Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Total Synthesis of (±)-Mersicarpine Following a 6-exo-trig Radical Cyclization

Wen-Ling Peng, Yin-Jia Jhang, Chieh-Yu Chang, Po-Kai Peng, Wei-Ting Zhao and Yen-Ku Wu*

Department of Applied Chemistry, National Yang Ming Chiao Tung University, 1001 University Road, Hsinchu 30010, Taiwan

E-mail: yenkuwu@nycu.edu.tw

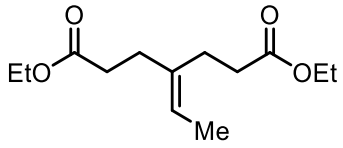
Supporting Information

Table of Contents

General Information

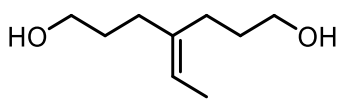
All air-sensitive reactions were conducted in flame-dried glassware under nitrogen atmosphere by using Schlenk techniques. Reactions were monitored by thin layer chromatography (Merck silica gel 60 F254) and visualized with 254 nm UV light or by staining with phosphomolybdic acid or potassium permanganate. Flash column chromatography was conducted by using 230-400 mesh silica gel with indicated eluents. Solvents including dichloromethane (DCM), 1,4-dioxane, tetrahydrofuran (THF), acetonitrile (MeCN), toluene, diethyl ether were dried by solvent purification system. All other solvents (etheyl acetate (EA), *N*,*N*-diethylformamide (DMF), etc.) and commercial reagents (ACS grade) were used as received. NMR spectra were recorded on Agilent 400-MR DD2 (400 MHz) in indicated deuterated solvent. Chemical shifts were recorded in ppm relative to residual non-deuterated solvent (δ 7.26 ppm for ^{1}H NMR and 77.16 for ^{13}C NMR in $CDCl_3$). Coupling constants were recorded in hertz (Hz) and multiplicities were abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on Thermo Nicolet iS5 FT-IR spectrometer with ATR sampling technique and were reported in wave number (cm^{-1}). High-resolution mass spectroscopy was performed on TOF instrument with CI or EI.

Diethyl 4-ethylideneheptanedioate (7)[1]



To a solution of ethyltriphenylphosphonium bromide (3.55 g, 9.55 mmol, 2.2 equiv) in toluene (62 mL) at room temperature was added *t*-BuOK (1.05 g, 9.33 mmol, 2.15 equiv). After 3 h at room temperature, the reaction was cooled to 0 ℃, and diethyl 4-oxopimelate (**6**) (1 g. 4.34 mmol, 1 equiv) was added. After 3 h at 0 ℃, the reaction was quenched by saturated aqueous ammonium chloride (50 mL). The resulting mixture was extracted with ethyl acetate (50 mL x3), and the combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/EA= 10:1 to 3:1) to afford **7** (877 mg, 83%) as yellowish oil. R_f : 0.75 (hexane/EA = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.28 (q, *J* = 6.8 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.42-2.27 (m, 8H), 1.59 (d, *J* = 6.8 Hz, 3H), 1.25 (d, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 173.05, 136.46, 120.77, 60.22, 60.13, 33.06, 32.75, 31.45, 25.07, 14.14, 13.05 [a carbonyl carbon signal and an aliphatic carbon signal are missing due to peak overlapping]; **IR** (film): 2979, 2927, 2866, 1731, 1445, 1369, 1249, 1160, 1036 cm^{-1}; **HRMS** (CI, $[M+H]^+$) for $C_{13}H_{23}O_4$ calcd. 243.1596, found: 243.1591.

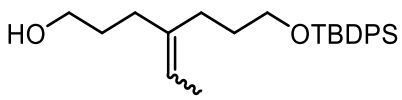
4-Ethylideneheptane-1,7-diol (8)[1]



To a solution of **7** (361 mg, 1.49 mmol, 1 equiv) in THF (15 mL) at 0 ℃ was slowly added lithium aluminum hydride (283.5 mg, 7.47 mmol, 5 equiv). After 4 h at 0 ℃,

ethyl acetate (15 mL) was slowly added under the same temperature. After the reaction was not vigorously bubbling, distilled water (5 mL) was added. The resulting gummy mixture was filtered through celite and eluted with ethyl acetate (100 mL). The filtrate was then dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to afford **8** (211 mg, 90%) as yellowish oil without further purification. R_f : 0.18 (hexane/EA = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.28 (q, *J* = 6.8 Hz, 1H), 3.63 (t, *J* = 6.5 Hz, 2H), 3.62 (t, *J* = 6.5 Hz, 2H), 2.14-2.03 (m, 4H), 1.74 (br, 2H), 1.69-1.62 (m, 4H), 1.60 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 139.16, 119.79, 63.08, 62.96, 33.18, 31.17, 25.98, 13.36 [an aliphatic carbon signal is missing due to peak overlapping]; **IR** (film): 3343, 2925, 2862, 1738, 1718, 1437, 1241, 1033 cm^{-1}; **HRMS** (CI, $[M+H]^+$) for $C_9H_{19}O_2$ calcd. 159.1385, found: 159.1380.

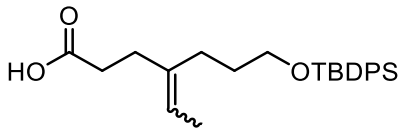
7-((*tert*-Butyldiphenylsilyl)oxy)-4-ethylideneheptan-1-ol (9)[1]



To a solution of **8** (405 mg, 2.56 mmol, 5 equiv) in DCM (10 mL) was added imidazole (47 mg, 0.68 mmol, 1.3 equiv). After 2 h at room temperature, the reaction was cooled to 0 ℃, and then *t*-butyl(chloro)diphenylsilane (TBDPSCl; 128.2 μL , 0.5 mmol, 1 equiv) was added. The reaction was allowed to stir at room temperature for 16 h, and distilled water (10 mL) was added. The resulting mixture was extracted with ethyl acetate (20 mL x3), and the combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/EA = 10:1 to 5:1) to afford **9** (141 mg, 71%) as yellowish oil. R_f: 0.25 (hexane/ EA = 10:1). Spectral data for the mixture of E/Z isomers: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.70-7.67 (m, 4H), 7.45-7.37 (m, 6H), 5.30-5.20 (m,

1H), 3.69-3.60 (m, 4H), 2.15-2.01 (m, 4H), 1.67-1.61 (m, 4H), 1.59 (d, J = 6.6 Hz, 3H), 1.49-1.32 (br, 1H), 1.07 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 139.30, 139.11 (minor), 135.64, 134.14 (minor), 134.10, 129.62, 129.59 (minor), 127.68, 127.67 (minor), 119.33 (minor), 119.31, 63.86, 63.68 (minor), 62.92 (minor), 62.82, 33.25, 32.99 (minor), 31.22, 31.11 (minor), 31.08, 26.96, 25.97, 25.95 (minor), 19.30 (minor), 19.29, 13.29; **IR** (film): 3344, 2927, 2855, 1716, 1462, 1111, 1052 cm^{-1}; **HRMS** (CI, $[M+H]^+$) for $C_{25}H_{37}O_2Si$ calcd. 397.2563, found: 397.2552.

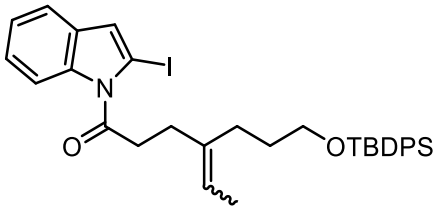
7-((*tert*-Butyldiphenylsilyl)oxy)-4-ethylideneheptanoic acid (10)



To a solution of **9** (2.75 g, 6.94 mmol, 1 equiv) in DMF (12 mL) and DCM (3 mL) at room temperature was added pyridinium chlorochromate (PCC; 8.00 g, 37.21 mmol, 1.3 equiv). After 12 h at room temperature, distilled water (20 mL) was added, and the resulting mixture was filtered through a pad of celite and extracted with ethyl acetate (50 mL x3). The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/EA = 5:1 to 1:1) to afford **10** (2.35 g, 82%) as yellowish oil. R_f : 0.15 (hexane/EA = 4:1). Spectral data for the mixture of E/Z isomers: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72-7.71 (m, 4H), 7.46-7.40 (m, 6H), 5.33-5.24 (m, 1H), 3.71-3.64 (m, 2H), 2.47 (t, J = 7.2 Hz, 1H), 2.43-2.36 (m, 2H), 2.33 (t, J = 7.5 Hz, 1H), 2.16 (t, J = 7.9 Hz, 1H), 2.10 (t, J = 7.8 Hz, 1H), 1.70-1.63 (m, 2H), 1.61 (t, J = 6.3 Hz, 3H), 1.10 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 179.66, 179.59 (minor), 137.85, 137.41 (minor), 135.69, 134.14 (minor), 134.11, 129.67, 129.65 (minor), 127.73 (minor), 127.72, 120.62 (minor), 119.83, 63.78, 63.57 (minor), 33.09 (minor), 32.80 (minor),

32.74, 31.68, 31.18, 31.15 (minor), 27.00, 26.23, 25.97 (minor), 24.97 (minor), 19.33, 19.32 (minor) 13.33, 13.28 (minor); **IR** (film): 3069, 2930, 2857, 1709, 1427, 1110 cm^{-1}; **HRMS** (CI, $[M-H]^-$) for $C_{25}H_{33}O_3Si$ calcd. 409.2199, found: 409.2194.

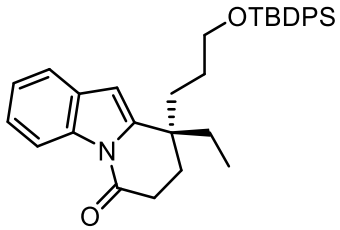
7-((*tert*-Butyldiphenylsilyl)oxy)-4-ethylidene-1-(2-iodo-1H-indol-1-yl)heptan-1-one (12)



To a solution of 2-iodoindole (**11**)[2] (59 mg, 0.24 mmol, 1 equiv), **10** (200 mg, 0.48 mmol, 2 equiv) and 4-dimethylaminopyridine (DMAP; 5 mg, 0.04 mmol, 0.15 equiv) in DCM (0.6 mL) was added dicyclohexyl carbodiimide (DCC; 101 mg, 0.48 mmol, 2 equiv) in one portion at 0 °C. After 10 min at 0 °C, the resulting mixture was warmed up to room temperature and stirred for 20 h. The reaction was filtered through a pad of celite and washed with DCM (10 mL). The filtrate was washed with saturated $NaHCO_3$ (10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/Et_2O/EA = 50:1:1 to 40:1:1) to afford **12** (139 mg, 88%) as yellowish oil. R_f: 0.38 (hexane/EA = 25:1). Data is reported for a mixture of E/Z isomers, and partial spectral data is reported. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.1 Hz, 1H; major), 8.01 (d, J = 8.3 Hz, 1H; minor), 7.70-7.67 (m, 8H), 7.50-7.47 (m, 2H), 7.42-7.35 (m, 12H), 7.25-7.20 (m, 4H), 7.04 (s, 2H), 5.33 (q, J = 6.7 Hz, 1H), 5.29 (q, J = 6.7 Hz, 1H), 3.73-3.68 (m, 4H), 3.30 – 3.25 (m, 2H; minor), 3.25 – 3.20 (m, 2H; major),, 2.60 – 2.56 (m, 2H; major), 2.55 – 2.50 (m, 2H; minor), 2.20 (t, J = 7.8 Hz, 2H; minor), 2.16 (t, J = 7.8 Hz, 2H; major), 1.75 – 1.69 (m, 2H; major), 1.69 – 1.64 (m, 2H; minor), 1.63

(d, J = 6.9 Hz, 3H; major), 1.60 (d, J = 6.9 Hz, 3H; minor), 1.10 (s, 9H; minor), 1.09 (s, 9H; major); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 173.13 (minor), 172.99, 138.02, 137.99 (minor), 137.73 (minor), 137.36, 135.70, 134.14, 134.12 (minor), 131.24, 131.21 (minor), 129.68 (minor), 129.66, 127.73, 124.81, 124.75 (minor), 123.52, 123.34, 123.27 (minor), 120.96, 120.35 (minor), 119.68, 114.98, 114.89 (minor), 73.56 (minor), 73.47, 63.79 (minor), 63.60, 39.05 (minor), 38.79, 33.01, 32.33 (minor), 31.28 (minor), 31.23, 27.04, 26.45 (minor), 25.37, 19.36, 19.35 (minor), 13.46, 13.42 (minor). **IR** (film): 3339, 2924, 2853, 1712, 1462, 1427, 1377, 1111 cm^{-1}; **HRMS** (CI, $[M+H]^+$) for $C_{33}H_{39}INO_2Si$ calcd. 636.1795, found: 636.1789.

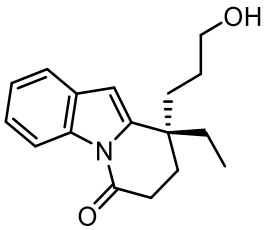
9-(3-((*tert*-Butyldiphenylsilyl)oxy)propyl)-9-ethyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one (13)



A flask containing **12** (42 mg, 0.07 mmol, 1 equiv) and azobisisobutyronitrile (AIBN; 11 mg, 0.07 mmol, 1 equiv) was vacuumed for 10 minutes. The whole system was then backfilled with N_2, and degassed anhydrous benzene (6.6 mL) was added. To the reaction was added nBu$_3$SnH (26.7 μL, 0.1 mmol, 1.5 equiv), and the resulting mixture was heated to 85 °C. After 6 h at 85 °C, the reaction was cooled to room temperature, filtered through a pad of celite, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ EA = 10:1 to 5:1) to afford **13** (20 mg, 59%) as yellowish oil. R_f: 0.18 (hexane/EA = 7.5:1) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.48 (d, J = 7.8 Hz, 1H), 7.65-7.62 (m, 4H), 7.46 (dd, J = 6.4, 1.5 Hz, 1H), 7.43-7.33 (m, 6H), 7.31-7.23 (m, 2H), 6.26 (s, 1H), 3.71-3.61 (m, 2H), 2.83 (ddd,

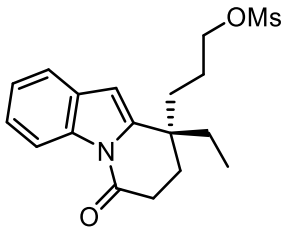
J = 6.7, 6.7, 3.8 Hz, 2H), 1.94 (ddd, *J* = 6.7, 6.7, 2.7 Hz, 2H), 1.82-1.64 (m, 5H), 1.52-1.44 (m, 1H), 1.04 (m, 9H), 0.89 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 169.29, 144.37, 135.70, 135.37, 134.00, 129.76, 129.73, 127.77, 124.29, 124.01, 119.69, 116.64, 105.25, 64.15, 34.50, 33.00, 30.50, 30.14, 27.02, 26.98, 19.33, 8.17; **IR** (film): 3340, 2915, 2849, 1735, 1455, 1376, 1183, 1111 cm^{-1}; **HRMS** (CI, $[M+H]^+$) for $C_{33}H_{40}NO_2Si$ calcd. 510.2828, found: 510.2823.

9-Ethyl-9-(3-hydroxypropyl)-8,9-dihydropyrido[1,2-a]indol-6(7H)-one (14)



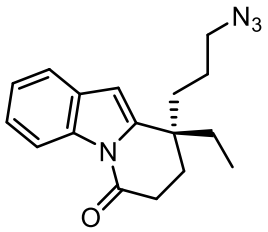
To a solution of **13** (32 mg, 0.06 mmol) in THF (1.3 mL) was added TBAF (1M in THF, 75 μL, 1.25 equiv), and the reaction was stirred at rt for 7 h. $NH_4Cl_{(aq)}$ (3 mL) was added, and the resulting mixture was extracted with ethyl acetate (10 mL x3). The combined organic layer was washed with brine (15 mL) and dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ EA = 10:1 to pure ethyl acetate) to afford **14** (13 mg, 79%) as yellowish oil. R_f : 0.33 (EA). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 6.9 Hz, 1H), 7.30-7.22 (m, 2H), 6.31 (s, 1H), 3.63 (t, *J* = 6.4 Hz, 2H), 2.85 (t, *J* = 6.7 Hz, 2H), 1.97 (t, *J* = 6.7 Hz, 2H), 1.83-1.68 (m, 5H), 1.65-1.46 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.28, 144.15, 135.30, 129.63, 124.32, 124.03, 119.94, 116.59, 105.26, 63.14, 37.47, 33.05, 30.42, 30.12, 30.06, 27.02, 8.15. **IR** (film): 3393, 2953, 2849, 1701, 1455, 1374, 1350, 1185, 1019 cm^{-1}; **HRMS** (EI, $[M]^+$) for $C_{17}H_{21}NO_2$ calcd. 271.1572, found: 271.1567.

3-(9-Ethyl-6-oxo-6,7,8,9-tetrahydropyrido[1,2-a]indol-9-yl)propylmethanesulfonate (S1)



To a solution of **14** (71 mg, 0.26 mmol, 1.0 equiv) in DCM (2.6 mL) at 0 °C was added triethylamine (43.9 μL, 0.32 mmol, 1.2 equiv) and methanesulfonyl chloride (25 μL, 0.32 mmol, 1.2 equiv). After 1 h at 0 °C, saturated $NaHCO_{3(aq)}$ (10 mL) was added, and the resulting mixture was extracted with ethyl acetate (10 mL x3). The combined organic layer was washed with brine (15 mL) and dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/EA = 5:1 to pure ethyl acetate) to afford **S1** (72 mg, 79%) as yellowish oil. R_f : 0.43 (hexane/EA = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 6.6 Hz, 1H), 7.32-7.24 (m, 2H), 6.31 (s, 1H), 4.26-4.17 (m, 2H), 2.98 (s, 3H), 2.87 (t, *J* = 6.8 Hz, 2H), 1.99 (t, *J* = 6.8 Hz, 2H), 1.84-1.70 (m, 6H), 0.93 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.90, 143.38, 135.25, 129.43, 124.42, 124.05, 119.99, 116.53, 105.31, 70.1, 37.36, 32.54, 30.27, 29.99, 27.89, 23.87, 13.72, 8.06. **IR** (film): 2956, 2932, 2868, 1699, 1455, 1350, 1174 cm^{-1}; **HRMS** (EI, $[M]^+$) for $C_{18}H_{23}NO_4S$ calcd. 349.1349, found: 349.1342.

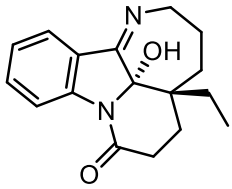
9-(3-Azidopropyl)-9-ethyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one (15)



To an aluminum foil wrapped flask containing **S1** (95 mg, 0.27 mmol, 1 equiv) in DMF

(27.4 mL) at room temperature was added sodium azide (89 mg, 1.37 mmol, 5 equiv). After 20 h at room temperature, deionized water (50 mL) was added, and the resulting mixture was extracted with ethyl acetate (100 mL x3). The combined organic layer was washed with brine (150 mL) and dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ EA = 20:1 to 5:1) to afford **15** (66 mg, 81%) as yellowish oil. R_f : 0.53 (hexane/EA = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 6.8 Hz, 1H), 7.32-7.24 (m, 2H), 6.32 (s, 1H), 3.35-3.23 (m, 2H), 2.87 (t, *J* = 6.7 Hz, 2H), 1.99 (t, *J* = 6.7 Hz, 2H), 1.86-1.69 (m, 4H), 1.67-1.50 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.02, 143.68, 135.36, 129.56, 124.49, 124.12, 120.04, 116.66, 105.36, 51.94, 37.57, 33.97, 30.41, 30.18, 30.14, 23.57, 8.18. **IR** (film): 2916, 2849, 2095, 1736, 1456, 1376, 1026 cm^{-1}; **HRMS** (EI, $[M]^+$) for $C_{17}H_{29}N_4O$ calcd. 296.1637, found: 296.1632.

(±)-**Mersicarpine (1)**



A stirring solution of compound (85 mg, 0.29 mmol) in MeCN (4.7 mL), acetone (4.7 mL) and distilled water (1.88 mL) was added tetrabutylammonium hydroxide (10.7 mg, 0.03 mmol, 0.1 equiv), $NaHCO_3$ (421 mg, 5 mmol, 17 equiv) and disodium ethylenediamininetetraacetic acid (Na_2·EDTA; 11 mg, 0.03 mmol, 1 equiv) under air. The reaction was then cooled to 0 °C, and a solution of potassium peroxymonosulfate (929 mg, 15.1 mmol, 52 equiv) in distilled water (2.8 mL) was slowly added over 14 min with vigorous stirring. After 2 h at 0 °C, the reaction was warmed up to room temperature, and ethyl acetate (30 mL) was added. The resulting mixture was washed

with brine (15 mL) and dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was directly used for the next step without purification.

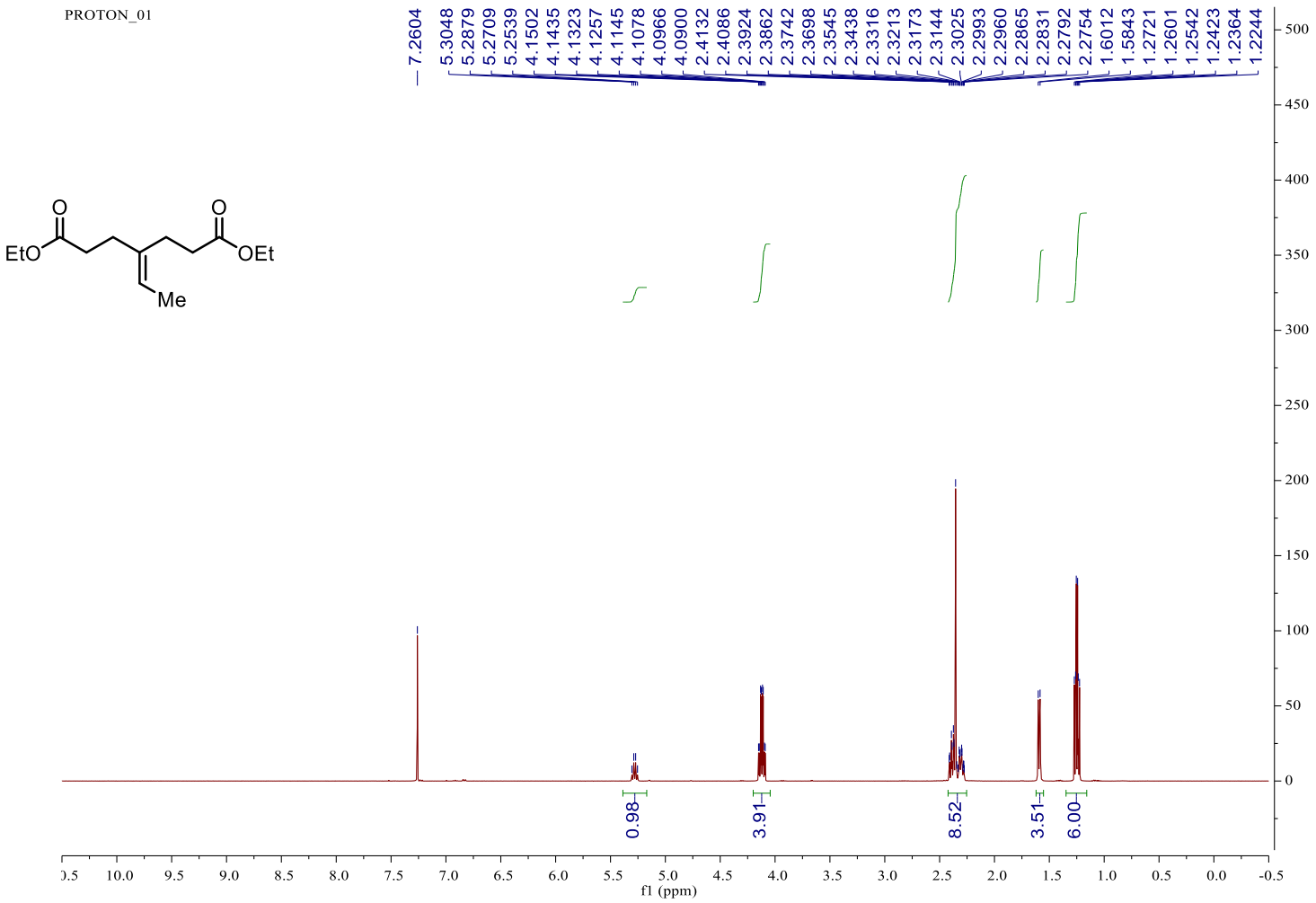
Under air, to a solution of crude mixture in THF (9 mL) and distilled water (0.6 mL) was added triphenylphosphine (158 mg, 0.6 mmol, 2 equiv) at room temperature. After 2 h at room temperature, the starting material was fully consumed (confirmed by TLC), and the reaction was directly concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ EA = 5:1 to 3:1) to afford **1** (25 mg, 31%) as white solid. m.p. 180 °C. R_f: 0.1 (hexane/EA = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (d, 1H, *J* = 8.2 Hz), 7.55 (d, *J* = 7.6 Hz, 1H), 7.32 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.03 (dd, *J* = 7.6, 7.6 Hz, 1H), 3.78 (t, *J* = 4.4 Hz, 2H), 2.56-2.48 (m, 1H), 2.39-2.30 (m, 1H), 2.07-1.99 (m, 1H), 1.92-1.84 (m, 1H), 1.73-1.58 (m, 4H), 1.29-1.20 (m, 1H), 1.10-1.01 (m, 1H), 0.72 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.64, 169.18, 146.67, 133.38, 124.39, 124.37, 122.34, 116.87, 94.00, 50.47, 39.43, 34.47, 29.25, 25.60, 23.01, 21.18, 7.01. **IR** (cast): 2923, 2852, 1660, 1467, 1389, 1303, 1127, 1069 cm^{-1}; **HRMS** (EI, $[M]^+$) for $C_{17}H_{20}N_2O_2$ calcd. 284.1525, found: 284.1519.

^{1}H/^{13}C NMR Spectral Comparison of Natural and Synthetic Mersicarpine (1)

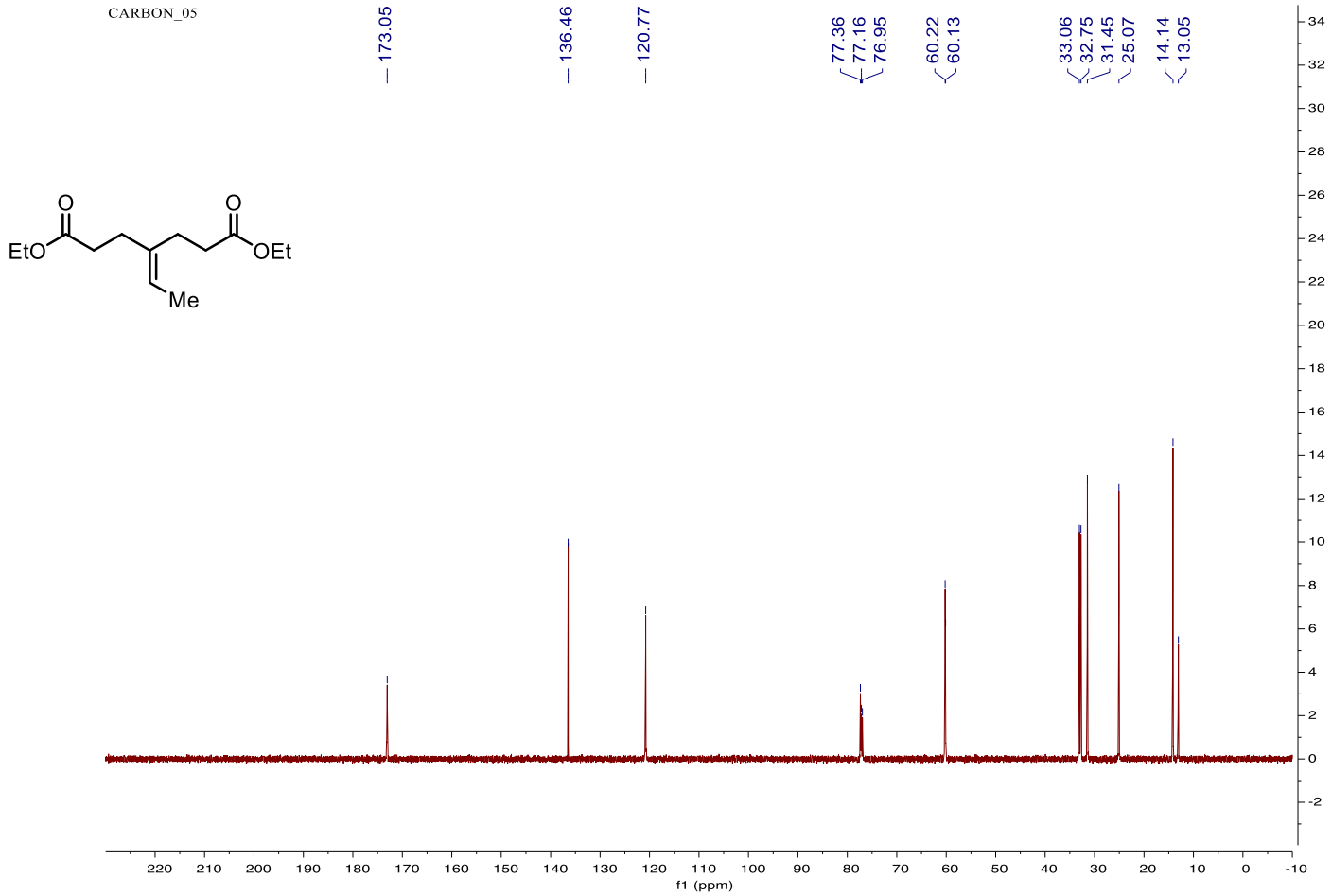
^{1}H NMR ($CDCl_3$, 400MHz)		^{13}C NMR ($CDCl_3$, 100MHz)	
Natural[3]	Synthetic	Natural[3]	Synthetic
8.14 (d, *J* = 8.2 Hz, 1H)	8.07 (d, *J* = 8.2 Hz, 1H)	169.6	169.64
7.60 (d, *J* = 7.5 Hz, 1H)	7.40 (d, *J* = 7.6 Hz, 1H)	169.0	169.18
7.36 (t, *J* = 7.3 Hz, 1H)	7.32 (dd, *J* = 8.0, 8.0 Hz,	146.7	146.67
	1H)	133.5	133.38
7.07 (t, *J* = 7.5 Hz, 1H)	7.03 (dd, *J* = 7.6, 7.6 Hz,	124.5	124.39
	1H)	124.4	124.37
3.93 – 3.78 (m, 2H)	3.78 (t, *J* = 4.4 Hz, 2H)	122.4	122.34
2.59 (ddd, *J* = 18.4, 9.6,	2.56-2.48 (m, 1H)	116.9	116.87
3.3 Hz, 1H)		94.0	94.00
2.44 – 2.35 (m, 1H)	2.39-2.30 (m, 1H)	50.6	50.47
2.10 – 2.02 (m, 1H)	2.07-1.99 (m, 1H)	39.4	39.43
1.96 – 1.85 (m, 1H)	1.92-1.84 (m, 1H)	34.5	34.47
1.77 – 1.72 (m, 1H)	1.73-1.58 (m, 4H)	29.3	29.25
1.70 – 1.62 (m, 3H)		25.6	25.60
1.34 – 1.28 (m, 1H)	1.29-1.20 (m, 1H)	23.1	23.01
1.16 – 1.07 (m, 1H)	1.10-1.01 (m, 1H)	21.3	21.18
0.74 (t, *J* = 7.4 Hz, 3H)	0.72 (3H, t, *J* = 7.4 Hz)	7.0	7.01

References:

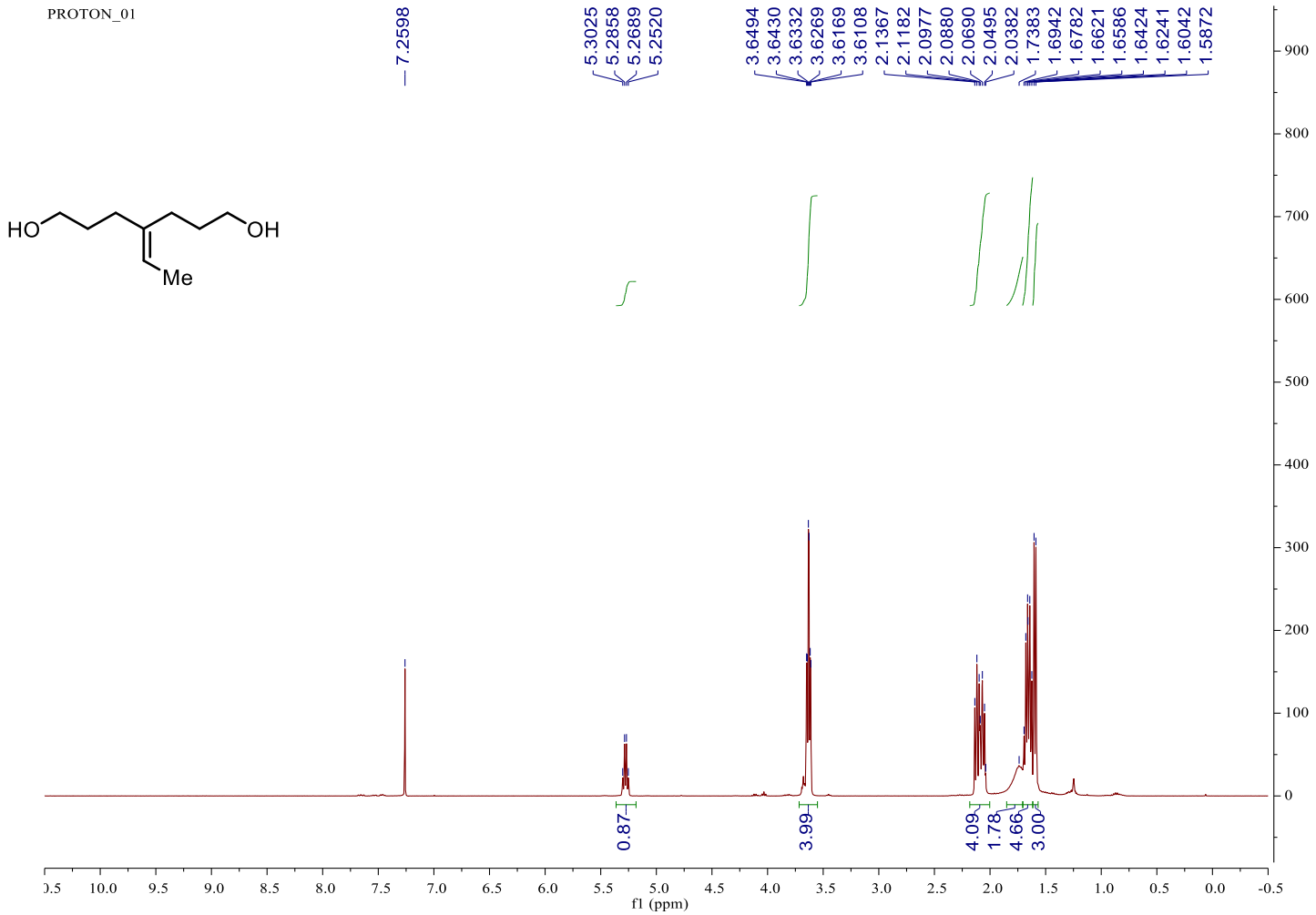
1. K. Harada, A. Imai, K. Uto, R. G. Carter, M. Kubo, H. Hioki and Y. Fukuyama, *Org. Lett.*, 2011, **13**, 988.
2. J. Bergman and L. Venemalm, *J. Org. Chem.*, 1992, **57**, 2495.
3. T.-S. Kam, G. Subramaniam, K.-H. Lim and Y.-M. Choo, *Tetrahedron Lett.*, **2004**, *45*, 599.



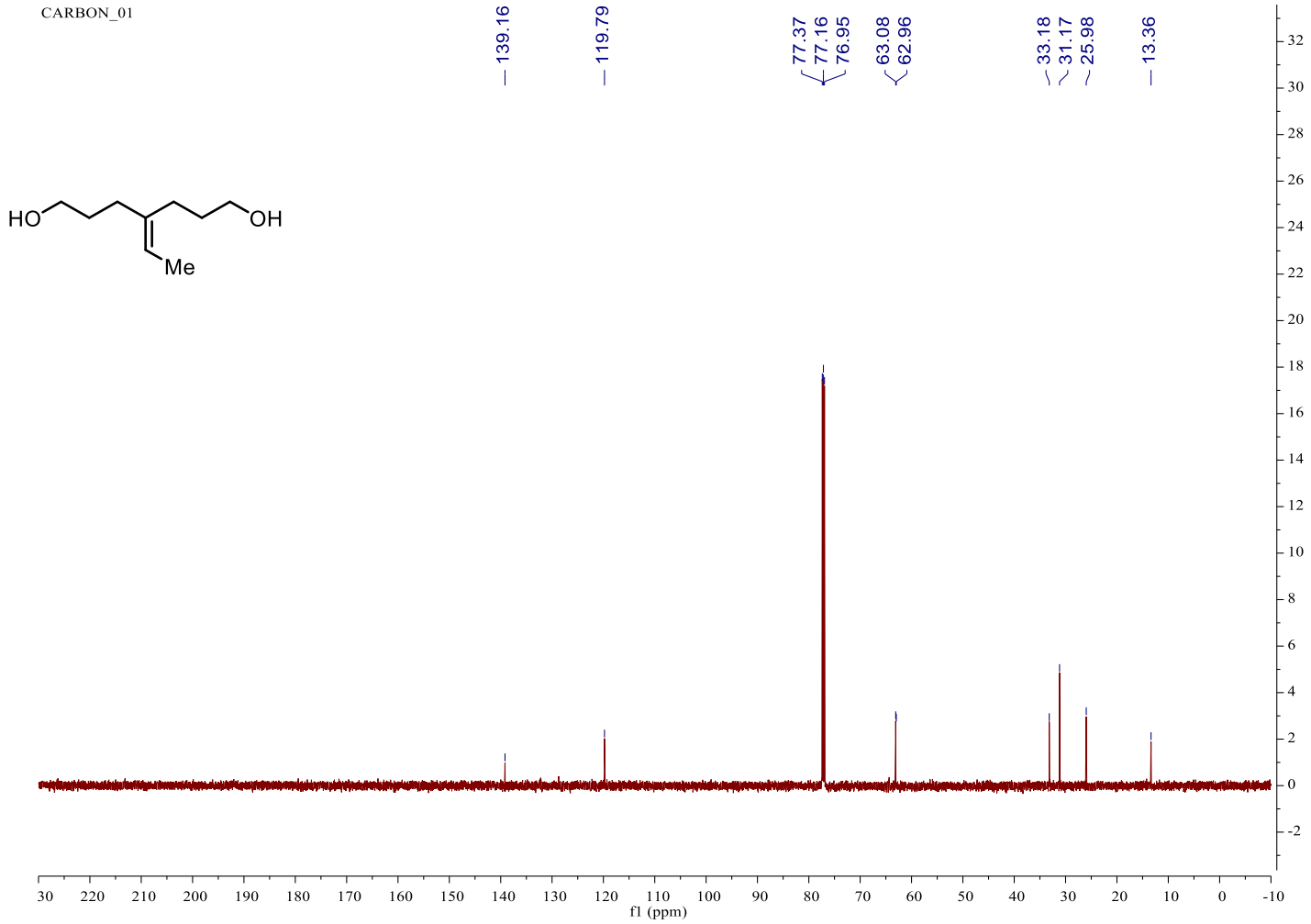
^{1}H NMR Spectrum of Compound 7



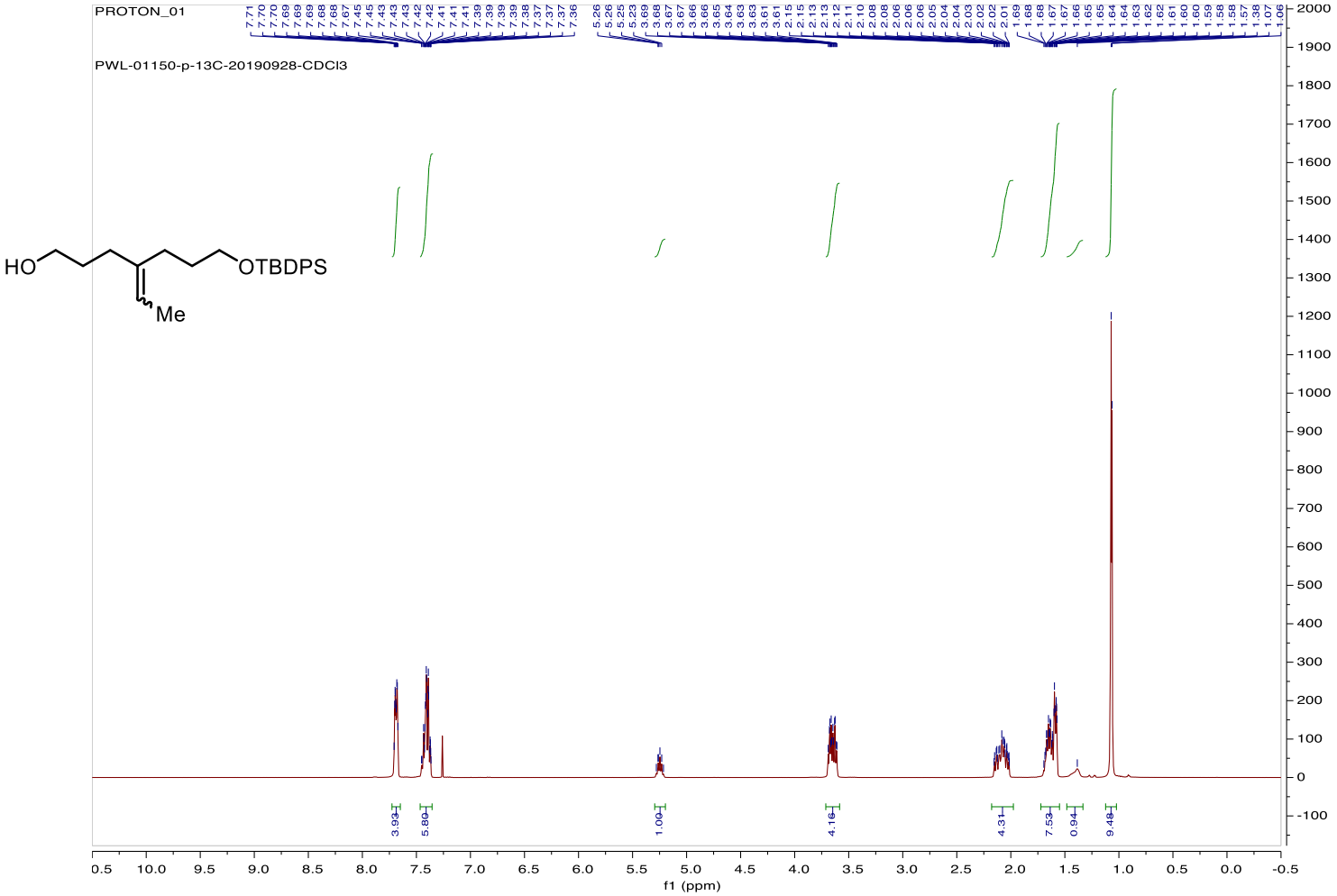
^{13}C NMR Spectrum of Compound 7



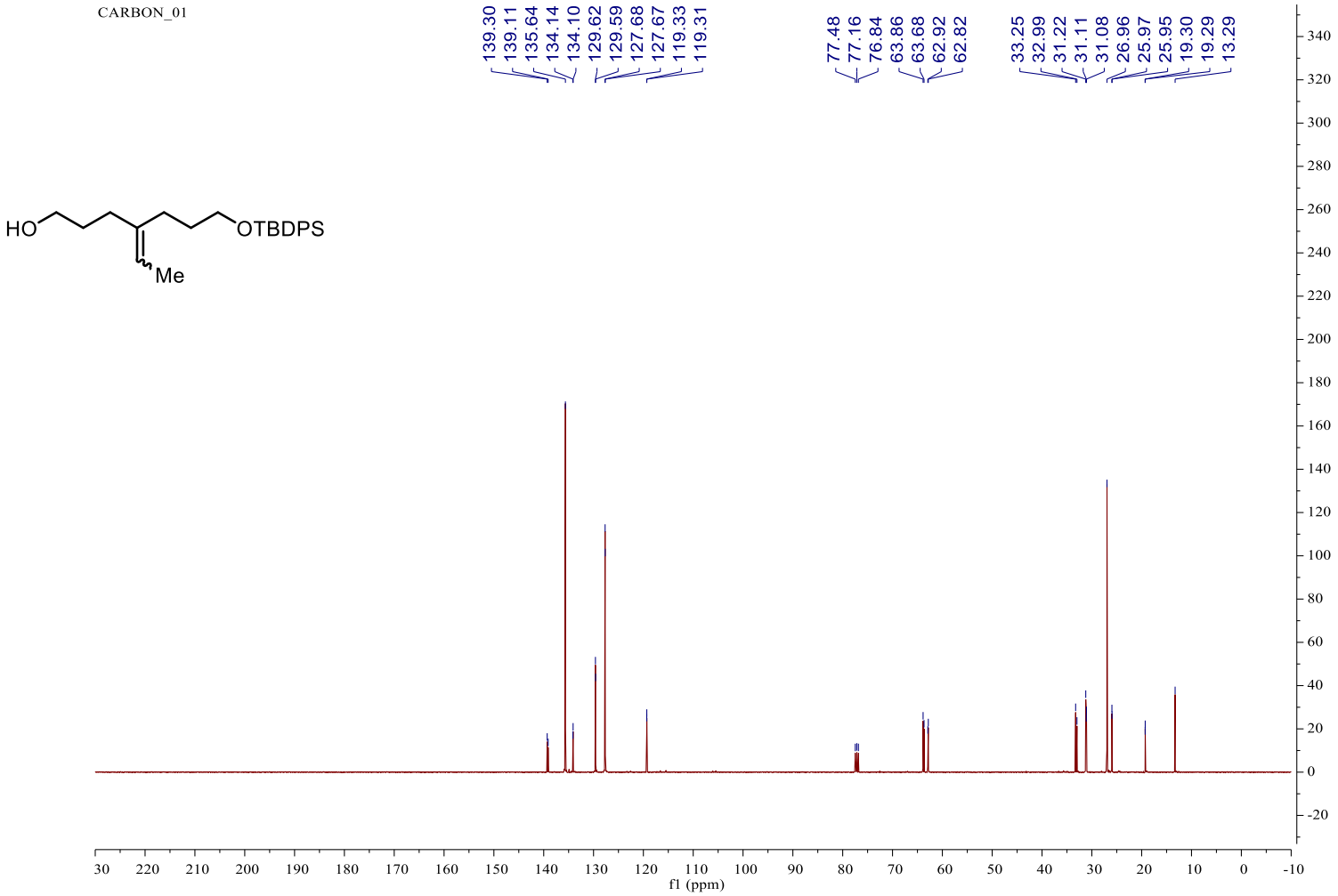
^{1}H NMR Spectrum of Compound 8



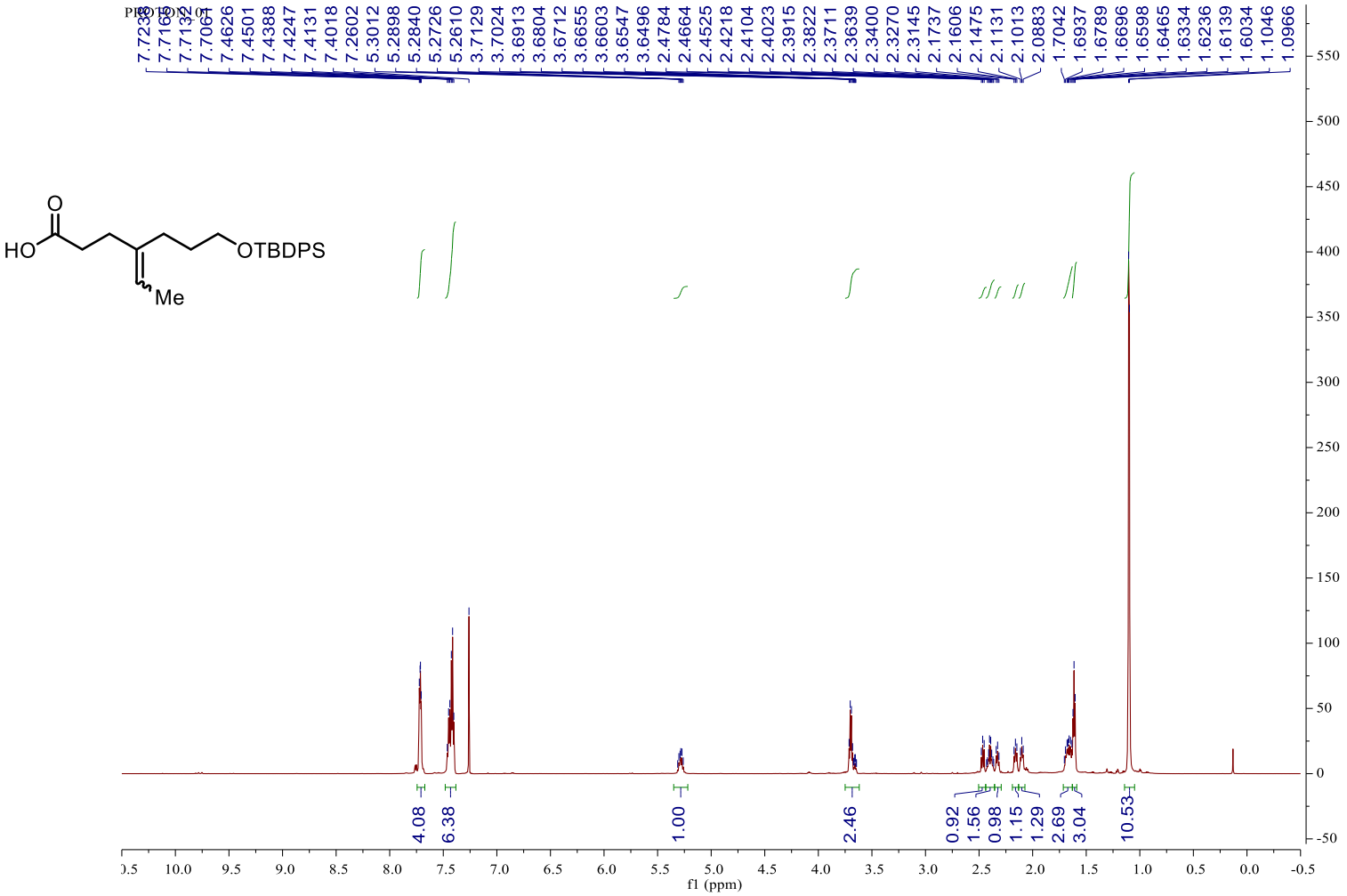
^{13}C NMR Spectrum of Compound 8



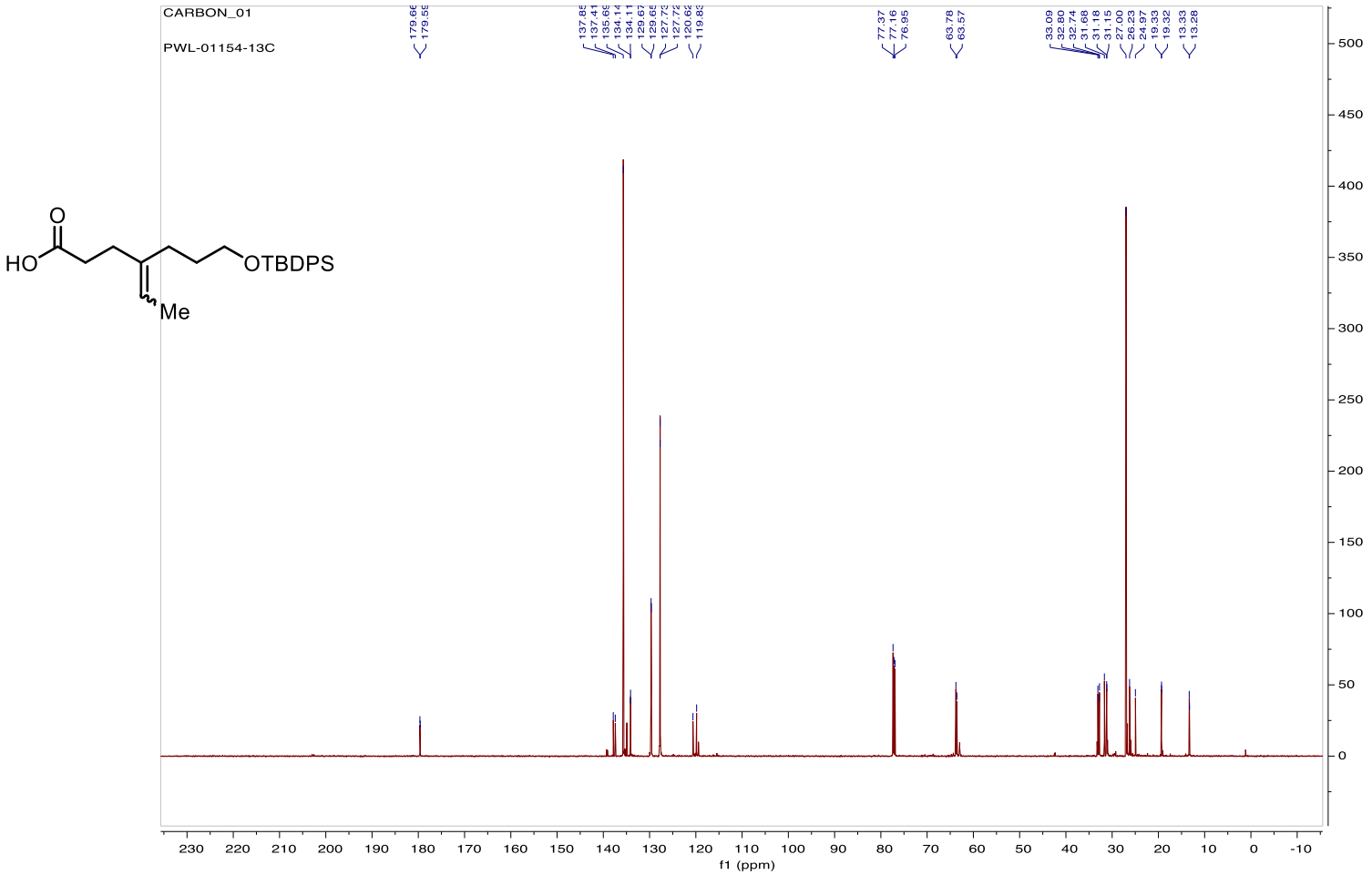
^{1}H NMR Spectrum of Compound 9



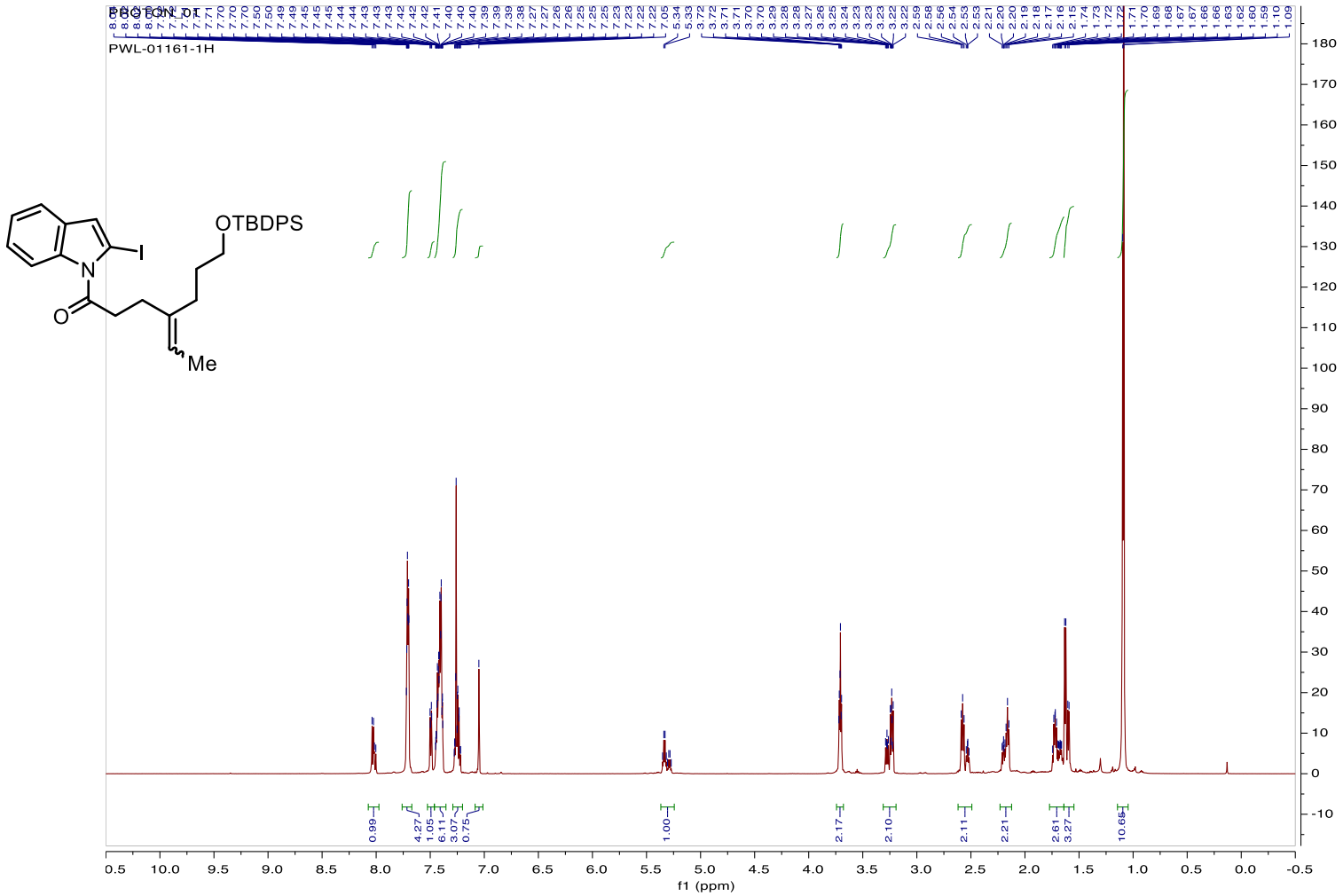
^{13}C NMR Spectrum of Compound 9



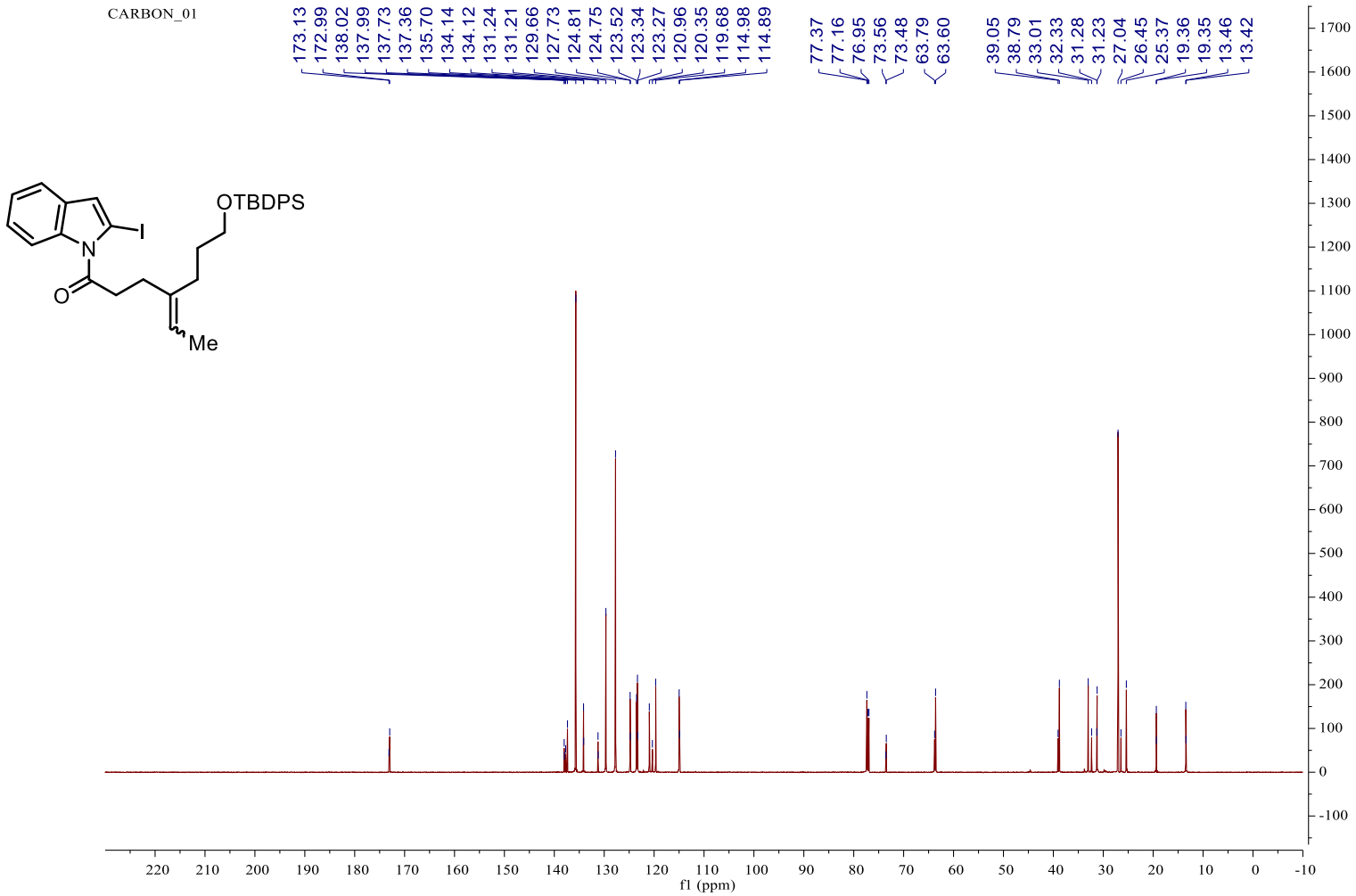
^{1}H NMR Spectrum of Compound 10



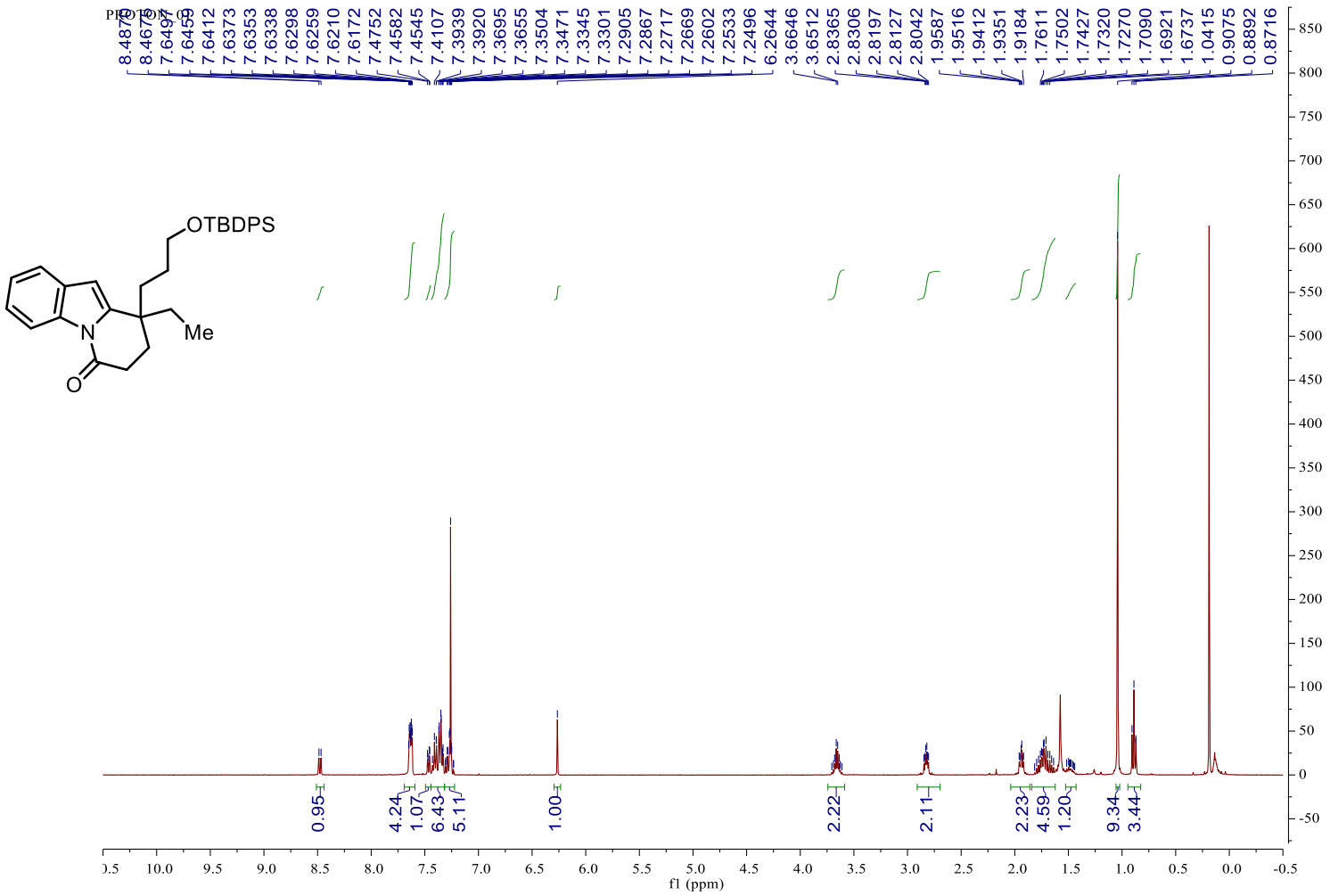
^{13}C NMR Spectrum of Compound 10



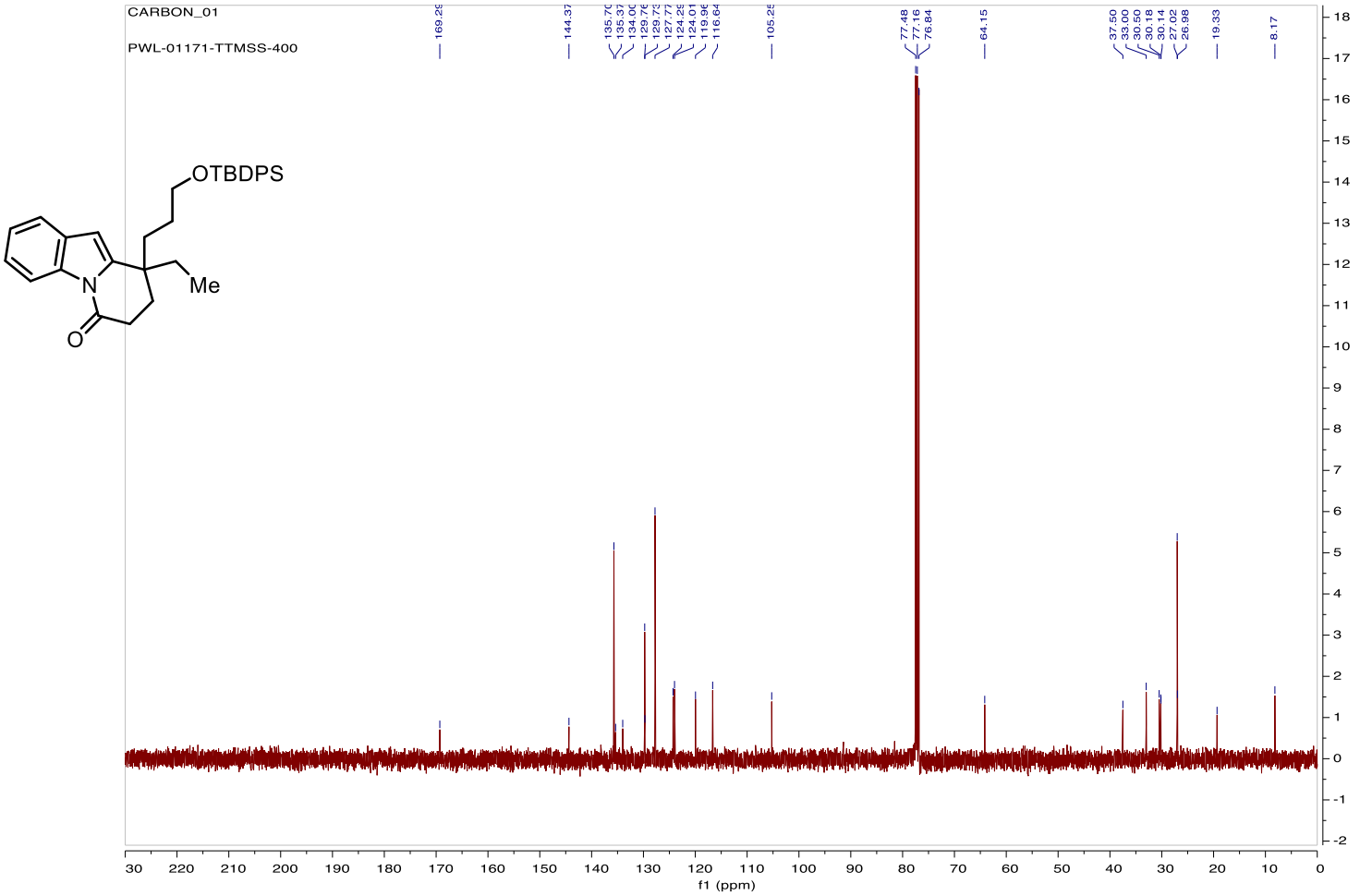
^{1}H NMR Spectrum of Compound 12



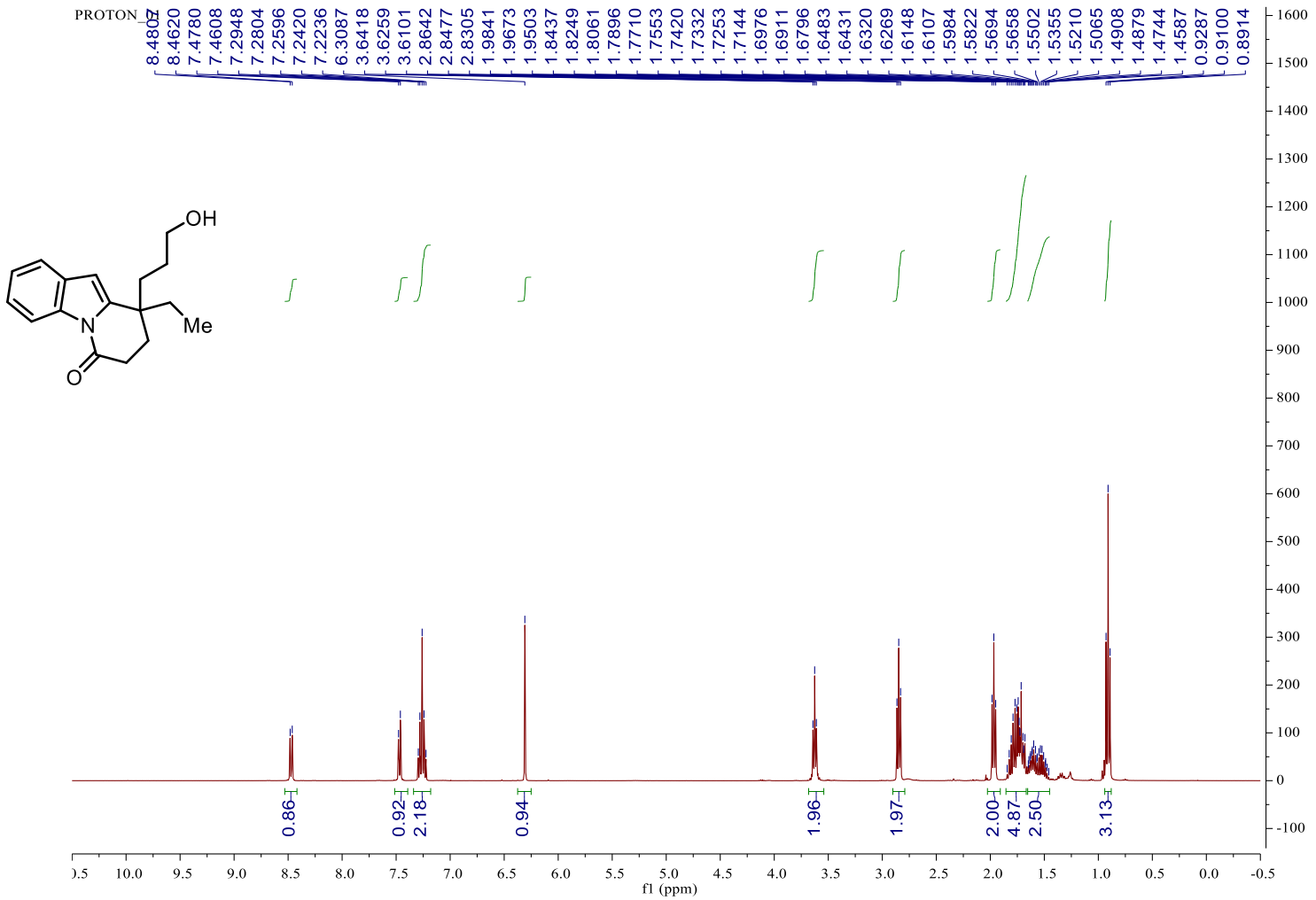
^{13}C NMR Spectrum of Compound 12



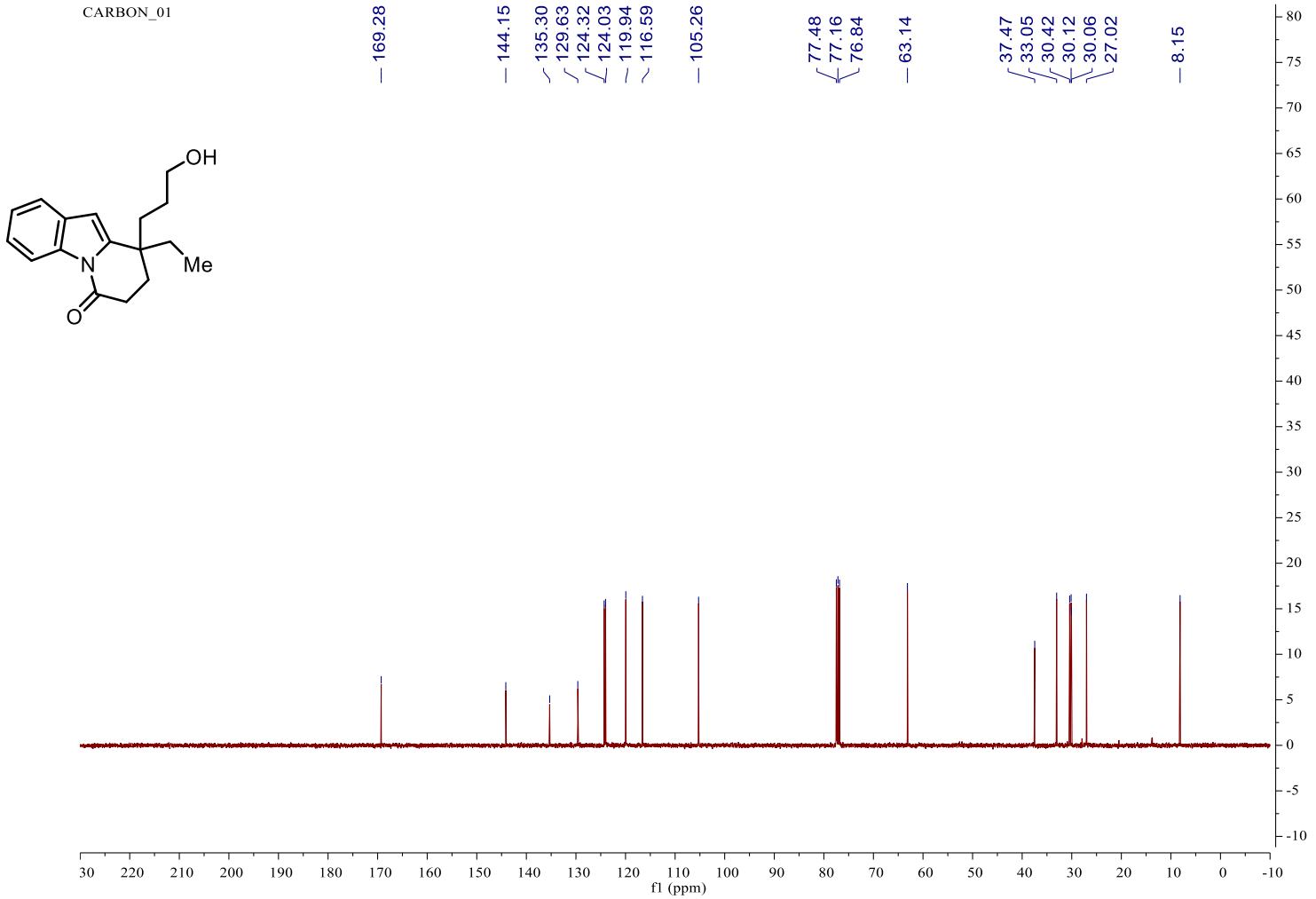
^{1}H NMR Spectrum of Compound 13



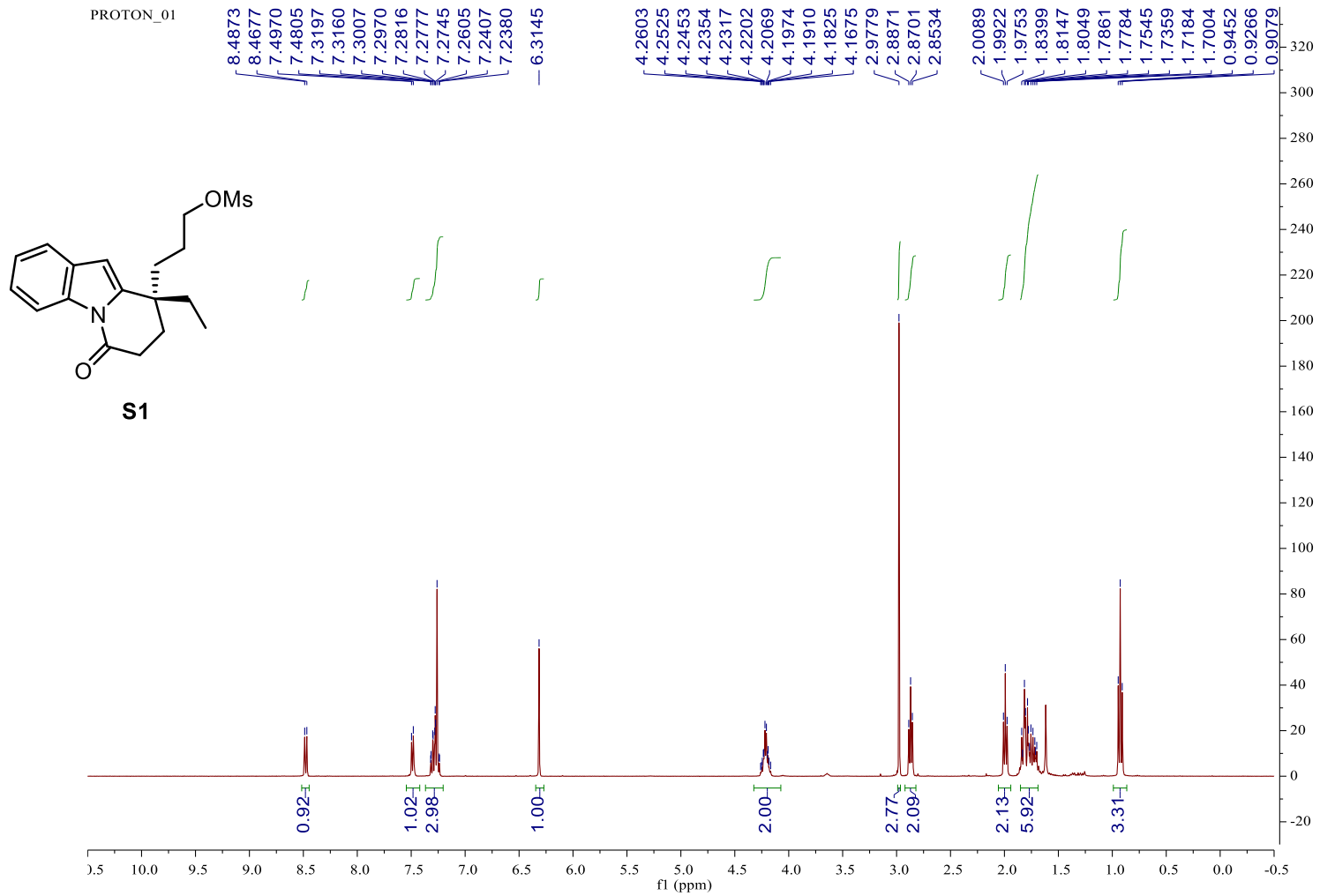
^{13}C NMR Spectrum of Compound 13



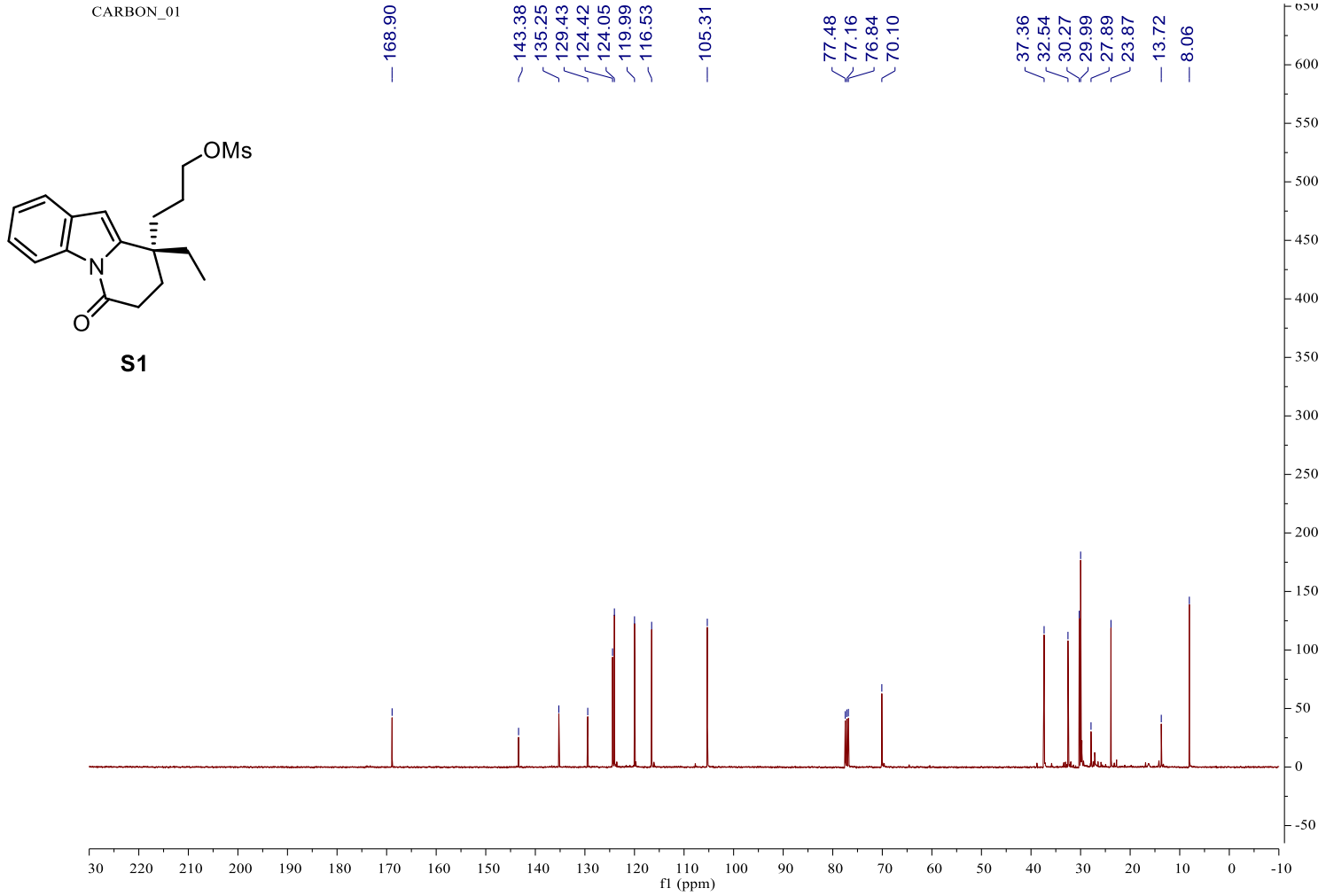
^{1}H NMR Spectrum of Compound 14



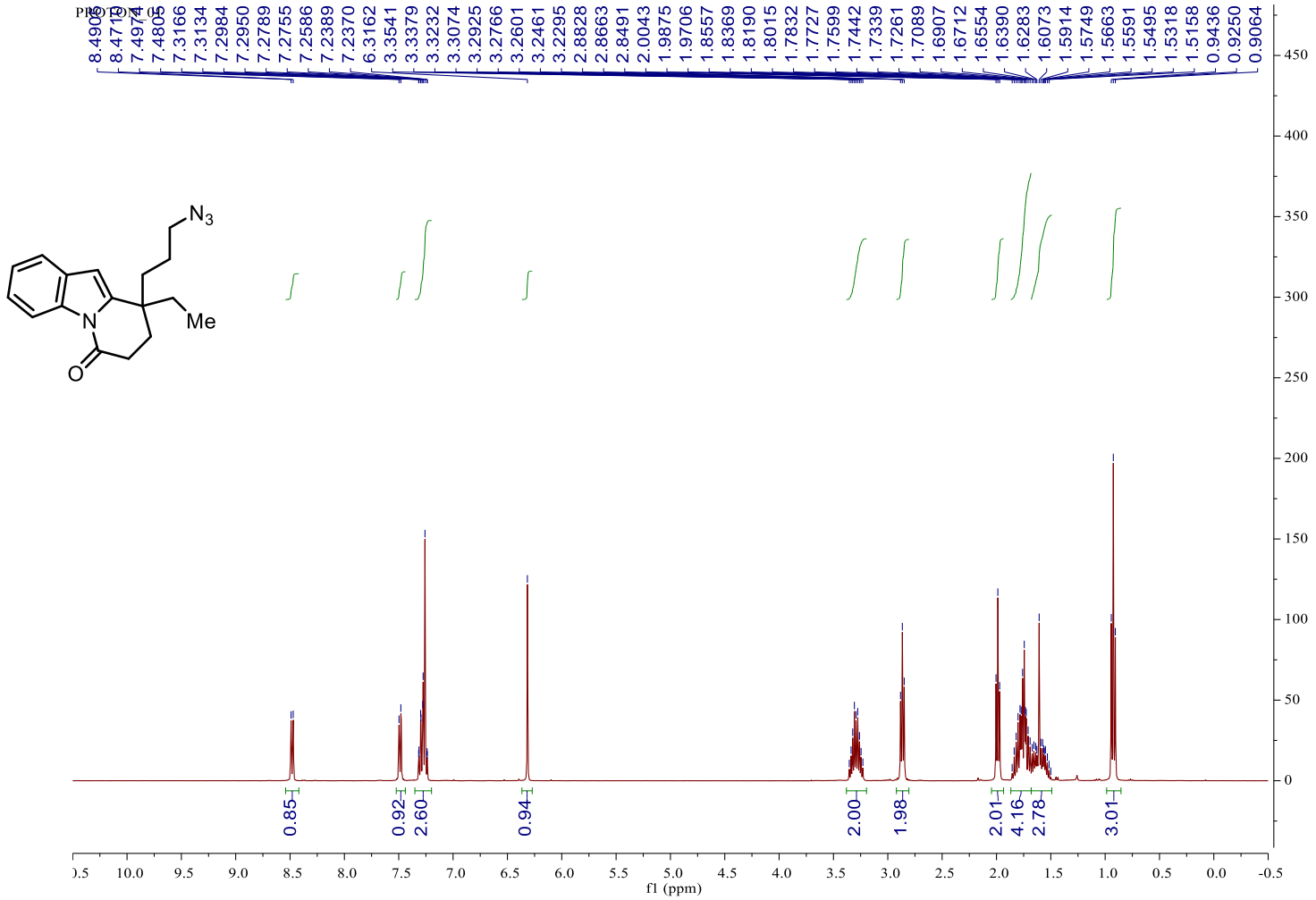
^{13}C NMR Spectrum of Compound 14



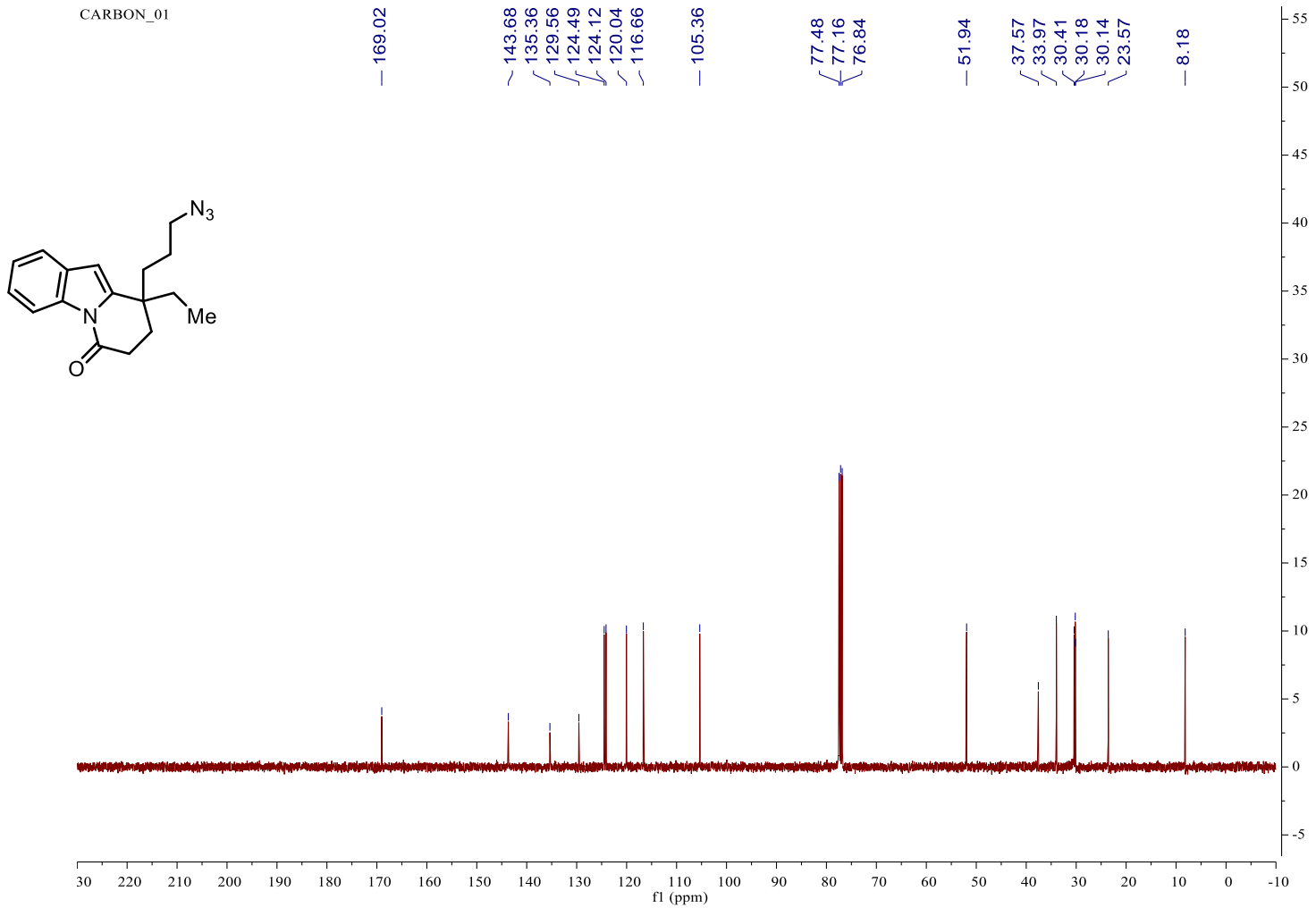
^{1}H NMR Spectrum of Compound S1



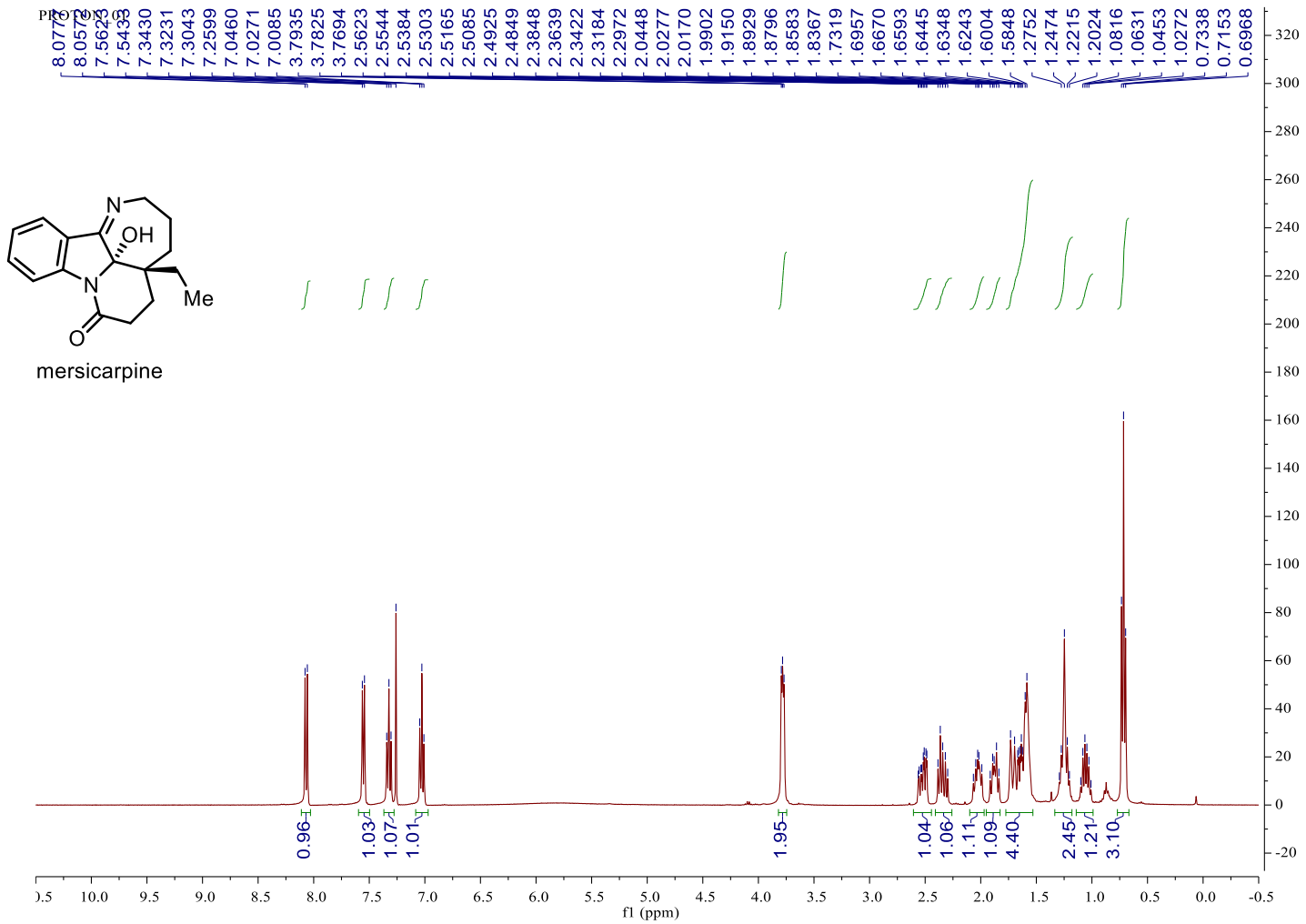
^{13}C NMR Spectrum of Compound S1



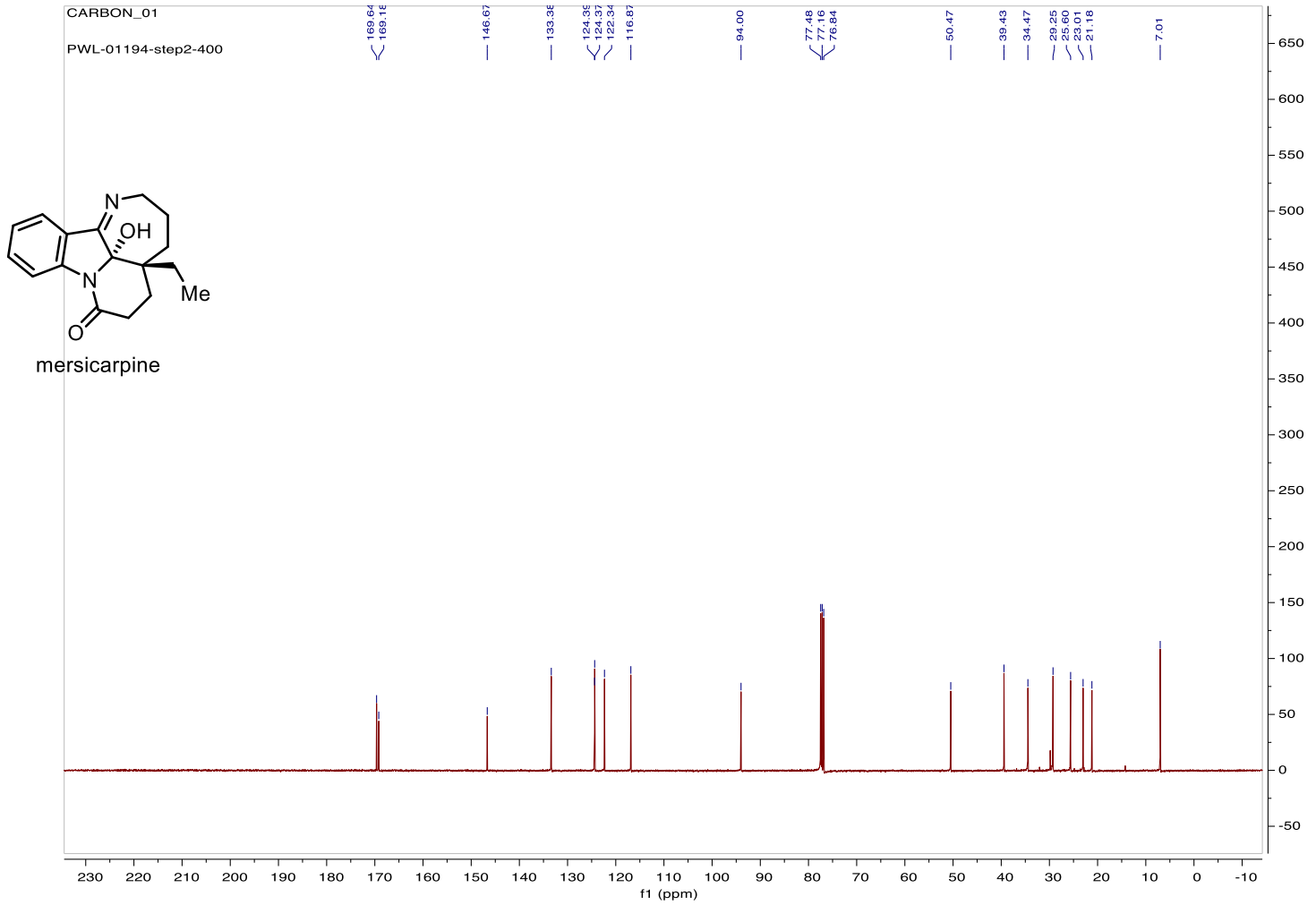
^{1}H NMR Spectrum of Compound 15



^{13}C NMR Spectrum of Compound 15



^{1}H NMR Spectrum of Mersicarpine 1



^{13}C NMR Spectrum of Mersicarpine 1