Supporting Information

Gold(I)-Catalyzed Tandem Cyclization Approach to Tetracyclic Indolines

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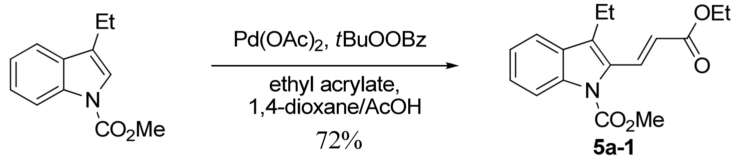
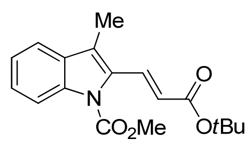
I. General information

Unless otherwise noted, reagents were obtained commercially and used without further purification. CH_2Cl_2 was distilled from CaH_2 under a nitrogen atmosphere. THF was distilled from sodium-benzophenone under a nitrogen atmosphere. Toluene was distilled from sodium under a nitrogen atmosphere. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed on Dynamicadsorbents silica gel F-254 TLC plates. Flash chromatography was carried out on Zeoprep 60 ECO silica gel. ^1H and ^{13}C NMR spectra were recorded with Varian INOVA 400, 500 and Bruker Avance-III 300 spectrometers. Mass spectral and analytical data were obtained *via* the PE SCIEX/ABI API QSTAR Pulsar i Hybrid LC/MS/MS, Applied Biosystems operated by the Central Analytical Laboratory, University of Colorado at Boulder. Infrared (IR) spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer. Melting point (mp) determinations were performed by using a Thomas Hoover capillary melting point apparatus and are uncorrected. High performance liquid chromatography (HPLC) analyses of chiral compounds were performed using a ChiralCel OD column (250 x 4.6 mm) and ChiralPak IA column (250 x 4.6 mm). Compounds were detected by monitoring UV absorbance at 254 nm. Optical rotations were determined on a JASCO 1030 polarimeter at 25 °C. X-Ray crystallographic analysis was carried out by Dr. Joseph Reibenspies at the X-ray Diffraction Laboratory, Texas A & M University.

II. General preparation of alkenylindoles (5a-1 – 5j-1) and characterization data

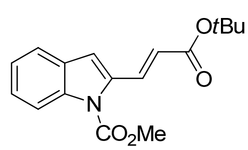


(*E*)-Methyl 2-(3-ethoxy-3-oxoprop-1-enyl)-3-ethyl-1H-indole-1-carboxylate (5a-1):[S1] To a solution of the protected indole (1.02 g, 5.0 mmol) in 1, 4-dioxane/AcOH (3:1, v:v, 10.0 mL) was added $Pd(OAc)_2$ (23 mg, 0.10 mmol), *tert*-butyl benzoyl peroxide (1.3 g, 6.5 mmol) and ethyl acrylate (2.9 mL, 20.0 mmol). The resulting mixture was heated to 80 °C under N_2 atmosphere for 24 h before it was cooled to RT, diluted with ethyl acetate, and filtered through a pad of celite. The filtrate was washed with saturated aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give a crude oil, which was purified by column chromatography (hexanes/ethyl acetate = 30:1) to afford **5a-1** (1.10 g, 3.6 mmol) as a white solid in 72% yield: m.p. 65–66 ºC; IR (thin film): ν 2967, 1740, 1713, 1629, 1455, 1441, 1359, 1176, 1037 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 16.1 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.31–7.27 (m, 1H), 6.11 (d, *J* = 16.1 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.05 (s, 3H), 2.84 (q, *J* = 7.6 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.92, 152.55, 136.54, 135.87, 131.00, 129.89, 127.31, 126.16, 123.43, 120.49, 119.73, 115.92, 60.84, 54.09, 18.31, 15.21, 14.56 ppm; HRMS (ESI): *m/z*: Calcd for $C_{17}H_{19}NNaO_4$ $[M+Na]^+$ 324.1206, Found 324.1196.



5b-1

(*E*)-Methyl 2-(3-*tert*-butoxy-3-oxoprop-1-enyl)-3-methyl-1H-indole-1-carboxylate (5b-1): A colorless oil was obtained in 75% yield by following general procedure. IR (thin film): ν = 3359, 3053, 2977, 1698, 1626, 1455, 1145, 1065, 1025 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* =16.0 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.39 – 7.34 (m, 1H), 7.32 – 7.27 (m, 1H), 6.03 (d, *J* = 16.0 Hz, 1H), 4.05 (s, 3H), 2.38 (s, 3H), 1.56 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.18, 152.39, 136.19, 134.88, 131.59, 130.70, 126.02, 123.30, 123.23, 120.68, 119.52, 115.71, 80.69, 53.93, 28.38, 10.78 ppm; HRMS (ESI): *m/z*: Calcd for $C_{18}H_{21}NNaO_4$ $[M+Na]^+$ 338.1362, Found 338.1372.

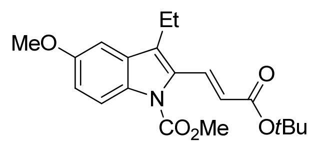


5c-1

(*E*)-Methyl 2-(3-*tert*-butoxy-3-oxoprop-1-enyl)-1H-indole-1-carboxylate (5c-1): A

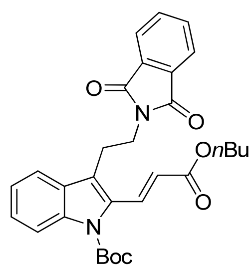
S1. Grimster, N. P.; Gauntlett, C.; Godfrey, C. R. A.; Gaunt, M. J. *Angew. Chem. Int. Ed.* **2005**, *44*, 3125.

colorless oil was obtained in 71% yield by following general procedure. IR (thin film): ν = 2977, 1715, 1625, 1440, 1368, 1160, 1121, 1072 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 15.8 Hz, 0.9 Hz, 1H), 8.13 (dd, *J* = 8.5 Hz, 0.9 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.35 (ddd, *J* = 8.5 Hz, 7.2 Hz, 1.3 Hz, 1H), 7.30 – 7.26 (m, 1H), 6.97 (s, 1H), 6.34 (d, *J* = 15.8 Hz, 1H), 4.09 (s, 3H), 1.54 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.82, 152.08, 137.31, 136.11, 134.63, 128.81, 125.66, 123.57, 121.73, 121.10, 115.82, 110.41, 80.55, 53.94, 28.23 ppm; HRMS (ESI): *m/z*: Calcd for $C_{17}H_{19}NNaO_4$ $[M+Na]^+$ 324.1206, Found 324.1192.



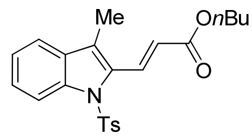
5d-1

(*E*)-Methyl 2-(3-*tert*-butoxy-3-oxoprop-1-enyl)-3-ethyl-5-methoxy-1H-indole-1-carboxylate (5d-1): A white solid was obtained in 78% yield by following general procedure. m.p. 116–118 ºC; IR (thin film): ν = 2971, 2934, 1737, 1705, 1625, 1479, 1366, 1144, 1025 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 16.1 Hz, 1H), 7.00 – 6.94 (m, 2H), 6.02 (d, *J* = 16.1 Hz, 1H), 4.03 (s, 3H), 3.88 (s, 3H), 2.80 (q, *J* = 7.6 Hz, 2H), 1.55 (s, 9H), 1.30 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.19, 156.29, 152.39, 134.82, 131.74, 131.13, 130.72, 126.61, 122.27, 116.74, 114.55, 101.88, 80.75, 55.84, 53.89, 28.39, 18.28, 15.00 ppm; HRMS (ESI): *m/z*: Calcd for $C_{20}H_{25}NNaO_5$ $[M+Na]^+$ 382.1624, Found 382.1623.



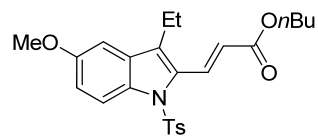
5f-1

(*E*)-*Tert*-butyl 2-(3-butoxy-3-oxoprop-1-enyl)-3-(2-(1, 3-dioxoisoindolin-2-yl)ethyl)-1H-indole-1-carboxylate (5f-1): A colorless oil was obtained in 73% yield by following general procedure. IR (thin film): ν = 2959, 1771, 1715, 1632, 1455, 1361, 1287, 1166, 1107 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 16.2 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.73 – 7.68 (m, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.31 – 7.26 (m, 1H), 6.35 (d, *J* = 16.2 Hz, 1H), 4.25 (t, *J* = 6.7 Hz, 2H), 4.09 – 3.88 (m, 2H), 3.24 – 3.09 (m, 2H), 1.76 – 1.70 (m, 2H), 1.66 (s, 9H), 1.53 – 1.44 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.09, 166.75, 150.09, 136.58, 135.86, 134.04, 132.35, 132.16, 129.48, 126.02, 123.34, 120.65, 119.77, 119.37, 115.69, 84.72, 64.61, 37.74, 30.90, 28.26, 24.34, 19.29, 13.95 ppm; HRMS (ESI): *m/z*: Calcd for $C_{30}H_{32}N_2NaO_6$ $[M+Na]^+$ 539.2125, Found 539.2172.



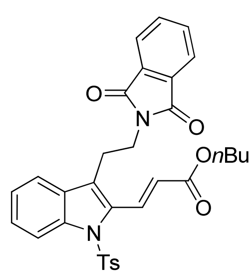
5g-1

(*E*)-Butyl 3-(3-methyl-1-(4-methylbenzene-sulfonyl)-1H-indol-2-yl)acrylate (5g-1): A colorless oil was obtained in 70% yield by following general procedure. IR (thin film): ν = 2959, 1712, 1628, 1450, 1372, 1311, 1175, 1133 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 – 8.21 (m, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.30 – 7.26 (m, 1H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.11 (d, *J* = 16.1 Hz, 1H), 4.27 (t, *J* = 6.7 Hz, 2H), 2.30 – 2.32 (m, 6H), 1.75 (dt, *J* = 14.6 Hz, 6.8 Hz, 2H), 1.52 – 1.43 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.62, 145.00, 137.20, 135.00, 134.64, 131.83, 131.49, 129.74, 126.77, 126.56, 124.15, 123.43, 122.55, 119.93, 115.49, 64.83, 30.88, 21.66, 19.36, 13.94, 11.04 ppm; HRMS (ESI): *m/z*: Calcd for $C_{23}H_{25}NNaO_4S$ $[M+Na]^+$ 434.1396, Found 434.1401.



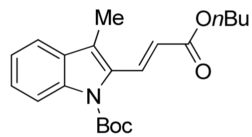
5h-1

(*E*)-Butyl 3-(3-ethyl-5-methoxy-1-(4-methylbenzenesulfonyl)-1H-indol-2-yl)acrylate (5h-1): A white solid was obtained in 76% yield by following general procedure. m.p. 146–147 ºC; IR (thin film): ν = 2954, 1713, 1630, 1450, 1311, 1176, 1163 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 16.1 Hz, 1H), 8.10 (d, *J* = 9.1 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.98 (dd, *J* = 9.1 Hz , 2.5 Hz, 1H), 6.85 (d, *J* = 2.5 Hz, 1H), 6.10 (d, *J* = 16.1 Hz, 1H), 4.26 (t, *J* = 6.8 Hz, 2H), 3.84 (s, 3H), 2.71 (q, *J* = 7.6 Hz, 2H), 2.30 (s, 3H), 1.74 (dt, *J* = 14.6 Hz, 6.8 Hz, 2H), 1.53 – 1.41 (m, 2H), 1.16 (t, *J* = 7.6 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.71, 157.05, 144.89, 134.70, 134.64, 132.28, 131.93, 130.09, 129.65, 126.83, 121.72, 116.92, 115.20, 102.21, 64.93, 55.83, 30.94, 21.74, 19.42, 18.52, 14.66, 14.01 ppm; HRMS (ESI): *m/z*: Calcd for $C_{25}H_{29}NNaO_5S$ $[M+Na]^+$ 478.1659, Found 478.1664.



5j-1

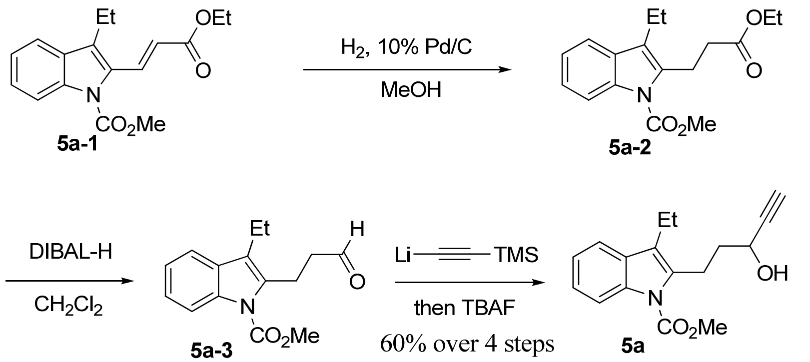
(*E*)-Butyl 3-(3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1-(4-methylbenzene-sulfonyl)-1H-indol-2-yl)acrylate (5j-1): A white solid was obtained in 76% yield by following general procedure. m.p. 149–151 ºC; IR (thin film): ν = 2959, 2873, 1771, 1713, 1632, 1449, 1174, 1090 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 16.2 Hz, 1H), 7.87 – 7.78 (m, 2H), 7.75 – 7.69 (m, 2H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.34 (m, 1H), 7.32 – 7.26 (m, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.38 (d, *J* = 16.2 Hz, 1H), 4.28 (t, *J* = 6.8 Hz, 2H), 3.84 – 3.79 (m, 2H), 3.14 – 3.06 (m, 2H), 2.32 (s, 3H), 1.76 (dt, J = 14.6 Hz, 6.8 Hz, 2H), 1.59 – 1.40 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.11, 166.37, 145.16, 137.27, 135.05, 134.21, 133.78, 133.01, 132.14, 130.48, 129.86, 126.87, 126.66, 124.46, 123.49, 123.02, 122.71, 119.89, 115.59, 64.95, 37.42, 30.93, 24.55, 21.78, 19.39, 14.05 ppm; HRMS (ESI): *m/z*: Calcd for $C_{32}H_{30}N_2NaO_6S$ $[M+Na]^+$ 593.1717, Found 593.1733.



5o-1

(*E*)-*Tert*-butyl 2-(3-butoxy-3-oxoprop-1-enyl)-3-methyl-1H-indole-1-carboxylate (5o-1): A white solid was obtained in 72% yield by following general procedure. m.p. 45–46 ºC; IR (thin film): ν = 2959, 2931, 2872, 1731, 1630, 1455, 1354, 1331, 1283, 1145, 1065cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.13 (m, 1H), 8.08 (dd, J = 16.1 Hz, 0.7 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.36 (ddd, J = 8.4 Hz, 7.2 Hz, 1.3 Hz, 1H), 7.31 – 7.25 (m, 1H), 6.10 (d, J = 16.1 Hz, 1H), 4.23 (t, J = 6.7 Hz, 2H), 2.39 (s, 3H), 1.78 – 1.67 (m, 2H), 1.67 (s, 9H), 1.52 – 1.38 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.06, 150.36, 136.77, 136.61, 131.41, 130.51, 126.01, 123.04, 120.56, 120.30, 119.50, 115.66, 84.50, 64.62, 30.96, 28.35, 19.38, 13.95, 10.73 ppm; HRMS (ESI): *m/z*: Calcd for $C_{21}H_{27}NNaO_4$ $[M+Na]^+$ 380.1832, Found 380.1832.

III. General preparation of alkynylindole substrates **5a**-**5j** (entries 1-10, Table 2) and characterization data

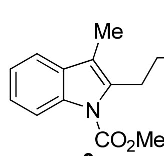


Methyl 2-(3-hydroxypent-4-ynyl)-3-methyl-1H-indole-1-carboxylate (5a, entry 1, Table 2): To a solution of **5a-1** (1.1 g, 3.6 mmol) in anhydrous methanol (10.0 mL) was added 10% Pd/C (110 mg). The resulting mixture was stirred under hydrogen atmosphere (56 psi) for 1 h before it was filtrated through a short pad of silica gel to afford **5a-2**, which was used for the next step without further purification.

5a-2 was dissolved in anhydrous dichloromethane and the solution was cooled to -78 °C before the addition of the solution of DIBAL-H (1.0 M in hexane, 4.3 mL, 4.3 mmol) dropwise. The reaction mixture was stirred for 2 h at -78 °C before it was treated with saturated aqueous solution of Rochelle salt (10.0 mL) at -78 °C. After being stirred for 1 h at RT, the layers were separated. The aqueous layer was extracted with ether, and the combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to give **5a-3** as a yellow oil, which was used for the next step without further purification.

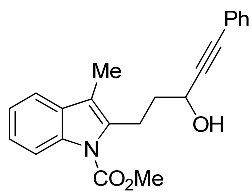
A solution of ^{n}BuLi (1.6 M in hexanes, 4.5 mL, 7.2 mmol) was added to a solution of trimethylsilylacetylene (1.06 mL, 7.5 mmol) in anhydrous THF (20.0 mL) at -78 °C. The resulting mixture was stirred for 30 min before the addition of the solution of **5a-3** in anhydrous THF (3.0 mL) dropwise. The reaction mixture was stirred for 1 hour at the same temperature before it was quenched with water, and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to afford a yellow oil, which was then dissolved in anhydrous THF (10.0 mL) and cooled to 0 °C. Tetrabutylammonium fluoride (1.0 M in THF, 3.6 mL, 3.6 mmol) was added dropwise to the above solution, and the resulting mixture was stirred for 10 min at 0 °C. After the reaction was terminated by the addition of water (20.0 mL), the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to produce a crude oil, which was purified by column chromatography (hexanes/ethyl acetate = 5:1) to afford alkynylindole **5a** (616 mg, 2.16 mmol) as a colorless oil in 60% yield over 4 steps: IR (thin film): ν = 3288, 2963, 1731, 1458, 1442, 1360, 1330, 1216, 1136 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 7.1 Hz, 2.1 Hz, 1H), 7.48 (dd, J = 6.5 Hz, 2.5 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.26 – 7.21 (m, 1H), 4.46 (td, J = 6.1 Hz, 2.9 Hz, 1H), 4.05 (s, 3H), 3.20 (m, 2H), 2.71 (q, J = 7.6 Hz, 2H), 2.53 – 2.49 (d, J = 4.0 Hz,1H), 2.23 (d, J = 5.5 Hz, 1H), 2.05 (dt, J = 10.8 Hz, 6.6 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.76, 135.88, 135.40, 130.02, 123.98, 122.97, 122.11, 118.45, 115.95, 84.84, 73.22, 61.78, 53.69, 37.90, 22.28, 17.38, 15.13 ppm; HRMS (ESI): *m/z*: Calcd for

$C_{17}H_{20}NO_3$ [M+H]$^+$ 286.1437, Found 286.1441.



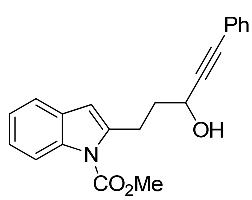
3

Methyl 2-(3-hydroxypent-4-ynyl)-3-methyl-1H-indole-1-carboxylate (3, Scheme 1): A colorless oil was obtained in 68% yield by following general procedure. IR (thin film): ν = 3435, 3288, 2955, 2864, 1732, 1459, 1379, 1254, 1221, 1136, 1057 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.02 (m, 1H), 7.46 – 7.42 (m, 1H), 7.32 – 7.23 (m, 1H), 7.27 – 7.21 (m, 1H), 4.42 (qd, *J* = 6.2 Hz, 2.0 Hz, 1H), 4.05 (s, 3H), 3.25 – 3.20 (m, 2H), 2.50 (d, *J* = 2.0 Hz, 1H), 2.23 (s, 3H), 2.09 – 2.00 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.60, 135.68, 135.55, 130.83, 123.95, 122.90, 118.21, 115.70, 115.67, 84.92, 73.07, 61.49, 53.56, 37.31, 22.33, 8.73 ppm; HRMS (ESI): *m/z*: Calcd for $C_{16}H_{17}NNaO_3$ [M+Na]$^+$ 294.1101, Found 294.1094.



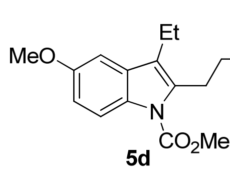
5b

Methyl 2-(3-hydroxy-5-phenylpent-4-ynyl)-3-methyl-1H-indole-1-carboxylate (5b, entry 2, Table 2): A white solid was obtained in 70% yield by following general procedure. m.p. 91–92 ºC; IR (thin film): ν = 3435, 3051, 2954, 2863, 1732, 1459, 1354, 1220, 1135, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 – 9.27 (m, 1H), 8.07 – 8.02 (m, 1H), 7.47 – 7.43 (m, 2H), 7.42 – 7.37 (m, 3H), 7.29 – 7.26 (m, 1H), 7.26 – 7.24 (m, 1H), 4.64 (q, *J* = 6.2 Hz, 1H), 4.05 (s, 3H), 3.28 (td, *J* = 8.8 Hz, 4.0 Hz, 2H), 2.26 (s, 3H), 2.13 (dd, *J* = 12.0 Hz, 8.0 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.75, 135.94, 135.70, 131.83, 130.99, 128.56, 128.46, 124.07, 123.00, 122.74, 118.34, 115.83, 115.80, 90.08, 85.15, 62.37, 53.66, 37.66, 22.59, 8.91 ppm; HRMS (ESI): *m/z*: Calcd for $C_{22}H_{21}NNaO_3$ [M+Na]$^+$ 370.1414, Found 370.1426.



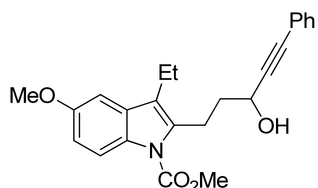
5c

Methyl 2-(3-hydroxy-5-phenylpent-4-ynyl)-1H-indole-1-carboxylate (5c, entry 3, Table 2): A colorless oil was obtained in 58% yield by following general procedure. IR (thin film): ν = 3434, 2954, 2853, 1739, 1456, 1332, 1214, 1059 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 1H), 7.47 (d, *J* = 7.1 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.35 – 7.31 (m, 3H), 7.30 – 7.26 (m, 1H), 7.26 – 7.19 (m, 1H), 6.46 (s, 1H), 4.71 (q, *J* = 6.1 Hz, 1H), 4.06 (s, 3H), 3.30 – 3.24 (m, 2H), 2.26 – 2.19 (m, 2H), 2.11 (d, *J* = 5.4 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.72, 141.09, 136.61, 131.89, 129.56, 128.66, 128.50, 123.89, 123.27, 122.68, 120.11, 115.87, 108.66, 89.87, 85.42, 62.44, 53.80, 37.18, 25.86 ppm; HRMS (ESI): *m/z*: Calcd for $C_{21}H_{19}NNaO_3$ $[M+Na]^+$ 356.1257, Found 356.1252.



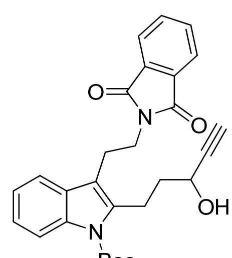
5d

Methyl 3-ethyl-2-(3-hydroxypent-4-ynyl)-5-methoxy-1H-indole-1-carboxylate (5d, entry 4, Table 2): A white solid was obtained in 72% yield by following general procedure. m.p. 69–70 ºC; IR (thin film): ν = 3451, 3284, 2961, 1731, 1608, 1478, 1442, 1364, 1262, 1131 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 9.0 Hz, 1H), 6.93 (d, *J* = 2.6 Hz, 1H), 6.86 (dd, *J* = 9.0 Hz, 2.6 Hz, 1H), 4.45 (m, 1H), 4.03 (s, 3H), 3.87 (s, 3H), 3.18 (td, *J* = 8.0 Hz, 4.0 Hz, 2H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.50 (d, *J* = 2.1 Hz, 1H), 2.04 (t, *J* = 8.0 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.09, 152.61, 136.24, 130.94, 130.43, 121.95, 116.73, 111.88, 101.56, 84.85, 73.19, 61.76, 55.89, 53.61, 37.85, 22.34, 17.37, 15.00 ppm; HRMS (ESI): *m/z*: Calcd for $C_{18}H_{21}NNaO_4$ $[M+Na]^+$ 338.1362, Found 338.1364.



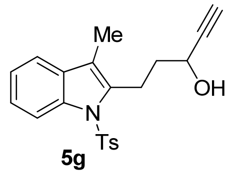
5e

Methyl 3-ethyl-2-(3-hydroxy-5-phenylpent-4-ynyl)-5-methoxy-1H-indole-1-carboxylate (5e, entry 5, Table 2): A colorless oil was obtained in 74% yield by following general procedure. IR (thin film): ν = 3442, 2956, 1731, 1454, 1333, 1221, 1067 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.0 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.34 – 7.28 (m, 3H), 6.93 (d, *J* = 2.6 Hz, 1H), 6.86 (dd, *J* = 9.0 Hz, 2.6 Hz, 1H), 4.69 (t, *J* = 5.5 Hz, 1H), 4.02 (s, 3H), 3.87 (s, 3H), 3.31 – 3.21 (m, 2H), 2.71 (q, *J* = 7.6 Hz, 2H), 2.13 (m, 2H), 1.23 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.09, 152.61, 136.40, 131.80, 130.96, 130.49, 128.53, 128.44, 122.75, 121.91, 116.73, 111.86, 101.55, 90.07, 85.12, 62.44, 55.88, 53.57, 38.11, 22.57, 17.41, 14.99 ppm; HRMS (ESI): *m/z*: Calcd for $C_{24}H_{25}NNaO_4$ $[M+Na]^+$ 414.1676, Found 414.1667.



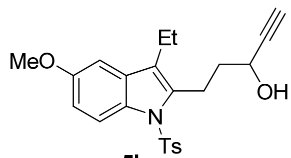
5f

***Tert*-butyl 3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-2-(3-hydroxypent-4-ynyl)-1H-indole-1-carboxylate (5f, entry 6, Table 2):** A white solid was obtained in 65% yield by following general procedure. m.p. 140–141 ºC; IR (thin film): ν = 3466, 3287, 2930, 2359, 1770, 1712, 1457, 1365, 1328, 1161 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 1H), 7.88 – 7.84 (m, 2H), 7.76 – 7.71 (m, 2H), 7.68 (dt, *J* = 7.9 Hz, 3.1 Hz, 1H), 7.26 – 7.21 (m, 2H), 4.52 – 4.42 (m, 1H), 3.98 – 3.81 (m, 2H), 3.35 – 3.20 (m, 2H), 3.06 (t, *J* = 8.3 Hz, 2H), 2.91 (d, *J* = 6.1 Hz, 1H), 2.50 (d, *J* = 2.1 Hz, 1H), 2.28 – 2.10 (m, 2H), 1.70 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.95, 142.71, 141.91, 137.62, 132.89, 129.31, 128.08, 127.96, 126.94, 125.83, 123.79, 121.69, 118.14, 90.00, 82.26, 58.02, 48.51, 33.08, 31.33, 29.91, 28.39, 23.64, 21.61 ppm; HRMS (ESI): *m/z*: Calcd for $C_{28}H_{29}N_2O_5$ $[M+H]^+$ 473.2086, Found 473.2088.



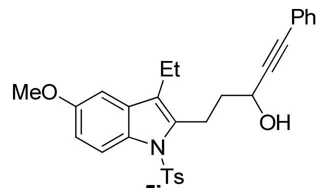
5g

5-(3-Methyl-1-(4-methylbenzene-sulfonyl)-1H-indol-2-yl)pent-1-yn-3-ol (5g, entry 7, Table 2): A colorless oil was obtained in 72% yield by following general procedure. IR (thin film): ν = 3291, 2924, 1453, 1360, 1232, 1170, 1042 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* =8.0 Hz, 1H), 7.56 (d, *J* = 8.2 Hz,, 2H), 7.37 (d, *J* =8.0 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 4.43 (m, 1H), 3.17 (td, *J* = 7.2 Hz, 3.0 Hz, 2H), 2.50 (d, *J* = 2.1 Hz, 1H), 2.31 (s, 3H), 2.22 – 2.10 (m, 5H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.75, 136.84, 135.93, 135.83, 131.60, 129.93, 126.41, 124.53, 123.71, 118.70, 117.98, 115.35, 84.72, 73.30, 61.65, 38.16, 22.20, 21.75, 9.16 ppm; HRMS (ESI): *m/z*: Calcd for $C_{21}H_{22}NO_3S$ $[M+H]^+$ 368.1315, Found 368.1317.



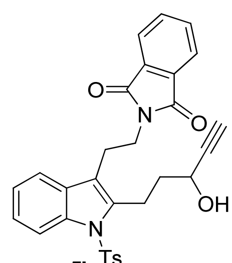
5h

5-(3-Ethyl-5-methoxy-1-(4-methylbenzene-sulfonyl)-1H-indol-2-yl)pent-1-yn-3-ol (5h, entry 8, Table 2): A colorless oil was obtained in 71% yield by following general procedure. IR (thin film): ν = 3289, 2966, 1598, 1447, 1359, 1214, 1175, 1036 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 9.0 Hz, 0.4 Hz, 1H), 7.51(d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.87 (dd, *J* = 9.0 Hz, 2.6 Hz, 1H), 6.83 (d, *J* = 2.2 Hz, 1H), 4.47 (td, *J* = 6.3 Hz, 2.1 Hz, 1H), 3.83 (s, 3H), 3.22 – 3.04 (m, 2H), 2.60 (m, 2H), 2.51 (d, *J* = 2.1 Hz, 1H), 2.30 (s, 3H), 2.16 (td, *J* = 7.8 Hz, 6.4 Hz, 2H), 1.13 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.71, 144.60, 136.47, 135.61, 131.86, 131.62, 129.80, 126.31, 124.48, 116.47, 112.40, 101.85, 84.68, 73.28, 61.73, 55.83, 38.71, 22.28, 21.70, 17.66, 14.77 ppm; HRMS (ESI): *m/z*: Calcd for $C_{23}H_{25}NNaO_4S$ $[M+Na]^+$ 434.1397, Found 434.1400.



5i

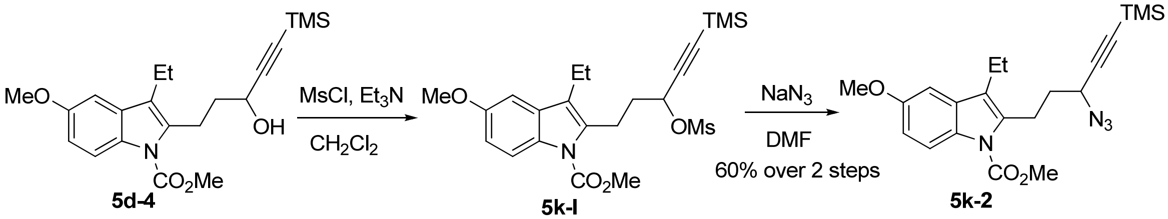
5-(3-Ethyl-5-methoxy-1-(4-methylbenzene-sulfonyl)-1H-indol-2-yl)-1-phenylpent-1-yn-3-ol (5i, entry 9, Table 2): A colorless oil was obtained in 77% yield by following general procedure. IR (thin film): ν = 3345, 3027, 2942, 2876, 1603, 1496, 1453, 1046, 747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 9.0 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.47 – 7.41 (m, 2H), 7.34 – 7.29 (m, 3H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.87 (dd, *J* = 9.0 Hz, 2.6 Hz, 1H), 6.84 – 6.80 (m, 1H), 4.69 (t, *J* = 6.2 Hz, 1H), 3.83 (s, 3H), 3.27 – 3.10 (m, 2H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.30 (s, 3H), 2.28 – 2.16 (m, 2H), 1.17 – 1.10 (m, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.73, 144.57, 136.64, 135.75, 131.89, 131.69, 129.81, 128.58, 128.47, 126.35, 124.39, 122.79, 116.50, 112.39, 101.85, 89.87, 85.25, 62.49, 55.84, 38.97, 22.49, 21.72, 17.73, 14.79 ppm; HRMS (ESI): *m/z*: Calcd for $C_{29}H_{29}NNaO_4S$ $[M+Na]^+$ 510.1509, Found 510.1514.



5j

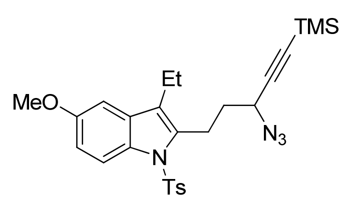
2-(2-(2-(3-Hydroxypent-4-ynyl)-1-(4-methylbenzene-sulfonyl)-1H-indol-3-yl)ethyl)-isoindoline-1,3-dione (5j, entry 10, Table 2): A colorless oil was obtained in 69% yield by following general procedure. IR (thin film): ν = 3349, 2963, 1713, 1596, 1447, 1358, 1218, 1180 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.15 (m, 1H), 7.89 – 7.78 (m, 2H), 7.77 – 7.70 (m, 2H), 7.65 – 7.60 (m, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.23 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.50 (tdd, *J* = 6.8 Hz, 4.6 Hz, 2.1 Hz, 1H), 3.88 – 3.78 (m, 2H), 3.31 – 3.13 (m, 2H), 3.03 – 2.97 (m, 2H), 2.53 (d, *J* = 2.1 Hz,1H), 2.33 (s, 3H), 2.28 – 2.11 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.46, 144.89, 137.56, 136.85, 1315.98, 134.33, 132.19, 130.28, 130.02, 126.45, 124.73, 123.97, 123.58, 118.81, 118.01, 115.36, 84.71, 73.26, 61.53, 39.00, 37.77, 29.92, 23.89, 22.21, 21.79 ppm; HRMS (ESI): *m/z*: Calcd for $C_{30}H_{27}N_2O_5S$ $[M+H]^+$ 527.1635, Found 527.1637.

IV. General preparation of alkynylindoles containing nitrogen nucleophiles **5k-5n** (entries 11-14, Table 2) and characterization data



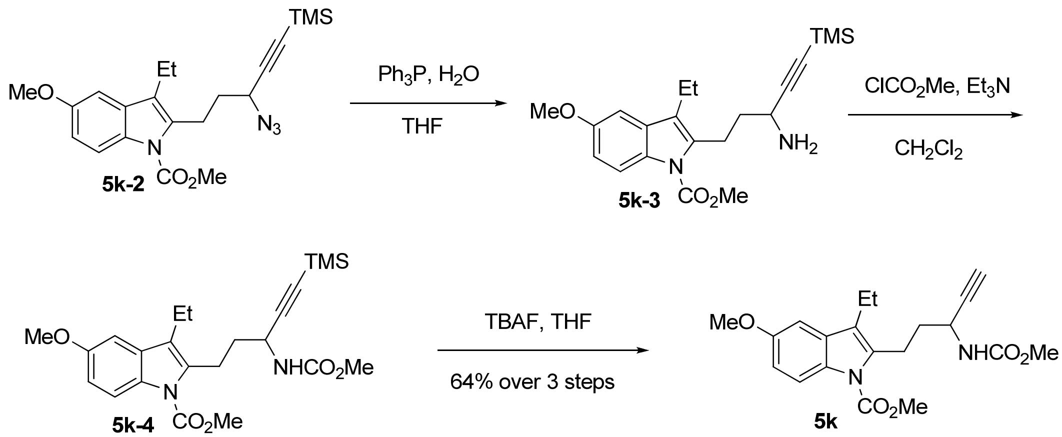
Methyl 2-(3-azido-5-(trimethylsilyl)pent-4-ynyl)-3-ethyl-5-methoxy-1H-indole-1-carboxylate (5k-2): A solution of alcohol **5d-4** (1.94 g, 5.0 mmol) in anhydrous dichloromethane (10.0 mL) was cooled to -20 ºC before triethylamine (1.70 mL, 12.0 mmol) was added dropwise. The mixture was stirred at -20 ºC for 10 min; then tosyl chloride (0.47 mL, 6.0 mmol) was added over a period of 10 min. The resulting mixture was stirred at 0 ºC for 2 h before quenched with saturated aqueous $NaHCO_3$ (10.0 mL) and extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4 and filtered through a pad of celite, and the solvent was removed *in vacuo* to yield crude **5k-1**.

A mixture of **5k-1** and sodium azide (0.98 g, 15.0 mmol) in anhydrous DMF (20.0 mL) was stirred at RT for 12 h. After removal of DMF *in vacuo*, water was added to the reaction solution and the mixture was extracted with ethyl acetate. The combined extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give a crude oil, which was purified by column chromatography (hexanes/ethyl acetate = 20:1) to afford azide **5k-2** (1.24 g, 3.0 mmol) as a yellowish oil in 60% yield (2 steps): IR (thin film): ν = 2961, 2106, 1732, 1478, 1442, 1363, 1262, 1217, 1131, 845 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 1H), 6.93 (d, *J* = 2.6 Hz, 1H), 6.87 (dd, *J* = 9.0 Hz, 2.6 Hz, 1H), 4.18 – 4.12 (m, 1H), 4.03 (s, 3H), 3.87 (s, 3H), 3.21 – 3.08 (m, 2H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.00 (q, *J* = 7.4 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H), 0.22 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.13, 152.39, 135.55, 130.83, 130.52, 122.11, 116.73, 112.03, 112.01, 101.56, 100.48, 92.73, , 55.88, 55.86, 53.53, 53.24, 35.51, 23.13, 17.38, 15.00, 0.05 ppm; HRMS (ESI): *m/z*: Calcd for $C_{21}H_{28}N_4NaO_3Si$ $[M+Na]^+$ 435.1823, Found 435.1840.



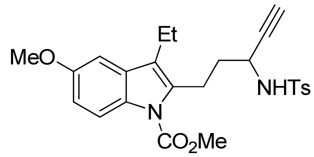
5m-2

2-(3-Azido-5-(trimethylsilyl)pent-4-ynyl)-3-ethyl-5-methoxy-1-tosyl-1H-indole(5m-2): A yellowish oil was obtained in 56% yield by following general procedure. IR (thin film): ν = 2964, 2106, 1599, 1475, 1362, 1216, 1035, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 9.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.85 (dd, *J* = 9.0 Hz, 2.6 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 4.12 (t, *J* = 6.7 Hz, 1H), 3.81 (s, 3H), 3.14 – 2.99 (m, 2H), 2.58 (q, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 2.15 – 2.05 (m, 2H), 1.11 (t, *J* = 7.6 Hz, 3H), 0.20 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.75, 144.59, 135.87, 135.67, 131.77, 131.66, 129.80, 126.33, 124.68, 116.51, 112.53, 101.87, 100.37, 92.70, 55.83, 55.81, 53.16, 36.26, 29.90, 23.03, 21.72, 17.68, 14.78, 0.07 ppm; HRMS (ESI): *m/z*: Calcd for $C_{26}H_{32}N_4NaO_3SSi$ $[M+Na]^+$ 531.1857, Found 531.1843.



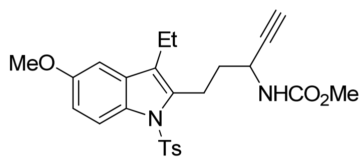
Methyl 3-ethyl-5-methoxy-2-(3-(methoxycarbonylamino)pent-4-ynyl)-1H-indole-1-carboxylate (5k, entry 11, Table 2): To the solution of the azide **5k-2** in anhydrous THF (10.0 mL) at RT was added triphenylphosphine (0.87 g, 3.3 mmol) and water (0.54 mL, 30.0 mmol). The resulting mixture was heated to 55 °C for 1.5 h before it was cooled to RT and concentrated *in vacuo*. The residue **5k-3** was then dissolved in anhydorus dichloromethane (10.0 mL) and cooled to 0 °C. To the cooled solution triethylamine (1.65 mL, 6.0 mmol) was added followed by the addition of methyl chloroformate (0.25 mL, 3.2 mmol). The resulting solution was stirred at RT for 3 h before quenched with saturated aqueous $NaHCO_3$. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, and the solvents were removed *in vacuo* to give the crude **5k-4**, which was used for the next step without further purification.

Tetrabutylammonium fluoride (1.0 M in THF, 3.0 mL, 3.0 mmol) was added to a solution of **5k-4** in THF at 0 °C, and the resulting mixture was stirred for 10 min at 0 °C. After the reaction was terminated by the addition of water, the organic layer was extracted with ethyl acetate. The combined organic parts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give a crude oil, which was purified by column chromatography (hexanes/ethyl acetate = 3:1) to afford propargyl carbamate **5k** (715 mg, 1.92 mmol) as a colorless oil in 64% yield over 3 steps: IR (thin film): ν = 3295, 2964, 1731, 1723, 1522, 1475, 1361, 1242 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 1H), 6.94 (d, *J* = 2.5 Hz, 1H), 6.88 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 5.25-5.15 (br, 1H), 4.60-4.50 (br, 1H), 4.05 (s, 3H), 3.88 (s, 3H), 3.72 (s, 3H), 3.17 – 3.04 (m, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 2.37 (d, *J* = 2.3 Hz, 1H), 2.04 – 1.94 (m, 2H), 1.22 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.38, 156.13, 152.48, 135.86, 130.89, 130.43, 121.89, 116.75, 111.98, 101.55, 83.23, 77.43, 71.58, 55.90, 55.88, 53.60, 52.53, 43.31, 35.78, 23.10, 17.40, 15.07 ppm; HRMS (ESI): *m/z*: Calcd for $C_{20}H_{25}N_2O_5$ $[M+H]^+$ 373.1758, Found 373.1759.



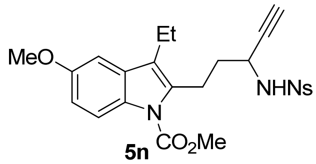
5l

Methyl 3-ethyl-5-methoxy-2-(3-(4-methylphenylsulfonamido)pent-4-ynyl)-1H-indole -1-carboxylatel (5l, entry 12, Table 2): A colorless oil was obtained in 69% yield by following general procedure. IR (thin film): ν = 3274, 2961, 2929, 1731, 1607, 1478, 1442, 1332, 1161, 1090 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.0 Hz, 1H), 7.77 (d, *J* = 6.4 Hz, 2H), 7.27 (d, *J* = 6.4 Hz, 2H), 6.92 (d, *J* = 2.6 Hz,1H), 6.86 (dd, *J* = 9.0 Hz, 2.6 Hz, 1H), 5.09 (d, *J* = 8.2 Hz, 1H), 4.15 (qd, *J* = 6.7 Hz, 2.3 Hz, 1H), 4.02 (s, 3H), 3.87 (s, 3H), 3.17 – 3.00 (m, 2H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 2.15 (d, *J* = 2.3 Hz, 1H), 1.99 – 1.96 (m, 2H), 1.17 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.07, 152.39, 143.60, 137.36, 135.45, 130.77, 130.39, 129.62, 127.49, 121.97, 116.71, 111.99, 101.52, 81.86, 72.88, 55.85, 53.63, 45.38, 36.45, 22.87, 21.68, 17.32, 15.00 ppm; HRMS (ESI): *m/z*: Calcd for $C_{25}H_{28}N_2NaO_5S$ $[M+Na]^+$ 491.1611, Found 491.1614.



5m

Methyl 5-(3-ethyl-5-methoxy-1-(4-methylbenzene-sulfoyl)-1H-indol-2-yl)pent-1-yn-3-ylcarbamate (5m, entry 13, Table 2): A colorless oil was obtained in 52% yield by following general procedure. IR (thin film): ν = 3294, 2965, 1723, 1599, 1520, 1475, 1360, 1246, 1163, 1047 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 9.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.87 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 6.83 (d, *J* = 2.5 Hz, 1H), 5.18 (d, *J* = 7.2 Hz, 1H), 4.55 – 4.45 (br, 1H), 3.83 (s, 3H), 3.72 (s, 3H), 3.10 – 2.96 (m, 2H), 2.57 (q, *J* = 7.6 Hz, 2H), 2.34 (d, *J* = 2.3 Hz, 1H), 2.31 (s, 3H), 2.19 – 2.06 (m, 2H), 1.12 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.74, 156.50, 144.64, 135.98, 135.74, 131.72, 131.63, 129.84, 126.29, 124.36, 116.39, 112.54, 101.88, 83.18, 71.57, 55.82, 52.55, 43.24, 36.61, 23.11, 21.69, 17.68, 14.81 ppm; HRMS (ESI): *m/z*: Calcd for $C_{25}H_{28}N_2NaO_5S$ $[M+Na]^+$ 491.1611, Found 491.1599.

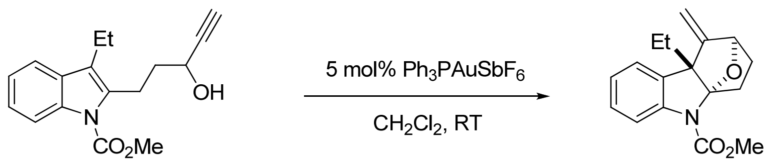


5n

Methyl 3-ethyl-5-methoxy-2-(3-(2-nitrophenylsulfonamido)pent-4-ynyl)-1H-indole-1-carboxylate (5n, entry 14, Table 2): A colorless oil was obtained in 65% yield by following general procedure. IR (thin film): ν = 3286, 2962, 2932, 1728, 1608, 1541, 1478, 1363, 1170, 1132 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.15 (m, 1H), 7.95 – 7.92 (m, 2H), 7.78 – 7.70 (m, 2H), 6.94 (d, *J* = 2.3 Hz, 1H), 6.89 (dd, *J* = 9.0 Hz, 2.6 Hz, 1H), 5.96 – 5.85 (br, 1H), 4.35 – 4.24 (br, 1H), 4.06 (s, 3H), 3.89 (s, 3H), 3.29 – 3.08 (m, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 2.11 – 2.02 (m, 3H), 1.21 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C

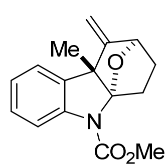
NMR (101 MHz, $CDCl_3$) δ 156.06, 152.33, 147.92, 135.16, 134.18, 133.84, 132.91, 131.66, 130.72, 130.37, 125.50, 122.08, 116.71, 112.07, 112.04, 101.48, 80.97, 73.40, 55.80, 53.65, 46.09, 36.26, 22.95, 17.34, 15.04 ppm; HRMS (ESI): *m/z*: Calcd for $C_{24}H_{26}N_3O_7$ $[M+H]^+$ 500.1486, Found 500.1473.

V. General procedure of gold(I)-catalyzed tandem cyclization reaction (Table 2)



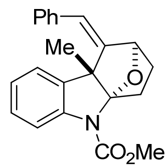
5a **6a**

The catalyst solution was prepared by addition of Ph_3PAuCl (2.5 mg, 0.005 mmol) to a suspension of $AgSbF_6$ (1.7 mg, 0.005 mmol) in anhydrous dichloromethane (0.50 mL) at RT. The suspension was stirred for 20 min at RT under Argon atmosphere. The resulting catalyst solution was then added to a solution of substrate **5a** (28.5 mg, 0.10 mmol) in anhydrous dichloromethane (0.50 mL) dropwise at RT. The resulting mixture was kept stirring at RT until TLC showed that there was no starting material **5a** left (about 1 h). The reaction mixture was then filtered through a short pad of silica gel. The filtrate was concentrated *in vacuo*, and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford tetracyclic indoline **6a** (entry 1, Table 2, 23.7 mg, 0.083 mmol) as a colorless oil in 83% yield: IR (thin film): ν = 2957, 2923, 1720, 1458, 1442, 1360, 1242, 1132 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.07 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 5.10 (d, *J* = 0.7 Hz, 1H), 5.01 (s, 1H), 4.59 (d, *J* = 6.1 Hz, 1H), 3.91 (s, 3H), 3.06 – 3.03 (m, 1H), 2.27 (tdd, *J* = 12.4 Hz, 6.1 Hz, 3.5 Hz, 1H), 2.10 (ddd, *J* = 12.4 Hz, 9.0 Hz, 3.5 Hz, 1H), 1.90 (dq, *J* = 15.2 Hz, 7.6 Hz, 1H), 1.79 (ddd, *J* = 12.2 Hz, 9.1 Hz, 5.5 Hz, 1H), 1.72 – 1.60 (m, 1H), 0.60 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.21, 154.02, 133.34, 128.04, 123.93, 123.29, 115.94, 105.62, 102.47, 77.15, 60.11, 53.09, 33.23, 30.82, 29.93, 23.54, 8.90 ppm; HRMS (ESI): *m/z*: Calcd for $C_{17}H_{20}NO_3$ $[M+H]^+$ 286.1437, Found 286.1443.



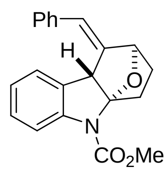
4

Tetracyclic indoline 4 (Scheme 1): A white solid was obtained in 83% yield by following general procedure. m.p. 105–106 ºC; IR (thin film): ν = 2956, 2924, 1720, 1479, 1440, 1361, 1316, 1240, 1101 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.19 (td, *J* = 8.2 Hz, 1.3 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 5.10 (s, 1H), 5.00 (s, 1H), 4.57 (t, *J* = 11.8 Hz, 1H), 3.89 (s, 3H), 2.99 (td, *J* = 12.1 Hz, 5.0 Hz, 1H), 2.23 (tdd, *J* = 12.4 Hz, 6.1 Hz, 3.6 Hz, 1H), 2.09 (ddd, *J* = 12.4 Hz, 9.0 Hz, 3.6 Hz, 1H), 1.76 (ddd, *J* = 12.3 Hz, 9.0 Hz, 5.4 Hz, 1H), 1.31 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.91, 154.36, 141.66, 136.09, 127.94, 123.96, 122.88, 116.20, 106.05, 102.42, 77.28, 56.86, 53.11, 30.62, 26.25, 23.40 ppm; HRMS (ESI): *m/z*: Calcd for $C_{16}H_{17}NNaO_3$ $[M+Na]^+$ 294.1101, Found 294.1090.



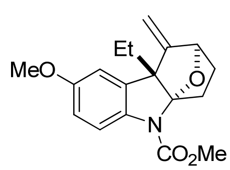
6b

Tetracyclic indoline 6b (entry 2, Table 2): A colorless oil was obtained in 65% yield by following general procedure. IR (thin film): ν = 3581, 2923, 1715, 1463, 1360, 1236 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 1H), 7.44 – 7.33 (m, 5H), 7.15 – 7.08 (m, 1H), 6.79 (td, J = 7.5 Hz, 1.0, 1H), 6.59 (dd, J = 7.6 Hz, 0.9 Hz, 1H), 5.96 (d, J = 4.9 Hz, 1H), 4.55 (dd, J = 6.3 Hz, 5.0 Hz, 1H), 3.93 (s, 3H), 3.38 – 3.29 (m, 1H), 2.52 – 2.37 (m, 1H), 2.37 – 2.29 (m, 1H), 2.04 (ddd, J = 11.7 Hz, 9.2 Hz, 2.7 Hz, 1H), 1.48 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.37, 143.06, 139.55, 134.45, 129.07, 128.09, 128.36, 128.09, 126.66, 124.34, 123.28, 115.48, 102.66, 72.79, 52.52, 33.82, 30.02, 26.17, 23.24 ppm; HRMS (ESI): *m/z*: Calcd for $C_{22}H_{21}NNaO_3$ $[M+Na]^+$ 370.1414, Found 370.1409.



6c

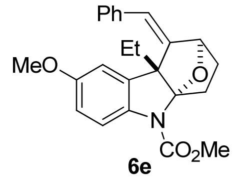
Tetracyclic indoline 6c (entry 3, Table 2): A colorless oil was obtained in 67% yield by following general procedure. IR (thin film): ν = 3608, 3583, 2924, 1714, 1477, 1358, 1259 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.6 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.45 – 7.36 (m, 3H), 7.14 (t, J = 7.9 Hz, 1H), 6.75 (td, J = 7.9 Hz, 5.0 Hz, 1H), 6.50 (d, J = 7.5 Hz, 1H), 6.41 (dd, J = 4.7 Hz, 1.9 Hz, 1H), 4.74 – 4.61 (m, 1H), 4.11 – 4.14 (m, 1H), 3.94 (s, 3H), 3.42 (t, J = 11.9 Hz, 1H), 2.37 (ddd, J = 11.5 Hz, 7.0 Hz, 4.4 Hz, 1H), 2.12 (td, J = 9.2 Hz, 4.6 Hz, 1H), 2.00 (dt, J = 12.6 Hz, 8.4 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.28, 142.97, 139.46, 134.36, 130.91, 129.48, 128.98, 128.36, 128.00, 126.57, 124.25, 123.19, 115.39, 99.91, 72.70, 52.43, 33.73, 29.93, 14.30 ppm; HRMS (ESI): *m/z*: Calcd for $C_{21}H_{19}NNaO_3$ $[M+Na]^+$ 356.1257, Found 356.1250.



6d

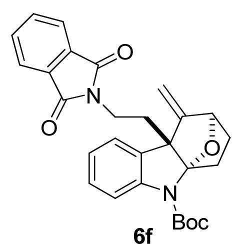
Tetracyclic indoline 6d (entry 4, Table 2): A colorless oil was obtained in 85% yield by following general procedure. IR (thin film): ν = 2964, 1720, 1484, 1367, 1114, 1087, 1025, 1065 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 8.9 Hz, 1H), 7.42 – 7.28 (m, 5H), 6.67 (dd, J = 8.9 Hz, 2.7 Hz, 1H), 6.18 (d, J = 2.7 Hz, 1H), 5.94 (d, J = 5.0 Hz, 1H), 4.53 – 4.49 (m, 1H), 3.90 (s, 3H), 3.56 (s, 3H), 3.36 (t, J = 10.7 Hz, 1H), 2.41 – 2.29 (m, 3H), 2.03 (dt, J = 11.5 Hz, 7.1 Hz, 2H), 1.95 (dt, J = 15.9 Hz, 7.9 Hz, 1H), 1.89 (dd, J = 14.1 Hz, 7.5 Hz, 1H), 0.54 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.12, 156.57, 153.92, 136.74, 134.82, 116.49, 112.24, 110.00, 109.97, 105.87, 102.49, 102.45, 77.10, 60.16, 55.87, 52.96, 33.11, 30.79, 23.59, 8.88 ppm; HRMS (ESI): *m/z*:

Calcd for $C_{18}H_{21}NNaO_4$ $[M+Na]^+$ 338.1362, Found 338.1353.



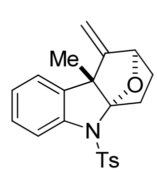
6e

Tetracyclic indoline 6e (entry 5, Table 2): A colorless oil was obtained in 75% yield by following general procedure. IR (thin film): ν = 2925, 1713, 1481, 1362, 1272, 1100, 1045 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.28 (m, 5H), 6.67 (dd, *J* = 8.2 Hz, 2.7 Hz, 1H), 6.18 (t, J = 2.7 Hz, 1H), 5.94 (d, *J* = 5.0 Hz, 1H), 4.53 – 4.49 (m, 1H), 3.90 (s, 3H), 3.56 (s, 3H), 3.36 (t, *J* = 10.7 Hz, 1H), 2.41 – 2.29 (m, 2H), 2.03 (dt, *J* = 11.5 Hz, 7.1 Hz, 1H), 1.95 (dt, *J* = 15.9 Hz, 7.9 Hz, 1H), 1.89 (dd, *J* = 14.1 Hz, 7.5 Hz, 1H), 0.54 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.99, 154.20, 141.31, 140.55, 136.66, 132.98, 130.78, 127.98, 127.68, 115.88, 112.67, 110.84, 102.73, 71.23, 56.60, 55.63, 52.86, 33.38, 31.41, 30.00, 23.31, 9.42 ppm; HRMS (ESI): *m/z*: Calcd for $C_{24}H_{26}NO_4$ $[M+H]^+$ 392.1856, Found 392.1854.



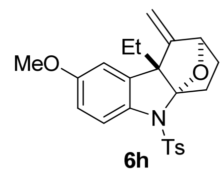
6f

Tetracyclic indoline 6f (entry 6, Table 2): A white solid was obtained in 84% yield by following general procedure. m.p. 165–167 ºC; IR (thin film): ν = 2978, 1772, 1713, 1477, 1398.95, 1368, 1247, 1161, 1075 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 3H), 7.72 – 7.65 (m, 2H), 7.36 (dd, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.11 (td, *J* = 8.0 Hz, 2.6 Hz, 1H), 5.10 (s, 1H), 5.01 (s, 1H), 4.59 (d, *J* = 6.0 Hz, 1H), 3.45 (td, *J* = 12.9 Hz, 4.1 Hz, 1H), 3.20 (td, *J* = 12.6 Hz, 5.5 Hz, 1H), 3.10 (ddd, *J* = 13.5 Hz, 12.1 Hz, 5.2 Hz, 1H), 2.44 (ddd, *J* = 12.4 Hz, 9.0 Hz, 3.4 Hz, 1H), 2.34 – 2.19 (m, 1H), 1.99 – 1.87 (m, 1H), 1.79 (ddd, *J* = 12.3 Hz, 9.1 Hz, 5.6 Hz, 1H), 1.63 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.11, 156.65, 152.32, 143.06, 134.14, 132.18, 132.03, 128.47, 124.12, 123.32, 123.24, 116.26, 105.51, 102.78, 82.85, 58.44, 38.39, 33.93, 30.86, 29.90, 28.59, 23.63 ppm; HRMS (ESI): *m/z*: Calcd for $C_{28}H_{29}N_2O_5$ $[M+H]^+$ 473.2071, Found 473.2086.



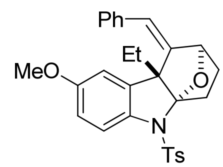
6g

Tetracyclic indoline 6g (entry 7, Table 2): A colorless oil was obtained in 85% yield by following general procedure. IR (thin film): ν = 2924, 1475, 1458, 1360, 1163, 1094, 1025 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.24 – 7.21 (m, 2H), 7.18 – 7.14 (m, 1H), 7.05 – 6.99 (m, 1H), 5.07 (s, 1H), 4.98 (s, 1H), 4.56 (d, J = 6.0 Hz, 1H), 3.04 – 2.93 (m, 1H), 2.36 (s, 3H), 2.20 (ddd, J = 15.7 Hz, 8.9 Hz, 3.6 Hz, 2H), 1.78 – 1.70 (m, 1H), 1.23 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.36, 144.26, 141.37, 136.65, 136.15, 129.64, 128.08, 127.97, 124.22, 123.29, 114.95, 107.58, 102.61, 77.34, 57.66, 30.39, 25.55, 24.05, 21.79 ppm; HRMS (ESI): *m/z*: Calcd for $C_{21}H_{22}NO_3S$ $[M+H]^+$ 368.1315, Found 368.1318.



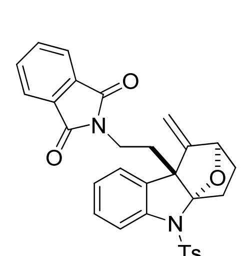
6h

Tetracyclic indoline 6h (entry 8, Table 2): A colorless oil was obtained in 88% yield by following general procedure. IR (thin film): ν = 2934, 1475, 1456, 1359, 1162, 1099, 1027 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 2H), 7.43 (d, J = 8.9 Hz, 1H), 7.25 – 7.21 (m, 2H), 6.75 (d, J = 2.6 Hz, 1H), 6.70 (dd, J = 8.9 Hz, 2.7 Hz, 1H), 5.02 (s, 1H), 4.95 (s, 1H), 4.53 (d, J = 5.8 Hz, 1H), 3.74 (s, 3H), 3.06 – 2.93 (m, 1H), 2.36 (s, 3H), 2.25 – 2.17 (m, 2H), 1.83 (dq, J = 15.2 Hz, 7.6 Hz, 1H), 1.77 – 1.70 (m, 1H), 1.67 – 1.58 (m, 1H), 0.66 (t, J = 7.5 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.63, 156.55, 144.06, 136.83, 136.34, 134.70, 129.56, 129.55, 129.53, 128.20, 128.19, 128.17, 114.71, 112.34, 110.63, 107.49, 102.62, 77.29, 60.95, 55.88, 32.82, 30.41, 24.28, 21.76, 8.74 ppm; HRMS (ESI): *m/z*: Calcd for $C_{23}H_{25}NNaO_4S$ $[M+Na]^+$ 434.1397, Found 434.1402.



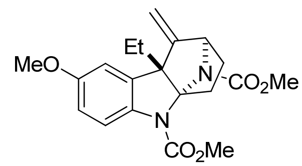
6i

Tetracyclic indoline 6i (entry 9, Table 2): A colorless oil was obtained in 64% yield by following general procedure. IR (thin film): ν = 2941, 1472, 1456, 1364, 1160, 1099 cm^{-1};^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 8.02 (m, 2H),7.53 (d, J = 8.1 Hz, 1H), 7.41 – 7.25 (m,5H),), 6.67 (dd, J = 8.1 Hz, 2.5 Hz, 1H), 6.15 (t, J = 2.5 Hz, 1H), 5.92 (d, J = 5.0 Hz, 1H), 4.52 – 4.43 (m, 1H), 3.56 (s, 3H), 3.36 (t, J = 10.8 Hz, 1H), 2.42 – 2.26 (m, 2H), 2.23 (s, 3H), 2.04 (dt, J = 11.5 Hz, 7.2 Hz, 2H), 1.95 (dt, J = 15.9 Hz, 7.6 Hz, 1H), 1.89 (dd, J = 14.2 Hz, 7.6 Hz, 1H), 0.54 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.92, 141.24, 140.48, 136.59, 132.91, 130.71, 127.82, 127.61,126.51, 124.23, 115.81, 112.60, 110.77, 102.66, 71.16, 56.53, 55.56, 52.79, 33.31, 31.34, 29.93, 23.24, 21.78, 9.35 ppm; HRMS (ESI): *m/z*: Calcd for $C_{29}H_{29}NNaO_4S$ $[M+Na]^+$ 510.1509, Found 510.1503.



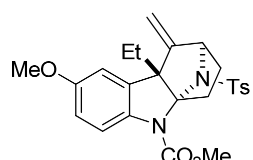
6j

Tetracyclic indoline 6j (entry 10, Table 2): A colorless oil was obtained in 82% yield by following general procedure. IR (thin film): ν = 2924, 1772, 1713, 1458, 1399, 1365, 1164, 1090, 1038 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.79 (m, 2H), 7.69 (m, 2H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.32 (dd, *J* = 7.5 Hz, 0.9 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.11 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 5.06 (s, 1H), 4.98 (s, 1H), 4.57 (d, *J* = 5.9 Hz, 1H), 3.57 – 3.45 (m, 1H), 3.15 (dd, *J* = 12.9 Hz, 5.7 Hz, 1H), 2.60 (td, *J* = 9.2 Hz, 4.5 Hz, 1H), 2.35 – 2.26 (m, 4H), 2.17 (td, *J* = 13.1 Hz, 4.9 Hz, 1H), 1.98 – 1.89 (m, 1H), 1.84 – 1.73 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.03, 155.80, 144.36, 142.27, 136.50, 134.17, 132.20, 131.89, 129.68, 128.67, 128.32, 124.62, 123.79, 123.37, 114.50, 106.94, 103.14, 59.44, 38.29, 33.61, 30.51, 29.93, 24.28, 21.77 ppm; HRMS (ESI): *m/z*: Calcd for $C_{30}H_{27}N_2O_5S$ $[M+H]^+$ 527.1635, Found 527.1636.



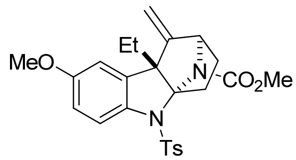
6k

Tetracyclic indoline 6k (entry 11, Table 2): A colorless oil was obtained in 78% yield by following general procedure. IR (thin film): ν = 3095, 1720, 1442, 1432, 1261, 1105, 1129 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 1H), 6.92 (d, *J* = 2.6 Hz, 1H), 6.79 (dd, *J* = 8.3 Hz, 2.6 Hz, 1H), 5.95 – 6.45 (br, 1H), 5.27 (s, 1H), 5.16 (s, 1H), 4.75 – 4.83 (br, 1H), 3.90 (s, 3H), 3.81 (s, 3H), 3.69 (s, 3H), 3.00 – 2.85 (m, 1H), 2.01-2.04 (m, 1H), 1.82 (t, *J* = 7.4 Hz, 2H), 0.78 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.65, 155.93, 153.08, 146.44, 144.36, 135.08, 134.42, 116.23, 112.32, 111.87, 108.23, 105.31, 55.85, 53.32, 53.04, 52.46, 48.78, 35.19, 32.60, 29.91, 8.59 ppm; HRMS (ESI): *m/z*: Calcd for $C_{20}H_{25}N_2O_5$ $[M+H]^+$ 373.1758, Found 373.1752.



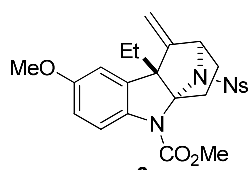
6l

Tetracyclic indoline 6l (entry 12, Table 2): A colorless oil was obtained in 75% yield by following general procedure. IR (thin film): ν = 3274, 2923, 1713, 1481.71, 1275, 1158, 1093, 1035 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (m, 3H), 7.28 – 7.21 (m, 2H), 6.74 (dd, *J* = 8.9 Hz, 2.7 Hz, 1H), 6.70 (d, *J* = 2.6 Hz, 1H), 5.92 (s, 1H), 5.20 (s, 1H), 5.10 (d, *J* = 1.2 Hz, 1H), 4.59 (d, *J* = 9.0 Hz, 1H), 4.33 (dd, *J* = 15.1 Hz, 6.2 Hz, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 2.65 (ddd, *J* = 17.1 Hz, 6.4 Hz, 3.2 Hz, 1H), 2.41 (s, 3H), 2.14 (dt, *J* = 17.1 Hz, 6.0 Hz, 1H), 1.79 – 1.68 (m, 1H), 1.66 – 1.57 (m, 1H), 0.62 (q, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.99, 153.01, 145.45, 144.24, 143.58, 138.12, 134.81, 134.53, 129.84, 127.23, 116.14, 111.99, 111.49, 111.15, 105.17, 60.63, 55.86, 53.06, 52.67, 52.04, 35.90, 32.74, 29.92, 29.59, 21.77, 21.29, 14.42, 8.60 ppm; HRMS (ESI): *m/z*: Calcd for $C_{25}H_{29}N_2O_5S$ $[M+H]^+$ 469.1792, Found 469.1778.



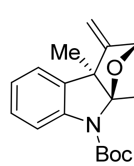
6m

Tetracyclic indoline 6m (entry 13, Table 2): A white solid was obtained in 79% yield by following general procedure. m.p. 129–130 ºC; IR (thin film): ν = 2924, 1724, 1525, 1476, 1363, 1252, 1171, 1088, 1037 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.44 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 6.80– 6.82 (m, 2H), 6.01 (dd, *J* = 5.3 Hz , 3.3 Hz, 1H), 5.11 (s, 1H), 5.05 (s, 1H), 4.70 – 4.53 (m, 1H), 3.79 (s, 3H), 3.68 (s, 3H), 2.85 (ddd, *J* = 17.7 Hz, 7.2 Hz, 3.3 Hz, 1H), 2.35 (s, 3H), 2.11 (dt, *J* = 17.7 Hz, 6.0 Hz, 1H), 1.35 – 1.27 (m, 1H), 0.60 – 0.53 (m, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.70, 156.56, 145.58, 144.80, 144.61, 135.49, 134.76, 134.63, 129.63, 129.39, 127.46, 116.93, 112.72, 112.05, 108.84, 108.27, 55.83, 54.01, 52.46, 48.54, 34.26, 32.71, 29.93, 21.77, 8.28 ppm; HRMS (ESI): *m/z*: Calcd for $C_{25}H_{28}N_2NaO_5S$ $[M+Na]^+$ 491.1611, Found 491.1598.



6n

Tetracyclic indoline 6n (entry 14, Table 2): A colorless oil was obtained in 70% yield by following general procedure. IR (thin film): ν = 2923, 2852, 1714, 1539, 148, 1363, 1275, 1165 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.8 Hz, 1.4 Hz, 1H), 7.70 (td, *J* = 7.6 Hz, 1.5 Hz, 1H), 7.62 (td, *J* = 7.7 Hz, 1.4 Hz, 2H), 7.56 (dd, *J* = 7.9 Hz, 1.4 Hz, 1H), 6.65 (dd, *J* = 8.9 Hz, 2.7 Hz, 1H), 6.15 (m, 2H), 5.79 (d, *J* = 9.5 Hz, 1H), 5.32 (s, 1H), 5.18 (s, 1H), 4.55 (dt, *J* = 9.2 Hz, 4.5 Hz, 1H), 3.92 (s, 3H), 3.74 (s, 3H), 2.65 (ddd, *J* = 16.6 Hz, 4.9 Hz, 3.1 Hz, 1H), 2.44 (ddd, *J* = 16.6 Hz, 7.1 Hz, 4.4 Hz, 1H), 1.71 (dq, *J* = 14.7 Hz, 7.3 Hz, 2H), 1.61 – 1.44 (m, 1H), 0.66 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.70, 152.94, 147.44, 145.25, 144.76, 135.02, 134.98, 134.63, 133.32, 132.56, 131.25, 125.67, 115.99, 113.80, 111.20, 109.87, 104.89, 60.63, 55.60, 54.88, 53.16, 51.46, 38.10, 29.93, 14.42, 8.91 ppm; HRMS (ESI): *m/z*: Calcd for $C_{24}H_{26}N_3O_7S$ $[M+H]^+$ 500.1486, Found 500.1481.

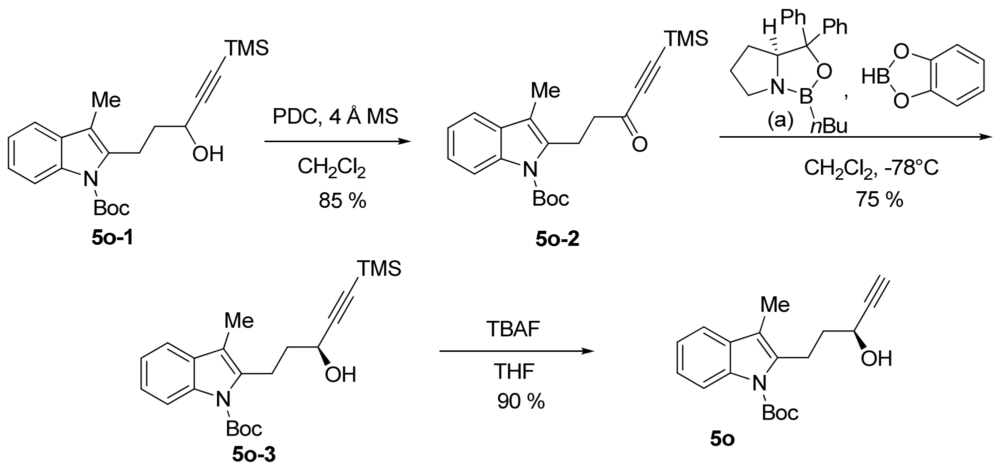


6o

Tetracyclic indoline 6o (Scheme 2): A colorless oil was obtained in 80% yield by following general procedure. The *ee* of **6o** was determined as 81% by chiral HPLC analysis (ChiralPak IA column, hexanes/*i*PrOH = 98:2, 0.50 mL/min, t_r for major isomer is 9.7 min, for minor isomer is 15.1 min). $[\alpha]_D^{20}$ = –26.5 cm^3 g^{-1} dm^{-1} (c = 1.43 g cm^{-3} in EtOAc). IR (thin film): ν = 2975, 1715., 1478, 1461, 1366, 1317, 1246, 1164, 1100, 750 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.20

(td, *J* = 8.2 Hz, 1.3 Hz, 1H), 7.02 (td, *J* = 7.5 Hz, 1.3 Hz, 1H), 5.11 (s, 1H), 5.01 (s, 1H), 4.59 (d, *J* = 6.0 Hz, 1H), 3.06 (td, *J* = 15.5 Hz, 5.0 Hz, 1H), 2.24 (tdd, *J* = 12.4 Hz, 6.1 Hz, 3.6 Hz, 1H), 2.17 – 2.02 (m, 1H), 1.76 (ddd, *J* = 12.1 Hz, 9.0 Hz, 5.4 Hz, 1H), 1.62 (s, 9H), 1.33 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.27, 152.75, 142.05, 136.12, 127.81, 123.55, 122.86, 116.23, 106.25, 102.17, 82.59, 77.13, 56.67, 30.68, 28.59, 26.17, 23.33 ppm; HRMS (ESI): *m/z*: Calcd for $C_{19}H_{24}NO_3$ $[M+H]^+$ 314.1751, Found 314.1748.

VI. Preparation of enantioenriched alkynylindole substrate **5o** and characterization data



***Tert*-butyl 3-methyl-2-(3-oxo-5-(trimethylsilyl)pent-4-ynyl)-1H-indole-1-carboxylate (5o-2):** PDC (376 mg, 1.0 mmol) was added to a stirred mixture of the alcohol **5o-1** (193 mg, 0.50 mmol) and activated 4 Å molecular sieves (400 mg) in anhydrous dichloromethane (5.0 ml). The resulting mixture was stirred for 5 h; then it was diluted with diethyl ether (15.0 mL). The resulting suspension was filtrated through a pad of silica gel. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate=20:1) to provide **5o-2** (163 mg, 0.43 mmol) as a colorless oil in 85% yield: IR (thin film): ν = 3050, 2975, 2150, 1731, 1681, 1456, 1332, 1252, 1135, 847 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 1H), 7.43 (dd, J = 7.7 Hz, 1.1 Hz, 1H), 7.27 – 7.20 (m, 2H), 3.36 – 3.33 (m, 2H), 2.95 – 2.90 (m, 2H), 2.21 (s, 3H), 1.68 (s, 9H), 0.21 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.94, 150.55, 135.93, 134.61, 130.63, 123.96, 122.62, 118.30, 115.72, 115.69, 115.22, 102.04, 98.29, 83.84, 45.50, 28.41, 21.53, 8.86, -0.66 ppm; HRMS (ESI): *m/z*: Calcd for $C_{22}H_{29}LiNO_3Si$ $[M+Li]^+$ 390.2072, Found 390.2084.

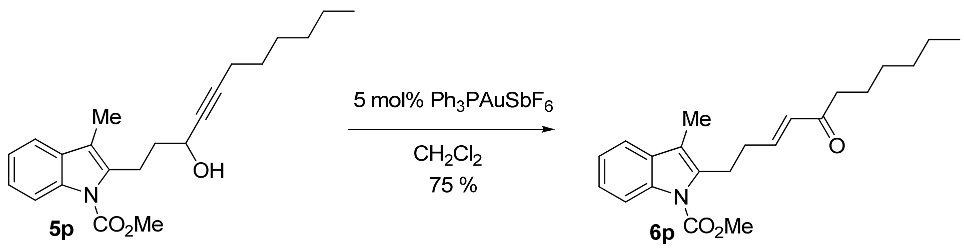
(*S*)-*Tert*-butyl 2-(3-hydroxy-5-(trimethylsilyl)pent-4-ynyl)-3-methyl-1H-indole-1-carboxylate (5o-3)[S2]: Ketone **5o-2** (163 mg, 0.43 mmol) (azeotropically dried with toluene under an inert atmosphere) was treated with catalyst a (108 µL, 0.20 M in toluene, 0.022 mmol). The toluene was removed *in vacuo* before anhydrous dichloromethane (1.0 mL) was added. The resulting solution was then cooled to -78 ºC. A solution of catecholborane (0.52 mmol, 54 µL) in anhydrous dichloromethane (200 µL) was then added dropwise over 10 min. The reaction mixture was stirred at -78 ºC for 5 h before quenched with MeOH (1.0 mL). The mixture was then warmed to RT, diluted with diethyl ether, washed with saturated aqueous $NaHCO_3$ until the aqueous layer was colorless. The organic phase was further washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo.* The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate=10:1) to provide **5o-1** (124 mg, 0.33 mmol) as a

S2. Helal, C. J.; Magriotis, P. A.; Corey, E. J. *J. Am. Chem. Soc.* **1996**, *118*,10938.

colorless oil in 75% yield: IR (thin film): ν = 3442, 3279, 1732, 1452, 1350, 1343, 1235 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 7.94 (m, 1H), 7.44 – 7.39 (m, 1H), 7.25 – 7.19 (m, 2H), 4.38 (t, J = 6.3 Hz, 1H), 3.21 (t, J = 7.3 Hz, 2H), 2.22 (s, 3H), 2.12 – 1.96 (m, 2H), 1.69 (s, 9H), 0.16 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.89, 136.10, 135.87, 130.83, 123.80, 122.63, 118.24, 115.78, 115.14, 106.81, 89.69, 83.95, 62.29, 37.81, 29.92, 28.50, 22.53, 8.89, 0.06 ppm; HRMS (ESI): *m/z*: Calcd for $C_{22}H_{32}NO_3Si$ $[M+H]^+$ 386.2146, Found 386.2139.

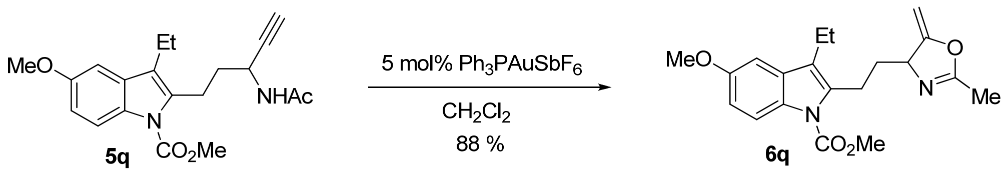
(*S*)-*Tert*-butyl 2-(3-hydroxypent-4-ynyl)-3-methyl-1H-indole-1-carboxylate (5o, Scheme 2): The TMS group was removed by following general procedure, and **5o** was obtained as a colorless oil in 95% yield: The *ee* of **5o** was determined as 81% by chiral HPLC analysis (ChiralCel OD column, hexanes/*i*PrOH = 97:3, 0.75 mL/min, t_r for major isomer is 16.4 min, for minor isomer is 18.5 min). $[\alpha]_D^{20}$ = –25.3 $cm^3\,g^{-1}\,dm^{-1}$ (c = 1.50 g cm^{-3} in EtOAc). IR (thin film): ν = 3435, 3289, 1732, 1459, 1354, 1333, 1221, 1136 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 1H), 7.45 – 7.41 (m, 1H), 7.25 – 7.20 (m, 2H), 4.42-4.35 (m, 1H), 3.22 (t, J = 7.2 Hz, 2H), 2.48 (d, J = 2.1 Hz, 1H), 2.34 (d, J = 5.9 Hz, 1H), 2.23 (s, 3H), 2.09-2.02 (m, 2H), 1.69 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ150.91, 135.93, 135.83, 130.80, 123.83, 122.65, 118.26, 115.77, 115.23, 85.01, 84.02, 73.13, 61.59, 37.70, 28.48, 22.38, 8.87 ppm; HRMS (ESI): *m/z*: Calcd for $C_{19}H_{23}NNaO_3$ $[M+Na]^+$ 336.1570, Found 336.1578.

VII. Unexpected gold(I)-catalyzed reactions and characterization data



Methyl 2-(3-hydroxydodec-4-ynyl)-3-methyl-1H-indole-1-carboxylate (5p): A colorless oil was obtained in 86% yield by following general procedure. IR (thin film): ν = 3446, 2929, 2857, 2359, 1735, 1458, 1353, 1220, 1139 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 1H), 7.48 – 7.40 (m, 1H), 7.29 – 7.21 (m, 2H), 4.36 (m 1H), 4.04 (s, 3H), 3.26 – 3.15 (m, 2H), 2.23 (s, 3H), 2.21 – 2.17 (m, 2H), 2.01 – 1.95 (m, 2H), 1.52 – 1.45 (m, 2H), 1.42 – 1.34 (m, 2H), 1.32 – 1.22 (m, 4H), 0.88 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.71, 136.17, 135.71, 131.01, 124.00, 122.97, 118.30, 115.77, 115.66, 85.96, 81.15, 62.16, 53.61, 38.00, 31.53, 28.82, 28.76, 22.74, 22.60, 18.90, 14.27, 8.86 ppm; HRMS (ESI): m/z: Calcd for $C_{22}H_{29}NNaO_3$ $[M+Na]^+$ 378.2040, Found 378.2035.

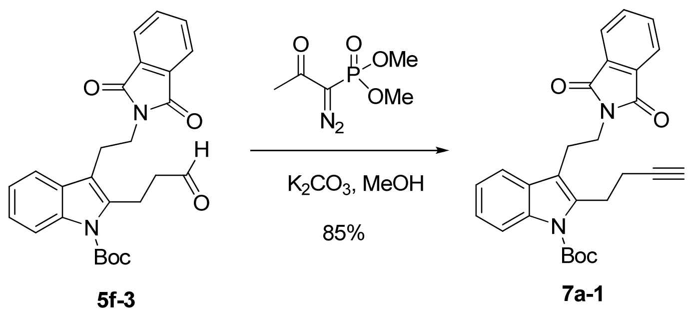
(*E*)-Methyl 3-methyl-2-(5-oxoundec-3-enyl)-1H-indole-1-carboxylate (6p): A colorless oil was obtained in 75% yield by following general procedure. IR (thin film): ν = 2924, 2852, 1736, 1458, 1355, 1220, 1134 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 1H), 7.48 – 7.42 (m, 1H), 7.33 – 7.20 (m, 2H), 6.87 (dt, J = 15.8 Hz, 7.0 Hz, 1H), 6.12 (dt, J = 15.9 Hz, 1.5 Hz, 1H), 4.05 (s, 3H), 3.22 – 3.16 (m, 2H), 2.57 – 2.52 (m, 2H), 2.52 – 2.47 (m, 2H), 2.19 (s, 3H), 1.33 – 1.23 (m, 8H), 0.93 – 0.82 (m, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.08, 152.65, 146.00, 135.63, 135.44, 131.01, 130.88, 124.23, 123.08, 118.47, 115.84, 115.80, 53.68, 40.33, 31.84, 29.93, 29.21, 25.79, 24.43, 22.74, 14.29, 9.01 ppm; HRMS (ESI): m/z: Calcd for $C_{22}H_{30}NO_3$ $[M+H]^+$ 356.2220, Found 356.2221.



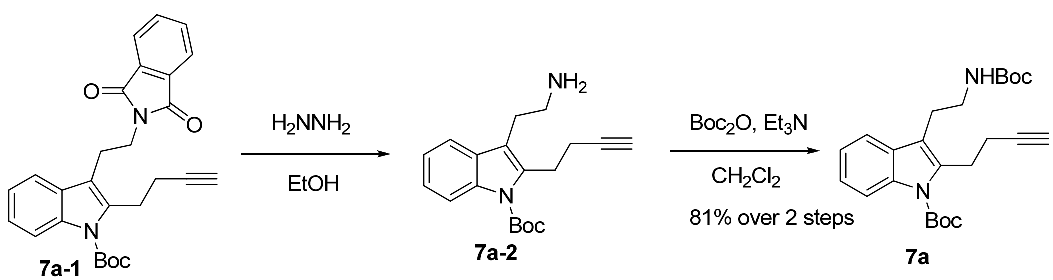
Methyl 2-(3-acetamidopent-4-ynyl)-3-ethyl-5-methoxy-1H-indole-1-carboxylate (5q): A colorless oil was obtained in 62% yield by following general procedure. IR (thin film): ν = 3282, 2962, 1731, 1651, 1538, 1364, 1133, 1089 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 9.0 Hz, 1H), 6.92 (d, J = 2.6 Hz, 1H), 6.86 (dd, J = 9.0 Hz, 2.6 Hz, 1H), 6.17 – 6.10 (br, 1H), 4.82 – 4.75 (m, 1H), 4.03 (s, 3H), 3.87 (s, 3H), 3.20 – 3.03 (m, 2H), 2.66 (q, J = 7.6 Hz, 2H), 2.32 (d, J = 2.3 Hz, 1H), 2.02 (s, 3H), 2.00 – 1.90 (m, 2H), 1.21 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.57, 156.13, 152.53, 135.96, 130.88, 130.32, 121.89, 116.74, 111.98, 101.51, 83.16, 71.26, 55.87, 53.58, 41.29, 35.38, 23.34, 23.04, 17.38, 15.07 ppm; HRMS (ESI): m/z: Calcd for $C_{20}H_{24}N_2NaO_4$ $[M+Na]^+$ 379.1628, Found 379.1632.

Methyl 3-ethyl-5-methoxy-2-(2-(2-methyl-5-methylene-4,5-dihydrooxazol-4-yl)ethyl)-1H-indole-1-carboxylate (6q): A colorless oil was obtained in 88% yield by following general procedure. IR (thin film) ν = 3012, 1732, 1677, 1478, 1440, 1386, 1263, 1216, 1130 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 9.0 Hz, 0.4 Hz, 1H), 6.92 (d, *J* = 2.3 Hz, 1H), 6.86 (dd, *J* = 9.0 Hz, 2.6 Hz, 1H), 4.69 (t, *J* = 2.8 Hz, 1H), 4.59 – 4.51 (m, 1H), 4.23 (t, *J* = 2.8 Hz, 1H), 4.02 (s, 3H), 3.86 (s, 3H), 3.15 – 3.11 (m, 2H), 2.77 – 2.56 (m, 2H), 2.11 (d, *J* = 1.6 Hz, 3H), 2.08 – 1.97 (m, 1H), 1.85 – 1.70 (m, 1H), 1.20 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.08, 163.00, 156.11, 152.46, 136.68, 130.99, 130.63, 121.70, 116.71, 116.65, 111.86, 111.81, 101.57, 101.50, 83.56, 68.01, 55.95, 55.90, 53.52, 53.49, 36.59, 22.95, 17.41, 15.05, 14.29 ppm; HRMS (ESI): *m/z*: Calcd for $C_{20}H_{25}N_2O_4$ $[M+H]^+$ 357.1809, Found 357.1808.

VIII. General preparation of alkynylindoles **7a-7h** (entries 1-8, Table 3) and characterization data

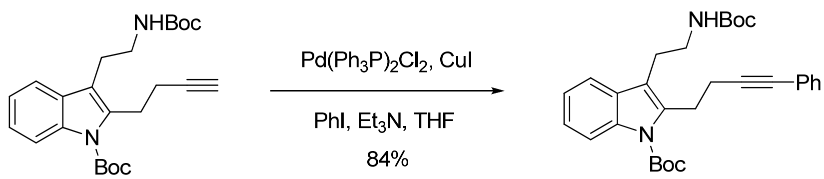


***Tert*-butyl 2-(but-3-ynyl)-3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1H-indole-1-carboxylate (7a-1):** To a solution of aldehyde **5f-3** (4.46 g. 10 mmol) in anhydrous MeOH (20 mL) was added a solution of Ohira-Bestmann Reagent (4.80 g, 25 mmol) in MeOH (5 mL) and K_2CO_3 (4.15 g, 30 mmol) at 0 °C. The resulting mixture was stirred at RT for 3 h before quenched with an aqueous solution of NH_4Cl. The aqueous phase was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to give an oil. Purification by column chromatography (hexanes/ethyl acetate = 3:1) afforded alkyne **7a-1** (3.76 g, 8.5 mmol) as a white solid in 85% yield: m.p. 183–184 °C. IR (thin film): ν = 3305, 2930, 1769, 1712, 1457, 1363, 1165, 1107 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 1H), 7.89 – 7.82 (m, 2H), 7.73 – 7.68 (m, 3H), 7.26 – 7.20 (m, 2H), 3.96 – 3.85 (m, 2H), 3.32 (t, *J* = 7.3 Hz, 2H), 3.17 – 3.04 (m, 2H), 2.59 (td, *J* = 7.3 Hz, 2.6 Hz, 2H), 1.99 (t, *J* = 2.6 Hz, 1H), 1.69 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.43, 150.52, 136.14, 136.09, 134.23, 134.16, 132.33, 129.56, 124.23, 123.44, 122.99, 118.58, 116.39, 115.96, 84.19, 83.70, 69.59, 38.09, 28.43, 26.25, 23.78, 19.62 ppm; HRMS (ESI): *m/z*: Calcd for $C_{27}H_{26}N_2NaO_4$ $[M+Na]^+$ 465.1785, Found 465.1779.



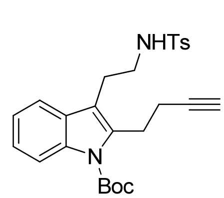
***Tert*-butyl 2-(but-3-ynyl)-3-(2-(tert-butoxycarbonylamino)ethyl)-1H-indole-1-carboxylate (7a, entry 1, Table 3):** To a solution of **7a-1** (3.76 g, 8.5 mmol) in absolute EtOH (20 mL) was added anhydrous hydrazine (3.0 mL, 85 mmol). The resulting mixture was heated to 60 °C for 1 h before it was cooled to RT, filtered through a pad of celite. The filtrate was concentrated *in vacuo* to give **7a-2** as colorless oil, which was used in the next step without purification.

To a solution of **7a-2** in anhydrous dichloromethane was added triethylamine (2.4 mL, 17.0 mmol) and Boc_2O (2.3 g, 10.2 mmol) at 0 °C. The resulting mixture was stirred at RT for 3 h before an aqueous solution of NH_4Cl was added. The aqueous phase was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to give an oil. Purification by column chromatography (hexanes/ethyl acetate = 5:1) afforded alkyne **7a** (2.84 g, 6.9 mmol) as a colorless oil in 81% yield over 2 steps: IR (thin film): ν = 2976, 2927, 1725, 1367, 1164, 1133 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.9 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.32 – 7.18 (m, 2H), 4.70 – 4.50 (br, 1H), 3.38 (d, J = 5.8 Hz, 2H), 3.24 (t, J = 7.4 Hz, 2H), 2.92 (t, J = 6.8 Hz, 2H), 2.53 (td, J = 7.4 Hz, 2.6 Hz, 2H), 1.96 (t, J = 2.6 Hz, 1H), 1.69 (s, 9H), 1.44 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.04, 150.51, 136.15, 136.05, 129.75, 124.20, 122.85, 118.62, 117.11, 115.91, 84.17, 83.75, 79.42, 69.49, 40.74, 28.61, 28.42, 26.25, 24.99, 19.62 ppm; HRMS (ESI): *m/z*: Calcd for $C_{24}H_{33}N_2O_4$ $[M+H]^+$ 413.2435, Found 413.2441.



7a **7b**

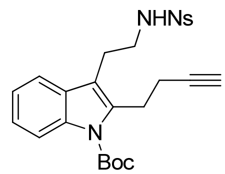
***Tert*-butyl 3-(2-(tert-butoxycarbonylamino)ethyl)-2-(4-phenylbut-3-ynyl)-1H-indole--1-carboxylate (7b, entry 2, Table 3):** A solution of alkyne **7a** (144 mg, 0.35 mmol) and iodobenzene (195 mg, 0.53 mmol) in THF (2 mL) was frozen with liquid nitrogen and thoroughly degassed under high vacuum. $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol) was added and the resulting suspension was degassed in the same way. Freshly purified copper(I) iodide (16 mg, 0.08 mmol) was added and degassing was repeated. Previously degassed triethylamine (0.5 mL, 3.5 mmol) was added and the mixture was heated at 70 °C for 2 h. The reaction was allowed to cool to RT, saturated aqueous $NaHCO_3$ was added and the mixture was extracted with ethyl acetate. The combined extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give brown foam, which was purified by column chromatography (hexanes/ethyl acetate = 10:1) to afford **7b** (140 mg, 0.29 mmol) as a colorless oil in 84% yield: IR (thin film): ν = 2974, 2928, 1708, 1476, 1382, 1172 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 7.4 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.27 – 7.16 (m, 5H), 4.68 – 4.45 (br, 1H), 3.50 – 3.27 (m, 4H), 2.97 (t, J = 6.8 Hz, 2H), 2.75 (t, J = 7.4 Hz, 2H), 1.71 (s, 9H), 1.44 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.05, 150.57, 136.28, 136.20, 131.65, 129.81, 128.39, 127.82, 124.18, 123.89, 122.86, 118.58, 117.13, 115.92, 89.43, 84.17, 81.65, 79.40, 40.75, 28.60, 28.44, 26.51, 24.97, 20.67 ppm; HRMS (ESI): Calcd for $C_{30}H_{36}N_2NaO_4$ $[M+Na]^+$ 511.2567, Found 511.2559.



7c

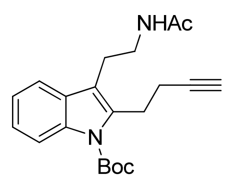
***Tert*-butyl 2-(but-3-ynyl)-3-(2-(4-methylphenylsulfonamido)ethyl)-1H-indole-1-carboxylate (7c, entry 3, Table 3) :** A colorless oil was obtained in 88% yield by following general procedure. IR (thin film): ν = 3291, 2927, 1727, 1457, 1325, 1158 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.3 Hz, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 7.7

Hz, 1H), 7.35 – 7.21 (m, 3H), 7.17 (t, *J* = 7.4 Hz, 1H), 4.51 (t, *J* = 6.3 Hz, 1H), 3.24 (q, *J* = 6.9 Hz, 2H), 3.18 (t, *J* = 7.2 Hz, 2H), 2.92 (t, *J* = 7.1 Hz, 2H), 2.49 (td, *J* = 7.2 Hz, 2.6 Hz, 2H), 2.40 (s, 3H), 1.90 (t, *J* = 2.6 Hz, 1H), 1.69 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.42, 143.63, 136.98, 136.41, 136.18, 129.87, 129.25, 127.25, 124.37, 122.98, 118.25, 116.08, 115.88, 84.44, 83.71, 69.72, 43.14, 28.46, 26.12, 25.07, 21.78, 19.51 ppm; HRMS (ESI): *m/z*: Calcd for $C_{26}H_{30}N_2NaO_4S$ $[M+Na]^+$ 489.1819, Found 489.1800.



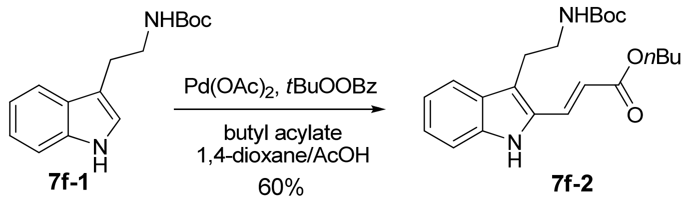
7d

***Tert*-butyl 2-(but-3-ynyl)-3-(2-(2-nitrophenylsulfonamido)ethyl)-1H-indole-1-carboxylate (7d, entry 4, Table 3):** A colorless oil was obtained in 80% yield by following general procedure. IR (thin film): ν = 3294, 2927, 1726, 1540, 1457, 1394, 1164 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.98 – 7.93 (m, 1H), 7.73 – 7.69 (m, 1H), 7.58 (pd, *J* = 7.5 Hz, 1.7 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.16 – 7.09 (m, 1H), 5.38 (t, *J* = 5.8 Hz, 1H), 3.42 (dd, *J* = 13.1 Hz, 7.1 Hz, 2H), 3.18 (t, *J* = 7.2 Hz, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.48 (td, *J* = 7.2 Hz, 2.6 Hz, 2H), 1.91 (t, *J* = 2.6 Hz, 1H), 1.68 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$)δ 150.27, 147.65, 136.50, 136.12, 133.74, 133.56, 132.84, 130.83, 129.01, 125.49, 124.29, 122.90, 118.08, 116.11, 115.58, 84.46, 83.58, 69.68, 43.77, 29.90, 28.41, 26.15, 25.12, 19.54 ppm; HRMS (ESI): *m/z*: Calcd for $C_{25}H_{27}N_3NaO_6S$ $[M+Na]^+$ 520.1513, Found 520.1531.

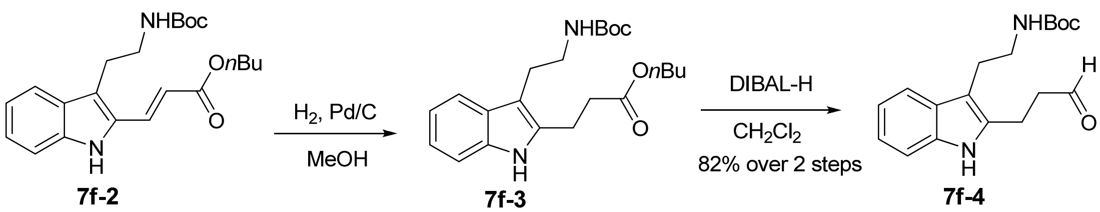


7e

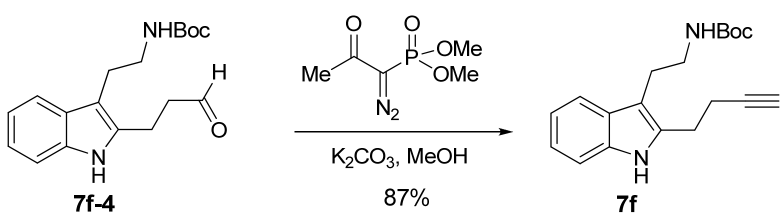
***Tert*-butyl 3-(2-acetamidoethyl)-2-(but-3-ynyl)-1H-indole-1-carboxylate (7e, entry 5, Table 3):** A colorless oil was obtained in 74% yield by following general procedure. IR (thin film): ν = 3290, 2922, 2851, 1726, 1650, 1457, 1341, 1163 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.4 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.33 – 7.26 (m, 1H), 7.26 – 7.20 (m, 1H), 5.65 – 5.56 (br, 1H), 3.52 (q, *J* = 6.8 Hz, 2H), 3.25 (t, *J* = 7.3 Hz, 2H), 2.94 (t, *J* = 7.0 Hz, 2H), 2.54 (td, *J* = 7.3 Hz, 2.6 Hz, 2H), 1.96 (t, *J* = 2.6 Hz, 1H), 1.93 (s, 3H), 1.70 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.35, 150.52, 136.14, 136.05, 129.81, 124.32, 122.97, 118.52, 117.12, 116.01, 110.84, 84.31, 83.70, 69.60, 39.95, 28.45, 26.16, 24.46, 23.58, 19.63 ppm; HRMS (ESI): *m/z*: Calcd for $C_{21}H_{26}N_2NaO_3$ $[M+Na]^+$ 377.1835, Found 377.1817.



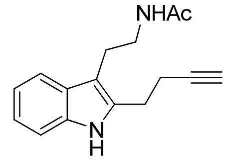
(*E*)-Butyl 3-(3-(2-(*tert*-butoxycarbonylamino)ethyl)-1H-indol-2-yl)acrylate (7f-2): A colorless oil was obtained in 60% yield by following general procedure. IR (thin film): ν = 3339, 2961, 1693, 1613, 1513, 1455, 1251, 1171, 1069, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.35 (br, 1H), 7.75 (d, *J* = 15.9 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.20 (d, *J* = 15.9 Hz, 1H), 4.65 – 4.52 (br, 1H), 4.22 (t, *J* = 6.6 Hz, 2H), 3.43 – 3.35 (m, 2H), 3.10 – 3.06 (m, 2H), 1.86 – 1.55 (m, 2H), 1.51 – 1.40 (m, 9H), 0.97 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.63, 156.13, 137.76, 132.06, 130.90, 128.48, 125.10, 120.14, 119.63, 114.97, 111.37, 79.40, 64.69, 41.66, 30.92, 28.57, 28.29, 25.03, 19.32, 19.22, 13.92 ppm; HRMS (ESI): Calcd for $C_{22}H_{31}N_2O_4$ $[M+H]^+$ 387.2278, Found 387.2289.



***Tert*-butyl 2-(2-(3-oxopropyl)-1H-indol-3-yl)ethylcarbamate (7f-4):** A colorless oil was obtained in 82% yield by following general procedure. IR (thin film): ν = 3402, 3055, 2976, 2931, 2727, 1689, 1513, 1462, 1366, 1169, 741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.40 – 8.31 (br, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.19 – 7.12 (m, 1H), 7.10 – 7.02 (m, 1H), 4.60 – 4.50 (br, 1H), 3.37 (dd, *J* = 12.6 Hz, 6.2 Hz, 2H), 3.12 – 2.97 (m, 2H), 2.94 – 2.86 (m, 4H), 1.43 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.34, 202.31, 156.13, 135.48, 134.99, 128.11, 121.43, 119.21, 118.20, 110.73, 108.43, 79.19, 44.27, 41.22, 28.50, 24.74, 18.08 ppm; HRMS (ESI): Calcd for $C_{18}H_{25}N_2O_3$ $[M+H]^+$ 317.1860, Found 317.1867.

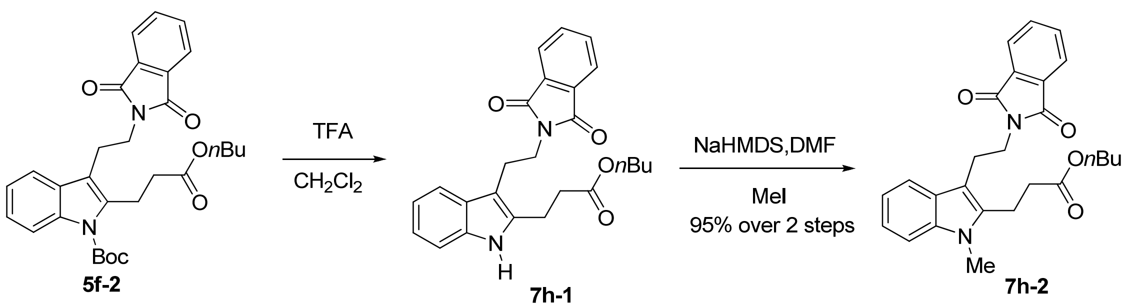


***Tert*-butyl 2-(2-(but-3-ynyl)-1H-indol-3-yl)ethylcarbamate (7f, entry 6, Table 3):** A colorless oil was obtained in 87 % yield by following general procedure. IR (thin film): ν = 3403, 3303, 2975, 2931, 1689, 1511, 1462, 1250, 1166 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.20 – 7.13 (m, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 4.70 – 4.56 (br, 1H), 3.38 (d, *J* = 6.4 Hz, 2H), 2.98 (t, *J* = 6.8 Hz, 2H), 2.91 (t, *J* = 6.6 Hz, 2H), 2.55 (td, *J* = 6.8 Hz, 2.6 Hz, 2H), 2.13 (t, *J* = 2.6 Hz, 1H), 1.44 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.14, 135.67, 135.00, 128.18, 121.77, 119.52, 118.54, 110.79, 109.19, 84.10, 79.29, 70.31, 41.20, 28.63, 25.00, 24.81, 19.47 ppm; HRMS (ESI): Calcd for $C_{19}H_{25}N_2O_2$ $[M+H]^+$ 313.1911, Found 313.1911.

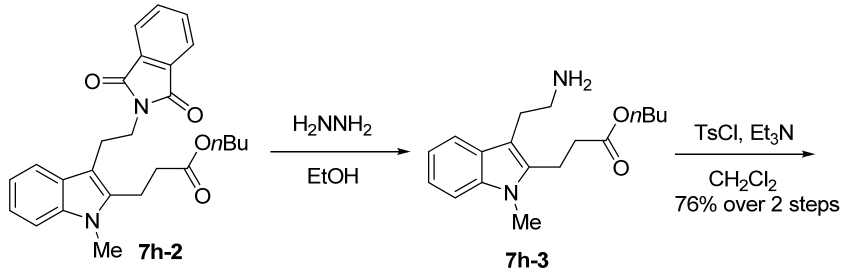


7g

***N*-(2-(2-(But-3-ynyl)-1H-indol-3-yl)ethyl)acetamide (7h, entry 7, Table 3):** A colorless oil was obtained in 84 % yield by following general procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 8.31 (br, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.75 – 5.62 (br, 1H), 3.53 (dd, *J* = 12.9 Hz, 6.4 Hz, 2H), 3.04 – 2.87 (m, 4H), 2.55 (td, *J* = 6.9 Hz, 2.6 Hz, 2H), 2.11 (t, *J* = 2.5 Hz, 1H), 1.93 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.13, 135.67, 135.02, 128.22, 121.94, 119.75, 118.33, 110.95, 108.95, 83.99, 70.48, 40.61, 29.92, 24.93, 24.18, 23.37, 19.46 ppm; HRMS (ESI): *m/z*: Calcd for $C_{16}H_{19}N_2O$ $[M+H]^+$ 255.1492, Found 255.1480.

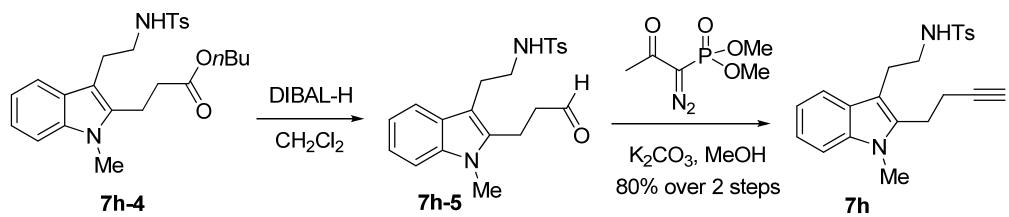


Butyl 3-(3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1-methyl-1H-indol-2-yl)propanoate (7h-2): To a solution of ester **5f-2** (1.56 g, 3.0 mmol) in anhydrous dichloromethane (10 mL) was added trifluoroacetic acid (2.3 mL, 30.0 mmol). The resulting mixture was stirred at RT for 2 h before the solvents were removed *in vacuo* to give an oil, which was dissolved in anhydrous DMF (10 mL) and cooled to -50 °C. A solution of NaHMDS (2.0 M in THF, 1.6 mL, 3.2 mmol) was added to the above solution. After 30 min, iodomethane (0.37 mL, 6.0 mmol) was added in one portion and the resulting mixture was slowly warmed to RT and stirred for 2 h before it was quenched with water, and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to afford a yellow oil, which was purified by column chromatography (hexanes/ethyl acetate = 10:1) to afford N-methyl indole **7h-2** (1.23 g, 2.85 mmol) as a colorless oil in 95% yield over 2 steps: IR (thin film): ν = 2957, 1770, 1712, 1470, 1396, 1258, 1171, 1024 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.86 (m, 2H), 7.77 – 7.76 (m, 3H), 7.31 (d, *J* = 5.8 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.16 – 7.11 (m, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 4.00 – 3.88 (m, 2H), 3.76 (s, 3H), 3.28 – 3.20 (m, 2H), 3.20 – 3.12 (m, 2H), 2.77 – 2.63 (m, 2H), 1.64 (dt, *J* = 14.6 Hz, 7.0 Hz, 2H), 1.46 – 1.34 (m, 2H), 0.99 – 0.92 (m, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.61, 168.48, 136.99, 135.98, 134.03, 132.40, 127.66, 123.33, 121.39, 119.42, 118.54, 109.04, 108.14, 64.85, 38.91, 34.75, 30.78, 29.92, 29.87, 24.02, 20.03, 19.29, 13.91 ppm; HRMS (ESI): *m/z*: Calcd for $C_{26}H_{28}N_2NaO_4$ $[M+Na]^+$ 455.1914, Found 455.1934.



4-Methyl-*N*-(2-(1-methyl-2-(3-oxopropyl)-1H-indol-3-yl)ethyl)benzenesulfonamide (7h-4): To a solution of **7h-2** (1.23 g, 2.85 mmol) in absolute EtOH (5 mL) was added anhydrous hydrazine (1.0 mL, 28.5 mmol). The resulting mixture was heated to 60 °C for 1 h before it was cooled to RT, filtered through a pad of celite. The filtrate was concentrated *in vacuo* to give amine **7h-3** as a crude oil, which was used in the next step without purification.

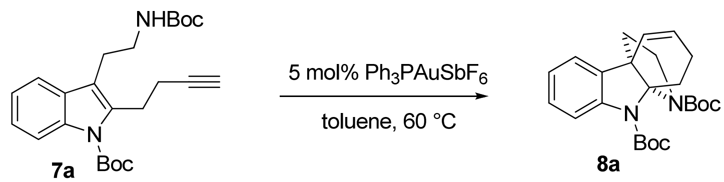
To a solution of **7h-3** in anhydrous dichloromethane was added triethylamine (0.8 mL, 5.7 mmol) and TsCl (0.77 g, 3.42mmol) at 0 °C. The resulting mixture was stirred at RT for 10 h before quenched with an aqueous solution of NH_4Cl. The aqueous phase was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to give an oil, which was purified by column chromatography (hexanes/ethyl acetate=5:1) to afford sulfonamide **7h-4** (1.05 g, 2.3 mmol) as a colorless oil in 81% yield over 2 steps: IR (thin film): ν = 3290, 2958, 2872, 1731, 1471, 1330, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 6.6 Hz, 2H), 7.21 – 7.15 (m, 2H), 7.07 – 7.00 (m, 1H), 4.45 (t, *J* = 6.2 Hz, 1H), 4.07 (t, *J* = 6.7 Hz, 2H), 3.67 (s, 3H), 3.21 (q, *J* = 6.7 Hz, 2H), 3.08 – 3.03 (m, 2H), 2.95 (t, *J* = 6.8 Hz, 2H), 2.56 – 2.50 (m, 2H), 2.40 (s, 3H), 1.62 – 1.53 (m, 2H), 1.32 (dt, *J* = 14.7 Hz, 7.5 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.44, 143.12, 136.91, 136.13, 129.72, 129.57, 127.14, 127.03, 121.30, 119.21, 118.06, 109.00, 107.36, 64.73, 43.58, 34.39, 30.59, 29.73, 29.67, 24.97, 21.53, 21.50, 19.74, 19.11, 13.75 ppm; HRMS (ESI): *m/z*: Calcd for $C_{25}H_{33}N_2O_4S$ $[M+Na]^+$ 457.2156, Found 457.2144.



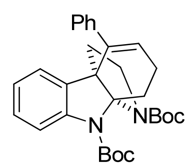
***N*-(2-(2-(But-3-ynyl)-1-methyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide (7h,entry 8, Table 3):** Ester **7h-4** (1.05 g, 2.3 mmol) was dissolved in anhydrous dichloromethane and the solution was cooled to -78 °C before the addition of the solution of DIBAL-H (1.0 M in hexane, 2.76 mL, 2.76 mmol) dropwise. The reaction mixture was stirred for 1 h at -78 °C before it was treated with saturated aqueous solution of Rochelle salt (5.0 mL) at -78 °C. After being stirred at RT for 1 h, the layers were separated. The aqueous layer was extracted with ether, and the combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to produce aldehyde **7h-5** as a yellow oil, which was used for the next step without further purification.

To a solution of aldehyde **7h-5** in anhydrous MeOH (5 mL) was added a solution of Ohira-Bestmann Reagent (1.03 g, 5.75 mmol) in MeOH (5 mL) and K_2CO_3 (0.96 g, 6.9 mmol) at 0 °C. The resulting mixture was stirred at RT for 3 h before quenched with an aqueous solution of NH_4Cl. The aqueous phase was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to give an oil, which was purified by column chromatography (hexanes/ethyl acetate = 5:1) to afford alkyne **7h** (0.70 g, 1.8 mmol) as a white solid in 80% yield over 2 steps: m.p. 160–161 °C. IR (thin film): ν = 3287, 2924, 1471, 1324.49, 1158, 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.37 – 7.32 (m, 1H), 7.27 – 7.20 (m, 3H), 7.17 (ddd, *J* = 8.2 Hz, 7.0 Hz, 1.1 Hz, 1H), 7.02 (ddd, *J* = 8.0 Hz, 7.0 Hz, 1.1 Hz, 1H), 4.35 (t, *J* = 6.1 Hz, 1H), 3.68 (s, 3H), 3.23 (q, *J* = 6.7 Hz, 2H), 3.02 – 2.91 (m, 4H), 2.48 – 2.34 (m, 5H), 1.96 (t, *J* = 2.7 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.41, 137.04, 136.90, 136.28, 129.78, 127.19, 127.16, 121.54, 119.39, 118.25, 109.20, 107.59, 82.96, 69.98, 43.63, 30.05, 30.00, 25.18, 23.64, 21.70, 21.67, 19.60 ppm; HRMS (ESI): *m/z*: Calcd for $C_{22}H_{24}N_2NaO_2S$ $[M+Na]^+$ 403.1450 , Found 403.1461.

IX. Gold(I)-catalyzed tandem cyclization studies for the synthesis of akuammilines (Table 3)

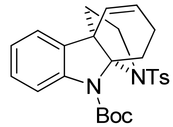


The catalyst solution was first prepared by addition of Ph_3PAuCl (2.5 mg, 0.005 mmol) to a suspension of $AgSbF_6$ (1.7 mg, 0.005 mmol) in anhydrous toluene (0.50 mL) at RT. The suspension was stirred for 20 min at RT under Argon atmosphere. The resulting catalyst solution was then added to a solution of substrate **7a** (41.2 mg, 0.10 mmol) in anhydrous toluene (0.50 mL) dropwise at RT. The resulting mixture was heated at 60 °C until TLC showed that there was no starting material **7a** left (about 1-2 h). The reaction mixture was cooled to RT, filtered through a short pad of silica gel. The filtrate was concentrated *in vacuo*, and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford **8a** (entry 1, Table 3, 23.7 mg, 0.083 mmol) as a colorless oil in 75% yield: IR (thin film): ν = 2973, 2927, 1708, 1477, 1376, 1172, 1144 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.23 – 7.12 (m, 2H), 7.00 (t, *J* =7.3 Hz, 1H), 5.74 – 5.70 (m, 1H), 5.60 (d, *J* = 10.0 Hz, 1H), 3.53 (t, *J* = 9.1 Hz, 2H), 3.00 (dt, *J* = 17.3 Hz, 8.7 Hz, 1H), 2.25 (dd, *J* = 13.1 Hz, 5.9 Hz, 2H), 2.16 – 2.11 (m, 1H), 2.07 – 1.97 (m, 2H), 1.57 (s, 9H), 1.45 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.29, 134.20, 128.15, 128.12, 126.40, 123.17, 122.27, 118.03, 117.95, 117.88, 117.81, 117.61, 87.70, 81.31, 76.75, 56.61, 56.57, 46.27, 33.93, 29.91, 29.58, 29.54, 29.41, 28.76, 28.63, 28.50, 27.99, 27.93, 27.88, 23.21, 22.91 ppm; HRMS (ESI): *m/z*: Calcd for $C_{24}H_{32}N_2NaO_4$ $[M+Na]^+$ 435.2254 , Found 435.2266.



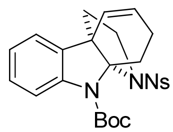
8b

Tetracyclic indoline 8b (entry 2, Table 3): A colorless oil was obtained in 84% yield by following general procedure. ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 3H), 7.14 – 7.05 (m, 1H), 6.97 – 6.92 (m, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.20 (d, *J* = 6.7 Hz, 1H), 5.60 (d, *J* = 3.9 Hz, 1H), 3.82 – 3.78 (m, 1H), 3.65 – 3.55 (m, 1H), 2.92 – 2.82 (m, 1H), 2.47 (dd, *J* = 12.3 Hz, 6.1 Hz, 2H), 2.35 (td, *J* = 12.0 Hz, 8.3 Hz, 1H), 2.26 (d, *J* = 18.5 Hz, 1H), 1.92 – 1.83 (m, 1H), 1.63 (s, 9H), 1.43 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.76, 141.17, 139.40, 131.52, 130.41, 129.94, 129.65, 128.10, 127.74, 126.98, 124.67, 122.36, 118.14, 110.31, 88.28, 81.30, 46.12, 33.21, 30.04, 28.89, 28.75, 24.00 ppm; HRMS (ESI): *m/z*: Calcd for $C_{30}H_{36}N_2NaO_4$ $[M+Na]^+$ 511.2567, Found 511.2577.



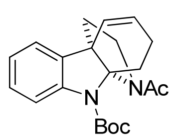
8c

Tetracyclic indoline 8c (entry 3, Table 3): A colorless oil was obtained in 81% yield by following general procedure. IR (thin film): ν = 2924, 1697, 1477, 1365, 1161, 1098, 1043 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* =8.3 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.09 – 7.04 (m, 1H), 6.98 (td, *J* = 7.8 Hz, 1.5 Hz, 1H), 6.93 (dt, *J* = 7.4 Hz, 3.7 Hz, 1H), 5.70 – 5.62 (m, 1H), 5.49 (dt, *J* = 9.9 Hz, 1.9 Hz, 1H), 3.83 – 3.71 (m, 2H), 2.92 (dd, *J* = 16.2 Hz, 10.2 Hz, 1H), 2.42 – 2.31 (m, 4H), 2.26 – 2.15 (m, 1H), 2.15 – 2.08 (m, 2H), 2.01 – 1.87 (m, 1H), 1.61 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.70, 141.90, 137.62, 132.88, 129.29, 128.07, 127.96, 127.03, 126.94, 125.83, 123.79, 121.69, 118.14, 89.99, 82.26, 58.02, 48.55, 48.49, 33.07, 31.40, 31.36, 31.30, 29.91, 28.38, 23.63, 21.60 ppm; HRMS (ESI): *m/z*: Calcd for $C_{26}H_{30}N_2NaO_4S$ $[M+Na]^+$ 489.1819, Found 489.1823.



8d

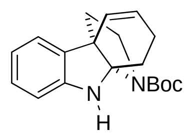
Tetracyclic indoline 8d (entry 4, Table 3): A colorless oil was obtained in 88% yield by following general procedure. IR (thin film): ν = 2925, 1711, 1544, 1366, 1164, 1035 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.62 (dd, *J* = 11.4 Hz, 3.8 Hz, 1H), 7.60 – 7.49 (m, 3H), 7.20 (ddd, *J* = 7.3 Hz, 4.3 Hz, 2.8 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 5.70 – 5.65 (m, 1H), 5.55 (d, *J* = 10.0 Hz, 1H), 3.93 – 3.82 (m, 1H), 3.66 (d, *J* = 13.8 Hz, 1H), 3.14 (m, 1H), 2.46 (dd, *J* = 12.7 Hz, 5.7 Hz, 1H), 2.24 (td, *J* = 12.1 Hz, 8.2 Hz, 1H), 2.11 – 2.07 (m, 2H), 1.95 – 1.86 (m, 1H), 1.56 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.97, 148.34, 141.89, 135.06, 133.19, 133.11, 131.74, 131.15, 128.67, 128.35, 125.74, 124.12, 122.29, 117.99, 90.61, 82.65, 58.54, 49.55, 32.80, 31.80, 29.91, 28.38, 28.26, 23.41, 22.87, 14.35 ppm; HRMS (ESI): *m/z*: Calcd for $C_{25}H_{27}N_3NaO_6S$ $[M+Na]^+$ 520.1513, Found 520.1517.



8e

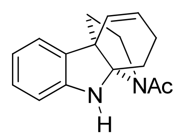
Tetracyclic indoline 8e (entry 5, Table 3): A colorless oil was obtained in 80% yield by following general procedure. IR (thin film): ν = 2927, 1698, 1664, 1477, 1404, 1364, 1167 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6, 60°C) δ 8.41 – 8.11 (m, 1H), 7.10 – 7.01 (m, 1H), 6.92 – 6.79 (m, 2H), 5.55 – 5.41 (m, 1H), 5.36 (d, *J* = 10.1 Hz, 1H), 3.69 (d, *J* = 14.3 Hz, 1H), 2.80 – 2.56 (m, 2H), 2.34 (t, *J* = 14.4 Hz, 1H), 1.87 (dd, *J* = 12.3 Hz, 7.4 Hz, 2H), 1.63 – 1.52 (m, 12H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.31, 143.17, 134.44, 134.30, 132.88, 132.20, 129.50, 129.39, 128.61, 128.34, 128.02, 126.41, 124.88, 124.63, 123.06, 122.37, 122.10, 119.44, 117.47, 88.15, 81.56, 55.88, 47.23, 46.05, 33.84, 31.68, 29.92, 29.20, 28.47, 28.13, 27.68, 24.71, 23.39, 23.25, 22.67 ppm; HRMS (ESI): *m/z*:

Calcd for $C_{21}H_{26}N_2NaO_3$ $[M+Na]^+$ 377.1835, Found 377.1846.



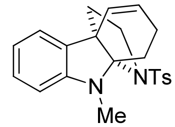
8f

Tetracyclic indoline 8f (entry 6, Table 3): A colorless oil was obtained in 87% yield by following general procedure. IR (thin film): ν = 3377, 2972, 2927, 1681, 1609, 1365, 1254, 1169, 951 cm^{-1}; ^{1}H NMR (400 MHz, Toluene-d_8, 95°C) δ 6.90 – 6.82 (m, 2H), 6.62 (t, *J* = 7.4 Hz, 1H), 6.35 (d, *J* = 7.6 Hz, 1H), 5.58 – 5.45 (m, 3H), 3.37 (s, 1H), 3.37 (t, *J* = 8.2 Hz, 1H), 3.10 – 3.02 (m, 1H), 2.80 – 2.68 (br, 1H), 2.23 (ddd, *J* = 16.3 Hz, 11.1 Hz, 5.1 Hz, 1H), 2.03 (ddd, *J* = 12.4 Hz, 6.8 Hz, 2.2 Hz, 1H), 1.88 – 1.61 (m, 4H), 1.37 (s, 9H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ 155.72, 155.68, 150.35, 149.86, 133.85, 133.59, 131.21, 131.20, 129.33, 126.66, 126.58, 124.05, 123.95, 123.92, 120.21, 120.19, 111.14, 111.02, 87.28, 86.91, 82.09, 80.97, 58.22, 57.08, 47.43, 47.38, 47.28, 35.33, 34.89, 30.28, 30.25, 29.30, 29.26, 29.03, 28.90, 23.78 ppm; HRMS (ESI): *m/z*: Calcd for $C_{19}H_{25}N_2O_2$ $[M+H]^+$ 313.1911, Found 313.1917.



8g

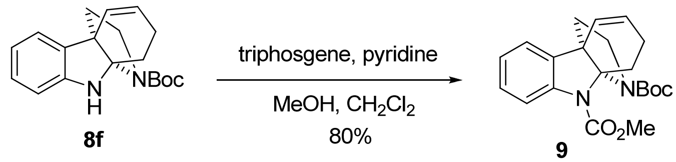
Tetracyclic indoline 8g (entry 7, Table 3): A colorless oil was obtained in 83% yield by following general procedure. ν = 3387, 2924, 1660, 1457, 1401, 1311, 1127 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 – 7.03 (m, 2H), 6.75 (dd, *J* = 7.4, 6.5 Hz, 1H), 6.62 (d, *J* = 7.7, 1H), 5.79 (s, 1H), 5.76 – 5.59 (m, 2H), 3.59 (t, *J* = 8.5 Hz, 1H), 3.29 – 3.17 (m, 1H), 2.92 (dd, *J* = 13.6 Hz, 3.2 Hz, 1H), 2.45 (dd, *J* = 12.7 Hz, 5.5 Hz, 1H), 2.41 – 2.26 (m, 2H), 2.23 – 2.11 (m, 1H), 1.97 (s, 3H), 1.78 – 1.67 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.56, 149.24, 131.90, 129.60, 128.58, 126.37, 123.04, 119.17, 110.61, 87.38, 55.46, 47.58, 34.49, 29.92, 27.70, 27.66, 23.91, 22.87 ppm; HRMS (ESI): *m/z*: Calcd for $C_{16}H_{19}N_2O$ $[M+H]^+$ 255.1492 , Found 255.1483.



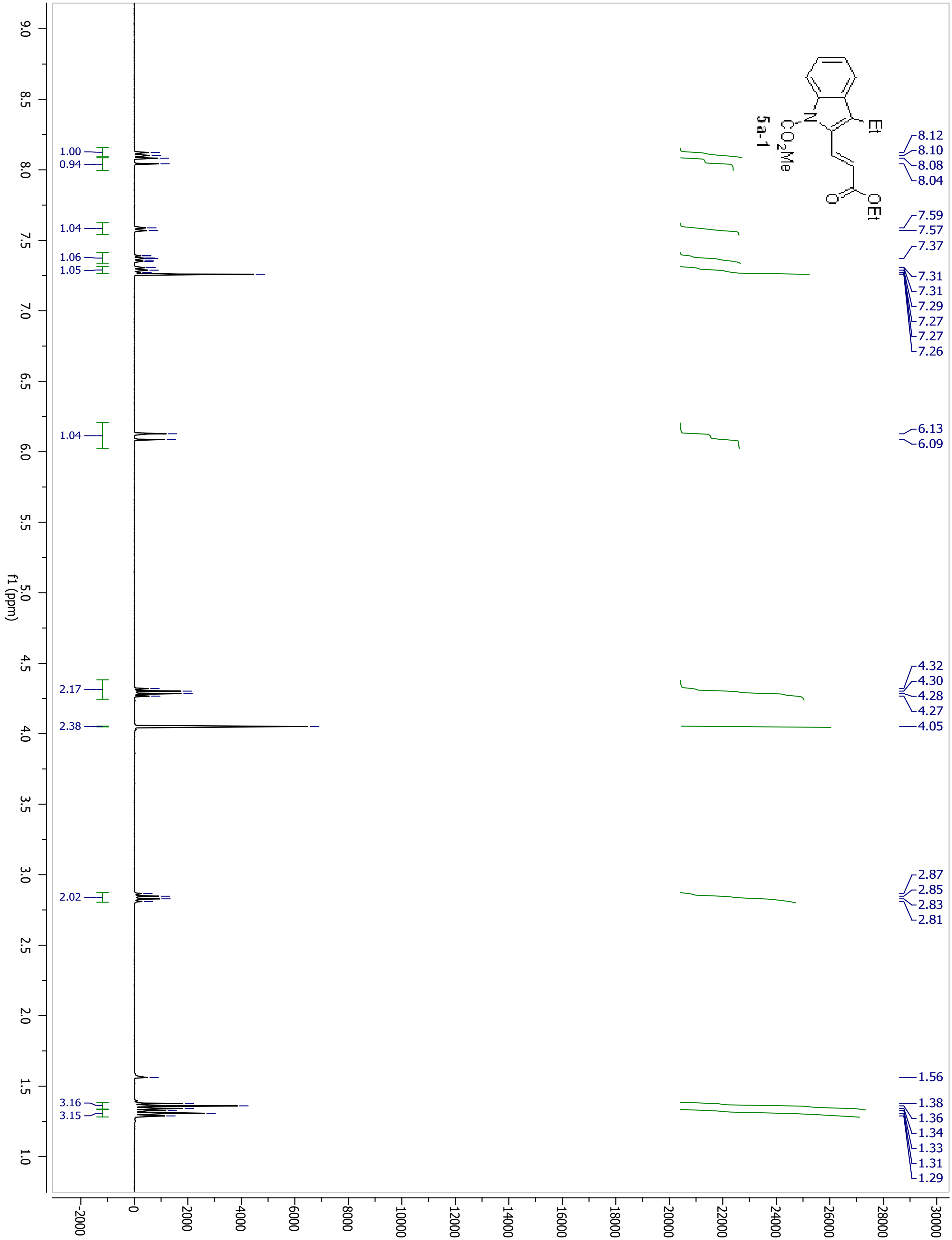
8h

Tetracyclic indoline 8h (entry 8, Table 3): A colorless oil was obtained in 86% yield by following general procedure. IR (thin film): ν = 2923, 1605, 1491, 1332, 1153, 1094, 920 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.12 (td, *J* = 7.7 Hz, 1.3Hz, 1H), 7.02 (dd, *J* = 7.2 Hz, 0.9 Hz, 1H), 6.69 (td, *J* = 7.4 Hz, 0.9 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 5.73 – 5.61 (m, 2H), 3.49 (td, *J* = 7.7 Hz, 3.8 Hz, 1H), 3.15 (d, *J* = 6.5 Hz, 1H), 3.01 (s, 3H), 3.00 – 2.92 (m, 1H), 2.38 (s, 3H), 2.36 – 2.29 (m, 1H), 2.10 – 1.95 (m, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.45, 142.89, 138.22, 131.22, 129.54, 129.49, 128.80, 127.02, 125.28, 122.00, 118.05, 106.57, 93.71, 57.62, 48.10, 34.80, 29.73, 29.70, 28.18, 22.65, 21.64, 21.62 ppm; HRMS (ESI): *m/z*: Calcd for

$C_{22}H_{24}N_2NaO_2S$ $[M+H]^+$ 403.1450, Found 403.1464.



To a solution of the substrate **8f** (31 mg, 0.1 mmol) in anhydrous dichloromethane (0.5 mL) was added pyridine (40 μL, 0.5 mmol) and a solution of triphosgene (89 mg, 0.3 mmol) in dichloromethane (0.2 mL) at -10 °C. The reaction was slowly warmed to RT and stirred for 30 min. MeOH (40 μL, 1 mmol) was added to the above solution and the reaction was stirred for another 2h before the solvents were removed *in vacuo* to give a crude oil, which was purified by column chromatography (petroleum ether/ethyl acetate=10:1) to produce **9** (29.6 mg, 0.08 mmol) as a colorless oil in 80% yield: IR (thin film): ν = 2927, 1708, 1479, 1439, 1378, 1242, 1169, 752 cm^{-1}; ^1H NMR (400 MHz, C_6D_6, 60 °C) δ 8.16 (d, *J* = 7.6 Hz, 1H), 7.12 – 7.05 (m, 1H), 6.97 – 6.83 (m, 2H), 5.59 – 5.51 (m, 1H), 5.47 (d, *J* = 10.0 Hz, 1H), 3.64 (s, 3H), 3.50 – 3.47 (m, 1H), 3.18 – 2.98 (m, 2H), 2.42 – 2.35 (m, 1H), 2.15 – 1.95 (m, 1H), 2.06 – 1.96 (m, 1H), 1.90 – 1.78 (m, 1H), 1.74 – 1.63 (m, 1H), 1.42 (s, 9H) ppm; ^{13}C NMR (101 MHz, C_6D_6,60 °C) δ 154.54, 153.76, 142.55, 135.21, 129.01, 128.89, 128.27, 127.04, 123.63, 122.61, 117.82, 89.34, 79.72, 56.92, 52.35, 52.29, 47.13, 35.35, 28.94, 28.73, 23.53 ppm; HRMS (ESI): *m/z*: Calcd for $C_{21}H_{27}N_2O_4$ $[M+H]^+$ 371.1965 , Found 371.1958.



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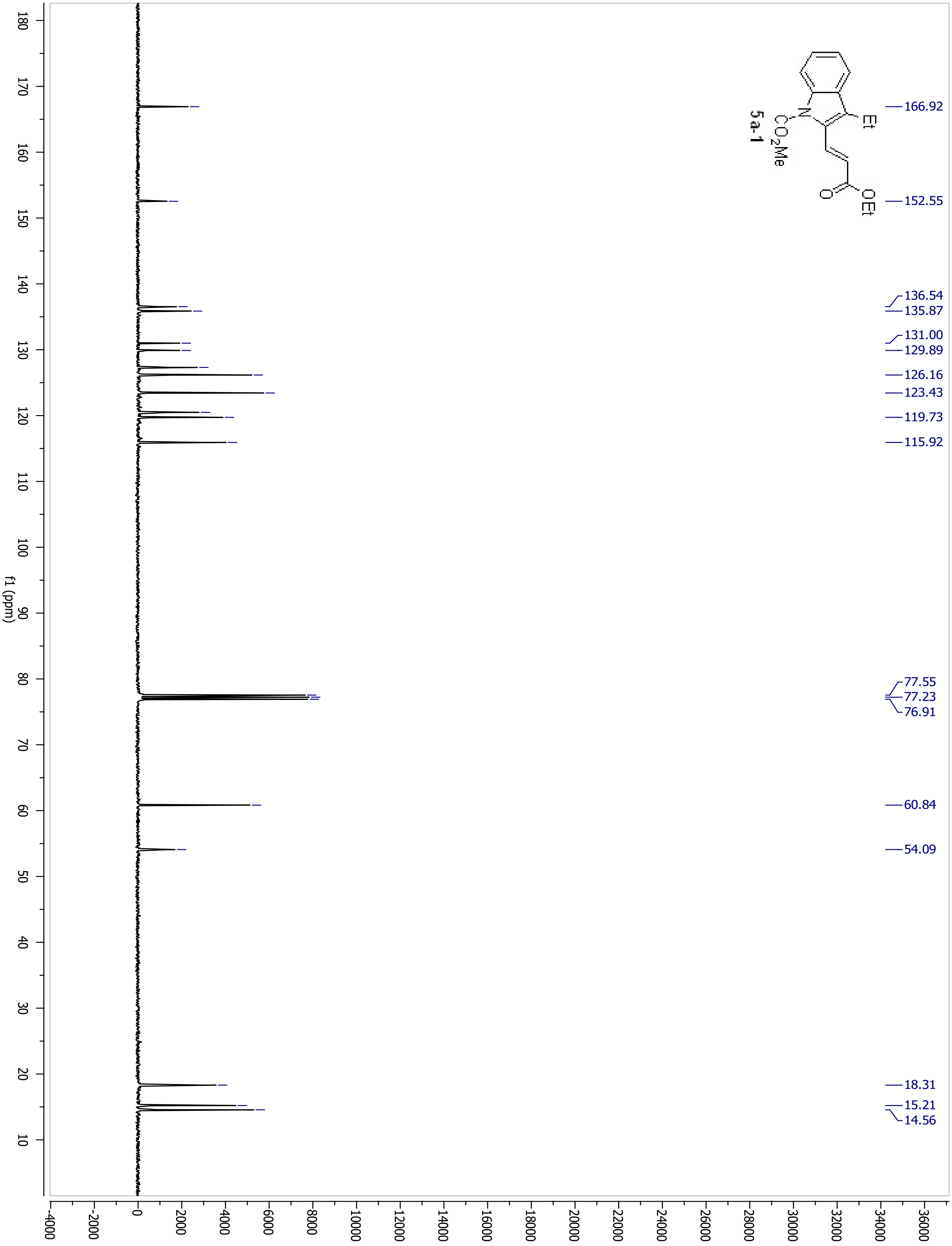
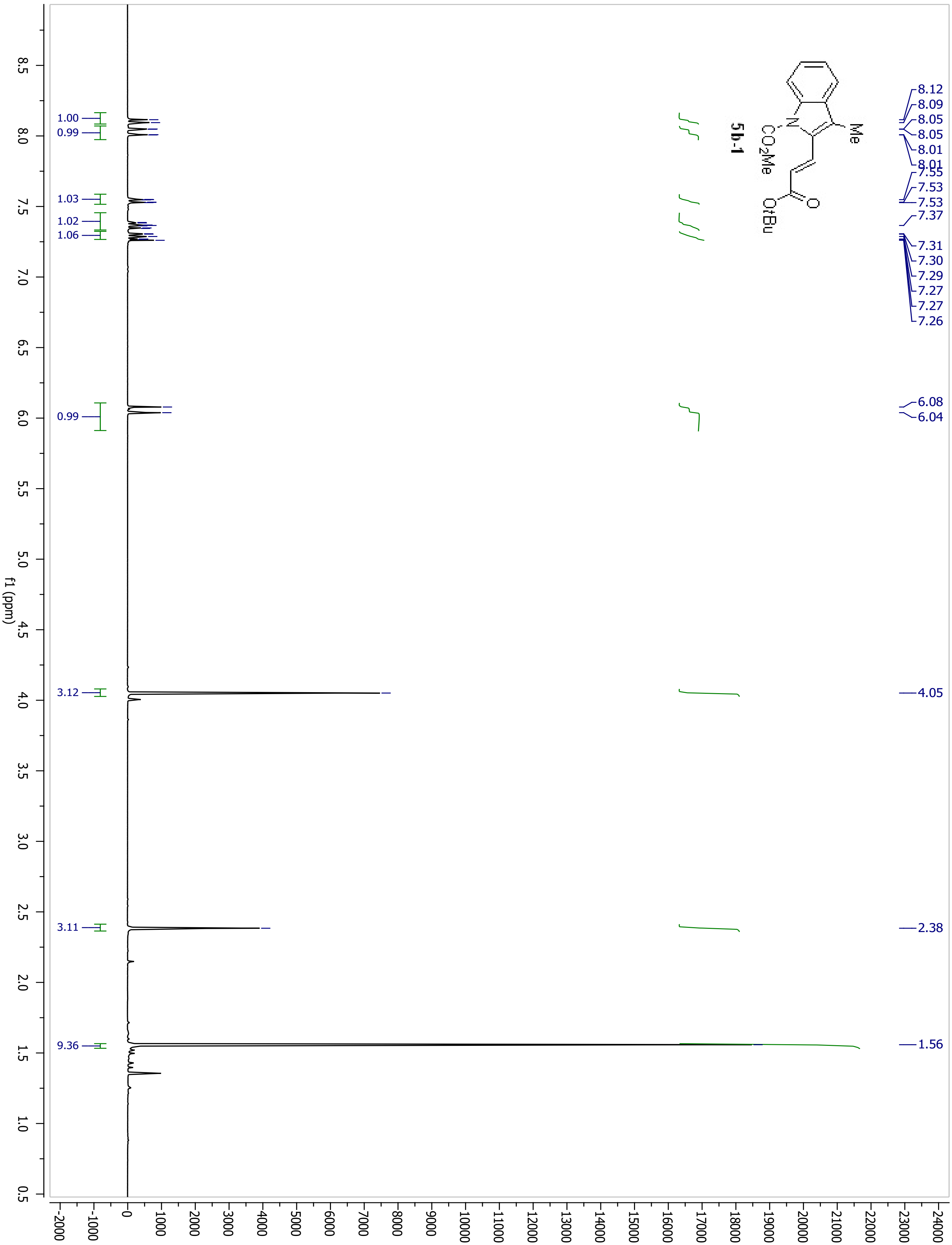
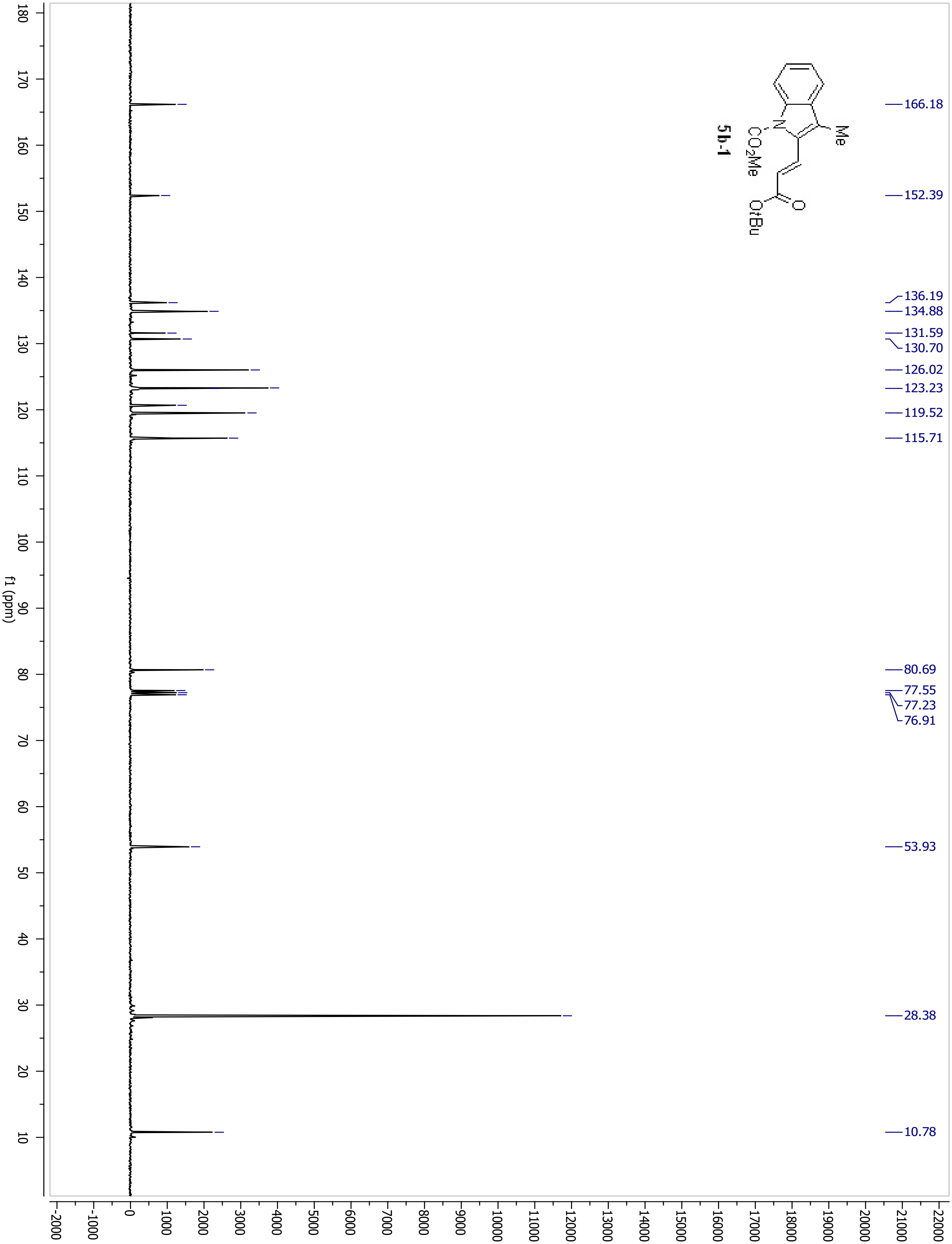
OEt
CO2Me
N
O
8.12
8.10
8.08
8.04
7.59
7.57
7.37
7.31
7.31
7.29
7.27
7.27
7.26
6.13
6.09
4.32
4.30
4.28
4.27
4.05
2.87
2.85
2.83
2.81
1.56
1.38
1.36
1.34
1.33
1.31
1.29
1.00
0.94
1.04
1.06
1.05
1.04
2.17
2.38
2.02
3.16
3.15
f1 (ppm)



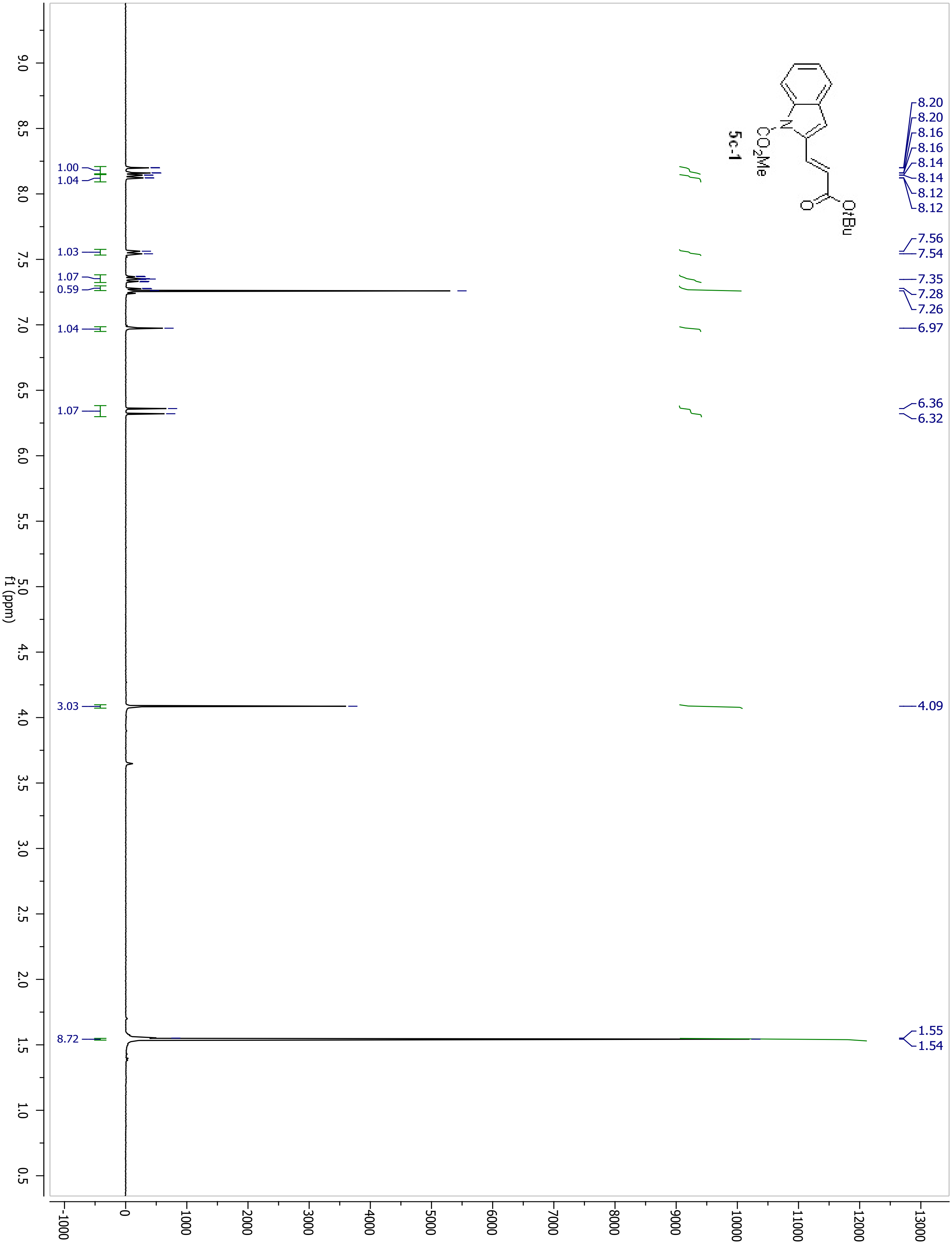
Et
N
CO_2Me
OEt
O
5a-1
166.92
152.55
136.54
135.87
131.00
129.89
126.16
123.43
119.73
115.92
77.55
77.23
76.91
60.84
54.09
18.31
15.21
14.56
f1 (ppm)



5b-1
Me
N
CO2Me
OtBu
O
8.12
8.09
8.05
8.05
8.01
8.01
7.55
7.53
7.53
7.37
7.31
7.30
7.29
7.27
7.27
7.26
6.08
6.04
4.05
2.38
1.56
1.00
0.99
1.03
1.02
1.06
0.99
3.12
3.11
9.36
f1 (ppm)



5b-1
Me
CO2Me
OtBu
O
N
166.18
152.39
136.19
134.88
131.59
130.70
126.02
123.23
119.52
115.71
80.69
77.55
77.23
76.91
53.93
28.38
10.78
f1 (ppm)


5c-1
CO2Me
N
OtBu
O
8.20
8.20
8.16
8.16
8.14
8.14
8.12
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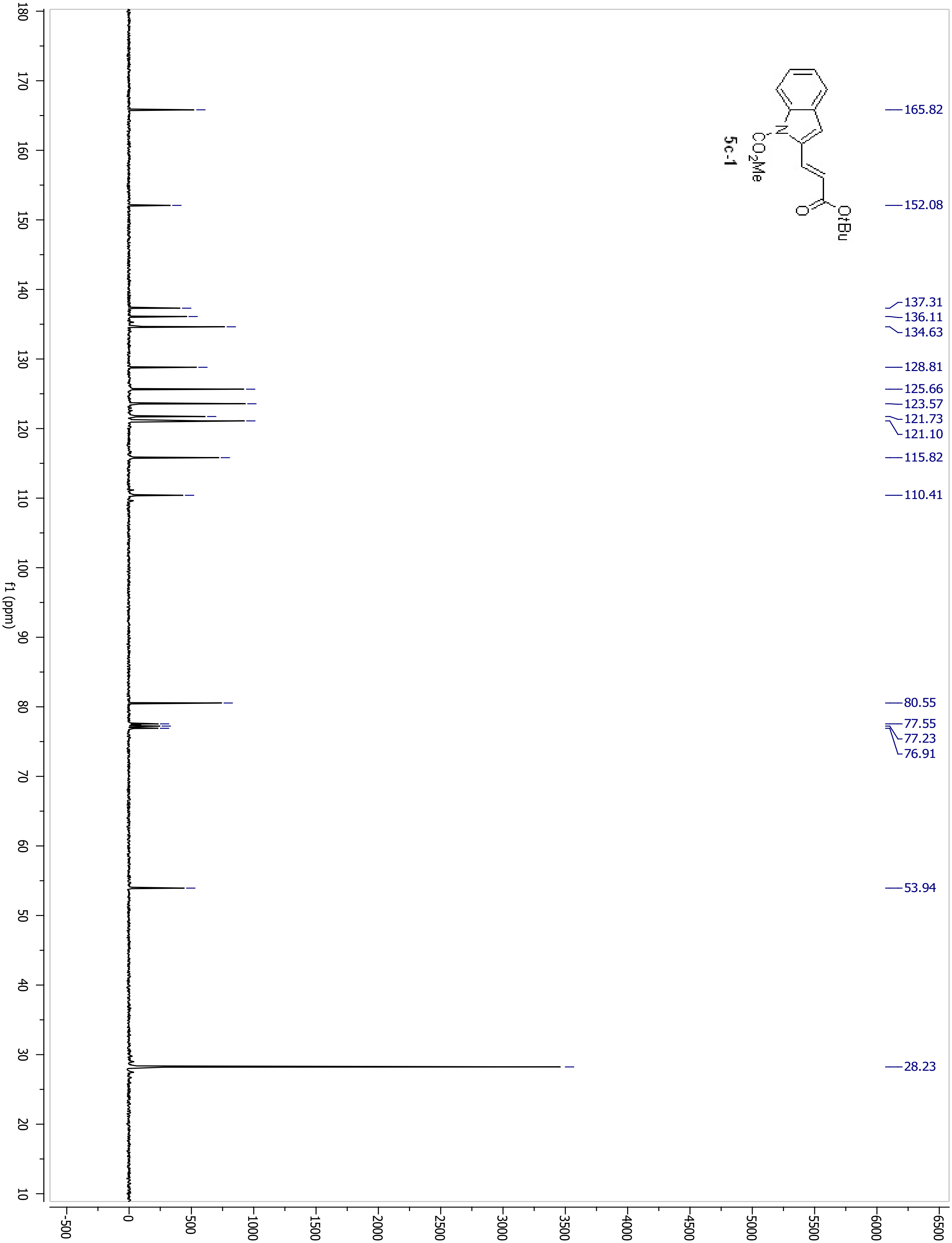
7.56
7.54
7.35
7.28
7.26
6.97
6.36
6.32
4.09
1.55
1.54
1.00
1.04
1.03
1.07
0.59
1.04
1.07
3.03
8.72
f1 (ppm)


5c-1
CO2Me
OtBu
165.82
152.08
137.31
136.11
134.63
128.81
125.66
123.57
121.73
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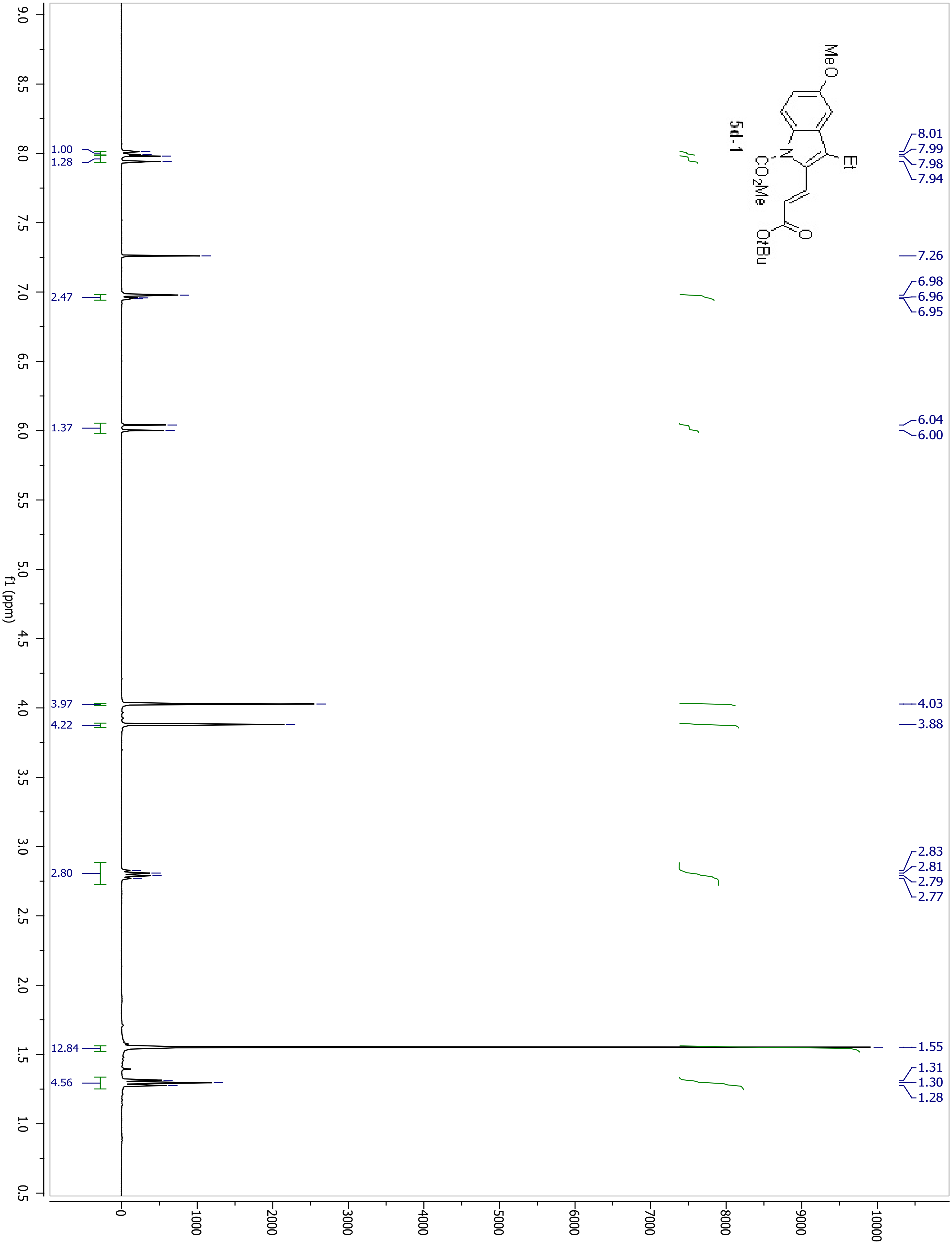
53.94
28.23
f1 (ppm)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MeO
Et
CO_2Me
OtBu
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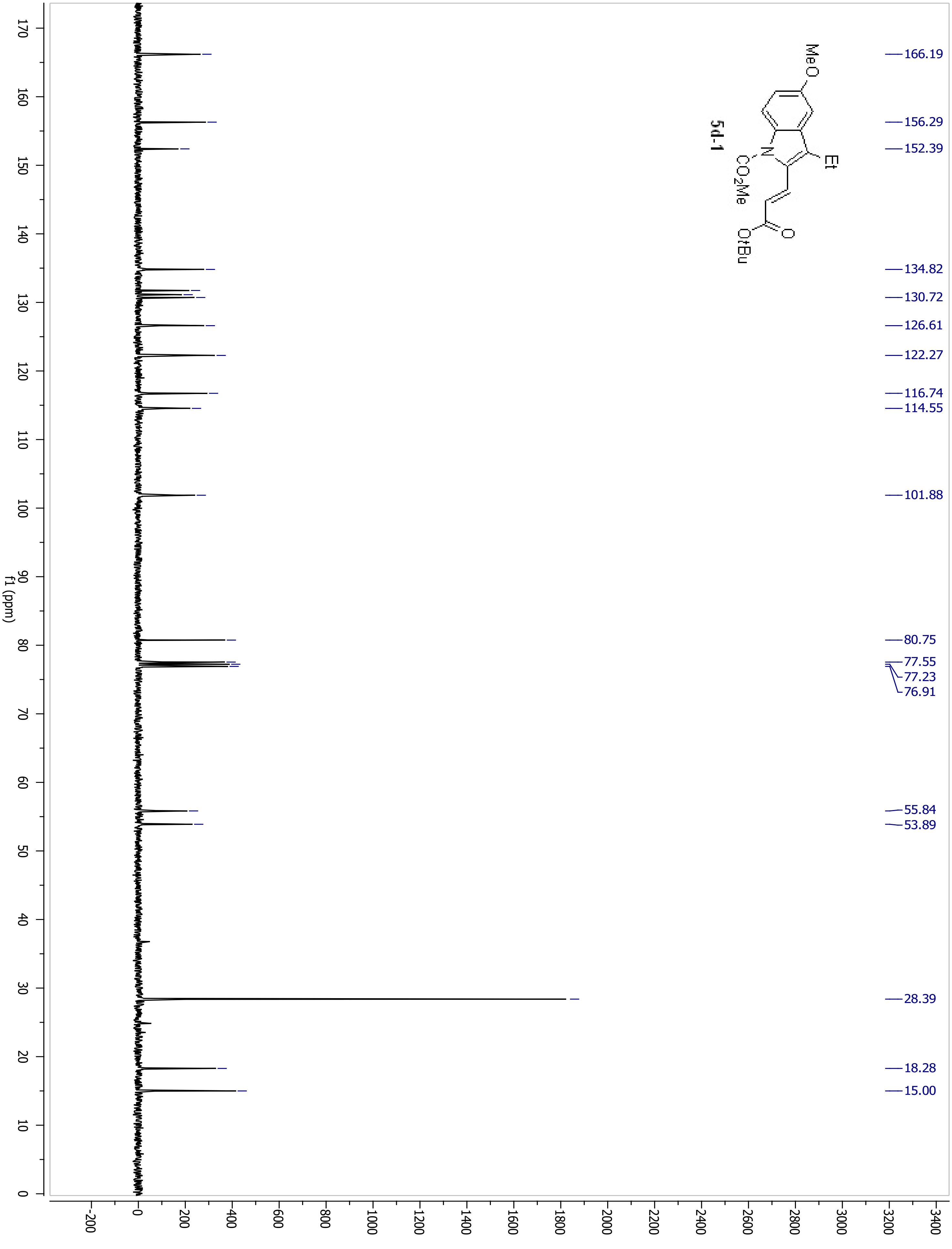
7.99
7.98
7.94
7.26
6.98
6.96
6.95
6.04
6.00
4.03
3.88
2.83
2.81
2.79
2.77
1.55
1.31
1.30
1.28
1.00
1.28
2.47
1.37
3.97
4.22
2.80
12.84
4.56
f1 (ppm)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156.29
152.39
134.82
130.72
126.61
122.27
116.74
114.55
101.88
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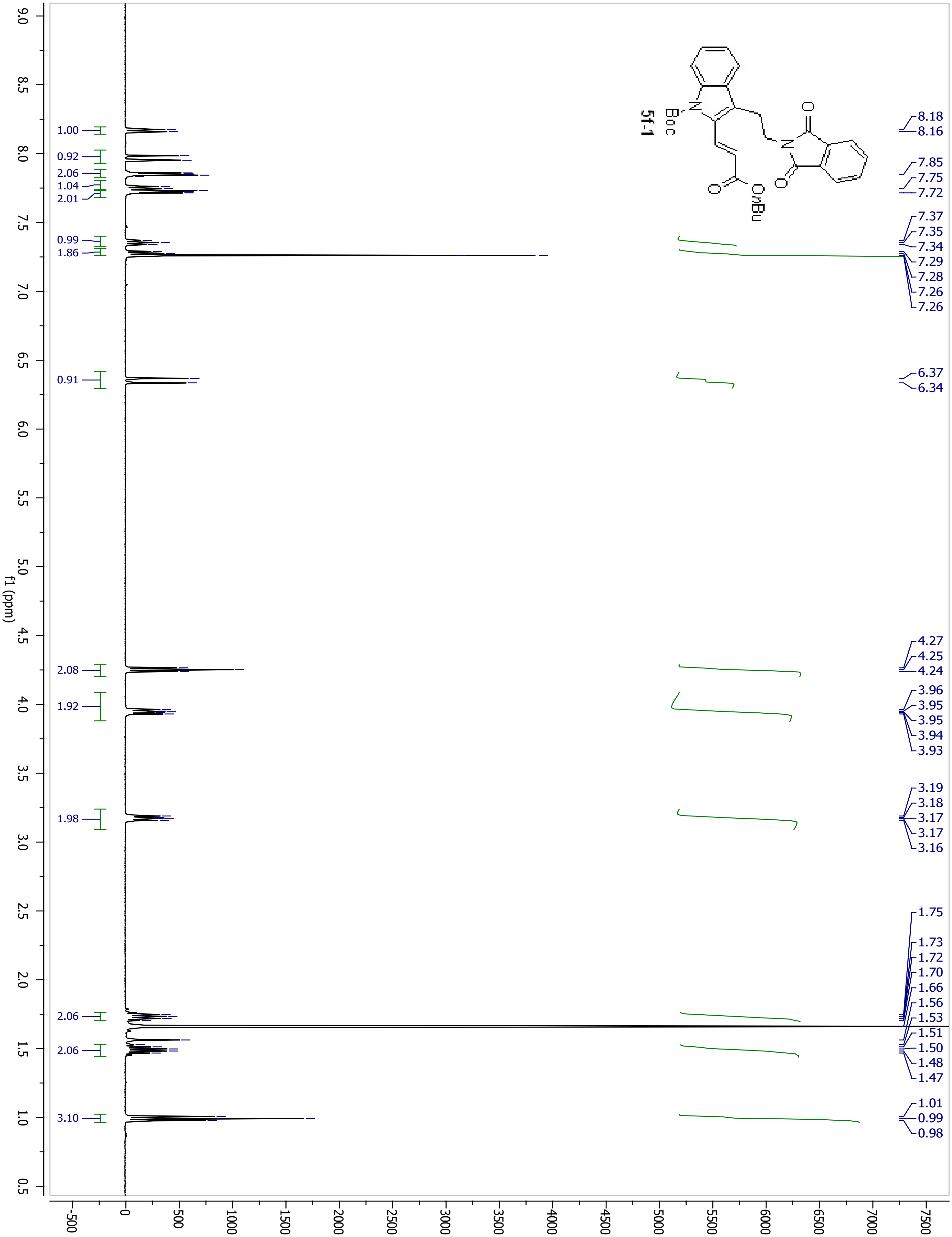
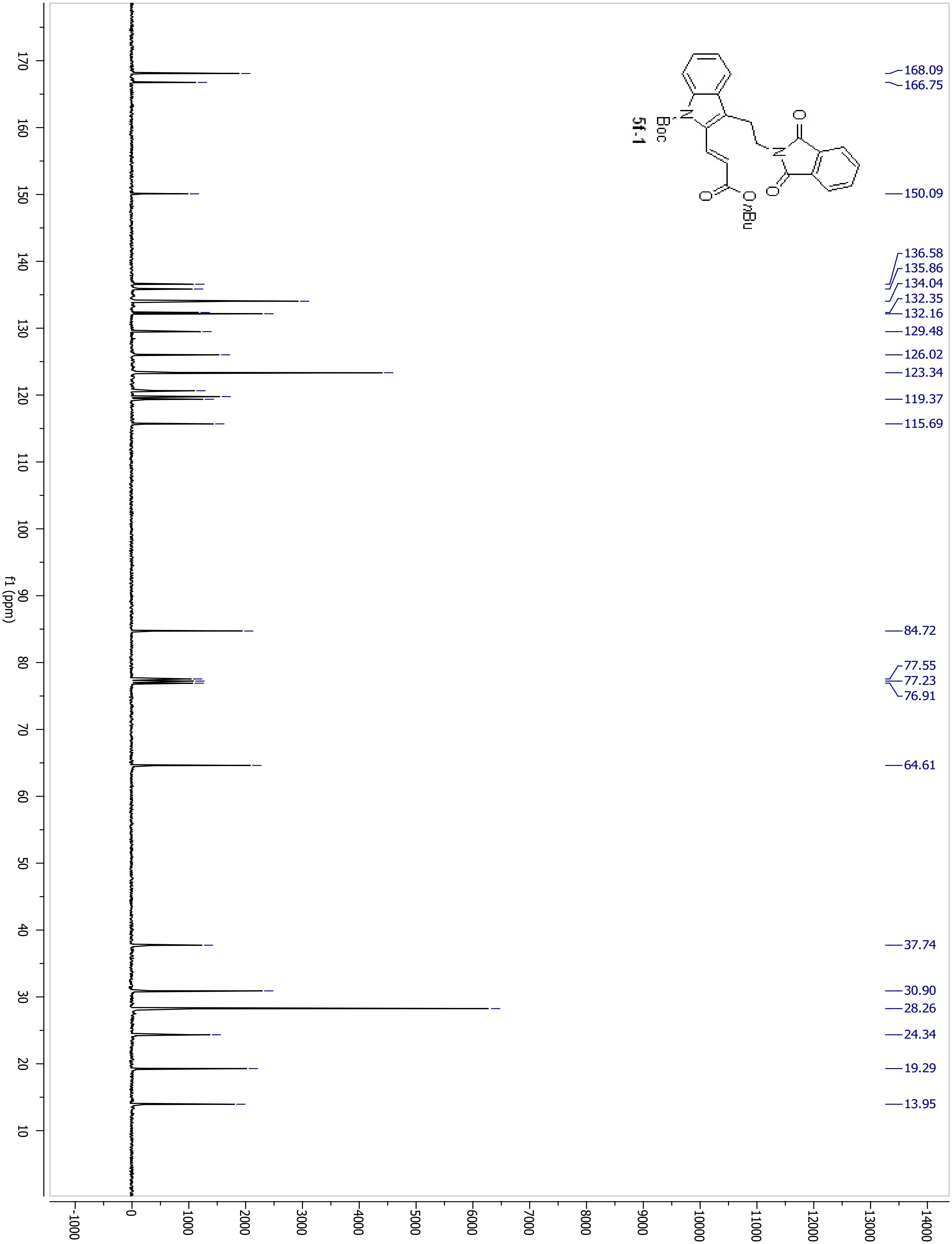
18.28
15.00
f1 (ppm)


5f-1
Boc
OnBu
f1 (ppm)
8.18
8.16
7.85
7.75
7.72
7.37
7.35
7.34
7.29
7.28
7.26
7.26
6.37
6.34
4.27
4.25
4.24
3.96
3.95
3.95
3.94
3.93
3.19
3.18
3.17
3.17
3.16
1.75
1.73
1.72
1.70
1.66
1.56
1.53
1.51
1.50
1.48
1.47
1.01
0.99
0.98
1.00
0.92
2.06
1.04
2.01
0.99
1.86
0.91
2.08
1.92
1.98
2.06
2.06
3.10


168.09
166.75
150.09
136.58
135.86
134.04
132.35
132.16
129.48
126.02
123.34
119.37
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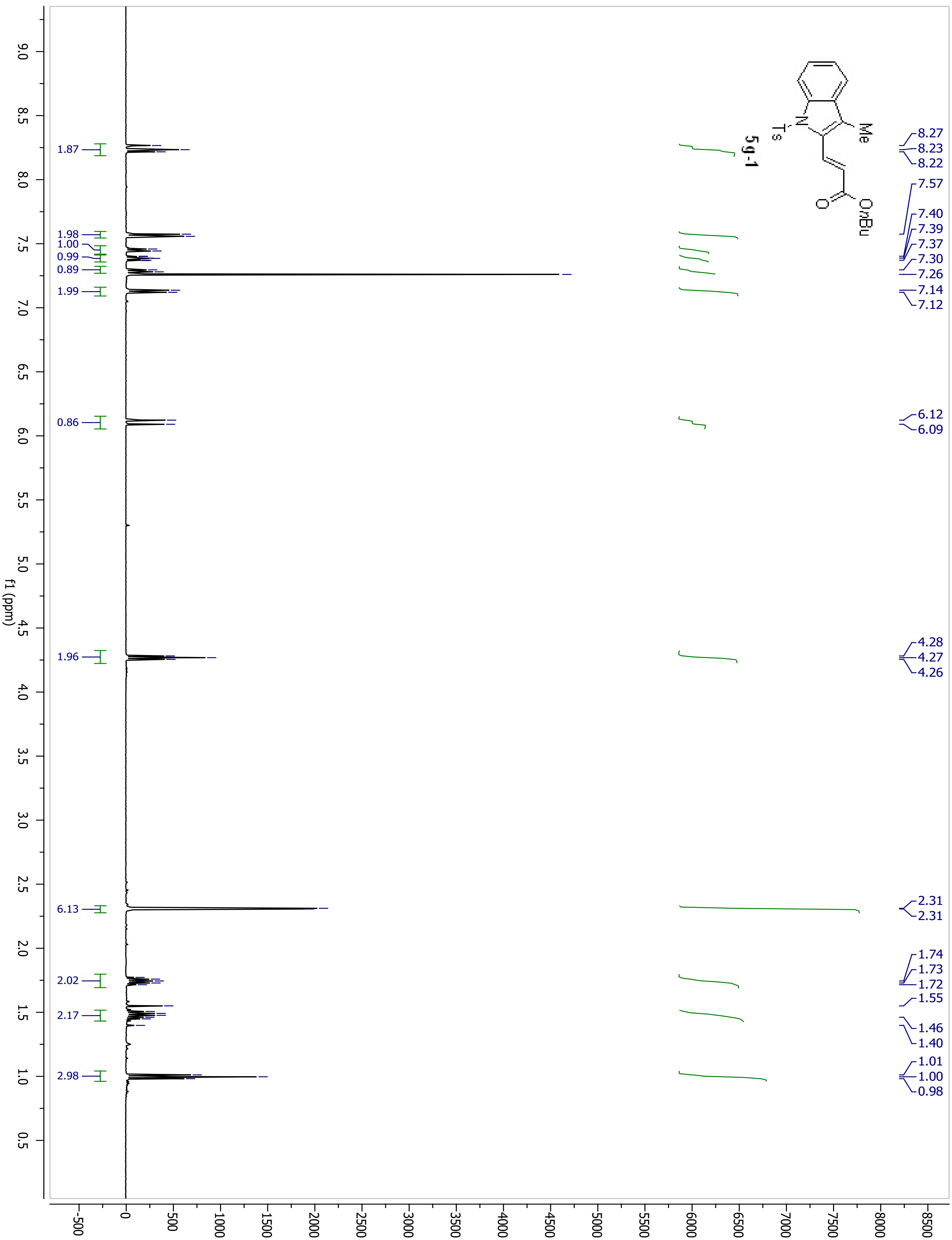
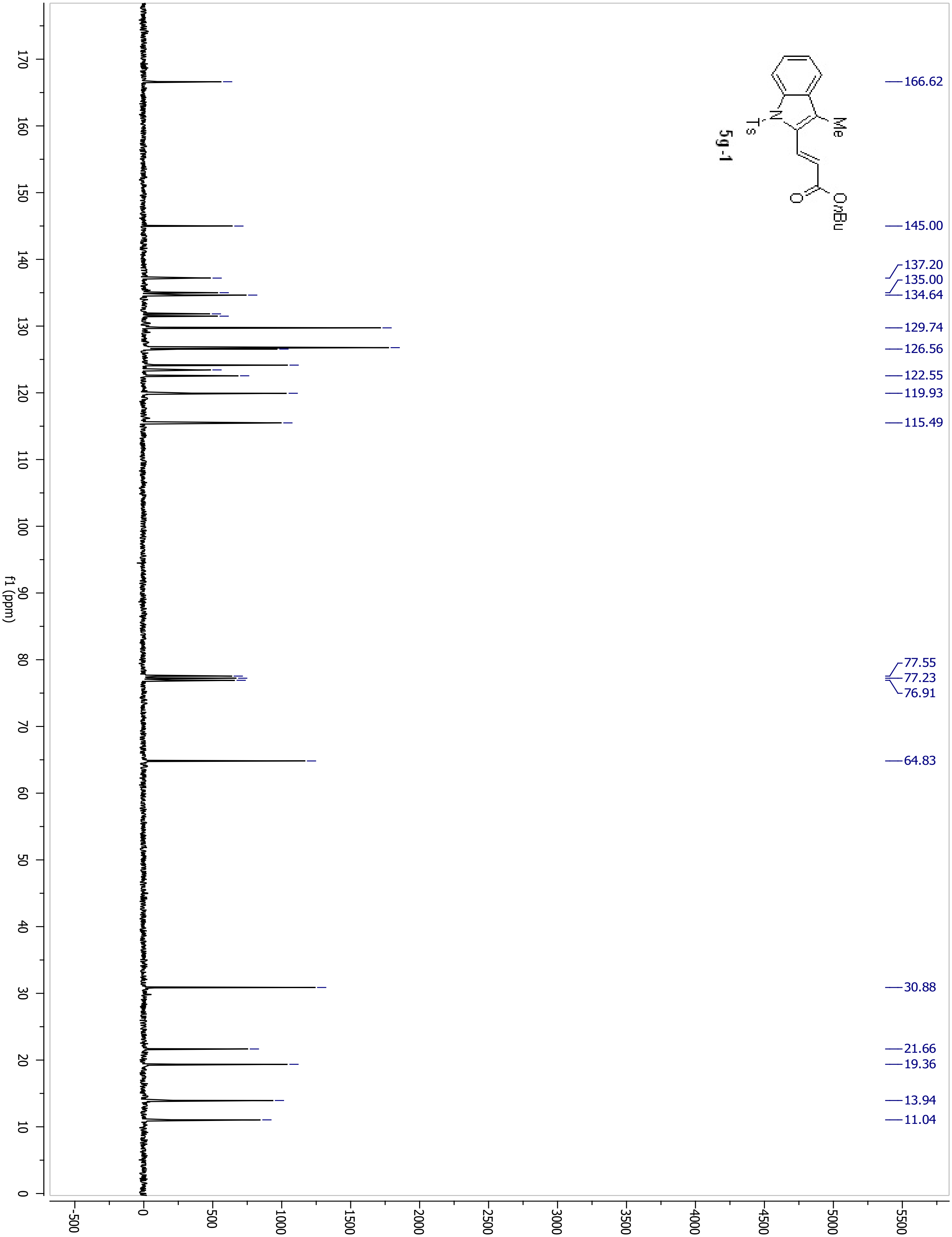
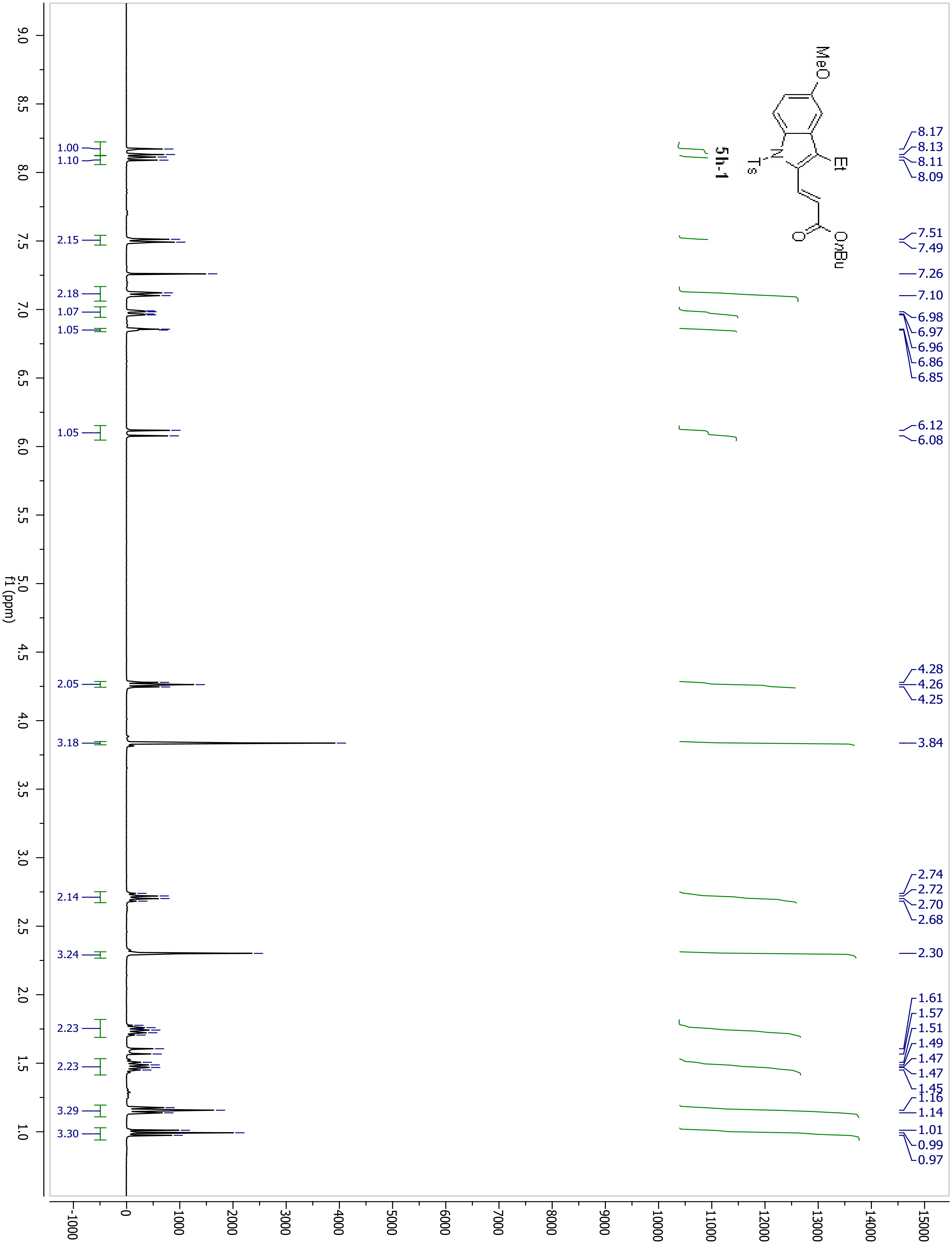
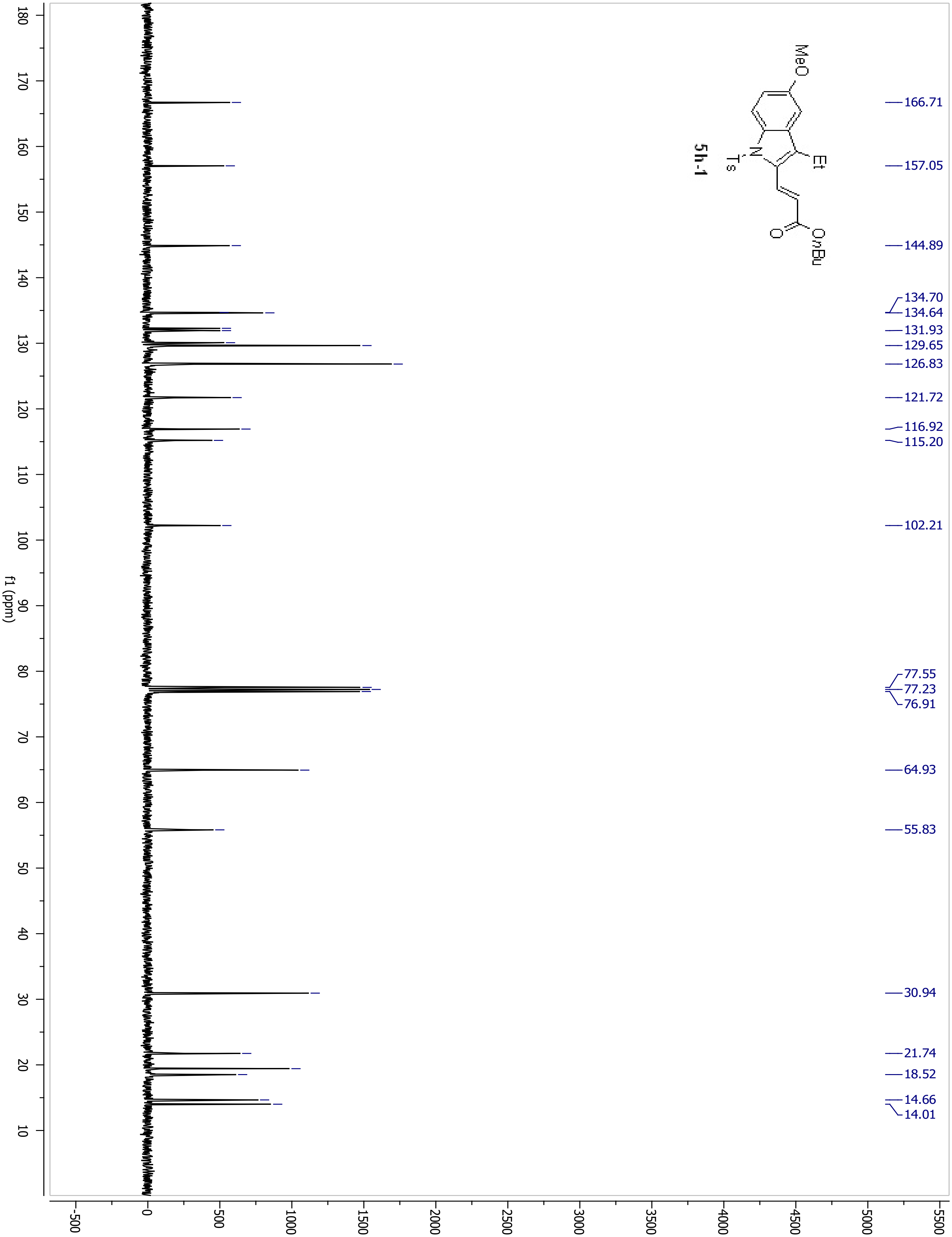
84.72
77.55
77.23
76.91
64.61
37.74
30.90
28.26
24.34
19.29
13.95
5f-1
Boc
OnBu
f1 (ppm)

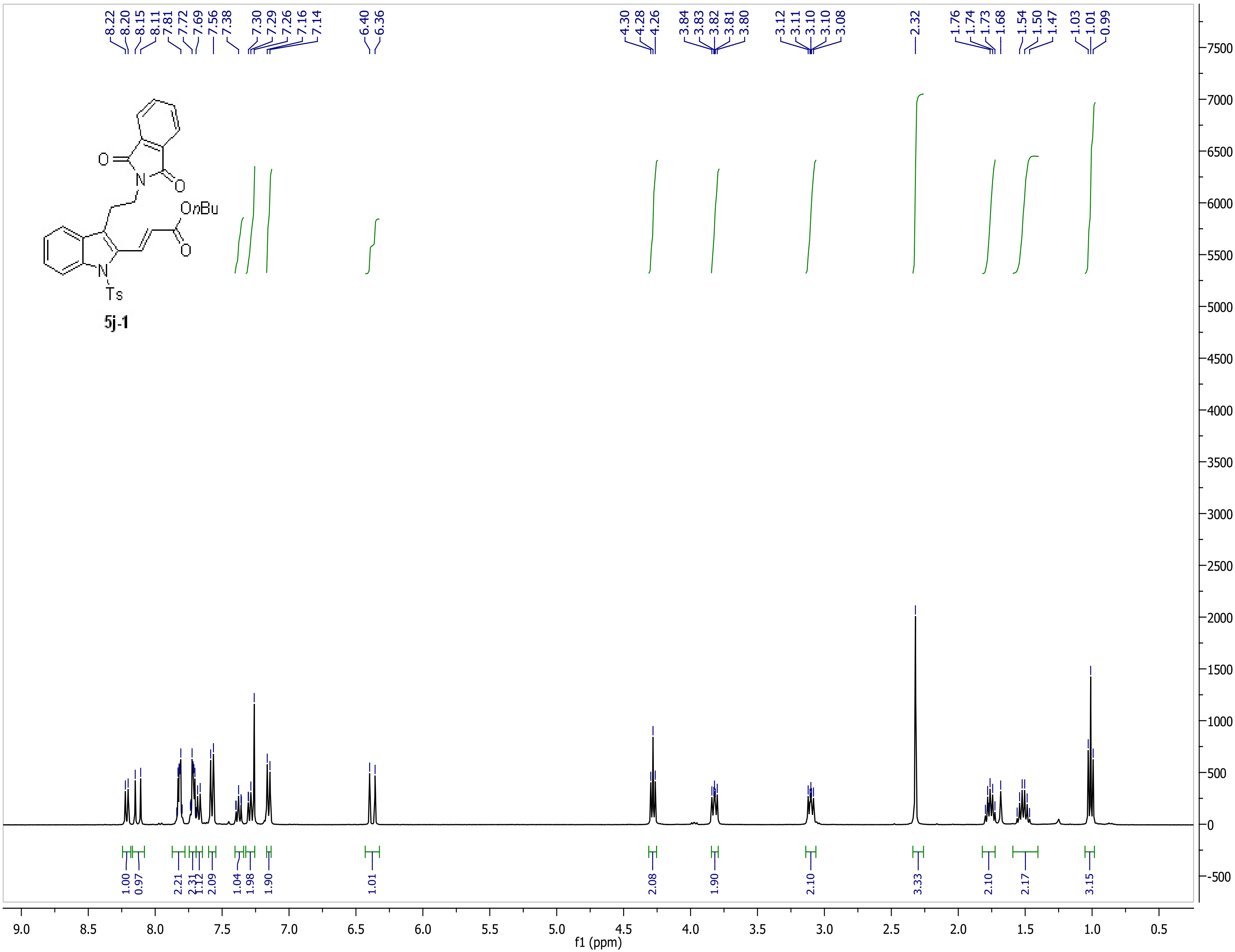

5g-1
Me
OnBu
O
N
Ts
f1 (ppm)


5g-1
Me
N
Ts
O
OnBu
166.62
145.00
137.20
135.00
134.64
129.74
126.56
122.55
119.93
115.49
77.55
77.23
76.91
64.83
30.88
21.66
19.36
13.94
11.04
f1 (ppm)

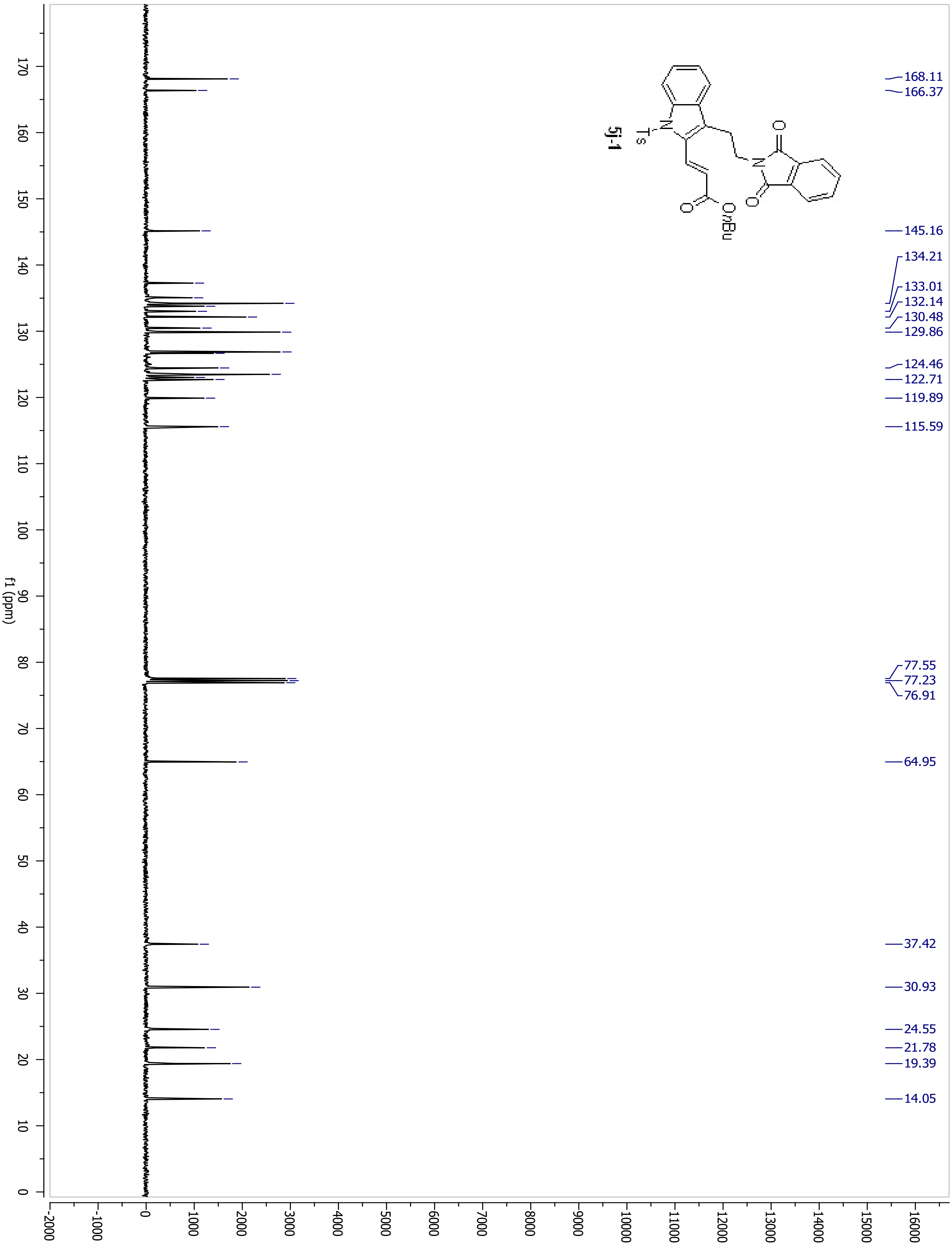

MeO
Et
N
Ts
OnBu
O
5h-1
8.17
8.13
8.11
8.09
7.51
7.49
7.26
7.10
6.98
6.97
6.96
6.86
6.85
6.12
6.08
4.28
4.26
4.25
3.84
2.74
2.72
2.70
2.68
2.30
1.61
1.57
1.51
1.49
1.47
1.47
1.45
1.16
1.14
1.01
0.99
0.97
1.00
1.10
2.15
2.18
1.07
1.05
1.05
2.05
3.18
2.14
3.24
2.23
2.23
3.29
3.30
f1 (ppm)

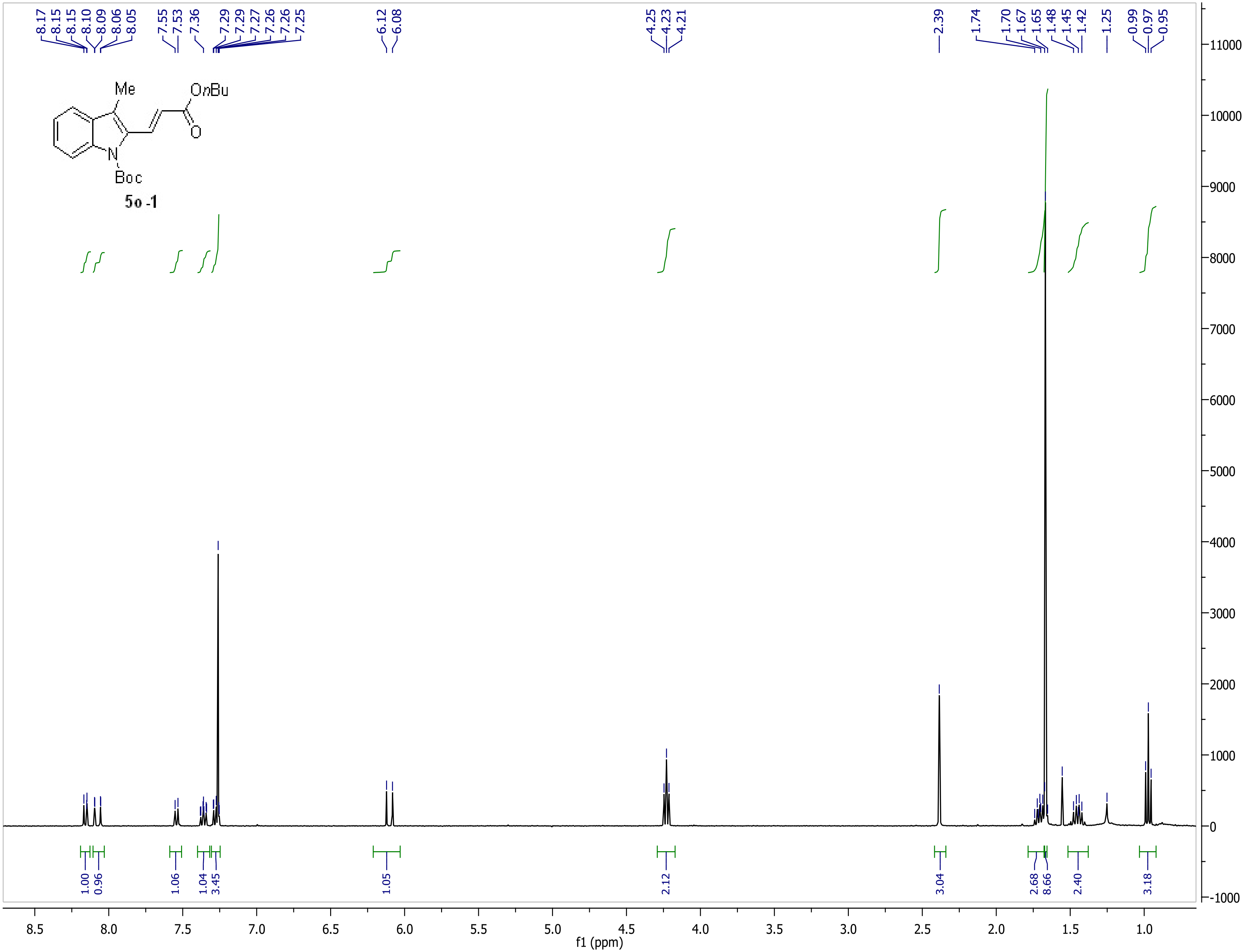


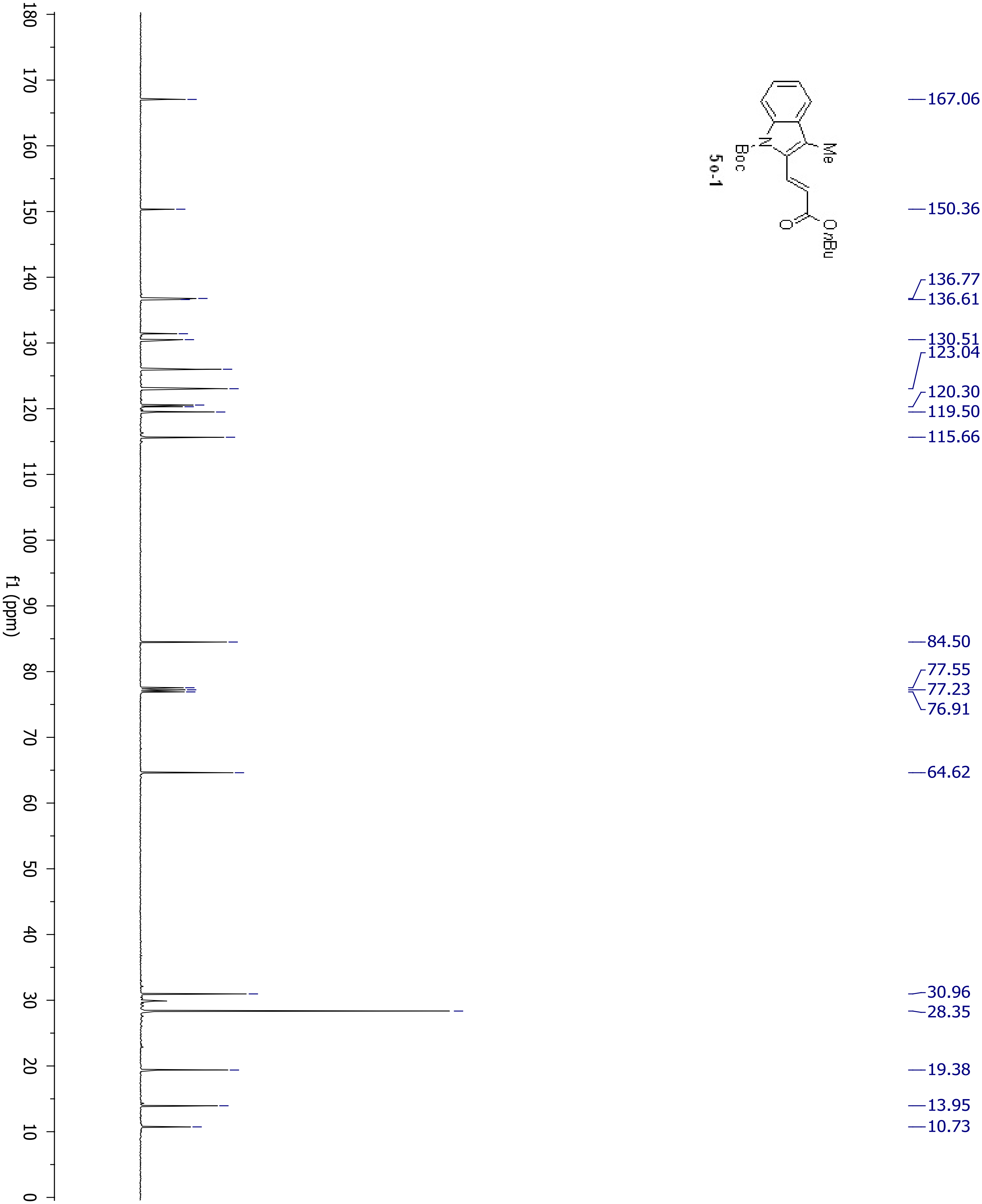
5h-1
MeO
Et
N
Ts
O
OnBu
166.71
157.05
144.89
134.70
134.64
131.93
129.65
126.83
121.72
116.92
115.20
102.21
77.55
77.23
76.91
64.93
55.83
30.94
21.74
18.52
14.66
14.01
f1 (ppm)



5j-1
OnBu
Ts
8.22 8.20 8.15 8.11 7.81 7.72 7.69 7.56 7.38 7.30 7.29 7.26 7.16 7.14 6.40 6.36 4.30 4.28 4.26 3.84 3.83 3.82 3.81 3.80 3.12 3.11 3.10 3.10 3.08 2.32 1.76 1.74 1.73 1.68 1.54 1.50 1.47 1.03 1.01 0.99
1.00 0.97 2.21 2.31 1.12 2.09 1.04 1.98 1.90 1.01 2.08 1.90 2.10 3.33 2.10 2.17 3.15
f1 (ppm)


5j-1
Ts
N
O
OnBu
168.11
166.37
145.16
134.21
133.01
132.14
130.48
129.86
124.46
122.71
119.89
115.59
77.55
77.23
76.91
64.95
37.42
30.93
24.55
21.78
19.39
14.05
f1 (ppm)


8.17 8.15 8.15 8.10 8.09 8.06 8.05
7.55 7.53 7.36
7.29 7.29 7.27 7.26 7.26 7.25
6.12 6.08
4.25 4.23 4.21
2.39
1.74 1.70 1.67 1.65 1.48 1.45 1.42
1.25
0.99 0.97 0.95
Me
OnBu
O
N
Boc
5o-1
1.00 0.96 1.06 1.04 3.45 1.05 2.12 3.04 2.68 8.66 2.40 3.18
f1 (ppm)


5o-1
Me
Boc
N
O
OnBu
167.06
150.36
136.77
136.61
130.51
123.04
120.30
119.50
115.66
84.50
77.55
77.23
76.91
64.62
30.96
28.35
19.38
13.95
10.73
f1 (ppm)
180
170
160
150
140
130
120
110
100
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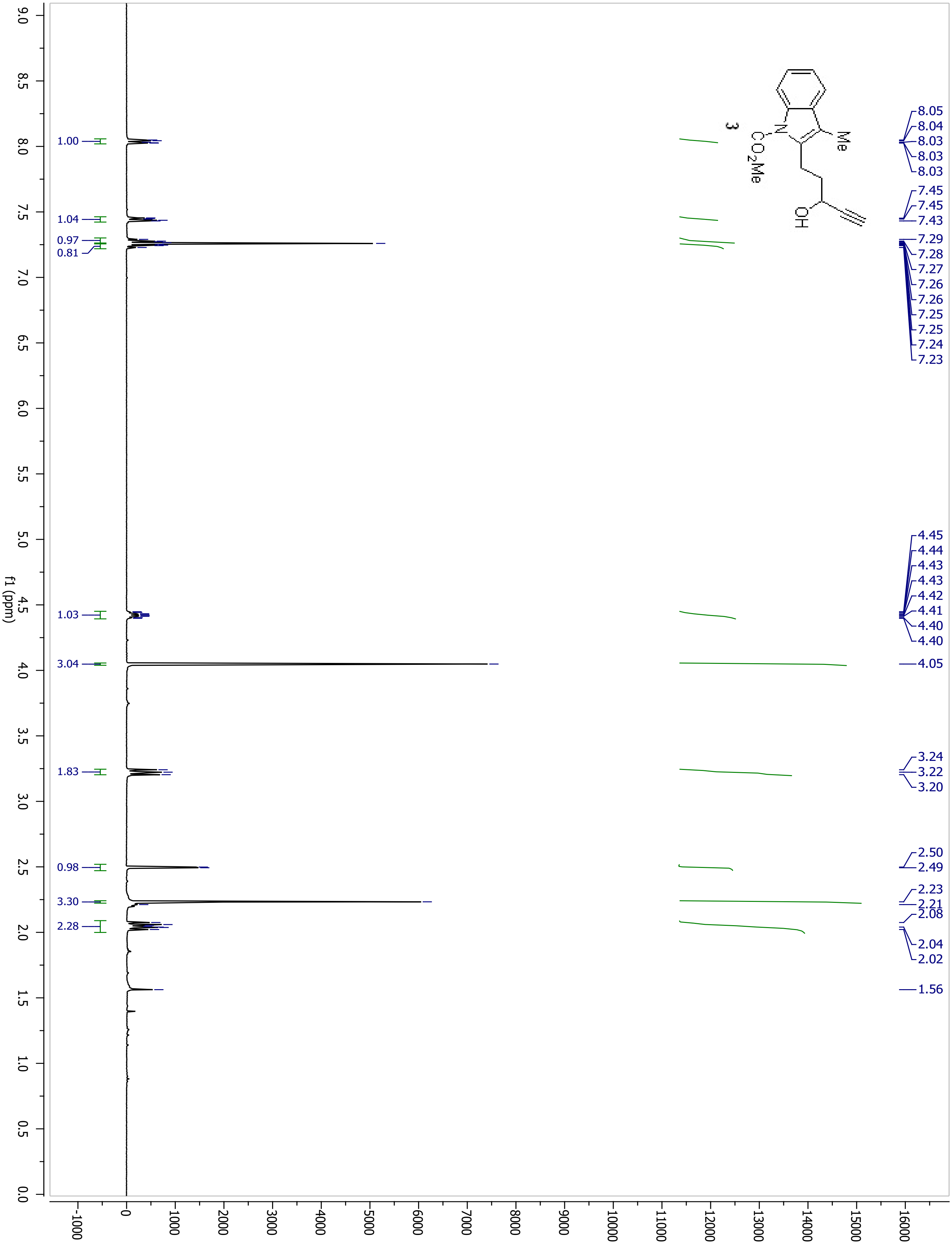
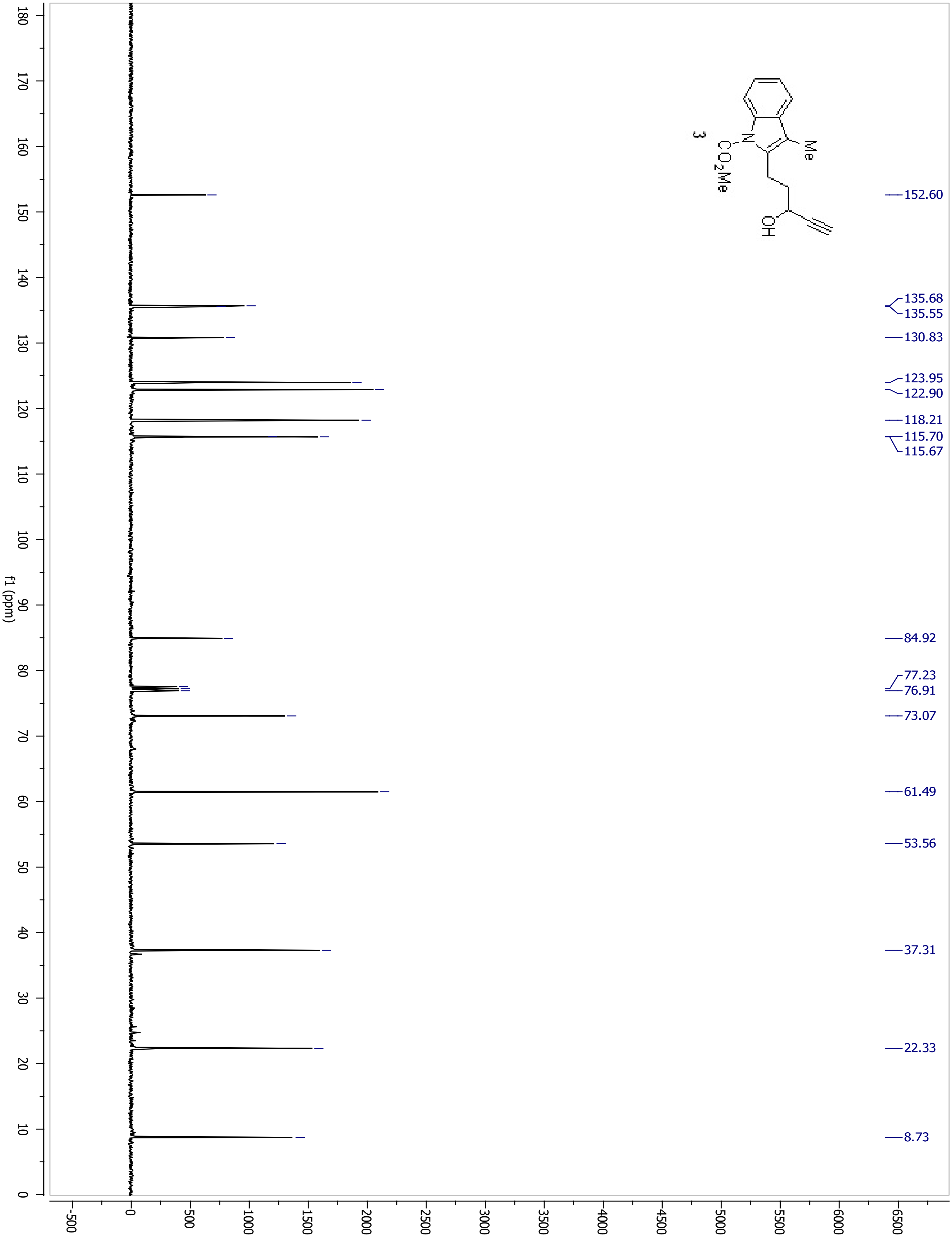
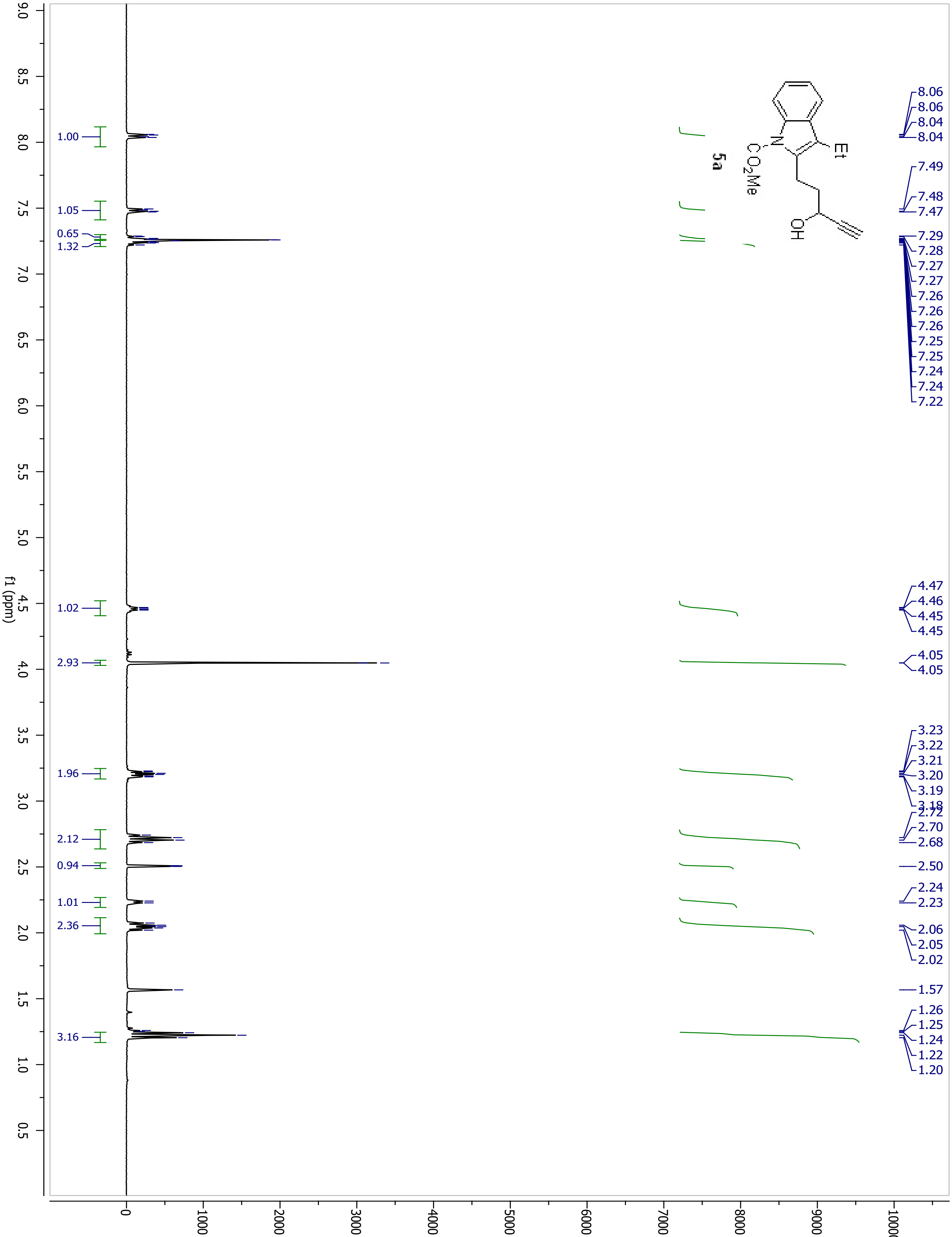
40
30
20
10
0

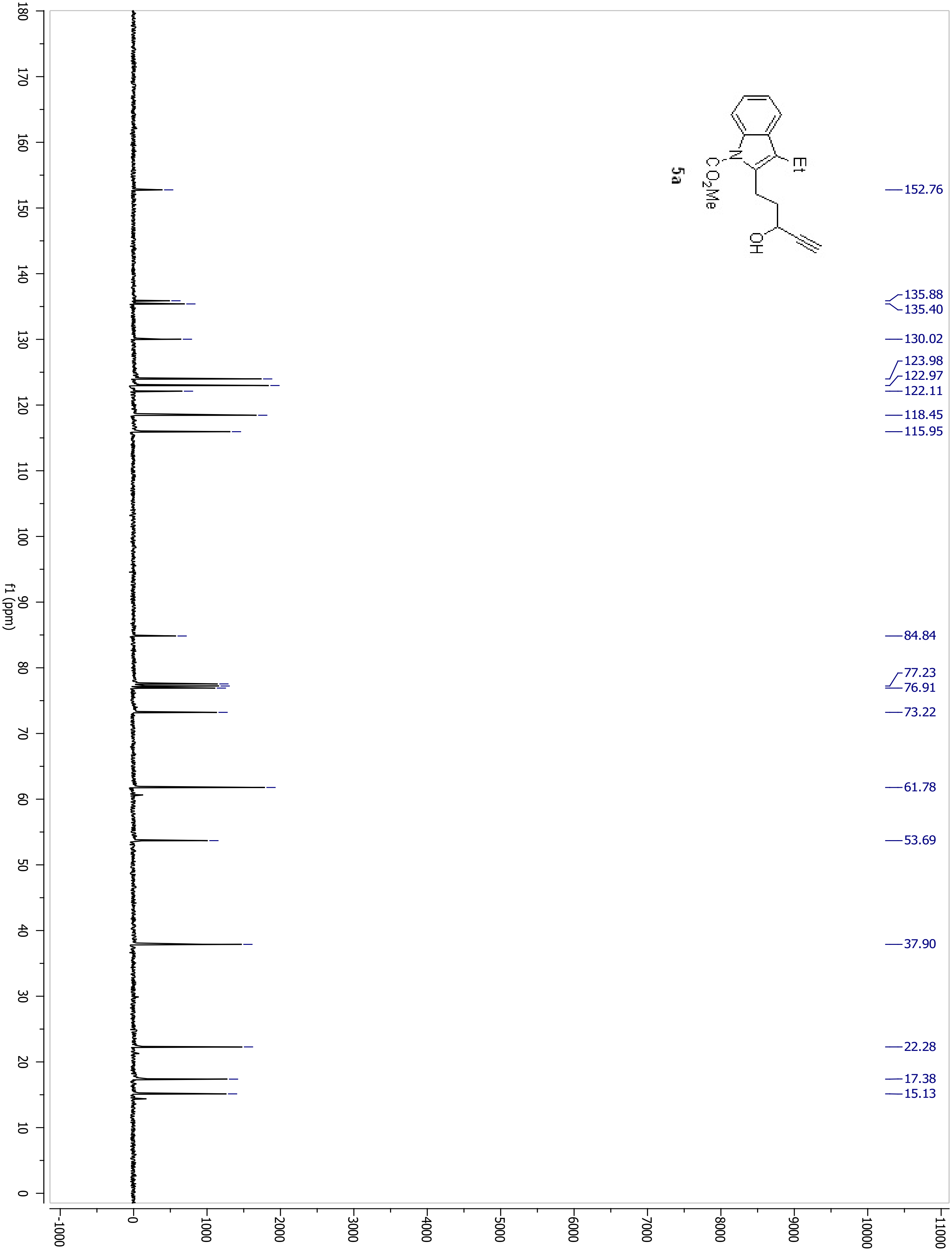


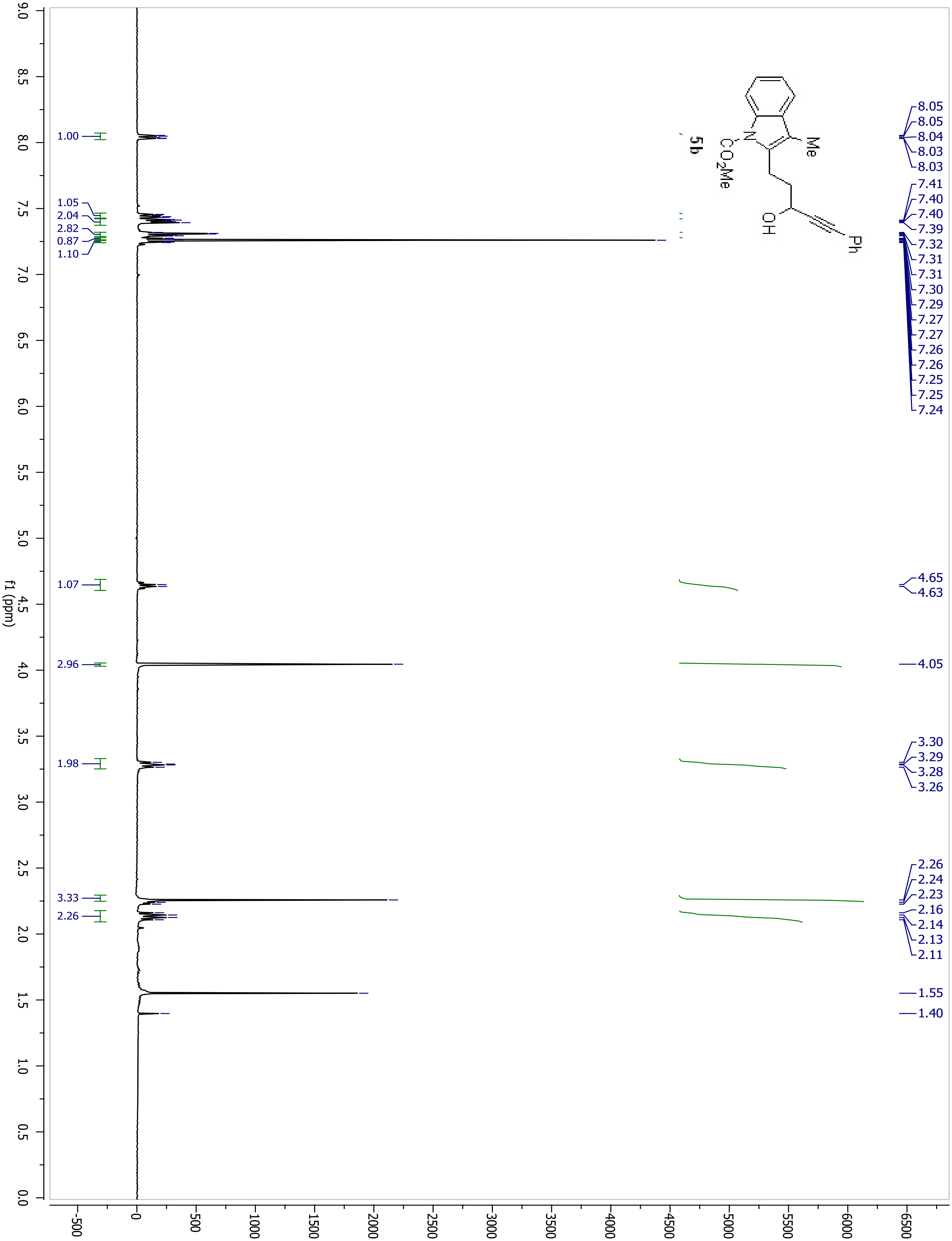
3
Me
N
CO_2Me
OH
f1 (ppm)

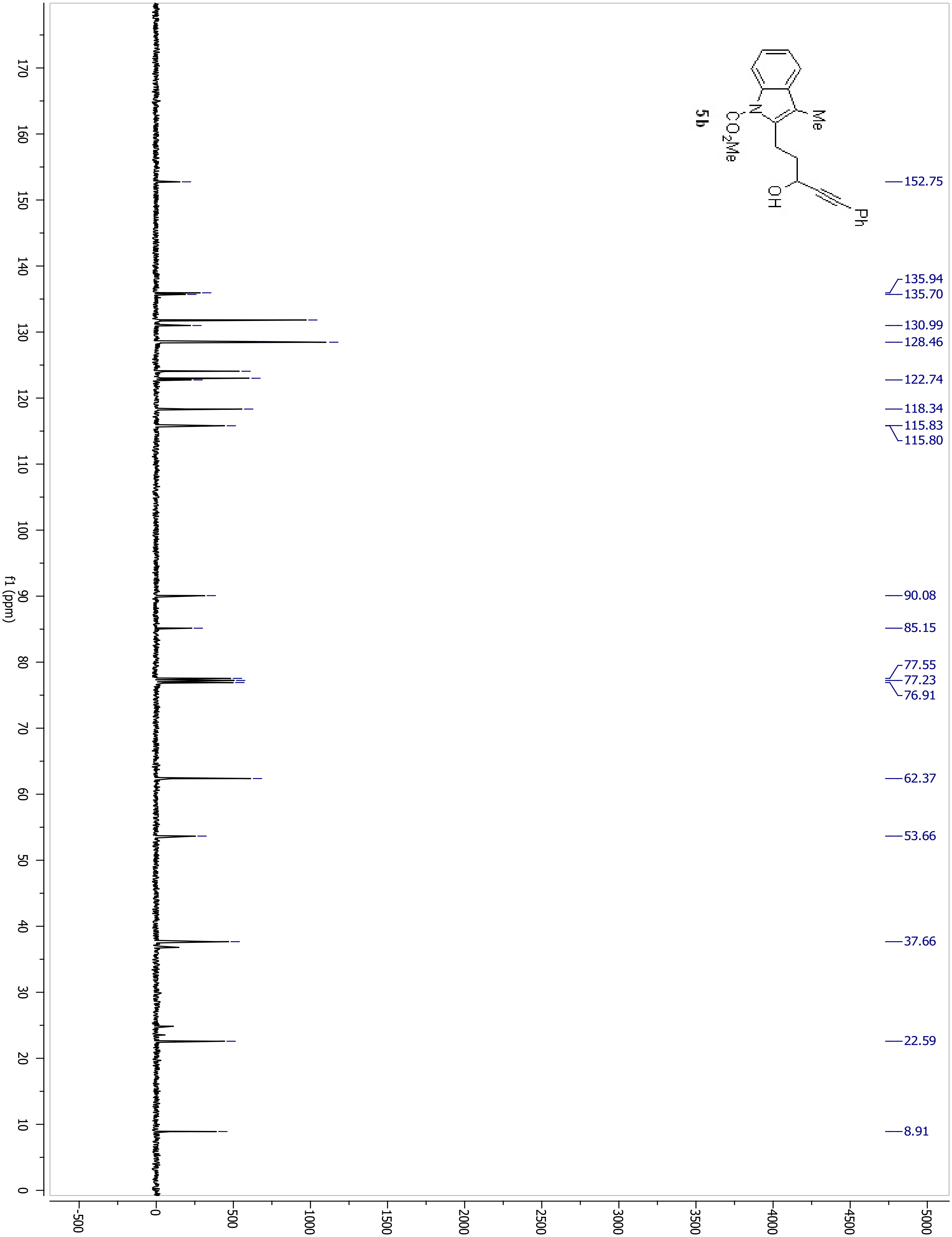


3
Me
N
CO2Me
OH
152.60
135.68
135.55
130.83
123.95
122.90
118.21
115.70
115.67
84.92
77.23
76.91
73.07
61.49
53.56
37.31
22.33
8.73
f1 (ppm)

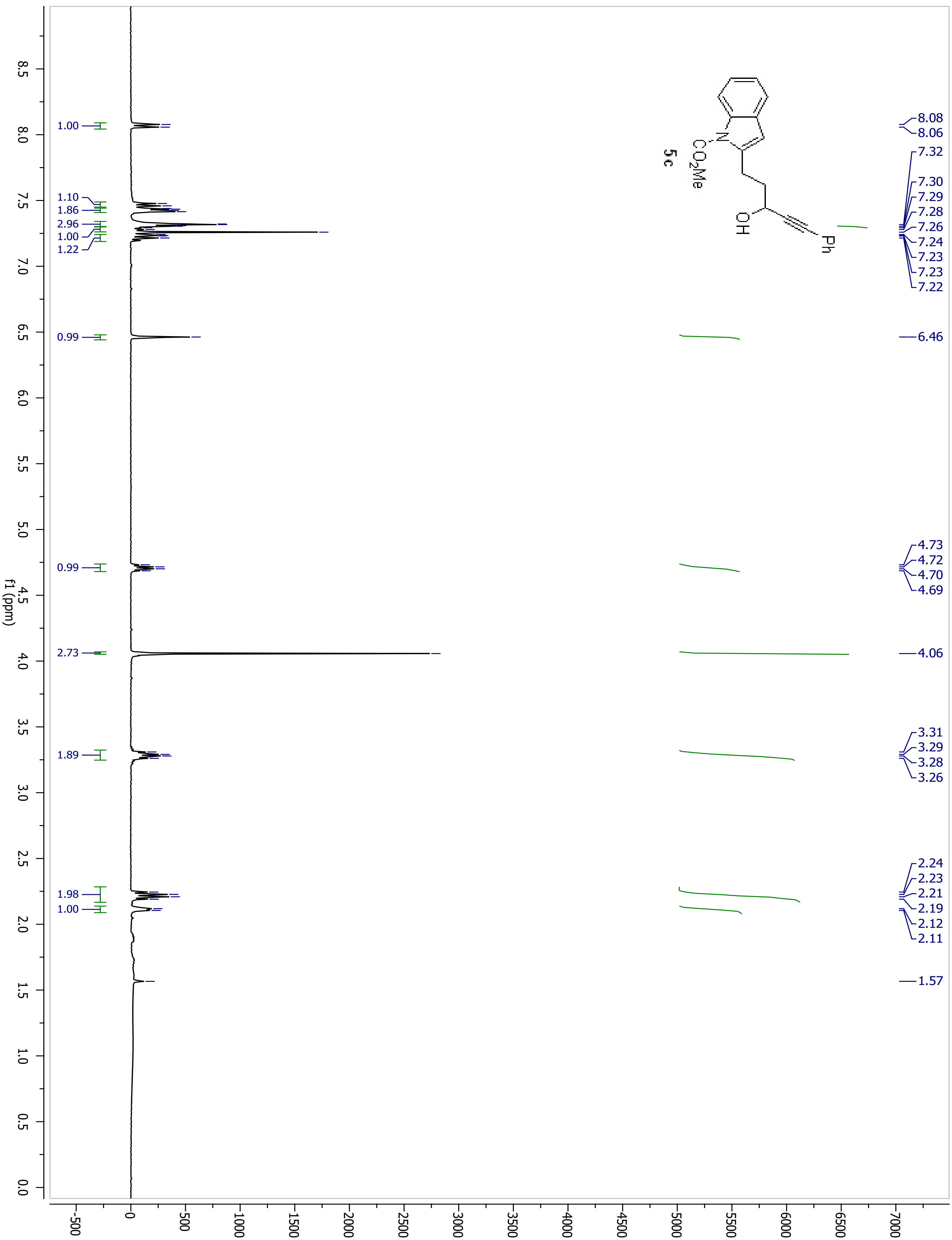

5a
f1 (ppm)

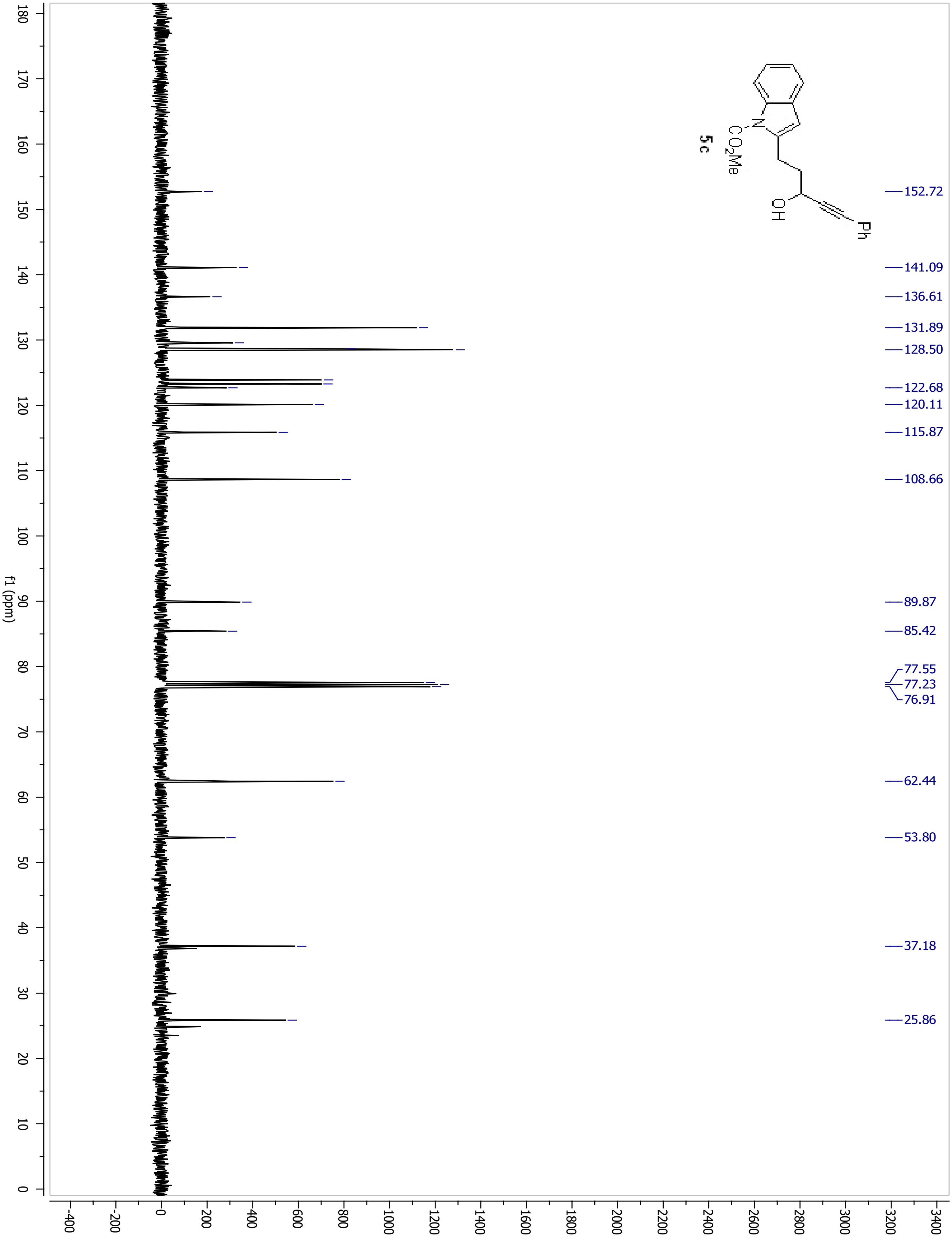

Et
N
CO2Me
OH
5a
152.76
135.88
135.40
130.02
123.98
122.97
122.11
118.45
115.95
84.84
77.23
76.91
73.22
61.78
53.69
37.90
22.28
17.38
15.13
f1 (ppm)


5b
Me
CO2Me
OH
Ph
f1 (ppm)
8.05
8.05
8.04
8.03
8.03
7.41
7.40
7.40
7.39
7.32
7.31
7.31
7.30
7.29
7.27
7.27
7.26
7.26
7.25
7.25
7.24
4.65
4.63
4.05
3.30
3.29
3.28
3.26
2.26
2.24
2.23
2.16
2.14
2.13
2.11
1.55
1.40
1.00
1.05
2.04
2.82
0.87
1.10
1.07
2.96
1.98
3.33
2.26



5b
Me
N
CO2Me
OH
Ph
152.75
135.94
135.70
130.99
128.46
122.74
118.34
115.83
115.80
90.08
85.15
77.55
77.23
76.91
62.37
53.66
37.66
22.59
8.91
f1 (ppm)


5c
CO2Me
OH
Ph
f1 (ppm)
8.08
8.06
7.32
7.30
7.29
7.28
7.26
7.24
7.23
7.23
7.22
6.46
4.73
4.72
4.70
4.69
4.06
3.31
3.29
3.28
3.26
2.24
2.23
2.21
2.19
2.12
2.11
1.57
1.00
1.10
1.86
2.96
1.00
1.22
0.99
0.99
2.73
1.89
1.98
1.00


5c
152.72
141.09
136.61
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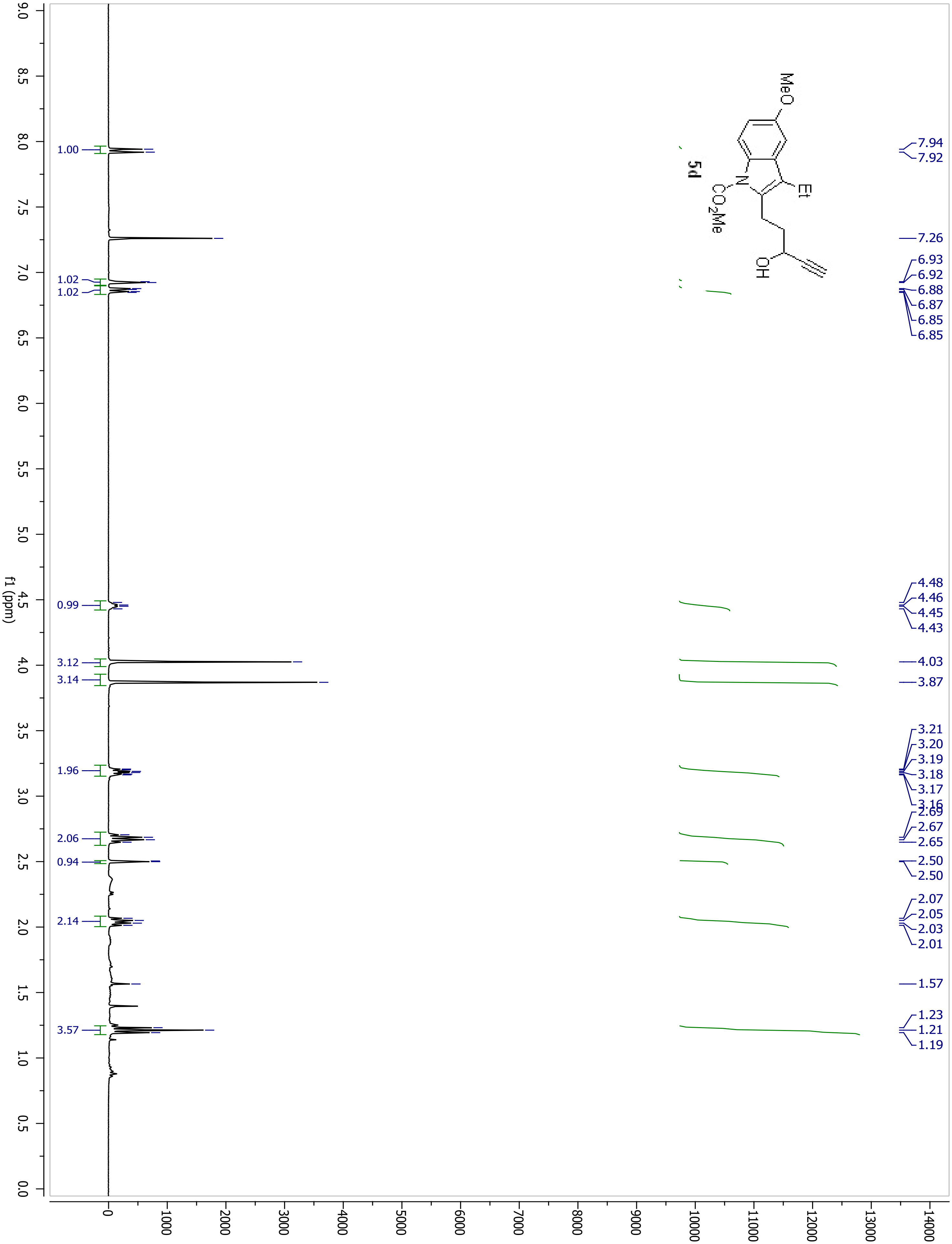
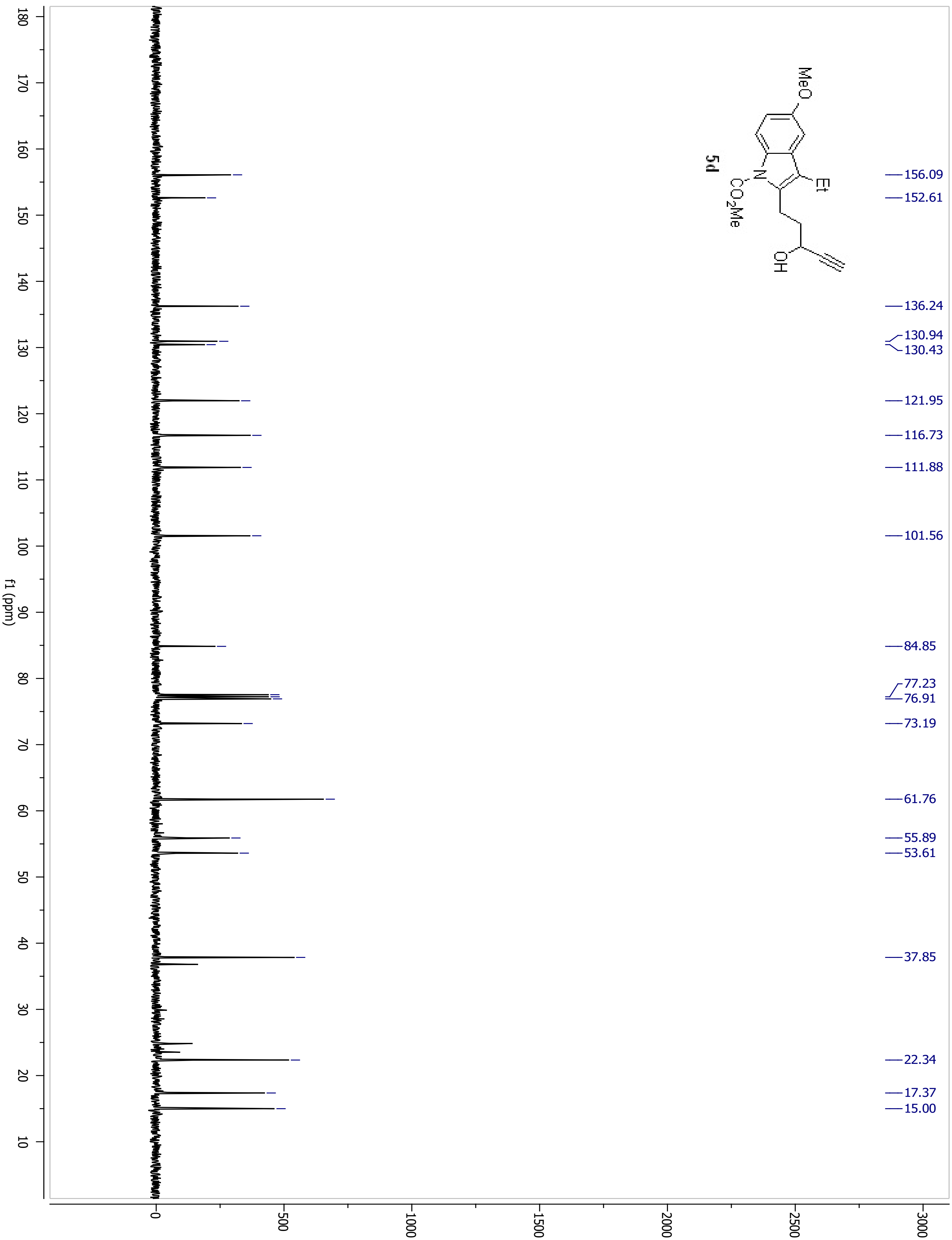
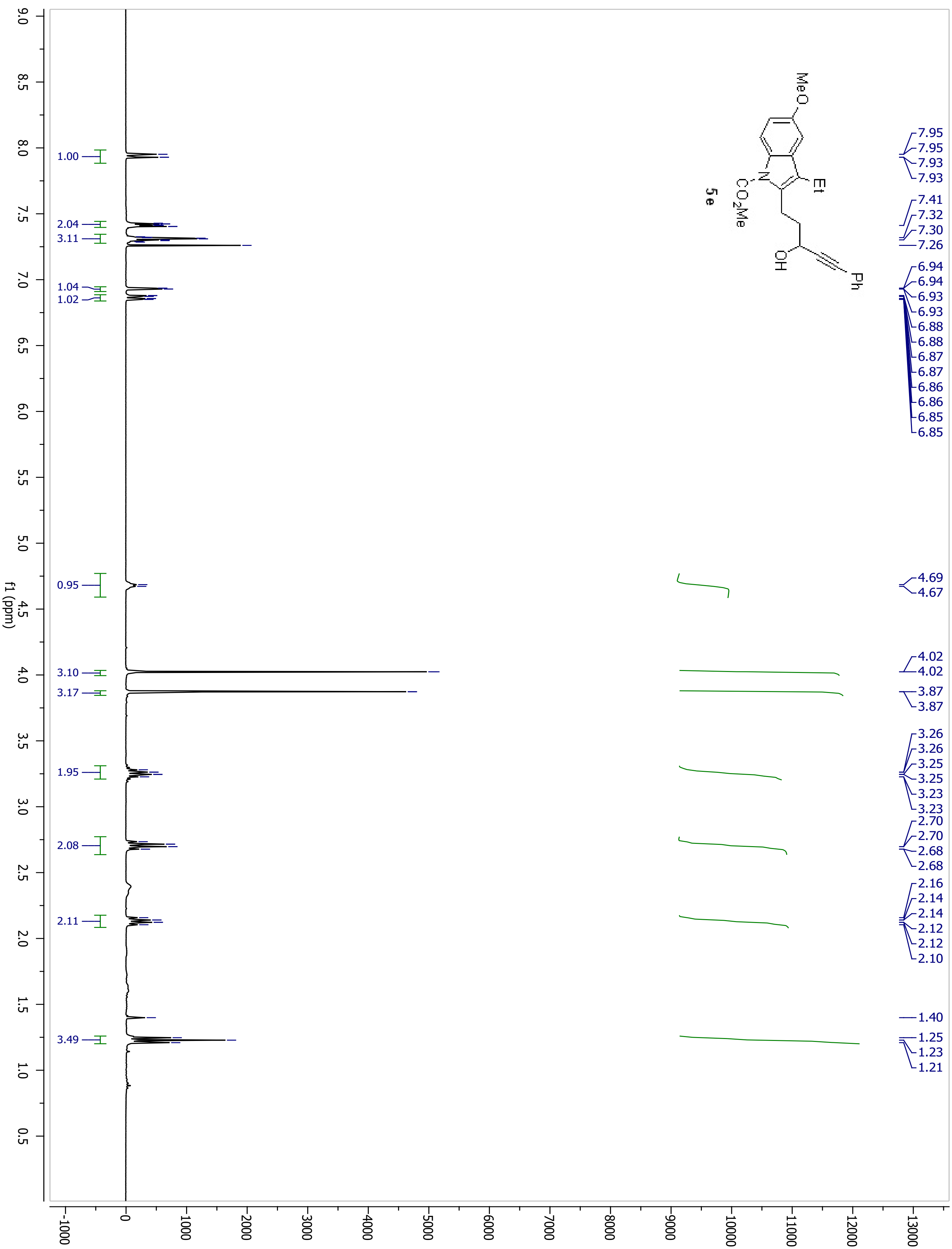
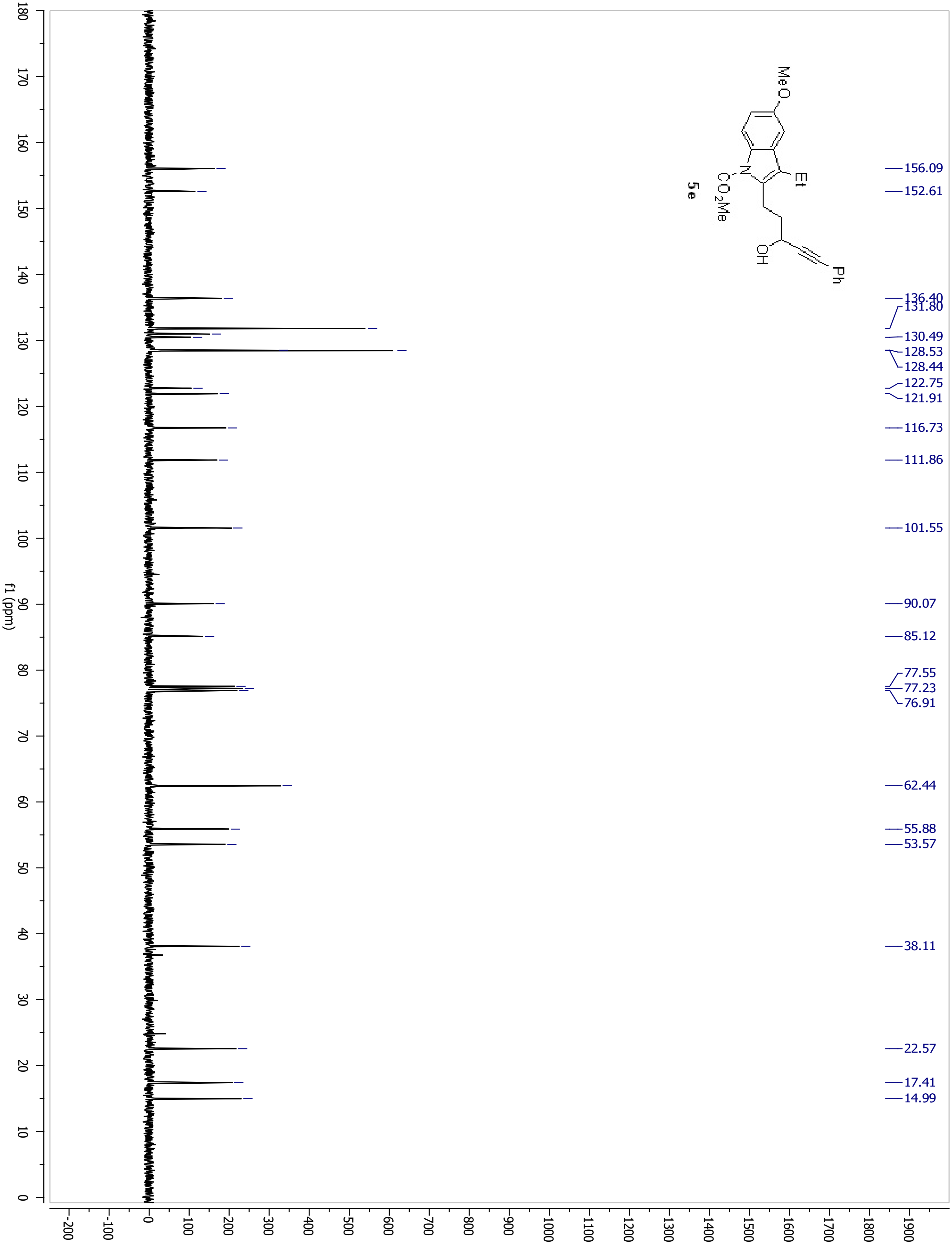
128.50
122.68
120.11
115.87
108.66
89.87
85.42
77.55
77.23
76.91
62.44
53.80
37.18
25.86
f1 (ppm)


MeO
Et
N
CO2Me
OH
5d
7.94
7.92
7.26
6.93
6.92
6.88
6.87
6.85
6.85
4.48
4.46
4.45
4.43
4.03
3.87
3.21
3.20
3.19
3.18
3.17
3.16
2.69
2.67
2.65
2.50
2.50
2.07
2.05
2.03
2.01
1.57
1.23
1.21
1.19
1.00
1.02
1.02
0.99
3.12
3.14
1.96
2.06
0.94
2.14
3.57
f1 (ppm)



5d
MeO
Et
N
CO_2Me
OH
156.09
152.61
136.24
130.94
130.43
121.95
116.73
111.88
101.56
84.85
77.23
76.91
73.19
61.76
55.89
53.61
37.85
22.34
17.37
15.00
f1 (ppm)


MeO
Et
N
CO_2Me
OH
Ph
5e
f1 (ppm)


MeO
Et
N
CO_2Me
5e
OH
Ph
156.09
152.61
136.40
131.80
130.49
128.53
128.44
122.75
121.91
116.73
111.86
101.55
90.07
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76.91
62.44
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53.57
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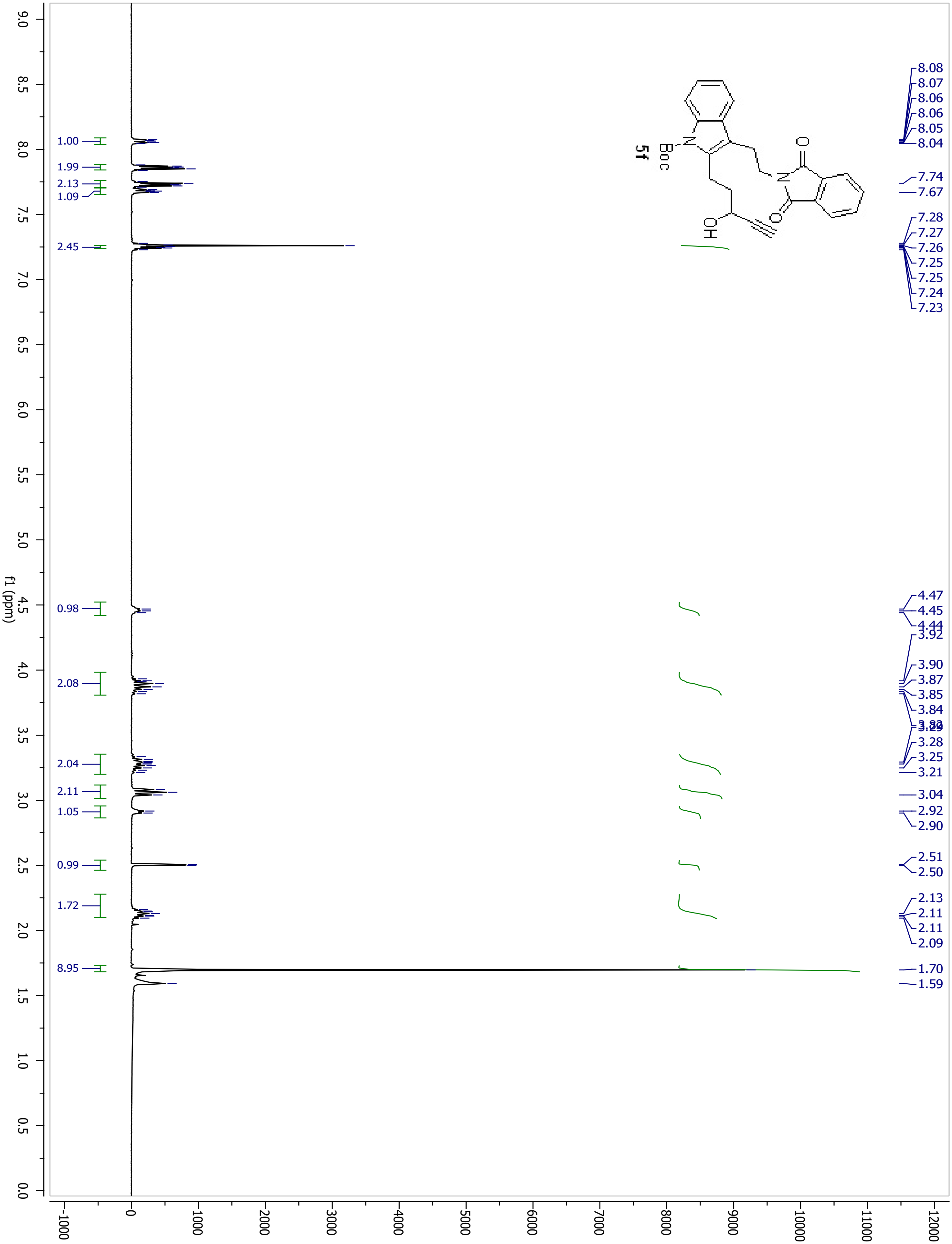
22.57
17.41
14.99
f1 (ppm)


5f
Boc
OH
8.08
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8.06
8.06
8.05
8.04
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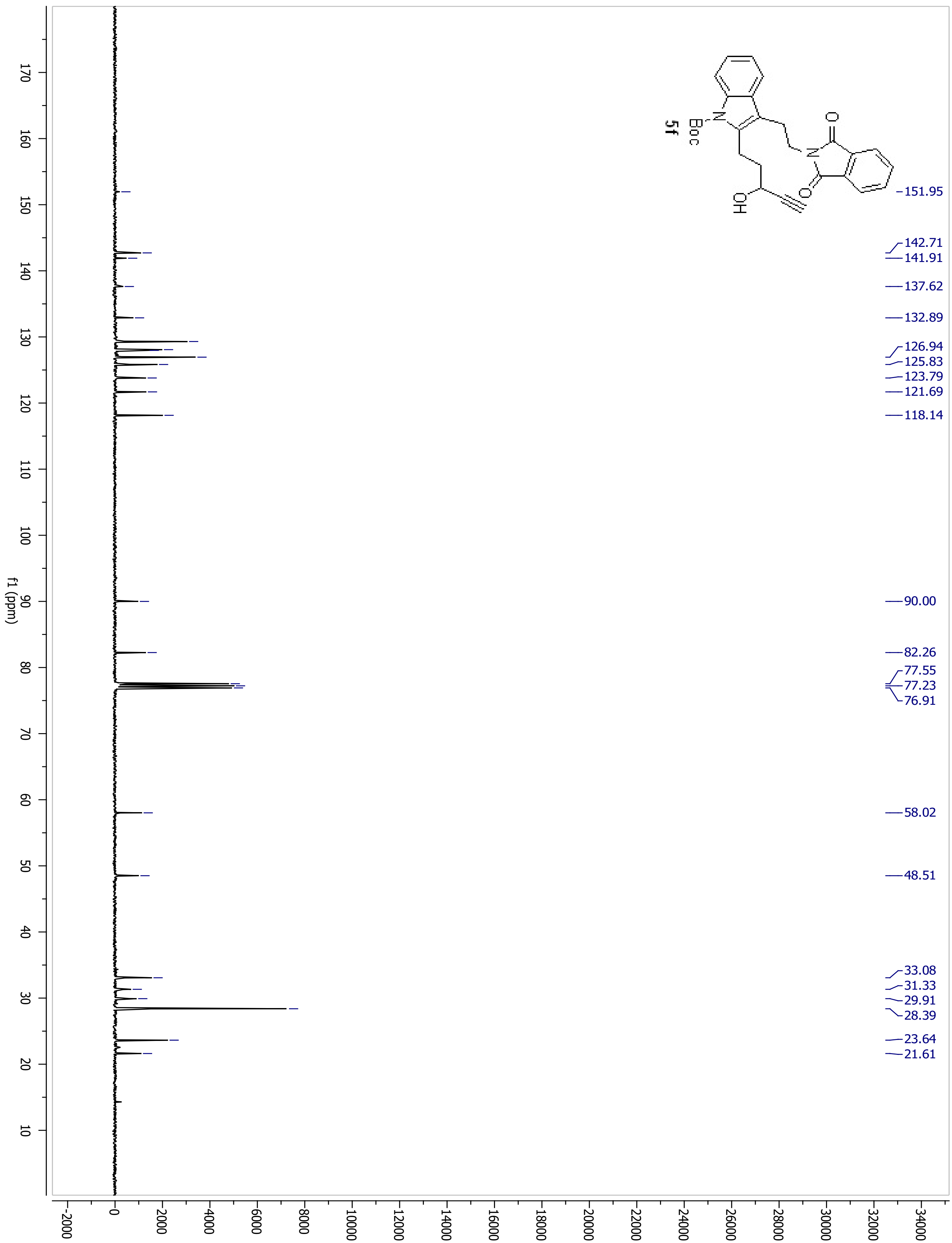
7.67
7.28
7.27
7.26
7.25
7.25
7.24
7.23
4.47
4.45
4.44
3.92
3.90
3.87
3.85
3.84
3.29
3.28
3.25
3.21
3.04
2.92
2.90
2.51
2.50
2.13
2.11
2.11
2.09
1.70
1.59
1.00
1.99
2.13
1.09
2.45
0.98
2.08
2.04
2.11
1.05
0.99
1.72
8.95
f1 (ppm)



5f
Boc
N
O
OH
151.95
142.71
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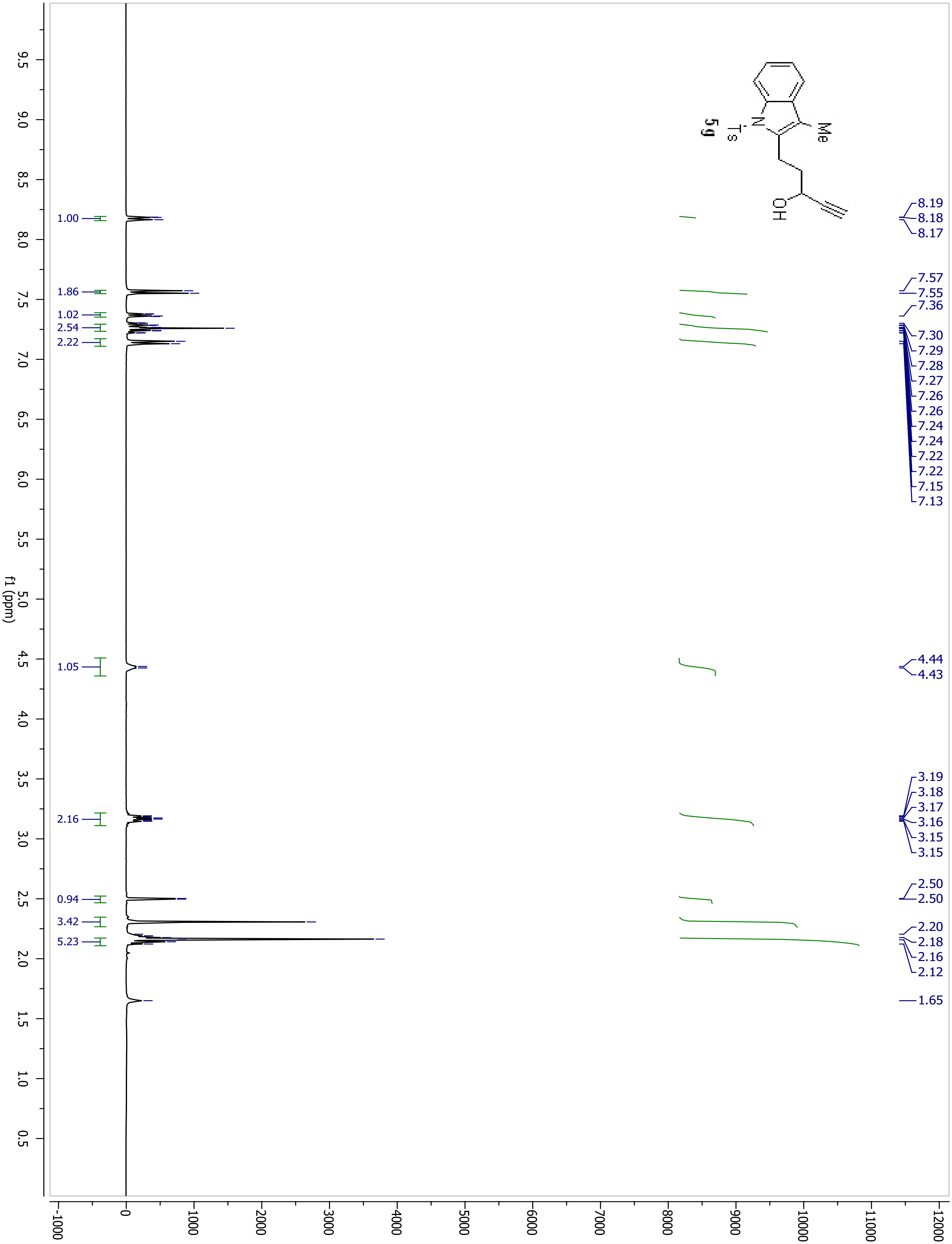
137.62
132.89
126.94
125.83
123.79
121.69
118.14
90.00
82.26
77.55
77.23
76.91
58.02
48.51
33.08
31.33
29.91
28.39
23.64
21.61
f1 (ppm)


Me
N
Ts
OH
5g
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7.30
7.29
7.28
7.27
7.26
7.26
7.24
7.24
7.22
7.22
7.15
7.13
4.44
4.43
3.19
3.18
3.17
3.16
3.15
3.15
2.50
2.50
2.20
2.18
2.16
2.12
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1.02
2.54
2.22
1.05
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0.94
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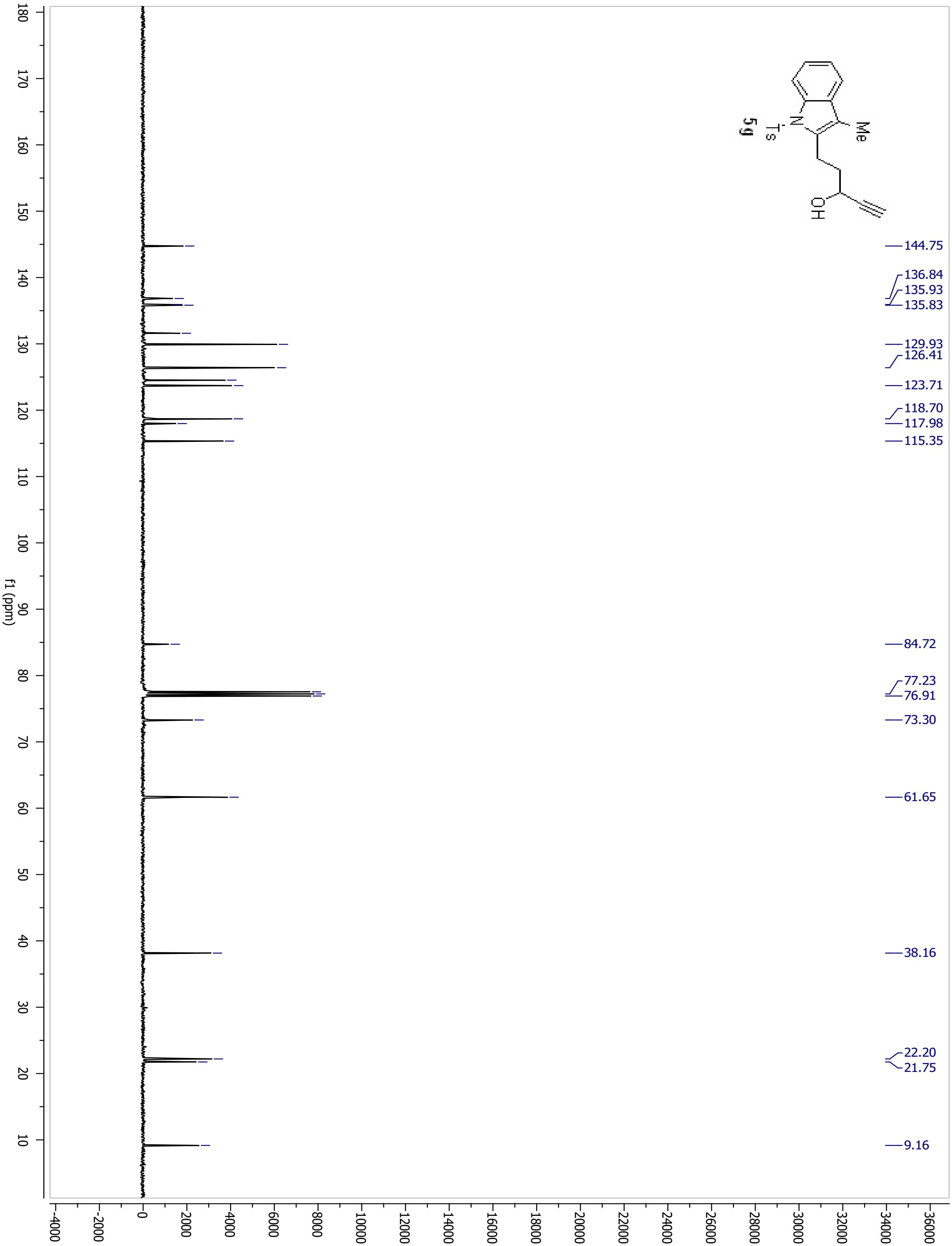
5.23
f1 (ppm)


5g
Ts
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115.35
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77.23
76.91
73.30
61.65
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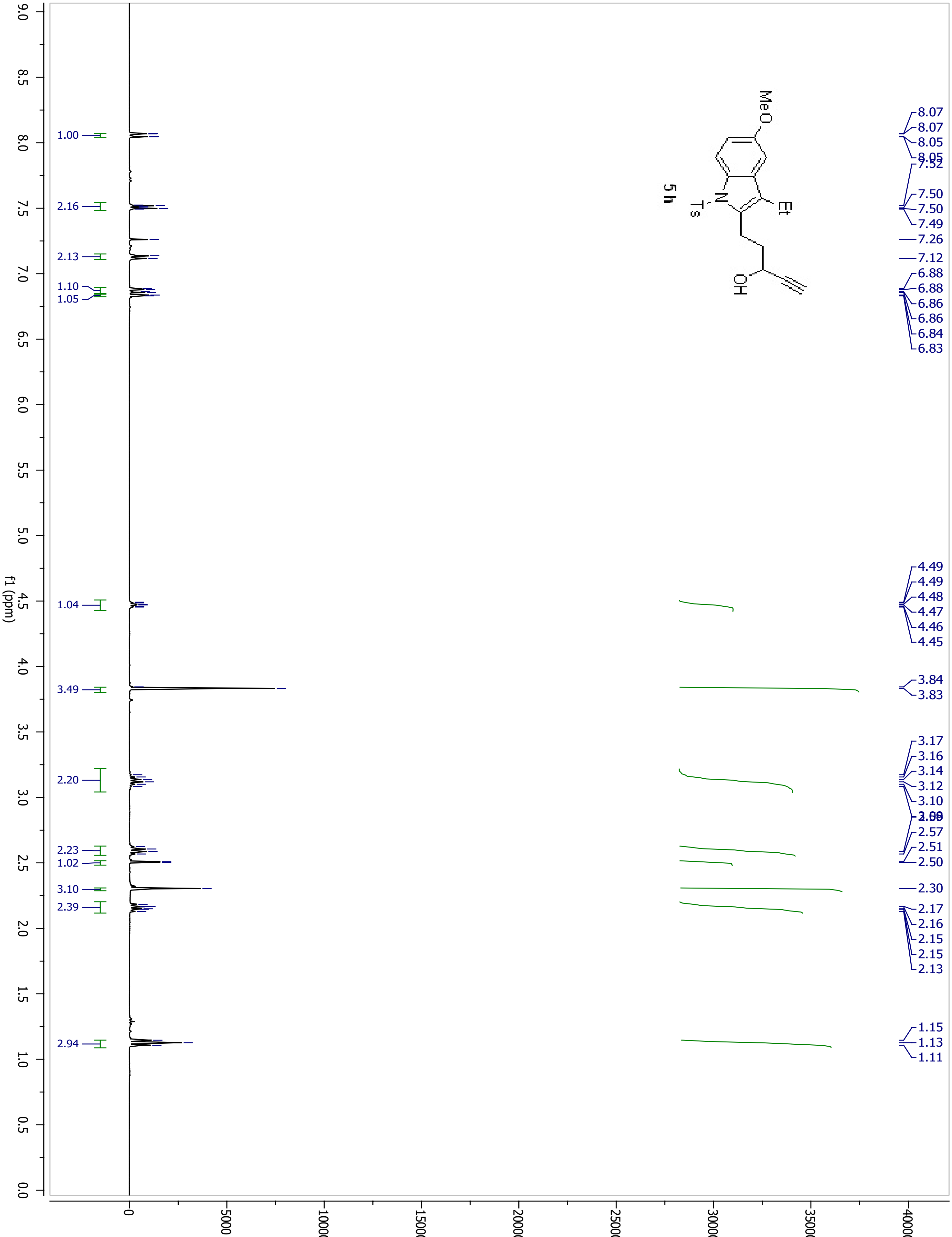
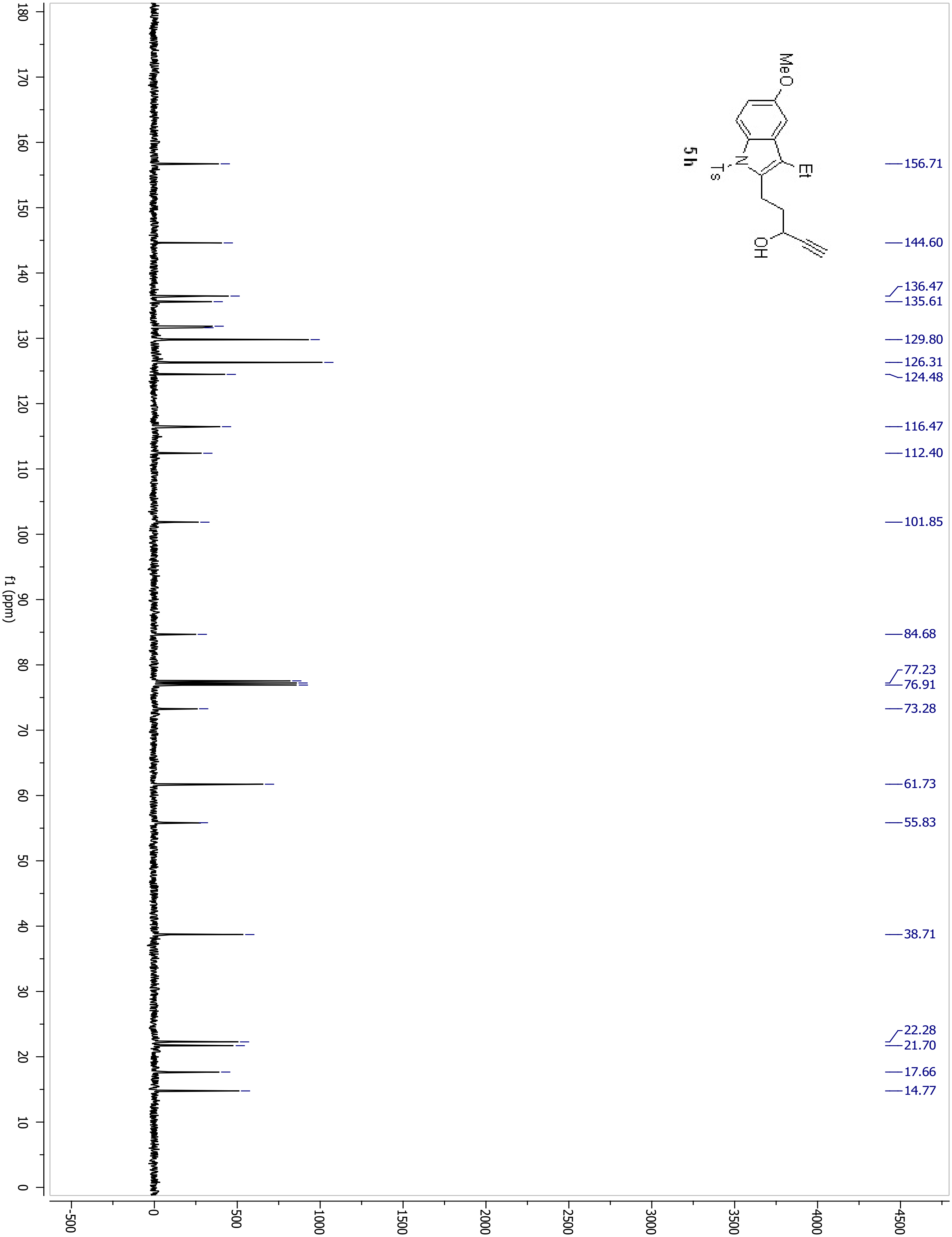
22.20
21.75
9.16
f1 (ppm)


5h
MeO
Et
N
Ts
OH
f1 (ppm)


5h
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Ts
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101.85
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55.83
38.71
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21.70
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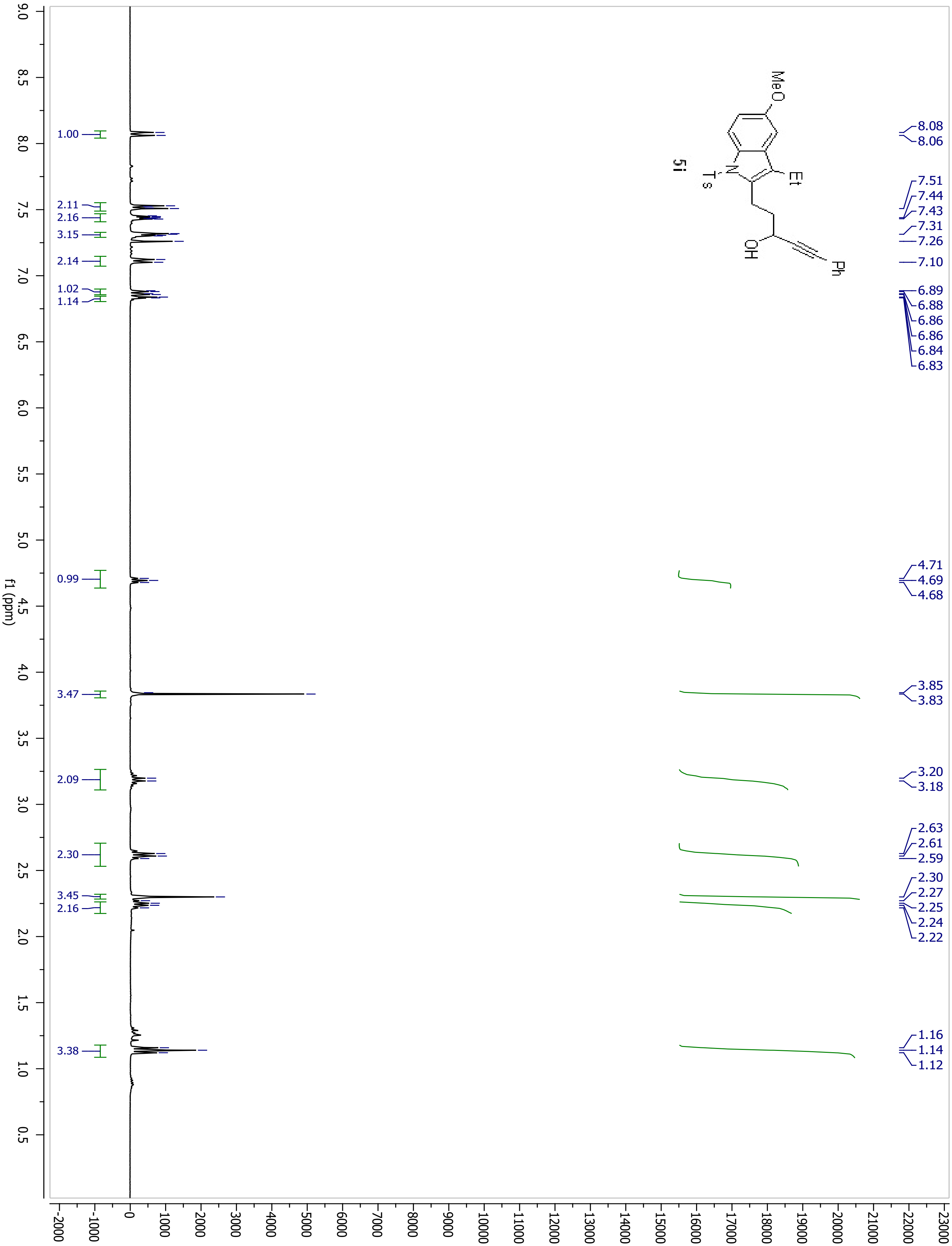
14.77
f1 (ppm)


MeO
Et
N
Ts
OH
Ph
5i
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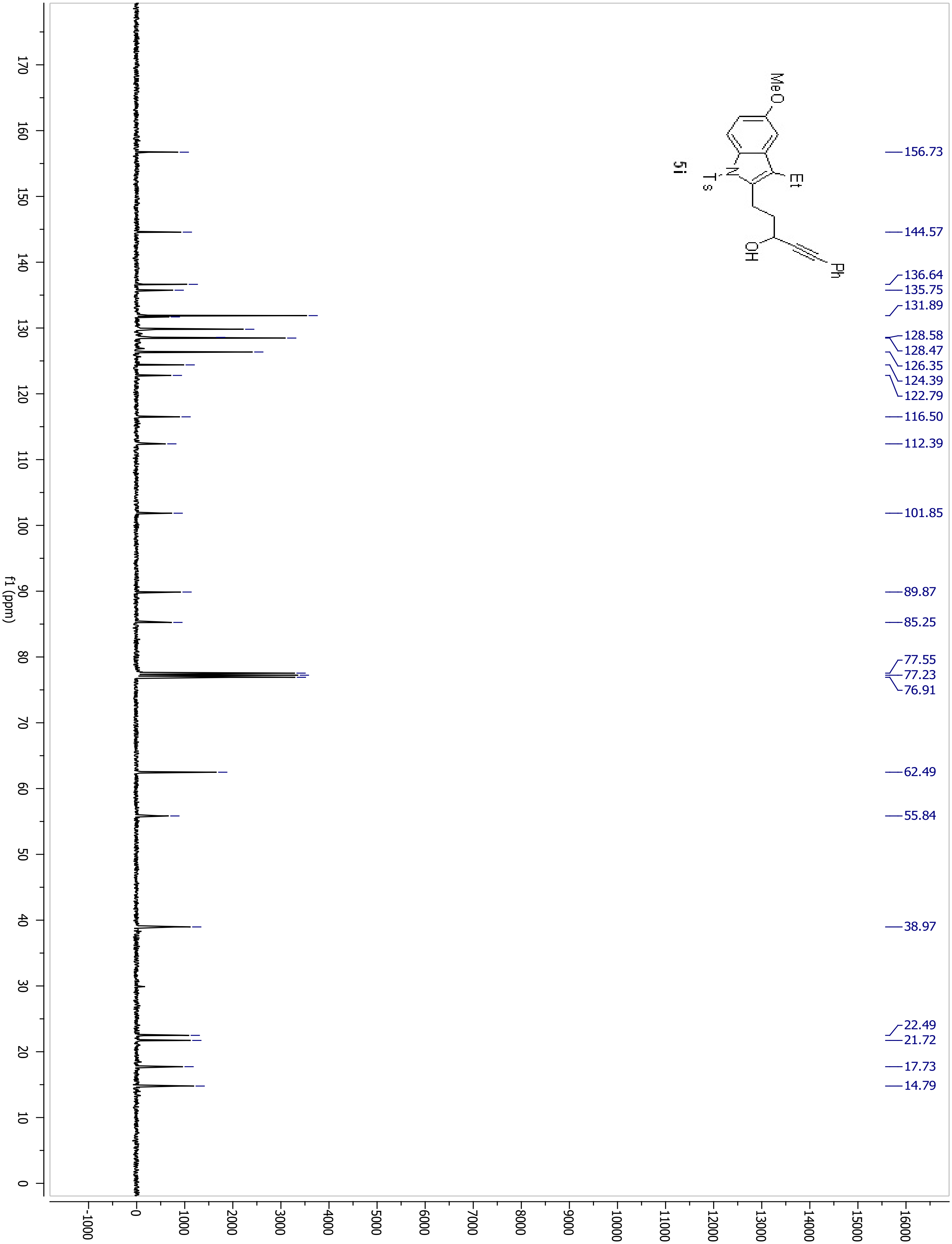
7.10
6.89
6.88
6.86
6.86
6.84
6.83
4.71
4.69
4.68
3.85
3.83
3.20
3.18
2.63
2.61
2.59
2.30
2.27
2.25
2.24
2.22
1.16
1.14
1.12
1.00
2.11
2.16
3.15
2.14
1.02
1.14
0.99
3.47
2.09
2.30
3.45
2.16
3.38
f1 (ppm)


5i
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Et
N
Ts
OH
Ph
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126.35
124.39
122.79
116.50
112.39
101.85
89.87
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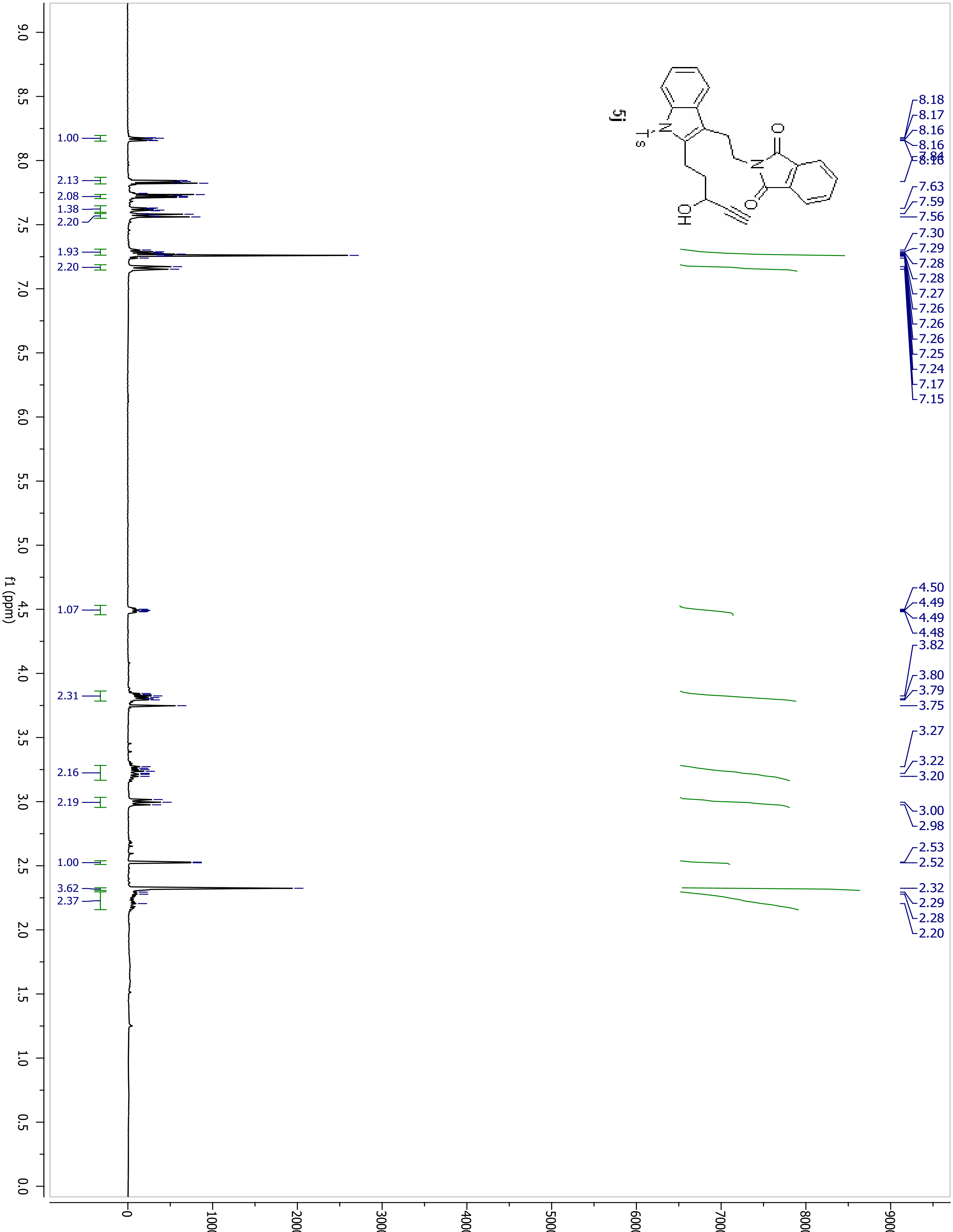
38.97
22.49
21.72
17.73
14.79
f1 (ppm)


5j
Ts
N
O
N
O
OH
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8.17
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8.16
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7.84
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7.59
7.56
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.26
7.25
7.24
7.17
7.15
4.50
4.49
4.49
4.48
3.82
3.80
3.79
3.75
3.27
3.22
3.20
3.00
2.98
2.53
2.52
2.32
2.29
2.28
2.20
1.00
2.13
2.08
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1.07
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1.00
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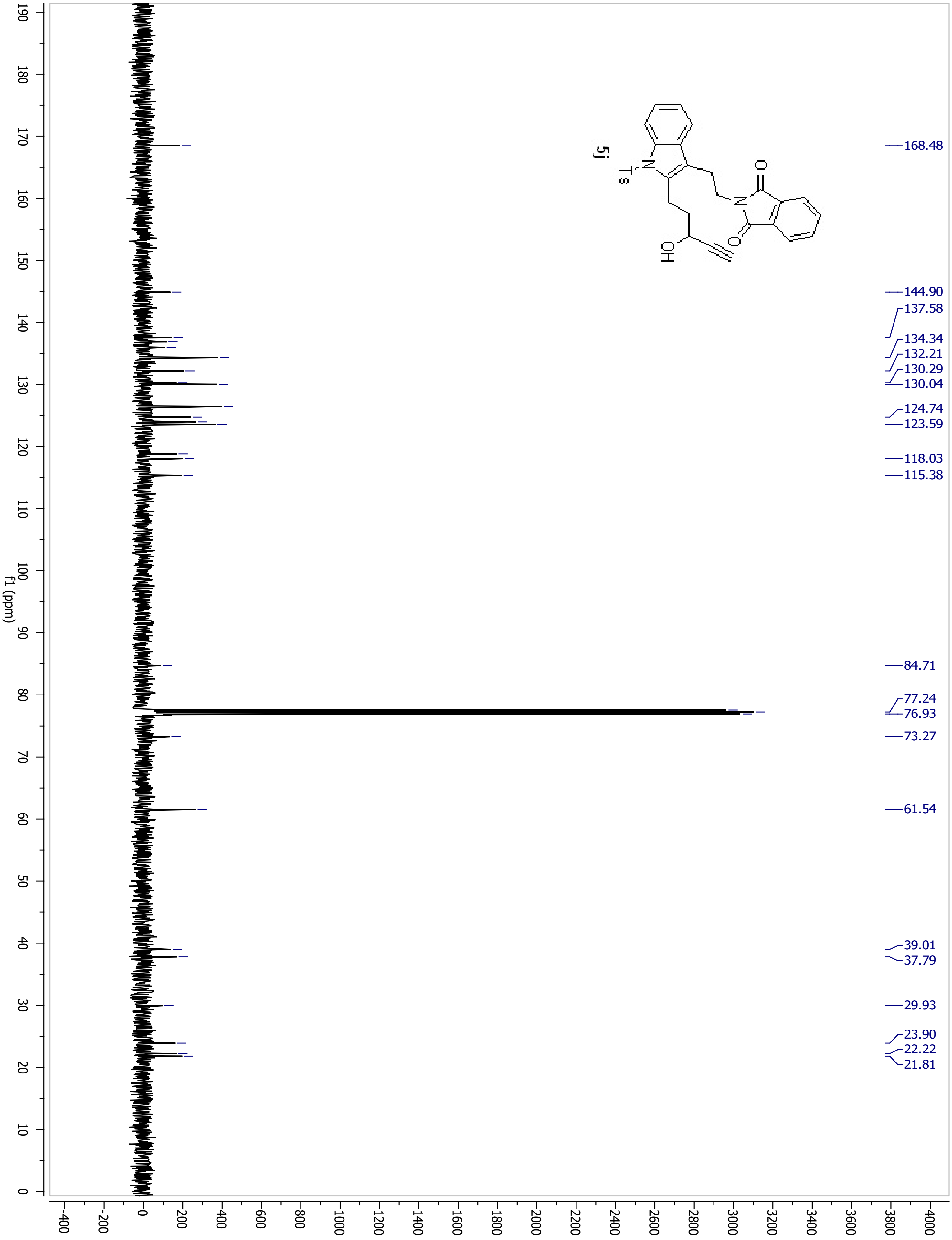
2.37
f1 (ppm)


5j
Ts
N
O
N
O
OH
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137.58
134.34
132.21
130.29
130.04
124.74
123.59
118.03
115.38
84.71
77.24
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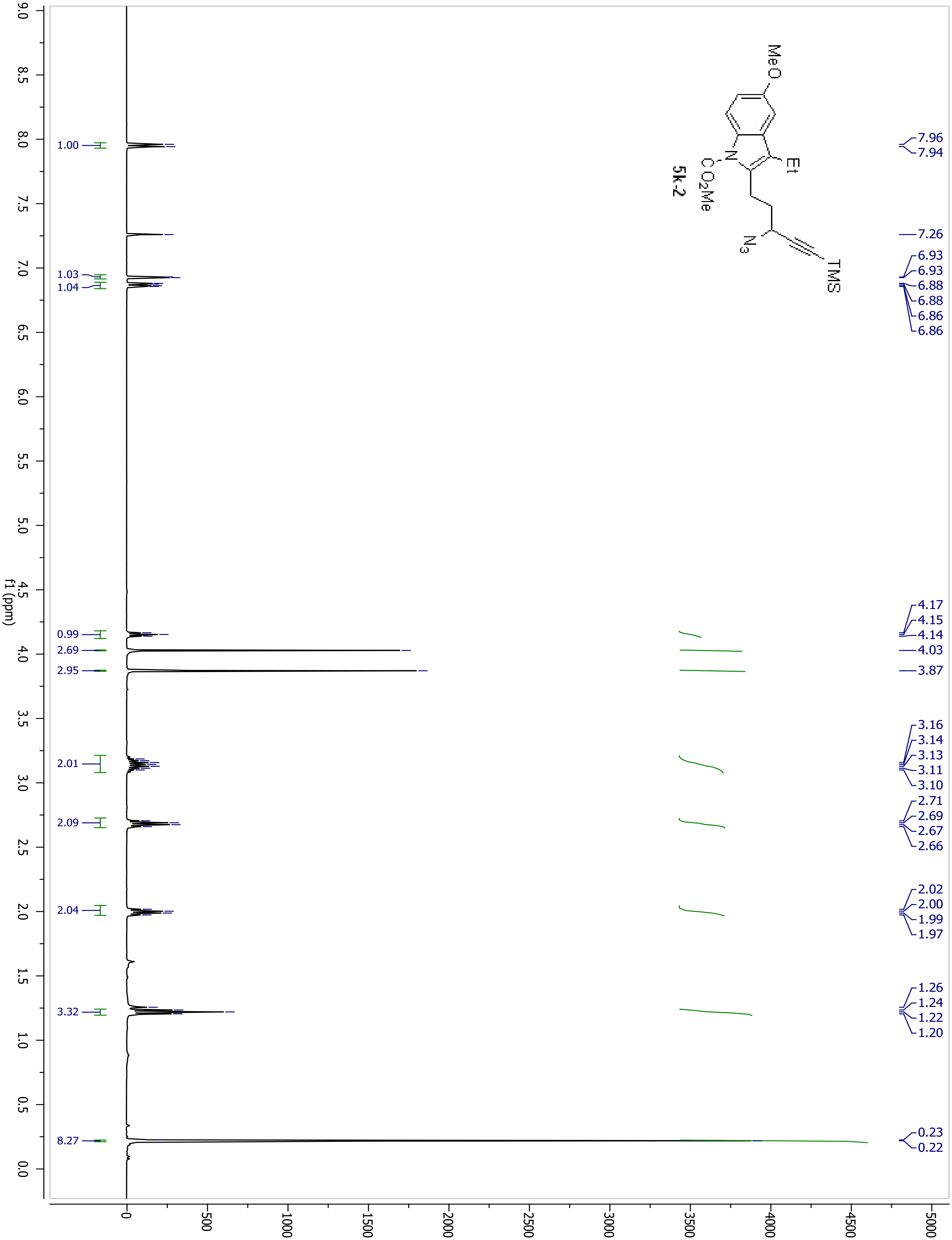
73.27
61.54
39.01
37.79
29.93
23.90
22.22
21.81
f1 (ppm)



MeO
Et
N
CO_2Me
N_3
TMS
5k-2
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6.93
6.88
6.88
6.86
6.86
4.17
4.15
4.14
4.03
3.87
3.16
3.14
3.13
3.11
3.10
2.71
2.69
2.67
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2.02
2.00
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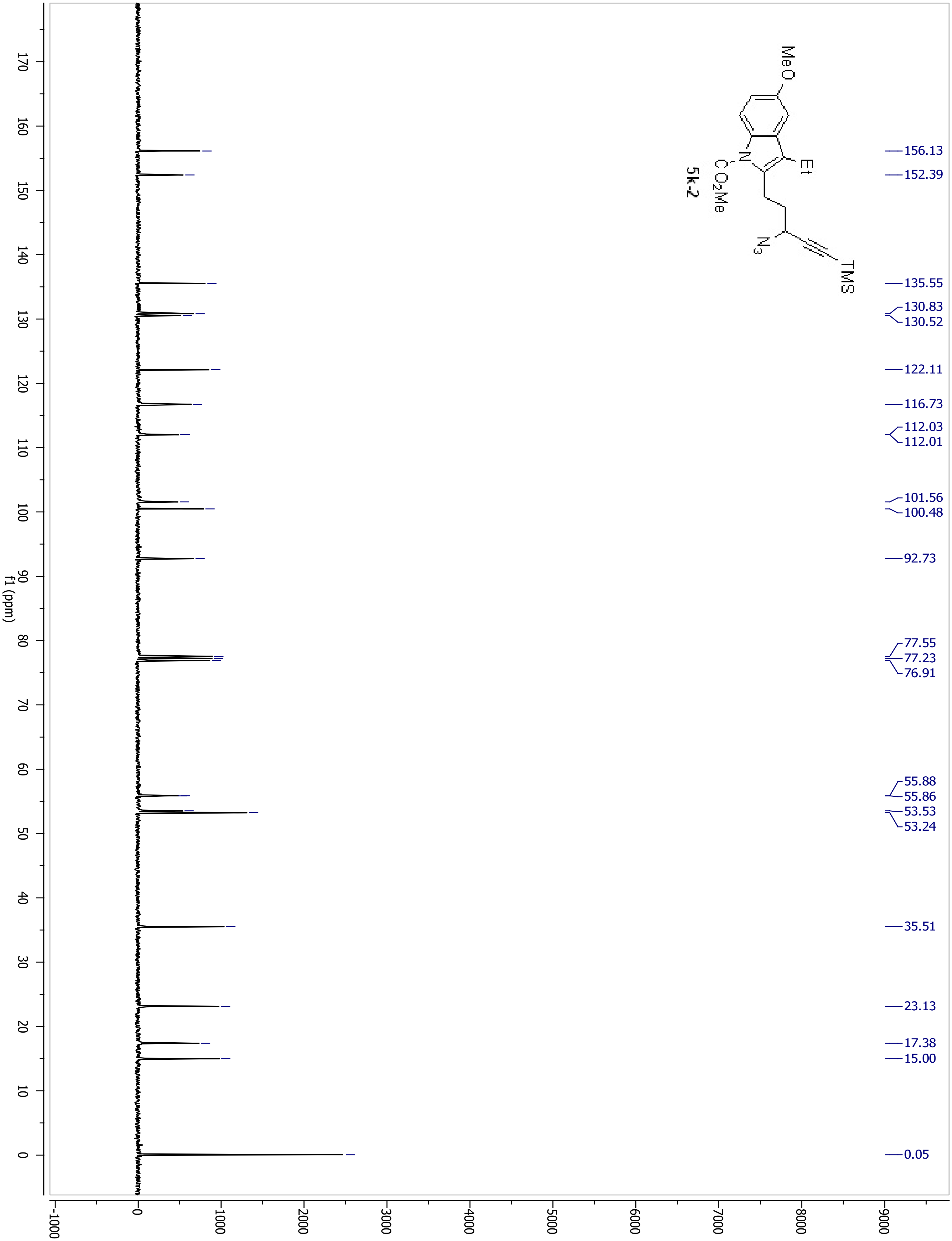
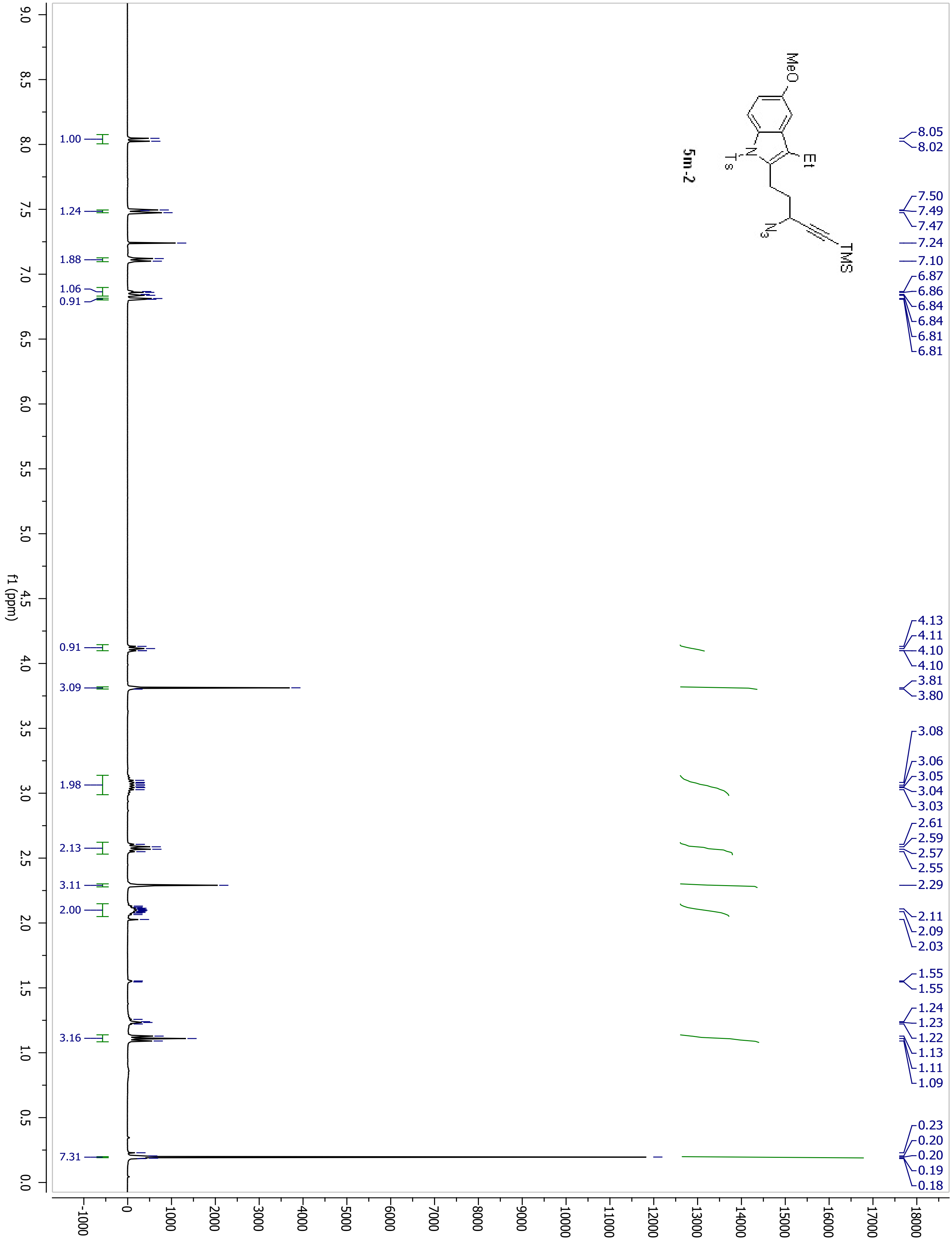
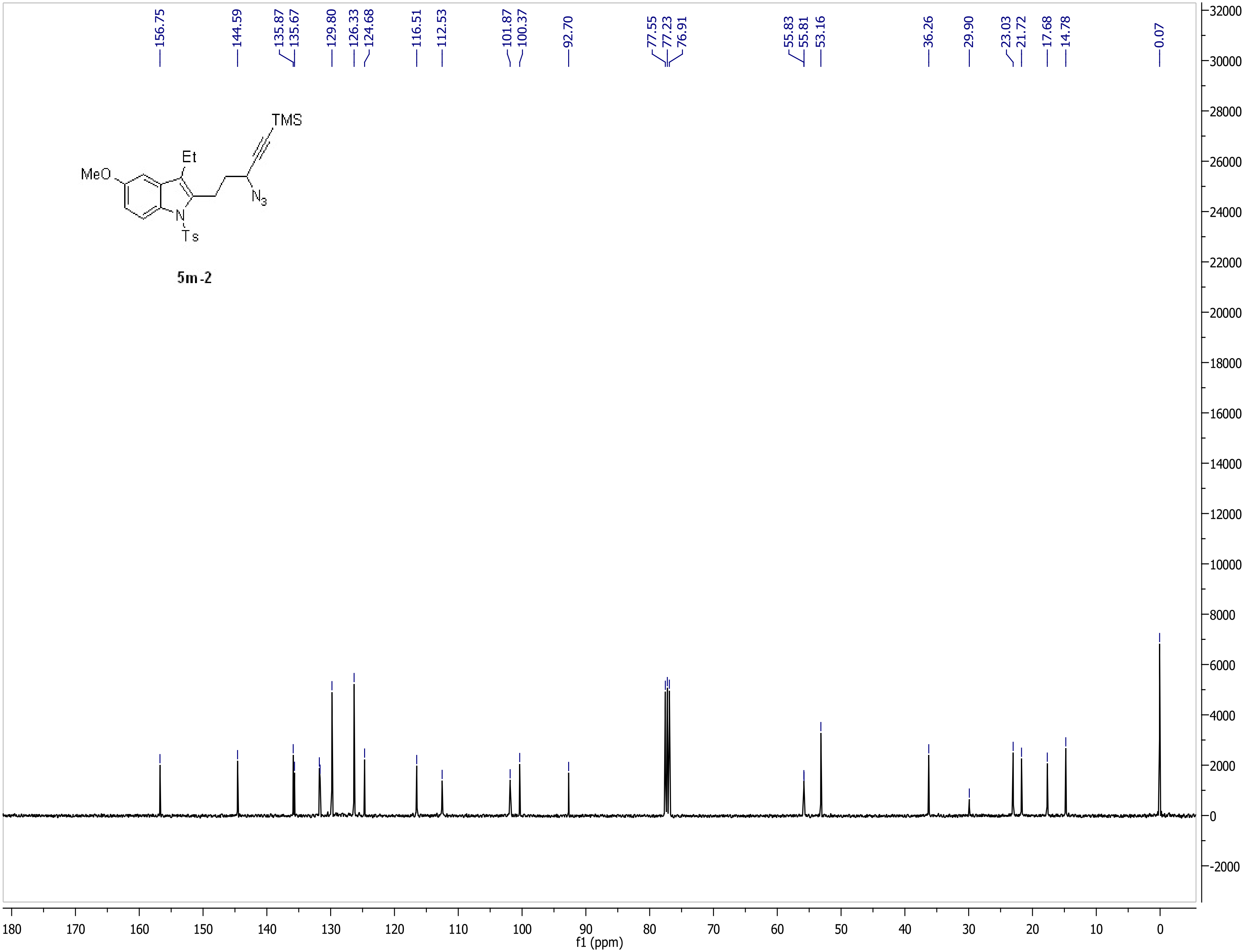
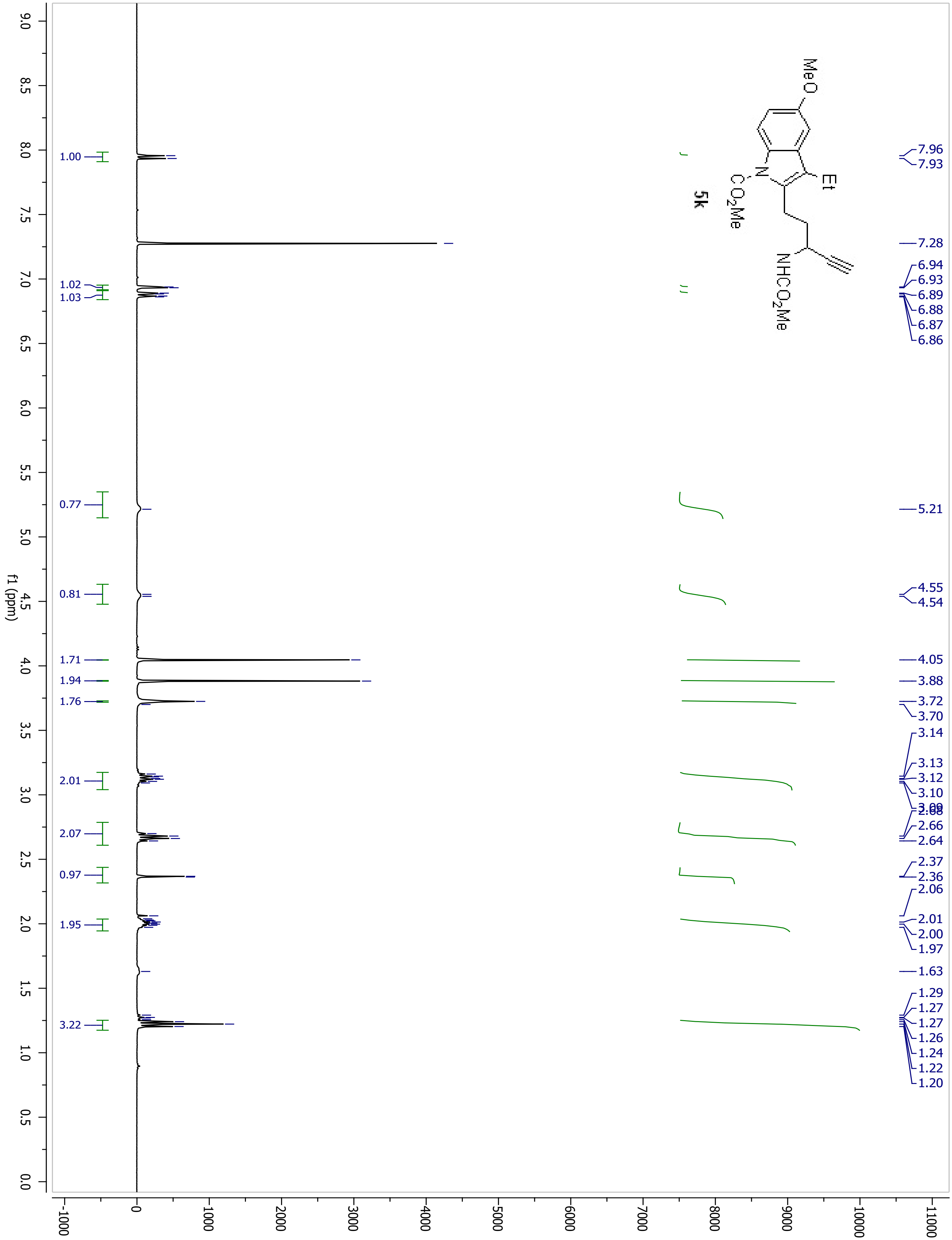
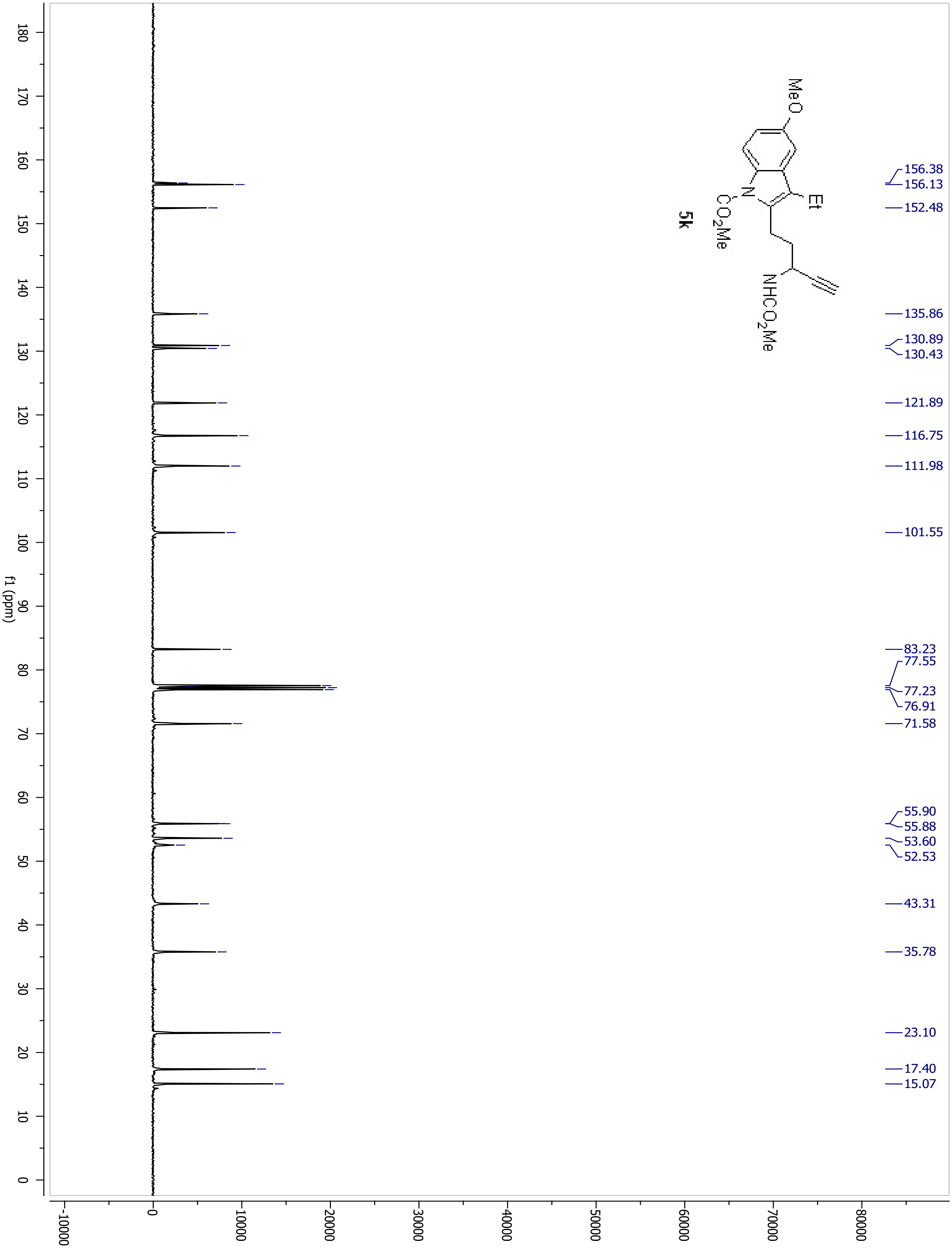
1.97
1.26
1.24
1.22
1.20
0.23
0.22
1.00
1.03
1.04
0.99
2.69
2.95
2.01
2.09
2.04
3.32
8.27
f1 (ppm)

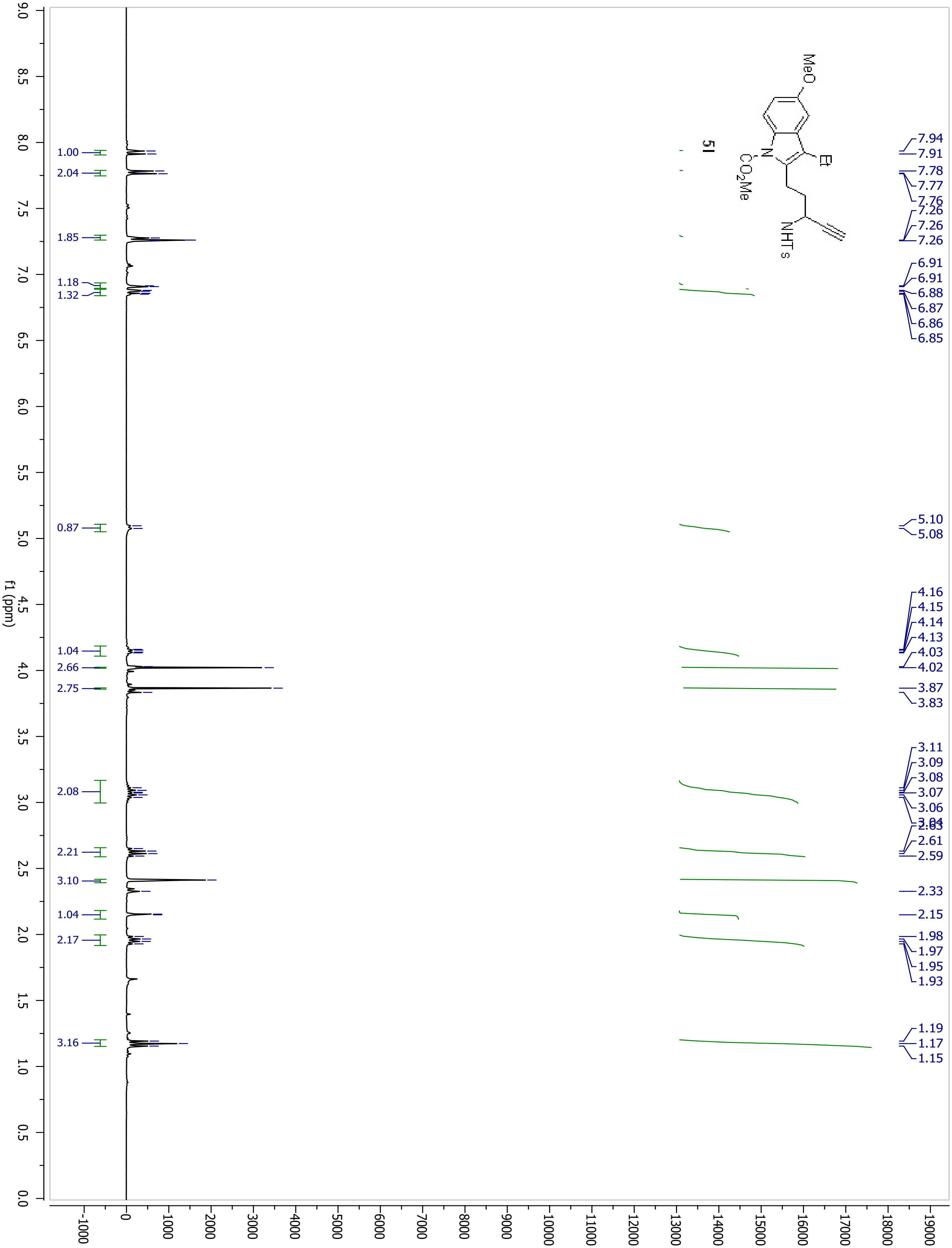

5k-2
MeO
Et
N
CO2Me
N3
TMS
156.13
152.39
135.55
130.83
130.52
122.11
116.73
112.03
112.01
101.56
100.48
92.73
77.55
77.23
76.91
55.88
55.86
53.53
53.24
35.51
23.13
17.38
15.00
0.05
f1 (ppm)


5m-2
MeO
Et
N
Ts
N3
TMS
f1 (ppm)

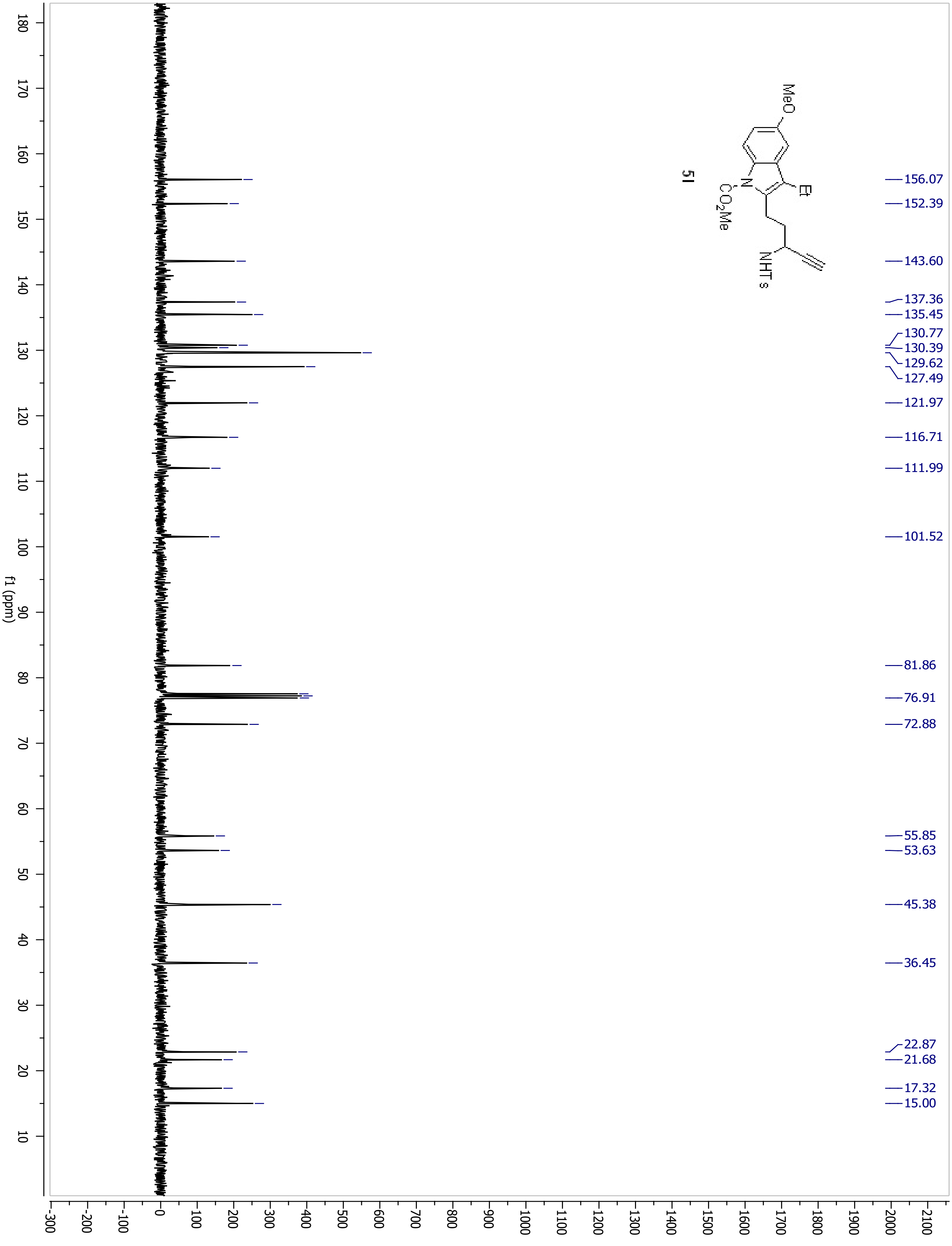

156.75
144.59
135.87
135.67
129.80
126.33
124.68
116.51
112.53
101.87
100.37
92.70
77.55
77.23
76.91
55.83
55.81
53.16
36.26
29.90
23.03
21.72
17.68
14.78
0.07
MeO
Et
TMS
N
Ts
N_3
5m-2
f1 (ppm)


5k
MeO
Et
NHCO2Me
CO2Me
f1 (ppm)


5k
MeO
Et
CO2Me
NHCO2Me
156.38
156.13
152.48
135.86
130.89
130.43
121.89
116.75
111.98
101.55
83.23
77.55
77.23
76.91
71.58
55.90
55.88
53.60
52.53
43.31
35.78
23.10
17.40
15.07
f1 (ppm)



MeO
Et
NHTs
CO_2Me
5l
f1 (ppm)


5l
MeO
Et
N
CO_2Me
NHTs
156.07
152.39
143.60
137.36
135.45
130.77
130.39
129.62
127.49
121.97
116.71
111.99
101.52
81.86
76.91
72.88
55.85
53.63
45.38
36.45
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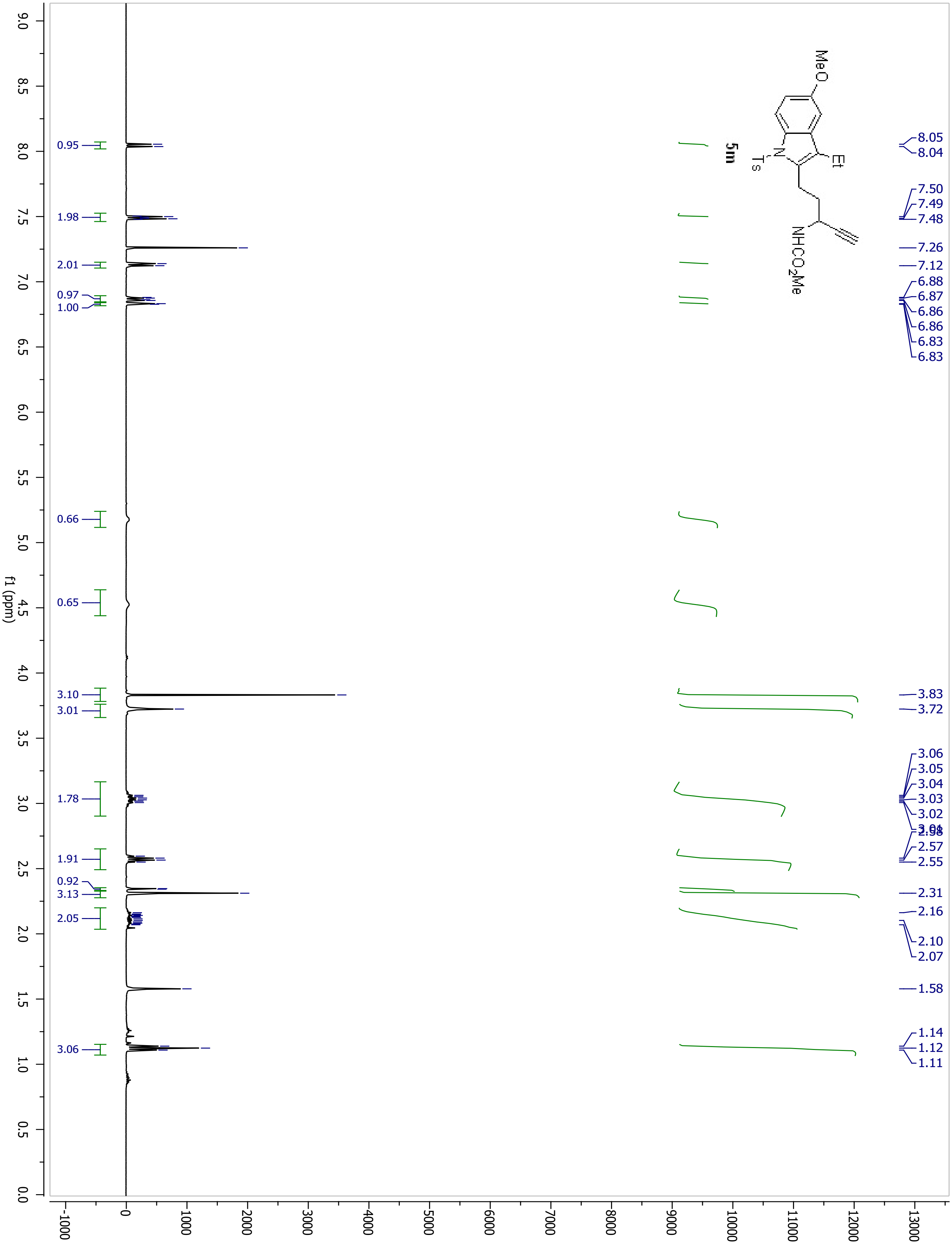
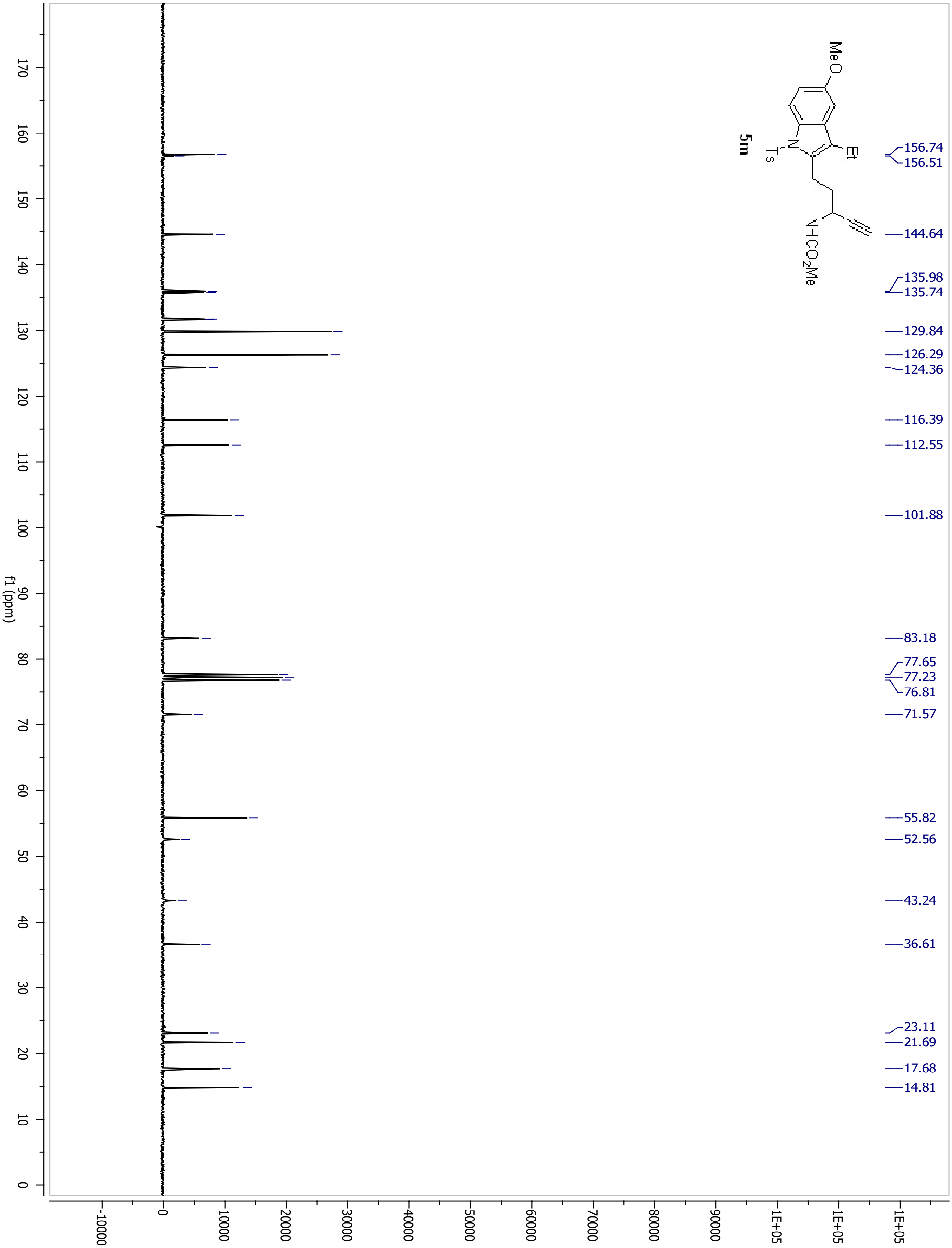
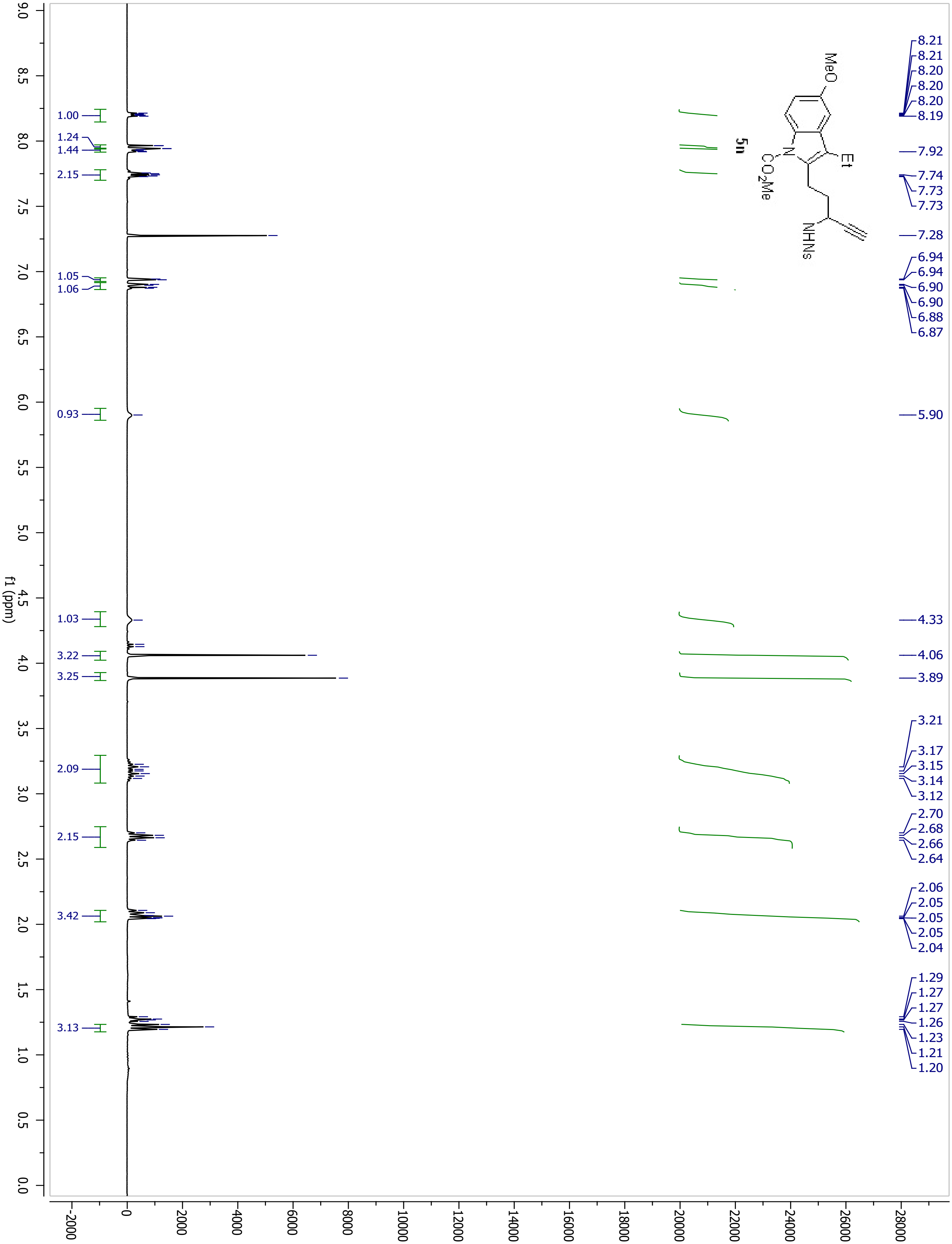
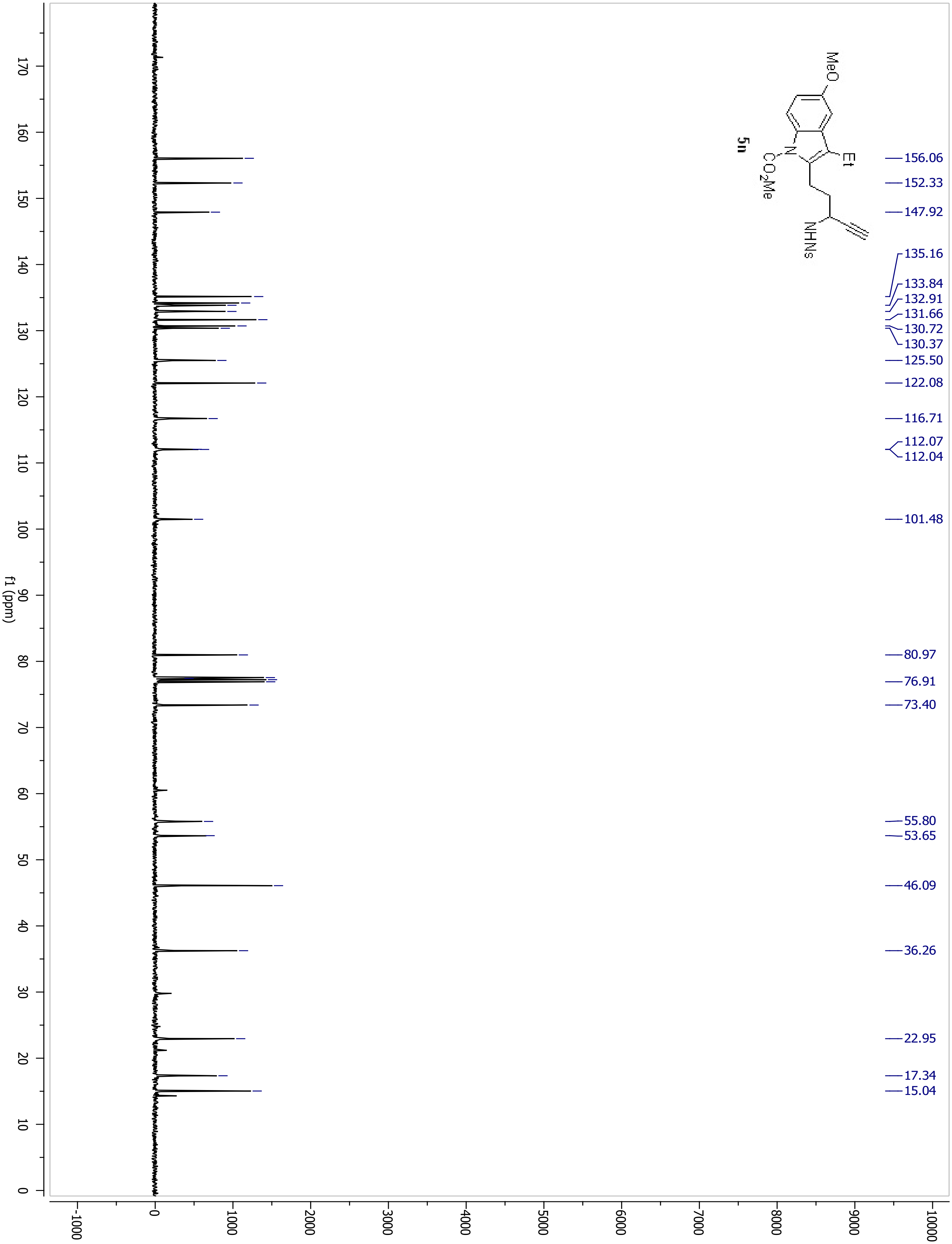
21.68
17.32
15.00
f1 (ppm)

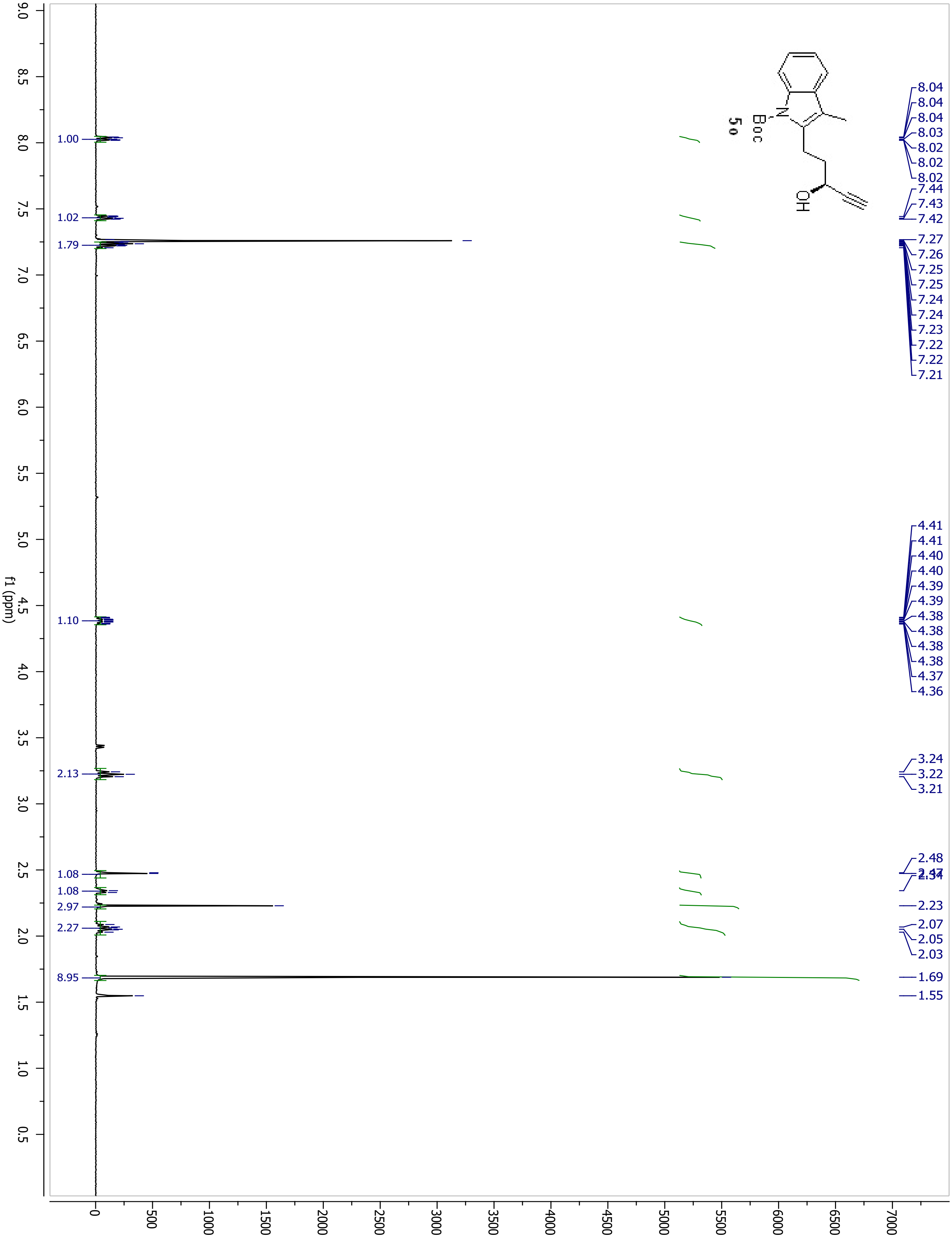

5m
MeO
Et
N
Ts
NHCO2Me
f1 (ppm)
8.05
8.04
7.50
7.49
7.48
7.26
7.12
6.88
6.87
6.86
6.86
6.83
6.83
3.83
3.72
3.06
3.05
3.04
3.03
3.02
2.57
2.55
2.31
2.16
2.10
2.07
1.58
1.14
1.12
1.11
0.95
1.98
2.01
0.97
1.00
0.66
0.65
3.10
3.01
1.78
1.91
0.92
3.13
2.05
3.06



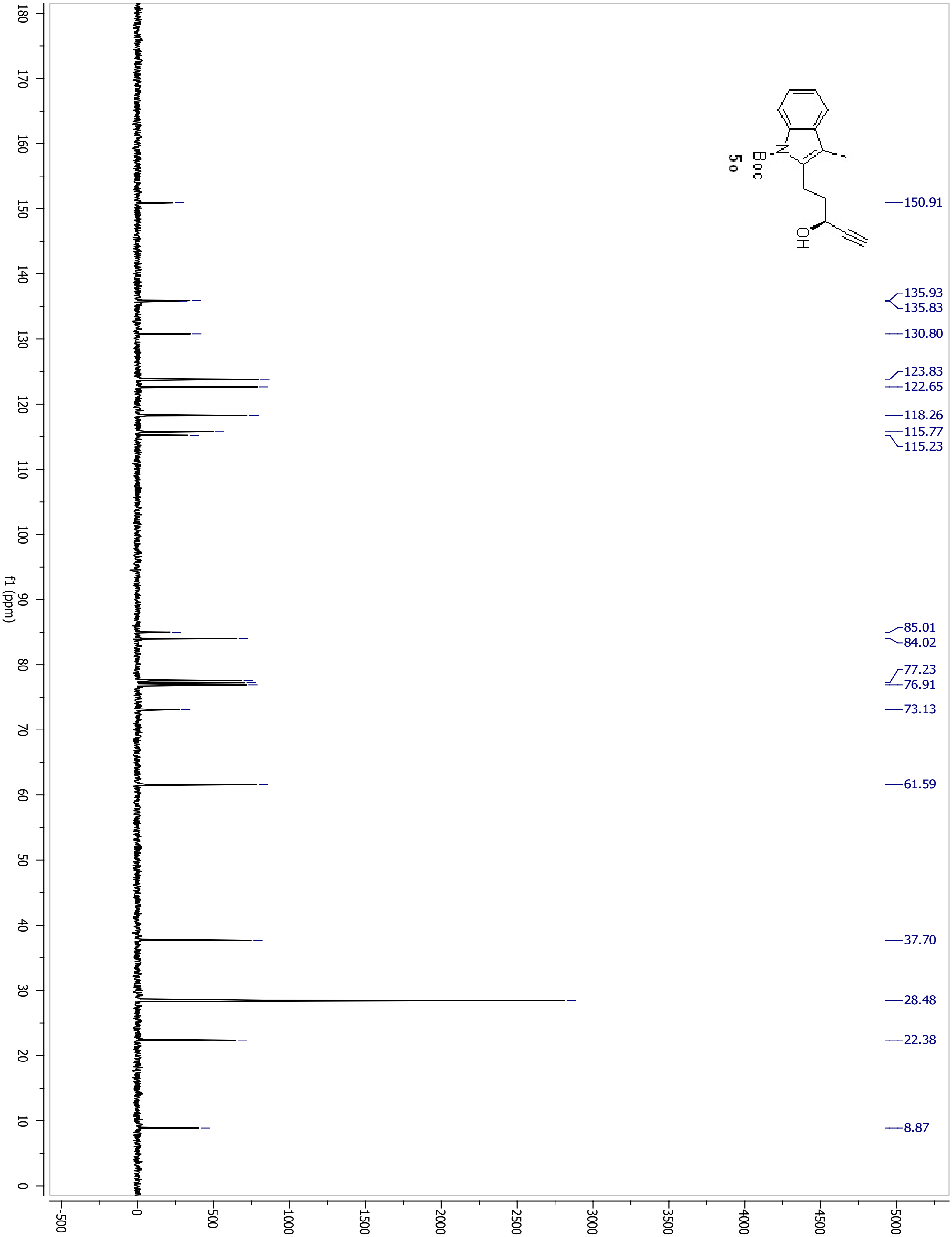
5m
MeO
Et
Ts
$NHCO_2Me$
156.74
156.51
144.64
135.98
135.74
129.84
126.29
124.36
116.39
112.55
101.88
83.18
77.65
77.23
76.81
71.57
55.82
52.56
43.24
36.61
23.11
21.69
17.68
14.81
f1 (ppm)

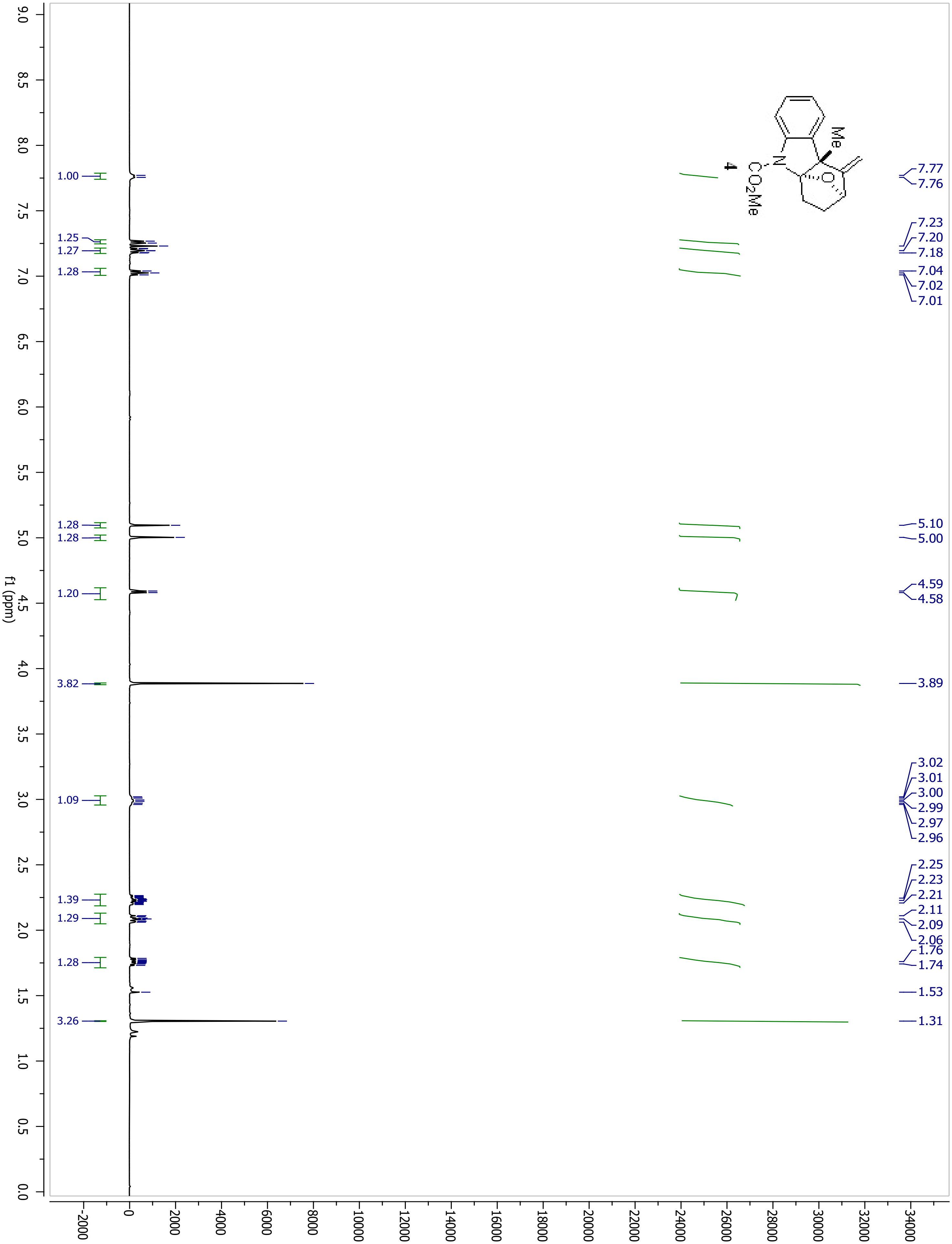

5n
MeO
Et
N
CO2Me
NHNs
f1 (ppm)
8.21
8.21
8.20
8.20
8.20
8.19
7.92
7.74
7.73
7.73
7.28
6.94
6.94
6.90
6.90
6.88
6.87
5.90
4.33
4.06
3.89
3.21
3.17
3.15
3.14
3.12
2.70
2.68
2.66
2.64
2.06
2.05
2.05
2.05
2.04
1.29
1.27
1.27
1.26
1.23
1.21
1.20
1.00
1.24
1.44
2.15
1.05
1.06
0.93
1.03
3.22
3.25
2.09
2.15
3.42
3.13


MeO
Et
N
CO2Me
NHNs
5n
156.06
152.33
147.92
135.16
133.84
132.91
131.66
130.72
130.37
125.50
122.08
116.71
112.07
112.04
101.48
80.97
76.91
73.40
55.80
53.65
46.09
36.26
22.95
17.34
15.04
f1 (ppm)

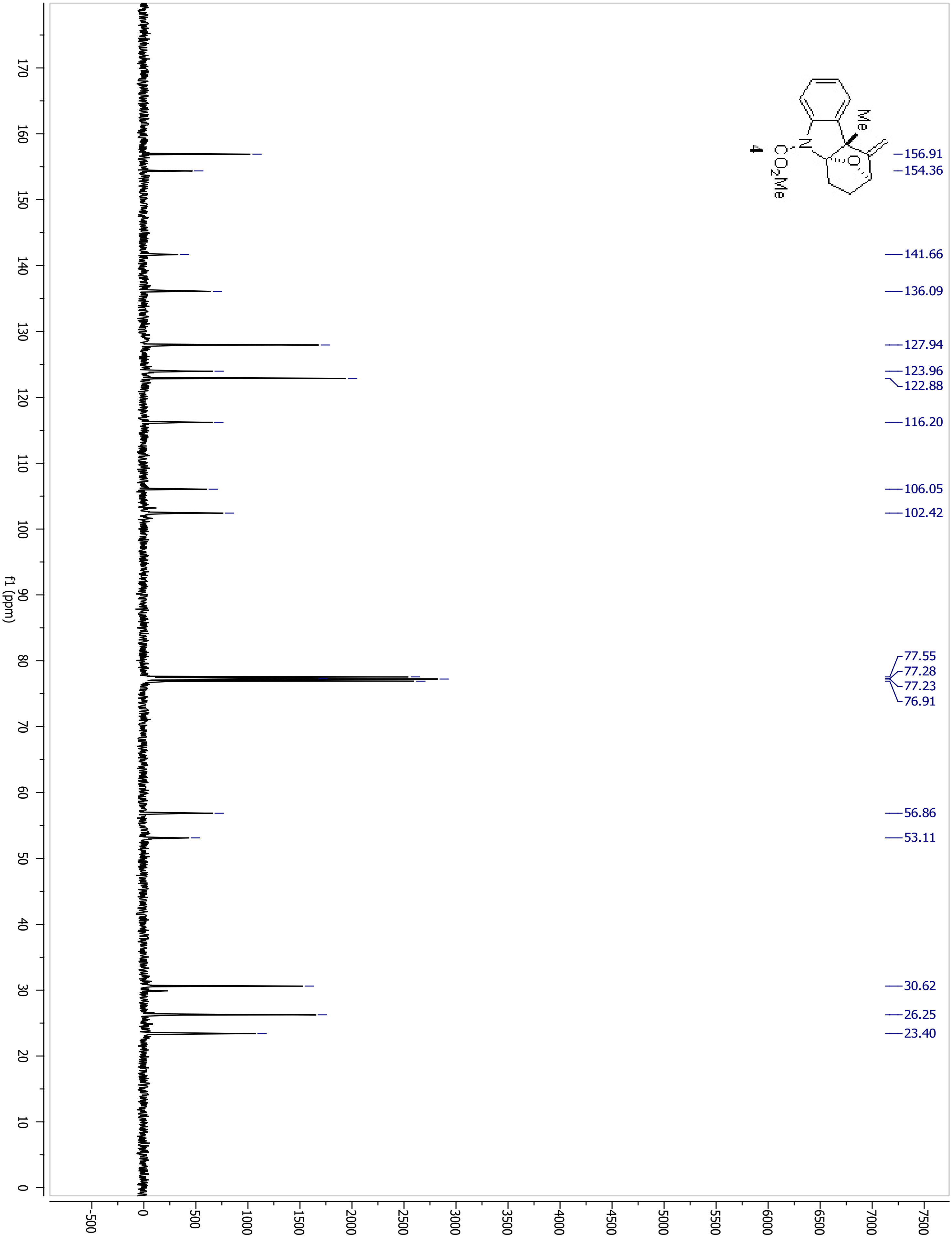


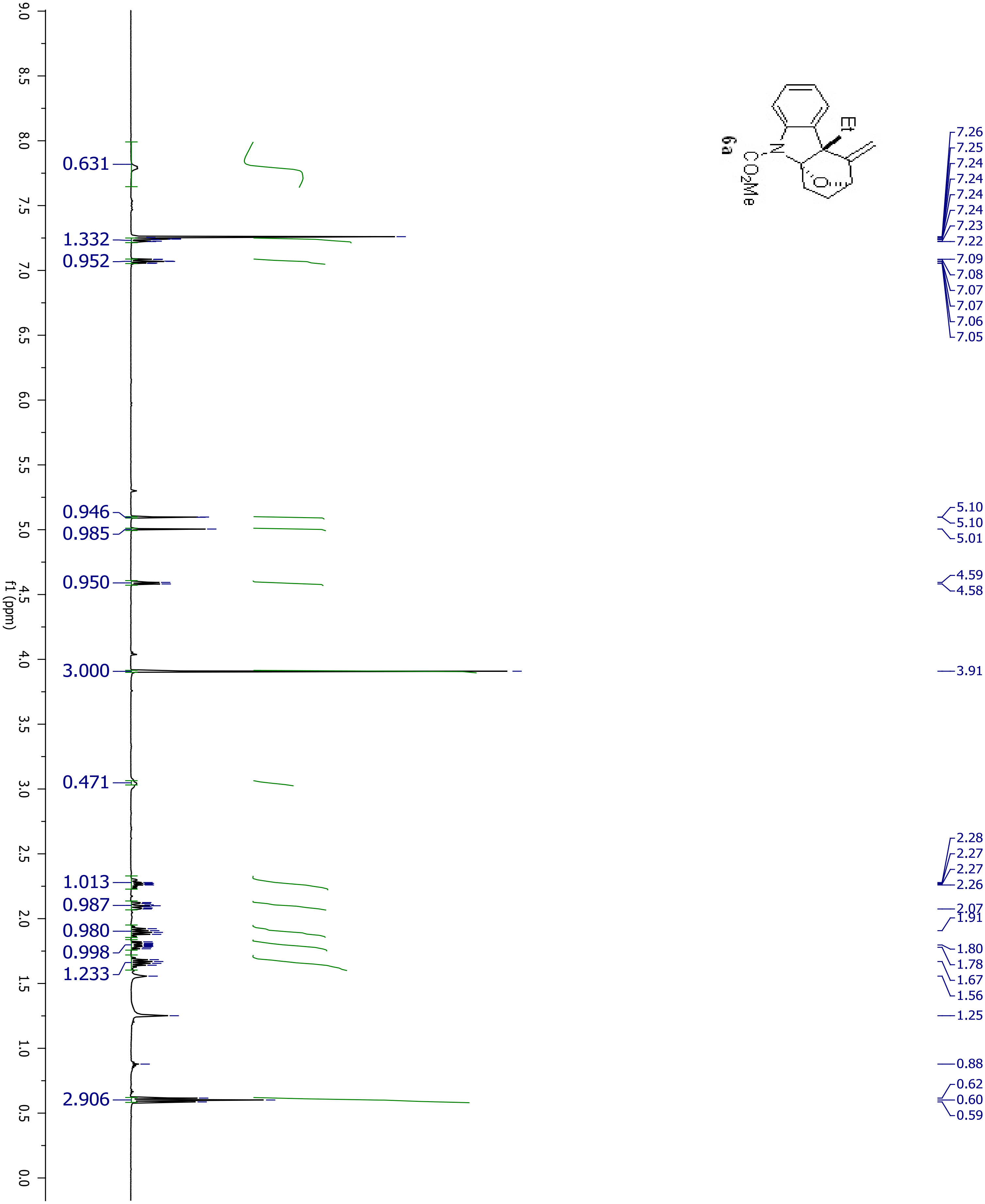
Boc
5o
OH
8.04
8.04
8.04
8.03
8.02
8.02
8.02
7.44
7.43
7.42
7.27
7.26
7.25
7.25
7.24
7.24
7.23
7.22
7.22
7.21
4.41
4.41
4.40
4.40
4.39
4.39
4.38
4.38
4.38
4.38
4.37
4.36
3.24
3.22
3.21
2.48
2.47
2.34
2.23
2.07
2.05
2.03
1.69
1.55
1.00
1.02
1.79
1.10
2.13
1.08
1.08
2.97
2.27
8.95
f1 (ppm)

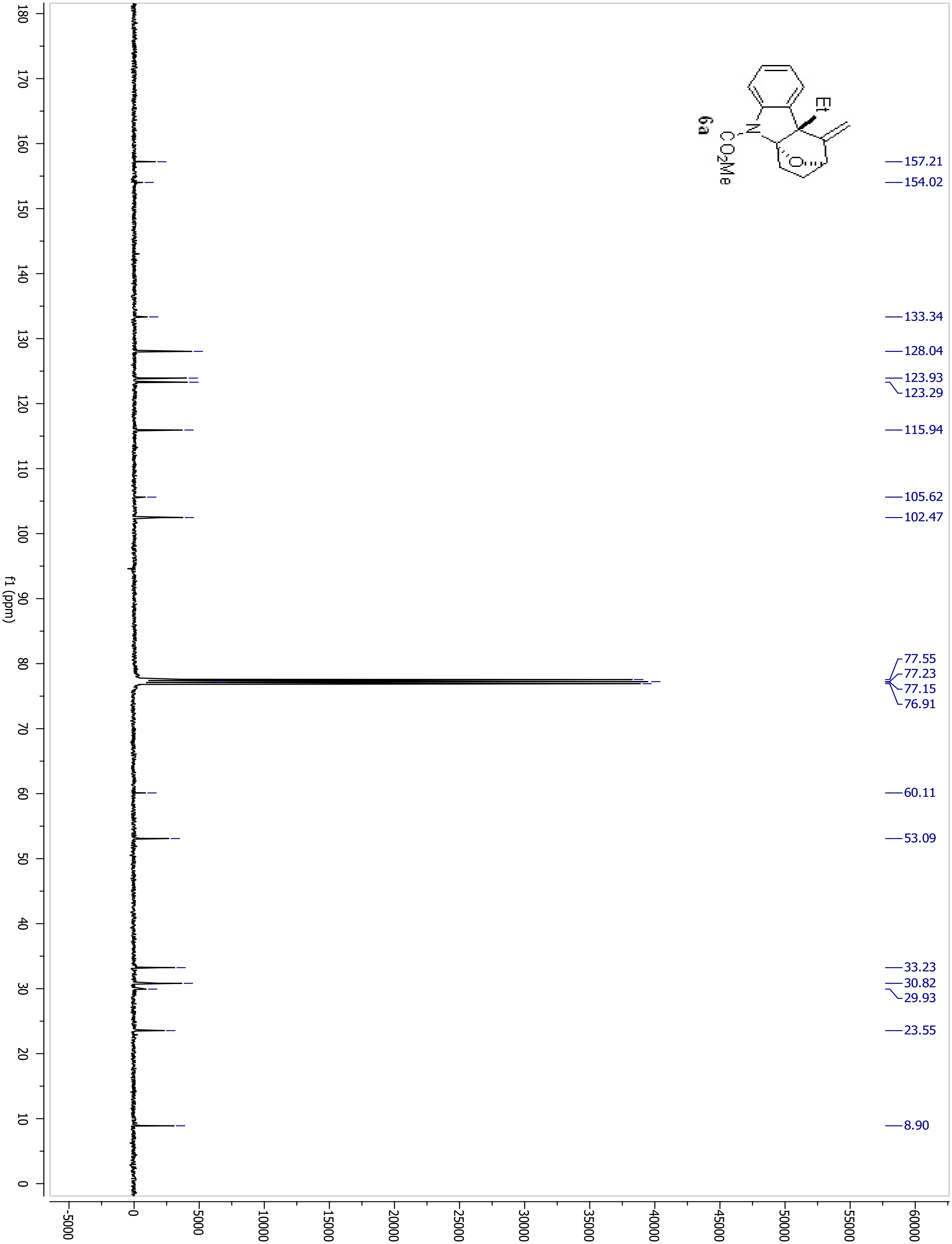

5o
Boc
OH
150.91
135.93
135.83
130.80
123.83
122.65
118.26
115.77
115.23
85.01
84.02
77.23
76.91
73.13
61.59
37.70
28.48
22.38
8.87
f1 (ppm)



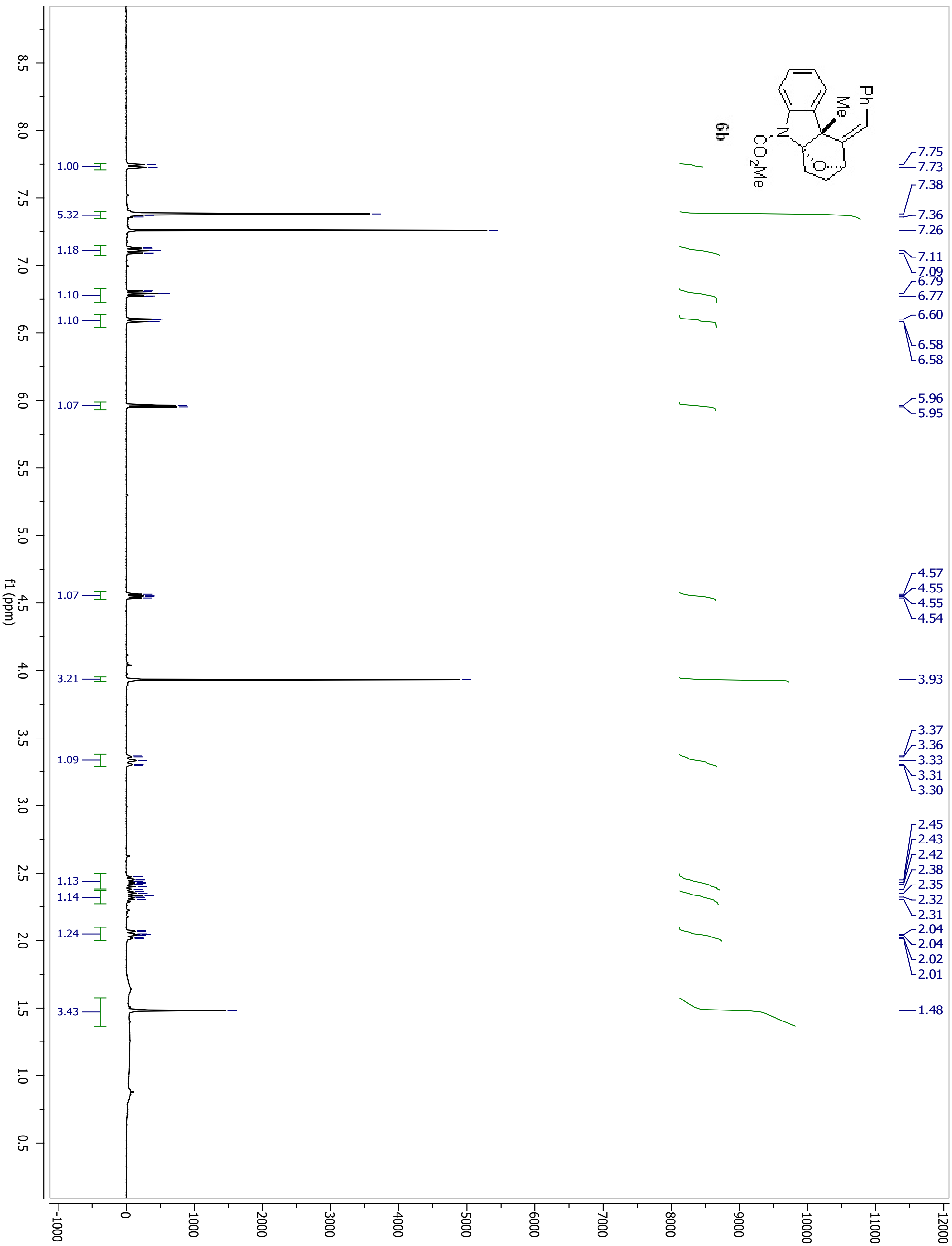
Me
N
CO_2Me
4
7.77
7.76
7.23
7.20
7.18
7.04
7.02
7.01
5.10
5.00
4.59
4.58
3.89
3.02
3.01
3.00
2.99
2.97
2.96
2.25
2.23
2.21
2.11
2.09
2.06
1.76
1.74
1.53
1.31
1.00
1.25
1.27
1.28
1.28
1.28
1.20
3.82
1.09
1.39
1.29
1.28
3.26
f1 (ppm)

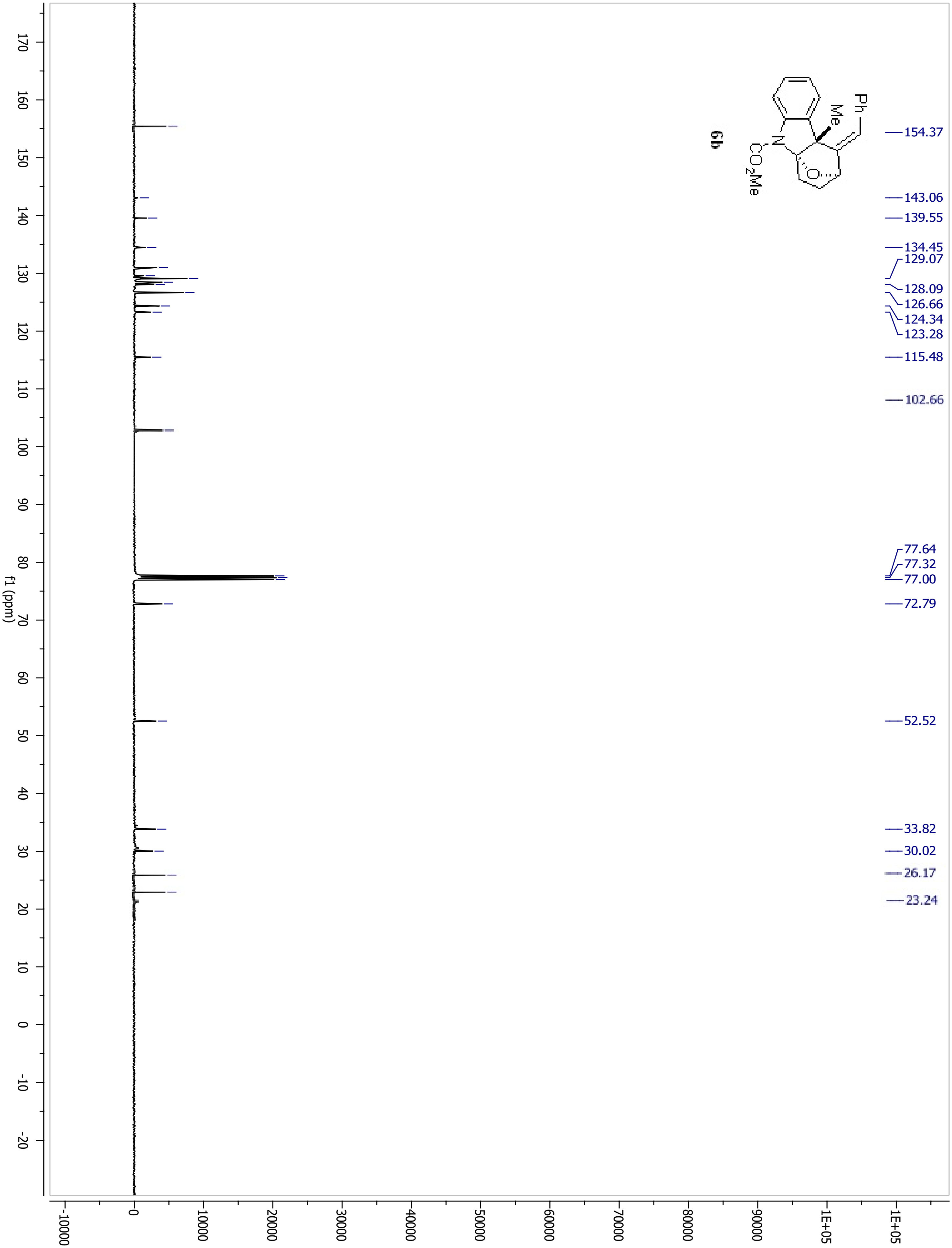

Me
O
N
CO2Me
4
156.91
154.36
141.66
136.09
127.94
123.96
122.88
116.20
106.05
102.42
77.55
77.28
77.23
76.91
56.86
53.11
30.62
26.25
23.40
f1 (ppm)


6a
Et
N
O
CO2Me
f1 (ppm)

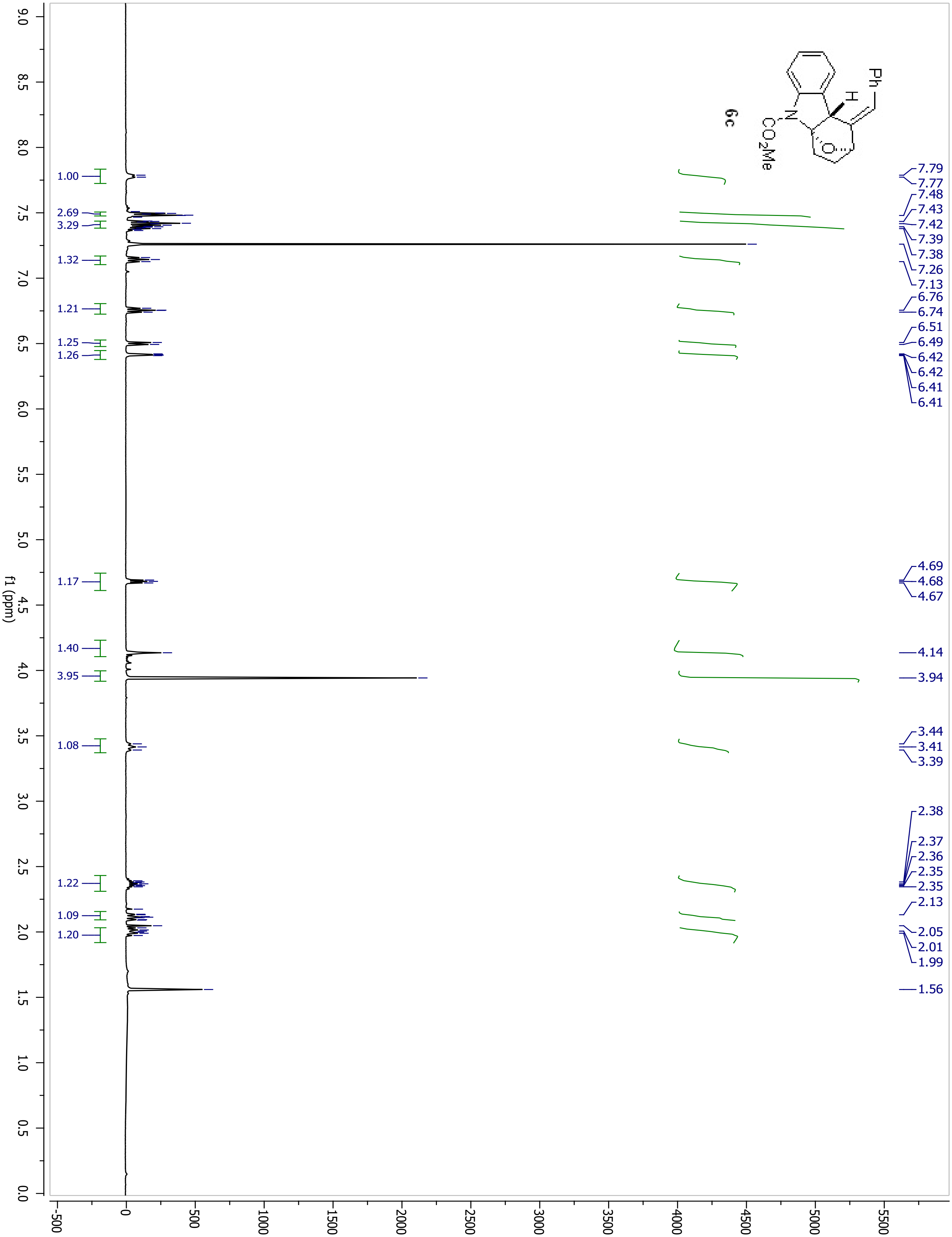


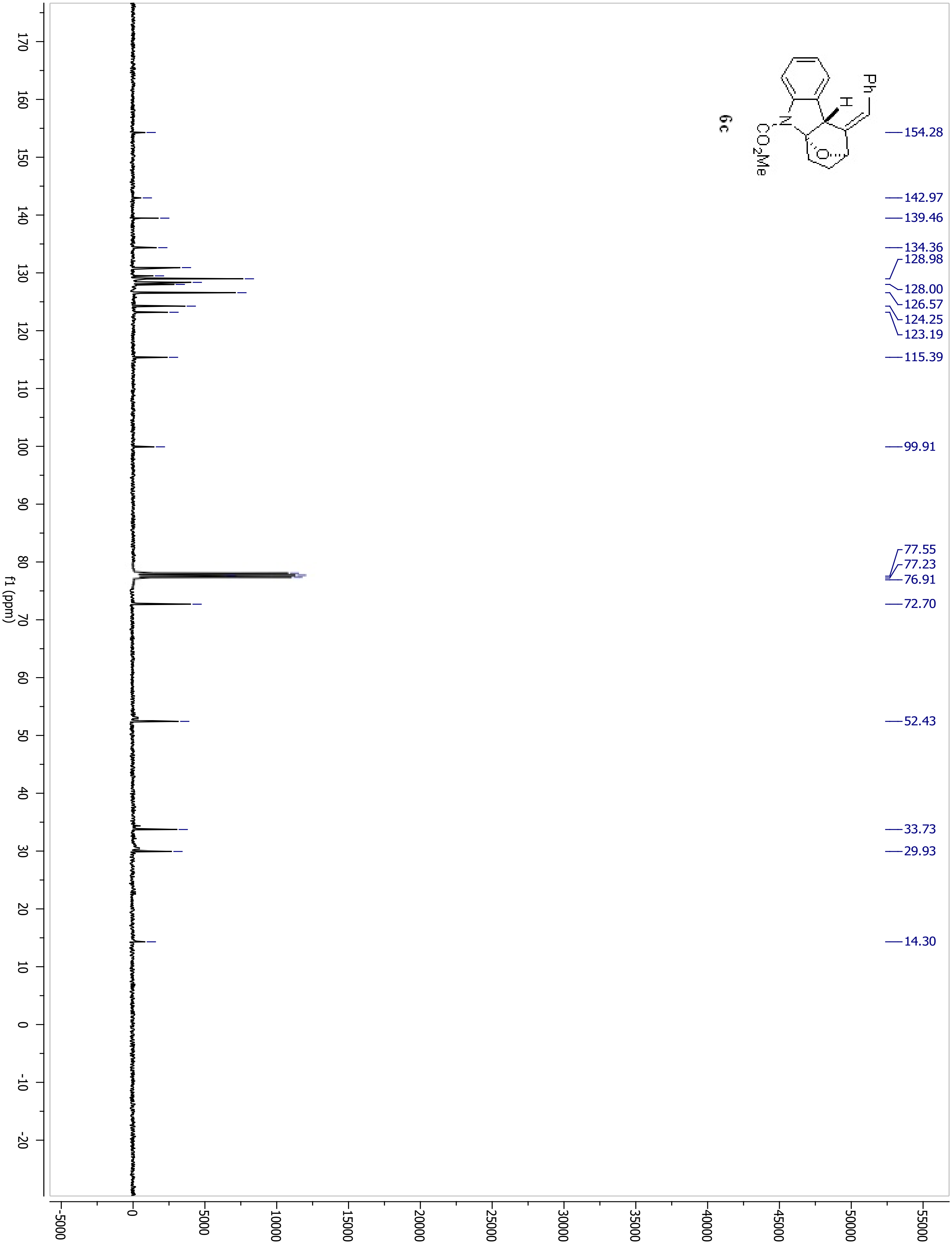
6a
Et
N
CO2Me
O
157.21
154.02
133.34
128.04
123.93
123.29
115.94
105.62
102.47
77.55
77.23
77.15
76.91
60.11
53.09
33.23
30.82
29.93
23.55
8.90
f1 (ppm)


6b
Ph
Me
N
O
CO2Me
7.75
7.73
7.38
7.36
7.26
7.11
7.09
6.79
6.77
6.60
6.58
6.58
5.96
5.95
4.57
4.55
4.55
4.54
3.93
3.37
3.36
3.33
3.31
3.30
2.45
2.43
2.42
2.38
2.35
2.32
2.31
2.04
2.04
2.02
2.01
1.48
1.00
5.32
1.18
1.10
1.10
1.07
1.07
3.21
1.09
1.13
1.14
1.24
3.43
f1 (ppm)



Ph
Me
N
O
CO_2Me
6b
154.37
143.06
139.55
134.45
129.07
128.09
126.66
124.34
123.28
115.48
102.66
77.64
77.32
77.00
72.79
52.52
33.82
30.02
26.17
23.24
f1 (ppm)


6c
f1 (ppm)


6c
Ph
H
N
O
CO2Me
154.28
142.97
139.46
134.36
128.98
128.00
126.57
124.25
123.19
115.39
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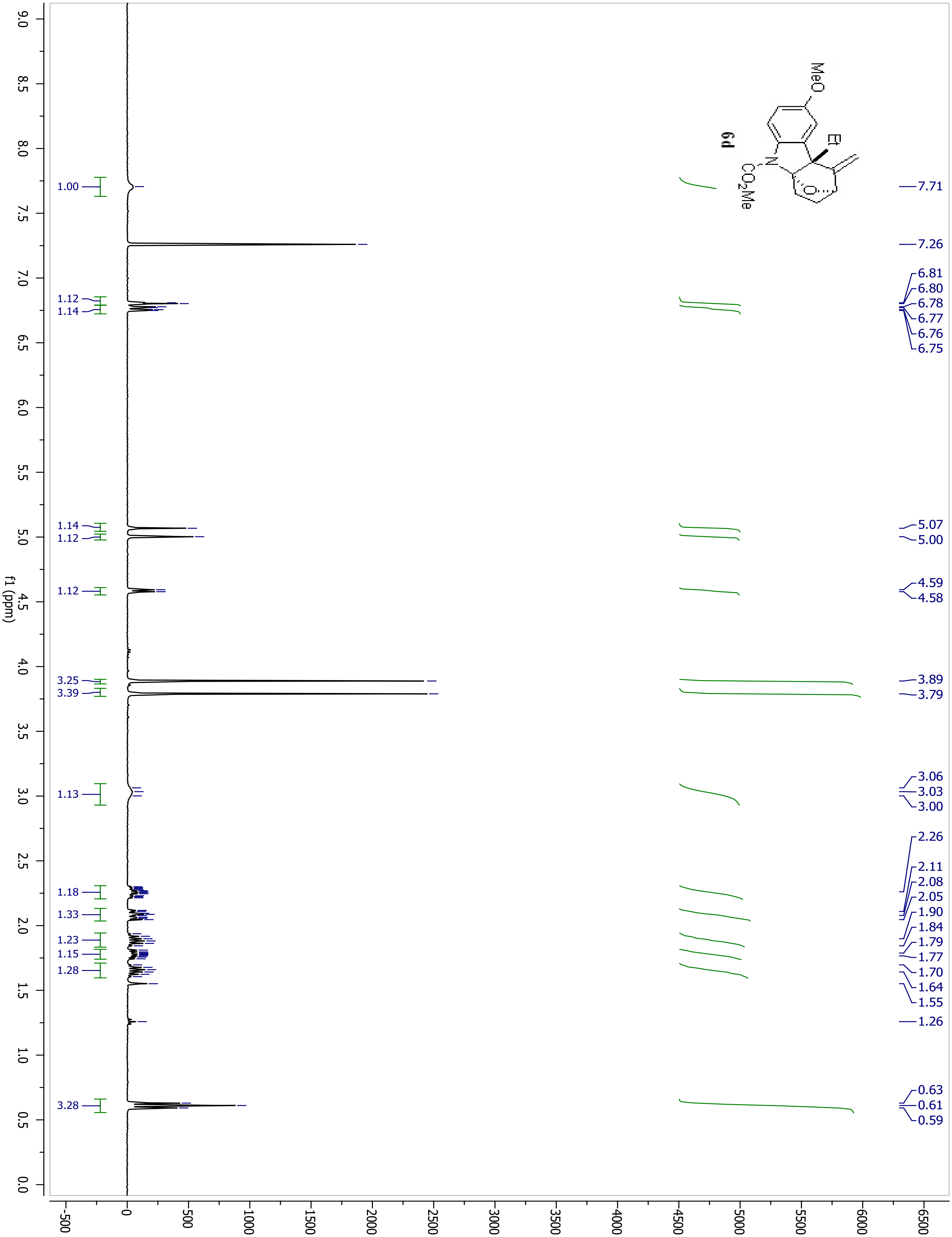
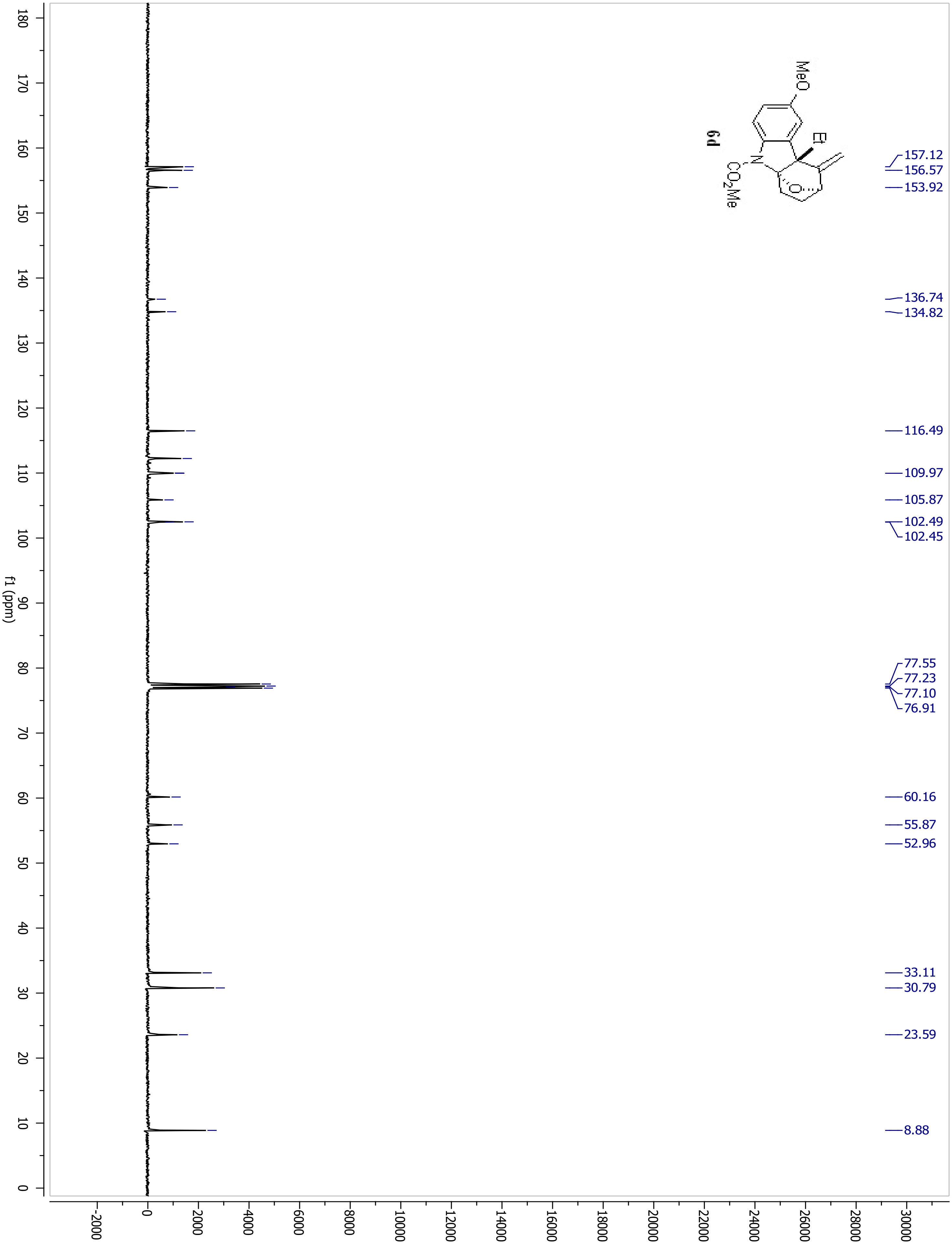
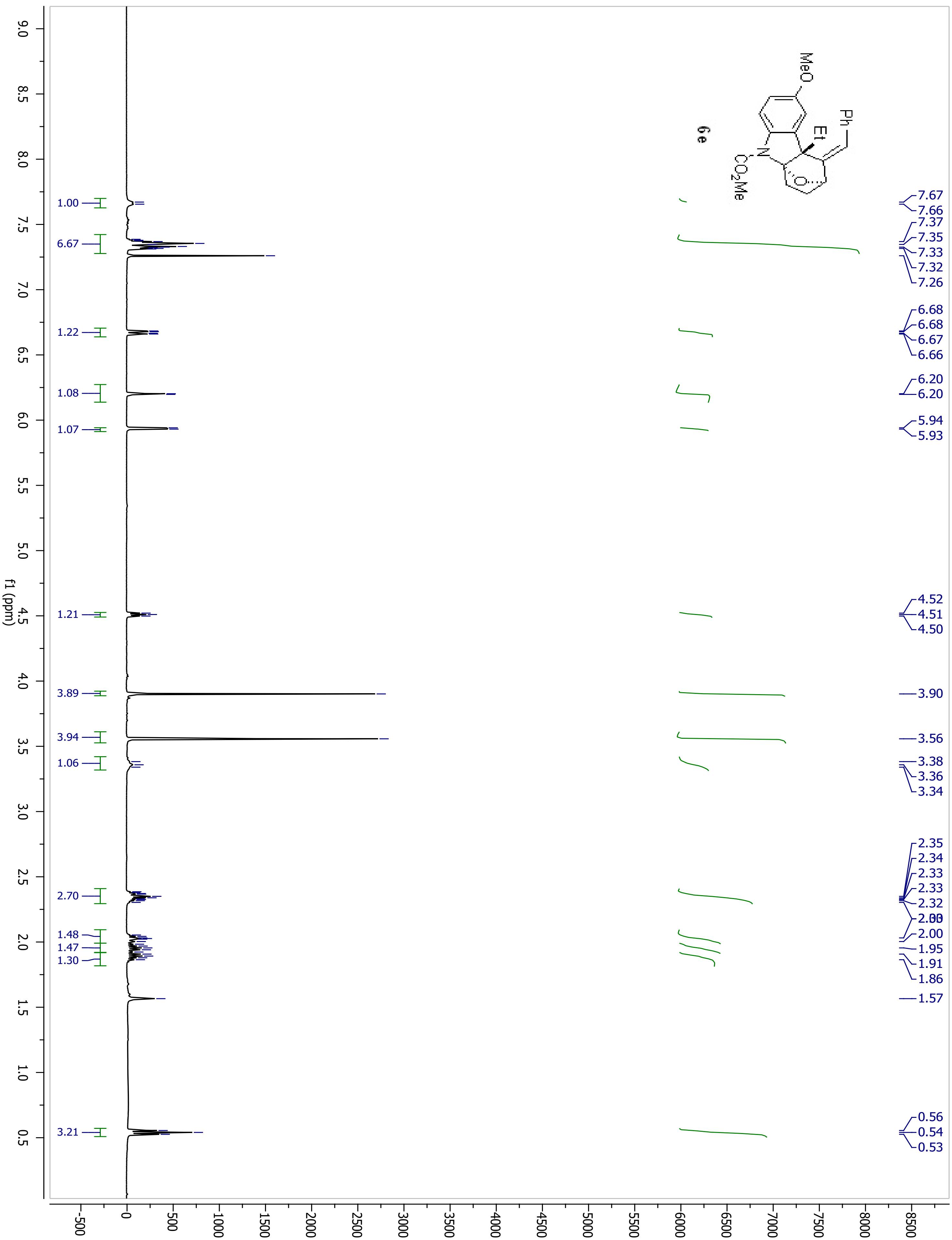
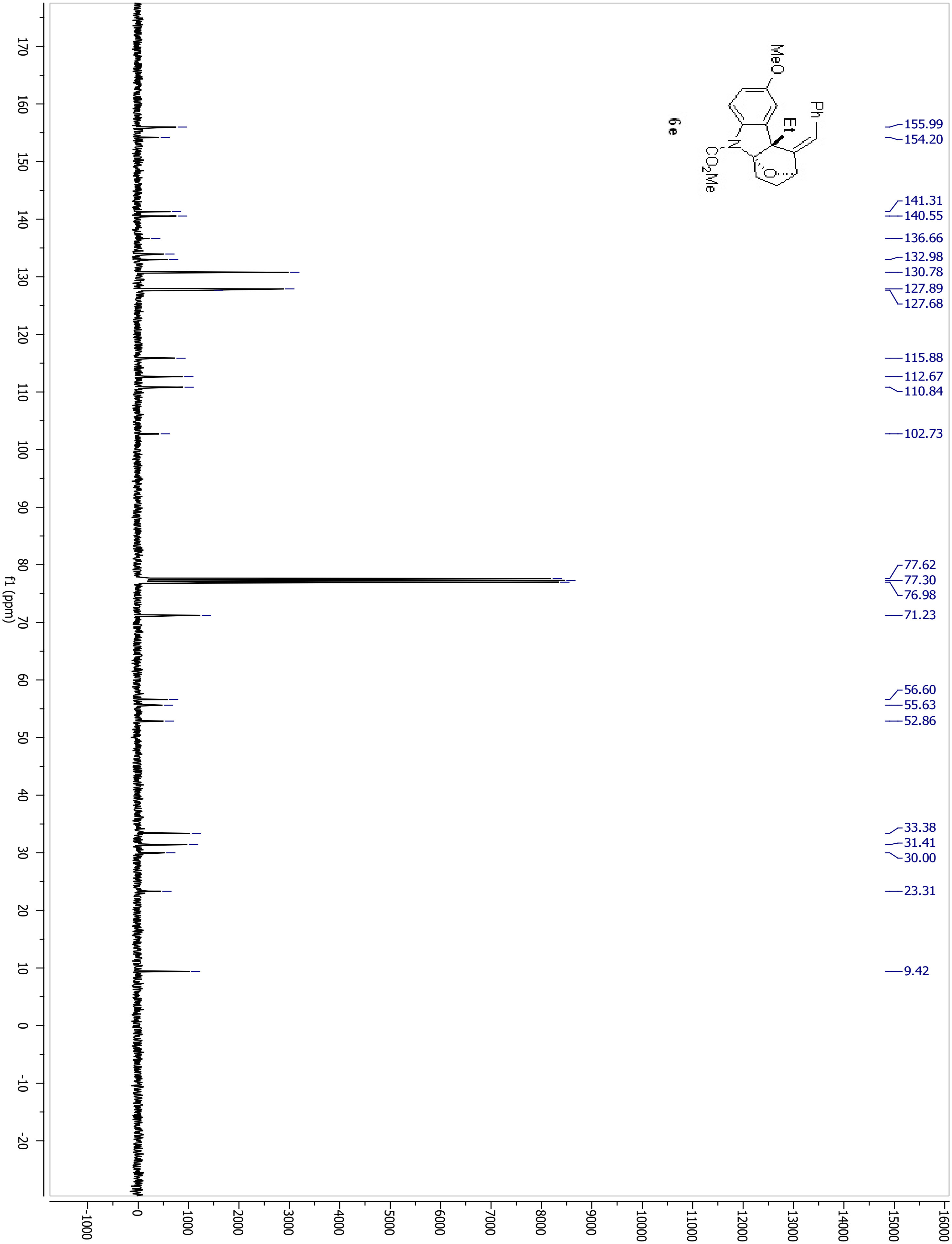
77.55
77.23
76.91
72.70
52.43
33.73
29.93
14.30
f1 (ppm)

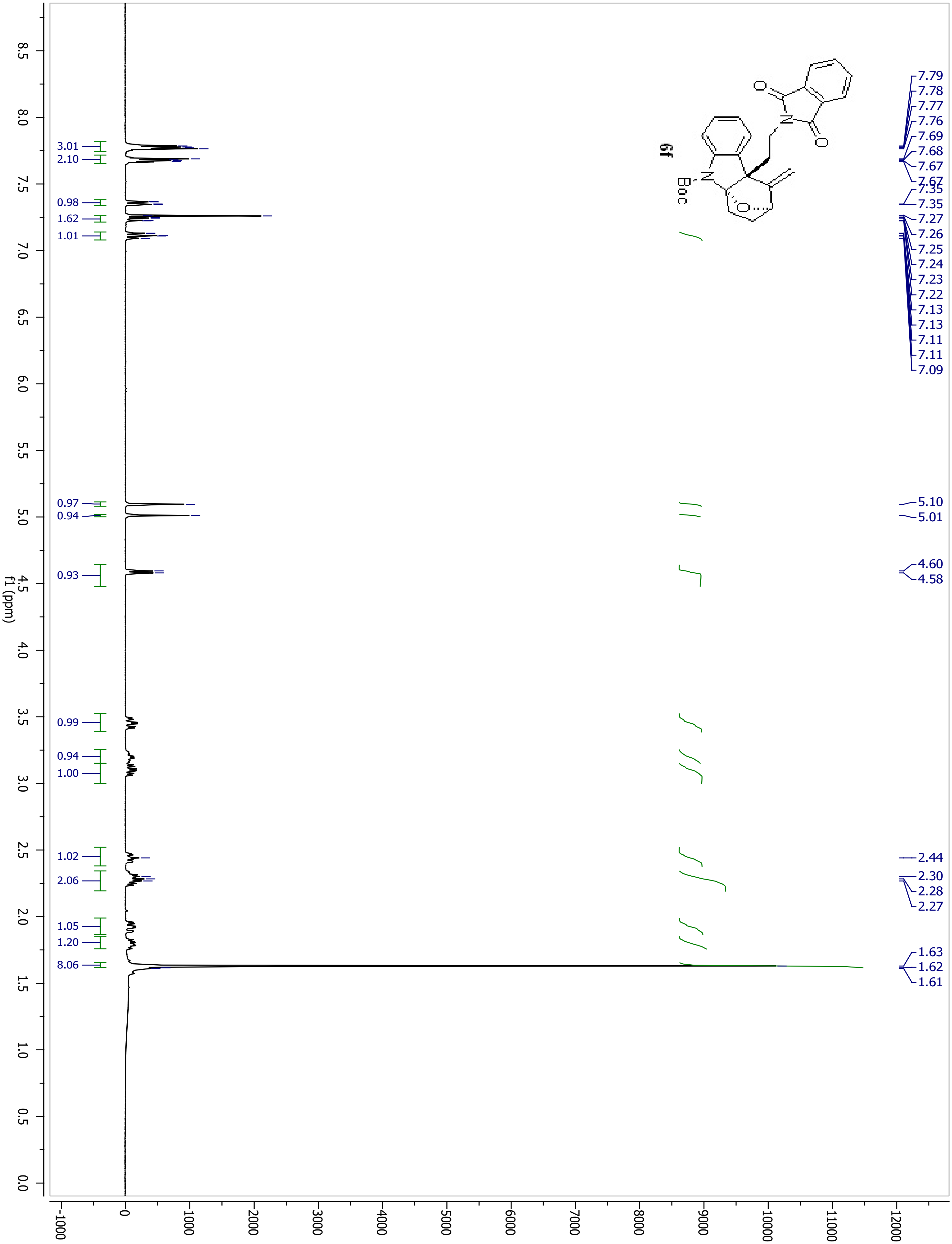

MeO
Et
N
O
CO2Me
6d
7.71
7.26
6.81
6.80
6.78
6.77
6.76
6.75
5.07
5.00
4.59
4.58
3.89
3.79
3.06
3.03
3.00
2.26
2.11
2.08
2.05
1.90
1.84
1.79
1.77
1.70
1.64
1.55
1.26
0.63
0.61
0.59
1.00
1.12
1.14
1.14
1.12
1.12
3.25
3.39
1.13
1.18
1.33
1.23
1.15
1.28
3.28
f1 (ppm)

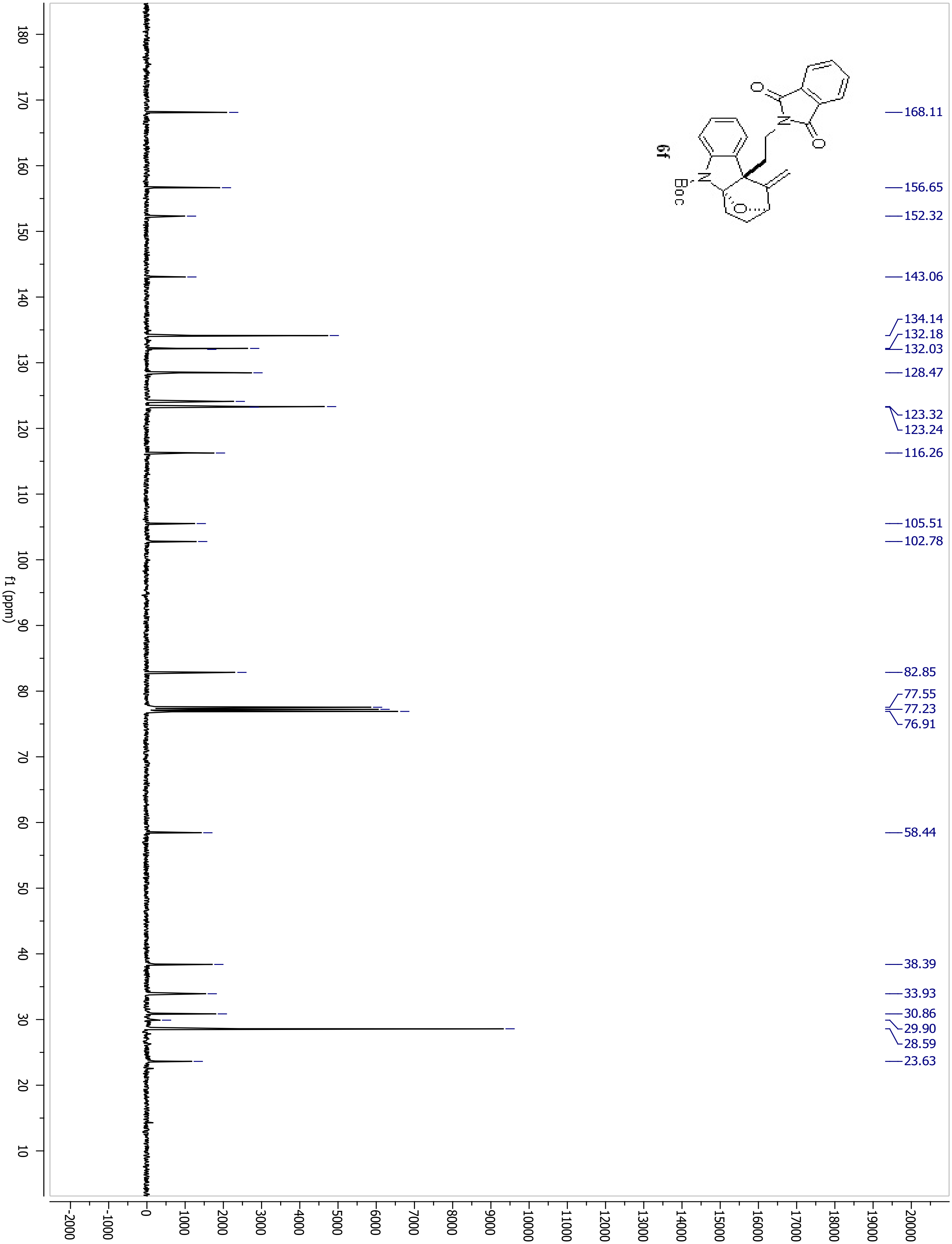

6d
MeO
Et
N
CO2Me
O
157.12
156.57
153.92
136.74
134.82
116.49
109.97
105.87
102.49
102.45
77.55
77.23
77.10
76.91
60.16
55.87
52.96
33.11
30.79
23.59
8.88
f1 (ppm)

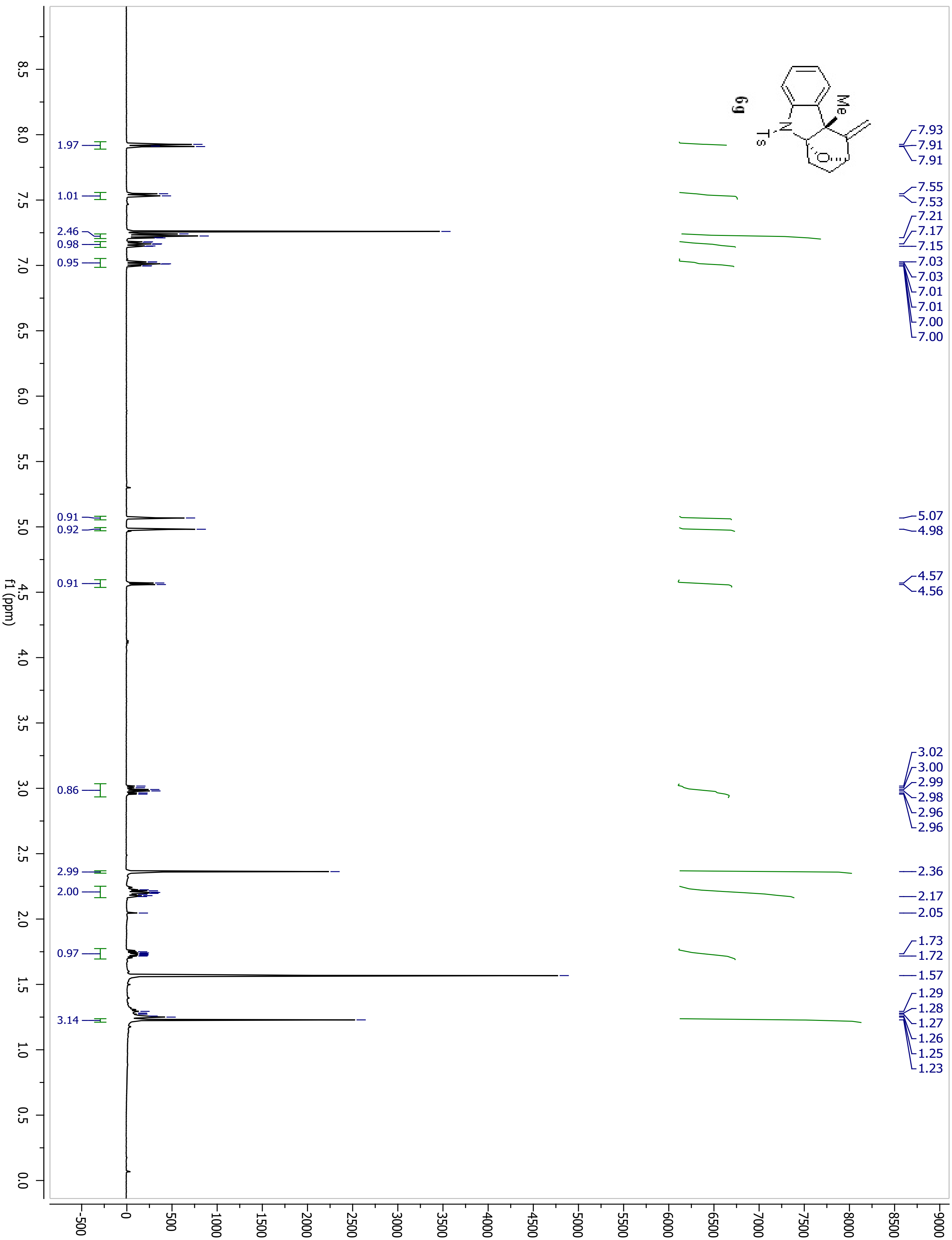

6e
MeO
Ph
Et
N
O
CO2Me
f1 (ppm)
1.00
6.67
1.22
1.08
1.07
1.21
3.89
3.94
1.06
2.70
1.48
1.47
1.30
3.21
7.67
7.66
7.37
7.35
7.33
7.32
7.26
6.68
6.68
6.67
6.66
6.20
6.20
5.94
5.93
4.52
4.51
4.50
3.90
3.56
3.38
3.36
3.34
2.35
2.34
2.33
2.33
2.32
2.00
2.00
1.95
1.91
1.86
1.57
0.56
0.54
0.53

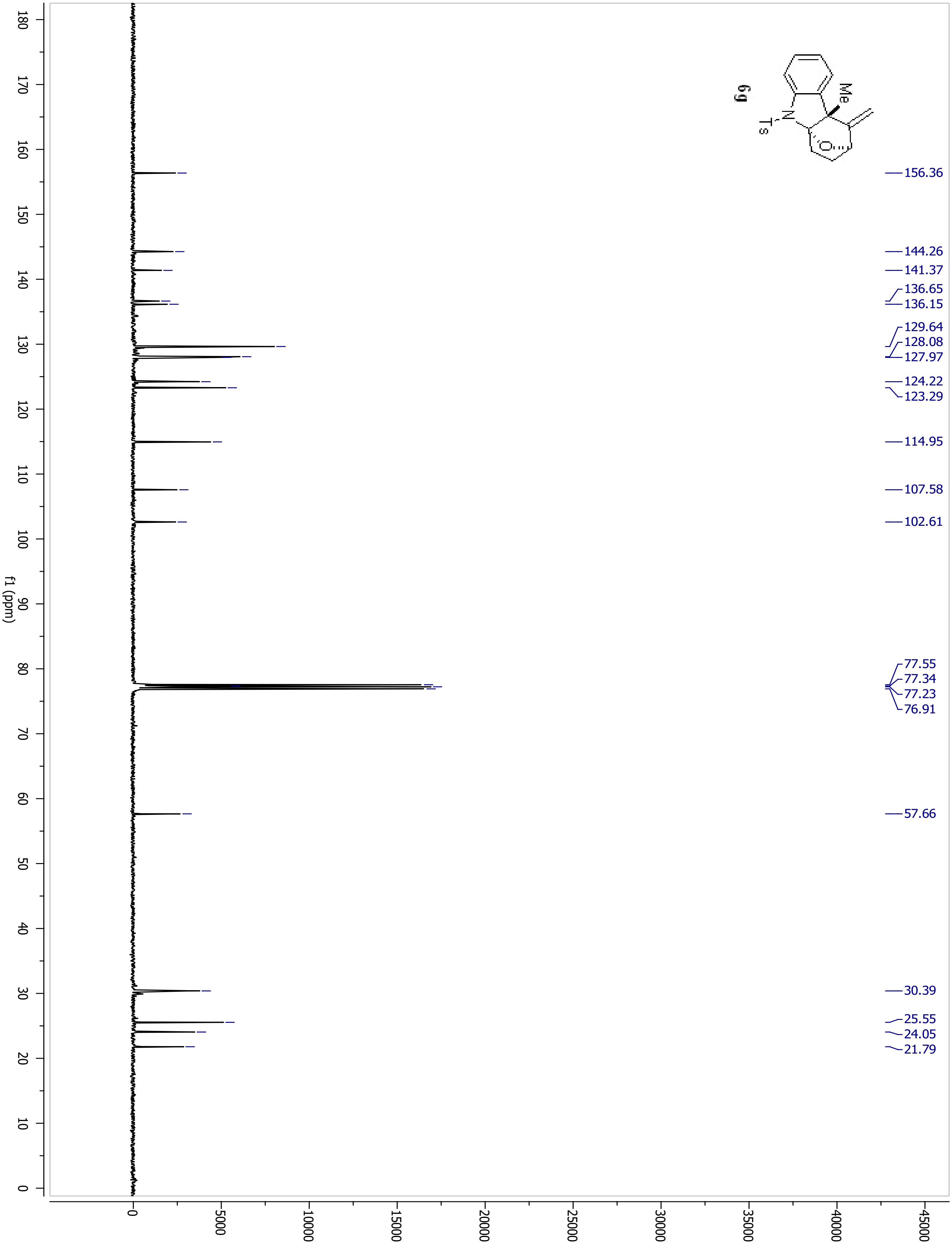


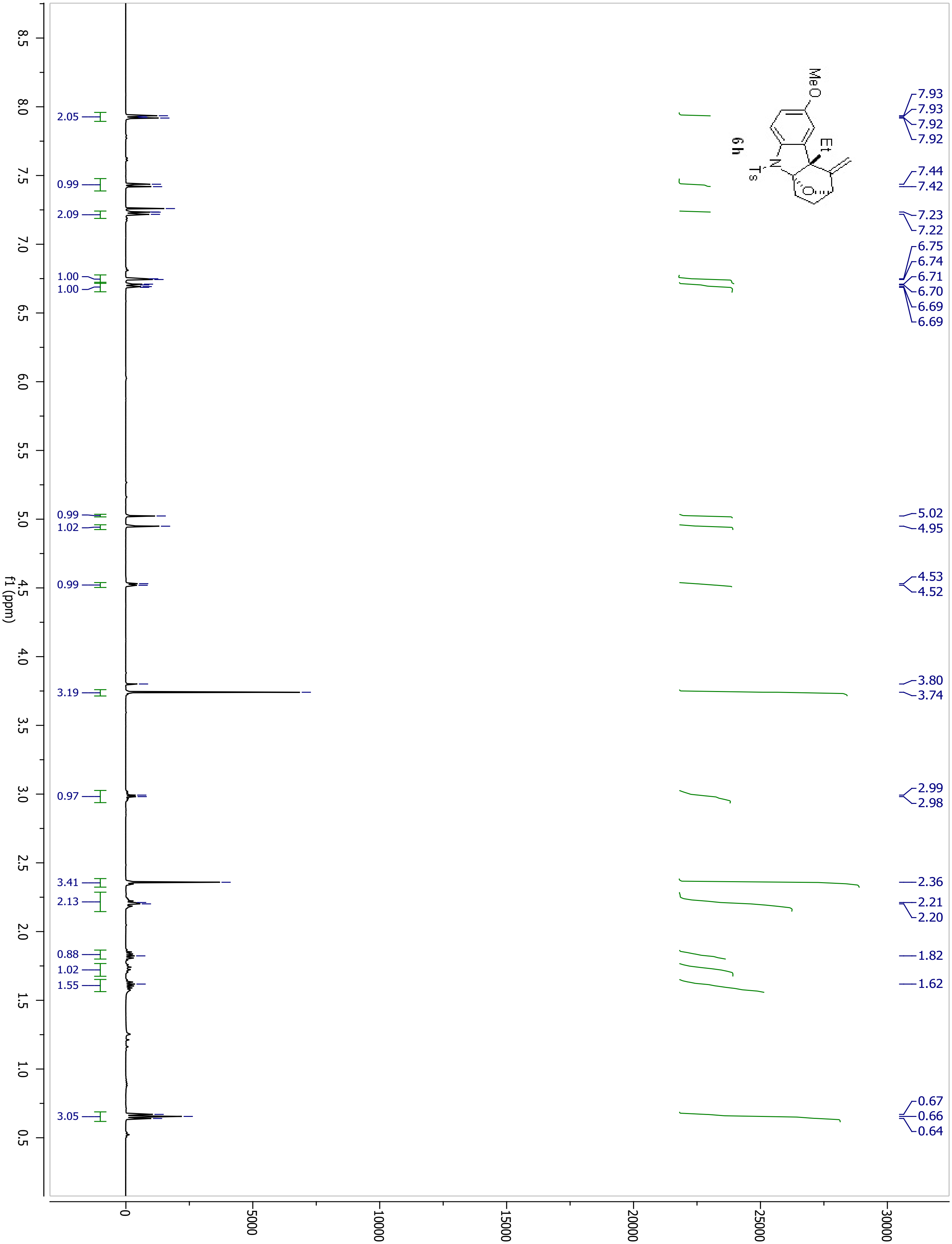
6e
MeO
Ph
Et
N
CO2Me
155.99
154.20
141.31
140.55
136.66
132.98
130.78
127.89
127.68
115.88
112.67
110.84
102.73
77.62
77.30
76.98
71.23
56.60
55.63
52.86
33.38
31.41
30.00
23.31
9.42
f1 (ppm)

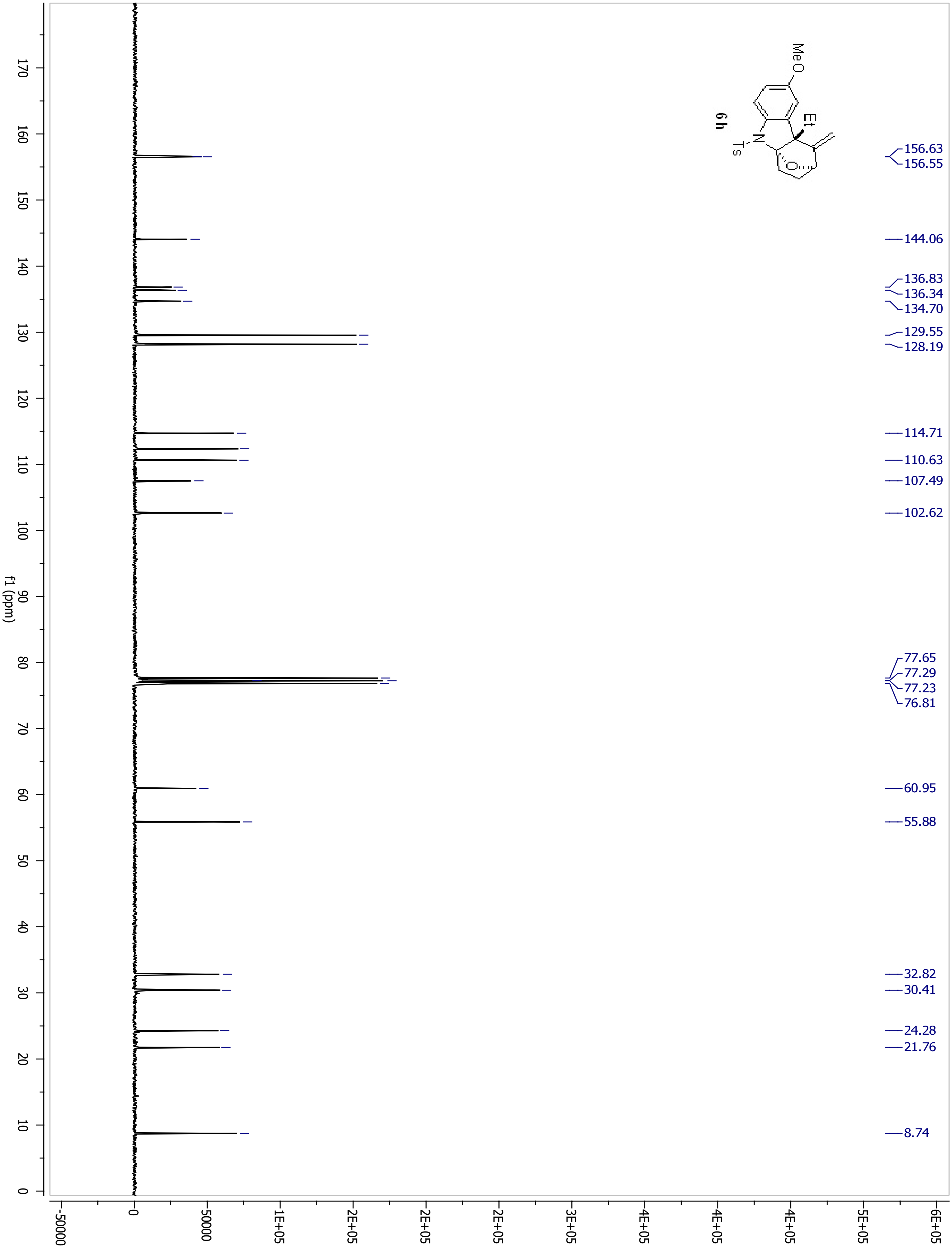

6f
Boc
f1 (ppm)
7.79
7.78
7.77
7.76
7.69
7.68
7.67
7.67
7.35
7.35
7.27
7.26
7.25
7.24
7.23
7.22
7.13
7.13
7.11
7.11
7.09
5.10
5.01
4.60
4.58
2.44
2.30
2.28
2.27
1.63
1.62
1.61
3.01
2.10
0.98
1.62
1.01
0.97
0.94
0.93
0.99
0.94
1.00
1.02
2.06
1.05
1.20
8.06

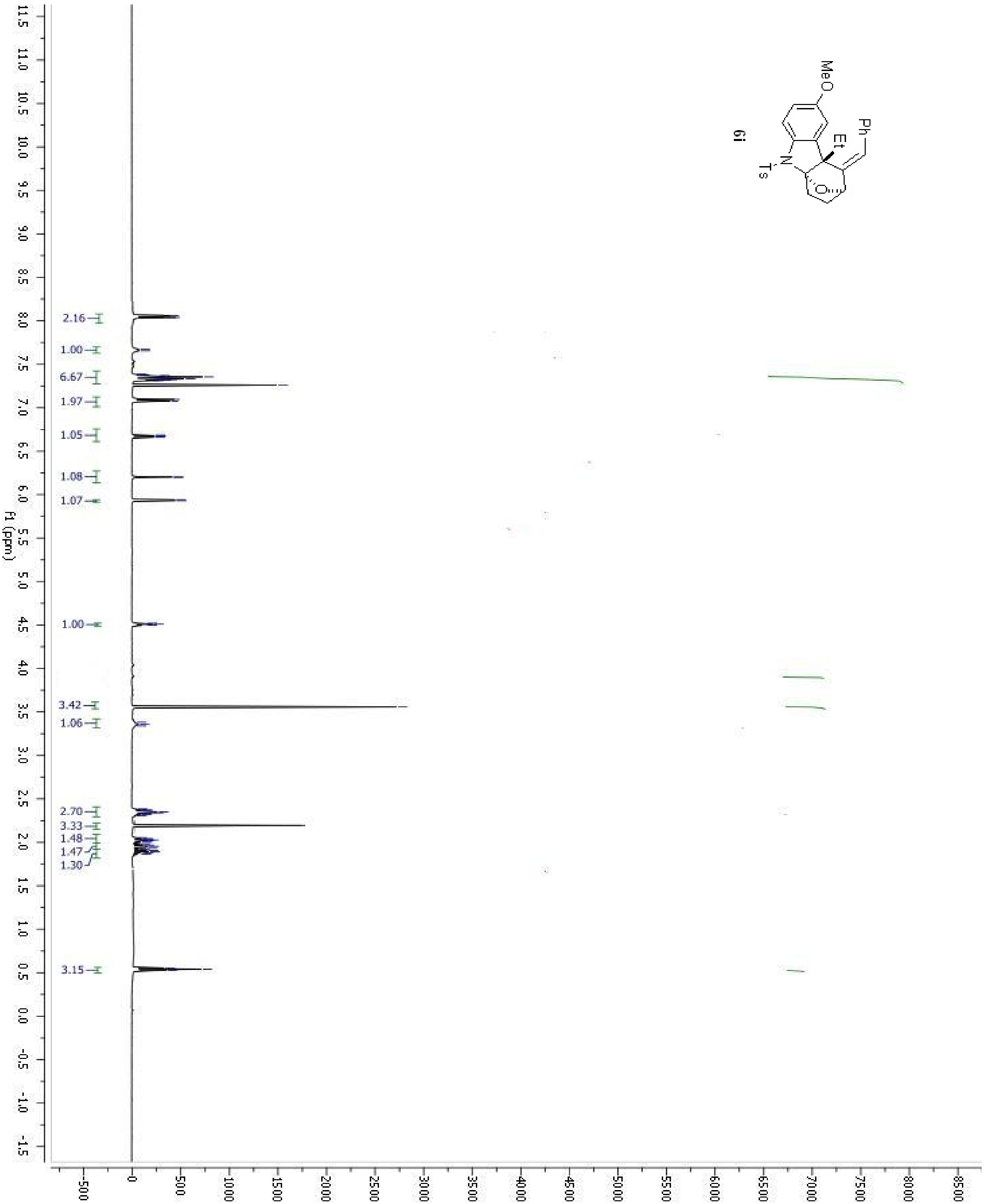

6f
Boc
168.11
156.65
152.32
143.06
134.14
132.18
132.03
128.47
123.32
123.24
116.26
105.51
102.78
82.85
77.55
77.23
76.91
58.44
38.39
33.93
30.86
29.90
28.59
23.63
f1 (ppm)

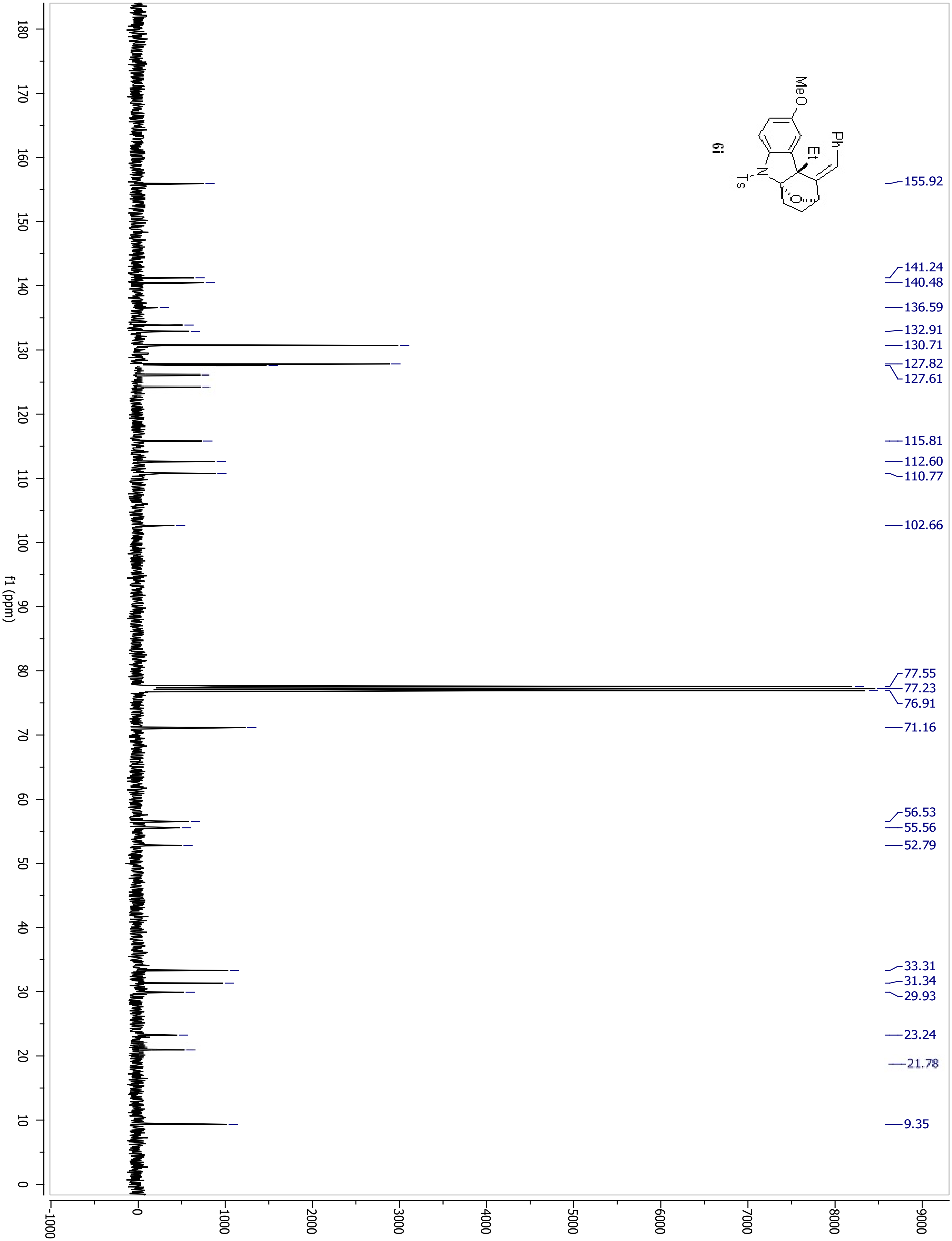

6g
Me
N
Ts
O
f1 (ppm)
7.93
7.91
7.91
7.55
7.53
7.21
7.17
7.15
7.03
7.03
7.01
7.01
7.00
7.00
5.07
4.98
4.57
4.56
3.02
3.00
2.99
2.98
2.96
2.96
2.36
2.17
2.05
1.73
1.72
1.57
1.29
1.28
1.27
1.26
1.25
1.23
1.97
1.01
2.46
0.98
0.95
0.91
0.92
0.91
0.86
2.99
2.00
0.97
3.14

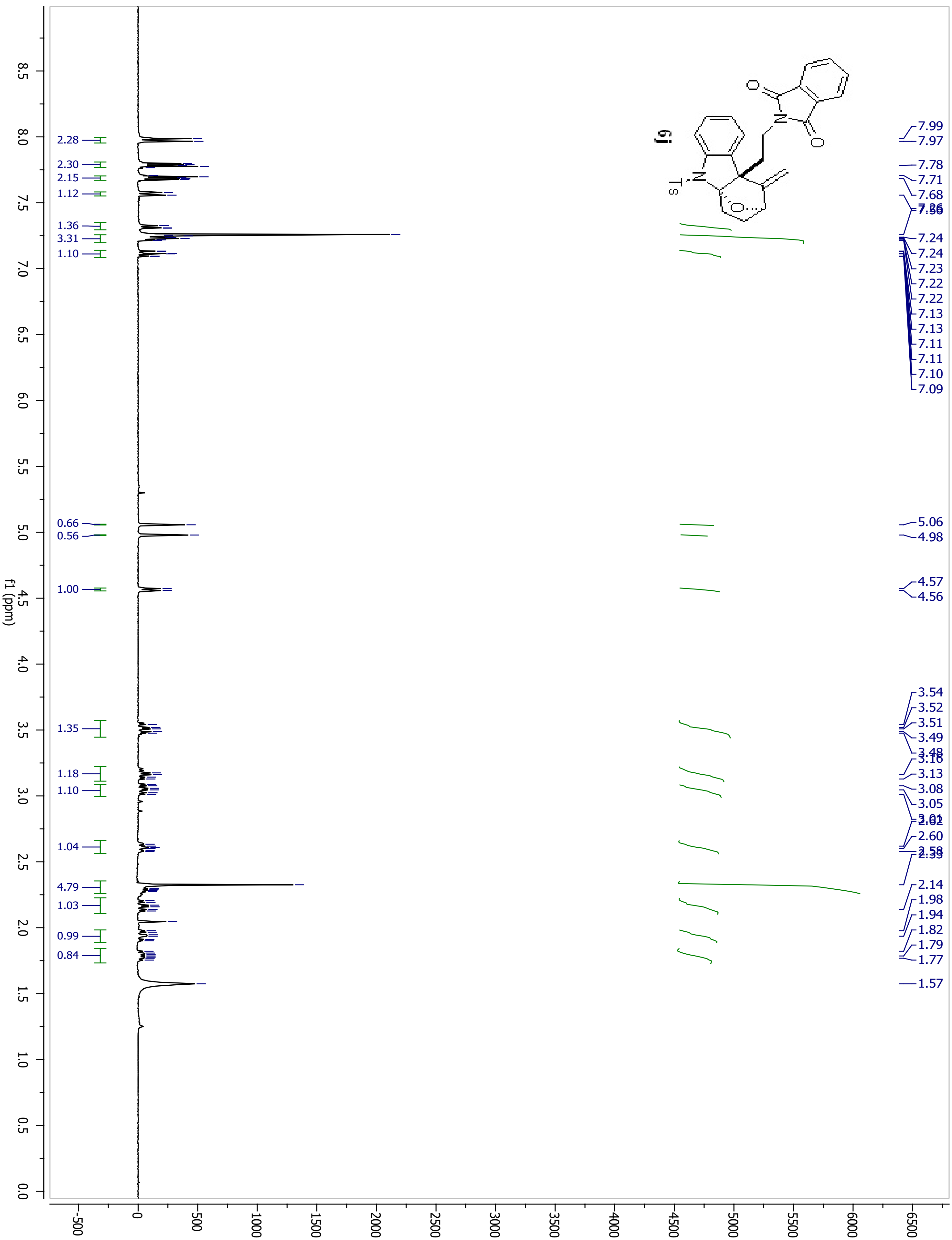

6g
Me
N
Ts
O
156.36
144.26
141.37
136.65
136.15
129.64
128.08
127.97
124.22
123.29
114.95
107.58
102.61
77.55
77.34
77.23
76.91
57.66
30.39
25.55
24.05
21.79
f1 (ppm)

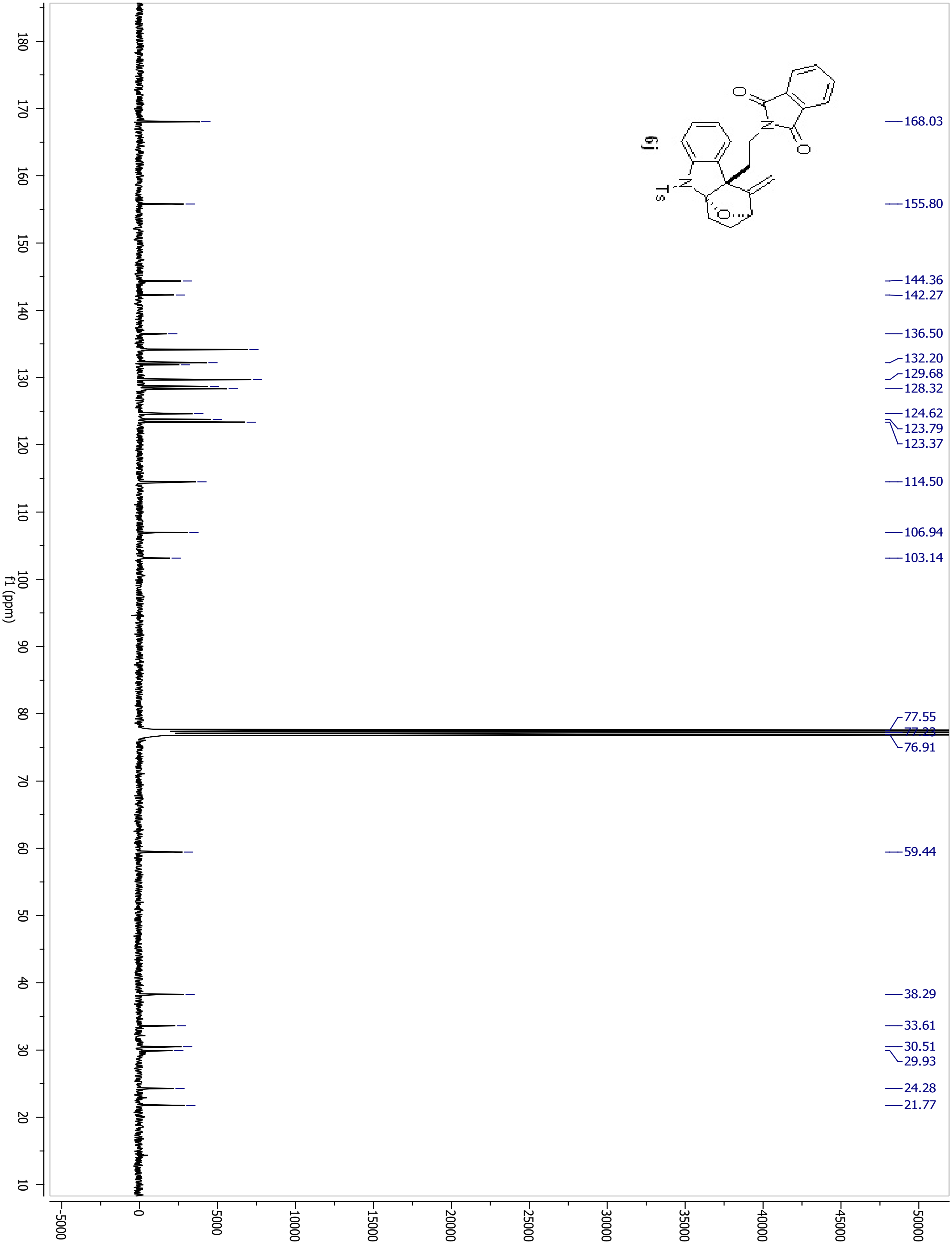

6h
MeO
Et
N
Ts
O
7.93
7.93
7.92
7.92
7.44
7.42
7.23
7.22
6.75
6.74
6.71
6.70
6.69
6.69
5.02
4.95
4.53
4.52
3.80
3.74
2.99
2.98
2.36
2.21
2.20
1.82
1.62
0.67
0.66
0.64
2.05
0.99
2.09
1.00
1.00
0.99
1.02
0.99
3.19
0.97
3.41
2.13
0.88
1.02
1.55
3.05
f1 (ppm)

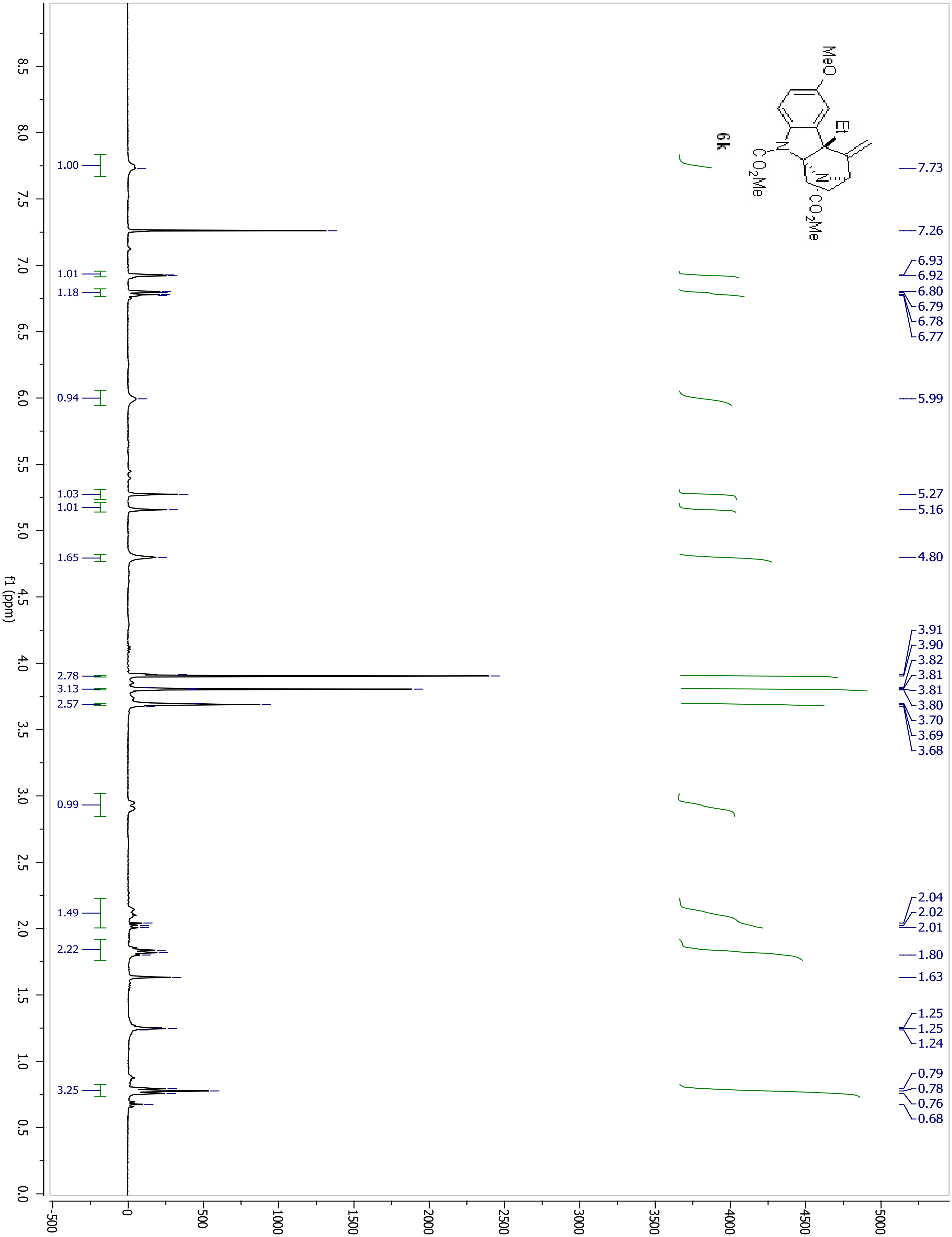

MeO
Et
N
Ts
6h
156.63
156.55
144.06
136.83
136.34
134.70
129.55
128.19
114.71
110.63
107.49
102.62
77.65
77.29
77.23
76.81
60.95
55.88
32.82
30.41
24.28
21.76
8.74
f1 (ppm)

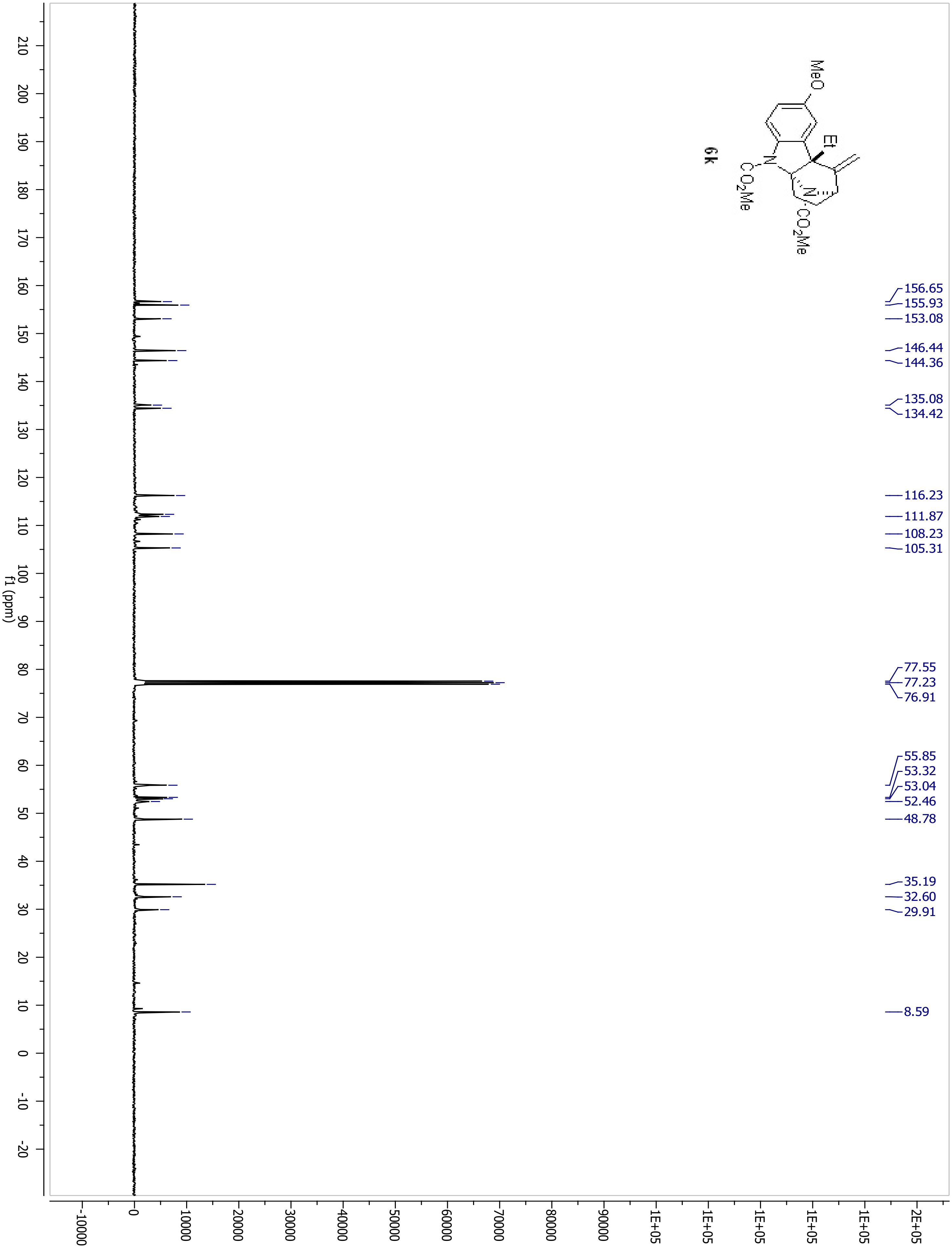

MeO
Ph
Et
N
Ts
O
6i
2.16
1.00
6.67
1.97
1.05
1.08
1.07
1.00
3.42
1.06
2.70
3.33
1.48
1.47
1.30
3.15
f1 (ppm)


6i
MeO
Ph
Et
N
Ts
O
155.92
141.24
140.48
136.59
132.91
130.71
127.82
127.61
115.81
112.60
110.77
102.66
77.55
77.23
76.91
71.16
56.53
55.56
52.79
33.31
31.34
29.93
23.24
21.78
9.35
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000

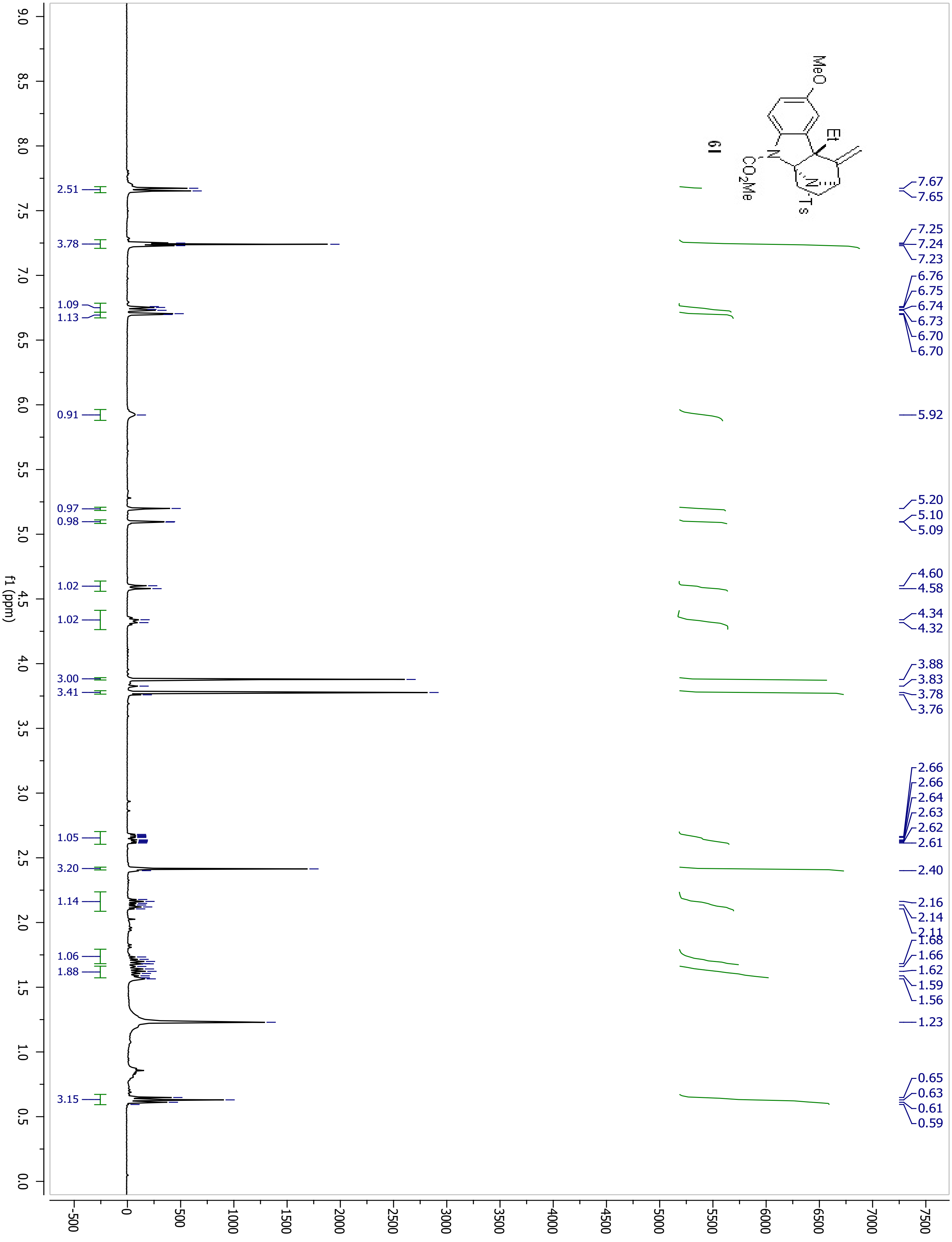

6j
Ts
f1 (ppm)

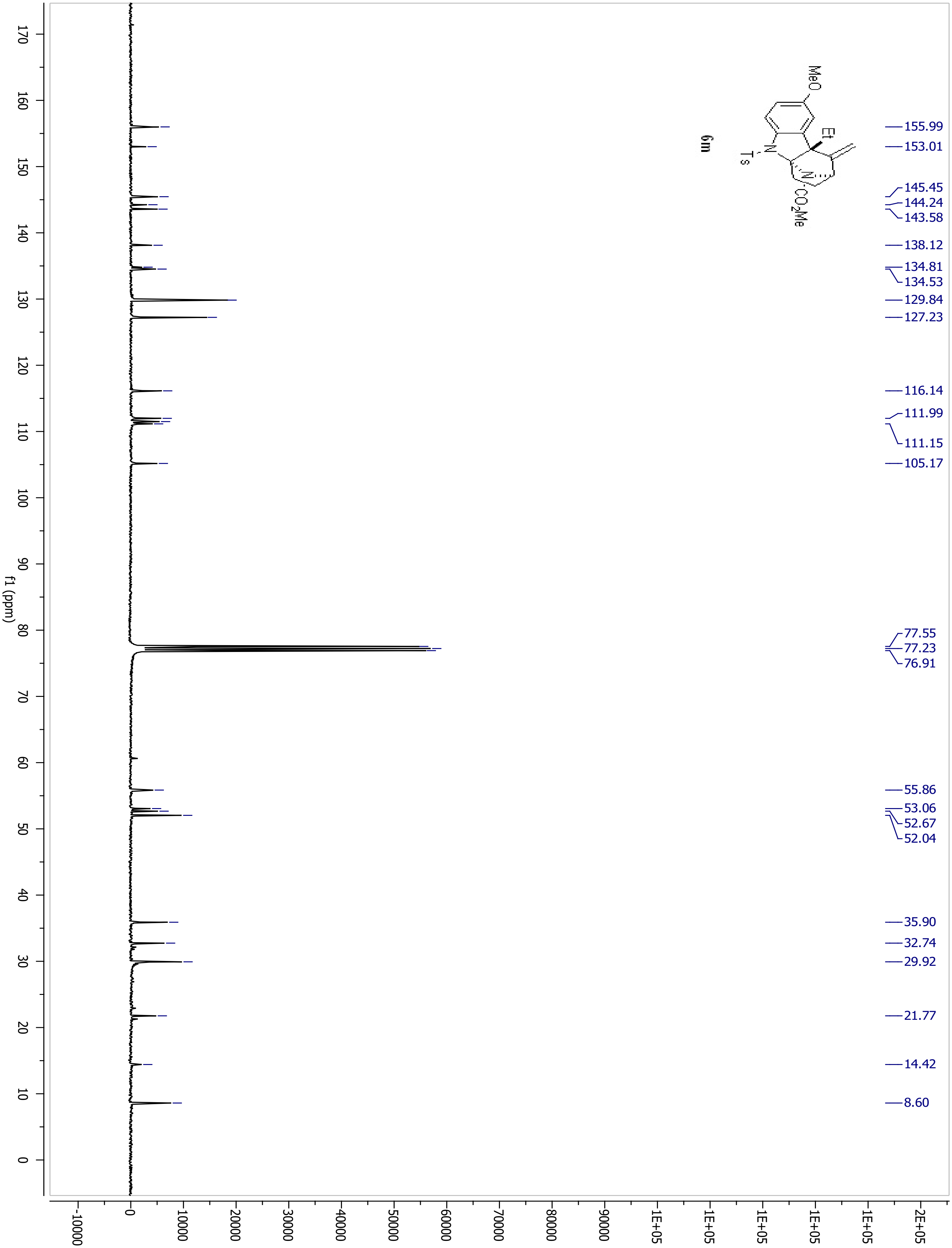

6j
Ts
N
O
168.03
155.80
144.36
142.27
136.50
132.20
129.68
128.32
124.62
123.79
123.37
114.50
106.94
103.14
77.55
77.23
76.91
59.44
38.29
33.61
30.51
29.93
24.28
21.77
f1 (ppm)

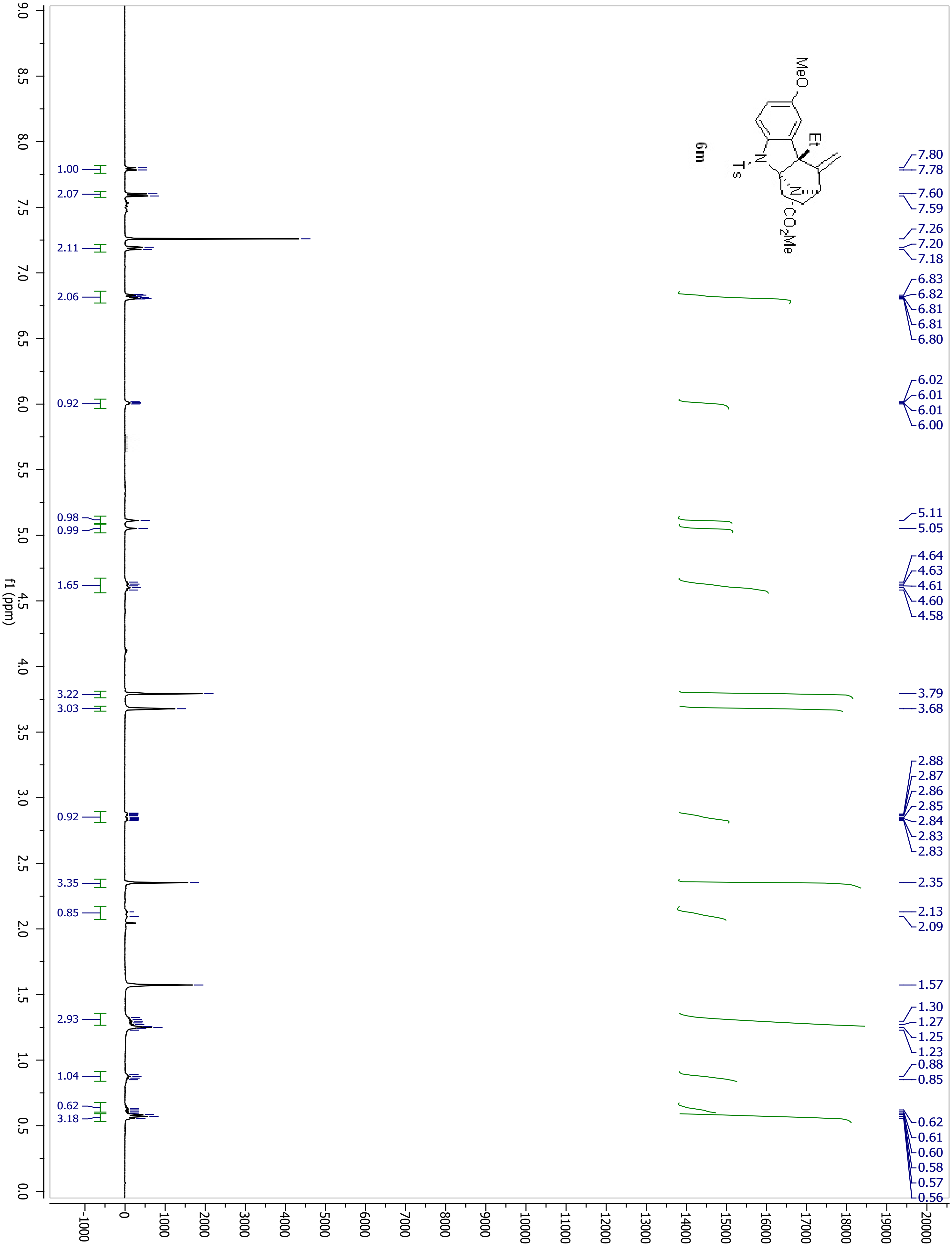

6k
MeO
Et
N
CO2Me
7.73
7.26
6.93
6.92
6.80
6.79
6.78
6.77
5.99
5.27
5.16
4.80
3.91
3.90
3.82
3.81
3.81
3.80
3.70
3.69
3.68
2.04
2.02
2.01
1.80
1.63
1.25
1.25
1.24
0.79
0.78
0.76
0.68
1.00
1.01
1.18
0.94
1.03
1.01
1.65
2.78
3.13
2.57
0.99
1.49
2.22
3.25
f1 (ppm)

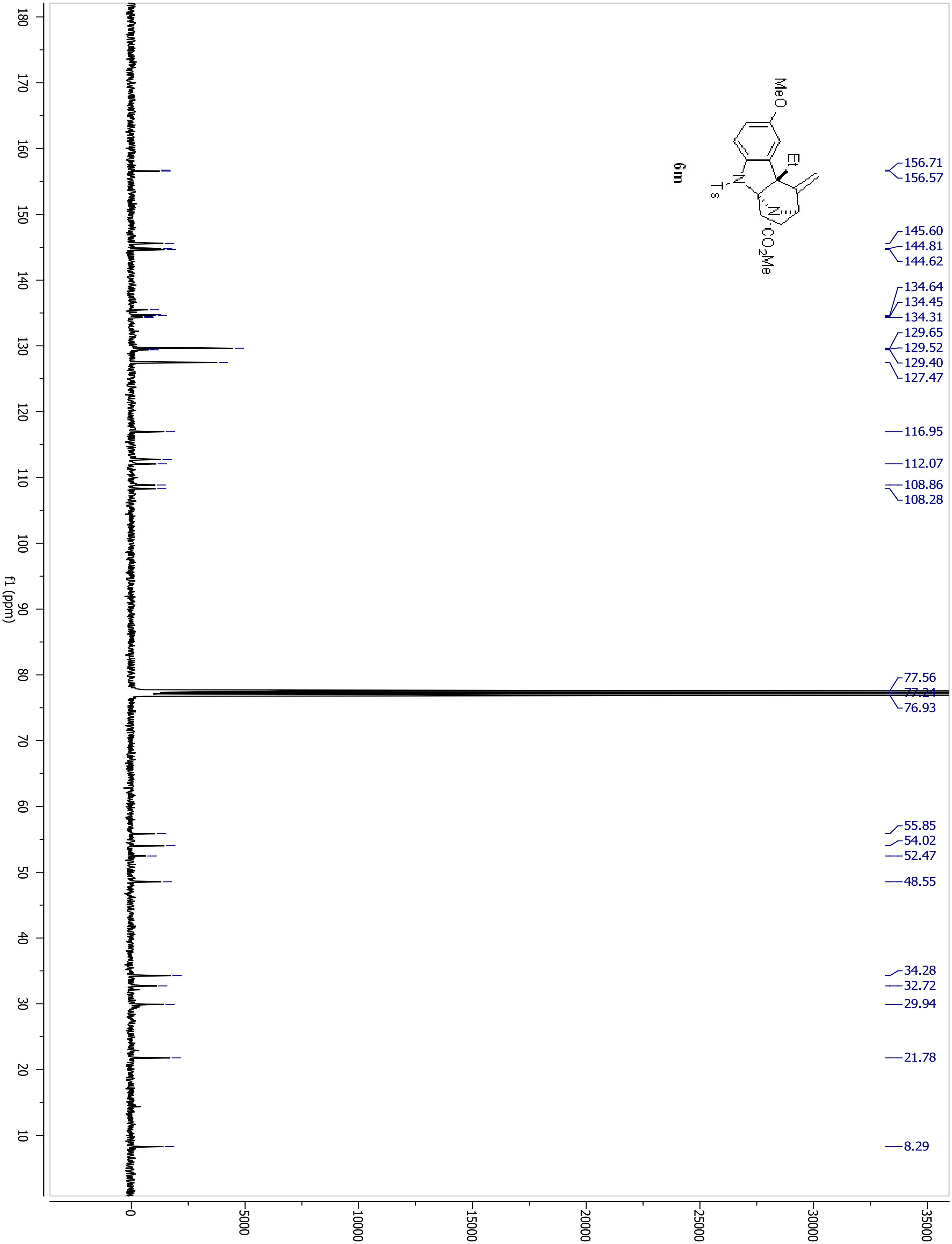


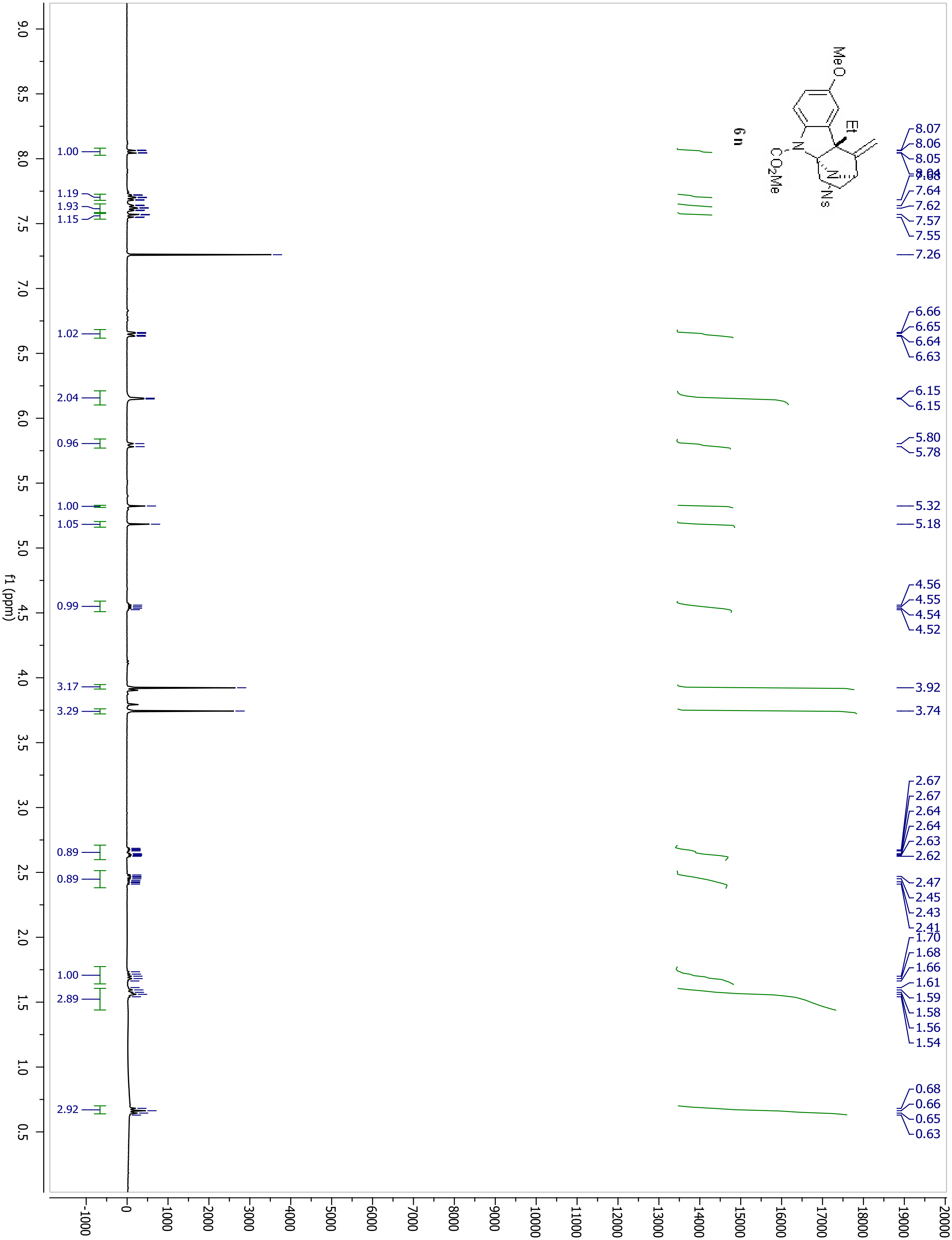
MeO
Et
N
CO2Me
N
CO2Me
6k
156.65
155.93
153.08
146.44
144.36
135.08
134.42
116.23
111.87
108.23
105.31
77.55
77.23
76.91
55.85
53.32
53.04
52.46
48.78
35.19
32.60
29.91
8.59
f1 (ppm)

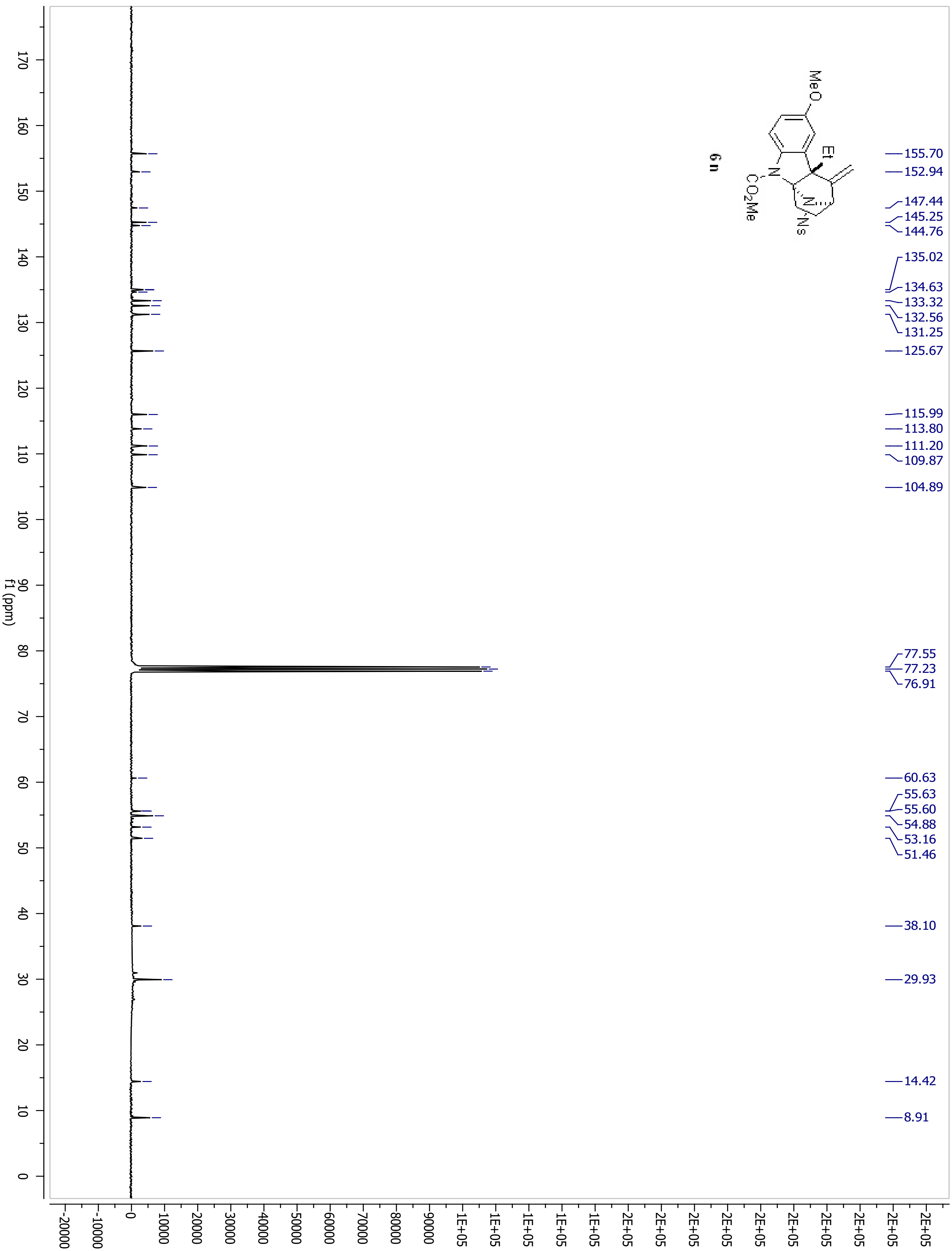

6l
MeO
Et
N
CO2Me
N-Ts
7.67
7.65
7.25
7.24
7.23
6.76
6.75
6.74
6.73
6.70
6.70
5.92
5.20
5.10
5.09
4.60
4.58
4.34
4.32
3.88
3.83
3.78
3.76
2.66
2.66
2.64
2.63
2.62
2.61
2.40
2.16
2.14
2.11
1.68
1.66
1.62
1.59
1.56
1.23
0.65
0.63
0.61
0.59
2.51
3.78
1.09
1.13
0.91
0.97
0.98
1.02
1.02
3.00
3.41
1.05
3.20
1.14
1.06
1.88
3.15
f1 (ppm)

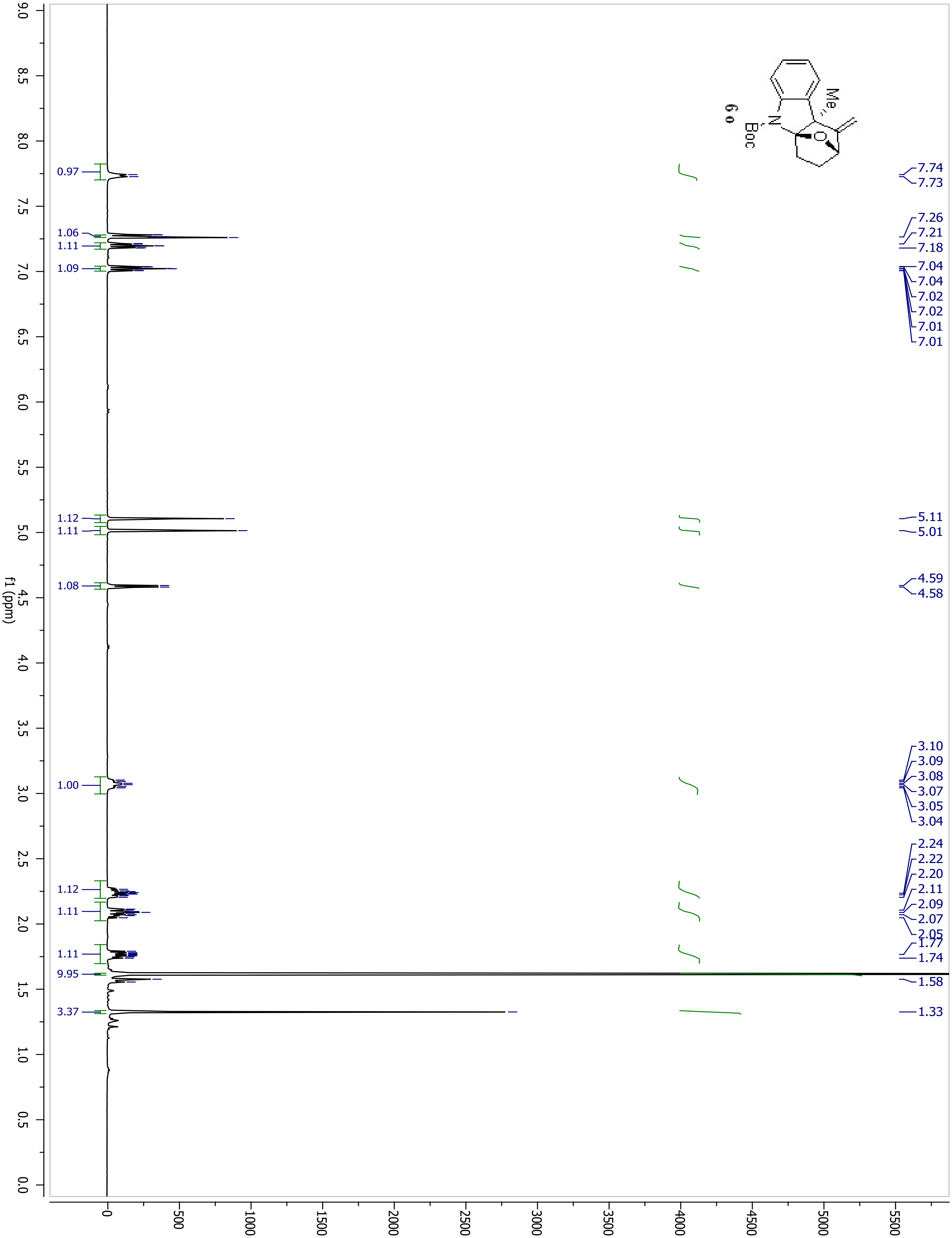

6m
MeO
Et
N
Ts
N
CO2Me
155.99
153.01
145.45
144.24
143.58
138.12
134.81
134.53
129.84
127.23
116.14
111.99
111.15
105.17
77.55
77.23
76.91
55.86
53.06
52.67
52.04
35.90
32.74
29.92
21.77
14.42
8.60
f1 (ppm)

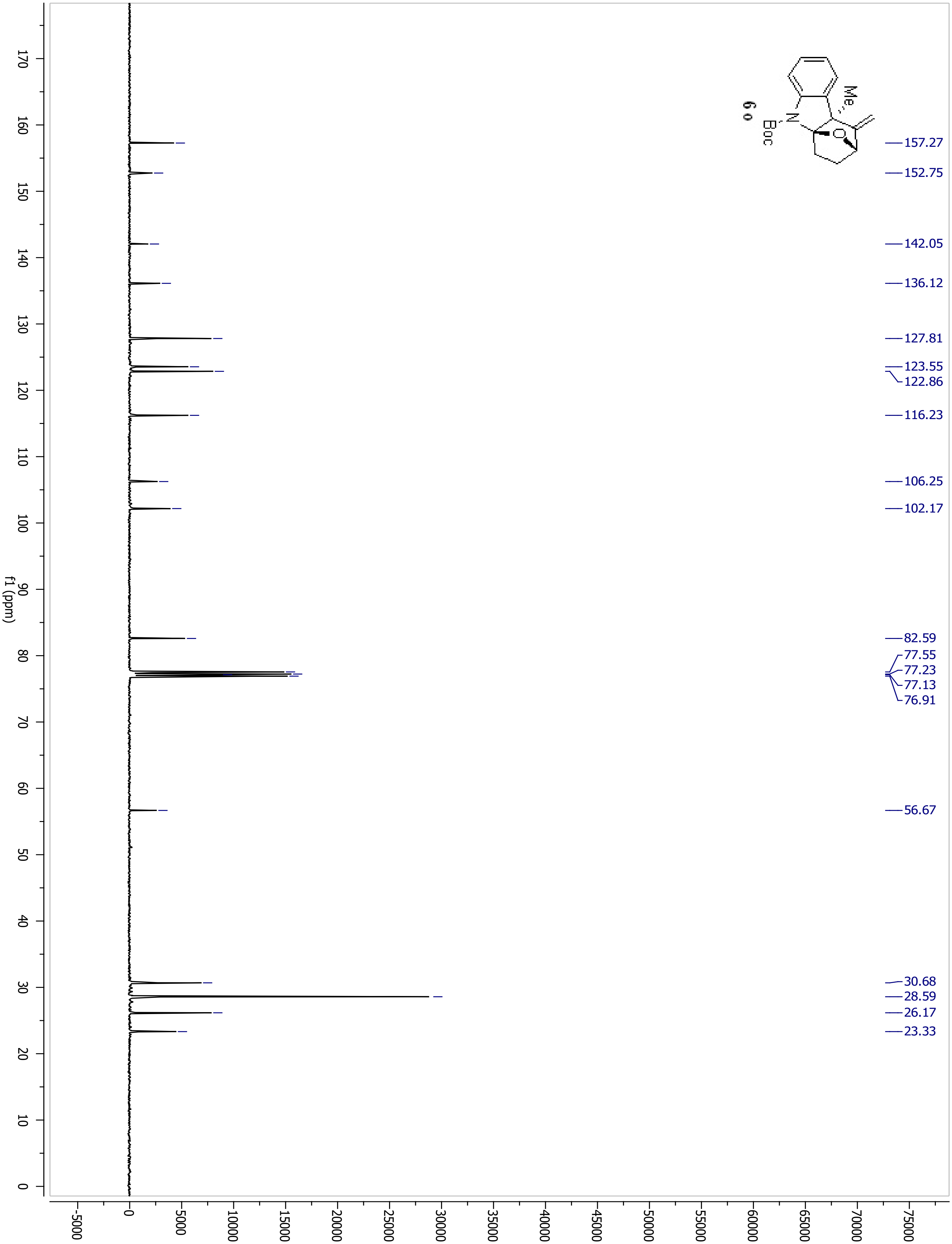

MeO
Et
N
Ts
N
CO2Me
6m
7.80
7.78
7.60
7.59
7.26
7.20
7.18
6.83
6.82
6.81
6.81
6.80
6.02
6.01
6.01
6.00
5.11
5.05
4.64
4.63
4.61
4.60
4.58
3.79
3.68
2.88
2.87
2.86
2.85
2.84
2.83
2.83
2.35
2.13
2.09
1.57
1.30
1.27
1.25
1.23
0.88
0.85
0.62
0.61
0.60
0.58
0.57
0.56
1.00
2.07
2.11
2.06
0.92
0.98
0.99
1.65
3.22
3.03
0.92
3.35
0.85
2.93
1.04
0.62
3.18
f1 (ppm)


6m
MeO
Et
N
Ts
N
CO2Me
156.71
156.57
145.60
144.81
144.62
134.64
134.45
134.31
129.65
129.52
129.40
127.47
116.95
112.07
108.86
108.28
77.56
77.24
76.93
55.85
54.02
52.47
48.55
34.28
32.72
29.94
21.78
8.29
f1 (ppm)

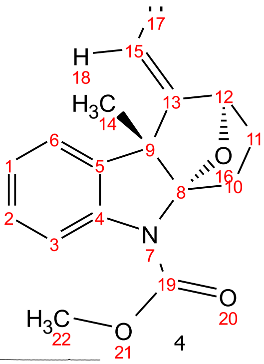

6n
MeO
Et
CO2Me
Ns
f1 (ppm)


6 n
MeO
Et
N
CO2Me
N
Ns
155.70
152.94
147.44
145.25
144.76
135.02
134.63
133.32
132.56
131.25
125.67
115.99
113.80
111.20
109.87
104.89
77.55
77.23
76.91
60.63
55.63
55.60
54.88
53.16
51.46
38.10
29.93
14.42
8.91
f1 (ppm)

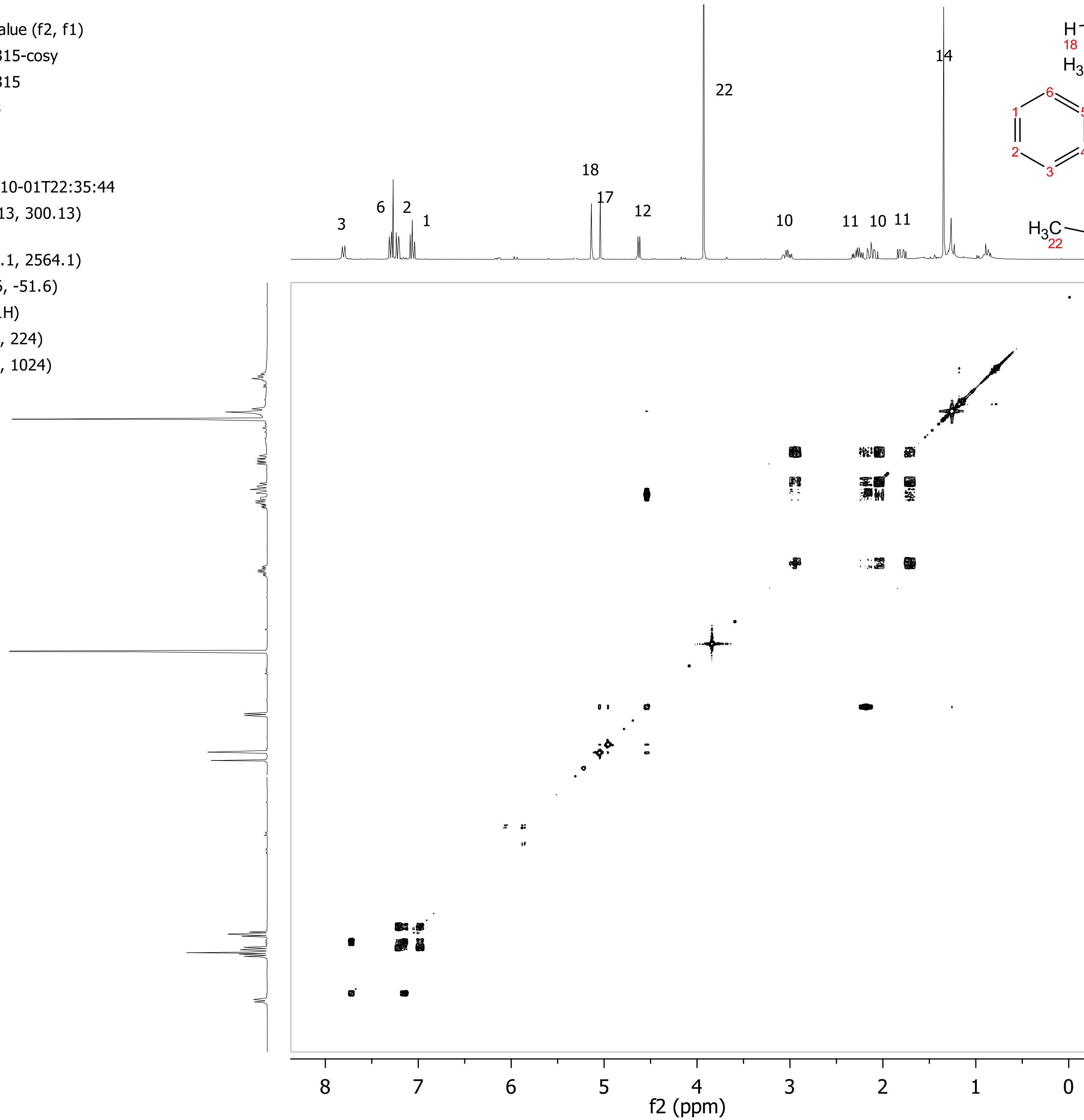

6o
Me
N
O
Boc
7.74
7.73
7.26
7.21
7.18
7.04
7.04
7.02
7.02
7.01
7.01
5.11
5.01
4.59
4.58
3.10
3.09
3.08
3.07
3.05
3.04
2.24
2.22
2.20
2.11
2.09
2.07
2.05
1.77
1.74
1.58
1.33
0.97
1.06
1.11
1.09
1.12
1.11
1.08
1.00
1.12
1.11
1.11
9.95
3.37
f1 (ppm)


6o
Me
N
Boc
O
157.27
152.75
142.05
136.12
127.81
123.55
122.86
116.23
106.25
102.17
82.59
77.55
77.23
77.13
76.91
56.67
30.68
28.59
26.17
23.33
f1 (ppm)

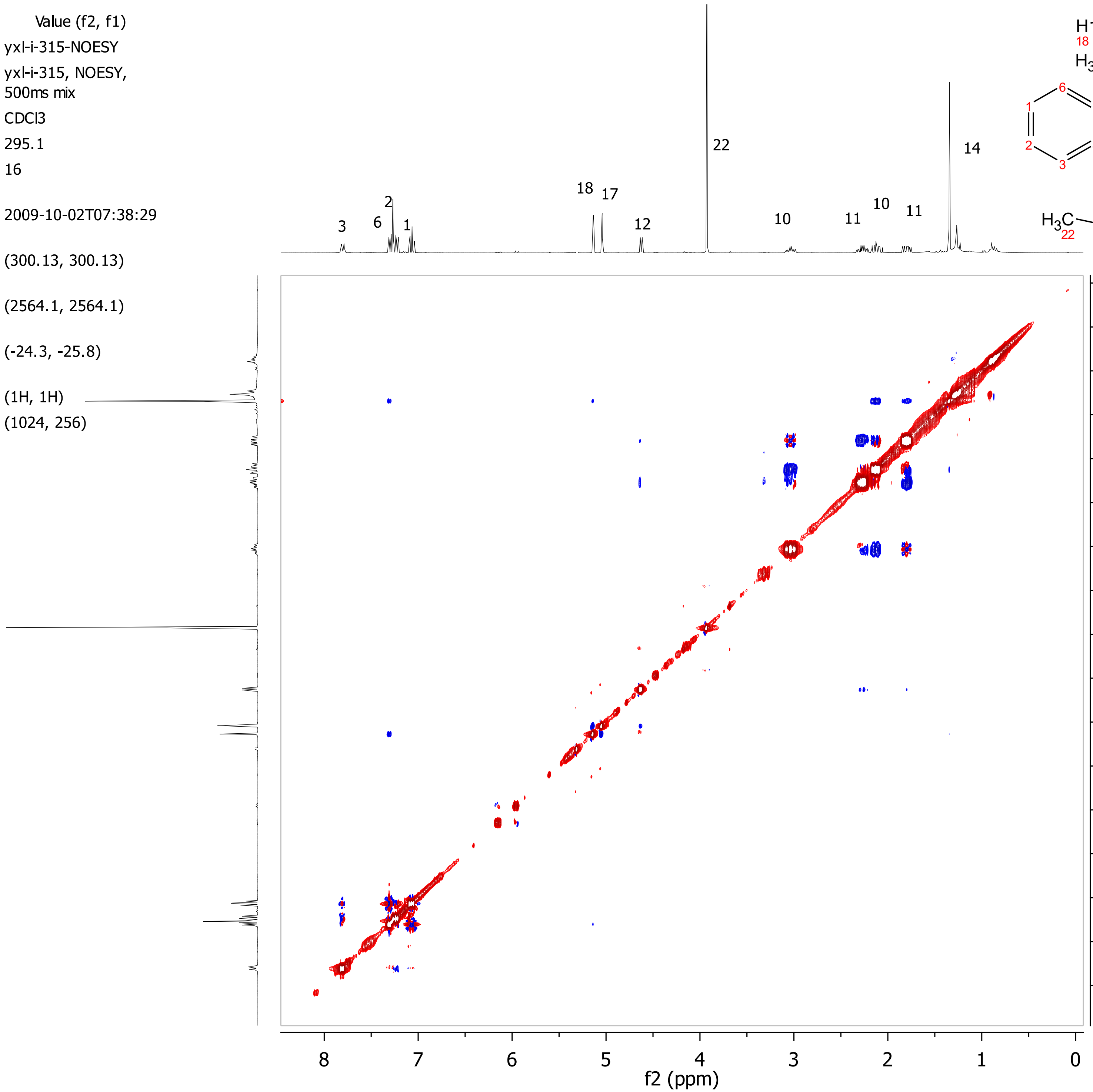
Parameter	Value (f2, f1)
Title	yxl-i-315-cosy
Comment	yxl-i-315
Solvent	CDCl3
Temperature	295.5
Number of Scans	4
Acquisition Date	2009-10-01T22:35:44
Spectrometer Frequency	(300.13, 300.13)
Spectral Width	(2564.1, 2564.1)
Lowest Frequency	(-51.6, -51.6)
Nucleus	(1H, 1H)
Acquired Size	(1024, 224)
Spectral Size	(1024, 1024)

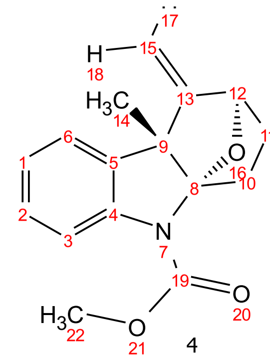


4



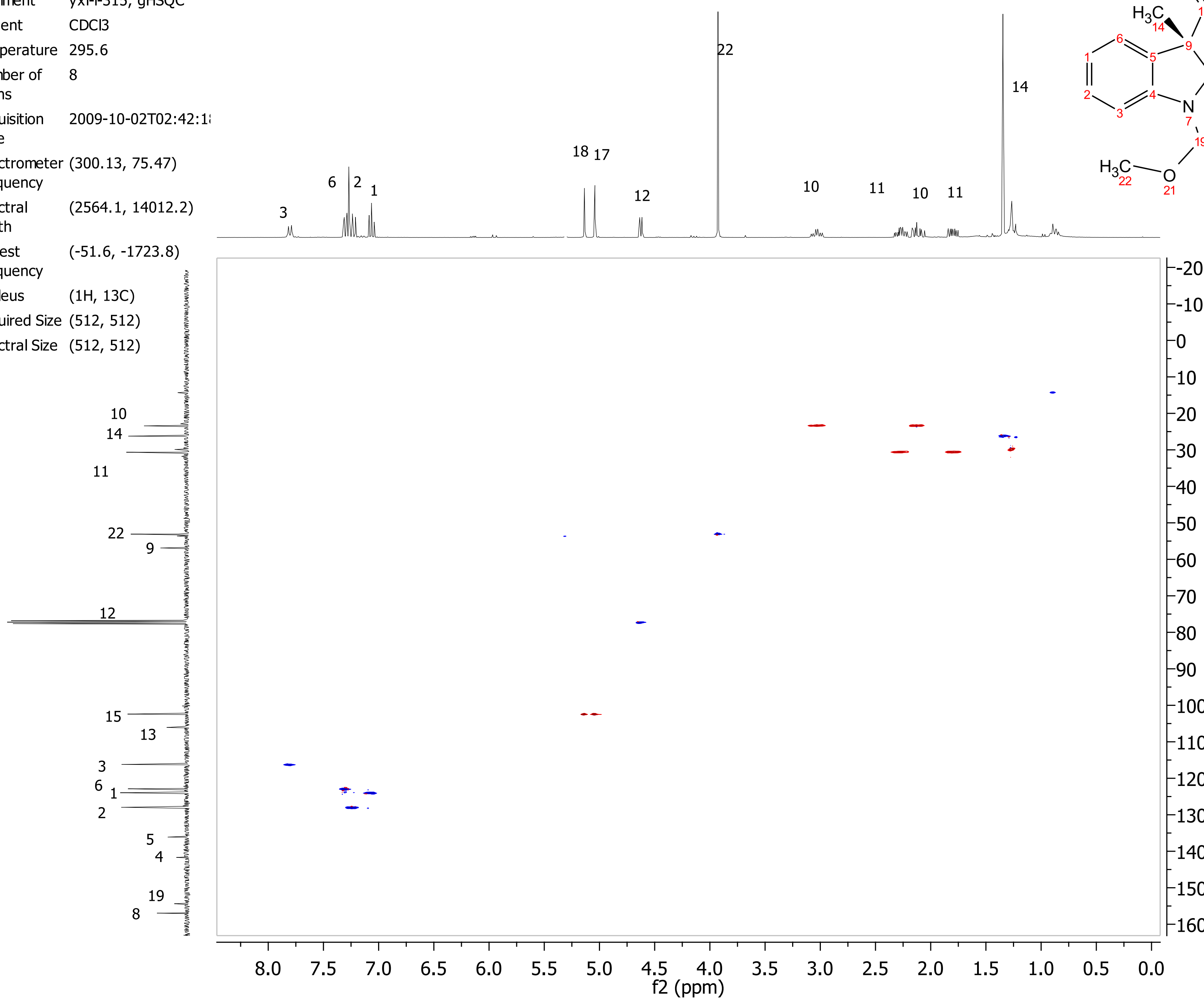
Parameter	Value (f2, f1)
Title	yxl-i-315-NOESY
Comment	yxl-i-315, NOESY, 500ms mix
Solvent	CDCl3
Temperature	295.1
Number of Scans	16
Acquisition Date	2009-10-02T07:38:29
Spectrometer Frequency	(300.13, 300.13)
Spectral Width	(2564.1, 2564.1)
Lowest Frequency	(-24.3, -25.8)
Nucleus	(1H, 1H)
Acquired Size	(1024, 256)

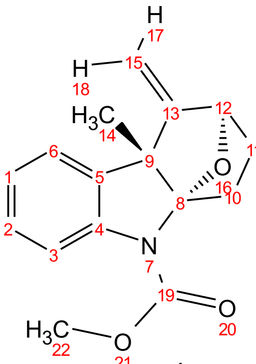




4

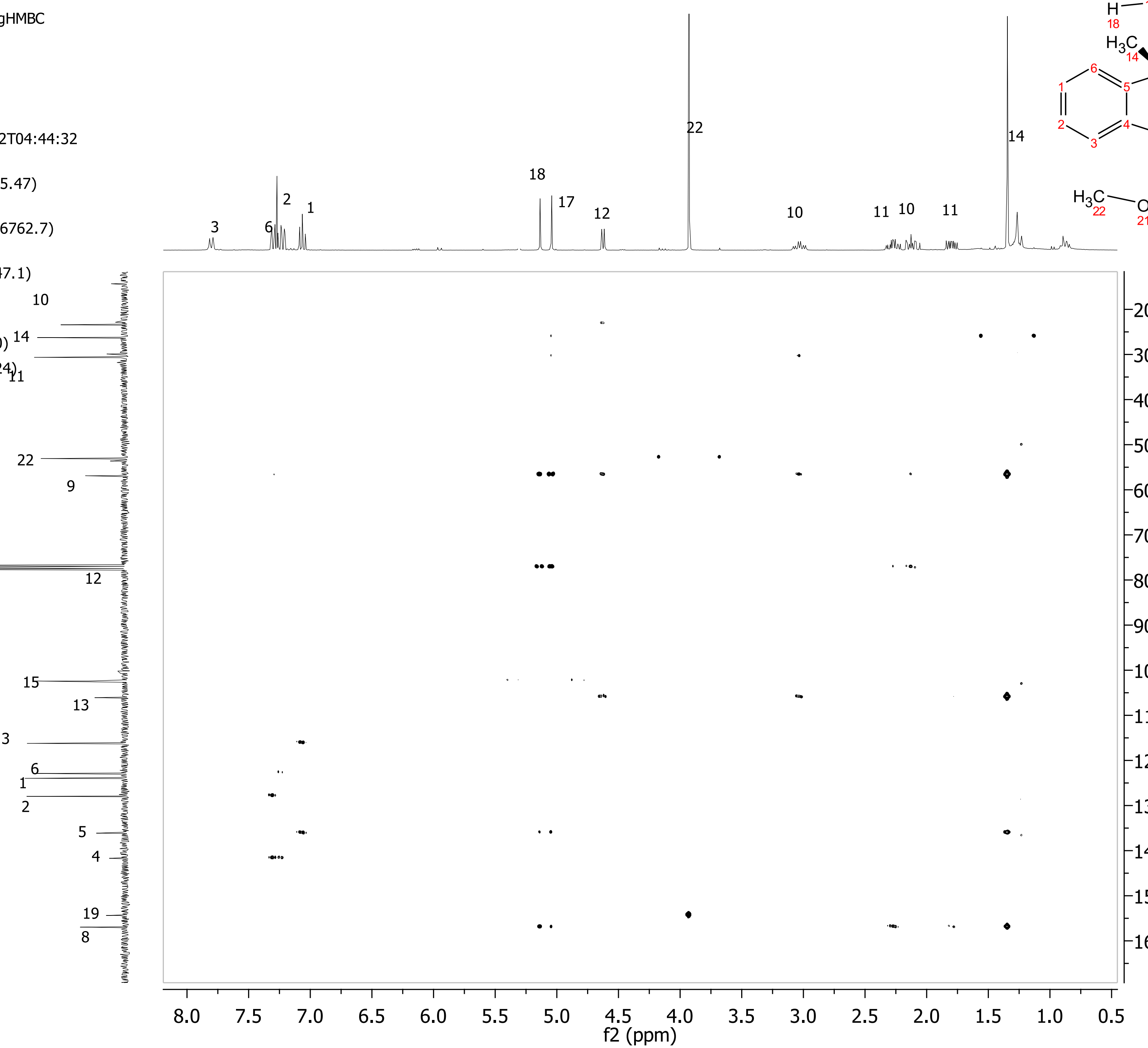
Parameter	Value (f2, f1)
Title	yxl-i-315-gHSQC
Comment	yxl-i-315, gHSQC
Solvent	CDCl3
Temperature	295.6
Number of Scans	8
Acquisition Date	2009-10-02T02:42:1
Spectrometer Frequency	(300.13, 75.47)
Spectral Width	(2564.1, 14012.2)
Lowest Frequency	(-51.6, -1723.8)
Nucleus	(1H, 13C)
Acquired Size	(512, 512)
Spectral Size	(512, 512)

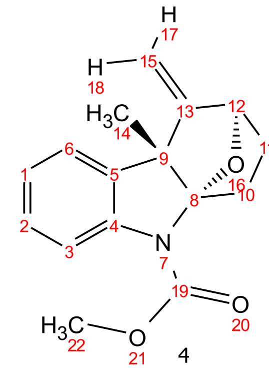




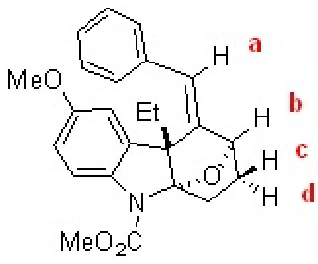
4

Parameter	Value (f2, f1)
Title	yxl-i-315-gHMBC
Comment	yxl-i-315, gHMBC
Solvent	CDCl3
Temperature	295.5
Number of Scans	16
Acquisition Date	2009-10-02T04:44:32
Spectrometer Frequency	(300.13, 75.47)
Spectral Width	(2564.1, 16762.7)
Lowest Frequency	(-51.6, -847.1)
Nucleus	(1H, 13C)
Acquired Size	(1024, 400)
Spectral Size	(1024, 1024)



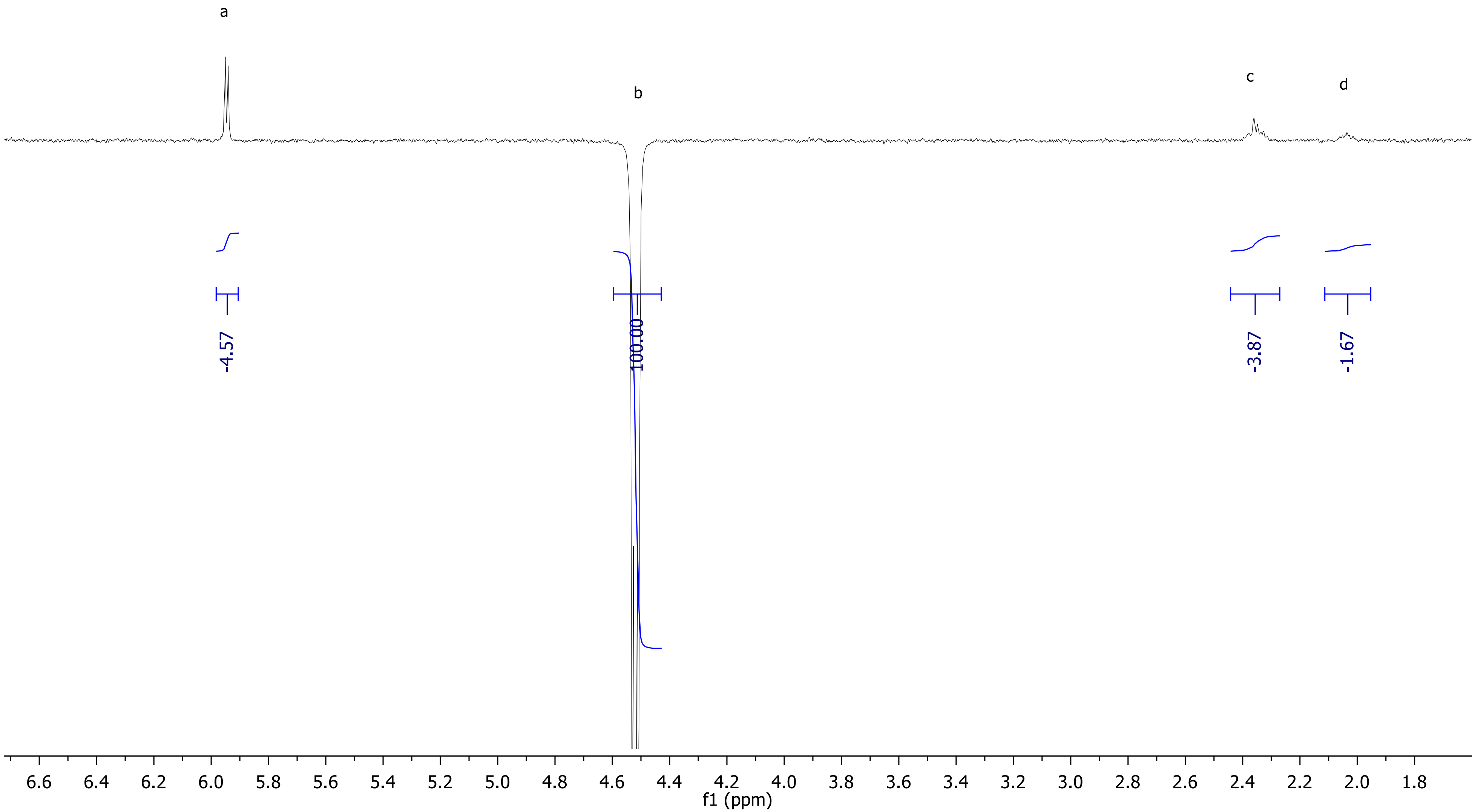


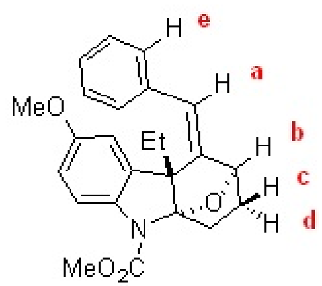
4



6e

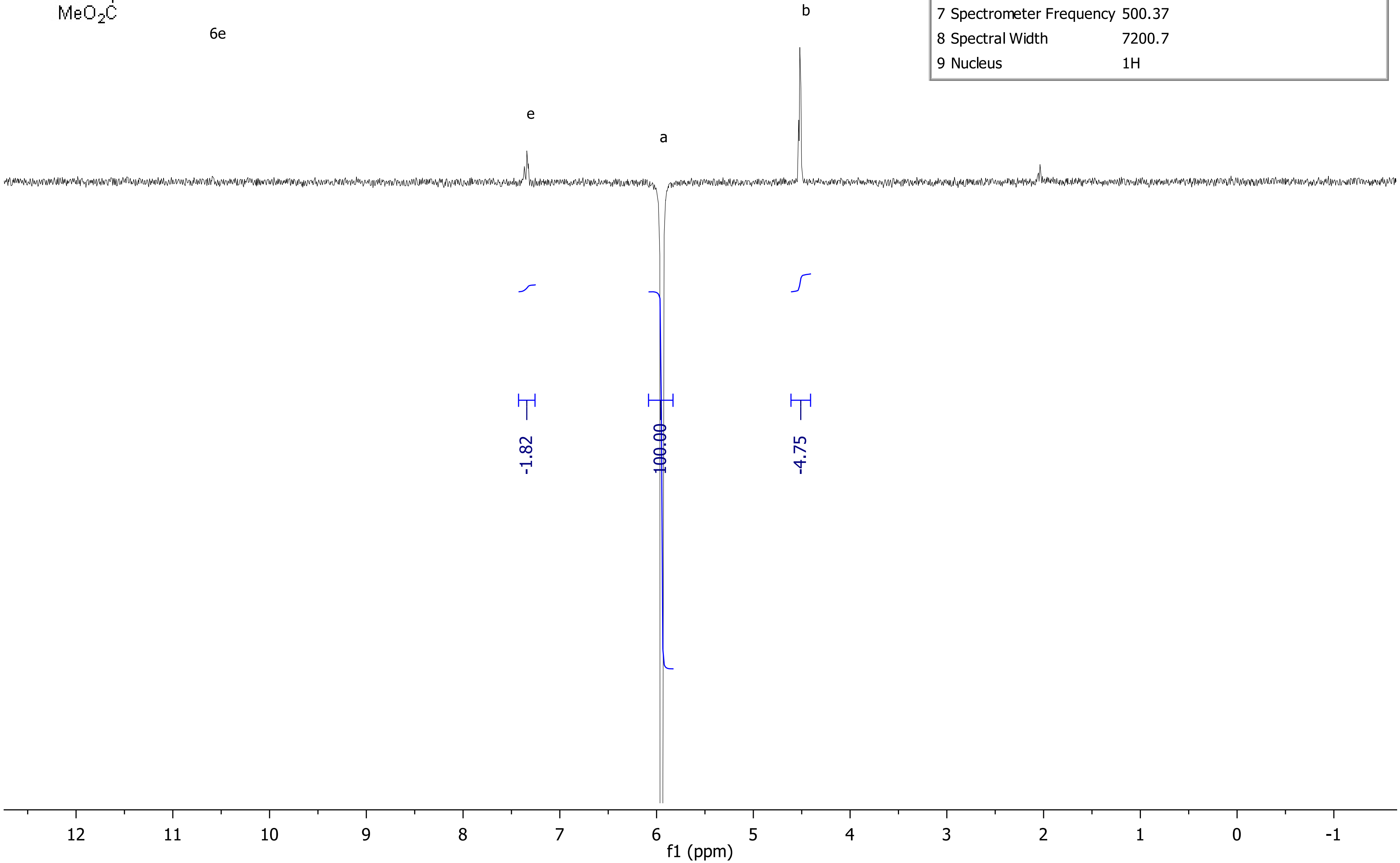
Parameter	Value
1 Data File Name	X:/ wang/ Liu/ yxl-i-341-goesy2.fid/ fid
2 Title	yxl-i-341, goesy @ 4.51ppm/ mix=0.7sec
3 Solvent	CDCl3
4 Acquisition Date	2009-10-14T06:07:28
5 Temperature	20.0
6 Number of Scans	32
7 Spectrometer Frequency	500.37
8 Spectral Width	7200.7
9 Nucleus	1H

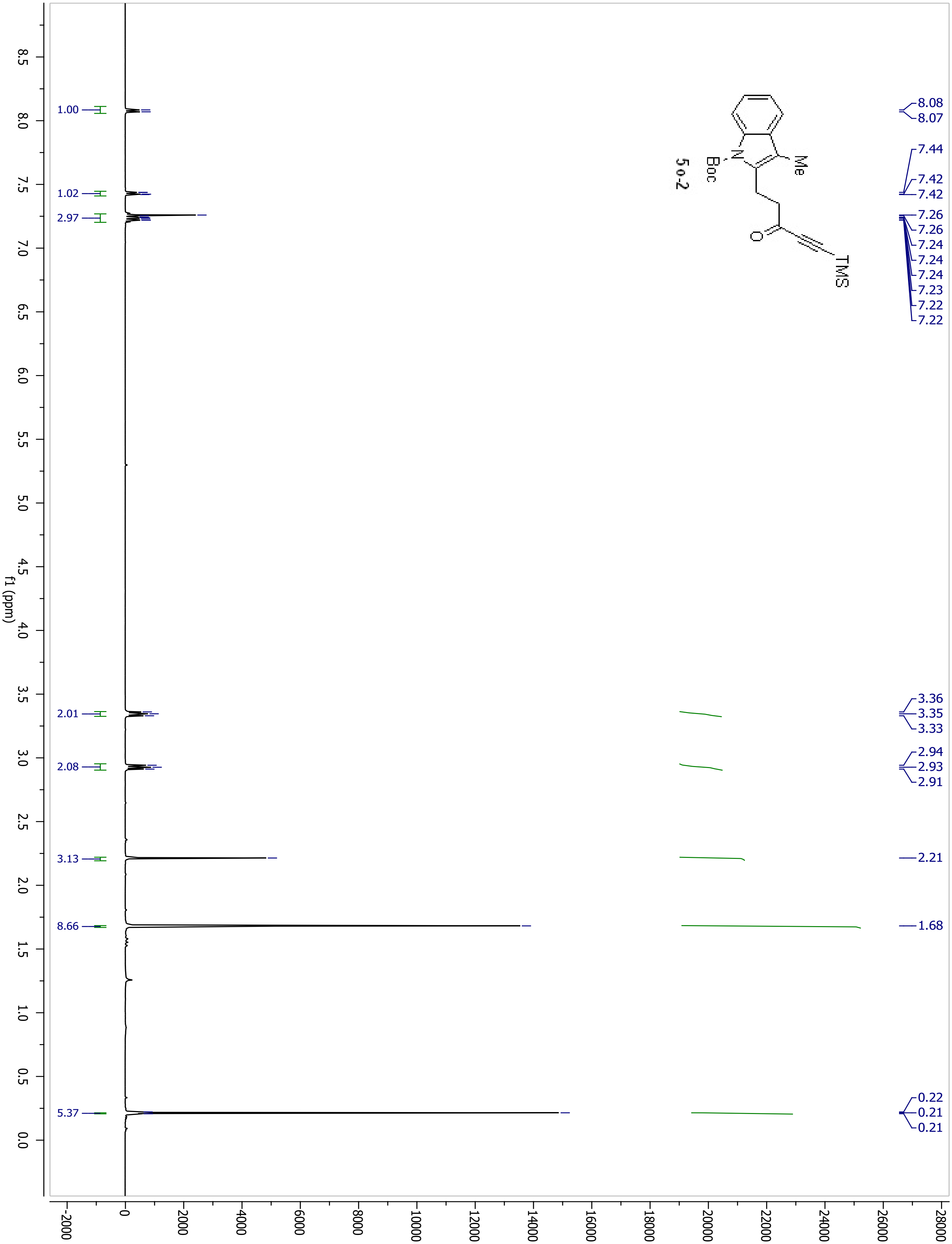




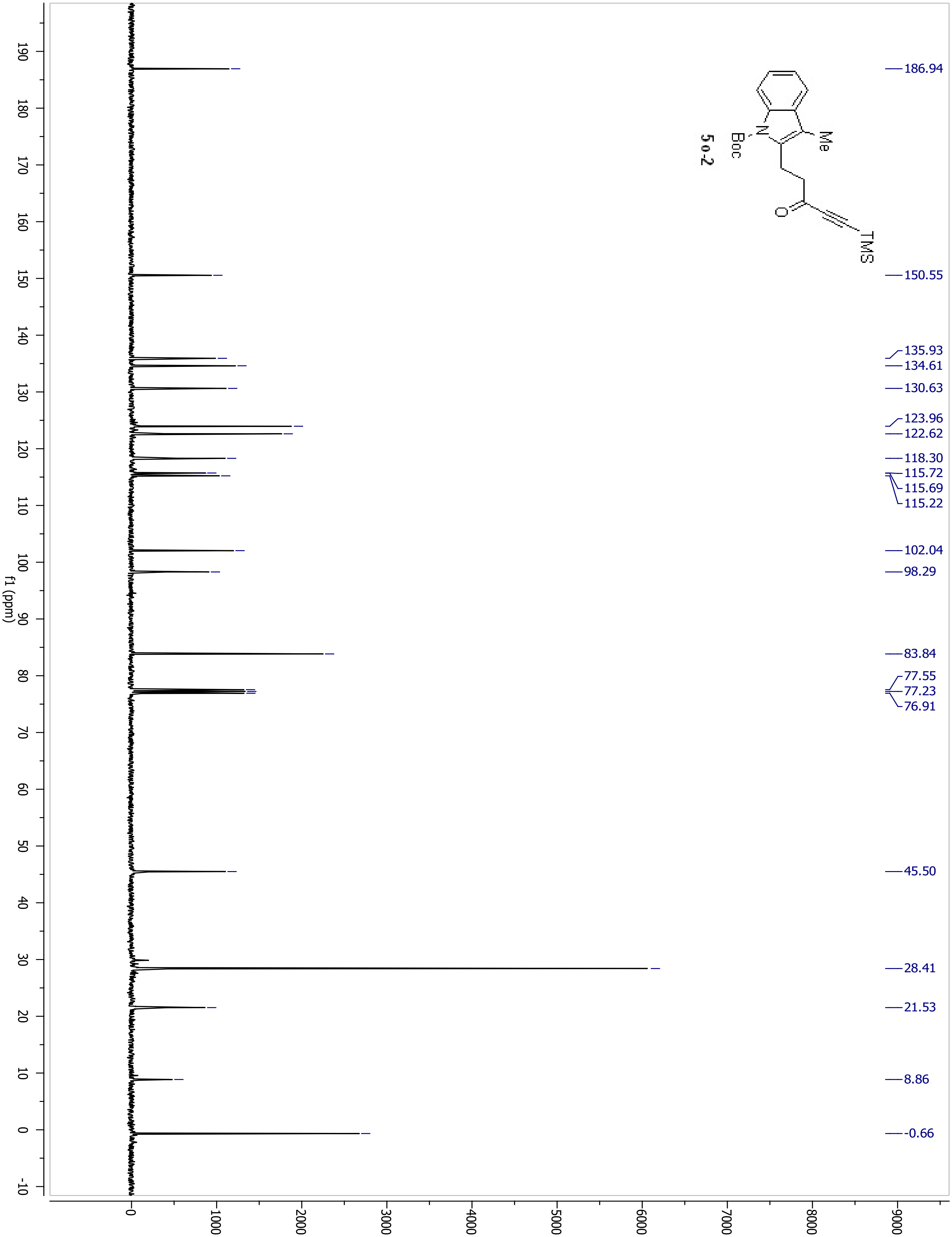
6e

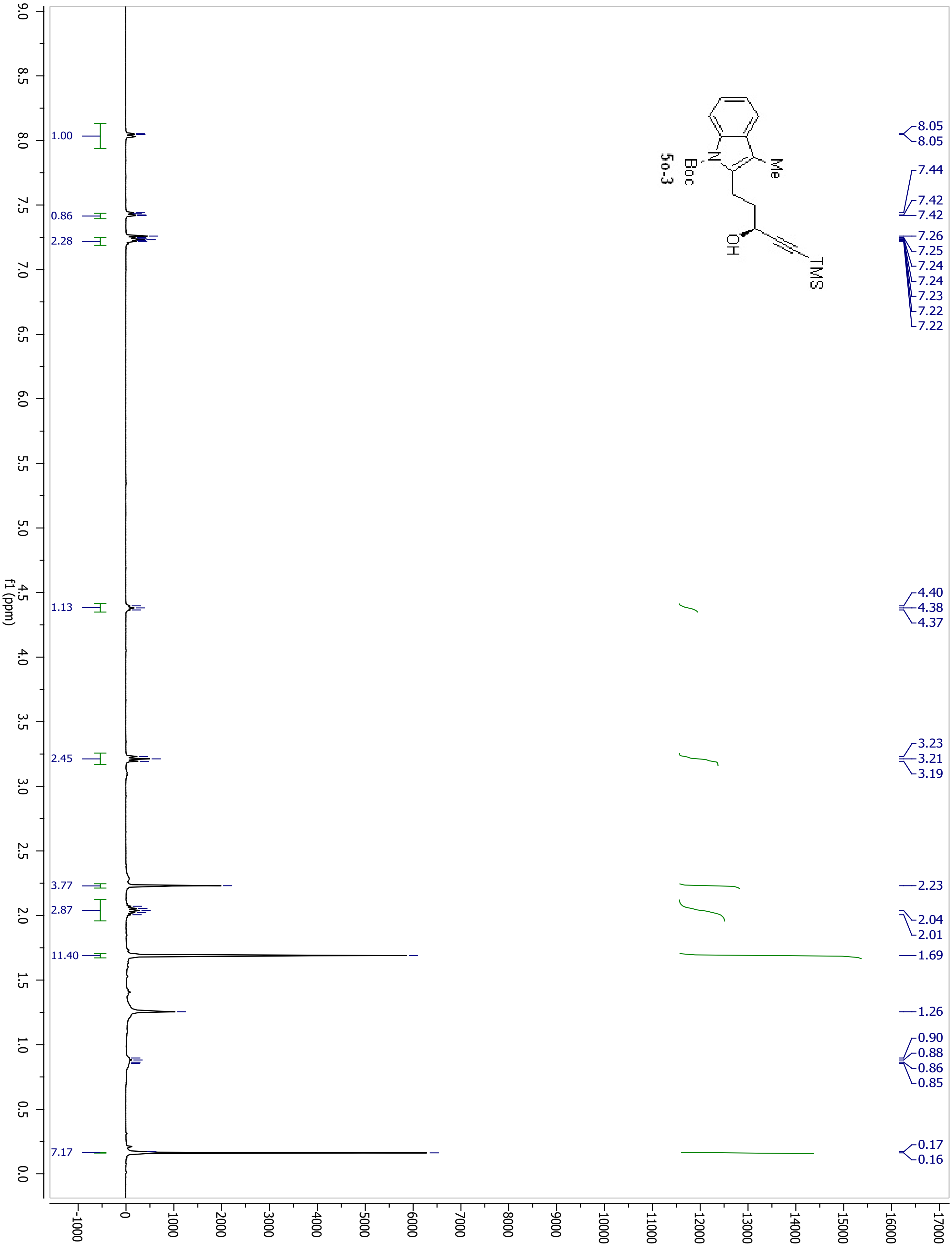
Parameter	Value
1 Data File Name	X:/ wang/ Liu/ yxl-i-341-goesy1.fid/ fid
2 Title	yxl-i-341, goesy @ 5.94 ppm/ mix=0.7
3 Solvent	CDCl3
4 Acquisition Date	2009-10-14T06:03:51
5 Temperature	20.0
6 Number of Scans	32
7 Spectrometer Frequency	500.37
8 Spectral Width	7200.7
9 Nucleus	1H

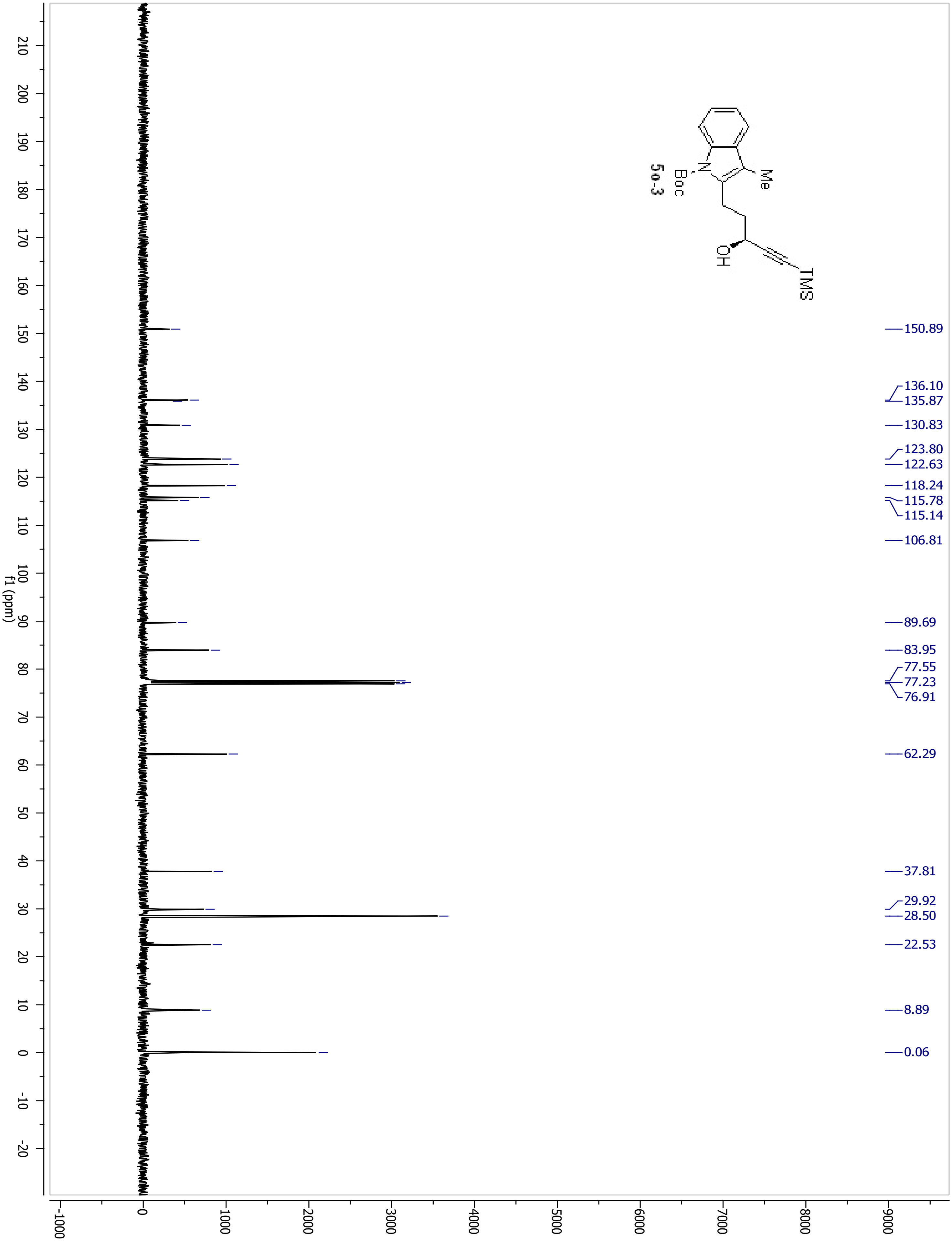


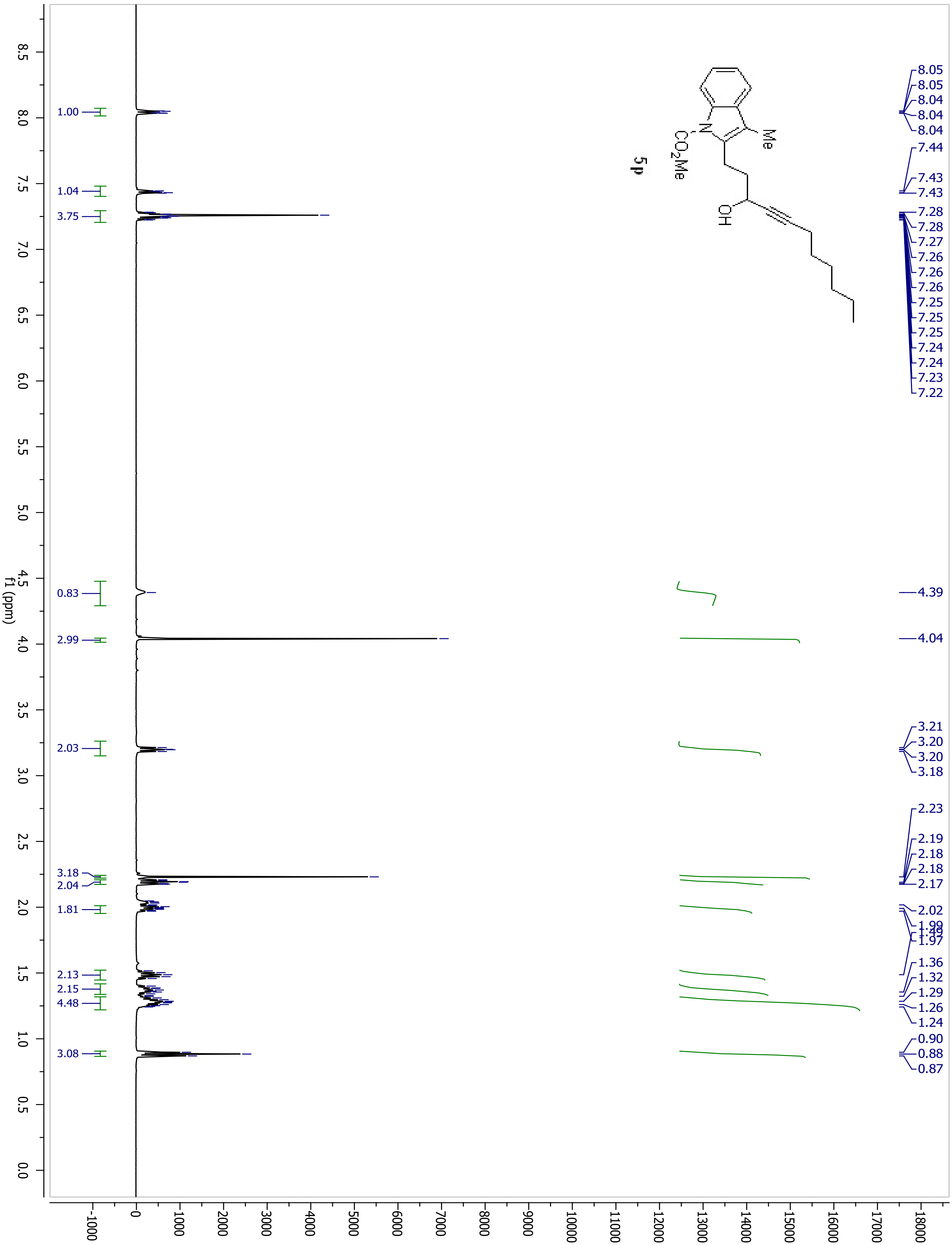


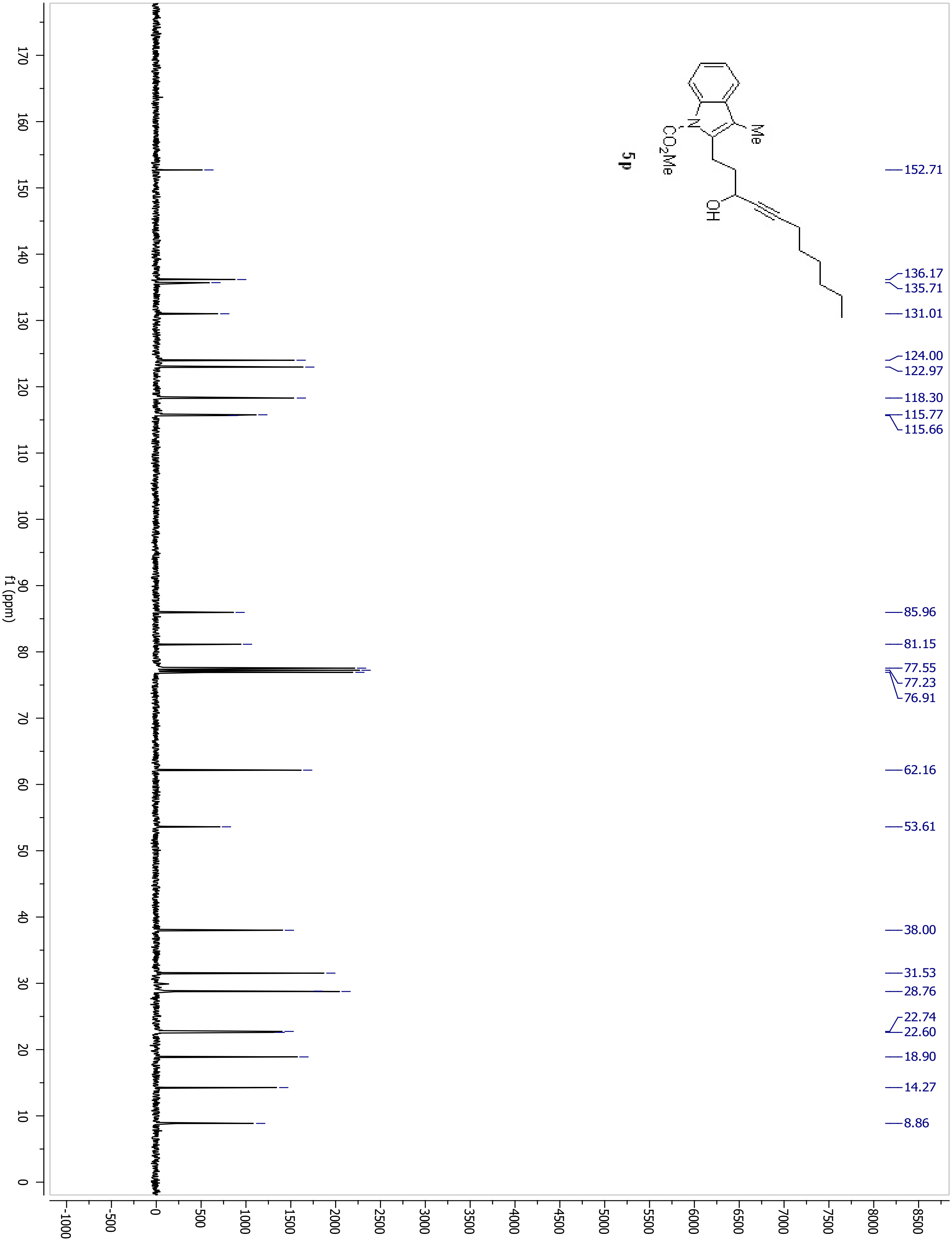
Me
N
Boc
O
TMS
5o-2
f1 (ppm)

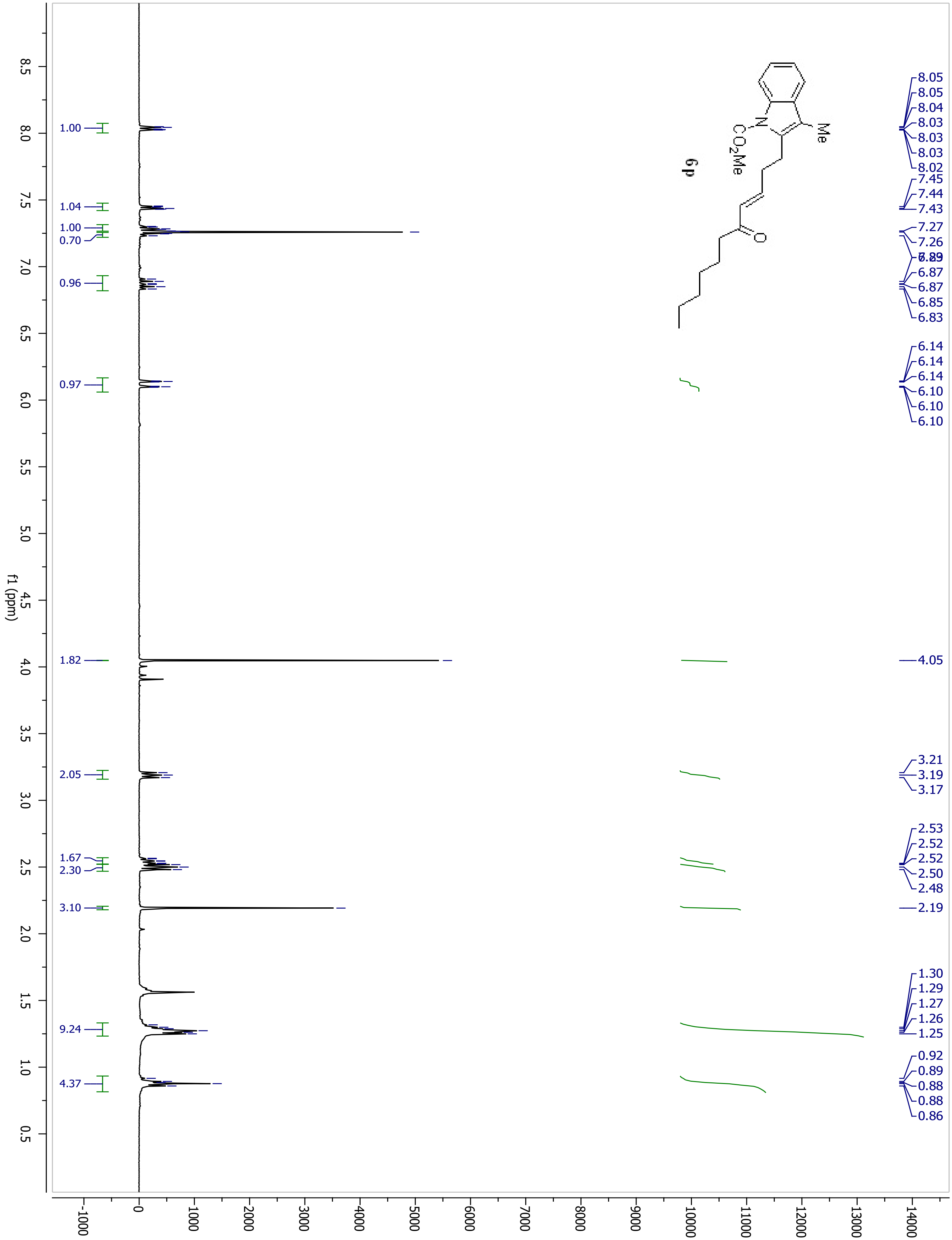

5o-2
Me
N
Boc
O
TMS
186.94
150.55
135.93
134.61
130.63
123.96
122.62
118.30
115.72
115.69
115.22
102.04
98.29
83.84
77.55
77.23
76.91
45.50
28.41
21.53
8.86
-0.66
f1 (ppm)

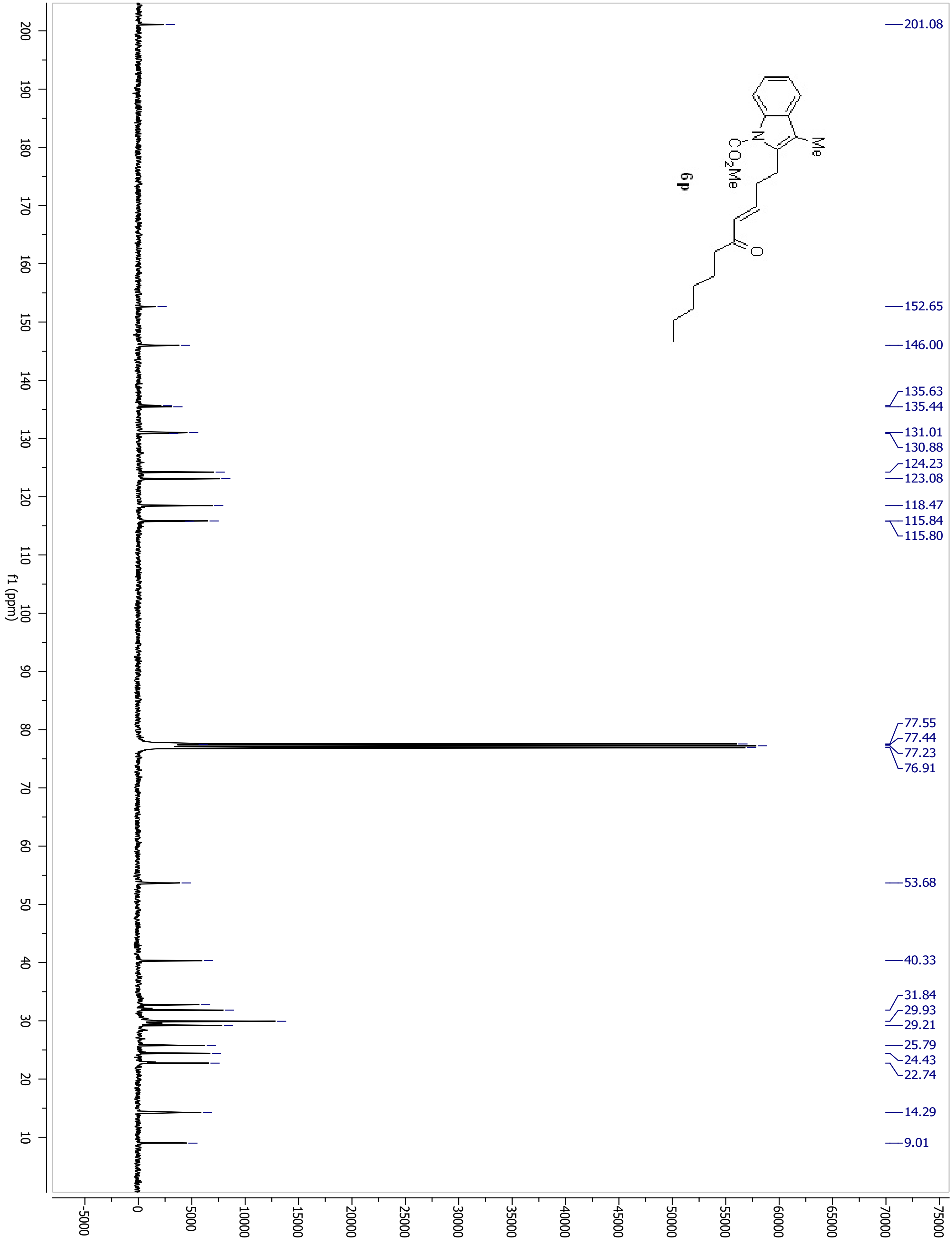

Me
N
Boc
5o-3
OH
TMS
f1 (ppm)


150.89
136.10
135.87
130.83
123.80
122.63
118.24
115.78
115.14
106.81
89.69
83.95
77.55
77.23
76.91
62.29
37.81
29.92
28.50
22.53
8.89
0.06
f1 (ppm)
Me
N
Boc
OH
TMS
5o-3

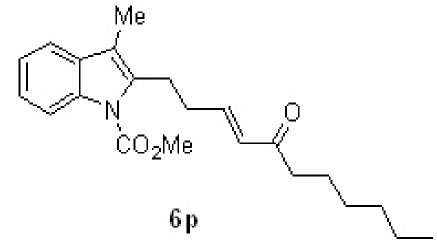

5p
Me
CO_2Me
OH
f1 (ppm)
1.00
1.04
3.75
0.83
2.99
2.03
3.18
2.04
1.81
2.13
2.15
4.48
3.08
8.05
8.05
8.04
8.04
8.04
7.44
7.43
7.43
7.28
7.28
7.27
7.26
7.26
7.26
7.25
7.25
7.25
7.24
7.24
7.23
7.22
4.39
4.04
3.21
3.20
3.20
3.18
2.23
2.19
2.18
2.18
2.17
2.02
1.99
1.97
1.36
1.32
1.29
1.26
1.24
0.90
0.88
0.87


5p
Me
CO2Me
N
OH
152.71
136.17
135.71
131.01
124.00
122.97
118.30
115.77
115.66
85.96
81.15
77.55
77.23
76.91
62.16
53.61
38.00
31.53
28.76
22.74
22.60
18.90
14.27
8.86
f1 (ppm)

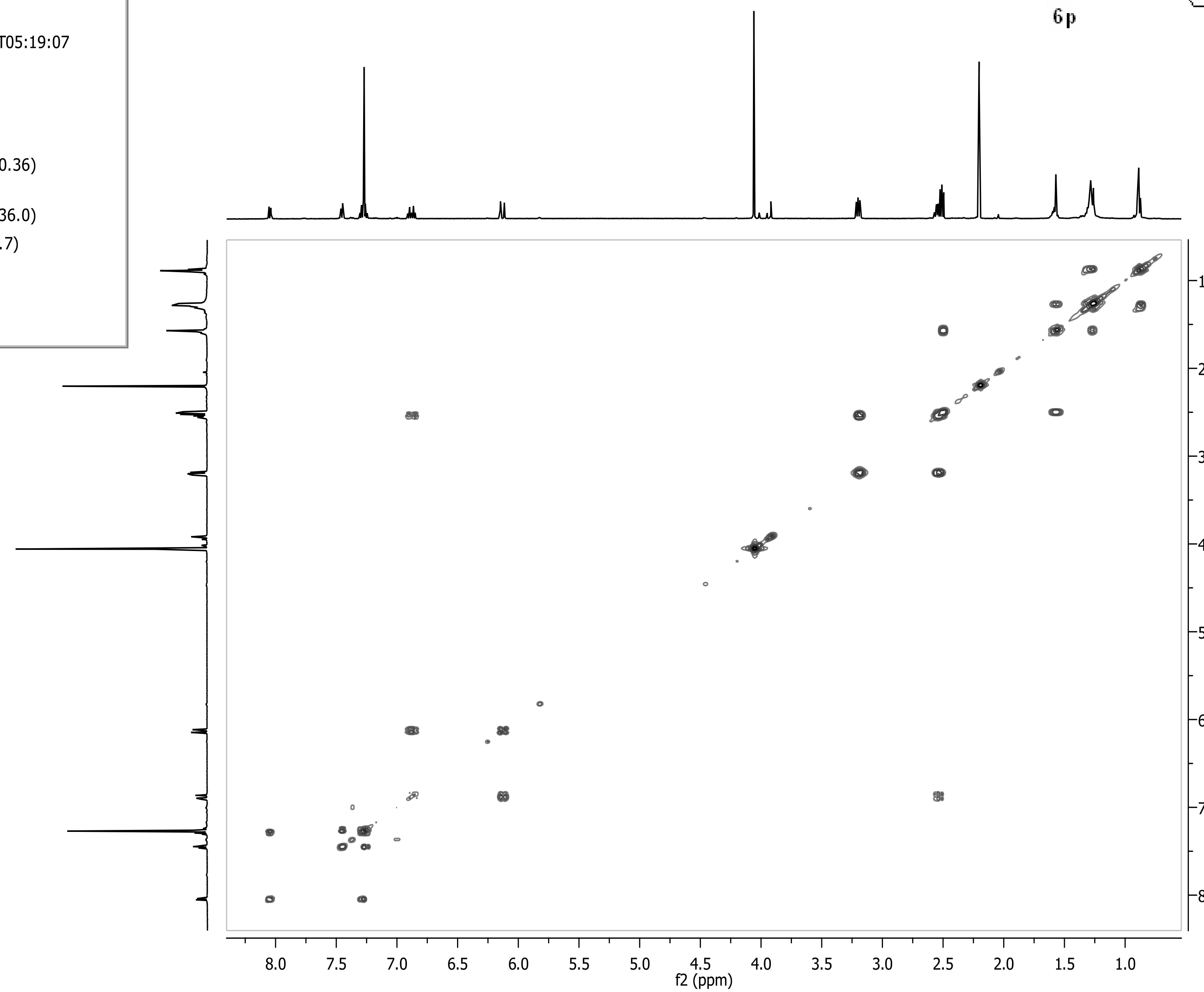

6p
Me
N
CO2Me
O
f1 (ppm)

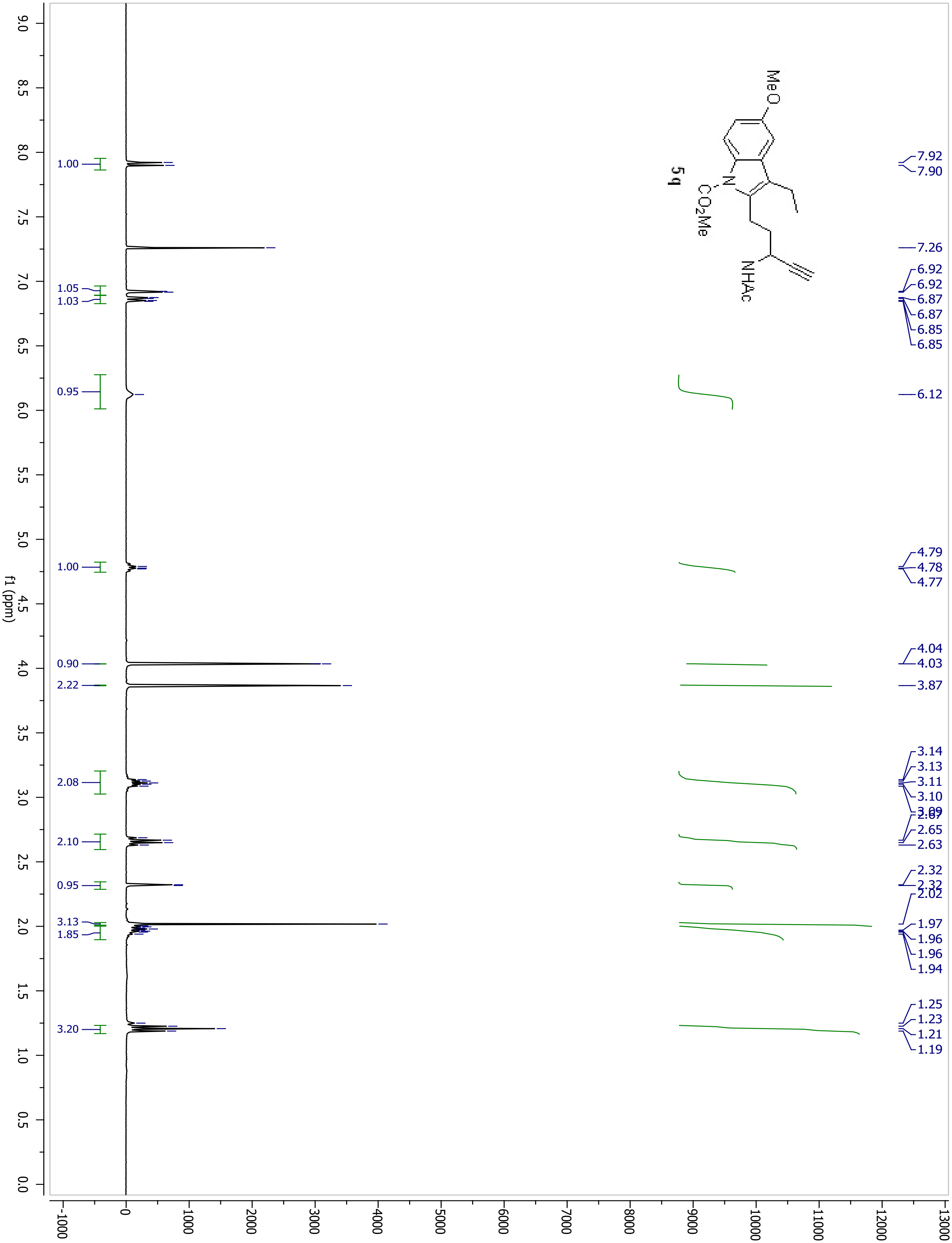

6p
CO2Me
Me
O
N
201.08
152.65
146.00
135.63
135.44
131.01
130.88
124.23
123.08
118.47
115.84
115.80
77.55
77.44
77.23
76.91
53.68
40.33
31.84
29.93
29.21
25.79
24.43
22.74
14.29
9.01
f1 (ppm)

	Parameter	Value (f2, f1)
1	Data File Name	E:/ NMR DATA/ yxl-i-216-gcosy.fid/ fid
2	Title	Proton NMR, Standard Parameters
3	Solvent	CDCl3
4	Pulse Sequence	gCOSY
5	Acquisition Date	2009-10-22T05:19:07
6	Modification Date	
7	Temperature	20.0
8	Number of Scans	2
9	Spectrometer Frequency	(500.36, 500.36)
10	Spectral Width	(3936.0, 3936.0)
11	Lowest Frequency	(268.7, 268.7)
12	Nucleus	(1H, 1H)
13	Acquired Size	(512, 256)
14	Spectral Size	(512, 512)

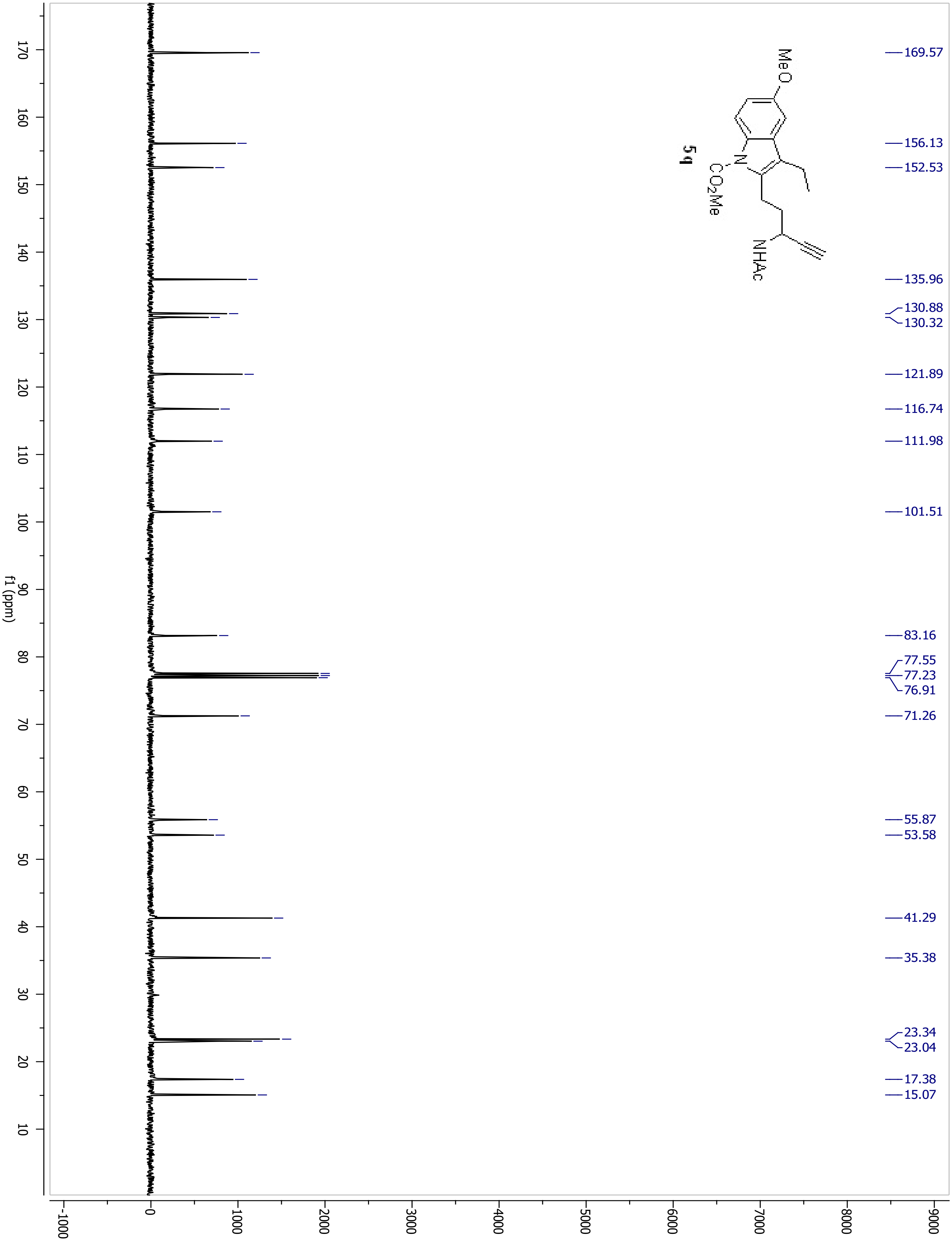


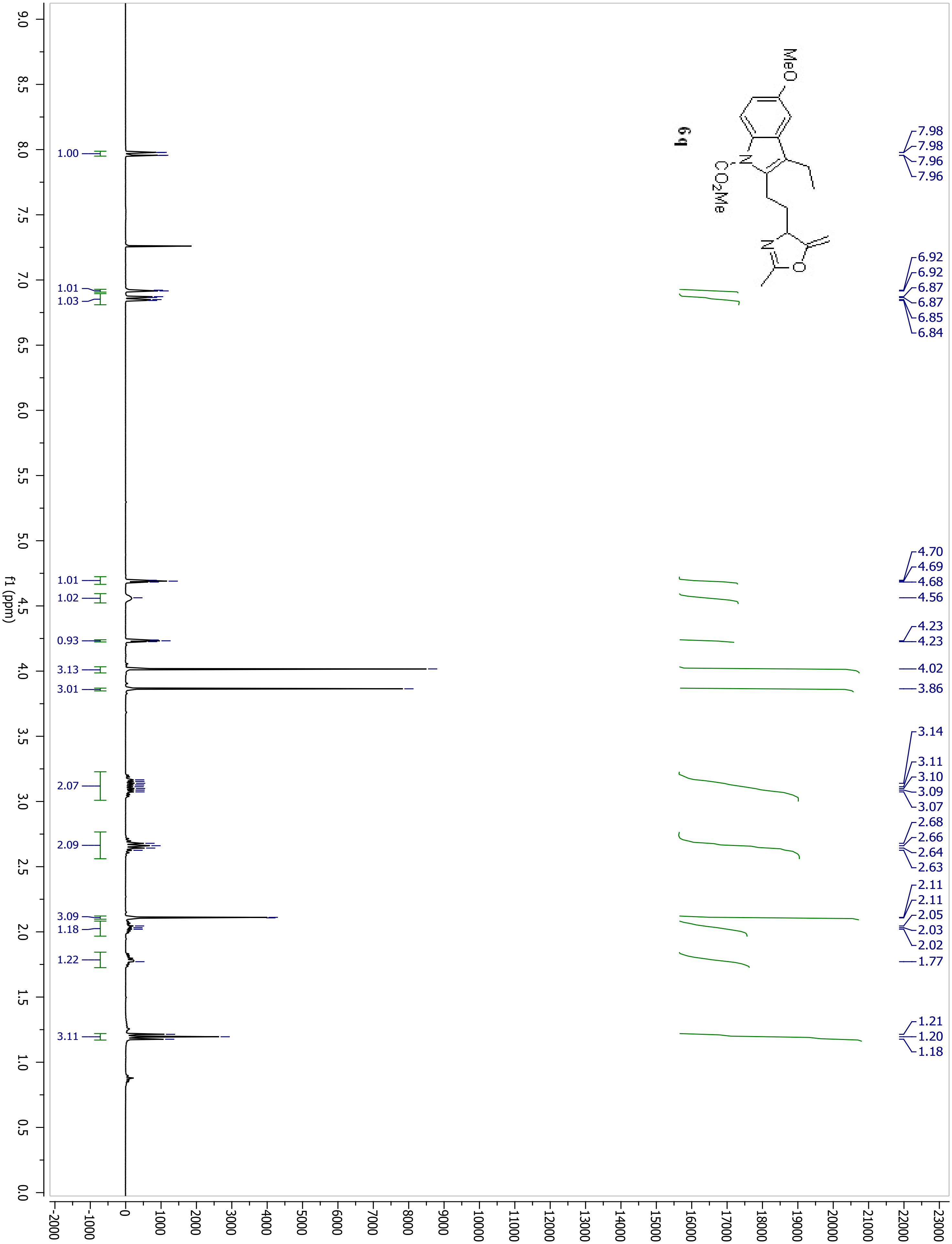
6p

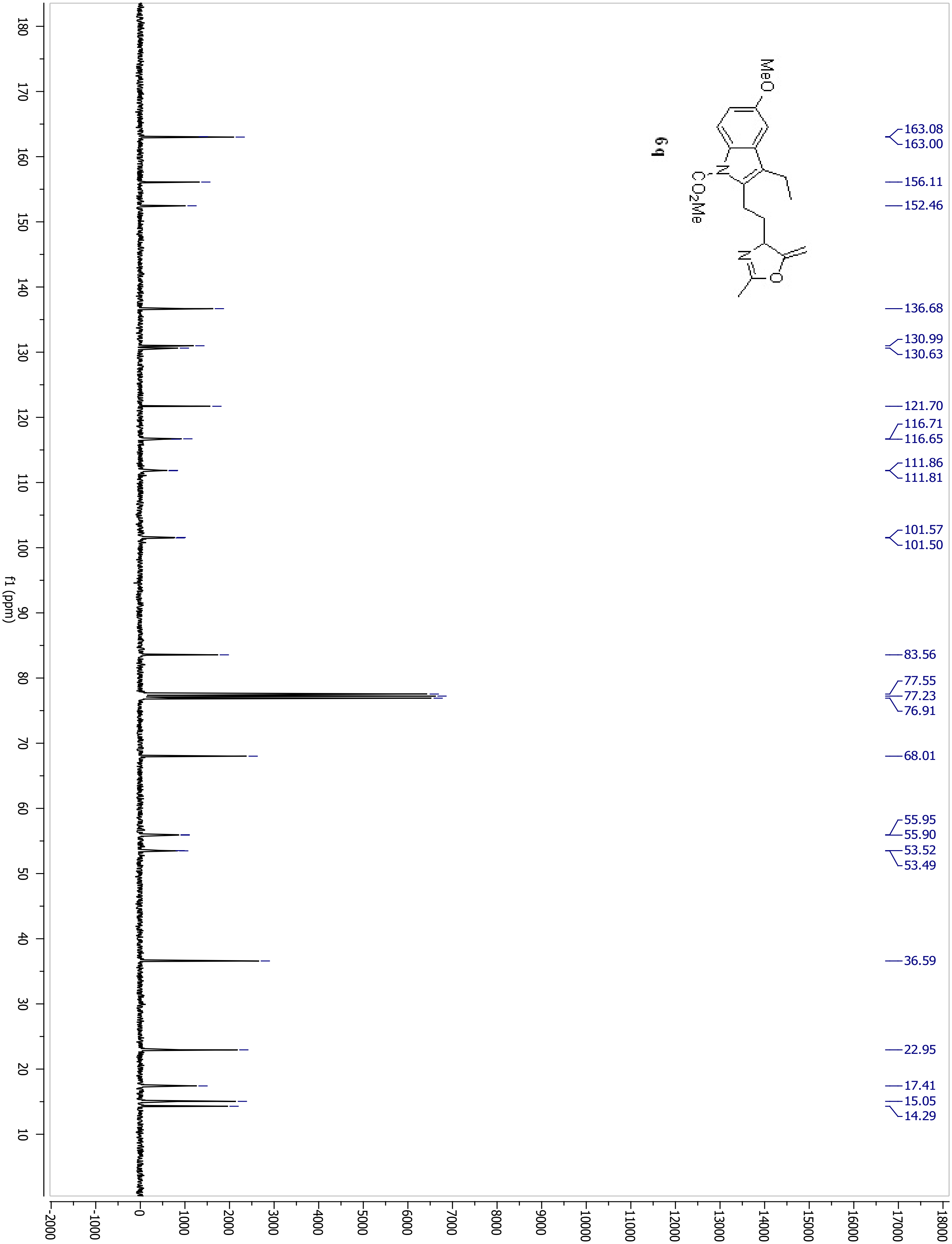


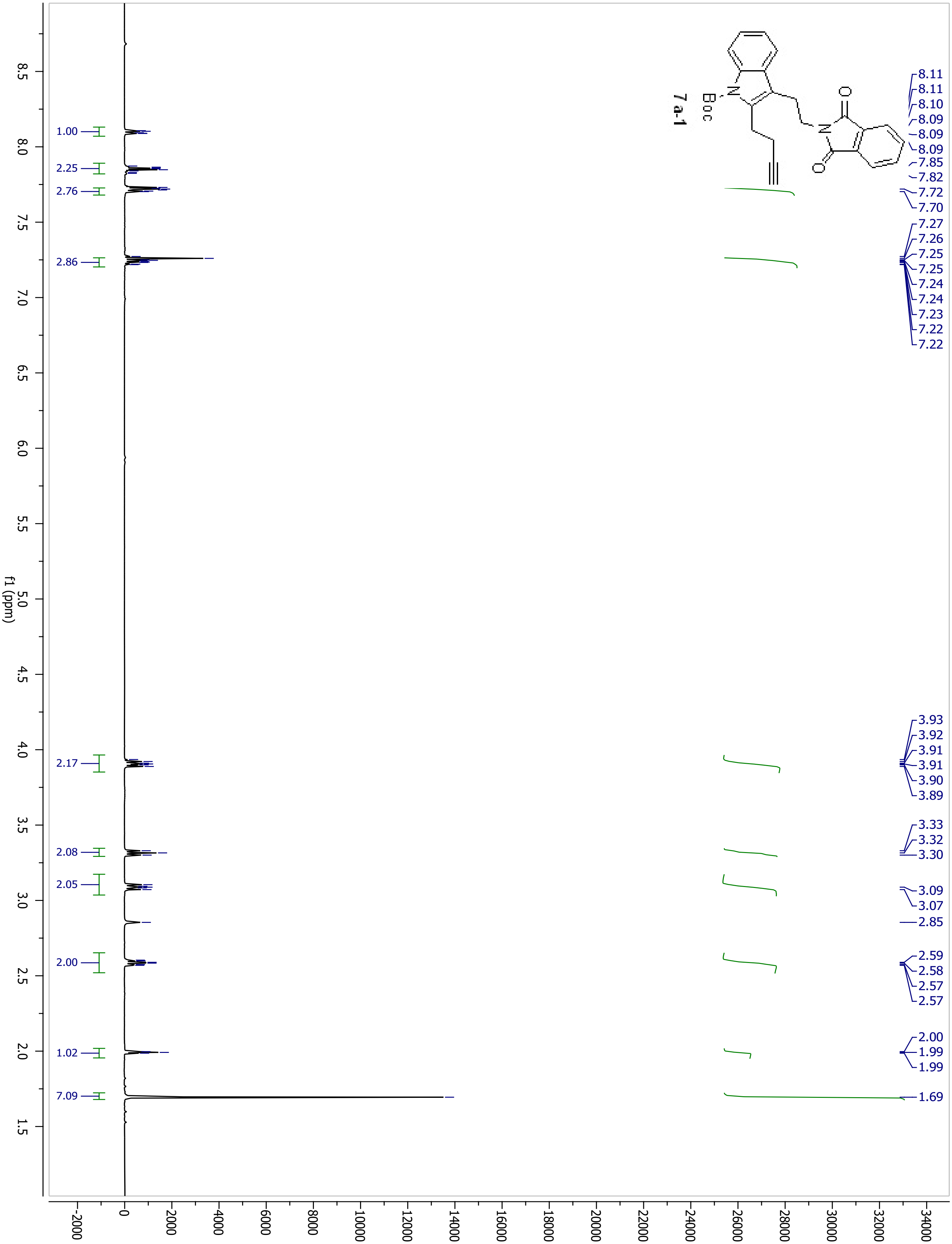


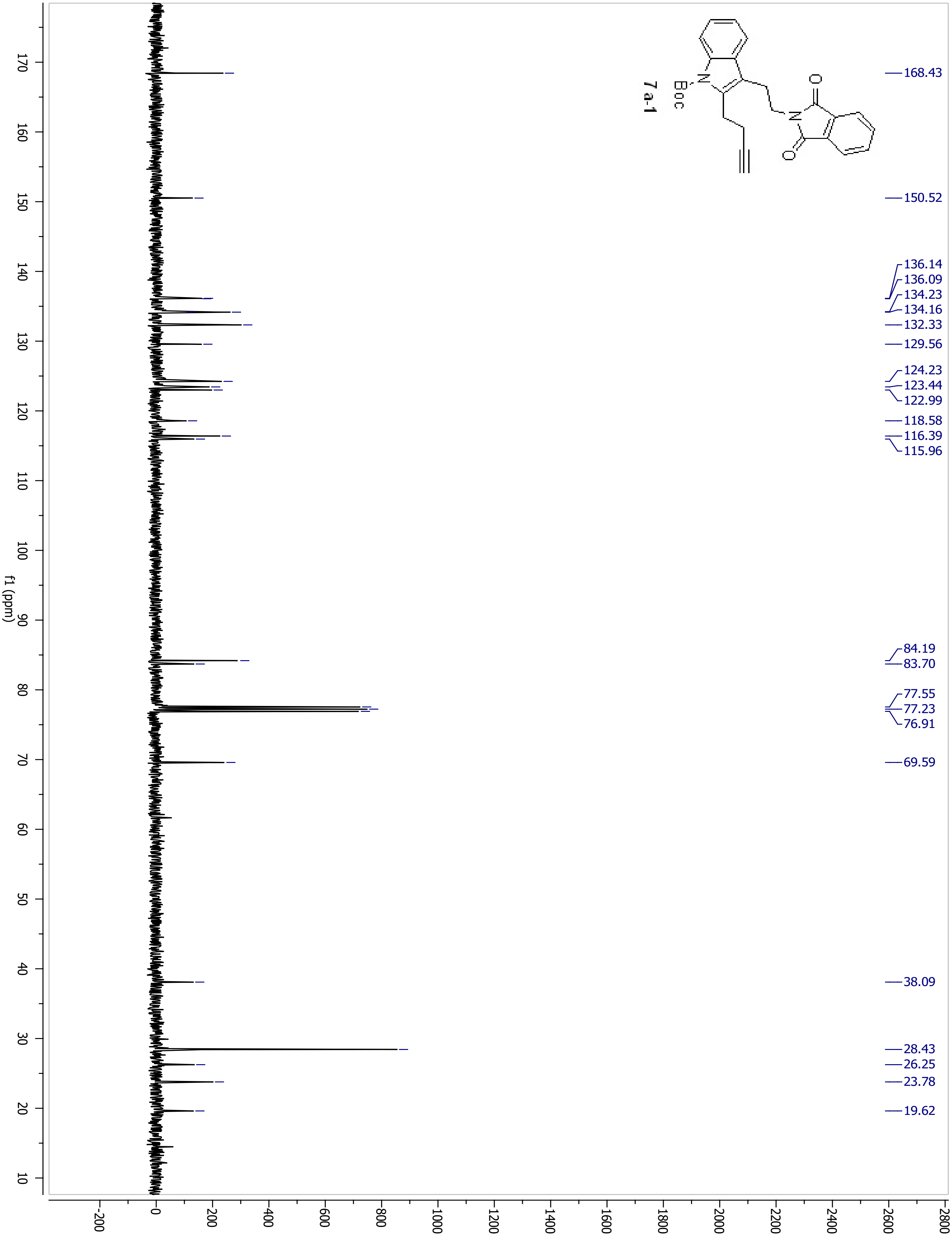
5q
MeO
CO2Me
NHAc
7.92
7.90
7.26
6.92
6.92
6.87
6.87
6.85
6.85
6.12
4.79
4.78
4.77
4.04
4.03
3.87
3.14
3.13
3.11
3.10
3.09
2.67
2.65
2.63
2.32
2.32
2.02
1.97
1.96
1.96
1.94
1.25
1.23
1.21
1.19
1.00
1.05
1.03
0.95
1.00
0.90
2.22
2.08
2.10
0.95
3.13
1.85
3.20
f1 (ppm)

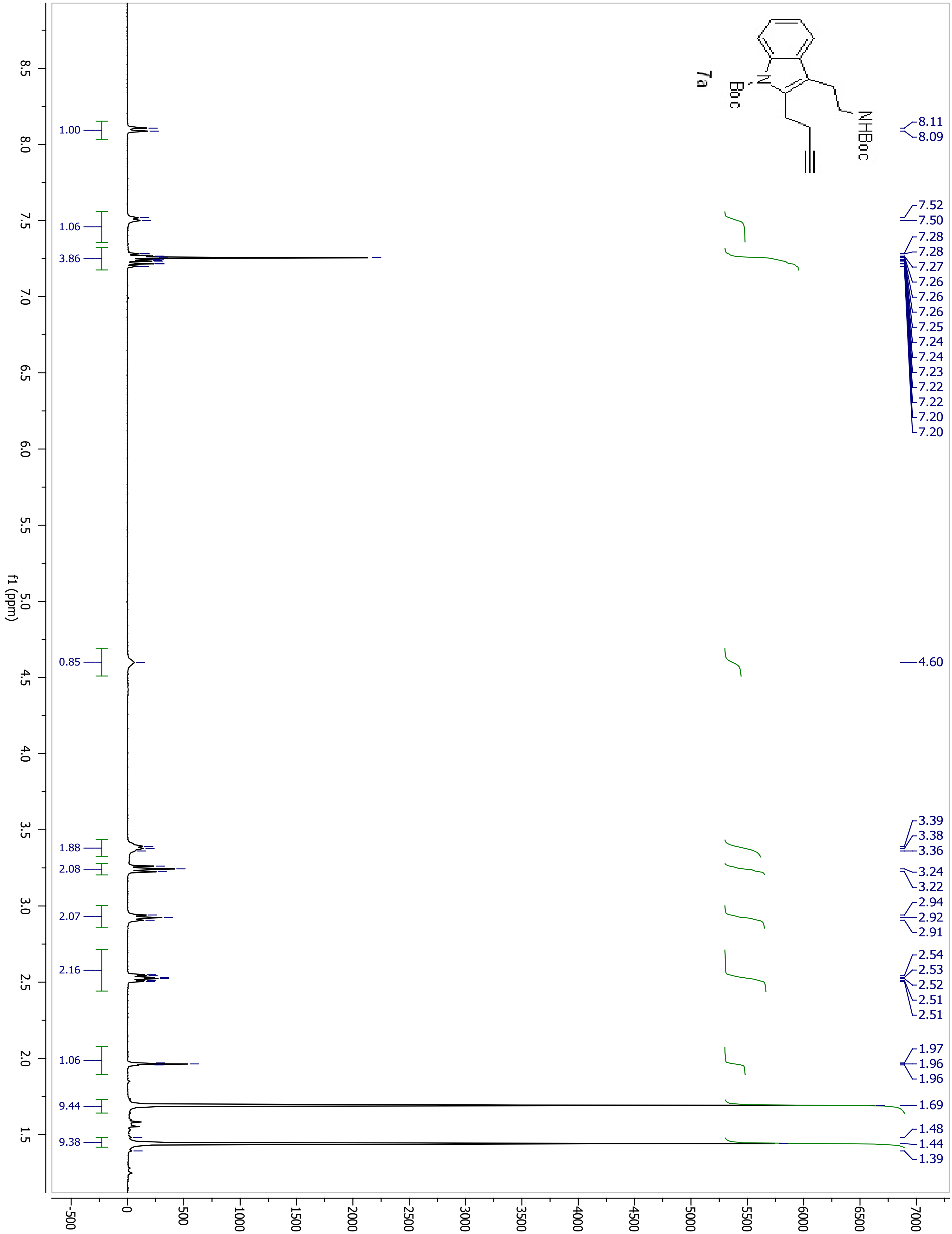

169.57
156.13
152.53
135.96
130.88
130.32
121.89
116.74
111.98
101.51
83.16
77.55
77.23
76.91
71.26
55.87
53.58
41.29
35.38
23.34
23.04
17.38
15.07
MeO
N
CO2Me
NHAc
5q
f1 (ppm)

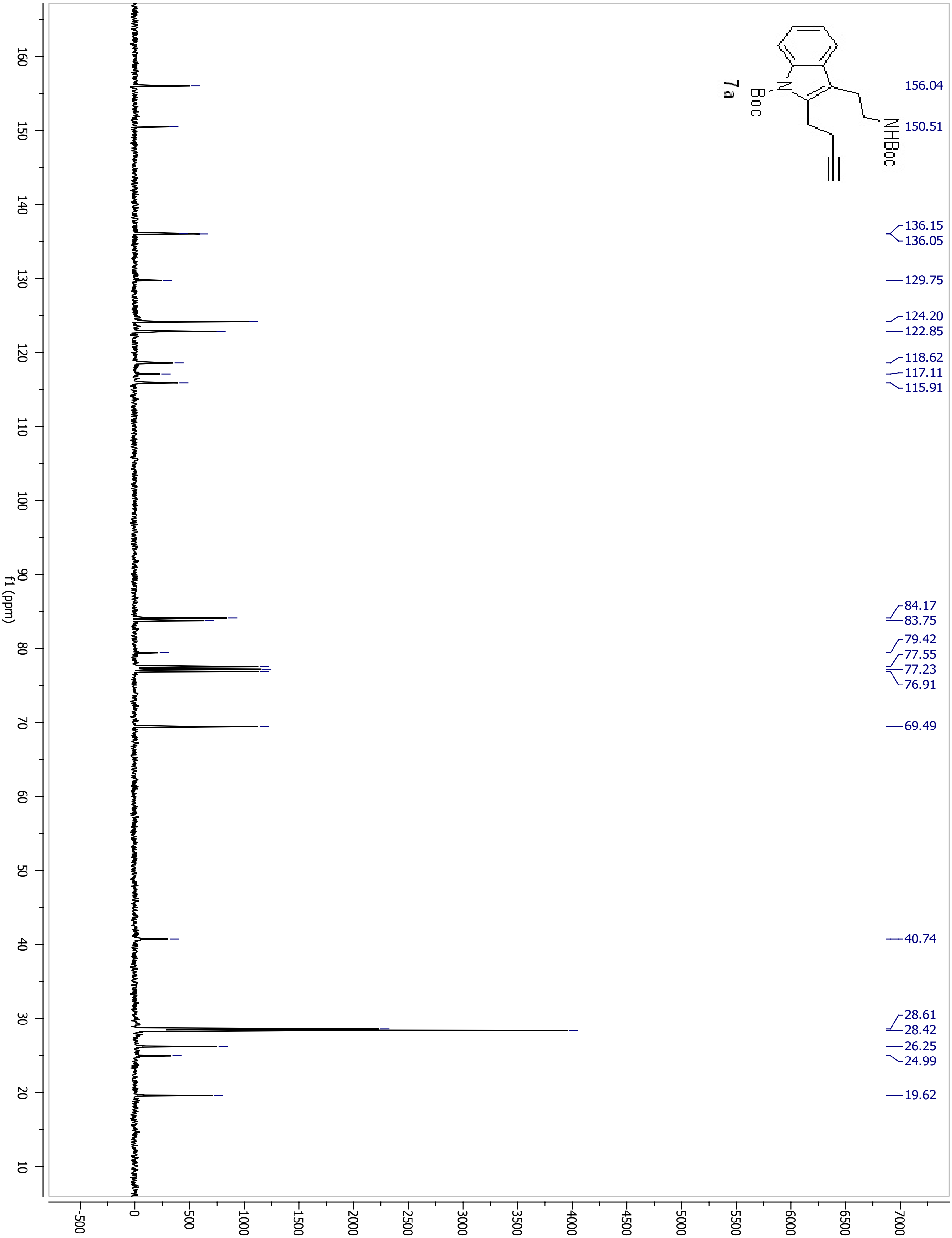

6q
MeO
CO2Me
f1 (ppm)

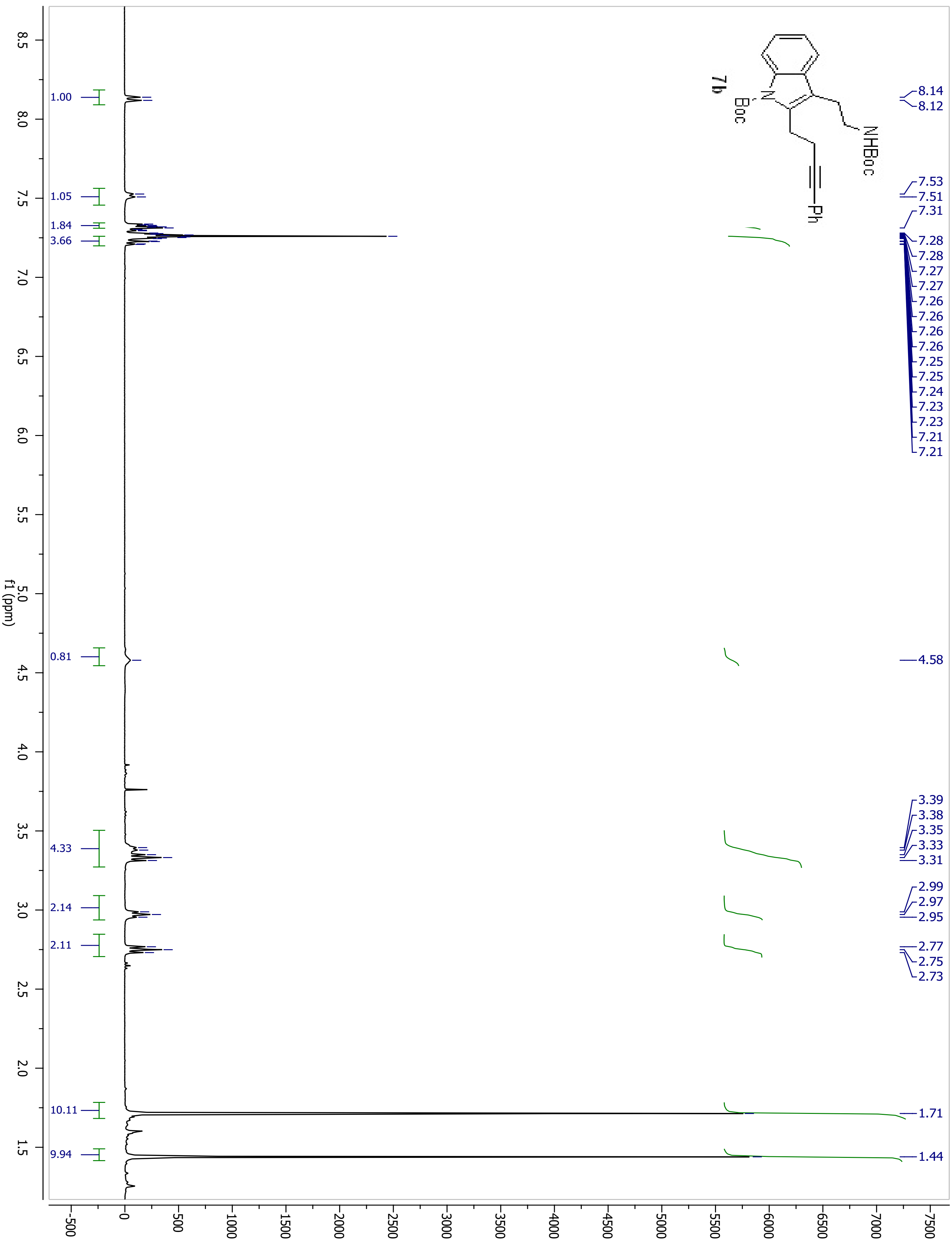

6q
MeO
N
CO_2Me
N
O
163.08
163.00
156.11
152.46
136.68
130.99
130.63
121.70
116.71
116.65
111.86
111.81
101.57
101.50
83.56
77.55
77.23
76.91
68.01
55.95
55.90
53.52
53.49
36.59
22.95
17.41
15.05
14.29
f1 (ppm)

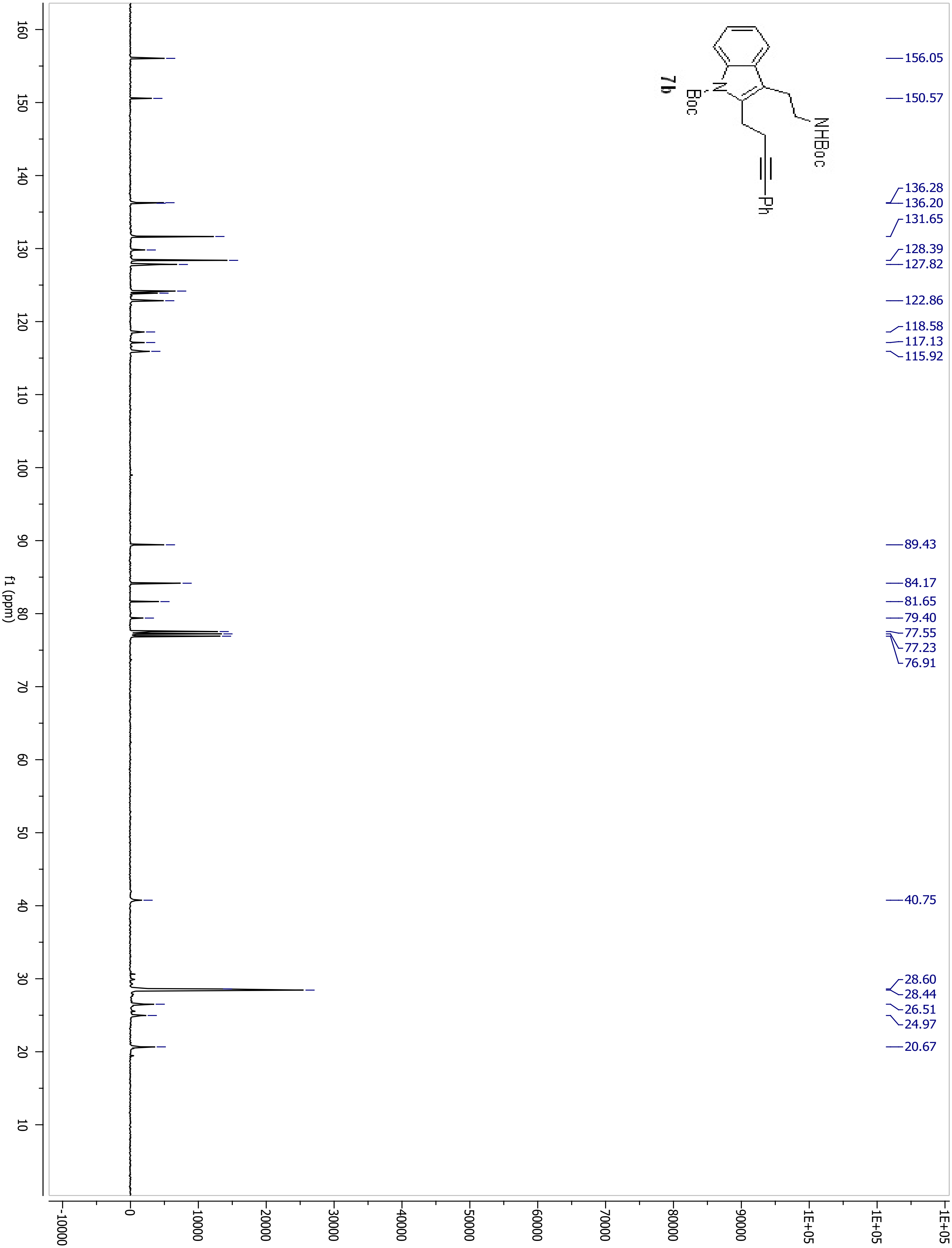

7a-1
Boc
f1 (ppm)
8.11
8.11
8.10
8.09
8.09
8.09
7.85
7.82
7.72
7.70
7.27
7.26
7.25
7.25
7.24
7.24
7.23
7.22
7.22
3.93
3.92
3.91
3.91
3.90
3.89
3.33
3.32
3.30
3.09
3.07
2.85
2.59
2.58
2.57
2.57
2.00
1.99
1.99
1.69
1.00
2.25
2.76
2.86
2.17
2.08
2.05
2.00
1.02
7.09

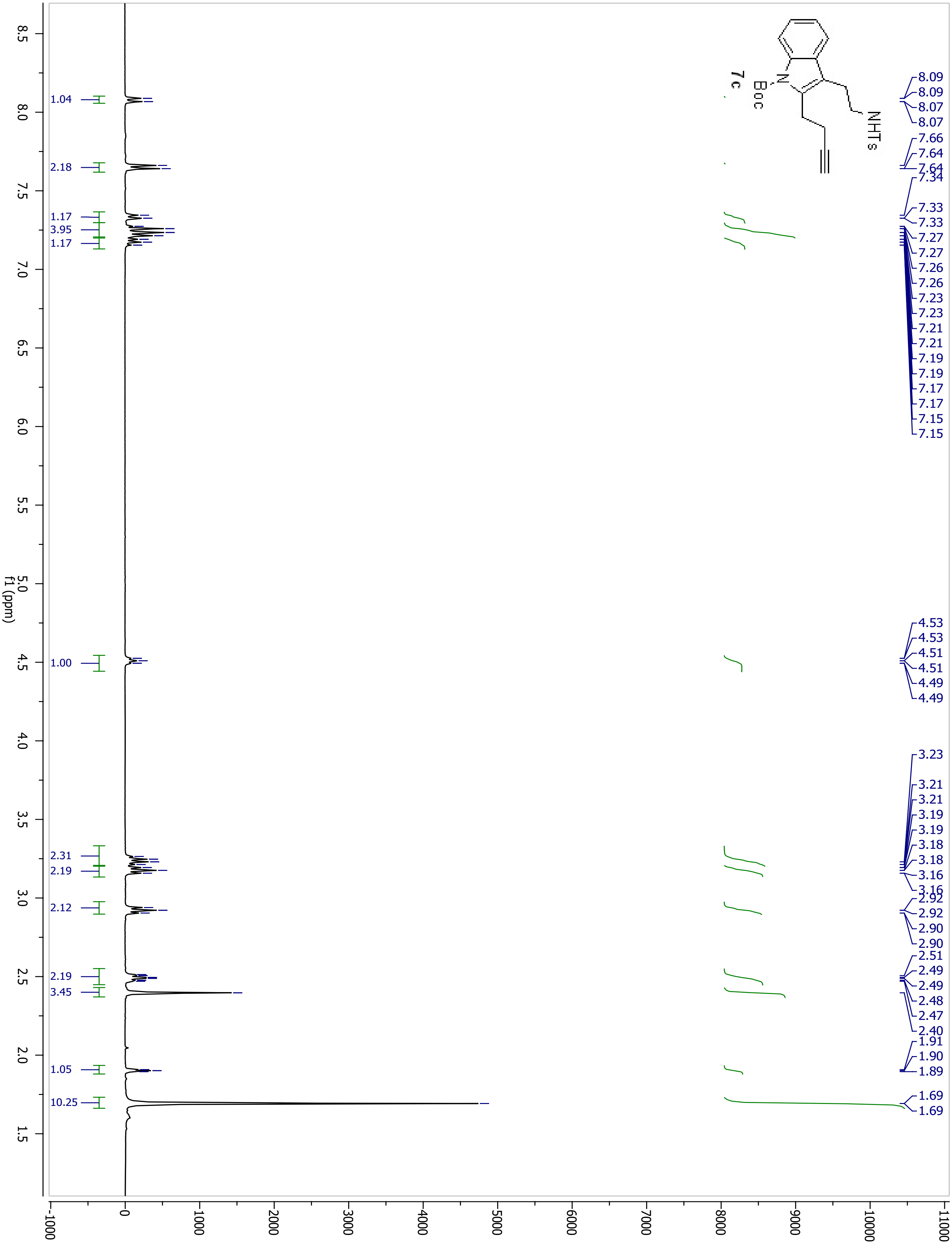

Boc
7a-1
168.43
150.52
136.14
136.09
134.23
134.16
132.33
129.56
124.23
123.44
122.99
118.58
116.39
115.96
84.19
83.70
77.55
77.23
76.91
69.59
38.09
28.43
26.25
23.78
19.62
f1 (ppm)

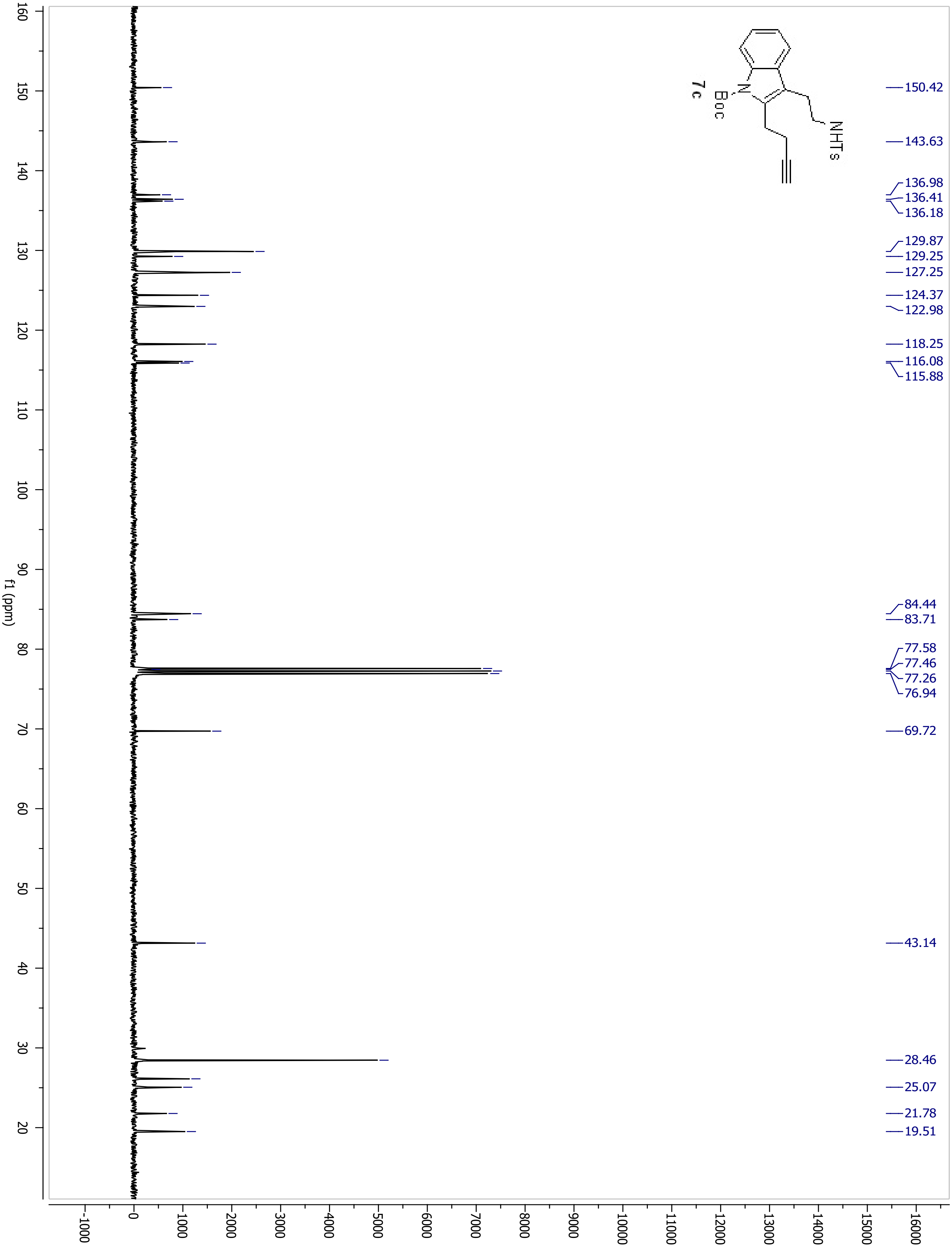

7a
NHBoc
N
Boc
8.11
8.09
7.52
7.50
7.28
7.28
7.27
7.26
7.26
7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.20
7.20
4.60
3.39
3.38
3.36
3.24
3.22
2.94
2.92
2.91
2.54
2.53
2.52
2.51
2.51
1.97
1.96
1.96
1.69
1.48
1.44
1.39
1.00
1.06
3.86
0.85
1.88
2.08
2.07
2.16
1.06
9.44
9.38
f1 (ppm)


7a
Boc
NHBoc
156.04
150.51
136.15
136.05
129.75
124.20
122.85
118.62
117.11
115.91
84.17
83.75
79.42
77.55
77.23
76.91
69.49
40.74
28.61
28.42
26.25
24.99
19.62
f1 (ppm)

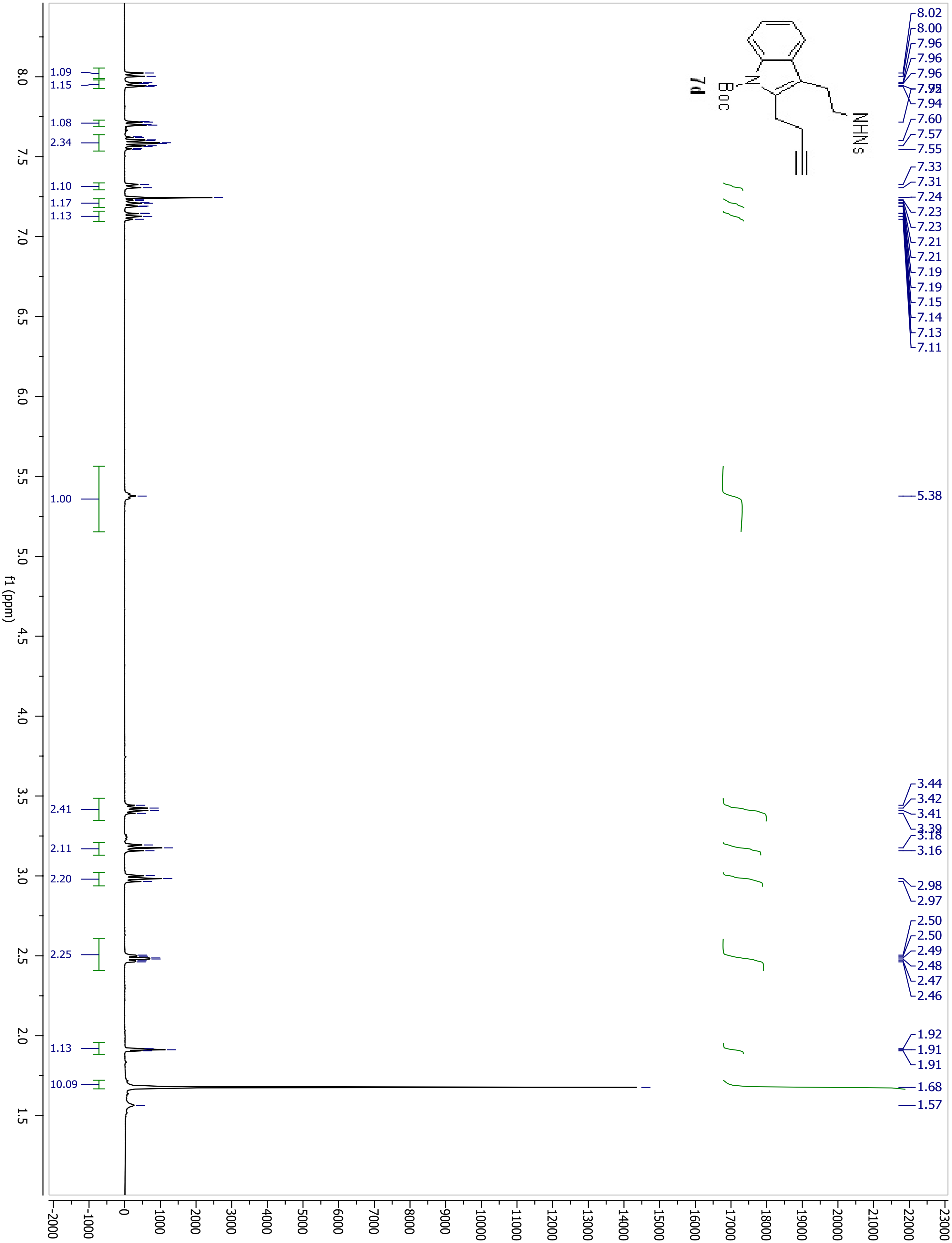

7b
NHBoc
Boc
Ph
N
8.14
8.12
7.53
7.51
7.31
7.28
7.28
7.27
7.27
7.26
7.26
7.26
7.26
7.25
7.25
7.24
7.23
7.23
7.21
7.21
4.58
3.39
3.38
3.35
3.33
3.31
2.99
2.97
2.95
2.77
2.75
2.73
1.71
1.44
1.00
1.05
1.84
3.66
0.81
4.33
2.14
2.11
10.11
9.94
f1 (ppm)


7b
Boc
NHBoc
Ph
156.05
150.57
136.28
136.20
131.65
128.39
127.82
122.86
118.58
117.13
115.92
89.43
84.17
81.65
79.40
77.55
77.23
76.91
40.75
28.60
28.44
26.51
24.97
20.67
f1 (ppm)

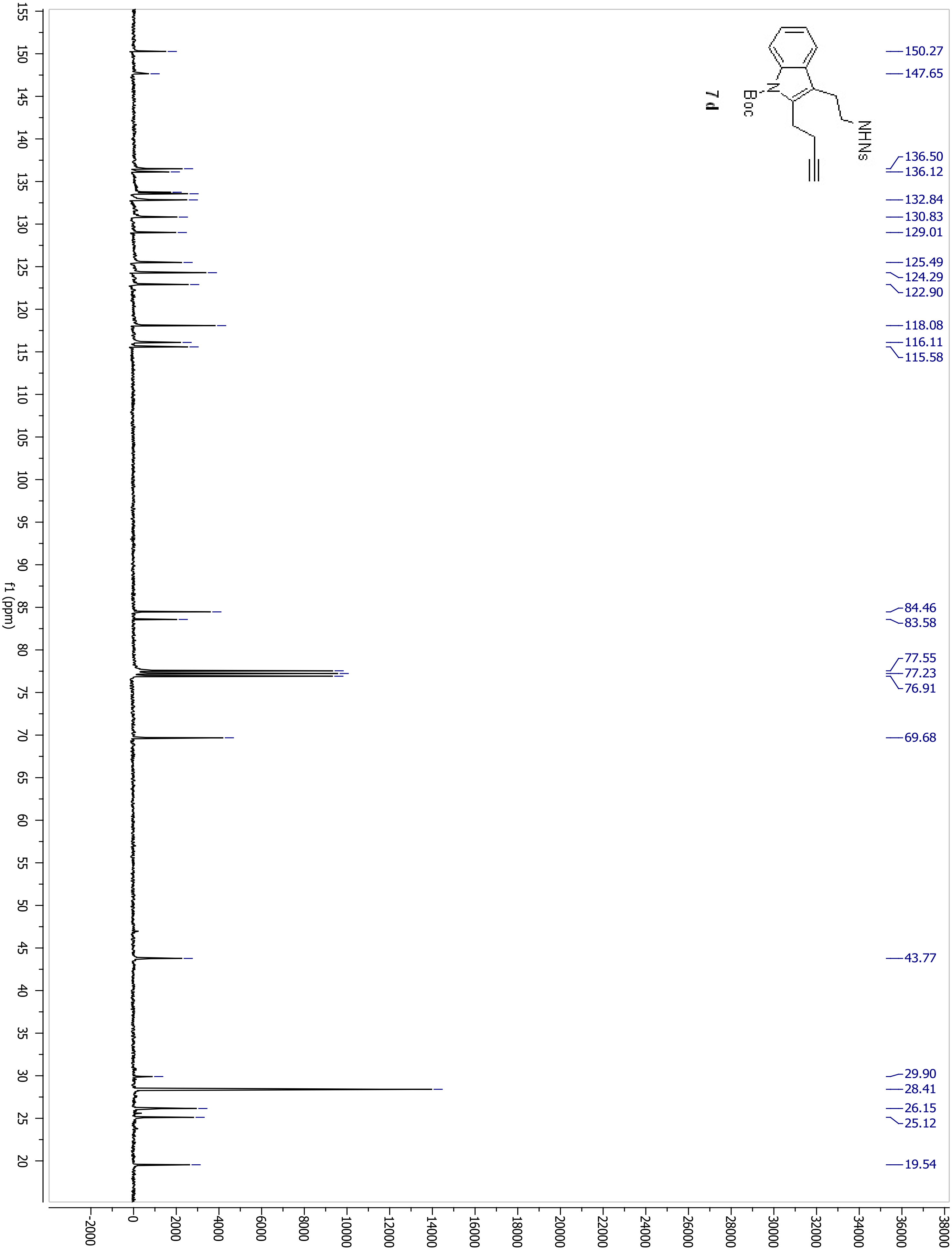

7c
Boc
NHTs
f1 (ppm)
8.09
8.09
8.07
8.07
7.66
7.64
7.64
7.34
7.33
7.33
7.27
7.27
7.26
7.26
7.23
7.23
7.21
7.21
7.19
7.19
7.17
7.17
7.15
7.15
4.53
4.53
4.51
4.51
4.49
4.49
3.23
3.21
3.21
3.19
3.19
3.18
3.18
3.16
3.16
2.92
2.92
2.90
2.90
2.51
2.49
2.49
2.48
2.47
2.40
1.91
1.90
1.89
1.69
1.69
1.04
2.18
1.17
3.95
1.17
1.00
2.31
2.19
2.12
2.19
3.45
1.05
10.25

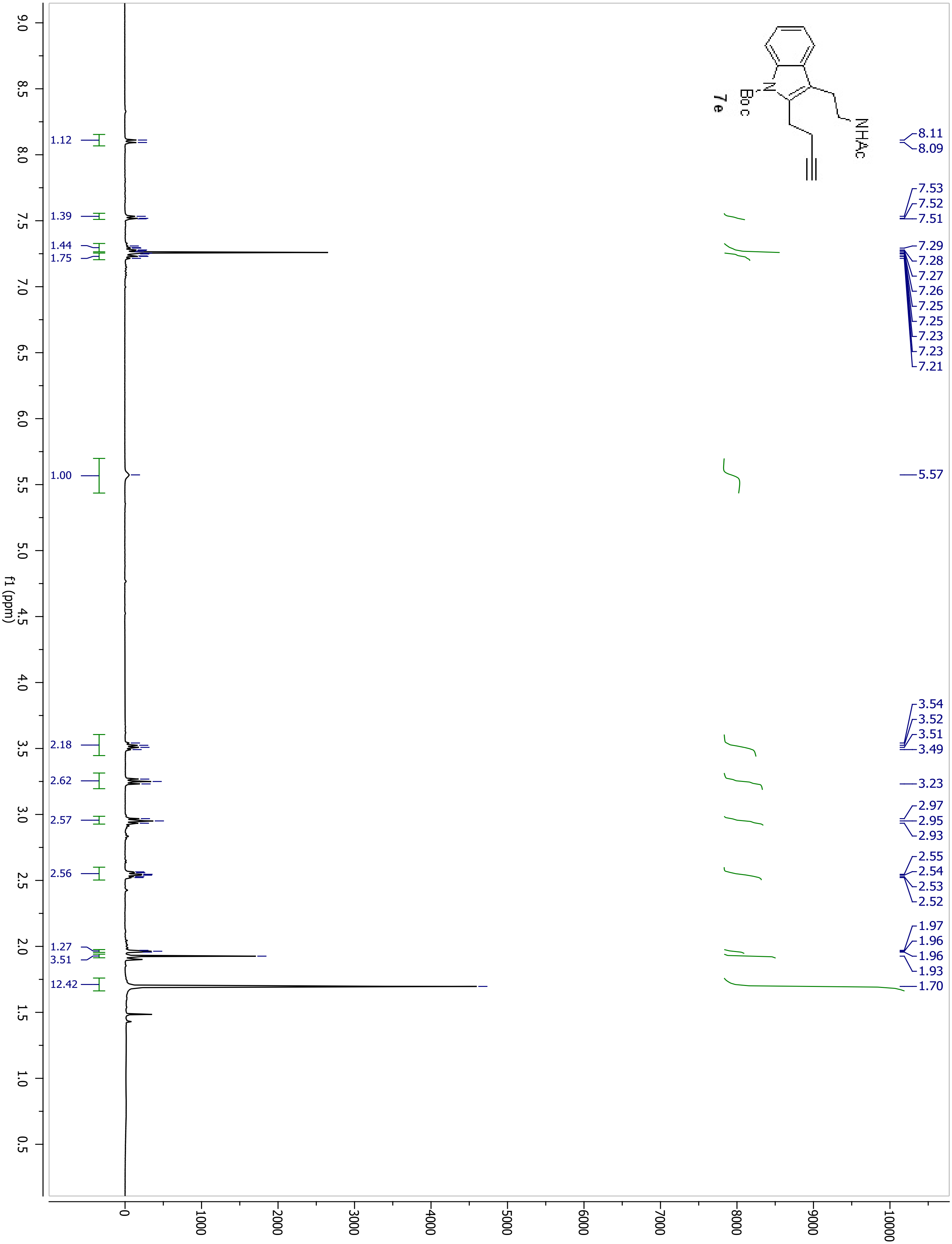


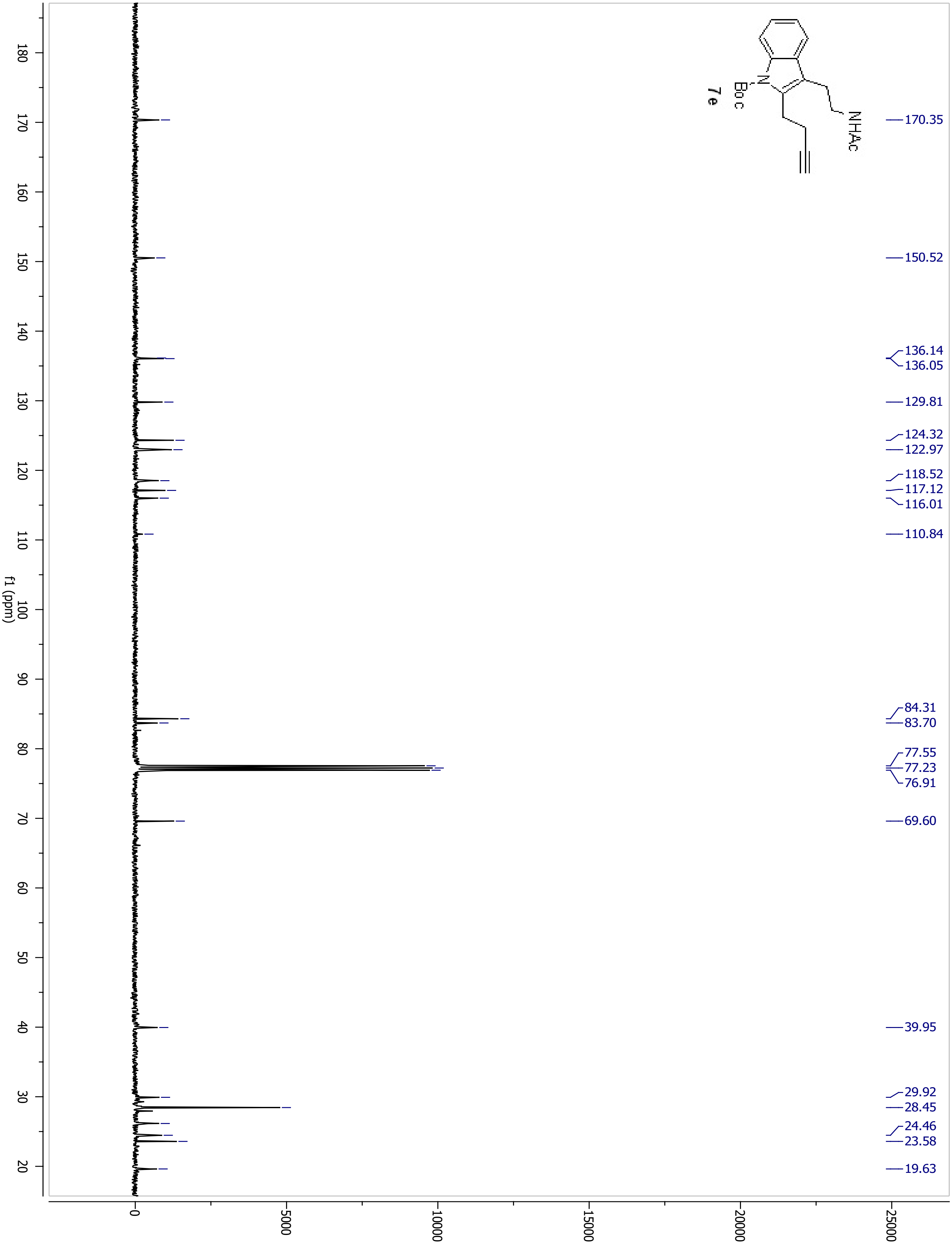
150.42
143.63
136.98
136.41
136.18
129.87
129.25
127.25
124.37
122.98
118.25
116.08
115.88
84.44
83.71
77.58
77.46
77.26
76.94
69.72
43.14
28.46
25.07
21.78
19.51
NHTs
N
Boc
7c
f1 (ppm)

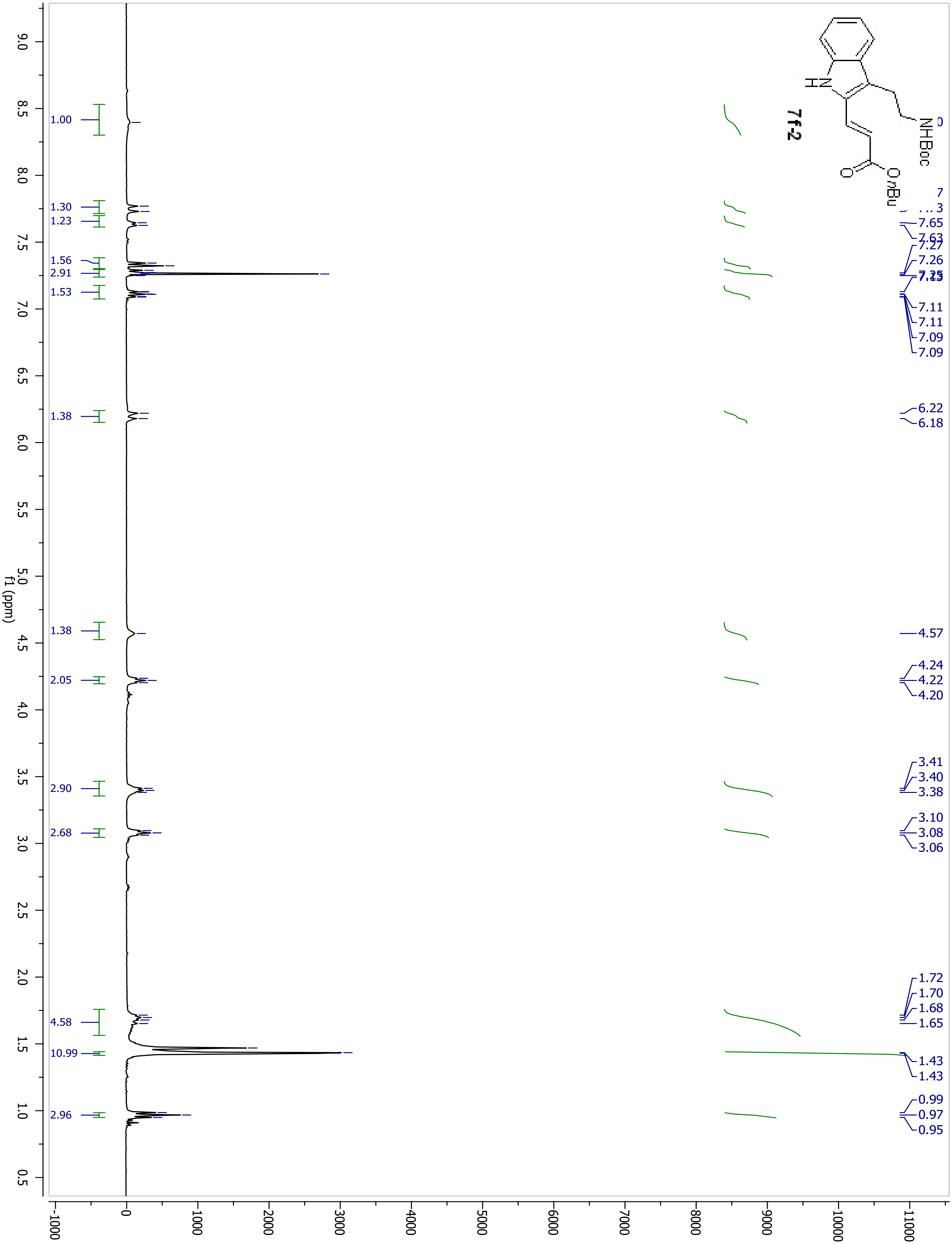


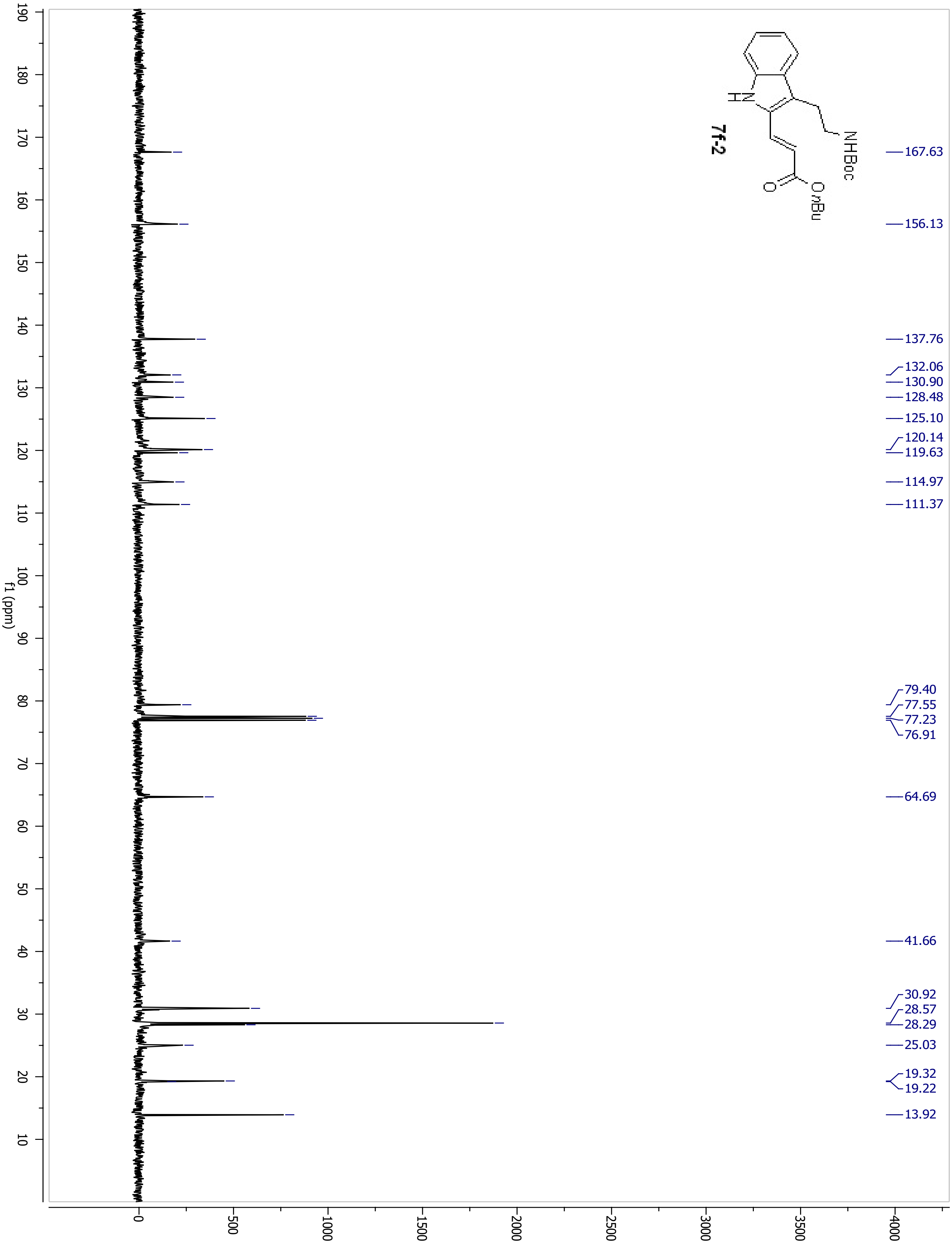
NHNs
Boc
7d
f1 (ppm)

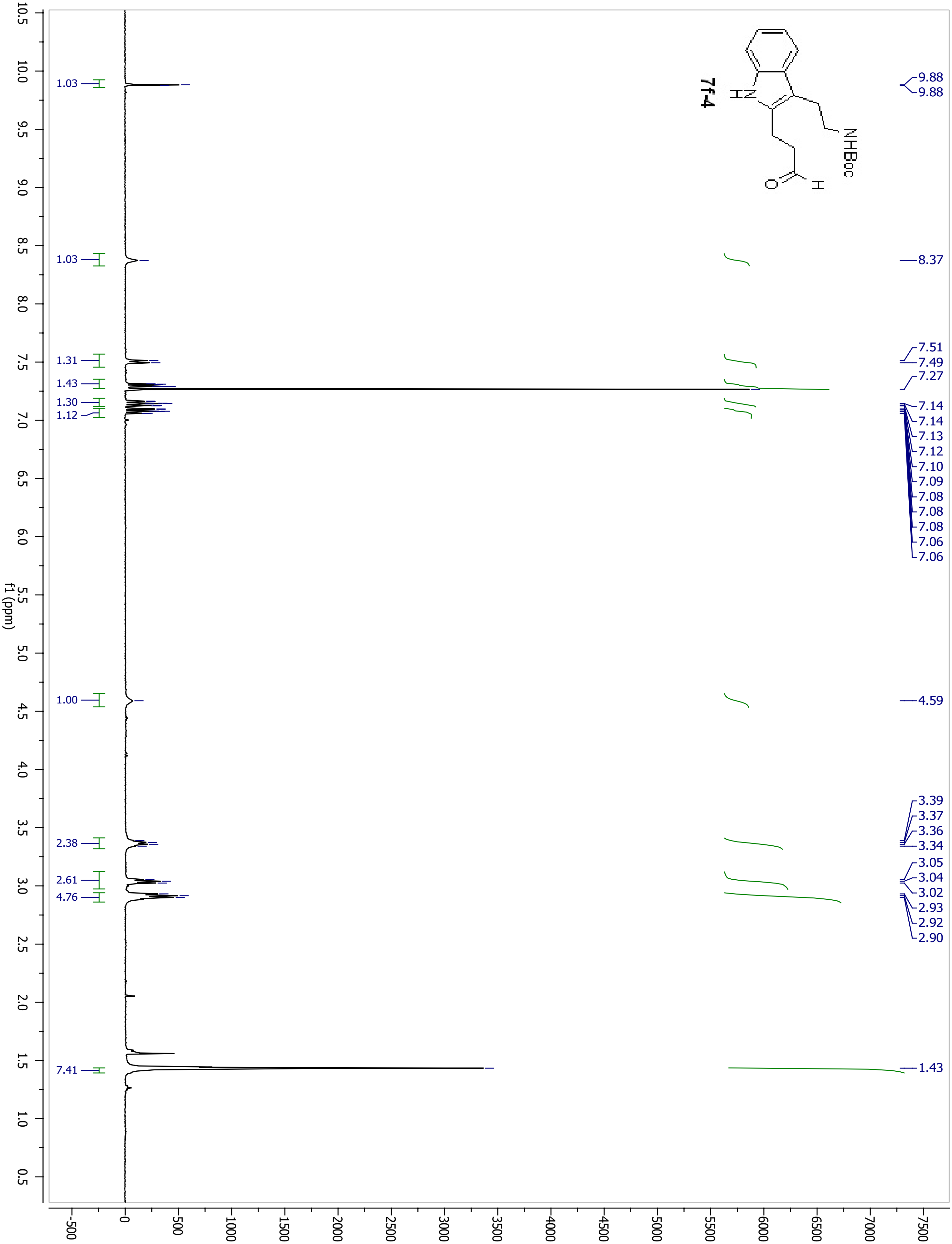

7d
Boc
NHNs
150.27
147.65
136.50
136.12
132.84
130.83
129.01
125.49
124.29
122.90
118.08
116.11
115.58
84.46
83.58
77.55
77.23
76.91
69.68
43.77
29.90
28.41
26.15
25.12
19.54
f1 (ppm)

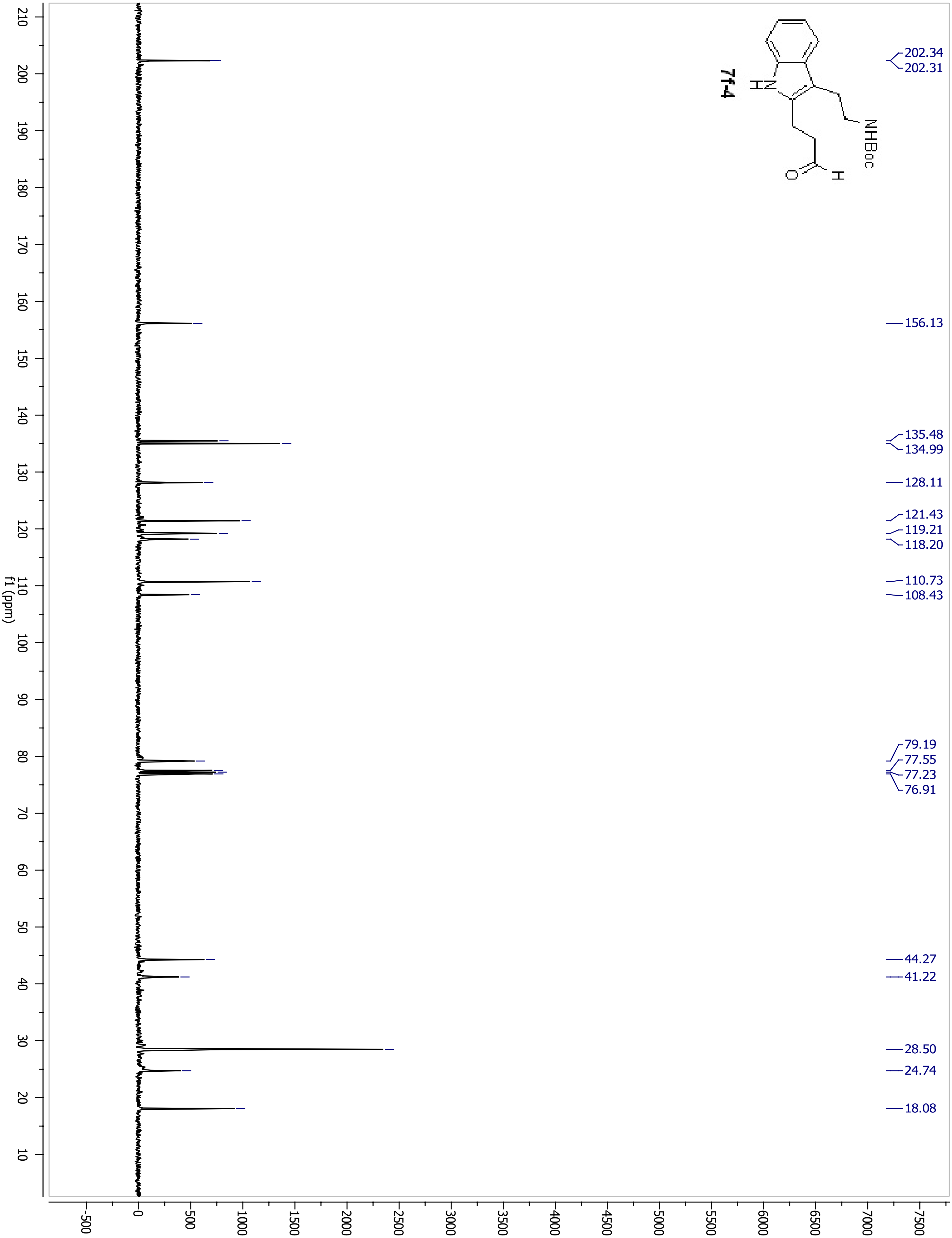

NHAc
N
Boc
7e
8.11
8.09
7.53
7.52
7.51
7.29
7.28
7.27
7.26
7.25
7.25
7.23
7.23
7.21
5.57
3.54
3.52
3.51
3.49
3.23
2.97
2.95
2.93
2.55
2.54
2.53
2.52
1.97
1.96
1.96
1.93
1.70
1.12
1.39
1.44
1.75
1.00
2.18
2.62
2.57
2.56
1.27
3.51
12.42
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000

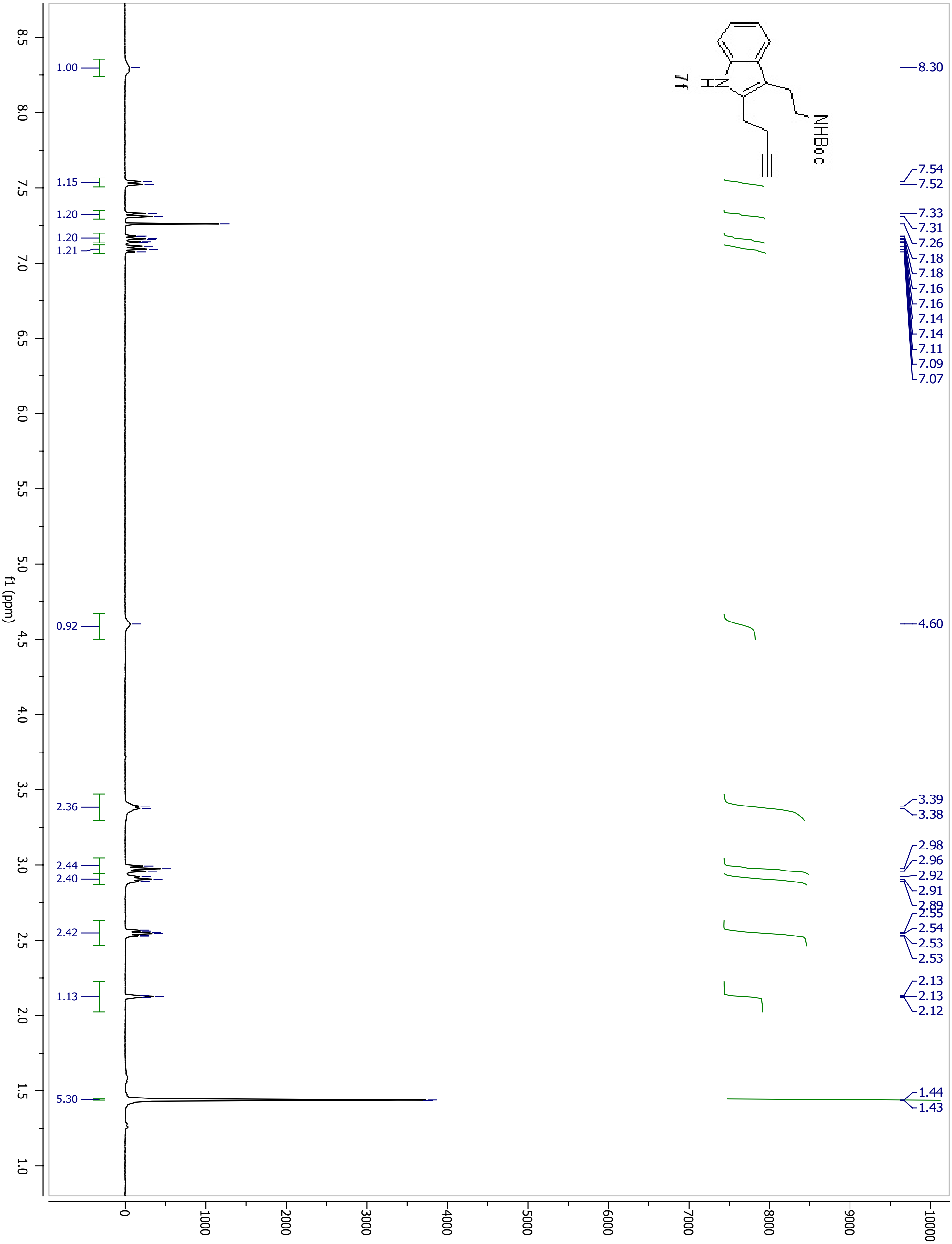

NHAc
Boc
7e
170.35
150.52
136.14
136.05
129.81
124.32
122.97
118.52
117.12
116.01
110.84
84.31
83.70
77.55
77.23
76.91
69.60
39.95
29.92
28.45
24.46
23.58
19.63
f1 (ppm)


7f-2
NHBoc
OnBu
HN
O
7.65
7.63
7.27
7.26
6.22
6.18
7.11
7.11
7.09
7.09
4.57
4.24
4.22
4.20
3.41
3.40
3.38
3.10
3.08
3.06
1.72
1.70
1.68
1.65
1.43
1.43
0.99
0.97
0.95
1.00
1.30
1.23
1.56
2.91
1.53
1.38
1.38
2.05
2.90
2.68
4.58
10.99
2.96
f1 (ppm)

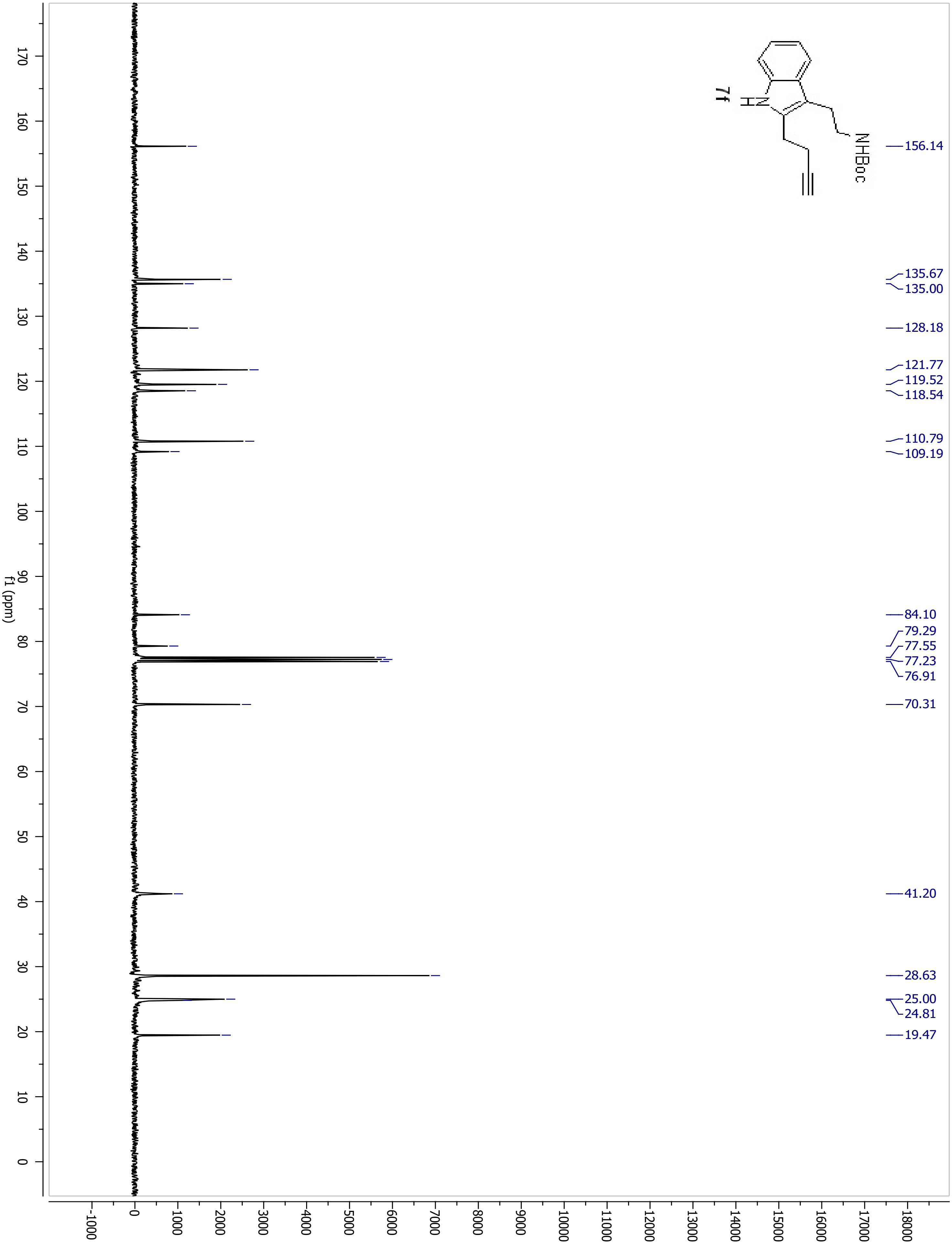

7f-2
NHBoc
OnBu
NH
O
167.63
156.13
137.76
132.06
130.90
128.48
125.10
120.14
119.63
114.97
111.37
79.40
77.55
77.23
76.91
64.69
41.66
30.92
28.57
28.29
25.03
19.32
19.22
13.92
f1 (ppm)

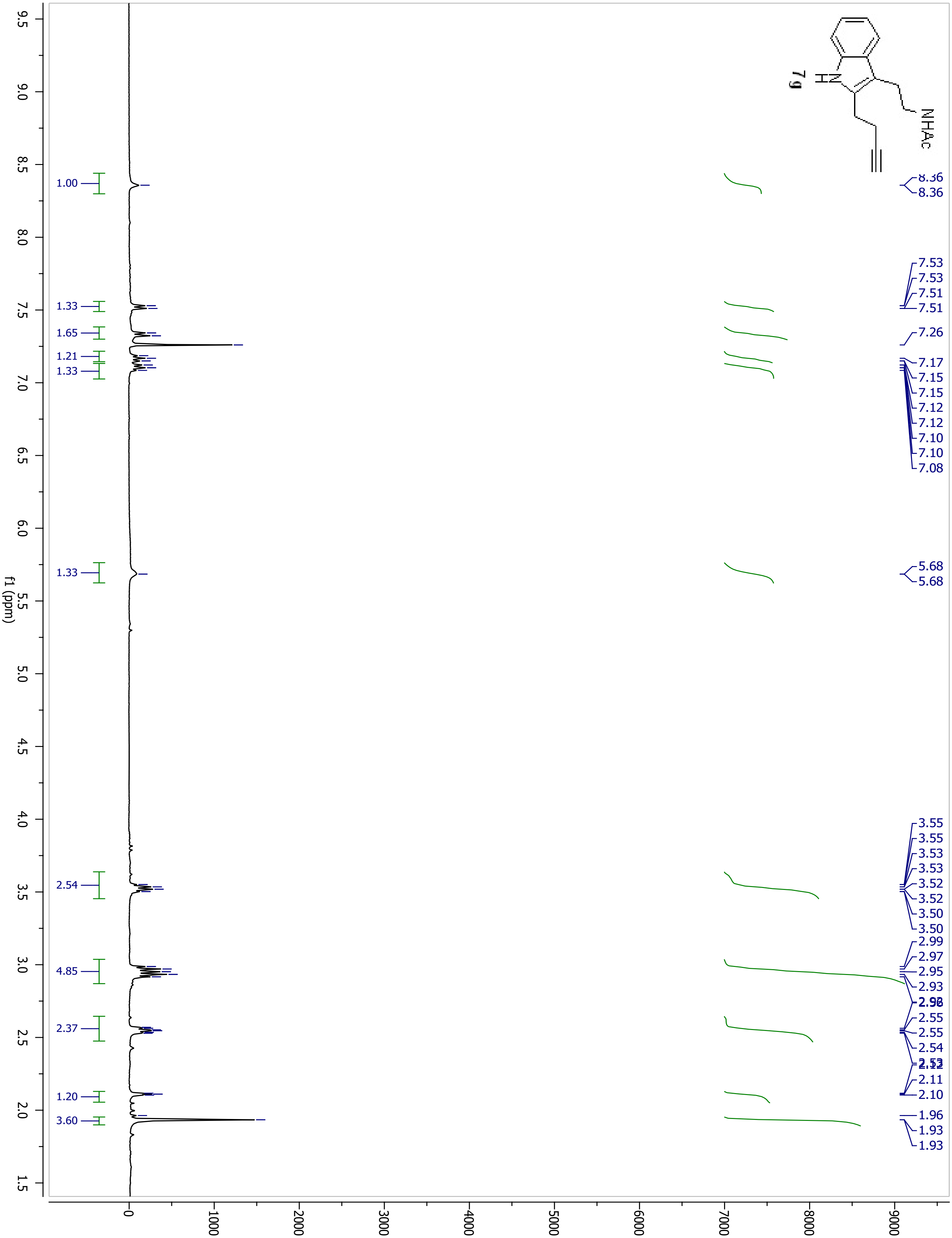

7f-4
NHBoc
f1 (ppm)

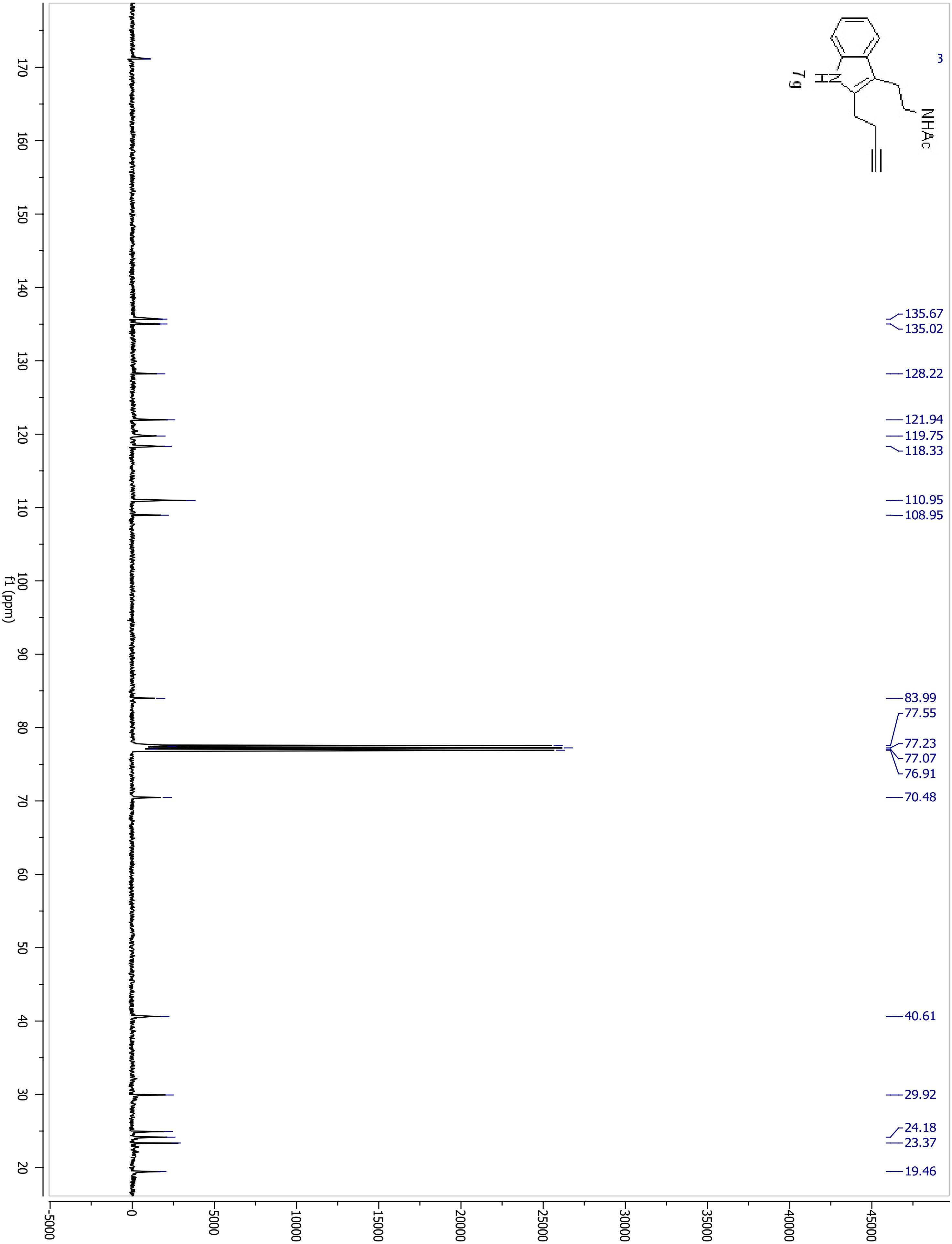

7f-4
NHBoc
202.34
202.31
156.13
135.48
134.99
128.11
121.43
119.21
118.20
110.73
108.43
79.19
77.55
77.23
76.91
44.27
41.22
28.50
24.74
18.08
f1 (ppm)

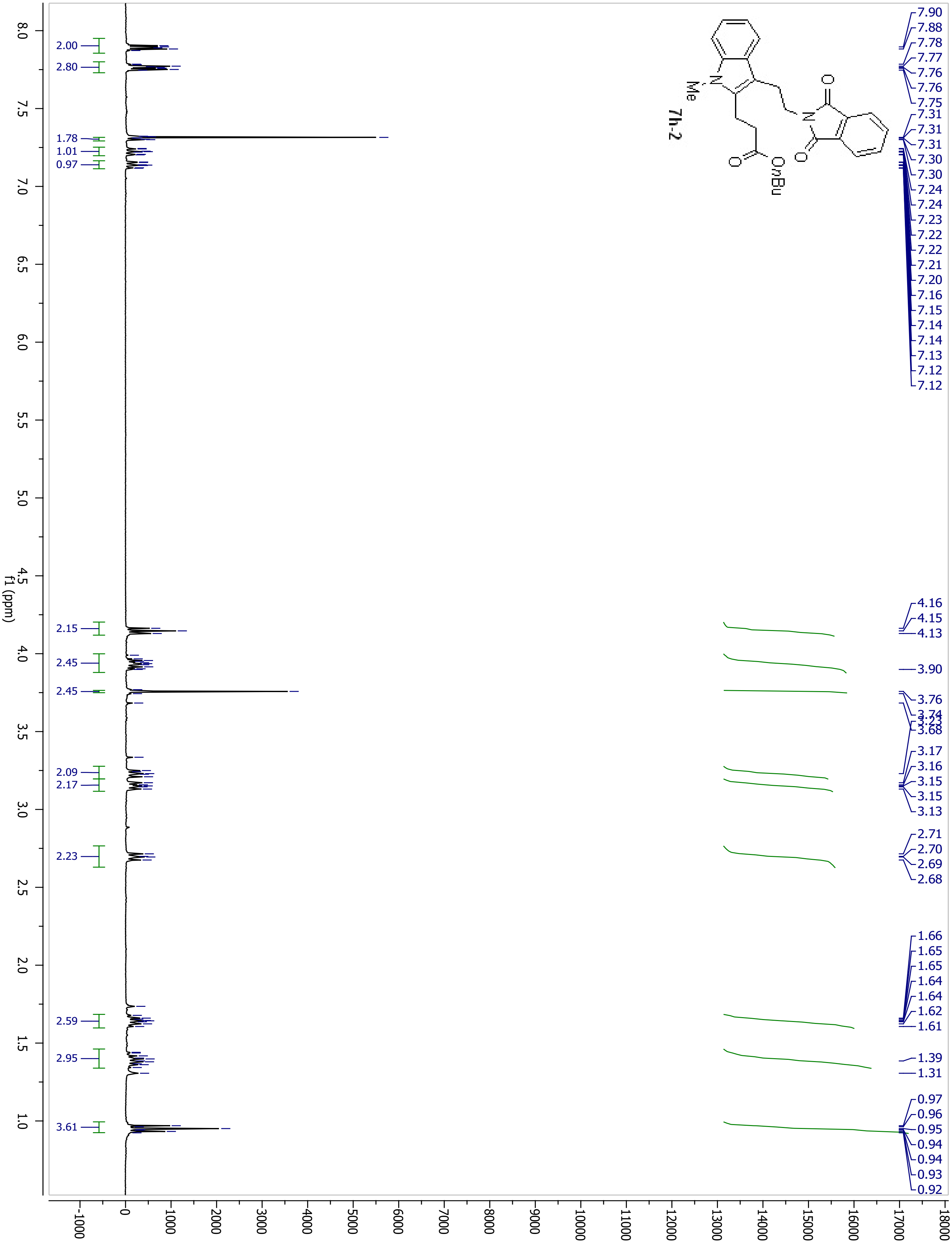


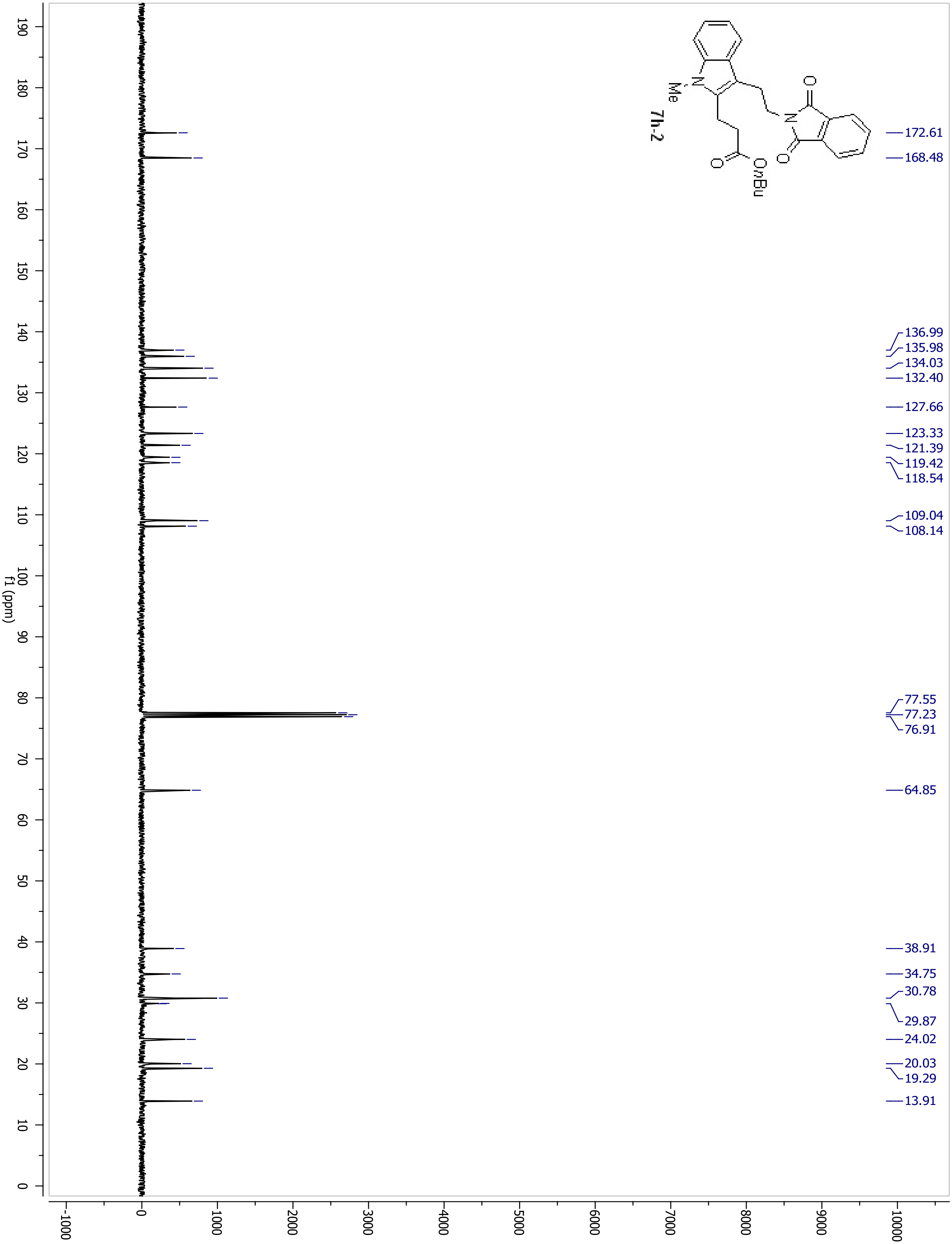
7f
NHBoc
f1 (ppm)
8.30
7.54
7.52
7.33
7.31
7.26
7.18
7.18
7.16
7.16
7.14
7.14
7.11
7.09
7.07
4.60
3.39
3.38
2.98
2.96
2.92
2.91
2.89
2.55
2.54
2.53
2.53
2.13
2.13
2.12
1.44
1.43
1.00
1.15
1.20
1.20
1.21
0.92
2.36
2.44
2.40
2.42
1.13
5.30

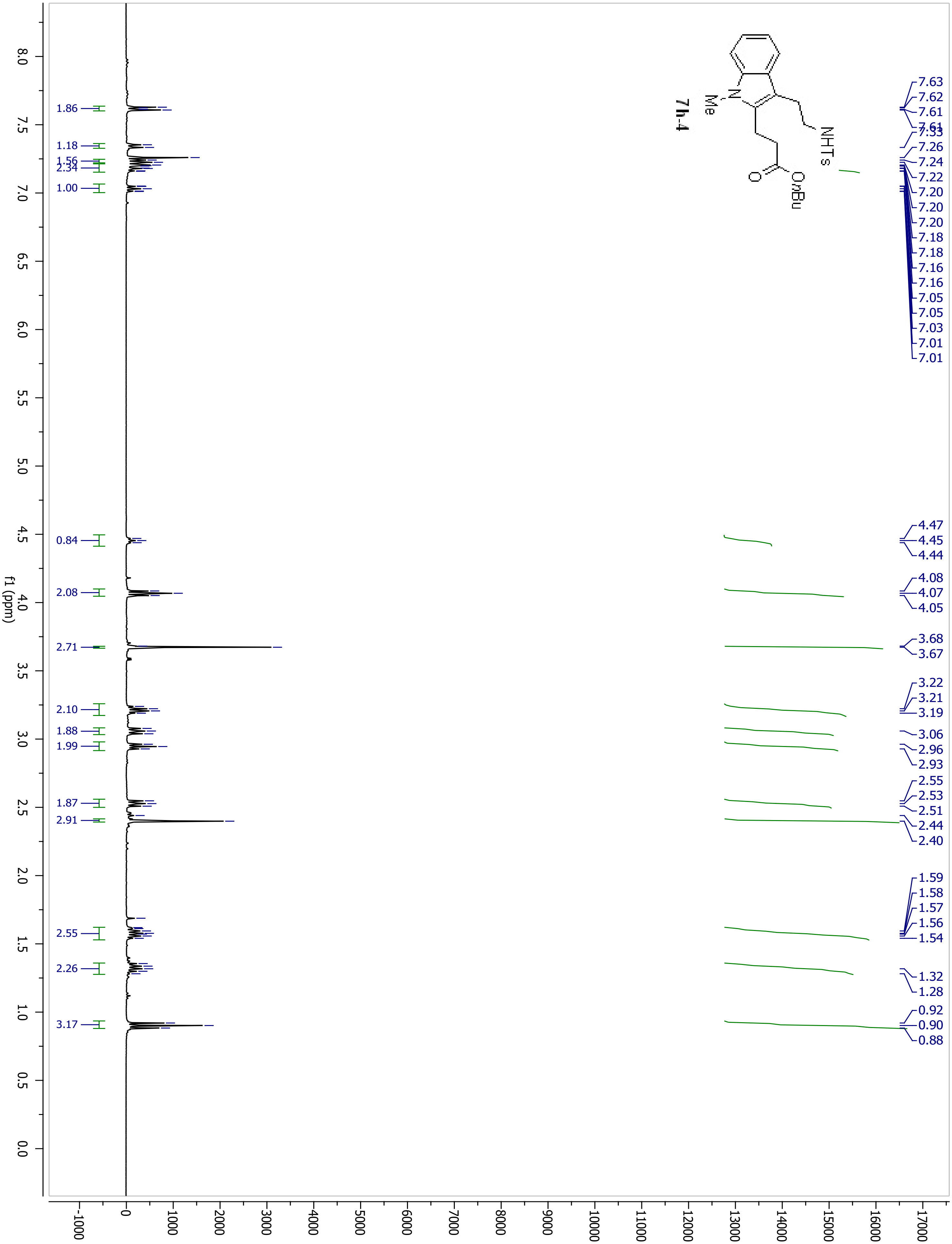

7f
NHBoc
156.14
135.67
135.00
128.18
121.77
119.52
118.54
110.79
109.19
84.10
79.29
77.55
77.23
76.91
70.31
41.20
28.63
25.00
24.81
19.47
f1 (ppm)

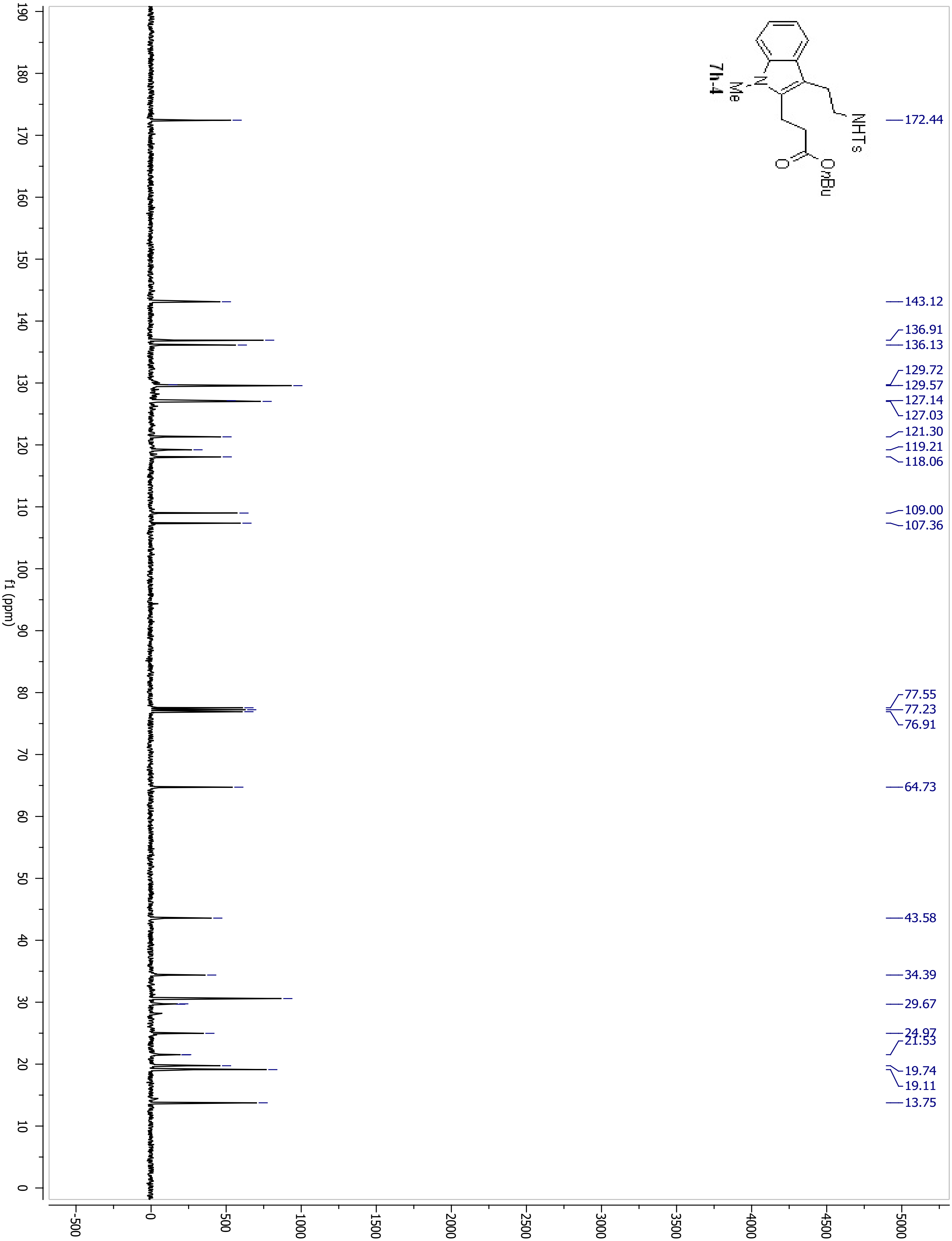

7g
NHAc
f1 (ppm)


7g
NHAc
135.67
135.02
128.22
121.94
119.75
118.33
110.95
108.95
83.99
77.55
77.23
77.07
76.91
70.48
40.61
29.92
24.18
23.37
19.46
f1 (ppm)

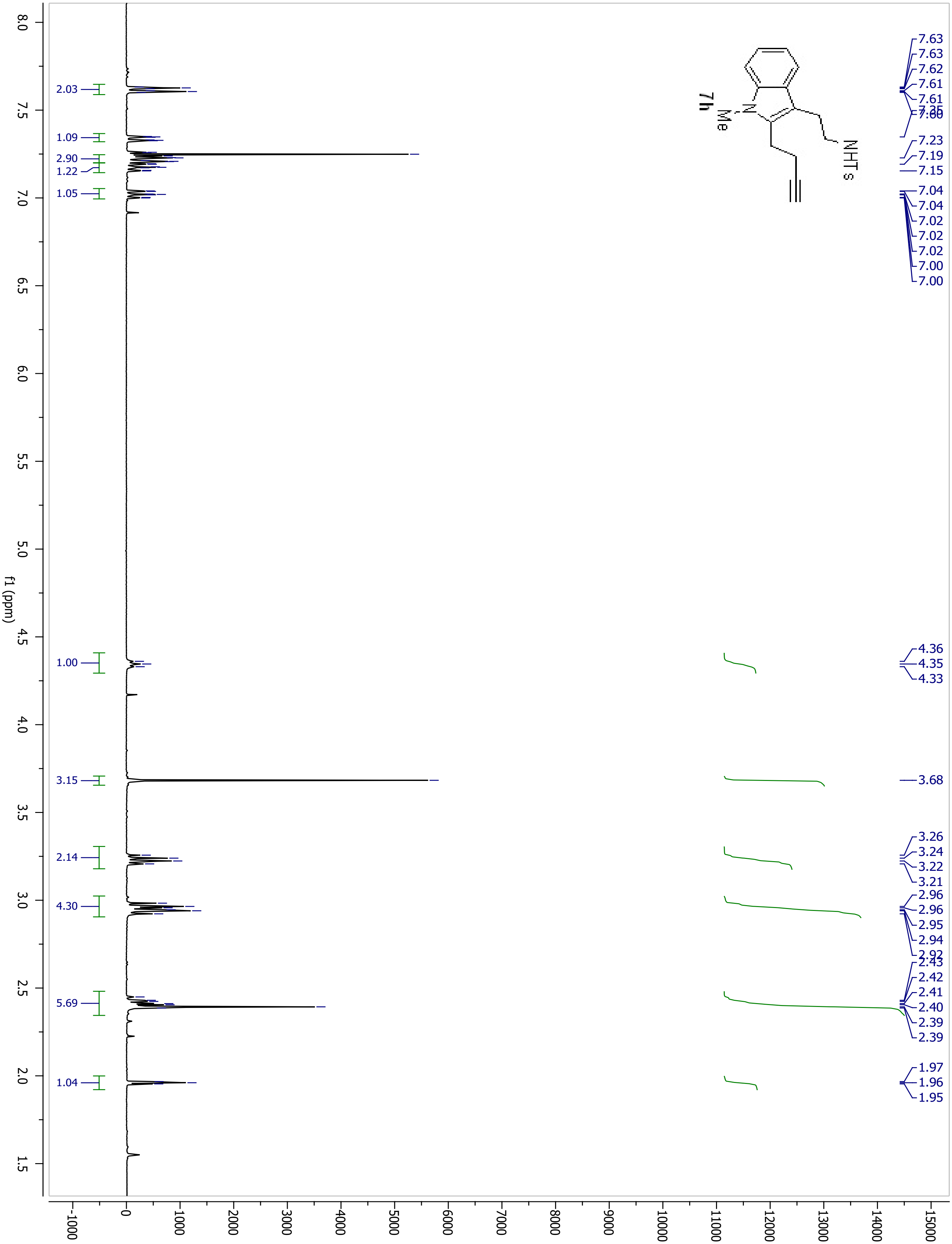

7h-2
OnBu
Me
f1 (ppm)

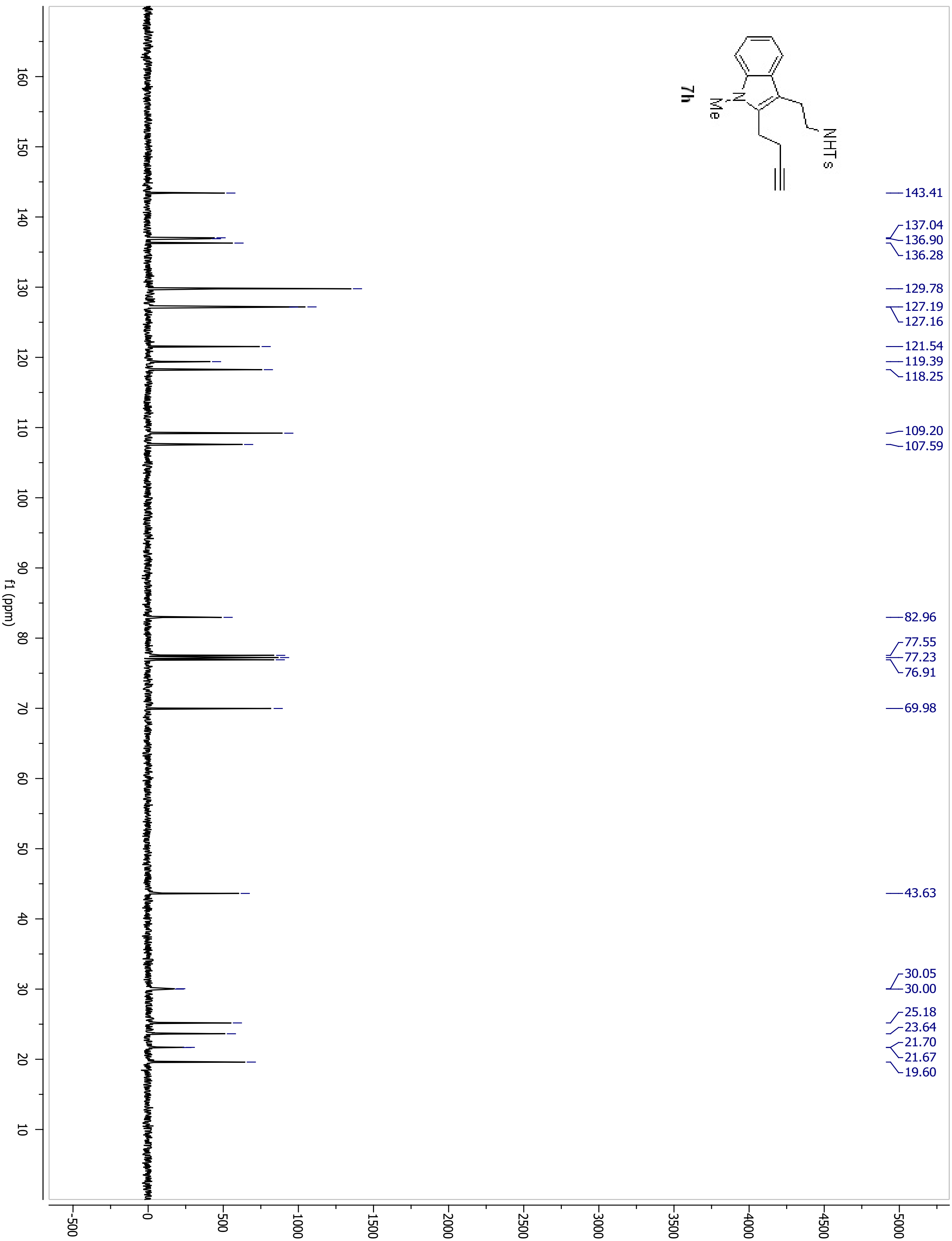

7h-2
Me
N
O
OnBu
172.61
168.48
136.99
135.98
134.03
132.40
127.66
123.33
121.39
119.42
118.54
109.04
108.14
77.55
77.23
76.91
64.85
38.91
34.75
30.78
29.87
24.02
20.03
19.29
13.91
f1 (ppm)

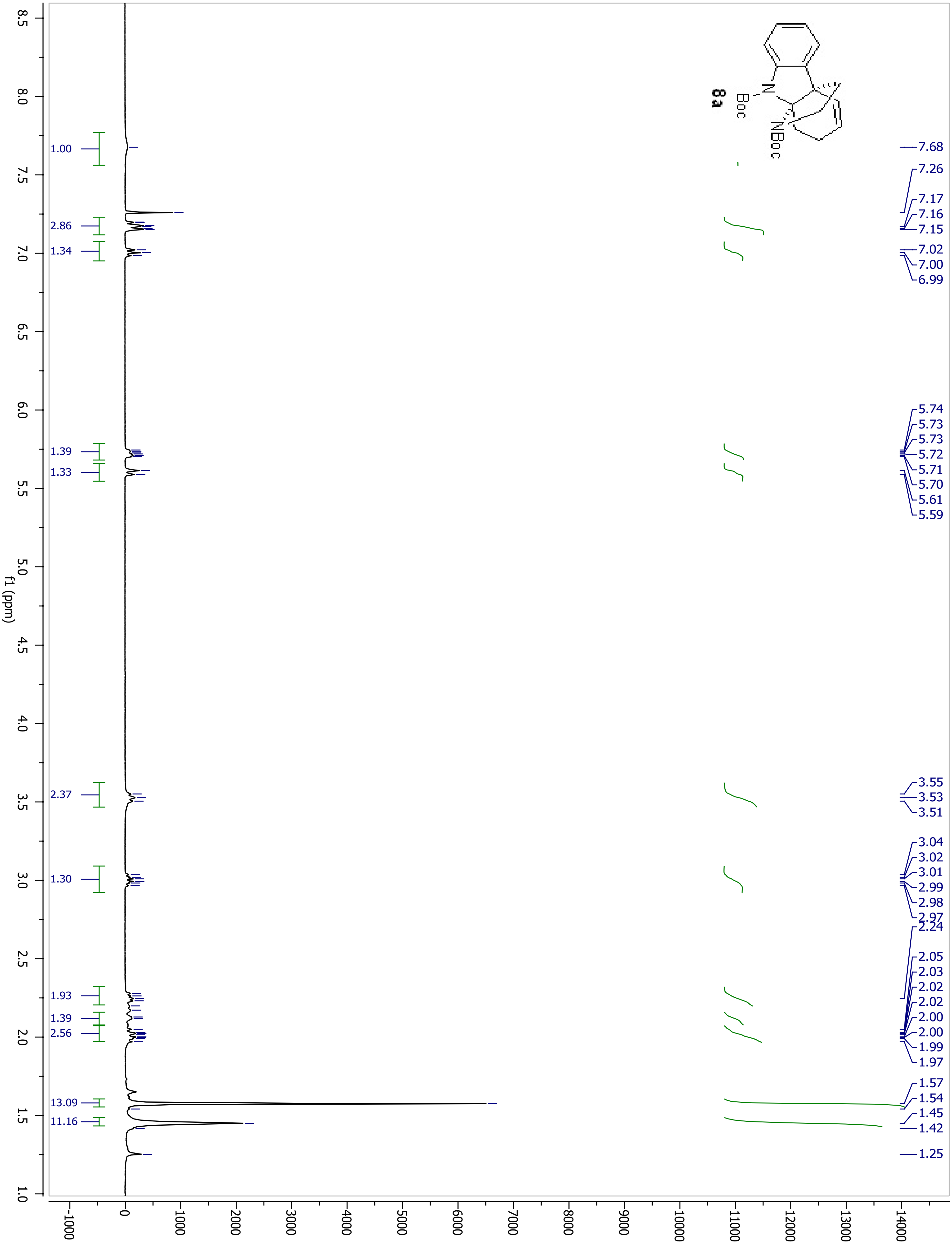

7h-4
NHTs
OnBu
Me
N
O
7.63
7.62
7.61
7.61
7.33
7.26
7.24
7.22
7.20
7.20
7.20
7.18
7.18
7.16
7.16
7.05
7.05
7.03
7.01
7.01
4.47
4.45
4.44
4.08
4.07
4.05
3.68
3.67
3.22
3.21
3.19
3.06
2.96
2.93
2.55
2.53
2.51
2.44
2.40
1.59
1.58
1.57
1.56
1.54
1.32
1.28
0.92
0.90
0.88
1.86
1.18
1.56
2.34
1.00
0.84
2.08
2.71
2.10
1.88
1.99
1.87
2.91
2.55
2.26
3.17
f1 (ppm)

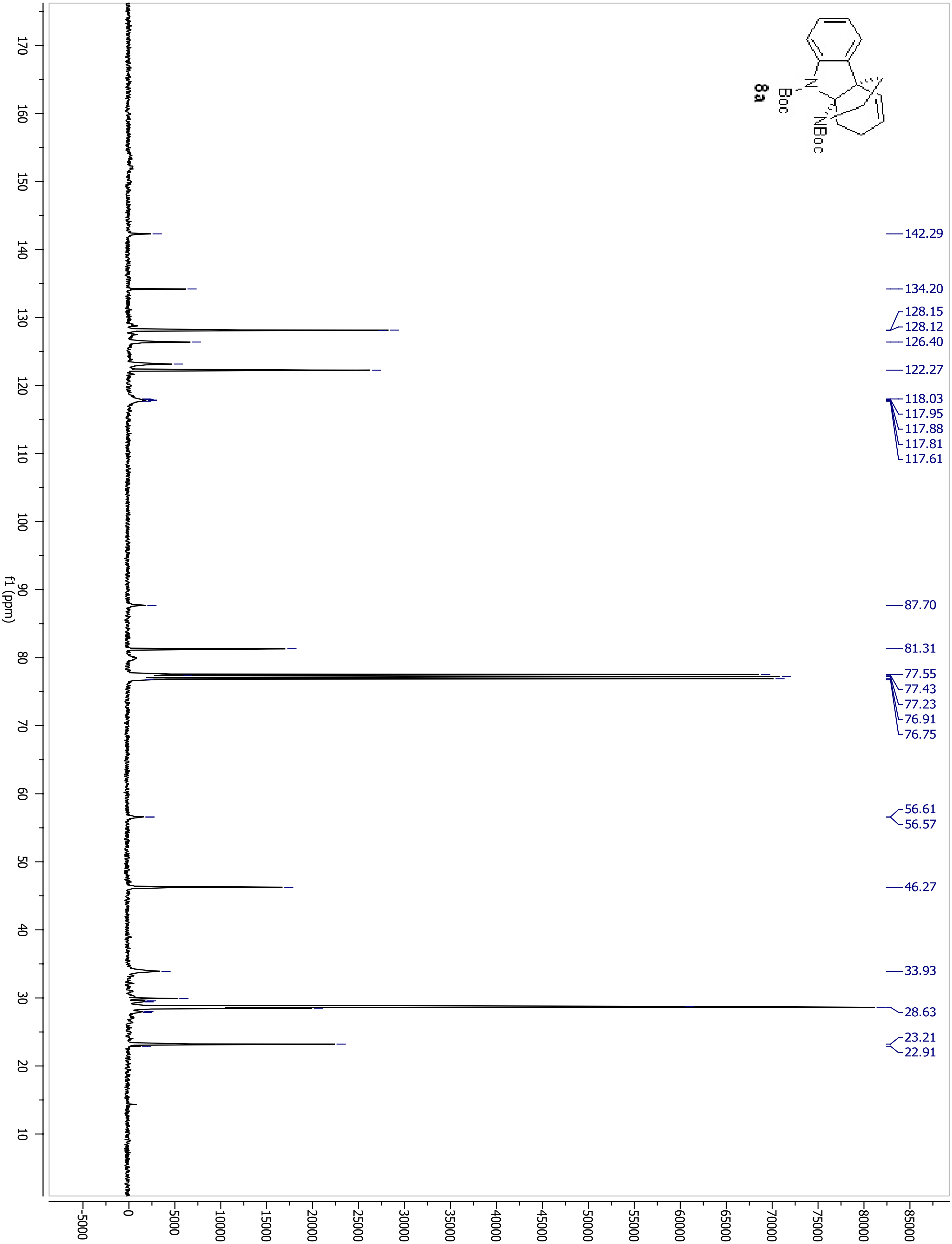


7h-4
Me
N
NHTs
O
OnBu
172.44
143.12
136.91
136.13
129.72
129.57
127.14
127.03
121.30
119.21
118.06
109.00
107.36
77.55
77.23
76.91
64.73
43.58
34.39
29.67
24.97
21.53
19.74
19.11
13.75
f1 (ppm)

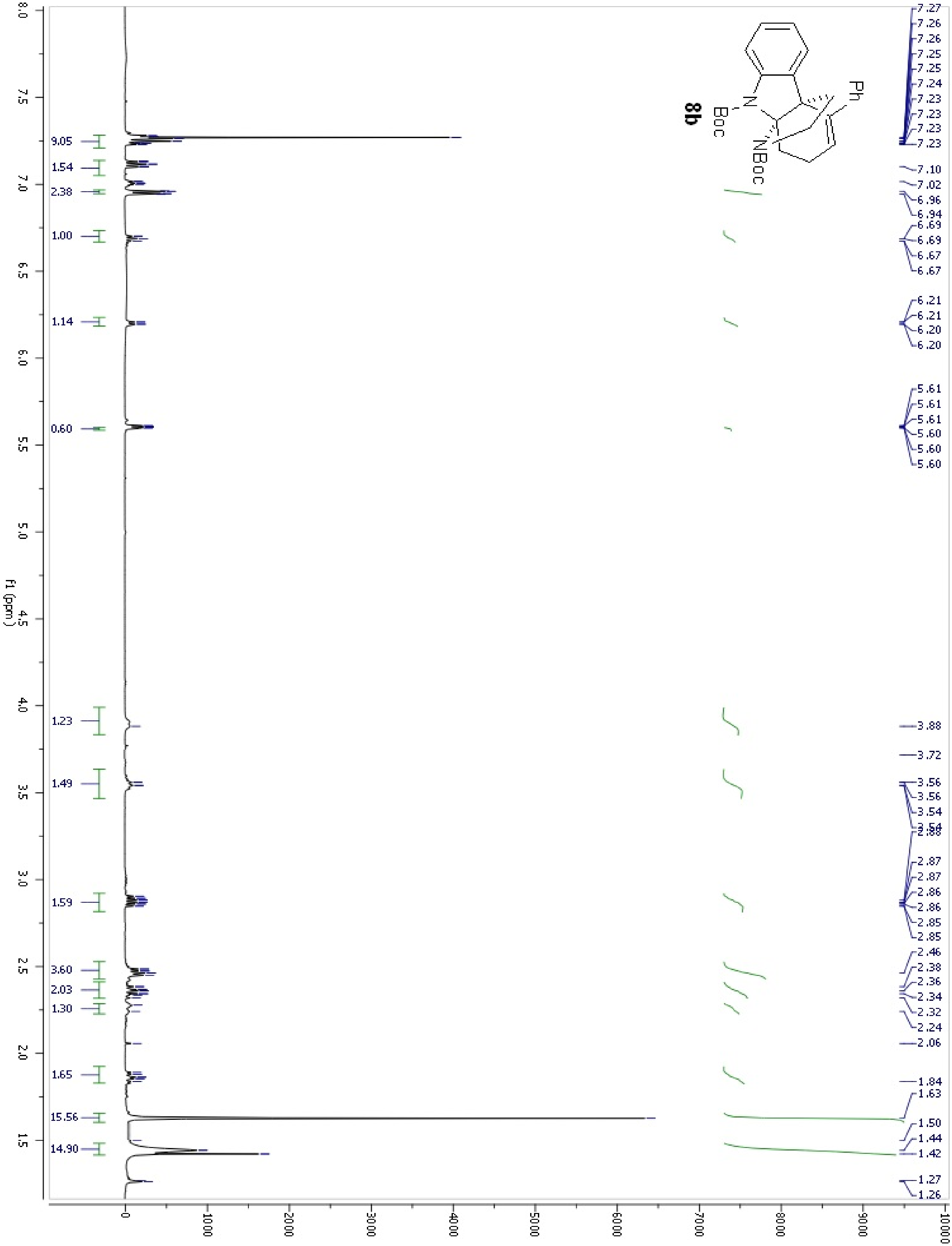

7h
NHTs
Me
f1 (ppm)


7h
Me
NHTs
143.41
137.04
136.90
136.28
129.78
127.19
127.16
121.54
119.39
118.25
109.20
107.59
82.96
77.55
77.23
76.91
69.98
43.63
30.05
30.00
25.18
23.64
21.70
21.67
19.60
f1 (ppm)

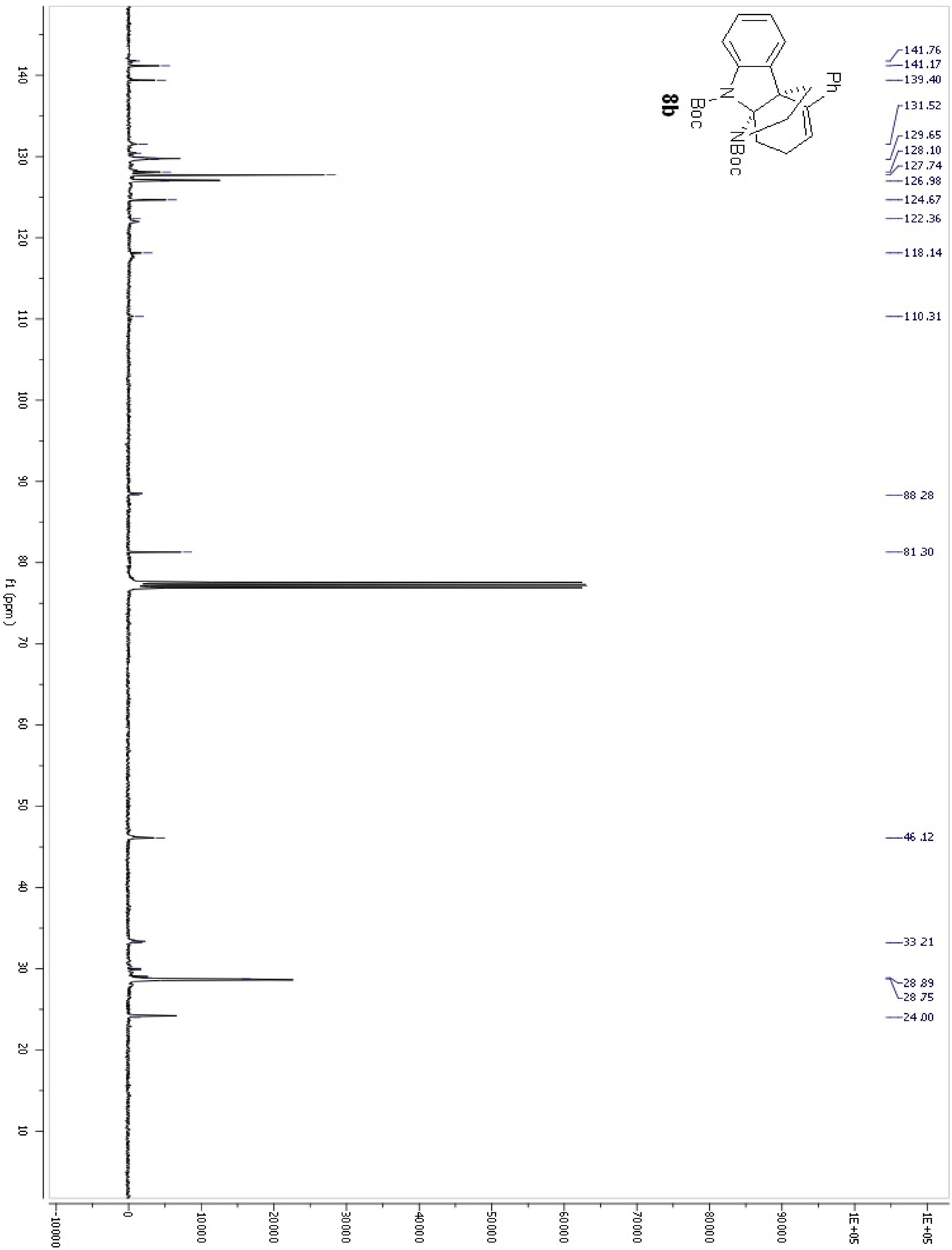

8a
Boc
NBoc
7.68
7.26
7.17
7.16
7.15
7.02
7.00
6.99
5.74
5.73
5.73
5.72
5.71
5.70
5.61
5.59
3.55
3.53
3.51
3.04
3.02
3.01
2.99
2.98
2.97
2.24
2.05
2.03
2.02
2.02
2.00
2.00
1.99
1.97
1.57
1.54
1.45
1.42
1.25
1.00
2.86
1.34
1.39
1.33
2.37
1.30
1.93
1.39
2.56
13.09
11.16
f1 (ppm)

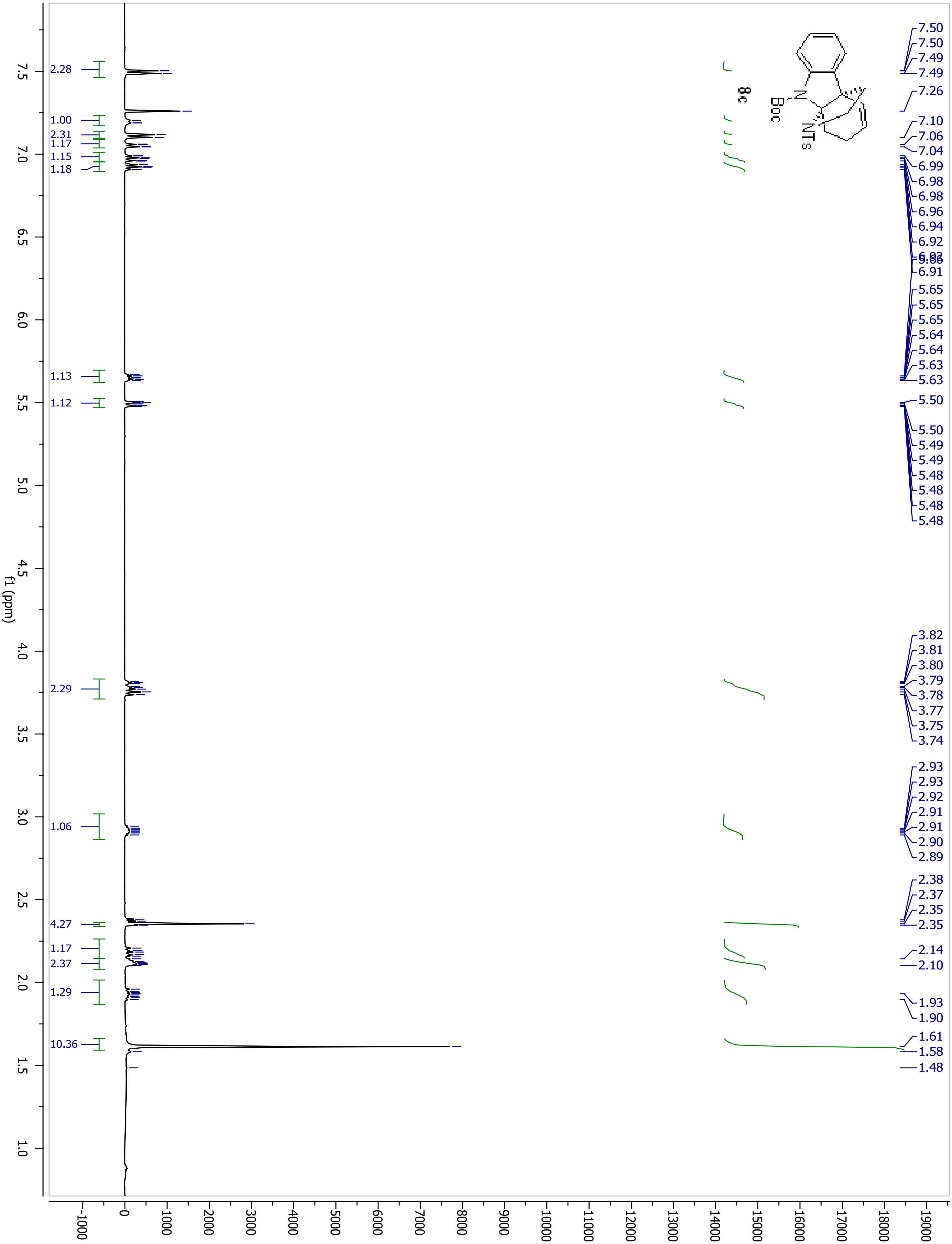


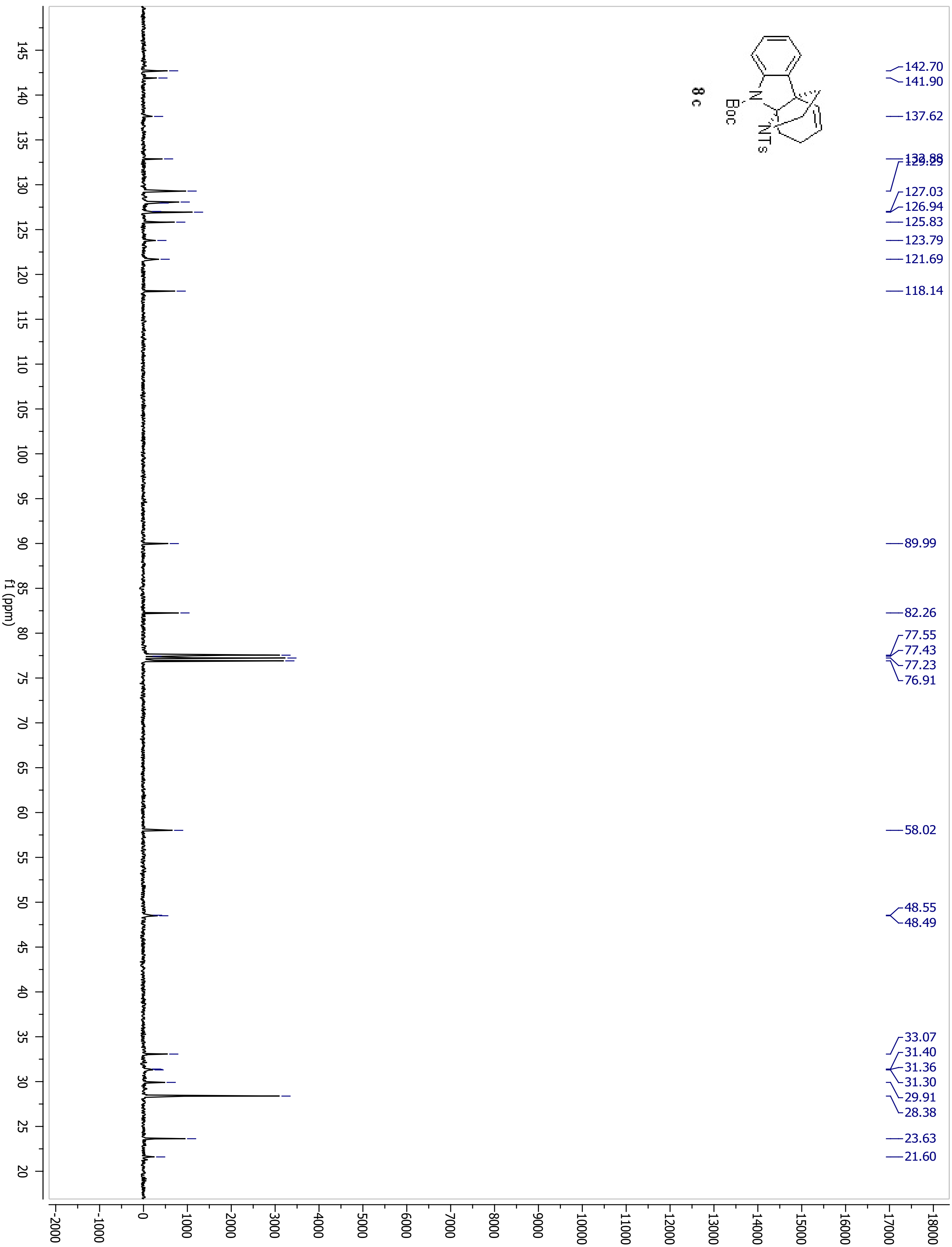
8a
Boc
NBoc
142.29
134.20
128.15
128.12
126.40
122.27
118.03
117.95
117.88
117.81
117.61
87.70
81.31
77.55
77.43
77.23
76.91
76.75
56.61
56.57
46.27
33.93
28.63
23.21
22.91
f1 (ppm)

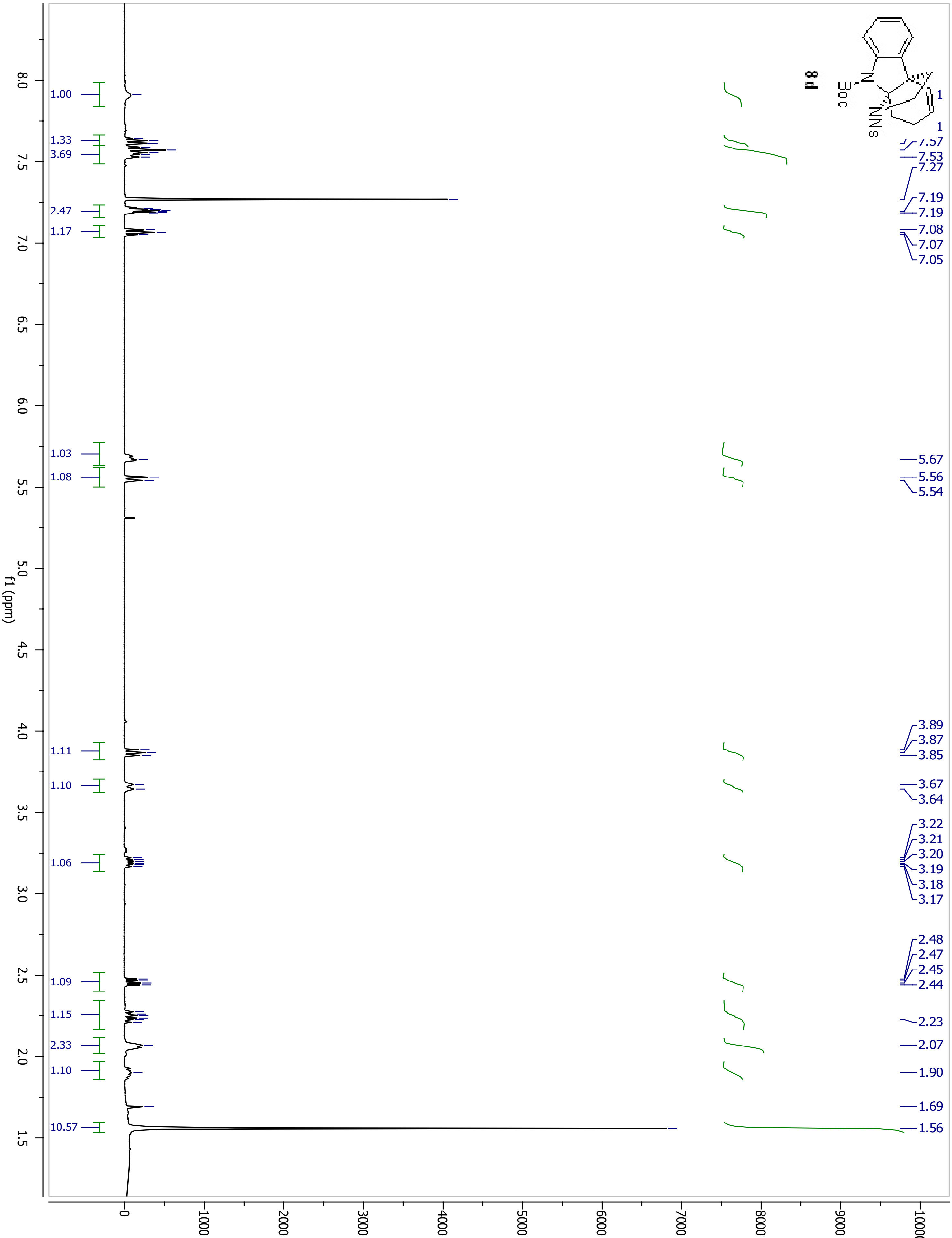


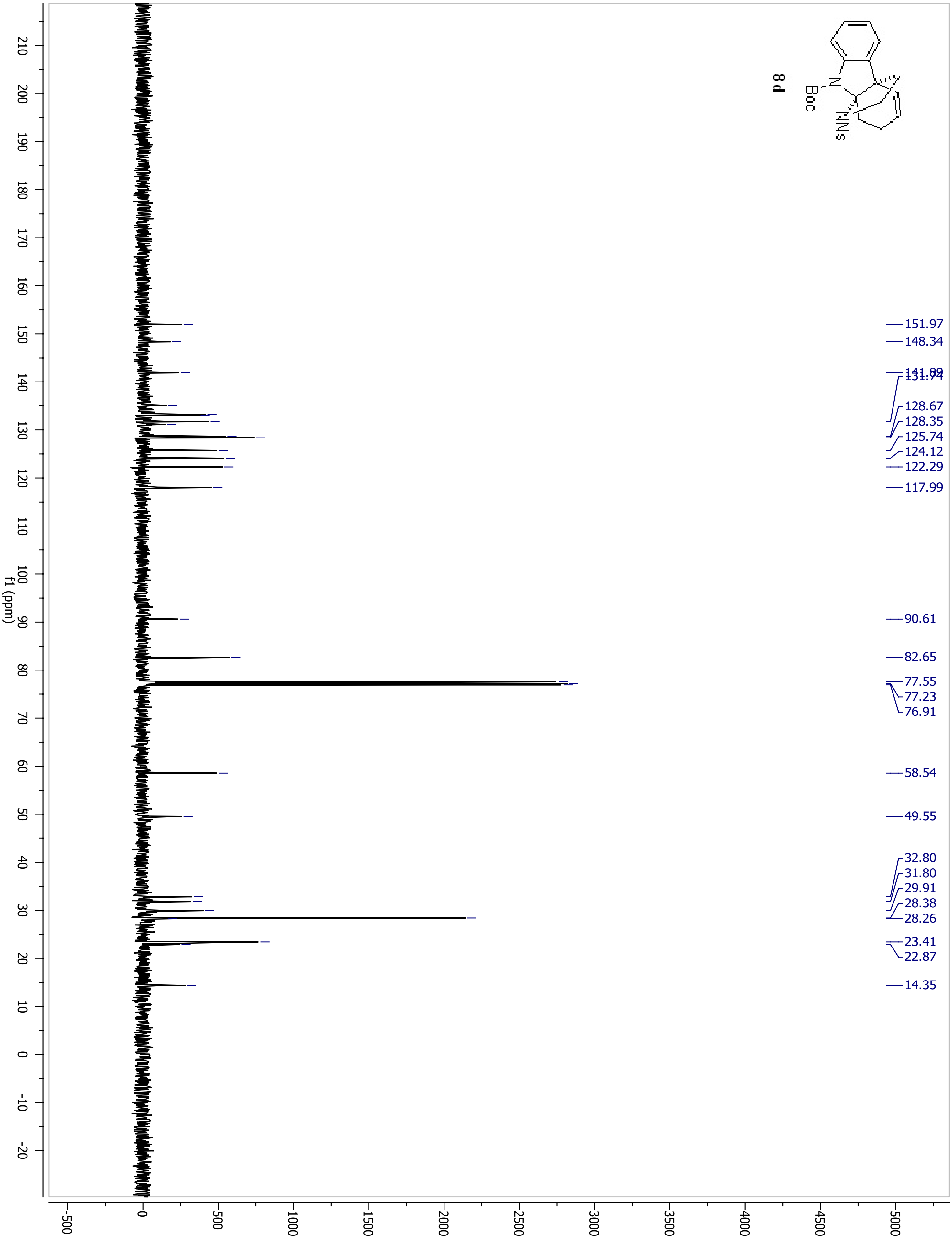
8b
Boc
NBoc
N
Ph
f1 (ppm)
9.05
1.54
2.38
1.00
1.14
0.60
1.23
1.49
1.59
3.60
2.03
1.30
1.65
15.56
14.90
7.27
7.26
7.26
7.25
7.25
7.24
7.23
7.23
7.23
7.23
7.10
7.02
6.96
6.94
6.69
6.69
6.67
6.67
6.21
6.21
6.20
6.20
5.61
5.61
5.61
5.60
5.60
5.60
3.88
3.72
3.56
3.56
3.54
3.54
2.88
2.87
2.87
2.86
2.86
2.85
2.85
2.46
2.38
2.36
2.34
2.32
2.24
2.06
1.84
1.63
1.50
1.44
1.42
1.27
1.26


8b
Boc
NBoc
Ph
141.76
141.17
139.40
131.52
129.65
128.10
127.74
126.98
124.67
122.36
118.14
110.31
88.28
81.30
46.12
33.21
28.89
28.75
24.00
f1 (ppm)

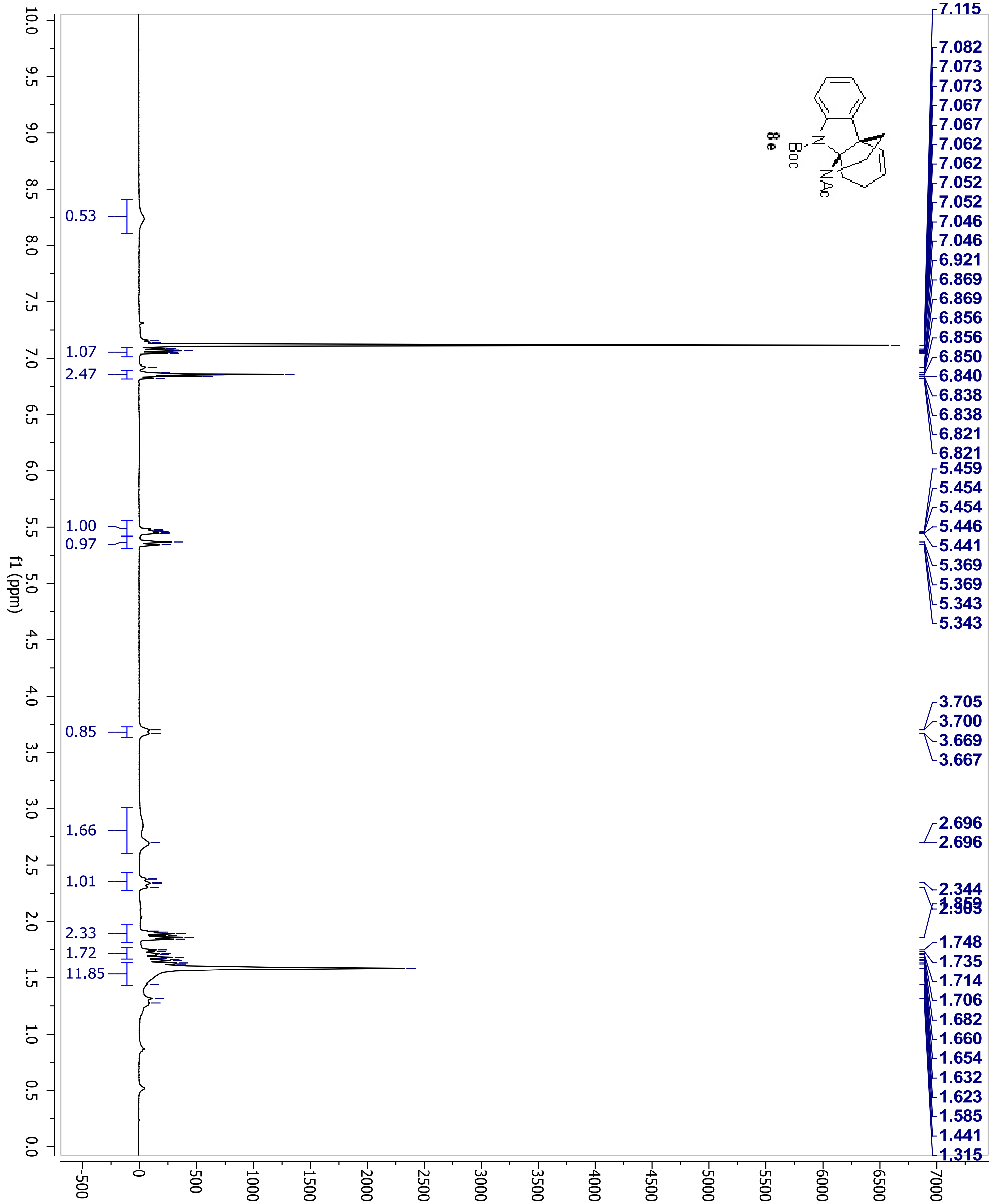

8c
Boc
NTs
f1 (ppm)
7.50
7.50
7.49
7.49
7.26
7.10
7.06
7.04
6.99
6.98
6.98
6.96
6.94
6.92
6.92
6.91
5.65
5.65
5.65
5.64
5.64
5.63
5.63
5.50
5.50
5.49
5.49
5.48
5.48
5.48
5.48
3.82
3.81
3.80
3.79
3.78
3.77
3.75
3.74
2.93
2.93
2.92
2.91
2.91
2.90
2.89
2.38
2.37
2.35
2.35
2.14
2.10
1.93
1.90
1.61
1.58
1.48
2.28
1.00
2.31
1.17
1.15
1.18
1.13
1.12
2.29
1.06
4.27
1.17
2.37
1.29
10.36


8c
N
Boc
NTs
142.70
141.90
137.62
132.88
129.29
127.03
126.94
125.83
123.79
121.69
118.14
89.99
82.26
77.55
77.43
77.23
76.91
58.02
48.55
48.49
33.07
31.40
31.36
31.30
29.91
28.38
23.63
21.60
f1 (ppm)





8d
N
Boc
NNs
151.97
148.34
141.89
131.74
128.67
128.35
125.74
124.12
122.29
117.99
90.61
82.65
77.55
77.23
76.91
58.54
49.55
32.80
31.80
29.91
28.38
28.26
23.41
22.87
14.35
f1 (ppm)


8e
Boc
N
NAc
7.115
7.082
7.073
7.073
7.067
7.067
7.062
7.062
7.052
7.052
7.046
7.046
6.921
6.869
6.869
6.856
6.856
6.850
6.840
6.838
6.838
6.821
6.821
5.459
5.454
5.454
5.446
5.441
5.369
5.369
5.343
5.343
3.705
3.700
3.669
3.667
2.696
2.696
2.344
1.859
2.303
1.748
1.735
1.714
1.706
1.682
1.660
1.654
1.632
1.623
1.585
1.441
1.315
0.53
1.07
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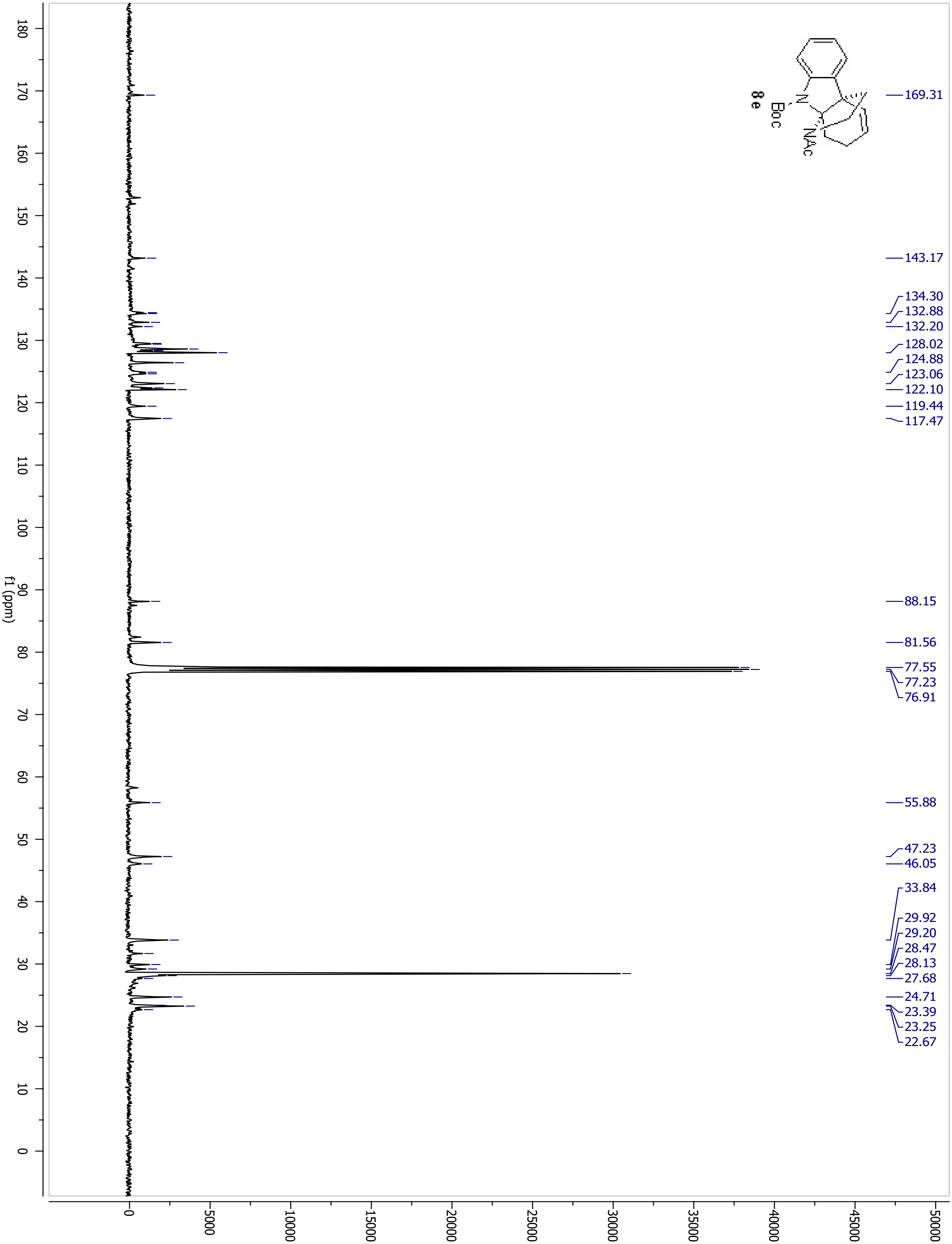
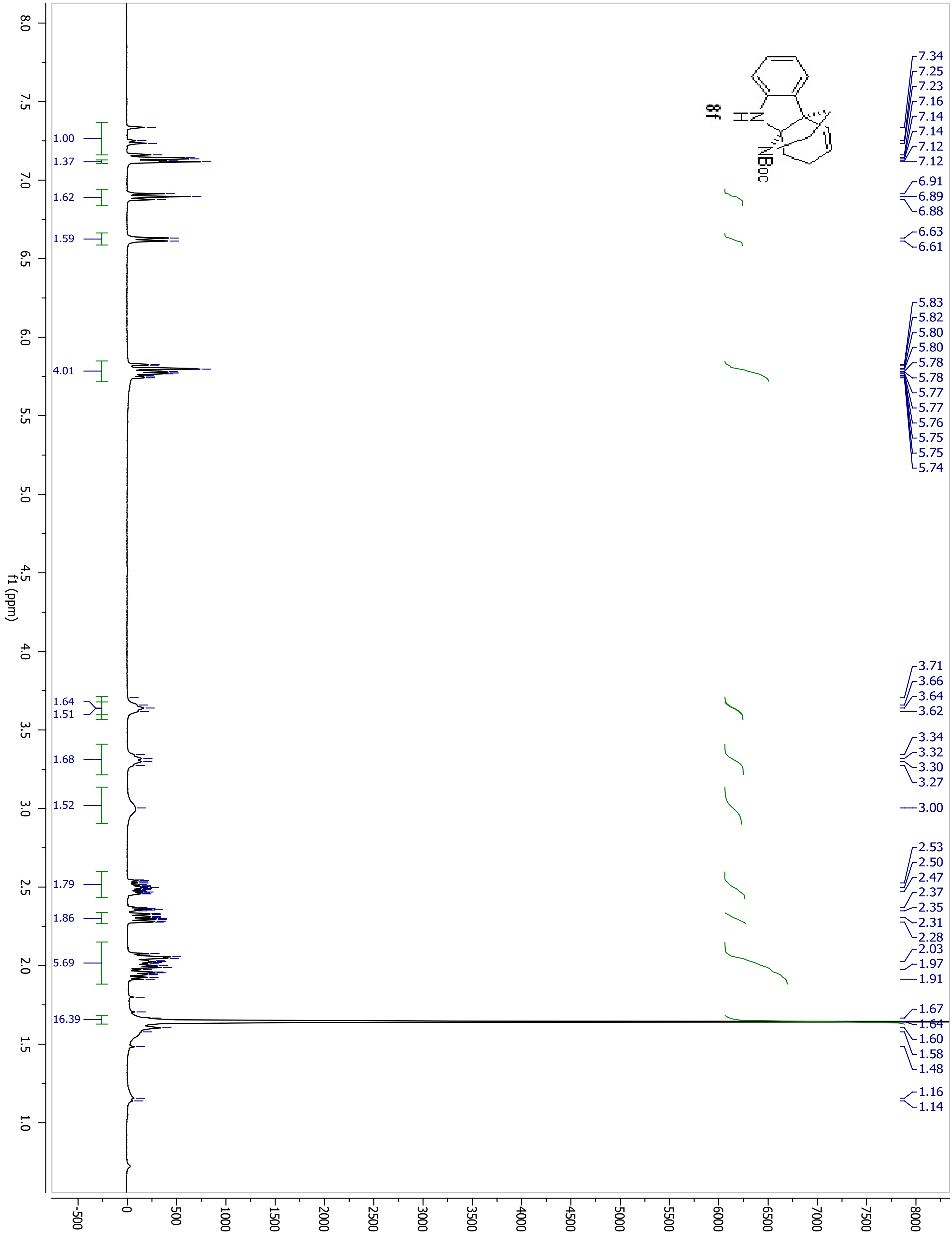
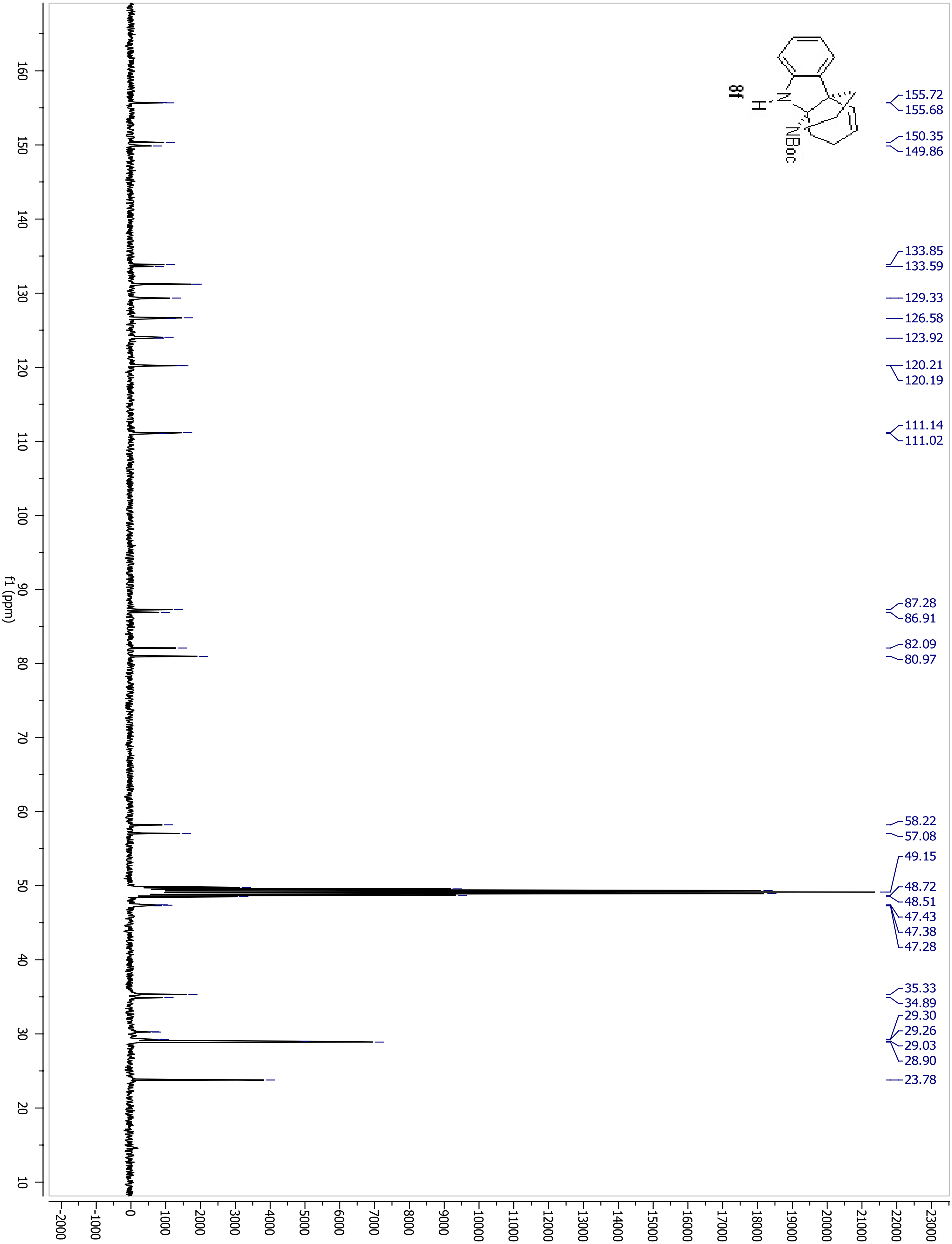
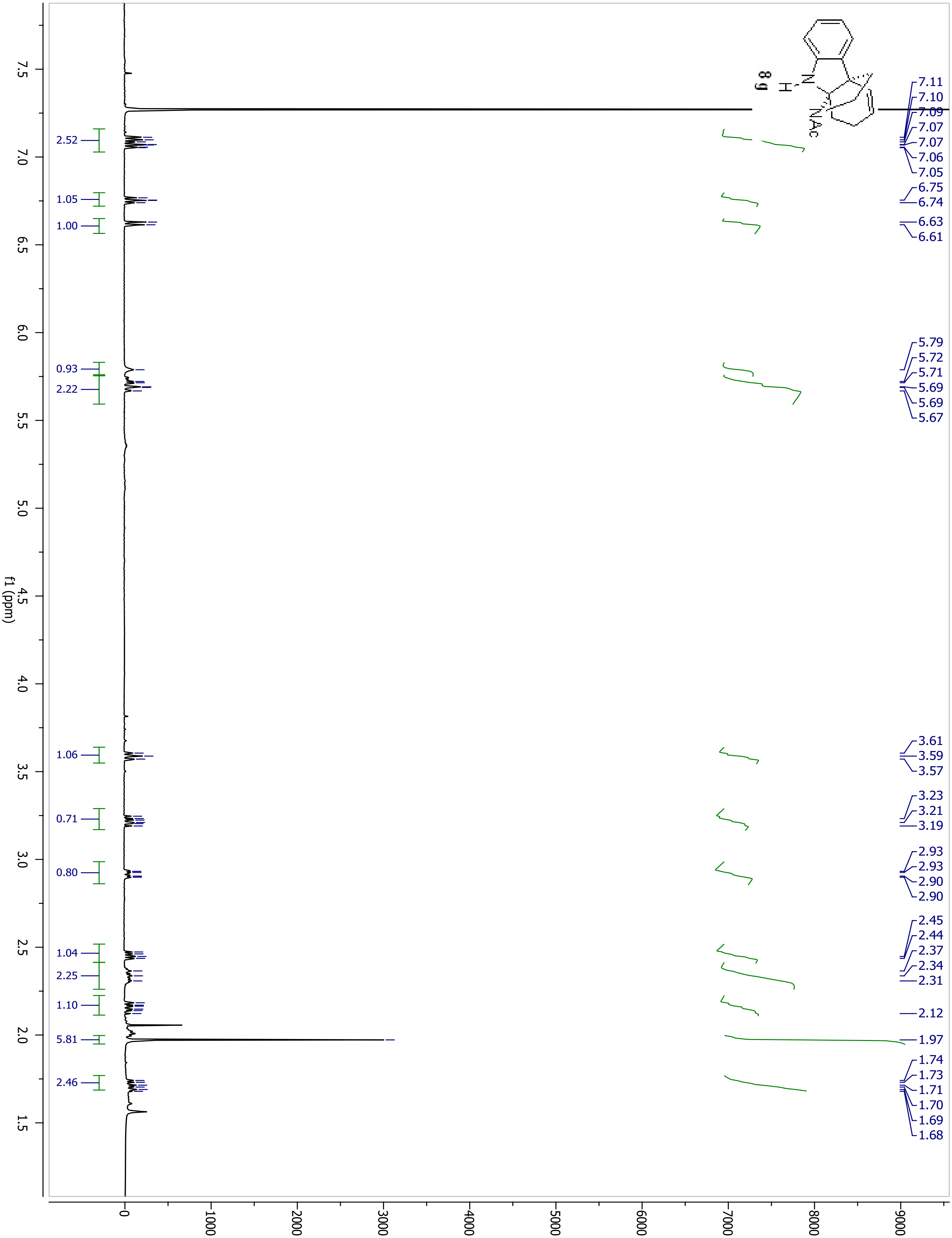
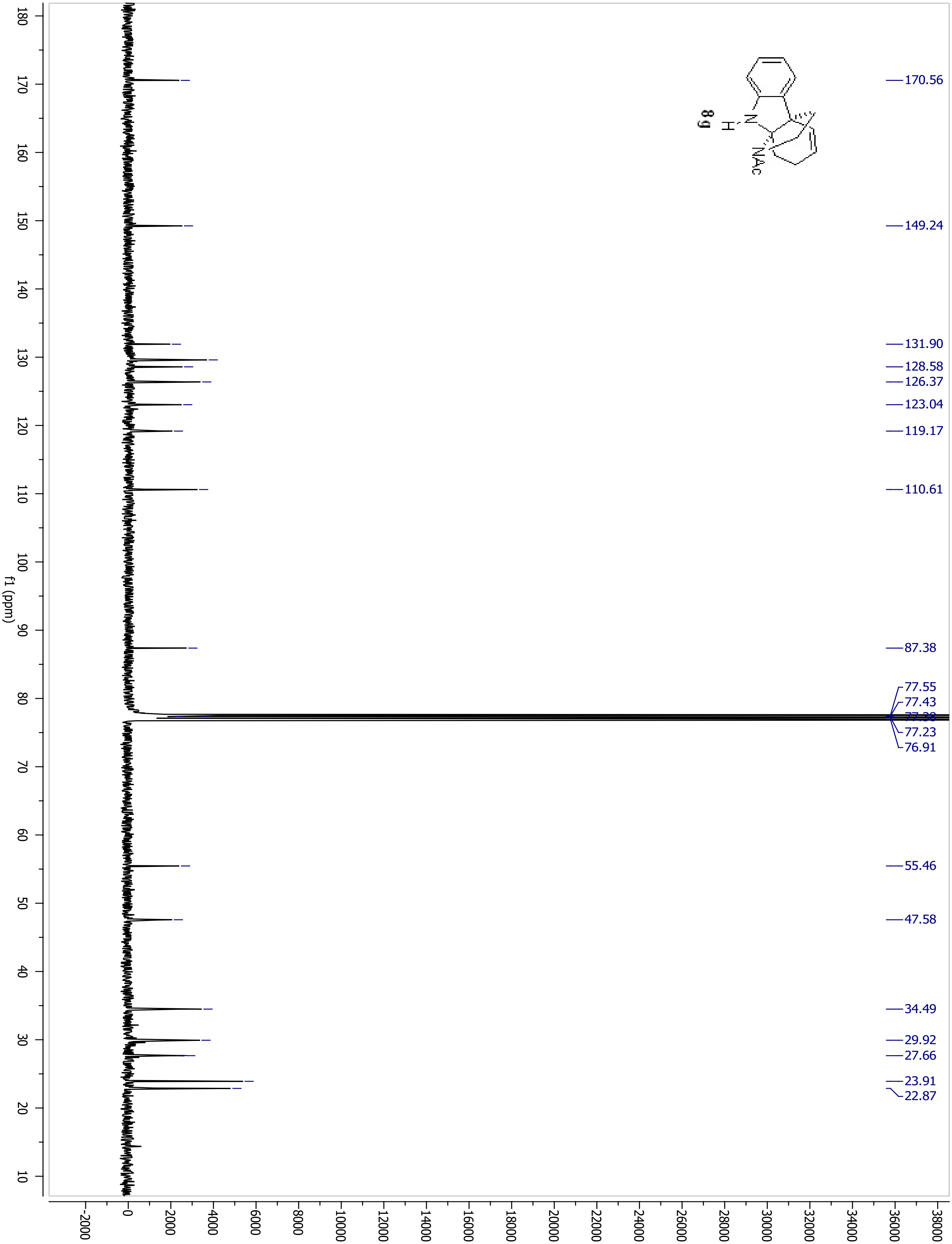
1.00
0.97
0.85
1.66
1.01
2.33
1.72
11.85
f1 (ppm)

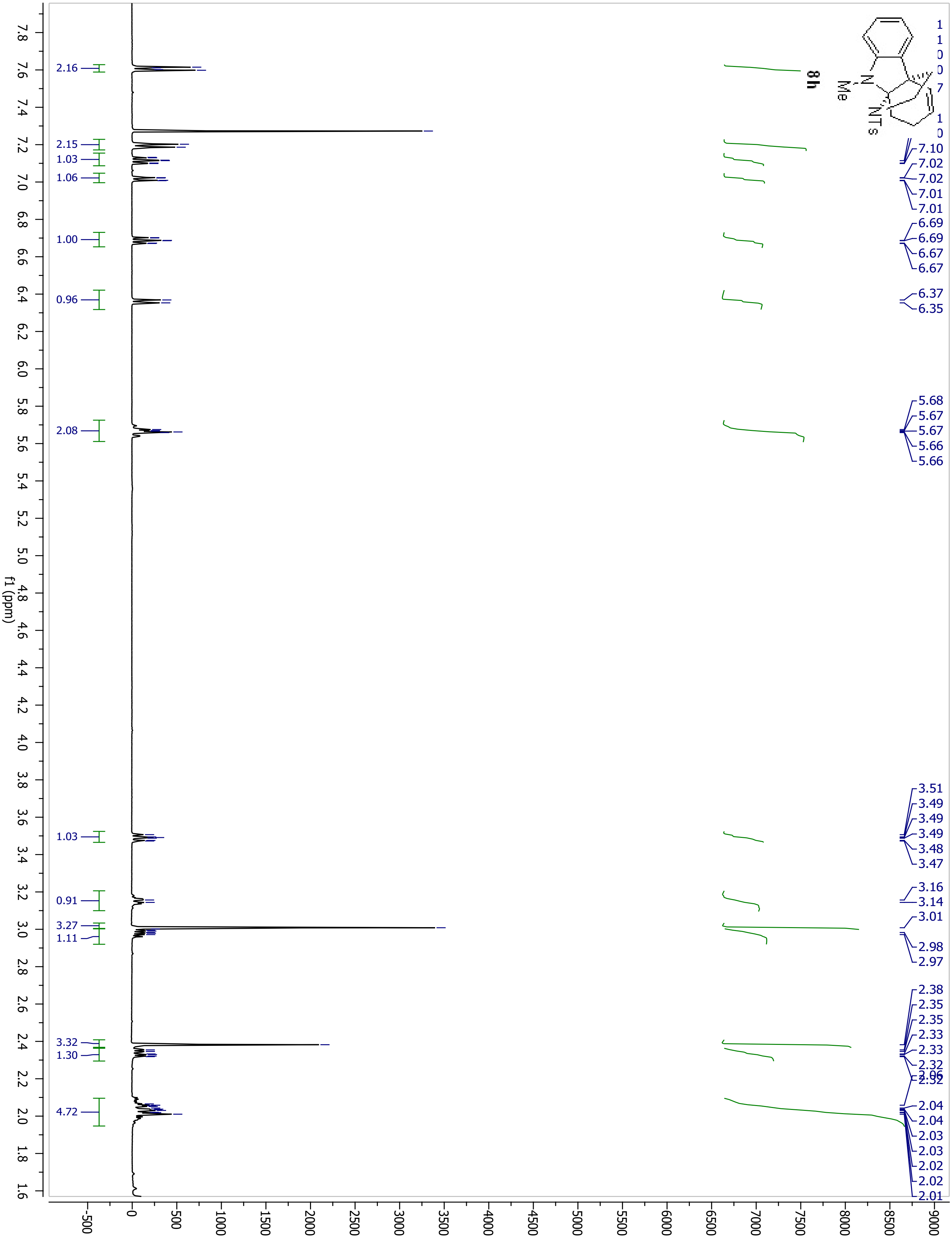

8e
Boc
NAc
169.31
143.17
134.30
132.88
132.20
128.02
124.88
123.06
122.10
119.44
117.47
88.15
81.56
77.55
77.23
76.91
55.88
47.23
46.05
33.84
29.92
29.20
28.47
28.13
27.68
24.71
23.39
23.25
22.67
f1 (ppm)

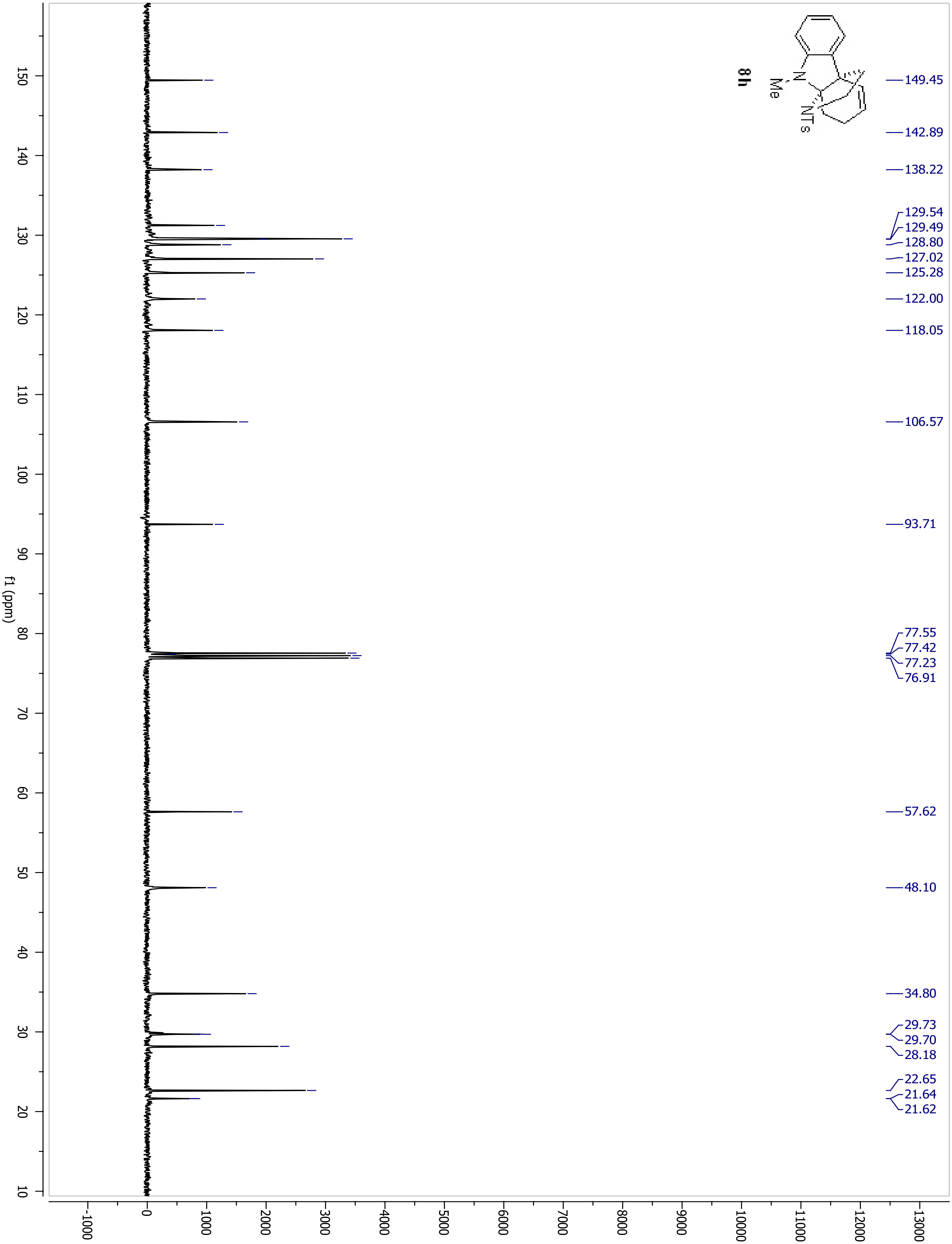

8f
NBoc
N
H
7.34
7.25
7.23
7.16
7.14
7.14
7.12
7.12
6.91
6.89
6.88
6.63
6.61
5.83
5.82
5.80
5.80
5.78
5.78
5.77
5.77
5.76
5.75
5.75
5.74
3.71
3.66
3.64
3.62
3.34
3.32
3.30
3.27
3.00
2.53
2.50
2.47
2.37
2.35
2.31
2.28
2.03
1.97
1.91
1.67
1.64
1.60
1.58
1.48
1.16
1.14
1.00
1.37
1.62
1.59
4.01
1.64
1.51
1.68
1.52
1.79
1.86
5.69
16.39
f1 (ppm)

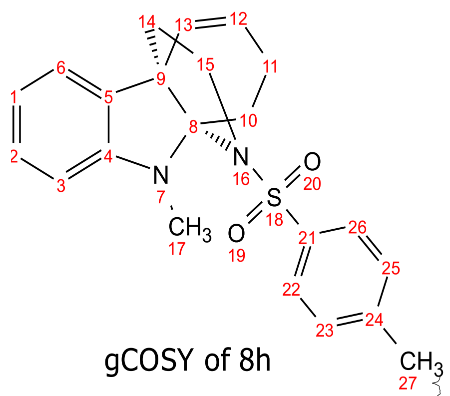

8f
NBoc
H
N
155.72
155.68
150.35
149.86
133.85
133.59
129.33
126.58
123.92
120.21
120.19
111.14
111.02
87.28
86.91
82.09
80.97
58.22
57.08
49.15
48.72
48.51
47.43
47.38
47.28
35.33
34.89
29.30
29.26
29.03
28.90
23.78
f1 (ppm)


8g
f1 (ppm)

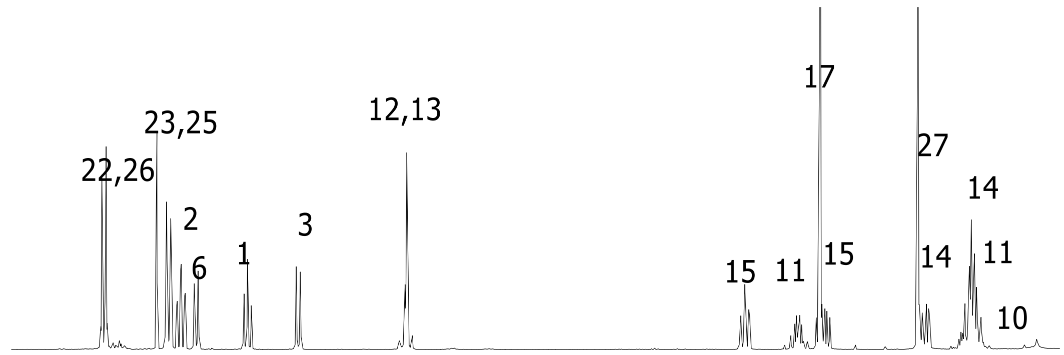

8g
NAc
N
H
170.56
149.24
131.90
128.58
126.37
123.04
119.17
110.61
87.38
77.55
77.43
77.23
76.91
55.46
47.58
34.49
29.92
27.66
23.91
22.87
f1 (ppm)

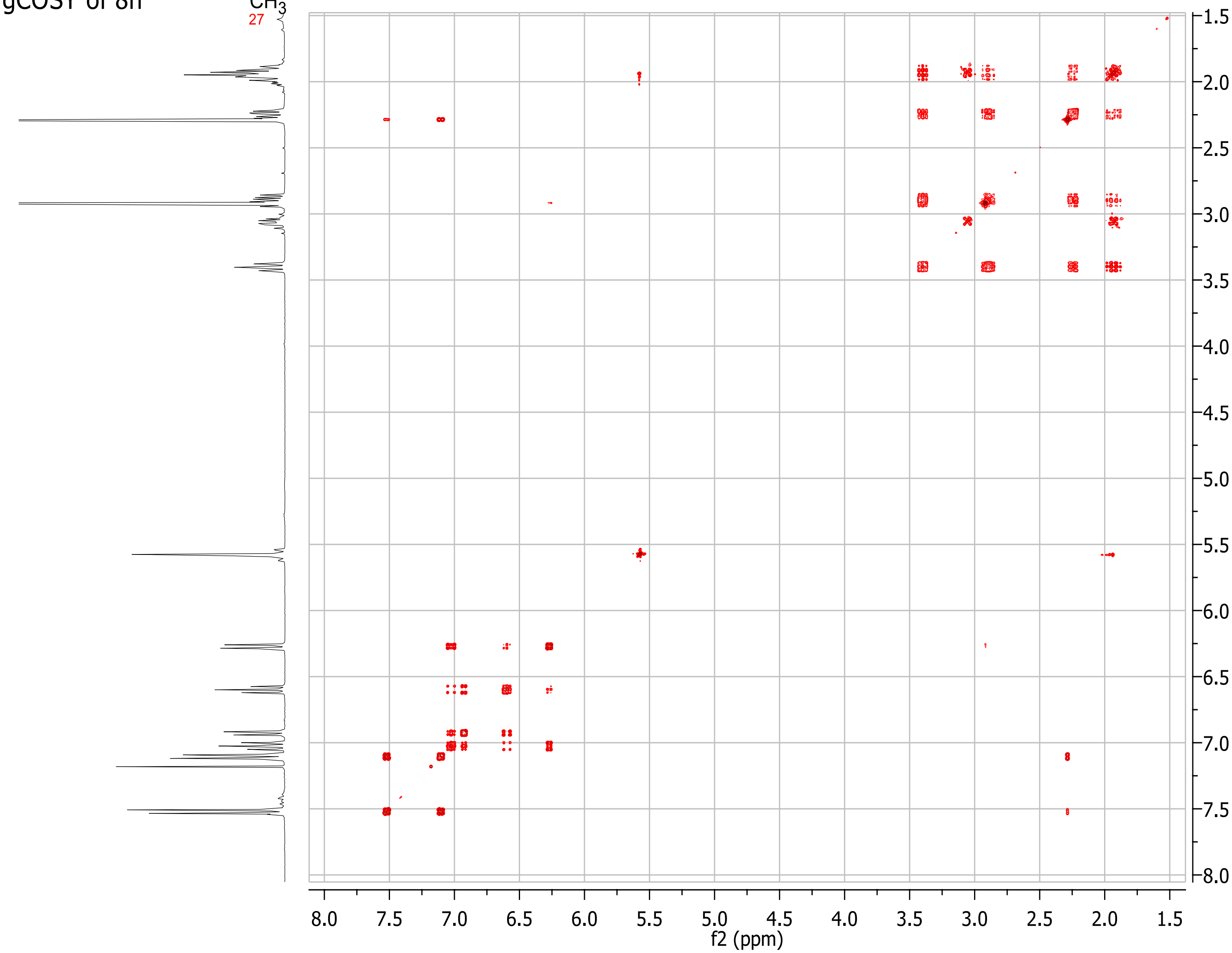

8h
NTs
Me
N
f1 (ppm)


8h
N
Me
NTs
149.45
142.89
138.22
129.54
129.49
128.80
127.02
125.28
122.00
118.05
106.57
93.71
77.55
77.42
77.23
76.91
57.62
48.10
34.80
29.73
29.70
28.18
22.65
21.64
21.62
f1 (ppm)

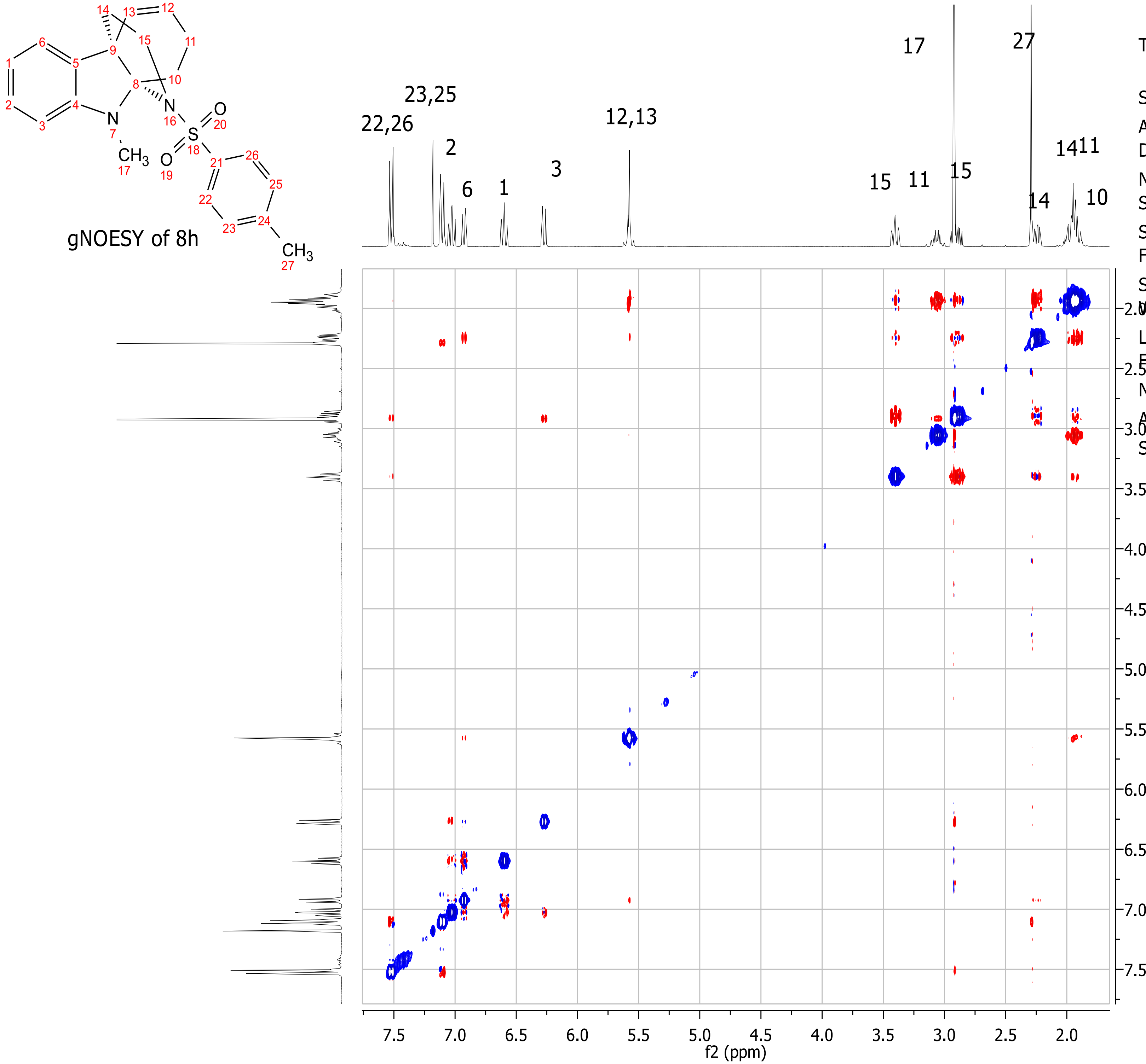


gCOSY of 8h



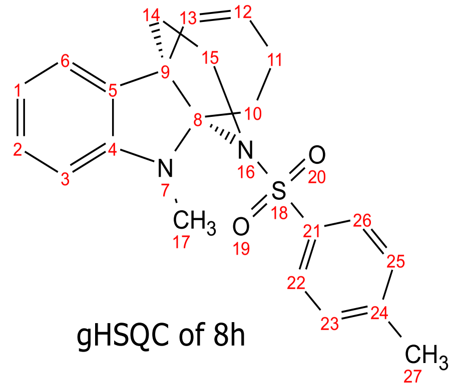


Parameter	Value (f2
Title	yxl-iii-me-ts-a gCOSY
Solvent	CDCl3
Acquisition Date	2009-12-23T
Number of Scans	1
Spectrometer Frequency	(300.13, 300.
Spectral Width	(2427.2, 242
Lowest Frequency	(27.9, 27.9)
Nucleus	(1H, 1H)
Acquired Size	(1024, 512)
Spectral Size	(1024, 1024)

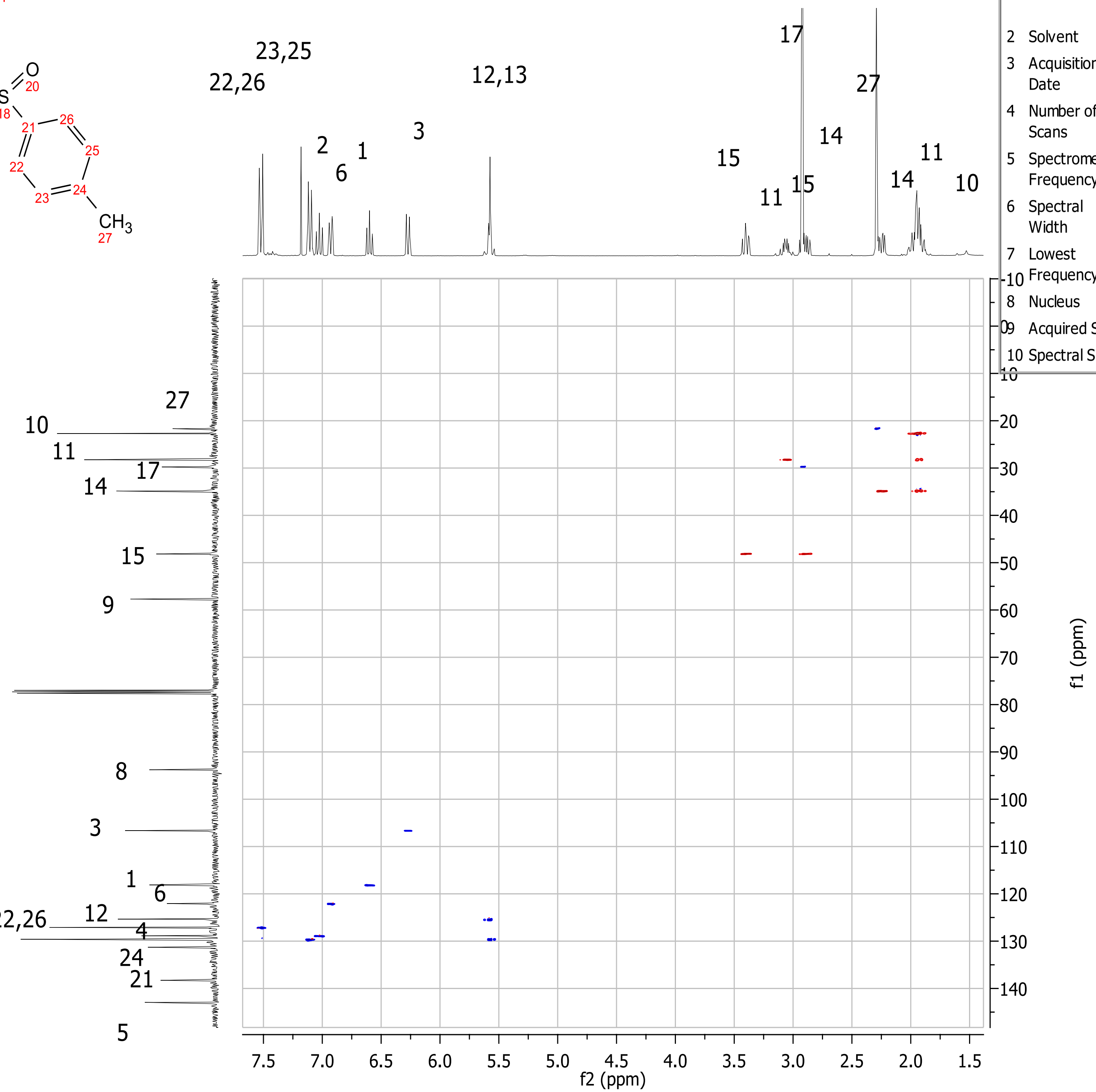


gNOESY of 8h

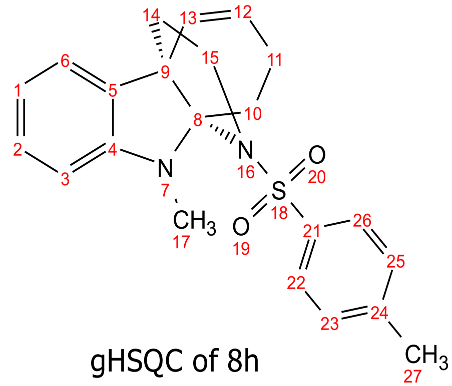
Parameter	Value
Title	yxl-iii-me-gHMBC
Solvent	CDCl3
Acquisition Date	2009-12-2
Number of Scans	8
Spectrometer Frequency	(300.13, 3
Spectral Width	(2427.2, 2
Lowest Frequency	(27.9, 27.
Nucleus	(1H, 1H)
Acquired Size	(1024, 25
Spectral Size	(1024, 10



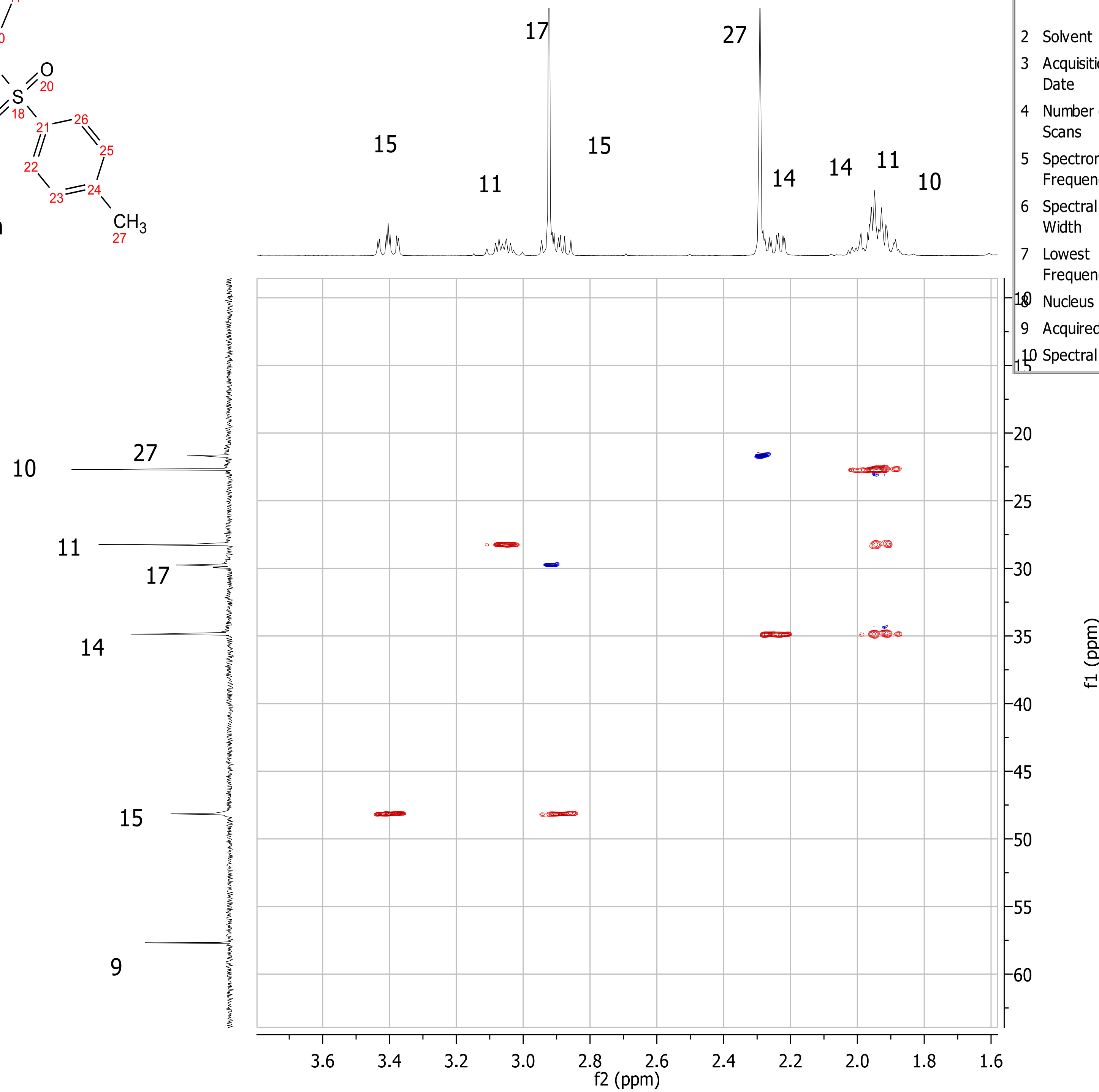
gHSQC of 8h



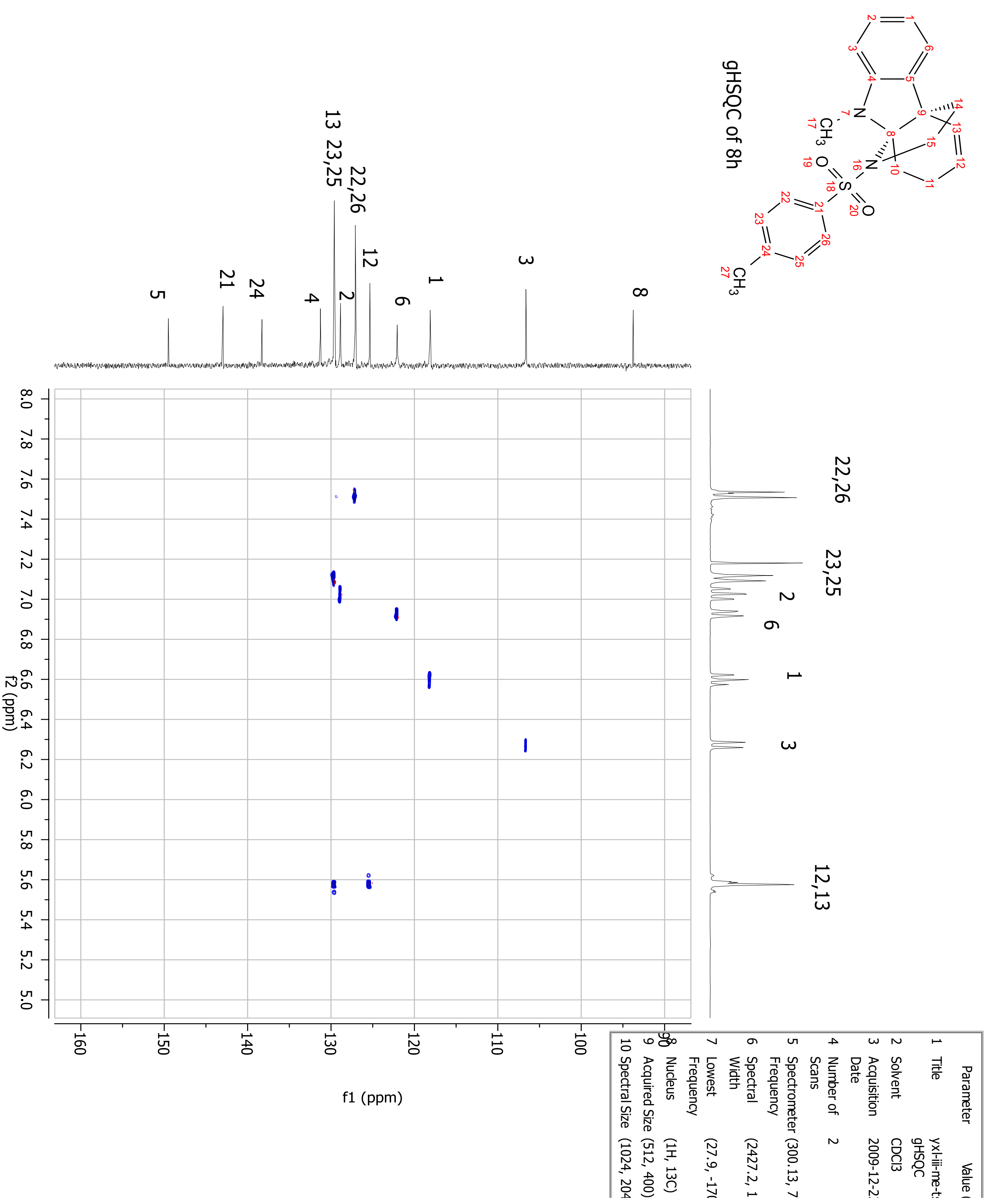
	Parameter	Value (
1	Title	yxl-iii-me-t: gHSQC
2	Solvent	CDCl3
3	Acquisition Date	2009-12-2:
4	Number of Scans	2
5	Spectrometer Frequency	(300.13, 7
6	Spectral Width	(2427.2, 1
7	Lowest Frequency	(27.9, -17(
8	Nucleus	(1H, 13C)
9	Acquired Size	(512, 400)
10	Spectral Size	(1024, 204

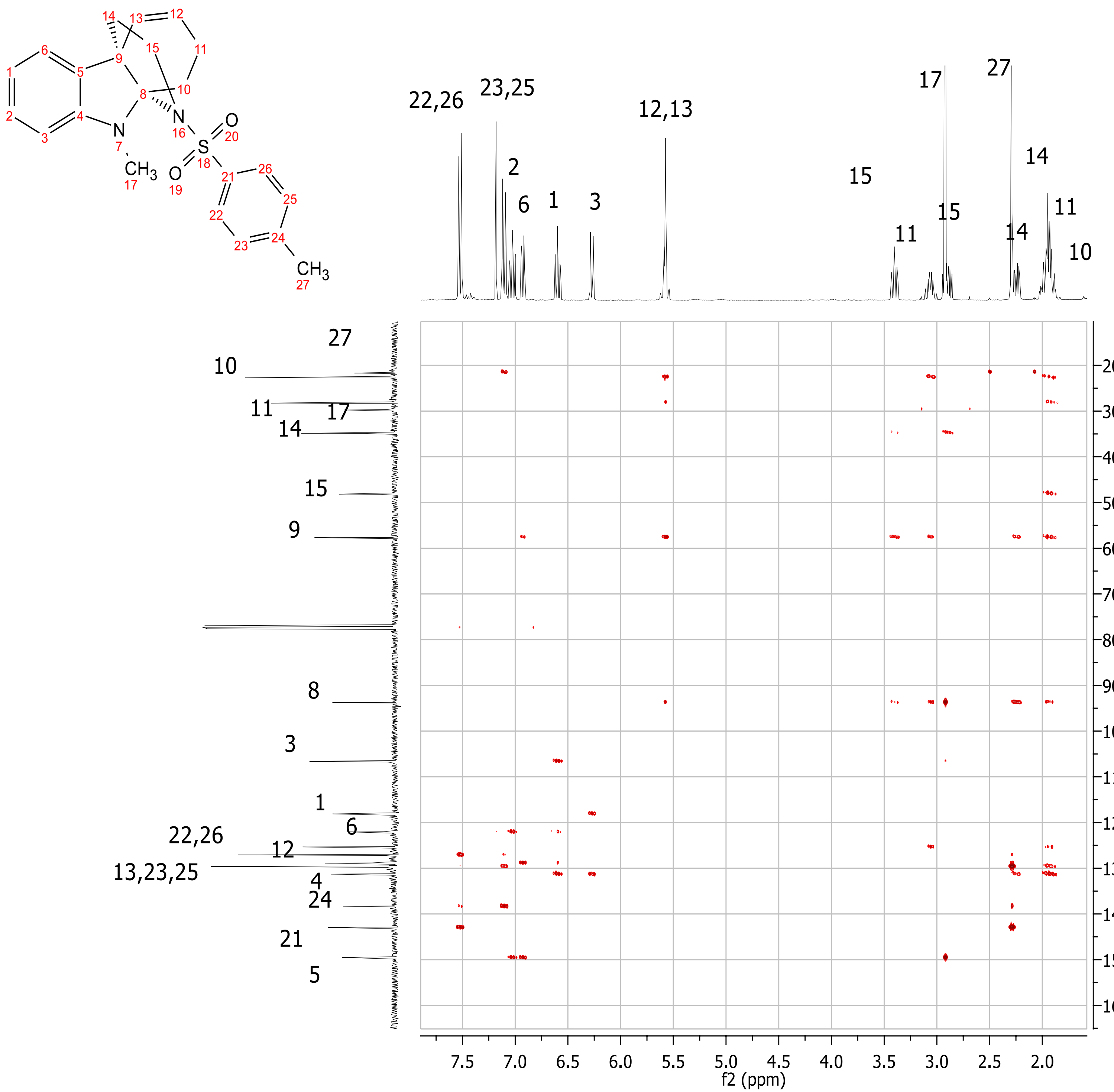


gHSQC of 8h

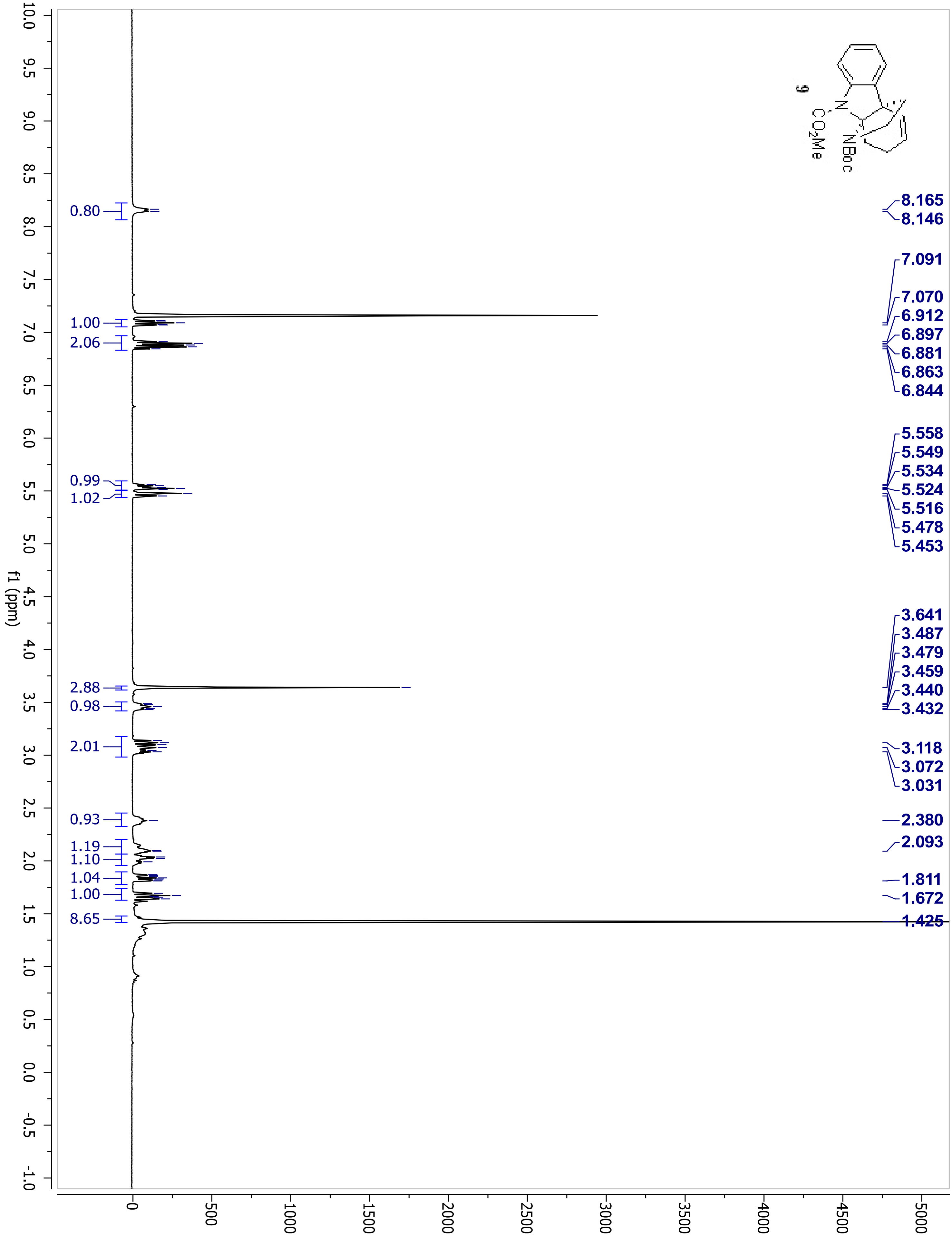


	Parameter	Value (
1	Title	yxl-iii-me-t: gHSQC
2	Solvent	CDCl3
3	Acquisition Date	2009-12-2:
4	Number of Scans	2
5	Spectrometer Frequency	(300.13, 7
6	Spectral Width	(2427.2, 1
7	Lowest Frequency	(27.9, -17(
8	Nucleus	(1H, 13C)
9	Acquired Size	(512, 400)
10	Spectral Size	(1024, 204


gHSQC of 8h
f1 (ppm)
f2 (ppm)
Parameter
Value
1 Title
2 Solvent
CDCl3
3 Acquisition Date
4 Number of Scans
2
5 Spectrometer Frequency
6 Spectral Width
7 Lowest Frequency
8 Nucleus
(1H, 13C)
9 Acquired Size
(512, 400)
10 Spectral Size

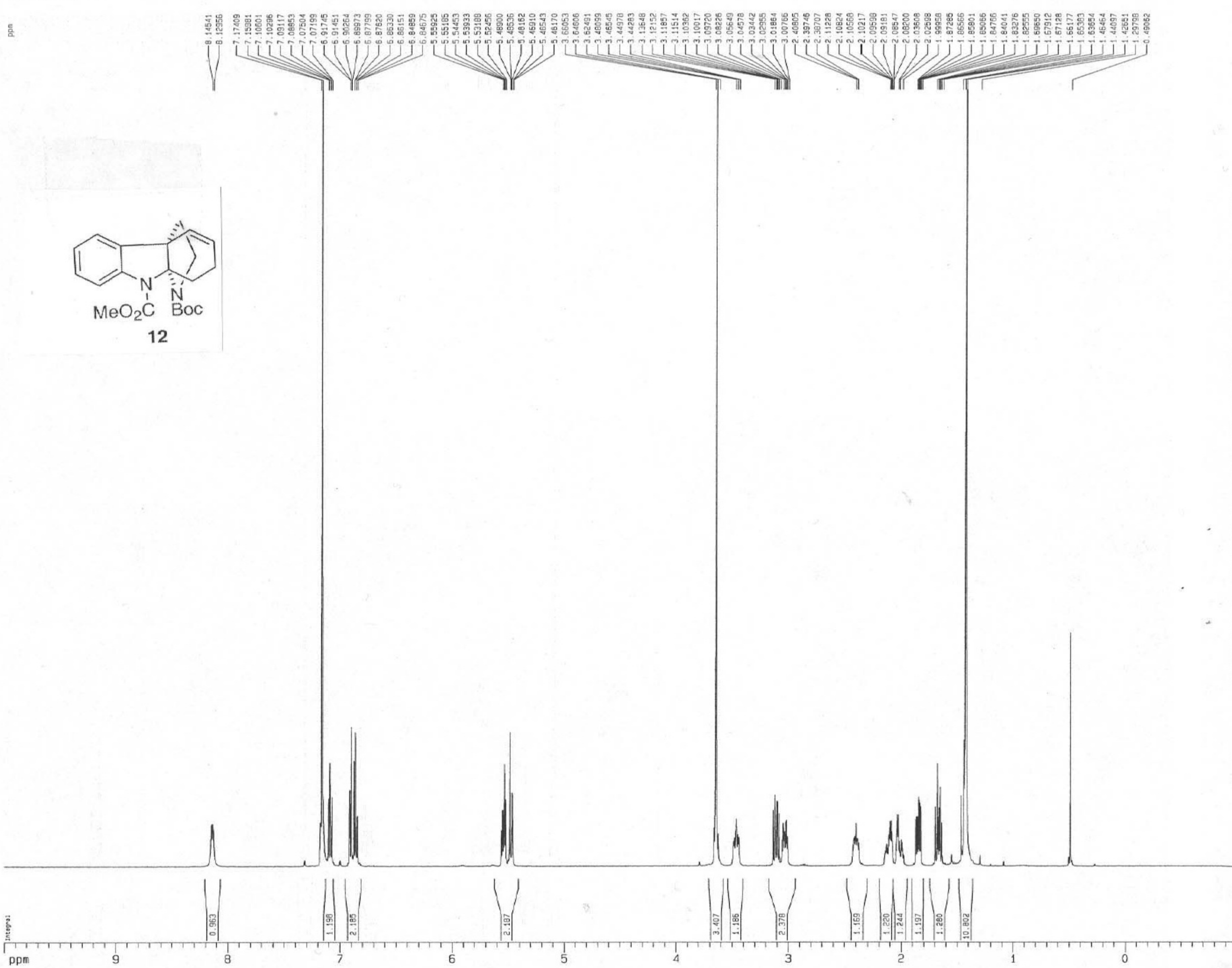


Parameter	Value
Title	yxl-iii-me-t gHMBC
Solvent	CDCl3
Acquisition Date	2009-12-2
Number of Scans	4
Spectrometer Frequency	(300.13, 7
Spectral Width	(2427.2, 1
Lowest Frequency	(27.9, -83
Nucleus	(1H, 13C)
Acquired Size	(1024, 472
Spectral Size	(1024, 102


9
CO2Me
NBoc
N
8.165
8.146
7.091
7.070
6.912
6.897
6.881
6.863
6.844
5.558
5.549
5.534
5.524
5.516
5.478
5.453
3.641
3.487
3.479
3.459
3.440
3.432
3.118
3.072
3.031
2.380
2.093
1.811
1.672
1.425
0.80
1.00
2.06
0.99
1.02
2.88
0.98
2.01
0.93
1.19
1.10
1.04
1.00
8.65
f1 (ppm)

Spectum of Overmann's intermediate

1H spectrum

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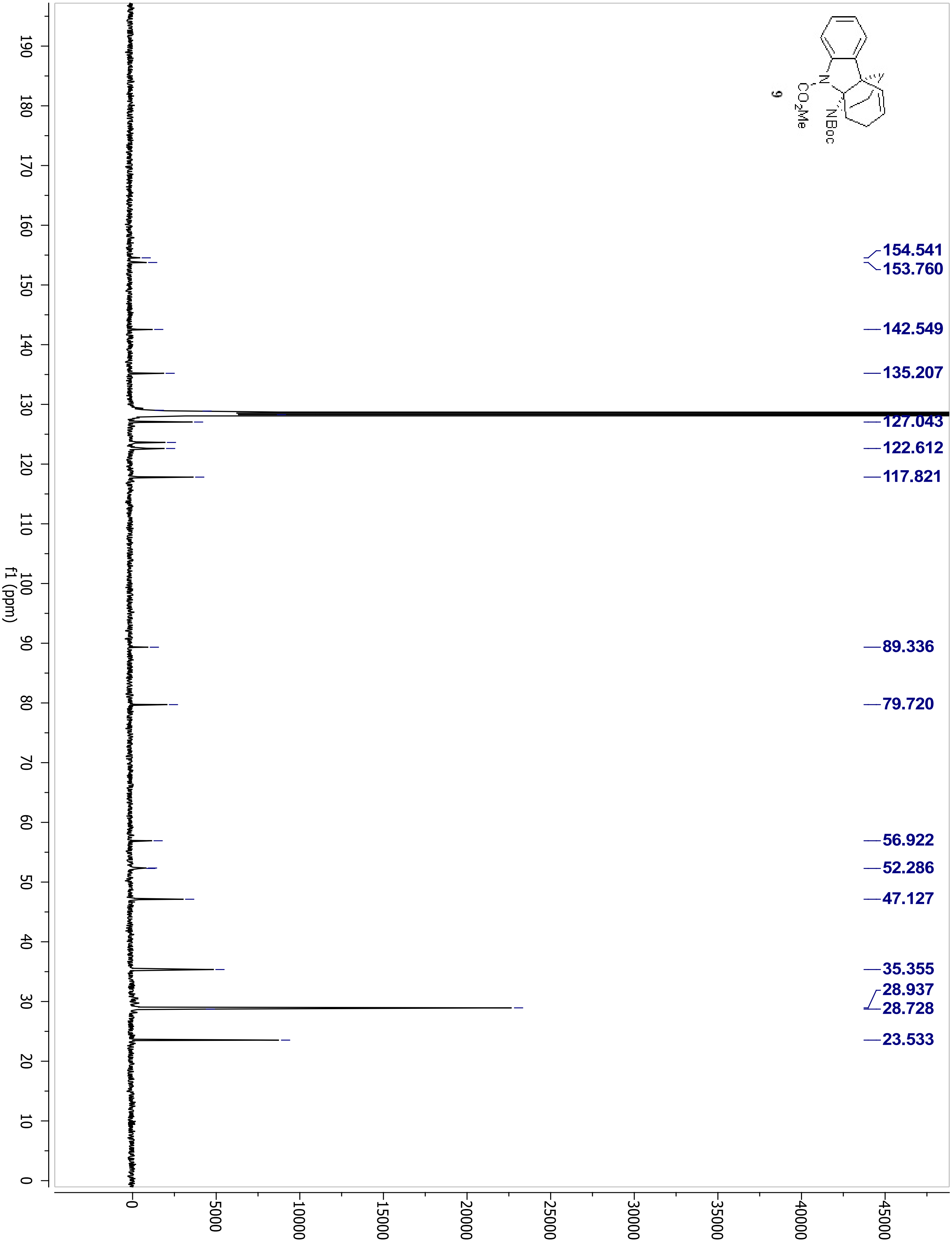
Current Data Parameters
USER              aaronw
NAME         abd-III-157-X
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030613
Time               18.08
INSTRUM            gn500
PROBHD   5 mm broadban
PULPROG             zg30
TD                 65536
SOLVENT             C6D6
NS                     8
DS                     2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 287.4
DW               62.400 usec
DE                 6.00 usec
TE                333.0 K
D1          0.10000000 sec

============ CHANNEL f1 =======
NUC1                  1H
P1                 12.00 usec
PL1                -3.00 dB
SFO1         499.8334988 MHz

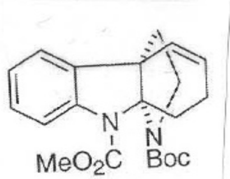
F2 - Processing parameters
SI                 65536
SF           499.8299942 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 49.85 cm
F1P               10.000 ppm
F1               4998.30 Hz
F2P               -1.000 ppm
F2               -499.83 Hz
PPMCM            0.48246 ppm/cm
HZCM           241.14606 Hz/cm
```

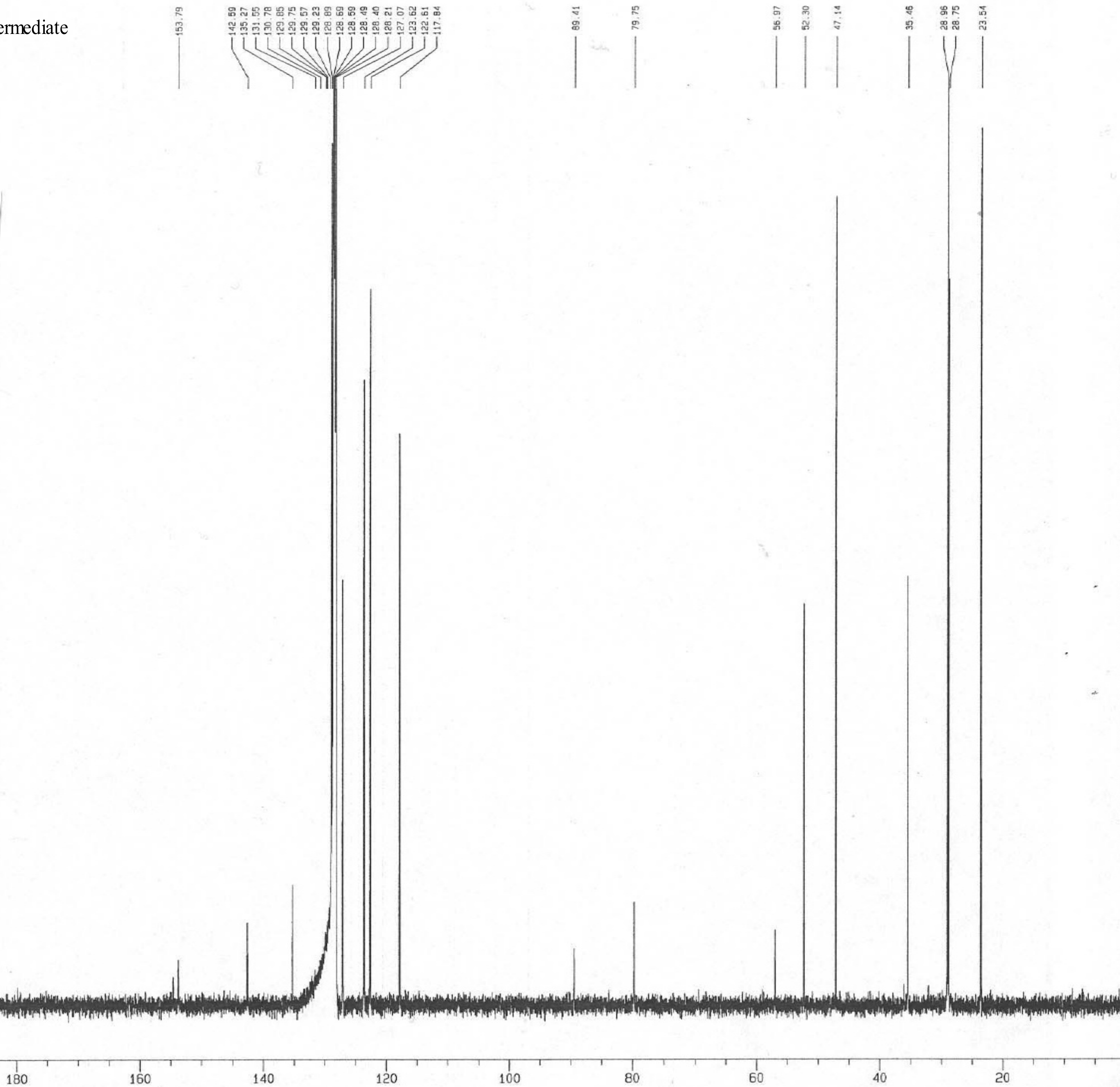

154.541
153.760
142.549
135.207
127.043
122.612
117.821
89.336
79.720
56.922
52.286
47.127
35.355
28.937
28.728
23.533
f1 (ppm)
NBoc
N
CO_2Me
9

13C spectrum with 1H decoupling

Spectum of Overmann's intermediate



12



Current Data Parameters

USER	aaronw
NAME	abd-III-157-X
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20030613
Time	18.14
INSTRUM	gn500
PROBHD	5 mm broadban
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	6428
DS	4
SWH	30303.031 Hz
FIDRES	0.462388 Hz
AQ	1.0813940 sec
RG	1290.2
DW	16.500 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
D11	0.03000000 sec

============ CHANNEL f1 =======

NUC1	13C
P1	15.00 usec
PL1	0.00 dB
SFO1	125.6961791 MHz

============ CHANNEL f2 =======

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-3.00 dB
PL12	15.10 dB
SFO2	499.8334988 MHz

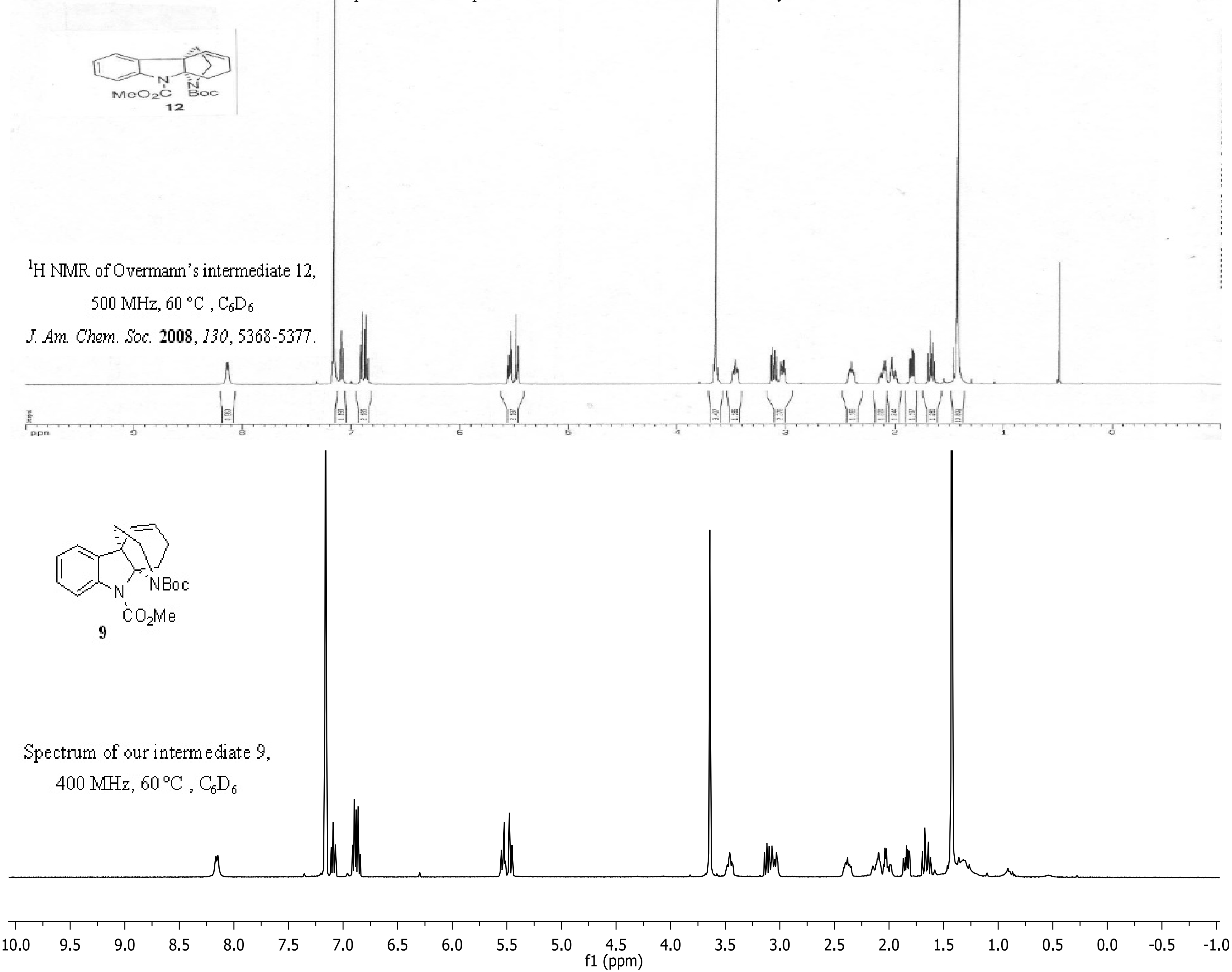
F2 - Processing parameters

SI	65536
SF	125.6822507 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	22.80 cm
CY	259.14 cm
F1P	220.000 ppm
F1	27650.10 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	9.64912 ppm/cm
HZCM	1212.72351 Hz/cm

Comparison between spectrum of Overmann's intermediate and our synthetic intermediate



Comparison between spectrum of Overmann's intermediate and our synthetic intermediate