Iron(II) Bromide-Catalyzed Synthesis of Benzimidazoles from Aryl Azides

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Supporting Information

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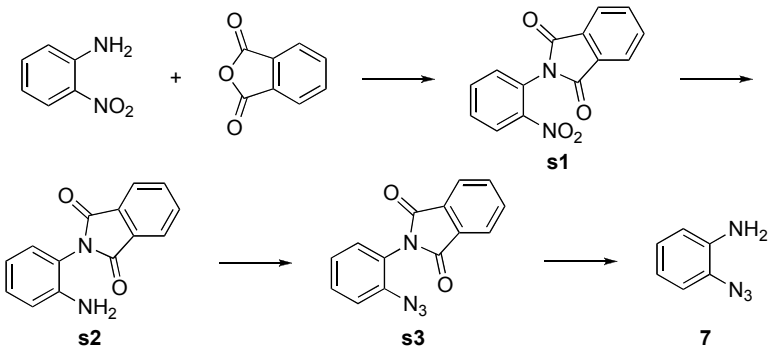
Typical information and materials

^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature using Bruker DRX 500 or Varian DRX 300 spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra were acquired on a JEOL GCMate II or Thermo Finnigan LTQ FT spectrometer, and were obtained by peak matching. Analytical thin layer chromatography was performed on Sorbent Technologies 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on Sorbent Technologies 60Å (40 – 60 μm) mesh silica gel (SiO_2). Medium pressure liquid chromatography (MPLC) was performed using Thomson SINGLE StEP pumps to force flow the indicated solvent system down columns that had been packed with Sorbent Technologies 60Å (40 – 60 μm) mesh silica gel (SiO_2). All reactions were carried out under an atmosphere of nitrogen in glassware, which had been oven-dried. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Acetonitrile, Methanol, Toluene, THF, Et_2O, and CH_2Cl_2 were dried by filtration through alumina according to the procedure of Grubbs.[1] Metal salts were stored in an MBraun labmaster nitrogen atmosphere dry box.

I. Preparation of 2-azidoanilines

A. Typical procedure for the preparation of 2-azidoanilines

The requisite 2-azidoanilines were prepared from 2-nitroanilines following the method reported by Hall and co-workers (Scheme s1).[2]



Scheme s1.

2-Phthalimidonitrobenzene (s1).[3] 13.81 g of phthalic anhydride (100.0 mmol) and 14.81 g of 2-nitroaniline (100.0 mmol) were melted together in an open flask and heated to 215 °C for 2h, at which time the evolution of water had ceased. The reaction mixture was allowed to cool somewhat, and 50 mL of glacial acetic acid was then added. The solution was refluxed to dissolve any phthalimide that had precipitated. After 5 minutes, the reaction mixture was slowly cooled. The resulting mixture was filtered and the precipitate was washed with portions of ethyl ether until the filtrate was colorless to provide **s1** as a yellow crystalline solid (19.16 g, 72%): mp 195–196 °C. The spectral data matched that reported by Cul and co-workers:[3] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.19 (d, J = 8.0 Hz, 1H), 7.96–7.98 (m, 2H), 7.78–7.84 (m, 3H), 7.63 (t, J = 8.0 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.3, 145.7, 134.8, 134.1, 131.8, 130.9, 129.7, 125.8, 125.6, 124.2; IR (thin film): 1714, 1600, 1523, 1467, 1379, 1344, 781, 706 cm^{-1}.

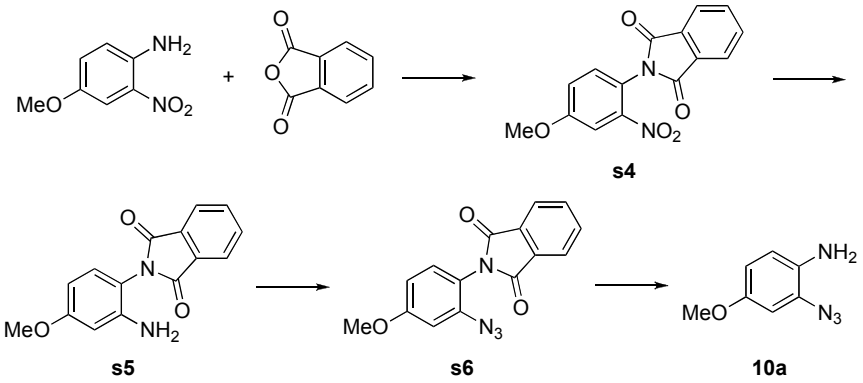
2-Phthalimidoaniline (s2).[4] To a solution of 10.73 g of **s1** (40.0 mmol) in 320 mL of acetone was added 32 mL of glacial acetic acid, 32 mL of water and 26.81 g of iron powder (480.0 mmol). The mixture was heated to reflux. After 8 h, the reaction mixture was cooled and filtered through a pad of Celite. The filtrate was concentrated *in vacuo*. The resulting residue was dissolved in 150 mL of acetone, and 200 mL of saturated solution of sodium carbonate was then added. Filtration afforded **s2** as a yellow solid (7.04 g, 74%): mp 184–184 °C. The spectral data matched that reported by Alkhathlan and co-workers:[4] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.94–7.96 (m, 2H), 7.79–7.81 (m, 2H), 7.24–7.27 (m, 1H), 7.12 (dd, J = 8.0, 1.0 Hz, 1H), 6.88–6.92 (m, 2H), 3.76 (br s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.4, 143.4, 134.5, 132.1, 130.2, 129.2, 123.9, 119.4, 118.0, 117.9; IR (thin film): 3379, 1707, 1623, 1503, 1379, 1100, 881, 716 cm^{-1}.

2-Phthalimidophenyl azide (s3). 5.96 g of **s2** (25.0 mmol) was suspended in 160 mL of glacial acetic acid and 160 mL of water. The mixture was cooled to 0 °C and 2.42 g of $NaNO_2$ (35.0 mmol) was added in one portion. After 3h, the remaining undissolved starting **s2** (approximately 0.16 g) was isolated by filtration. To the filtrate, 2.44 g of NaN_3 (37.5 mmol) was slowly added. During this addition, small portions of ethyl ether were added to prevent excessive foaming. After 0.5 h, the reaction mixture was filtered to give **s3** as a light yellow solid (6.37 g, 99%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95–7.96 (m, 2H), 7.79–7.80 (m, 2H), 7.50–7.53 (m, 1H), 7.26–7.33 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.9, 137.8, 134.4, 131.9, 130.6, 130.5, 125.3, 123.8, 122.5, 119.3;

IR (thin film): 2117, 2088, 1712, 1501, 1380, 1077, 753, 711 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{14}H_8N_4O_2$ $(M)^+$ 264.0647, found 264.0647.

2-Azidoaniline (7). 5.55 g of **s3** (21.0 mmol) was suspended in 14 mL of methanol. To this slurry was added 1.5 mL of hydrazine hydrate (31.5 mmol) in one portion. The resulting reaction mixture was stirred rapidly. After 20 min, the reaction became very thick. Any lumps were broken up with a spatula. An additional 10 mL of methanol was added and stirring was continued for 1 h. To the resulting paste, 40 mL of a 1.0 M aqueous solution of NaOH was added. The mixture was diluted with 30 mL of water and 60 mL of CH_2Cl_2. The resulting two phases were separated, and the aqueous phase was extracted with an additional 2 × 30 mL of CH_2Cl_2. The combined organic phases were washed with 1 × 30 mL of distilled water and 1 × 30 mL of brine. The resulting organic phase was dried over Na_2SO_4 and the heterogeneous mixture was filtered. The filtrate was concentrated *in vacuo*. Purification of the resulting residue by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded **7** as a yellow solid (1.76 g, 62%): R_f = 0.6 (14:86 EtOAc:hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.97 (td, *J* = 7.7, 1.2 Hz, 1H), 6.80 (td, *J* = 7.7, 1.2 Hz, 1H), 6.70 (dd, *J* = 7.8, 1.2 Hz, 1H), 3.81 (br s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.0, 125.5, 125.1, 119.0, 118.3, 115.8; IR (thin film): 3386, 3194, 2132, 1502, 1304, 1262, 822, 746 cm^{-1}; HRMS (EI) *m / z* calcd for $C_6H_6N_4$ $(M)^+$ 134.0592, found 134.0594.

B. Substituted 2-azidoaniline syntheses



Scheme s2.

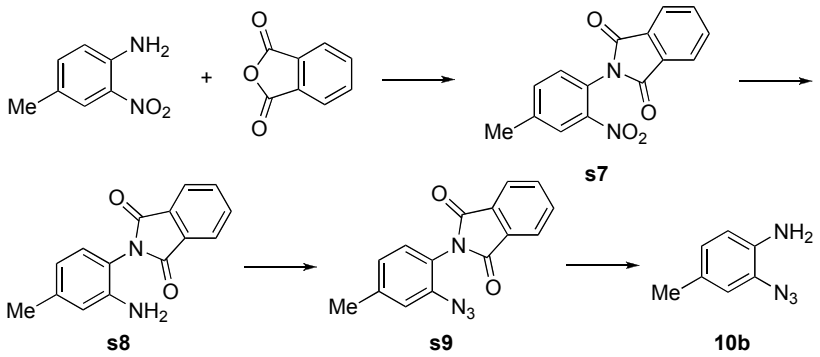
5-Methoxy-2-phthalimidonitrobenzene (s4). The typical procedure was followed using 7.41 g of phthalic anhydride (50.0 mmol) and 8.41 g of 4-methoxy-2-nitroaniline (50.0 mmol). Purification by recrystallization from 25 mL of glacial acetic acid afforded **s4** as a yellow crystalline solid (11.80 g, 79%): mp 147–148 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.94–7.96 (m, 2H), 7.80–7.82 (m, 2H), 7.70 (d, *J* = 2.5 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.26–7.29 (m, 1H), 3.93 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.7, 160.1, 146.2, 134.6, 131.93, 131.88, 124.0, 120.1, 117.9, 110.8, 56.2; IR (thin film): 1736, 1536, 1509, 1386, 1313, 1244, 1029, 720 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{15}H_{10}O_5N_2$ $(M)^+$ 298.0590, found 298.0592.

5-Methoxy-2-phthalimidoaniline (s5). The typical procedure was followed using 5.96 g of **s4** (20.0 mmol) and 13.40 g of iron powder (240.0 mmol) in 160 mL of acetone, 16 mL of glacial acetic acid, and 16 mL of water. Purification by recrystallization from 70 mL of acetone and 100 mL of saturated solution of sodium carbonate afforded **s5** as a yellow solid (3.71 g, 69%): mp 181–182 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.94 (br s, 2H), 7.78 (br s, 2H), 7.02 (d, *J* = 8.5 Hz, 1H), 6.46 (d, *J* = 7.5 Hz, 1H), 6.41 (s, 1H), 3.80 (s, 3H), 3.73 (br s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.7, 161.1, 144.5, 134.4, 132.1, 130.1, 123.8, 111.0, 105.3, 102.7, 55.4;

IR (thin film): 3444, 3366, 1715, 1630, 1515, 1385, 1212, 880 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{15}H_{12}O_3N_2$ $(M)^+$ 268.0848, found 268.0851.

5-Methoxy-2-phthalimidophenyl azide (s6). The typical procedure was followed using 2.68 g of **s5** (10.0 mmol), 0.97 g of $NaNO_2$ (14.0 mmol) and 0.98 g of NaN_3 (15.0 mmol) in 60 mL of glacial acetic acid and 60 mL of water. Purification using MPLC (0:100 – 20:80 EtOAc:hexanes) afforded **s6** as a light yellow solid (2.94 g, 100%): R_f = 0.5 (16:84 EtOAc:hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.93–7.95 (m, 2H), 7.78–7.79 (m, 2H), 7.19 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.79–6.81 (m, 2H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.3, 161.3, 138.9, 134.3, 132.0, 131.3, 123.8, 115.3, 110.9, 105.2, 55.8; IR (thin film): 2113, 1705, 1511, 1389, 1232, 1078, 881, 717 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{15}H_{10}O_3N_4$ $(M)^+$ 294.0753, found 294.0755.

2-Azido-4-methoxyaniline (10a). The typical procedure was followed using 2.94 g of **s6** (10.0 mmol) and 0.7 mL of hydrazine hydrate (15.0 mmol) in 15 mL of methanol. Purification using MPLC (0:100 – 15:85 EtOAc:hexanes) afforded **10a** as a yellow solid (1.31 g, 80%): R_f = 0.4 (14:86 EtOAc:hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.62–6.65 (m, 2H), 6.54–6.57 (m, 1H), 3.76 (s, 3H), 3.52 (br s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.2, 131.8, 126.1, 117.0, 111.2, 104.6, 55.9; IR (thin film): 3404, 3187, 2114, 1509, 1254, 1042, 826, 714 cm^{-1}; HRMS (EI) *m / z* calcd for $C_7H_8ON_4$ $(M)^+$ 164.0698, found 164.0697.



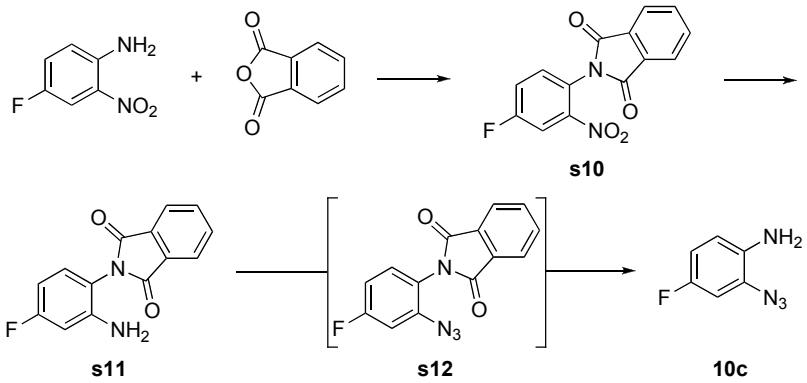
Scheme s3.

5-Methyl-2-phthalimidonitrobenzene (s7).[3] The typical procedure was followed using 7.41 g of phthalic anhydride (50.0 mmol) and 7.76 g of 4-methyl-2-nitroaniline (50.0 mmol). Purification by recrystallization from 25 mL of glacial acetic acid afforded **s7** as a yellow crystalline solid (11.50 g, 81%): mp 134–135 °C. The spectral data matched that reported by Cul and co-workers:[3] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.00 (s, 1H), 7.94–7.96 (m, 2H), 7.80–7.82 (m, 2H), 7.58 (dt, *J* = 8.0, 0.5 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.6, 145.4, 140.8, 134.8, 134.7, 131.9, 130.7, 126.2, 124.1, 122.9, 21.1; IR (thin film): 1734, 1716, 1533, 1381, 1350, 1226, 1101, 719 cm^{-1}.

5-Methyl-2-phthalimidoaniline (s8). The typical procedure was followed using 5.64 g of **s7** (20.0 mmol) and 13.40 g of iron powder (240.0 mmol) in 160 mL of acetone, 16 mL of glacial acetic acid and 16 mL of water. Purification by recrystallization from 70 mL of acetone and 100 mL of saturated solution of sodium carbonate afforded **s8** as a yellow solid (4.01 g, 79%): mp 157–158 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.93–7.95 (m, 2H), 7.78–7.79 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.71–6.72 (m, 2H), 3.70 (br s, 2H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.5, 143.0, 140.5, 134.4, 132.1, 128.9, 123.8, 120.4, 118.4, 115.5, 21.4; IR (thin film): 3421, 3350, 1724, 1512, 1383, 1103, 883, 717 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{15}H_{12}O_2N_2$ $(M)^+$ 252.0899, found 252.0899.

5-Methyl-2-phthalimidophenyl azide (s9). The typical procedure was followed using 2.52 g of **s8** (10.0 mmol), 0.97 g of $NaNO_2$ (14.0 mmol) and 0.98 g of NaN_3 (15.0 mmol) in 60 mL of glacial acetic acid and 60 mL of water. Filtration afforded **s9** as a yellow solid (2.73 g, 98%): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.94–7.96 (m, 2H), 7.78–7.80 (m, 2H), 7.17 (d, J = 8.0 Hz, 1H), 7.07–7.11 (m, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.2, 141.3, 137.4, 134.3, 132.0, 130.2, 126.3, 123.8, 120.0, 119.9, 21.4; IR (thin film): 2112, 1734, 1716, 1514, 1385, 1306, 1105, 717 cm^{-1}; HRMS (EI) m / z calcd for $C_{15}H_{10}O_2N_4$ $(M)^+$ 278.0804, found 278.0805.

2-Azido-4-methylaniline (10b).[5] The typical procedure was followed using 2.18 g of **s9** (7.8 mmol) and 0.6 mL of hydrazine hydrate (12.3 mmol) in 15 mL of methanol. Purification using MPLC (0:100 – 10:90 EtOAc:hexanes) afforded **10b** as an orange oil (0.92 g, 79%): R_f = 0.5 (14:86 EtOAc:hexanes). The spectral data matched that reported by Novak and co-workers:[5] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.87 (s, 1H), 6.80 (d, J = 8.0 Hz, 1H), 6.62 (dd, J = 8.0, 2.0 Hz, 1H), 3.71 (br s, 2H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.7, 128.8, 126.3, 125.0, 118.8, 116.1, 20.6; IR (thin film): 3462, 3371, 2110, 1624, 1516, 1306, 1261, 810 cm^{-1}.



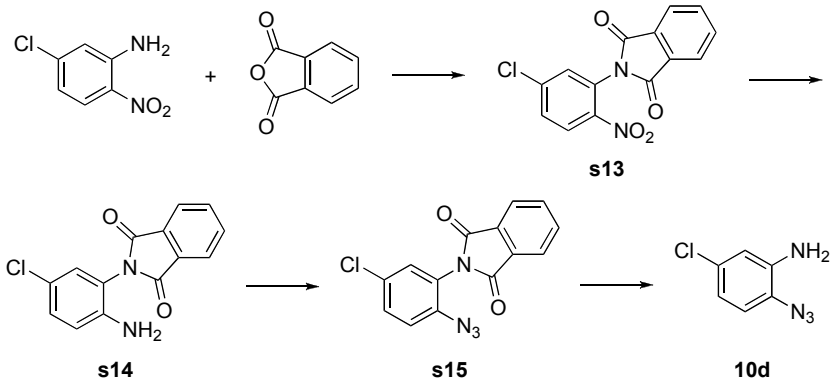
Scheme s4.

5-Fluoro-2-phthalimidonitrobenzene (s10). The typical procedure was followed using 7.41 g of phthalic anhydride (50.0 mmol) and 8.05 g of 4-fluoro-2-nitroaniline (50.0 mmol). Purification by recrystallization from 40 mL of glacial acetic acid afforded **s10** as a brown crystalline solid (9.40 g, 66%): mp 230–231 °C; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.21 (dd, J = 8.5, 2.5 Hz, 1H), 8.01–8.04 (m, 2H), 7.95–7.97 (m, 2H), 7.84–7.91 (m, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 166.5, 161.5 (d, J_{CF} = 250.0 Hz), 146.6 (d, J_{CF} = 10.0 Hz), 135.9, 133.7 (d, J_{CF} = 8.8 Hz), 131.7, 124.5, 122.4 (d, J_{CF} = 22.5 Hz), 121.7, 114.0 (d, J_{CF} = 27.5 Hz); IR (thin film): 1739, 1537, 1502, 1466, 1383, 1234, 878, 714 cm^{-1}; HRMS (EI) m / z calcd for $C_{14}H_7O_4N_2F$ $(M)^+$ 286.0390, found 286.0392.

5-Fluoro-2-phthalimidoaniline (s11). The typical procedure was followed using 2.86 g of **s10** (10.0 mmol) and 6.70 g of iron powder (120.0 mmol) in 80 mL of acetone, 8 mL of glacial acetic acid and 8 mL of water. Purification by recrystallization from 35 mL of acetone and 50 mL of saturated solution of sodium carbonate afforded **s11** as a brown solid (0.74 g, 29%): mp 182–183 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.94–7.95 (m, 2H), 7.79–7.81 (m, 2H), 7.04–7.07 (m, 1H), 6.56–6.59 (m, 2H), 3.85 (br s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.4, 163.7 (d, J_{CF} = 245.0 Hz), 145.2 (d, J_{CF} = 11.2 Hz), 134.6, 131.9, 130.8 (d, J_{CF} = 10.0 Hz), 123.9, 113.7, 106.2 (d, J_{CF} = 22.5 Hz), 104.2 (d, J_{CF} = 25.0 Hz); IR (thin film): 3454, 3375, 2125, 1722, 1622, 1513, 1385, 717 cm^{-1}; HRMS (EI) m / z calcd for $C_{14}H_9O_2N_2F$ $(M)^+$ 256.0648, found 256.0650.

5-Fluoro-2-phthalimidophenyl azide (s12). The typical procedure was followed using 0.73 g of **s11** (2.8 mmol), 0.28 g of $NaNO_2$ (4.0 mmol) and 0.28 g of NaN_3 (4.3 mmol) in 20 mL of glacial acetic acid and 20 mL of water. Filtration afforded crude **s12** as a yellow solid (0.62 g, 77%): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.94–7.96 (m, 2H), 7.79–7.81 (m, 2H), 7.25–7.28 (m, 1H), 7.02 (dd, J = 8.5, 2.5 Hz, 1H), 6.96–7.00 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.9, 163.4 (d, J_{CF} = 248.8 Hz), 139.8 (d, J_{CF} = 10.0 Hz), 134.5, 132.1 (d, J_{CF} = 10.0 Hz), 131.9, 123.9, 118.7, 112.6 (d, J_{CF} = 22.5 Hz), 107.0 (d, J_{CF} = 25.0 Hz). This material was used directly in the next step without further purification.

2-azido-4-fluoroaniline (10c). The typical procedure was followed using 0.62 g of unpurified **s12** (2.2 mmol) and 0.16 mL of hydrazine hydrate (3.3 mmol) in 8 mL of methanol. Purification by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded **10c** as a red oil (0.32 g, 97%) (***Caution*** **10c** is volatile): R_f = 0.5 (16:84 EtOAc:hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.77 (dd, J = 8.8, 2.2 Hz, 1H), 6.68 (td, J = 8.5, 2.5 Hz, 1H), 6.60–6.63 (m, 1H), 3.67 (br s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 156.1 (d, J_{CF} = 237.5 Hz), 134.3, 126.0 (d, J_{CF} = 8.8 Hz), 116.4 (d, J_{CF} = 8.8 Hz), 112.2 (d, J_{CF} = 22.5 Hz), 105.6 (d, J_{CF} = 25.0 Hz); IR (thin film): 3456, 3373, 2114, 1599, 1510, 1311, 1255, 950 cm^{-1}; HRMS (EI) m / z calcd for $C_6H_5N_4F$ $(M)^+$ 152.0498, found 152.0497.



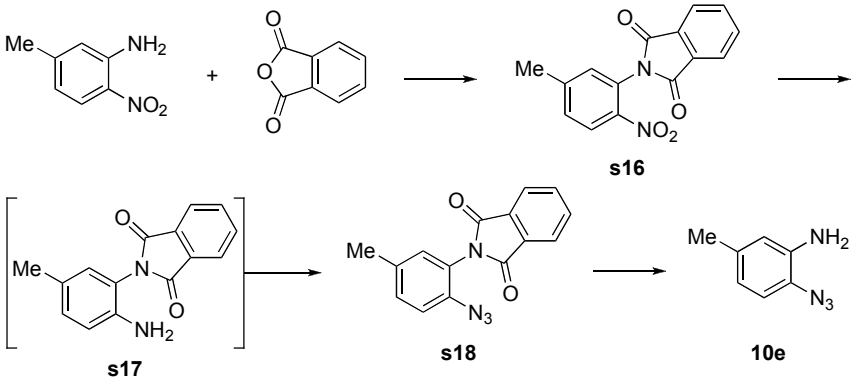
Scheme s5.

4-Chloro-2-phthalimidonitrobenzene (s13). The typical procedure was followed using 7.41 g of phthalic anhydride (50.0 mmol), and 8.63 g of 5-chloro-2-nitroaniline (50.0 mmol). Purification by recrystallization from 25 mL of glacial acetic acid afforded **s13** as a yellow crystalline solid (5.10 g, 34%): mp 192–193 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.16 (d, J = 8.5 Hz, 1H), 7.97–7.99 (m, 2H), 7.83–7.85 (m, 2H), 7.59 (dd, J = 8.8, 2.2 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.9, 144.0, 140.3, 135.0, 131.7, 131.0, 129.8, 127.0, 126.8, 124.4; IR (thin film): 1727, 1600, 1525, 1347, 1224, 1109, 780, 716 cm^{-1}; HRMS (EI) m / z calcd for $C_{14}H_7O_4N_2Cl$ $(M)^+$ 302.0094, found 302.0091.

4-Chloro-2-phthalimidoaniline (s14). The typical procedure was followed using 4.54 g of **s13** (15.0 mmol) and 10.05 g of iron powder (180.0 mmol) in 120 mL of acetone, 12 mL of glacial acetic acid, and 12 mL of water. Purification by recrystallization from 50 mL of acetone and 80 mL of saturated solution of sodium carbonate afforded **s14** as a yellow solid (3.77 g, 92%): mp 165–166 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95–7.96 (m, 2H), 7.80–7.82 (m, 2H), 7.21 (dd, J = 8.8, 2.2 Hz, 1H), 7.13 (d, J = 2.0 Hz, 1H); 6.82 (d, J = 8.5 Hz, 1H), 3.76 (br s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.9, 142.2, 134.6 (2C), 131.9, 130.2, 129.0, 124.0, 123.5, 118.7; IR (thin film): 3433, 3360, 1717, 1630, 1496, 1376, 1102, 722 cm^{-1}; HRMS (EI) m / z calcd for $C_{14}H_9O_2N_2Cl$ $(M)^+$ 272.0353, found 272.0352.

4-Chloro-2-phthalimidophenyl azide (s15). The typical procedure was followed using 2.73 g of **s14** (10.0 mmol), 0.97 g of $NaNO_2$ (14.0 mmol) and 0.98 g of NaN_3 (15.0 mmol) in 60 mL of glacial acetic acid and 60 mL of water. Filtration afforded **s15** as a light yellow solid (2.12 g, 71%): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95–7.97 (m, 2H), 7.80–7.82 (m, 2H), 7.48 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.31 (d, *J* = 2.0 Hz, 1H); 7.24 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.5, 136.7, 134.6 (2C), 131.8, 130.8, 130.3, 124.0, 123.5, 120.3; IR (thin film): 2131, 2099, 1725, 1492, 1371, 1305, 1111, 717 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{14}H_7O_2N_4Cl$ $(M)^+$ 298.0258, found 298.0262.

2-azido-5-chloroaniline (10d). The typical procedure was followed using 1.49 g of **s15** (5.0 mmol) and 0.4 mL of hydrazine hydrate (7.5 mmol) in 5 mL of methanol. Purification by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded **10d** as an orange oil (0.76 g, 91%): R_f = 0.5 (13:87 EtOAc:hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.92 (d, *J* = 8.5 Hz, 1H), 6.74 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.66 (d, *J* = 2.5 Hz, 1H), 3.88 (br s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 139.1, 130.7, 123.8, 119.2, 118.7, 115.4; IR (thin film): 3392, 3299, 2128, 2087, 1494, 1297, 1252, 796 cm^{-1}; HRMS (EI) *m / z* calcd for $C_6H_5N_4Cl$ $(M)^+$ 168.0203, found 168.0205.



Scheme s6.

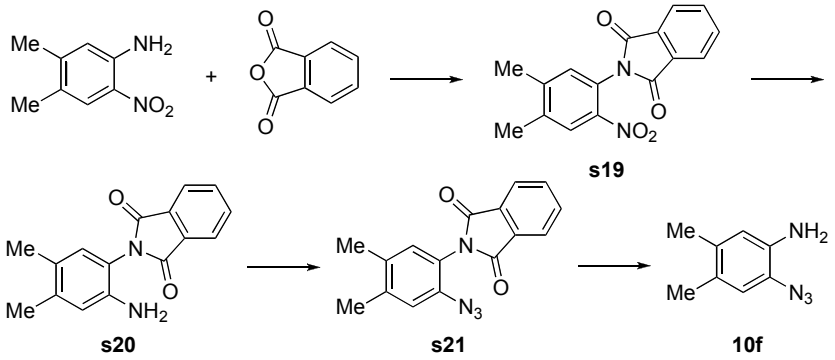
4-Methyl-2-phthalimidonitrobenzene (s16). The typical procedure was followed using 1.30 g of phthalic anhydride (8.8 mmol) and 1.34 g of 5-methyl-2-nitroaniline (8.8 mmol). Purification by recrystallization from 5 mL of glacial acetic acid afforded **s16** as a light yellow crystalline solid (1.02 g, 41%): mp 147–148 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.94–7.96 (m, 2H), 7.80–7.82 (m, 2H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.30 (s, 1H), 2.50 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.5, 145.9, 143.4, 134.7, 131.9, 131.5, 130.4, 125.9, 125.5, 124.1, 21.5; IR (thin film): 1724, 1604, 1520, 1371, 1348, 1306, 1105, 719 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{15}H_{10}O_4N_2$ $(M)^+$ 282.0641, found 282.0638.

4-Methyl-2-phthalimidoaniline (s17). The typical procedure was followed using 2.17 g of **s16** (7.7 mmol) and 5.13 g of iron powder (92.3 mmol) in 60 mL of acetone, 6 mL of glacial acetic acid, and 6 mL of water. Purification by recrystallization from 15 mL of acetone and 50 mL of saturated solution of sodium carbonate afforded crude **s17** as a brown solid (0.69 g, 40%): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.94–7.95 (m, 2H), 7.78–7.79 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 3.67 (br s, 2H), 2.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.4, 140.8, 134.4 (2C), 132.1, 131.0, 129.4, 129.0, 123.8, 118.0, 20.4. Unpurified **s17** was used directly to next step.

4-Methyl-2-phthalimidophenyl azide (s18). The typical procedure was followed using 0.69 g of **s17** (2.7 mmol), 0.26 g of $NaNO_2$ (3.8 mmol), and 0.26 g of NaN_3 (4.1 mmol) in 16 mL of glacial acetic acid and 16 mL of water. Purification using MPLC (0:100 – 20:80 EtOAc:hexanes) afforded **s18** as a light yellow solid (0.68 g,

89%): R_f = 0.5 (14:86 EtOAc:hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.92–7.94 (m, 2H), 7.77–7.78 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.0, 135.6, 135.0, 134.4, 132.0, 131.5, 131.0, 123.8, 122.3, 119.2, 20.8; IR (thin film): 2129, 2100, 1722, 1502, 1375, 1302, 1109, 717 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{15}H_{10}O_2N_4$ $(M)^+$ 278.0804, found 278.0802.

2-azido-5-methylaniline (10e). The typical procedure was followed using 0.67 g of **s18** (2.4 mmol) and 0.2 mL of hydrazine hydrate (3.6 mmol) in 10 mL of methanol. Purification using MPLC (0:100 – 10:90 EtOAc:hexanes) afforded **10e** as a pink solid (0.34 g, 96%): R_f = 0.4 (14:86 EtOAc:hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.93 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 7.5 Hz, 1H), 6.53 (s, 1H), 3.76 (br s, 2H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.9, 135.6, 122.5, 119.9, 118.2, 116.6, 21.0; IR (thin film): 3388, 2130, 2092, 1633, 1506, 1308, 1273, 798 cm^{-1}; HRMS (EI) *m / z* calcd for $C_7H_8N_4$ $(M)^+$ 148.0749, found 148.0748.



Scheme s7.

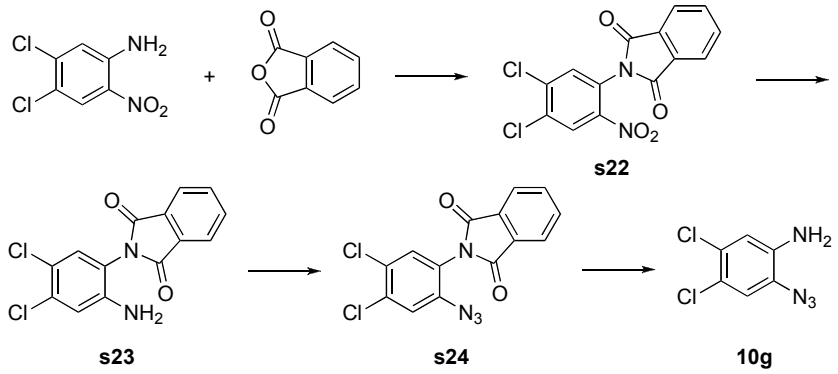
4,5-Dimethyl-2-phthalimidonitrobenzene (s19). The typical procedure was followed using 3.70 g of phthalic anhydride (25.0 mmol) and 4.28 g of 4,5-dimethyl-2-nitroaniline (25.0 mmol). Purification by recrystallization from 5 mL of glacial acetic acid afforded **s19** as a brown crystalline solid (4.01 g, 54%): mp 158–159 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.00 (s, 1H), 7.92–7.94 (m, 2H), 7.79–7.80 (m, 2H), 7.24 (s, 1H), 2.39 (s, 3H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.7, 144.6, 143.2, 139.4, 134.6, 132.0, 131.8, 126.7, 124.1, 123.0, 20.0, 19.6; IR (thin film): 1726, 1525, 1408, 1365, 1350, 1248, 1103, 719 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{16}H_{12}O_4N_2$ $(M)^+$ 296.0797, found 296.0799.

4,5-Dimethyl-2-phthalimidoaniline (s20). The typical procedure was followed using 2.96 g of **s19** (10.0 mmol) and 6.70 g of iron powder (120.0 mmol) in 80 mL of acetone, 8 mL of glacial acetic acid and 8 mL of water. Purification by recrystallization from 15 mL of acetone and 80 mL of saturated solution of sodium carbonate afforded **s20** as a brown solid (2.09 g, 78%): mp 180–181 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.93–7.95 (m, 2H), 7.77–7.79 (m, 2H), 6.88 (s, 1H), 6.71 (s, 1H), 3.55 (br s, 2H), 2.22 (s, 3H), 2.18 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.6, 141.0, 139.0, 134.4, 132.1, 129.6, 127.8, 123.8, 119.4, 115.5, 19.7, 18.8; IR (thin film): 1708, 1610, 1511, 1381, 1099, 1068, 872, 717 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{16}H_{14}O_2N_2$ $(M)^+$ 266.1055, found 266.1057.

4,5-Dimethyl-2-phthalimidophenyl azide (s21). The typical procedure was followed using 1.48 g of **s20** (5.5 mmol), 0.54 g of $NaNO_2$ (7.8 mmol) and 0.54 g of NaN_3 (8.3 mmol) in 30 mL of glacial acetic acid and 30 mL of water. Filtration afforded **s21** as a light brown solid (1.52 g, 94%): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.94 (d, *J* = 2.5 Hz, 2H), 7.77–7.79 (m, 2H), 7.07 (s, 1H), 7.05 (s, 1H), 2.33 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.3, 140.0, 134.8, 134.34, 134.28, 132.0, 131.2, 123.8, 120.4, 119.8, 19.9, 19.3; IR (thin film): 2112,

1714, 1508, 1379, 1306, 1105, 872, 723 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{16}H_{12}O_2N_4$ $(M)^+$ 292.0960, found 292.0957.

2-azido-4,5-dimethylaniline (10f). The typical procedure was followed using 1.45 g of **s21** (5.0 mmol) and 0.4 mL of hydrazine hydrate (7.5 mmol) in 10 mL of methanol. Purification using MPLC (0:100 – 10:90 EtOAc:hexanes) afforded **10f** as a yellow solid (0.68 g, 84%): R_f = 0.6 (16:84 EtOAc:hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.80 (s, 1H), 6.52 (s, 1H), 3.61 (br s, 2H), 2.19 (s, 3H), 2.17 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.7, 133.9, 127.4, 122.5, 119.4, 117.4, 19.3, 18.9; IR (thin film): 2117, 2100, 1512, 1448, 1318, 1261, 865, 768 cm^{-1}; HRMS (EI) *m / z* calcd for $C_8H_{10}N_4$ $(M)^+$ 162.0905, found 162.0906.



Scheme s8.

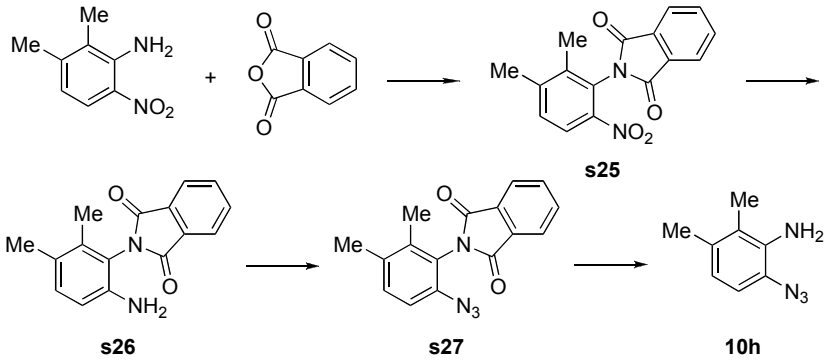
4,5-Dichloro-2-phthalimidonitrobenzene (s22). The typical procedure was followed using 3.70 g of phthalic anhydride (25.0 mmol) and 5.39 g of 4,5-dichloro-2-nitroaniline (25.0 mmol). Purification by recrystallization from 25 mL of glacial acetic acid afforded **s22** as a brown crystalline solid (2.36 g, 28%): mp 170–171 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.31 (s, 1H), 7.97–7.98 (m, 2H), 7.84–7.86 (m, 2H), 7.67 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.8, 143.8, 138.9, 135.1, 134.1, 132.2, 131.6, 127.5, 124.7, 124.5; IR (thin film): 1726, 1533, 1473, 1394, 1346, 1224, 1105, 717 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{14}H_6O_4N_2Cl_2$ $(M)^+$ 335.9705, found 335.9702.

4,5-Dichloro-2-phthalimidoaniline (s23). The typical procedure was followed using 2.18 g of **s22** (6.5 mmol) and 4.33 g of iron powder (78.0 mmol) in 60 mL of acetone, 6 mL of glacial acetic acid, and 6 mL of water. Purification by recrystallization from 20 mL of acetone and 80 mL of saturated solution of sodium carbonate afforded **s23** as a light brown solid (1.58 g, 80%): mp 222–223 °C; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 7.91 (s, 2H), 7.86 (s, 2H), 7.42 (s, 1H), 6.94 (s, 1H), 5.88 (s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 167.6, 147.5, 134.7, 133.0, 132.5, 132.0, 123.7, 116.2, 115.9, 115.7; IR (thin film): 3348, 1722, 1708, 1626, 1491, 1375, 862, 714 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{14}H_8O_2N_2Cl_2$ $(M)^+$ 305.9963, found 305.9962.

4,5-Dichloro-2-phthalimidophenyl azide (s24). The typical procedure did not work because of the poor solubility of **s23** in acetic acid and water. This azide was obtained following the method reported by Goddard-Borger and co-workers:[6] 1.33 g of imidazole-1-sulfonyl azide hydrochloride (6.3 mmol) was added to 1.30 g of aniline **s23** (4.2 mmol), 1.16 g of K_2CO_3 (8.4 mmol), and 0.16 g of $CuSO_4 \cdot 5H_2O$ (0.63 mmol) in 21 mL of MeOH and 21 mL of acetone. After 36h, visualization of the reaction progress using thin layer chromatography revealed only about 50% completion. Nevertheless, the resulting mixture was diluted with 50 mL of water and 50 mL of CH_2Cl_2. The phases were separated and the resulting aqueous phase was extracted with an additional 2 × 50 mL of CH_2Cl_2. The combined organic phases were washed with 1 × 30 mL of distilled water and 1 × 30 mL of brine. The resulting organic phase was dried over Na_2SO_4, and the heterogeneous mixture was filtered.

The filtrate was concentrated *in vacuo*. Purification using MPLC (0:100 – 10:90 EtOAc:hexanes) afforded **s24** as a yellow solid (0.28 g, 20%): R_f = 0.6 (16:84 EtOAc:hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95–7.97 (m, 2H), 7.81–7.83 (m, 2H), 7.41 (s, 1H), 7.39 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.3, 137.6, 134.7 (2C), 132.0, 131.7, 128.9, 124.1, 122.0, 120.9; IR (thin film): 2111, 1713, 1487, 1395, 1294, 1102, 872, 725 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{14}H_6O_2N_4Cl_2$ $(M)^+$ 331.9868, found 331.9871.

2-azido-4, 5-dichlorolaniline (10g). The typical procedure was followed using 0.42 g of **s24** (1.3 mmol) and 0.1 mL of hydrazine hydrate (2.0 mmol) in 5 mL of methanol. Purification using MPLC (0:100 – 10:90 EtOAc:hexanes) afforded **10g** as a light red solid (0.18 g, 71%): R_f = 0.5 (15:85 EtOAc:hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.04 (s, 1H), 6.74 (s, 1H), 3.82 (br s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.7, 128.8, 124.9, 121.0, 119.5, 116.4; IR (thin film): 2116, 1619, 1491, 1390, 1271, 1242, 1126, 862 cm^{-1}; HRMS (EI) *m / z* calcd for $C_6H_4N_4Cl_2$ $(M)^+$ 201.9813, found 201.9815.



Scheme s9.

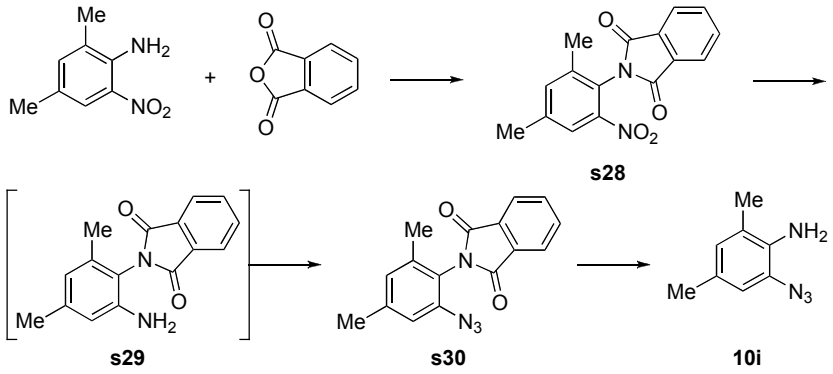
3,4-Dimethyl-2-phthalimidonitrobenzene (s25). The typical procedure was followed using 3.70 g of phthalic anhydride (25.0 mmol) and 4.28 g of 2,3-dimethyl-6-nitroaniline (25.0 mmol). Purification by recrystallization from 20 mL of glacial acetic acid afforded **s25** as a deep brown crystalline solid (3.61 g, 49%): mp 168–169 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95–7.97 (m, 2H), 7.80–7.82 (m, 2H), 7.43 (s, 1H), 7.41 (s, 1H), 2.43 (s, 3H), 2.19 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.8, 145.1, 144.7, 139.1, 134.7, 132.1, 131.0, 124.5, 124.1, 123.2, 21.1, 15.0; IR (thin film): 1720, 1583, 1516, 1468, 1369, 1334, 876, 719 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{16}H_{12}O_4N_2$ $(M)^+$ 296.0797, found 296.0794.

3,4-Dimethyl-2-phthalimidoaniline (s26). The typical procedure was followed using 2.96 g of **s25** (10.0 mmol) and 6.70 g of iron powder (120.0 mmol) in 80 mL of acetone, 8 mL of glacial acetic acid and 8 mL of water. Purification by recrystallization from 15 mL of acetone and 80 mL of saturated solution of sodium carbonate afforded **s26** as a brown solid (0.96 g, 36%): mp 176–177 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.96 (s, 2H), 7.81 (m, 2H), 7.06 (d, *J* = 7.0 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 3.47 (br s, 2H), 2.23 (s, 3H), 1.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.4, 141.7, 135.7, 134.4, 132.0, 131.7, 127.8, 123.9, 117.4, 114.4, 19.7, 14.8; IR (thin film): 3373, 1714, 1626, 1494, 1375, 1105, 883, 721 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{16}H_{14}O_2N_2$ $(M)^+$ 266.1055, found 266.1055.

3,4-Dimethyl-2-phthalimidophenyl azide (s27). The typical procedure was followed using 0.68 g of **s26** (2.3 mmol), 0.22 g of $NaNO_2$ (3.2 mmol) and 0.23 g of NaN_3 (3.5 mmol) in 15 mL of glacial acetic acid and 15 mL of water. Purification using MPLC (0:100 – 11:89 EtOAc:hexanes) afforded **s27** as a yellow solid (0.67 g, 100%): R_f = 0.4 (15:85 EtOAc:hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.94–7.96 (m, 2H), 7.78–7.80 (m, 2H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 2.30 (s, 3H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ

167.2, 137.8, 135.6, 134.4 (2C), 132.1, 131.8, 123.9, 121.6, 116.0, 20.1, 14.8; IR (thin film): 2121, 1722, 1485, 1371, 1304, 1107, 885, 721 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{16}H_{12}O_2N_4$ $(M)^+$ 292.0960, found 292.0963.

6-azido-2,3-dimethylaniline (10h). The typical procedure was followed using 0.83 g of **s27** (2.8 mmol) and 0.2 mL of hydrazine hydrate (3.4 mmol) in 10 mL of methanol. Purification using MPLC (0:100 – 10:90 EtOAc:hexanes) afforded **10h** as a pink solid (0.26 g, 57%): R_f = 0.5 (14:86 EtOAc:hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.86 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 3.78 (br s, 2H), 2.29 (s, 3H), 2.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.2, 133.6, 122.9, 121.9, 120.3, 115.1, 20.3, 13.1; IR (thin film): 2109, 2062, 1460, 1271, 1072, 1020, 849, 788 cm^{-1}; HRMS (EI) *m / z* calcd for $C_8H_{10}N_4$ $(M)^+$ 162.0905, found 162.0907.



Scheme s10.

3,5-Dimethyl-2-phthalimidonitrobenzene (s28). The typical procedure was followed using 4.46 g of phthalic anhydride (30.1 mmol) and 5.00 g of 4,6-dimethyl-2-nitroaniline (30.1 mmol). Purification by recrystallization from 15 mL of glacial acetic acid afforded **s28** as a brown crystalline solid (5.55 g, 62%): mp 213–214 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95–7.97 (m, 2H), 7.85 (s, 1H), 7.81–7.82 (m, 2H), 7.47 (s, 1H), 2.47 (s, 3H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.7, 146.5, 140.7, 140.2, 136.7 (2C), 134.6, 132.1, 124.1, 122.1, 21.1, 18.1; IR (thin film): 1728, 1707, 1529, 1375, 1350, 1218, 1103, 715 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{16}H_{12}O_4N_2$ $(M)^+$ 296.0797, found 296.0799.

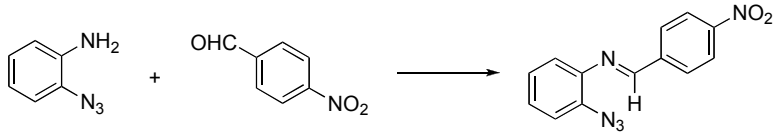
3,5-Dimethyl-2-phthalimidoaniline (s29). The typical procedure was followed using 2.96 g of **s28** (10.0 mmol) and 6.70 g of iron powder (120.0 mmol) in 80 mL of acetone, 8 mL of glacial acetic acid, and 8 mL of water. Purification by recrystallization from 15 mL of acetone and 80 mL of saturated solution of sodium carbonate afforded crude **s29** as a brown solid (2.58 g, 97%): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95 (s, 2H), 7.80 (m, 2H), 6.58 (s, 1H), 6.54 (s, 1H), 3.56 (br s, 2H), 2.27 (s, 3H), 2.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.5, 143.7, 140.3, 137.2, 134.4, 132.0, 123.8, 122.0, 115.4, 114.4, 21.3, 18.0. Unpurified **s29** was used directly in the next step.

3,5-Dimethyl-2-phthalimidophenyl azide (s30). The typical procedure was followed using 2.58 g of **s29** (9.7 mmol), 0.94 g of $NaNO_2$ (13.6 mmol), and 0.94 g of NaN_3 (14.5 mmol) in 58 mL of glacial acetic acid and 58 mL of water. Purification using MPLC (0:100 – 20:80 EtOAc:hexanes) afforded **s30** a pale yellow solid (0.96 g, 34%): R_f = 0.4 (15:85 EtOAc:hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.93–7.94 (m, 2H), 7.77–7.78 (m, 2H), 6.944 (s, 1H), 6.938 (s, 1H), 2.37 (s, 3H), 2.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.1, 140.9, 138.9, 137.8, 134.4, 132.1, 127.9, 123.8, 119.2, 117.2, 21.4, 17.8; IR (thin film): 2112, 1732, 1713, 1377, 1317, 1107, 845, 717 cm^{-1}; HRMS (EI) *m / z* calcd for $C_{16}H_{12}O_2N_4$ $(M)^+$ 292.0960, found 292.0956.

2-azido-4,6-dimethylaniline (10i). The typical procedure was followed using 0.95 g of **s30** (3.2 mmol) and 0.2 mL of hydrazine hydrate (3.9 mmol) in 12 mL of methanol. Purification using MPLC (0:100 – 10:90 EtOAc:hexanes) afforded **10i** as a yellow solid (0.45 g, 86%): R_f = 0.4 (15:85 EtOAc:hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.79 (s, 1H), 6.74 (s, 1H), 3.68 (br s, 2H), 2.32 (s, 3H), 2.18 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 134.0, 128.0, 127.7, 124.7, 123.7, 116.4, 20.6, 17.3; IR (thin film): 3420, 3322, 2114, 1636, 1498, 1318, 1267, 828 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_8H_{10}N_4$ $(M)^+$ 162.0905, found 162.0895.

II. Preparation of 2-azidoarylimines

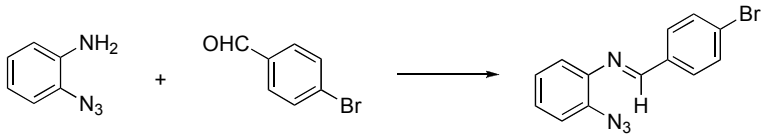
A. Typical procedure for the preparation of 2-azidoarylimines



7 **5**

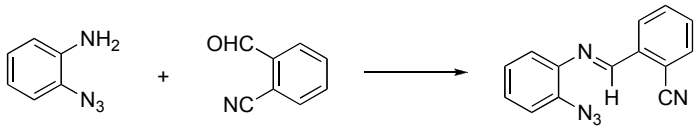
(*E*)-2-azido-*N*-(4-nitrobenzylidene)aniline (5). To a solution of 0.27 g of 2-azidoaniline **(7)** (2.0 mmol) and 0.31 g of 4-nitrobenzaldehyde (2.0 mmol) in 2 mL of CH_2Cl_2 was added 0.6 g of anhydrous $MgSO_4$. The mixture was stirred at room temperature. After 36 h, the heterogeneous mixture was filtered. The filtrate was concentrated *in vacuo*. The crude product was recrystallized from CH_2Cl_2 and hexanes to afford **5** as an orange crystalline solid (0.39 g, 73%): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.55 (s, 1H), 8.32 (d, *J* = 8.5 Hz, 2H), 8.08 (d, *J* = 9.0 Hz, 2H), 7.24–7.28 (m, 1H), 7.18 (td, *J* = 7.5, 1.0 Hz, 1H), 7.08–7.12 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.7, 149.4, 143.1, 141.1, 134.0, 129.7, 128.2, 125.6, 124.0, 120.6, 119.0; IR (thin film): 2122, 2094, 1560, 1520, 1340, 1096, 853, 766 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{13}H_9O_2N_5$ $(M)^+$ 267.0756, found 267.0755.

B. 2-Azidoarylimine syntheses



7 **8b**

(*E*)-2-azido-*N*-(4-bromobenzylidene)aniline (8b). The typical procedure was followed using 0.27 g of 2-azidoaniline **(7)** (2.0 mmol), 0.37 g of 4-bromobenzaldehyde (2.0 mmol) and 0.6 g of anhydrous $MgSO_4$ in 2 mL of CH_2Cl_2. Purification by recrystallization afforded **8b** as a yellow crystalline solid (0.22 g, 36%): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.39 (s, 1H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.21 (td, *J* = 7.6, 1.2 Hz, 1H), 7.15 (td, *J* = 7.5, 1.5 Hz, 1H), 7.06 (td, *J* = 7.8, 1.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.3, 143.9, 134.7, 133.5, 132.1, 130.4, 127.2, 126.3, 125.5, 120.4, 119.2; IR (thin film): 2120, 2092, 1624, 1488, 1299, 1068, 820, 751 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{13}H_9N_4Br$ $(M)^+$ 300.0010, found 300.0012.

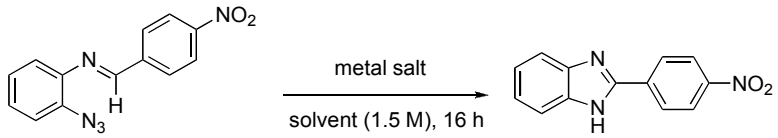


7 **8j**

(*E*)-2-azido-*N*-(2-cyanobenzylidene)aniline (8j). The typical procedure was followed using 0.13 g of 2-azidoaniline **(7)** (1.0 mmol), 0.16 g of 2-cyanobenzaldehyde (1.2 mmol) and 0.3 g of anhydrous $MgSO_4$ in 1 mL of CH_2Cl_2. Purification by recrystallization afforded **8j** as a yellow crystalline solid (0.24 g, 96%): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.86 (s, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 7.00–7.76 (m, 2H), 7.58 (td, *J* = 7.5, 1.0 Hz, 1H), 7.24–7.28 (m, 1H), 7.14–7.20 (m, 2H), 7.08–7.10 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.9, 143.0, 137.8, 134.0, 133.1, 133.0, 131.5, 128.2, 127.9, 125.6, 120.5, 119.3, 116.8, 113.6; IR (thin film): 2154, 2121, 1487, 1446, 1350, 1097, 766, 737 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{14}H_9N_5$ $(M)^+$ 247.0858, found 247.0858.

III. $FeBr_2$-catalyzed synthesis of benzimidazoles from aryl azides

A. General procedure for the screening of catalysts to promote the decomposition of aryl azides



5 **6**

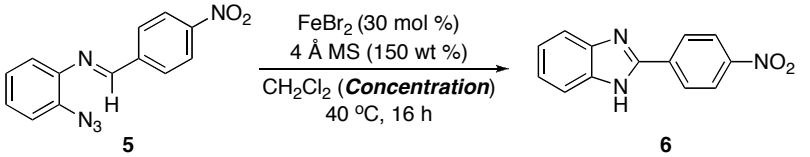
To a mixture of 0.021 g of aryl azide **5** (0.078 mmol), metal salt (5–30 mol %) and crushed 4Å molecular sieves (100 wt %) was added 0.05 mL of solvent. After 16 h, the heterogenous mixture was filtered through SiO_2. The filtrate was concentrated *in vacuo*. The resulting mixture was dissolved in 0.8 mL of DMSO-d_6 and 0.007 mL of dibromomethane (0.1 mmol) was added. The area of NH peak in benzimidazole **6** was compared with the area of the peak of dibromomethane to derive a ^{1}H NMR yield.

Table s1. Optimization of reaction conditions

entry	metal salt	mol %	4Å MS (wt %)	Temp (ºC)	yield (%)[a]
1	None	n.a.	0	145	89[b]
2[d]	None	n.a.	100	40	0
3[c]	None	n.a.	100	60	0
4[c]	$Rh_2(O_2CC_3F_7)_4$	5	0	60	trace
5[c]	$Rh_2(O_2CC_3F_7)_4$	5	100	60	36
6[c]	$Rh_2(O_2CC_7H_{15})_4$	5	100	60	31
7[c]	ZnI_2	10	100	60	trace
8[c]	$Cu(OTf)_2$	10	100	60	trace
9[c]	AgOTf	5	100	60	5
10[c]	AuCl	5	100	60	trace
11[c]	$Pd(PPh_3)_4$	5	100	60	trace
12[c]	$Pd(PhCN)_2Cl_2$	5	100	60	0
13[c]	$Pd(OCOCF_3)_2$	5	100	60	0
14[c]	Co(salen)[e]	5	100	60	28
15[c]	$Ni(COD)_2$[f]	5	100	60	8
16[c]	$Fe(F_3COCHCOCF_3)_3$	5	100	60	43
17[d]	$Fe(F_3COCHCOCF_3)_3$	30	100	40	60
18[d]	$Fe(acac)_3$	30	100	40	40
19[d]	$Fe(OCOCH_3)_3$	30	100	40	10
20[d]	FeF_3	30	100	40	11
21[d]	$FeCl_3$	30	100	40	27
22[d]	$FeBr_3$	30	100	40	77
23[d]	$AlCl_3$	30	100	40	53
24[d]	$BF_3{\bullet}Et_2O$	30	100	40	trace
25[d]	$FeCl_2$	30	100	40	49
26[d]	$FeBr_2$	30	100	40	>95
27[d]	$FeBr_2$	30	30	40	62
28[d]	$FeBr_2$	30	150	40	>95[g]
29[d]	$FeBr_2$	10	150	40	55
30[d]	$FeBr_2$	100	150	40	91

[a] as determined using ^{1}H NMR spectroscopy. [b] xylenes was employed as solvent (0.2 M) and after 2 h. [c] Reaction performed in PhMe. [d] Reaction performed in CH_2Cl_2. [e] Salen = (1*S*,2*S*)-*N,N'*-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-1,2-diphenylethylenediamine. [f] COD = 1,5-cyclooctadiene. [g] Isolated yield after chromatography on SiO_2 was 91%.

B. Examination of concentration

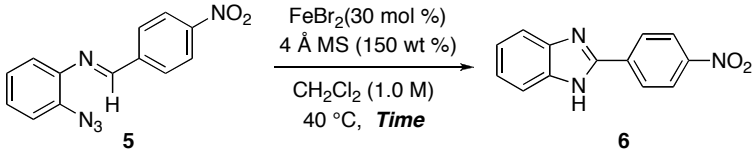


5 **6**

0.5 M >95%
1.0 M >95%

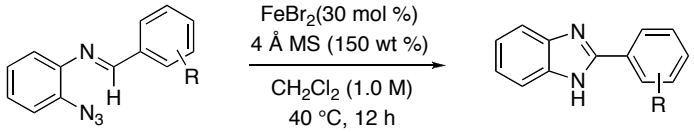
as determined by ^{1}H NMR spectroscopy

C. Examination of reaction time



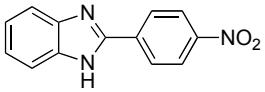
8h 89%
12h >95%
as determined by ^{1}H NMR spectroscopy

D. Optimized general procedure



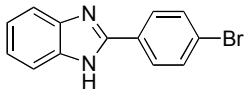
To a mixture of 0.080 g of 2-azidoarylimine, $FeBr_2$ (30 mol %) and 0.120 g of crushed 4Å molecular sieves (150 wt %) was added CH_2Cl_2 to make a 1.0 M solution. The resulting mixture was heated to 40 °C. After 12 h, the reaction mixture was cooled to room temperature, and the heterogenous mixture was filtered through SiO_2. The filtrate was concentrated *in vacuo*. Purification using MPLC (0:100 – 2:98 MeOH:CH_2Cl_2) provided the benzimidazole as a solid.

E. Benzimidazole synthesis from 2-azidoarylimine



6

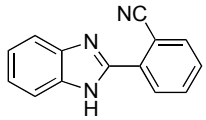
Benzimidazole (6).[7] The general procedure was followed with 0.080 g of azide **5** (0.299 mmol), 0.019 g of $FeBr_2$ (0.090 mmol), and 0.120 g of crushed 4Å molecular sieves in 0.30 mL of CH_2Cl_2. Purification by MPLC (0:100 – 2:98 MeOH:CH_2Cl_2) afforded benzimidazole **6** as an orange solid (0.066 g, 93%): R_f = 0.5 (9:91 MeOH:CH_2Cl_2); mp 321–322 °C. The spectral data matched that reported by Bellona and co-workers:[7] ^{1}H NMR (DMSO-d_6, 500 MHz): δ 13.27 (br s, 1H), 8.36–8.41 (m, 4H), 7.70 (br s, 1H), 7.57 (br s, 1H), 7.24 (br s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 149.5, 148.2, 144.3, 136.5, 135.7, 127.8, 124.8, 124.0, 122.8, 119.9, 112.3; IR (thin film): 3421, 3296, 1587, 1512, 1338, 852, 744, 708 cm^{-1}.



9b

Benzimidazole (9b).[8] The general procedure was followed with 0.080 g of azide **8b** (0.266 mmol), 0.017 g of $FeBr_2$ (0.080 mmol), and 0.120 g of crushed 4Å molecular sieves in 0.27 mL of CH_2Cl_2. Purification by MPLC (0:100 – 3:97 MeOH:CH_2Cl_2) afforded benzimidazole **9b** as a light yellow solid (0.072 g, 99%): R_f = 0.4 (9:91 MeOH:CH_2Cl_2); mp 298–299 °C. The spectral data matched that reported by Itoh and co-workers:[8] ^{1}H NMR

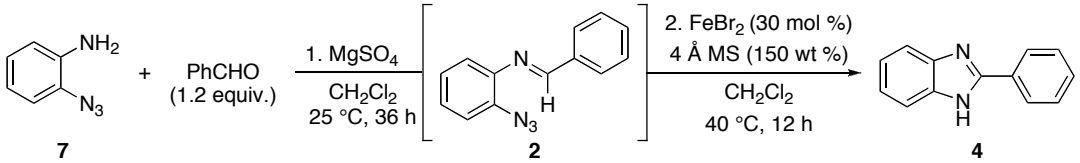
(DMSO-d_6, 500 MHz): δ 12.97 (br s, 1H), 8.10 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H), 7.60 (br s, 2H), 7.20 (br s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 150.7, 144.2, 135.5, 132.4, 129.9, 128.8, 123.7, 123.3, 122.3, 119.4, 111.9; IR (thin film): 3466, 3396, 1639, 1594, 1312, 1274, 1084, 764 cm^{-1}.



9j

Benzimidazole (9j). The general procedure was followed with 0.080 g of azide **8j** (0.323 mmol), 0.021 g of $FeBr_2$ (0.097 mmol), and 0.120 g of crushed 4Å molecular sieves in 0.32 mL of CH_2Cl_2. Purification by MPLC (0:100 – 2:98 MeOH:CH_2Cl_2) afforded benzimidazole **9j** as a light yellow solid (0.065 g, 92%): R_f = 0.6 (9:91 MeOH:CH_2Cl_2); mp 252–253 °C; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 13.09 (s, 1H), 8.07 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 7.5 Hz, 1H), 7.87 (t, J = 7.5 Hz, 1H), 7.73 (d, J = 7.5 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.24–7.28 (m, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 148.9, 144.0, 135.7, 135.3, 133.8, 133.1, 130.6, 129.7, 123.9, 122.6, 120.0, 118.7, 112.2, 110.6; IR (thin film): 3400, 3368, 1453, 1400, 1283, 1136, 970, 746 cm^{-1}; HRMS (EI) m / z calcd for $C_{14}H_9N_3$ $(M)^+$ 219.0796, found 219.0796.

F. Optimized two step typical procedure



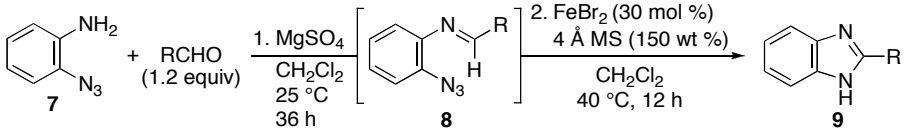
7 **2** **4**

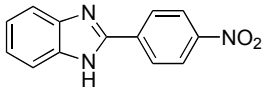
Step 1: To a solution of 0.067 g of 2-azidoaniline **7** (0.50 mmol) and 0.056 mL of benzaldehyde (0.60 mmol) in 0.5 mL of CH_2Cl_2 was added 0.20 g of anhydrous $MgSO_4$. The mixture was stirred at room temperature. After 36 h, the heterogeneous mixture was filtered. The filtrate was concentrated *in vacuo*. The resulting mixture was dissolved in 0.6 mL of $CDCl_3$ and 0.007 mL of dibromomethane (0.10 mmol) was added. The area of N=CH peak in 2-azidoarylimine **2** was compared with the area of the peak of dibromomethane to derive a ^{1}H NMR yield: 93%. The solution was concentrated *in vacuo* once more to afford crude 2-azidoarylimine **2**.

Step 2: To the unpurified product **2**, 0.032 g of $FeBr_2$ (0.15 mmol), 0.167 g of crushed 4Å molecular sieves, and 0.50 mL of CH_2Cl_2 was added. The resulting mixture was heated to 40 °C. After 12 h, the reaction mixture was cooled to room temperature, and the heterogenous mixture was filtered through SiO_2. The filtrate was concentrated *in vacuo*. Purification by MPLC (0:100 – 2:98 MeOH:CH_2Cl_2) provided the benzimidazole **4**[9] as a white solid (0.084 g, 86%): R_f = 0.5 (7:93 MeOH:CH_2Cl_2); mp 299–300 °C. The spectral data matched that reported by Sezen and co-workers:[9] ^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.91 (br s, 1H), 8.17 (d, J = 8.0 Hz, 2H), 7.46–7.58 (m, 5H), 7.18–7.19 (m, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 151.8, 144.4, 135.5, 130.7, 130.3, 129.4, 127.0, 123.0, 122.2, 119.4, 111.8; IR (thin film): 3047, 2966, 1462, 1411, 1276, 970, 744, 703 cm^{-1}.

Note: (a) When 1.0 equiv of benzaldehyde was employed, ^{1}H NMR yield of step 1 was 81% and the yield of two steps was only 72%; (b) Without filtration in step 1, the yield of two steps was only 76%.

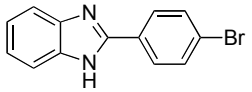
G. Benzimidazole synthesis from 2-azidoaniline 7 (two step procedure)





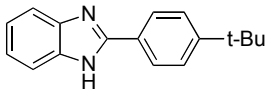
9a

Benzimidazole (9a). The typical procedure was followed with 0.067 g of 2-azidoaniline **7** (0.50 mmol), 0.091 g of 4-nitrobenzaldehyde (0.6 mmol), and 0.20 g of anhydrous $MgSO_4$ in 0.5 mL of CH_2Cl_2 to afford **8a** (>95% as determined by ^{1}H NMR spectroscopy). 0.032 g of $FeBr_2$ (0.15 mmol) and 0.200 g of crushed 4Å molecular sieves in 0.50 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 2:98 MeOH:CH_2Cl_2) afforded benzimidazole **9a** as an orange solid (0.111 g, 93%).



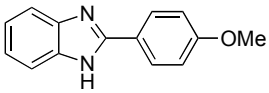
9b

Benzimidazole (9b). The typical procedure was followed with 0.067 g of 2-azidoaniline **7** (0.50 mmol), 0.111 g of 4-bromobenzaldehyde (0.6 mmol), and 0.20 g of anhydrous $MgSO_4$ in 0.5 mL of CH_2Cl_2 to afford **8b** (95% as determined by ^{1}H NMR spectroscopy. 0.032 g of $FeBr_2$ (0.15 mmol) and 0.226 g of crushed 4Å molecular sieves in 0.50 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 3:97 MeOH:CH_2Cl_2) afforded benzimidazole **9b** as a light yellow solid (0.128 g, 94%).



9c

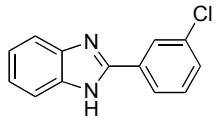
Benzimidazole (9c). The typical procedure was followed with 0.067 g of 2-azidoaniline **7** (0.50 mmol), 0.100 mL of 4-*tert*-butylbenzaldehyde (0.6 mmol), and 0.20 g of anhydrous $MgSO_4$ in 0.5 mL of CH_2Cl_2 to afford **8c** (89% as determined by ^{1}H NMR spectroscopy). 0.032 g of $FeBr_2$ (0.15 mmol), and 0.209 g of crushed 4Å molecular sieves in 0.50 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 1:99 MeOH:CH_2Cl_2) afforded benzimidazole **9c** as a white solid (0.061 g, 49%): R_f = 0.7 (6:94 MeOH:CH_2Cl_2); mp 250–251 °C; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.85 (br s, 1H), 8.10 (d, J = 4.5 Hz, 2H), 7.53–7.56 (m, 4H), 7.17 (br s, 2H), 1.29 (s, 9H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 153.0 (2C), 151.8 (2C), 127.9, 126.7, 126.2, 122.4 (4C), 35.0, 31.4; IR (thin film): 3560, 2962, 1724, 1589, 1450, 1427, 970, 740 cm^{-1}; HRMS (EI) m / z calcd for $C_{17}H_{18}N_2$ $(M)^+$ 250.1470, found 250.1469.



9d

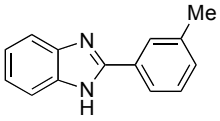
Benzimidazole (9d).[10] The typical procedure was followed with 0.067 g of 2-azidoaniline **7** (0.50 mmol), 0.073 mL of 4-methoxybenzaldehyde (0.6 mmol), and 0.20 g of anhydrous $MgSO_4$ in 0.5 mL of CH_2Cl_2 to afford **8d** (80% as determined by ^{1}H NMR spectroscopy). 0.032 g of $FeBr_2$ (0.15 mmol), and 0.189 g of crushed 4Å molecular sieves in 0.50 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 1:99 MeOH:CH_2Cl_2) afforded benzimidazole **9d** as a white solid (0.041 g, 36%): R_f = 0.7 (5:95 MeOH:CH_2Cl_2);

mp 224–225 °C. The spectral data matched that reported by Bellina and co-workers:[10] ^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.74 (s, 1H), 8.10–8.12 (m, 2H), 7.60 (d, J = 7.0 Hz, 1H), 7.48 (d, J = 7.0 Hz, 1H), 7.13–7.18 (m, 2H), 7.09 (d, J = 9.0 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 161.1, 151.8, 144.4, 135.4, 128.5, 123.2, 122.5, 121.9, 119.0, 114.8, 112.5, 55.8; IR (thin film): 3674, 3345, 1652, 1558, 1419, 1180, 808, 742 cm^{-1}.



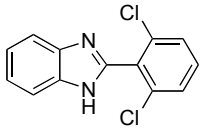
9e

Benzimidazole (9e). The typical procedure was followed with 0.067 g of 2-azidoaniline **7** (0.50 mmol), 0.068 mL of 3-chlorobenzaldehyde (0.6 mmol), and 0.20 g of anhydrous $MgSO_4$ in 0.5 mL of CH_2Cl_2 to afford **8e** (>95% as determined using ^{1}H NMR spectroscopy). 0.032 g of $FeBr_2$ (0.15 mmol), and 0.192 g of crushed 4Å molecular sieves in 0.50 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 3:97 MeOH:CH_2Cl_2) afforded benzimidazole **9e** as a light yellow solid (0.093 g, 81%): R_f = 0.5 (5:95 MeOH:CH_2Cl_2); mp 232–233 °C; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 13.04 (br s, 1H), 8.23 (s, 1H), 8.14 (d, J = 7.5 Hz, 1H), 7.61 (br s, 2H), 7.48–7.57 (m, 2H), 7.20–7.22 (m, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 150.2 (3C), 134.3, 132.7, 131.4, 130.0, 126.5, 125.5, 122.9 (4C); IR (thin film): 3610, 1558, 1442, 1402, 1228, 1124, 893, 744 cm^{-1}; HRMS (EI) m / z calcd for $C_{13}H_9N_2Cl$ $(M)^+$ 228.0454, found 228.0453.



9f

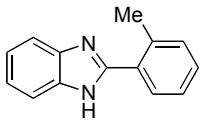
Benzimidazole (9f).[11] The typical procedure was followed with 0.067 g of 2-azidoaniline **7** (0.50 mmol), 0.070 mL of 3-methylbenzaldehyde (0.6 mmol) and 0.20 g of anhydrous $MgSO_4$ in 0.5 mL of CH_2Cl_2 to afford **8f** (94% as determined using ^{1}H NMR spectroscopy). 0.032 g of $FeBr_2$ (0.15 mmol) and 0.177 g of crushed 4Å molecular sieves in 0.50 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 1:99 MeOH:CH_2Cl_2) afforded benzimidazole **9f** as a white solid (0.064 g, 61%): R_f = 0.6 (6:94 MeOH:CH_2Cl_2); mp 219–220 °C. The spectral data matched that reported by Lewis and co-workers:[11] ^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.89 (br s, 1H), 8.03 (s, 1H), 7.97 (d, J = 7.5 Hz, 1H), 7.59 (br s, 2H), 7.41 (t, J = 7.8 Hz, 1H), 7.27 (d, J = 7.0 Hz, 1H), 7.18–7.19 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 151.8 (2C), 138.6 (2C), 130.9, 130.6, 129.3, 127.5, 124.1, 122.5 (4C), 21.5; IR (thin film): 3442, 2873, 1402, 1357, 1274, 1228, 1110, 740 cm^{-1}.



9g

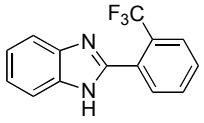
Benzimidazole (9g). The typical procedure was followed with 0.067 g of 2-azidoaniline **7** (0.50 mmol), 0.105 g of 2,6-dichlorobenzaldehyde (0.6 mmol), and 0.20 g of anhydrous $MgSO_4$ in 0.5 mL of CH_2Cl_2 to afford **8g** (>95% as determined using ^{1}H NMR spectroscopy). 0.032 g of $FeBr_2$ (0.15 mmol) and 0.218 g of crushed 4Å molecular sieves in 0.50 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 3:97 MeOH:CH_2Cl_2) afforded benzimidazole **9g** as a white solid (0.129 g, 98%): R_f = 0.5 (7:93 MeOH:CH_2Cl_2); mp 275–276 °C; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.90 (br s, 1H), 7.55–7.70 (m, 5H), 7.23 (br s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 147.2, 143.7, 135.6, 134.6, 132.8, 131.1, 128.8, 123.2, 122.1, 119.8, 112.1; IR (thin

film): 3428, 3297, 1587, 1481, 1410, 1265, 1132, 735 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{13}H_8N_2Cl_2$ $(M)^+$ 262.0065, found 262.0067.



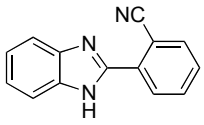
9h

Benzimidazole (9h).[12] The typical procedure was followed with 0.067 g of 2-azidoaniline **7** (0.50 mmol), 0.070 mL of 2-methylbenzaldehyde (0.6 mmol) and 0.20 g of anhydrous $MgSO_4$ in 0.5 mL of CH_2Cl_2 to afford **8h** (90% as determined using ^1H NMR spectroscopy). 0.032 g of $FeBr_2$ (0.15 mmol) and 0.177 g of crushed 4Å molecular sieves in 0.50 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 1:99 MeOH:CH_2Cl_2) afforded benzimidazole **9h** as a white solid (0.068 g, 65%): R_f = 0.6 (8:92 MeOH:CH_2Cl_2); mp 213–214 °C. The spectral data matched that reported by Du and co-workers:[12] ^1H NMR (DMSO-d_6, 500 MHz): δ 12.63 (br s, 1H), 7.73 (d, *J* = 7.0 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 7.0 Hz, 1H), 7.17–7.21 (m, 3H), 7.17–7.21 (m, 2H), 2.60 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 152.4, 144.2, 137.5, 134.9, 131.7, 130.6, 129.9, 129.8, 126.4, 122.8, 121.9, 119.4, 111.7, 21.5; IR (thin film): 3544, 1724, 1612, 1442, 1407, 1273, 958, 744 cm^{-1}.



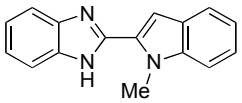
9i

Benzimidazole (9i). The typical procedure was followed with 0.067 g of 2-azidoaniline **7** (0.50 mmol), 0.079 mL of 2-trifluoromethylbenzaldehyde (0.6 mmol), and 0.20 g of anhydrous $MgSO_4$ in 0.5 mL of CH_2Cl_2 to afford **8i** (92% as determined using ^1H NMR spectroscopy). 0.032 g of $FeBr_2$ (0.15 mmol) and 0.218 g of crushed 4Å molecular sieves in 0.50 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 3:97 MeOH:CH_2Cl_2) afforded benzimidazole **9i** as a white solid (0.121 g, 92%): R_f = 0.5 (8:92 MeOH:CH_2Cl_2); mp 273–274 °C; ^1H NMR (DMSO-d_6, 500 MHz): δ 12.77 (s, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.45–7.83 (m, 3H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.20–7.25 (m, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 149.8, 143.9, 135.0, 132.8, 132.7, 130.8, 130.7, 128.3 (q, J_{CF} = 30.0 Hz), 127.1 (d, J_{CF} = 7.5 Hz), 124.2 (q, J_{CF} = 265.0 Hz), 123.2, 122.1, 119.6, 112.0; IR (thin film): 2920, 2850, 1493, 1408, 1311, 1121, 1034, 746 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{14}H_9N_2F_3$ $(M)^+$ 262.0718, found 262.0720.



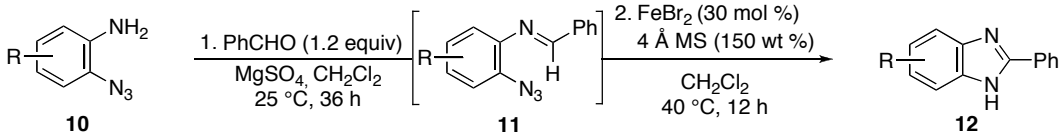
9j

Benzimidazole (9j). The typical procedure was followed with 0.067 g of 2-azidoaniline **7** (0.50 mmol), 0.079 g of 2-cyanobenzaldehyde (0.6 mmol), and 0.20 g of anhydrous $MgSO_4$ in 0.5 mL of CH_2Cl_2 to afford **8j** (>95% as determined using ^1H NMR spectroscopy). 0.032 g of $FeBr_2$ (0.15 mmol) and 0.185 g of crushed 4Å molecular sieves in 0.50 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 2:98 MeOH:CH_2Cl_2) afforded benzimidazole **9j** as a light yellow solid (0.099 g, 90%).

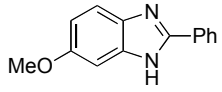


9k

Benzimidazole (9k). The typical procedure was followed with 0.067 g of 2-azidoaniline **7** (0.50 mmol), 0.096 g of 1-methylindole-2-carboxaldehyde (0.6 mmol), and 0.20 g of anhydrous $MgSO_4$ in 0.5 mL of CH_2Cl_2 to afford **8k** (78% as determined using ^{1}H NMR spectroscopy). 0.032 g of $FeBr_2$ (0.15 mmol) and 0.206 g of crushed 4Å molecular sieves in 0.50 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 1:99 MeOH:CH_2Cl_2) afforded benzimidazole **9k** as a white solid (0.051 g, 41%): R_f = 0.7 (8:92 MeOH:CH_2Cl_2); mp 202–203 °C; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.92 (s, 1H), 7.72 (d, J = 7.0 Hz, 1H), 7.66 (d, J = 7.0 Hz, 1H), 7.54 (d, J = 7.0 Hz, 2H), 7.20–7.27 (m, 4H), 7.10–7.12 (m, 1H), 4.30 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 146.3, 144.2, 139.3, 134.6, 129.9, 127.2, 123.5, 123.4, 122.2, 121.4, 120.6, 119.4, 111.5, 110.8, 104.0, 32.5; IR (thin film): 3027, 2809, 1576, 1402, 1337, 1287, 973, 741 cm^{-1}; HRMS (EI) m / z calcd for $C_{16}H_{13}N_3$ $(M)^+$ 247.1110, found 247.1106.

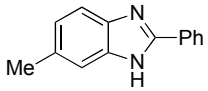


10 **11** **12**



12a

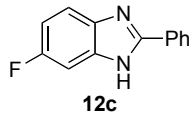
Benzimidazole (12a). The typical procedure was followed with 0.164 g of 2-azido-4-methoxyaniline **10a** (1.00 mmol), 0.121 mL of benzaldehyde (1.20 mmol), and 0.40 g of anhydrous $MgSO_4$ in 1.0 mL of CH_2Cl_2 to afford **11a** [66% as determined using ^{1}H NMR spectroscopy; 0.070 mL of dibromomethane (1.0 mmol) was used]. 0.065 g of $FeBr_2$ (0.30 mmol) and 0.378 g of crushed 4Å molecular sieves in 1.0 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 2:98 MeOH:CH_2Cl_2) afforded benzimidazole **12a** as a white solid (0.126 g, 56%): R_f = 0.7 (2:98 MeOH:CH_2Cl_2); mp 149–150 °C; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.76 (br s, 1H), 8.13 (d, J = 6.5 Hz, 2H), 7.43–7.50 (m, 4H), 7.04 (br s, 1H), 6.82 (d, J = 6.5 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 156.3, 151.0 (3C), 130.8, 130.0, 129.4 (2C), 126.6 (2C), 111.8 (3C), 55.9; IR (thin film): 3055, 2931, 1630, 1456, 1404, 1269, 1159, 702 cm^{-1}; HRMS (EI) m / z calcd for $C_{14}H_{12}ON_2$ $(M)^+$ 224.0950, found 224.0949.



12b

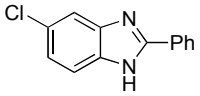
Benzimidazole (12b).[13] The typical procedure was followed with 0.148 g of 2-azido-4-methylaniline **10b** (1.00 mmol), 0.121 mL of benzaldehyde (1.20 mmol), and 0.40 g of anhydrous $MgSO_4$ in 1.0 mL of CH_2Cl_2 to afford **11b** (92% as determined using ^{1}H NMR spectroscopy; 0.070 mL of dibromomethane (1.0 mmol) was used). 0.065 g of $FeBr_2$ (0.30 mmol) and 0.354 g of crushed 4Å molecular sieves in 1.0 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 1:99 MeOH:CH_2Cl_2) afforded benzimidazole **12b** as a white solid (0.156 g, 75%). Alternatively, the typical procedure was followed with 0.148 g of 2-azido-5-methylaniline **10e** (1.00 mmol), 0.121 mL of benzaldehyde (1.20 mmol) and 0.40 g of anhydrous $MgSO_4$ in 1.0 mL of CH_2Cl_2 to afford **11e** [>95% as determined using ^{1}H NMR spectroscopy; 0.070 mL of dibromomethane (1.0 mmol) was used]. 0.065 g of $FeBr_2$ (0.30 mmol) and 0.354 g of crushed 4Å molecular sieves in 1.0 mL of CH_2Cl_2 were

used in next step. Purification by MPLC (0:100 – 1:99 MeOH:CH_2Cl_2) afforded benzimidazole **12b** as a white solid (0.187 g, 90%): R_f = 0.6 (2:98 MeOH:CH_2Cl_2); mp 243–244 °C. The spectral data matched that reported by Wang and co-workers:[13] ^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.80 (br s, 1H), 8.18 (d, *J* = 6.5 Hz, 2H), 7.39–7.51 (m, 5H), 7.00 (d, *J* = 7.0 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 151.4, 131.8 (3C), 130.8, 130.1, 129.4 (2C), 126.8 (2C), 124.0 (3C), 21.8; IR (thin film): 3265, 1743, 1587, 1442, 1265, 1111, 968, 748 cm^{-1}.



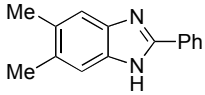
12c

Benzimidazole (12c). The typical procedure was followed with 0.172 g of 2-azido-4-fluoroaniline **10c** (1.13 mmol), 0.137 mL of benzaldehyde (1.36 mmol) and 0.45 g of anhydrous $MgSO_4$ in 1.1 mL of CH_2Cl_2 to afford **11c** [94% as determined using ^{1}H NMR spectroscopy; 0.070 mL of dibromomethane (1.0 mmol) was used]. 0.073 g of $FeBr_2$ (0.30 mmol) and 0.407 g of crushed 4Å molecular sieves in 1.1 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 2:98 MeOH:CH_2Cl_2) afforded benzimidazole **12c** as a white solid (0.114 g, 54%): R_f = 0.6 (2:98 MeOH:CH_2Cl_2); mp 242–243 °C; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 13.06 (br s, 1H), 8.18 (d, *J* = 7.5 Hz, 2H), 7.45–7.53 (m, 5H), 7.05 (br s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 159.2 (d, J_{CF} = 237.5 Hz), 153.2 (d, J_{CF} = 42.5 Hz), 153.0 (2C), 130.4 (2C), 129.4 (2C), 126.9 (2C), 110.9 (3C); IR (thin film): 3543, 1587, 1408, 1254, 1144, 1103, 837, 739 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{13}H_9N_2F$ $(M)^+$ 212.0750, found 212.0754.



12d

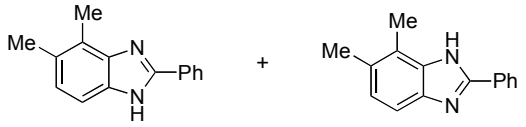
Benzimidazole (12d).[14] The typical procedure was followed with 0.168 g of 2-azido-5-chloroaniline **10d** (1.00 mmol), 0.121 mL of benzaldehyde (1.20 mmol), and 0.40 g of anhydrous $MgSO_4$ in 1.0 mL of CH_2Cl_2 to afford **11d** [84% as determined using ^{1}H NMR spectroscopy; 0.070 mL of dibromomethane (1.0 mmol) was used]. 0.065 g of $FeBr_2$ (0.30 mmol) and 0.385 g of crushed 4Å molecular sieves in 1.0 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 2:98 MeOH:CH_2Cl_2) afforded benzimidazole **12d** as a light yellow solid (0.188 g, 82%): R_f = 0.6 (3:97 MeOH:CH_2Cl_2); mp 212–213 °C. The spectral data matched that reported by Perry and co-workers:[14] ^{1}H NMR (DMSO-d_6, 500 MHz): δ 13.09 (br s, 1H), 8.17 (d, *J* = 7.5 Hz, 2H), 7.47–7.59 (m, 5H), 7.20 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 153.1 (4C), 130.6, 130.2, 129.5 (2C), 127.1 (2C), 122.8 (3C); IR (thin film): 3579, 2916, 1583, 1429, 1274, 1103, 806, 690 cm^{-1}.



12e

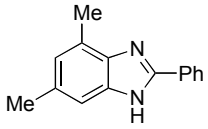
Benzimidazole (12e).[13] The typical procedure was followed with 0.162 g of 2-azido-4,5-dimethylaniline **10f** (1.00 mmol), 0.121 mL of benzaldehyde (1.20 mmol), and 0.40 g of anhydrous $MgSO_4$ in 1.0 mL of CH_2Cl_2 to afford **11f** [>95% as determined using ^{1}H NMR spectroccopy; 0.070 mL of dibromomethane (1.0 mmol) was used). 0.065 g of $FeBr_2$ (0.30 mmol) and 0.375 g of crushed 4Å molecular sieves in 1.0 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 2:98 MeOH:CH_2Cl_2) afforded benzimidazole **12e** as a pale white solid (0.205 g, 92%): R_f = 0.6 (8:92 MeOH:CH_2Cl_2); mp 253–254 °C. The spectral data matched that reported by Perry and co-workers:[13] ^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.66 (s, 1H), 8.15 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.29 (br s, 1H), 2.30 (s, 6H); ^{13}C NMR (DMSO-d_6, 125

MHz): δ 150.8, 143.0, 134.0, 131.6, 131.0, 130.4, 129.9, 129.3, 126.7, 119.4, 111.8, 20.5 (2C); IR (thin film): 3362, 1584, 1446, 1398, 1286, 1115, 968, 851 cm^{-1}.



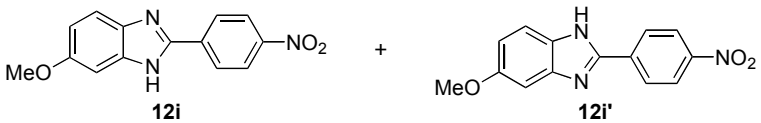
12g **12g'**

Benzimidazole (12g). The typical procedure was optimized using 0.111 g of 6-azido-2,3-dimethylaniline **10h** (0.68 mmol), 0.34 mL of benzaldehyde (3.42 mmol), and 0.27 g of anhydrous $MgSO_4$ in 0.50 mL of CH_2Cl_2. After the reaction, excessive benzaldehyde was removed under reduced pressure (~1 mm Hg) to afford **11g** (% as determined using ^1H NMR spectroscopy; 0.070 mL of dibromomethane (1.0 mmol) was used. Without excess benzaldehyde, the yield of this step was only 29%. 0.044 g of $FeBr_2$ (0.20 mmol) and 0.257 g of crushed 4Å molecular sieves in 0.68 mL of CH_2Cl_2 were used in the next step. Purification by MPLC (0:100 – 2:98 MeOH:CH_2Cl_2) afforded benzimidazole **12g**, an inseparable mixture of tautomers (ratio: 48:52), as a white solid (0.092 g, 60%): R_f = 0.7 (8:92 MeOH:CH_2Cl_2); mp 200–201 °C. One isomer: ^1H NMR (DMSO-d_6, 500 MHz): δ 12.69 (br s, 1H), 8.19 (br s, 2H), 7.52 (t, J = 7.5 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.23 (br s, 1H), 6.98 (d, J = 8.0 Hz, 1H), 2.48 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 150.8, 142.1 (4C), 131.0, 130.0 (2C), 129.3 (2C), 126.9, 125.0, 116.1, 19.5, 13.7. The other isomer: ^1H NMR (DMSO-d_6, 500 MHz): δ 12.35 (br s, 1H), 8.19 (br s, 2H), 7.52 (t, J = 7.5 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.33 (br s, 1H), 6.98 (d, J = 8.0 Hz, 1H), 2.48 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 150.7, 144.5 (4C), 131.0, 130.0 (2C), 129.3 (2C), 126.9, 124.7, 108.3, 19.5, 14.5. IR (thin film): 3056, 2918, 1706, 1457, 1362, 1311, 1226, 694 cm^{-1}; HRMS (EI) m / z calcd for $C_{15}H_{14}N_2$ $(M)^+$ 222.1157, found 222.1158.



12h

Benzimidazole (12h). The optimized two step typical procedure was followed with 0.162 g of 2-azido-4,6-dimethylaniline **10i** (1.00 mmol), 0.121 mL of benzaldehyde (1.20 mmol), and 0.40 g of anhydrous $MgSO_4$ in 1.0 mL of CH_2Cl_2 to afford **11h** [91% as determined using ^1H NMR spectroscopy; 0.070 mL of dibromomethane (1.0 mmol) was used). 0.065 g of $FeBr_2$ (0.30 mmol) and 0.375 g of crushed 4Å molecular sieves in 1.0 mL of CH_2Cl_2 were used in next step. Purification by MPLC (0:100 – 2:98 MeOH:CH_2Cl_2) afforded benzimidazole **12h** as a white solid (0.146 g, 66%): R_f = 0.5 (6:94 MeOH:CH_2Cl_2); mp 187–188 °C; ^1H NMR (DMSO-d_6, 500 MHz): δ 12.65 (br s, 1H), 8.21 (d, J = 7.5 Hz, 2H), 7.52 (t, J = 7.5 Hz, 2H), 7.44 (t, J = 7.0 Hz, 1H), 7.19 (br s, 1H), 6.79 (s, 1H), 2.53 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 150.8, 131.7 (4C), 131.0, 129.9, 129.3 (2C), 126.9 (2C), 124.5 (2C), 21.8, 17.3; IR (thin film): 2972, 2918, 1705, 1455, 1406, 1221, 840, 694 cm^{-1}; HRMS (EI) m / z calcd for $C_{15}H_{14}N_2$ $(M)^+$ 222.1157, found 222.1155.

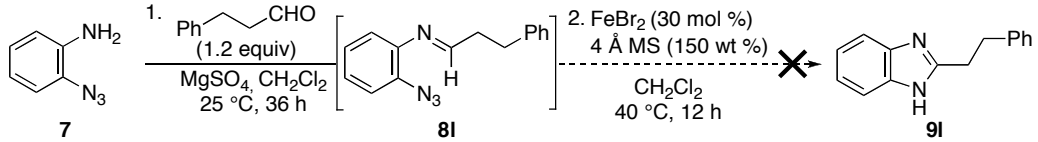


12i **12i'**

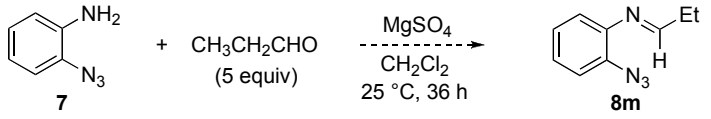
Benzimidazole (12i). The typical procedure was followed with 0.164 g of 2-azido-4-methoxyaniline **10a** (1.00 mmol), 0.183 g of 4-nitrobenzaldehyde (1.20 mmol) and 0.40 g of anhydrous $MgSO_4$ in 1.0 mL of CH_2Cl_2 10 afford **11i** [>95% as determined using ^1H NMR spectroscopy; 0.070 mL of dibromomethane (1.0 mmol) was used]. 0.065 g of $FeBr_2$ (0.30 mmol) and 0.444 g of crushed 4Å molecular sieves in 1.0 mL of CH_2Cl_2 were

used in the next step. Purification by MPLC (0:100 – 2:98 MeOH:CH_2Cl_2) afforded benzimidazole **12i**, an inseparable mixture of tautomers (ratio: 35/65), as an orange solid (0.266 g, 99%): R_f = 0.4 (8:92 MeOH:CH_2Cl_2); mp 245–246 °C. Major isomer: ^{1}H NMR (DMSO-d_6, 500 MHz): δ 13.05 (br s, 1H), 8.30 (s, 4H), 7.56 (br s, 1H), 6.97 (br s, 1H), 6.84 (br s, 1H), 3.79 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 157.3, 148.5, 147.8, 138.9 (2C), 136.6, 127.2 (2C), 124.6 (2C), 120.5, 112.8, 94.7, 55.9. Minor isomer: ^{1}H NMR (DMSO-d_6, 500 MHz): δ 13.10 (br s, 1H), 8.30 (s, 4H), 7.42 (br s, 1H), 7.20 (br s, 1H), 6.84 (br s, 1H), 3.79 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 156.3, 149.5, 145.2, 136.4, 130.2 (2C), 127.4 (2C), 124.6 (2C), 114.3, 112.6, 101.7, 55.9. IR (thin film): 3534, 1597, 1512, 1423, 1342, 1254, 856, 811 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{14}H_{11}O_3N_3$ $(M)^+$ 269.0800, found 269.0797.

H. Reactivity of alkyl aldehydes with 2-azidoaniline 7



The typical two-step procedure was followed with 0.067 g of 2-azidoaniline **7** (0.50 mmol), 0.081 mL of hydrocinnamaldehyde (0.6 mmol), and 0.20 g of anhydrous $MgSO_4$ in 0.5 mL of CH_2Cl_2 to afford **8l** (24% as determined by ^{1}H NMR spectroscopy). 0.032 g of $FeBr_2$ (0.15 mmol) and 0.209 g of crushed 4Å molecular sieves in 0.50 mL of CH_2Cl_2 were used in the next step. The ^{1}H NMR spectroscopy of crude product did not reveal any characteristic benzimidazole peaks.

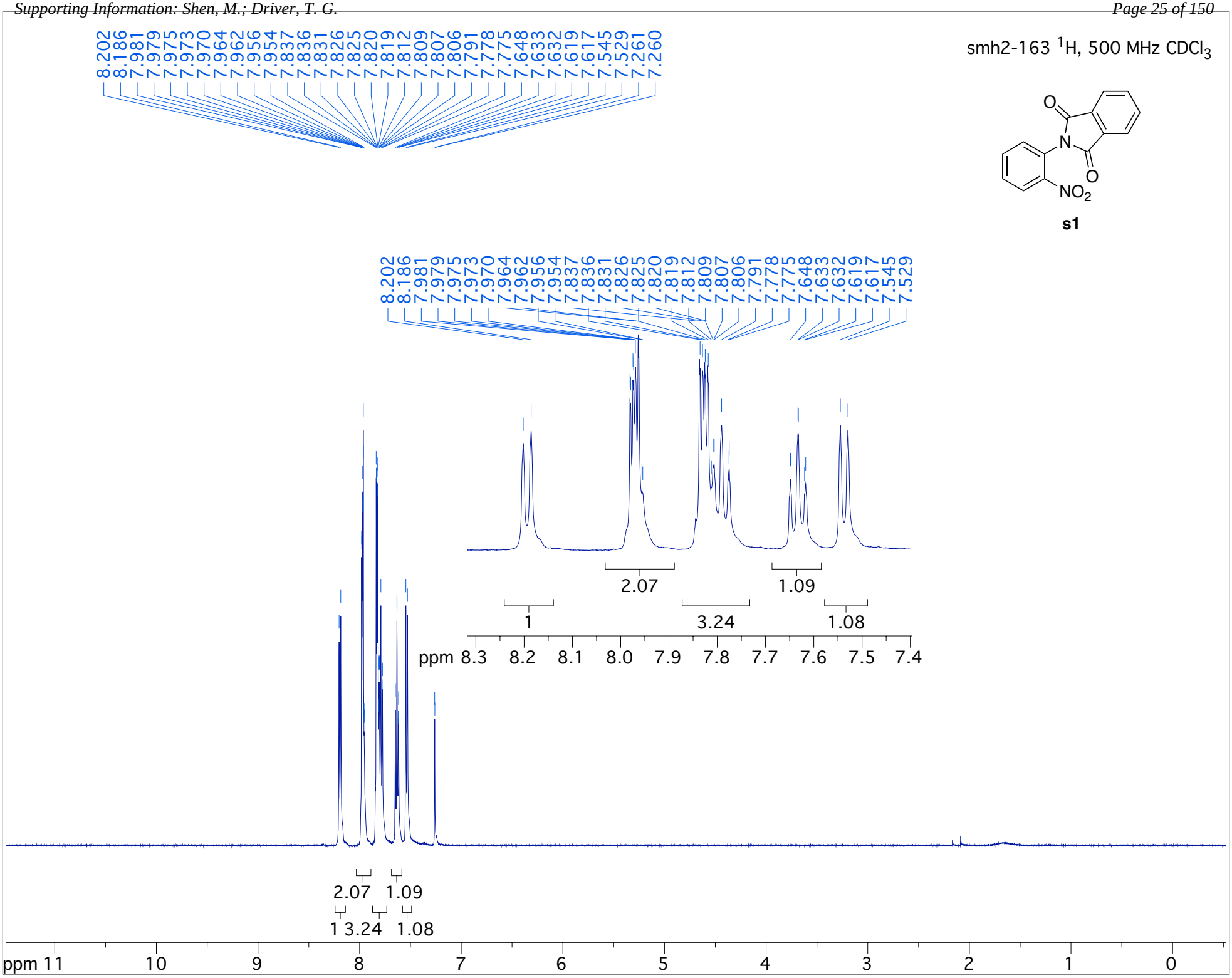


<10%
as determined by ^{1}H NMR spectroscopy

The optimized, typical step 1 condensation procedure was followed with 0.067 g of 2-azidoaniline **7** (0.50 mmol), 0.018 mL of propionaldehyde (2.5 mmol), and 0.20 g of anhydrous $MgSO_4$ in 0.5 mL of CH_2Cl_2. ^{1}H NMR spectroscopy of the crude reaction mixture revealed a complex mixture of products consisting of less than 10% of **8m**. Further optimization was not performed.

IV. References

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520
[2] Hall, J. H.; Patterson, E. *J. Am. Chem. Soc.* **1967**, *89*, 5856-5861.
[3] Cul, A.; Daich, A.; Decroix, B.; Sanz, G.; Hijfte, L. V. *Tetrahedron* **2004**, *60*, 11029-11040.
[4] Alkhathlan, H. A.; Al-Lohedan, H. A. *Phosphorous, Sulfur Silicon Relat. Elem.* **1991**, *61*, 367-372.
[5] Novak, M; Kahley, M. J.; Lin, J.; Kennedy, S. A.; James, T. G. *J. Org. Chem.* **1995**, *60*, 8294-8304.
[6] Goddard-Borger, E. D.; Stick, R. V. *Org. Lett.* **2007**, *9*, 3797-3800.
[7] Bellona, F.; Calandri, C.; Cauteruccio, S.; Rossi, R. *Tetrahedron* **2007**, *63*, 1970-1980.
[8] Itoh, T; Nagata, K.; Ishikawa, H.; Ohsawa, A. *Heterocycles* **2004**, *63*, 2769-2784.
[9] Sezen, B; Sames, D. *J. Am. Chem. Soc.* **2003**, *125*, 5274-5275.
[10] Bellina, F.; Cauteruccio, S.; Rossi, R. *Eur. J. Org. Chem.* **2006**, *6*, 1379-1382.
[11] Lewis, J.; Jessica Y., W.; Robert, G., B.; Jonathan A., E. *Angew. Chem., Int. Ed.* **2006**, *118*, 1619-1621.
[12] Du, L.-H.; Wang, Y.-G. *Synthesis* **2007**, *5*, 675-678.
[13] Wang, Y.; Sarris, K.; Sauer, D. R.; Djuric, S. W. *Tetrahedron Lett.* **2006**, *47*, 4823-4826.
[14] Perry, R.; Wilson, B. D. *J. Org. Chem.* **1993**, *58*, 7016-7021.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7.975
7.973
7.970
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7.962
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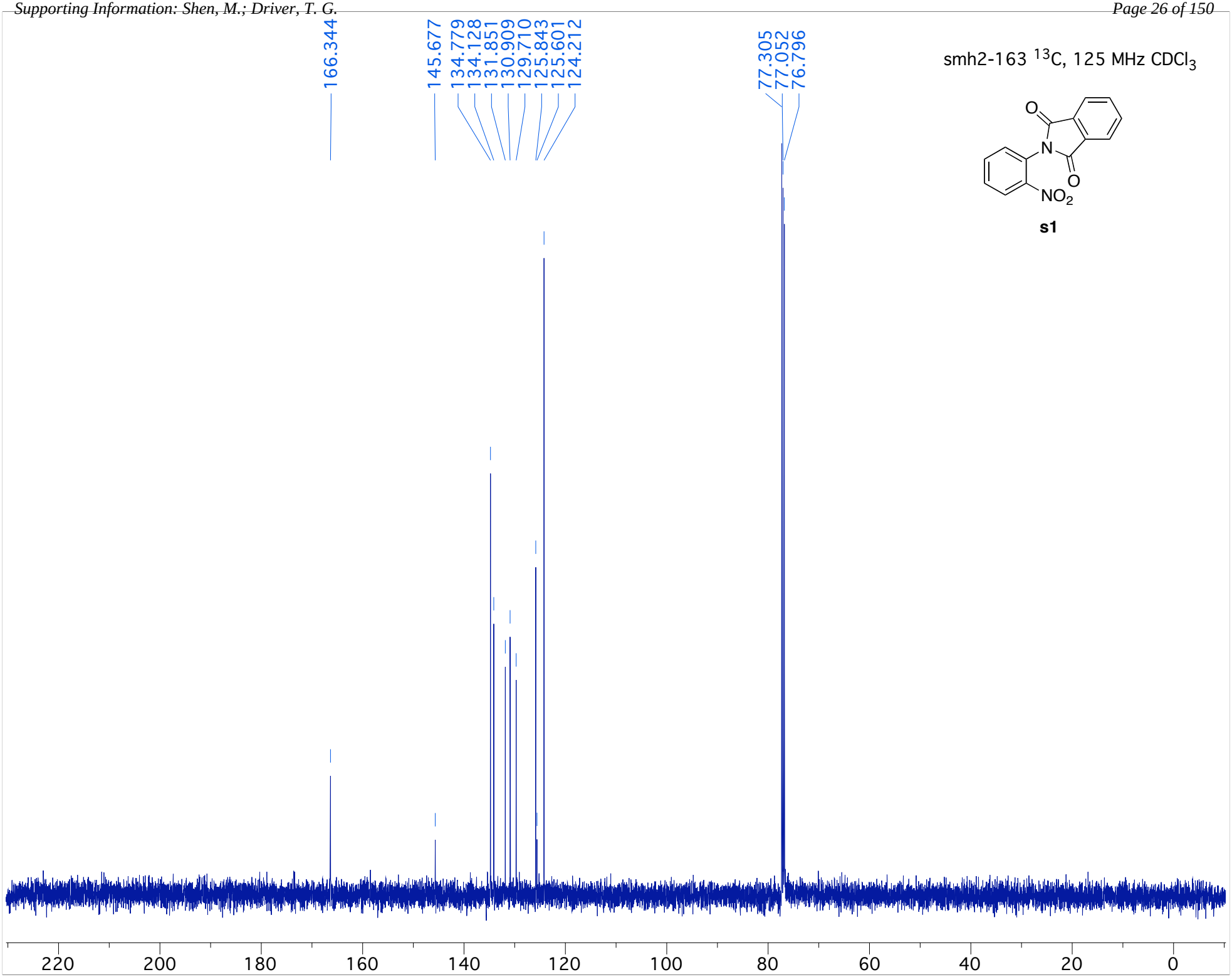
7.837
7.836
7.831
7.826
7.825
7.820
7.819
7.812
7.809
7.807
7.806
7.791
7.778
7.775
7.648
7.633
7.632
7.619
7.617
7.545
7.529
7.261
7.260
smh2-163 ^{1}H, 500 MHz $CDCl_3$
O
N
O
NO_2
s1
2.07
1.09
1
3.24
1.08
ppm 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4
2.07 1.09
1 3.24 1.08
ppm 11 10 9 8 7 6 5 4 3 2 1 0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131.851
130.909
129.710
125.843
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124.212
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77.052
76.796
smh2-163 ^{13}C, 125 MHz $CDCl_3$
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N
O
NO_2
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180
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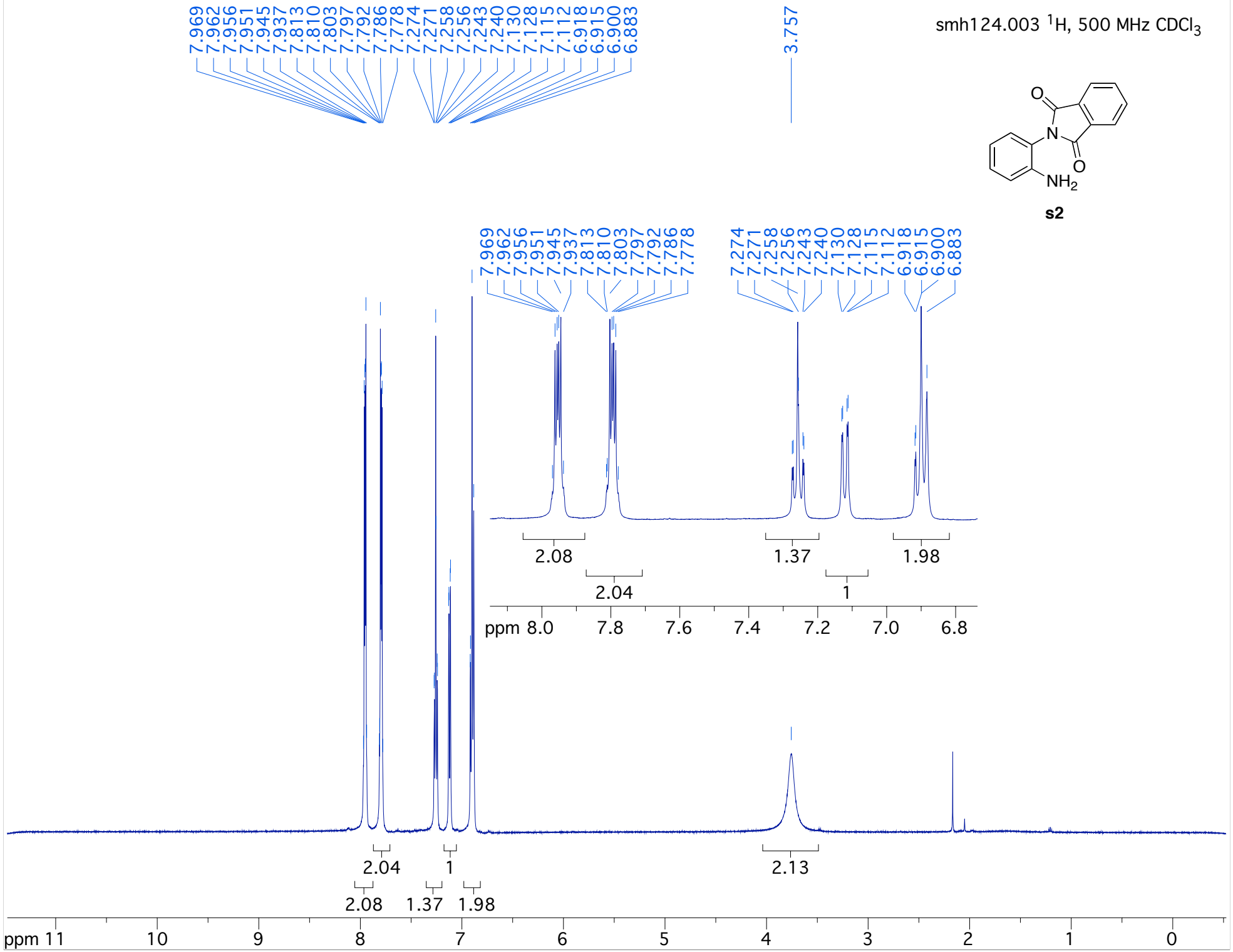
140
120
100
80
60
40
20
0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7.813
7.810
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7.792
7.786
7.778
7.274
7.271
7.258
7.256
7.243
7.240
7.130
7.128
7.115
7.112
6.918
6.915
6.900
6.883
3.757
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O
NH_2
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2.04
1.37
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1.98
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7.6
7.4
7.2
7.0
6.8
2.04
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2.08
1.37
1.98
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3
2
1
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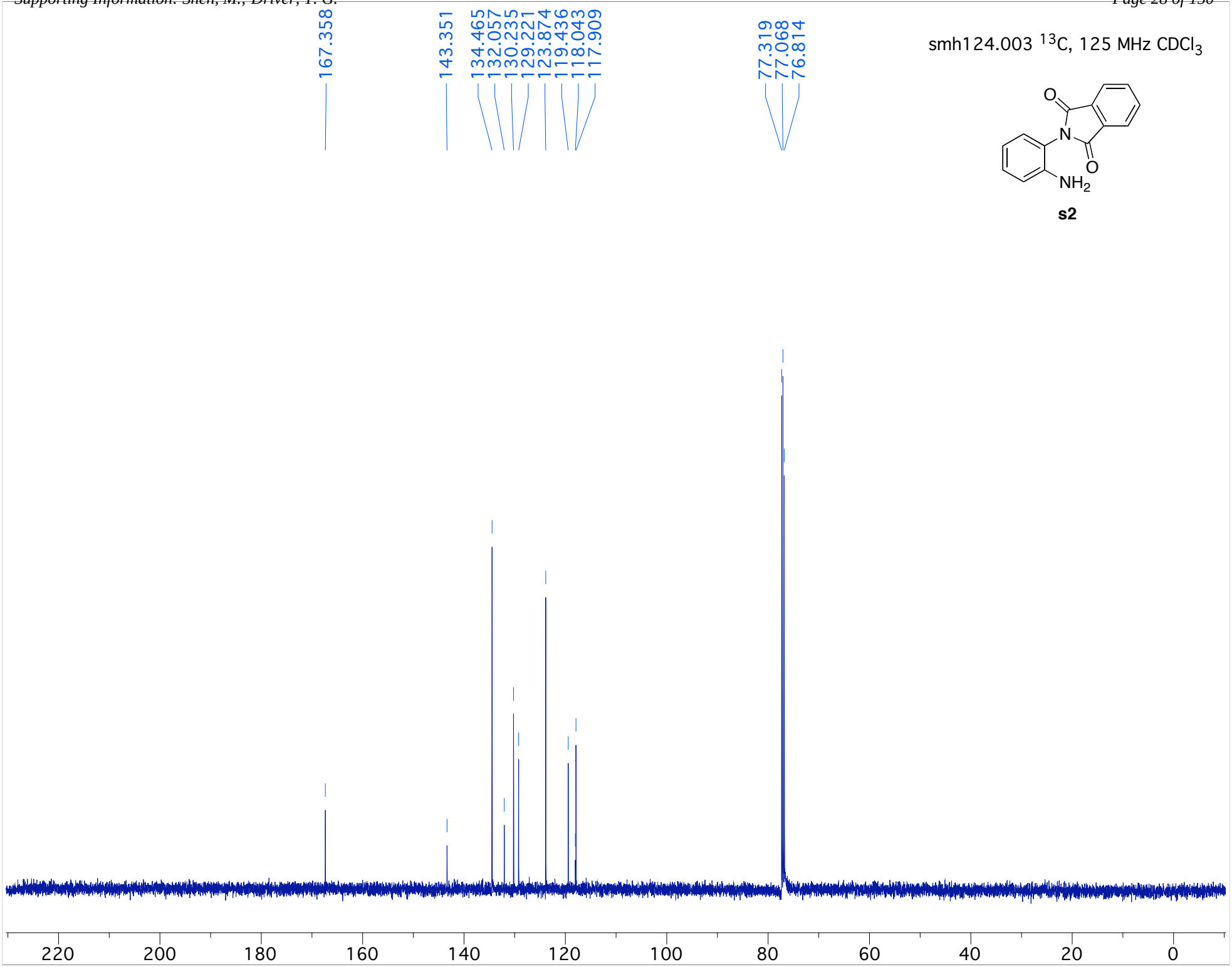
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130.235
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76.814
smh124.003 ^{13}C, 125 MHz $CDCl_3$
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O
NH_2
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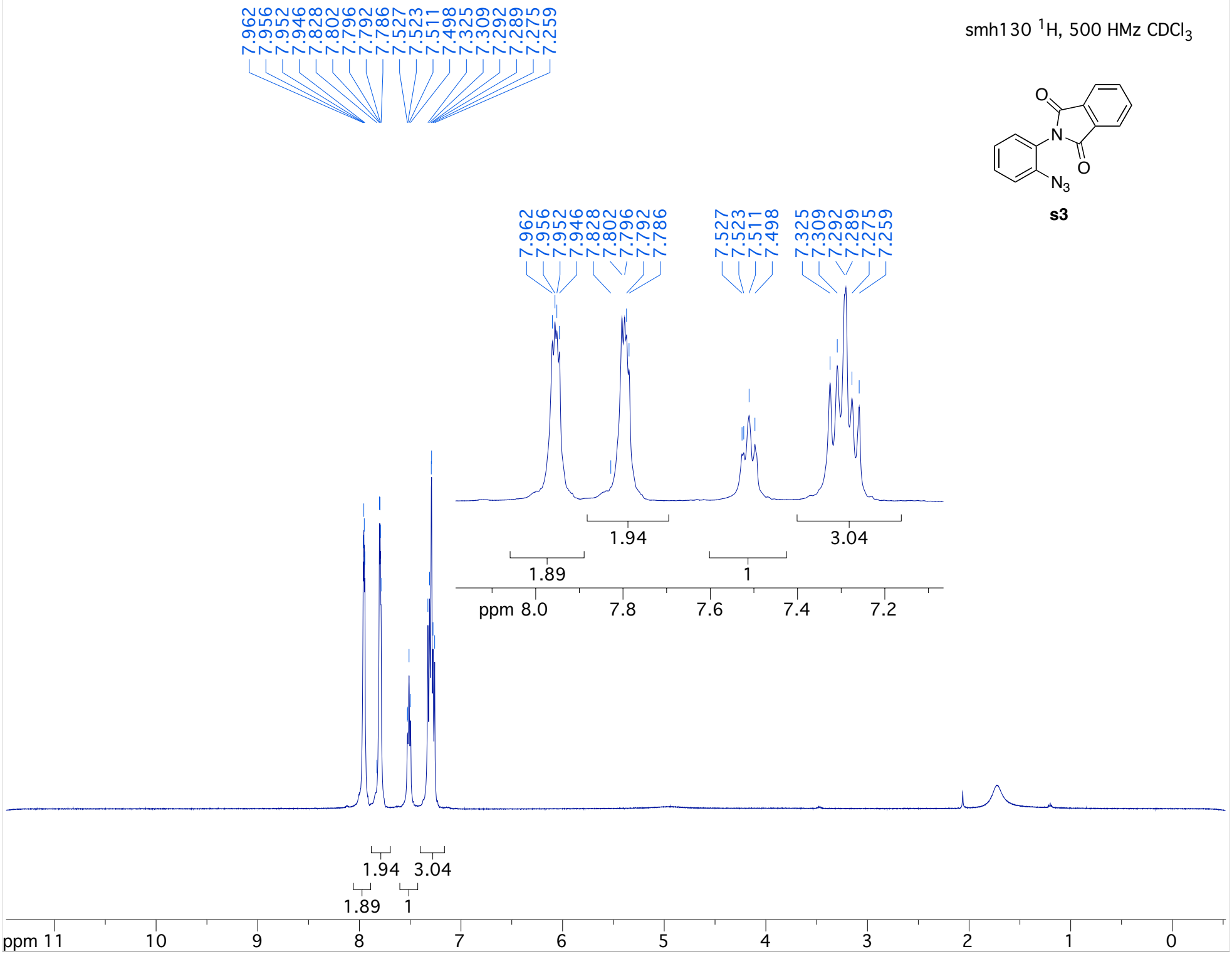
140
120
100
80
60
40
20
0

s2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7.309
7.292
7.289
7.275
7.259
smh130 ^{1}H, 500 HMz $CDCl_3$
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N
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N_3
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3.04
1.89
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7.8
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7.4
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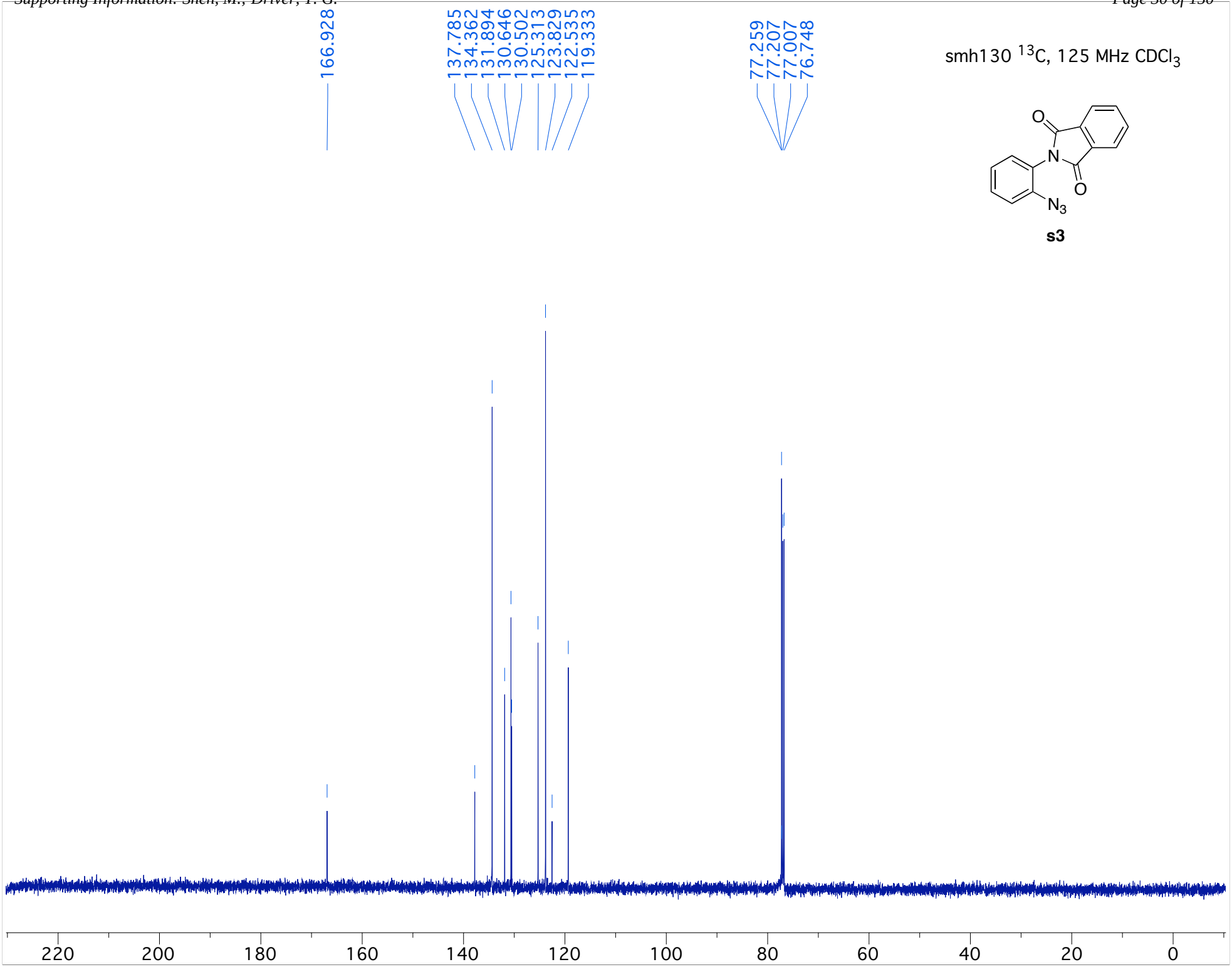
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77.007
76.748
smh130 ^{13}C, 125 MHz $CDCl_3$
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O
N_3
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120
100
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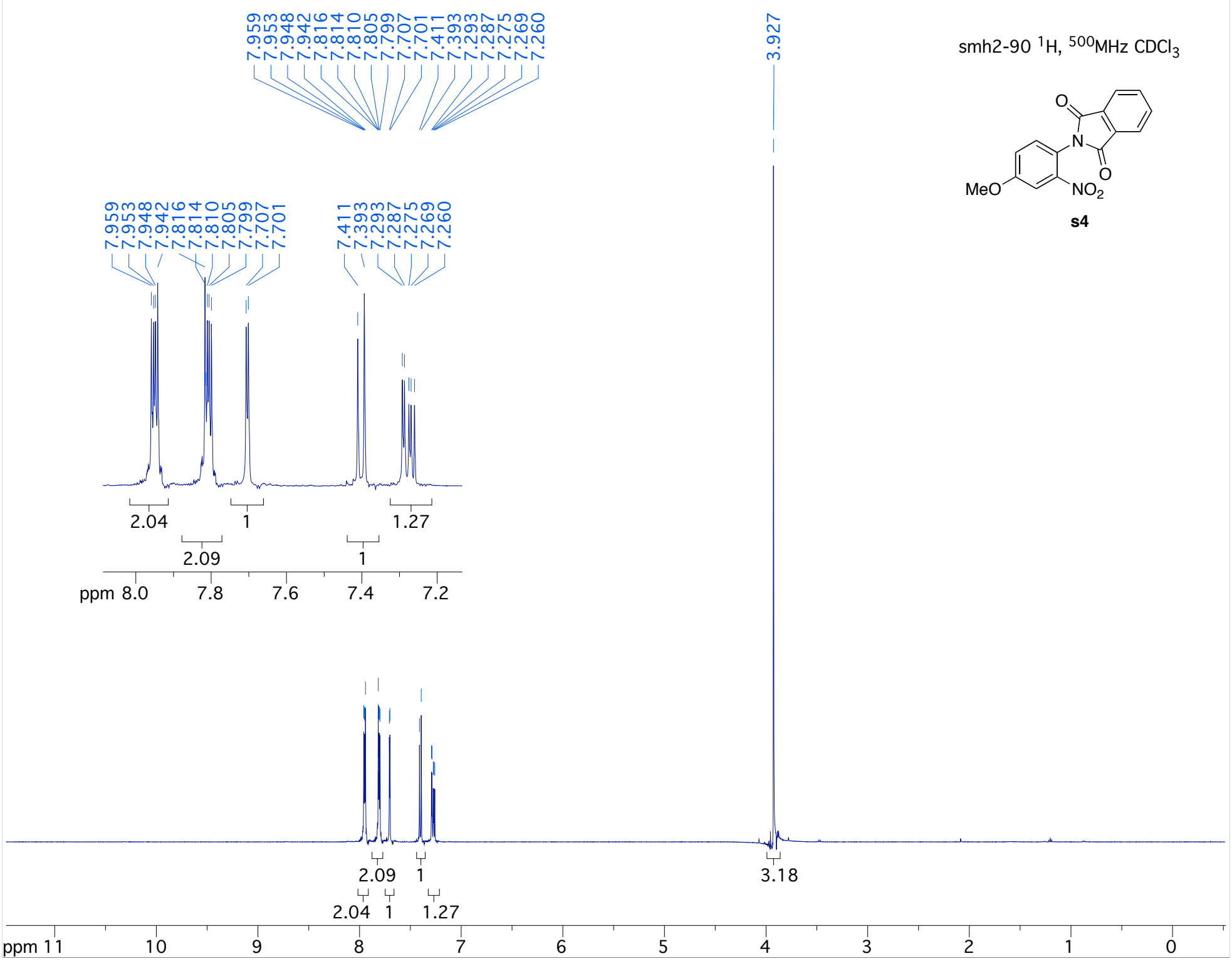
60
40
20
0

s3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7.810
7.805
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7.707
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7.293
7.287
7.275
7.269
7.260
3.927
smh2-90 ^{1}H, ^{500}MHz $CDCl_3$
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O
MeO
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s4
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2.09
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ppm 8.0
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7.2
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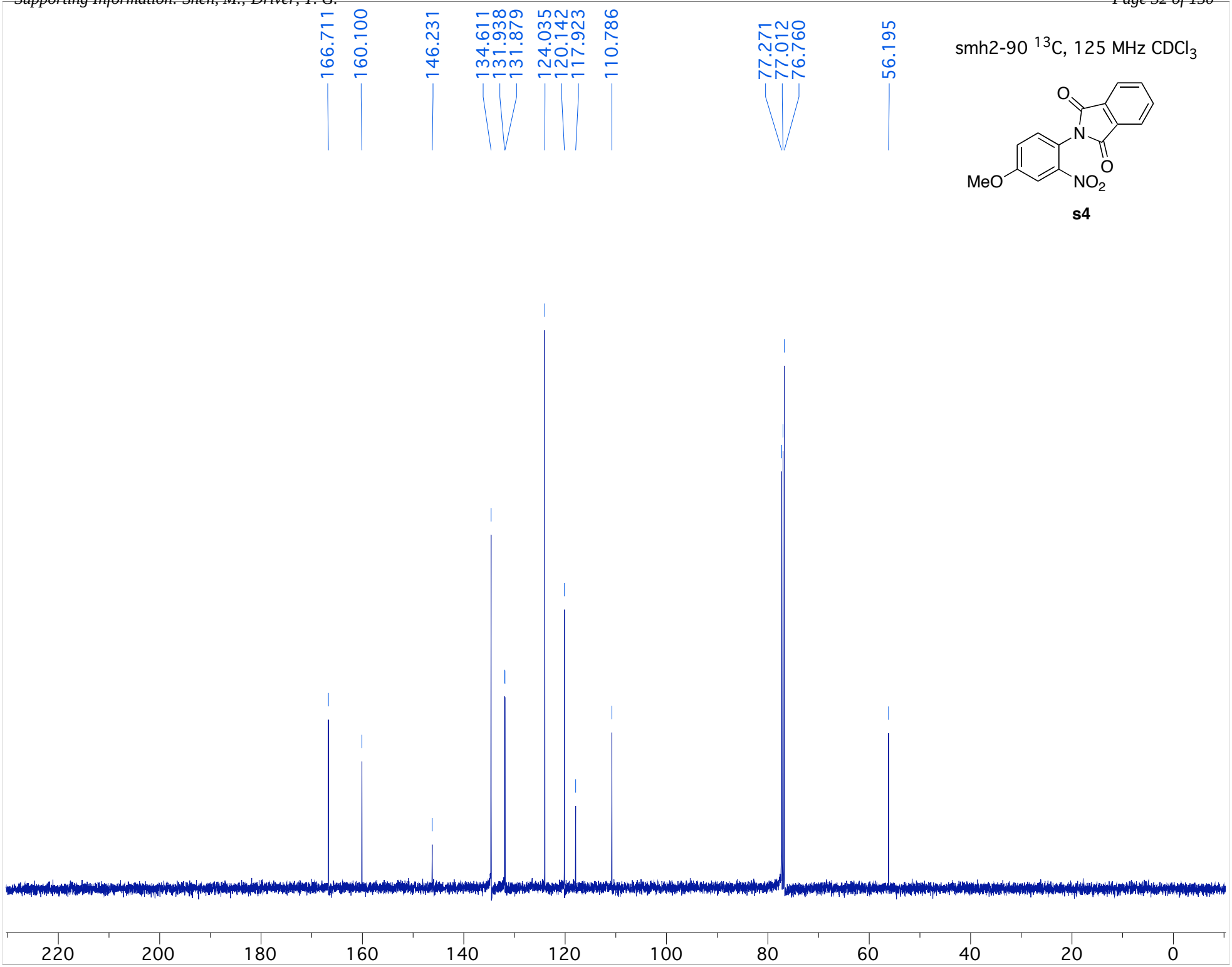
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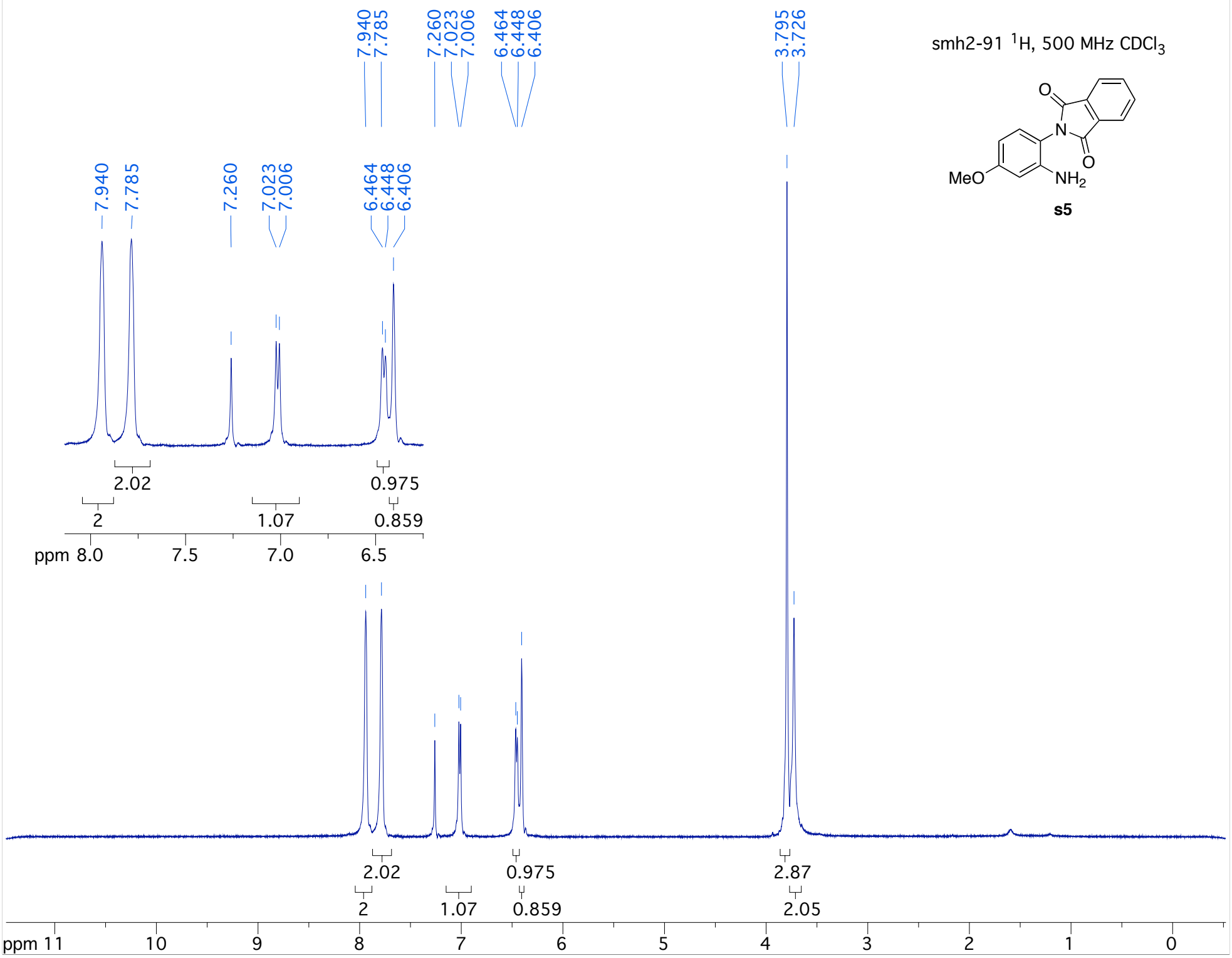
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O
MeO
NH_2
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2
1.07
0.859
ppm 8.0
7.5
7.0
6.5
2.02
0.975
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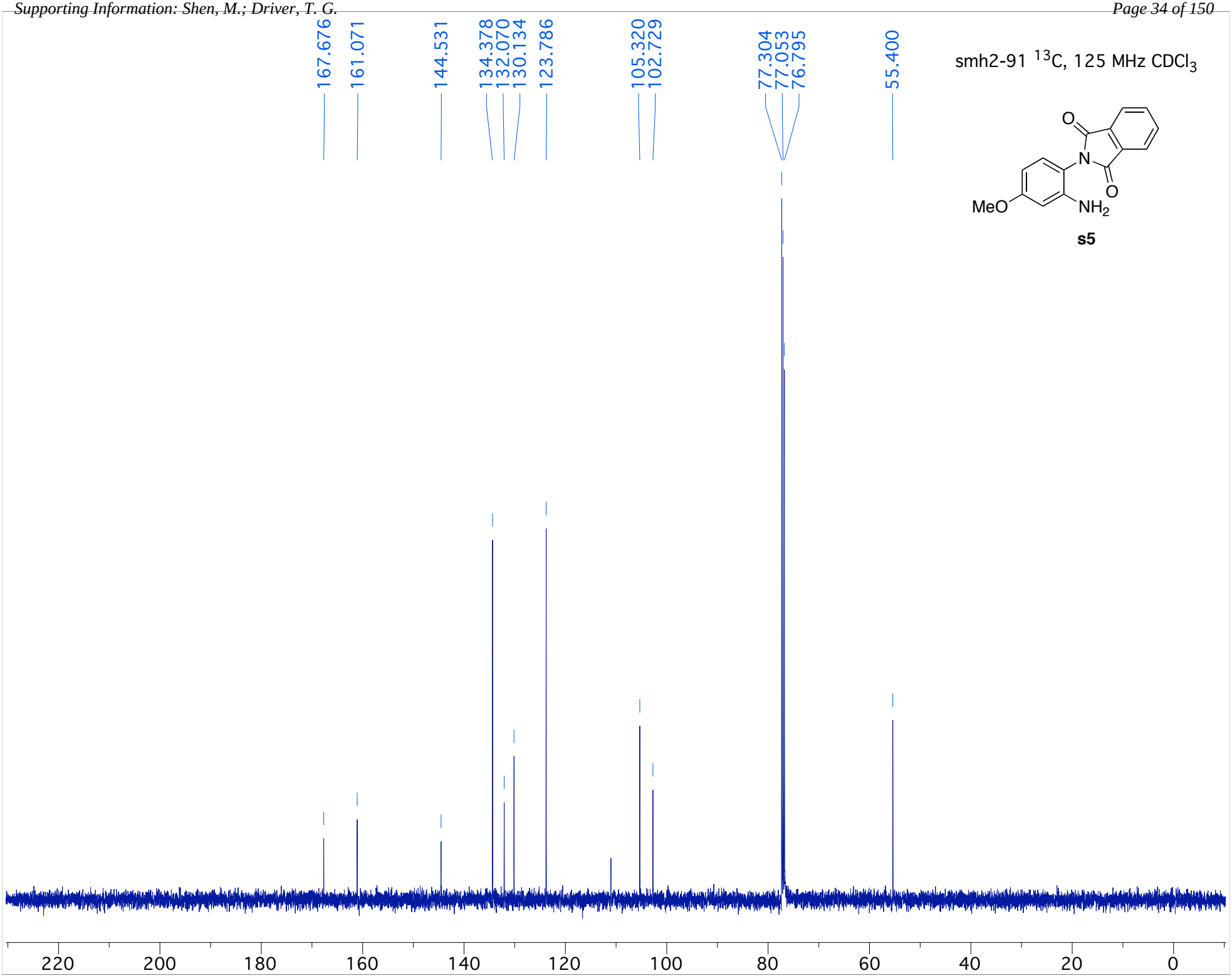
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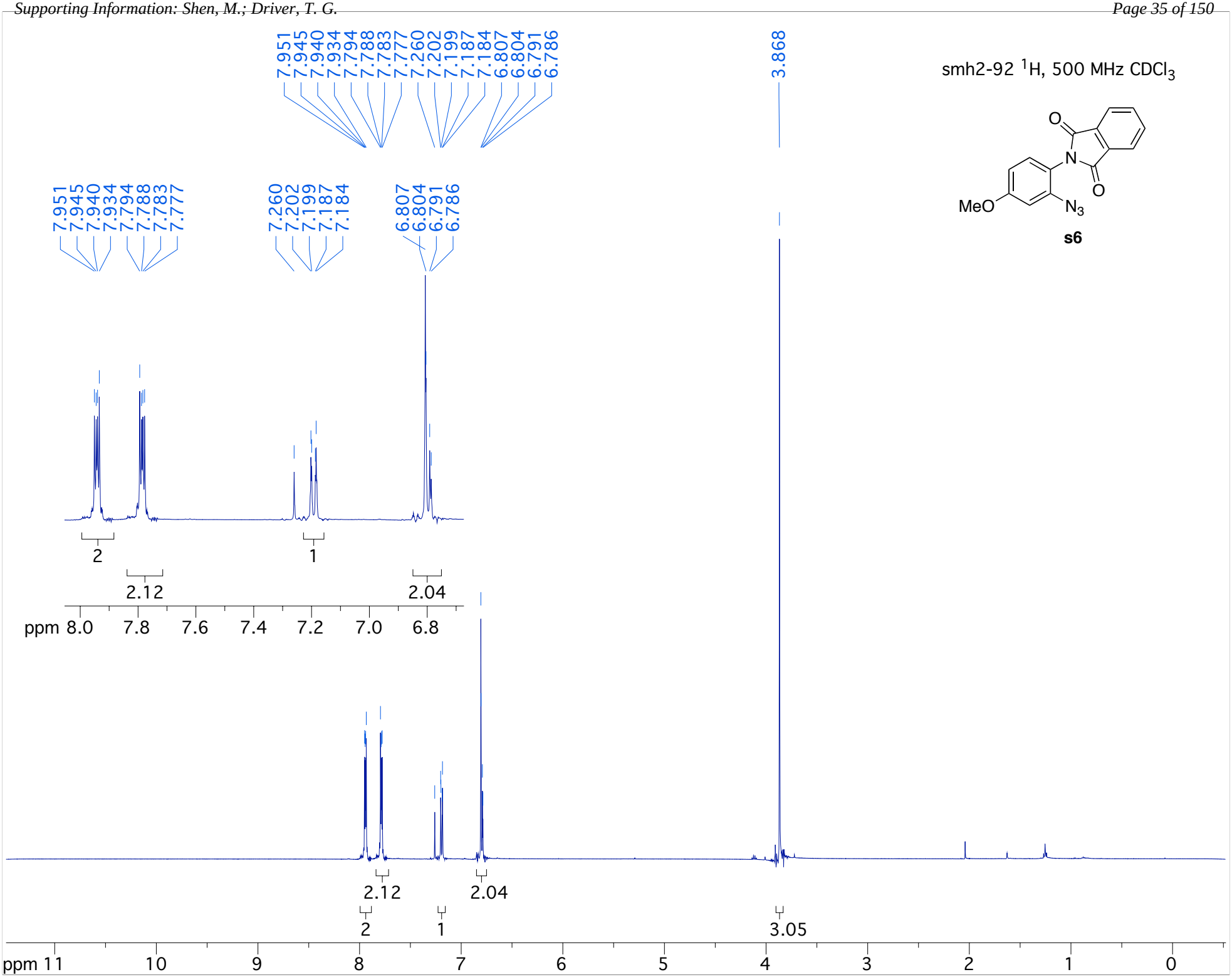
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7.184
6.807
6.804
6.791
6.786
3.868
smh2-92 ^{1}H, 500 MHz $CDCl_3$
O
N
O
MeO
N_3
s6
2
1
2.12
2.04
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2
1
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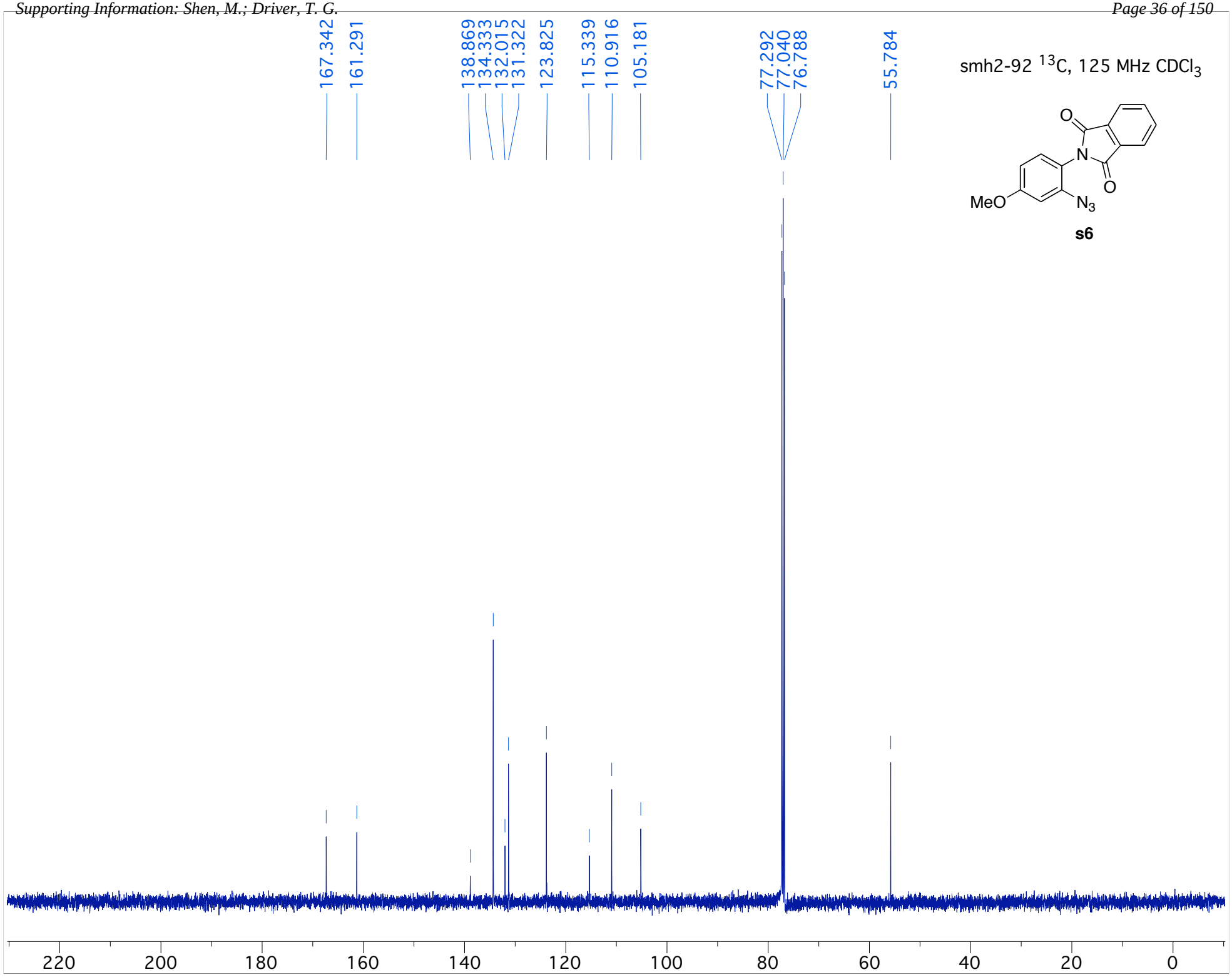
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76.788
55.784
smh2-92 ^{13}C, 125 MHz $CDCl_3$
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MeO
N_3
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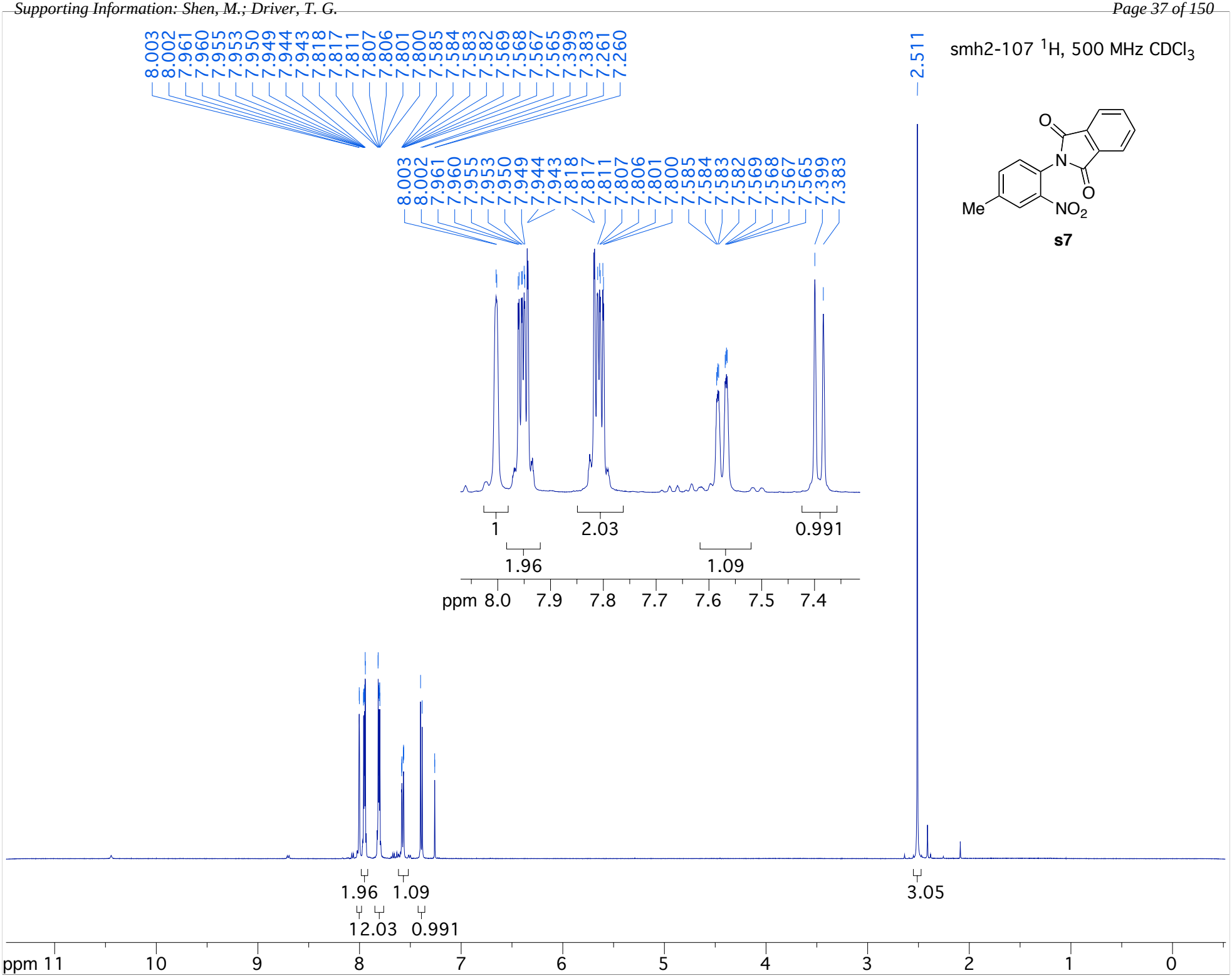
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7.585
7.584
7.583
7.582
7.569
7.568
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7.565
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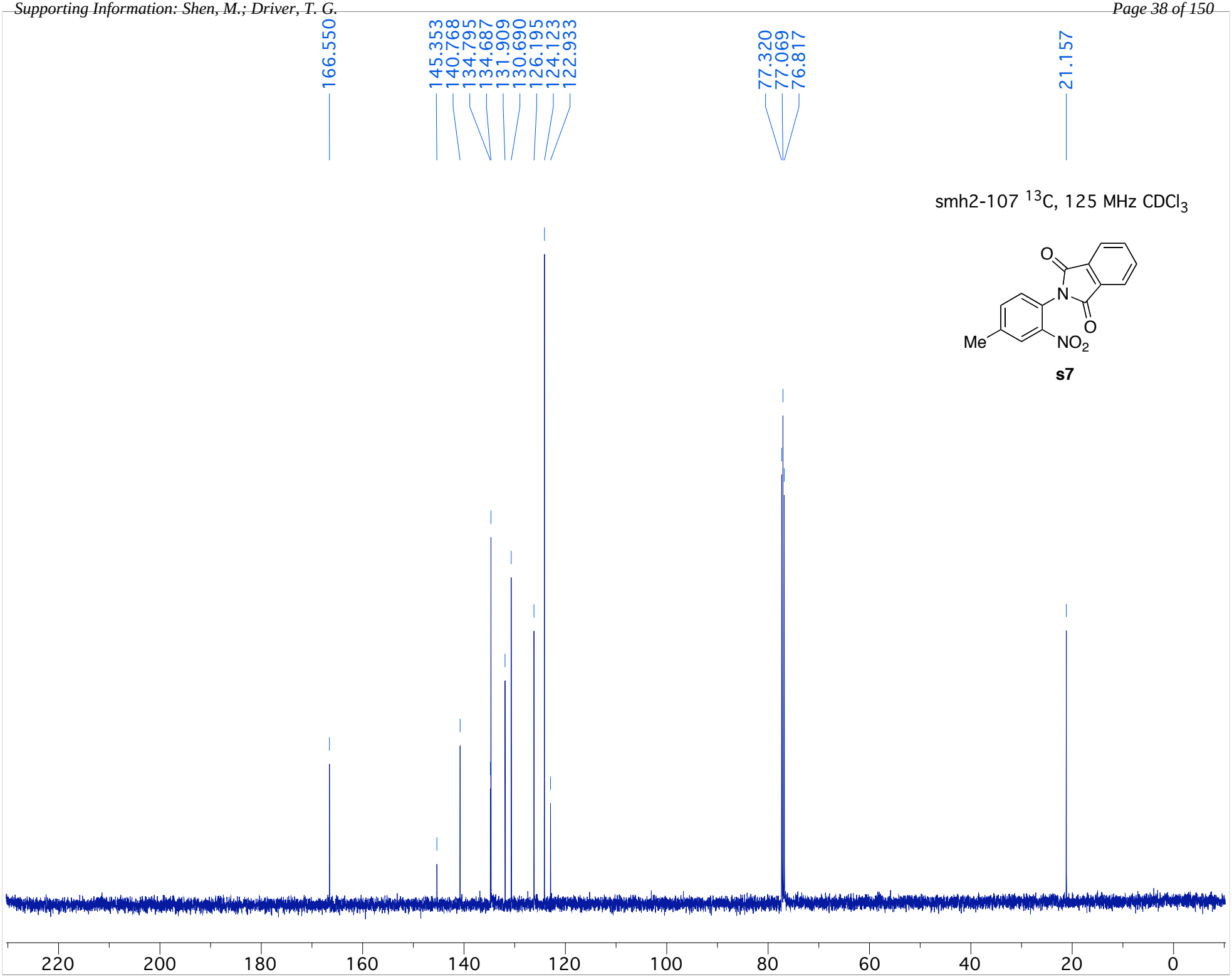
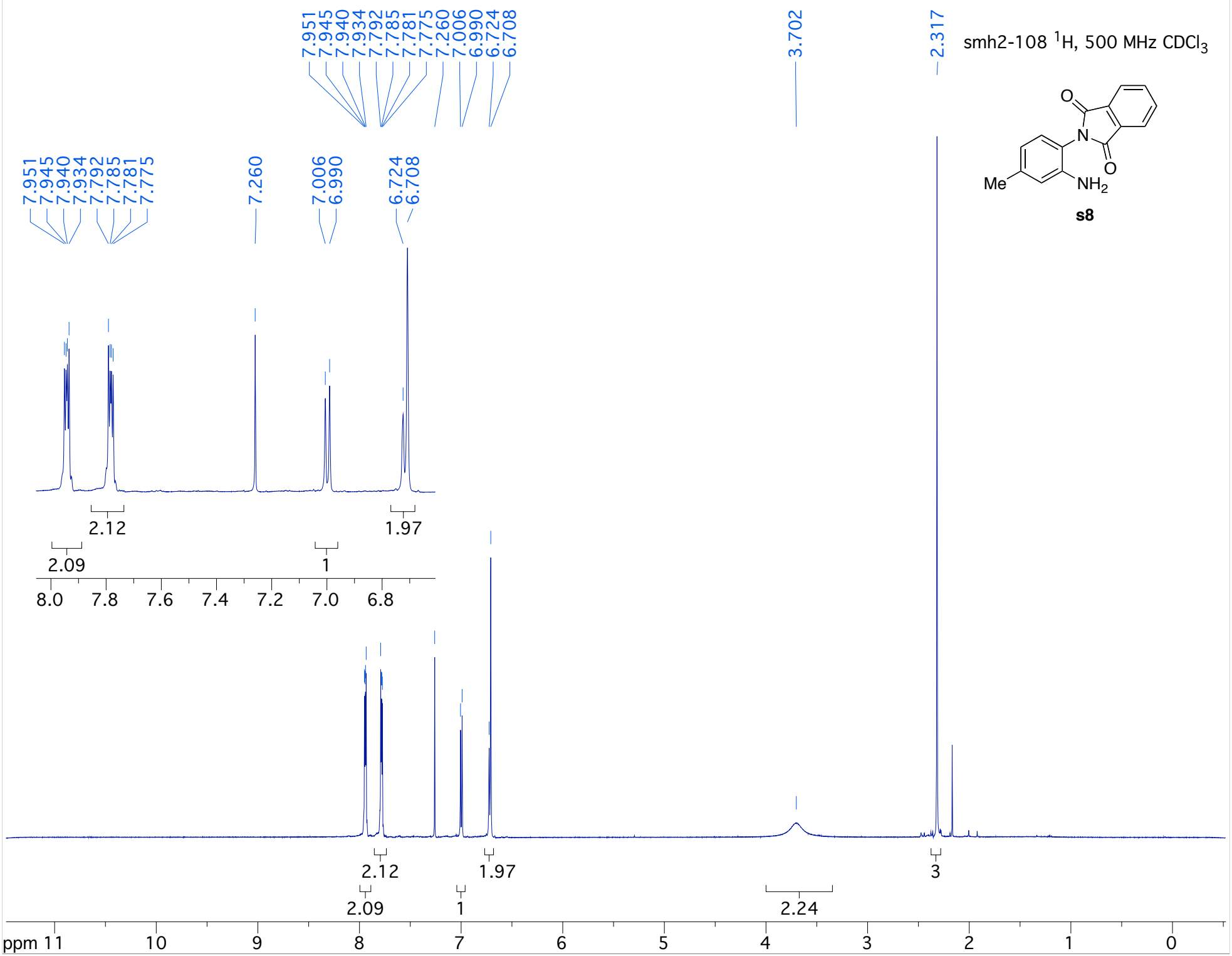
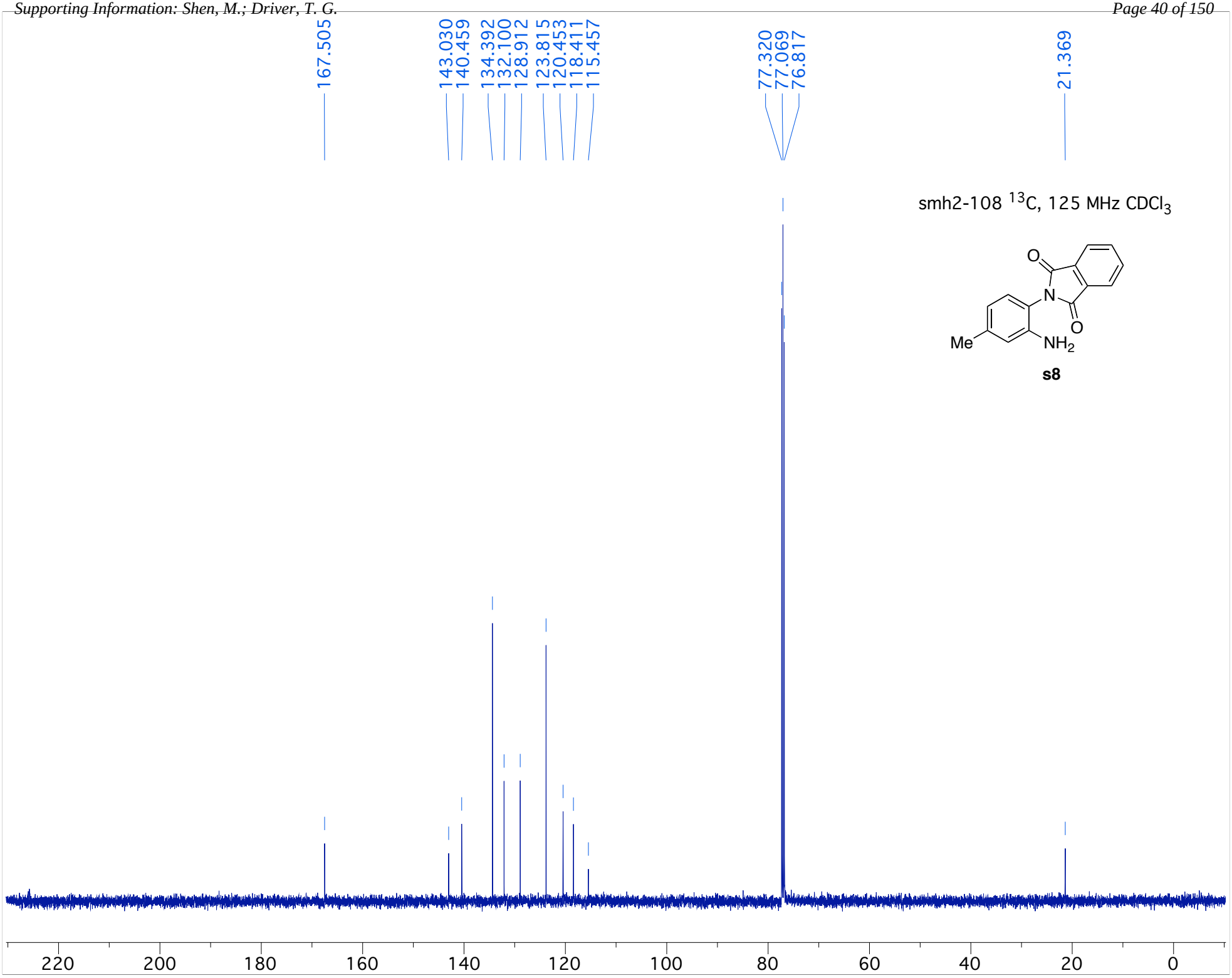
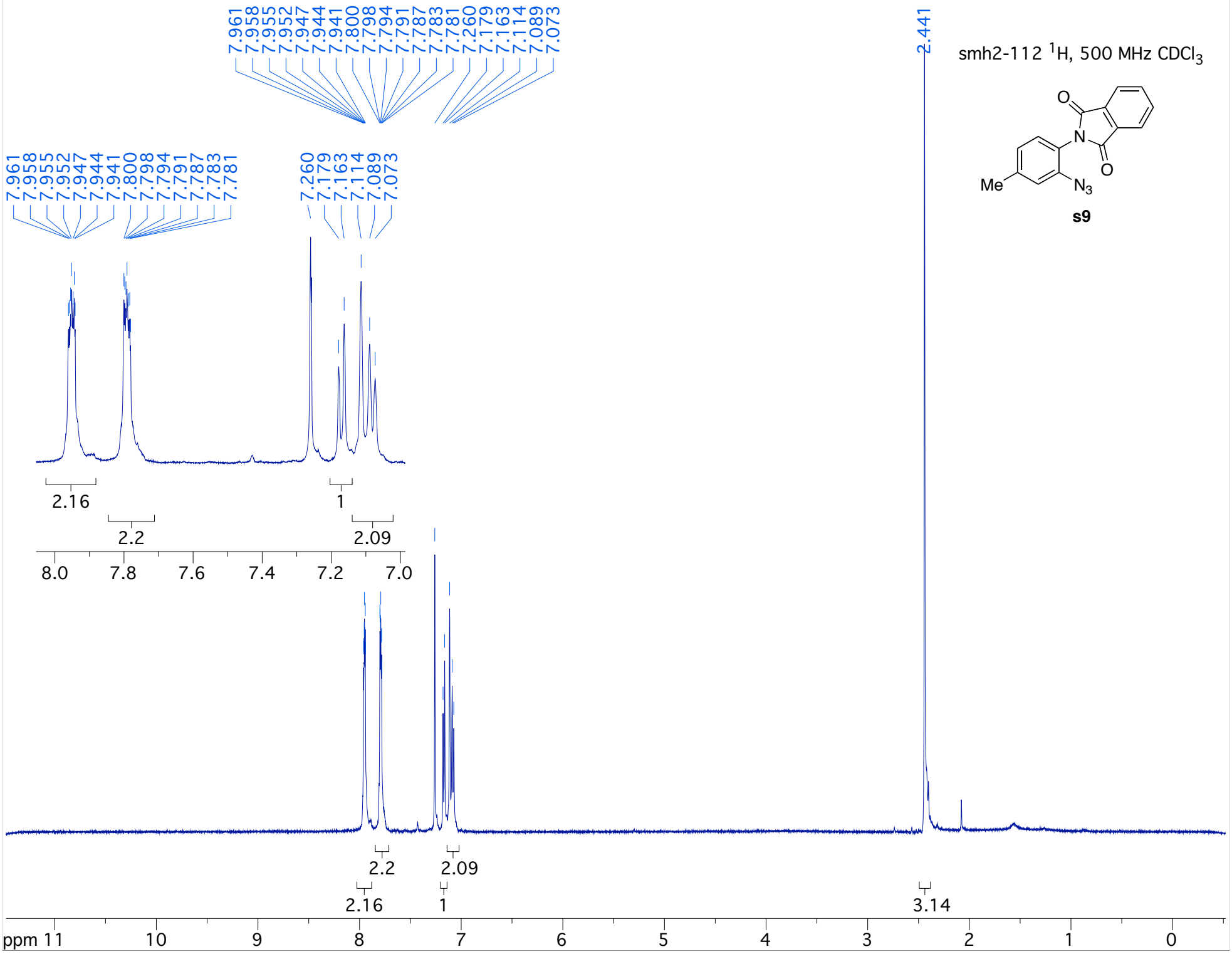
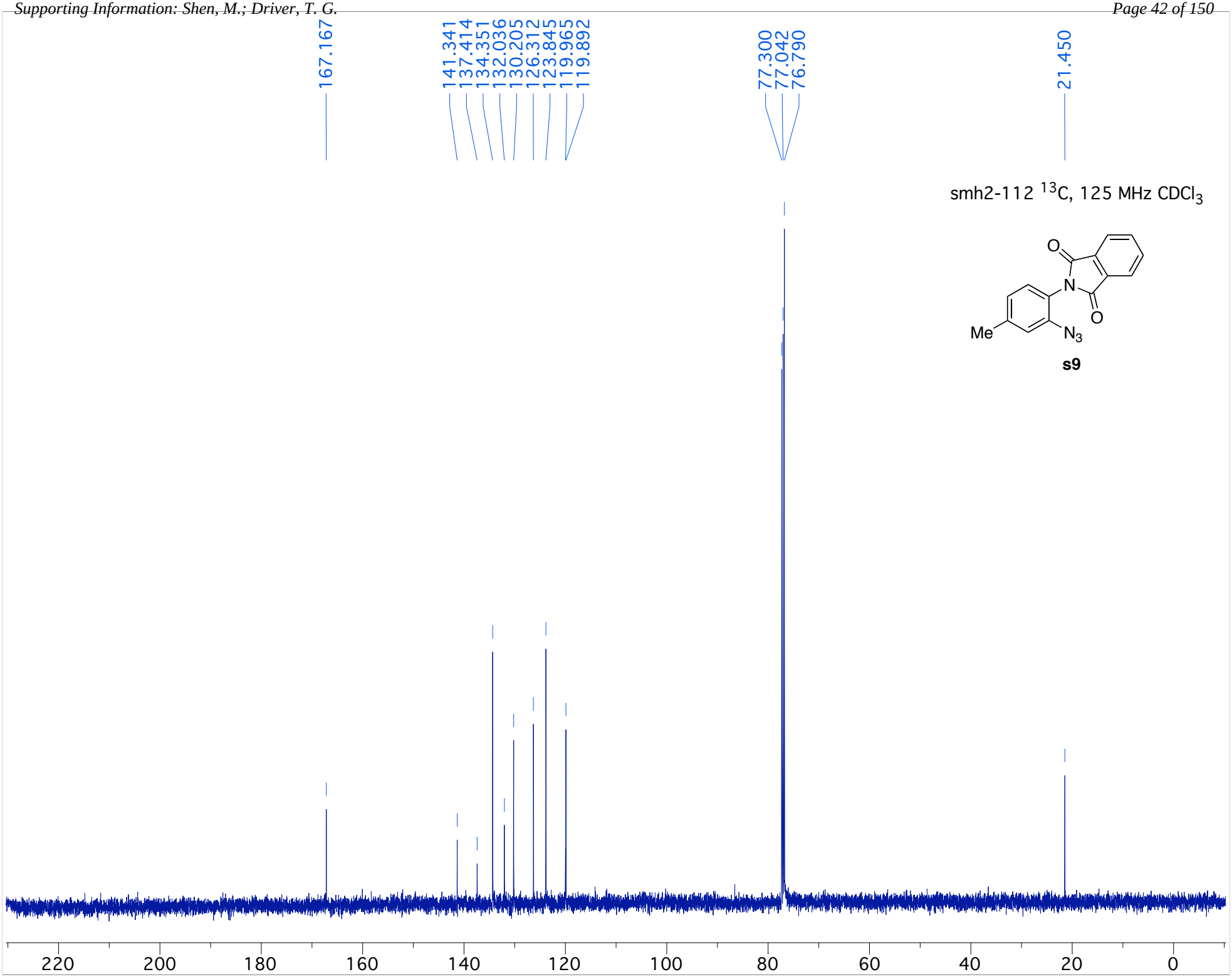
7.261
7.260
2.511
smh2-107 ^{1}H, 500 MHz $CDCl_3$
Me
NO_2
s7
1
2.03
0.991
1.96
1.09
ppm 8.0 7.9 7.8 7.7 7.6 7.5 7.4
1.96
1.09
12.03
0.991
3.05
ppm 11 10 9 8 7 6 5 4 3 2 1 0

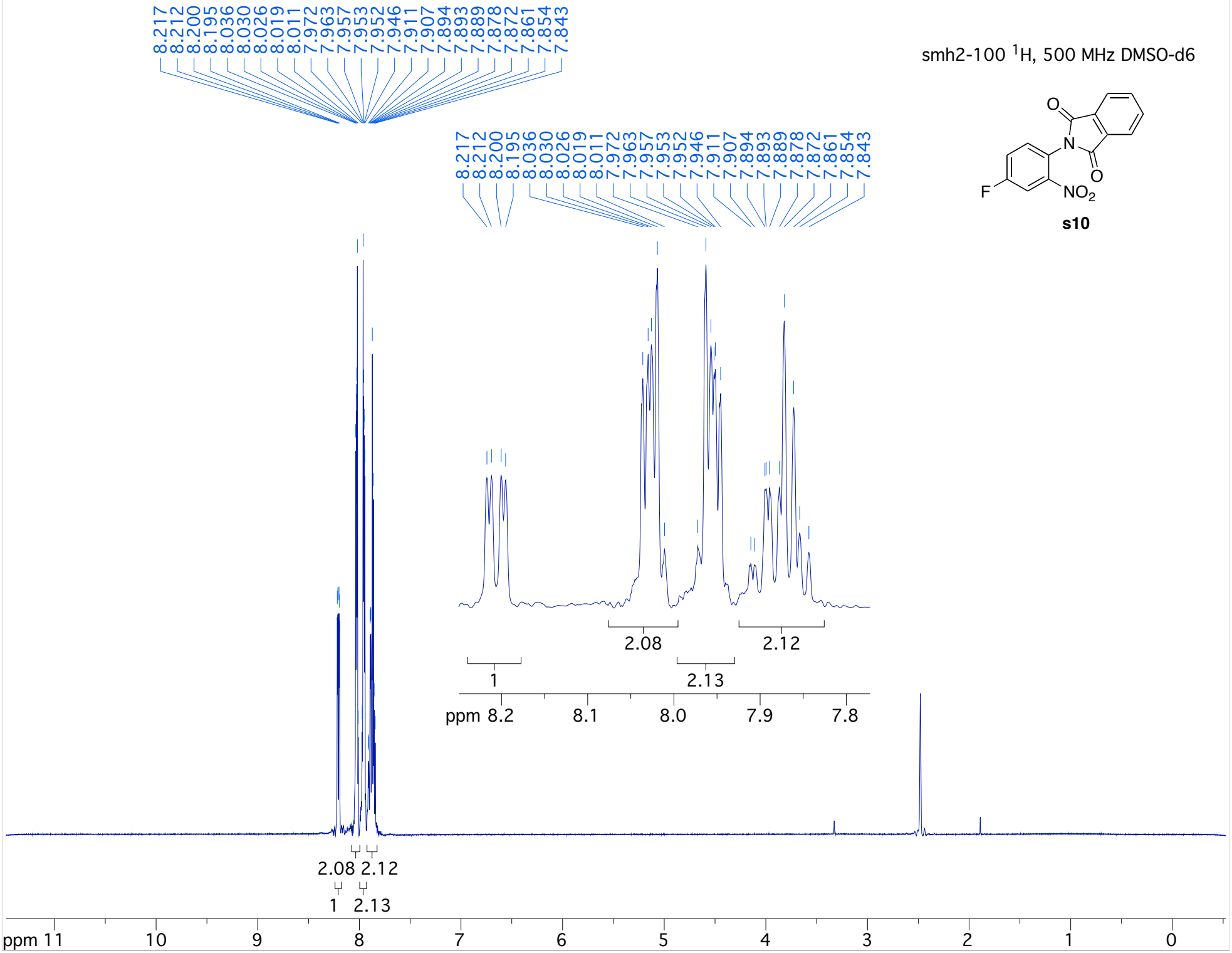

166.550
145.353
140.768
134.795
134.687
131.909
130.690
126.195
124.123
122.933
77.320
77.069
76.817
21.157
smh2-107 ^{13}C, 125 MHz $CDCl_3$
O
N
O
Me
NO_2
s7
220
200
180
160
140
120
100
80
60
40
20
0

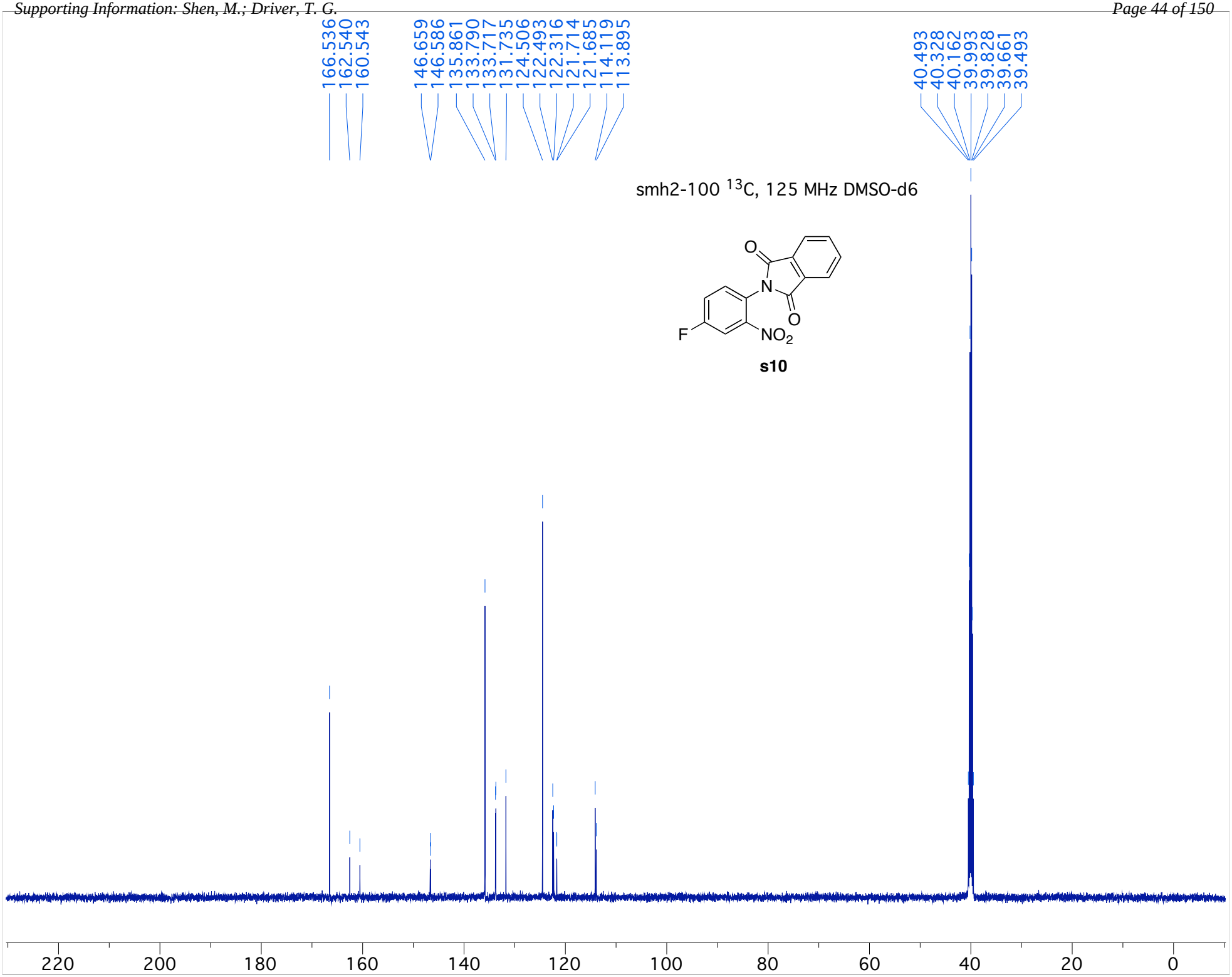

7.951
7.945
7.940
7.934
7.792
7.785
7.781
7.775
7.260
7.006
6.990
6.724
6.708
3.702
2.317
smh2-108 ^{1}H, 500 MHz $CDCl_3$
O
N
O
Me
NH_2
s8
2.12
1.97
2.09
1
2.12
1.97
3
2.09
1
2.24
8.0
7.8
7.6
7.4
7.2
7.0
6.8
ppm 11
10
9
8
7
6
5
4
3
2
1
0

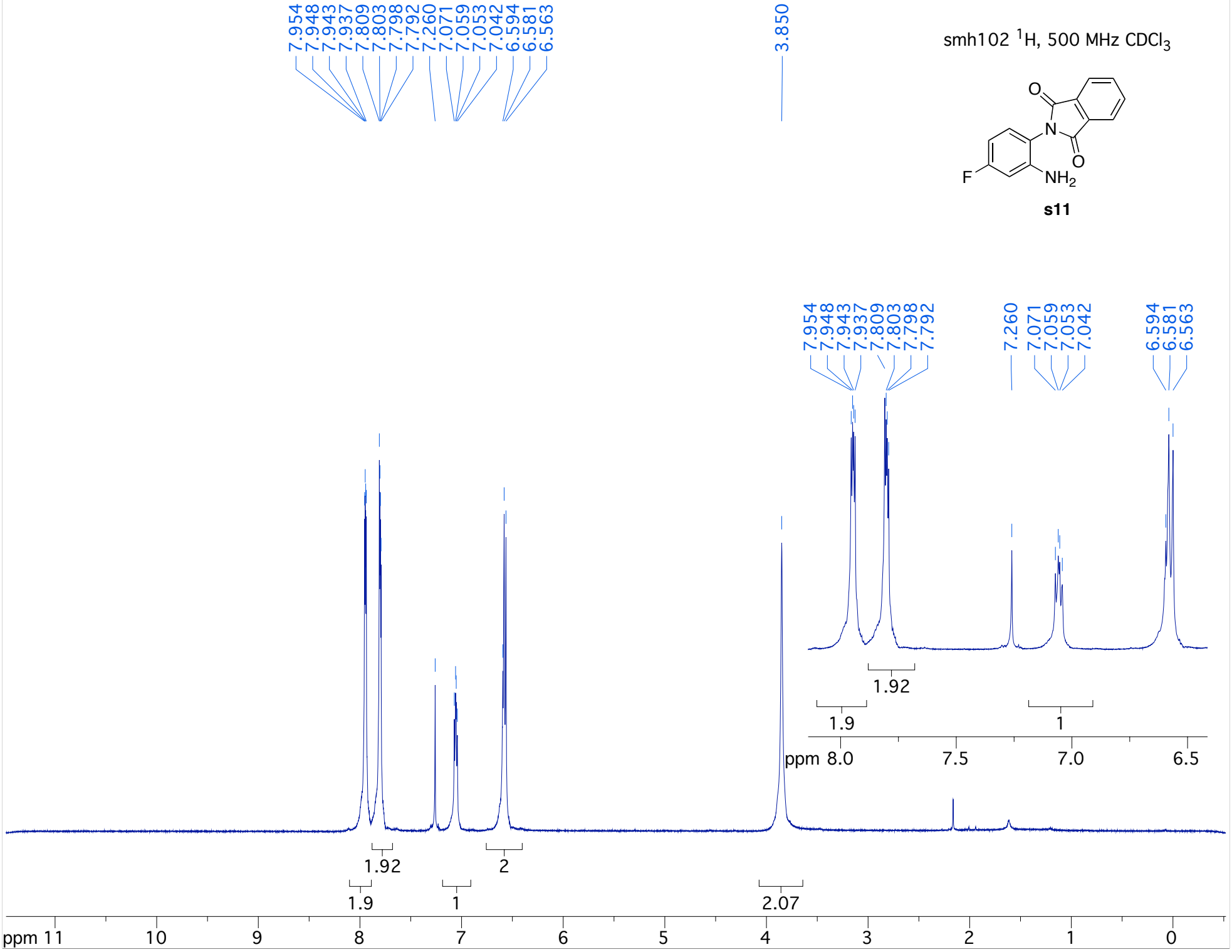

167.505
143.030
140.459
134.392
132.100
128.912
123.815
120.453
118.411
115.457
77.320
77.069
76.817
21.369
smh2-108 ^{13}C, 125 MHz $CDCl_3$
O
N
O
Me
NH_2
s8
220
200
180
160
140
120
100
80
60
40
20
0

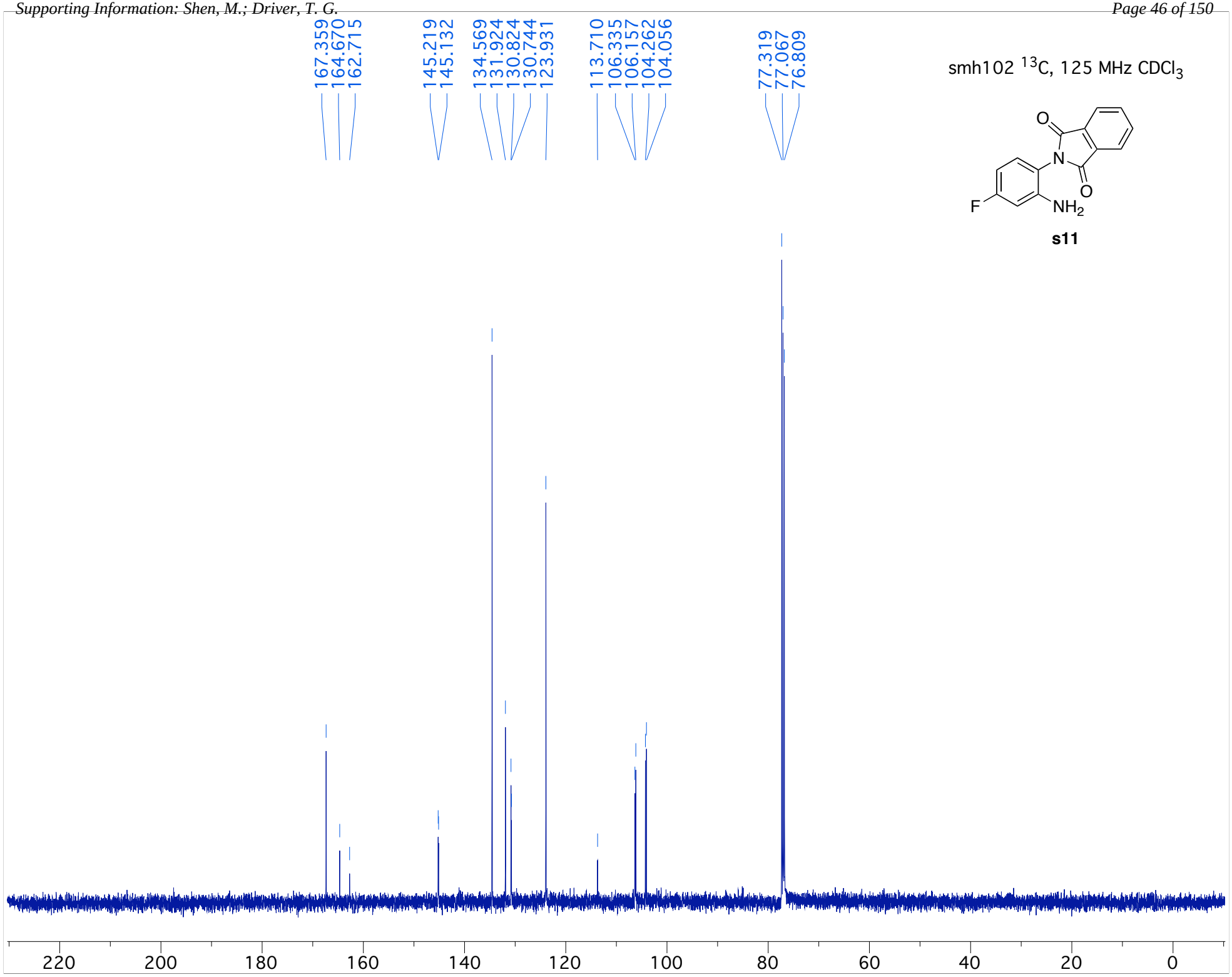

7.961
7.958
7.955
7.952
7.947
7.944
7.941
7.800
7.798
7.794
7.791
7.787
7.783
7.781
7.260
7.179
7.163
7.114
7.089
7.073
2.441
smh2-112 ^{1}H, 500 MHz $CDCl_3$
Me
N_3
O
N
O
s9
2.16
1
2.2
2.09
8.0
7.8
7.6
7.4
7.2
7.0
2.2
2.09
2.16
1
3.14
ppm 11
10
9
8
7
6
5
4
3
2
1
0

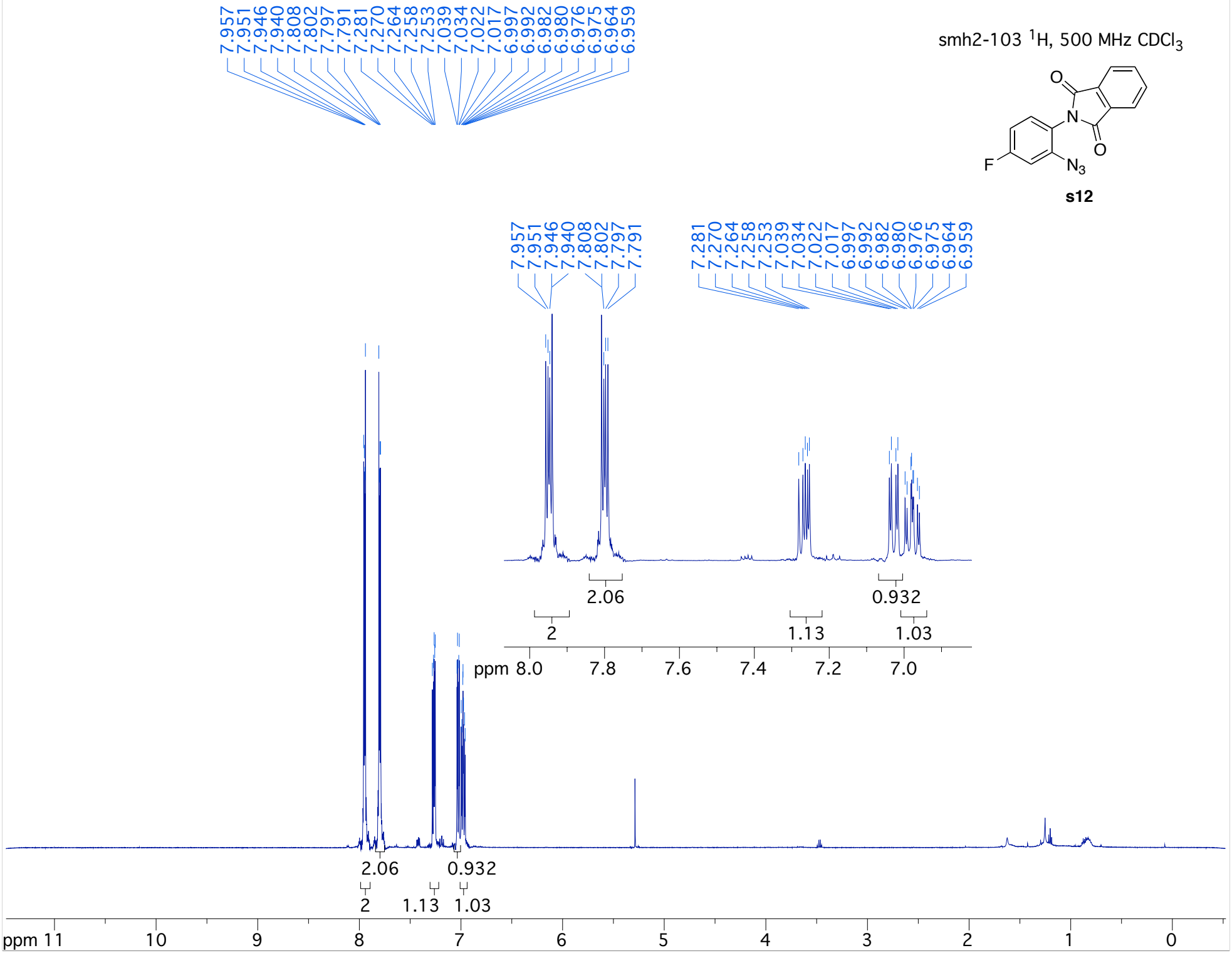

167.167
141.341
137.414
134.351
132.036
130.205
126.312
123.845
119.965
119.892
77.300
77.042
76.790
21.450
smh2-112 ^{13}C, 125 MHz $CDCl_3$
O
N
O
Me
N_3
s9
220
200
180
160
140
120
100
80
60
40
20
0

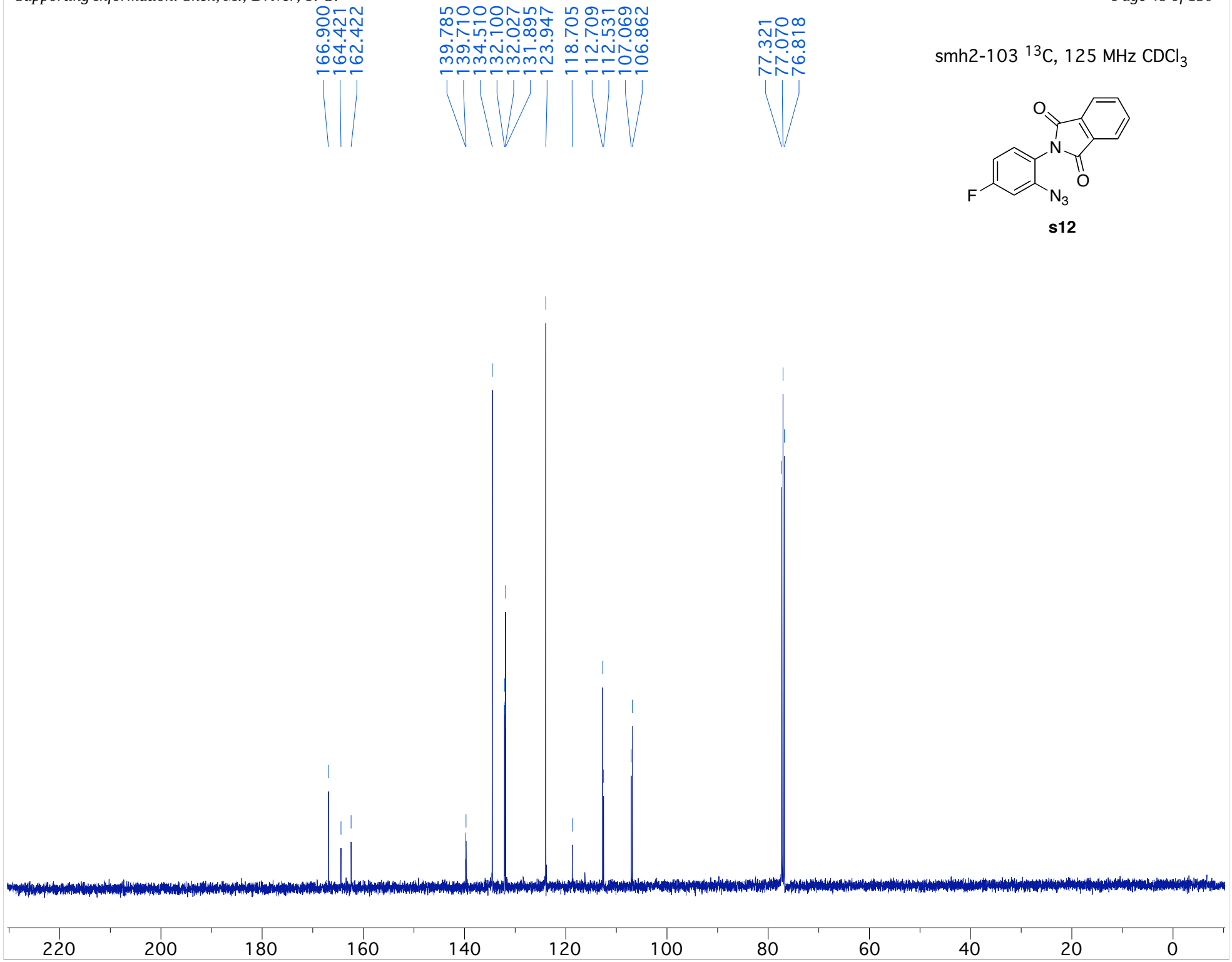

8.217
8.212
8.200
8.195
8.036
8.030
8.026
8.019
8.011
7.972
7.963
7.957
7.953
7.952
7.946
7.911
7.907
7.894
7.893
7.889
7.878
7.872
7.861
7.854
7.843
smh2-100 1H, 500 MHz DMSO-d6
O
N
O
F
NO2
s10
2.08
2.12
1
2.13
ppm 8.2
8.1
8.0
7.9
7.8
2.08 2.12
1 2.13
ppm 11
10
9
8
7
6
5
4
3
2
1
0

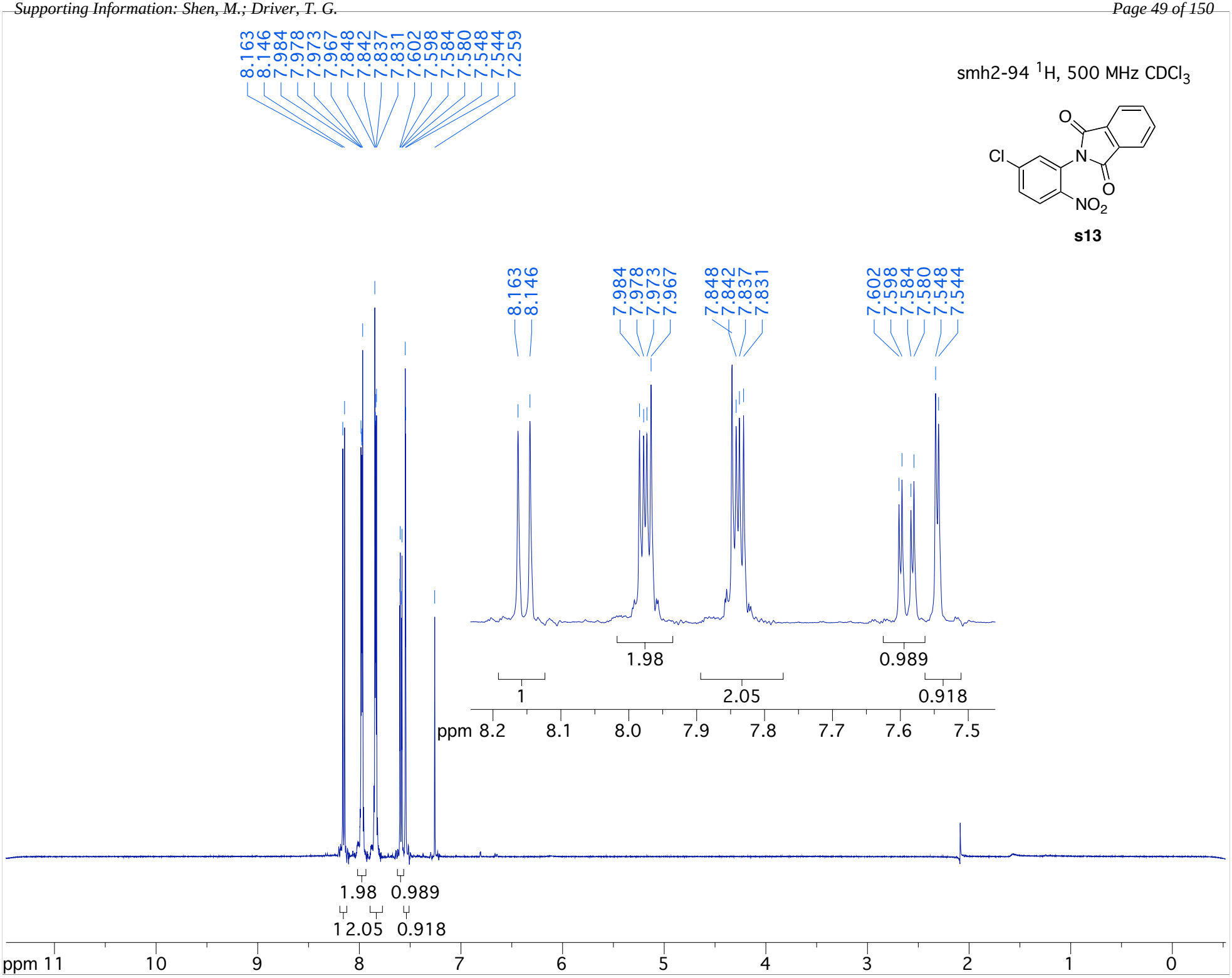

166.536
162.540
160.543
146.659
146.586
135.861
133.790
133.717
131.735
124.506
122.493
122.316
121.714
121.685
114.119
113.895
40.493
40.328
40.162
39.993
39.828
39.661
39.493
smh2-100 13C, 125 MHz DMSO-d6
O
N
O
F
NO2
s10
220
200
180
160
140
120
100
80
60
40
20
0

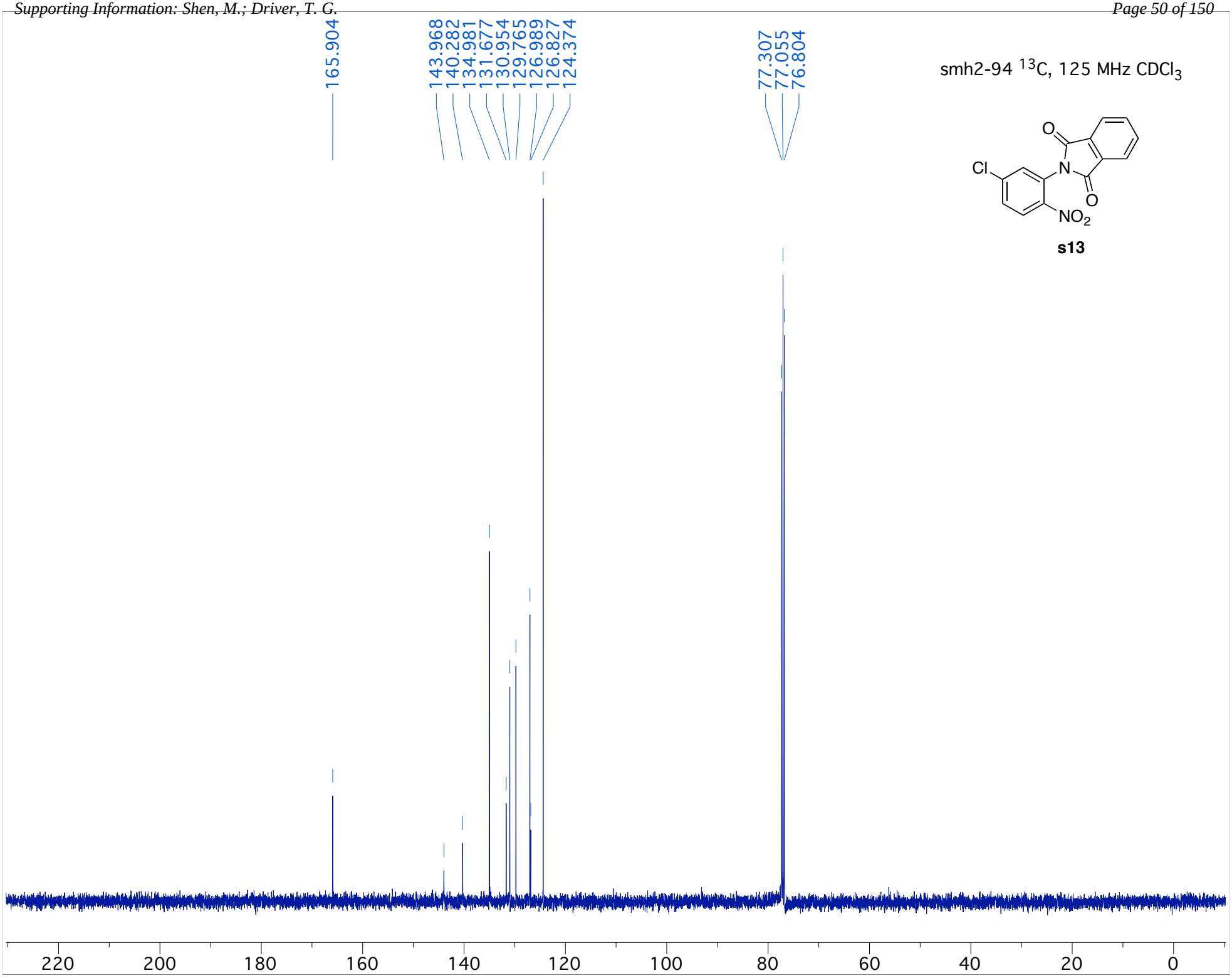

7.954
7.948
7.943
7.937
7.809
7.803
7.798
7.792
7.260
7.071
7.059
7.053
7.042
6.594
6.581
6.563
3.850
smh102 ^{1}H, 500 MHz $CDCl_3$
O
N
O
F
NH_2
s11
1.92
2
1.9
1
2.07
ppm 11
10
9
8
7
6
5
4
3
2
1
0
1.92
1.9
1
ppm 8.0
7.5
7.0
6.5

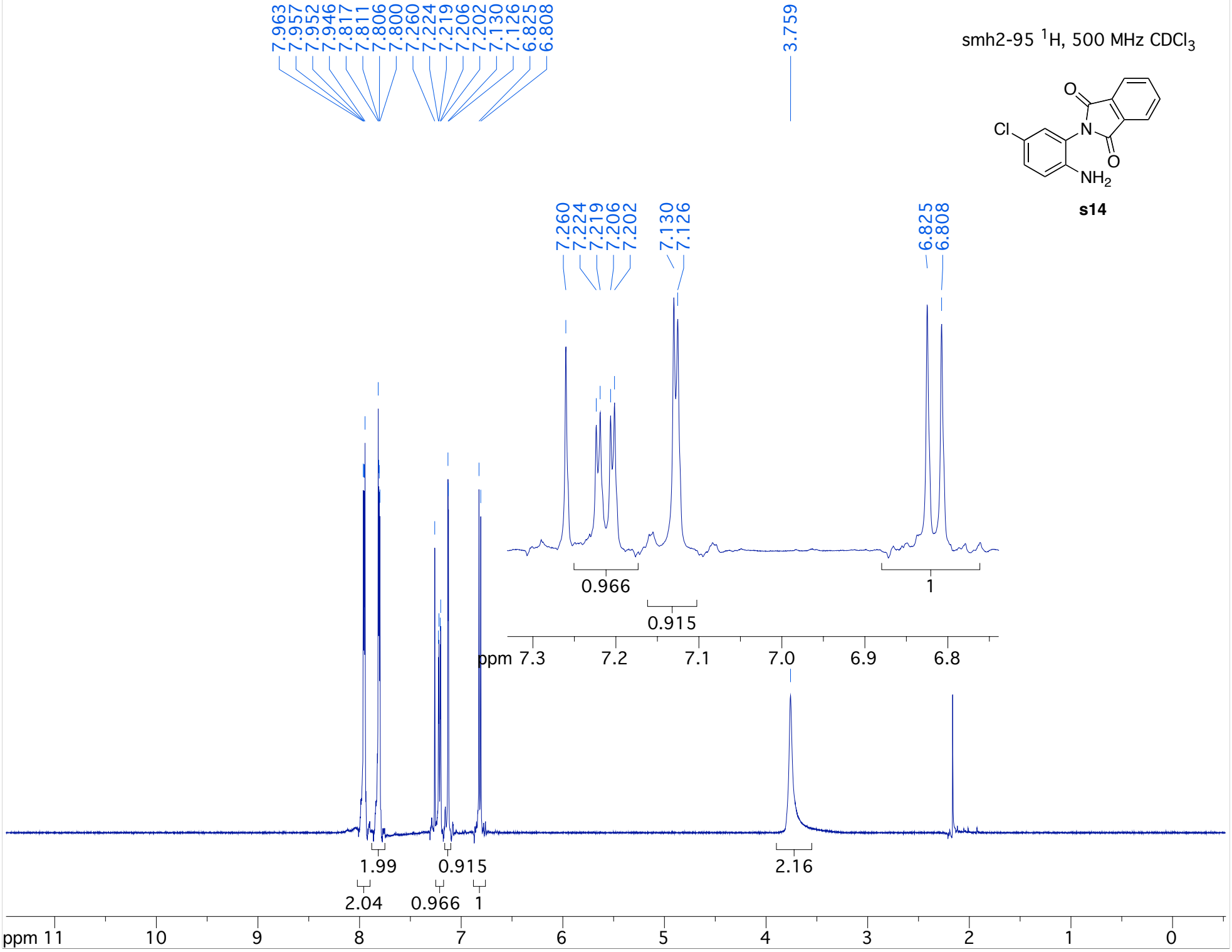

167.359
164.670
162.715
145.219
145.132
134.569
131.924
130.824
130.744
123.931
113.710
106.335
106.157
104.262
104.056
77.319
77.067
76.809
smh102 ^{13}C, 125 MHz $CDCl_3$
O
N
O
F
NH_2
s11
220
200
180
160
140
120
100
80
60
40
20
0

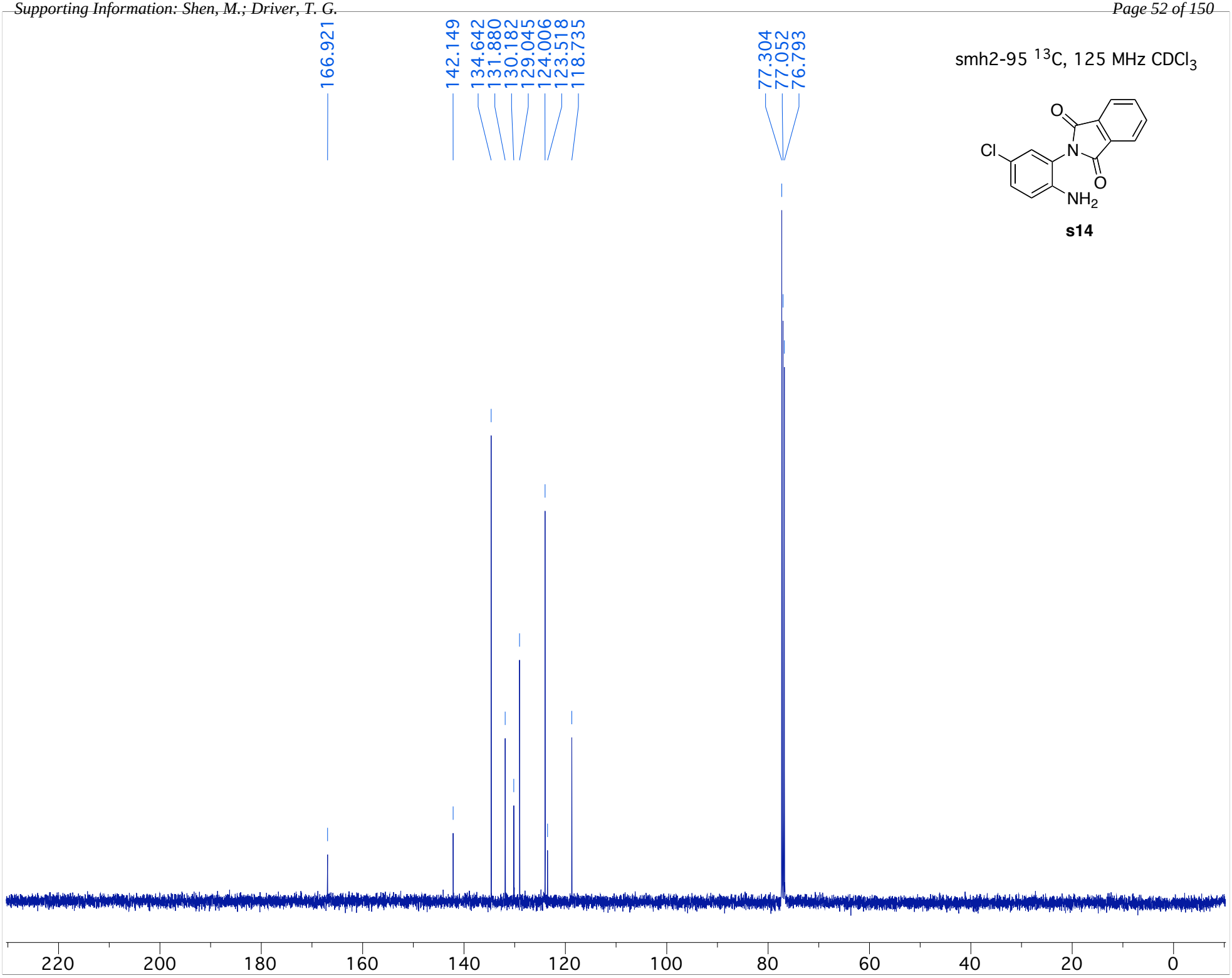

7.957
7.951
7.946
7.940
7.808
7.802
7.797
7.791
7.281
7.270
7.264
7.258
7.253
7.039
7.034
7.022
7.017
6.997
6.992
6.982
6.980
6.976
6.975
6.964
6.959
smh2-103 ^{1}H, 500 MHz $CDCl_3$
O
N
O
F
N_3
s12
2.06
0.932
2
1.13
1.03
ppm 8.0
7.8
7.6
7.4
7.2
7.0
2.06
0.932
2
1.13
1.03
ppm 11
10
9
8
7
6
5
4
3
2
1
0


166.900
164.421
162.422
139.785
139.710
134.510
132.100
132.027
131.895
123.947
118.705
112.709
112.531
107.069
106.862
77.321
77.070
76.818
smh2-103 ^{13}C, 125 MHz $CDCl_3$
O
N
O
F
N_3
s12
220
200
180
160
140
120
100
80
60
40
20
0

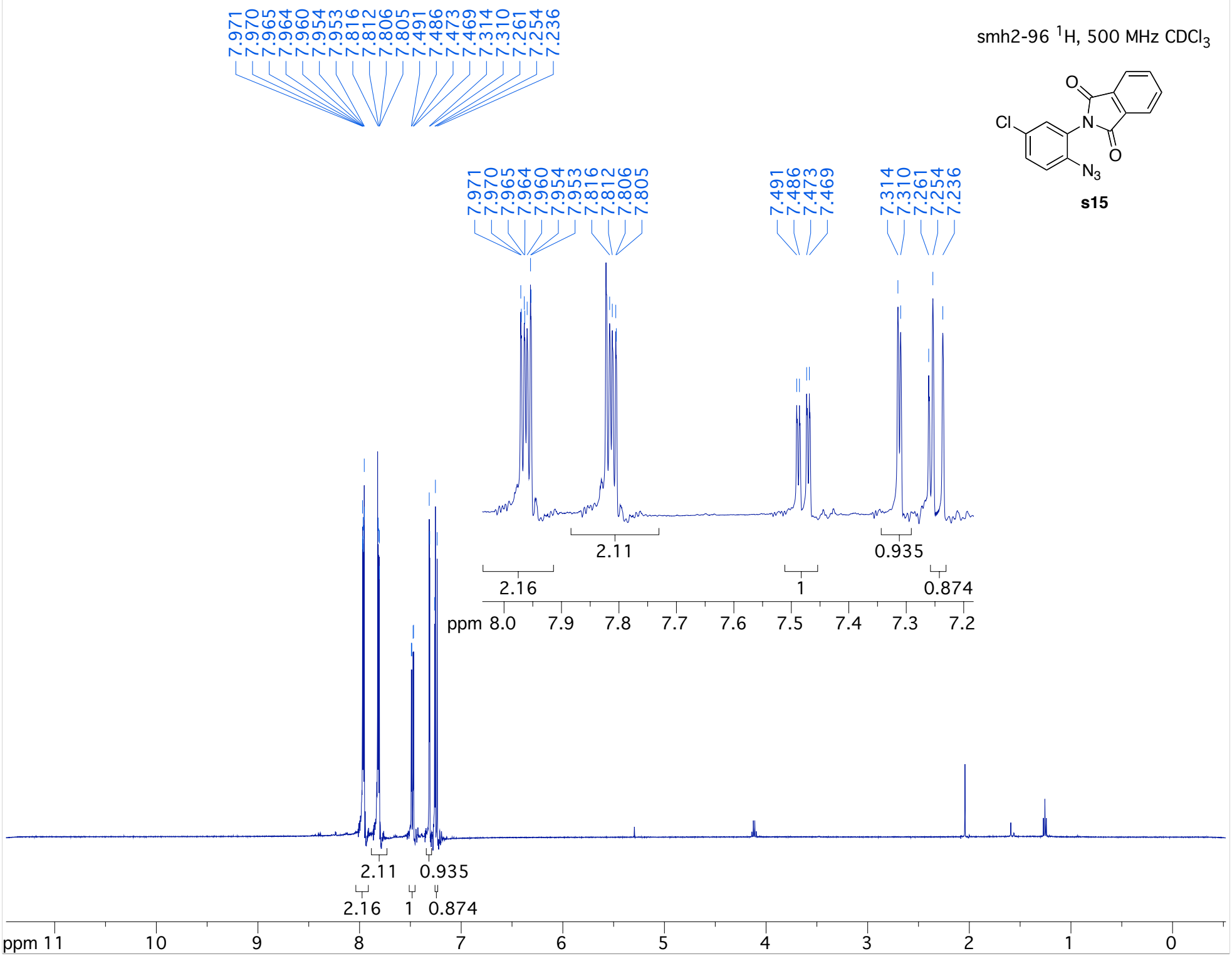

8.163
8.146
7.984
7.978
7.973
7.967
7.848
7.842
7.837
7.831
7.602
7.598
7.584
7.580
7.548
7.544
7.259
smh2-94 ^{1}H, 500 MHz $CDCl_3$
Cl
N
O
O
NO_2
s13
1.98
0.989
1
2.05
0.918
ppm 8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
1.98
0.989
12.05
0.918
ppm 11
10
9
8
7
6
5
4
3
2
1
0

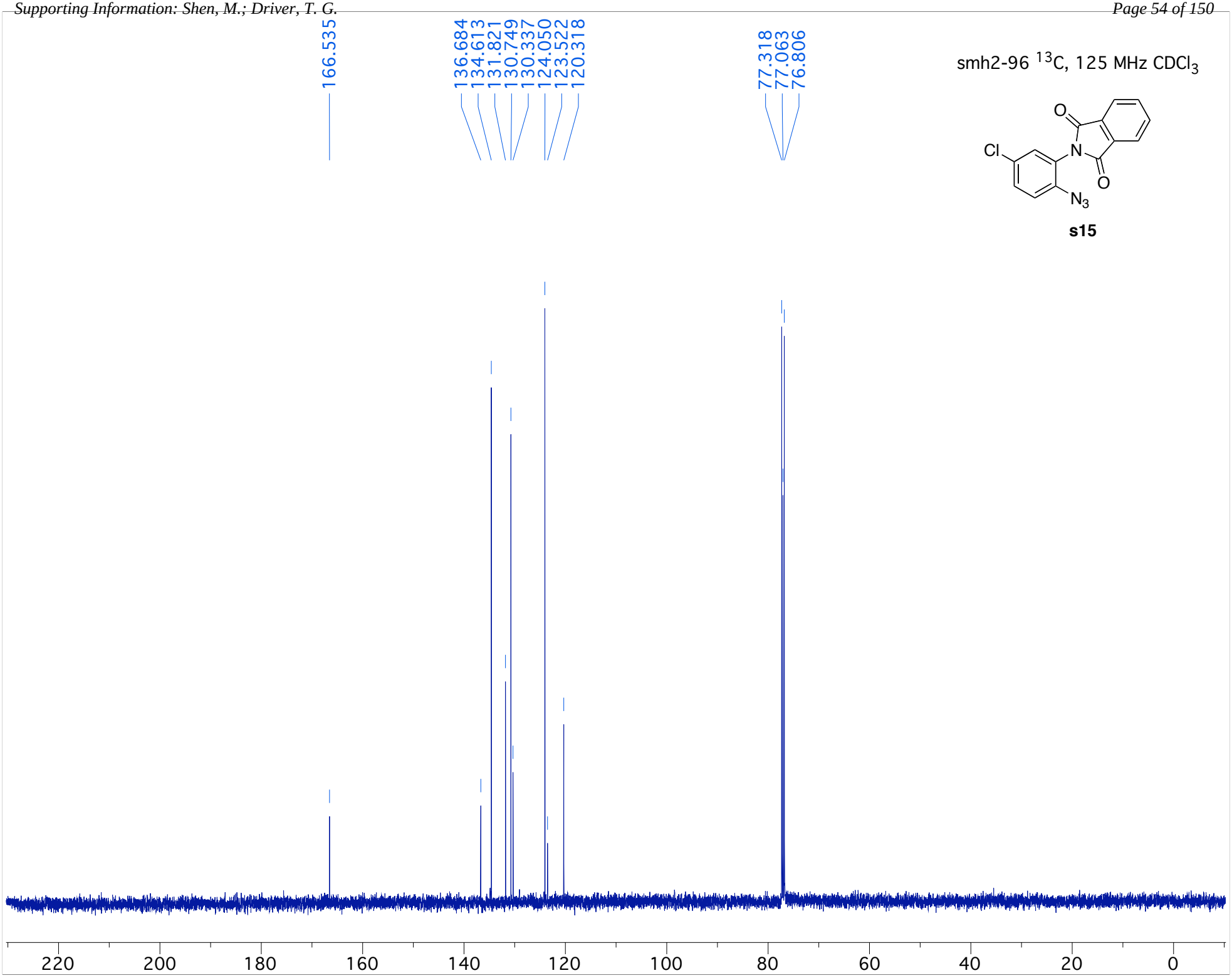

165.904
143.968
140.282
134.981
131.677
130.954
129.765
126.989
126.827
124.374
77.307
77.055
76.804
smh2-94 ^{13}C, 125 MHz $CDCl_3$
Cl
N
O
O
NO_2
s13
220
200
180
160
140
120
100
80
60
40
20
0


7.963
7.957
7.952
7.946
7.817
7.811
7.806
7.800
7.260
7.224
7.219
7.206
7.202
7.130
7.126
6.825
6.808
3.759
smh2-95 ^{1}H, 500 MHz $CDCl_3$
Cl
N
O
O
NH_2
s14
0.966
1
0.915
ppm 7.3
7.2
7.1
7.0
6.9
6.8
1.99
0.915
2.16
2.04
0.966
1
ppm 11
10
9
8
7
6
5
4
3
2
1
0

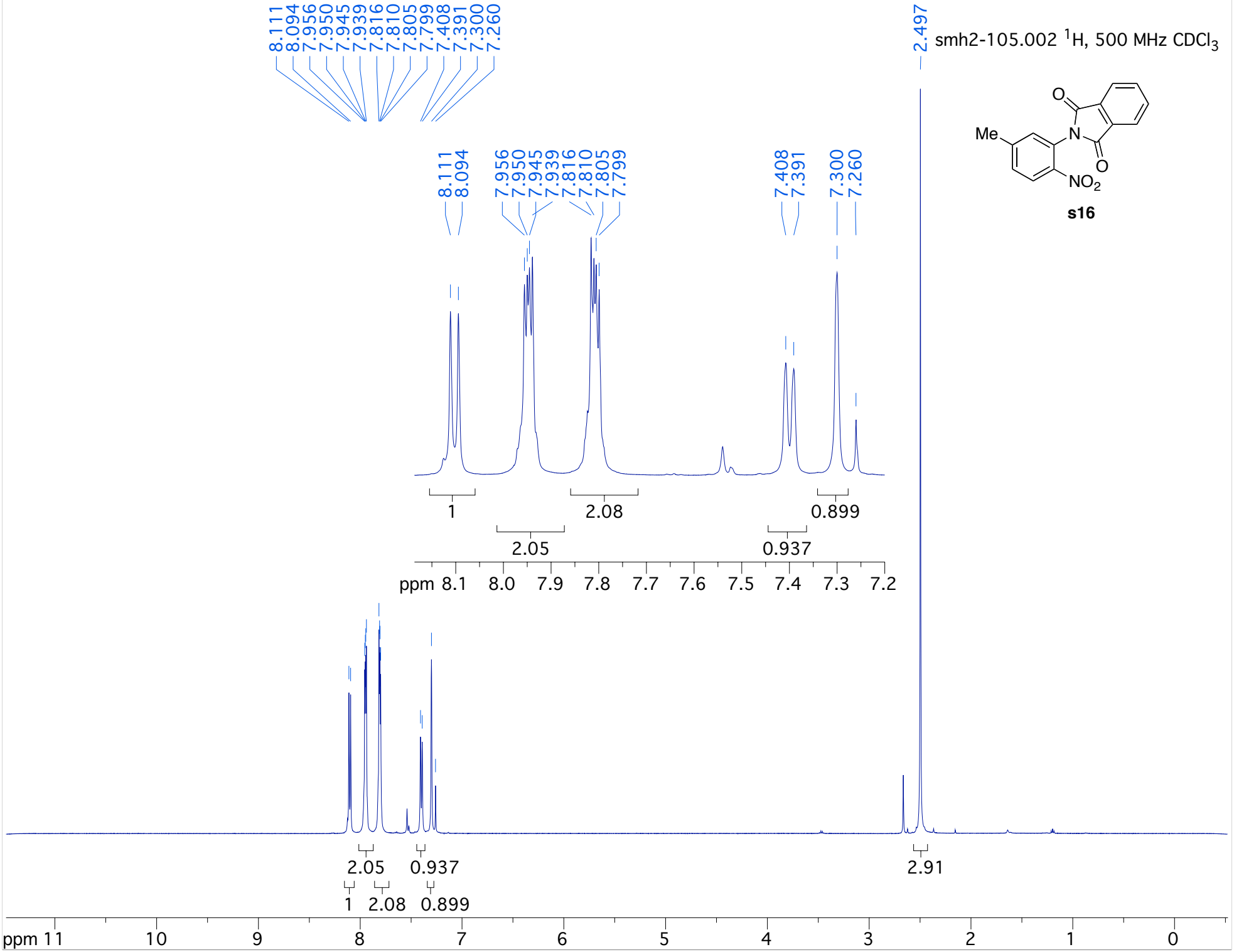

166.921
142.149
134.642
131.880
130.182
129.045
124.006
123.518
118.735
77.304
77.052
76.793
smh2-95 ^{13}C, 125 MHz $CDCl_3$
Cl
N
O
O
NH_2
220
200
180
160
140
120
100
80
60
40
20
0

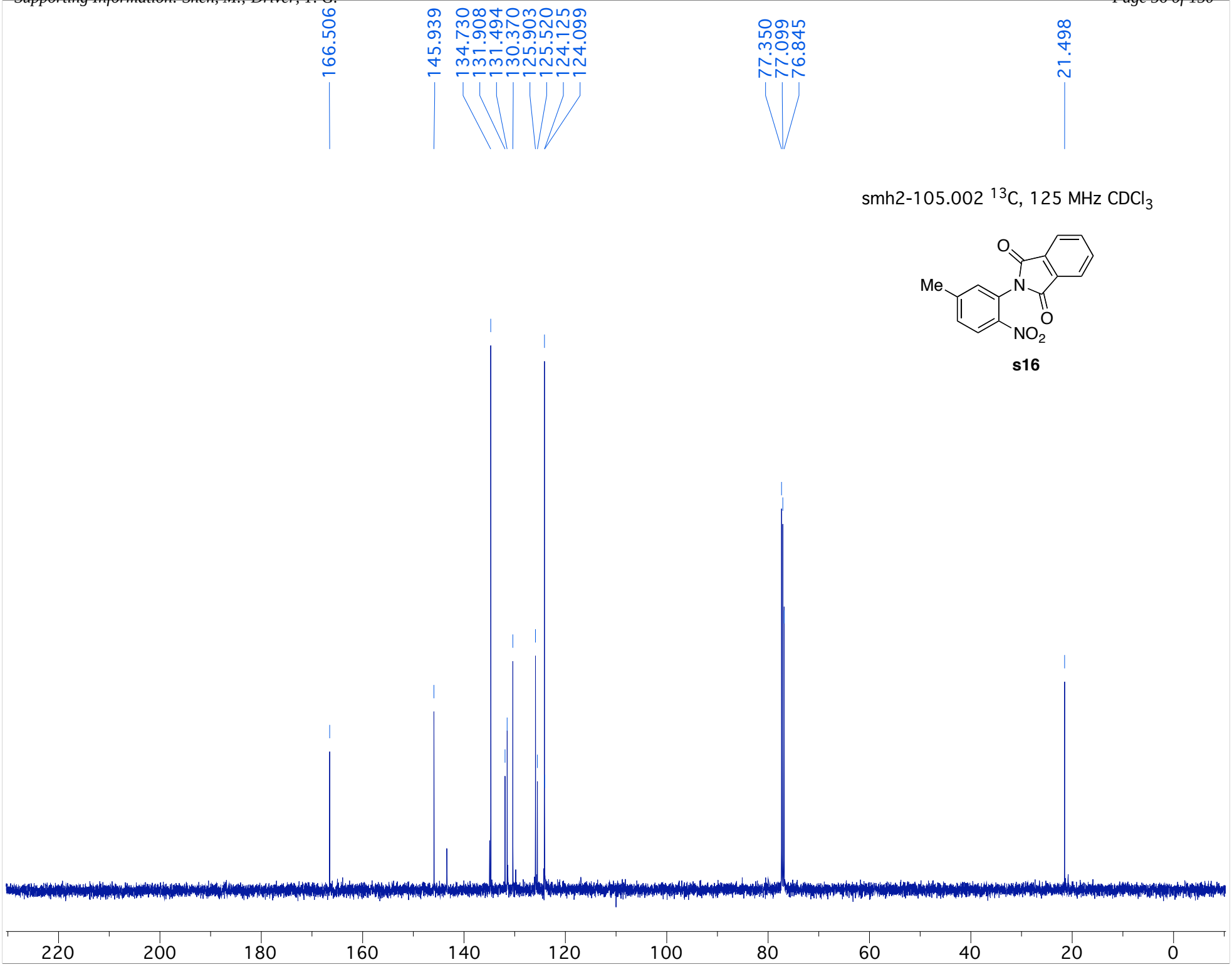
s14


7.971
7.970
7.965
7.964
7.960
7.954
7.953
7.816
7.812
7.806
7.805
7.491
7.486
7.473
7.469
7.314
7.310
7.261
7.254
7.236
smh2-96 ^{1}H, 500 MHz $CDCl_3$
Cl
N
O
O
N_3
s15
2.11
0.935
2.16
1
0.874
ppm 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
2.11
0.935
2.16
1
0.874
ppm 11 10 9 8 7 6 5 4 3 2 1 0

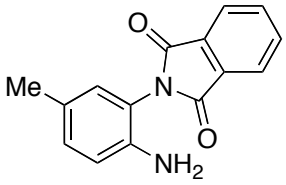

166.535
136.684
134.613
131.821
130.749
130.337
124.050
123.522
120.318
77.318
77.063
76.806
smh2-96 ^{13}C, 125 MHz $CDCl_3$
Cl
N
O
O
N_3
220
200
180
160
140
120
100
80
60
40
20
0

s15

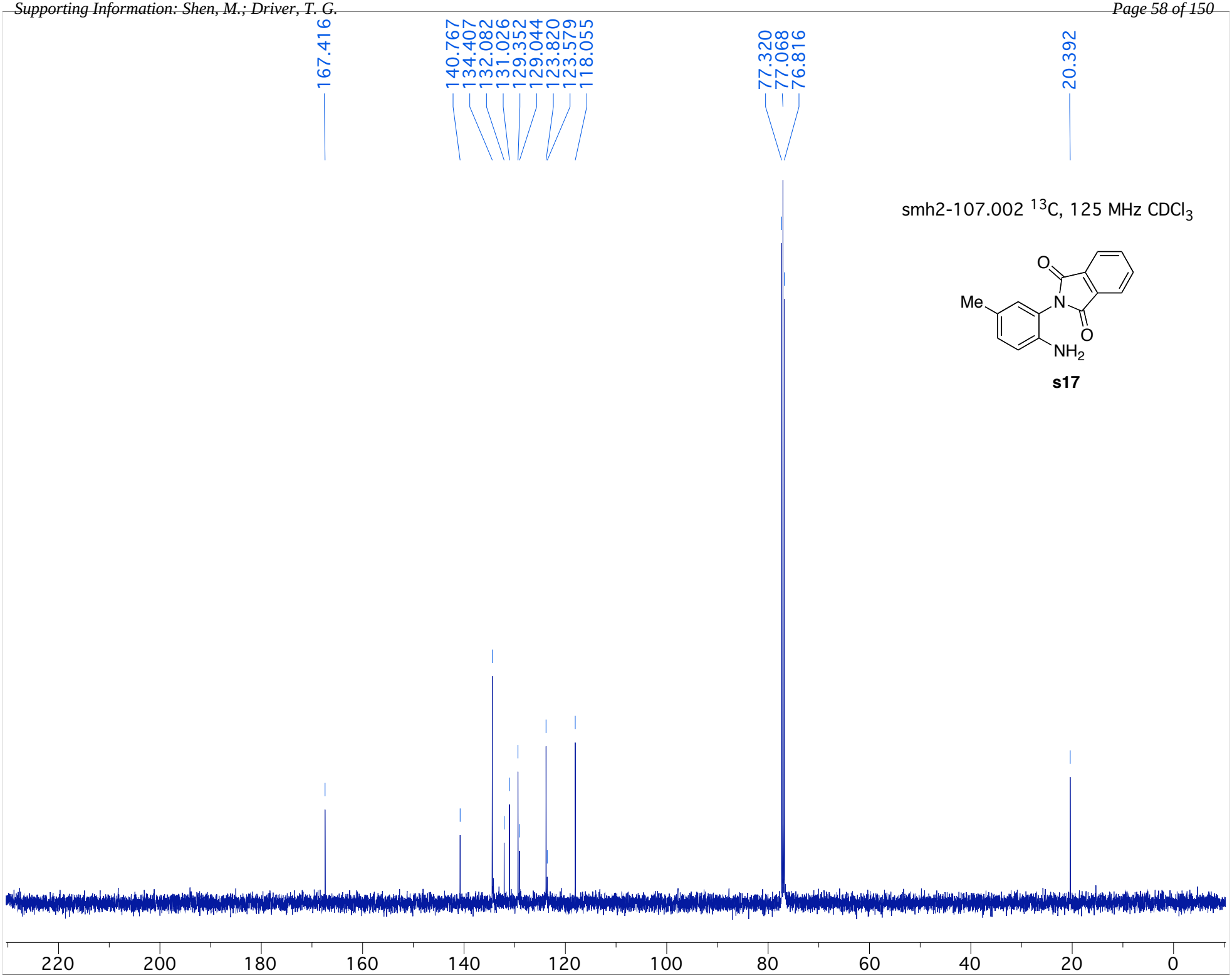

8.111
8.094
7.956
7.950
7.945
7.939
7.816
7.810
7.805
7.799
7.408
7.391
7.300
7.260
2.497
smh2-105.002 ^{1}H, 500 MHz $CDCl_3$
Me
N
O
O
NO_2
s16
1
2.08
0.899
2.05
0.937
ppm 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
2.05
0.937
2.91
1
2.08
0.899
ppm 11 10 9 8 7 6 5 4 3 2 1 0

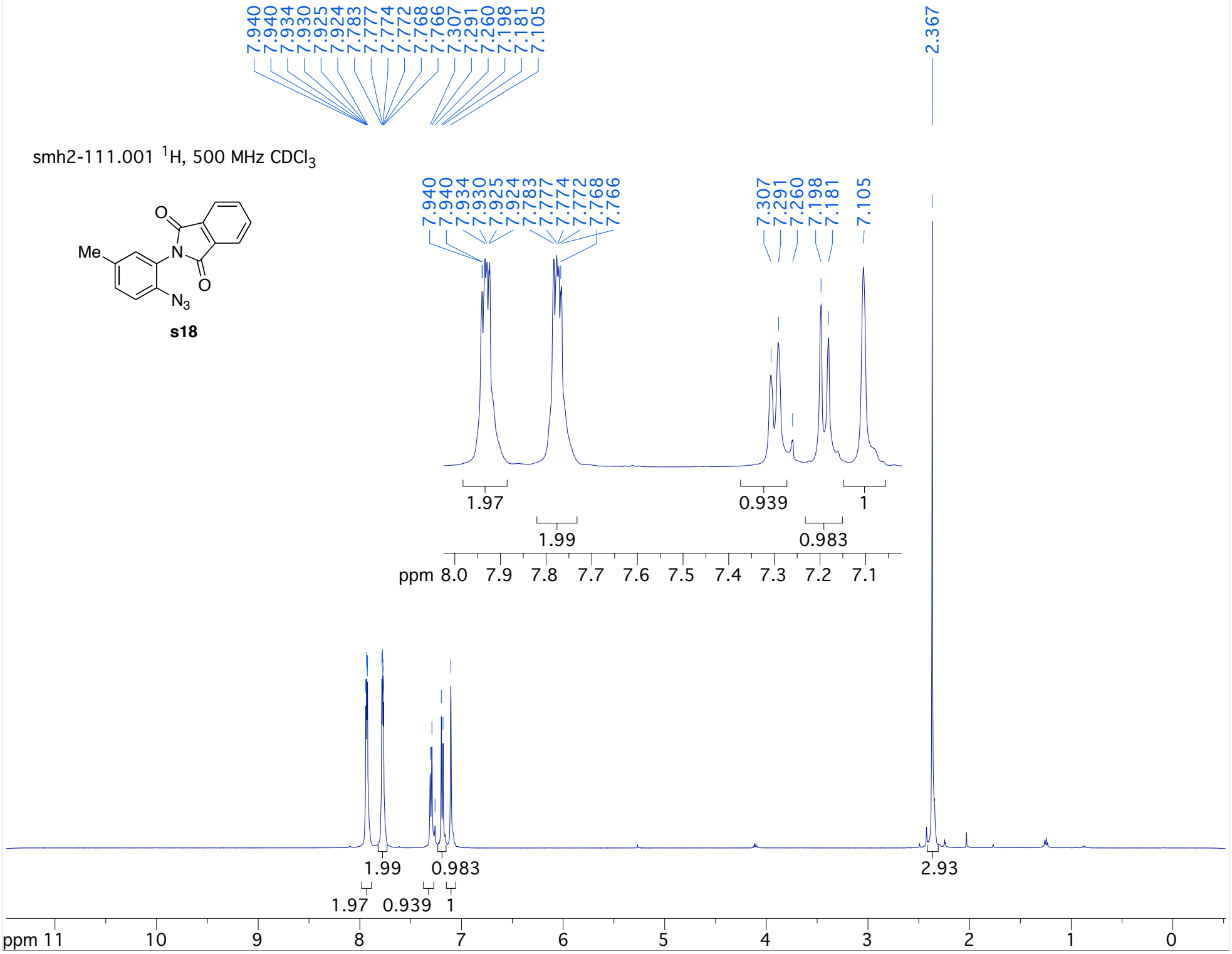

166.506
145.939
134.730
131.908
131.494
130.370
125.903
125.520
124.125
124.099
77.350
77.099
76.845
21.498
smh2-105.002 13C, 125 MHz CDCl3
Me
N
O
O
NO2
s16
220
200
180
160
140
120
100
80
60
40
20
0

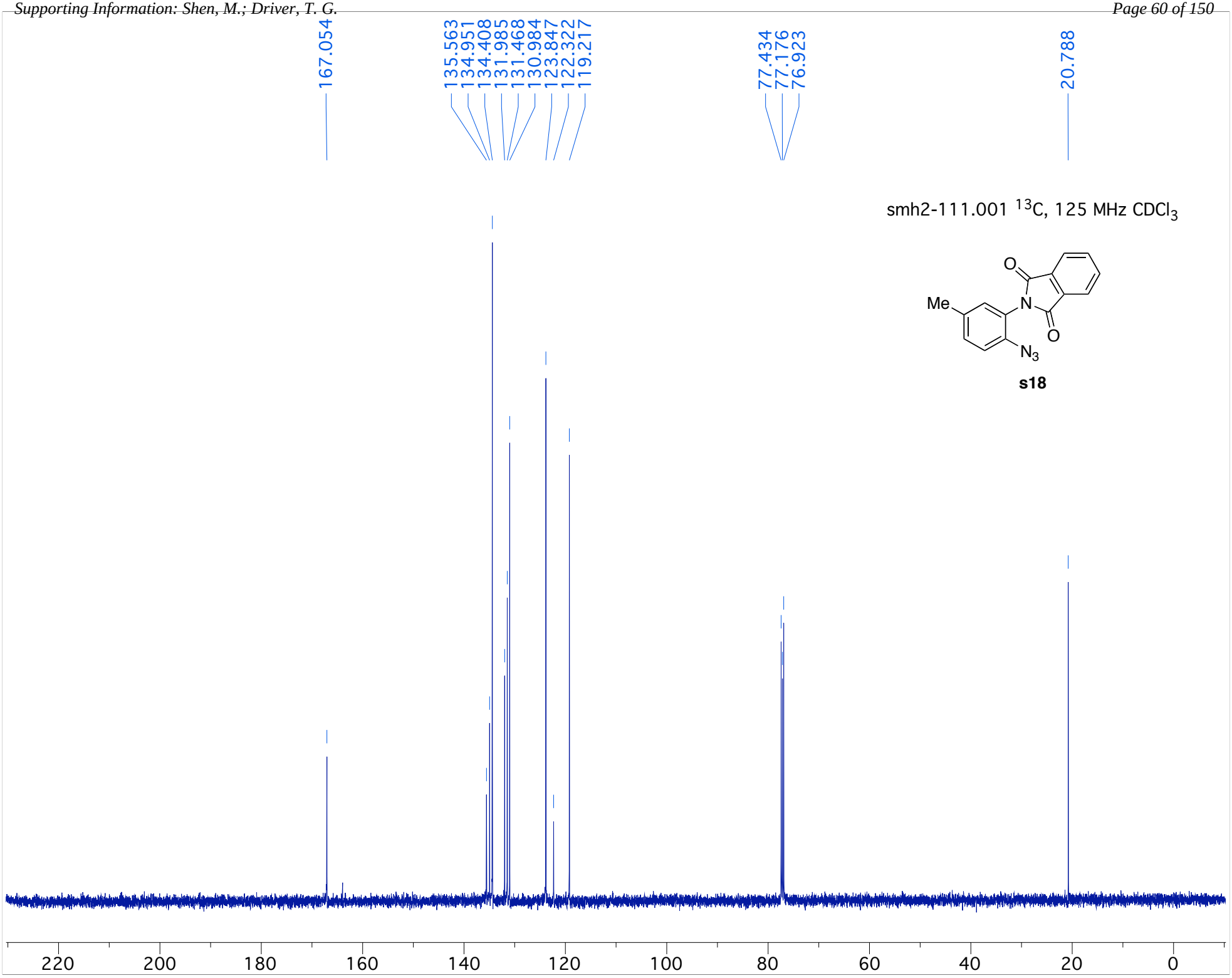
smh2-107.002 ^{1}H, 500 MHz $CDCl_3$

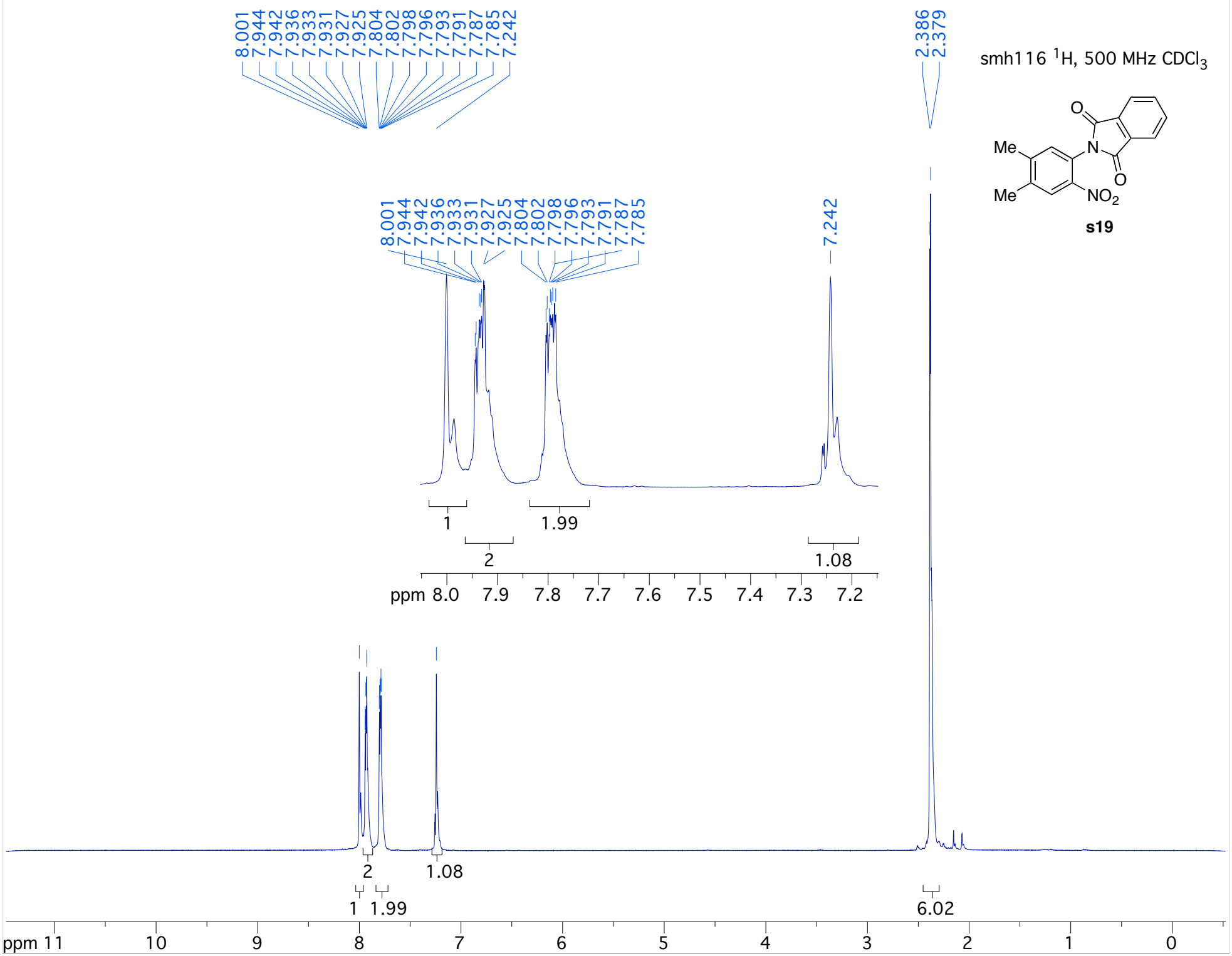


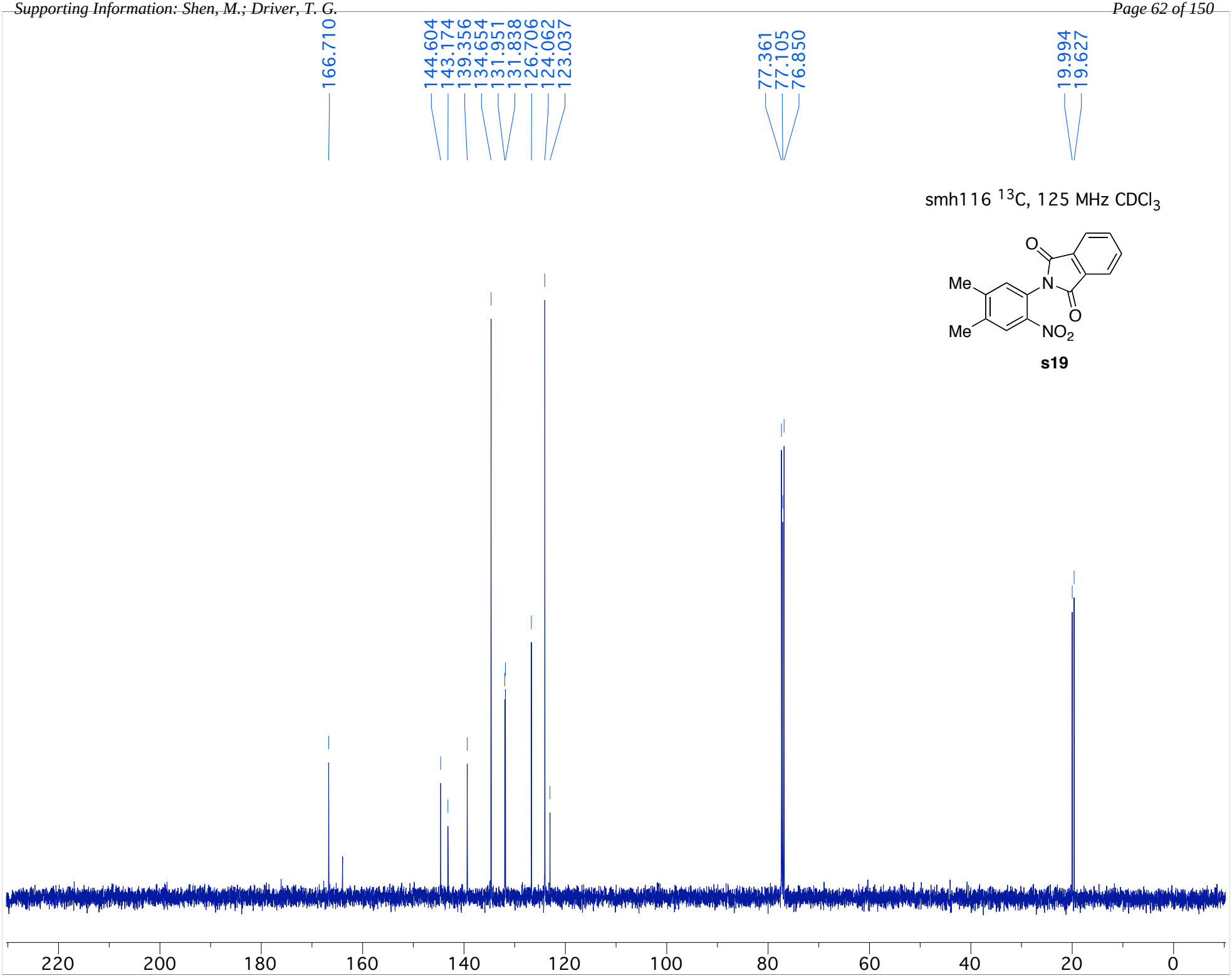
s17

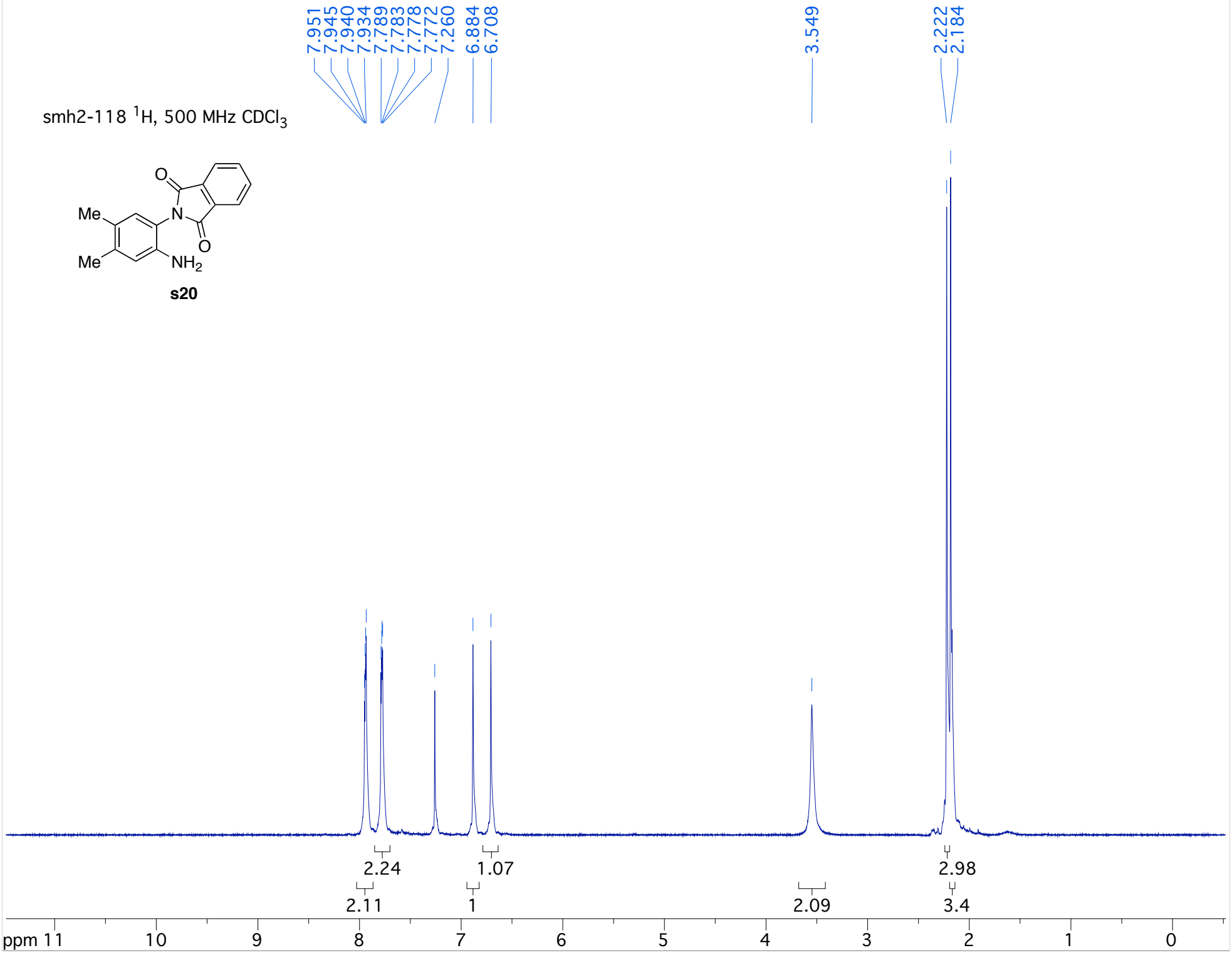

167.416
140.767
134.407
132.082
131.026
129.352
129.044
123.820
123.579
118.055
77.320
77.068
76.816
20.392
smh2-107.002 ^{13}C, 125 MHz $CDCl_3$
Me
O
N
O
NH_2
s17
220
200
180
160
140
120
100
80
60
40
20
0

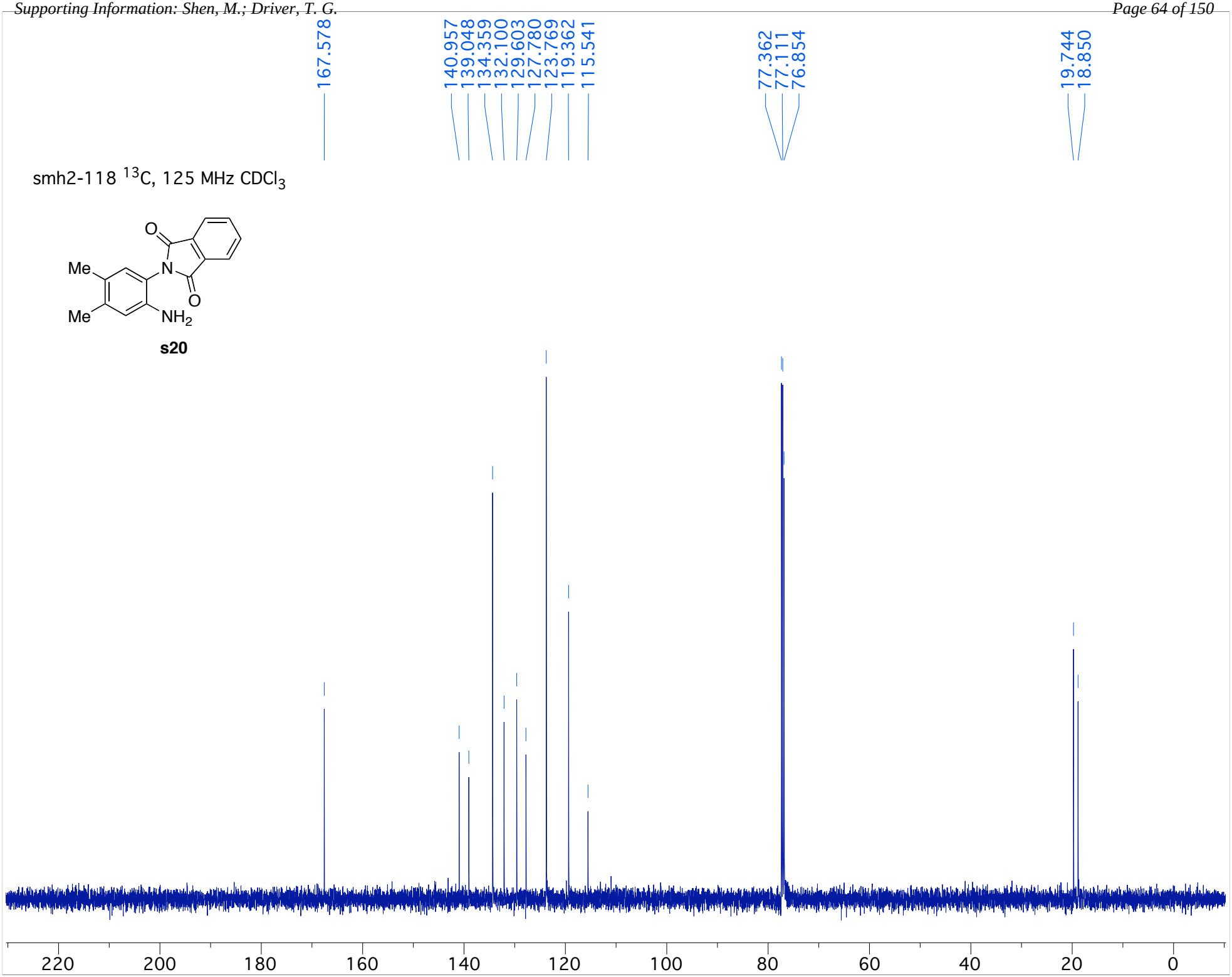

7.940
7.940
7.934
7.930
7.925
7.924
7.783
7.777
7.774
7.772
7.768
7.766
7.307
7.291
7.260
7.198
7.181
7.105
2.367
smh2-111.001 ^{1}H, 500 MHz $CDCl_3$
Me
N
O
O
N_3
s18
1.97
0.939
1
1.99
0.983
ppm 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
1.99
0.983
2.93
1.97
0.939
1
ppm 11 10 9 8 7 6 5 4 3 2 1 0


167.054
135.563
134.951
134.408
131.985
131.468
130.984
123.847
122.322
119.217
77.434
77.176
76.923
20.788
smh2-111.001 ^{13}C, 125 MHz $CDCl_3$
Me
N
O
O
N_3
s18
220
200
180
160
140
120
100
80
60
40
20
0

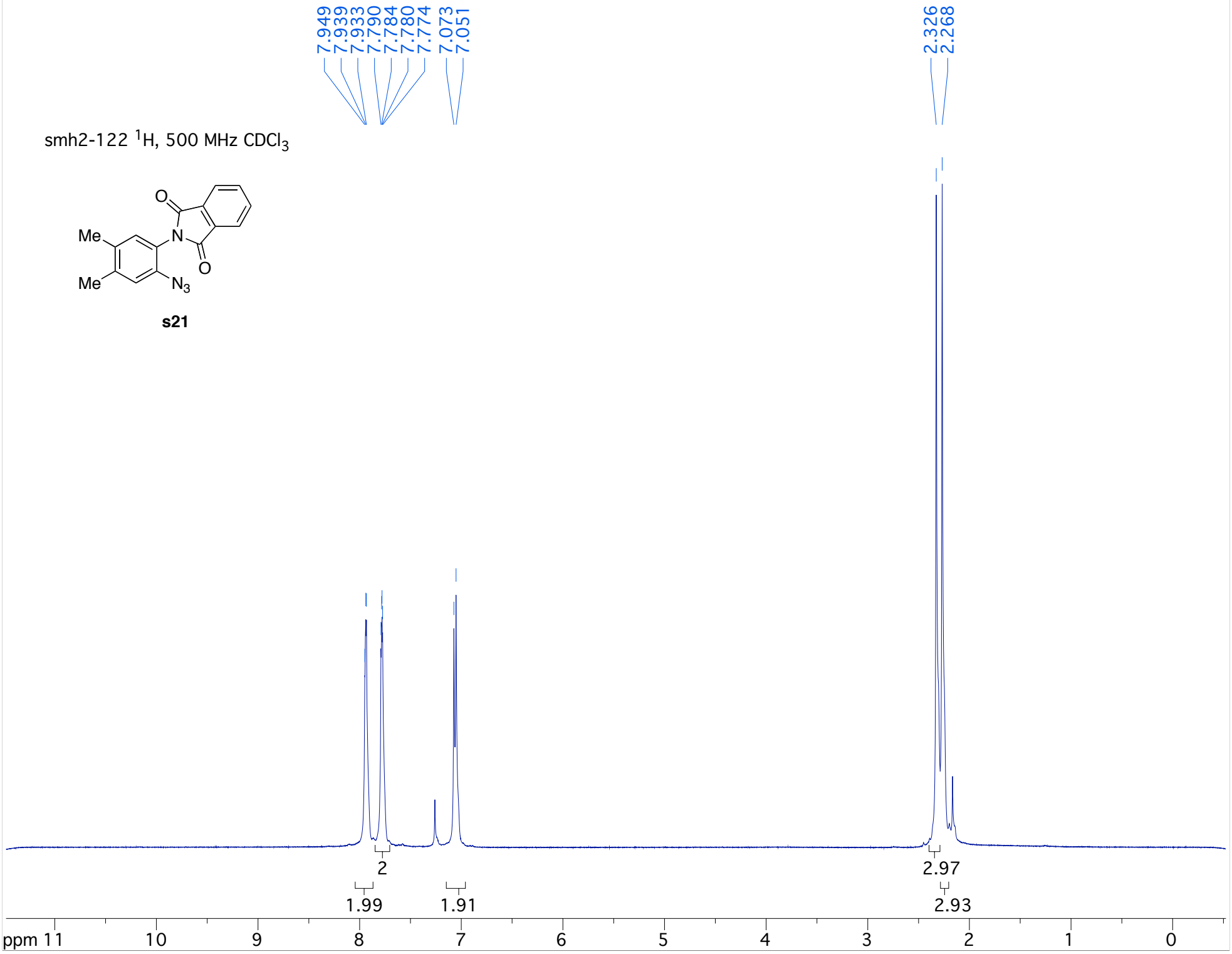

8.001
7.944
7.942
7.936
7.933
7.931
7.927
7.925
7.804
7.802
7.798
7.796
7.793
7.791
7.787
7.785
7.242
2.386
2.379
smh116 ^{1}H, 500 MHz $CDCl_3$
Me
Me
N
O
O
O
NO_2
s19
1
1.99
2
1.08
ppm 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
2
1.08
1
1.99
6.02
ppm 11 10 9 8 7 6 5 4 3 2 1 0


166.710
144.604
143.174
139.356
134.654
131.951
131.838
126.706
124.062
123.037
77.361
77.105
76.850
19.994
19.627
smh116 13C, 125 MHz CDCl3
O
N
O
Me
Me
NO2
s19
220
200
180
160
140
120
100
80
60
40
20
0

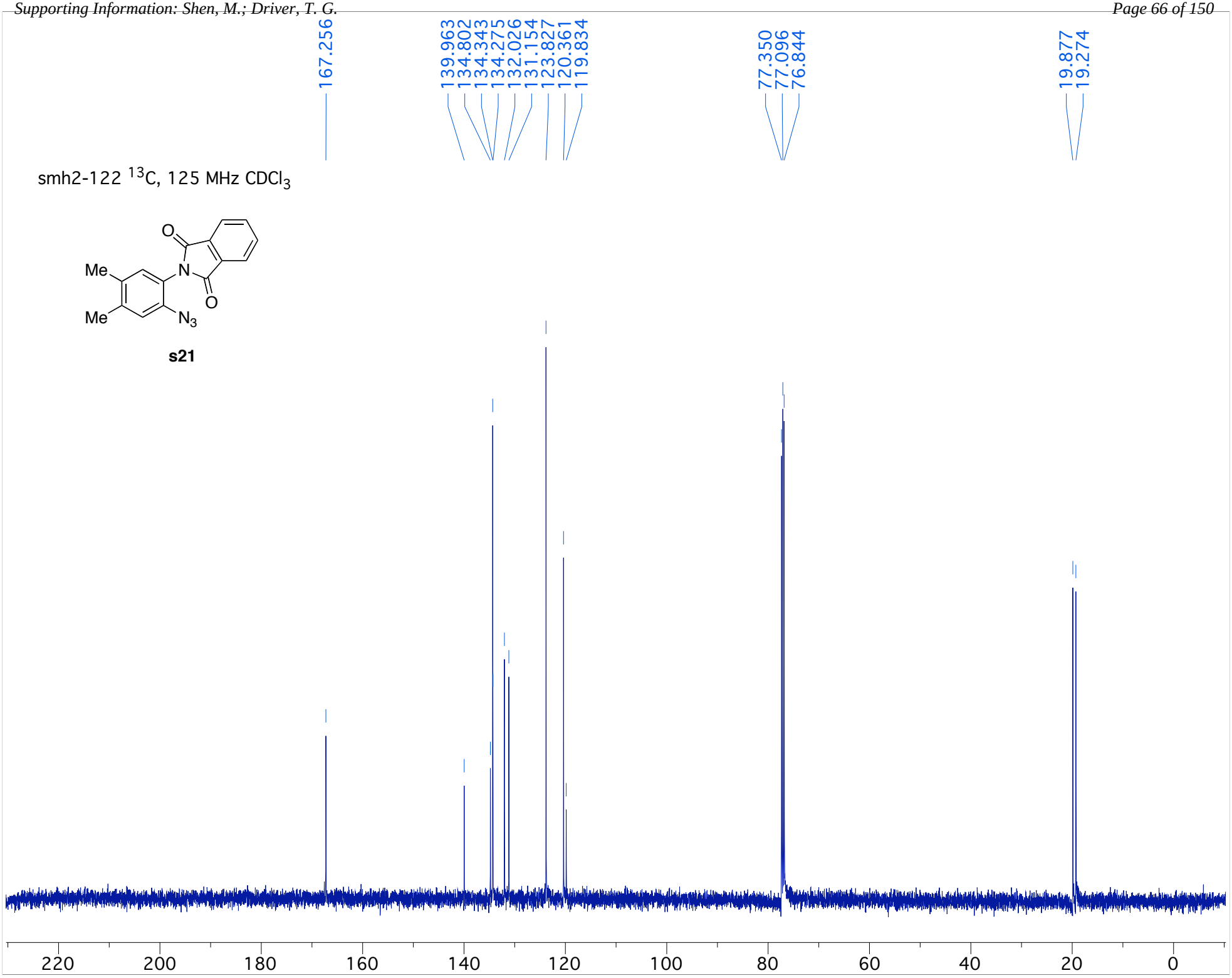

7.951
7.945
7.940
7.934
7.789
7.783
7.778
7.772
7.260
6.884
6.708
3.549
2.222
2.184
smh2-118 ^{1}H, 500 MHz $CDCl_3$
O
N
O
Me
Me
NH_2
s20
2.24
1.07
2.98
2.11
1
2.09
3.4
ppm 11
10
9
8
7
6
5
4
3
2
1
0


167.578
140.957
139.048
134.359
132.100
129.603
127.780
123.769
119.362
115.541
77.362
77.111
76.854
19.744
18.850
smh2-118 ^{13}C, 125 MHz $CDCl_3$
O
N
O
Me
Me
NH_2
220
200
180
160
140
120
100
80
60
40
20
0

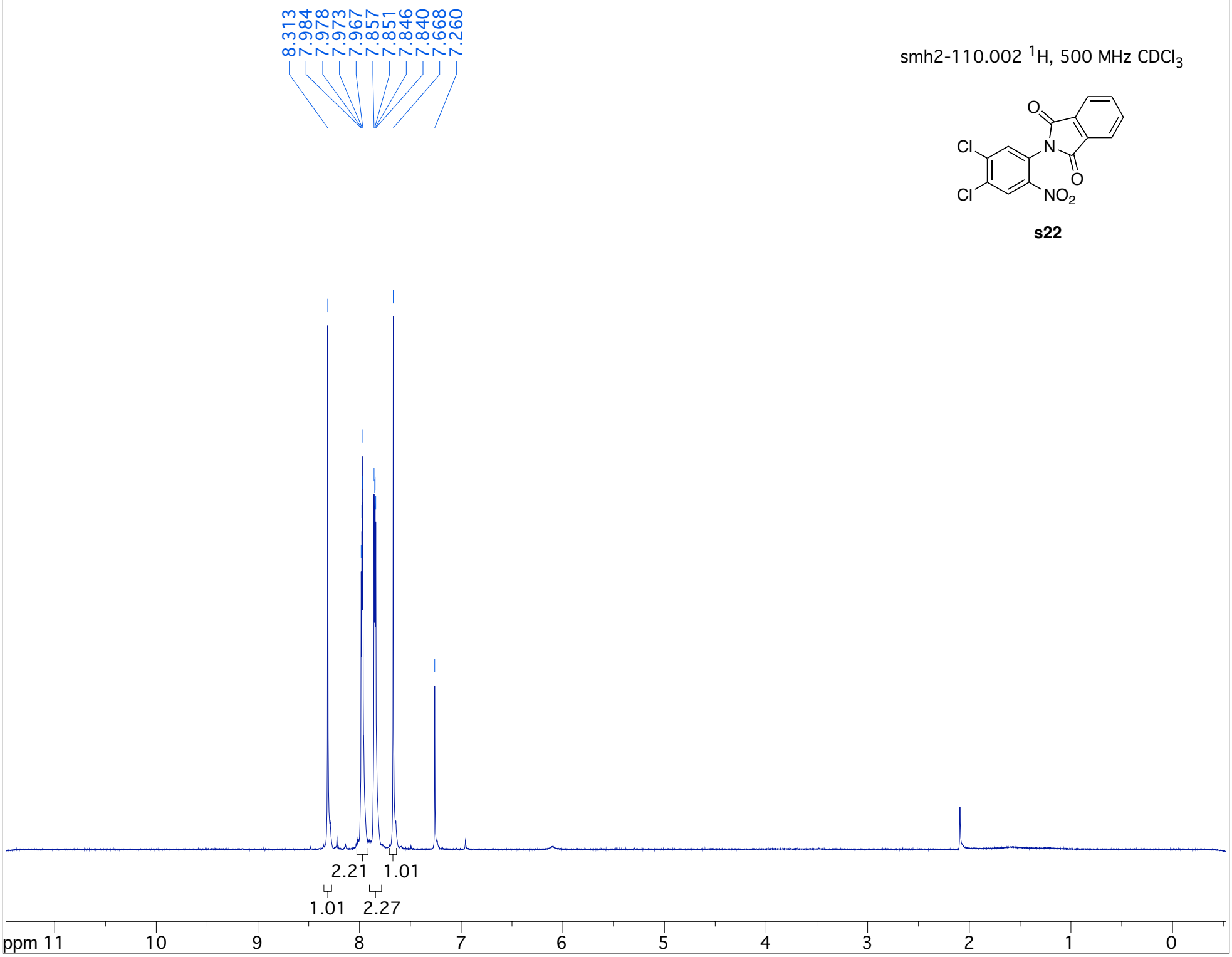
s20

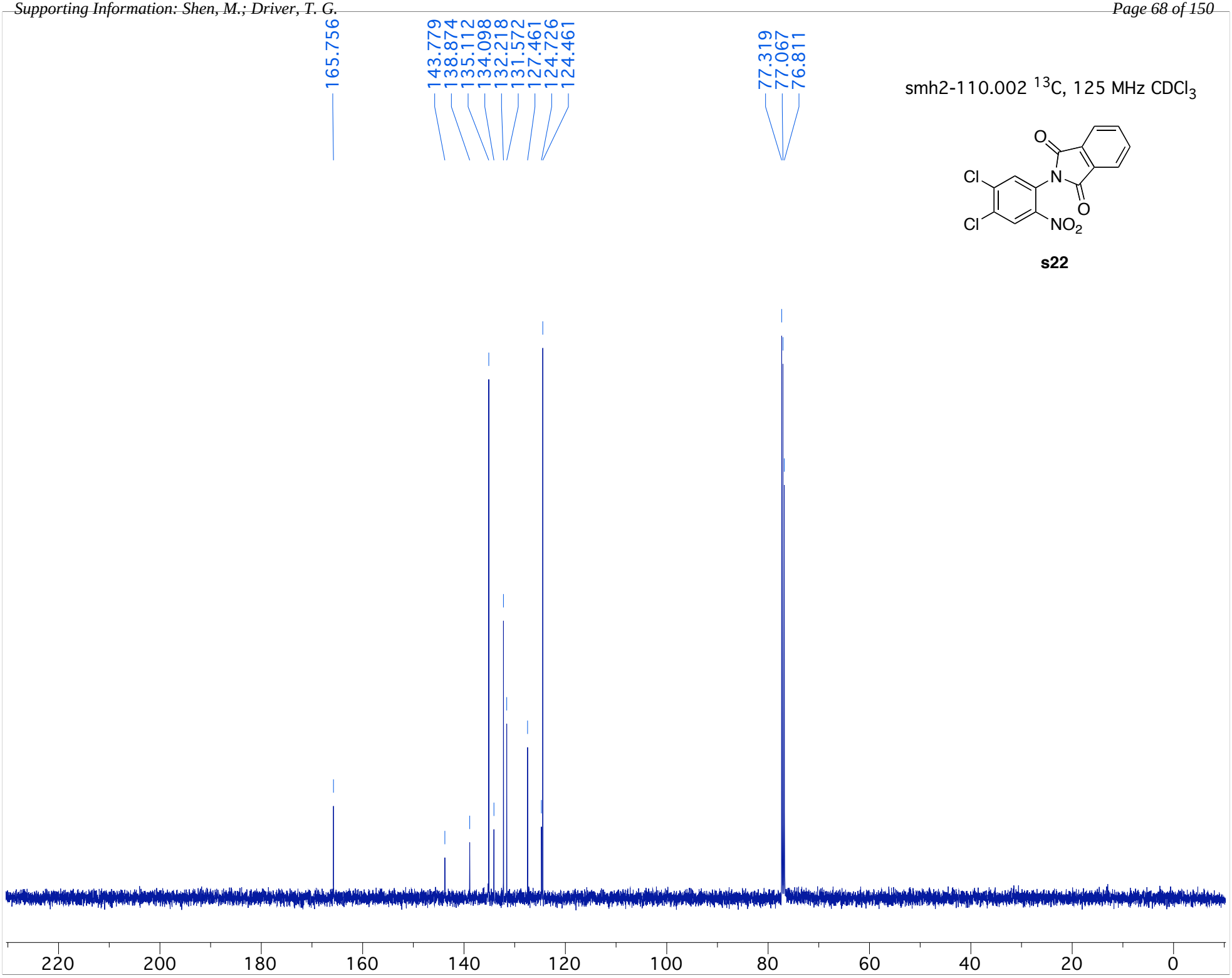

7.949
7.939
7.933
7.790
7.784
7.780
7.774
7.073
7.051
2.326
2.268
smh2-122 ^{1}H, 500 MHz $CDCl_3$
O
N
O
Me
Me
N_3
2
1.99
1.91
2.97
2.93
ppm 11
10
9
8
7
6
5
4
3
2
1
0

s21

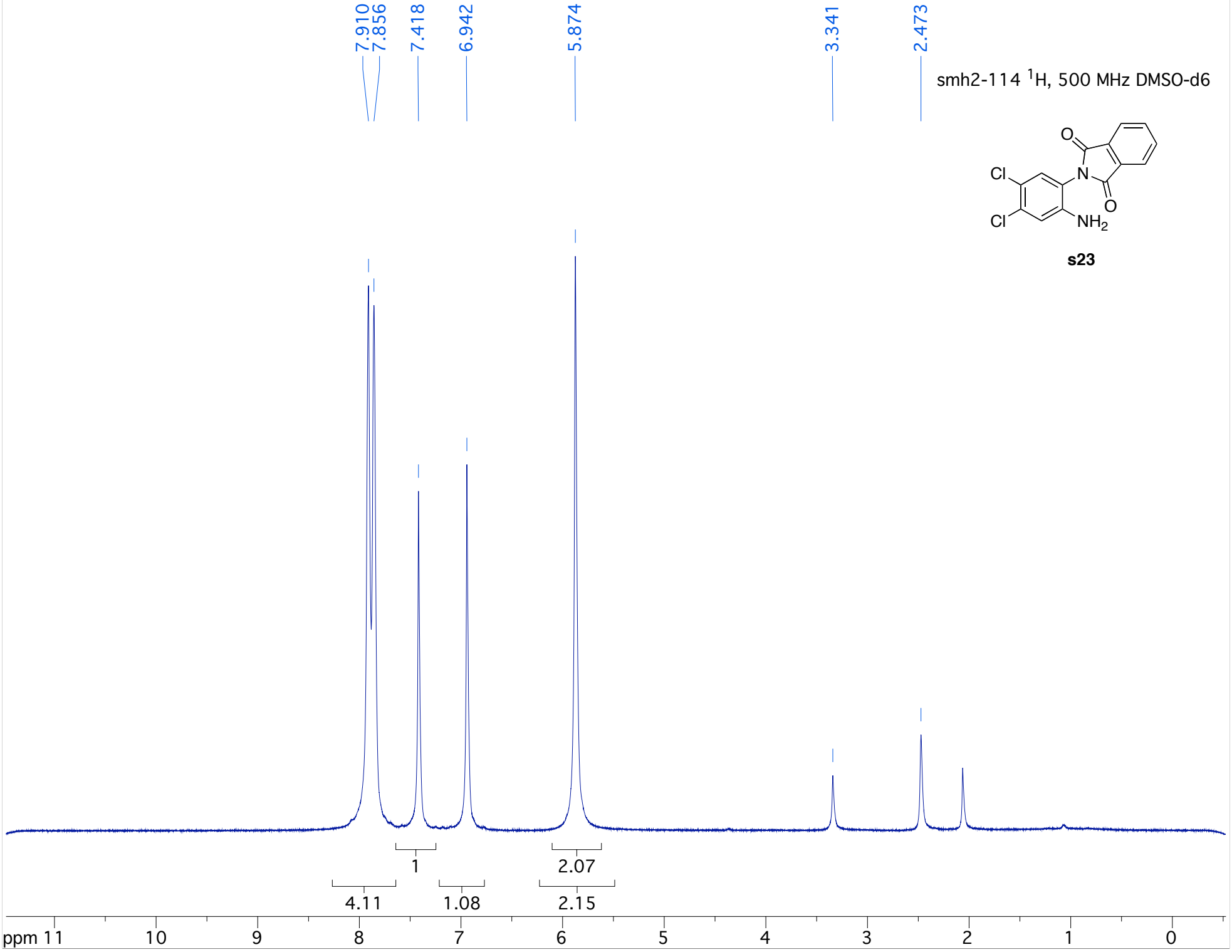

167.256
139.963
134.802
134.343
134.275
132.026
131.154
123.827
120.361
119.834
77.350
77.096
76.844
19.877
19.274
smh2-122 ^{13}C, 125 MHz $CDCl_3$
O
N
O
Me
Me
N_3
220
200
180
160
140
120
100
80
60
40
20
0

s21

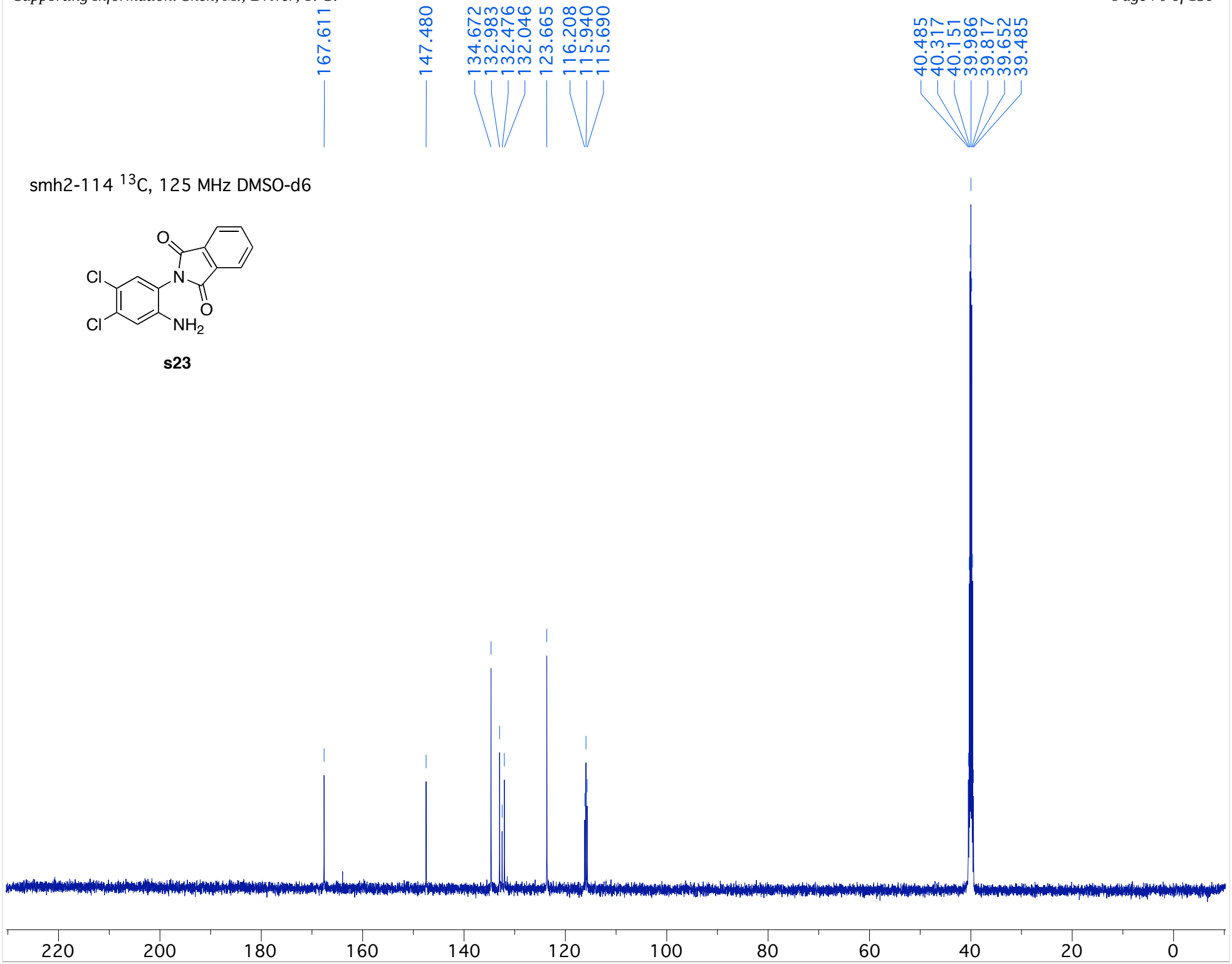

8.313
7.984
7.978
7.973
7.967
7.857
7.851
7.846
7.840
7.668
7.260
smh2-110.002 ^{1}H, 500 MHz $CDCl_3$
O
N
O
Cl
Cl
NO_2
s22
2.21
1.01
1.01
2.27
ppm 11
10
9
8
7
6
5
4
3
2
1
0

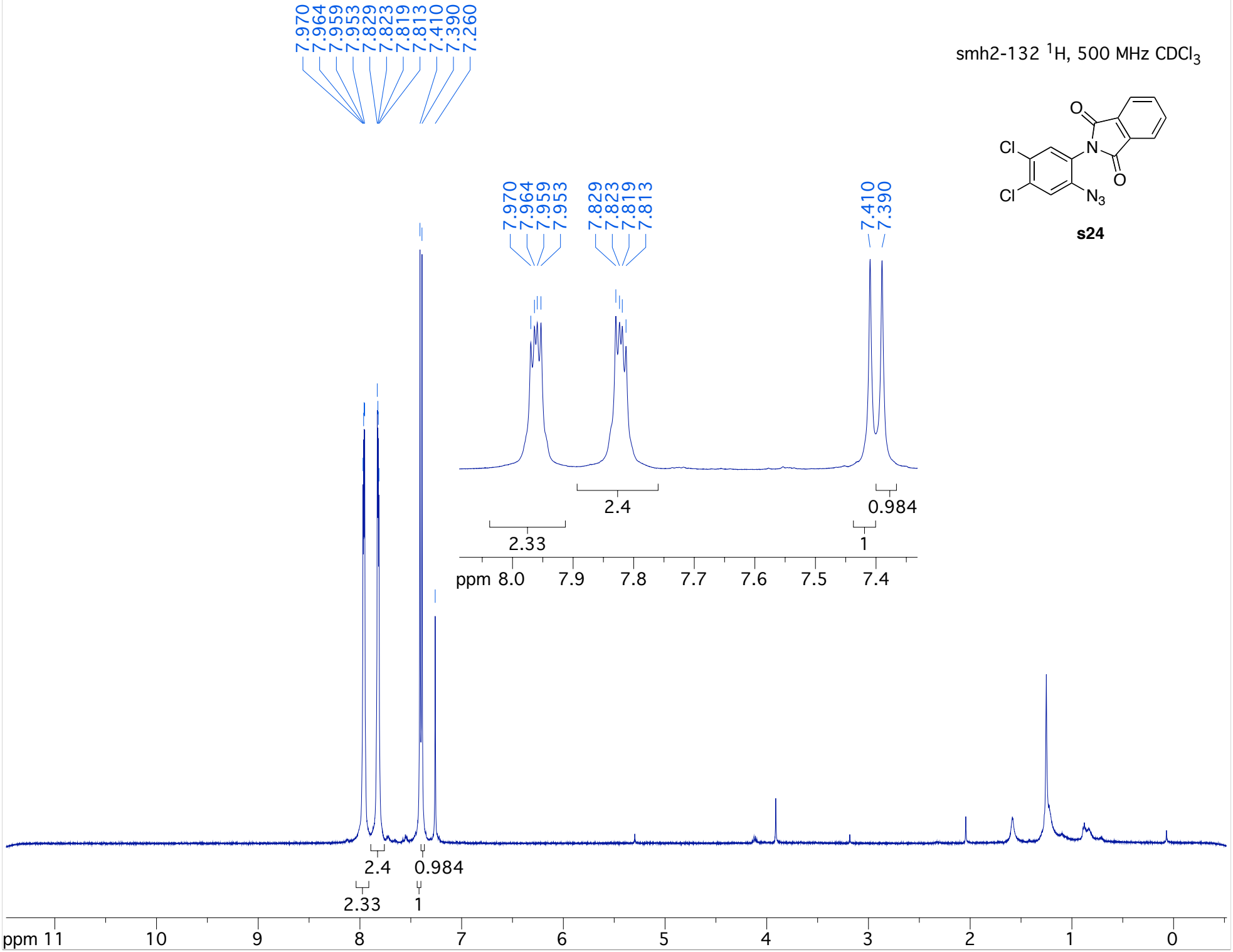

165.756
143.779
138.874
135.112
134.098
132.218
131.572
127.461
124.726
124.461
77.319
77.067
76.811
smh2-110.002 ^{13}C, 125 MHz $CDCl_3$
O
N
O
Cl
Cl
NO_2
220
200
180
160
140
120
100
80
60
40
20
0

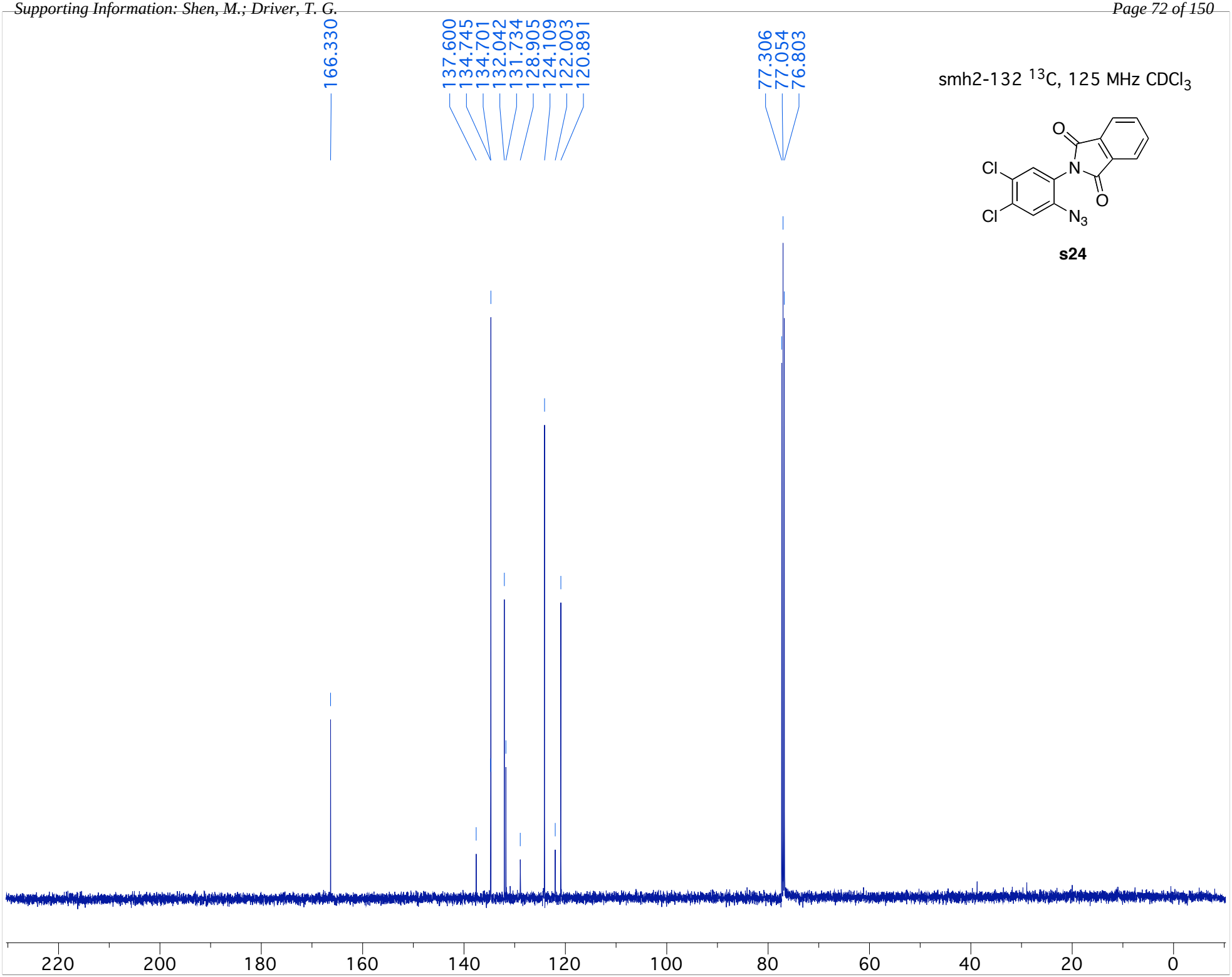
s22


7.910
7.856
7.418
6.942
5.874
3.341
2.473
smh2-114 ^{1}H, 500 MHz DMSO-d6
O
N
O
Cl
Cl
NH$_2$
1
2.07
4.11
1.08
2.15
ppm 11
10
9
8
7
6
5
4
3
2
1
0

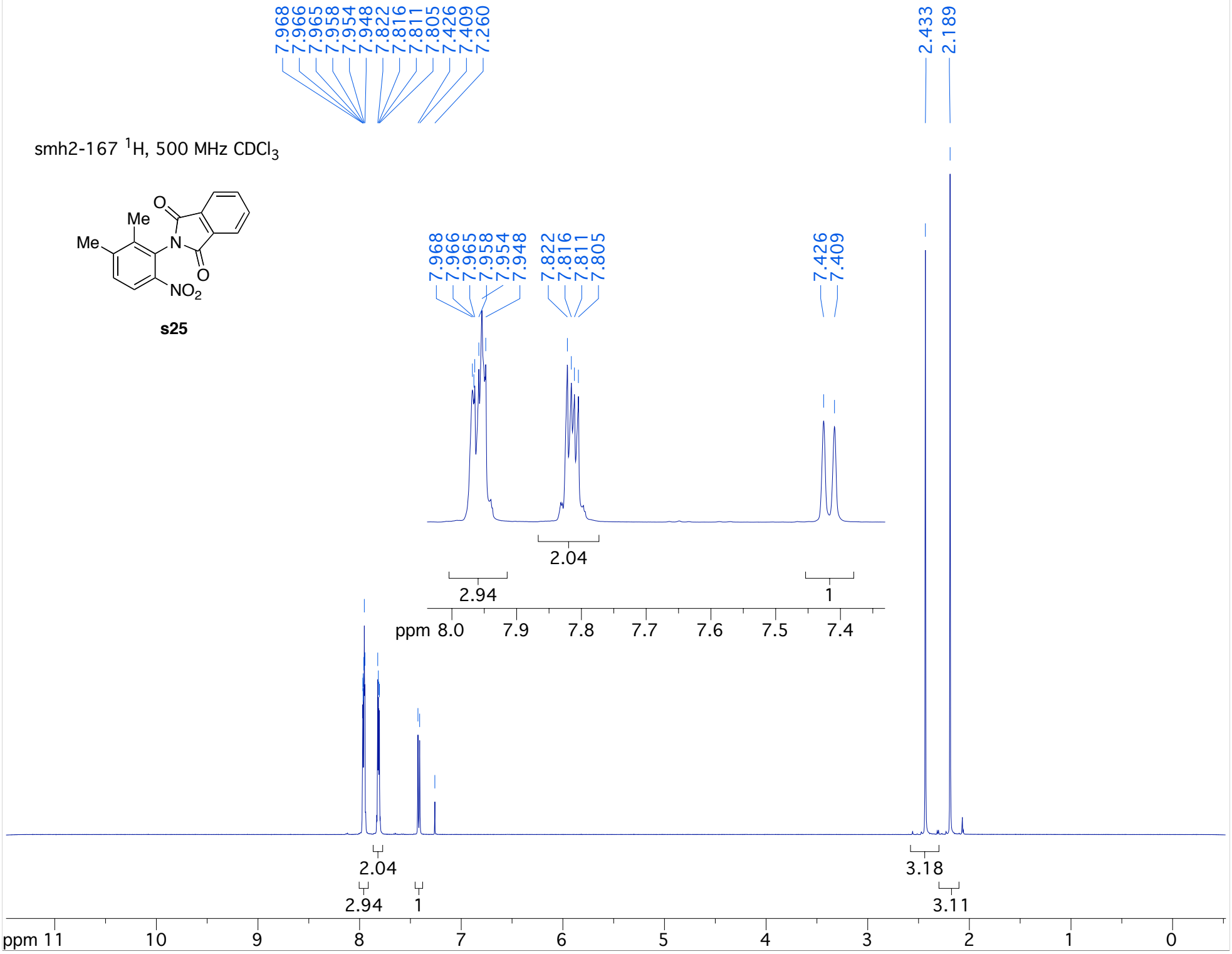
s23


167.611
147.480
134.672
132.983
132.476
132.046
123.665
116.208
115.940
115.690
40.485
40.317
40.151
39.986
39.817
39.652
39.485
smh2-114 13C, 125 MHz DMSO-d6
O
N
O
Cl
Cl
NH2
s23
220
200
180
160
140
120
100
80
60
40
20
0


7.970
7.964
7.959
7.953
7.829
7.823
7.819
7.813
7.410
7.390
7.260
smh2-132 ^{1}H, 500 MHz $CDCl_3$
O
N
O
Cl
Cl
N_3
s24
2.4
0.984
2.33
1
ppm 8.0 7.9 7.8 7.7 7.6 7.5 7.4
2.4
0.984
2.33
1
ppm 11 10 9 8 7 6 5 4 3 2 1 0

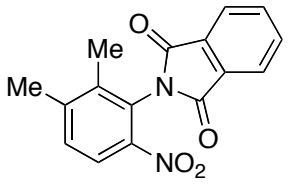

166.330
137.600
134.745
134.701
132.042
131.734
128.905
124.109
122.003
120.891
77.306
77.054
76.803
smh2-132 ^{13}C, 125 MHz $CDCl_3$
O
N
O
Cl
Cl
N_3
220
200
180
160
140
120
100
80
60
40
20
0

s24

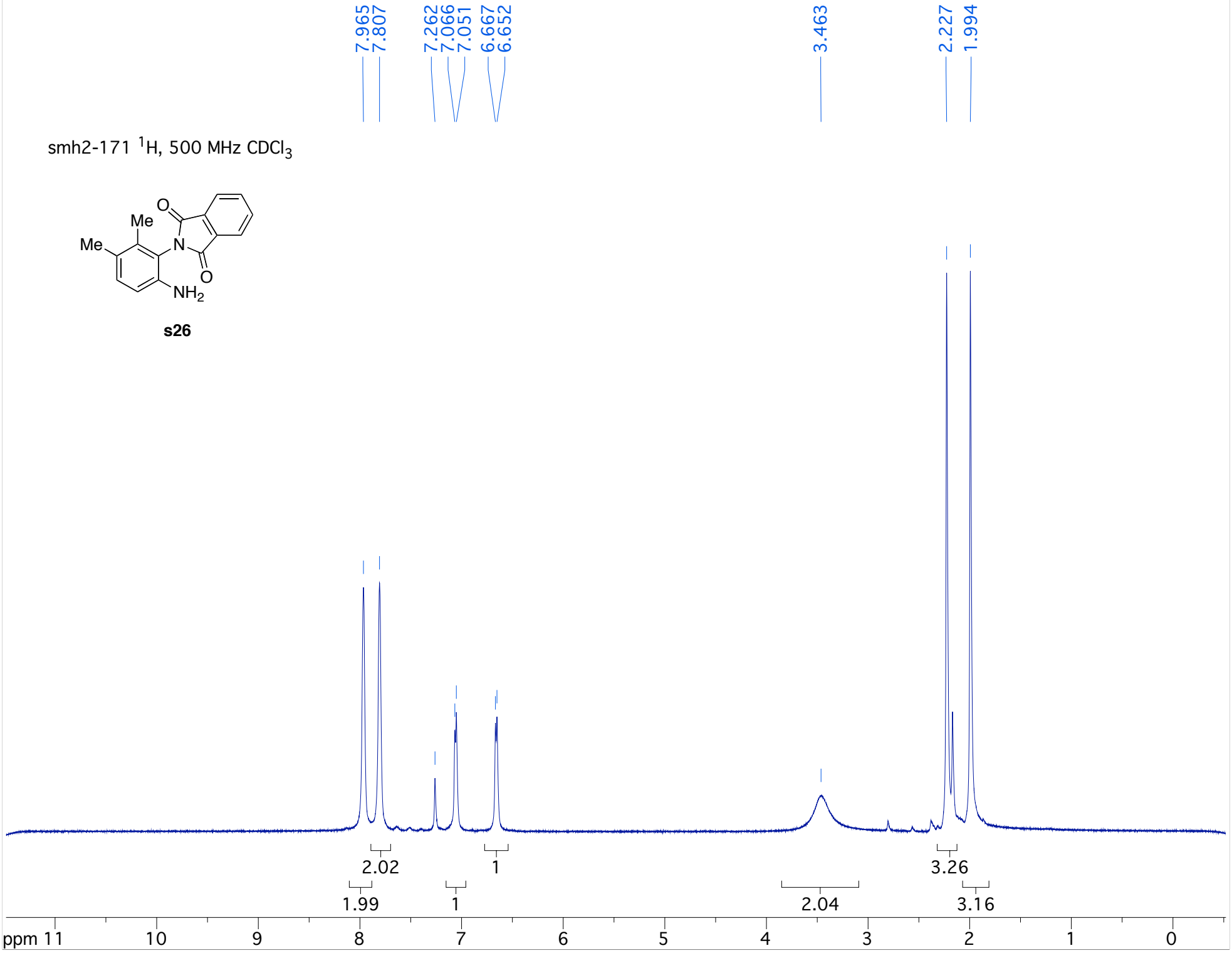

7.968
7.966
7.965
7.958
7.954
7.948
7.822
7.816
7.811
7.805
7.426
7.409
7.260
2.433
2.189
smh2-167 ^{1}H, 500 MHz $CDCl_3$
Me
Me
N
O
O
NO_2
s25
2.04
2.94
1
ppm 8.0 7.9 7.8 7.7 7.6 7.5 7.4
2.04
2.94
1
3.18
3.11
ppm 11 10 9 8 7 6 5 4 3 2 1 0

166.830
145.134
144.720
139.110
134.672
132.117
131.058
124.524
124.124
123.198
77.357
77.100
76.849
21.131
14.987

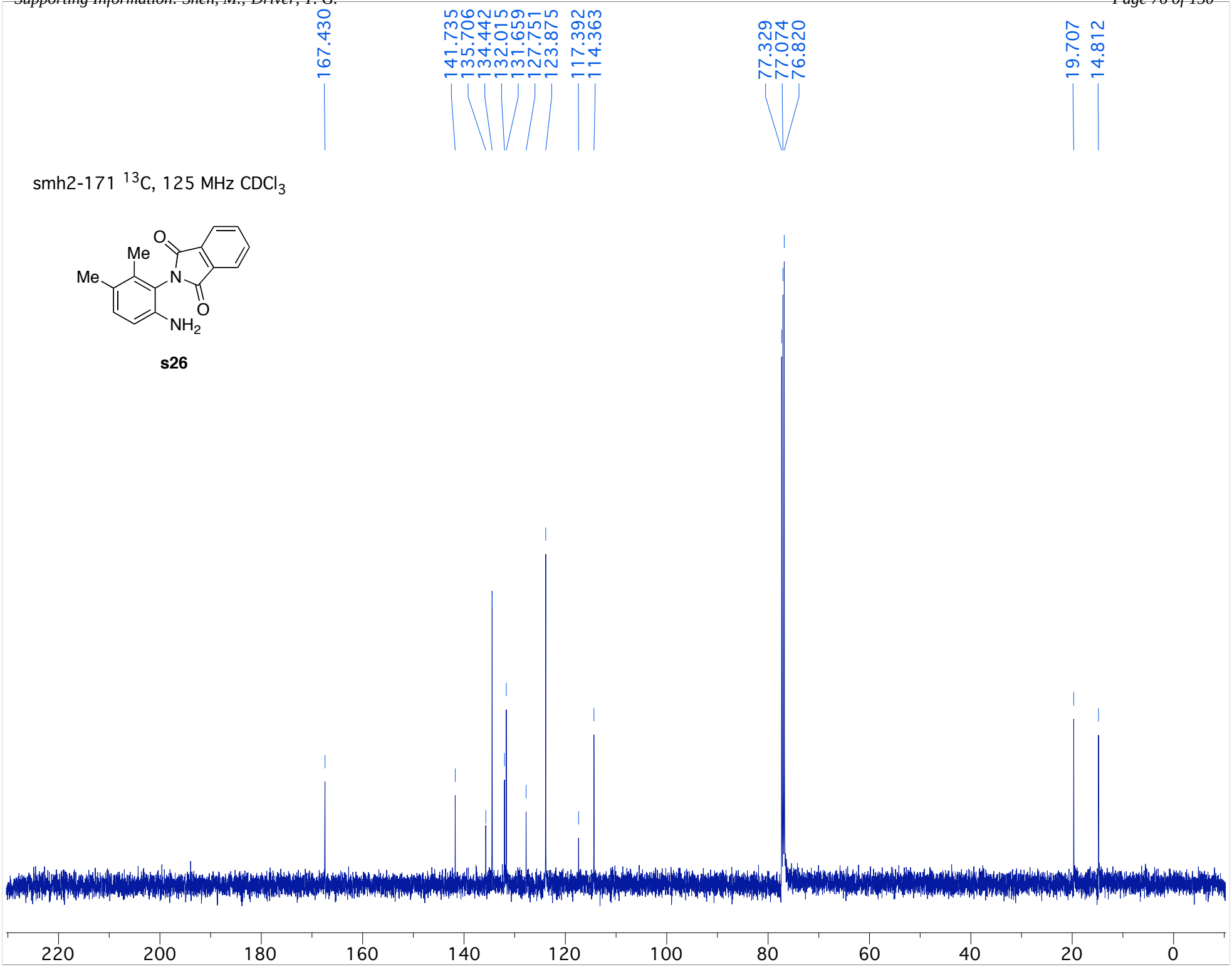
smh2-167 ^{13}C, 125 MHz $CDCl_3$



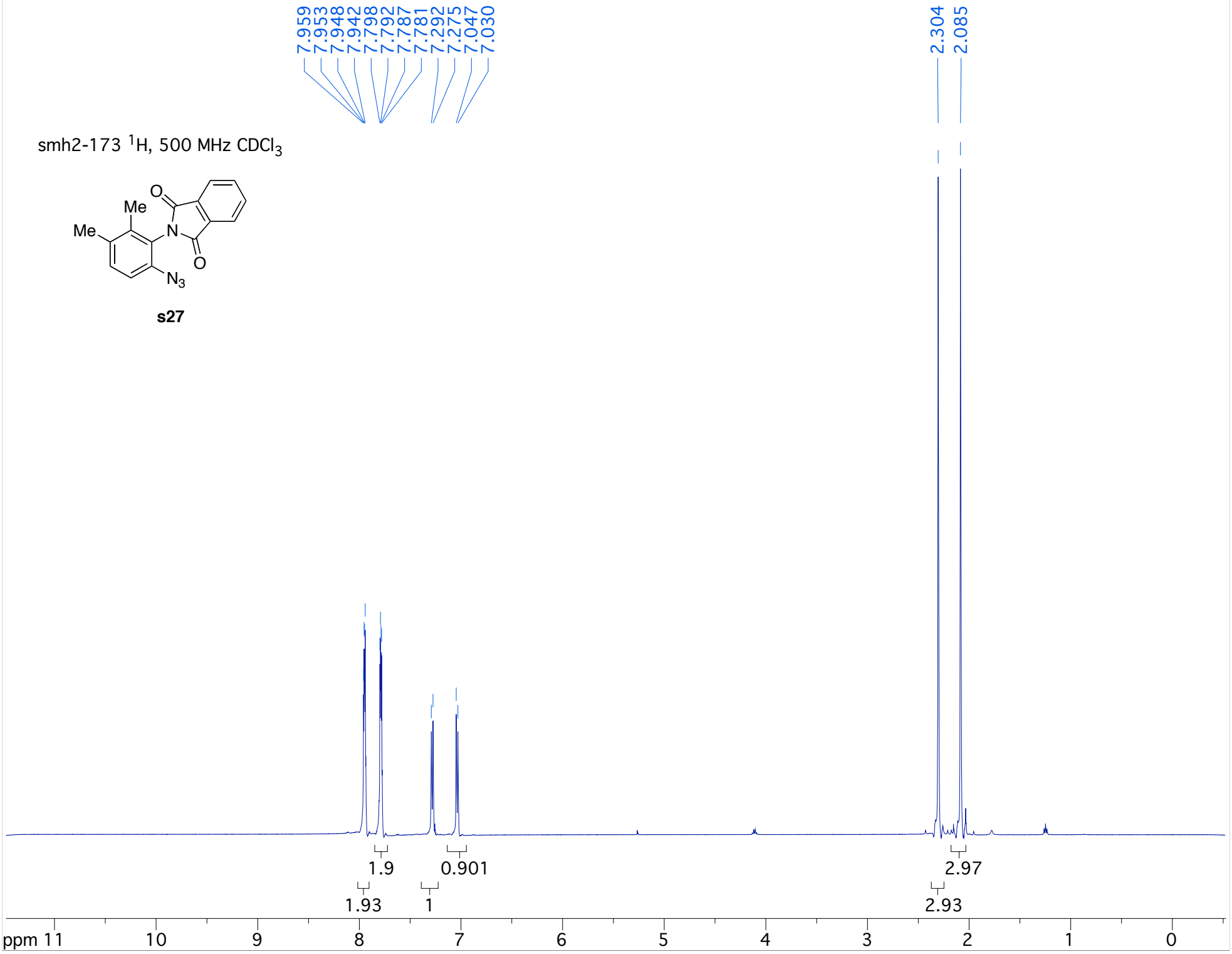
s25


7.965
7.807
7.262
7.066
7.051
6.667
6.652
3.463
2.227
1.994
smh2-171 ^{1}H, 500 MHz $CDCl_3$
Me
Me
N
O
O
NH_2
2.02
1
3.26
1.99
1
2.04
3.16
ppm 11
10
9
8
7
6
5
4
3
2
1
0

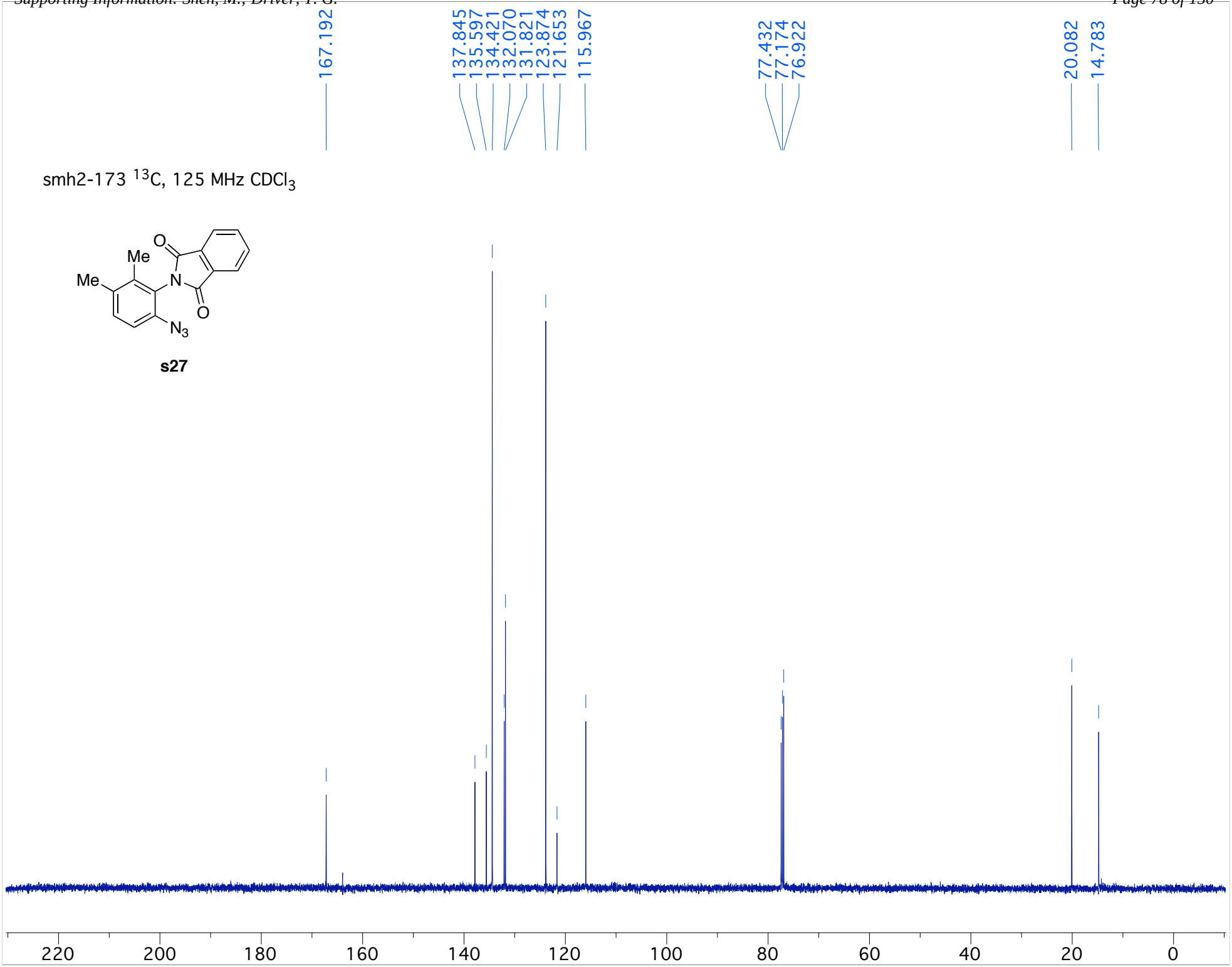
s26

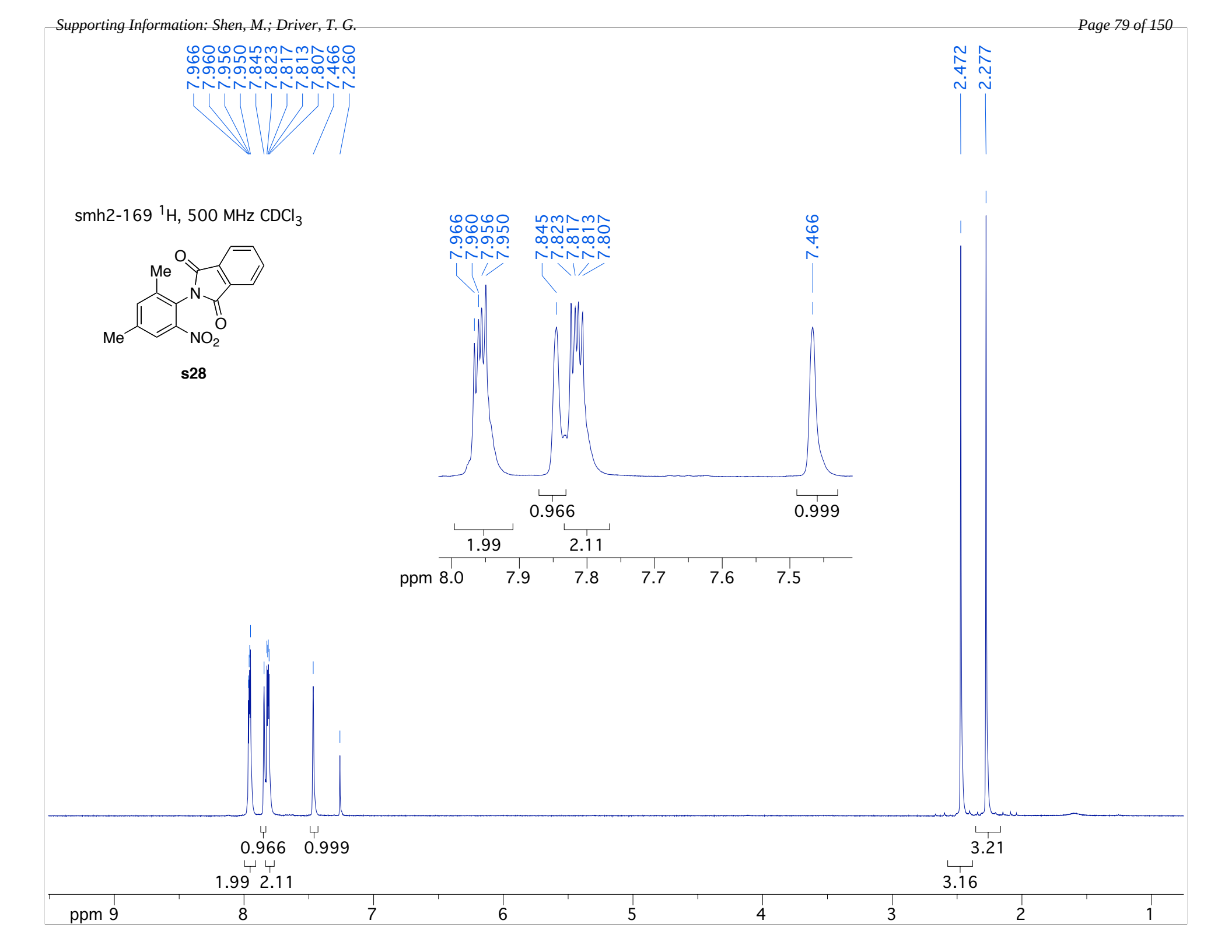

167.430
141.735
135.706
134.442
132.015
131.659
127.751
123.875
117.392
114.363
77.329
77.074
76.820
19.707
14.812
smh2-171 ^{13}C, 125 MHz $CDCl_3$
Me
Me
N
O
O
NH_2
220
200
180
160
140
120
100
80
60
40
20
0

s26

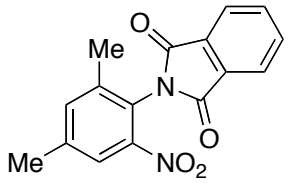

7.959
7.953
7.948
7.942
7.798
7.792
7.787
7.781
7.292
7.275
7.047
7.030
2.304
2.085
smh2-173 ^{1}H, 500 MHz $CDCl_3$
Me
Me
O
N
O
N_3
1.9
0.901
2.97
1.93
1
2.93
ppm 11
10
9
8
7
6
5
4
3
2
1
0

s27

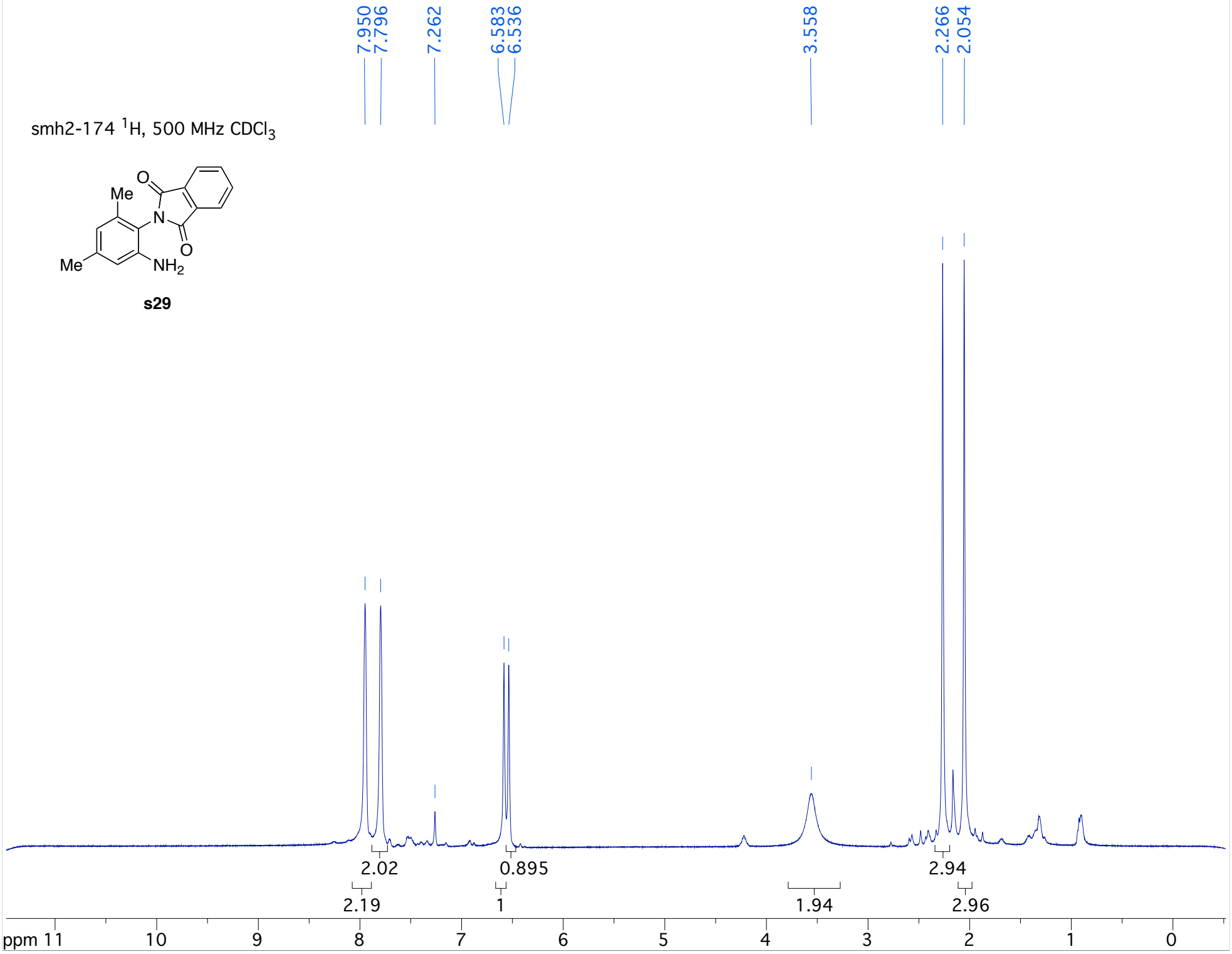

167.192
137.845
135.597
134.421
132.070
131.821
123.874
121.653
115.967
77.432
77.174
76.922
20.082
14.783
smh2-173 ^{13}C, 125 MHz $CDCl_3$
Me
Me
N
O
O
N_3
s27
220
200
180
160
140
120
100
80
60
40
20
0


7.966
7.960
7.956
7.950
7.845
7.823
7.817
7.813
7.807
7.466
7.260
2.472
2.277
smh2-169 ^{1}H, 500 MHz $CDCl_3$
Me
N
O
O
Me
NO_2
s28
0.966
0.999
1.99
2.11
ppm 8.0
7.9
7.8
7.7
7.6
7.5
0.966
0.999
3.21
1.99
2.11
3.16
ppm 9
8
7
6
5
4
3
2
1

smh2-169 ^{13}C, 125 MHz $CDCl_3$

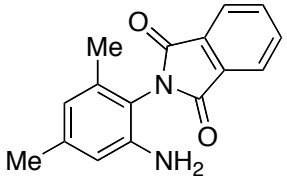


s28

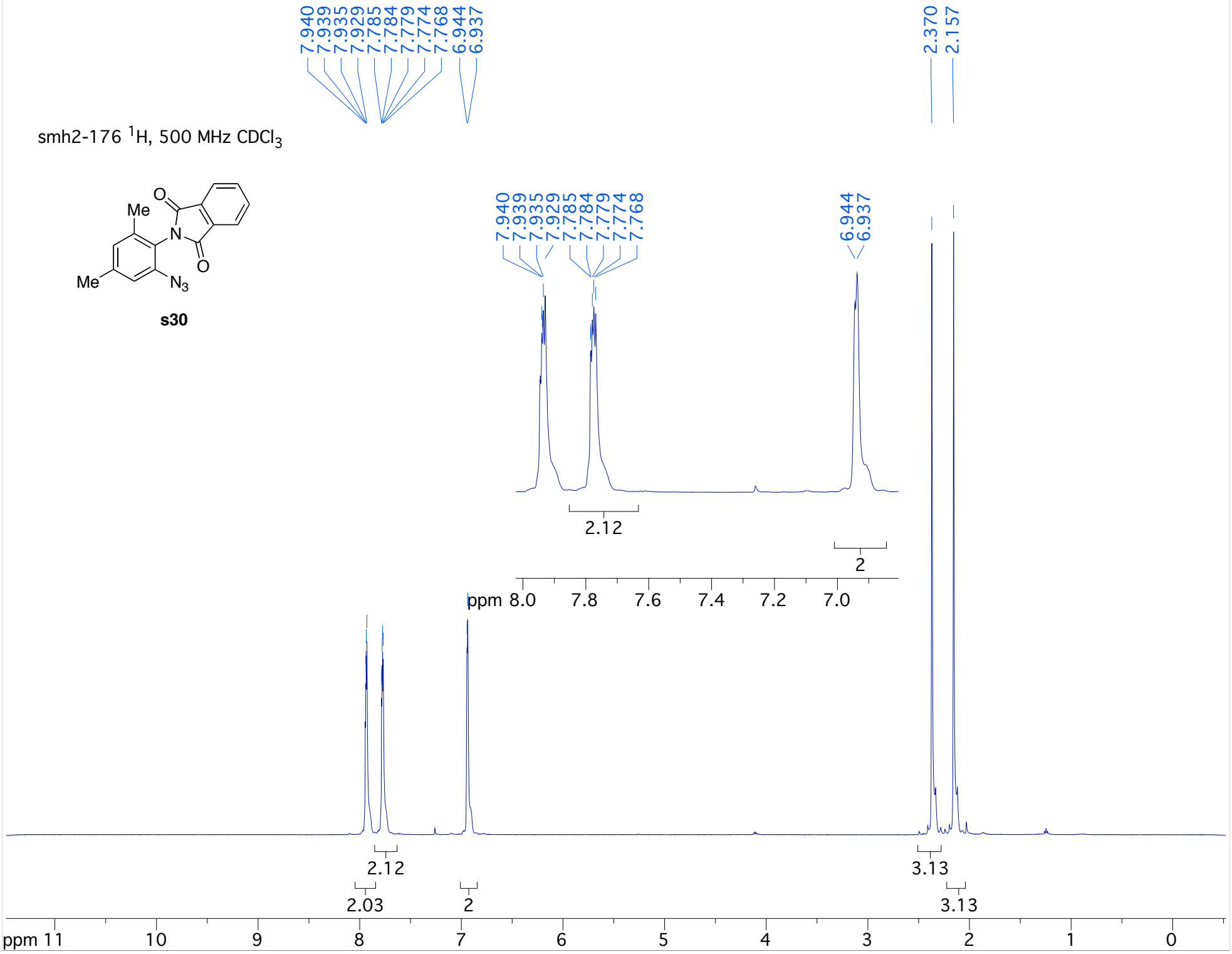

7.950
7.796
7.262
6.583
6.536
3.558
2.266
2.054
smh2-174 ^{1}H, 500 MHz $CDCl_3$
O
Me
N
O
Me
NH_2
2.02
0.895
2.94
2.19
1
1.94
2.96
ppm 11
10
9
8
7
6
5
4
3
2
1
0

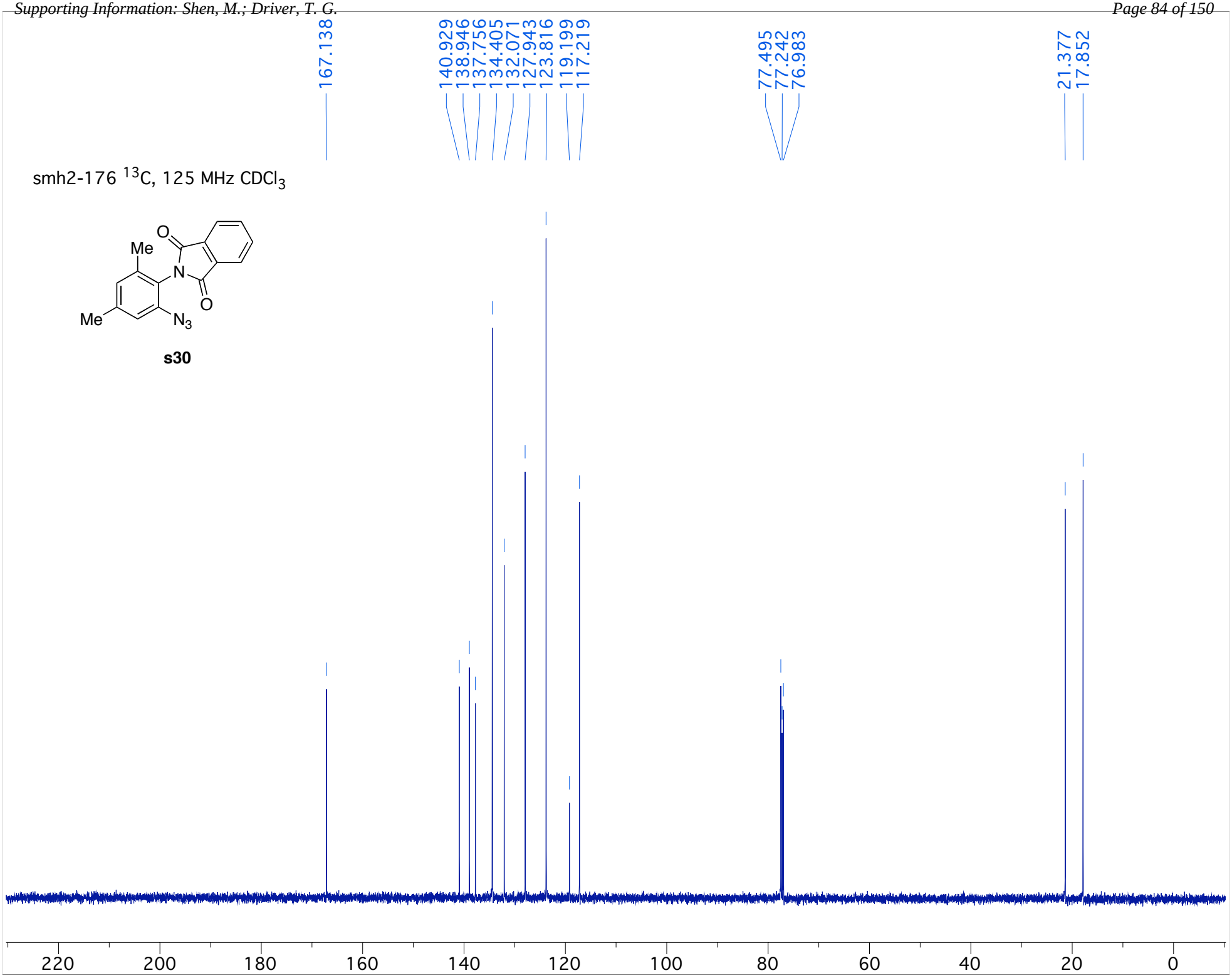
s29

smh2-174 ^{13}C, 125 MHz $CDCl_3$

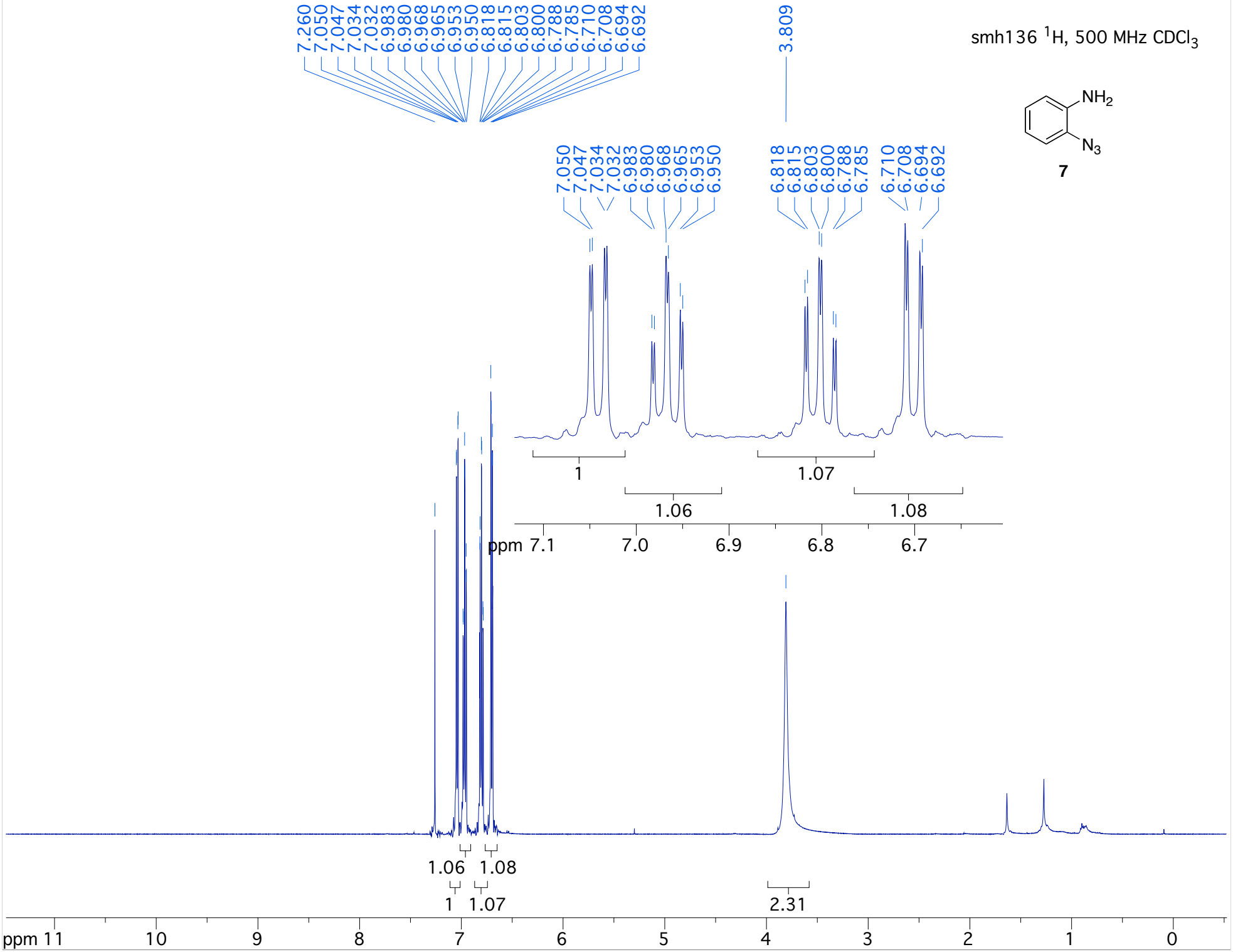


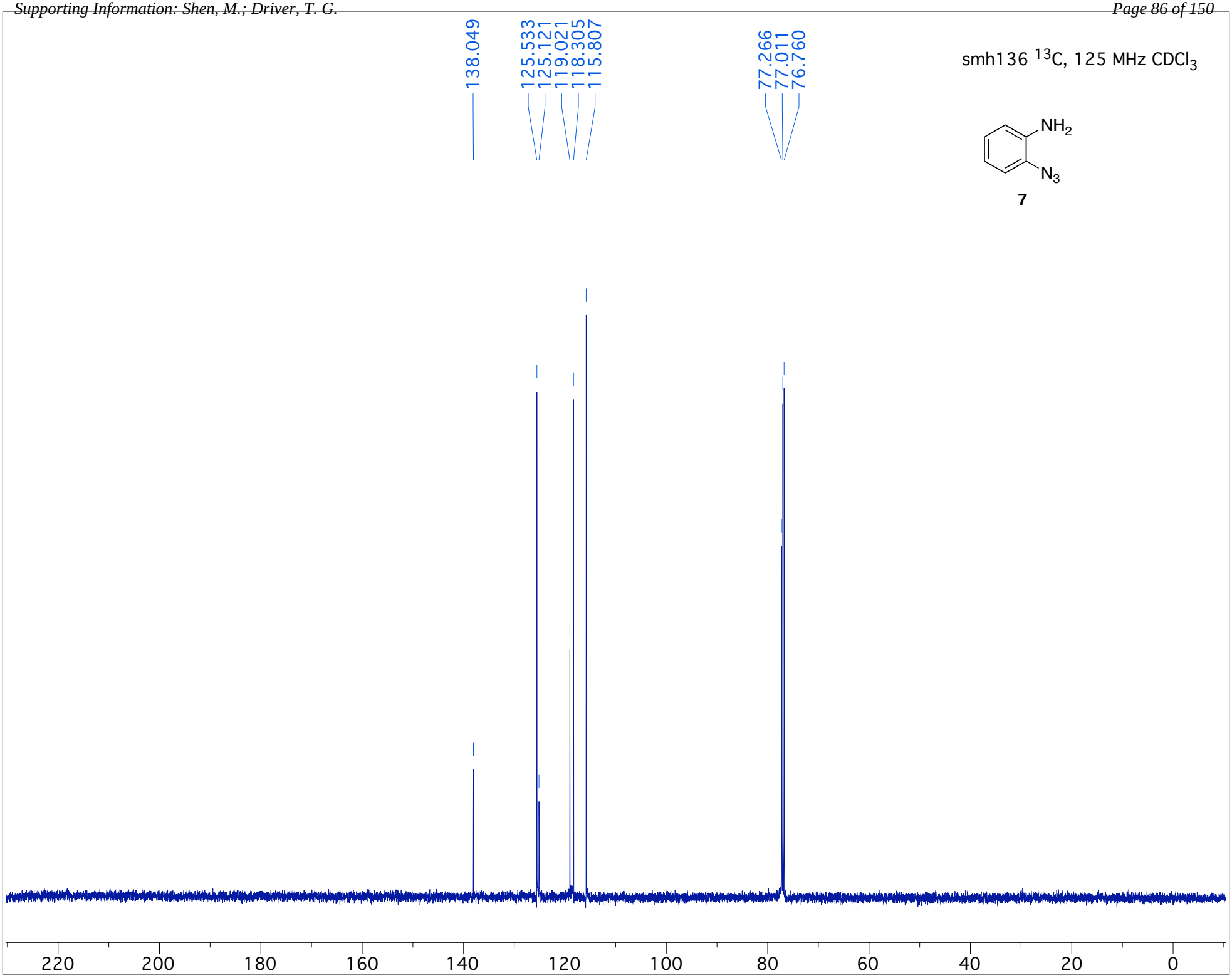
s29

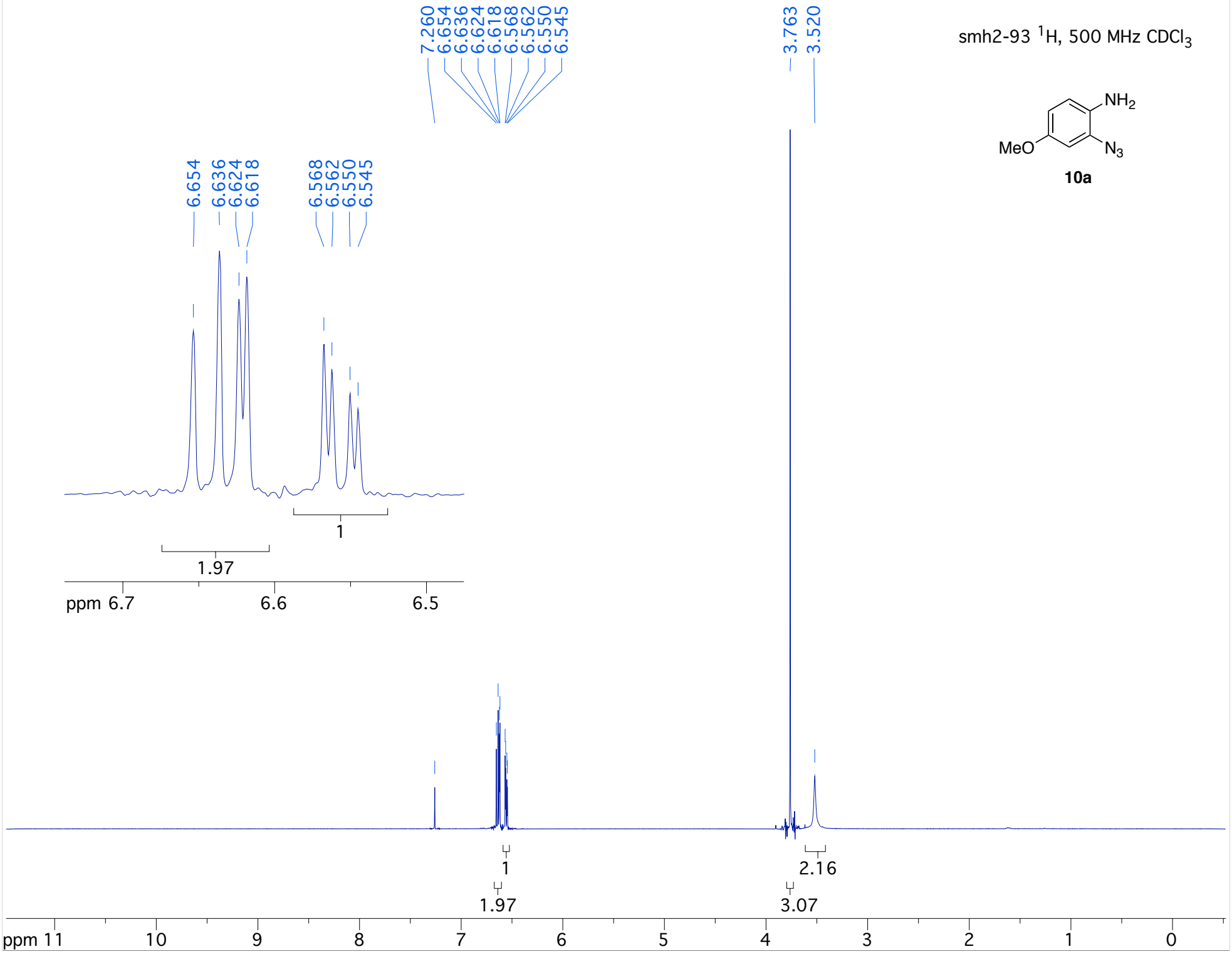

7.940
7.939
7.935
7.929
7.785
7.784
7.779
7.774
7.768
6.944
6.937
2.370
2.157
smh2-176 ^{1}H, 500 MHz $CDCl_3$
Me
O
N
O
Me
N_3
s30
2.12
2
ppm 8.0
7.8
7.6
7.4
7.2
7.0
2.12
3.13
2.03
2
3.13
ppm 11
10
9
8
7
6
5
4
3
2
1
0

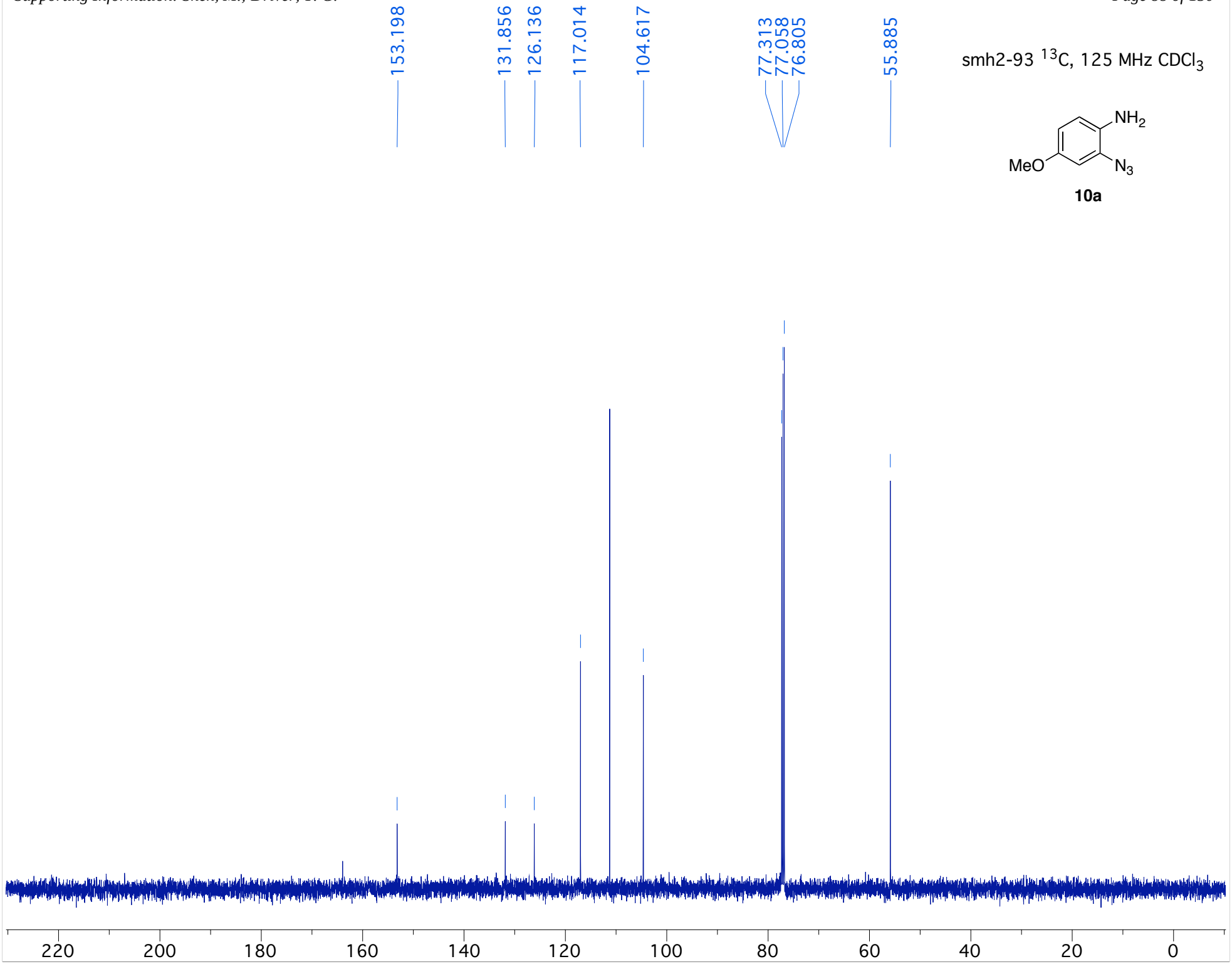

167.138
140.929
138.946
137.756
134.405
132.071
127.943
123.816
119.199
117.219
77.495
77.242
76.983
21.377
17.852
smh2-176 ^{13}C, 125 MHz $CDCl_3$
Me
O
N
O
Me
N_3
220
200
180
160
140
120
100
80
60
40
20
0

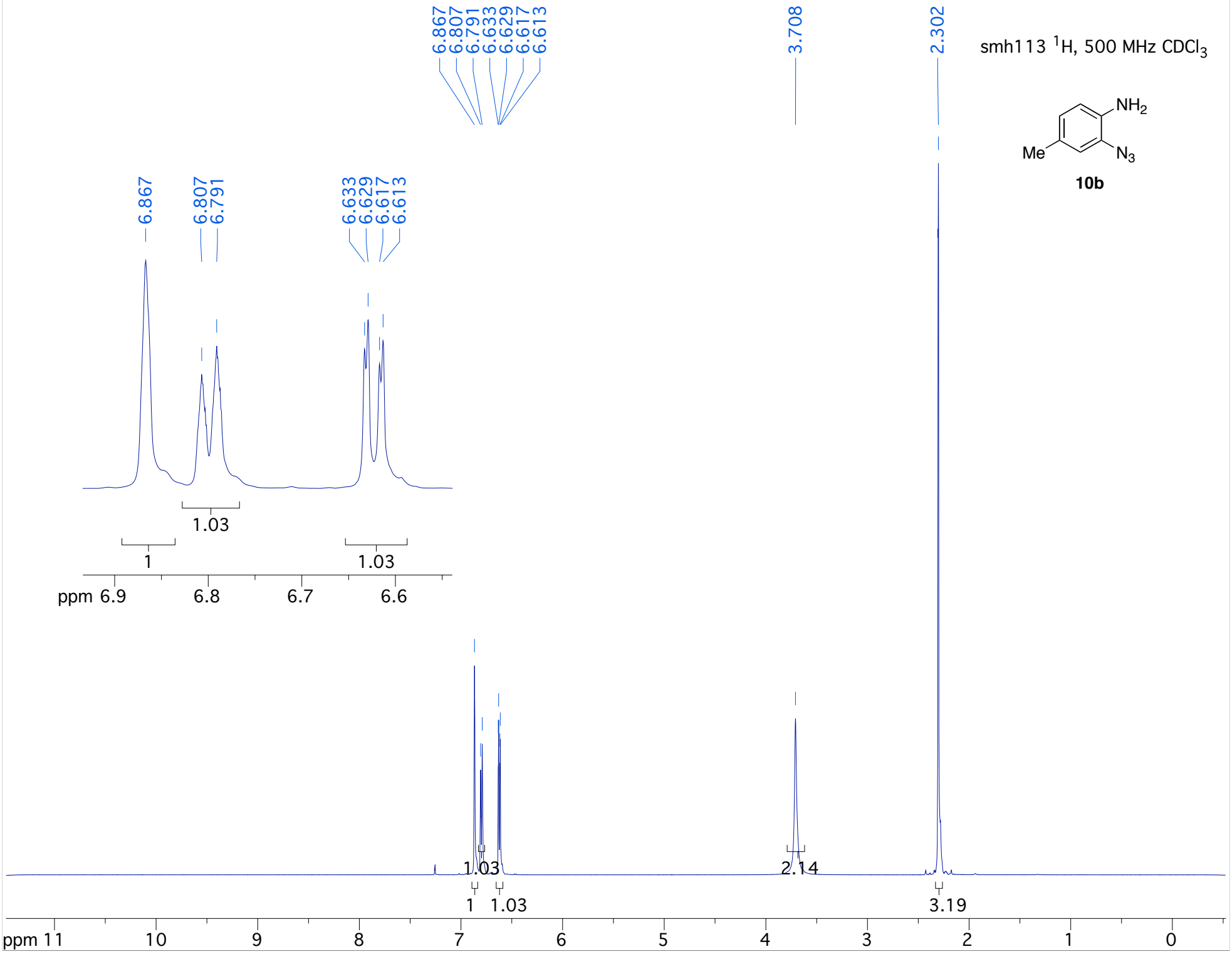
s30

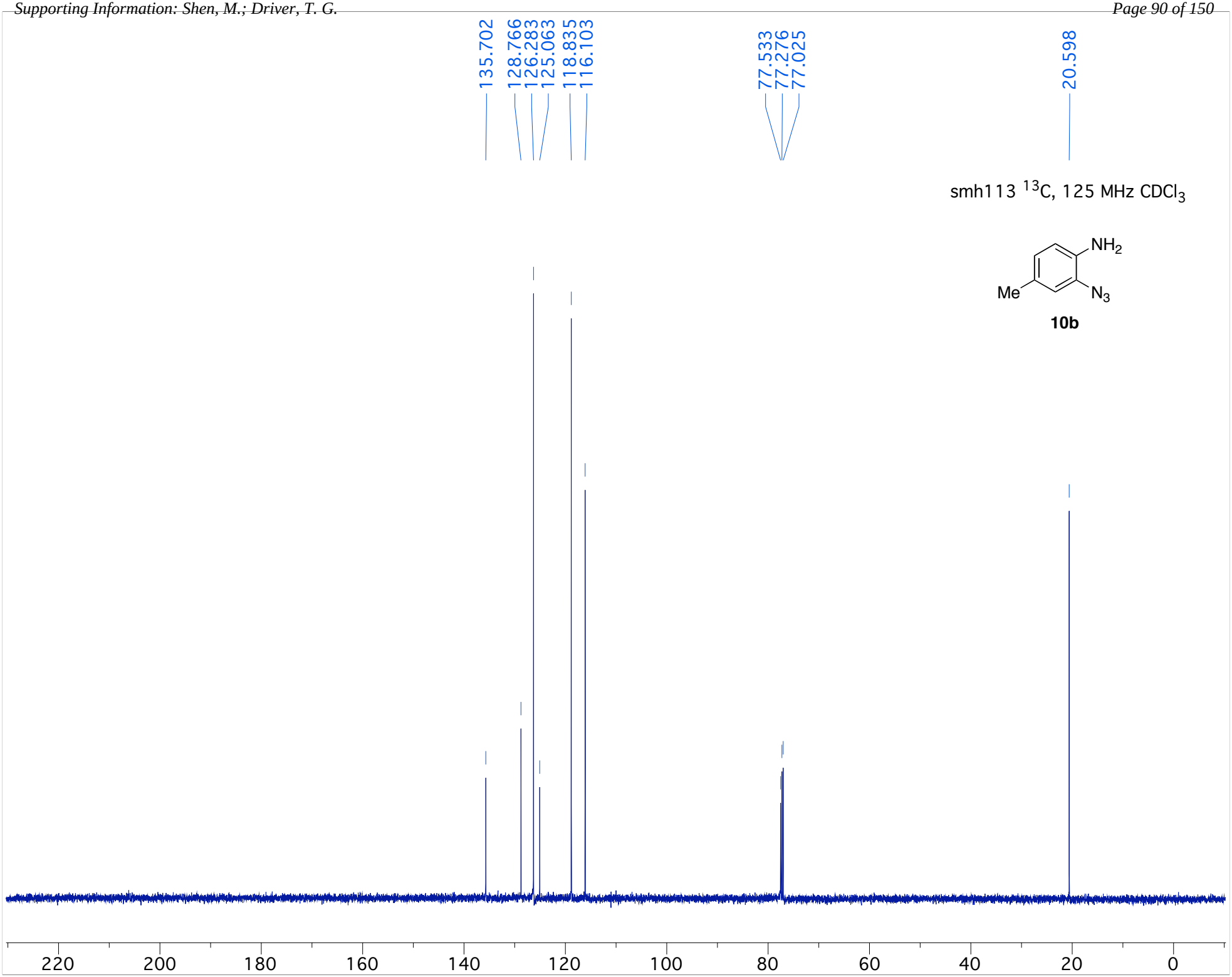

7.260
7.050
7.047
7.034
7.032
6.983
6.980
6.968
6.965
6.953
6.950
6.818
6.815
6.803
6.800
6.788
6.785
6.710
6.708
6.694
6.692
3.809
smh136 ^{1}H, 500 MHz $CDCl_3$
NH_2
N_3
7
1
1.07
1.06
1.08
ppm 7.1
7.0
6.9
6.8
6.7
1.06
1.08
1
1.07
2.31
ppm 11
10
9
8
7
6
5
4
3
2
1
0

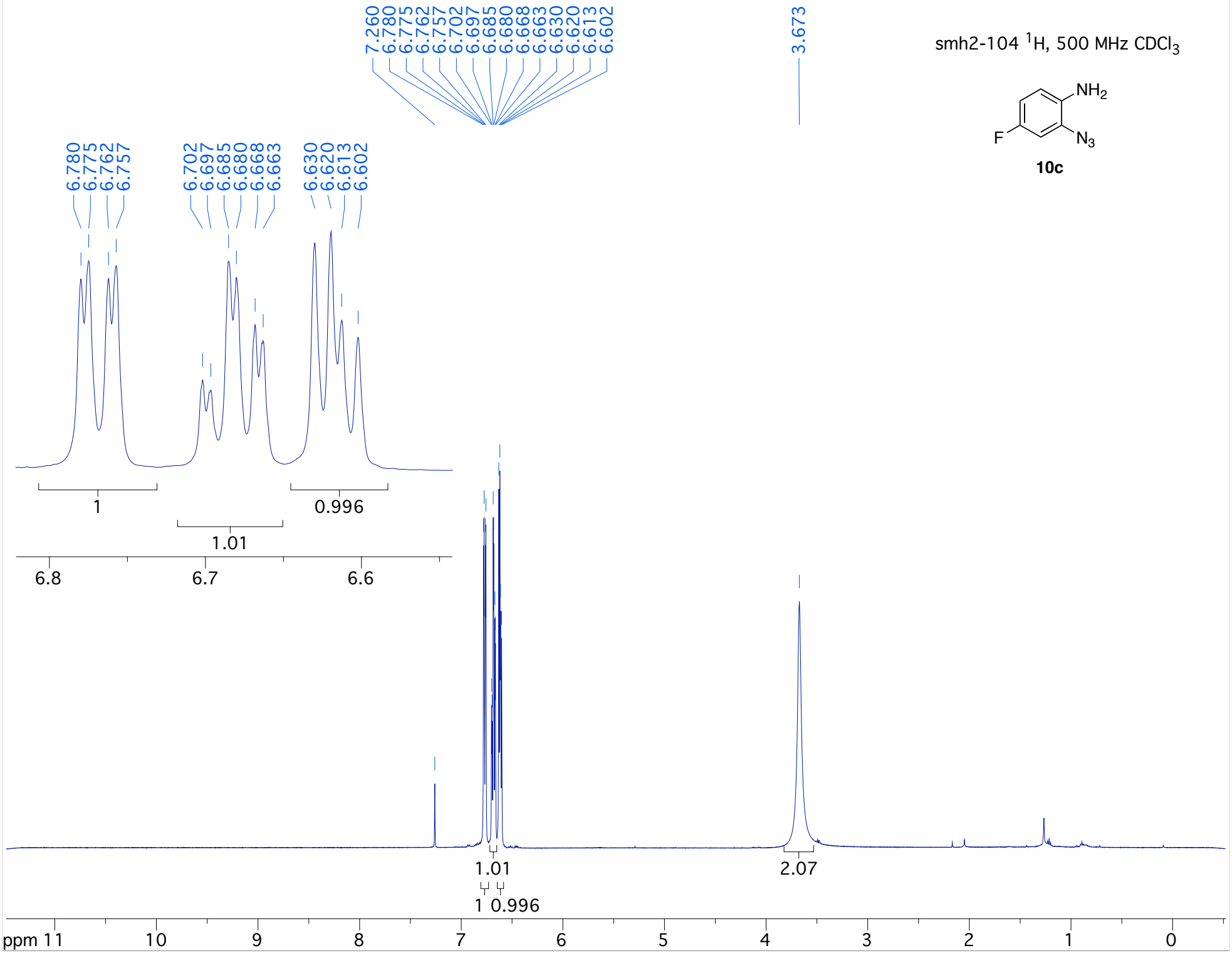

138.049
125.533
125.121
119.021
118.305
115.807
77.266
77.011
76.760
smh136 ^{13}C, 125 MHz $CDCl_3$
NH_2
N_3
7
220
200
180
160
140
120
100
80
60
40
20
0

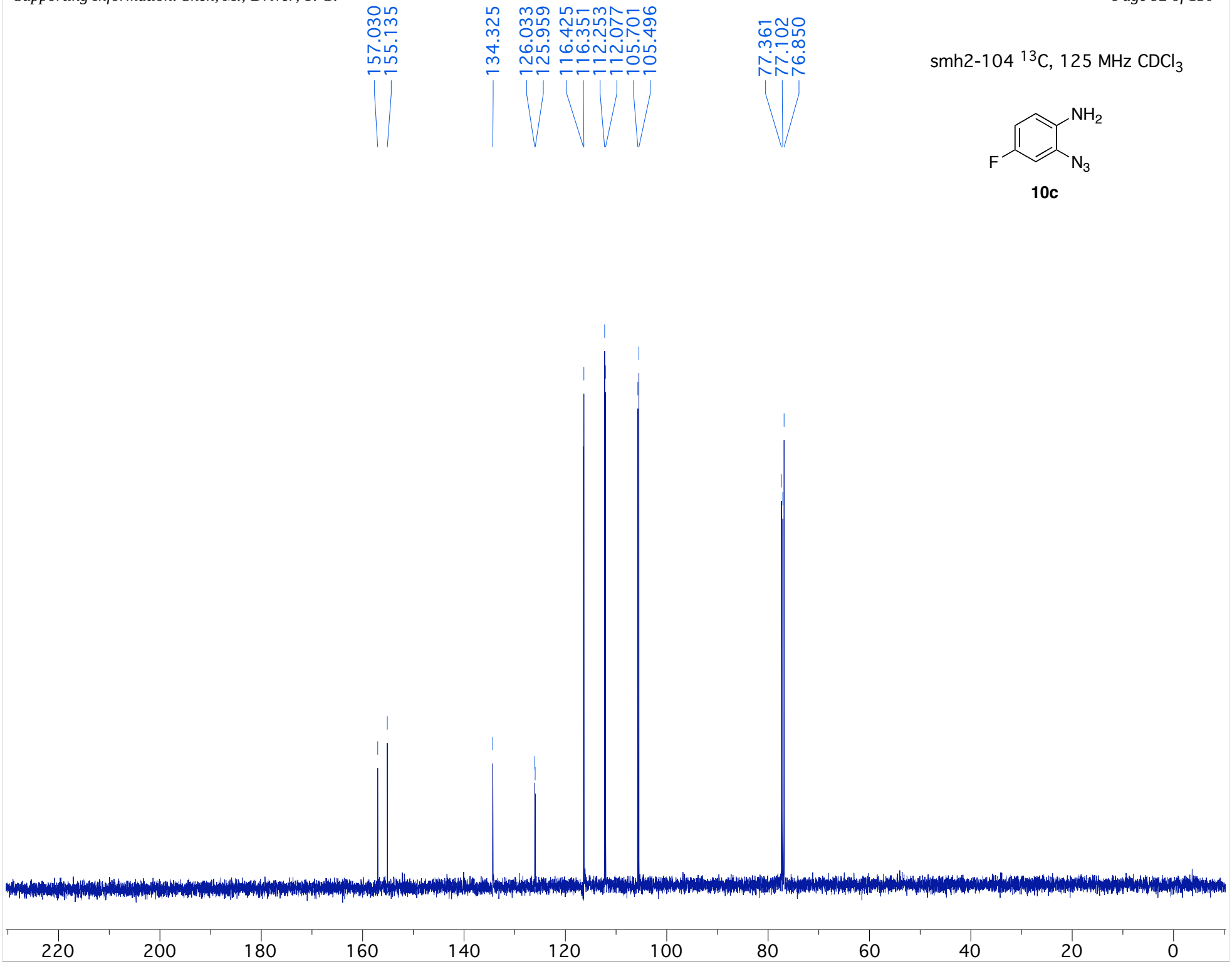

7.260
6.654
6.636
6.624
6.618
6.568
6.562
6.550
6.545
3.763
3.520
smh2-93 ^{1}H, 500 MHz $CDCl_3$
NH_2
MeO
N_3
10a
6.654
6.636
6.624
6.618
6.568
6.562
6.550
6.545
1
1.97
ppm 6.7
6.6
6.5
1
2.16
1.97
3.07
ppm 11
10
9
8
7
6
5
4
3
2
1
0

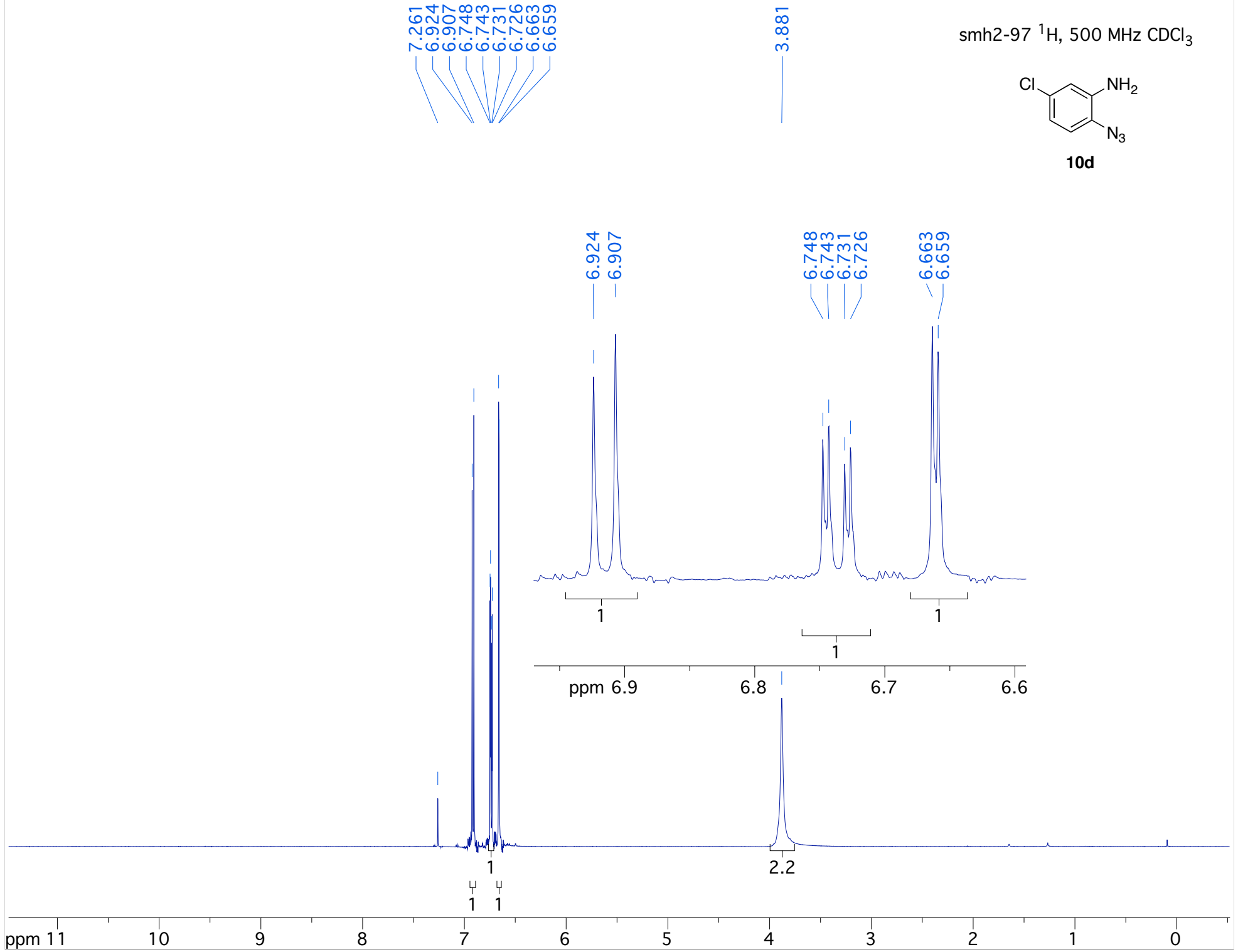

153.198
131.856
126.136
117.014
104.617
77.313
77.058
76.805
55.885
smh2-93 13C, 125 MHz CDCl3
NH2
MeO
N3
10a
220
200
180
160
140
120
100
80
60
40
20
0

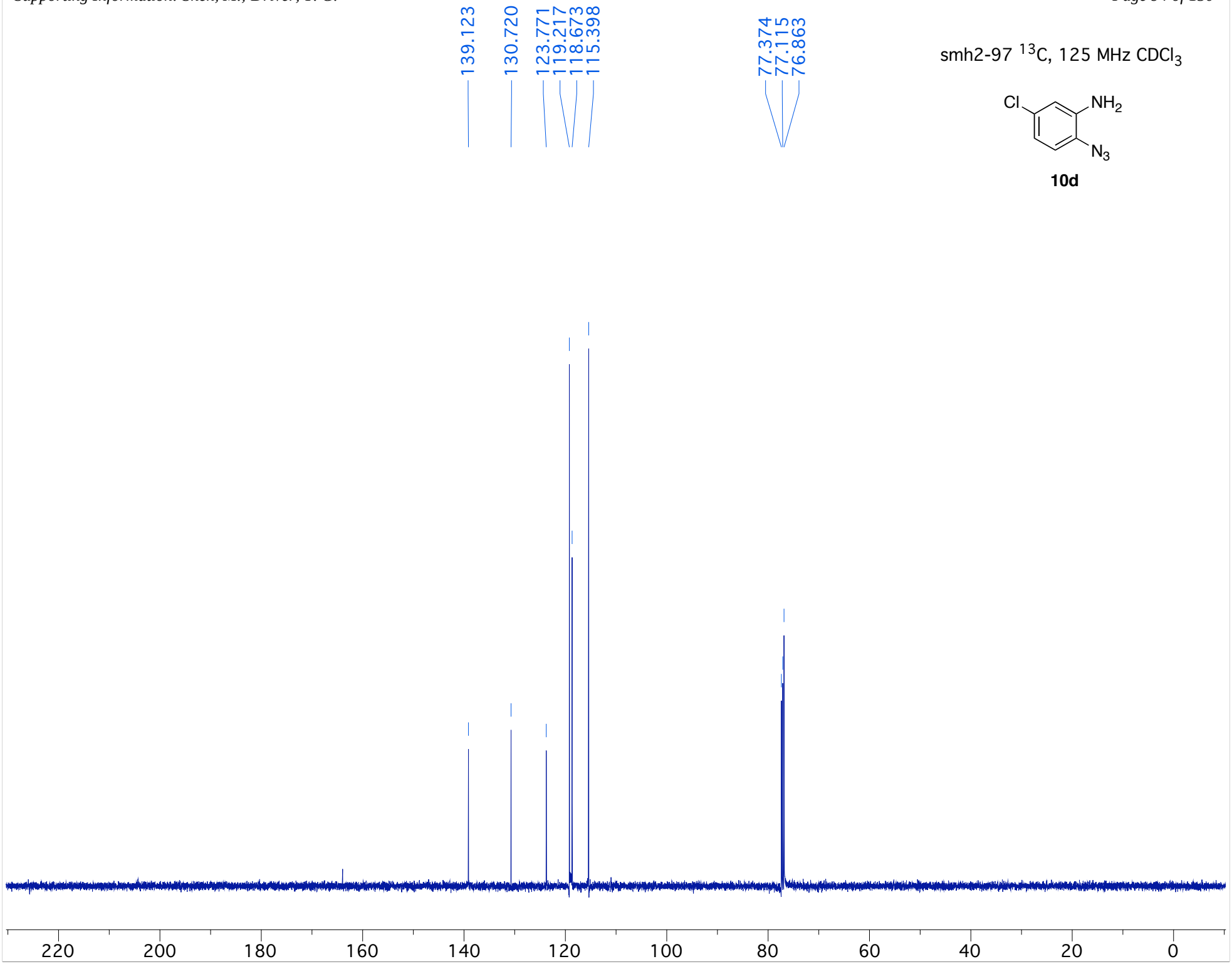

6.867
6.807
6.791
6.633
6.629
6.617
6.613
3.708
2.302
smh113 ^{1}H, 500 MHz $CDCl_3$
NH_2
Me
N_3
10b
1.03
1
1.03
ppm 6.9
6.8
6.7
6.6
1.03
2.14
1
1.03
3.19
ppm 11
10
9
8
7
6
5
4
3
2
1
0

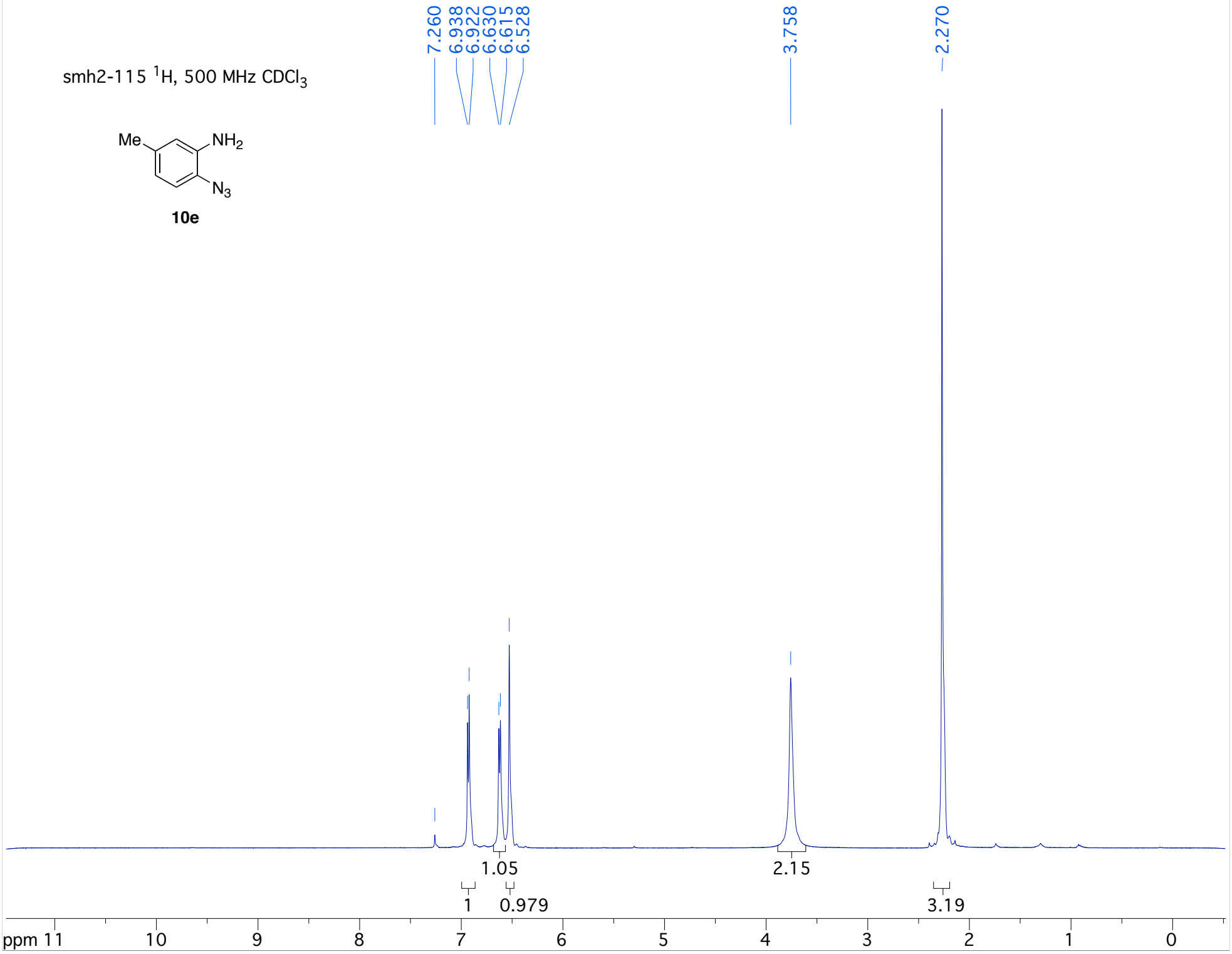

135.702
128.766
126.283
125.063
118.835
116.103
77.533
77.276
77.025
20.598
smh113 ^{13}C, 125 MHz $CDCl_3$
NH_2
Me
N_3
10b
220
200
180
160
140
120
100
80
60
40
20
0


7.260
6.780
6.775
6.762
6.757
6.702
6.697
6.685
6.680
6.668
6.663
6.630
6.620
6.613
6.602
3.673
smh2-104 ^{1}H, 500 MHz $CDCl_3$
NH_2
F
N_3
10c
1
0.996
1.01
6.8
6.7
6.6
1.01
2.07
1 0.996
ppm 11
10
9
8
7
6
5
4
3
2
1
0

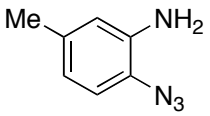

157.030
155.135
134.325
126.033
125.959
116.425
116.351
112.253
112.077
105.701
105.496
77.361
77.102
76.850
smh2-104 ^{13}C, 125 MHz $CDCl_3$
NH_2
F
N_3
10c
220
200
180
160
140
120
100
80
60
40
20
0


7.261
6.924
6.907
6.748
6.743
6.731
6.726
6.663
6.659
3.881
smh2-97 ^{1}H, 500 MHz $CDCl_3$
Cl
NH_2
N_3
10d
6.924
6.907
6.748
6.743
6.731
6.726
6.663
6.659
1
1
1
ppm 6.9
6.8
6.7
6.6
1
1
1
2.2
ppm 11
10
9
8
7
6
5
4
3
2
1
0

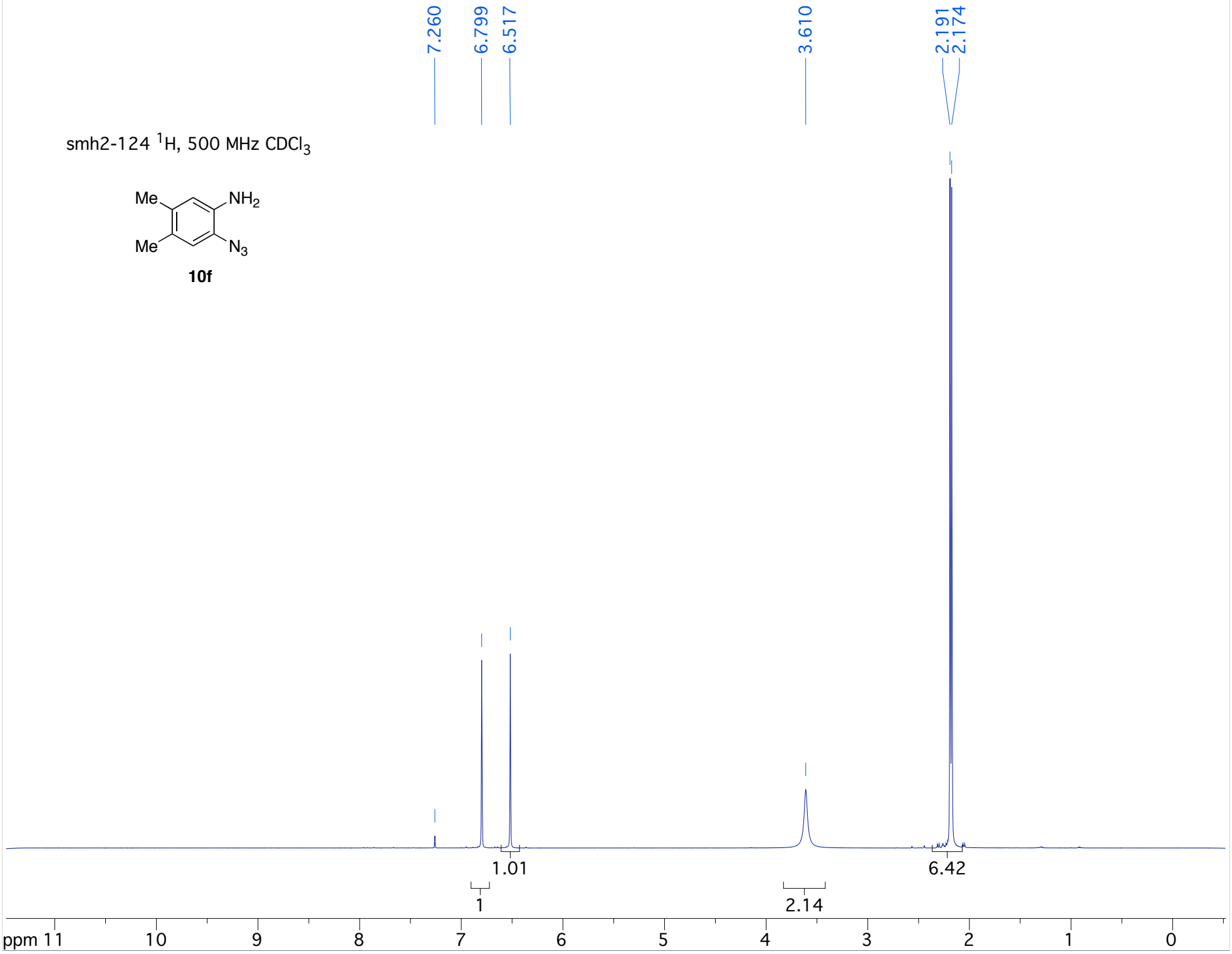

139.123
130.720
123.771
119.217
118.673
115.398
77.374
77.115
76.863
smh2-97 ^{13}C, 125 MHz $CDCl_3$
Cl
NH_2
N_3
10d
220
200
180
160
140
120
100
80
60
40
20
0


7.260
6.938
6.922
6.630
6.615
6.528
3.758
2.270
smh2-115 ^{1}H, 500 MHz $CDCl_3$
Me
NH_2
N_3
10e
1.05
2.15
1
0.979
3.19
ppm 11
10
9
8
7
6
5
4
3
2
1
0

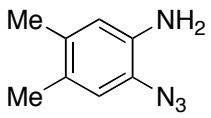
smh2-115 ^{13}C, 125 MHz $CDCl_3$



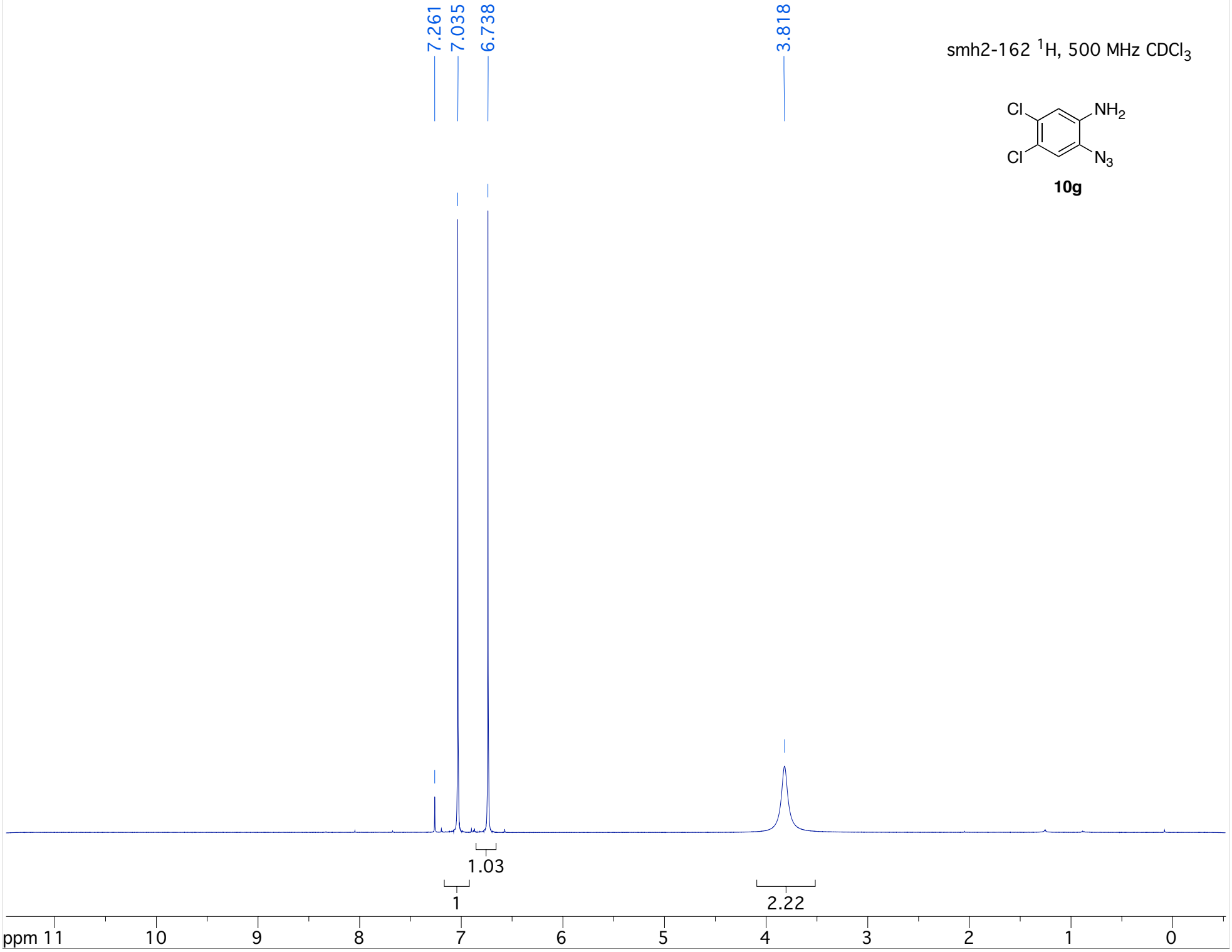
10e

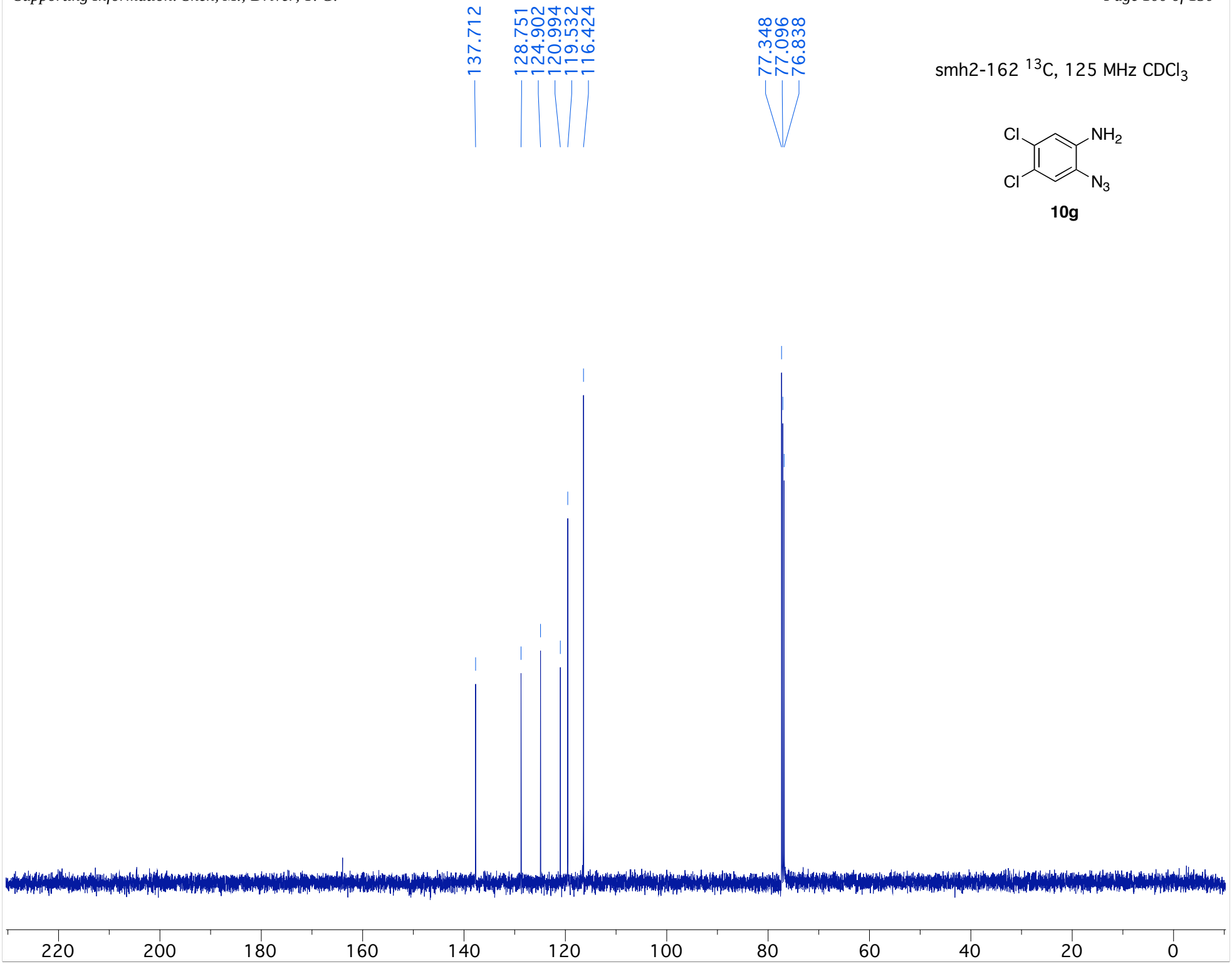

7.260
6.799
6.517
3.610
2.191
2.174
smh2-124 ^{1}H, 500 MHz $CDCl_3$
Me
NH_2
Me
N_3
10f
1.01
6.42
1
2.14
ppm 11
10
9
8
7
6
5
4
3
2
1
0

smh2-124 ^{13}C, 125 MHz $CDCl_3$

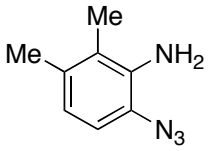


10f


7.261
7.035
6.738
3.818
smh2-162 ^{1}H, 500 MHz $CDCl_3$
Cl
NH_2
Cl
N_3
10g
1.03
1
2.22
ppm 11
10
9
8
7
6
5
4
3
2
1
0

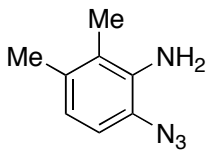

137.712
128.751
124.902
120.994
119.532
116.424
77.348
77.096
76.838
smh2-162 ^{13}C, 125 MHz $CDCl_3$
Cl
NH$_2$
Cl
N$_3$
10g
220
200
180
160
140
120
100
80
60
40
20
0

smh2-175 ^{1}H, 500 MHz $CDCl_3$



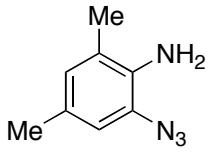
10h

smh2-175 ^{13}C, 125 MHz $CDCl_3$



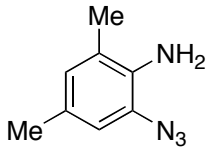
10h

smh2-181 ^{1}H, 500 MHz $CDCl_3$

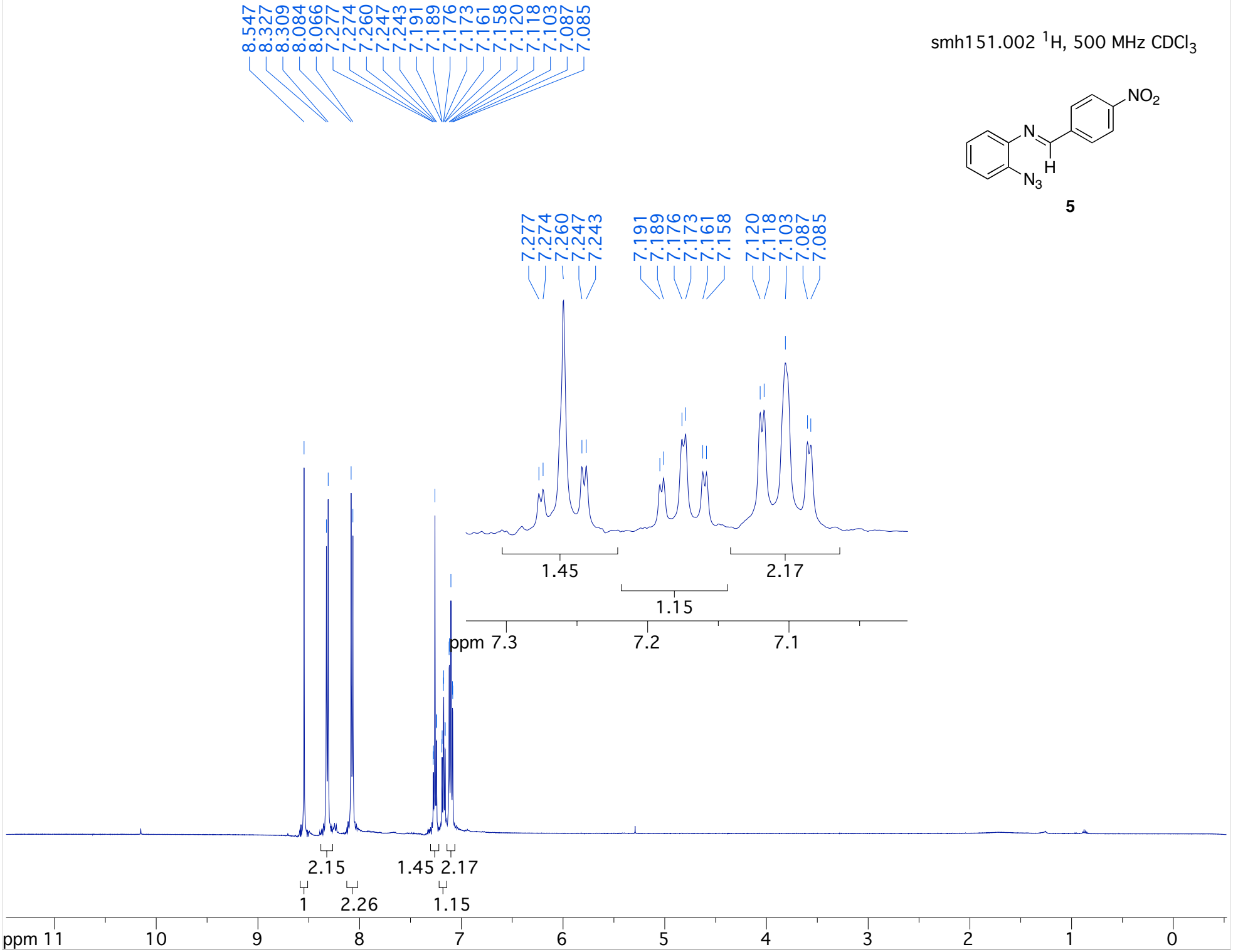


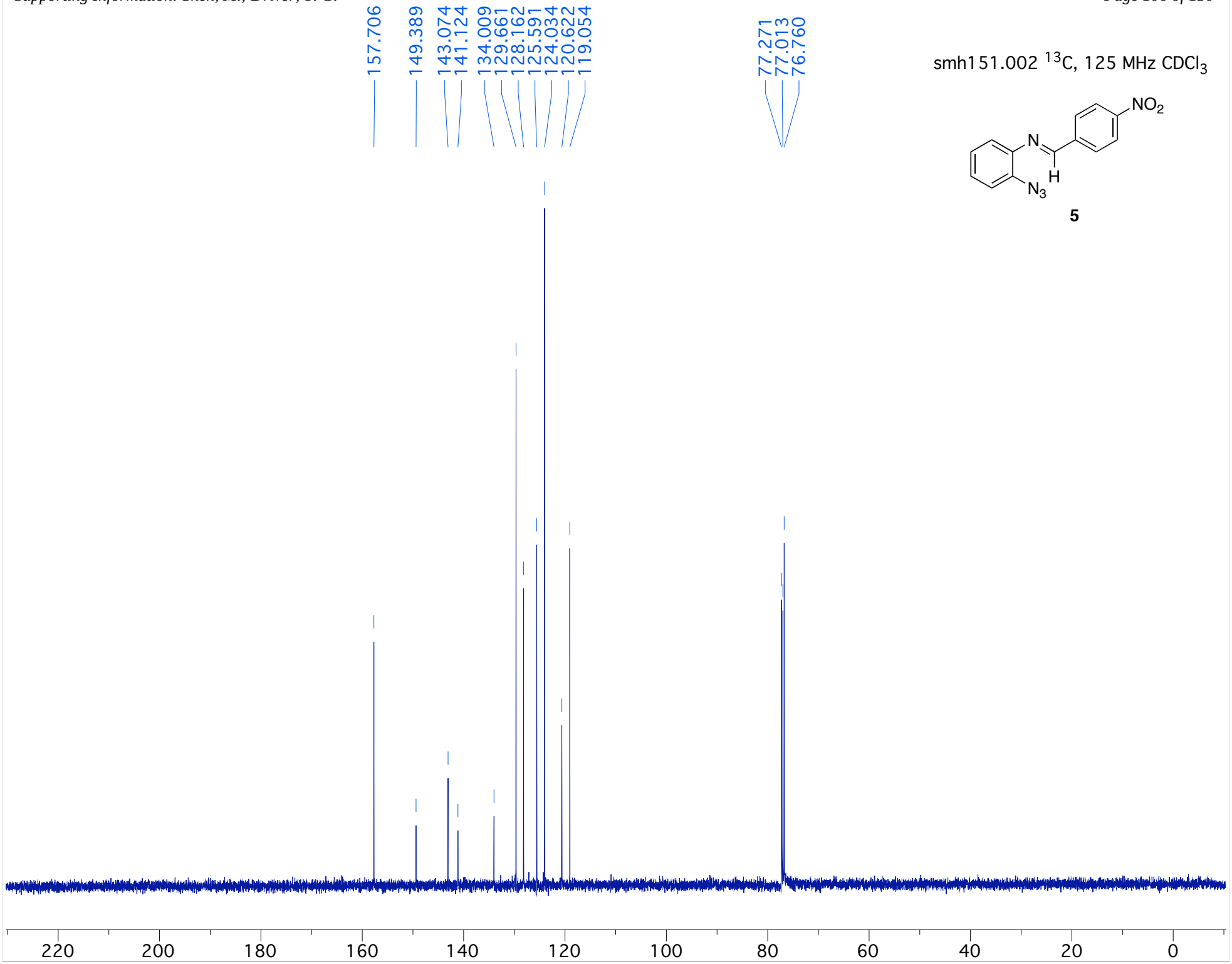
10i

smh2-181 ^{13}C, 125 MHz $CDCl_3$

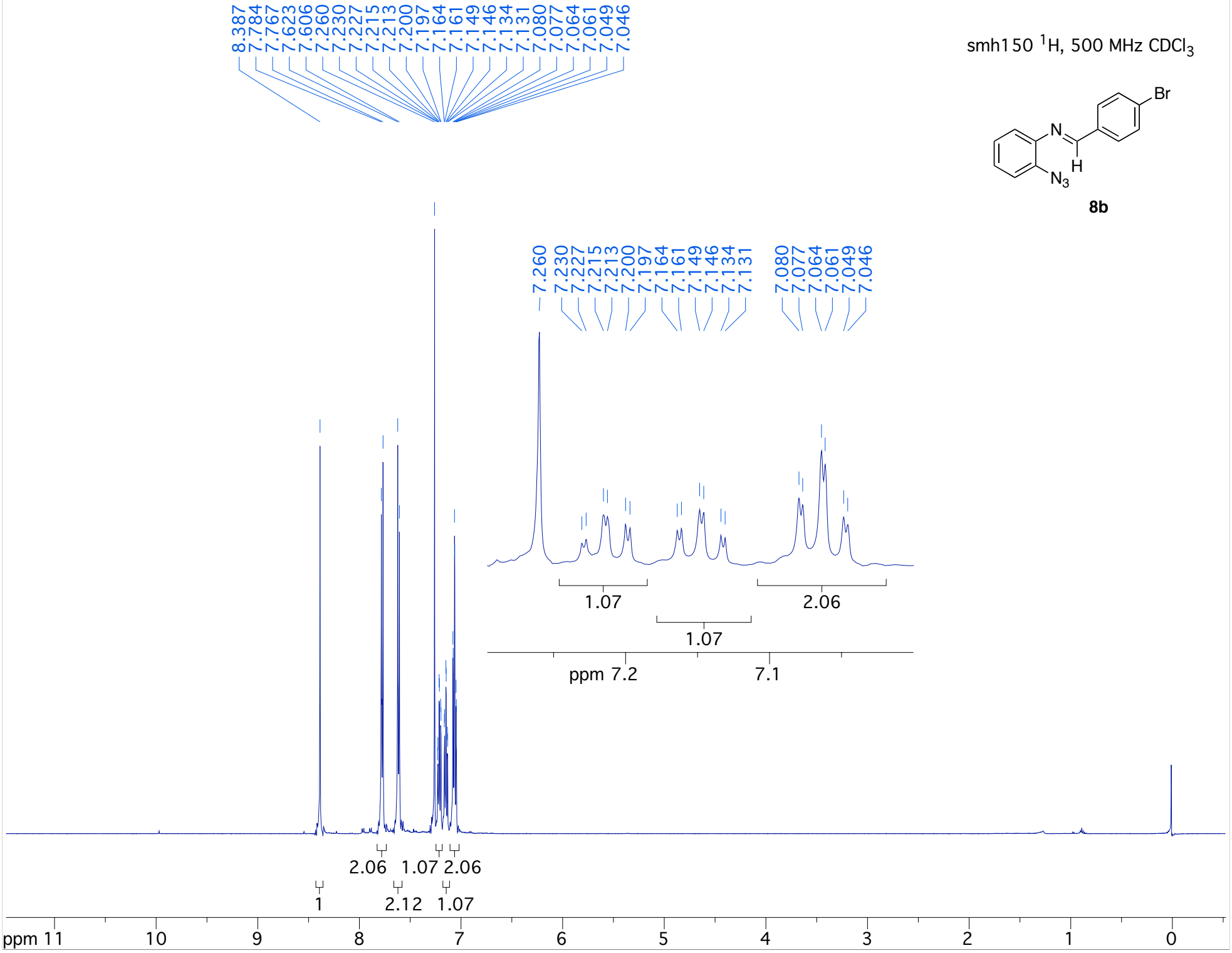


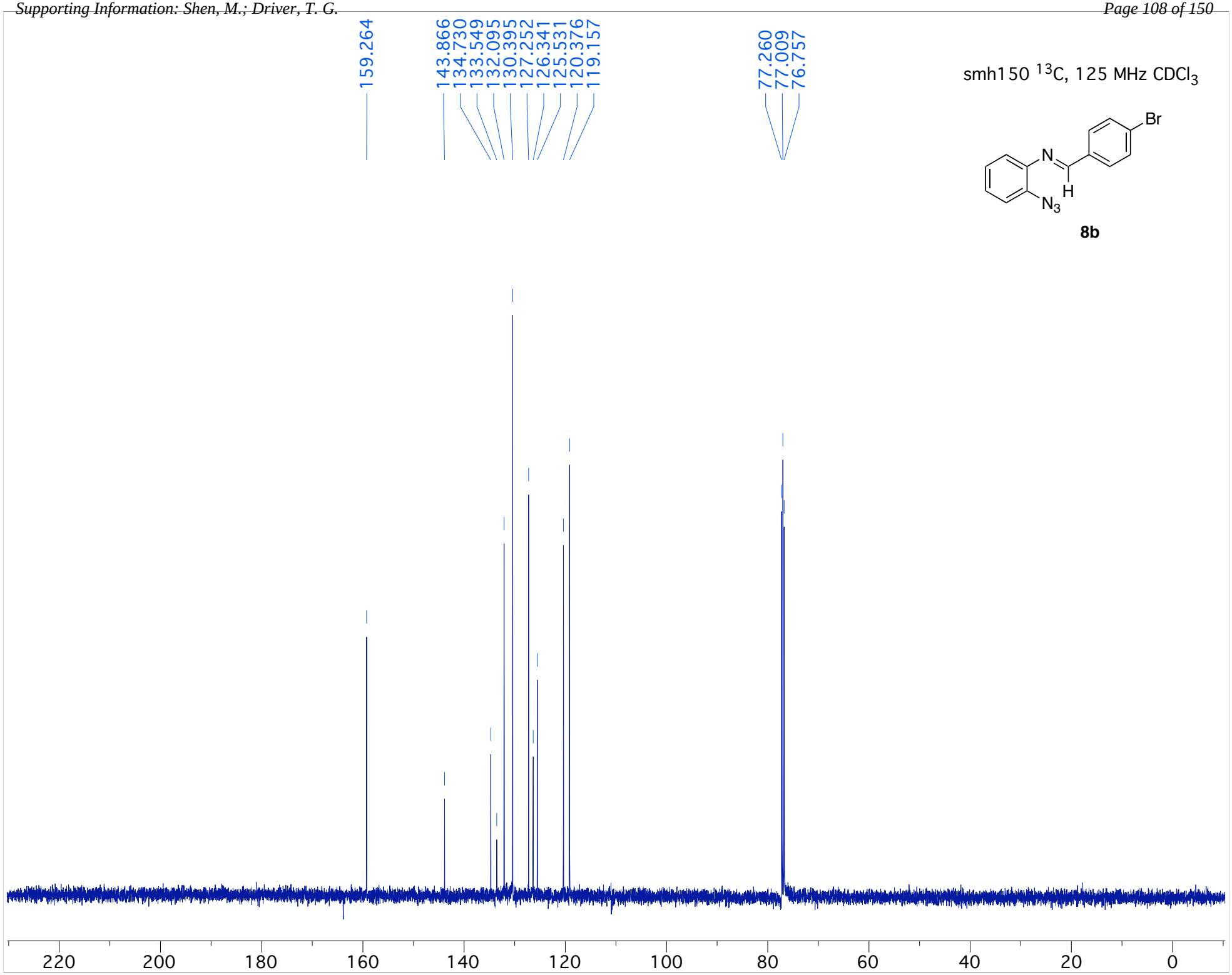
10i

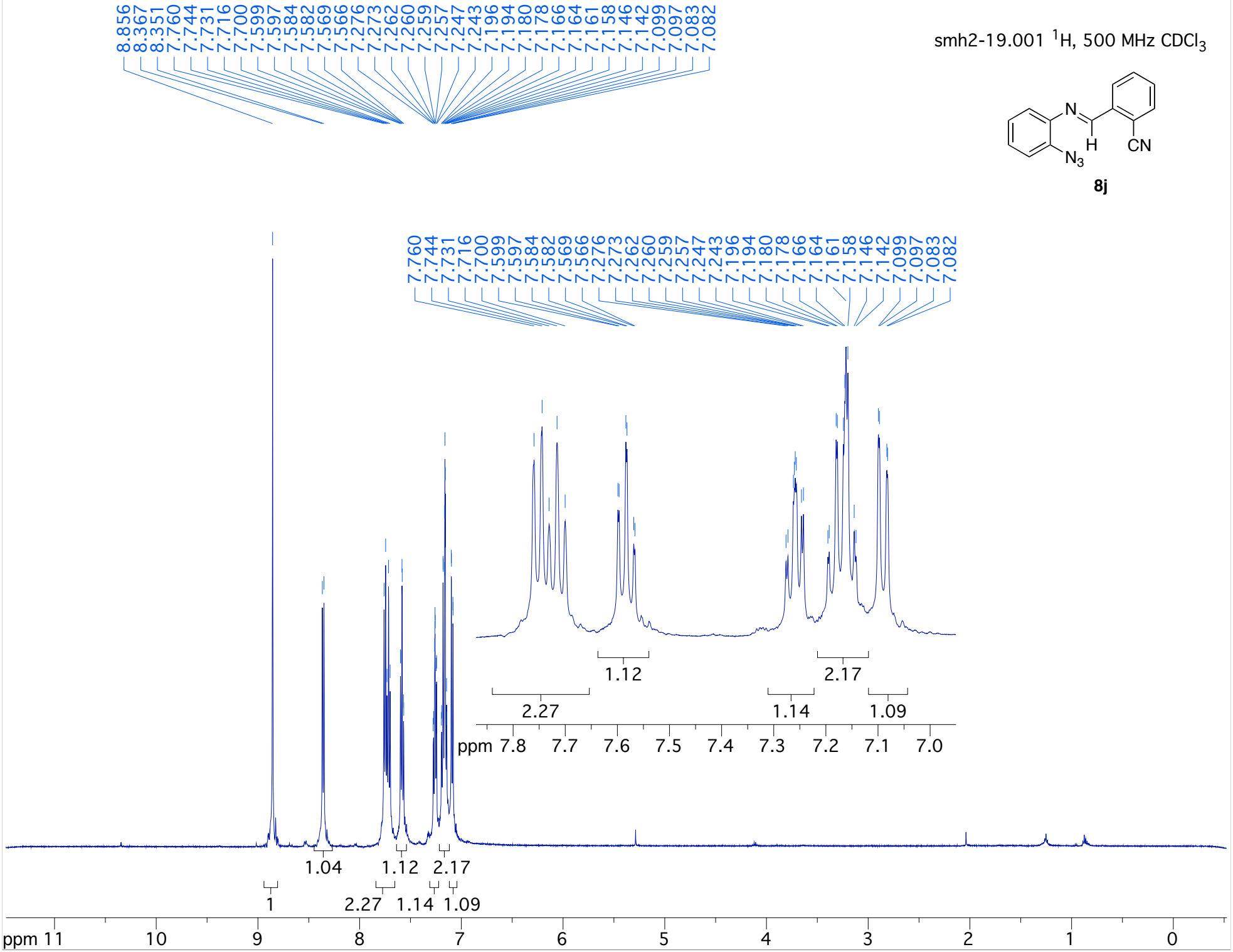

8.547
8.327
8.309
8.084
8.066
7.277
7.274
7.260
7.247
7.243
7.191
7.189
7.176
7.173
7.161
7.158
7.120
7.118
7.103
7.087
7.085
smh151.002 ^{1}H, 500 MHz $CDCl_3$
NO_2
N
H
N_3
5
1.45
2.17
1.15
ppm 7.3
7.2
7.1
2.15
1.45
2.17
1
2.26
1.15
ppm 11
10
9
8
7
6
5
4
3
2
1
0

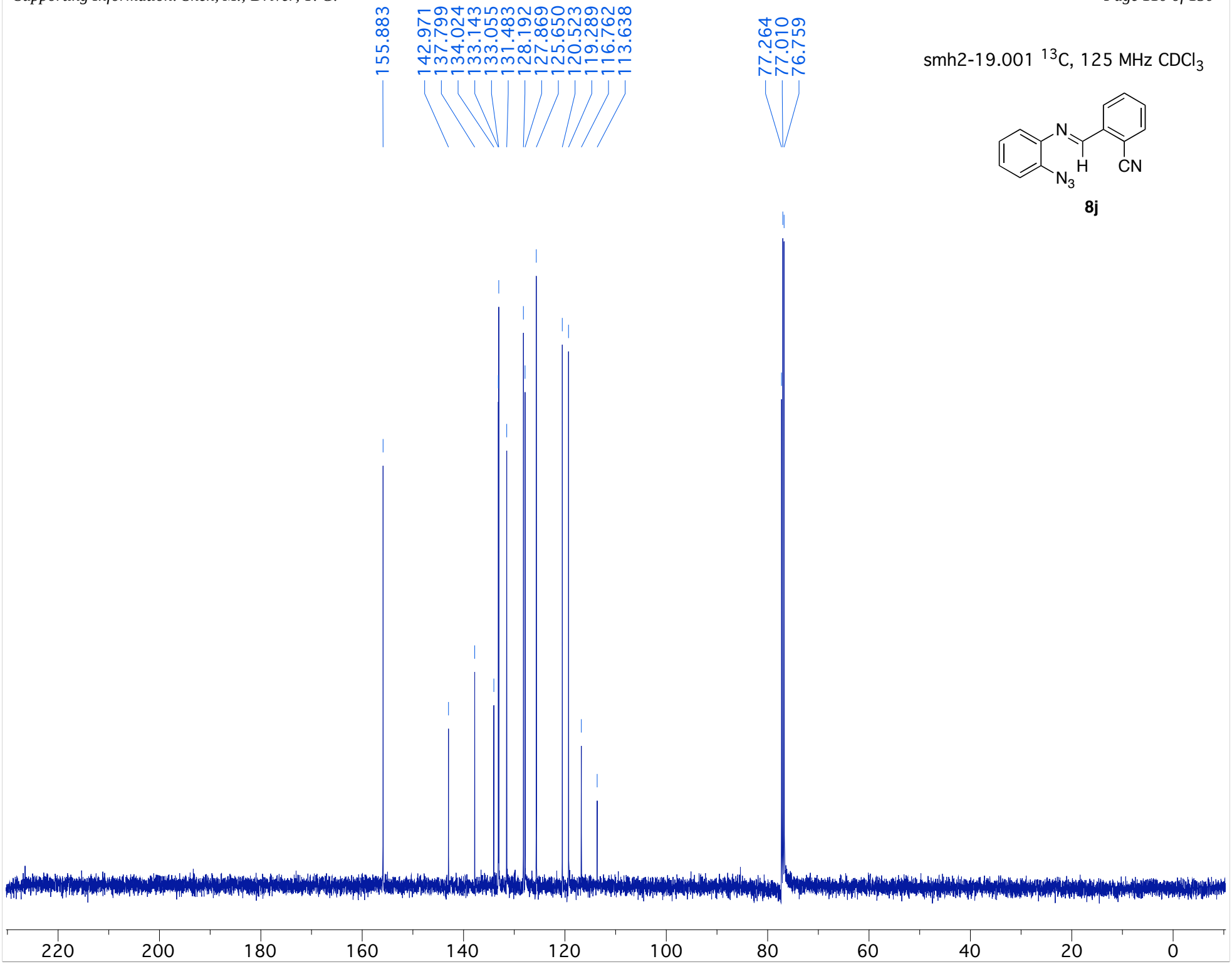

157.706
149.389
143.074
141.124
134.009
129.661
128.162
125.591
124.034
120.622
119.054
77.271
77.013
76.760
smh151.002 ^{13}C, 125 MHz $CDCl_3$
NO_2
N
H
N_3
220
200
180
160
140
120
100
80
60
40
20
0

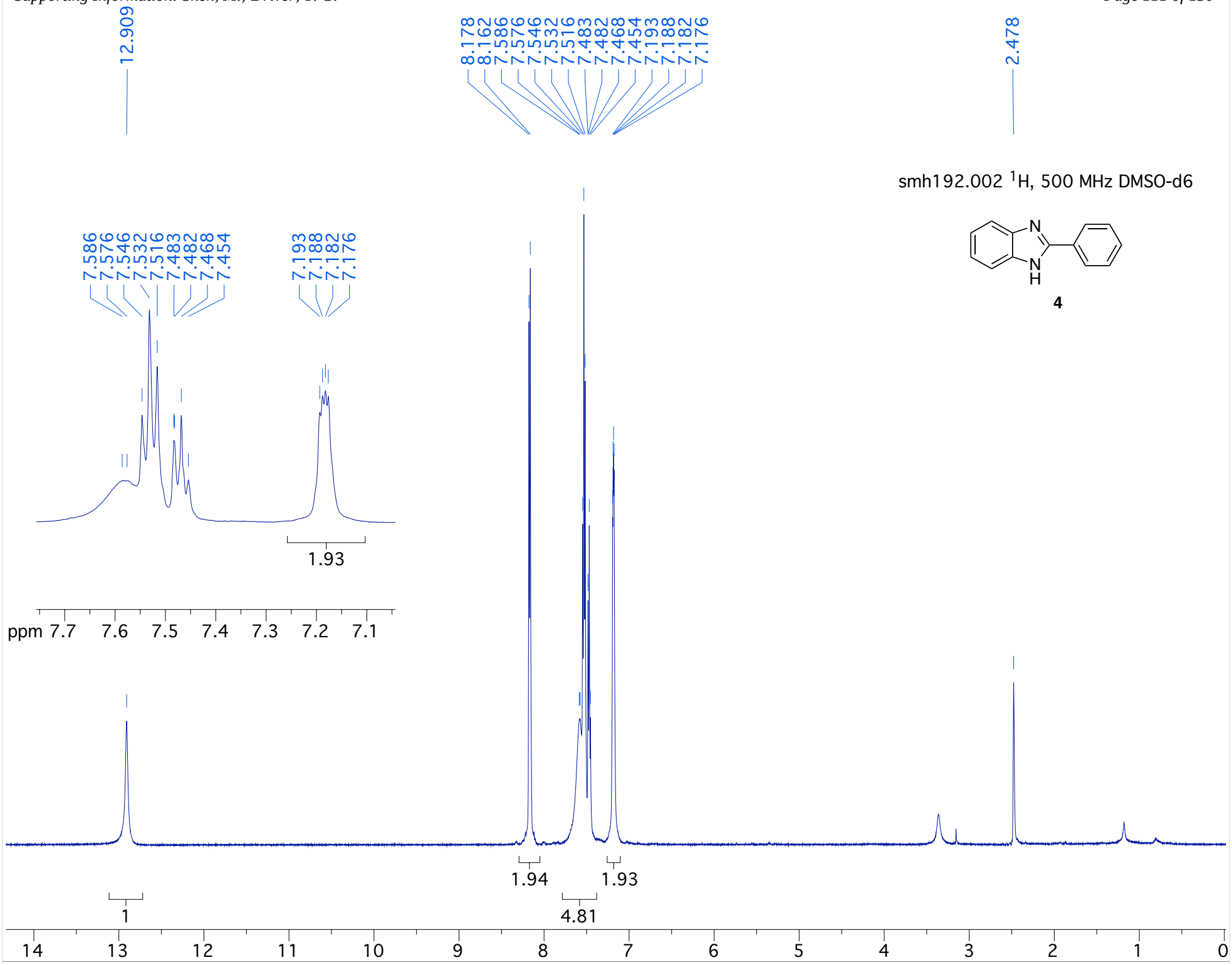
5


8.387
7.784
7.767
7.623
7.606
7.260
7.230
7.227
7.215
7.213
7.200
7.197
7.164
7.161
7.149
7.146
7.134
7.131
7.080
7.077
7.064
7.061
7.049
7.046
smh150 ^{1}H, 500 MHz $CDCl_3$
Br
N
H
N_3
8b
1.07
2.06
1.07
ppm 7.2
7.1
2.06
1.07
2.06
1
2.12
1.07
ppm 11
10
9
8
7
6
5
4
3
2
1
0

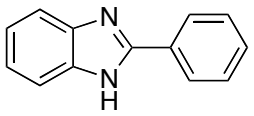

159.264
143.866
134.730
133.549
132.095
130.395
127.252
126.341
125.531
120.376
119.157
77.260
77.009
76.757
smh150 ^{13}C, 125 MHz $CDCl_3$
Br
N
H
N_3
8b
220
200
180
160
140
120
100
80
60
40
20
0


8.856
8.367
8.351
7.760
7.744
7.731
7.716
7.700
7.599
7.597
7.584
7.582
7.569
7.566
7.276
7.273
7.262
7.260
7.259
7.257
7.247
7.243
7.196
7.194
7.180
7.178
7.166
7.164
7.161
7.158
7.146
7.142
7.099
7.097
7.083
7.082
smh2-19.001 ^{1}H, 500 MHz $CDCl_3$
N
H
CN
N_3
8j
1.04
1.12
2.17
1
2.27
1.14
1.09
ppm 11
10
9
8
7
6
5
4
3
2
1
0
ppm 7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0

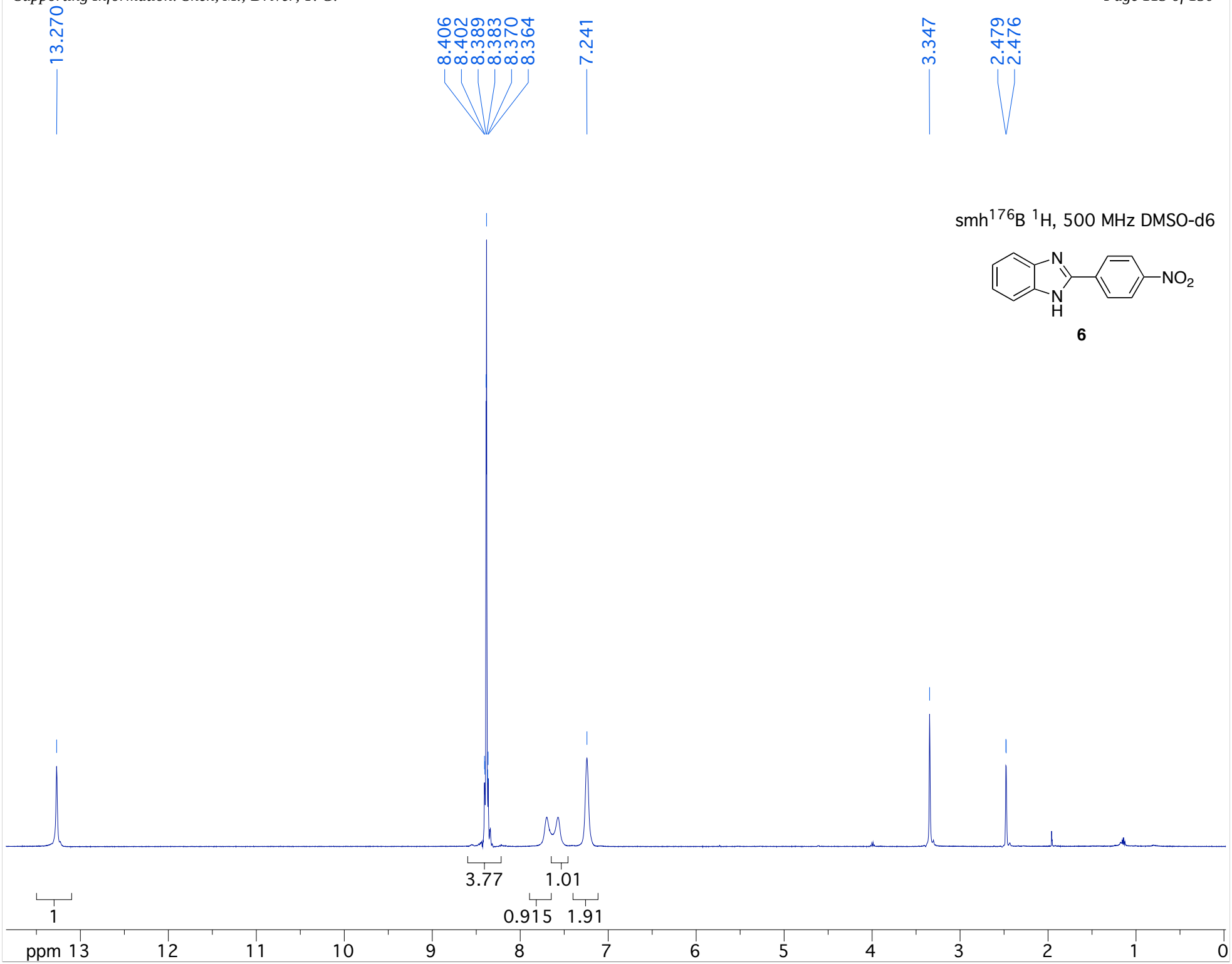

155.883
142.971
137.799
134.024
133.143
133.055
131.483
128.192
127.869
125.650
120.523
119.289
116.762
113.638
77.264
77.010
76.759
smh2-19.001 13C, 125 MHz CDCl3
N
H
N3
CN
8j
220
200
180
160
140
120
100
80
60
40
20
0

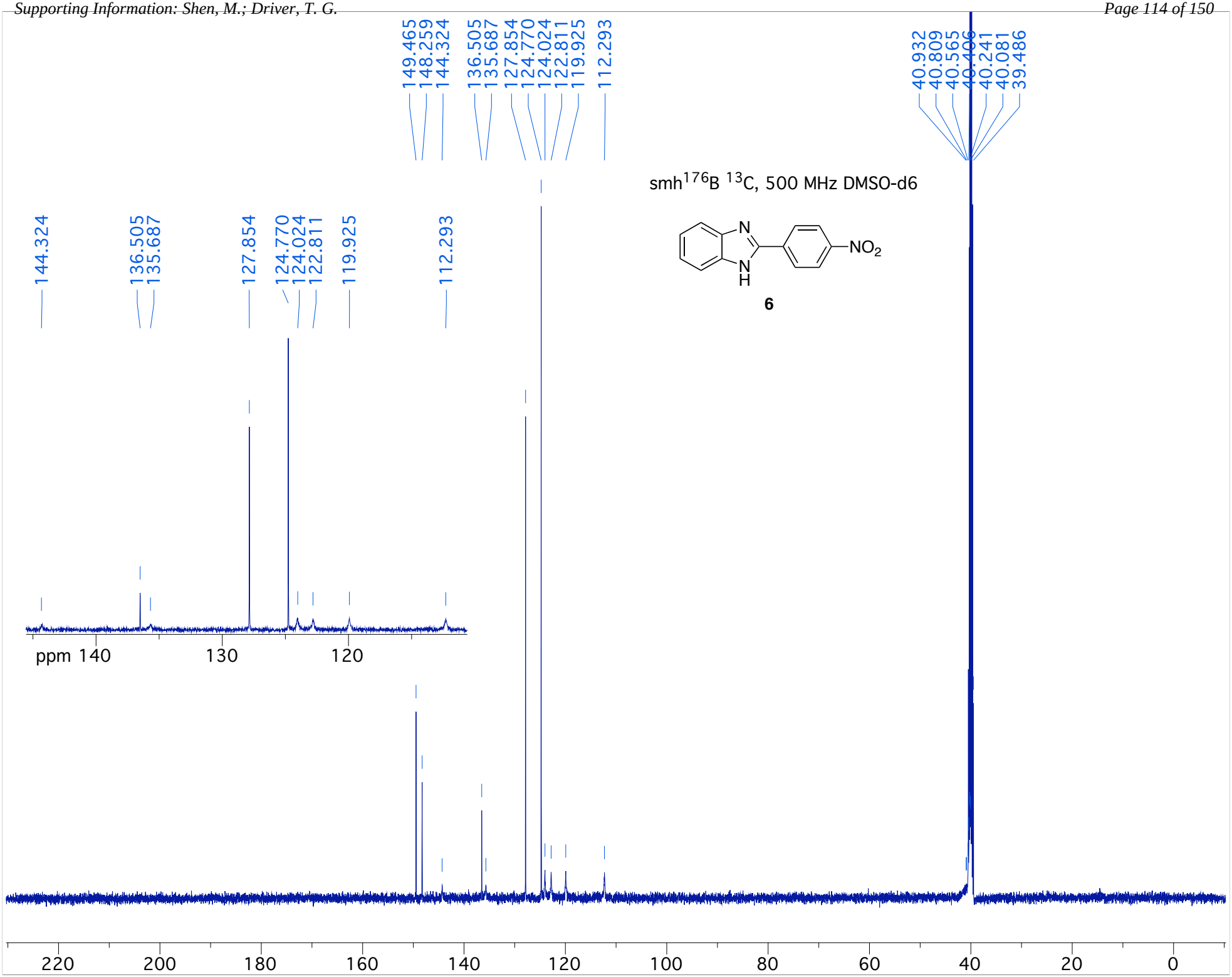

12.909
8.178
8.162
7.586
7.576
7.546
7.532
7.516
7.483
7.482
7.468
7.454
7.193
7.188
7.182
7.176
2.478
smh192.002 1H, 500 MHz DMSO-d6
N
N
H
4
7.586
7.576
7.546
7.532
7.516
7.483
7.482
7.468
7.454
7.193
7.188
7.182
7.176
1.93
ppm 7.7 7.6 7.5 7.4 7.3 7.2 7.1
1.94
1.93
1
4.81
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0

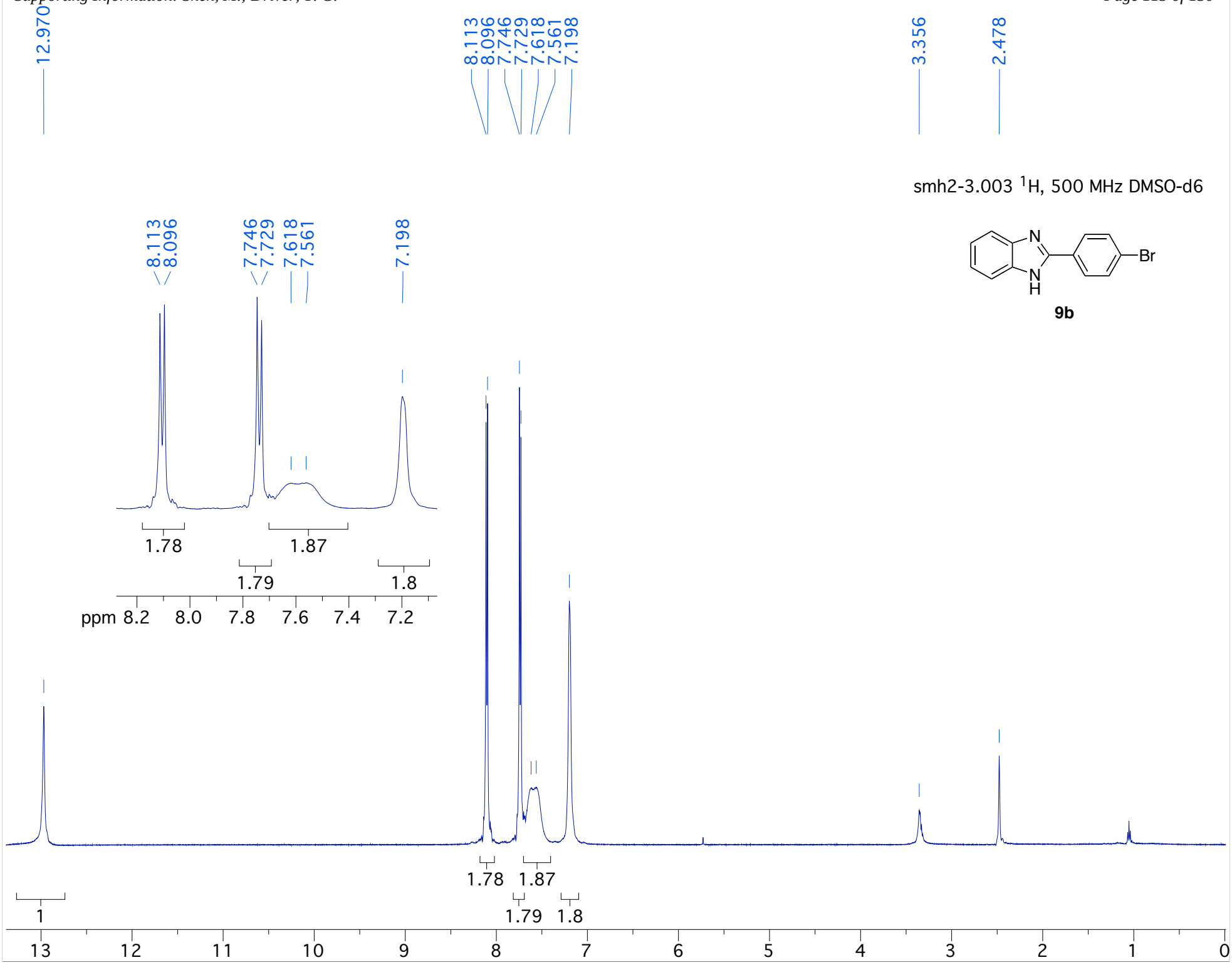
smh192.003 ^{13}C, 125 MHz DMSO-d6

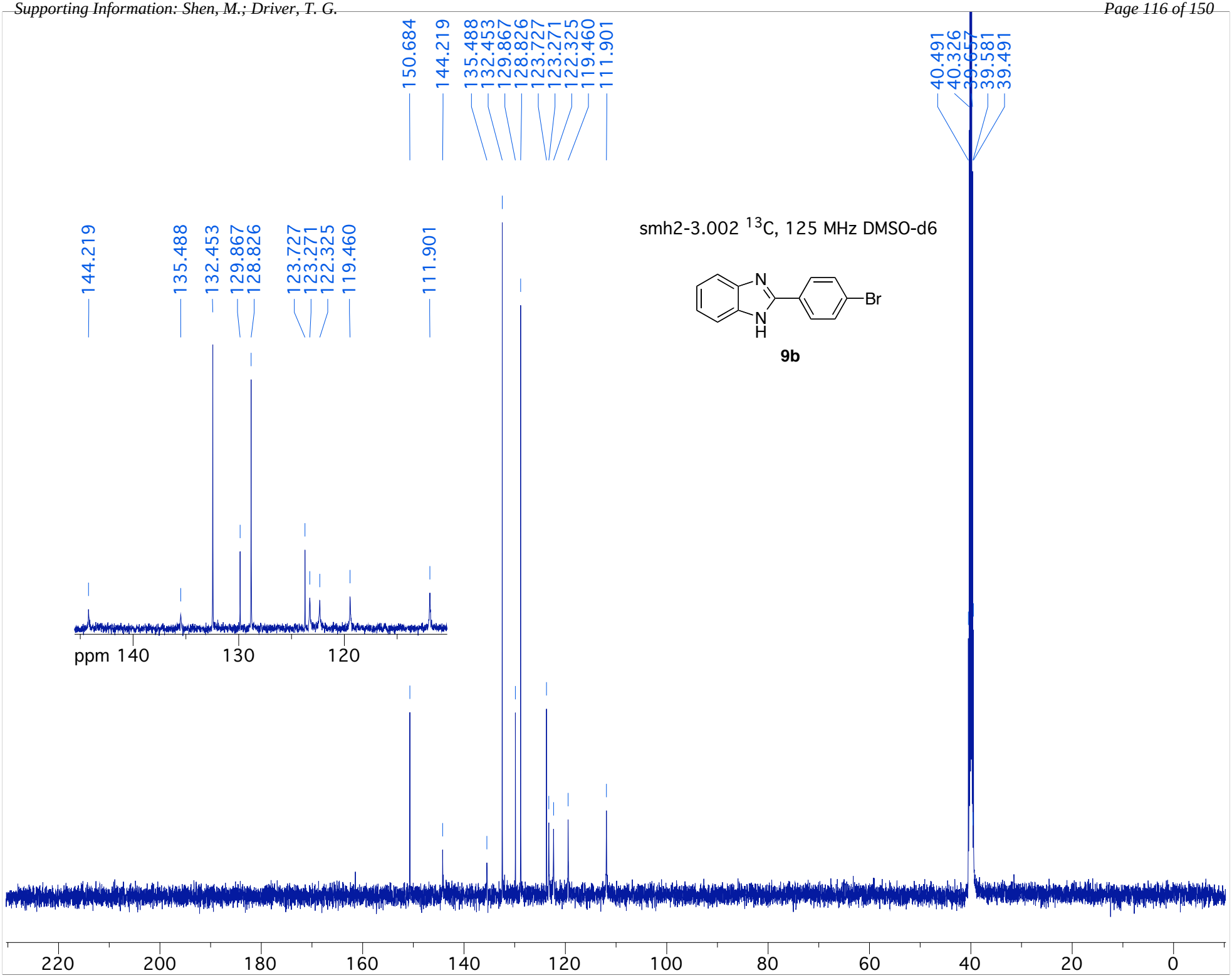


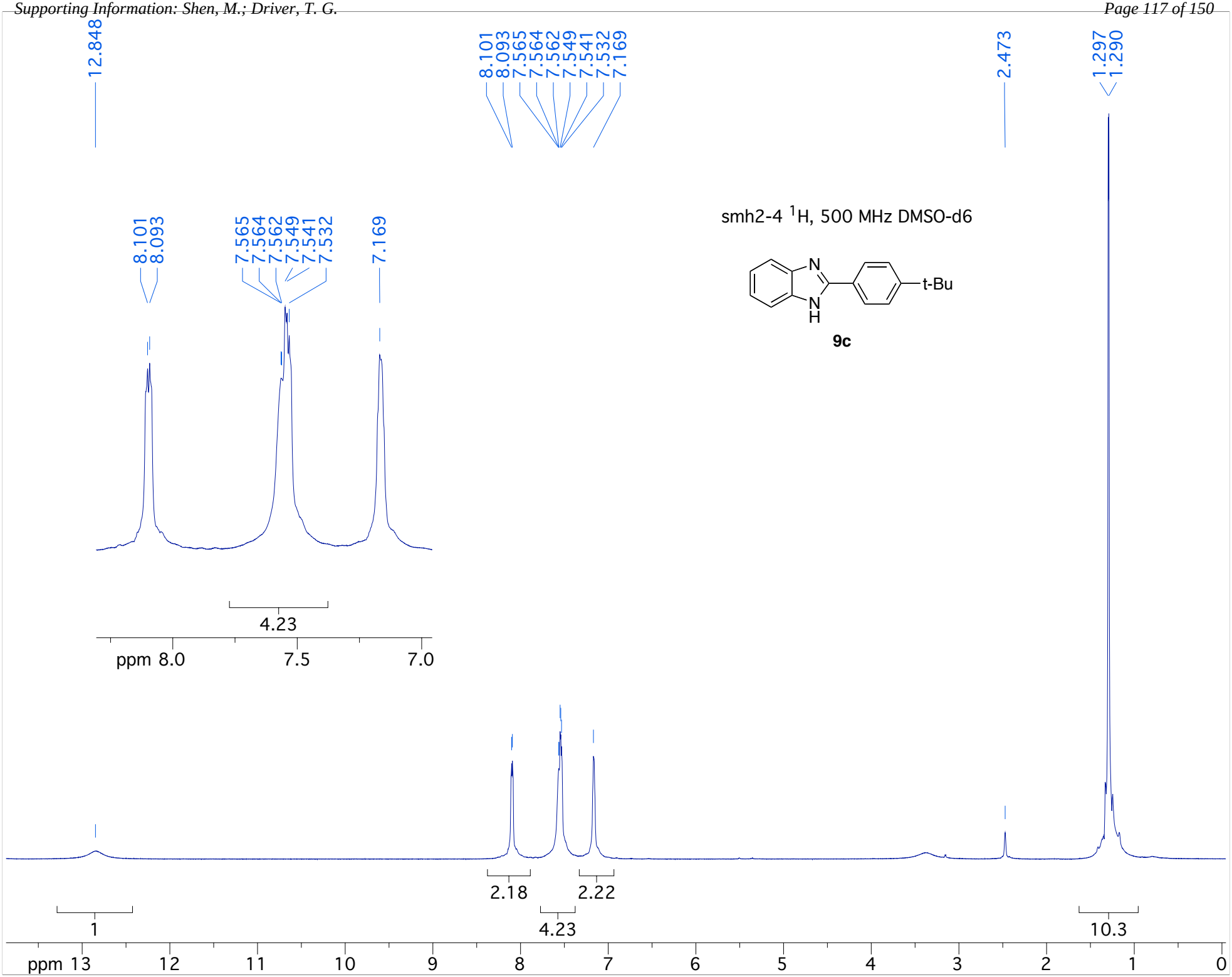
4


13.270
8.406
8.402
8.389
8.383
8.370
8.364
7.241
3.347
2.479
2.476
smh176B 1H, 500 MHz DMSO-d6
N
N
H
NO2
6
3.77
1.01
1
0.915
1.91
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0

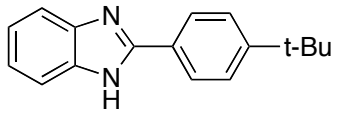

149.465
148.259
144.324
136.505
135.687
127.854
124.770
124.024
122.811
119.925
112.293
40.932
40.809
40.565
40.406
40.241
40.081
39.486
smh176B 13C, 500 MHz DMSO-d6
N
N
H
NO2
6
144.324
136.505
135.687
127.854
124.770
124.024
122.811
119.925
112.293
ppm 140
130
120
220
200
180
160
140
120
100
80
60
40
20
0


12.970
8.113
8.096
7.746
7.729
7.618
7.561
7.198
3.356
2.478
smh2-3.003 ^{1}H, 500 MHz DMSO-d6
N
N
H
Br
9b
1.78
1.87
1.79
1.8
ppm 8.2 8.0 7.8 7.6 7.4 7.2
1
1.78 1.87
1.79 1.8
13 12 11 10 9 8 7 6 5 4 3 2 1 0

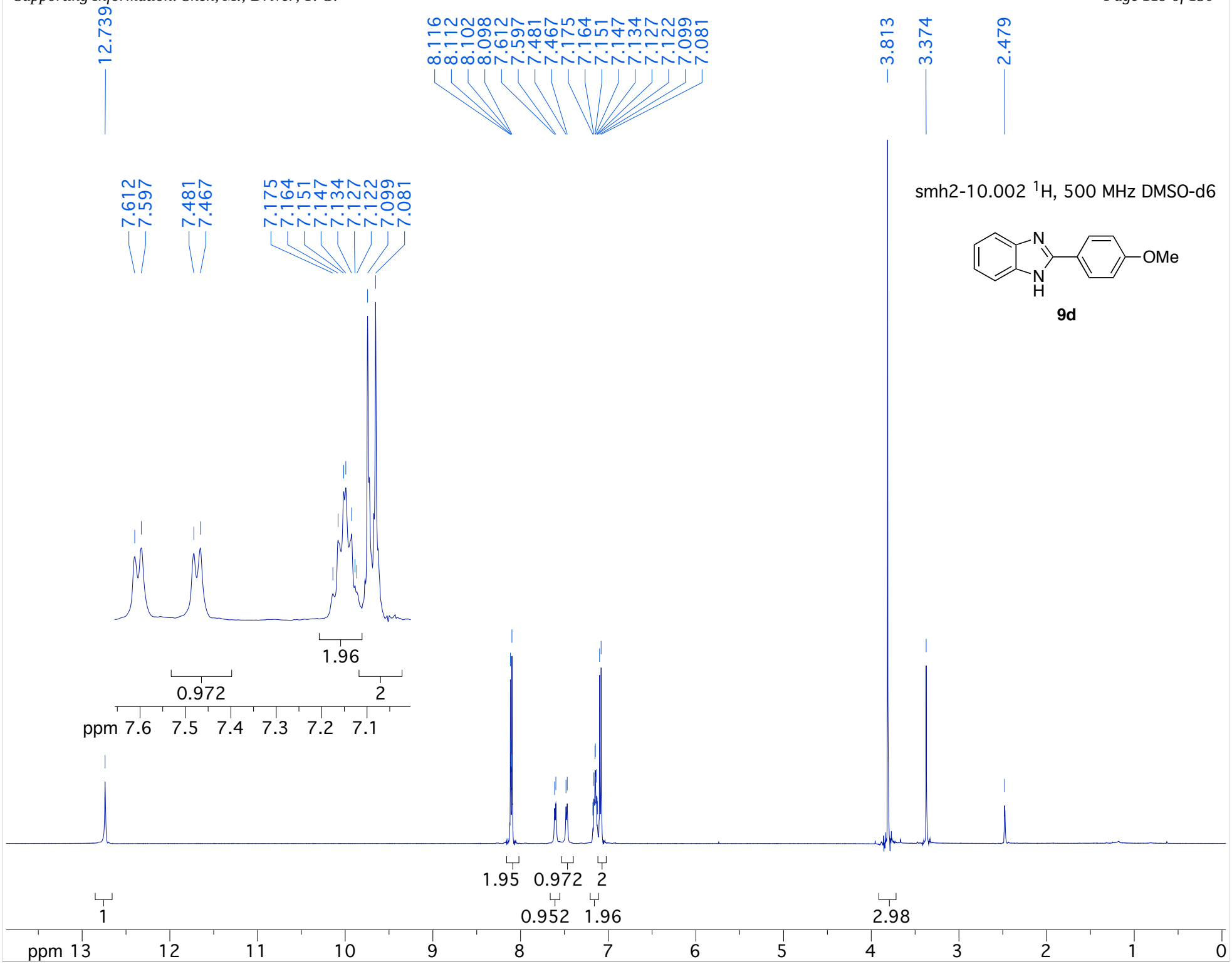

150.684
144.219
135.488
132.453
129.867
128.826
123.727
123.271
122.325
119.460
111.901
40.491
40.326
39.657
39.581
39.491
smh2-3.002 13C, 125 MHz DMSO-d6
N
N
H
Br
9b
144.219
135.488
132.453
129.867
128.826
123.727
123.271
122.325
119.460
111.901
ppm 140
130
120
220
200
180
160
140
120
100
80
60
40
20
0

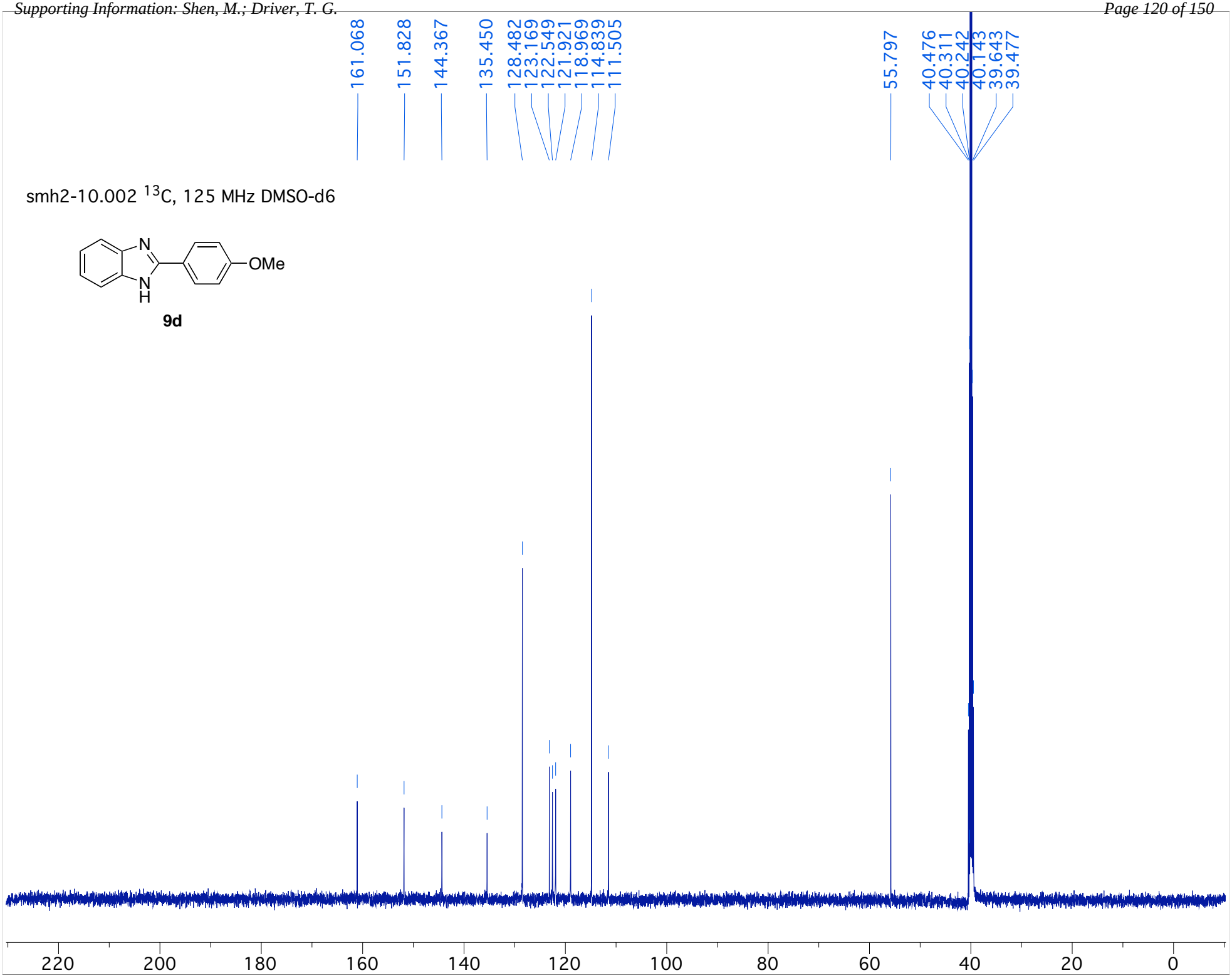

12.848
8.101
8.093
7.565
7.564
7.562
7.549
7.541
7.532
7.169
2.473
1.297
1.290
smh2-4 ^{1}H, 500 MHz DMSO-d6
N
N
H
t-Bu
9c
4.23
ppm 8.0
7.5
7.0
2.18
2.22
1
4.23
10.3
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0

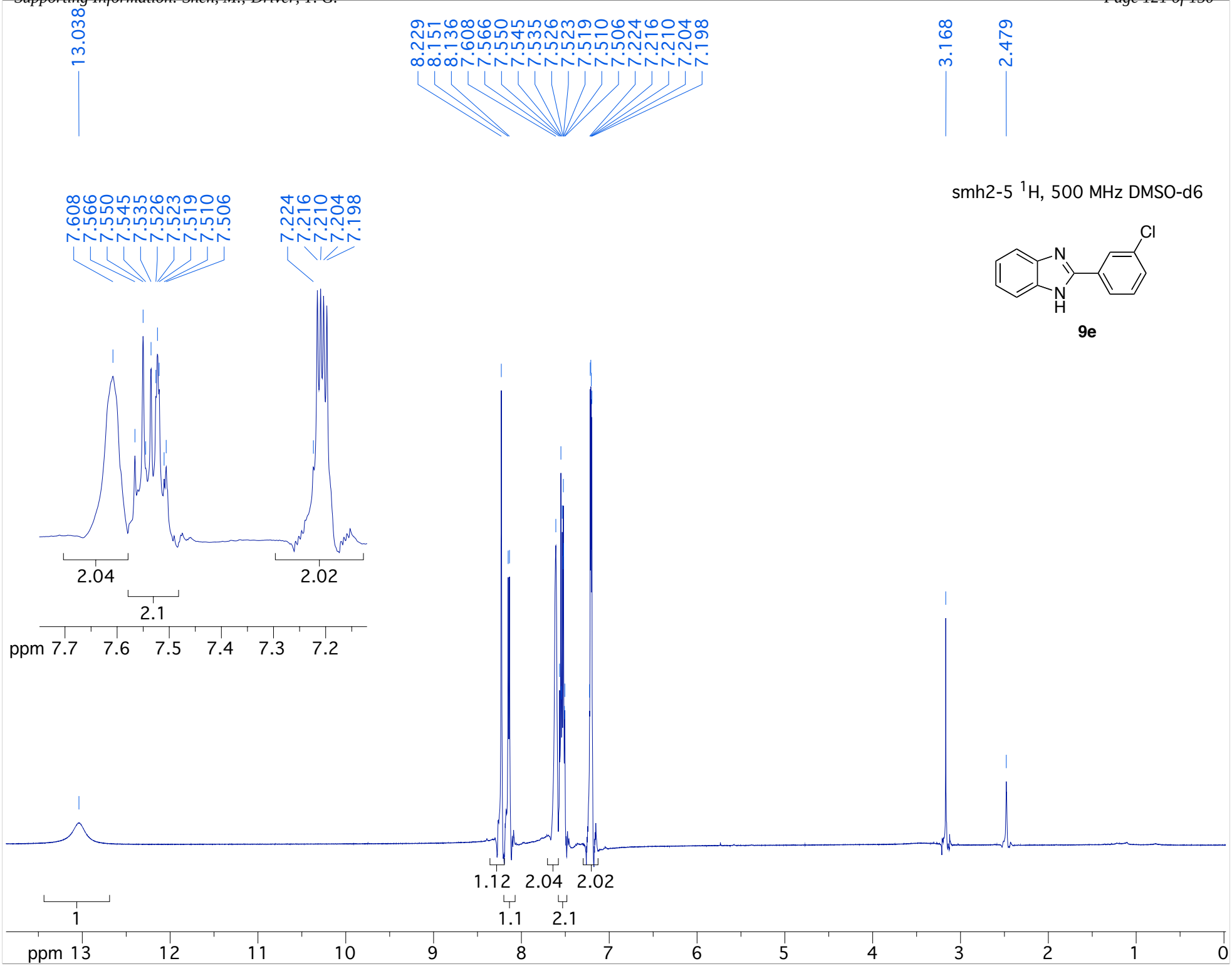
smh2-4 ^{13}C, 125 MHz DMSO-d6



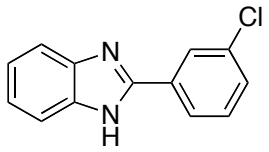
9c


12.739
8.116
8.112
8.102
8.098
7.612
7.597
7.481
7.467
7.175
7.164
7.151
7.147
7.134
7.127
7.122
7.099
7.081
3.813
3.374
2.479
smh2-10.002 1H, 500 MHz DMSO-d6
N
N
H
OMe
9d
1.96
0.972
2
ppm 7.6 7.5 7.4 7.3 7.2 7.1
1.95 0.972 2
1
0.952 1.96
2.98
ppm 13 12 11 10 9 8 7 6 5 4 3 2 1 0

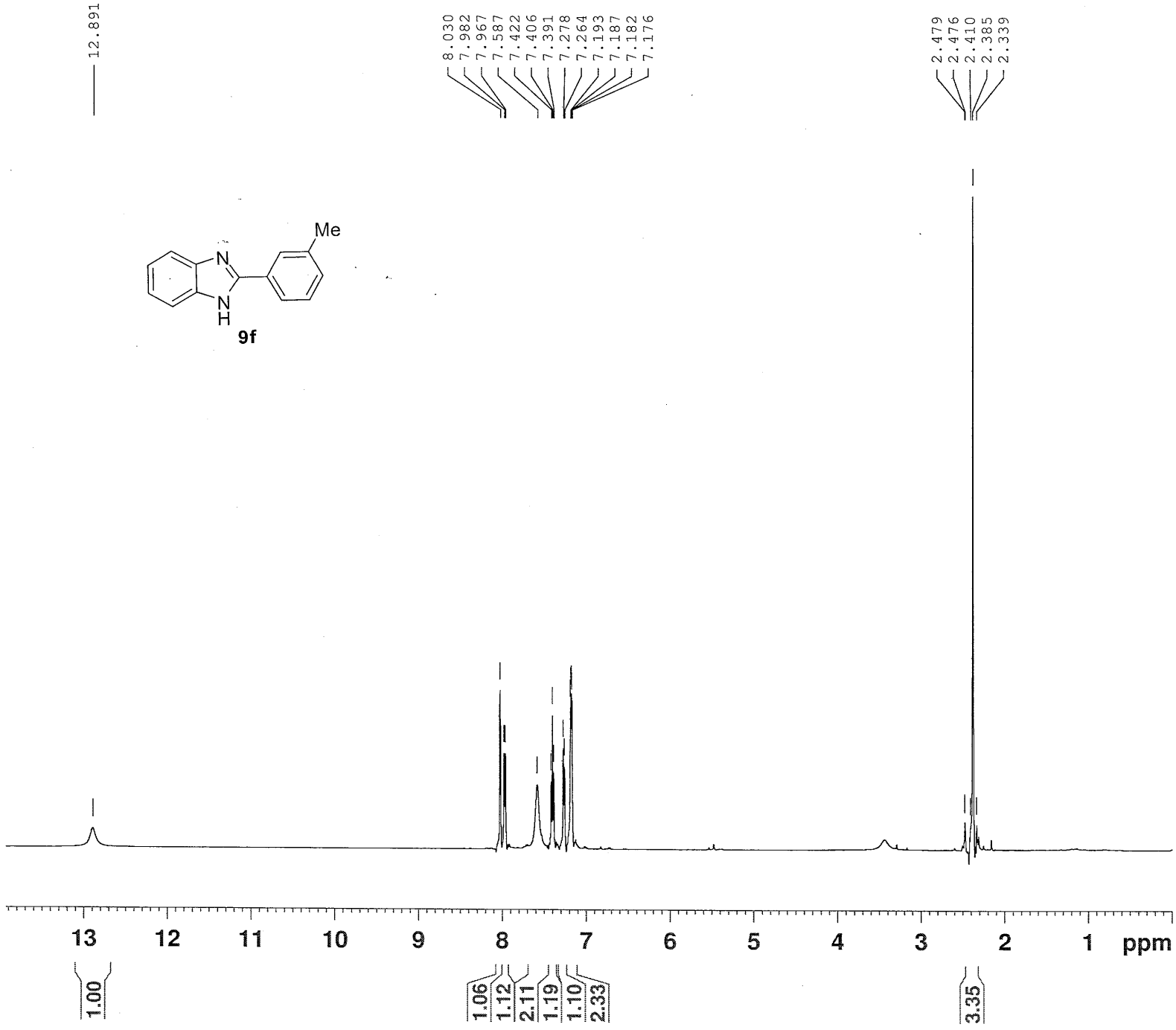

161.068
151.828
144.367
135.450
128.482
123.169
122.549
121.921
118.969
114.839
111.505
55.797
40.476
40.311
40.242
40.143
39.643
39.477
smh2-10.002 13C, 125 MHz DMSO-d6
N
N
H
OMe
9d
220
200
180
160
140
120
100
80
60
40
20
0


13.038
8.229
8.151
8.136
7.608
7.566
7.550
7.545
7.535
7.526
7.523
7.519
7.510
7.506
7.224
7.216
7.210
7.204
7.198
3.168
2.479
smh2-5 1H, 500 MHz DMSO-d6
Cl
N
N
H
9e
2.04
2.02
2.1
ppm 7.7 7.6 7.5 7.4 7.3 7.2
1.12
2.04
2.02
1
1.1
2.1
ppm 13 12 11 10 9 8 7 6 5 4 3 2 1 0

smh2-5 ^{13}C, 125 MHz DMSO-d6



9e

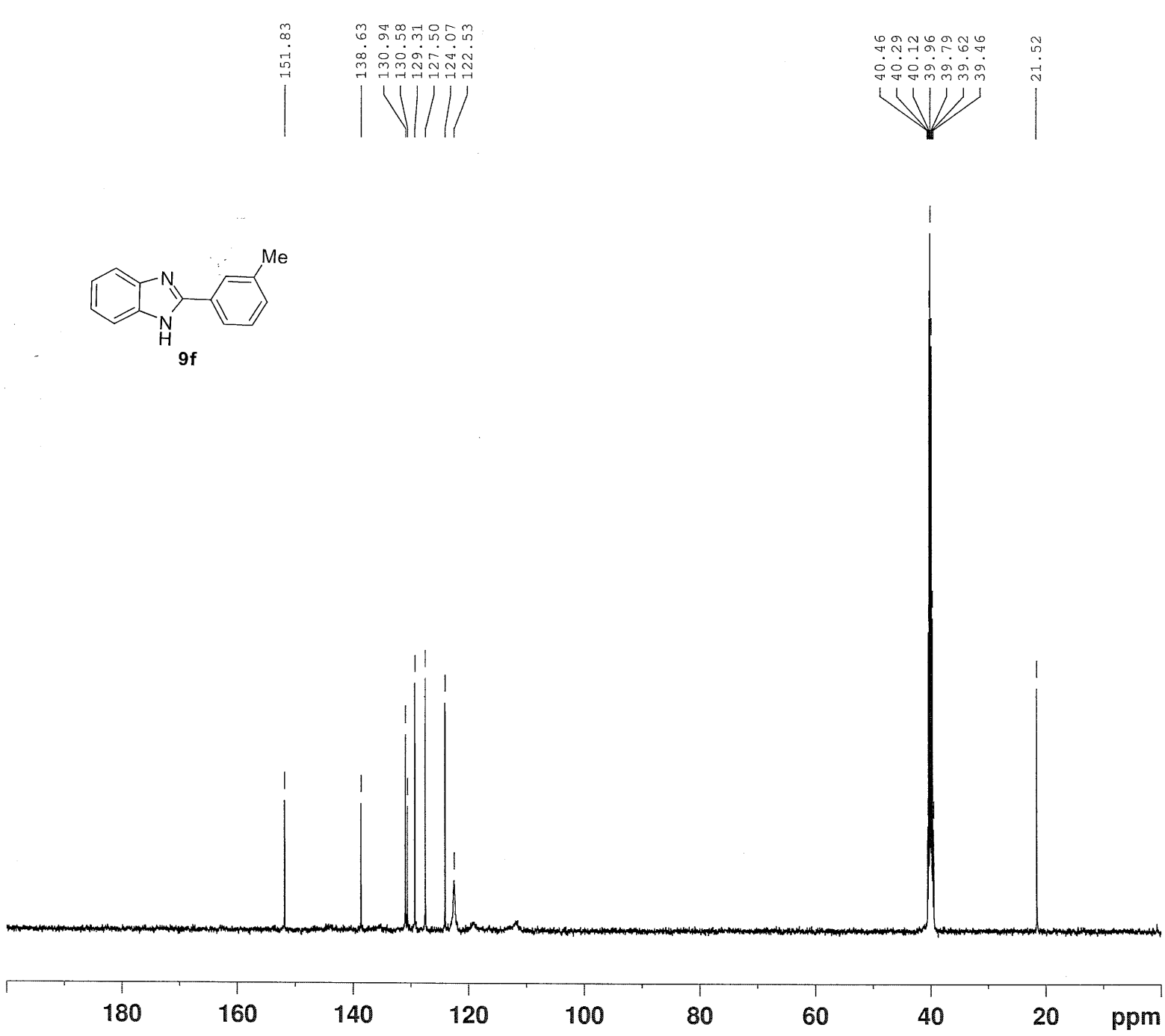


Current Data Parameters
NAME .smh2-13.002
EXPNO 1
PROCNO 1

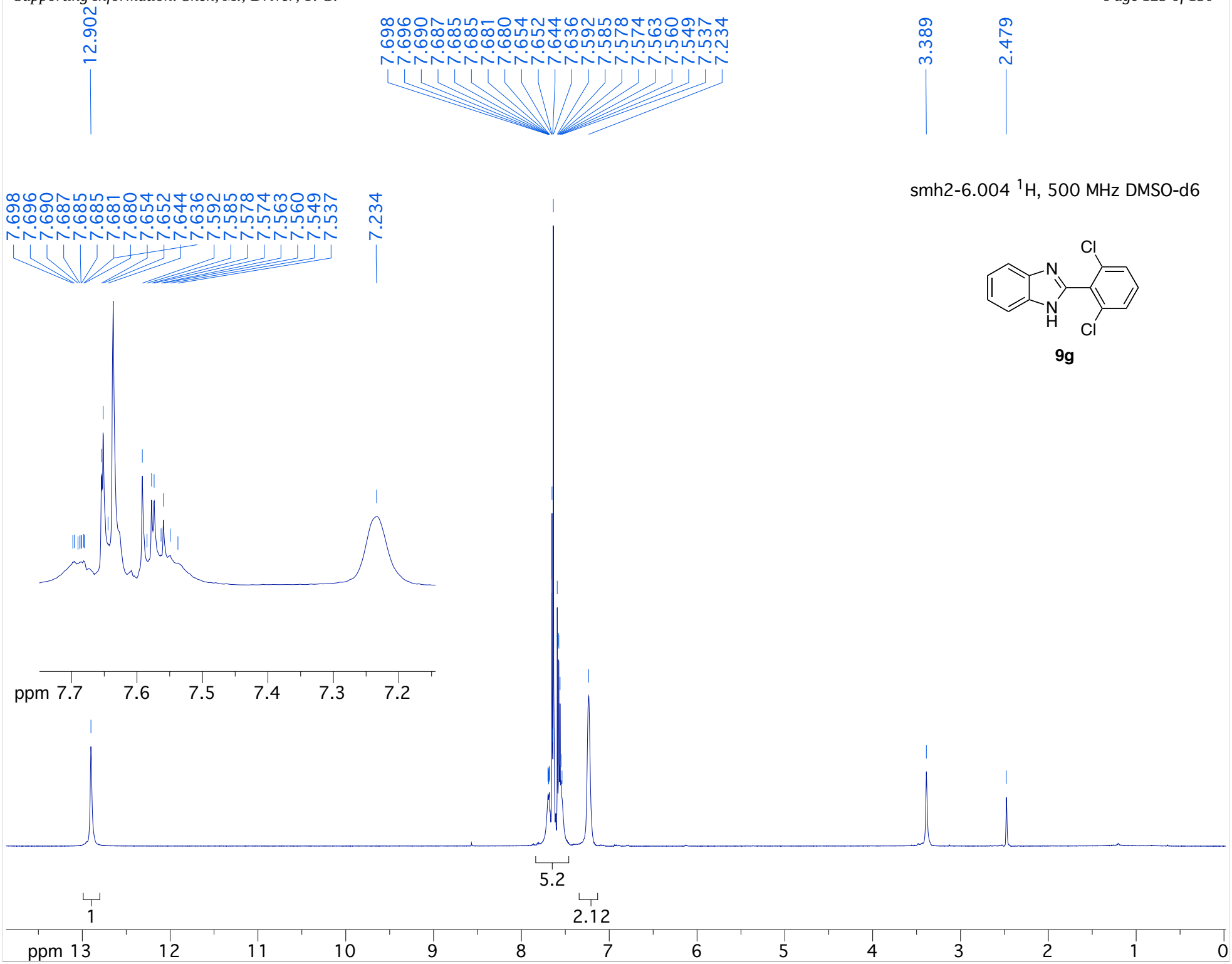
F2 - Acquisition Parameters
Date_ 20071108
Time 16.27
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8503.401 Hz
FIDRES 0.259503 Hz
AQ 1.9268672 sec
RG 80.6
DW 58.800 use
DE 6.00 use
TE 300.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

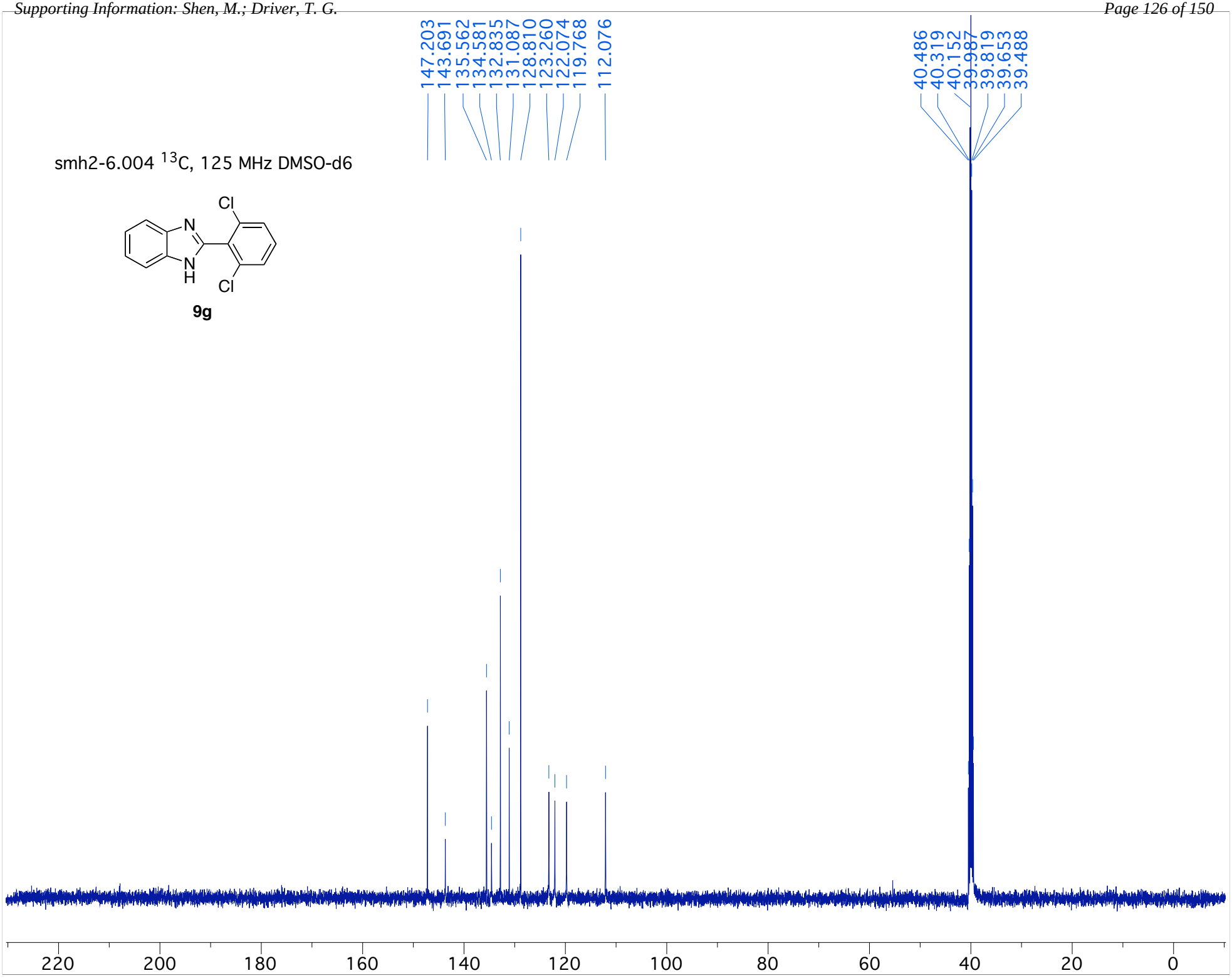
======== CHANNEL f1 ========
NUC1 1H
P1 3.50 use
PL1 -2.00 dB
SFO1 500.6427535 MHz

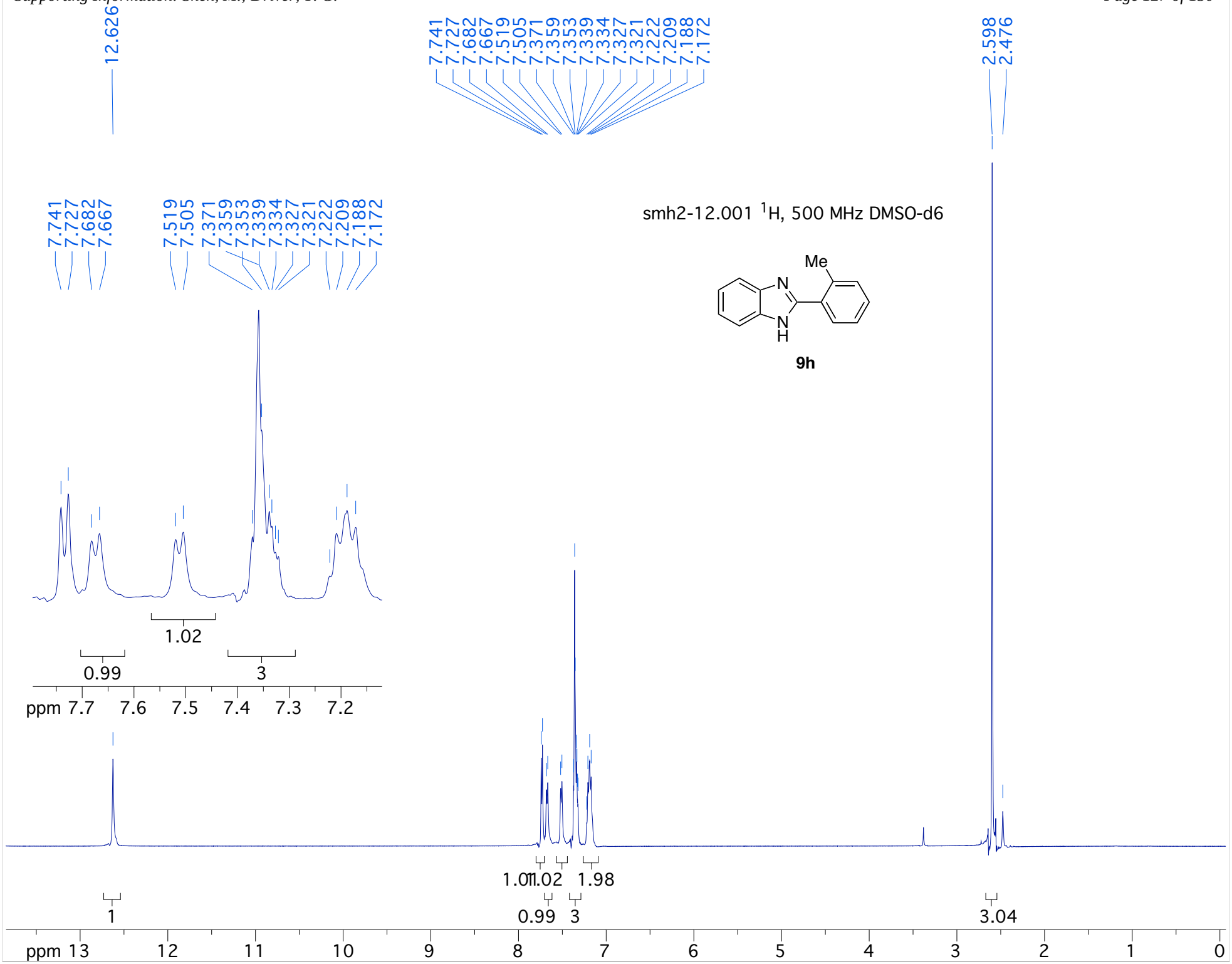
F2 - Processing parameters
SI 32768
SF 500.6400128 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



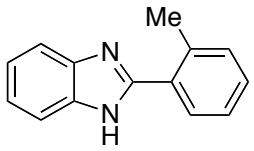

```
Current Data Parameters
NAME          .smh2-13.002
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20071108
Time                 16.32
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG              zgpg
TD                  32768
SOLVENT             CDCl3
NS                    164
DS                      2
SWH             30303.031 Hz
FIDRES          0.924775 Hz
AQ              0.5407385 sec
RG                  16384
DW                16.500 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                 2.70 usec
PL1                1.00 dB
SFO1        125.8998755 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             83.00 usec
PL2               -2.00 dB
PL12              15.40 dB
PL13              20.00 dB
SFO2        500.6422529 MHz

F2 - Processing parameters
SI                  16384
SF          125.8860280 MHz
WDW                    EM
SSB                     0
LB                 3.00 Hz
GB                      0
PC                   1.00
```


12.902
7.698
7.696
7.690
7.687
7.685
7.685
7.681
7.680
7.654
7.652
7.644
7.636
7.592
7.585
7.578
7.574
7.563
7.560
7.549
7.537
7.234
3.389
2.479
smh2-6.004 1H, 500 MHz DMSO-d6
Cl
N
N
H
Cl
9g
ppm 7.7
7.6
7.5
7.4
7.3
7.2
5.2
1
2.12
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0

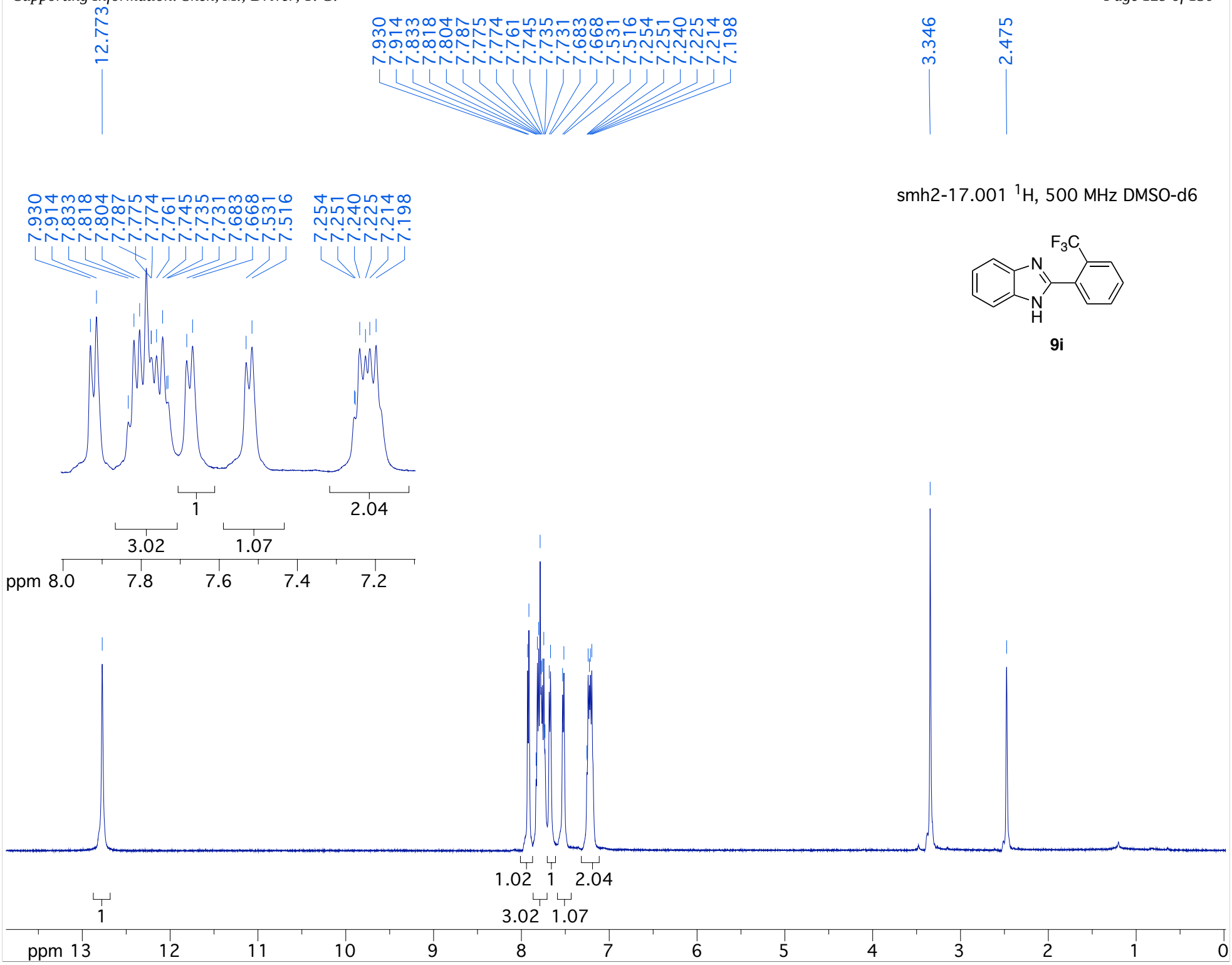

147.203
143.691
135.562
134.581
132.835
131.087
128.810
123.260
122.074
119.768
112.076
40.486
40.319
40.152
39.987
39.819
39.653
39.488
smh2-6.004 13C, 125 MHz DMSO-d6
Cl
N
N
H
Cl
9g
220
200
180
160
140
120
100
80
60
40
20
0


12.626
7.741
7.727
7.682
7.667
7.519
7.505
7.371
7.359
7.353
7.339
7.334
7.327
7.321
7.222
7.209
7.188
7.172
2.598
2.476
smh2-12.001 ^{1}H, 500 MHz DMSO-d6
Me
N
N
H
9h
1.02
0.99
3
ppm 7.7 7.6 7.5 7.4 7.3 7.2
1.01
1.02
1.98
1
0.99
3
3.04
ppm 13 12 11 10 9 8 7 6 5 4 3 2 1 0

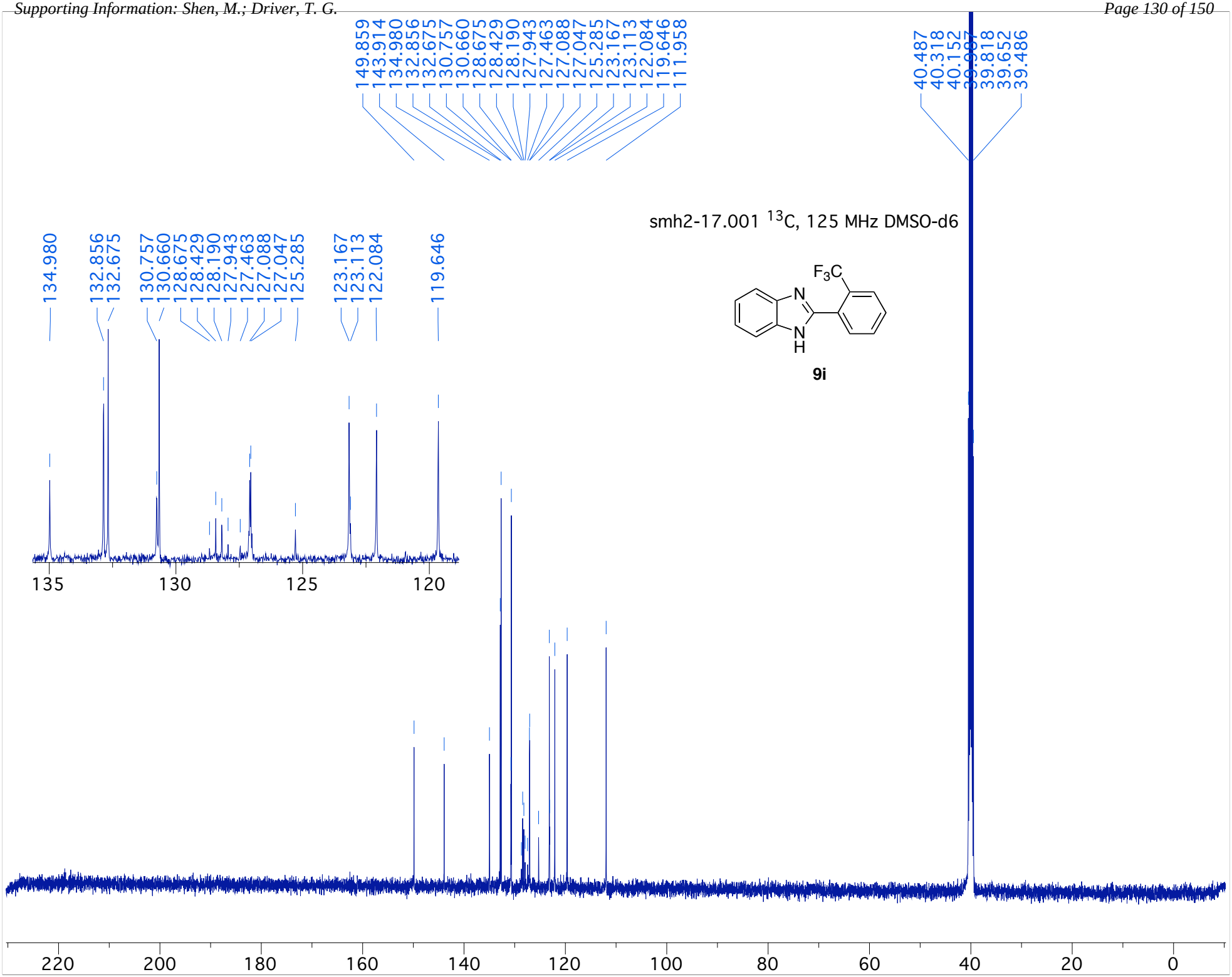
smh2-12.001 ^{13}C, 125 MHz DMSO-d6

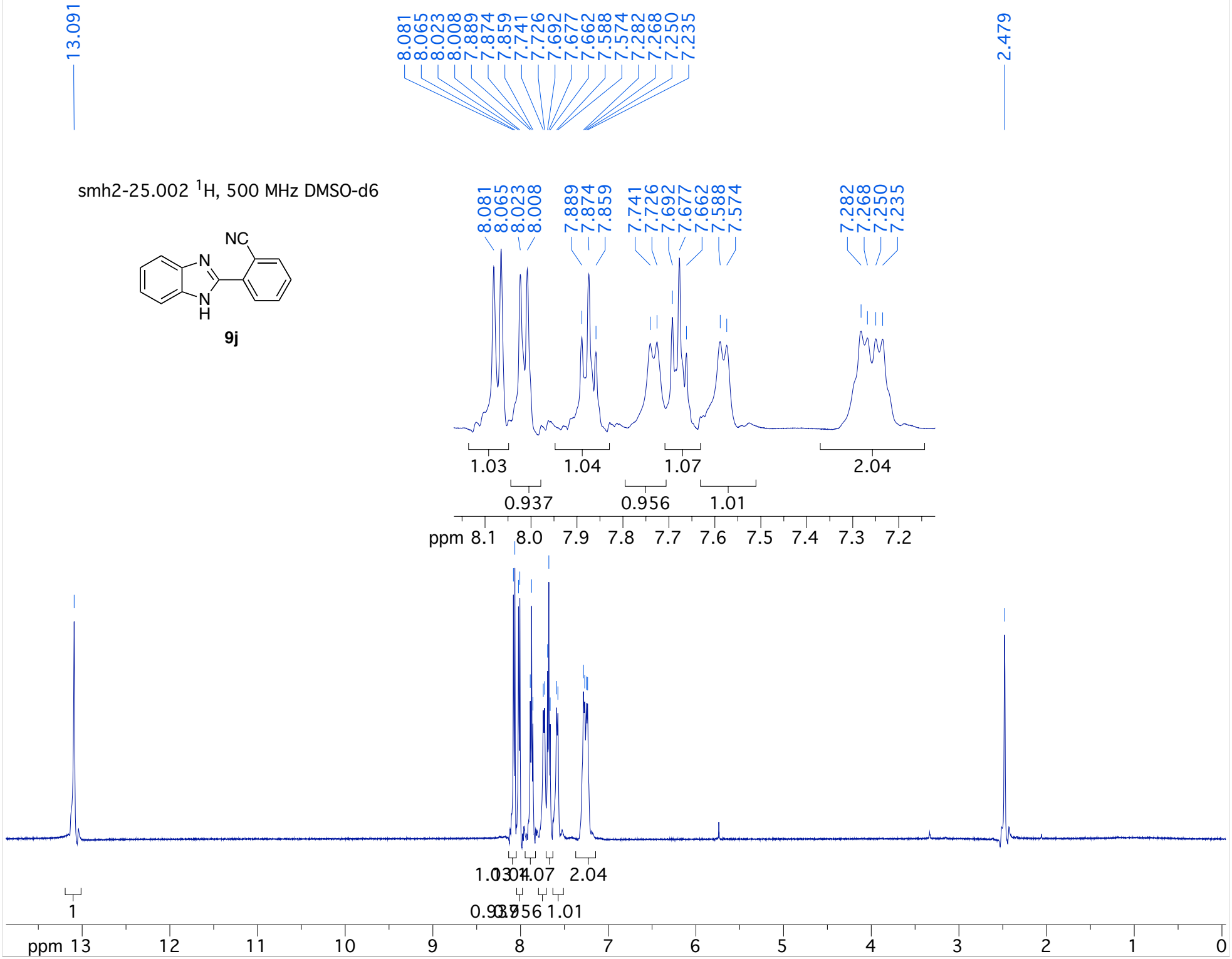


9h

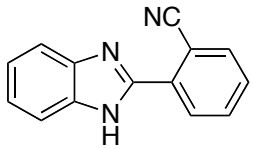

12.773
7.930
7.914
7.833
7.818
7.804
7.787
7.775
7.774
7.761
7.745
7.735
7.731
7.683
7.668
7.531
7.516
7.254
7.251
7.240
7.225
7.214
7.198
3.346
2.475
smh2-17.001 ^{1}H, 500 MHz DMSO-d6
F_3C
N
N
H
1
2.04
3.02
1.07
ppm 8.0
7.8
7.6
7.4
7.2
1.02
1
2.04
1
3.02
1.07
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0

9i


149.859
143.914
134.980
132.856
132.675
130.757
130.660
128.675
128.429
128.190
127.943
127.463
127.088
127.047
125.285
123.167
123.113
122.084
119.646
111.958
40.487
40.318
40.152
39.818
39.652
39.486
smh2-17.001 13C, 125 MHz DMSO-d6
F3C
N
N
H
9i
220
200
180
160
140
120
100
80
60
40
20
0
135
130
125
120


13.091
8.081
8.065
8.023
8.008
7.889
7.874
7.859
7.741
7.726
7.692
7.677
7.662
7.588
7.574
7.282
7.268
7.250
7.235
2.479
smh2-25.002 1H, 500 MHz DMSO-d6
NC
N
N
H
9j
1.03
1.04
1.07
2.04
0.937
0.956
1.01
ppm 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
1
ppm 13 12 11 10 9 8 7 6 5 4 3 2 1 0

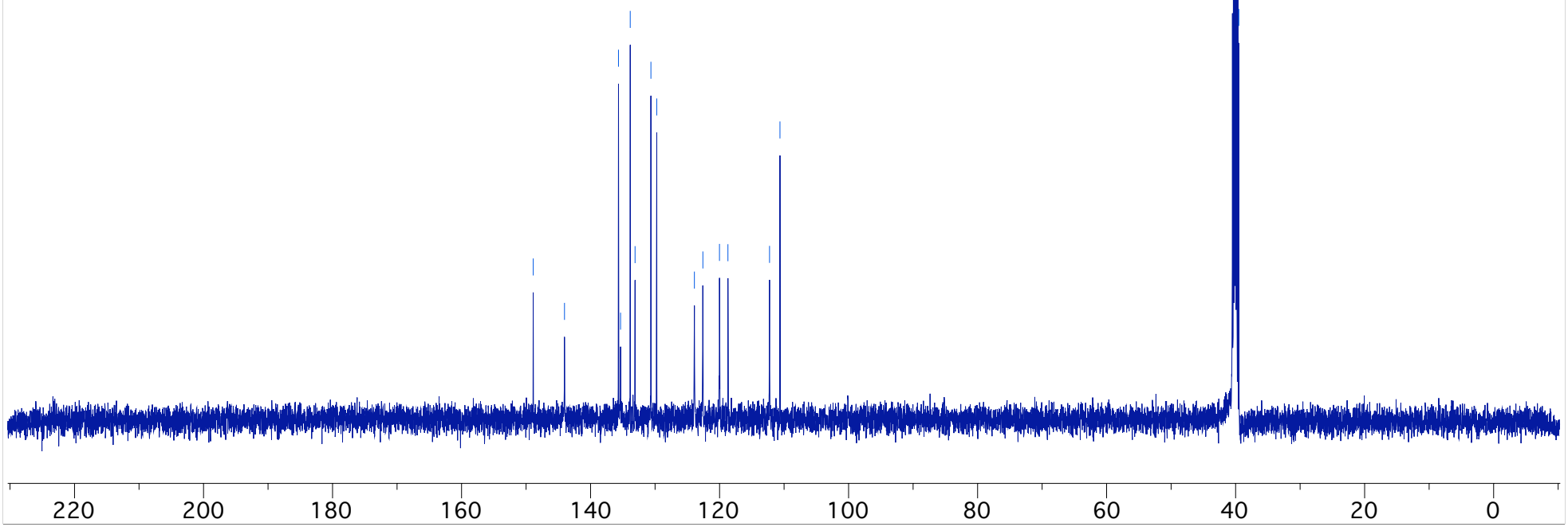
smh2-25.002 ^{13}C, 125 MHz DMSO-d6

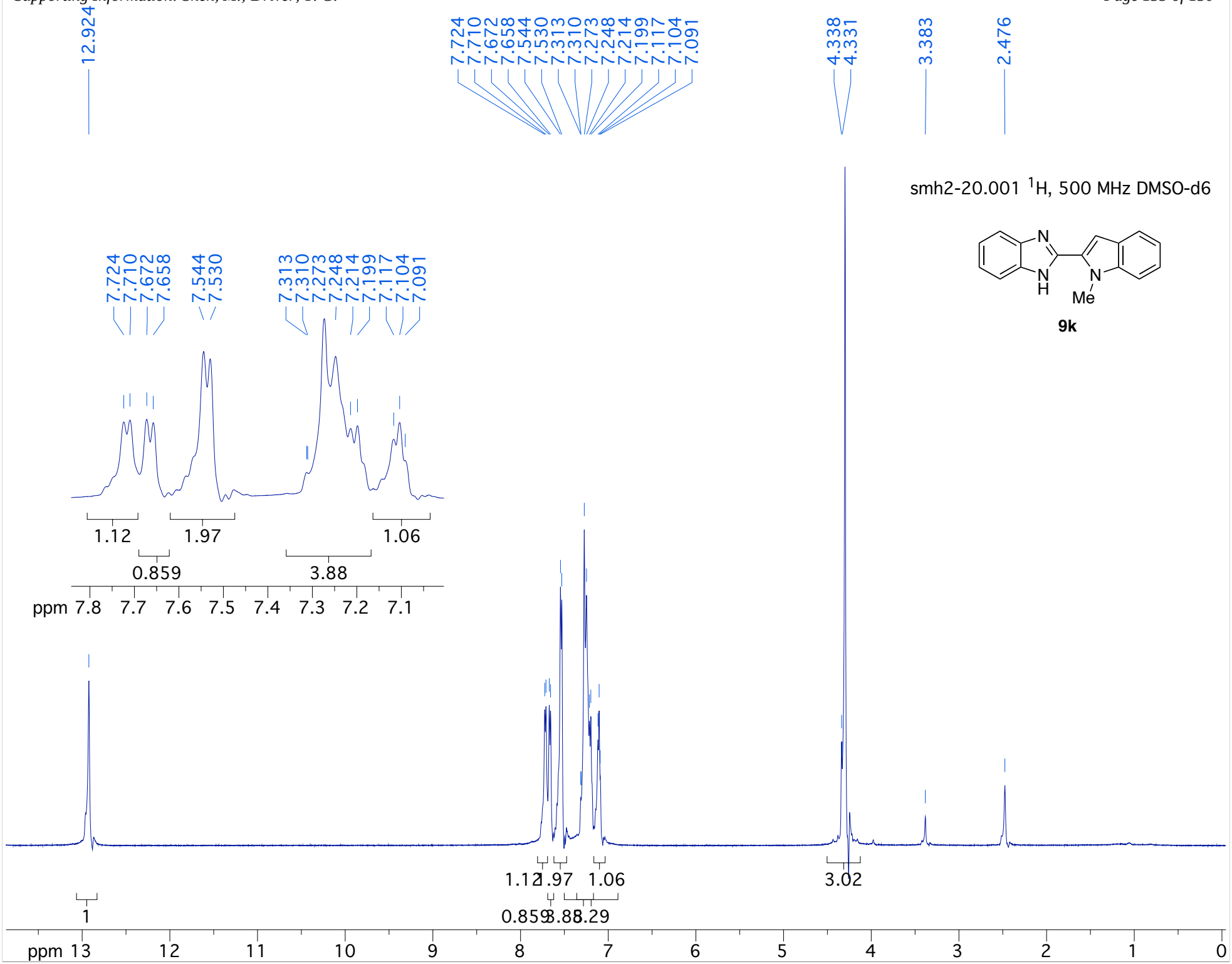


9j

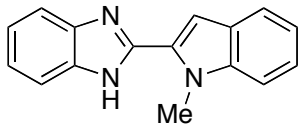
148.888
144.041
135.673
135.349
133.850
133.102
130.644
129.740
123.904
122.589
120.015
118.705
112.255
110.638

40.497
40.330
40.165
39.996
39.830
39.665
39.495

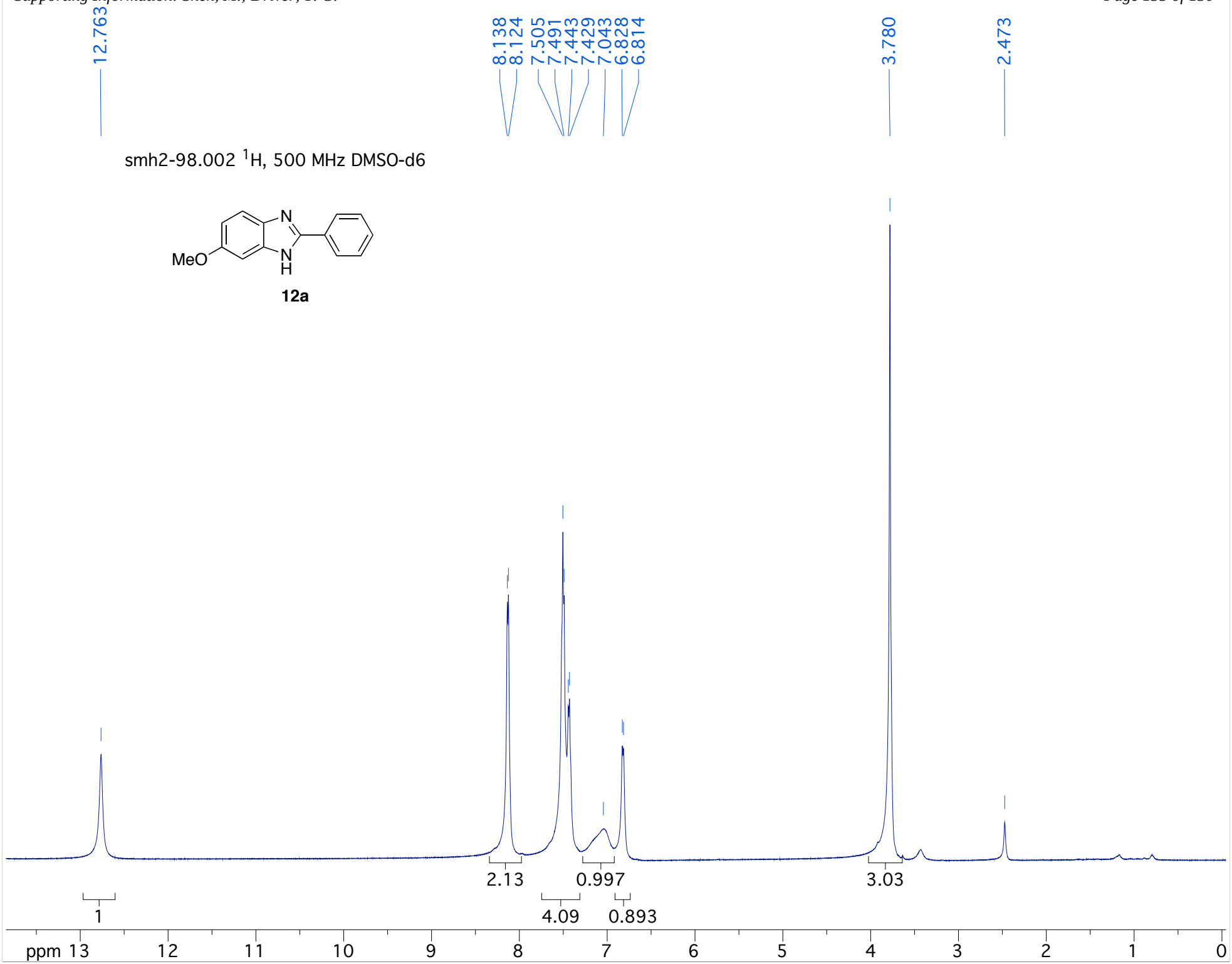



12.924
7.724
7.710
7.672
7.658
7.544
7.530
7.313
7.310
7.273
7.248
7.214
7.199
7.117
7.104
7.091
4.338
4.331
3.383
2.476
smh2-20.001 1H, 500 MHz DMSO-d6
N
N
H
N
Me
9k
1.12
1.97
1.06
0.859
3.88
ppm 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
1.12
1.97
1.06
3.02
1
0.859
3.88
3.29
ppm 13 12 11 10 9 8 7 6 5 4 3 2 1 0

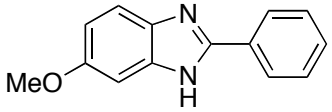
smh2-20.002 ^{13}C, 125 MHz DMSO-d6



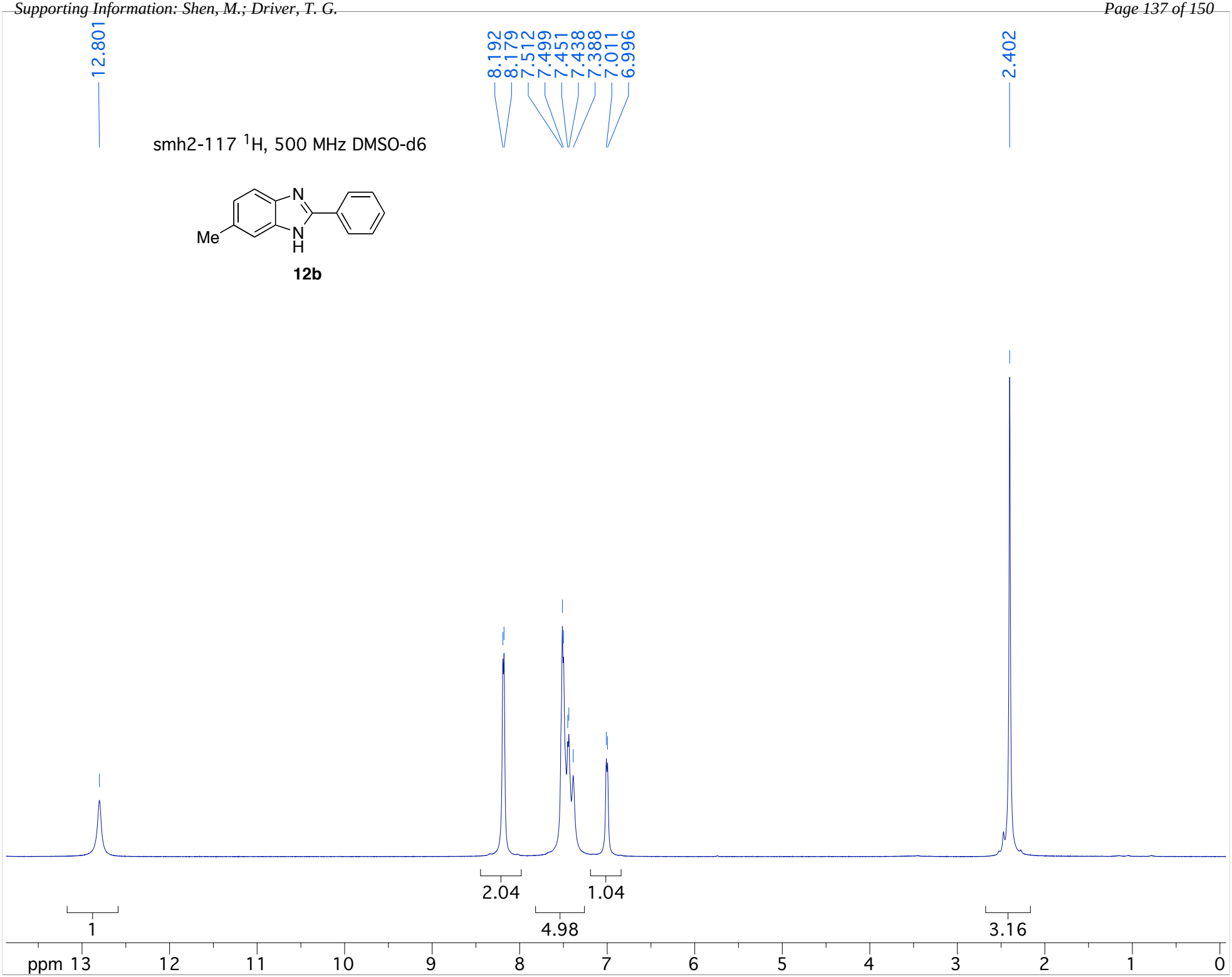
9k


12.763
8.138
8.124
7.505
7.491
7.443
7.429
7.043
6.828
6.814
3.780
2.473
smh2-98.002 ^{1}H, 500 MHz DMSO-d6
MeO
N
N
H
12a
2.13
0.997
3.03
1
4.09
0.893
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0

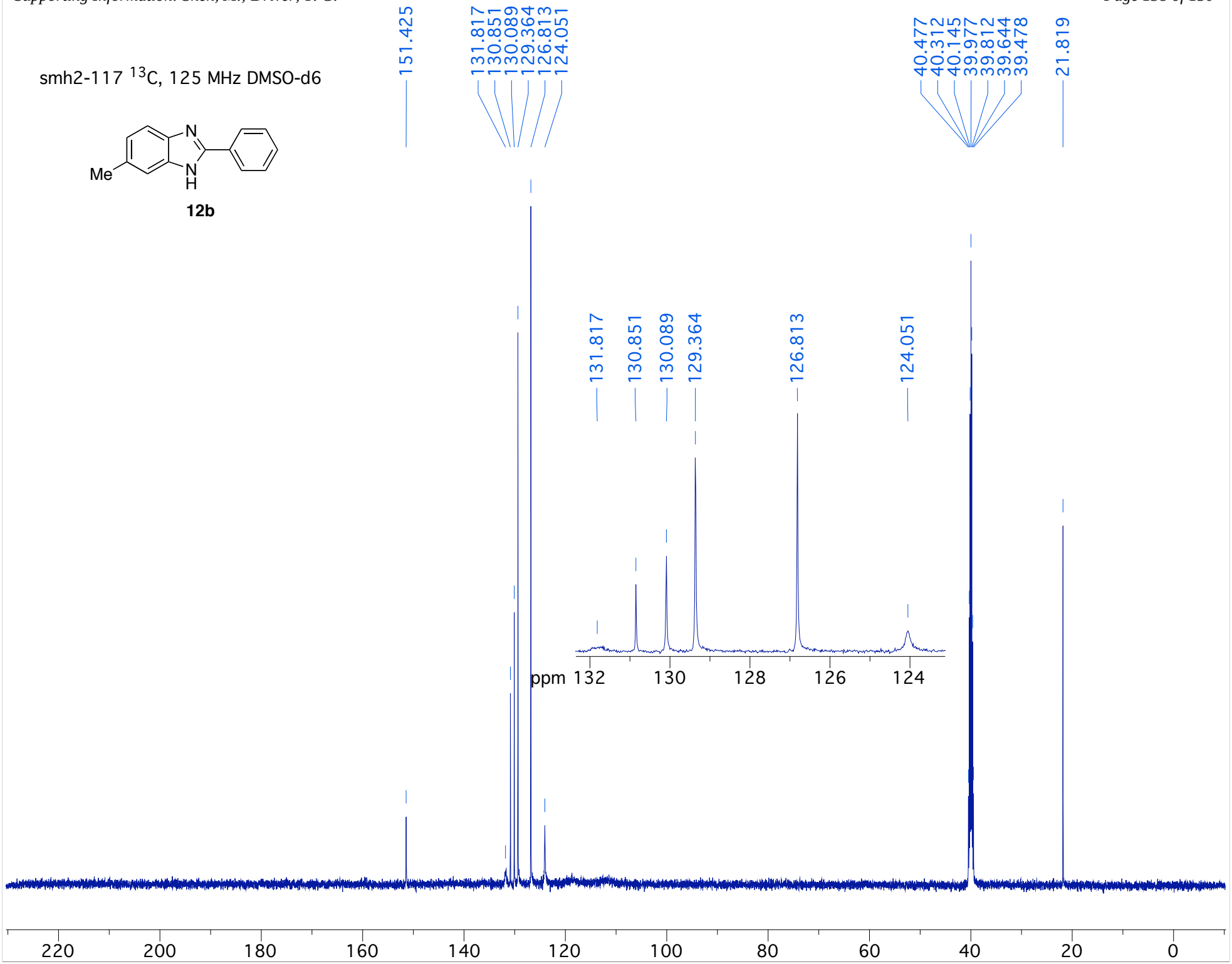
smh2-98.002 ^{13}C, 125 MHz DMSO-d6

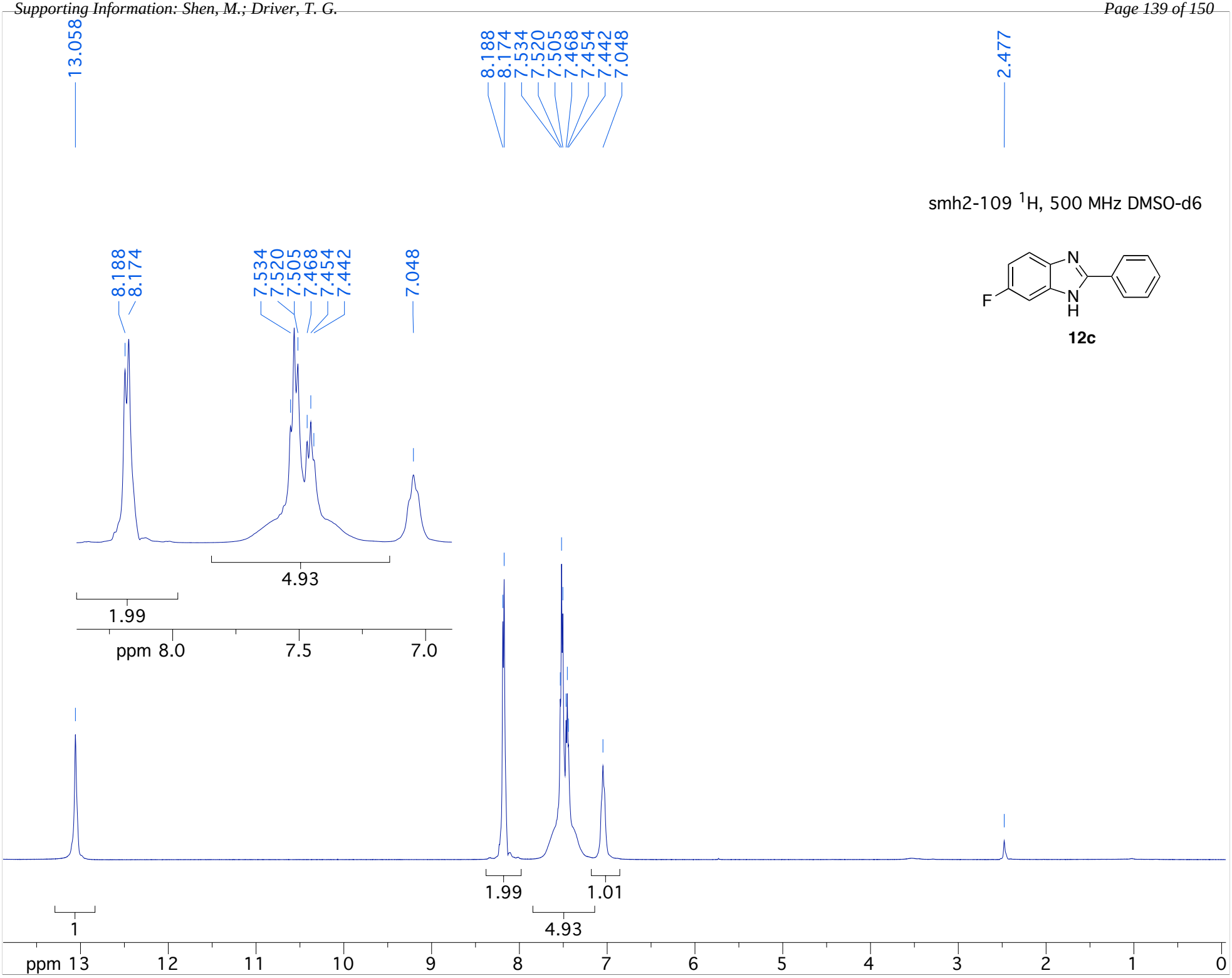


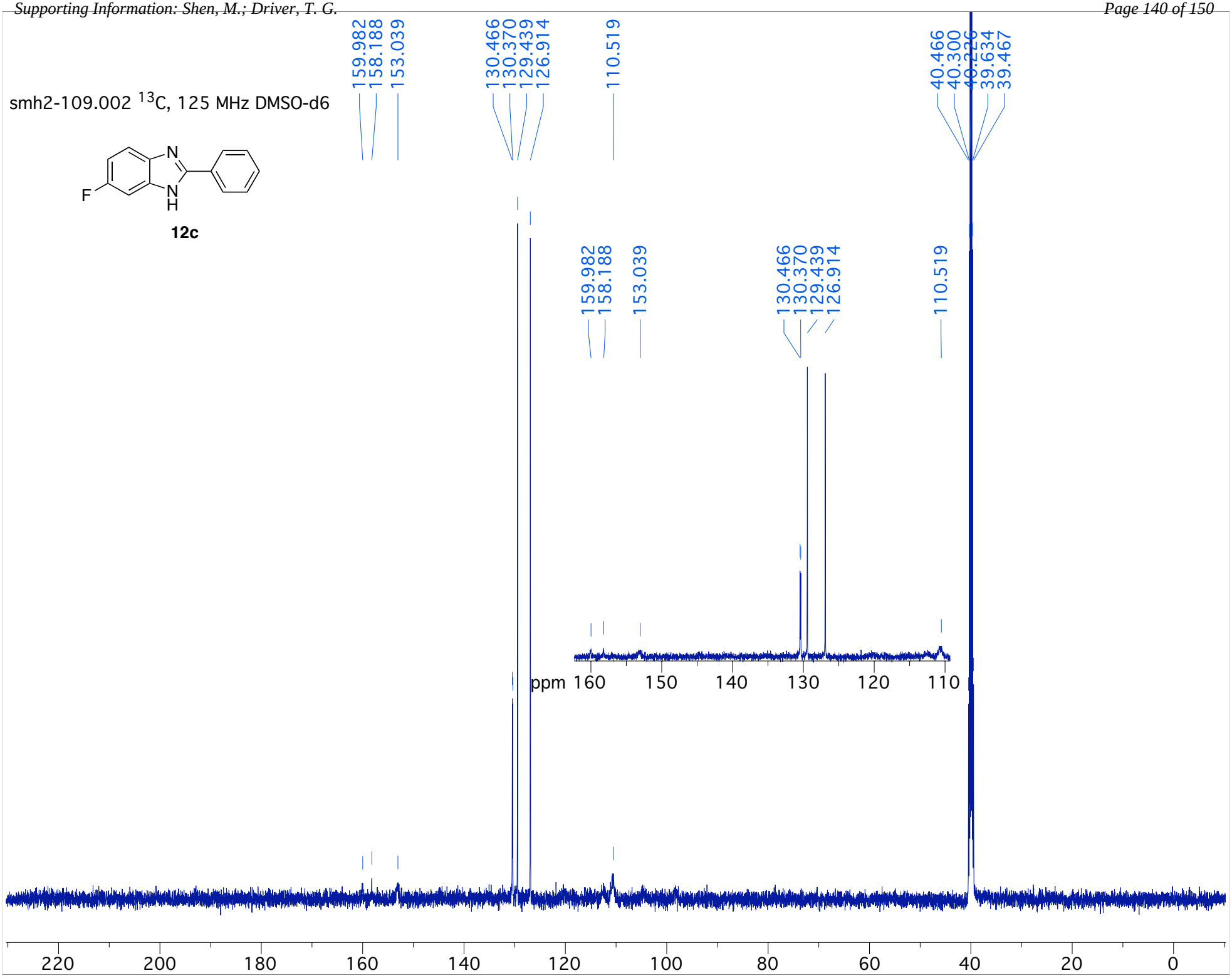
12a

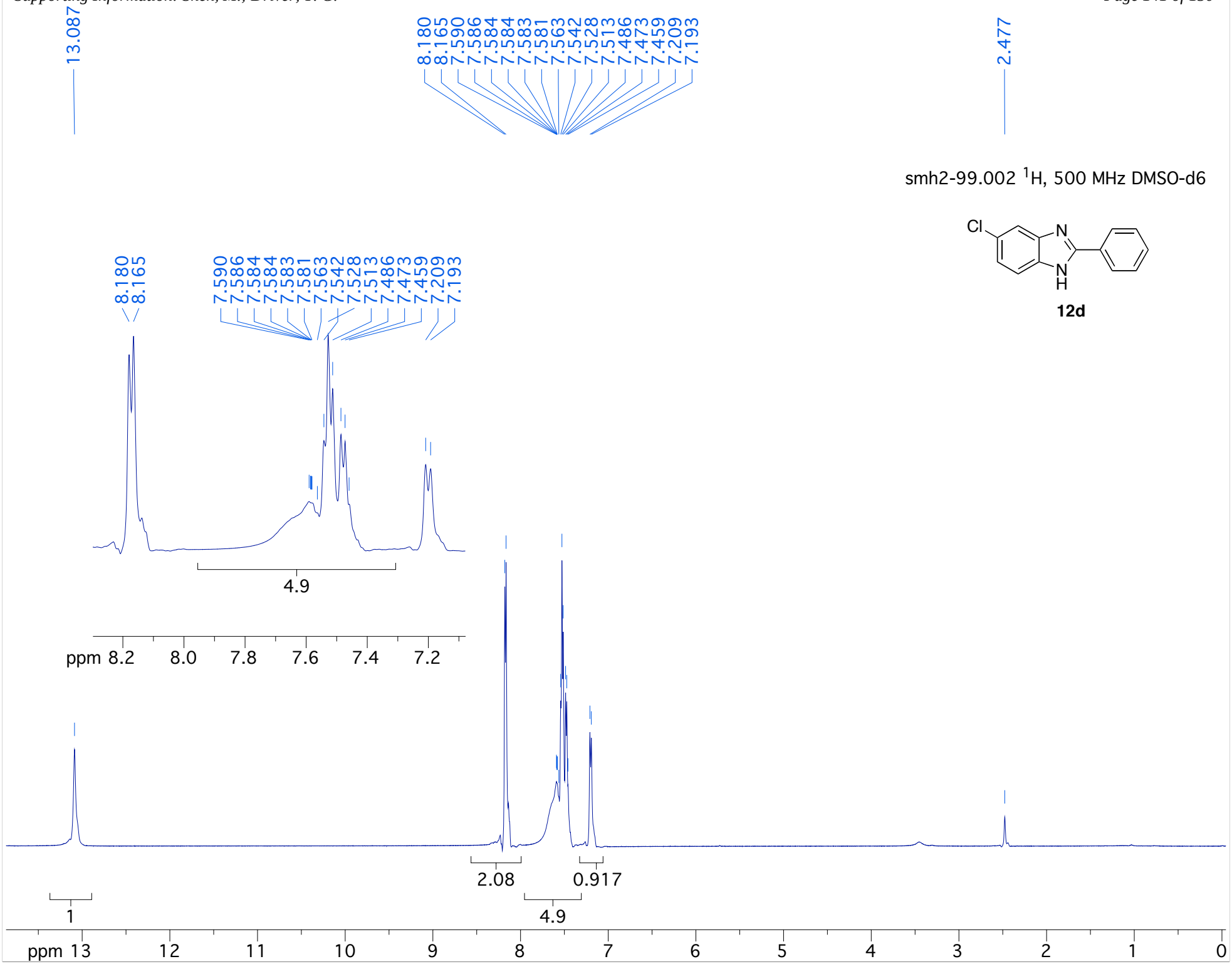

12.801
8.192
8.179
7.512
7.499
7.451
7.438
7.388
7.011
6.996
2.402
smh2-117 ^{1}H, 500 MHz DMSO-d6
N
N
H
Me
2.04
1.04
1
4.98
3.16
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0

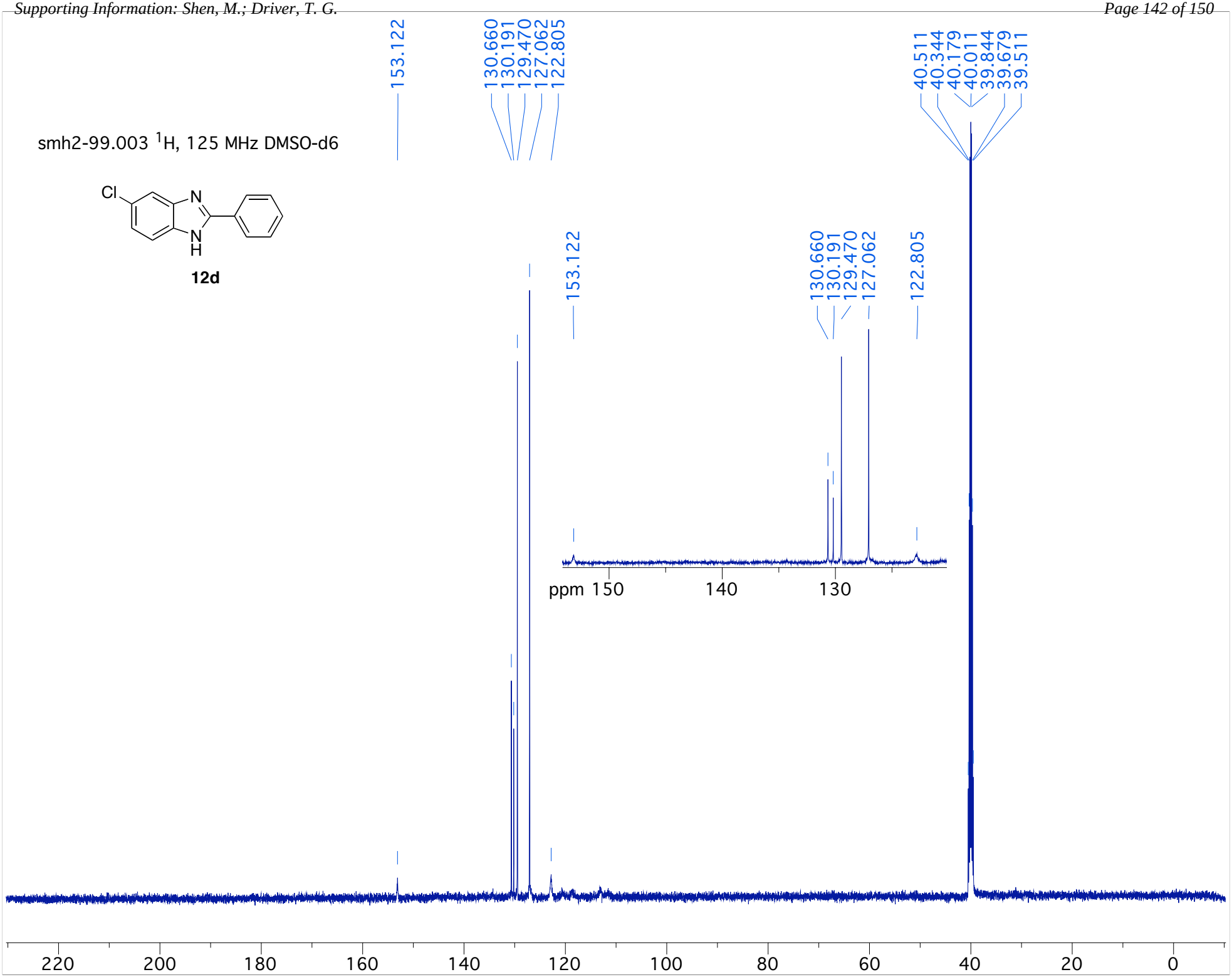
12b

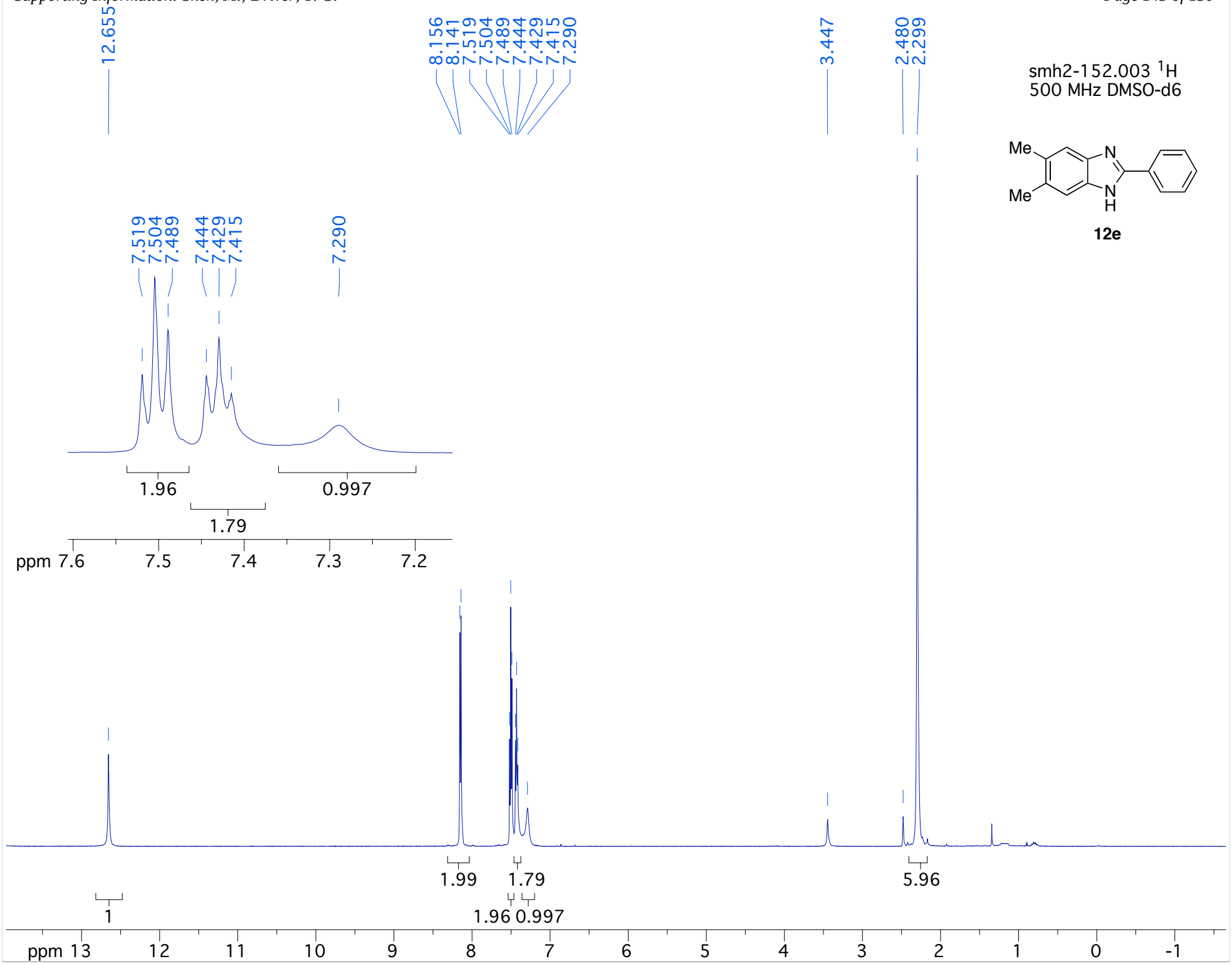

smh2-117 13C, 125 MHz DMSO-d6
Me
N
N
H
12b
151.425
131.817
130.851
130.089
129.364
126.813
124.051
40.477
40.312
40.145
39.977
39.812
39.644
39.478
21.819
ppm 132
130
128
126
124
220
200
180
160
140
120
100
80
60
40
20
0

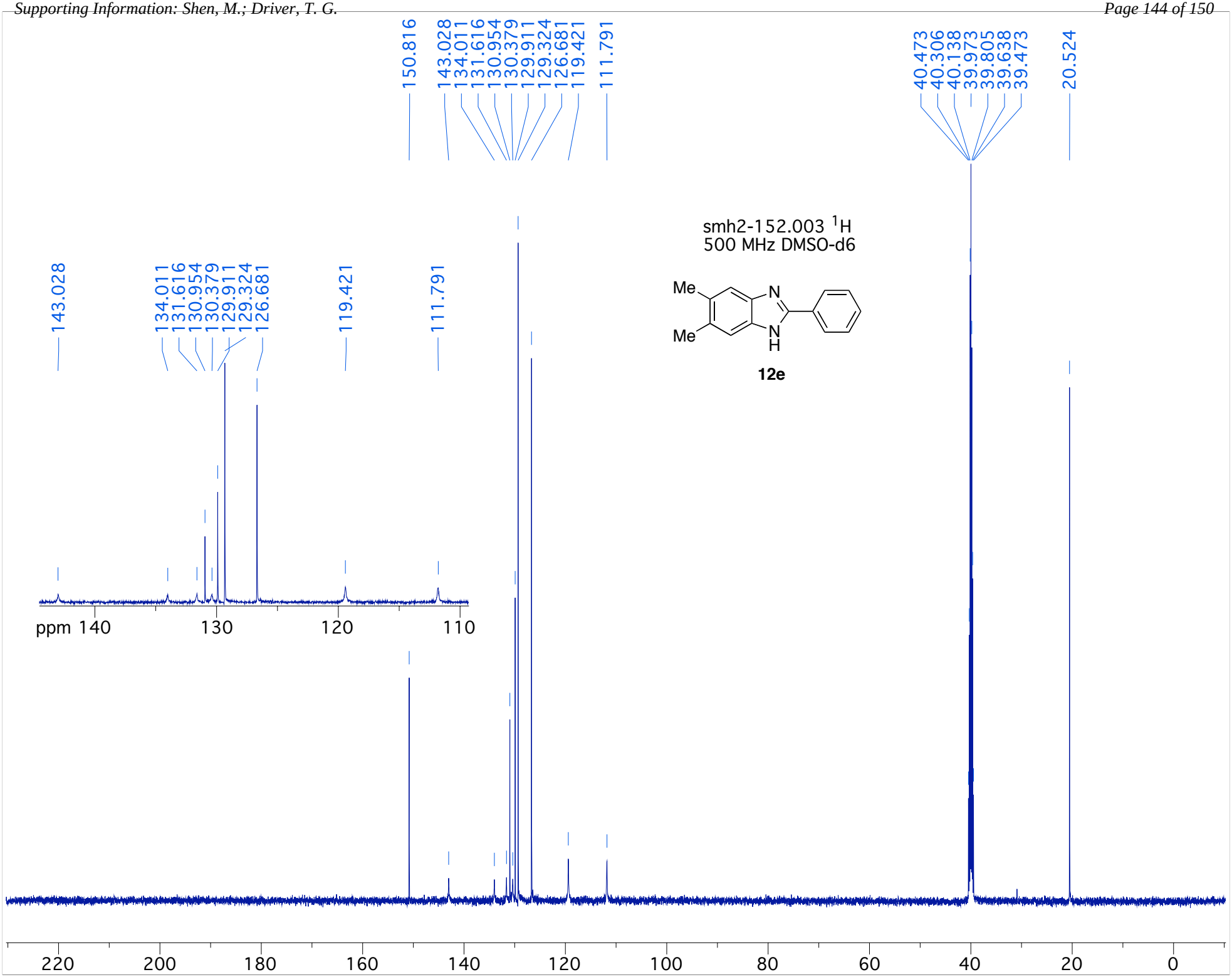

13.058
8.188
8.174
7.534
7.520
7.505
7.468
7.454
7.442
7.048
2.477
smh2-109 ^{1}H, 500 MHz DMSO-d6
F
N
N
H
12c
1.99
4.93
ppm 8.0
7.5
7.0
1
1.99
1.01
4.93
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0

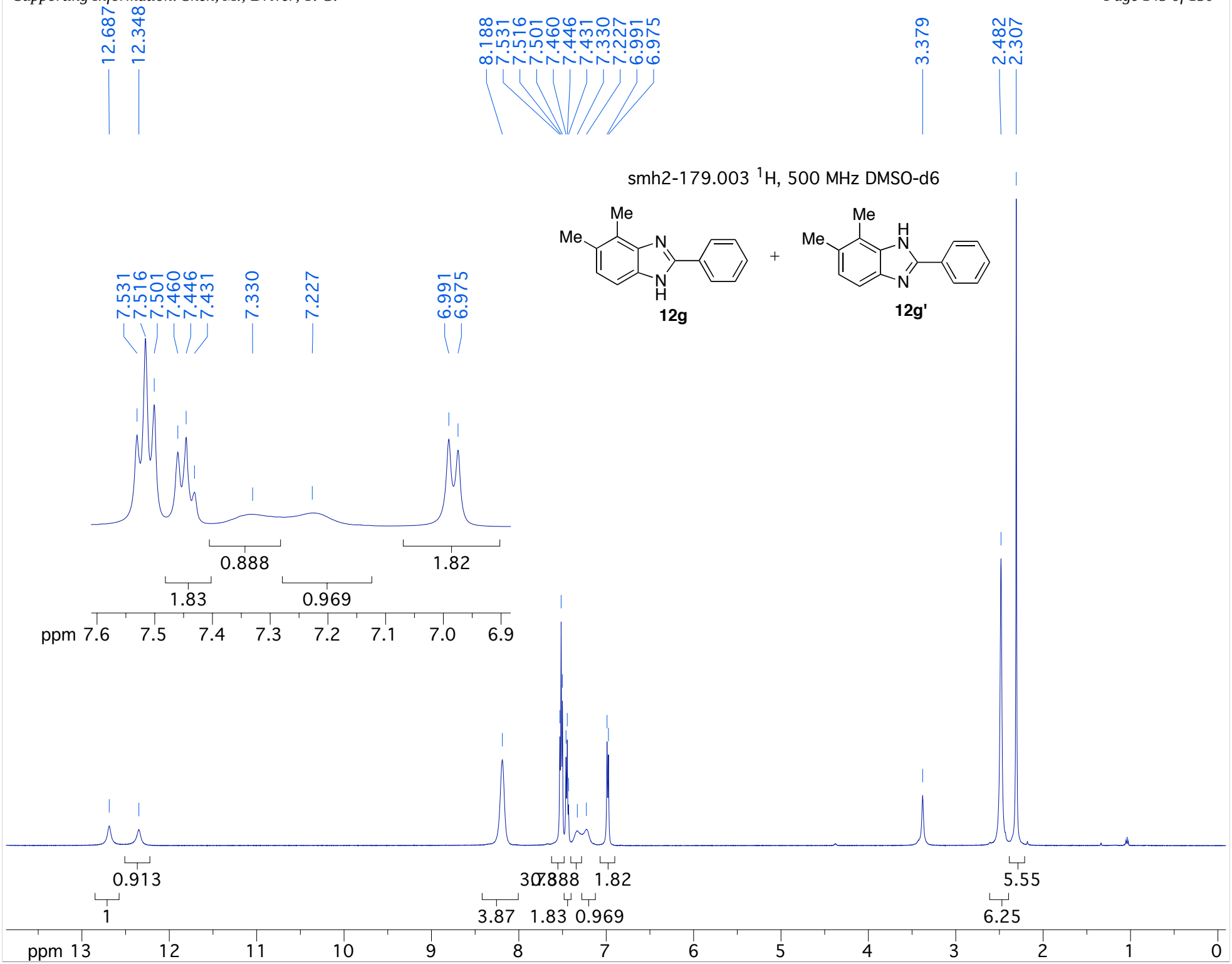

smh2-109.002 13C, 125 MHz DMSO-d6
159.982
158.188
153.039
130.466
130.370
129.439
126.914
110.519
40.466
40.300
40.226
39.634
39.467
F
N
N
H
12c
ppm 160
150
140
130
120
110
220
200
180
160
140
120
100
80
60
40
20
0

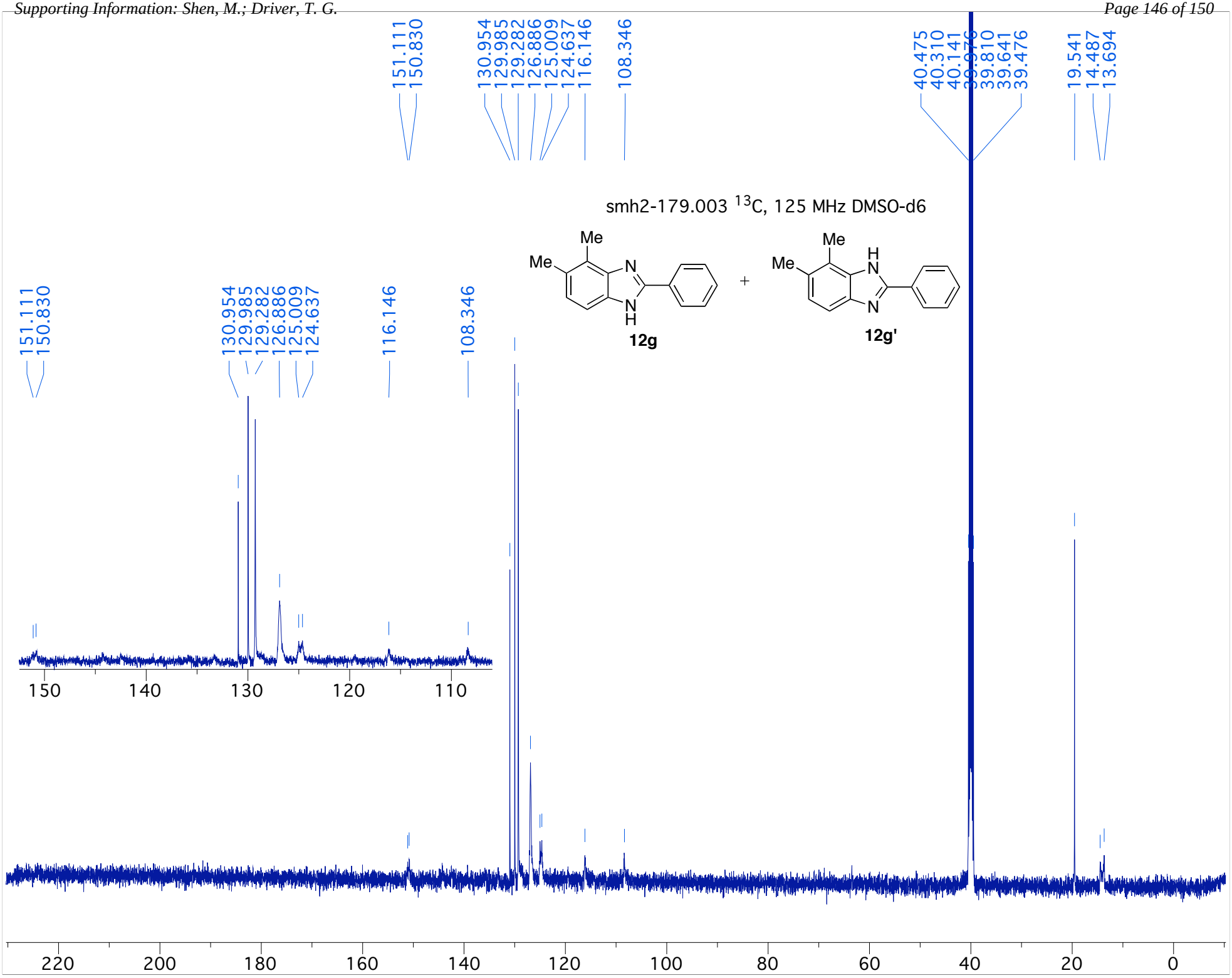

13.087
8.180
8.165
7.590
7.586
7.584
7.584
7.583
7.581
7.563
7.542
7.528
7.513
7.486
7.473
7.459
7.209
7.193
2.477
smh2-99.002 1H, 500 MHz DMSO-d6
Cl
N
N
H
12d
4.9
ppm 8.2 8.0 7.8 7.6 7.4 7.2
2.08
0.917
1
4.9
ppm 13 12 11 10 9 8 7 6 5 4 3 2 1 0

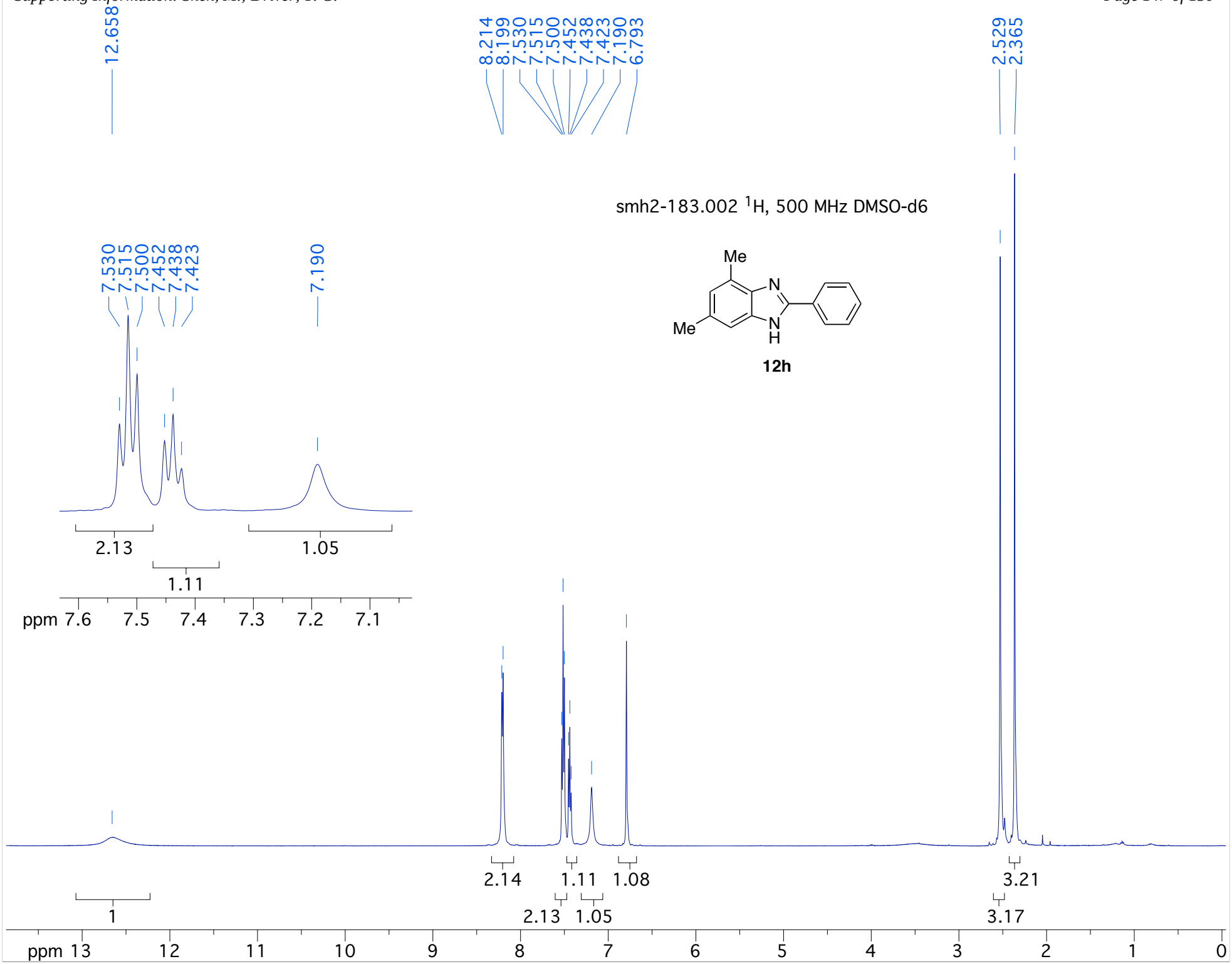

153.122
130.660
130.191
129.470
127.062
122.805
40.511
40.344
40.179
40.011
39.844
39.679
39.511
smh2-99.003 ^{1}H, 125 MHz DMSO-d6
Cl
N
N
H
12d
ppm 150
140
130
220
200
180
160
140
120
100
80
60
40
20
0

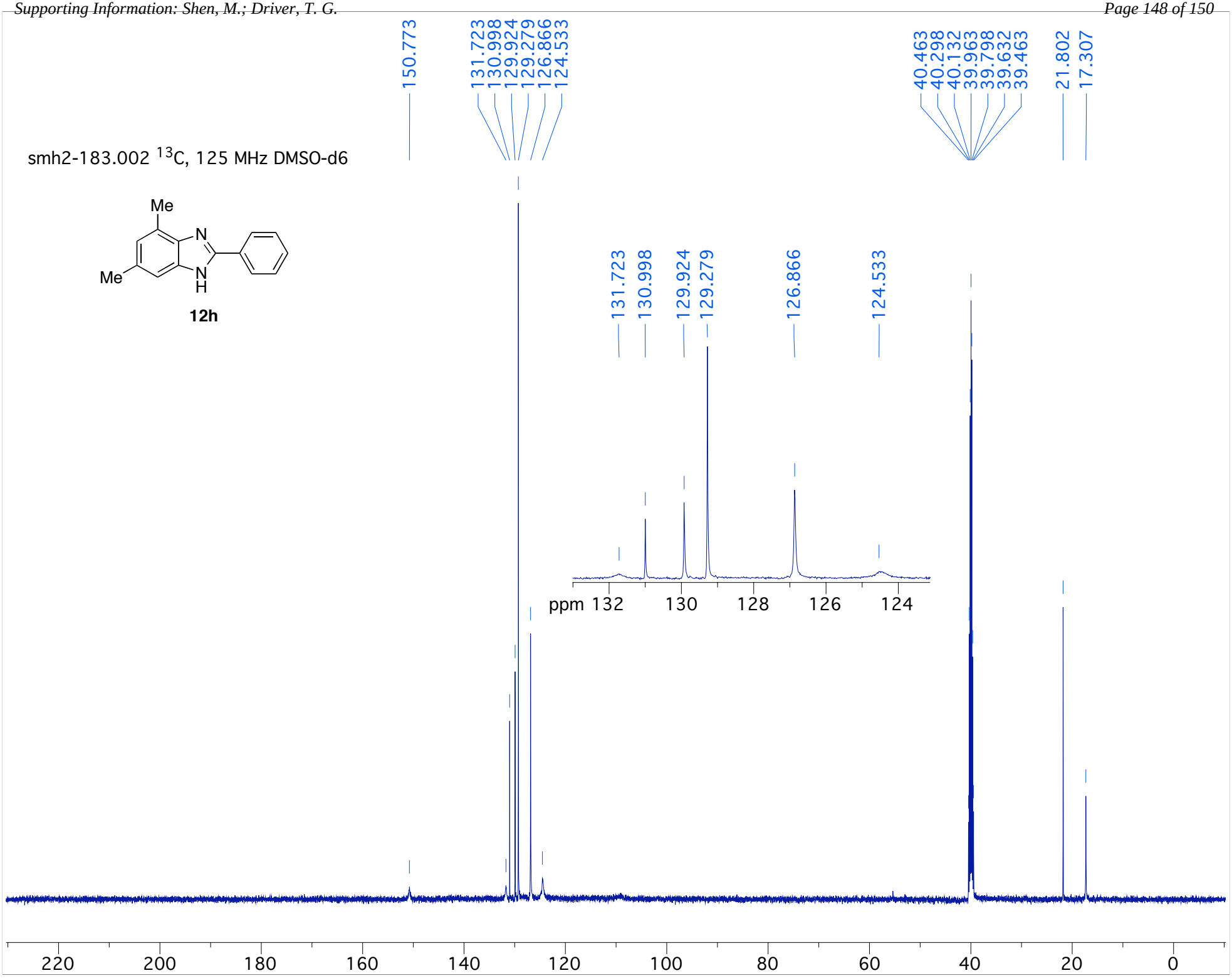

12.655
8.156
8.141
7.519
7.504
7.489
7.444
7.429
7.415
7.290
3.447
2.480
2.299
smh2-152.003 ^{1}H
500 MHz DMSO-d6
Me
Me
N
N
H
12e
7.519
7.504
7.489
7.444
7.429
7.415
7.290
1.96
0.997
1.79
ppm 7.6
7.5
7.4
7.3
7.2
1.99
1.79
5.96
1
1.96
0.997
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1

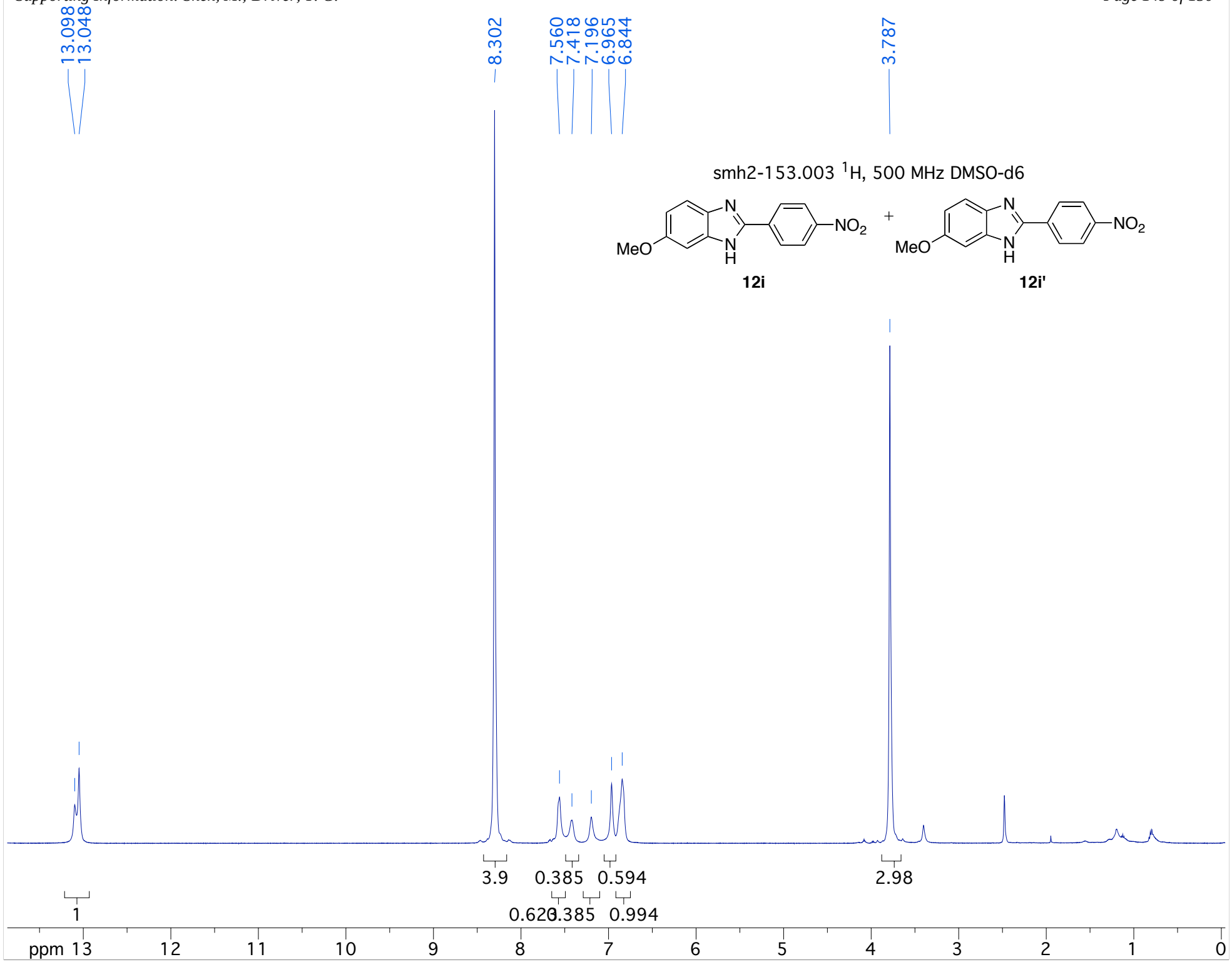

150.816
143.028
134.011
131.616
130.954
130.379
129.911
129.324
126.681
119.421
111.791
40.473
40.306
40.138
39.973
39.805
39.638
39.473
20.524
smh2-152.003 1H
500 MHz DMSO-d6
Me
Me
N
N
H
12e
ppm 140
130
120
110
220
200
180
160
140
120
100
80
60
40
20
0

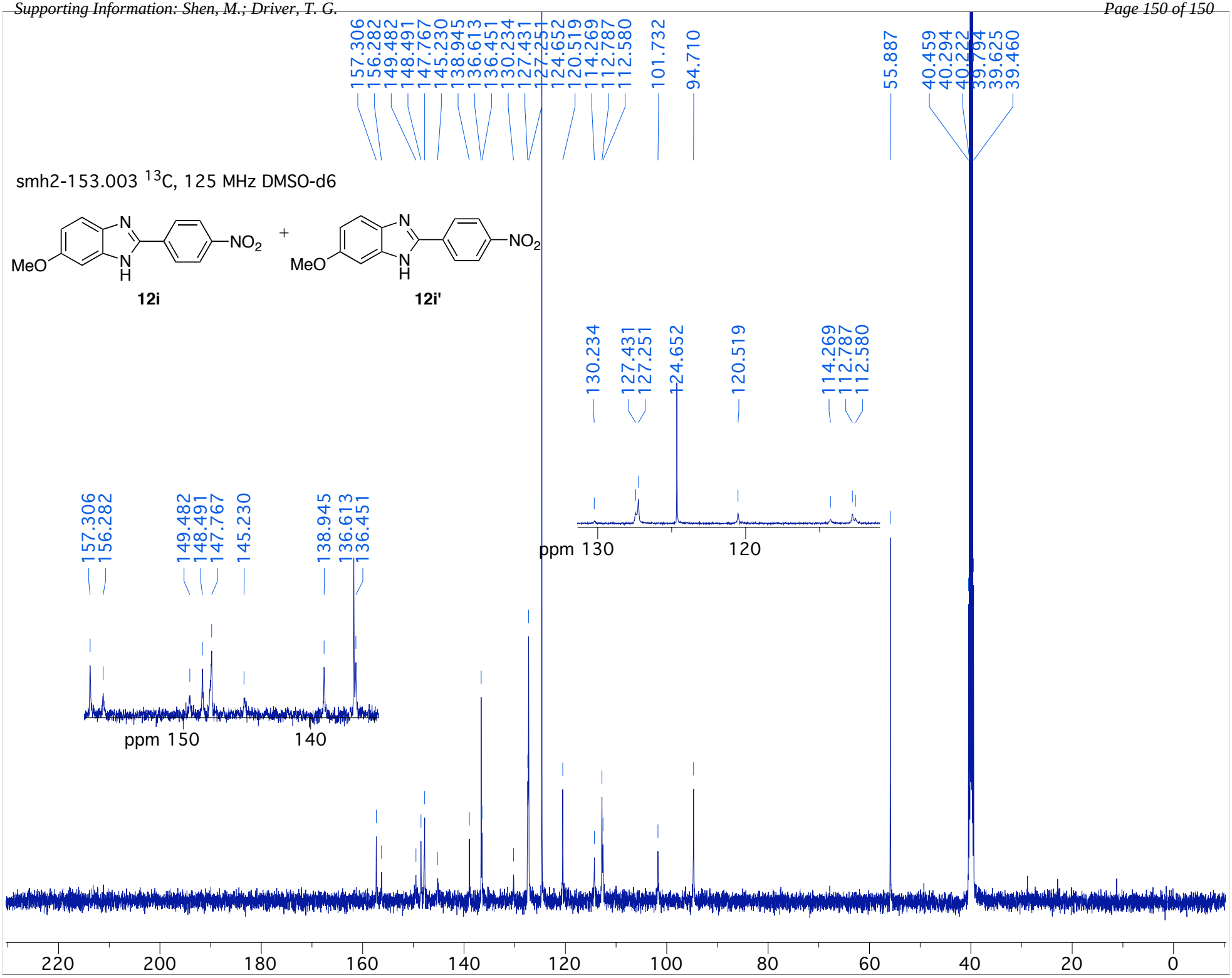

12.687
12.348
8.188
7.531
7.516
7.501
7.460
7.446
7.431
7.330
7.227
6.991
6.975
3.379
2.482
2.307
smh2-179.003 1H, 500 MHz DMSO-d6
Me
Me
N
N
H
12g
+
Me
Me
H
N
N
12g'
0.888
1.82
1.83
0.969
ppm 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
0.913
1
3.87
1.83
0.969
1.82
5.55
6.25
ppm 13 12 11 10 9 8 7 6 5 4 3 2 1 0


151.111
150.830
130.954
129.985
129.282
126.886
125.009
124.637
116.146
108.346
40.475
40.310
40.141
39.976
39.810
39.641
39.476
19.541
14.487
13.694
smh2-179.003 13C, 125 MHz DMSO-d6
Me
Me
N
N
H
12g
+
Me
Me
H
N
N
12g'
150
140
130
120
110
220
200
180
160
140
120
100
80
60
40
20
0


12.658
8.214
8.199
7.530
7.515
7.500
7.452
7.438
7.423
7.190
6.793
2.529
2.365
smh2-183.002 1H, 500 MHz DMSO-d6
Me
N
N
H
Me
12h
2.14
1.11
1.08
3.21
2.13
1.05
3.17
1
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0


150.773
131.723
130.998
129.924
129.279
126.866
124.533
40.463
40.298
40.132
39.963
39.798
39.632
39.463
21.802
17.307
smh2-183.002 13C, 125 MHz DMSO-d6
Me
N
N
H
Me
12h
ppm 132
130
128
126
124
220
200
180
160
140
120
100
80
60
40
20
0


13.098
13.048
8.302
7.560
7.418
7.196
6.965
6.844
3.787
smh2-153.003 ^{1}H, 500 MHz DMSO-d6
MeO
N
N
H
NO$_2$
+
MeO
N
N
H
NO$_2$
12i
12i'
3.9
0.385
0.594
2.98
1
0.620
0.385
0.994
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0


157.306
156.282
149.482
148.491
147.767
145.230
138.945
136.613
136.451
130.234
127.431
127.251
124.652
120.519
114.269
112.787
112.580
101.732
94.710
55.887
40.459
40.294
40.222
39.794
39.625
39.460
smh2-153.003 13C, 125 MHz DMSO-d6
MeO
NO2
12i
12i'
ppm 150
140
ppm 130
120
220
200
180
160
140
120
100
80
60
40
20
0