Highly Reactive, General and Long-Lived Catalysts for Palladium-Catalyzed Amination of Heteroaryl and Aryl Chlorides, Bromides and Iodides: Scope and Structure-Activity Relationships

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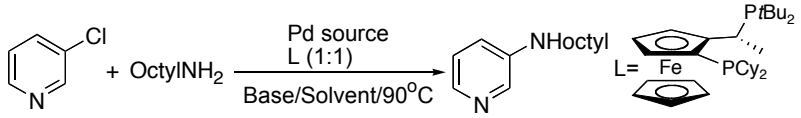
Supporting Information

General Methods. Unless otherwise noted, all manipulation were conducted inside an inert atmosphere glovebox, but procedures for conducting reations without a glovebox 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 with tetramethylsilane or residual protiated solvent 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. Shifts downfield of the standard are reported as positive. 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) was 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.

Table S1. Optimization of Palladium-catalyzed Coupling Reaction of 3-Chloropyridine with 1-Octylamine Catalyzed by Palladium Precursors and CyPF-*t*-Bu (1:1).[a]



Entry	Palladium	Base	Solvent	Loading (mol %)	Time (h)	Conversion [%] (Yield)[b]
1	$Pd(dba)_2$	NaO*t*Bu	DME	1	10	100
2	$PdCl_2(PhCN)_2$	NaO*t*Bu	DME	1	10	96
3	$Pd_2(dba)_3$	NaO*t*Bu	DME	1	10	100
4	$Pd(OAc)_2$	NaO*t*Bu	DME	1	1	100 (99)
5	$Pd(OAc)_2$	NaO*t*Bu	DME	0.05	1	100
6	$Pd(OAc)_2$	K_3PO_4	DME	0.05	24	trace
7	$Pd(OAc)_2$	Cs_2CO_3	DME	0.05	24	NR
8	$Pd(OAc)_2$	K_2CO_3	DME	0.05	24	NR
9	$Pd(OAc)_2$	NaO*t*Bu	Toluene	0.05	5	100
10	$Pd(OAc)_2$	NaO*t*Bu	THF	0.05	1	100
11	$Pd(OAc)_2$	NaO*t*Bu	1,4-dioxane	0.05	5	100
12	$Pd(OAc)_2$	NaO*t*Bu	DME	0.01	5	100 (99)
13	$Pd(OAc)_2$	NaO*t*Bu	Toluene	0.01	48	81
14	$Pd(OAc)_2$	NaO*t*Bu	THF	0.01	48	97
15	$Pd(OAc)_2$	NaO*t*Bu	1,4-dioxane	0.01	48	87
16	$Pd(OAc)_2$	NaO*t*Bu	DME	0.005	24	100 (93)

[a] All the experiments were conducted with a 1:1 ratio of metal to ligand, 1 mmol of 3-chloropyridine and 1.2 equiv 1-octylamine, and 1.4 equiv base in 1.0 mL solvent. [c] Determined by GC analysis. Isolated yields are indicated in parentheses.

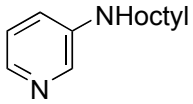
Stability of Josiphos CyPF-*t*-Bu. The Josiphos ligand CyPF-*t*-Bu (11.0 mg, 2.00×10^{-5} mmol) was dissolved in C_6D_6 (0.5 mL) in an uncapped NMR tube in air. The ^{1}H NMR and ^{31}P NMR spectra of CyPF-*t*-Bu were unchanged after 24 h. Alternatively, CyPF-*t*-Bu (11.0 mg, 2.00×10^{-5} mmol) was weighed into an open vial in air. The solid was dissolved in C_6D_6 (0.5 mL) after 24 h. The ^{1}H NMR and ^{31}P NMR spectra of Josiphos CyPF-*t*-Bu also were unchanged.

General Procedure A for Catalytic Amination of Heteroaryl and Aryl Halides in DME. The reaction conditions and average yields for each reaction are shown in Table 1 and 2. A typical procedure is given for the eleventh entry in Table 1.

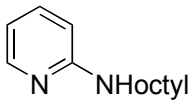
Stock Solution A (1.0×10^{-2} M): DME (1.0 mL) was added to the mixture of $Pd(OAc)_2$ (2.2 mg, 1.0×10^{-2} mmol) and CyPF-*t*-Bu (5.5 mg, 1.0×10^{-2} mmol). The resulting orange colored solution was stirred at room temperature for one minute before using.

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.

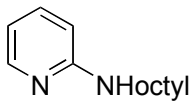
***N*-Octyl-3-aminopyridine. (Table 1, entry 11).** A solution of $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-5} mmol) was added to a 4 mL vial containing 3-chloropyridine (0.114 g, 1.00 mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) in 1.0 mL of DME. Octylamine (0.155 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 90 ºC until 3-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 197.2 mg (93%) 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.



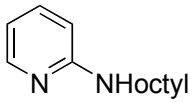
***N*-Octyl-2-aminopyridine. (Table 1, entry 1).** The general procedure A conducted with 2-chloropyridine (0.114 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (100.0 μL from stock solution **B**, 1.0×10^{-5} mmol) gave 176.3 mg (86%) of *N*-benzyl-2-aminopyridine as a colorless liquid. ^{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, 12.32, 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.



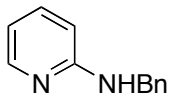
***N*-Octyl-2-aminopyridine. (Table 1, entry 2).** The general procedure A conducted with 2-iodopyridine (0.205 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-5} mmol) gave 12.2 mg (84%) of *N*-octyl-2-aminopyridine as a yellow solid.of *N*-octyl-2-aminopyridine as a yellow solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 1, entry 1.)



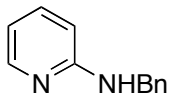
***N*-Octyl-2-aminopyridine. (Table 1, entry 3).** The general procedure A conducted with 2-bromopyridine (0.158 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **B**, 5.0×10^{-6} mmol) gave 196.8 mg (96%) of *N*-octyl-2-aminopyridine as a yellow solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 1, entry 1.)



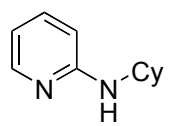
***N*-benzyl-2-aminopyridine.**[1] **(Table 1, entry 4).** The general procedure A conducted with 2-chloropyridine (0.114 g, 1.00 mmol), benzylamine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (100.0 μL from stock solution **B**, 1.0×10^{-5} mmol) gave 173.6 mg (85%) of *N*-benzyl-2-aminopyridine as a colorless liquid. ^{1}H NMR ($CDCl_3$) δ 7.95 (dt, *J* = 4.8 1.0 Hz, 1 H), 7.26 (td, *J* = 8.0, 1.2 Hz, 1 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 7.21 (t, *J* = 8.0 Hz, 2 H), 7.15 (t, *J* = 7.2 Hz, 1 H), 6.45 (dd, *J* = 7.2, 4.8 Hz, 1 H), 6.23 (dd, *J* = 8.0, 0.8 Hz, 1 H), 5.13 (s, 1 H), 4.38 (d, *J* = 5.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 158.63, 148.08, 139.14, 137.31, 128.49, 127.28, 127.06, 112.92, 106.60, 46.17.



***N*-Benzyl-2-aminopyridine.**[1] **(Table 1, entry 5).** The general procedure A conducted with 2-bromopyridine (0.158 g, 1.00 mmol), benzylamine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **B**, 5.0×10^{-6} mmol) gave 152.7 mg (83%) of *N*-benzyl-2-aminopyridine as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 1, entry 4.)

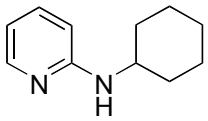


***N*-Cyclohexyl-2-aminopyridine.**[1] **(Table 1, entry 6).** The general procedure A conducted with 2-chloropyridine (0.114 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (10.0 μL from stock solution **A**, 1.0×10^{-4} mmol) gave 173.1 mg (98%) of *N*-cyclonexyl-2-aminopyridine 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.

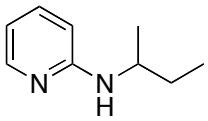


***N*-Cyclohexyl-2-aminopyridine.**[1] **(Table 1, entry 7).** The general procedure A conducted with 2-bromopyridine (0.158 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-5} mmol) gave 168.4 mg (96%) of *N*-cyclonexyl-2-

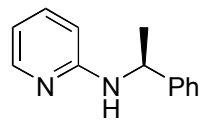
aminopyridine as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 2, entry 4.)



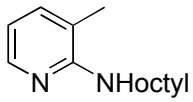
***N*-*sec*-Butyl-2-aminopyridine. (Table 1, entry 8).** The general procedure conducted with 2-iodopyridine (0.125 g, 1.00 mmol), *sec*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-5} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 146.8 mg (98%) of *N*-*sec*-butyl-2-aminopyridine as a colorless liquid. ^{1}H NMR ($CDCl_3$) δ 7.98 (dt, *J* = 5.0, 0.8 Hz, 1 H), 7.30 (ddd, *J* = 8.8, 7.6, 2.0 Hz, 1 H), 6.43 (ddd, *J* = 7.2, 4.8, 0.8 Hz, 1 H), 6.26 (d, *J* = 8.4 Hz, 1 H), 4.37 (d, *J* = 4.8 Hz, 1 H), 3.57-3.62 (m, 1 H), 1.42-1.52 (m, 2 H), 1.11 (d, *J* = 6.4 Hz, 3 H), 0.87 (t, *J* = 7.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 158.37, 148.17, 137.23, 112.20, 106.52, 48.38, 29.69, 20.28, 10.27. Anal. Calcd. For $C_9H_{14}N_2$: C, 71.96; H, 9.39; N, 18.65. Found: C, 72.01; H, 9.58; N, 18.51.



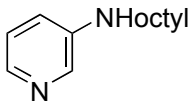
***N*-(2-Pyridyl)-α-methyl-benzylamine. (Table 1, entry 9).).** The general procedure A conducted with 2-chloropyridine (0.114 g, 1.00 mmol), α-methyl-benzylamine (0.145 g, 1.20 mmol, 99 % ee), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) gave 181.3 mg (91%, 94.5% ee) of *N*-(2-pyridyl)-α-methyl-benzylamine. The ee was determined on Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 1.0 ml/min, wavelength = 254 nm. Retention time 5.71 mins (S-isomer), 9.28 mins (R-isomer). ^{1}H NMR ($CDCl_3$) δ 7.97 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1 H), 7.28 (dd, *J* = 7.5, 1.0 Hz, 2 H), 7.22 (d, *J* = 7.5 Hz, 1 H), 7.17-7.21 (m, 2 H), 7.12 (t, *J* = 7.0 Hz, 1 H), 6.42 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1 H), 6.08 (d, *J* = 8.0 Hz, 1 H), 5.19 (d, *J* = 5.5 Hz, 1 H), 4.62 (quint, *J* = 6.5 Hz, 1 H), 1.44 (d, *J* = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 158.03, 148.08, 144.63, 137.33, 128.52, 126.87, 127.45, 112.87, 106.51, 51.81, 24.30. Anal. Calcd. For $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.67; H, 7.11; N, 14.13.



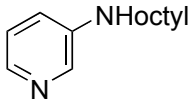
***N*-Octyl-2-amino-3-methylpyridine. (Table 1, entry 10).** The general procedure A conducted with 2-chloro-3-methylpyridine (0.126 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-5} mmol) gave 211.6 mg (96%) of *N*-octyl-2-amino-3-methylpyridine as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.98 (d, *J* = 4.2 Hz, 1 H), 7.14 (d, *J* = 7.2 Hz, 1 H), 6.44 (dd, *J* = 6.8, 5.2 Hz, 1 H), 4.03 (s, b, 1 H), 3.41 (q, *J* = 6.5 Hz, 2 H), 2.02 (s, 3 H), 1.60 (quint, *J* = 7.2 Hz, 2 H), 1.19-1.40 (m, 10 H), 0.84 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 156.90, 145.38, 136.44, 116.18, 112.10, 41.68, 31.75, 29.81, 29.35, 29.19, 27.11, 22.57, 16.86, 14.00. Anal. Calcd. For $C_{14}H_{24}N_2$: C, 76.31; H, 10.98; N, 12.71. Found: C, 76.25; H, 10.99; N, 12.41.



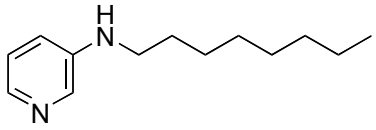
***N*-Octyl-3-aminopyridine. (Table 1, entry 11).** The general procedure A conducted with 3-chloropyridine (0.114 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-5} mmol) gave 197.2 mg (93%) of *N*-octyl-3-aminopyridine as a yellow 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.



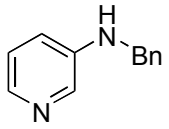
***N*-Octyl-3-aminopyridine. (Table 1, entry 12).** The following procedure was performed without a drybox. An oven-dried resealable Schlenk flask capped with a rubber septum was evacuated and backfilled with N_2. To the flask was added NaO*t*Bu (0.135 g, 1.40 mmol) and a stir bar. The flask was evacuated and backfilled with N_2 three times. To the flask was then added 3-chloropyridine (0.114 g, 1.00 mmol, 95.0 μL), DME (1.0 mL), a stock solution (5.0 μL) containing $Pd(OAc)_2$ (5.0×10^{-5} mmol) and CyPF-*t*-Bu (5.0×10^{-5} mmol) and octylamine (0.155 g, 1.20 mmol). The rubber septum was wrapped with vinyl electrical tape to prevent leaking. The resulting mixture was stirred for 48 h at 100 °C until the 3-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 204.3 mg (99%) of *N*-octyl-3-aminopyridine as a yellow solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 1, entry 11.)



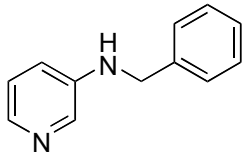
***N*-octyl-3-aminopyridine. (Table 1, entry 13).** The general procedure A conducted with 3-bromopyridine (0.158 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-5} mmol) gave 207.7 mg (99%) of *N*-octyl-3-aminopyridine as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 1, entry 11.)



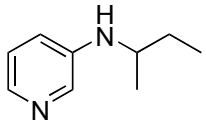
***N*-Benzyl-3-aminopyridine.**[2] **(Table 1, entry 14).** The general procedure A conducted with 3-chloropyridine (0.114 g, 1.00 mmol), benzylamine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (10.0 μL from stock solution **A**, 1.0×10^{-4} mmol) gave 174.8 mg (95%) of *N*-benzyl-3-aminopyridine as a yellow solid. ^{1}H NMR ($CDCl_3$) δ 7.93 (d, *J* = 2.8 Hz, 1 H), 7.83 (dd, *J* = 4.8, 1.6 Hz, 1 H), 7.23 (d, *J* = 4.4 Hz, 4 H), 7.14-7.19 (m, 1 H), 6.91 (dd, *J* = 8.0, 4.4 Hz, 1 H), 6.72 (ddd, *J* = 8.4, 2.8, 1.2 Hz, 1 H), 4.37 (s, b, 1 H), 4.19 (d, *J* = 6.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 143.97, 138.51, 138.45, 135.97, 128.54, 127.23, 127.19, 123.52, 118.26, 47.54.



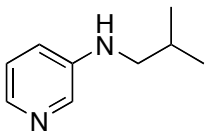
***N*-Benzyl-3-aminopyridine.**[2] **(Table 1, entry 15).** The general procedure A conducted with 3-bromopyridine (0.158 g, 1.00 mmol), benzylamine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-5} mmol) gave 183.3 mg (99%) of *N*-benzyl-3-aminopyridine as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 1, entry 14.)



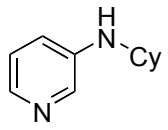
***N*-*sec*-Butyl-3-aminopyridine. (Table 1, entry 16).** The general procedure A conducted with 3-bromopyridine (0.158 g, 1.00 mmol), *sec*-butylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-5} mmol) gave 139.3 mg (93%) of *N*-*sec*-butyl-3-aminopyridine as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.91 (d, J = 2.8 Hz, 1 H), 7.80 (dd, J = 4.4, 1.2 Hz, 1 H), 6.95 (ddd, J = 8.0, 4.4, 0.8 Hz, 1 H), 6.73 (ddd, J = 8.4, 2.8, 1.4 Hz, 1 H), 3.74 (s, b, 1 H), 3.28-3.31 (m, 1 H), 1.44-1.55 (m, 1 H), 1.33-1.42 (m, 1 H), 1.07 (d, J = 6.4 Hz, 3 H), 0.85 (t, J = 7.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.61, 137.62, 135.99, 123.48, 118.32, 49.30, 29.18, 19.76, 10.08; Anal. Calcd. For $C_9H_{14}N_2$: C, 71.96; H, 9.39; N, 18.65. Found: C, 71.69; H, 9.41; N, 18.65.



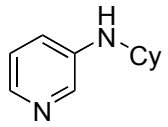
***N*-*iso*-Butyl-2-aminopyridine. (Table 1, entry 17).** The general procedure conducted with 3-iodopyridine (0.125 g, 1.00 mmol), *iso*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 144.0 mg (96%) of *N*-*iso*-butyl-2-aminopyridine as a colorless liquid. ^{1}H NMR ($CDCl_3$) δ 7.93 (d, J = 2.8 Hz, 1 H), 7.82 (dd, J = 4.8, 1.2 Hz, 1 H), 6.95 (dd, J = 8.4, 4.4 Hz, 1 H), 6.75 (ddd, J = 8.0, 2.8, 1.2 Hz, 1 H), 4.01 (s, 1 H), 2.82 (t, J = 4.8 Hz, 2 H), 1.73-1.84 (m, 1 H), 0.89 (d, J = 6.7 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 144.44, 137.86, 135.67, 123.47, 117.90, 51.06, 27.74, 20.18. Anal. Calcd. For $C_9H_{14}N_2$: C, 71.96; H, 9.39; N, 18.65. Found: C, 71.88; H, 9.42; N, 18.54.



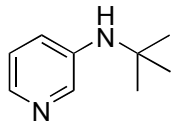
***N*-Cyclohexyl-3-aminopyridine.**[1] **(Table 1, entry 18).** The general procedure A conducted with 3-chloropyridine (0.114 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (10.0 μL from stock solution **A**, 1.0×10^{-4} mmol) gave 138.4 mg (79%) of *N*-cyclohexyl-3-aminopyridine 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.



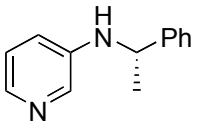
***N*-Cyclohexyl-3-aminopyridine.**[1] **(Table 1, entry 19).** The general procedure conducted with 3-iodopyridine (0.205 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 137.5 mg (78%) of *N*-cyclohexyl-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 18.)



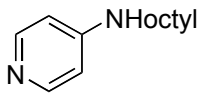
***N-tert*-Butyl-3-aminopyridine.**[3] **(Table 1, entry 20).** The general procedure A conducted with 3-chloropyridine (0.114 g, 1.00 mmol), *tert*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0×10^{-2} mmol) and CyPF-*t*-Bu (5.5 mg, 1.0×10^{-2} mmol) gave 100.3 mg (67%) of *N-tert*-butyl-3-aminopyridine as a colorless liquid. ^{1}H NMR ($CDCl_3$) δ 8.03 (s, 1 H), 7.91 (t, J = 3.0 Hz, 1 H), 6.98 (d, J = 3.2 Hz, 1 H), 6.97 (d, J = 3.6 Hz, 1 H), 3.55 (s, b, 1 H), 1.27 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 142.89, 139.32, 139.03, 123.21, 122.42, 51.36, 29.66.



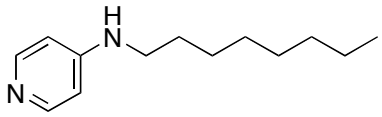
***N*-(3-Pyridyl)-α-methyl-benzylamine. (Table 1, entry 21).).** The general procedure A conducted with 3-chloropyridine (0.114 g, 1.00 mmol), α-methyl-benzylamine (0.145 g, 1.20 mmol, 99 % ee), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) gave 181.3 mg (91%, 94.5% ee) of *N*-(3-pyridyl)-α-methyl-benzylamine. The ee was determined on Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 1.0 ml/min, wavelength = 254 nm. Retention time 15.83 mins (S-isomer), 33.17 mins (R-isomer). ^{1}H NMR ($CDCl_3$) δ 7.90 (d, J = 2.8 Hz, 1 H), 7.78 (dd, J = 4.8, 1.2 Hz, 1 H), 7.09-7.24 (m, 5 H), 6.83 (dd, J = 8.4, 4.8 Hz, 1 H), 6.58 (ddd, J = 8.4, 2.8, 1.2 Hz, 1 H), 4.39 (s, b, 1 H), 4.30-4.38 (m, 1 H), 1.40 (d, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 144.15, 143.18, 138.16, 136.33, 128.58, 126.93, 125.57, 123.41, 118.71, 53.03, 24.75. Anal. Calcd. For $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.44; H, 7.35; N, 13.84.



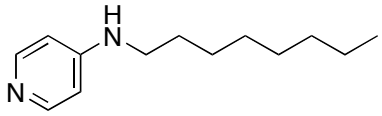
***N*-Octyl-4-aminopyridine. (Table 1, entry 22).** The general procedure A conducted with 4-chloropyridine hydrochloride (0.150 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (10.0 μL from stock solution **A**, 1.0×10^{-4} mmol) gave 171.5 mg (83%) of *N*-octyl-4-aminopyridine as a yellow 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.



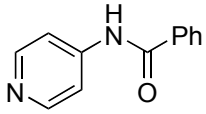
***N*-Octyl-4-aminopyridine. (Table 1, entry 23).** The general procedure A conducted with 4-bromopyridine hydrochloride (0.195 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-5} mmol) gave 192.3 mg (93%) of *N*-octyl-4-aminopyridine as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 1, entry 22.)



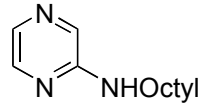
***N*-Octyl-4-aminopyridine. (Table 1, entry 24).** The general procedure A conducted with 4 -iodopyridine (0.205 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 164.6 mg (80%) of *N*-octyl-4-aminopyridine as a yellow solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 1, entry 22.)



4-Benzamidopyridine.[4] **(Table 1, entry 25).** The same procedure A conducted with 4-chloropyridine hydrochloride (0.150 g, 1.00 mmol), benzamide (0.145 g, 1.20 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0×10^{-2} mmol) and CyPF-*t*-Bu (5.5 mg, 1.0×10^{-2} mmol) gave 148.5 mg (75%) of 4-benzamidopyridine as a white solid. ^{1}H NMR (CD_3COCD_3) δ 9.82 (s, b, 1 H), 8.48 (d, J = 6.4 Hz, 2 H), 8.00 (dt, J = 7.2, 2.0 Hz, 2 H), 7.81 (dd, J = 6.8, 2.0 Hz, 2 H), 7.60 (tt, J = 7.2, 1.4 Hz, 1 H), 7.52 (tt, J = 7.6, 1.2 Hz, 2 H); ^{13}C NMR (CD_3COCD_3) δ 166.95, 151.20, 146.76, 135.36, 132.74, 129.24, 128.34, 114.54.

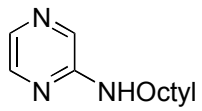


***N*-Octylaminopyrazine. (Table 1, entry 26).** The general procedure A conducted with chloropyrazine (0.115 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-5} mmol) gave 170.0 mg (82%) of *N*-octylaminopyrazine as a pale yellow solid. ^{1}H NMR ($CDCl_3$) δ 7.89 (dd, J = 2.8, 1.6 Hz, 1 H), 7.80 (d, J = 1.6 Hz, 1 H), 7.69 (d, J = 2.8 Hz, 1 H), 4.94 (s, b, 1 H), 3.24 (q, J = 6.7 Hz, 2 H), 1.54 (quint, J = 7.3 Hz, 2 H), 1.20-1.42 (m, 10 H), 0.80 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 154.70, 141.83, 132.16, 131.72, 41.40, 31.65, 29.28, 29.17, 29.09, 26.87, 22.50, 13.96; Anal. Calcd. For $C_{12}H_{21}N_3$: C, 69.52; H, 10.21; N, 20.27. Found: C, 69.58; H, 10.26; N, 20.45.

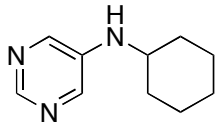


***N*-Octylaminopyrazine. (Table 1, entry 27).** The general procedure A conducted with iodopyrazine (0.206 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock

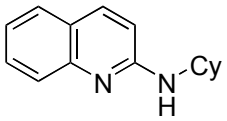
solution **A**, 5.0×10^{-45} mmol) gave 172.1 mg (83%) of *N*-octylaminopyrazine as a pale yellow solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 1, entry 26.)



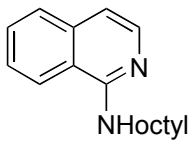
5-(Cyclohexylamino)pyrimidine.[5] **(Table 1, entry 28).** The general procedure A conducted with 5-bromopyrimidine (0.158 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0 mmol) and CyPF-*t*-Bu (5.5 mg, 1.0 mmol) gave 141.2 mg (80%) of 5-(cyclohexylamino)pyrimidine as a pale yellow plate. ^{1}H NMR ($CDCl_3$) δ 8.53 (s, 1 H), 8.07 (s, 2 H), 3.63 (s, b, 1 H), 3.23-3.30 (m, 1 H), 2.03-2.06 (m, 2 H), 1.65-1.80 (m, 3 H), 1.15-1.43 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 148.01, 140.96, 105.28, 51.12, 32.94, 25.58, 24.66.



***N*-Cyclohexyl-2-aminoquinoline. (Table 1, entry 29).** The general procedure A conducted with 2-chloroquinoline (0.163 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (10.0 μL from stock solution **A**, 1.0×10^{-4} mmol) gave 138.4 mg (79%) 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.

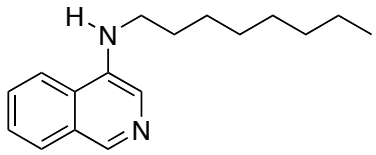


***N*-Octyl-1-aminoisoquinoline. (Table 1, entry 30).** The general procedure A conducted with 1-chloroisoquinoline (0.164 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-5} mmol) gave 233.8 mg (91%) of *N*-octyl-1-aminoisoquinoline as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.98 (d, J = 6.0 Hz, 1 H), 7.72 (d, J = 7.6 Hz, 1 H), 7.65 (d, J = 8.4 Hz, 1 H), 7.56 (dd, J = 8.0, 6.8 Hz, 1 H), 7.43 (dd, J = 8.2, 6.8 Hz, 1 H), 6.89 (d, J = 5.6 Hz, 1 H), 5.16 (s, b, 1 H), 3.58 (q, J = 7.6 Hz, 2 H), 1.72 (quint, J = 7.6 Hz, 2 H), 1.45 (quint, J = 7.6 Hz, 2 H), 1.23-1.37 (m, 8 H), 0.86 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 155.07, 141.22, 136.82, 129.32, 126.87, 125.49, 121.25, 117.96, 110.32, 41.77, 31.66, 29.43, 29.27, 29.11, 27.09, 22.49, 13.95; Anal. Calcd. For $C_{17}H_{24}N_2$: C, 79.64; H, 9.44; N, 10.93. Found: C, 79.56; H, 9.57; N, 10.90.

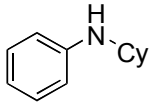


***N*-Octyl-4-amino-*iso*quinoline. (Table 1, entry 31).** The general procedure A conducted with 4-bromo-*iso*quinoline (0.208 g, 1.00 mmol), cyclohexylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and

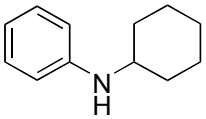
CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-5} mmol) gave 237.0 mg (93%) of *N*-Octyl-4-amino-*iso*quinoline as a white solid. ^{1}H NMR ($CDCl_3$) δ 8.65 (s, 1 H), 7.86 (d, *J* = 8.0 Hz, 1 H), 7.84 (s, 1 H), 7.75 (d, *J* = 8.5 Hz, 1 H), 7.60 (t, *J* = 8.0 Hz, 1 H), 7.53 (t, *J* = 7.5 Hz, 1 H), 4.19 (s,1 H), 3.27 (q, *J* = 7.0 Hz, 2 H), 1.74 (quint, *J* = 8.0 Hz, 2 H), 1.45 (quint, *J* = 7.0 Hz, 2 H), 1.27-1.36 (m, 8 H), 0.87 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 141.70, 137.84, 128.73, 128.38, 127.93, 126.76, 125.64, 123.26, 119.04, 43.87, 31.75, 29.35, 29.32, 29.19, 27.18, 22.59, 14.05. Anal. Calcd. For $C_{17}H_{24}N_2$: C, 79.64; H, 9.44; N, 10.93. Found: C, 79.52; H, 9.82; N, 10.90.



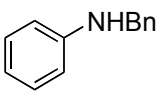
***N*-(Phenyl)cyclohexylamime.**[6] **(Table 3, entry 1).** The general procedure A conducted with phenylchloride (0.113 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A** , 5.0×10^{-5} mmol) gave 174.7 mg (99%) of *N*-(phenyl)cyclohexylamine as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.05 (t, *J* = 7.6 Hz, 2 H), 6.56 (td, *J* = 7.2, 1.2 Hz, 1 H), 6.48 (dd, *J* = 7.6, 0.8 Hz, 2 H), 3.38 (s, b, 1 H), 3.11-3.18 (m, 1 H), 1.94-1.97 (m, 2 H), 1.66 (dt, *J* = 13.2, 4.0 Hz, 2 H), 1.55 (dt, *J* = 12.0, 3.6 Hz, 1 H), 1.22-1.32 (m, 2 H), 0.99-1.18 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 147.31, 129.16, 116.71, 113.02, 51.56, 33.39, 25.88, 24.96.



***N*-cyclohexyl-aniline.**[6] **(Table 3, entry 2).** The general procedure A conducted with phenyl bromide (0.157 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (10.0 μL from stock solution **A**, 1.0×10^{-4} mmol) gave 168.9 mg (96%) of N-cyclohexyl-aniline as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 3, entry 1.)

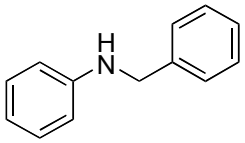


***N*-(Phenyl)benzylamine.**[6] **(Table 3, entry 3).** The general procedure A conducted with phenyl chloride (0.113 g, 1.00 mmol), benzylamine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-5} mmol) gave 183.0 mg (99%) of *N*-(Phenyl)benzylamine as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.49 (d, *J* = 6.0 Hz, 2 H), 7.46 (d, *J* = 7.2 Hz, 2 H), 7.38-7.41 (m, 1 H), 7.30 (t, *J* = 7.2 Hz, 2 H), 6.86 (td, *J* = 7.2, 1.2 Hz, 1 H), 6.74 (dd, *J* = 7.6, 1.2 Hz, 2 H), 4.42 (s, 2 H), 4.09 (s, b, 1 H); ^{13}C NMR ($CDCl_3$) δ 148.04, 139.36, 129.15, 128.51, 127.37, 127.09, 117.41, 112.73, 48.13.

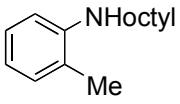


***N*-Benzylaniline.**[6] **(Table 3, entry 4).** The general procedure A conducted with phenyl bromide (0.157 g, 1.00 mmol), benzylamine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (100.0 μL from stock

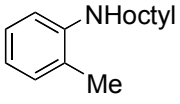
solution **B**, 1.0×10^{-5} mmol) gave 178.1 mg (97%) of *N*-Benzylaniline as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 3, entry 3.)



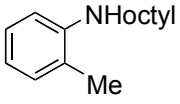
***N*-(*o*-Tolyl)octylamine. (Table 3, entry 5).** The general procedure A conducted with 2-chlorotoluene (0.127 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (10.0 μL from stock solution **A**, 1.0×10^{-4} mmol) gave 214.1 mg (98%) of *N*-(*o*-tolyl)octylamine as a yellow 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*-(*o*-Tolyl)octylamine. (Table 3, entry 6).** The general procedure A conducted with 2-bromotoluene (0.171 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-5} mmol) gave 218.4 mg (99%) of *N*-(*o*-tolyl)octylamine as a yellow solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 3, entry 5.)

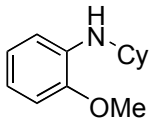


***N*-(*o*-Tolyl)octylamine. (Table 3, entry 7).** The general procedure conducted with 2-iodotoluene (0.218 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 203.7 mg (93%) of *N*-(*o*-tolyl)octylamine as a yellow solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 3, entry 5.)

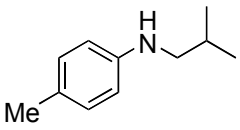


***N*-(Cyclohexylamino)-*o*-anisidine. (Table 3, entry 8).** The general procedure A conducted with 2-bromoanisole (0.187 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) gave 192.0 mg (94%) of *N*-(cyclohexylamino)-*o*-anisidine as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 6.88 (td, *J* = 8.0, 1.6 Hz, 1 H), 6.78 (dd, *J* = 8.4, 1.2 Hz, 1 H), 6.23-6.67 (m, 2 H), 4.17 (s, b, 1 H), 3.86 (s, 3 H), 3.28 (tt, *J* = 10.0, 3.8 Hz, 1 H), 2.10 (dd, *J* = 12.0, 3.0 Hz, 2 H), 1.80 (dt, *J* = 12.8, 3.6 Hz, 2 H), 1.68 (dt, *J* = 12.8, 4.0 Hz, 1 H), 1.35-1.46 (m, 2 H), 1.18-1.31 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 146.62, 137.19, 121.16, 115.67, 110.09, 109.47,

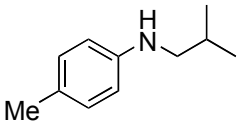
55.28, 51.25, 33.37, 25.96, 25.03; Anal. Calcd. For $C_{13}H_{19}N_2O$: C, 76.06; H, 9.33; N, 6.82. Found: C, 76.04; H, 9.32; N, 6.71.



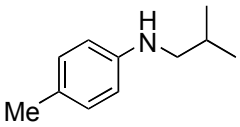
***N*-*p*-Tolyl-*iso*-butylamine.**[7] **(Table 3, entry 9).** The general procedure A conducted with 4-chlorotoluene (0.127 g, 1.00 mmol), *iso*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) gave 135.5 mg (83%) of *N*-*p*-tolyl-*iso*-butylamine as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 6.99 (d, *J* = 8.0 Hz, 2 H), 6.54 (d, *J* = 7.8 Hz, 2 H), 3.47 (s, b, 1 H), 2.92 (d, *J* = 6.8 Hz, 2 H), 2.25 (s, 3 H), 1.78 (nonet, *J* = 6.8 Hz, 1 H), 0.99 (d, *J* = 6.8 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 146.29, 129.66, 126.11, 112.83, 52.20, 27.97, 20.46, 20.33.



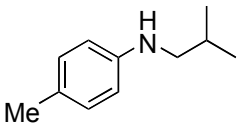
***N*-*p*-Tolyl-*iso*-butylamine. (Table 3, entry 10).** The general procedure A conducted with 4-bromotoluene (0.171 g, 1.00 mmol), *iso*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) gave 147.1 mg (90%) of *N*-*p*-tolyl-*iso*-butylamine as a pale yellow liquid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 3, entry 9.)



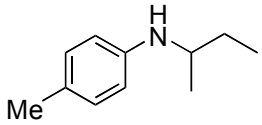
***N*-*p*-Tolyl-*iso*-butylamine. (Table 3, entry 11).** The general procedure conducted with 4-iodotoluene (0.218 g, 1.00 mmol), *iso*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 122.5 mg (75%) of *N*-*p*-tolyl-*iso*-butylamine as a pale yellow liquid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 3, entry 9.)



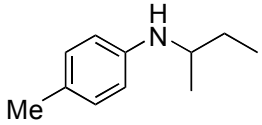
***N*-*p*-Tolyl-*iso*-butylamine. (Table 3, entry 12).** The general procedure conducted with 4-iodotoluene (5.50 g, 25.0 mmol), *iso*-butylamine (2.20 g, 30.0 mmol), $Pd(OAc)_2$ (1.1 mg, 0.50 mmol) and CyPF-*t*-Bu (2.7 mg, 0.50 mmol) and sodium *tert*-butoxide (3.38 g, 35.0 mmol) gave 3.30 g (81%) of *N*-*p*-tolyl-*iso*-butylamine as a pale yellow liquid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 3, entry 9.)



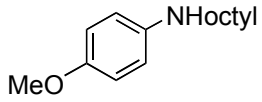
***N*-(*p*-Tolyl)-*sec*-butylamine. (Table 3, entry 13).** The general procedure A conducted with 4-bromotoluene (0.171 g, 1.00 mmol), *sec*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) gave 142.2 mg (87%) of *N*-(*p*-tolyl)-*sec*-butylamine 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.



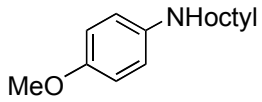
***N*-(*p*-Tolyl)-*sec*-butylamine. (Table 3, entry 14).** The general procedure conducted with 4-iodotoluene (0.218 g, 1.00 mmol), *sec*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 0.50 mmol%) and CyPF-*t*-Bu (2.7 mg, 0.50 mmol%) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 133.8 mg (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 3, entry 13.)



***N*-(4-Methoxyphenyl)octylamine. (Table 3, entry 15).** The general procedure A conducted with 4-chloroanisole (0.143 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (100.0 μL from stock solution **A**, 1.0×10^{-3} mmol) gave 217.2 mg (92%) of *N*-(4-methoxyphenyl)octylamine as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 6.68 (d, *J* = 6.4 Hz, 2 H), 6.47 (d, *J* = 6.8 Hz, 2 H), 3.63 (s, 3 H), 3.17 (s, b, 1 H), 2.94 (t, *J* = 7.0 Hz, 2 H), 1.49 (quint, *J* = 7.0 Hz, 2 H), 1.20-1.28 (m, 10 H), 0.80 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 151.77, 142.76, 114.71, 113.83, 55.60, 44.88, 31.75, 29.58, 29.37, 29.20, 27.13, 22.58, 14.02. Anal. Calcd. For $C_{15}H_{25}NO$: C, 76.55; H, 10.71; N, 5.95. Found: C, 76.46; H, 10.41; N, 6.04.

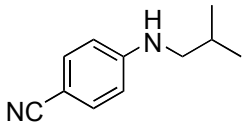


***N*-(4-Methoxyphenyl)octylamine. (Table 3, entry 16).** The general procedure conducted with 4-iodoanisole (0.234 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0 mmol%) and CyPF-*t*-Bu (5.5 mg, 1.0 mmol%) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 158.3 mg (67%) of *N*-(4-methoxyphenyl)octylamine as a pale yellow liquid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 3, entry 15.)

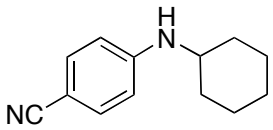


***N*-(4-Cyanophenyl)-*iso*-butylamine. (Table 3, entry 17).** The general procedure A conducted with 4-cyano-1-chlorobenzene (0.138 g, 1.00 mmol), *iso*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-5} mmol) gave 156.0 mg (90%) of *N*-(4-cyanoxyphenyl)-*iso*-butylamine as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.27 (d, *J* = 8.8 Hz, 2 H), 7.46 (d, *J* = 8.8 Hz, 2 H), 4.32 (s, b, 1 H), 2.87 (d, *J* = 6.8 Hz, 2 H), 1.80 (nonet, *J* = 6.8 Hz, 1 H), 0.89

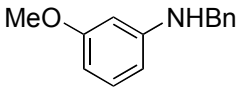
(d, J = 6.8 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 151.74, 133.43, 120.38, 112.01, 98.00, 50.86, 27.90, 20.12; Anal. Calcd. For $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.96; H, 8.03; N, 16.01.



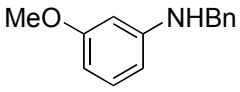
***N*-(4-Cyanophenyl)-cyclohexylamine. (Table 3, entry 18).** The general procedure A conducted with 4-cyano-1-bromobenzene (0.182 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0 × 10^{-5} mmol) gave 184.2 mg (92%) of *N*-(4-Cyanophenyl)-cyclohexylamine 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*-(Benzylamino)-*m*-anisidine. (Table 3, entry 19).** The general procedure A conducted with 3-chloroanisole (0.143 g, 1.00 mmol), benzylamine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0 × 10^{-5} mmol) gave 208.0 mg (98%) of *N*-(benzylamino)-*m*-anisidine as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.45 (dd, J = 8.4, 2.0 Hz, 2 H), 7.42 (t, J = 7.6 Hz, 2 H), 7.36 (tt, J = 6.4, 2.0 Hz, 1 H), 7.17 (t, J = 8.0 Hz, 1 H), 6.39 (dd, J = 8.0, 1.6 Hz, 1 H), 6.34 (dd, J = 8.0, 1.6 Hz, 1 H), 6.28 (t, J = 1.6 Hz, 1 H), 4.37 (s, 2 H), 4.13 (s, b, 1 H), 3.81 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 160.65, 149.42, 139.23, 129.84, 128.46, 127.33, 127.05, 105.80, 102.45, 98.70, 54.85, 48.06. Anal. Calcd. For $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.83; H, 7.13; N, 6.54.

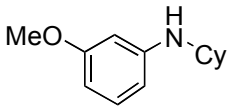


***N*-(Benzylamino)-*m*-anisidine. (Table 3, entry 20).** The general procedure conducted with 3-iodoanisole (0.234 g, 1.00 mmol), benzylamine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0 × 10^{-5} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 211.6 mg (99%) of *N*-(benzylamino)-*m*-anisidine as a pale yellow liquid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 3, entry 19.)

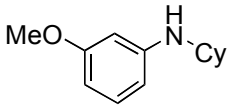


***N*-(Cyclohexylamino)-*m*-anisidine.[8] (Table 3, entry 21).** The general procedure A conducted with 3-bromoanisole (0.143 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (10.0 μL from stock solution **A**, 1.0 × 10^{-4} mmol) gave 207.2 mg (99%) of *N*-(cyclohexylamino)-*m*-anisidine 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 =

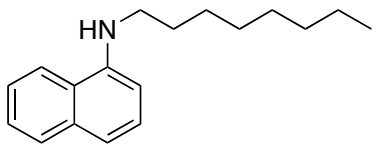
12.4, 3.6 Hz, 1 H), 1.33-1.44 (m, 2 H), 1.25 (tt, *J* = 12.0, 3.6 Hz, 1 H), 1.11-1.21 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 160.74, 148.67, 129.82, 106.24, 101.61, 98.98, 54.90, 51.57, 33.32, 25.82, 24.92.



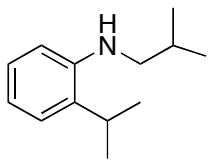
***N*-(Cyclohexylamino)-*m*-anisidine.**[8] **(Table 3, entry 22).** The general procedure conducted with 3-iodoanisole (0.234 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 196.7 mg (94%) of *N*-(cyclohexylamino)-*m*-anisidine as a pale yellow liquid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 3, entry 21.)



***N*-Octyl-1-aminonaphathlene.**[9] **(Table 3, entry 23).** The general procedure conducted with 1-iodonaphathlene (0.254 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 249.9 mg (98%) of *N*-octyl-1-aminonaphathlene as a pale yellow solid. ^{1}H NMR ($CDCl_3$) δ 7.81-7.84 (m, 2 H), 7.42-7.50 (m, 2 H), 7.39 (t, *J* = 8.0 Hz, 1 H), 7.26 (d, *J* = 8.4 Hz, 1 H), 6.64 (d, *J* = 7.6 Hz, 1 H), 4.33 (s, br, 1 H), 3.28 (t, *J* = 7.2 Hz, 2 H), 1.78 (quint, *J* = 7.6 Hz, 2 H), 1.35-1.55 (m, 10 H), 0.95 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.60, 134.26, 128.62, 126.65, 125.59, 124.52, 123.27, 119.74, 116.98, 104.11, 44.20, 31.85, 29.47, 29.41, 29.28, 27.36, 22.68, 14.12.

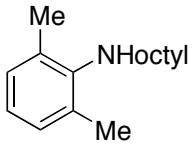


***N*-(*iso*butyl)-2-*iso*propylaniline. (Table 3, entry 24).** The general procedure A conducted with 1-bromo-2-*iso*propylbenzene (0.199 g, 1.00 mmol), *iso*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) gave 181.2 mg (95%) of N-(isobutyl)-2-isopropylaniline as a pale yellow liquid. . ^{1}H NMR ($CDCl_3$) δ 7.21 (dd, *J* = 7.5, 1.5 Hz, 1 H), 7.17 (td, *J* = 7.5, 1.5 Hz, 1 H), 6.78 (td, *J* = 7.5, 1.0 Hz, 1 H), 6.62 (d, *J* = 7.5 Hz, 1 H), 3.79 (s, b, 1 H), 3.03 (d, *J* = 6.5 Hz, 2 H), 2.92 (hept, *J* = 7.0 Hz, 1 H), 2.01 (hept, *J* = 6.5 Hz, 1 H), 1.33 (d, *J* = 7.0 Hz, 6 H), 1.08 (d, *J* = 6.5 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 145.05, 131.67, 126.70, 124.80, 116.76, 110.15, 51.83, 27.89, 27.18, 22.18, 20.58.

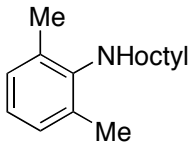


***N*-(2, 6-Xylyl)octylamine. (Table 3, entry 25).** The general procedure A conducted with 2, 6-dimethyl-1-chloro-benzene (0.141 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (100.0 μL from stock solution **A,** 1.0×10^{-3} mmol) gave 226.3 mg (97%) of *N*-(2, 6-xylyl)octylamine as a yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.10 (d, *J* = 7.6 Hz, 2 H), 6.92 (t, *J* = 7.6 Hz, 1 H), 3.10 (t, *J* = 7.2 Hz, 2 H), 3.07 (s, b, 1 H), 2.41 (s, 6 H), 1.71 (quint, *J* = 7.2 Hz, 2 H), 1.43-1.53 (m,

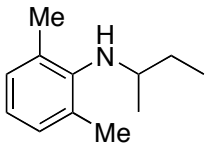
10 H), 1.04 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 146.34, 128.91, 128.66, 121.41, 48.56, 31.77, 31.16, 29.46, 29.24, 27.13, 22.60, 18.43, 14.01; Anal. Calcd. For $C_{16}H_{27}N$: C, 82.34; H, 11.66; N, 6.00. Found: C, 82.16; H, 11.78; N, 5.94.



***N*-(2, 6-Xylyl)octylamine. (Table 3, entry 26).** The general procedure A conducted with 2, 6-dimethyl-1-chloro-benzene (0.185 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A,** 5.0 × 10^{-4} mmol) gave 228.3 mg (98%) of *N*-(2, 6-xylyl)octylamine as a yellow liquid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 3, entry 25.)

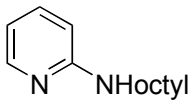


***N*-(2, 6-Xylyl)-*sec*butylamine. (Table 3, entry 27).** The general procedure A conducted with 2, 6-dimethyl-1-chloro-benzene (0.185 g, 1.00 mmol), *sec*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0 × 10^{-3} mmol) and CyPF-*t*-Bu (2.8 mg, 5.0 × 10^{-3} mmol) gave 172.7 mg (97%) of *N*-(2, 6-Xylyl)-*sec*butylamine as a yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.01 (d, J = 7.2 Hz, 2 H), 6.82 (t, J = 7.2 Hz, 1 H), 3.24 (sext, J = 6.4 Hz, 1 H), 2.82 (s, 1 H), 2.30 (s, 6 H), 1.58-1.68 (m, 1 H), 1.37-1.48 (m, 1 H), 1.10 (d, J = 6.8 Hz, 3 H), 1.00 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 145.17, 128.86, 128.78,121.02, 53.52, 30.90, 20.80, 19.03, 10.78. Anal. Calcd. For $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.37; H, 11.09; N, 8.14.

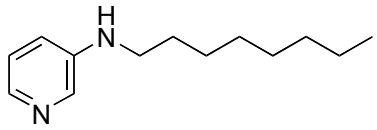


General Procedure B for Catalytic Amination of Heteroaryl and Aryl Halides in Toluene. The reaction conditions and average yields for each reaction are shown in Table 1 and 3. A typical procedure is given for the first entry in Table 5.

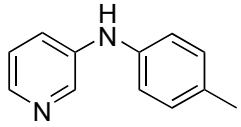
***N*-Octyl-2-aminopyridine. (Table 5, entry 1).** A solution of $Pd(OAc)_2$ and CyPF-*t*-Bu (10.0 μL from stock solution **A**, 1.0 × 10^{-4} mmol) was added to a 4 mL vial containing 2-chloropyridine (0.114 g, 1.00 mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) in 1.0 mL of toluene. Octylamine (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 3-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 200.9 mg (98%) of *N*-octyl-2-aminopyridine as a yellow solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 1, entry 1.)



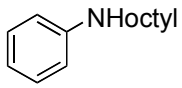
***N*-octyl-3-aminopyridine. (Table 5, entry 2).** The general procedure B conducted with 3-chloropyridine (0.114 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) gave 210.0 mg (98%) of *N*-octyl-3-aminopyridine as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 1, entry 11.)



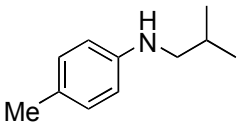
***N*-(3-Pyridinyl)-*p*-toluidine. (Table 5, entry 3).** The general procedure B conducted with 3-chloropyridine (0.114 g, 1.00 mmol), *p*-toluidine (0.130 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (100.0 μL from stock solution **A**, 1.0×10^{-3} mmol) gave 121.1 mg (66%) of *N*-(3-pyridyl)-*p*-toluidine as a yellow solid. ^{1}H NMR ($CDCl_3$) δ 8.34 (s, 1 H), 8.12 (d, *J* = 4.4 Hz, 1 H), 7.35 (t, *J* = 7.6 Hz, 1 H), 7.10-7.19 (m, 3 H), 7.02 (d, *J* = 8.0 Hz, 2 H), 5.75 (s, b, 1 H), 2.33 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 140.79, 140.42, 139.10, 138.87, 131.46, 129.81, 123.56, 121.97, 119.02, 20.54; Anal. Calcd. For $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C, 78.19; H, 6.61; N, 15.01.



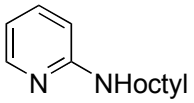
***N*-Phenyloctylamine.**[10] **(Table 5, entry 4).** The general procedure B conducted with phenyl chloride (0.113 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) gave 203.8 mg (99%) of *N*-phenyloctylamine as a colorless 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.



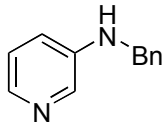
***N*-*p*-Tolyl-*iso*-butylamine.**[7] **(Table 5, entry 5).** The general procedure B conducted with 4-chlorotoluene (0.127 g, 1.00 mmol), *iso*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (20.0 μL from stock solution **A**, 2.0×10^{-4} mmol) gave 161.6 mg (99%) of *N*-*p*-tolyl-*iso*-butylamine as a pale yellow liquid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 3, entry 9.)



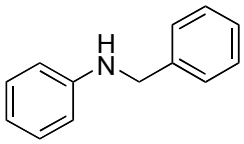
***N*-Octyl-2-aminopyridine. (Table 5, entry 6).** The general procedure B conducted with 2-bromopyridine (0.158 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (10.0 μL from stock solution **A**, 1.0×10^{-4} mmol) gave 188.6 mg (92%) of *N*-octyl-2-aminopyridine as a yellow solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 1, entry 1.)



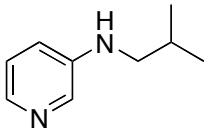
***N*-Benzyl-3-aminopyridine. (Table 5, entry 7).** The general procedure B conducted with 3-chloropyridine (0.114 g, 1.00 mmol), benzylamine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (10.0 μL from stock solution **A**, 1.0×10^{-4} mmol) gave 182.2 mg (99%) of *N*-benzyl-3-aminopyridine as a yellow solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 1, entry 14.)



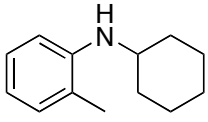
***N*-Benzylaniline. (Table 5, entry 8).** The general procedure B conducted with phenyl bromide (0.157 g, 1.00 mmol), benzylamine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **B**, 5.0×10^{-5} mmol) gave 181.8 mg (99%) of *N*-Benzylaniline as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 3, entry 3.)



***N*-*iso*-Butyl-2-aminopyridine. (Table 5, entry 9).** The general procedure B conducted with 3-iodopyridine (0.125 g, 1.00 mmol), *iso*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (200.0 μL from stock solution **A**, 2.0×10^{-3} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 148.5 mg (99%) of *N*-*iso*-butyl-2-aminopyridine as a colorless liquid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 1, entry 17.)

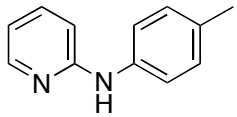


***N*-(Cyclohexylamino)-*o*-toluidine.[11] (Table 5, entry 10).** The general procedure B conducted with 2-iodotoluene (0.218 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 175.0 mg (93%) of *N*-(cyclohexylamino)-*o*-toluidine as a yellow solid. ^{1}H NMR ($CDCl_3$) δ 6.95-7.04 (m, 2 H), 6.52-6.56 (m, 2 H), 3.21-3.26 (m, 2 H), 2.04 (s, 3 H), 1.97-2.04 (m, 2 H), 1.56-1.71 (m, 3 H), 1.08-1.34 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 145.18, 135.16, 126.96, 121.46, 116.17, 110.07, 51.38, 33.53, 25.93, 24.95, 17.46.

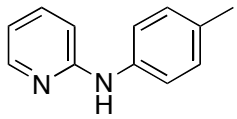


***N*-2-pyridyl-*p*-toluidine. (Table 6, entry 1).** The general procedure A conducted with 2-chloropyridine (0.114 g, 1.00 mmol), *p*-toluidine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (100.0 μL from stock solution **A,** 1.0×10^{-3} mmol) gave 158.8 mg (86%) of *N*-2-pyridyl-*p*-toluidine as

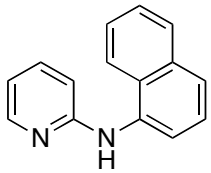
a white solid. ^{1}H NMR ($CDCl_3$) δ 8.18 (dd, *J* = 5.2, 1.2 Hz, 1 H), 7.47 (ddd, *J* = 8.6, 6.6, 1.6 Hz, 1 H), 7.21 (d, *J* = 8.4 Hz, 2 H), 7.15 (d, *J* = 8.4 Hz, 2 H), 6.83 (d, *J* = 8.4 Hz, 1 H), 6.70 (dd, *J* = 6.6, 5.4 Hz, 1 H), 6.85 (s, br, 1 H), 2.34 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 156.73, 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.



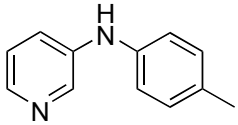
***N*-2-pyridyl-*p*-toluidine. (Table 6, entry 2).** The general procedure A conducted with 2-bromopyridine (0.158 g, 1.00 mmol), *p*-toluidine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A,** 5.0×10^{-4} mmol) gave 175.4 mg (95%) of *N*-2-pyridyl-*p*-toluidine as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 6, entry 1.)



2-α-Naphthylaminopyridine.[12] **(Table 6, entry 3).** The general procedure A conducted with 2-chloropyridine (0.114 g, 1.00 mmol), 1-naphthylamine (0.172 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) gave 214.9 mg (98%) of 2-α-naphthylaminopyridine as a colorless solid. ^{1}H NMR ($CDCl_3$) δ 8.17 (d, *J* = 5.0 Hz, 1 H), 8.10 (d, *J* = 8.5 Hz, 1 H), 7.90 (d, *J* = 7.0 Hz, 1 H), 7.72 (d, *J* = 8.5 Hz, 1 H), 7.58 (d, *J* = 7.5 Hz, 1 H), 7.39-7.54 (m, 4 H), 7.35 (s, b, 1 H), 6.69 (t, *J* = 5.0 Hz, 1 H), 6.62 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 157.85, 148.48, 137.73, 136.11, 134.69, 129.28, 128.46, 126.29, 126.16, 125.89, 125.28, 122.43, 120, 52, 114.59, 107.63.

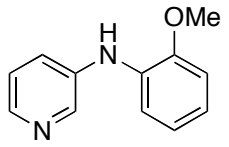


***N*-(3-Pyridinyl)-*p*-toluidine. (Table 6, entry 4).** The general procedure A conducted with 3-chloropyridine (0.114 g, 1.00 mmol), *p*-toluidine (0.130 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) gave 181.6 mg (93%) of *N*-(3-pyridyl)-*p*-toluidine as a yellow solid. ^{1}H NMR ($CDCl_3$) δ 8.34 (s, 1 H), 8.12 (d, *J* = 4.4 Hz, 1 H), 7.35 (t, *J* = 7.6 Hz, 1 H), 7.10-7.19 (m, 3 H), 7.02 (d, *J* = 8.0 Hz, 2 H), 5.75 (s, b, 1 H), 2.33 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 140.79, 140.42, 139.10, 138.87, 131.46, 129.81, 123.56, 121.97, 119.02, 20.54; Anal. Calcd. For $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C, 78.19; H, 6.61; N, 15.01.

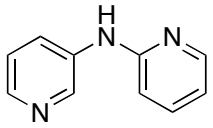


***N*-3-pyridyl-*o*-anisidine. (Table 6, entry 5).** The general procedure A conducted with 3-chloropyridine (0.114 g, 1.00 mmol), *o*-anisidine (0.148 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A**, 5.0×10^{-4} mmol) gave 197.1 mg (99%) of *N*-3-pyridyl-*o*-anisidine as colorless needles. ^{1}H NMR ($CDCl_3$) δ 8.44 (d, *J* = 2.5 Hz, 1 H), 8.17 (dd, *J* = 4.5, 1.5 Hz, 1 H), 7.48

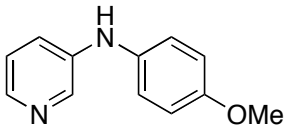
(ddd, J = 8.0, 2.5, 1.5 Hz, 1 H), 7.16-7.26 (m, 1 H), 7.17 (dd, J = 8.0, 4.5 Hz, 1 H), 6.88-6.93 (m, 3 H), 6.16 (s, b, 1 H), 3.89 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 148.67, 142.03, 140.85, 139.31, 131.63, 123.97, 123.58, 121.06, 120.77, 115.03, 110.67, 55.53; Anal. Calcd. For $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 72.05; H, 6.09; N, 13.89.



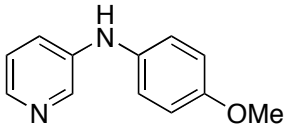
2,3'-Dipyridylamine.[13] **(Table 6, entry 6).** The general procedure A conducted with 3-chloropyridine (0.114 g, 1.00 mmol), 2-aminopyridine (0.113 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol) and CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) gave 165.0 mg (97%) of 2,3'-dipyridylamine as a colorless solid. ^{1}H NMR ($CDCl_3$) δ 8.69 (d, J = 2.5 Hz, 1 H), 8.25 (dd, J = 4.5, 1.5 Hz, 1 H), 8.23 (dd, J = 5.0, 1.0 Hz, 1 H), 8.00 (ddd, J = 8.0, 2.5, 1.5 Hz, 1 H), 7.50-7.54 (m, 1 H), 7.32 (s, b, 1 H), 7.23-7.27 (m, 1 H), 6.81 (d, J = 8.0 Hz, 1 H), 6.77-6.80 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 155.33, 148.12, 143.09, 141.48, 137.83, 137.56, 126.18, 123.66, 115.70, 109.30.



***N*-3-pyridyl-*p*-anisidine. (Table 6, entry 7).** The general procedure A conducted with 3-bromopyridine (0.158 g, 1.00 mmol), *p*-anisidine (0.148 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A,** 5.0×10^{-4} mmol) gave 161.0 mg (80%) 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.

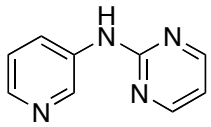


***N*-3-pyridyl-*p*-anisidine. (Table 6, entry 8).** The general procedure A conducted with 3-iodopyridine (0.205 g, 1.00 mmol), *p*-anisidine (0.148 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A,** 5.0×10^{-4} mmol) gave 195.2 mg (97%) of *N*-3-pyridyl-*p*-anisidine as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 6, entry 7.)

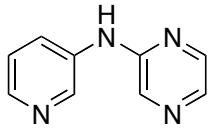


***N*-3-pyridyl-2-pyrimidinamine.**[14] **(Table 6, entry 9).** The general procedure A conducted with 3-bromopyridine (0.158 g, 1.00 mmol), 2-aminopyrimidine (0.113 g, 1.20 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0×10^{-2} mmol) and CyPF-*t*-Bu (5.5 mg, 1.0×10^{-2} mmol) gave 165.1 mg (96%) of *N*-3-pyridyl-2-pyrimidinamine as a white solid. ^{1}H NMR ($CDCl_3$) δ 8.70 (d, J = 2.0 Hz, 1 H), 8.42 (d, J = 4.5 Hz, 2

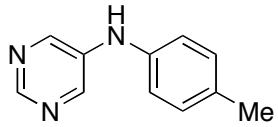
H), 8.26 (d, *J* = 4.5 Hz, 1 H), 8.24 (ddd, *J* = 8.5, 2.5, 1.5 Hz, 2 H), 7.24 (dd, *J* = 8.0, 5.0 Hz, 1 H), 6.74 (t, *J* = 5.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 160.01, 158.01, 143.48, 141.18, 136.40, 126.26, 123.41, 113.12.



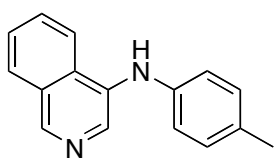
***N*-3-pyridyl-2-pyrazinamine. (Table 6, entry 10).** The general procedure A conducted with 3-bromopyridine (0.158 g, 1.00 mmol), 2-aminopyrazine (0.113 g, 1.20 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0×10^{-2} mmol) and CyPF-*t*-Bu (5.5 mg, 1.0×10^{-2} mmol) gave 158.1 mg (92%) of *N*-3-pyridyl-2-pyrazinamine 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.



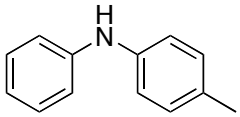
***N*-pyrimidyl-*p*-toluidine. (Table 6, entry 11).** The general procedure A conducted with 5-bromopyrimidine (0.158 g, 1.00 mmol), *p*-toluidine (0.128 g, 1.20 mmol), potassium phosphate (0.254 g, 1.40 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0 mmol) and CyPF-*t*-Bu (5.5 mg, 1.0 mmol) gave 96.5 mg (52%) of *N*-pyrimidyl-*p*-toluidine as a colorless powder. ^{1}H NMR ($CDCl_3$) δ 8.72 (s, 1 H), 8.45 (s, 2 H), 7.15 (d, *J* = 8.5 Hz, 2 H), 7.03 (d, *J* = 8.5 Hz, 2 H), 5.68 (s, b, 1 H), 2.33 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 150.45, 143.99, 138.99, 133.39, 130.33, 120.04, 105.29, 20.76; Anal. Calcd. For $C_{11}H_{11}N_3$: C, 71.33; H, 5.99; N, 22.69. Found: C, 71.11; H, 5.96; N, 22.23.



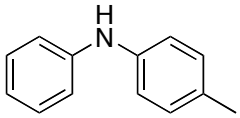
***N*-(4-*iso*quinolinyl)-*p*-toluidine. (Table 6, entry 12).** The general procedure A conducted with 4-bromoisoquinoline (0.104 g, 0.500 mmol), p-toluidine (65.0 mg, 0.600 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (25.0 μL from stock solution **A,** 2.5×10^{-4} mmol) gave 98.9 mg (84%) of *N*-(4-*iso*quinolinyl)-*p*-toluidine as a white solid. ^{1}H NMR ($CDCl_3$) δ 8.91(s, 1 H), 8.41 (S, 1 H), 7.94 (d, *J* = 8.4 Hz, 2 H), 7.56-7.65 (m, 2 H), 7.07 (d, *J* = 8.4 Hz, 2 H), 6.93 (d, *J* = 8.4 Hz, 2 H), 6.04 (S, 1 H), 2.30 (S, 3 H); ^{13}C NMR ($CDCl_3$) δ 146.14, 141.02, 134.39, 132.42, 130.99, 129.91, 129.63, 129.57, 128.97, 127.88, 127.24, 120.96, 118.42, 20.64. Anal. Calcd. For $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.69; H, 6.13; N, 11.88.



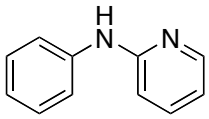
***N*-Phenyl-*p*-toluidine**[15]**. (Table 6, entry 13).** The general procedure A conducted with phenyl chloride (0.113 g, 1.00 mmol), *p*-toluidine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A,** 5.0×10^{-4} mmol) gave 182.3 mg (99%) of *N*-phenyl-*p*-toluidine as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.28 (t, *J* = 8.4 Hz, 2 H), 7.13(d, *J* = 8.0 Hz, 2 H), 7.03-7.06 (m, 4 H), 6.92 (t, *J* = 7.2 Hz, 1 H), 5.62 (s, br, 1 H), 2.35 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.84, 140.18, 130.83, 129.79, 129.24, 120.21, 118.82, 116.76, 20.65.



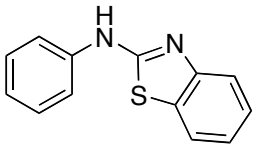
***N*-Phenyl-*p*-toluidine**[15]**. (Table 6, entry 14).** The general procedure A conducted with phenyl bromide (0.157 g, 1.00 mmol), *p*-toluidine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (5.0 μL from stock solution **A,** 5.0×10^{-5} mmol) gave 174.9 mg (95%) of *N*-phenyl-*p*-toluidine as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 6, entry 13.)



***N*-(2-Pyridyl)-aniline**[16]**. (Table 6, entry 15).** The general procedure A conducted with phenyl bromide (0.157 g, 1.00 mmol), 2-aminopyridine (0.113 g, 1.20 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0×10^{-2} mmol) and CyPF-*t*-Bu (5.5 mg, 1.0×10^{-2} mmol) gave 138.0 mg (81%) of *N*-(2-pyridyl)-aniline as a white solid. ^{1}H NMR ($CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 1 H), 7.44-7.50 (m, 1 H), 7.33-7.34 (m, 2 H), 7.30-7.32 (m, 2 H), 7.02-7.07 (m, 2 H), 6.88 (d, *J* = 8.0 Hz, 1 H), 6.71 (t, *J* = 7.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 155.99, 148.32, 140.42, 137.70, 129.26, 122.78, 120.34, 114.95, 108.14.

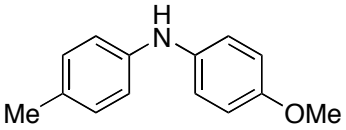


***N*-Phenylaminobenzothiazole. (Table 6, entry 16).** The general procedure A conducted with phenyl bromide (0.157 g, 1.00 mmol), 2-aminobenzothiazole (0.180 g, 1.20 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0×10^{-2} mmol) and CyPF-*t*-Bu (5.5 mg, 1.0×10^{-2} mmol) gave 139.6 mg (62%) of *N*-phenylaminobenzothiazole**.** as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.58 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.49 (td, *J* = 8.0, 1.5 Hz, 1 H), 7.34 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.25 (t, *J* = 7.5 Hz, 2 H), 7.17 (t, *J* = 7.5 Hz, 1 H), 7.12 (td, *J* = 8.0, 1.0 Hz, 1 H), 7.03 (d, *J* = 7.5 Hz, 2 H), 6.95-7.05 (s, br, 1 H); ^{13}C NMR ($CDCl_3$) δ 139.67, 137.51, 134.87, 131.73, 129.38, 126.85, 126.46, 124.09, 117.24, 115.17, 110.04. Anal. Calcd. For $C_{13}H_{10}N_2S$: C, 69.00; H, 4.45; N, 12.38. Found: C, 69.02; H, 4.49; N, 12.38.

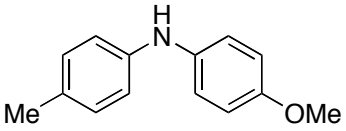


***N*-*p*-tolyl-*p*-anisidine.**[17] **(Table 6, entry 17).** The general procedure A conducted with *p*-tolyl chloride (0.127 g, 1.00 mmol), *p*-anisidine (0.148 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A,** 5.0×10^{-4} mmol) gave 210.6 mg (99%) of *N*-*p*-tolyl-*p*-anisidine 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),

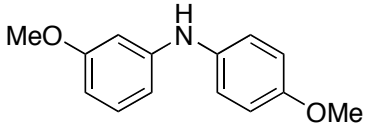
3.80 (s, 3 H), 2.27 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 154.64, 142.27, 136.50, 129.72, 129.17, 120.95, 116.43, 114.55, 55.48, 20.49.



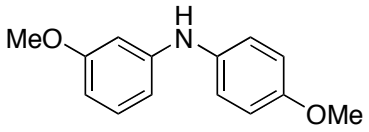
***N*-*p*-tolyl-*p*-anisidine. (Table 6, entry 18).** The general procedure A conducted with *p*-tolyl bromide (0.171 g, 1.00 mmol), *p*-anisidine (0.148 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A,** 5.0×10^{-4} mmol) gave 206.3 mg (97%) of *N*-*p*-tolyl-*p*-anisidine as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 6, entry 18.)



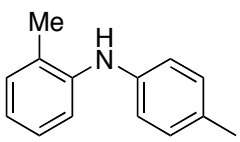
3,4'-Dimethoxydiphenylamine.[18]**(Table 6, entry 19).** The general procedure A conducted with 3-chloroanisole (0.143 g, 1.00 mmol), *p*-anisidine (0.148 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A,** 5.0×10^{-4} mmol) gave 227.9 mg (99%) of 3,4'-Dimethoxydiphenylamine as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.13 (t, *J* = 8.0 Hz, 1 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 6.87 (d, *J* = 8.4 Hz, 2 H), 6.48-6.51 (m, 2 H), 6.41 (d, *J* = 8.4 Hz, 1 H), 5.54(s, br, 1 H), 3.80 (s, 3 H), 3.76 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 160.66, 155.30, 146.60, 135.33, 129.97, 122.57, 114.55, 108.21, 104.59, 101.19, 55.45, 55.03.



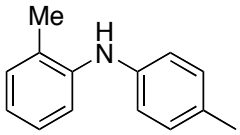
3,4'-Dimethoxydiphenylamine. (Table 6, entry 20). The general procedure A conducted with 3-bromoanisole (0.187 g, 1.00 mmol), *p*-anisidine (0.148 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A,** 5.0×10^{-4} mmol) gave 216.4 mg (94%) of 3,4'-Dimethoxydiphenylamine as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 6, entry 19.)



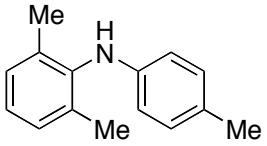
***N*-(*o*-Tolyl)-*p*-toluidine**[18]**. (Table 6, entry 21).** The general procedure A conducted with *o*-tolyl bromide (0.171 g, 1.00 mmol), *p*-toluidine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A,** 5.0×10^{-4} mmol) gave 189.8 mg (96%) of *N*-(*o*-Tolyl)-*p*-toluidine 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.



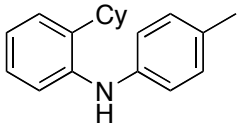
***N*-(*o*-Tolyl)-*p*-toluidine[18]. (Table 6, entry 22).** The general procedure A conducted with *o*-tolyl iodide (0.219 g, 1.00 mmol), *p*-toluidine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A,** 5.0×10^{-4} mmol) gave 195.7 mg (99%) of *N*-(*o*-Tolyl)-*p*-toluidine as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 6, entry 21.)



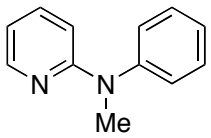
2-*N*-(*p*-Tolyl)-1,3-xylidine. (Table 6, entry 23). The general procedure A conducted with 2-bromo-1,2-dimethylbenzene (0.185 g, 1.00 mmol), *p*-toluidine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol) and CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) gave 188.4 mg (89%) of 2-*N*-(*p*-Tolyl)-1,3-xylidine as a white solid. ^{1}H NMR ($CDCl_3$) δ 6.92-7.00 (m, 3 H), 6.85 (d, J = 8.4 Hz, 2 H), 6.31 (d, J = 8.0 Hz, 2 H), 4.95 (s, br, 1 H), 2.12 (s, 3 H), 2.09 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 143.85, 138.65, 135.50, 129.71, 128.51, 127.38, 125.39, 113.73, 20.43, 18.34. Anal. Calcd. For $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.53; H, 8.03; N, 6.76.



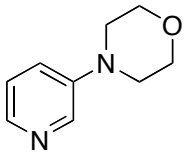
***N*-(*p*-Tolyl)-2-cyclohexylaniline. (Table 6, entry 24).** The general procedure A conducted with 1-bromo-2-cyclohexylbenzene (0.239 g, 1.00 mmol), *p*-toluidine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A,** 5.0×10^{-4} mmol) gave 235.2 mg (89%) of *N*-(*p*-Tolyl)-2-cyclohexylaniline as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.30 (dd, J = 8.0, 1.2 Hz, 1 H), 7.24 (d, J = 8.4, 1.2 Hz, 1 H), 7.14 (td, J = 7.2, 1.2 Hz, 1 H), 7.10 (d, J = 8.0 Hz, 2 H), 7.03 (td, J = 7.2, 1.2 Hz, 1 H), 6.90 (d, J = 8.4 Hz, 2 H), 5.42 (s, br, 1 H), 2.13-2.78 (m, 1 H), 2.34 (s, 3 H), 1.88-1.92 (m, 4 H), 1.79-1.82 (m, 1 H), 1.13-1.54 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 140.23, 140.53, 138.08, 129.77, 129.69, 126.46, 126.26, 122.27, 119.98, 117.76, 38.25, 33.39, 27.05, 26.27, 20.57.



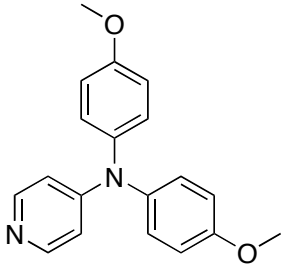
2-(*N*-Methylanilino)pyridine.[11] (Table 7, entry 1). The general procedure A conducted with 2-chloropyridine (0.125 mg, 1.10 mmol), *N*-methylaniline (0.106 mg, 1.00 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0×10^{-2} mmol) and CyPF-*t*-Bu (5.5 mg, 1.0×10^{-2} mmol) gave 105 mg (57%) of 2-(N-Methylanilino)pyridine as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 8.21 (ddd, J = 5.2, 1.6, 0.8 Hz, 1 H), 7.38 (tt, J = 8.0, 2.0 Hz, 2 H), 7.29 (ddd, J = 8.4, 6.8, 2.0 Hz, 1 H), 7.25 (dd, J = 8.4, 2.0 Hz, 2 H), 7.19 (tt, J = 7.2, 1.2 Hz, 1 H), 6.59 (ddd, J = 7.6, 5.2, 0.8 Hz, 1 H), 6.51 (dt, J = 8.4, 0.8 Hz, 1 H), 3.46 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 158.74, 147.70, 146.75, 136.52, 129.64, 126.27, 125.38, 113.05, 109.11, 38.36.



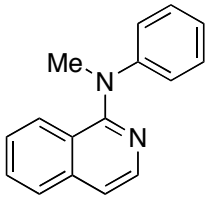
***N*-(3-Pyridyl)morpholine.**[1] **(Table 7, entry 2).** The general procedure A conducted with 3-chloropyridine (0.114 mg, 1.00 mmol), morpholine (0.105 mg, 1.20 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0×10^{-2} mmol) and CyPF-*t*-Bu (5.5 mg, 1.0×10^{-2} mmol) gave 113 mg (69%) of *N*-(3-Pyridyl)morpholine as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 8.31 (s, 1 H), 8.13 (t, *J* = 2.8 Hz, 1 H), 7.19 (d, *J* = 2.4 Hz, 1 H), 7.18 (d, *J* = 1.6 Hz, 1 H), 3.88 (t, *J* = 4.8 Hz, 4 H), 3.19 (t, *J* = 4.8 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 147.0, 141.2, 138.4, 123.7, 122.3, 66.8, 48.7.



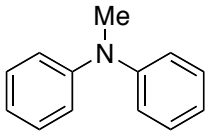
***N*,*N*-Di-(4'-methoxyphenyl)-4-pyridinamine. (Table 7, entry 3).** The general procedure A conducted with 4-chloropyridine hydrochloride 4,4'-dimethoxyphenylamine (0.150 g, 1.00 mmol), (0.275 g, 1.20 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0×10^{-2} mmol) and CyPF-*t*-Bu (5.5 mg, 1.0×10^{-2} mmol) gave 152.0 mg (50%) of *N*,*N*-Di-(4'-methoxyphenyl)-4-pyridinamine as a white solid. ^{1}H NMR ($CDCl_3$) δ 8.16 (s, b, 2 H), 7.13 (d, *J* = 8.8 Hz, 4 H), 7.89 (d, *J* = 8.8 Hz, 4 H), 6.59 (s, b, 2 H), 3.80 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 157.41, 154.23, 149.52, 137.70, 128.16, 114.96, 110.66, 55.38. Anal. Calcd. For $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.14. Found: C, 74.44; H, 6.02; N, 8.99.



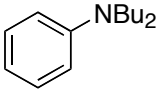
***N*-methyl-*N*-phenyl-1-isoquinolinamine (Table 7, entry 4).** The general procedure A conducted with 1-chloroisoquinoline (0.164 g, 1.00 mmol), *N*-methylaniline (0.214 mg, 2.00 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0×10^{-2} mmol) and CyPF-*t*-Bu (5.5 mg, 1.0×10^{-2} mmol) gave 150.3 mg (64%) of *N*-methyl-*N*-phenyl-1-isoquinolinamine as a yellow solid. ^{1}H NMR ($CDCl_3$) δ 8.20 (d, *J* = 6.0 Hz, 1 H), 7.63 (d, *J* = 7.6 Hz, 1 H), 7.60 (d, *J* = 8.4 Hz, 1 H), 7.42 (td, *J* = 8.2, 0.8 Hz, 1 H), 7.24 (d, *J* = 5.6 Hz, 1 H), 7.15 (td, *J* = 8.0, 1.2 Hz, 1 H), 7.12 (t, *J* = 8.0 Hz, 2 H), 6.87 (tt, *J* = 7.6, 1.2 Hz, 1 H), 6.82 (d, *J* = 8.4 Hz, 2 H), 3.50 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 158.38, 150.68, 141.11, 138.19, 129.48, 129.18, 126.87, 126.68, 126.09, 122.77, 122.13, 121.15, 116.69, 41.34. Anal. Calcd. For $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 82.01; H, 6.10; N, 11.85.



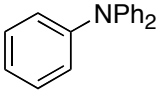
***N*-Methyldiphenylamine.**[19] **(Table 7, entry 5).** The general procedure A conducted with phenyl bromide (0.157 g, 1.00 mm0l), *N*-methylaniline (0.129 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A,** 5.0×10^{-4} mmol) gave 102.3 mg (56%) of *N*-Methyldiphenylamine 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.



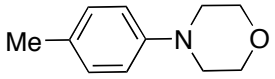
***N, N*-Di-butylaniline.**[20] **(Table 7, entry 6).** The general procedure A conducted with phenyl bromide (0.157 g, 1.00 mm0l), dibutylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol) and CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) gave 140.5 mg (69%) of *N, N*-Di-butylaniline as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.19 (t, *J* = 9.0 Hz, 2 H), 6.64 (d, *J* = 9.5 Hz, 2 H), 6.62 (t, *J* = 9.0 Hz, 1 H), 3.26 (t, *J* = 8.0 Hz, 4 H), 1.53-1.60 (m, 4 H), 1.35 (sext, *J* = 7.5 Hz, 4 H), 0.95 (t, *J* = 7.5 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 148.25, 129.17, 115.11, 111.76, 50.79, 29.45, 20.39, 14.02.



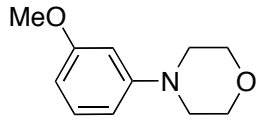
Triphenylamine.[19] **(Table 7, entry 7).** The general procedure A conducted with phenyl bromide (0.157 g, 1.00 mm0l), diphenylamine (0.203 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol) and CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) gave 211.3 mg (86%) of triphenylamine 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.



***p*-Tolylmorpholine.**[11] **(Table 7, entry 8).** The general procedure A conducted with *p*-tolyl bromide (0.171 g, 1.00 mm0l), morpholine (0.105 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol) and CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) gave 152.5 mg (86%) 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.

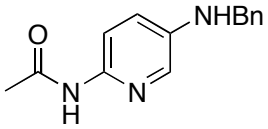


***N*-(3-Methoxyphenyl)morpholine.**[11] **(Table 7, entry 9).** The general procedure A conducted with 3-bromoanisole (0.187 g, 1.00 mm0l), morpholine (0.105 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A,** 5.0×10^{-4} mmol) gave 158.9 mg (82%) of *N*-(3-methoxyphenyl)morpholine 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.

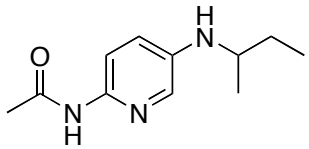


General Procedure C Using $LiN(SiMe_3)_2$ as the Base for Catalytic Amination of Functionalized Aryl Chlorides. The reaction conditions and average yields for each reaction are shown in Table 8-10. A typical procedure is given for the first entry in Table 8.

2-Acetamido-5-*N*-benzylaminopyridine (Table 8, entry 1) 2-Acetamido-5-chloropyridine (0.168 g, 1.00 mmol) was added to a 4 mL vial containing lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) in 1.0 mL of DME. $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) were then added by syringe, followed by octylamine (0.155g, 1.20 mmol). The vial was sealed with a cap containing a PTFE septum, and the reaction mixture was stirred at 100° C for 24 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 eluting with ethyl acetate to give 142.4 mg (59%) of 2-Acetamido-5-*N*-benzylaminopyridine as a white solid. ^{1}H NMR ($CDCl_3$) δ 9.12 (s, 1 H), 7.94 (d, J = 9.0 Hz, 1 H), 7.60 (d, J = 2.5 Hz, 1 H), 7.27 (d, J = 4.5 Hz, 4 H), 7.20-7.22 (m, 1 H), 6.93 (dd, J = 9.0, 3.0 Hz, 1 H), 4.25 (s, 2 H), 4.10 (s, br, 1 H), 1.98 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 168.27, 143.19, 141.09, 138.47, 131.36, 128.65, 127.37, 127.23, 122.50, 115.16, 48.18, 24.22. Anal. Calcd. For $C_{14}H_{15}N_3O$: C, 69.69; H, 6.27; N, 17.41. Found: C, 69.59; H, 6.33; N, 17.20.

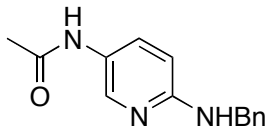


2-Acetamido-5-*N*-*sec*-butylaminopyridine (Table 8, entry 2) The general procedure C conducted with 2-acetamido-5-chloropyridine (0.168 g, 1.00 mmol), *sec*-butylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 198.3 mg (96%) of 2-Acetamido-5-*N*-*sec*-butylaminopyridine as a white solid. ^{1}H NMR ($CDCl_3$) δ 9.35(s, 1 H), 7.95 (d, J = 9.0 Hz, 1 H), 7.60 (d, J = 2.5 Hz, 1 H), 6.91 (dd, J = 9.0, 2.5 Hz, 1 H), 3.40 (s, br, 1 H), 3.30 (sext, J = 6.5 Hz, 1 H), 2.09 (s, 3 H), 1.50-1.56 (m, 1 H), 1.39-1.44 (m, 1 H), 1.11 (d, J = 6.5 Hz, 3 H), 0.89 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 168.22, 142.62, 140.83, 132.14, 122.53, 115.36, 50.05, 29.32, 24.19, 19.91, 10.15.

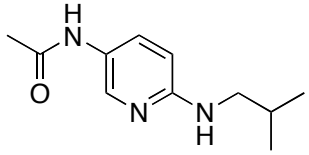


5-Acetamido-2-*N*-benzylaminopyridine (Table 8, entry 3) The general procedure C conducted with 5-acetamido-2-chloropyridine (0.168 g, 1.00 mmol), benzylamine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 175.5 mg (73%) of 2-Acetamido-5-*N*-benzylaminopyridine as a white solid. ^{1}H NMR (CD_3OD) δ 8.05 (dd, J = 2.5, 1.0 Hz, 1 H), 7.59 (dd, J = 9.0, 3.0 Hz, 1 H), 7.32 (d, J = 7.5 Hz, 2 H), 7.28 (td, J = 7.0, 1.5 Hz, 2 H), 7.20 (t, J = 7.5 Hz, 1 H), 6.50 (dd, J = 9.0, 1.0 Hz, 1 H), 4.46

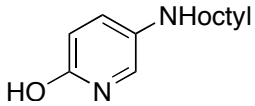
(s, 2 H), 2.07 (s, 3 H); ^{13}C NMR (CD_3OD) δ 171.70, 157.55, 141.10, 140.92, 133.18, 129.42, 128.32, 127.90, 126.57, 109.24, 46.54, 23.26.



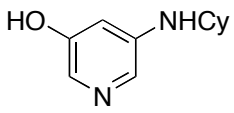
5-Acetamido-2-*N*-*iso*-butylaminopyridine (Table 8, entry 4) The general procedure C conducted with 5-acetamido-2-chloropyridine (0.168 g, 1.00 mmol), *iso*-butylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 121.1 mg (67%) of 5-Acetamido-2-*N*-*iso*-butylaminopyridine as a white solid. ^{1}H NMR (CD_3OD) δ 7.60 (d, J = 9.0 Hz, 1 H), 7.58 (s, 1 H), 6.91 (dd, J = 9.0, 3.0 Hz, 1 H), 2.78 (d, J = 8.5 Hz, 2 H), 2.02 (s, 3 H), 1.72-1.79 (m, 1 H), 0.87 (d, J = 6.5 Hz, 6 H); ^{13}C NMR (CD_3OD) δ 171.24, 144.42, 142.28, 132.98, 122.08, 117.44, 52.49, 29.02, 23.58, 20.76.



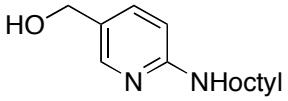
2-Hydroxy-5-*N*-octylaminopyridine (Table 8, entry 5) The general procedure C conducted with 5-chloro-2-hydroxypyridine (0.130 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 117.6 mg (53%) of 2-Hydroxy-5-*N*-octylaminopyridine as a white solid. ^{1}H NMR ($CDCl_3$) δ 13.63 (s. br, 1 H), 7.07 (dd, J = 9.5, 2.5 Hz, 1 H), 6.62 (d, J = 2.5 Hz, 1 H), 6.48 (d, J = 10.0 Hz, 1 H), 3.20 (s, br, 1 H), 2.83 (t, J = 7.0 Hz, 2 H), 1.53 (quint, J = 7.0 Hz, 2 H), 1.23-1.32 (m, 10 H), 0.84 (d, J = 67.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 162.35, 135.37, 131.93, 120.31, 114.20, 45.06, 31.72, 29.29, 29.19, 29.15, 27.07, 22.57, 14.02. Anal. Calcd. For $C_{13}H_{22}N_2O$: C, 70.23; H, 9.97; N, 12.60. Found: C, 69.96; H, 10.01; N, 12.42.



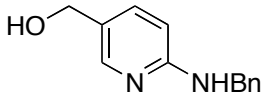
3-Hydroxy-5-*N*-cyclohexylaminopyridine (Table 8, entry 6) The general procedure C conducted with 5-chloro-3-hydroxypyridine (0.130 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 110.6 mg (67%) of 3-Hydroxy-5-*N*-cyclohexylaminopyridine as a white solid. ^{1}H NMR (CD_3OD) δ 7.40 (d, J = 2.5 Hz, 1 H), 7.30 (d, J = 2.5 Hz, 1 H), 6.43 (t, J = 2.5 Hz, 1 H), 3.15 (tt, J = 10.0, 4.0 Hz, 1 H), 1.98 (dd, J = 12.5, 3.0 Hz, 2 H), 1.76 (dt, J = 13.5, 3.5 Hz, 2 H), 1.65 (dt, J = 12.5, 3.5 Hz, 1 H), 1.33-1.42 (m, 2 H), 1.14-1.27 (m, 3 H); ^{13}C NMR (CD_3OD) δ 156.57, 147.27, 127.85, 125.42, 106.94, 52.42, 33.92, 27.00, 26.09.



5-Hydroxymethyl-2-*N*-octylaminopyridine (Table 8, entry 7) The general procedure C conducted with 2-chloro-5-hydroxymethylpyridine (0.144 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 187.0 mg (79%) of 5-Hydroxymethyl-2-*N*-octylaminopyridine as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.85 (d, *J* = 2.0 Hz, 1 H), 7.42 (dd, *J* = 8.5, 2.0 Hz, 1 H), 6.32 (d, *J* = 8.5 Hz, 1 H), 4.59 (s, 1 H), 4.44 (s, 2 H), 3.35 (s, br, 1 H), 3.15 (td, *J* = 7.0, 5.0 Hz, 2 H), 1.55 (quint, *J* = 7.5 Hz, 2 H), 1.23-1.35 (m, 10 H), 0.84 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 158.45, 147.28, 137.78, 125.07, 106.10, 62.47, 42.37, 31.76, 29.43, 29.31, 29.19, 27.00, 22.59, 14.04. Anal. Calcd. For $C_{14}H_{24}N_2O$: C, 71.14; H, 10.23; N, 11.85. Found: C, 71.39; H, 10.26; N, 11.46.

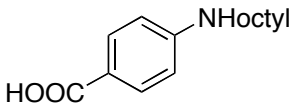


5-Hydroxymethyl-2-*N*-benzylaminopyridine (Table 8, entry 8) The general procedure C conducted with 2-chloro-5-hydroxymethylpyridine (0.144 g, 1.00 mmol), benzylamine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 117.9 mg (55%) of 5-Hydroxymethyl-2-*N*-benzylaminopyridine as a white solid. ^{1}H NMR (CD_3OD) δ 7.89 (d, *J* = 2.0 Hz, 1 H), 7.43 (dd, *J* = 9.0, 2.0 Hz, 1 H), 7.32 (d, *J* = 7.0 Hz, 2 H), 7.27 (t, *J* = 7.0 Hz, 2 H), 7.19 (t, *J* = 7.0 Hz, 1 H), 6.52 (d, *J* = 9.0 Hz, 1 H), 4.89 (s, 2 H), 4.47 (s, 2 H), 4.41 (s, 2 H); ^{13}C NMR (CD_3OD) δ 159.82, 147.27, 140.99, 138.96, 129.40, 128.28, 127.89, 126.32, 109.54, 62.74, 46.38. Anal. Calcd. For $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.60; H, 6.58; N, 12.90.

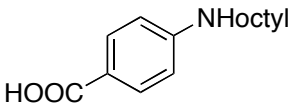


General Procedure D Using K_3PO_4 as the Base for Catalytic Amination of Functionalized Aryl Iodides. The reaction conditions and average yields for each reaction are shown in Table 9. A typical procedure is given Table 6, entry 5.

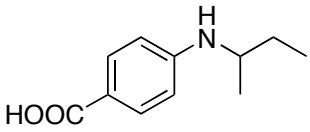
4-*N*-Octylamino-benzoic acid. (Table 9, entry 1) 4-Chlorobenzoic acid (0.157 g, 1.00 mmol) was added to a 4 mL vial containing lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) in 1.0 mL of DME. $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) were then added by syringe, followed by octylamine (0.155g, 1.20 mmol). 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 eluting with hexane/ethyl acetate (50/50) to give 202.2 mg (81%) of *N*-octyl-aminobenzoic 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.



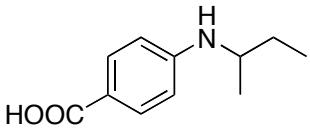
4-*N*-Octylamino-benzoic acid. (Table 9, entry 2) The general procedure C conducted with 4-bromobenzoic acid (0.201 g, 1.00 mmol), octylamine (0.155g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) gave 179.4 mg (72%) of *N*-octyl-aminobenzoic acid as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 9, entry 1.)



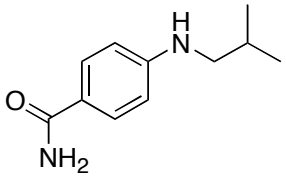
4-*N*-*sec*-butylamino-benzoic acid (Table 9, entry 3) The general procedure C conducted with 4-bromobenzoic acid (0.201 g, 1.00 mmol), sec-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 178.4 mg (92%) of 4-*N*-*sec*-butylbenzoic acid as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.25-9.00 (s, b, 1 H), 7.89 (d, *J* = 6.8 Hz, 2 H), 6.52 (d, *J* = 6.8 Hz, 2 H), 4.70-5.20 (s, b, 1H), 3.47 (sext, *J* = 5.2 Hz, 1 H), 1.46-1.62 (m, 2 H), 1.19 (d, *J* = 4.8 Hz, 3 H), 0.94 (t, *J* = 6.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 172.55, 152.03, 132.37, 116.67, 111.61, 49.53, 29.51, 20.04, 10.29. Anal. Calcd. For $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.35; H, 7.80; N, 7.17.



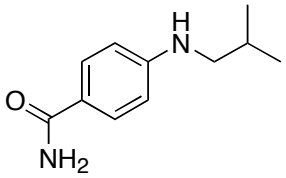
4-*N*-*sec*-butylamino-benzoic acid (Table 9, entry 4) The general procedure C conducted with 4-iodobenzoic acid (0.248 g, 1.00 mmol), sec-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 151.3 mg (92%) of 4-*N*-*sec*-butylbenzoic acid as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 9, entry 3.)



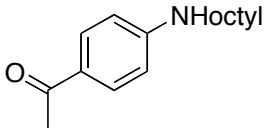
4-*N*-*Iso*-Butylamino-benzamide (Table 9, entry 5) The general procedure C conducted with 4-chlorobenzamide (0.156 g, 1.00 mmol), *iso*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 129.6 mg (67%) of 4-*N*-*iso*-butylamino-benzamide as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 2 H), 6.53 (d, *J* = 7.2 Hz, 2 H), 5.96 (s, b, 2 H), 4.04 (s, b, 1 H), 2.94 (d, *J* = 5.2 Hz, 2 H), 1.86 (nonet, *J* = 5.2 Hz, 1 H), 0.95 (d, *J* = 5.6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 169.50, 151.52, 129.23, 120.87, 111.48, 51.13, 27.98, 20.33. Anal. Calcd. For $C_{11}H_{16}N_2O$: C, 68.72; H, 8.39; N, 14.57. Found: C, 68.70; H, 8.43; N, 14.32.



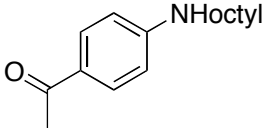
4-*N*-*Iso*-Butylamino-benzamide (Table 9, entry 6) The general procedure B conducted with 4-bromobenzamide (0.200 g, 1.00 mmol), *iso*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 162.5 mg (85%) of 4-*N*-*Iso*-Butylamino-benzamide as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 9, entry 6.)



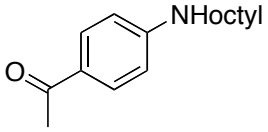
4-*N*-octylamino-acetophenone (Table 9, entry 7) The general procedure B conducted with 4'-chloro-acetophenone (0.155 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) in DME (5.0 mL) gave 225.6 mg (91%) 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.



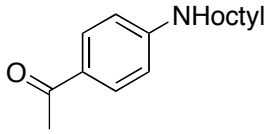
4'-*N*-octylamino-acetophenone (Table 9, entry 8). The general procedure D conducted with 4'-chloro-acetophenone (0.155 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and potassium phosphate (0.254 g, 1.40 mmol) gave 178.5 mg (74%) of 4'-*N*-octylamino-acetophenone as a pale yellow liquid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 9, entry 7.)



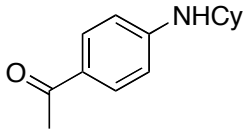
4-*N*-octylamino-acetophenone (Table 9, entry 9) The general procedure C conducted with 4'-chloro-acetophenone (0.155 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 151.2 mg (61%) of 4'-*N*-octylamino-acetophenone as a pale yellow liquid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 9, entry 7.)



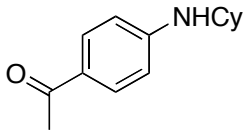
4'-*N*-octylamino-acetophenone (Table 9, entry 10). The general procedure D conducted with 4'-iodoacetophenone (0.246 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and potassium phosphate (0.254 g, 1.40 mmol) gave 192.9 mg (78%) of 4'-*N*-octylamino-acetophenone as a pale yellow liquid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 9, entry 7.)



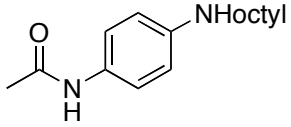
4-*N*-cyclohexylamino-acetophenone (Table 9, entry 11) The general procedure C conducted with 4'-chloro-acetophenone (0.155 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 151.6 mg (87%) 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.



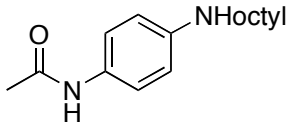
4'-*N*-octylamino-acetophenone (Table 9, entry 12). The general procedure D conducted with 4'-bromo-acetophenone (0.199 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0×10^{-2} mmol), CyPF-*t*-Bu (5.5 mg, 1.0×10^{-2} mmol) and potassium phosphate (0.254 g, 1.40 mmol) gave 142.9 mg (82%) of 4'-*N*-octylamino-acetophenone as a pale yellow liquid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 9, entry 11.)



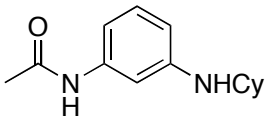
4-*N*-Octylamino-acetanilide (Table 9, entry 13) The general procedure C conducted with 4-bromoacetanilide (0.214 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 257 mg (98%) of 4-*N*-octyl-amino-acetanilide as a yelow solid. ^{1}H NMR (CD_3OD) δ 7.18 (d, *J* = 8.5 Hz, 2 H), 6.51 (d, *J* = 8.5 Hz, 2 H), 2.95 (t, *J* = 7.2 Hz, 2 H), 1.99 (s, 3 H), 1.51 (quint, *J* = 7.2 Hz, 2 H), 1.23-1.33 (m, 10 H), 0.83 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (CD_3OD) δ 171.08, 147.56, 129.43, 123,29, 114.00, 45.35, 33.01, 30.62, 30.43, 30.39, 28.32, 23.72, 23.48, 14.48. Anal. Calcd. For $C_{16}H_{26}N_2O$: C, 73.24; H, 9.99; N, 10.68. Found: C, 73.22; H, 10.10; N, 10.71.



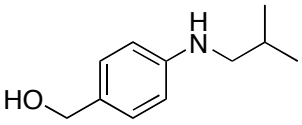
4-*N*-Octylamino-acetanilide (Table 9, entry 14). The general procedure C conducted with 4-iodoacetanilide (0.261 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 0.50 mmol%), CyPF-*t*-Bu (2.7 mg, 0.50 mmol%) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 176.2 mg (67%) of 4-*N*-octyl-amino-acetanilide as a yellow solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 9, entry 13.)



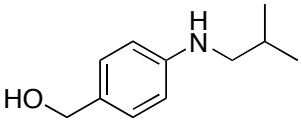
3-*N*-cyclohexylamino-acetanilide (Table 9, entry 15) The general procedure C conducted with 3-chloroacetanilide (0.170 g, 1.00 mmol), cyclohexylamine (0.119g, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 172.6 mg (74%) of 3-*N*-cyclohexylamino-acetanilide as a yellow solid. ^{1}H NMR ($CDCl_3$) δ 7.81 (s, 1H), 7.02 (t, *J* = 6.4 Hz, 1 H), 6.99 (s, 1 H), 6.62 (d, *J* = 6.4 Hz, 1 H), 6.29 (d, *J* = 6.4 Hz, 1 H), 3.40 (s, b, 1H), 3.18 (tt, *J* = 8.0, 3.0 Hz, 1 H), 2.08 (s, 3 H), 1.98 (dd, *J* = 10.0, 2.0 Hz, 2 H), 1.70 (dt, *J* = 10.8, 2.8 Hz, 2 H), 1.59 (dt, *J* = 10.0, 3.0 Hz, 1 H), 1.26-1.34 (m, 2 H), 1.04-1.23 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 168.64, 147.95, 139.03, 129.43, 108.80, 108.17, 104.75, 51.52, 31.22, 25.78, 24.84, 24.47. Anal. Calcd. For $C_{14}H_{20}N_2O$: C, 72.38; H, 8.68; N, 12.06. Found: C, 72.24; H, 8.64; N, 11.85.



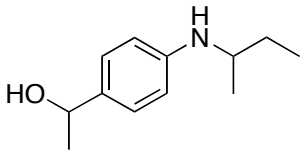
4-*N*-*iso*Butylamino-benzylalcohol (Table 9, entry 16) The general procedure C conducted with 4-bromobenzylalcohol (0.187 g, 1.00 mmol), *iso*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ and CyPF-*t*-Bu (50.0 μL from stock solution **A**, 5.0×10^{-4} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 128.7 mg (72%) of 4-*N*-*iso*butylamino-benzylalcohol as a yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.15 (d, *J* = 8.0 Hz, 2 H), 6.56 (d, *J* = 8.0 Hz, 2 H), 4.50 (s, 2 H), 3.00-3.80 (s, br, 1 H), 2.91 (d, *J* = 7.2 Hz, 2 H), 1.84-1.91 (m, 1 H), 1.10-2.10 (s, br, 1 H), 0.96 (d, *J* = 7.2 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 148.25, 129.30, 128.82, 112.57, 65.35, 51.77, 27.93, 20.40.



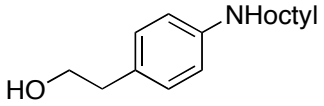
4-*N*-*iso*Butylamino-benzylalcohol (Table 9, entry 17) The general procedure C conducted with 4-iodobenzylalcohol (0.234 g, 1.00 mmol), *iso*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 0.50 mmol%),CyPF-*t*-Bu (2.7 mg, 0.50 mmol%) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 84.0 mg (47%) of 4-*N*-*iso*butylamino-benzylalcohol as a yellow liquid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 9, entry 16.)



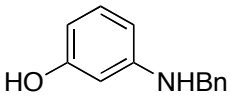
1-(4-*N*-*sec*-Butylamino-phenyl)-ethanol. (Table 9, entry 18) The general procedure C conducted with 4-chlorophenyl-1-ethanol (0.157 g, 1.00 mmol), *sec*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 160.7 mg (83%) of 1-(*N*-*sec*-butylamino-phenyl)-ethanol as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.15 (d, *J* = 8.8 Hz, 2 H), 6.54 (d, *J* = 8.0 Hz, 2 H), 4.74 (q, *J* = 6.6 Hz, 1 H), 3.38 (sext, *J* = 6.2 Hz, 1 H), 3.00 (s, b, 1H), 2.20 (s, b, 1 H), 1.54-1.62 (m, 1 H), 1.41-1.51 (m, 1 H), 1.44 (d, *J* = 6.4 Hz, 3 H), 1.16 (d, *J* = 6.0 Hz, 3 H), 0.95 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 147.03, 133.93, 126.56, 112.84, 69.93, 49.73, 29.46, 24.52, 20.08, 10.26. Anal. Calcd. For $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.20; H, 9.86; N, 7.20.



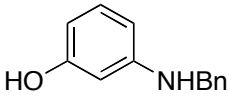
1-(4-*N*-octylamino-phenyl)-ethanol. (Table 9, entry 19) The general procedure C conducted with 4-chlorophenyl-1-ethanol (0.157 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 219.8 mg (89%) of 1-(*N*-octylamino-phenyl)-ethanol as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.01 (d, *J* = 8.4 Hz, 2 H), 6.55 (d, *J* = 8.0 Hz, 2 H), 3.77 (t, *J* = 6.4 Hz, 2 H), 3.40 (s, b, 1 H), 3.07 (t, *J* = 6.8 Hz, 2 H), 2.73 (t, *J* = 6.4 Hz, 2 H), 1.58 (quint, *J* = 7.2 Hz, 2 H), 1.28-1.40 (m, 11 H), 0.88 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 147.19, 129.76, 126.56, 112.97, 63.92, 44.19, 38.27, 31.79, 29.59, 29.38, 29.22, 27.15, 22.61, 14.04. Anal. Calcd. For $C_{16}H_{27}NO$: C, 77.06; H, 10.91; N, 5.62. Found: C, 77.21; H, 11.13; N, 5.61.



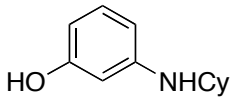
3-Hydroxy-*N*-benzyl-aniline (Table 9, entry 20) The general procedure C conducted with 3-chlorophenol (0.129 g, 1.00 mmol), benzylamine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 168.1 mg (84%) of 3-hydroxy-*N*-benzyl-aniline as a pale yellow solid. ^{1}H NMR ($CDCl_3$) δ 7.34-7.42 (m, 5 H), 7.07 (t, *J* = 8.0 Hz, 1 H), 6.29 (dd, *J* = 8.6, 1.8 Hz, 1 H), 6.26 (dd, *J* = 8.0, 2.4 Hz, 1 H), 6.16 (t, *J* = 2.2 Hz, 1 H), 4.50-5.50 (s, b, 2H), 4.29 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 156.47, 149.46, 139.01, 130.18, 128.53, 127.44, 127.16, 106.01, 104.92, 100.12, 48.17. Anal. Calcd. For $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.17; H, 6.51; N, 6.84.



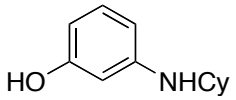
3-Hydroxy-*N*-benzyl-aniline (Table 9, entry 21) The general procedure C conducted with 3-bromophenol (0.172 g, 1.00 mmol), benzylamine (0.129 g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 170.1 mg (85%) of 3-hydroxy-*N*-benzyl-aniline as a pale yellow solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 9, entry 20.)



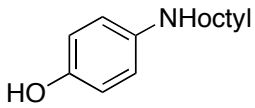
3-Hydroxy-*N*-cyclohexyl-aniline[21] **(Table 9, entry 22)** The general procedure C conducted with 3-bromophenol (0.172 g, 1.00 mmol), cyclohexylamine (0.119g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 154.6 mg (81%) of 3-hydroxy-*N*-cyclohexyl-aniline as a pale yellow solid. ^{1}H NMR ($CDCl_3$) δ 6.98 (t, *J* = 7.6 Hz, 1 H), 6.19 (dd, *J* = 8.0, 1.6 Hz, 1 H), 6.16 (dd, *J* = 8.0, 1.6 Hz, 1 H), 6.05 (t, *J* = 2.0 Hz, 1 H), 4.70 (s, br, 2 H), 3.15 (tt, *J* = 10.0, 4.0 Hz, 1 H), 2.02 (dd, *J* = 12.8, 2.4 Hz, 2 H), 1.72 (dt, *J* = 13.2, 3.6 Hz, 2 H), 1.62 (dt, *J* = 12.0, 3.6 Hz, 1 H), 1.26-1.37 (m, 2 H), 1.04-1.23 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 148.25, 129.30, 128.82, 112.57, 65.35, 51.77, 27.93, 20.40.



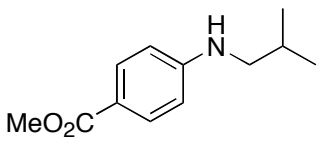
3-Hydroxy-*N*-cyclohexyl-aniline[21] **(Table 9, entry 23).** The general procedure C conducted with 3-iodophenol (0.220 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0 mmol%), CyPF-*t*-Bu (5.5 mg, 1.0 mmol%) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 133.8 mg (70%) of 3-hydroxy-*N*-cyclohexyl-aniline as a pale yellow solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 9, entry 22.)



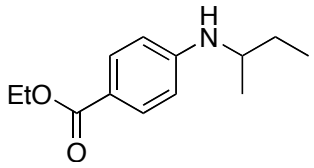
4-Hydroxy-*N*-octyl-aniline (Table 9, entry 24) The general procedure C conducted with 4-chlorophenol (0.129 g, 1.00 mmol), octylamine (0.155g, 1.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0×10^{-3} mmol), CyPF-*t*-Bu (2.8 mg, 5.0×10^{-3} mmol) and lithium bis(trimethylsilyl)amide (0.402 g, 2.40 mmol) gave 159.6 mg (72%) of 4-hydroxy-*N*-octyl-aniline as a white solid. ^{1}H NMR ($CDCl_3$) δ 6.62 (d, *J* = 6.4 Hz, 2 H), 6.53 (d, *J* = 6.4 Hz, 2 H), 4.50-5.20 (s, b, 2 H), 3.02 (t, *J* = 6.8 Hz, 2 H), 1.56 (quint, *J* = 7.0 Hz, 2 H), 1.27-1.35 (m, 10 H), 0.88 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 148.45, 141.73, 116.28, 115.29, 45.68, 31.76, 29.42, 29.35, 29.19, 27.11, 22.60, 14.06. Anal. Calcd. For $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33. Found: C, 75.88; H, 10.57; N, 6.33.



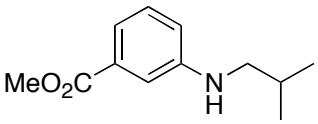
Methyl-4-(*iso*butylamino)-benzoate (Table 9, entry 25). The general procedure D conducted with methyl-4-chlorobenzoate (0.1719 mg, 1.00 mmol), *iso*butylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0×10^{-2} mmol), CyPF-*t*-Bu (5.5 mg, 1.0×10^{-2} mmol) and potassium phosphate (0.254 mg, 1.40 mmol) gave 194.4 mg (94%) of methyl-4-(*iso*butylamino)-benzoate as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.83 (d, *J* = 8.5 Hz, 2 H), 6.51 (d, *J* = 8.5 Hz, 2 H), 4.32 (s, 1 H), 3.81 (s, 3 H), 2.93 (t, *J* = 6.5 Hz, 2 H), 1.86 (nonet, *J* = 6.8 Hz, 1 H), 0.95 (d, *J* = 6.5 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 167.30, 152.23, 131.41, 117.54, 111.14, 51.32, 50.88, 27.84, 20.21. Anal. Calcd. For: $C_{12}H_{17}NO_2$ C, 69.54; H, 8.27; N, 6.76. Found: C, 69.46; H, 8.39; N, 6.80.



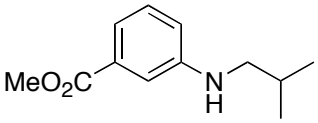
Ethyl-4-(*sec*-butylamino)-benzoate (Table 9, entry 26). The general procedure D conducted with ethyl-4-iodobenzoate (0.276 mg, 1.00 mmol), *sec*-butylamine (87.8 mg, 1.20 mmol), $Pd(OAc)_2$ (4.4 mg, 2.0 mmol%) and CyPF-*t*-Bu (11.0 mg, 2.0 mmol%) and potassium phosphate (0.254 g, 1.40 mmol) gave 169.7 mg (77%) 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.



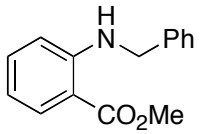
Methyl-3-(*iso*butylamino)-benzoate (Table 9, entry 27). The general procedure D conducted with methyl-3-chlorobenzoate (0.172 mg, 1.00 mmol), *iso*butylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0×10^{-2} mmol), CyPF-*t*-Bu (5.5 mg, 1.0×10^{-2} mmol) and potassium phosphate (0.254 mg, 1.40 mmol) gave 187.7 mg (91%) of methyl-3-(*iso*butylamino)-benzoate as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.26 (d, *J* = 7.6 Hz, 1 H), 7.18 (t, *J* = 2.0 Hz, 1 H), 7.12 (t, *J* = 7.6 Hz, 1 H), 6.68 (dd, *J* = 7.6, 2.0 Hz, 1 H), 3.80 (s, 3 H), 3.75-3.95 (s, br, 1 H), 2.87 (d, *J* = 6.8 Hz, 2 H), 1.80 (nonet, *J* = 6.8 Hz, 1 H), 0.90 (d, *J* = 6.8 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 167.54, 148.47, 130.86, 129.04, 117.95, 117.02, 113.03, 51.94, 51.55, 27.89, 20.37. Anal. Calcd. For: $C_{12}H_{17}NO_2$ C, 69.54; H, 8.27; N, 6.76. Found: C, 69.38; H, 8.27; N, 6.69.



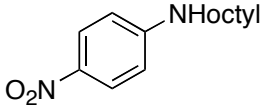
Ethyl-3-(*iso*butylamino)-benzoate (Table 9, entry 28). The general procedure D conducted with ethyl-3-bromobenzoate (0.215 mg, 1.00 mmol), *iso*butylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0×10^{-2} mmol), CyPF-*t*-Bu (5.5 mg, 1.0×10^{-2} mmol) and potassium phosphate (0.254 mg, 1.40 mmol) gave 167.5 mg (81%) of Ethyl-3-(*iso*butylamino)-benzoate as a white solid. (^{1}H and ^{13}C NMR spectra are the same as those for the product in Table 9, entry 27.)

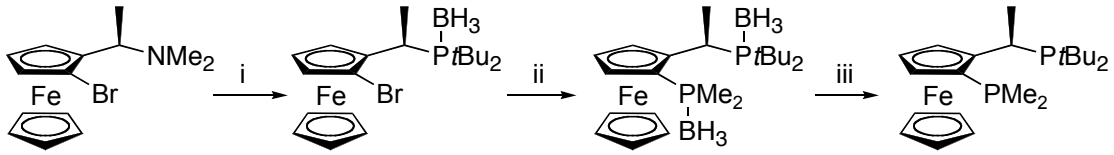


Methyl-2-(benzylamino)-benzoate (Table 9, entry 29). The general procedure D conducted with methyl-2-chlorobenzoate (0.172 mg, 1.00 mmol), benzylamine (0.119 g, 1.20 mmol), $Pd(OAc)_2$ (4.4 mg, 2.0×10^{-2} mmol), CyPF-*t*-Bu (11.0 mg, 2.00×10^{-2} mmol) and potassium phosphate (0.254 mg, 1.40 mmol) gave 197.7 mg (82%) of methyl-2-(benzylamino)-benzoate as a white solid. ^{1}H NMR ($CDCl_3$) δ 8.22 (s, 1 H), 7.96 (dd, *J* = 8.0, 2.0 Hz, 1 H), 7.26-7.39 (m, 6 H), 6.66 (d, *J* = 8.5 Hz, 1 H), 6.62 (td, *J* = 8.0, 1.0 Hz, 1 H), 4.47 (d, *J* = 5.5 Hz, 2 H), 3.88 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.06, 150.89, 138.79, 134.56, 131.56, 128.62, 127.08, 127.00, 114.79, 111.59, 110.07, 51.42, 46.86.



4-Nitro-*N*-octyl-aniline (Table 9, entry 30). The general procedure conducted with 4-nitro-1-iodobenzene (0.249 mg, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), $Pd(OAc)_2$ (2.2 mg, 1.0 mmol%), CyPF-*t*-Bu (5.5 mg, 1.0 mmol%) and potassium phosphate (0.254 g, 1.40 mmol) gave 198.0 mg (79%) 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.

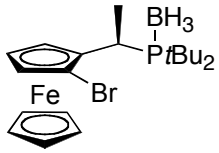




5a **5b** **5c** **5**

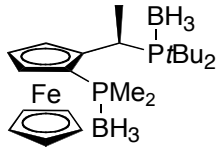
Reagents and conditions: Compound **5a** was prepared according to the reported procedure. i. a) $HPtBu_2$, AcOH, 100 ºC, 3 h; b) BH_3, THF, 10 min; ii. a) *t*BuLi, THF, _78°C, 35 min, $ClPMe_2$, overnight, RT; b) BH_3, THF, 10 min; iii. Morpholine, 100 °C, 4 h.

Preparation of Racemic MePF-*t*-Bu 5 [CpFe(C_5H_3(CH(Me)P*t*Bu_2(PMe_2)-1,2]. A red solution of compound **5a** (0.182 g, 0.540 mmol) and $HPtBu_2$ (79.3 mg, 0.540 mmol) in 2.0 mL acetic acid was heated at 100 ºC for 3 h. The solvent was removed under reduced pressure, and 2 mL of THF was added. To the solution was added 5.0 mL of BH_3• THF (1.0 M). The resulting solution was stirred for 10 min, after which time 5 mL of MeOH was added slowly with cooling in an ice bath to quench the excess BH_3. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (hexane/ethyl acetate, 90/10) to give 231.4 mg (95%) to give the product **5b** as an orange solid. ^{1}H NMR (C_6D_6) δ 4.30-4.31 (m, 1 H), 4.26-4.28 (m, 1 H), 4.08 (s, 5 H), 3.87-3.88 (m, 1 H), 3.28 (dq, *J* = 11.0, 7.5 Hz, 1 H), 1.94 (dd, *J* = 12.2, 7.4 Hz, 3 H), 1.35 (d, *J* = 12.0 Hz, 9 H), 1.26 (d, *J* = 12.0 Hz, 9 H), -0.2-1.0 (br, 3 H); ^{31}P {^{1}H} NMR (C_6D_6) δ 60.3 (m). Anal. Calcd. For $C_{20}H_{33}BBrFeP$: C, 53.26; H, 7.38. Found: C, 53.47; H, 7.51.

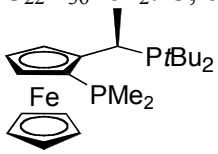


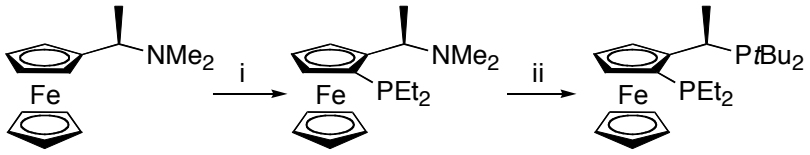
To a solution of **5b** (0.143 mg, 0.320 mmol) in THF (6.0 mL) was added a solution of *t*BuLi (1.5 M in hexane) in hexane (227 μL, 0.340 mmol) at _78°C. The resulting solution was stirred for 2 h at _78°C. A solution of $ClPMe_2$ (33.0 mg, 27.0 μL, 0.350 mmol) in 3.0 mL of Et_2O was added by syringe. The mixture was stirred overnight, and 5.0 mL of BH_3•THF (1.0 M) was added. After 10 min, aqueous

saturated $NaHCO_3$ (10 mL) was slowly added with cooling in an ice bath. The resulting organic layer and Et_2O extracts from the aqueous layer were combined, washed with 2 × 20 mL of water, dried over $MgSO_4$, and concentrated to afford an organic powder. The BH_3 protected compound **5c** was purified by flash chromatography (hexane/ethyl acetate, 90/10) to give 121.4 mg (85%) of the product **5c** as an orange solid. ^{1}H NMR (C_6D_6) δ 4.72 (s, 1 H), 4.45 (t, *J* = 3.0 Hz, 1 H), 4.27 (s, 5 H), 4.16-4.17 (m, 1 H), 3.71 (dq, *J* = 11.0, 7.5 Hz, 1 H), 2.00 (dd, *J* = 11.0, 7.5 Hz, 3 H), 1.66 (d, *J* = 10.0 Hz, 3 H), 1.50 (d, *J* = 10.0 Hz, 3 H), 1.40 (, d, *J* = 12.0 Hz, 9 H), 1.27 (d, *J* = 12.0 Hz, 9 H), -0.5-1.3 (br, 6 H); ^{31}P {^{1}H} NMR (C_6D_6) δ -3.03 (m), 57.3 (m).



A red solution of **5c** (43.0 mg, 0.096 mmol) in 1.0 mL of morpholine was heated at 100 °C for 3 h. The solvent was removed, and 5.0 mL of hexane was added. The red solution was filtered through a short plug of Celite, and the solvent was evaporated under reduced pressure. Ligand **5** was recrystalized from 5 mL of degassed EtOH to yield 38.1 mg (95%) of orange, microcrystalline product. ^{1}H NMR (C_6D_6) δ 4.07-4.09 (m, 1 H), 4.05-4.06 (m, 1 H), 4.01-4.02 (m, 1 H), 3.99 (s, 5 H), 3.63 (qd, *J* = 7.0, 2.5 Hz, 1 H), 1.74 (dd, *J* = 7.5, 3.0 Hz, 3 H), 1.49 (d, *J* = 2.5 Hz, 3 H), 1.37 (d, *J* = 10.5 Hz, 9 H), 1.26 (d, *J* = 4.5 Hz, 3 H), 1.10 (d, *J* = 11.0 Hz, 9 H); ^{31}P {^{1}H} NMR (C_6D_6) δ -65.04 (d, *J* = 36 Hz), 51.96 (d, *J* = 36 Hz). ^{13}C NMR δ 101.98 (t, *J* = 24.2 Hz), 79.90 (dd, *J* = 16.6, 3.9 Hz), 69.65 (d, *J* = 4.0 Hz), 67.68, 67.74 (d, *J* = 7.3 Hz), 67.68, 33.78 (d, *J* = 29.6 Hz), 33.86 (d, *J* = 29.6 Hz), 31.86 (d, *J* = 13.6 Hz), 31.60 (dd, *J* = 13.3 Hz), 30.78 (dd, *J* = 33.7, 6.9 Hz), 19.52 (t, *J* = 13.0 Hz), 17.02 (d, *J* = 3.0 Hz), 3.42 (dd, *J* = 11.3, 1.6Hz). Anal. Calcd. For $C_{22}H_{36}FeP_2$: C, 63.17; H, 8.67. Found: C, 62.94; H, 8.40.



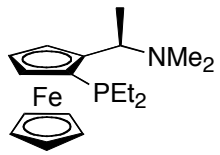


6a **6b** **6**

Reagents and conditions: i. a) *n*BuLi, Et_2O, rt, overnight; b) $ClPEt_2$, Et_2O/THF, rt, overnight; ii. $HPtBu_2$, HOAc, 100 °C, 1 h.

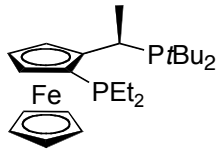
Preparation of Racemic EtPF-*t*-Bu (6) [CpFe(C_5H_3(CH(Me)P*t*Bu$_2$(PEt$_2$)-1,2]. To a solution of **6a** (1.43 g, 5.00 mmol) in Et_2O (10.0 mL) was added a solution of *n*BuLi (2.5 M in hexane) in hexane (2.10 mL, 5.25 mmol) at room temperature. The resulting solution was stirred overnight, and the clear orange solution became orange cloudy. A solution of $ClPEt_2$ (0.620 g, 5.00 mmol) in 10.0 mL of Et_2O was added through syringe. The mixture was stirred overnight. Aqueous saturated $NaHCO_3$ (10 mL) was slowly added with cooling in an ice bath. The resulting organic layer and Et_2O extracts from the aqueous layer were combined, washed with 2 × 20 mL of water, dried over $MgSO_4$, and concentrated to afford an orange powder. Compound **6b** was purified by flash chromatography (hexane/ethyl acetate, 90/10) to give 0.863g (50%) of the product **6b** as an orange solid. ^{1}H NMR (C_6D_6) δ 4.30 (dd, *J* = 6.7, 3.0 Hz, 1 H), 4.20 (s, 1 H), 4.15 (d, *J* = 2.4 Hz, 1 H), 4.13 (s, 1 H), 4.07 (s, 5 H), 2.20 (s, 6 H),

1.83-1.88 (m, 4 H), 1.34 (dt, J = 16.2, 7.7 Hz, 3 H), 1.23 (d, J = 6.8 Hz, 3 H), 1.34 (dt, J = 15.3, 7.7 Hz, 3 H); ^{31}P {^{1}H} NMR (C_6D_6) δ -31.6 (s).



6b

A red solution of compound **6b** (0.358 g, 1.04 mmol) and HP*t*Bu$_2$ (152.5 mg, 1.04 mmol) in 5.0 mL acetic acid was heated at 100 ºC for 1 h. The solvent was removed under reduced pressure and 1.0 mL of Et_3N and 10 mL of pentane was added. The red solution was filtered through a short plug of Celite and the solvent was evaporated. Ligand **6** was recrystalized from 5 mL of degassed EtOH yield 139.2 mg (30%) of orange, microcrystalline product. ^{1}H NMR (C_6D_6) δ 4.07-4.10 (m, 1 H), 4.02-4.04 (m, 2 H), 4.00 (s, 5 H), 3.64 (qd, J = 7.0, 2.5 Hz, 1 H), 2.27 (dqd, J = 14.0, 7.5, 1.5 Hz, 1 H), 1.77-1.89 (m, 3 H), 1.75 (dd, J = 7.5, 3.0 Hz, 3 H), 1.21 (dt, J = 16.5, 8.0 Hz, 3 H), 1.10 (d, J = 10.5 Hz, 9 H), 1.05 (dt, J = 9.5, 7.5 Hz, 3 H), 1.10 (d, J = 10.5 Hz, 9 H); ^{31}P {^{1}H} NMR (C_6D_6) δ -35.75 (d, J = 25.7 Hz), 51.73 (d, J = 25.3 Hz). ^{13}C NMR (C_6D_6) δ 102.00 (t, J = 23.0 Hz), 77.10 (dd, J = 16.3, 3.8 Hz), 70.04 (d, J = 4.7 Hz), 69.73, 69.55 (d, J = 3.6 Hz), 67.52, 34.13 (d, J = 30.1 Hz), 33.80 (d, J = 30.1 Hz), 31.93 (d, J = 14.1 Hz), 31.65 (dd, J = 7.5, 2.5 Hz), 30.79 (dd, J = 33.8, 7.5 Hz), 21.10 (d, J = 14.5 Hz), 20.99 (d, J = 14.5 Hz), 17.17 (dd, J = 8.5, 2.1 Hz), 11.82 (d, J = 23.9 Hz), 8.97 (d, J = 4.2 Hz). Anal. Calcd. For $C_{24}H_{40}FeP_2$: C, 64.58; H, 9.03. Found: C, 64.60; H, 8.75.



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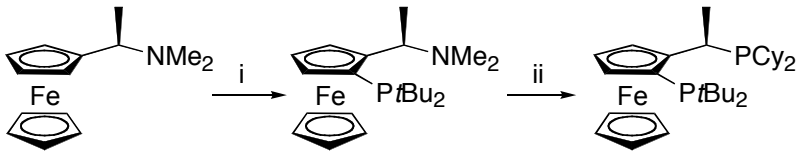
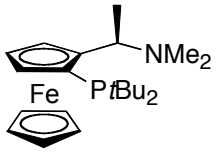


6a **9a** **9**

Reagents and conditions: i. a) *n*BuLi, Et_2O, rt, overnight; b) ClP*t*Bu$_2$, Et_2O/THF, rt, overnight; ii. HPCy$_2$, HOAc, 100 °C, 1 h.

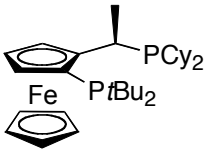
Preparation of Racemic *t*BuPFCy (9) [CpFe(C$_5$H$_3$(CH(Me)PCy$_2$(P*t*Bu$_2$)-1,2]. To a solution of **6a** (0.257 g, 1.00 mmol) in Et_2O (5.0 mL) was added a solution of *n*BuLi (2.5 M in hexane) in hexane (0.44 mL, 1.10 mmol) at room temperature. The resulting solution was stirred overnight, and the clear orange solution became orange cloudy. A solution of ClP*t*Bu$_2$ (0.180 g, 1.00 mmol) in 5.0 mL of Et_2O was added through syringe. The mixture was stirred overnight. Aqueous saturated $NaHCO_3$ (10 mL) was slowly added with cooling in an ice bath. The resulting organic layer and Et_2O extracts from the aqueous layer were combined, washed with 2 × 20 mL of water, dried over $MgSO_4$, and concentrated to afford an orange powder. Compound **9a** was purified by flash chromatography (hexane/ethyl acetate, 40/60) to give 0.381 g (95%) of the product **9a** as an orange solid. ^{1}H NMR ($CDCl_3$) δ 4.25-4.30 (m, 1 H), 4.18-4.20 (m, 1 H), 4.12-4.15 (m, 1H), 4.06 (s, 5 H), 3.95-4.02 (m, 1 H), 2.25 (s, 6 H), 1.58 (d, J = 12.0 Hz, 9 H), 1.28 (d, J = 7.2 Hz, 3 H), 1.14 (d, J = 12.0 hz, 9 H); ^{31}P {^{1}H} NMR ($CDCl_3$) δ 13.8 (s). ^{13}C NMR (C_6D_6) δ 100.12 (d, J = 27.9 Hz), 78.88 (d, J = 40.6 Hz), 72.64 (d, J = 6.3 Hz),

70.44, 68.78, 68.01 (d, J = 4.6 Hz), 56.30 (d, J = 13.1 Hz), 40.33, 33.30 (d, J = 23.3 Hz), 31.80 (d, J = 21.2 Hz), 31.21 (d, J = 15.7 Hz), 30.80 (d, J = 14.4 Hz), 26.75 (d, J = 5.2 Hz).



9a

A red solution of compound **9a** (0.100 g, 0.250 mmol) and $HPCy_2$ (250 mg, 1.25 mmol) in 2.0 mL acetic acid was heated at 100 °C for 1 h. The solvent was removed under reduced pressure, and 1.0 mL of Et_3N and 10 mL of pentane was added. The red solution was filtered through a short plug of Celite, and the solvent was evaporated. Ligand **9** was recrystalized from 5 mL of degassed EtOH to yield 131.2 mg (95%) of orange, microcrystalline product. ^{1}H NMR (C_6D_6) δ 4.35-4.39 (m, 1 H), 4.13-4.15 (m, 1 H), 4.12-4.13 (m, 1 H), 4.09 (s, 5 H), 3.22 (qd, J = 7.5, 4.0 Hz, 1 H), 1.85-2.10 (m, 4 H), 1.65-1.82 (m, 6 H), 1.62 (dd, J = 7.5, 4.0 Hz, 3 H), 1.53 (d, J = 12.0 Hz, 9 H), 1.42-1.60 (m, 5 H), 1.20-1.40 (m, 7 H), 1.15 (dt, J = 11.0 Hz, 9 H); ^{31}P {^{1}H} NMR (C_6D_6) δ 12.12 (d, J = 24.4 Hz), 9.52 (d, J = 24.4 Hz). ^{13}C NMR (C_6D_6) δ 103.55 (dd, J = 28.7, 18.5 Hz), 78.09 (dd, J = 37.7, 1.8 Hz), 72.00 (d, J = 6.5 Hz), 70.25, 68.50 (dd, J = 9.3, 4.6 Hz), 68.23, 34.25 (d, J = 25.9 Hz), 33.35 (d, J = 23.0 Hz), 32.67 (dd, J = 19.4, 1.9 Hz), 31.94 (d, J = 24.0 Hz), 31.77 (d, J = 21.2 Hz), 31.29 (d, J = 4.6 Hz), 31.18 (d, J = 4.6 Hz), 30.76 (d, J = 14.8 Hz), 30.21 (d, J = 4.6 Hz), 30.00 (d, J = 8.3 Hz), 28.30 (d, J = 14.7 Hz), 28.13 (d, J = 4.6 Hz), 27.71 (d, J = 6.4 Hz), 27.43 (d, J = 12.1 Hz), 26.90, 26.30 (d, J = 13.8 Hz), 26.11 (d, J = 12.8 Hz), 19.54 (d, J = 1.8 Hz). Anal. Calcd. For $C_{32}H_{52}FeP_2$: C, 69.31; H, 9.45. Found: C, 69.08; H, 9.83.



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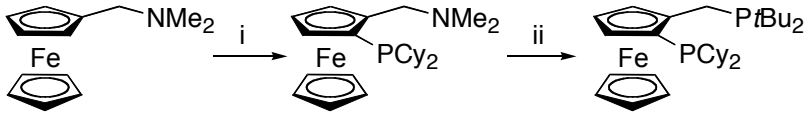
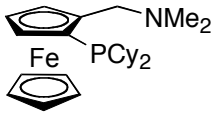


10a **10b** **10**

Reagents and conditions: i. a) *n*BuLi, Et_2O, rt, overnight; b) $ClPCy_2$, Et_2O/THF, rt, overnight; ii. $HPtBu_2$, HOAc, 100 °C, 1 h.

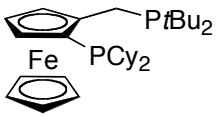
Preparation of Racemic Ligand (10) [CpFe(C_5H_3(CH_2PCy_2)($PtBu_2$)-1,2]. To a solution of **10a** (0.243 g, 1.00 mmol) in Et_2O (5.0 mL) was added a solution of *n*BuLi (2.5 M in hexane) in hexane (0.44 mL, 1.10 mmol) at room temperature. The resulting solution was stirred overnight, and the clear orange solution became orange cloudy. A solution of $ClPCy_2$ (0.233 g, 1.00 mmol) in 5.0 mL of Et_2O was added through syringe. The mixture was stirred overnight. Aqueous saturated $NaHCO_3$ (10 mL) was slowly added with cooling in an ice bath. The resulting organic layer and Et_2O extracts from the aqueous layer were combined, washed with 2 × 20 mL of water, dried over $MgSO_4$, and concentrated to afford an orange powder. Compound **10b** was purified by flash chromatography (hexane/ethyl acetate, 50/50) to give 0.350 g (83%) of the product **10b** as an orange solid. ^{1}H NMR ($CDCl_3$) δ 4.31 (s, 1 H), 4.18 (t, J = 2.4 Hz, 1 H), 4.01 (s, 6 H), 3.61 (dd, J = 13.2, 2.0 Hz, 1 H), 3.03 (d, J = 12.8 Hz, 1

H), 2.28-2.29 (m, 1 H), 2.13 (s, 6 H), 1.94-1.98 (m, 3 H), 1.80-1.82 (m, 3 H), 1.54-1.71 (m, 6 H), 1.15-1.39 (m, 5 H), 1.04-1.06 (m, 4 H). ^{31}P {^{1}H} NMR ($CDCl_3$) δ -12.13 (s).



10b

A red solution of compound **10b** (43.9 mg, 0.100 mmol) and HP*t*Bu$_2$ (16.2 mg, 0.100 mmol) in 1.0 mL acetic acid was heated at 80 ºC for 5 h. The solvent was removed under reduced pressure, and 1.0 mL of Et_3N and 10 mL of pentane was added. The red solution was filtered through a short plug of Celite, and the solvent was evaporated. Ligand **10** was recrystalized from 5 mL of degassed EtOH to yield 52.2 mg (95%) of orange, microcrystalline product. ^{1}H NMR (C_6D_6) 4.65-4.68 (m, 1 H), 4.15-4.17 (m, 1 H), 4.10 (s, 5 H), 4.05-4.08 (m, 1 H), 2.74 (d, *J* = 16.8 Hz, 1 H), 2.63 (dd, *J* = 16.4, 4.4 Hz, 1 H), 2.26-2.30 (m, 1 H), 2.05-2.13 (m, 2 H), 1.61-1.87 (m, 9 H), 1.32-1.48 (m, 6 H), 1.21 (d, *J* = 10.8 Hz, 9 H), 1.10-1.22 (m, 4 H), 1.07 (d, *J* = 10.8 Hz, 9 H). ^{31}P {^{1}H} NMR (C_6D_6) δ 23.39 (s), -14.37 (s). ^{13}C NMR (C_6D_6) δ 94.26 (dd, *J* = 23.6, 19.8 Hz), 79.64 (dd, *J* = 20.6, 3.8 Hz), 71.97 (dd, *J* = 13.7, 3.0 Hz), 70.23, 70.08, 67.87, 36.56 (dd, *J* = 14.6, 2.3 Hz), 35.90 (d, *J* = 13.0 Hz), 33.88 (d, *J* = 23.6 Hz), 32.05 (d, *J* = 24.4 Hz), 31.70 (d, *J* = 22.8 Hz), 31.64 (d, *J* = 13.0 Hz), 31.39 (d, *J* = 15.3 Hz), 30.47 (d, *J* = 4.6 Hz), 30.30 (d, *J* = 13.8 Hz), 30.14 (d, *J* = 14.5 Hz), 28.43 (d, *J* = 15.3 Hz), 27.99, 27.91 (d, *J* = 3.0 Hz), 27.64 (d, *J* = 10.0 Hz), 26.90, 22.38 (d, *J* = 10.7 Hz), 22.13 (d, *J* = 10.7 Hz); Anal. Calcd. For $C_{31}H_{50}FeP_2$: C, 68.88; H, 9.32. Found: C, 68.85; H, 9.47.



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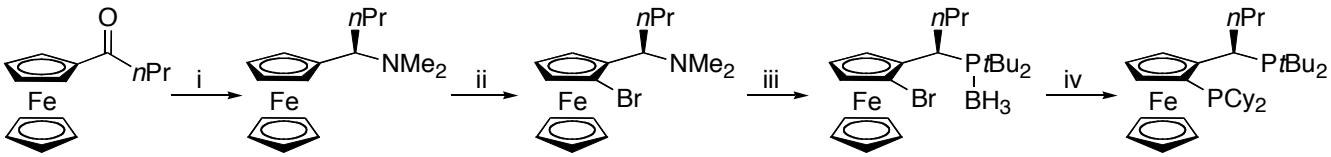
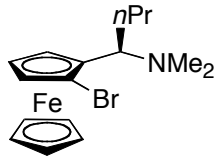


11a **11b** **11c** **11d** **11**

Reagents and conditions: Compound **11a** was prepared according to the reported procedure. i. a) $HNMe_2$, Et_3N, $TiCl_4$, CH_2Cl_2, overnight; b) $NaCNBH_3$, MeOH, 0°C, 1 h; ii. a) Li_2PdCl_4, Et_3N, MeOH, overnight; Br_2, CH_2Cl_2, 30 min; iii. a) HP*t*Bu$_2$, AcOH, 100 ºC, 3 h; b) BH_3, THF, 10 min; ii. *t*BuLi, THF, _78°C, 2 h, $ClPCy_2$, overnight, RT; iv. Morpholine, 100 °C, 4 h.

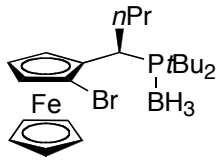
Preparation of Racemic Ligand (11) [CpFe(C_5H_3(CH(*n*Pr)PCy$_2$)(P*t*Bu$_2$)-1,2]. To a dry 500 mL flask with septum was added compound **11a** (2.56 g, 10.0 mmol), dimethylamine hydrochloride (0.816 g, 10.0 mmol), triethylamine (3.0 g, 30 mmol) and CH_2Cl_2 (60 mL) under nitrogen atmosphere. Titanium tetrachloride (0.6 mL, 5.0 mmol) was added slowly via syringe. The reaction was stirred overnight and quenched with a solution of $NaCNBH_3$ (1.80 g, 30.0 mmol) in 30 mL of MeOH with cooling in an ice bath. The resulting mixture was allowed to stir for 1 h, and the pH was adjusted to 13 with 5 N NaOH. The resulting organic layer and EtOAc extracts from the aqueous layer were combined, washed with 2 × 50 mL of water, dried over $MgSO_4$, and concentrated to afford **11b** as a red oil. This compound was used without further purification.

A solution of **11b** (1.00 g, 3.52 mmol) in 70 mL of MeOH was added to the solution of triethyl amine (1.06 mL, 7.00 mmol) and Li_2PdCl_4 (0.926 g, 3.52 mmol) in 70 mL of MeOH. Orange precipitates formed after 0.5 h, and the mixture was allowed to stir overnight. The precipitate was filtered and washed with MeOH. The resulting orange solid was dissolved in 60.0 mL of CH_2Cl_2, and bromine (0.2 mL) in 70 mL of CH_2Cl_2 was added dropwise. After stirring for 30 min, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography (hexane/triethylamine, 80/20) to give 350 mg (40%) of the desired compound **11c** as an red oil. ^{1}H NMR ($CDCl_3$) δ 4.43 (dd, *J* = 2.0, 1.0 Hz, 1 H), 4.13 (s, 5 H), 4.10 (t, *J* = 2.5 Hz, 1 H), 3.97 (dd, *J* = 2.5, 1.0 Hz, 1 H), 3.60 (dd, *J* = 11.0, 3.5 Hz, 1 H), 2.03 (s, 6 H), 1.93-2.01 (m, 1 H), 1.77-1.85 (m, 1 H), 1.61-1.68 (m, 1 H), 1.49-1.56 (m, 1 H), 1.04 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 85.79, 79.51, 71.14, 69.47, 65.68, 65.50, 59.44, 40.89, 35.01, 20.57, 14.25. MS (m/e) 318 (100), 320 (100) (M^+-NMe_2).



11c

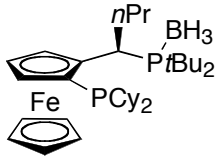
A red solution of compound **11c** (0.273 g, 0.750 mmol) and HP*t*Bu_2 (0.122 g, 0.750 mmol) in 5.0 mL acetic acid was heated at 100 ºC for 1 h. The solvent was removed under reduced pressure, and 2 mL of THF was added. To the solution was added 5.0 mL of BH_3•THF (1.0 M). The resulting solution was stirred for 10 min, and 5 mL of MeOH was added slowly with cooling in an ice bath to quench the excess BH_3. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (hexane/ethyl acetate, 30/70) to give 341.3 mg (95%) of the product **11d** as an orange solid. ^{1}H NMR ($CDCl_3$) δ 4.28 (s, 1 H), 4.15 (s, 1 H), 4.00 (s, 6 H), 2.55-2.59 (m, 1 H), 2.30-2.33 (m, 1 H), 1.51-1.87 (m, 3 H), 1.66 (d, *J* = 12.3 Hz, 9 H), 1.01 (d, *J* = 12.3 Hz, 9 H), 0.86 (t, *J* = 7.2 Hz, 3 H), -0.5-0.8 (m, 3 H); ^{31}P {^{1}H} NMR ($CDCl_3$) δ 46.4 (m). Anal. Calcd. For $C_{22}H_{37}BBrFeP$: C, 55.16; H, 7.78. Found: C, 55.45; H, 7.89.



11d

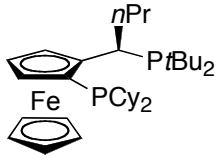
To a solution of **11d** (0.149 g, 0.310 mmol) in THF (6.0 mL) was added a solution of *t*BuLi (1.5 M in hexane) in hexane (227 μL, 0.340 mmol) at _78 °C. The resulting solution was stirred for 2 h at _78°C. A solution of $ClPCy_2$ (79.3 g, 0.340 mmol) in 3.0 mL of Et_2O was added through syringe. The mixture was stirred overnight. Aqueous saturated $NaHCO_3$ (10 mL) was slowly added with cooling in an ice bath. The resulting organic layer and Et_2O extracts from the aqueous layer were combined, washed with 2 × 20 mL of water, dried over $MgSO_4$, and concentrated to afford an organic powder. The BH_3 protected compound **11**•BH_3 was purified by flash chromatography (hexane/ethyl acetate, 95/5) to give 157.2 mg (85%) of the product as an orange solid. ^{1}H NMR ($CDCl_3$) δ 4.55-5.59 (m, 1 H), 4.24 (t, *J* = 2.5 Hz, 1 H), 4.18-4.20 (m, 1 H), 4.08 (s, 5 H), 3.20 (dt, *J* = 12.0, 9.5 Hz, 1 H), 2.31-2.41 (m, 2 H), 2.15-2.23 (m, 1 H), 1.98-2.05 (m, 3 H), 1.61-1.87 (m, 6 H), 1.32-1.54 (m, 6 H), 1.29 (d, *J* = 12.0 Hz, 9 H), 1.22 (d, *J* = 12.5 Hz, 9 H), 1.12-1.32 (m, 5 H), 1.00-1.10 (m, 3 H), 0.98 (t, *J* = 7.0 Hz, 3 H), -0.50-0.80 (m, 3 H); ^{31}P {^{1}H} NMR ($CDCl_3$) δ -20.38 (s), 61.08 (m). ^{13}C NMR ($CDCl_3$) δ 99.83 (dd, *J* = 28.0, 4.2 Hz), 84.78 (dd, *J* = 23.9, 4.7 Hz), 71.45 (d, *J* = 4.7 Hz), 70.94 (t, *J* = 3.1 Hz), 69.50, 67.45,

41.42 (d, *J* = 13.5 Hz), 40.47, 34.98 (d, *J* = 23.3 Hz), 34.27-34.59 (4 C overlap), 32.88 (d, *J* = 14.8 Hz), 32.50 (dd, *J* = 20.6, 15.1 Hz), 31.34 (d, *J* = 13.0 Hz), 30.14, 29.19 (d, *J* = 17.9 Hz), 29.03, 28.25 (d, *J* = 2.9 Hz), 27.73 (d, *J* = 3.1 Hz), 27.60 (d, *J* = 10.9 Hz), 27.31 (d, *J* = 11.3 Hz), 26.90 (d, *J* = 2.8 Hz), 24.56 (d, *J* = 3.3 Hz), 24.49 (d, *J* = 3.3 Hz), 14.43.

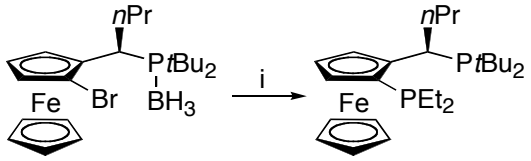


11•BH3

A red solution of **11•**BH_3 (50 mg, 0.083 mmol) in 1.0 mL of morpholine was heated at 100 °C for 1 h. The solvent was removed and 5.0 mL of hexane was added. The red solution was filtered through a short plug of Celite, and the solvent was evaporated under reduced pressure. Recrystallization of the residue from 3.0 mL of degassed EtOH yields 46.0 mg (95%) of ligand **11** as orange, microcrystalline product. ^{1}H NMR (C_6D_6) δ 4.24-5.27 (m, 1 H), 4.08 (s, 6 H), 4.07-4.09 (m, 1 H), 3.24-3.29 (m, 1 H), 2.22-2.25 (m, 3 H), 2.12-2.24 (m, 2 H), 2.04-2.13 (m, 2 H), 1.90-2.03 (m, 1 H), 1.45-1.87 (m, 13 H), 1.39 (d, *J* = 10.0 Hz, 9 H), 1.22 (d, *J* = 12.5 Hz, 9 H), 1.12-1.32 (m, 5 H), 1.05 (t, *J* = 7.0 Hz, 3 H); ^{31}P {^{1}H} NMR (C_6D_6) δ -17.66 (d, *J* = 31.9 Hz), 56.79 (d, *J* = 31.5 Hz). ^{13}C NMR (C_6D_6) δ 102.93 (dd, *J* = 26.0, 23.6 Hz), 80.00 (dd, *J* = 24.7, 3.0 Hz), 72.09 (d, *J* = 4.3 Hz), 69.69, 69.08 (t, *J* = 3.6 Hz), 67.49, 39.30 (d, *J* = 16.0, 3.4 Hz), 36.51 (d, *J* = 1.7 Hz), 35.97 (d, *J* = 6.2 Hz), 35.82 (d, *J* = 6.6 Hz), 35.52 (d, *J* = 7.0 Hz), 35.16 (d, *J* = 7.5 Hz), 33.92-34 31 (2 C overlap), 32.50 (d, *J* = 15.1 Hz), 31.62-32.20 (3 C overlap), 30.12, 28.92 (d, *J* = 16.7 Hz), 28.45 (d, *J* = 10.0 Hz), 28.13 (d, *J* = 3.2 Hz), 27.95 (d, *J* = 13.0 Hz), 27.01 (d, *J* = 23.1 Hz), 24.75, 15.01.



11

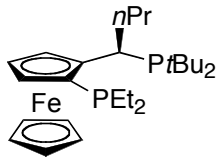


11d **12**

Reagents and conditions: i. a) *n*BuLi, THF, _78°C, 2 h, $ClPEt_2$, overnight, RT; iv. Morpholine, 100 °C, 1 h.

To a solution of **11d** (90.2 mg, 0.200 mmol) in THF (1.0 mL) was added a solution of *n*BuLi (1.6 M in hexane) in hexane (133 μL, 0.220 mmol) at _78°C. The resulting solution was stirred for 2 h at _78°C. A solution of $ClPEt_2$ (24.9 g, 0.200 mmol) in 2.0 mL of Et_2O was added through syringe. The mixture was stirred overnight. Aqueous saturated $NaHCO_3$ (10 mL) was slowly added with cooling in an ice bath. The resulting organic layer and Et_2O extracts from the aqueous layer were combined, washed with 2 × 20 mL of water, dried over $MgSO_4$, and concentrated to afford an organic powder. A red solution of the organic powder in 1.0 mL of morpholine was heated at 100 °C for 1 h. The solvent was removed and 5.0 mL of hexane was added. The red solution was filtered through a short plug of Celite, and the solvent was evaporated under reduced pressure. Recrystallization of the residue from 2.0 mL

of degassed EtOH yields 76.0 mg (80%) of ligand **12** as orange, microcrystalline product. ^{1}H NMR (C_6D_6) δ 4.00-4.08 (m, 3 H), 3.98 (s, 5 H), 3.35-3.45 (m, 1 H), 2.08-2.32 (m, 3 H), 1.70-2.06 (m, 4 H), 1.46-1.66 (m, 1 H), 1.34 (d, *J* = 10.0 Hz, 9 H), 1.20 (dt, *J* = 8.0, 7.6 Hz, 2 H), 0.95-1.18 (m, 7 H), 1.04 (t, *J* = 10.0 Hz, 9 H); ^{31}P {^{1}H} NMR (C_6D_6) δ -35.55 (d, *J* = 54.0 Hz), 60.45 (d, *J* = 54.0 Hz). ^{13}C NMR (C_6D_6) δ 100.44 (t, *J* = 23.6 Hz), 76.66 (dd, *J* = 18.3, 6.0 Hz), 70.41 (d, *J* = 4.6 Hz), 70.02, 68.74, 67.02, 36.31 (d, *J* = 33.6 Hz), 34.47, 34.10 (dd, *J* = 36.6, 3.0 Hz), 33.99 (d, *J* = 32.1 Hz), 31.97 (d, *J* = 15.3 Hz), 31.69 (d, *J* = 13.8 Hz), 24.39, 21.74 (t, *J* = 13.8 Hz), 18.33 (d, *J* = 9.9, 4.6 Hz), 15.13, 11.95 (d, *J* = 23.7 Hz), 9.64 (d, *J* = 6.0 Hz). Anal. Calcd. For $C_{26}H_{44}FeP$: C, 65.82; H, 9.35. Found: C, 65.94; H, 9.13.



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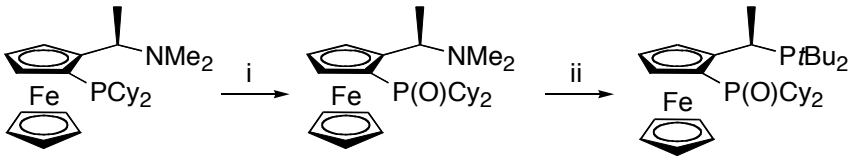
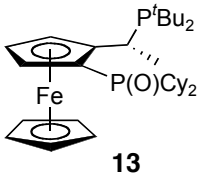


13a **13b** **13**

Reagents and conditions: i. a) H_2O_2, MeOH, room temperature, 1 h; ii. HP*t*Bu$_2$, HOAc, 100 °C, 1 h.

Preparation of Racemic Ligand 13 [CpFe(C$_5$H$_3$(CH(Me)P(O)Cy$_2$)(P*t*Bu$_2$)-1,2]. To a solution of **13a** (88.0 mg, 0.200 mmol) in 3 mL MeOH, one drop of 30% H_2O_2 was added at 0 °C and stirred for 1 h at room temperature. The product was partitioned between 30 mL $CHCl_3$ and 10 mL H_2O. The phase was separated, and the organic layer was washed with brine (20 mL), dried over $MgSO_4$ and evaporated *in vacuo* to give 90.0 mg (99%) **13b** as an orange powder. ^{1}H NMR ($CDCl_3$) δ 4.99 (s, 1 H), 4.53 (q, *J* = 6.7, 1 H), 4.47-4.50 (m, 1 H), 4.22 (s, 5 H), 4.11-4.15 (m, 1 H), 2.51 (s, 3 H), 2.32 (s, 3 H), 1.86 (d, *J* = 6.8 Hz, 3 H), 1.00-2.30 (m, 22 H from Cy); ^{31}P {^{1}H} NMR (C_6D_6) δ 49.29 (s).

A red solution of compound **13b** (90.0 mg, 0.200 mmol) and HP*t*Bu$_2$ (32.4 mg, 0.200 mmol) in 2.0 mL acetic acid was heated at 100 ºC for 30 h. The solvent was removed under reduced pressure, and 1.0 mL of Et_3N and 10 mL of pentane was added. The red solution was filtered through a short plug of Celite, and the solvent was evaporated. Ligand **13** was recrystalized from 5 mL of degassed EtOH to give 82.2 mg (73%) of orange, microcrystalline product. ^{1}H NMR (C_6D_6) δ 4.25 (s, 5 H), 4.13-4.16 (m, 1 H), 4.03-4.06 (m, 1 H), 3.99-4.02 (m, 1 H), 3.67 (dq, *J* = 22.4, 10.4 Hz, 1 H), 2.84-2.94 (m, 1 H), 2.61-2.66 (m, 1 H), 2.37-2.50 (m, 1 H), 1.75 (dd, *J* = 7.6, 3.2 Hz, 3 H), 1.44 (d, *J* = 10.4 Hz, 9 H), 1.15 (d, *J* = 10.8 Hz, 9 H), 1.20-2.03 (m, 19 H from PCy$_2$); ^{31}P {^{1}H} NMR (C_6D_6) δ 49.68 (s), 42.50 (s);). ^{13}C NMR (C_6D_6) δ 101.62 (dd, *J* = 22.9, 12.9 Hz), 74.17 (dd, *J* = 93.1, 3.1 Hz), 70.89 (d, *J* = 12,2Hz), 70.56, 70.38 (d, *J* = 8.3 Hz), 68.34 (d, *J* = 10.0 Hz), 42.83 (d, *J* = 64.8 Hz), 42.39 (d, *J* = 21.42 Hz), 41.72 (d, *J* = 21.32 Hz), 34.18 (d, *J* = 33.6 Hz), 33.32 (d, *J* = 29.8 Hz), 32.14 (d, *J* = 14.5 Hz), 31.75 (d, *J* = 13.7 Hz), 30.11, 29.79 (d, *J* = 35.1 Hz), 28.26 (d, *J* = 11.4 Hz), 27.94 (d, *J* = 12.3 Hz), 27.70 (d, *J* = 3.1 Hz), 27.58, 27.34, 27.21, 27.04, 26.78, 26.66 (d, *J* = 1.5 Hz).



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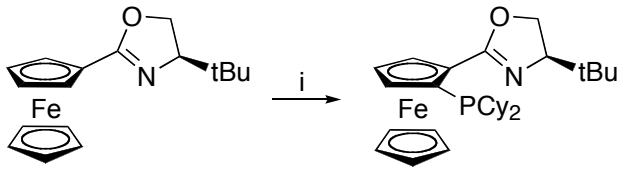
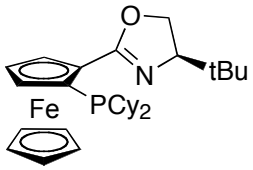


14a **14**

Reagents and conditions: Compound **14a** was prepared according to the reported procedure. i. *n*BuLi, THF, room temperature, 2 h, $ClPCy_2$, overnight, RT.

Preparation of Ligand 14. A 2.5 M solution of *n*BuLi (80 μL, 0.20 mmol) was added dropwise to the solution of **14a** (62.2 mg, 0.200 mmol) in 1.0 mL of Et_2O at room temperature. The resulting mixture was stirred for 2 h at room temperature. A solution of $ClPCy_2$ (46.5 mg, 0.200 mmol) in 2.0 mL of Et_2O was added through syringe. The mixture was stirred overnight. Aqueous saturated $NaHCO_3$ (10 mL) was slowly added with cooling in an ice bath. The resulting organic layer and Et_2O extracts from the aqueous layer were combined, washed with 2 × 20 mL of water, dried over $MgSO_4$, and concentrated to afford an organic powder. The crude product was purified by flash chromatography (hexane/ethyl acetate, 95/5) to give 89.3 mg (88%) of the product as an orange solid. ^1H NMR (C_6D_6) δ 4.95-5.01 (m, 1 H), 4.15 (s, 5 H), 4.13-4.14 (m, 2 H), 3.86-3.94 (m, 2 H), 3.77 (dd, *J* = 9.5, 8.0 Hz, 1 H), 2.58-2.61 (m, 1 H), 1.00-2.00 (m, 21 H), 0.95 (s, 9 H); ^{31}P {^1H} NMR (C_6D_6) δ -10.14 (s). ^{13}C NMR (C_6D_6) δ 165.12 (d, *J* = 1.5 Hz), 80.82 (d, *J* = 32.2 Hz), 76.88, 75.23 (d, *J* = 15.5 Hz), 72.23, 72.19, 71.26 (d, *J* = 17.5 Hz), 71.20, 70.34, 68.00, 37.86 (d, *J* = 19.2 Hz), 33.92 (d, *J* = 16.0 Hz), 33.72, 32.48 (d, *J* = 19.7 Hz), 31.02 (d, *J* = 12.8 Hz), 30.40 (d, *J* = 13.1 Hz), 29.88 (d, *J* = 9.4 Hz), 28.55 (d, *J* = 9.7 Hz), 28.32 (d, *J* = 8.4 Hz), 27.56 (d, *J* = 10.8 Hz), 27.42 (d, *J* = 9.7 Hz), 26.97 (d, *J* = 8.7 Hz), 26.25. Anal. Calcd. For $C_{29}H_{42}FeNOP$: C, 68.64; H, 8.34. Found: C, 68.55; H, 8.13.



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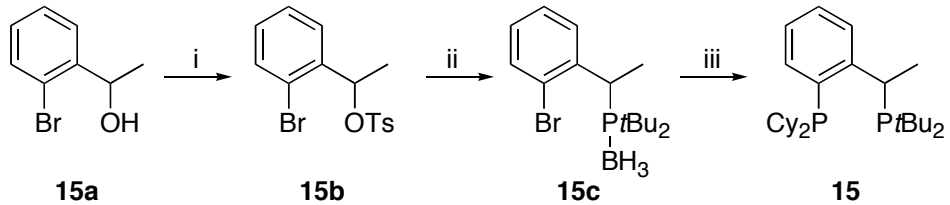
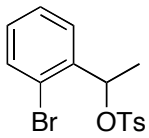


15a **15b** **15c** **15**

Reagents and conditions: i. a) NaH, Et_2O, reflux, 5 h; b) TsCl, 0°C, 1 h; ii. a) $LiPtBu_2{\bullet}BH_3$, -78°C→reflux, 10 h; iii. a) *t*BuLi, THF, _78°C, 35 min, $ClPCy_2$, overnight, RT; b) Morpholine, 100 °C, 1 h.

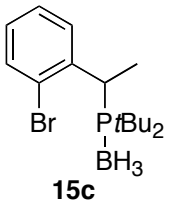
Preparatiion of Ligand 15. A solution of 2-bromo-α-methylbenzylaocohol **15a** (0.400 g, 2.00 mmol) in 2.0 mL of Et_2O was added dropwise to a suspension of NaH (50.0 mg, 2.00 mmol) in 3.0 mL of Et_2O in a schlenk's tube nunder nitrogen atmosphere. The resulting mixture was stirred for 30 min at room temperature and heated to reflux for 5 h. The mixture was cooled to 0 °C and tosyl chloride (1.9

mmol) in 5.0 mL Et_2O was added dropwise. The mixture was stirred for another hour at 0 °C. The mixture was filtered through a short-pass funnel with Celite. The solvent was evaporated under reduced pressure. Recrystallizition from Et_2O/hexane at -10 °C gave 675 mg (95%) of compound **15b** as white crystals. ^{1}H NMR ($CDCl_3$) δ 7.65 (d, J = 8.5 Hz, 2 H), 7.34 (ddd, J = 8.0, 5.5, 1.0 Hz, 2 h), 7.14-7.18 (m, 3 H), 7.03 (td, J = 8.0, 1.5 Hz, 1 H), 5.89 (t, J = 6.5 Hz, 1 H), 2.32 (s, 3 H), 1.50 (d, J = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 144.49, 139.16, 133.44, 132.32, 129.47, 129.36, 127.72, 127.66, 127.35, 120.82, 79.09, 22.80, 21.40. Anal. Calcd. For $C_{15}H_{15}BrO_3S$: C, 50.71; H, 4.26. Found: C, 50.67; H, 4.23.



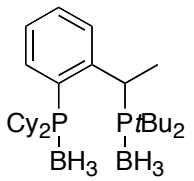
15b

A 1.0 M solution of *n*BuLi (0.4 mL, 1.0 mmol) was added dropwise to a solution of HP*t*Bu$_2$•BH$_3$ (0.160 g, 1.00 mmol) in 2.0 mL of THF at -78°C. The resulting mixture was stirred for 0.5 h at -78°C and 0.5 h at room temperature. The resulting solution was then added to a solution of **15b** (0.354 g, 1.00 mmol) in 3.0 mL of THF at -78°C. The mixture was stirred for 0.5 h at room temperature and heated to reflux for 10 h. White precipitate was formed during this time. After cooling to room temperature, the mixture was filtered through a short-pass funnel containing Celite. The solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (hexane/ethyl acetate, 99/1) to give 295.3 mg (92%) of **15c** as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.85 (d, J = 8.4 Hz, 1 H), 7.43 (d, J = 8.0 Hz, 1 H), 7.18-7.22 (m, 1 H), 6.97-7.01 (m, 1 H), 4.06 (dq, J = 14.4, 7.2 Hz, 1 H), 1.52 (dd, J = 13.2, 7.2 Hz, 3 H), 1.37 (d, J = 12.0 Hz, 9 H), 1.01 (d, J = 12.0 Hz, 9 H), 0.10-1.00 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 142.80, 132.67 (d, J = 2.7 Hz), 131.82 (d, J = 2.2 Hz), 128.33 (d, J = 1.5 Hz), 127.58 (d, J = 1.7 Hz), 124.03 (d, J = 6.2 Hz), 34.49 (d, J = 23.6 Hz), 34.17 (d, J = 24.5 Hz), 31.98 (d, J = 22.5 Hz), 29.22, 29.14, 22.55 (d, J = 1.3 Hz). ^{31}P {^{1}H} NMR ($CDCl_3$) δ 58.5 (m).



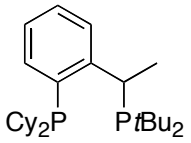
15c

A 1.5 M solution of *t*BuLi (0.54 mL, 0.81 mmol) was added dropwise to the solution of **15c** (0.278 g, 0.810 mmol) in 2.0 mL of THF at -78°C. The resulting mixture was stirred for 1 h at -78°C. To this yellow solution, $ClPCy_2$ (0.189 g, 0.900 mmol) was added. The resulting mixture was stirred at -78°C for 2 h and then heated to 60 °C for 5 h. The solution was cooled to room temperature, and 3.0 mL of BH_3•THF (1.0 M) was added. The resulting solution was stirred for 10 min, and 5.0 mL of MeOH was added slowly with cooling in an ice bath to quench the excess BH_3. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (hexane/ethyl acetate, 90/00) to give 203.3 mg (53%) of **15**•BH_3 as a white solid. ^{1}H NMR ($CDCl_3$) δ 8.22 (dd, J = 7.6, 4.4 Hz, 1 H), 7.45 (t, J = 8.0 Hz, 1 H), 7.38 (t, J = 8.0 Hz, 1 H), 7.23 (t, J = 7.6 Hz, 1 H), 4.89 (dq, J = 14.4, 6.8 Hz, 1 H), 2.18-2.30 (m, 1 H), 1.71-1.98 (m, 9 H), 1.58 (dd, J = 13.2, 7.2 Hz, 3 H), 1.40-1.60 (m, 3 H), 1.41 (d, J = 12.0 Hz, 9 H), 1.00-1.26 (m, 9 H), 1.00 (d, J = 12.0 Hz, 9 H), 0.00-1.00 (m, 6 H); ^{31}P {^{1}H} NMR ($CDCl_3$) δ 24.79 (m), 58.75 (m).



15·2BH$_3$

A colorless solution of **15**•2BH$_3$ (100.0 mg, 0.224 mmol) in 1.0 mL of morpholine was heated at 100 °C for 1 h. The solvent was evaporated, and 5.0 mL of hexane was added. The solution was filtered through a short plug of Celite, and the solvent was evaporated under reduced pressure. Recrystallization of the residue from 3.0 mL of degassed EtOH yielded 85.0 mg (85%) of ligand **15** as white crystals. ^{1}H NMR (C_6D_6) δ 7.60-7.64 (m, 1 H), 7.07 (d, *J* = 8.0 Hz, 1 H), 6.86-6.88 (m, 1 H), 6.71 (td, *J* = 7.5, 1.5 Hz, 1 H), 4.47-4.55 (m, 1 H), 1.68-1.78 (m, 3 H), 1.37-1.49 (m, 6 H), 1.32 (dd, *J* = 8.5, 7.0 Hz, 3 H), 1.17-1.26 (m, 2 H), 1.03 (d, *J* = 10.0 Hz, 9 H), 1.00-1.26 (m, 9 H), 0.80-1.00 (m, 2 H), 0.89 (d, *J* = 10.0 Hz, 9 H); ^{13}C NMR (C_6D_6) δ 156.07 (dd, *J* = 24.9, 9.2 Hz), 133.25 (d, *J* = 17.5 Hz), 133.12 (d, *J* = 2.8 Hz), 130.38 (dd, *J* = 14.7, 4.6 Hz), 128.74, 124.99 (d, *J* = 1.8 Hz), 36.16 (d, *J* = 15.6 Hz), 32.61-32.09 (4 C), 31.97 (dd, *J* = 11.9, 2.6 Hz), 31.83 (d, *J* = 12.9 Hz), 31.40 (d, *J* = 15.7 Hz), 30.99 (d, *J* = 13.8 Hz), 30.71 (d, *J* = 17.5 Hz), 29.59 (d, *J* = 6.5 Hz), 27.77 (d, *J* = 11.9 Hz), 27.68 (d, *J* = 6.4 Hz), 27.52 (d, *J* = 10.2 Hz), 27.34 (d, *J* = 11.1 Hz), 26.64 (d, *J* = 26.77 Hz), 24.81 (d, *J* = 12.8 Hz), 10.5. ^{31}P {^{1}H} NMR ($CDCl_3$) δ -16.98 (s), 53.59 (s). Anal. Calcd. For $C_{28}H_{48}P_2$: C, 75.30; H, 10.83. Found: C, 74.87; H, 11.27.



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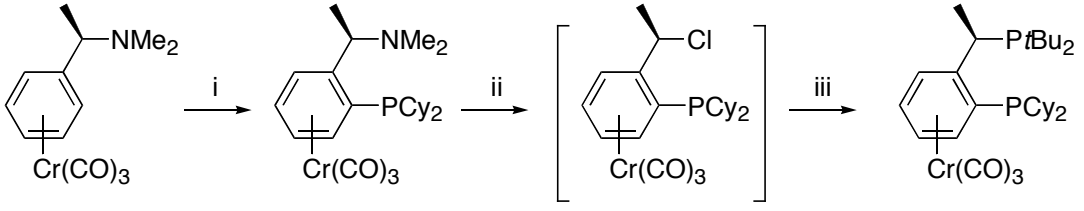
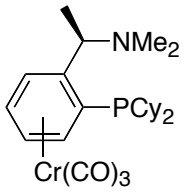


16a **16b** **16c** **16**

Reagents and conditions: i. *t*BuLi, THF, _78°C, 1 h, $ClPCy_2$, overnight, RT; ii. 1-Chloroethyl chloroformate, THF, -40 °C→room temperature, overnight; iii. a) $HPtBu_2$, $TlPF_6$, acetone, room temperature, overnight; b) Et_3N, room temperature, 15 min.

Preparation of Ligand 16. A 1.5 M solution of *t*BuLi (0.73 mL, 1.00 mmol) was added dropwise to the solution of **16a** (0.285 g, 1.00 mmol) in 2.0 mL of THF at -78°C. The resulting mixture was stirred for 1 h at -78 °C. To this yellow solution, $ClPCy_2$ (0.210 g, 1.00 mmol) was added. The resulting mixture was stirred at -78 °C for 2 h and then room temperature overnight. Aqueous saturated $NaHCO_3$ (10 mL) was slowly added with cooling in an ice bath. The resulting organic layer and Et_2O extracts from the aqueous layer were combined, washed with 2 × 20 mL of water, dried over $MgSO_4$, and concentrated to afford a yellow powder. Compound **16b** was purified by flash chromatography (hexane/diethyl ether, 80/20) to give 0.397 g (80%) of the product **16b** as a yellow solid. ^{1}H NMR (C_6D_6) δ 5.03 (d, *J* = 5.5 Hz, 1 H), 4.63 (t, *J* = 6.0 Hz, 1 H), 4.41-4.48 (m, 3 H), 2.52-2.55 (m, 1 H),

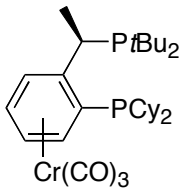
1.93 (s, 6 H), 1.36-1.87 (m, 14 H), 1.01-1.25 (m, 7 H), 0.83 (d, J = 7.0 Hz, 3 H); $^{31}P\{^{1}H\}$ NMR (C_6D_6) δ -6.52 ppm.



16b

1-Chloroethyl chloroformate (0.143 g, 1.00 mmol) was added dropwise to a stirring solution of **16b** (0.100 g, 0.250 mmol) in 5.0 mL of THF at -40°C. The solution was warmed to room temperature and kept stirring overnight. The solvent was evaporated and the residue was dissolved in 5.0 mL of Et_2O. The solution was filtered through a short pad of Celite, and the solvent was evaporated under reduced pressure to give a yellow solid. Attempts at purification by flash chromatography resulted in decomposition. The crude material was used without further purification.

HP*t*Bu$_2$ (36.6 mg, 0.250mmol) was added to the solution of the crude product dissolved in 5.0 mL of dry acetone. To this solution was added dropwise a suspension of $TlPF_6$ (88.0 mg, 0.250 mmol) in 1.0 mL of dry acetone. A fine white formed immediately. The solution was stirred at room temperature overnight. NEt_3 (0.5 mL) was added, and the solution was further stirred for 15 min and then filtered through a short plug of Celite. The solvent and excess NEt_3 were evaporated under reduced pressure. The residue was purified by flash chromatography (hexane/Et_2O, 95/5) to give 104.5 mg (70%) of ligand **16** as a yellow solid. ^{1}H NMR (C_6D_6) δ 5.12 (d, J = 6.5 Hz, 1 H), 4.67-4.71 (m, 2 H), 4.35 (td, J = 6.0, 2.0 Hz, 1 H), 4.12 (quintet, J = 6.5 Hz, 1 H), 1.53 (dd, J = 7.5, 2.5 Hz, 3 H), 1.1-2.5 (m, 22 H), 1.30 (d, J = 11.0 Hz, 9 H), 1.02 (d, J = 11.0 Hz, 9 H); ^{31}P $\{^{1}H\}$ NMR (C_6D_6) δ 50.23 (d, J = 52.67 Hz), -13.66 (d, J = 52.67 Hz) ppm. ^{13}C NMR (C_6D_6) δ 233.79, 125.62 (dd, J = 20.5, 16.5 Hz), 107.57 (d, J = 38.5 Hz), 98.18 (d, J = 2.1 Hz), 94.18, 90.40 (t, J = 5.5 Hz), 89.03, 38.30 (dd, J = 13.8, 9.6 Hz), 36.46 (dd, J = 19.2, 4.5 Hz), 35.25 (d, J = 16.7 Hz), 35.14 (d, J = 33.1 Hz), 34.93 (d, J = 16.9 Hz), 34.63 (d, J = 32.1 Hz), 33.11 (d, J = 23.5 Hz), 32.55 (dd, J = 15.6, 7.3 Hz), 32.42 (d, J = 13.5 Hz), 31.74 (dd, J = 12.5, 2.9 Hz), 30.03 (d, J = 12.2 Hz), 28.81 (d, J = 9.3 Hz), 28.68 (d, J = 12.8 Hz), 28.01 (d, J = 7.3 Hz), 27.45 (d, J = 6.9 Hz), 27.41 (d, J = 13.7 Hz), 26.89, 26.72 (d, J = 1.6 Hz). Anal. Calcd. For $C_{32}H_{51}CrO_3P_2$: C, 64.30; H, 8.60. Found: C, 63.87; H, 9.05.



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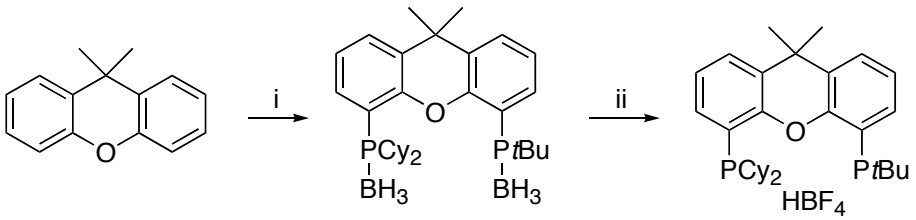
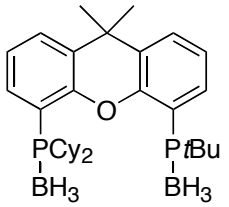


17a **17**

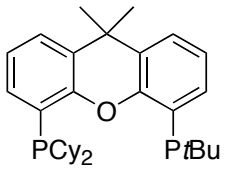
Reagents and conditions: i. a) BuLi/TMEDA, Et_2O, -78 °C→room temperature for 16 h; b) Cl*P*tBu_2, -78 °C→room temperature, 16 h; c) BuLi/TMEDA, Et_2O, -78 °C→room temperature for 16 h; d) $ClPCy_2$, -78 °C→room temperature, 16 h; e) BH_3/THF, room temperature, 10 min; ii. a) TMEDA, reflux, 10 h; b) HBF_4/CH_2Cl_2, room temperature, 30 min.

Preparatiion of Ligand 17. A solution (1.40 M) of *sec*-Butyllithium (1.50 mL, 2.10 mmol) was added dropwise to a mixture of Xanthene (0.420 g, 2.0 mmol) and TMEDA (0.244 g, 2.10 mmol) in Et_2O (5.0 mL). The resulting mixture was stirred for 16 h at room temperature. The mixture was cooled to -78 °C, and di-*tert*-butyl-chlorophosphine (0.361g, 2.00 mmol) in 5.0 mL Et_2O was added dropwise. The mixture was stirred for 16 h at room temeperature before it was cooled to -78 °C. TMEDA (0.244 g, 2.10 mmol) was added, followed by a solution (1.40 M) of *sec*-butyllithium (1.50 mL, 2.10 mmol). The resulting mixture was stirred for 16 h at room temperature. The mixture was cooled to -78 °C and di-cyclohexyl-chlorophosphine (0.465 g, 2.00 mmol) in 5.0 mL Et_2O was added dropwise. The mixture was stirred for 16 h at room temeperature. BH_3 in THF (30.0 mL, 1.0 M) was added, and the mixture was stirred for another 2 h at room temperature. The excess BH_3 was quenched by methanol. The solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography (hexane/ethyl acetate, 90/10) to give a white solid. The white solid was further purified by recrystallization from ethyl acetate to give **17a** (300.9 mg, 26%) as colorless crystals. ^{1}H NMR ($CDCl_3$) δ 7.91 (ddd, *J* = 13.2, 7.2, 1.2 Hz, 1 H), 7.63 (dt, *J* = 7.6, 1.6 Hz, 1 H), 7.54 (d, *J* = 7.2 Hz, 1 H), 7.46 (dd, *J* = 7.6, 1.6 Hz 1H), 7.10-7.14 (m, 2 H), 3.60-3.64 (m, 2 H), 2.13 (d, *J* = 11.6 Hz, 2 H), 1.73-1.82 (m, 4 H), 1.57 (s, 6 H), 1.26 (d, *J* = 12.0 Hz, 18 H), 1.10-1.62 (m, 14 H), 0.01-1.00 (m, 6 H); ^{31}P {^{1}H} NMR ($CDCl_3$) δ 38.4 (br), 10.54 (br).



17a

A colorless solution of **17a** (100.0 mg, 0.173 mmol) in 10.0 mL of TMEDA was heated at 110°C for 5 h. The solvent was removed, and 5.0 mL of hexane was added. The solution was filtered through a short plug of Celite, and the solvent was evaporated under reduced pressure. The residue was dissolved in 3.0 mL of CH_2Cl_2, and aqueous HBF_4 (43% w/w, 0.2 mL) was added. After vigiously stirring for 10 min, the organic layer was separated and dried over $MgSO_4$. Filtration, followed by removal of the solvent and recrystallization of the residue form CH_2Cl_2 by the addition of pentane afforded the product as colorless crystals. ^{1}H NMR (CD_2Cl_2) δ 8.48 (dd, *J* = 478.3, 7.2 Hz, 1 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.65 (t, *J* = 8.4 Hz, 1 H), 7.48-7.54 (m, 2 H), 7.38 (d, *J* = 7.6 Hz, 1 H), 7.27 (t, *J* = 7.6 Hz, 1 H), 2.06 (t, *J* = 7.2 Hz, 2 H), 1.95 (d, *J* = 7.5 Hz, 2 H), 1.79 (d, *J* = 12.8 Hz, 2 H), 1.65 (s, 6 H), 1.57 (d, *J* = 13.2 Hz, 18 H), 1.50-1.70 (m, 5 H), 0.95-1.42 (m, 11 H); ^{31}P {^{1}H} NMR (CD_2Cl_2) δ 22.0 (d, *J* = 89.0 Hz), -16.55 (d, *J* = 89.0 Hz). ^{13}C NMR (CD_2Cl_2) δ 154.60 (d, *J* = 3.0 Hz), 154.30 (d, *J* = 18.4 Hz), 134.76 (d, *J* = 4.5 Hz), 133.14, 132.41 (d, *J* = 3.0 Hz), 131.37, 130.73 (d, *J* = 5.3 Hz), 126.95, 125.63 (d, *J* = 11.4 Hz), 124.94, 122.19 (d, *J* = 19.1 Hz), 103.52 (d, *J* = 70.4 Hz), 35.81, 35.13 (d, J = 33.5 Hz), 33.24 (d, J = 9.9 Hz), 30.98 (d, *J* = 16.0 Hz), 30.01, 29.53 (d, *J* = 6.8 Hz), 27.93, 27.29 (d, *J* = 13.0 Hz), 27.11 (d, *J* = 8.3 Hz), 26.53.



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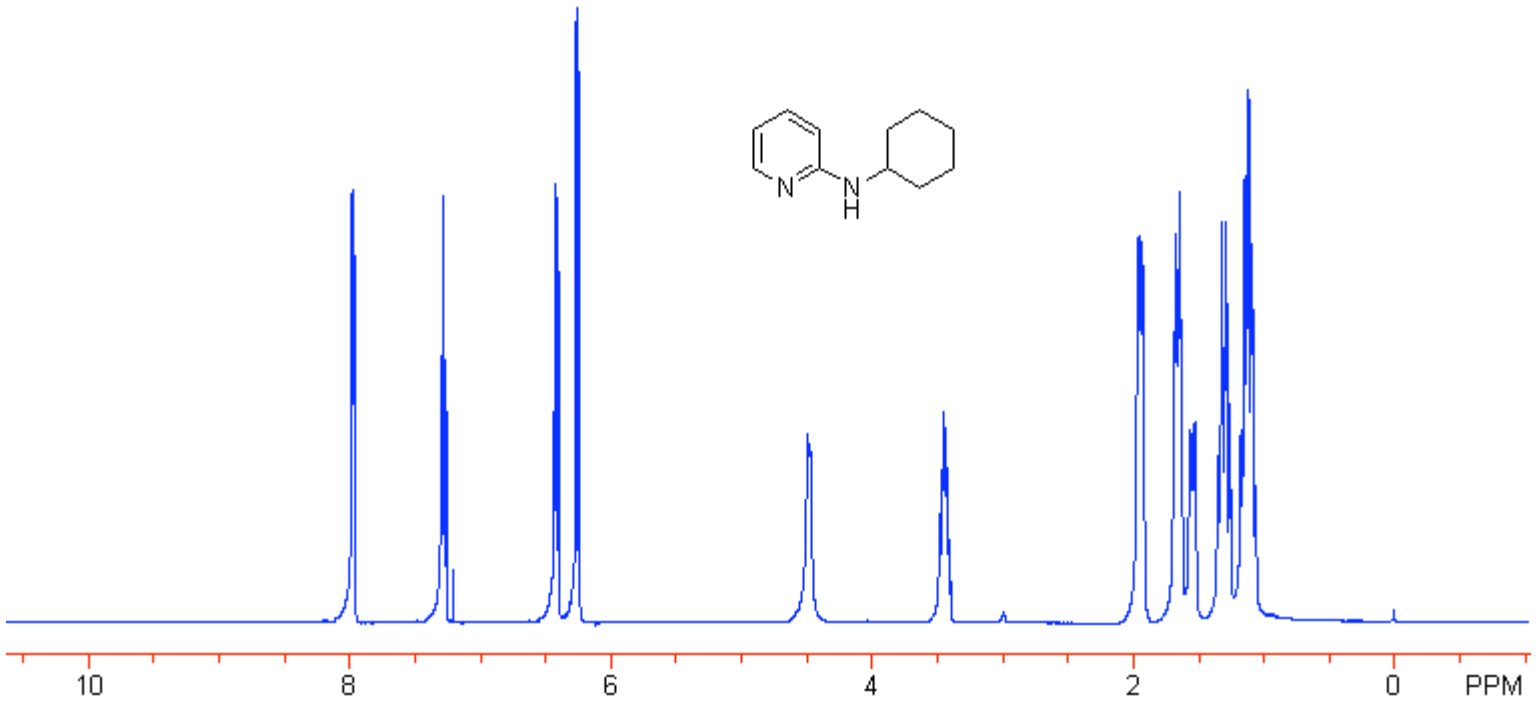
21. Ryoichi, H.; Masahiro, K.; Tetsutaro, K.; Kiyoshi, T.; Fumio, Y. *J. Heterocyclic Chem.* **1989**, *26*, 1255-1259.

Table 1, entry 6, *N*-Cyclohexyl-2-aminopyridine



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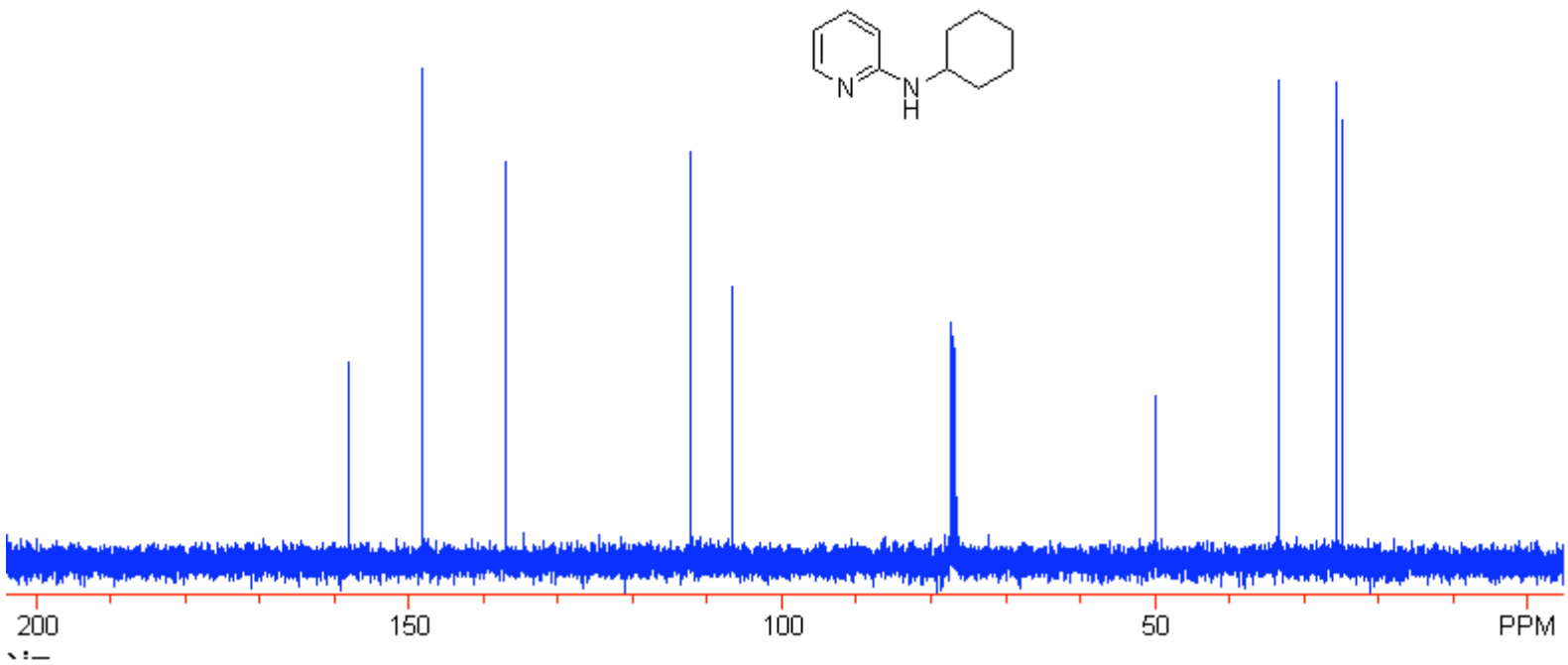

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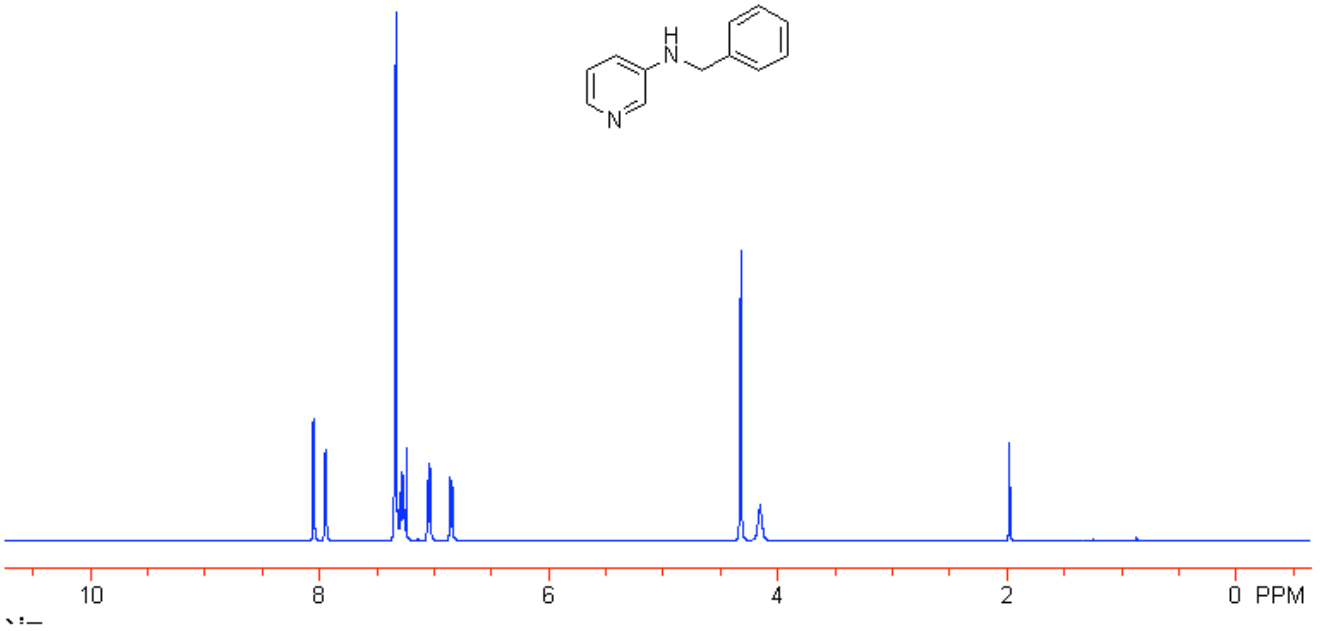

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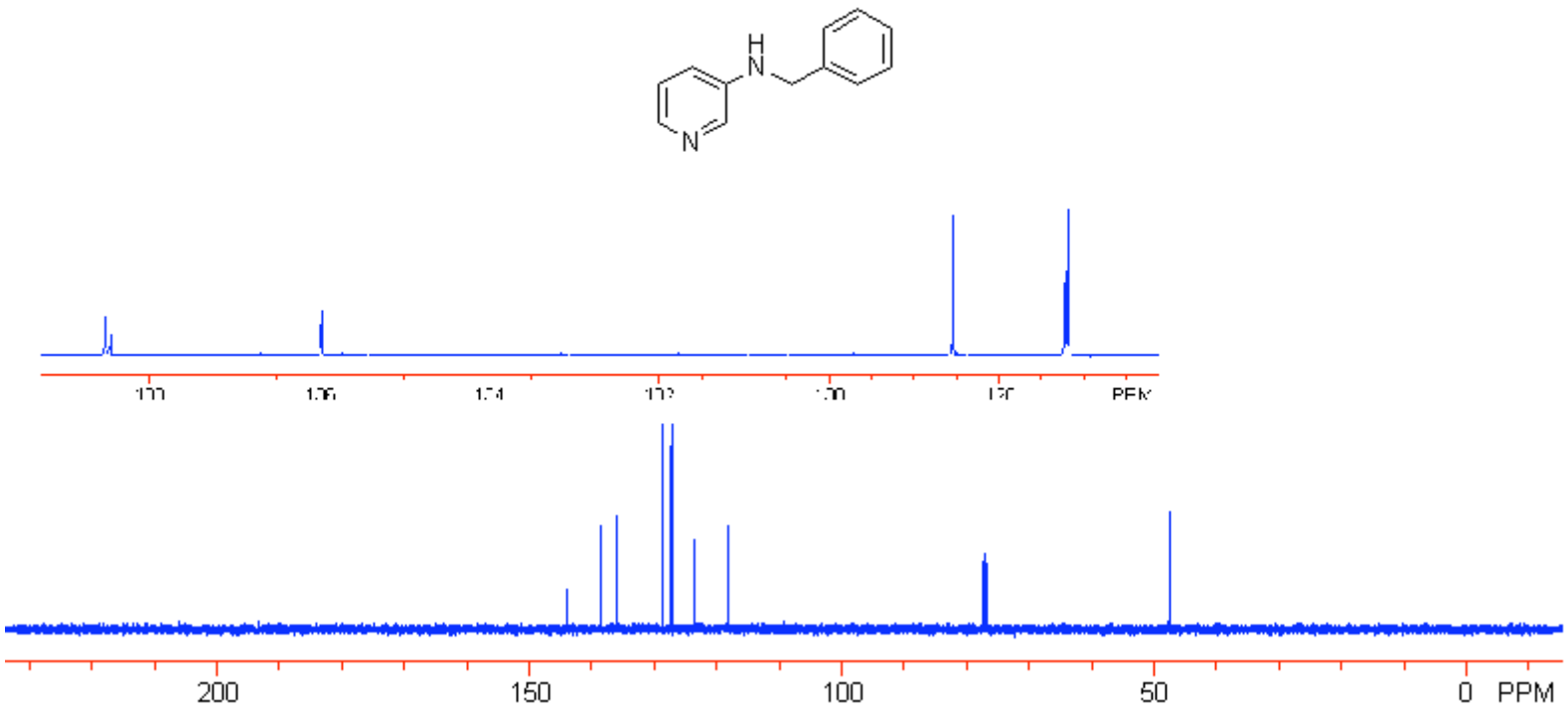
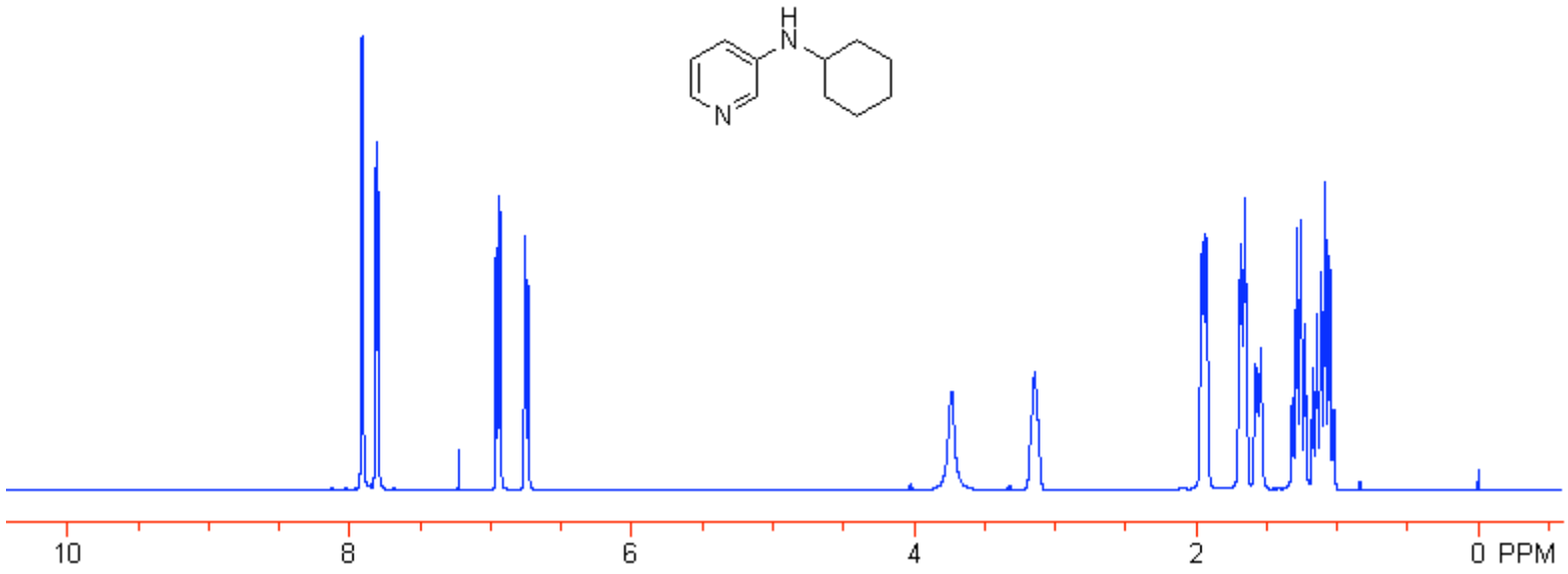


Table 1, entry 18, N-Cyclohexyl-3-aminopyridine



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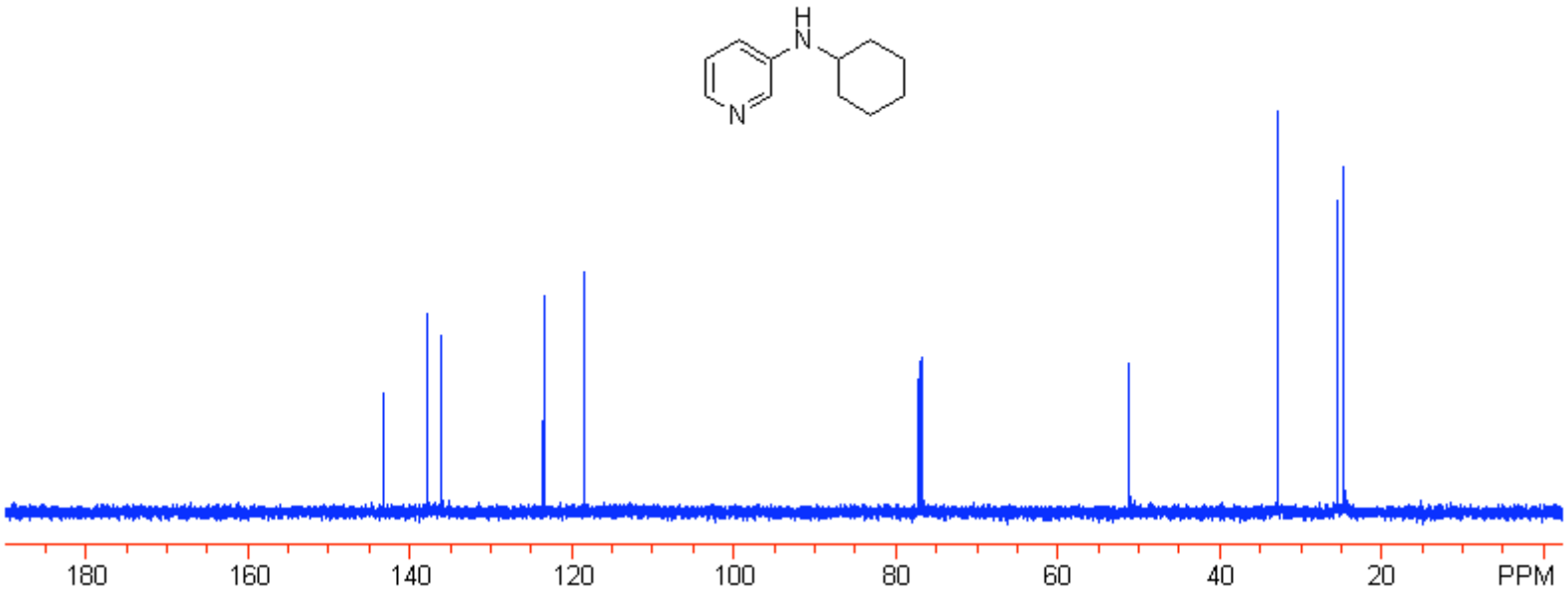

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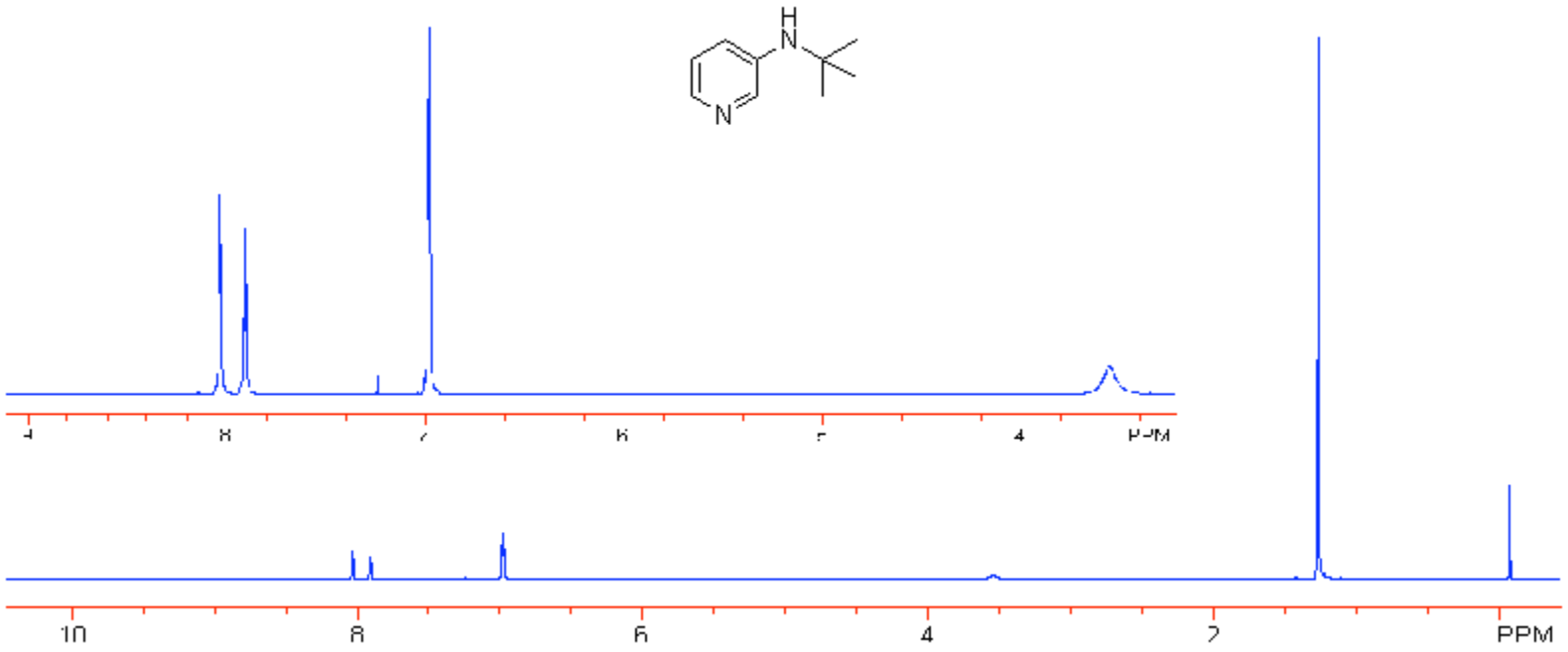
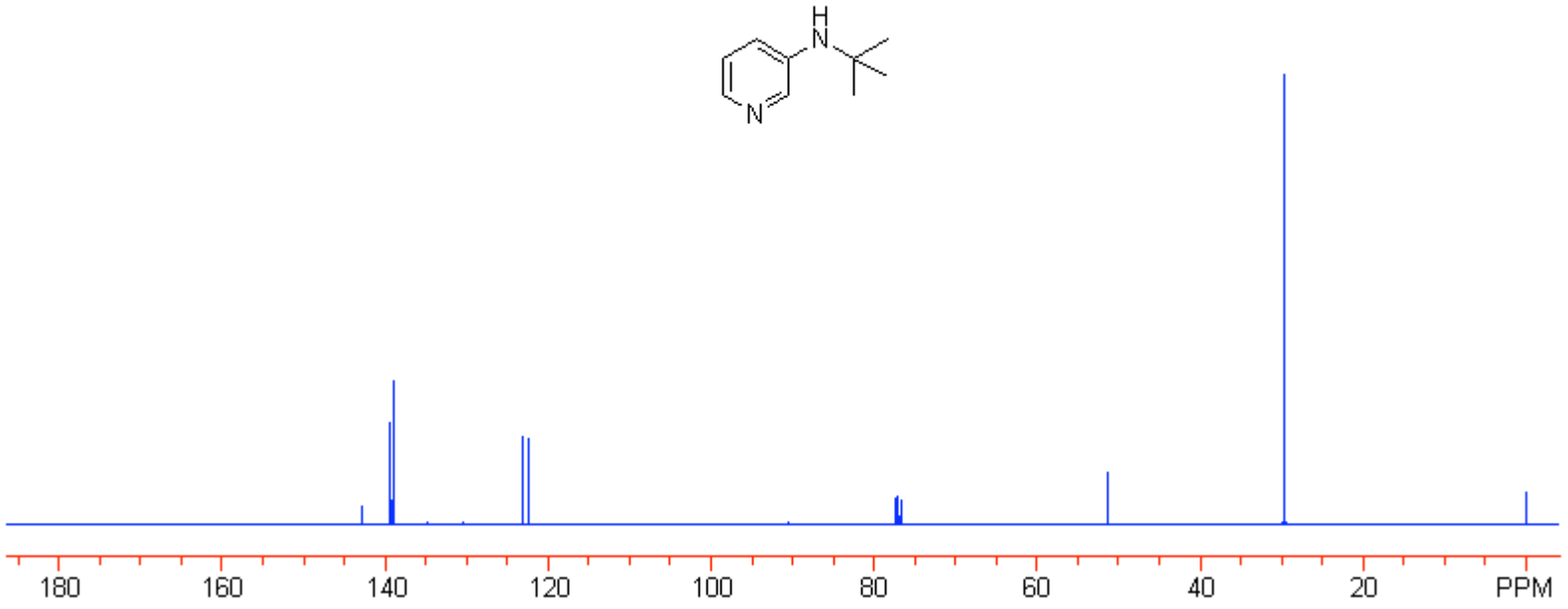


Table 1, entry 20, *N-tert*-butyl-3-aminopyridine



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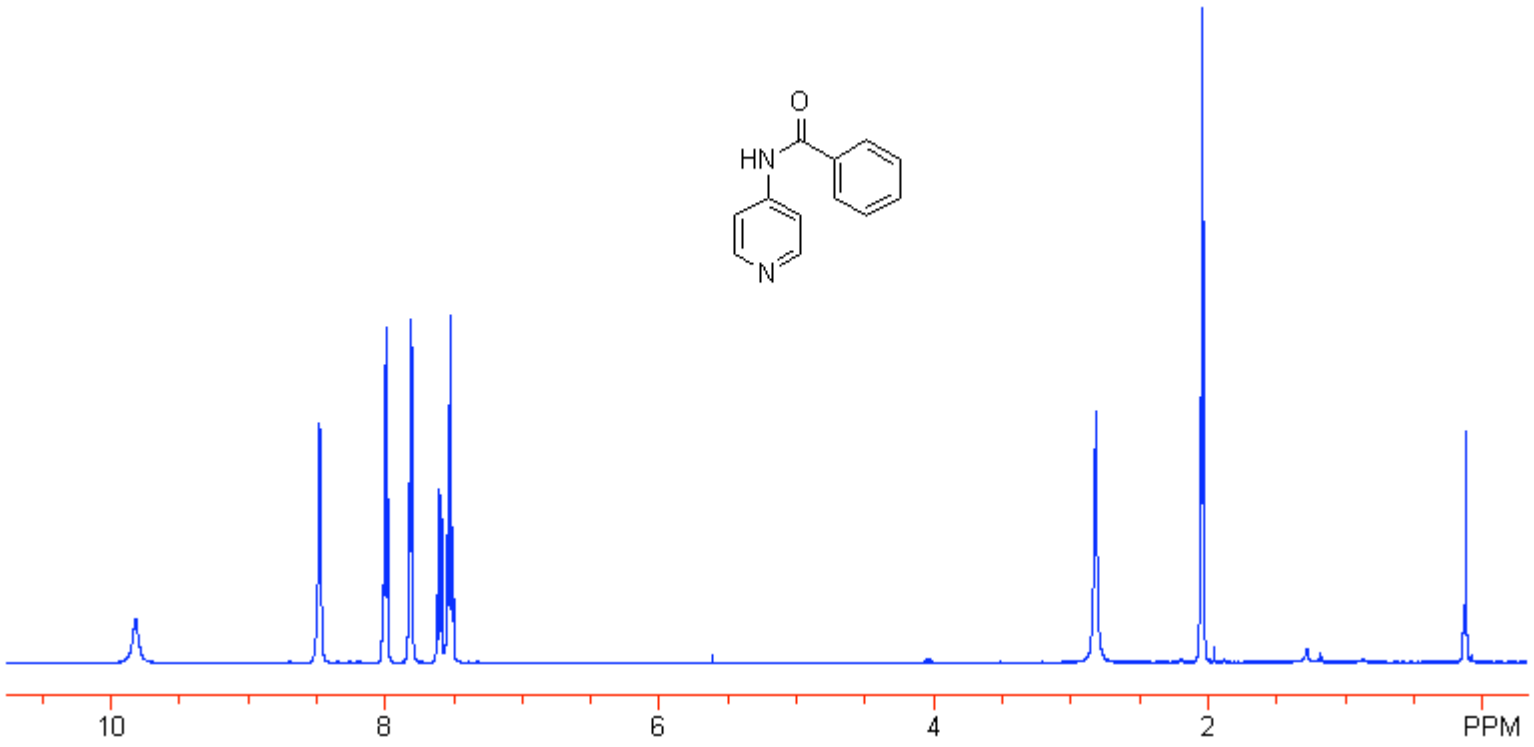


Table 1, entry 25, 4-benzamidopyridine

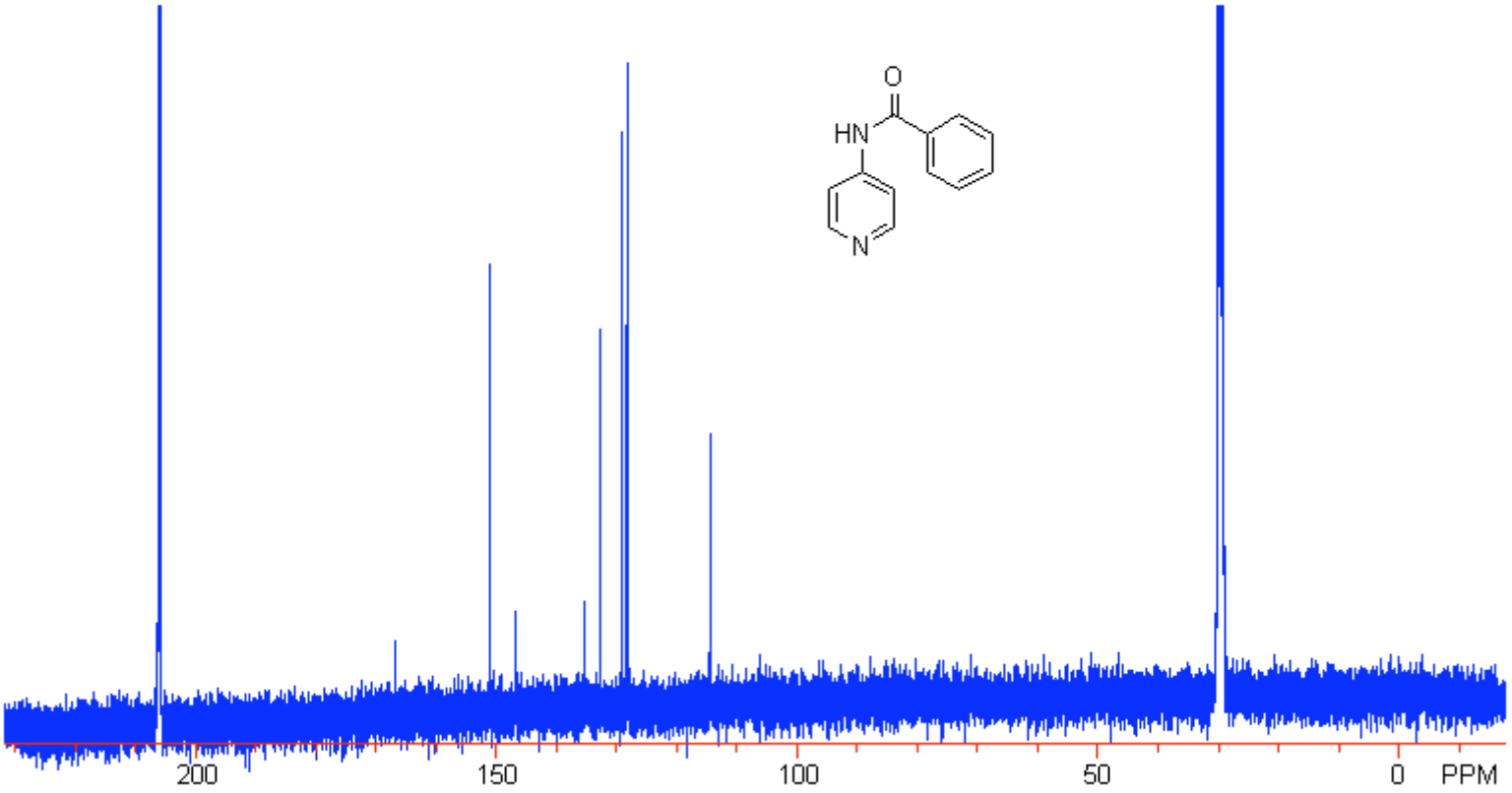


Table 1, entry 28, 5-(Cyclohexylamino)pyrimidine

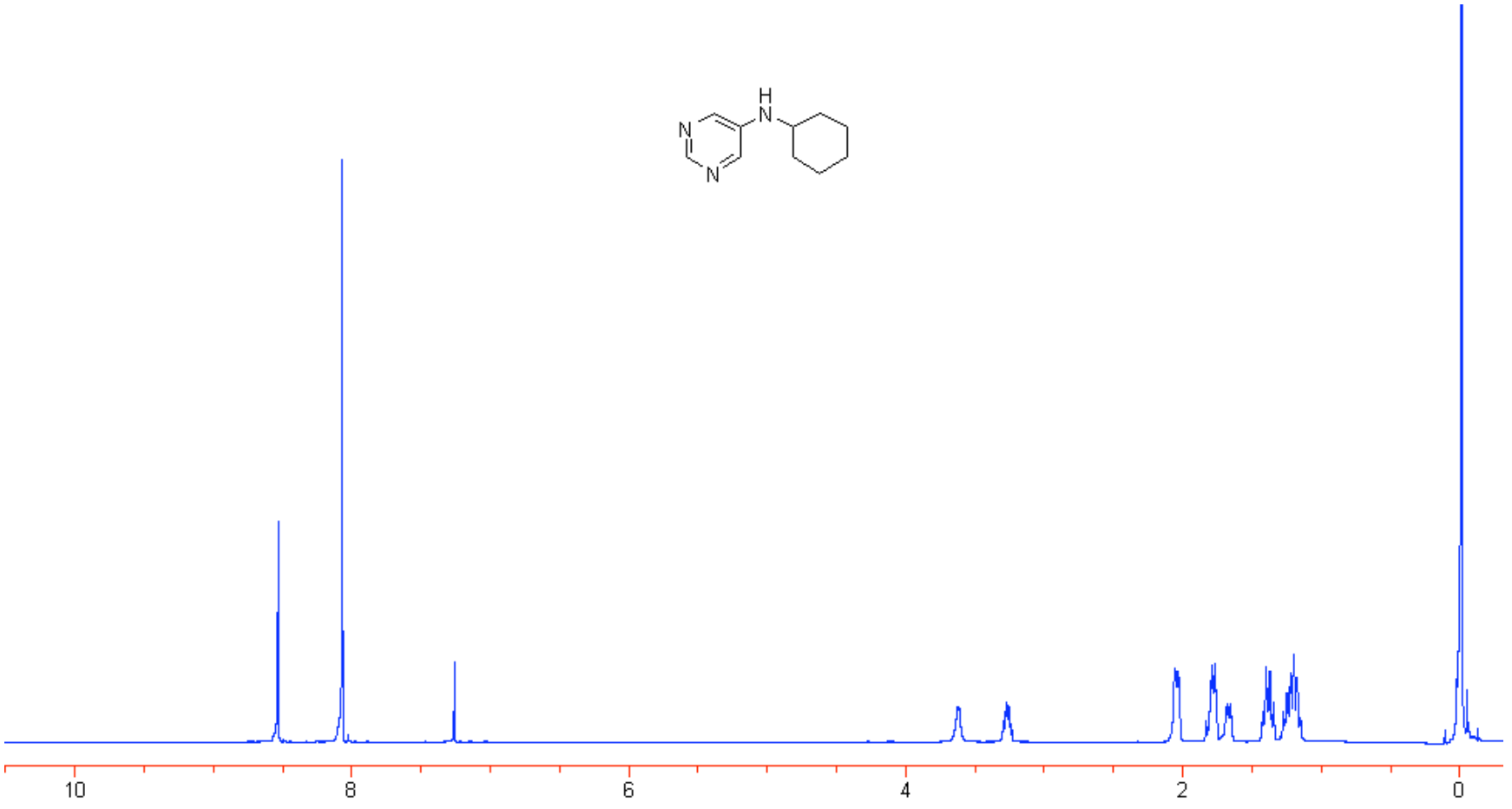
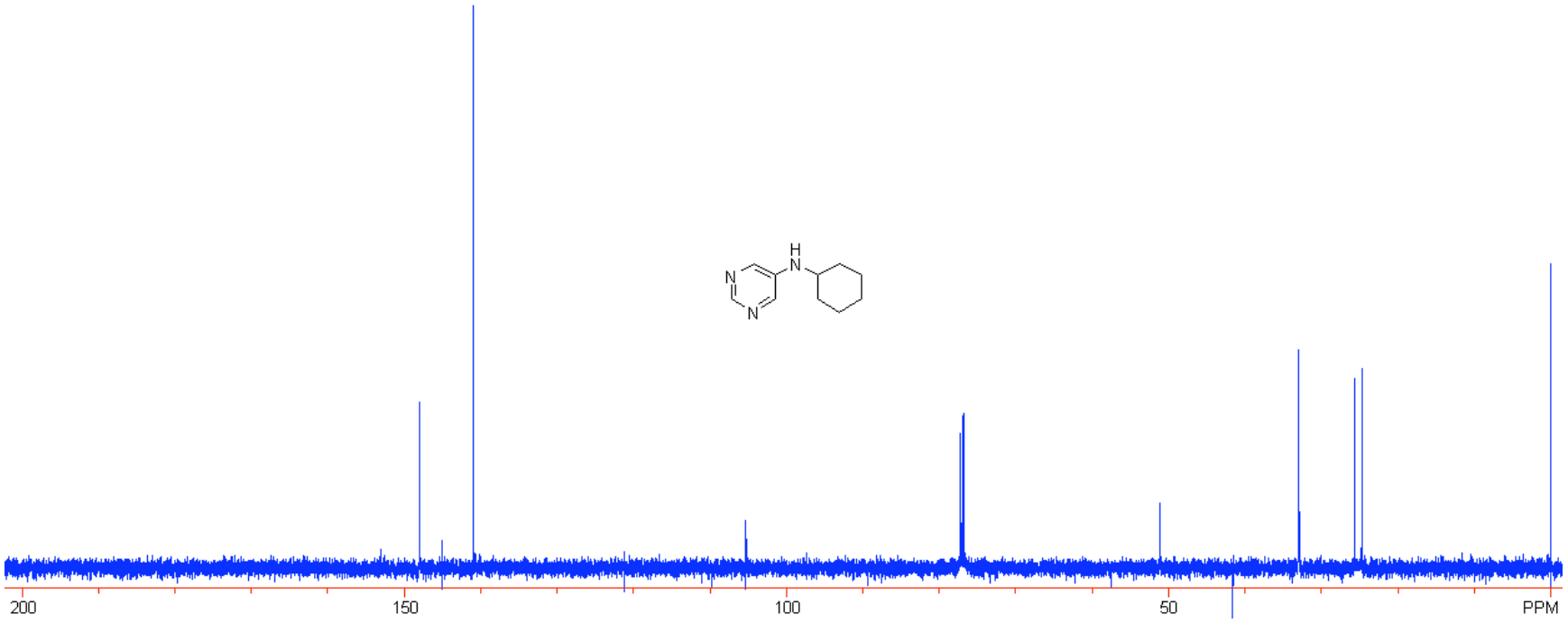


Table 1, entry 28, 5-(Cyclohexylamino)pyrimidine



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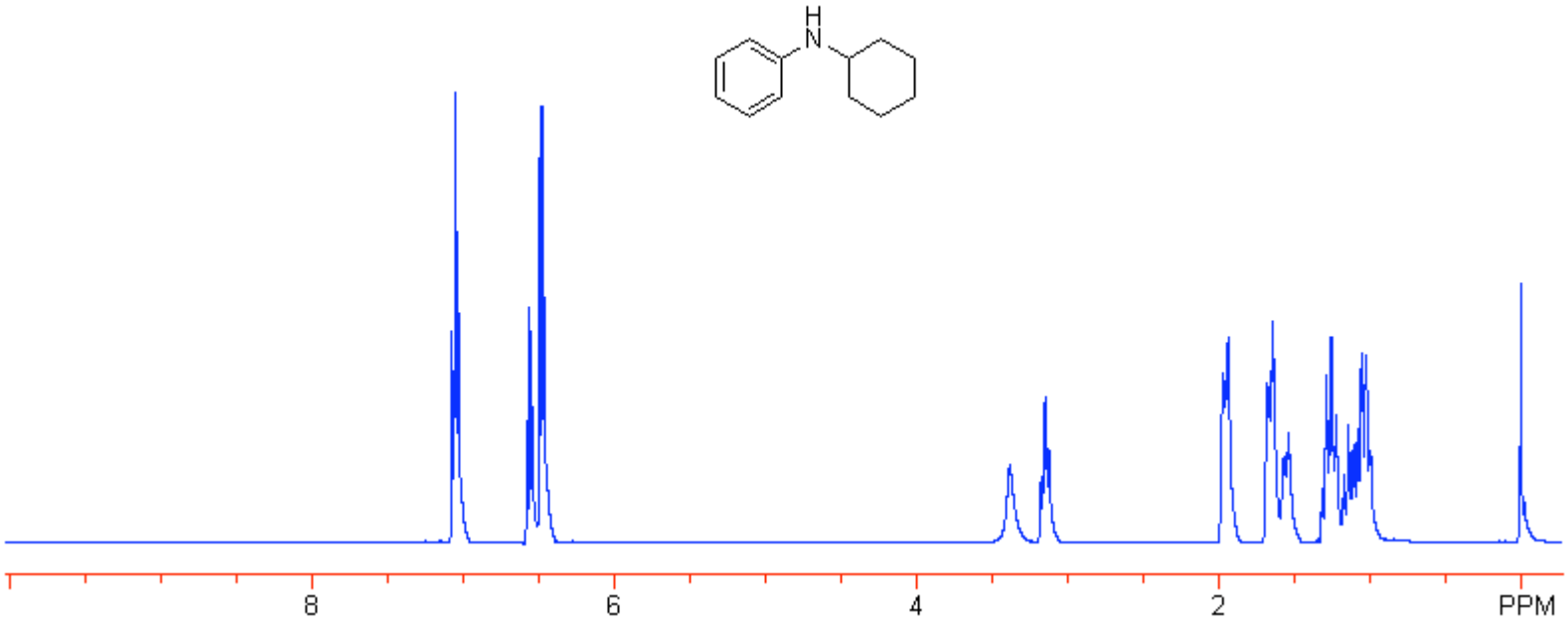
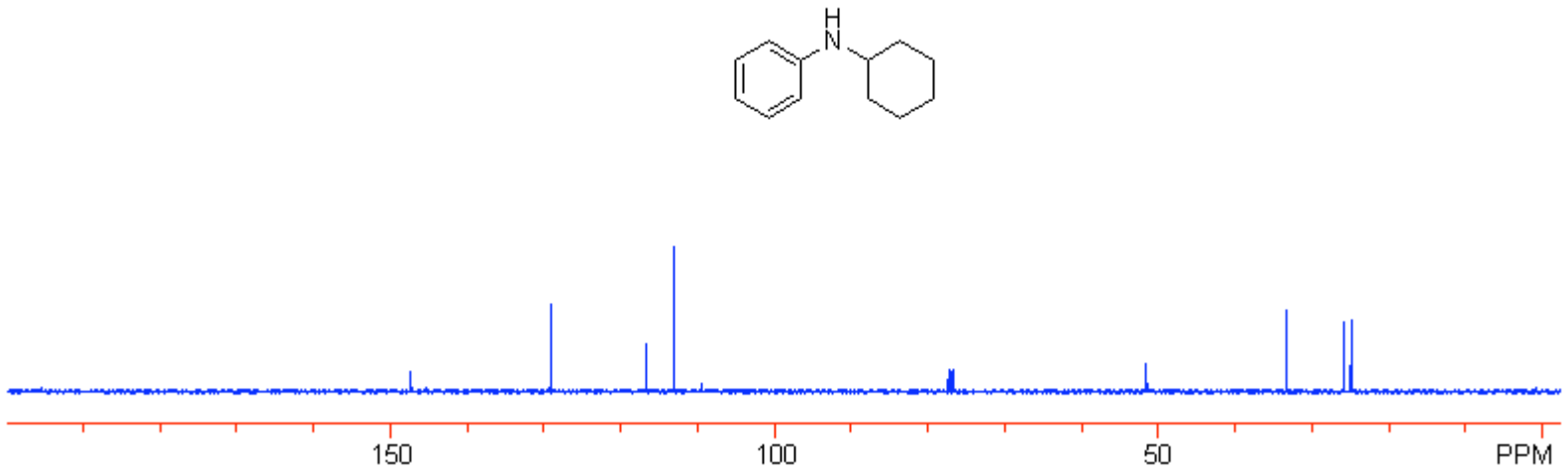


Table 3, entry 1, *N*-(Phenyl)-cyclohexylamine



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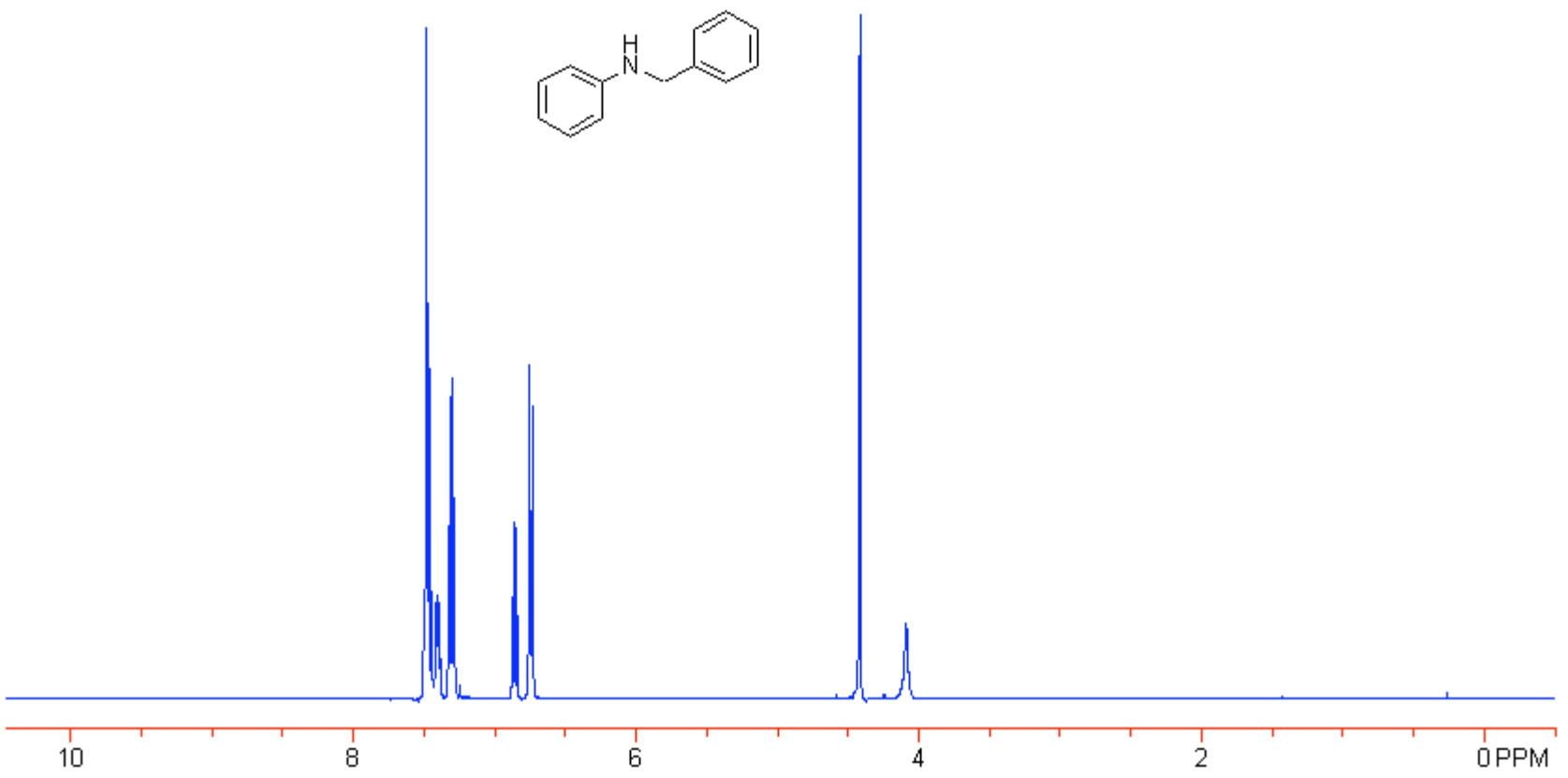

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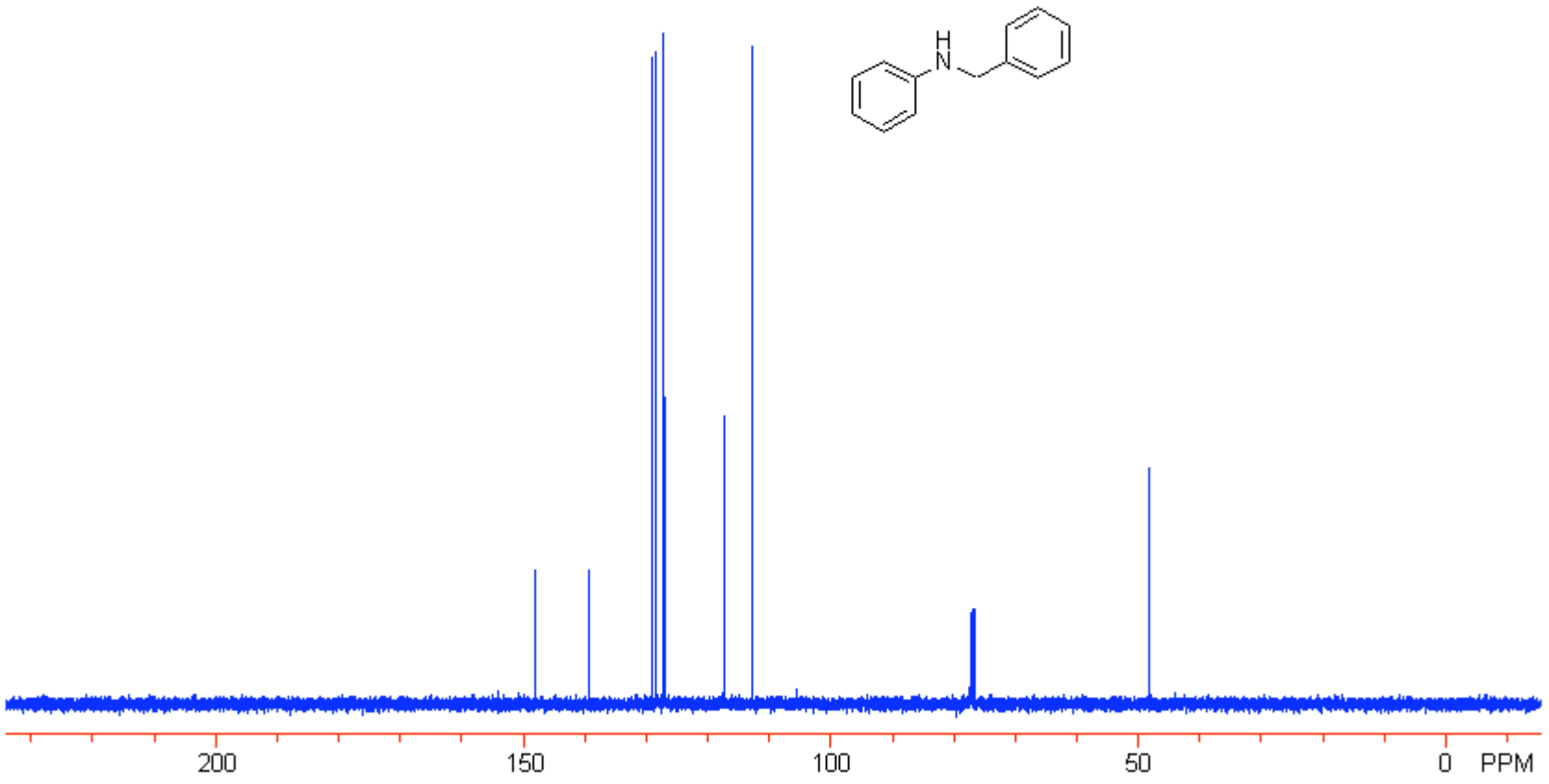
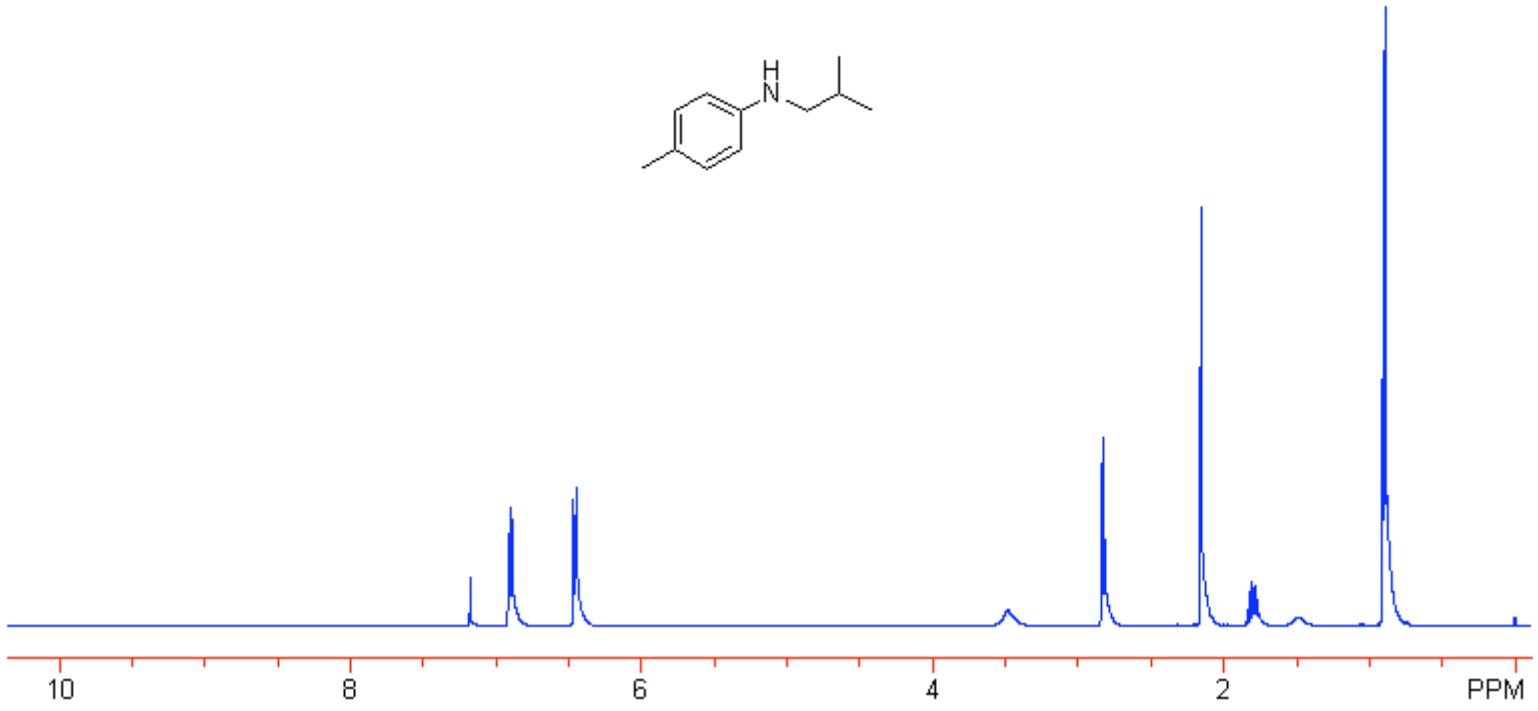


Table 3, entry 9, *N*-(*p*-Tolyl)-*iso*-butylamine



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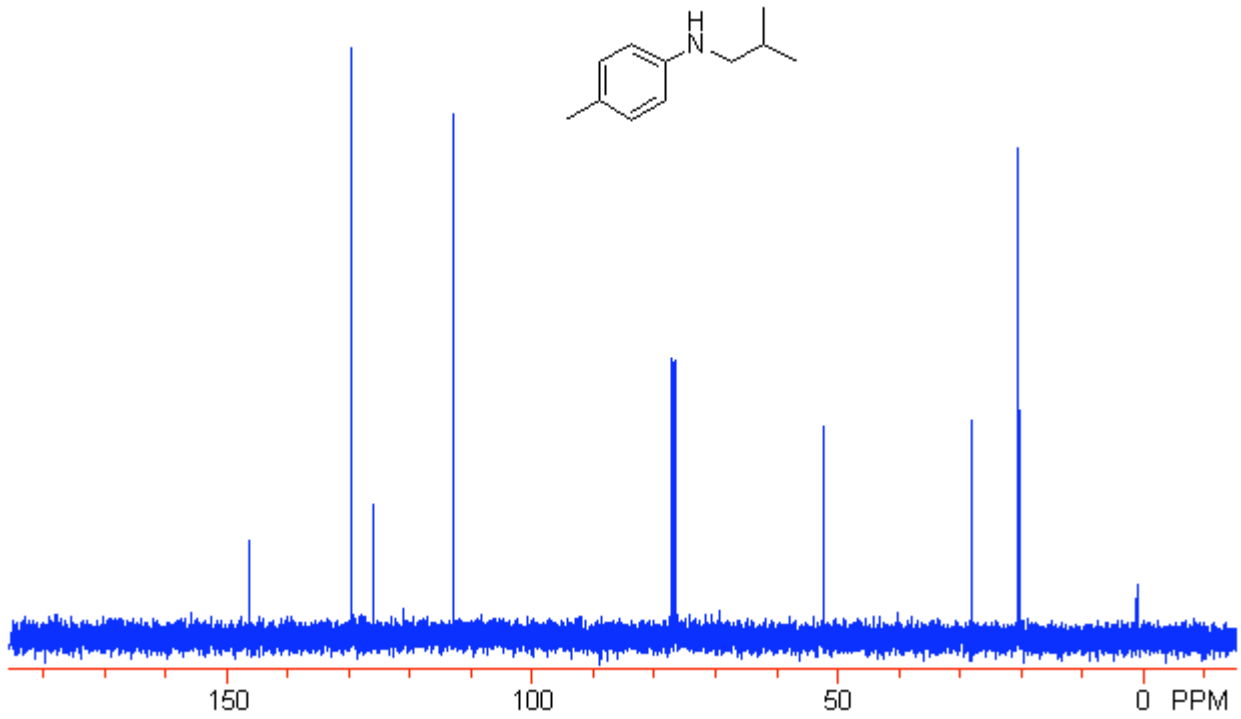
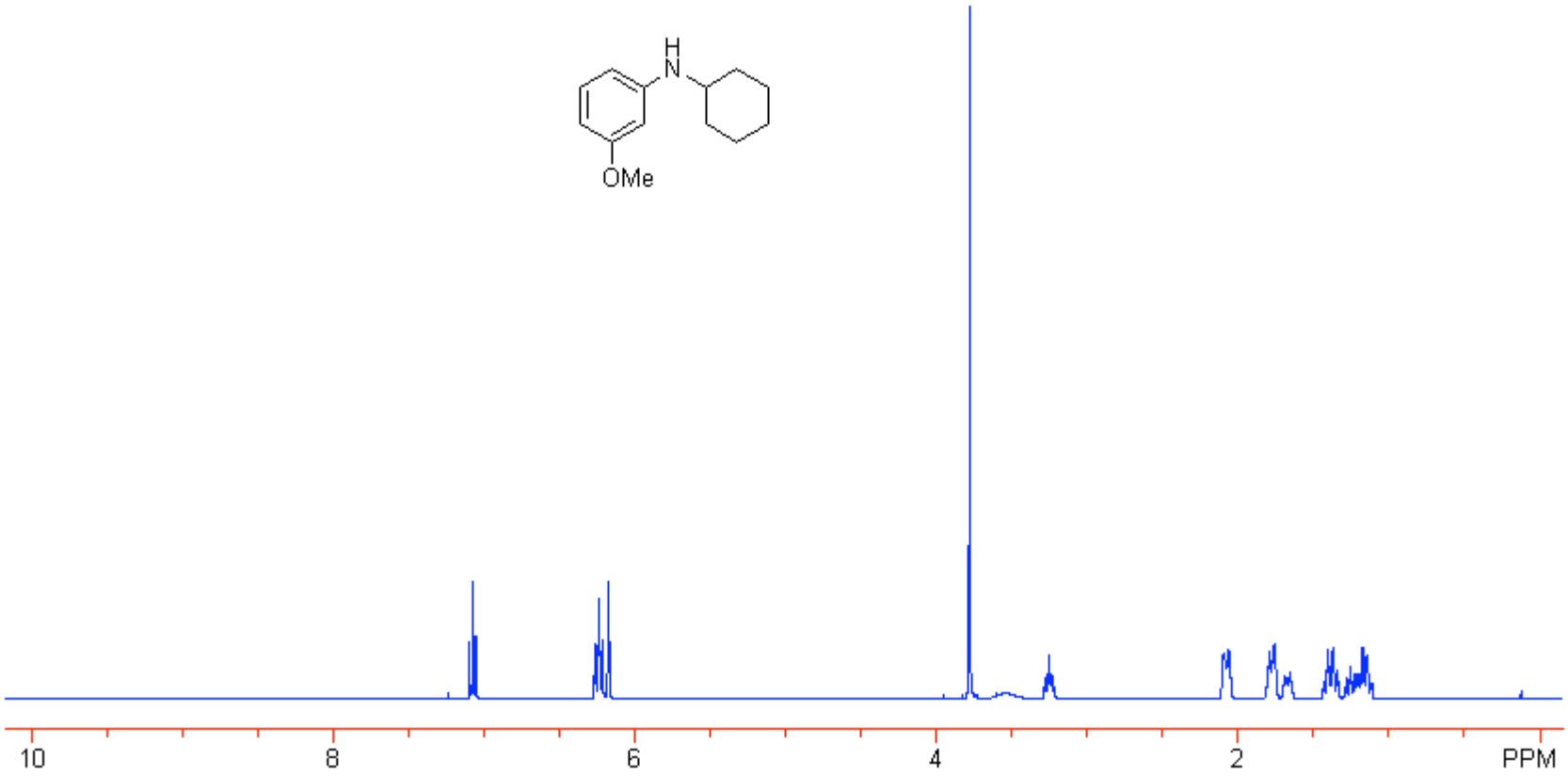


Table 3, entry 21, *N*-(Cyclohexylamino)-*m*-anisidine



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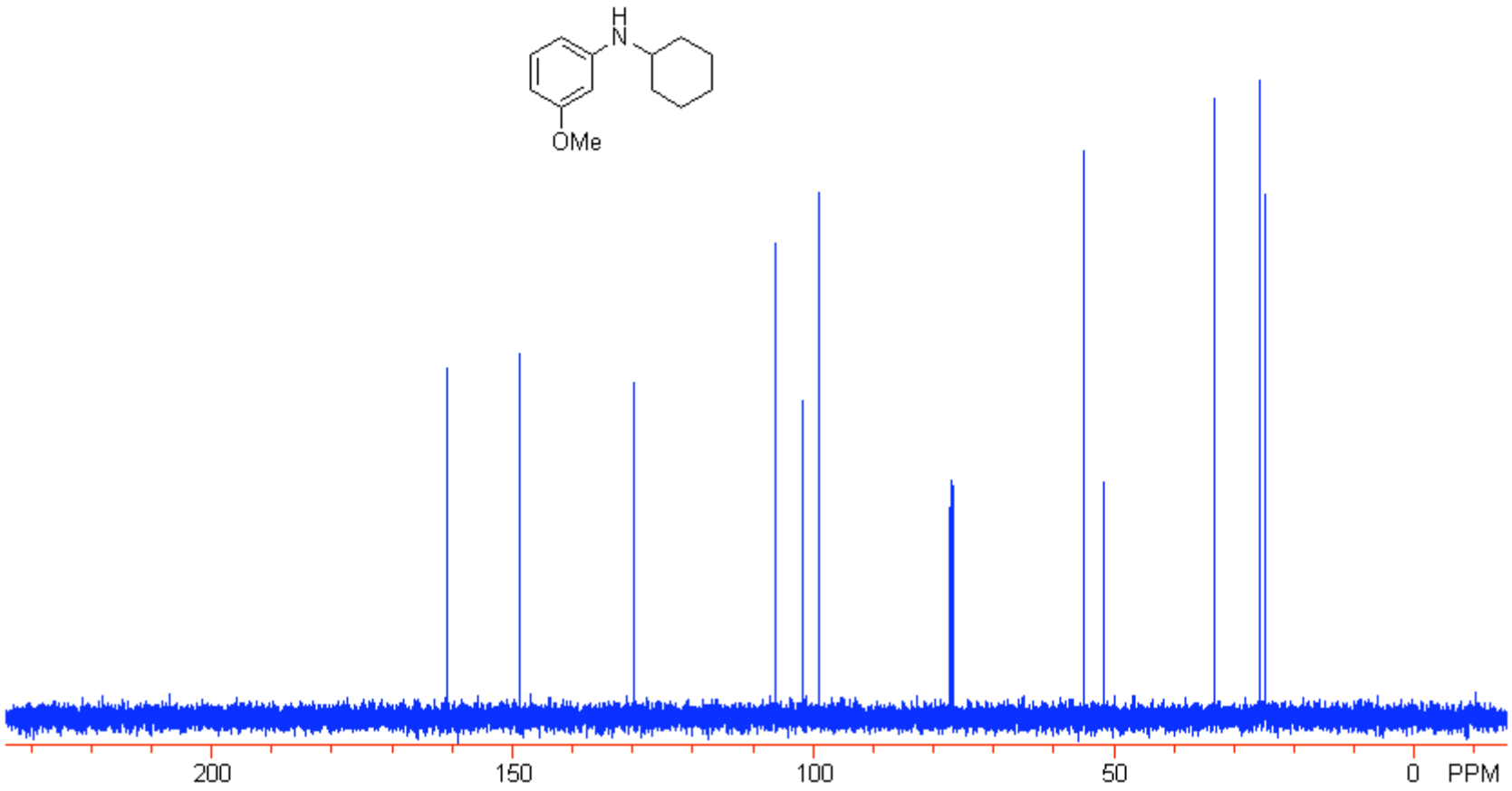
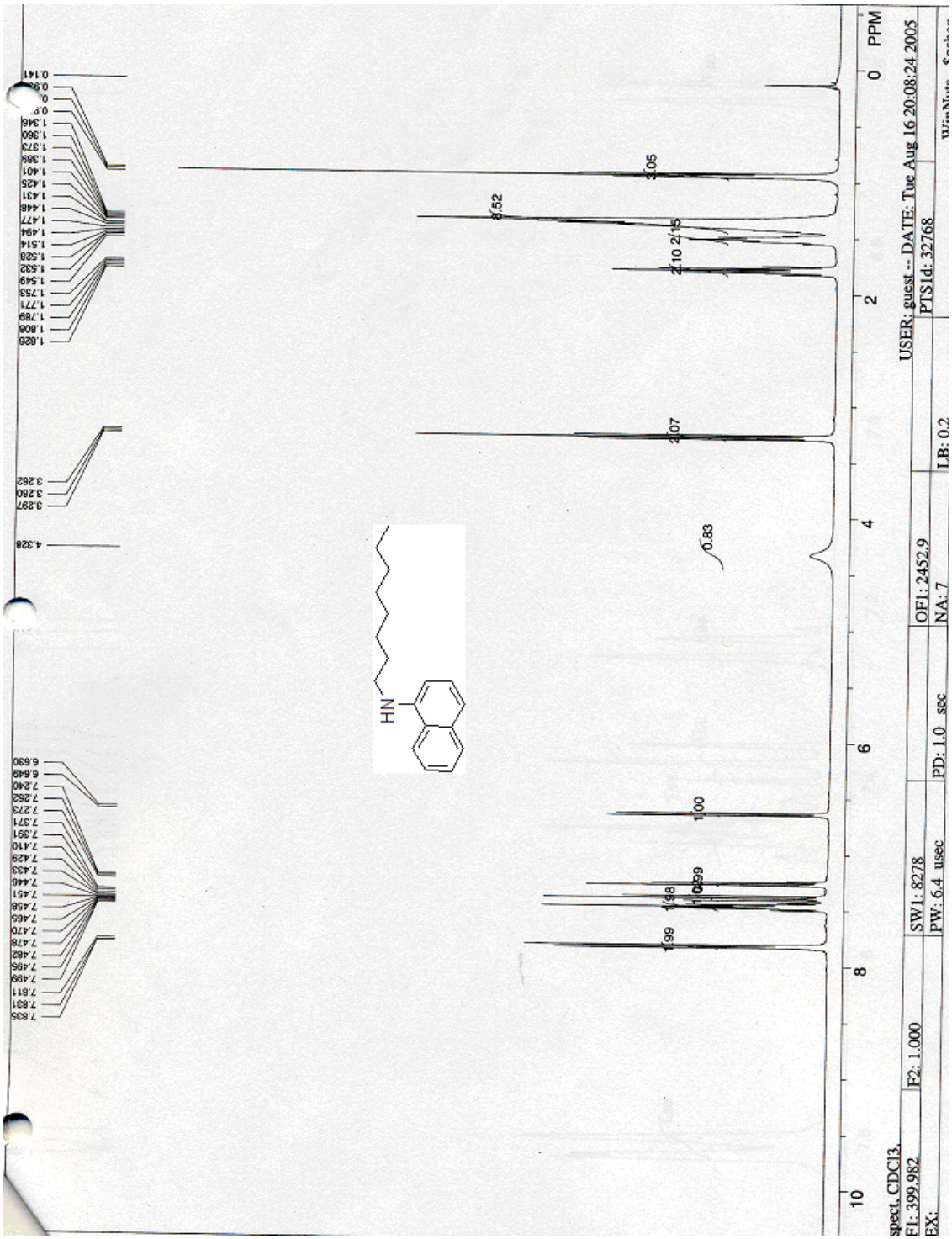


Table 3, entry 23 , *N*-octyl-1-qminonaphathlene



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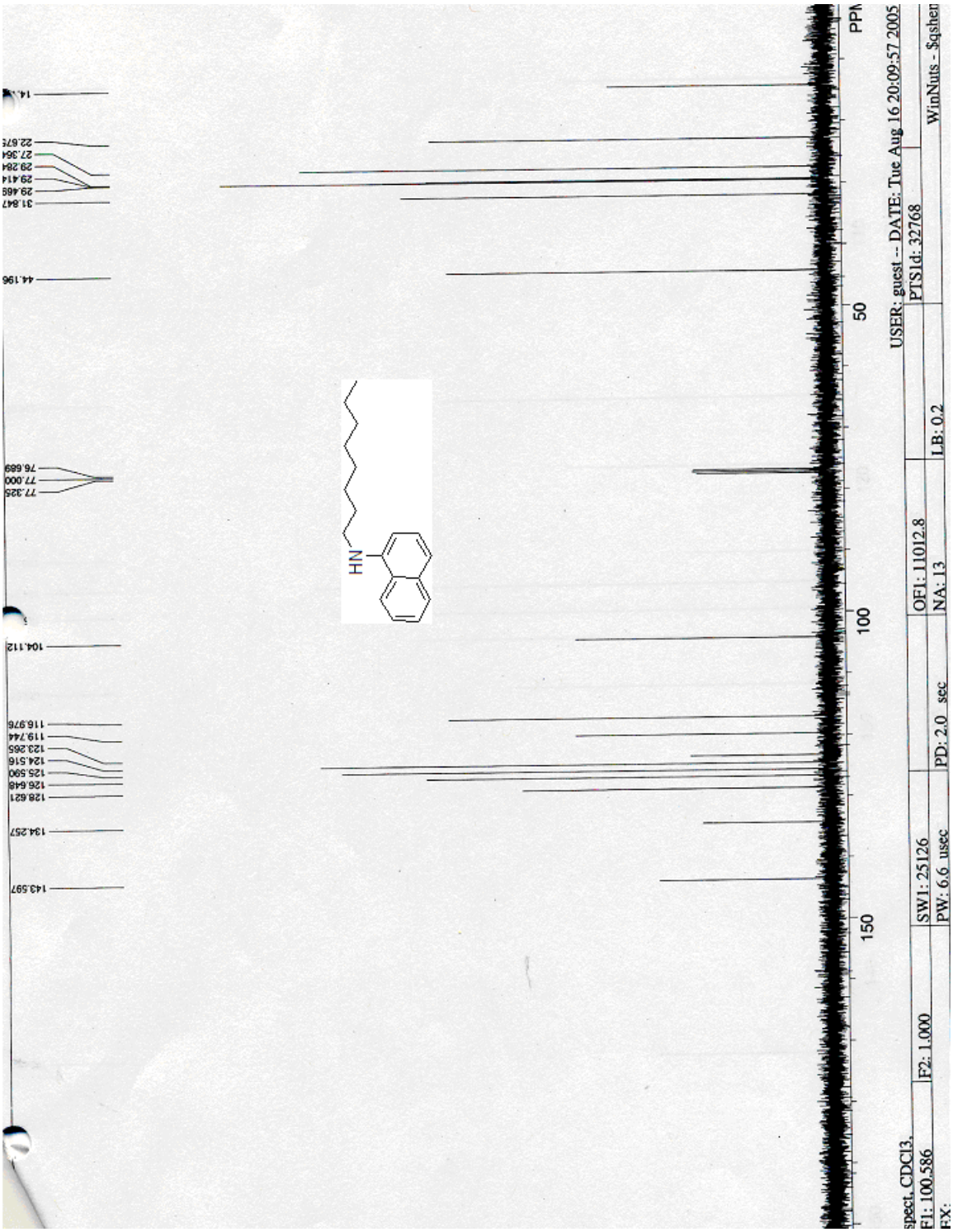


Table 3, entry 24, *N*-(*iso*butyl)-2-*iso*propylaniline

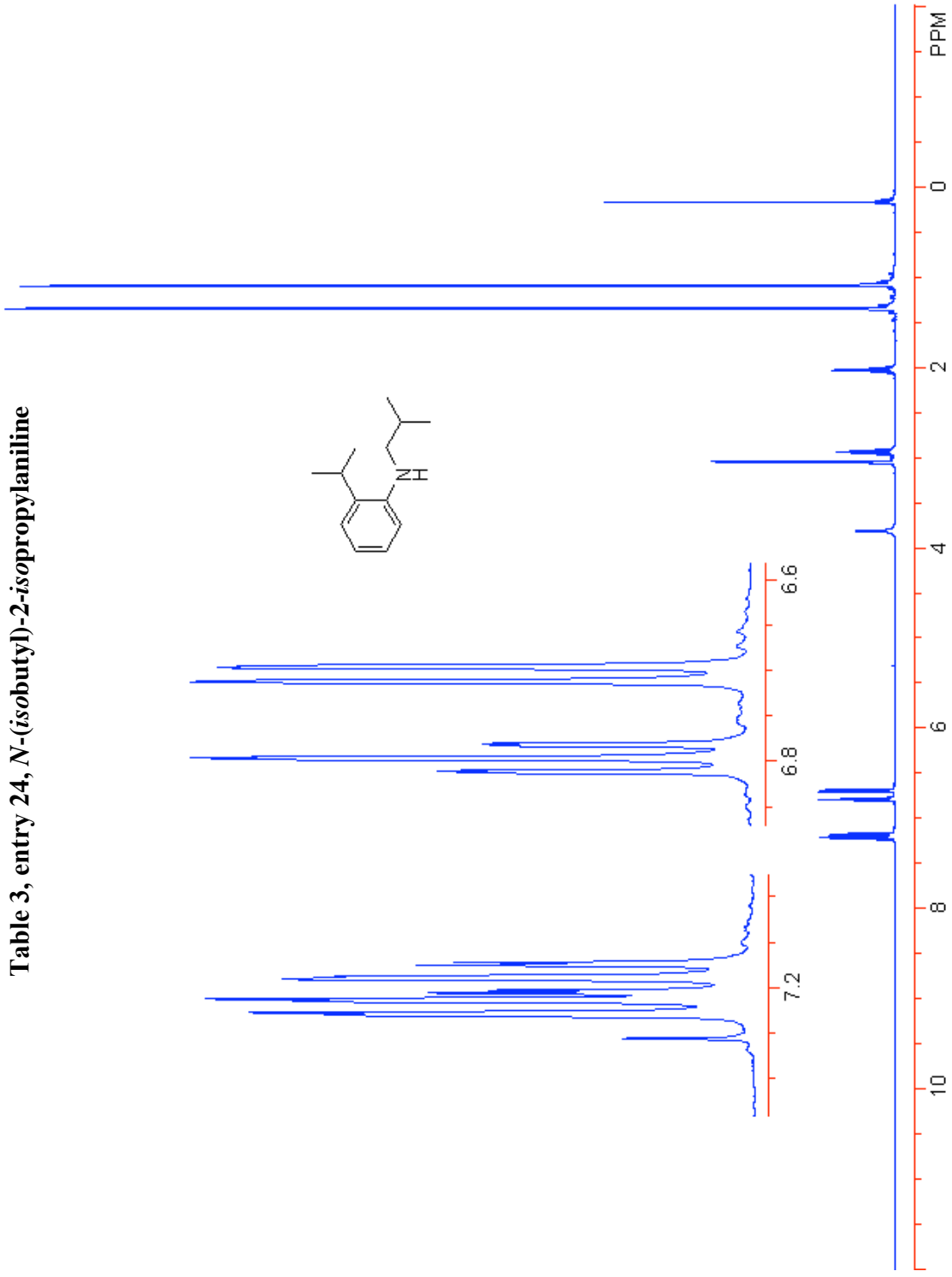
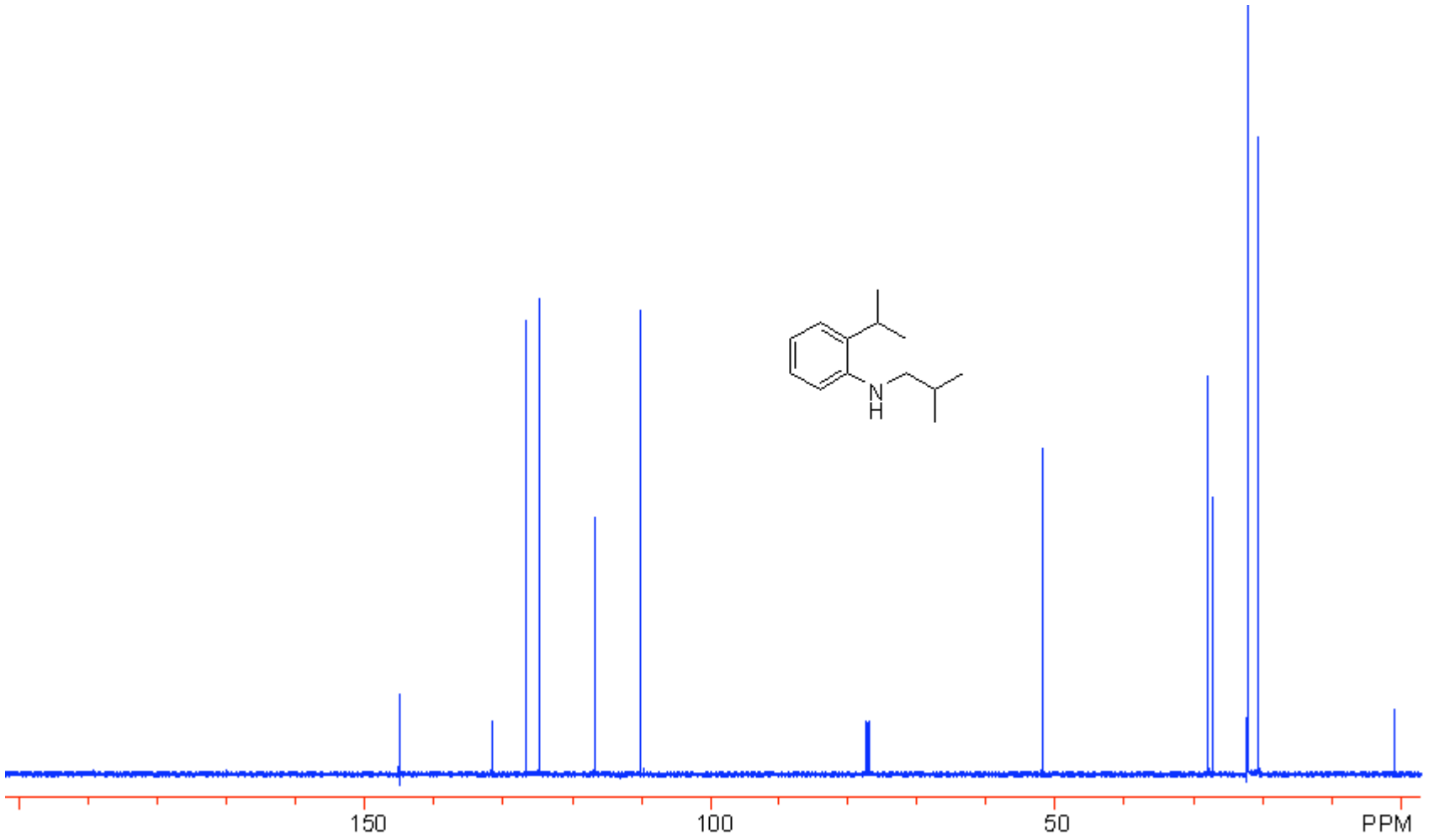


Table 3, entry 24, *N*-(*iso*butyl)-2-*iso*propylaniline



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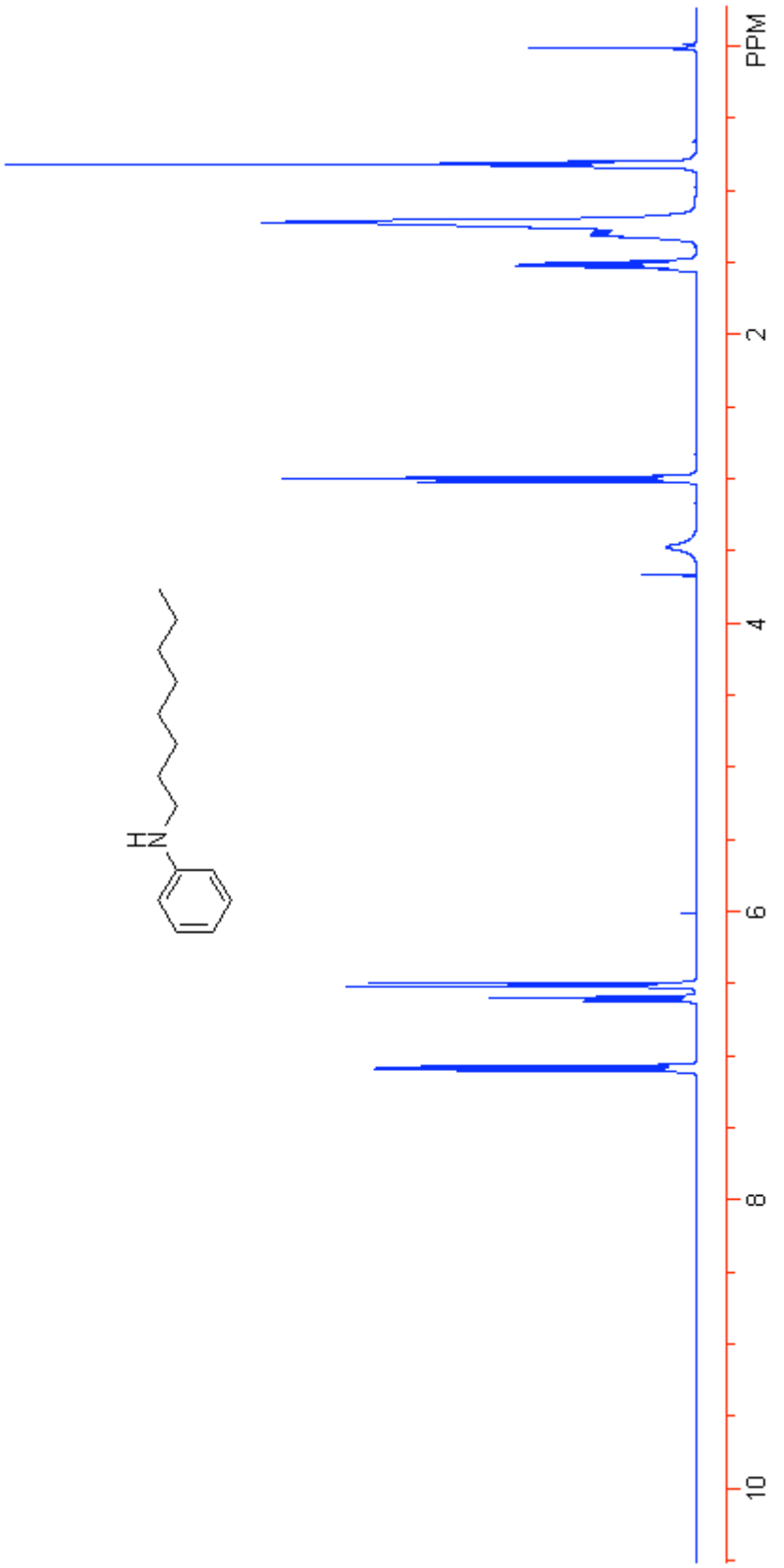

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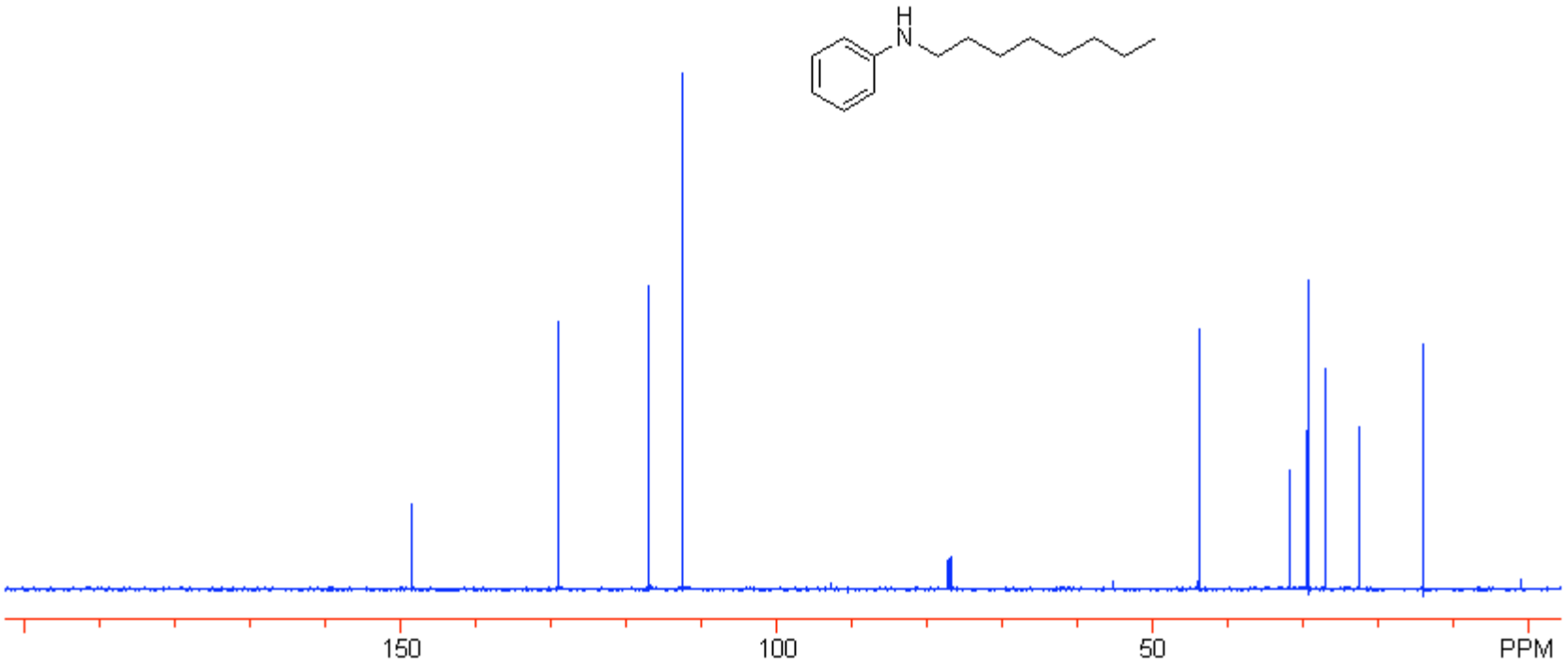
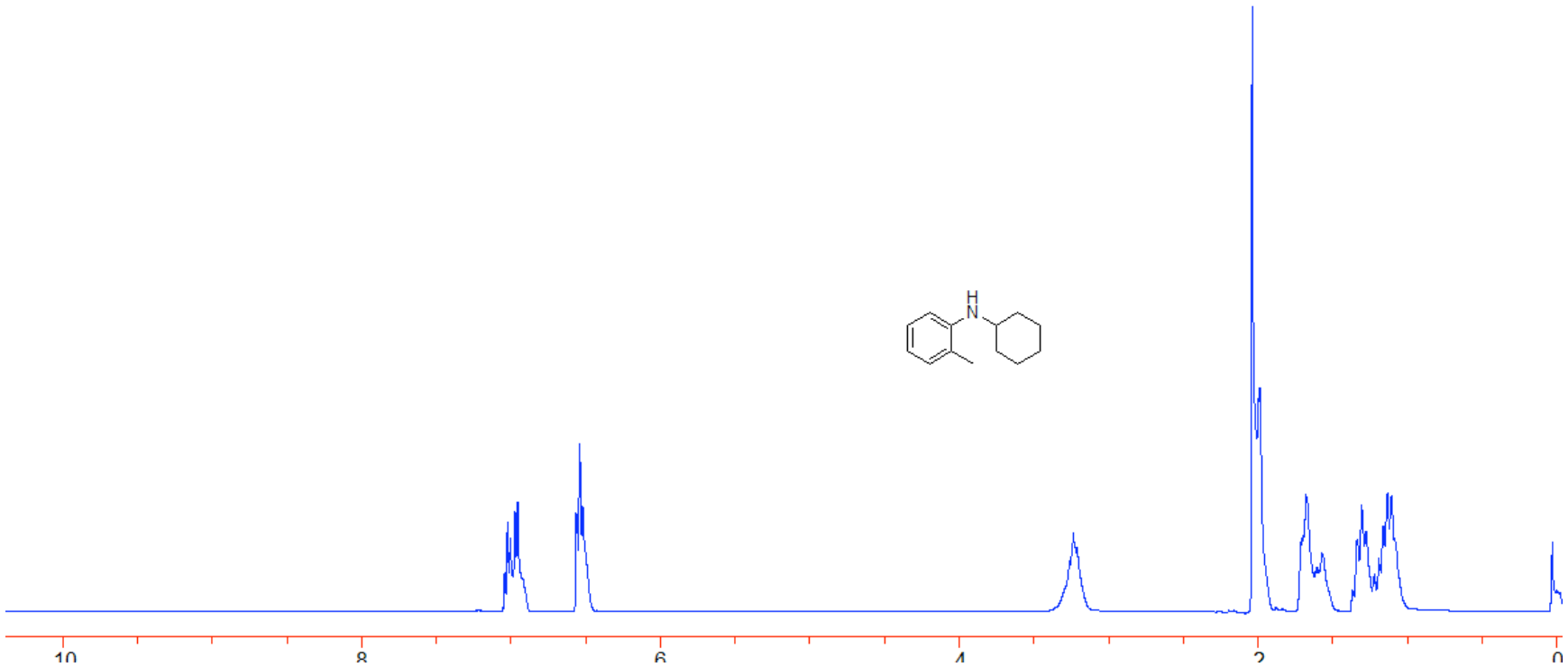


Table 5, entry 10 , *N*-(Cyclohexylamino)-*o*-toluidine



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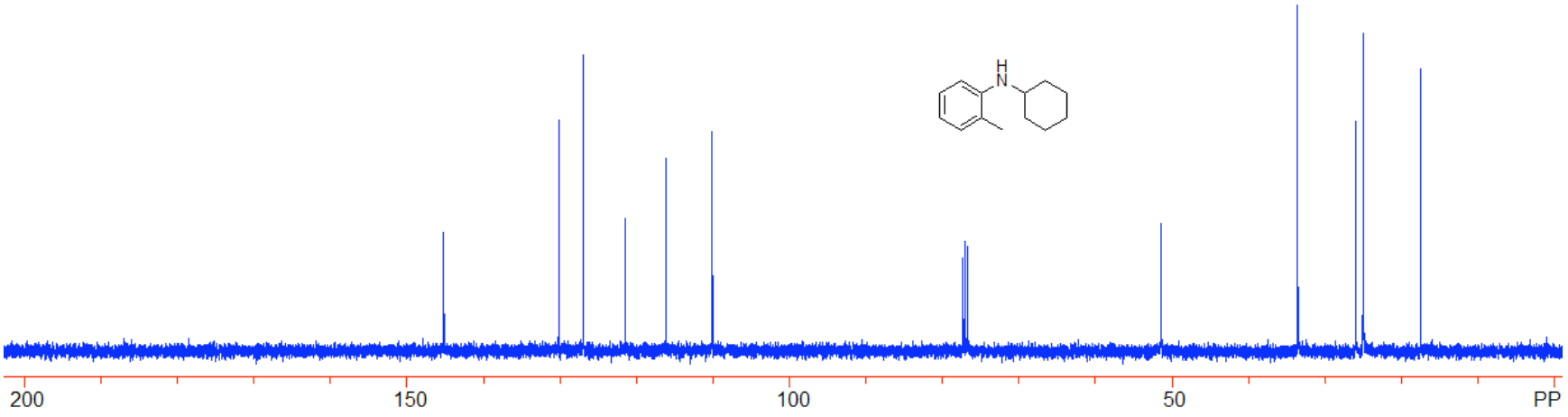
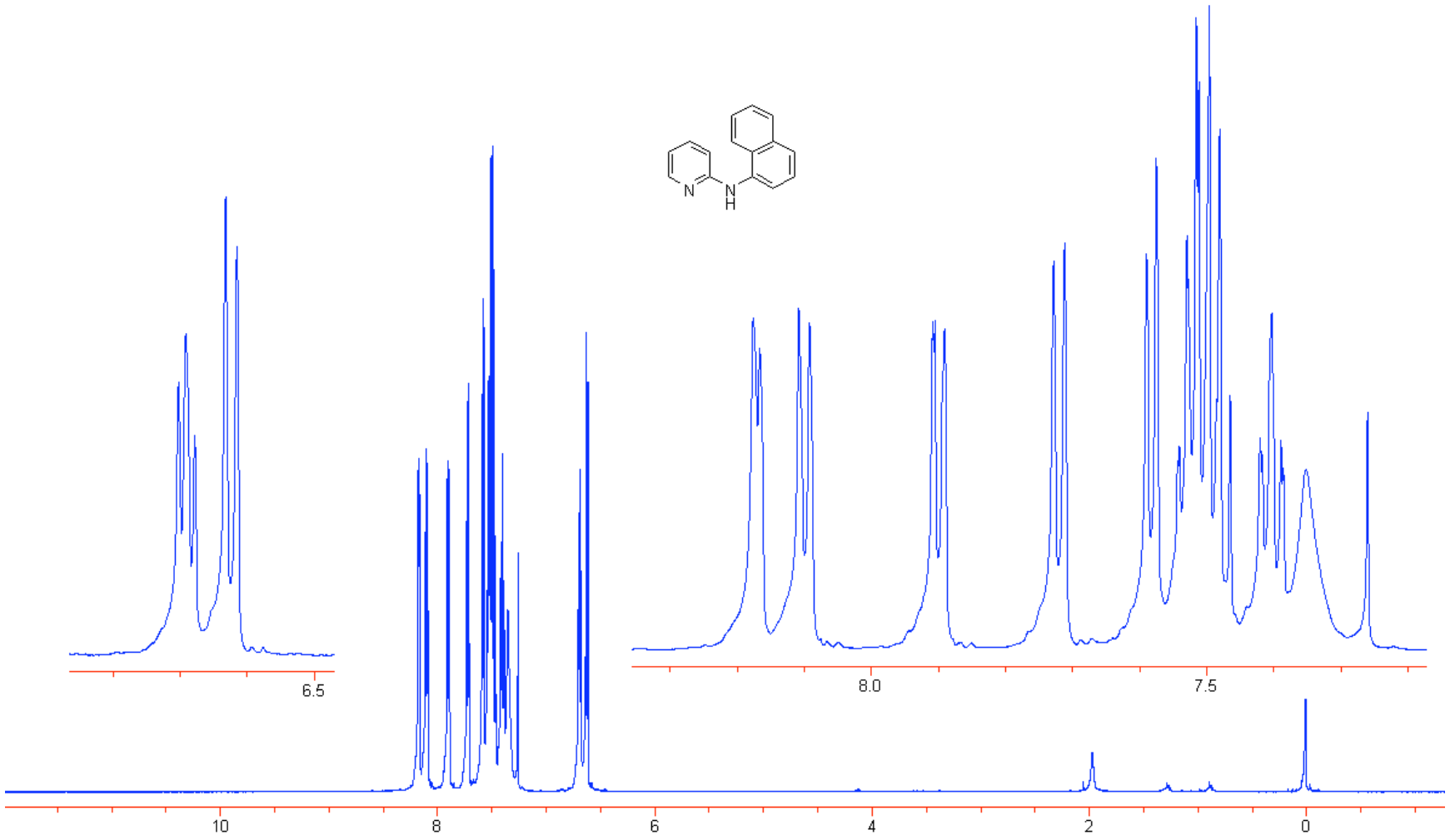


Table 6, entry 3 , 2-α-Naphthylaminopyridine



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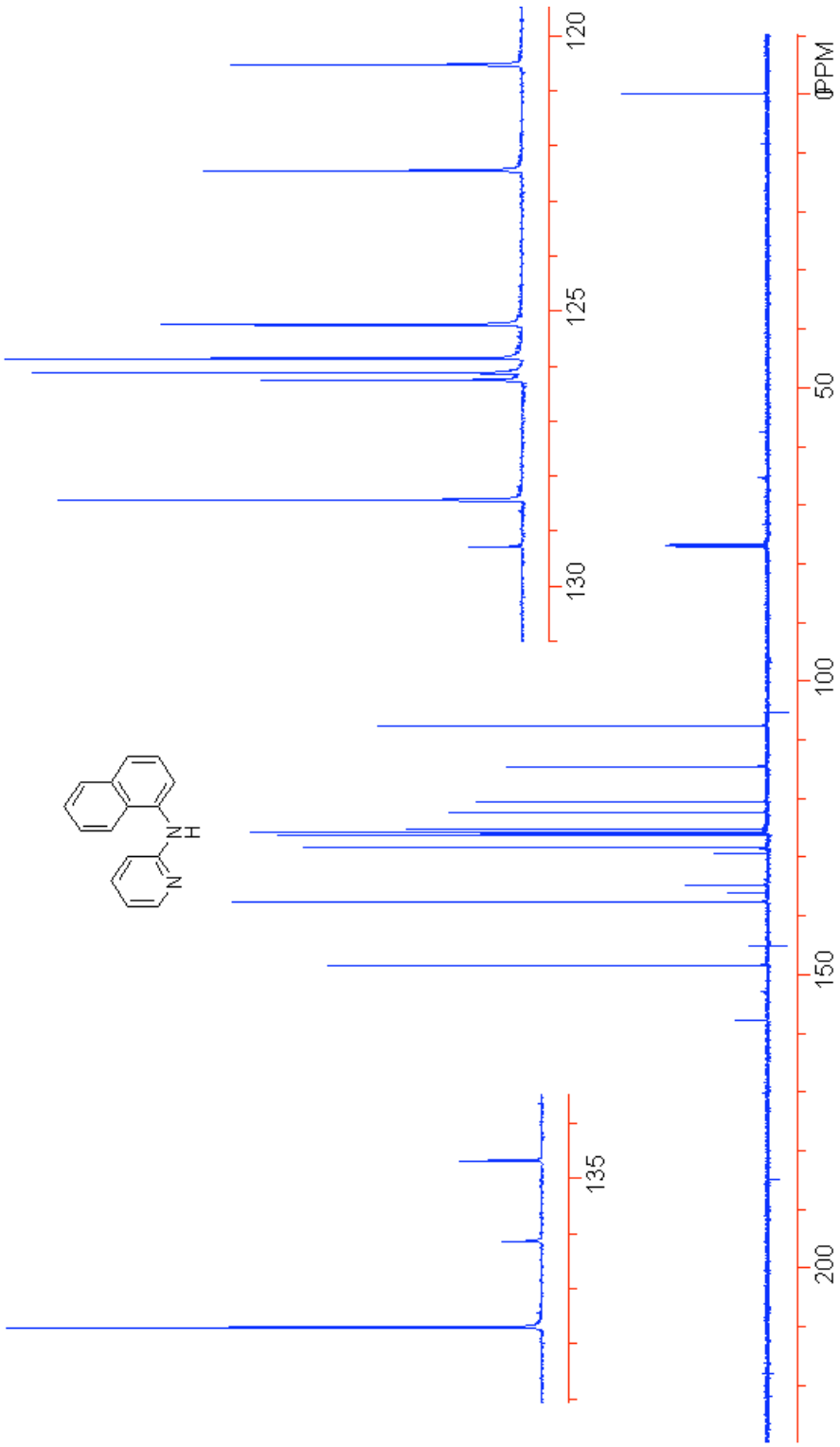


Table 6, entry 6 , 2,3'-Dipyridylamine

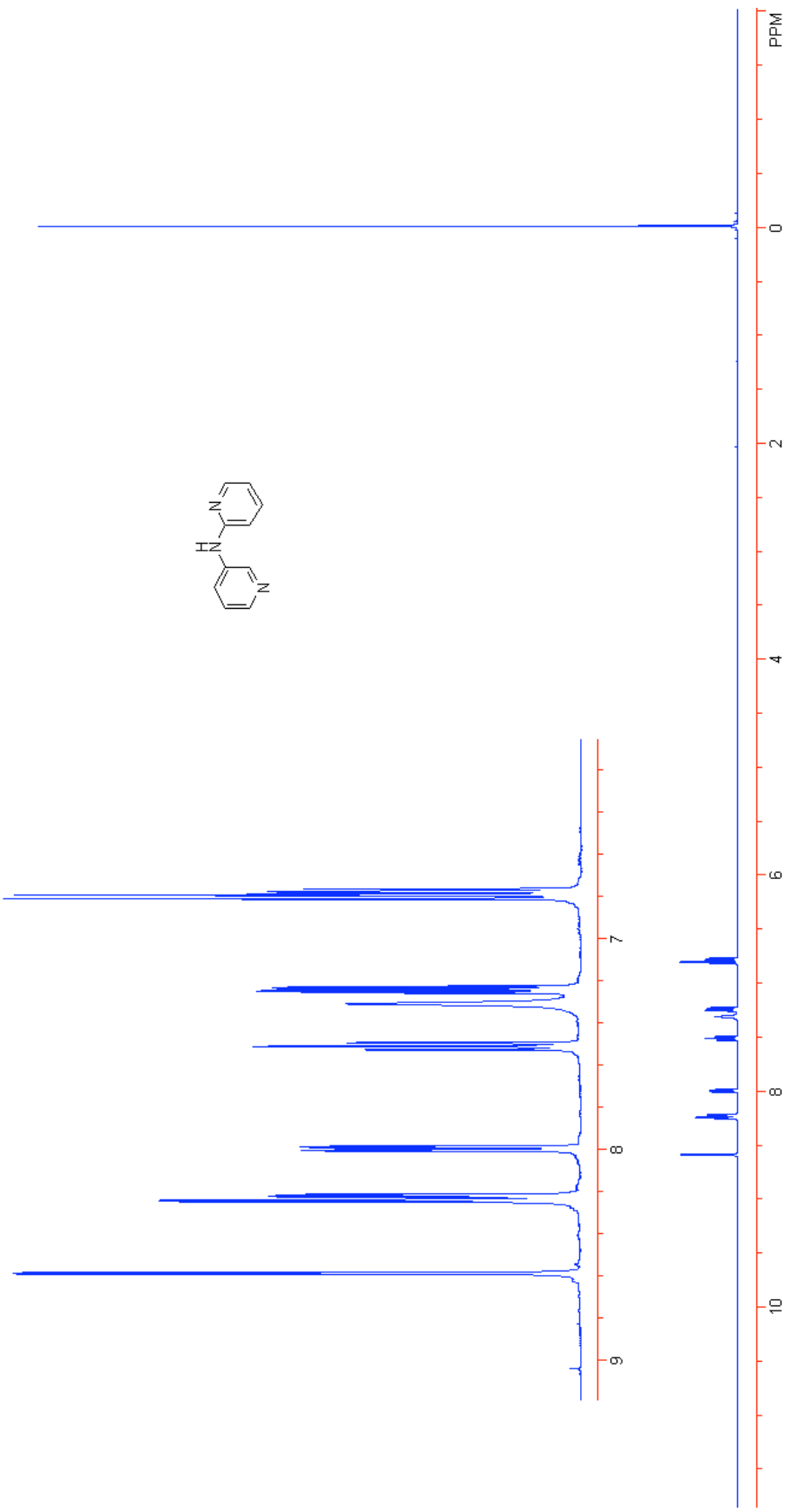
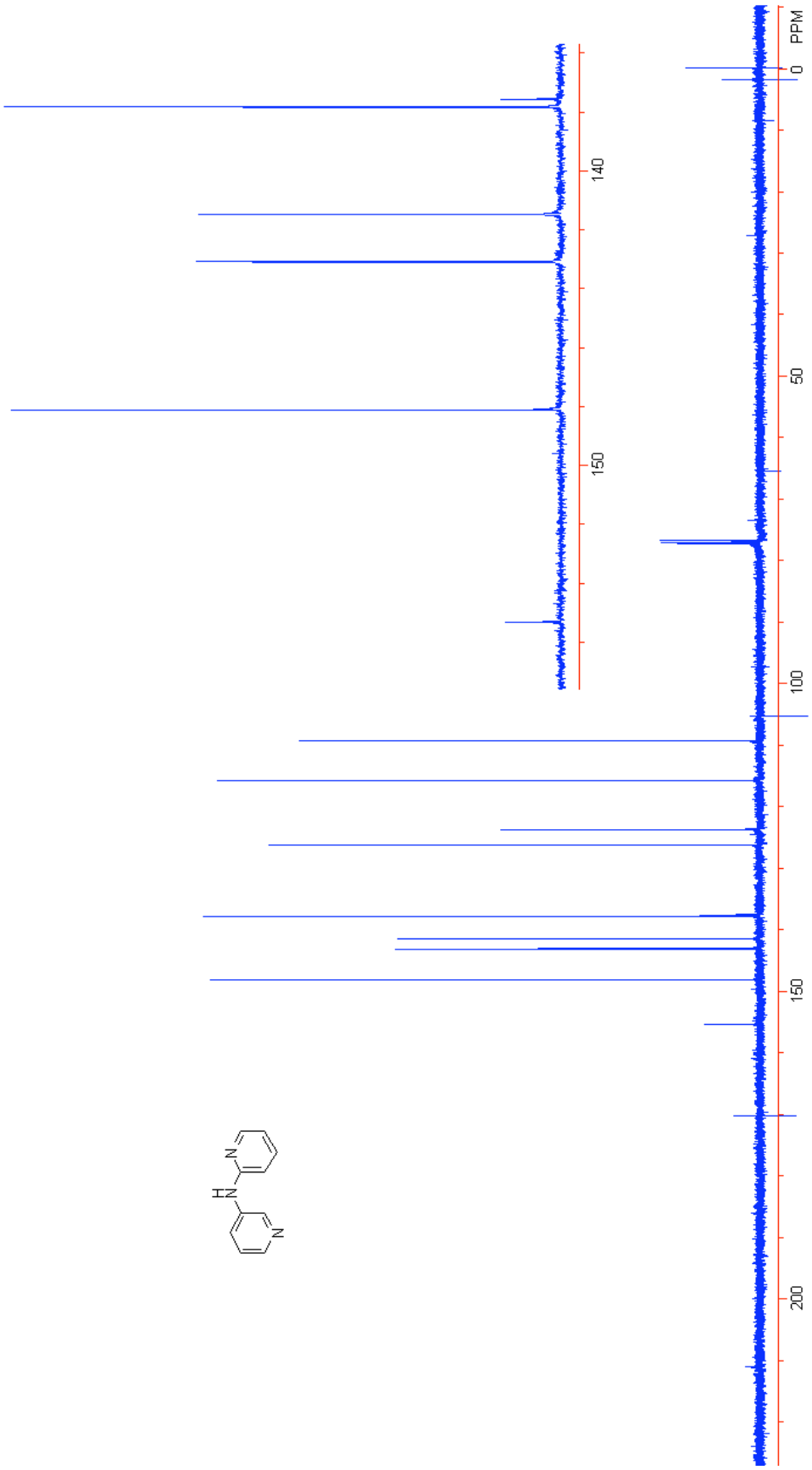


Table 6, entry 6 , 2,3'-Dipyridylamine



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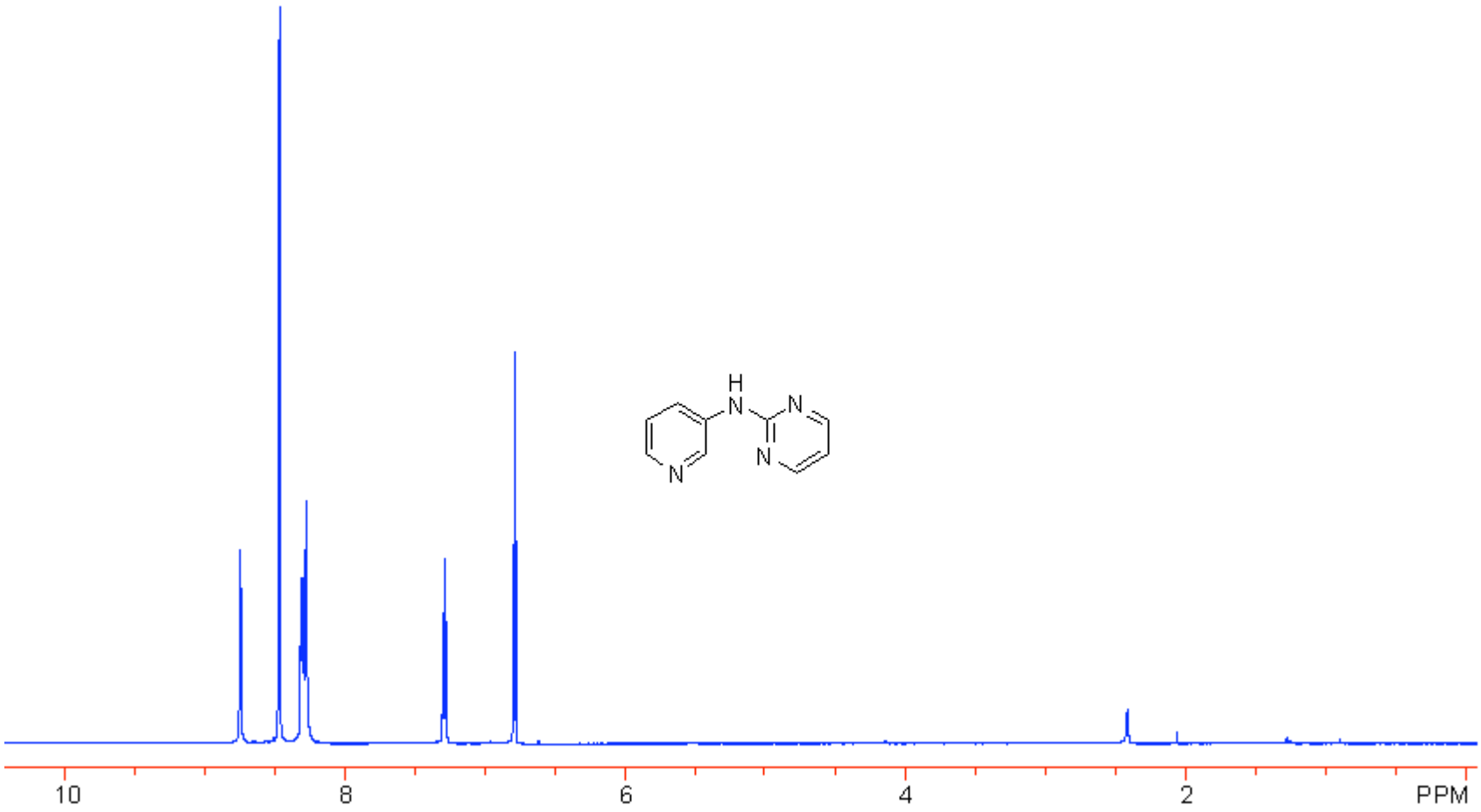
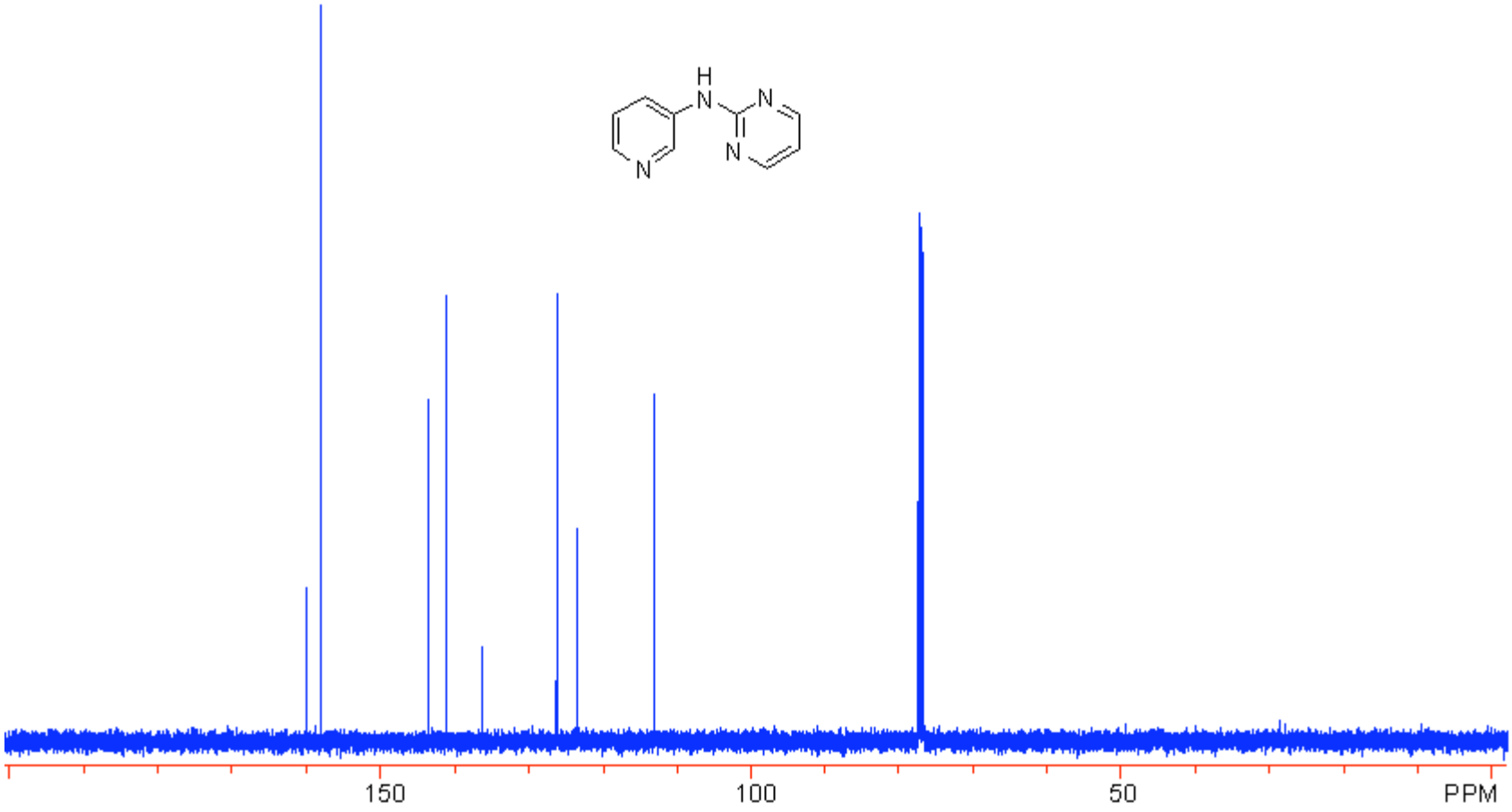


Table 6, entry 9, *N*-3-pyridyl-2-pyrimidinamine



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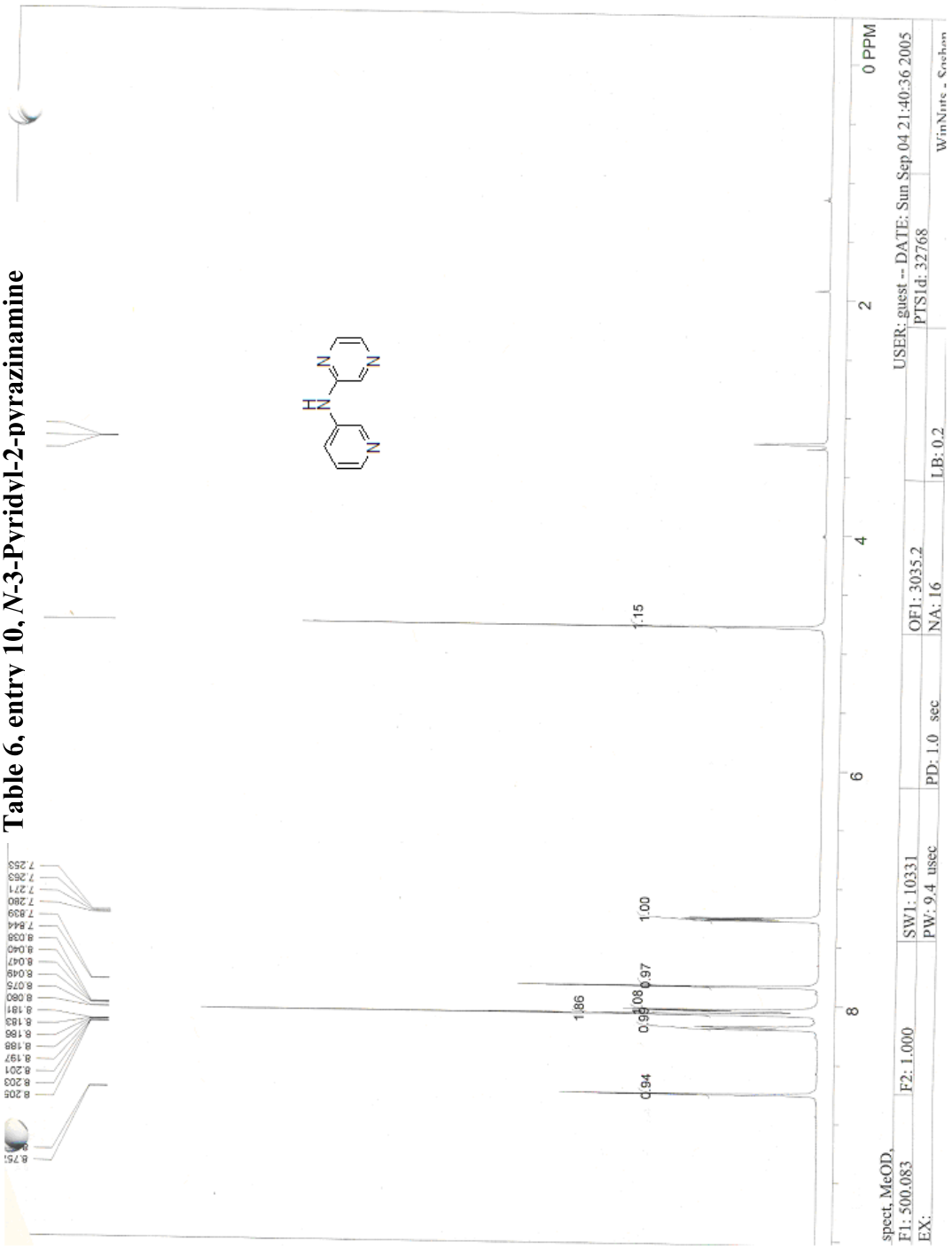

Table 6, entry 10, *N*-3-Pyridyl-2-pyrazinamine

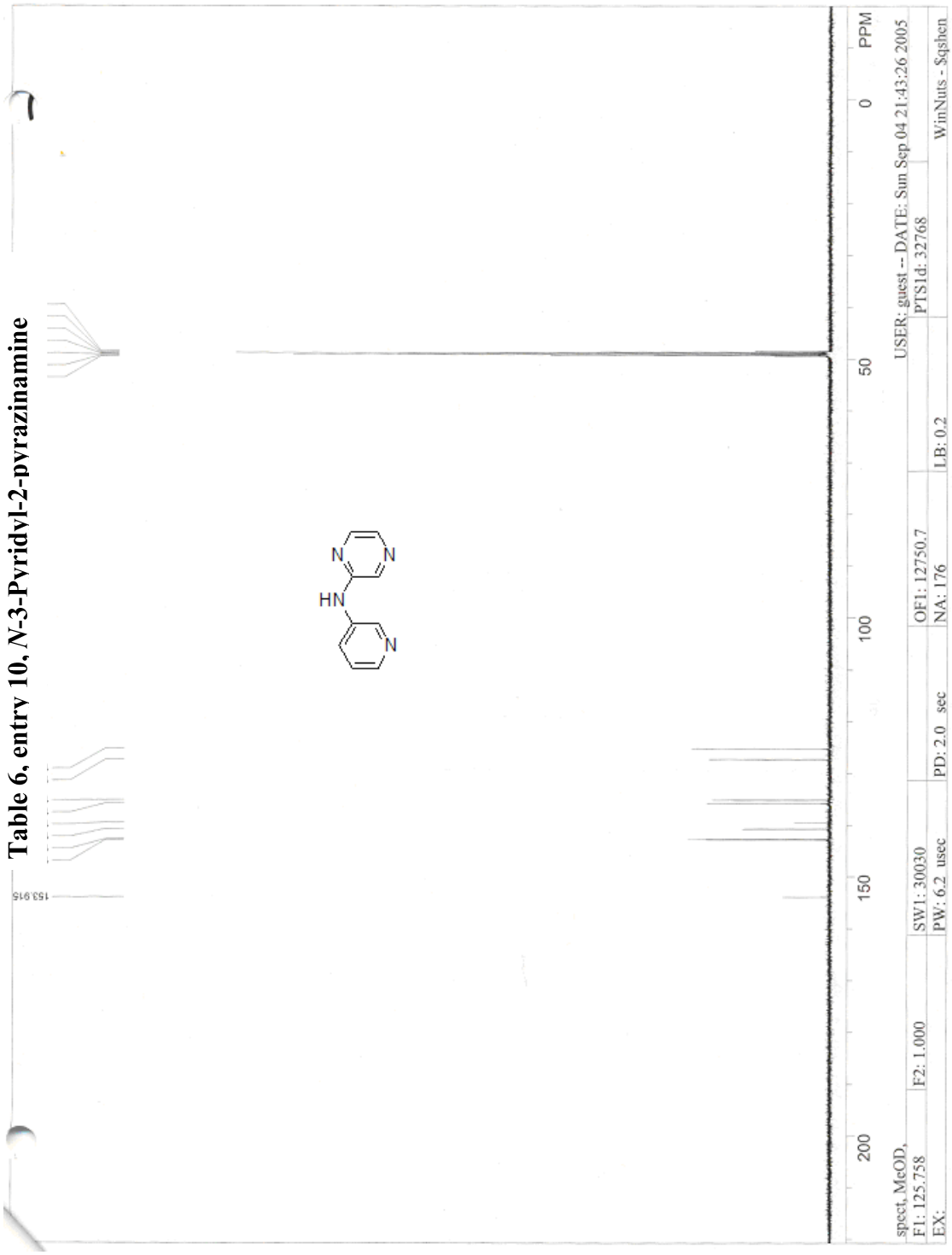

Table 6, entry 13, *N*-Phenyl-*p*-toluidine

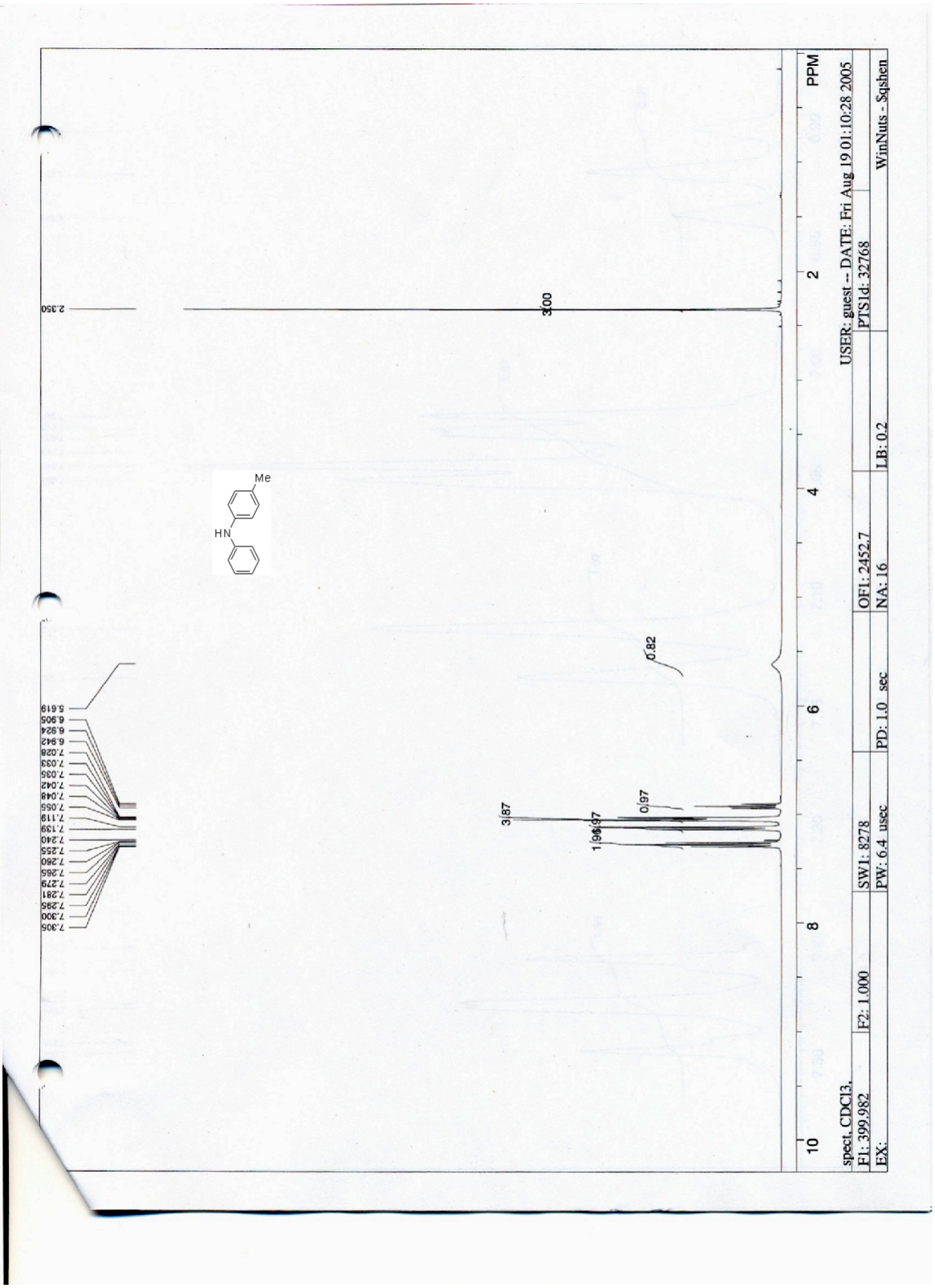

Table 6, entry 13, *N*-Phenyl-*p*-toluidine

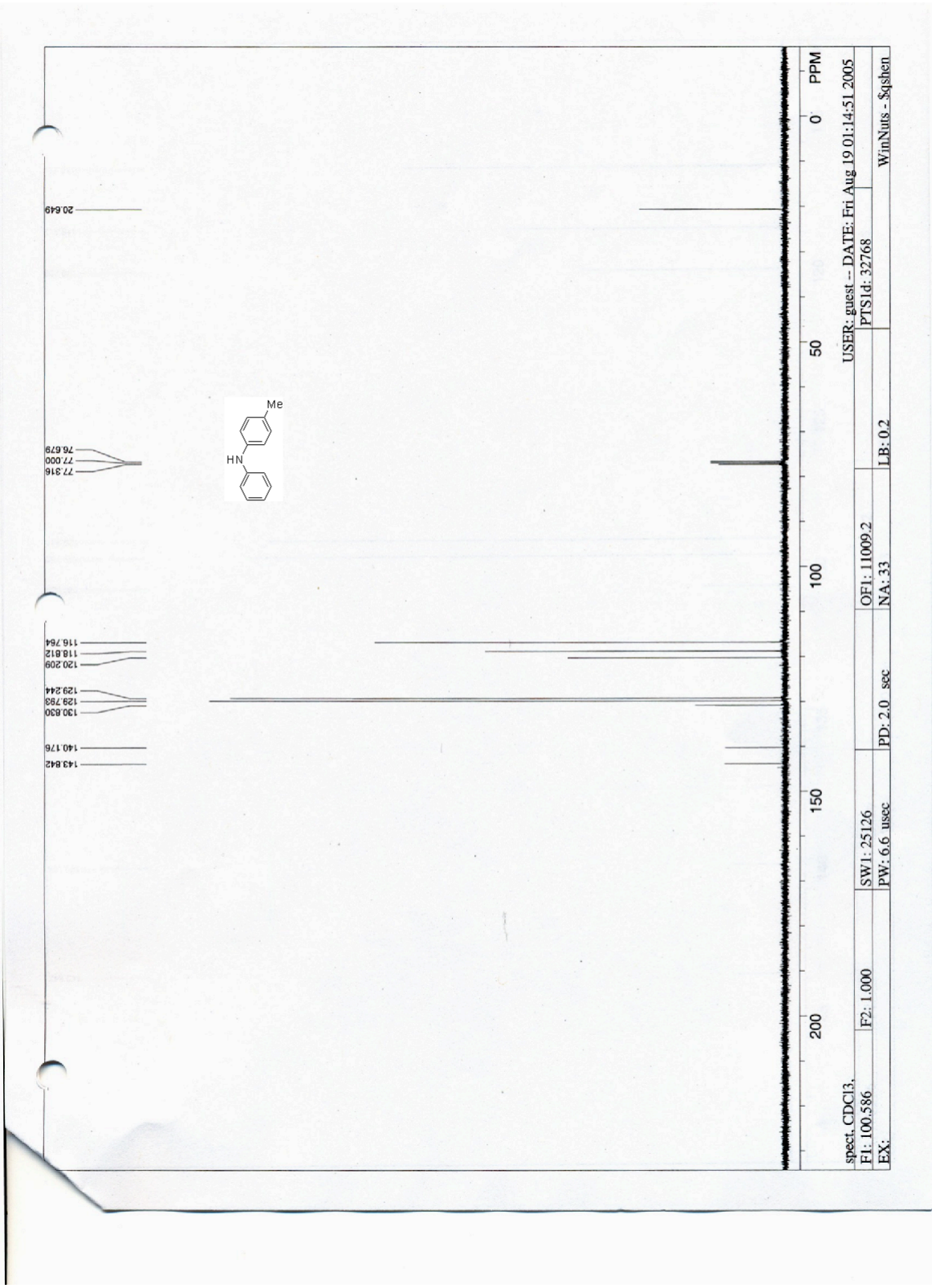

Table 6, entry 15, *N*-(2-Pyridyl)-aniline

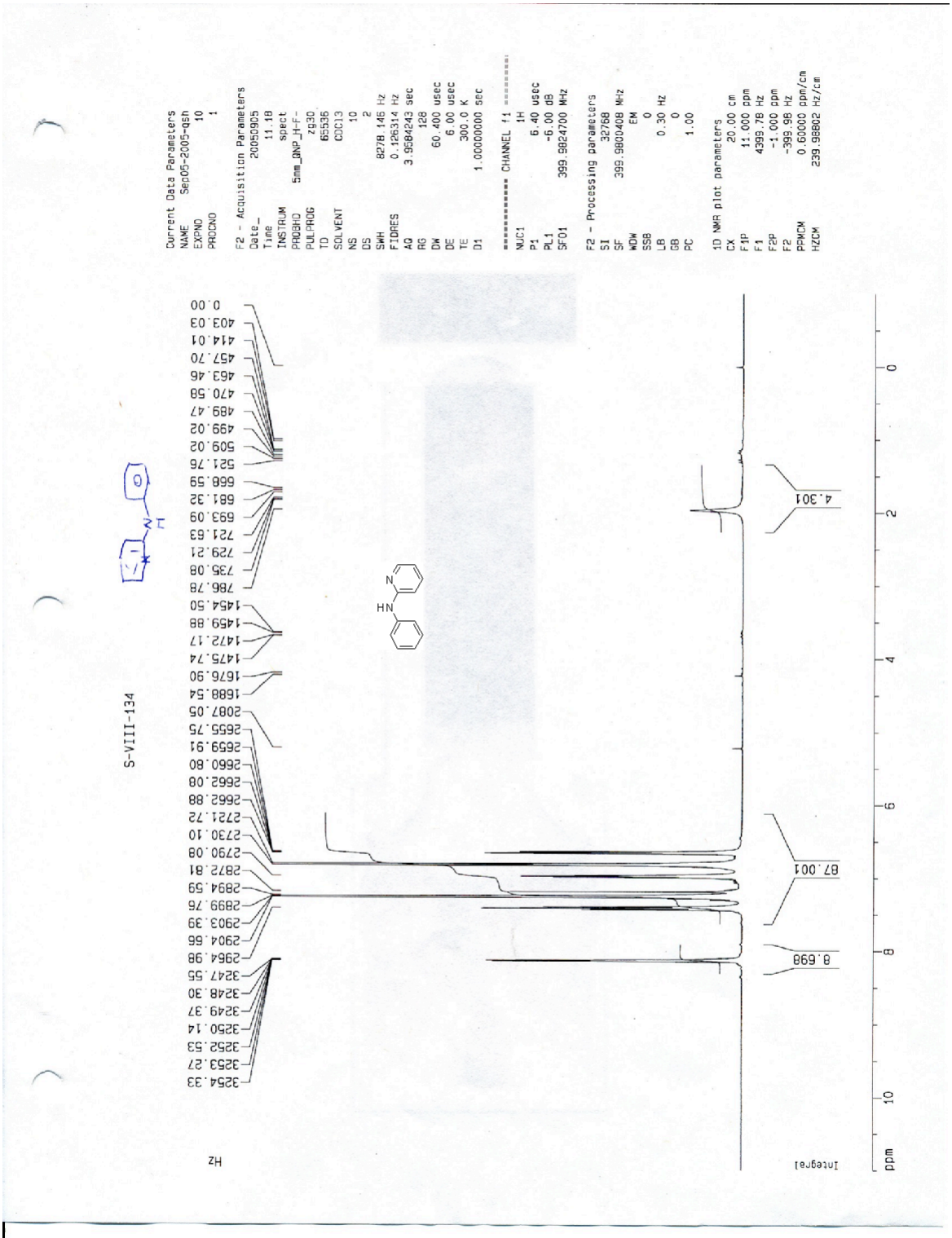

Table 6, entry 15, *N*-(2-Pyridyl)-aniline

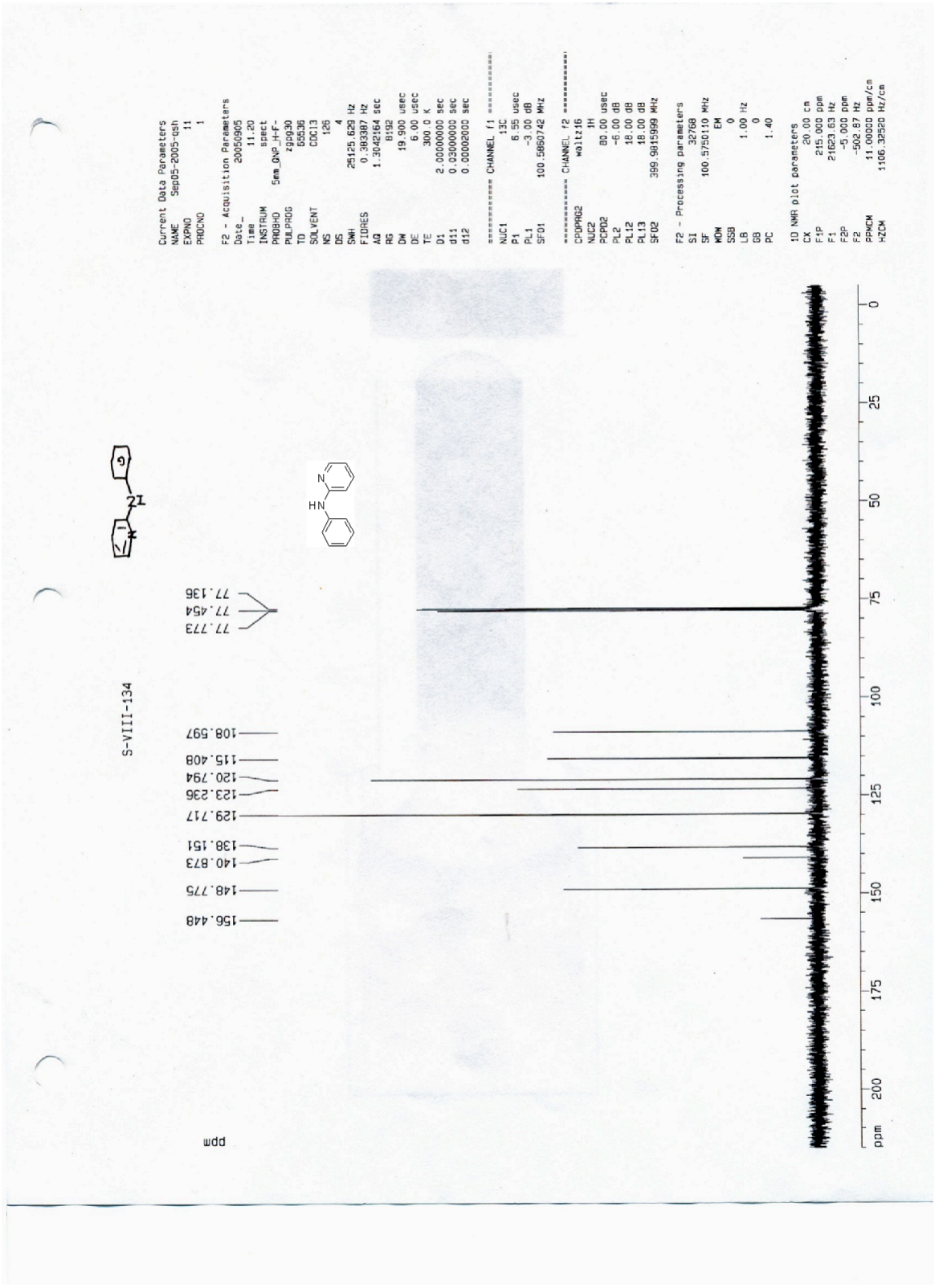

Table 6, entry 18, *N*-(*p*-Tolyl)-*p*-anisidine

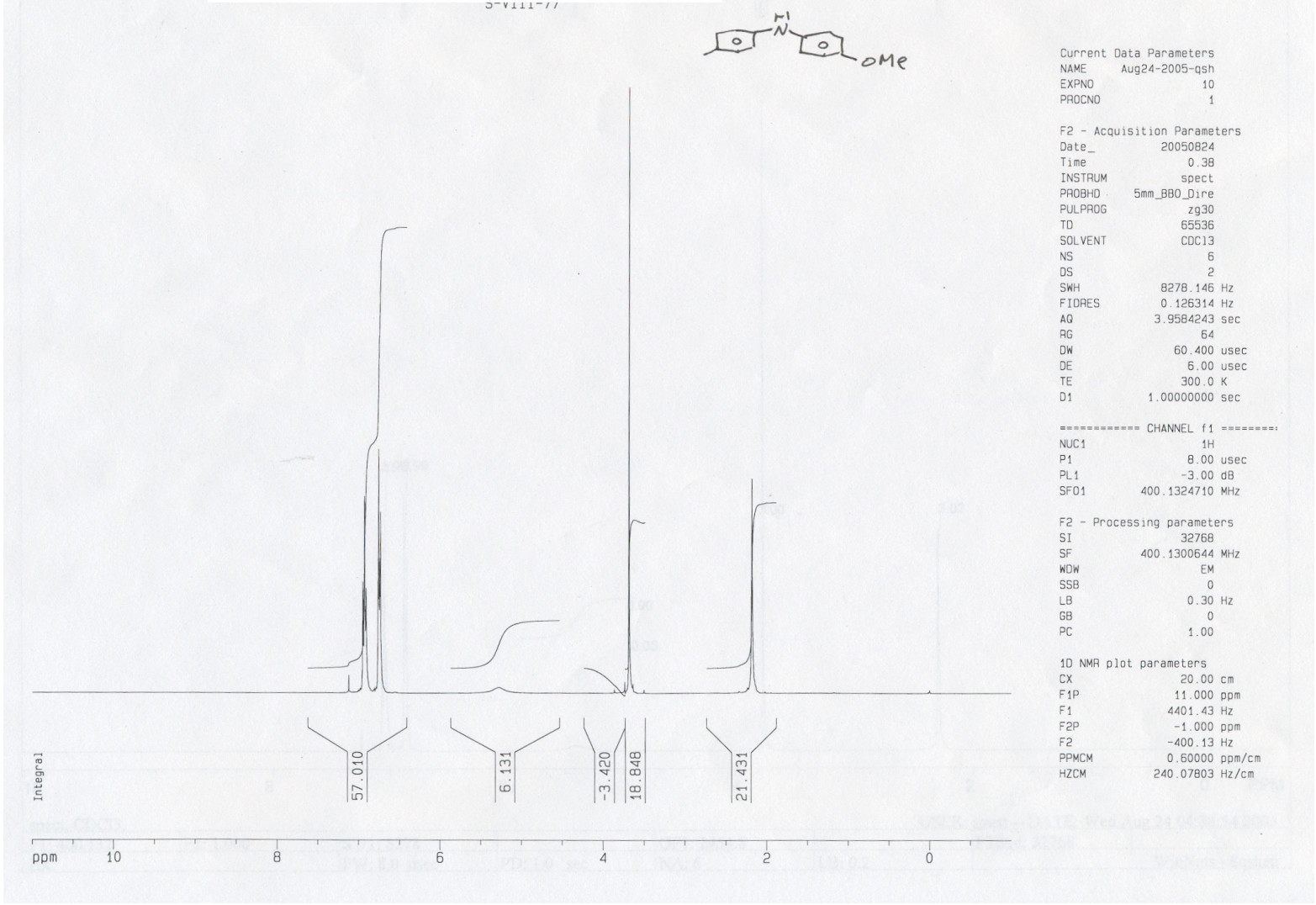


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Table 6, entry 18, *N*-(*p*-Tolyl)-*p*-anisidine

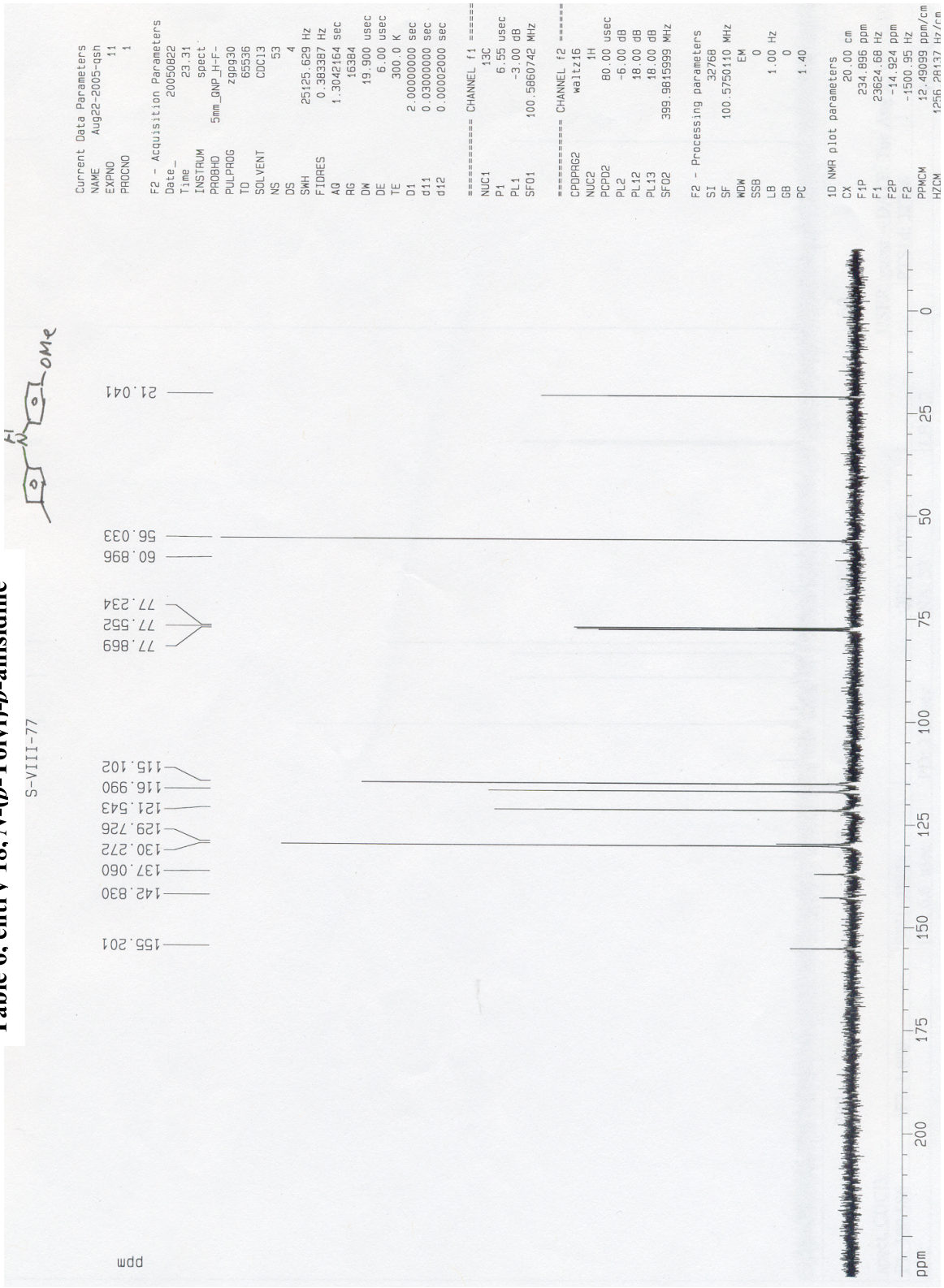


Table 6, entry 19, 3,4'-Dimethoxydiphenylamine aniline

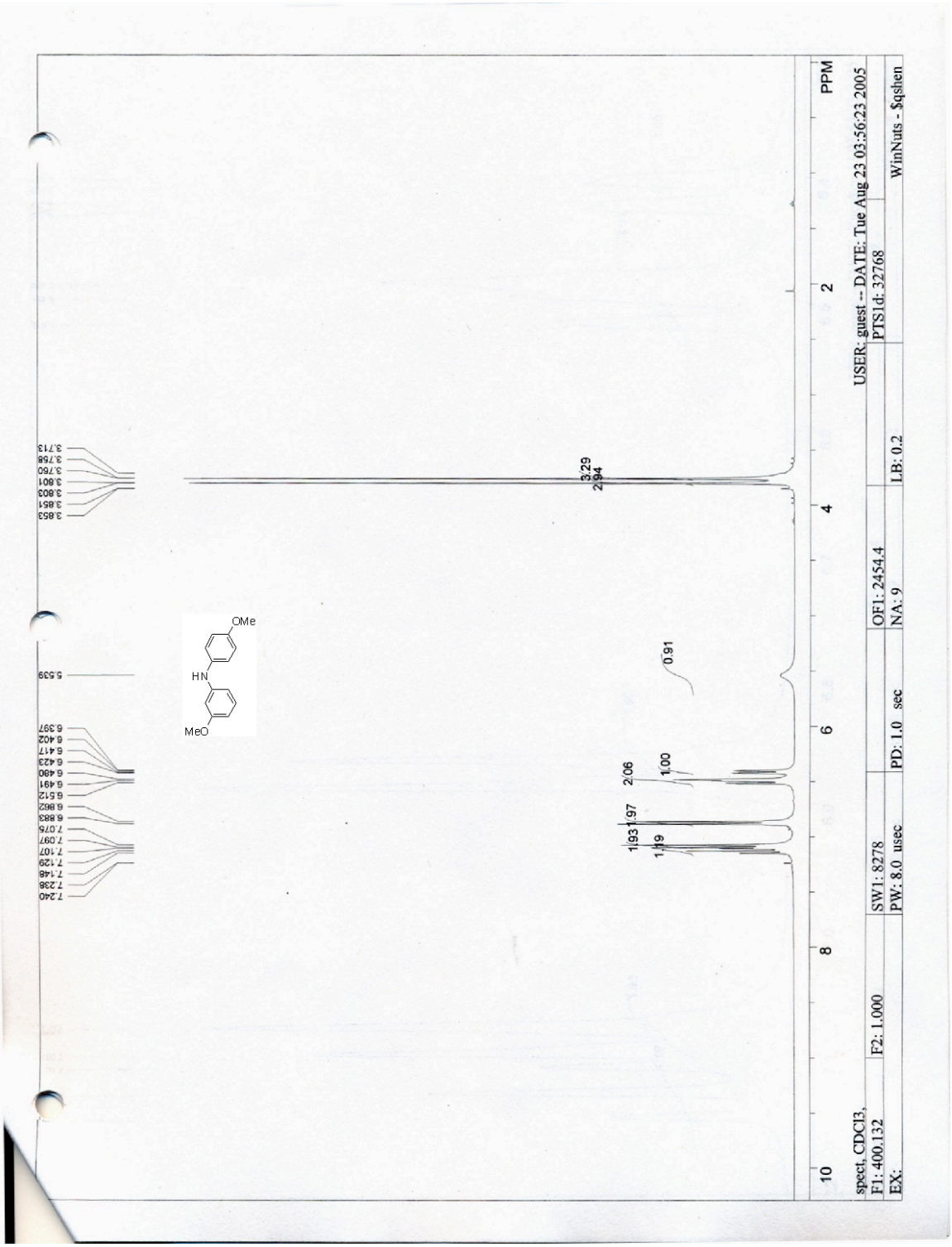


Table 6, entry 19, 3,4'-Dimethoxydiphenylamine aniline

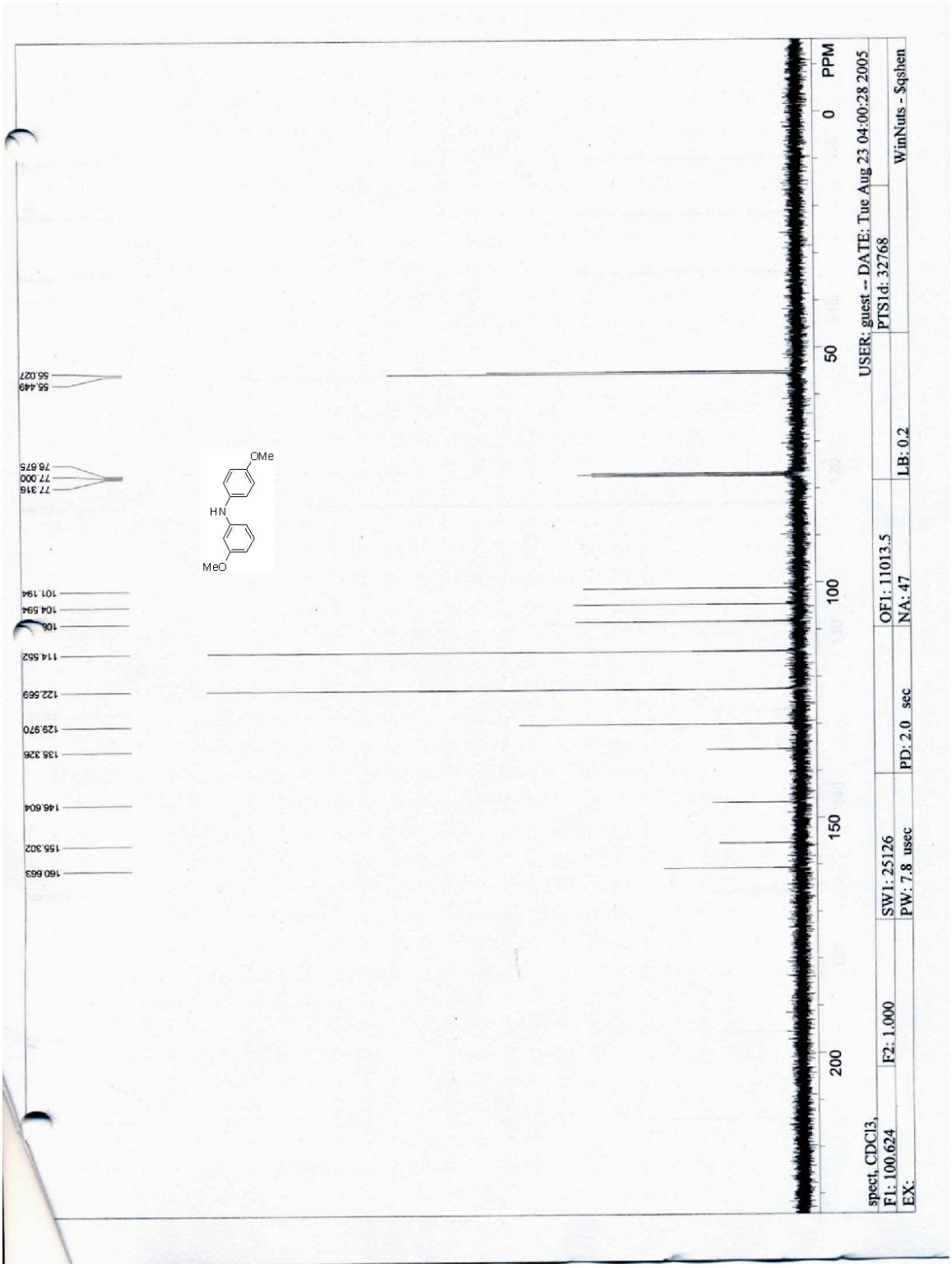


Table 6, entry 21, *N*-(*o*-Tolyl)-*p*-toluidine

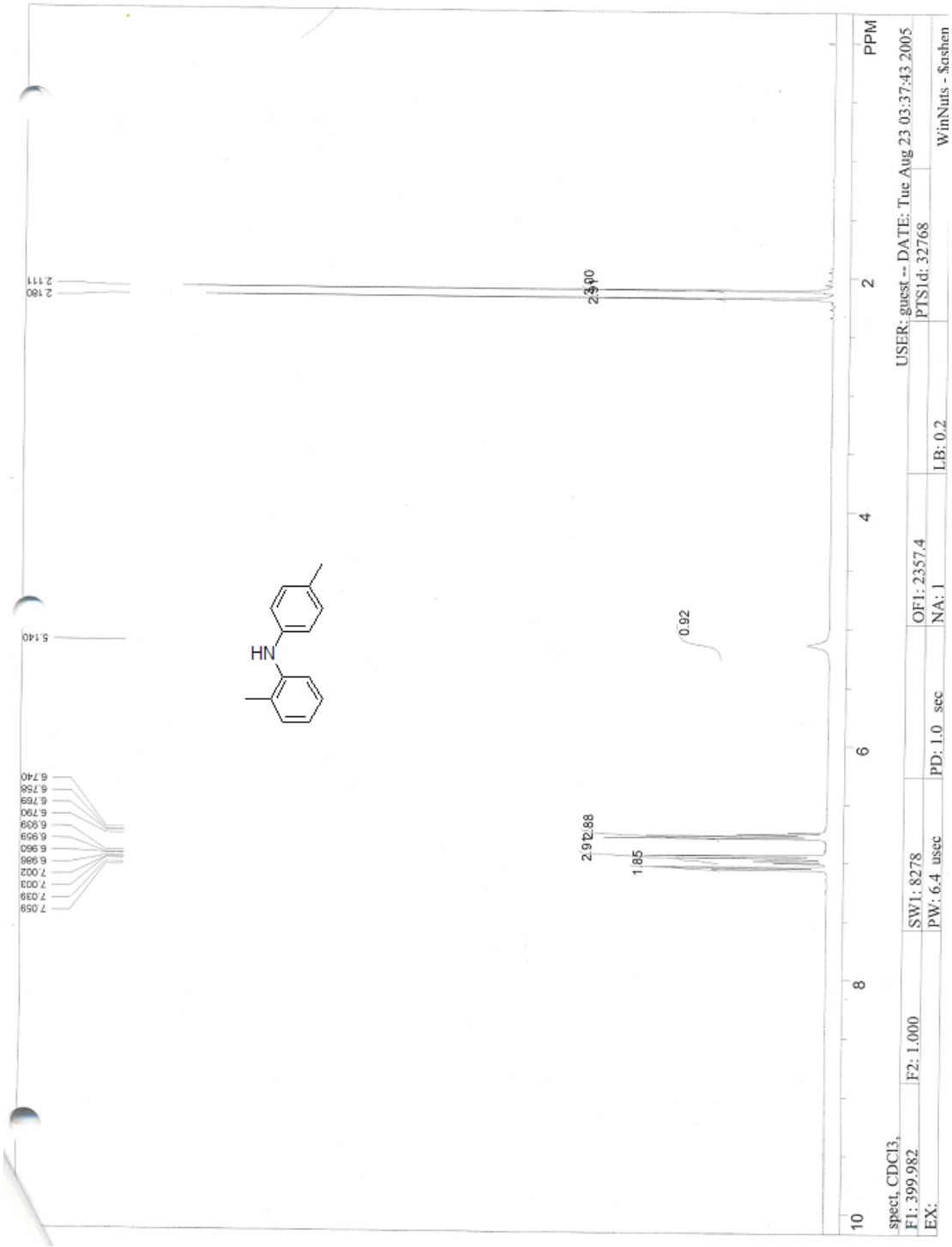


Table 6, entry 21, *N*-(*o*-Tolyl)-*p*-toluidine

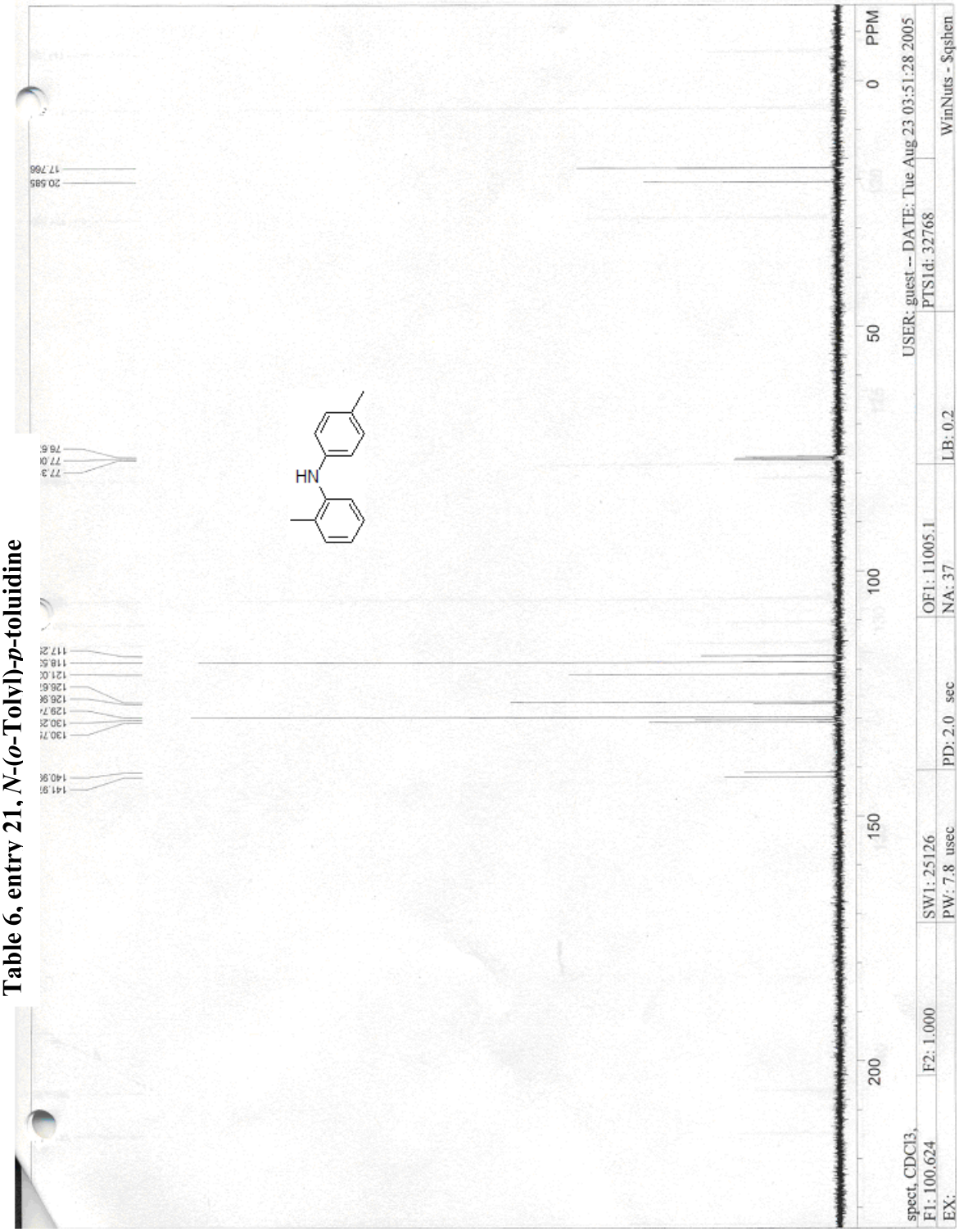


Table 6, entry 24, *N*-(*p*-Tolyl)-2-cyclohexylaniline

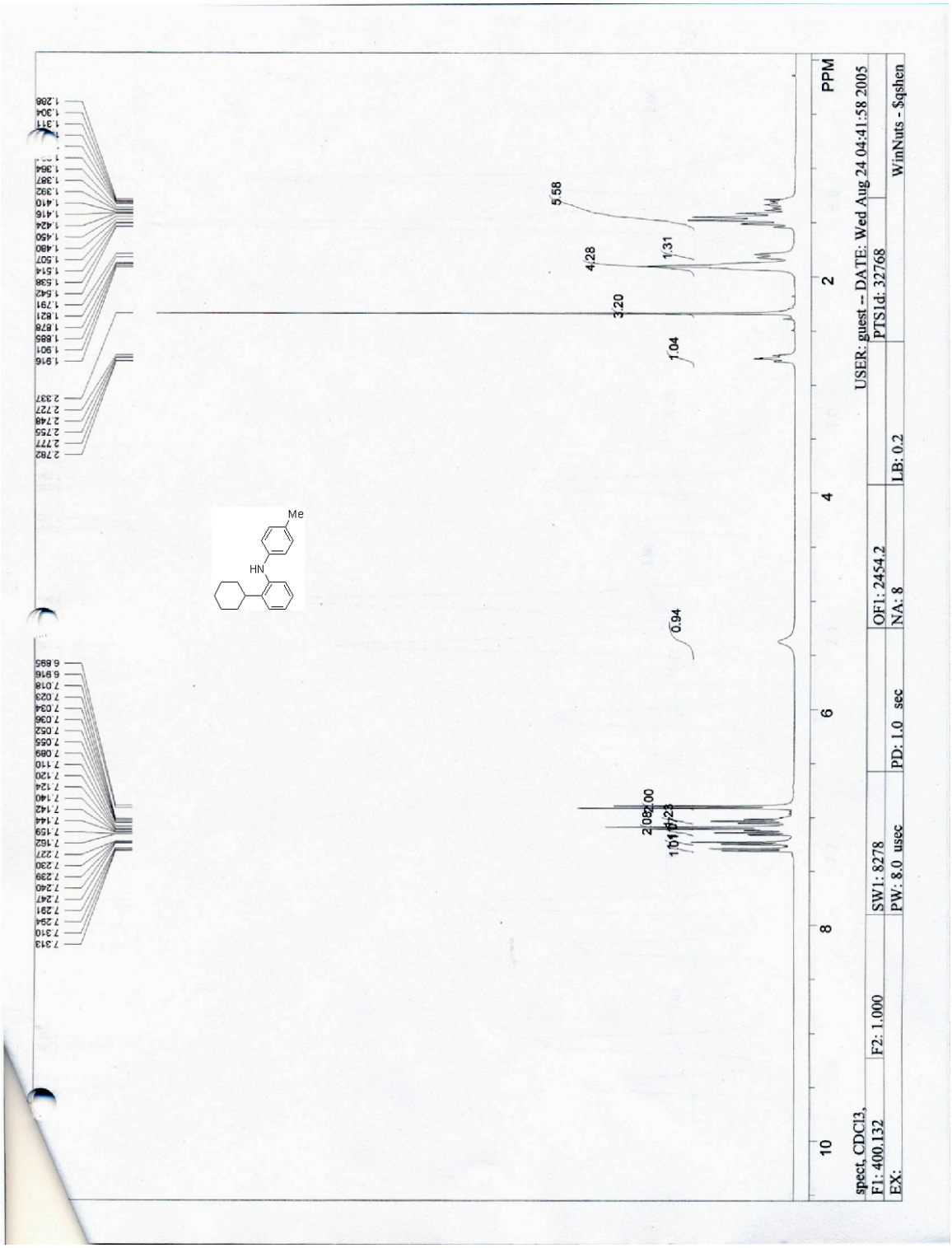


Table 6, entry 24, *N*-(*p*-Tolyl)-2-cyclohexylaniline

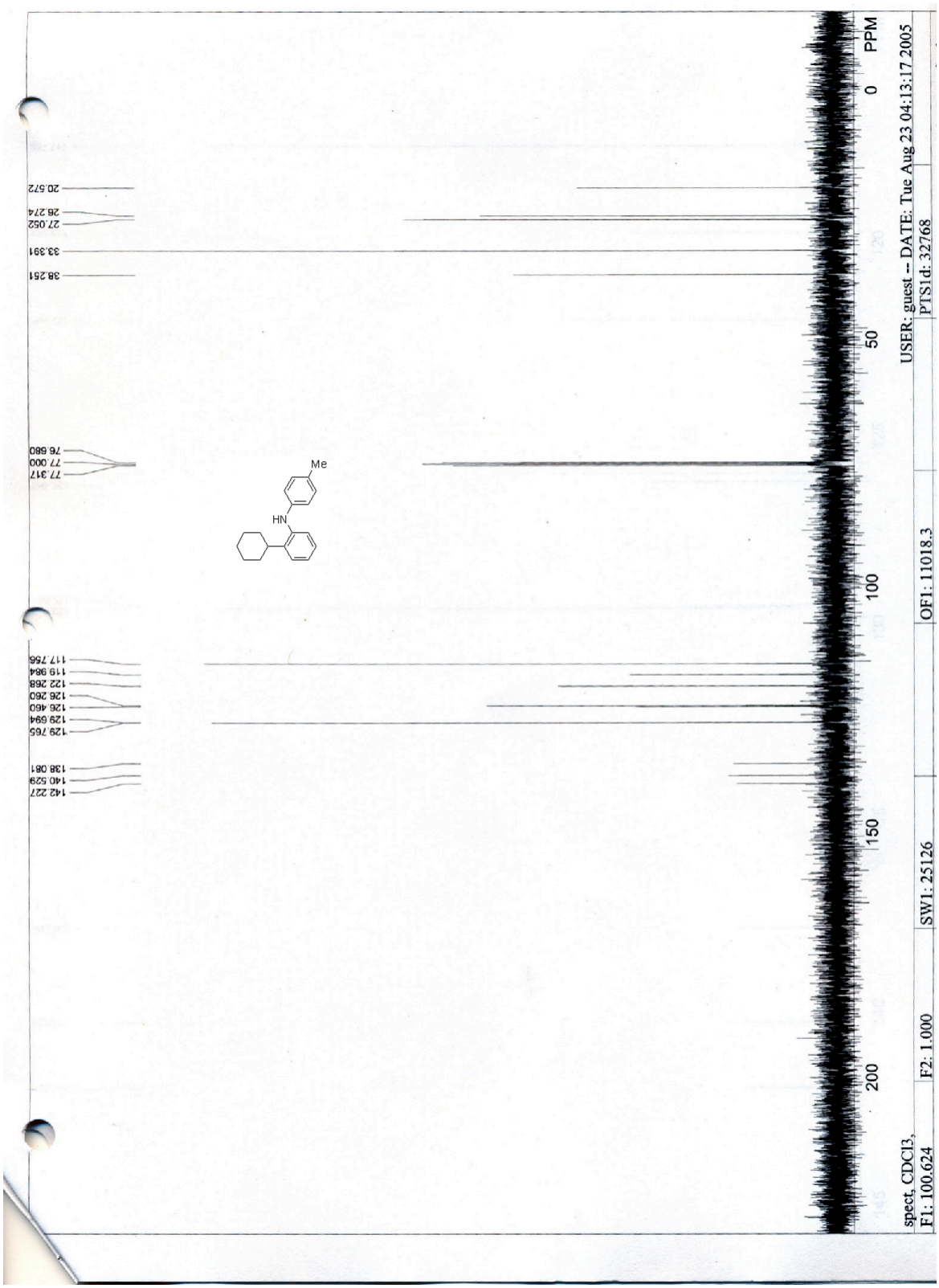


Table 7, entry 1, 2-(*N*-Methylanilino)pyridine

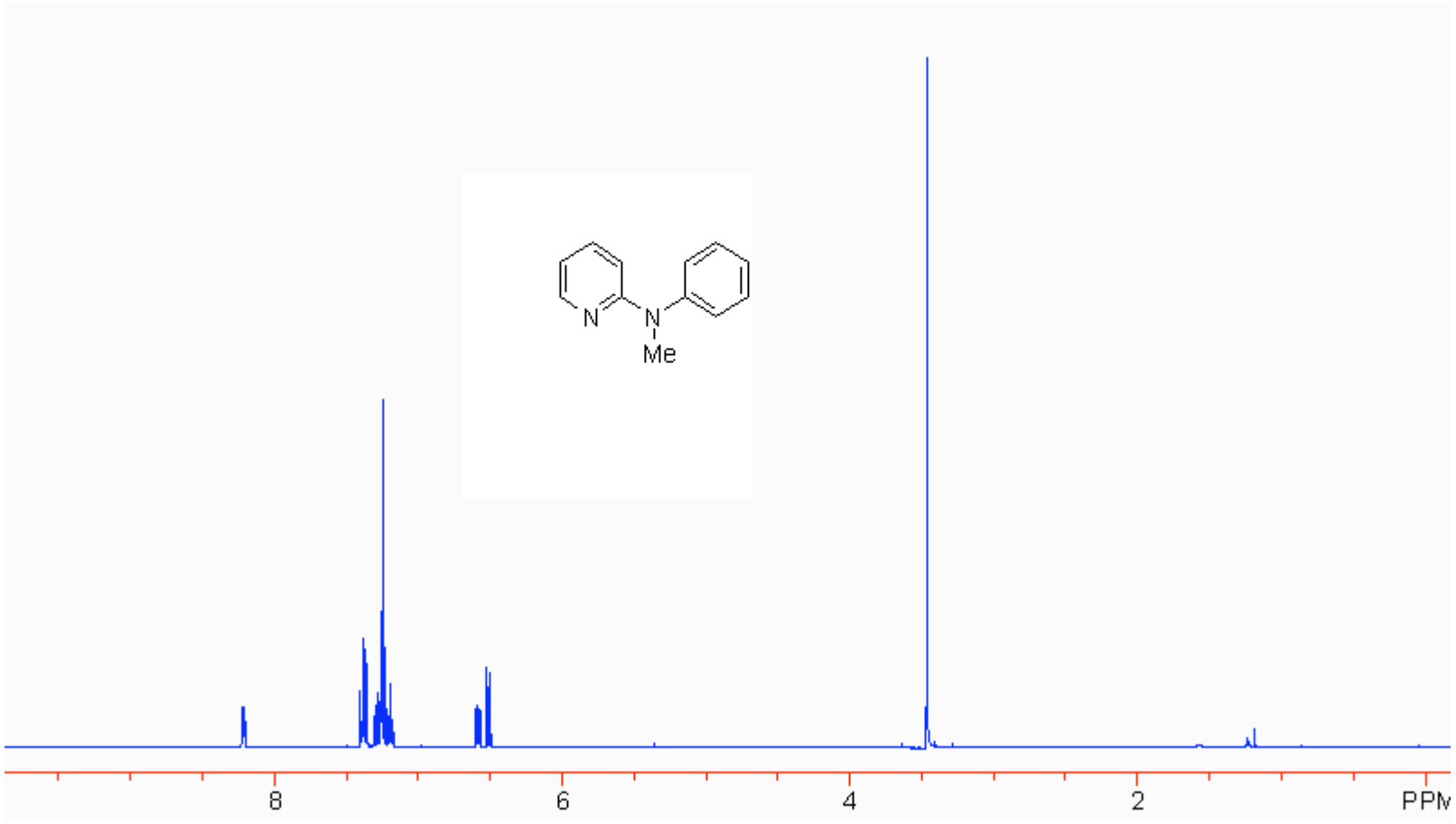


Table 7, entry 1, 2-(*N*-Methylanilino)pyridine

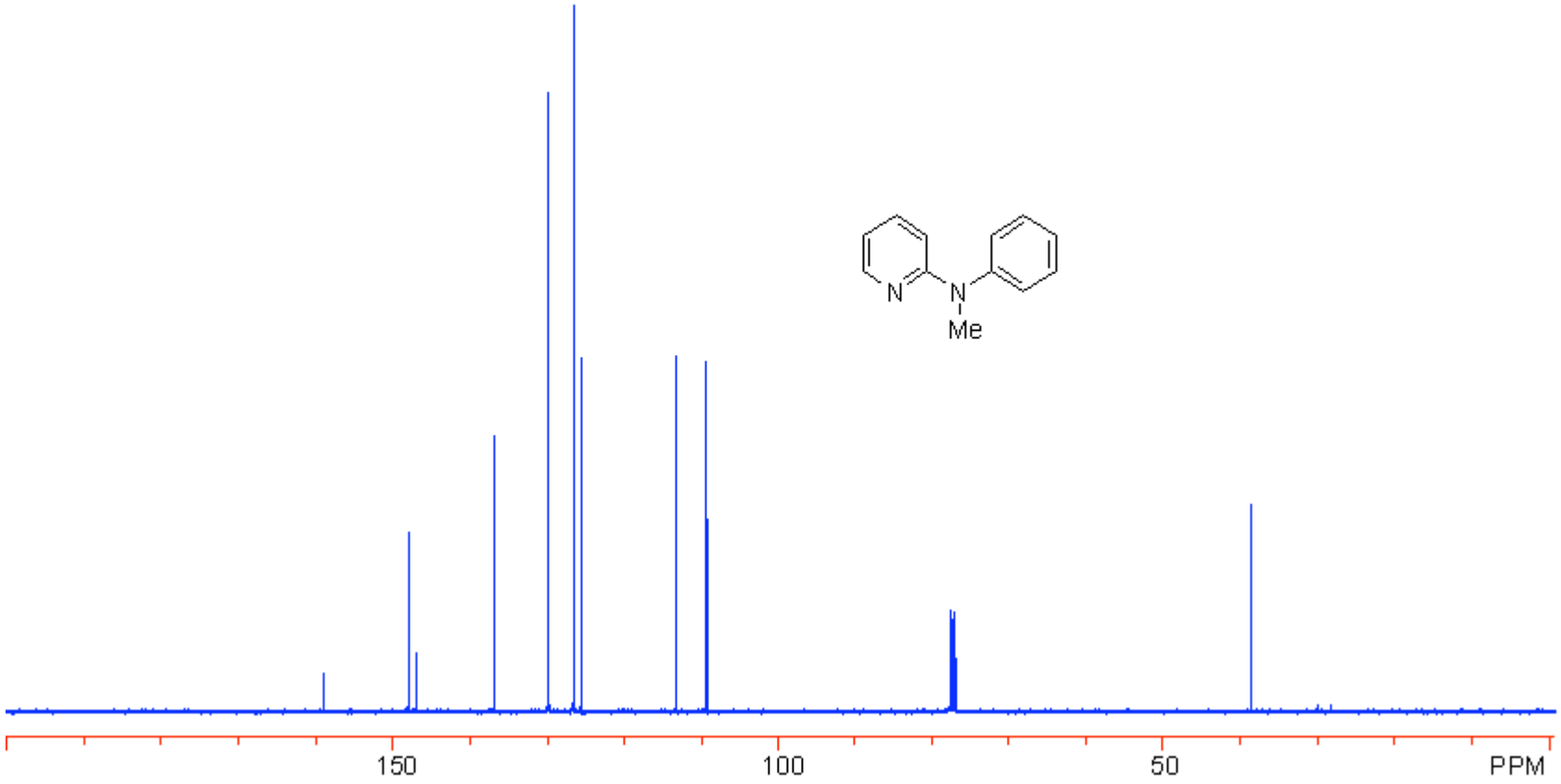


Table 7, entry 2, 3-Pyridylmorpholine

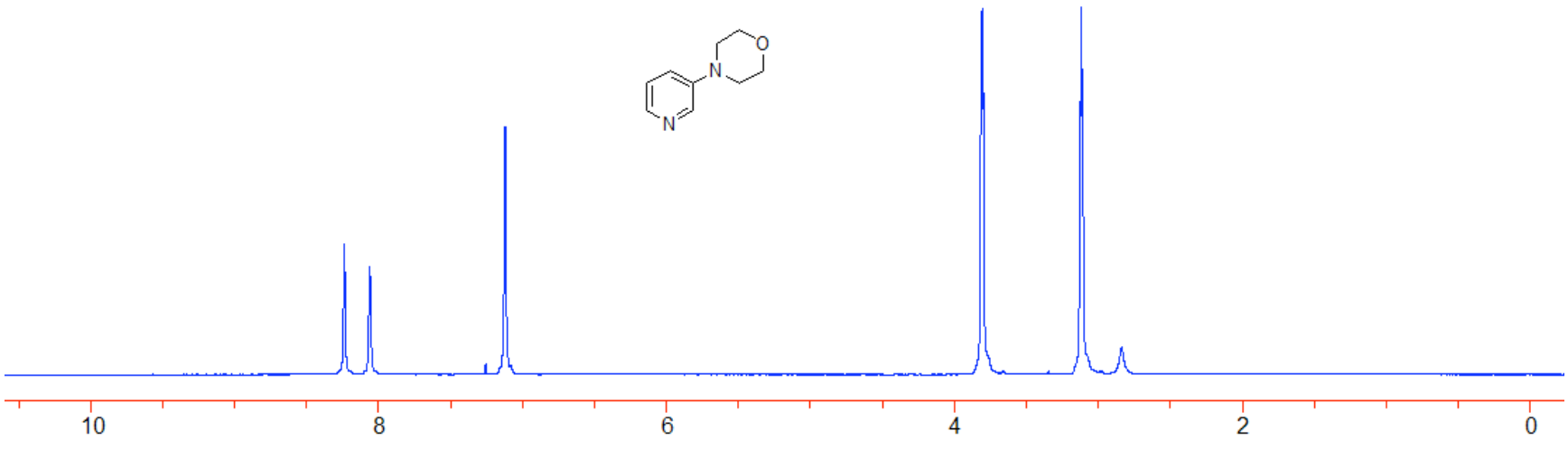


Table 7, entry 2, 3-Pyridylmorpholine

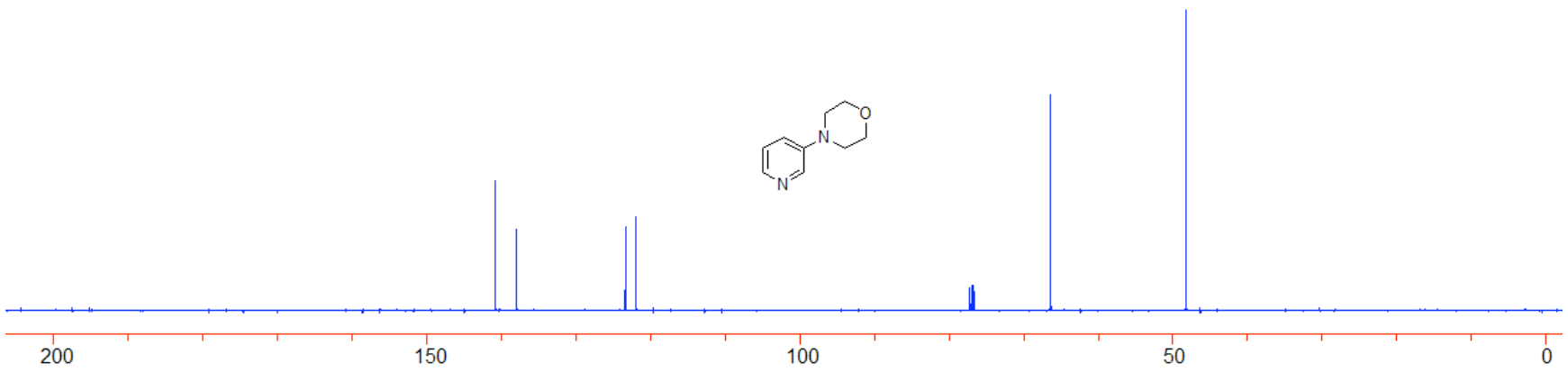


Table 7, entry 5, *N*-Methyldiphenylamine

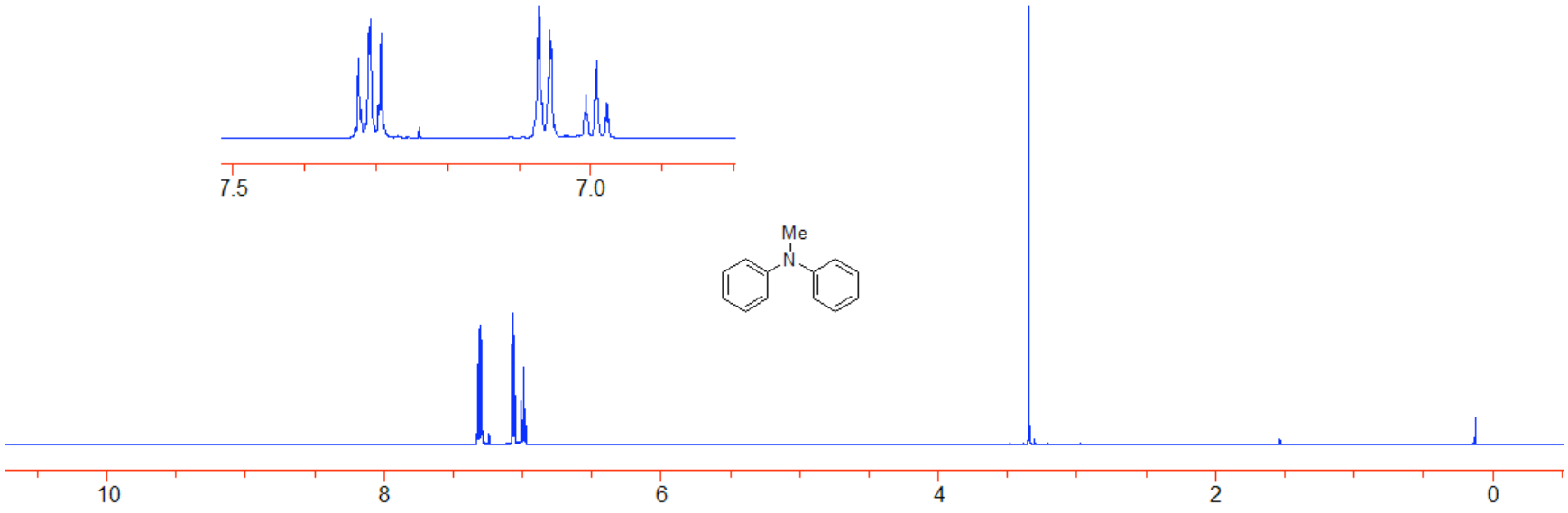


Table 7, entry 5, *N*-Methyldiphenylamine

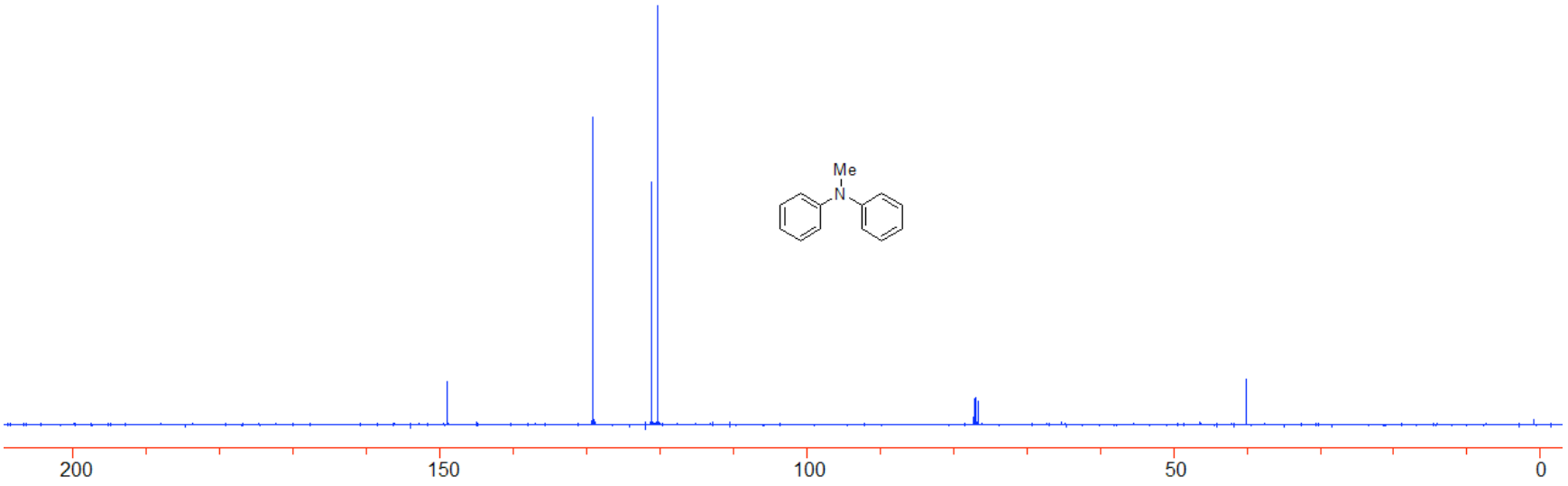


Table 7, entry 6, *N*, *N*-Di-butylaniline

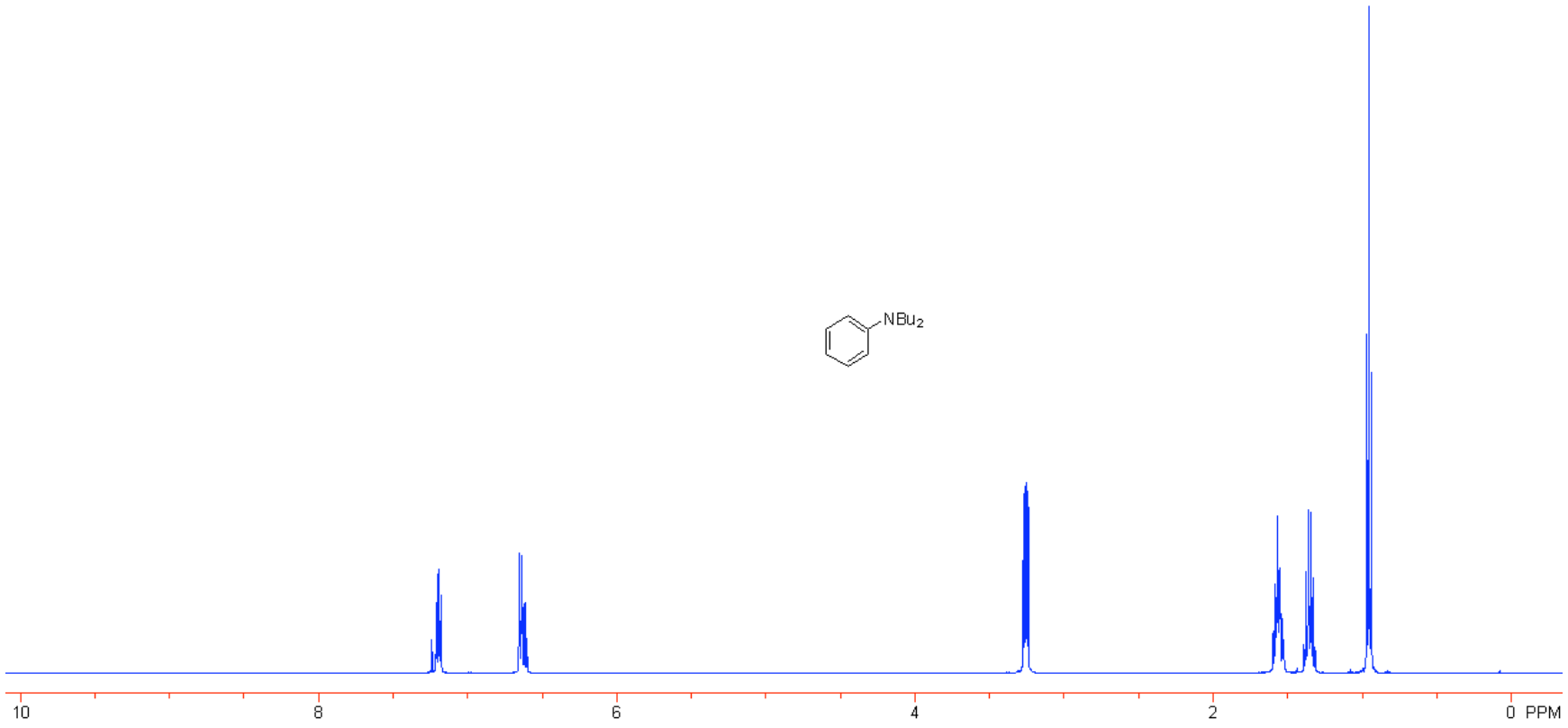


Table 7, entry 6, *N*, *N*-Di-butylaniline

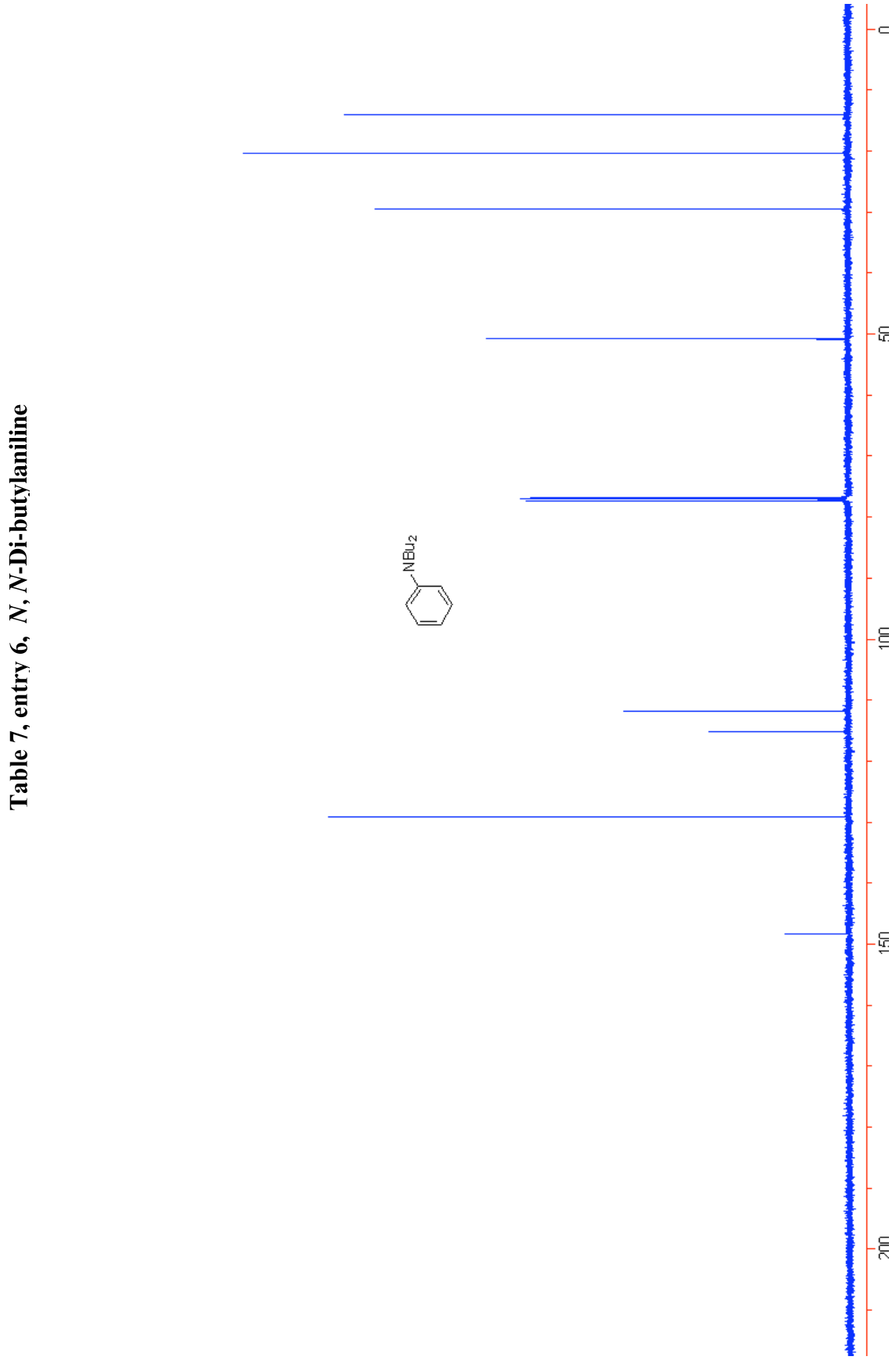


Table 7, entry 7, Triphenylamine

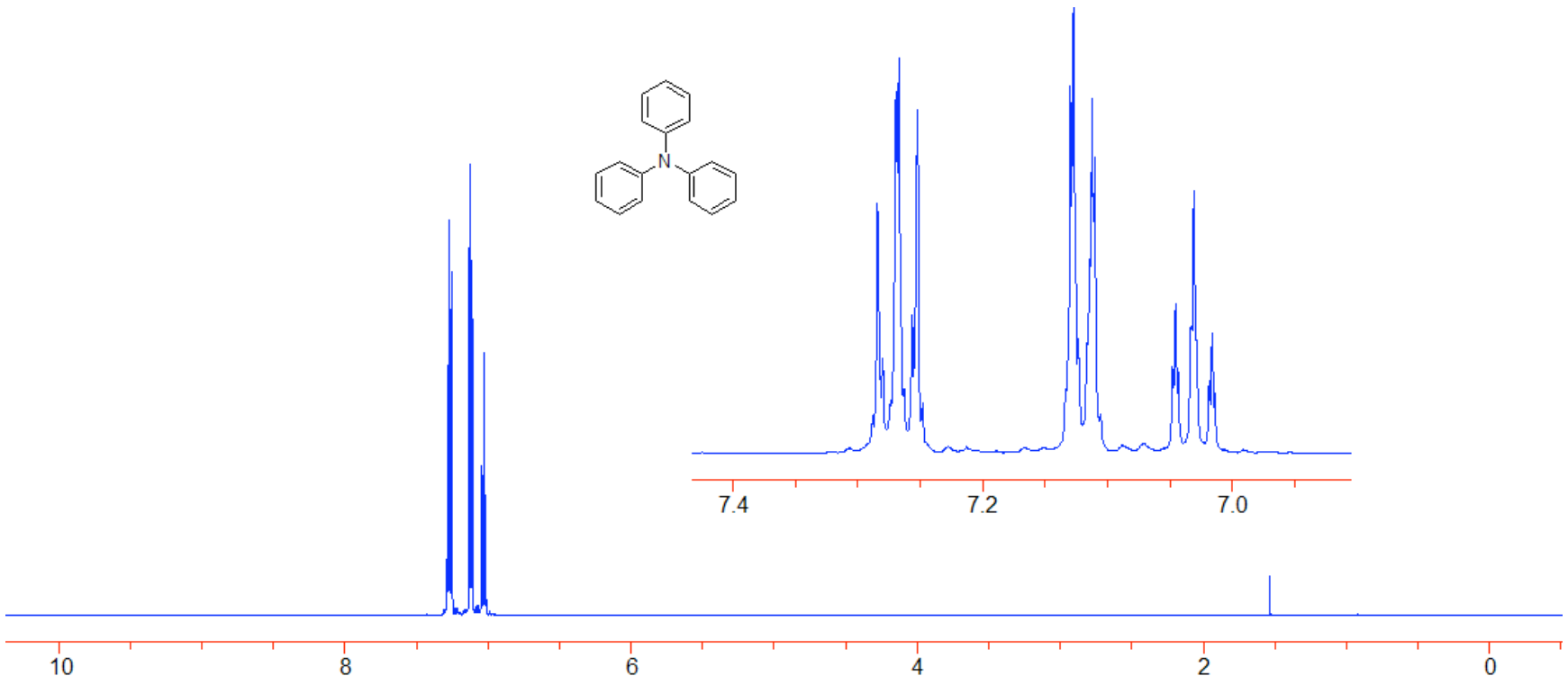


Table 7, entry 7, Triphenylamine

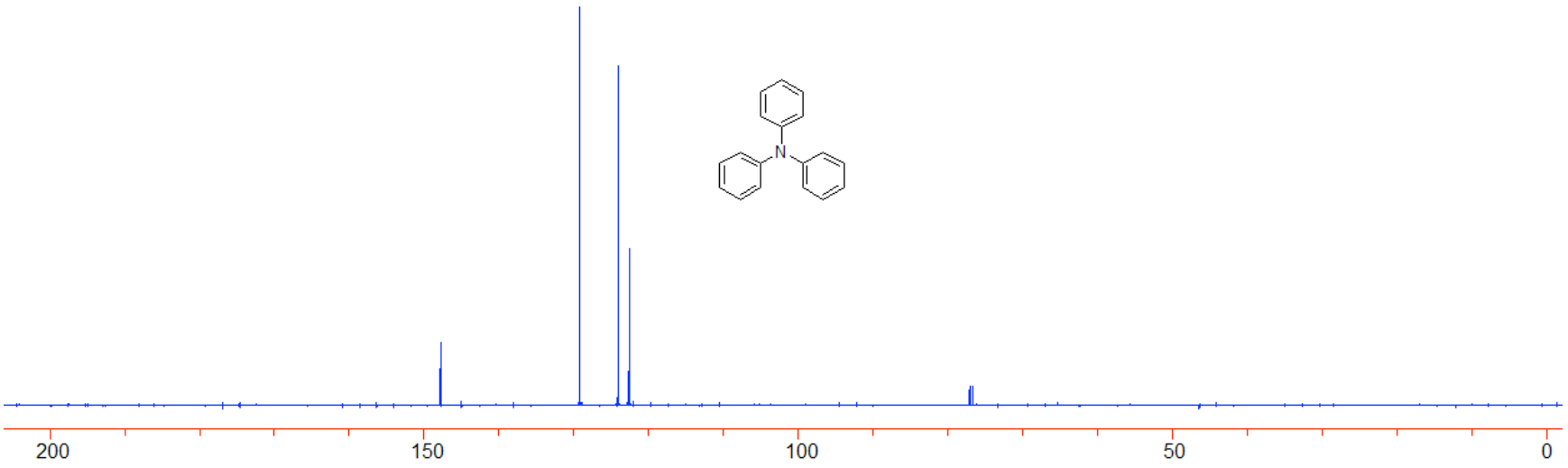


Table 18, entry 8, *p*-Tolylmorpholine

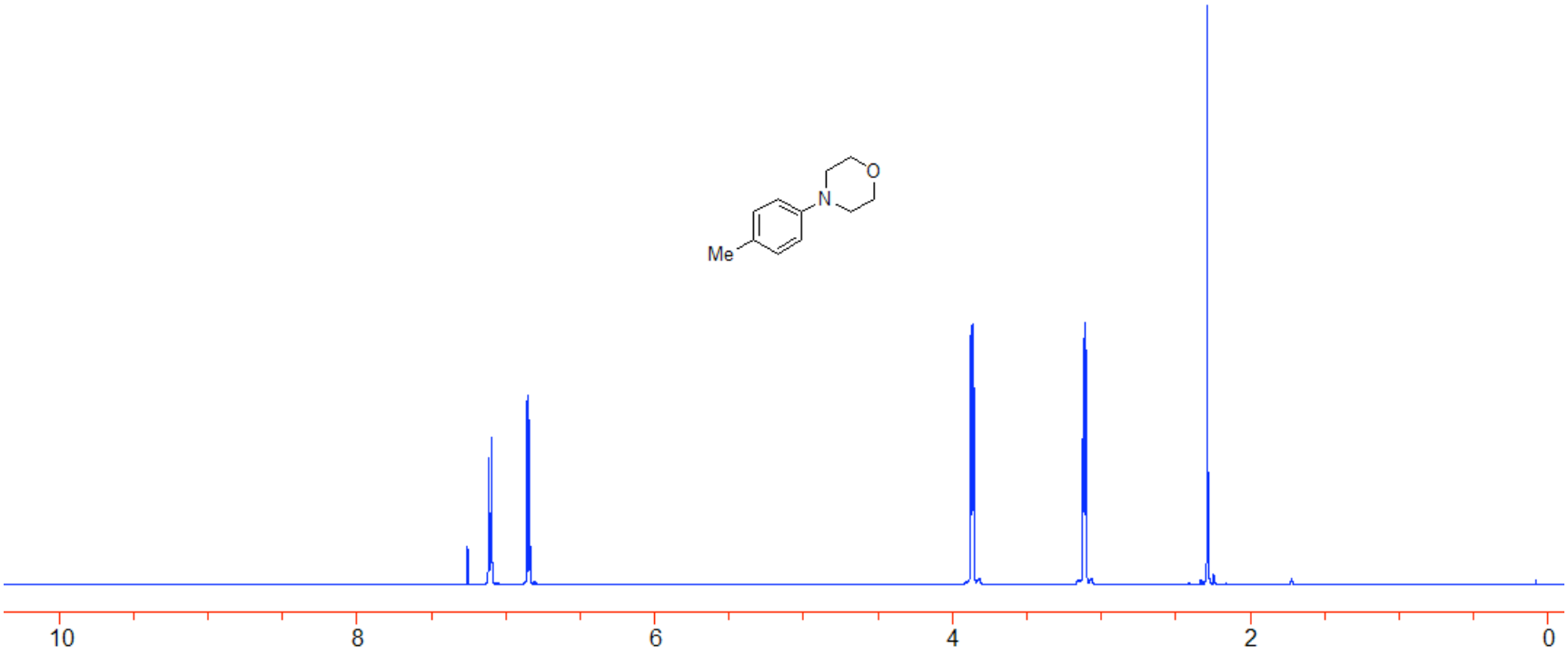


Table 18, entry 8, *p*-Tolylmorpholine

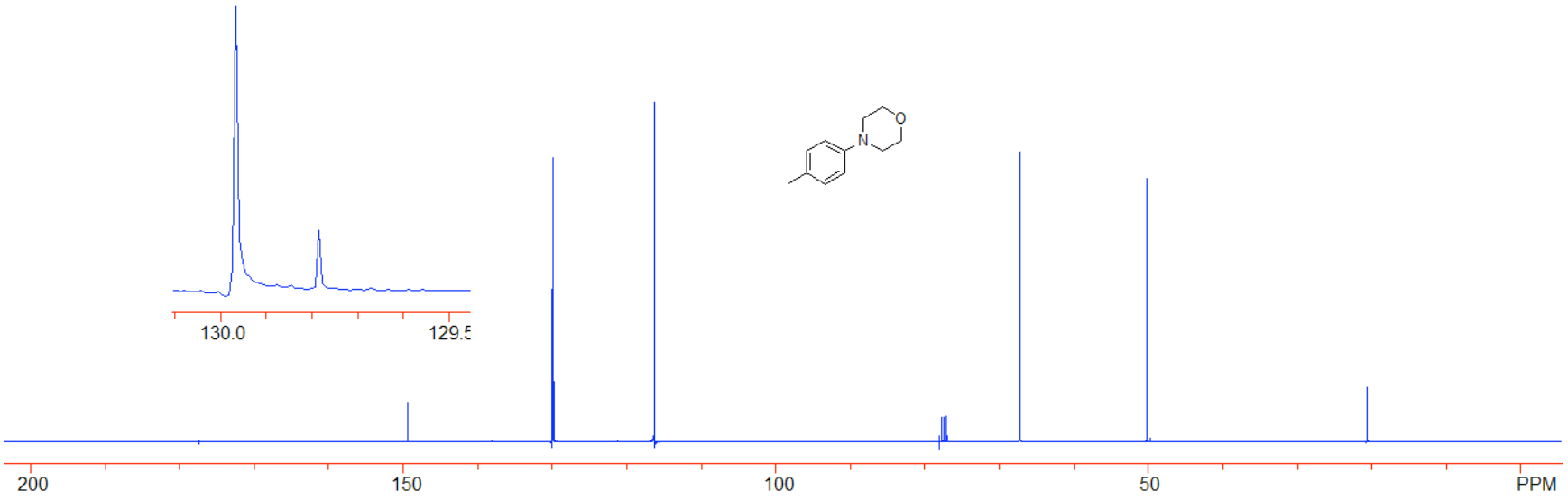


Table 7, entry 9, *N*-(3-Methoxyphenyl)-morpholine

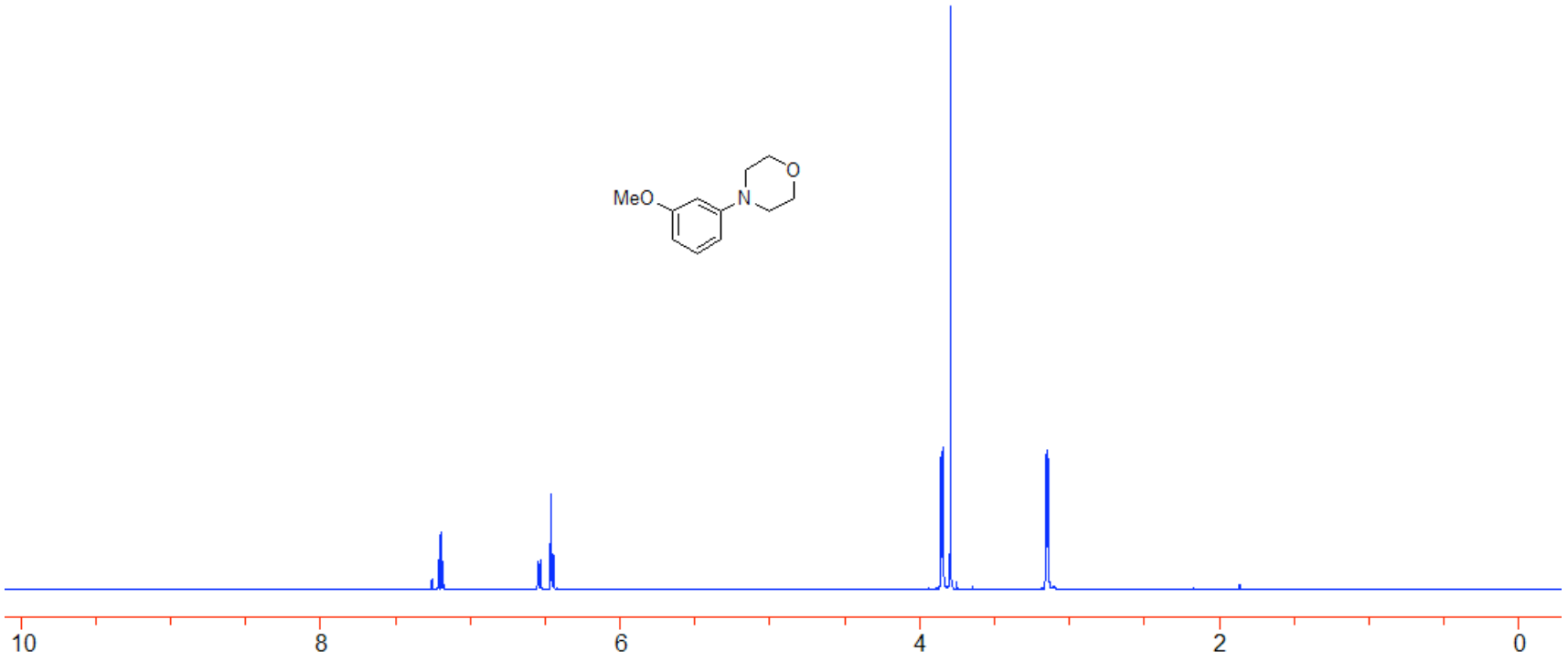


Table 7, entry 9, *N*-(3-Methoxyphenyl)-morpholine

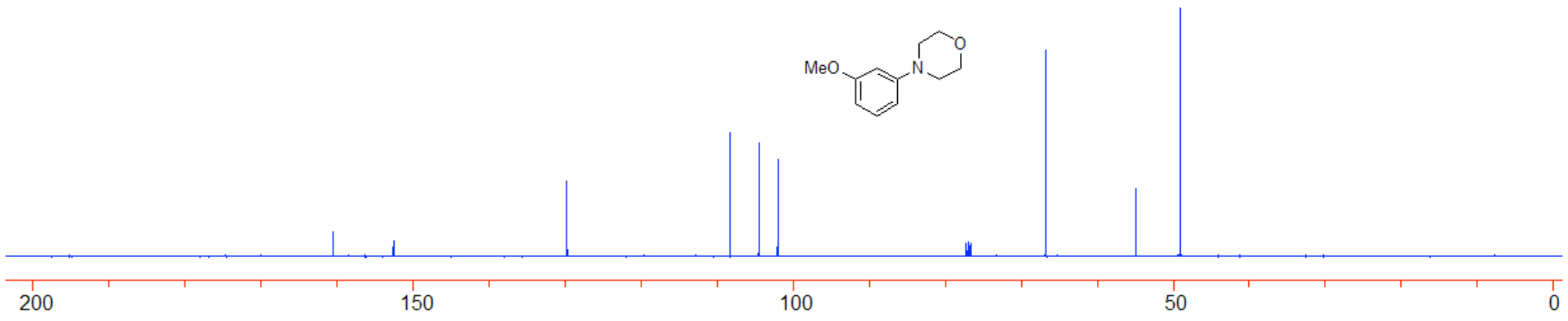


Table 8, entry 2, 2-Acetamido-5-*N*-*sec*-butylaminopyridine

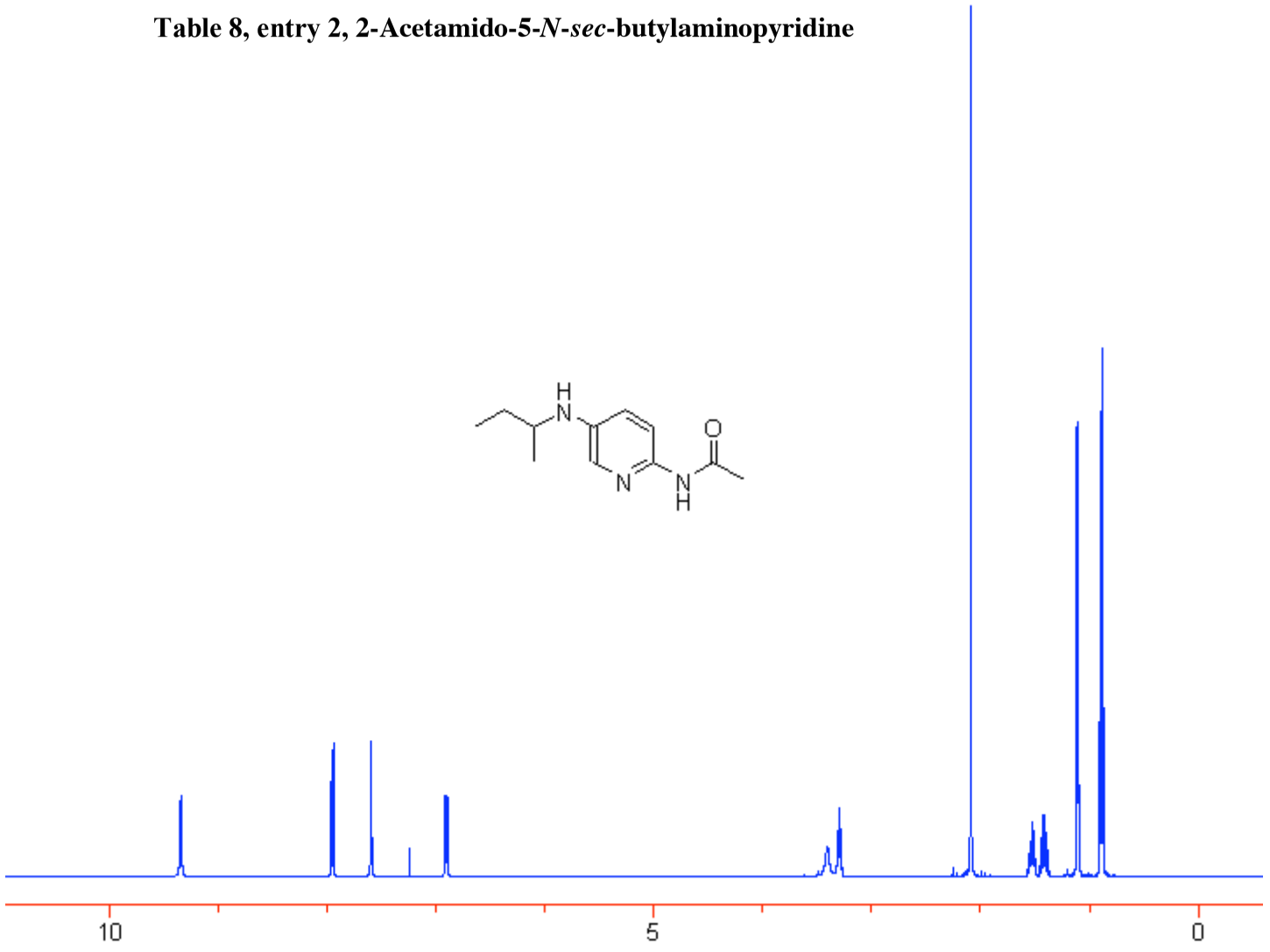


Table 8, entry 2, 2-Acetamido-5-*N*-*sec*-butylaminopyridine

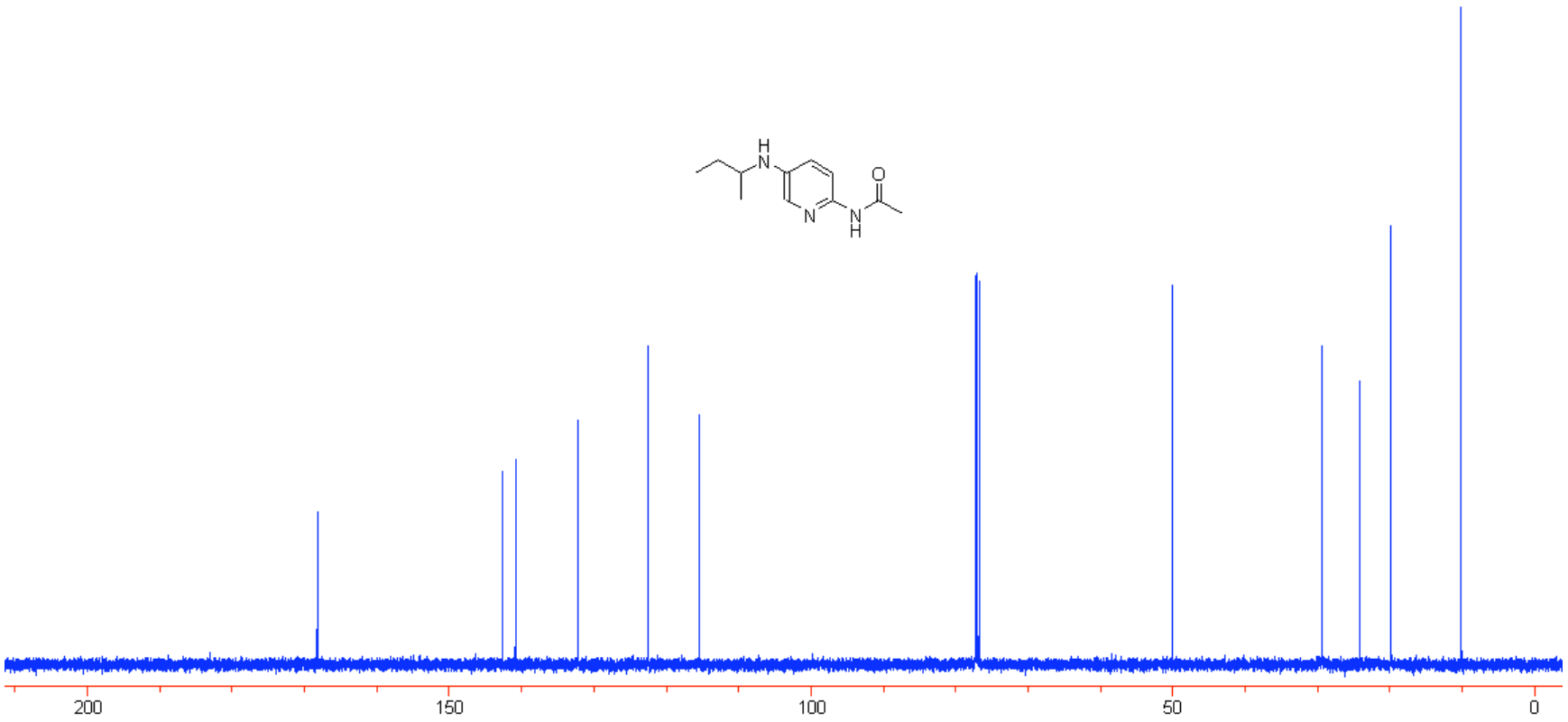


Table 8, entry 3, 5-Acetamido-2-*N*-benzylaminopyridine

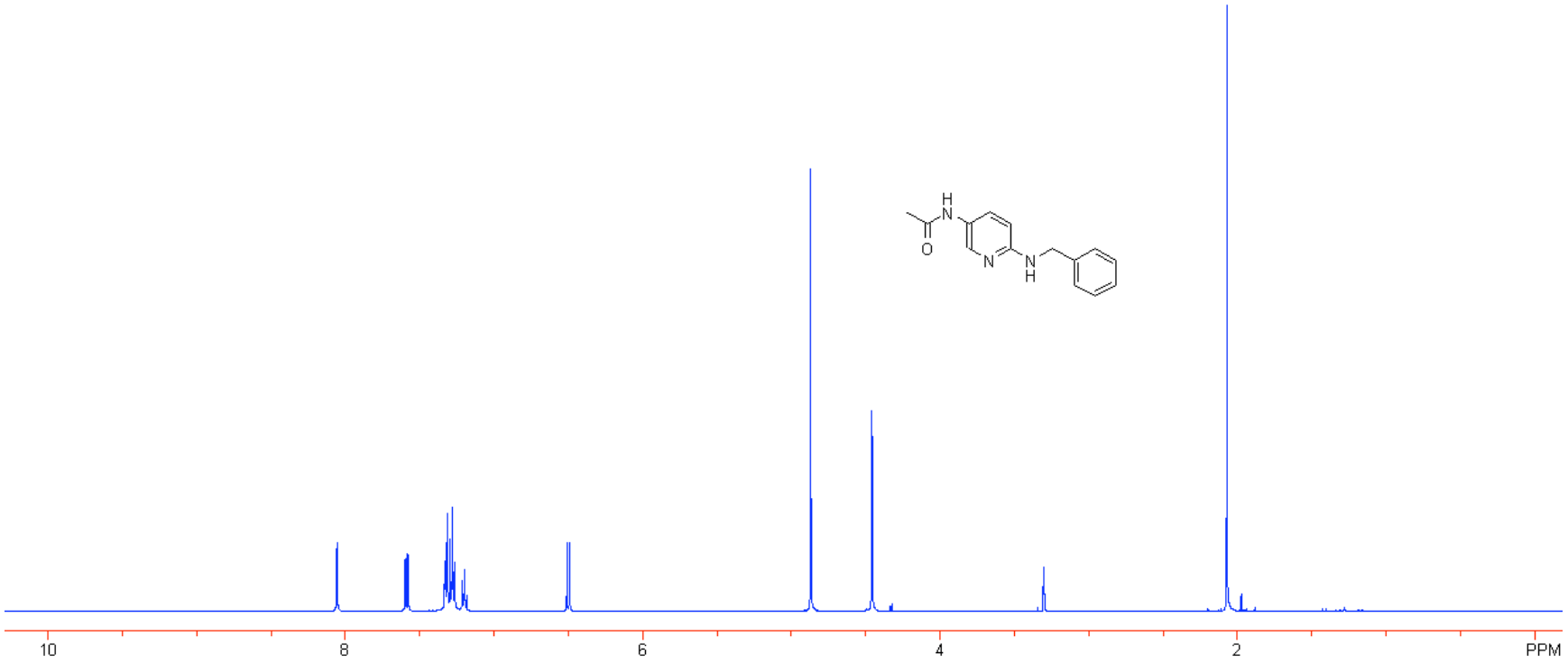


Table 8, entry 3, 5-Acetamido-2-*N*-benzylaminopyridine

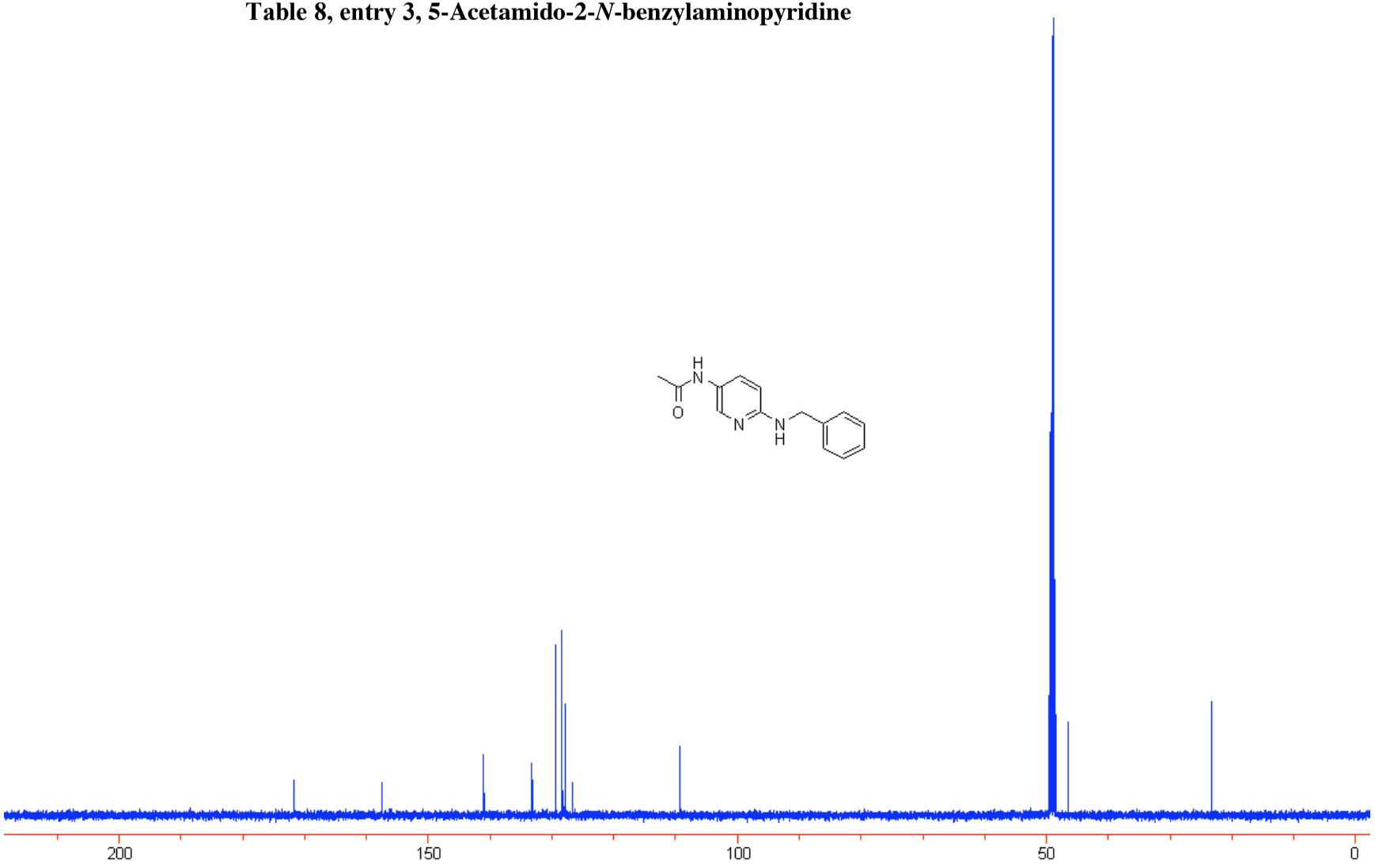


Table 8, entry 4, 5-Acetamido-2-*N*-*iso*-butylaminopyridine

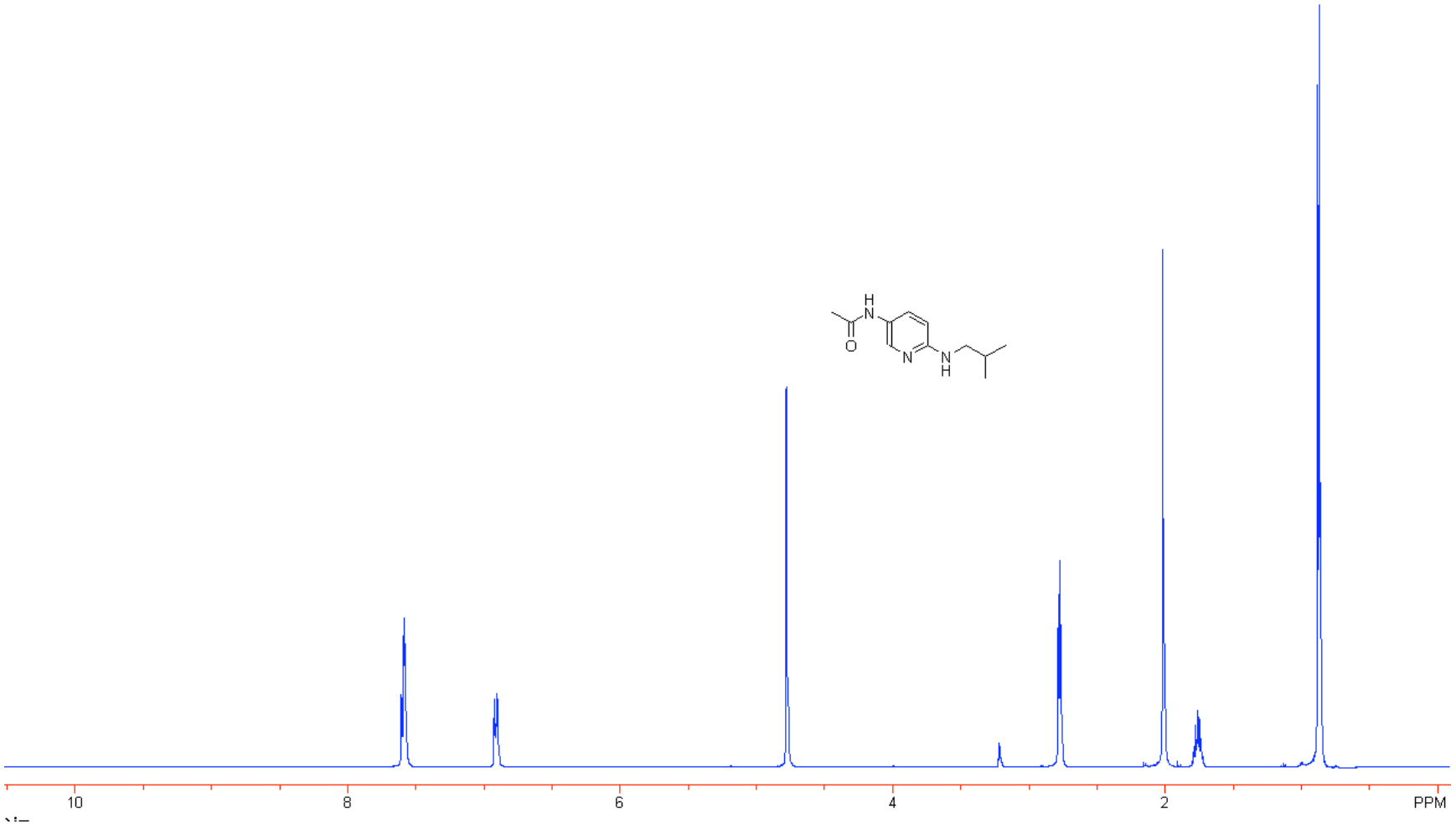


Table 8, entry 4, 5-Acetamido-2-*N*-*iso*-butylaminopyridine

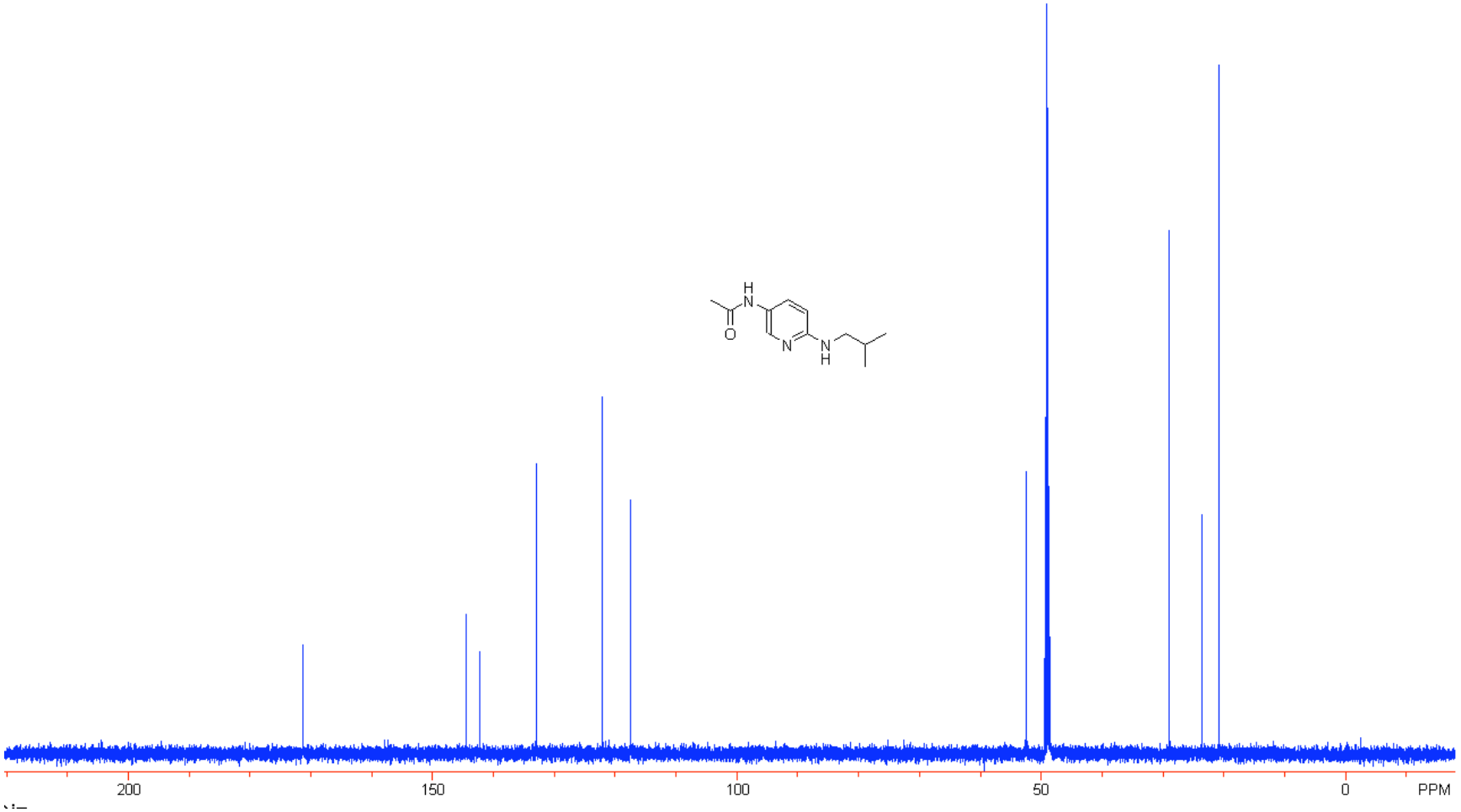


Table 8, entry 6, 3-Hydroxy-5-*N*-cyclohexylaminopyridine

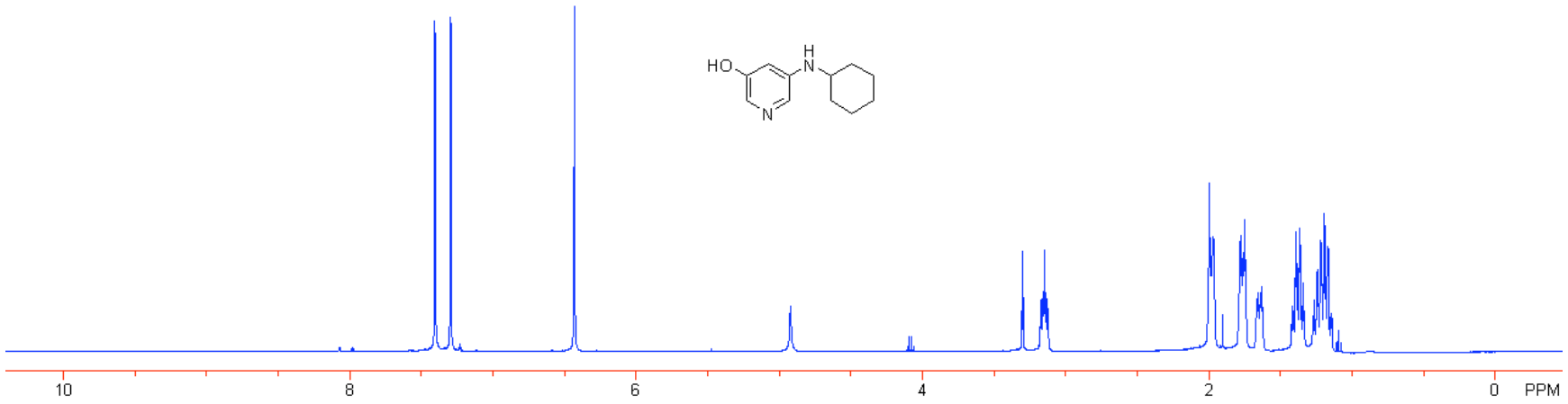


Table 8, entry 6, 3-Hydroxy-5-*N*-cyclohexylaminopyridine

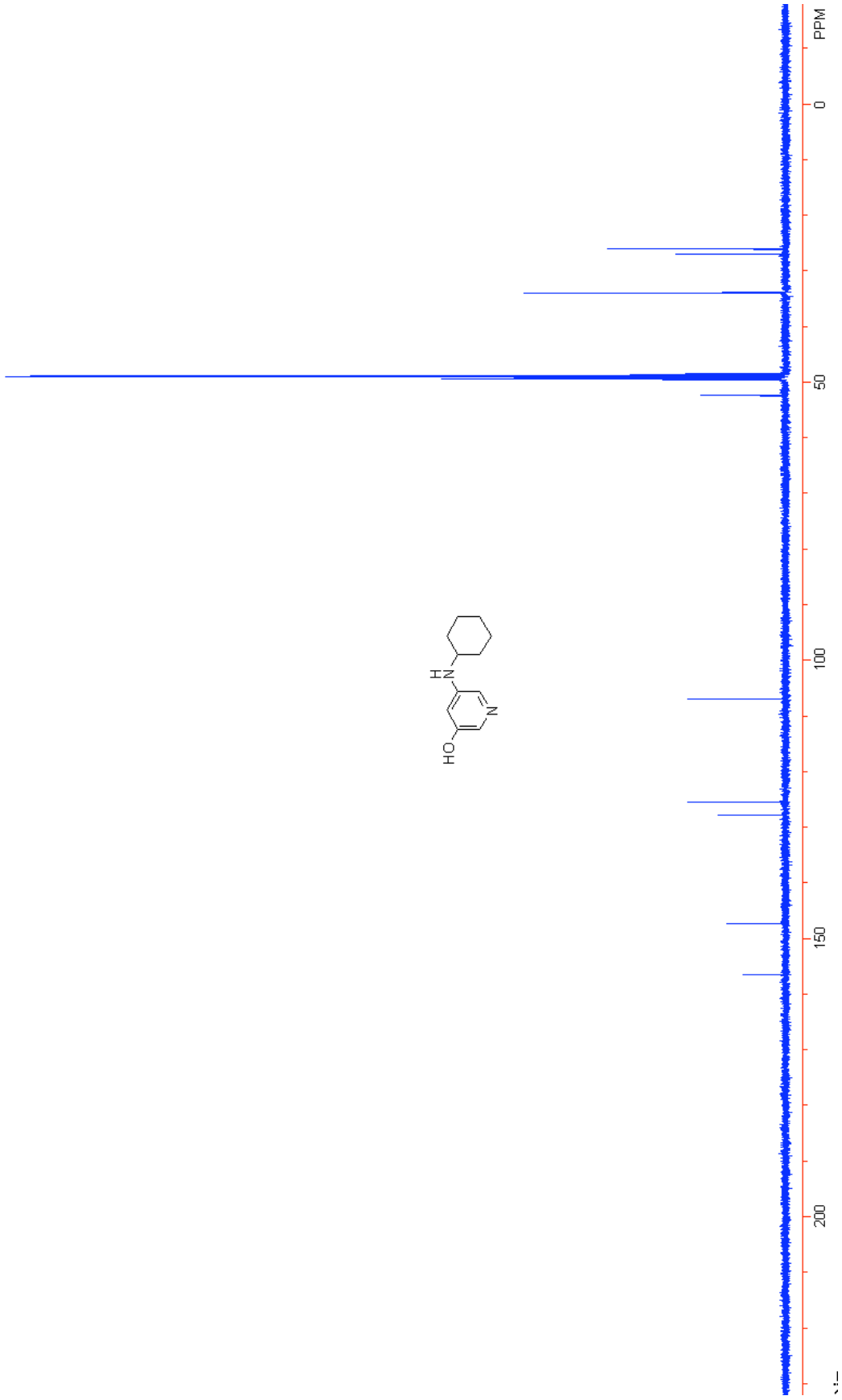


Table 9, entry 16, *N-iso*-Butylamino-benzylalcohol

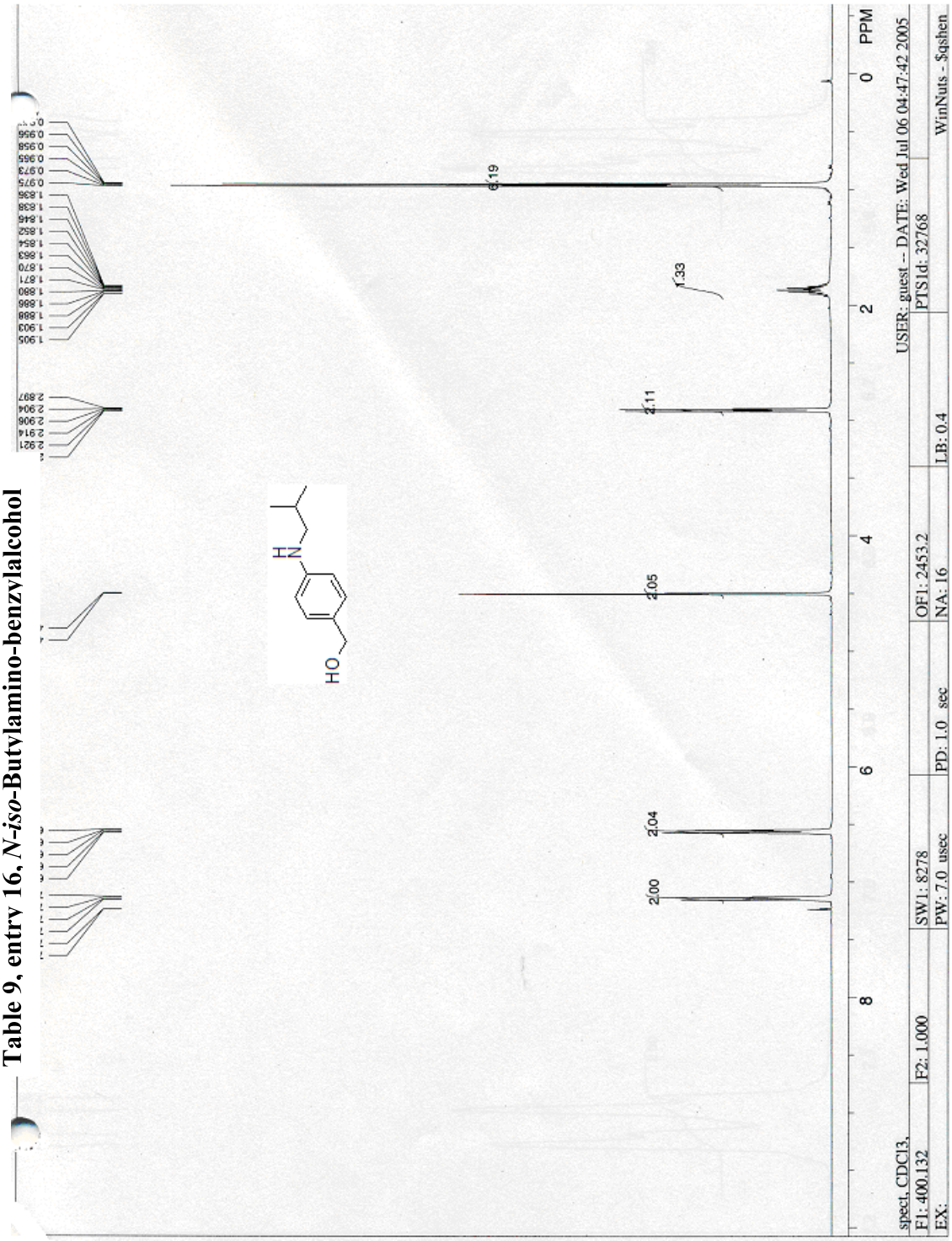


Table 9, entry 16, *N-iso*-Butylamino-benzylalcohol

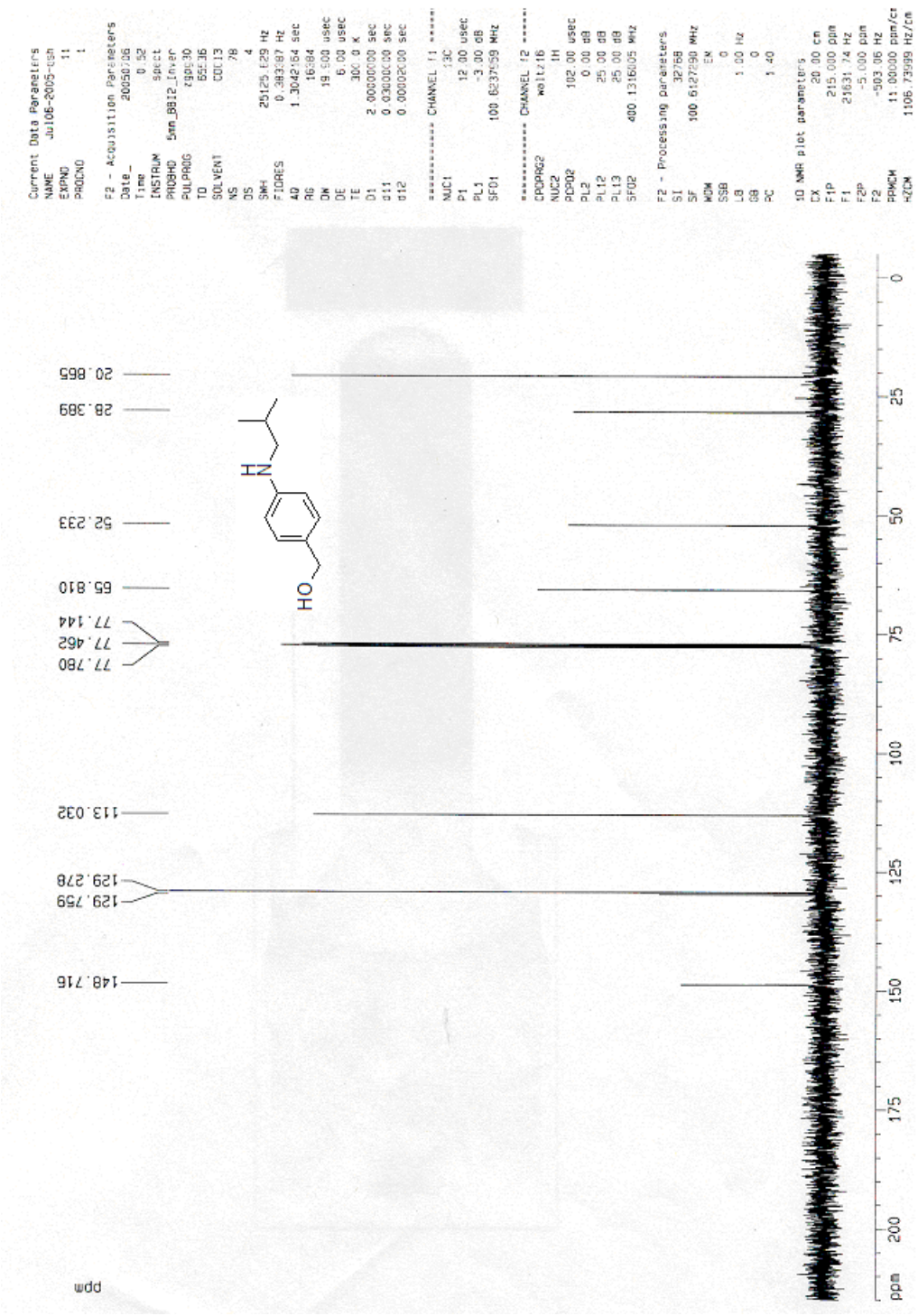


Table 9, entry 22, 3-Hydroxy-*N*-cyclohexyl-aniline

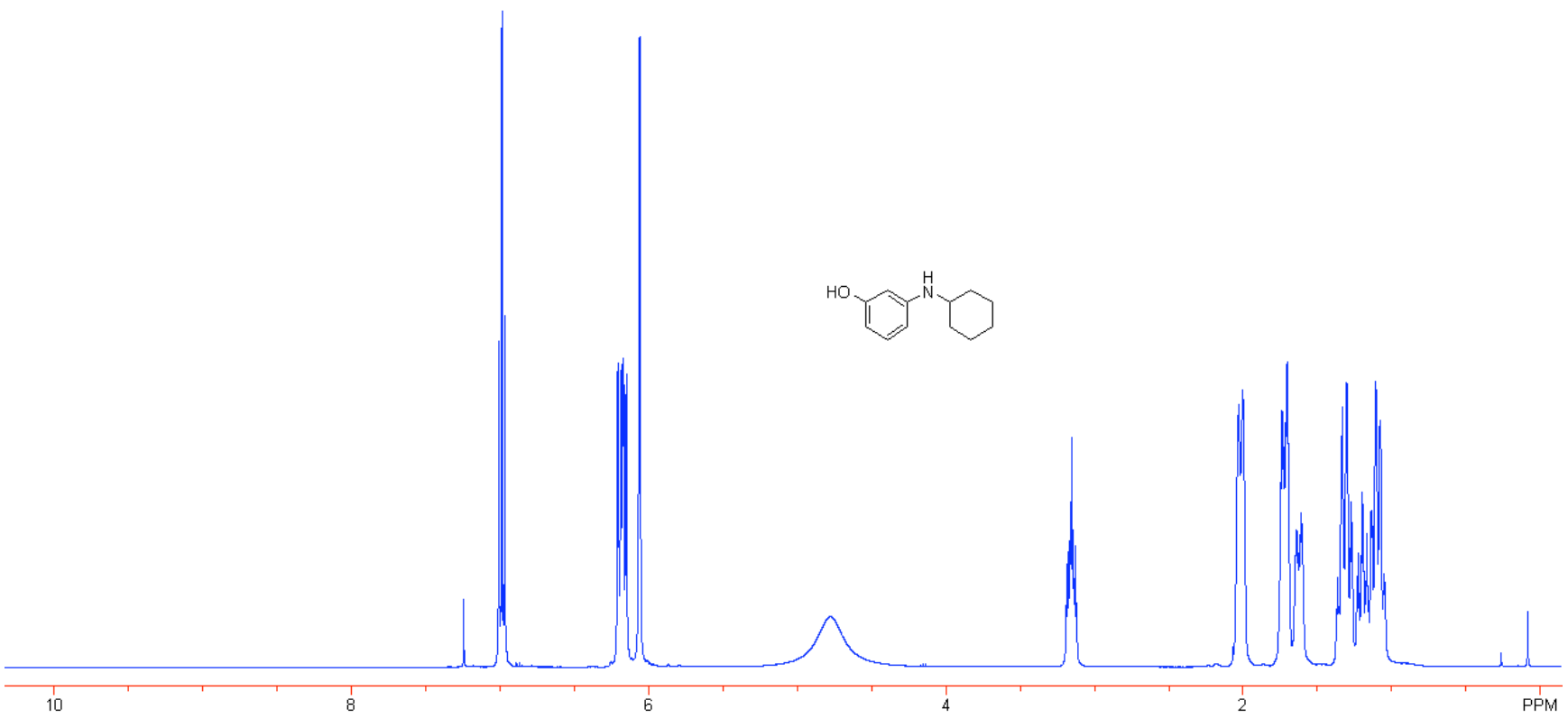


Table 9, entry 22, 3-Hydroxy-*N*-cyclohexyl-aniline

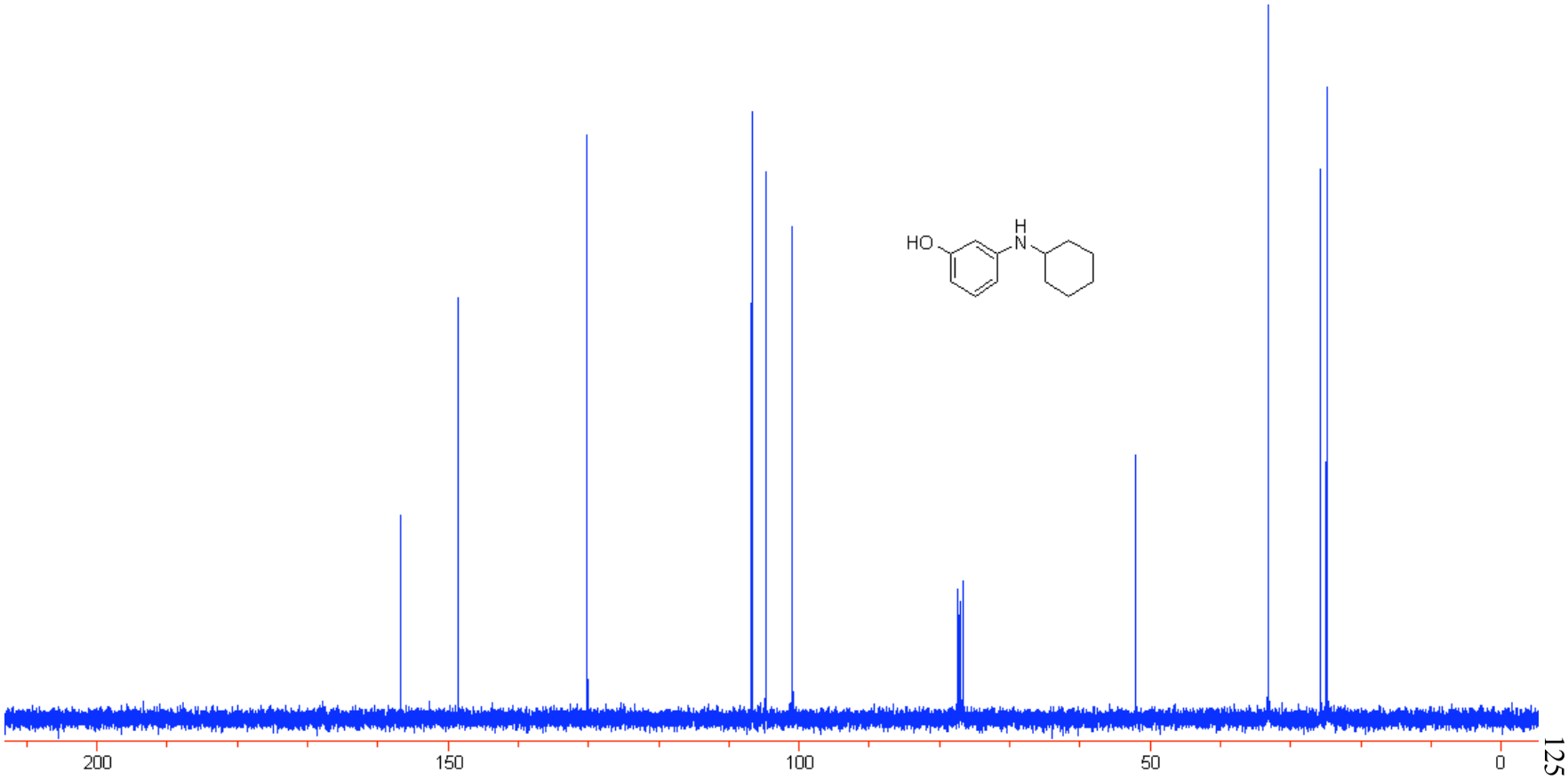


Table 9, entry 29, Methyl-2-(benzylamino)-benzoate

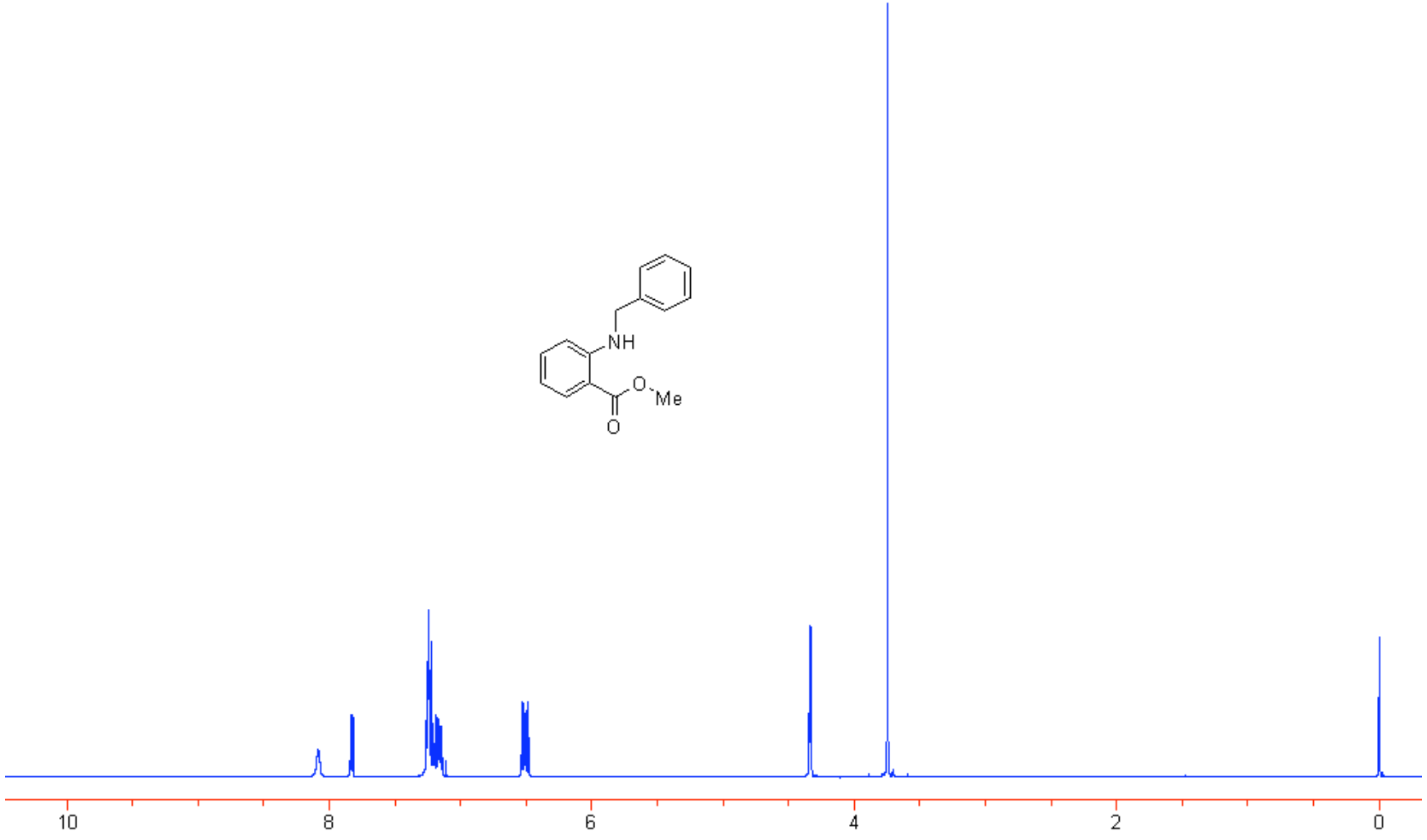
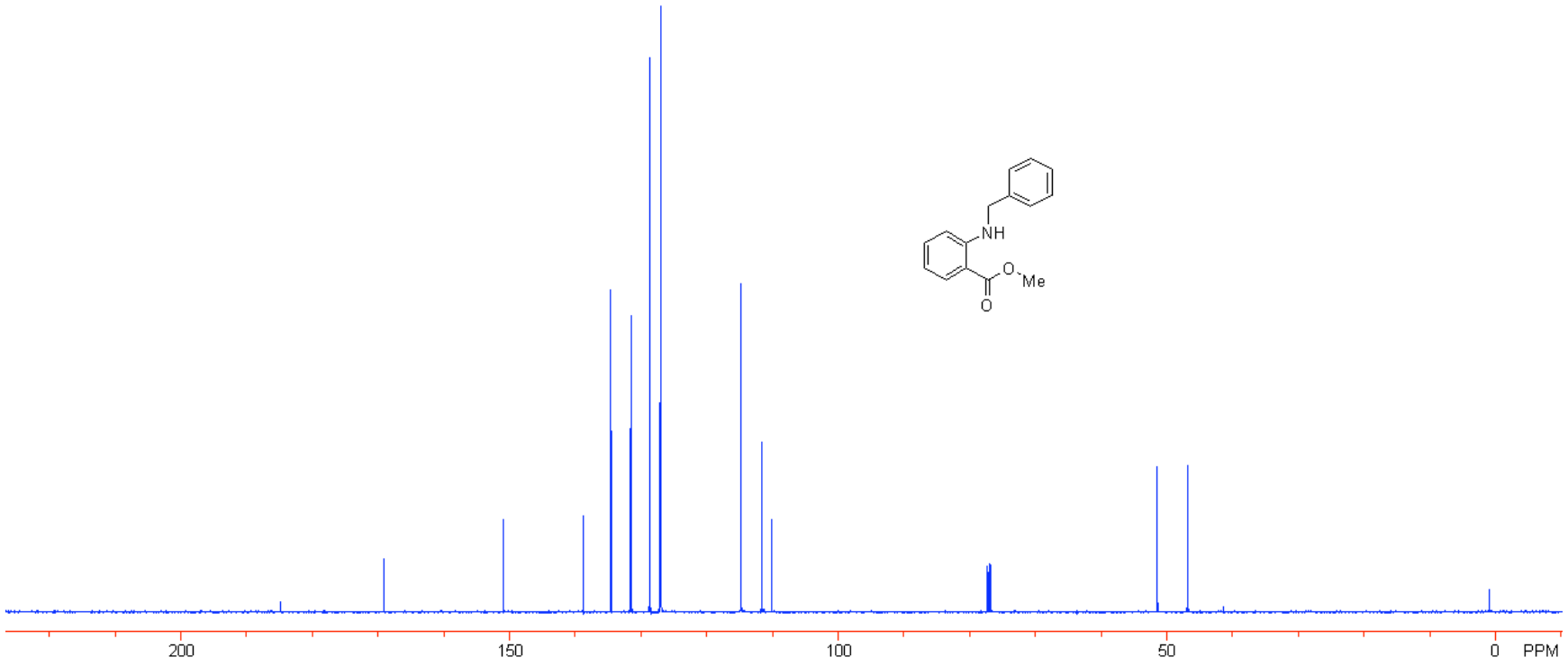
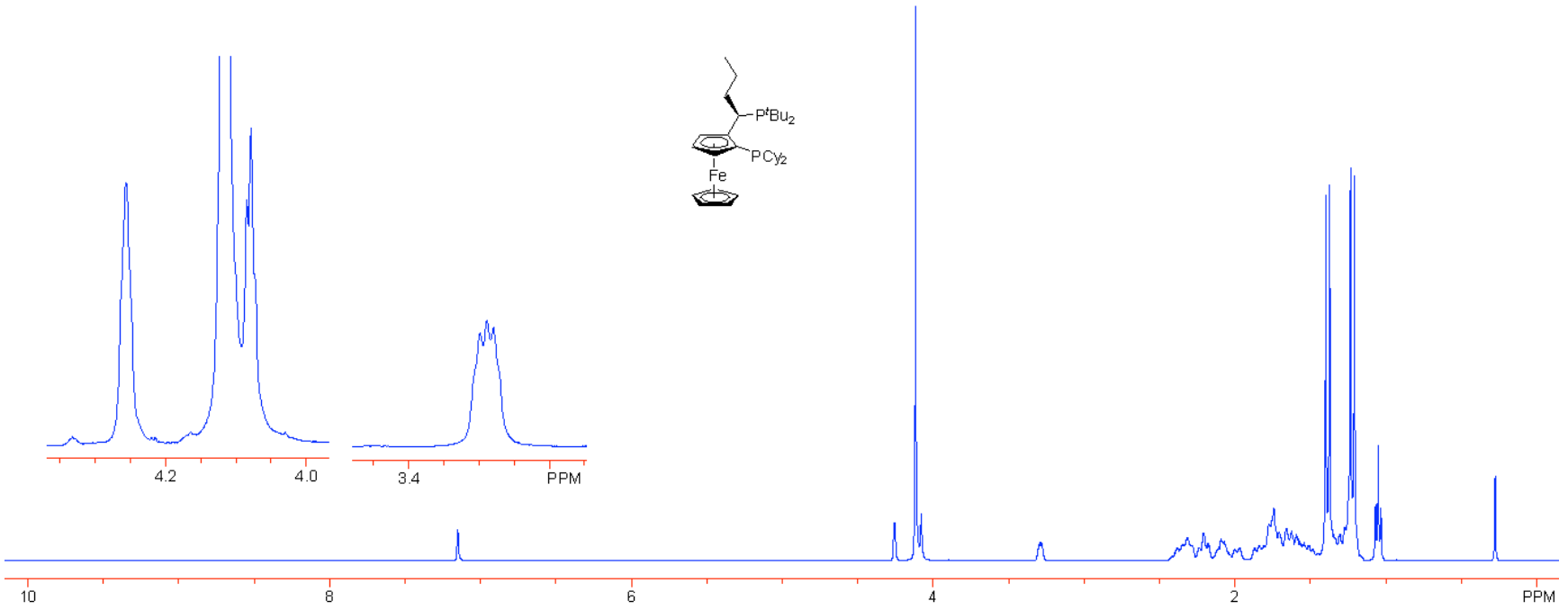


Table 9, entry 29, Methyl-2-(benzylamino)-benzoate

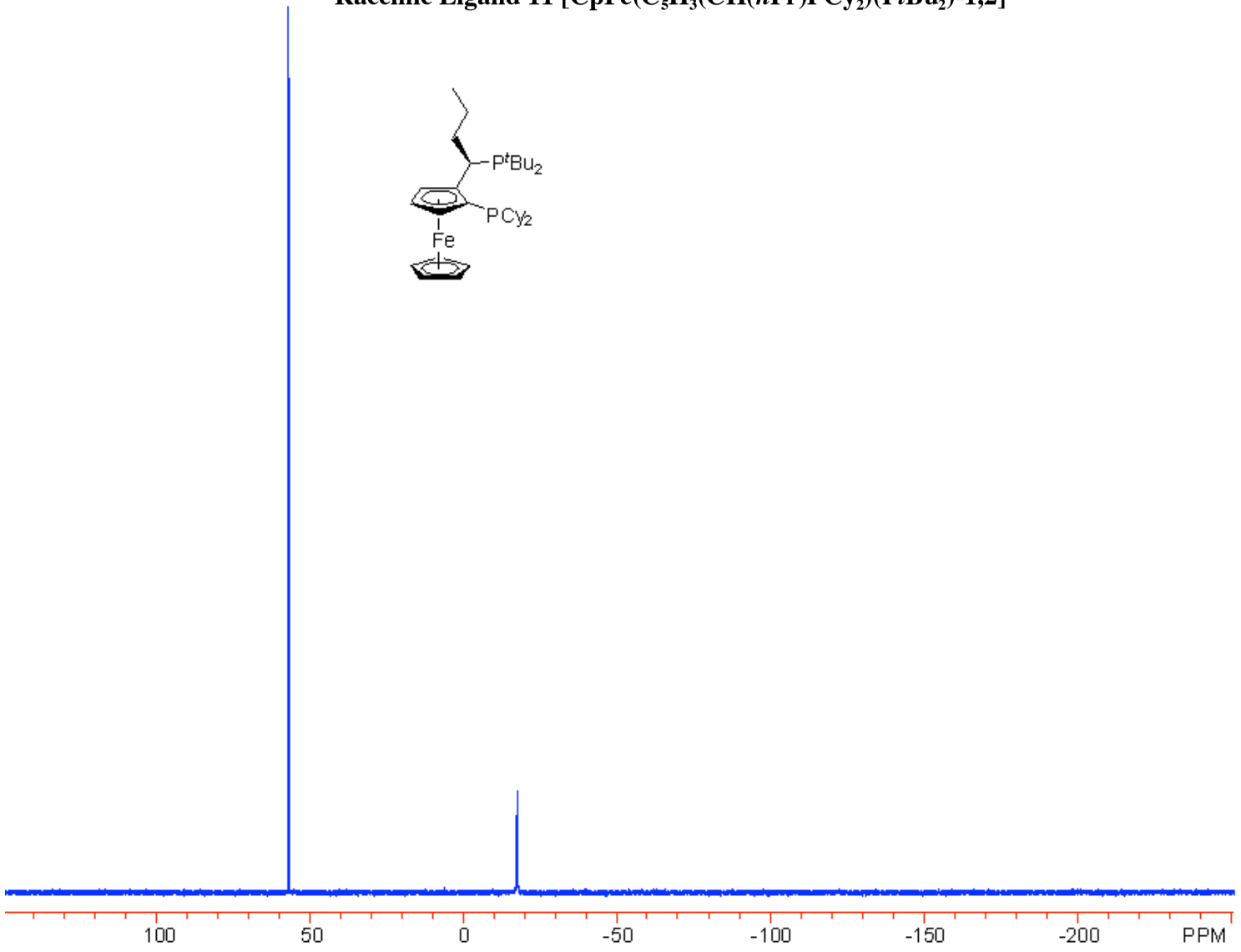


2,2_,2__-

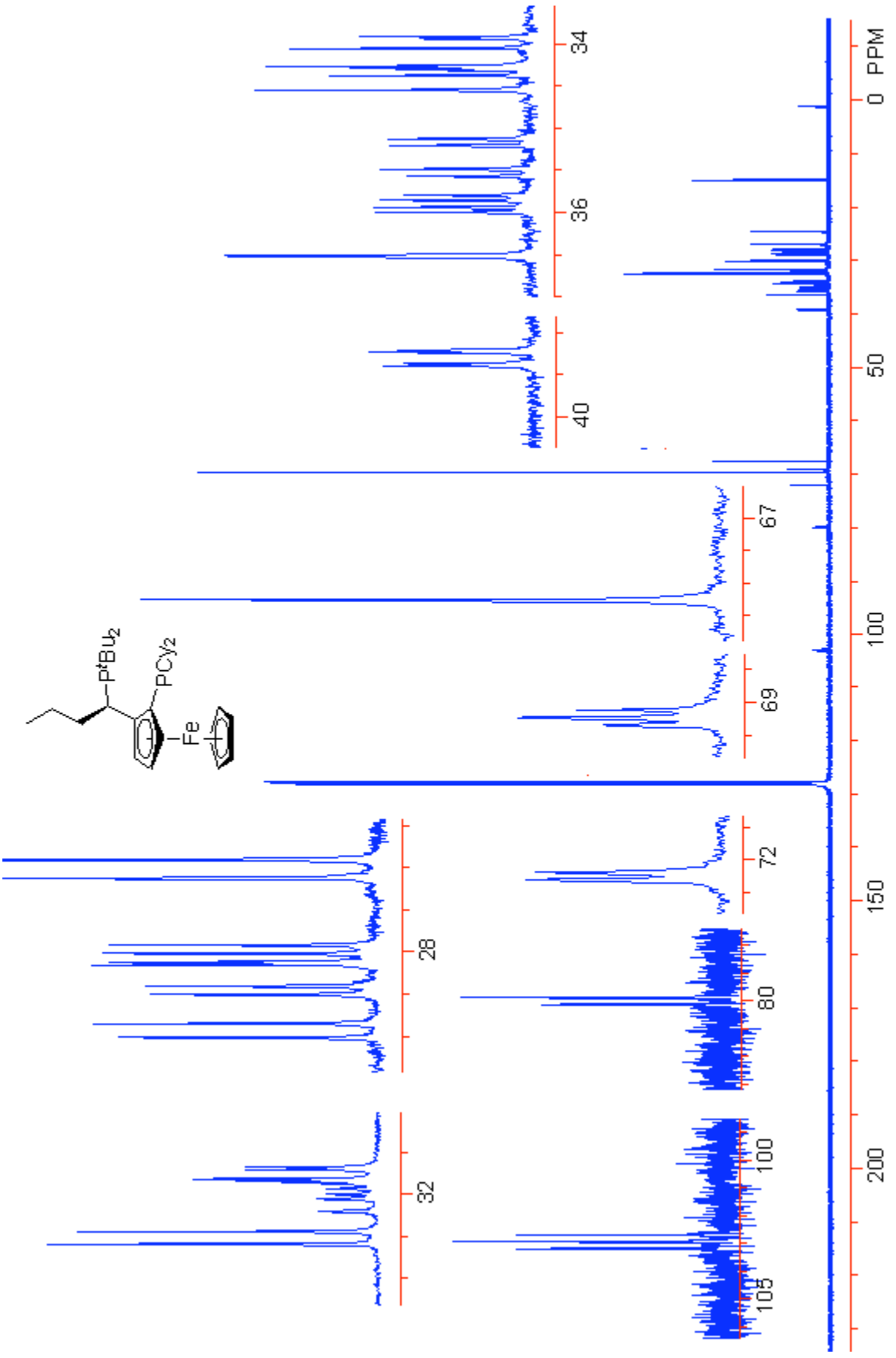
Racemic Ligand 11 [CpFe(C_5H_3(CH(*n*Pr)PCy_2)(P*t*Bu_2)-1,2]



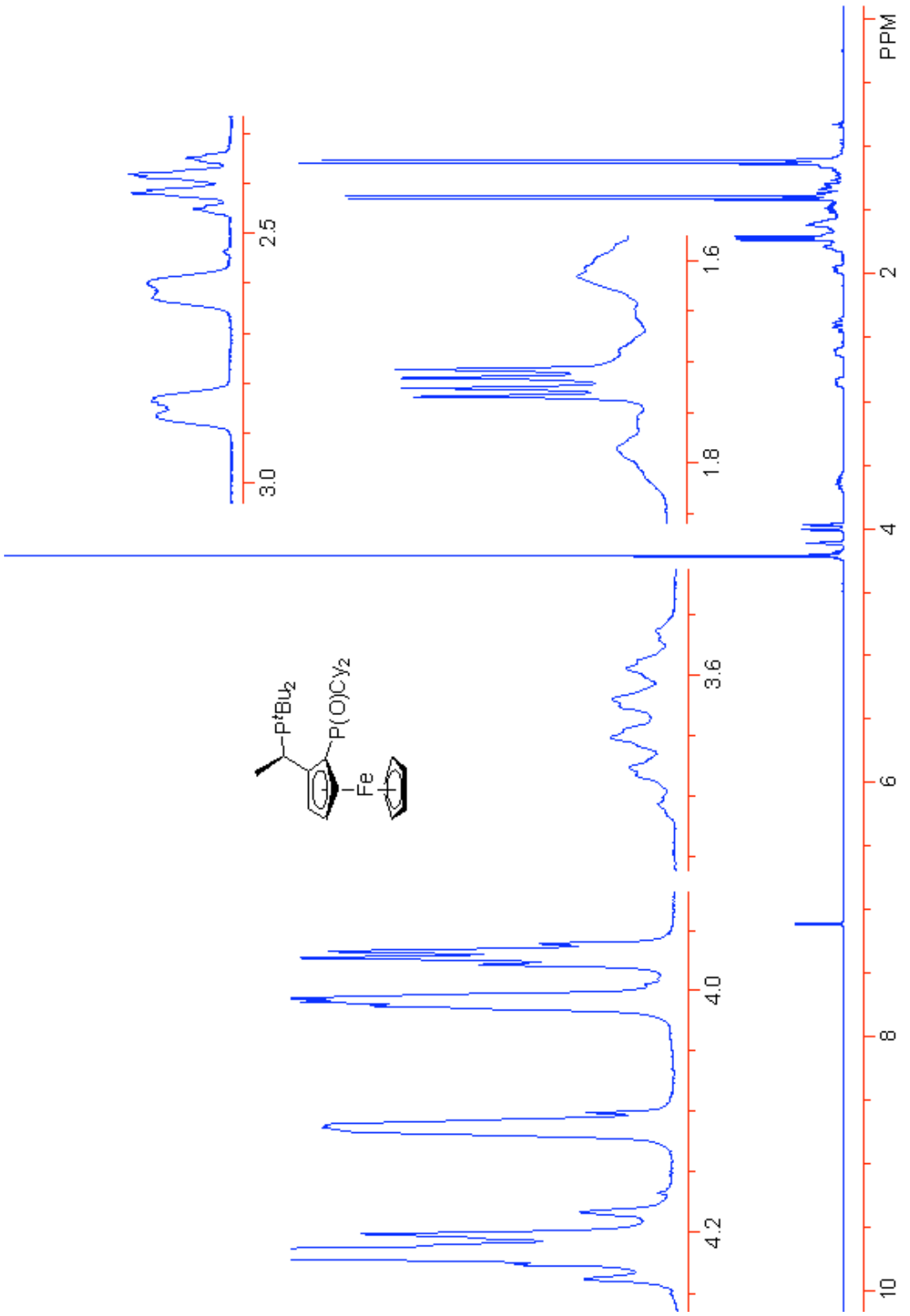
Racemic Ligand 11 [CpFe(C_5H_3(CH(*n*Pr)PCy_2)(P*t*Bu_2)-1,2]



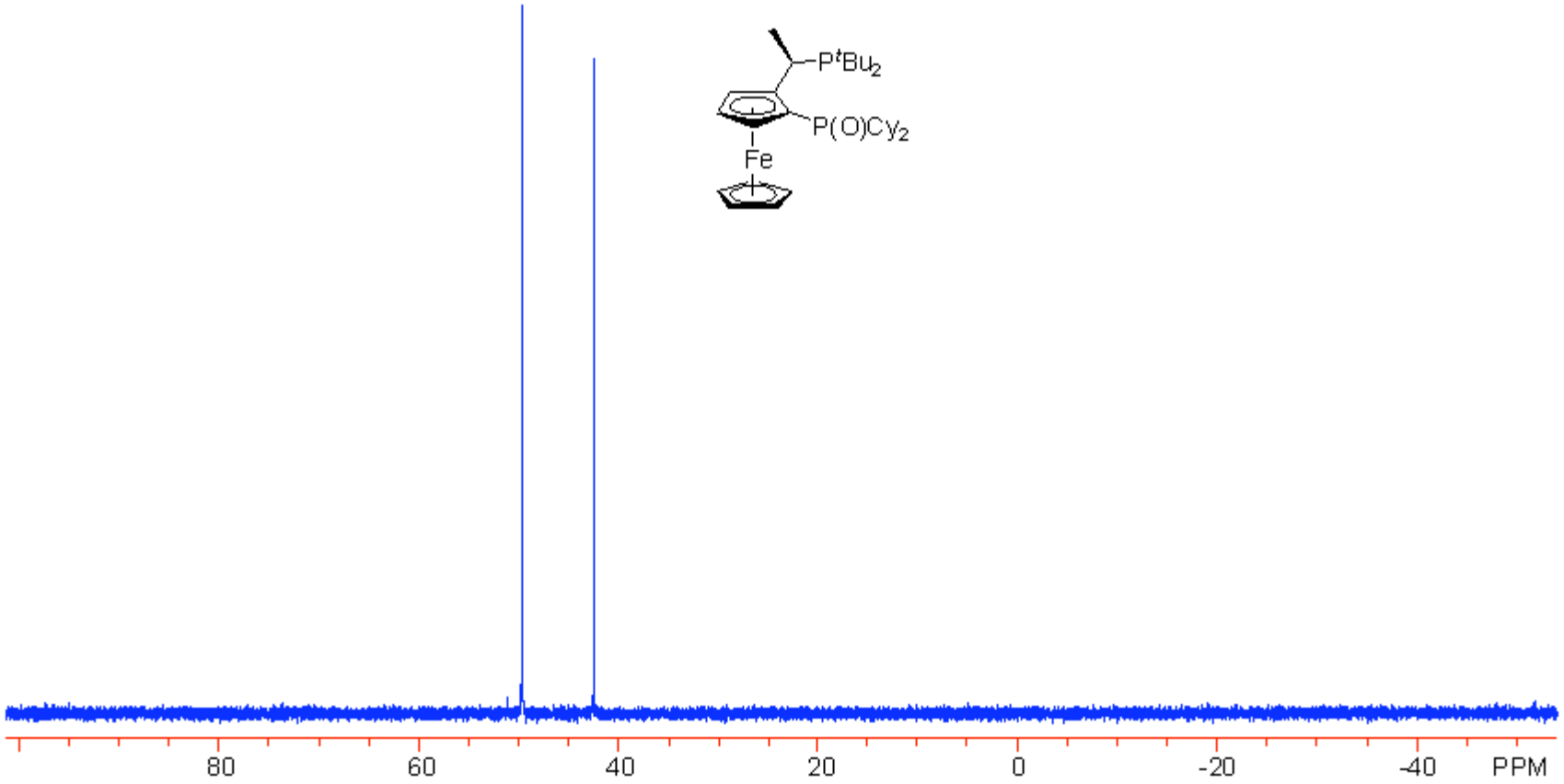
Racemic Ligand 11 [CpFe(C_5H_3(CH(*n*Pr)PCy_2)($PtBu_2$)-1,2]



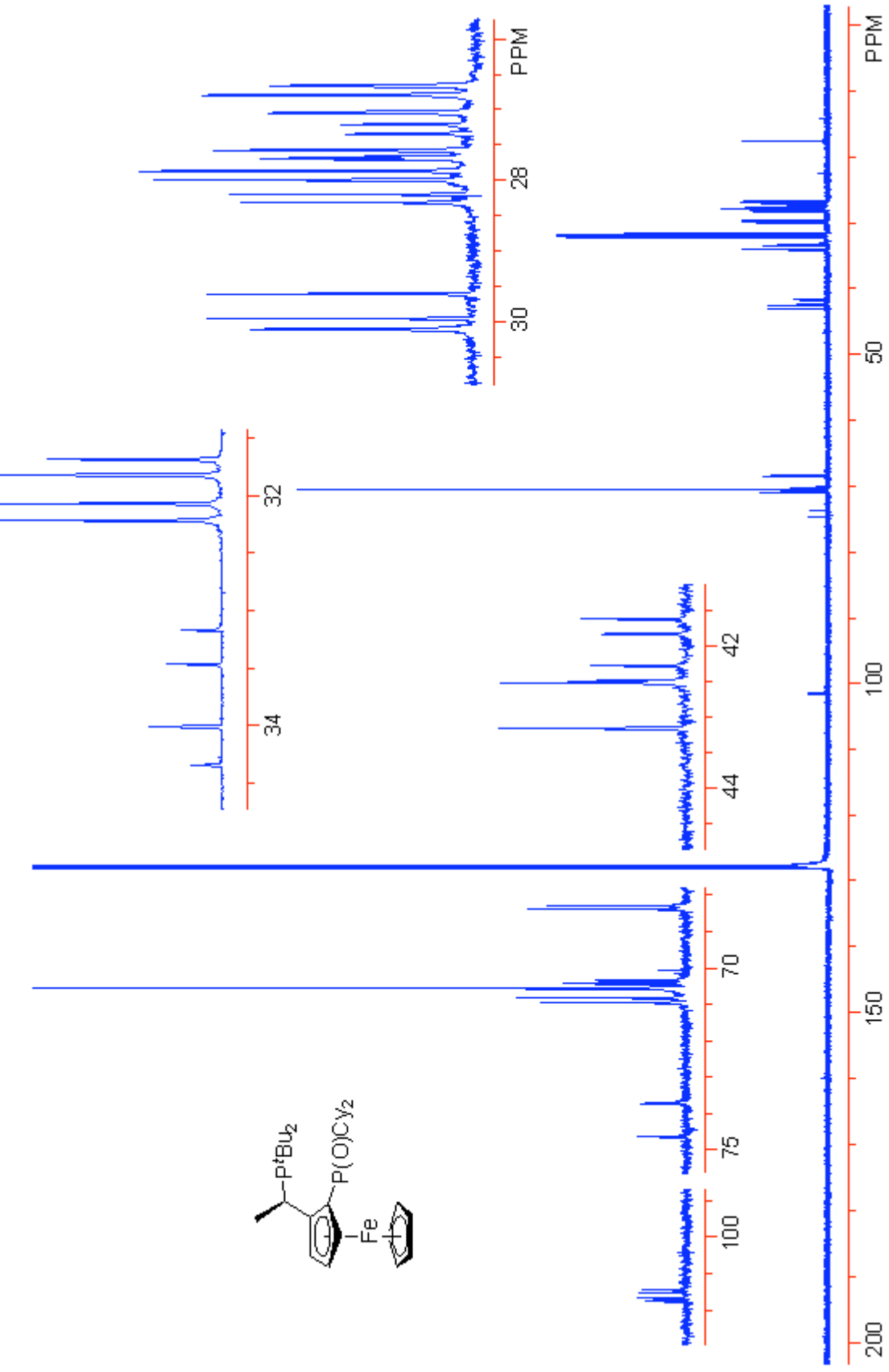
Ligand 13 [CpFe(C_5H_3(CH(Me)P(O)Cy_2)(P$t$$Bu_2$)-1,2]



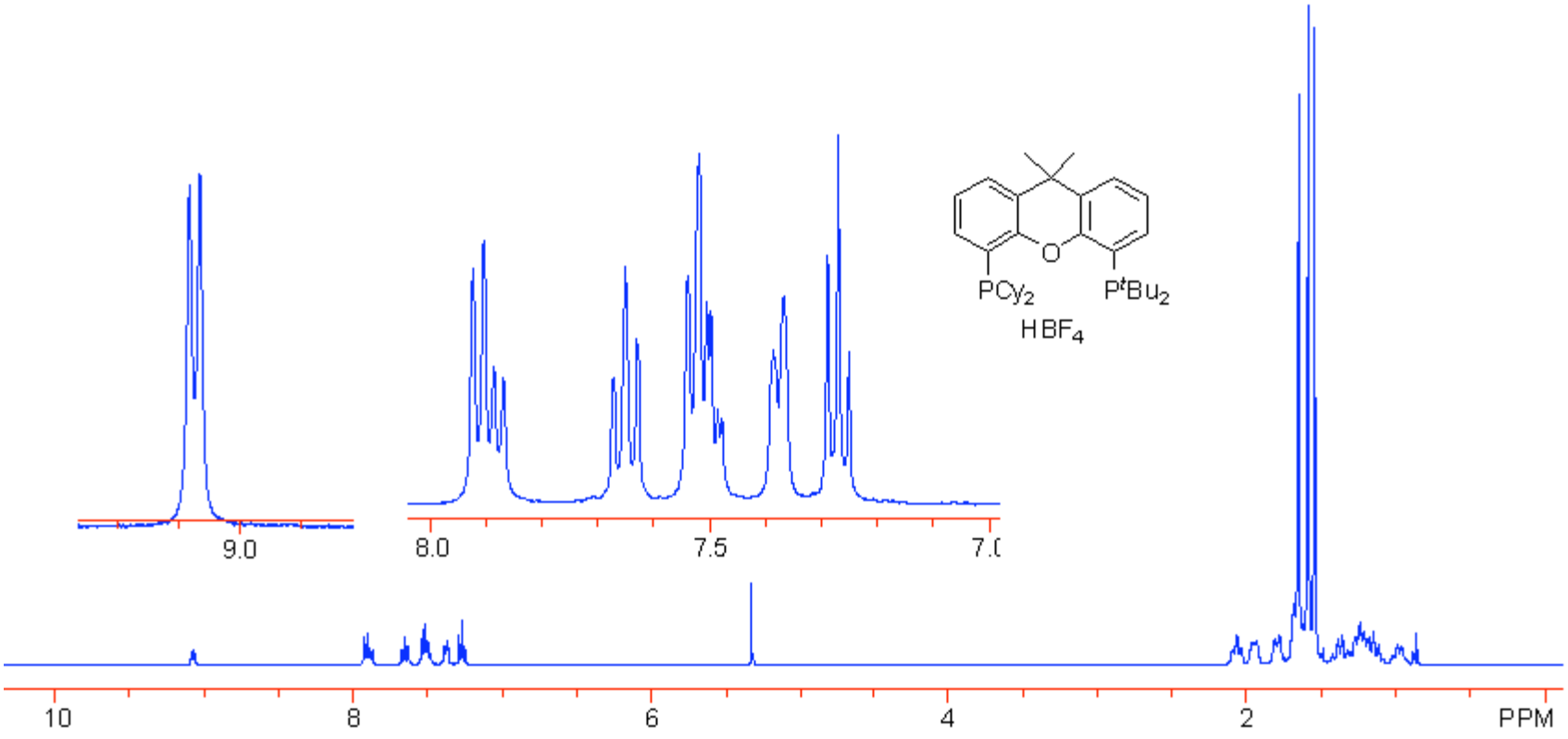
Ligand 13 [CpFe(C_5H_3(CH(Me)P(O)Cy_2)(P*t*Bu_2)-1,2]



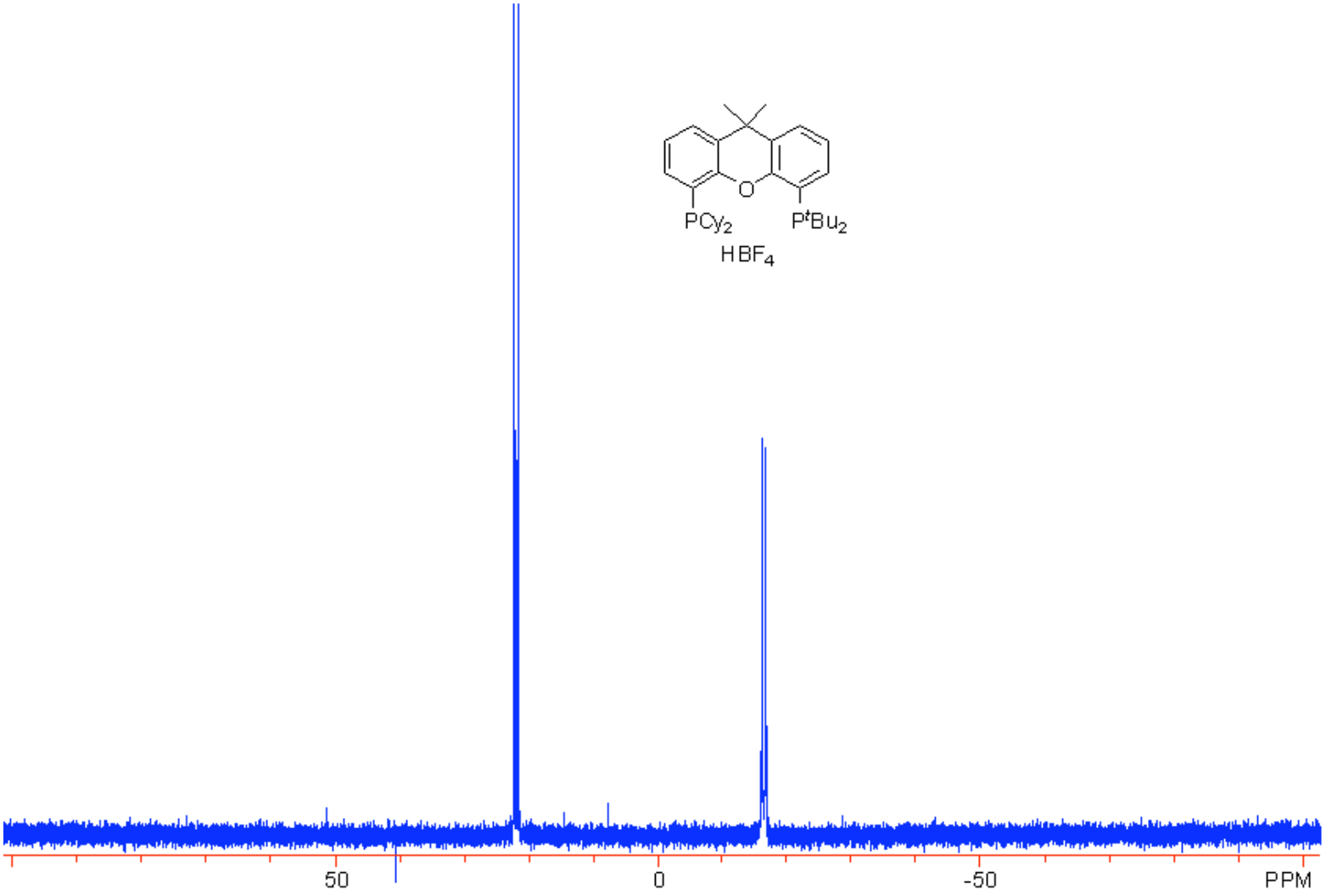
Ligand 13 [CpFe(C_5H_3(CH(Me)P(O)Cy_2)(P*t*Bu_2)-1,2]

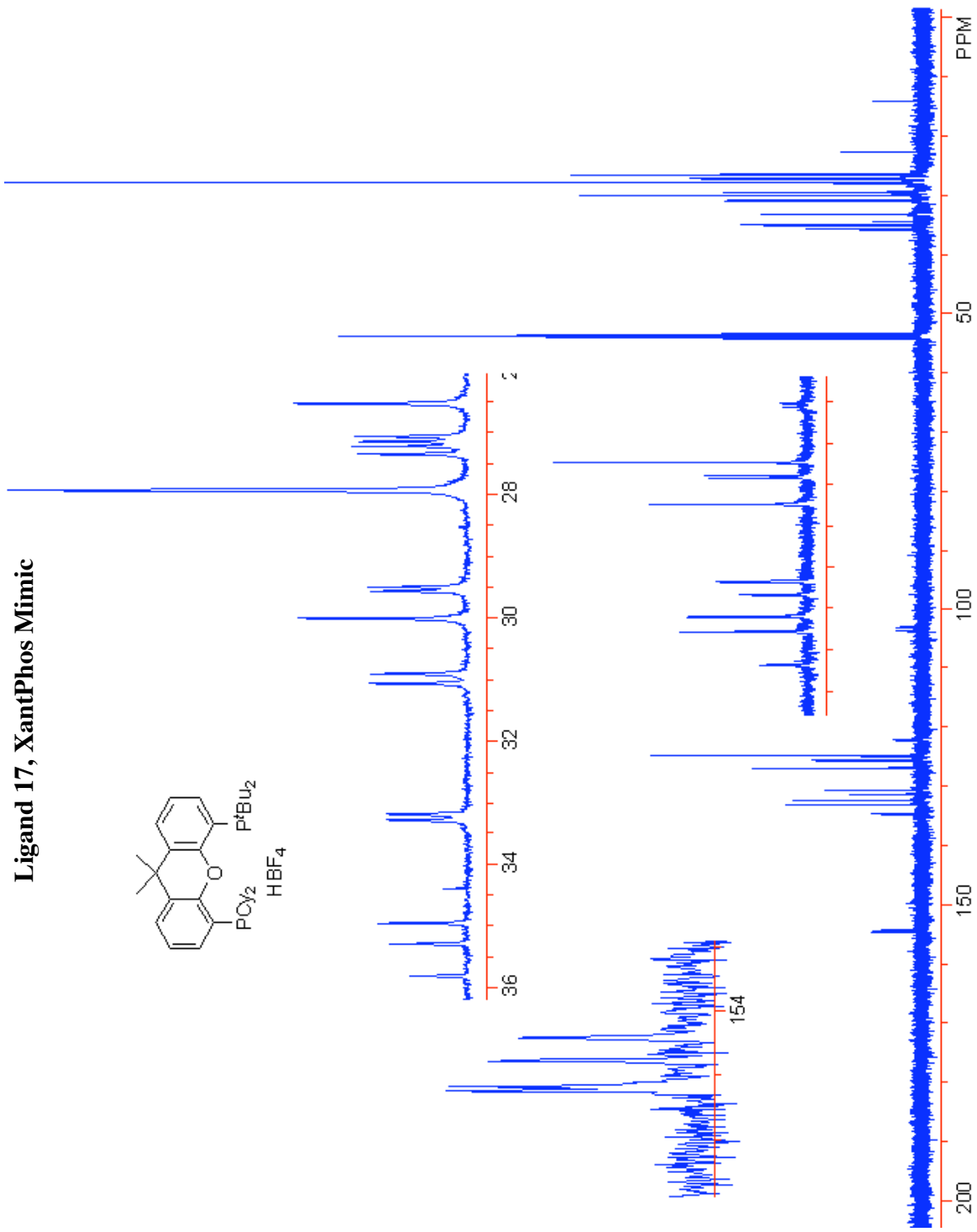


Ligand 17, XantPhos Mimic



Ligand 17, XantPhos Mimic




Ligand 17, XantPhos Mimic
PCy2
PtBu2
HBF4
O
36
34
32
30
28
154
200
150
100
50
PPM