[(CyPF-^{t}Bu)PdCl$_2$]: An Air-Stable, One-Component, Highly Efficient Complex for Amination of Heteroaryl and Aryl Halides

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Supporting Information

General Methods. Unless otherwise noted, all manipulation were conducted under an inert atmosphere, but procedures for conducting reactions without access to a drybox are provided below. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 or 500 MHz Spectrometer, and ^{31}P {^{1}H} NMR spectra were recorded on a General Electric QE 300 MHz spectrometer. All ^{1}H and ^{13}C{^{1}H} chemical shifts are reported downfield of tetramethylsilane using tetramethylsilane or residual protiated solvent (for ^{1}H NMR spectroscopy) or the resonance of deutrated solvent (for ^{13}C NMR spectroscopy) as a reference. All ^{31}P{^{1}H} NMR chemical shifts are reported in parts per million relative to an 85% H_3PO_4 external standard. Chemical shifts downfield of the standard are reported with positive values. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA or Robertson Microlab, Inc., Madison, NJ. GC and GC/MS analyses were conducted with an HP-1 methyl silicone column. CyPF-^{t}Bu (CyPF-^{t}Bu = 1-dicyclohexylphosphino-2-di-*t*-butylphosphinoethylferrocene) and Pd(CH$_3$CN)$_2$Cl$_2$ were obtained from Solvias AG and Strem Chemicals and used without further purification. Ethylene glycol dimethyl ether (DME, 99.9% purity, HPLC grade) was purchased and used without further purification. All other chemicals were used as received from commercial sources.

Synthesis of (CyPF-^{t}Bu)PdCl$_2$. A mixture of $PdCl_2$ (90.0 mg, 0.500 mmol) in CH_3CN (5.0 mL) was refluxed for 8 h under nitrogen. The clear orange solution was cooled to room temperature, and CyPF-^{t}Bu (290 mg 0.550 mmol) was added. The resulting mixture was stirred for 1 h at room temperature. The reaction mixture was filtered through a medium fritted funnel containing Celite. The solvent was evaporated under vacuum. The residue was dissolved in 1 mL THF, 20 mL of hexane was added slowly, and the resulting solution was cooled at -10 °C. After 12 h, red/orange crystals formed, and these crystals were isolated by filteration, and washed with hexane to afford (CyPF-^{t}Bu)PdCl$_2$ (330 mg, 91%). ^{1}H NMR ($CDCl_3$) δ 4.85 (s, 1 H), 4.55 (s, 1 H), 4.53 (s, 1 H), 4.25 (s, 5 H), 3.60-3.75 (m, 1 H), 3.00-3.10 (m, 1 H), 2.50-2.60 (m, 1 H), 2.27-2.90 (m, 1 H), 2.13-2.25 (m, 2 H), 2.00-2.10 (m, 1 H), 1.97 (dd, J = 9.0, 7.5 Hz, 3 H), 1.70-1.95 (m, 4 H), 1.20-1.30 (m, 8 H), 1.63 (d, J = 13.0 Hz, 9 H), 1.30-1.45 (m, 4 H), 1.23 (d, J = 14.5 Hz, 9 H); ^{13}C NMR ($CDCl_3$) δ 96.49 (dd, J = 13.3, 5.5 Hz), 71.92 (d, J = 2.5 Hz), 69.90 (d, J = 9.1 Hz), 69.78, 69.63 (d, J = 9.2 Hz), 69.34 (t, J = 5.7 Hz), 41.6 (d, J = 35.5 Hz), 41.57 (d, J = 8.2 Hz), 40.55 (d, J = 11.2 Hz), 37.56 (d, J = 35.5 Hz), 34.48 (t, J = 9.1 Hz), 31.97 (d, J = 1.9 Hz), 31.05 (d, J = 1.9 Hz), 29.99, 29.19, 28.06, 27.55 (d, J = 6.8 Hz), 27.32 (d, J = 10.2 Hz), 26.98 (d, J = 12.6 Hz), 26.89 (d, J = 5.2 Hz), 26.78 (d, J = 3.8 Hz), 26.12 (d, J = 1.9 Hz), 25.55, 18.02 (d, J = 6.7 Hz). ^{31}P {^{1}H} NMR ($CDCl_3$) δ 113.83 (d, J = 9.7

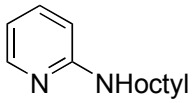
Hz), 31.74 (d, J = 9.7 Hz). Anal. Calcd. For $C_{32}H_{52}Cl_2FeP_2Pd$: C, 52.51; H, 7.16. Found: C, 52.72; H, 7.38.

General Procedure for Catalytic Amination of Heteroaryl and Aryl Chlorides, Bromides and Iodides. The reaction conditions and average yields for each reaction are shown in Table 1 and 2. A typical procedure is given for the first entry in Table 1.

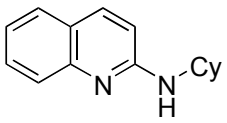
Stock Solution A (1.0×10^{-2} M): THF (1.0 mL) was added to (CyPF-^{t}Bu)$PdCl_2$ (7.3 mg, 1.0 mmol). The resulting orange colored solution was stirred at room temperature for one minute before using.

Stock Solution B (1.0×10^{-4} M): 10.0 μL of the stock solution **A** was diluted to 1.0 mL with DME. The resulting pale yellow colored solution was stirred at room temperature for one minute before using.

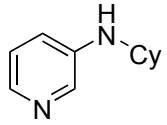
***N*-Octyl-2-aminopyridine. (Table 1, entry 1).** A solution of (CyPF-^{t}Bu)$PdCl_2$ (100.0 μL from stock solution **B**, 1.0×10^{-5} mmol) was added to a 4 mL vial containing 2-chloropyridine (0.114 g, 1.00 mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) in 1.0 mL of DME. Octylamine (0.155 g, 1.20 mmol) was then added by syringe. The vial was sealed with a cap containing a PTFE septum, and the reaction mixture was stirred at 100 °C until 2-chloropyridine was consumed, as determined by GC. The reaction solution was directly adsorbed onto silica gel, and the product was isolated by eluting with hexane/ethyl acetate (85/15) to give 189.1 mg (92%) of *N*-octyl-2-aminopyridine as a yellow solid. ^{1}H NMR ($CDCl_3$) δ 8.07 (d, J = 4.8 Hz, 1 H), 7.42 (dd, J = 8.6, 7.2 Hz, 1 H), 6.38 (d, J = 8.4 Hz, 1 H), 6.55 (dd, J = 7.0, 4.8 Hz, 1 H), 4.55 (s, b, 1 H), 3.24 (q, J = 6.8 Hz, 2 H), 1.62 (quint, J = 7.2 Hz, 2 H), 1.20-1.42 (m, 10 H), 0.89 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 158.88, 148.14, 137.19, 112.32, 106.1, 42.32, 31.68, 29.59, 29.42, 29.24, 27.11, 22.51, 13.95; Anal. Calcd. For $C_{13}H_{22}N_2$: C, 75.68; H, 10.75; N, 13.58. Found: C, 75.71; H, 10.67; N, 13.74.



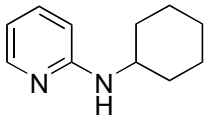
***N*-Cyclohexyl-2-aminoquinoline. (Table 1, entry 2).** The general procedure conducted with 2-chloroquinoline (0.163 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (10.0 μL from stock solution **A**, 1.0×10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 193.3 mg (85%) of *N*-cyclohexyl-2-aminoquinoline as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.67 (d, J = 9.2 Hz, 1 H), 7.56 (dd, J = 8.4, 0.4 Hz, 1 H), 7.45 (dd, J = 8.4, 1.2 Hz, 1 H), 7.40 (d, J = 8.8 Hz, 1 H), 7.07 (ddd, J = 8.0, 7.0, 1.2 Hz, 1 H), 6.50 (d, J = 8.8 Hz, 1 H), 4.66 (d, J = 8.0 Hz, 1 H), 3.71-3.78 (m, 1 H), 1.97-2.01 (m, 2 H), 1.66 (dt, J = 13.6, 4.9 Hz, 2 H), 1.55 (dt, J = 13.2, 4.9 Hz, 1 H), 1.27-1.38 (m, 2 H), 1.06-1.17 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 156.26, 148.15, 137.14, 129.34, 127.28, 125.85, 123.17, 121.60, 111.02, 49.70, 33.38, 25.66, 24.82; Anal. Calcd. For $C_{15}H_{18}N_2$: C, 79.61; H, 8.02; N, 12.38. Found: C, 79.49; H, 8.03; N, 12.23.



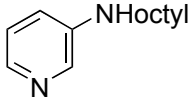
***N*-Cyclohexyl-3-aminopyridine.**[1] **(Table 1, entry 3).** The general procedure conducted with 3-chloropyridine (0.114 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), (CyPF-^{t}Bu)PdCl$_2$ (50.0 μL from stock solution **A**, 5.0 × 10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 155.8 mg (88%) of *N*-cyclohexyl-3-aminopyridine as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.91 (d, *J* = 2.4 Hz, 1 H), 7.81 (dd, *J* = 4.8, 1.4 Hz, 1 H), 6.95 (dd, *J* = 8.0, 4.8 Hz, 1 H), 6.75 (ddd, *J* = 8.0, 2.8, 1.2 Hz, 1 H), 3.73 (s, b, 1 H), 3.10-3.21 (m, 1 H), 1.94 (dd, *J* = 13.2, 3.2 Hz, 2 H), 1.67 (dt, *J* = 13.2, 3.6 Hz, 2 H), 1.56 (dd, *J* = 12.4, 3.6 Hz, 1 H), 1.22-1.33 (m, 2 H), 1.02-1.18 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.25, 137.77, 136.09, 123.48, 118.39, 51.16, 32.94, 25.59, 24.68.



***N*-Cyclohexyl-2-aminopyridine.**[1] **(Table 1, entry 4).** The general procedure conducted with 2-bromopyridine (0.158 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), (CyPF-^{t}Bu)PdCl$_2$ (5.0 μL from stock solution **A**, 5.0 × 10^{-5} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 149 mg (86%) of *N*-cyclonexyl-2-aminopyridine as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.97 (dt, *J* = 5.0, 0.8 Hz, 1 H), 7.28 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1 H), 6.42 (dd, *J* = 6.8, 5.0 Hz, 1 H), 6.26 (d, *J* = 8.0 Hz, 1 H), 4.48 (d, *J* = 6.4 Hz, 1 H), 3.41-3.49 (m, 1 H), 1.93-1.97 (m, 2 H), 1.66 (dt, *J* = 13.2, 3.6 Hz, 2 H), 1.55 (dt, *J* = 12.4, 4.0 Hz, 1 H), 1.25-1.36 (m, 2 H), 1.06-1.19 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 158.03, 148.13, 137.11, 112.14, 106.57, 49.95, 33.23, 25.67, 24.78.

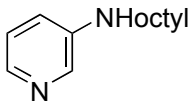


***N*-Octyl-3-aminopyridine. (Table 1, entry 5).** The general procedure conducted with 3-bromopyridine (0.158 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), (CyPF-^{t}Bu)PdCl$_2$ (5.0 μL from stock solution **A**, 5.0 × 10^{-5} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 152.6 mg (74%) of *N*-octyl-3-aminopyridine as a yellow solid. ^{1}H NMR ($CDCl_3$) δ 8.02 (d, *J* = 2.8 Hz, 1 H), 7.93 (dd, *J* = 4.4, 1.6 Hz, 1 H), 7.07 (dd, *J* = 8.4, 4.6 Hz, 1 H), 6.86 (ddd, *J* = 8.8, 3.2, 1.6 Hz, 1 H), 3.72 (s, b, 1 H), 3.11 (t, *J* = 7.2 Hz, 2 H), 1.63 (quint, *J* = 7.2 Hz, 2 H), 1.26-1.42 (m, 10 H), 0.89 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 144.37, 138.0, 135.69, 123.49, 118.01, 43.35, 31.63, 29.19, 29.16, 29.06, 26.92, 22.47, 13.91; Anal. Calcd. For $C_{13}H_{22}N_2$: C, 75.68; H, 10.75; N, 13.58. Found: C, 75.74; H, 10.94; N, 13.79.

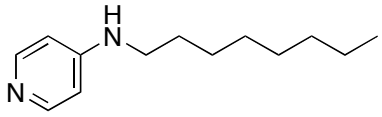


Representative procedure using Schlenk procedures on large scale. (Table 1, entry 6) An oven-dried resealable Schlenk flask capped with a rubber septum was evacuated and backfilled with N_2. To the flask was added NaO*t*Bu (6.8 g, 7.0 mmol) and (CyPF-

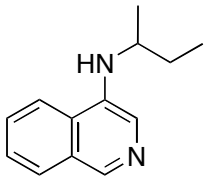
(^{t}Bu)$PdCl_2$ (1.5 mg, 0.25 mmol) and a stirring bar. To the flask was then added 3-bromopyridine (7.90 g, 50.0 mmol), DME (50.0 mL and octylamine (10.0 mL, 60.0 mmol). The rubber septum was wrapped with vinyl electrical tape to prevent leaking. The solution was bubbled with nitrogen for 10 min. The resulting mixture was stirred for 12 h at 110 °C until the 3-bromopyridine was consumed, as determined by GC. Water (50 mL) was added after the mixture was cooled to room temperature. The mixture was then extracted with CH_2Cl_2 (3 × 30.0 mL). The organic layer was separated and dried over Na_2SO_4. The solvent was evaporated, and the crude product was isolated by eluting with hexane/ethyl acetate (85/15) to give 8.87 g (87%) of *N*-octyl-3-aminopyridine as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 1, entry 5.)



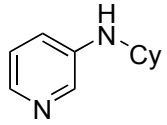
***N*-Octyl-4-aminopyridine. (Table 1, entry 7).** The general procedure conducted with 4-bromopyridine hydrochloride (0.195 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (5.0 μL from stock solution **A**, 5.0 × 10^{-5} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 179.4 mg (88%) of *N*-octyl-4-aminopyridine as a white solid. ^{1}H NMR ($CDCl_3$) δ 8.11 (d, *J* = 4.8 Hz, 2 H), 6.37 (d, *J* = 4.8 Hz, 2 H), 4.44 (s, b, 1 H), 3.08 (q, *J* = 7.2 Hz, 2 H), 1.55 (quint, *J* = 7.2 Hz, 2 H), 1.19-1.39 (m, 10 H), 0.84 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 153.50, 149.48, 107.18, 42.38, 31.59, 29.12, 29.02, 28.84, 26.85, 22.44, 13.89; Anal. Calcd. For $C_{13}H_{22}N_2$: C, 75.68; H, 10.75; N, 13.58. Found: C, 75.45; H, 10.80; N, 13.62.



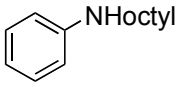
***N*-*sec*-Butyl-3-amino-*iso*quinoline. (Table 1, entry 8).** The general procedure conducted with 3-bromopyridine (0.158 g, 1.00 mmol), *sec*-butylamine (0.119 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (50.0 μL from stock solution **A**, 5.0 × 10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 198.3 mg (99%) of *N*-*sec*-butyl-3-amino-*iso*quinoline as a white solid. ^{1}H NMR ($CDCl_3$) δ 8.62 (s, 1 H), 7.86 (d, *J* = 7.5 Hz, 1 H), 7.85 (s, 1 H), 7.75 (d, *J* = 9.0 Hz, 1 H), 7.59 (td, *J* = 7.0, 1.5 Hz, 1 H), 7.52 (t, *J* = 7.5 Hz, 1 H), 4.05 (d, *J* = 7.0 Hz, 1 H), 3.61 (hept, *J* = 6.5 Hz, 1 H), 1.73 (hept, *J* = 6.0 Hz, 1 H), 1.58 (hept, *J* = 6.5 Hz, 1 H), 1.28 (d, *J* = 6.5 Hz, 3 H), 0.99 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 141.13, 136.93, 128.59, 128.56, 127.94, 126.70, 125.68, 123.72, 118.98, 49.69, 29.40, 19.98, 10.33. Anal. Calcd. For $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.98; H, 8.25; N, 13.82.



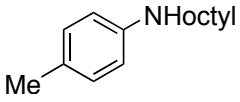
***N*-Cyclohexyl-3-aminopyridine.**[1] **(Table 1, entry 9).** The general procedure conducted with 3-iodopyridine (0.205 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), (CyPF-^{t}Bu)PdCl$_2$ (50.0 μL from stock solution **A**, 5.0 × 10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 124.0 mg (70%) of *N*-cyclohexyl-3-aminopyridine as a white solid. ^{1}H NMR (CDCl$_3$) δ 7.91 (d, *J* = 2.4 Hz, 1 H), 7.81 (dd, *J* = 4.8, 1.4 Hz, 1 H), 6.95 (dd, *J* = 8.0, 4.8 Hz, 1 H), 6.75 (ddd, *J* = 8.0, 2.8, 1.2 Hz, 1 H), 3.73 (s, b, 1 H), 3.10-3.21 (m, 1 H), 1.94 (dd, *J* = 13.2, 3.2 Hz, 2 H), 1.67 (dt, *J* = 13.2, 3.6 Hz, 2 H), 1.56 (dd, *J* = 12.4, 3.6 Hz, 1 H), 1.22-1.33 (m, 2 H), 1.02-1.18 (m, 3 H); ^{13}C NMR (CDCl$_3$) δ 143.25, 137.77, 136.09, 123.48, 118.39, 51.16, 32.94, 25.59, 24.68.



***N*-Phenyloctylamine.**[2] **(Table 2, entry 1).** The general procedure conducted with phenyl Chloride (0.113 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), (CyPF-^{t}Bu)PdCl$_2$ (5.0 μL from stock solution **A**, 5.0 × 10^{-5} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 203.0 mg (98%) of *N*-phenyloctylamine as a colorless liquid. ^{1}H NMR (CDCl$_3$) δ 7.09 (tt, *J* = 7.2, 2.0 Hz, 2 H), 6.60 (tt, *J* = 7.2, 1.0 Hz, 1 H), 6.50 (dd, *J* = 7.2, 2.0 Hz, 2 H), 3.47 (s, b, 1 H), 3.00 (t, *J* = 7.2 Hz, 2 H), 1.52 (quint, *J* = 7.2 Hz, 2 H), 1.21-1.32 (m, 10 H), 0.82 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (CDCl$_3$) δ 148.45, 129.11, 116.94, 112.57, 43.90, 31.79, 29.51, 29.39, 29.23, 27.14, 22.62, 14.07.

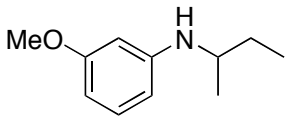


***N*-octyl-4-toluidine. (Table 2, entry 2).** The general procedure conducted with 4-chlorotoluene (0.126 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), (CyPF-^{t}Bu)PdCl$_2$ (50.0 μL from stock solution **A**, 5.0 × 10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 210 mg (96%) of *N*-octyl-4-toluidine as a colorless liquid. ^{1}H NMR (CDCl$_3$) δ 7.00 (d, *J* = 8.4 Hz, 2 H), 6.55 (d, *J* = 8.4 Hz, 2 H), 3.41 (s, b, 1 H), 3.10 (t, *J* = 7.2 Hz, 2 H), 2.26 (s, 3 H), 1.62 (quint, *J* = 7.2 Hz, 2 H), 1.31-1.43 (m, 10 H), 0.92 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (CDCl$_3$) δ 146.28, 129.65, 126.19, 112.85, 44.36, 31.81, 29.62, 29.42, 29.25, 27.18, 22.64, 20.33, 14.07. Anal. Calcd. For C$_{15}$H$_{25}$N: C, 82.13; H, 11.94; N, 6.39. Found: C, 82.33; H, 11.55; N, 6.10.

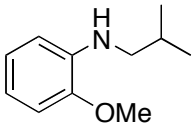


***N-sec*Butyl-3-anisidine.**[3] **(Table 2, entry 3).** The general procedure conducted with 3-chloroanisole (0.143 g, 1.00 mmol), *sec*-butylamine (0.119 g, 1.20 mmol), (CyPF-^{t}Bu)PdCl$_2$ (50.0 μL from stock solution **A**, 5.0 × 10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 133.9 mg (75%) of *N-sec*Butyl-3-anisidine as a colorless liquid. ^{1}H NMR (CDCl$_3$) δ 7.10 (t, *J* = 8.4 Hz, 1 H), 6.27 (ddd, *J* = 8.0, 2.0, 0.8 Hz, 1 H), 6.23 (ddd, *J* = 8.0, 2.0, 0.8 Hz, 1 H), 6.18 (t, *J* = 2.0 Hz, 1 H), 3.79 (s, 1 H), 3.50 (s, b, 1

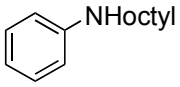
H), 3.41 (sext, J = 6.4 Hz, 1 H), 1.51-1.66 (m, 1 H), 1.44-1.55 (m, 1 H), 1.20 (d, J = 6.4 Hz, 3 H), 0.98 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 160.74, 149.00, 129.84, 106.18, 101.61, 98.86, 54.88, 49.68, 29.52, 20.12, 10.30.



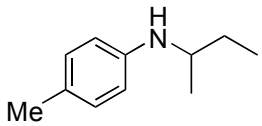
***N*-(2-Methoxyphenyl)-*iso*-butylamine. (Table 2, entry 4).** The general procedure conducted with 2-chloroanisole (0.143 g, 1.00 mmol), *iso*-butylamine (87.8 mg, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (50.0 μL from stock solution **A**, 5.0 × 10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 175.6 mg (98%) of *N*-(2-methoxyphenyl)-*iso*-butylamine as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 6.89 (td, J = 7.6, 1.2 Hz, 1 H), 6.79 (dd, J = 8.0, 1.2 Hz, 1 H), 6.67 (td, J = 7.6, 1.6 Hz, 1 H), 6.62 (dd, J = 7.6, 1.2 Hz, 1 H), 4.32 (s, b, 1 H), 3.87 (s, 3 H), 2.97 (t, J = 6.8 Hz, 2 H), 1.91-2.01 (m, 1 H), 1.02 (d, J = 6.4 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 146.63, 138.50, 121.25, 115.87, 109.65, 109.34, 55.35, 51.55, 27.95, 20.52.



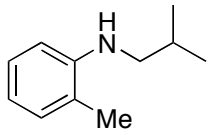
***N*-Phenyloctylamine.**[2] **(Table 2, entry 5).** The general procedure conducted with phenyl bromide (0.158 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (5.0 μL from stock solution **A**, 5.0 × 10^{-5} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 166.1mg (66%) of *N*-phenyloctylamine as a colorless liquid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 2, entry 1.)



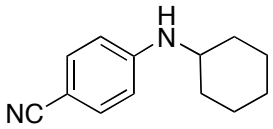
***N*-(*p*-Tolyl)-*sec*-butylamine. (Table 2, entry 6).** The general procedure conducted with 4-bromotoluene (0.171 g, 1.00 mmol), *sec*-butylamine (87.8 mg, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (50.0 μL from stock solution **A**, 5.0 × 10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 132.7 mg (81%) of *N*-(*p*-tolyl)-*sec*-butylamine as a colorless liquid. ^{1}H NMR ($CDCl_3$) δ 7.01 (d, J = 8.4 Hz, 2 H), 6.65 (dd, J = 8.4 Hz, 2 H), 3.40 (sext, J = 6.0 Hz, 1 H), 3.22 (s, b, 1 H), 2.27 (s, 3 H), 1.63 (sept, J = 6.0 Hz, 1 H), 1.49 (sept, J = 7.0 Hz, 1 H), 1.19 (d, J = 6.4 Hz, 3 H), 0.98 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 145.40, 129.70, 125.91, 113.33, 50.04, 29.59, 20.30, 20.22, 10.32; Anal. Calcd. For $C_{11}H_{17}N$: C, 80.93; H, 10.50; N, 8.58. Found: C, 80.71; H, 10.24; N, 8.66.



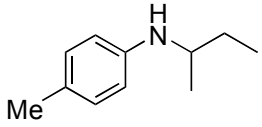
***N*-*o*-tolyl-*iso*butylamine.**[4] **(Table 2, entry 7).** The general procedure conducted with *o*-tolyl bromide (0.171 g, 1.00 mmol), *iso*-butylamine (87.8 mg, 1.20 mmol), (CyPF-^{t}Bu)PdCl$_2$ (50.0 μL from stock solution **A,** 5.0 × 10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 160.7 mg (98%) of *N*-*o*-tolyl-*iso*butylamine as a pale yellow liquid. ^{1}H NMR (CDCl$_3$) δ 7.01 (td, *J* = 7.8, 1.2 Hz, 1 H), 6.94 (dd, *J* = 7.2, 0.4 Hz, 1 H), 6.53 (td, *J* = 7.6, 1.2 Hz, 1 H), 6.49 (d, *J* = 8.0 Hz, 1 H), 3.43 (s, b, 1 H), 2.86 (d, *J* = 6.8 Hz, 2 H), 2.02 (s, 3 H), 1.78-1.88 (m, 1 H), 0.90 (d, *J* = 6.8 Hz, 6 H); ^{13}C NMR (CDCl$_3$) δ 146.28, 129.93, 127.03, 121.46, 116.43, 109.49, 51.66, 27.87, 20.48, 17.33.



***N*-(4-Cyanophenyl)-cyclohexylamine. (Table 2, entry 8).** The general procedure conducted with 4-cyano-1-bromobenzene (0.182 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), (CyPF-^{t}Bu)PdCl$_2$ (5.0 μL from stock solution **A**, 5.0 × 10^{-5} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 118.2 mg (59%) of *N*-(4-Cyanophenyl)-cyclohexylamine as a pale yellow liquid. ^{1}H NMR (CDCl$_3$) δ 7.34 (d, *J* = 8.4 Hz, 2 H), 6.49 (d, *J* = 8.4 Hz, 2 H), 4.21 (d, *J* = 7.6 Hz, 1 H), 3.21-3.29 (m, 1 H), 1.97-2.01 (m, 2 H), 1.74 (dt, *J* = 13.2, 4.0 Hz, 2 H), 1.63 (dt, *J* = 12.8, 4.0 Hz, 1 H), 1.29-1.40 (m, 2 H), 1.11-1.26 (m, 3 H); ^{13}C NMR (CDCl$_3$) δ 150.42, 133.58, 120.66, 112.19, 97.47, 51.08, 32.80, 25.54, 24.70. Anal. Calcd. For $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.85; H, 8.08; N, 13.78.

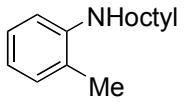


***N*-(*p*-Tolyl)-*sec*-butylamine. (Table 2, entry 9).** The general procedure conducted with 4-iodootoluene (0.228 g, 1.00 mmol), *sec*-butylamine (87.8 mg, 1.20 mmol), (CyPF-^{t}Bu)PdCl$_2$ (300.0 μL from stock solution **A**, 0.300 % mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 134.7 mg (82%) of *N*-(*p*-tolyl)-*sec*-butylamine as a colorless liquid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 2, entry 5.)

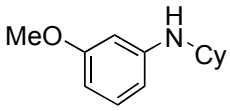


***N*-(*o*-Tolyl)octylamine. (Table 2, entry 10).** The general procedure conducted with 2-iodotoluene (0.218 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), (CyPF-^{t}Bu)PdCl$_2$ (50.0 μL from stock solution **A**, 5.0 × 10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 220 mg (98%) of *N*-(*o*-tolyl)octylamine as a yellow solid. ^{1}H NMR (CDCl$_3$) δ 7.20 (t, *J* = 7.6 Hz, 1 H), 7.12 (d, *J* = 7.2 Hz, 1 H), 6.72 (d, *J* = 7.4 Hz, 1 H), 6.69 (d, *J*

= 8.0 Hz, 1 H), 3.50 (s, b, 1 H), 3.22 (t, *J* = 7.2 Hz, 2 H), 2.21 (s, 3 H), 1.74 (quint, *J* = 7.3 Hz, 2 H), 1.38-1.52 (m, 10 H), 0.99 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 146.35, 129.92, 127.07, 121.55, 116.53, 109.52, 43.91, 31.82, 29.59, 29.42, 29.26, 27.23, 22.65, 17.38, 14.00; Anal. Calcd. For $C_{15}H_{25}N$: C, 82.13; H, 11.94; N, 6.39. Found: C, 82.23; H, 11.67; N, 6.10.



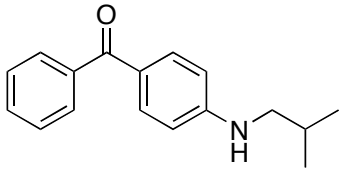
***N*-(Cyclohexylamino)-*m*-anisidine.**[2] **(Table 2, entry 11).** The general procedure conducted with 3-iodoanisole (0.234 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (50.0 μL from stock solution **A**, 5.0 × 10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 197.9 mg (96%) of *N*-(cyclohexylamino)-*m*-anisidine as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.08 (t, *J* = 8.4 Hz, 1 H), 6.26 (dd, *J* = 8.4, 2.0 Hz, 1 H), 6.23 (dd, *J* = 8.0, 2.0 Hz, 1 H), 6.18 (7, *J* = 2.0 Hz, 1 H), 3.78 (s, 3 H), 3.52 (s, b, 1 H), 3.28 (tt, *J* = 10.0, 3.8 Hz, 1 H), 2.08 (dd, *J* = 12.6, 3.0 Hz, 2 H), 1.78 (dt, *J* = 13.2, 3.6 Hz, 2 H), 1.67 (dt, *J* = 12.4, 3.6 Hz, 1 H), 1.33-1.44 (m, 2 H), 1.25 (tt, *J* = 12.0, 3.6 Hz, 1 H), 1.11-1.21 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 160.74, 148.67, 129.82, 106.24, 101.61, 98.98, 54.90, 51.57, 33.32, 25.82, 24.92.



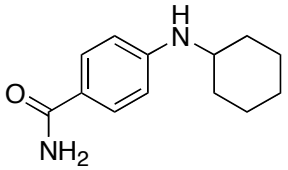
General Procedure Using $LiN(SiMe_3)_2$ as the Base for Catalytic Amination of Functionalized Aryl Iodides. The reaction conditions and average yields for each reaction are shown in Table 3. A typical procedure is given in Table 3, entry 2.

General Procedure Using K_3PO_4 as the Base for Catalytic Amination of Functionalized Aryl Iodides. The reaction conditions and average yields for each reaction are shown in Table 3. A typical procedure is given in Table 3, entry 3.

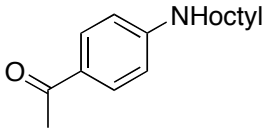
***N-iso*Butyl-4-aminobenzophenone. (Table 3, entry 1).** A solution of (CyPF-^{t}Bu)$PdCl_2$ (5.0 μL from stock solution **A**, 5.0 × 10^{-5} mmol) was added to a 4 mL vial containing 4-chlorobenzophenone (0.217 g, 1.00 mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) in 1.0 mL of DME. *iso*-Butylamine (87.8 mg, 1.20 mmol), was then added by syringe. The vial was sealed with a cap containing a PTFE septum, and the reaction mixture was stirred at 100 ºC until 4-chloro-benzophenone was consumed, as determined by GC. The reaction solution was directly adsorbed onto silica gel, and the product was isolated by silica gel chromatography, eluting with hexane/ethyl acetate (85/15) to give 200.0 mg (87%) of *N-iso*-butyl-4-aminobenzophenone as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.68-7.73 (m, 4 H), 7.50 (tt, *J* = 7.6, 2.0 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 6.55 (d, *J* = 8.8 Hz, 2 H), 4.40 (t, *J* = 5.6 Hz, 1 H), 2.99 (t, *J* = 6.4 Hz, 2 H), 1.89 (hept, *J* = 6.8 Hz, 1 H), 0.97 (d, *J* = 6.8 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 195.06, 152.33, 139.14, 132.99, 131.08, 129.36, 127.94, 125.56, 111.10, 50.93, 27.97, 20.32. Anal. Calcd. For $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.57; H, 7.63; N, 5.65.



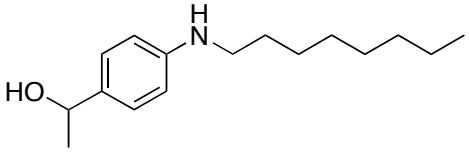
4-*N*-Cyclohexylamino-benzamide (Table 3, entry 2). 4-Chlorobenzamide (0.170 g, 1.00 mmol) was added to a 4 mL vial containing (CyPF-^{t}Bu)$PdCl_2$ (3.7 mg, 0.5 mmol%) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) in 1.0 mL of DME. Cyclohexylamine (0.119 g, 1.20 mmol) was then added by syringe. The vial was sealed with a cap containing a PTFE septum, and the reaction mixture was stirred at 100° C for 20 h. The reaction mixture then was allowed to cool to room temperature. To the reaction mixture was added 1 M HCl (0.5-1.0 mL). The mixture was stirred at room temperature for 5 min and was then extracted with CH_2Cl_2 (3 × 30.0 mL). The organic layer was separated and dried over Na_2SO_4. The solvent was evaporated, and the crude product was isolated by silica gel chromatography, eluting with hexane/ethyl acetate (50/50) to give 114.4 mg (52%) of 4-*N*-cyclohexylamino-benzamide as a white solid. ^{1}H NMR (CD_3OD) δ 7.59 (d, *J* = 8.5 Hz, 2 H), 6.50 (d, *J* = 8.5 Hz, 2 H), 3.17-3.24 (m, 1 H), 1.93 (dd, *J* = 12.0, 2.5 Hz, 2 H), 1.70 (dt, *J* = 13.5, 3.5 Hz, 2 H), 1.58 (dt, *J* = 12.5, 3.5 Hz, 1 H), 1.28-1.37 (m, 2 H), 1.09-1.20 (m, 3 H); ^{13}C NMR (CD_3OD) δ 172.80, 152.80, 130.52, 120.66, 112.56, 52.28, 33.97, 26.97, 26.09.



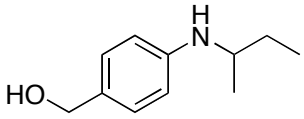
4'-*N*-octylamino-acetophenone (Table 3, entry 3). Octylamine (0.155 g, 1.20 mmol) was added to a 4 mL vial containing (CyPF-^{t}Bu)$PdCl_2$ (3.7 mg, 0.5 mmol%), 4'-Chloro-acetophenone (0.155 g, 1.00 mmol) and potassium phosphate (0.254 g, 1.40 mmol) in 1.0 mL of DME. The vial was sealed with a cap containing a PTFE septum, and the reaction mixture was stirred at 110 ºC until 4'-iodoacetophenone was consumed, as determined by GC. The reaction solution was directly adsorbed onto silica gel, and the product was isolated by eluting with hexane/ethyl acetate (75/25) to give 164.7 mg (67%) of 4'-*N*-octylamino-acetophenone as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.78 (d, *J* = 8.8 Hz, 2 H), 6.51 (d, *J* = 8.8 Hz, 2 H), 4.1 (s, b, 1H), 3.13 (q, *J* = 6.4 Hz, 2 H), 2.46 (s, 3 H), 1.60 (quint, *J* = 7.2 Hz, 2 H), 1.25-1.36 (m, 10 H), 0.86 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 196.13, 152.34, 130.72, 126.25, 111.13, 43.23, 31.70, 29.25, 29.21, 29.13, 26.98, 25.84, 22.55, 13.98. Anal. Calcd. For $C_{16}H_{25}NO$: C, 77.68; H, 10.19; N, 5.66. Found: C, 77.59; H, 10.32; N, 5.58.



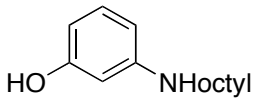
1-(4-*N*-octylamino-phenyl)-ethanol. (Table 3, entry 4) The general procedure conducted with 4-chlorophenyl-1-ethanol (0.157 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), (CyPF-^{t}Bu)PdCl$_2$ (3.7 mg, 0.5 mmol%) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 192.6 mg (77%) of 1-(4-*N*-octylamino-phenyl)-ethanol as a pale yellow liquid. ^{1}H NMR (CDCl$_3$) δ 7.16 (d, *J* = 8.4 Hz, 2 H), 6.56 (d, *J* = 8.4 Hz, 2 H), 4.75 (q, *J* = 6.4 Hz, 1 H), 3.20-4.20 (s, b, 1 H), 3.07 (t, *J* = 7.0 Hz, 2 H), 1.6-2.1 (s, b, 1 H), 1.59 (quint, *J* = 7.0 Hz, 2 H), 1.44 (d, *J* = 6.4 Hz, 3 H), 1.23-1.40 (m, 10 H), 0.88 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (CDCl$_3$) δ 147.96, 134.23, 126.56, 112.51, 70.09, 44.01, 31.76, 29.45, 29.35, 29.20, 27.10, 24.61, 22.60, 14.06. Anal. Calcd. For $C_{16}H_{27}NO$: C, 77.06; H, 10.91; N, 5.62. Found: C, 77.36; H, 11.00; N, 5.61.



4-*N*-*sec*-Butylamino-benzylalcohol (Table 3, entry 5) The general procedure conducted with 4-bromobenzylalcohol (0.187 g, 1.00 mmol), *sec*-butylamine (87.8 mg, 1.20 mmol), (CyPF-^{t}Bu)PdCl$_2$ (3.7 mg, 0.5 mmol%) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 127.1 mg (71%) of 4-*N*-*sec*butylamino-benzylalcohol as a yellow liquid. ^{1}H NMR (CDCl$_3$) δ 7.14 (d, *J* = 8.5 Hz, 2 H), 6.54 (dd, *J* = 8.5 Hz, 2 H), 4.50 (s, 2 H), 3.40-3.90 (s, br, 1 H), 3.38 (sext, *J* = 6.5 Hz, 1 H), 1.50-1.90 (s, br, 1 H), 1.54-1.62 (m, 1 H), 1.41-1.50 (m, 1 H), 1.15 (d, *J* = 6.5 Hz, 3 H), 0.93 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (CDCl$_3$) δ 147.40, 129.08, 128.90, 112.98, 65.31, 49.74, 29.47, 20.10, 10.27. Anal. Calcd. For $C_{10}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.22; H, 9.68; N, 7.64.

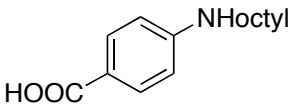


3-Hydroxy-*N*-octyl-aniline.[5] **(Table 3, entry 6)** The general procedure conducted with 3-bromophenol (0.172 g, 1.00 mmol), octylamine (0.155g, 1.20 mmol), (CyPF-^{t}Bu)PdCl$_2$ (50.0 μL from stock solution **A**, 5.0 × 10^{-4} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 179.3 mg (81%) of 3-hydroxy-*N*-octyl-aniline as a pale yellow solid. ^{1}H NMR (CDCl$_3$) δ 6.99 (t, *J* = 8.0 Hz, 1 H), 6.20 (dd, *J* = 7.4, 2.0 Hz, 1 H), 6.17 (dd, *J* = 7.4, 2.0 Hz, 1 H), 6.06 (t, *J* = 2.0 Hz, 1 H), 4.20-5.20 (s, b, 2H), 3.00 (t, *J* = 7.2 Hz, 2 H), 1.56 (quint, *J* = 7.2 Hz, 2 H), 1.27-1.35 (m, 10 H), 0.89 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (CDCl$_3$) δ 156.67, 149.73, 130.11, 106.10, 104.93, 100.40, 44.24, 31.76, 29.34, 29.32, 29.21, 27.07, 22.60, 14.05.

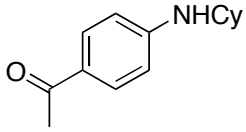


4-*N*-Octylamino-benzoic acid. (Table 3, entry 7) The general procedure conducted with 4-bromobenzoic acid (0.201 g, 1.00 mmol), octylamine (0.155g, 1.20 mmol), (CyPF-^{t}Bu)PdCl$_2$ (50.0 μL from stock solution **A**, 5.0 × 10^{-4} mmol) and lithium

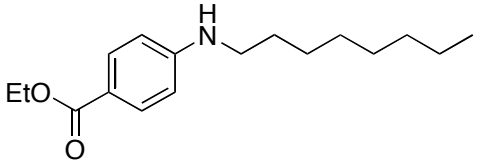
bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 178.4 mg (92%) 4-*N*-Octylamino-benzoic acid as a white solid. ^{1}H NMR (CD_3OD) δ 7.75 (d, *J* = 9.2 Hz, 2 H), 6.55 (d, *J* = 9.2 Hz, 2 H), 4.70-5.20 (s, b, 2 H), 3.09 (t, *J* = 7.2 Hz, 2 H), 1.59 (quint, *J* = 7.2 Hz, 2 H), 1.27-1.35 (m, 10 H), 0.88 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (CD_3OD) δ 171.02, 154.82, 132.92, 117.93, 112.09, 44.15, 33.17, 30.72, 30.60, 30.31, 28.40, 23.89, 14.62. Anal. Calcd. For: $C_{15}H_{23}NO_2$ C, 72.25; H, 9.30; N, 5.62. Found: C, 72.19; H, 9.43; N, 5.56.



4-*N*-cyclohexylamino-acetophenone (Table 3, entry 8) The general procedure conducted with 4'-bromo-acetophenone (0.199 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (5.5 mg, 1.0 mmol%) and potassium phosphate (0.254 g, 1.40 mmol) gave 163.6 mg (75%) of 4-*N*-cyclohexylamino-acetophenone as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.76 (dt, *J* = 9.0, 2.0 Hz, 2 H), 6.49 (dt, *J* = 9.0, 2.0 Hz, 2 H), 4.27 (s, b, 1H), 3.28-3.32 (m, 1 H), 2.44 (s, 3 H), 2.00 (dd, *J* = 12.5, 3.0 Hz, 2 H), 1.73 (dt, *J* = 13.0, 4.0 Hz, 2 H), 1.62 (dt, *J* = 13.0, 4.0 Hz, 1 H), 1.30-1.39 (m, 2 H), 1.12-1.23 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 196.09, 151.29, 130.75, 125.88, 111.36, 51.09, 32.92, 25.79, 25.57, 24.70. Anal. Calcd. For: $C_{14}H_{19}NO$ C, 77.38; H, 8.81; N, 6.45. Found: C, 77.44; H, 8.95; N, 6.55.

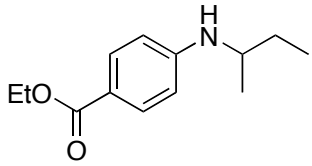


Ethyl-4-(octylamino)-benzoate (Table 3, entry 9). The general procedure conducted with ethyl-4-bromobenzoate (0.229 mg, 1.00 mmol), octylamine (0.155g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (3.7 mg, 0.5 mmol%) and potassium phosphate (0.254 mg, 1.40 mmol) gave 243.5 mg (88%) of Ethyl-4-(octylamino)-benzoate as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.84 (d, *J* = 8.8 Hz, 2 H), 6.51 (d, *J* = 8.8 Hz, 2 H), 4.29 (q, *J* = 6.8 Hz, 2 H), 4.12 (t, J = 5.0 Hz, 1 H), 3.12 (q, *J* = 6.8 Hz, 2 H), 1.59 (hept, *J* = 7.2 Hz, 2 H), 1.25-1.40 (m, 10 H), 0.86 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.87, 152.02, 131.41, 118.14, 111.16, 60.07, 43.29, 31.74, 29.30, 29.22, 29.17, 27.01, 22.59, 14.40, 14.05. Anal. Calcd. For: $C_{17}H_{27}NO_2$ C, 73.61; H, 9.81; N, 5.05. Found: C, 73.95; H, 9.88; N, 5.22.

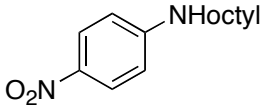


Ethyl-4-(*sec*-butylamino)-benzoate (Table 3, entry 10). The general procedure conducted with ethyl-4-iodobenzoate (0.276 mg, 1.00 mmol), *sec*-butylamine (87.8 mg, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (11.0 mg, 2.0 mmol%) and potassium phosphate (0.254 mg, 1.40 mmol) gave 157.0 mg (71%) of Ethyl-4-(*sec*-butylamino)-benzoate as a white

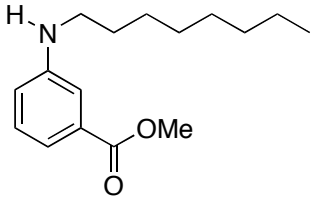
solid. ^{1}H NMR ($CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2 H), 6.49 (d, *J* = 8.5 Hz, 2 H), 4.29 (q, *J* = 7.0 Hz, 2 H), 3.98 (d, *J* = 6.0 Hz, 1 H), 3.44 (hept, *J* = 6.5 Hz, 1 H), 1.44-1.62 (m, 2 H), 1.33 (t, *J* = 7.0 Hz, 3 H), 1.16 (d, *J* = 6.5 Hz, 3 H), 0.93 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.87, 151.36, 131.50, 117.84, 111.50, 60.02, 49.36, 29.43, 19.98, 14.38, 10.24. Anal. Calcd. For: $C_{13}H_{19}NO_2$ C, 70.56; H, 8.65; N, 6.33. Found: C, 70.46; H, 8.64; N, 6.23.



4-Nitro-*N*-octyl-aniline (Table 3, entry 11). The general procedure conducted with 4-Nitro-1-iodobenzene (0.249 mg, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (5.5 mg, 1.0 mmol%) and potassium phosphate (0.254 g, 1.40 mmol) gave 213.6 mg (85%) of 4-Nitro-*N*-octyl-aniline as a white solid. ^{1}H NMR ($CDCl_3$) δ 8.05 (d, *J* = 9.0 Hz, 2 H), 6.49 (d, *J* = 9.0 Hz, 2 H), 4.55 (s, 1 H), 3.17 (q, *J* = 7.0 Hz, 2 H), 1.62 (quint, *J* = 7.0 Hz, 2 H), 1.21-1.39 (m, 10 H), 0.86 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 153.49, 137.60, 126.46, 110.83, 43.35, 31.70, 29.21, 29.13, 29.02, 26.92, 22.57, 14.03. Anal. Calcd. For $C_{14}H_{22}N_2O_2$: C, 67.17; H, 8.86; N, 11.19. Found: C, 67.09; H, 8.99; N, 11.11.

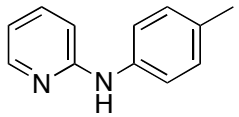


Ethyl-3-(octylamino)-benzoate (Table 3, entry 12). The general procedure conducted with ethyl-4-chlorobenzoate (0.171 mg, 1.00 mmol), octylamine (0.155g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (7.4 mg, 1.0 mmol%) and potassium phosphate (0.254 g, 1.40 mmol) gave 233.9 mg (89%) of Ethyl-3-(octylamino)-benzoate as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.26 (d, *J* = 7.6 Hz, 1 H), 7.18 (d, *J* = 2.4 Hz, 1 H), 7.12 (t, *J* = 7.6 Hz, 1 H), 6.68 (dd, *J* = 8.0, 2.4 Hz, 1 H), 3.80 (s, 3 H), 3.70 (s, b, 1 H), 3.04 (t, *J* = 7.0 Hz, 2 H), 1.53 (quint, *J* = 7.2 Hz, 2 H), 1.10-1.35 (m, 10 H), 0.81 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 167.53, 148.43, 130.86, 129.01, 118.04, 117.07, 113.03, 51.93, 43.80, 31.75, 29.32, 29.36, 29.19, 27.06, 22.59, 14.04. Anal. Calcd. For: $C_{17}H_{27}NO_2$ C, 72.96; H, 9.57; N, 5.32. Found: C, 72.75; H,9.68; N, 5.31.

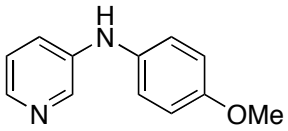


***N*-2-pyridyl-*p*-toluidine. (Table 4, entry 1).** The general procedure conducted with 2-bromopyridine (0.158 g, 1.00 mmol), *p*-toluidine (0.129 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (50.0 μL from stock solution **A**, 5.0 × 10^{-5} mmol) and sodium *tert*-butoxide (0.135 g, 1.40

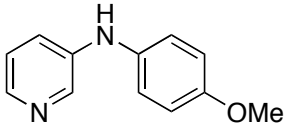
mmol) gave 168.4 mg (92%) of *N*-2-pyridyl-*p*-toluidine as a white solid. ^{1}H NMR ($CDCl_3$) δ 8.18 (dd, *J* = 5.2, 1.2 Hz, 1 H), 7.47 (ddd, *J* = 8.6, 6.6, 1.6 Hz, 1 H), 7.21 (d, *J* = 8.4 Hz, 2 H), 7.15 (d, *J* = 8.4 Hz, 2 H), 6.83 (d, *J* = 8.4 Hz, 1 H), 6.70 (dd, *J* = 6.6, 5.4 Hz, 1 H), 6.85 (s, br, 1 H), 2.34 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 156.73, 148.02, 137.83, 137.59, 132.47, 129.68, 121.21, 114.14, 107.45, 20.71. Anal. Calcd. For $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C, 73.08; H, 6.50; N, 15.14.



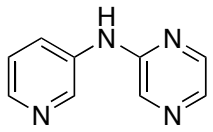
***N*-3-pyridyl-*p*-anisidine. (Table 4, entry 2).** The general procedure conducted with 3-chloropyridine (0.113 g, 1.00 mmol), *p*-anisidine (0.148 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (100.0 μL from stock solution **A**, 5.0 × 10^{-5} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 177.2 mg (89%) of *N*-3-pyridyl-*p*-anisidine as a white solid. ^{1}H NMR ($CDCl_3$) δ 8.22 (d, *J* = 2.8 Hz, 1 H), 8.03 (dd, *J* = 4.4, 1.0 Hz, 1 H), 7.18 (ddd, *J* = 8.0, 2.4, 1.4 Hz, 1 H), 7.05-7.09 (m, 1 H), 7.05 (d, *J* = 8.8 Hz, 2 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 5.84 (s, br, 1 H), 3.77 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 155.73, 141.70, 140.33, 138.17, 134.32, 123.64, 122.55, 121.02, 114.74, 55.49. Anal. Calcd. For $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 71.93; H, 6.08; N, 14.03.



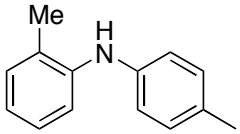
***N*-3-pyridyl-*p*-anisidine. (Table 4, entry 3).** The general procedure conducted with 3-bromopyridine (0.158 g, 1.00 mmol), *p*-anisidine (0.148 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (50.0 μL from stock solution **A**, 5.0 × 10^{-5} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 164.5 mg (83%) of *N*-3-pyridyl-*p*-anisidine as a white solid. (^{1}H and ^{13}CNMR spectra are the same as those for the product in Table 4, entry 2.)



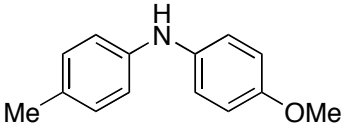
***N*-3-pyridyl-2-pyrazinamine. (Table 4, entry 4).** The general procedure conducted with 3-bromopyridine (0.158 g, 1.00 mmol), 2-aminopyrazine (0.113 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (7.3 mg, 1.0 × 10^{-2} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 158.1 mg (92%) of *N*-3-pyridyl-2-pyrazinamine as a white solid. ^{1}H NMR (CD_3OD) δ 8.75 (d, *J* = 2.5 Hz, 1 H), 8.42 (ddd, *J* = 8.0, 2.5, 1.0 Hz, 1 H), 8.07-8.08 (m, 2 H), 8.04 (dd, *J* = 4.5, 1.0 Hz, 1 H), 7.84 (d, *J* = 4.5 Hz, 1 H), 7.27 (dd, *J* = 8.5, 4.5Hz, 1 H); ^{13}C NMR (CD_3OD) δ 153.92, 142.80, 142.69, 140.70, 139.47, 135.77, 135.08, 127.24, 125.15.



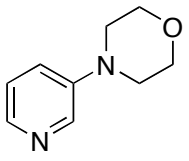
***N*-(*o*-Tolyl)-*p*-toluidine[4]. (Table 4, entry 5).** The general procedure conducted with *o*-tolyl bromide (0.171 g, 1.00 mmol), *p*-toluidine (0.129 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (50.0 μL from stock solution **A,** 5.0×10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 188.1 mg (95%) of *N*-(*o*-Tolyl)-*p*-toluidine as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.05 (d, *J* = 8.0 Hz, 2 H), 6.99 (t, *J* = 6.8 Hz, 1 H), 6.95 (d, *J* = 8.0 Hz, 2 H), 6.74-6.79 (m, 3 H), 5.14 (s, br, 1 H), 2.18 (s, 3 H), 2.11 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 141.97, 140.99, 130.76, 130.29, 129.75, 126.98, 126.67, 121.03, 118.54, 117.25, 20.59, 17.77.



***N*-*p*-tolyl-*p*-anisidine[6]. (Table 4, entry 6).** The general procedure conducted with *p*-tolyl bromide (0.171 g, 1.00 mmol), *p*-anisidine (0.148 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (50.0 μL from stock solution **A,** 5.0×10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 209.8 mg (98%) of *N*-*p*-tolyl-*p*-anisidine as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.05 (d, *J* = 8.4 Hz, 2 H), 7.03 (d, *J* = 7.6 Hz, 2 H), 6.84-6.88 (m, 4 H), 5.40 (s, br, 1 H), 3.80 (s, 3 H), 2.27 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 154.64, 142.27, 136.50, 129.72, 129.17, 120.95, 116.43, 114.55, 55.48, 20.49.

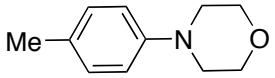


3-Pyridylmorpholine.[1] (Table 5, entry 1). The general procedure conducted with 3-bromopryidine (0.58 g, 1.00 mm0l), morpholine (0.105 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (3.7 mg, 5.0×10^{-3} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 125.0 mg (76%) of 3-Pyridylmorpholine as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 8.22 (s, 1 H), 8.04 (s, 1 H), 7.10 (s, 2 H), 3.79 (t, *J* = 4.5 Hz, 4 H), 3.11 (t, *J* = 4.5 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 146.75, 140.83, 138.00, 123.41, 121.99, 66.46, 48.34.

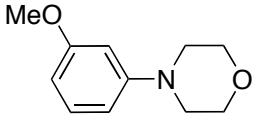


***p*-Tolylmorpholine.[7] (Table 5, entry 2).** The general procedure conducted with *p*-tolyl bromide (0.171 g, 1.00 mm0l), morpholine (0.105 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (3.7 mg, 5.0×10^{-3} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 158.9 mg

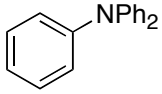
(90%) of *p*-tolylmorpholine as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.09 (d, J = 8.0 Hz, 2 H), 6.83 (d, J = 8.5 Hz, 2 H), 3.85 (t, J = 5.0 Hz, 4 H), 3.10 (t, J = 5.0 Hz, 4 H), 2.27 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 149.16, 129.68, 129.53, 115.99, 66.92, 49.84, 20.36.



***N*-(3-Methoxyphenyl)morpholine.[7] (Table 5, entry 3).** The general procedure conducted with 3-bromoanisole (0.187 g, 1.00 mm0l), morpholine (0.105 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (50.0 μL from stock solution **A,** 5.0 × 10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 171.7 mg (89%) of *N*-(3-methoxyphenyl)morpholine as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.18 (t, J = 8.5 Hz, 1 H), 6.53 (ddd, J = 8.0, 2.0, 1.0 Hz, 1 H), 6.42-6.45 (m, 2 H), 3.84 (t, J = 5.0 Hz, 4 H), 3.78 (s, 3 H), 3.14 (t, J = 5.0 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 160.00, 152.67, 129.83, 108.43, 104.68, 102.18, 66.86, 55.15, 49.25.



Triphenylamine.[8] (Table 5, entry 4). The general procedure conducted with phenyl bromide (0.157 g, 1.00 mm0l), diphenylamine (0.203 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (3.7 mg, 5.0 × 10^{-3} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 197.8 mg (81%) of triphenylamine as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.27 (tt, J = 7.5, 2.0 Hz, 6 H), 7.12 (dd, J = 8.5, 1.0 Hz, 6 H), 7.03 (tt, J = 7.5, 1.5 Hz, 3 H), 3.35 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 147.82, 129.18, 124.13, 122.63.



***N*-Methyldiphenylamine.[8] (Table 5, entry 5).** The general procedure conducted with phenyl bromide (0.157 g, 1.00 mm0l), *N*-methylaniline (0.129 g, 1.20 mmol), (CyPF-^{t}Bu)$PdCl_2$ (50.0 μL from stock solution **A,** 5.0 × 10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 126.0 mg (69%) of *N*-Methyldiphenylamine as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.31 (t, J = 8.5 Hz, 4 H), 7.06 (dd, J = 8.5, 1.0 Hz, 4 H), 6.99 (tt, J = 8.5, 1.0 Hz, 2 H), 3.35 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 148.97, 129.16, 121.21, 120.39, 40.18.

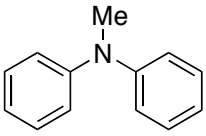


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Table 1, entry 3, N-Cyclohexyl-3-aminopyridine

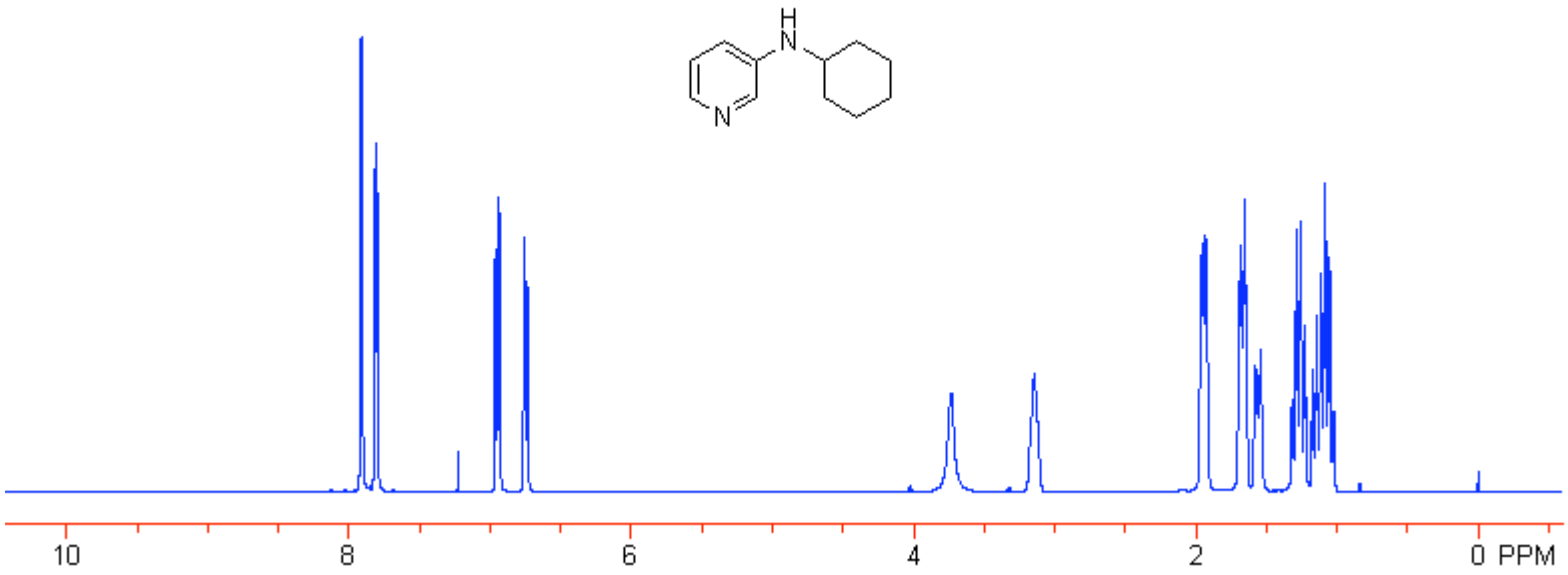


Table 1, entry 3, *N*-Cyclohexyl-3-aminopyridine

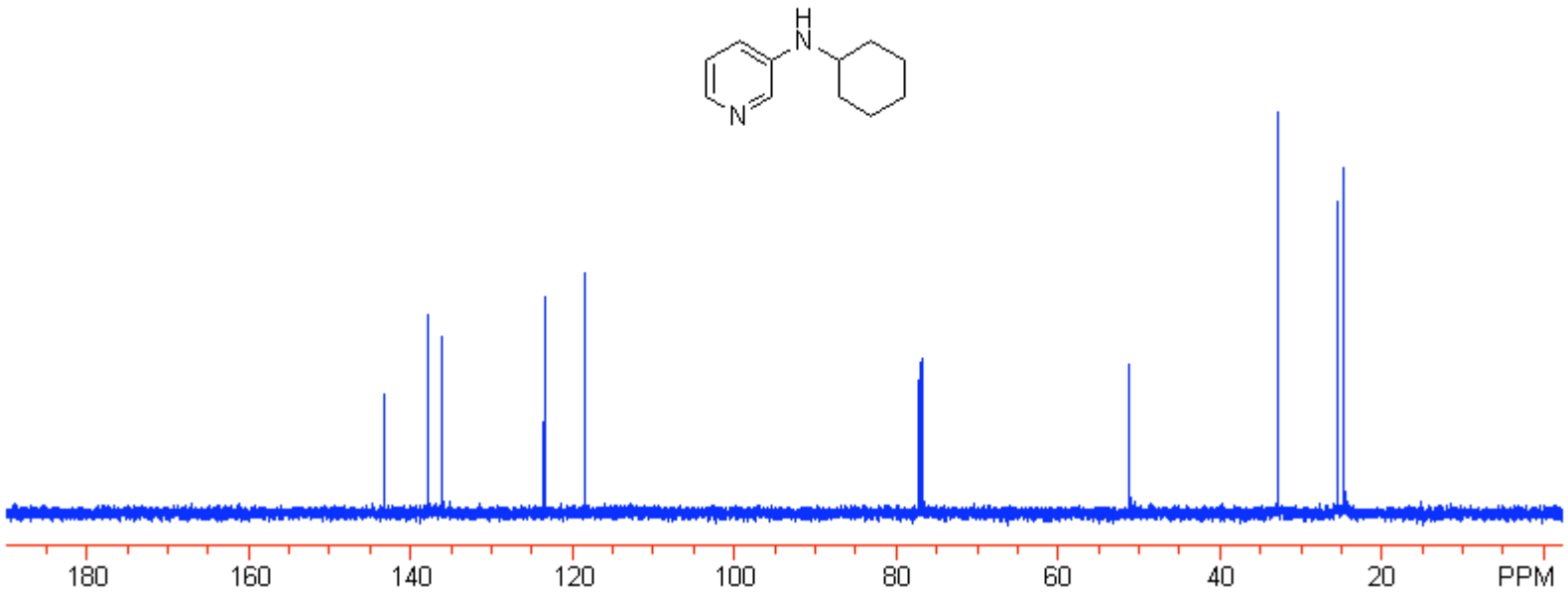
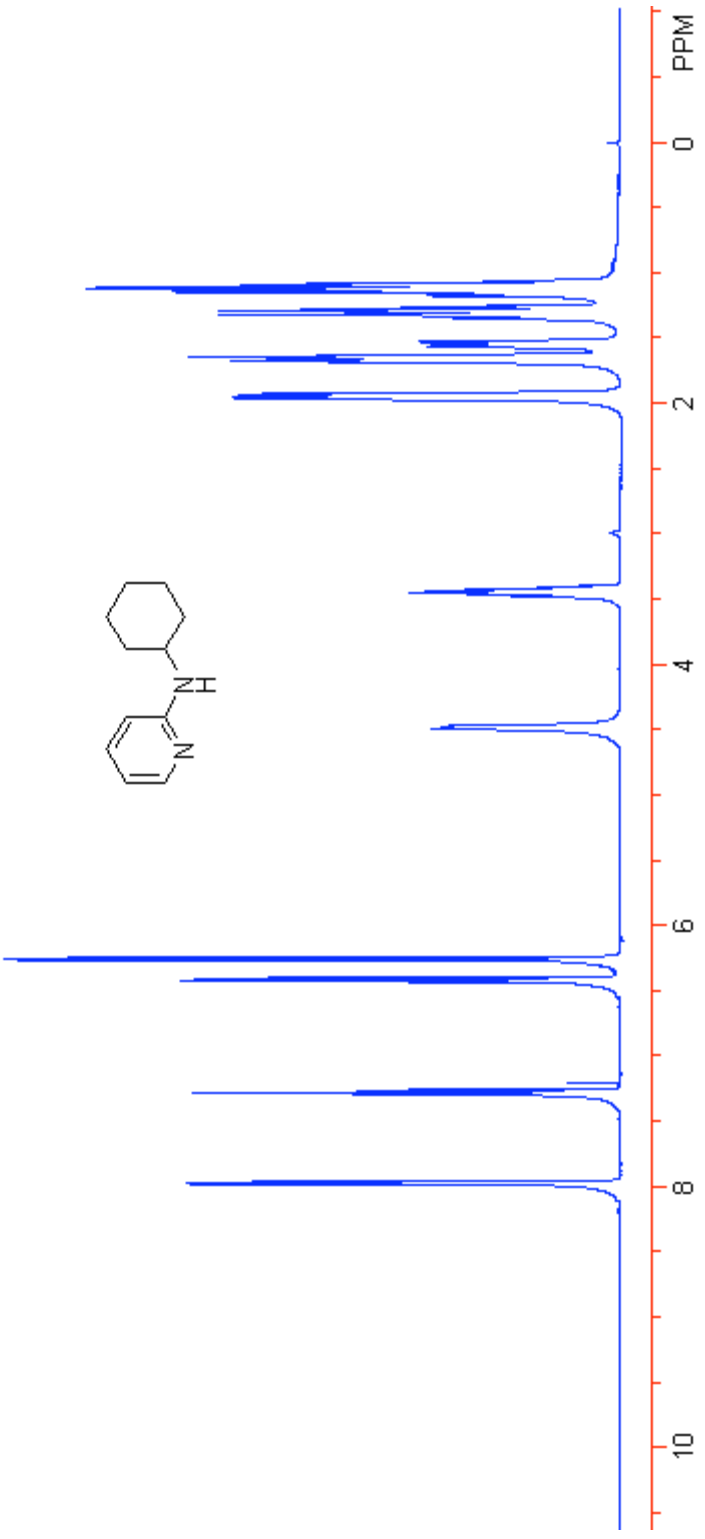


Table 1, entry 4, *N*-Cyclohexyl-2-aminopyridine



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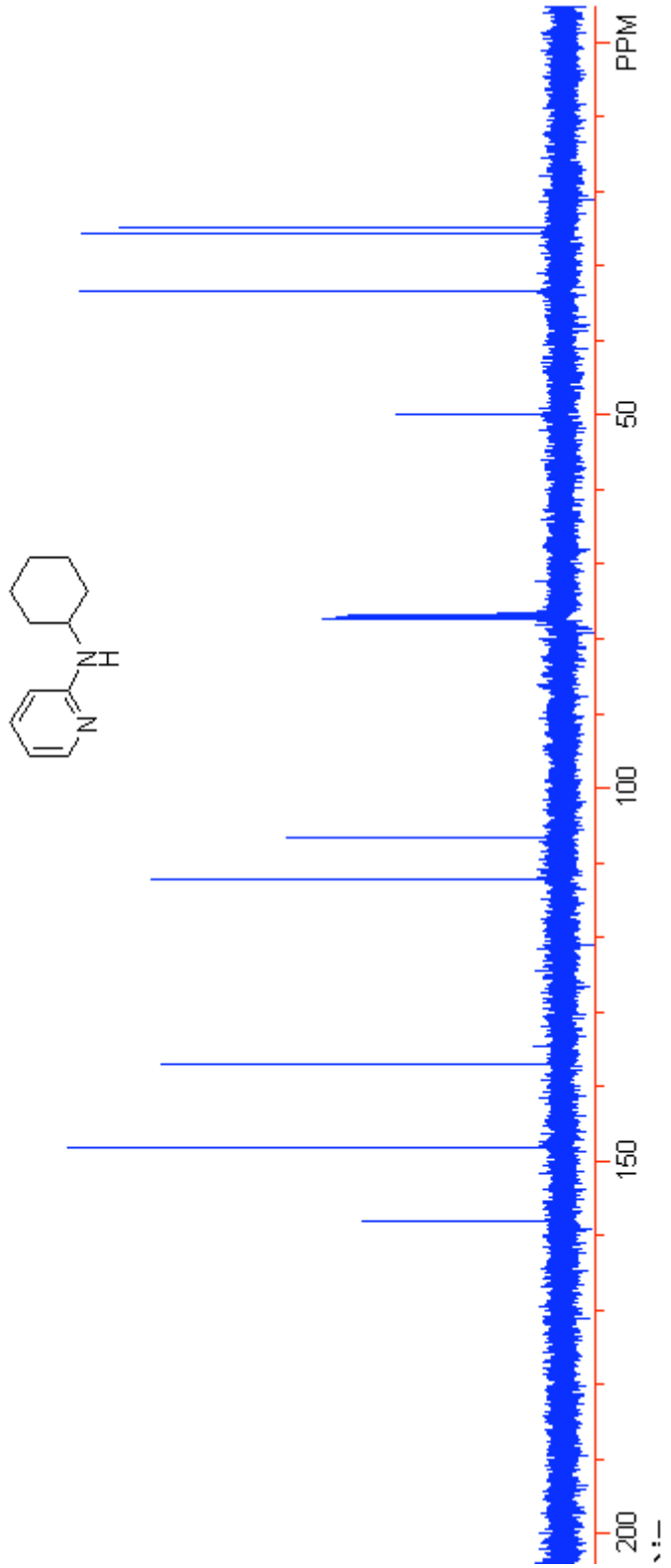


Table 2, entry 1, *N*-Phenyloctylamine

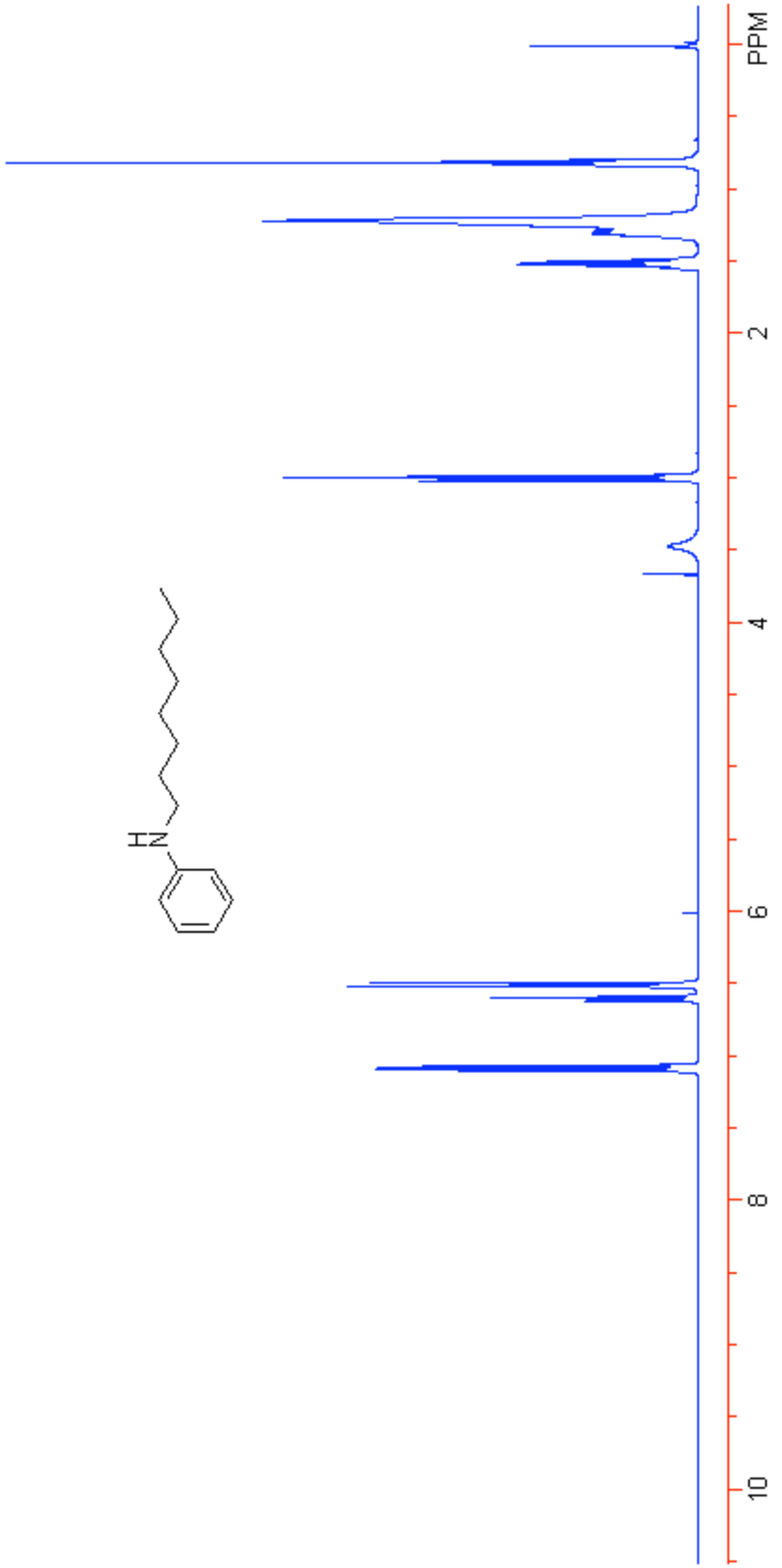


Table 2, entry 1, *N*-Phenyloctylamine

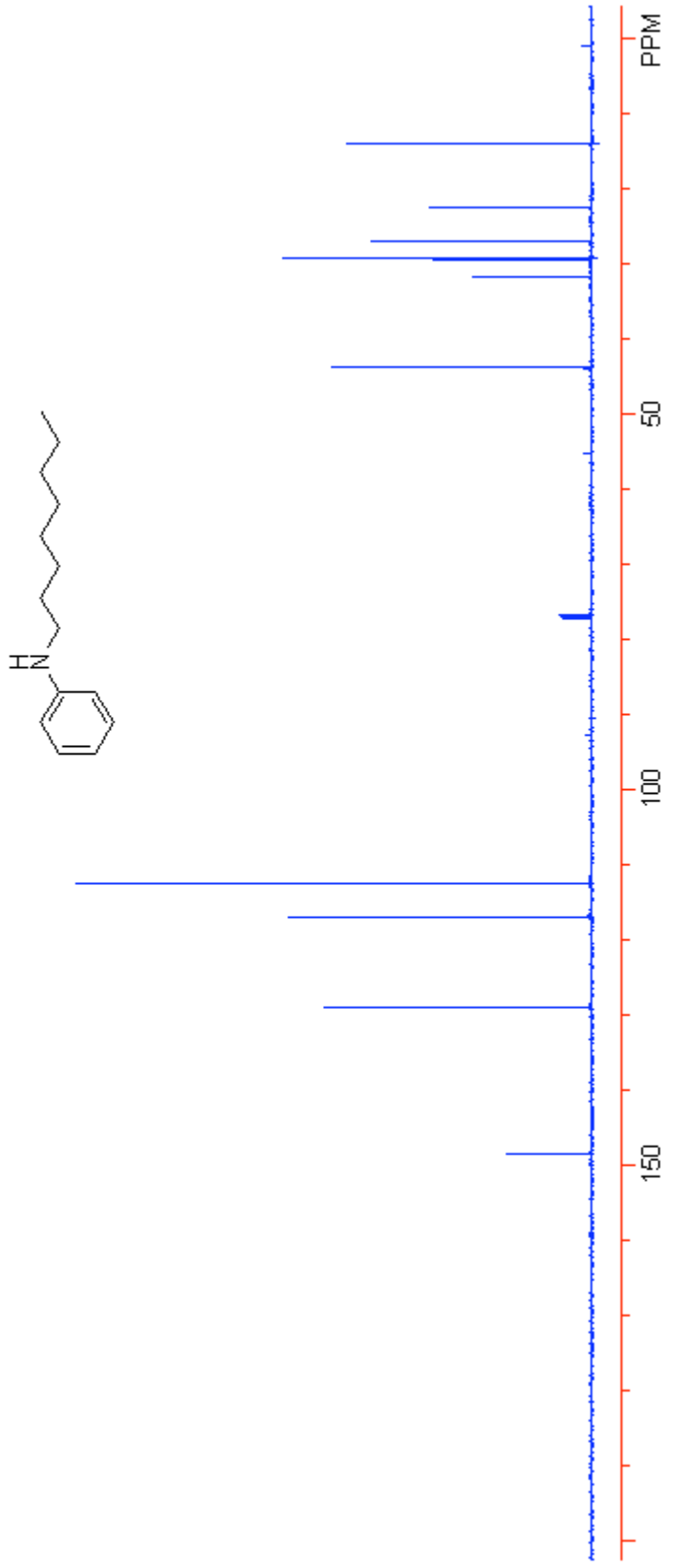


Table 2, entry 3, *N-sec*Butyl-3-anisidine

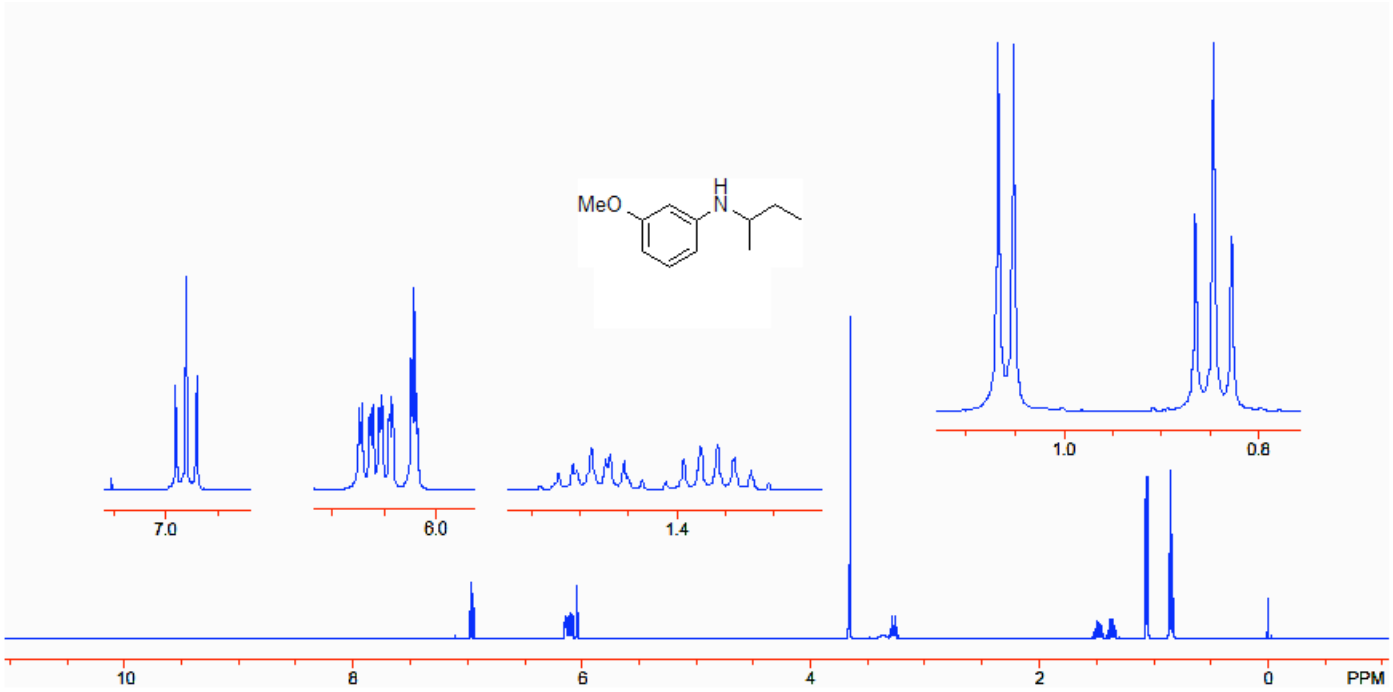


Table 2, entry 3, *N-sec*Butyl-3-anisidine

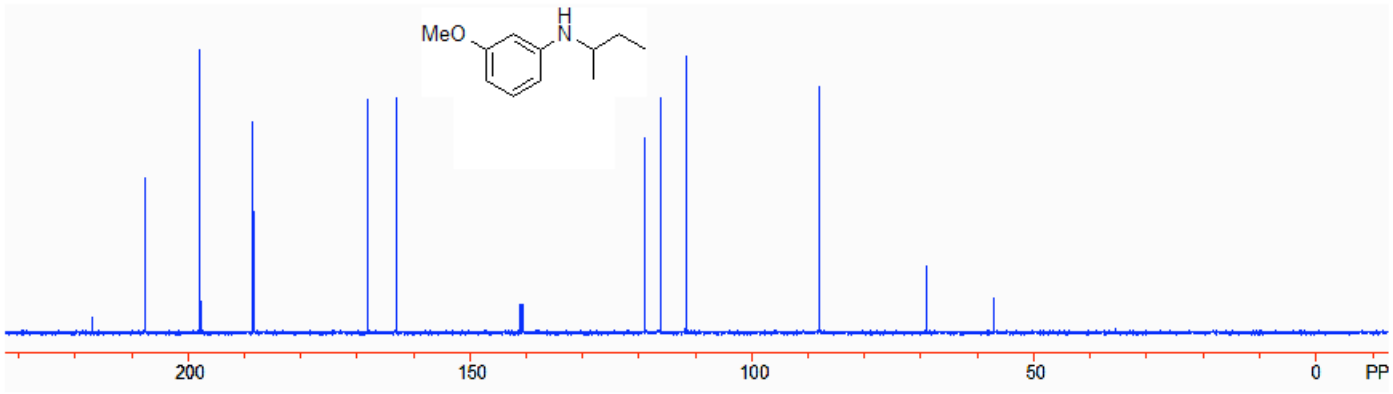


Table 2, entry 7, N-*o*-Tolyl-*iso*butylamine

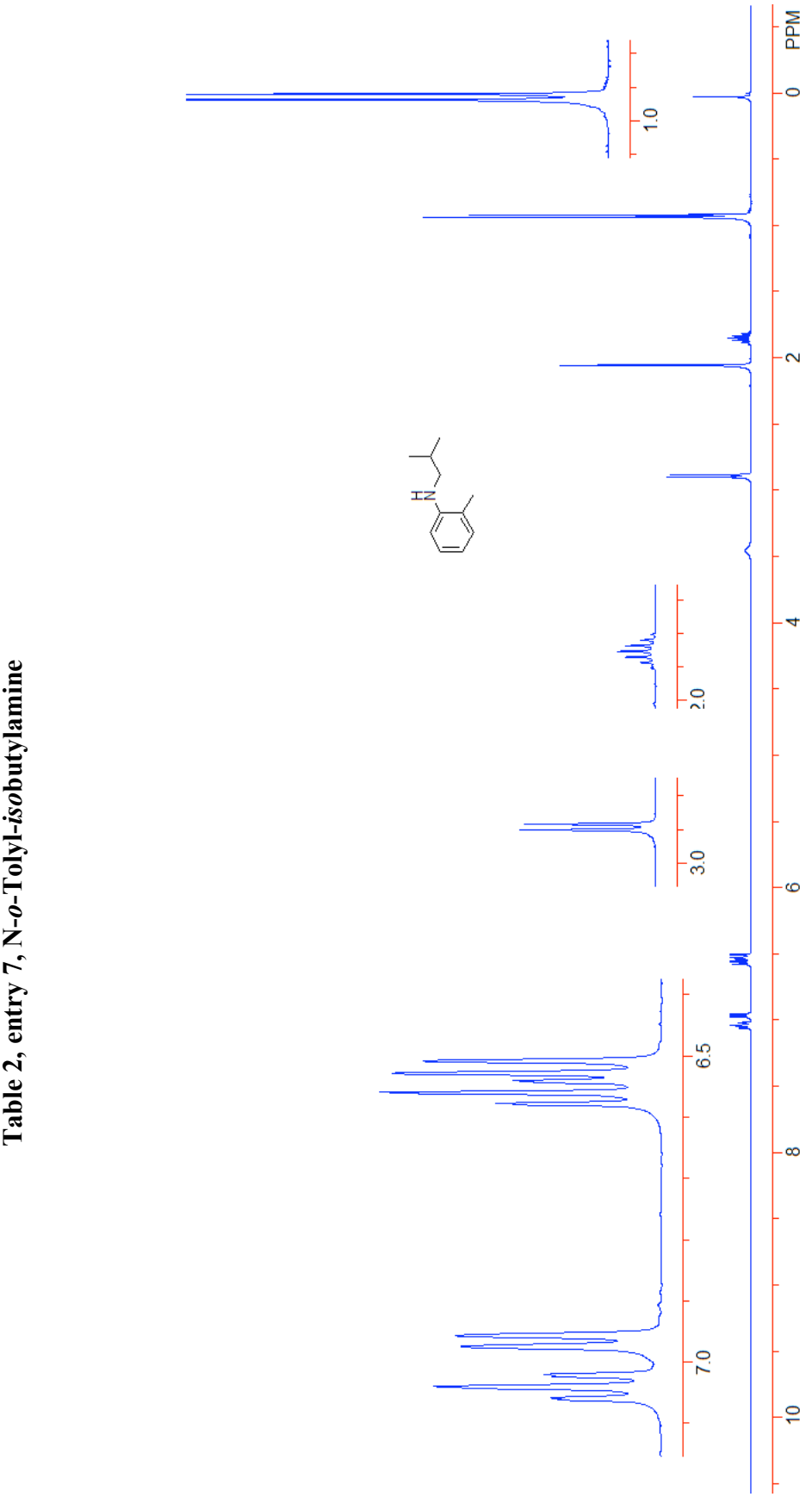


Table 2, entry 7, N-*o*-Tolyl-*iso*butylamine

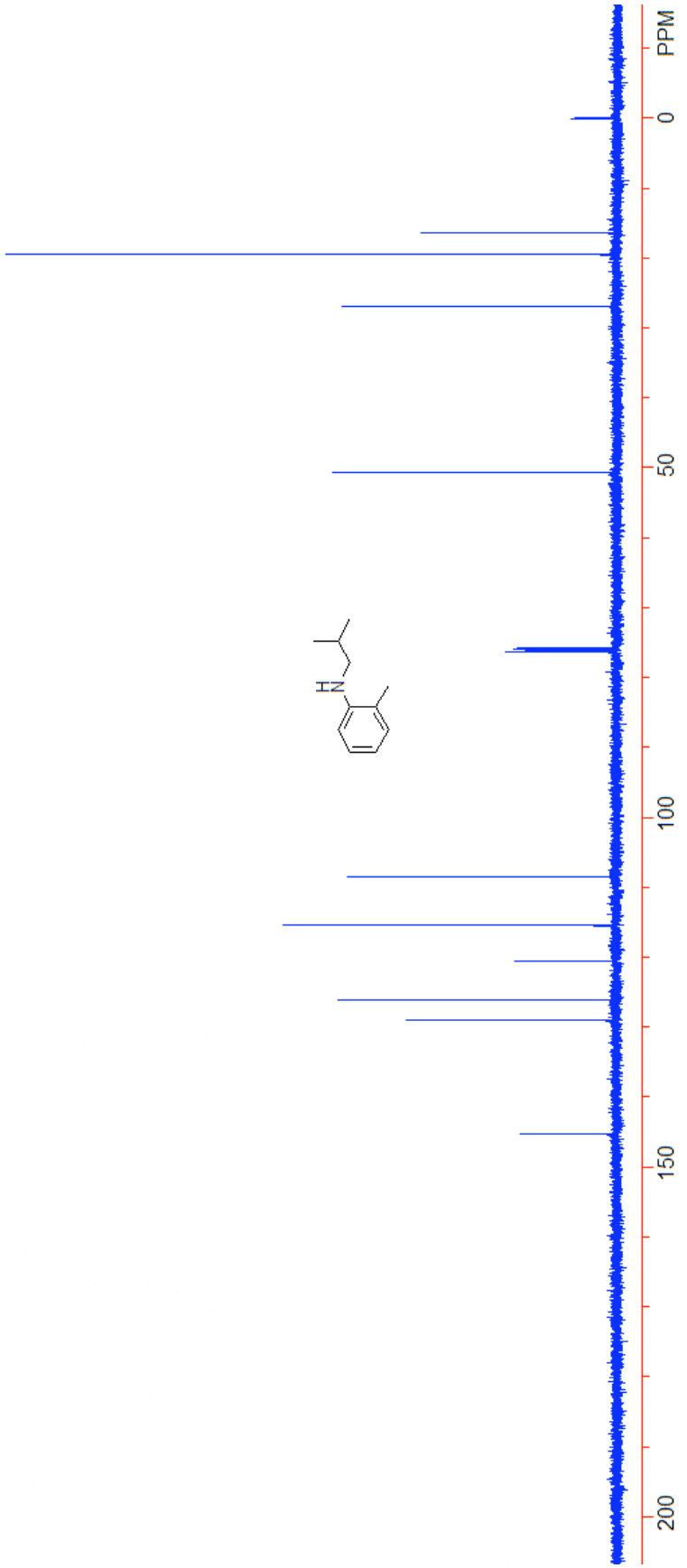


Table 2, entry 11, *N*-(Cyclohexylamino)-*m*-anisidine

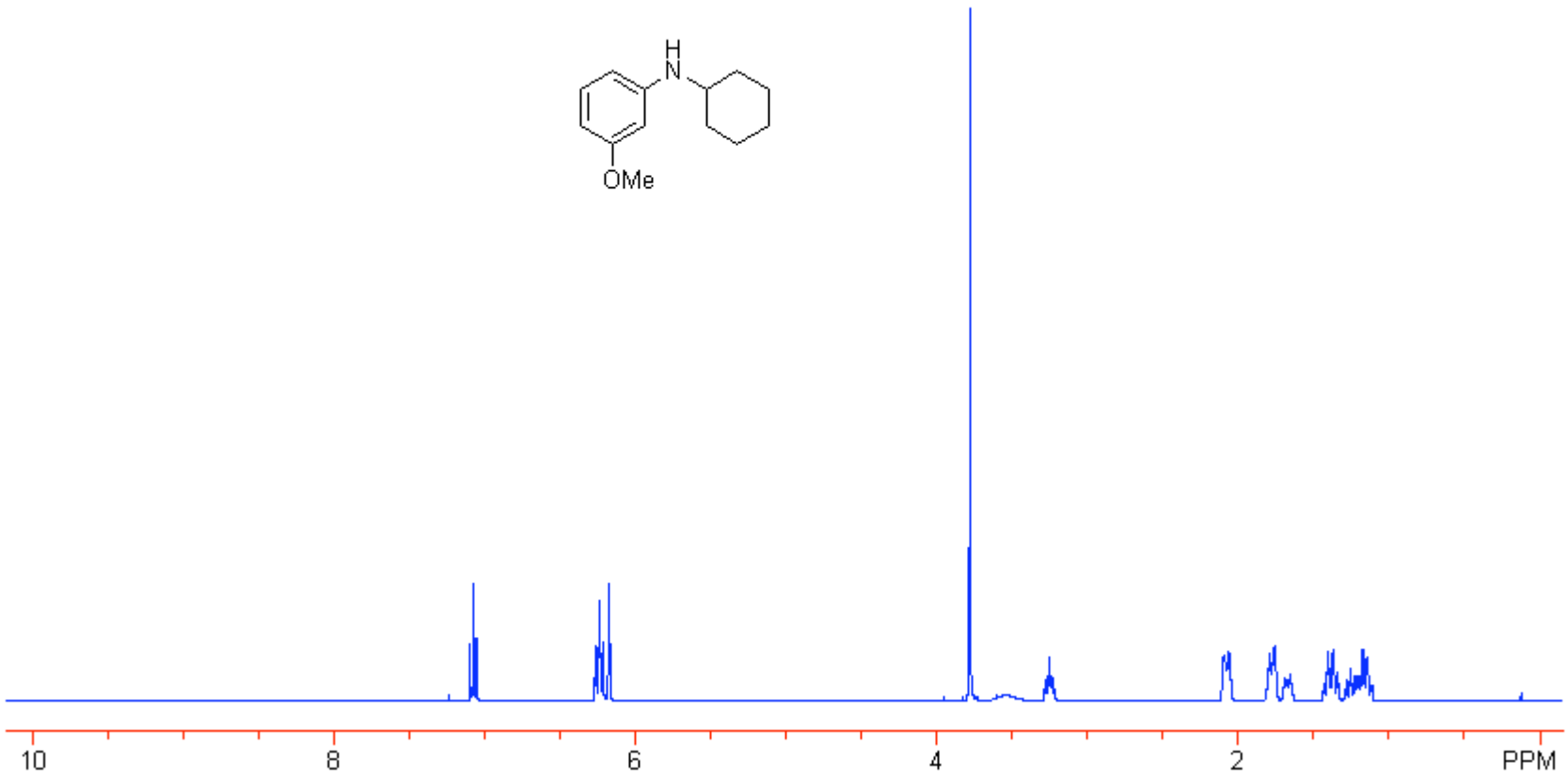


Table 2, entry 11, *N*-(Cyclohexylamino)-*m*-anisidine

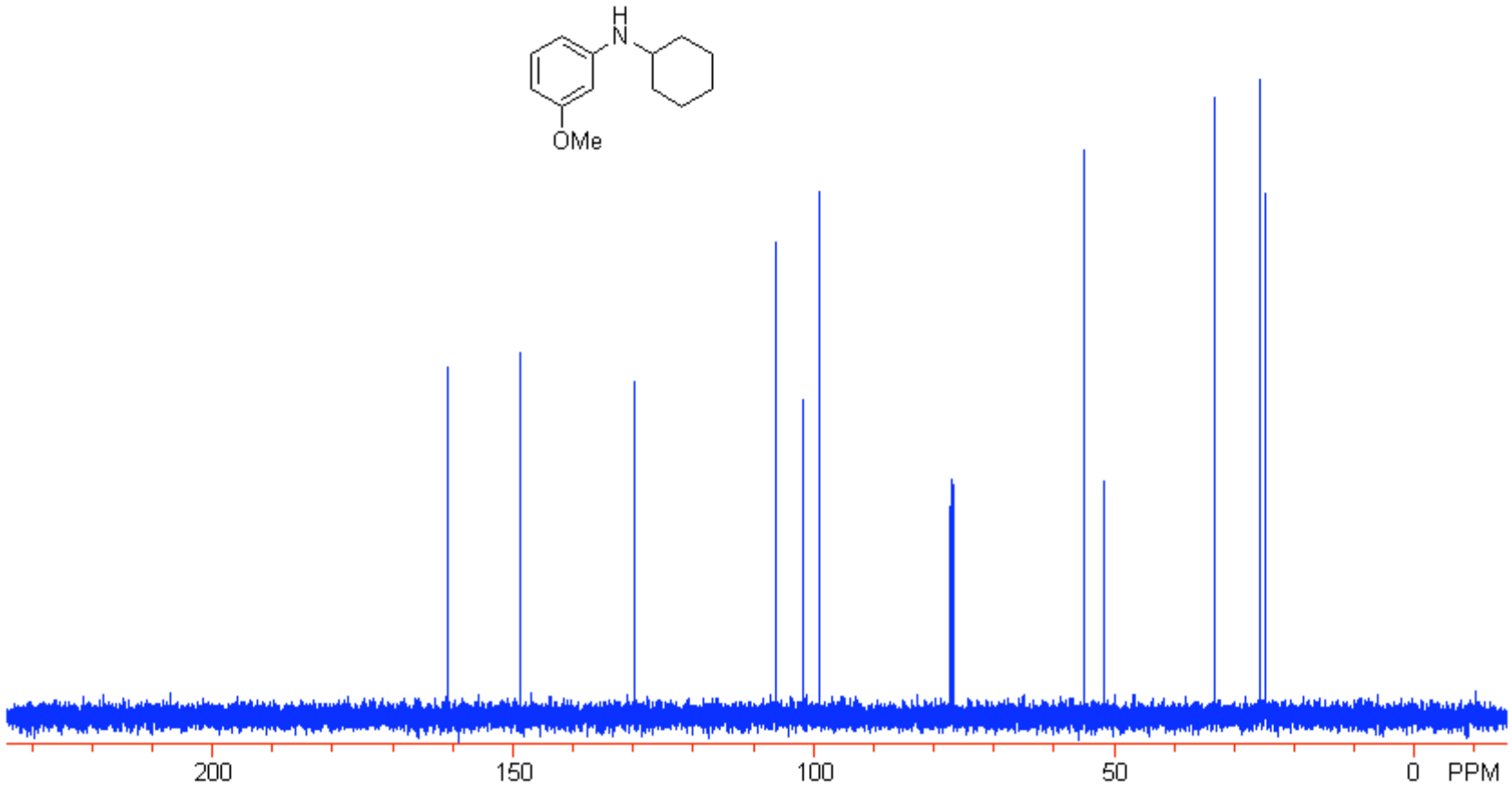
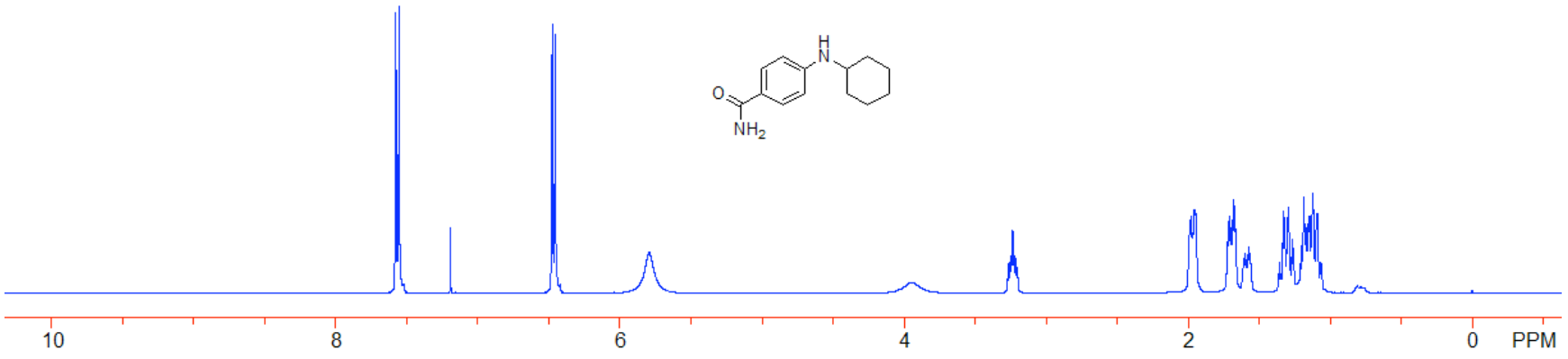


Table 4, entry 2, *N*-Cyclohexylamino-benzamide



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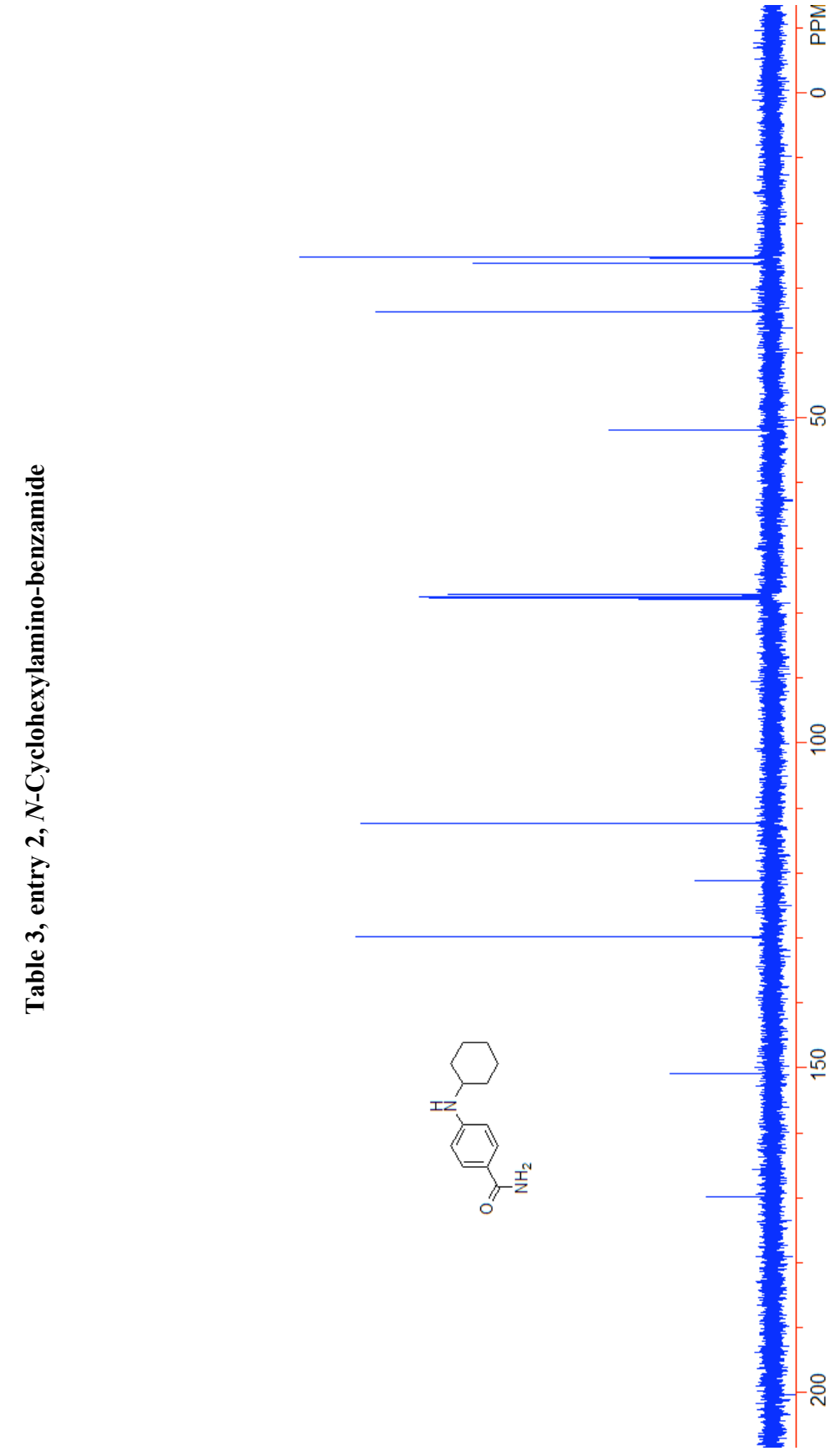


Table3, entry 6, 3-Hydoxy-*N*-octyl-aniline

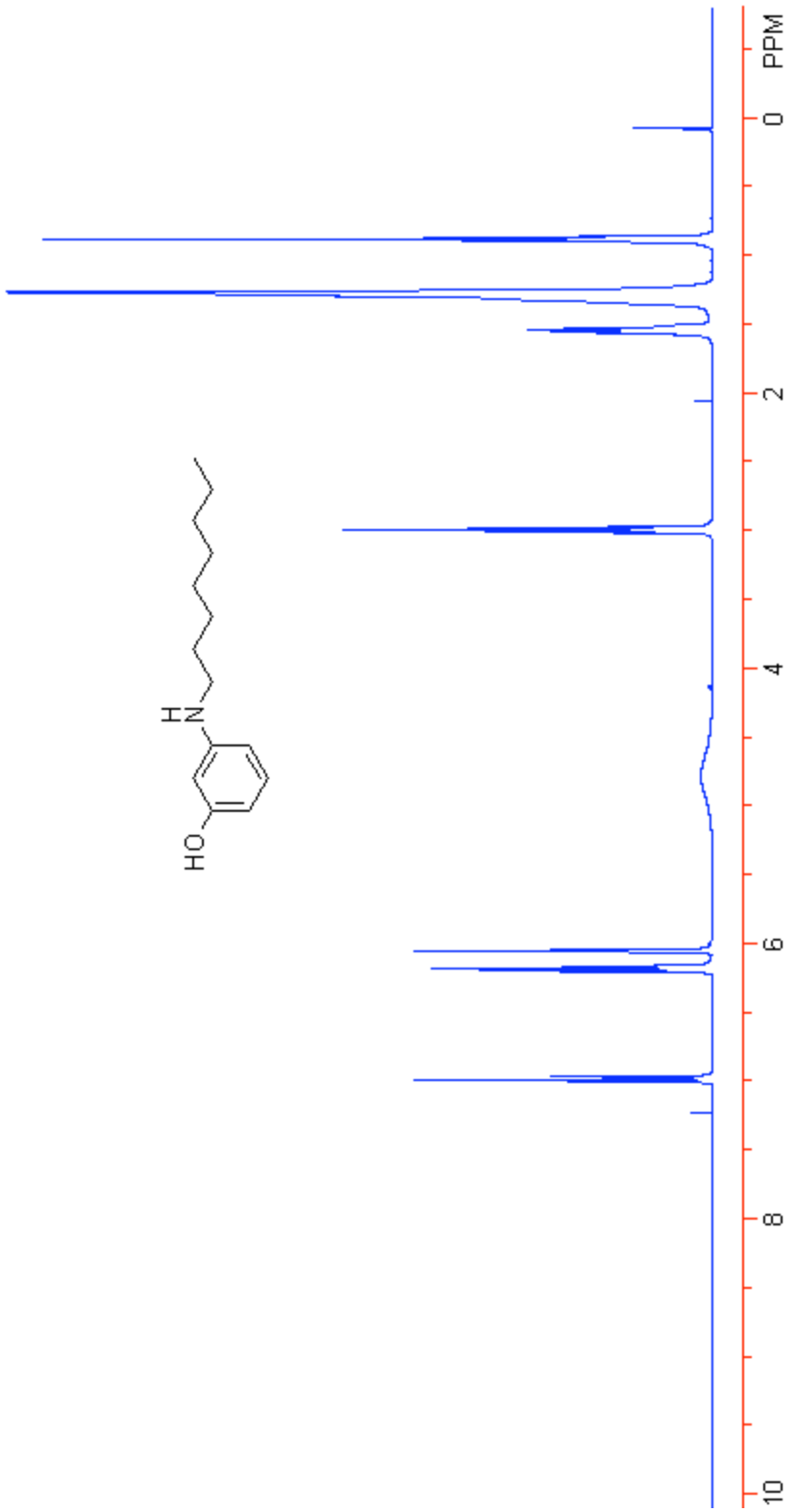


Table 3, entry 6, 3-Hydoxy-*N*-octyl-aniline

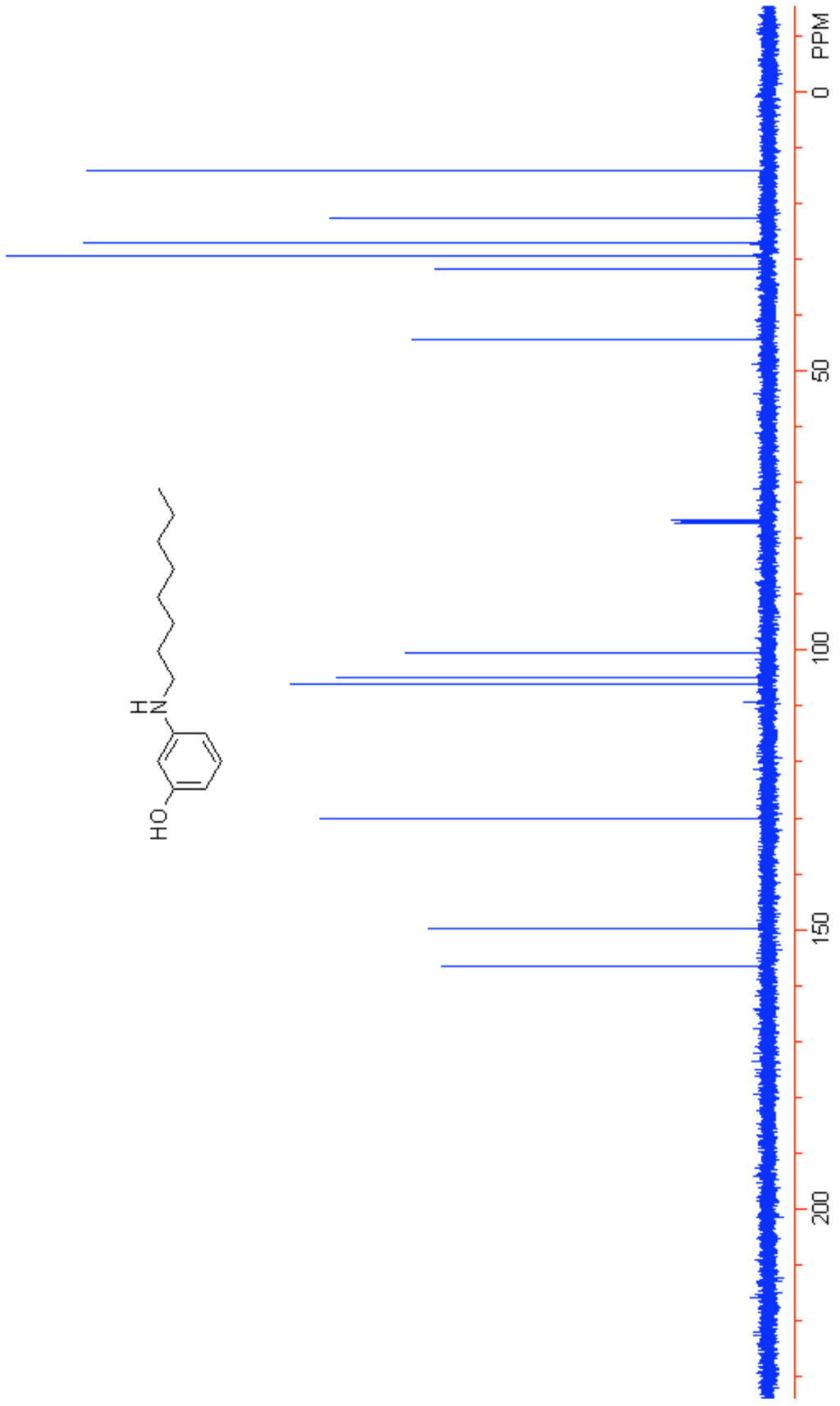


Table 4, entry 4, *N*-3-Pyridyl-2-pyrazinamine

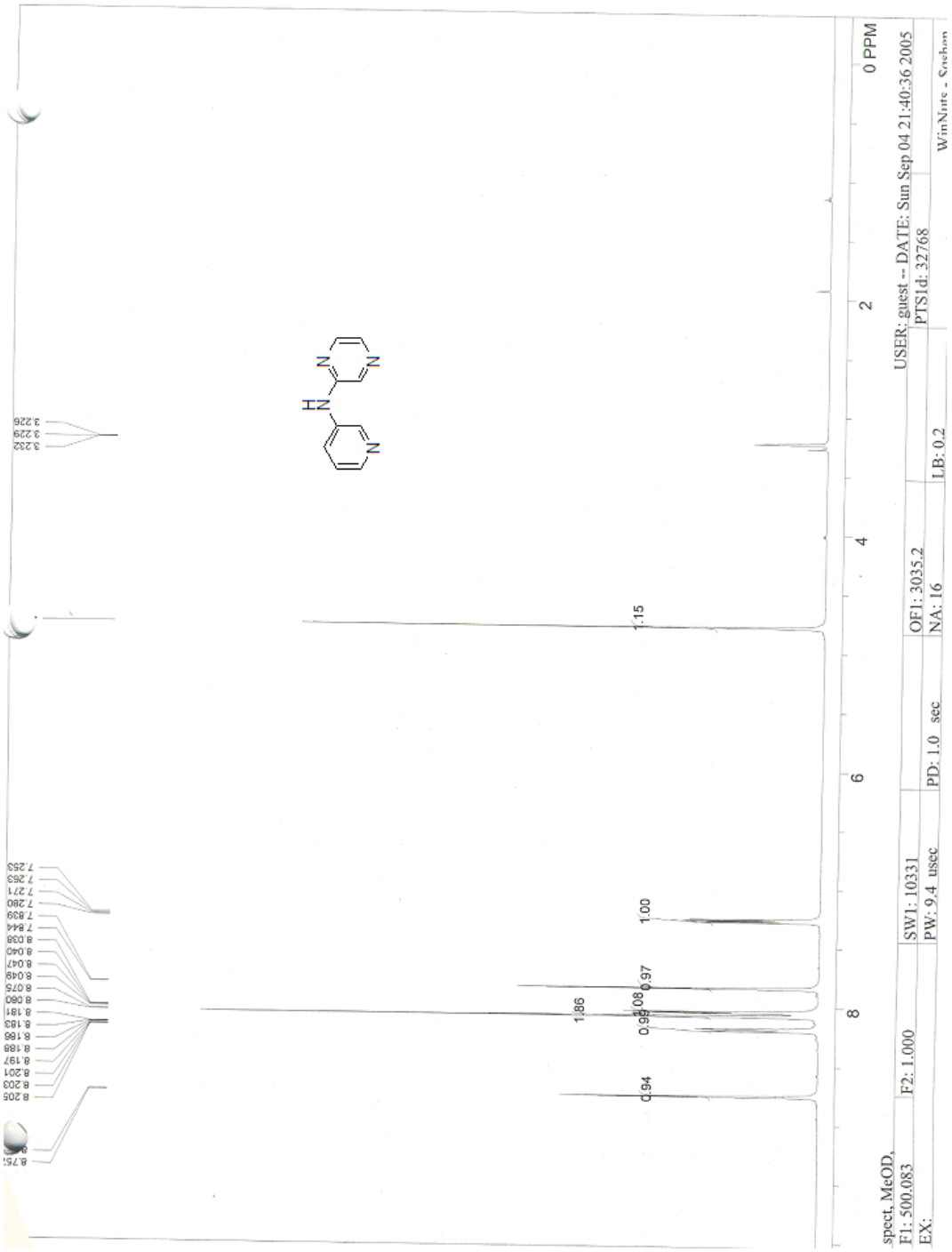


Table 4, entry 4, *N*-3-Pyridyl-2-pyrazinamine

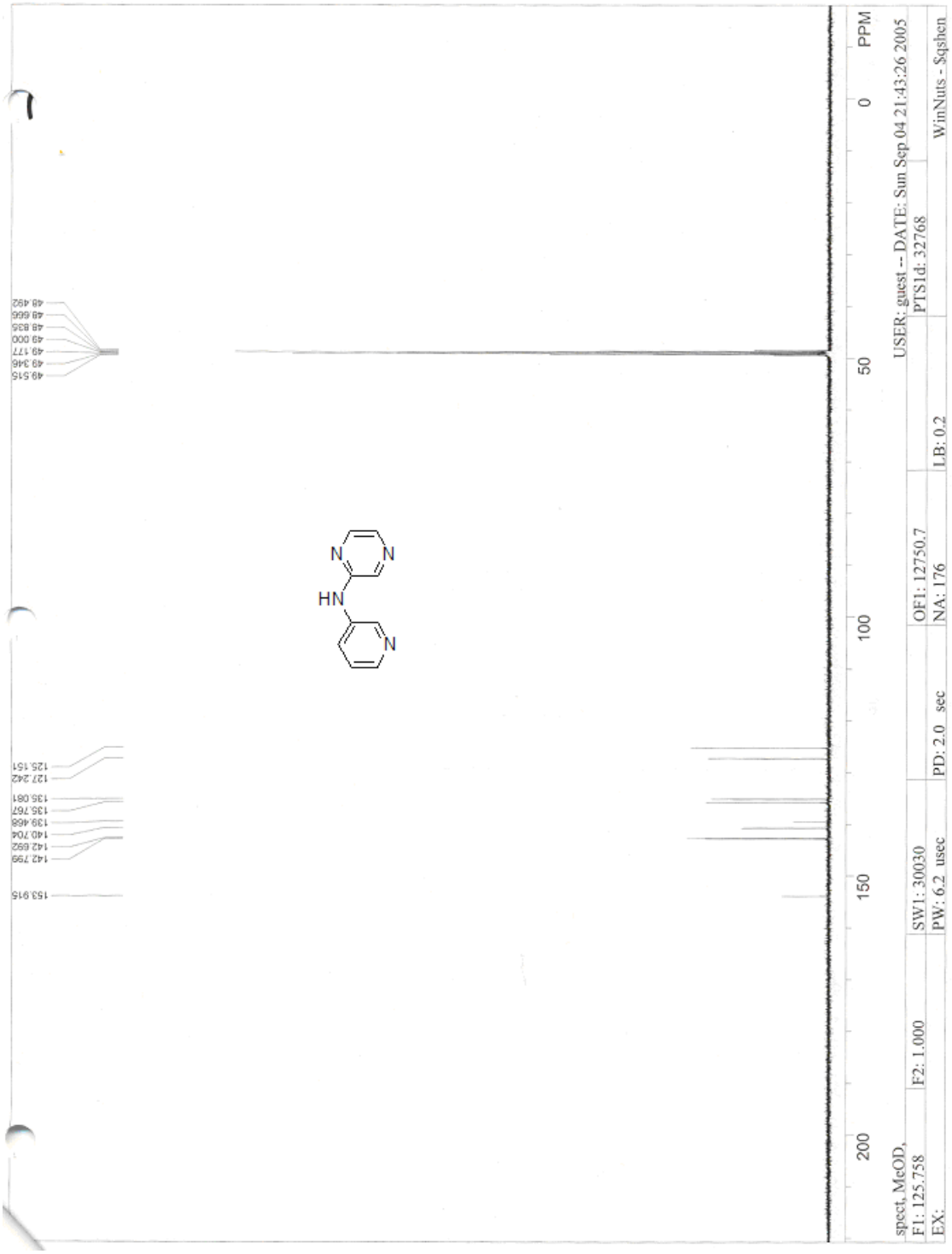


Table 4, entry 5, *N*-(*o*-Tolyl)-*p*-toluidine

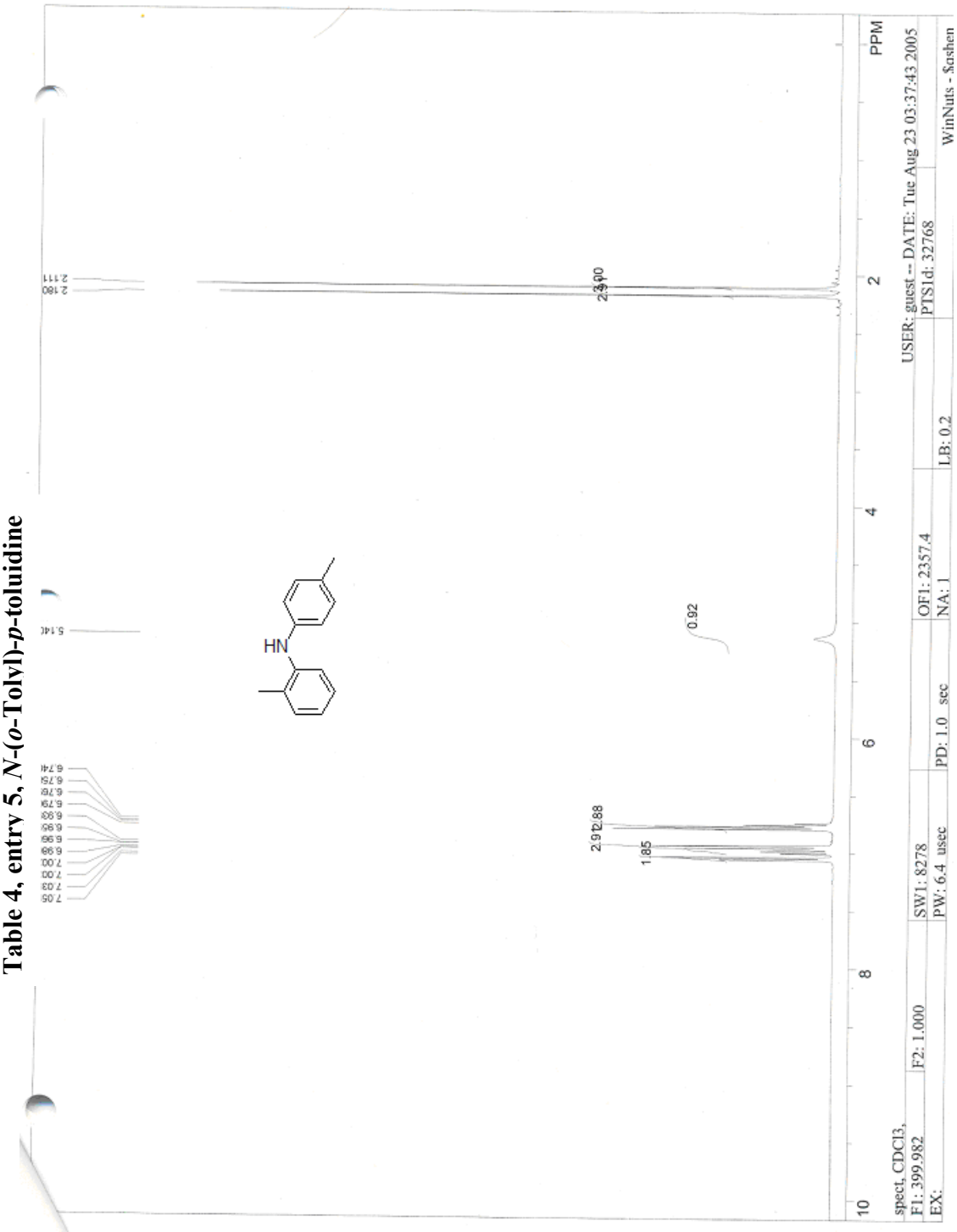


Table 4, entry 5, *N*-(*o*-Tolyl)-*p*-toluidine

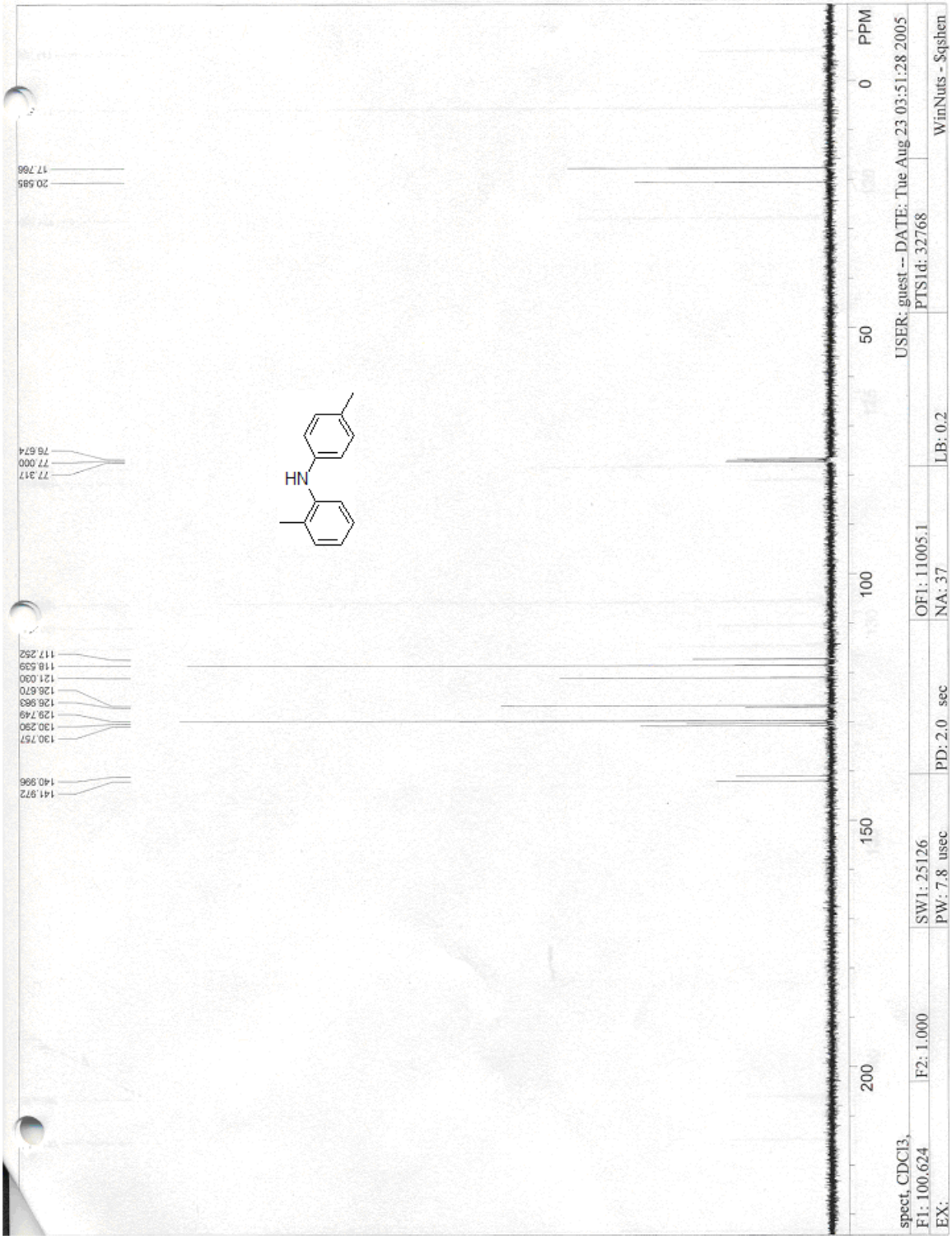
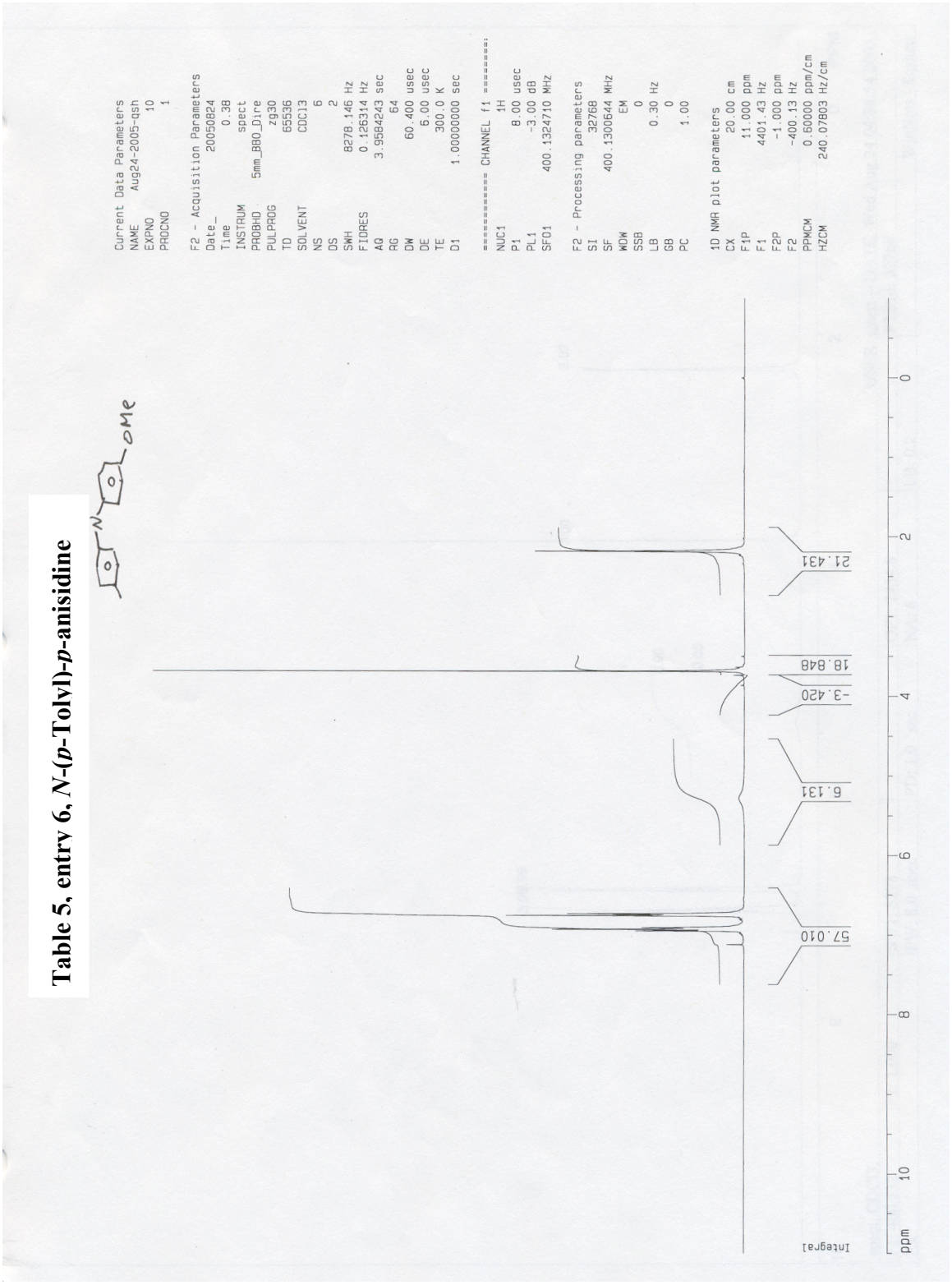


Table 5, entry 6, *N*-(*p*-Tolyl)-*p*-anisidine



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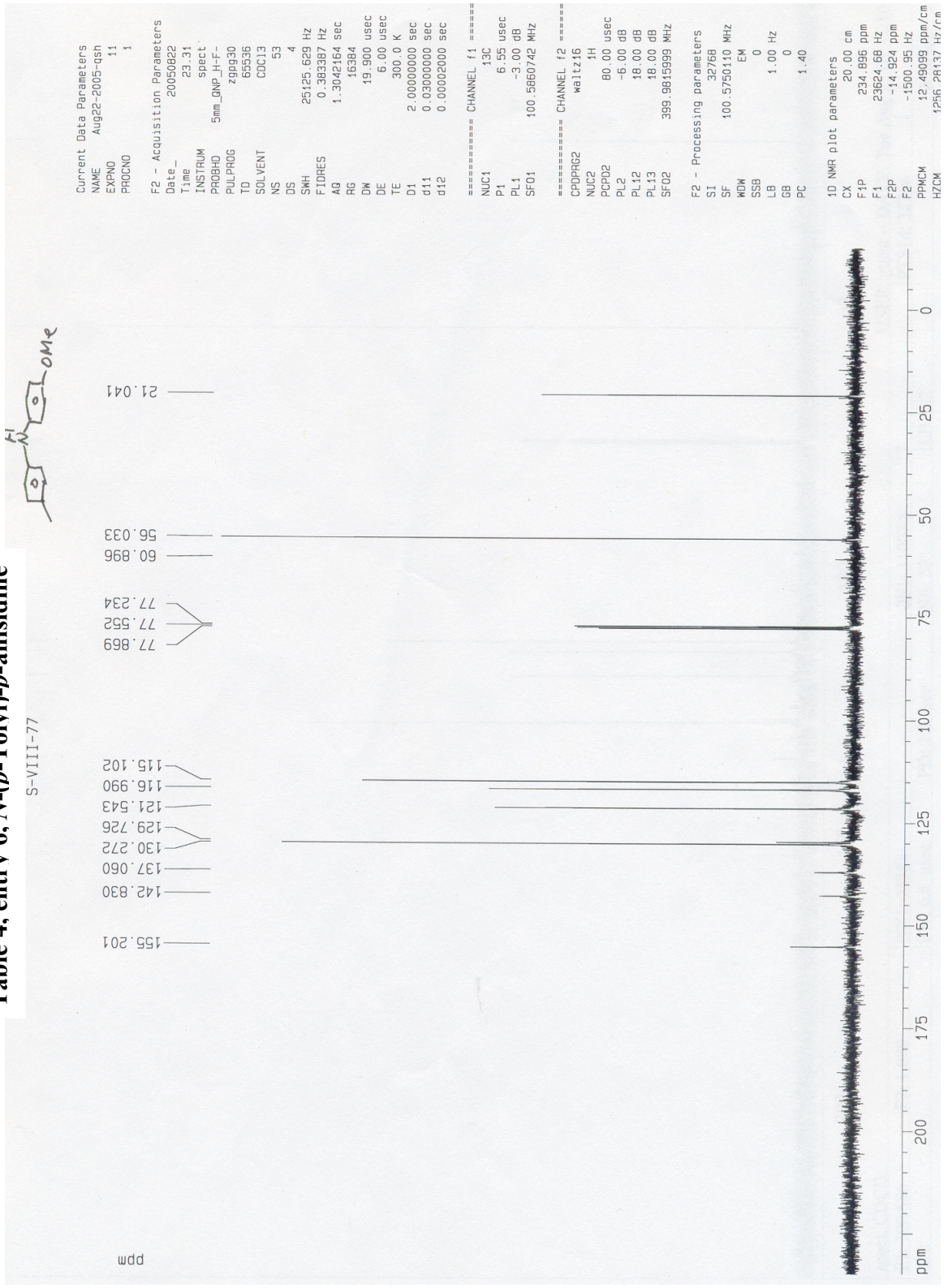


Table 5, entry 1, 3-Pyridylmorpholine

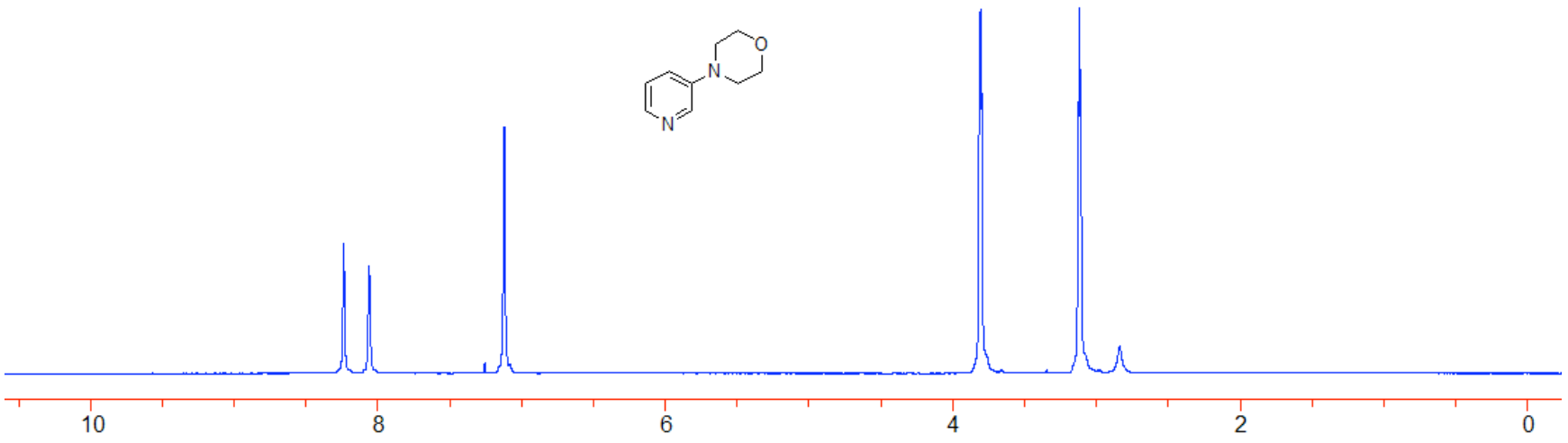
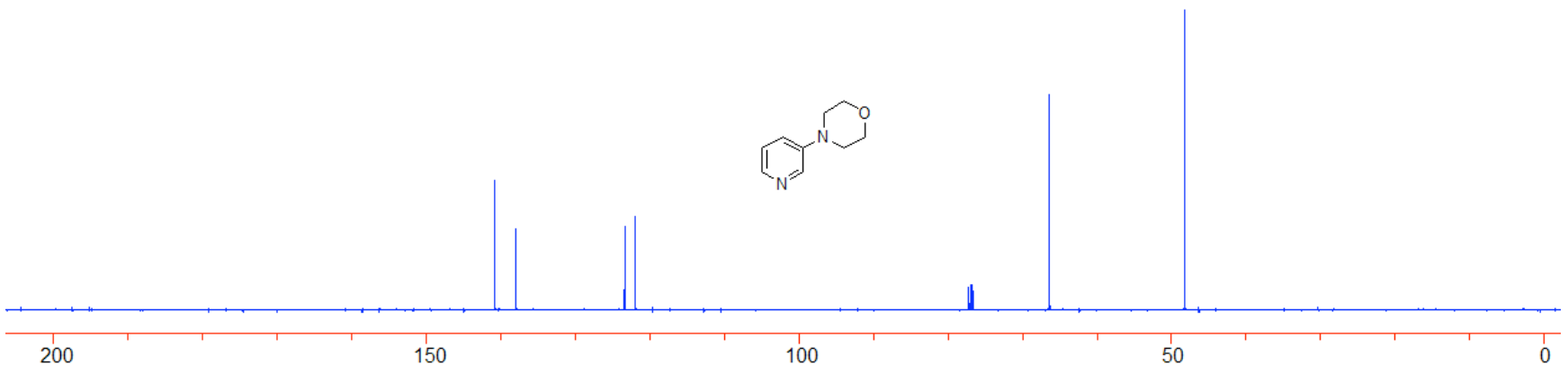


Table 5, entry 1, 3-Pyridylmorpholine



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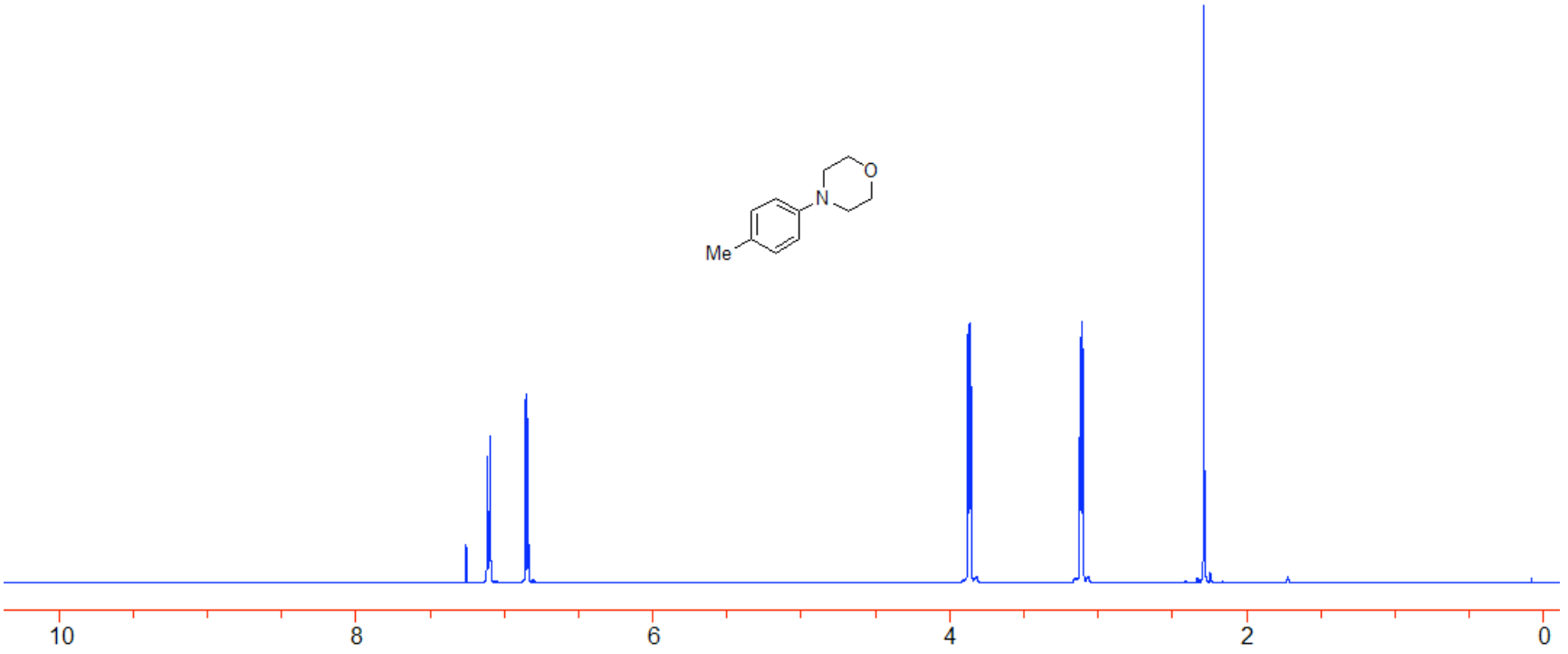

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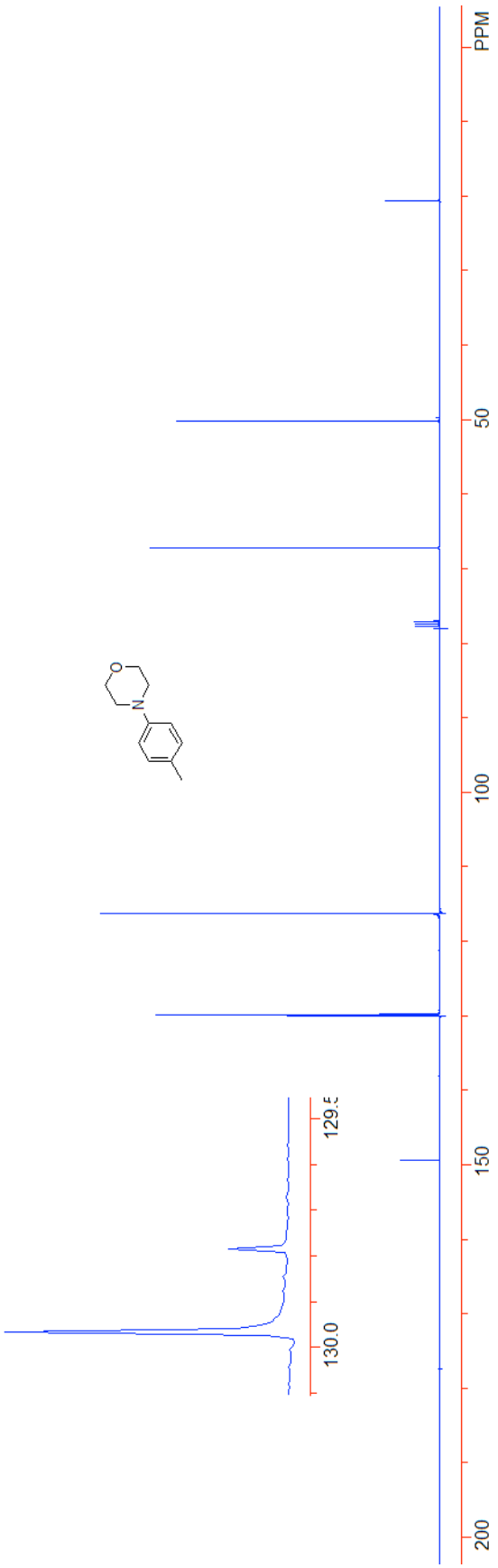


Table 6, entry 3, *N*-(3-Methoxyphenyl)-morpholine

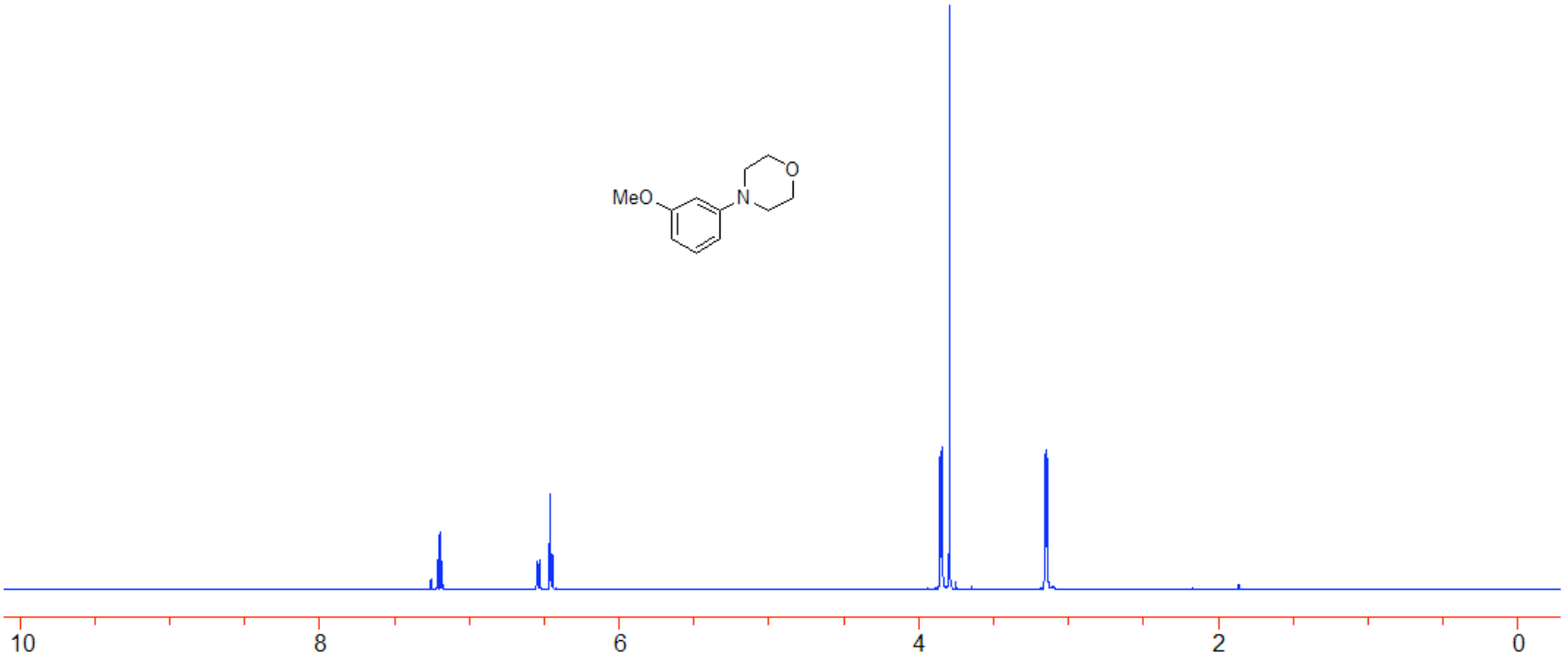


Table 5, entry 3, *N*-(3-Methoxyphenyl)-morpholine

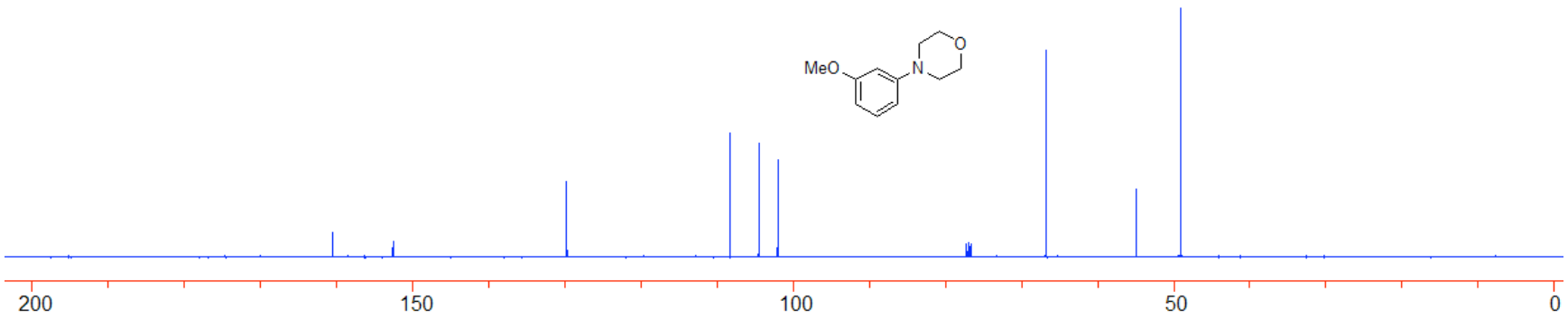
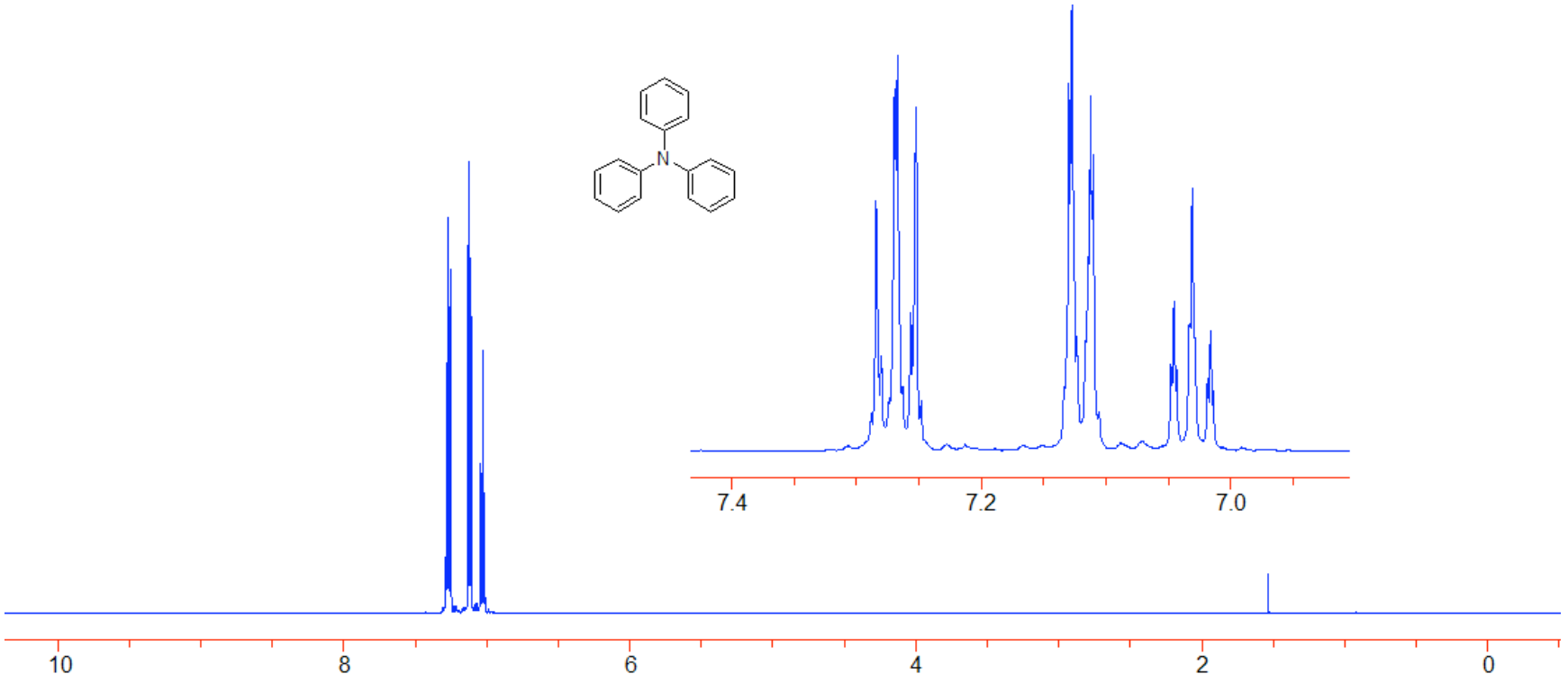


Table 5, entry 4, Triphenylamine



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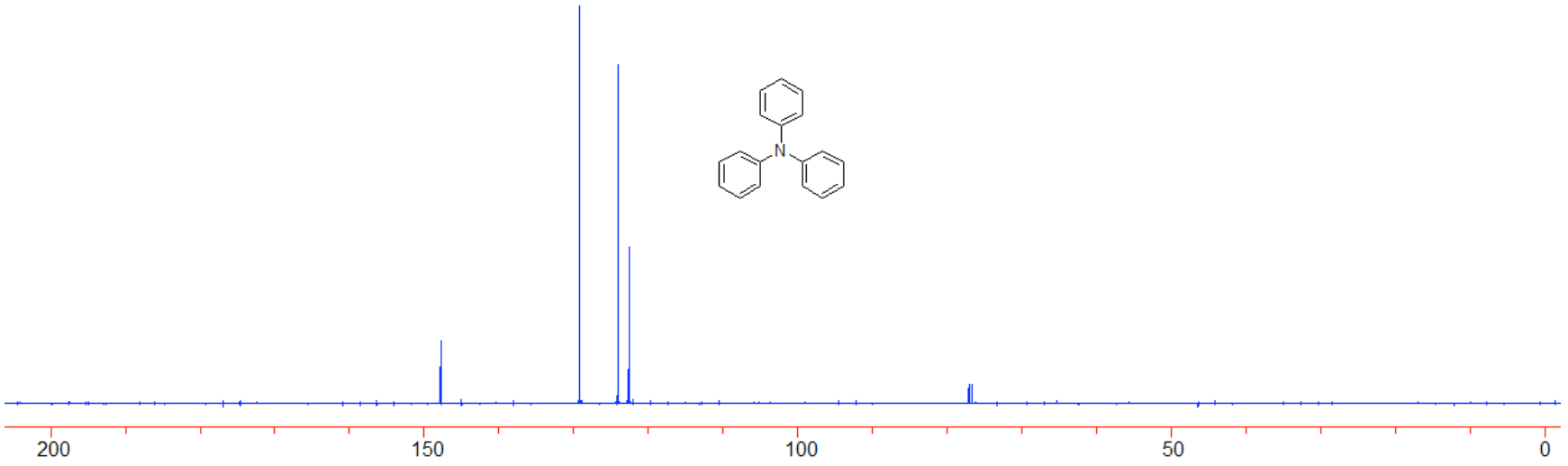


Table 5, entry 5, *N*-Methyldiphenylamine

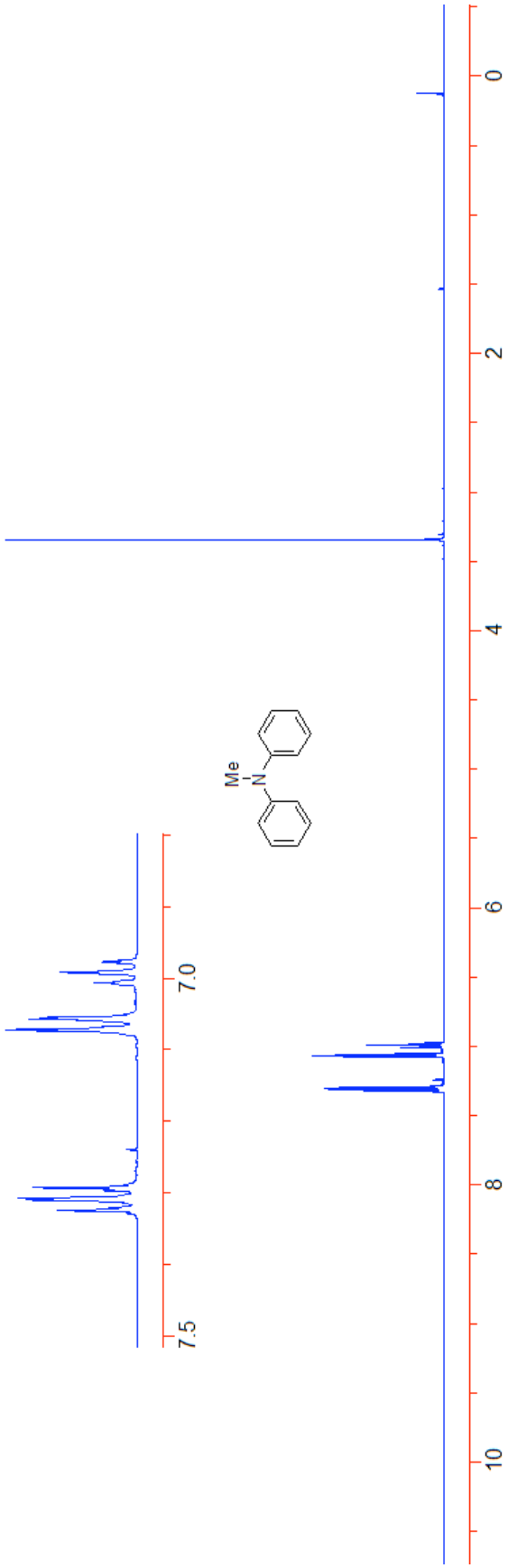
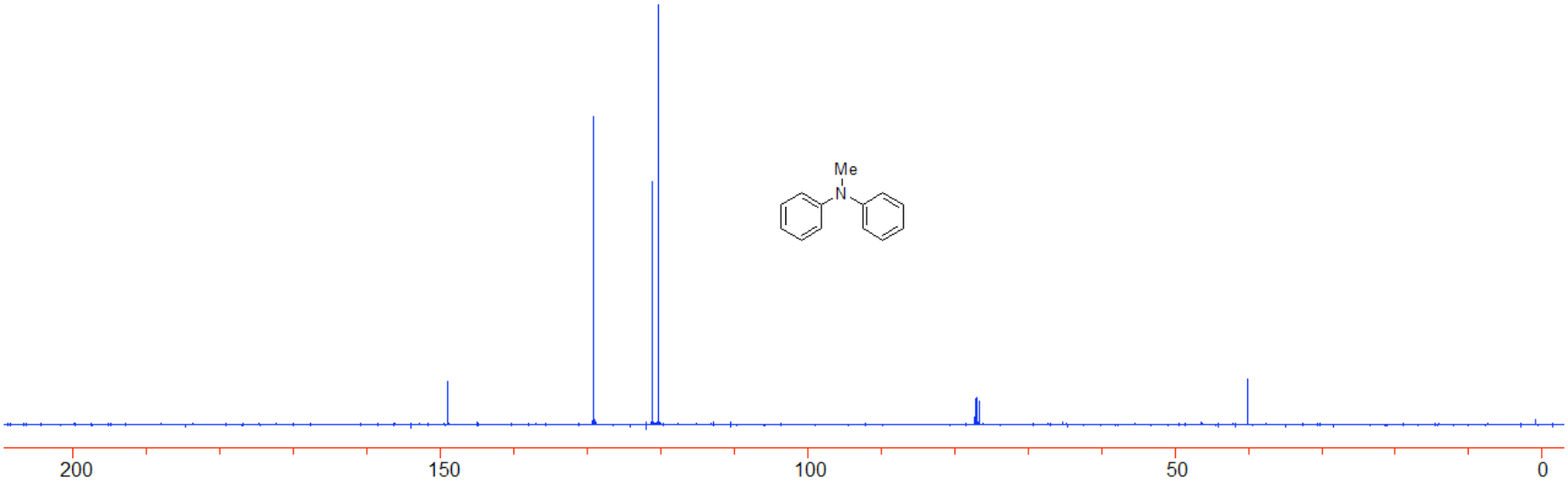


Table 5, entry 5, *N*-Methyldiphenylamine



^{1}H NMR spectroscopy of (CYPF-*t*-Bu)PdCl$_2$