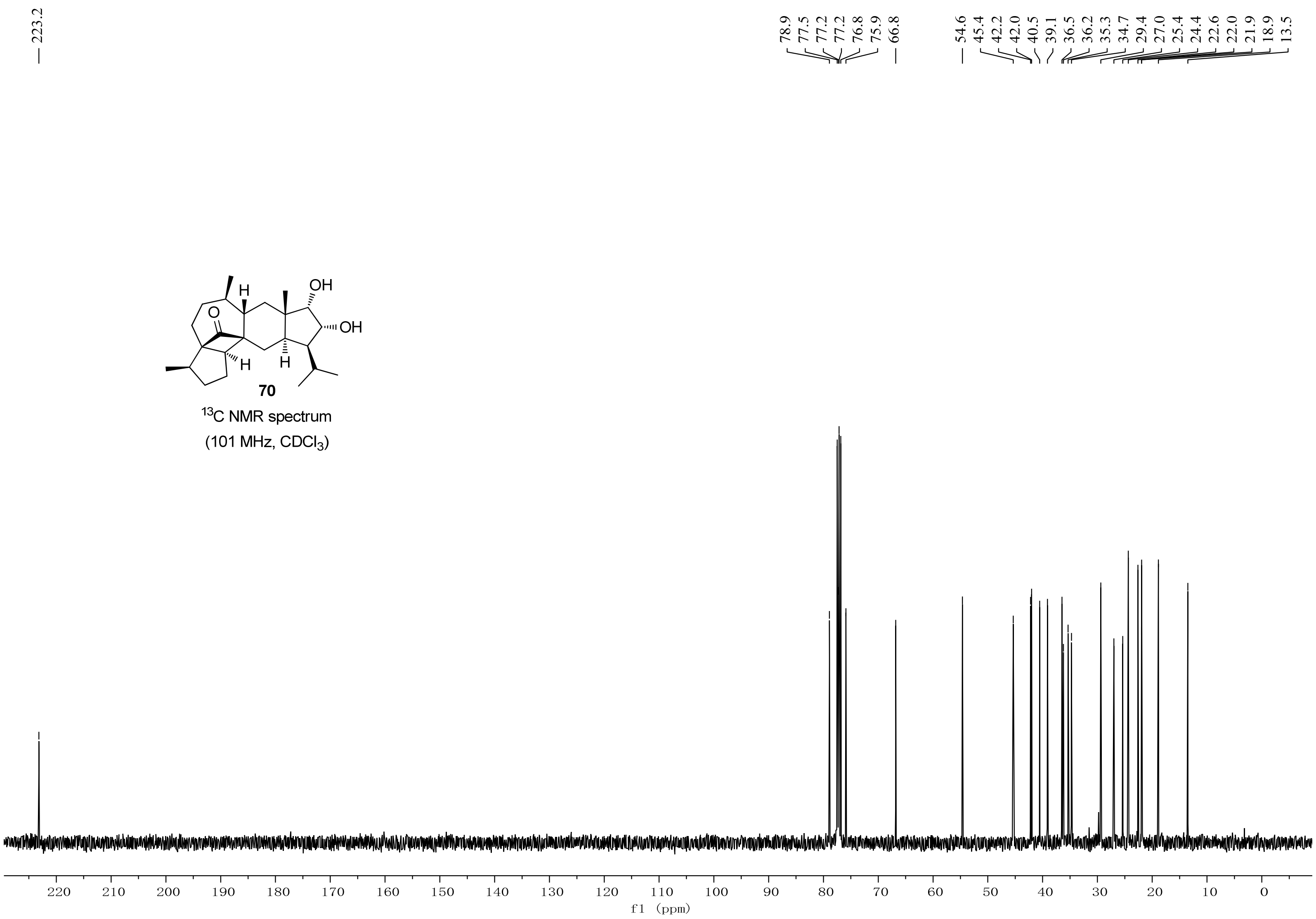


68

^{13}C NMR spectrum

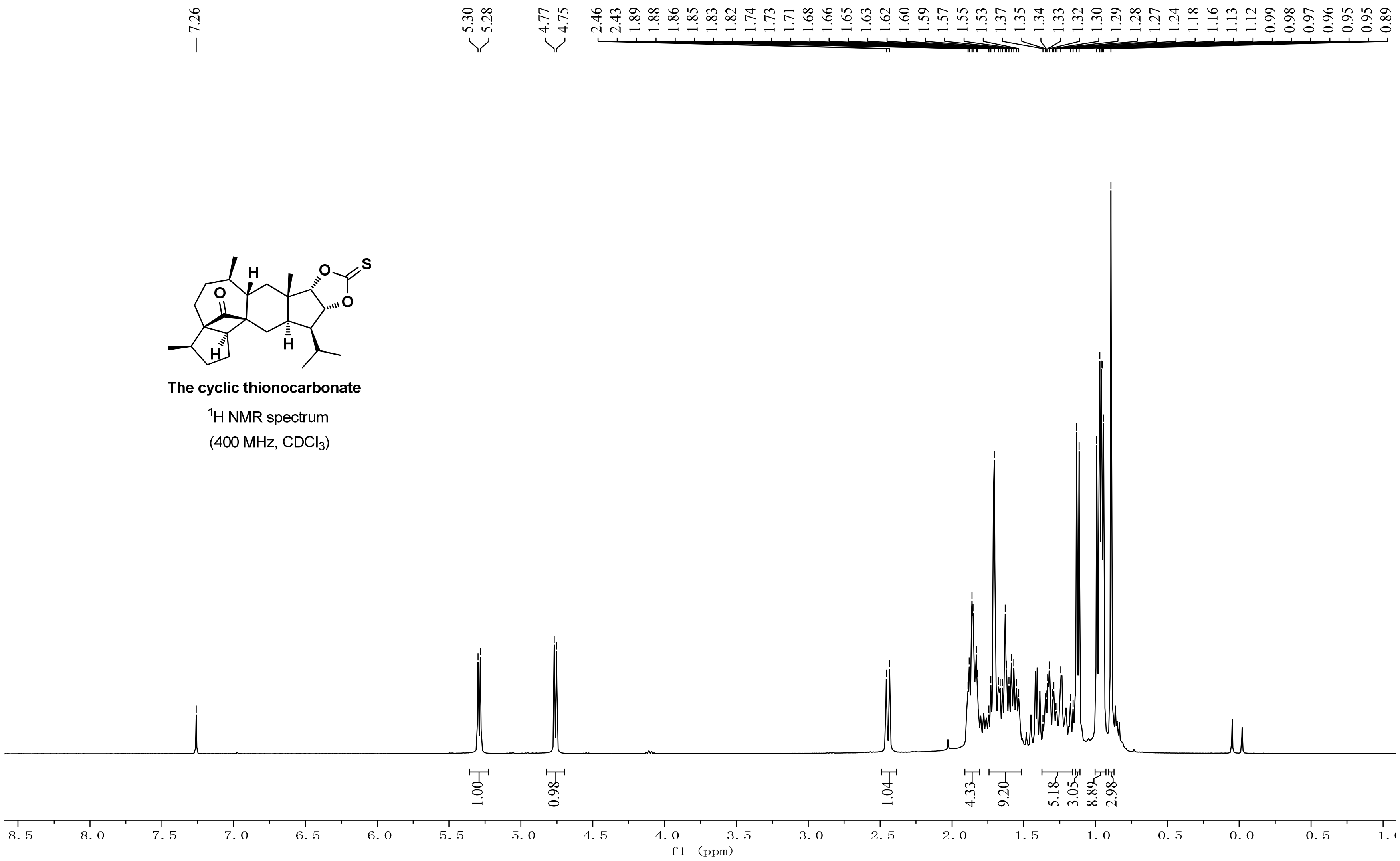
(101 MHz, CDCl$_3$)


7.26
4.23
3.57
3.56
2.84
2.52
2.46
2.43
2.12
2.11
2.08
2.06
2.05
1.87
1.85
1.84
1.82
1.80
1.76
1.74
1.73
1.71
1.67
1.64
1.63
1.61
1.59
1.57
1.56
1.54
1.49
1.46
1.43
1.42
1.40
1.39
1.35
1.35
1.32
1.30
1.29
1.26
1.23
1.13
1.11
0.98
0.97
0.95
0.94
0.92
0.78
OH
OH
H
O
H
H
70
^{1}H NMR spectrum
(400 MHz, CDCl$_3$)
1.00
0.96
1.02
0.92
1.03
1.17
2.03
1.03
7.95
2.02
4.06
3.08
8.75
2.99
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
−1.
f1 (ppm)



70

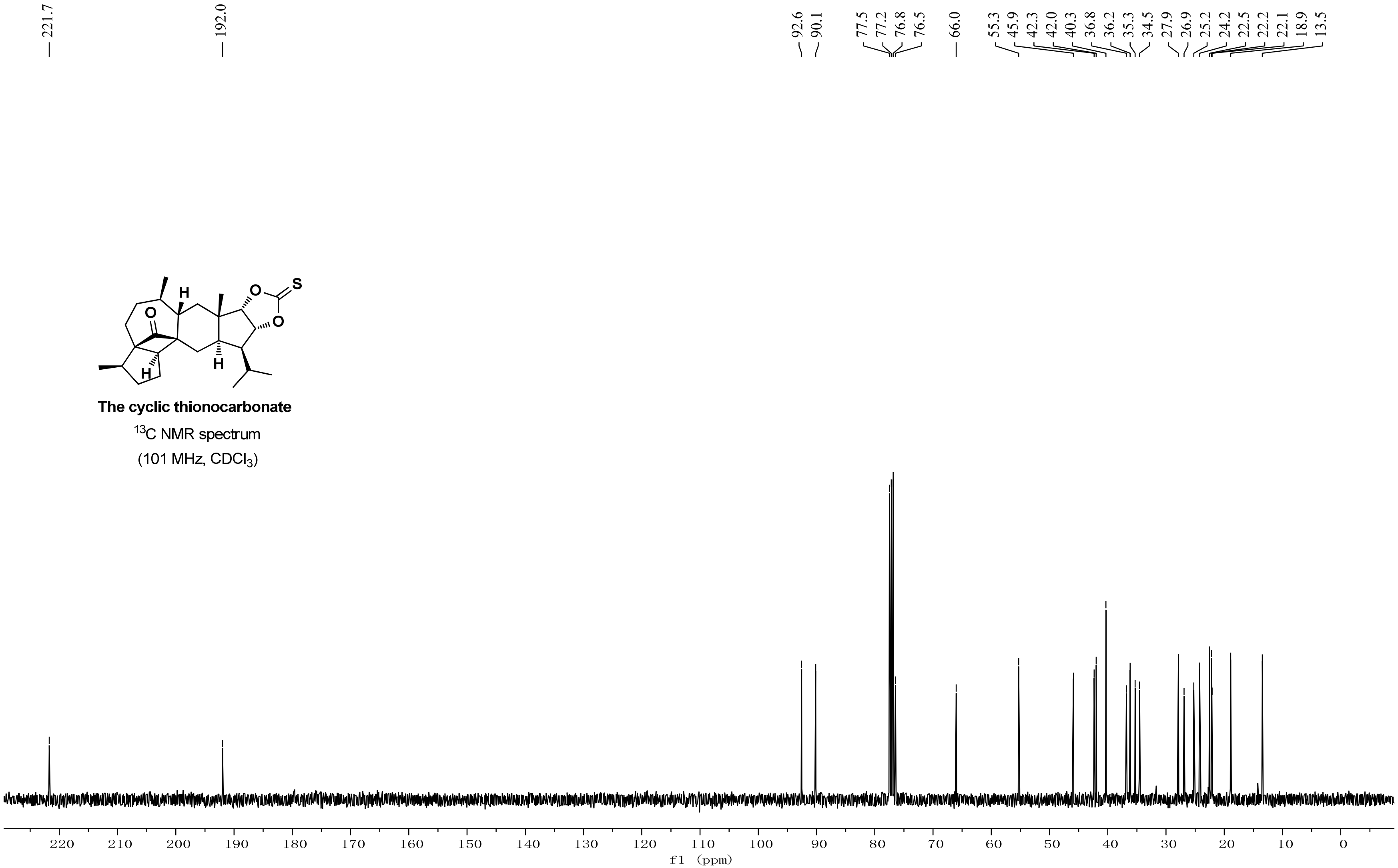
^{13}C NMR spectrum
(101 MHz, $CDCl_3$)



The cyclic thionocarbonate

^{1}H NMR spectrum

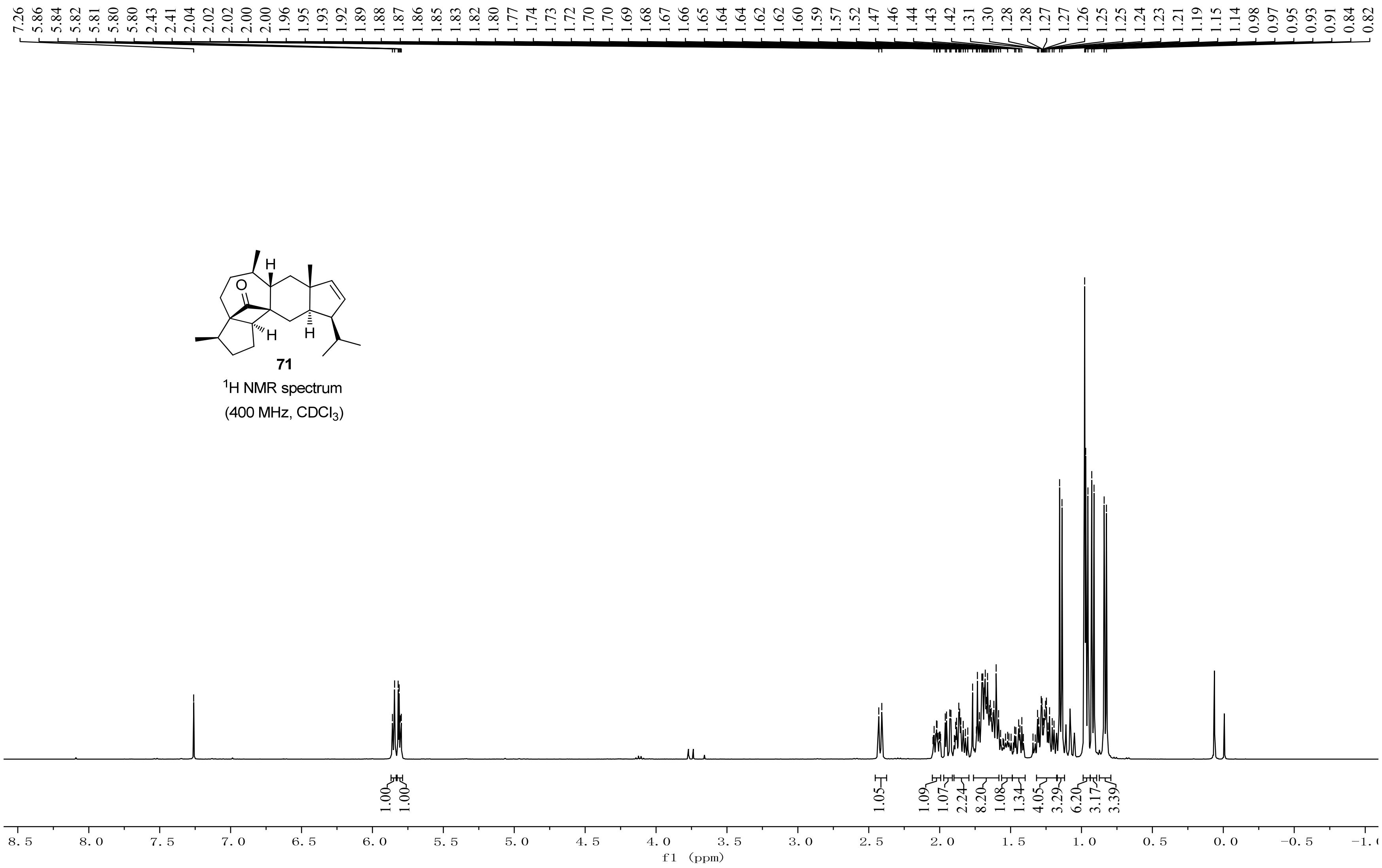
(400 MHz, $CDCl_3$)



The cyclic thionocarbonate

^{13}C NMR spectrum

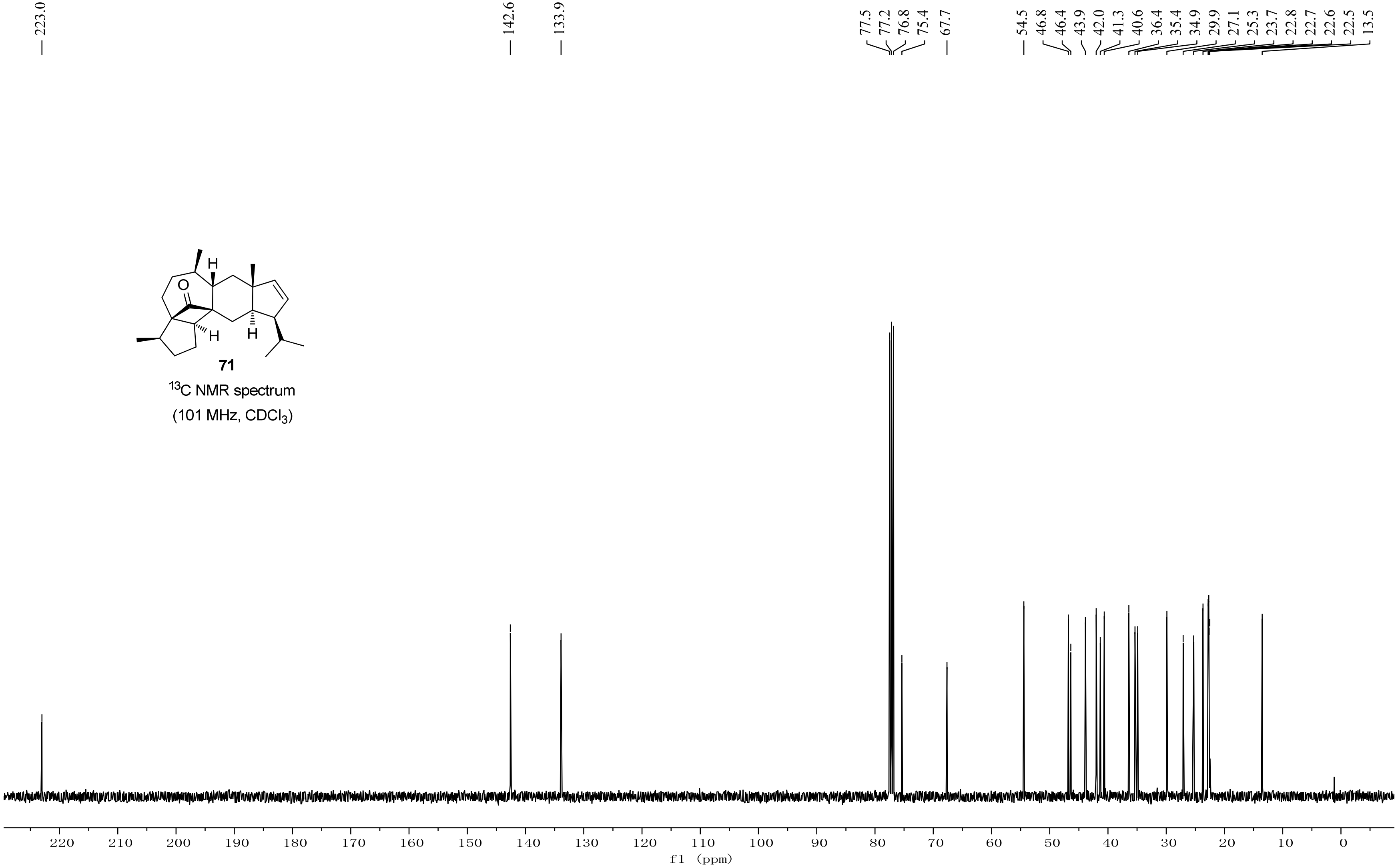
(101 MHz, $CDCl_3$)



71

^{1}H NMR spectrum

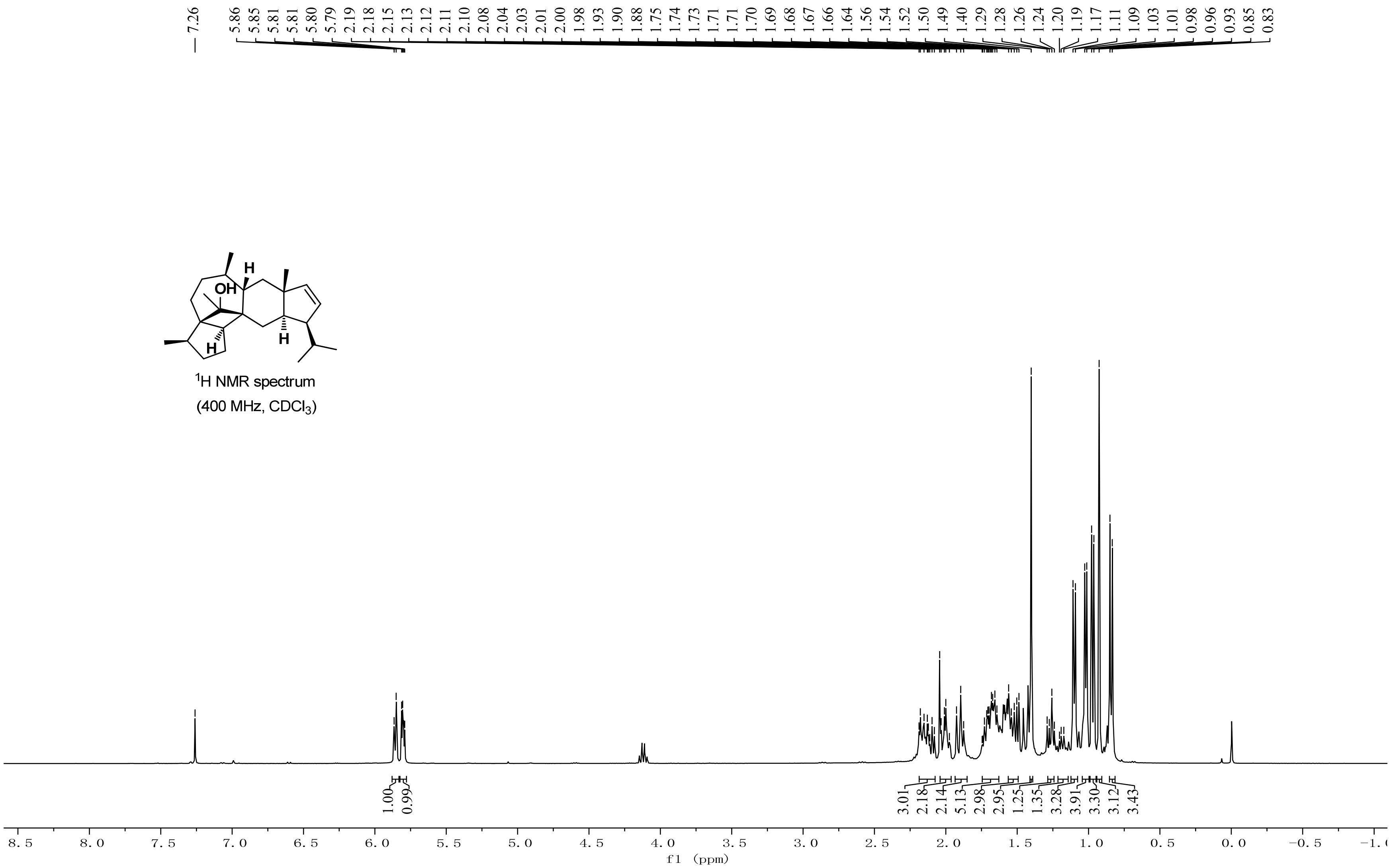
(400 MHz, $CDCl_3$)



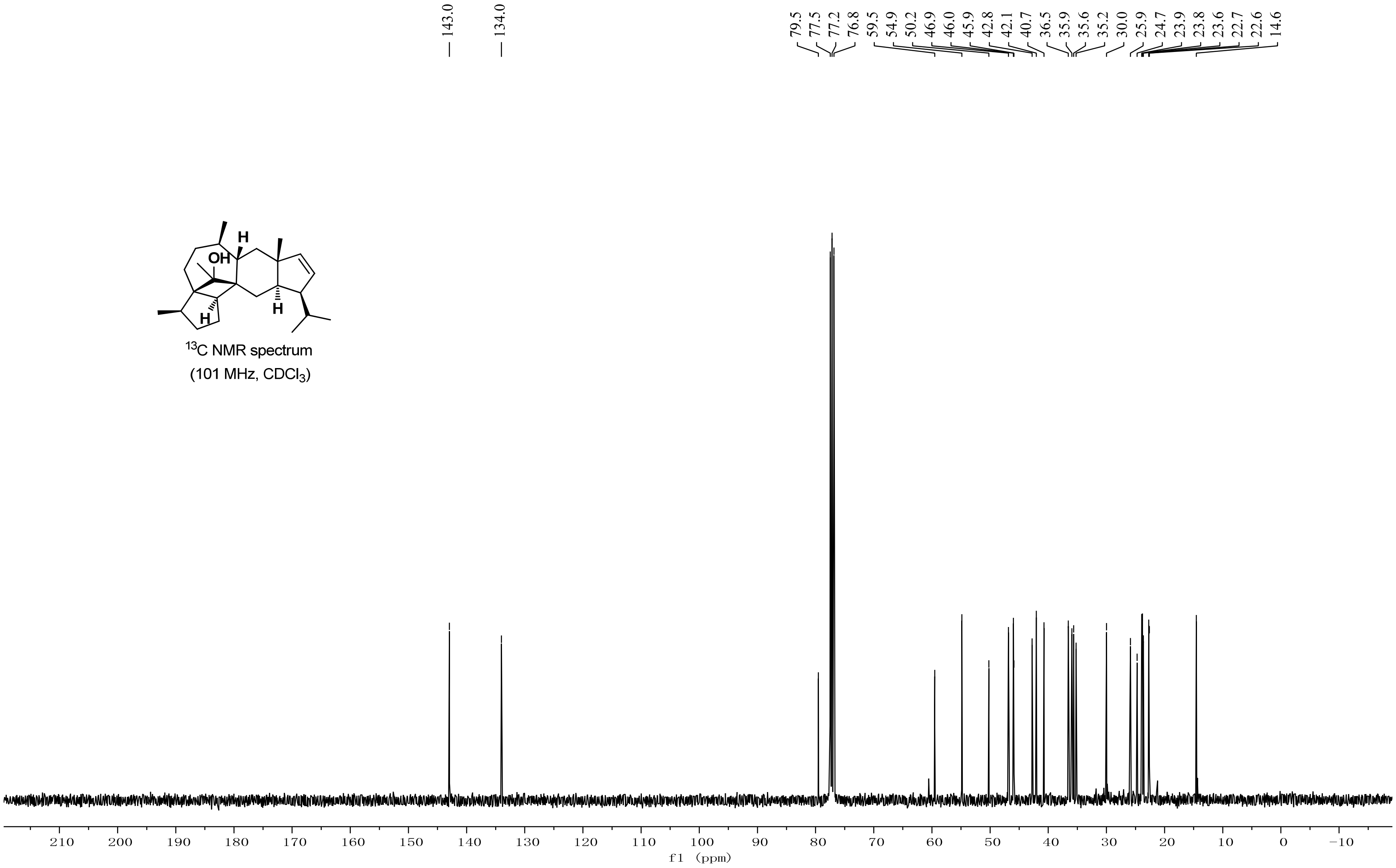
71

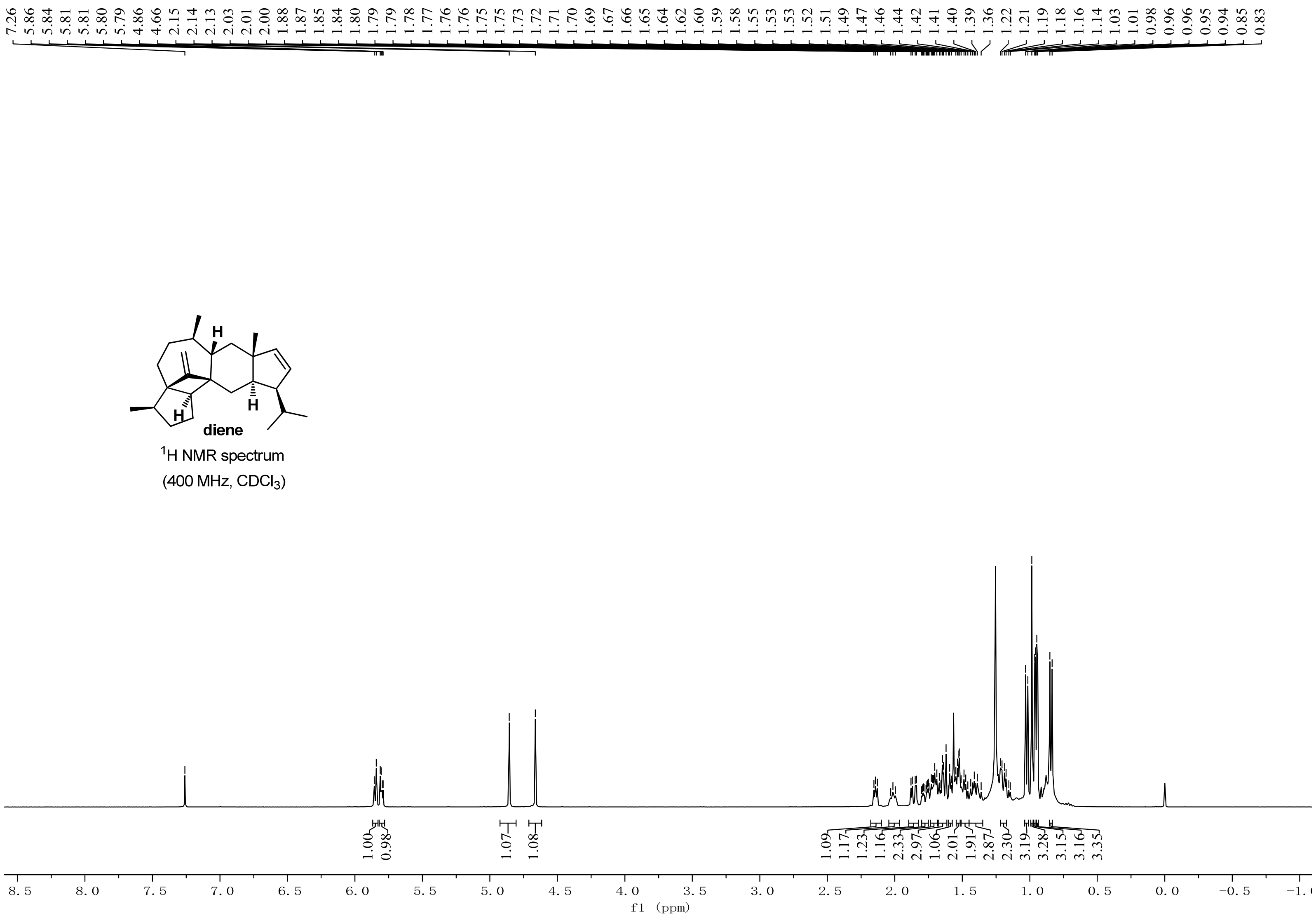
^{13}C NMR spectrum

(101 MHz, $CDCl_3$)


^{1}H NMR spectrum

(400 MHz, $CDCl_3$)

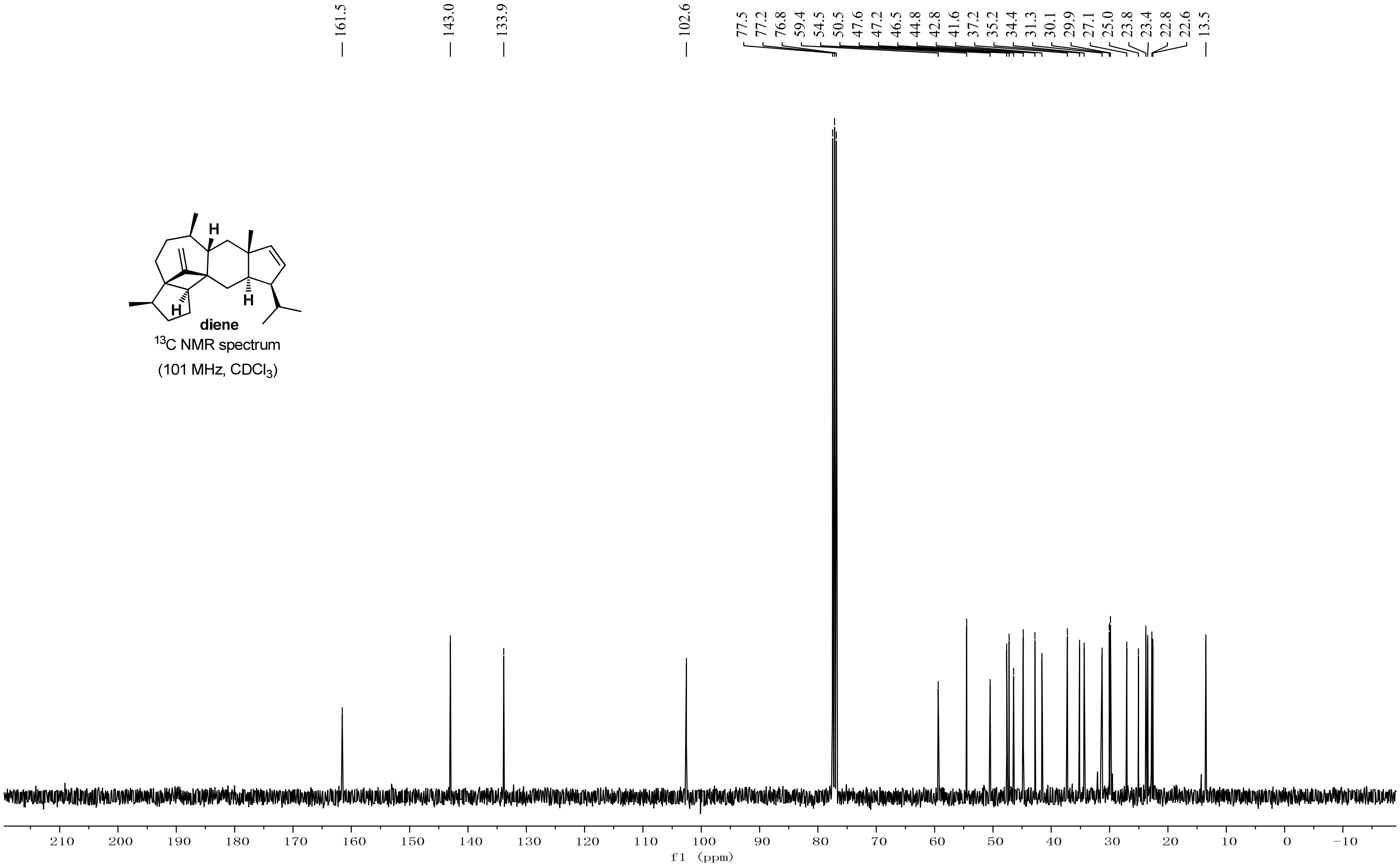

143.0
134.0
79.5
77.5
77.2
76.8
59.5
54.9
50.2
46.9
46.0
45.9
42.8
42.1
40.7
36.5
35.9
35.6
35.2
30.0
25.9
24.7
23.9
23.8
23.6
22.7
22.6
14.6
OH
H
H
H
^{13}C NMR spectrum
(101 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



diene

^{1}H NMR spectrum

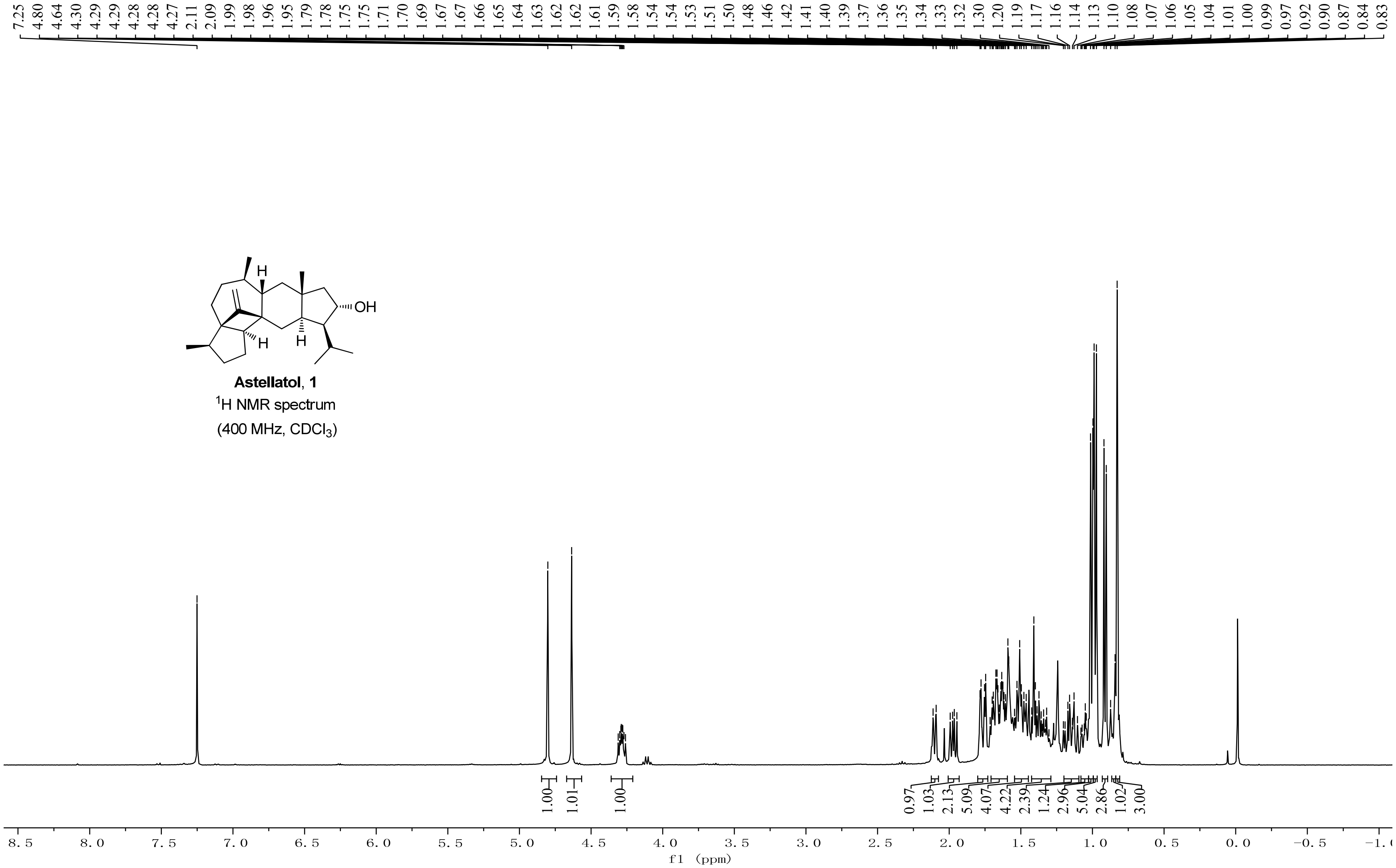
(400 MHz, $CDCl_3$)

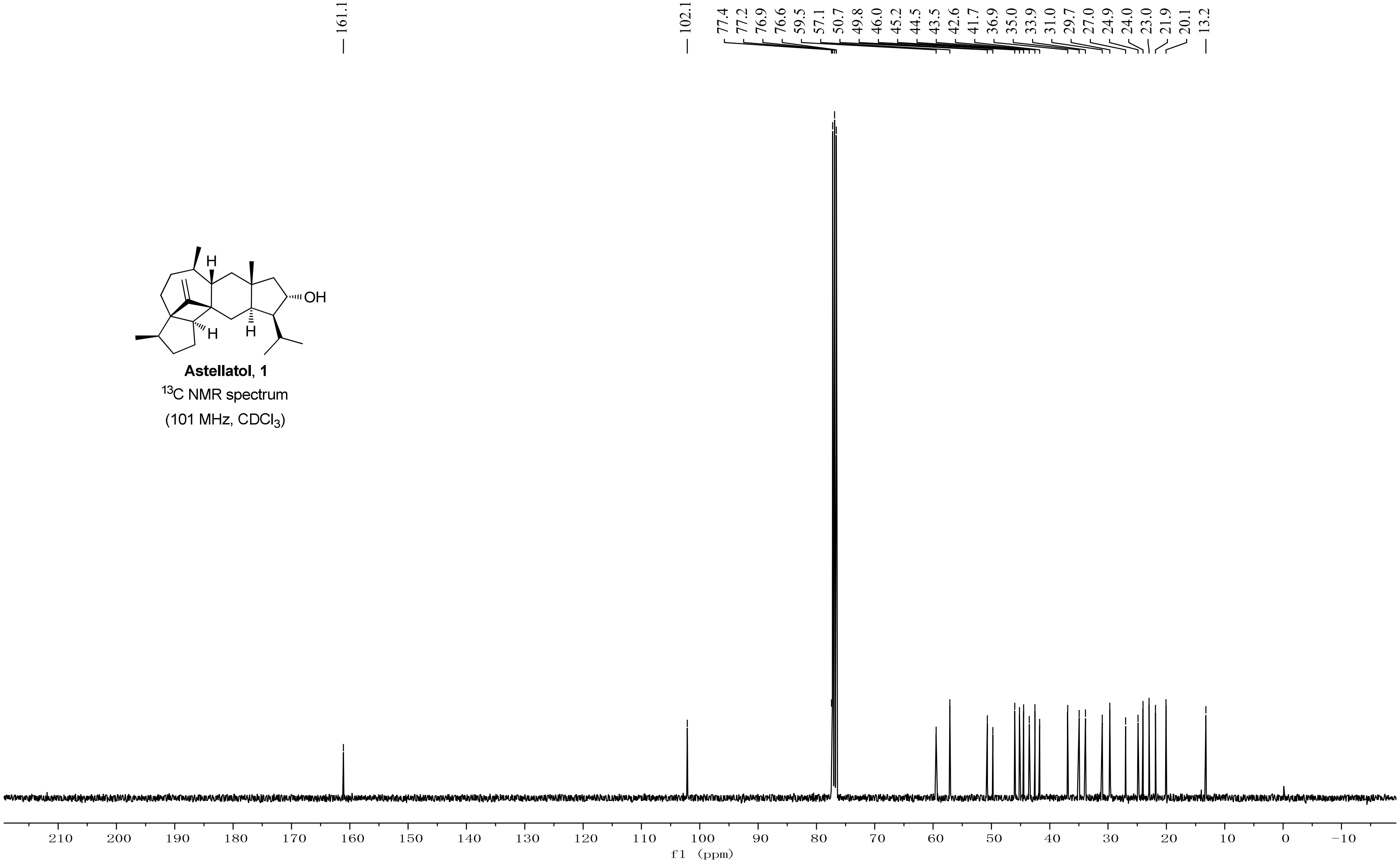


diene

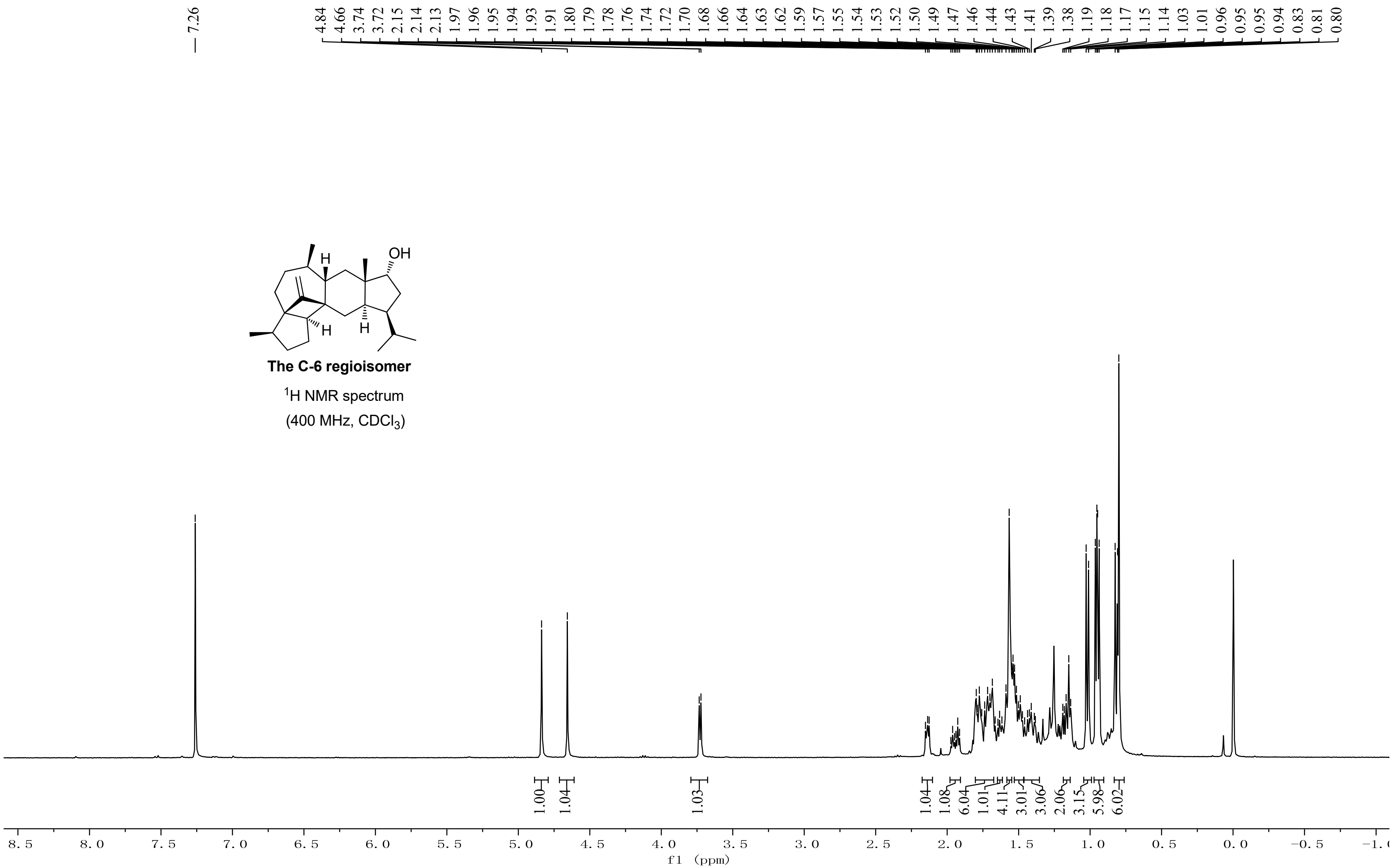
^{13}C NMR spectrum

(101 MHz, CDCl$_3$)


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

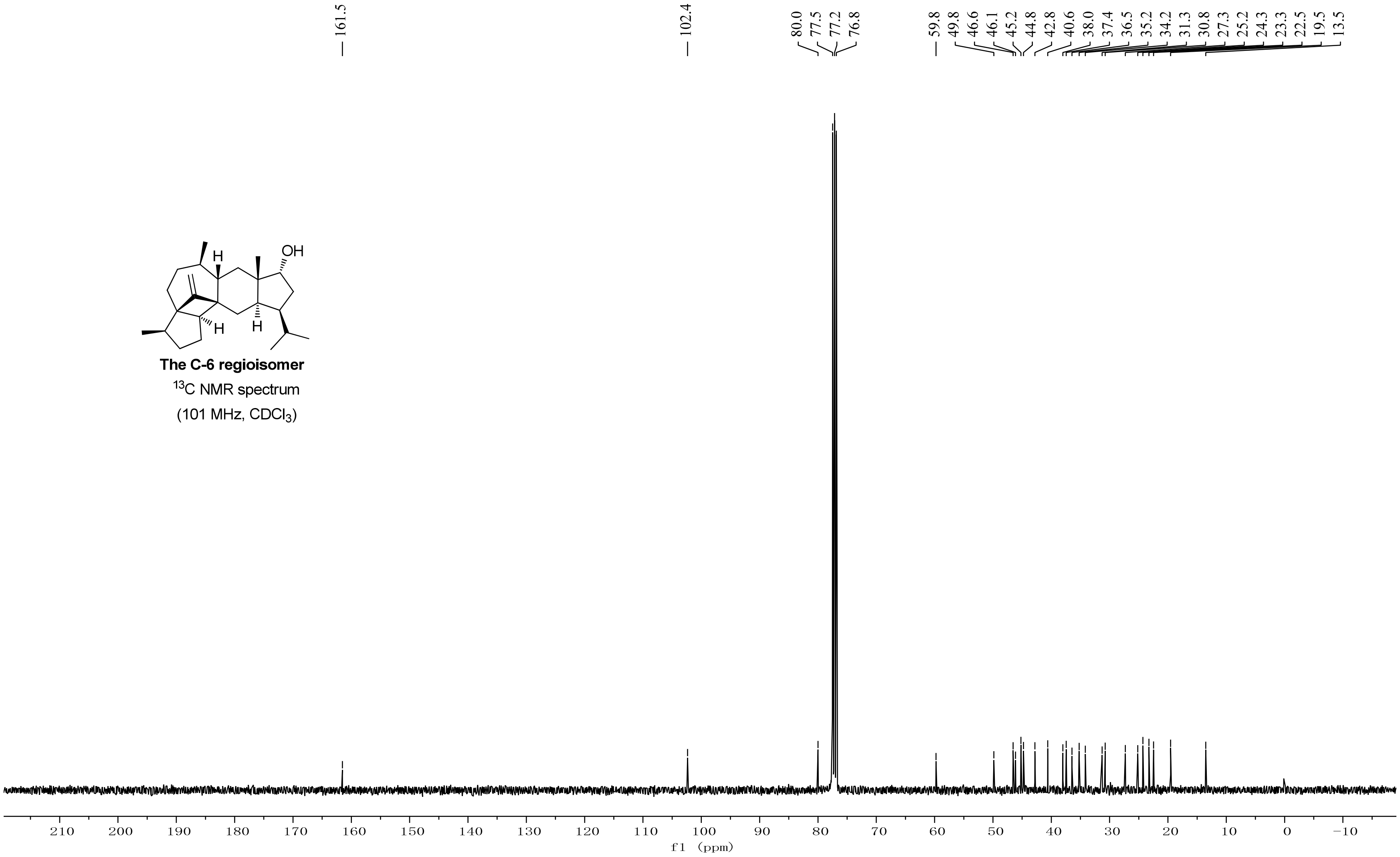


Astellatol, **1**
^{13}C NMR spectrum
(101 MHz, $CDCl_3$)


The C-6 regioisomer

^{1}H NMR spectrum

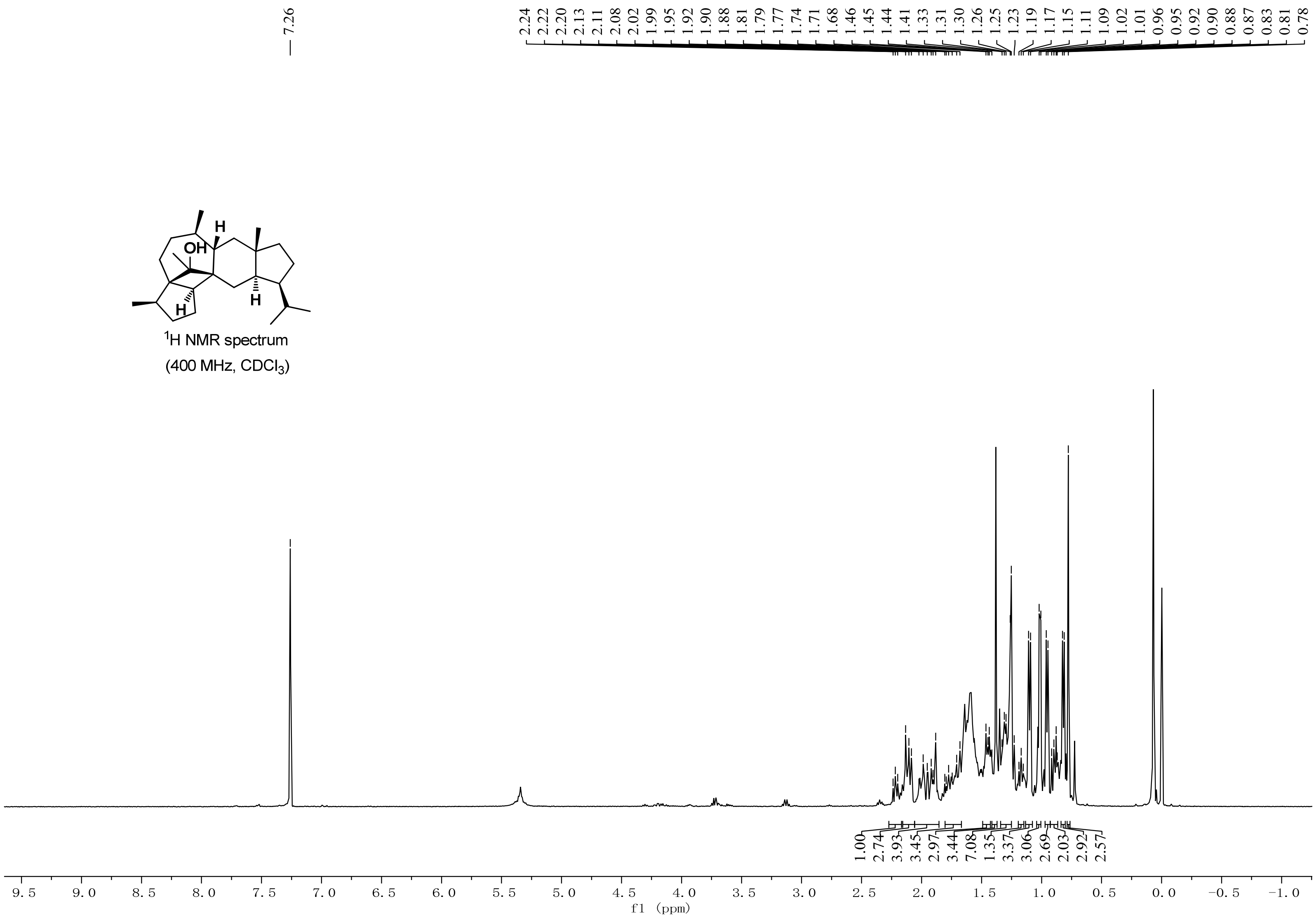
(400 MHz, $CDCl_3$)



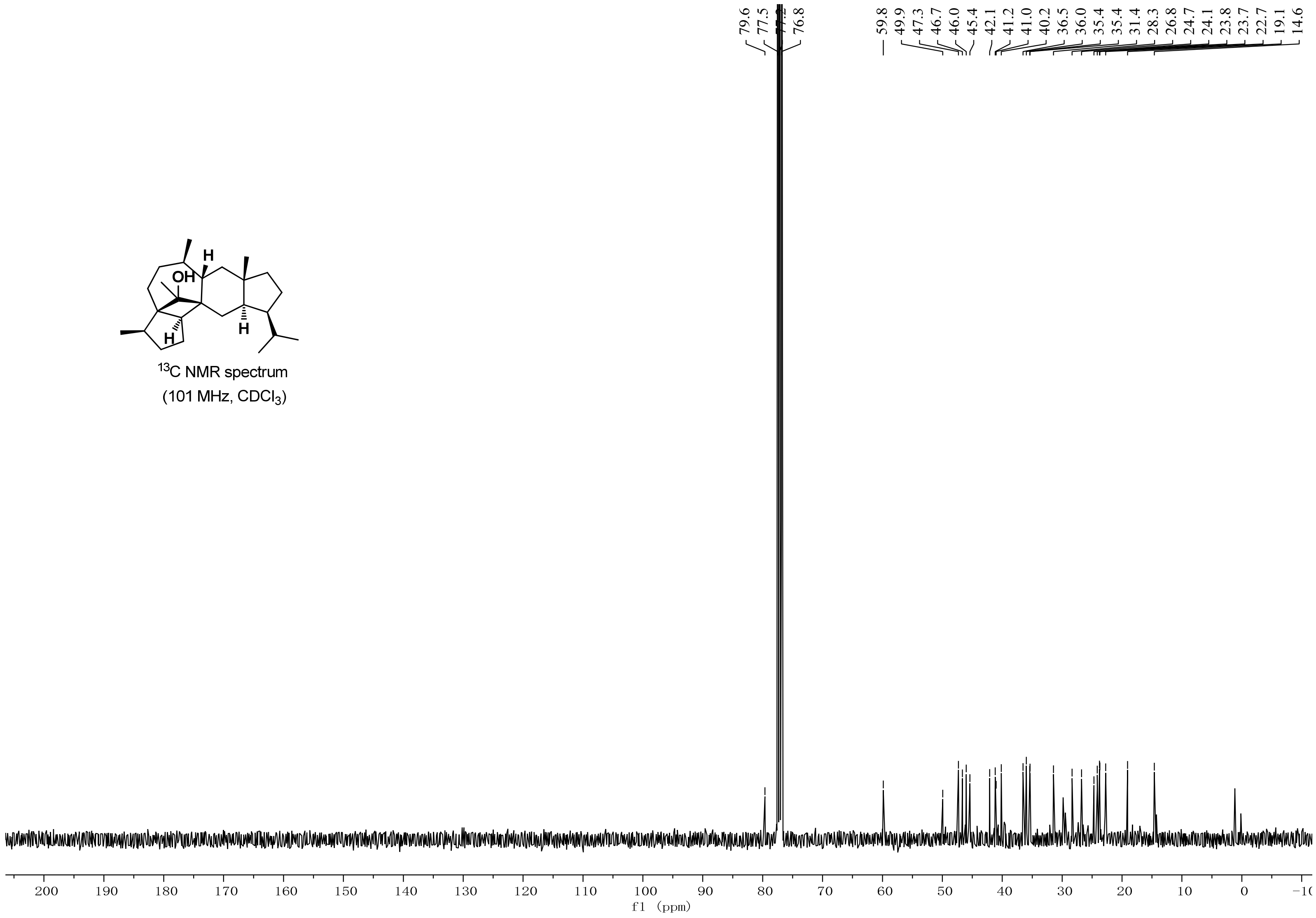
The C-6 regioisomer

^{13}C NMR spectrum

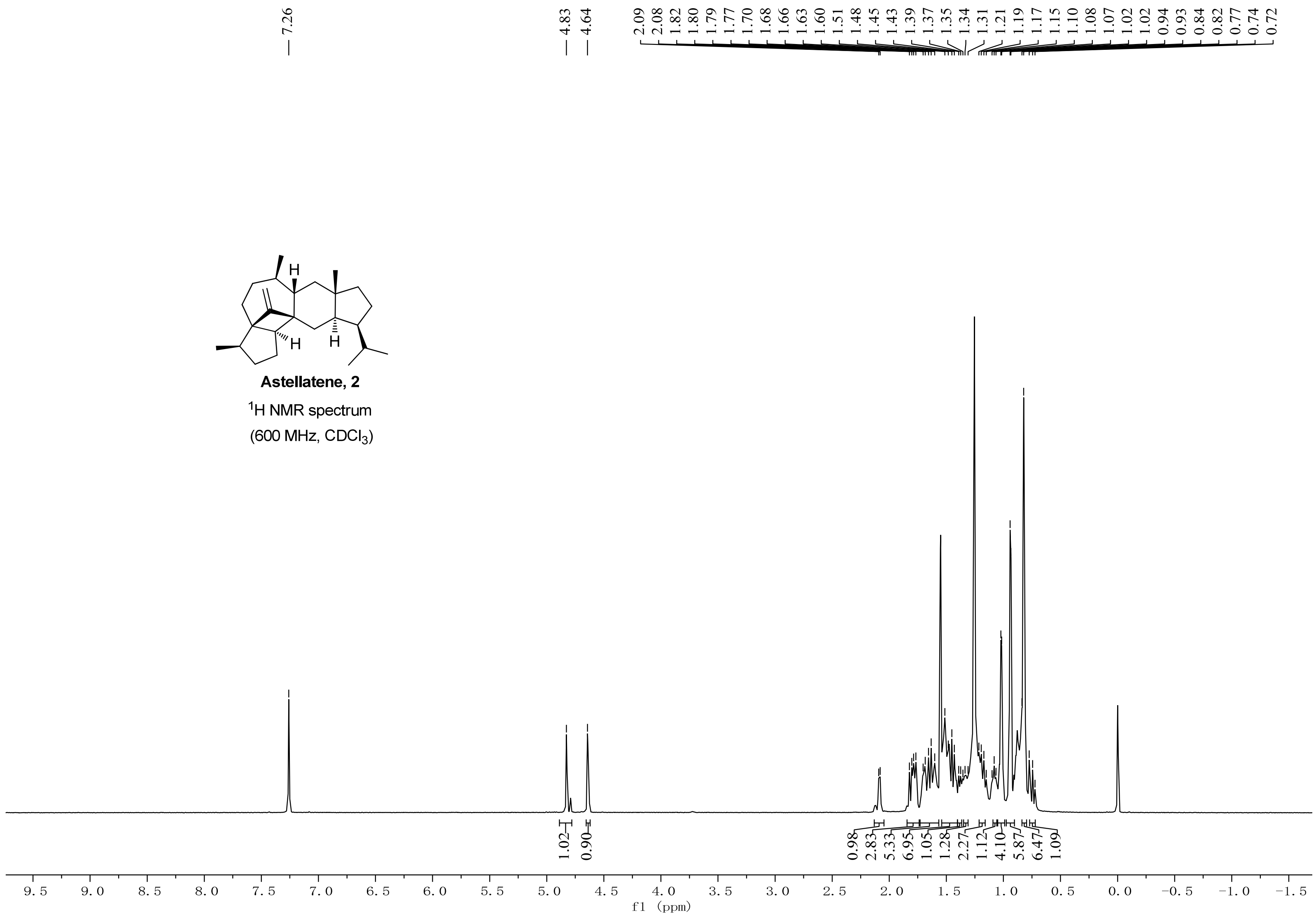
(101 MHz, $CDCl_3$)



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



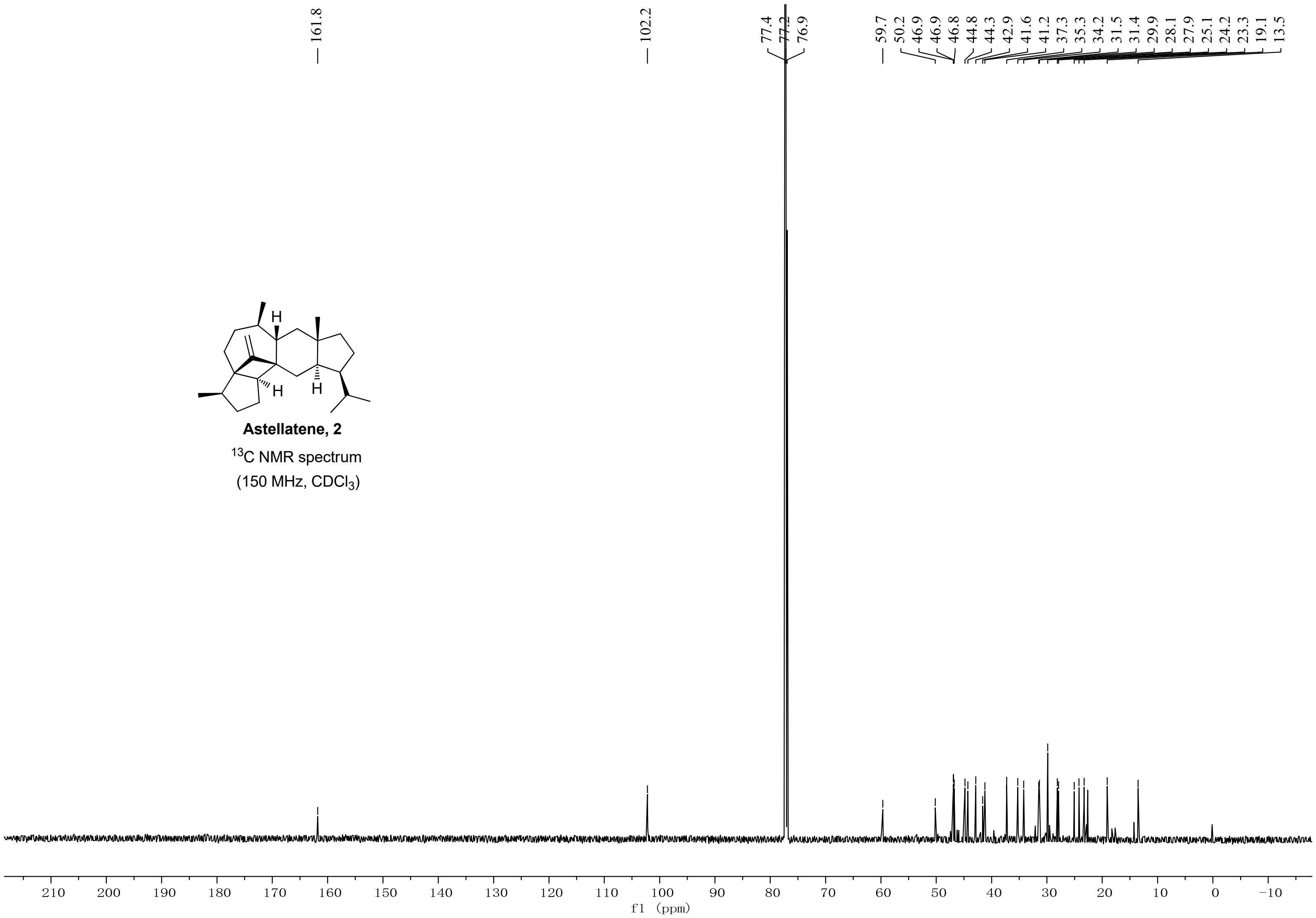
^{13}C NMR spectrum
(101 MHz, $CDCl_3$)



Astellatene, 2

^1H NMR spectrum

(600 MHz, $CDCl_3$)



Astellatene, 2

^{13}C NMR spectrum

(150 MHz, $CDCl_3$)

IV. Comparison of NMR Data of Natural and Synthetic Astellatol

Table S1. NMR data[a] for natural Astellatol and synthetic Astellatol in $CDCl_3$.

position	Natural Astellatol [b]		Synthetic Astellatol [c]	
	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)
1	49.8		49.8	
2a	27.0	1.41 (t, 13.5)	27.0	1.30–1.44 (m)[d]
2b		1.60 (dd, 2.7)		1.58–1.71 (m)[d]
3	45.3	1.66 (ddd, 10.2)	45.2	1.58–1.71 (m)[d]
4	57.2	1.41(td, 4.2, 10.2)	57.1	1.30–1.44 (m)[d]
5	77.4	4.28 (ddd, 7.1, 8.7)	77.4	4.29 (ddd, 4.2, 7.4, 8.6)
6a	50.9	1.13 (dd, 11.5)	50.7	1.10–1.20 (m)[d]
6b		1.97 (dd)		1.97 (dd, 7.1, 11.5)
7	41.7		41.7	
8a	43.6	0.84 (t, 12.2)	43.5	0.84 (t, 12.0)
8b		1.76 (ddd, 3.4)		1.77 (dd, 3.2, 12.9)
9	46.0	1.06 (ddd, 9.0)	46.0	1.03–1.08 (m)[d]
10	37.0	1.34 (m)	36.9	1.30–1.44 (m)[d]
11a	33.9	1.48 (ddt, 12.7, 4.5, 2.4)	33.9	1.46–1.56 (m)[d]
11b		1.65 (qd, 12.8, 4.7)		1.58–1.71 (m)[d]
12a	31.1	1.17 (td, 12.8)	31.0	1.10–1.20 (m)[d]
12b		1.76 (ddd)		1.77 (dd, 3.2, 12.9)
13	59.5		59.5	
14	42.6	1.47 (m)	42.6	1.46–1.56 (m)[d]
15a	35.0	1.37 (qd, 12.1, 7.2)	35.0	1.30–1.44 (m)[d]
15b		1.70 (dt)		1.58–1.71 (m)[d]
16a	24.9	1.48–1.58 (d, 9.0)	24.9	1.46–1.56 (m)[d]
16b		1.48–1.58 (d, 1.7)		1.46–1.56 (m)[d]
17	44.6	2.10 (dd)	44.5	2.10 (d, 8.7)
18	161.1		161.1	
19a	102.1	4.63 (s)	102.1	4.64 (s)
19b		4.80 (s)		4.80 (s)
20	29.7	1.67 (m)	29.7	1.58–1.71 (m)[d]
21	24.0	0.98 (d)	24.0	0.98 (d, 8.0)
22	21.8	0.98 (d)	21.9	0.98 (d, 8.0)
23	20.1	0.83 (s)	20.1	0.83 (s)
24	23.0	0.91 (d)	23.0	0.91 (d, 6.4)
25	13.2	1.00 (d)	13.2	1.00 (d, 6.4)

[a] δ_C is relative to $CDCl_3$ at $\delta 76.9$, δ_H is relative to $CDCl_3$ at $\delta 7.25$.

[b] ^{1}H NMR spectra were recorded at 600 MHz; ^{13}C NMR spectra were recorded at 150 MHz;

[c] ^{1}H NMR spectra were recorded at 400 MHz; ^{13}C NMR spectra were recorded at 101 MHz;

[d] Overlapped

Table S2. NMR data[a] for natural (+)-Astellatene and synthetic (-)-Astellatene in $CDCl_3$.

position	Natural Astellatene [b]		Synthetic Astellatene [c]	
	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)
1a	44.13	1.81 (dd, 12.4, 3.2)	44.13	1.74–1.84 (m)[d]
1b		0.75 (t, 12.4)		0.72–0.77 (m)
2	46.76	1.08 (m)	46.76	1.06–1.09 (m)[d]
3	37.13	1.34(m)	37.13	1.31–1.35 (m)
4a	34.04	1.69 (m)	34.05	1.56–1.73 (m)[d]
4b		1.49 (m)		1.40–1.54 (m)[d]
5a	31.20	1.77 (m)	31.21	1.74–1.84 (m)[d]
5b		1.19 (dd, 8.4, 4.8)		1.16–1.22 (m)[d]
6	59.52		59.52	
7	42.70	1.47 (m)	42.71	1.40–1.54 (m)[d]
8a	35.11	1.71 (m)	35.11	1.56–1.73 (m)[d]
8b		1.40 (m)		1.36–1.40 (m)
9a	27.76	1.53 (m)	27.76	1.40–1.54 (m)[d]
9b		1.53 (m)		1.40–1.54 (m)[d]
10	44.67	2.09 (m)	44.67	2.09 (d, 7.4)
11	161.65		161.65	
12	50.01		50.02	
13a	27.97	1.64 (m)	27.97	1.56–1.73 (m)[d]
13b		1.47 (m)		1.40–1.54 (m)[d]
14	46.61	1.22 (m)	46.61	1.16–1.22 (m)[d]
15	41.47		41.47	
16a	41.06	1.45 (m)	41.07	1.40–1.54 (m)[d]
16b		1.03 (m)		0.99–1.05 (m)[d]
17a	29.7	1.78 (m)	29.71	1.74–1.84 (m)[d]
17b		1.49 (m)		1.40–1.54 (m)[d]
18	46.72	1.62 (m)	46.73	1.56–1.73 (m)[d]
19	31.31	1.60 (m)	31.32	1.56–1.73 (m)[d]
20	24.05	0.94 (d, 6.4)	24.05	0.94 (d, 4.3)
21	13.36	1.02 (d, 6.4)	13.37	0.99–1.05 (m)[d]
22a	102.06	4.83 (s)	102.07	4.83 (s)
22b		4.64 (s)		4.64 (s)
23	18.94	0.82 (s)	18.95	0.82 (s)
24	24.91	0.94 (d, 6.4)	24.92	0.94 (d, 4.3)
25	23.13	0.82 (d, 6.4)	23.14	0.82 (s)

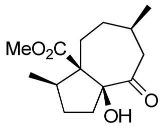
[a] δ_C is relative to $CDCl_3$ at δ77.0, δ_H is relative to $CDCl_3$ at δ7.26.

[b] ^{1}H NMR spectra were recorded at 400 MHz; ^{13}C NMR spectra were recorded at 100 MHz;

[c] ^{1}H NMR spectra were recorded at 600 MHz; ^{13}C NMR spectra were recorded at 150 MHz;

[d] Overlapped

V. Crystallographic Data



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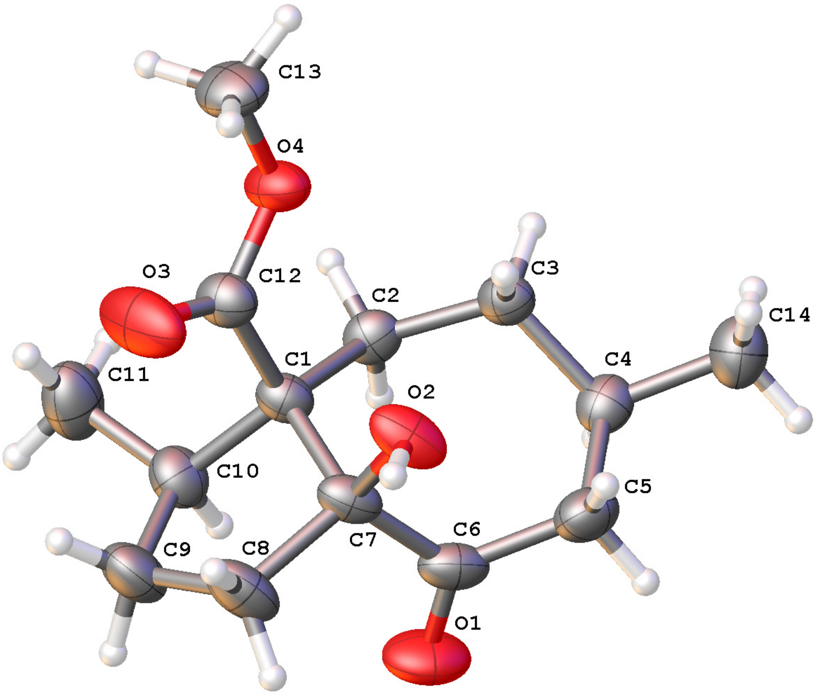


ORTEP of **(–)-43**

*Crystal data and structure refinement for compound (–)-**43***

Identification code	cu_dm16384_0m	
Empirical formula	C14 H22 O4	
Formula weight	254.31	
Temperature	296 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.7082(4) Å	a= 90°.
	b = 9.8033(6) Å	b= 90°.
	c = 17.7454(10) Å	g = 90°.
Volume	1340.95(13) Å^3	
Z	4	
Density (calculated)	1.260 Mg/m^3	
Absorption coefficient	0.742 mm^{-1}	
F(000)	552	
Crystal size	0.3 x 0.25 x 0.2 mm^3	
Theta range for data collection	4.984 to 69.644°.	
Index ranges	-8<=h<=9, -11<=k<=11, -21<=l<=21	
Reflections collected	9607	
Independent reflections	2473 [R(int) = 0.0419]	

Completeness to theta = 67.679°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7532 and 0.5253
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2473 / 0 / 168
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0979
R indices (all data)	R1 = 0.0377, wR2 = 0.0987
Absolute structure parameter	0.04(7)
Extinction coefficient	0.0092(12)
Largest diff. peak and hole	0.294 and -0.153 e.Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å2)

	x	y	z	U(eq)
O(1)	4895(2)	3925(2)	2048(1)	65(1)
O(2)	2825(2)	6650(1)	2944(1)	49(1)
O(3)	3004(2)	5903(2)	4619(1)	77(1)
O(4)	362(2)	5363(2)	4228(1)	45(1)
C(1)	2728(2)	4403(2)	3545(1)	33(1)
C(2)	1262(3)	3563(2)	3179(1)	36(1)
C(3)	64(2)	4273(2)	2616(1)	36(1)
C(4)	693(3)	4204(2)	1799(1)	39(1)
C(5)	2328(3)	5066(3)	1662(1)	48(1)
C(6)	3760(3)	4728(2)	2209(1)	42(1)
C(7)	3732(2)	5392(2)	2995(1)	36(1)
C(8)	5571(3)	5529(2)	3331(2)	53(1)
C(9)	5834(3)	4339(3)	3873(2)	54(1)
C(10)	4207(3)	3451(2)	3828(1)	43(1)
C(11)	3812(4)	2661(3)	4544(2)	61(1)
C(12)	2079(3)	5314(2)	4186(1)	40(1)
C(13)	-351(3)	6260(3)	4797(1)	56(1)
C(14)	-729(3)	4636(3)	1257(1)	53(1)

Atomic displacement parameters (Å2)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	52(1)	59(1)	84(1)	-7(1)	22(1)	19(1)
O(2)	36(1)	24(1)	86(1)	-1(1)	-4(1)	2(1)
O(3)	47(1)	98(2)	86(1)	-53(1)	-10(1)	-5(1)
O(4)	35(1)	55(1)	46(1)	-14(1)	6(1)	-2(1)
C(1)	29(1)	29(1)	42(1)	-2(1)	1(1)	-1(1)
C(2)	39(1)	30(1)	38(1)	-2(1)	3(1)	-7(1)
C(3)	33(1)	38(1)	38(1)	-4(1)	1(1)	-4(1)
C(4)	48(1)	34(1)	37(1)	-4(1)	1(1)	3(1)
C(5)	48(1)	54(1)	42(1)	5(1)	12(1)	2(1)
C(6)	34(1)	36(1)	56(1)	2(1)	15(1)	1(1)
C(7)	27(1)	27(1)	55(1)	2(1)	4(1)	1(1)
C(8)	29(1)	47(1)	83(2)	7(1)	-6(1)	-4(1)

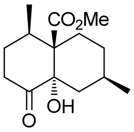
C(9)	32(1)	62(1)	68(1)	9(1)	-5(1)	4(1)
C(10)	43(1)	37(1)	50(1)	1(1)	-4(1)	6(1)
C(11)	62(1)	58(1)	63(1)	18(1)	-14(1)	-7(1)
C(12)	35(1)	39(1)	45(1)	-8(1)	0(1)	-4(1)
C(13)	51(1)	64(1)	52(1)	-16(1)	11(1)	8(1)
C(14)	61(1)	52(1)	44(1)	1(1)	-8(1)	-1(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å2x 10^3)

	x	y	z	U(eq)
H(2)	3519	7283	2965	73
H(2A)	1790	2792	2924	43
H(2B)	545	3198	3581	43
H(3A)	-53	5223	2760	44
H(3B)	-1077	3859	2646	44
H(4)	985	3251	1689	47
H(5A)	2737	4913	1152	58
H(5B)	2035	6025	1710	58
H(8A)	6433	5501	2933	64
H(8B)	5683	6389	3597	64
H(9A)	5997	4673	4382	65
H(9B)	6850	3816	3730	65
H(10)	4411	2776	3430	52
H(11A)	4747	2042	4648	91
H(11B)	2756	2155	4479	91
H(11C)	3683	3285	4956	91
H(13A)	-196	5858	5286	84
H(13B)	-1566	6395	4704	84
H(13C)	237	7123	4779	84
H(14A)	-1696	4025	1302	79
H(14B)	-293	4609	750	79
H(14C)	-1095	5547	1375	79

*Hydrogen bonds for compound (–)-**43**[Å and °].*

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(1)#1	0.82	2.02	2.839(2)	175.2



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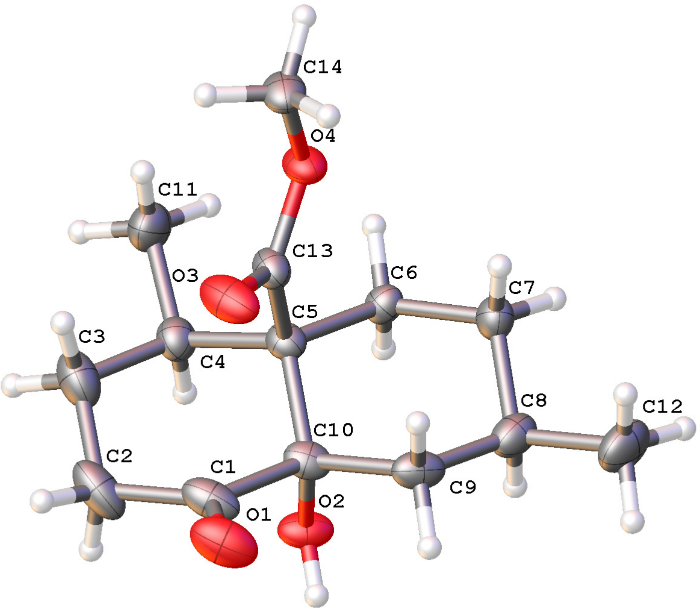


ORTEP of (+)-**44**

*Crystal data and structure refinement for compound (+)-**44***

Identification code	cu_dm16391_0m	
Empirical formula	C14 H22 O4	
Formula weight	254.31	
Temperature	130 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 11.5456(4) Å	a= 90°.
	b = 8.4616(2) Å	b= 91.069(2)°.
	c = 13.8894(4) Å	g = 90°.
Volume	1356.68(7) Å^3	
Z	4	
Density (calculated)	1.245 Mg/m^3	
Absorption coefficient	0.734 mm^{-1}	
F(000)	552	
Crystal size	0.2 x 0.15 x 0.11 mm^3	
Theta range for data collection	4.936 to 69.404°.	
Index ranges	-13<=h<=12, -9<=k<=10, -16<=l<=16	
Reflections collected	10460	
Independent reflections	4331 [R(int) = 0.0562]	
Completeness to theta = 67.679°	95.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7532 and 0.5348	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4331 / 1 / 333	

Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0468, wR2 = 0.1173
R indices (all data)	R1 = 0.0495, wR2 = 0.1200
Absolute structure parameter	-0.10(14)
Extinction coefficient	n/a
Largest diff. peak and hole	0.211 and -0.236 e.Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å2)

	x	y	z	U(eq)
O(1)	-2876(2)	-336(3)	2560(2)	46(1)
O(2)	-702(2)	-2699(2)	2200(2)	31(1)
O(3)	-1134(2)	2152(3)	2218(2)	42(1)
O(4)	768(2)	2544(2)	2246(1)	29(1)
C(1)	-2063(3)	-627(4)	2062(3)	35(1)
C(2)	-2166(3)	-713(5)	979(3)	44(1)
C(3)	-1149(3)	40(5)	459(2)	42(1)
C(4)	42(3)	-405(4)	894(2)	30(1)
C(5)	94(2)	-111(3)	2004(2)	23(1)
C(6)	1282(2)	-611(3)	2436(2)	24(1)
C(7)	1333(2)	-537(4)	3532(2)	28(1)
C(8)	363(3)	-1488(4)	3992(2)	33(1)
C(9)	-812(3)	-956(4)	3584(2)	31(1)
C(10)	-871(2)	-1089(3)	2488(2)	26(1)
C(11)	996(3)	432(4)	345(2)	41(1)
C(12)	404(4)	-1345(5)	5091(2)	47(1)
C(13)	-170(2)	1625(3)	2181(2)	26(1)
C(14)	528(3)	4218(3)	2344(2)	32(1)
O(1A)	7415(2)	5712(3)	3059(2)	41(1)
O(2A)	6060(2)	2432(2)	3242(1)	29(1)
O(3A)	3147(2)	6109(3)	2263(2)	39(1)
O(4A)	4894(2)	6955(2)	2735(1)	26(1)
C(1A)	6579(3)	5082(3)	3388(2)	29(1)
C(2A)	6286(3)	5190(4)	4448(2)	39(1)
C(3A)	4997(3)	5323(4)	4629(2)	39(1)
C(4A)	4250(3)	4150(3)	4057(2)	30(1)
C(5A)	4500(2)	4220(3)	2954(2)	23(1)
C(6A)	3820(3)	2932(3)	2405(2)	32(1)
C(7A)	4110(3)	2909(4)	1332(2)	41(1)
C(8A)	5394(3)	2705(4)	1167(2)	40(1)
C(9A)	6101(3)	3927(4)	1732(2)	30(1)
C(10A)	5812(2)	3938(3)	2802(2)	24(1)
C(11A)	2973(3)	4362(5)	4294(3)	49(1)
C(12A)	5679(5)	2810(5)	91(2)	60(1)
C(13A)	4095(2)	5831(3)	2594(2)	23(1)
C(14A)	4519(3)	8557(3)	2558(2)	29(1)

Atomic displacement parameters (Å2)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}

O(1)	28(1)	41(1)	70(2)	-20(1)	8(1)	2(1)
O(2)	32(1)	19(1)	42(1)	-7(1)	12(1)	-2(1)
O(3)	30(1)	23(1)	72(2)	-9(1)	-9(1)	7(1)
O(4)	33(1)	18(1)	37(1)	-1(1)	-5(1)	-1(1)
C(1)	23(2)	27(2)	55(2)	-15(1)	2(1)	1(1)
C(2)	32(2)	48(2)	53(2)	-22(2)	-14(1)	6(2)
C(3)	42(2)	44(2)	40(2)	-9(2)	-14(1)	7(2)
C(4)	34(2)	27(1)	27(1)	-2(1)	-4(1)	1(1)
C(5)	24(1)	18(1)	28(1)	-3(1)	-1(1)	2(1)
C(6)	24(1)	22(1)	25(1)	2(1)	2(1)	4(1)
C(7)	30(2)	30(1)	26(1)	2(1)	-3(1)	2(1)
C(8)	46(2)	26(2)	27(1)	0(1)	6(1)	-1(1)
C(9)	34(2)	26(1)	34(1)	-7(1)	13(1)	-5(1)
C(10)	25(1)	20(1)	34(1)	-9(1)	5(1)	2(1)
C(11)	50(2)	45(2)	27(1)	4(1)	-1(1)	-7(2)
C(12)	68(2)	44(2)	28(1)	5(1)	10(2)	-5(2)
C(13)	28(1)	21(1)	30(1)	-2(1)	-7(1)	2(1)
C(14)	41(2)	18(1)	36(1)	-1(1)	-6(1)	0(1)
O(1A)	30(1)	30(1)	64(1)	6(1)	0(1)	-2(1)
O(2A)	38(1)	20(1)	31(1)	4(1)	1(1)	8(1)
O(3A)	31(1)	25(1)	60(1)	5(1)	-13(1)	1(1)
O(4A)	26(1)	15(1)	37(1)	3(1)	-2(1)	2(1)
C(1A)	30(2)	20(1)	37(1)	2(1)	-5(1)	4(1)
C(2A)	44(2)	38(2)	33(2)	-7(1)	-14(1)	3(1)
C(3A)	55(2)	36(2)	24(1)	-3(1)	1(1)	7(2)
C(4A)	40(2)	26(2)	26(1)	7(1)	8(1)	4(1)
C(5A)	27(1)	17(1)	26(1)	2(1)	2(1)	0(1)
C(6A)	33(2)	18(1)	44(2)	0(1)	-4(1)	-1(1)
C(7A)	57(2)	26(2)	39(2)	-10(1)	-20(2)	3(1)
C(8A)	65(2)	29(2)	24(1)	-3(1)	-1(1)	11(2)
C(9A)	37(2)	27(1)	26(1)	3(1)	5(1)	9(1)
C(10A)	31(2)	17(1)	24(1)	4(1)	0(1)	5(1)
C(11A)	48(2)	50(2)	50(2)	12(2)	20(2)	3(2)
C(12A)	104(4)	48(2)	26(2)	-8(2)	1(2)	17(2)
C(13A)	26(1)	18(1)	26(1)	1(1)	3(1)	0(1)
C(14A)	29(1)	15(1)	42(2)	5(1)	-2(1)	2(1)

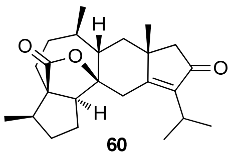
Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å2x 10^3)

	x	y	z	U(eq)
H(2)	-1213	-3271	2445	46
H(2A)	-2890	-179	769	53
H(2B)	-2226	-1837	785	53
H(3A)	-1236	1203	479	50
H(3B)	-1179	-289	-225	50
H(4)	147	-1566	792	36
H(6A)	1455	-1704	2228	28
H(6B)	1889	88	2176	28
H(7A)	1275	579	3739	34
H(7B)	2090	-951	3764	34
H(8)	472	-2625	3821	40
H(9A)	-1430	-1614	3864	37

H(9B)	-952	155	3773	37
H(11A)	914	192	-343	61
H(11B)	1755	67	583	61
H(11C)	933	1576	443	61
H(12A)	335	-231	5274	70
H(12B)	1141	-1767	5340	70
H(12C)	-238	-1946	5363	70
H(14A)	14	4562	1815	47
H(14B)	1256	4813	2322	47
H(14C)	153	4412	2960	47
H(2AA)	6621	2007	2966	44
H(2AB)	6683	6123	4730	46
H(2AC)	6591	4240	4782	46
H(3AA)	4741	6409	4465	46
H(3AB)	4865	5160	5324	46
H(4A)	4477	3070	4283	37
H(6AA)	4005	1888	2691	38
H(6AB)	2980	3119	2476	38
H(7AA)	3683	2032	1013	49
H(7AB)	3846	3910	1031	49
H(8A)	5625	1632	1403	47
H(9AA)	5949	4988	1458	36
H(9AB)	6936	3696	1662	36
H(11D)	2881	4331	4994	73
H(11E)	2519	3508	3995	73
H(11F)	2700	5382	4045	73
H(12D)	5219	2030	-270	89
H(12E)	6505	2596	5	89
H(12F)	5496	3873	-148	89
H(14D)	4210	8646	1899	43
H(14E)	5178	9277	2643	43
H(14F)	3914	8838	3014	43

*Hydrogen bonds for compound (+)-**44**[Å and °].*

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(1A)#1	0.84	2.01	2.838(3)	170.1
O(2A)-H(2AA)...O(1)#2	0.84	2.14	2.817(3)	137.0



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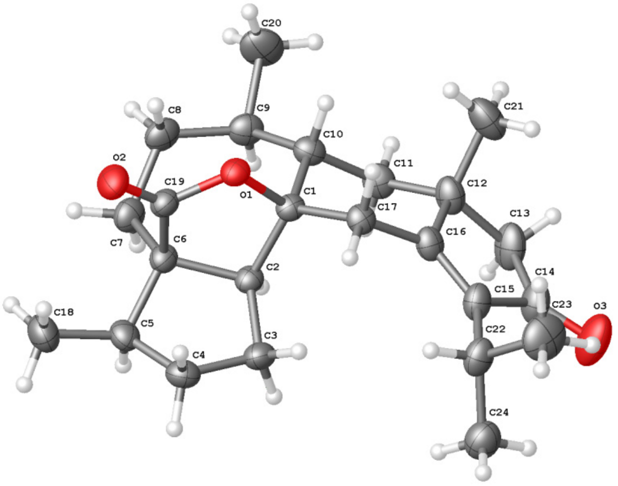


ORTEP of (–)-**60**

*Crystal data and structure refinement for compound (–)-**60***

Identification code	cu_dm17282_0m	
Empirical formula	C24 H34 O3	
Formula weight	370.51	
Temperature	296 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 6.6500(2) Å	a= 90°.
	b = 11.1580(3) Å	b= 101.781(2)°.
	c = 14.5580(4) Å	g = 90°.
Volume	1057.46(5) Å^3	
Z	2	
Density (calculated)	1.164 Mg/m^3	
Absorption coefficient	0.585 mm^{-1}	
F(000)	404	
Crystal size	0.15 x 0.08 x 0.02 mm^3	
Theta range for data collection	3.101 to 69.615°.	
Index ranges	-7<=h<=6, -13<=k<=13, -17<=l<=17	
Reflections collected	8052	
Independent reflections	3544 [R(int) = 0.0421]	
Completeness to theta = 67.679°	95.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7532 and 0.5187	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3544 / 1 / 249	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0438, wR2 = 0.1191	
R indices (all data)	R1 = 0.0472, wR2 = 0.1225	

Absolute structure parameter	0.24(17)
Extinction coefficient	n/a
Largest diff. peak and hole	0.116 and -0.187 e.$Å^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å2)

	x	y	z	U(eq)
O(1)	4233(3)	5964(2)	5987(1)	46(1)
O(2)	4101(3)	6651(2)	4544(1)	67(1)
O(3)	9450(6)	2942(3)	10098(2)	112(1)
C(1)	5682(4)	5886(2)	6893(2)	42(1)
C(2)	7772(4)	6236(2)	6669(2)	44(1)
C(3)	9174(5)	5246(3)	6399(2)	57(1)
C(4)	9203(5)	5432(3)	5373(2)	58(1)
C(5)	8832(4)	6771(3)	5217(2)	56(1)
C(6)	7149(4)	7025(2)	5780(2)	47(1)
C(7)	6827(5)	8347(3)	5973(2)	59(1)
C(8)	4993(5)	8605(3)	6437(2)	62(1)
C(9)	5133(5)	8128(3)	7427(2)	59(1)
C(10)	5012(4)	6756(2)	7595(2)	50(1)
C(11)	6260(5)	6488(3)	8591(2)	58(1)
C(12)	6089(6)	5209(3)	8923(2)	62(1)
C(13)	7791(7)	4864(3)	9775(2)	80(1)
C(14)	8498(7)	3641(3)	9537(2)	76(1)
C(15)	7798(5)	3462(2)	8511(2)	58(1)
C(16)	6509(5)	4344(2)	8180(2)	51(1)
C(17)	5413(4)	4584(2)	7197(2)	45(1)
C(18)	8424(6)	7160(4)	4192(2)	78(1)
C(19)	5061(4)	6534(2)	5332(2)	48(1)
C(20)	3415(8)	8729(4)	7834(3)	91(1)
C(21)	3942(7)	4979(4)	9142(3)	86(1)
C(22)	8424(6)	2398(3)	8003(2)	64(1)
C(23)	7348(9)	1268(4)	8245(4)	102(1)
C(24)	10741(7)	2228(4)	8178(3)	81(1)

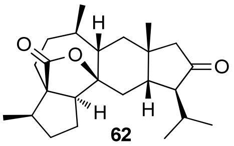
Atomic displacement parameters (Å2)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	38(1)	47(1)	52(1)	2(1)	4(1)	-4(1)
O(2)	57(1)	85(2)	53(1)	12(1)	-1(1)	0(1)
O(3)	162(3)	105(3)	59(2)	15(2)	-2(2)	34(2)
C(1)	39(1)	38(1)	48(1)	-3(1)	5(1)	-3(1)
C(2)	38(1)	43(1)	48(1)	1(1)	4(1)	-3(1)
C(3)	46(2)	58(2)	68(2)	8(1)	13(1)	9(1)
C(4)	46(2)	62(2)	67(2)	-3(1)	15(1)	1(1)
C(5)	48(2)	62(2)	58(2)	5(1)	13(1)	-8(1)
C(6)	43(1)	44(1)	52(1)	6(1)	7(1)	-3(1)
C(7)	64(2)	43(2)	68(2)	6(1)	10(1)	-3(1)
C(8)	66(2)	41(1)	77(2)	0(1)	9(1)	6(1)
C(9)	62(2)	43(1)	72(2)	-9(1)	15(1)	2(1)

C(10)	50(2)	45(1)	58(1)	-7(1)	15(1)	-3(1)
C(11)	73(2)	50(1)	51(1)	-12(1)	16(1)	-4(1)
C(12)	86(2)	55(2)	47(1)	-3(1)	20(1)	-7(1)
C(13)	126(3)	69(2)	40(1)	-4(1)	10(2)	-6(2)
C(14)	104(3)	71(2)	49(2)	12(1)	9(2)	3(2)
C(15)	76(2)	46(2)	49(1)	5(1)	8(1)	-5(1)
C(16)	65(2)	41(1)	48(1)	-1(1)	15(1)	-10(1)
C(17)	49(2)	38(1)	49(1)	-4(1)	10(1)	-8(1)
C(18)	79(3)	92(3)	68(2)	16(2)	27(2)	-5(2)
C(19)	44(2)	48(1)	50(1)	5(1)	4(1)	3(1)
C(20)	111(3)	57(2)	116(3)	-15(2)	49(3)	18(2)
C(21)	110(3)	80(2)	84(2)	-9(2)	55(2)	-16(2)
C(22)	85(2)	46(2)	58(2)	4(1)	7(1)	3(1)
C(23)	118(4)	54(2)	131(4)	-2(2)	19(3)	-14(2)
C(24)	91(3)	72(2)	80(2)	6(2)	16(2)	11(2)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å2x 10^3)

	x	y	z	U(eq)
H(2)	8550	6719	7183	53
H(3A)	10551	5312	6777	69
H(3B)	8635	4459	6497	69
H(4A)	8129	4969	4977	70
H(4B)	10520	5201	5238	70
H(5)	10079	7185	5537	67
H(7A)	6631	8782	5384	71
H(7B)	8063	8654	6376	71
H(8A)	4806	9467	6450	74
H(8B)	3770	8272	6040	74
H(9)	6444	8406	7802	71
H(10)	3573	6572	7602	60
H(11A)	7696	6662	8604	69
H(11B)	5806	7027	9030	69
H(13A)	8913	5435	9858	95
H(13B)	7250	4836	10345	95
H(17A)	3961	4420	7142	54
H(17B)	5930	4045	6776	54
H(18A)	7292	6710	3842	117
H(18B)	9626	7016	3938	117
H(18C)	8098	7999	4149	117
H(20A)	2107	8557	7438	136
H(20B)	3629	9580	7864	136
H(20C)	3442	8424	8453	136
H(21A)	2908	5107	8586	129
H(21B)	3719	5519	9625	129
H(21C)	3865	4168	9352	129
H(22)	7949	2543	7330	77
H(23A)	7814	1084	8898	153
H(23B)	7663	612	7873	153
H(23C)	5890	1398	8117	153
H(24A)	11363	2928	7972	121
H(24B)	11055	1541	7836	121
H(24C)	11265	2109	8837	121



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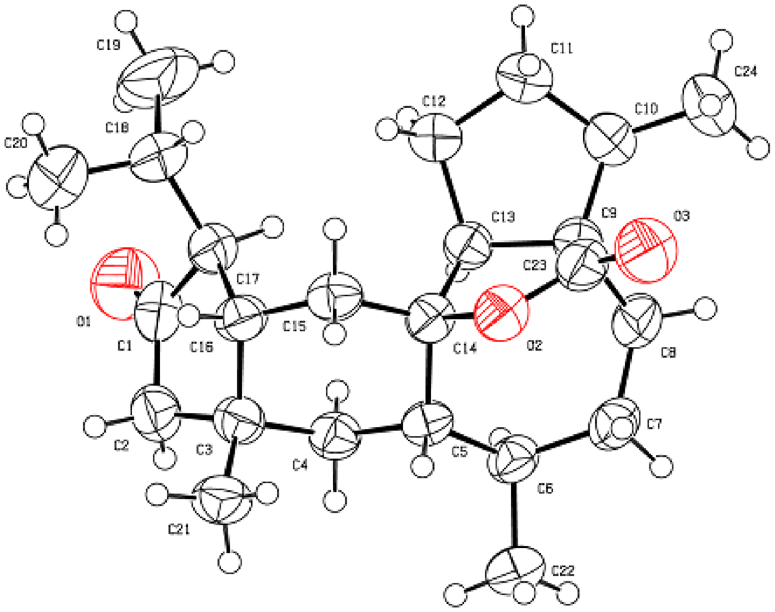


ORTEP of (–)-**62**

Crystal data and structure refinement for compound (–)-*62*

Identification code	cu_d8v17002_0m
Empirical formula	C24 H36 O3
Formula weight	372.53
Temperature	293.15 K
Wavelength	1.54184 Å
Crystal system	Orthorhombic
Space group	P212121
Unit cell dimensions	a = 8.9194(8) Å = 90°.
	b = 12.8315(12) Å = 90°.
	c = 18.5057(18) Å = 90°.
Volume	2118.0(3) Å3
Z	4
Density (calculated)	1.168 Mg/m3
Absorption coefficient	0.584 mm-1
F(000)	816
Crystal size	0.3 x 0.18 x 0.15 mm3
Theta range for data collection	4.193 to 70.136°.
Index ranges	-10<=h<=10, -15<=k<=15, -22<=l<=22
Reflections collected	11725
Independent reflections	3872 [R(int) = 0.0398]
Completeness to theta = 67.684°	98.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7533 and 0.5138
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	3872 / 0 / 249

Goodness-of-fit on F2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0659, wR2 = 0.1672
R indices (all data)	R1 = 0.0724, wR2 = 0.1734
Absolute structure parameter	0.10(16)
Extinction coefficient	n/a
Largest diff. peak and hole	0.398 and -0.219 e.Å-3

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å2)

	x	y	z	U(eq)
O(1)	4825(6)	1796(3)	5188(2)	93(1)
O(2)	2749(3)	6688(2)	6089(2)	57(1)
O(3)	1046(5)	7571(3)	6715(2)	84(1)
C(1)	5114(5)	2721(4)	5222(3)	64(1)
C(2)	5650(5)	3380(4)	4612(2)	63(1)
C(3)	5223(5)	4495(3)	4815(2)	51(1)
C(4)	3565(5)	4695(3)	4636(2)	50(1)
C(5)	2881(4)	5695(3)	4955(2)	46(1)
C(6)	1313(5)	5841(3)	4603(2)	51(1)
C(7)	184(5)	6530(4)	4996(2)	61(1)
C(8)	-567(5)	6029(4)	5647(2)	65(1)
C(9)	488(5)	5802(3)	6287(2)	53(1)
C(10)	-346(5)	5387(4)	6957(2)	67(1)
C(11)	917(6)	4921(5)	7410(3)	74(1)
C(12)	1975(6)	4425(4)	6866(2)	63(1)
C(13)	1716(4)	4986(3)	6126(2)	48(1)
C(14)	2981(5)	5633(3)	5789(2)	46(1)
C(15)	4614(5)	5408(3)	6007(2)	52(1)
C(16)	5390(5)	4483(3)	5645(2)	52(1)
C(17)	4909(5)	3384(3)	5889(2)	55(1)
C(18)	5748(6)	3008(4)	6582(3)	72(1)
C(19)	4927(9)	2078(6)	6924(4)	132(3)
C(20)	7324(7)	2724(5)	6443(3)	91(2)
C(21)	6246(5)	5300(4)	4448(2)	67(1)
C(22)	1509(6)	6279(5)	3834(3)	77(2)
C(23)	1391(6)	6777(4)	6414(2)	59(1)
C(24)	-1378(8)	6147(6)	7362(4)	108(2)

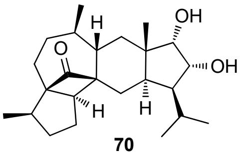
Atomic displacement parameters (Å2)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	120(3)	57(2)	103(3)	-9(2)	3(3)	4(2)
O(2)	69(2)	46(2)	56(2)	-10(1)	-7(1)	1(1)
O(3)	116(3)	65(2)	70(2)	-20(2)	1(2)	20(2)
C(1)	54(2)	63(3)	74(3)	-2(2)	-3(2)	13(2)
C(2)	60(2)	68(3)	60(2)	-7(2)	3(2)	11(2)
C(3)	51(2)	55(2)	48(2)	2(2)	3(2)	-2(2)
C(4)	56(2)	54(2)	40(2)	-4(2)	-4(2)	1(2)
C(5)	50(2)	48(2)	41(2)	2(2)	-6(2)	-3(2)
C(6)	58(2)	53(2)	42(2)	1(2)	-9(2)	6(2)
C(7)	72(3)	62(3)	49(2)	-1(2)	-12(2)	19(2)
C(8)	58(2)	83(3)	54(2)	2(2)	-9(2)	19(2)

C(9)	55(2)	62(2)	41(2)	-6(2)	-4(2)	10(2)
C(10)	60(3)	85(3)	55(2)	3(2)	7(2)	12(2)
C(11)	77(3)	92(4)	52(2)	9(3)	9(2)	19(3)
C(12)	67(3)	69(3)	53(2)	12(2)	9(2)	12(2)
C(13)	54(2)	49(2)	42(2)	-4(2)	-2(2)	4(2)
C(14)	54(2)	40(2)	45(2)	-6(2)	-5(2)	2(2)
C(15)	53(2)	57(2)	47(2)	3(2)	-6(2)	-9(2)
C(16)	51(2)	59(2)	47(2)	9(2)	-4(2)	-1(2)
C(17)	48(2)	59(2)	57(2)	8(2)	4(2)	3(2)
C(18)	78(3)	75(3)	63(3)	23(2)	4(2)	11(3)
C(19)	129(6)	132(6)	136(6)	91(5)	16(5)	3(5)
C(20)	85(4)	102(4)	85(4)	11(4)	-9(3)	22(3)
C(21)	60(2)	82(3)	58(2)	18(2)	6(2)	-7(2)
C(22)	80(3)	100(4)	50(2)	17(3)	-4(2)	20(3)
C(23)	75(3)	58(3)	45(2)	-7(2)	-8(2)	16(2)
C(24)	101(5)	144(6)	78(4)	11(4)	29(3)	57(5)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å2x 10^3)

	x	y	z	U(eq)
H(2A)	5168	3176	4164	75
H(2B)	6727	3316	4554	75
H(4A)	2984	4105	4807	60
H(4B)	3459	4721	4115	60
H(5)	3510	6280	4799	56
H(6)	862	5148	4556	62
H(7A)	692	7158	5154	73
H(7B)	-588	6737	4656	73
H(8A)	-1026	5380	5495	78
H(8B)	-1363	6486	5813	78
H(10)	-973	4806	6794	80
H(11A)	1426	5459	7684	89
H(11B)	529	4402	7742	89
H(12A)	1766	3686	6821	75
H(12B)	3007	4510	7021	75
H(13)	1342	4483	5770	58
H(15A)	5201	6028	5907	63
H(15B)	4639	5297	6525	63
H(16)	6463	4547	5750	63
H(17)	3835	3407	6000	65
H(18)	5741	3582	6931	86
H(19A)	4910	1508	6589	198
H(19B)	3918	2277	7041	198
H(19C)	5440	1870	7357	198
H(20A)	7854	2676	6893	136
H(20B)	7784	3247	6145	136
H(20C)	7362	2063	6200	136
H(21A)	7273	5091	4503	100
H(21B)	6100	5969	4668	100
H(21C)	6003	5340	3943	100
H(22A)	543	6359	3611	115
H(22B)	2106	5807	3553	115
H(22C)	1999	6944	3858	115
H(24A)	-1854	5791	7756	162
H(24B)	-2128	6407	7037	162
H(24C)	-796	6718	7545	162



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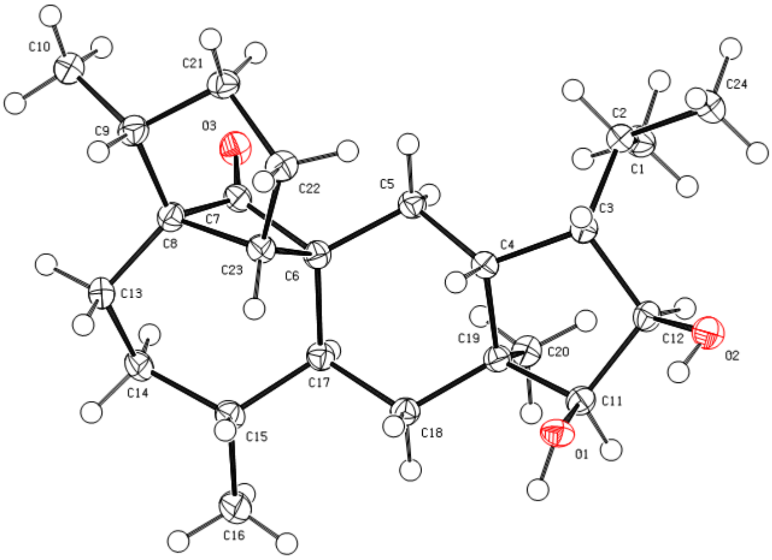

ORTEP of (–)-**70**

*Crystal data and structure refinement for compound (–)-**70***

Identification code	cu_cxy0173_0m
Empirical formula	$C_{24}H_{38}O_3$
Formula weight	374.54
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.4921(16)
b/Å	9.3712(19)
c/Å	33.896(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2062.2(8)
Z	4
ρ_{calc}g/cm^3	1.206
μ/mm^{-1}	0.600
F(000)	824.0
Crystal size/mm^3	0.41 × 0.36 × 0.35
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.214 to 136.42
Index ranges	$-7 \leq h \leq 7$, $-10 \leq k \leq 11$, $-40 \leq l \leq 40$
Reflections collected	20427

Independent reflections	3772 [R_{int} = 0.0278, R_{sigma} = 0.0203]
Data/restraints/parameters	3772/0/250
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0280, wR_2 = 0.0739
Final R indexes [all data]	R_1 = 0.0287, wR_2 = 0.0743
Largest diff. peak/hole / e Å^{-3}	0.23/-0.15
Flack parameter	0.07(5)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å2)

	x	*y*	*z*	U(eq)
O1	608.0(18)	10364.1(13)	2713.0(3)	20.2(3)
O2	-1504(2)	12507.7(13)	2448.5(3)	23.2(3)
O3	-3151.5(19)	9568.5(13)	4668.1(3)	21.4(3)
C1	-6301(3)	12573(2)	3298.7(5)	22.4(4)
C2	-4194(3)	13296.3(18)	3296.3(5)	18.5(3)
C3	-2358(3)	12361.0(17)	3167.5(4)	16.5(3)
C4	-1709(3)	11079.5(17)	3433.2(5)	15.7(3)
C5	-2386(3)	10913.7(18)	3860.6(5)	17.0(3)
C6	-1040(2)	9757.0(17)	4054.6(5)	16.7(3)
C7	-1536(3)	9545.8(17)	4491.1(5)	16.8(3)
C8	749(3)	9522.5(18)	4611.7(5)	17.9(3)
C9	1395(3)	10641.4(18)	4916.3(5)	20.2(4)
C10	446(3)	10477(2)	5325.4(5)	24.0(4)
C11	-1558(3)	10180.3(18)	2777.2(5)	17.8(3)
C12	-2520(3)	11690.4(18)	2749.2(5)	18.2(3)
C13	1496(3)	8004.3(18)	4678.5(5)	19.8(4)
C14	387(3)	6893.2(18)	4423.4(5)	20.9(4)
C15	456(3)	7151.6(17)	3975.8(5)	19.6(4)
C16	63(3)	5714(2)	3770.6(5)	29.3(4)
C17	-1072(3)	8308.9(17)	3822.6(5)	16.7(3)
C18	-716(3)	8540.2(17)	3375.3(5)	18.1(3)
C19	-2101(3)	9697.2(17)	3198.3(4)	16.6(3)
C20	-4350(3)	9169.8(18)	3190.0(5)	19.5(3)
C21	867(3)	12035.7(18)	4701.5(5)	20.4(4)
C22	1638(3)	11773.5(18)	4278.1(5)	20.2(4)
C23	1189(2)	10183.1(17)	4192.7(5)	17.3(4)
C24	-4285(3)	14642.7(19)	3037.5(5)	23.4(4)

Atomic displacement parameters (Å2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	19.9(6)	18.3(6)	22.4(6)	-1.4(5)	4.9(5)	0.9(5)
O2	29.1(7)	20.6(6)	19.9(6)	4.8(5)	6.8(5)	1.1(5)
O3	19.0(6)	23.9(6)	21.2(6)	3.6(5)	3.1(5)	-0.3(5)

C1	19.5(8)	23.4(9)	24.4(8)	0.0(7)	1.1(7)	3.3(7)
C2	21.0(8)	17.9(8)	16.5(7)	-0.5(6)	-0.6(7)	1.5(7)
C3	17.1(8)	16.4(8)	15.9(7)	0.5(6)	-0.7(6)	-1.8(6)
C4	14.8(7)	15.4(8)	16.9(8)	0.1(6)	0.0(6)	-0.2(6)
C5	18.0(8)	16.1(8)	17.0(8)	0.7(6)	0.7(6)	0.7(7)
C6	17.4(8)	16.2(8)	16.4(8)	0.8(6)	0.5(6)	-0.6(6)
C7	19.6(8)	12.6(8)	18.3(8)	1.6(6)	0.0(6)	-0.6(6)
C8	17.7(8)	19.6(8)	16.3(8)	0.4(6)	0.2(6)	0.1(7)
C9	18.3(8)	22.9(9)	19.6(8)	-1.9(7)	-1.6(6)	0.2(7)
C10	26.6(9)	25.9(9)	19.5(8)	-1.0(7)	-1.6(7)	4.9(8)
C11	18.1(8)	18.2(8)	17.3(8)	-0.6(6)	0.3(6)	-1.2(6)
C12	19.8(8)	18.9(8)	15.9(8)	2.3(6)	1.2(6)	-0.7(7)
C13	21.1(8)	20.6(8)	17.5(8)	2.4(6)	-2.3(7)	2.4(7)
C14	25.3(9)	15.2(8)	22.2(8)	2.8(6)	-1.7(7)	1.9(7)
C15	21.3(8)	16.3(8)	21.3(8)	0.1(6)	-0.9(7)	1.3(7)
C16	43.8(12)	17.4(9)	26.6(9)	-0.8(7)	-6.9(8)	4.4(8)
C17	17.6(8)	14.9(8)	17.6(8)	0.8(6)	-0.3(6)	-1.2(6)
C18	20.5(8)	16.4(8)	17.5(8)	-0.5(6)	0.9(7)	-0.5(7)
C19	18.6(8)	15.8(8)	15.5(7)	-0.6(6)	0.2(6)	-0.3(6)
C20	20.8(8)	18.7(8)	18.9(8)	0.7(6)	-0.8(7)	-3.7(7)
C21	21.2(8)	19.2(8)	20.9(8)	-3.5(6)	-0.8(7)	-0.9(7)
C22	21.3(8)	18.3(8)	20.8(8)	-0.4(6)	1.2(7)	-4.0(7)
C23	16.4(8)	17.5(8)	18.0(8)	0.5(6)	1.3(6)	0.0(6)
C24	23.8(9)	20.0(8)	26.5(9)	2.7(7)	-0.8(7)	3.5(8)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å2x 10^3)

Atom	*x*	*y*	*z*	U(eq)
H1	1085	9540	2645	30
H2	-350	12110	2431	35
H1A	-7320	13232	3393	34
H1B	-6259	11754	3469	34
H1C	-6648	12277	3036	34
H2A	-3917	13611	3567	22
H3	-1163	12999	3159	20
H4	-204	11150	3448	19
H5A	-3825	10638	3872	20
H5B	-2226	11812	4000	20
H9	2896	10594	4945	24
H10A	-1028	10511	5305	36
H10B	914	11239	5492	36
H10C	855	9579	5436	36
H11	-2157	9537	2580	21
H12	-3979	11596	2680	22
H13A	1302	7761	4954	24
H13B	2960	7961	4623	24
H14A	-1044	6855	4505	25
H14B	988	5966	4477	25
H15	1853	7460	3908	24

H16A	990	5010	3874	44
H16B	287	5816	3492	44
H16C	-1332	5420	3817	44
H17	-2462	7913	3852	20
H18A	713	8801	3333	22
H18B	-965	7649	3238	22
H20A	-4429	8297	3042	29
H20B	-5204	9879	3068	29
H20C	-4816	9005	3455	29
H21A	1571	12841	4821	25
H21B	-605	12212	4705	25
H22A	3102	11968	4258	24
H22B	912	12380	4093	24
H23	2290	9698	4047	21
H24A	-4518	14374	2768	35
H24B	-3004	15150	3057	35
H24C	-5388	15245	3126	35