

The Pd-Catalyzed Conversion of Aryl Chlorides, Triflates, and Nonaflates to Nitroaromatics

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Supporting Information

General Reagent Information

All reactions were carried out under an argon atmosphere. The *tert*-butanol was purchased from Aldrich Chemical Company in Sure-Seal bottles and were used as received. Aryl halides and aryl triflates were purchased from Aldrich Chemical Co., Alfa Aesar, Acros Organics or TCI America and used as received without further purification. Aryl triflates and aryl nonaflates that were not commercially available were synthesized using literature procedures.¹ Sodium nitrite and tetrabutylammonium nitrite were purchased from Aldrich Chemical Company. Tris(3,5-dioxaheptyl)amine was purchased from Alfa Aesar and was used as received. Ligands **1**,² **2**,³ and **3**⁴ were synthesized using literature procedures. Ligands **4** and **5** were purchased from Strem Chemicals and the Pd₂(dba)₃ was purchased from Aldrich Chemical Company. Flash chromatography was performed using a Biotage SP4 instrument with prepacked silica cartridges.

General Analytical Information

All compounds were characterized by ¹H NMR, ¹³C NMR, IR spectroscopy, as well as, in most instances, elemental analysis. Copies of the ¹H and ¹³C spectra can be found at the end of the Supporting Information. Nuclear Magnetic Resonance spectra were recorded on a Varian 300 MHz instrument and a Varian 500 MHz instrument. All ¹H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ¹³C NMR spectra are reported in ppm relative to deuteriochloroform (77.23 ppm), unless otherwise stated, and all were obtained with ¹H decoupling. All IR spectra were taken on a Perkin – Elmer 2000 FTIR. All GC analyses were performed on a Agilent 6890 gas chromatograph with an FID detector using a J & W DB-1 column (10

m, 0.1 mm I.D.). Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA.

General Procedure for Table 1 and Figure 1

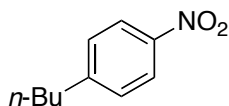
An oven-dried sealable Schlenk tube, which was equipped with a magnetic stir bar and fitted with a rubber septum, was charged with the Pd₂(dba)₃ (0.5 mol%), ligand (1.2 mol%), and nitrite source (2.0 mmol). The vessel was evacuated and backfilled with argon (this process was repeated a total of 3 times) and then the 4-chloro-*n*-butylbenzene (169 μL, 1.0 mmol), phase transfer catalyst (0-100 mol%), and *t*-BuOH (2 mL) were added via syringe. The Schlenk tube was sealed with a Teflon screw cap and the solution was heated to 110 °C for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc, and washed with water. Dodecane was then added as an internal standard and the reaction was analyzed by GC.

Note: Use of KNO₂ under optimal conditions gave a 10% GC yield for the above reaction.

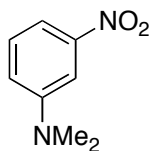
General Procedure for Tables 2 and 3

An oven-dried sealable Schlenk tube, which was equipped with a magnetic stir bar and fitted with a rubber septum, was charged with the Pd₂(dba)₃ (0.5 – 2.5 mol%), **1** (1.2 - 6 mol%), and sodium nitrite (138 mg, 2.0 mmol). The vessel was evacuated and backfilled with argon (this process was repeated a total of 3 times) and then the aryl halide or pseudo halide (1.0 mmol), tris(3,5-dioxaheptyl)amine (16 μL, 5 mol%), and *t*-BuOH (2 mL) were added via syringe (aryl chlorides, triflates, or nonaflates that were solids at room temperature were added with the catalyst and sodium nitrite). The Schlenk tube was sealed with a Teflon screw cap and the solution was heated to 130 °C for 24 h. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate, washed with water, concentrated in vacuo, and purified via the Biotage SP4 (silica-packed 50 or 100 g snap cartridge).

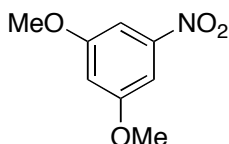
Experimental Procedures for Examples Described in Table 2



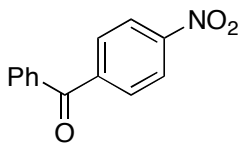
1-Butyl-4-nitrobenzene (Table 2) Following the general procedure, a mixture of 4-chloro-*n*-butylbenzene (169 μ L, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), Pd₂(dba)₃ (4.5 mg, 0.5 mol%), **1** (6 mg, 1.2 mol%), tris(3,5-dioxaheptyl)amine (16 μ L, 5 mol%), and *t*-BuOH (2 mL) was heated to 130 °C for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-25% EtOAc/hexanes) to provide the title compound as a yellow oil (155 mg, 87%). ¹H NMR (300 MHz, CDCl₃) δ : 8.11 (d, J = 8.7 Hz, 2H), 7.31 (d, J = 8.7 Hz, 2H), 2.70 (t, J = 7.5 Hz, 2H), 1.61 (pentet, J = 7.5 Hz, 2H), 1.36 (sextet, J = 7.5 Hz, 2H), 0.92 (t, J = 7.2 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ : 151.1, 146.4, 129.4, 123.8, 35.8, 33.3, 22.5, 14.1 ppm. IR (neat, cm⁻¹): 3439, 2932, 2862, 1605, 1518, 1345, 1110, 856, 746, 697. Anal. Calcd. for C₁₀H₁₃NO₂: C, 67.02; H, 7.31. Found: C, 67.00; H, 7.40.



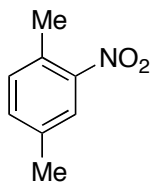
***N,N*-Dimethyl-3-nitroaniline**⁵ (Table 2) Following the general procedure, a mixture of *N,N*-dimethylamino-3-chlorobenzene (156 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), Pd₂(dba)₃ (4.5 mg, 0.5 mol%), **1** (6 mg, 1.2 mol%), tris(3,5-dioxaheptyl)amine (16 μ L, 5 mol%), and *t*-BuOH (2 mL) was heated to 130 °C for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-50% EtOAc/hexanes) to provide the title compound as a red solid (166 mg, 99%), mp = 53-56 °C (lit 56 – 58 °C). ¹H NMR (500 MHz, CDCl₃) δ : 7.51 (d, J = 8.0 Hz, 1H), 7.48 (s, 1H), 7.33 (t, J = 8.0 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 3.04 (s, 6H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ : 151.0, 129.8, 117.8, 110.8, 106.2, 40.5 ppm. IR (neat, cm⁻¹): 2908, 1620, 1568, 1529, 1342, 1232, 1067, 994, 875, 837, 732.



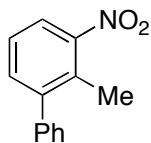
1,3-Dimethoxy-5-nitrobenzene (Table 2) Following the general procedure, a mixture of 1,3-dimethoxy-5-chlorobenzene (172 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), Pd₂(dba)₃ (4.5 mg, 0.5 mol%), **1** (6 mg, 1.2 mol%), tris(3,5-dioxaheptyl)amine (16 μL, 5 mol%), and *t*-BuOH (2 mL) was heated to 130 °C for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-40% EtOAc/hexanes) to provide the title compound as a yellow solid (155 mg, 84%), mp = 87 – 89 °C. ¹H NMR (300 MHz, CDCl₃) δ: 7.31 (d, *J* = 2.4 Hz, 2H), 6.70 (t, *J* = 2.4 Hz, 1H), 3.83 (s, 6H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ: 161.1, 150.0, 107.3, 101.6, 56.1 ppm. IR (neat, cm⁻¹): 2961, 1589, 1535, 1452, 1356, 1210, 1044, 854, 745, 665. Anal. Calcd. for C₈H₉NO₄: C, 52.46; H, 4.95. Found: C, 52.90; H, 4.98.



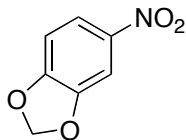
(4-Nitrophenyl)(phenyl)methanone (Table 2) Following the general procedure, a mixture of 4-chlorobenzophenone (217 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), Pd₂(dba)₃ (4.5 mg, 0.5 mol%), **1** (6 mg, 1.2 mol%), tris(3,5-dioxaheptyl)amine (16 μL, 5 mol%), and *t*-BuOH (2 mL) was heated to 130 °C for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-50% EtOAc/hexanes) to provide the title compound as a white solid (214 mg, 94%), mp = 132 – 135 °C. ¹H NMR (300 MHz, CDCl₃) δ: 8.31 (d, *J* = 8.1 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ: 195.0, 150.0, 143.1, 136.5, 133.7, 131.0, 130.3, 128.9, 123.8 ppm. IR (neat, cm⁻¹): 3101, 1651, 1594, 1514, 1359, 1318, 1107, 872, 705, 692. Anal. Calcd. for C₁₃H₉NO₃: C, 68.72; H, 3.99. Found: C, 69.19; H, 3.99.



1,4-Dimethyl-2-nitrobenzene (Table 2) Following the general procedure, a mixture of 2-chloro-*p*-xylene (134 μ L, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), Pd₂(dba)₃ (4.5 mg, 0.5 mol%), **1** (6 mg, 1.2 mol%), tris(3,5-dioxaheptyl)amine (16 μ L, 5 mol%), and *t*-BuOH (2 mL) was heated to 130 °C for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-40% EtOAc/hexanes) to provide the title compound as a yellow oil (106 mg, 70%). ¹H NMR (300 MHz, CDCl₃) δ : 7.76 (s, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 2.53 (s, 3H), 2.38 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ : 137.3, 134.1, 132.8, 125.1, 20.9, 20.3 ppm. IR (neat, cm⁻¹): 2930, 1654, 1527, 1346, 1293, 1156, 917, 810. Anal. Calcd. for C₈H₉NO₂: C, 63.56; H, 6.00. Found: C, 63.15; H, 6.04.

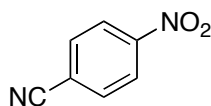


2-Methyl-3-nitrobiphenyl (Table 2) Following the general procedure, a mixture of 3-chloro-2-methylbiphenyl (203 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), Pd₂(dba)₃ (4.5 mg, 0.5 mol%), **1** (6 mg, 1.2 mol%), tris(3,5-dioxaheptyl)amine (16 μ L, 5 mol%), and *t*-BuOH (2 mL) was heated to 130 °C for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-40% EtOAc/hexanes) to provide the title compound as a yellow oil (212 mg, 99%). ¹H NMR (300 MHz, CDCl₃) δ : 7.80 (d, *J* = 8.10 Hz, 1H), 7.49 – 7.27 (m, 7H), 2.37 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ : 151.5, 145.2, 140.2, 134.2, 130.3, 129.5, 128.7, 128.0, 126.4, 123.3, 17.2 ppm. IR (neat, cm⁻¹): 3075, 1536, 1464, 1366, 869, 812, 760, 733, 706, 575. Anal. Calcd. for C₁₃H₁₁NO₂: C, 73.23; H, 5.20. Found: C, 73.48; H, 5.16.

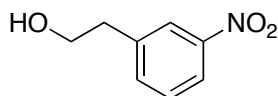


5-Nitro-1,3-benzodioxole⁶ (Table 2) Following the general procedure, a mixture of 5-

chloro-1,3-benzodioxole (117 μL , 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), $\text{Pd}_2(\text{dba})_3$ (23 mg, 2.5 mol%), **1** (30 mg, 6 mol%), tris(3,5-dioxaheptyl)amine (16 μL , 5 mol%), and *t*-BuOH (2 mL) was heated to 130 $^\circ\text{C}$ for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-50% EtOAc/hexanes) to provide the title compound as a white solid (166 mg, 99%), mp = 144 – 146 $^\circ\text{C}$ (literature 146 – 147 $^\circ\text{C}$). ^1H NMR (300 MHz, CDCl_3) δ : 7.87 (dd, $J = 2.4$ Hz, $J = 8.7$ Hz, 1H), 7.64 (d, $J = 2.4$ Hz, 1H), 6.85 (d, $J = 8.7$ Hz, 1H), 6.14 (s, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ : 153.4, 148.4, 120.1, 107.8, 104.7, 103.3 ppm. IR (neat, cm^{-1}): 1504, 1488, 1343, 1274, 1239, 1036, 919, 870, 825, 742.

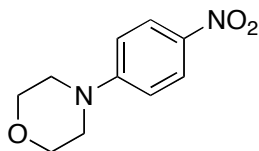


4-Nitrobenzonitrile⁷ (Table 2) Following the general procedure, a mixture of 4-chlorobenzonitrile (138 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), $\text{Pd}_2(\text{dba})_3$ (23 mg, 2.5 mol%), **1** (30 mg, 6 mol%), tris(3,5-dioxaheptyl)amine (16 μL , 5 mol%), and *t*-BuOH (2 mL) was heated to 130 $^\circ\text{C}$ for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-50% EtOAc/hexanes) to provide the title compound as a white solid (112 mg, 76%), mp = 141 – 145 $^\circ\text{C}$ (literature 143 – 144 $^\circ\text{C}$). ^1H NMR (300 MHz, CDCl_3) δ : 8.35 (d, $J = 8.7$ Hz, 2H), 7.89 (d, $J = 8.4$ Hz, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ : 133.7, 124.5, 118.6, 117.1 ppm. IR (neat, cm^{-1}): 2233, 1601, 1526, 1489, 1349, 1295, 860, 748, 683, 540.

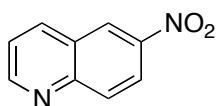


2-(3-Nitrophenyl)ethanol (Table 2) Following the general procedure, a mixture of 3-chlorophenethylalcohol (133 μL , 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), $\text{Pd}_2(\text{dba})_3$ (23 mg, 2.5 mol%), **1** (30 mg, 6 mol%), tris(3,5-dioxaheptyl)amine (16 μL , 5 mol%), and *t*-BuOH (2 mL) was heated to 130 $^\circ\text{C}$ for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-50% EtOAc/hexanes) to provide the title compound as a white solid (135 mg, 80%), mp = 47 – 49 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) δ : 8.06 (m, 2H), 7.55 (d, $J = 7.8$ Hz, 1H), 7.44 (t, $J = 7.8$ Hz, 1H),

3.87 (t, $J = 6.3$ Hz, 2H), 2.93 (t, $J = 6.3$ Hz, 2H), 2.23 (s, 1H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ : 148.5, 141.2, 135.7, 129.6, 124.1, 121.8, 63.1, 38.8 ppm. IR (neat, cm^{-1}): 3427, 1640, 1525, 1351, 1047, 735, 688. Anal. Calcd. for $\text{C}_8\text{H}_9\text{NO}_3$: C, 57.48; H, 5.43. Found: C, 57.73; H, 5.40.

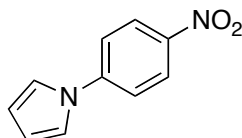


4-(4-Nitrophenyl)morpholine (Table 2) Following the general procedure, a mixture of 4-(4-chlorophenyl)morpholine (198 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), $\text{Pd}_2(\text{dba})_3$ (4.5 mg, 0.5 mol%), **1** (6 mg, 1.2 mol%), tris(3,5-dioxaheptyl)amine (16 μL , 5 mol%), and *t*-BuOH (2 mL) was heated to 130 $^\circ\text{C}$ for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-50% EtOAc/hexanes) to provide the title compound as a red solid (207 mg, 99%), mp = 148 – 150 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) δ : 8.05 (d, $J = 9.0$ Hz, 2H), 6.77 (d, $J = 9.3$ Hz, 2H), 3.82 (t, $J = 4.8$ Hz, 4H), 3.34 (t, $J = 4.8$ Hz, 4H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ : 155.2, 138.9, 126.1, 112.7, 66.6, 47.2 ppm. IR (neat, cm^{-1}): 1602, 1511, 1490, 1331, 1243, 1119, 1109, 1052, 927, 825. Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$: C, 57.68; H, 5.81. Found: C, 57.82; H, 5.82.

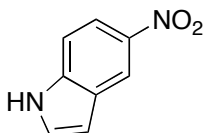


6-Nitroquinoline⁸ (Table 2) Following the general procedure, a mixture of 6-chloroquinoline (164 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), $\text{Pd}_2(\text{dba})_3$ (4.5 mg, 0.5 mol%), **1** (6 mg, 1.2 mol%), tris(3,5-dioxaheptyl)amine (16 μL , 5 mol%), and *t*-BuOH (2 mL) was heated to 130 $^\circ\text{C}$ for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 25-75% EtOAc/hexanes) to provide the title compound as a white solid (168 mg, 97%), mp = 149 – 151 $^\circ\text{C}$ (literature 150 $^\circ\text{C}$). ^1H NMR (300 MHz, CDCl_3) δ : 9.06 (s, 1H), 8.76 (s, 1H), 8.45 (d, $J = 9.3$ Hz, 1H), 8.33 (d, $J = 9.6$ Hz, 1H), 8.19 (d, $J = 9.3$ Hz, 1H), 7.5 (dd, $J = 5.4$ Hz, $J = 8.4$ Hz, 1H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ : 154.1, 150.4, 145.7, 138.1, 131.6, 127.2, 124.9, 123.1,

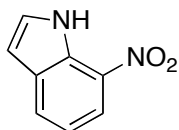
123.1 ppm. IR (neat, cm^{-1}): 1606, 1519, 1492, 1385, 1344, 1324, 903, 853, 809, 791, 777.



1-(4-Nitrophenyl)-1H-pyrrole⁹ (Table 2) Following the general procedure, a mixture of 1-(4-chlorophenyl)-1H-pyrrole (177 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), $\text{Pd}_2(\text{dba})_3$ (4.5 mg, 0.5 mol%), **1** (6 mg, 1.2 mol%), tris(3,5-dioxaheptyl)amine (16 μL , 5 mol%), and *t*-BuOH (2 mL) was heated to 130 $^\circ\text{C}$ for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-50% EtOAc/hexanes) to provide the title compound as an off-white solid (141 mg, 99%), mp = 179 – 180 $^\circ\text{C}$ (literature 178 – 180 $^\circ\text{C}$). ^1H NMR (300 MHz, DMSO) δ : 8.25 (d, $J = 9.3$ Hz, 2H), 7.85 (d, $J = 9.3$ Hz, 2H), 7.56 (m, 2H), 6.35 (s, 2H) ppm. ^{13}C NMR (75 MHz, DMSO) δ : 145.3, 144.5, 126.1, 120.1, 119.6, 112.9 ppm. IR (neat, cm^{-1}): 8438, 1598, 1507, 1334, 1110, 1063, 847, 737.

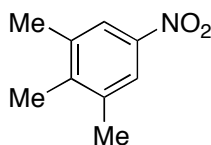


5-Nitro-1H-indole (Table 2) Following the general procedure, a mixture of 5-chloroindole (151 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), $\text{Pd}_2(\text{dba})_3$ (23 mg, 2.5 mol%), **1** (30 mg, 6 mol%), tris(3,5-dioxaheptyl)amine (16 μL , 5 mol%), and *t*-BuOH (2 mL) was heated to 130 $^\circ\text{C}$ for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-75% EtOAc/hexanes) to provide the title compound as a yellow solid (134 mg, 83%), mp = 140 – 141 $^\circ\text{C}$. ^1H NMR (300 MHz, DMSO) δ : 11.82 (s, 1H), 8.55 (s, 1H), 7.97 (dd, $J = 2.4$ Hz, $J = 9.0$ Hz, 1H), 7.60 (t, $J = 2.7$ Hz, 1H), 7.54 (d, $J = 9.0$ Hz, 1H), 6.71 (s, 1H) ppm. ^{13}C NMR (75 MHz, DMSO) δ : 141.7, 139.7, 130.0, 127.7, 118.0, 117.1, 112.5, 104.6 ppm. IR (neat, cm^{-1}): 3337, 1504, 1476, 1347, 1334, 1100, 892, 765, 744, 422. Anal. Calcd. for $\text{C}_8\text{H}_6\text{N}_2\text{O}_2$: C, 59.26; H, 3.73. Found: C, 59.34; H, 3.68.

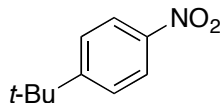


7-Nitro-1H-indole (Table 2) Following the general procedure, a mixture of 7-chloroindole (151 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), Pd₂(dba)₃ (23 mg, 2.5 mol%), **1** (30 mg, 6 mol%), tris(3,5-dioxaheptyl)amine (16 μL, 5 mol%), and *t*-BuOH (2 mL) was heated to 130 °C for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-75% EtOAc/hexanes) to provide the title compound as a yellow solid (116 mg, 72%), mp = 96 – 98 °C. ¹H NMR (300 MHz, CDCl₃) δ: 9.96 (s, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.40 (m, 1H), 7.20 (t, *J* = 8.1 Hz, 1H), 6.71 (m, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ: 131.9, 129.5, 129.2, 126.9, 119.5, 119.4, 104.3, 104.2 ppm. IR (neat, cm⁻¹): 3395, 1502, 1479, 1337, 1321, 1272, 1098, 1066, 736, 719. Anal. Calcd. for C₈H₆N₂O₂: C, 59.26; H, 3.73. Found: C, 59.38; H, 3.65.

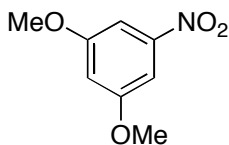
Experimental Procedures for Examples Described in Table 3



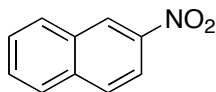
1,2,3-Trimethyl-5-nitrobenzene (Table 2) Following the general procedure, a mixture of 3,4,5-trimethylphenyl triflate (268 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), Pd₂(dba)₃ (4.5 mg, 0.5 mol%), **1** (6 mg, 1.2 mol%), tris(3,5-dioxaheptyl)amine (16 μL, 5 mol%), and *t*-BuOH (2 mL) was heated to 130 °C for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-40% EtOAc/hexanes) to provide the title compound as a yellow solid (156 mg, 95%), mp = 69 – 71 °C. ¹H NMR (300 MHz, CDCl₃) δ: 7.81 (s, 2H), 2.34 (s, 6H), 2.23 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ: 145.5, 143.6, 138.1, 122.4, 20.9, 16.2 ppm. IR (neat, cm⁻¹): 2962, 1536, 1453, 1357, 1211, 1159, 1044, 919, 855, 746. Anal. Calcd. for C₉H₁₁NO₂: C, 65.44; H, 6.71. Found: C, 65.54; H, 6.69.



1-*tert*-Butyl-4-nitrobenzene (Table 2) Following the general procedure, a mixture of 4-*tert*-butylphenyl triflate (433 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), Pd₂(dba)₃ (4.5 mg, 0.5 mol%), **1** (6 mg, 1.2 mol%), tris(3,5-dioxaheptyl)amine (16 μ L, 5 mol%), and *t*-BuOH (2 mL) was heated to 130 °C for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-40% EtOAc/hexanes) to provide the title compound as a yellow oil (161 mg, 90%). ¹H NMR (300 MHz, CDCl₃) δ : 8.13 (d, *J* = 9.0 Hz, 2H), 7.53 (d, *J* = 9.0 Hz, 2H), 1.35 (s, 9H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ : 159.1, 146.1, 126.5, 123.6, 35.6, 31.3 ppm. IR (neat, cm⁻¹): 2966, 1604, 1520, 1343, 1268, 1103, 853, 758, 727, 700. Anal. Calcd. for C₁₀H₁₃NO₂: C, 67.02; H, 7.31. Found: C, 66.86; H, 7.32.

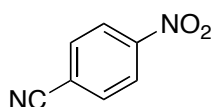


1,3-Dimethoxy-5-nitrobenzene (Table 2) Following the general procedure, a mixture of 3,5-dimethoxyphenyl triflate (286 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), Pd₂(dba)₃ (4.5 mg, 0.5 mol%), **1** (6 mg, 1.2 mol%), tris(3,5-dioxaheptyl)amine (16 μ L, 5 mol%), and *t*-BuOH (2 mL) was heated to 130 °C for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-40% EtOAc/hexanes) to provide the title compound as a yellow solid (179 mg, 98%), mp = 88 – 90 °C. ¹H NMR (300 MHz, CDCl₃) δ : 7.30 (s, 2H), 6.70 (s, 1H), 3.83 (s, 6H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ : 161.0, 150.0, 107.3, 101.6, 56.1 ppm. IR (neat, cm⁻¹): 2961, 1589, 1535, 1452, 1356, 1210, 1044, 854, 745, 665. Anal. Calcd. for C₈H₉NO₄: C, 52.46; H, 4.95. Found: C, 52.98; H, 4.97.

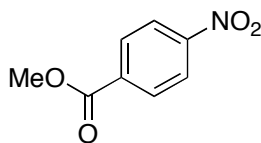


2-Nitronaphthalene (Table 2) Following the general procedure, a mixture of 2-naphthyl triflate (276 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), Pd₂(dba)₃ (4.5 mg, 0.5

mol%), **1** (6 mg, 1.2 mol%), tris(3,5-dioxaheptyl)amine (16 μ L, 5 mol%), and *t*-BuOH (2 mL) was heated to 130 $^{\circ}$ C for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-40% EtOAc/hexanes) to provide the title compound as a yellow solid (150 mg, 87%), mp = 74 – 76 $^{\circ}$ C. 1 H NMR (300 MHz, CDCl₃) δ : 8.72 (s, 1H), 8.18 (d, J = 9.0 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.7 Hz, 2H), 7.64 (m, 2H) ppm. 13 C NMR (75 MHz, CDCl₃) δ : 136.0, 132.1, 130.2, 130.0, 129.7, 128.2, 128.2, 124.8, 124.8, 119.4 ppm. IR (neat, cm⁻¹): 1603, 1530, 1501, 1351, 1081, 903, 869, 820, 766, 466. Anal. Calcd. for C₁₀H₇NO₂: C, 69.36; H, 4.07. Found: C, 69.88; H, 4.13.

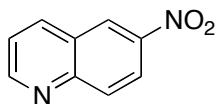


4-Nitrobenzonitrile⁷ (Table 2) Following the general procedure, a mixture of 4-cyanophenyl triflate (251 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), Pd₂(dba)₃ (23 mg, 2.5 mol%), **1** (30 mg, 6 mol%), tris(3,5-dioxaheptyl)amine (16 μ L, 5 mol%), and *t*-BuOH (2 mL) was heated to 130 $^{\circ}$ C for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-40% EtOAc/hexanes) to provide the title compound as a white solid (112 mg, 75%), mp = 141 – 145 $^{\circ}$ C (literature 143 – 144 $^{\circ}$ C). 1 H NMR (300 MHz, CDCl₃) δ : 8.36 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H) ppm. 13 C NMR (75 MHz, CDCl₃) δ : 133.7, 124.5, 118.6, 117.1 ppm. IR (neat, cm⁻¹): 2233, 1603, 1533, 1526, 1489, 1349, 1296, 860, 748, 683.

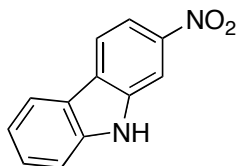


Methyl 4-nitrobenzoate¹⁰ (Table 2) Following the general procedure, a mixture of methyl 4-(perfluorobutoxy)benzoate (434 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), Pd₂(dba)₃ (4.5 mg, 0.5 mol%), **1** (6 mg, 1.2 mol%), tris(3,5-dioxaheptyl)amine (16 μ L, 5 mol%), and *t*-BuOH (2 mL) was heated to 130 $^{\circ}$ C for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 0-50% EtOAc/hexanes) to provide the title compound as a white solid (153 mg, 85%), mp = 94 – 95 $^{\circ}$ C (literature 95 – 96 $^{\circ}$ C). 1 H NMR (300 MHz, CDCl₃) δ : 8.25 (d, J = 9.0 Hz, 2H), 8.18 (d, J = 9.0 Hz, 2H), 3.95 (s, 3H) ppm. 13 C NMR (75 MHz, CDCl₃) δ : 165.4, 150.7,

135.7, 130.9, 123.8, 53.1 ppm. IR (neat, cm^{-1}): 1719, 1609, 1526, 1434, 1351, 1282, 1104, 956, 872, 717.



6-Nitroquinoline⁸ (Table 2) Following the general procedure, a mixture of quinolin-6-yl trifluoromethanesulfonate (277 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), Pd₂(dba)₃ (4.5 mg, 0.5 mol%), **1** (6 mg, 1.2 mol%), tris(3,5-dioxaheptyl)amine (16 μL , 5 mol%), and *t*-BuOH (2 mL) was heated to 130 °C for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 25-75% EtOAc/hexanes) to provide the title compound as a white solid (152 mg, 94%), mp = 150 – 151 °C. ¹H NMR (300 MHz, CDCl₃) δ : 9.06 (s, 1H), 8.76 (s, 1H), 8.45 (d, $J = 9.3$ Hz, 1H), 8.33 (d, $J = 9.6$ Hz, 1H), 8.19 (d, $J = 9.3$ Hz, 1H), 7.5 (dd, $J = 5.4$ Hz, $J = 8.4$ Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ : 154.1, 150.4, 145.7, 138.1, 131.6, 127.2, 124.9, 123.1, 123.1 ppm. IR (neat, cm^{-1}): 1606, 1519, 1492, 1344, 1324, 903, 853, 809, 791, 777. Anal. Calcd. for C₉H₆N₂O₂: C, 62.07; H, 3.47. Found: C, 61.97; H, 3.36.

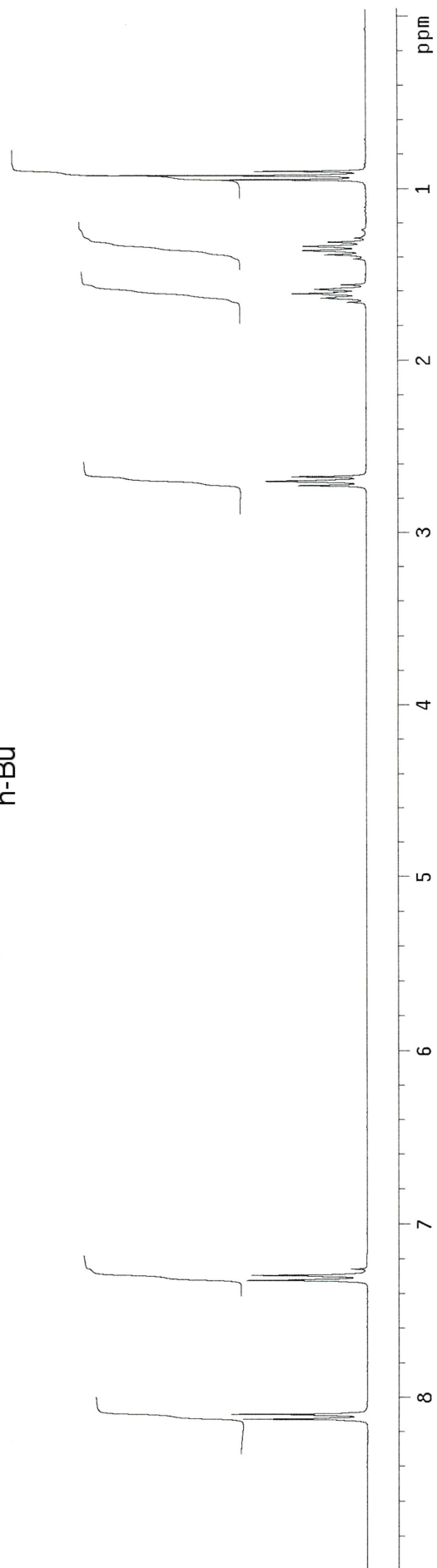
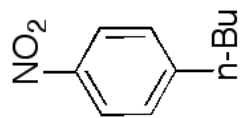


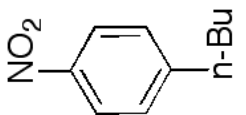
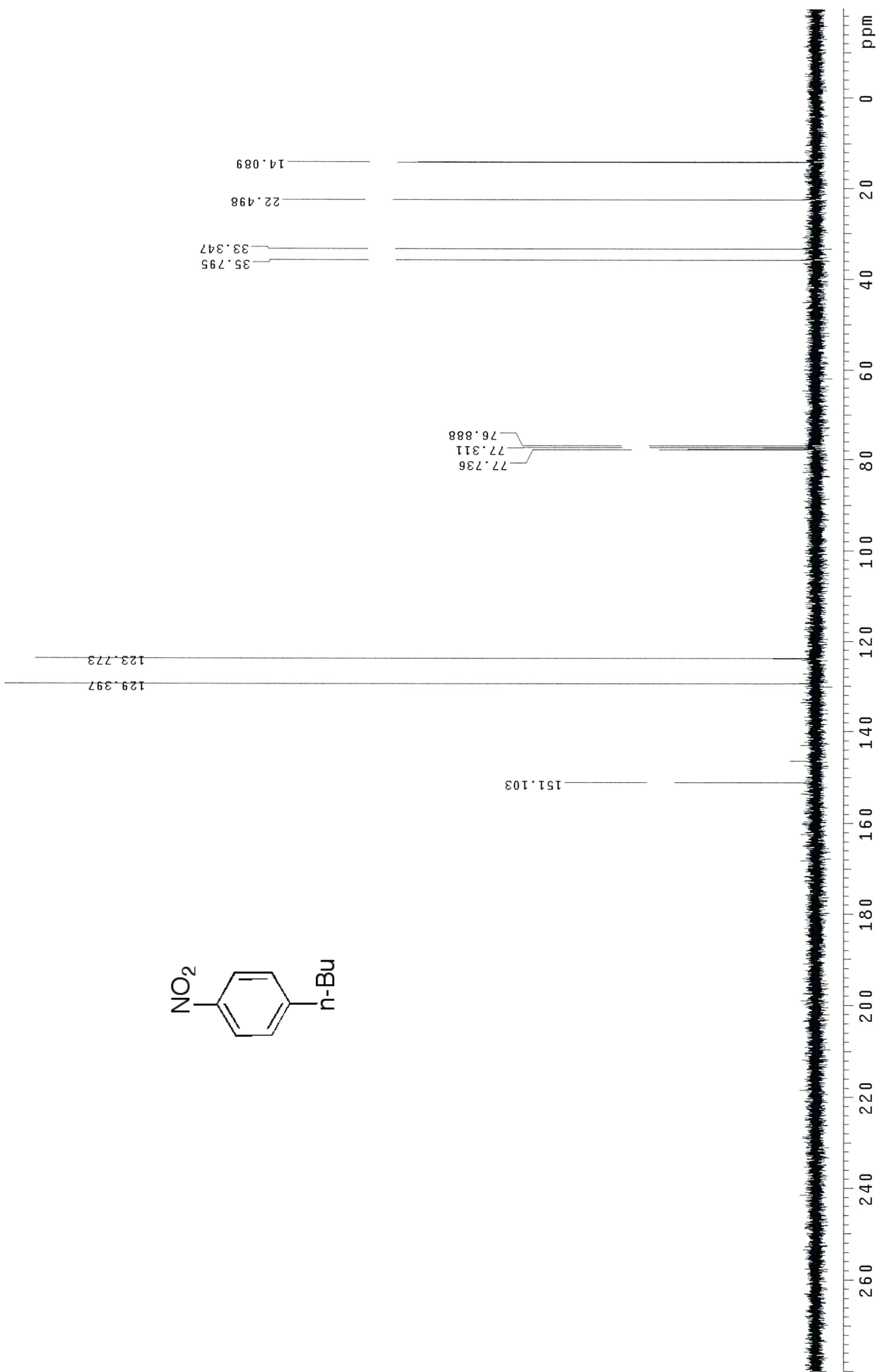
2-Nitro-9H-carbazole (Table 2) Following the general procedure, a mixture of 9H-carbazol-2-yl trifluoromethanesulfonate (315 mg, 1.0 mmol), sodium nitrite (138 mg, 2.0 mmol), Pd₂(dba)₃ (23 mg, 2.5 mol%), **1** (30 mg, 6 mol%), tris(3,5-dioxaheptyl)amine (16 μL , 5 mol%), and *t*-BuOH (2 mL) was heated to 130 °C for 24 h. The crude product was purified via the Biotage SP4 (silica-packed 50 g snap column; 25-75% EtOAc/hexanes) to provide the title compound as a off-white solid (162 mg, 76%), mp = 172 – 174 °C. ¹H NMR (300 MHz, DMSO) δ : 11.82 (s, 1H), 8.34 (s, 1H), 8.26 (d, $J = 8.4$ Hz, 1H), 8.20 (d, $J = 7.8$ Hz, 1H), 7.99 (d, $J = 8.7$ Hz, 1H), 7.60 (d, $J = 8.1$ Hz, 1H), 7.50 (t, $J = 7.2$ Hz, 1H), 7.22 (d, $J = 7.5$ Hz, 1H) ppm. ¹³C NMR (75 MHz, DMSO) δ : 145.6, 142.8, 139.1, 128.7, 128.2, 122.3, 121.7, 121.2, 120.4, 114.2, 112.4, 107.5 ppm. IR (neat, cm^{-1}): 3374, 1632, 1513, 1455, 1384, 1343, 1324, 874, 734, 719. Anal. Calcd. for C₁₂H₈N₂O₂: C,

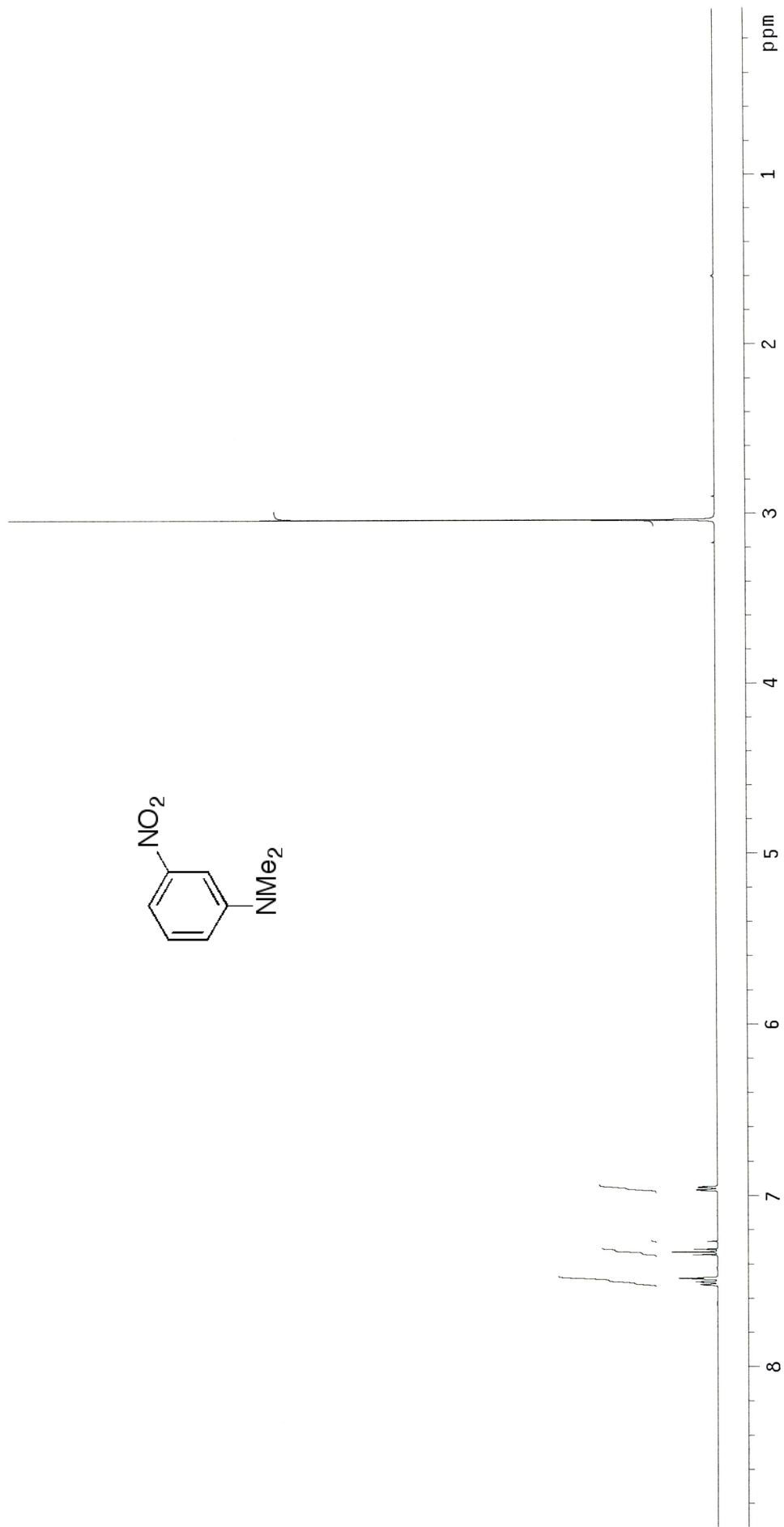
67.92; H, 3.80. Found: C, 68.23; H, 3.89.

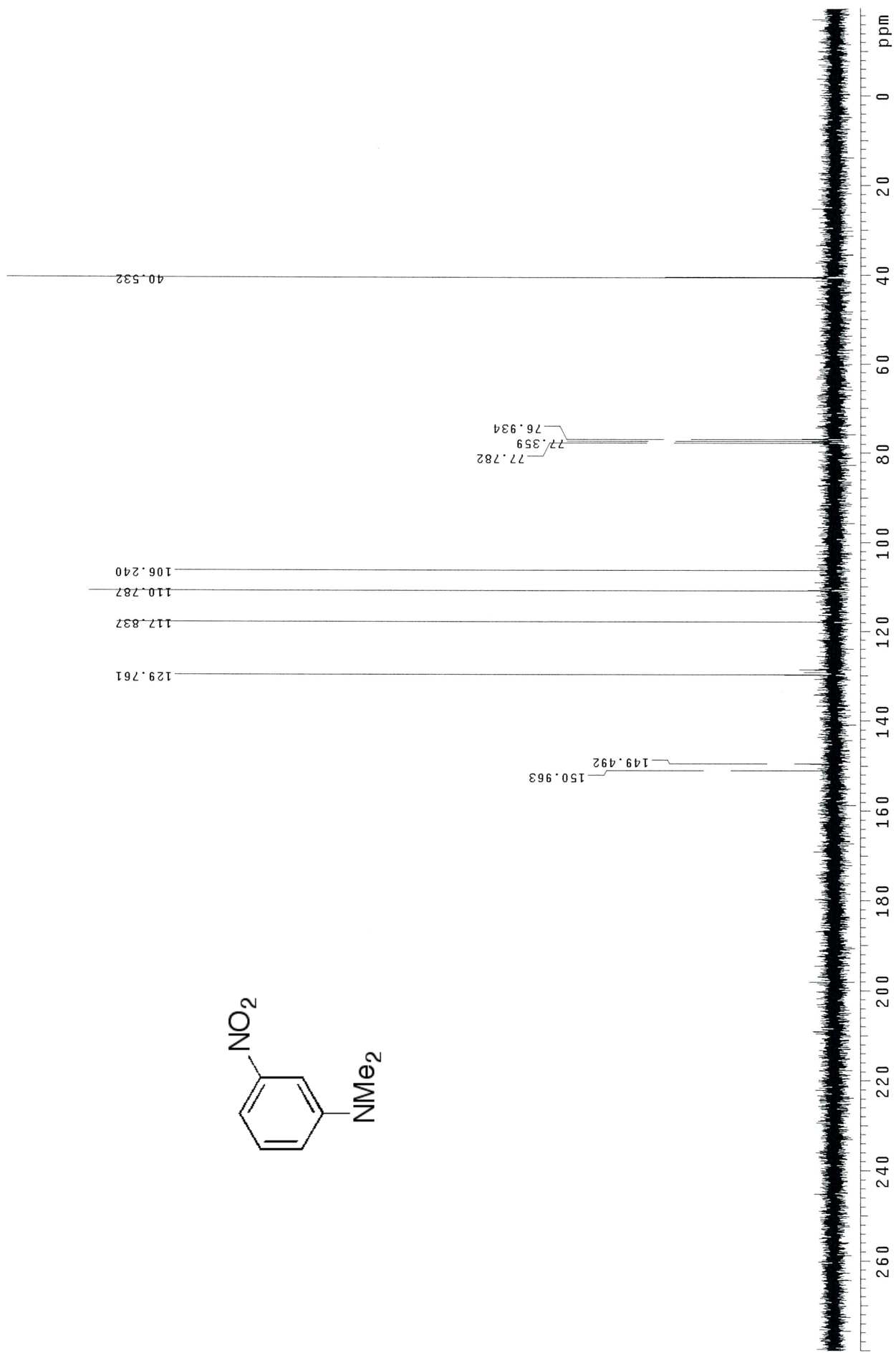
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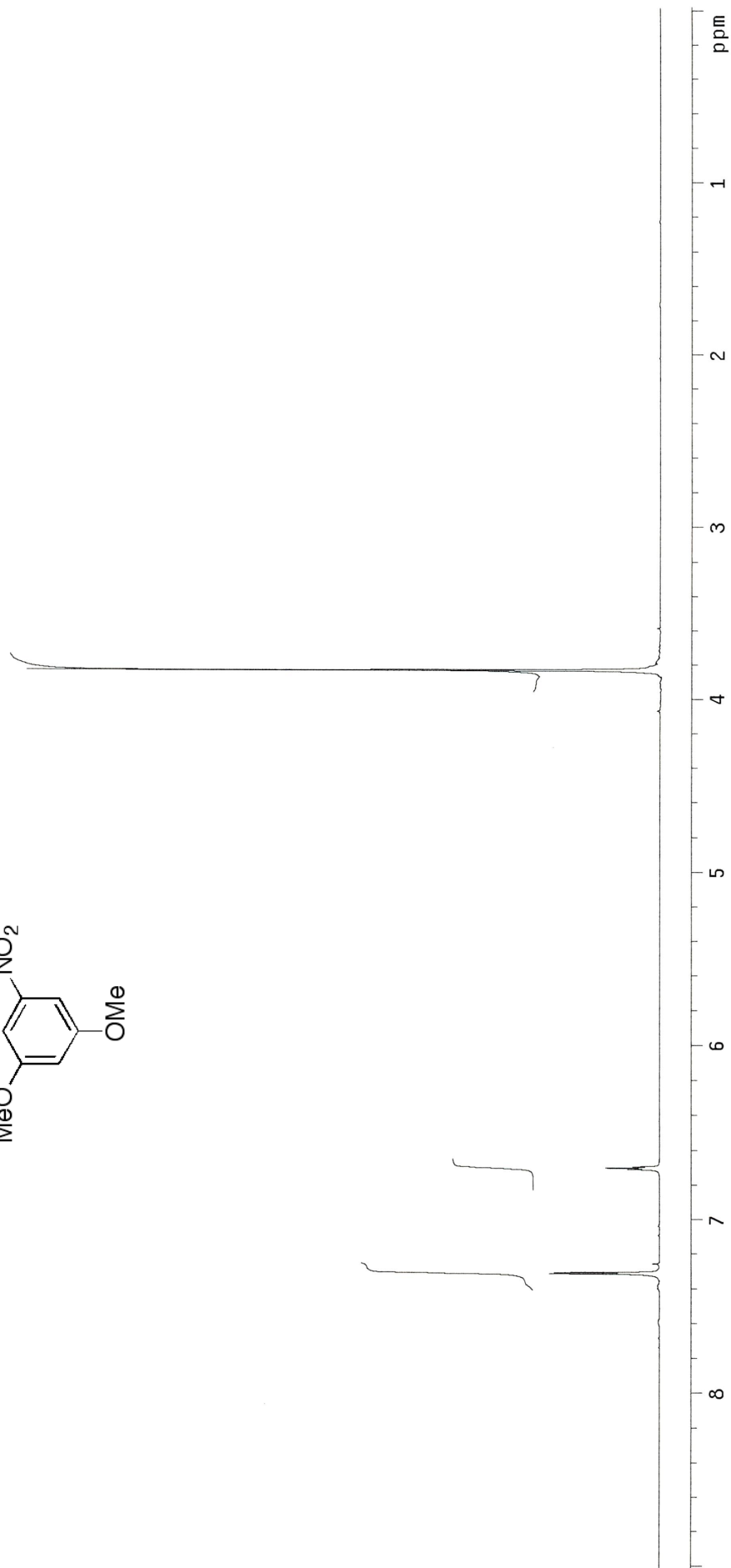
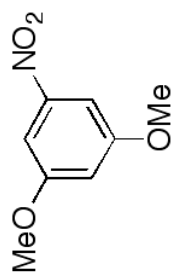
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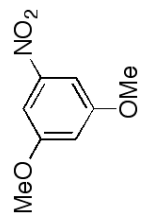
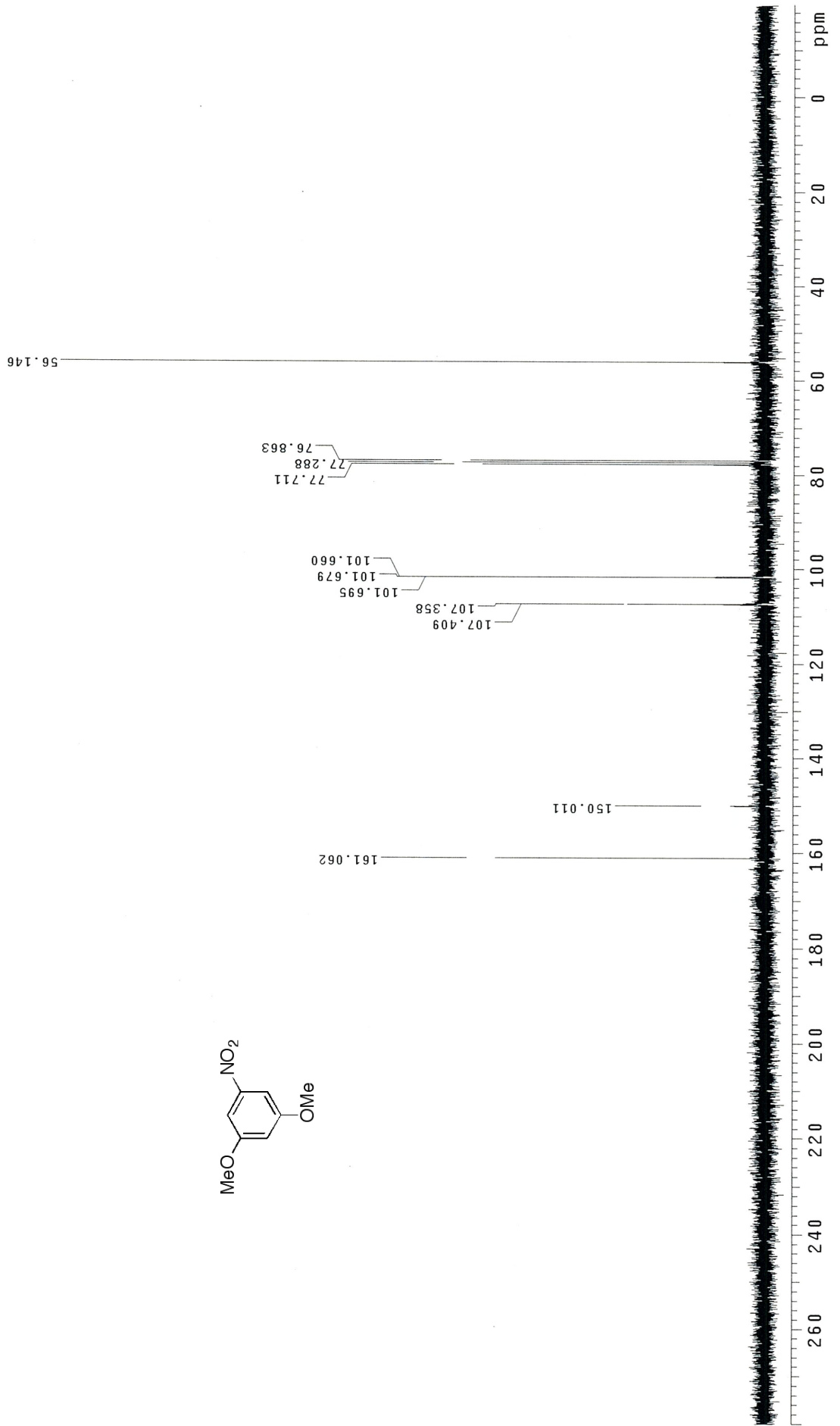


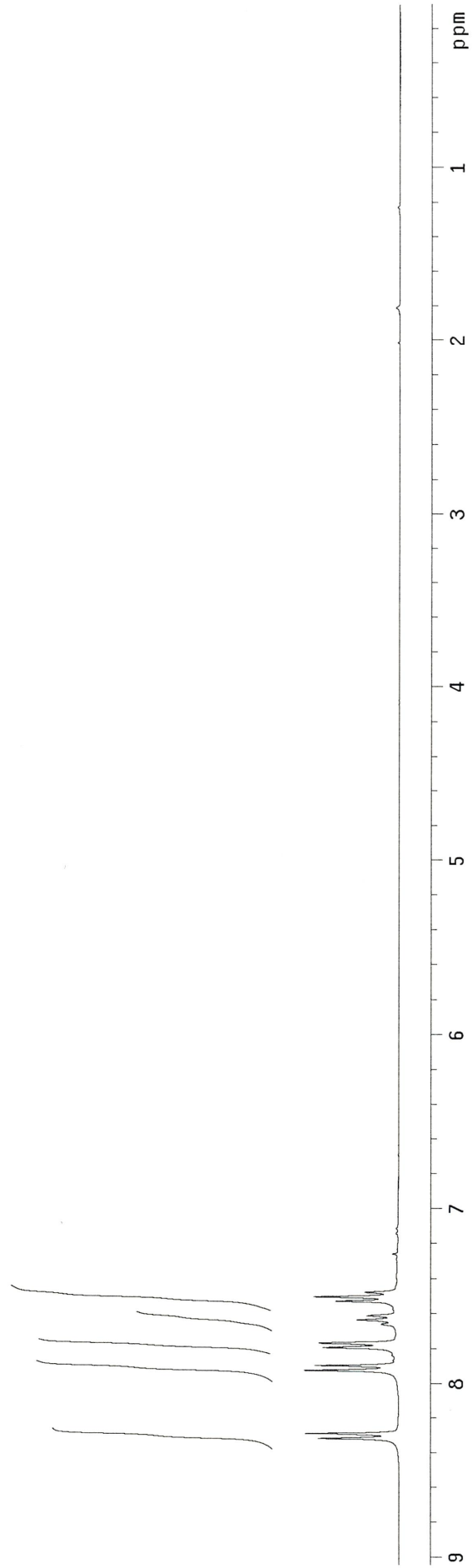
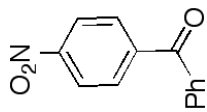


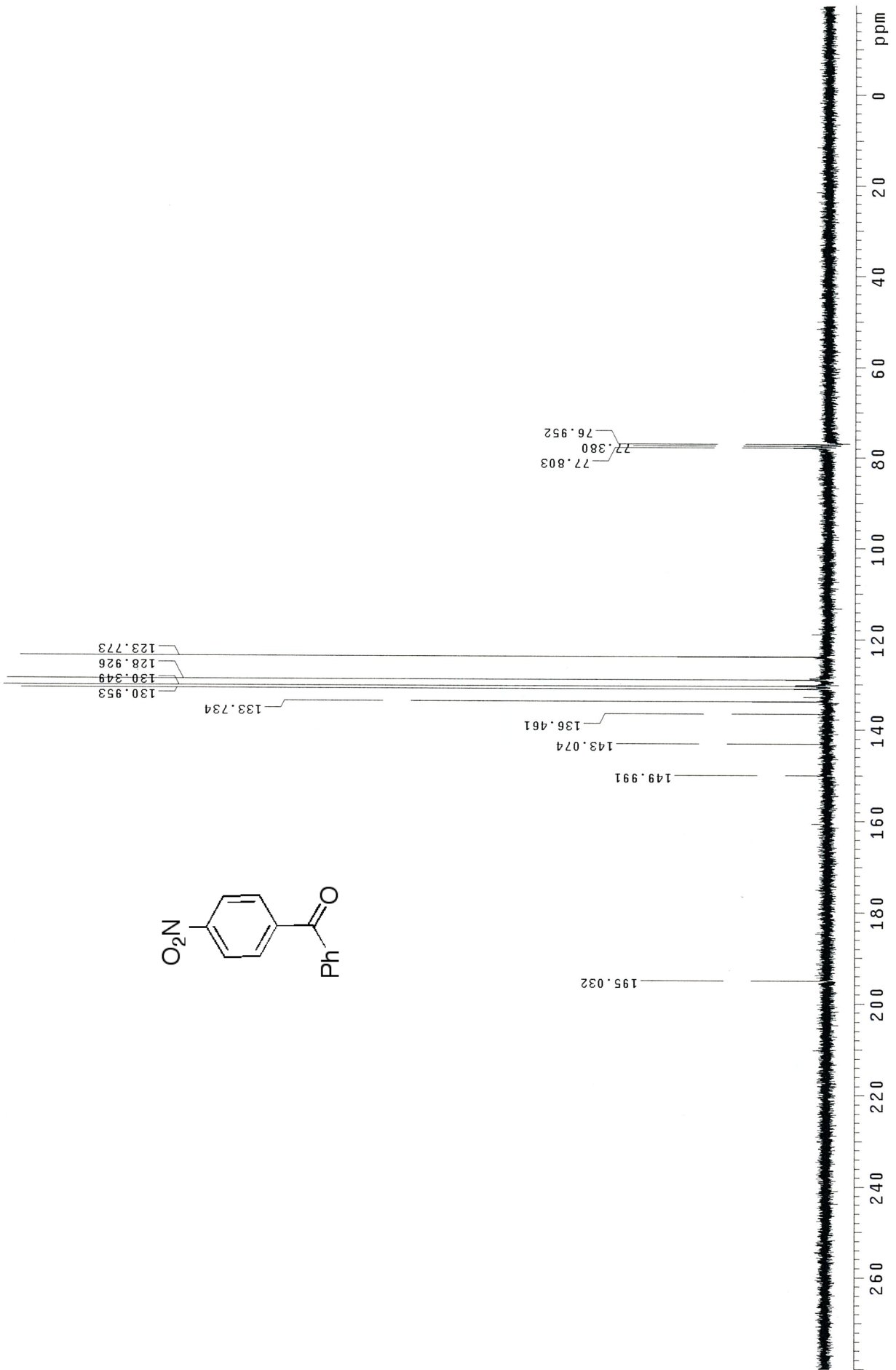


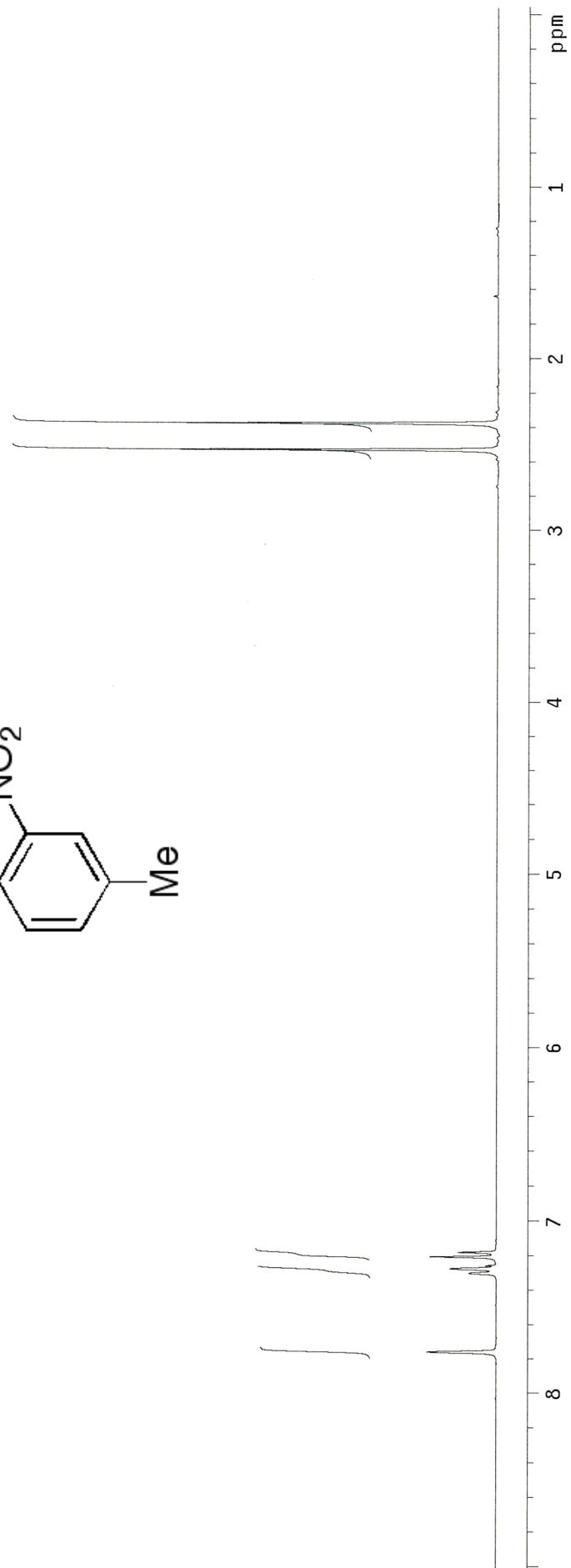
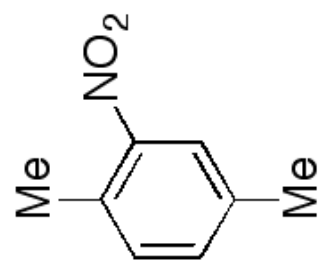


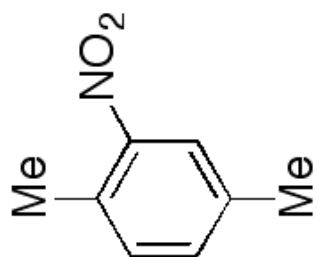
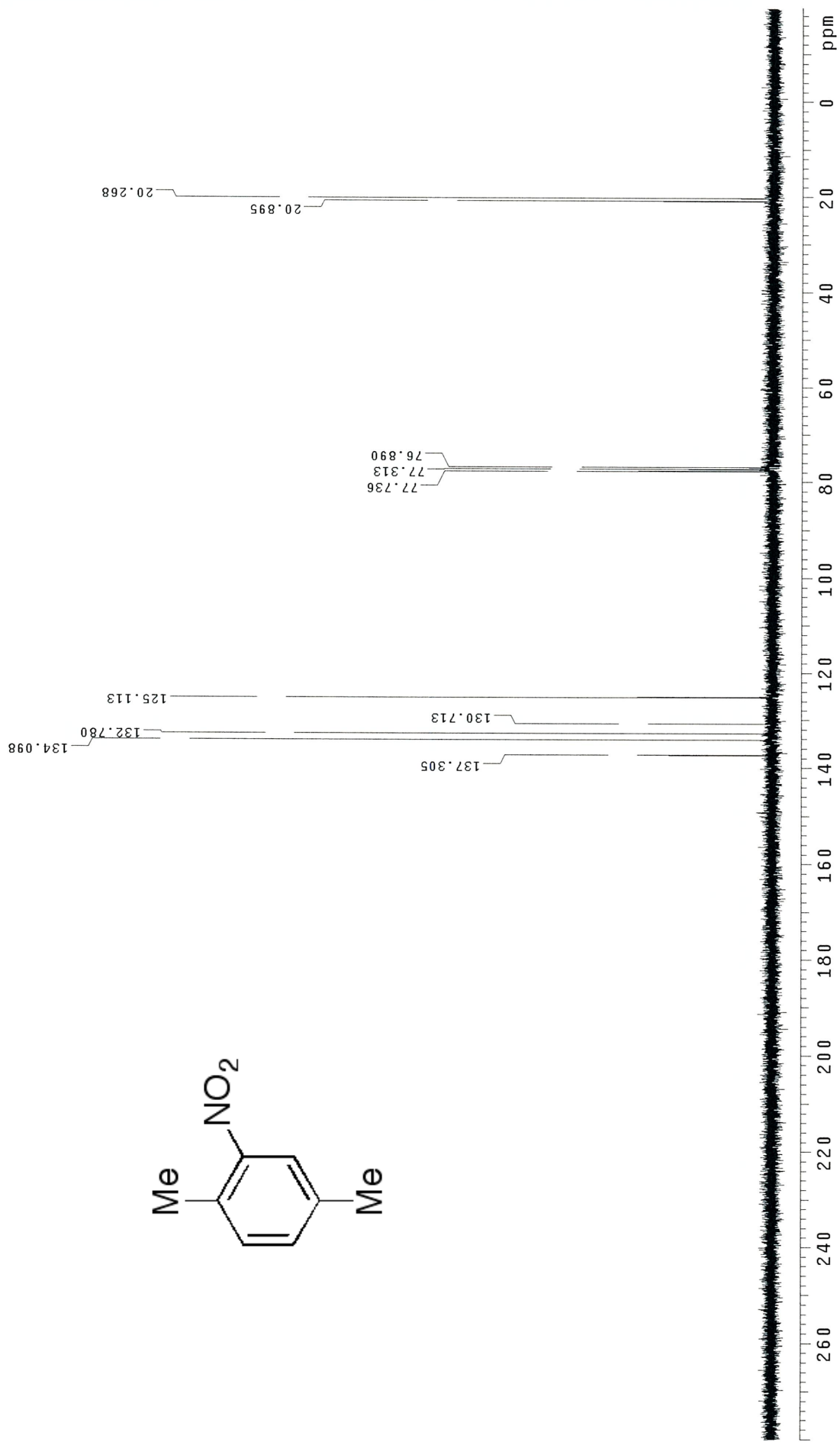


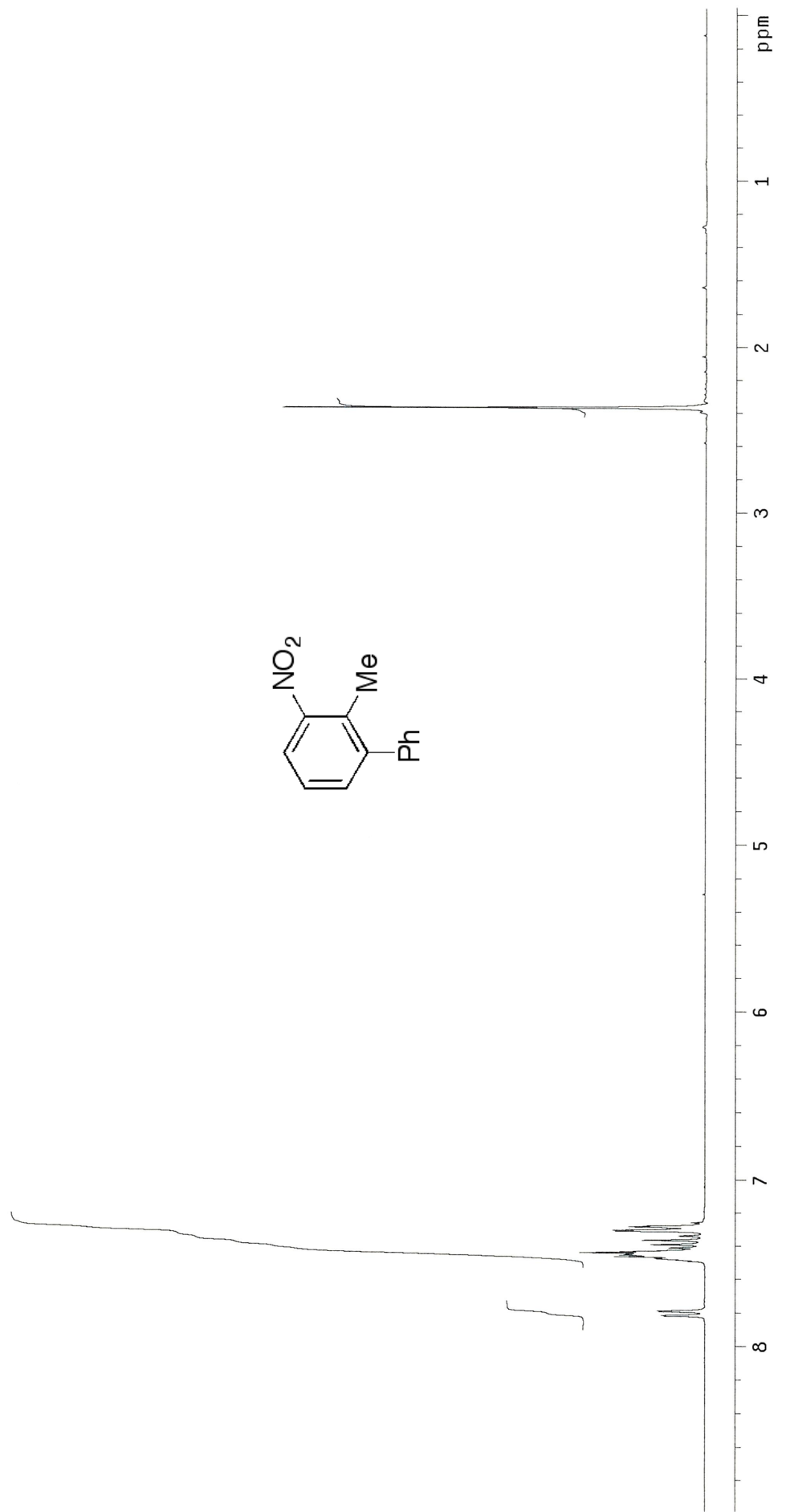


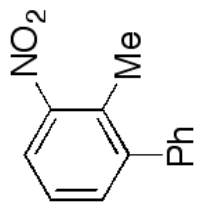
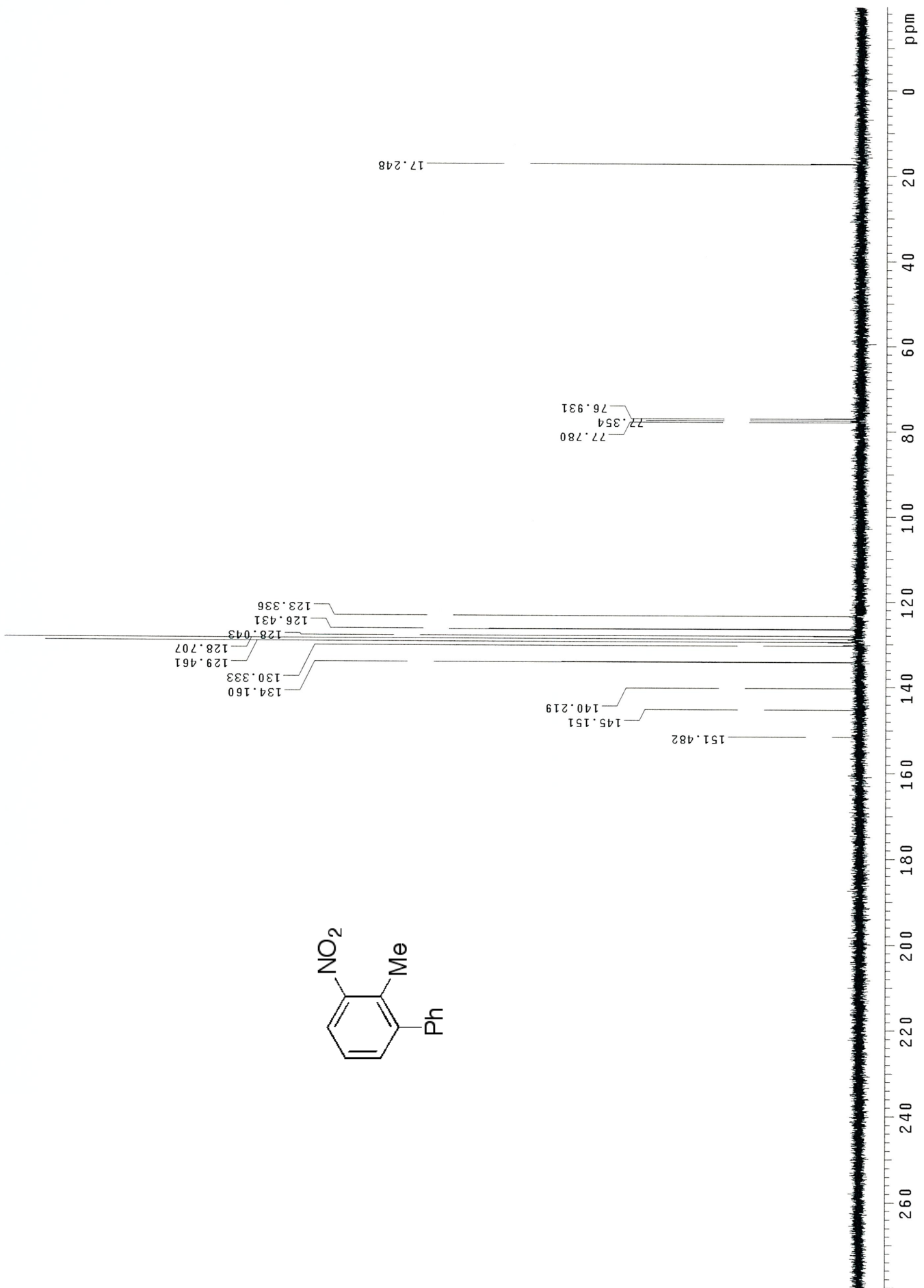


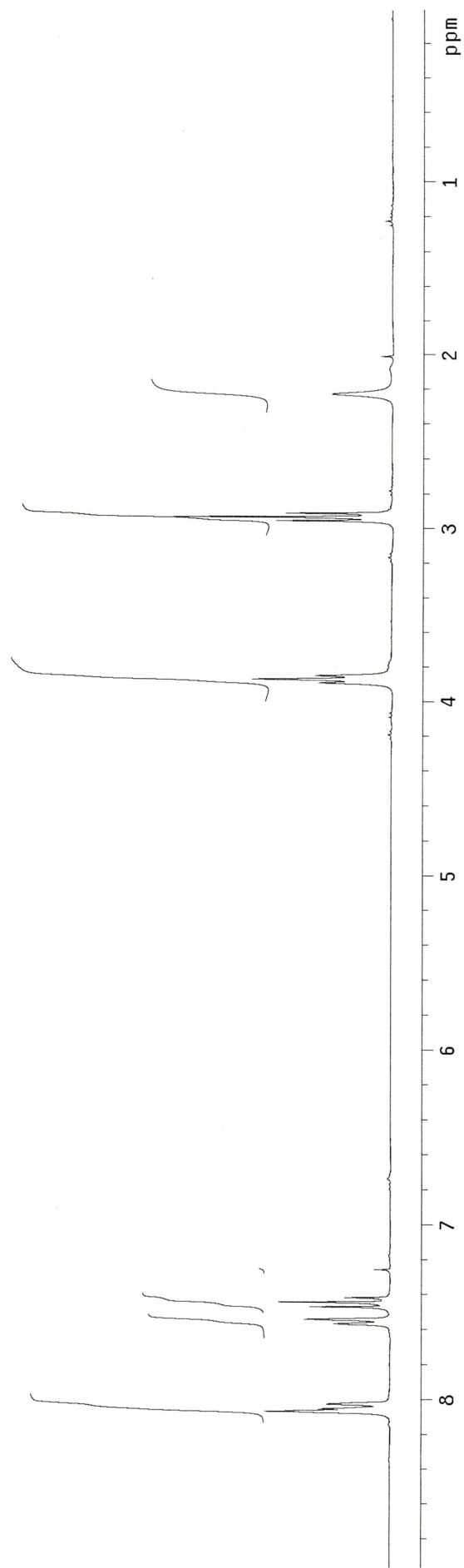
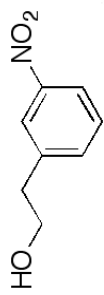


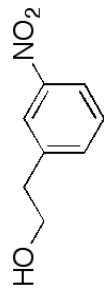
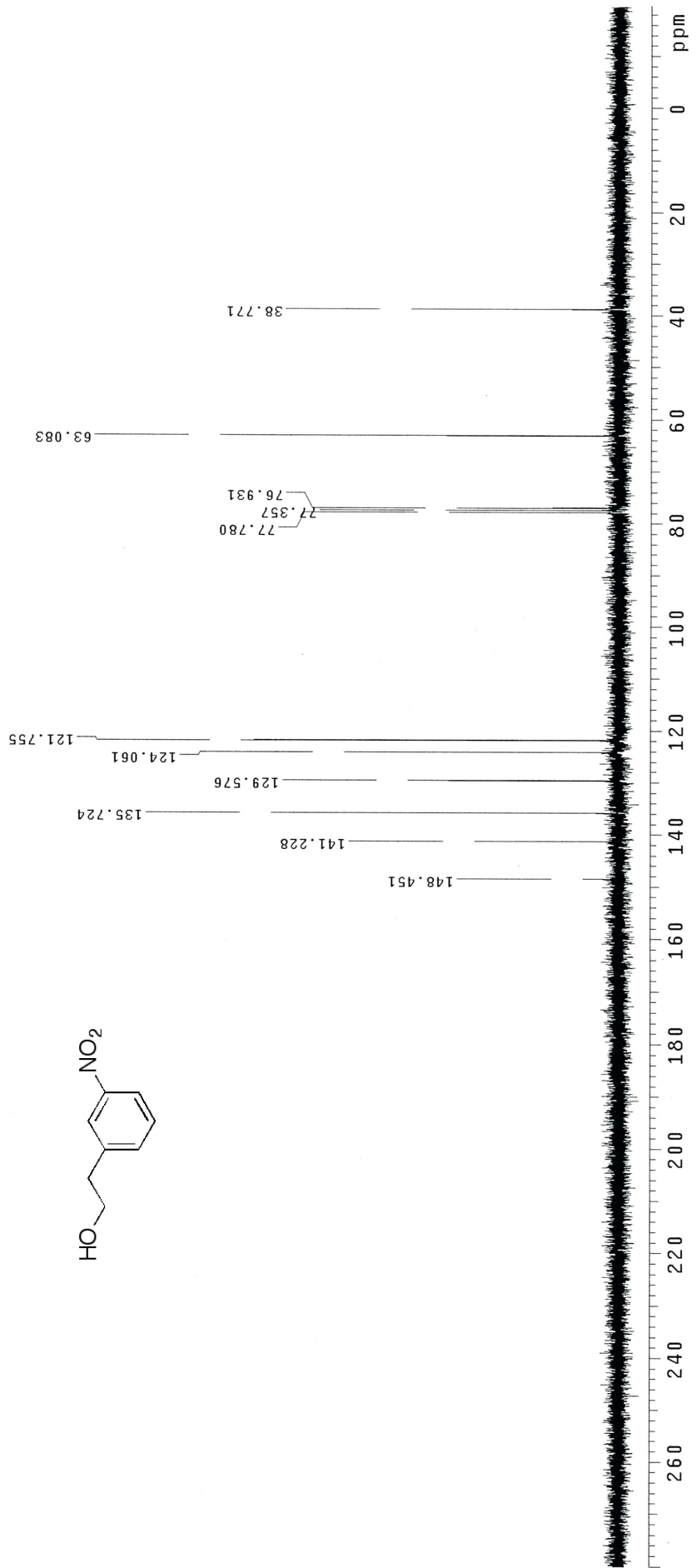


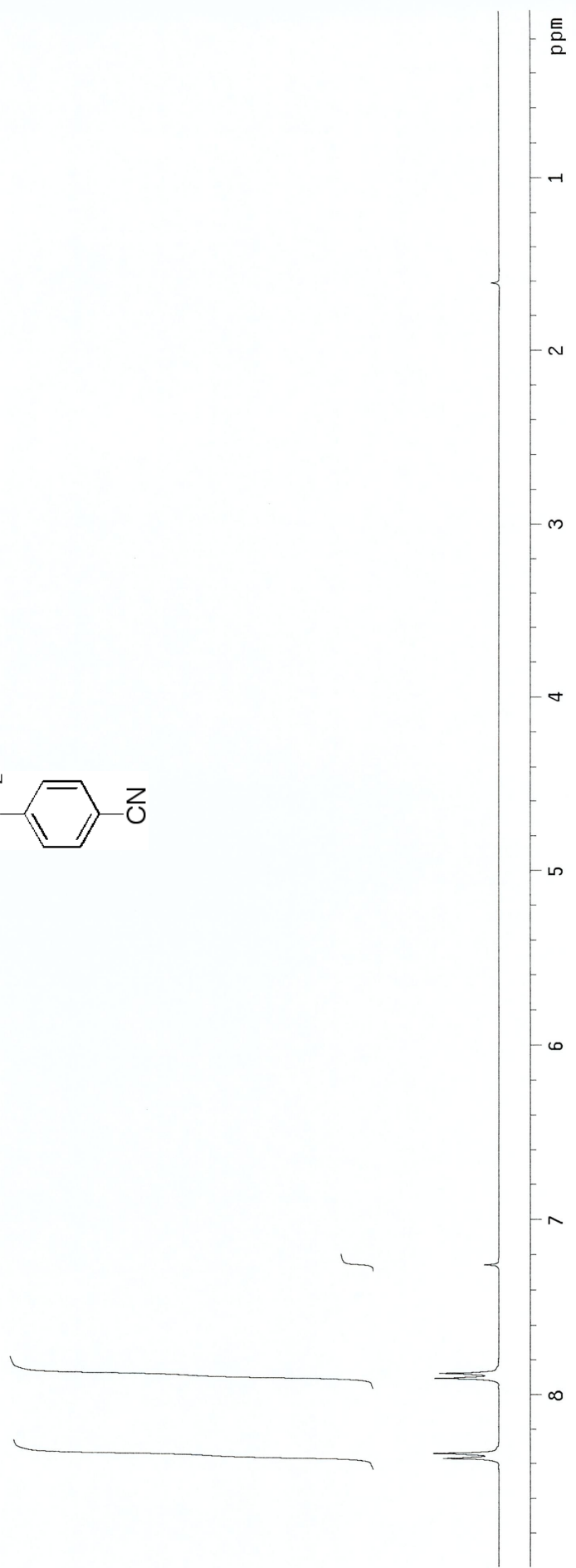
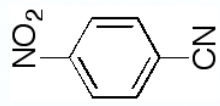


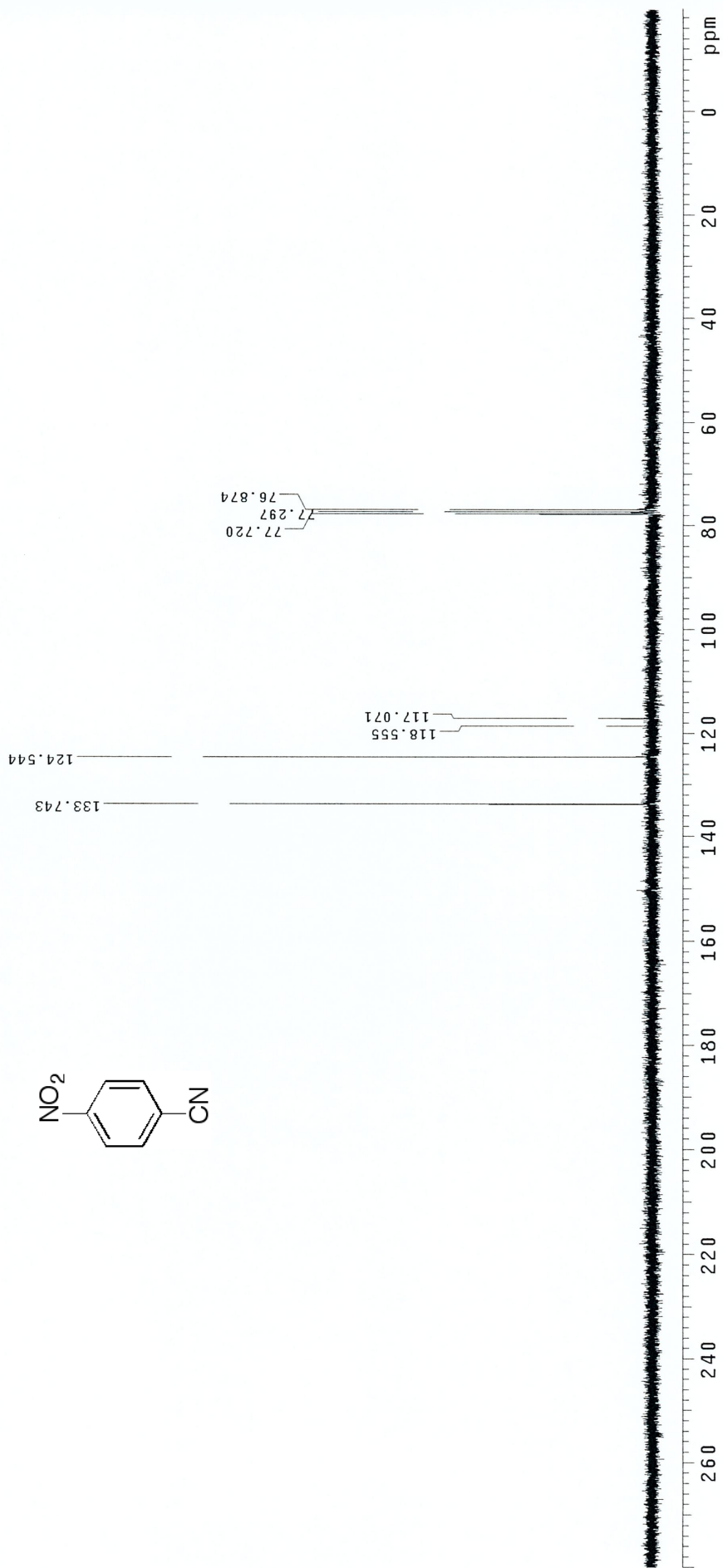


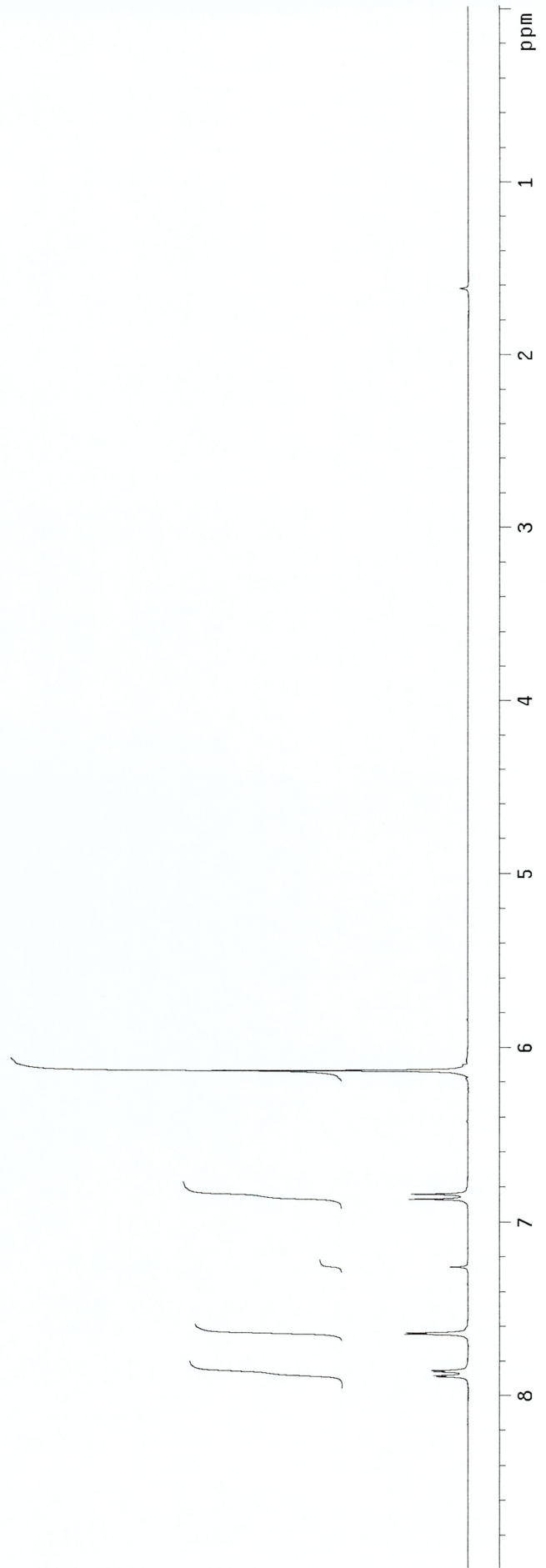
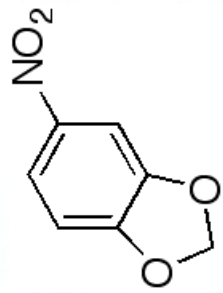


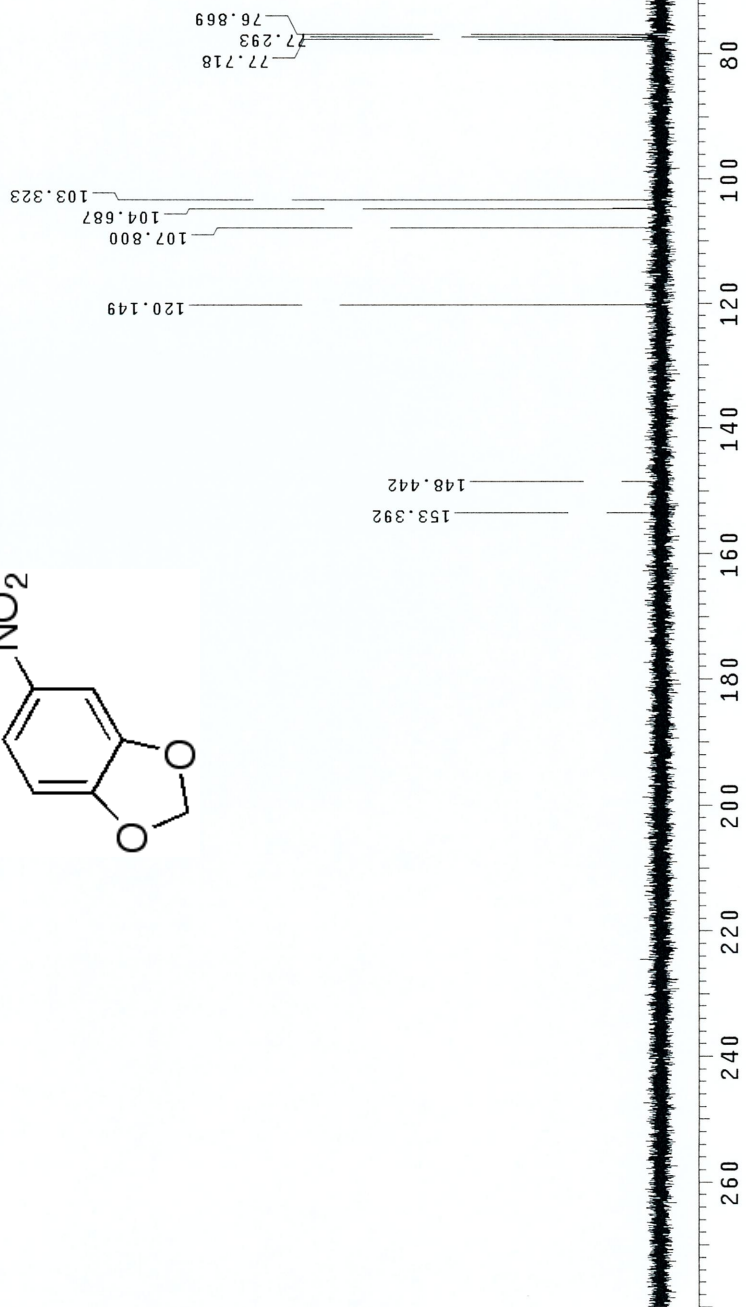
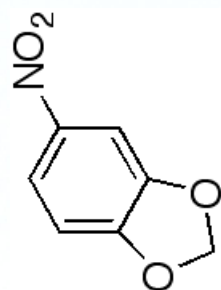


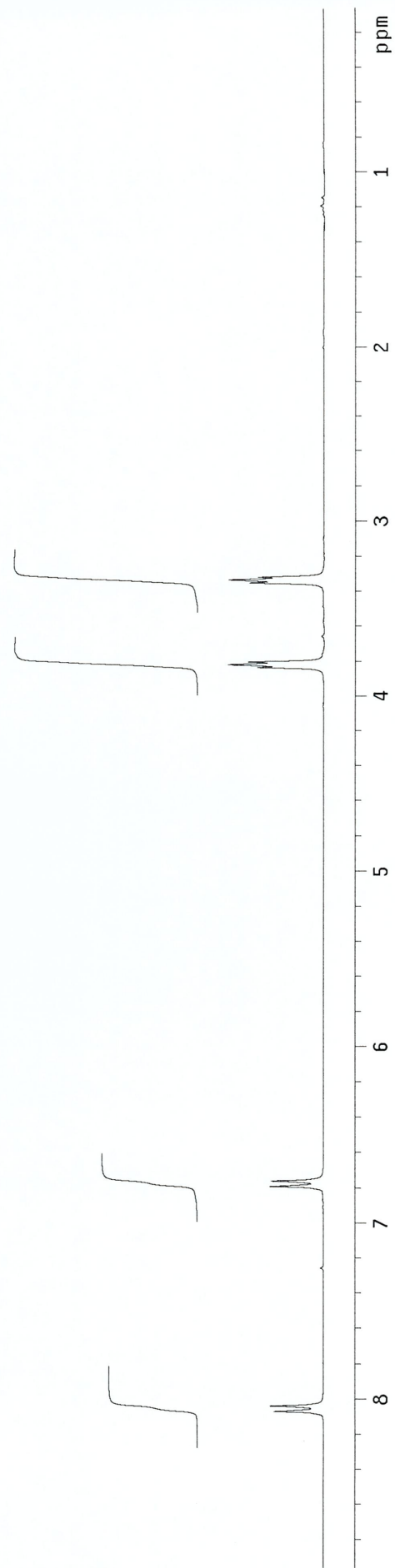
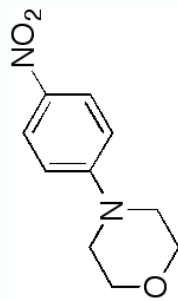


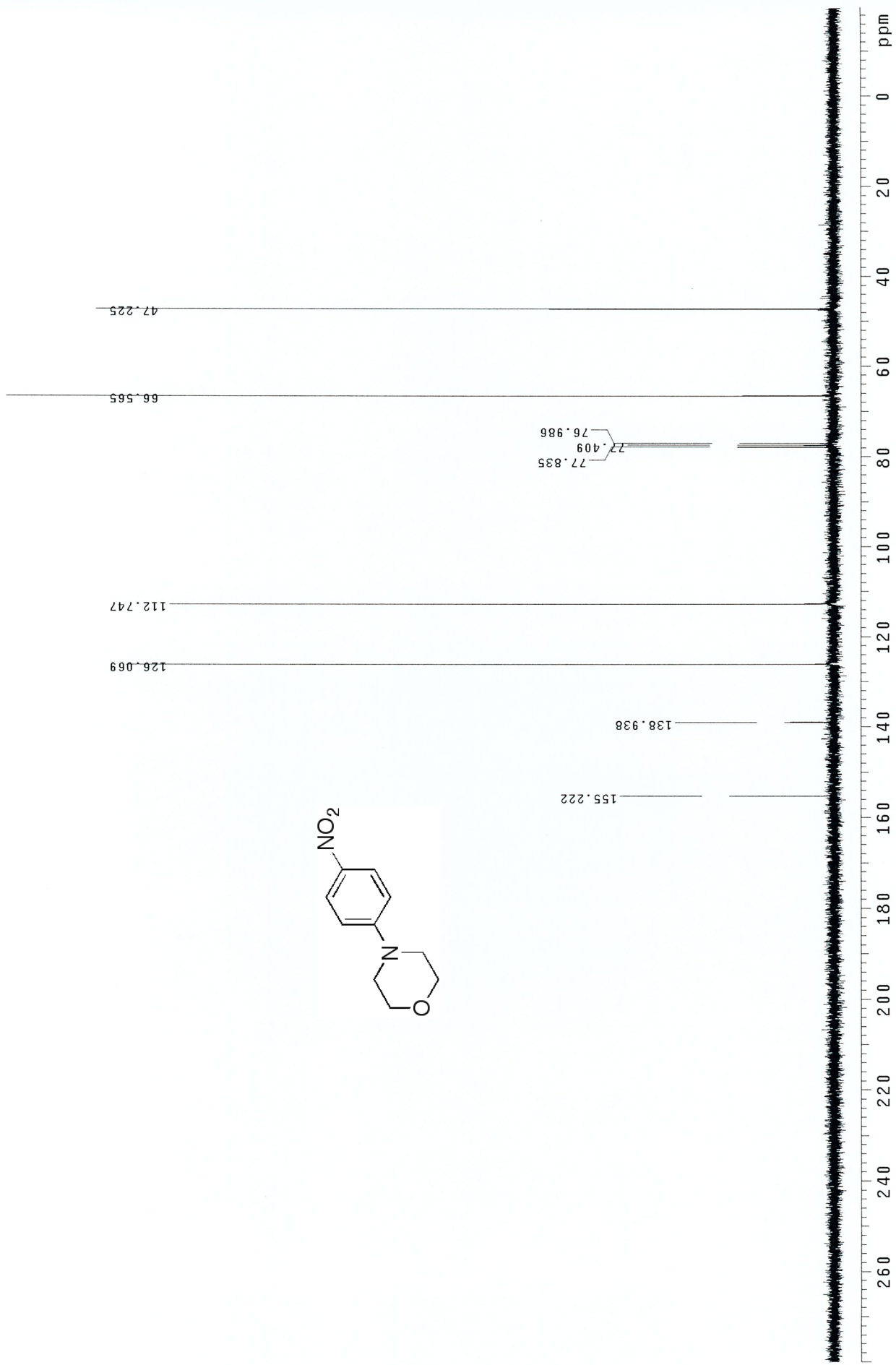


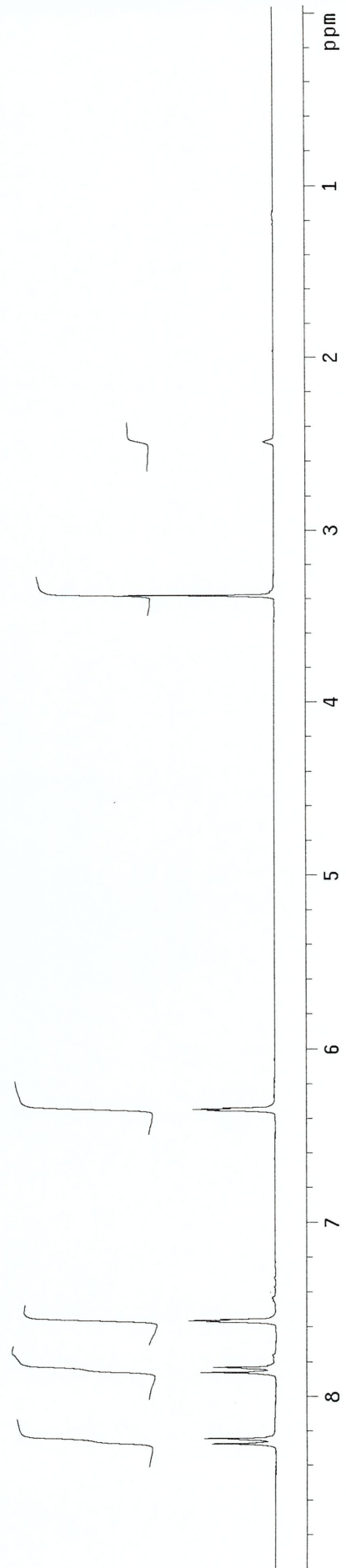
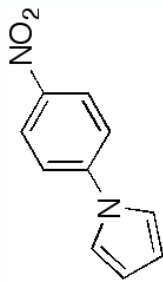


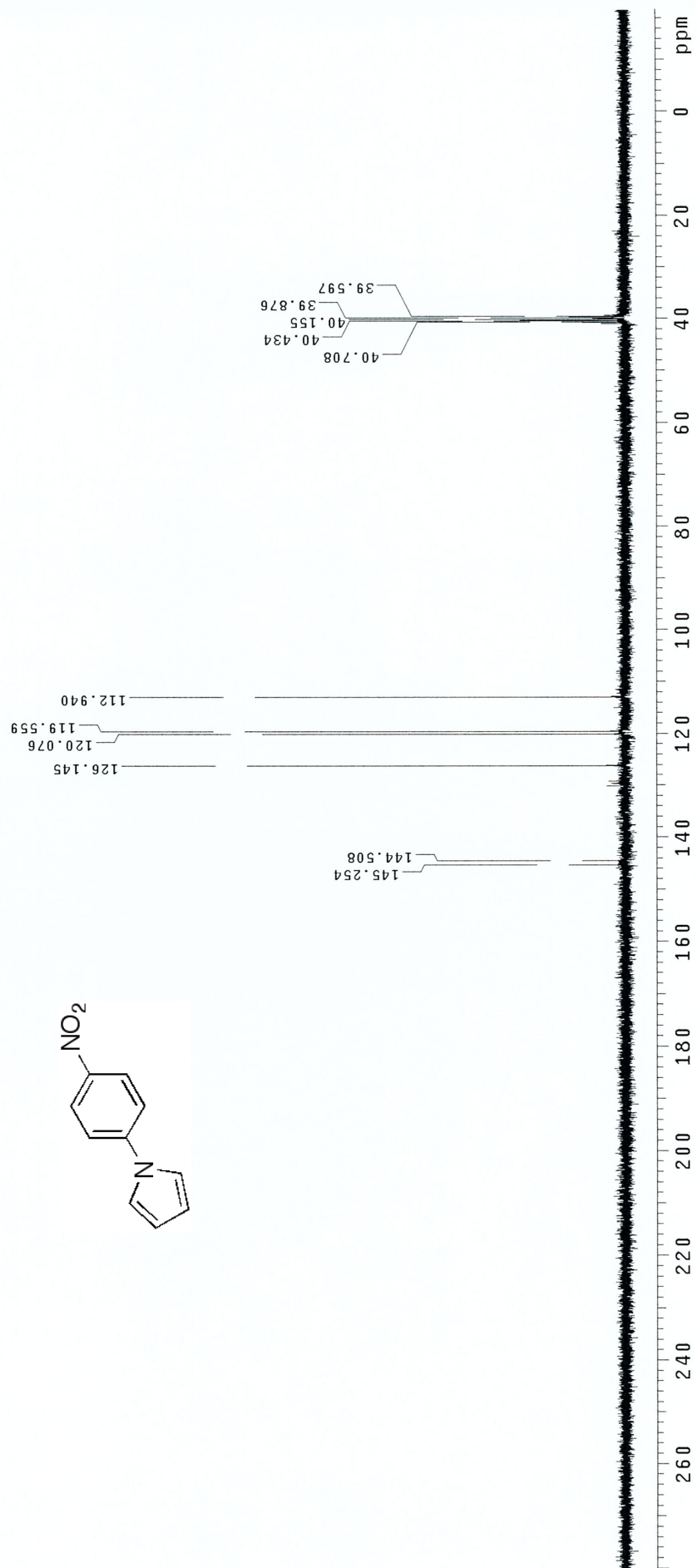


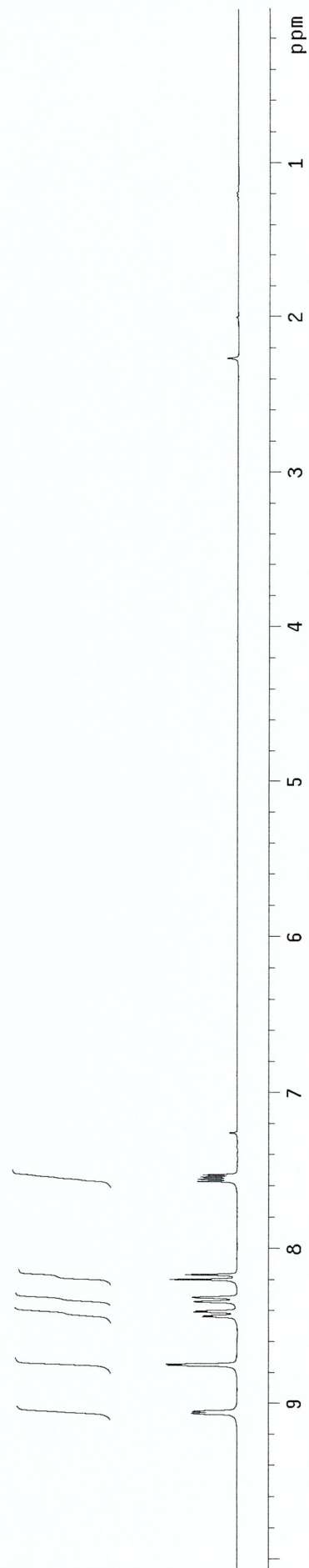
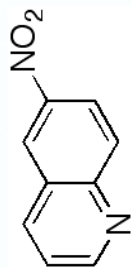


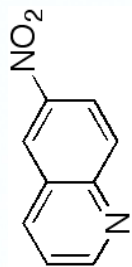
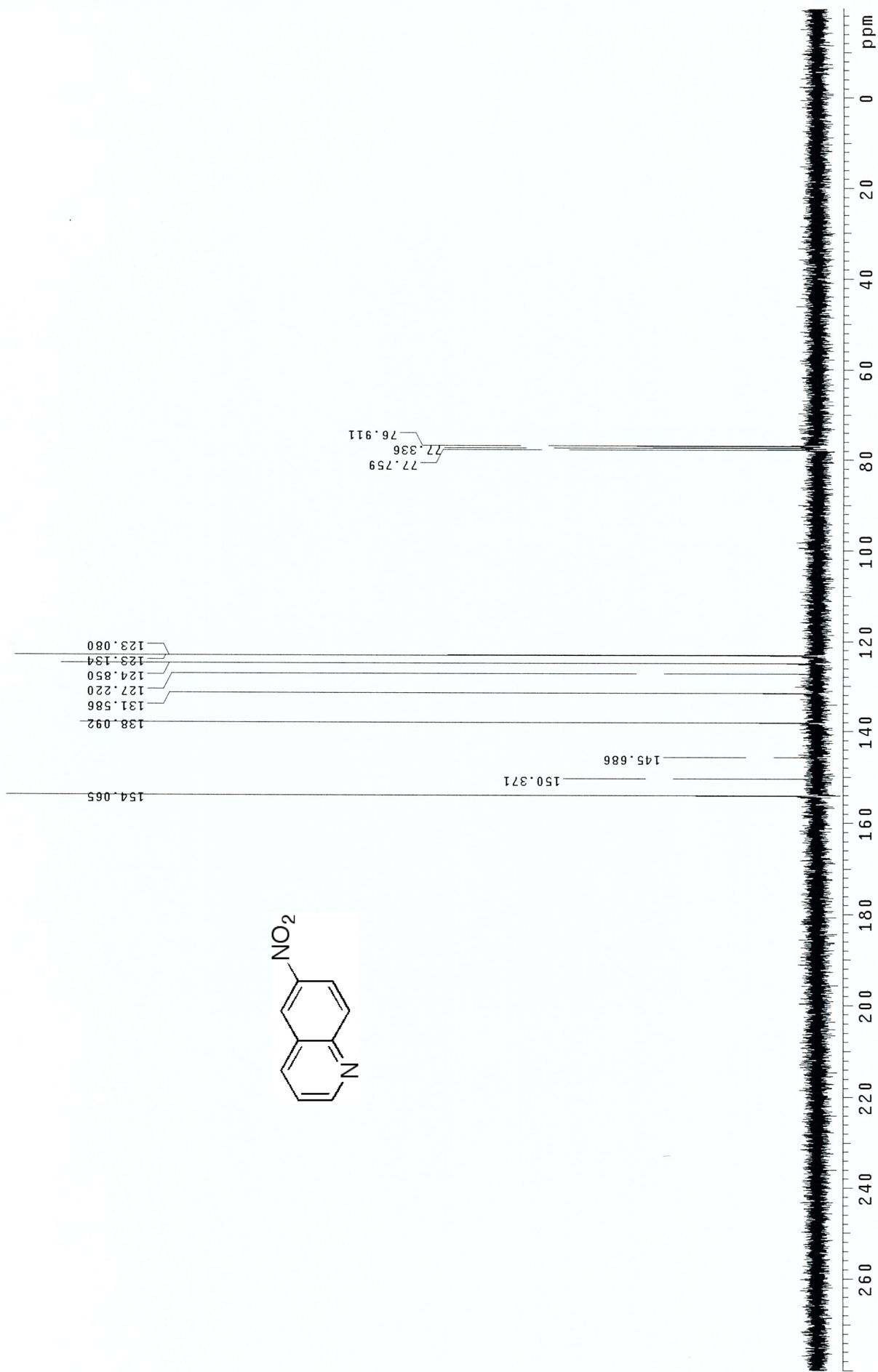


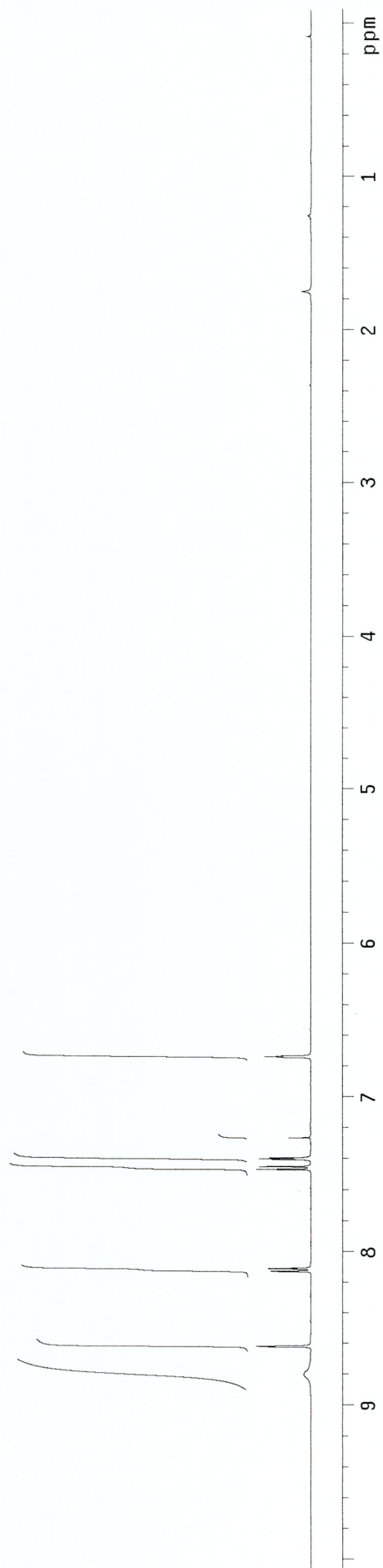
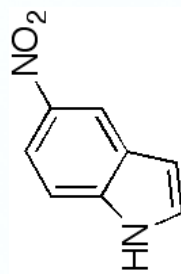


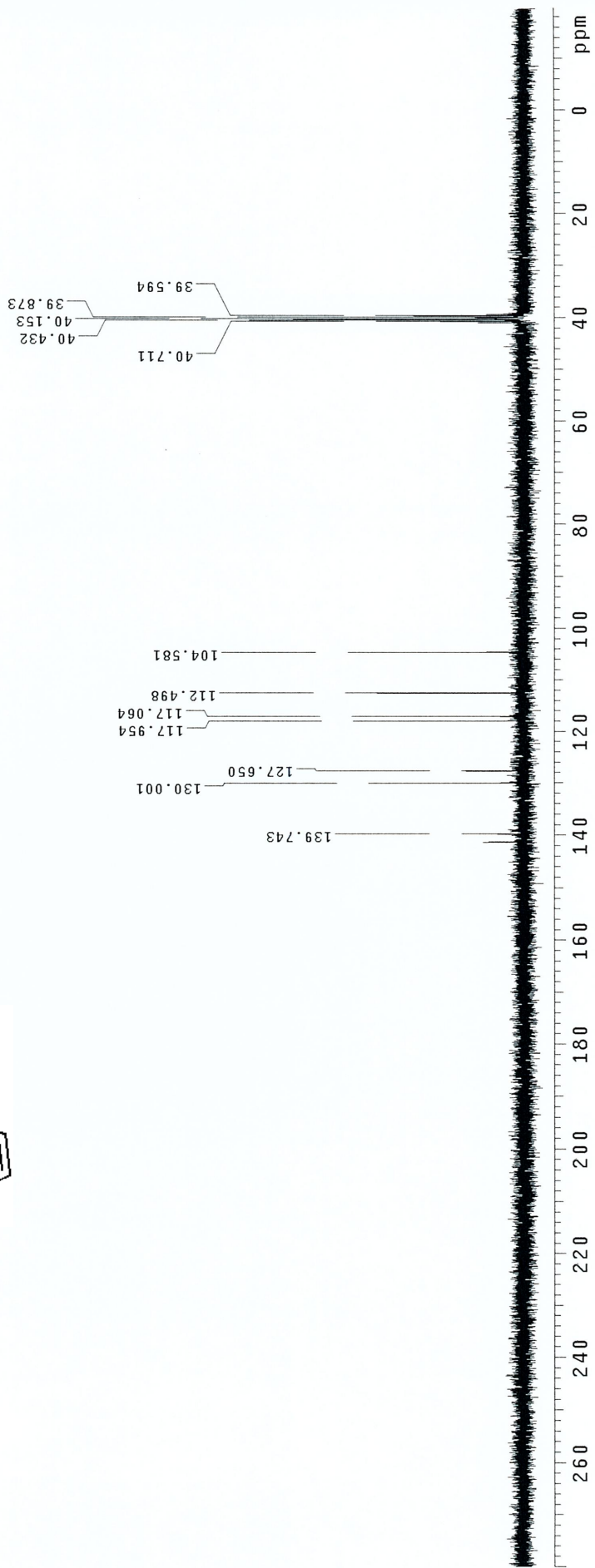
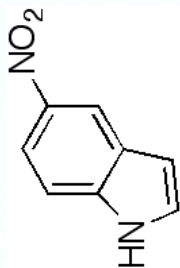


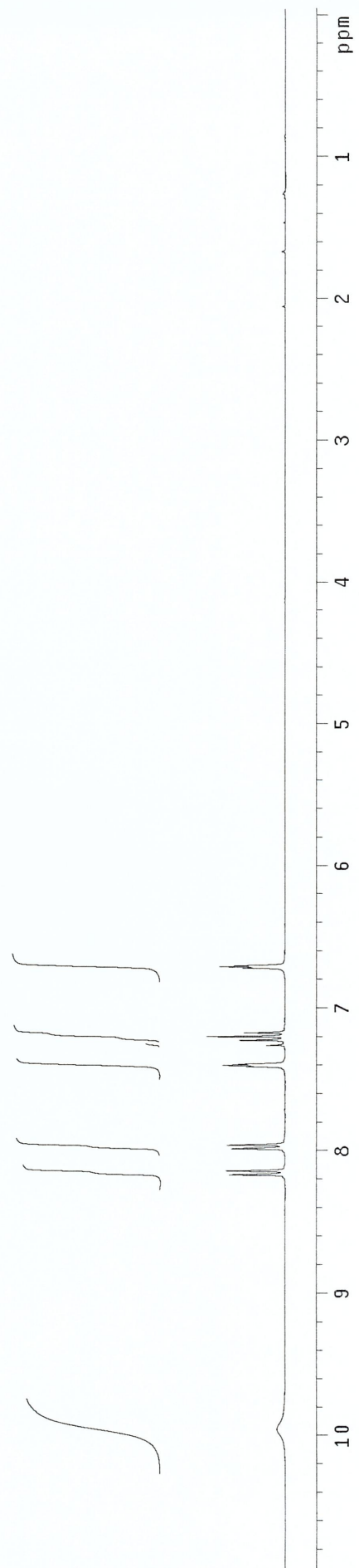
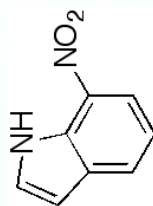


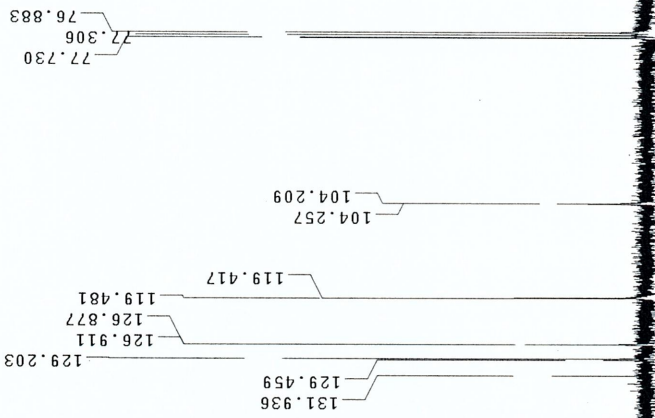
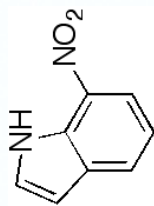


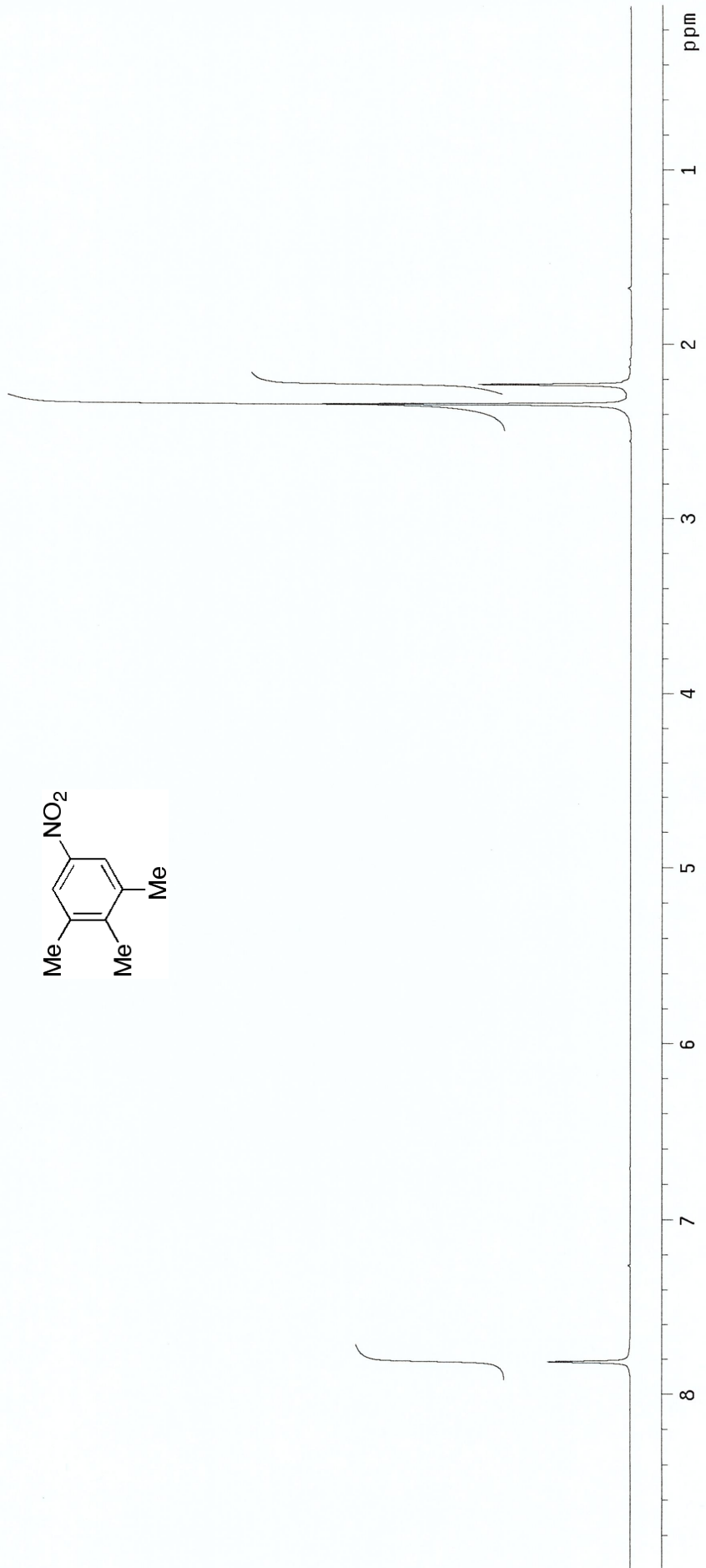
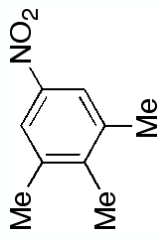


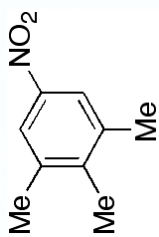
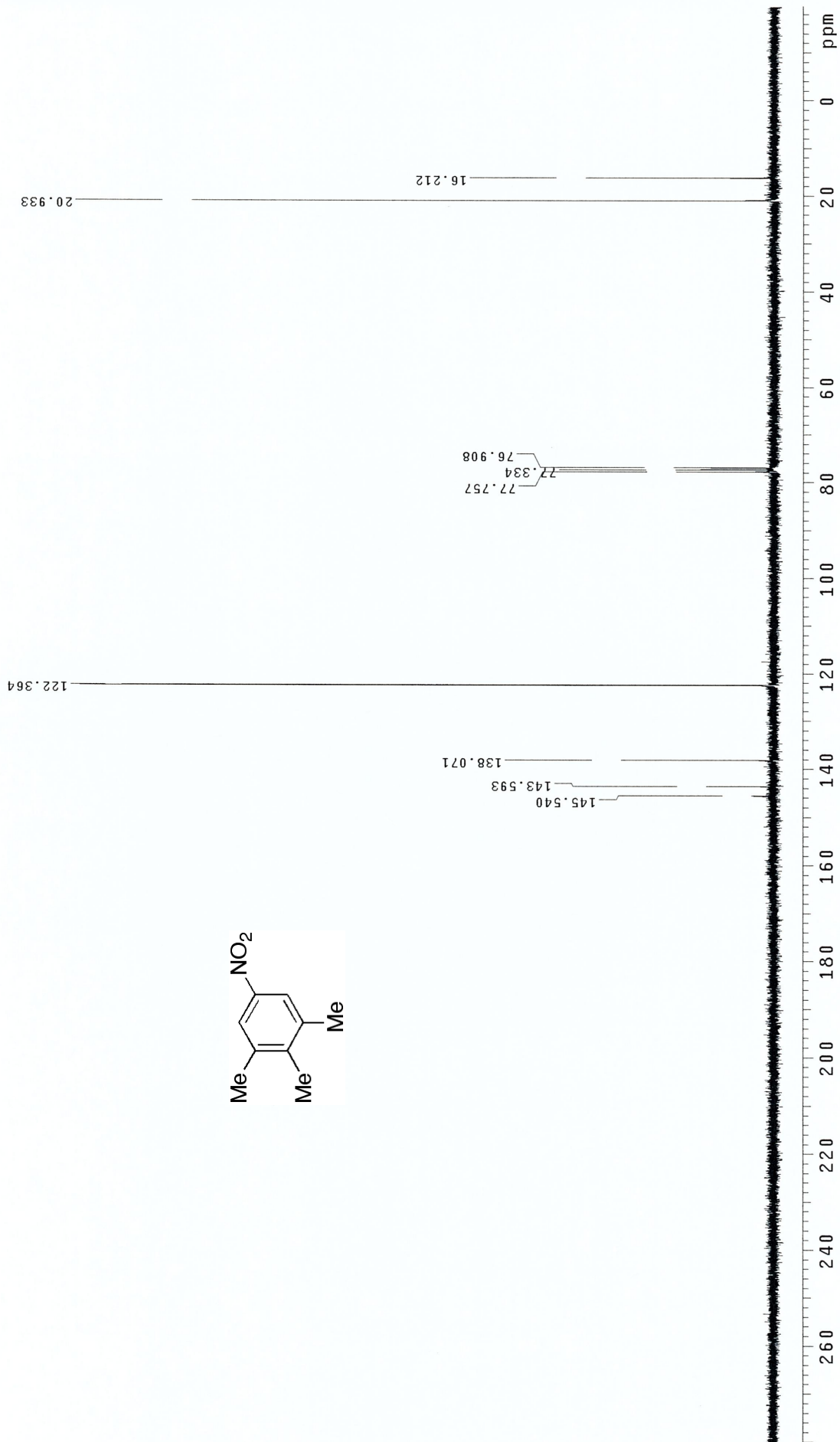


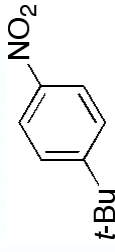
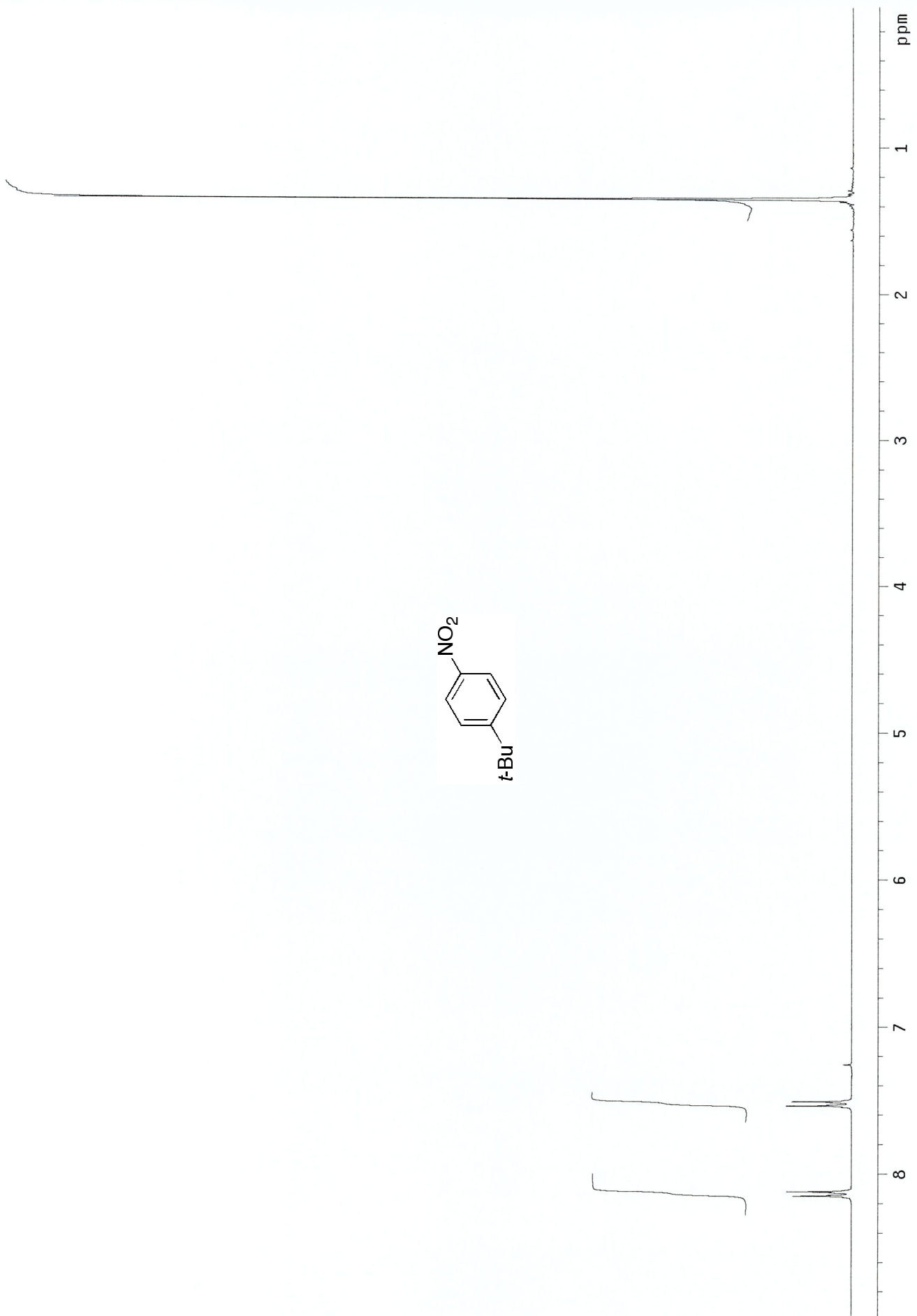


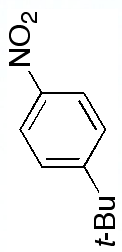
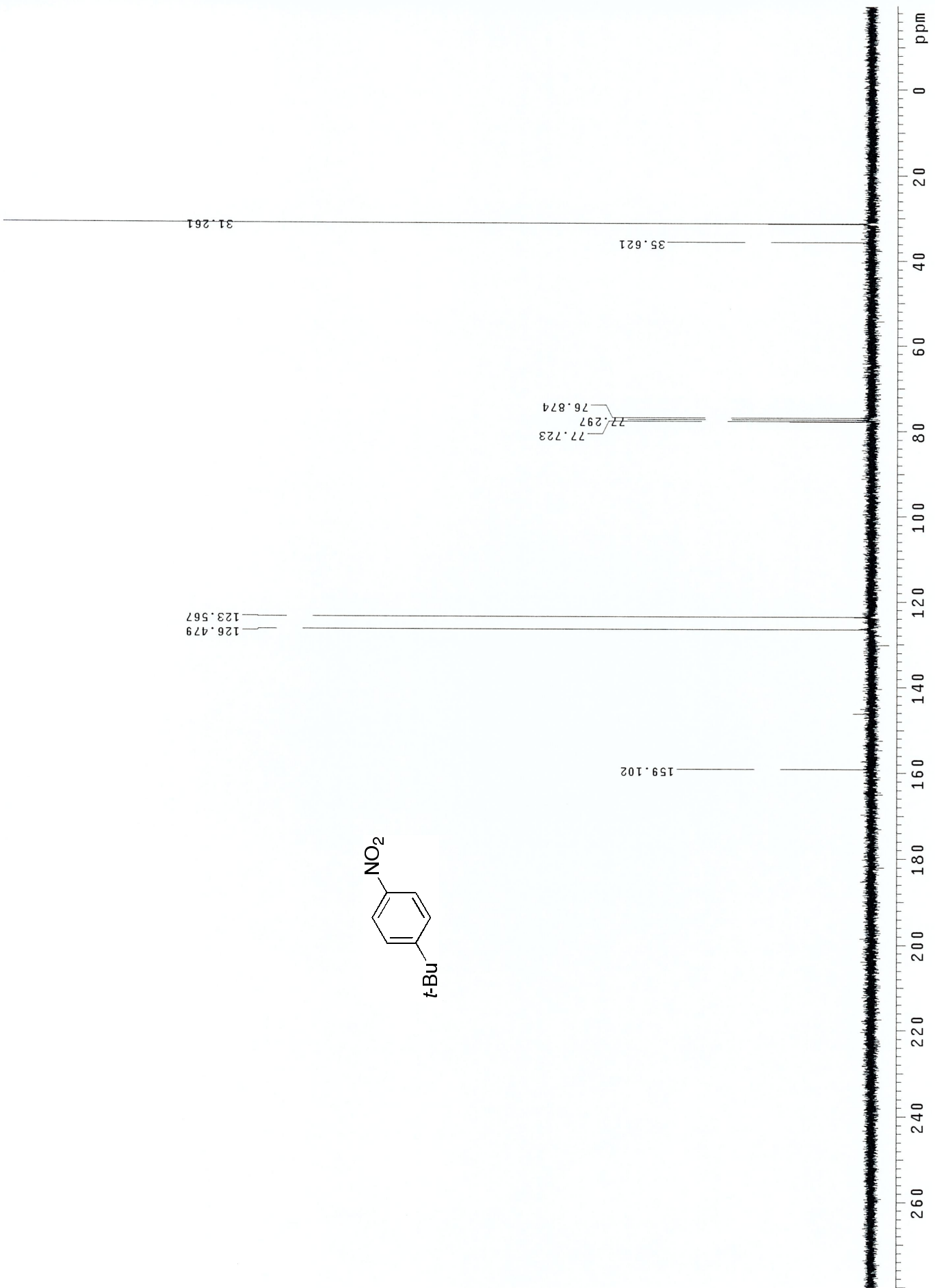


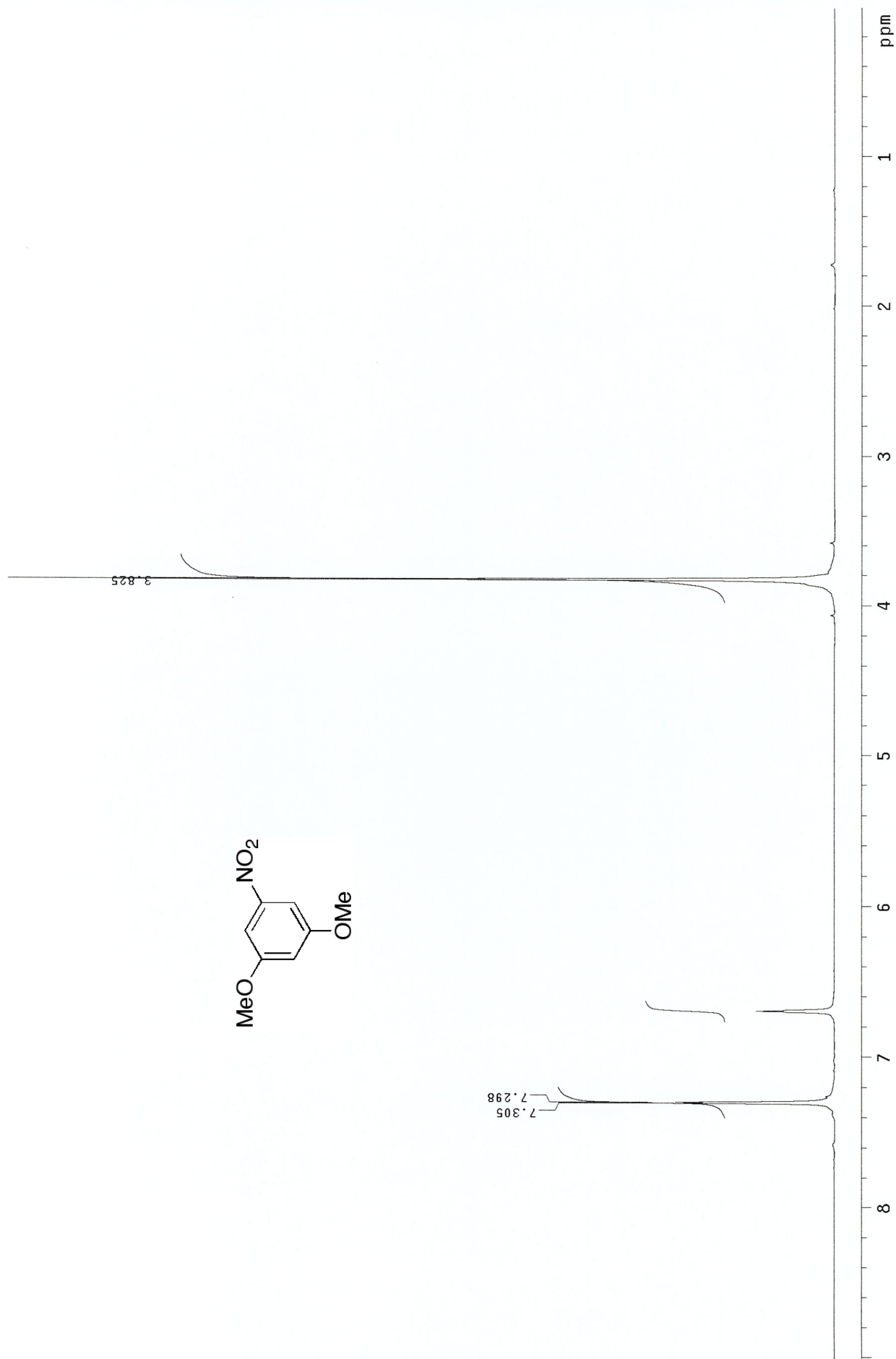


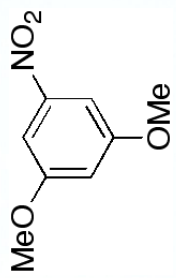
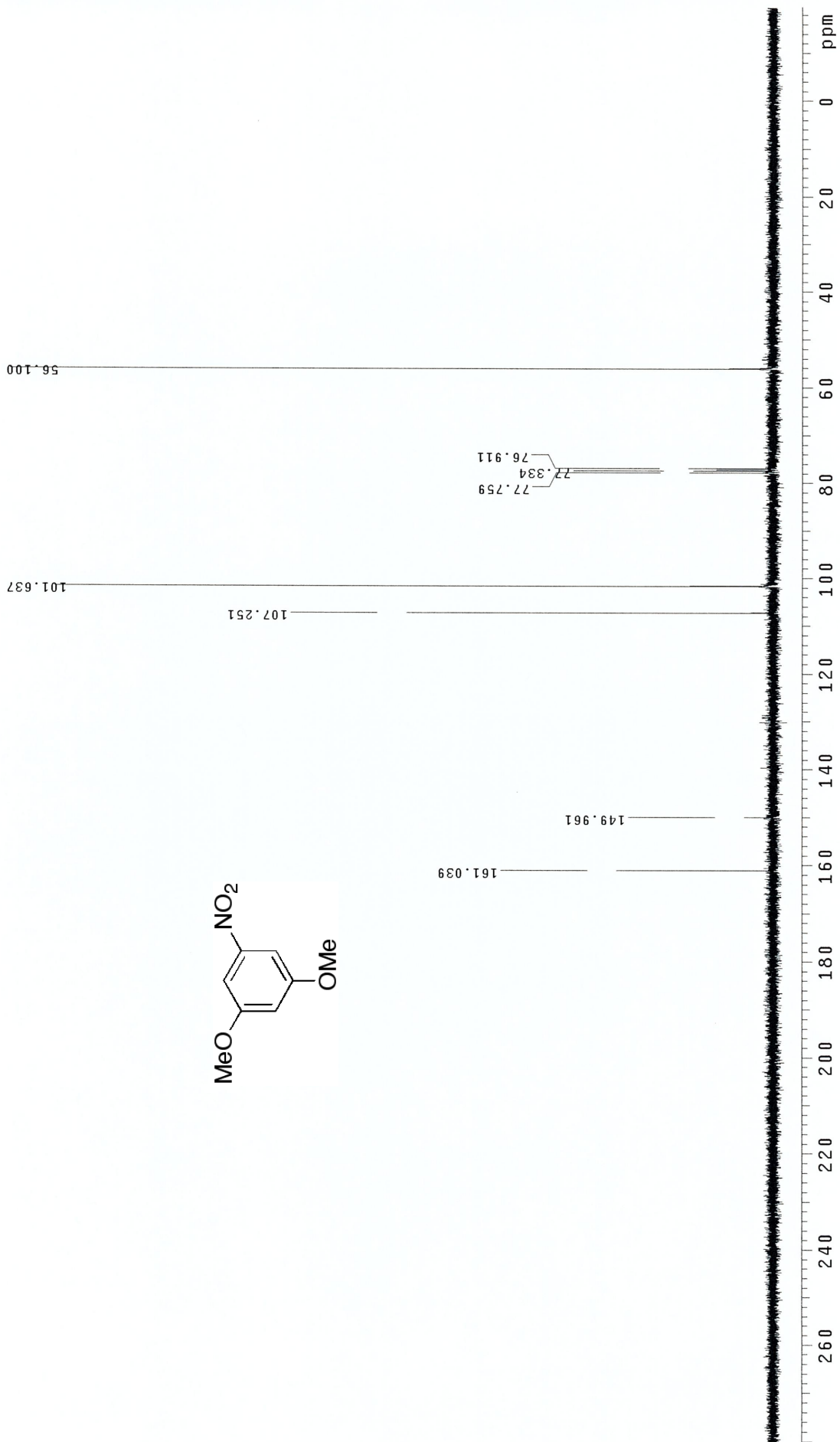


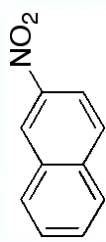
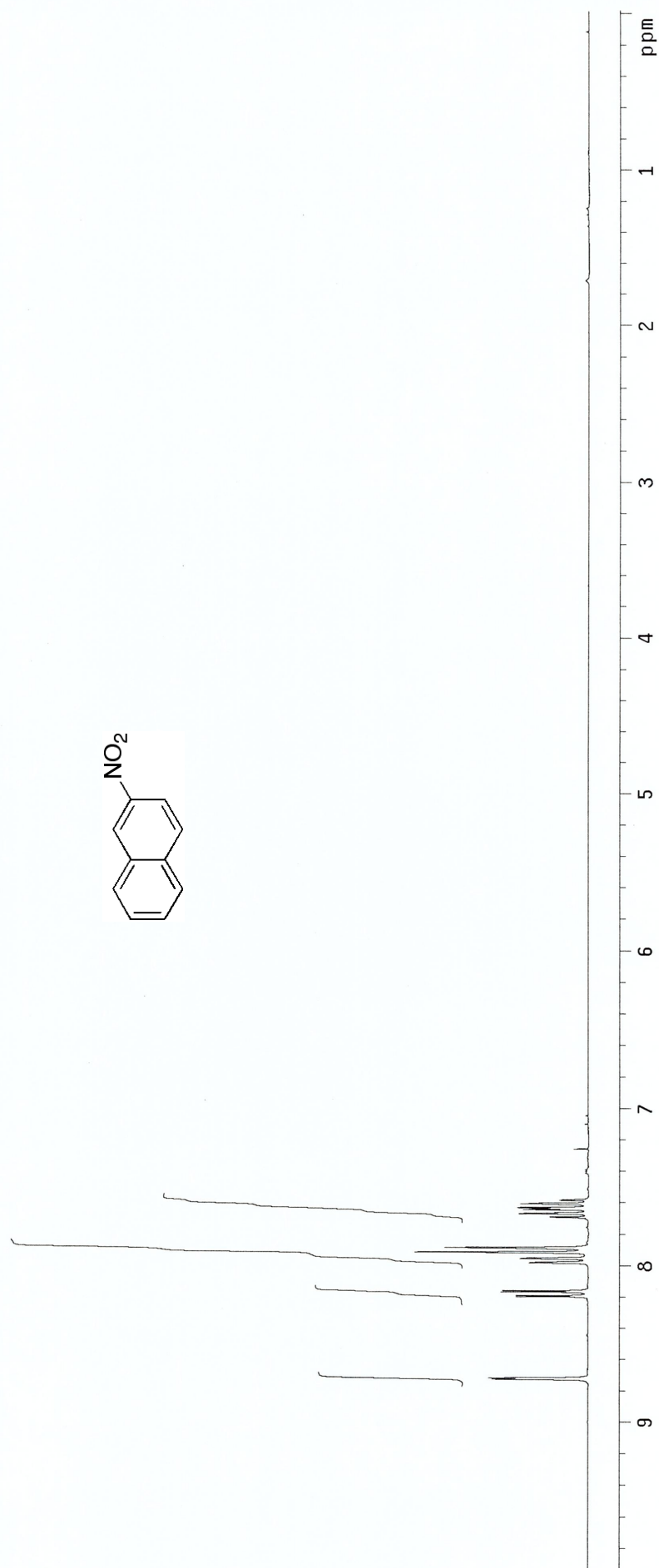


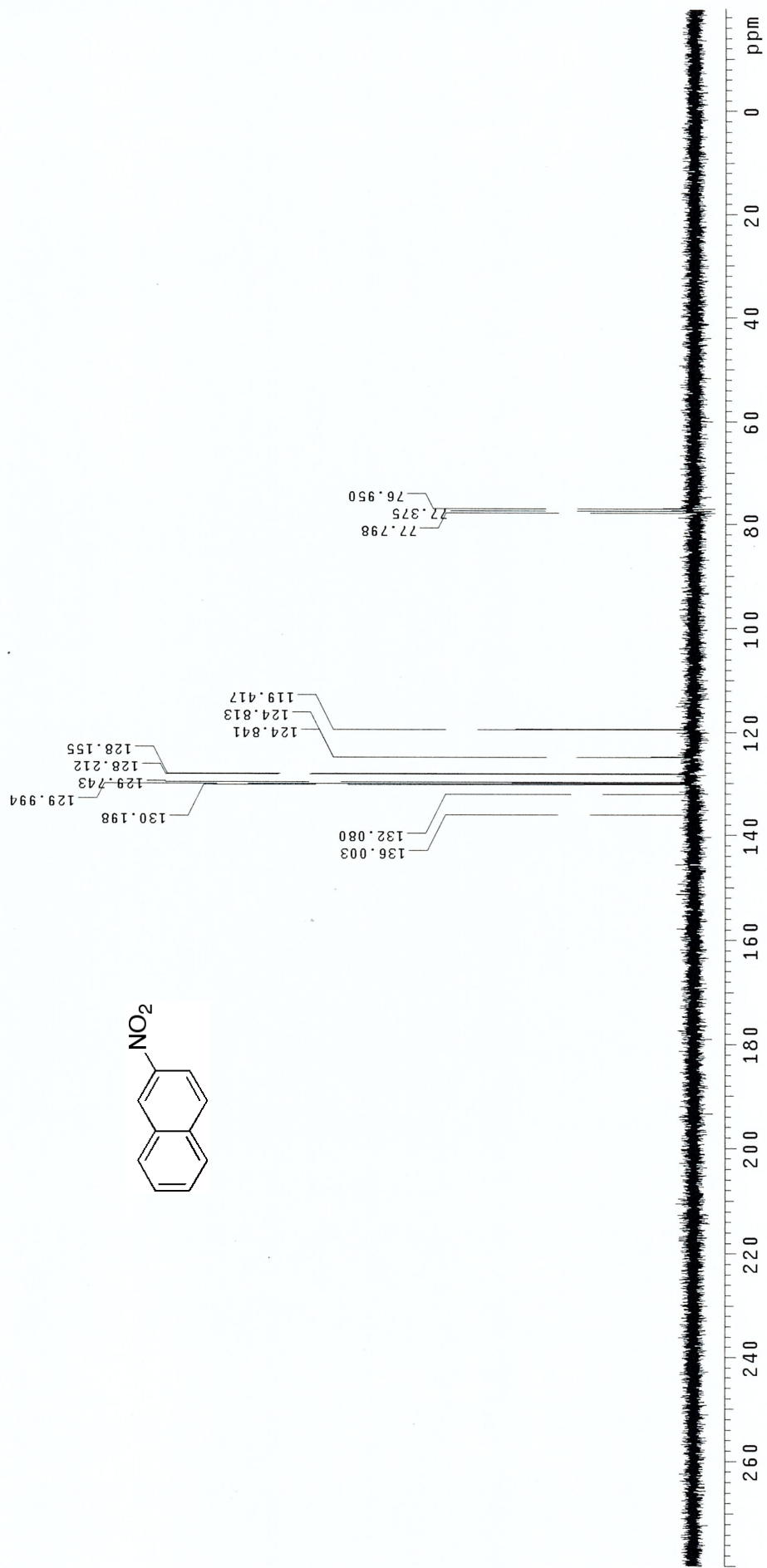


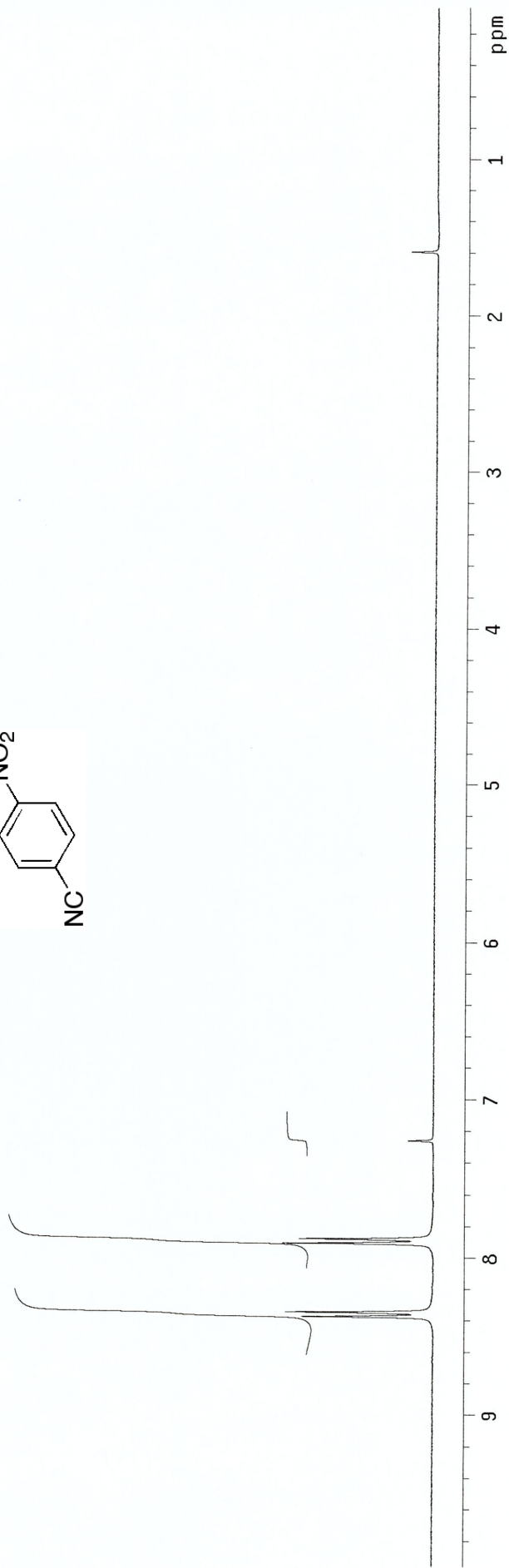
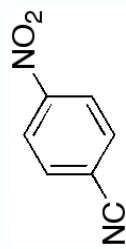


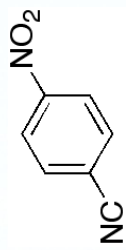
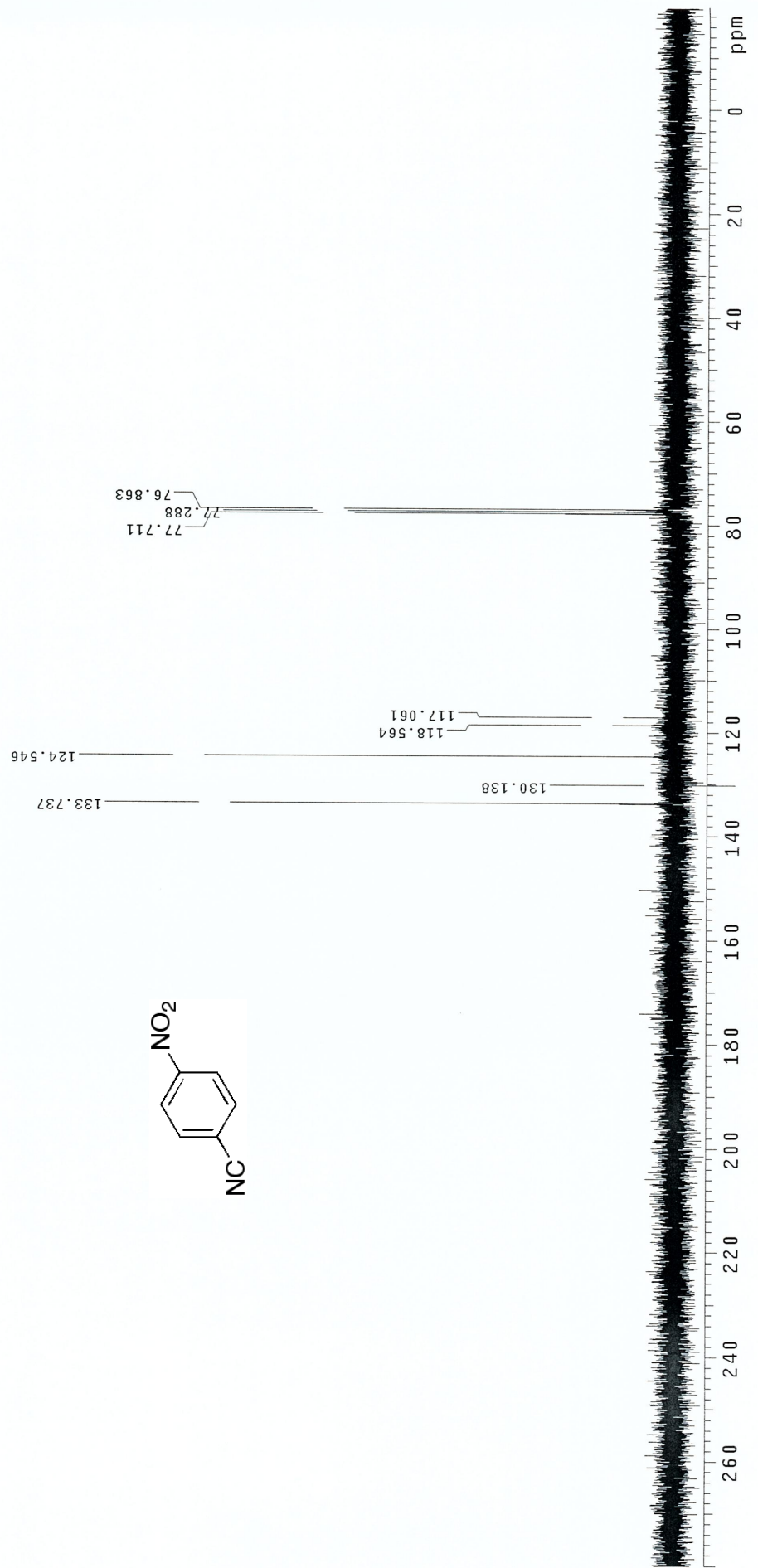


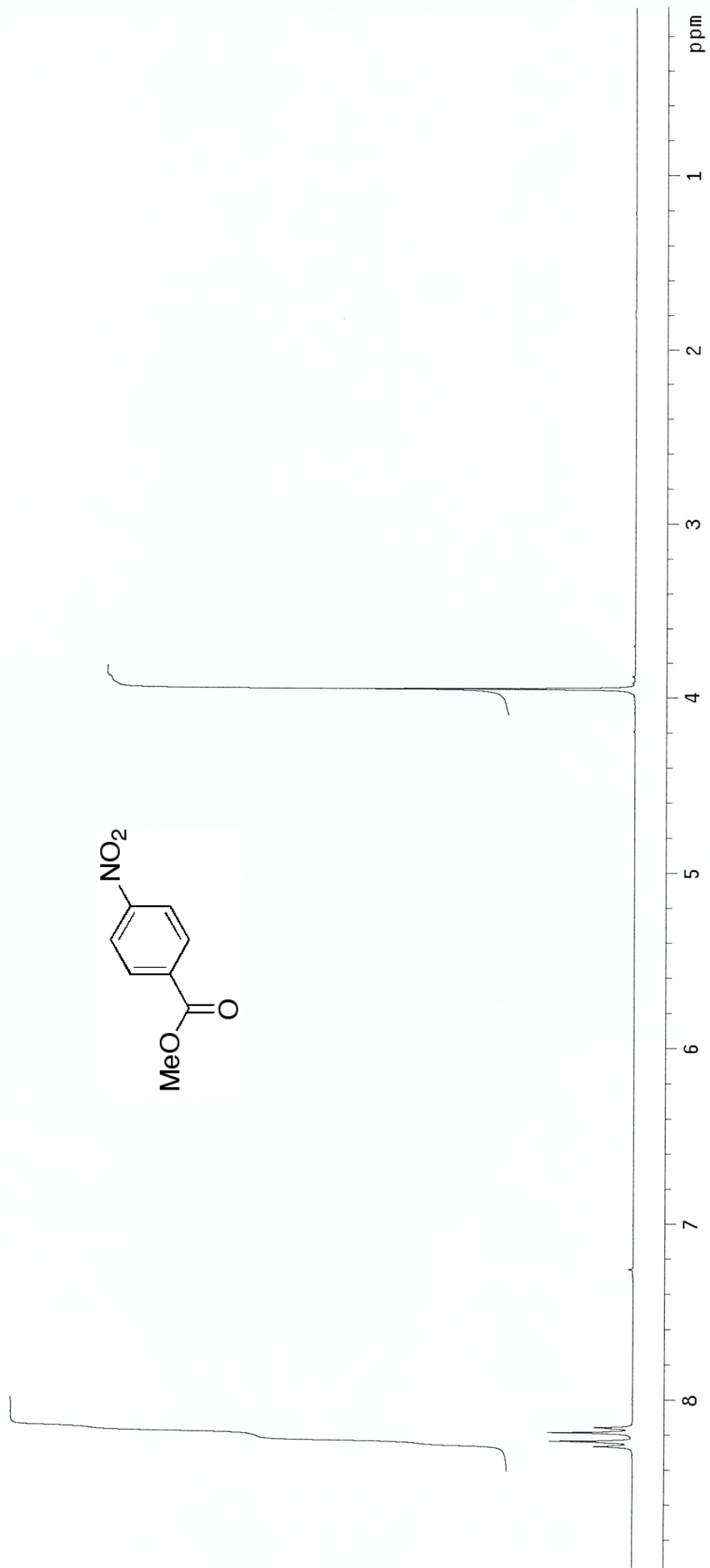


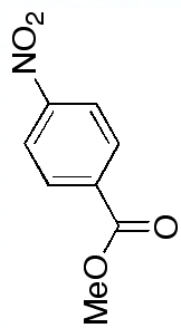
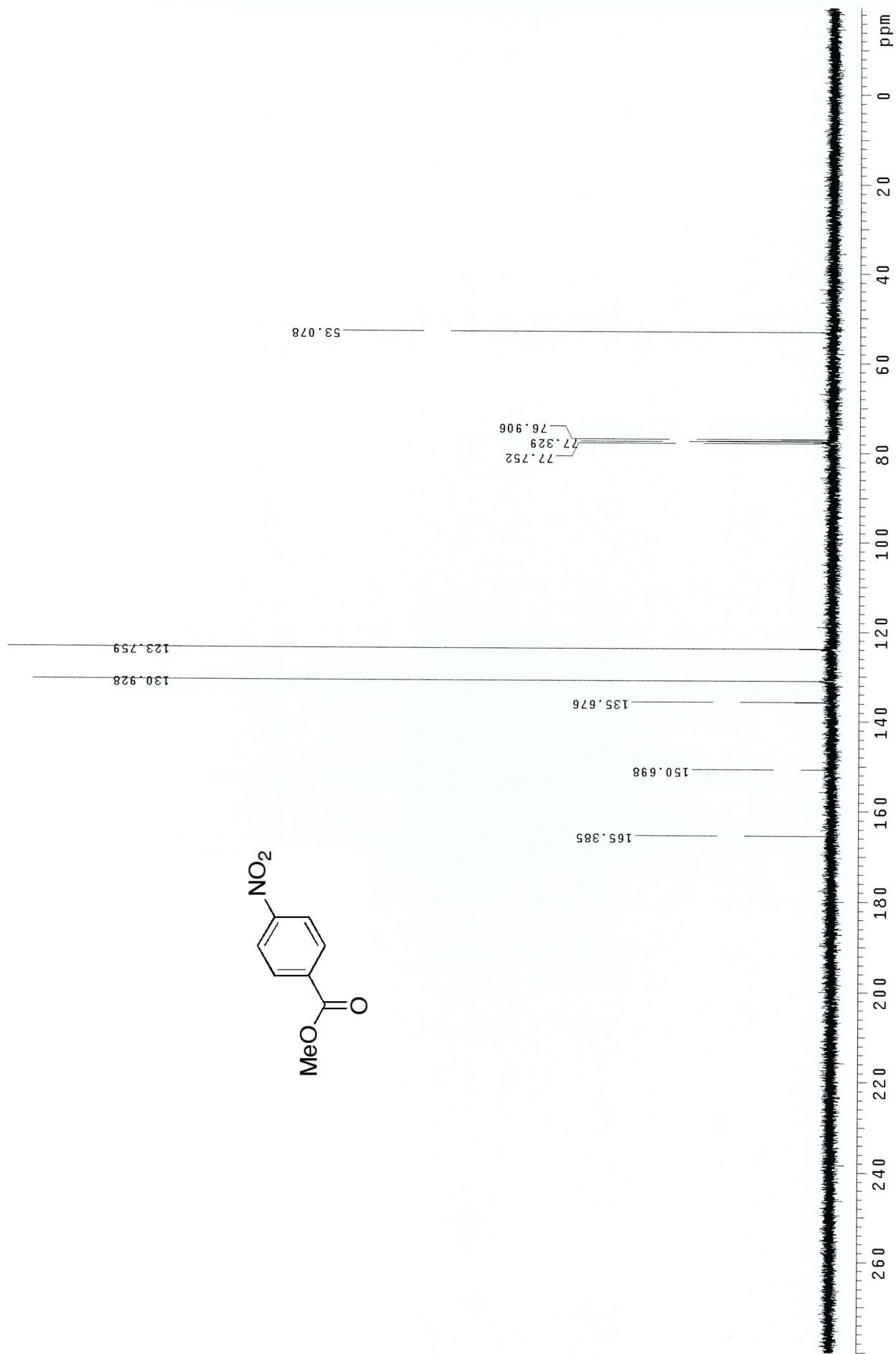






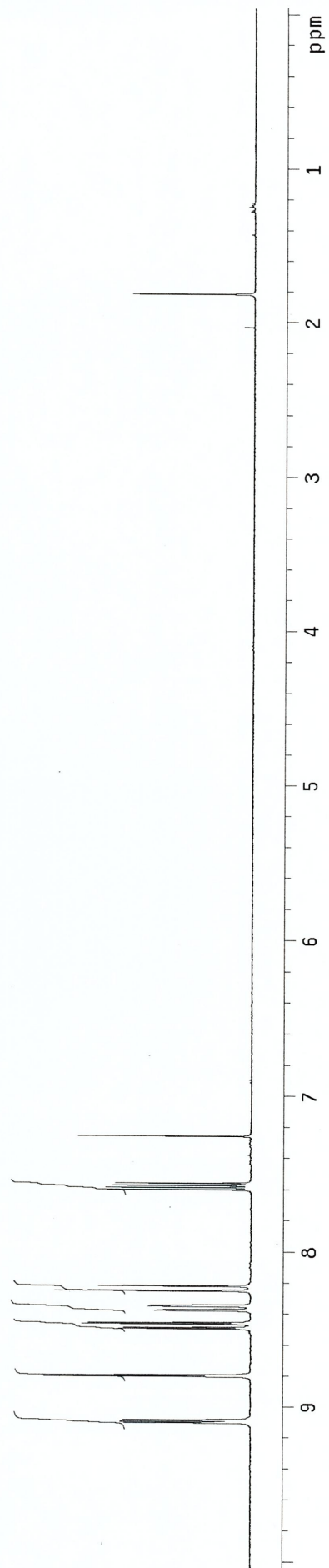
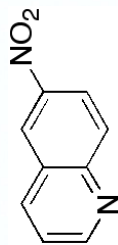


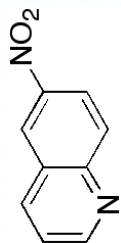




BF-IV-230

Pulse Sequence: s2pu1





77.704
77.279
76.856

123.150
124.864

124.891
127.263
131.653

138.117

150.435
154.072
154.094

