Supporting Information

Pd-Catalyzed Efficient Synthesis of Benzo[4,5]imidazo[1,2-*a*]indoles with Diaziridinone

Jianjun Wang, Xiao Zhang, Shiwei Zhang, Wei Liu, and Yian Shi*

Jiangsu Key Laboratory of Advanced Catalytic Materials & Technology, School of Petrochemical Engineering, Institute of Natural and Synthetic Organic Chemistry, Changzhou University, Changzhou 213164, P. R. China.

Email: shiyian@cczu.edu.cn

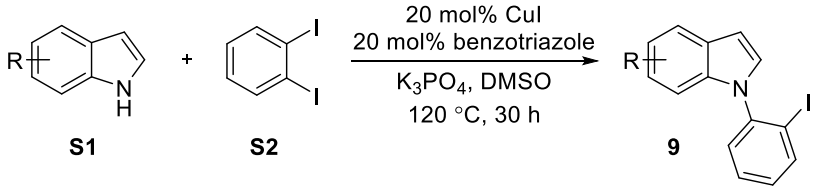
Table of Contents

General Methods

All reactions were carried out with oven-dried glassware. All commercially available reagents were used without further purification unless otherwise noted. All dry solvents were purified with solvent purification system before use. Column chromatography was performed on silica gel (300-400 mesh). ^{1}H NMR spectra were recorded on a 400 MHz NMR spectrometer, and ^{13}C NMR spectra were recorded on a 100 MHz NMR spectrometer. IR spectra were recorded on a FT-IR spectrometer. Melting points were uncorrected. High resolution mass spectra (HRMS, ESI) were recorded using an ion trap mass spectrometer. Di-*t*-butyldiaziridinone was prepared according to the reported procedure.[1] 1-(2-Iodophenyl)-1*H*-indole substrates **9** were prepared via copper-catalyzed coupling between indoles **S1** and 1,2-diiodobenzene (**S2**) based on reported procedures[2] (Scheme S-1).

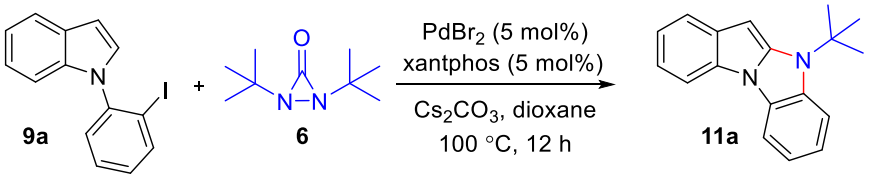
1) Du, H.; Zhao, B.; Shi, Y. *Org. Synth.* **2009**, *86*, 315-324.

2) Sun, M.; Chen, X.; Feng, Z.; Deng, G.; Yang, Y.; Liang, Y. *Org. Chem. Front.* **2021**, *8*, 6535-6540.



Scheme S-1. Preparation of indole substrates **9**

Representative procedure for benzo[4,5]imidazo[1,2-*a*]indole synthesis (Table 2, 11a)



To an oven-dried 4 mL pressure tube were added indole **9a** (0.0957 g, 0.30 mmol), $PdBr_2$ (0.0040 g, 0.015 mmol), xantphos (0.0087 g, 0.015 mmol), and Cs_2CO_3 (0.1955 g, 0.60 mmol), successively. The tube was fitted with rubber septum, evacuated under high vacuum, and refilled with N_2 for three time, followed by addition of dry 1,4-dioxane (1.0 mL) and di-*t*-butyldiaziridinone **6** (0.0766 g, 0.45 mmol). The rubber septum was rapidly replaced with Teflon-coated screw cap. The reaction mixture was placed in a pre-heated oil bath (100 °C), stirred for 12 h, cooled to room temperature, diluted with EtOAc, filtered over a

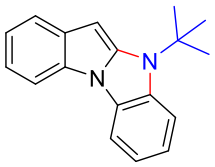
plug of silica gel, washed with EtOAc, concentrated under reduced pressure, and purified by flash chromatography (silica gel, eluent: petroleum ether/EtOAc = 100:1) to give benzo[4,5]imidazo[1,2-*a*]indole **11a** as yellow solid (0.065 g, 83% yield).

Procedure for benzo[4,5]imidazo[1,2-*a*]indole synthesis on gram scale (Scheme 4, 11a)

To an oven-dried 50 mL pressure tube were added indole **9a** (1.53 g, 4.80 mmol), $PdBr_2$ (0.0639 g, 0.24 mmol), xantphos (0.1389 g, 0.24 mmol), and Cs_2CO_3 (3.13 g, 9.60 mmol), successively. The tube was fitted with rubber septum, evacuated under high vacuum, and refilled with N_2 for three time, followed by addition of dry 1,4-dioxane (16 mL) and di-*t*-butyldiaziridinone **6** (1.226 g, 7.20 mmol). The rubber septum was rapidly replaced with Teflon-coated screw cap. The reaction mixture was placed in a pre-heated oil bath (100 ^oC), stirred for 20 h, cooled to room temperature, diluted with EtOAc, filtered over a plug of silica gel, washed with EtOAc, concentrated under reduced pressure, and purified by flash chromatography (silica gel, eluent: petroleum ether/EtOAc = 100:1 to 80:1) to give benzo[4,5]imidazo[1,2-*a*]indole **11a** as yellow solid (1.03 g, 82% yield).

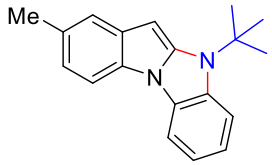
Characterization data for benzo[4,5]imidazo[1,2-*a*]indoles 11

Table 2, 11a



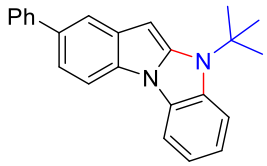
Yellow solid; 0.0650 g (83%); 0.0241 g (31%, from **9a-Br**). eluent: petroleum ether/EtOAc = 100:1; mp. 100-101 ^oC; IR (film) 1607, 1538, 1456, 1209, 1080 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 1H), 7.68-7.63 (m, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.40-7.34 (m, 1H), 7.11 (t, J = 7.2 Hz, 1H), 7.08-7.00 (m, 3H), 5.74 (s, 1H), 1.75 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.5, 133.5, 128.5, 125.5, 121.6, 121.3, 119.6, 118.9, 117.7, 112.3, 110.3, 110.0, 74.7, 57.5, 29.3; HRMS (ESI) m/z: Calcd for $C_{18}H_{19}N_2$ $[M+H]^+$: 263.1543; found: 263.1549.

Table 2, 11b



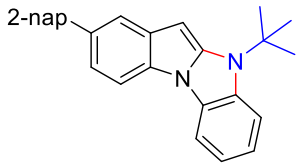
Yellow solid; 0.047 g (57%); eluent: petroleum ether/EtOAc = 40:1 to 20:1; mp. 104-105 °C; IR (film) 1607, 1544, 1501, 1215, 1189 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83-7.77 (m, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.56-7.49 (m, 1H), 7.43 (s, 1H), 7.25-7.17 (m, 2H), 7.02 (d, J = 8.0 Hz, 1H), 5.83 (s, 1H), 2.56 (s, 3H), 1.92 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 136.5, 133.8, 130.6, 128.6, 123.8, 121.3, 119.5, 119.0, 118.9, 112.2, 109.9, 109.85, 74.4, 57.5, 29.3, 21.9; HRMS (ESI) m/z: Calcd for $C_{19}H_{21}N_2$ $[M+H]^+$: 277.1699; found: 277.1691.

Table 2, 11c



Light yellow solid; 0.0702 g (69%); eluent: petroleum ether/EtOAc = 100:1; mp. 51-52 °C; IR (film) 1607, 1538, 1494, 1378, 1296, 1203, 1078 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 1.6 Hz, 1H), 7.74-7.69 (m, 1H), 7.68-7.61 (m, 2H), 7.45-7.36 (m, 3H), 7.32 (dd, J = 8.4, 1.6 Hz, 1H), 7.26 (tt, J = 6.8, 1.6 Hz, 1H), 7.15-7.07 (m, 2H), 5.84 (s, 1H), 1.80 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 143.0, 136.6, 134.7, 134.0, 128.7, 128.4, 127.6, 126.4, 125.0, 121.7, 119.7, 117.5, 117.4, 112.4, 110.4, 110.1, 75.1, 57.5, 29.3; HRMS (ESI) m/z: Calcd for $C_{24}H_{23}N_2$ $[M+H]^+$: 339.1856; found: 339.1854.

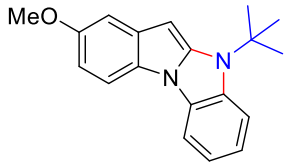
Table 2, 11d



Light yellow solid; 0.1037 g (89%); eluent: petroleum ether/EtOAc = 45:1 to 30:1; mp. 78-79 °C; IR (film) 1607, 1542, 1499, 1457, 1380, 1193 cm^{-1}; ^1H NMR (400 MHz,

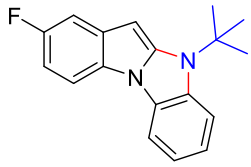
$CDCl_3$) δ 7.97 (s, 1H), 7.83-7.65 (m, 6H), 7.64-7.58 (m, 1H), 7.40-7.23 (m, 4H), 7.04-6.96 (m, 2H), 5.75 (s, 1H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 140.3, 136.6, 134.5, 134.2, 134.0, 132.3, 128.4, 128.3, 128.2, 127.7, 126.5, 126.2, 125.7, 125.5, 125.1, 121.7, 119.7, 117.8, 117.6, 112.4, 110.5, 110.1, 75.2, 57.6, 29.3; HRMS (ESI) m/z: Calcd for $C_{28}H_{25}N_2$ $[M+H]^+$: 389.2012; found: 389.2013.

Table 2, 11e



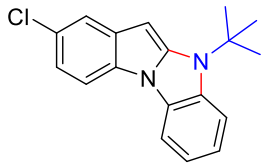
Yellow solid; 0.0345 g (39%); eluent: petroleum ether/EtOAc = 40:1; mp. 109-110 °C; IR (film) 1610, 1542, 1202, 1148 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76-7.69 (m, 2H), 7.53-7.47 (m, 1H), 7.21-7.15 (m, 2H), 7.10 (d, J = 2.4 Hz, 1H), 6.79 (dd, J = 8.4, 2.4 Hz, 1H), 5.82 (s, 1H), 3.91 (s, 3H), 1.89 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 144.1, 136.2, 134.4, 128.4, 121.3, 120.8, 119.6, 112.3, 110.8, 109.6, 106.4, 102.0, 74.9, 57.5, 56.0, 29.3; HRMS (ESI) m/z: Calcd for $C_{19}H_{21}N_2O$ $[M+H]^+$: 293.1648; found: 293.1653.

Table 2, 11f



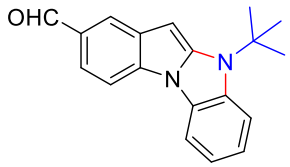
White solid; 0.0765 g (91%); eluent: petroleum ether/EtOAc = 70:1; mp. 67-69 °C; IR (film) 1610, 1542, 1183, 1131 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82-7.65 (m, 2H), 7.57-7.49 (m, 1H), 7.29-7.17 (m, 3H), 6.87 (td, J = 8.8, 2.4 Hz, 1H), 5.86 (s, 1H), 1.89 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0 (d, J = 233.4 Hz), 144.6, 136.2, 134.3 (d, J = 10.6 Hz), 128.2, 122.2, 121.7, 119.8, 112.5, 110.6 (d, J = 10.2 Hz), 109.8, 105.1 (d, J = 26.0 Hz), 104.2 (d, J = 24.2 Hz), 75.3 (d, J = 3.8 Hz), 57.6, 29.3; HRMS (ESI) m/z: Calcd for $C_{18}H_{18}FN_2$ $[M+H]^+$: 281.1449; found: 281.1451.

Table 2, 11g



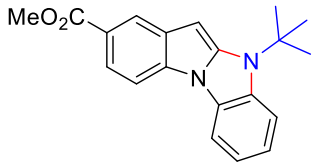
Yellow solid; 0.081 g (91%); eluent: petroleum ether/EtOAc = 100:1; mp. 95-96 °C; IR (film) 1607, 1456, 1209, 1080 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79-7.72 (m, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.55 (d, J = 2.4 Hz, 1H), 7.54-7.48 (m, 1H), 7.26-7.16 (m, 2H), 7.10 (dd, J = 8.4, 2.0 Hz, 1H), 5.83 (s, 1H), 1.89 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 136.3, 134.6, 128.1, 126.8, 123.9, 121.9, 119.8, 118.2, 117.5, 112.6, 111.0, 110.0, 74.7, 57.6, 29.3; HRMS (ESI) m/z: Calcd for $C_{18}H_{18}ClN_2$ $[M+H]^+$: 297.1153; found: 297.1159.

Table 2, 11h



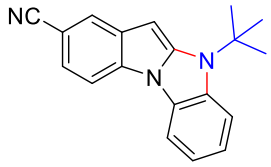
Yellow solid; 0.062 g (71%); eluent: petroleum ether/CH_2Cl_2, 3:1 to 1:1; mp. 105-106 °C; IR (film) 1685, 1603, 1542, 1212 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.07 (s, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.78 (dd, J = 7.6, 1.6 Hz, 1H), 7.66 (dd, J = 8.4, 1.6 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.28-7.16 (m, 2H), 5.96 (s, 1H), 1.88 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 144.4, 136.7, 133.3, 130.4, 128.5, 127.7, 122.79, 122.77, 120.0, 118.9, 122.7, 110.7, 110.4, 76.0, 57.7, 29.3; HRMS (ESI) m/z: Calcd for $C_{19}H_{19}N_2O$ $[M+H]^+$: 291.1492; found: 291.1494.

Table 2, 11i



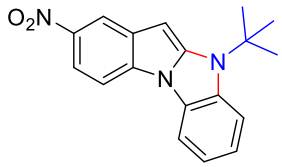
Light yellow solid; 0.0918 g (96%); eluent: petroleum ether/EtOAc = 40:1 to 30:1; mp. 104-105 °C; IR (film) 1711, 1608, 1545, 1292, 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 1.6 Hz, 1H), 7.88 (dd, J = 8.4, 1.6 Hz, 1H), 7.82-7.75 (m, 2H), 7.50 (dd, J = 7.2, 1.2 Hz, 1H), 7.24-7.16 (m, 2H), 5.93 (s, 1H), 3.98 (s, 3H), 1.87 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 144.1, 136.6, 133.0, 127.9, 127.7, 122.8, 122.3, 121.4, 119.8, 119.2, 112.5, 110.4, 109.7, 75.6, 57.6, 51.9, 29.2; HRMS (ESI) m/z: Calcd for $C_{20}H_{21}N_2O_2$ $[M+H]^+$: 321.1598; found: 321.1595.

Table 2, 11j



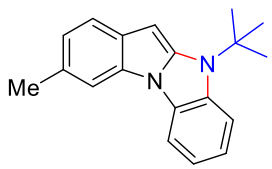
White solid; 0.075 g (87%); eluent: petroleum ether/CH_2Cl_2 = 2:1 to 1:1; mp. 174-175 ^oC; IR (film) 2216, 1608, 1542, 1378, 1214 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89-7.86 (m, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.81-7.77 (m, 1H), 7.57-7.53 (m, 1H), 7.39-7.34 (m, 1H), 7.30-7.20 (m, 2H), 5.92 (s, 1H), 1.89 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 136.6, 133.2, 127.7, 126.9, 123.6, 122.9, 121.2, 120.8, 120.2, 113.0, 110.7, 104.0, 75.3, 57.9, 29.4; HRMS (ESI) m/z: Calcd for $C_{19}H_{18}N_3$ $[M+H]^+$: 288.1495; found: 288.1496.

Table 2, 11k



Orange solid; 0.0844 g (92%); eluent: petroleum ether/CH_2Cl_2 = 2:1; mp. 159-160 ^oC; IR (film) 1609, 1548, 1335, 1212 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 2.4 Hz, 1H), 7.99 (dd, J = 8.8, 2.4 Hz, 1H), 7.78 (dd, J = 7.6, 1.6 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.28 (td, J = 7.6, 1.2 Hz, 1H), 7.22 (td, J = 7.6, 1.2 Hz, 1H), 5.98 (s, 1H), 1.89 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 142.6, 136.7, 132.9, 128.0, 127.5, 123.2, 120.3, 115.3, 113.2, 113.0, 110.7, 109.6, 76.6, 58.0, 29.3; HRMS (ESI) m/z: Calcd for $C_{18}H_{18}N_3O_2$ $[M+H]^+$: 308.1394; found: 308.1392.

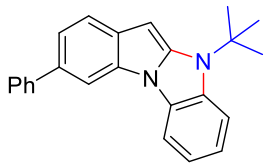
Table 2, 11l



Green oil; 0.0594 g (72%); eluent: petroleum ether/EtOAc = 60:1 to 50:1; IR (film) 1608, 1557, 1211 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85-7.80 (m, 1H), 7.68 (s, 1H), 7.54-7.48 (m, 2H), 7.23-7.18 (m, 2H), 7.11 (dd, J = 8.4, 1.6 Hz, 1H), 5.85 (s, 1H), 2.62 (s, 3H), 1.91 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 136.7, 131.2, 128.6, 127.4, 125.9,

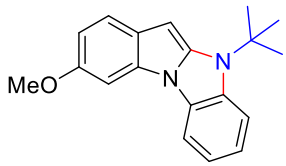
122.7, 121.4, 119.4, 118.6, 112.1, 110.7, 110.0, 74.4, 57.4, 29.3, 21.9; HRMS (ESI) m/z: Calcd for $C_{19}H_{21}N_2$ $[M+H]^+$: 277.1699; found: 277.1697.

Table 2, 11m



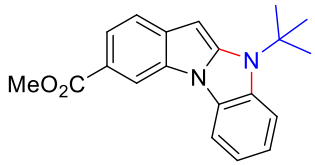
Light yellow solid; 0.0907 g (89%); eluent: petroleum ether/EtOAc = 100:1 to 60:1; mp. 49-50 °C; IR (film) 1608, 1545, 1465, 1371, 1210, 1178 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.95-7.88 (m, 1H), 7.81 (d, J = 6.8 Hz, 2H), 7.69 (d, J = 8.4 Hz, 1H), 7.60-7.51 (m, 4H), 7.39 (tt, J = 6.8, 1.2 Hz, 1H), 7.28-7.22 (m, 2H), 5.94 (s, 1H), 1.93 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 142.7, 136.6, 132.9, 131.2, 128.8, 128.5, 127.4, 126.24, 126.2, 121.7, 120.9, 119.7, 119.0, 112.4, 110.2, 109.0, 74.8, 57.6, 29.3; HRMS (ESI) m/z: Calcd for $C_{24}H_{23}N_2$ $[M+H]^+$: 339.1856; found: 339.1850.

Table 2, 11n



Brown solid; 0.058 g (66%); eluent: petroleum ether/EtOAc = 60:1; mp. 83-84 °C; IR (film) 1608, 1557, 1207, 1159 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79-7.72 (m, 1H), 7.53-7.47 (m, 2H), 7.41 (d, J = 2.4 Hz, 1H), 7.22-7.16 (m, 2H), 6.95 (dd, J = 8.4, 2.4 Hz, 1H), 5.81 (s, 1H), 3.98 (s, 3H), 1.89 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 143.0, 136.8, 128.4, 127.7, 125.8, 121.6, 119.3, 119.2, 112.1, 109.8, 109.7, 96.1, 73.9, 57.4, 56.3, 29.2; HRMS (ESI) m/z: Calcd for $C_{19}H_{21}N_2O$ $[M+H]^+$: 293.1648; found: 293.1653.

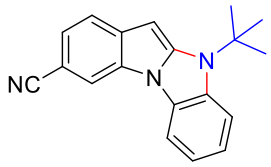
Table 2, 11o



Light yellow solid; 0.0862 g (90%); eluent: petroleum ether/EtOAc = 50:1 to 30:1; mp. 160-161 °C; IR (film) 1704, 1531, 1290, 1242 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.00-7.91 (m, 2H), 7.59-7.51 (m, 2H), 7.29-7.22 (m, 2H), 5.95 (s, 1H), 4.01 (s, 3H),

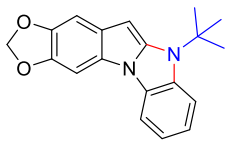
1.90 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 145.7, 137.5, 136.1, 128.1, 124.7, 122.8, 122.2, 120.3, 118.5, 117.8, 112.8, 112.2, 110.6, 76.4, 57.8, 51.8, 29.3; HRMS (ESI) m/z: Calcd for $C_{20}H_{21}N_2O_2$ $[M+H]^+$: 321.1598; found: 321.1595.

Table 2, 11p



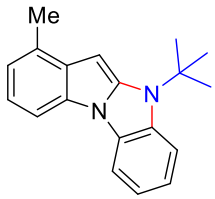
Light yellow solid; 0.0748 g (87%); eluent: petroleum ether/EtOAc = 40:1; mp. 145-146 °C; IR (film) 2211, 1532, 1459, 1195 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.10-8.03 (m, 1H), 7.93-7.87 (m, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.73 (dd, J = 8.0, 1.2 Hz, 1H), 7.62-7.55 (m, 2H), 6.28 (s, 1H), 2.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 136.7, 136.0, 127.6, 124.5, 124.1, 122.7, 121.7, 120.6, 118.8, 114.3, 113.1, 110.5, 98.3, 76.8, 58.1, 29.3; HRMS (ESI) m/z: Calcd for $C_{19}H_{18}N_3$ $[M+H]^+$: 288.1495; found: 288.1498.

Table 2, 11q



Light yellow solid; 0.0449 g (49%); eluent: petroleum ether/EtOAc = 100:1 to 80:1; mp. 60-61 °C; IR (film) 1611, 1557, 1466, 1288, 1151, 1040 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.63 (m, 1H), 7.51-7.45 (m, 1H), 7.36 (s, 1H), 7.21-7.12 (m, 2H), 7.04 (s, 1H), 5.98 (s, 2H), 5.77 (s, 1H), 1.87 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.6, 141.3, 136.3, 128.1, 127.4, 121.4, 119.3, 119.2, 112.2, 109.6, 100.5, 98.7, 92.4, 75.0, 57.3, 29.2; HRMS (ESI) m/z: Calcd for $C_{19}H_{18}N_2O_2Na$ $[M+Na]^+$: 329.1260; found: 329.1260.

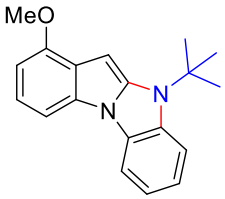
Table 2, 11r



Yellow oil; 0.0428 g (52%); eluent: petroleum ether/EtOAc = 80:1 to 60:1; IR (film) 1607, 1546, 1387, 1204, 1093 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.79 (m, 1H), 7.72

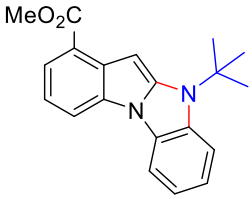
(d, J = 7.6 Hz, 1H), 7.56-7.50 (m, 1H), 7.24-7.18 (m, 2H), 7.14-7.05 (m, 2H), 5.86 (s, 1H), 2.63 (s, 3H), 1.93 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 136.6, 133.0, 128.6, 128.2, 125.1, 121.59, 121.55, 119.5, 117.8, 112.3, 110.1, 108.0, 73.3, 57.5, 29.3, 19.2; HRMS (ESI) m/z: Calcd for $C_{19}H_{21}N_2$ $[M+H]^+$: 277.1699; found: 277.1696.

Table 2, 11s



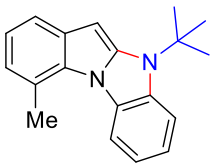
Brown solid; 0.0667 g (76%); eluent: petroleum ether/EtOAc = 80:1 to 60:1; mp. 131-132 ^{o}C; IR (film) 1605, 1543, 1504, 1253, 1073 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.78 (m, 1H), 7.55-7.50 (m, 2H), 7.23-7.17 (m, 2H), 7.13 (t, J = 8.0 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 6.00 (s, 1H), 4.05 (s, 3H), 1.91 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 142.3, 136.7, 128.4, 126.4, 123.3, 121.7, 119.4, 118.4, 112.2, 110.2, 104.2, 101.6, 71.6, 57.5, 55.5, 29.3; HRMS (ESI) m/z: Calcd for $C_{19}H_{21}N_2O$ $[M+H]^+$: 293.1648; found: 293.1655.

Table 2, 11t



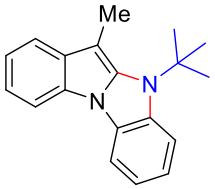
Yellow solid; 0.0802 g (83%); eluent: petroleum ether/EtOAc = 30:1; mp. 115-116 ^{o}C; IR (film) 1704, 1538, 1259, 1198, 1136 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 7.6, 1.2 Hz, 1H), 7.98 (dt, J = 7.6, 1.2 Hz, 1H), 7.83-7.76 (m, 1H), 7.58-7.52 (m, 1H), 7.25-7.19 (m, 2H), 7.14 (t, J = 7.6 Hz, 1H), 6.68 (d, J = 0.8 Hz, 1H), 4.01 (s, 3H), 1.92 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 145.5, 136.4, 134.0, 128.2, 126.8, 124.5, 122.1, 120.1, 118.4, 116.3, 114.4, 112.9, 110.3, 77.2, 57.9, 51.7, 29.4; HRMS (ESI) m/z: Calcd for $C_{20}H_{21}N_2O_2$ $[M+H]^+$: 321.1598; found: 321.1588.

Table 2, 11u



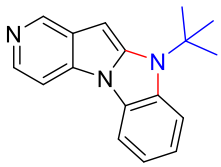
Green solid; 0.0547 g (66%); eluent: petroleum ether/EtOAc = 100:1; mp. 99-100 ^{o}C; IR (film) 1608, 1557, 1487, 1159 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.20 (td, J = 7.6, 1.2 Hz, 1H), 7.17-7.09 (m, 2H), 6.89 (d, J = 7.2 Hz, 1H), 5.97 (s, 1H), 3.15 (s, 3H), 1.92 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 136.7, 134.5, 129.3, 126.3, 121.7, 121.6, 120.8, 120.5, 119.0, 116.7, 112.1, 112.0, 75.4, 57.7, 29.4, 24.1; HRMS (ESI) m/z: Calcd for $C_{19}H_{21}N_2$ $[M+H]^+$: 277.1699; found: 277.1692.

Table 2, 11v



Yellow solid; 0.0237 g (29%); eluent: petroleum ether/EtOAc = 80:1 to 40:1; mp. 81-82 ^{o}C; IR (film) 1606, 1550, 1509, 1461, 1193 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.6 Hz, 1H), 7.79-7.74 (m, 1H), 7.65-7.59 (m, 2H), 7.31 (ddd, J = 7.6, 6.8, 1.2 Hz, 1H), 7.22 (ddd, J = 8.0, 7.2, 1.2 Hz, 1H), 7.18-7.09 (m, 2H), 2.62 (s, 3H), 1.89 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 138.2, 134.9, 128.4, 125.5, 121.3, 120.7, 119.6, 118.2, 117.4, 112.6, 110.1, 109.6, 81.8, 58.1, 31.3, 12.9; HRMS (ESI) m/z: Calcd for $C_{19}H_{21}N_2$ $[M+H]^+$: 277.1699; found: 277.1296.

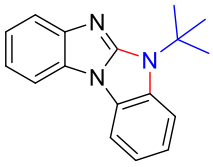
Table 2, 11w



Brown oil; 0.0697 g (88%); eluent: petroleum ether/EtOAc = 2:1 to 1:1; IR (film) 1604, 1542, 1372, 1208 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.30 (d, J = 5.6 Hz, 1H), 7.72 (d, J = 7.2 Hz, 1H), 7.64 (d. J = 5.6 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.26-7.17 (m, 2H), 5.86 (s, 1H), 1.84 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 141.1, 137.1, 136.7, 129.7, 128.6, 127.5, 122.8, 119.9, 112.7, 110.7, 105.3, 72.9, 57.6, 29.1; HRMS (ESI) m/z: Calcd

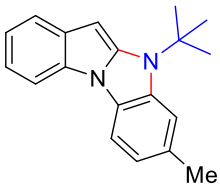
for $C_{17}H_{18}N_3$ $[M+H]^+$: 264.1495; found: 264.1497.

Table 2, 11x



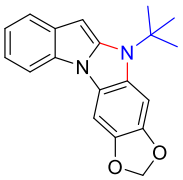
Light yellow oil; 0.064 g (81%); eluent: petroleum ether/EtOAc = 30:1 to 20:1; IR (film) 1621, 1538, 1453, 1393, 1204 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81-7.73 (m, 2H), 7.73-7.69 (m, 1H), 7.67-7.62 (m, 1H), 7.33 (td, *J* = 7.6, 1.6 Hz, 1H), 7.26-7.18 (m, 3H), 1.99 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 147.3, 135.2, 127.1, 125.7, 122.9, 122.5, 120.6, 119.5, 118.3, 113.6, 110.4, 109.9, 58.9, 29.7; HRMS (ESI) m/z: Calcd for $C_{17}H_{18}N_3$ $[M+H]^+$: 264.1495; found: 264.1498.

Table 2, 11y



Light yellow oil; 0.0505 g (61%); eluent: petroleum ether/EtOAc = 100:1 to 60:1; IR (film) 1611, 1548, 1463, 1390, 1214 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.31 (s, 1H), 7.23-7.18 (m, 1H), 7.16-7.10 (m, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 5.85 (s, 1H), 2.51 (s, 3H), 1.88 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 136.8, 133.3, 131.2, 126.5, 125.5, 121.0, 120.1, 118.8, 117.5, 113.0, 110.2, 109.6, 74.6, 57.4, 29.3, 22.2; HRMS (ESI) m/z: Calcd for $C_{19}H_{20}N_2Na$ $[M+Na]^+$: 299.1519; found: 299.1518.

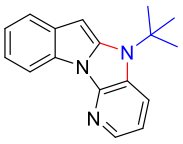
Table 2, 11z



Light yellow solid; 0.0347 g (38%); eluent: petroleum ether/EtOAc = 70:1 to 50:1; mp. 130-131 ^oC; IR (film) 1611, 1552, 1467, 1342, 1158, 1039 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.36 (s, 1H), 7.22-7.17 (m, 1H),

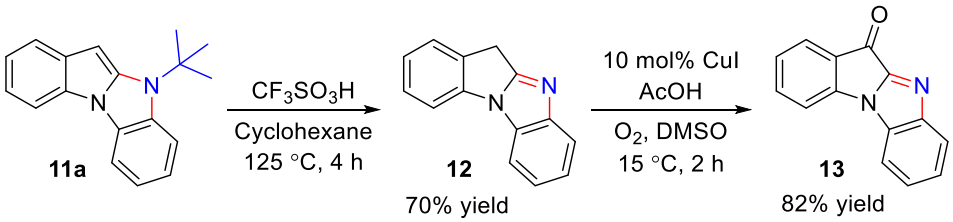
7.14-7.06 (m, 2H), 6.01 (s, 2H), 5.83 (s, 1H), 1.84 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 142.9, 141.2, 133.1, 130.5, 124.9, 122.4, 121.1, 118.8, 117.3, 109.9, 101.4, 95.5, 92.9, 74.4, 57.5, 29.3; HRMS (ESI) m/z: Calcd for $C_{19}H_{18}N_2O_2Na$ $[M+Na]^+$: 329.1260; found: 329.1263.

Table 2, 11aa



White solid; 0.0726 g (92%); eluent: petroleum ether/EtOAc = 80:1 to 60:1; mp. 96-97 ^{o}C; IR (film) 1585, 1552, 1500, 1391, 1203 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 5.2 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.29-7.23 (m, 1H), 7.22-7.17 (m, 1H), 7.06 (dd, J = 8.0, 4.8 Hz, 1H), 5.87 (s, 1H), 1.86 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 142.3, 138.4, 133.5, 130.3, 125.5, 122.2, 118.9, 118.87, 117.3, 116.7, 112.3, 76.4, 58.0, 29.1; HRMS (ESI) m/z: Calcd for $C_{17}H_{17}N_3Na$ $[M+Na]^+$: 286.1315; found: 286.1320.

Synthetic transformations of 11a (Scheme 5)



Compound 12. To an oven-dried 15 mL pressure tube was added benzo[4,5]imidazo[1,2-*a*]indole **11a** (0.1312 g, 0.50 mmol).[1] The tube was fitted with rubber septum, evacuated under high vacuum, and refilled with N_2 for three time. Cyclohexane (5.0 mL) was added, followed by slow addition of CF_3SO_3H (1.32 mL, 15.0 mmol) at room temperature. The rubber septum was rapidly replaced with Teflon-coated screw cap. The reaction mixture was placed in a pre-heated oil bath (125 ^{o}C), stirred for 4 h, cooled to room temperature, neutralized with saturated aqueous $NaHCO_3$ (pH = 9), extracted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, concentrated under reduced pressure, and purified by flash chromatography (silica gel, eluent: petroleum ether/EtOAc = 5:1 to 3:1) to give imidazole **12**[2] as yellow solid (0.0726 g, 70% yield). mp. 173-174 ^{o}C; IR (film) 1610, 1538, 1495, 1470, 1348, 1227 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.81-7.74 (m, 1H), 7.70-7.65 (m, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.34-7.26 (m, 2H), 7.16 (td, *J* = 7.6, 1.2 Hz 1H), 3.99 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 148.0, 139.2, 132.0, 129.6, 128.2, 126.1, 124.1, 122.9, 122.6, 120.2, 110.8, 110.4, 29.0; HRMS (ESI) m/z: Calcd for $C_{14}H_{11}N_2$ $[M+H]^+$: 207.0917; found: 207.0919.

1) Zheng, H.; Zhu, Y.; Shi, Y. *Angew. Chem. Int. Ed.* **2014**, *53*, 11280-11284.

2) Sharma, Y.; Kaur, S.; Kandhasamy, H.; Sahoo, S. C.; Chaudhari, V. D. *Org. Lett.* **2025**, *27*, 517-521.

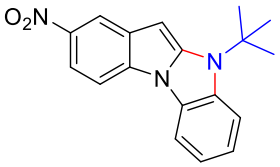
Compound 13. To an oven-dried 4 mL pressure tube were added imidazole **12** (0.021 g, 0.10 mmol) and CuI (0.0019 g, 0.010 mmol). The tube was fitted with rubber septum, evacuated under high vacuum, and refilled with O_2 for three time, followed by addition of DMSO (0.40 mL) and AcOH (5.7 uL, 0.10 mmol).[1] The reaction mixture was placed water bath (15 ^{o}C), stirred under O_2 atmosphere (balloon) for 2 h, neutralized with saturated aqueous $NaHCO_3$, extracted with CH_2Cl_2, washed with brine, dried over Na_2SO_4, filtered, concentrated under reduced pressure, and purified by flash chromatography (silica gel, eluent: petroleum ether/EtOAc = 3:1) to give imidazole **13**[2] as yellow solid (0.018 g, 82% yield). mp. 215-216 ^{o}C; IR (film) 1725, 1606, 1515, 1471, 1341, 1172 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d6) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.91-7.81 (m, 2H), 7.73 (td, *J* = 8.0, 1.6 Hz, 1H), 7.68 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.54 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.35 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.29 (t, *J* = 7.6 Hz 1H); ^{13}C NMR (100 MHz, DMSO-d6) δ 180.1, 149.1, 148.1, 142.8, 137.2, 129.6, 127.7, 127.0, 126.0, 125.2, 124.2, 123.0, 112.6, 112.2; HRMS (ESI) m/z: Calcd for $C_{14}H_8N_2ONa$ $[M+Na]^+$: 243.0529; found: 243.0529.

1. Sterckx, H.; Houwer, J. D.; Mensch, C.; Caretti, I.; Tehrani, A. T.; Herrebout, W. A.; Doorslaer, S. V.; Maes, B. U. W. *Chem. Sci.* **2016**, *7*, 346-357.

2. Sharma, Y.; Kaur, S.; Kandhasamy, H.; Sahoo, S. C.; Chaudhari, V. D. *Org. Lett.* **2025**, *27*, 517-521.

The X-ray structure of compound **11k**

Compound **11k** (0.010 g) was dissolved in petroleum ether/CH_2Cl_2 (4 mL, 3:1) and the solvent was allowed to slowly evaporated at room temperature to give a yellow crystal suitable for X-ray diffraction analysis. The intensity data was collected on a D8 VENTURE instrument. The data were outlined below.



11k

CCDC: 2372228

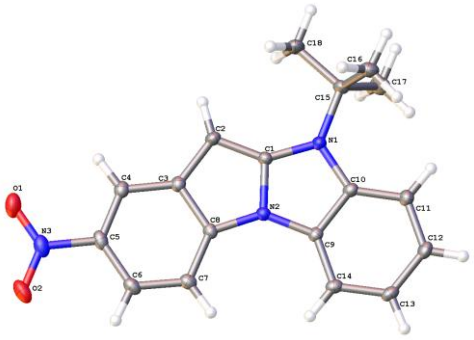


Figure S-1. Ortep diagram of compound **11k** (the thermal ellipsoids are drawn at the 30% probability level).

Table S-1. Crystal data and structure refinement for **11k**.

Identification code	**11k**	
Empirical formula	C18 H17 N3 O2	
Formula weight	307.34	
Temperature	170.00 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 6.8712(2) Å	α= 90°.
	b = 24.6723(7) Å	β= 91.358(2)°.
	c = 9.0721(3) Å	γ = 90°.
Volume	1537.55(8) $Å^3$	
Z	4	
Density (calculated)	1.328 Mg/m^3	
Absorption coefficient	0.457 mm^{-1}	
F(000)	648	
Crystal size	0.17 x 0.17 x 0.05 mm^3	
Theta range for data collection	4.519 to 54.868°.	
Index ranges	-8<=h<=8, -29<=k<=28, -11<=l<=10	
Reflections collected	14979	
Independent reflections	2899 [R(int) = 0.0748]	
Completeness to theta = 53.594°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.5693	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2899 / 0 / 212	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0459, wR2 = 0.1176	
R indices (all data)	R1 = 0.0616, wR2 = 0.1300	
Extinction coefficient	0.0029(6)	
Largest diff. peak and hole	0.301 and -0.225 $e.Å^{-3}$	

Table S-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **11k**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	9124(2)	6000(1)	9925(2)	51(1)
O(2)	8821(2)	6620(1)	8241(2)	50(1)
N(1)	7129(2)	3586(1)	4702(1)	28(1)
N(2)	7306(2)	4494(1)	4631(1)	24(1)
N(3)	8828(2)	6140(1)	8633(2)	38(1)
C(1)	7492(2)	4045(1)	5552(2)	25(1)
C(2)	7990(2)	4211(1)	6962(2)	28(1)
C(3)	8082(2)	4790(1)	6896(2)	26(1)
C(4)	8496(2)	5187(1)	7959(2)	28(1)
C(5)	8445(2)	5722(1)	7520(2)	30(1)
C(6)	8028(2)	5890(1)	6076(2)	30(1)
C(7)	7620(2)	5503(1)	5004(2)	28(1)
C(8)	7647(2)	4963(1)	5425(2)	24(1)
C(9)	6822(2)	4330(1)	3201(2)	23(1)
C(10)	6690(2)	3762(1)	3251(2)	25(1)
C(11)	6187(2)	3479(1)	1969(2)	30(1)
C(12)	5861(2)	3775(1)	684(2)	32(1)
C(13)	6028(2)	4334(1)	650(2)	30(1)
C(14)	6518(2)	4624(1)	1918(2)	27(1)
C(15)	6966(2)	3015(1)	5229(2)	30(1)
C(16)	4849(3)	2830(1)	5049(2)	39(1)
C(17)	8355(3)	2655(1)	4366(2)	45(1)
C(18)	7549(3)	2977(1)	6854(2)	42(1)

Table S-3. Bond lengths [Å] and angles [°] for **11k**.

O(1)-N(3)	1.234(2)
O(2)-N(3)	1.236(2)
N(1)-C(1)	1.388(2)
N(1)-C(10)	1.4118(19)
N(1)-C(15)	1.493(2)
N(2)-C(1)	1.3924(19)
N(2)-C(8)	1.3795(19)
N(2)-C(9)	1.3920(19)
N(3)-C(5)	1.463(2)
C(1)-C(2)	1.378(2)
C(2)-H(2)	0.9500
C(2)-C(3)	1.430(2)
C(3)-C(4)	1.400(2)
C(3)-C(8)	1.427(2)
C(4)-H(4)	0.9500
C(4)-C(5)	1.378(2)
C(5)-C(6)	1.397(2)
C(6)-H(6)	0.9500
C(6)-C(7)	1.386(2)
C(7)-H(7)	0.9500
C(7)-C(8)	1.387(2)
C(9)-C(10)	1.404(2)
C(9)-C(14)	1.383(2)
C(10)-C(11)	1.392(2)
C(11)-H(11)	0.9500
C(11)-C(12)	1.391(2)
C(12)-H(12)	0.9500
C(12)-C(13)	1.385(2)
C(13)-H(13)	0.9500
C(13)-C(14)	1.388(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.530(2)
C(15)-C(17)	1.533(2)
C(15)-C(18)	1.522(2)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800

C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800

C(1)-N(1)-C(10)	107.44(12)
C(1)-N(1)-C(15)	127.25(13)
C(10)-N(1)-C(15)	124.87(13)
C(8)-N(2)-C(1)	109.99(12)
C(8)-N(2)-C(9)	139.93(13)
C(9)-N(2)-C(1)	110.07(12)
O(1)-N(3)-O(2)	122.75(15)
O(1)-N(3)-C(5)	118.72(15)
O(2)-N(3)-C(5)	118.53(15)
N(1)-C(1)-N(2)	107.62(13)
C(2)-C(1)-N(1)	142.68(14)
C(2)-C(1)-N(2)	109.69(13)
C(1)-C(2)-H(2)	127.2
C(1)-C(2)-C(3)	105.62(13)
C(3)-C(2)-H(2)	127.2
C(4)-C(3)-C(2)	132.77(14)
C(4)-C(3)-C(8)	118.04(15)
C(8)-C(3)-C(2)	109.19(13)
C(3)-C(4)-H(4)	121.1
C(5)-C(4)-C(3)	117.90(15)
C(5)-C(4)-H(4)	121.1
C(4)-C(5)-N(3)	118.22(15)
C(4)-C(5)-C(6)	123.91(15)
C(6)-C(5)-N(3)	117.86(15)
C(5)-C(6)-H(6)	120.4
C(7)-C(6)-C(5)	119.20(15)
C(7)-C(6)-H(6)	120.4
C(6)-C(7)-H(7)	121.1
C(6)-C(7)-C(8)	117.84(15)
C(8)-C(7)-H(7)	121.1

N(2)-C(8)-C(3)	105.50(13)
N(2)-C(8)-C(7)	131.39(14)
C(7)-C(8)-C(3)	123.11(14)
N(2)-C(9)-C(10)	106.00(12)
C(14)-C(9)-N(2)	131.21(15)
C(14)-C(9)-C(10)	122.79(14)
C(9)-C(10)-N(1)	108.86(13)
C(11)-C(10)-N(1)	131.93(15)
C(11)-C(10)-C(9)	119.21(13)
C(10)-C(11)-H(11)	121.0
C(12)-C(11)-C(10)	117.95(15)
C(12)-C(11)-H(11)	121.0
C(11)-C(12)-H(12)	119.0
C(13)-C(12)-C(11)	122.04(15)
C(13)-C(12)-H(12)	119.0
C(12)-C(13)-H(13)	119.6
C(12)-C(13)-C(14)	120.82(14)
C(14)-C(13)-H(13)	119.6
C(9)-C(14)-C(13)	117.18(15)
C(9)-C(14)-H(14)	121.4
C(13)-C(14)-H(14)	121.4
N(1)-C(15)-C(16)	109.08(13)
N(1)-C(15)-C(17)	109.37(13)
N(1)-C(15)-C(18)	110.40(13)
C(16)-C(15)-C(17)	111.96(15)
C(18)-C(15)-C(16)	108.23(14)
C(18)-C(15)-C(17)	107.79(14)
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17C)	109.5

H(17B)-C(17)-H(17C)	109.5
C(15)-C(18)-H(18A)	109.5
C(15)-C(18)-H(18B)	109.5
C(15)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S-4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **11k**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	57(1)	50(1)	45(1)	-18(1)	-10(1)	1(1)
O(2)	55(1)	28(1)	67(1)	-14(1)	4(1)	-3(1)
N(1)	40(1)	21(1)	22(1)	1(1)	0(1)	0(1)
N(2)	26(1)	21(1)	23(1)	2(1)	2(1)	1(1)
N(3)	29(1)	37(1)	48(1)	-14(1)	1(1)	-1(1)
C(1)	30(1)	20(1)	25(1)	2(1)	4(1)	0(1)
C(2)	36(1)	27(1)	21(1)	3(1)	2(1)	1(1)
C(3)	24(1)	28(1)	25(1)	-1(1)	4(1)	0(1)
C(4)	26(1)	33(1)	27(1)	-4(1)	4(1)	-2(1)
C(5)	23(1)	28(1)	39(1)	-10(1)	4(1)	-1(1)
C(6)	26(1)	23(1)	42(1)	-1(1)	4(1)	1(1)
C(7)	25(1)	25(1)	34(1)	2(1)	3(1)	1(1)
C(8)	22(1)	24(1)	27(1)	-3(1)	4(1)	0(1)
C(9)	21(1)	27(1)	22(1)	0(1)	4(1)	0(1)
C(10)	27(1)	26(1)	23(1)	2(1)	4(1)	2(1)
C(11)	37(1)	28(1)	26(1)	-2(1)	4(1)	0(1)
C(12)	35(1)	38(1)	22(1)	-4(1)	4(1)	0(1)
C(13)	31(1)	38(1)	22(1)	6(1)	2(1)	2(1)
C(14)	25(1)	29(1)	27(1)	6(1)	4(1)	1(1)
C(15)	42(1)	21(1)	28(1)	3(1)	2(1)	2(1)
C(16)	48(1)	31(1)	39(1)	8(1)	1(1)	-4(1)
C(17)	58(1)	31(1)	46(1)	3(1)	9(1)	14(1)
C(18)	66(1)	27(1)	34(1)	8(1)	-7(1)	-1(1)

Table S-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **11k**.

	x	y	z	U(eq)
H(2)	8224	3988	7801	34
H(4)	8804	5092	8952	34
H(6)	8024	6264	5833	36
H(7)	7332	5605	4013	34
H(11)	6071	3095	1974	36
H(12)	5512	3588	-199	38
H(13)	5804	4523	-252	36
H(14)	6638	5007	1905	32
H(16A)	4028	3045	5696	59
H(16B)	4752	2446	5314	59
H(16C)	4412	2879	4022	59
H(17A)	8037	2681	3310	67
H(17B)	8219	2278	4688	67
H(17C)	9699	2775	4549	67
H(18A)	8889	3106	6997	64
H(18B)	7461	2599	7178	64
H(18C)	6673	3201	7433	64

Table S-6. Torsion angles [°] for **11k**.

O(1)-N(3)-C(5)-C(4)	-2.1(2)
O(1)-N(3)-C(5)-C(6)	177.24(14)
O(2)-N(3)-C(5)-C(4)	178.61(14)
O(2)-N(3)-C(5)-C(6)	-2.0(2)
N(1)-C(1)-C(2)-C(3)	179.7(2)
N(1)-C(10)-C(11)-C(12)	-179.20(15)
N(2)-C(1)-C(2)-C(3)	0.88(17)
N(2)-C(9)-C(10)-N(1)	-1.08(16)
N(2)-C(9)-C(10)-C(11)	178.93(13)
N(2)-C(9)-C(14)-C(13)	-179.40(14)
N(3)-C(5)-C(6)-C(7)	-178.71(13)
C(1)-N(1)-C(10)-C(9)	1.20(16)
C(1)-N(1)-C(10)-C(11)	-178.82(16)
C(1)-N(1)-C(15)-C(16)	110.49(17)
C(1)-N(1)-C(15)-C(17)	-126.75(17)
C(1)-N(1)-C(15)-C(18)	-8.3(2)
C(1)-N(2)-C(8)-C(3)	0.63(16)
C(1)-N(2)-C(8)-C(7)	-179.57(15)
C(1)-N(2)-C(9)-C(10)	0.58(16)
C(1)-N(2)-C(9)-C(14)	-178.91(15)
C(1)-C(2)-C(3)-C(4)	179.50(16)
C(1)-C(2)-C(3)-C(8)	-0.49(17)
C(2)-C(3)-C(4)-C(5)	-179.51(16)
C(2)-C(3)-C(8)-N(2)	-0.08(16)
C(2)-C(3)-C(8)-C(7)	-179.90(14)
C(3)-C(4)-C(5)-N(3)	178.45(13)
C(3)-C(4)-C(5)-C(6)	-0.8(2)
C(4)-C(3)-C(8)-N(2)	179.93(12)
C(4)-C(3)-C(8)-C(7)	0.1(2)
C(4)-C(5)-C(6)-C(7)	0.6(2)
C(5)-C(6)-C(7)-C(8)	0.0(2)
C(6)-C(7)-C(8)-N(2)	179.86(14)
C(6)-C(7)-C(8)-C(3)	-0.4(2)
C(8)-N(2)-C(1)-N(1)	179.78(11)
C(8)-N(2)-C(1)-C(2)	-0.97(17)
C(8)-N(2)-C(9)-C(10)	-178.87(16)

C(8)-N(2)-C(9)-C(14)	1.6(3)
C(8)-C(3)-C(4)-C(5)	0.5(2)
C(9)-N(2)-C(1)-N(1)	0.16(16)
C(9)-N(2)-C(1)-C(2)	179.41(12)
C(9)-N(2)-C(8)-C(3)	-179.93(16)
C(9)-N(2)-C(8)-C(7)	-0.1(3)
C(9)-C(10)-C(11)-C(12)	0.8(2)
C(10)-N(1)-C(1)-N(2)	-0.82(16)
C(10)-N(1)-C(1)-C(2)	-179.7(2)
C(10)-N(1)-C(15)-C(16)	-60.96(19)
C(10)-N(1)-C(15)-C(17)	61.79(19)
C(10)-N(1)-C(15)-C(18)	-179.77(14)
C(10)-C(9)-C(14)-C(13)	1.2(2)
C(10)-C(11)-C(12)-C(13)	0.2(2)
C(11)-C(12)-C(13)-C(14)	-0.5(2)
C(12)-C(13)-C(14)-C(9)	-0.2(2)
C(14)-C(9)-C(10)-N(1)	178.45(13)
C(14)-C(9)-C(10)-C(11)	-1.5(2)
C(15)-N(1)-C(1)-N(2)	-173.48(13)
C(15)-N(1)-C(1)-C(2)	7.7(3)
C(15)-N(1)-C(10)-C(9)	174.07(13)
C(15)-N(1)-C(10)-C(11)	-5.9(3)

Symmetry transformations used to generate equivalent atoms:

Table S-7. Hydrogen bonds for **11k** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

NMR Spectra

^{1}H NMR Spectrum of **11a** ($CDCl_3$, 400 MHz)

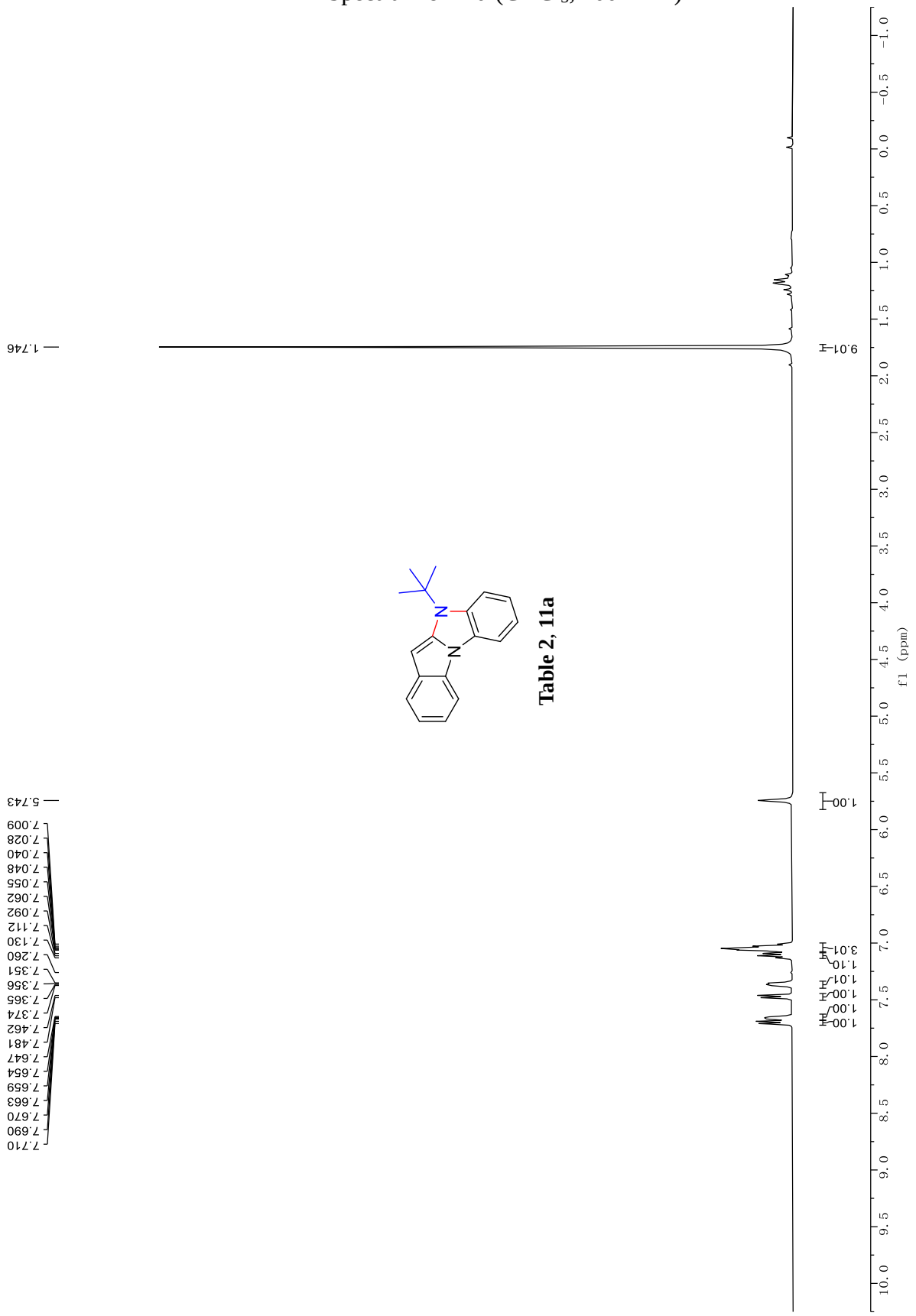


Table 2, 11a

^{13}C NMR Spectrum of **11a** ($CDCl_3$, 100 MHz)

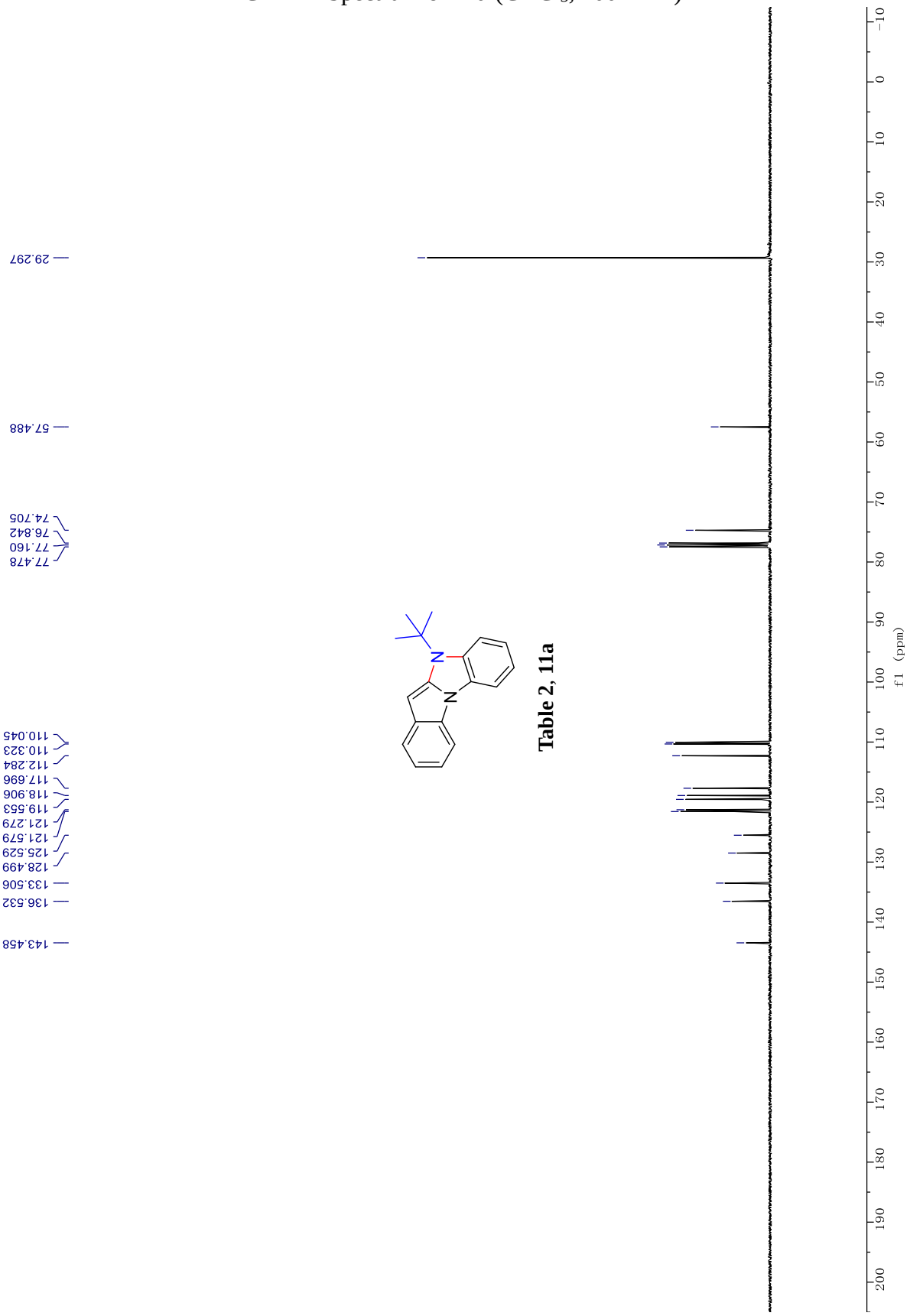
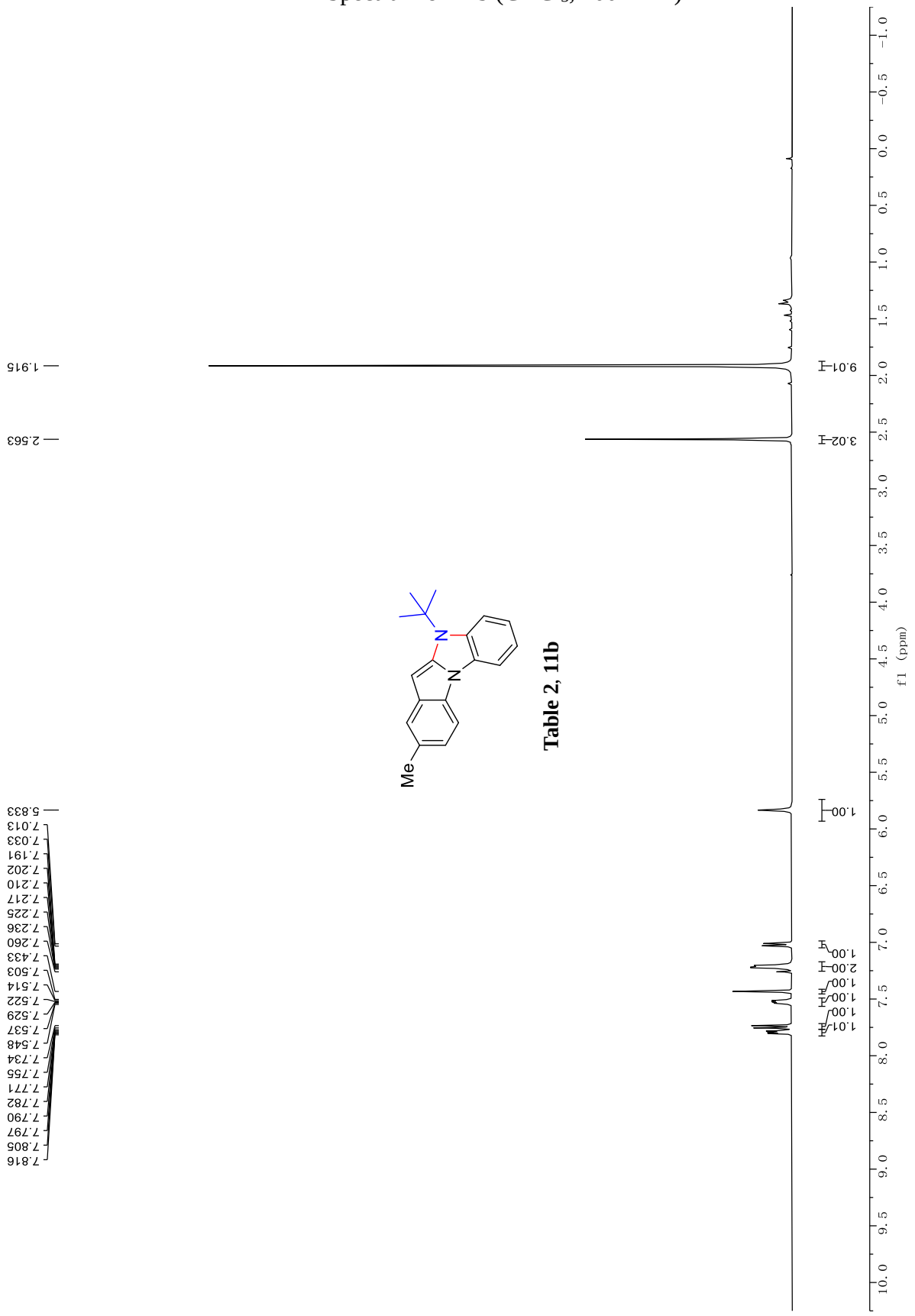


Table 2, 11a

^{1}H NMR Spectrum of **11b** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **11b** ($CDCl_3$, 100 MHz)

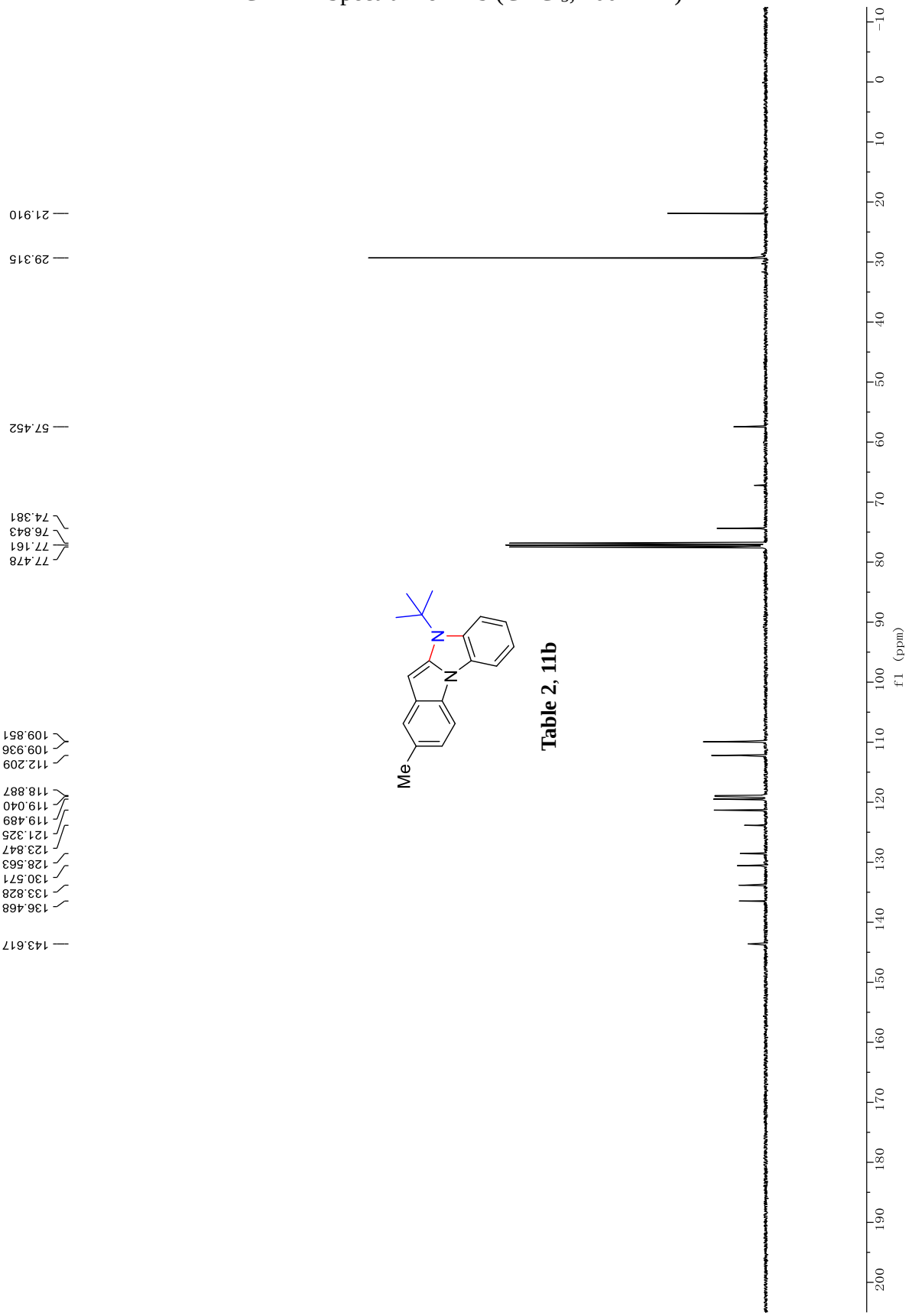


Table 2, 11b

^{1}H NMR Spectrum of **11c** ($CDCl_3$, 400 MHz)

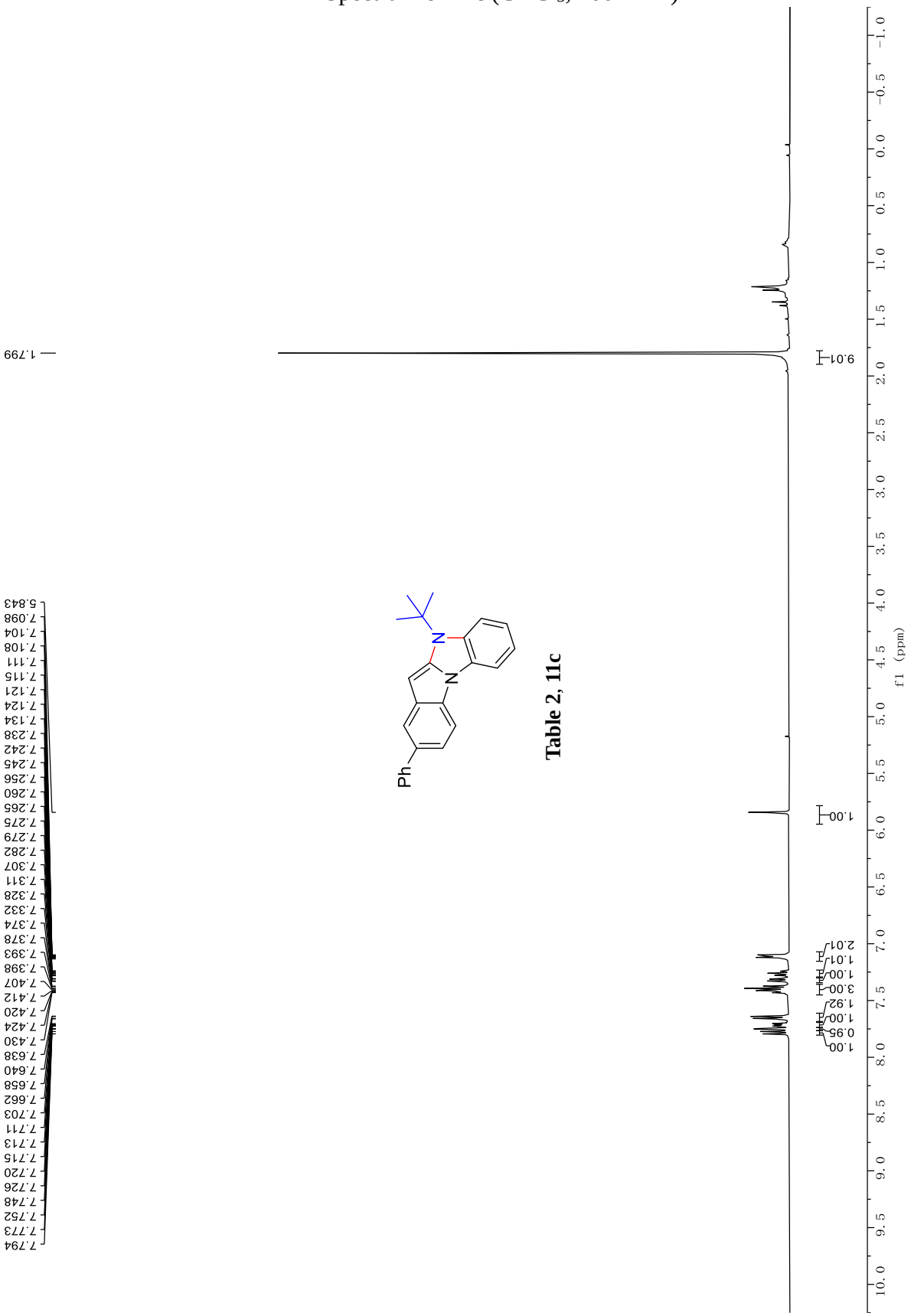
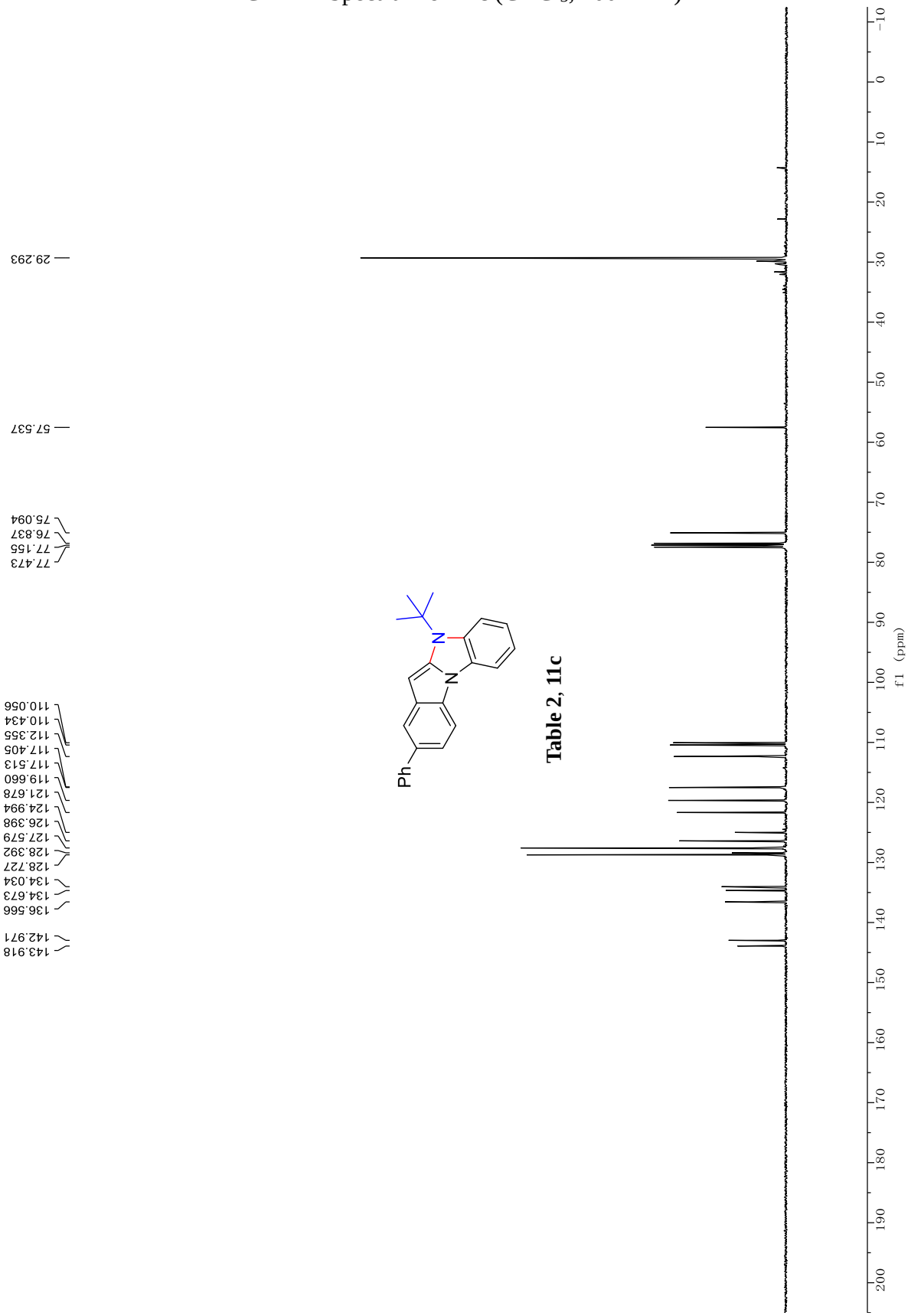
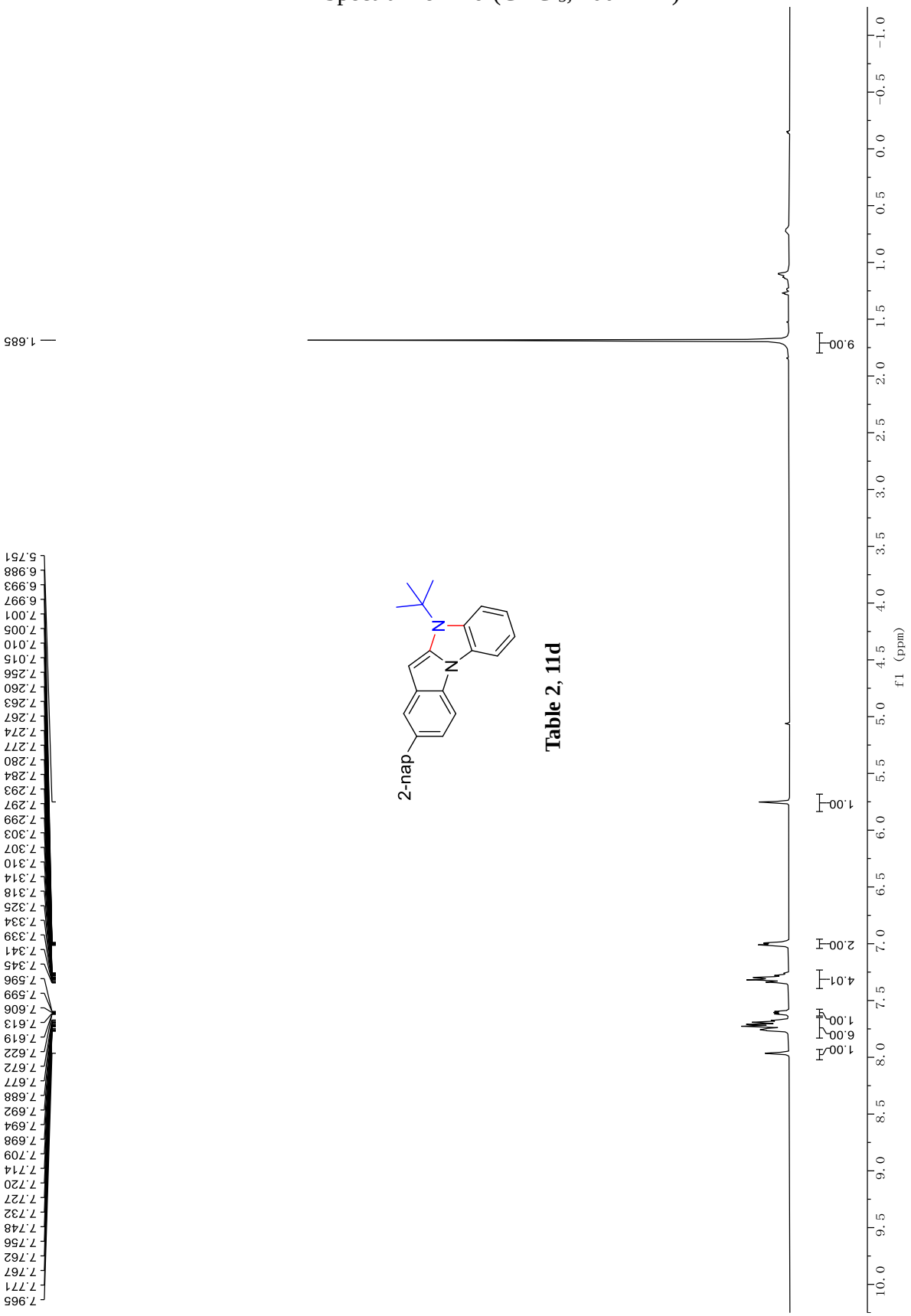


Table 2, 11c

^{13}C NMR Spectrum of **11c** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **11d** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **11d** ($CDCl_3$, 100 MHz)

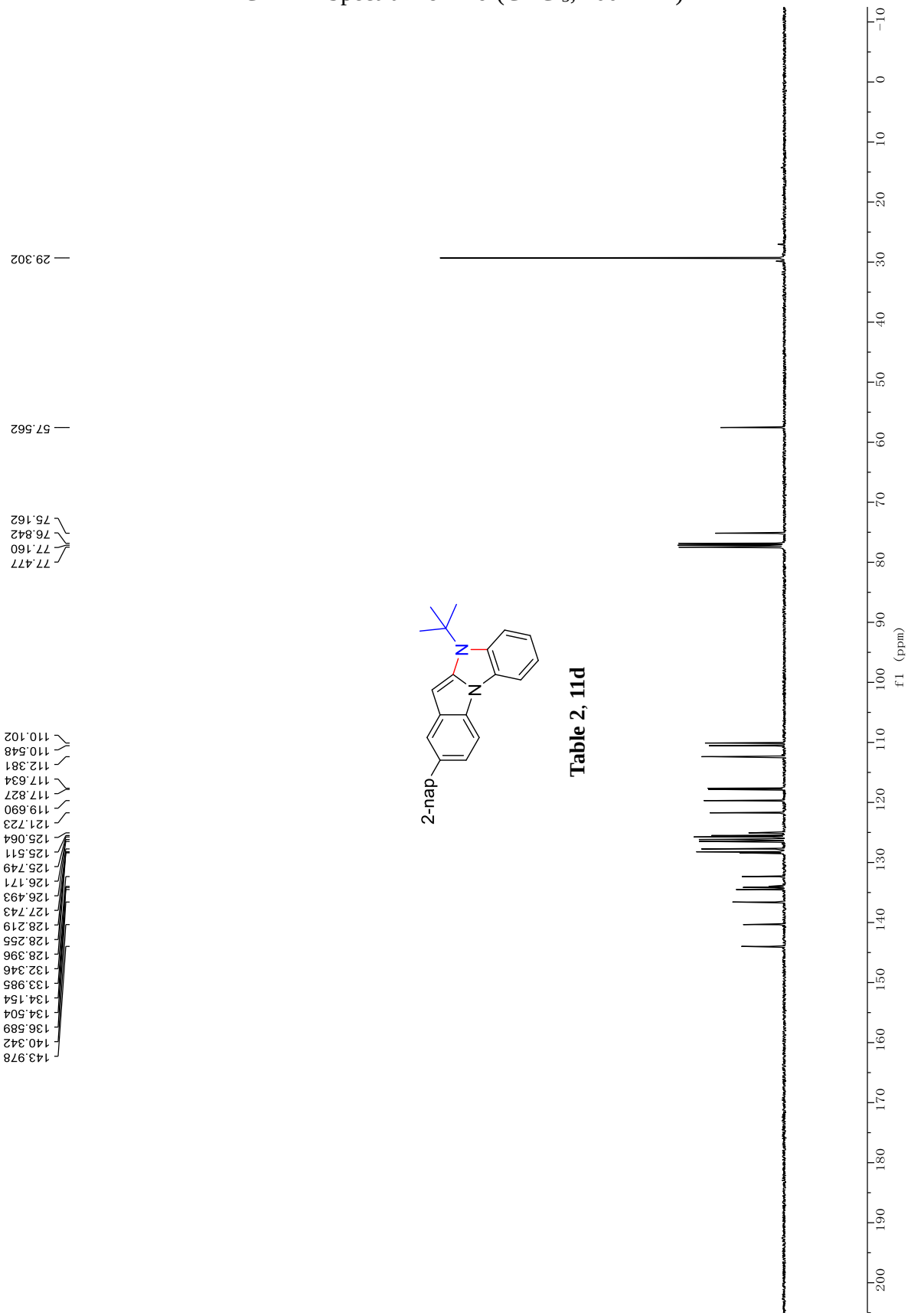


Table 2, 11d

^{1}H NMR Spectrum of **11e** ($CDCl_3$, 400 MHz)

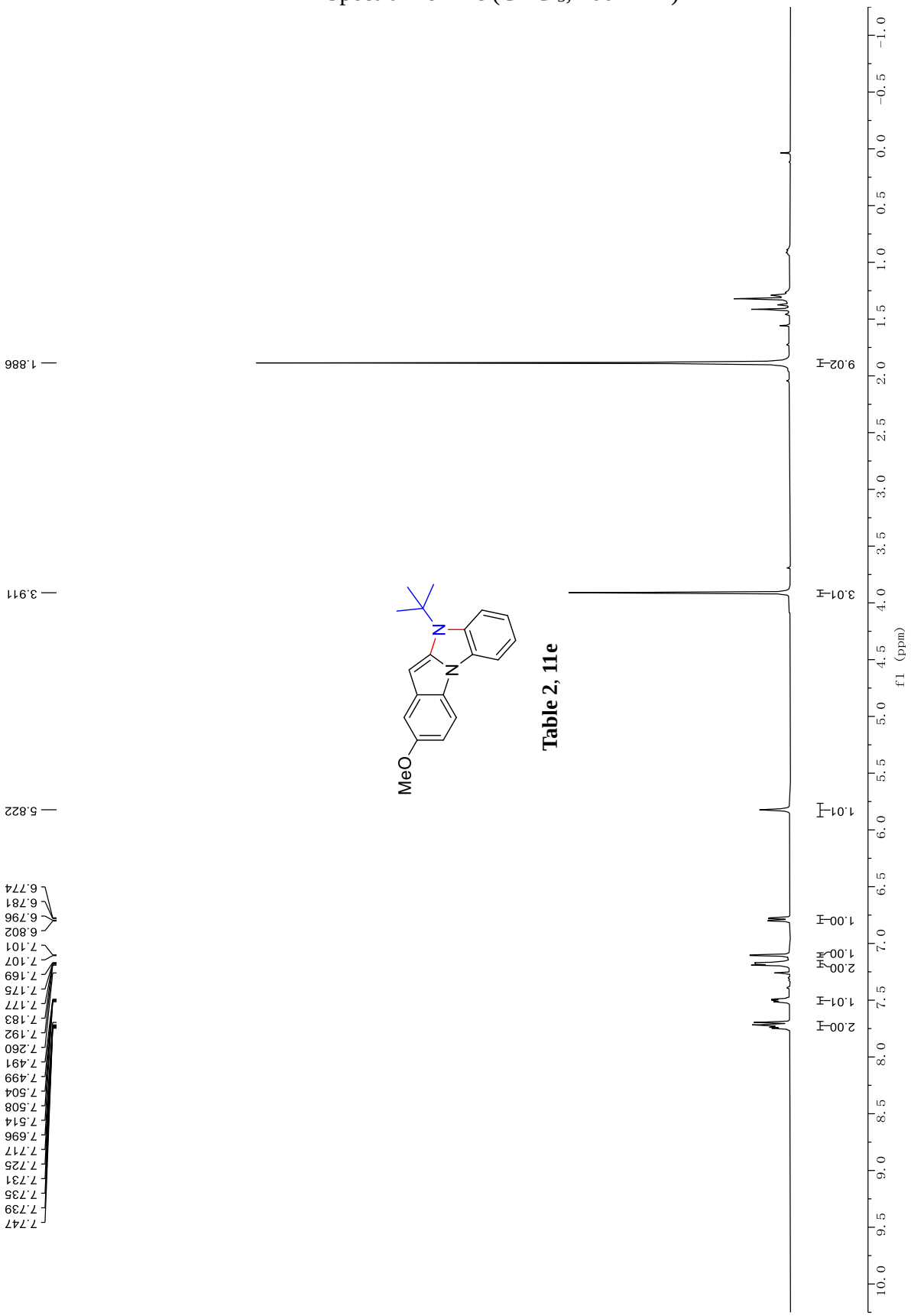
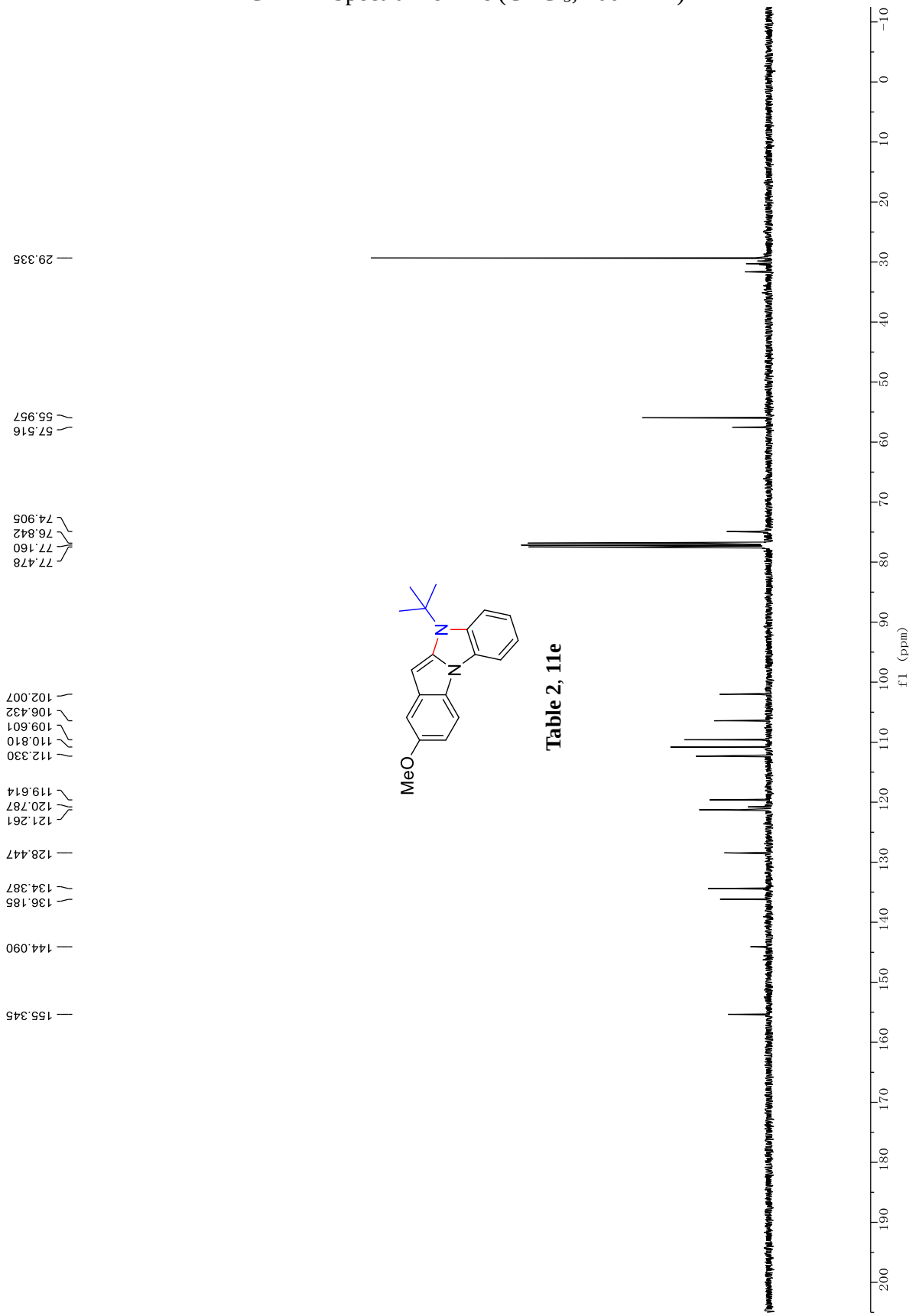


Table 2, 11e

^{13}C NMR Spectrum of **11e** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **11f** ($CDCl_3$, 400 MHz)

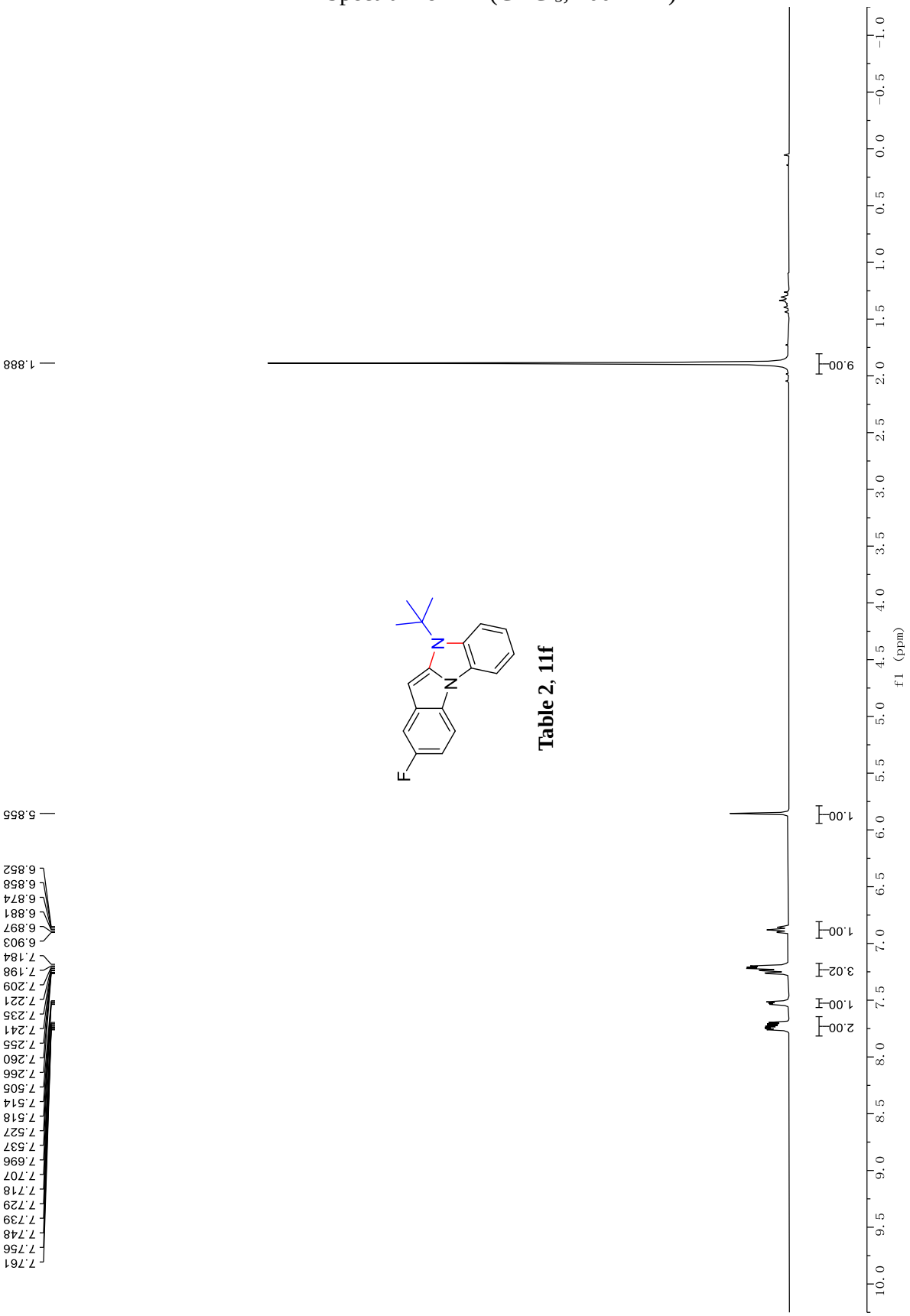
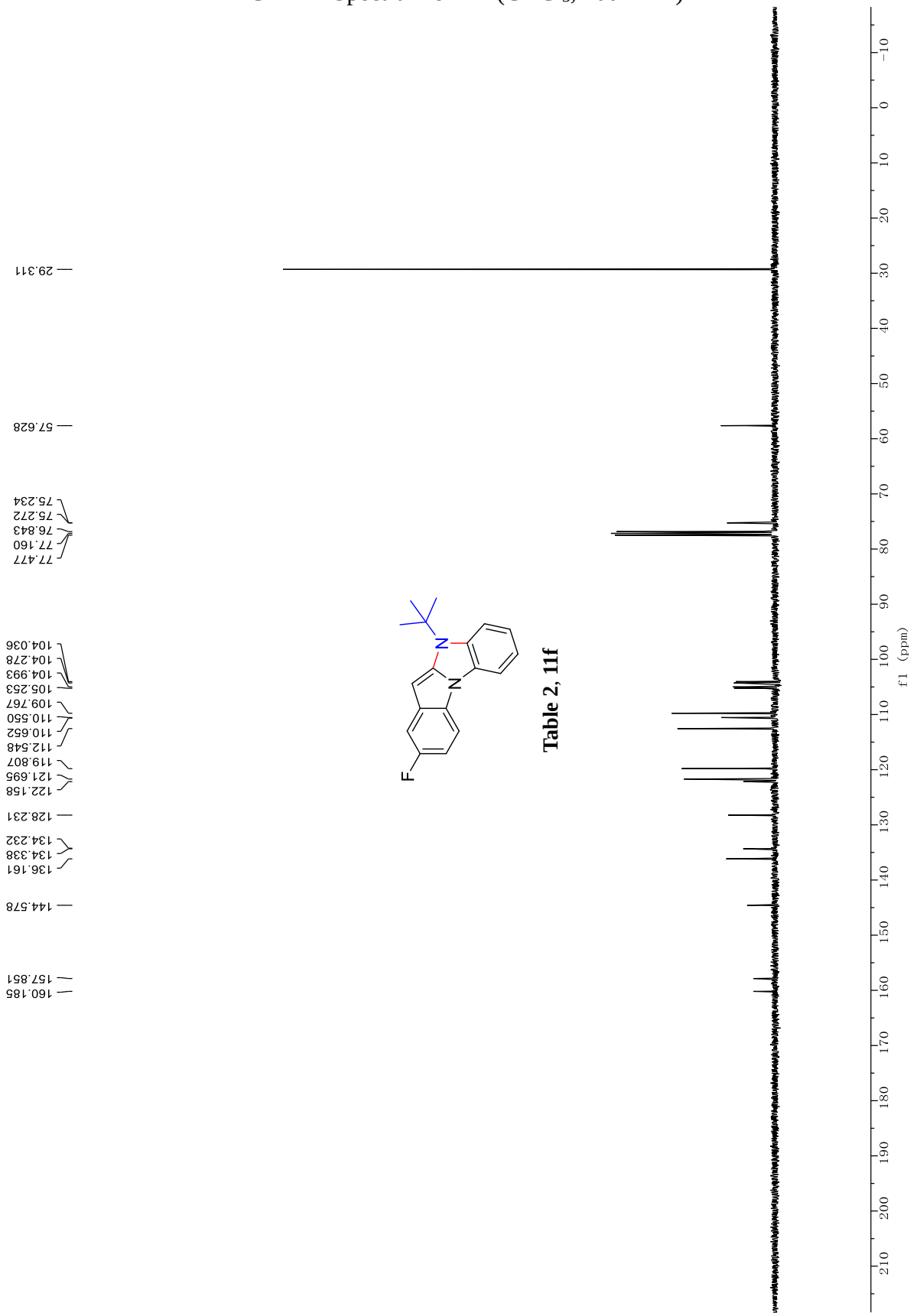


Table 2, 11f

^{13}C NMR Spectrum of **11f** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **11g** ($CDCl_3$, 400 MHz)

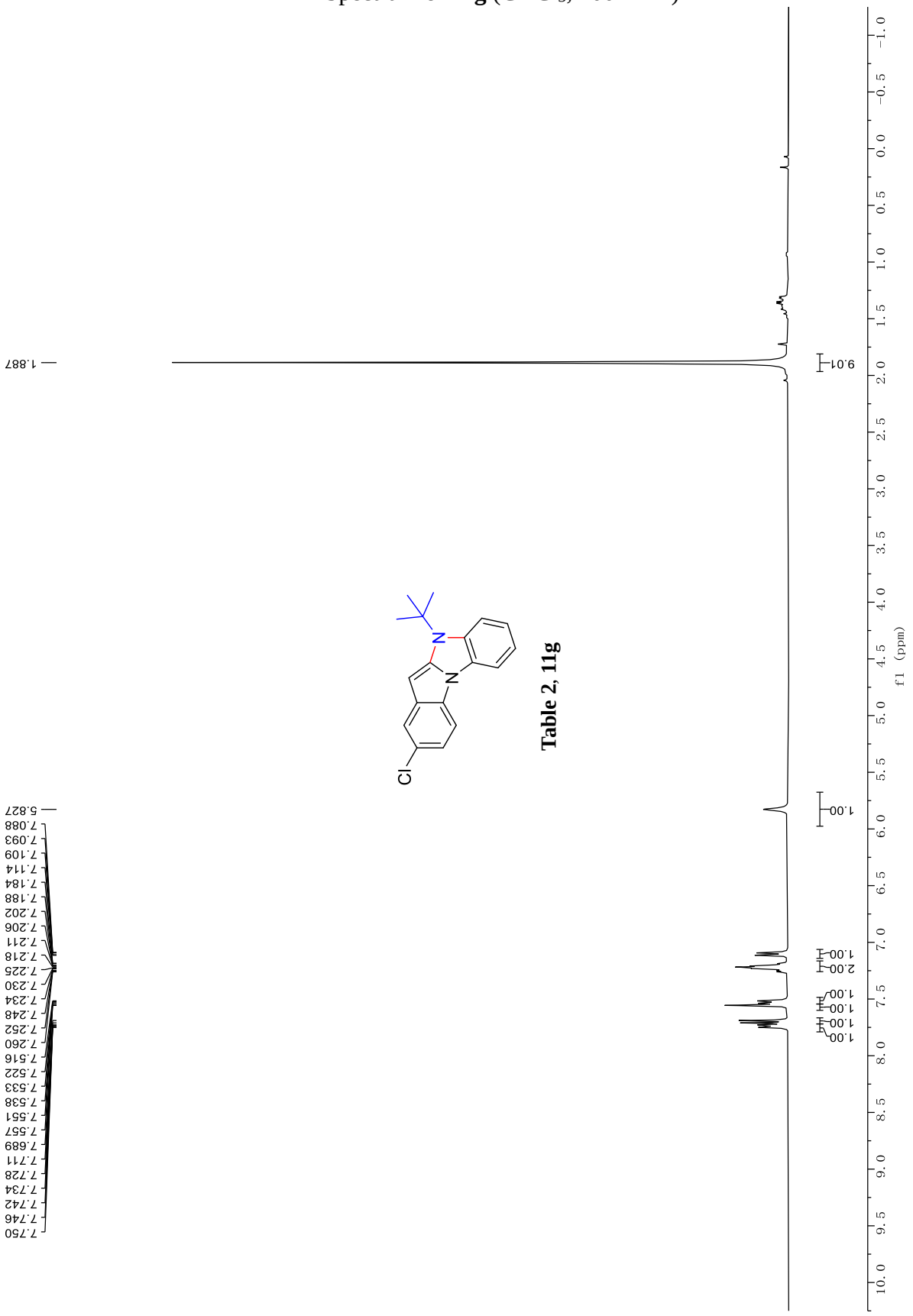


Table 2, 11g

^{13}C NMR Spectrum of **11g** ($CDCl_3$, 100 MHz)

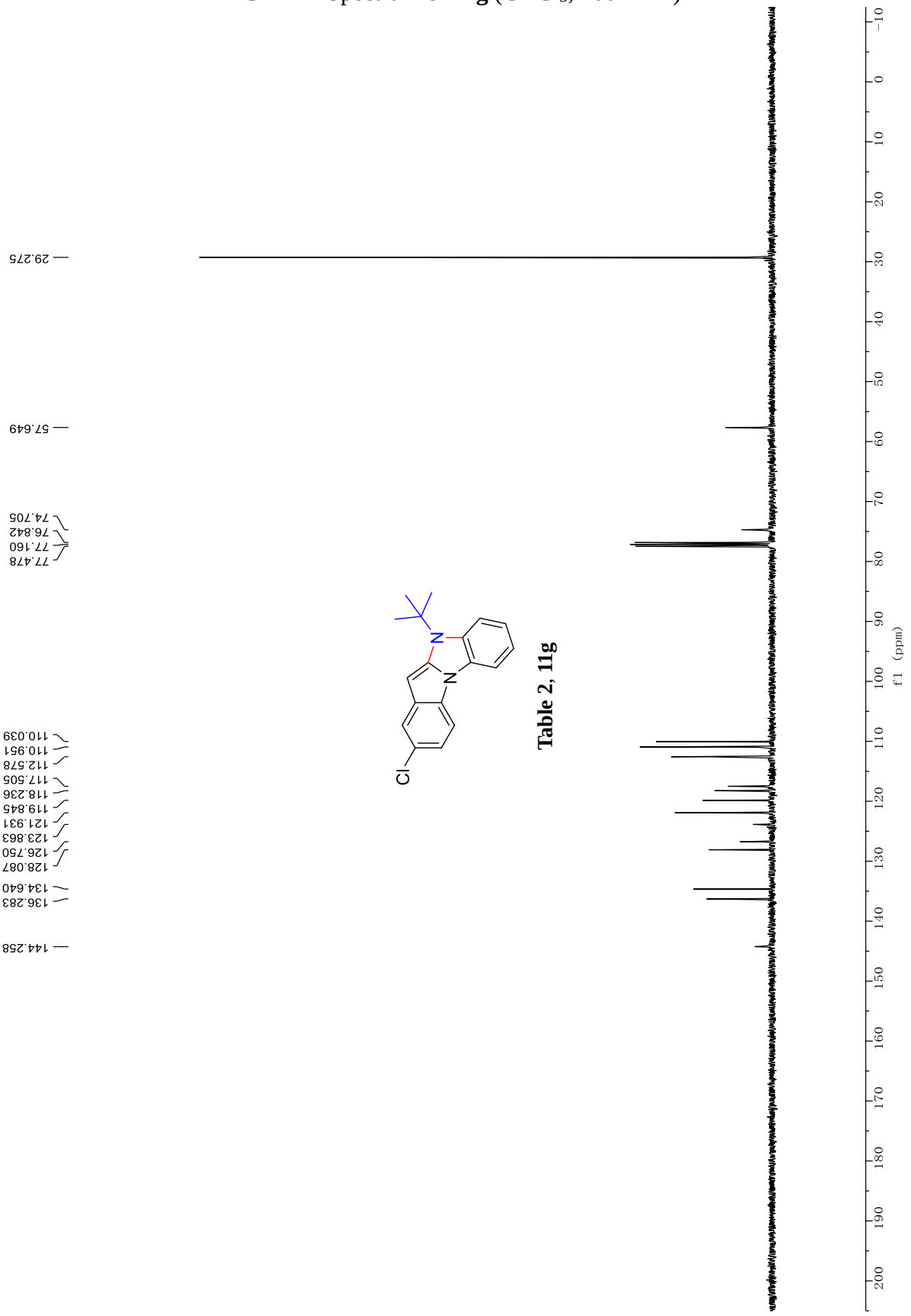
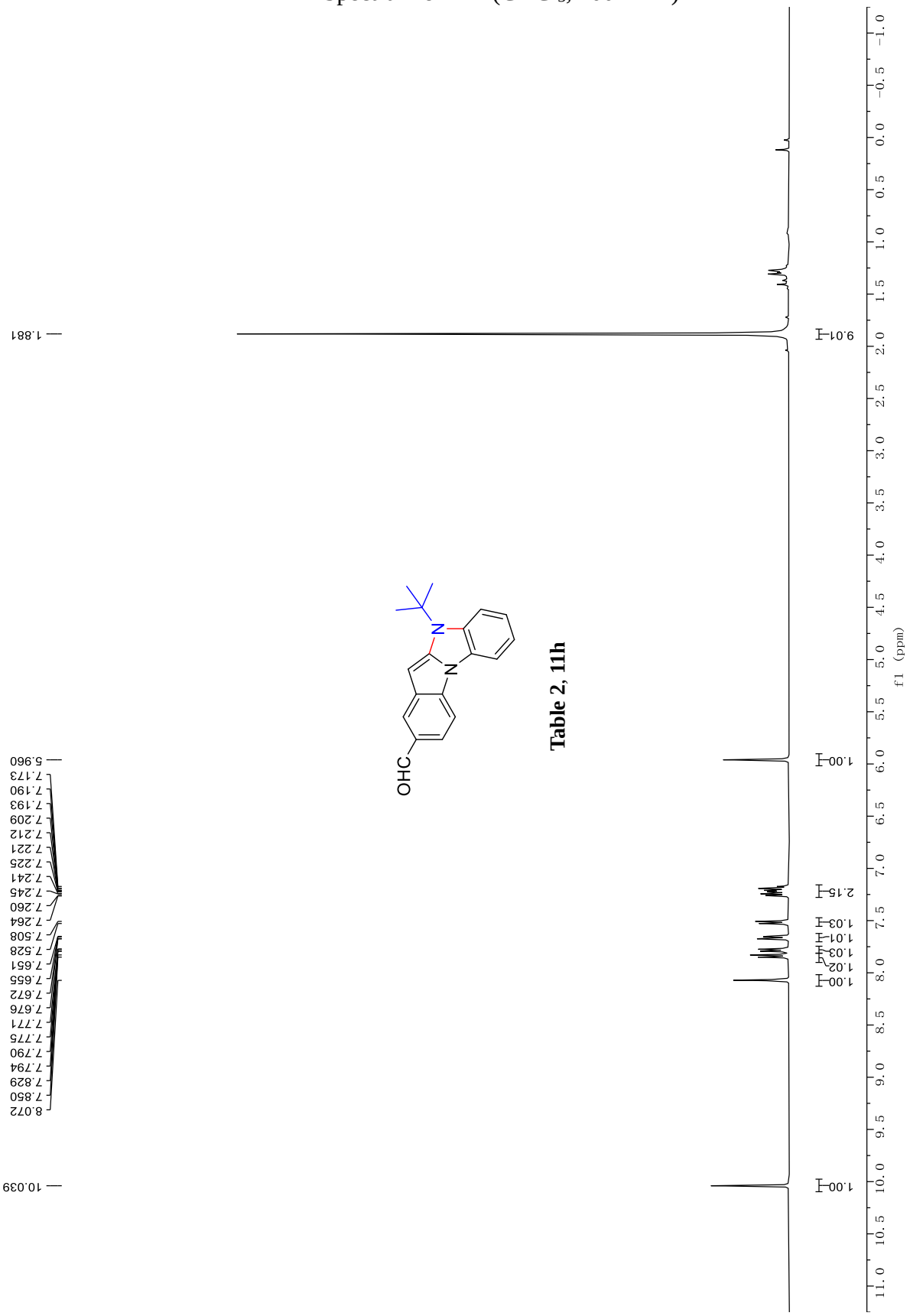


Table 2, 11g

^{1}H NMR Spectrum of **11h** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **11h** ($CDCl_3$, 100 MHz)

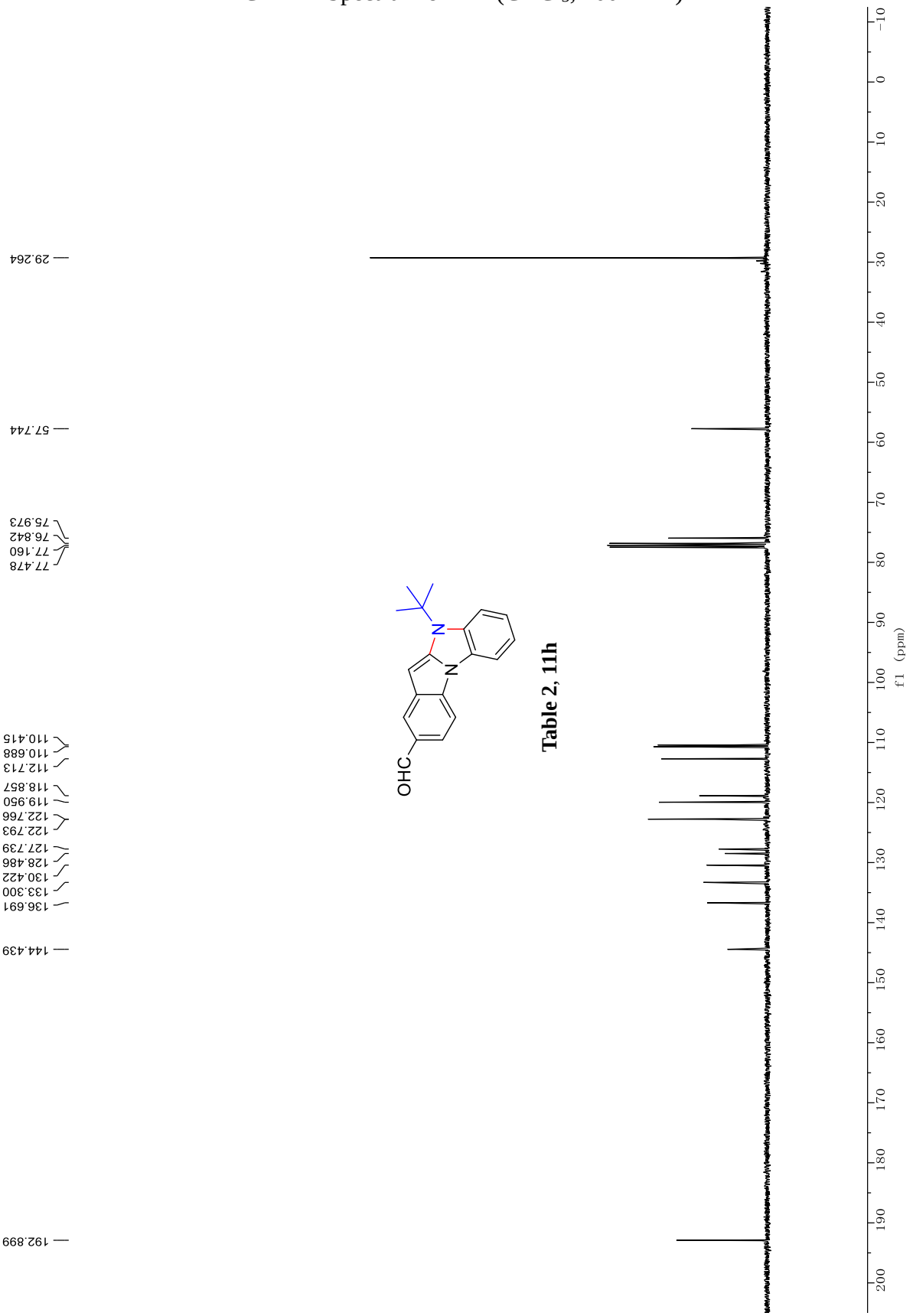


Table 2, 11h

^{1}H NMR Spectrum of **11i** ($CDCl_3$, 400 MHz)

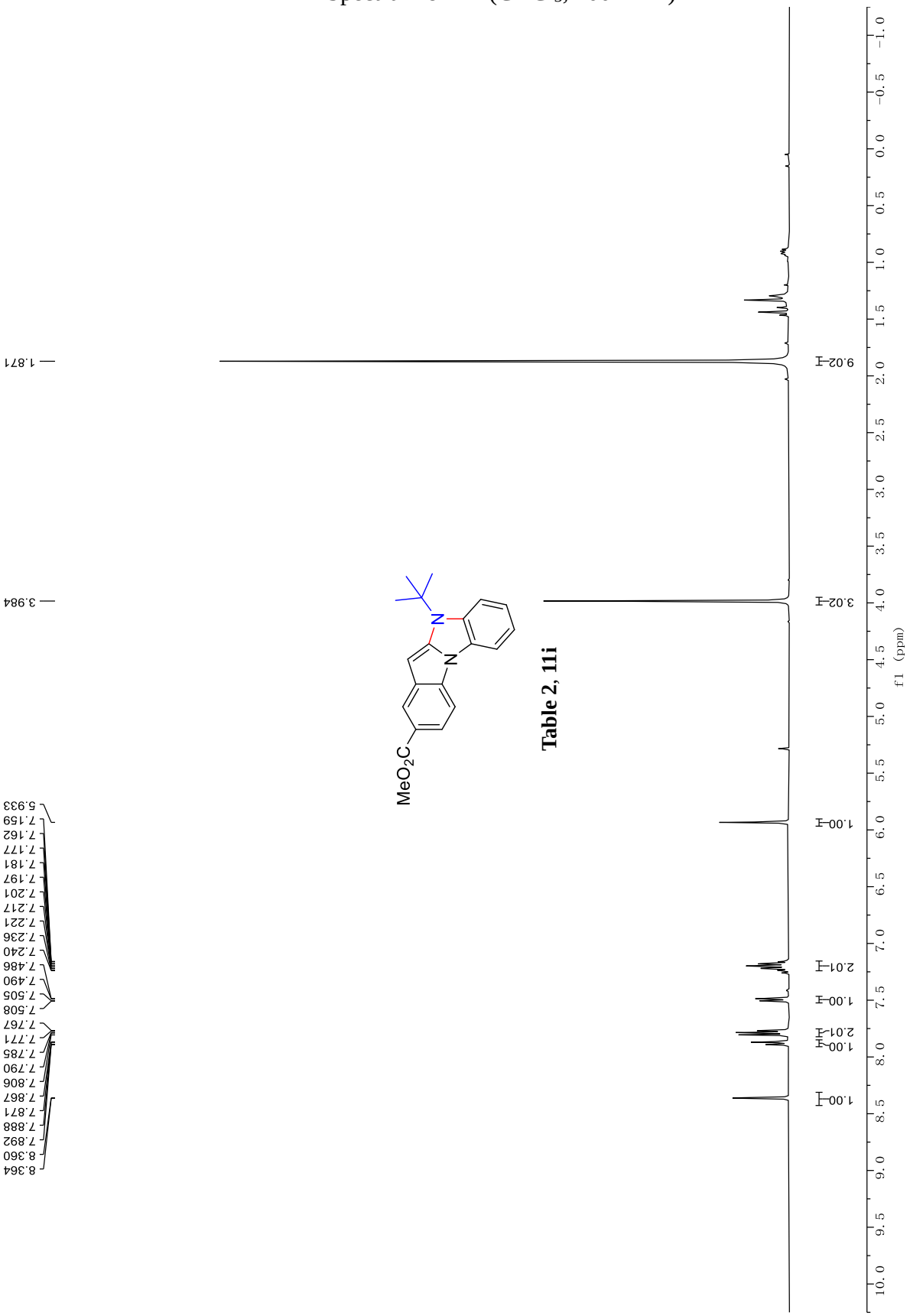


Table 2, 11i

^{13}C NMR Spectrum of **11i** ($CDCl_3$, 100 MHz)

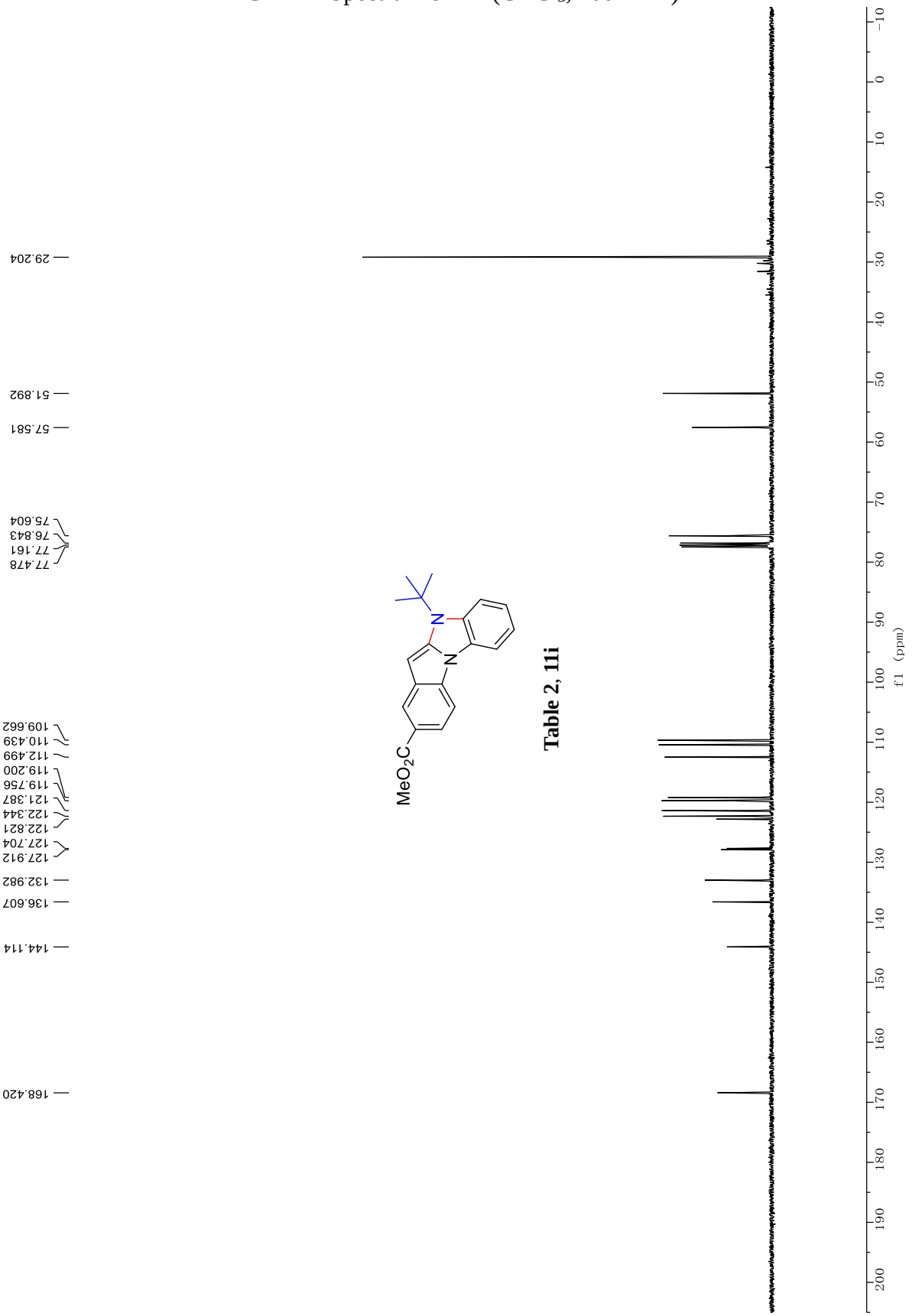
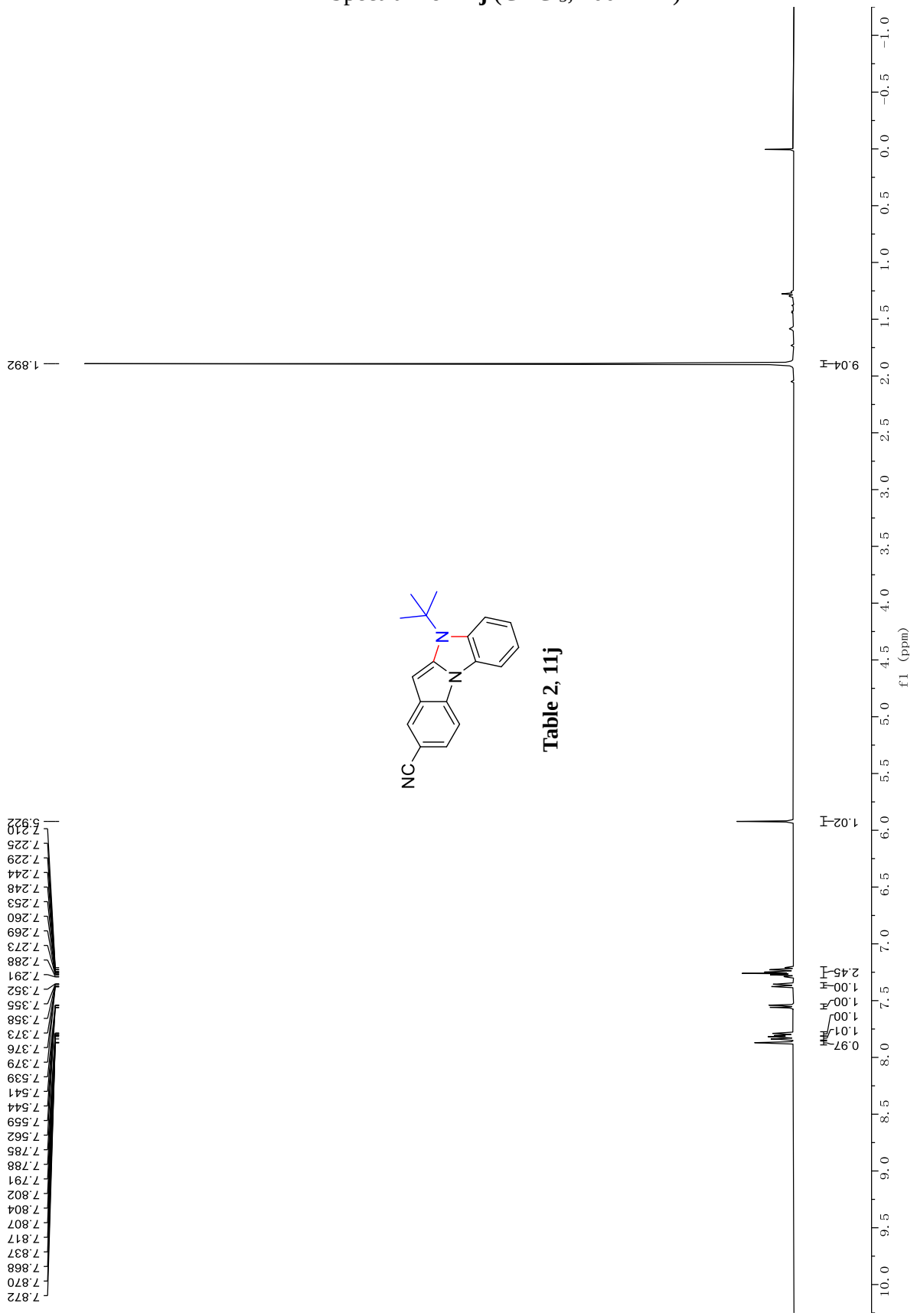
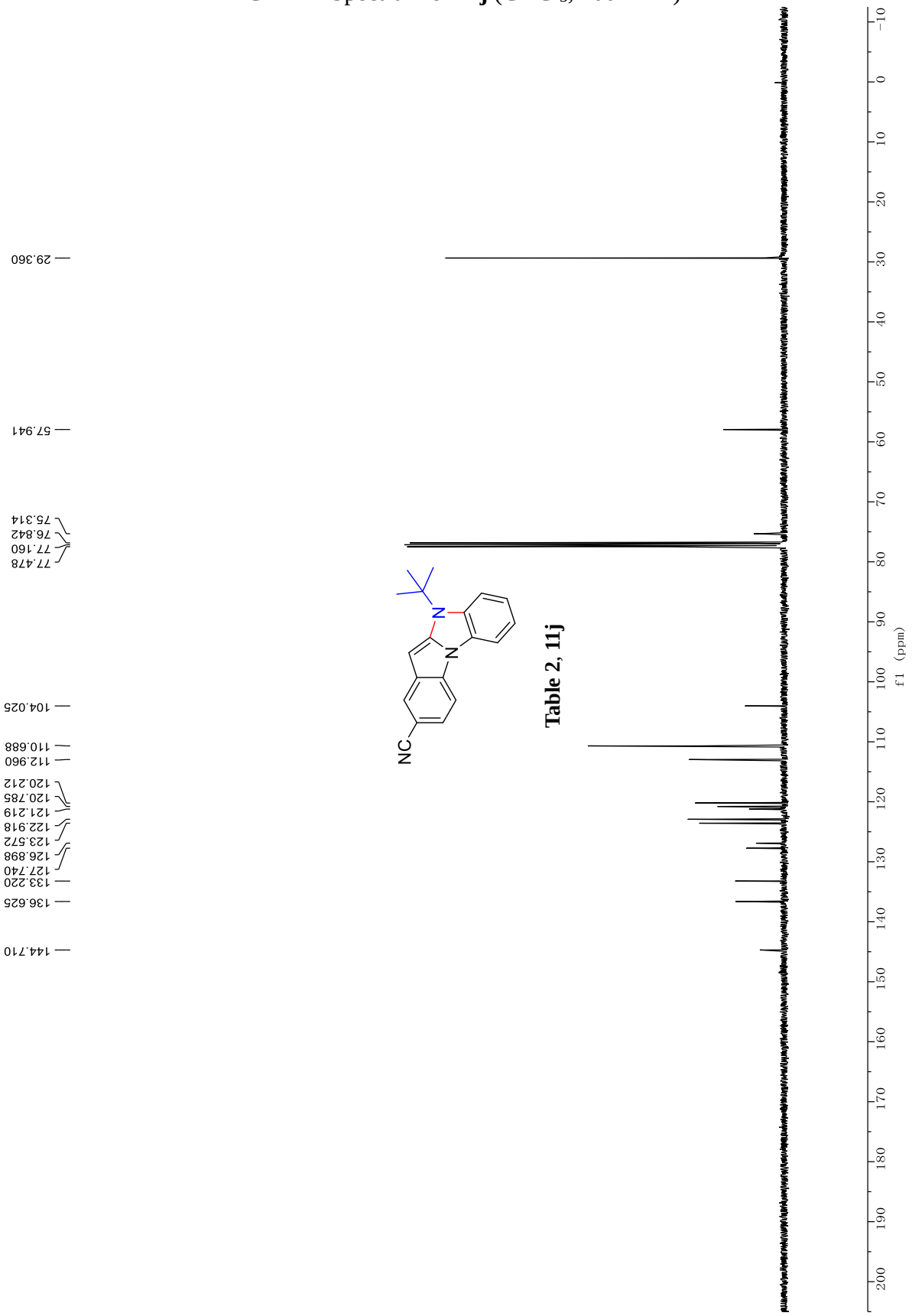


Table 2, 11i

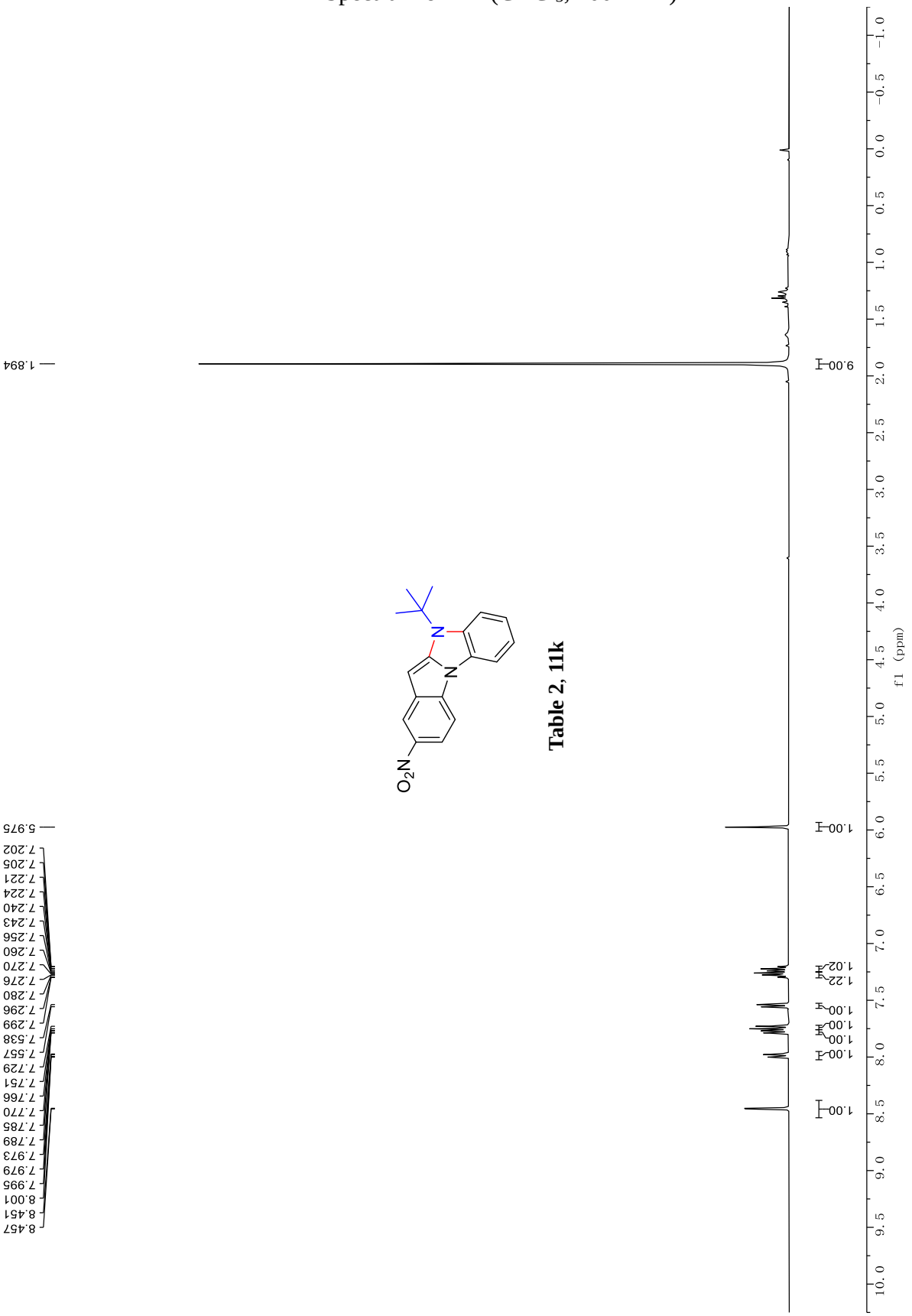
^{1}H NMR Spectrum of **11j** ($CDCl_3$, 400 MHz)



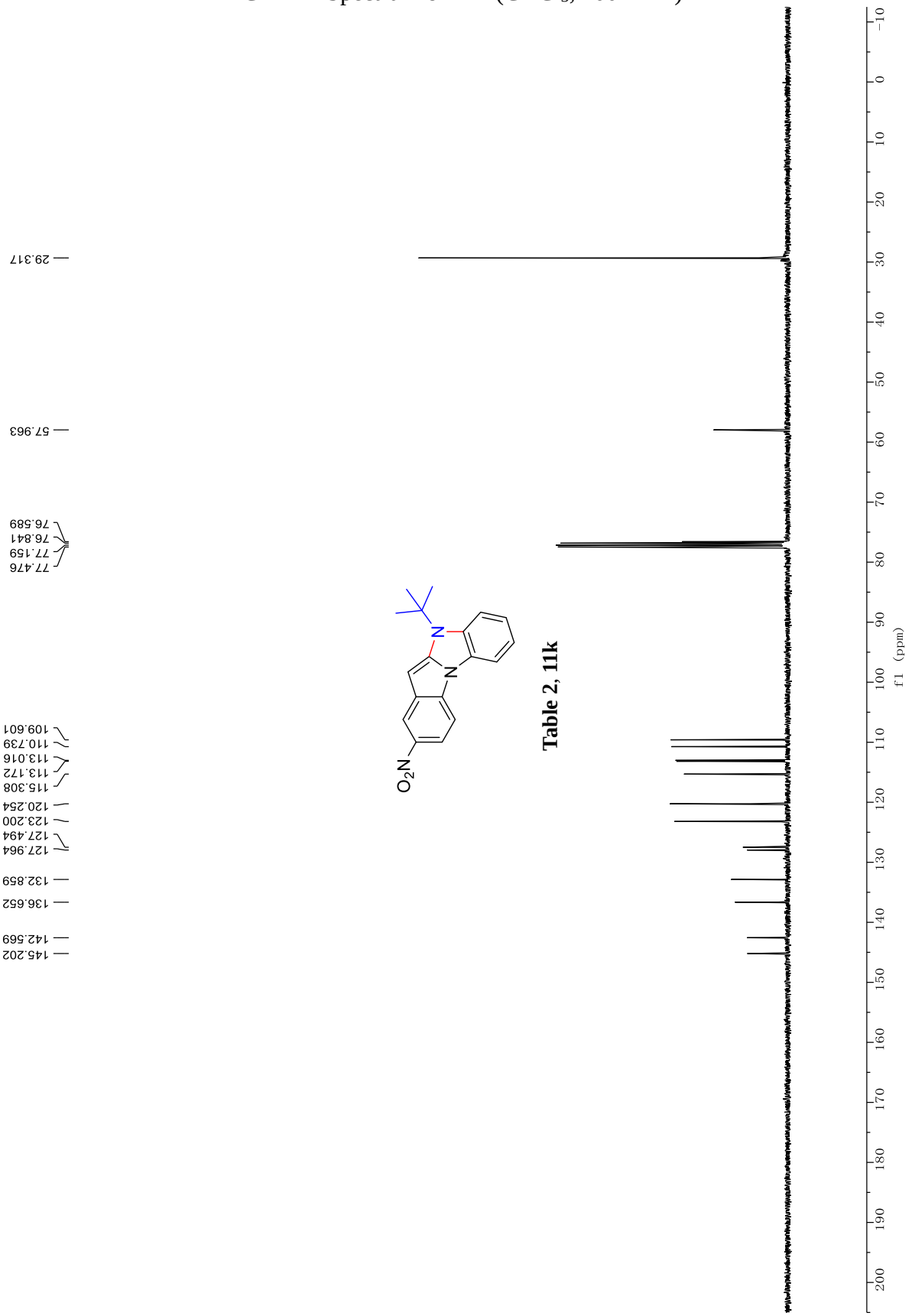
^{13}C NMR Spectrum of **11j** ($CDCl_3$, 100 MHz)



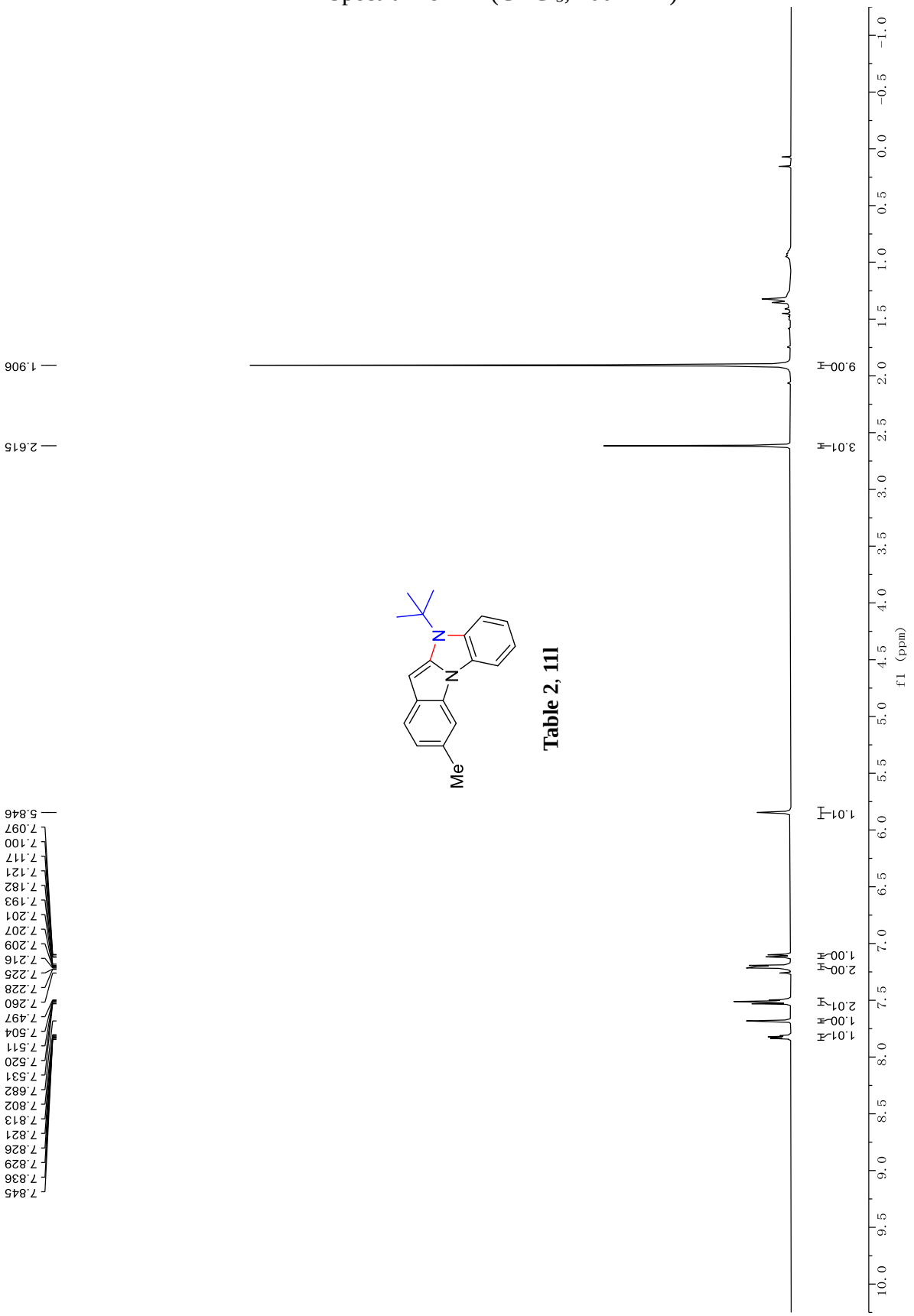
^{1}H NMR Spectrum of **1lk** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **11k** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **11l** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **11l** ($CDCl_3$, 100 MHz)

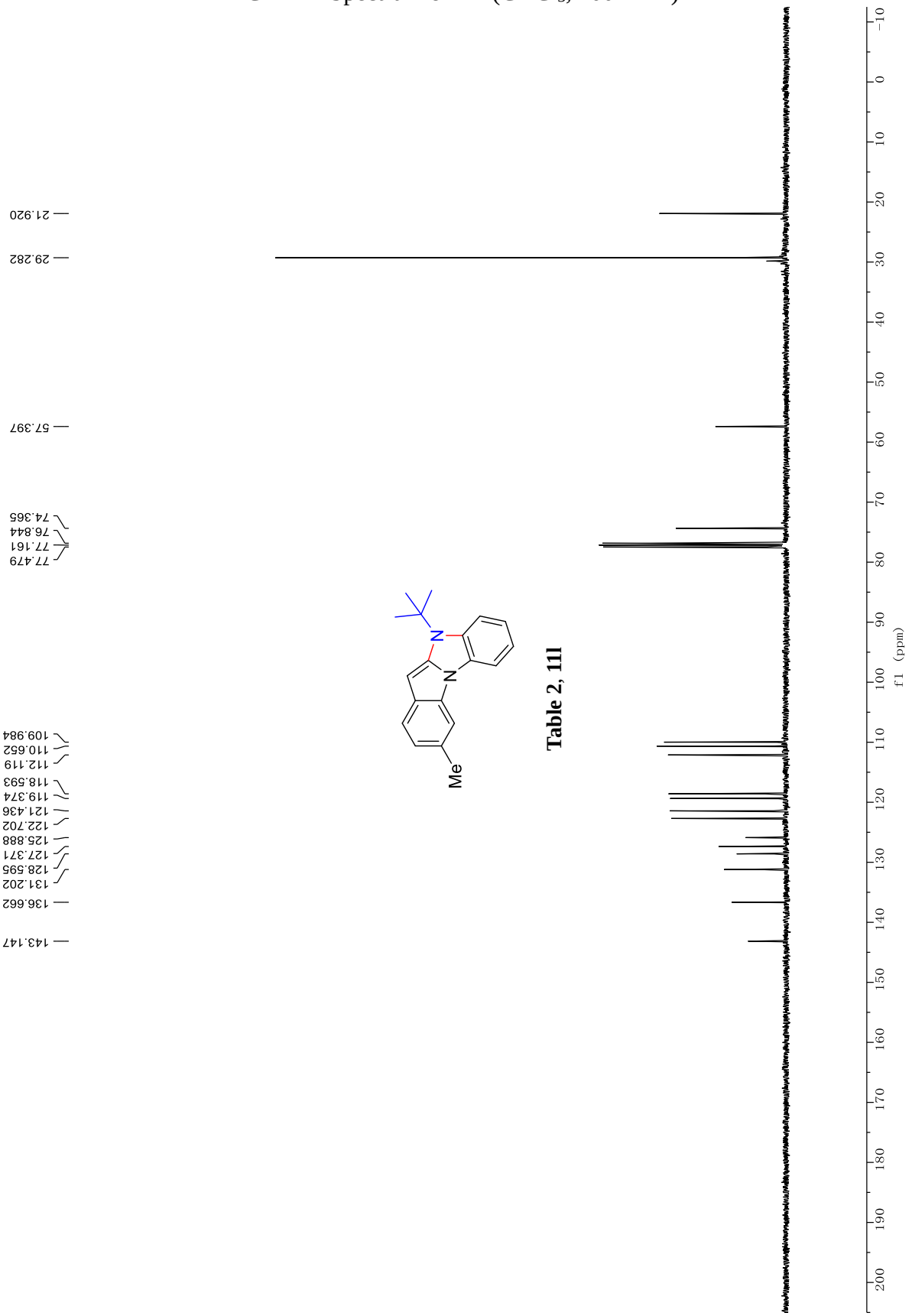
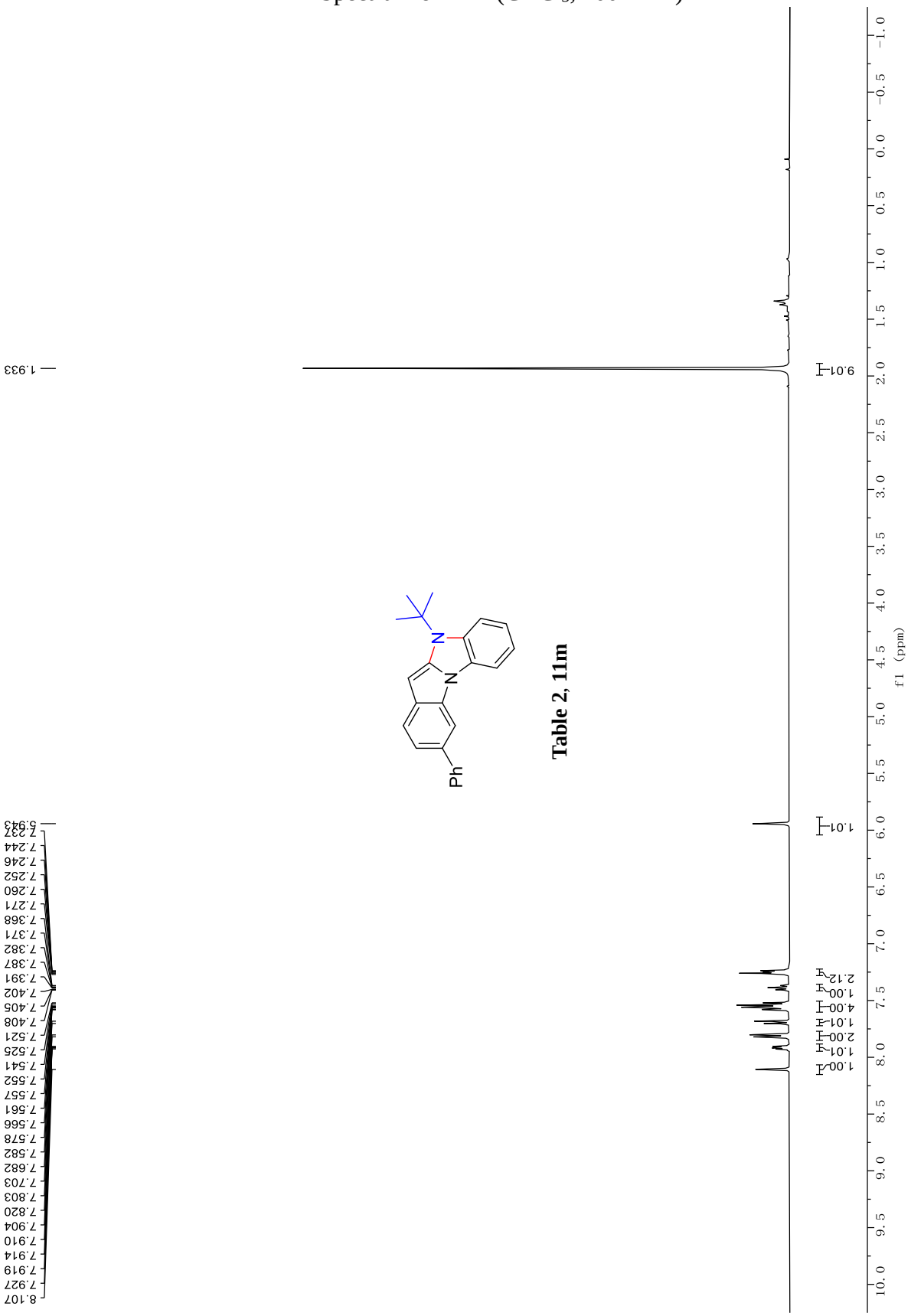
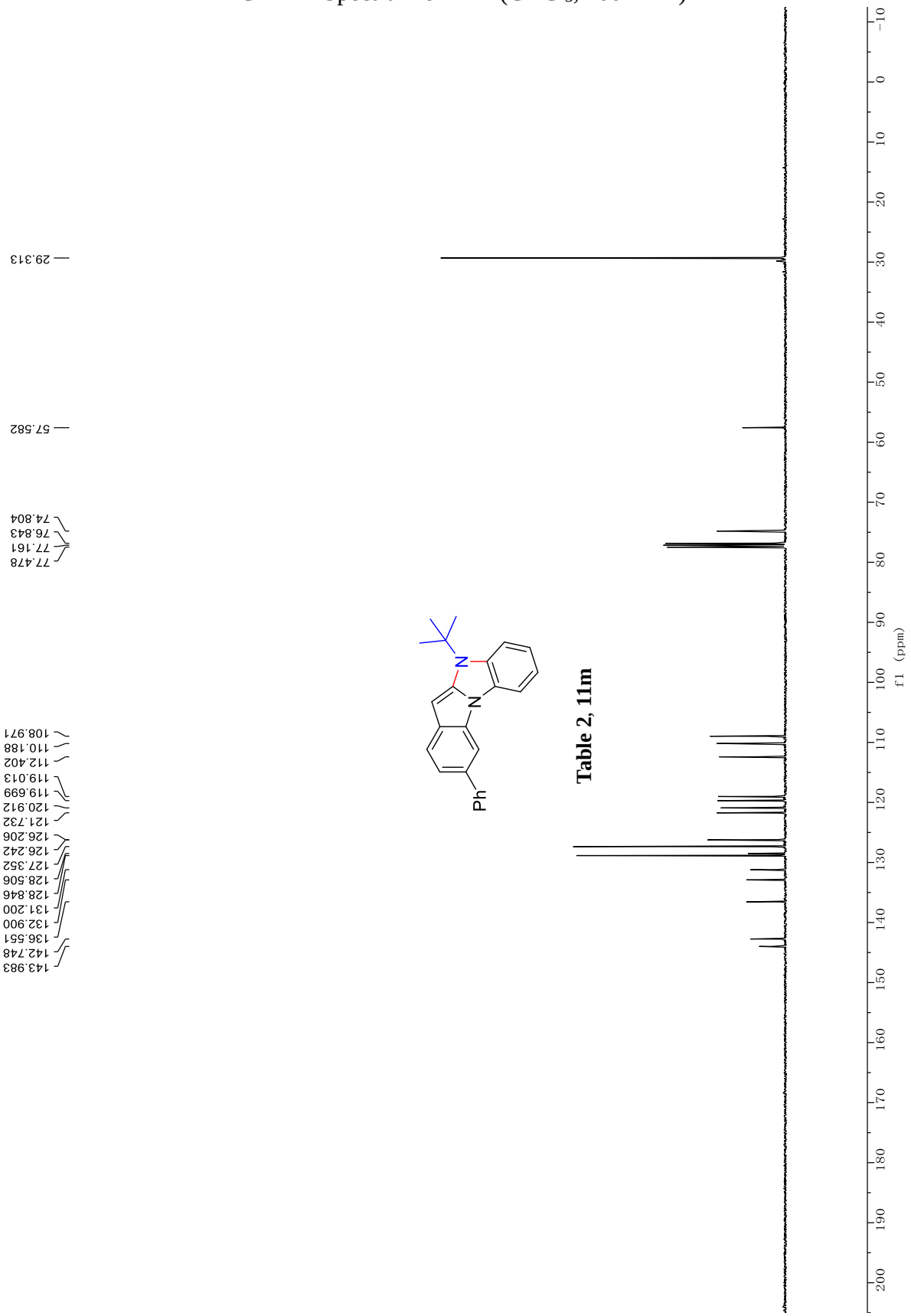


Table 2, 11l

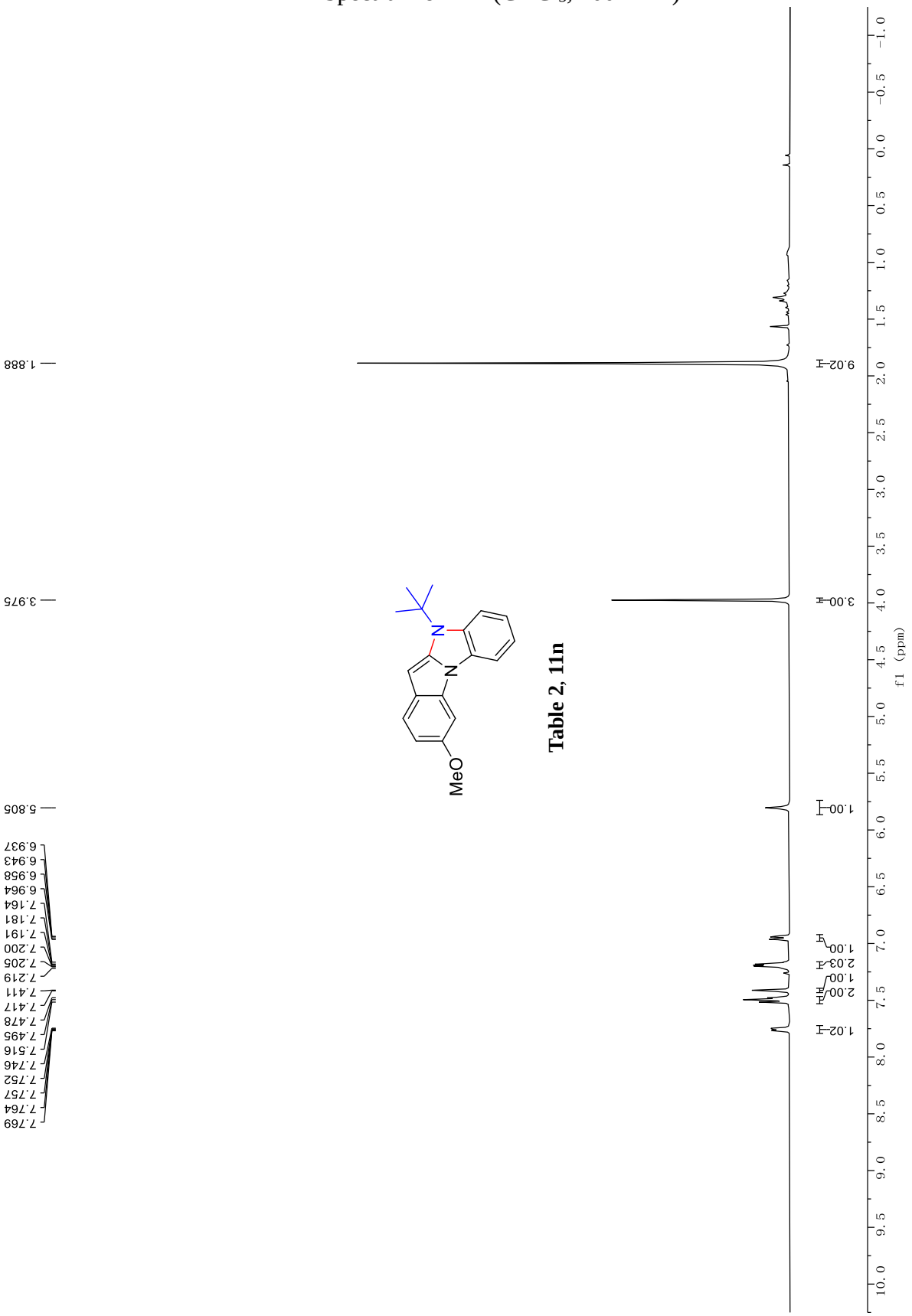
^{1}H NMR Spectrum of **11m** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **11m** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **11n** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **11n** ($CDCl_3$, 100 MHz)

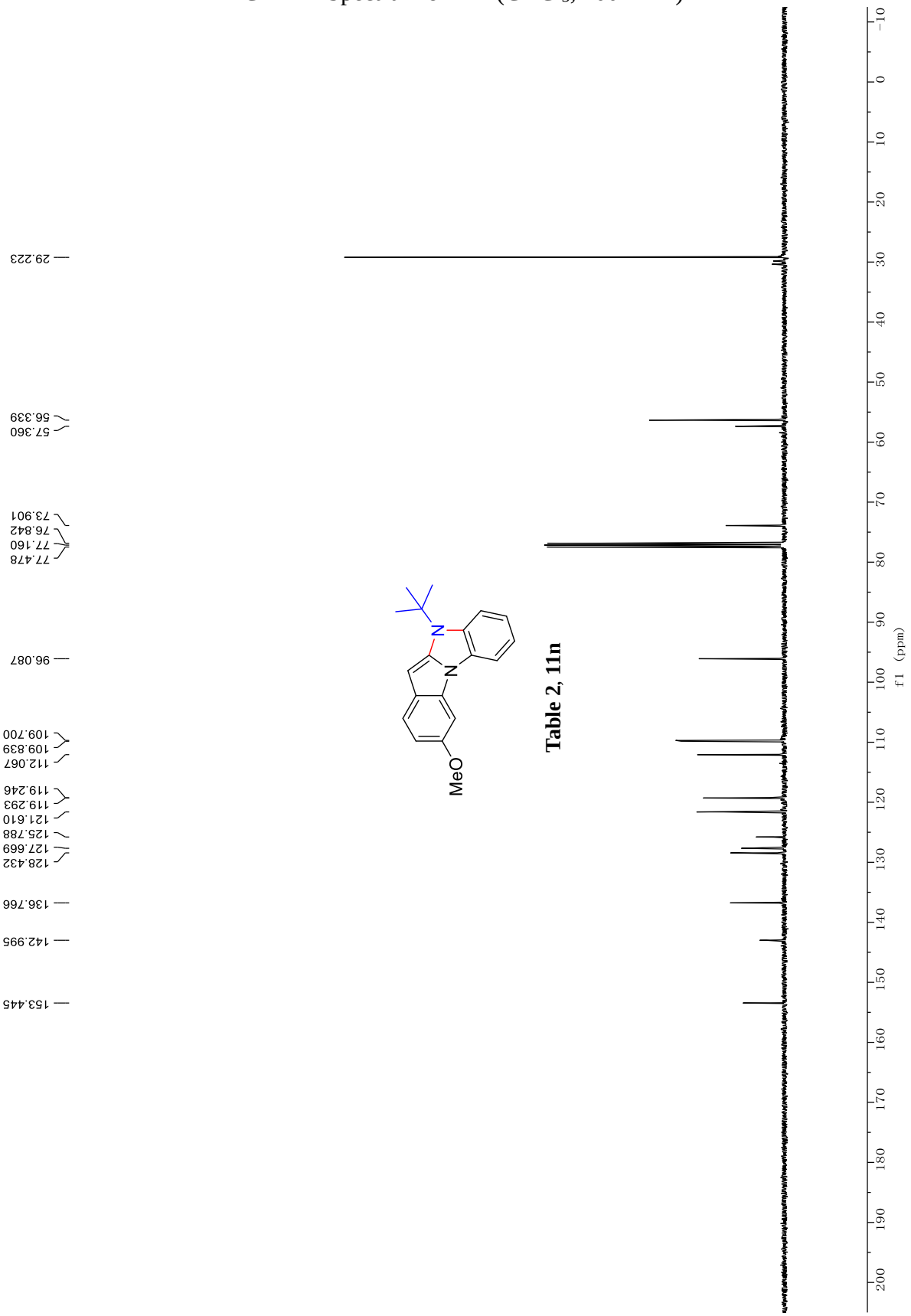
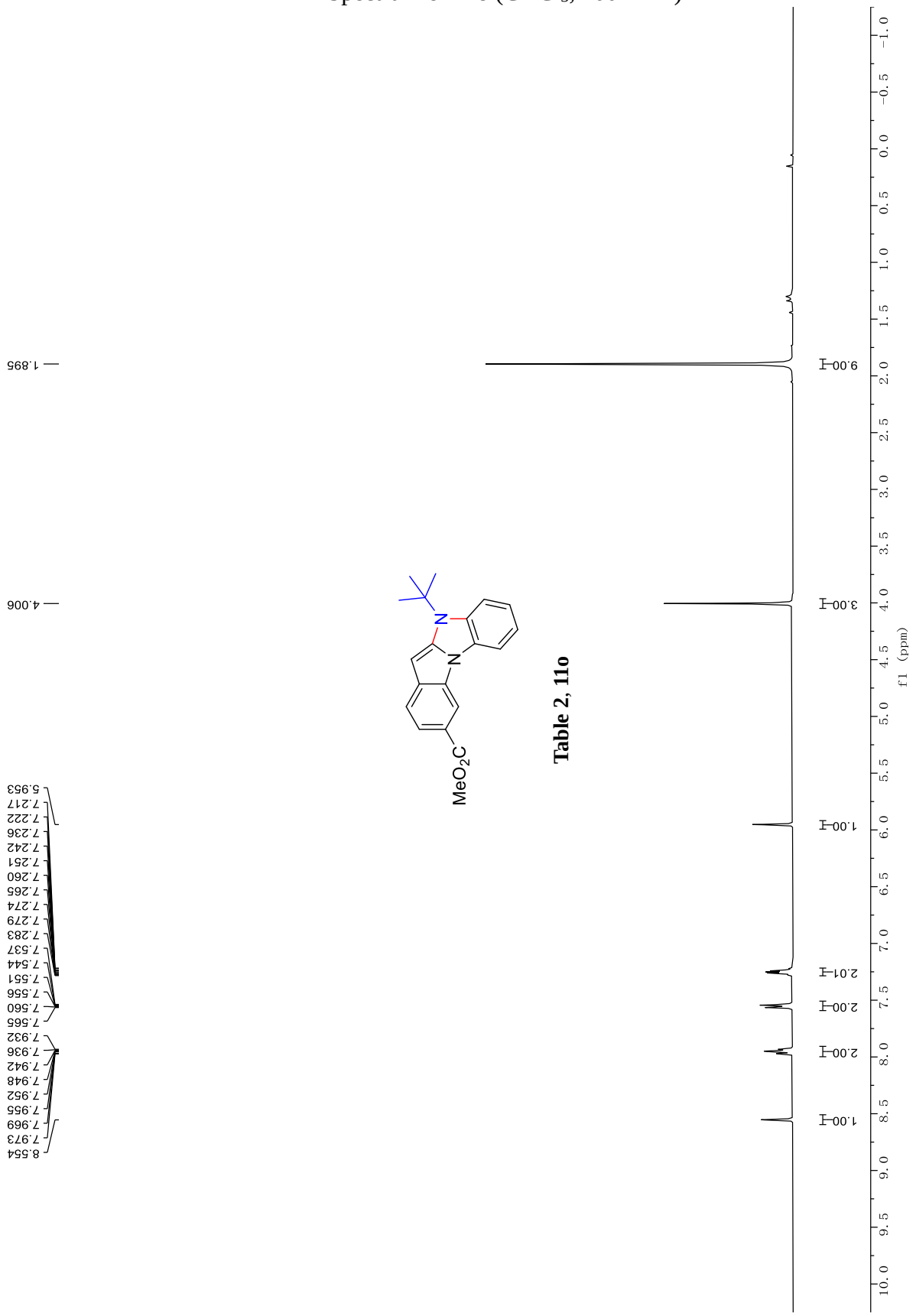
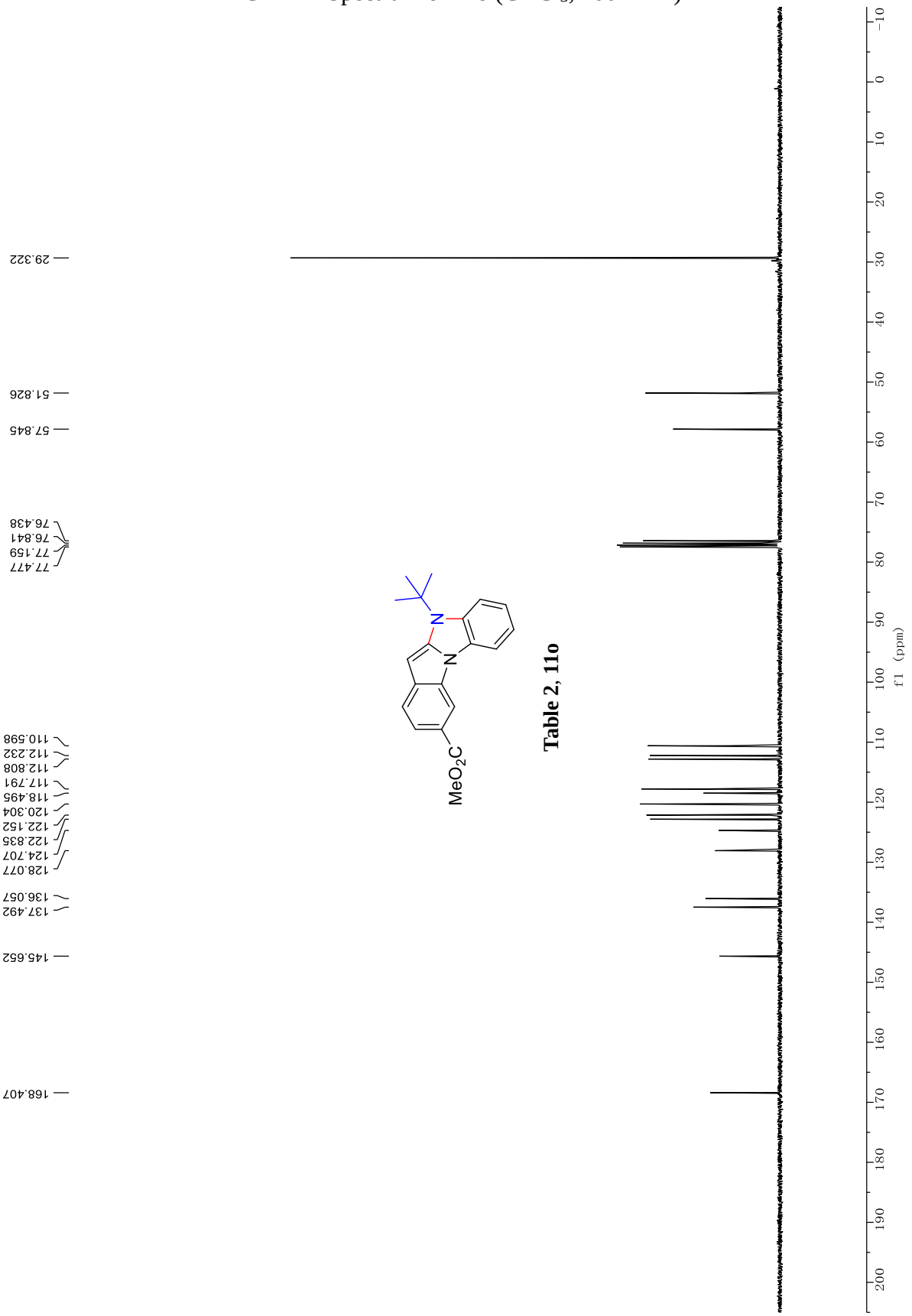


Table 2, 11n

^{1}H NMR Spectrum of **11o** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **11o** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **11p** ($CDCl_3$, 400 MHz)

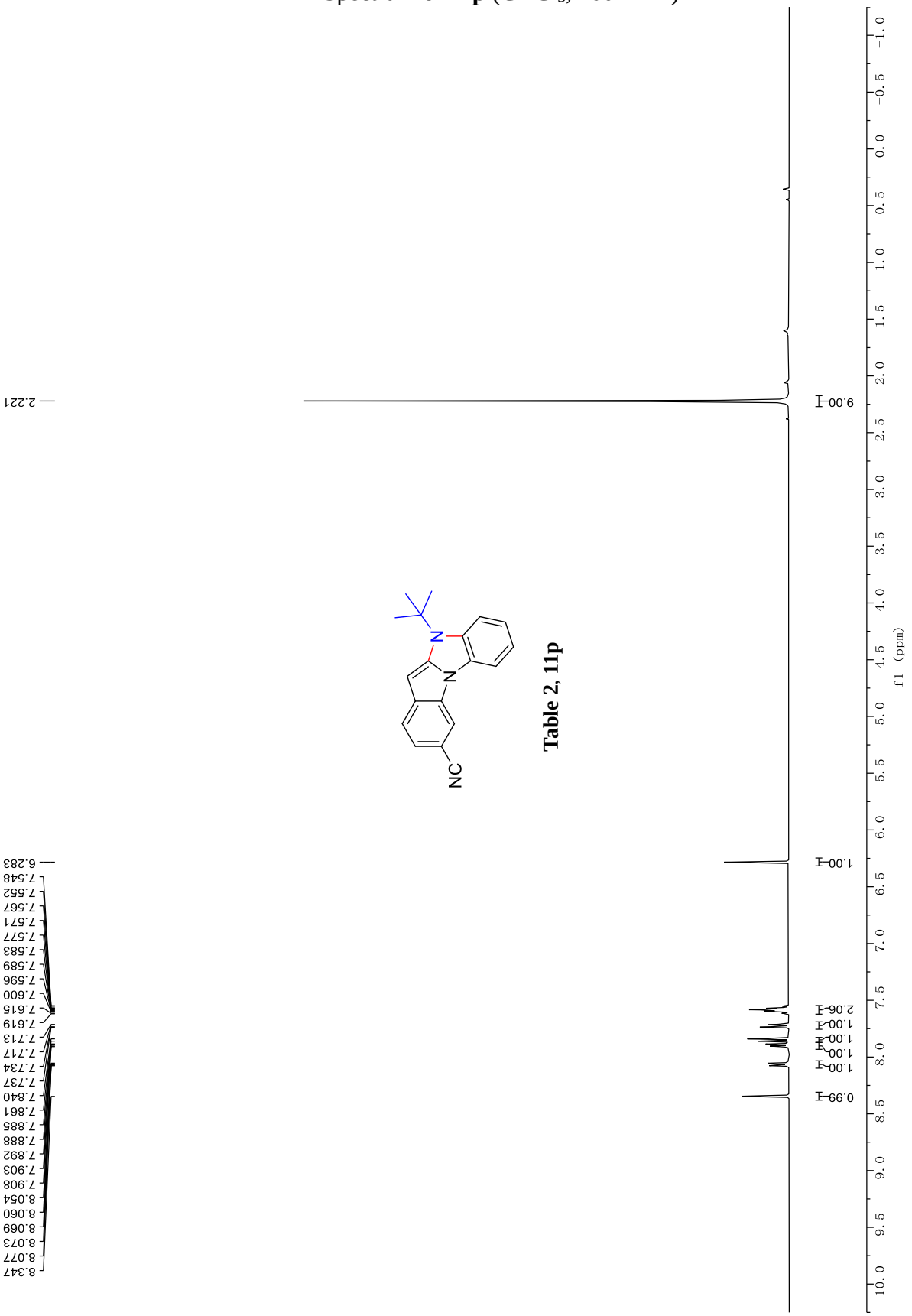
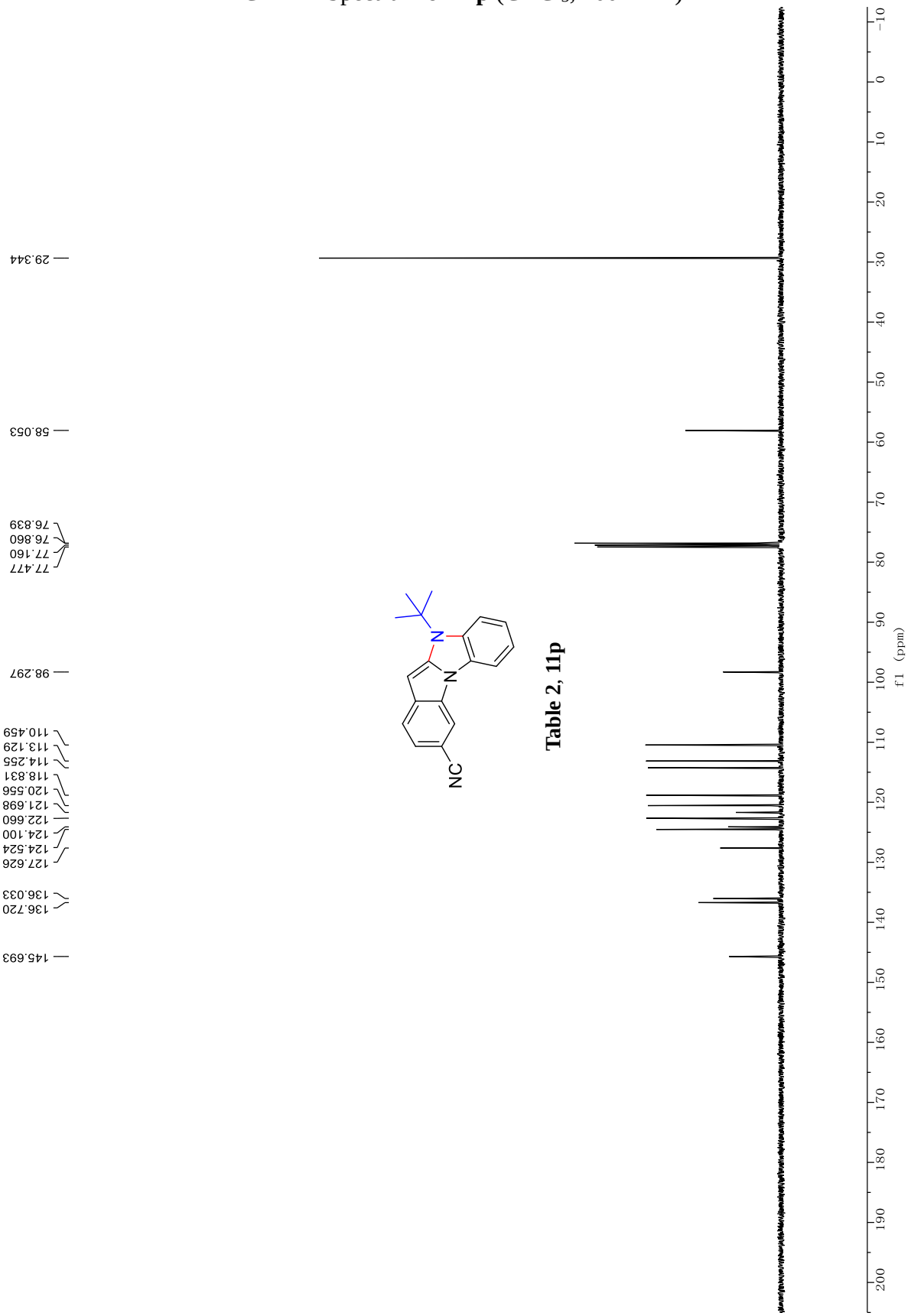


Table 2, 11p

^{13}C NMR Spectrum of **11p** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **11q** ($CDCl_3$, 400 MHz)

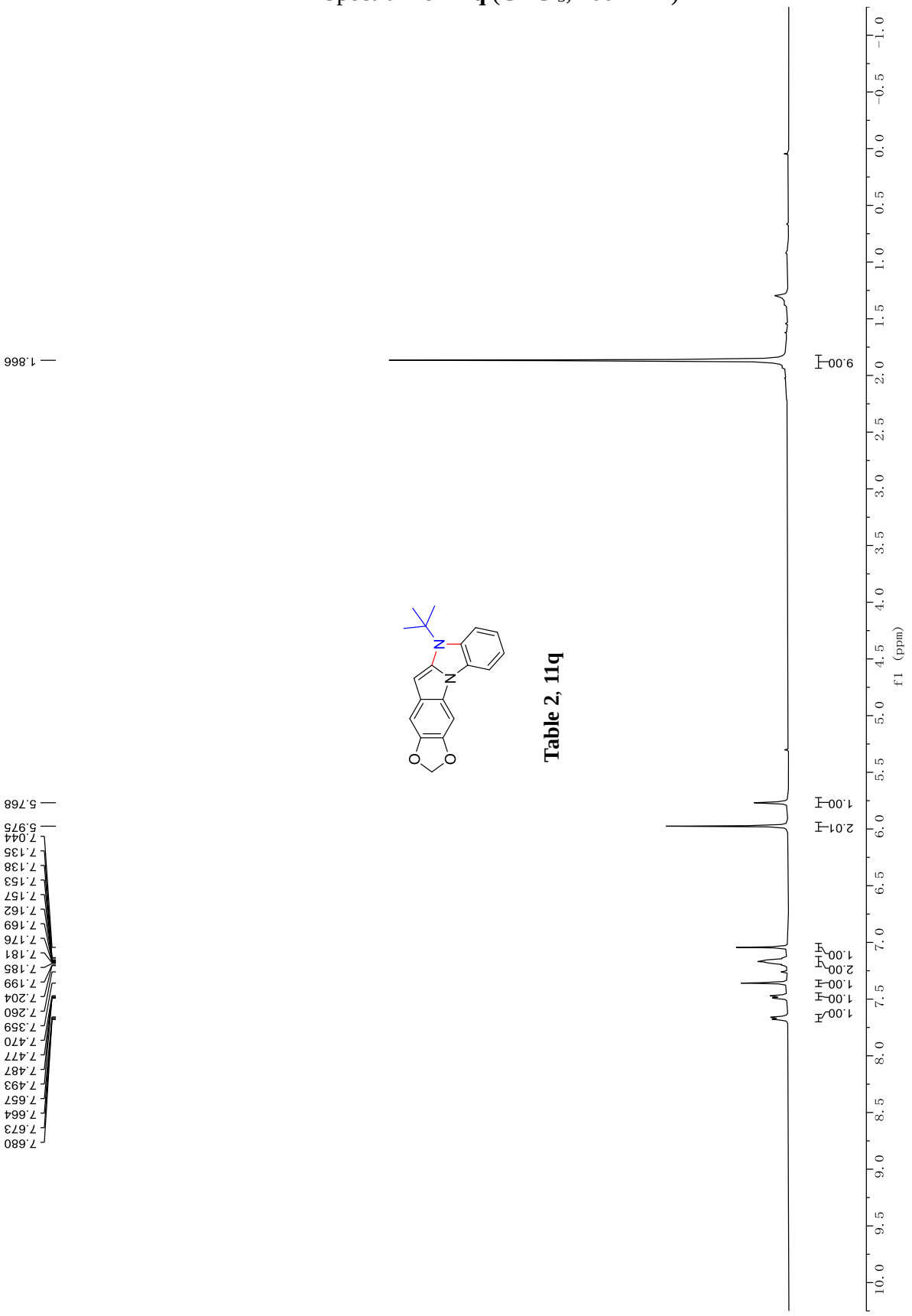


Table 2, 11q

^{13}C NMR Spectrum of **11q** ($CDCl_3$, 100 MHz)

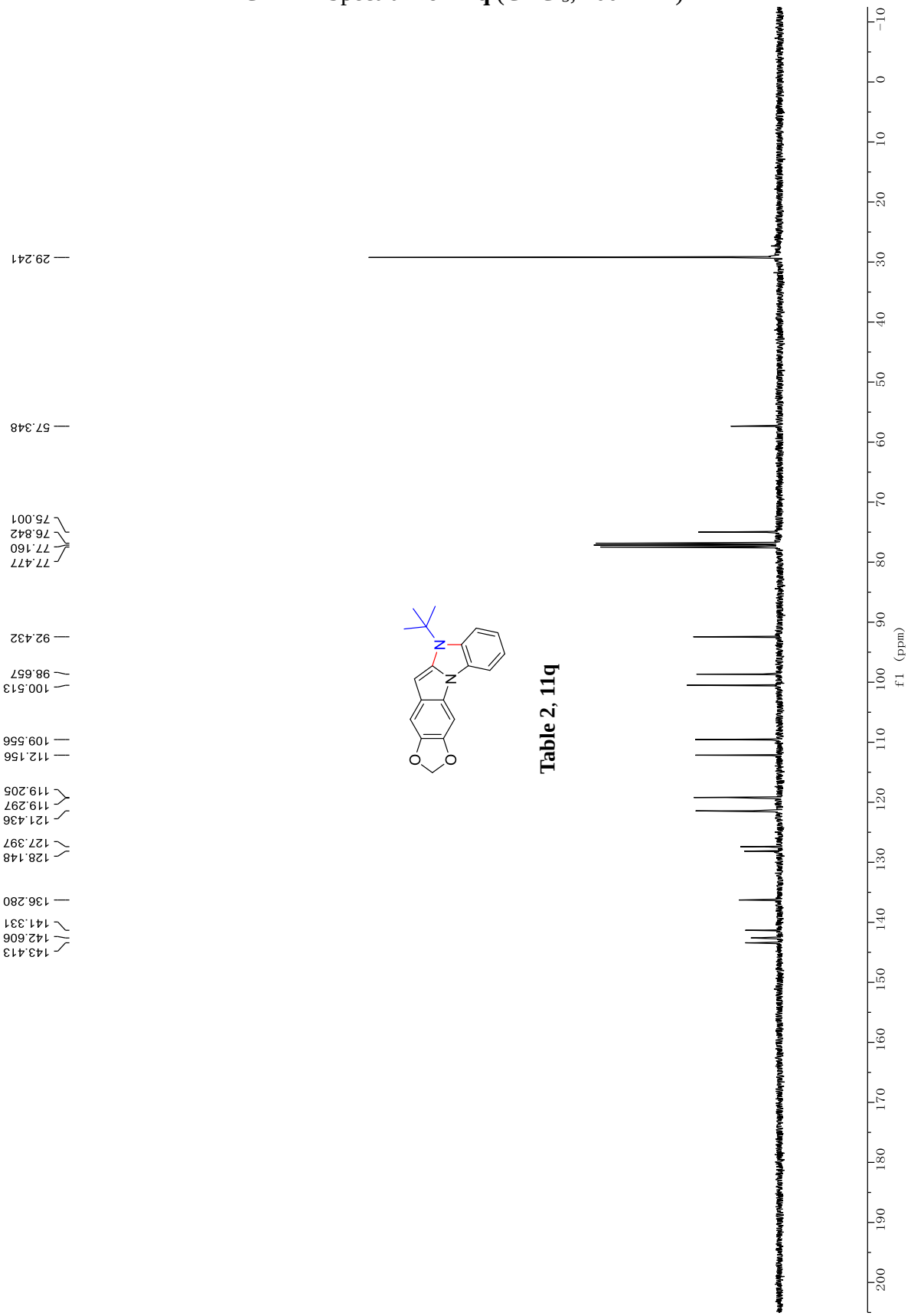
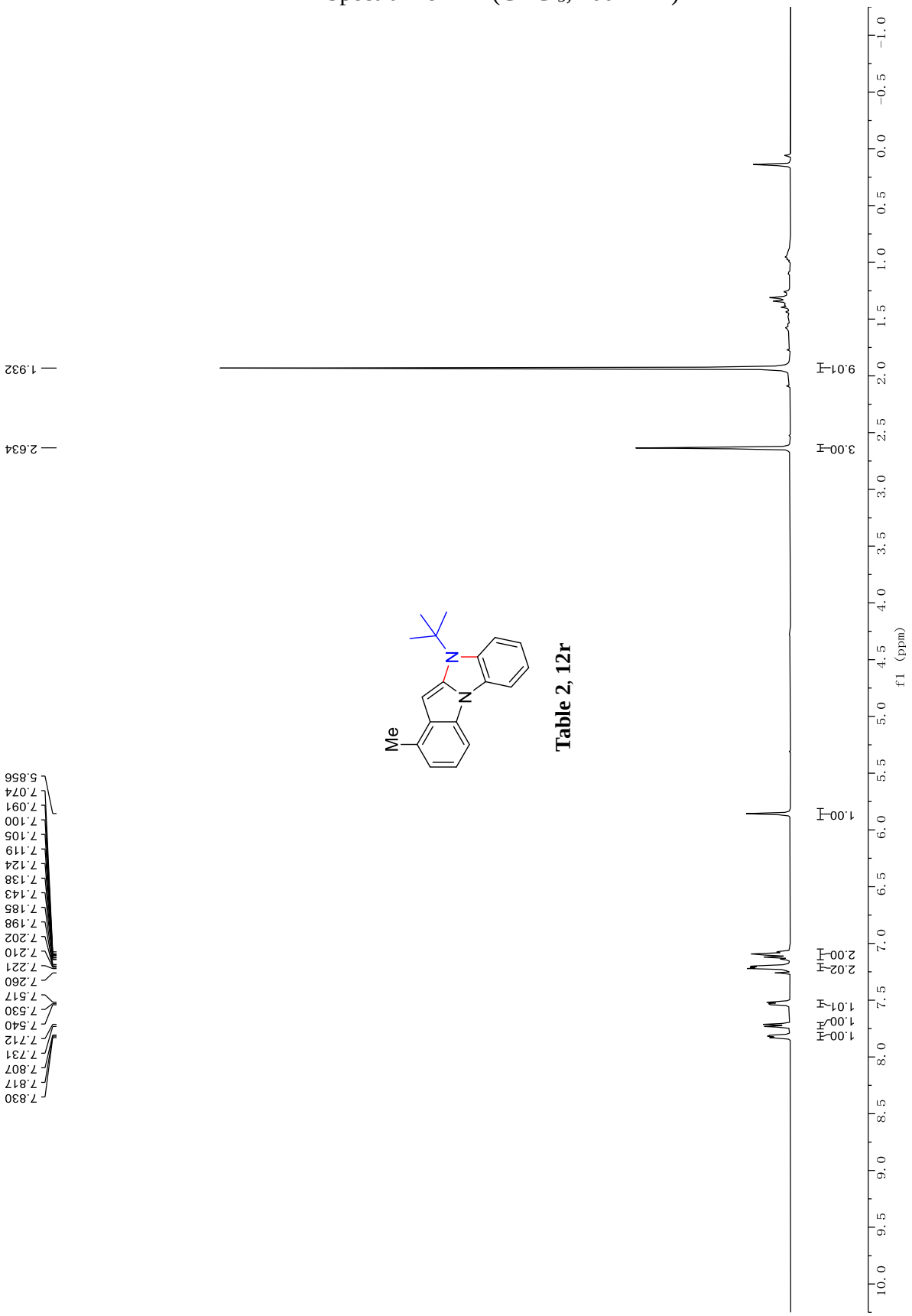
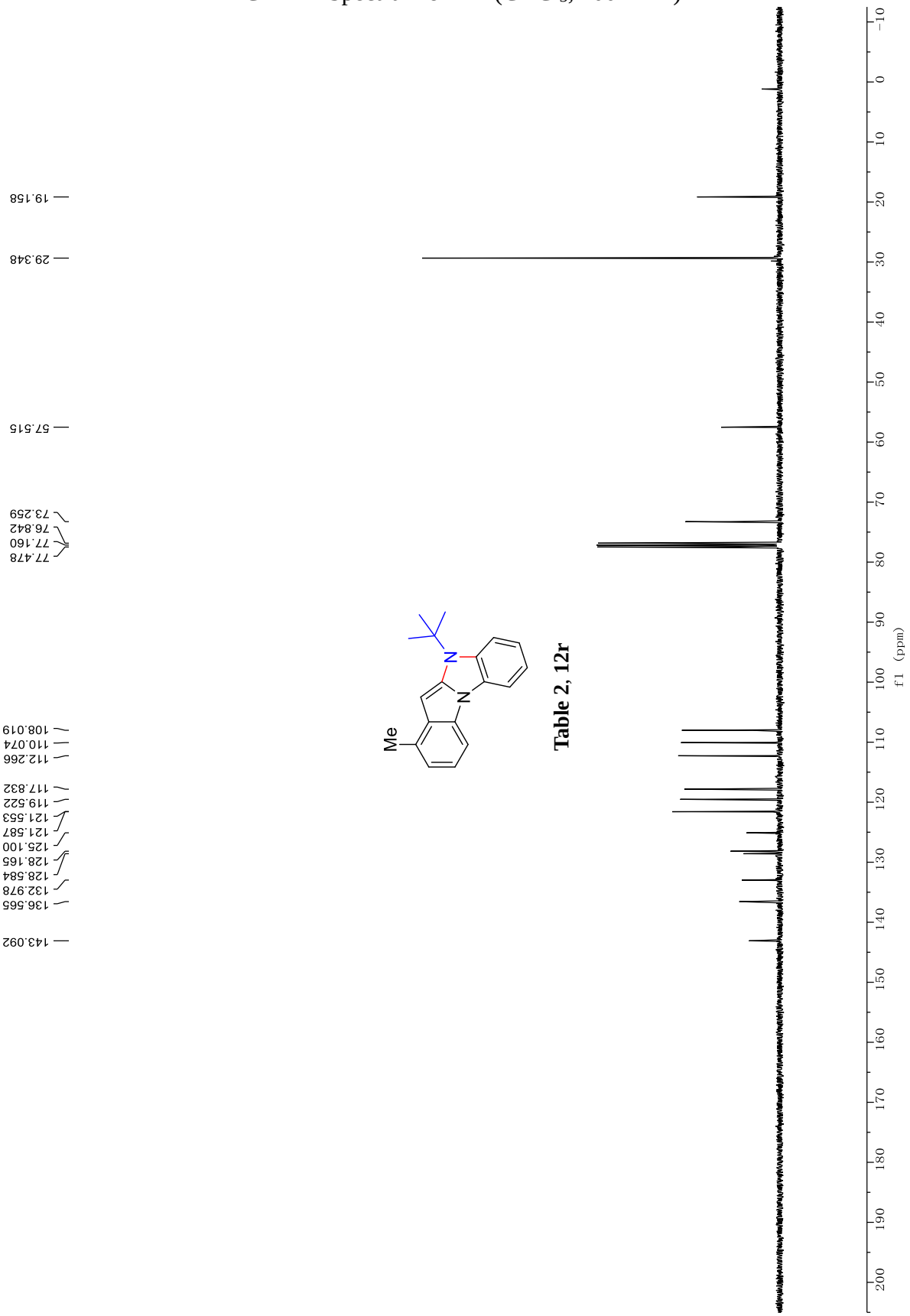


Table 2, 11q

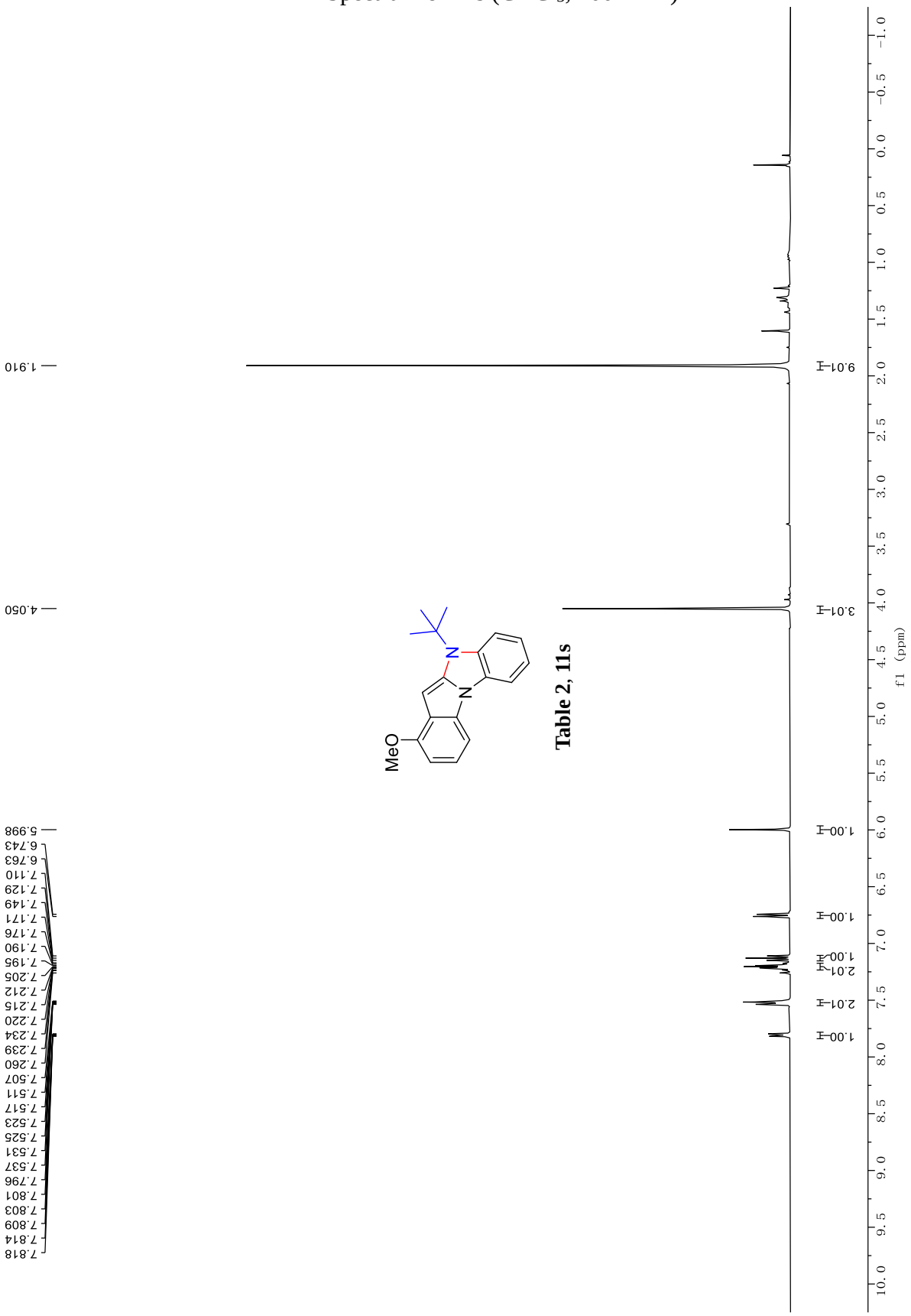
^{1}H NMR Spectrum of **11r** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **11r** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **11s** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **11s** ($CDCl_3$, 100 MHz)

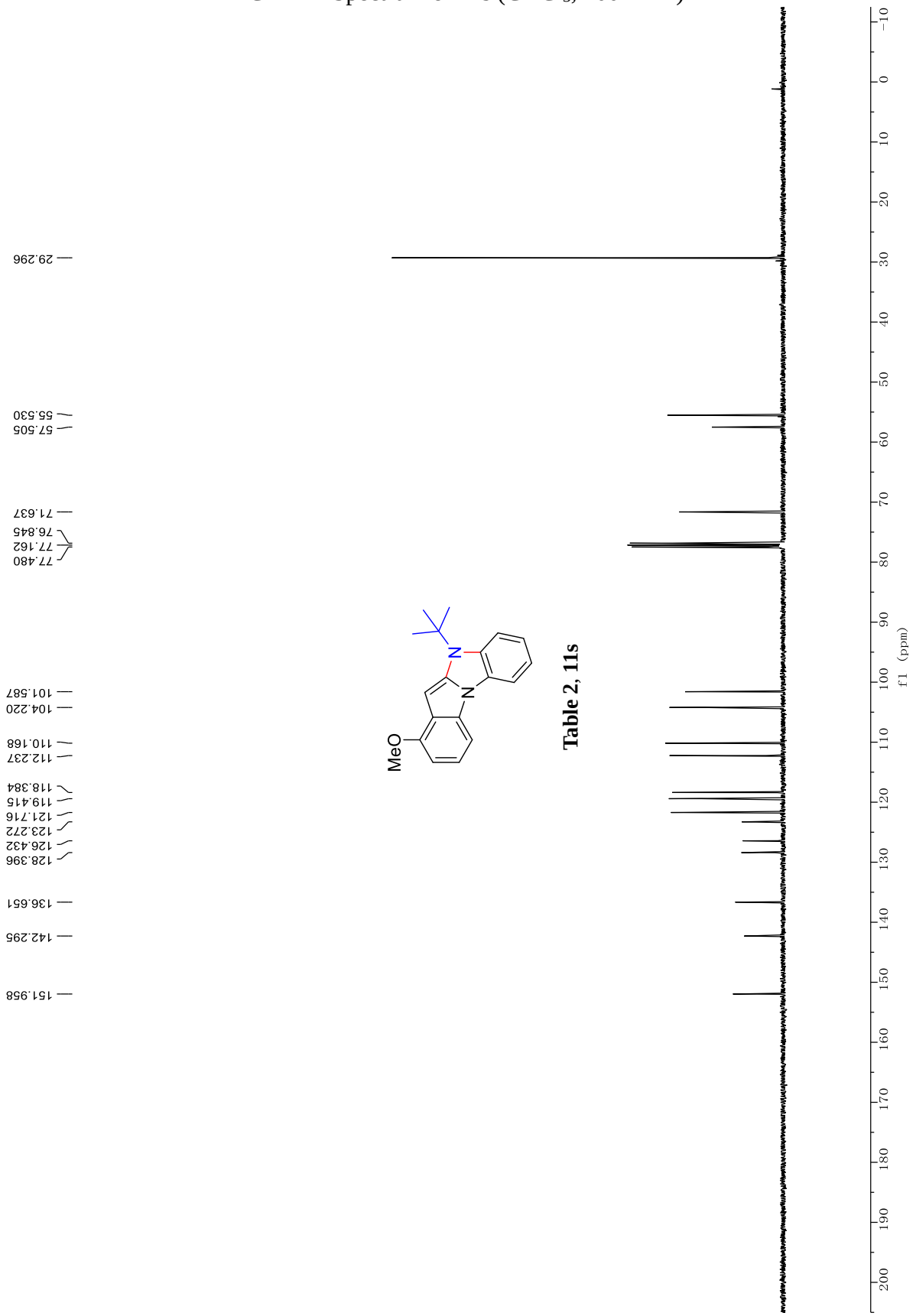
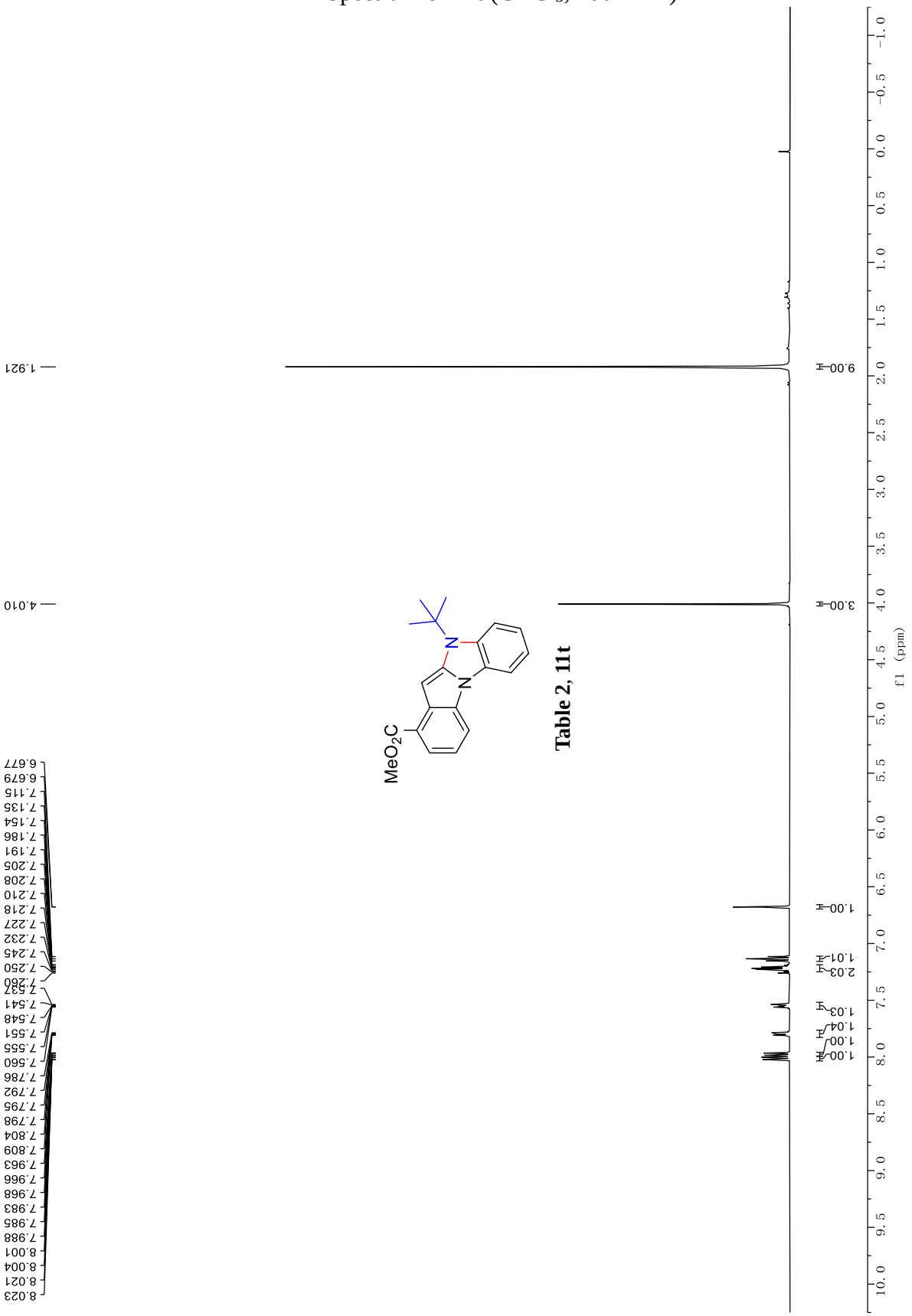
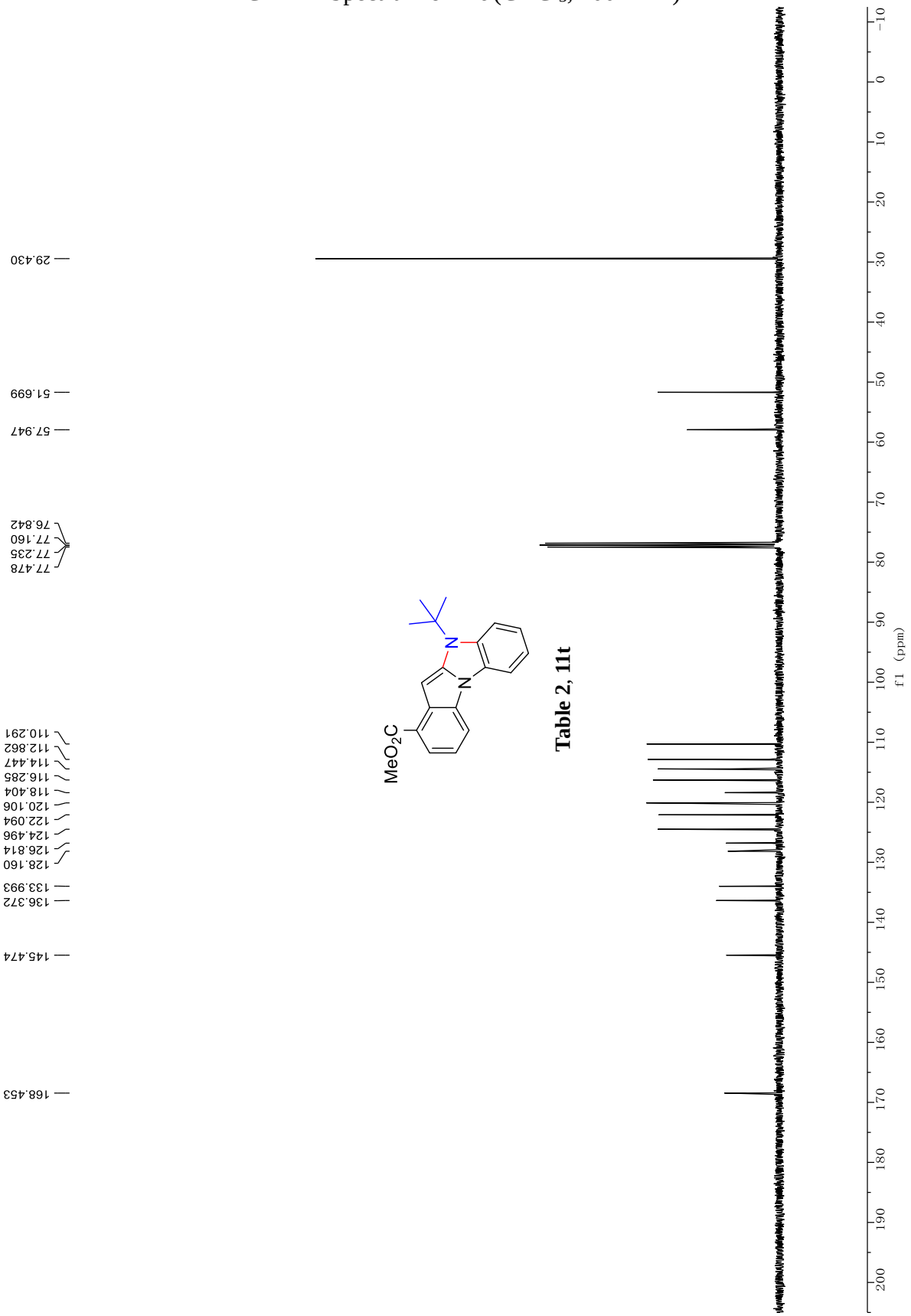


Table 2, 11s

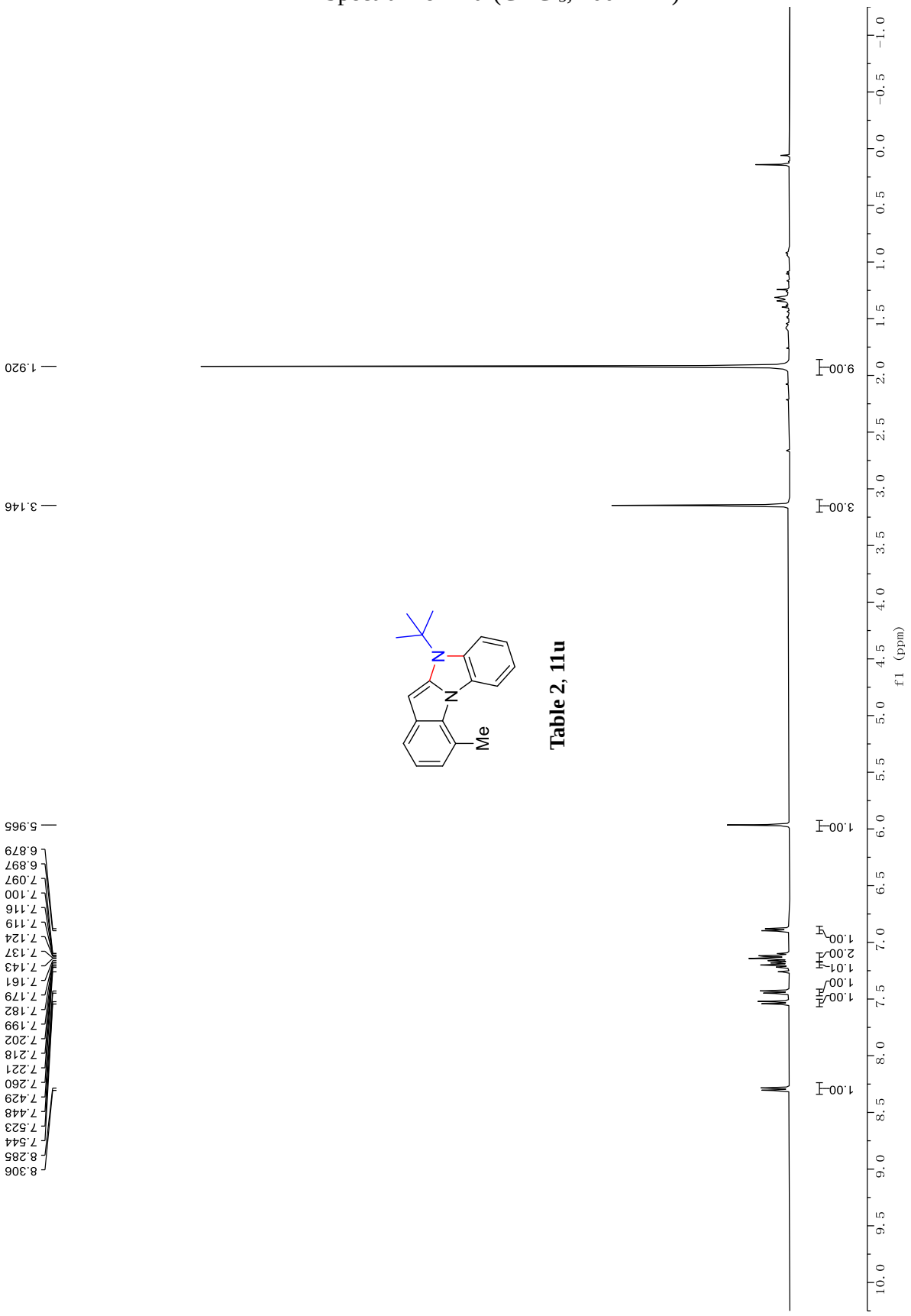
^{1}H NMR Spectrum of **11t** ($CDCl_3$, 400 MHz)



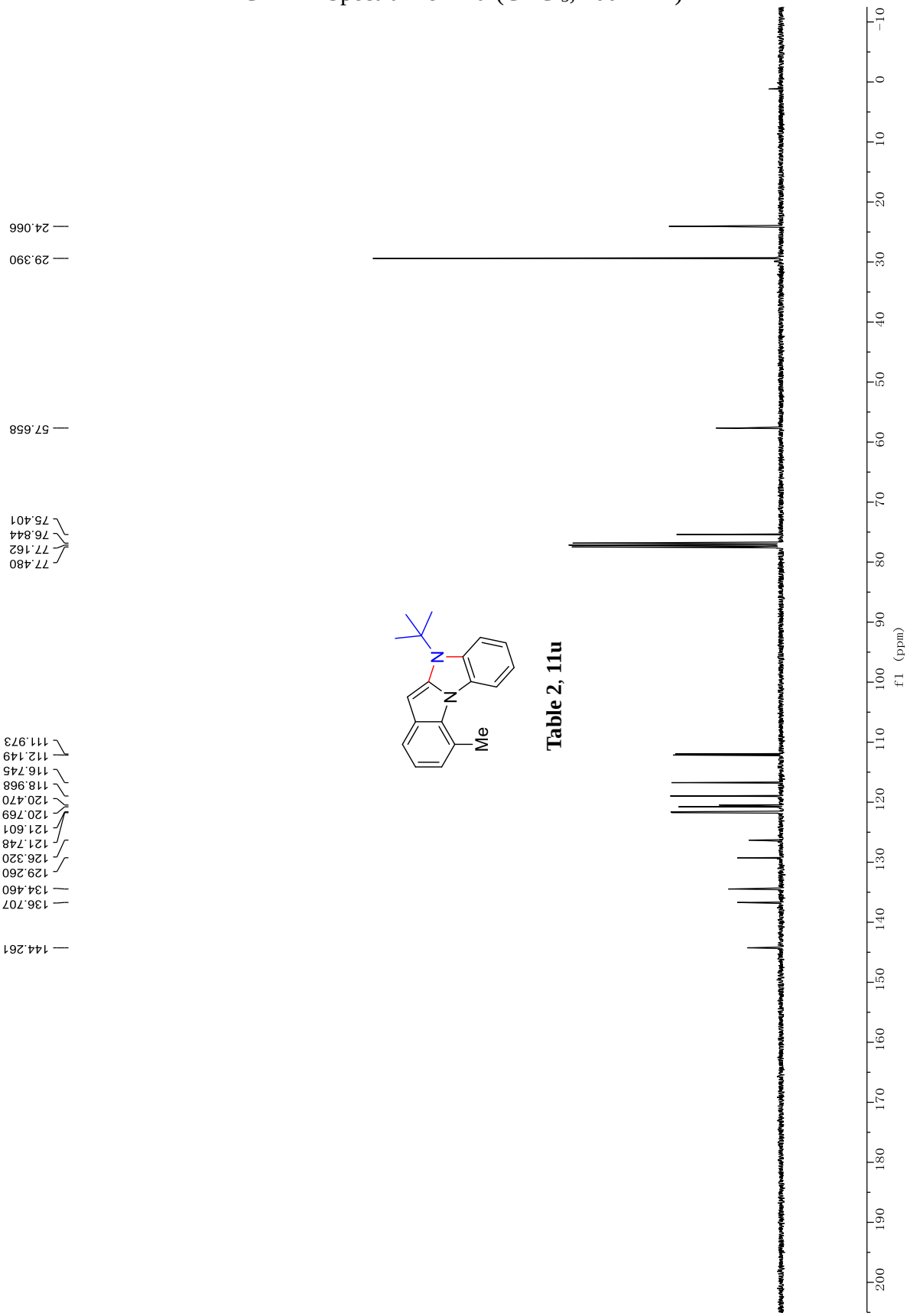
^{13}C NMR Spectrum of **11t** ($CDCl_3$, 100 MHz)



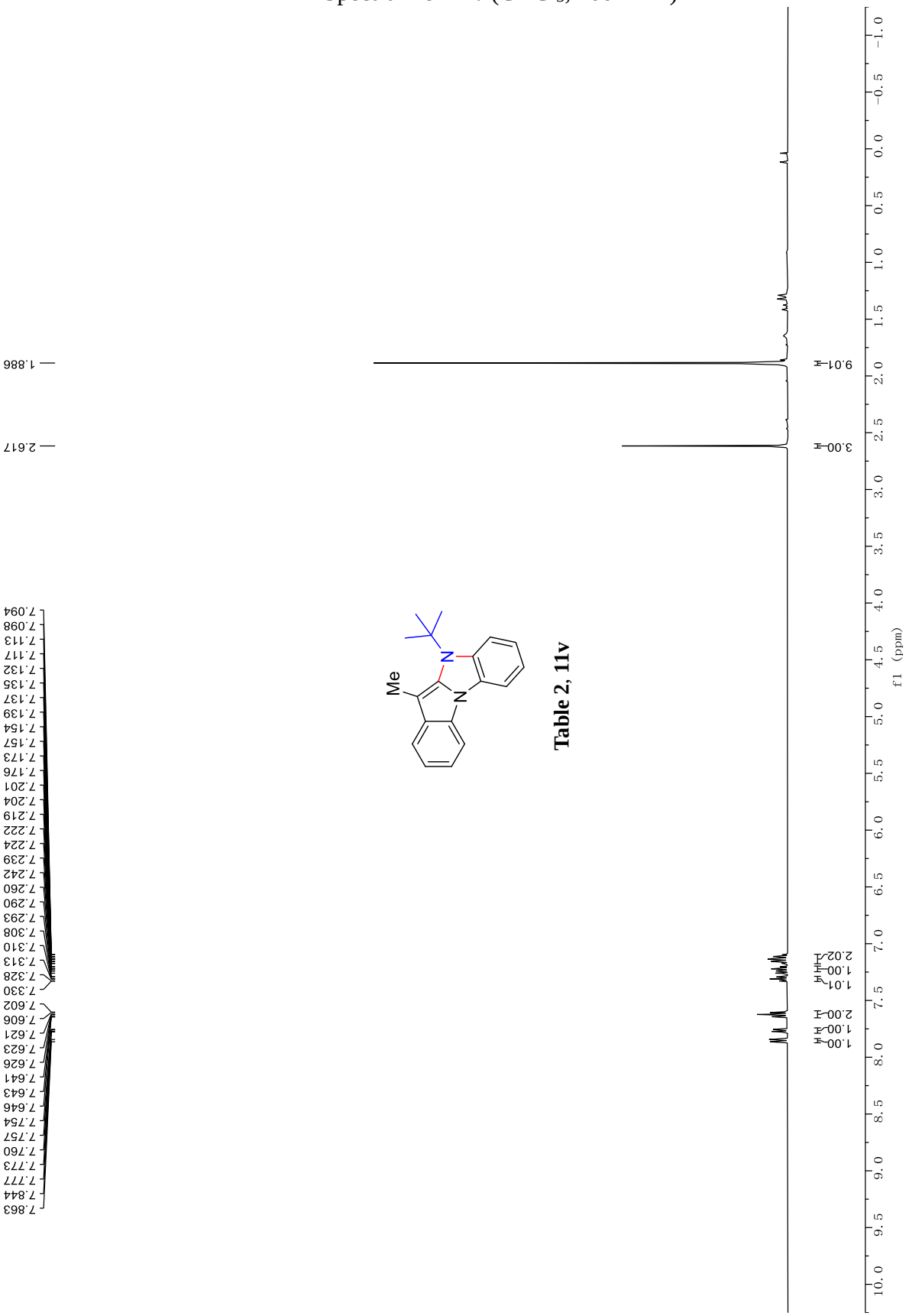
^{1}H NMR Spectrum of **11u** ($CDCl_3$, 400 MHz)



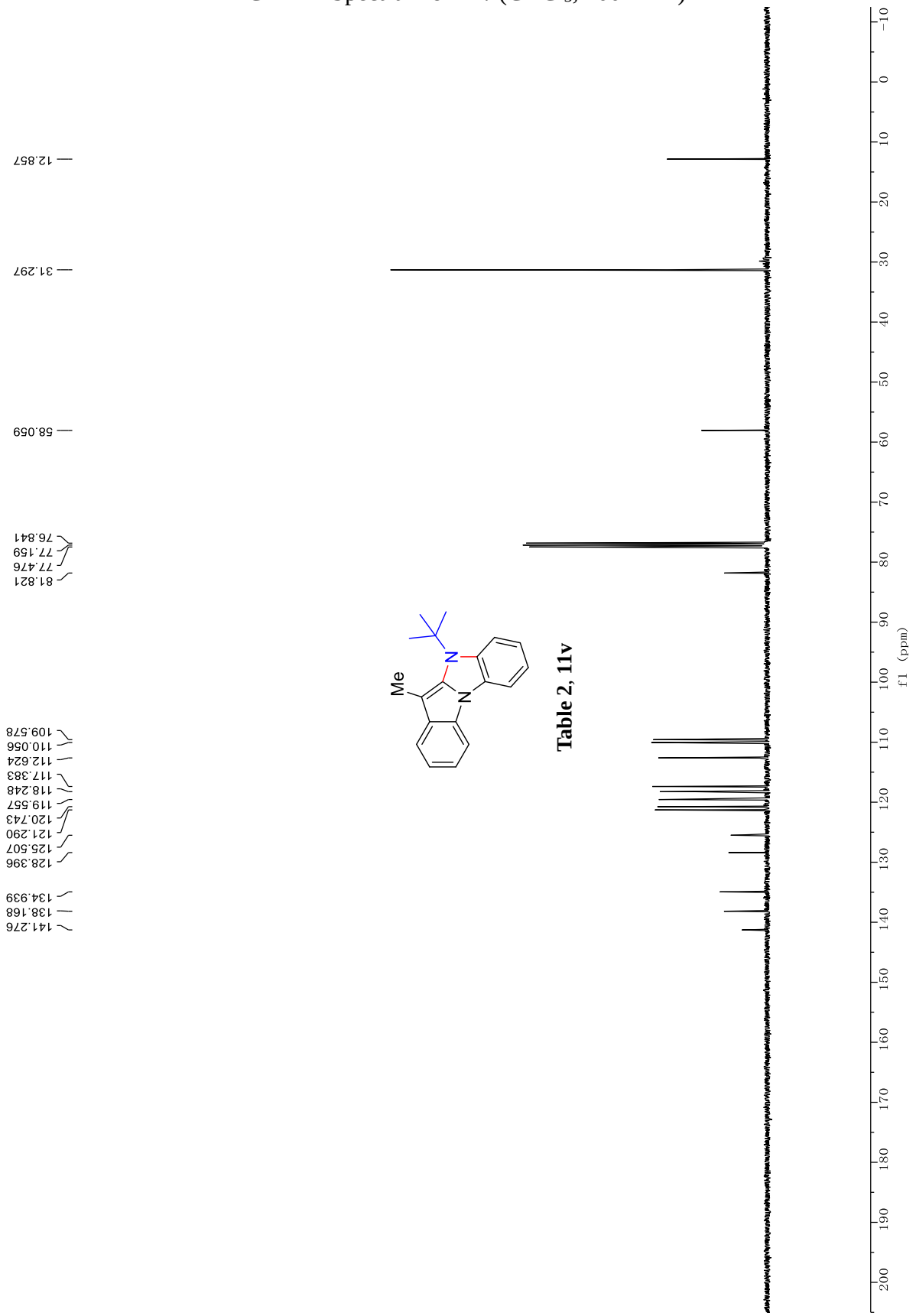
^{13}C NMR Spectrum of **11u** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **11v** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **11v** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **11w** ($CDCl_3$, 400 MHz)

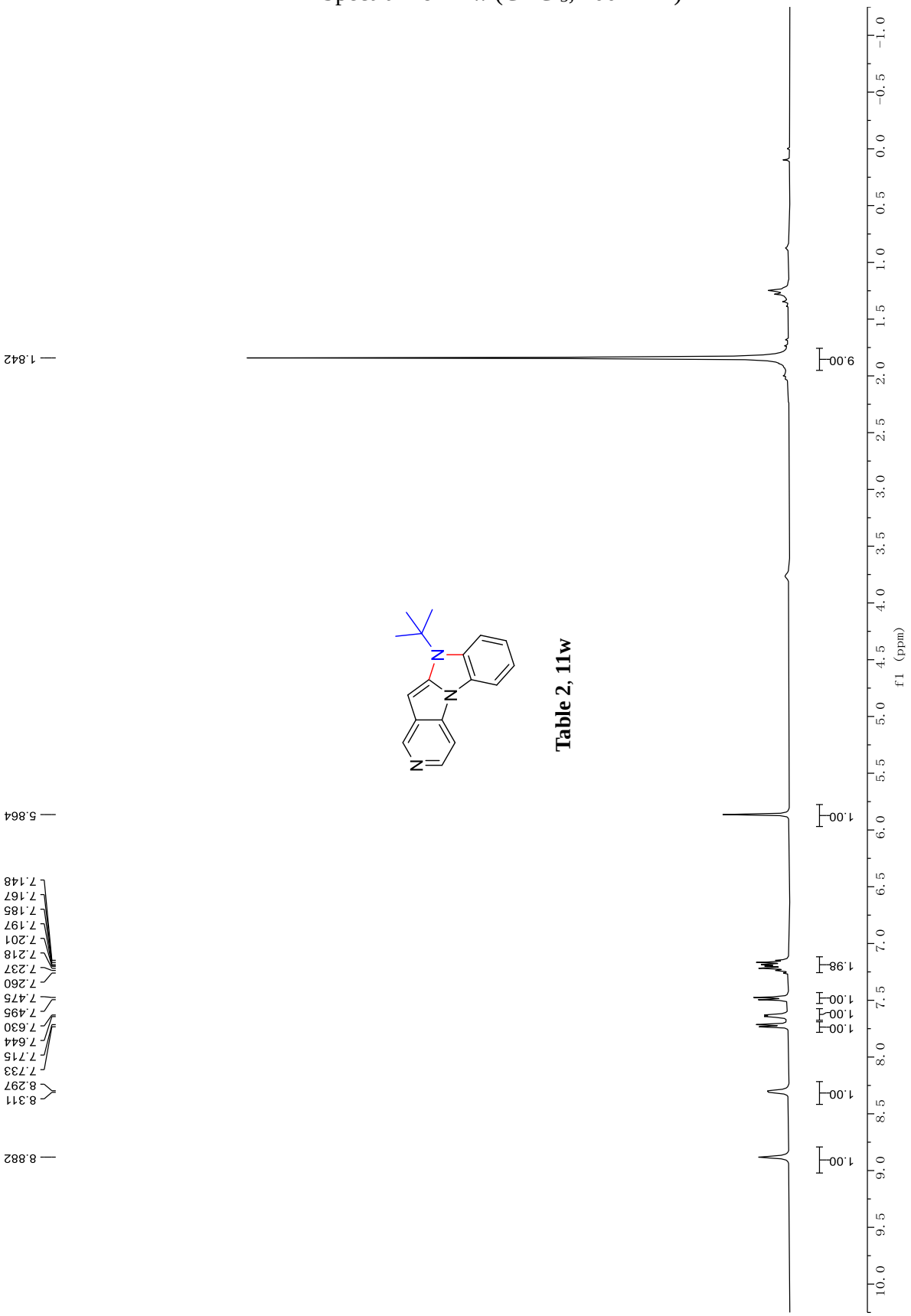


Table 2, 11w

^{13}C NMR Spectrum of **11w** ($CDCl_3$, 100 MHz)

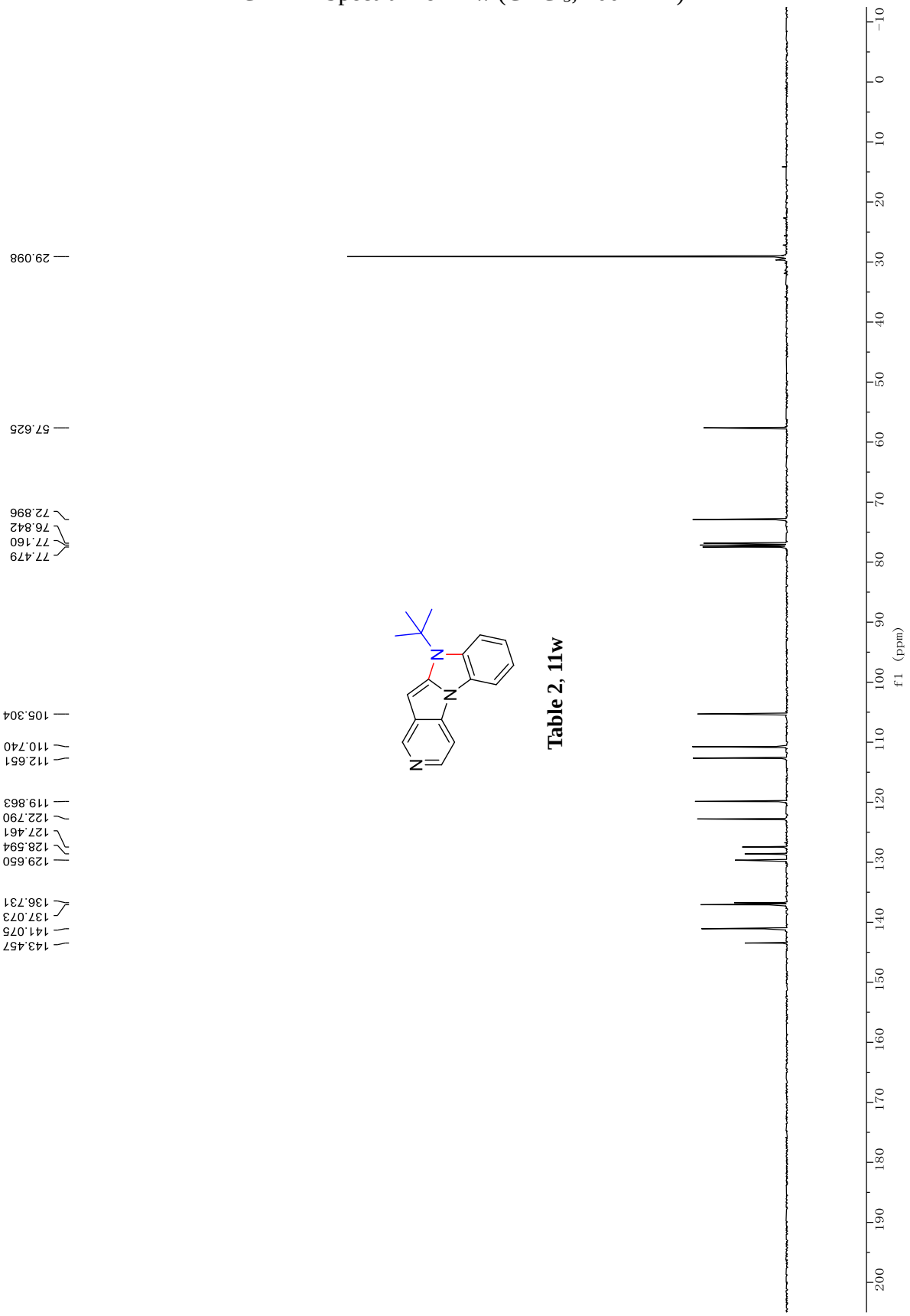
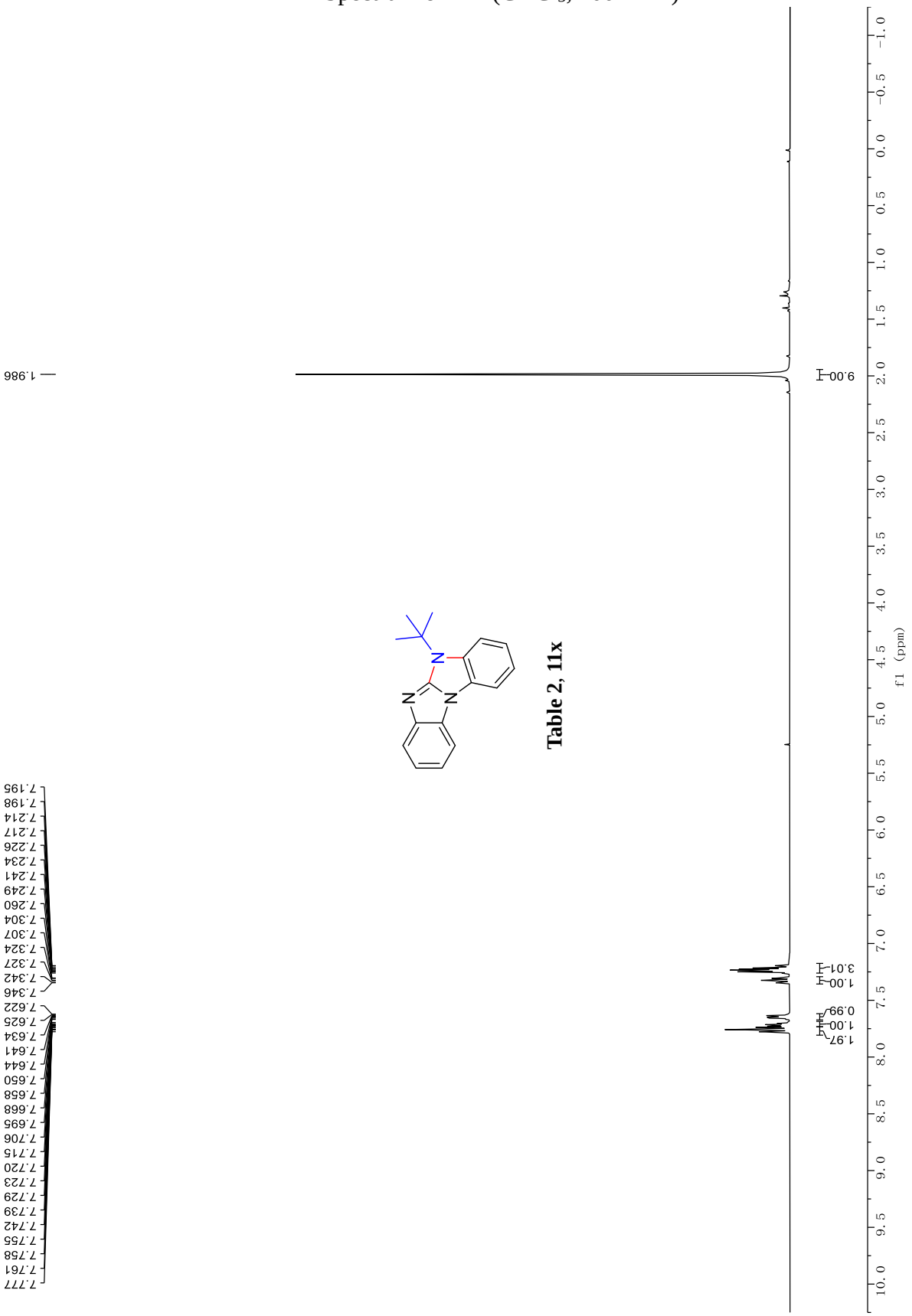


Table 2, 11w

^{1}H NMR Spectrum of **11x** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **11x** ($CDCl_3$, 100 MHz)

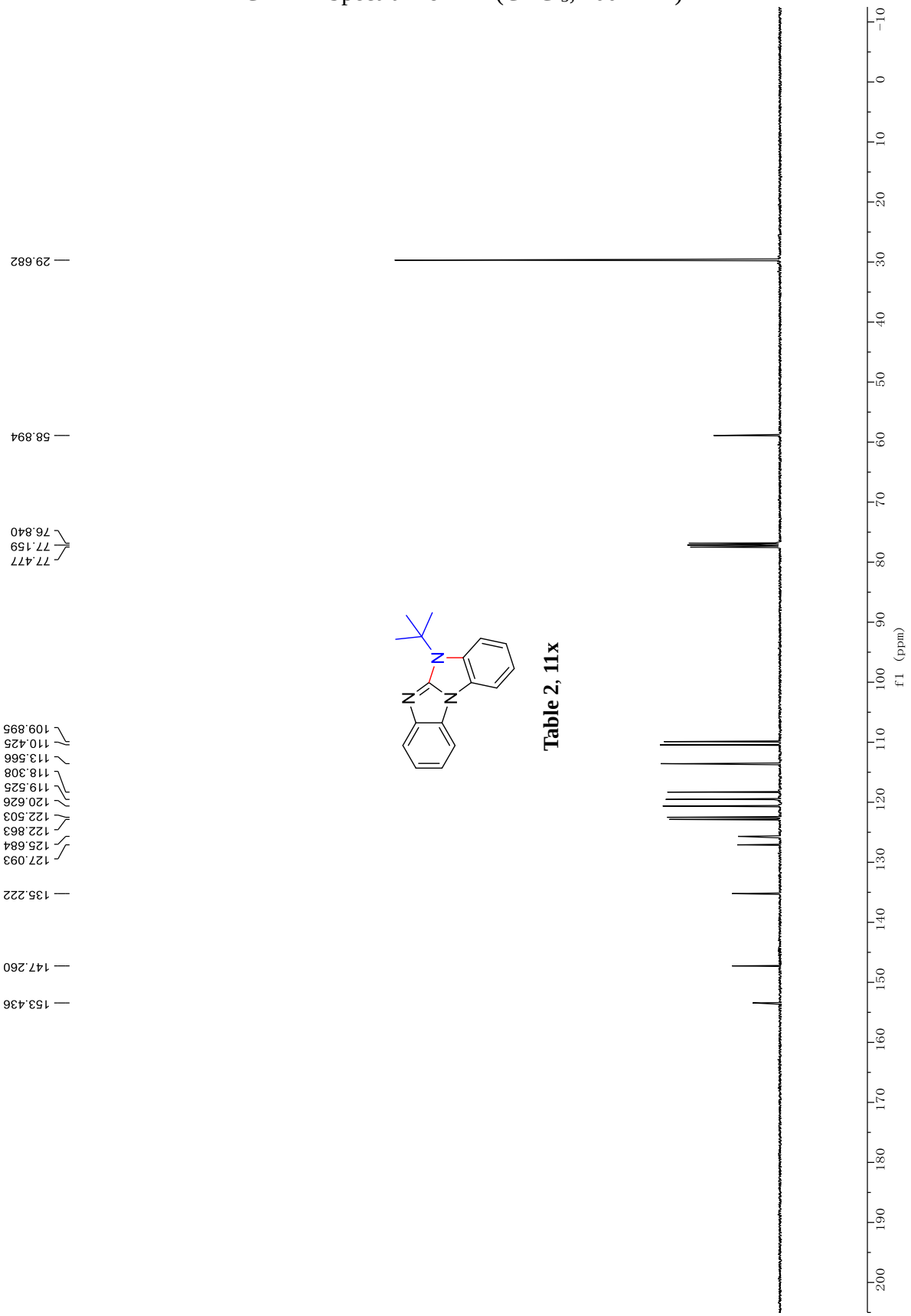


Table 2, 11x

^{1}H NMR Spectrum of **11y** ($CDCl_3$, 400 MHz)

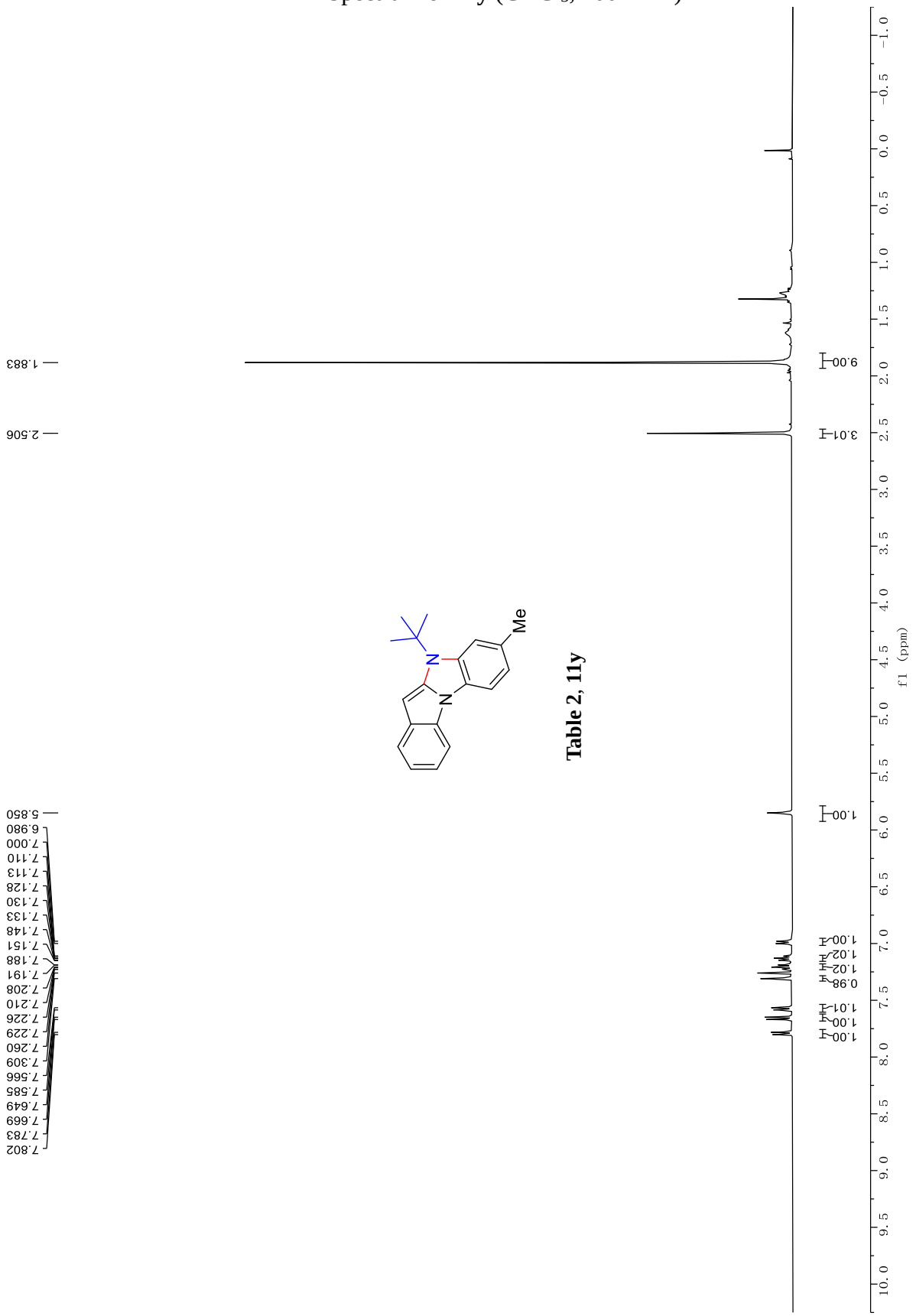


Table 2, 11y

^{13}C NMR Spectrum of **11y** ($CDCl_3$, 100 MHz)

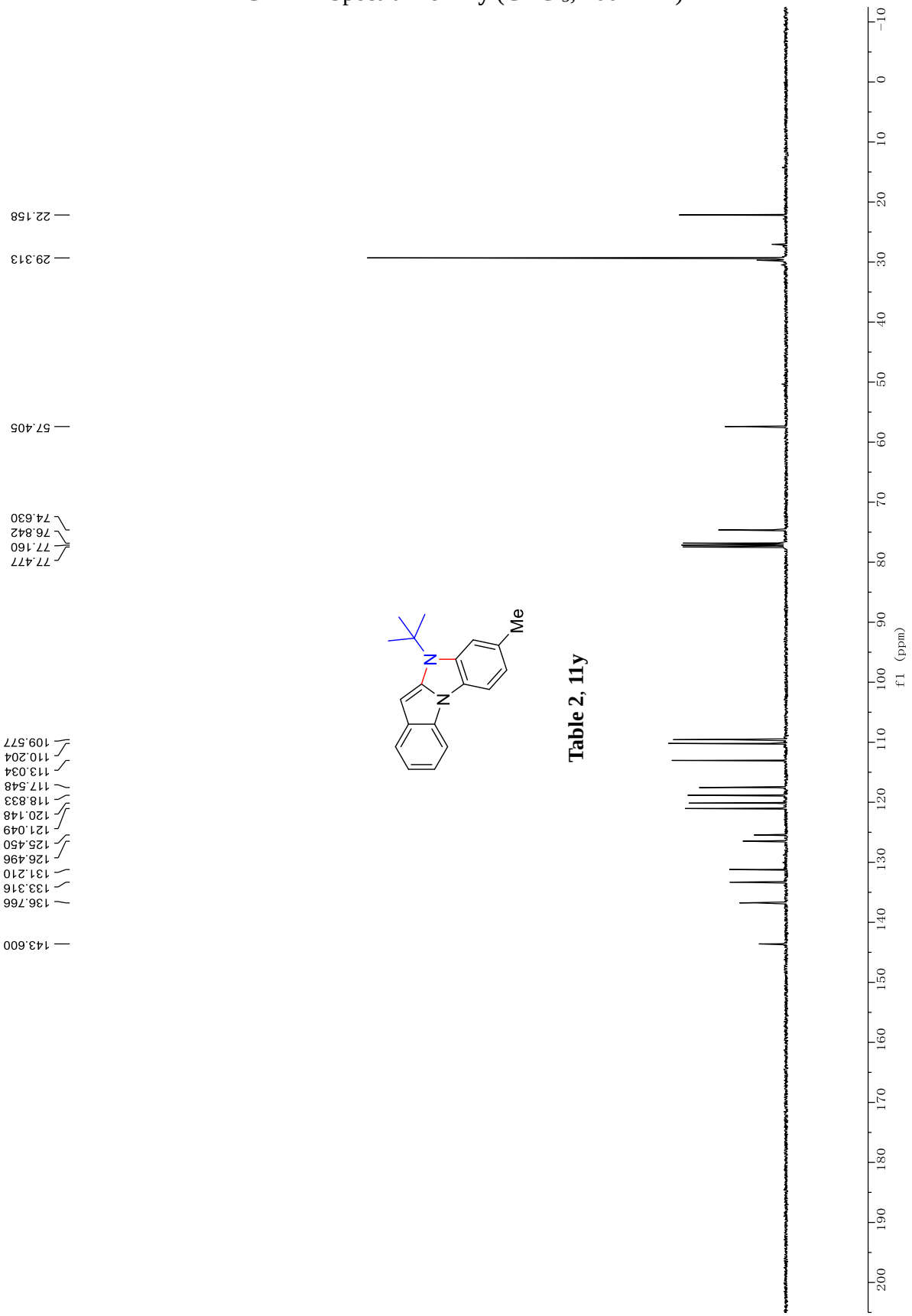


Table 2, 11y

^{1}H NMR Spectrum of **11z** ($CDCl_3$, 400 MHz)

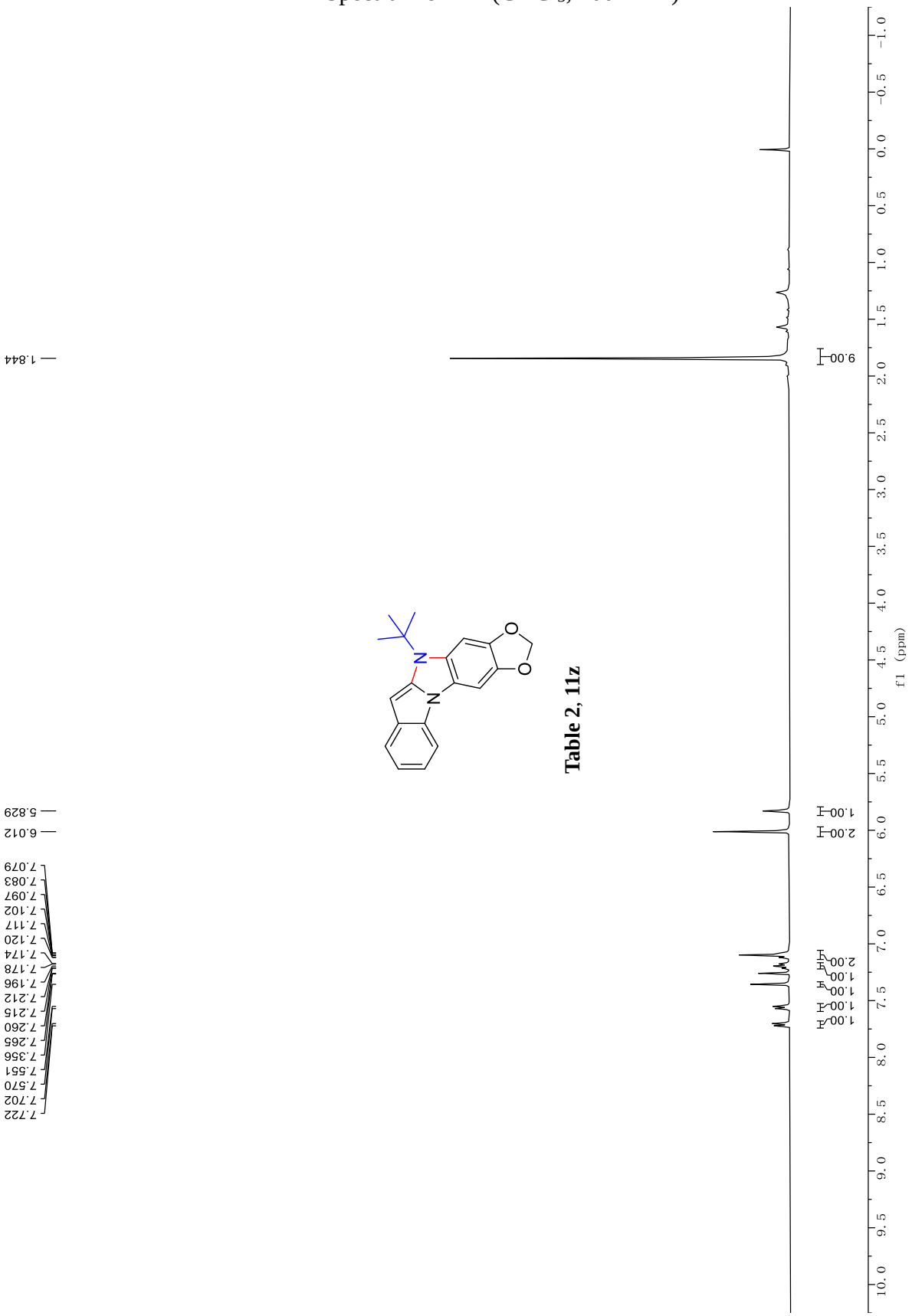


Table 2, 11z

^{13}C NMR Spectrum of **11z** ($CDCl_3$, 100 MHz)

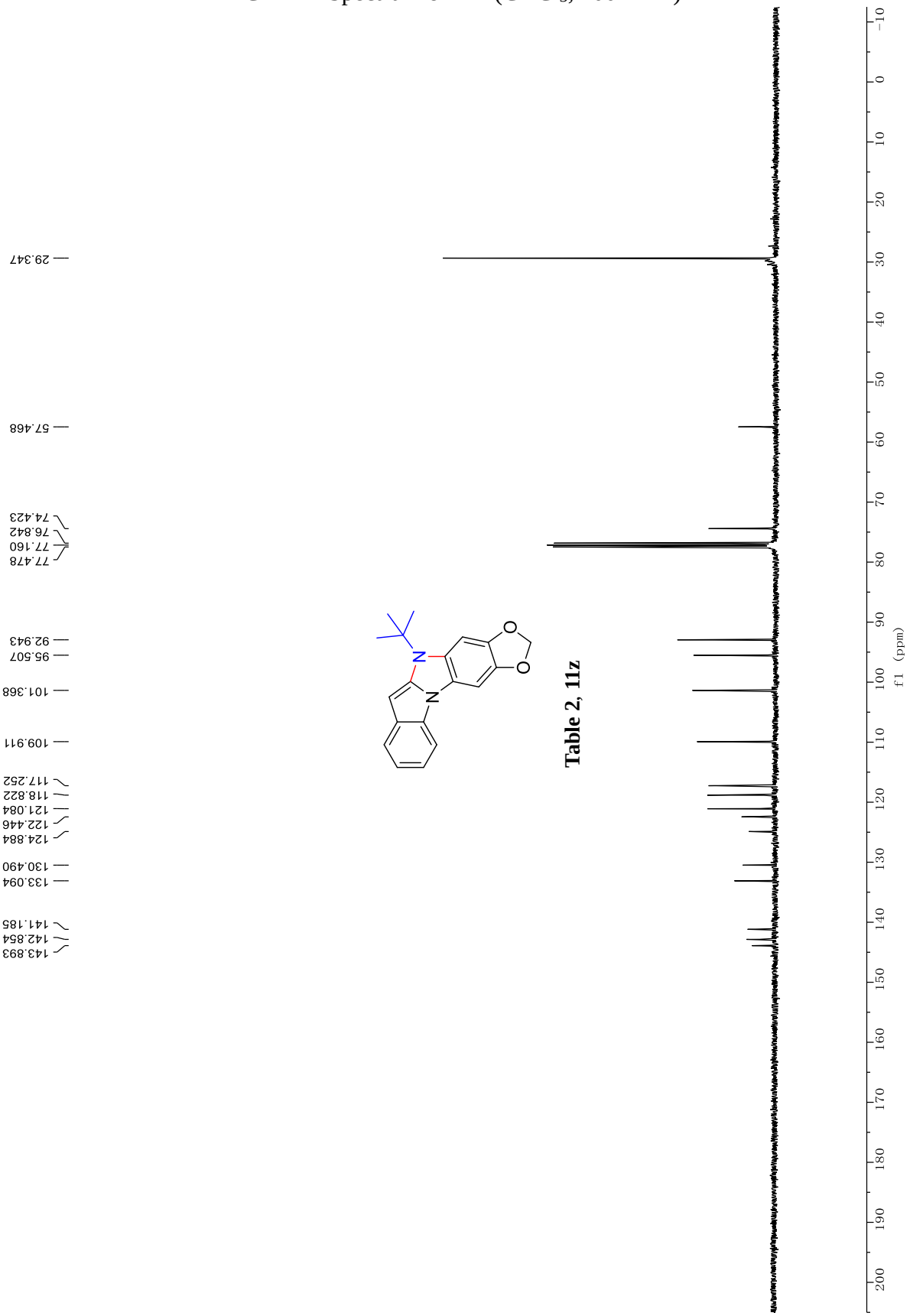


Table 2, 11z

^{1}H NMR Spectrum of **11aa** ($CDCl_3$, 400 MHz)

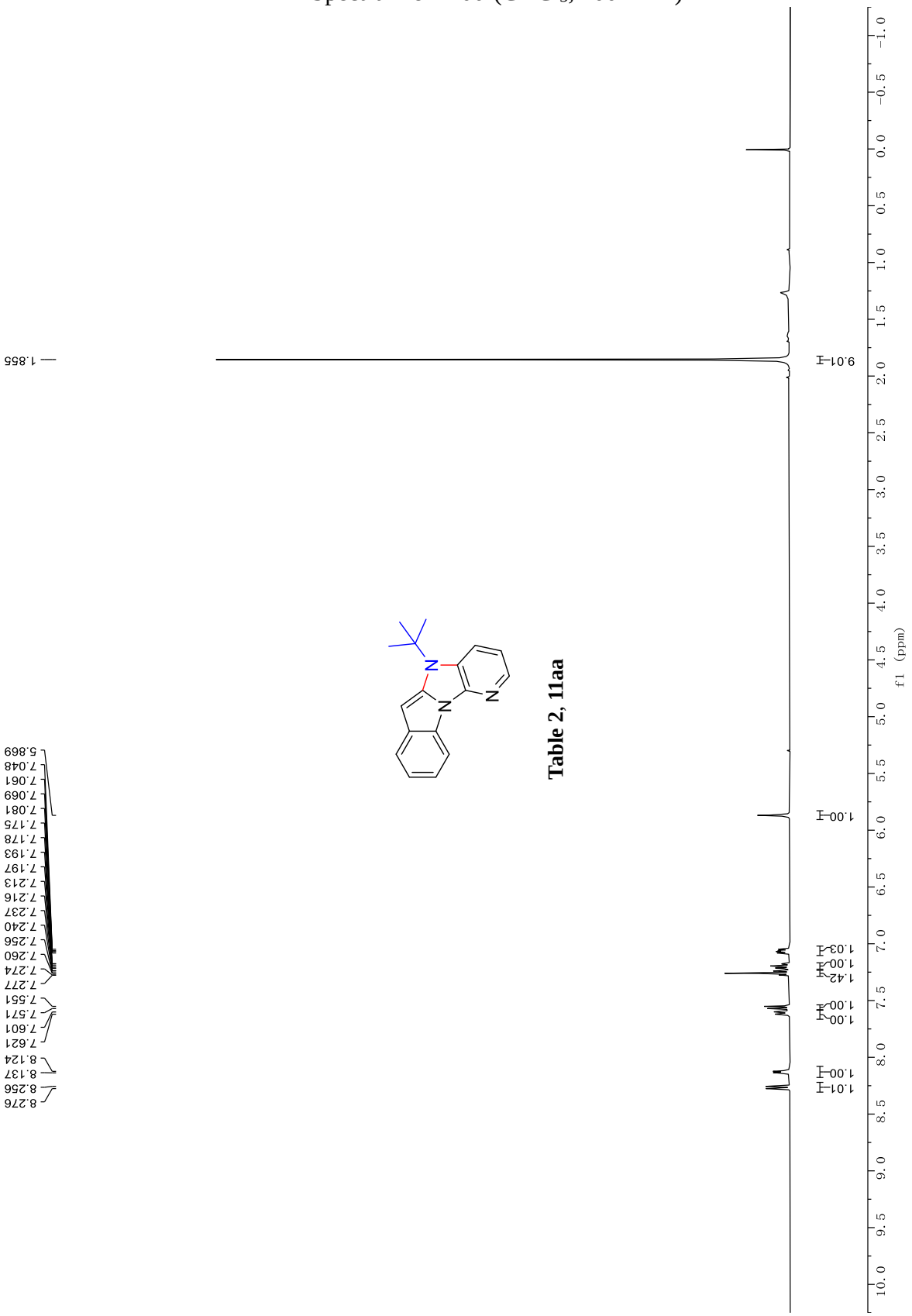


Table 2, 11aa

^{13}C NMR Spectrum of **11aa** ($CDCl_3$, 100 MHz)

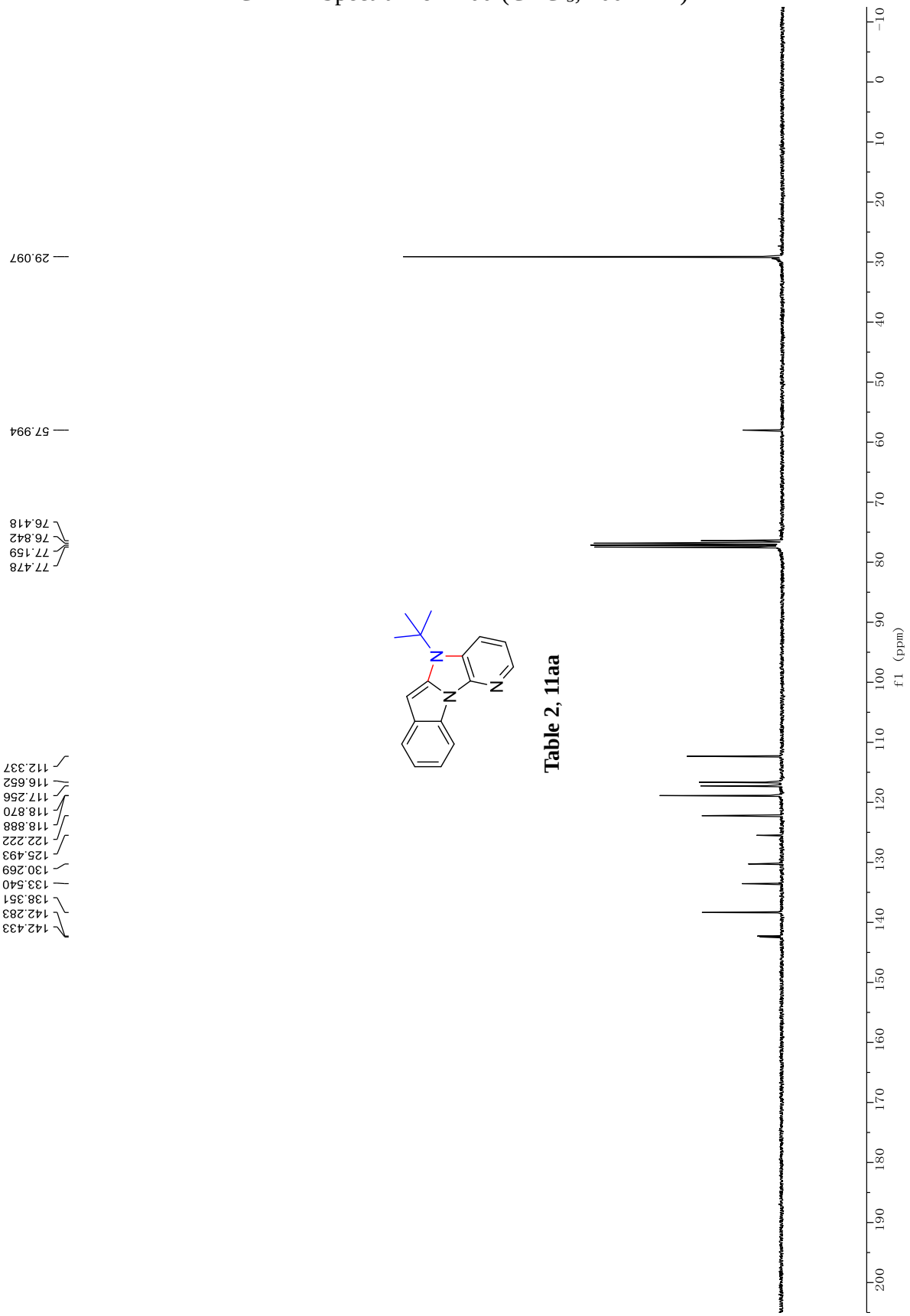
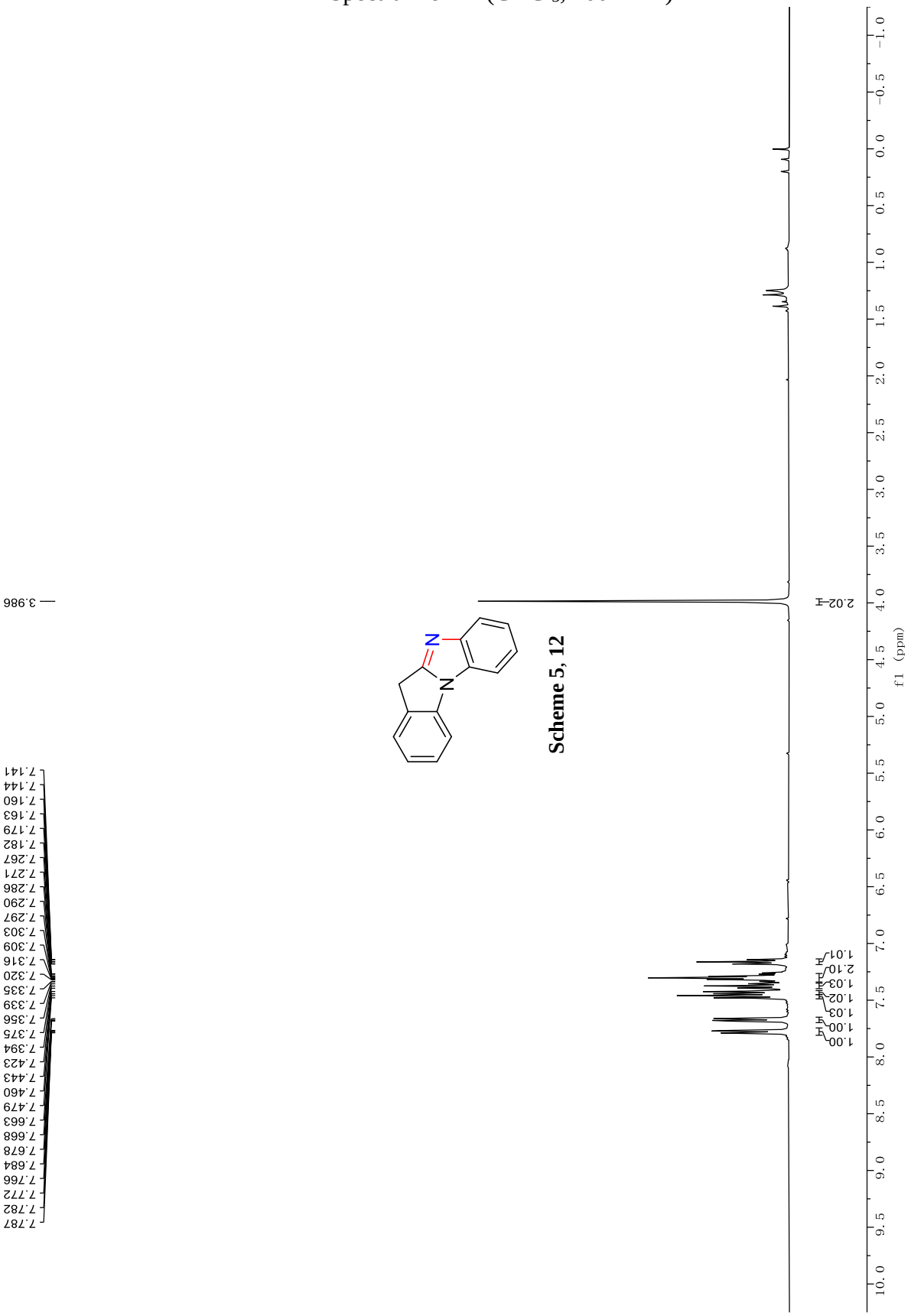


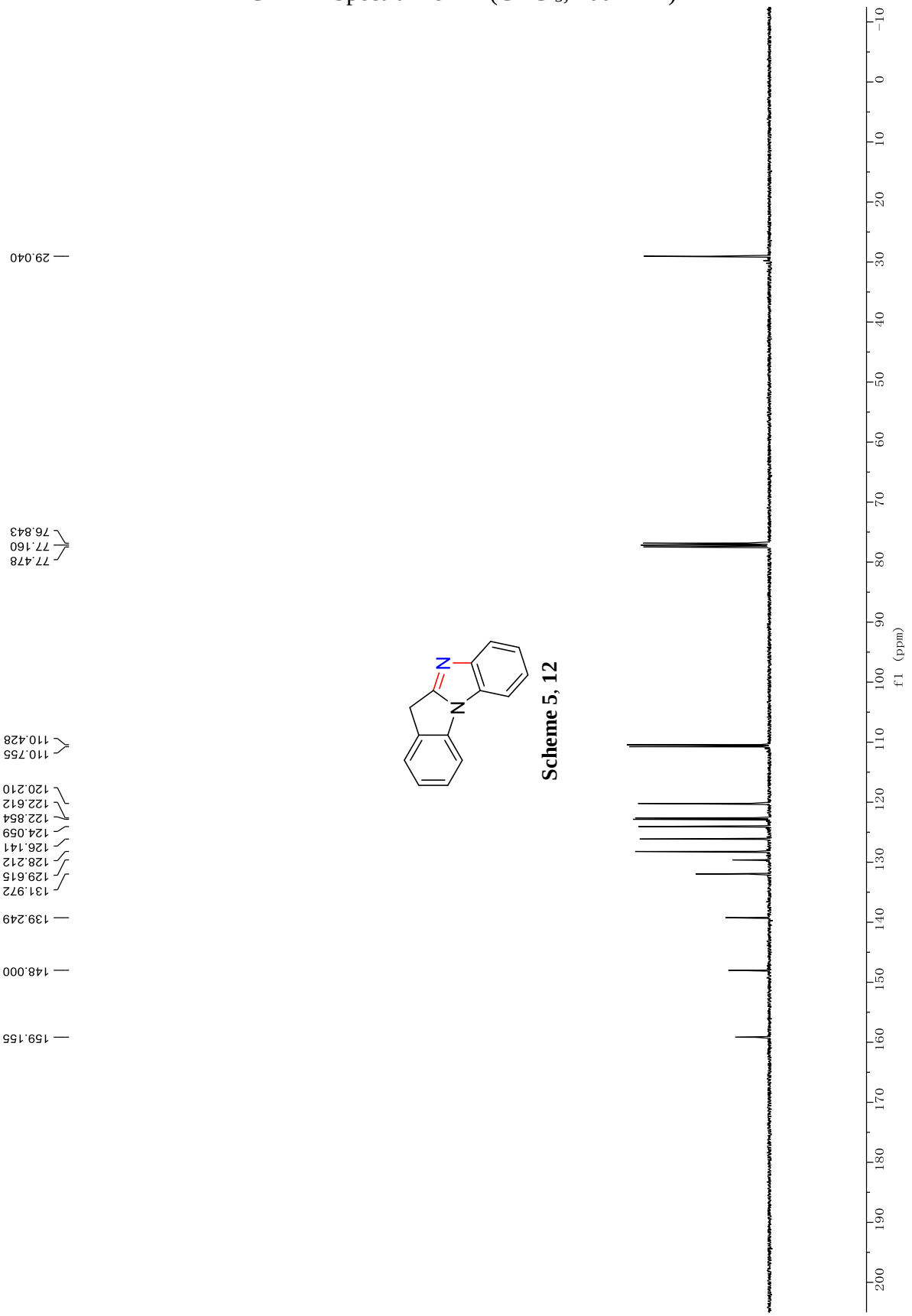
Table 2, 11aa

^{1}H NMR Spectrum of **12** ($CDCl_3$, 400 MHz)



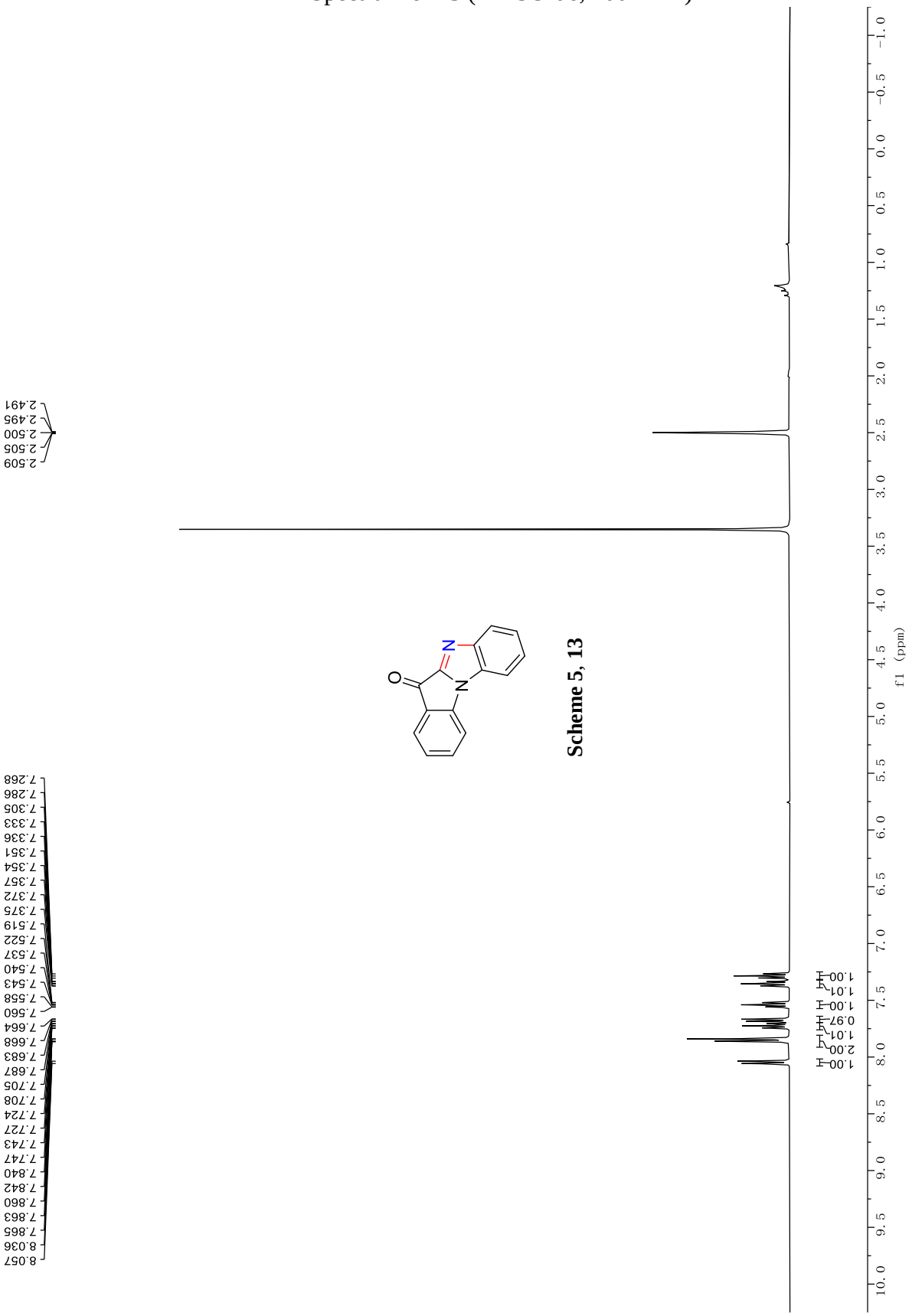
Scheme 5, 12

^{13}C NMR Spectrum of **12** ($CDCl_3$, 100 MHz)



Scheme 5, 12

^{1}H NMR Spectrum of **13** (DMSO-d6, 400 MHz)



Scheme 5, 13

^{13}C NMR Spectrum of **13** (DMSO-d6, 100 MHz)