Supporting Information

Super Electron Donor-mediated Reductive Transformation of Nitrobenzenes: A Novel Strategy to Synthesize Azobenzenes and Phenazines

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1. General Comments

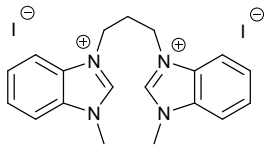
Melting points (mp) were determined with a Yazawa micro melting point apparatus and uncorrected. Infrared (IR) data were recorded on SensIR ATR (Attenuated Total Reflectance) FT-IR. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). NMR data were recorded on a JEOL AL400 spectrometer or a JEOL ECA600 spectrometer. Chemical shifts are expressed in δ (parts per million, ppm) values and coupling constants are expressed in herts (Hz). ^{1}H NMR spectra were referenced to tetramethylsilane as an internal standard or to a solvent signal ($CDCl_3$: 7.26 ppm, DMSO-d_6: 2.49 ppm). ^{13}C NMR spectra were referenced to a solvent signal ($CDCl_3$: 77.0 ppm, DMSO-d_6: 39.5 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet. Low and high resolution mass spectra (LRMS and HRMS) were obtained from Mass Spectrometry Resource, Graduate School of Pharmaceutical Sciences, Tohoku University, on a JEOL JMS-DX 303 and JMS-700/JMS-T 100 GC spectrometer.

2. Materials

Nitrobenzenes and other commercially available materials were purchased from Tokyo Kasei Co., Aldrich Inc. and other commercial suppliers and were used as received. Flash column chromatography was performed with Kanto silica gel 60 N (spherical, neutral, 70−230 mesh).

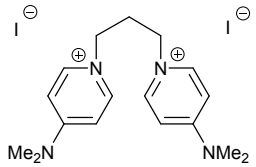
3. Preparation of Starting Materials

Preparation of 1,3-*bis*(3-methyl-3*H*-benzimidazolium)propane diiodide (1')[1]



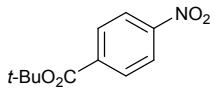
Under an Ar atmosphere, 1,3-diiodopropane (39 mmol, 8.7 g) was added to a solution of 1-methyl-1*H*-benzimidazole (90 mmol, 12 g) in acetonitrile (400 mL). The mixture was heated under reflux for 2 days. After cooling, diethyl ether (200 mL) was added to the mixture. The resulting precipitates were filtered and washed with diethyl ether (100 mL × 3). Recrystallization from CH_2Cl_2/ethanol to give **1'** (85%, 14 g) as colorless prisms. mp 268−273 °C; IR (neat, cm^{-1}): 2361, 2344, 1570, 1487, 1351, 1201, 1126, 1008, 857, 762; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.73 (2H, s), 8.09−8.02 (4H, m), 7.73−7.67 (4H, m), 4.68 (4H, t, J = 7.3 Hz), 4.07 (6H, s), 2.59 (2H, quint, J = 7.3 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm):142.8, 131.8, 130.8, 126.6, 126.5, 113.6, 113.5, 43.8, 33.4, 28.1; LRMS (FAB) m/z: 433 $(M–I)^+$; HRMS (FAB-EB) m/z: $(M–I)^+$ Calcd. for $C_{19}H_{22}IN_4^+$: 433.0884, found: 433.0894.

Preparation of 1,3-*bis*(*N*,*N*-dimethyl-4-aminopyridinium)propane diiodide (2')[2]



Under an Ar atmosphere, 1,3-diiodopropane (30 mmol, 8.9 g) was added to a solution of 4-dimethylaminopyridine (75 mmol, 8.4 g) in acetonitrile (300 mL). The mixture was heated under reflux overnight. After cooling, diethyl ether (100 mL) was added to the mixture. The resulting precipitates were filtered and washed with diethyl ether (30 mL × 3). Recrystallization from CH_2Cl_2/ethanol to gave **2'** (77%, 12 g) as colorless prisms. mp 303–308 °C (dec.); IR (neat, cm^{-1}): 1645, 1570, 1539, 1404, 1374, 1236, 1202, 1174, 1036, 946, 830, 743, 738; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.29 (4H, d, J = 7.3 Hz), 7.04 (4H, d, J = 7.3 Hz), 4.27–4.23 (4H, m), 3.18 (12H, s), 2.36–2.32 (2H, m); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 155.9, 141.9, 107.8, 53.8, 39.8, 31.0; LRMS (FAB) m/z: 413 $(M–I)^+$; HRMS (FAB-EB) m/z: $(M–I)^+$ Calcd. for $C_{17}H_{26}IN_4^+$: 413.1197, found: 413.1212.

***tert*-Butyl 4-nitrobenzoate (4o)**[3]



To a slurry of 4-nitrobenzoic acid (10 mmol, 1.8 g) in pyridine (20 mL), tosyl chloride (20 mmol, 3.8 g) was added with stirring. Once the solid was completely dissolved, the solution was cooled to 0 °C, and *t*-butanol (2 mL) was added. After stirring at 0 °C for 2 h, the reaction mixture was allowed to warm to rt. After an additional 2 h of stirring, another portion of *t*-butanol (2 mL) was added. The reaction mixture was stirred for additional 14 h. The solvent was evaporated, and the residue was partitioned between ethyl acetate (30 mL), and sat. $NaHCO_3$ (30 mL). The organic layer was washed with sat. $NaHCO_3$ (30 mL × 3), and the pooled aqueous layer was washed with ethyl acetate (30 mL). The organic layer was pooled and washed with brine (30 mL), sat. $NaHSO_4$ (30 mL × 4), and brine (30 mL), and then dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was recrystallized from CH_2Cl_2/hexane to give **4o** (43%, 0.97 g) as colorless prisms. mp 122–123 °C (lit.[4] 114–116 °C); IR (neat, cm^{-1}): 2980, 1711, 1608, 1521, 1461, 1396, 1373, 1365, 1345, 1324, 1298, 1254, 1156, 1123, 1103, 1010, 874, 841, 786, 716, 707; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.26 (2H, d, J = 8.8 Hz), 8.15 (2H, d, J = 8.8 Hz), 1.62 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 163.7, 150.3, 137.4 130.5, 123.3, 82.6, 28.1; LRMS (EI) m/z: 223 (M^+); HRMS (EI-TOF) m/z: (M^+) Calcd. for $C_{11}H_{13}NO_4$: 223.0845, found: 223.0817.

4. General Procedure for the Synthesis of Azobenzenes

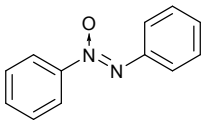
Method in a glove box

In a glove box, A mixture of **2'** (0.40 mmol, 0.22 g) and NaH (paraffin oil free, 1.0 mmol, 25 mg) in DMF (2.9 mL) was stirred at rt for 1 h. After the SED generated, nitrobenzene **4** (0.20 mmol) was added to the mixture and stirred at rt for 15 min. The reaction mixture was quenched with saturated NH_4Cl aq. and extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed by water (30 mL × 3) and brine (30 mL), and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to give the azobenzene **6**.

Method using a manifold

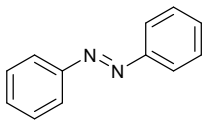
Under an Ar atmosphere, a mixture of **2'** (0.42 mmol, 0.23 g) and NaH (60% dispersion in paraffin oil, 0.82 mmol, 33 mg) in DMF (2.9 mL) was stirred at rt for 1 h. After the SED generated, nitrobenzene (0.20 mmol) was added to the mixture and stirred at rt for 15 min. The reaction mixture was quenched with H_2O at 0 °C and extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed by water (30 mL × 3) and brine (30 mL), and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to give the azobenzene **6**.

Azoxybenzene (5a)



Obtained as yellow oil; IR (neat, cm^{-1}): 3063, 3027, 2946, 2871, 1600, 1586, 1496, 1468, 1454, 1244, 1171, 1038, 750; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.32–8.30 (2H, m), 8.16 (2H, dd, J = 1.5, 8.8 Hz), 7.58–7.47 (5H, m), 7.39 (1H, t, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 148.4, 144.0, 131.6, 129.6, 128.8, 128.7, 125.5, 122.4; LRMS (EI) *m*/*z*: 198 (M^+); HRMS (EI-EB) *m*/*z*: Calcd. for $C_{12}H_{10}N_2O$: 198.0793, found: 198.0795.

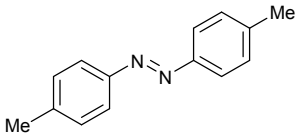
Azobenzene (6a)



Obtained in 98% yield (13.4 mg, 0.15 mmol scale); Recrystallized from hexane, orange plates, mp 66–70 °C (lit.[6] 65–66 °C); IR (neat, cm^{-1}): 3061, 2956, 2924, 2855, 2358, 2323, 1483, 1452, 1299, 1222, 1151, 1071, 1019, 926, 773; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.94–7.91 (4H, m),

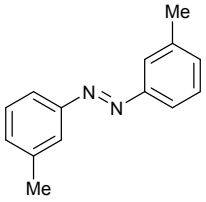
7.54–7.45 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 152.7, 131.0, 129.1, 122.8; LRMS (EI) *m*/*z*: 182 (M^+); HRMS (EI-TOF) *m*/*z*: (M^+) Calcd. for $C_{12}H_{10}N_2$: 182.0844, found: 182.0847.

4,4′-Dimethylazobenzene (6b)



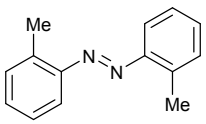
Obtained in 70% yield (14.6 mg); Recrystallized from methanol/hexane, orange plates, mp 146–147 °C (lit.[5] 145–146 °C); IR (neat, cm^{-1}): 3023, 2922, 1598, 1580, 1503, 1412, 1296, 1209, 1153, 1110, 1037, 1011, 840; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.81 (4H, d, *J* = 8.3 Hz), 7.30 (4H, d, *J* = 8.3 Hz), 2.43 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 150.8, 141.2, 129.7, 122.7, 21.5; LRMS (EI) *m*/*z*: 210 (M^+); HRMS (EI-TOF) *m*/*z*: (M^+) Calcd. for $C_{14}H_{14}N_2$: 210.1157, found: 210.1180.

3,3′-Dimethylazobenzene (6c)



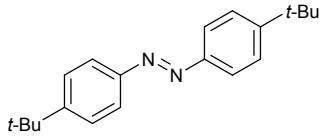
Obtained as orange oil in 98% yield (20.6 mg); IR (neat, cm^{-1}): 2919, 1607, 1599, 1481, 1457, 1378, 1306, 1250, 1144, 1084, 1041, 999, 914, 881, 790; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.76–7.69 (4H, m), 7.39 (2H, t, *J* = 7.8 Hz), 7.27 (2H, d, *J* = 7.8 Hz), 2.45 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 152.9, 139.0, 131.6, 128.9, 122.9, 120.4, 21.3; LRMS (EI) *m*/*z*: 210 (M^+); HRMS (EI-EB) *m*/*z*: (M^+) Calcd. for $C_{14}H_{14}N_2$: 210.1157, found: 210.1157.

2,2′-Dimethylazobenzene (6d)



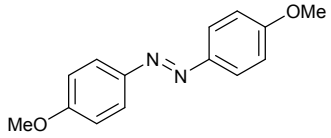
Obtained in 38% yield (8.0 mg); Recrystallized from methanol/hexane, orange plates, mp 55–57 °C (lit.[6] 53–54 °C); IR (neat, cm^{-1}): 2926, 1597, 1479, 1456, 1376, 1303, 1278, 1218, 1194, 1150, 1120, 1041, 950, 865, 769, 717; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.62 (2H, d, *J* = 8.3 Hz), 7.35–7.33 (4H, m), 7.28–7.25 (2H, m), 2.74 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 151.1, 138.0, 131.3, 130.7, 126.3, 115.9, 17.6; LRMS (EI) *m*/*z*: 210 (M^+); HRMS (EI-TOF) *m*/*z*: (M^+) Calcd. for $C_{14}H_{14}N_2$: 210.1157, found: 210.1176.

4,4′-Di-*tert*-butylazobenzene (6e)



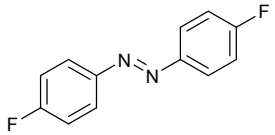
Obtained in 95% yield (27.9 mg); Recrystallized from methanol/hexane, orange prisms, mp 188–192 °C; IR (neat, cm^{-1}): 2959, 2904, 2867, 1602, 1497, 1473, 1458, 1404, 1362, 1268, 1161, 1107, 1010, 845; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.84 (4H, d, J = 8.6 Hz), 7.52 (4H, d, J = 8.6 Hz) 1.37 (18H, s); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 154.2, 150.8, 126.0, 122.4, 35.0, 31.3; LRMS (EI, *m*/*z*): 294 (M^+); HRMS (EI-TOF) *m*/*z*: (M^+) Calcd. for $C_{20}H_{26}N_2$: 294.2096, found: 294.2091.

4,4′-Dimethoxyazobenzene (6f)



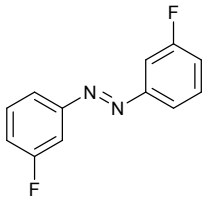
Obtained in 79% yield (18.8 mg); Recrystallized from ethanol/hexane, orange prisms, mp 169–171 °C (lit.[7] 166.5–167 °C); IR (neat, cm^{-1}): 2970, 2840, 1598, 1578, 1496, 1456, 1439, 1421, 1317, 1293, 1242, 1178, 1143, 1102, 1023, 839, 823, 745, 733; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.89–7.85 (4H, m), 7.01–6.98 (4H, m), 3.88 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 161.5, 147.1, 124.3, 114.1, 55.5; LRMS (EI) *m*/*z*: 242 (M^+); HRMS (EI-TOF) *m*/*z*: (M^+) Calcd. for $C_{14}H_{14}N_2O_2$: 242.1055, found: 242.1045.

4,4′-Difluoroazobenzene (6g)



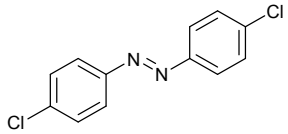
Obtained in 51% yield (11.3 mg); Orange plates, mp 102–104 °C (lit.[8] 97–100 °C); IR (neat, cm^{-1}): 3112, 3062, 2924, 1896, 1592, 1496, 1415, 1289, 1229, 1201, 1140, 1094, 1008, 892, 839, 801, 754, 720; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.94–7.91 (4H, m), 7.22–7.7.18 (4H, m); ^{13}C NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 164.4 (d, J_{FC} = 252.4 Hz), 149.0, 124.8 (d, J_{FC} = 8.6 Hz), 116.1 (d, J_{FC} = 21.5 Hz); LRMS (EI) *m*/*z*: 218 (M^+); HRMS (EI-TOF) *m*/*z*: (M^+) Calcd. for $C_{12}H_8F_2N_2$: 218.0656, found: 218.0615.

3,3′-Difluoroazobenzene (6h)



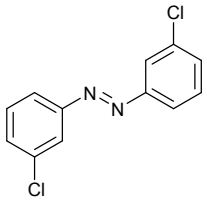
Obtained in 65% yield (14.2 mg) as a orange plates; mp 66–74 °C (lit.[9] 77–79 °C); IR (neat, cm^{-1}): 3080, 2924, 2854, 2364, 2323, 1582, 1479, 1465, 1315, 1240, 1111, 951, 887, 798, 743; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.78–7.76 (2H, m), 7.61 (2H, dt, J = 2.4, 9.8 Hz), 7.54–7.48 (2H, m), 7.23–7.18 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 163.3 (d, J_{FC} = 249.4 Hz), 153.8 (d, J_{FC} = 7.4 Hz), 130.3 (d, J_{FC} = 9.1 Hz), 120.8 (d, J_{FC} = 3.3 Hz), 118.2 (d, J_{FC} = 22.2 Hz), 108.1 (d, J_{FC} = 23.0 Hz); LRMS (EI) *m*/*z*: 218 (M^+); HRMS (EI-TOF) *m*/*z*: (M^+) Calcd. for $C_{12}H_8F_2N_2$: 218.0656, found: 218.0665.

4,4′-Dichloroazobenzene (6i)



Obtained in 80% yield (20.2 mg); Recrystallized from ethyl acetate/hexane, orange prisms, mp 186–190 °C (lit.[5] 184.5–185.5 °C); IR (neat, cm^{-1}): 3086, 2360, 2343, 1923, 1585, 1570, 1479, 1404, 1295, 1209, 1145, 1105, 1082, 1004, 846, 823, 717; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.88–7.84 (4H, m), 7.51–7.47 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm):150.8, 137.2, 129.4, 124.2; LRMS (EI) *m*/*z*: 250 (M^+); HRMS (EI-TOF) *m*/*z*: (M^+) Calcd. for $C_{12}H_8{}^{35}Cl_2N_2$: 250.0065, found: 250.0045.

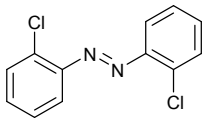
3,3′-Dichloroazobenzene (6j)



Obtained in 71% yield (18.0 mg); Recrystallized from methanol/hexane, orange plates, mp 104–105 °C (lit.[8] 100–102 °C); IR (neat, cm^{-1}): 3079, 3072, 2356, 2325, 1955, 1889, 1820, 1704, 1585, 1568, 1462, 1416, 1303, 1196, 1154, 1066, 996, 885, 791; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.90 (2H, s), 7.85–7.82 (2H, m), 7.48–7.46 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm):

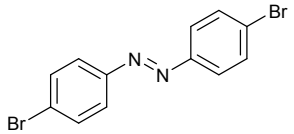
153.1, 135.2, 131.2, 130.2, 122.6, 121.9; LRMS (EI) *m*/*z*: 250 (M^+); HRMS (EI-TOF) *m*/*z*: Calcd. for $C_{12}H_8{}^{35}Cl_2N_2$: 250.0065, found: 250.0093.

2,2′-Dichloroazobenzene (6k)



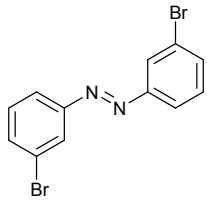
Obtained in 74% yield (18.5 mg); Recrystallized from ethanol (orange prisms); mp 133–134 °C (lit.[5] 137–139 °C); IR (neat, cm^{-1}): 2923, 1723, 1582, 1574, 1465, 1443, 1433, 1288, 1220, 1159, 1129, 1059, 1032, 952, 942, 833, 763, 725, 747; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.77 (2H, dd, *J* = 2.0, 7.8 Hz), 7.57 (2H, dd, *J* = 1.5, 7.8 Hz), 7.42 (2H, td, *J* = 2.0, 7.8 Hz), 7.36 (2H, td, *J* = 1.5, 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 148.8, 135.8, 132.2, 130.8, 127.4, 118.1; LRMS (EI) *m*/*z*: 250 (M^+); HRMS (EI-TOF) *m*/*z*: (M^+) Calcd. for $C_{12}H_8{}^{35}Cl_2N_2$: 250.0065, found: 250.0070.

4,4′-Dibromoazobenzene (6l)



Obtained in 68% yield (23.2 mg); Recrystallized from chloroform/hexane, orange plates, mp 208–210 °C (lit.[5] 203–204.5 °C); IR (neat, cm^{-1}): 3088, 1907, 1773, 1646, 1570, 1473, 1398, 1282, 1218, 1154, 1098, 1065, 1006, 833, 816, 711; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.79 (4H, d, *J* = 8.8 Hz), 7.65 (4H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 151.2, 132.4, 125.8, 124.4; LRMS (EI) *m*/*z*: 338 (M^+); HRMS (EI-TOF) *m*/*z*: (M^+) Calcd. for $C_{12}H_8{}^{79}Br_2N_2$: 337.9054, found: 337.9064.

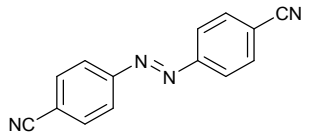
3,3′-Dibromoazobenzene (6m)



Obtained in 71% yield (24.1 mg); Recrystallized from methanol/chloroform, orange needles, mp 129–130 °C (lit.[10] 139–141 °C); IR (neat, cm^{-1}): 3065, 1759, 1564, 1458, 1411, 1300, 1207, 1197, 1147, 1058, 995, 882, 867, 859, 794; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.05 (2H, s), 7.88 (2H, d, *J* = 8.0 Hz), 7.62 (2H, d, *J* = 8.0 Hz), 7.41 (2H, t, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ

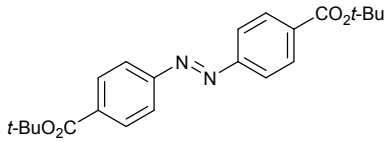
(ppm): 153.2, 134.1, 130.5, 124.8, 123.2 (2C); LRMS (EI) *m*/*z*: 338 (M^+); HRMS (EI-TOF) *m*/*z*: (M^+) Calcd. for $C_{12}H_8{}^{79}Br_2N_2$: 337.9054, found: 337.9027.

4,4′-Dicyanoazobenzene (6n)



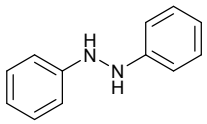
Obtained in 72% yield (16.8 mg); Recrystallized from ethyl acetate/hexane, red needles; IR (neat, cm^{-1}): 3092, 2358, 2228, 1931, 1801, 1598, 1491, 1408, 1306, 1296, 1219, 1163, 1099, 1011; ^1H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 8.04 (4H, d, *J* = 8.8 Hz), 7.85 (4H, d, *J* = 8.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 154.0, 133.4, 123.7, 118.1, 115.2; LRMS (EI) *m*/*z*: 232 (M^+); HRMS (EI-EB) *m*/*z*: (M^+) Calcd. for $C_{14}H_8N_4$: 232.0749, found: 232.0747.

Di-*tert*-buthylazobenzene-4,4'-dicarboxylate (6o)



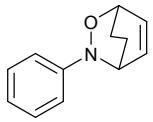
Obtained in 57% yield (21.9 mg); Recrystallized from hexane, orange needles; mp 186–188 °C; IR (neat, cm^{-1}): 2979, 1705, 1367, 1288, 1256, 1170, 1118, 1098, 1010, 870, 850, 781, 700; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.14 (4H, d, *J* = 8.3 Hz), 7.96 (4H, d, *J* = 8.3 Hz), 1.63 (18H, s); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 165.1, 154.7, 134.3, 130.4, 122.7, 81.6, 28.2; LRMS (EI) *m*/*z*: 382 (M^+); HRMS (EI-EB) *m*/*z*: (M^+) Calcd. for $C_{22}H_{26}N_2O_4$: 382.1893, found: 382.1888.

Hydrazobenzene (7a)



Colorlss solid; mp 127–129 °C (lit.[11] 124–125 °C); IR (neat, cm^{-1}): 3327, 2925, 1598, 1586, 1478, 1304, 1246, 1073, 888, 750; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.22–7.19 (4H, m), 6.86–6.82 (4H, m), 5.59 (2H, br.s); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 148.8, 129.3, 119.9, 112.3; LRMS (EI) *m*/*z*: 184 (M^+); HRMS (EI-EB) *m*/*z*: (M^+) Calcd. for $C_{12}H_{12}N_2$: 184.1000, found: 183.0993.

3-Phenyl-2-oxa-3-azabicyclo[2.2.2]oct-5-ene (9)

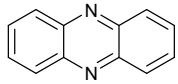


Obtained in 9% yield (3.4 mg); IR (neat, cm^{-1}): 2960, 2930, 2853, 1595, 1489, 1450, 1369, 1237, 1228, 1179, 1164, 1151, 1085, 1060, 1026, 956, 950, 937, 900, 874, 821, 806, 762, 719; ^1H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 7.21 (2H, t, J = 7.4 Hz), 7.01 (2H, d, J = 2.8, 8.3 Hz), 6.92 (1H, t, J = 7.3 Hz), 6.59–6.57 (1H, m), 6.15 (1H, t, J = 7.9 Hz), 4.70 (1H, t, J = 2.8 Hz), 4.44–4.42 (1H, m), 2.32–2.27 (1H, m), 2.25–2.21 (1H, m), 1.60–1.57 (1H, m), 1.37 (1H, td, J = 3.7, 11.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 152.3, 131.6, 130.0, 128.3, 122.0, 117.4, 69.1, 56.5, 24.0, 21.4; LRMS (EI) m/z: 187 (M^+); HRMS (EI-EB) m/z: (M^+) Calcd. for $C_{12}H_{13}NO$: 187.0997, found: 187.0990.

5. General Procedure for the Synthesis of Phenazines

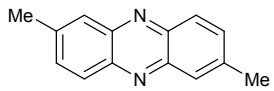
Under an Ar atmosphere, a mixture of **2'** (0.40 mmol, 0.23 g) and NaH (60% dispersion in paraffin oil, 0.80 mmol, 33 mg) in DMF (2.9 mL) was stirred at rt for 1 h. After the SED generated, 2-fluoronitrobenzene (0.20 mmol) was added to the mixture and stirred at rt for 15 min. The reaction mixture was quenched with H_2O at 0 °C and extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed by water (30 mL × 3) and brine (30 mL), and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to give the phnazine **11**.

Phenazine (11a)



Obtained in 68% yield (12.1 mg); Recrystallized from CH_2Cl_2/hexane, yellow prisms, mp 177–179 °C (lit.[9] 172–175 °C); IR (neat, cm^{-1}): 3060, 1627, 1513, 1472, 1431, 1361, 1210, 1147, 1109, 997, 957, 903, 858, 820, 741; ^1H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 8.28–8.25 (4H, m), 7.87–7.84 (4H, m); ^{13}C NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 143.6, 130.5, 129.7; LRMS (EI) m/z: 180 (M^+); HRMS (EI-TOF) m/z: (M^+) Calcd. for $C_{12}H_8N_2$: 180.0687, found: 180.0702.

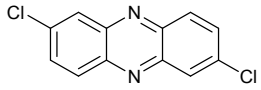
2,7-Dimethylphenazine (11b)



Obtained as orange solid (**10b**: 30% yield, 6.3 mg, **10b'**: 22% yield, 4.6 mg); mp 169–170 °C (lit.[9] 161–163 °C); IR (neat, cm^{-1}): 2970, 2944, 2910, 1639, 1515, 1507, 1481, 1449, 1418, 1379, 1356,

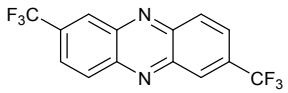
1133, 1037, 1009, 881, 874, 863, 801, 768, 749; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.12 (2H, d, J = 8.8 Hz), 7.97 (2H, s), 7.67–7.65 (2H, m), 2.65 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 143.2, 142.3, 140.5, 133.3, 129.0, 127.7, 22.2; LRMS (EI) *m*/*z*: 208 (M^+); HRMS (EI-TOF) *m*/*z*: (M^+) Calcd. for $C_{14}H_{12}N_2$: 208.1000, found: 208.1000.

2,7-Dichlorophenazine (11c)



10c: 43% yield, 10.7 mg, **10c'**: 45% yield, 11.2 mg; Recrystallized from methanol/hexane, yellow prisms; IR (neat, cm^{-1}): 3054, 1924, 1773, 1618, 1506, 1458, 1412, 1399, 1373, 1351, 1320, 1285, 1258, 1180, 1166, 1127, 1067, 1049, 951, 935, 921, 884, 855, 846, 809, 740, 730; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.24 (2H, d, J = 2.2 Hz), 8.18 (2H, d, J = 9.3 Hz), 7.80 (2H, dd, J = 2.2, 9.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 143.3, 142.3, 136.9, 132.6, 130.9, 128.1; LRMS (EI) *m*/*z*: 248 (M^+); HRMS (EI-TOF) *m*/*z*: (M^+) Calcd. for $C_{12}H_6{}^{35}Cl_2N_2$: 247.9908, found: 247.9920.

2,7-*Bis*(trifluoromethyl)phenazine (11d)



Obtained in 28% yield as yellow solid (8.6 mg); mp 119–122 °C; IR (neat, cm^{-1}): 3031, 1517, 1487, 1428, 1326, 1288, 1256, 1206, 1162, 1139, 1130, 1046, 984, 935, 915, 892, 856, 836, 807, 771, 755; ^{1}H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 8.63 (2H, s), 8.43 (2H, d, J = 8.9 Hz), 8.04 (2H, dd, 1.4, 8.9 Hz); ^{13}C NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 144.4, 143.1, 133.1 (q, J_{FC} = 33.0 Hz), 131.5, 128.2 (q, J_{FC} = 5.7 Hz), 126.5, 123.4 (q, J_{FC} = 272.5 Hz); LRMS (EI) *m*/*z*: 316 (M^+); HRMS (EI-EB) *m*/*z*: (M^+) Calcd. for $C_{14}H_6F_6N_2$: 316.0435, found: 316.0433.

6. References

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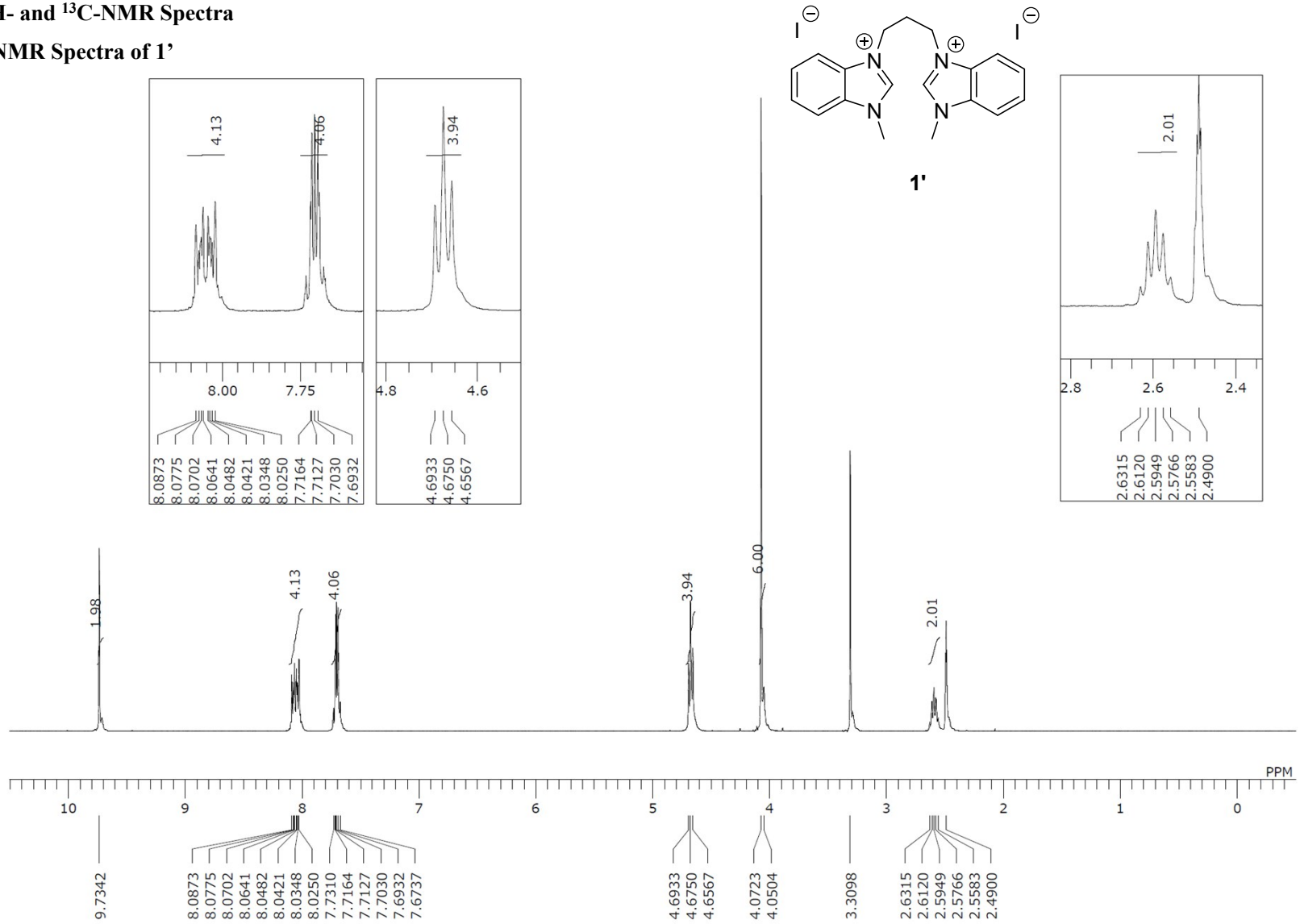
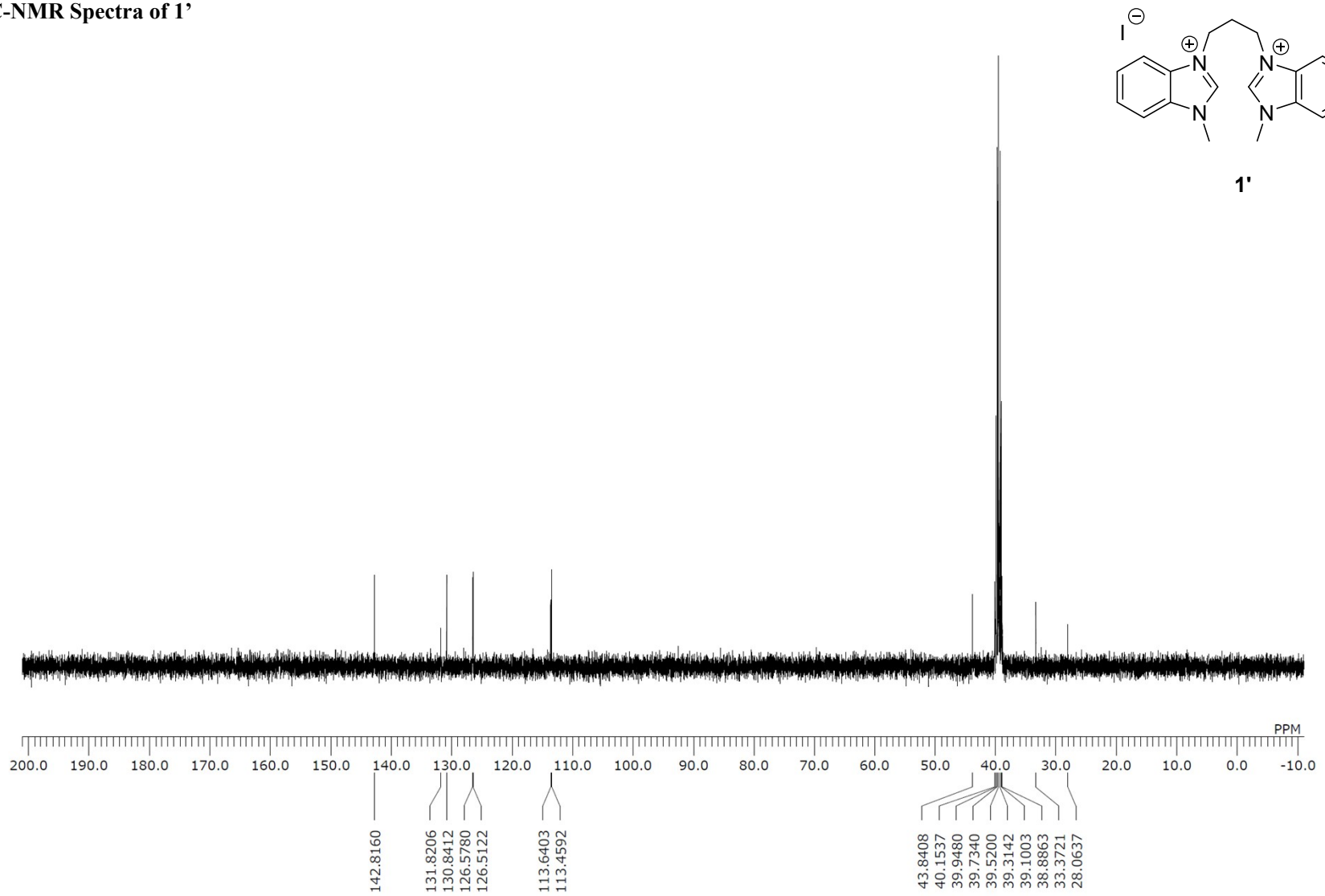
7. ^{1}H- and ^{13}C-NMR Spectra

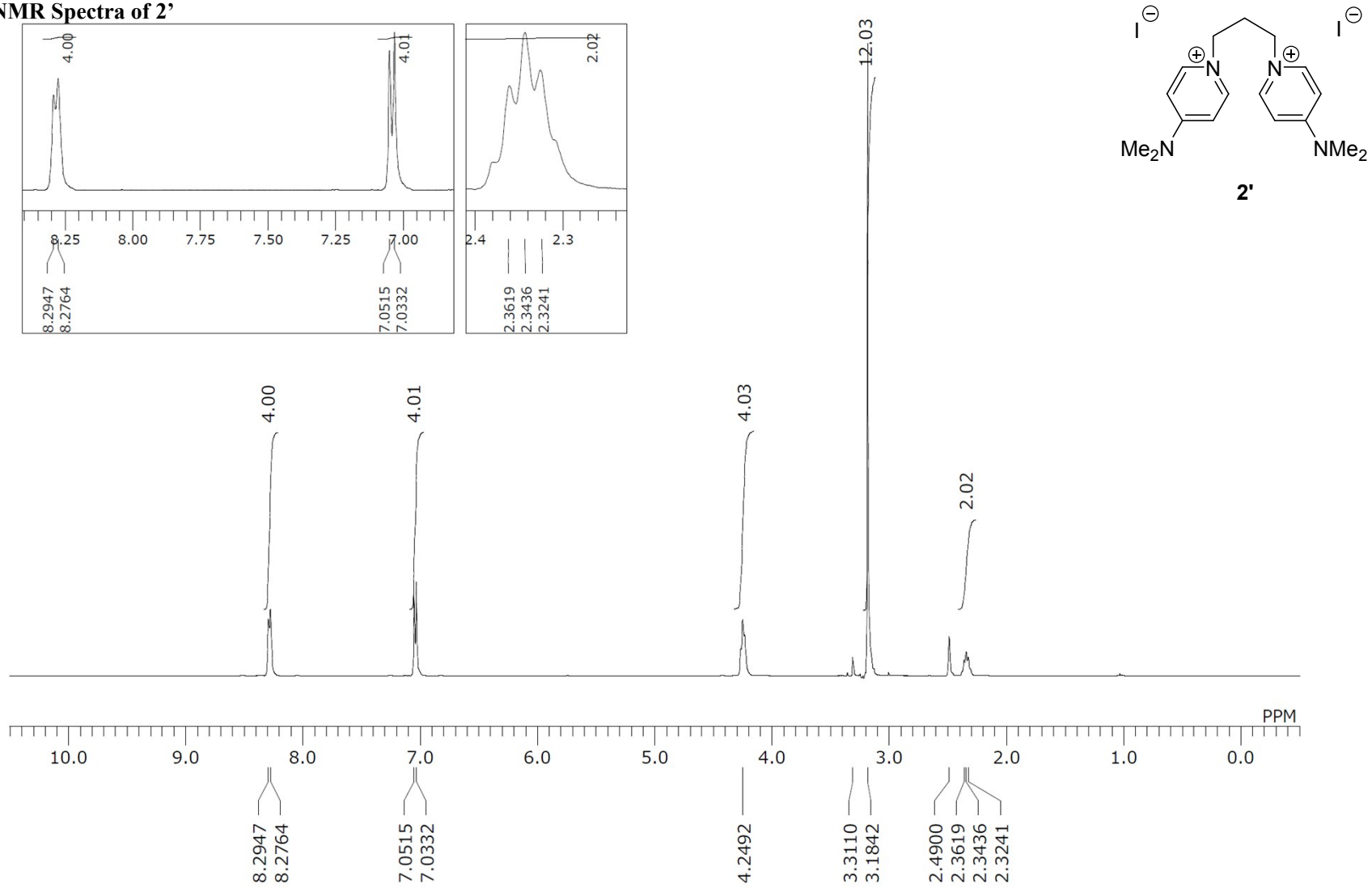
^{1}H-NMR Spectra of 1’



^{13}C-NMR Spectra of 1'

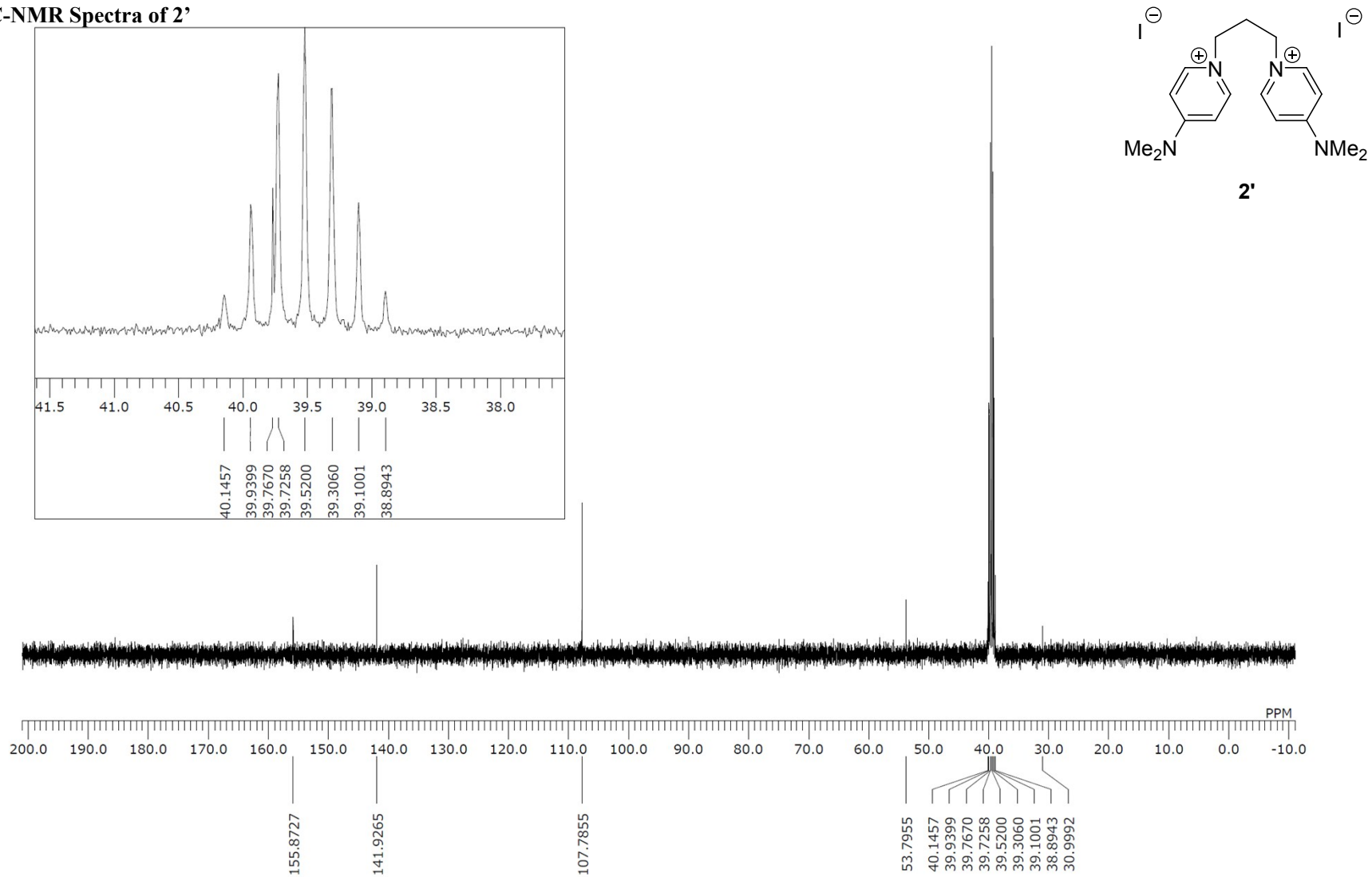


^{1}H-NMR Spectra of 2'

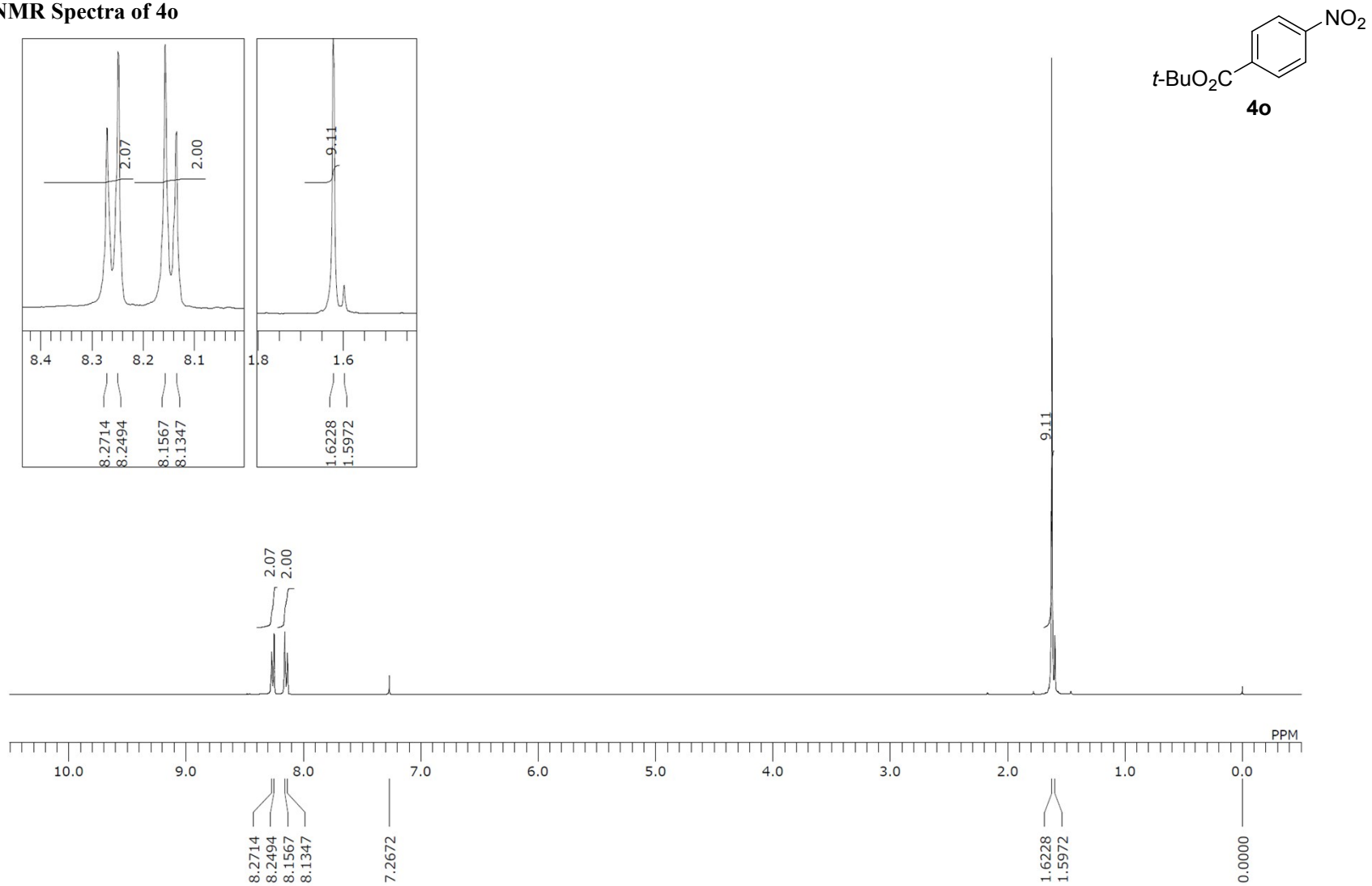


2'

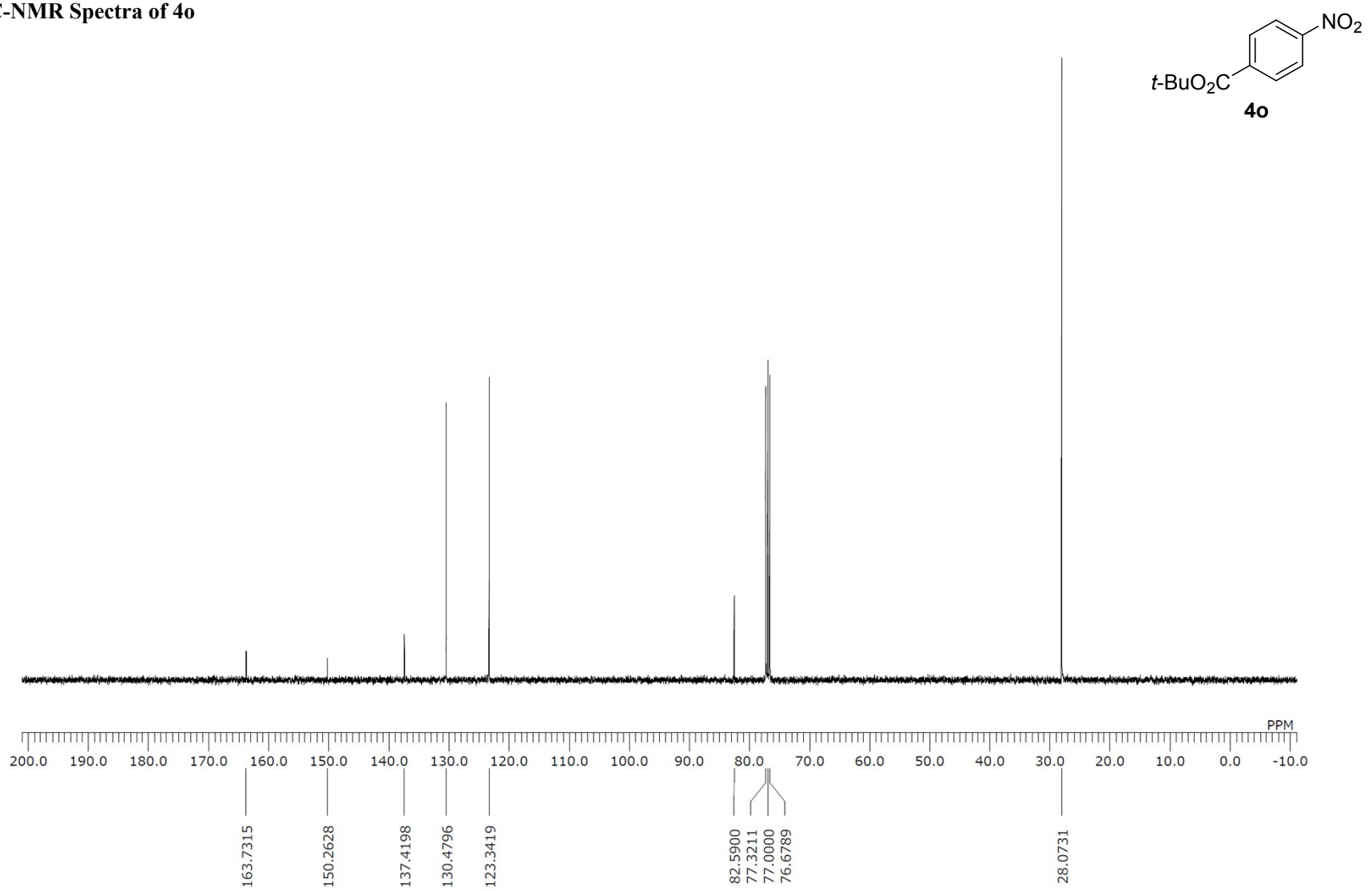
^{13}C-NMR Spectra of 2'



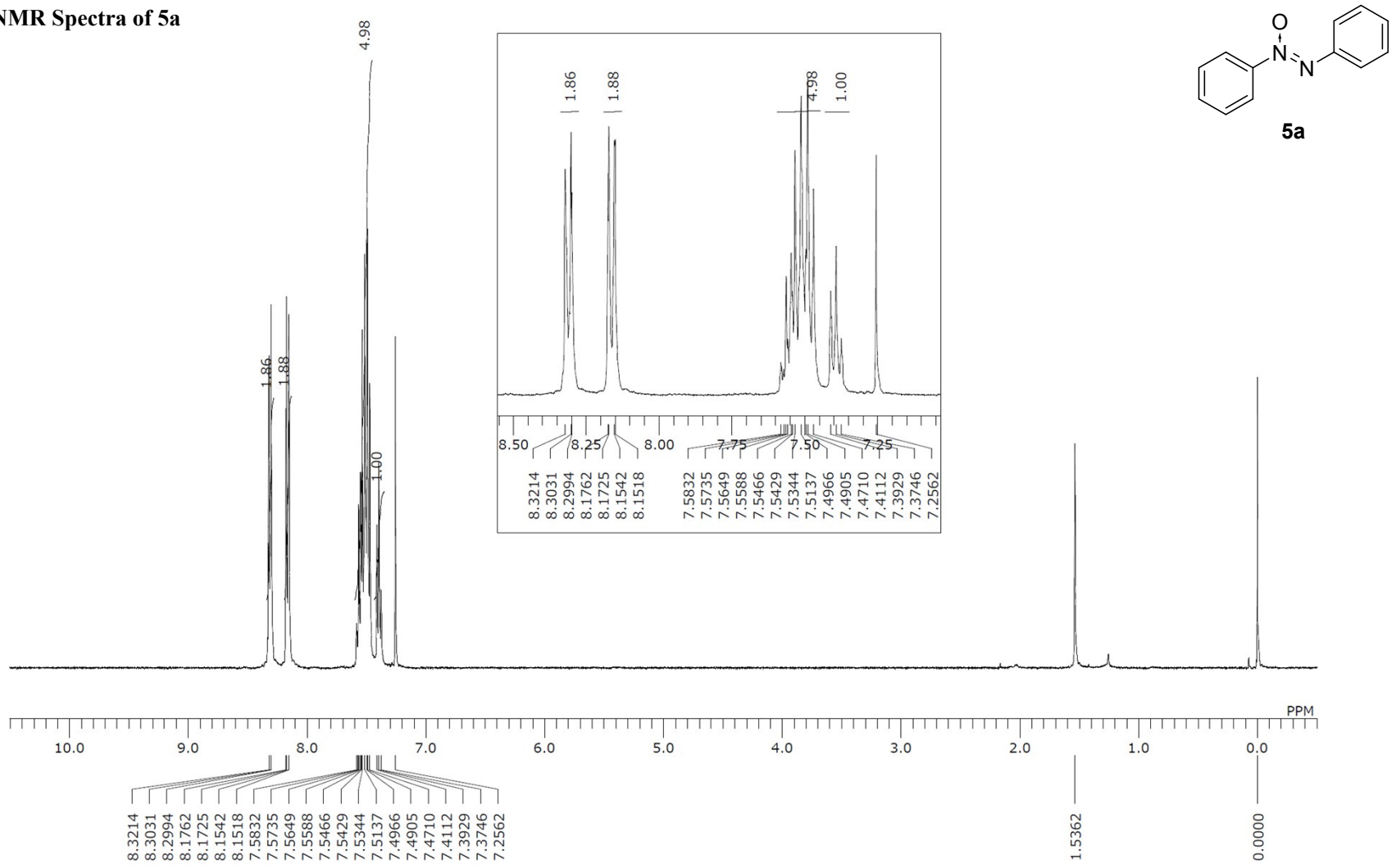
[1]H-NMR Spectra of 4o



^{13}C-NMR Spectra of 4o

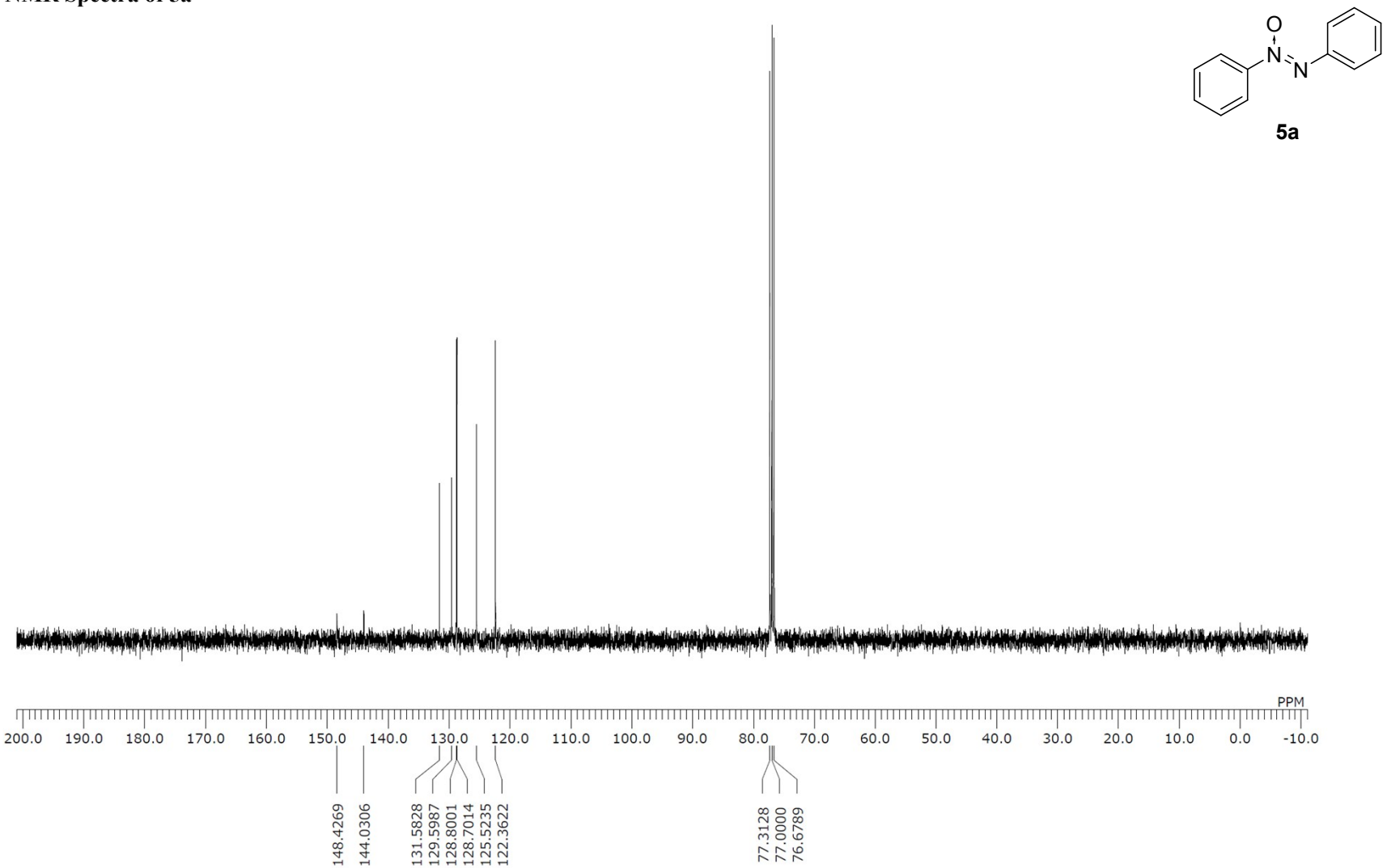


[1]H-NMR Spectra of 5a

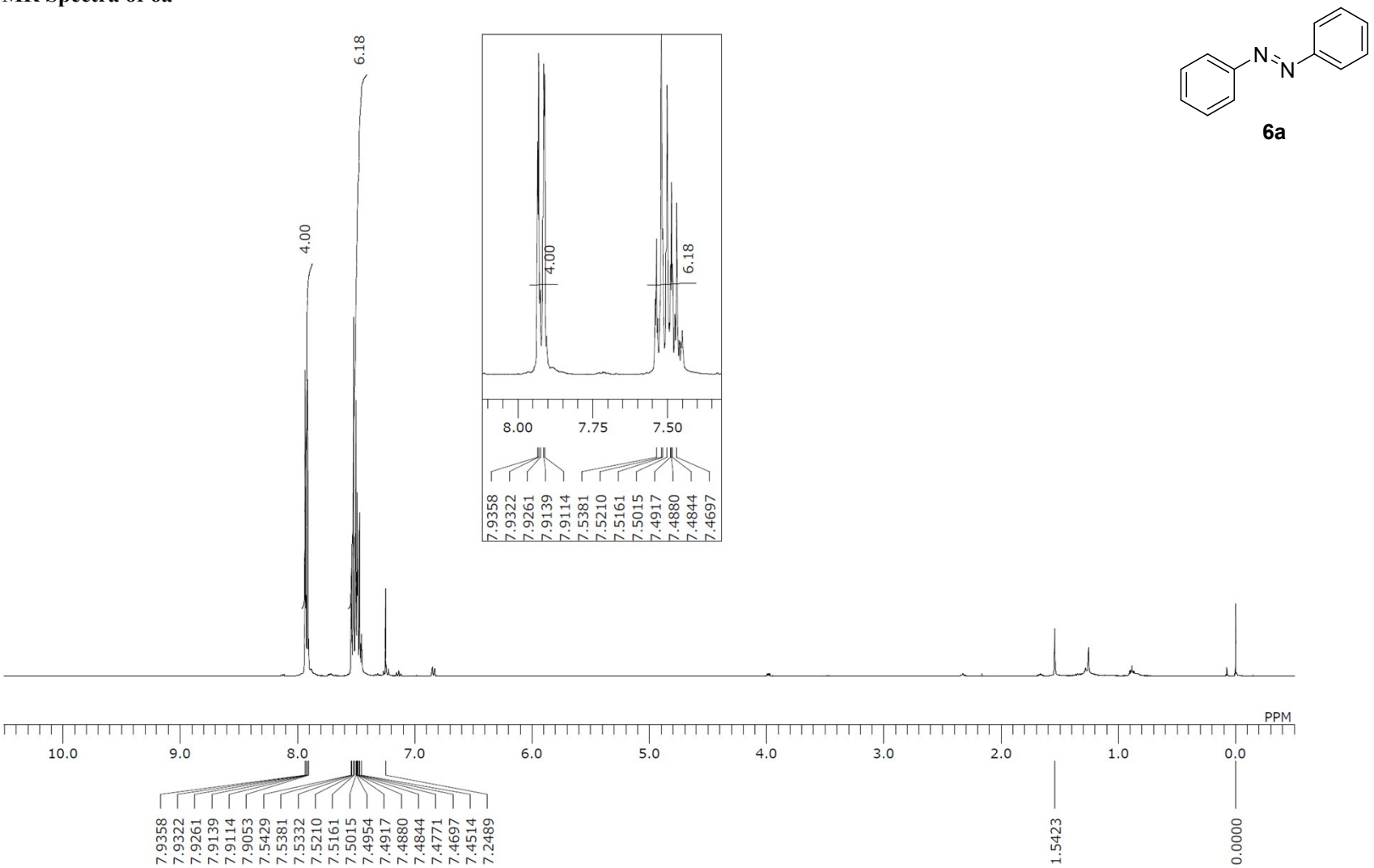


5a

^{13}C-NMR Spectra of 5a

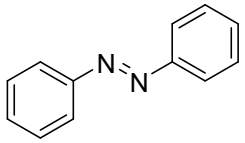


[1]H-NMR Spectra of 6a

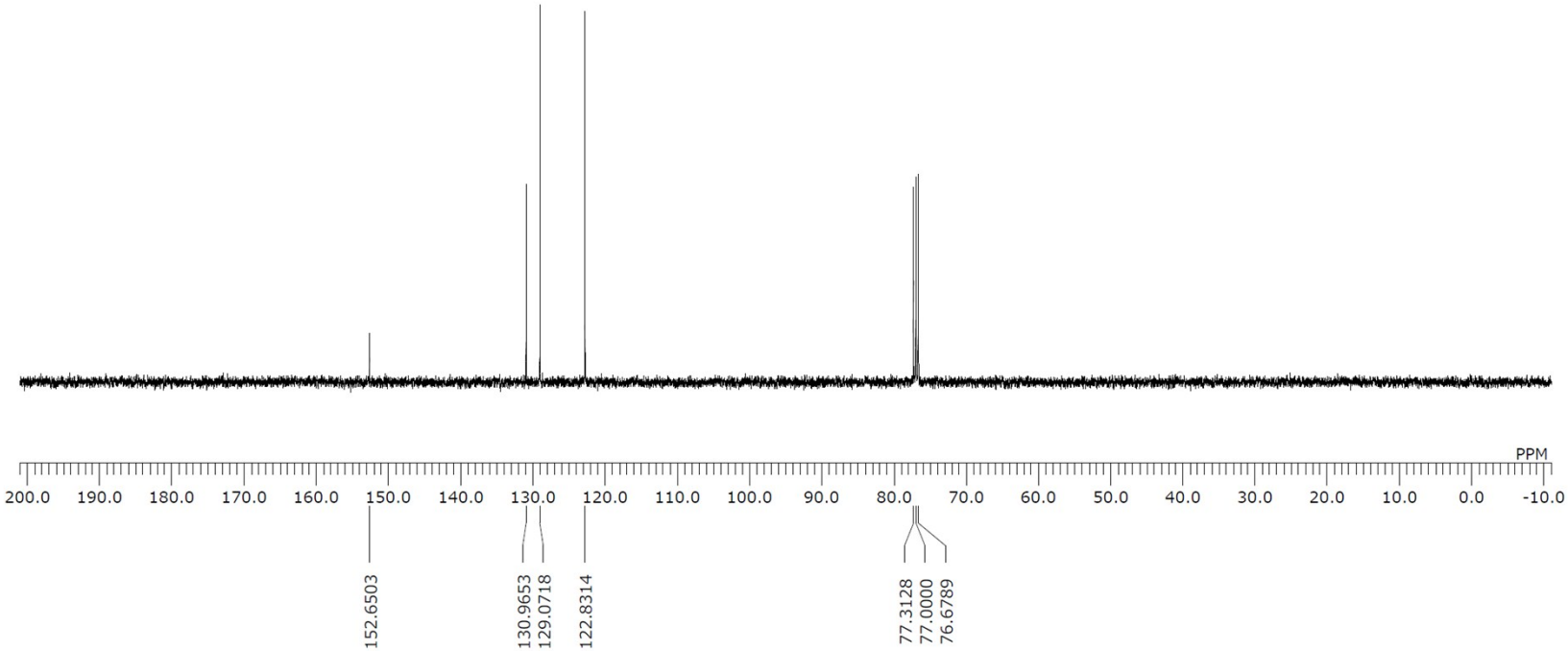


6a

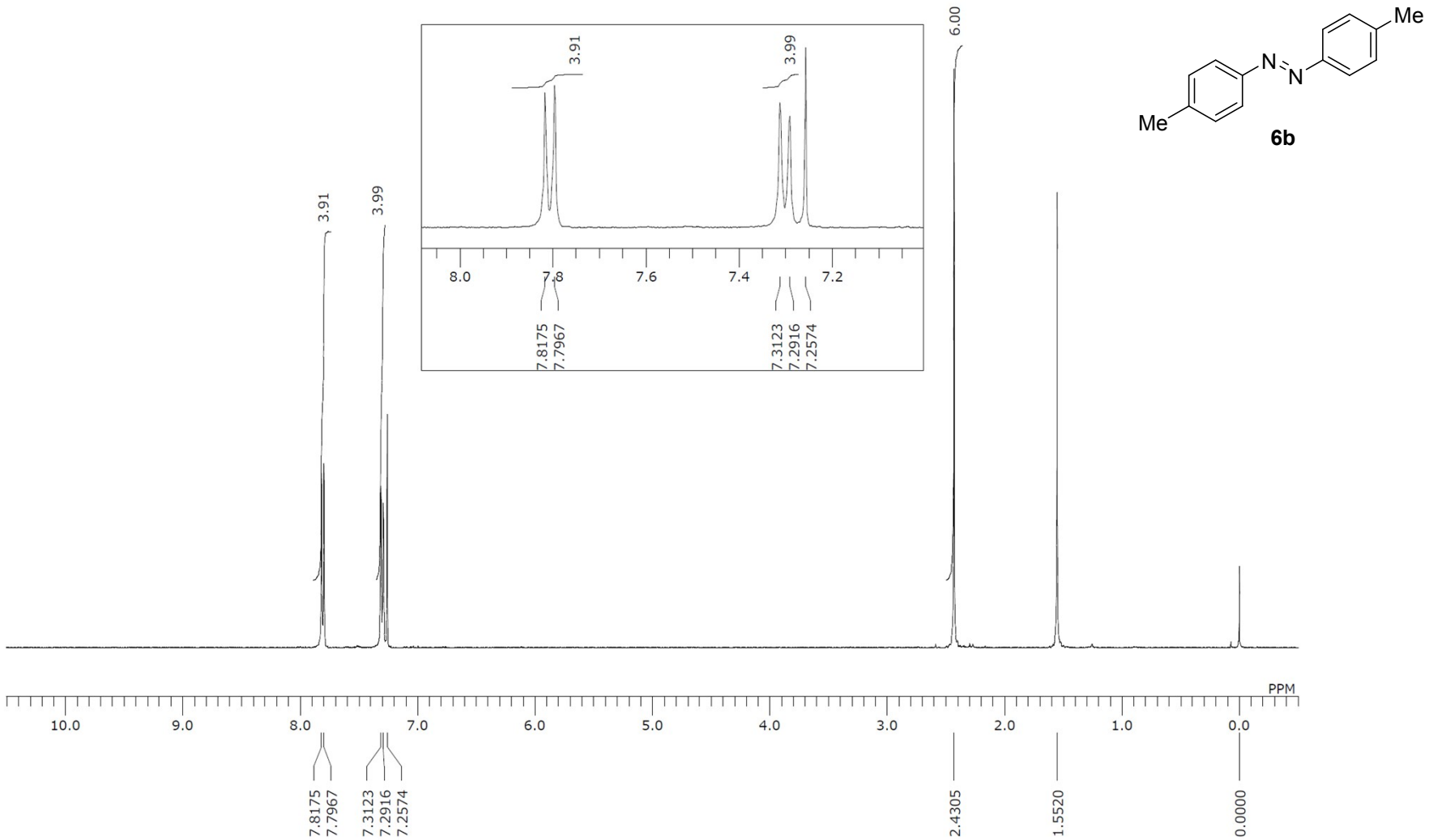
^{13}C-NMR Spectra of 6a



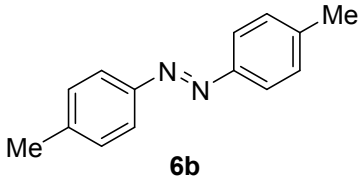
6a



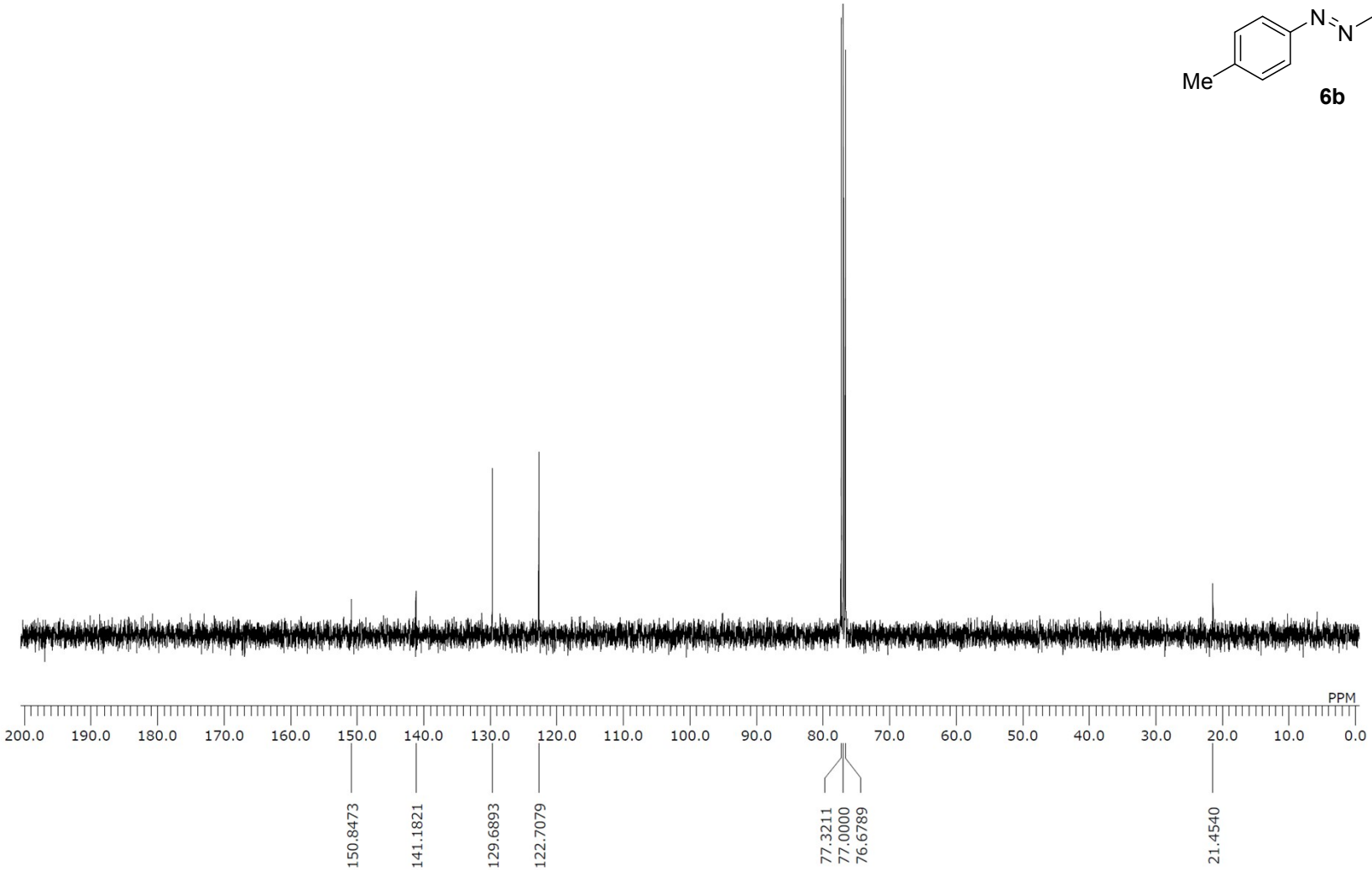
[1]H-NMR Spectra of 6b



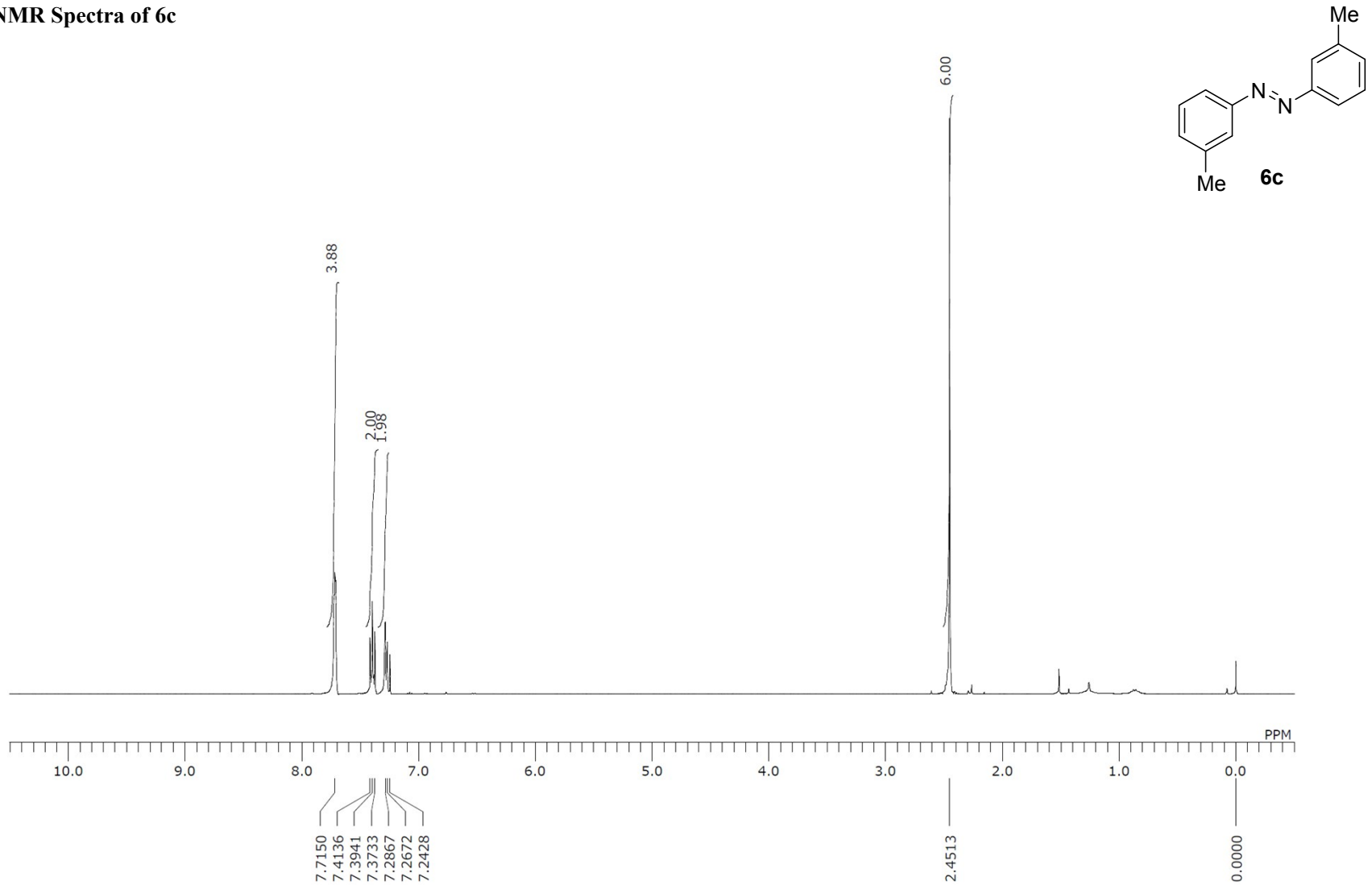
^{13}C-NMR Spectra of 6b



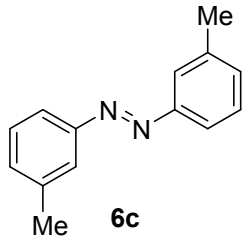
6b



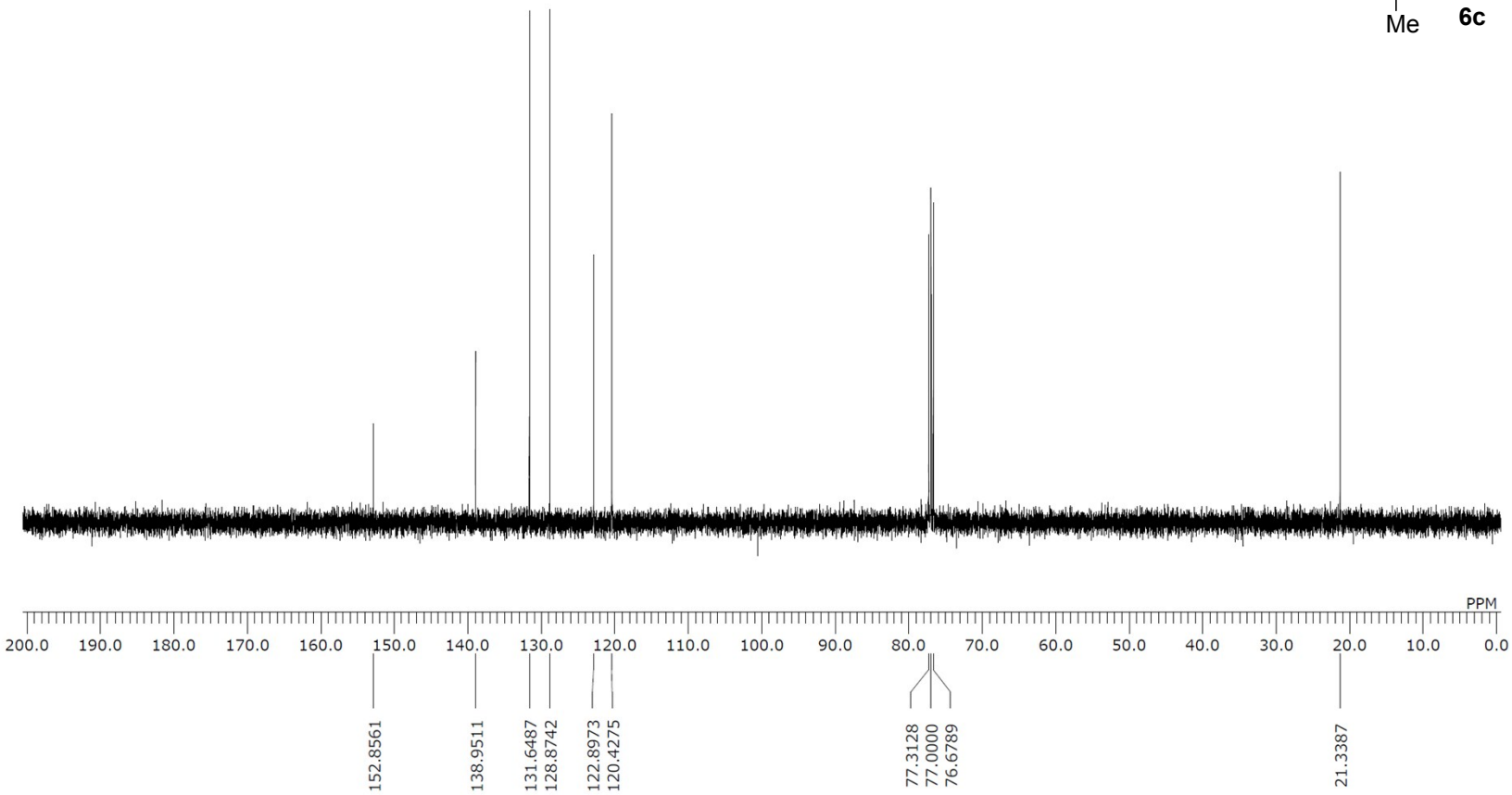
[1]H-NMR Spectra of 6c



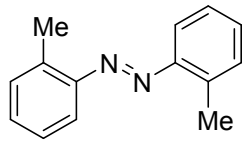
^{13}C-NMR Spectra of 6c



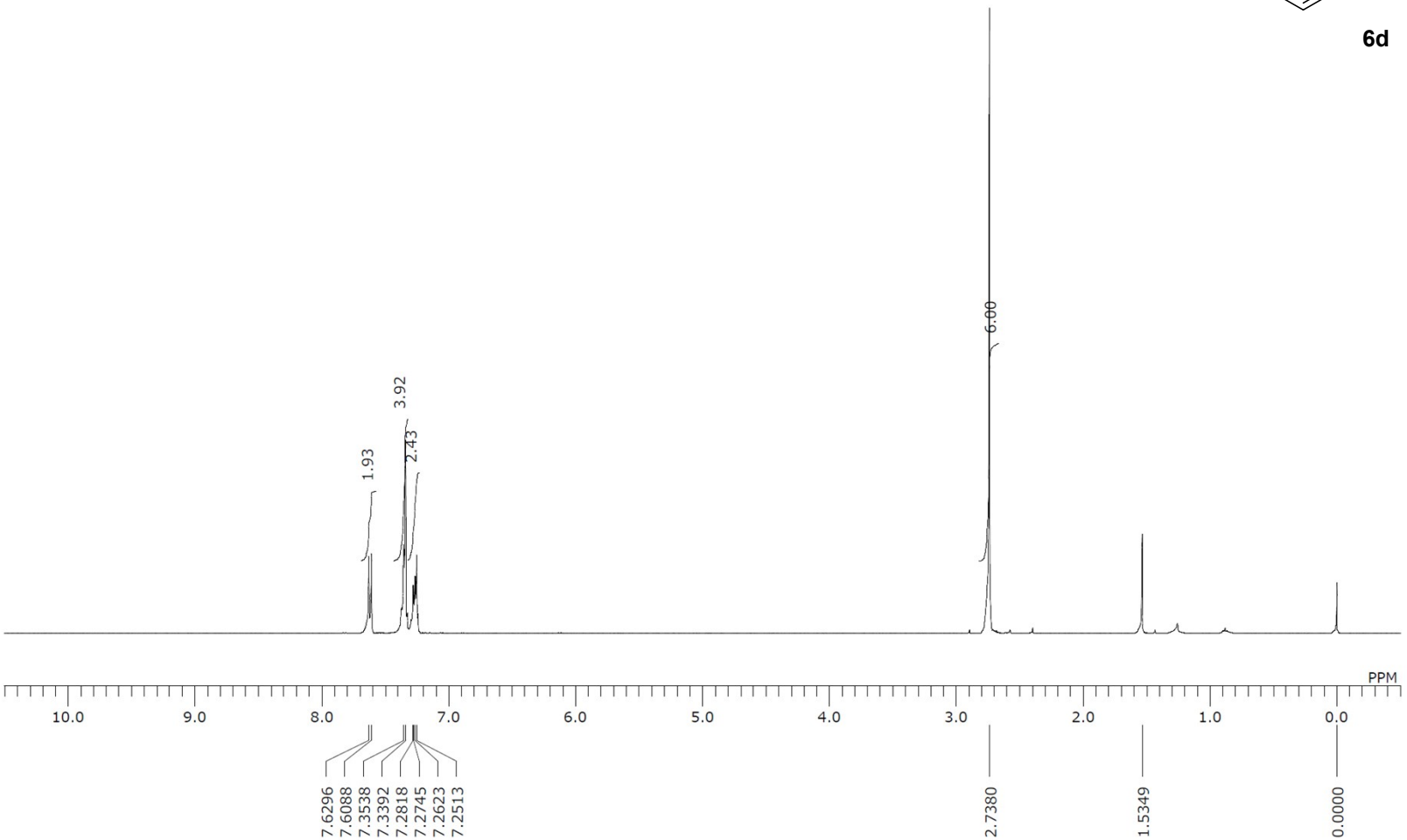
6c



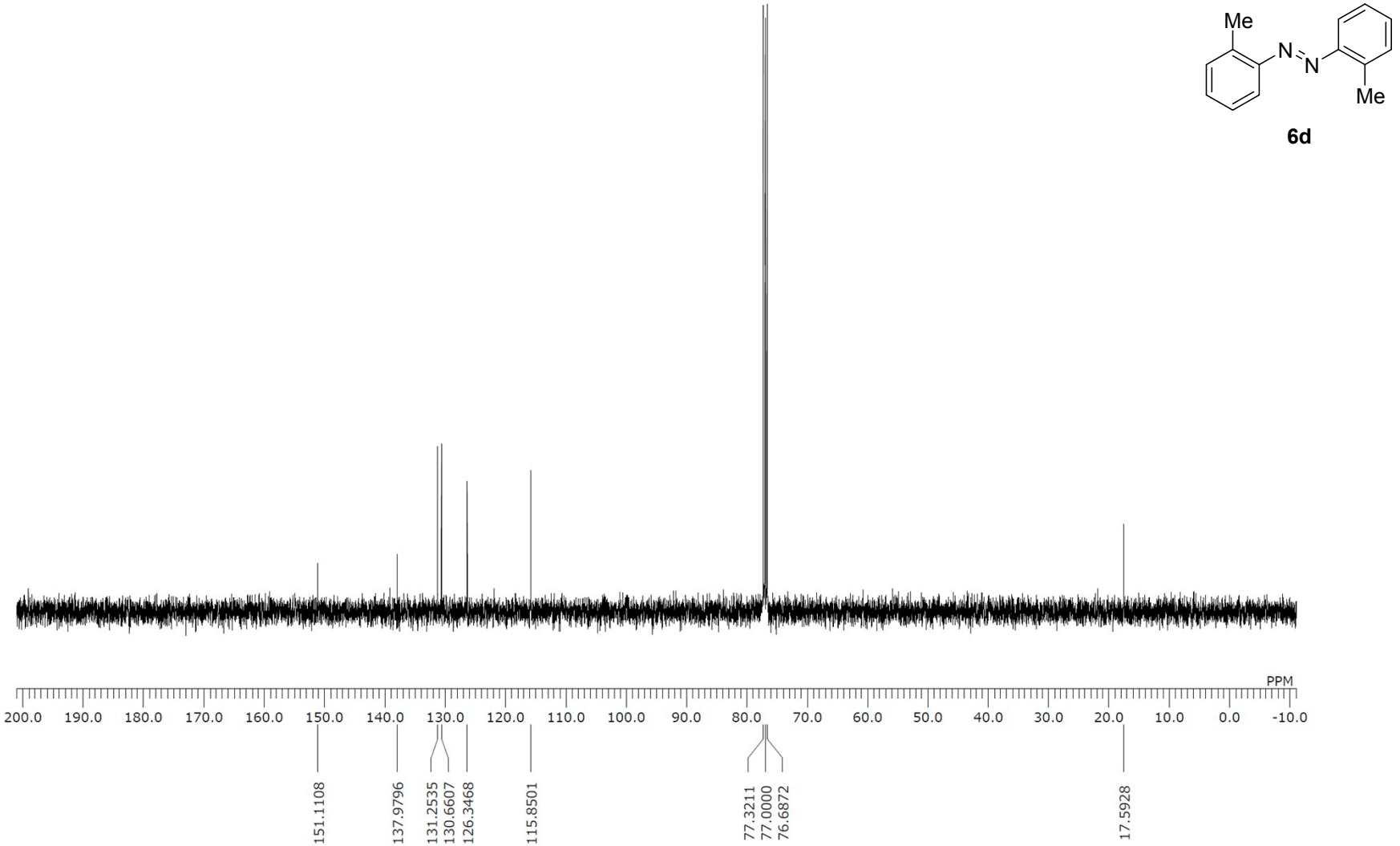
[1]H-NMR Spectra of 6d



6d



^{13}C-NMR Spectra of 6d



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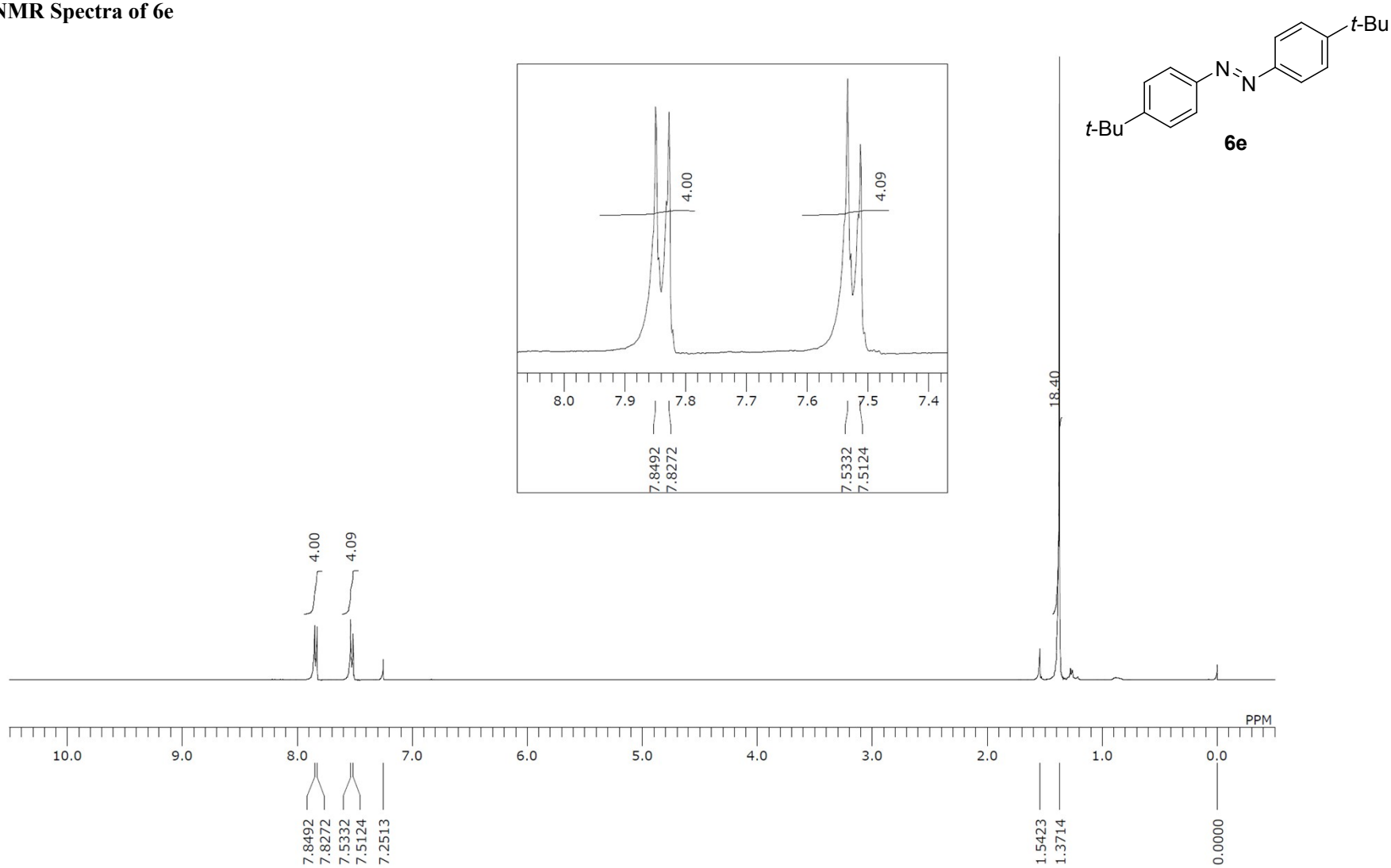
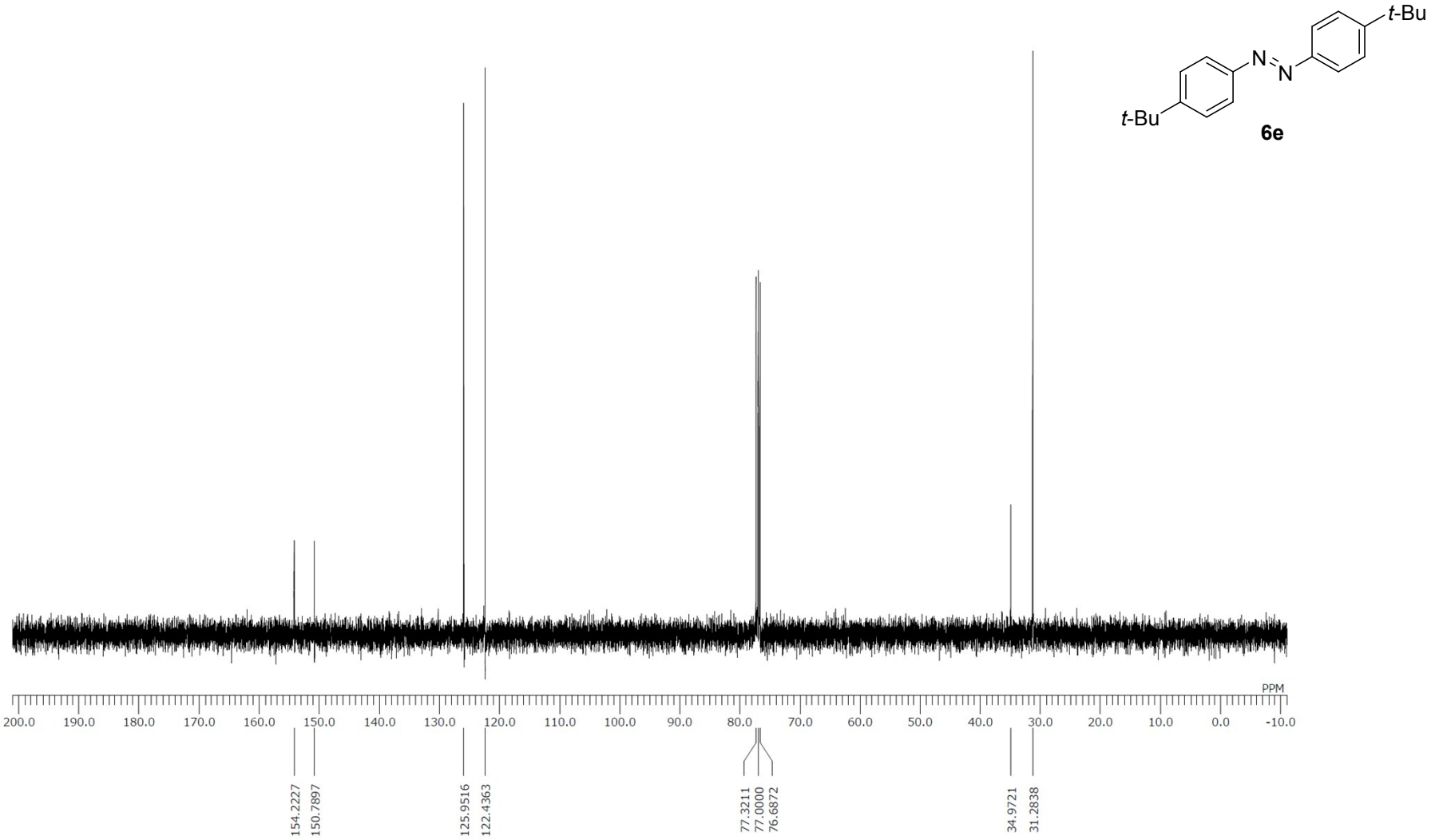
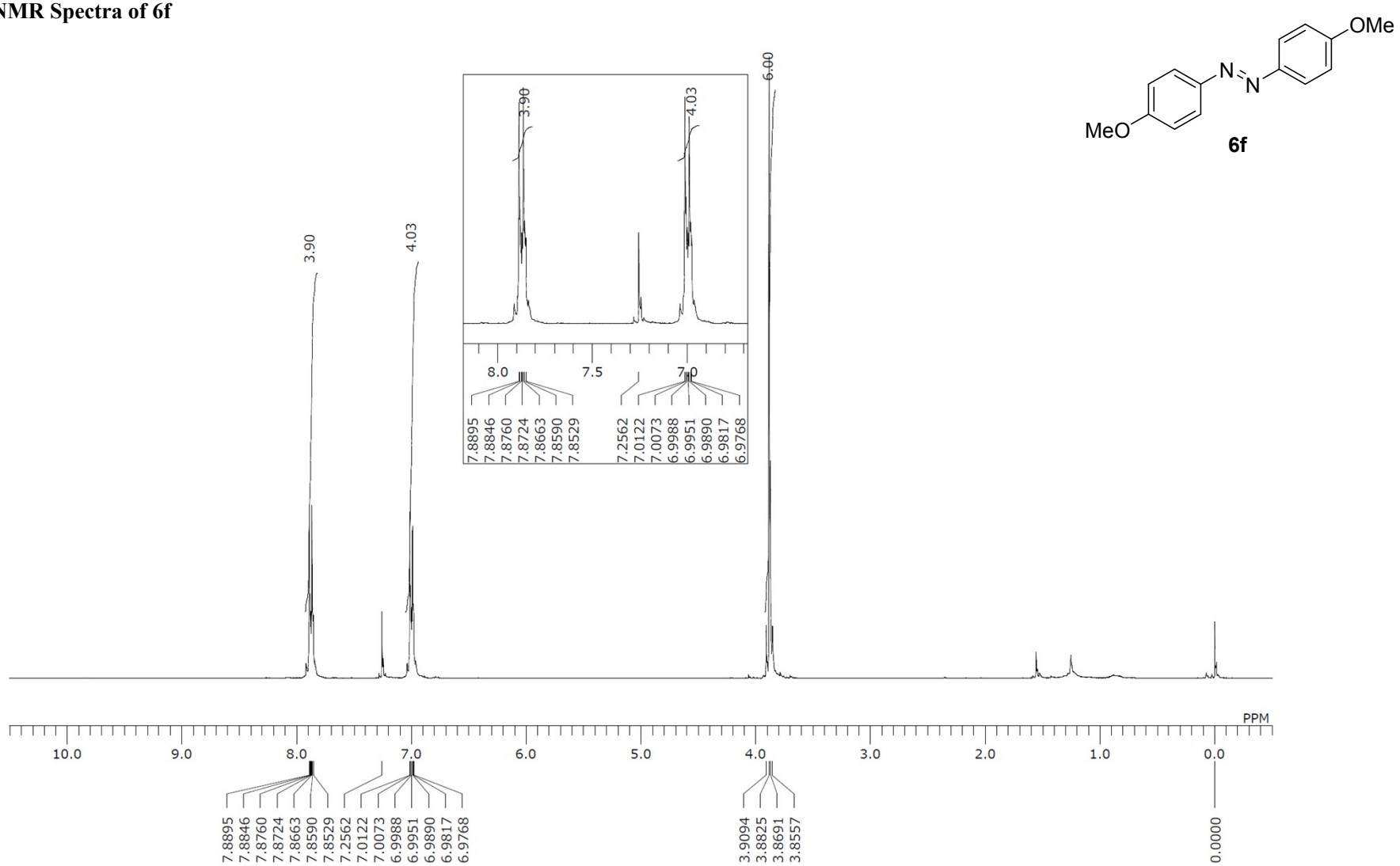


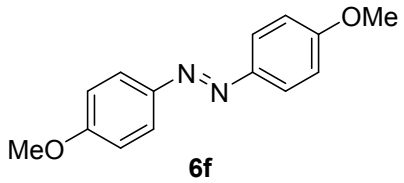
^{13}C-NMR Spectra of 6e



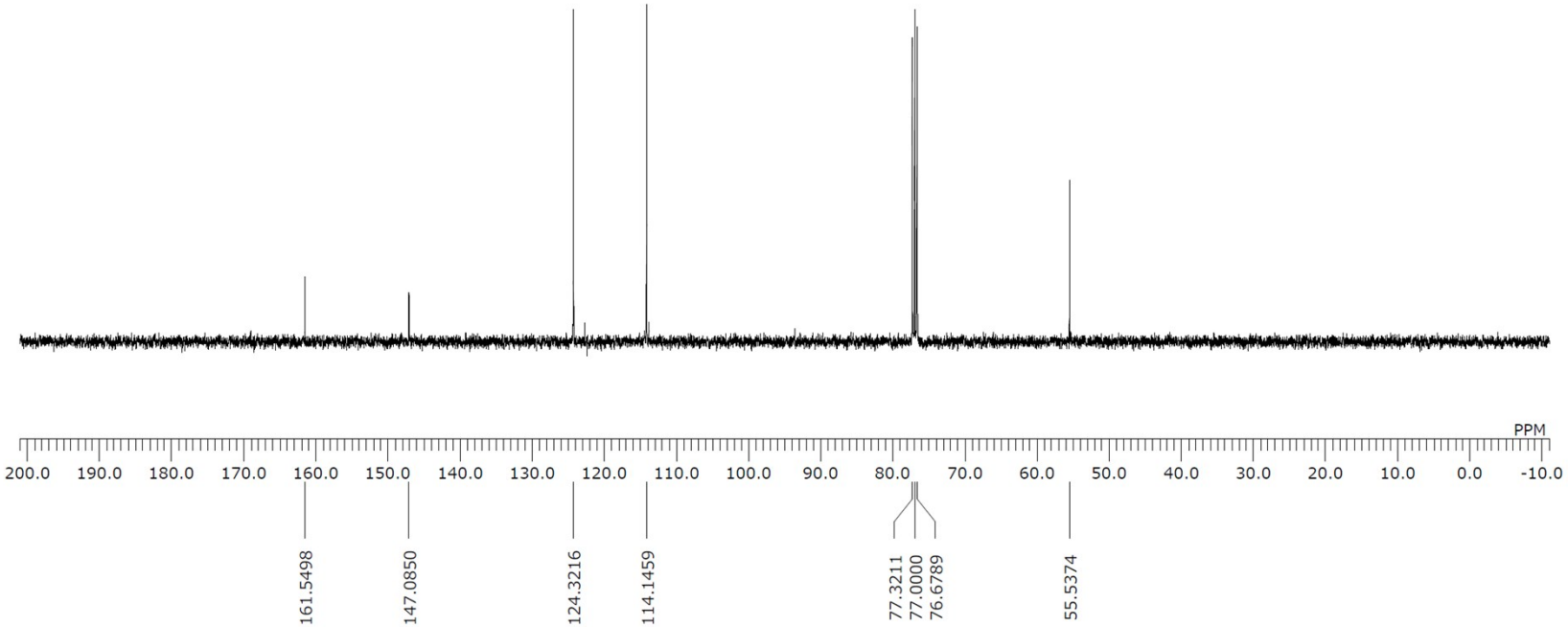
[1]H-NMR Spectra of 6f



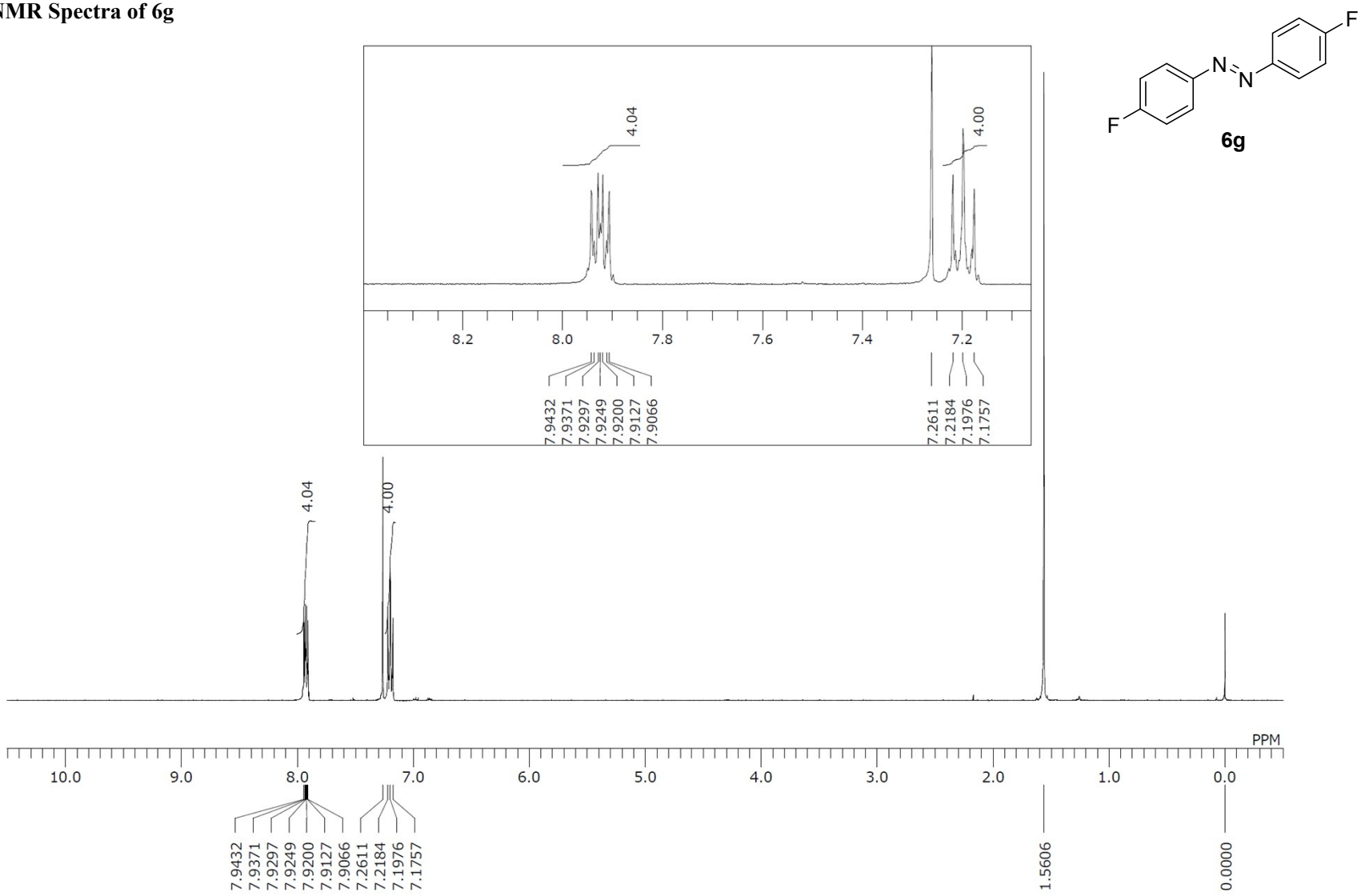
^{13}C-NMR Spectra of 6f



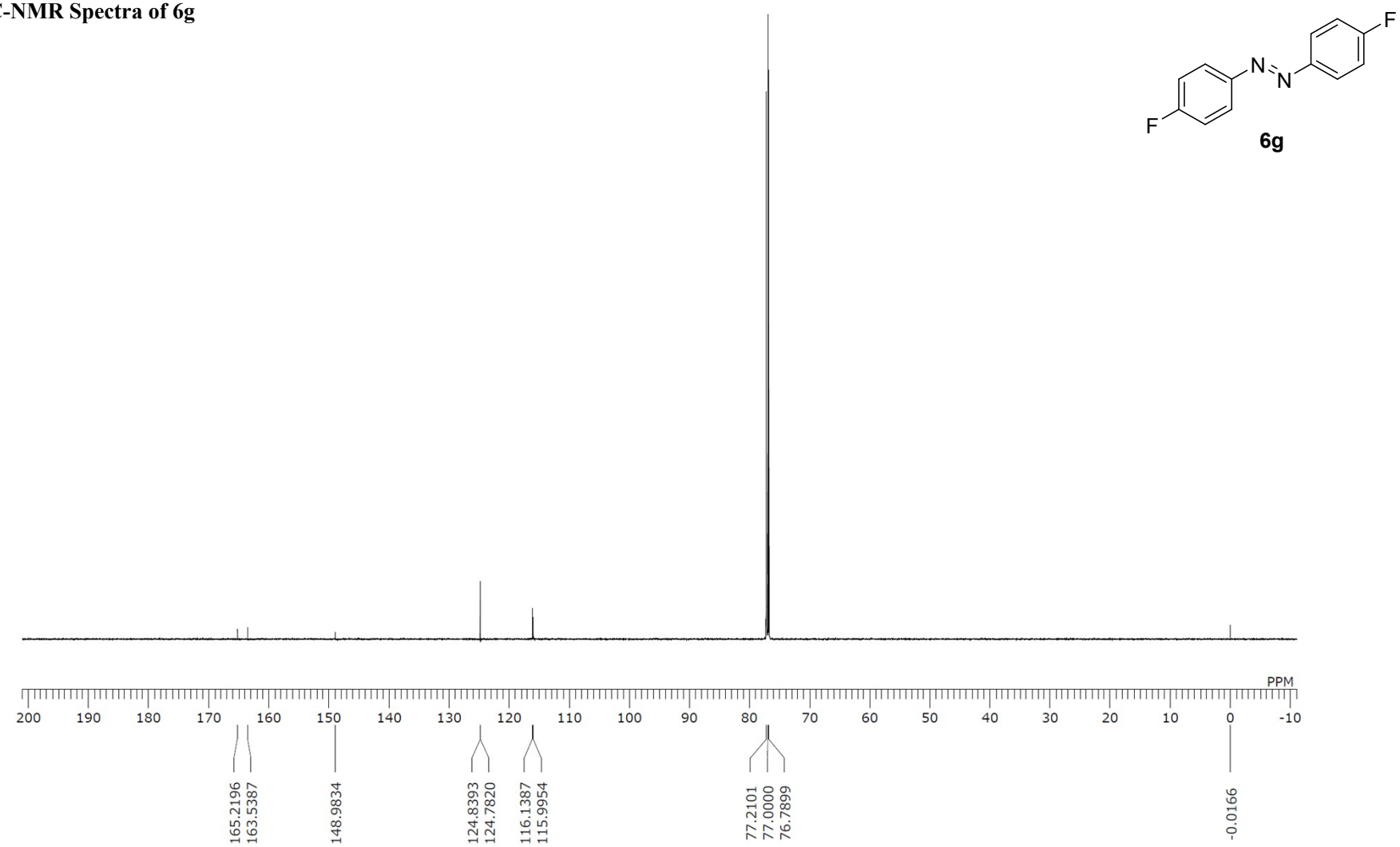
6f



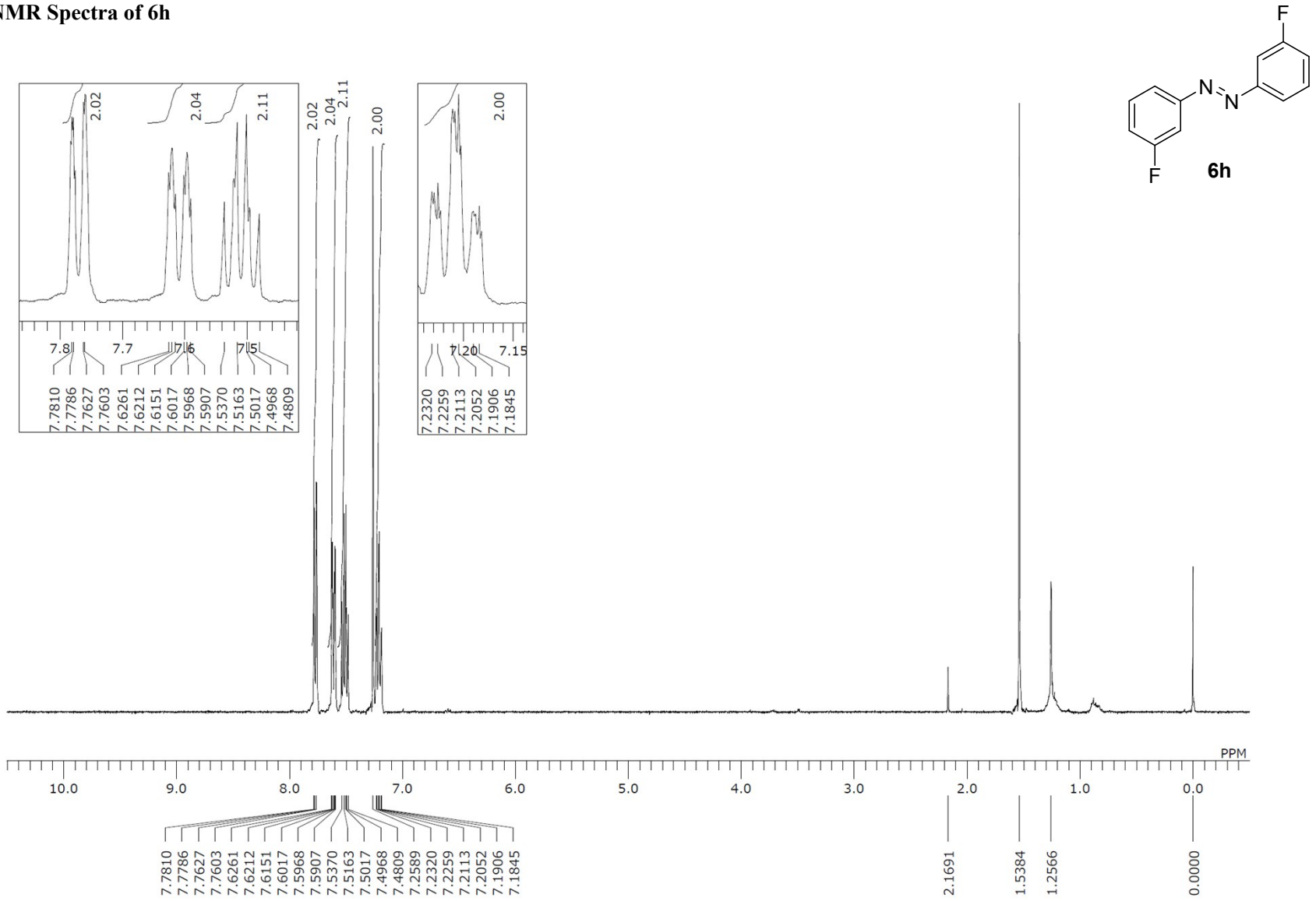
[1]H-NMR Spectra of 6g



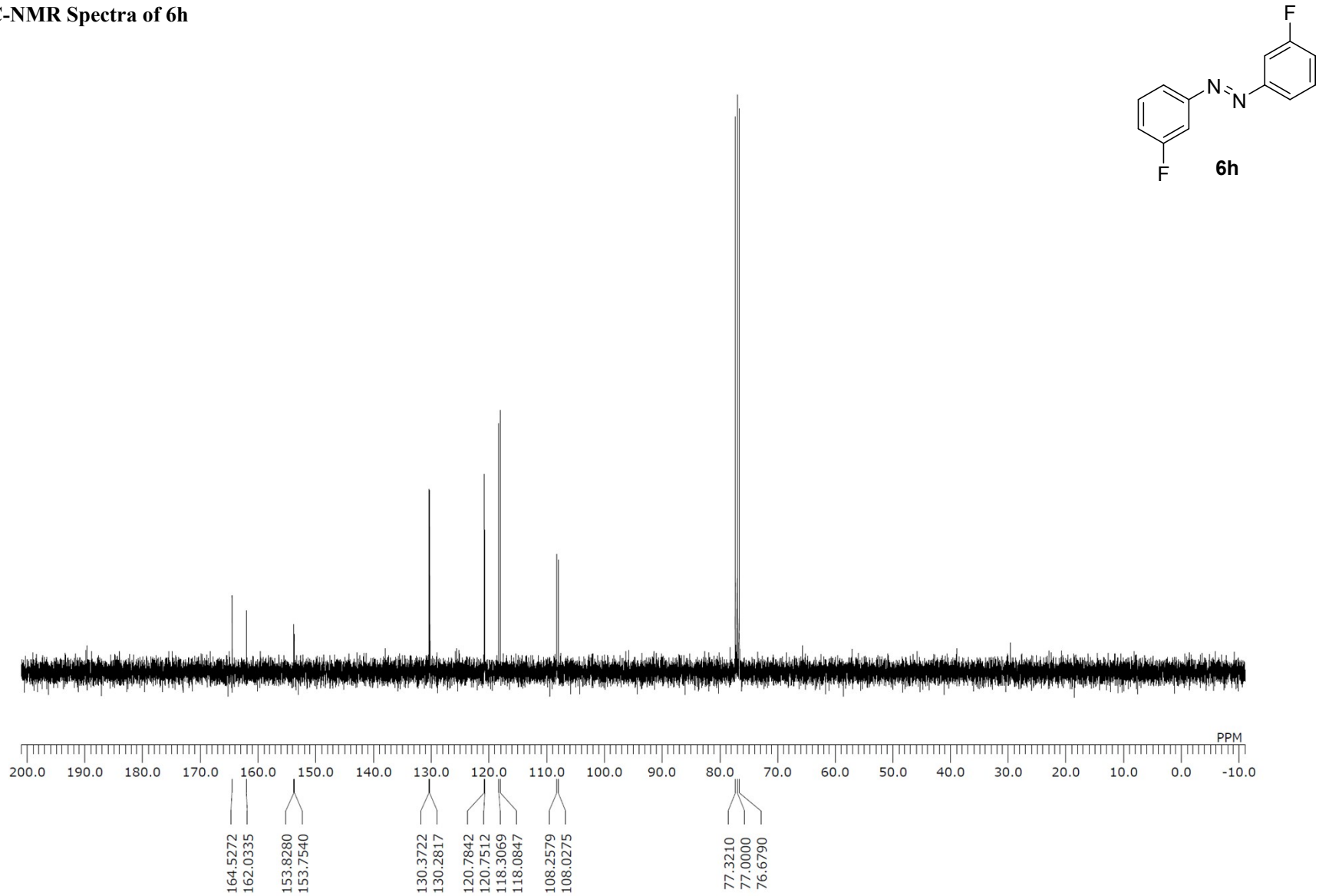
^{13}C-NMR Spectra of 6g



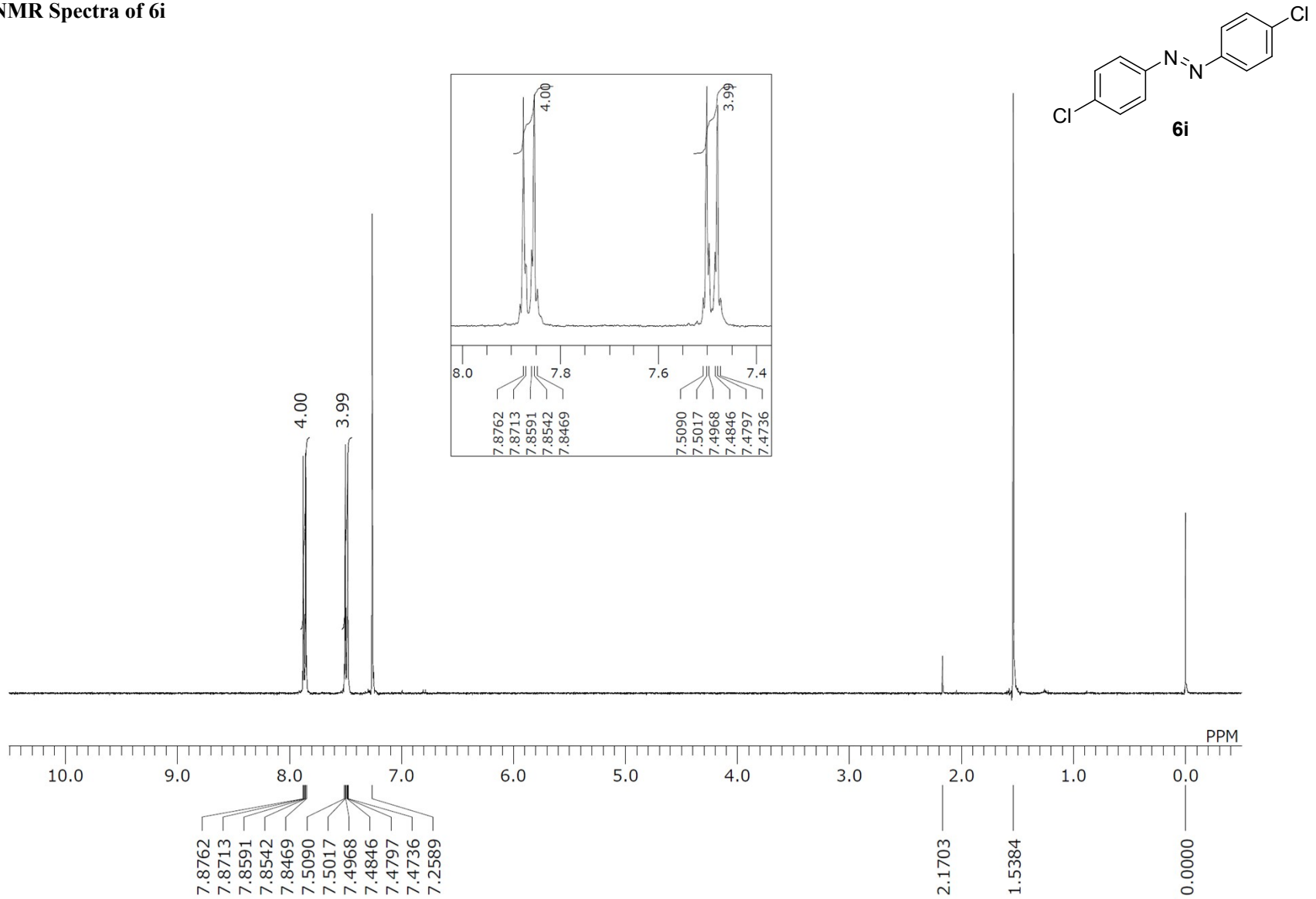
[1]H-NMR Spectra of 6h



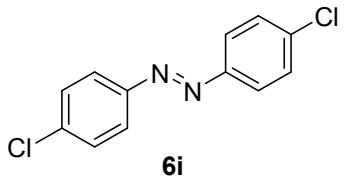
^{13}C-NMR Spectra of 6h



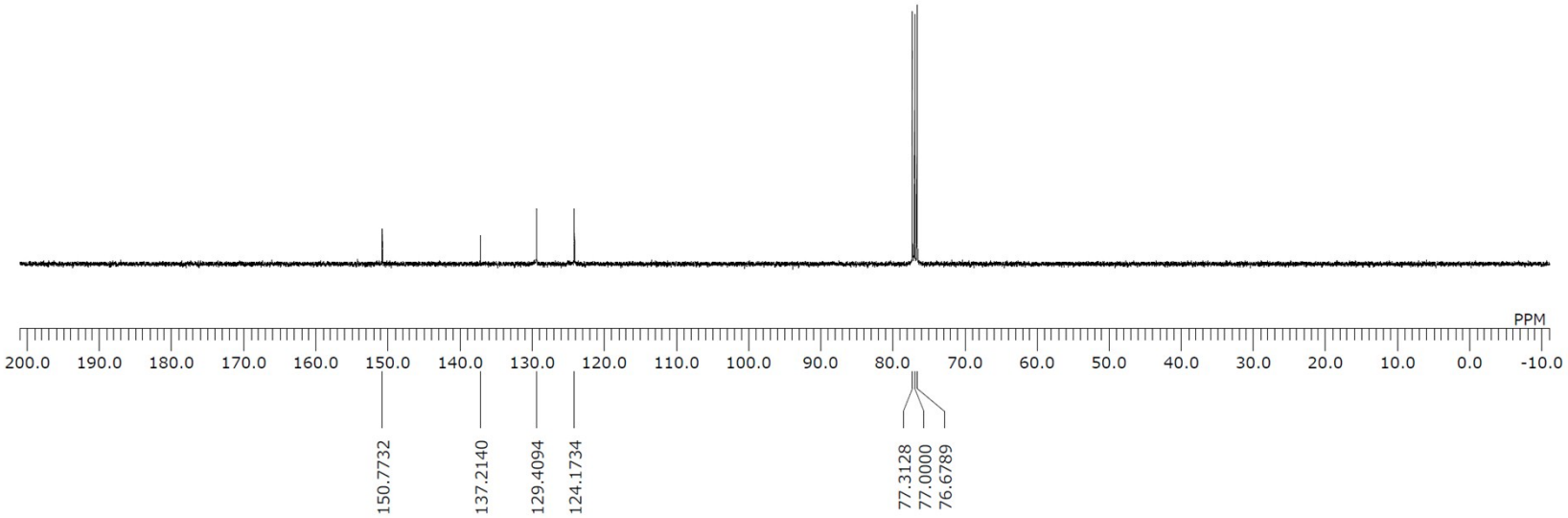
[1]H-NMR Spectra of 6i



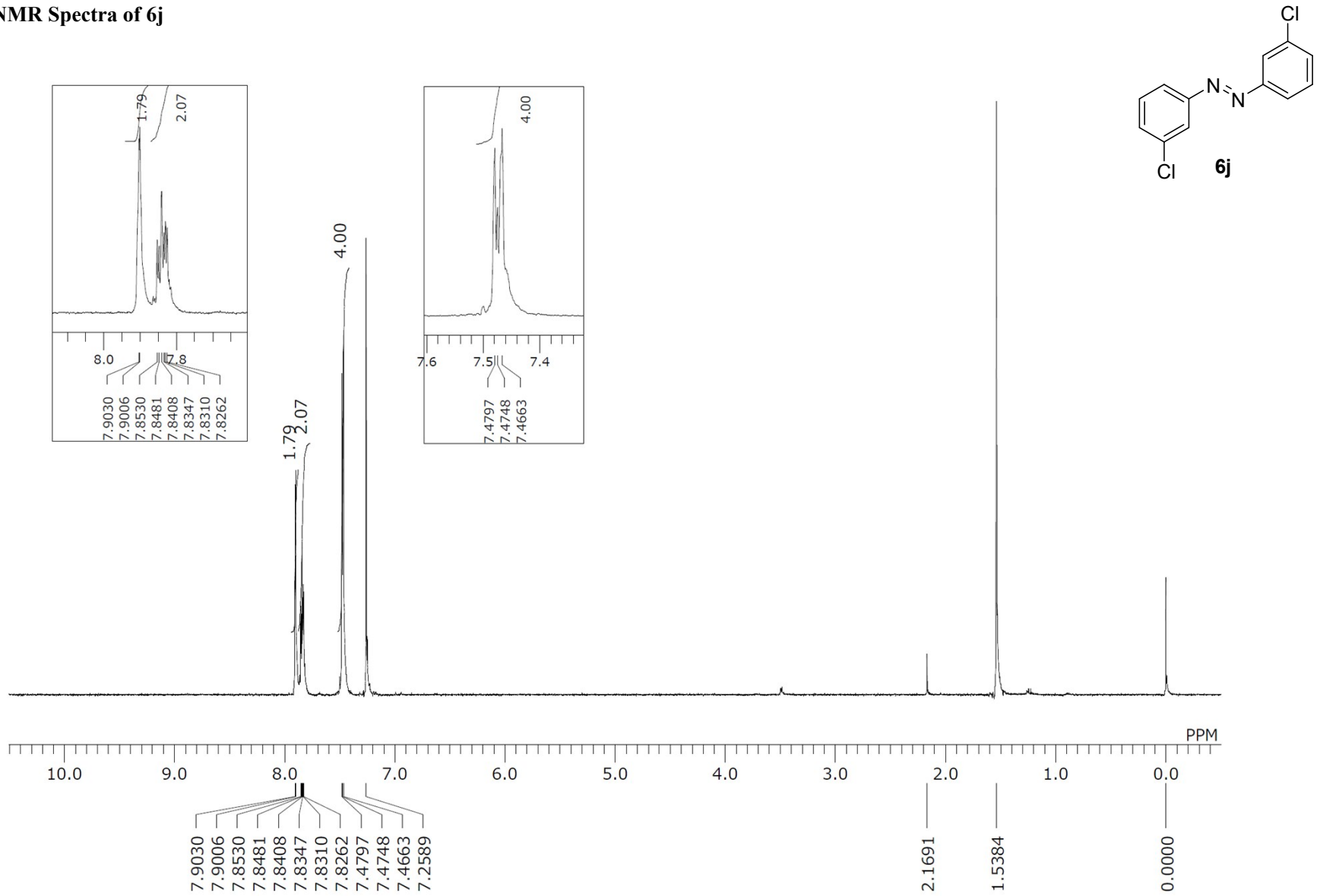
^{13}C-NMR Spectra of 6i



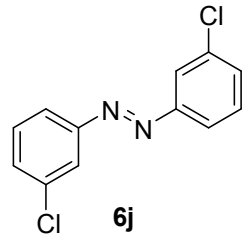
6i



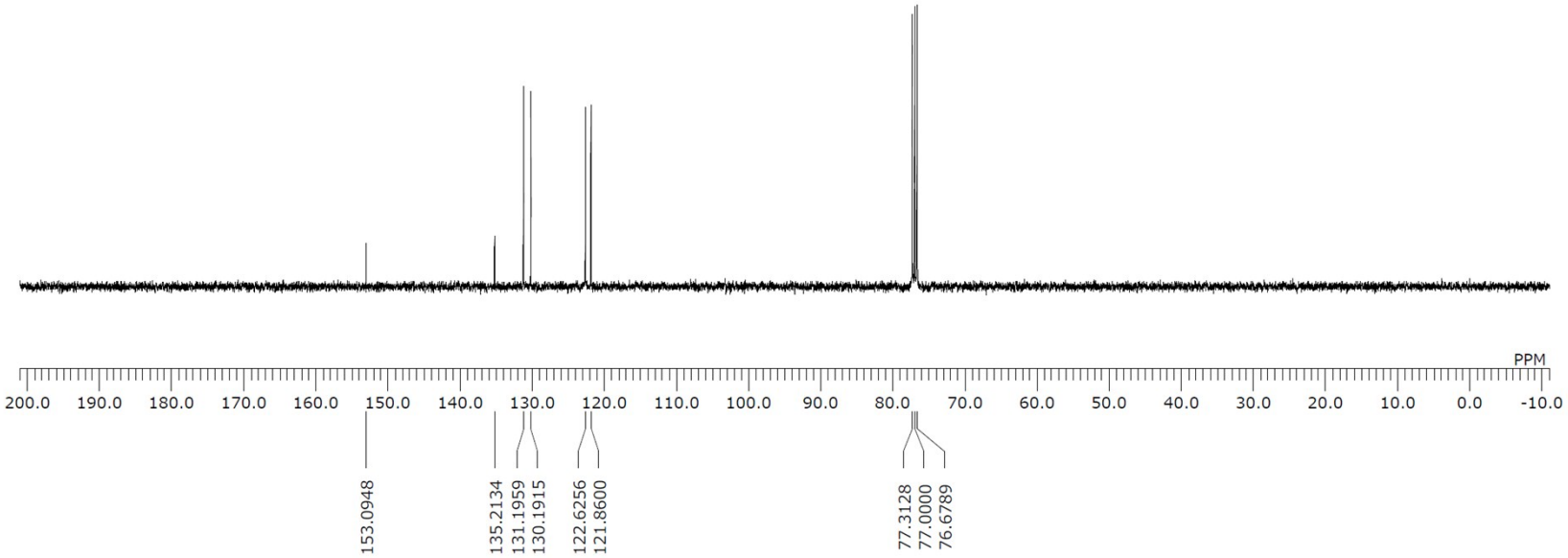
[1]H-NMR Spectra of 6j



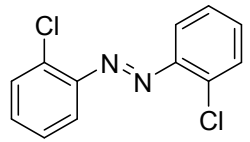
^{13}C-NMR Spectra of 6j



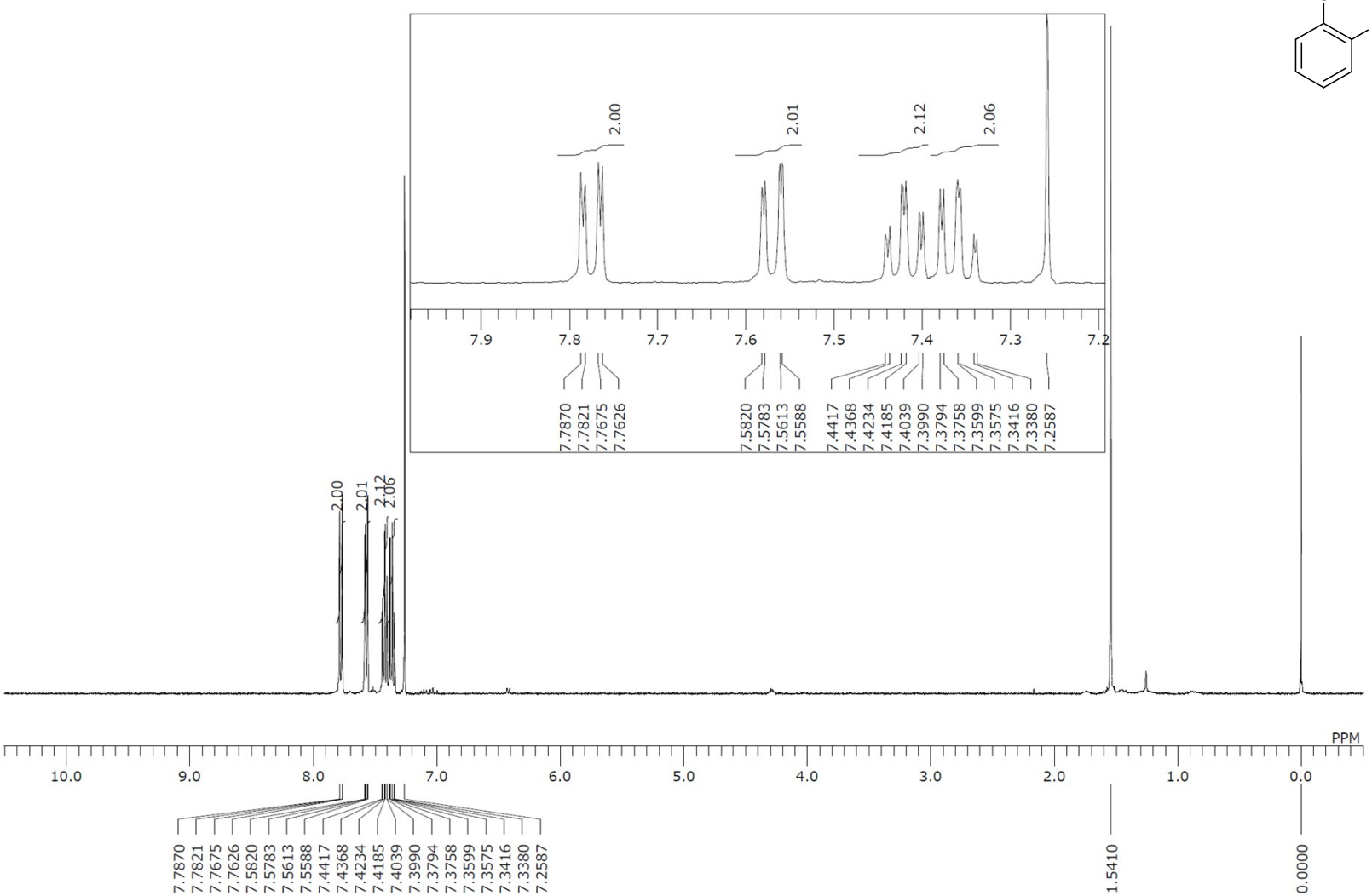
6j



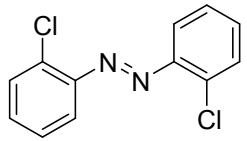
[1]H-NMR Spectra of 6k



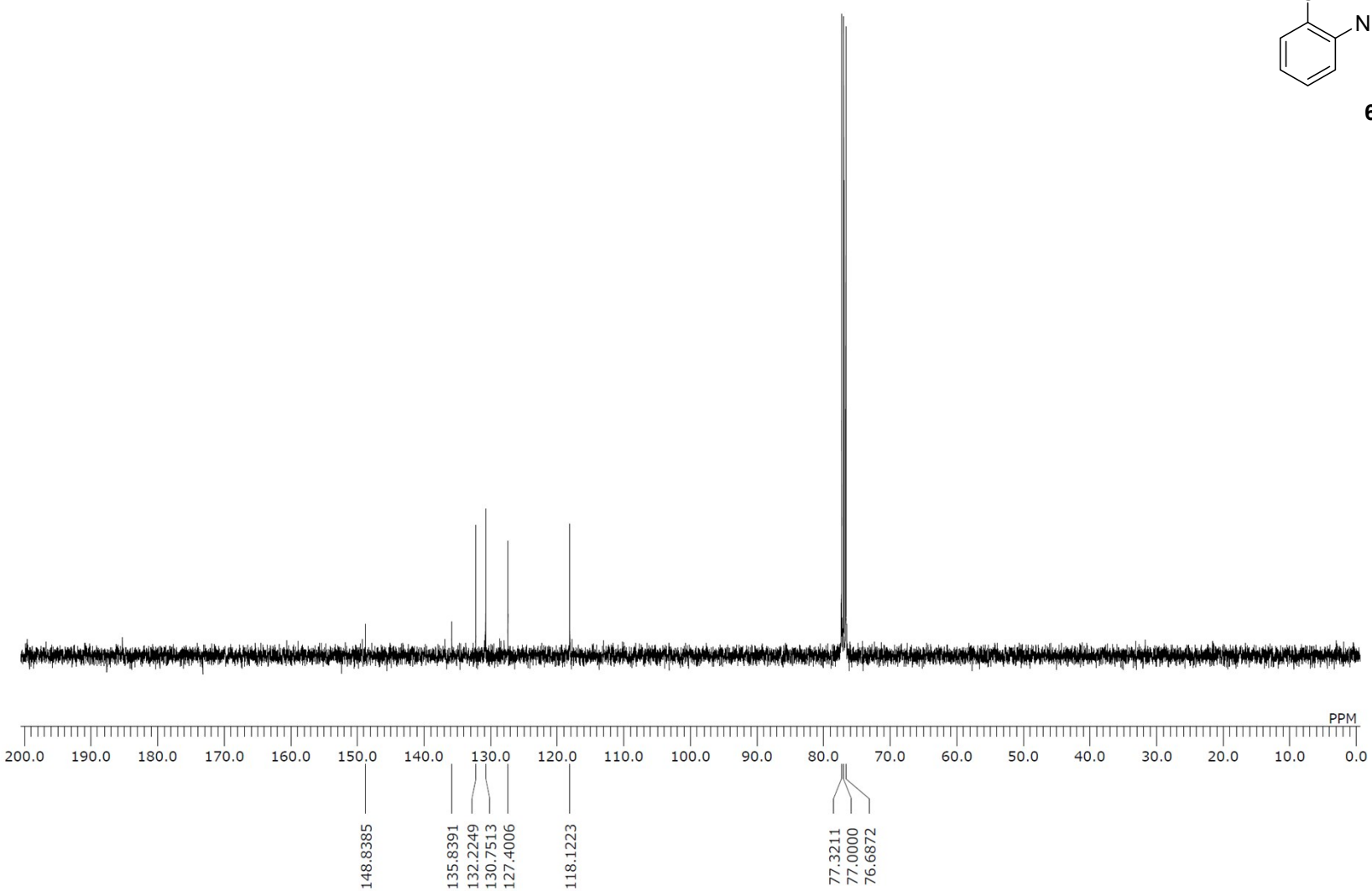
6k



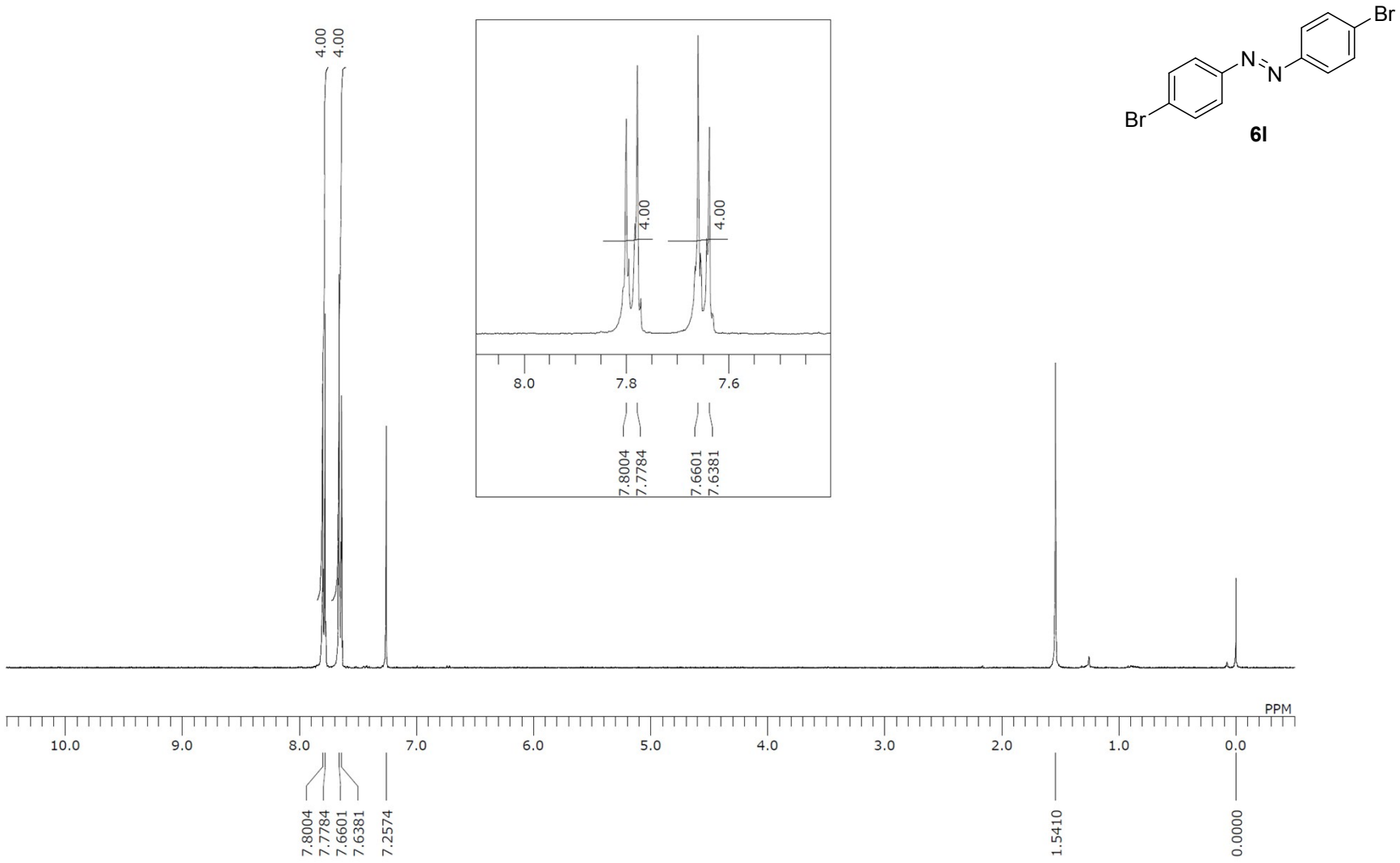
^{13}C-NMR Spectra of 6k



6k

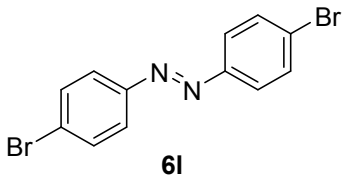


^{1}H-NMR Spectra of 6l

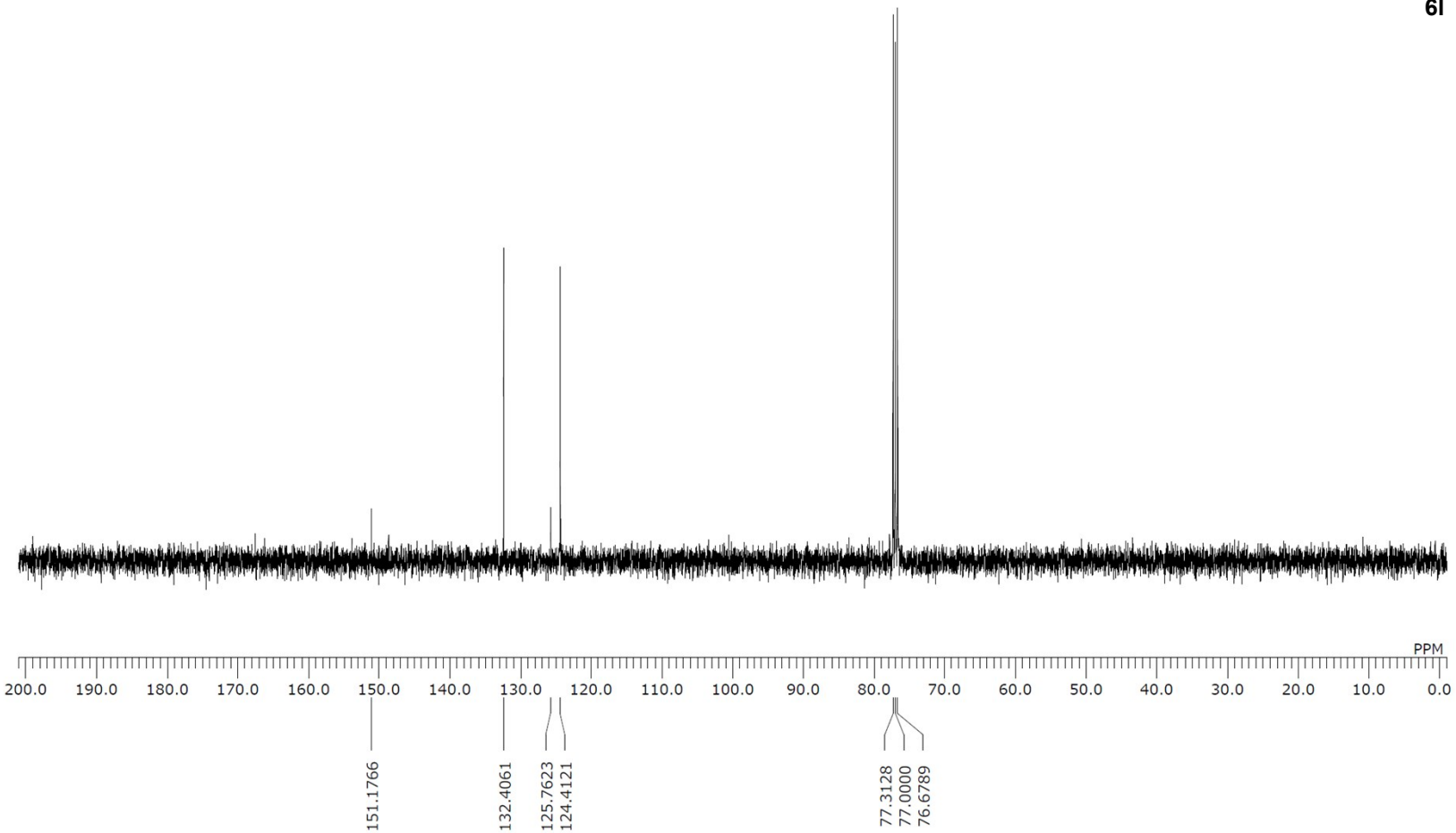


6l

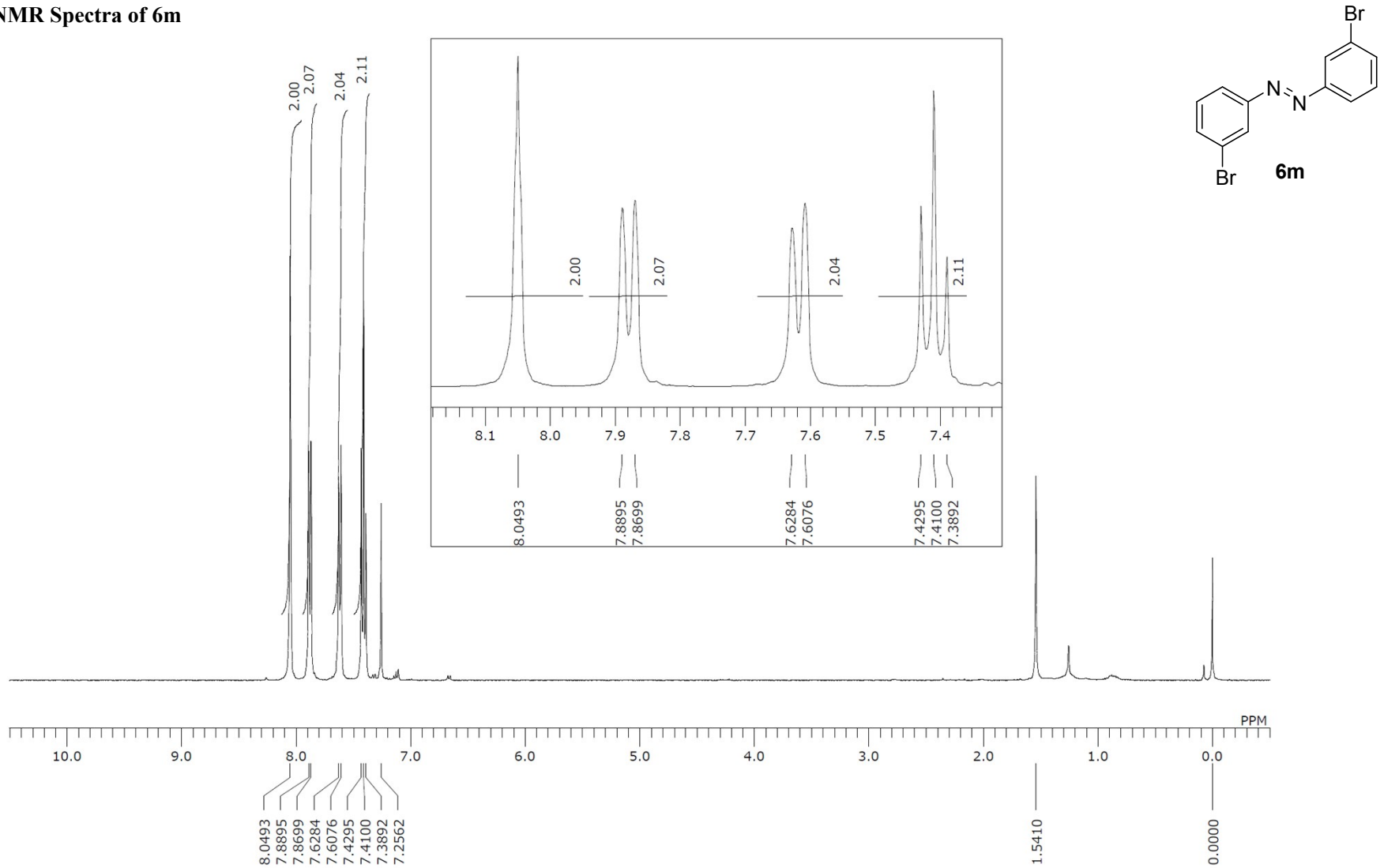
^{13}C-NMR Spectra of 6l



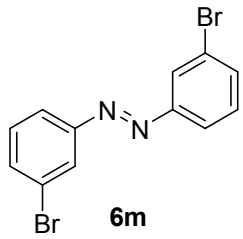
6l



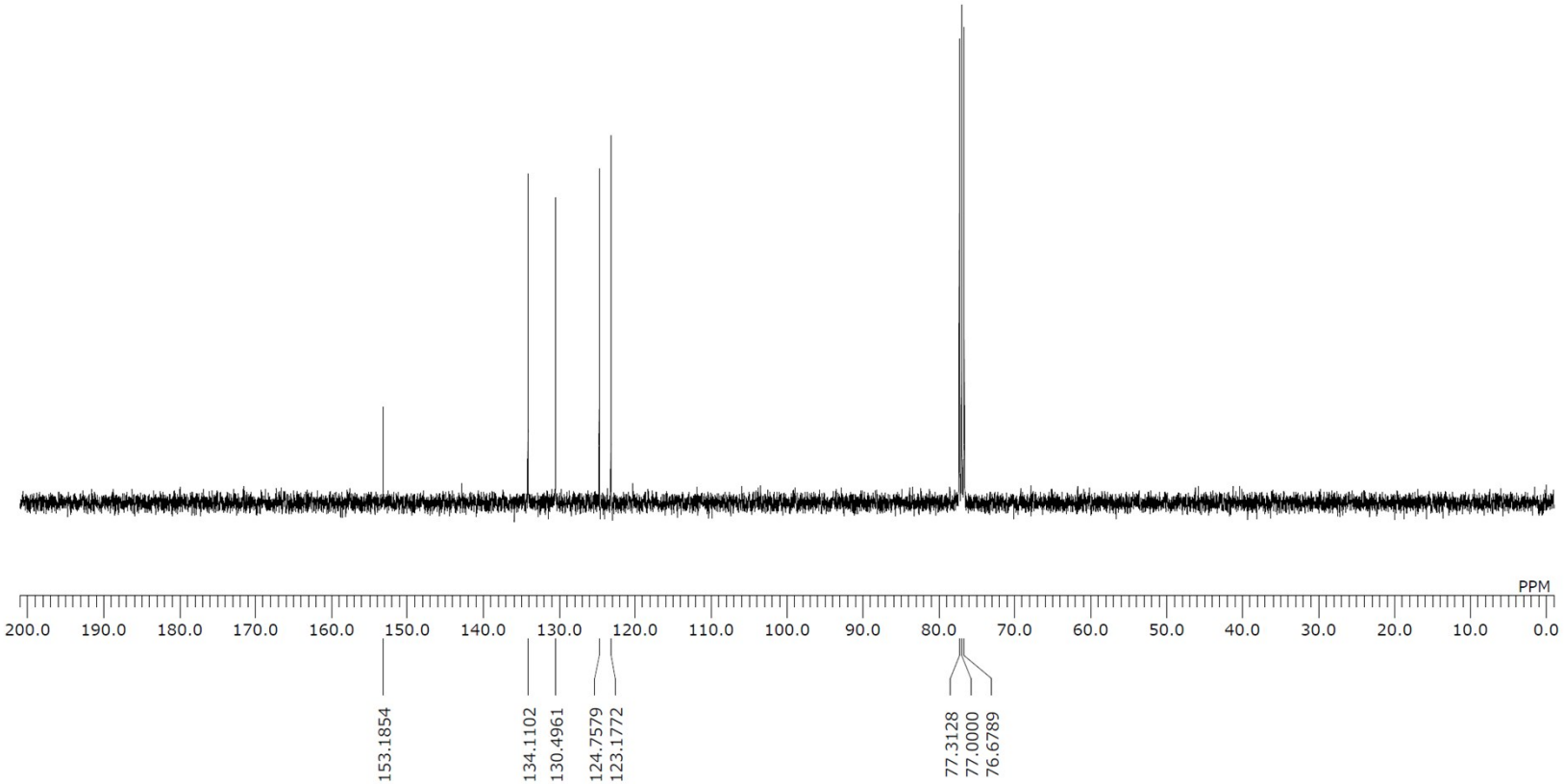
[1]H-NMR Spectra of 6m



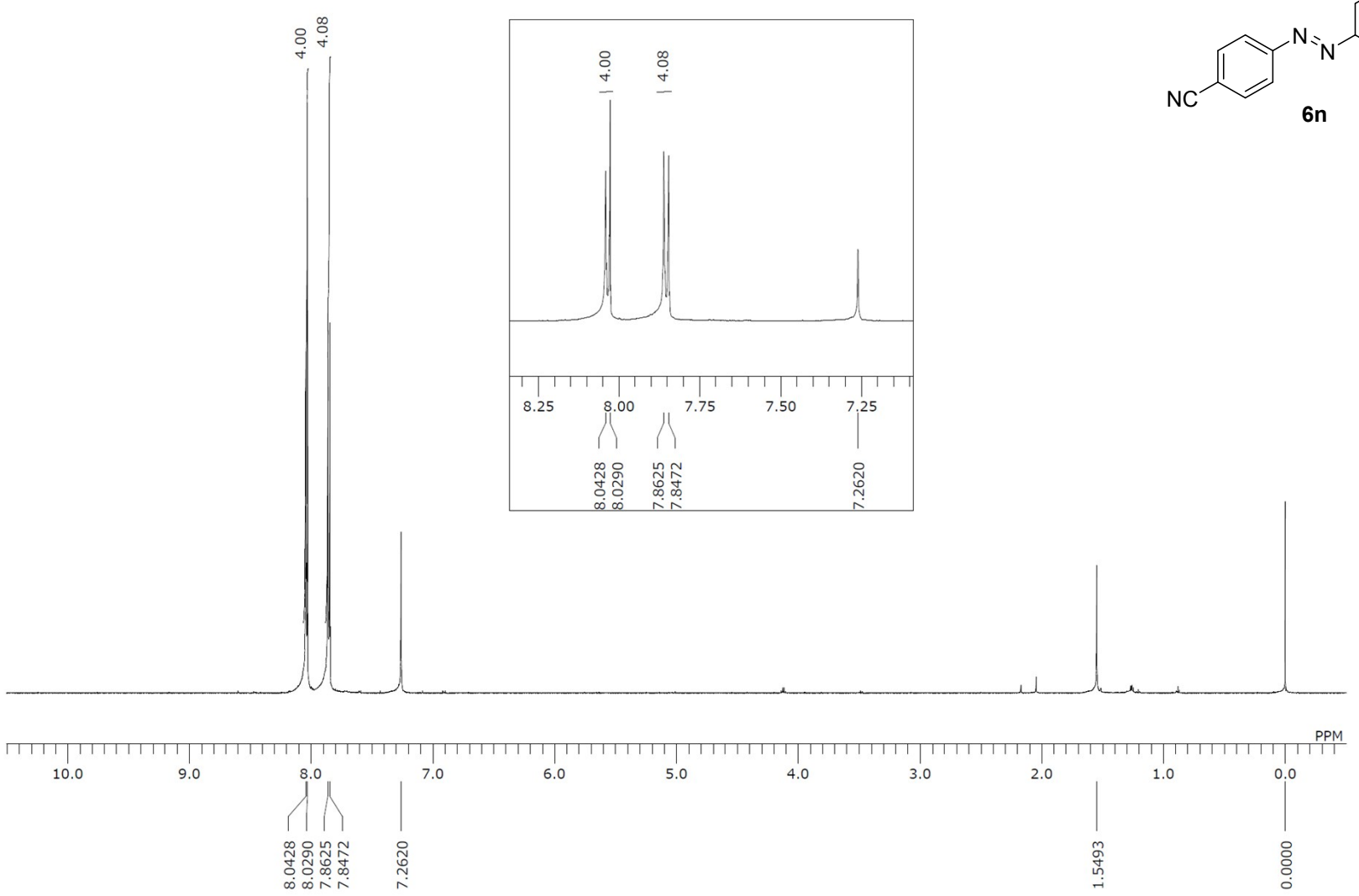
^{13}C-NMR Spectra of 6m

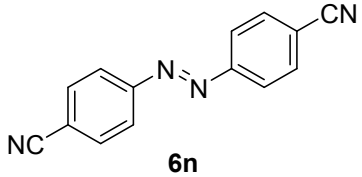


6m



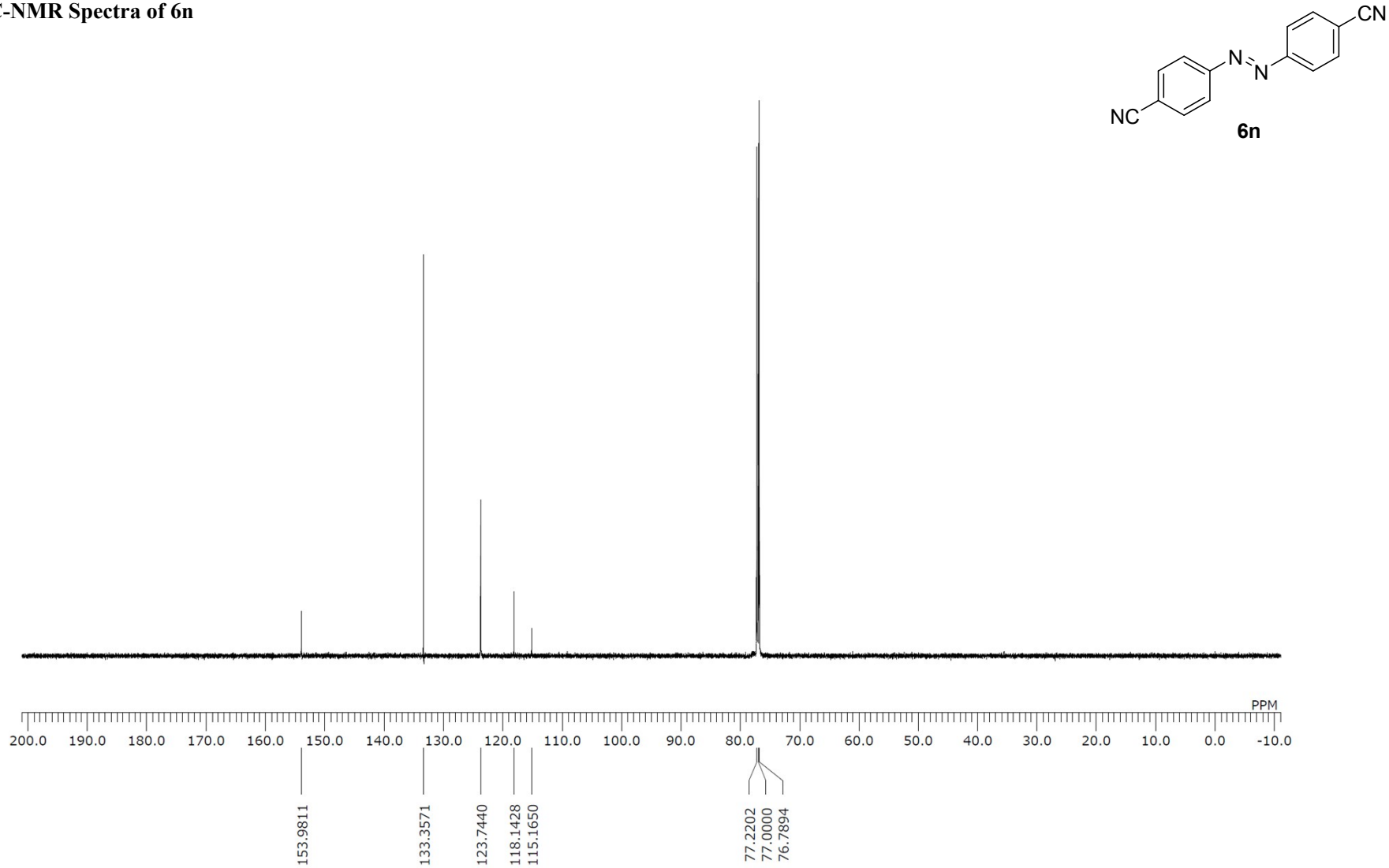
[1]H-NMR Spectra of 6n



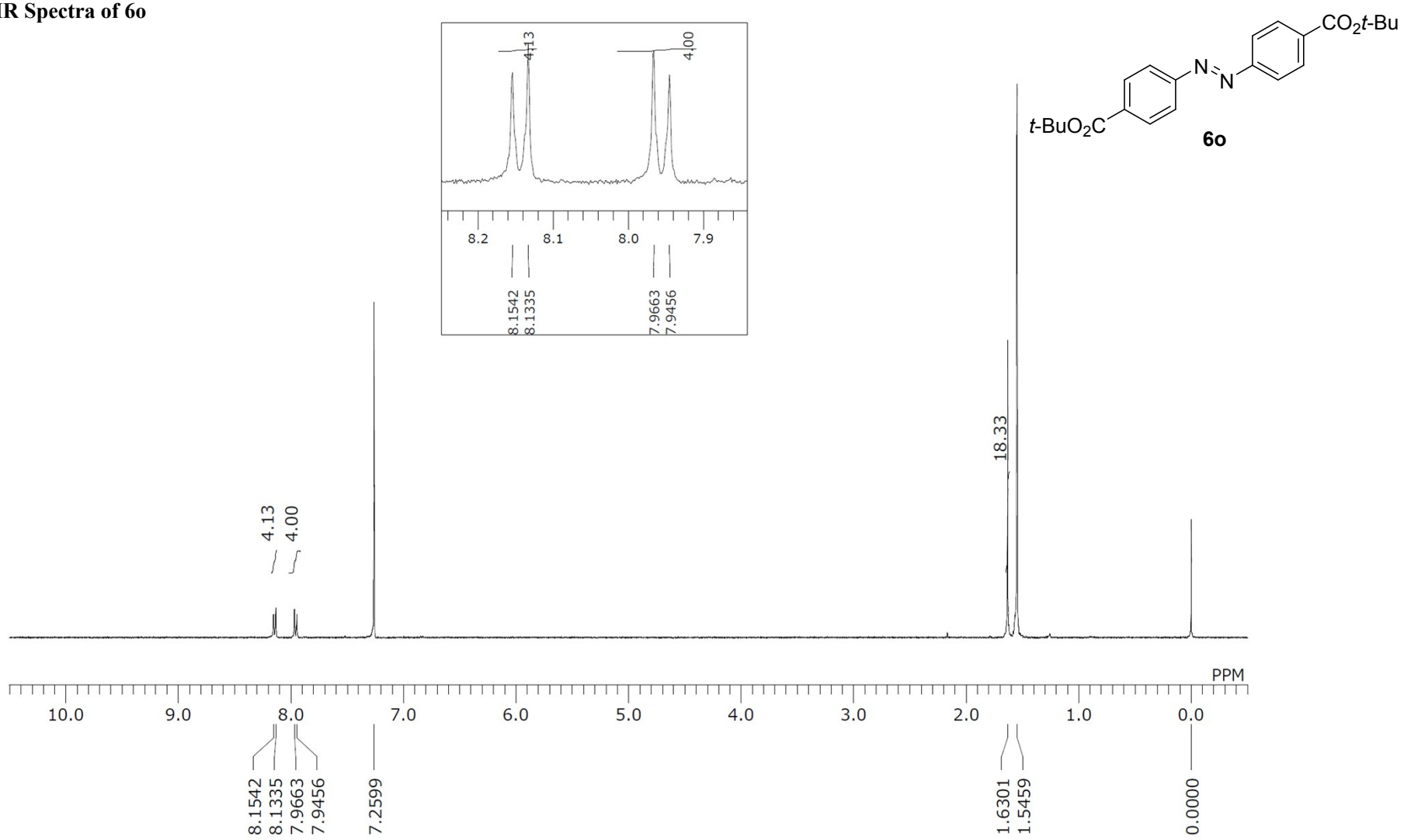


6n

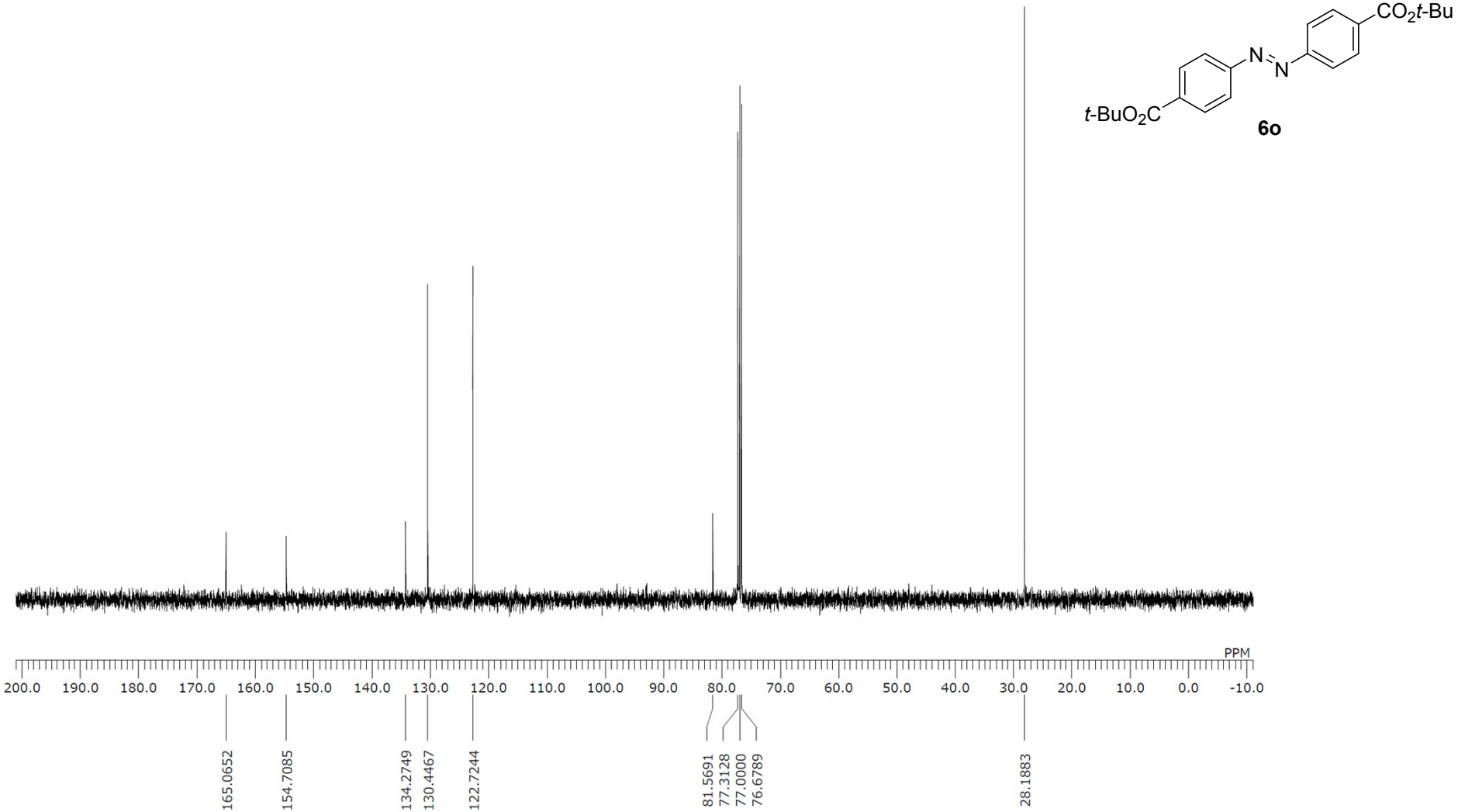
^{13}C-NMR Spectra of 6n



[1]H-NMR Spectra of 6o



^{13}C-NMR Spectra of 6o



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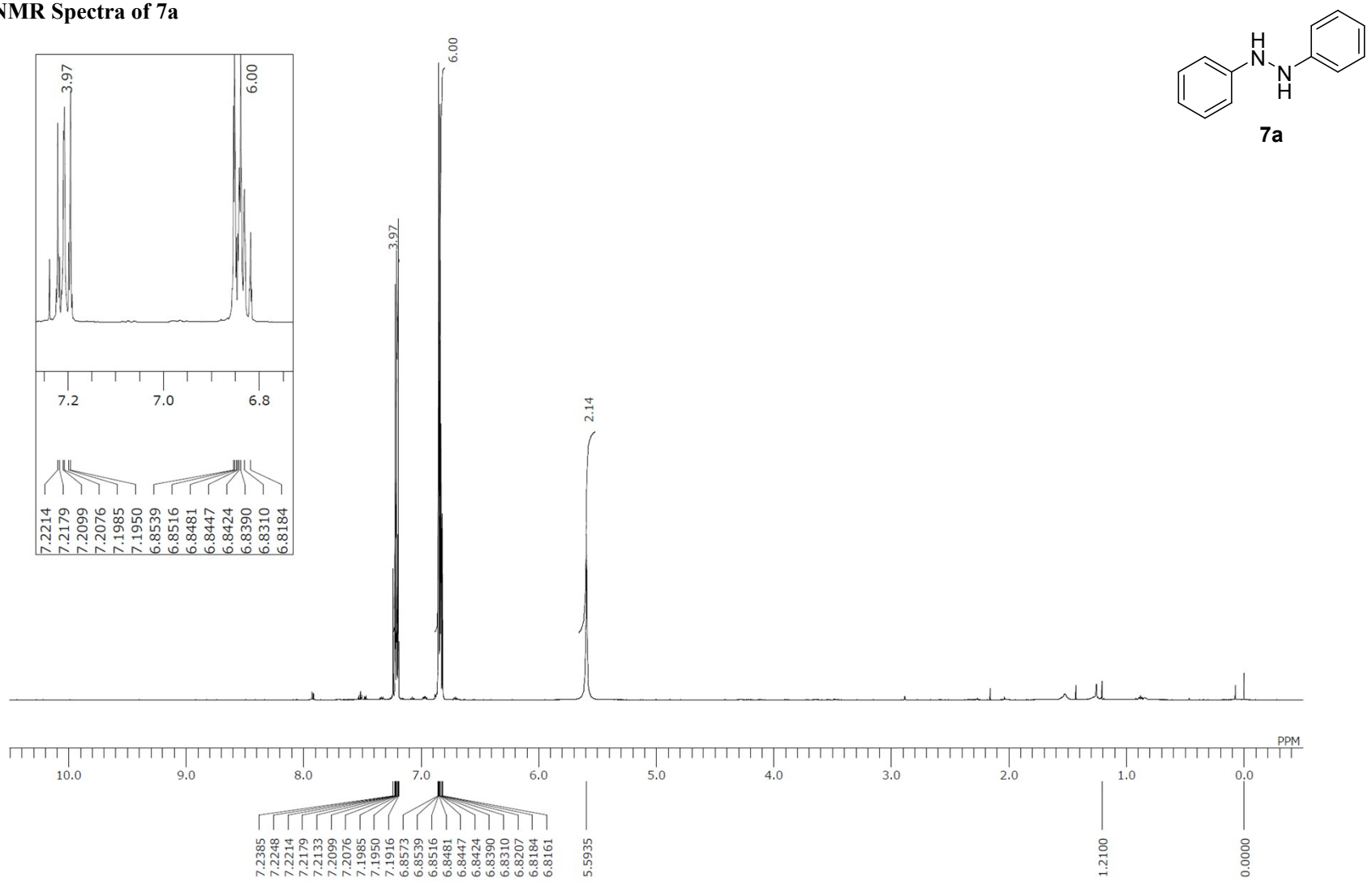
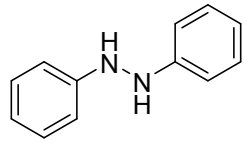
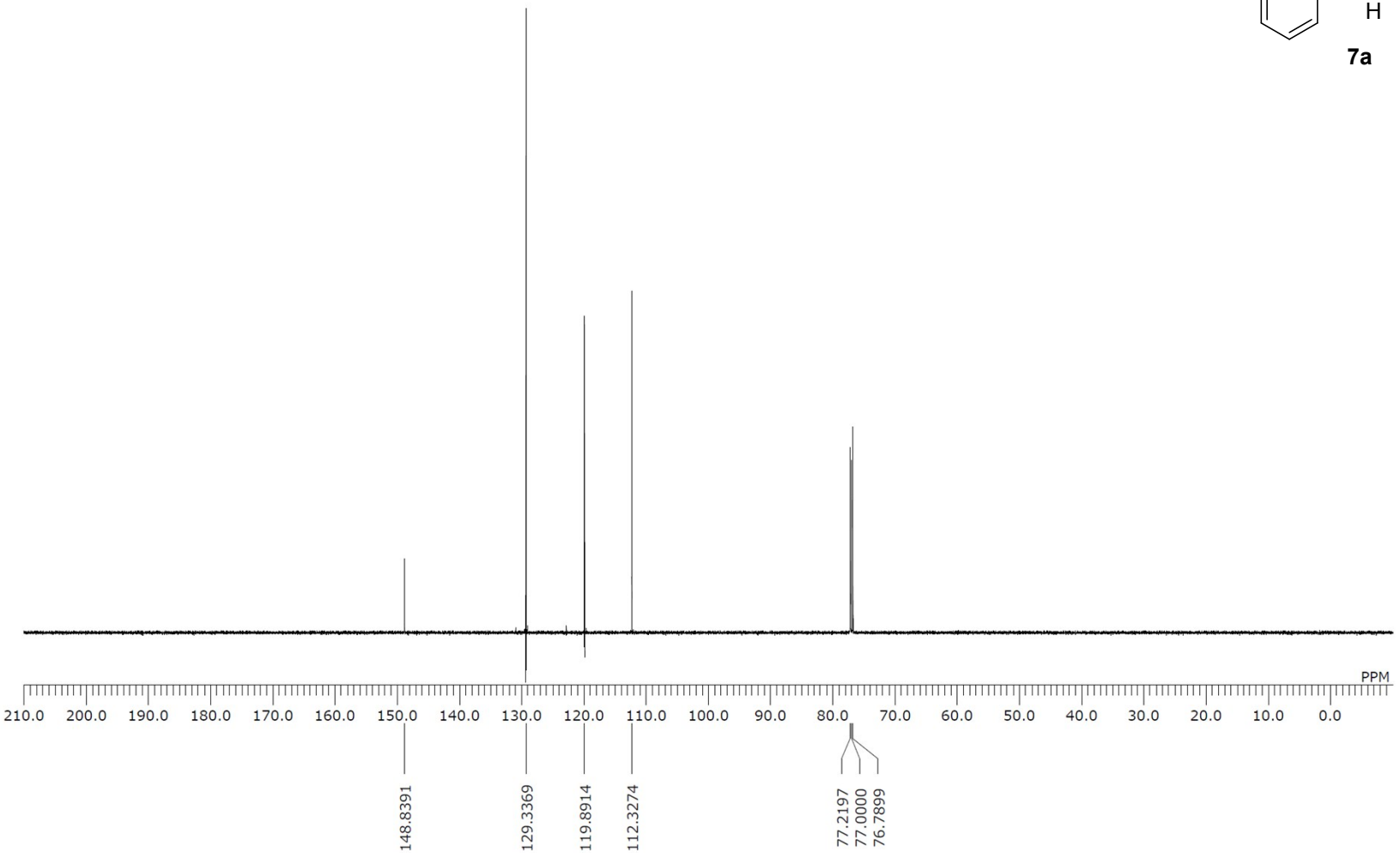


7a

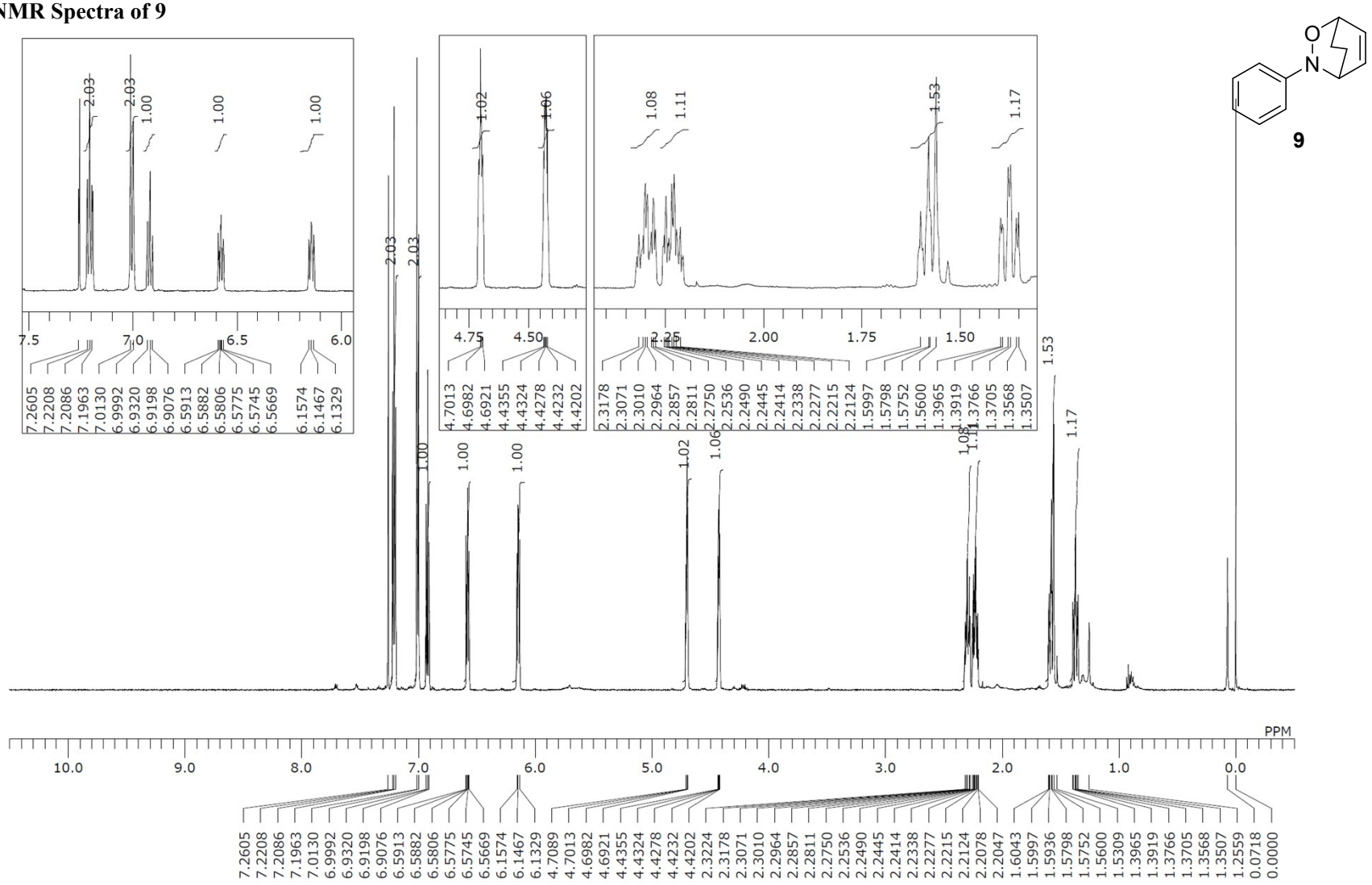
^{13}C-NMR Spectra of 7a



7a



[1]H-NMR Spectra of 9



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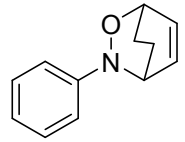
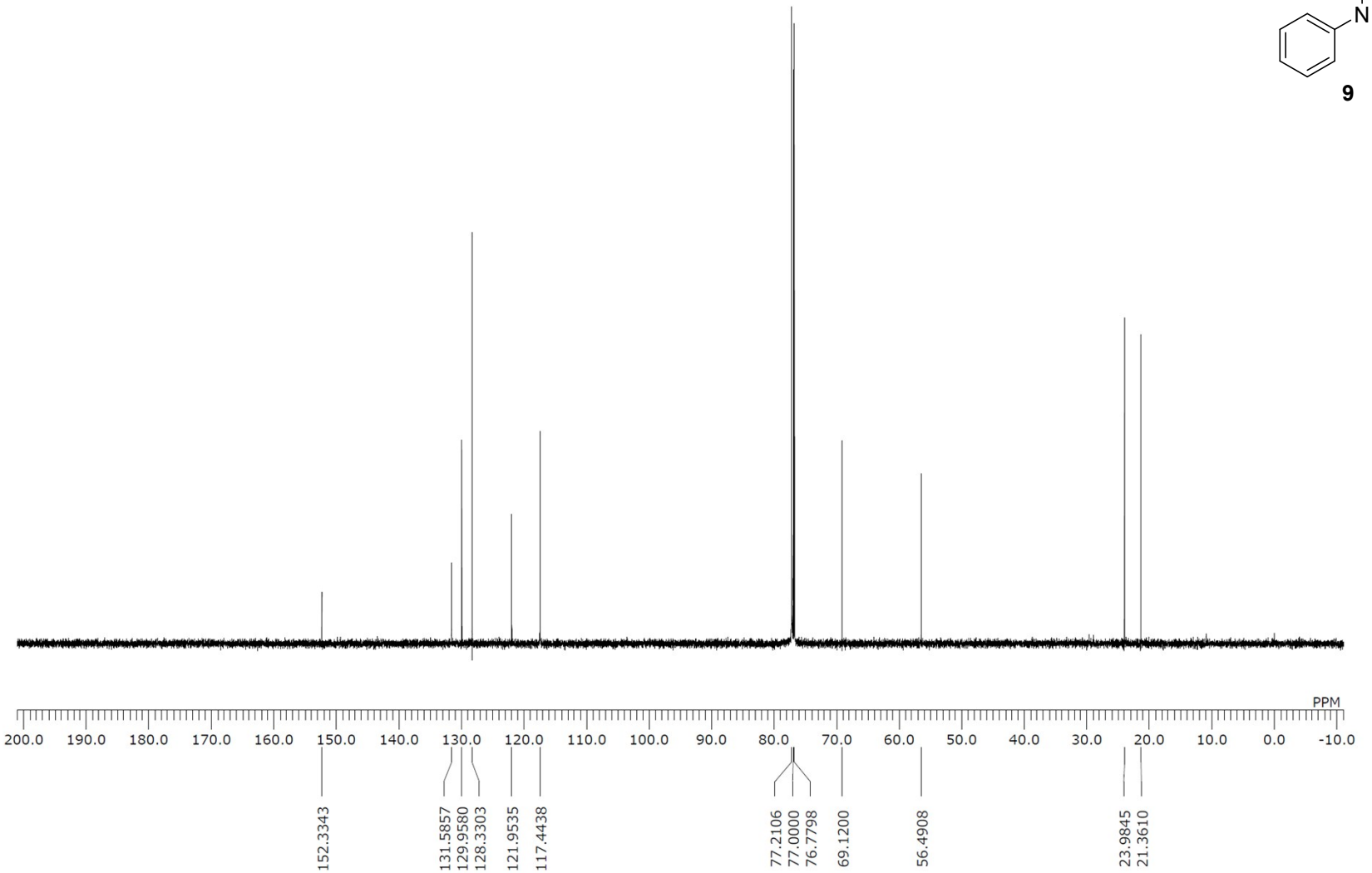
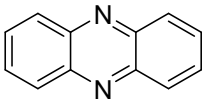


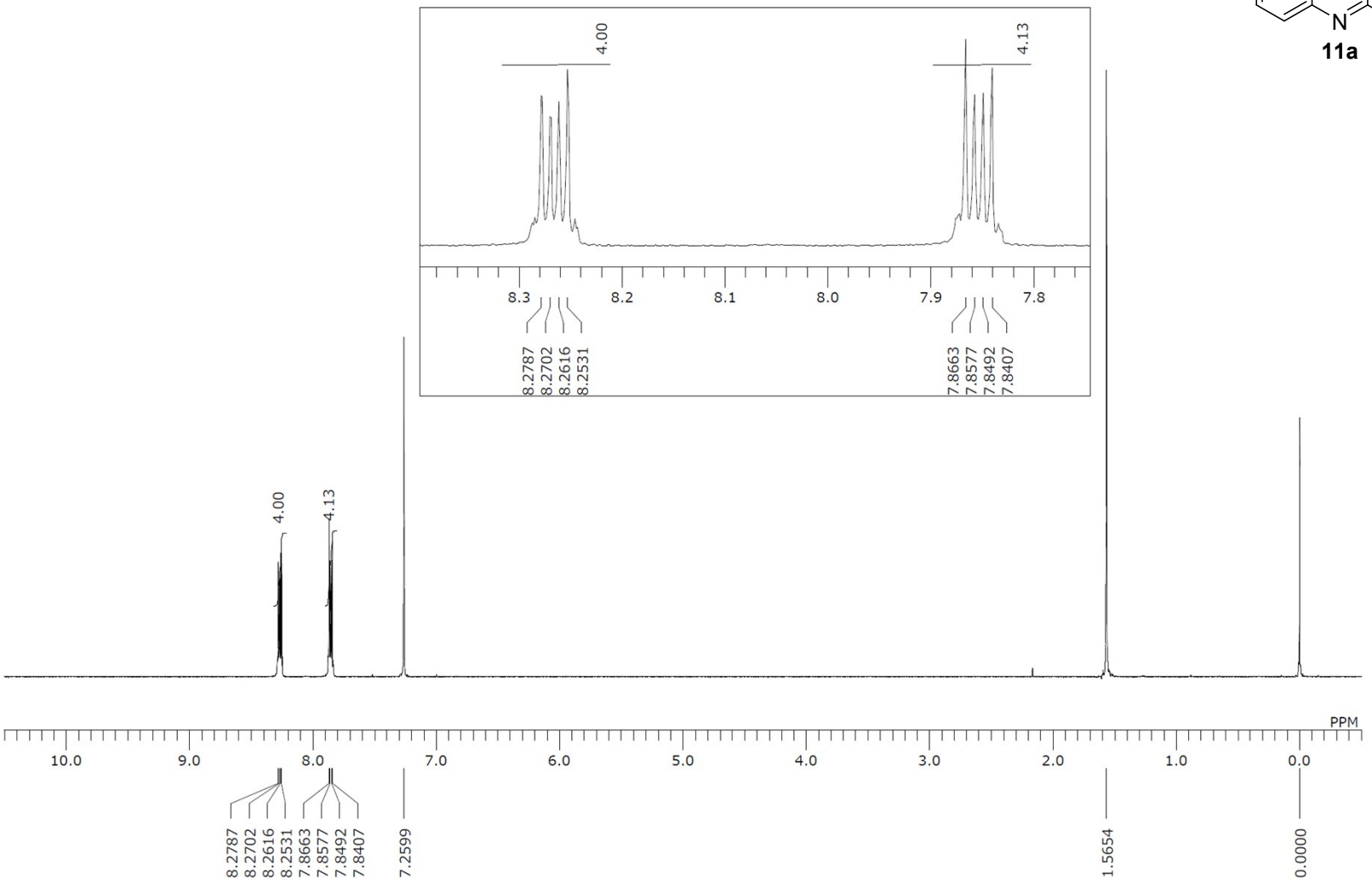
9



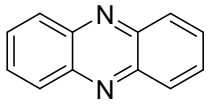
[1]H-NMR Spectra of 11a



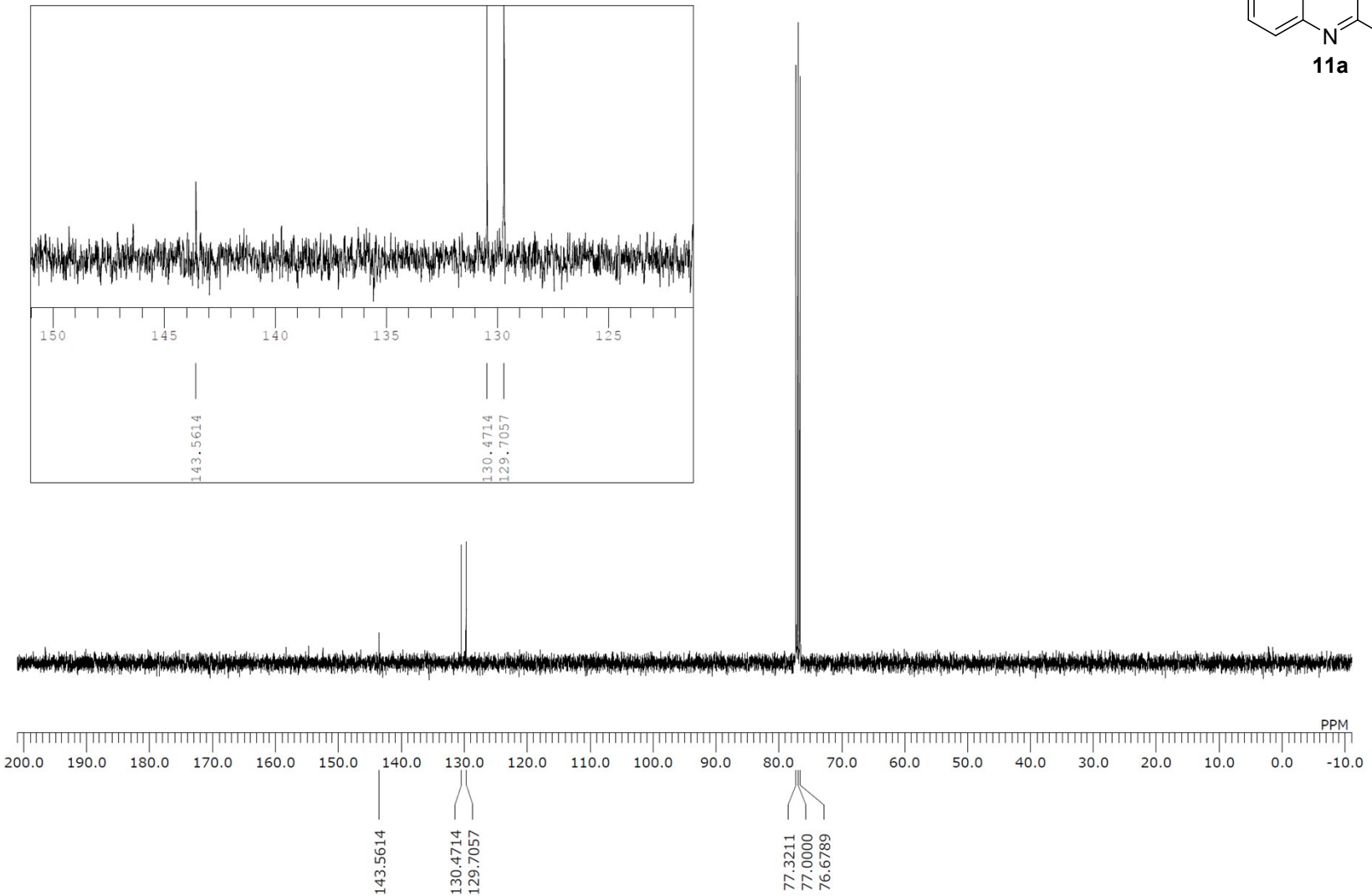
11a



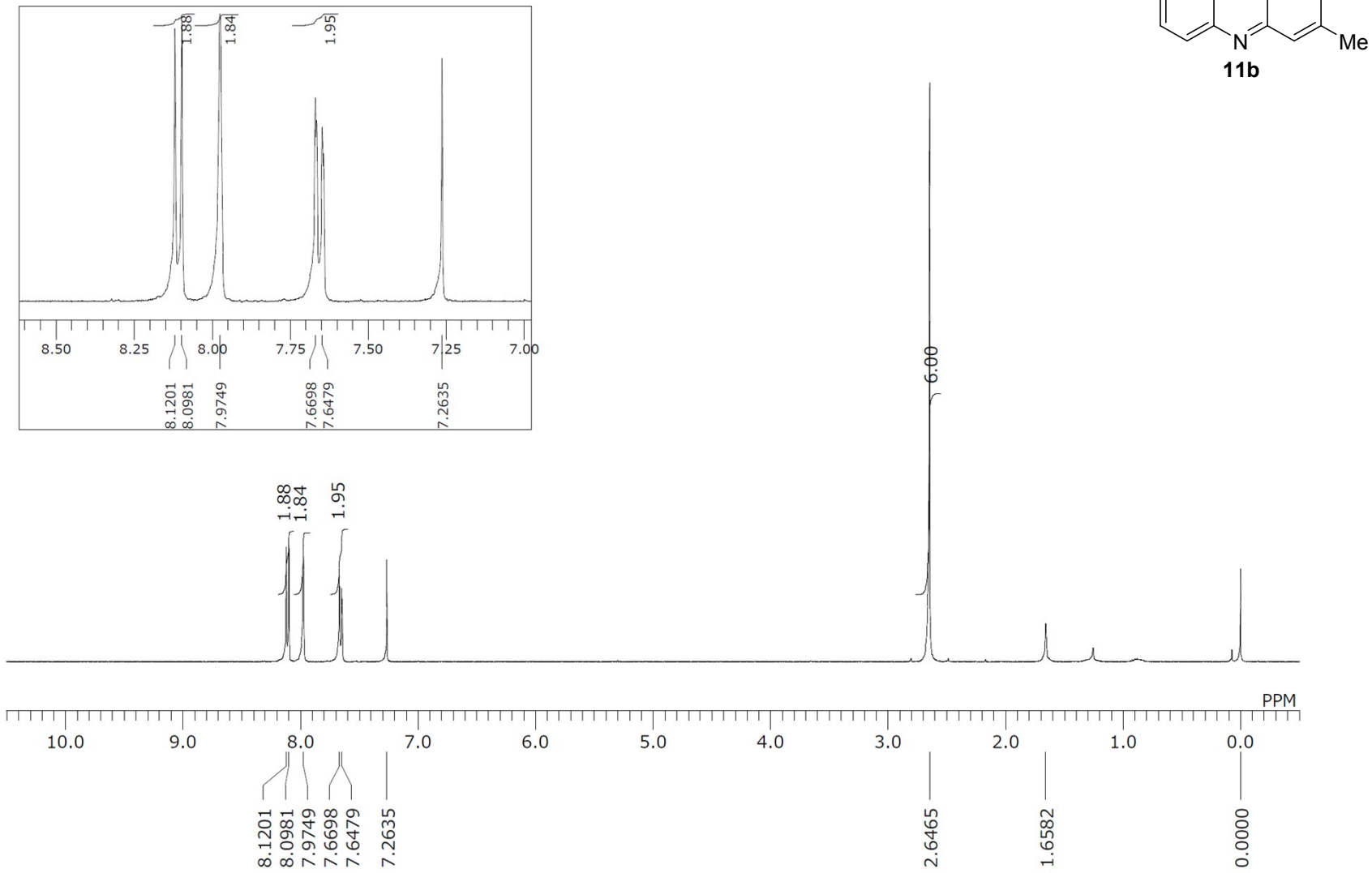
^{13}C-NMR Spectra of 11a



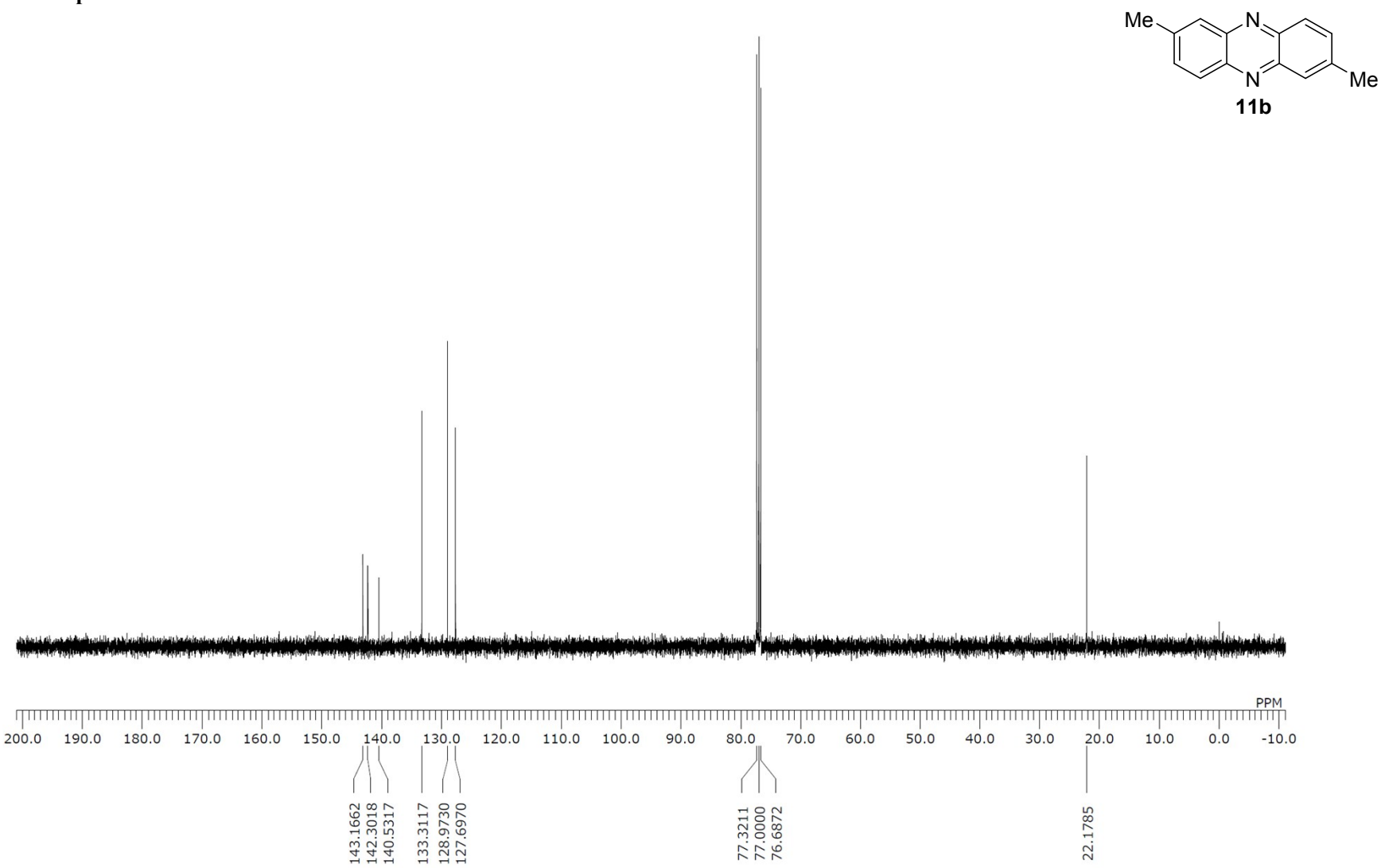
11a



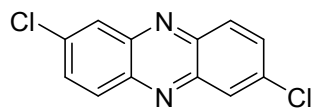
[1]H-NMR Spectra of 11b



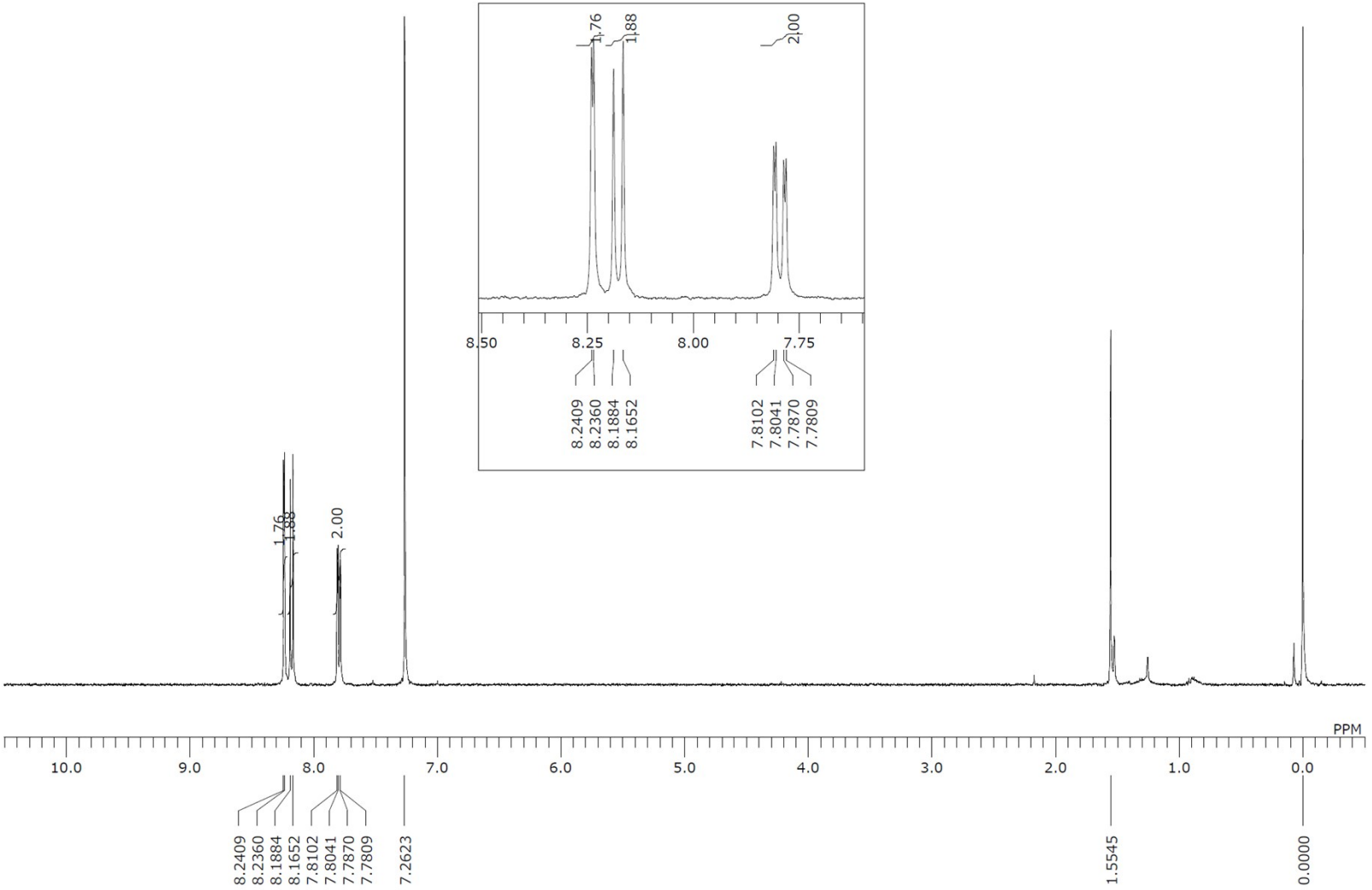
^{13}C-NMR Spectra of 11b



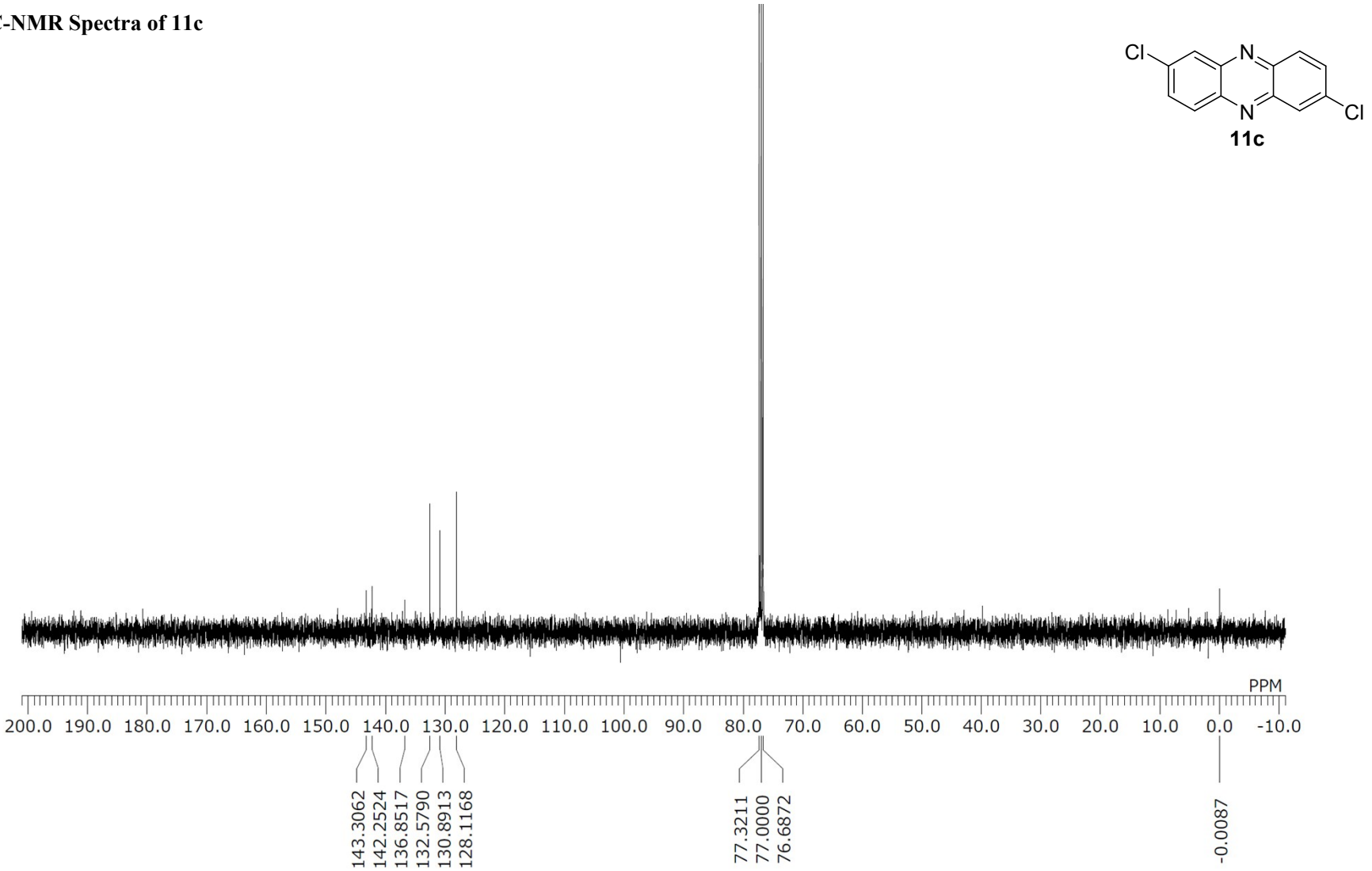
^{1}H-NMR Spectra of 11c



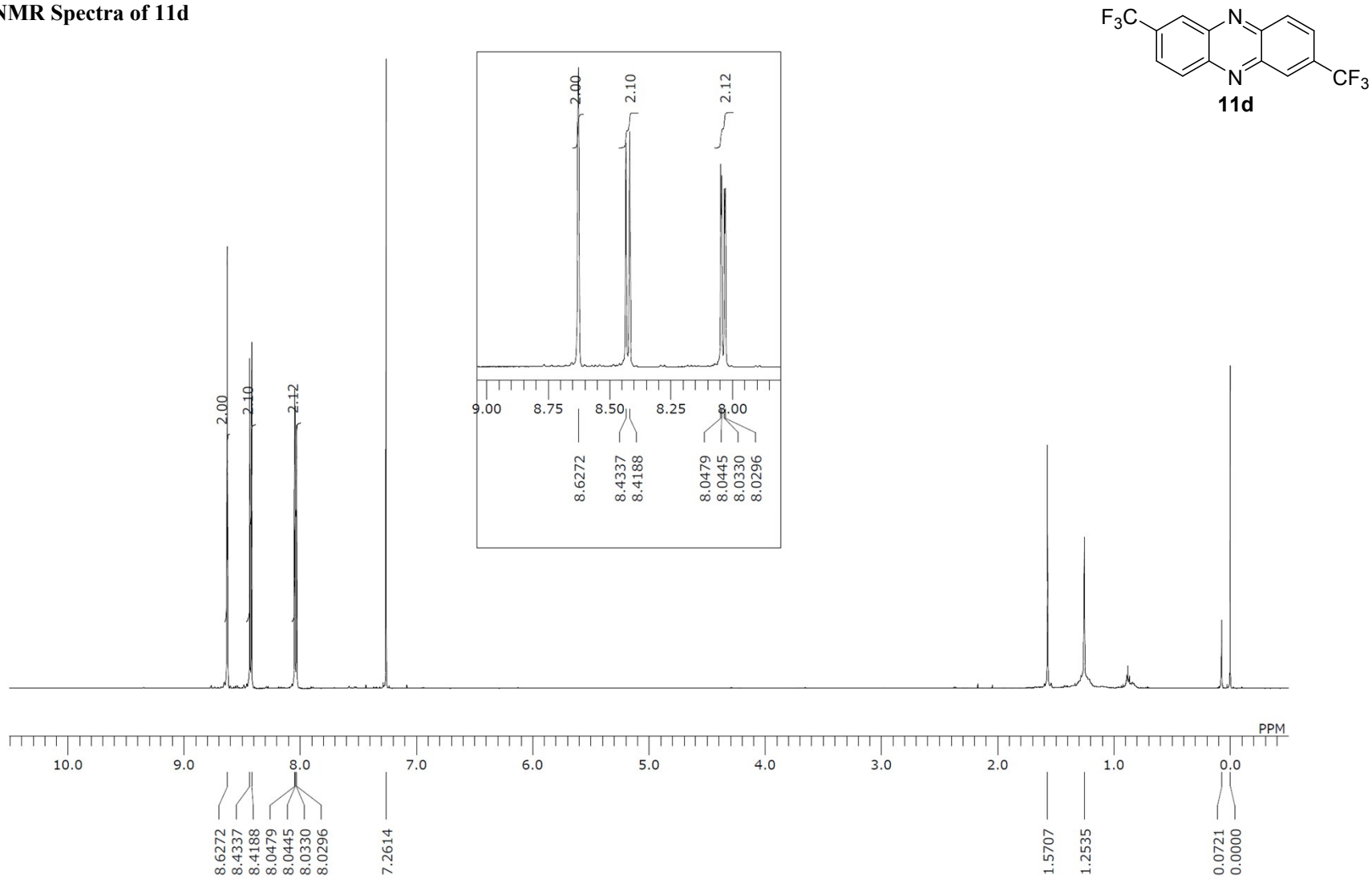
11c



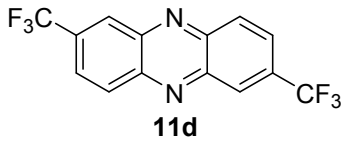
^{13}C-NMR Spectra of 11c



[1]H-NMR Spectra of 11d



^{13}C-NMR Spectra of 11d



11d