

Supporting Information

**New Catalysts for Suzuki-Miyaura Coupling Reactions of Heteroatom-Substituted
Heteroaryl Chlorides**

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Experimental Section

General. All experiments were performed under nitrogen atmosphere in screw-cap vials. All reagents including di-*tert*-butylphosphine, dicyclohexylphosphine, Pd₂dba₃, PdCl₂(COD), aryl- and heteroaryl halides, aryl- and heteroaryl boronic acids/esters, and organic/inorganic bases were purchased from commercial sources and used as received. Anhydrous, sure-seal grade organic solvents including toluene, tetrahydrofuran (THF), acetonitrile (CH₃CN), dioxane, 1-butanol (1-BuOH), dimethoxyethane (DME), dimethylacetamide (DMAC), and pentane were used as purchased. Distilled water purged with nitrogen was used. Stock solutions of catalysts were generally used particularly for high TON experiments. Commercially available pre-packed silica gel plugs and hexanes/ethyl acetate solvents were used for column chromatographic purification of organic products. The syntheses of PdCl₂{PR₂(Ph-R')₂} complexes were typically performed on 4.0 – 5.0 mmol scale of the aryl halide. Few of the PdCl₂{PR₂(Ph-R')₂} complexes are now commercially available. The Suzuki coupling reactions were typically performed on 1.0 mmol scale of the aryl halide. The yields correspond to isolated products of > 95 % purity as determined by NMR, GCMS and/or HPLC. The conversions were determined by GCMS area% in the presence of a standard (BHT). The catalyst turnover numbers (TON) were determined in some cases using calibrated LC area% (calibrated using purified product). NMR spectra were recorded on 400 MHz instrument and all NMR (¹H, ¹³C, ³¹P, and ¹⁹F) chemical shifts are reported in parts per million (ppm) and all coupling constants are reported in Hertz (Hz).

Syntheses of PdCl₂{PR₂(Ph-R')₂} complexes (A: R = ^tBu, R' = *p*-CF₃; B: R = ^tBu, R' = H; B': R = Cy, R' = H; C: R = ^tBu, R' = 3,4,5-tri-OMe; D: R = ^tBu, R' = *p*-OMe; E: R = ^tBu, R' = *p*-NMe₂; E': R = Cy,

$R' = p\text{-NMe}_2$). The syntheses were typically performed on a 4.0 – 5.0 mmol scale of the aryl halide. A toluene or xylene solution of di-alkylphosphine (1.0 equiv), aryl bromide (1.0 equiv), NaO^tBu (1.5 equiv) and Pd_2dba_3 (1 mol %) was stirred at 90 – 130 °C for 12 h. The reaction was cooled to ambient temperature and filtered through a short silica gel plug. The silica gel plug was rinsed with toluene or dioxane. The combined filtrate was concentrated under vacuum and the residue was dissolved in THF. Alternatively, the combined filtrate was used as such. The $\text{PdCl}_2(\text{COD})$ (0.35 – 0.40 equiv) complex was added as a solid and the reaction mixture was stirred at ambient temperature for 12 h. For complex **B'**, a 2:1 reaction mixture of commercially available PCy_2Ph and $\text{PdCl}_2(\text{COD})$ in THF was stirred at ambient temperature for 12 h. The reaction mixture was filtered, and the yellow solid was washed with pentane and dried under vacuum. The desired complexes were typically obtained in about 85% isolated yields.

PdCl₂{P'^tBu₂(Ph-*p*-CF₃)₂}₂ (A): **¹H NMR** (CDCl_3): δ 8.00 (br. s, 4H), 7.59 (br. d, $J = 7.9$, 4H), 1.62 (br. t, $J_{PH} = 7.0$, 36H). **³¹P NMR** (CDCl_3): δ 55.7. **¹⁹F NMR** (CDCl_3): δ - 63.4. **Elemental Analysis:** Calculated: C 47.54, H 5.85; Found: C 47.57, H 6.05. **Raman:** cm^{-1} 297.9 (Pd-Cl).

PdCl₂{P'^tBu₂(Ph)}₂ (B): **¹H NMR** (CD_2Cl_2): δ 7.9 – 7.8 (m, 4H), 7.36 – 7.30 (m, 6H), 1.56 (br. t, $J_{PH} = 6.9$, 36H). **³¹P NMR** (CD_2Cl_2): δ 54.4. **Raman:** cm^{-1} 300.9 (Pd-Cl).

PdCl₂{PCy₂(Ph)}₂ (B'): ¹H NMR (C_6D_6): δ 7.90 (m, 4H), 7.29 – 7.18 (m, 6H), 2.93 – 1.16 (m, 44H). **³¹P NMR** (C_6D_6): δ 41.9. **Elemental Analysis:** Calculated: C 59.55, H 7.50; Found: C 59.38, H 7.01.

PdCl₂{P'^tBu₂(Ph-3,4,5-tri-OMe)}₂ (C): **¹H NMR** (C_6D_6): δ 7.41 (t, $J_{PH} = 4.7$, 4H), 3.93 (s, 6H), 3.71 (s, 12H), 1.76 (br. t, $J_{PH} = 6.8$, 36 H). **³¹P NMR** (C_6D_6): δ 69.4. **Elemental Analysis:** Calculated: C 50.91, H 7.29; Found: C 50.74, H 7.03.

PdCl₂{P'^tBu₂(Ph-*p*-OMe)}₂ (D): Isolated material contained 1,4-dioxane (0.25 mol equiv). **¹H NMR** (C_6D_6): δ 8.06 – 8.02 (p, $J = 4.3$, 4H), 6.85 (d, $J = 8.6$, 4H), 3.32 (s, 6H), 1.77 (br. t, $J = 6.8$, 36H). **Elemental Analysis:** Calculated: C 53.28, H 7.45; Found: C 53.36, H 7.03.

PdCl₂{P'Bu₂(Ph-*p*-NMe₂)₂}₂ (E): **¹H NMR** (CDCl₃): δ 7.5 (br. s, 4H), 6.42 (d, *J* = 8.3, 4H), 2.75 (s, 12H), 1.38 (t, *J_{PH}* = 6.6, 36H). **³¹P NMR** (CDCl₃): δ 52.1. **Elemental Analysis:** Calculated: C 54.28, H 7.97; Found: C 53.17, H 7.58. **Raman:** cm⁻¹ 295.8 (Pd-Cl).

PdCl₂{PCy₂(Ph-*p*-NMe₂)₂}₂ (E'): **¹H NMR** (C₆D₆): δ 7.91 (m, 4H), 6.64 (d, *J* = 8.8, 4H), 3.03 – 1.28 (m, 44H), 2.52 (s, 12H). **³¹P NMR** (C₆D₆): δ 39.2. **Elemental Analysis:** Calculated: C 59.15, H 7.94; Found: C 58.85, H 7.63.

General procedure for the Suzuki-Miyaura coupling reactions. All Suzuki-Miyaura coupling reactions (Tables 1 – 9, equations 1 and 2) were typically performed on a 1.0 mmol scale of the aryl halide. A mixture of aryl halide (1.0 equiv), aryl boronic acid/ester (1.2 – 1.5 equiv), base (2.0 – 3.0 equiv.) and catalyst (0.01 – 2.0 mol %) in aqueous solvent (~ 3-4 mL for 1.0 mmol starting substrate, ~ 10 % water) was stirred at 80 – 100 °C in screw-capped glass vials for 5 h – 20 h. The reaction was cooled to ambient temperature and extracted in organic solvent (ether or dichloromethane). The organic extract was subjected to an aqueous work-up (when product stability permitted, 1N NaOH was used to facilitate removal of excess boronic acid), dried over anhydrous Na₂SO₄, and concentrated under vacuum. The crude material was purified by column chromatography on silica gel using hexanes and hexanes/ethyl acetate or 5 % methanol in ethyl acetate as eluents. High TON experiments were stirred at 80 – 100 °C for 24 h. Additional details are provided in the schematics and text.

2-(*o*-Tolyl)-3-pyridinamine (Table 5, entry 1). This compound was isolated as a white solid (93 % yield) from the reaction of 2-chloropyridin-3-amine and *o*-tolylboronic acid using the general procedure. **¹H NMR** (CDCl₃): δ 8.08 (d, *J* = 4.5, 1H), 7.29-7.26 (m, 4H), 7.08-7.00 (m, 2H), 3.59 (s br, 2H), 2.17 (s, 3H). **¹³C NMR** (CDCl₃): δ 146.0, 140.3, 139.2, 137.4, 136.7, 130.7, 129.1, 128.5, 126.3, 123.2, 121.9, 19.3.

2-(*p*-Tolyl)-3-pyridinamine (Table 5, entry 2). This compound was isolated as a white solid (95 % yield) from the reaction of 2-chloropyridin-3-amine and *p*-tolylboronic acid using the general procedure. **¹H NMR** (CDCl₃): δ 8.1 (d/d, *J* = 4.1/1.8, 1H), 7.55 (d, *J* = 8.2, 2H), 7.26 (d, *J* = 7.8, 2H), 7.04 – 6.98 (m,

2H), 3.84 (s br, 2H), 2.39 (s, 3H). **¹³C NMR** (CDCl₃): δ 145.1, 140.0, 139.9, 138.0, 135.7, 129.4, 128.3, 122.8, 122.6, 21.3.

2-{4-(Trifluoromethyl)phenyl}-3-pyridinamine (Table 5, entry 3). This compound was isolated as a white solid (92 % yield) from the reaction of 2-chloropyridin-3-amine and 4-(trifluoromethyl)phenylboronic acid using the general procedure. **¹H NMR** (CDCl₃): δ 8.12 (d/d, *J* = 4.5/1.6, 1H), 7.81 (d, *J* = 8.0, 2H), 7.71 (d, *J* = 8.3, 2H), 7.10 – 7.02 (m, 2H), 3.85 (s br). **¹³C NMR** (CDCl₃): δ 143.1, 142.3, 140.2, 140.2, 130.1 (q, ²*J*_{CF} = 32.5), 128.9, 125.7 (q, ³*J*_{CF} = 3.5), 123.8, 123.2, 124.2 (q, ¹*J*_{CF} = 272).

2-(4-Methoxyphenyl)-3-pyridinamine (Table 5, entry 4). This compound was isolated as a white solid (93 % yield) from the reaction of 2-chloropyridin-3-amine and 4-methoxyphenylboronic acid using the general procedure. **¹H NMR** (CDCl₃): δ 8.08 (d/d, *J* = 3.7/1.1, 1H), 7.60 (d, *J* = 8.4, 2H), 7.01 – 6.96 (m, 4H), 3.85 (s br, 2H, partially overlapped), 3.82 (s, 3H). **¹³C NMR** (CDCl₃): δ 159.5, 144.8, 140.1, 139.8, 131.1, 129.8, 122.7, 122.6, 114.2, 55.4.

2-{4-(Trifluoromethyl)phenyl}-4-pyridinamine (Table 5, entry 5). This compound was isolated as a white solid (90 % yield) from the reaction of 2-chloropyridin-4-amine and 4-(trifluoromethyl)phenylboronic acid using the general procedure. **¹H NMR** (CDCl₃): δ 8.31 (d, *J* = 5.4, 1H), 8.0 (d, *J* = 8.2, 2H), 7.67 (d, *J* = 8.2, 2H), 6.93 (s, 1H), 6.51 (br d, *J* = 5.5, 1H), 4.39 (br s, 2H). **¹³C NMR** (CDCl₃): δ 156.8, 153.7, 150.3, 143.2, 130.5 (q, ²*J*_{CF} = 32.2), 127.2, 125.5 (q, ³*J*_{CF} = 3.5), 124.3 (q, ¹*J*_{CF} = 272), 109.0, 106.9.

2-(4-Fluorophenyl)-4-pyridinamine (Table 5, entry 6). This compound was isolated as a white solid (93 % yield) from the reaction of 2-chloropyridin-4-amine and 4-fluorophenylboronic acid using the general procedure. **¹H NMR** (CDCl₃): δ 7.46 – 7.42 (m, 2H), 7.14 – 7.10 (m, 2H), 6.97 – 6.92 (m, 3H), signal for NH₂ protons not observed. **¹³C NMR** (CDCl₃): δ 161.3 (d, ¹*J*_{CF} = 246.0), 142.3, 129.6 (d, ³*J*_{CF} = 3.4), 127.0, 126.58, 126.54 (d, ³*J*_{CF} = 7.8), 123.73, 122.1, 114.76 (d, ²*J*_{CF} = 21.5).

2-Mesyl-4-pyridinamine (Table 5, entry 7). This compound was isolated as a white solid (98 % yield) from the reaction of 2-chloropyridin-4-amine and mesylboronic acid using the general procedure. **¹H NMR** (CDCl_3): δ 8.02 (d, $J = 5.5$, 1H), 6.75 (s, 2H), 6.23 (d, $J = 5.4$, 1H), 6.20 (s, 1H), 4.57 (s br, 2H), 2.17 (s, 3H), 1.90 (s, 6H). **¹³C NMR** (CDCl_3): δ 159.0, 152.7, 148.4, 137.1, 135.9, 134.5, 127.0, 109.1, 106.8, 20.0, 18.9.

2-Mesyl-3-pyridinamine (Table 5, entry 8). This compound was isolated as a white solid (92 % yield) from the reaction of 2-chloropyridin-3-amine and mesylboronic acid using the general procedure. **¹H NMR** (CDCl_3): δ 7.98 (d, $J = 4.5$, 1H), 6.92 (d/d, $J = 8.0/5.0$, 1H), 6.84 (d, $J = 8.0$, 1H), 6.82 (s, 2H), 3.45 (s br, 2H), 2.20 (s, 3H), 1.88 (s, 6H). **¹³C NMR** (CDCl_3): δ 145.8, 140.5, 139.4, 137.6, 136.5, 133.8, 128.6, 122.8, 121.3, 21.2, 19.4.

3-Methoxy-6-(4-methoxyphenyl)pyridazine (Table 6, entry 1). This compound was isolated as a white solid (97 % yield) from the reaction of 3-chloro-6-methoxypyridazine and 4-methoxyphenylboronic acid using the general procedure. **¹H NMR** (CDCl_3): δ 7.96 (d, $J = 8.8$, 2H), 7.72 (d, $J = 9.2$, 1H), 7.27 – 6.99 (m, 3H), 4.17 (s, 3H), 3.86 (s, 3H). **¹³C NMR** (CDCl_3): δ 164.0, 160.8, 154.9, 128.8, 127.8, 126.6, 117.7, 114.4, 55.4, 54.8.

4-(4-Methoxyphenyl)-2-methylthiopyrimidine (Table 6, entry 2). This compound was isolated as a white solid (95 % yield) from the reaction of 4-chloro-2-(methylthio)pyrimidine and 4-methoxyphenylboronic acid using the general procedure. **¹H NMR** (CDCl_3): δ 8.45 (d, $J = 5.3$, 1H), 8.05 (d, $J = 9.0$, 2H), 7.26 (d, $J = 5.8$, 1H), 6.97 (d, $J = 9.0$, 2H), 3.85 (s, 3H), 2.62 (s, 3H). **¹³C NMR** (CDCl_3): δ 172.5, 163.3, 162.2, 157.4, 128.8, 128.7, 114.3, 111.0, 55.5, 14.2.

4-{2-(Methylthio)pyrimidin-4-yl}benzonitrile (Table 6, entry 3). This compound was isolated as an off-white solid (94 % yield) from the reaction of 4-chloro-2-(methylthio)pyrimidine and 4-cyanophenylboronic acid using the general procedure. **¹H NMR** (CDCl_3): δ 8.64 (d, $J = 5.3$, 1H), 8.20 (d, $J = 8.6$, 2H), 7.79 (d, $J = 8.4$, 2H), 7.40 (d, $J = 5.3$, 1H), 2.65 (s, 3H). **¹³C NMR** (CDCl_3): δ 173.5, 161.8, 158.3, 140.5, 132.7, 127.8, 118.4, 114.5, 112.2, 14.3.

Methyl 2-(4-Methoxyphenyl)-6-methylpyrimidine-4-carboxylate (Table 6, entry 4). This compound was isolated as an off-white solid (89 % yield) from the reaction of methyl 2-chloro-6-methylpyrimidine-4-carboxylate and 4-methoxyphenylboronic acid using the general procedure except (i) anhydrous toluene was used as solvent and (ii) 0.01 mol% catalyst was used. **¹H NMR** (CDCl_3): δ 8.47 (d, $J = 8.8$, 2H), 7.63 (s, 1H), 6.98 (d, $J = 8.6$, 2H), 4.02 (s, 3H), 3.86 (s, 3H), 2.63 (s, 3H). **¹³C NMR** (CDCl_3): δ 169.5, 165.5, 164.8, 162.1, 154.9, 130.2, 129.8, 117.3, 113.9, 55.4, 53.1, 24.6.

4-(2,6-Dimethylphenyl)-2-(methylthio)pyrimidine (Table 6, entry 5). This compound was isolated as a colorless oil (99 % yield) from the reaction of 4-chloro-2-(methylthio)pyrimidine and 2,6-dimethylphenylboronic acid using the general procedure except 0.1 mol% catalyst was used. **¹H NMR** (CDCl_3): δ 8.47 (d, $J = 4.9$, 1H), 7.12 (t, $J = 7.6$, 1H), 7.01 (d, $J = 7.5$, 2H), 6.80 (d, $J = 5.0$, 1H), 2.47 (s, 3H), 2.01 (s, 6H). **¹³C NMR** (CDCl_3): δ 171.9, 166.8, 156.1, 136.9, 134.2, 127.6, 126.8, 116.1, 19.2, 13.1.

2,4-Dimethoxy-6-(4-methoxyphenyl)pyrimidine (Table 6, entry 6). This compound was isolated as an off-white solid (98 % yield) from the reaction of 6-chloro-2,4-dimethoxypyrimidine and 4-methoxyphenylboronic acid using the general procedure except 0.1 mol% catalyst was used. **¹H NMR** (CDCl_3): δ 8.02 (d, $J = 8.6$, 2H), 6.97 (d, $J = 8.6$, 2H), 6.7 (s, 1H), 4.07 (s, 3H), 3.99 (s, 3H), 3.86 (s, 3H). **¹³C NMR** (CDCl_3): δ 172.5, 165.6, 165.4, 161.7, 129.3, 128.6, 114.0, 95.9, 55.4, 54.7, 53.9.

5-(6-Methoxypyridin-3-yl)pyridin-2-amine (Table 7, entry 1). This compound was isolated as a white solid (97 % yield) from the reaction of 5-chloropyridin-2-amine and 6-methoxypyridin-3-ylboronic acid using the general procedure. **¹H NMR** (CDCl_3): δ 8.27 (d/d, $J = 8/2.3$, 2H), 7.70 (d/d, $J = 8.6/2.6$, 1H), 7.59 (d/d, $J = 8.6/2.5$, 1H), 6.80 (d, $J = 8.6$, 1H), 6.58 (d, $J = 8.4$, 1H), 4.53 (br s, 2H), 3.97 (s, 3H). **¹³C NMR** (CDCl_3): δ 163.4, 157.7, 146.1, 144.2, 136.8, 136.2, 127.4, 124.2, 110.9, 108.6, 53.5.

4-(Pyridin-3-yl)pyridin-2-amine (Table 7, entry 2). This compound was isolated as an off-white solid (95 % yield) from the reaction of 4-chloropyridin-2-amine and pyridin-3-ylboronic acid using the general

procedure. **¹H NMR** (CDCl₃): δ 8.84 (s, 1H), 8.65 (d, *J* = 3.5 Hz, 1H), 8.17 (d, *J* = 5.0, 1H), 7.87 (d, *J* = 7.5, 1H), 7.34 - 7.45 (m, 1H), 6.86 (d, *J* = 5.0, 1H), 6.69 (s, 1H), 4.68 (br. s, 2H). **¹³C NMR** (CDCl₃): δ 158.3, 149.1, 148.2, 147.3, 146.3, 133.6, 133.4, 122.9, 111.6, 105.4.

2-(Pyridin-3-yl)pyridin-3-amine (Table 7, entry 3). This compound was isolated as a white solid (88 % yield) from the reaction of chloropyridin-3-amine and pyridin-3-ylboronic acid using the general procedure. **¹H NMR** (CDCl₃): δ 8.96 (s, 1H), 8.63 (d, *J* = 4.0, 1H), 8.15 (d, *J* = 3.5, 1H), 8.03 (d, *J* = 7.5, 1H), 7.40-7.42 (m, 1H), 7.05 - 7.17 (m, 2H), 3.79 (s, br, 2H). **¹³C NMR** (CDCl₃): δ 147.2, 146.9, 139.0, 138.1, 138.1, 133.9, 132.2, 121.4, 121.3, 120.8.

4-(2-Fluoropyridin-3-yl)-2,6-dimethoxypyrimidine (Table 7, entry 4). This compound was isolated as an off-white solid (97 % yield) from the reaction of Cl-chloro-2,4-dimethoxypyrimidine and 2-fluoropyridin-3-ylboronic acid using the general procedure. **¹H NMR** (CDCl₃): δ 8.92-8.99 (m, 1H), 8.53 (d, *J* = 5.0, 1H), 7.60-7.57 (m, 1H), 7.02 (s, 1H), 4.31 (s, 3H), 4.26 (s, 3H). **¹³C NMR** (CDCl₃): δ 172.7, 165.2, 161.2 (d, *J_{CF}* = 244), 159.1 (d, *J_{CF}* = 7.8), 148.8 (d, *J_{CF}* = 15.6), 141.2, 121.9 (d, *J_{CF}* = 4.3), 119.8 (d, *J_{CF}* = 25.2), 101.7 (d, *J_{CF}* = 13.9), 54.8, 54.1.

4-(2-Fluoropyridin-3-yl)-2-(methylthio)pyrimidine (Table 7, entry 5). This compound was isolated as a white solid (92 % yield) from the reaction of 4-chloro-2-(methylthio)pyrimidine and 2-fluoropyridin-3-ylboronic acid using the general procedure. **¹H NMR** (CDCl₃): δ 8.71 (t, *J* = 8.8, 1H), 8.61 (d, *J* = 5.5, 1H), 8.33 (s, 1H), 7.56 (d, *J* = 3.5, 1H), 7.33-7.42 (m, 1H), 2.62 (s, 3H). **¹³C NMR** (CDCl₃): δ 172.3, 161.2 (d, *J_{CF}* = 243), 158.1, 158.0 (d, *J_{CF}* = 7.8), 149.5 (d, *J_{CF}* = 15.6), 141.2, 122.1, 119.4 (d, *J_{CF}* = 26.0), 115.5 (d, *J_{CF}* = 13.0), 14.2.

3-(2-Fluoropyridin-3-yl)-6-methoxypyridazine (Table 7, entry 6). This compound was isolated as a white solid (99 % yield) from the reaction of 3-chloro-6-methoxypyridazine and 2-fluoropyridin-3-ylboronic acid using the general procedure. **¹H NMR** (CDCl₃): δ 8.60 - 8.70 (m, 1H), 8.31 (d, *J* = 4.5, 1H), 7.97 (d/d, *J* = 9.5/2.0, 1H), 7.35 - 7.45 (m, 1H), 7.10 (d, *J* = 9.0, 1H), 4.21 (s, 3H). **¹³C NMR** (CDCl₃):

δ 164.4, 160.5 (d, $J_{CF} = 240$), 150.4 (d, $J_{CF} = 6.1$), 148.4 (d, $J_{CF} = 15.6$), 140.9, 130.0 (d, $J_{CF} = 11.3$), 122.3, 119.4 (d, $J_{CF} = 26.8$), 117.3, 55.0.

2-(*p*-Tolyl)thiophene (Table 8, entry 1). This compound was isolated as a white solid (96 % yield) from the reaction of 2-chlorothiophene and *p*-tolylboronic acid using the general procedure. **$^1\text{H NMR}$** (CDCl_3): δ 7.48 (d, $J = 8.2$, 2H), 7.24 (d, $J = 3.5$, 1H), 7.2 (d, $J = 5$, 1H), 7.15 (d, $J = 7.9$, 2H), 7.03 (d/d, $J = 5.1/3.6$, 1H), 2.33 (s, 3H). **$^{13}\text{C NMR}$** (CDCl_3): δ 144.6, 137.3, 131.6, 129.5, 127.9, 125.8, 124.2, 122.6, 21.2.

4-(4-Methoxyphenyl)-1,3,5-trimethyl-1*H*-pyrazole (Table 8, entry 2). This compound was isolated as a white solid (93 % yield) from the reaction of 4-bromo-1,3,5-trimethylpyrazole and 4-methoxyphenylboronic acid using the general procedure. **$^1\text{H NMR}$** (CDCl_3): δ 7.15 (d, $J = 8.6$, 2H), 6.94 ($J = 8.6$, 2H), 3.82 (s, 3H), 3.76 (s, 3H), 2.22 (s, 3H), 2.20 (s, 3H). **$^{13}\text{C NMR}$** (CDCl_3): δ 158.1, 145.0, 136.0, 130.5, 126.6, 118.8, 113.9, 55.3, 36.0, 12.4, 10.2.

4-(4-Fluorophenyl)-1,3,5-trimethyl-1*H*-pyrazole (Table 8, entry 3). This compound was isolated as a white solid (95 % yield) from the reaction of 4-bromo-1,3,5-trimethylpyrazole and 4-fluorophenylboronic acid using the general procedure. **$^1\text{H NMR}$** (CDCl_3): δ 7.10 (d/d, $J = 8.8/5.7$, 2H), 6.99 (t, $J = 8.8$, 2H), 3.69 (s, 3H), 2.13 (s, 3H), 2.12 (s, 3H). **$^{13}\text{C NMR}$** (CDCl_3): δ 160.5 (d, $J = 244$), 143.9, 135.1, 129.9 (d, $J = 7.7$), 129.2 (d, $J = 2.6$), 117.3, 114.2 (d, $J = 20.7$), 35.0, 11.3, 9.1. **$^{19}\text{F NMR}$** (CDCl_3): δ -116.

3-(1,3,5-Trimethyl-1*H*-pyrazol-4-yl)pyridine (Table 8, entry 4). This compound was isolated as an off-white solid (95% yield) from the reaction of 4-bromo-1,3,5-trimethylpyrazole and pyridine-3-ylboronic acid using the general procedure. **$^1\text{H NMR}$** (CDCl_3): δ 8.50-8.52 (m, 2H), 7.57 (d, $J = 8.0$, 1H), 7.33 (d/d, $J = 7.5$, 5.0, 1H), 3.80 (s, 3H), 2.25 (s, 6 H). **$^{13}\text{C NMR}$** (CDCl_3): δ 150.3, 147.3, 145.2, 136.7, 136.5, 130.2, 123.4, 115.6, 36.1, 12.4, 10.2.

2-(6-Methoxypyridin-3-yl)benzo[d]oxazole (Table 8, entry 5). This compound was isolated as an off-white solid (88 % yield) from the reaction of 2-chlorobenzoxazole and 6-methoxypyridin-3-ylboronic acid

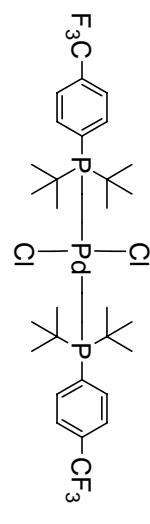
using the general synthetic procedure with a modified work-up procedure where the product was precipitated by adding water to the reaction mixture in dioxane. The precipitated product was washed with water (5 mL), cold pentane (1 mL), and dried under vacuum. ¹H NMR (CDCl₃): δ 9.04 (br. s, 1H), 8.36 (br. d, *J* = 11.0, 1H), 7.75 (br. s, 1H), 7.56 (br. s, 1H), 7.34 (m, 2H), 6.88 (d, *J* = 8.8, 1H), 4.03 (s, 3H). ¹³C NMR (CDCl₃): δ 166.0, 161.4, 150.6, 147.2, 142.0, 137.5, 125.0, 124.7, 119.8, 117.1, 111.4, 110.5, 54.0.

2-(Thiophen-2-yl)benzo[d]oxazole (Table 8, entry 6). This compound was isolated as a white solid (95 % yield) from the reaction of 2-chlorobenzooxazole and 2-thiopheneboronic acid using the general procedure. ¹H NMR (CDCl₃): δ 7.89 (d, *J* = 4.0, 1H), 7.67 - 7.78 (m, 1 H), 7.49 - 7.58 (m, 2H), 7.28 - 7.37 (m, 2H), 7.11 - 7.21 (m, 1H). ¹³C NMR (CDCl₃): δ 159.1, 150.4, 142.0, 130.3, 130.0, 129.7, 128.3, 125.1, 124.8, 119.8, 110.5.

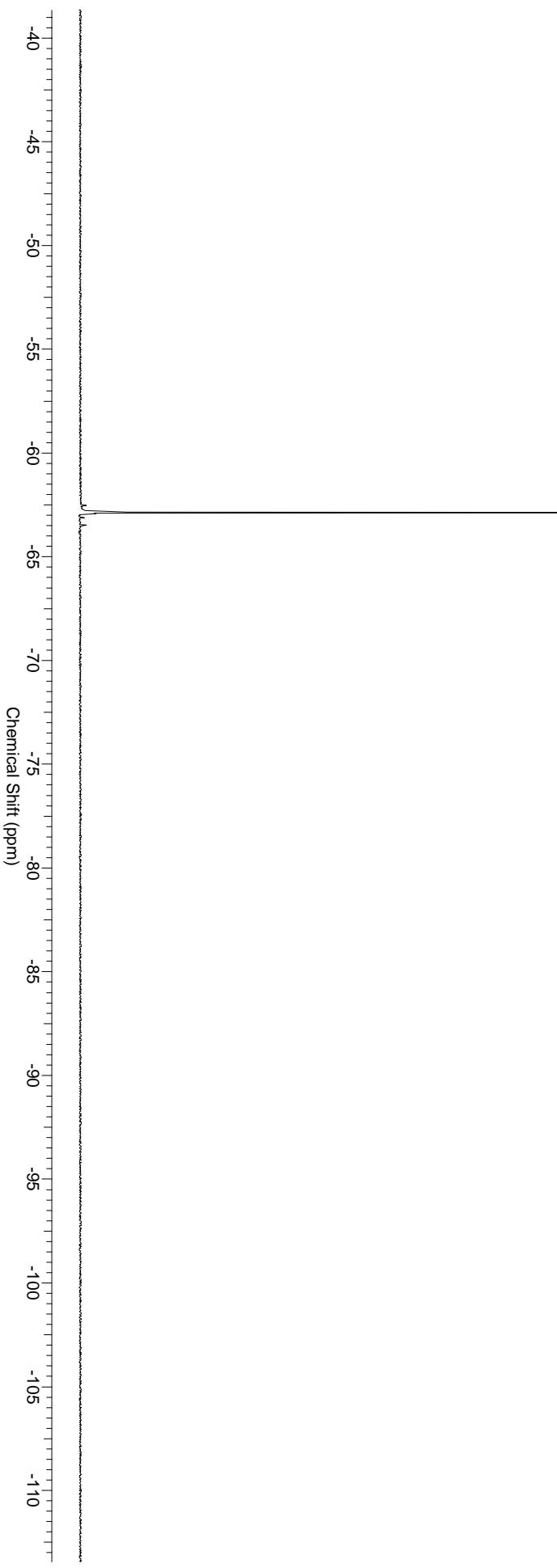
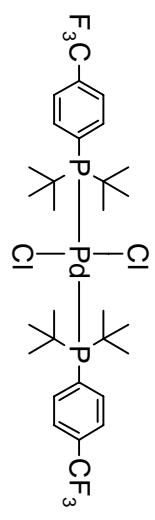
2-(*p*-Tolyl)-3-pyridinamine (Equation 1). This compound was isolated as a white solid (96 % yield) from the reaction of 2-chloro-3-pyridinamine and 4,4,5,5-tetramethyl-2-*p*-tolyl-1,3,2-dioxaborolane using the general procedure. Isolated material contained some 2,3-dimethylbutane-2,3-diol. The ¹H and ¹³C NMR data matched entry 2, Table 5.

2-(Quinolin-6-yl)pyridine-4-amine (Equation 2). This compound was isolated as a white solid (92 % yield) from the reaction of 2-chloro-4-pyridinamine and 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinoline using the general procedure. ¹H NMR (CD₃OD): δ 8.88 (d, *J* = 4.0, 1H), 8.45 (d, *J* = 8.0, 1H), 8.35 (s, 1 H), 8.19 (d, 8.6, 1H), 8.12 (d, 6.1, 2H), 7.60 - 7.57 (dd, *J* = 8.2, 4.2, 1H), 7.14 (s, 1H), 6.66 (d, *J* = 5.5, 1H), -NH₂ protons not observed. ¹³C NMR (CDCl₃): δ 157.1, 155.5, 150.6, 147.5, 147.2, 137.6, 136.9, 128.5, 128.4, 128.3, 126.4, 121.8, 108.0, 107.0.

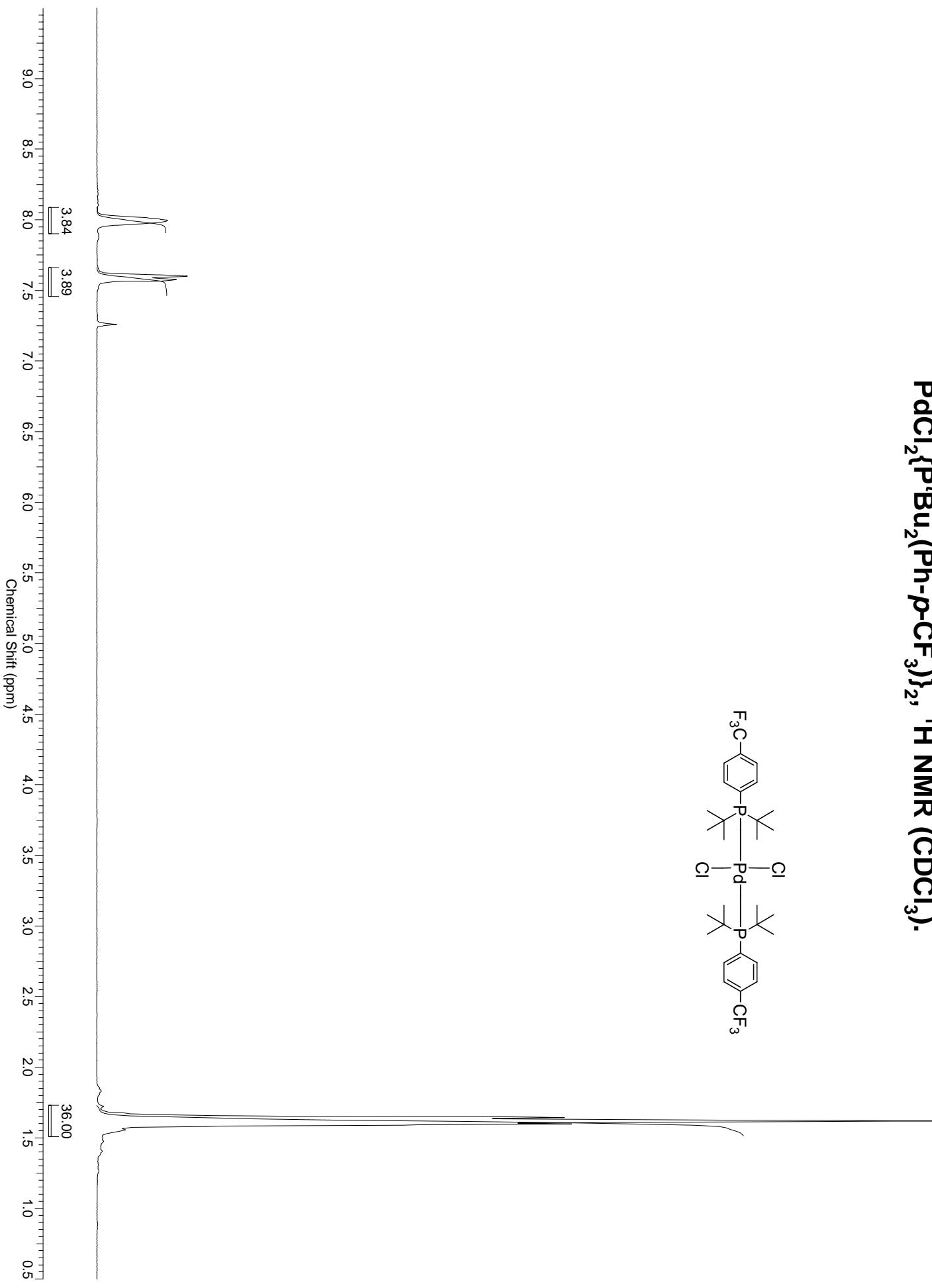
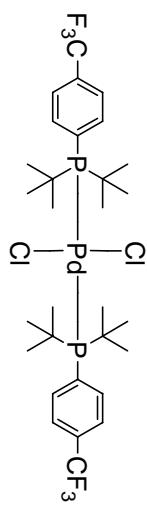
PdCl₂{P^tBu₂(Ph-*p*-CF₃)}₂, ³¹P NMR (CDCl₃).



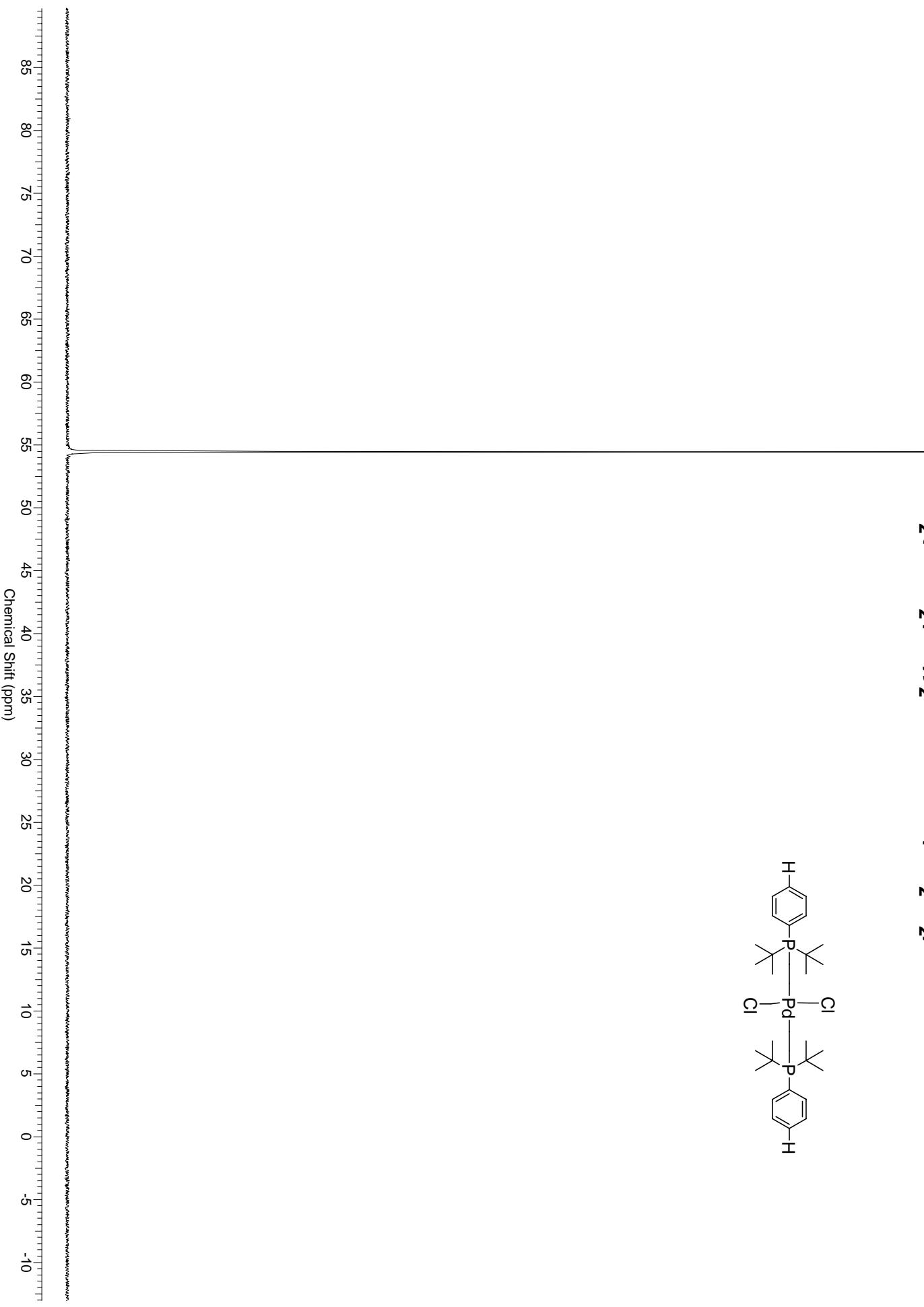
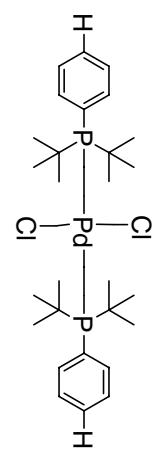
PdCl₂{P^tBu₂(Ph-*p*-CF₃)₂}₂, ¹⁹F NMR (CDCl₃).



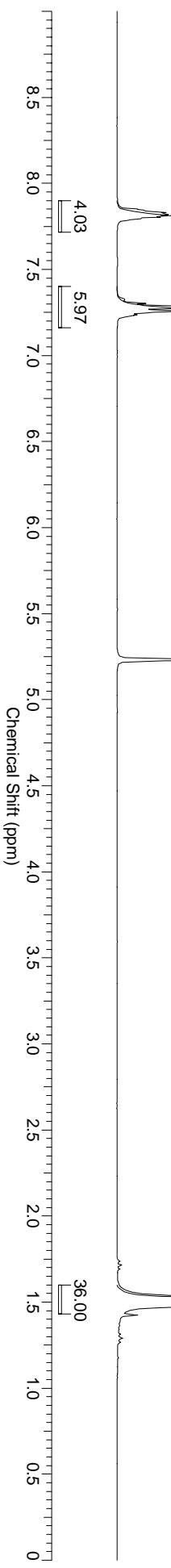
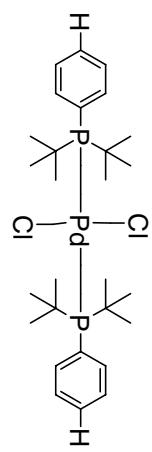
PdCl₂{P^tBu₂(Ph-*p*-CF₃)}₂, ¹H NMR (CDCl₃).



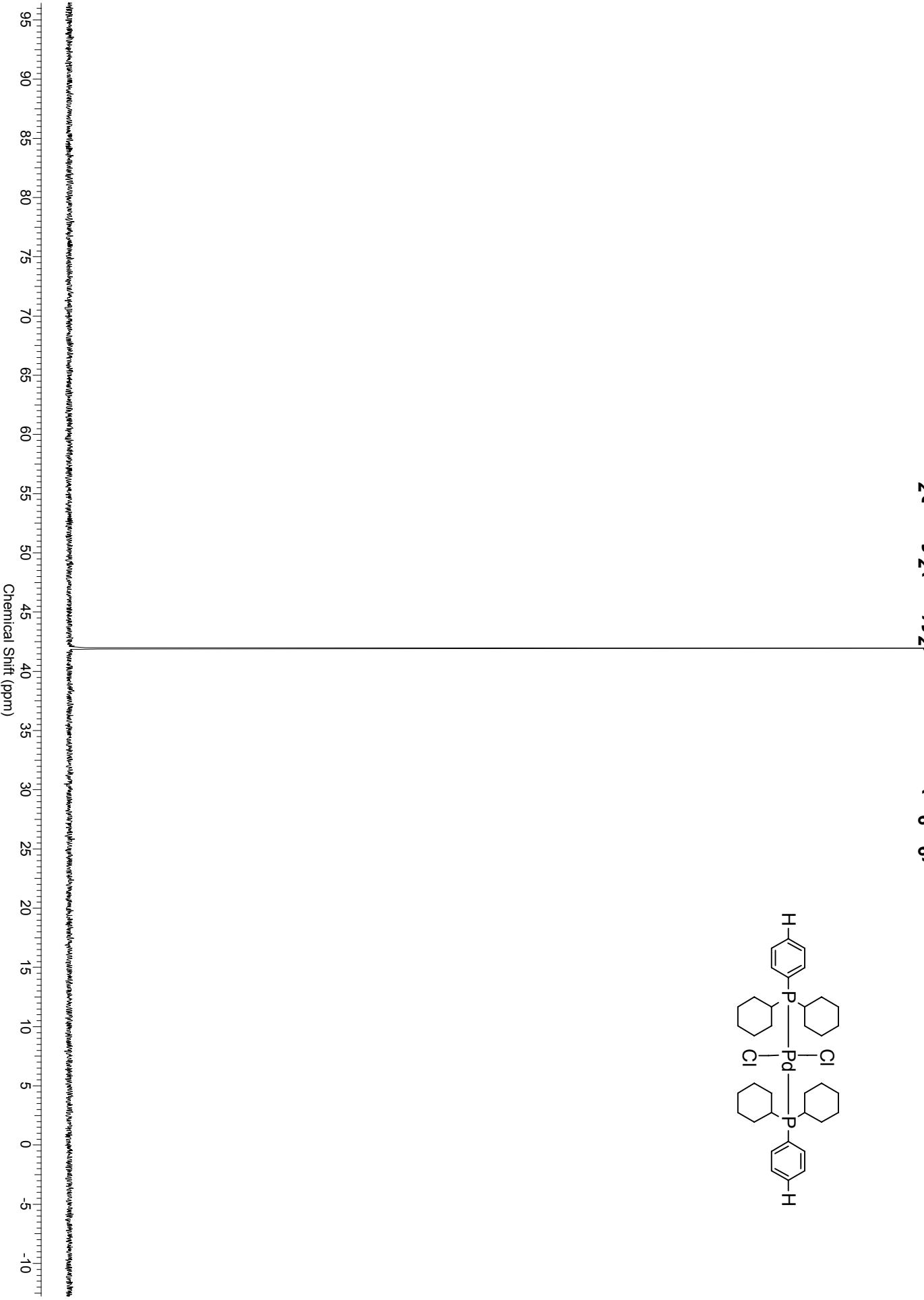
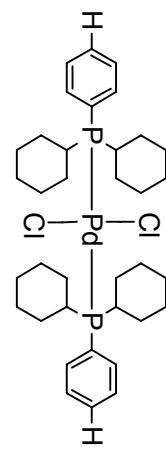
PdCl₂{P^tBu₂(Ph)}₂, ³¹P NMR (CD₂Cl₂).



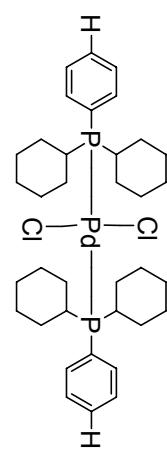
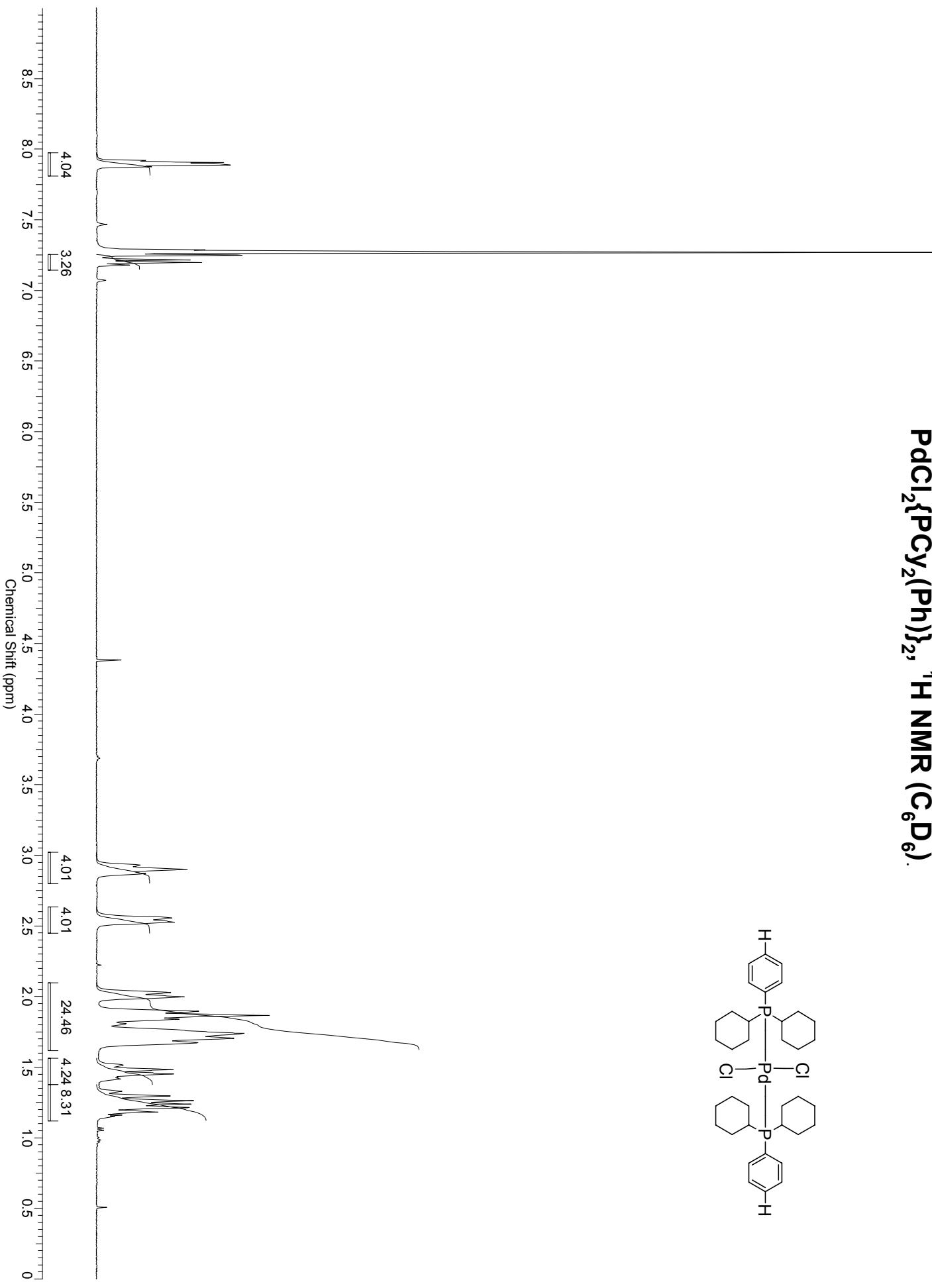
PdCl₂{P^tBu₂(Ph)}₂, ¹H NMR (CD₂Cl₂).



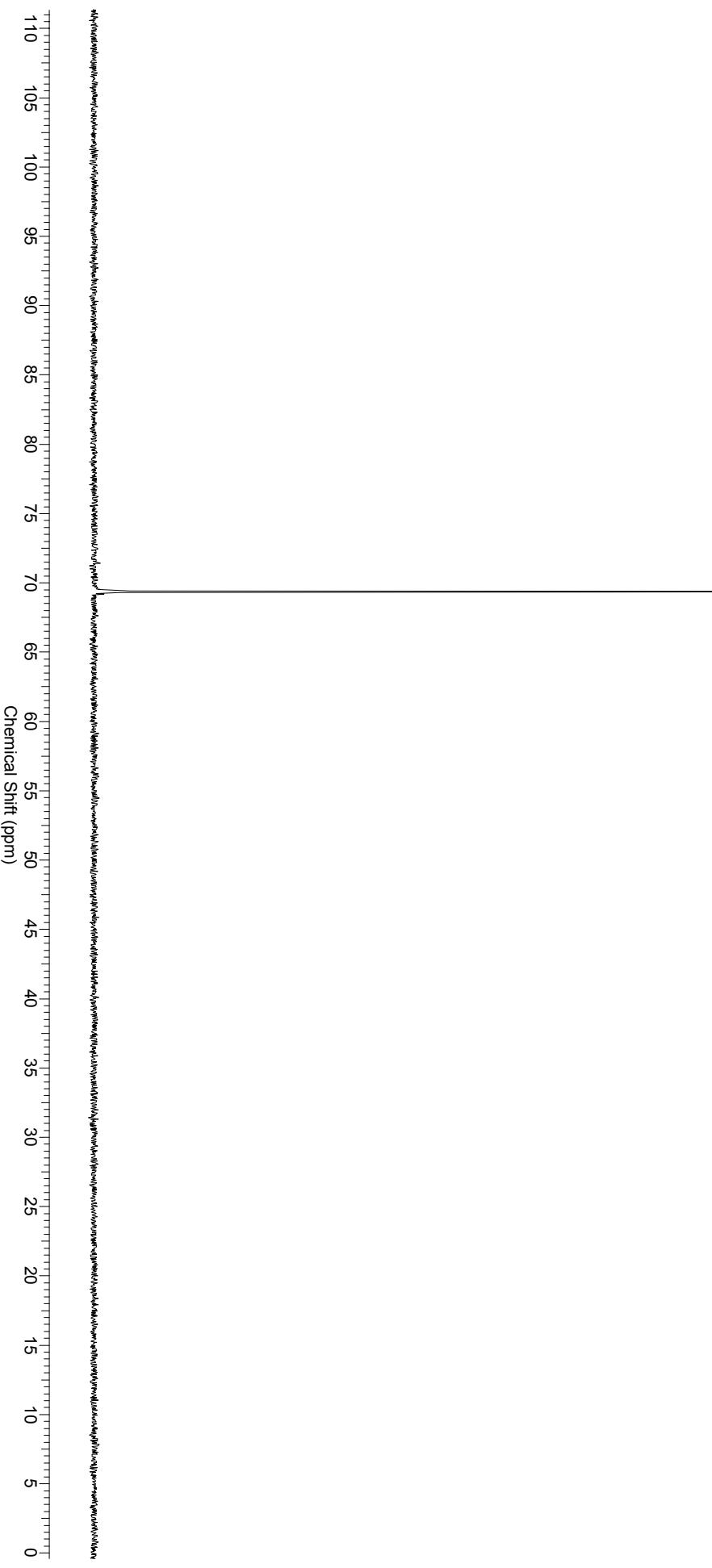
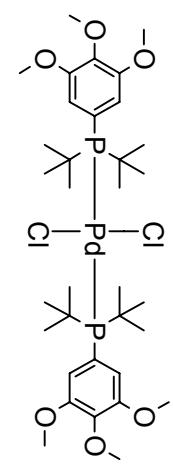
PdCl₂{PCy₂(Ph)}₂, ³¹P NMR (C₆D₆).



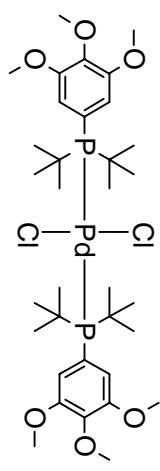
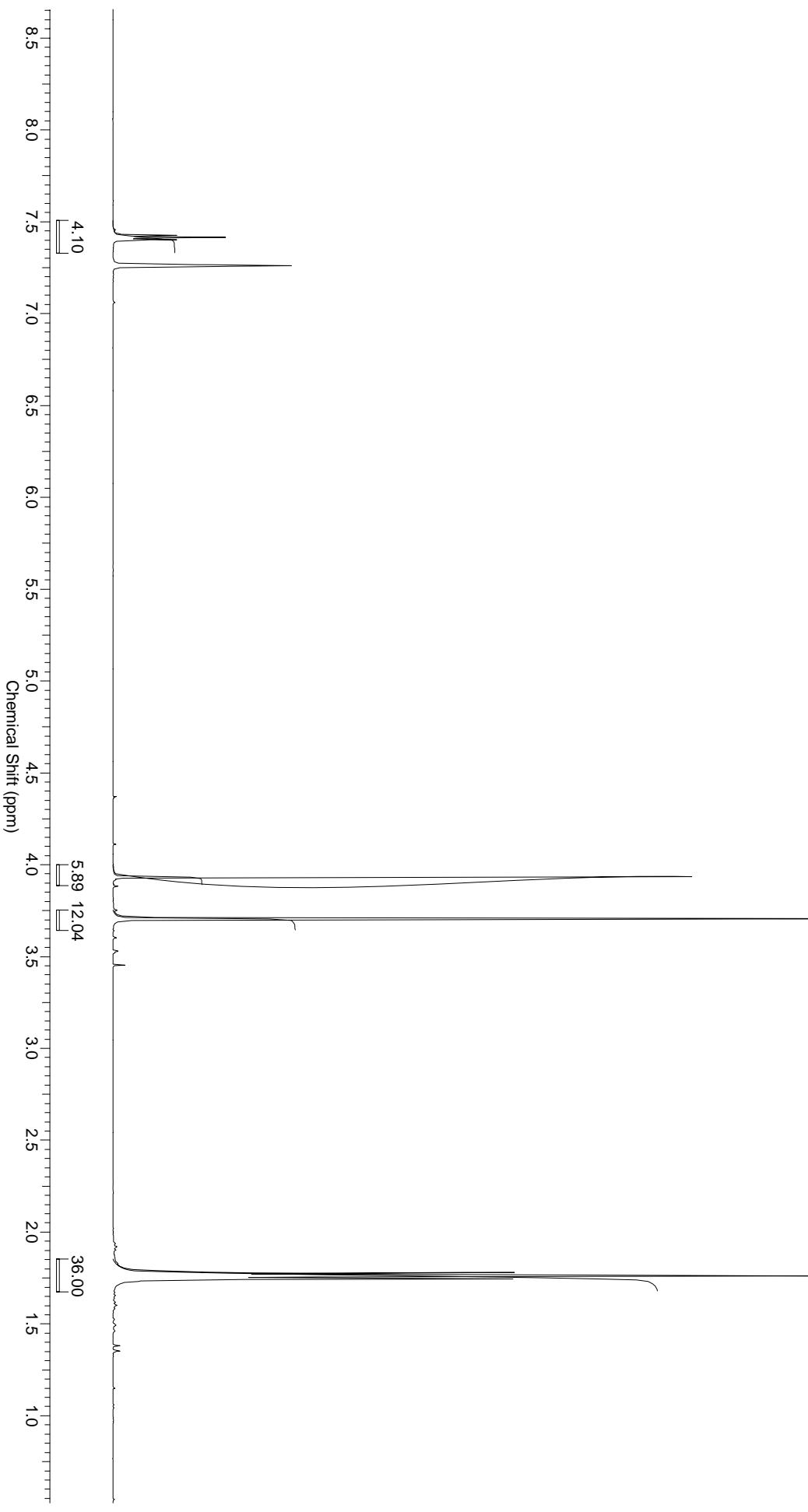
$\text{PdCl}_2\{\text{PCy}_2(\text{Ph})\}_2$, ^1H NMR (C_6D_6).



PdCl₂{P^tBu₂(Ph-*p,m,m*-tri-OMe)}₂, ³¹P NMR (C₆D₆)



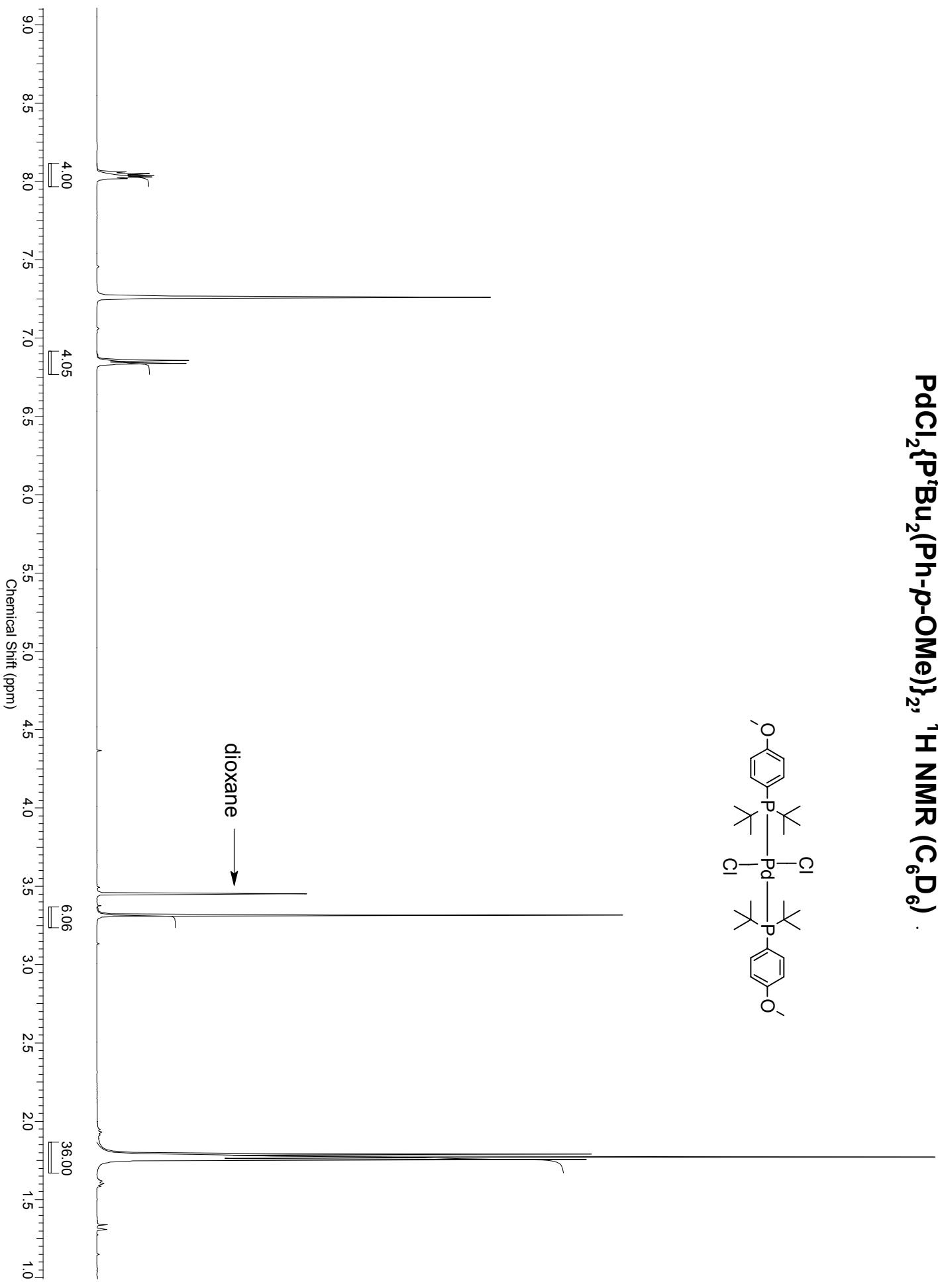
$\text{PdCl}_2\{\text{P}^t\text{Bu}_2(\text{Ph}-m,m,\rho\text{-tri-OMe})\}_2$, ^1H NMR (C_6D_6).



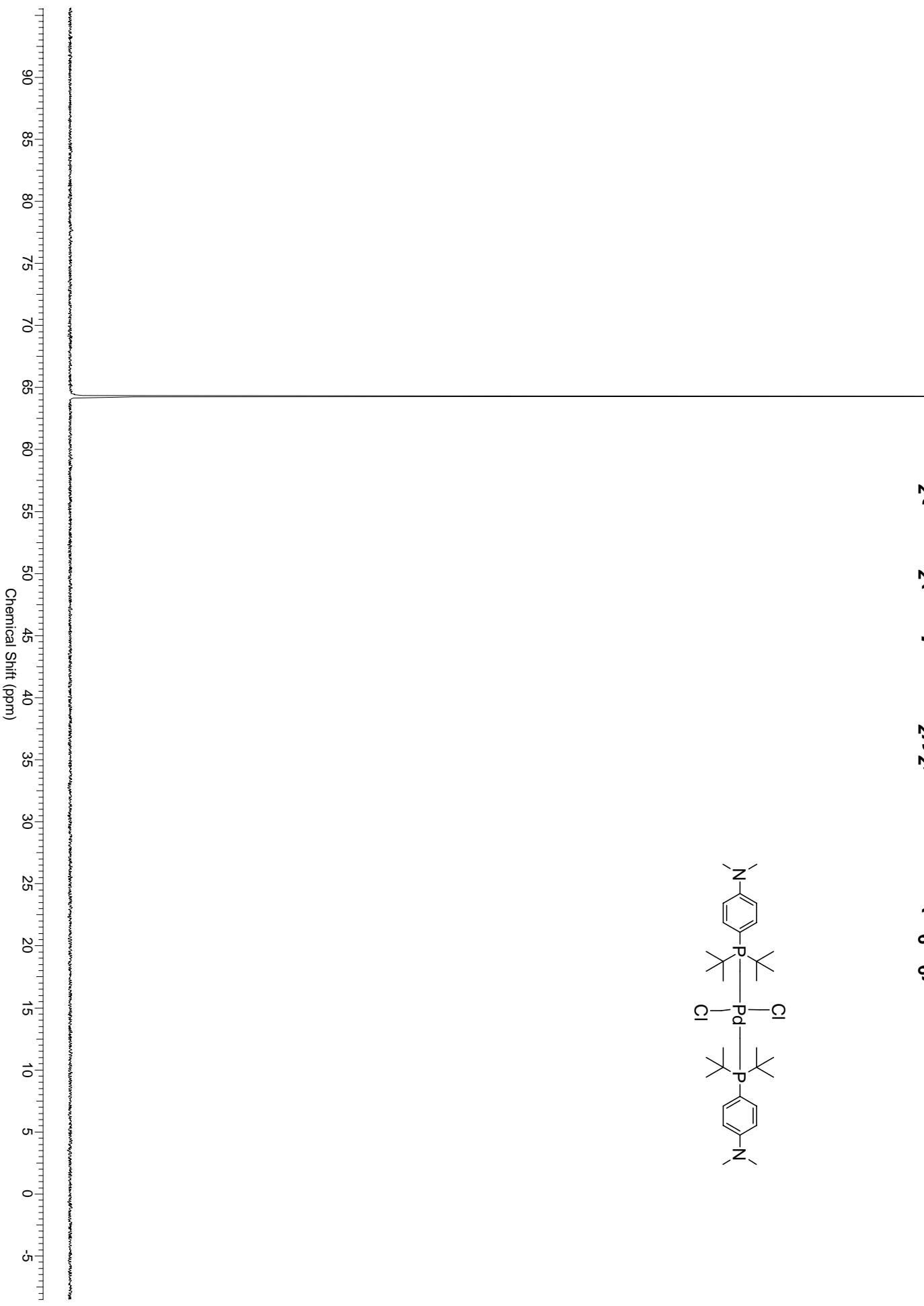
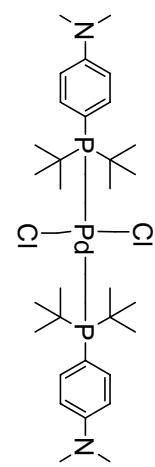
$\text{PdCl}_2\{\text{P}^t\text{Bu}_2(\text{Ph}-p\text{-OMe})\}_2$, ^{31}P NMR (C_6D_6).



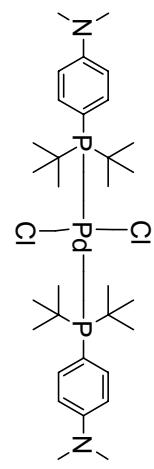
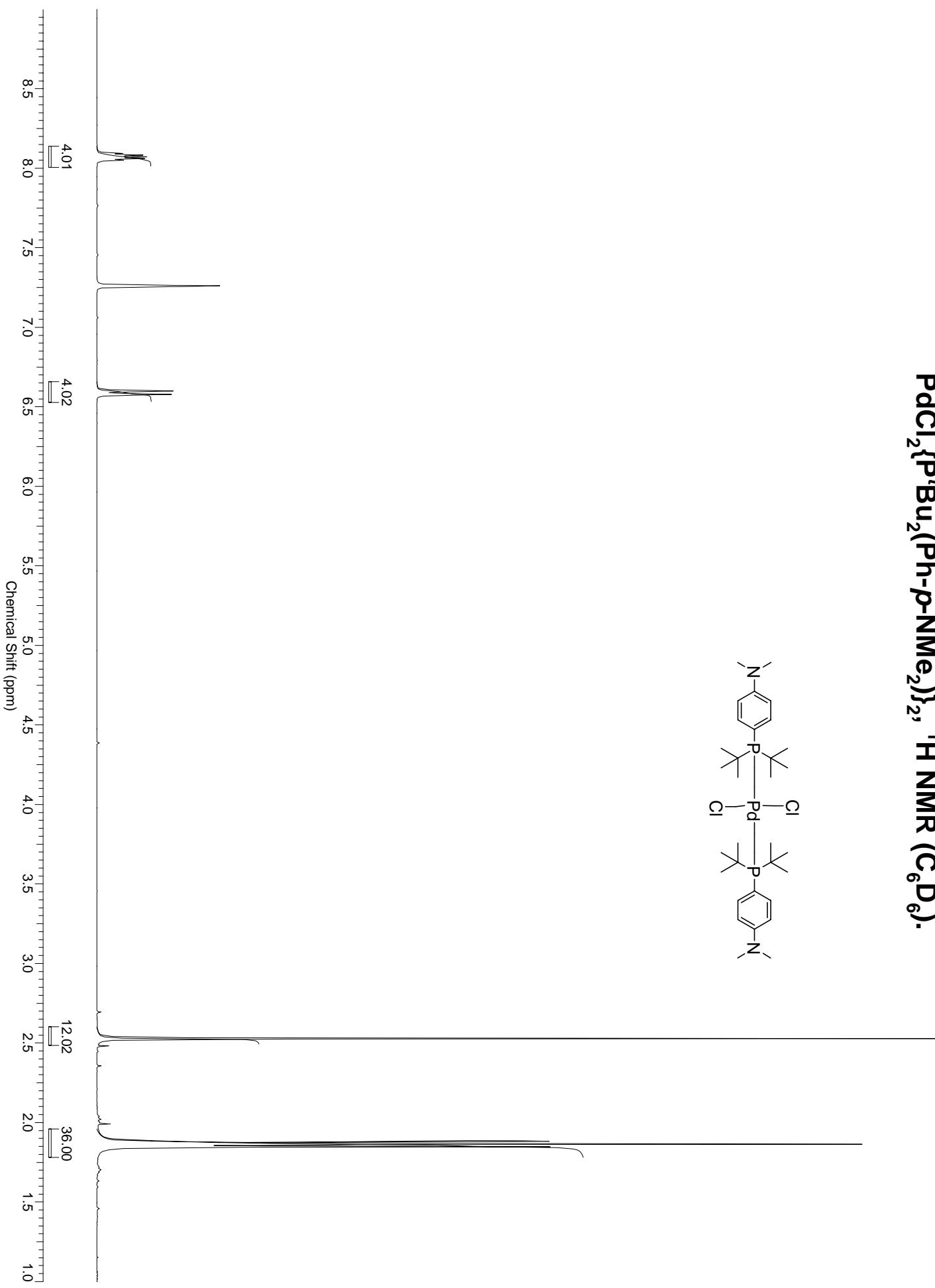
$\text{PdCl}_2\{\text{P}^t\text{Bu}_2(\text{Ph}-\rho\text{-OMe})\}_2$, ^1H NMR (C_6D_6) .



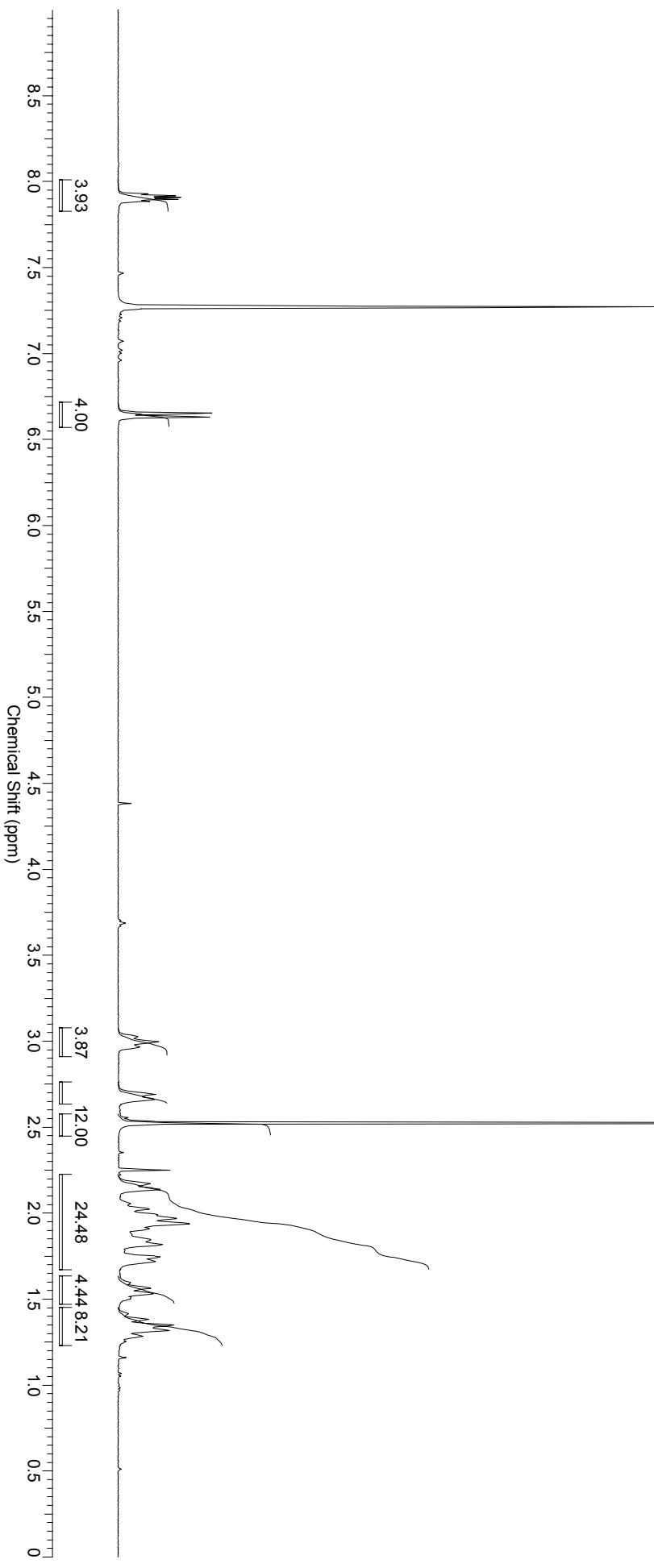
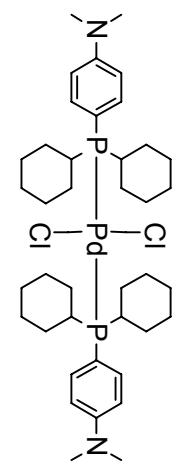
PdCl₂{P^tBu₂(Ph-*p*-NMe₂)}₂, ³¹P NMR (C₆D₆).



PdCl₂{P'Bu₂(Ph-*p*-NMe₂)}₂, ¹H NMR (C₆D₆).



PdCl₂{PCy₂(Ph-*p*-NMe₂)₂}, ¹H NMR (C₆D₆).



PdCl₂{PCy₂(Ph-*p*-NMe₂)}₂, ³¹P NMR (C₆D₆).

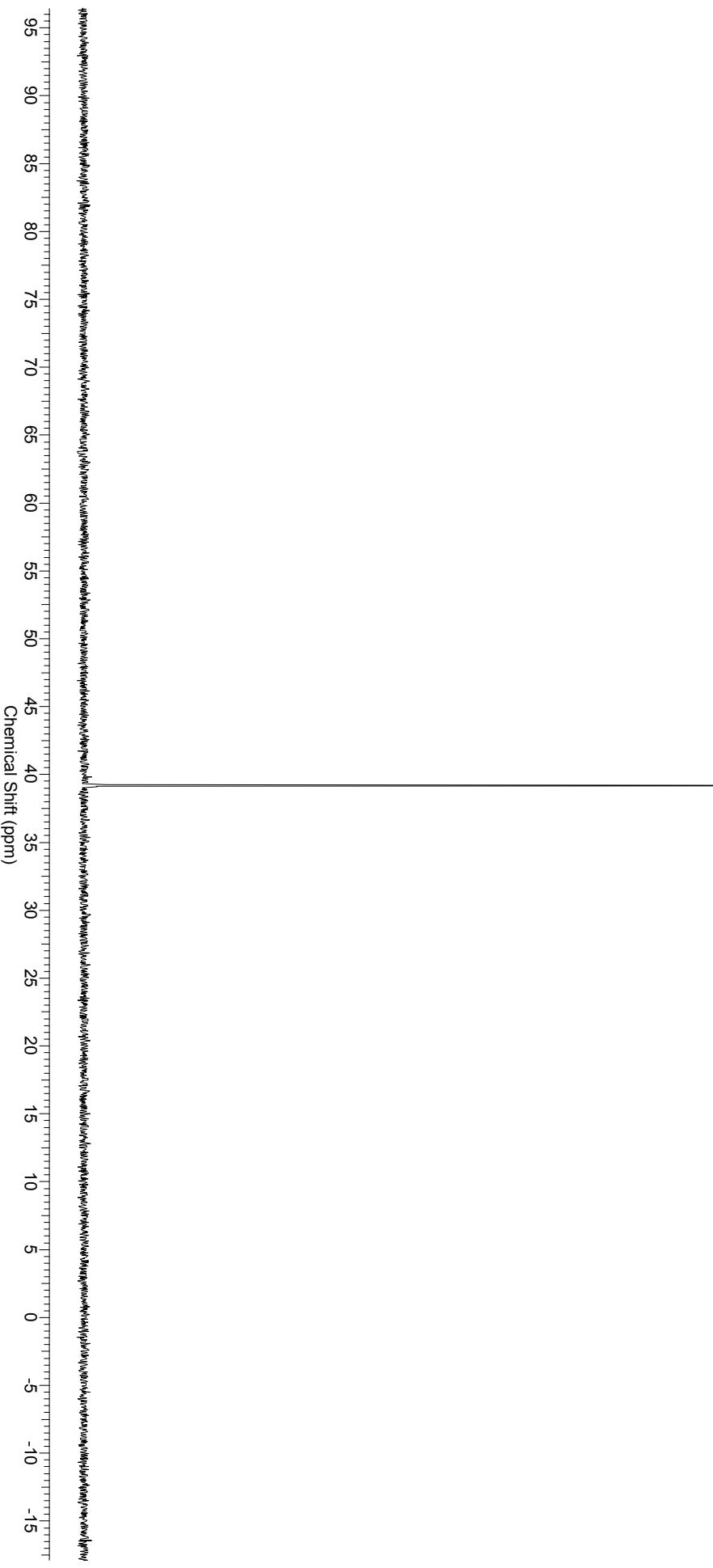
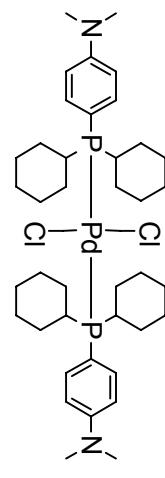


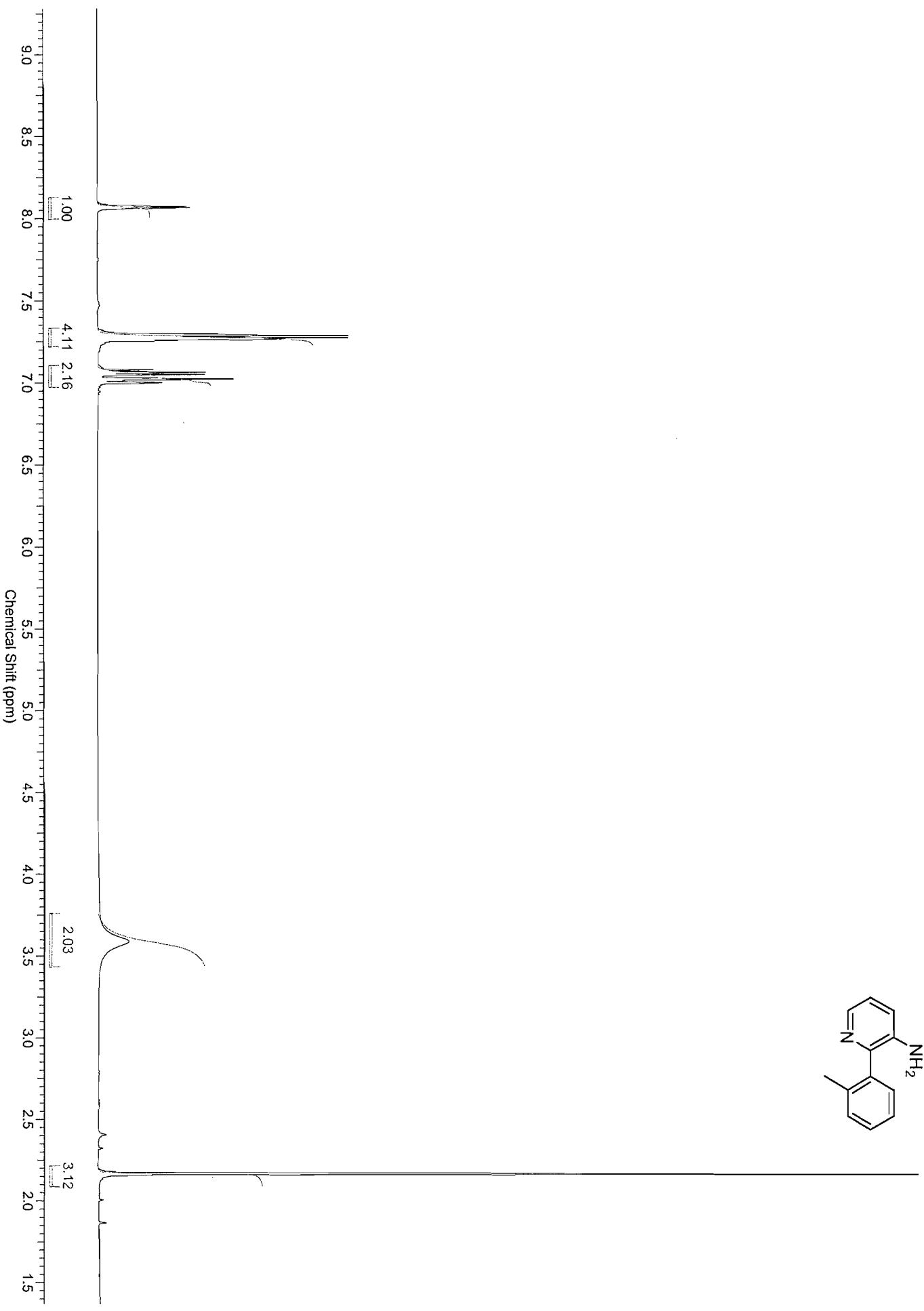
Table 1, entry 1, ^1H NMR (CDCl_3).

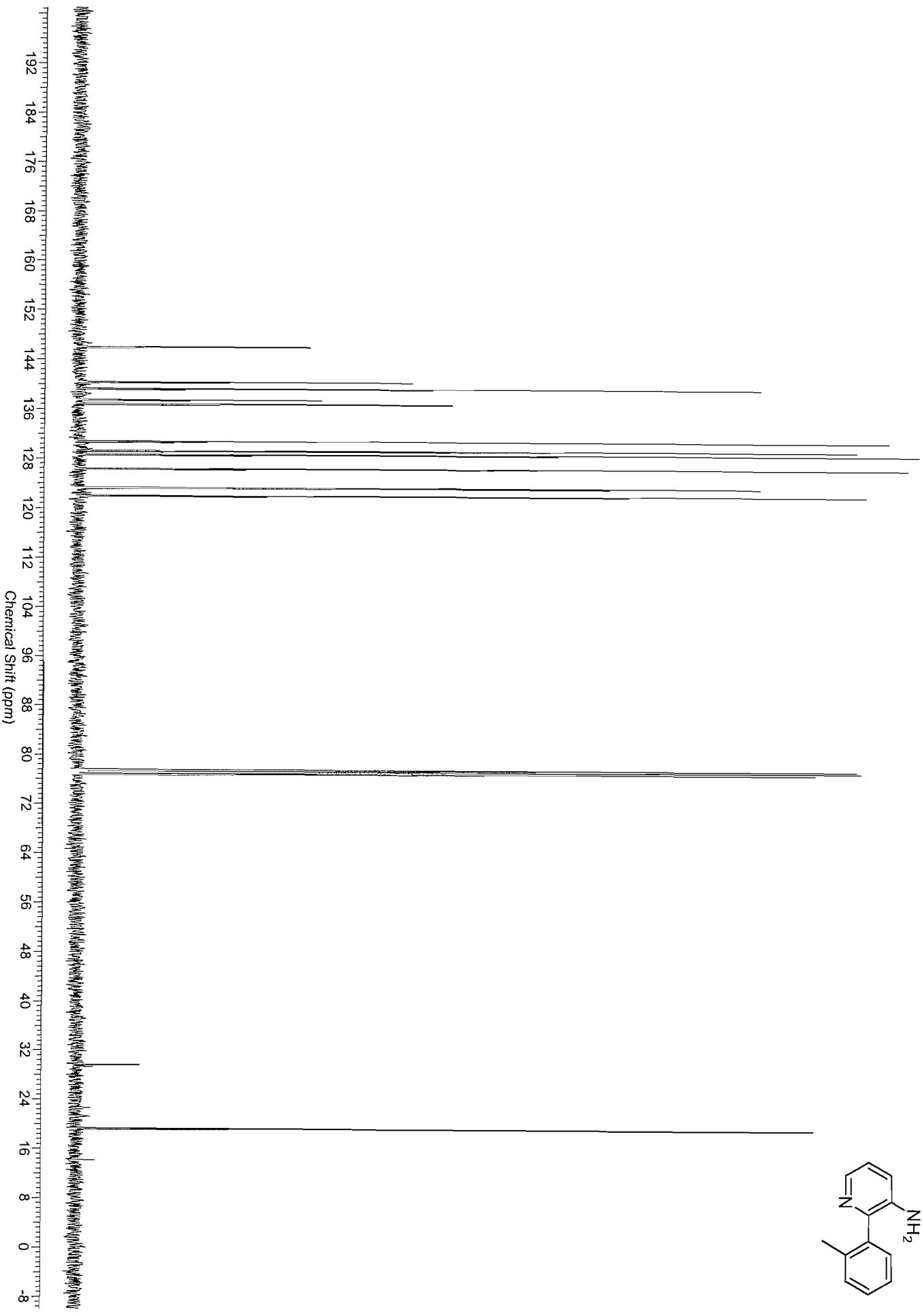
Table 1, entry 1, ^{13}C NMR (CDCl_3).

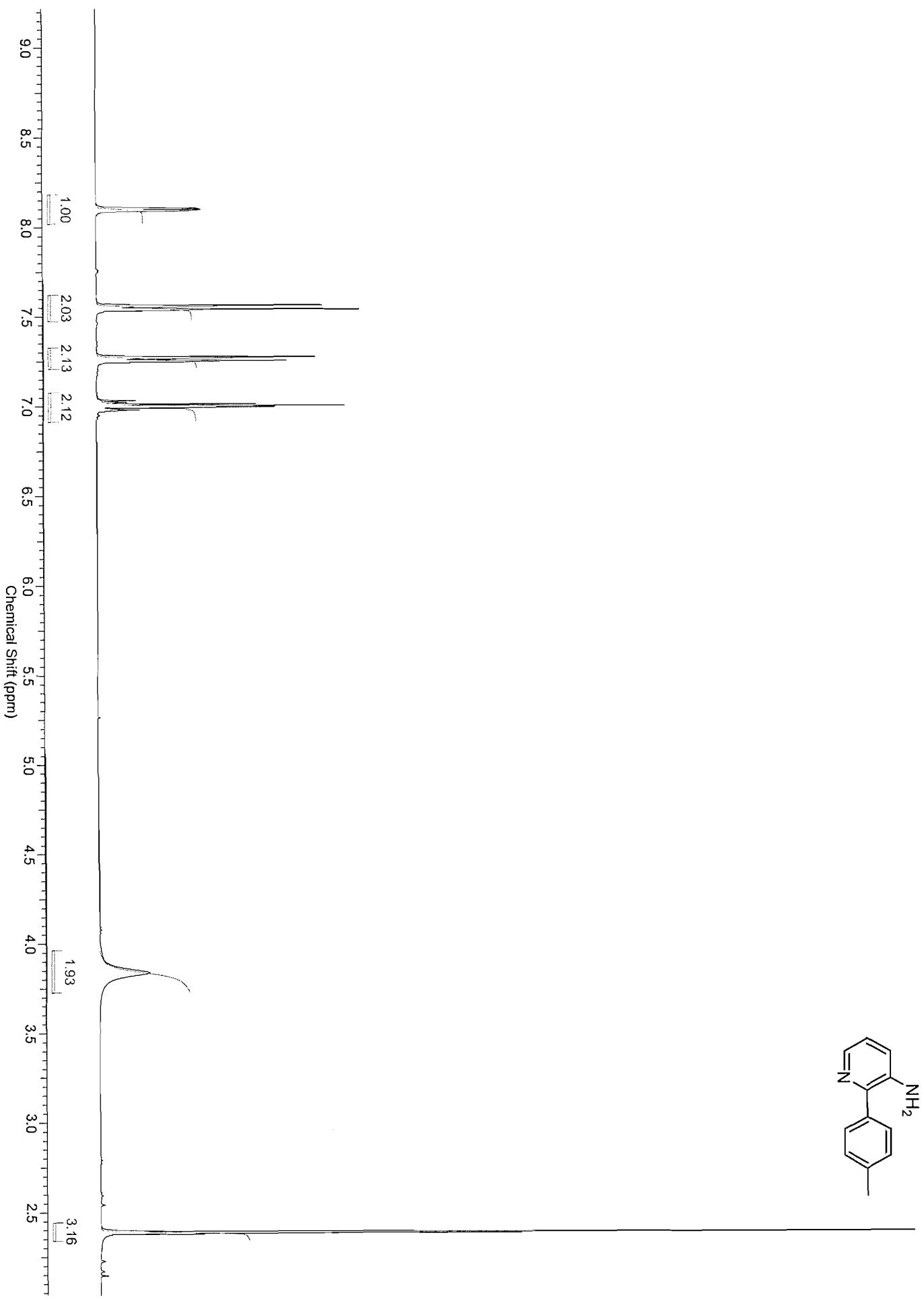
Table 1, entry 2, ^1H NMR (CDCl_3).

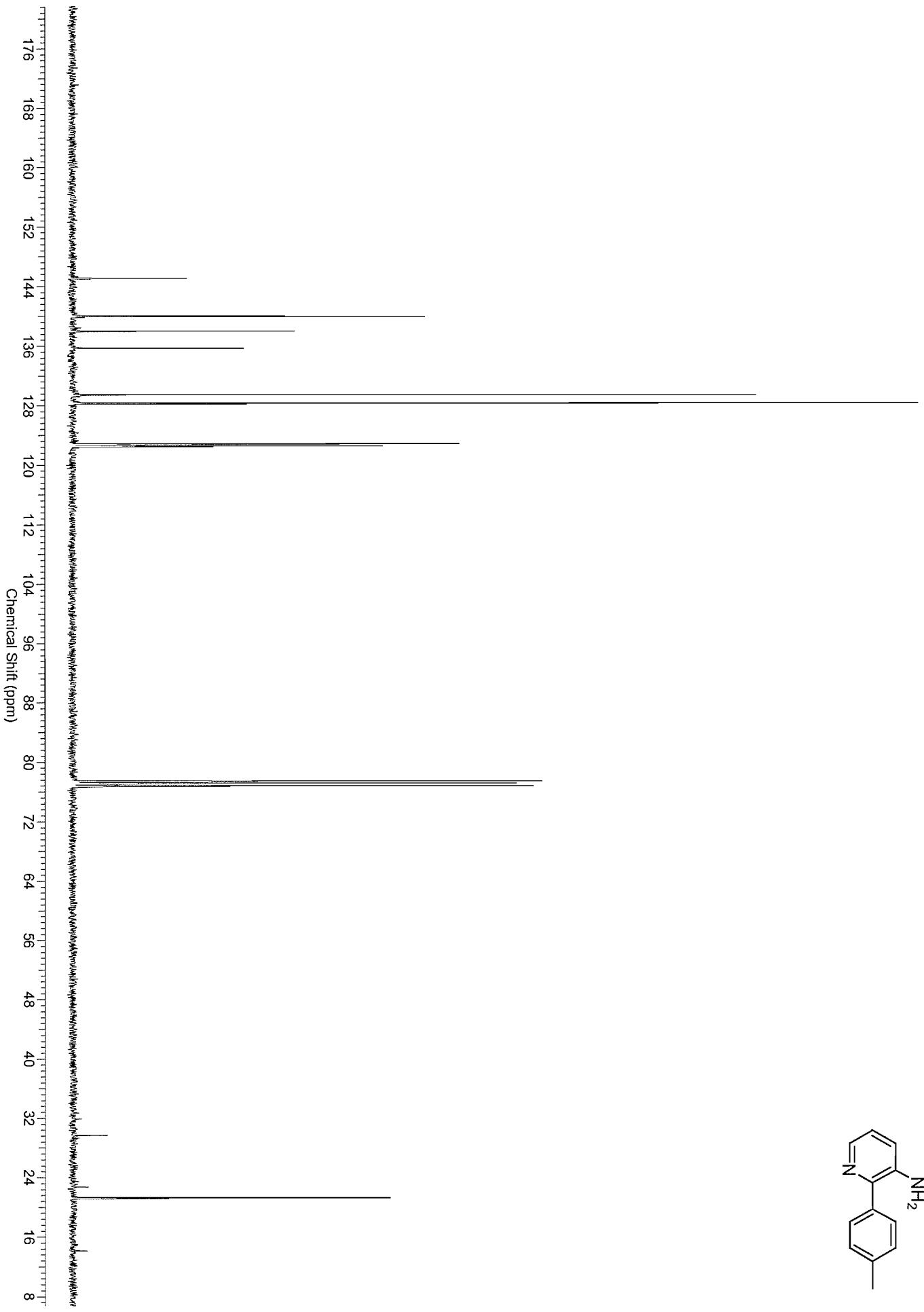
Table 1, entry 2, ^{13}C NMR (CDCl_3).

Table 1, entry 3, ^1H NMR (CDCl_3).

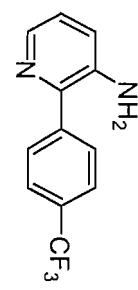
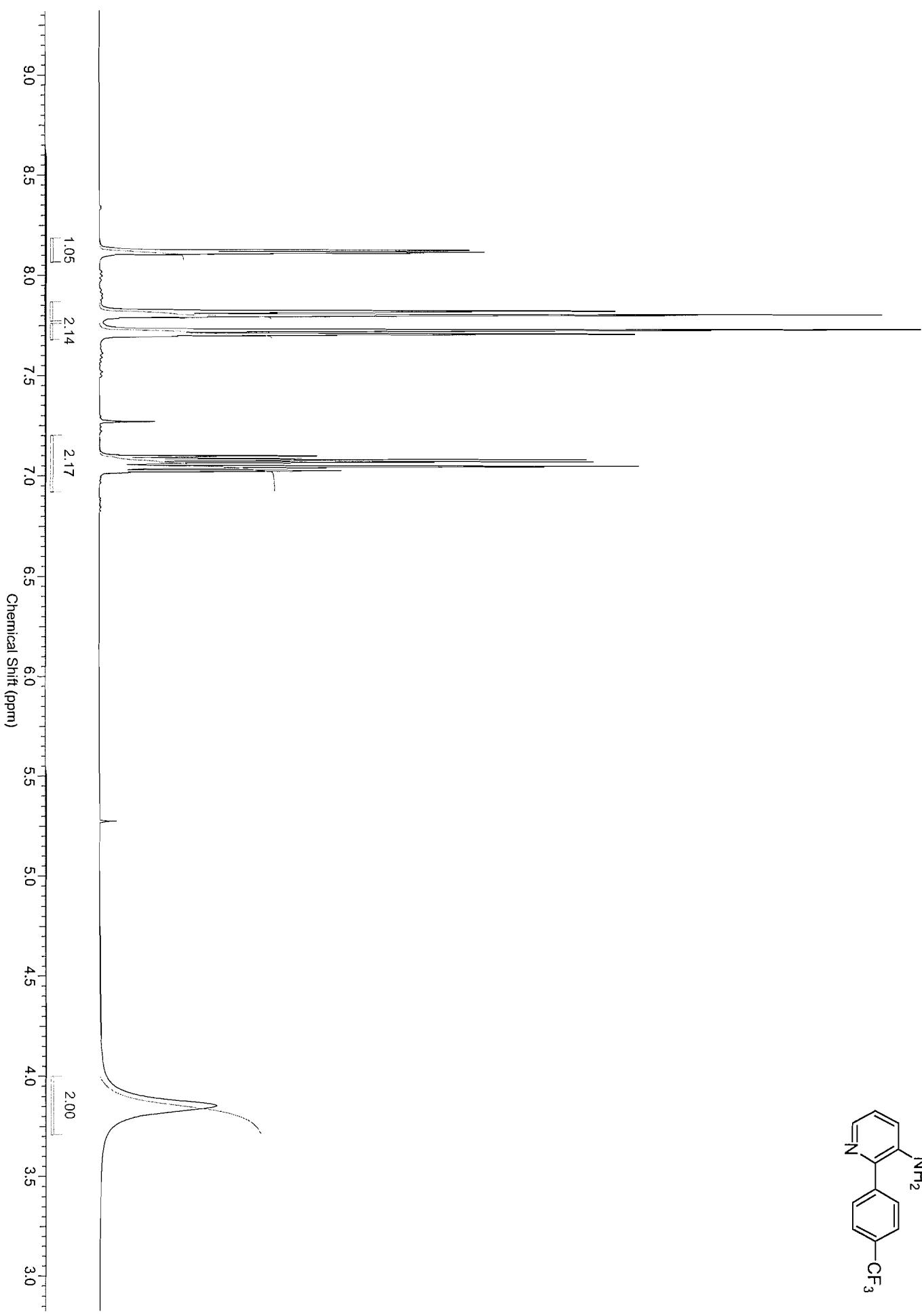


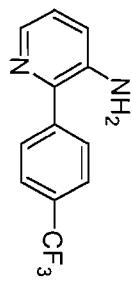
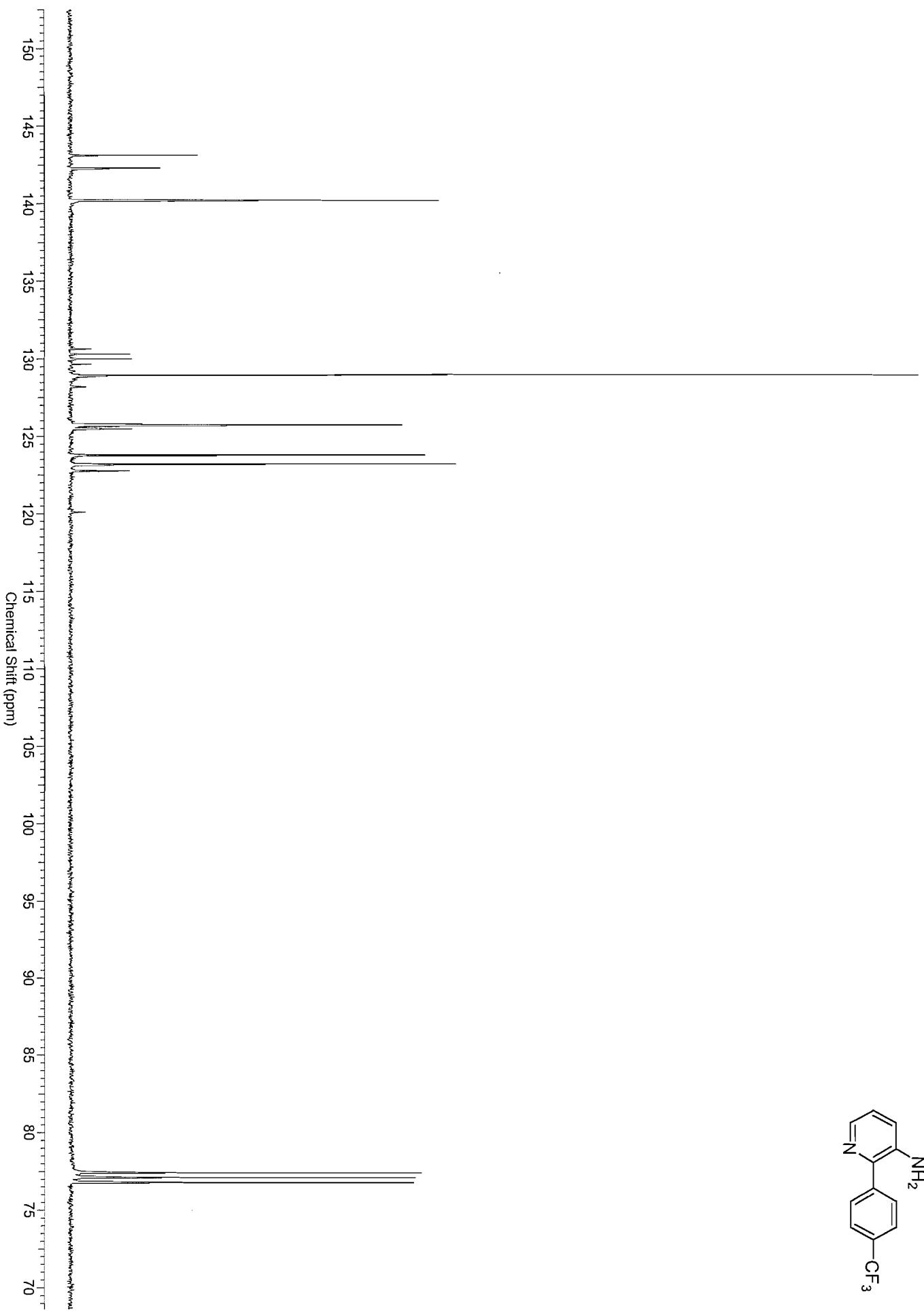
Table 1, entry 3, ^{13}C NMR (CDCl_3).

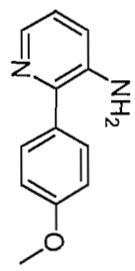
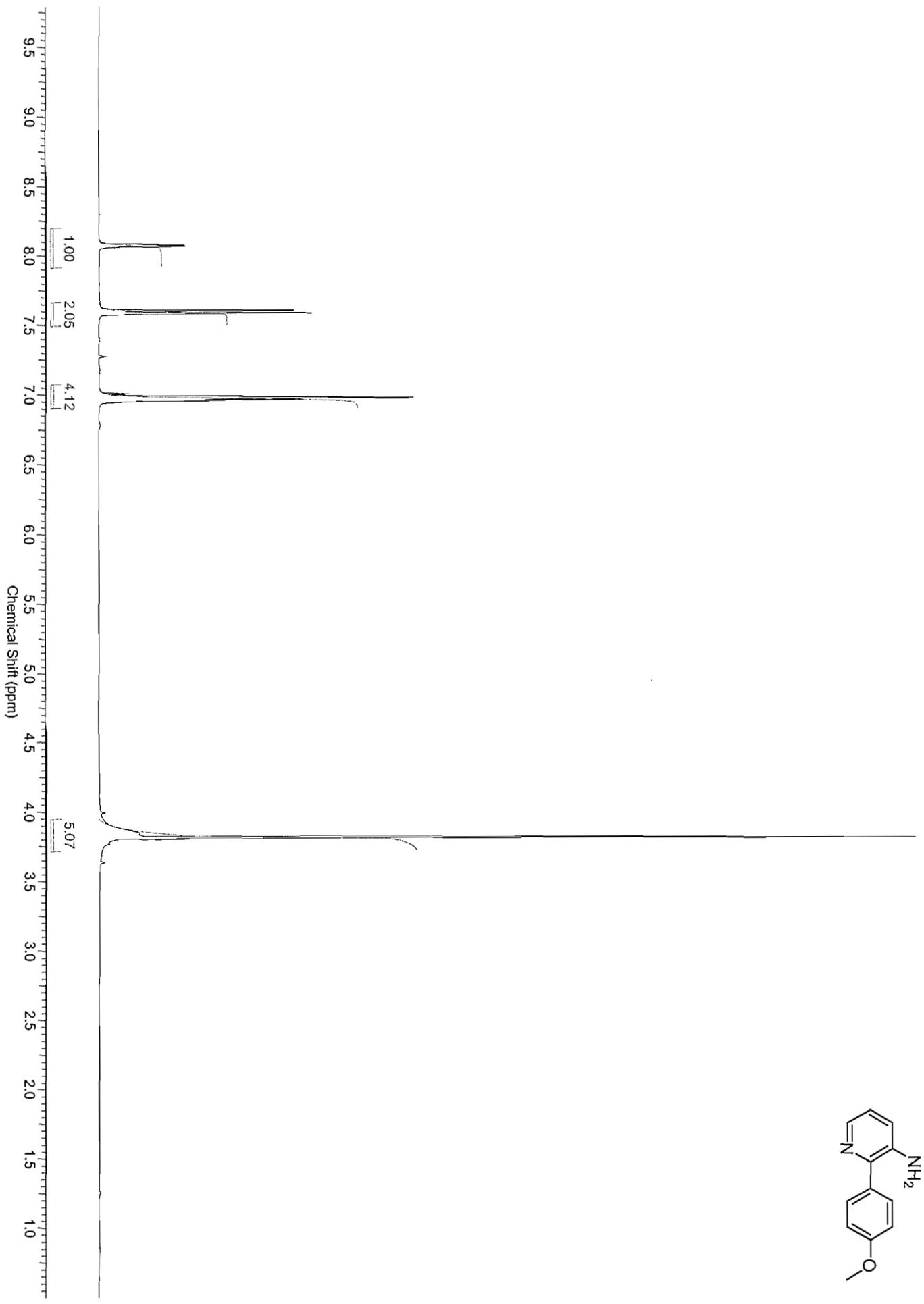
Table 1, entry 4, ^1H NMR (CDCl_3).

Table 1, entry 4, ^{13}C NMR (CDCl_3).

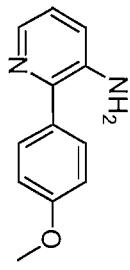
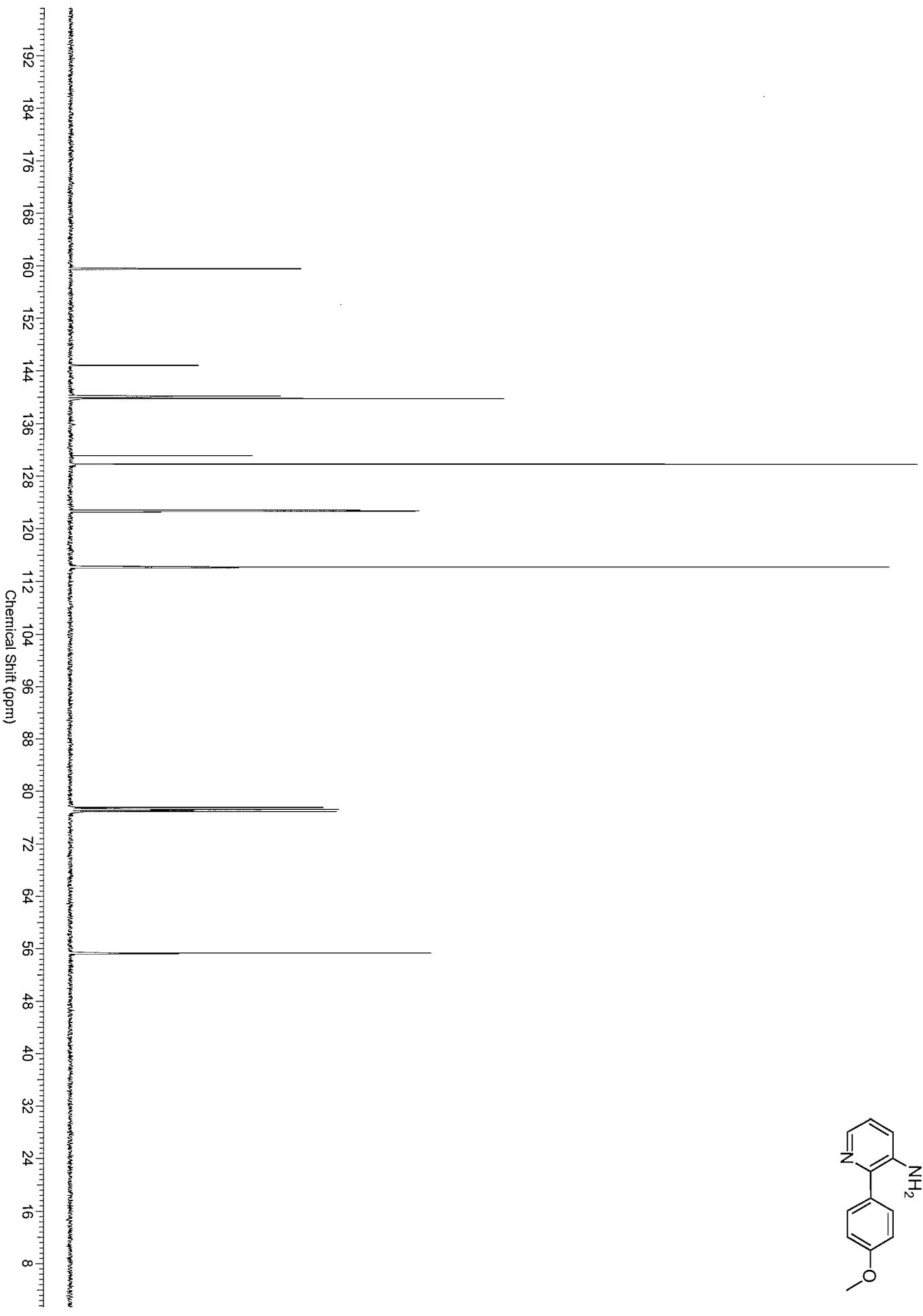


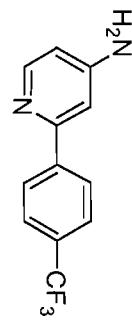
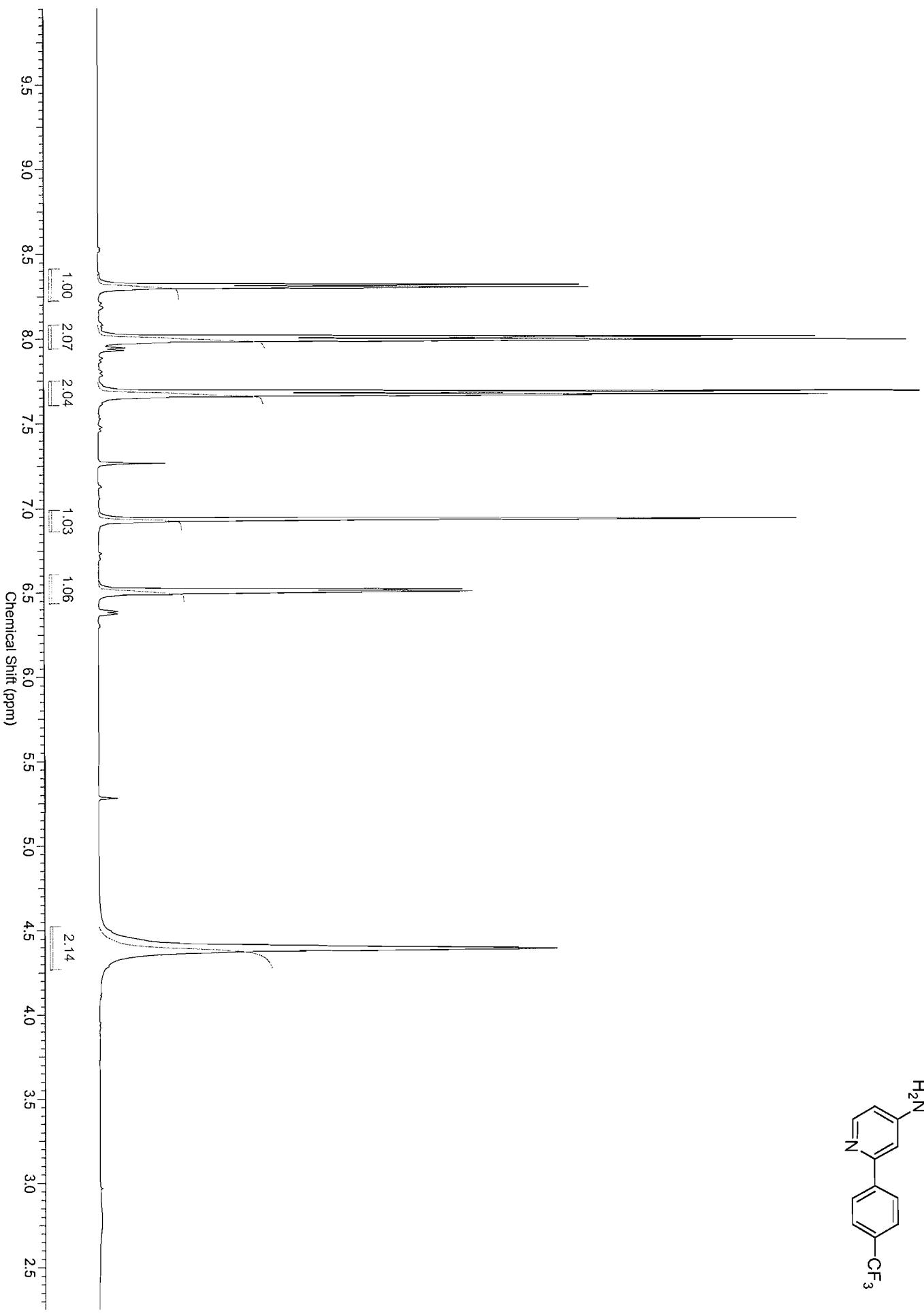
Table 1, entry 6, ^1H NMR (CDCl_3).

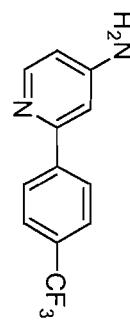
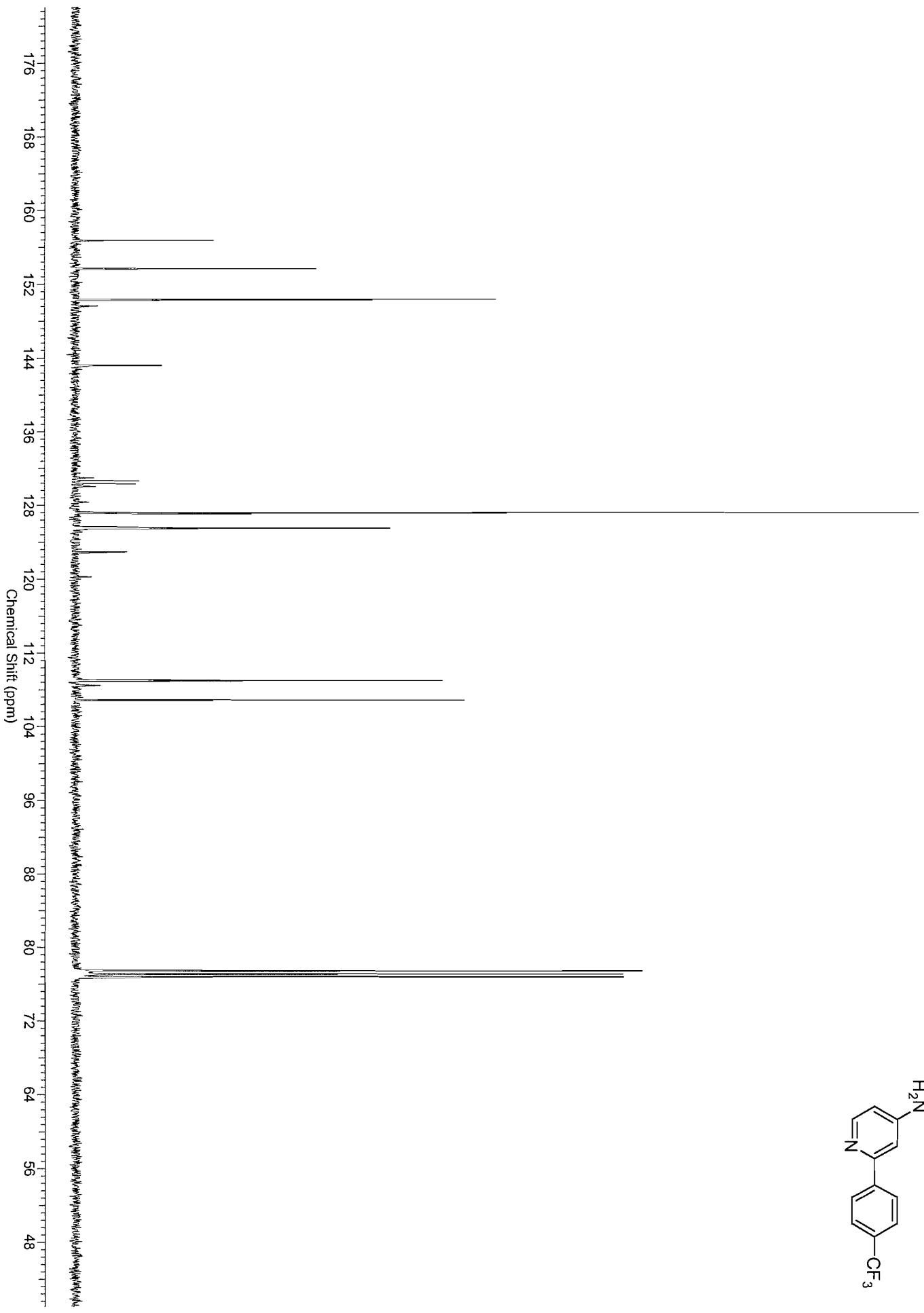
Table 1, entry 6, ^{13}C NMR (CDCl_3).

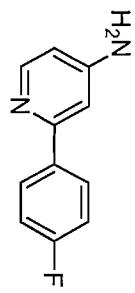
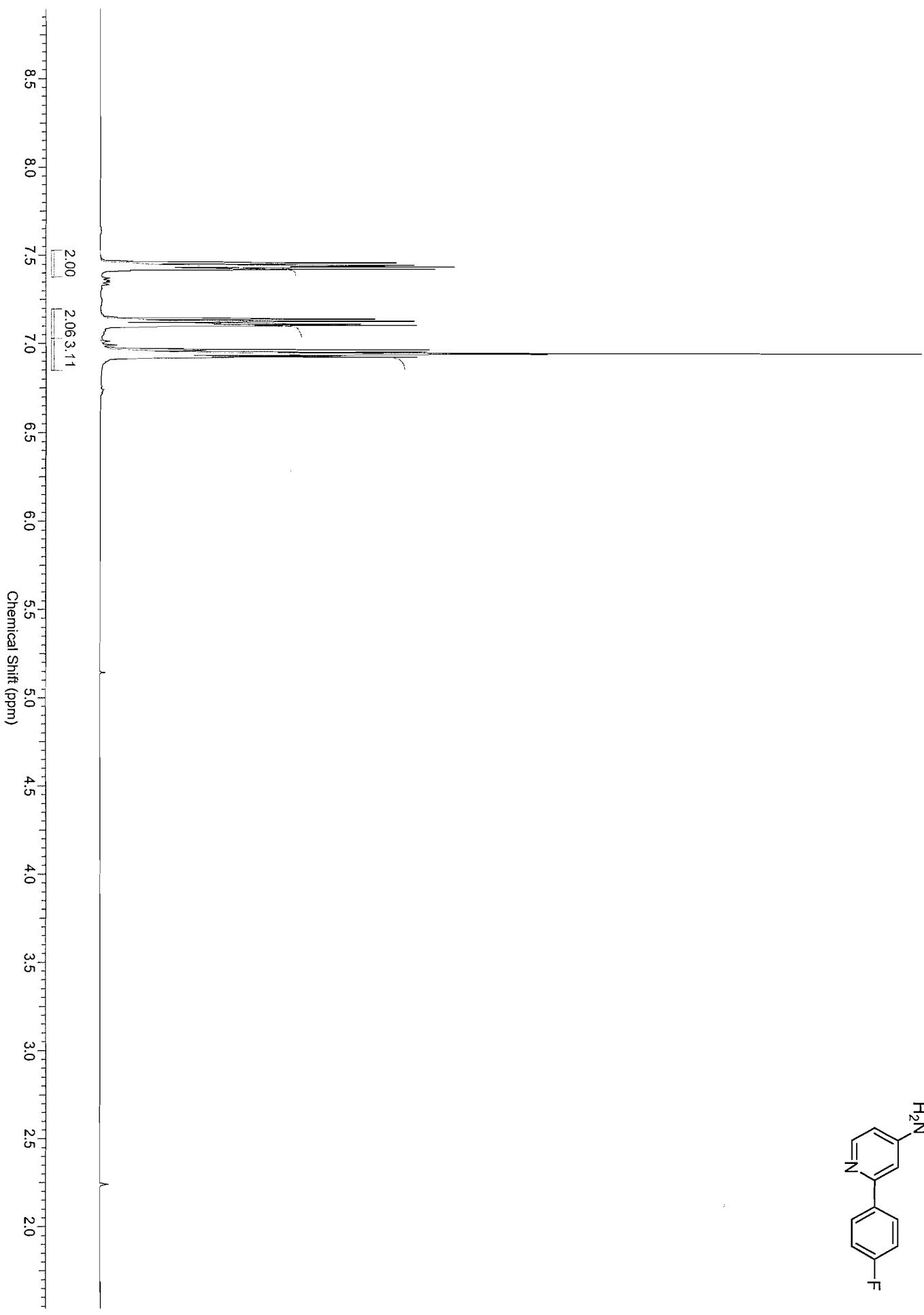
Table 1, entry 5, ^1H NMR (CDCl_3).

Table 1, entry 5, ^{13}C NMR (CDCl_3).

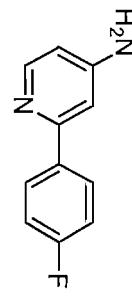
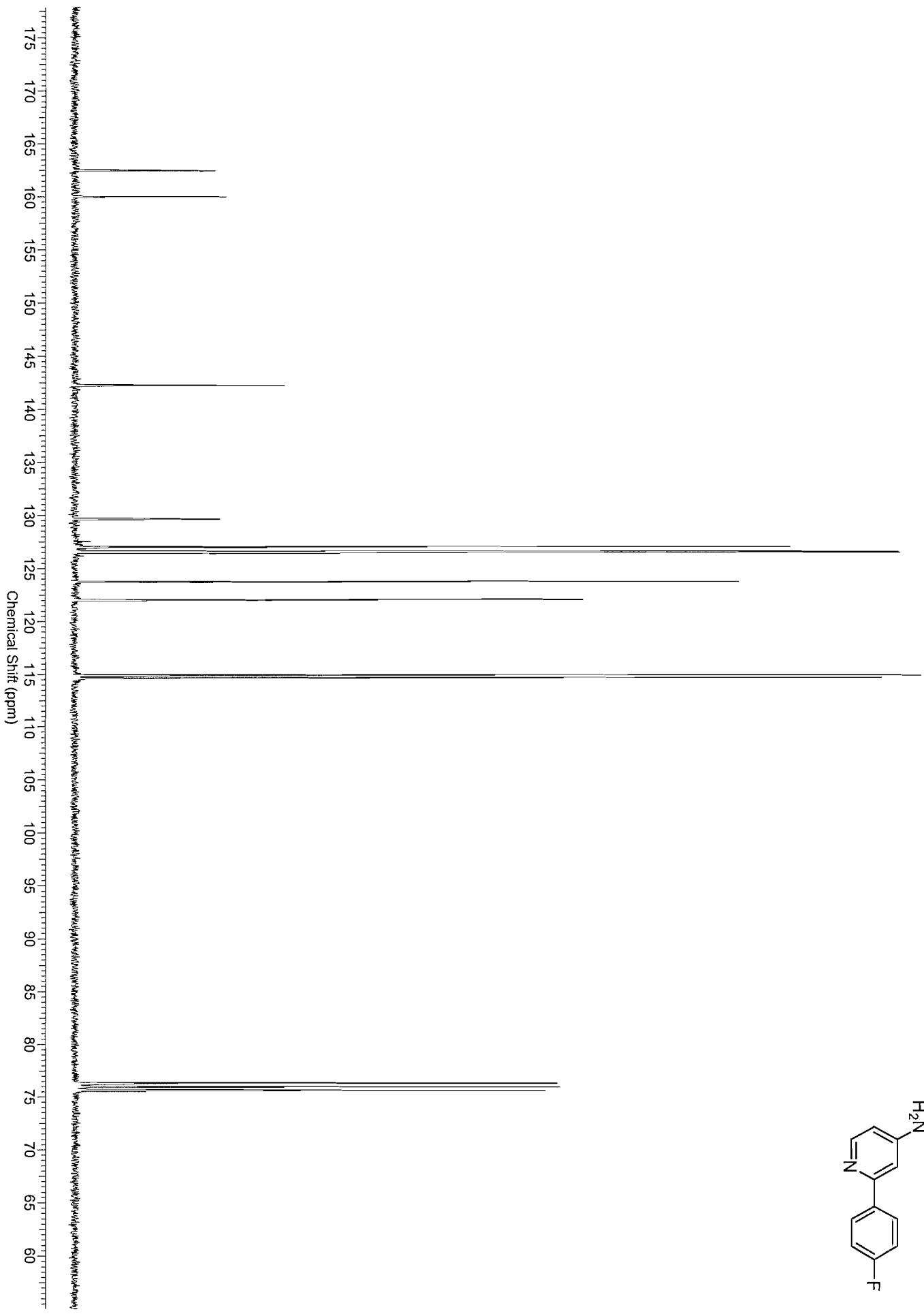


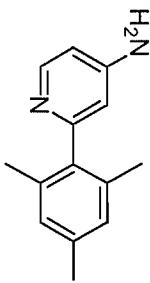
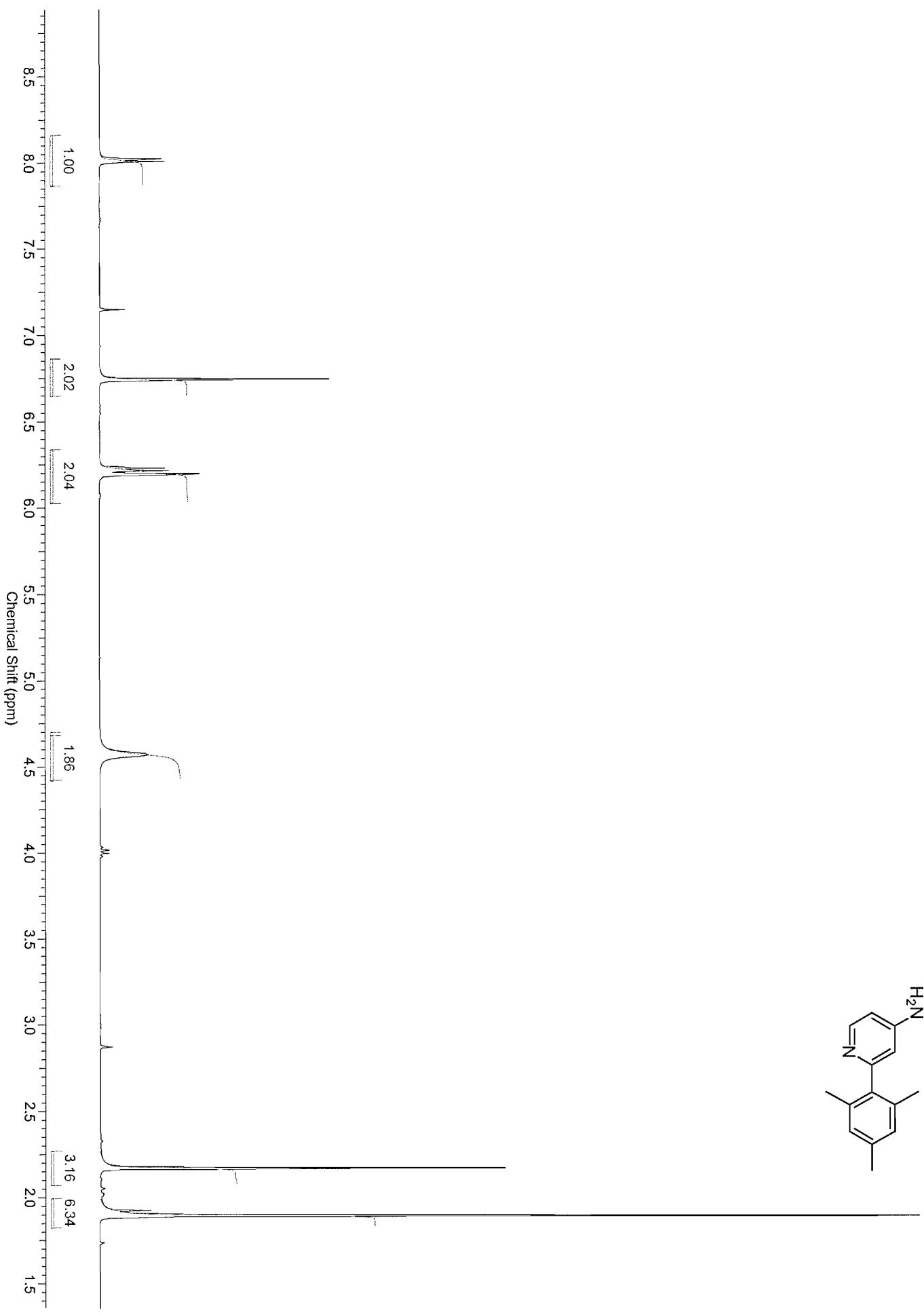
Table 1, entry 7, ^1H NMR (CDCl_3).

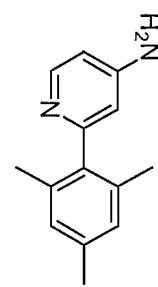
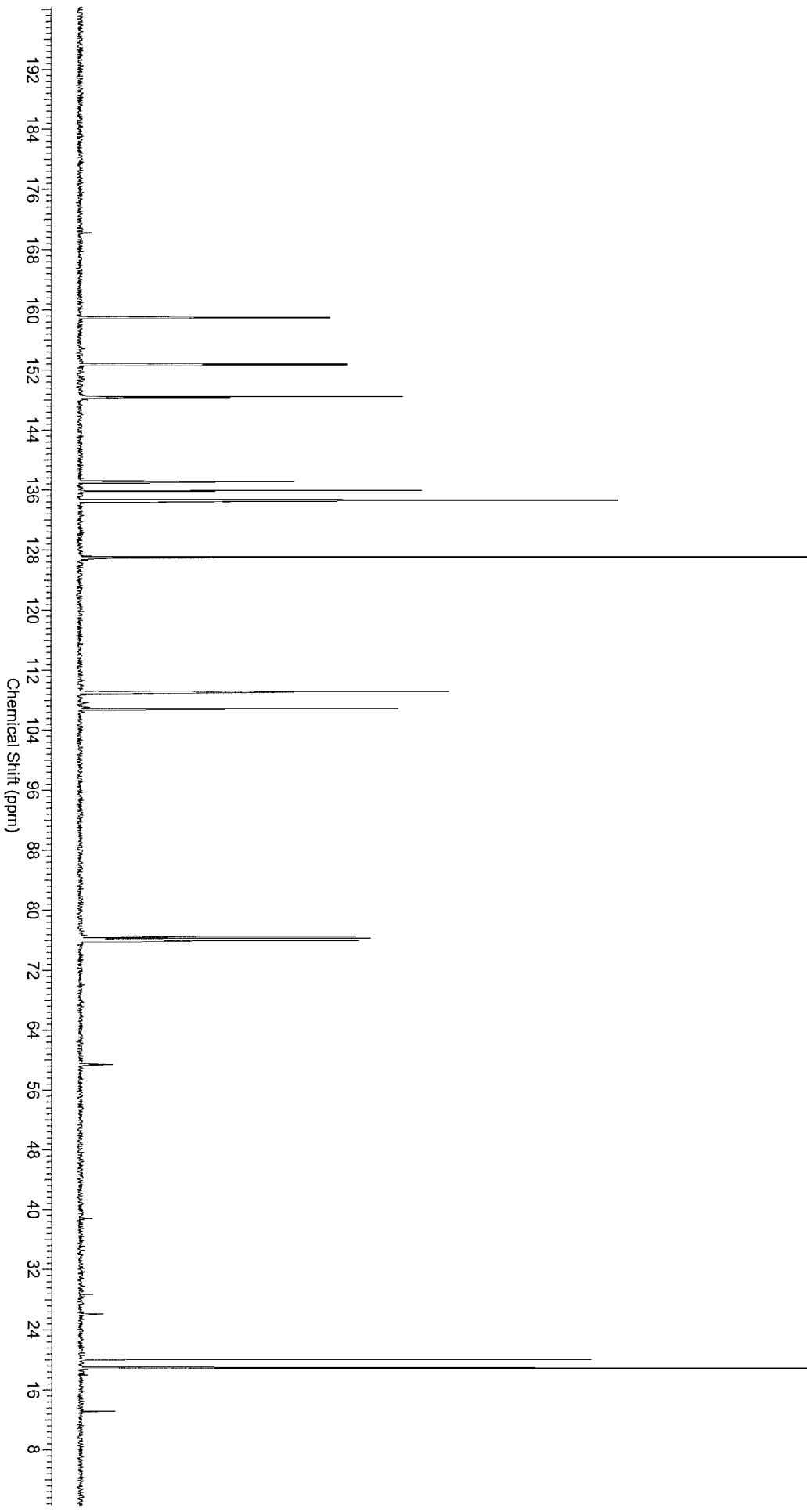
Table 1, entry 7, ^{13}C NMR (CDCl_3).

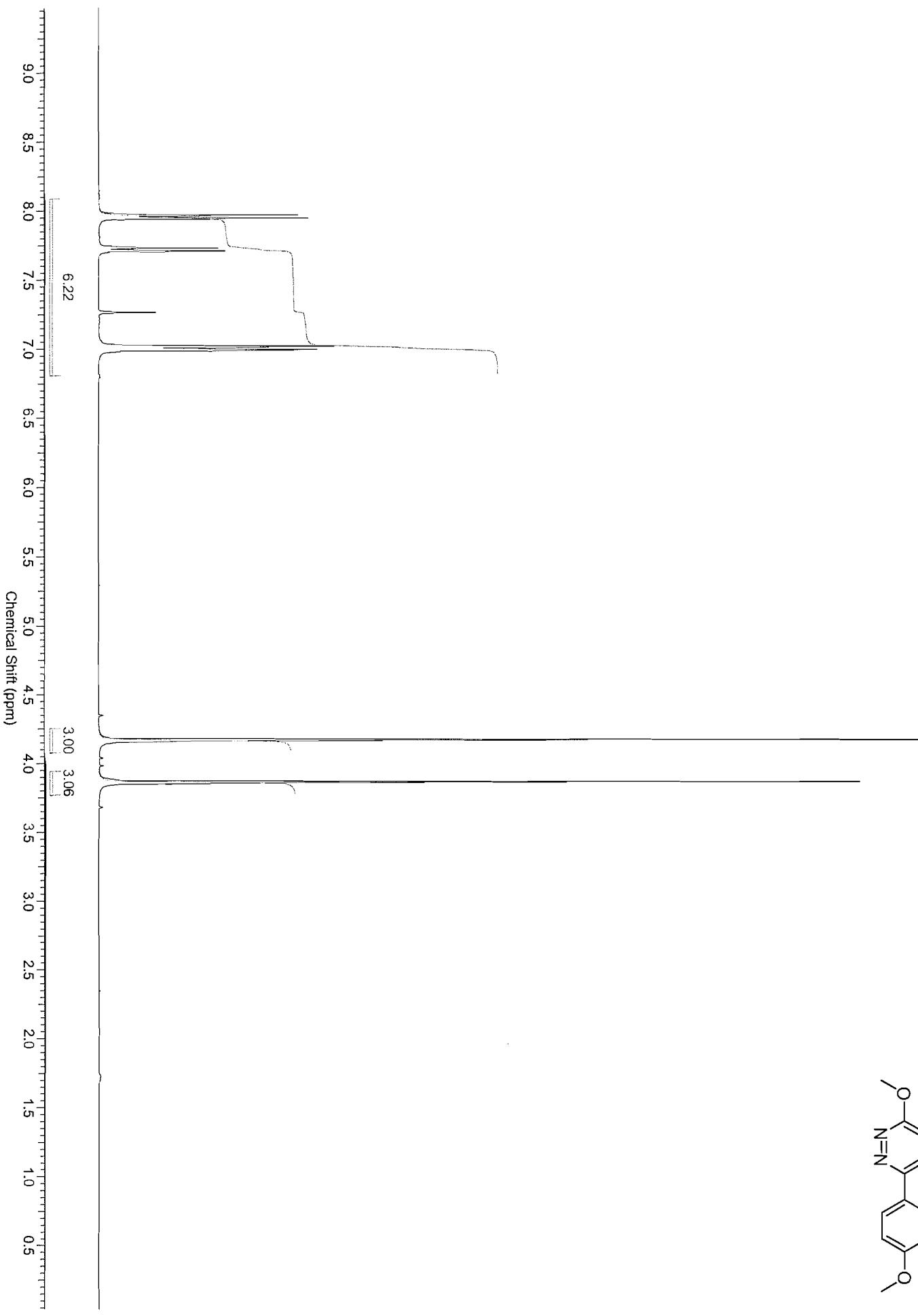
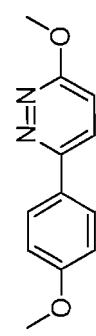
Table 1, entry 13, ^1H NMR (CDCl_3).

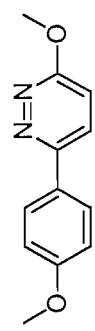
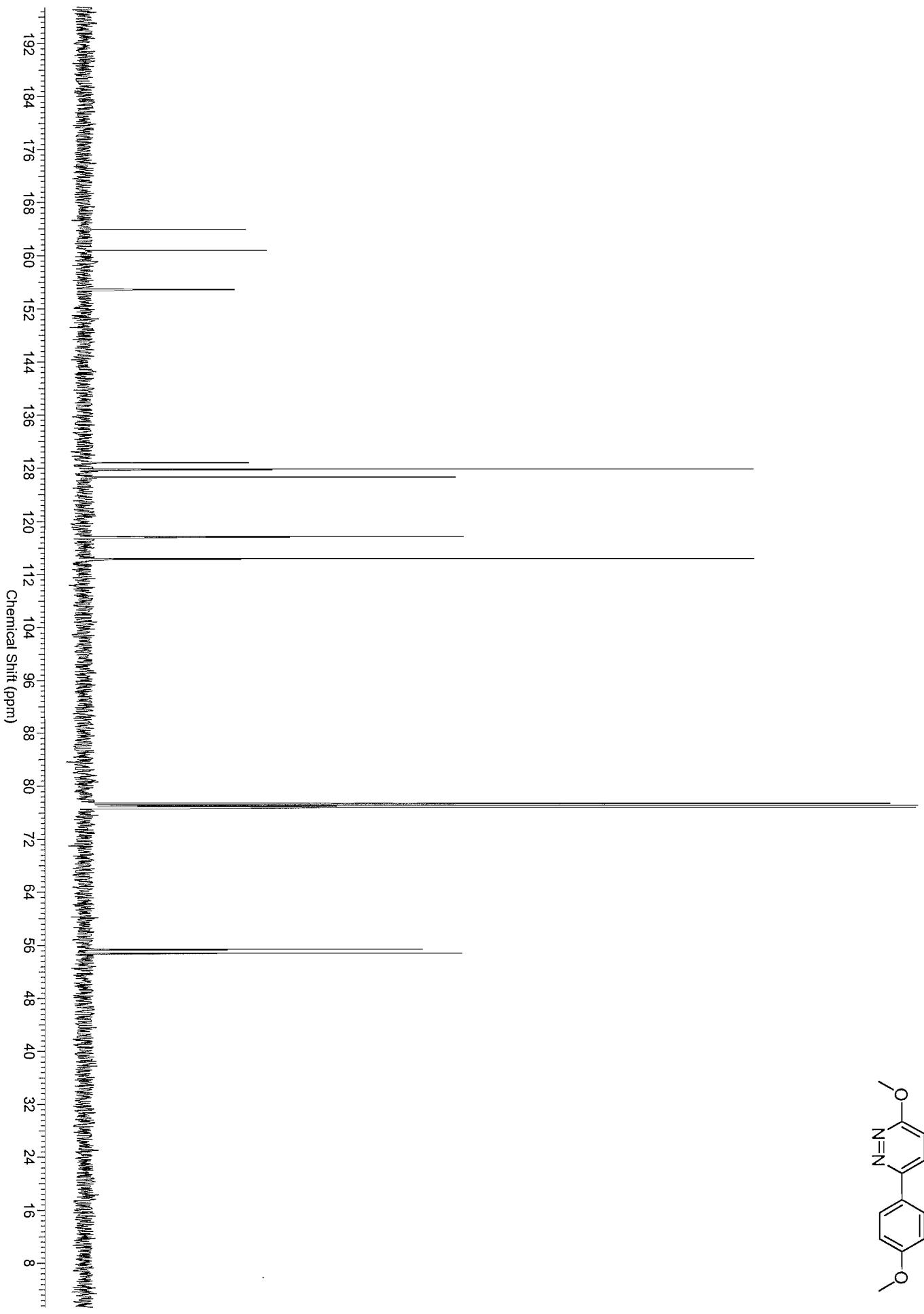
Table 1, entry 13, ^{13}C NMR (CDCl_3).

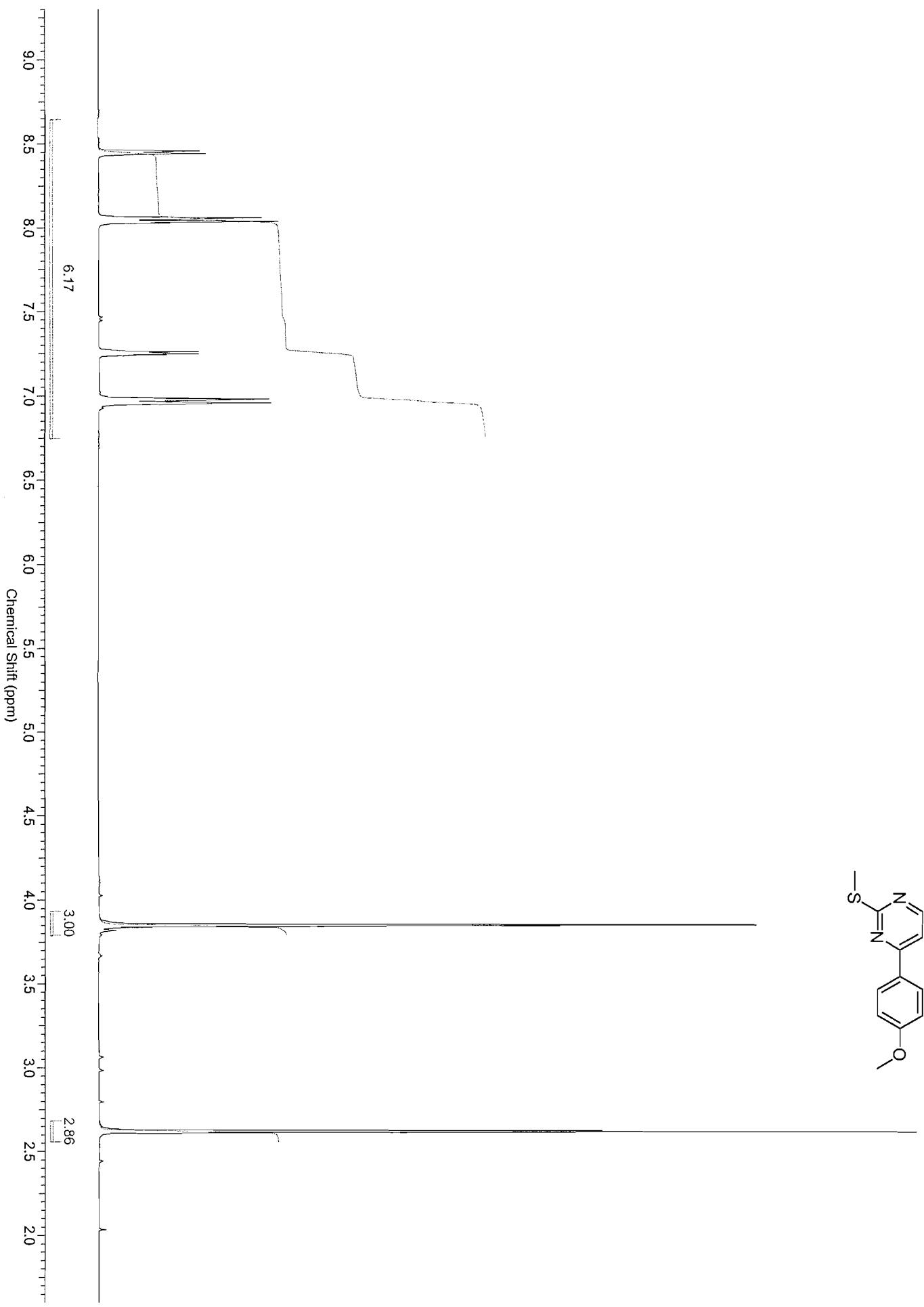
Table 1, entry 8, ^1H NMR (CDCl_3).

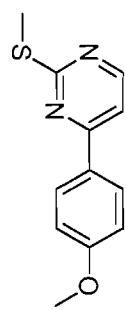
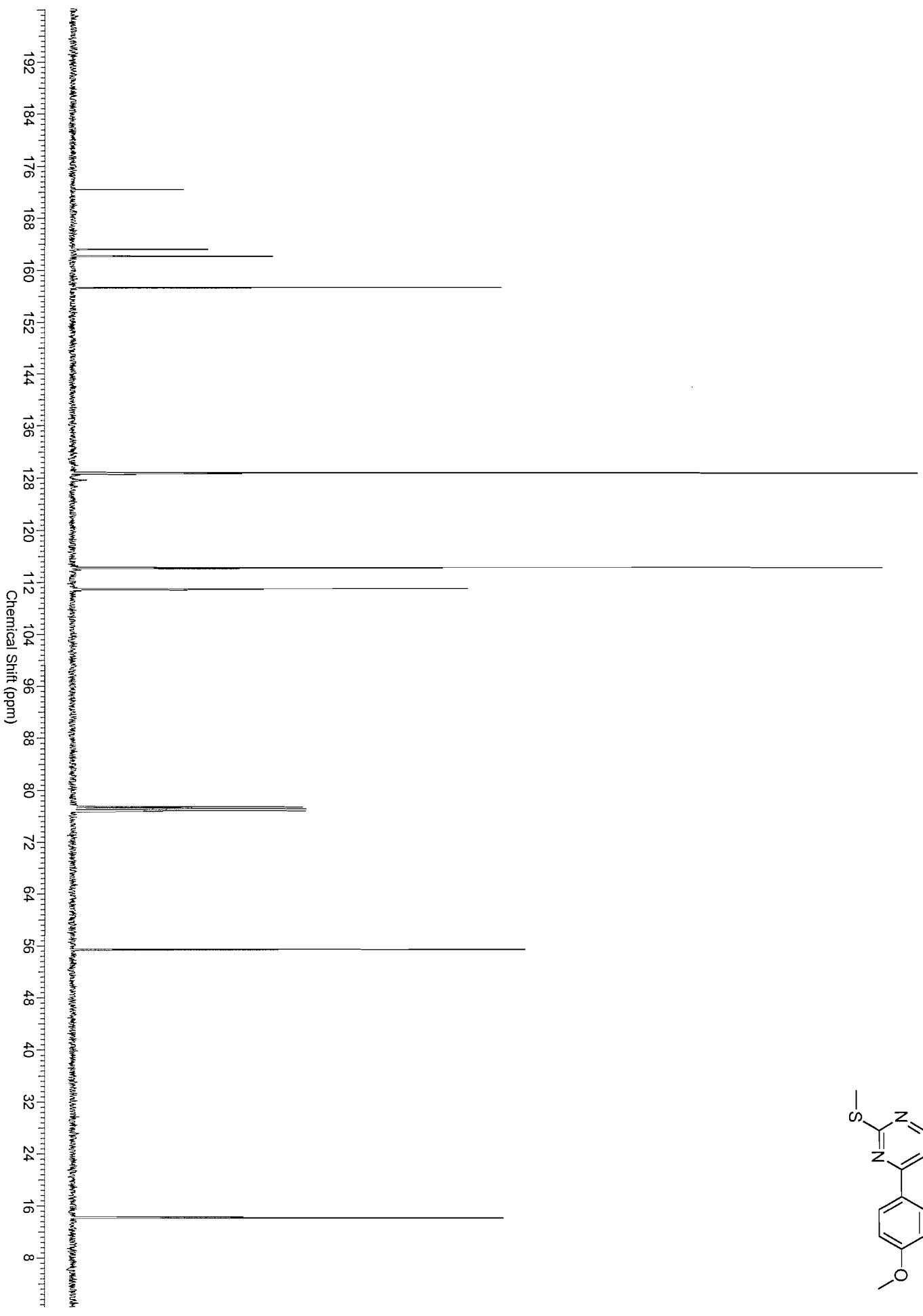
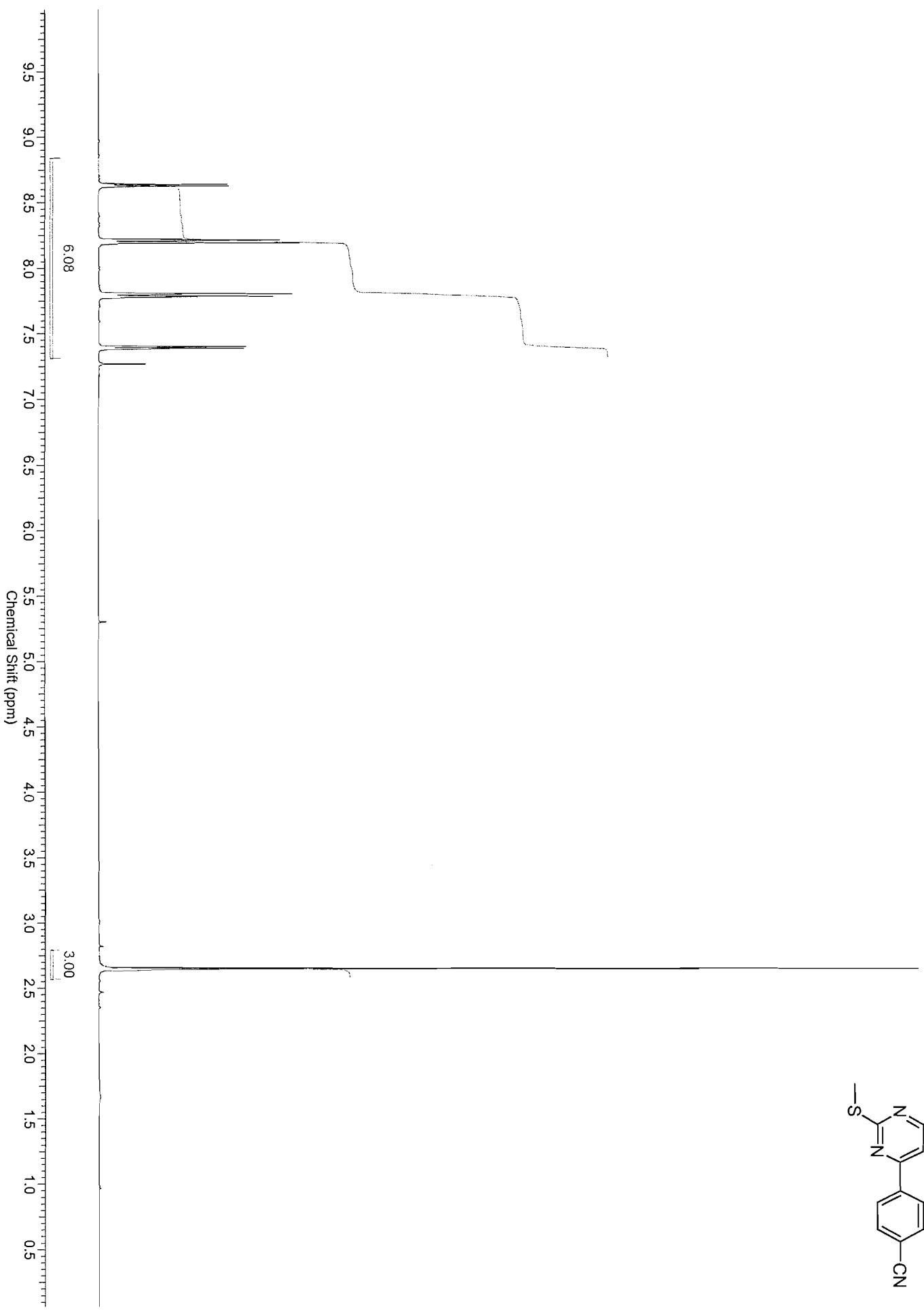
Table 1, entry 8, ^{13}C NMR (CDCl_3).

Table 1, entry 9, ^1H NMR (CDCl_3).

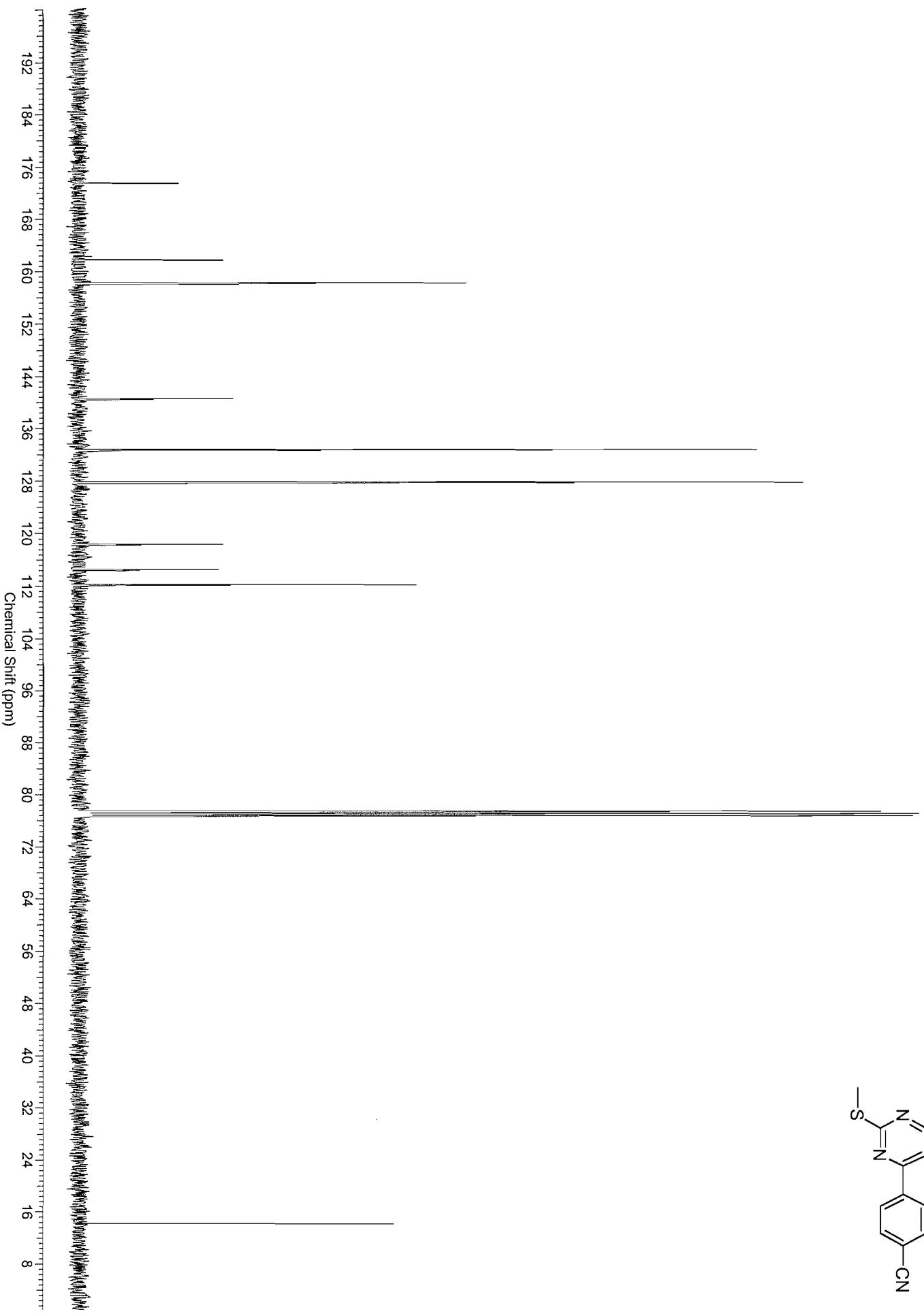


Table 1, entry 9, ^{13}C NMR (CDCl_3).

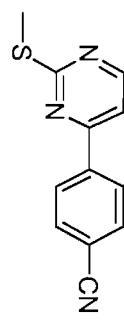


Table 1, entry 12, ^1H NMR (CDCl_3).

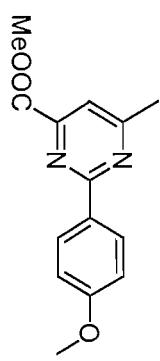
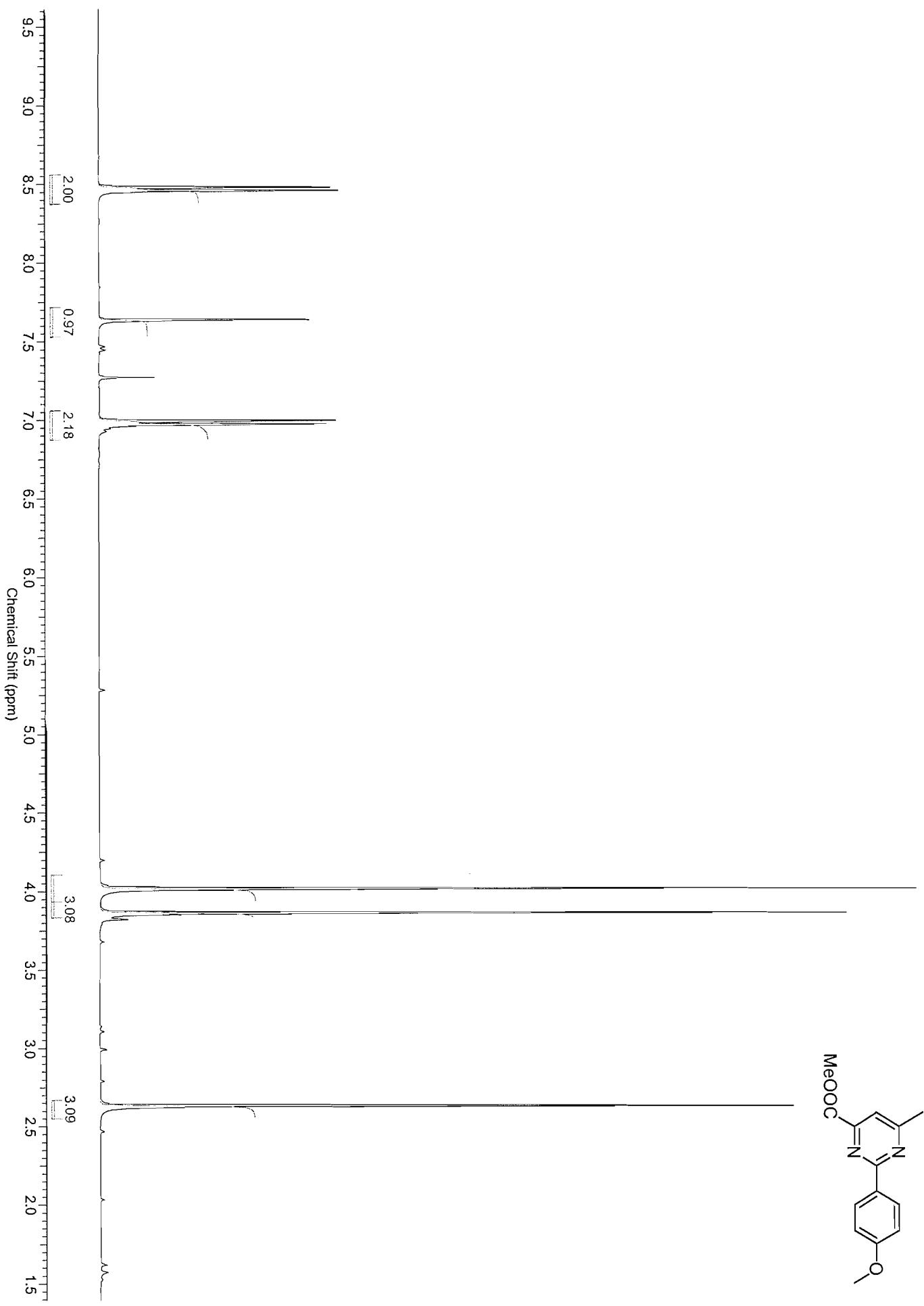


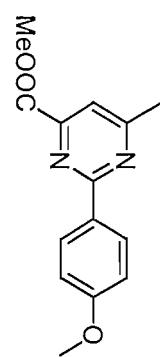
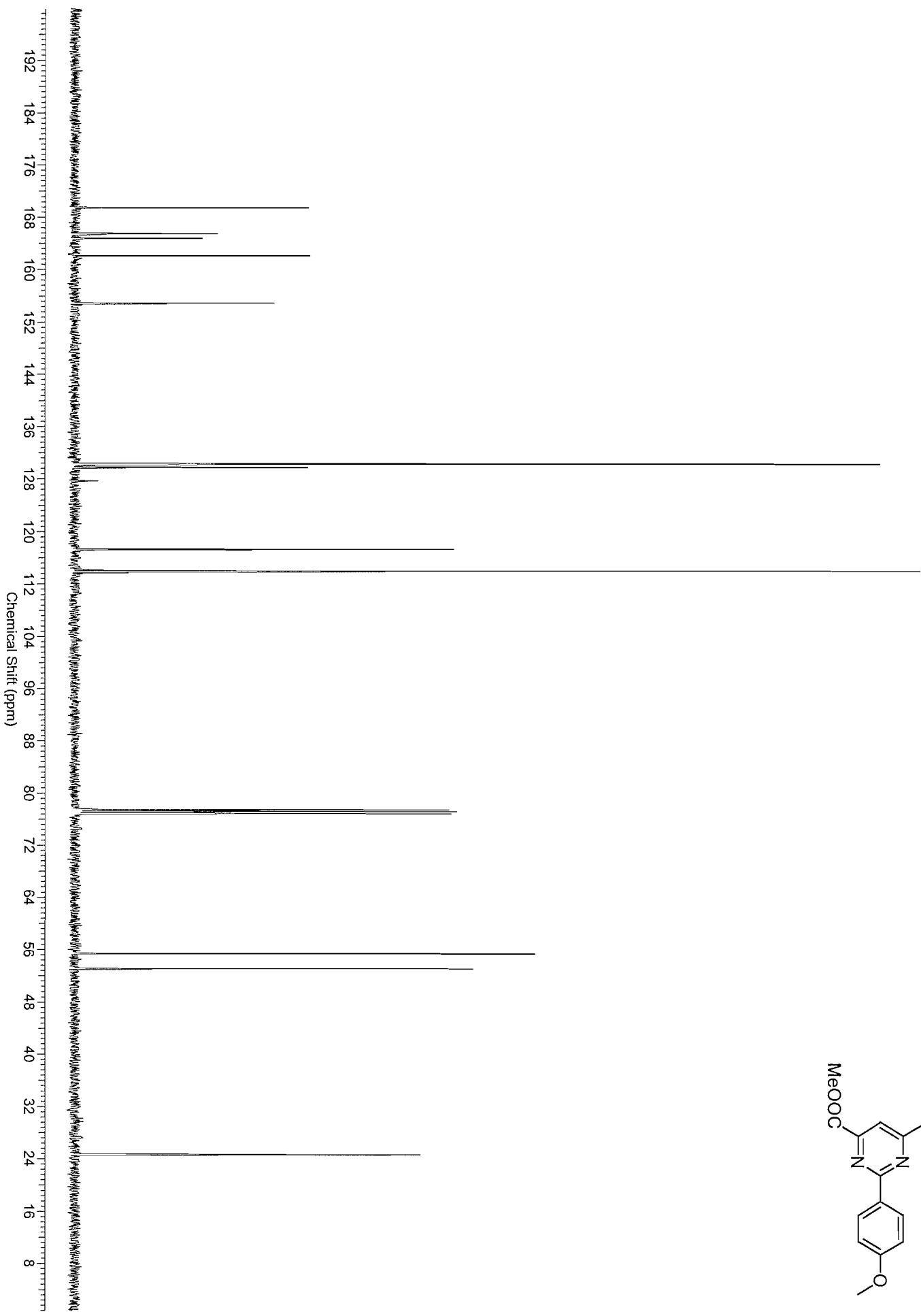
Table 1, entry 12, ^{13}C NMR (CDCl_3).

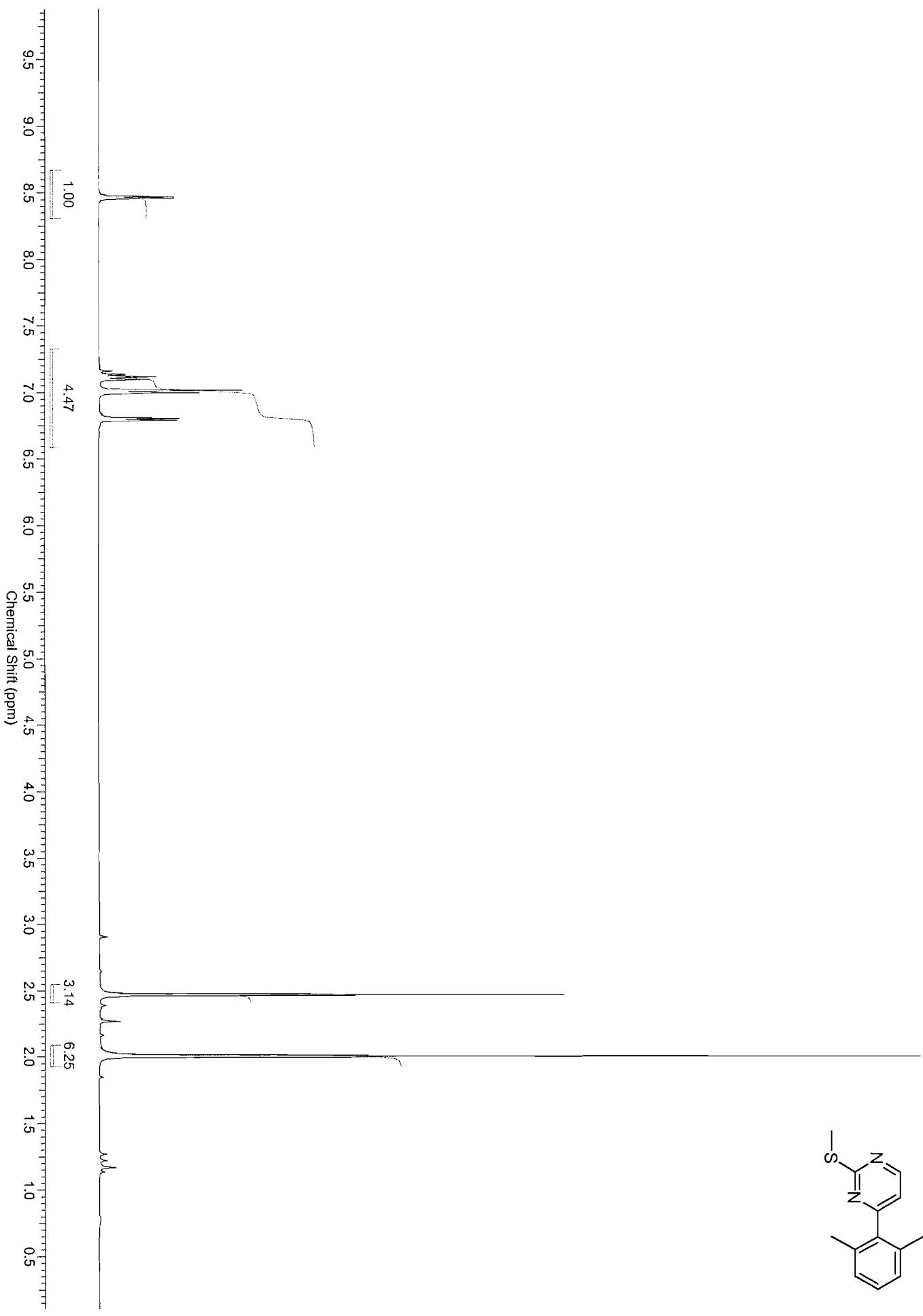
Table 1, entry 10, ^1H NMR (CDCl_3).

Table 1, entry 10, ^{13}C NMR (CDCl_3).

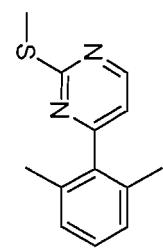
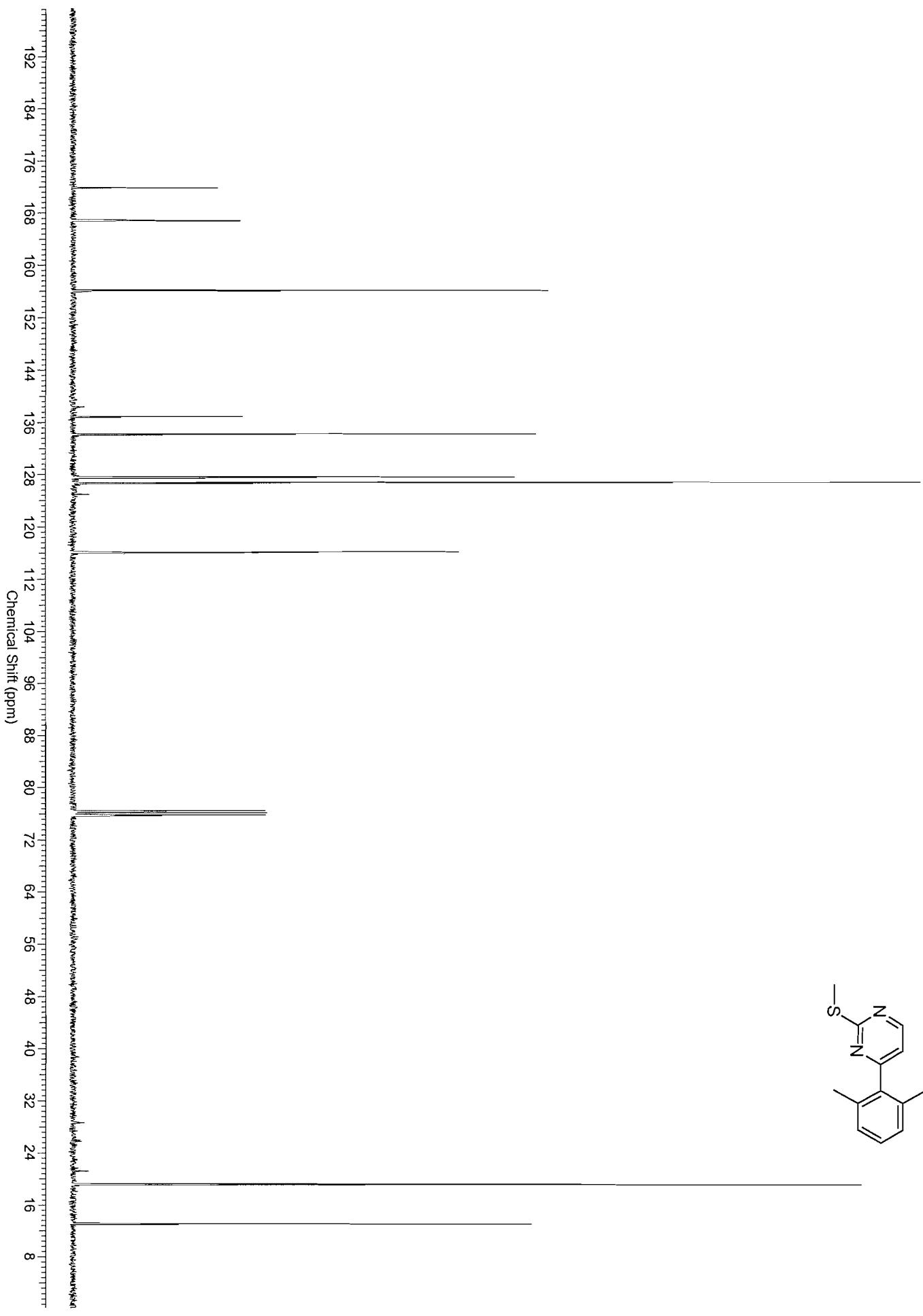


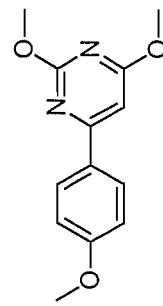
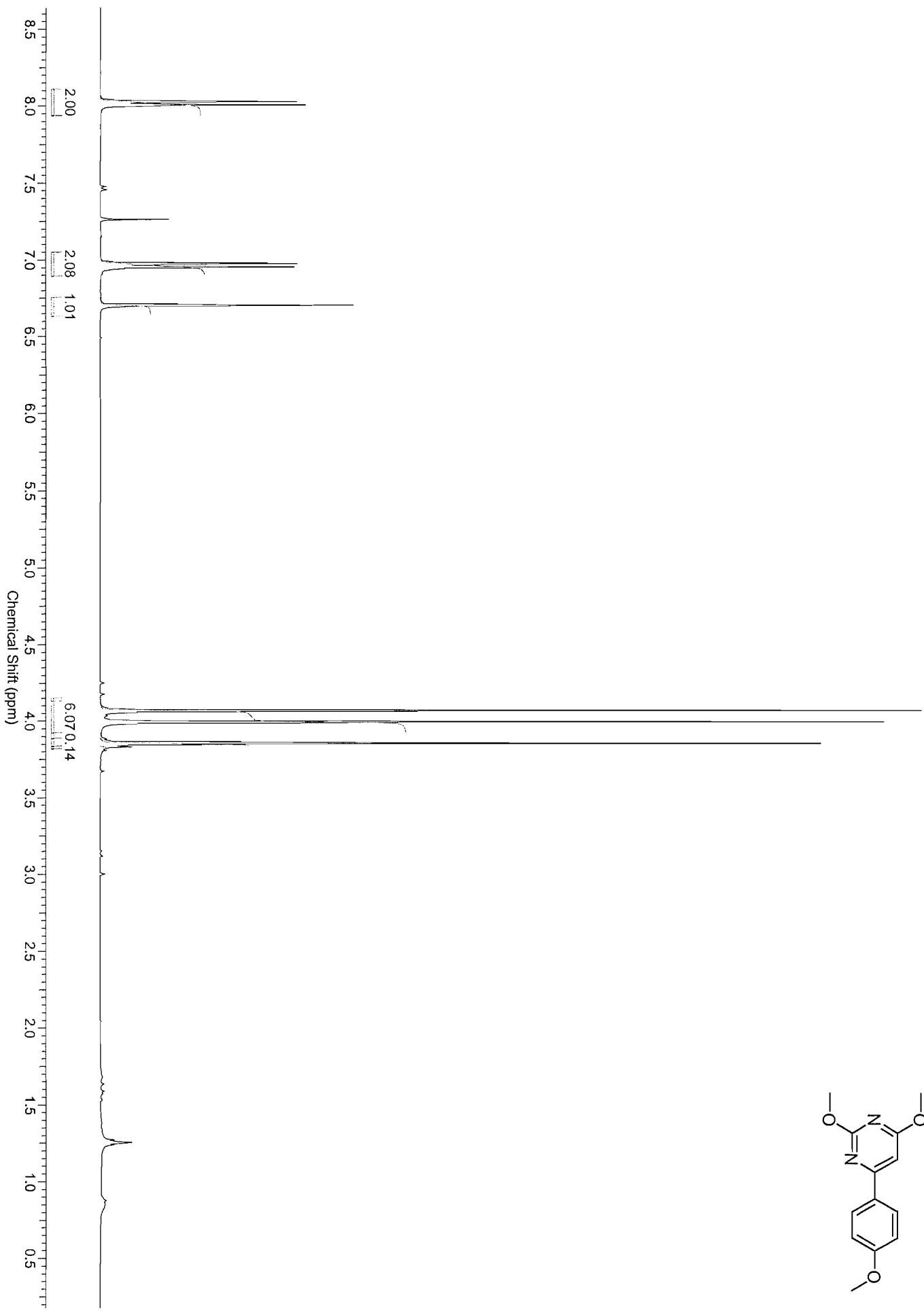
Table 1, entry 11, ^1H NMR (CDCl_3).

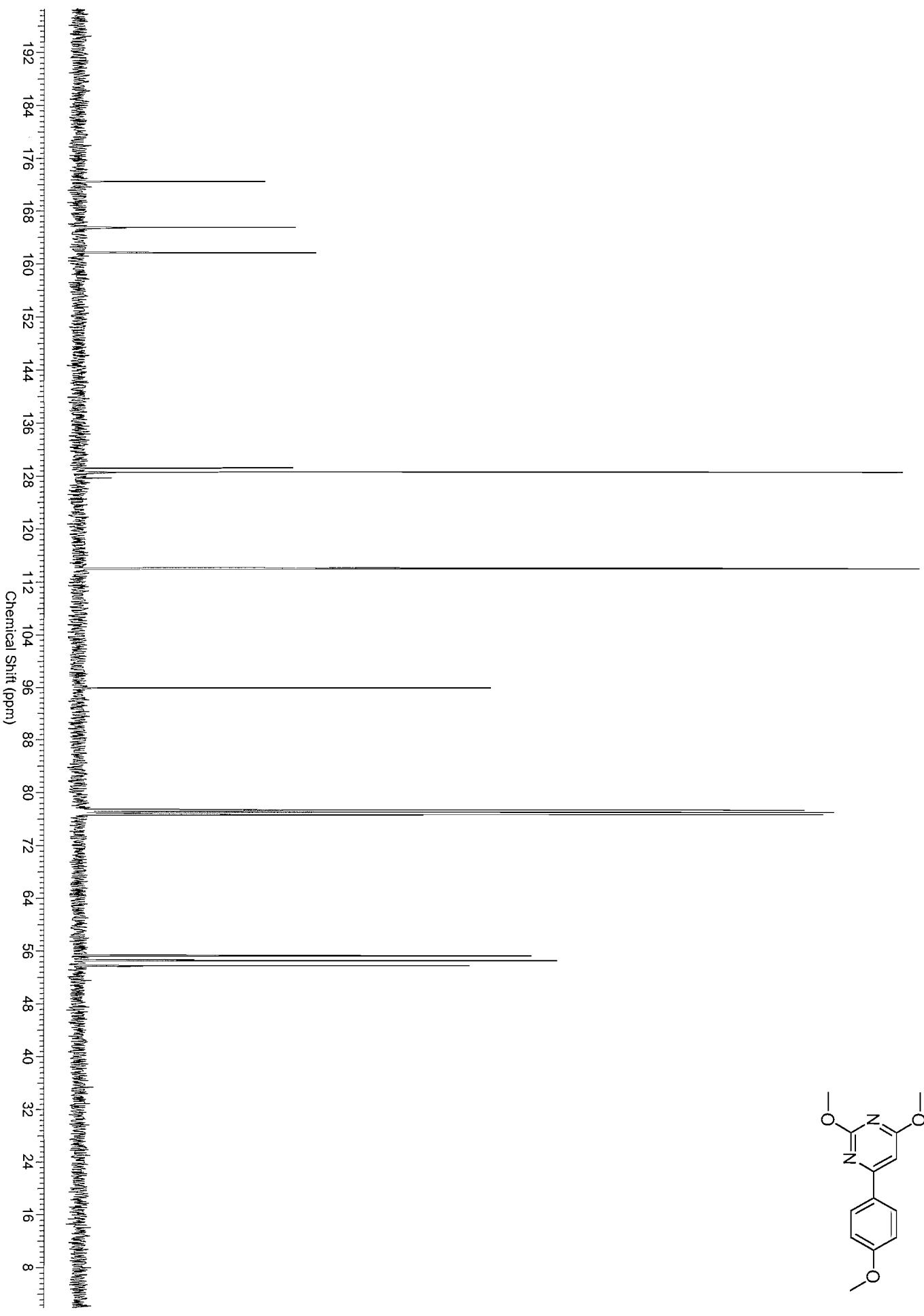
Table 1, entry 11, ^{13}C NMR (CDCl_3).

Table 7, entry 1, ^1H NMR (CDCl_3)

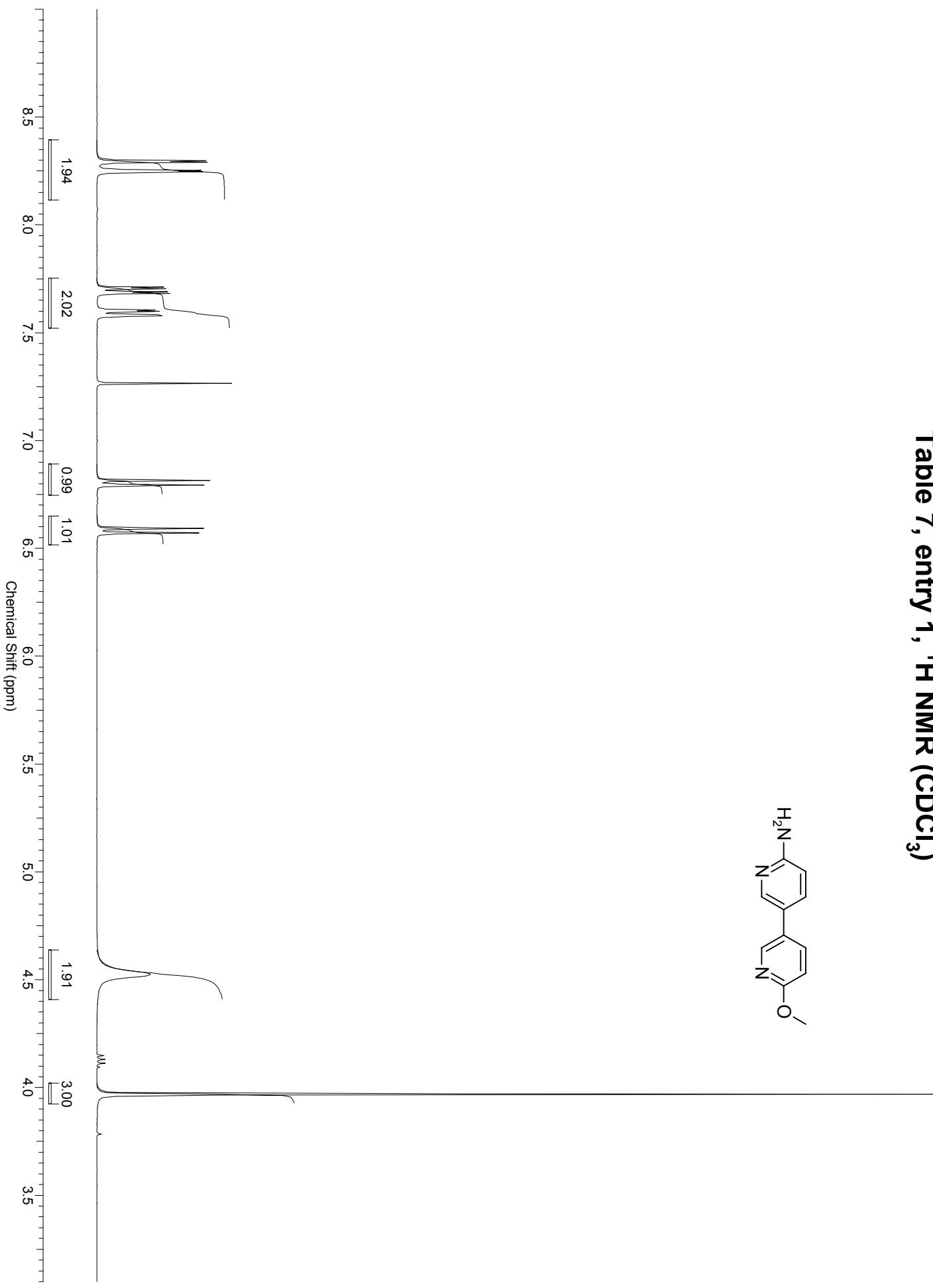


Table 7, entry 1, ^{13}C NMR (CDCl_3).

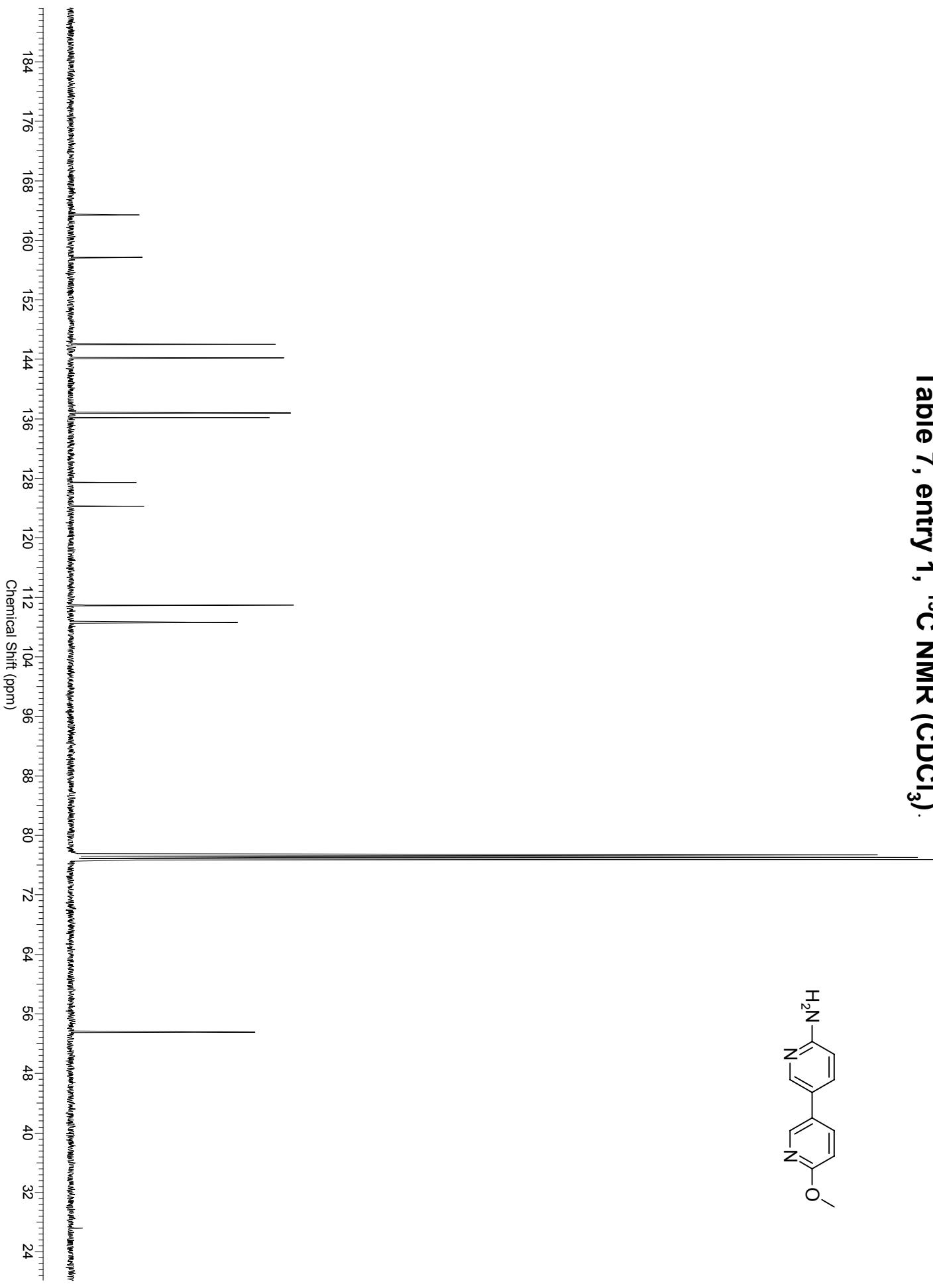


Table 7, entry 2, ^1H NMR (CDCl_3).

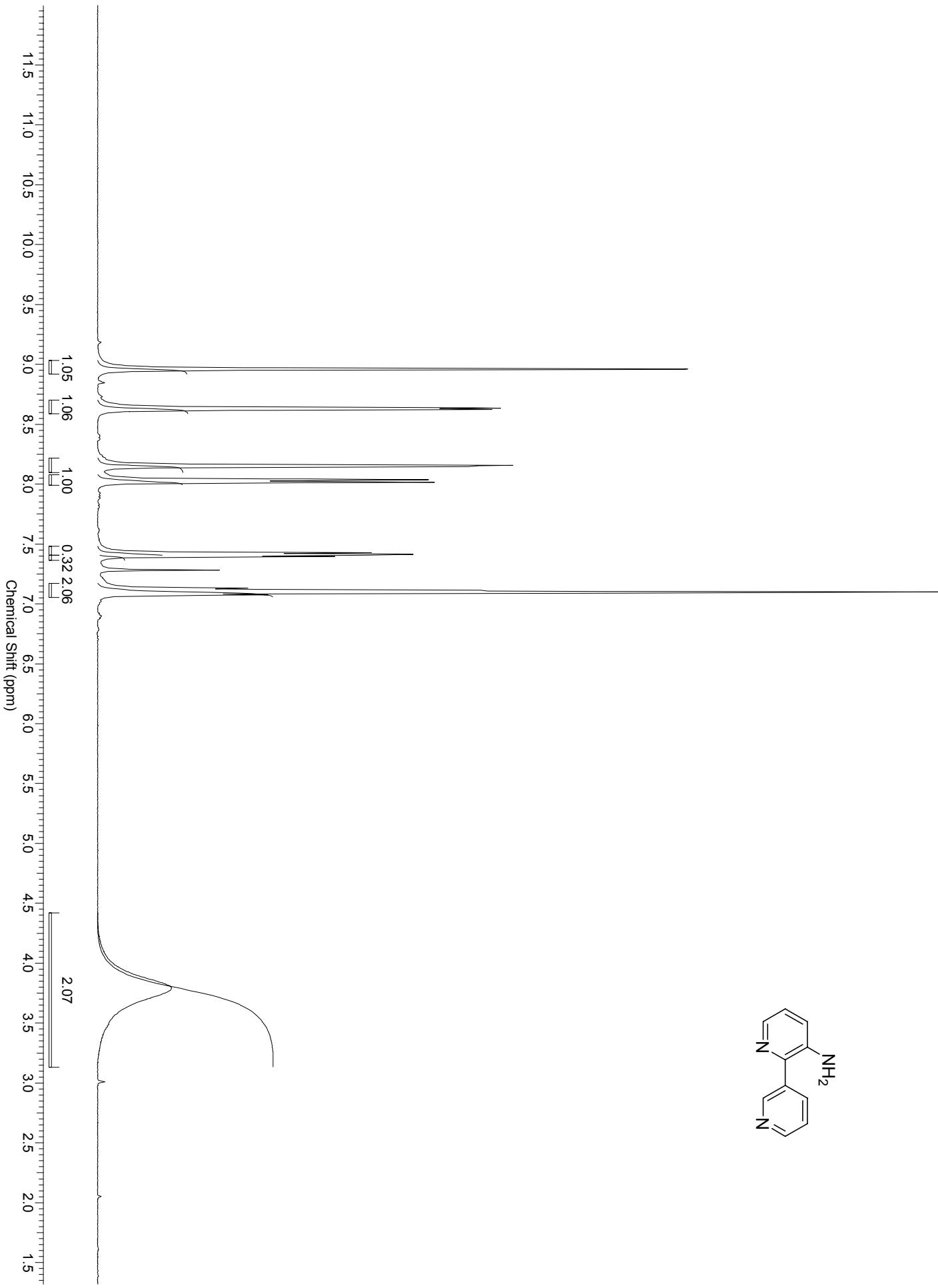


Table 7, entry 2, ^{13}C NMR (CDCl_3)

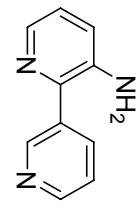
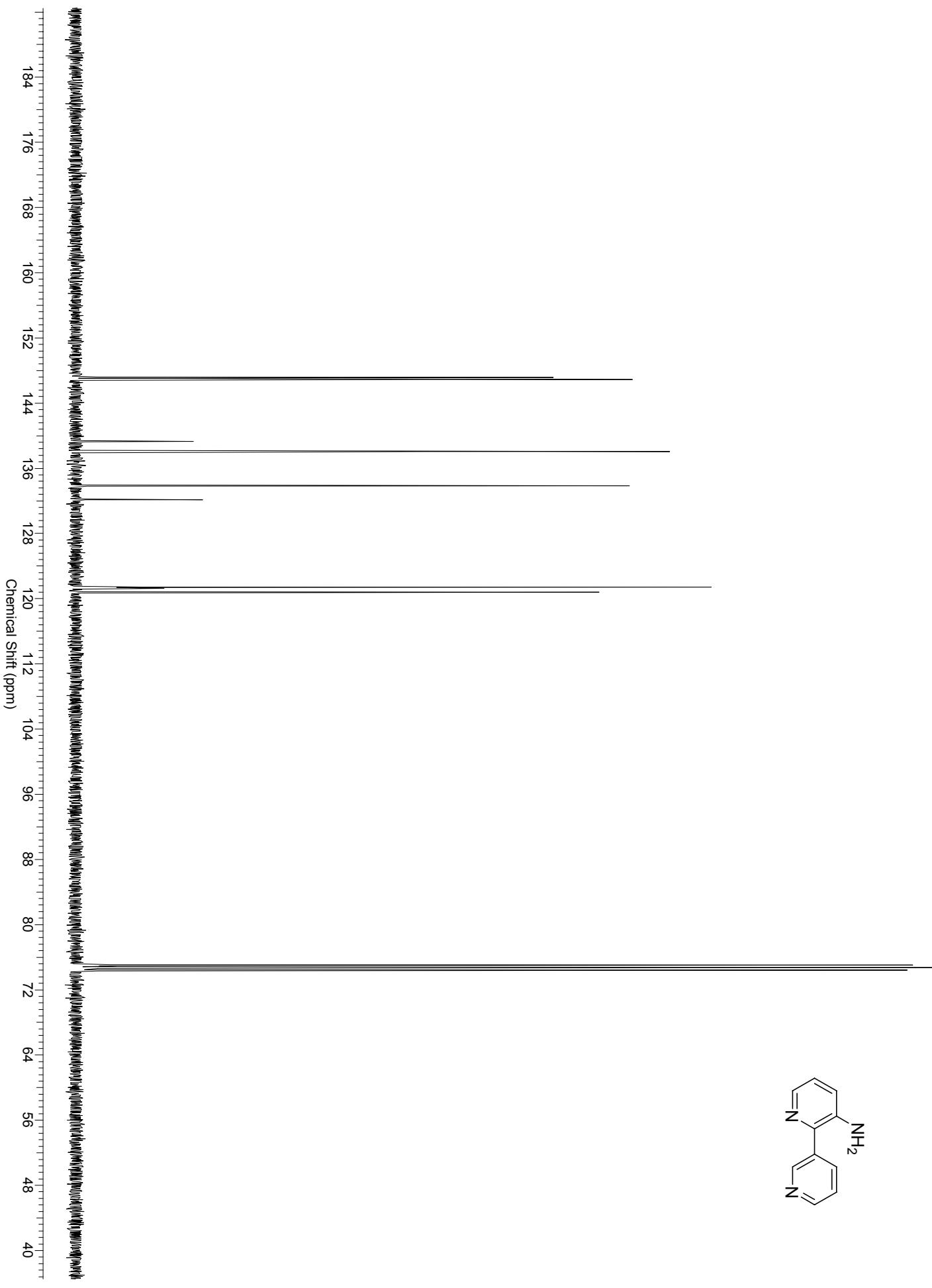


Table 7, entry 3, ^1H NMR (CDCl_3).

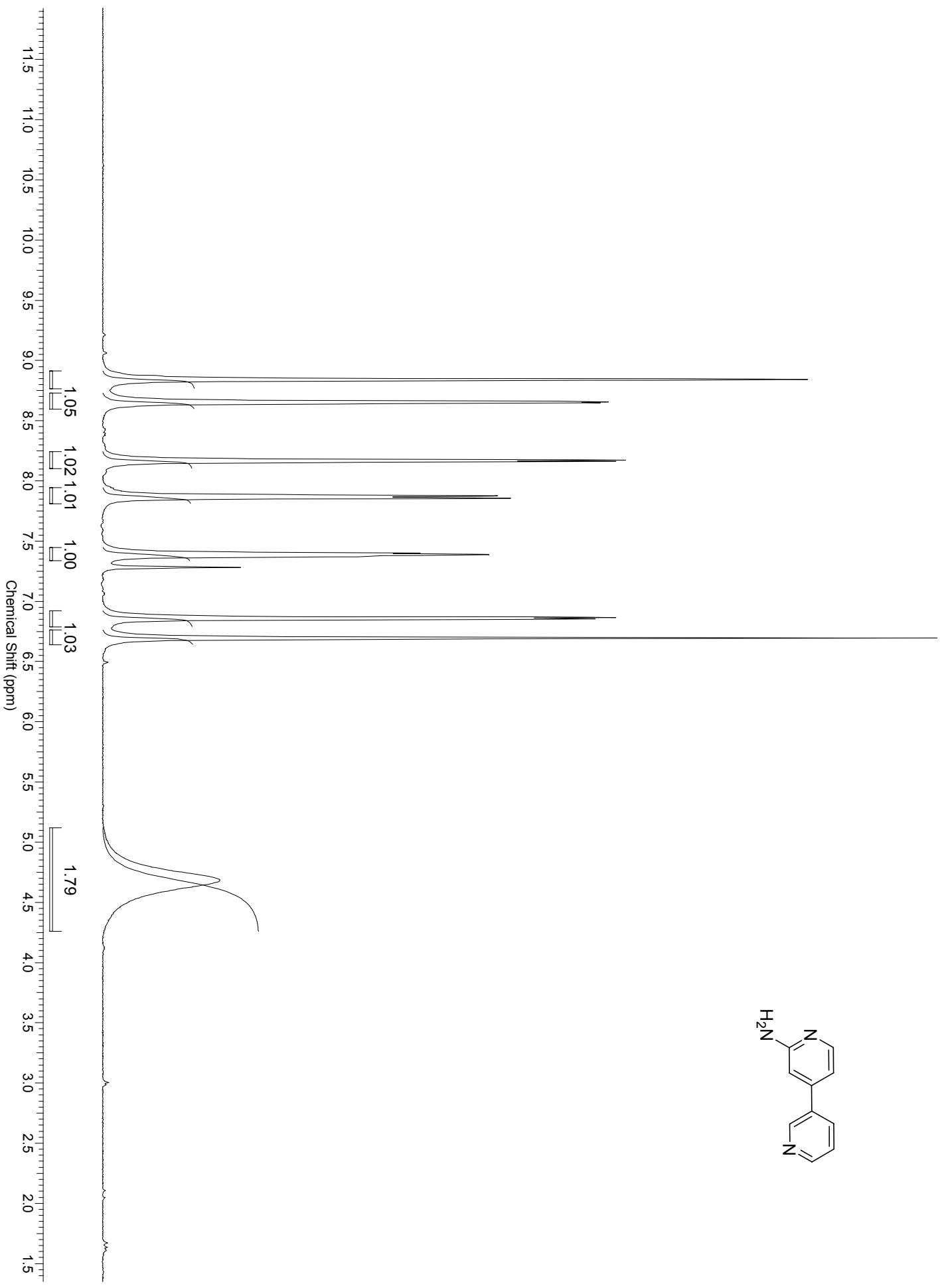


Table 7, entry 3, ^{13}C NMR (CDCl_3).

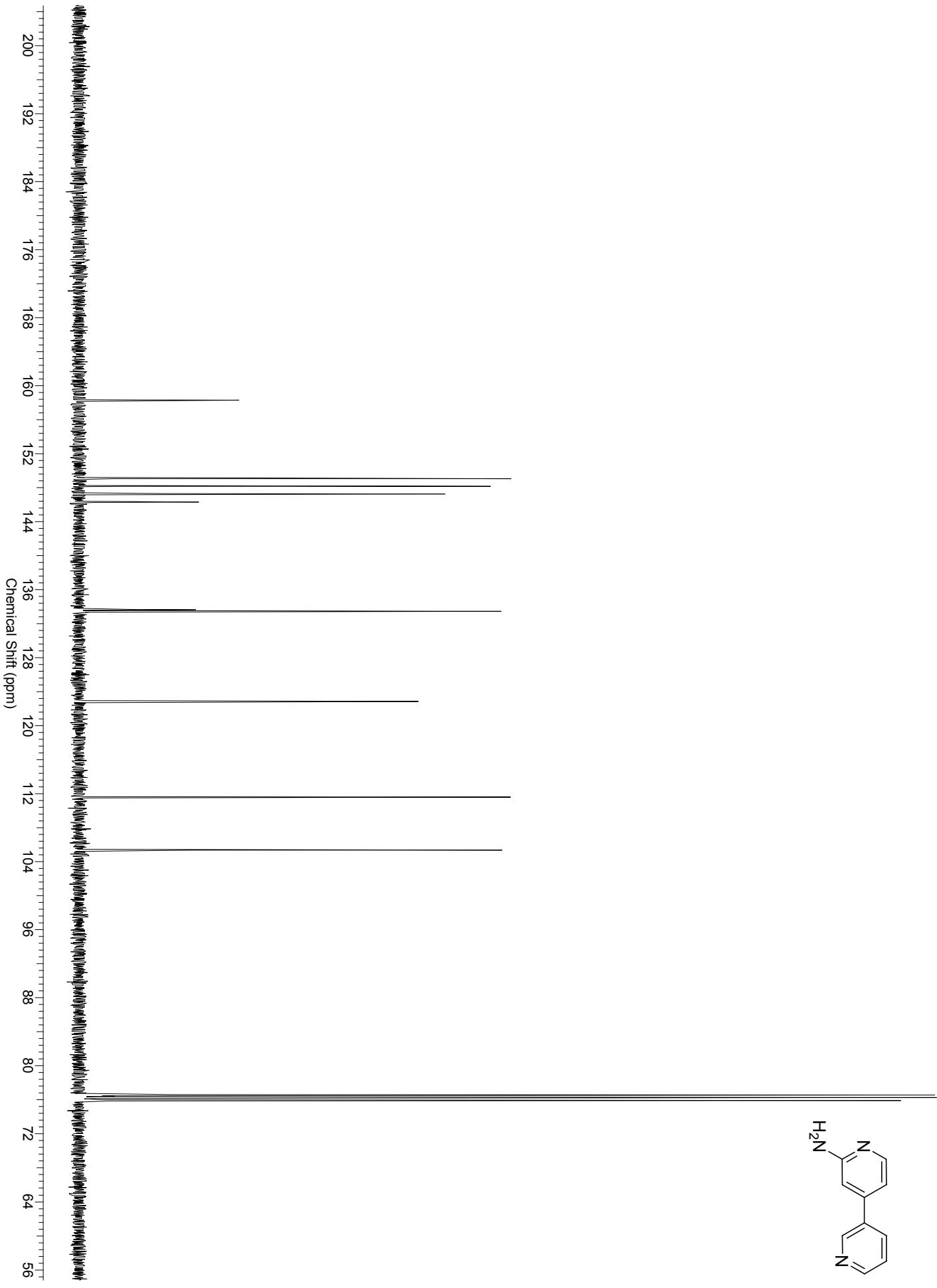


Table 7, entry 4, ^1H NMR (CDCl_3).

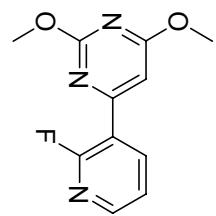
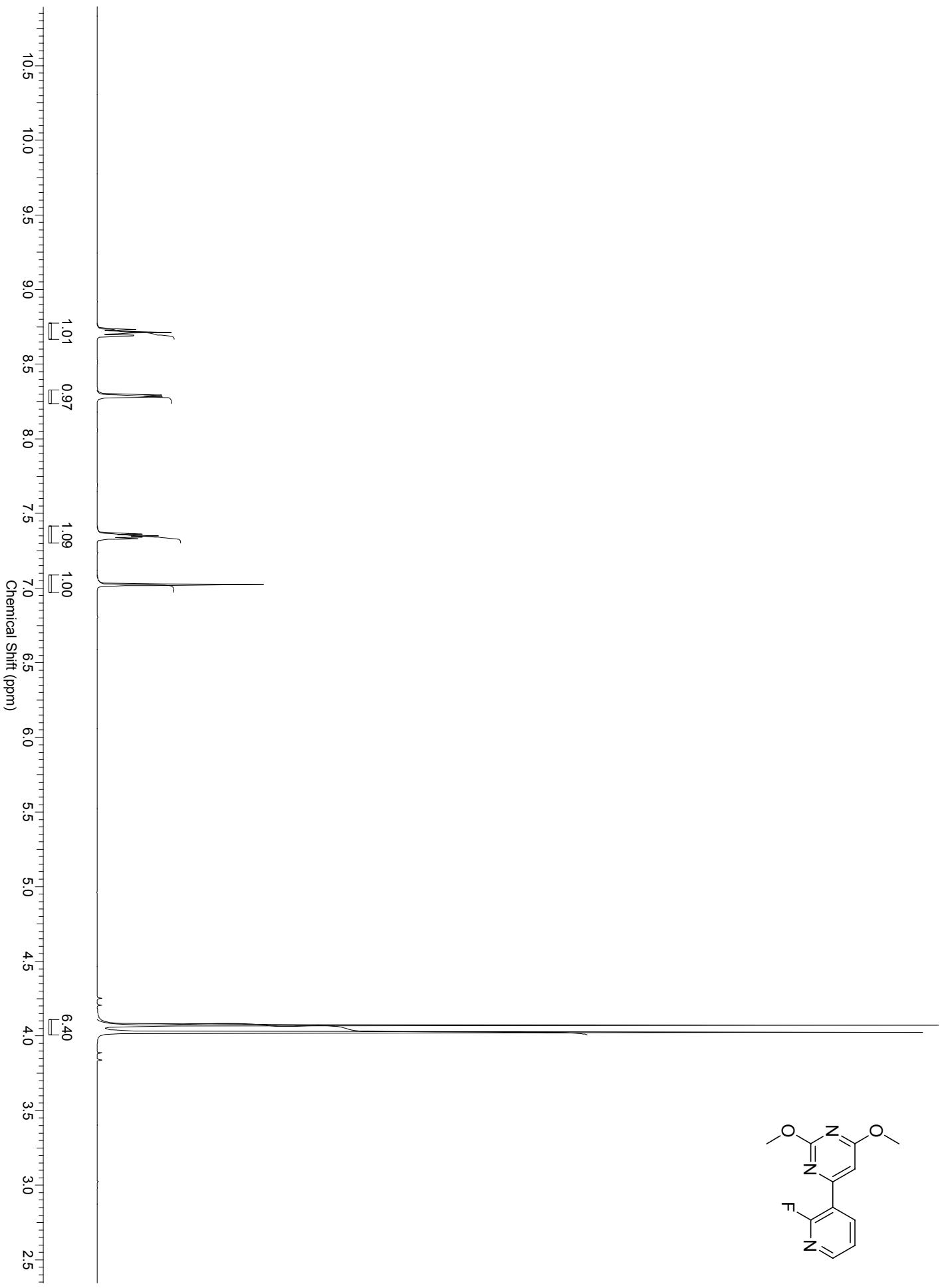


Table 7, entry 4, ^{13}C NMR (CDCl_3).

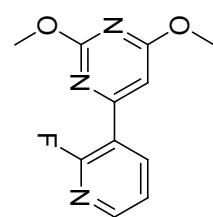
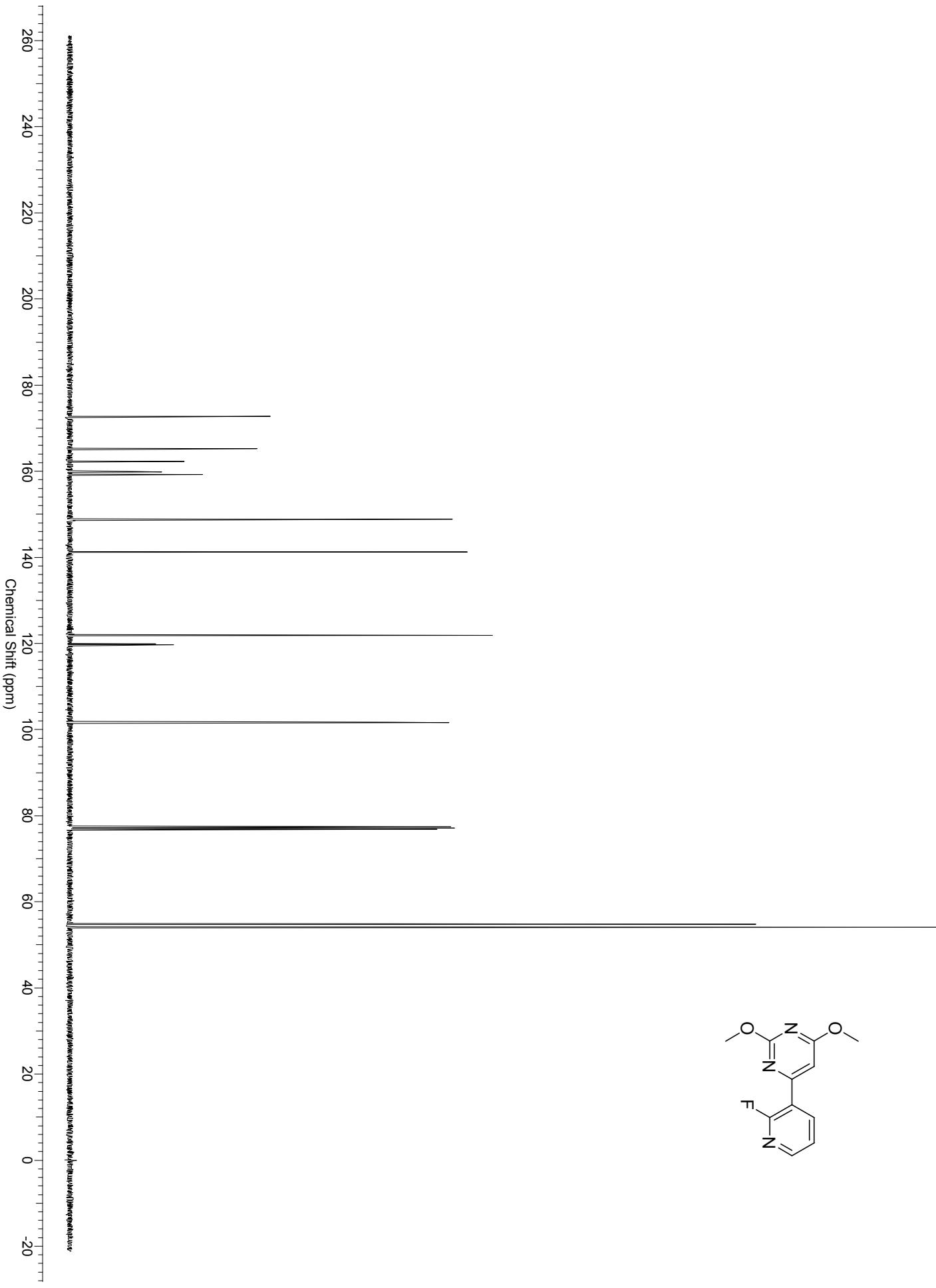


Table 7, entry 6, ^1H NMR (CDCl_3).

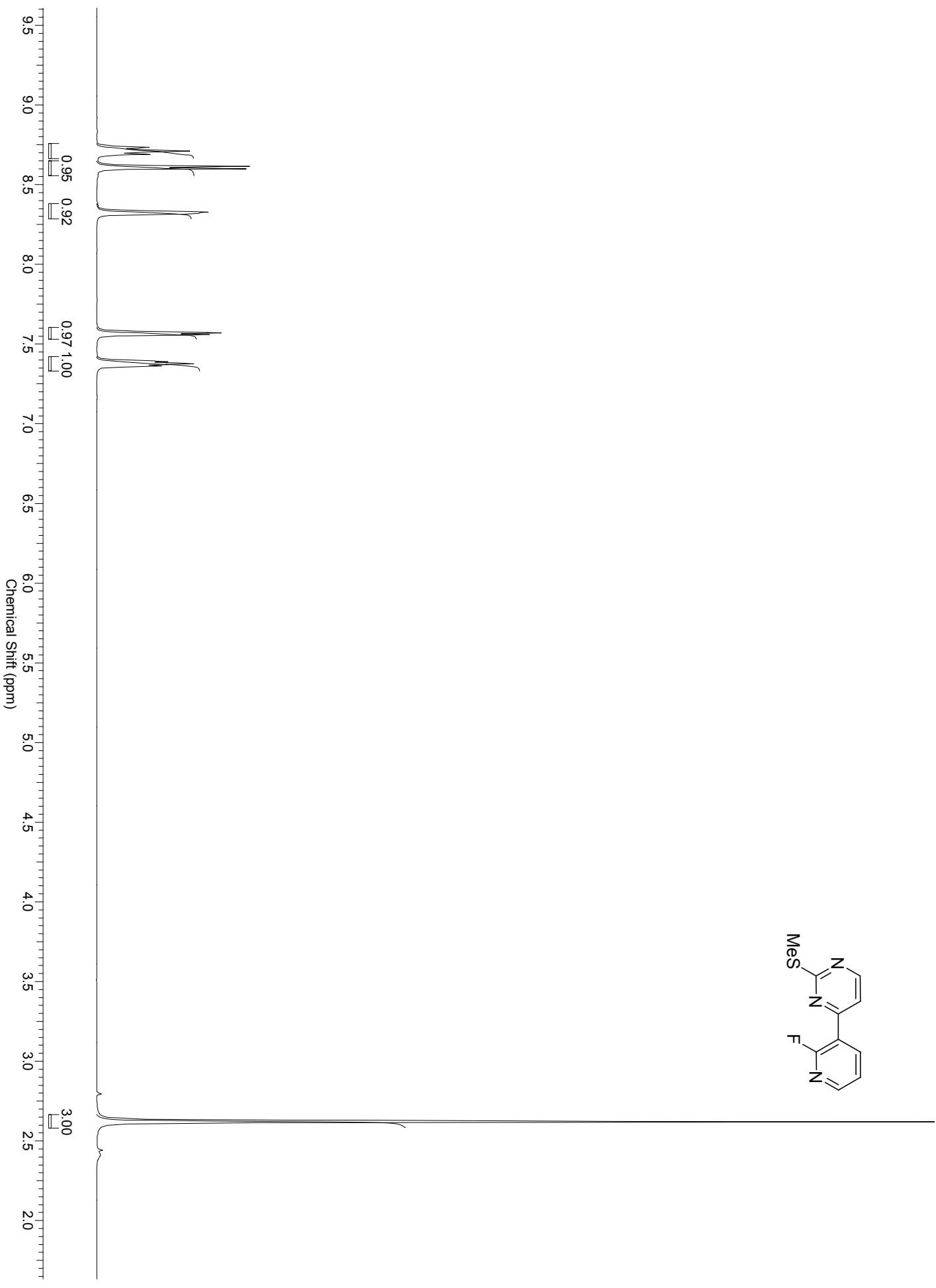


Table 7, entry 6, ^1H NMR (CDCl_3).

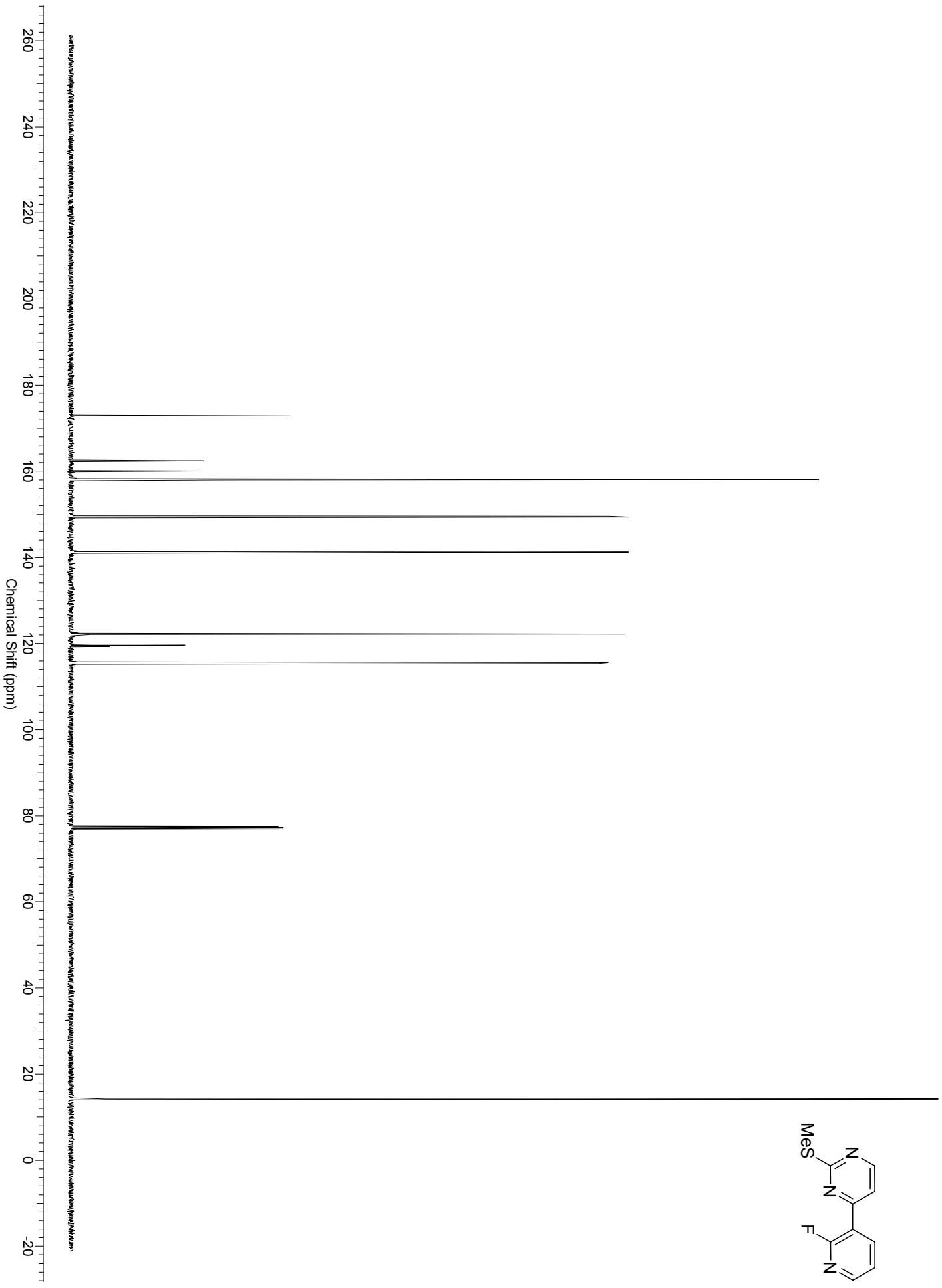


Table 7, entry 7, ^1H NMR (CDCl_3).

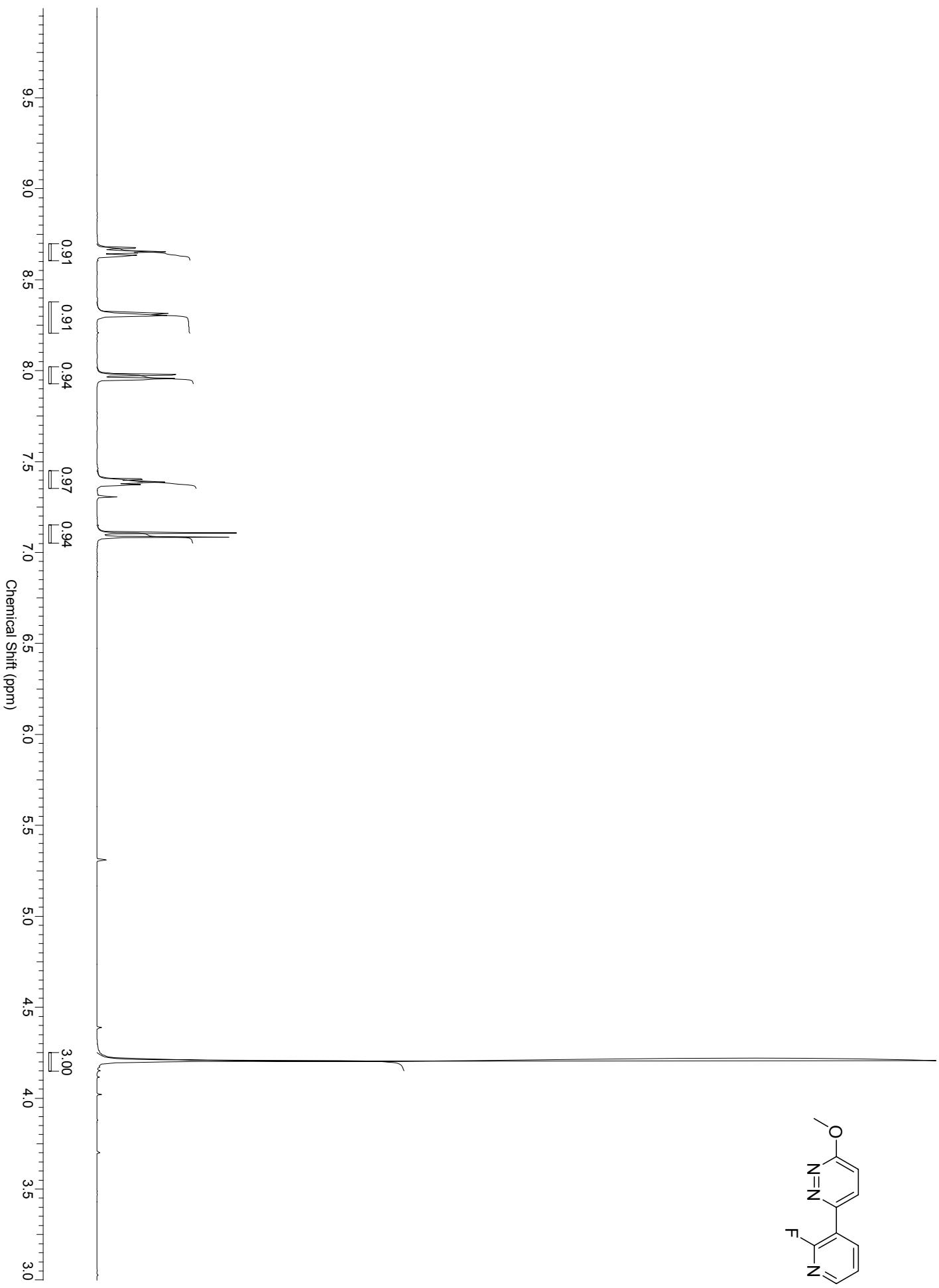
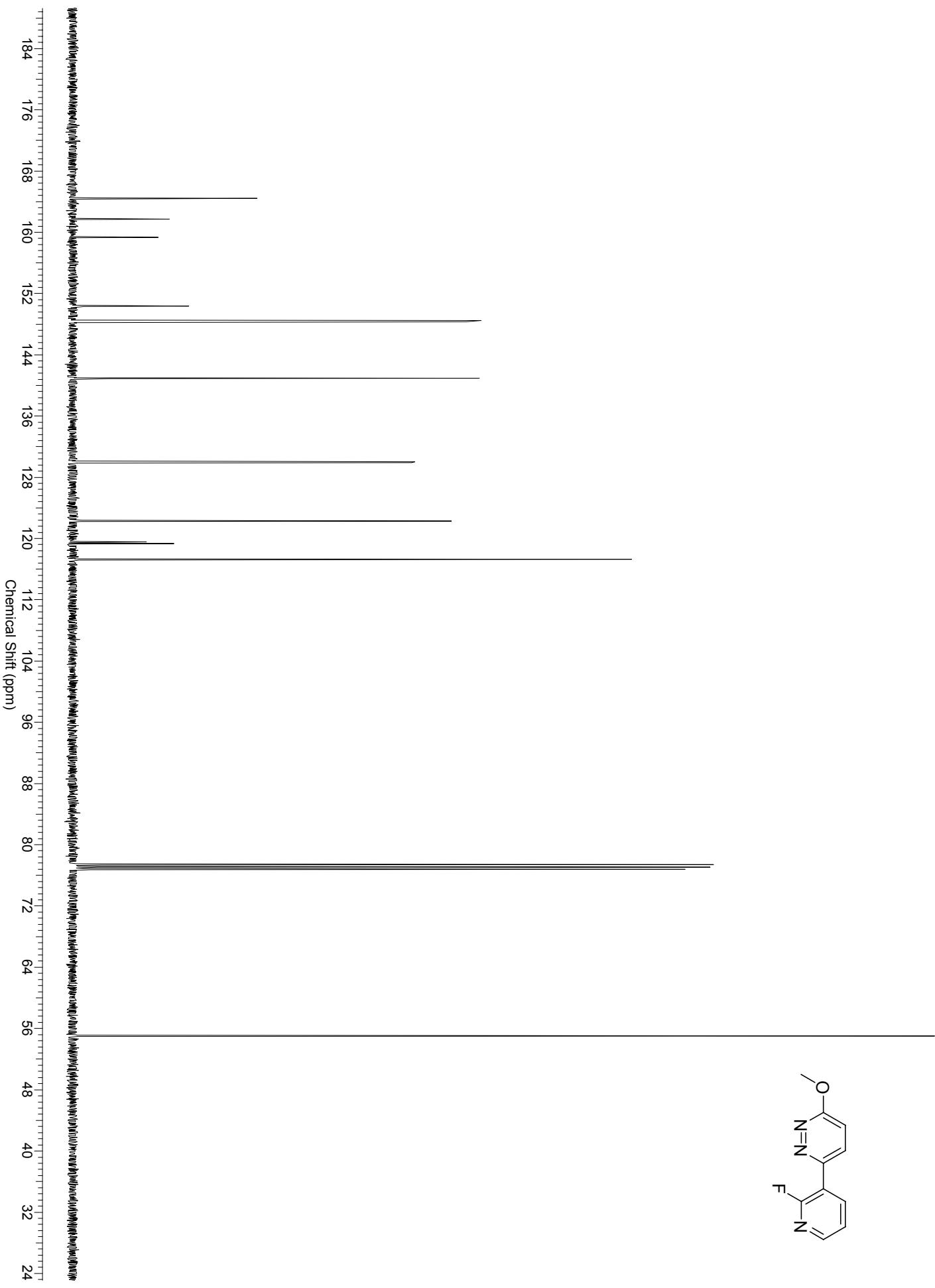


Table 7, entry 7, ^{13}C NMR (CDCl_3).



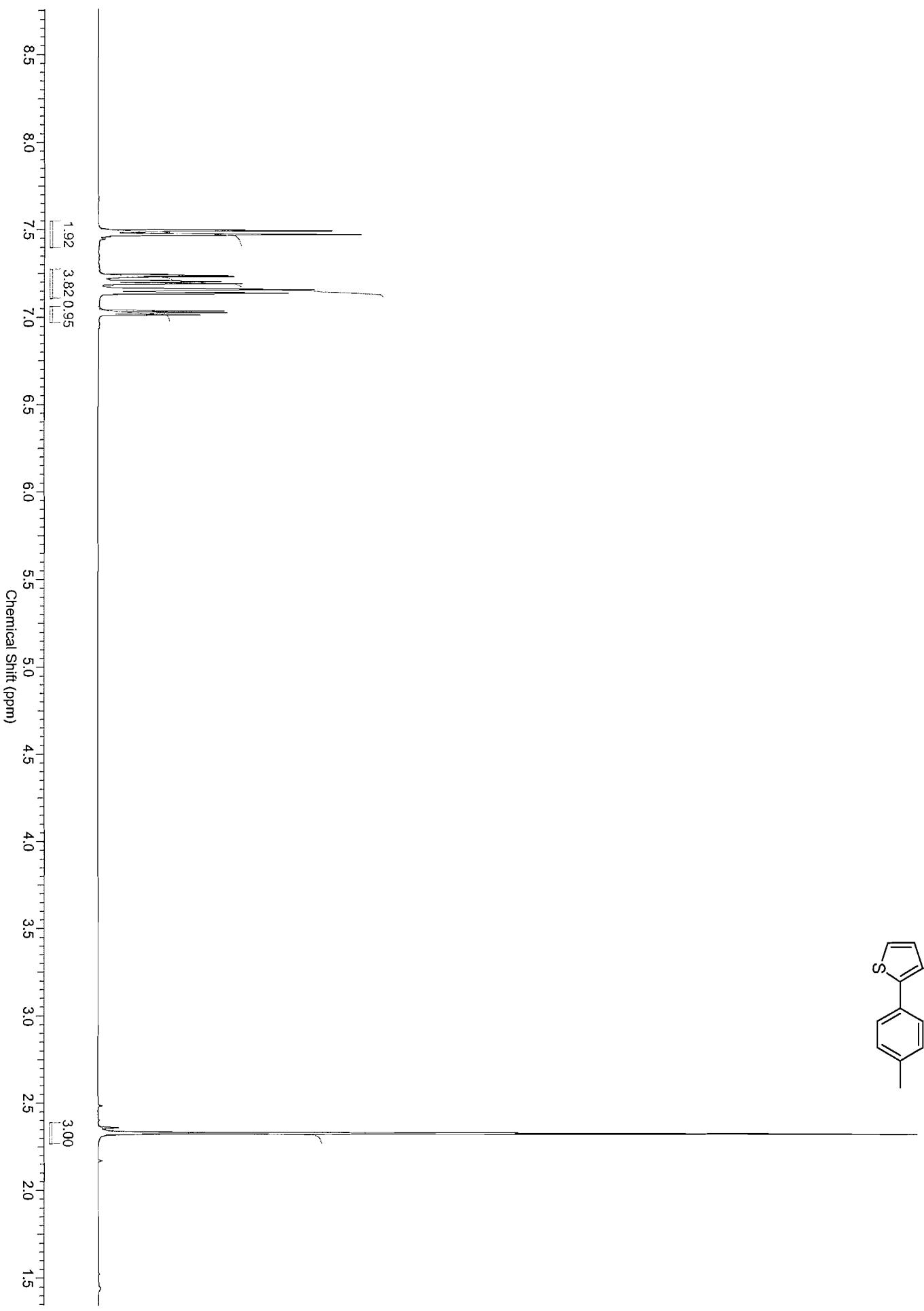


Table 8, entry 1, ^1H NMR (CDCl_3).

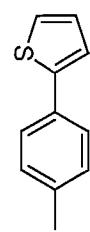


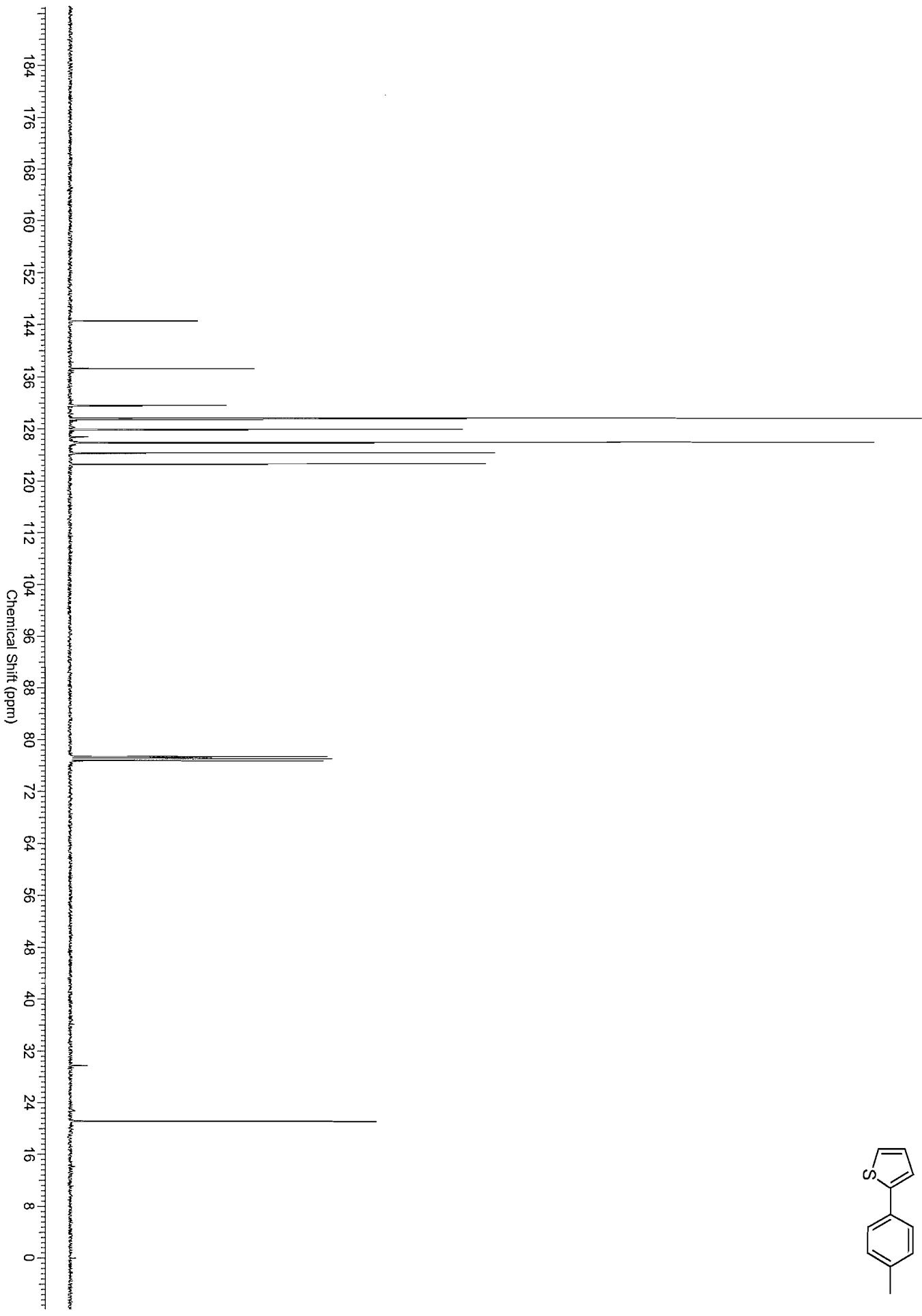
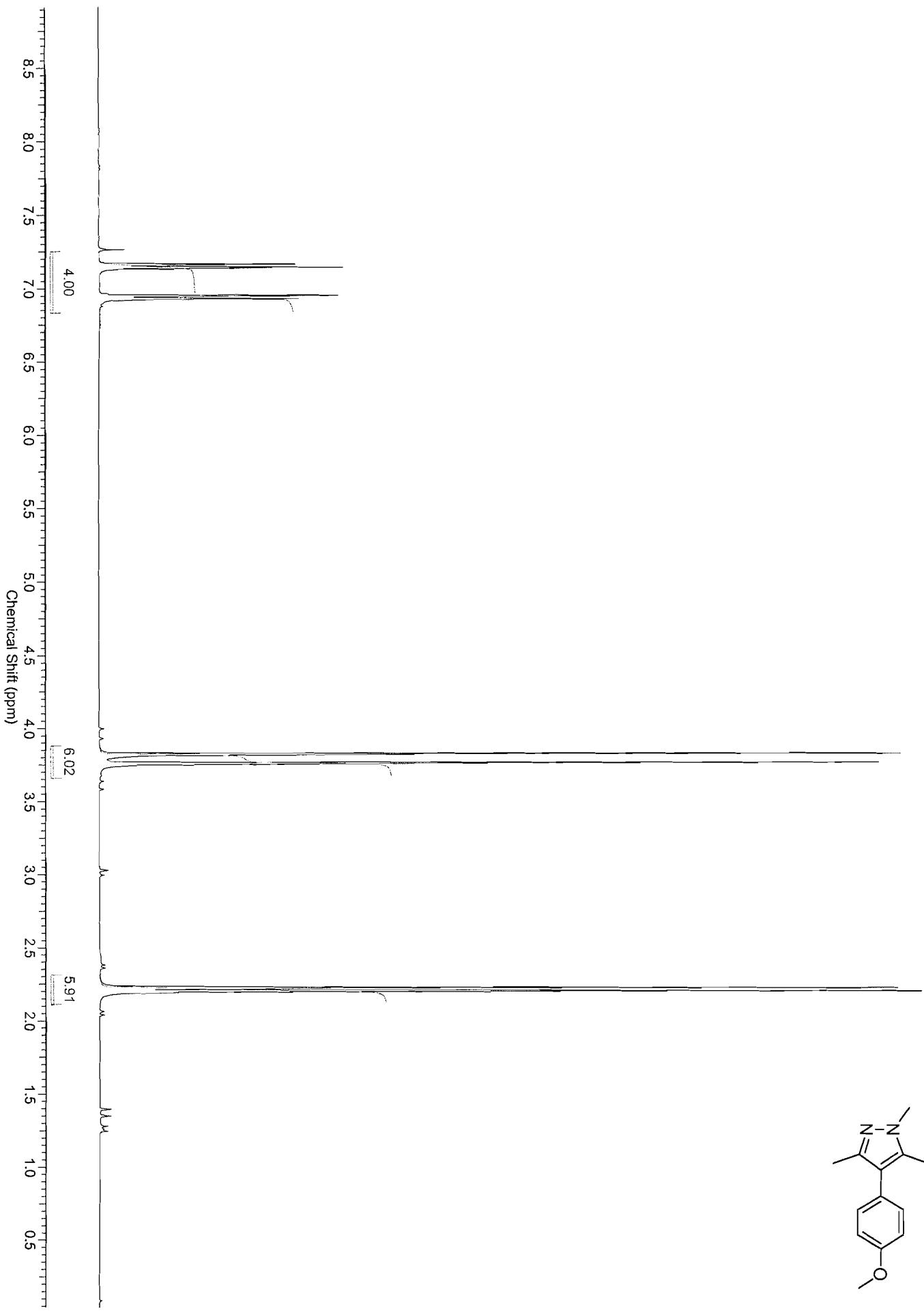
Table 8, entry 1, ^{13}C NMR (CDCl_3).

Table 8, entry 2, ^1H NMR (CDCl_3).

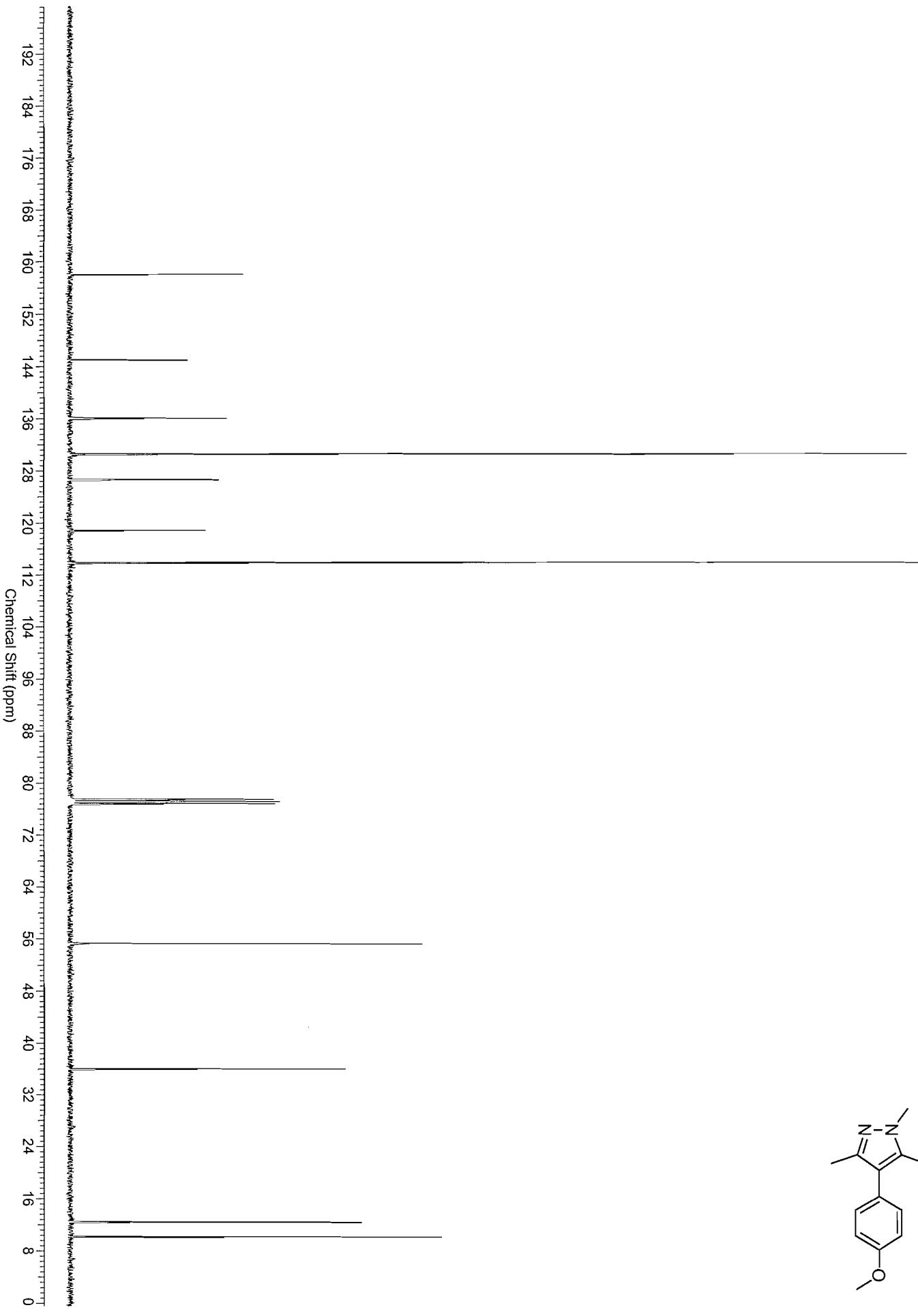


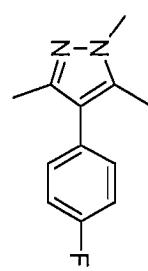
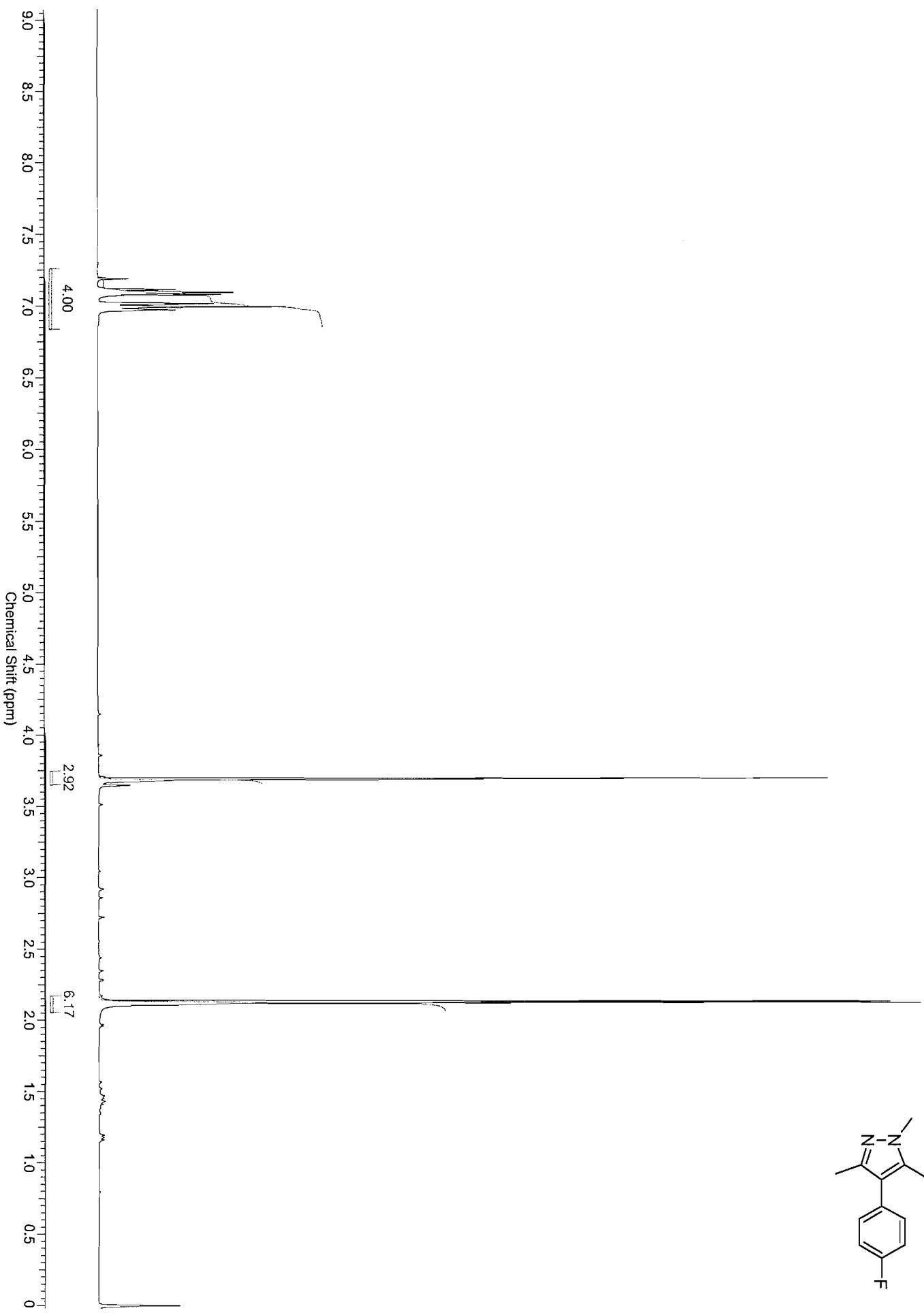
Table 8, entry 3, ^1H NMR (CDCl_3).

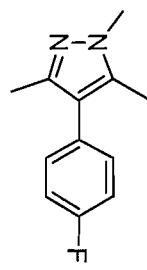
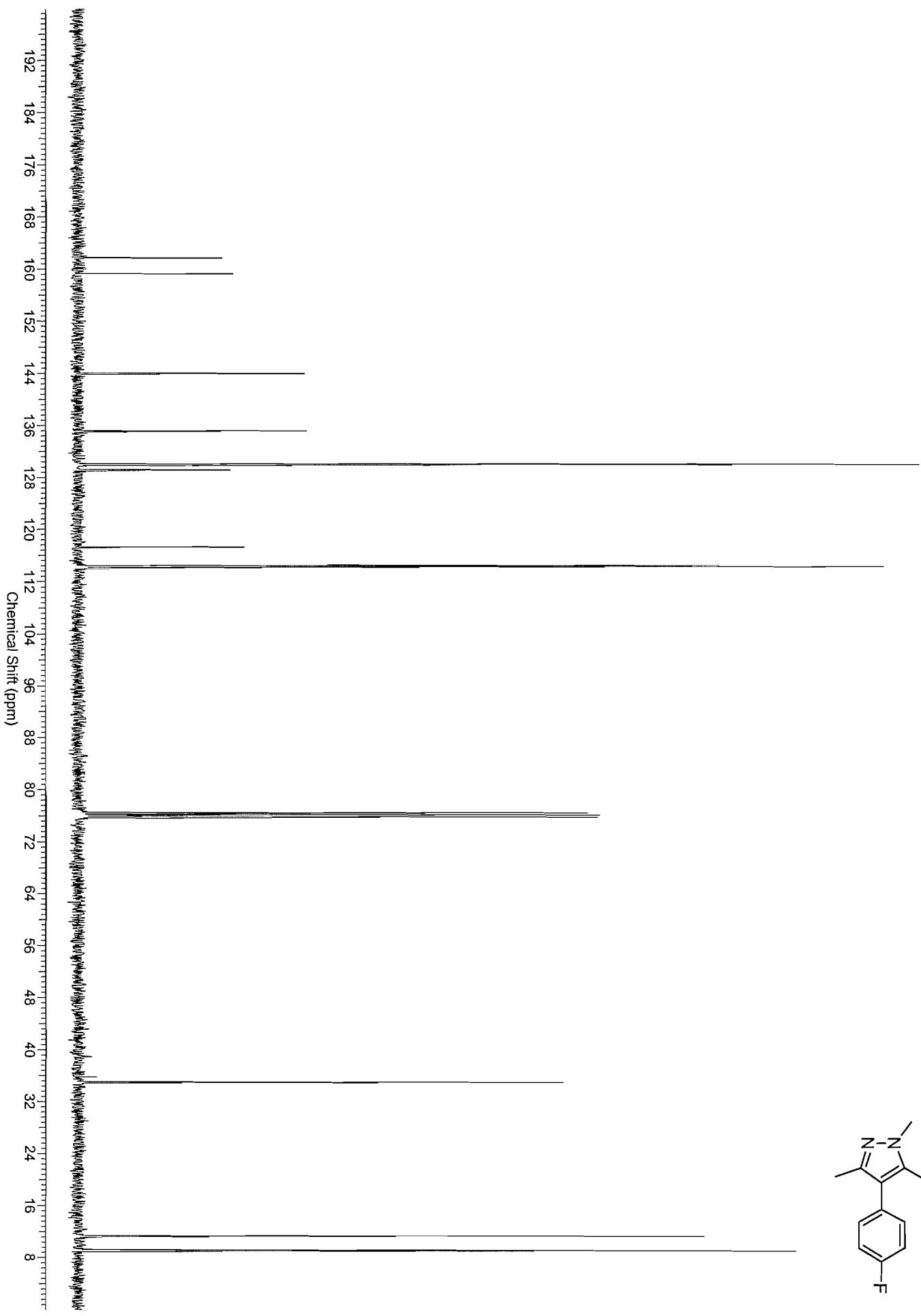
Table 8, entry 3, ^{13}C NMR (CDCl_3).

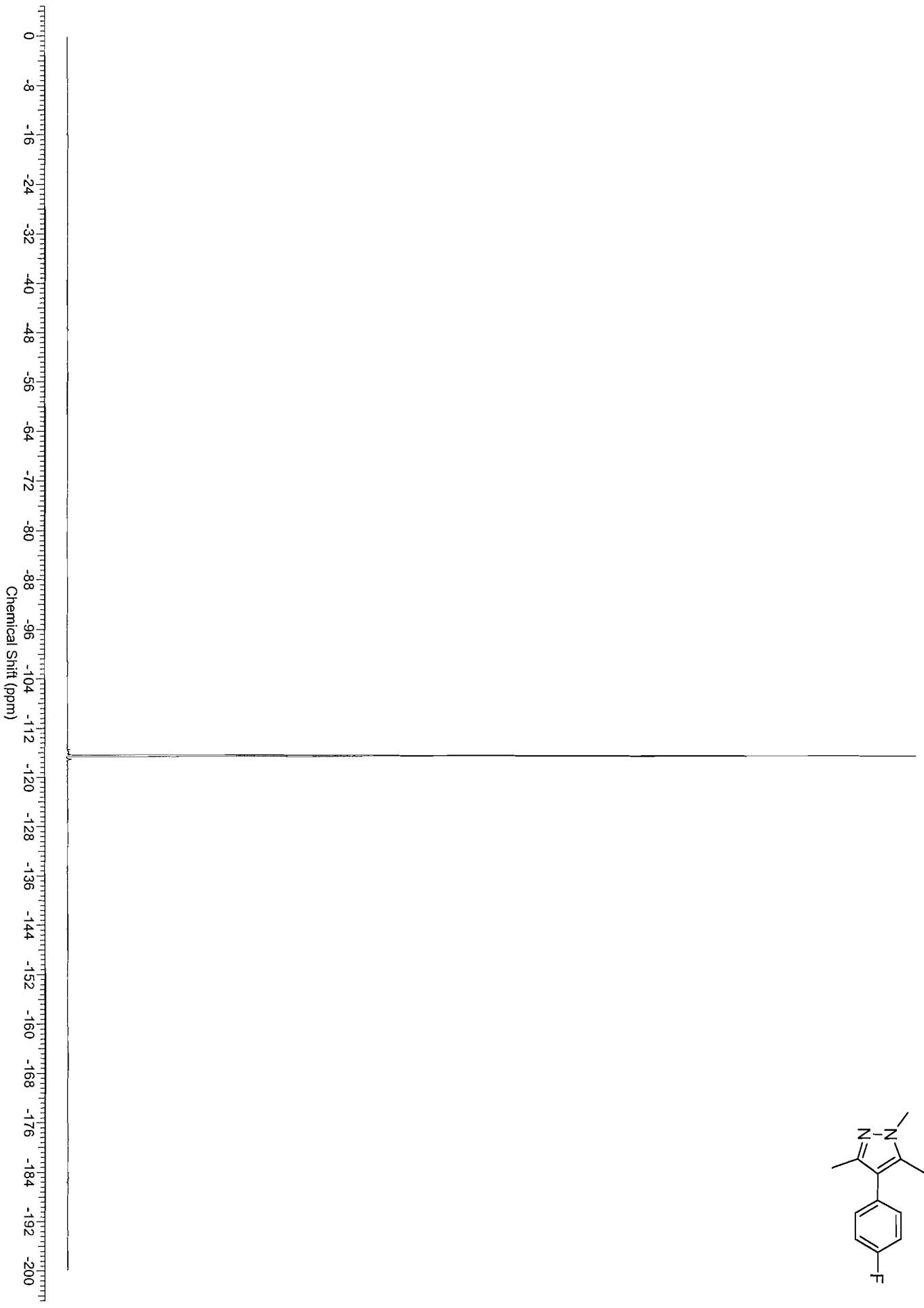
Table 8, entry 3, ^{19}F NMR (CDCl_3).

Table 8, entry 4, ^1H NMR (CDCl_3).

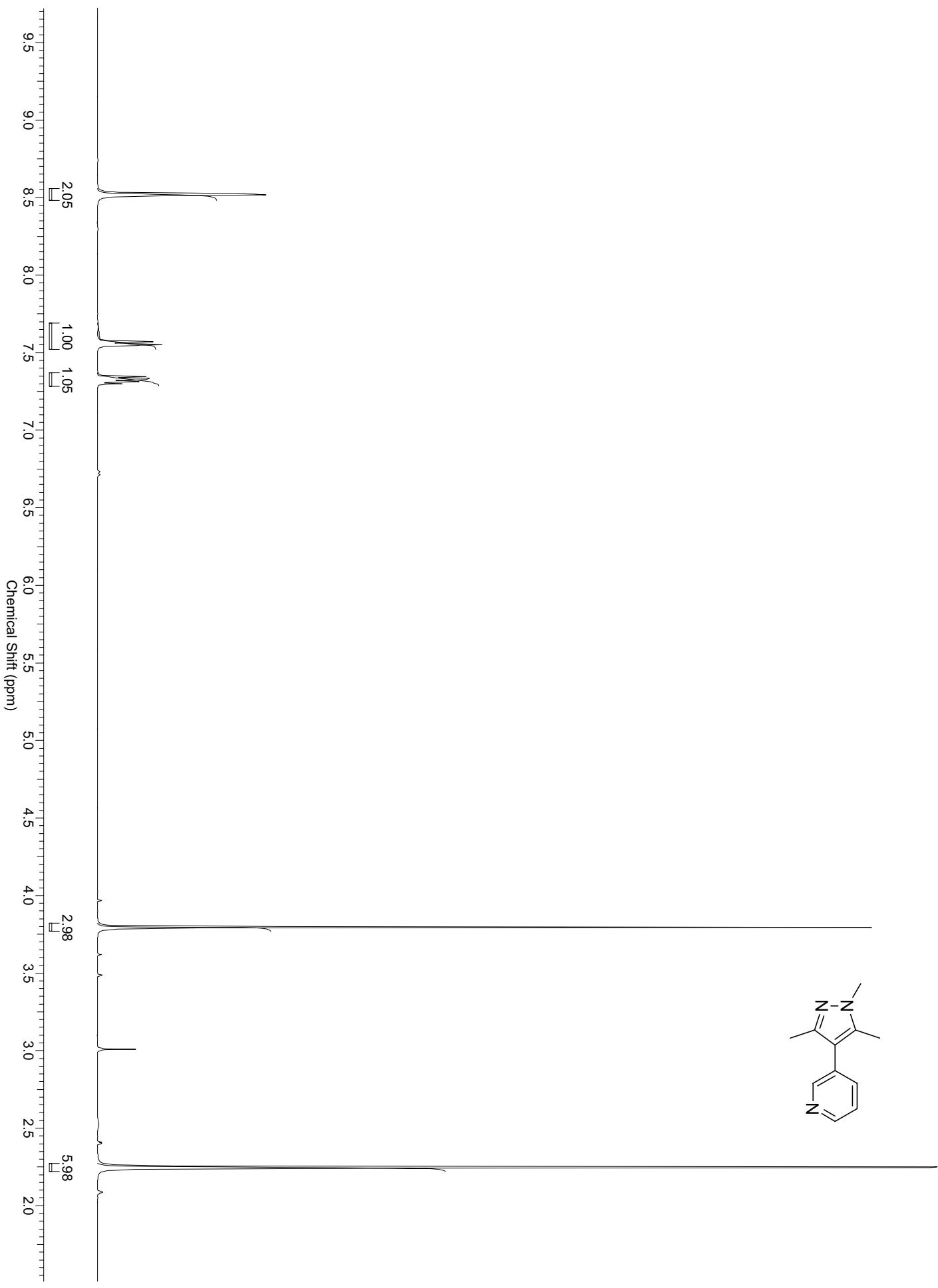


Table 8, entry 4, ^{13}C NMR (CDCl_3).

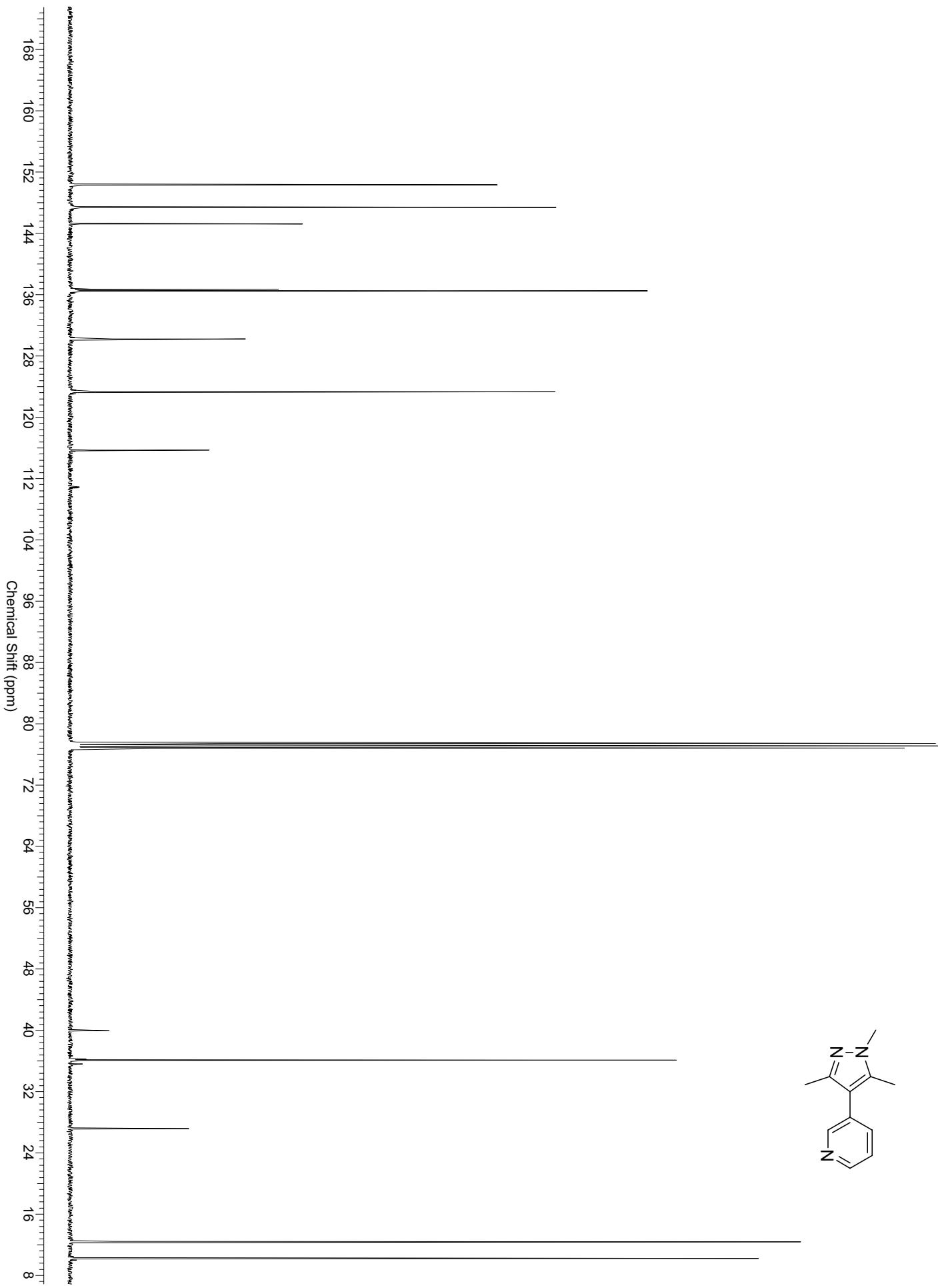


Table 8, entry 5, ^1H NMR (CDCl_3).

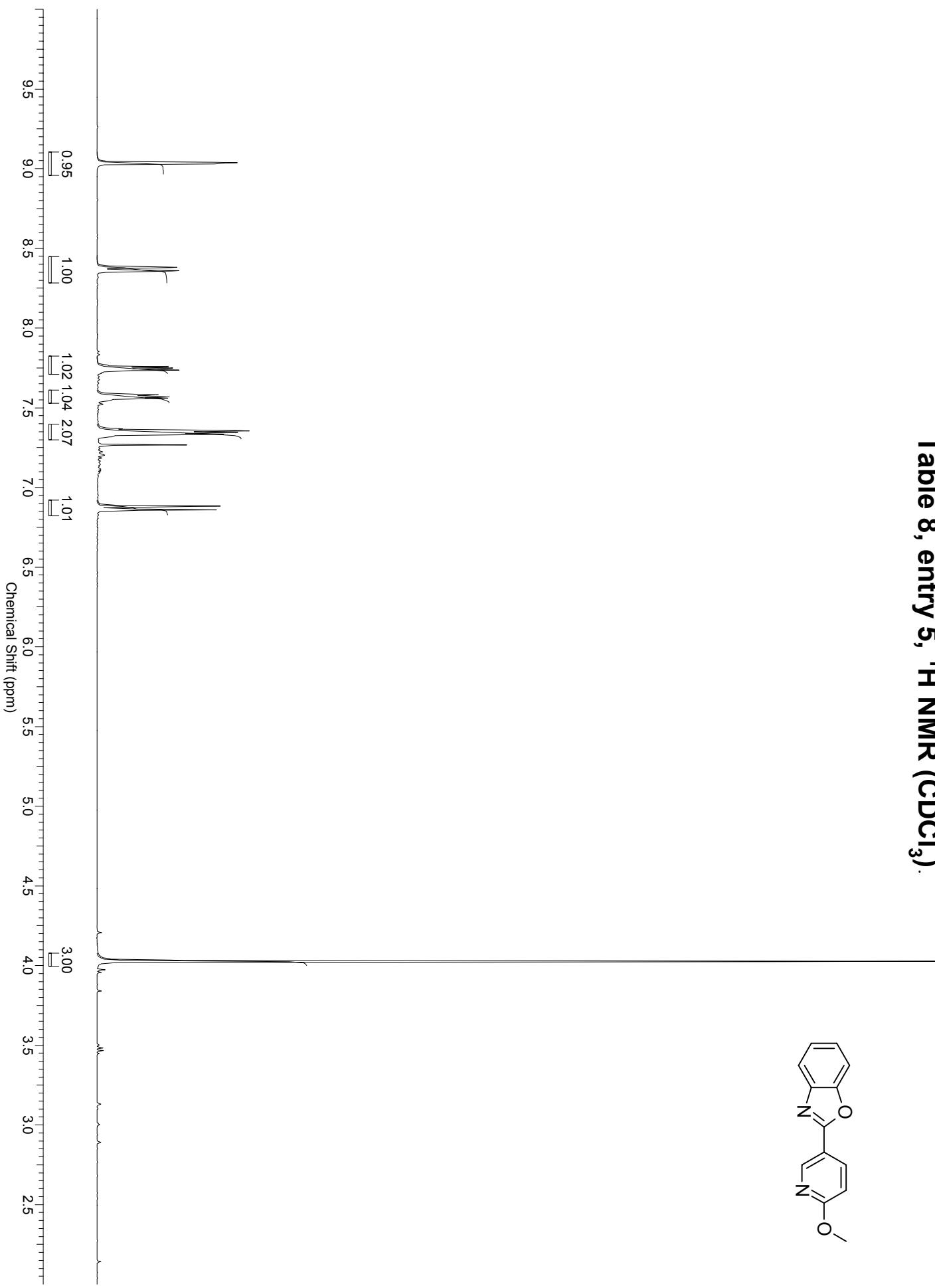


Table 8, entry 5, ^{13}C NMR (CDCl_3)

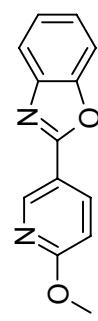
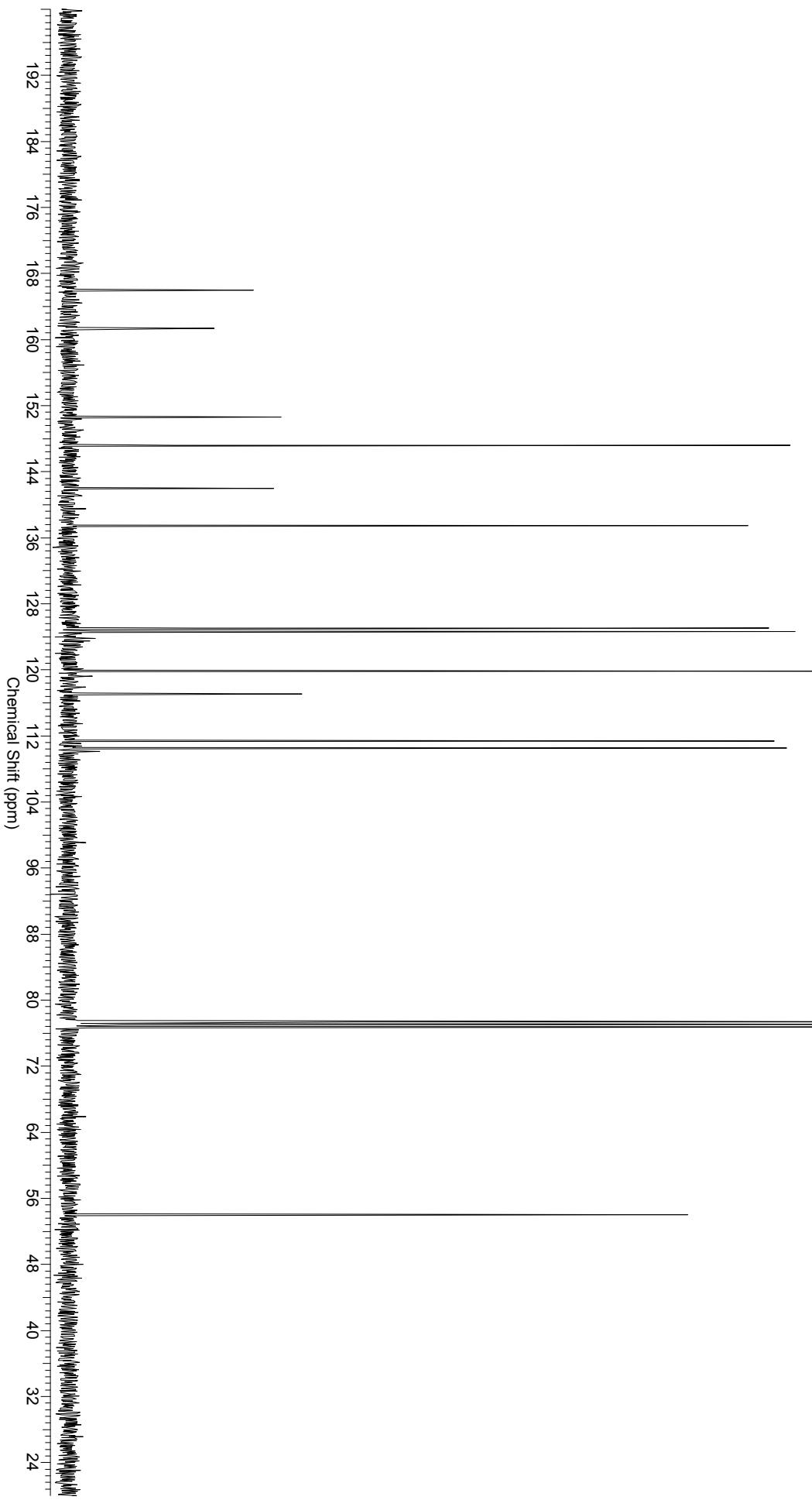


Table 8, entry 6, ^1H NMR (CDCl_3).

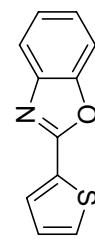
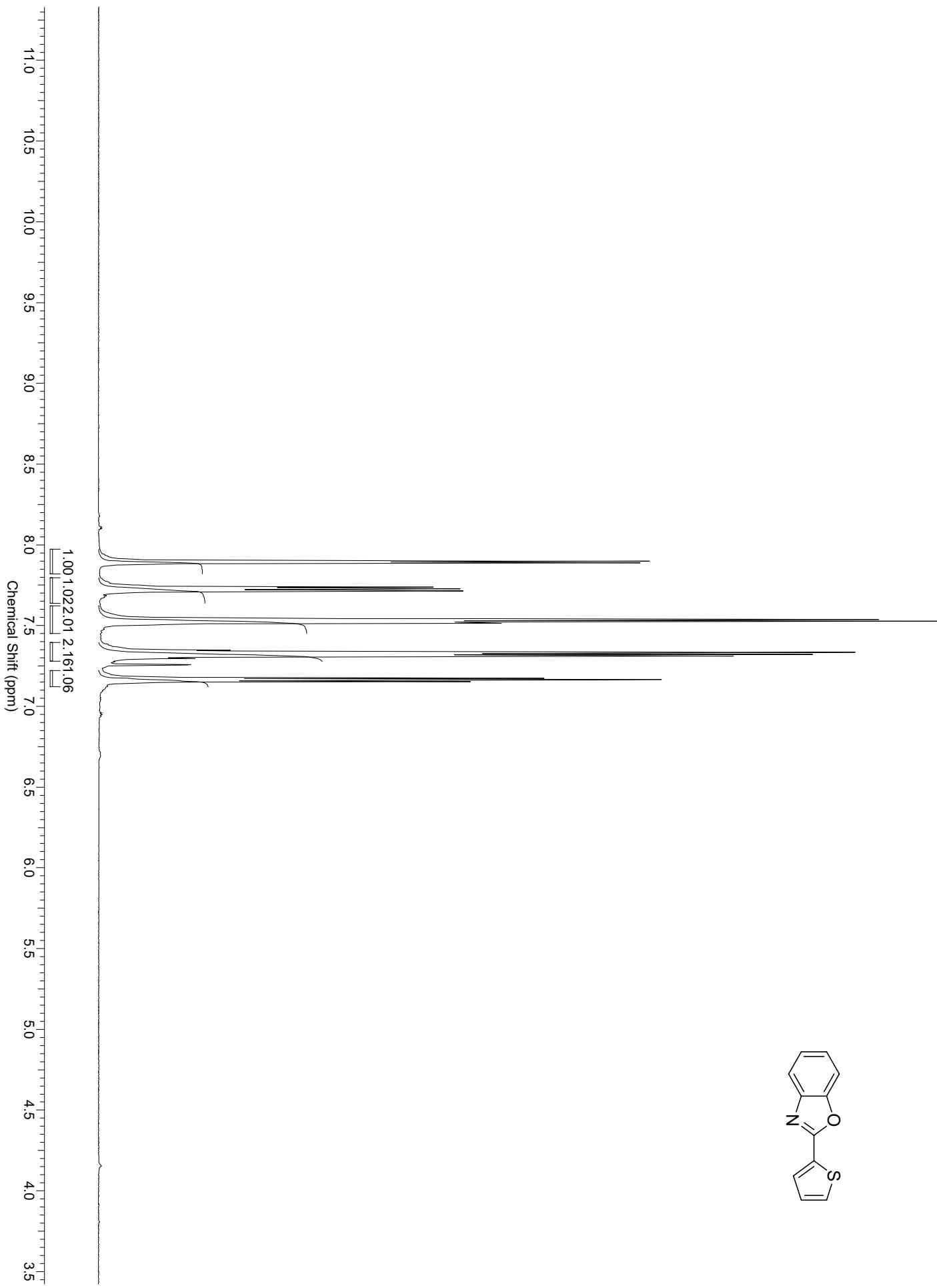
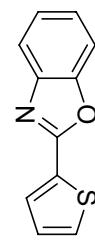
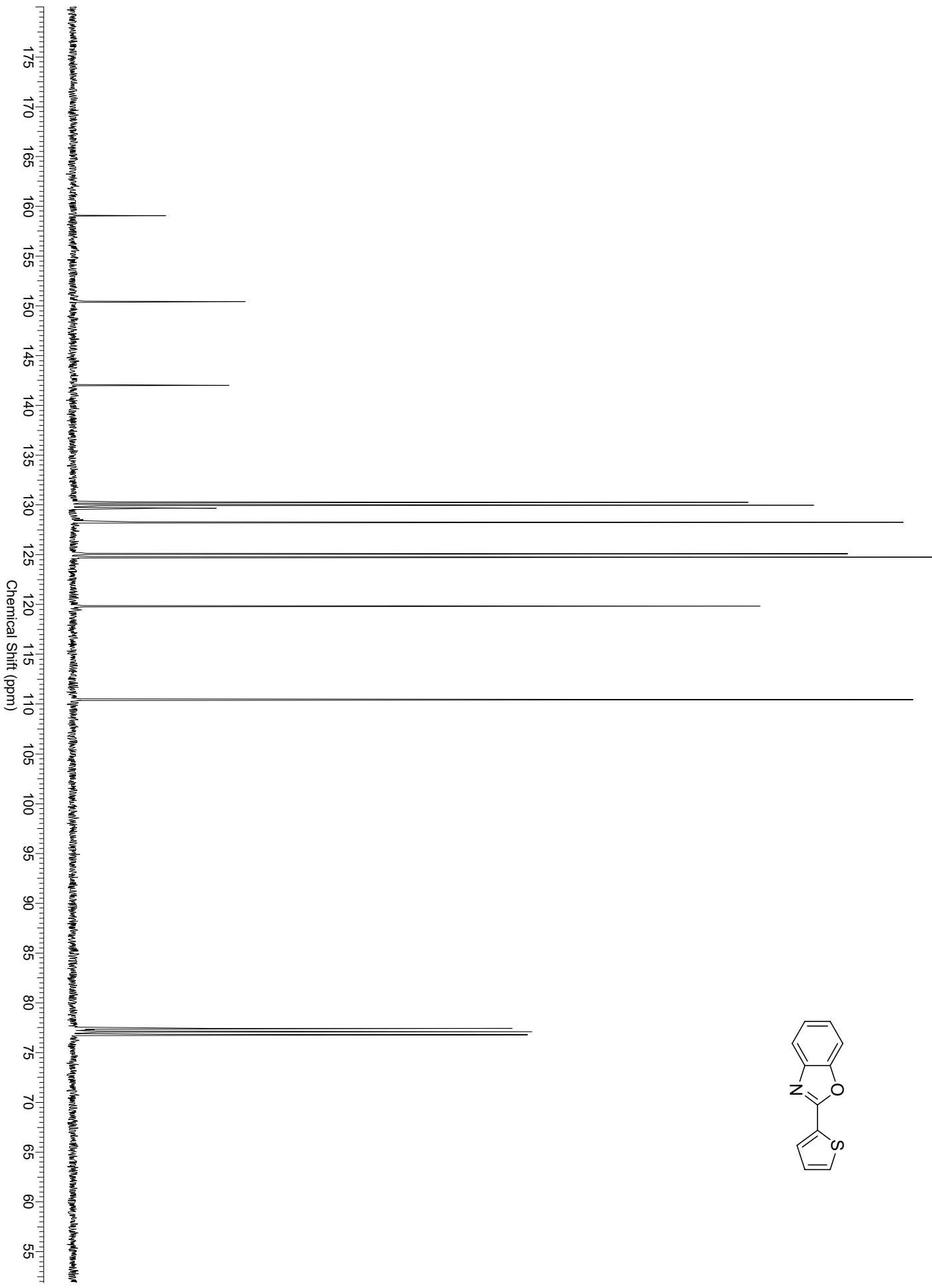
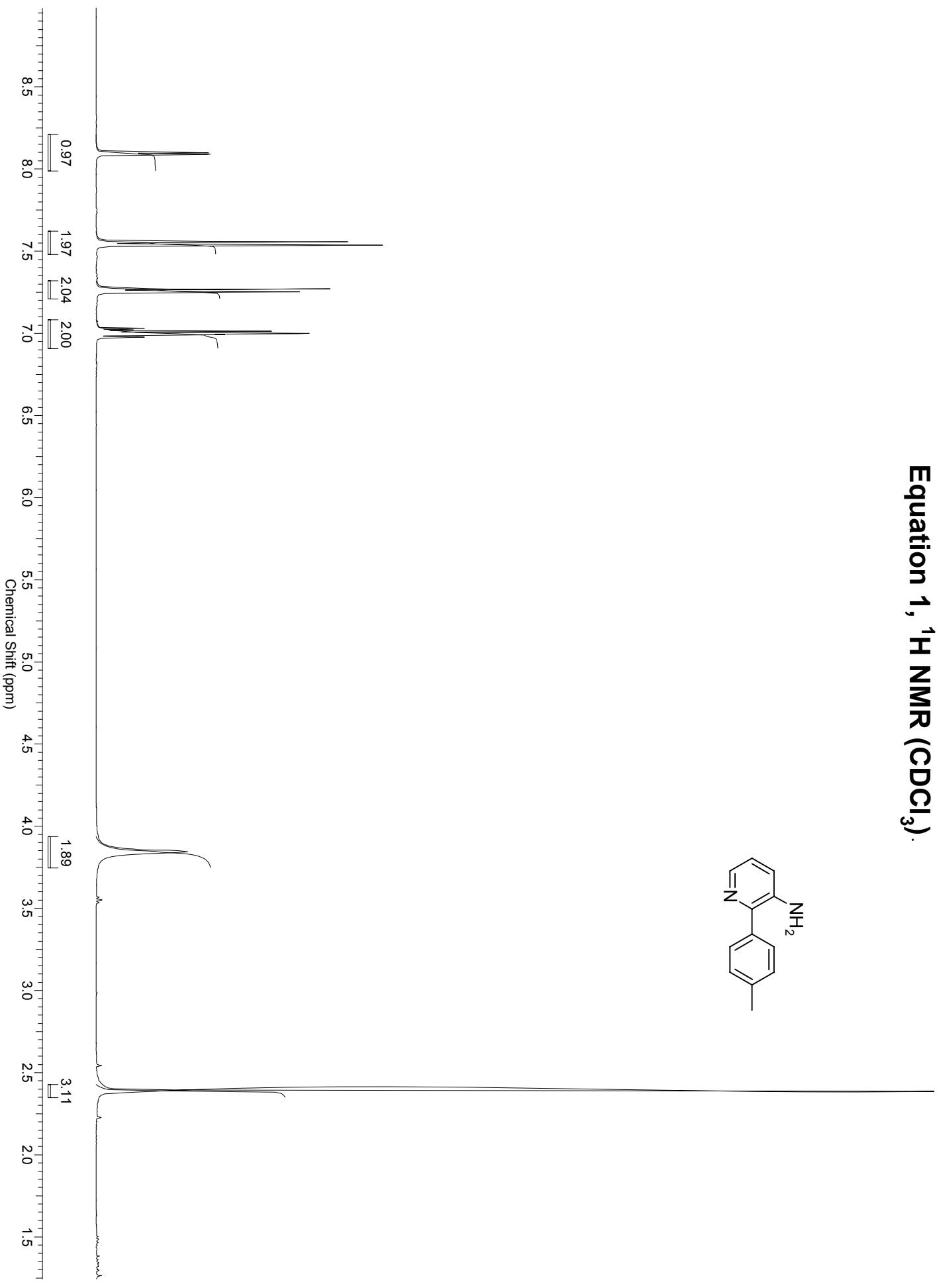


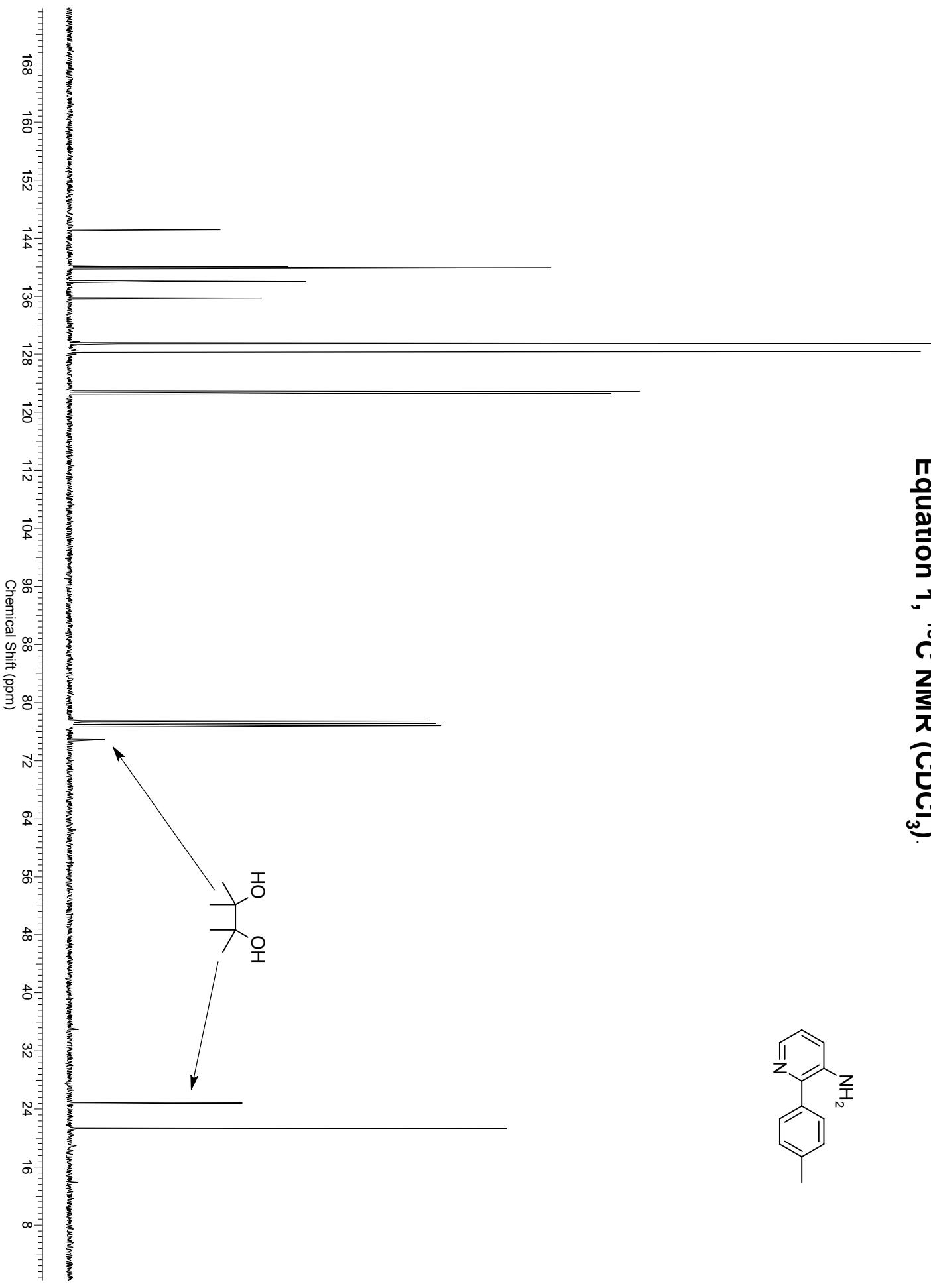
Table 8, entry 6, ^{13}C NMR (CDCl_3).



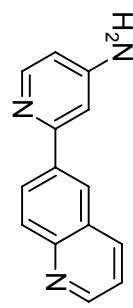
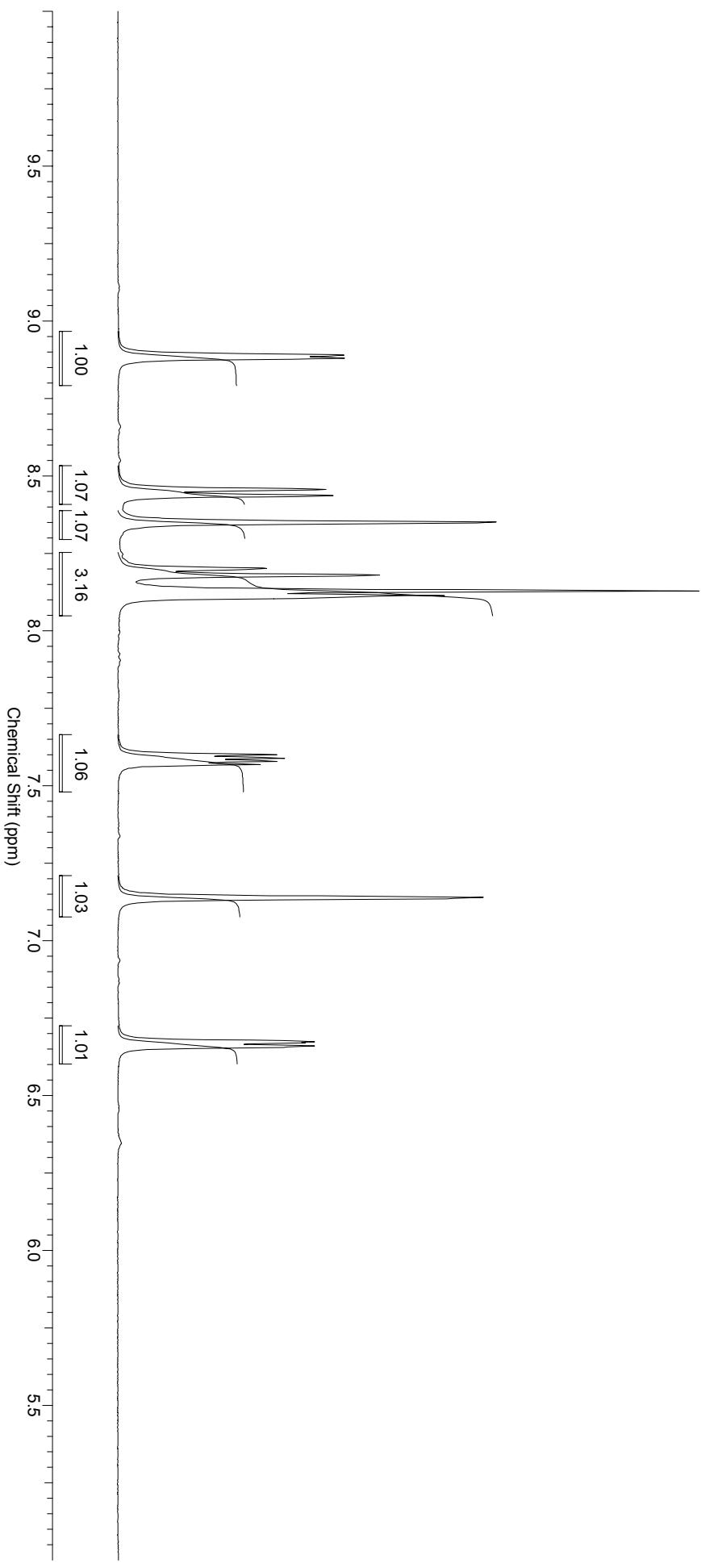
Equation 1, ^1H NMR (CDCl_3).



Equation 1, ^{13}C NMR (CDCl_3).



Equation 2, ^1H NMR (CD_3OD).



Equation 2, ^{13}C NMR (CD_3OD).

