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Construction of the Tricyclic Core of Rhamnofolane-type Diterpenoids

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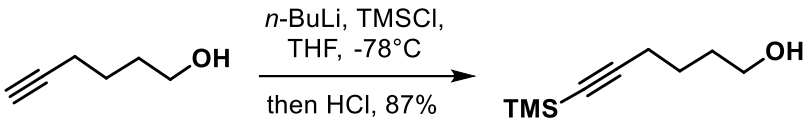
1. General Information

All reactions were performed under an argon atmosphere with dry solvents under anhydrous conditions unless otherwise stated. Dichloromethane (DCM), benzene and 1,4-dioxane were distilled from calcium hydride under argon; tetrahydrofuran (THF) was sequentially distilled from sodium and then from $LiAlH_4$ under argon. Unless otherwise noted, all the other chemicals were obtained from commercial sources and used without further purification. Reactions requiring anhydrous conditions were run under a dry atmosphere of argon; glassware was either flame dried immediately prior to use after placing in an oven (120 °C) for at least 2 h and allowed to cool under an atmosphere of argon; liquid reagents, solutions or solvents were added via syringe through a rubber septum. Column chromatography was performed using silica gel (200-300 mesh). Thin layer chromatography (TLC) was used for monitoring reactions and visualized by a UV lamp (254 nm and 365 nm), I_2 and developing the plates with p-anisaldehyde. ^1H and ^{13}C NMR were recorded on Bruker DRX-400 MHz NMR spectrometer with TMS as the internal standard and were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: ^1H NMR = 7.26 ppm, ^{13}C NMR = 77.16 ppm; Pyridine-d_5: ^1H NMR = 8.74 ppm, ^{13}C NMR = 150.35 ppm). Abbreviations in ^1H NMR data are illustrated as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dt = doublet of triplet, td = triplet of doublet, tdd = triplet of doublet of doublet, m = multiplet, br = broad. Coupling constants (J) are reported in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on Bruker-FT-MS spectrometers (ESI-TOF). Infrared (IR) spectra were recorded on a NEXUS 670 FT-IR device and are reported in wavenumbers (cm^{-1}). Only the strongest and/or structurally important absorption of infrared (IR) spectra are reported.

The LEDs used in this work (emitting at 395 nm, 430 nm, 450 nm, 470 nm, and 495 nm) were supplied by Shenzhen Fengsheng Jingguang Technology Co., Ltd., with the LED chips sourced from Taiwan Lextar Electronics Corporation. Each LED had a power of 20 W.

2. Experimental Procedure

Procedure for preparation of alcohol 16



15 **16**

According to an optimized procedure based on the literature[1], to a 150 mL round-bottom flask were added alcohol **15** (1.0 g, 10 mmol, 1.0 equiv.) and THF (30 mL). The reaction mixture was cooled to –78 °C, and a solution of *n*-BuLi (2.5 M in hexane, 8.6 mL, 21 mmol, 2.1 equiv.) was added dropwise to the reaction mixture. After stirring for 30 min, TMSCl (3.2 mL, 25 mmol, 2.5 equiv.) was added. The reaction was stirred for an additional 1 h, then quenched with 10 mL of 1 M HCl and diluted with 30 mL of water. The mixture was extracted with ethyl acetate (3 × 50 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography (eluent: ethyl acetate / petroleum ether = 1:4) afforded alcohol **16** as a colorless liquid (1.50 g, 87% yield).

TLC: R_f = 0.5 (ethyl acetate / petroleum ether = 1:3; *p*-anisaldehyde).

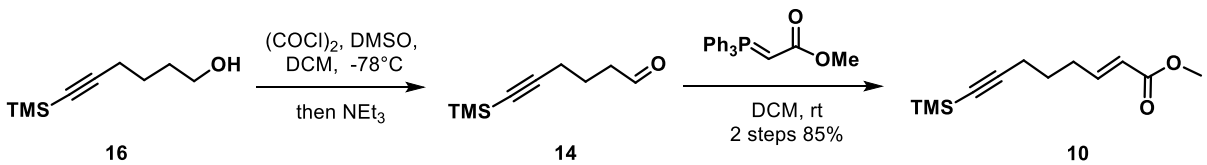
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (t, *J* = 6.2 Hz, 2H), 2.27 (t, *J* = 6.7 Hz, 2H), 1.74 – 1.54 (m, 4H), 0.14 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 107.30, 84.95, 62.55, 31.94, 25.01, 19.75, 0.28.

HRMS (ESI-TOF) m/z calcd for $[M - H]^-$: 169.1054, found 169.1061.

IR (thin film): 3744, 2954, 2903, 2362, 2335, 2174, 1436, 1268, 844 cm^{-1}

Procedure for preparation of α, β-unsaturated ester 10



16 **14** **10**

Step 1. Oxidation to aldehyde.

To a 500 mL round-bottom flask were added dichloromethane (130 mL) and the mixture was cooled to –78 °C. Oxalyl chloride (6.8 mL, 80 mmol, 2.0 equiv.) was added, followed by dropwise addition of DMSO (11.5 mL, 161 mmol, 4.0 equiv.) at the same temperature. After stirring for 30 min, a solution of alcohol **16** (6.87 g, 40.3 mmol, 1.0 equiv.) in DCM (20 mL) was added dropwise to the reaction mixture. The reaction mixture was stirred at –78 °C for an additional 30 min, then triethylamine (33.6 mL, 242 mmol, 6.0 equiv.) was added, resulting in the formation of a white pasty precipitate. The mixture was allowed to warm to room temperature and stirred vigorously for 15 min. The reaction was quenched with water (200 mL) and extracted with DCM (3 × 100 mL). The combined organic layers were washed successively with 1 M HCl (100 mL), saturated $NaHCO_3$ solution (100 mL), and saturated NaCl solution (100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude aldehyde **14** as a colorless liquid, which was used directly in the next step without further purification.

Step 2. Wittig reaction.

The crude aldehyde **14** was dissolved in DCM (120 mL) in a 1 L round-bottom flask. Methyl (triphenylphosphoranylidene)acetate (33.7 g, 101 mmol, 2.5 equiv.) was added, and the reaction mixture was stirred at room temperature for 2 h. The mixture was diluted with petroleum ether (500 mL), concentrated, and a large amount of white solid precipitated. Additional petroleum ether (500 mL) was added, and the mixture was filtered through a pad of Celite. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (eluent: ethyl acetate / petroleum ether = 1:15) to afford the desired α, β-unsaturated ester **10** as a colorless liquid (7.69 g, 85% yield over two steps).

TLC: R_f = 0.4 (ethyl acetate/petroleum ether = 1:10; *p*-anisaldehyde).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (dt, *J* = 14.7, 7.0 Hz, 1H), 5.90 – 5.82 (m, 1H), 3.73 (s, 3H), 2.32 (q, *J* = 7.3 Hz, 2H), 2.26 (t, *J* = 7.0 Hz, 2H), 1.64 – 1.71 (m, *J* = 7.2 Hz, 2H), 0.15 (s, 9H).

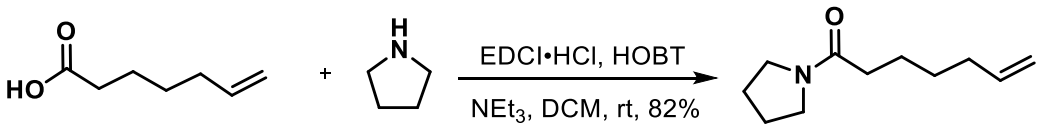
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.14, 148.54, 121.70, 106.38, 85.53, 51.58, 31.17, 26.95,

19.40, 0.24.

HRMS (ESI-TOF) m/z calcd for $[M + Na]^+$: 247.1125, found 247.1125.

IR (thin film): 2954, 2903, 2174, 1726, 1436, 1272, 1203, 1097, 842 cm^{-1}

Procedure for preparation of amide 11



12 **13** **11**

To a 2 L round-bottom flask were added acid **12** (50 g, 0.39 mol, 1.0 equiv.) and the mixture was cooled in an ice–water bath. Pyrrolidine **13** (48 mL, 0.59 mol, 1.5 equiv.), 1-hydroxybenzotriazole (HOBt, 79 g, 0.56 mol, 1.5 equiv.), and EDCI·HCl (112 g, 0.585 mol, 1.5 equiv.) were added successively under stirring. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. TLC analysis indicated complete consumption of the starting material. The reaction was quenched with 1 M HCl (1 L) and stirred vigorously for 10 min, during which a large amount of white precipitate formed. The mixture was filtered through a Celite pad, and the filtrate was extracted with DCM (3 × 300 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (3 × 500 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:3 → 1:1, gradient) afforded amide **11** as a colorless liquid (57.99 g, 82%).

TLC: R_f = 0.3 (ethyl acetate/petroleum ether = 1:1; *p*-anisaldehyde).

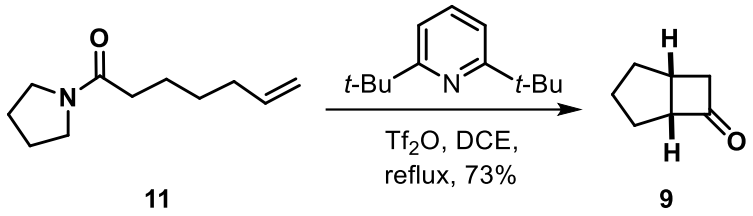
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.04 – 4.90 (m, 2H), 3.45 (t, *J* = 6.9 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.25 (t, *J* = 7.6 Hz, 2H), 2.07 (m, 2H), 1.98 – 1.90 (m, 2H), 1.88 – 1.80 (m, 2H), 1.72 – 1.60 (m, 2H), 1.43 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.78, 138.82, 114.64, 46.74, 45.72, 34.78, 33.73, 28.89, 26.26, 24.56, 24.55.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 182.1539, found 182.1534.

IR (thin film): 2972, 2937, 2872, 1641, 1548, 1432, 1268, 995 cm^{-1}

Procedure for preparation of cyclobutanone 9



According to an optimized procedure based on the literature[2], a 3 L three-neck round-bottom flask was charged with 2,6-di-*tert*-butyl-4-methylpyridine (57.7 g, 0.281 mol, 1.2 equiv.), amide **11**, and 1.2 L of 1,2-dichloroethane (DCE). A reflux condenser and a constant-pressure dropping funnel were attached. A solution of trifluoromethanesulfonic anhydride (Tf_2O, 43.3 mL, 0.258 mol, 1.1 equiv.) in DCE (350 mL) was placed in the dropping funnel and added dropwise to the reaction mixture at 95 °C over 12 h under reflux. After TLC monitoring indicated completion, the reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure.

To the residue were added tetrahydrofuran (1.0 L), water (1.0 L), and potassium carbonate (80 g, 0.59 mol, 2.5 equiv.). The mixture was heated at reflux (85 °C) for 3 h and then cooled to room temperature. The layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 500 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by distillation under reduced pressure (oil bath 110 °C, 4.21 kPa) to collect the fraction at 74 °C, affording cyclobutanone **9** as a colorless liquid (18.57 g, 73%).

TLC: R_f = 0.5 (ethyl acetate / petroleum ether = 1:10; 2,4-dinitrophenylhydrazine).

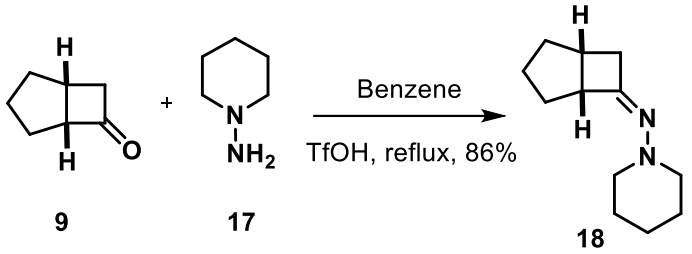
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.60 – 3.49 (m, 1H), 3.19 (ddd, *J* = 18.4, 9.3, 4.5 Hz, 1H), 2.94 – 2.83 (m, 1H), 2.49 (ddd, *J* = 18.4, 4.6, 3.4 Hz, 1H), 2.11 – 1.98 (m, 1H), 1.89 – 1.79 (m, 2H), 1.78 – 1.70 (m, 1H), 1.69 – 1.59 (m, 1H), 1.57 – 1.51 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 215.17, 64.97, 51.67, 32.90, 29.99, 29.06, 24.87.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 111.0804, found 111.0802.

IR (thin film): 2948, 2865, 1771, 1077, 756 cm^{-1}

Procedure for preparation of hydrazone 18



To a 250 mL round-bottom flask were added cyclobutanone **9** (6.50 g, 59.0 mmol, 1.0 equiv.), 1-Aminopiperidine **17** (9.6 mL, 89 mmol, 1.5 equiv.), benzene (100 mL), and trifluoroacetic acid (0.10 mL, 1.3 mmol, 0.022 equiv.). The mixture was heated at reflux under a Dean–Stark apparatus for 1 h to remove water, and then cooled to room temperature. The crude reaction mixture was directly subjected to column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:2) to afford hydrazone **18** as a colorless liquid (9.76 g, 86%). The product was obtained as an inseparable mixture of *Z/E* isomers in an approximate ratio of 1:3. The mixture of isomers was used directly in the next step without further purification.

TLC: R_f = 0.5 (ethyl acetate / petroleum ether = 1:1; *p*-anisaldehyde).

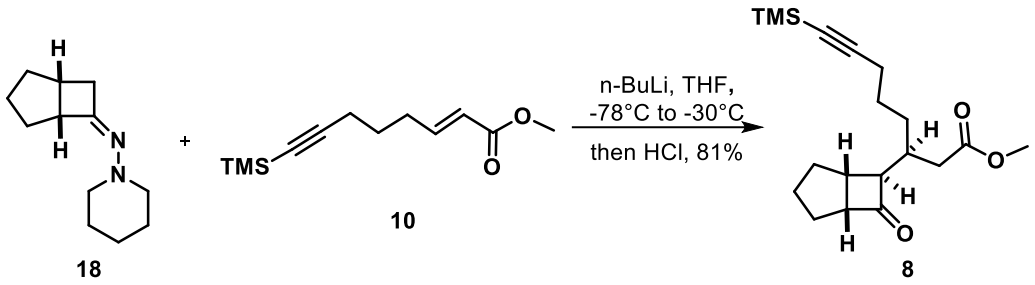
^{1}H NMR (400 MHz, Pyridine-d_5) δ 3.61 – 3.54 (m, 0.25H), 3.48 – 3.41 (m, 0.75H), 3.09 – 2.85 (m, 5H), 2.63 – 2.49 (m, 1H), 2.37 (dt, *J* = 17.3, 3.9 Hz, 0.75H), 2.28 (dt, *J* = 17.0, 4.1 Hz, 0.25H), 2.25 – 2.20 (m, 0.25H), 1.98 (dd, *J* = 12.5, 5.5 Hz, 0.75H), 1.77 – 1.51 (m, 7H), 1.49 – 1.31 (m, 4H).

^{13}C NMR (101 MHz, Pyridine-d_5) δ 160.34, 159.63, 56.56, 56.19, 53.88, 53.33, 40.48, 40.10, 33.73, 33.65, 33.47, 32.77, 32.64, 29.85, 26.15, 26.11, 25.51, 25.26, 24.83, 24.79.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 193.1699, found 193.1695.

IR (thin film): 2933, 2856, 2803, 1677, 1448, 1268, 756 cm^{-1}

Procedure for preparation of ester 8



To a 500 mL round-bottom flask were added hydrazone **18** (1.00 g, 5.20 mmol, 1.1 equiv.) and THF (35 mL). The mixture was cooled to 0 °C, and *n*-BuLi (2.5 M in hexane, 2.0 mL, 5.0 mmol, 1.05 equiv.) was added dropwise to the reaction mixture. The mixture was stirred for 1 h to give a yellow suspension. The reaction mixture was then cooled to –78 °C, and a solution of α, β-unsaturated ester **10** (1.06 g, 4.73 mmol, 1.0 equiv.) in THF (20 mL) was added. The mixture was allowed to warm to –30 °C over 2 h and maintained at –30 °C for an additional 1 h. The reaction was quenched by the addition of 10% aqueous HCl (160 mL), warmed to room temperature, and stirred for 1 h. The layers were separated, and the aqueous layer was extracted with ethyl acetate (3 × 150 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (500 mL) and saturated NaCl solution (500 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: ethyl acetate / petroleum ether = 1:10) afforded ester **8** as a colorless liquid (6.27 g, 81%).

TLC: R_f = 0.6 (ethyl acetate / petroleum ether = 1:5; *p*-anisaldehyde).

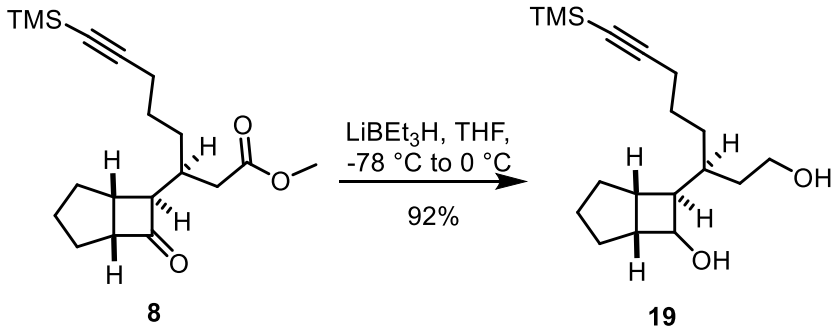
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3H), 3.39 (ddd, *J* = 10.2, 7.1, 3.0 Hz, 1H), 2.73 – 2.66 (m, 1H), 2.66 – 2.58 (m, 1H), 2.41 – 2.31 (m, 2H), 2.31 – 2.24 (m, 1H), 2.21 (t, *J* = 6.8 Hz, 2H), 2.06 – 1.94 (m, 1H), 1.85 (m, 2H), 1.79 – 1.65 (m, 2H), 1.62 – 1.50 (m, 3H), 1.49 – 1.35 (m, 2H), 0.14 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 216.18, 173.08, 107.09, 84.92, 67.22, 62.01, 51.75, 36.57, 35.34, 34.17, 33.06, 31.01, 29.46, 25.78, 25.29, 20.03, 0.27.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 335.2037, found 335.2038.

IR (thin film): 2953, 2173, 1769, 1739, 1256, 845, 756 cm^{-1}

Procedure for preparation of diol 19



To a 250 mL round-bottom flask were added ester **8** (1.00 g, 2.99 mmol, 1.0 equiv.) and THF (15 mL). The solution was cooled to –78 °C, and lithium triethylborohydride ($LiBEt_3H$, 1 M in THF, 17.9 mL, 17.9 mmol, 6.0 equiv.) was added dropwise to the reaction mixture. The mixture was stirred at –78 °C for 30 min, then gradually warmed to 0 °C and stirred for an additional 2 h. TLC analysis indicated complete conversion of the starting material. The reaction was carefully quenched with saturated NH_4Cl solution (100 mL) — **Caution: vigorous gas evolution observed** — and the layers were separated. The aqueous phase was extracted with ethyl acetate (3 × 100 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: ethyl acetate / petroleum ether = 1:3 → 1:2, gradient) afforded diol **19** as a colorless liquid (4.04 g, 92%).

TLC: R_f = 0.3 (ethyl acetate / petroleum ether = 1:2; *p*-anisaldehyde).

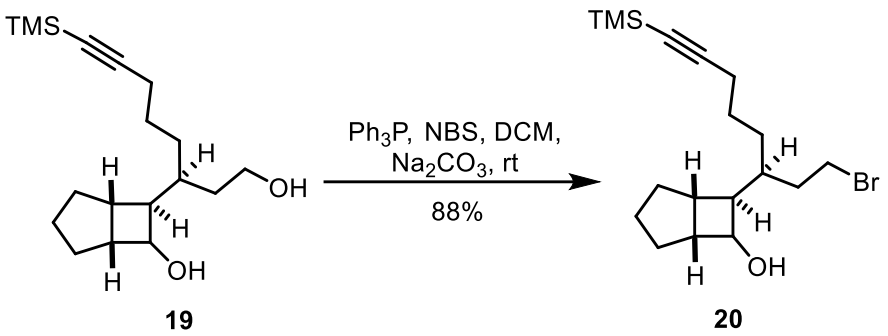
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 – 3.91 (m, 1H), 3.75 – 3.60 (m, 2H), 2.79 – 2.69 (m, 1H), 2.30 – 2.15 (m, 2H), 2.13 – 2.03 (m, 1H), 1.95 – 1.85 (m, 1H), 1.84 – 1.74 (m, 1H), 1.74 – 1.64 (m, 1H), 1.60 (m, 2H), 1.56 – 1.40 (m, 11H), 0.14 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 107.72, 84.85, 69.23, 61.10, 53.23, 41.17, 38.83, 37.76, 34.02, 33.00, 29.84, 26.52, 25.11, 24.47, 20.32, 0.29.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 309.2244, found 309.2241.

IR (thin film): 3335, 2942, 2862, 2172, 1251, 1048, 844, 758, 643 cm^{-1}

Procedure for preparation of bromide 20



To a 250 mL round-bottom flask were added diol **19** (2.90 g, 9.40 mmol, 1.0 equiv.), dichloromethane (100 mL), and Na_2CO_3 (19.9 g, 188 mmol, 20.0 equiv.). The reaction mixture was cooled to 0 °C, and triphenylphosphine (12.3 g, 47.0 mmol, 5.0 equiv.) and *N*-bromosuccinimide (8.36 g, 47.0 mmol, 5.0 equiv.) were added successively. The reaction was stirred at 0 °C for 3 h, after which TLC analysis indicated complete consumption of the starting material. The solvent was removed under reduced pressure, and the residue was diluted with petroleum ether (500 mL), resulting in the formation of a white precipitate. The precipitate was collected by filtration and washed with petroleum ether (2 × 500 mL). The combined filtrates were concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel (eluent: ethyl acetate /petroleum ether = 1:10) to afford bromide **20** as a colorless liquid (3.04 g, 88%).

TLC: R_f = 0.7 (ethyl acetate / petroleum ether = 1:2; *p*-anisaldehyde).

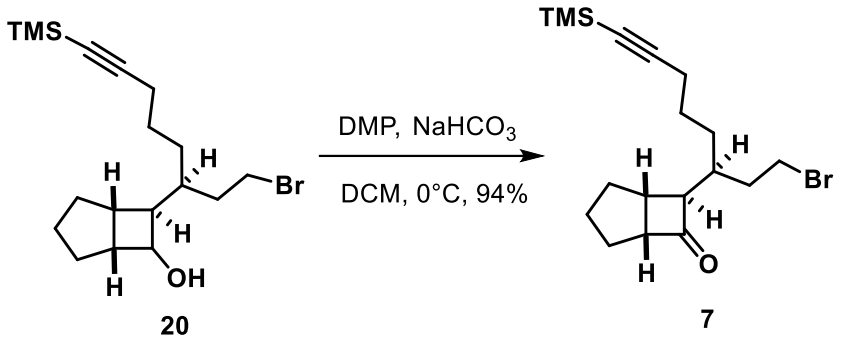
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (t, *J* = 7.3 Hz, 1H), 3.51 – 3.33 (m, 2H), 2.76 (q, *J* = 8.1 Hz, 1H), 2.23 (t, *J* = 6.1 Hz, 2H), 2.08 (q, *J* = 6.3 Hz, 1H), 1.95 – 1.84 (m, 2H), 1.83 – 1.72 (m, 2H), 1.71 – 1.58 (m, 2H), 1.58 – 1.40 (m, 9H), 0.15 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 107.51, 85.01, 69.24, 52.77, 41.31, 40.94, 37.78, 34.47, 32.98, 31.82, 29.02, 26.50, 24.70, 24.40, 20.29, 0.29.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 371.1400, found 371.1394.

IR (thin film): 2945, 2864, 2172, 1256, 845, 756 cm^{-1}

Procedure for preparation of silylalkyne 7



To a 500 mL round-bottom flask were added bromide **20** (1.82 g, 4.90 mmol, 1.0 equiv.) and dichloromethane (40 mL). The mixture was cooled to 0 °C, $NaHCO_3$ (1.23 g, 7.35 mmol, 1.5 equiv.) and Dess–Martin periodinane (3.12 g, 7.35 mmol, 1.5 equiv.) were added successively. The reaction mixture was stirred for 1 h, during which time TLC analysis indicated completion of the reaction. The mixture was then carefully quenched with saturated Na_2SO_3 solution (100 mL) — **caution: vigorous gas evolution observed**. The layers were separated, and the aqueous phase was extracted with DCM (3 × 100 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: ethyl acetate /petroleum ether = 1:20) afforded silylalkyne **7** as a colorless liquid (1.71 g, 94%).

TLC: R_f = 0.7 (ethyl acetate / petroleum ether = 1:5; *p*-anisaldehyde).

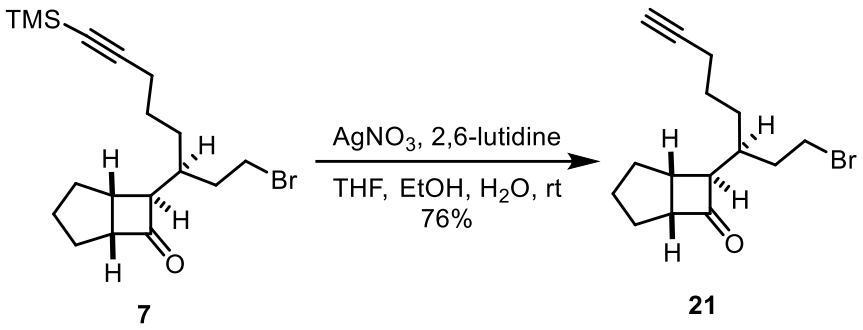
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.50 – 3.34 (m, 3H), 2.70 – 2.59 (m, 2H), 2.32 – 2.14 (m, 2H), 2.04 – 1.91 (m, 3H), 1.90 – 1.82 (m, 2H), 1.82 – 1.71 (m, 2H), 1.68 – 1.55 (m, 3H), 1.55 – 1.42 (m, 3H), 0.15 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 216.64, 107.07, 85.09, 66.93, 62.13, 36.93, 34.79, 34.26, 33.17, 31.18, 29.51, 29.49, 25.33, 25.27, 20.05, 0.28.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 369.1244, found 369.1242.

IR (thin film): 2951, 2866, 2173, 1767, 1450, 1250, 844, 760, 642 cm^{-1}

Procedure for preparation of alkyne 21



To a 25 mL round-bottom flask were added silylalkyne **7** (150 mg, 0.406 mmol, 1.0 equiv.), THF (1.5 mL), EtOH (1.5 mL), H_2O (1.5 mL), and 2,6-lutidine (0.15 mL). The mixture was cooled to 0 °C, and $AgNO_3$ was added. After 10 min, the reaction mixture was allowed to warm to room temperature and stirred for an additional 30 min, at which point TLC indicated complete conversion of the starting material. The reaction was quenched with saturated NaH_2PO_4 solution (15 mL), producing a yellow precipitate. The mixture was extracted with MTBE (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:30) afforded alkyne **21** as a colorless liquid (97 mg, 76%).

TLC: R_f = 0.3 (ethyl acetate / petroleum ether = 1:10; *p*-anisaldehyde).

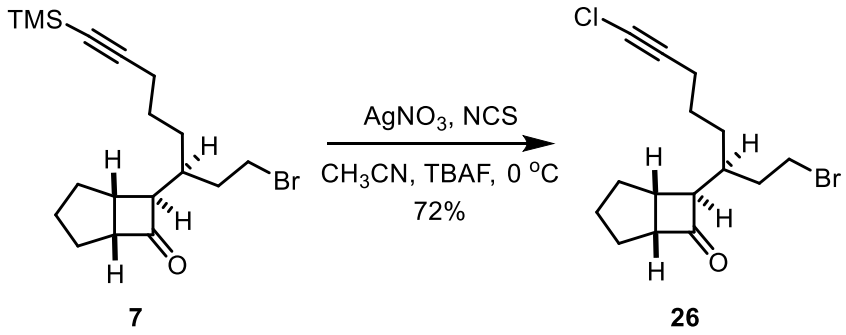
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.50 – 3.34 (m, 3H), 2.70 – 2.58 (m, 2H), 2.20 (m, 2H), 2.04 – 1.90 (m, 4H), 1.91 – 1.71 (m, 4H), 1.67 – 1.53 (m, 4H), 1.53 – 1.44 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 216.63, 84.21, 68.79, 66.96, 62.14, 37.01, 34.89, 34.27, 33.18, 31.23, 29.71, 29.51, 25.33, 25.31, 18.70.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$:297.0849, found 297.0848.

IR (thin film): 3295, 2942, 2865, 1765, 1453, 1267, 755, 642 cm^{-1}

Procedure for preparation of chloroalkyne 26



7 **26**

To a 50 mL round-bottom flask were added silylalkyne **7** (100 mg, 0.271 mmol, 1.0 equiv.) and MeCN (3 mL). The mixture was cooled to 0 °C, followed by the addition of $AgNO_3$ (14 mg, 0.081 mmol, 0.3 equiv.) and NCS (72 mg, 0.54 mmol, 2.0 equiv.). After 5 min, TBAF (1.0 M in THF, 0.3 mL, 0.3 mmol, 1.1 equiv.) was added. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. Upon completion (monitored by TLC), the reaction was quenched with water (20 mL) and extracted with petroleum ether (3 × 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: ethyl acetate /petroleum ether = 1:20) to afford the title chloroalkyne **26** as a colorless liquid (65 mg, 72% yield).

TLC: R_f = 0.3 (ethyl acetate / petroleum ether = 1:10; *p*-anisaldehyde).

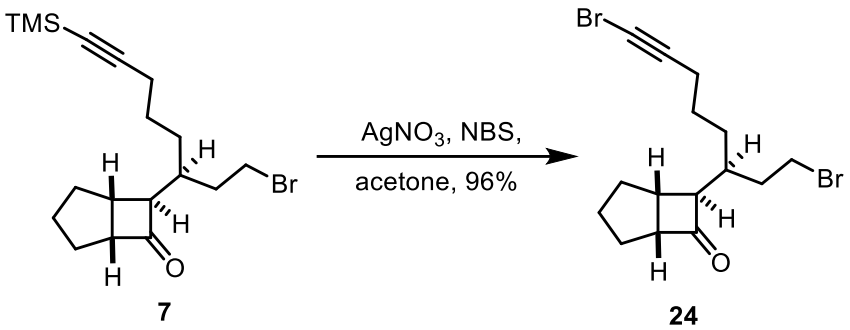
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 – 3.33 (m, 3H), 2.70 – 2.57 (m, 2H), 2.26 – 2.09 (m, 2H), 2.05 – 1.91 (m, 3H), 1.90 – 1.83 (m, 2H), 1.83 – 1.72 (m, 2H), 1.67 – 1.50 (m, 4H), 1.50 – 1.42 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 216.55, 69.29, 66.96, 62.15, 57.76, 37.01, 34.91, 34.30, 33.19, 31.20, 29.82, 29.52, 25.34, 25.27, 19.07.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$:331.0459, found 331.0462.

IR (thin film): 2942.33, 2864.82, 1765.69, 1452.04, 755.62 cm^{-1}

Procedure for preparation of bromoalkyne 24



7 **24**

To a 500 mL round-bottom flask were added silylalkyne **7** (1.22 g, 3.30 mmol, 1.0 equiv.), acetone (16 mL), and $AgNO_3$ (280 mg, 1.65 mmol, 0.5 equiv.). The mixture was cooled to 0 °C, and *N*-bromosuccinimide (880 mg, 4.95 mmol, 1.5 equiv.) was added. The reaction mixture was stirred at 0 °C for 1 h, resulting in a white suspension. TLC analysis indicated complete consumption of the starting material. The reaction was quenched with water (200 mL) and extracted with petroleum ether (3 × 200 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:20) afforded bromoalkyne **24** as a colorless liquid (1.19 g, 96%).

TLC: R_f = 0.5 (ethyl acetate / petroleum ether = 1:10; *p*-anisaldehyde).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 – 3.33 (m, 3H), 2.70 – 2.57 (m, 2H), 2.30 – 2.13 (m, 2H), 2.05 – 1.91 (m, 3H), 1.90 – 1.83 (m, 2H), 1.83 – 1.72 (m, 2H), 1.67 – 1.51 (m, 4H), 1.50 – 1.41 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 216.59, 79.98, 66.94, 62.14, 38.38, 36.98, 34.89, 34.29, 33.18, 31.20, 29.78, 29.52, 25.33, 25.18, 19.98.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$:374.9954, found 374.9953.

IR (thin film): 2942, 2864, 1765, 1452, 756 cm^{-1}

General procedure A for photochemical reactions:

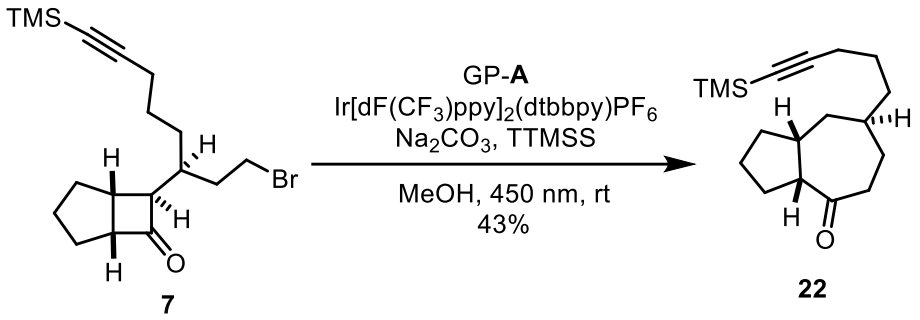
To a 10 mL reaction tube were added the substrate (0.0133 mmol, 1.0 equiv.), MeOH (1 mL), Na_2CO_3 (7.0 mg, 0.067 mmol, 5.0 equiv.), tris(trimethylsilyl)silane (TTMSS, 21 μL, 0.067 mmol, 5.0 equiv.), and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.3 mg, 0.3 μmol, 0.02 equiv.). The

reaction vessel was purged with argon three times. The mixture was then irradiated at room temperature with a 20 W 450 nm LED for 2 h. After completion (monitored by TLC), the solvent was removed under reduced pressure, and the crude residue was directly purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:40) to afford the corresponding product.

General procedure B for photochemical reactions:

To a 10 mL reaction tube were added the substrate (0.0133 mmol, 1.0 equiv.), 1,4-dioxane (0.3 mL), 2,6-lutidine (1.5 μL, 0.013 mmol, 1.0 equiv.), tris(trimethylsilyl)silane (TTMSS, 21 μL, 0.067 mmol, 5.0 equiv.), and $Ir(dFppy)_2(dtbbpy)PF_6$ (0.3 mg, 0.3 μmol, 0.02 equiv.). The reaction vessel was purged with argon three times. The mixture was then irradiated at room temperature with a 20 W 450 nm LED for 2 h. After completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure, and the crude residue was directly purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:40) to afford the corresponding product.

Synthesis of bicyclic ketone 22



Bicyclic ketone **22** was obtained from silylalkyne **7** (4.8 mg, 0.013 mmol) according to the experimental procedure described in General Procedure **A**, affording a colorless liquid (1.7 mg, 43%). When General Procedure **B** was used, the yield was 82%.

TLC: R_f = 0.5 (ethyl acetate / petroleum ether = 1:10; *p*-anisaldehyde).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.15 (dt, *J* = 11.3, 8.1 Hz, 1H), 2.45 (ddd, *J* = 17.2, 6.1, 3.0 Hz, 1H), 2.39 – 2.28 (m, 2H), 2.23 (t, *J* = 6.8 Hz, 2H), 2.19 – 2.07 (m, 1H), 1.85 – 1.64 (m, 5H),

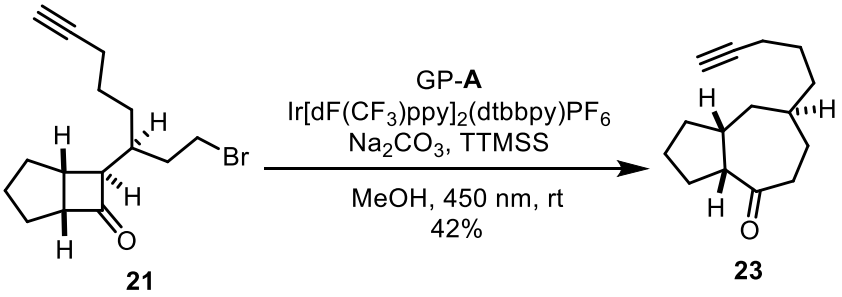
1.64 – 1.50 (m, 4H), 1.50 – 1.41 (m, 2H), 1.42 – 1.29 (m, 2H), 1.12 – 0.99 (m, 1H), 0.15 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 213.89, 107.51, 84.78, 52.45, 41.22, 36.11, 35.18, 35.10, 34.99, 34.05, 28.56, 26.79, 26.28, 25.68, 20.16, 0.31.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 291.2139, found 291.2138.

IR (thin film): 2937, 2865, 2173, 1704, 1456, 1248, 843, 759, 643 cm^{-1}

Synthesis of bicyclic ketone 23



Bicyclic ketone **23** was obtained from alkyne **21** (4 mg, 0.013 mmol) according to the experimental procedure described in General Procedure **A** (GP-**A**), affording a colorless liquid (1.3 mg, 42%). When General Procedure **B** (GP-**B**) was used, the yield was 78%.

TLC: R_f = 0.3 (ethyl acetate / petroleum ether = 1:10; *p*-anisaldehyde).

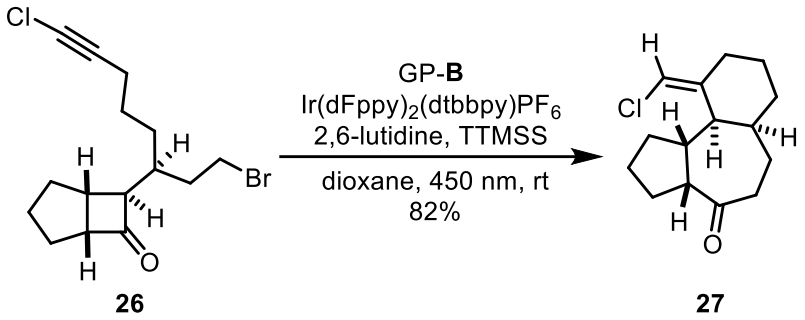
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.15 (dt, *J* = 11.3, 8.1 Hz, 1H), 2.51 – 2.41 (m, 1H), 2.40 – 2.25 (m, 2H), 2.20 (td, *J* = 6.8, 2.7 Hz, 2H), 2.17 – 2.08 (m, 1H), 1.96 (t, *J* = 2.7 Hz, 1H), 1.84 – 1.66 (m, 5H), 1.64 – 1.45 (m, 6H), 1.43 – 1.30 (m, 2H), 1.05 (tdd, *J* = 12.3, 10.6, 6.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 213.87, 84.58, 68.54, 52.42, 41.22, 36.15, 35.22, 35.17, 35.06, 34.08, 28.44, 26.63, 26.28, 25.68, 18.76.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 219.1744, found 219.1739.

IR (thin film): 3299, 2937, 2865, 1701, 1457, 1269, 1184, 755, 637 cm^{-1}

Synthesis of vinyl chloride 27



Vinyl chloride **27** was obtained from chloroalkyne **26** (4.4 mg, 0.013 mmol) according to the experimental procedure described in General Procedure **B**, affording a colorless liquid (2.8 mg, 82%).

TLC: R_f = 0.3 (ethyl acetate / petroleum ether = 1:20; *p*-anisaldehyde).

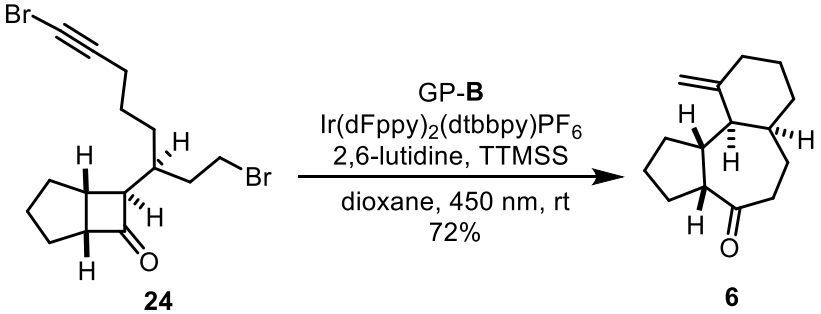
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (d, *J* = 1.9 Hz, 1H), 3.27 (dt, *J* = 11.3, 8.1 Hz, 1H), 2.84 (dd, *J* = 11.9, 5.0 Hz, 1H), 2.52 (qd, *J* = 11.5, 6.7 Hz, 1H), 2.44 – 2.35 (m, 2H), 2.23 (tt, *J* = 12.4, 7.5 Hz, 1H), 2.12 (ddt, *J* = 13.5, 4.6, 1.9 Hz, 1H), 2.00 (tdd, *J* = 13.4, 4.4, 2.0 Hz, 1H), 1.90 – 1.77 (m, 3H), 1.76 – 1.66 (m, 2H), 1.65 – 1.56 (m, 2H), 1.56 – 1.44 (m, 2H), 1.36 – 1.19 (m, 2H), 1.09 (qd, *J* = 12.1, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 213.21, 143.30, 110.52, 51.23, 40.97, 40.29, 39.23, 38.95, 31.29, 31.01, 29.56, 28.88, 27.36, 25.93, 25.30.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 253.1354, found 253.1350.

IR (thin film): 2932.25, 2862.37, 1703.33, 1452.11, 755.77 cm^{-1}

Synthesis of alkene 6



Alkene **6** was obtained from bromoalkyne **24** (5.0 mg, 0.014 mmol) according to the experimental procedure described in General Procedure **B**, affording a colorless liquid (2.2 mg,

72%). When General Procedure **A** was used, the yield was 39%.

TLC: R_f = 0.5 (ethyl acetate / petroleum ether = 1:10; *p*-anisaldehyde).

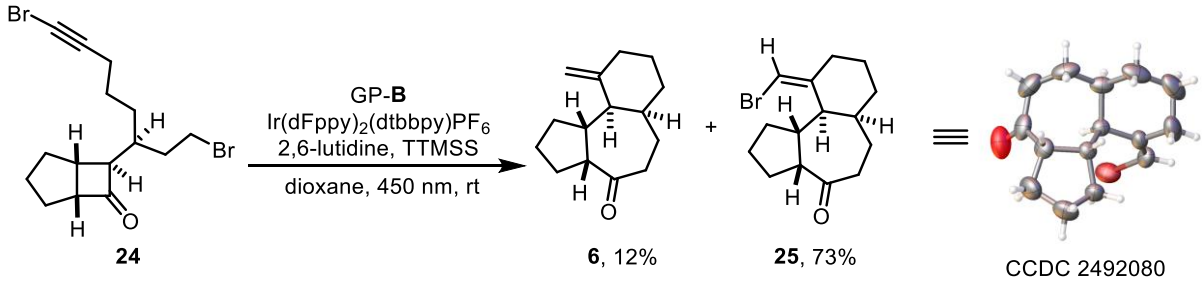
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.60 (t, *J* = 2.2 Hz, 1H), 4.57 – 4.51 (m, 1H), 3.28 (dt, *J* = 11.4, 8.2 Hz, 1H), 2.48 (qd, *J* = 11.6, 6.5 Hz, 1H), 2.38 – 2.32 (m, 2H), 2.26 – 2.16 (m, 1H), 2.16 – 2.08 (m, 1H), 2.01 (dd, *J* = 11.9, 4.7 Hz, 1H), 1.93 (td, *J* = 13.1, 4.5 Hz, 1H), 1.87 – 1.68 (m, 5H), 1.65 – 1.56 (m, 2H), 1.53 – 1.41 (m, 2H), 1.29 (m, 2H), 0.97 (qd, *J* = 12.3, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 214.01, 150.67, 109.23, 51.03, 48.99, 40.57, 40.50, 38.93, 32.68, 31.70, 29.62, 28.81, 27.71, 25.83, 25.28.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 219.1744, found 219.1739.

IR (thin film): 2929, 1705, 1516, 1269, 756 cm^{-1}

Synthesis of vinyl bromide 25



Bromoalkyne **24** (4.8 mg, 0.013mmol) was subjected to the experimental procedure described in General Procedure **A**, except that the reaction time was shortened to 20 min, affording vinyl bromide **25** as a white solid (2.8 mg, 72%). In addition, alkene **6** was obtained as a minor product (0.3 mg, 12%).

Vinyl bromide **25:**

TLC: R_f = 0.6 (ethyl acetate / petroleum ether = 1:10; *p*-anisaldehyde).

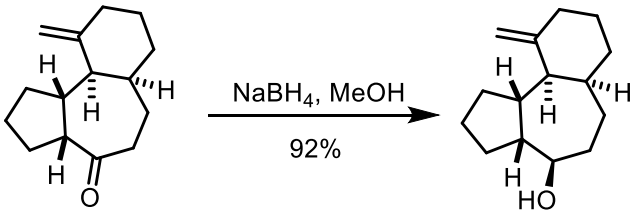
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (d, *J* = 1.9 Hz, 1H), 3.27 (dt, *J* = 11.2, 8.1 Hz, 1H), 2.82 (dd, *J* = 11.8, 5.0 Hz, 1H), 2.54 (qd, *J* = 11.4, 6.6 Hz, 1H), 2.45 – 2.33 (m, 2H), 2.30 – 2.15 (m, 2H), 2.01 (tdd, *J* = 13.3, 4.4, 1.9 Hz, 1H), 1.86 (qd, *J* = 5.6, 3.1 Hz, 2H), 1.83 – 1.68 (m, 3H), 1.66 – 1.58 (m, 2H), 1.56 – 1.47 (m, 2H), 1.37 – 1.19 (m, 2H), 1.12 (qd, *J* = 11.9, 5.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 213.12, 146.23, 100.02, 51.25, 43.42, 40.27, 39.29, 38.94, 32.48, 31.19, 29.39, 28.83, 27.37, 25.91, 25.34.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 297.0849, found 297.0845.

IR (thin film): 2932, 2861, 1704, 1453, 1269, 755 cm^{-1}

Synthesis of alcohol 28



6 **28**

To a 100 mL round-bottom flask were added alkene **6** (800 mg, 3.66 mmol, 1.0 equiv.) and MeOH (20 mL). The solution was cooled to 0 °C, followed by the addition of $NaBH_4$ (400 mg, 11.0 mmol, 3.0 equiv.). The reaction mixture was stirred at 0 °C for 30 min. Upon completion, the reaction was quenched with water (400 mL) and extracted with petroleum ether (3 × 200 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:8) to afford the title alcohol **28** as a white solid (742 mg, 92% yield).

TLC: R_f = 0.4 (ethyl acetate / petroleum ether = 1:3; *p*-anisaldehyde).

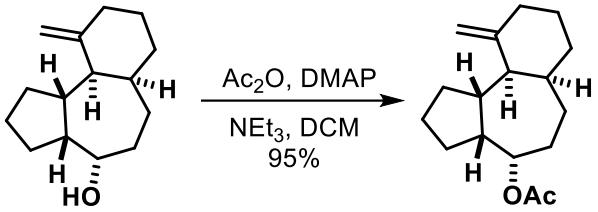
^{1}H NMR (400 MHz, C_6D_6) δ 4.79 (d, *J* = 2.7 Hz, 1H), 4.72 (dd, *J* = 2.7, 1.3 Hz, 1H), 3.66 (brs, 1H), 2.83 (dd, *J* = 9.9, 4.1 Hz, 1H), 2.00 (ddt, *J* = 21.8, 8.7, 3.8 Hz, 4H), 1.82 – 1.65 (m, 5H), 1.67 – 1.53 (m, 4H), 1.44 – 1.28 (m, 5H), 1.27 – 1.16 (m, 1H), 0.80 (d, *J* = 4.0 Hz, 1H).

^{13}C NMR (101 MHz, C_6D_6) δ 153.20, 107.54, 72.91, 48.90, 44.73, 42.38, 39.61, 35.04, 32.51, 31.78, 30.29, 30.16, 29.33, 27.94, 25.46.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 243.1719, found 243.1712.

IR (thin film): 3397.45, 2927.67, 2858.3, 1652.08, 1446.97, 885.72 cm^{-1}

Synthesis of acetate 30



28 **30**

To a 50 mL round-bottom flask were added alcohol **28** (400 mg, 1.82 mmol, 1.0 equiv.), CH_2Cl_2 (15 mL), Et_3N (1.26 mL, 9.08 mmol, 5.0 equiv.), DMAP (111 mg, 0.908 mmol, 0.5 equiv.), and Ac_2O (0.51 mL, 5.4 mmol, 3.0 equiv.). The reaction mixture was stirred at room temperature for 30 min. Upon completion, the mixture was concentrated under reduced pressure. The residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:80) to afford acetate **30** as a colorless liquid (452 mg, 95% yield).

TLC: R_f = 0.6 (ethyl acetate / petroleum ether = 1:10; *p*-anisaldehyde).

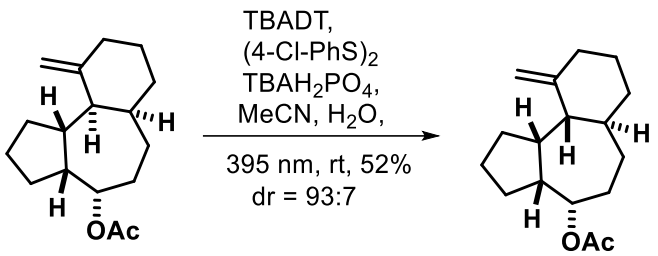
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.03 (td, *J* = 5.8, 3.4 Hz, 1H), 4.65 – 4.58 (m, 2H), 2.61 (dd, *J* = 10.4, 4.2 Hz, 1H), 2.38 (qd, *J* = 8.9, 3.4 Hz, 1H), 2.21 (qd, *J* = 10.3, 6.5 Hz, 1H), 2.11 – 2.02 (m, 5H), 1.92 (dddd, *J* = 14.6, 8.4, 6.0, 2.5 Hz, 1H), 1.84 – 1.60 (m, 6H), 1.58 – 1.40 (m, 4H), 1.41 – 1.17 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.03, 152.97, 107.38, 76.35, 48.44, 42.45, 41.76, 39.11, 34.31, 31.68, 29.98, 29.95, 29.43, 29.33, 27.55, 24.94, 21.60.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 263.2006, found 263.2004.

IR (thin film): 2929.01, 2860.55, 1735.54, 1446.61, 1368.97, 1242.00, 1022.47, 886.52 cm^{-1}

Synthesis of acetate 31



30 **31**

To a 10 mL reaction tube were added acetate **30** (10 mg, 0.038 mmol, 1.0 equiv.), TBADT (1.0 mg, 0.38 μmol, 0.01 equiv.), bis(4-chlorophenyl) disulfide (1.1 mg, 3.8 μmol, 0.1 equiv.), and $TBAH_2PO_4$ (1.3 mg, 3.8 μmol, 0.1 equiv.). The reaction vessel was evacuated and backfilled with argon. MeCN (0.4 mL) and H_2O (0.1 mL) were added via syringe. The mixture was stirred at room temperature under 395 nm LED irradiation for 8 h. Upon completion, the reaction was quenched with water (5 mL) and extracted with petroleum ether (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:80) to afford the title acetate **31** as a colorless liquid (5.2 mg, 52% yield, dr = 93:7).

TLC: R_f = 0.5 (ethyl acetate / petroleum ether = 1:20; *p*-anisaldehyde).

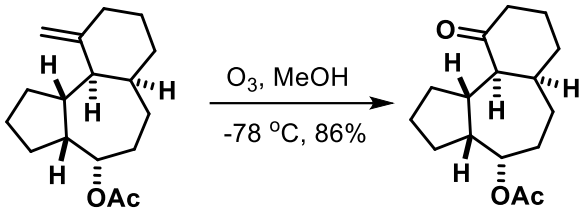
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.03 (ddd, *J* = 10.8, 5.4, 1.9 Hz, 1H), 4.75 (t, *J* = 1.5 Hz, 1H), 4.66 (d, *J* = 1.8 Hz, 1H), 2.65 – 2.52 (m, 1H), 2.48 – 2.34 (m, 1H), 2.30 – 2.15 (m, 2H), 2.09 – 1.96 (m, 4H), 1.95 – 1.84 (m, 1H), 1.83 – 1.71 (m, 4H), 1.71 – 1.52 (m, 5H), 1.51 – 1.34 (m, 3H), 1.33 – 1.24 (m, 1H), 1.23 – 1.09 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.50, 152.96, 108.04, 77.26, 47.37, 44.23, 42.46, 37.19, 35.60, 34.69, 33.55, 29.22, 28.90, 27.45, 25.82, 25.12, 21.51.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 263.2006, found 263.2009.

IR (thin film): 2933.84, 2863.61, 1732.00, 1640.99, 1450.71, 1368.45, 1243.78, 1020.75, 888.52 cm^{-1}

Synthesis of ketone 33



30 **33**

To a 25 mL round-bottom flask were added acetate **30** (25 mg, 0.095 mmol, 1.0 equiv.) and MeOH (0.8 mL). The solution was cooled to –78 °C. Ozone was bubbled through the solution until a pale blue color persisted. After 30 s, oxygen was bubbled through the mixture until the blue color disappeared. PPh_3 (75 mg, 0.29 mmol, 3.0 equiv.) was added to the reaction. The mixture was allowed to warm to room temperature and stirred for 30 min. Upon completion, the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:8) to afford ketone **33** as a colorless liquid (22 mg, 86% yield).

TLC: R_f = 0.5 (ethyl acetate / petroleum ether = 1:20; *p*-anisaldehyde).

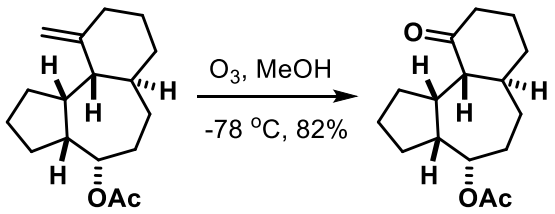
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.97 (dt, *J* = 6.6, 4.1 Hz, 1H), 2.76 (dd, *J* = 9.6, 4.1 Hz, 1H), 2.54 – 2.33 (m, 3H), 2.26 – 2.16 (m, 1H), 2.13 – 1.96 (m, 5H), 1.89 – 1.65 (m, 7H), 1.64 – 1.57 (m, 1H), 1.54 – 1.40 (m, 3H), 1.39 – 1.22 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 214.59, 170.86, 75.52, 57.06, 43.63, 41.16, 38.71, 38.57, 33.22, 29.54, 29.38, 28.99, 28.51, 25.40, 25.38, 21.51.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 265.1798, found 265.1801.

IR (thin film): 2939.60, 2864.88, 1731.65, 1706.29, 1448.87, 1370.00, 1244.36, 1021.48 cm^{-1}

Synthesis of ketone 32



31 **32**

To a 25 mL round-bottom flask were added acetate **31** (5.0 mg, 0.019 mmol, 1.0 equiv.)

and MeOH (0.5 mL). The solution was cooled to –78 °C. Ozone was bubbled through the solution until a pale blue color persisted. After 30 s, oxygen was bubbled through the mixture until the blue color disappeared. PPh_3 (15 mg, 0.057 mmol, 3.0 equiv.) was added to the reaction. The mixture was allowed to warm to room temperature and stirred for 30 min. Upon completion, the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:8) to afford ketone **32** as a colorless liquid (4.1 mg, 82% yield).

TLC: R_f = 0.5 (ethyl acetate / petroleum ether = 1:20; *p*-anisaldehyde).

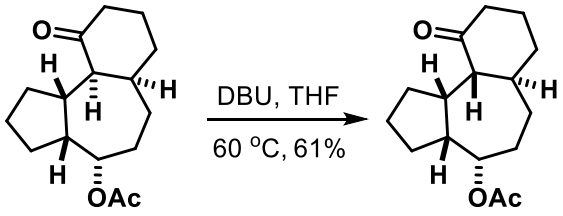
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.89 (ddd, *J* = 10.8, 5.3, 1.7 Hz, 1H), 2.90 (tdd, *J* = 11.7, 7.0, 2.5 Hz, 1H), 2.60 – 2.47 (m, 1H), 2.39 (dddd, *J* = 14.9, 5.1, 3.4, 1.9 Hz, 1H), 2.29 (dt, *J* = 10.1, 1.8 Hz, 1H), 2.24 – 2.14 (m, 1H), 1.99 (s, 3H), 1.97 – 1.81 (m, 5H), 1.80 – 1.65 (m, 3H), 1.64 – 1.51 (m, 3H), 1.50 – 1.32 (m, 3H), 1.24 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 212.46, 170.53, 77.34, 55.60, 41.55, 41.49, 38.60, 38.38, 36.58, 33.86, 29.78, 29.21, 27.77, 25.95, 23.61, 21.55.

HRMS (ESI-TOF) m/z calcd for $[M + H]^+$: 265.1798, found 265.1791.

IR (thin film): 2940.21, 2867.92, 1728.61, 1703.48, 1452.84, 1368.96, 1245.01, 1020.73 cm^{-1}

Thermodynamic Equilibrium of ketone 33



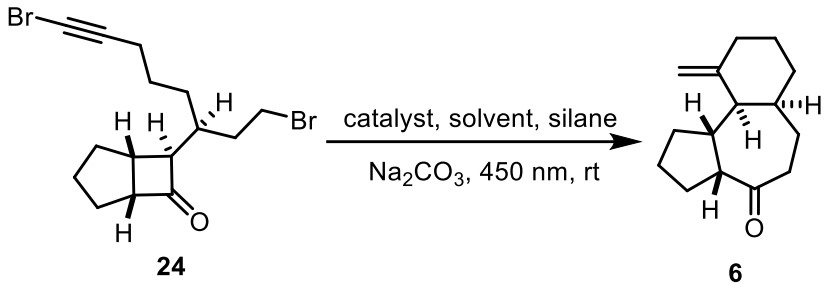
33 **32**

To a 10 mL reaction tube were added ketone **33** (7.5 mg, 0.02837 mmol, 1.0 equiv) and THF (0.2 mL), followed by the addition of DBU (0.02 mL, 0.1 mmol, 5.0 equiv). The reaction vessel was purged with argon, and the mixture was stirred at 60 °C for 10 h. The mixture was concentrated under reduced pressure. The residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:8) to afford compound

32 as a colorless liquid (4.8 mg, 61% yield). The NMR spectrum was consistent with that of ketone **32** obtained from the ozonolysis of ketone **31**.

3. Screening of Photoreaction Conditions

Table S1. Screening of photocatalysts, solvents, and silanes



24 **6**

entry[a]	catalyst	solvent	silane	yield[b]
1	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MeCN	TTMSS	46
2	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MeOH	TTMSS	41
3	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	iPrOH	TTMSS	42
4	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	HFIP[c]	TTMSS	45
5	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	THF	TTMSS	34
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	Et_2O	TTMSS	62
7	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DME	TTMSS	41
8	**$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$**	**1,4-dioxane**	**TTMSS**	**67**
9	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MTBE	TTMSS	61
10	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MOE[d]	TTMSS	59
11	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	benzene	TTMSS	39
12	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	PhMe	TTMSS	45
13	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	n-hexane	TTMSS	52
14	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	acetone	TTMSS	45
15	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$CHCl_3$	TTMSS	0

16	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DCM	TTMSS	0
17	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMSO	TTMSS	38
18	$Ru(bpy)_3(PF_6)_2$	1,4-dioxane	TTMSS	0
19	$Ru(bpz)_3(PF_6)_2$	1,4-dioxane	TTMSS	0
20	$Ir[(dFFppy)_2(4,4'\text{-}dCF_3bpy)]PF_6$	1,4-dioxane	TTMSS	39
21	$Ir[dF(Me)ppy]_2(dtbbpy)PF_6$	1,4-dioxane	TTMSS	65
22	$Ir(dFCF_3ppy)_2(5,5'\text{-}dCF_3bpy)PF_6$	1,4-dioxane	TTMSS	59
23	**$Ir(dFppy)_2(dtbbpy)PF_6$**	1,4-**dioxane**	**TTMSS**	**71**
24	$Ir(dFppy)_2(dtbbpy)PF_6$	1,4-dioxane	Ph_3SiH	0
25	$Ir(dFppy)_2(dtbbpy)PF_6$	1,4-dioxane	t-$BuPh_2SiH$	0
26	$Ir(dFppy)_2(dtbbpy)PF_6$	1,4-dioxane	$(Me_3SiO)_3SiH$	0
27	$Ir(dFppy)_2(dtbbpy)PF_6$	1,4-dioxane	Et_3SiH	0
28	$Ir(dFppy)_2(dtbbpy)PF_6$	1,4-dioxane	i-Pr_3SiH	0

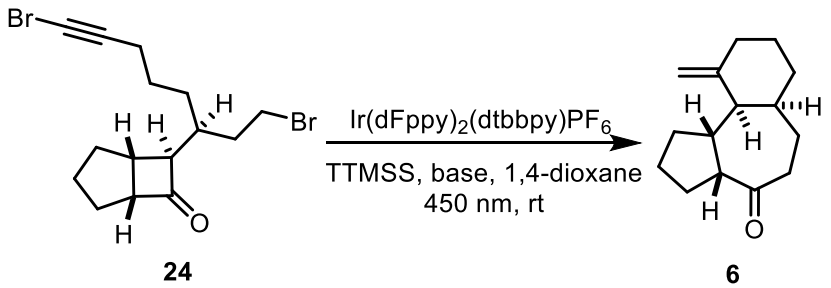
[a] The reaction was conducted using bromide **24** (5.0 mg, 0.013 mmol, 1.0 equiv.), the appropriate catalyst (0.3 μmol, 0.02 equiv.), solvent (1 mL), silane (0.066 mmol, 5 equiv.), and Na_2CO_3 (0.066 mmol, 5 equiv.). The mixture was irradiated with a 20 W, 450 nm LED for 2 h at room temperature.

[b] NMR yield.

[c] HFIP = 1,1,1,3,3,3-Hexafluoro-2-propanol.

[d] MOE = 2-Methoxyethanol.

Table S2. Screening of photocatalysts, solvents, and silanes



24 **6**

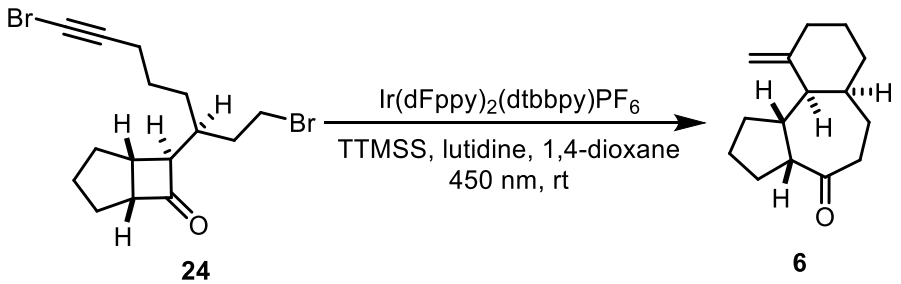
entry[a]	base	yield[b]

1	no base	45
2	Na_2CO_3	71
3	K_2CO_3	65
4	$NaHCO_3$	55
5	KH_2PO_4	49
6	Li_2CO_3	65
7	CsF	66
8	Cs_2CO_3	63
9	NaOAc	58
10	**2,6-lutidine**	**79**
11	proton sponge	21
12	pyridine	74
13	2,6-Di-tert-butylpyridine	74
14	NEt_3	65
15	DIPEA	53

[a] The reaction was carried out with bromide **24** (5.0 mg, 0.013 mmol, 1.0 equiv.), $Ir(dFppy)_2(dtbbpy)PF_6$ (0.3 mg, 0.3 μmol, 0.02 equiv.), TTMSS (21 μL, 0.066 mmol, 5 equiv.), the appropriate base (0.066 mmol, 5 equiv.), and 1,4-dioxane (1 mL). The mixture was irradiated with a 20 W, 450 nm LED for 2 h.

[b] NMR yield.

Table S3. Screening of silane, base, catalyst equivalents, and reaction concentration.



entry[a]	$(Me_3Si)_3SiH$	lutidine	Ir catalyst	concentration	yield[b]

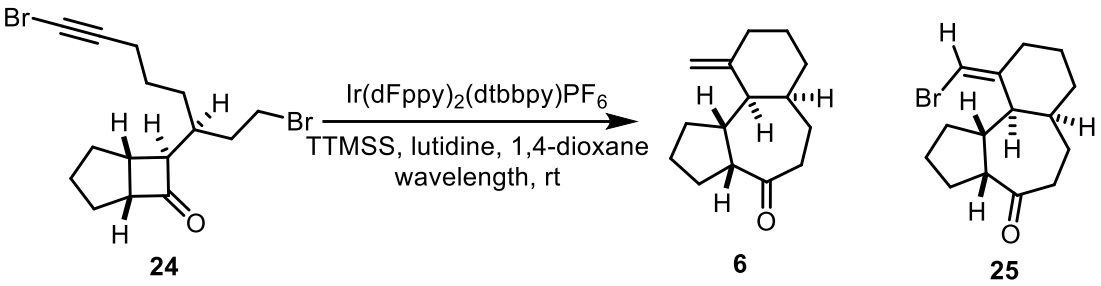
	(equiv.)	(equiv.)	(equiv.)	(mol/L)	
1	20.0	5.0	0.02	0.01	80
2	10.0	5.0	0.02	0.01	78
3	5.0	5.0	0.02	0.01	79
4	3.0	5.0	0.02	0.01	64
5	2.0	5.0	0.02	0.01	49
6	1.0	5.0	0.02	0.01	10
7	0.5	5.0	0.02	0.01	0
8	5.0	3.0	0.02	0.01	79
9	5.0	2.0	0.02	0.01	78
10	5.0	1.0	0.02	0.01	79
11	5.0	5.0	0.1	0.01	80
12	5.0	5.0	0.05	0.01	78
13	5.0	5.0	0.02	0.01	80
14	5.0	5.0	0.01	0.01	75
15	5.0	5.0	0.02	0.02	76
16	5.0	5.0	0.02	0.04	77
17	5.0	5.0	0.02	0.08	70
18	**5.0**	**1.0**	**0.02**	**0.04**	**79 (72[c])**

[a] The reaction was performed with bromide **24** (5.0 mg, 0.013 mmol, 1.0 equiv.), the appropriate amount of $Ir(dFppy)_2(dtbbpy)PF_6$, TTMSS, lutidine, and 1,4-dioxane (volume as appropriate). The mixture was irradiated with a 20 W, 450 nm LED for 2 h.

[b] NMR yield.

[c] Isolated yield.

Table S4. Screening of LED wavelength and reaction time.



entry[a]	wavelength	time (min)	Yield (**6**)[b]	Yield (**25**)[b]
1	395 nm	120	78	-
2	430 nm	120	77	-
3	450 nm	120	79	-
4	470 nm	120	76	-
5	495 nm	120	43	-
6	450 nm	5	0[c]	24[c]
7	450 nm	20	12[c]	73[c]
8	450 nm	60	77	-
9	450 nm	240	79	-

[a] The reaction was carried out with bromide **24** (5.0 mg, 0.013 mmol, 1.0 equiv.), $Ir(dFppy)_2(dtbbpy)PF_6$ (0.3 mg, 0.3 μmol, 0.02 equiv.), TTMSS (21 μL, 0.066 mmol, 5 equiv.), lutidine (1.5 μL, 0.013 mmol, 1.0 equiv.), and 1,4-dioxane (0.3 mL, 0.04 mol/L). The mixture was irradiated with the appropriate wavelength of LED (20 W) for appropriate time.

[b] NMR yield.

[c] Isolated yield.

4. Photoreaction Set-Up

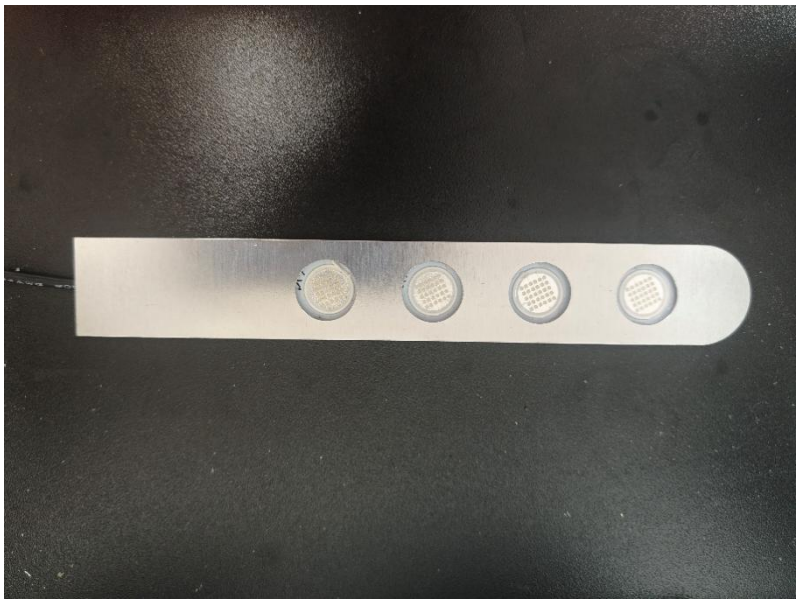


Figure S1. LED light source used in this work.

Figure S2. 16-position high-throughput photoreactor.

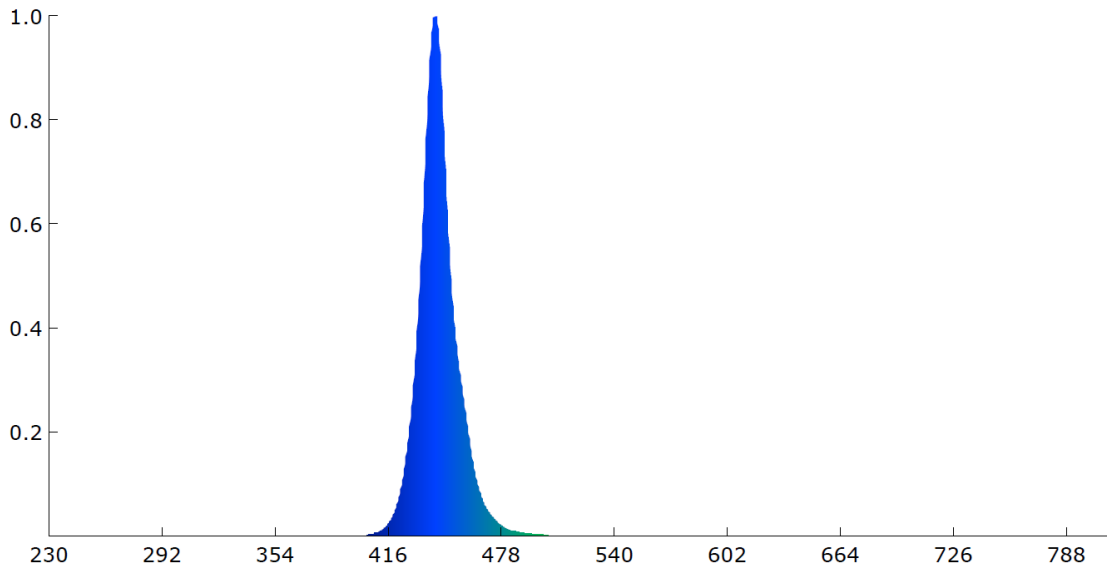


Figure S3. Emission spectrum of the 450 nm LED, with a full width at half maximum (FWHM) of 16.2 nm.

5. Computational Details

To gain deeper insight into the regioselectivity, stereoselectivity, and electronic effects on the reactivity of substrates, DFT calculations were performed. The geometric optimizations were conducted at B3LYP-D3/6-31+G(d,p) level with the PCM:dioxane solvent model.[3] The single point calculation was performed on the optimized geometries at the B3LYP-D3(PCM: dioxane) /cc-pVTZ level.[4] Unless otherwise specified, the relative Gibbs free energies in the following were B3LYP single-point energies corrected by the B3LYP zero-Gibbs energies. All calculations were performed using Gaussian 09 software.[5]

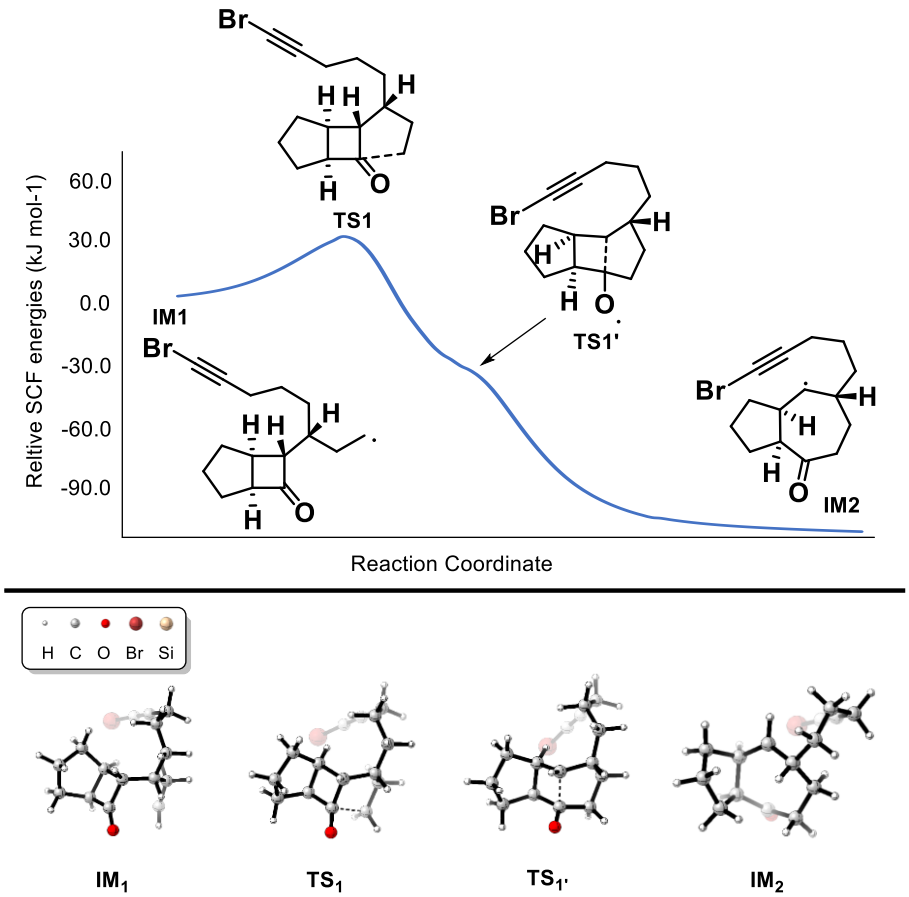


Figure S4. Intrinsic Reaction Coordinate (IRC) calculation profile for the transformation from **IM1** to **IM2** calculated at the B3LYP-D3(PCM)/6-31+G(d,p) level. The energy profile reveals a monotonically decreasing path from **TS1** to **IM2** with a distinct inflection point (**TS1'**), supporting a one-step, two-stage mechanism that involves initial radical attack followed by asynchronous ring-expansion.

Cartesian Coordinates and Energies of Optimized Structures

1. Br-system

23

6	0	2.785810	-0.220945	-0.448601
6	0	3.614434	-1.396928	-1.008001
6	0	2.743546	-1.966746	-2.148401
6	0	1.281442	-1.767876	-1.676901
6	0	1.332320	-0.710975	-0.510601
6	0	0.734162	-2.770488	-0.662901
6	0	0.923743	-1.821284	0.524799
8	0	0.238485	-3.873498	-0.760201
1	0	0.608703	0.098510	-0.585301
1	0	0.595438	-1.590490	-2.512001

6	0	-0.249160	-1.685108	1.524599
6	0	0.235333	-1.348898	2.956699
6	0	-1.394679	-0.758831	1.058399
1	0	1.808150	-2.164065	1.082499
1	0	-0.674739	-2.697117	1.598099
6	0	-2.071069	-1.247045	-0.213001
6	0	1.129508	-0.117079	3.192299
6	0	0.450879	1.279807	3.104999
6	0	0.548866	1.930809	1.799199
6	0	0.649155	2.455011	0.712499
35	0	0.788040	3.178914	-0.929901
1	0	2.897692	0.657457	-1.095901
1	0	3.090504	0.079661	0.558799
1	0	3.766650	-2.157925	-0.232201
1	0	4.607028	-1.090908	-1.352701
1	0	2.894234	-1.378643	-3.060801
1	0	2.968567	-3.010542	-2.389001
1	0	0.804051	-2.220086	3.307799
1	0	-0.642068	-1.279316	3.614399
1	0	-1.035000	0.260276	0.905599
1	0	-2.144580	-0.714347	1.856099
1	0	-1.419369	-1.233132	-1.084401
1	0	1.995908	-0.141662	2.522699
1	0	1.530610	-0.212371	4.207899
1	0	0.913665	1.946016	3.843699
1	0	-0.605919	1.200085	3.391899
1	0	-2.511749	-2.238254	-0.105601
35	0	-3.577794	-0.043076	-0.716401

Thermal correction to Gibbs Free Energy= 0.268948

$(TMSi)_3SiH$

14	0	-0.027109	-0.038016	-0.794118
14	0	1.768228	-1.380466	-0.046308
14	0	-2.076186	-0.849436	0.059088
14	0	0.297504	2.215479	-0.160063
6	0	2.103091	2.742243	-0.427297
1	0	2.241349	3.792900	-0.142560
1	0	2.787085	2.136660	0.177808
1	0	2.398580	2.634338	-1.477009
6	0	-0.834446	3.361737	-1.164488
1	0	-1.888626	3.096857	-1.027541
1	0	-0.701866	4.404334	-0.848833
1	0	-0.608590	3.300276	-2.235006
6	0	-0.119845	2.404662	1.684534
1	0	0.055833	3.436678	2.012760
1	0	-1.170784	2.164274	1.880815
1	0	0.496630	1.743628	2.303842
6	0	2.159249	-0.939385	1.760830
1	0	2.963184	-1.579422	2.145137

1	0	2.485880	0.102390	1.854813
1	0	1.282782	-1.075121	2.404159
6	0	1.317175	-3.223926	-0.132251
1	0	1.063380	-3.525140	-1.154840
1	0	2.160897	-3.840159	0.203132
1	0	0.457842	-3.452762	0.507975
6	0	3.317994	-1.075277	-1.099430
1	0	3.141993	-1.341911	-2.147617
1	0	3.618479	-0.022276	-1.066277
1	0	4.156523	-1.679986	-0.731433
6	0	-2.597973	-2.436535	-0.842422
1	0	-1.835102	-3.216664	-0.744199
1	0	-3.535940	-2.823582	-0.424499
1	0	-2.753873	-2.251133	-1.911100
6	0	-3.450273	0.448683	-0.130959
1	0	-3.213146	1.362230	0.425806
1	0	-3.595758	0.724252	-1.181555
1	0	-4.401537	0.057999	0.251856
6	0	-1.864715	-1.237513	1.907831
1	0	-2.815989	-1.572772	2.339479
1	0	-1.126264	-2.031593	2.065677
1	0	-1.532613	-0.355305	2.466305
1	0	-0.077322	-0.105779	-2.293383

$(TMSi)_3Si\cdot$

14	0	-0.006107	-0.006070	-0.624368
14	0	1.453416	-1.763695	-0.055598
14	0	-2.254682	-0.377324	-0.032928
14	0	0.800067	2.137990	-0.078429
6	0	2.684539	2.204141	-0.303708
1	0	3.063946	3.203091	-0.054417
1	0	3.186858	1.480683	0.348298
1	0	2.970129	1.980682	-1.337591
6	0	-0.007777	3.463439	-1.170809
1	0	-1.098266	3.449726	-1.066002
1	0	0.348659	4.461642	-0.886511
1	0	0.230954	3.304819	-2.228268
6	0	0.392353	2.527221	1.739200
1	0	0.767459	3.522527	2.010729
1	0	-0.689438	2.514018	1.913231
1	0	0.850179	1.794409	2.412825
6	0	1.996171	-1.577532	1.759119
1	0	2.669303	-2.396944	2.042948
1	0	2.527417	-0.632476	1.918693
1	0	1.132974	-1.595903	2.433650
6	0	0.573653	-3.435050	-0.252914
1	0	0.231922	-3.587146	-1.282688
1	0	1.253577	-4.256832	0.004687
1	0	-0.299926	-3.502113	0.405277

6	0	3.004545	-1.738858	-1.149330
1	0	2.748104	-1.880519	-2.205029
1	0	3.536743	-0.785679	-1.056795
1	0	3.691832	-2.541968	-0.854423
6	0	-3.015855	-1.752549	-1.097104
1	0	-2.457432	-2.689050	-0.989835
1	0	-4.053916	-1.939140	-0.793931
1	0	-3.014736	-1.479371	-2.158111
6	0	-3.260749	1.217661	-0.258475
1	0	-2.876670	2.022348	0.378606
1	0	-3.228011	1.565627	-1.296870
1	0	-4.310934	1.047367	0.010041
6	0	-2.358973	-0.904869	1.792864
1	0	-3.404659	-1.072002	2.082275
1	0	-1.806464	-1.834489	1.970210
1	0	-1.941880	-0.135081	2.451476

$(TMSi)_3SiBr$

14	0	-0.024987	-0.031108	-0.619580
14	0	1.797051	-1.408555	-0.007360
14	0	-2.118638	-0.853200	0.109108
14	0	0.315356	2.253179	-0.112457
6	0	2.101613	2.740131	-0.517881
1	0	2.252391	3.814262	-0.353645
1	0	2.814681	2.198923	0.113705
1	0	2.340229	2.519688	-1.564050
6	0	-0.879641	3.312174	-1.129450
1	0	-1.922303	3.079155	-0.889371
1	0	-0.711634	4.377462	-0.928464
1	0	-0.734432	3.137925	-2.200863
6	0	-0.009680	2.507352	1.741539
1	0	0.173035	3.553087	2.018298
1	0	-1.047295	2.268381	2.000592
1	0	0.644704	1.878224	2.355375
6	0	2.194292	-1.087115	1.821806
1	0	3.017222	-1.733441	2.151230
1	0	2.497527	-0.047238	1.987627
1	0	1.329007	-1.292100	2.462173
6	0	1.334847	-3.230913	-0.247118
1	0	1.009821	-3.420743	-1.275857
1	0	2.198314	-3.874867	-0.039024
1	0	0.522746	-3.527966	0.425567
6	0	3.297609	-0.988004	-1.082085
1	0	3.061024	-1.119610	-2.143286
1	0	3.616611	0.049032	-0.934902
1	0	4.140733	-1.644518	-0.833907
6	0	-2.516715	-2.464361	-0.801599
1	0	-1.772554	-3.238270	-0.586417
1	0	-3.501260	-2.841754	-0.498758

1	0	-2.529549	-2.302411	-1.884674
6	0	-3.466984	0.430437	-0.246426
1	0	-3.306166	1.347102	0.331684
1	0	-3.482907	0.697990	-1.308563
1	0	-4.454277	0.032570	0.019048
6	0	-2.017556	-1.169662	1.978967
1	0	-2.986108	-1.519173	2.357449
1	0	-1.269637	-1.935107	2.214328
1	0	-1.751590	-0.258769	2.527001
35	0	-0.109918	-0.132087	-2.948712

TS0

6	0	-1.061500	-1.700300	-1.330100
6	0	-2.445500	-2.155700	-1.842200
6	0	-3.317800	-2.198400	-0.569700
6	0	-2.809200	-1.018300	0.292400
6	0	-1.375600	-0.653900	-0.249500
6	0	-3.262300	0.378700	-0.137500
6	0	-1.907100	0.733900	-0.760000
8	0	-4.302600	0.993000	-0.021000
1	0	-0.598200	-0.565400	0.505100
1	0	-2.930200	-1.197700	1.365500
6	0	-1.262400	2.079800	-0.356800
6	0	-0.262900	2.594700	-1.423200
6	0	-0.637600	2.112500	1.064900
1	0	-2.031200	0.736700	-1.853600
1	0	-2.090500	2.804000	-0.353500
6	0	-1.588900	1.807000	2.185900
6	0	0.913800	1.695400	-1.851900
6	0	2.106500	1.545200	-0.860800
6	0	2.057600	0.310100	-0.076200
6	0	1.975200	-0.741800	0.518800
35	0	1.773100	-2.310000	1.380800
1	0	-0.536500	-2.547900	-0.871000
1	0	-0.417600	-1.310800	-2.126000
1	0	-2.849200	-1.419500	-2.549500
1	0	-2.411700	-3.117900	-2.363200
1	0	-3.134000	-3.132100	-0.024600
1	0	-4.392200	-2.136500	-0.771600
1	0	-0.838300	2.801300	-2.335900
1	0	0.127400	3.566000	-1.088100
1	0	0.204300	1.416900	1.124900
1	0	-0.223100	3.118100	1.208000
1	0	-2.038500	0.817600	2.191000

1	0	0.548700	0.698100	-2.118100
1	0	1.313200	2.127400	-2.777000
1	0	3.046300	1.541100	-1.427400
1	0	2.160100	2.413100	-0.191300
1	0	-2.288600	2.586000	2.484300
14	0	1.295100	1.485900	6.297800
35	0	-0.211900	1.653700	4.149200
14	0	0.804800	-0.756000	6.832600
14	0	3.373700	1.994600	5.310600
14	0	0.398200	3.199500	7.645300
6	0	3.631400	0.926400	3.774400
1	0	4.604700	1.139200	3.314500
1	0	3.590400	-0.142000	4.007200
1	0	2.851400	1.138100	3.037100
6	0	4.790300	1.713100	6.544900
1	0	5.753300	1.966700	6.083500
1	0	4.668500	2.332500	7.440800
1	0	4.834200	0.665000	6.863100
6	0	3.327900	3.819700	4.793800
1	0	4.256600	4.099100	4.280500
1	0	2.490200	3.998500	4.110700
1	0	3.206700	4.480800	5.659300
6	0	1.452000	-1.183700	8.567200
1	0	1.208200	-2.223000	8.822000
1	0	2.540300	-1.066000	8.627400
1	0	0.999500	-0.535300	9.326500
6	0	1.632800	-1.872700	5.541200
1	0	1.430500	-1.512900	4.526900
1	0	2.720000	-1.897500	5.680400
1	0	1.255700	-2.900100	5.621500
6	0	-1.073100	-1.000900	6.781500
1	0	-1.477800	-0.658700	5.823500
1	0	-1.322000	-2.062000	6.907500
1	0	-1.567100	-0.436300	7.580200
6	0	-0.137800	4.638900	6.537500
1	0	0.702300	5.009100	5.939800
1	0	-0.922800	4.318300	5.844900
1	0	-0.520700	5.468600	7.145100
6	0	-1.092700	2.536500	8.611900
1	0	-1.871200	2.179600	7.928600
1	0	-0.803600	1.701200	9.260000
1	0	-1.525800	3.322100	9.243700
6	0	1.728900	3.800600	8.861900
1	0	1.331600	4.604800	9.494300

1	0	2.067700	2.990100	9.517200
1	0	2.603900	4.190500	8.329000

IM1

6	0	0.302508	-1.462403	-1.480708
6	0	1.475507	-2.398503	-1.844308
6	0	1.951907	-2.953004	-0.484408
6	0	1.747108	-1.786104	0.510492
6	0	0.735508	-0.791003	-0.168608
6	0	2.785308	-0.666004	0.473692
6	0	1.862909	0.296796	-0.282808
8	0	3.917208	-0.559205	0.898792
1	0	-0.100392	-0.483803	0.454792
1	0	1.528507	-2.124403	1.528092
6	0	1.719509	1.727296	0.285992
6	0	1.347510	2.766097	-0.797508
6	0	0.826009	1.804297	1.548292
1	0	2.230909	0.373196	-1.317408
1	0	2.733710	2.002096	0.612992
6	0	1.302109	0.955897	2.679092
6	0	0.098410	2.544597	-1.671808
6	0	-1.285090	2.788698	-1.000808
6	0	-1.943791	1.581998	-0.502508
6	0	-2.471391	0.563599	-0.114508
35	0	-3.196492	-0.975301	0.475892
1	0	-0.604993	-2.053002	-1.303208
1	0	0.069408	-0.741703	-2.271708
1	0	2.282808	-1.826504	-2.319808
1	0	1.188407	-3.189203	-2.544608
1	0	1.312707	-3.789503	-0.178508
1	0	2.984907	-3.315404	-0.499908
1	0	2.202610	2.826796	-1.484008
1	0	1.274410	3.754897	-0.322908
1	0	-0.210591	1.554797	1.306692
1	0	0.811610	2.864497	1.861892
1	0	2.358409	0.913496	2.927792
1	0	0.602809	0.453597	3.339592
1	0	0.115709	1.542097	-2.112308
1	0	0.172810	3.245497	-2.511108
1	0	-1.958190	3.257198	-1.729708
1	0	-1.180190	3.510998	-0.180708

TS1

6	0	1.397511	-1.006978	-2.134999

6	0	2.463725	-2.064764	-1.775199
6	0	1.946334	-2.678571	-0.456799
6	0	1.304618	-1.495079	0.291401
6	0	0.976203	-0.400684	-0.784899
6	0	2.342805	-0.503166	0.893301
6	0	2.001390	0.602730	-0.154299
8	0	3.444908	-0.769451	1.418401
1	0	-0.051501	-0.045197	-0.781599
1	0	0.488422	-1.796690	0.952301
6	0	1.497473	1.889123	0.512501
6	0	0.993358	3.008516	-0.419399
6	0	0.561379	1.452611	1.661501
1	0	2.856987	0.814441	-0.808299
1	0	2.387167	2.314535	1.003201
6	0	1.289993	0.411620	2.460001
6	0	-0.188739	2.785001	-1.386199
6	0	-1.617639	2.788482	-0.767699
6	0	-2.150522	1.475175	-0.406899
6	0	-2.559607	0.370569	-0.125199
35	0	-3.095385	-1.293038	0.307901
1	0	0.532118	-1.498390	-2.598499
1	0	1.763201	-0.251573	-2.840499
1	0	3.432719	-1.579751	-1.603399
1	0	2.608435	-2.809362	-2.564599
1	0	1.177844	-3.432481	-0.669099
1	0	2.734340	-3.157560	0.132901
1	0	1.851754	3.301128	-1.038999
1	0	0.764646	3.886913	0.201901
1	0	-0.378116	1.051698	1.278301
1	0	0.315367	2.318407	2.295001
1	0	2.147988	0.740732	3.040601
1	0	0.750204	-0.430287	2.884701
1	0	-0.042727	1.878603	-1.981099
1	0	-0.162250	3.618701	-2.097499
1	0	-2.311945	3.239773	-1.487499
1	0	-1.635148	3.440782	0.115701

IM2

6	0	-2.101088	2.770799	0.227508
6	0	-2.374990	1.344900	0.044808
6	0	-2.527892	0.156500	-0.129092
35	0	-2.665795	-1.621200	-0.373792
1	0	-1.926688	2.975799	1.292308
1	0	-3.000287	3.335500	-0.049292

6	0	-0.906587	3.289597	-0.614892
6	0	0.512812	3.078095	-0.048492
6	0	3.684008	-0.222109	-1.380492
6	0	3.524607	-0.757109	0.072708
6	0	2.084606	-1.343607	0.148208
6	0	1.316507	-0.692406	-1.043092
6	0	2.428107	-0.703407	-2.133192
6	0	1.333406	-1.267606	1.468108
6	0	1.357208	0.009994	2.288208
6	0	0.522510	1.150595	1.668008
6	0	1.019910	1.645095	0.278308
6	0	0.754209	0.685195	-0.845792
1	0	3.712409	0.873491	-1.375592
1	0	4.609707	-0.565311	-1.852592
1	0	4.257006	-1.535910	0.306508
1	0	3.682808	0.045691	0.797108
1	0	2.134504	-2.413407	-0.079292
1	0	0.490906	-1.353605	-1.341292
1	0	2.565905	-1.730708	-2.495592
1	0	2.174508	-0.076507	-2.993992
1	0	0.957608	-0.236305	3.275808
1	0	2.391308	0.351393	2.415608
1	0	-0.520091	0.832397	1.605908
1	0	0.565611	1.994495	2.367908
1	0	2.113610	1.754993	0.393108
1	0	0.134009	1.028396	-1.668692
8	0	0.674705	-2.230905	1.844808
1	0	-1.037886	4.372398	-0.730392
1	0	1.203013	3.511994	-0.783692
1	0	0.618213	3.687295	0.859208
1	0	-0.984988	2.869998	-1.623792

TS2

6	0	-0.694665	3.058818	0.024723
6	0	-1.138076	1.649121	-0.196177
6	0	-2.101582	0.864629	-0.162277
35	0	-3.050094	-0.676064	-0.224777
1	0	-0.640664	3.235517	1.107423
1	0	-1.490160	3.711824	-0.353377
6	0	0.639338	3.456507	-0.625077
6	0	1.886533	2.768898	-0.032477
6	0	2.856198	-1.639610	-1.631177
6	0	2.614495	-2.106308	-0.168077
6	0	1.099697	-1.863496	0.112323

6	0	0.631904	-0.866692	-0.994077
6	0	1.451000	-1.388899	-2.206677
6	0	0.691400	-1.469193	1.522123
6	0	1.497708	-0.428399	2.276223
6	0	1.309219	1.004002	1.737423
6	0	1.742521	1.246799	0.268323
6	0	0.853616	0.612006	-0.776277
1	0	3.430506	-0.705714	-1.638877
1	0	3.424793	-2.369914	-2.214977
1	0	2.849686	-3.166510	-0.033077
1	0	3.258399	-1.555613	0.521823
1	0	0.558089	-2.795192	-0.080677
1	0	-0.434497	-1.021784	-1.183477
1	0	1.008493	-2.331595	-2.554277
1	0	1.445506	-0.691799	-3.050977
1	0	1.175907	-0.465697	3.320623
1	0	2.562106	-0.686708	2.241323
1	0	0.262321	1.289310	1.872023
1	0	1.905924	1.663998	2.378223
1	0	2.753917	0.809991	0.178423
1	0	0.838720	1.144306	-1.725677
8	0	-0.302004	-1.974385	2.032223
1	0	0.758346	4.541207	-0.521077
1	0	2.715134	2.914391	-0.736377
1	0	2.177537	3.283495	0.891323
1	0	0.573437	3.264708	-1.701977

IM3

6	0	-0.448975	2.660705	0.651193
6	0	-0.902588	1.262609	0.247993
6	0	-2.155790	0.942819	0.526993
35	0	-3.283103	-0.517571	0.290893
1	0	0.233424	2.560899	1.502693
1	0	-1.305070	3.232812	1.018193
6	0	0.256331	3.415798	-0.503807
6	0	0.909523	2.467493	-1.536407
6	0	0.822380	-2.432207	-1.808607
6	0	2.112182	-2.251918	-0.960407
6	0	1.618386	-1.707913	0.408793
6	0	0.209092	-1.083601	0.130693
6	0	-0.342518	-2.162596	-0.835607
6	0	2.567494	-0.857222	1.229893
6	0	3.362303	0.236771	0.554393
6	0	2.449014	1.418879	0.177893

6	0	1.380811	1.139889	-0.904207
6	0	0.092304	0.350000	-0.510607
1	0	0.803186	-1.697606	-2.623007
1	0	0.756071	-3.420906	-2.272307
1	0	2.650473	-3.194122	-0.818007
1	0	2.806588	-1.567324	-1.453307
1	0	1.407179	-2.566912	1.055093
1	0	-0.346108	-1.078196	1.071693
1	0	-0.580825	-3.068694	-0.265107
1	0	-1.257015	-1.851388	-1.345507
1	0	4.129206	0.572865	1.257293
1	0	3.861100	-0.142533	-0.344007
1	0	1.995317	1.802783	1.094793
1	0	3.097821	2.219174	-0.198207
1	0	1.870006	0.554184	-1.693807
1	0	-0.392897	0.184204	-1.481607
8	0	2.639592	-1.020722	2.443393
1	0	1.012937	4.080592	-0.072107
1	0	0.185121	2.234299	-2.327007
1	0	1.751527	2.970285	-2.026007
1	0	-0.465863	4.059305	-1.017307

TS3

14	0	2.621599	0.134703	-0.145897
1	0	1.152599	-0.016897	-0.626297
6	0	-5.178801	-1.838998	1.377203
6	0	-6.061401	-0.936298	0.473203
6	0	-5.196401	-0.660698	-0.789597
6	0	-3.716701	-0.962898	-0.368197
6	0	-3.969101	-2.219298	0.503903
6	0	-5.410601	0.640302	-1.536597
6	0	-5.566501	1.925502	-0.756597
6	0	-4.212901	2.368602	-0.170497
6	0	-3.573901	1.438402	0.887703
6	0	-2.884401	0.114602	0.424303
1	0	-4.838101	-1.273998	2.253703
1	0	-5.715001	-2.715498	1.753403
1	0	-6.995901	-1.428098	0.185103
1	0	-6.341101	-0.019298	0.996903
1	0	-5.425901	-1.433998	-1.530897
1	0	-3.159101	-1.218598	-1.271697
1	0	-4.220101	-3.064798	-0.148497
1	0	-3.096601	-2.511598	1.091503
1	0	-5.936801	2.691502	-1.443397

1	0	-6.296201	1.805702	0.051003
1	0	-3.529301	2.547702	-1.003297
1	0	-4.373302	3.343602	0.305703
1	0	-4.372301	1.142702	1.581103
1	0	-2.639301	-0.374298	1.377503
8	0	-5.393001	0.652502	-2.763097
6	0	-1.093901	1.851203	-0.430297
6	0	-1.496501	0.400703	-0.200397
6	0	-0.586801	-0.524297	-0.486797
35	0	-0.548001	-2.395397	-0.267497
1	0	-1.641401	2.225003	-1.302397
1	0	-0.037701	1.898803	-0.702797
6	0	-1.375501	2.753603	0.797903
6	0	-2.517301	2.222602	1.694003
1	0	-2.989901	3.053802	2.230003
1	0	-2.098401	1.556502	2.458603
1	0	-1.611602	3.762803	0.442303
1	0	-0.468001	2.842103	1.402203
14	0	3.328599	2.344303	-0.586197
14	0	3.947699	-1.436097	-1.307197
14	0	2.509399	-0.347797	2.163503
6	0	5.221099	2.429603	-0.435697
1	0	5.554399	2.125004	0.562903
1	0	5.572698	3.453704	-0.612597
1	0	5.708799	1.775004	-1.166597
6	0	2.820299	2.851403	-2.343397
1	0	3.167198	3.868303	-2.565897
1	0	1.730699	2.832003	-2.459397
1	0	3.248099	2.174803	-3.091197
6	0	2.570398	3.577503	0.643403
1	0	1.481498	3.622803	0.539803
1	0	2.966998	4.584503	0.462603
1	0	2.798998	3.306103	1.680003
6	0	4.285599	-0.843397	-3.079497
1	0	4.889099	-1.582297	-3.621497
1	0	4.831599	0.106603	-3.084697
1	0	3.351399	-0.697597	-3.633397
6	0	3.097299	-3.129397	-1.370297
1	0	2.882599	-3.502697	-0.363497
1	0	3.742400	-3.858397	-1.877097
1	0	2.147399	-3.074097	-1.911697
6	0	5.606299	-1.614696	-0.394697
1	0	6.131499	-0.655596	-0.325997
1	0	6.259399	-2.321796	-0.921497

1	0	5.457699	-1.989396	0.624403
6	0	4.027499	0.371103	3.052903
1	0	4.956299	-0.049197	2.650403
1	0	3.989999	0.142103	4.125303
1	0	4.076999	1.460203	2.942103
6	0	0.931099	0.417603	2.889603
1	0	0.948399	1.510103	2.810703
1	0	0.822399	0.154303	3.949203
1	0	0.049099	0.056703	2.350203
6	0	2.467199	-2.223297	2.454103
1	0	3.378999	-2.704797	2.083503
1	0	1.612599	-2.677597	1.942103
1	0	2.381599	-2.441397	3.526103

24

6	0	-0.363195	2.623611	0.678007
6	0	-0.889997	1.246812	0.315307
6	0	-2.169297	1.011414	0.630007
35	0	-3.192900	-0.559684	0.225207
1	0	0.403505	2.510710	1.451807
1	0	-1.155593	3.227413	1.130007
6	0	0.227207	3.357410	-0.555293
6	0	0.773605	2.382309	-1.626893
6	0	0.866696	-2.512591	-1.688093
6	0	2.143296	-2.307194	-0.832193
6	0	1.644598	-1.676293	0.500207
6	0	0.210699	-1.112190	0.202607
6	0	-0.303203	-2.241489	-0.727693
6	0	2.570799	-0.727694	1.232407
6	0	3.375401	0.273104	0.436807
6	0	2.469103	1.423806	-0.038793
6	0	1.302503	1.074508	-0.996893
6	0	0.041101	0.307210	-0.467393
1	0	0.844397	-1.786791	-2.510693
1	0	0.814894	-3.507191	-2.141293
1	0	2.657295	-3.251394	-0.625993
1	0	2.860198	-1.671295	-1.355793
1	0	1.469496	-2.487592	1.215007
1	0	-0.344101	-1.101589	1.143407
1	0	-0.512505	-3.132689	-0.122593
1	0	-1.226003	-1.979687	-1.247193
1	0	4.156802	0.673603	1.088507
1	0	3.855300	-0.202197	-0.423893
1	0	2.108904	1.945607	0.849307

1	0	3.111205	2.138405	-0.568293
1	0	1.724401	0.454807	-1.799093
1	0	-0.515899	0.101711	-1.392093
8	0	2.609199	-0.729194	2.458507
1	0	1.022208	4.030509	-0.215493
1	0	-0.025995	2.130510	-2.334593
1	0	1.562606	2.870808	-2.210093
1	0	-0.544892	3.989311	-1.006893
1	0	-2.784196	1.733116	1.153007

TS2’

6	0	2.017304	-1.868894	2.812591
6	0	2.704904	-2.041592	1.533091
6	0	3.214005	-2.166490	0.441491
35	0	3.939505	-2.324988	-1.195509
1	0	2.677402	-1.355692	3.524091
1	0	1.832707	-2.865394	3.233491
6	0	0.665202	-1.114498	2.697391
6	0	0.684297	0.415302	2.843791
6	0	1.116885	4.407704	-0.017009
6	0	2.221086	4.147507	-1.055209
6	0	2.329491	2.600207	-1.186509
6	0	0.921992	2.035203	-0.708609
6	0	0.101189	3.289401	-0.288309
6	0	3.513892	2.024711	-0.419909
6	0	3.668291	2.321211	1.065991
6	0	2.925794	1.289609	1.942891
6	0	1.383694	1.285004	1.767891
1	0	1.514086	4.330105	1.001191
1	0	0.681682	5.408202	-0.113309
1	0	1.914185	4.555306	-2.025209
1	0	3.176585	4.620310	-0.800909
1	0	2.501291	2.311008	-2.226309
1	0	0.457694	1.581002	-1.590709
1	0	-0.543112	3.593499	-1.117109
1	0	-0.557211	3.085699	0.560391
1	0	4.737592	2.274114	1.291291
1	0	3.311688	3.328210	1.301591
1	0	3.332597	0.301110	1.720091
1	0	3.158794	1.510610	2.992591
1	0	1.048791	2.309403	1.978591
8	0	4.338794	1.321213	-0.990409
1	0	0.013503	-1.498300	3.491291
1	0	-0.363704	0.734299	2.877191

1	0	1.110396	0.672504	3.823791
1	0	0.188402	-1.387699	1.753791
6	0	0.991596	0.943303	0.341691
1	0	1.421598	0.007105	-0.019709
14	0	-2.049601	-0.200906	-0.088209
14	0	-2.725003	0.544192	-2.235809
14	0	-1.847094	-2.565005	-0.242709
14	0	-3.475103	0.591790	1.622491
6	0	-3.039809	2.401391	2.012691
1	0	-3.729610	2.804989	2.764591
1	0	-3.106611	3.030991	1.118291
1	0	-2.021809	2.489594	2.407991
6	0	-3.289000	-0.420409	3.219991
1	0	-3.638797	-1.448310	3.080891
1	0	-3.886002	0.035989	4.019791
1	0	-2.249300	-0.466406	3.559291
6	0	-5.302703	0.528685	1.104191
1	0	-5.942304	0.812083	1.949791
1	0	-5.597800	-0.474416	0.776991
1	0	-5.505705	1.223284	0.281991
6	0	-4.493702	-0.042213	-2.619809
1	0	-4.751702	0.239286	-3.649009
1	0	-5.220503	0.429885	-1.950809
1	0	-4.606398	-1.125713	-2.526809
6	0	-1.555701	-0.178904	-3.549809
1	0	-0.517802	0.124699	-3.371809
1	0	-1.844202	0.171795	-4.548709
1	0	-1.585298	-1.273804	-3.556509
6	0	-2.736409	2.433692	-2.445209
1	0	-1.727410	2.822195	-2.610709
1	0	-3.160710	2.948891	-1.576809
1	0	-3.342110	2.693991	-3.322509
6	0	-0.146993	-2.974600	-0.978409
1	0	-0.011594	-2.488500	-1.950909
1	0	-0.046890	-4.057600	-1.125209
1	0	0.669106	-2.647898	-0.327909
6	0	-2.045592	-3.462606	1.421691
1	0	-3.079492	-3.395409	1.777591
1	0	-1.394293	-3.065804	2.204691
1	0	-1.807288	-4.525505	1.287091
6	0	-3.166292	-3.307009	-1.395209
1	0	-3.055589	-4.398909	-1.410809
1	0	-3.062893	-2.946309	-2.423609
1	0	-4.181893	-3.077112	-1.054509

1	0	-0.548403	0.398199	0.258491

IM3’

6	0	-1.955846	2.823923	0.377903
6	0	-2.385265	1.443229	0.155503
6	0	-2.720681	0.297834	-0.050797
35	0	-3.188004	-1.413960	-0.349497
1	0	-1.726545	2.968320	1.442303
1	0	-2.808338	3.479735	0.159903
6	0	-0.746340	3.272207	-0.486697
6	0	0.663457	3.043188	0.094503
6	0	4.183109	-0.428460	-0.160797
6	0	3.512191	-1.787351	0.097703
6	0	2.017893	-1.611631	-0.310797
6	0	1.990710	-0.384430	-1.303897
6	0	3.468016	0.091749	-1.417097
6	0	1.089995	-1.475518	0.886803
6	0	1.356409	-0.398622	1.926303
6	0	0.664128	0.930988	1.554603
6	0	1.203137	1.599880	0.275603
1	0	4.015118	0.251642	0.682303
1	0	5.267308	-0.515275	-0.290097
1	0	3.960580	-2.547157	-0.552697
1	0	3.634386	-2.142153	1.127303
1	0	1.662881	-2.504226	-0.831897
1	0	1.675204	-0.782226	-2.274297
1	0	3.929010	-0.354957	-2.306397
1	0	3.543531	1.179048	-1.531197
1	0	0.953105	-0.760116	2.876903
1	0	2.430812	-0.229636	2.048703
1	0	-0.408575	0.742502	1.462303
1	0	0.799337	1.620386	2.397303
1	0	2.285539	1.725266	0.421803
8	0	0.121985	-2.217105	1.008803
1	0	-0.847626	4.353408	-0.640097
1	0	1.358664	3.563278	-0.578497
1	0	0.731864	3.566287	1.058903
1	0	-0.831347	2.816708	-1.479397
6	0	0.988325	0.753383	-1.000597
1	0	-0.030180	0.346697	-0.993197
1	0	1.034134	1.425683	-1.867497

Zero-point Gibbs free energy (ZPG in a.u.), single-point energy (Esp in a.u.) and ΔG (in kJ/mol) for Br-system

species	ZPG	Esp	Esp +ZPG	ΔG
23	0.268948	-5807.506387	-5807.237439	84.5
TS0	0.565295	-7325.099564	-7324.534269	103.1
IM1	0.265039	-3233.203433	-3232.938394	0.0
TS1	0.268225	-3233.191003	-3232.922778	41.0
IM2	0.269697	-3233.229633	-3232.959936	-56.5
TS2	0.271538	-3233.213463	-3232.941925	-9.3
TS2'	0.584977	-4751.457762	-4750.872785	-0.5
TS3	0.584103	-4751.491721	-4750.907618	-91.9
IM3	0.276884	-3233.259695	-3232.982811	-116.6
24	0.290772	-3233.940225	-3233.649453	-212.9
IM3'	0.28625	-3233.897207	-3233.610957	-111.0
TMSiH	0.289512	-1518.223712	-1517.934200	-
TMSi	0.280039	-1517.583972	-1517.303933	-
TMSiBr	0.278856	-4091.914025	-4091.635169	-

2 H-system

H-TS2

6	0	-3.191398	0.223916	0.510303
6	0	-1.992497	0.454713	1.373103
6	0	-1.532996	1.030012	2.374003
1	0	-3.333695	1.107916	-0.125597
1	0	-4.063898	0.181018	1.172803
6	0	-3.154301	-1.036084	-0.367197
6	0	-2.100801	-1.008787	-1.493797
6	0	2.381896	-2.091299	-0.199297
6	0	2.730800	-0.646400	-0.656297
6	0	2.013902	0.301402	0.352003
6	0	0.922200	-0.579095	1.038403
6	0	1.688797	-1.922397	1.165503
6	0	1.498506	1.637004	-0.155197
6	0	0.782206	1.708805	-1.489597
6	0	-0.632595	1.095809	-1.446497
6	0	-0.713599	-0.414191	-1.104397

6	0	-0.405000	-0.766091	0.335003
1	0	1.688495	-2.554397	-0.911097
1	0	3.263394	-2.737401	-0.144897
1	0	3.809000	-0.460203	-0.636997
1	0	2.406000	-0.480299	-1.686197
1	0	2.723003	0.562500	1.144403
1	0	0.716801	-0.172394	2.035603
1	0	2.437897	-1.831099	1.963003
1	0	1.033194	-2.760095	1.425103
1	0	0.709809	2.764906	-1.763397
1	0	1.371605	1.198104	-2.259297
1	0	-1.238294	1.674011	-0.743397
1	0	-1.070595	1.240510	-2.440997
1	0	0.033499	-0.909493	-1.750397
1	0	-0.882803	-1.687190	0.665403
8	0	1.629809	2.641803	0.535103
1	0	-4.144401	-1.171781	-0.817397
1	0	-1.959304	-2.037187	-1.848297
1	0	-2.497700	-0.444486	-2.346297
1	0	-2.997503	-1.906684	0.279903
1	0	-0.813695	1.365410	3.091003

H-TS2'

6	0	-2.047846	-2.796178	2.461025
6	0	-2.747630	-3.144526	3.697920
6	0	-3.337307	-3.416187	4.720583
6	0	-2.645305	-1.559855	1.753122
6	0	-1.837538	-1.181884	0.506208
6	0	-2.926264	3.560156	-0.929216
6	0	-3.339015	3.453625	-2.406691
6	0	-2.665747	2.158380	-2.947431
6	0	-1.455348	1.859112	-1.957635
6	0	-1.491356	3.018764	-0.921699
6	0	-3.623625	0.985064	-3.066221
6	0	-4.459904	0.581003	-1.861126
6	0	-3.736530	-0.479675	-1.006321
6	0	-2.420070	-0.014898	-0.325864
1	0	-3.570465	2.937187	-0.297941
1	0	-2.998101	4.583849	-0.547005
1	0	-2.937023	4.309338	-2.960882
1	0	-4.424579	3.462137	-2.556368
1	0	-2.275699	2.315325	-3.956108
1	0	-0.543319	1.942010	-2.555679

1	0	-0.808990	3.810277	-1.251718
1	0	-1.155485	2.700364	0.067778
1	0	-5.392008	0.153180	-2.242208
1	0	-4.708231	1.446040	-1.240212
1	0	-3.511430	-1.345714	-1.642232
1	0	-4.440706	-0.822429	-0.240623
1	0	-2.658164	0.811967	0.359453
8	0	-3.702552	0.342990	-4.107107
1	0	-3.688717	-1.777789	1.503205
1	0	-1.737769	-2.059559	-0.148062
1	0	-0.822163	-0.924765	0.820603
1	0	-2.661343	-0.714046	2.452506
6	0	-1.414845	0.468286	-1.354255
1	0	-1.113987	-0.311282	-2.060349
1	0	-2.073783	-3.653397	1.775399
1	0	-0.988948	-2.619032	2.686843
14	0	1.501474	0.738535	0.085069
14	0	2.739804	2.444279	-0.987323
14	0	2.594385	-1.332673	-0.226906
14	0	1.315945	1.254566	2.384720
6	0	0.071659	2.659592	2.679828
1	0	0.076249	2.952042	3.737455
1	0	0.311142	3.544944	2.081301
1	0	-0.945951	2.343374	2.424114
6	0	0.751474	-0.243303	3.407321
1	0	1.360399	-1.131128	3.204701
1	0	0.828822	-0.018765	4.478390
1	0	-0.293169	-0.491238	3.196367
6	0	3.016662	1.803849	3.034510
1	0	2.960704	2.014581	4.110010
1	0	3.771179	1.024878	2.879900
1	0	3.365678	2.711852	2.531043
6	0	4.593878	2.167246	-0.663718
1	0	5.180244	2.981355	-1.108426
1	0	4.812136	2.139177	0.409400
1	0	4.940961	1.225063	-1.101544
6	0	2.464050	2.435018	-2.866831
1	0	1.442588	2.733888	-3.125424
1	0	3.152601	3.138736	-3.351508
1	0	2.641646	1.440880	-3.291479
6	0	2.289216	4.162401	-0.310770
1	0	1.224521	4.383223	-0.435594
1	0	2.524082	4.241813	0.756311
1	0	2.860774	4.936120	-0.838754

6	0	3.158843	-1.505817	-2.033176
1	0	3.871398	-0.720244	-2.307954
1	0	3.648237	-2.475236	-2.190194
1	0	2.308098	-1.441576	-2.721191
6	0	1.456066	-2.796891	0.183064
1	0	1.085136	-2.742759	1.212116
1	0	0.588205	-2.827390	-0.483523
1	0	2.004721	-3.740501	0.070664
6	0	4.116727	-1.436852	0.906965
1	0	4.660399	-2.373841	0.731810
1	0	4.806634	-0.604912	0.730237
1	0	3.822992	-1.410899	1.962529
1	0	0.018763	0.599619	-0.587744
1	0	-3.853481	-3.659744	5.621846

TMS-system
TMS-TS2

6	0	-0.148679	3.117103	-0.084998
6	0	-0.673384	1.735905	-0.320898
6	0	-1.661787	0.976609	-0.316798
1	0	-0.180878	3.306503	0.997002
1	0	-0.865476	3.814906	-0.535298
6	0	1.259523	3.428498	-0.612098
6	0	2.396320	2.643793	0.074202
6	0	3.077502	-1.827209	-1.534498
6	0	2.694201	-2.277808	-0.096498
6	0	1.192202	-1.899902	0.080802
6	0	0.896806	-0.851901	-1.037398
6	0	1.744704	-1.435504	-2.198198
6	0	0.716304	-1.479400	1.460102
6	0	1.562207	-0.535603	2.292302
6	0	1.556513	0.915797	1.769702
6	0	2.103914	1.134994	0.335702
6	0	1.229512	0.598598	-0.776398
1	0	3.739506	-0.954312	-1.491498
1	0	3.610299	-2.606011	-2.088898
1	0	2.823597	-3.355608	0.042702
1	0	3.335203	-1.790510	0.641902
1	0	0.585399	-2.776900	-0.167198
1	0	-0.165594	-0.896697	-1.293698
1	0	1.240100	-2.327402	-2.592998
1	0	1.864407	-0.731505	-3.028498
1	0	1.161107	-0.553502	3.309502

1	0	2.595306	-0.898907	2.329602
1	0	0.538014	1.305800	1.844102
1	0	2.175615	1.501294	2.459602
1	0	3.076112	0.610691	0.300202
1	0	1.348214	1.132797	-1.717698
8	0	-0.364698	-1.880096	1.879502
1	0	1.445927	4.500897	-0.480498
1	0	3.292520	2.730090	-0.552398
1	0	2.643521	3.125792	1.028002
1	0	1.275022	3.253198	-1.693798
14	0	-3.077491	-0.189986	-0.195598
6	0	-2.652698	-1.895687	-0.890798
1	0	-1.870700	-2.365090	-0.285898
1	0	-2.316598	-1.844789	-1.932498
1	0	-3.542600	-2.536484	-0.854198
6	0	-4.522388	0.540420	-1.175798
1	0	-4.809185	1.522621	-0.783798
1	0	-5.396891	-0.118977	-1.116798
1	0	-4.259488	0.661719	-2.232898
6	0	-3.522392	-0.358084	1.630302
1	0	-3.787788	0.611617	2.066002
1	0	-2.668394	-0.767487	2.180202
1	0	-4.374095	-1.036881	1.759702

TMS-TS2’

6	0	-2.834464	-2.236667	2.532087
6	0	-3.645155	-2.662679	3.673506
6	0	-4.326782	-3.002694	4.627399
6	0	-3.050932	-0.755443	2.147371
6	0	-2.182666	-0.335711	0.951966
6	0	-1.348191	4.675400	1.132897
6	0	-1.829372	5.222993	-0.221878
6	0	-1.791055	4.023623	-1.214176
6	0	-0.760140	2.984824	-0.588225
6	0	-0.291514	3.626750	0.751850
6	0	-3.165054	3.423409	-1.491487
6	0	-4.018360	2.928560	-0.329547
6	0	-3.729613	1.454095	0.025819
6	0	-2.298724	1.154809	0.551360
1	0	-2.175306	4.205111	1.677803
1	0	-0.949182	5.461905	1.782524
1	0	-1.131057	5.989519	-0.577719
1	0	-2.815361	5.699059	-0.169432
1	0	-1.428688	4.347185	-2.193310

1	0	0.089056	2.953208	-1.277791
1	0	0.670691	4.127386	0.592631
1	0	-0.128634	2.881059	1.535186
1	0	-5.063580	3.017388	-0.640903
1	0	-3.872094	3.552998	0.557910
1	0	-3.914454	0.835763	-0.862686
1	0	-4.464558	1.150672	0.779355
1	0	-2.139647	1.752461	1.460790
8	0	-3.576265	3.319726	-2.638392
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1	0	-2.432260	-0.957940	0.080846
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1	0	-2.818330	-0.125944	3.016046
6	0	-1.259282	1.552744	-0.486451
1	0	-1.440058	1.093954	-1.463986
14	0	-5.346816	-3.534589	6.065766
6	0	-4.652776	-2.736546	7.633169
1	0	-4.678952	-1.643354	7.564327
1	0	-5.235698	-3.033415	8.513442
1	0	-3.612275	-3.036070	7.800761
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1	0	-7.544775	-3.417965	4.873093
1	0	-7.770399	-3.278958	6.626090
1	0	-7.194909	-1.887379	5.690598
6	0	-5.266039	-5.418443	6.202698
1	0	-5.862263	-5.774122	7.051693
1	0	-5.651565	-5.896663	5.295473
1	0	-4.235012	-5.759548	6.347689
1	0	-3.064170	-2.874952	1.667873
1	0	-1.773821	-2.406940	2.761362
14	0	1.632323	0.014920	-0.369114
14	0	3.102617	1.412924	-1.622102
14	0	1.366453	-2.061508	-1.508177
14	0	2.480375	-0.318209	1.832249
6	0	2.173407	1.206640	2.927639
1	0	2.622111	1.054142	3.917559
1	0	2.610201	2.114908	2.498853
1	0	1.102760	1.387653	3.073369
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1	0	4.720533	-0.832593	2.814842

1	0	4.608470	-1.514985	1.184239
1	0	4.910609	0.215264	1.401632
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1	0	5.372554	1.138642	-2.629377
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1	0	4.470121	-0.376791	-2.762188
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1	0	1.421212	2.639140	-3.064490
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1	0	1.995001	1.180098	-3.878258
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1	0	2.773129	3.562060	-0.335573
1	0	4.165674	2.670181	0.292927
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1	0	0.178065	-1.158213	-3.544366
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1	0	3.125288	-3.388769	-0.277059
1	0	0.143001	0.757972	-0.277828

6. References

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[3] a) A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648−5652. b) A. D. Becke, Density-functional thermochemistry. IV.A new dynamical correlation functional and implications for exact-exchange mixing. *J. Chem. Phys*. **1996**, *104*, 1040−1046.

[4] J. Zhang, X. Xu, D.G. Truhlar, *Theo. Chem. Account.* **2011**, *128*, 295−305.

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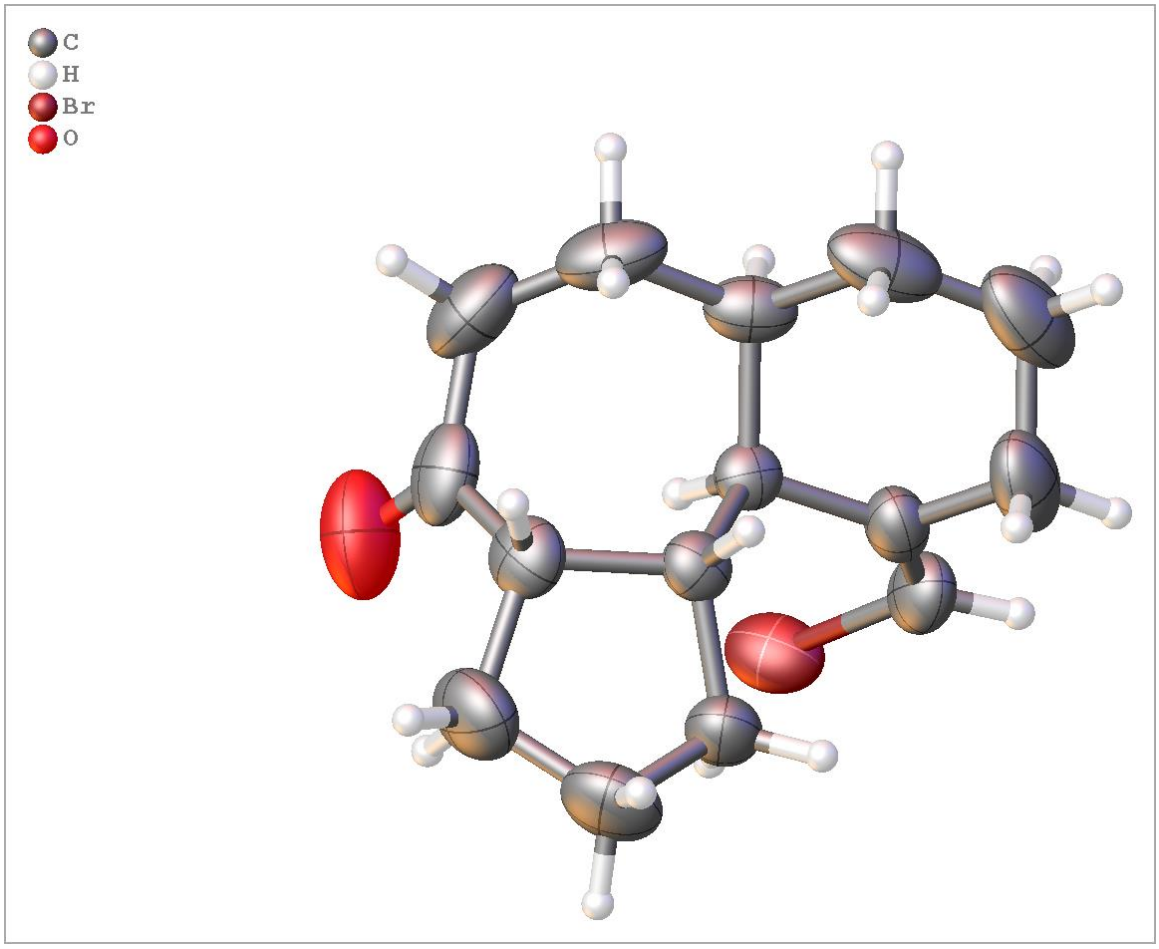
Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 09 E01,Gaussian, Inc., Wallingford CT, **2016**.

7. X-ray Crystallographic Data



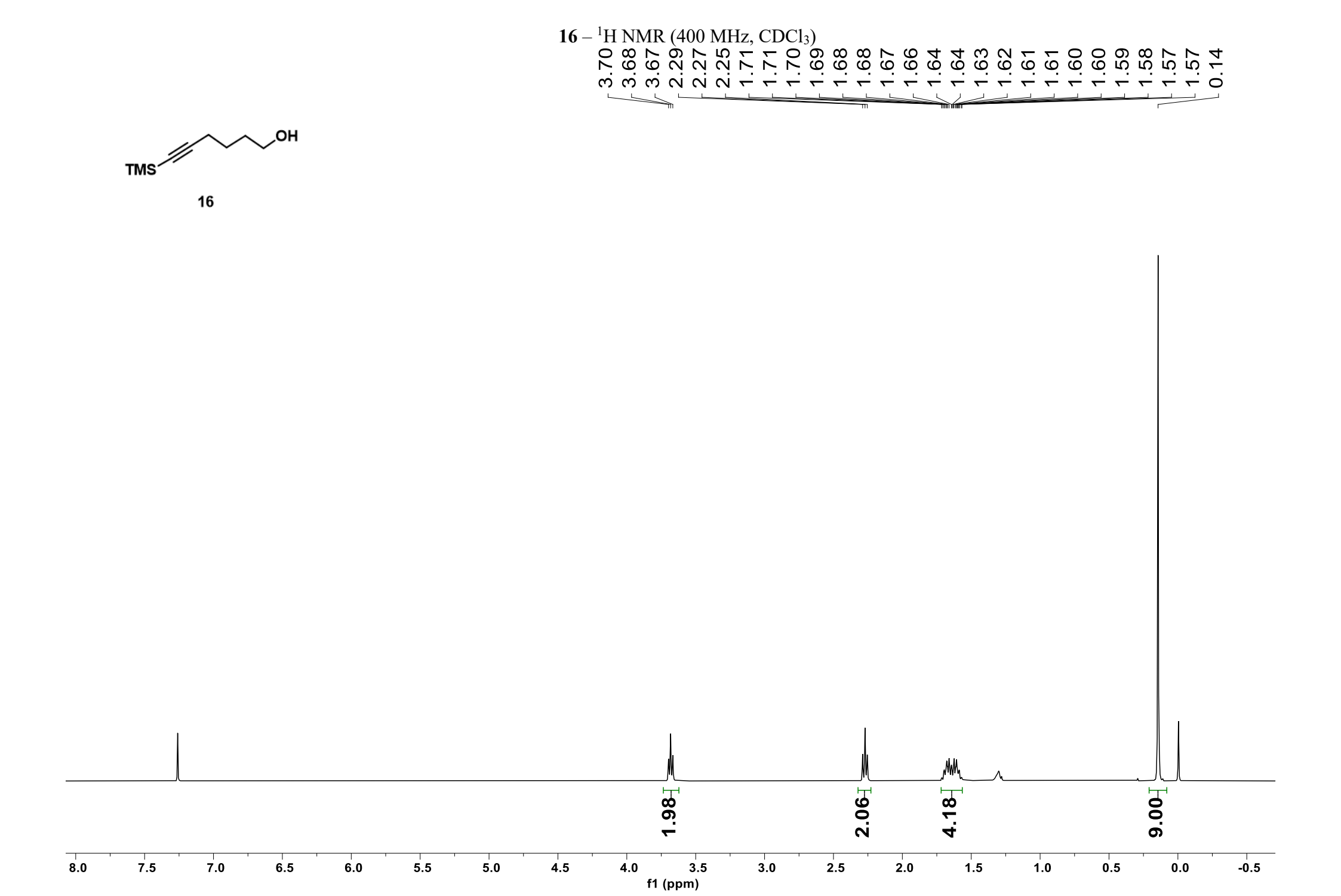
The single crystal for compound **25** was obtained by slow evaporation of *n*-hexane. The data were collected on a Bruker APEX-IICCD diffractometer equipped with MoKα X-ray sources. Displacement ellipsoids are drawn at the 30% probability level. Structure deposited at the Cambridge Crystallographic Data Centre (CCDC 2492080).

Empirical formula	$C_{15}H_{21}BrO$
Formula weight	297.24
Temperature/K	294.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.7790(16)
b/Å	13.881(2)
c/Å	11.429(2)
α/°	90
β/°	92.759(7)
γ/°	90
Volume/Å^3	1391.2(4)
Z	4
ρ_{calc} g/cm^3	1.424
μ/mm^{-1}	2.940
F(000)	616.0
Crystal size/mm^3	0.45 × 0.38 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.62 to 55.054
Index ranges	$-11 \leqslant h \leqslant 11, -17 \leqslant k \leqslant 18, -14 \leqslant l \leqslant 14$
Reflections collected	34092
Independent reflections	3204 [R_{int} = 0.1085, R_{sigma} = 0.0550]
Data/restraints/parameters	3204/0/154
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0440, wR_2 = 0.1136
Final R indexes [all data]	R_1 = 0.0660, wR_2 = 0.1270

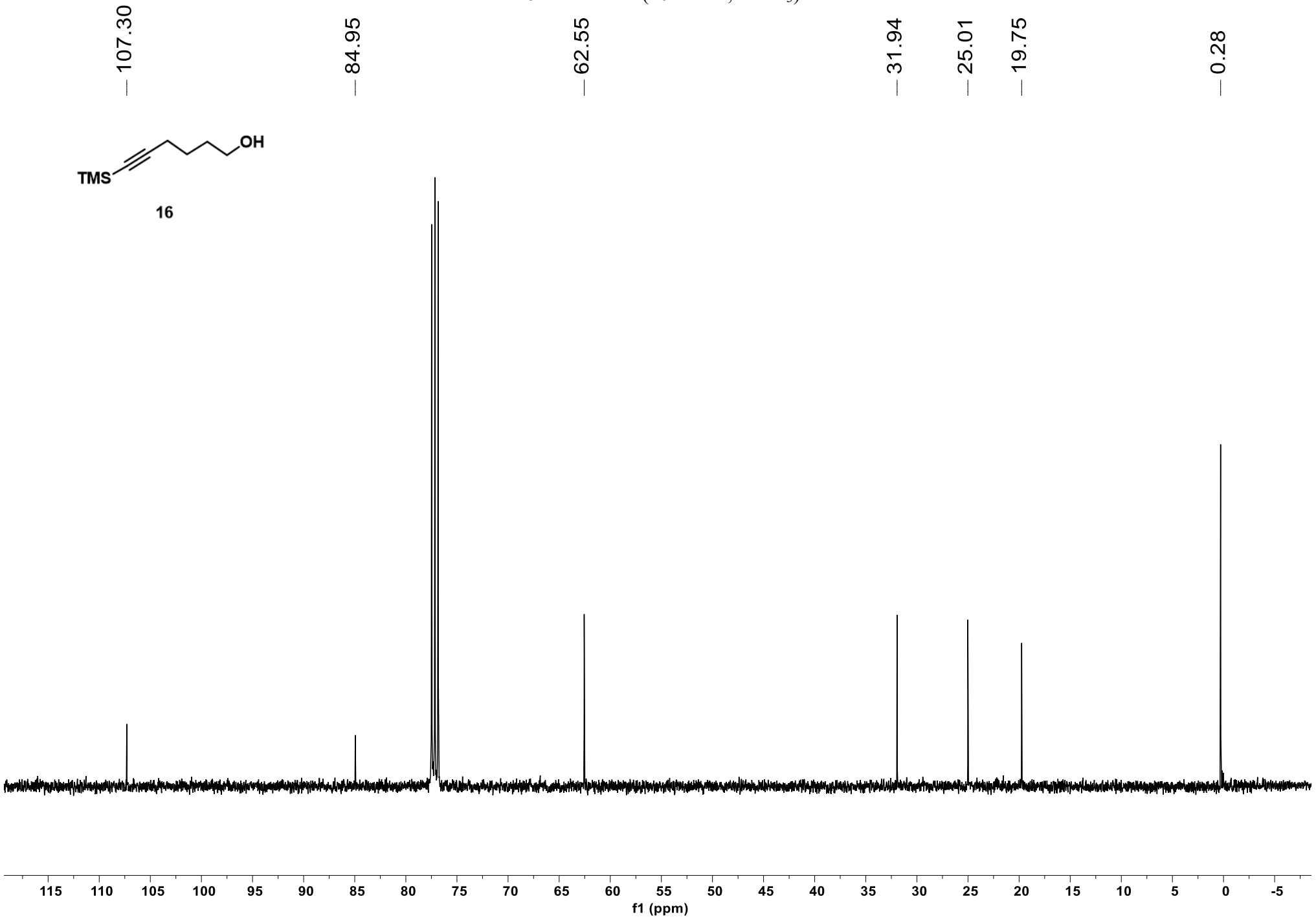
Largest diff. peak/hole / e $Å^{-3}$	0.54/-0.76

8. NMR Spectra

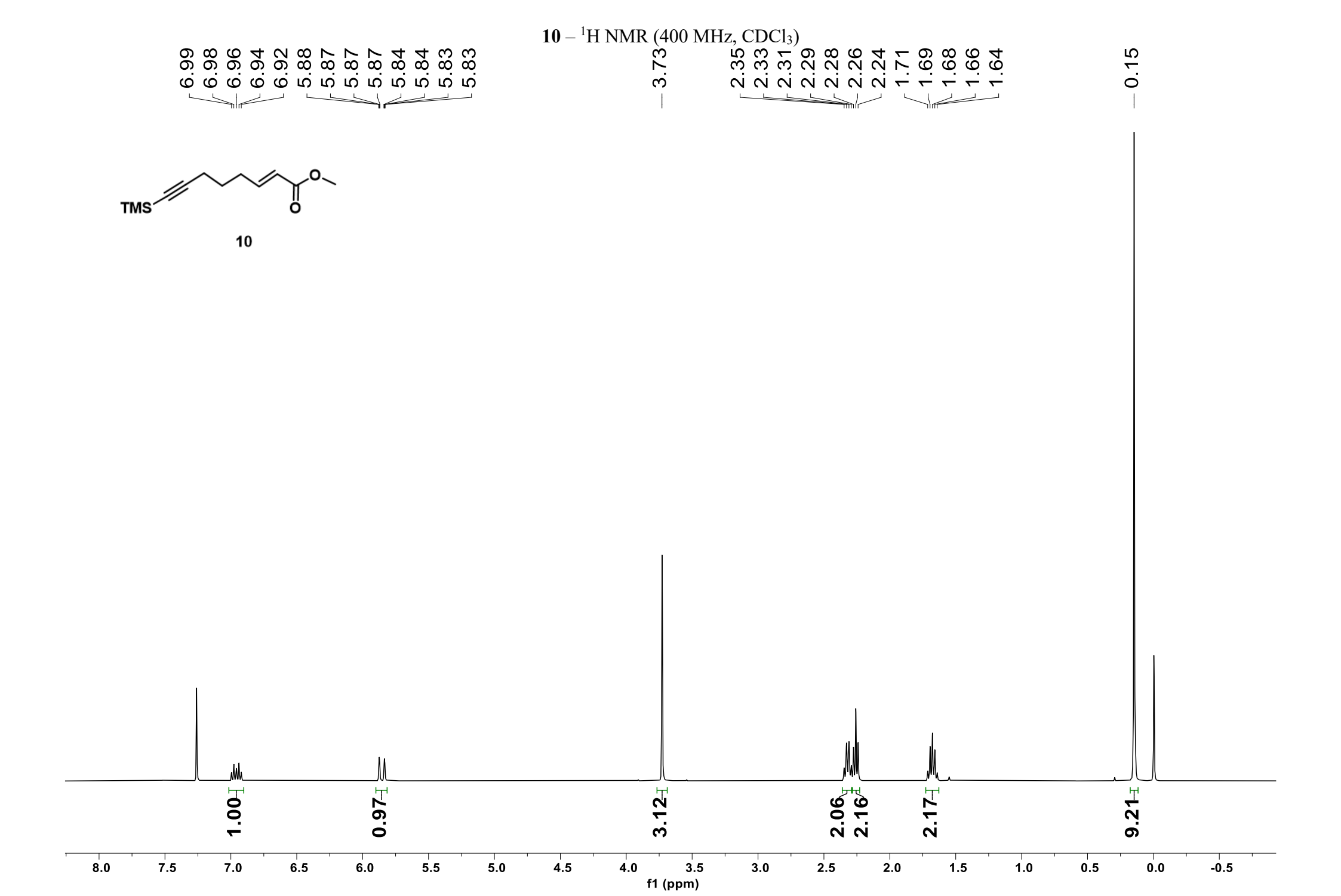
16 – ^{1}H NMR (400 MHz, $CDCl_3$)



16 – ^{13}C NMR (101 MHz, $CDCl_3$)

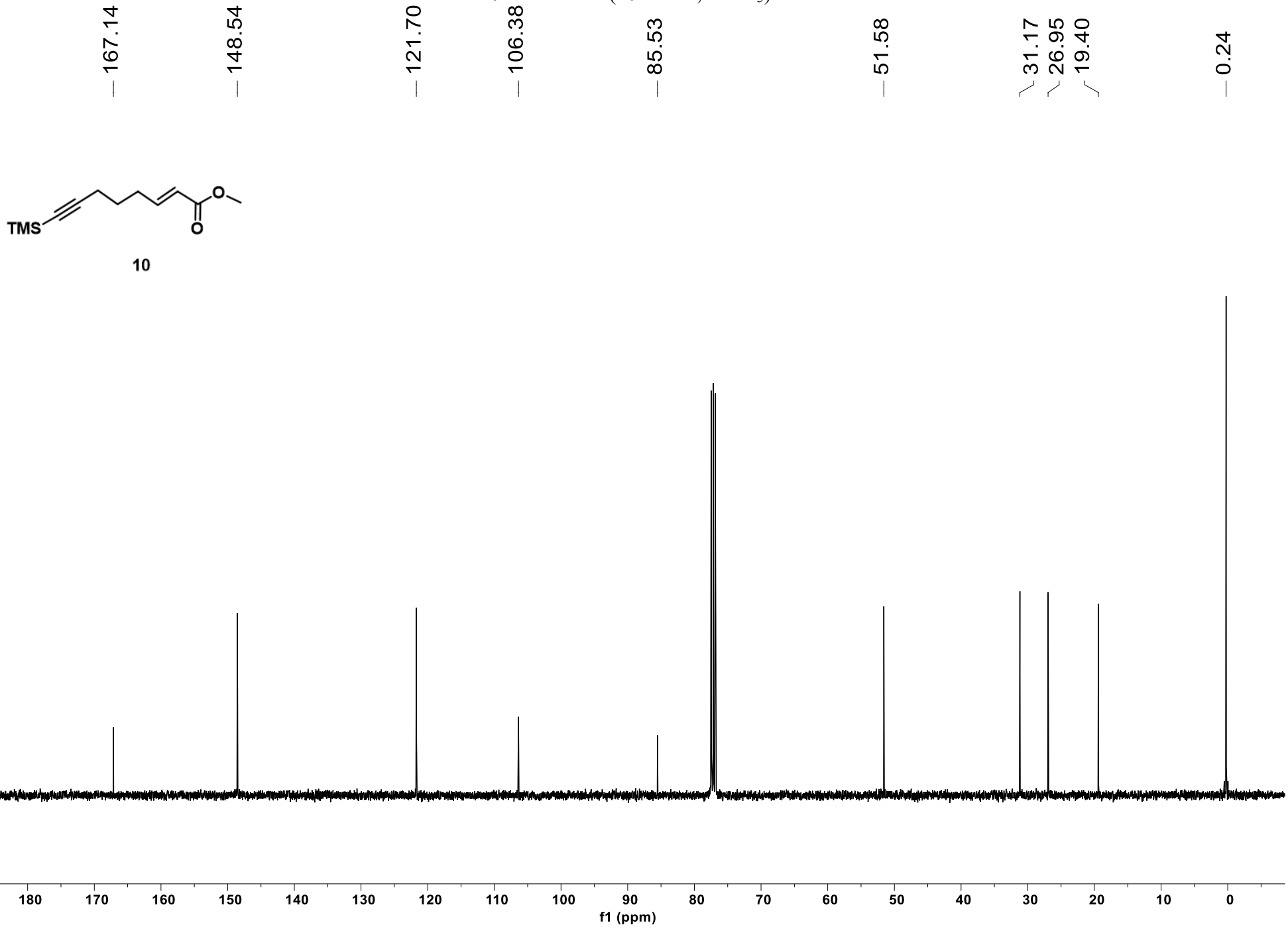


10 – ^{1}H NMR (400 MHz, $CDCl_3$)

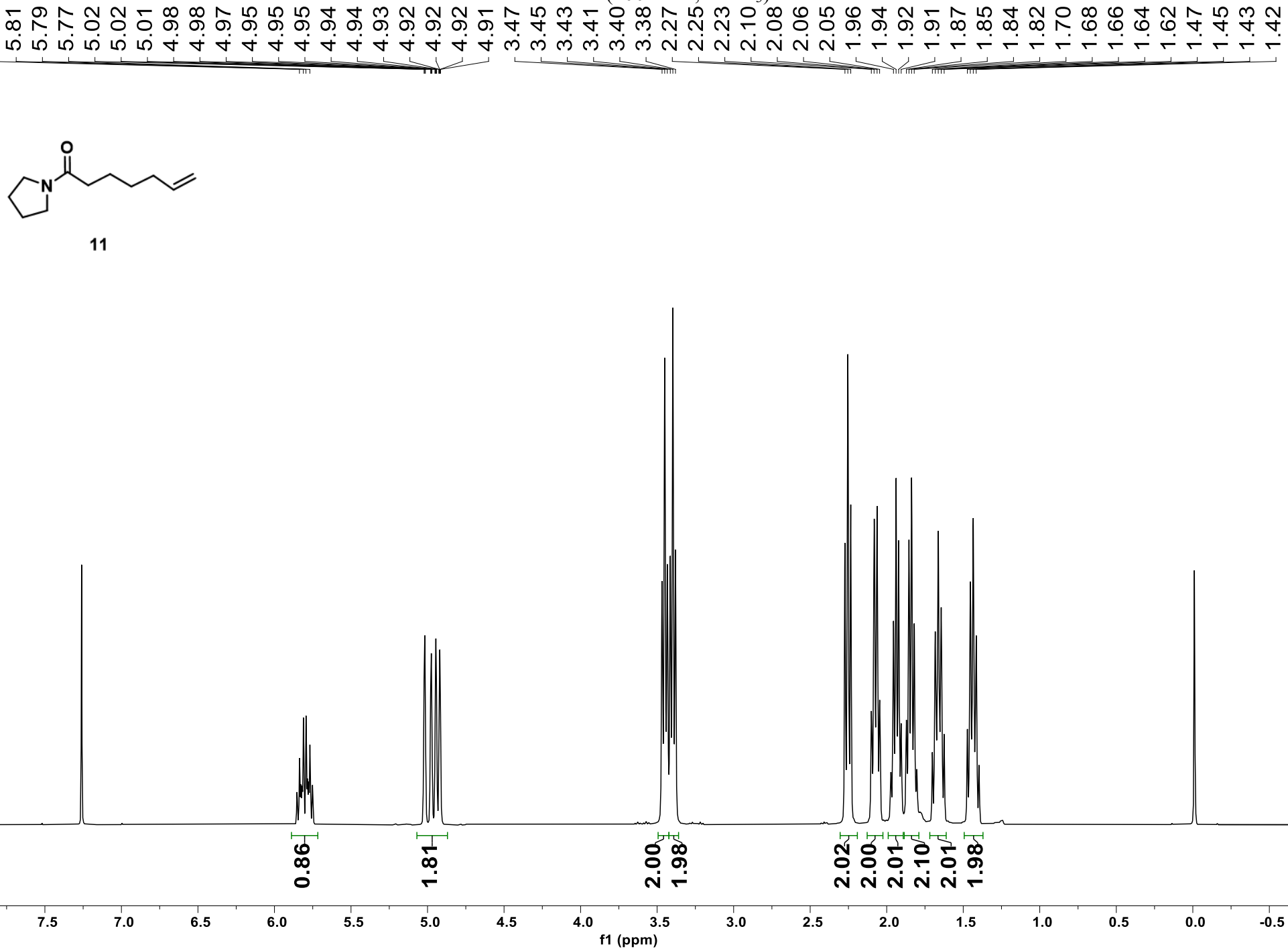


10

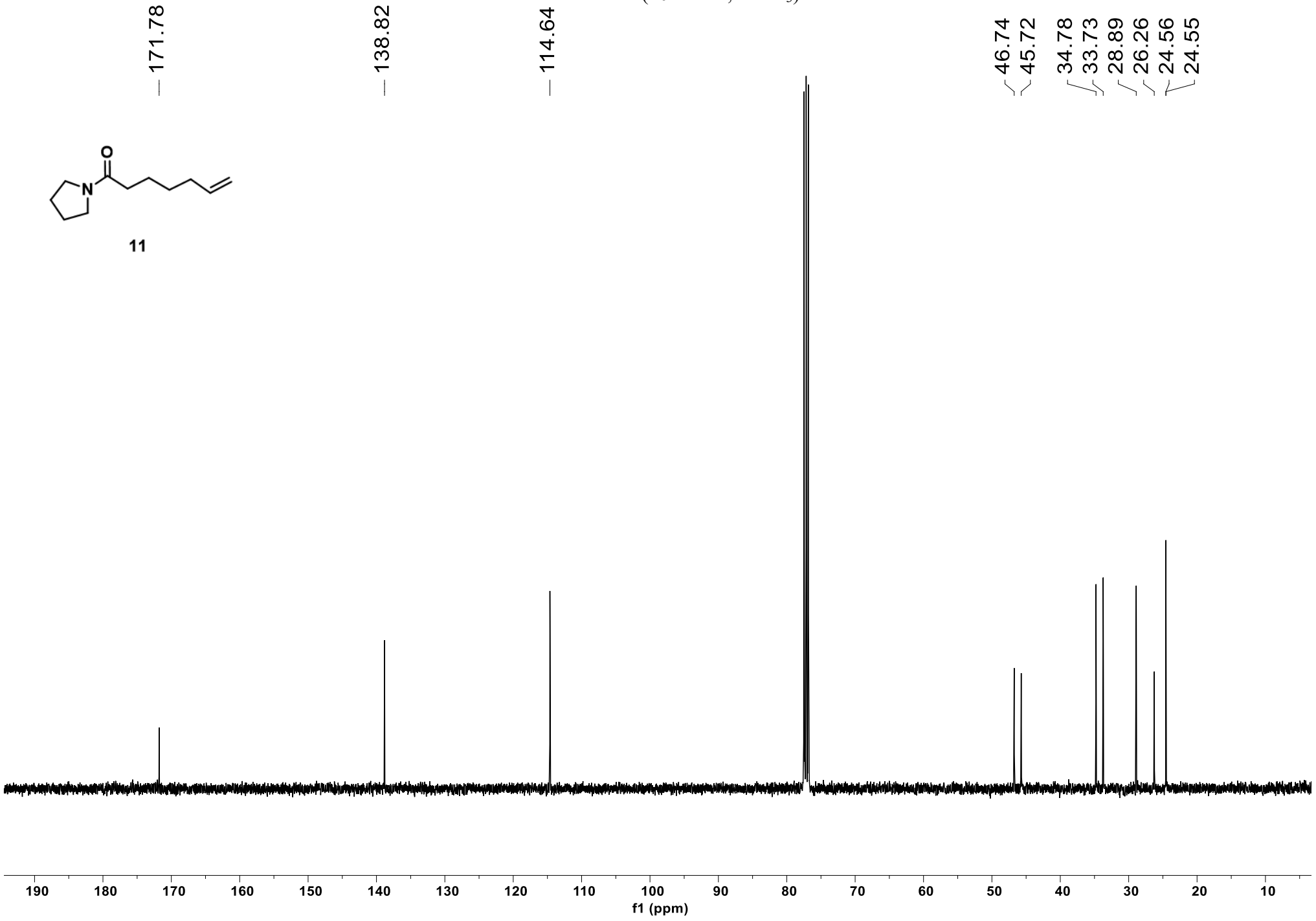
10 – ^{13}C NMR (101 MHz, $CDCl_3$)



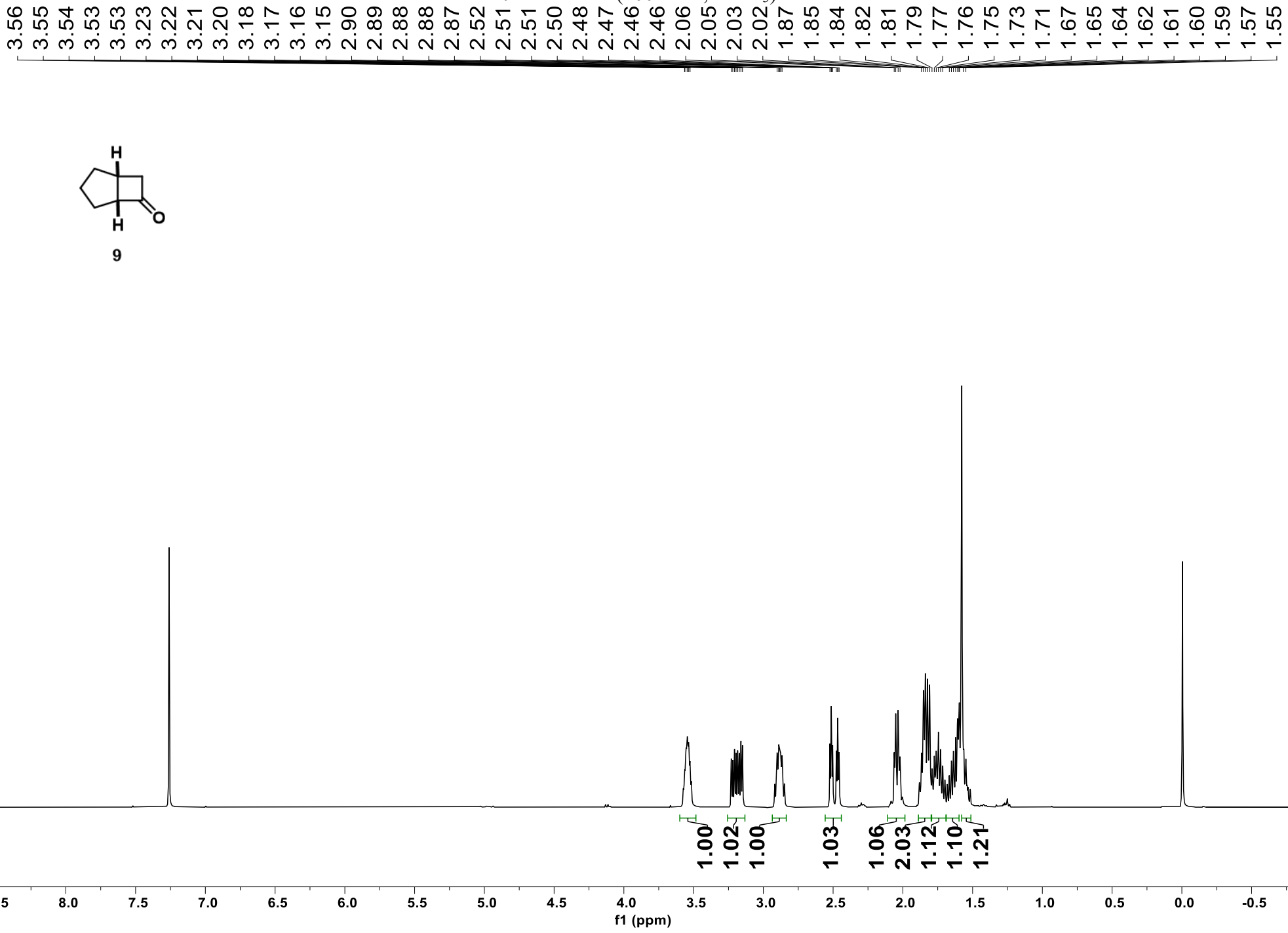
11 – ^{1}H NMR (400 MHz, $CDCl_3$)



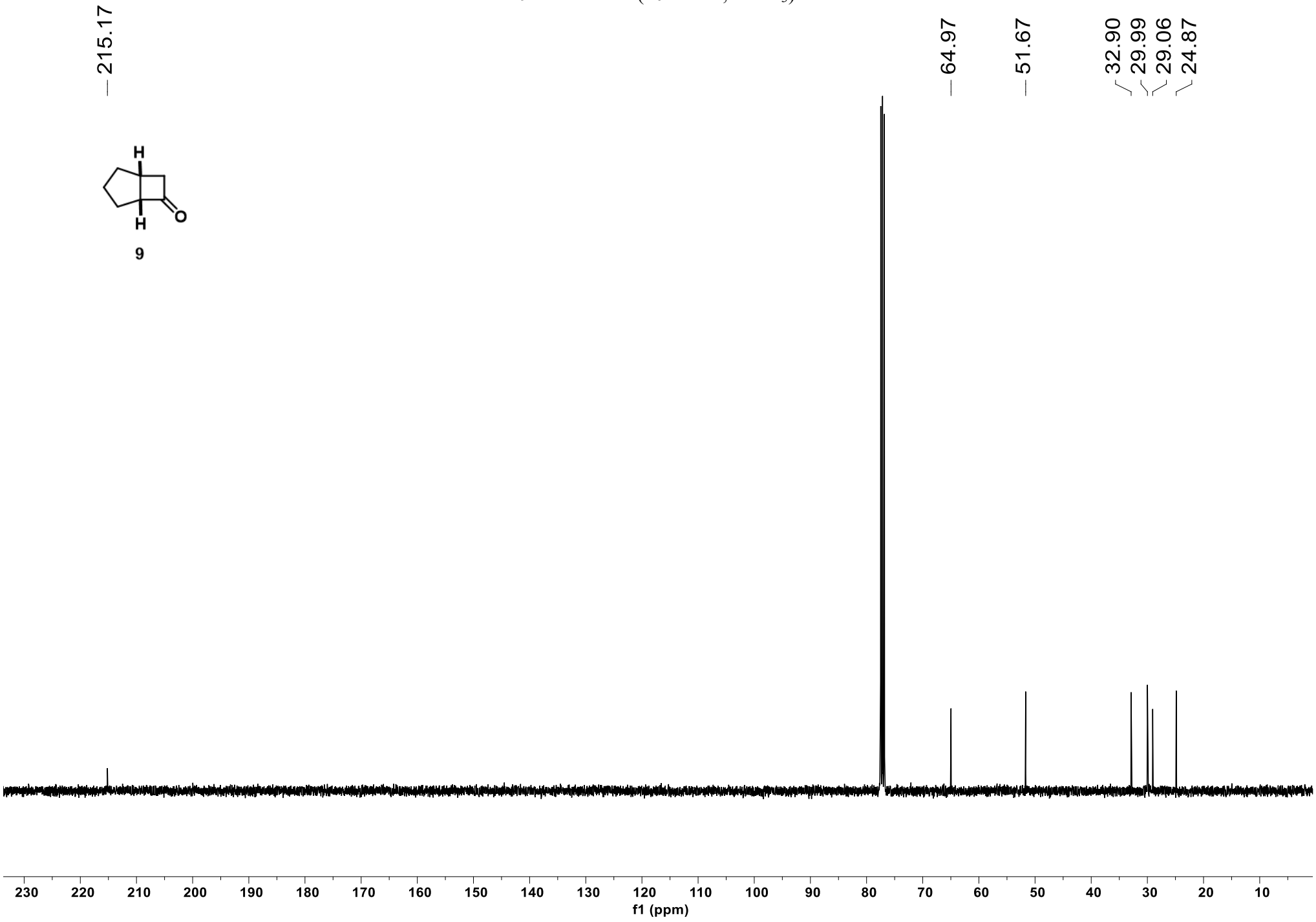
11 – ^{13}C NMR (101 MHz, $CDCl_3$)



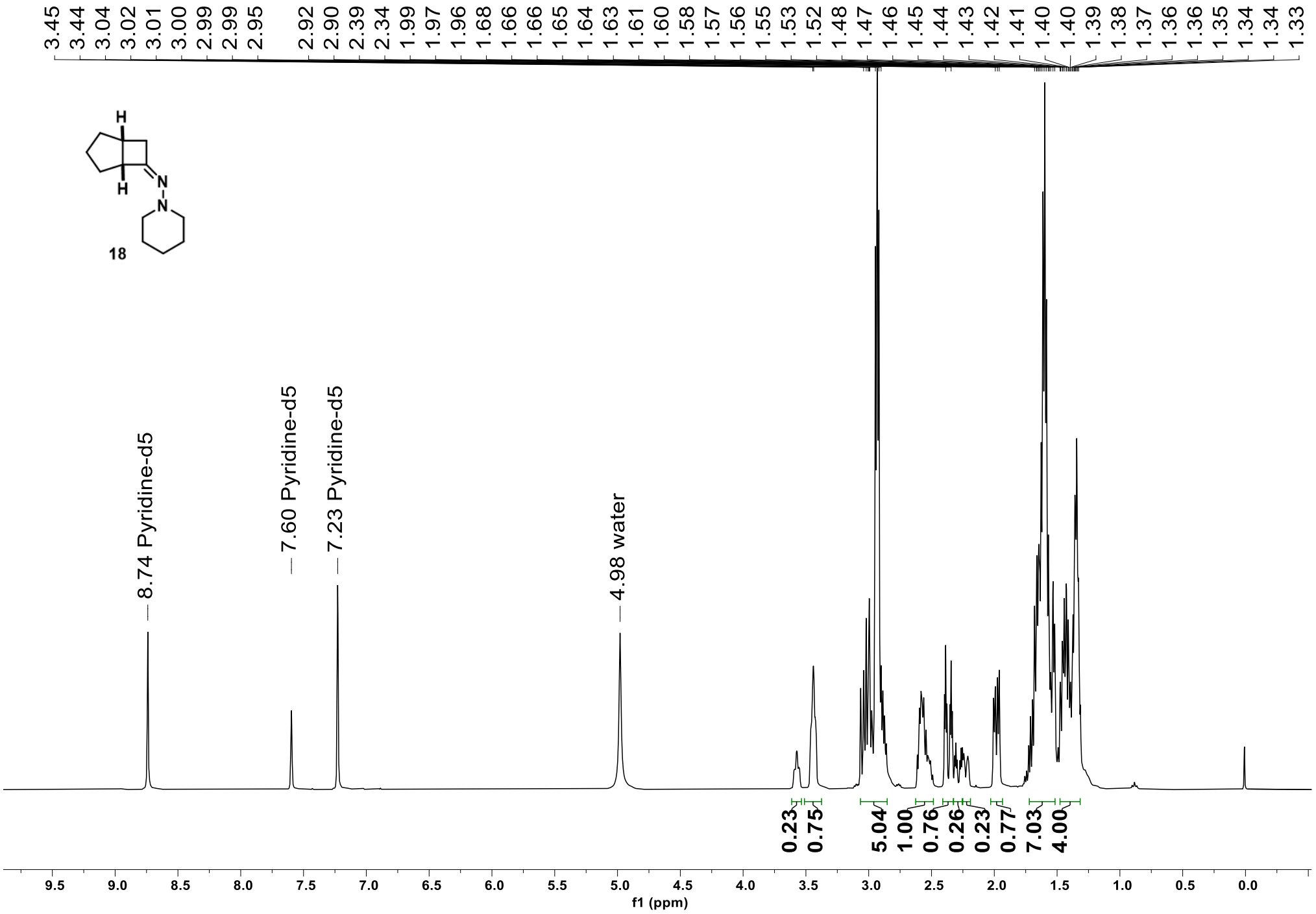
9 – ^{1}H NMR (400 MHz, $CDCl_3$)



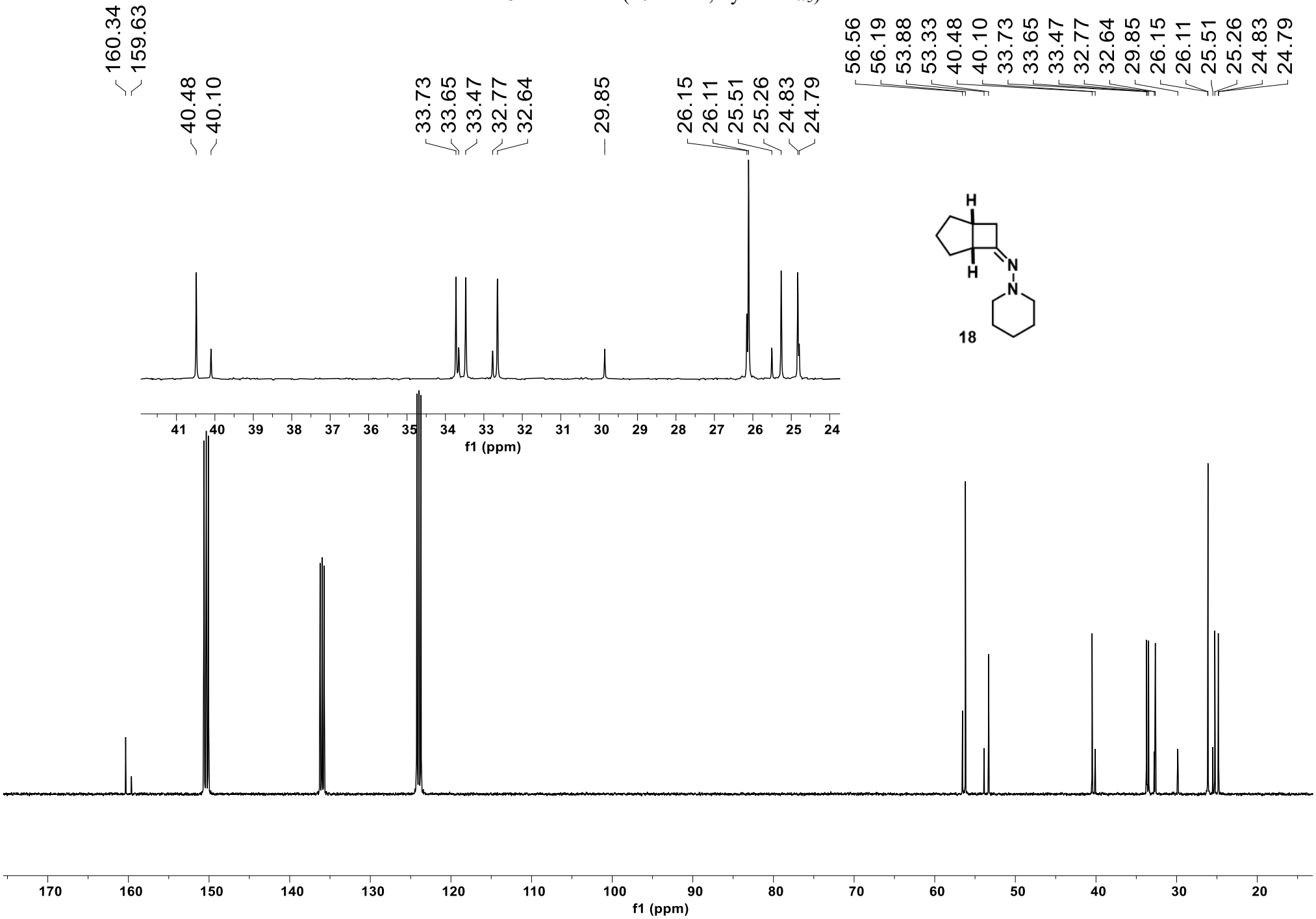
9 – ^{13}C NMR (101 MHz, $CDCl_3$)



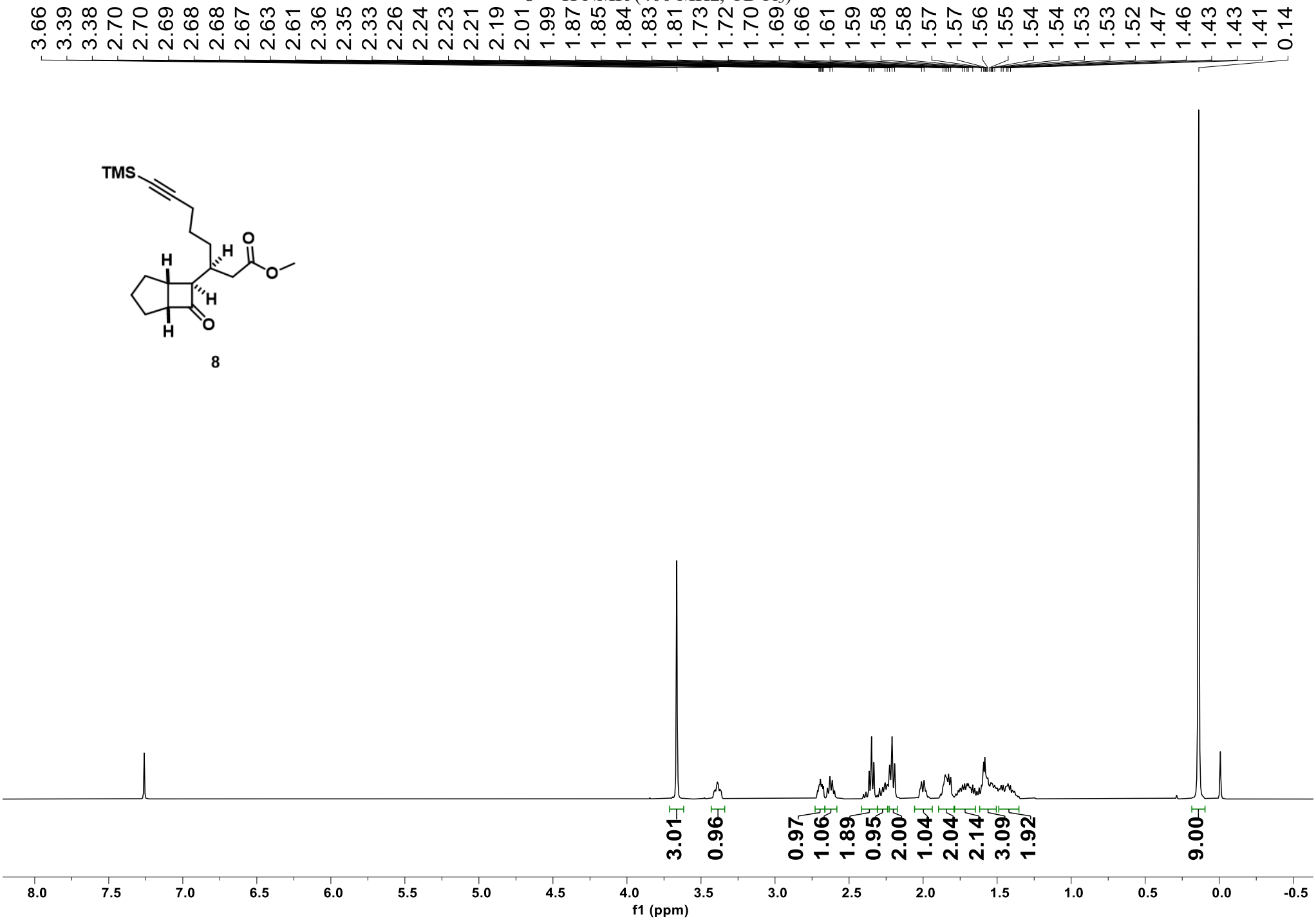
18 – ^{1}H NMR (400 MHz, Pyridine-d_5)



18 – ^{13}C NMR (101 MHz, Pyridine-d_5)

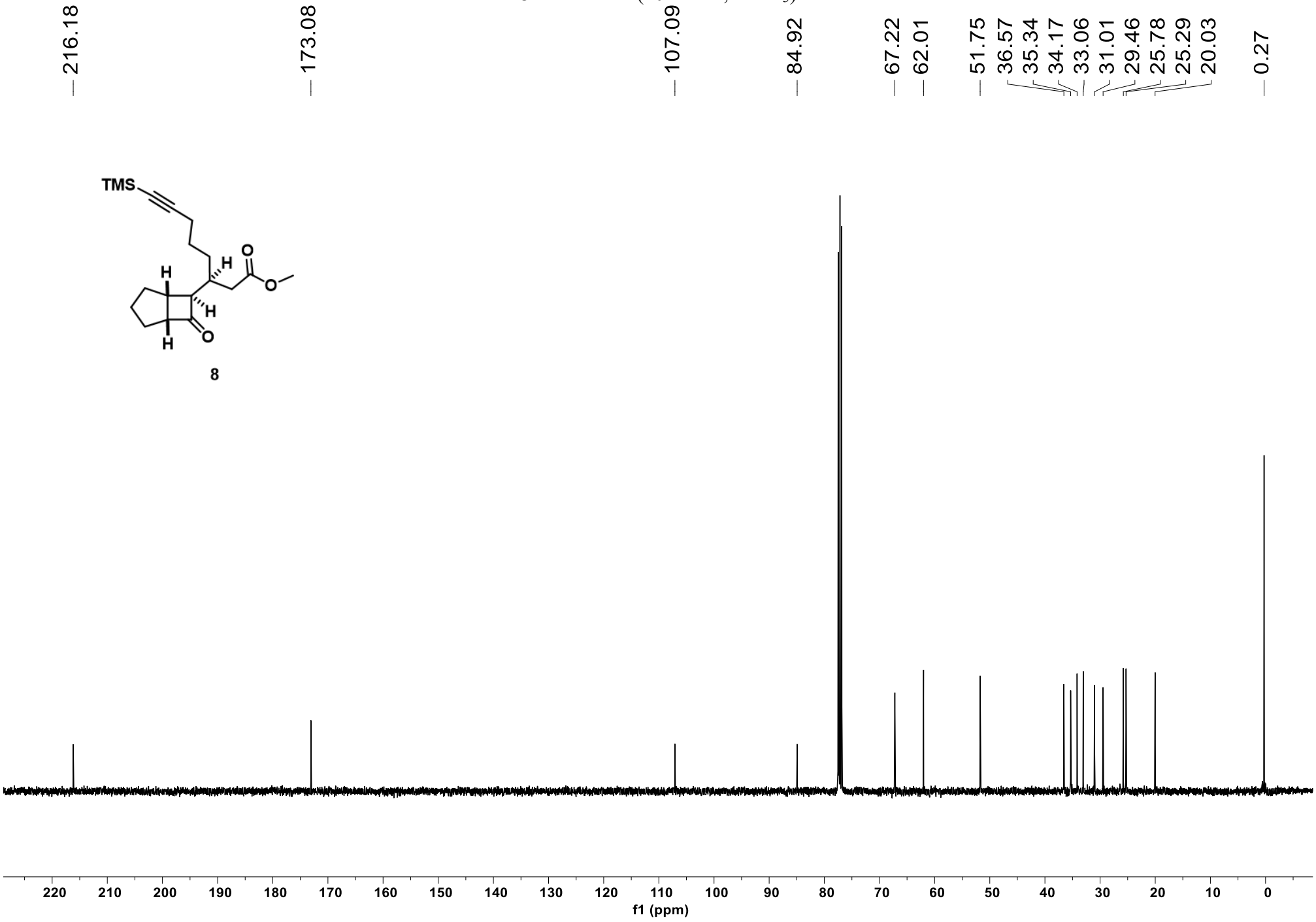


8 – ^{1}H NMR (400 MHz, $CDCl_3$)

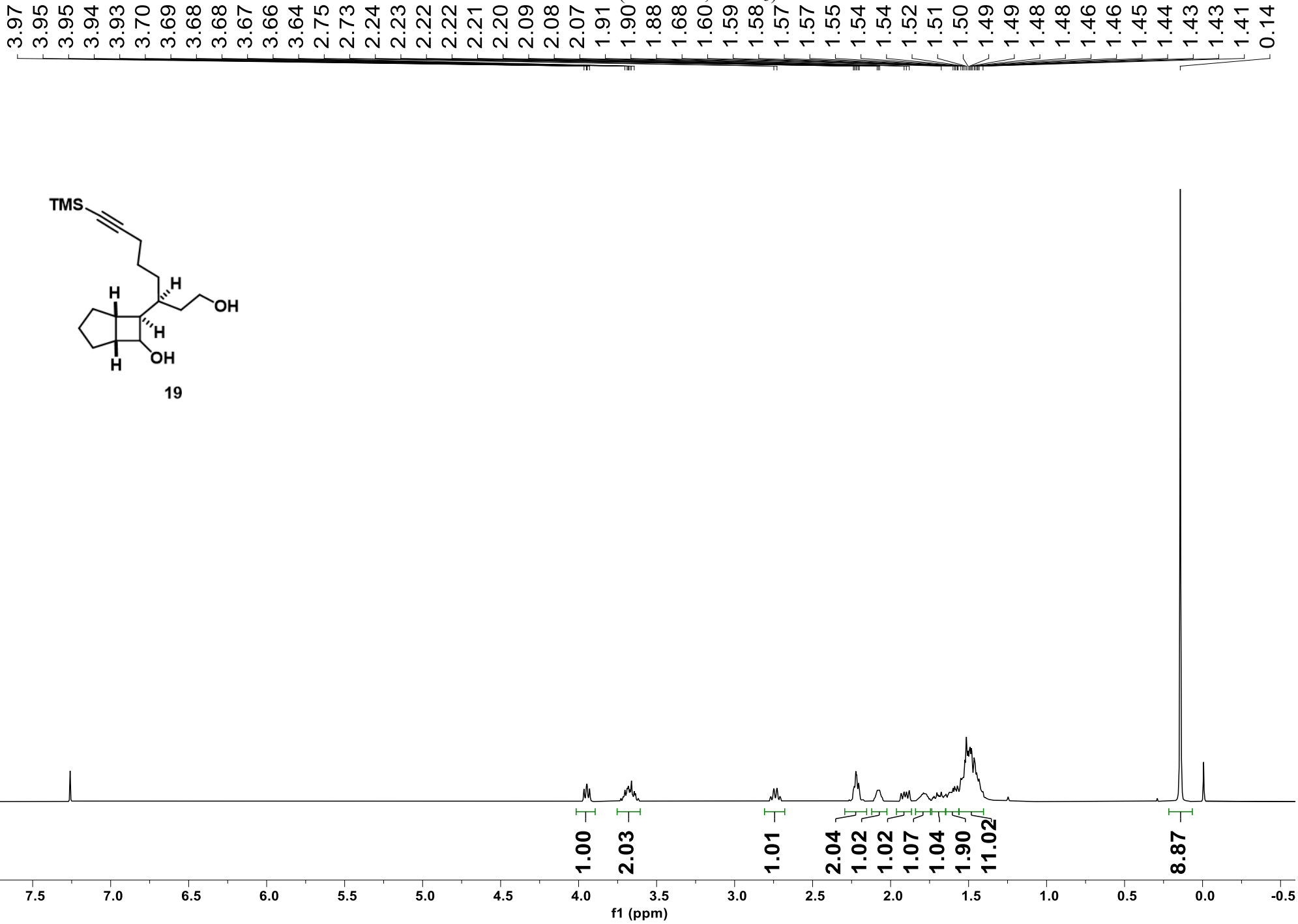


8

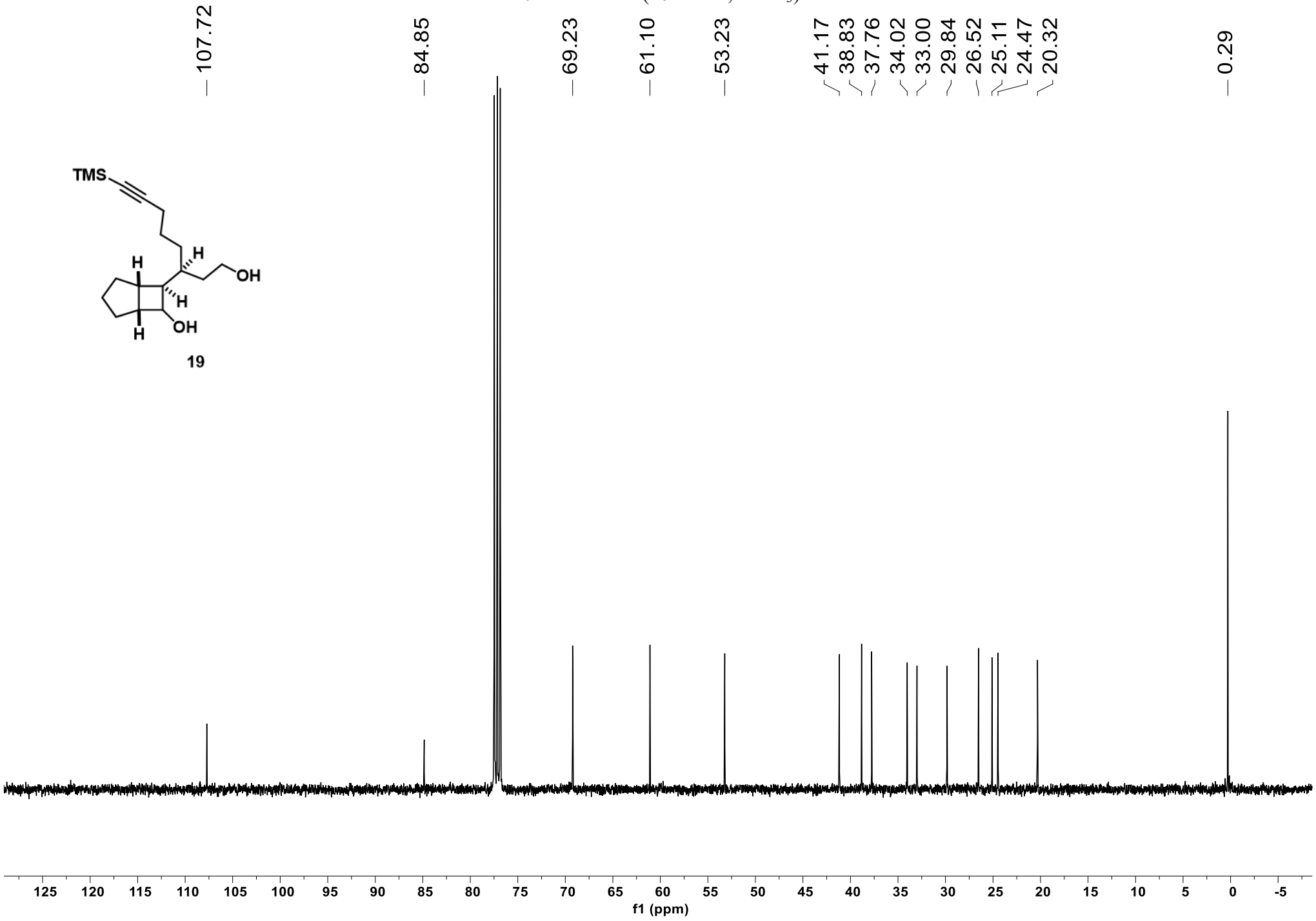
8 – ^{13}C NMR (101 MHz, $CDCl_3$)



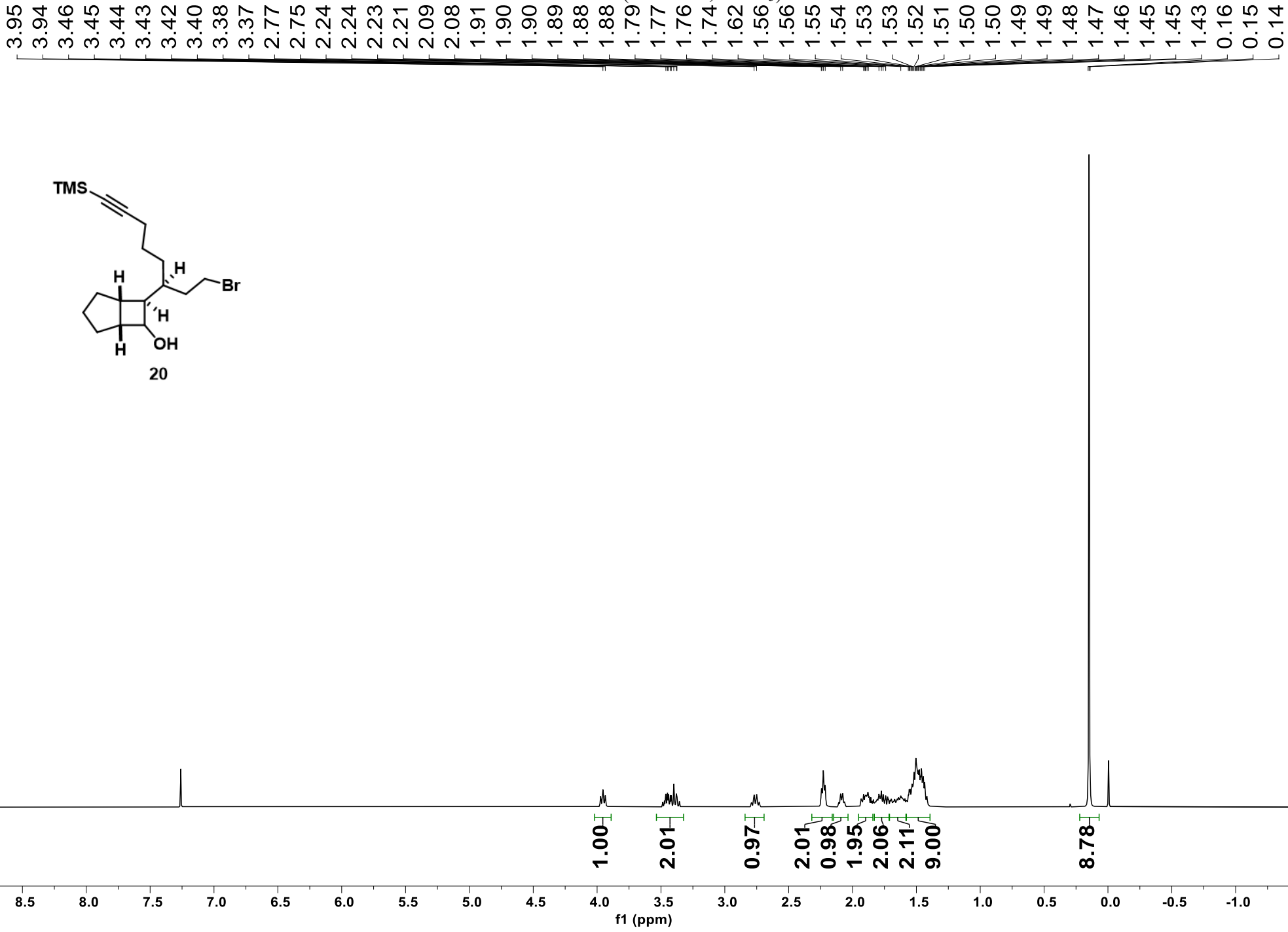
19 – ^{1}H NMR (400 MHz, $CDCl_3$)



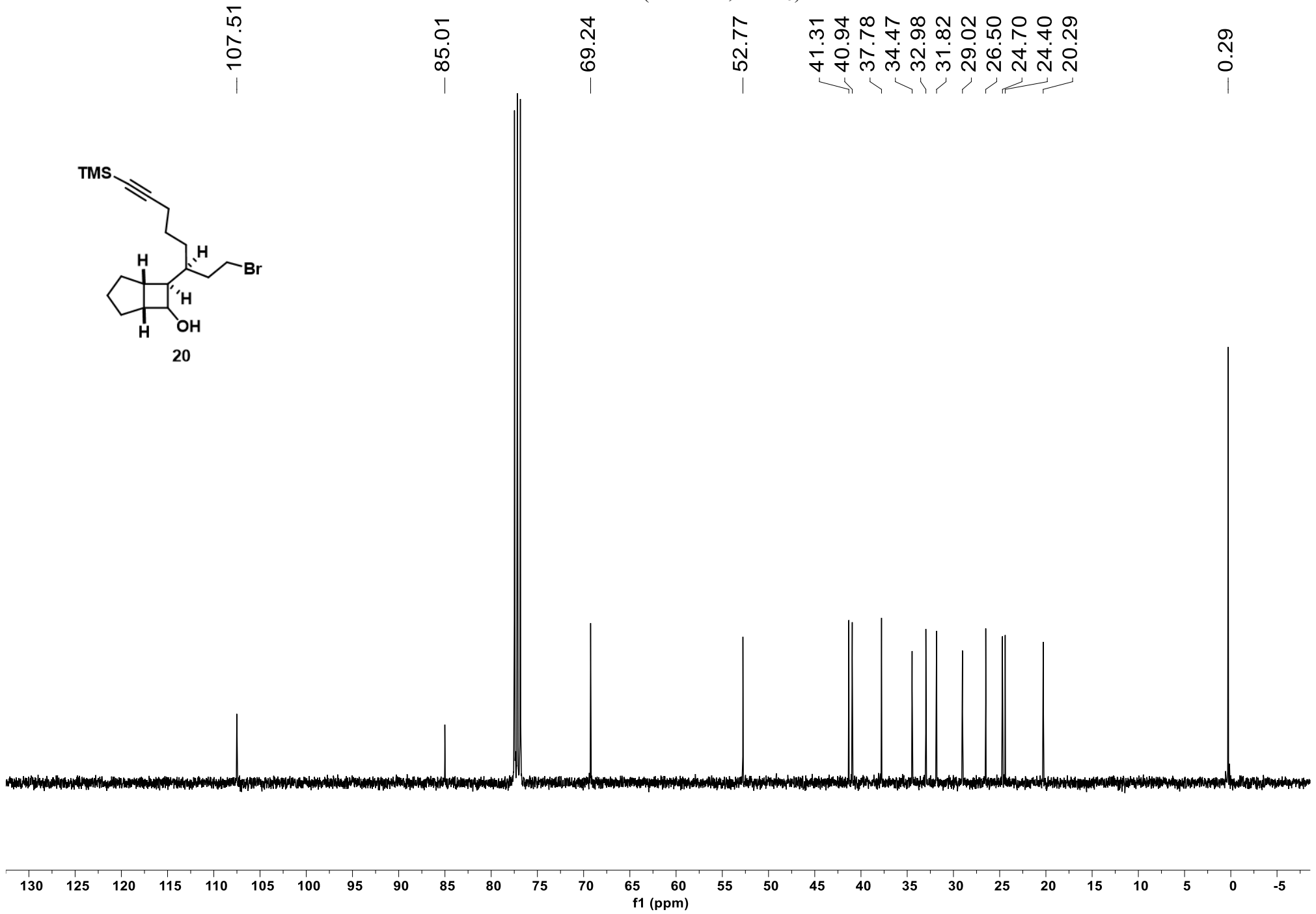
19 – ^{13}C NMR (101 MHz, $CDCl_3$)



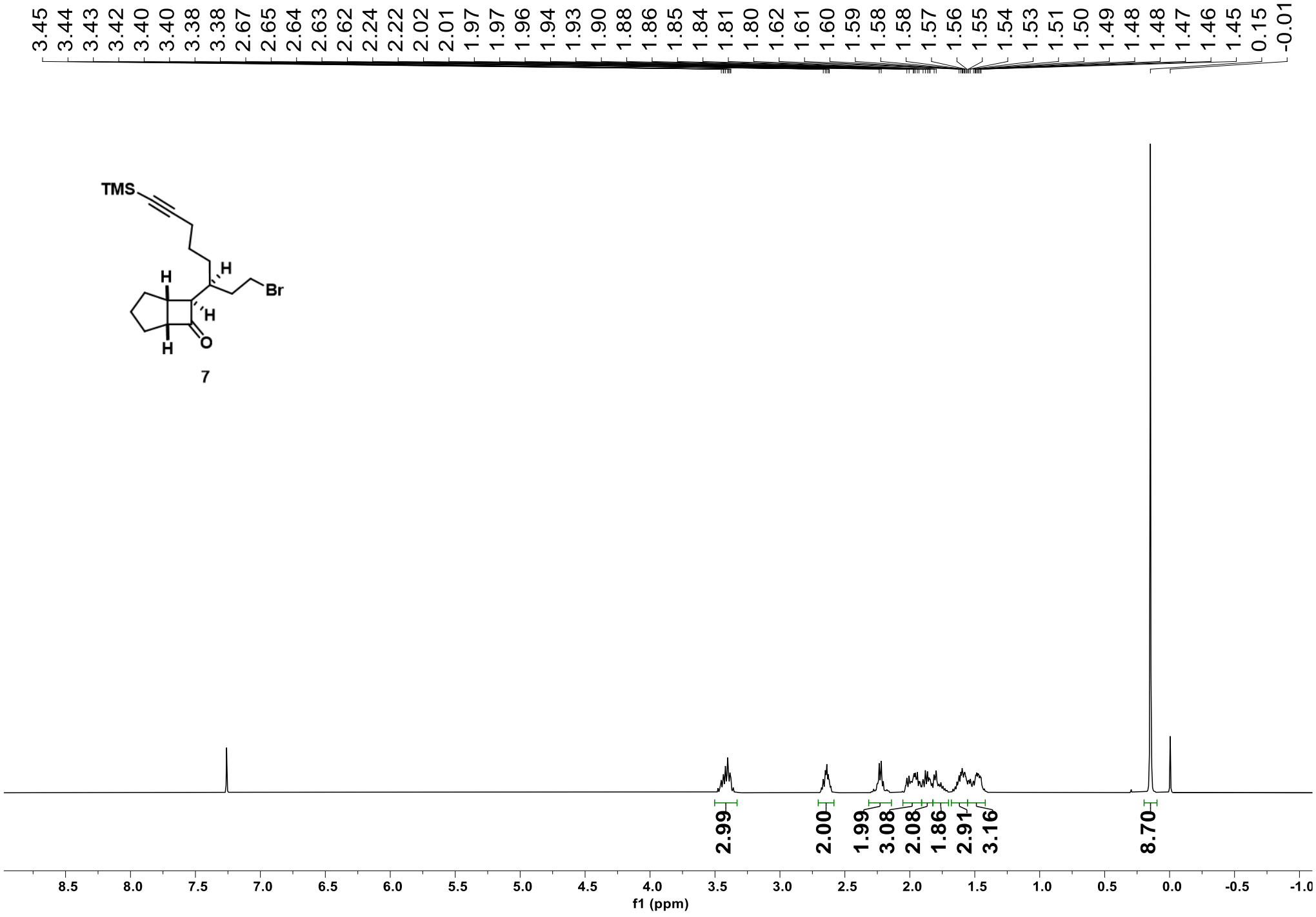
20 – ^{1}H NMR (400 MHz, $CDCl_3$)



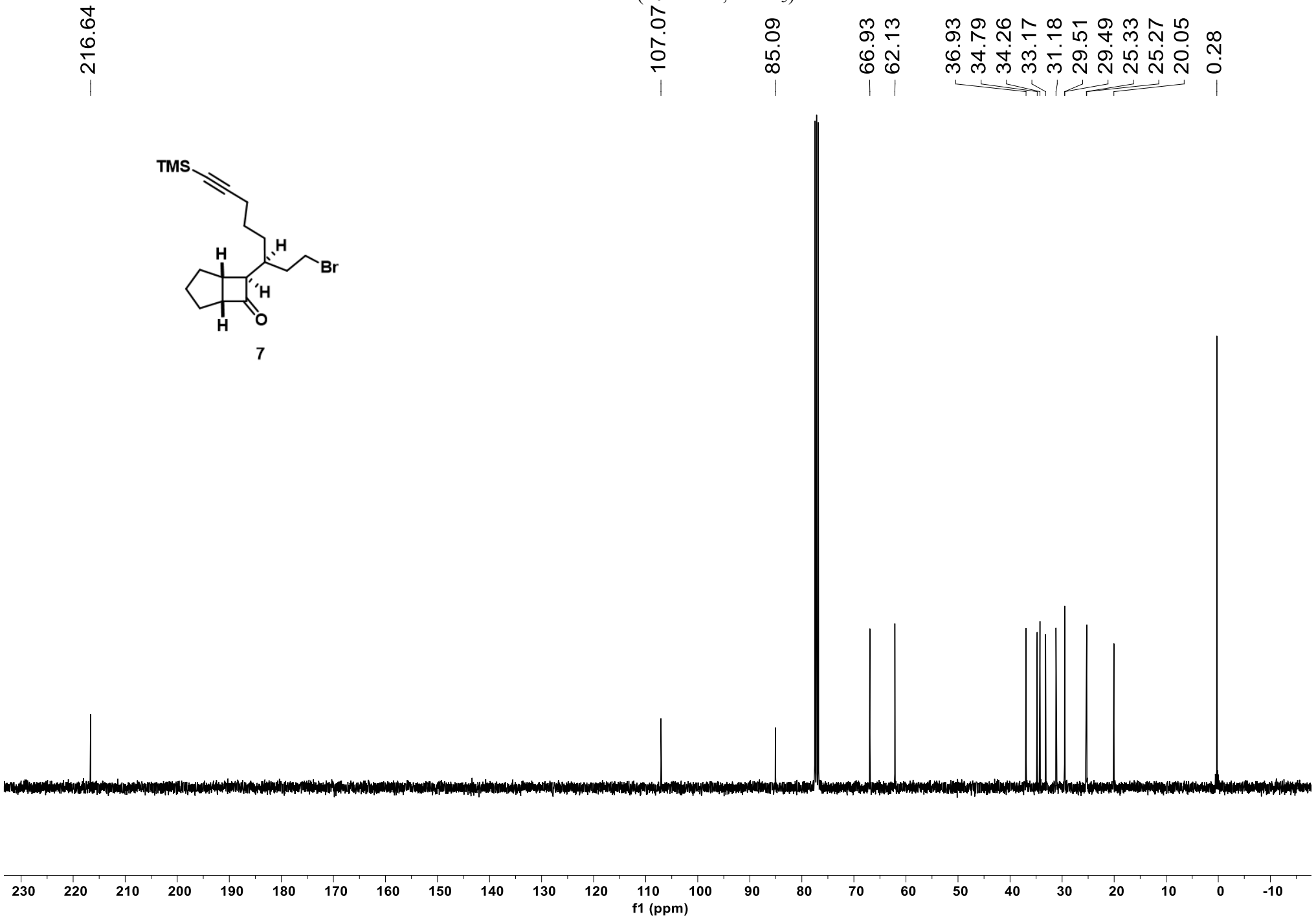
20 – ^{13}C NMR (101 MHz, $CDCl_3$)



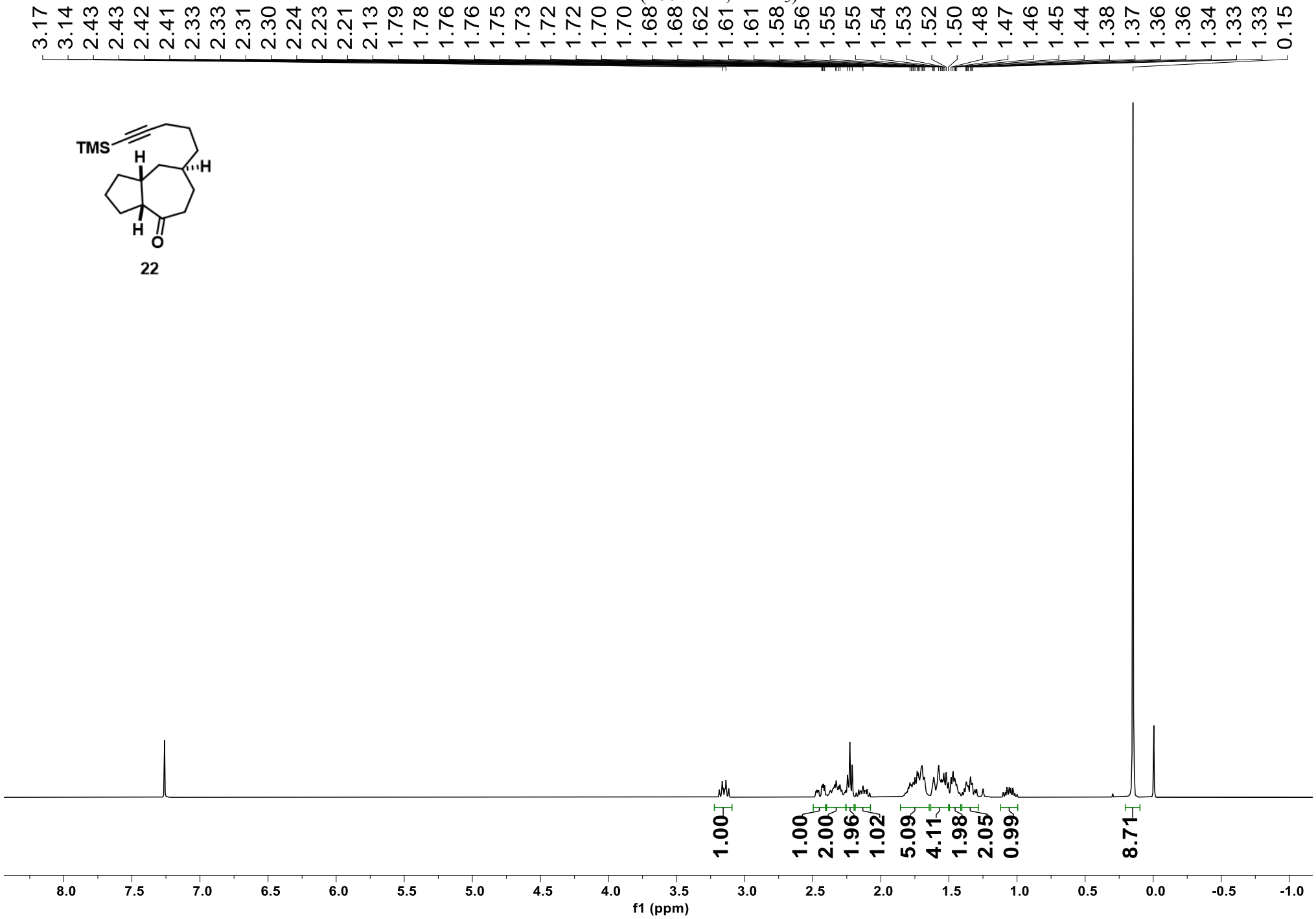
7 – ^{1}H NMR (400 MHz, $CDCl_3$)



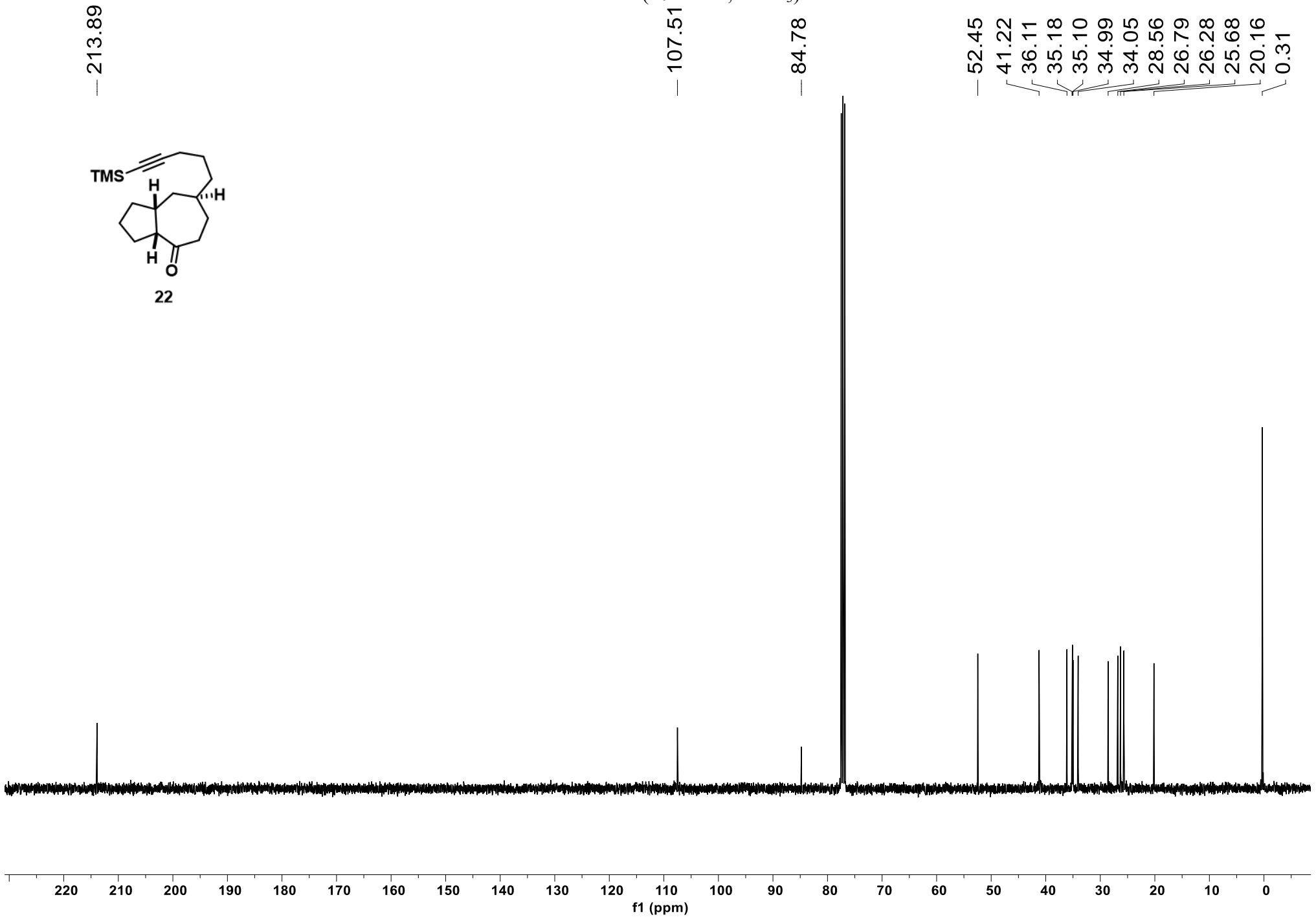
7 – ^{13}C NMR (101 MHz, $CDCl_3$)



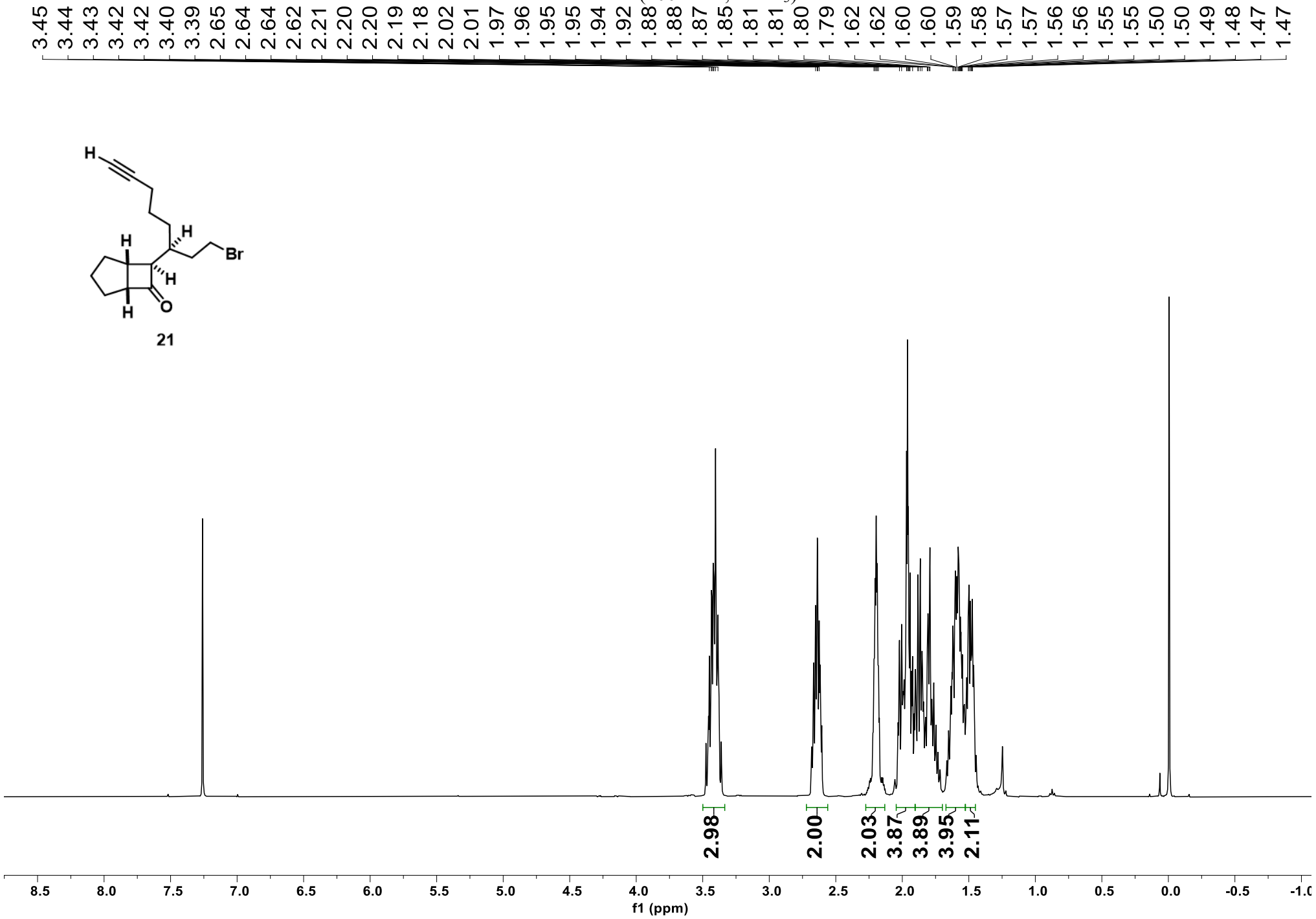
22 – ^{1}H NMR (400 MHz, $CDCl_3$)



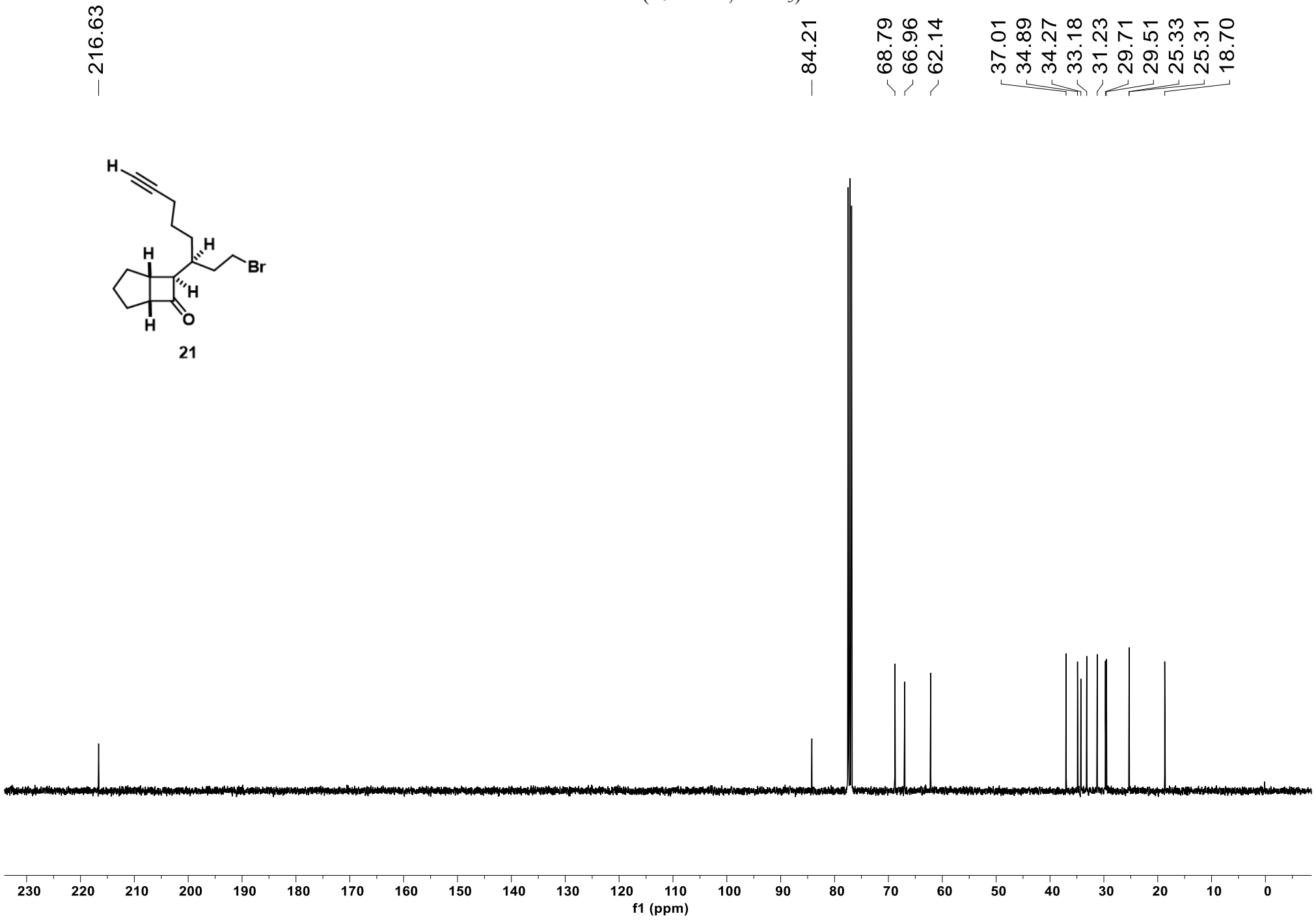
22 – ^{13}C NMR (101 MHz, $CDCl_3$)



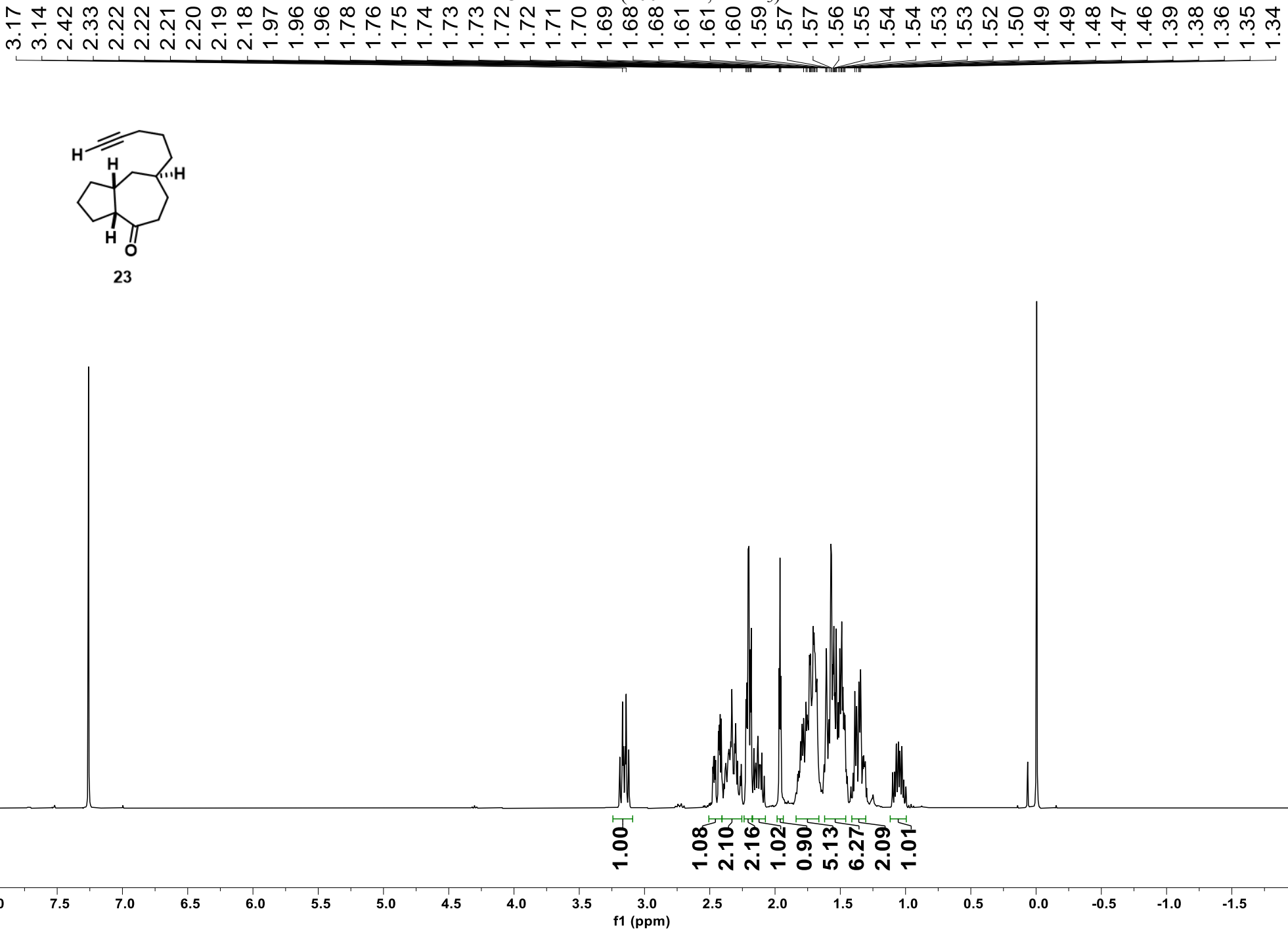
21 – ^{1}H NMR (400 MHz, $CDCl_3$)



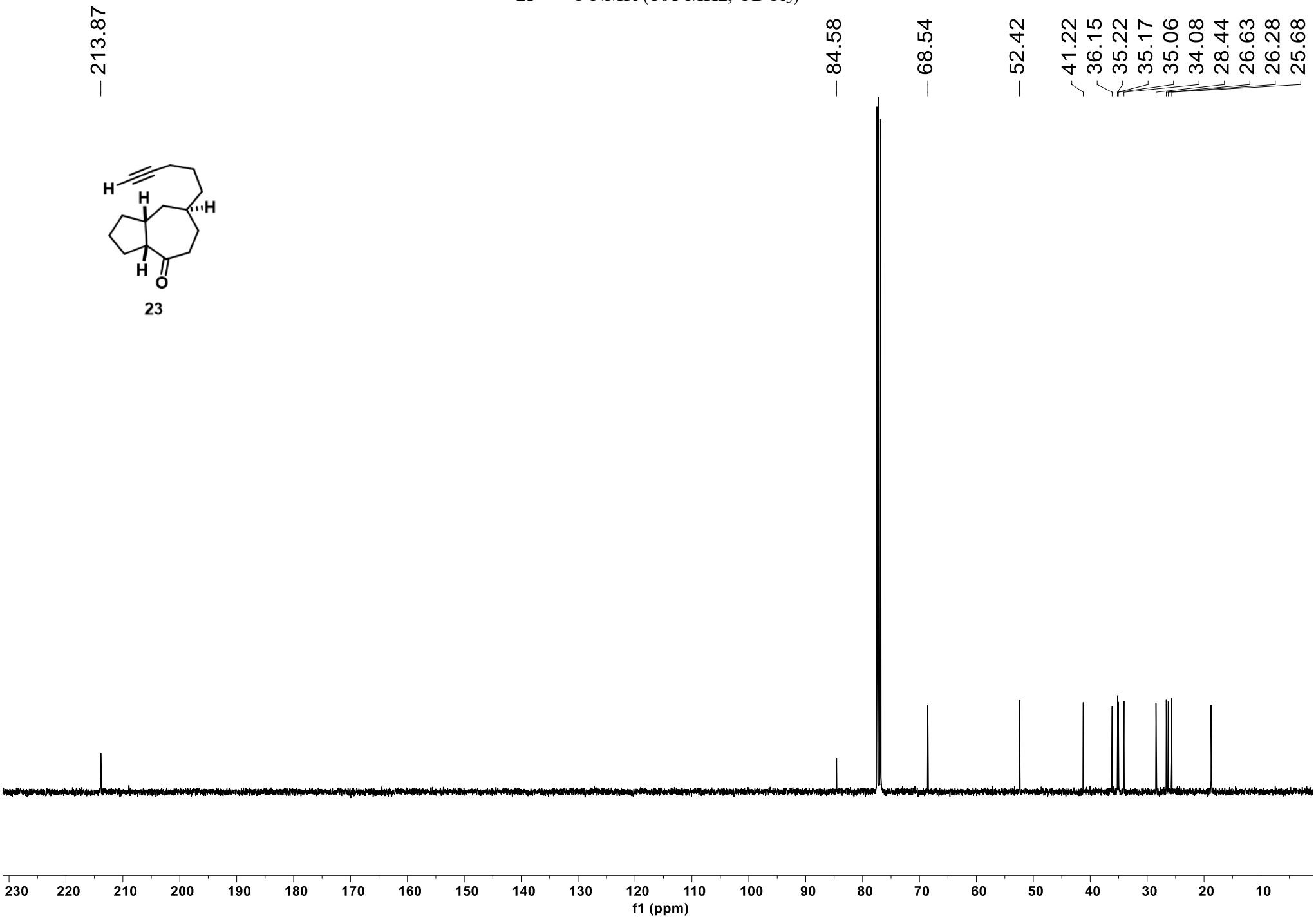
21 – ^{13}C NMR (101 MHz, $CDCl_3$)



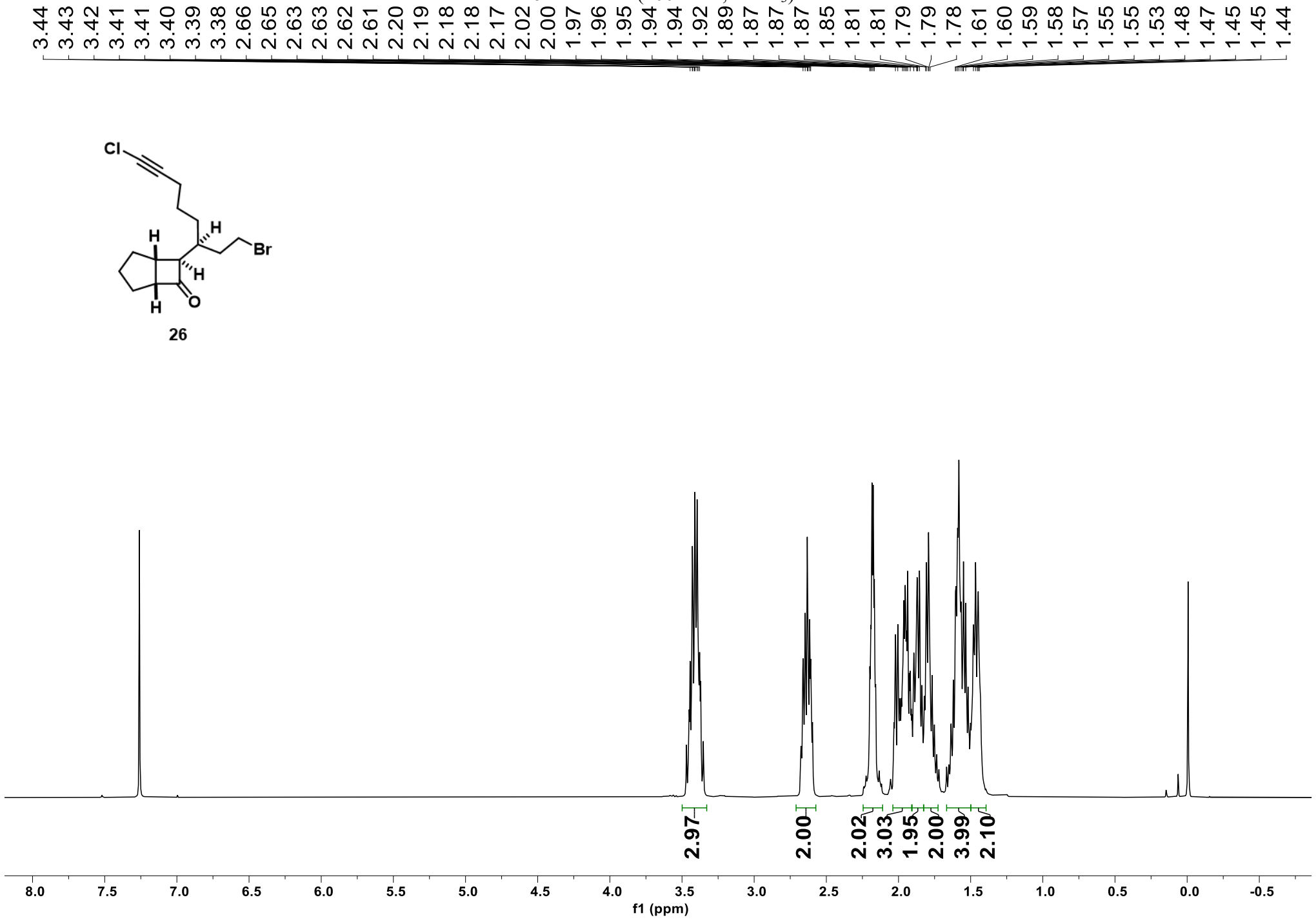
23 – ^{1}H NMR (400 MHz, $CDCl_3$)



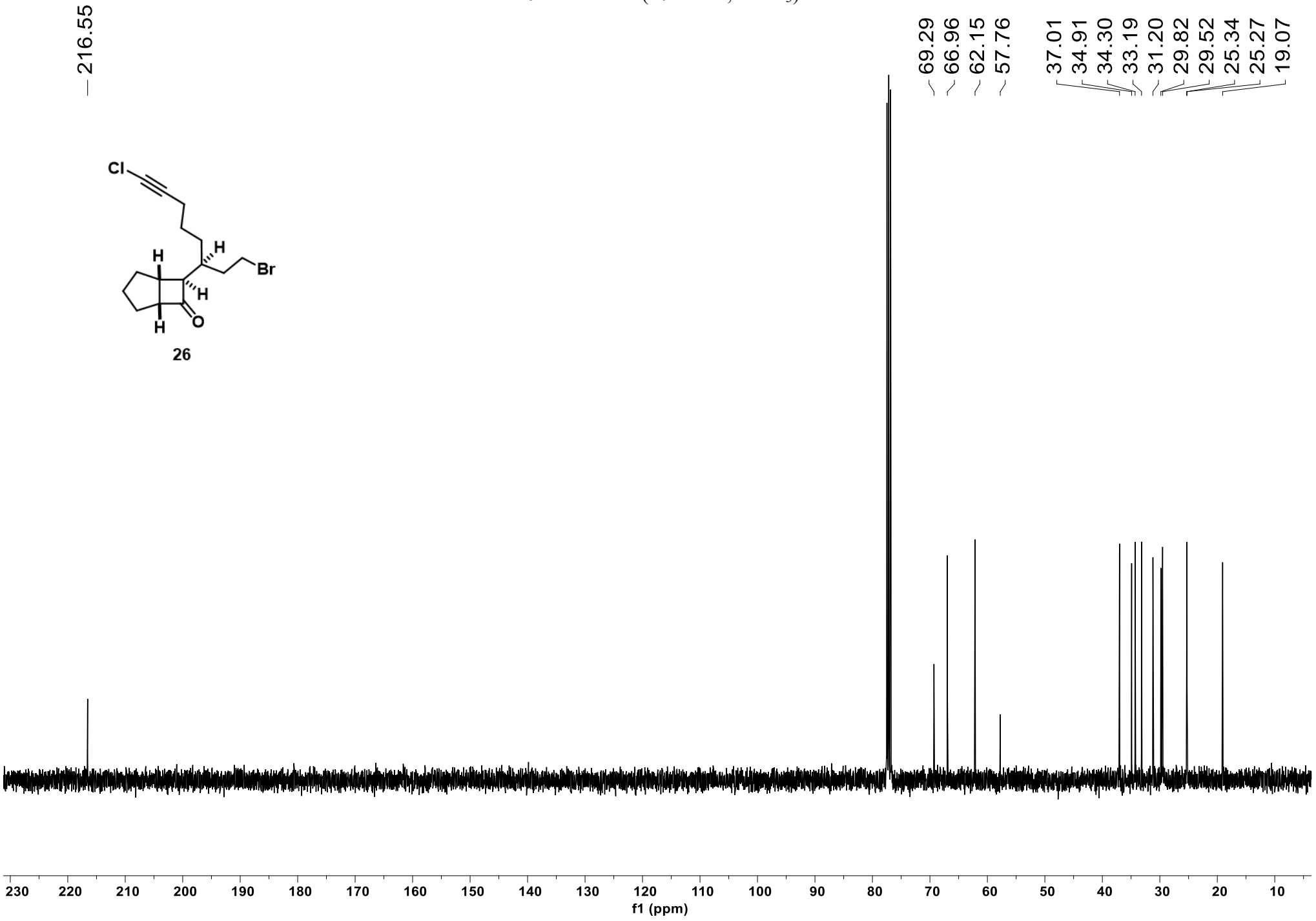
23 – ^{13}C NMR (101 MHz, $CDCl_3$)



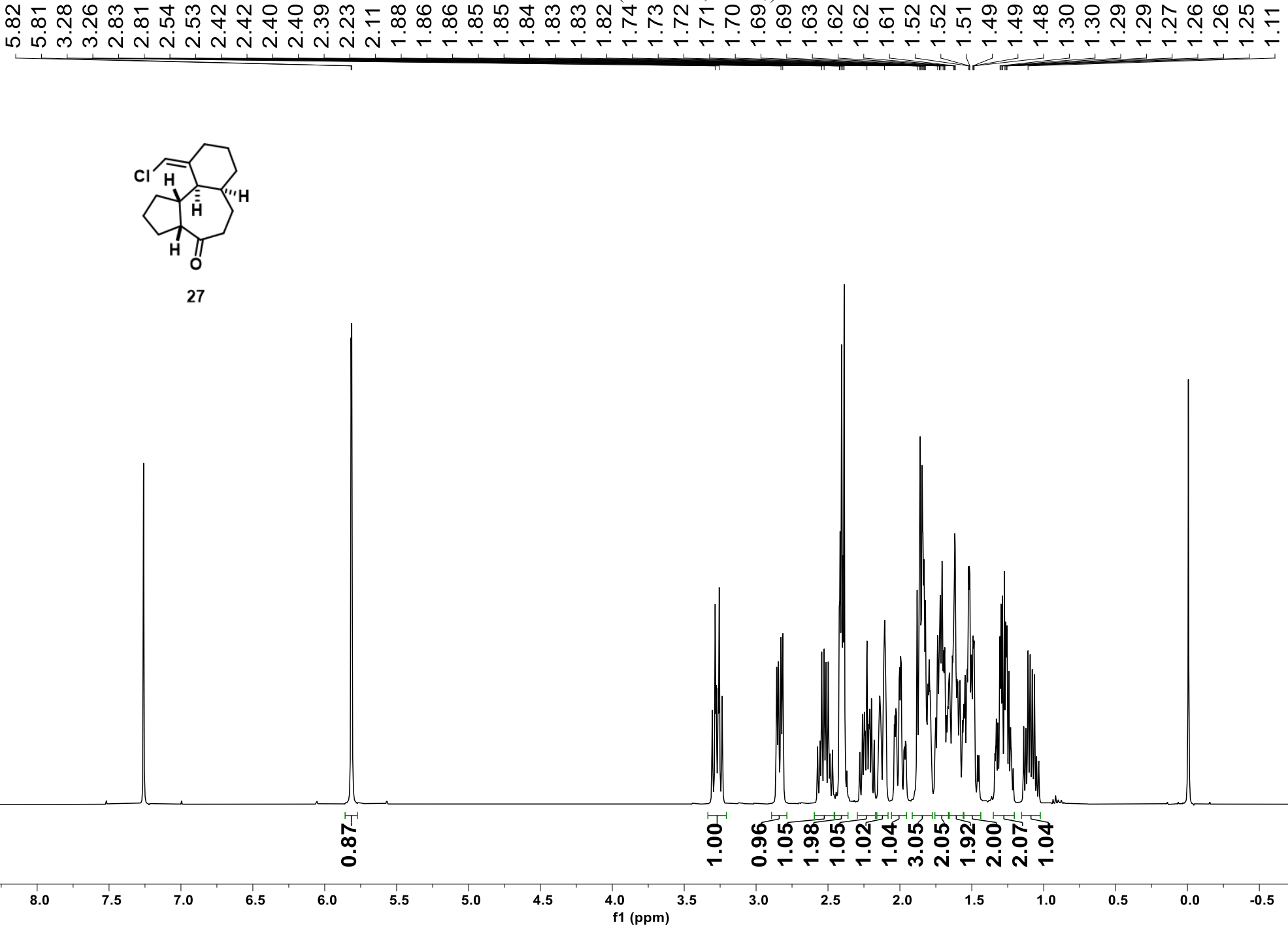
26– ^{1}H NMR (400 MHz, $CDCl_3$)



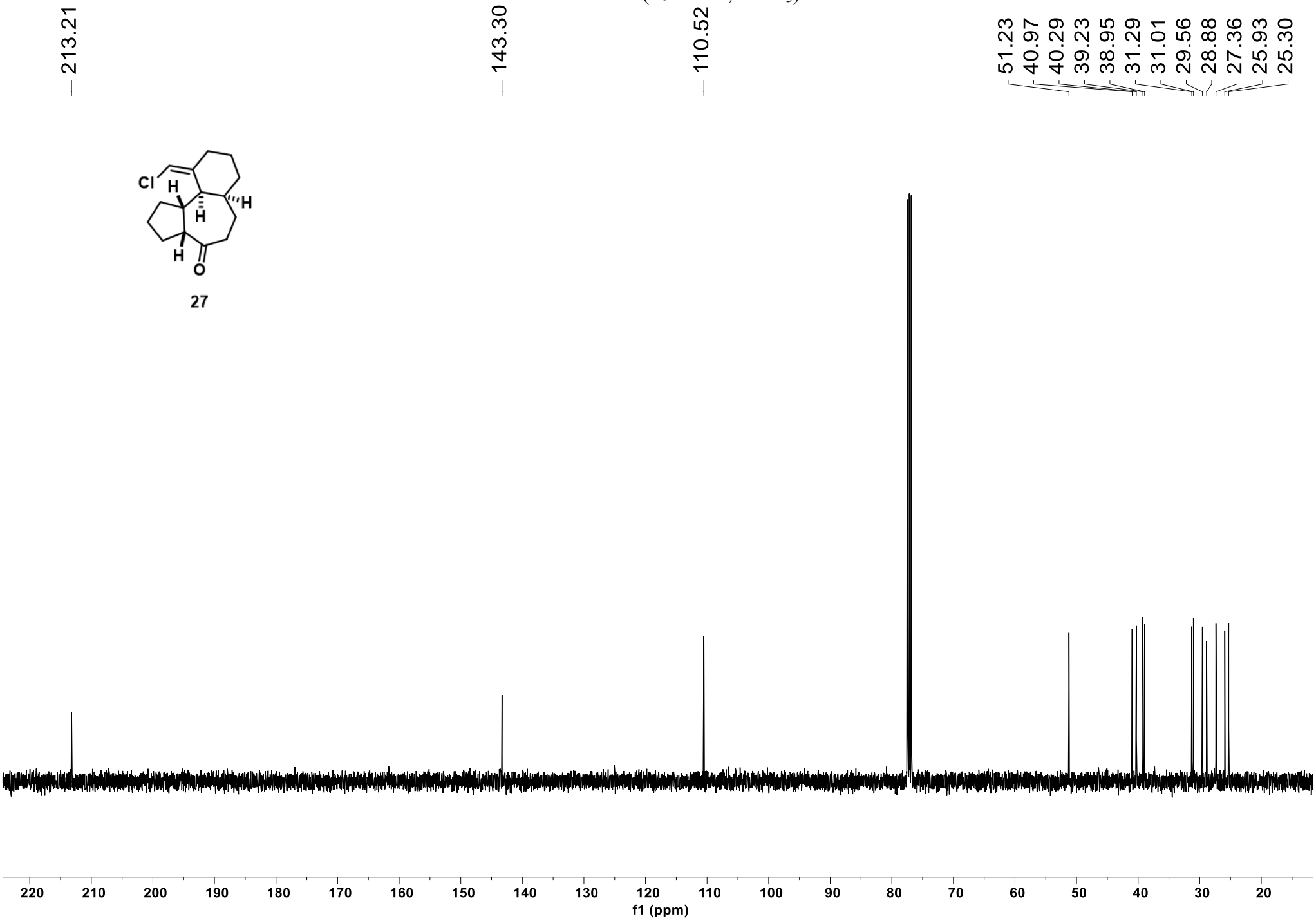
26 – ^{13}C NMR (101 MHz, $CDCl_3$)



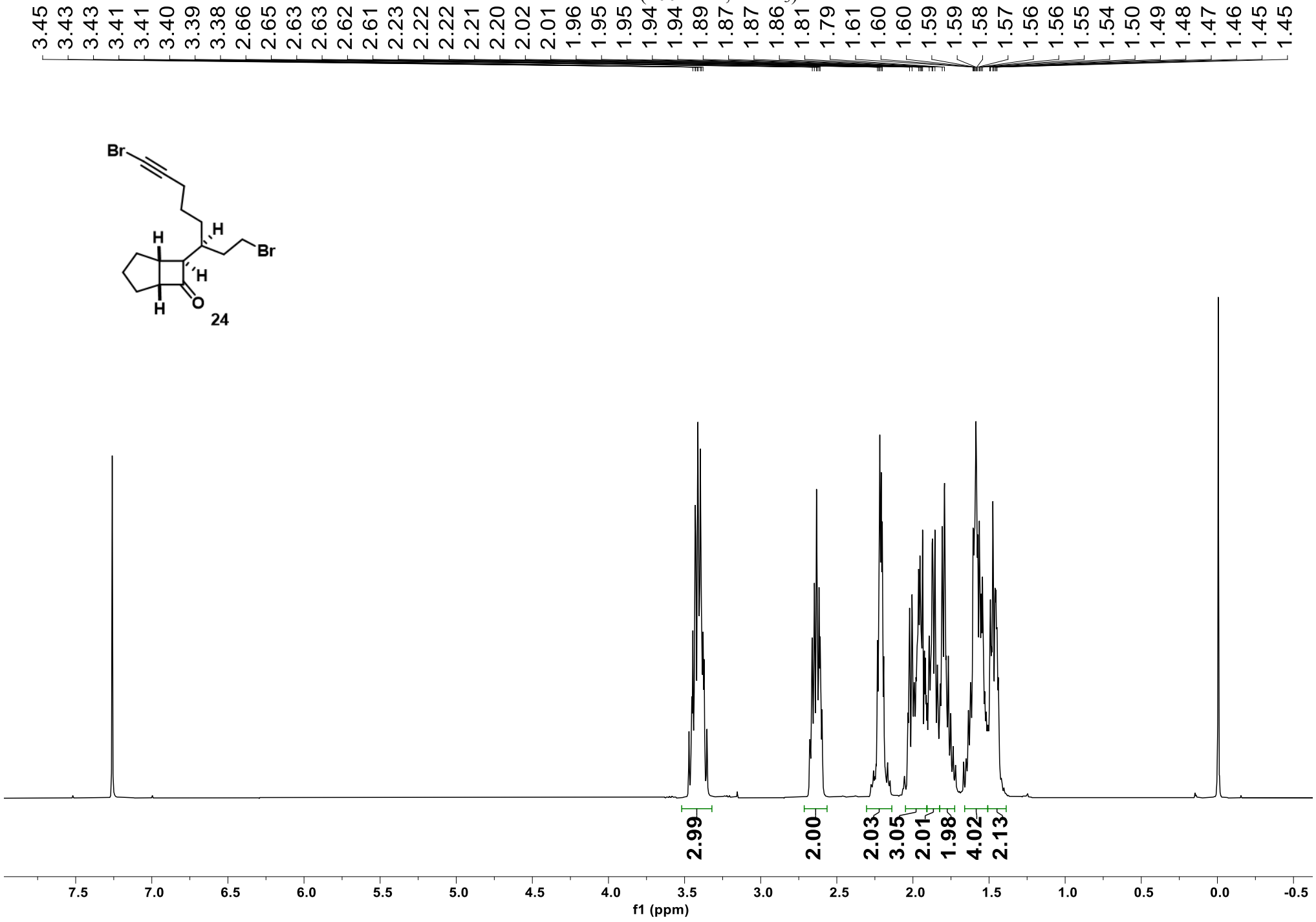
27– ^{1}H NMR (400 MHz, $CDCl_3$)



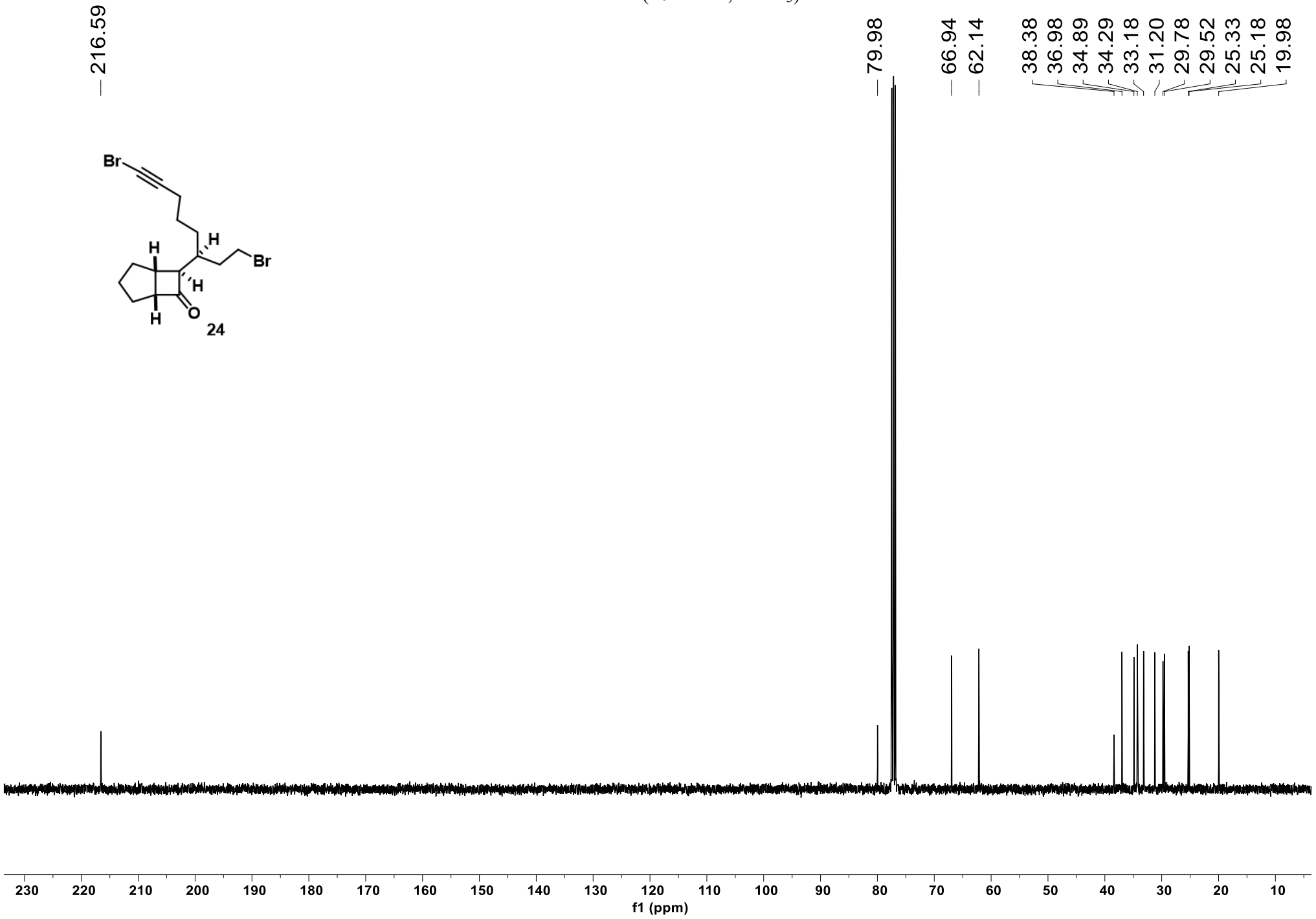
27 – ^{13}C NMR (101 MHz, $CDCl_3$)



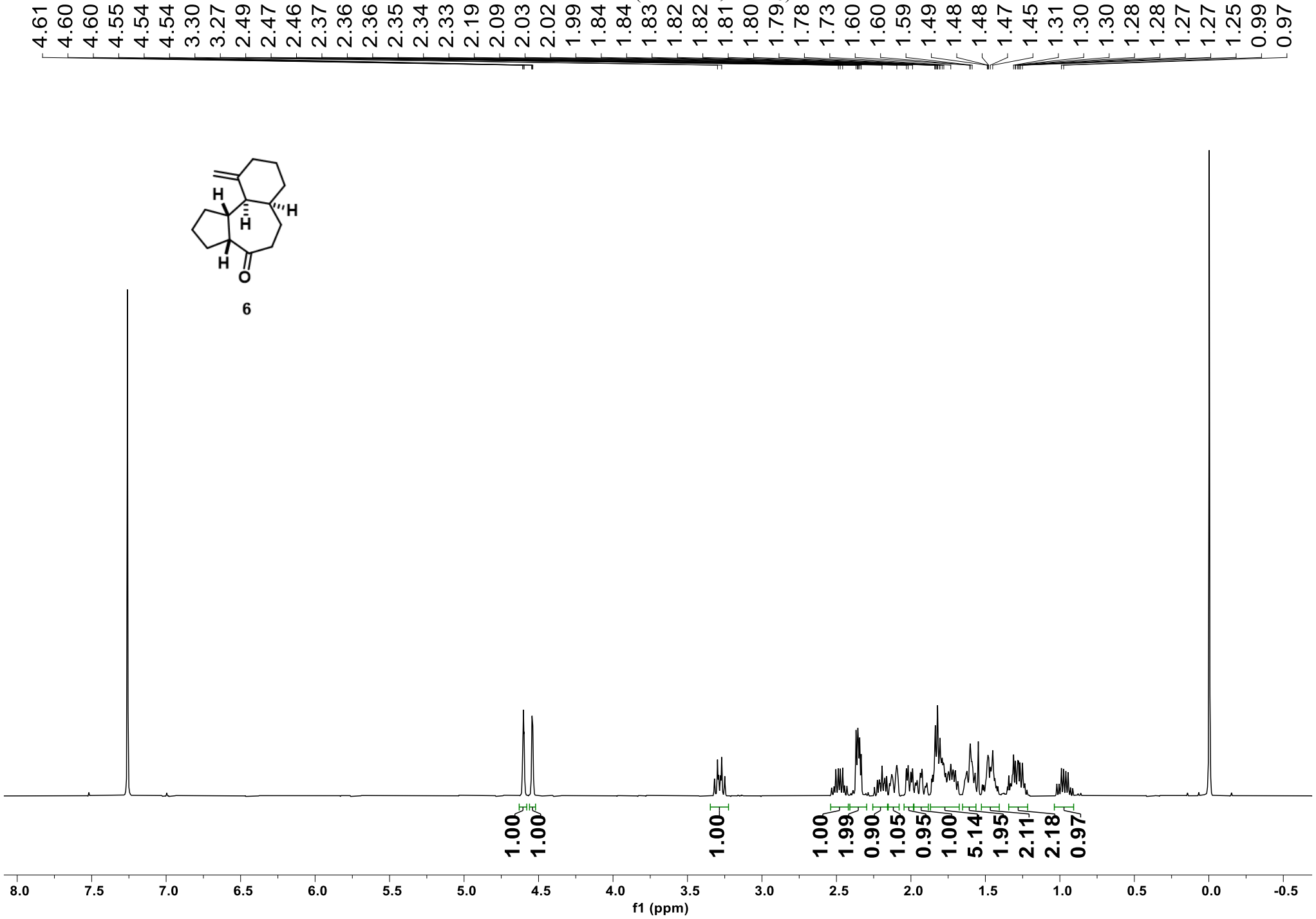
24 – ^{1}H NMR (400 MHz, $CDCl_3$)



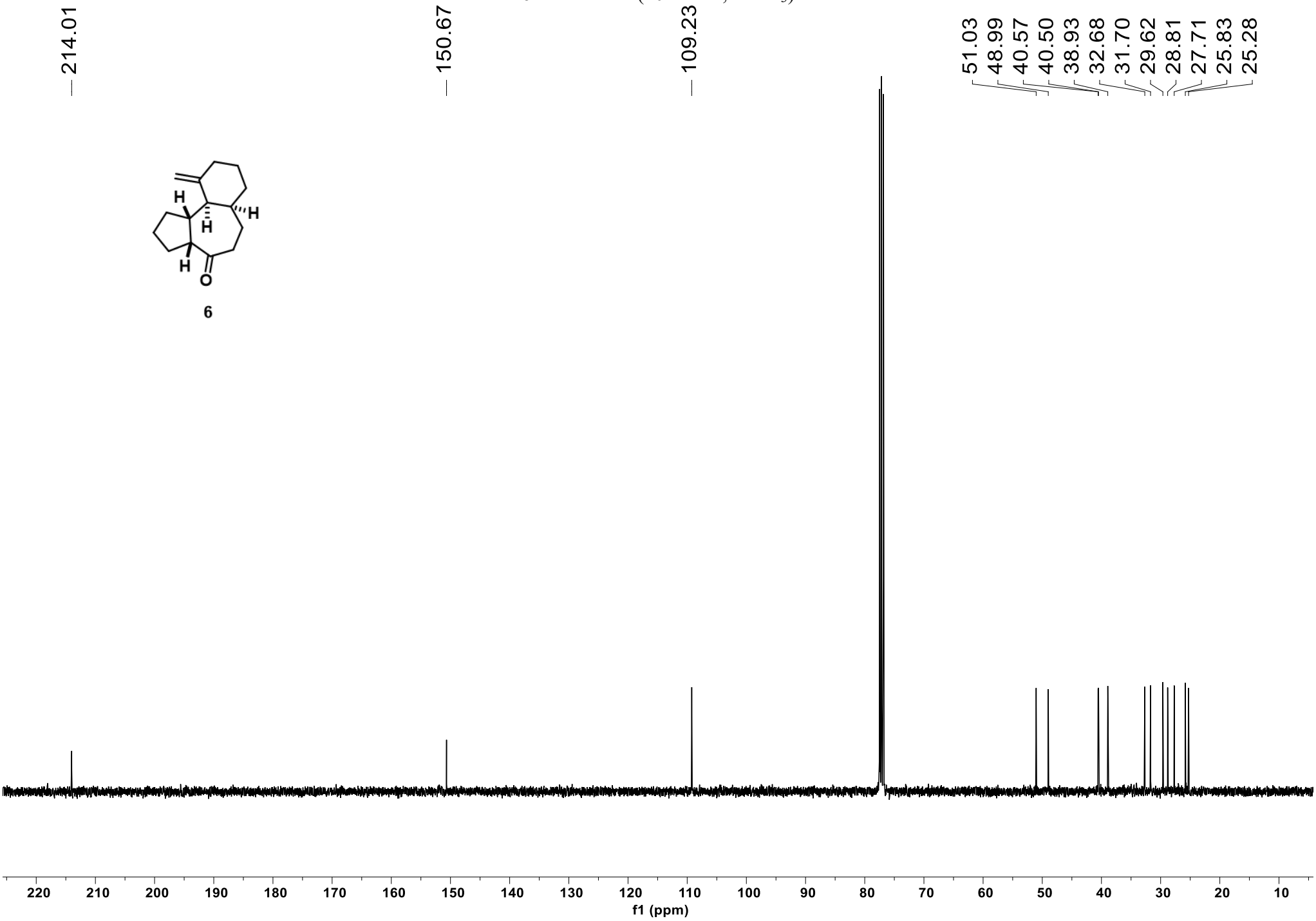
24 – ^{13}C NMR (101 MHz, $CDCl_3$)



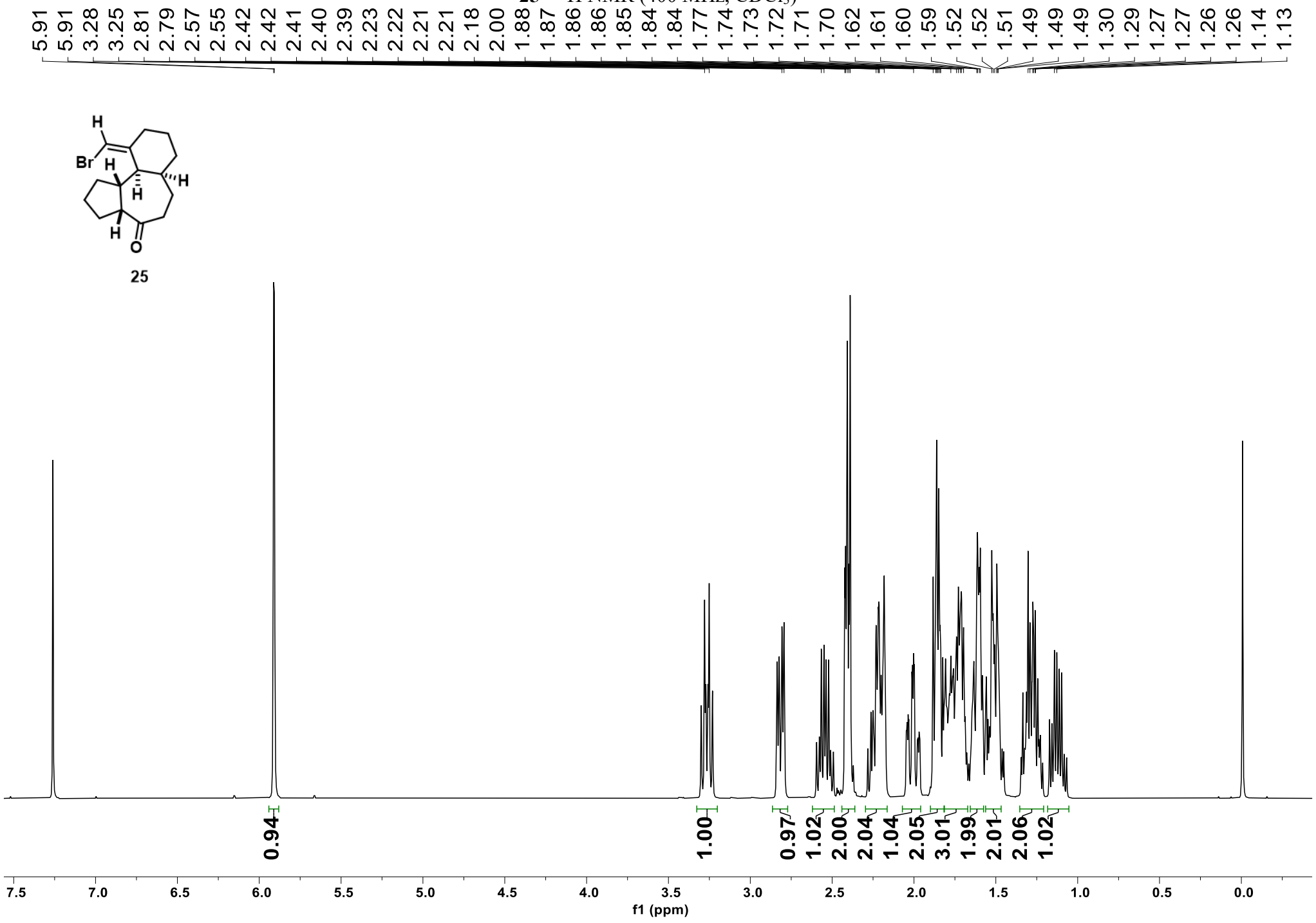
6 – ^{1}H NMR (400 MHz, $CDCl_3$)



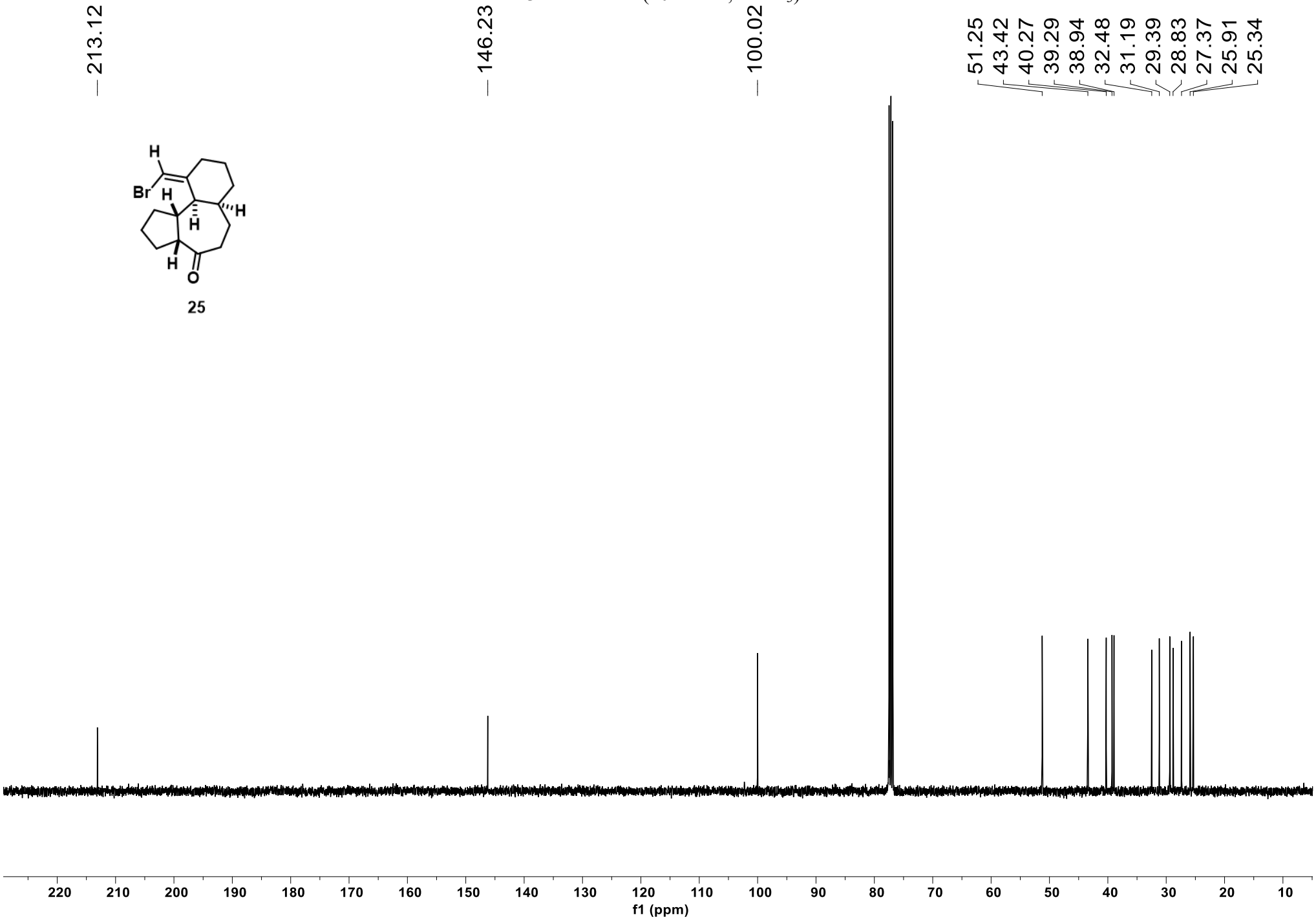
6 – ^{13}C NMR (101 MHz, $CDCl_3$)



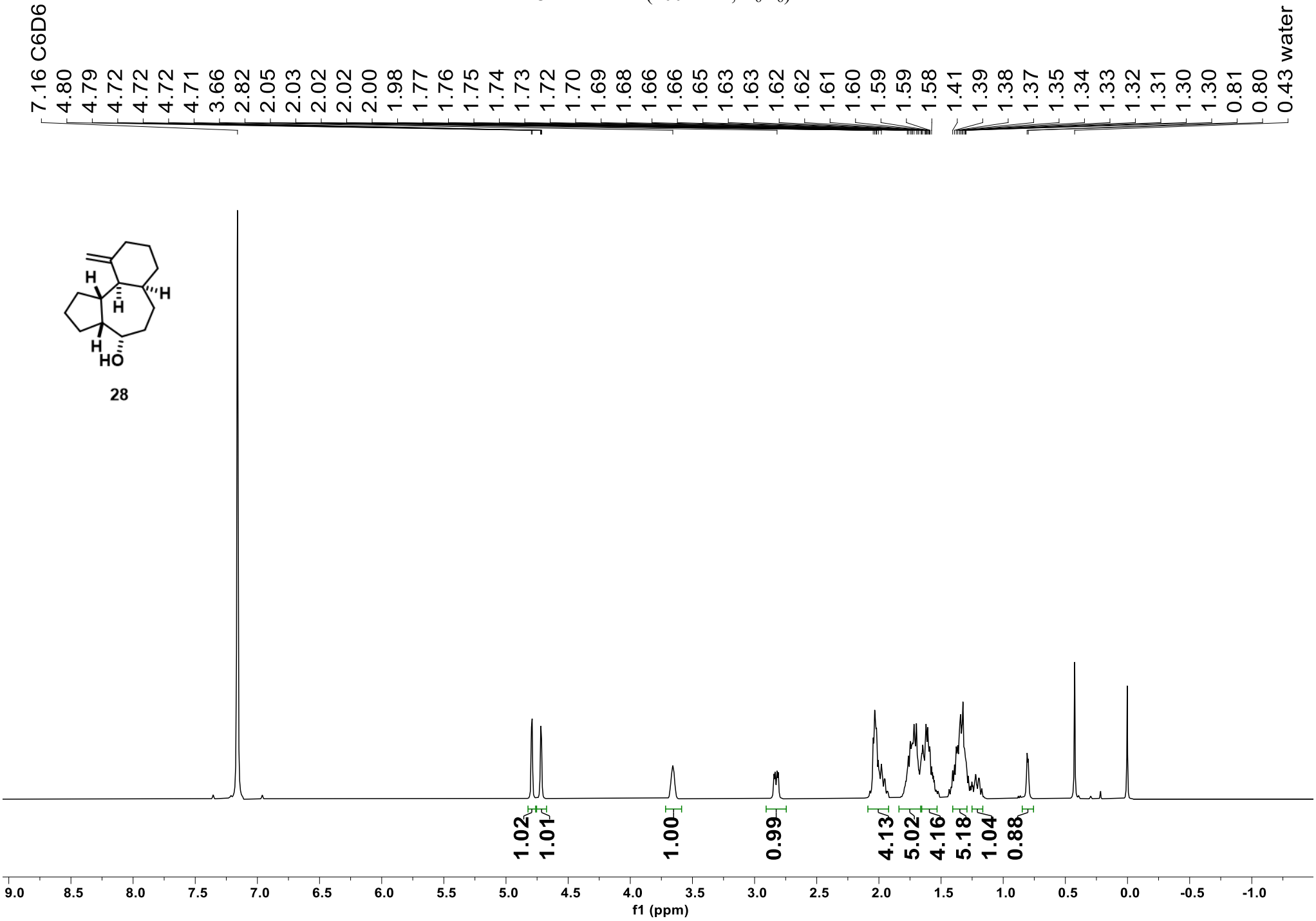
25 – ^{1}H NMR (400 MHz, $CDCl_3$)



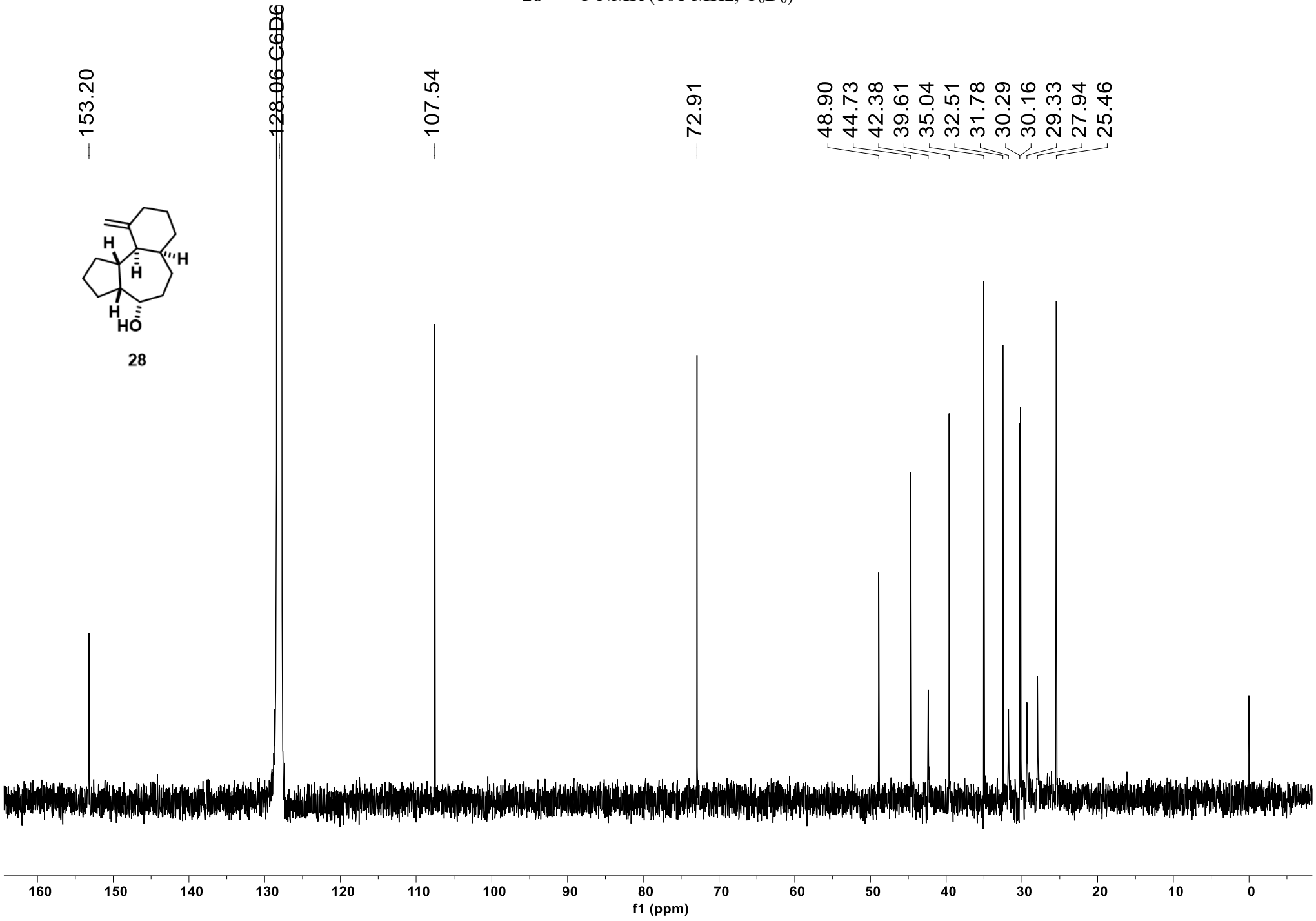
25 – ^{13}C NMR (101 MHz, $CDCl_3$)



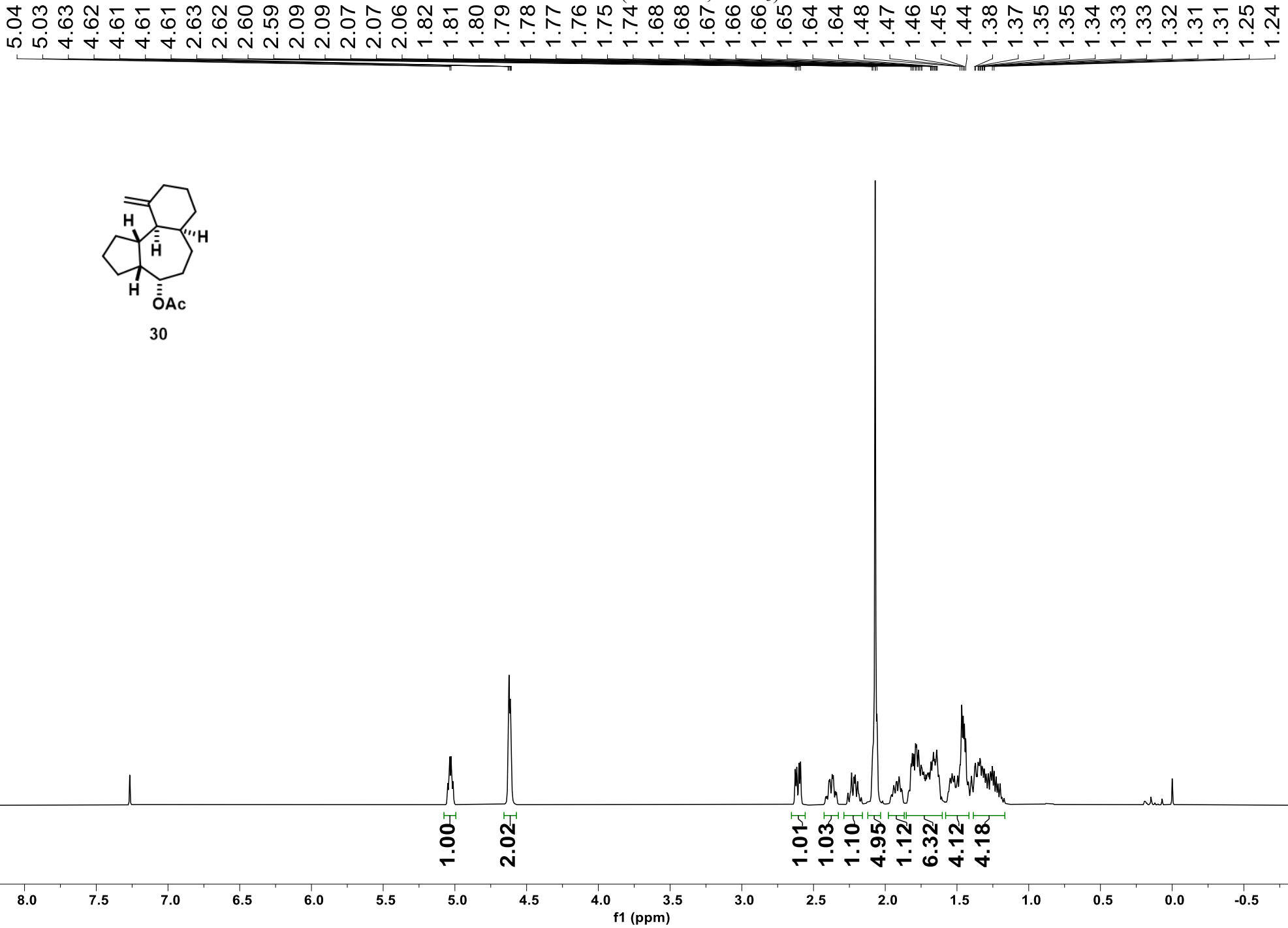
28 – ^{1}H NMR (400 MHz, C_6D_6)



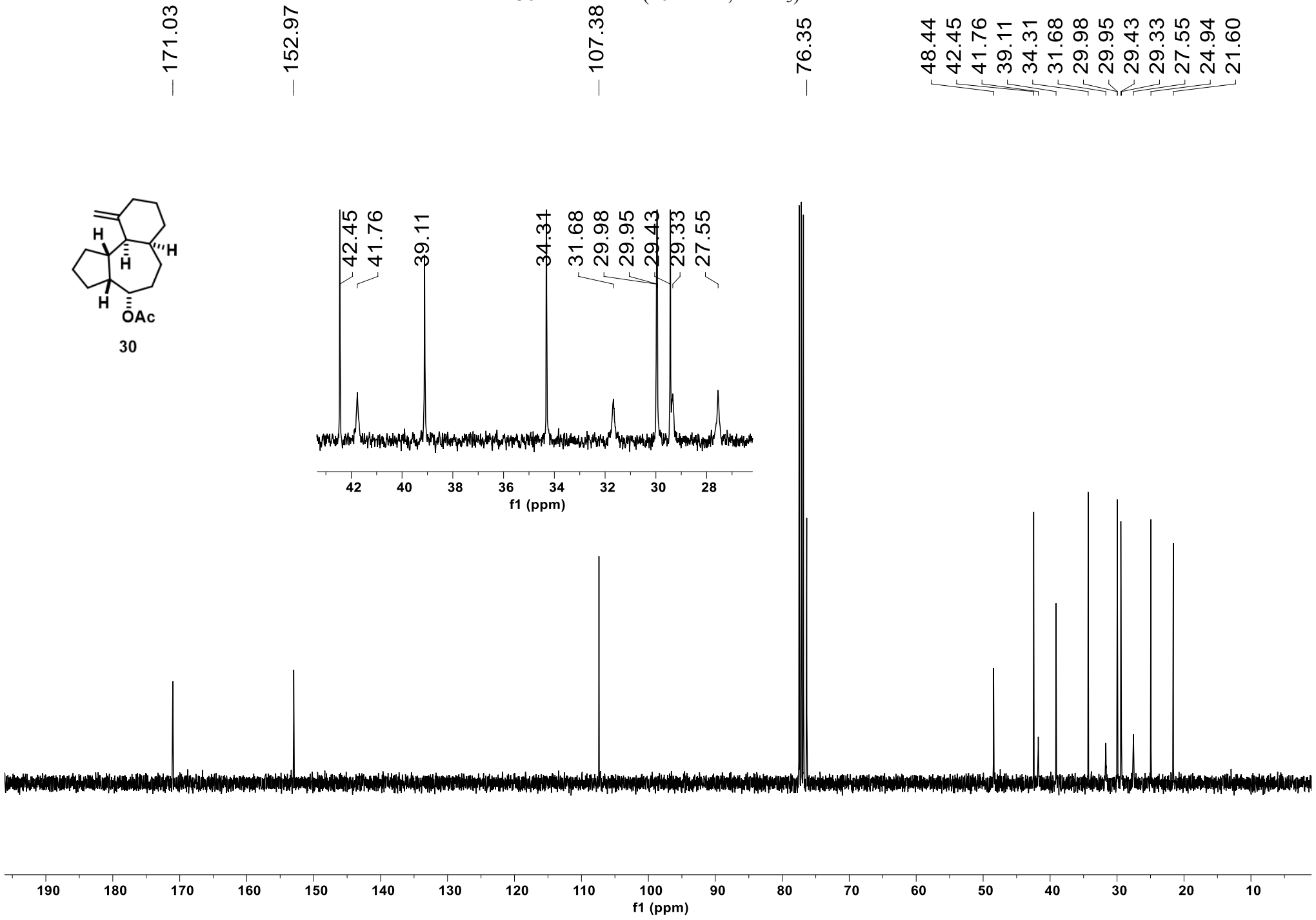
28 – ^{13}C NMR (101 MHz, C_6D_6)



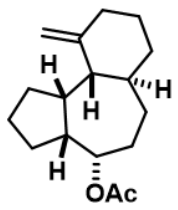
30 – ^{1}H NMR (400 MHz, $CDCl_3$)



30 – ^{13}C NMR (101 MHz, $CDCl_3$)

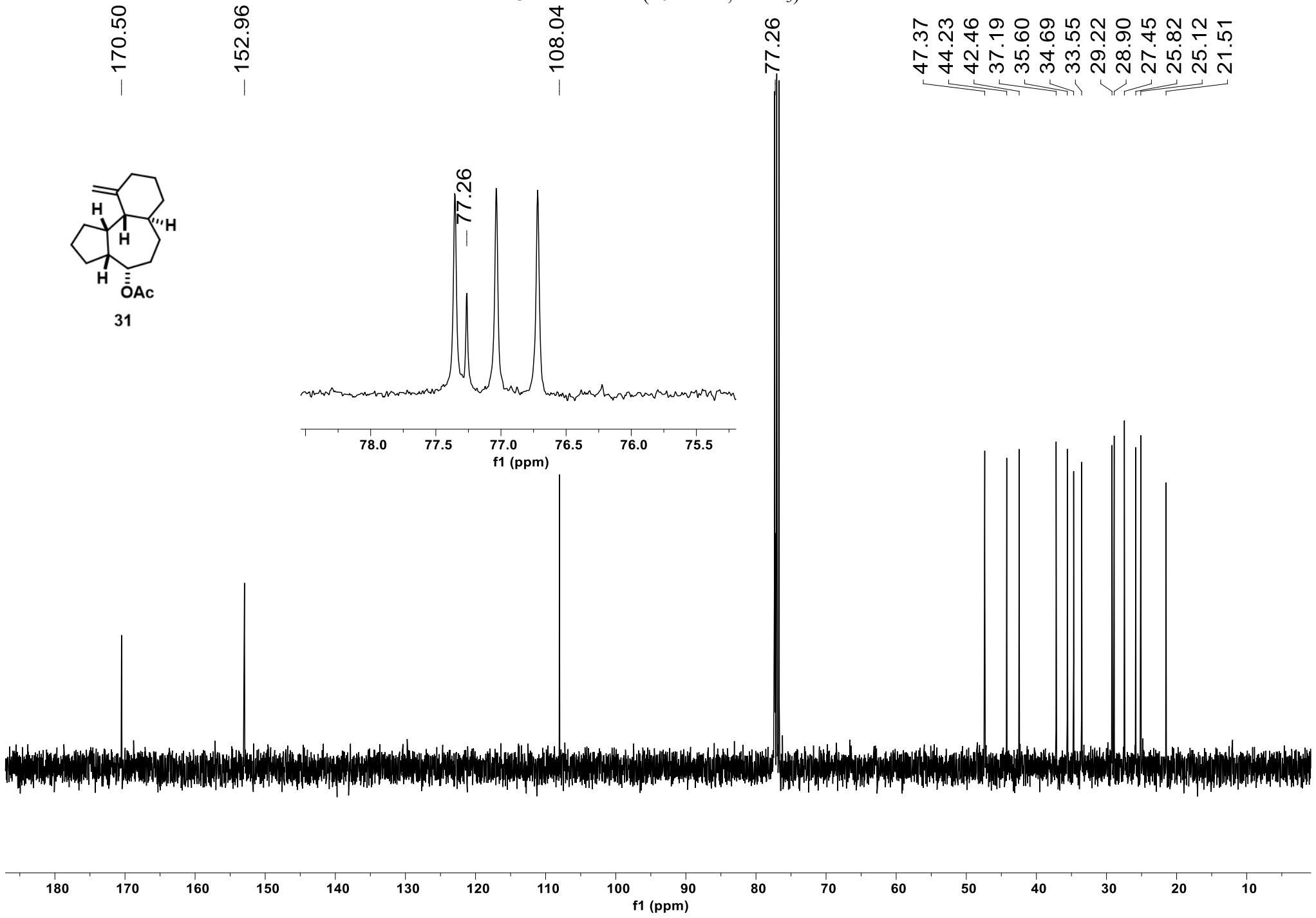


31 – ^{1}H NMR (400 MHz, $CDCl_3$)

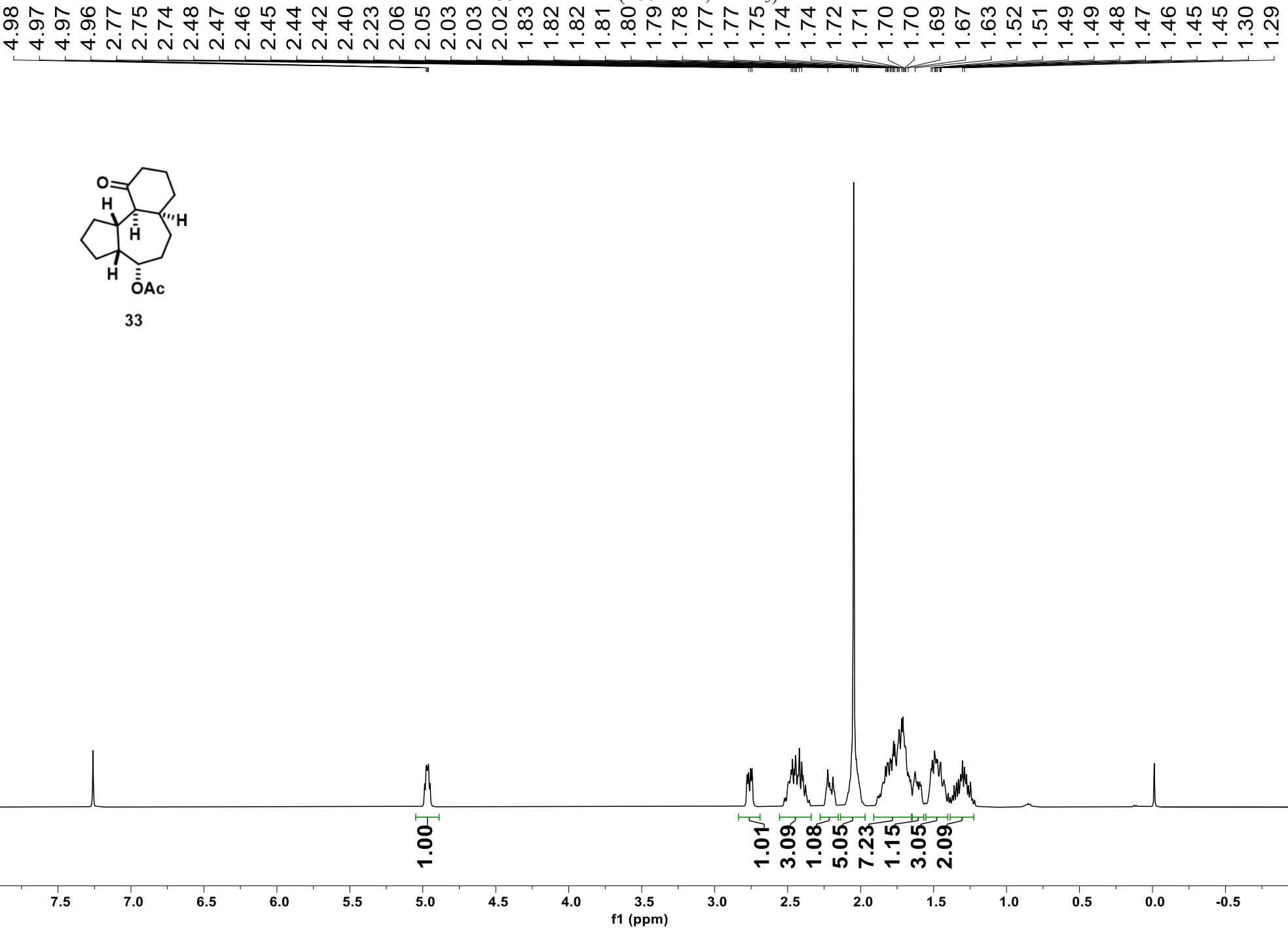


31

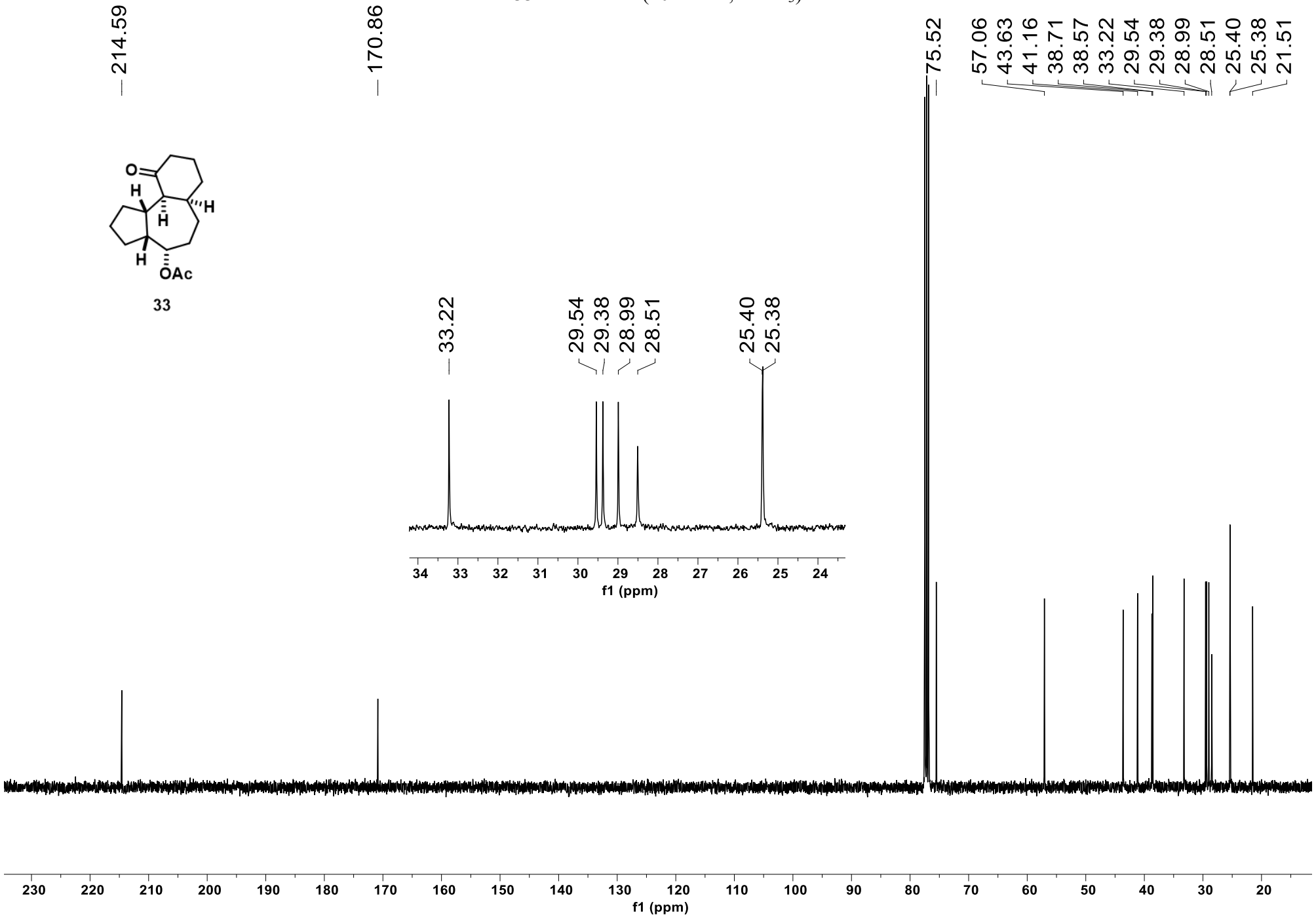
31 – ^{13}C NMR (101 MHz, $CDCl_3$)



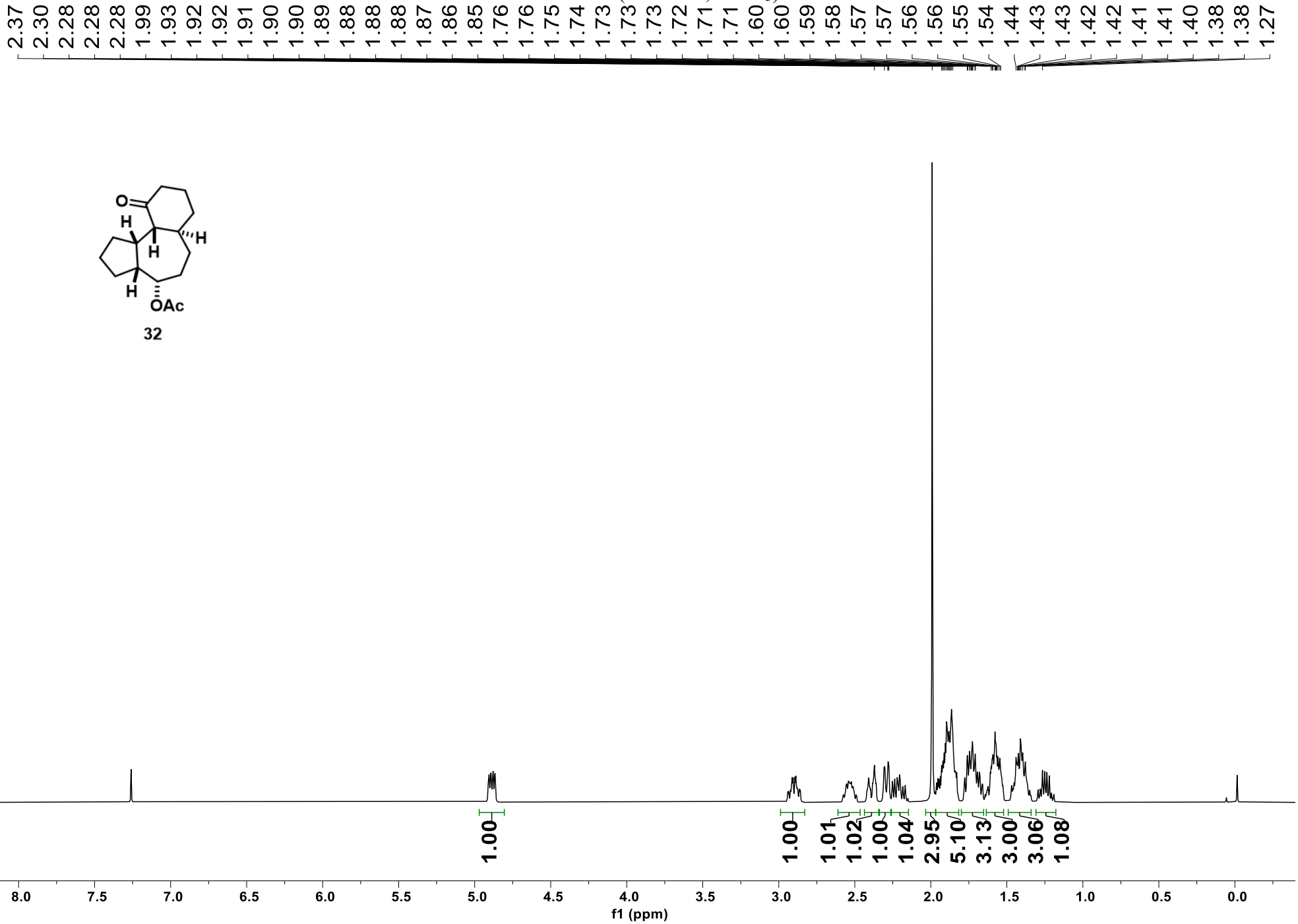
33 – ^{1}H NMR (400 MHz, $CDCl_3$)



33 – ^{13}C NMR (101 MHz, $CDCl_3$)



32 – ^{1}H NMR (400 MHz, $CDCl_3$)



32 – ^{13}C NMR (101 MHz, $CDCl_3$)