Palladium-Catalyzed Coupling of Ammonia and Lithium Amide with Aryl Halides

Qilong Shen and John F. Hartwig*

Department of Chemistry, Yale University,
P.O. Box 208107, New Haven, Connecticut 06520-8107

Supporting Information

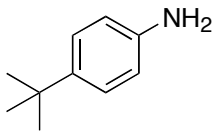
General Methods. Unless otherwise noted, all manipulation were conducted under an inert atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 or 500 MHz Spectrometer, and ^{31}P {^{1}H} NMR spectra were recorded on a General Electric QE 300 MHz spectrometer with tetramethylsilane 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. Chemical shifts downfield of the standard are reported with positive values. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA or Robertson Microlab, Inc., Madison, NJ. GC and GC/MS analyses were conducted with an HP-1 methyl silicone column. CyPF-*t*-Bu (CyPF-*t*-Bu = 1-dicyclohexylphosphino-2-di-*t*-butylphosphinoethylferrocene) and $Pd(CH_3CN)_2Cl_2$ were obtained from Solvias AG and Strem Chemicals and used without further purification. Ethylene glycol dimethyl ether (DME, 99.9% purity, HPLC grade) was purchased and used without further purification. All other chemicals were used as received from commercial sources.

Synthesis of (CyPF-*t*-Bu)$PdCl_2$. Josiphos CyPF-*t*-Bu (55.4 mg 0.100 mmol) was added to a solution of $Pd(CH_3CN)_2Cl_2$ (26.0 mg, 0.100 mmol) in CH_2Cl_2 (5.0 mL). The resulting mixture was stirred for 30 min at room temperature. The reaction mixture was filtered through a medium fritted funnel containing Celite. The resulting solution was concentrated under vacuum. Crystalline material was obtained by layering with hexane and cooling at -10 °C (65.0 mg, 90%). ^{1}H NMR ($CDCl_3$) δ 4.85 (s, 1 H), 4.55 (s, 1 H), 4.53 (s, 1 H), 4.25 (s, 5 H), 3.60-3.75 (m, 1 H), 3.00-3.10 (m, 1 H), 2.50-2.60 (m, 1 H), 2.27-2.90 (m, 1 H), 2.13-2.25 (m, 2 H), 2.00-2.10 (m, 1 H), 1.97 (dd, *J* = 9.0, 7.5 Hz, 3 H), 1.70-1.95 (m, 4 H), 1.20-1.30 (m, 8 H), 1.63 (d, *J* = 13.0 Hz, 9 H), 1.30-1.45 (m, 4 H), 1.23 (d, *J* = 14.5 Hz, 9 H); ^{31}P {^{1}H] NMR (CH_2Cl_2) δ 113.83 (d, *J* = 9.7 Hz), 31.78 (d, *J* = 9.7 Hz); ^{13}C NMR ($CDCl_3$) δ 96.49 (dd, *J* = 13.3, 5.5 Hz), 71.92 (d, *J* = 2.5 Hz), 69.90 (d, *J* = 9.1 Hz), 69.78, 69.63 (d, *J* = 9.2 Hz), 69.34 (t, *J* = 5.7 Hz), 41.6 (d, *J* = 35.5 Hz), 41.57 (d, *J* = 8.2 Hz), 40.55 (d, *J* = 11.2 Hz), 37.56 (d, *J* = 35.5 Hz), 34.48 (t, *J* = 9.1 Hz), 31.97 (d, *J* = 1.9 Hz), 31.05 (d, *J* = 1.9 Hz), 29.99, 29.19, 28.06, 27.55 (d, *J* = 6.8 Hz), 27.32 (d, *J* = 10.2 Hz), 26.98 (d, *J* = 12.6 Hz), 26.89 (d, *J* = 5.2 Hz), 26.78 (d, *J* = 3.8 Hz), 26.12 (d, *J* = 1.9 Hz), 25.55, 18.02 (d, *J* = 6.7 Hz). Anal. Calcd. For $C_{32}H_{52}Cl_2FeP_2Pd$: C, 52.51; H, 7.16. Found: C, 52.72; H, 7.38.

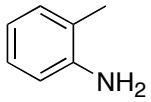
General Procedure for Catalytic Amination of Heteroaryl and Aryl Chlorides, Bromides and Iodides with Ammonia in a Parr Bomb. The reaction conditions and average yields for each reaction are shown in Table 1. A typical procedure is given for the first entry in Table 1.

4-*tert*-butylaniline (Table 1, entry 1). (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00×10^{-2} mmol), NaO*t*Bu (0.192 g, 2.00 mmol) and 4-*tert*-butyl-1-bromobenzene (0.213 g, 1.00 mmol)

were weighed into a Parr Bomb inside a dry box. DME (20.0 mL) was then added. The Parr bomb was closed and removed from the dry box. Ammonia was added with stirring by connecting to an ammonia tank and maintaining the pressure at 80 psi for 30 min. The resulting reaction mixture was allowed to stir for 24 h at 90 °C. Pressure was built up to 200 psi during the reaction. The reaction mixture was then cooled to room temperature before being poured into ice water (20.0 mL). To this mixture was added HCl aqueous solution (10.0 mL, 1.0 M)). The mixture was stirred at room temperature for 5 min and was then neutralized with a saturated solution of $NaHCO_3$ (5.00-10.0 mL). After extraction with CH_2Cl_2 (3 × 20.0 mL), the organic layer was separated and dried over $MgSO_4$. The solvent was evaporated, and the crude product isolated by eluting with hexane/ethyl acetate (70/30) to give 128.1 mg (86%) of 4-*tert*-butylaniline as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.05 (d, J = 8.4 Hz, 2 H), 6.55 (d, J = 8.8 Hz, 2 H), 3.44 (s, br, 2 H), 1.20 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 143.74, 141.32, 125.98, 114.86, 33.85, 31.49.



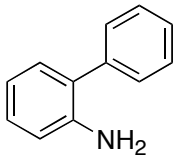
***o*-Toluidine (Table 1, entry 3).** 2-Chlorotoluene (0.126 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00 × 10^{-2} mmol), and NaO*t*Bu (0.192 g, 2.00 mmol) in 20.0 mL DME gave 73.6 mg (69%) of *o*-toluidine as a colorless liquid (hexane/ethyl acetate: 70/30). ^{1}H NMR ($CDCl_3$) δ 7.08 (d, J = 6.4 Hz, 1 H), 7.07 (t, J = 6.4 Hz, 1 H), 6.74 (t, J = 6.0 Hz, 1 H), 6.70 (d, J = 6.0 Hz, 1 H), 3.62 (s, br, 2 H), 2.19 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 144.41, 130.36, 126.87, 122.26, 118.57, 114.88, 17.25.



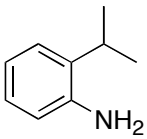
***o*-Toluidine (Table 1, entry 4).** 2-Bromotoluene (0.171 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00 × 10^{-2} mmol), and NaO*t*Bu (0.192 g, 2.00 mmol) in 20.0 mL DME gave 89.1 mg (86%) of *o*-toluidine as a colorless liquid.

***o*-Toluidine (Table 1, entry 5).** 2-Iodotoluene (0.217 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00 × 10^{-2} mmol), and NaO*t*Bu (0.192 g, 2.00 mmol) in 20.0 mL DME gave 84.7 mg (79%) of *o*-toluidine as a colorless liquid.

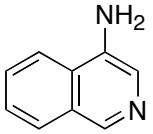
2-Aminobiphenyl (Table 1, entry 6). 2-Bromobiphenyl (0.233 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00 × 10^{-2} mmol), and NaO*t*Bu (0.192 g, 2.00 mmol) in 20.0 mL DME gave 0.160 g (94%) of 2-aminobiphenyl as a solid (hexane/ethyl acetate: 70/30). ^{1}H NMR ($CDCl_3$) δ 7.28-7.34 (m, 4 H), 7.19-7.25 (m, 1 H), 6.98-7.07 (m, 2H), 6.71 (t, J = 7.2 Hz, 1 H), 6.62 (d, J = 8.0 Hz, 1 H), 3.60 (s, br, 2 H); ^{13}C NMR ($CDCl_3$) δ 140.40, 139.44, 130.36, 129.00, 128.71, 128.41, 127.52, 127.06, 118.54, 115.50.



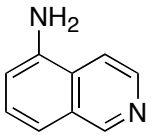
2-*iso*-Propylaniline (Table 1, entry 7). 1-Bromo-2-*iso*-propylbenzene (0.199 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00×10^{-2} mmol), and NaO*t*Bu (0.192 g, 2.00 mmol) in 4.0 mL DME gave 0.120 g (89%) of 2-*iso*-propylaniline as a solid (hexane/ethyl acetate: 70/30). ^{1}H NMR ($CDCl_3$) δ 7.08 (dd, J = 6.0, 1.2 Hz, 1 H), 6.96 (td, J = 6.0, 1.2 Hz, 1 H), 6.73 (td, J = 6.0, 0.8 Hz, 1 H), 6.60 (dd, J = 6.0, 1.2 Hz, 1 H), 3.56 (s, br, 2 H), 2.83 (sept, J = 5.2 Hz, 1 H), 1.20 (J = 5.2 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 143.22, 132.55, 126.44, 125.30, 118.92, 115.74, 27.56, 22.20.



4-Amino-*iso*-quinoline (Table 1, entry 8). 4-Bromo-*iso*-quinoline (0.208 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00×10^{-2} mmol), and NaO*t*Bu (0.192 g, 2.00 mmol) in 20.0 mL DME gave 0.115 g (80%) of 4-amino-*iso*-quinoline as a solid Ethyl acetate/methanol: 50/50). ^{1}H NMR ($CDCl_3$) δ 8.70 (s, 1 H), 8.00 (s, 1 H), 7.84 (d, J = 8.0 Hz, 1 H), 7.76 (d, J = 8.5 Hz, 1 H), 7.58 (dd, J = 8.0, 7.0 Hz, 1 H), 7.51 (dd, J = 8.0, 7.5 Hz, 1 H), 4.21 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 142.99, 136.86, 128.86, 128.54, 127.99, 127.65, 126.93, 125.95, 119.97.

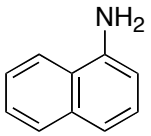


5-Amino-*iso*-quinoline (Table 1, entry 9). 5-Bromo-*iso*-quinoline (0.208 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00×10^{-2} mmol), and NaO*t*Bu (0.192 g, 2.00 mmol) in 4.0 mL DME gave 0.101 g (70%) of 5-Amino-*iso*-quinoline as a solid (Ethyl acetate/methanol: 90/10). ^{1}H NMR ($CDCl_3$) δ 9.15 (s, 1 H), 8.45 (d, J = 5.6 Hz, 1 H), 7.55 (d, J = 6.0 Hz, 1 H), 7.37 (d, J = 5.2 Hz, 2 H), 6.91 (t, J = 4.8 Hz, 1 H), 4.26 (s, br, 2 H); ^{13}C NMR ($CDCl_3$) δ 152.85, 141.88, 141.30, 129.33, 127.72, 125.88, 117.80, 114.06, 112.96.



1-Aminonaphthalene (Table 1, entry 10). 1-Bromonapthathene (0.207 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00×10^{-2} mmol), and NaO*t*Bu (0.192 g, 2.00 mmol) in 4.0

mL DME gave 0.132 g (92%) of 1-Aminonaphthalene as a solid (hexane/ethyl acetate: 70/30). ^{1}H NMR ($CDCl_3$) δ 7.78-7.82 (m, 2 H), 7.40-7.7.47 (m, 2 H), 7.25-7.34 (m, 2 H), 6.76 (dd, J = 6.8, 1.2 Hz, 1 H), 4.10 (s, br, 2 H); ^{13}C NMR ($CDCl_3$) δ 140.02, 134.32, 128.49, 126.29, 125.79, 124.80, 123.58, 120.74, 118.90, 109.62.



General Procedure for Catalytic Amination of Heteroaryl and Aryl Chlorides, Bromides and Iodides with Lithium Amide ($LiNH_2$). The reaction conditions and average yields for each reaction are shown in 2. A typical procedure is given for the first entry in Table 2.

4-*tert*-butylaniline (Table 2, entry 1). (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00 × 10^{-2} mmol), $LiNH_2$ (0.230 g, 10.0 mmol) and 4-*tert*-butyl-1-bromobenzene (0.213 g, 1.00 mmol) were weighed into a 24 mL vial. DME (20.0 mL) was then added. The vial was sealed with a cap containing a PTFE septum, and the reaction mixture was stirred for 24 h at 80 °C. The reaction mixture was allowed to cool to room temperature before pouring into ice water (20.0 mL). To this mixture was added HCl aqueous solution (10.0 mL, 1.0 M). The mixture was stirred at room temperature for 5 min and was then neutralized with a saturated solution of $NaHCO_3$ (5.00-10.0 mL). After extraction with CH_2Cl_2 (3 × 20.0 mL), the organic layer was separated and dried over $MgSO_4$. The solvent was evaporated, and the crude product isolated by eluting with hexane/ethyl acetate (80/20) to give 107.0 mg (72%) of 4-*tert*-butylaniline as a pale yellow liquid.

***o*-Toluidine (Table 2, entry 4).** 2-Chlorotoluene (0.126 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00 × 10^{-2} mmol), and $LiNH_2$ (0.230 g, 10.0 mmol) in 20.0 mL DME gave 74.9 mg (70%) of *o*-toluidine as a colorless liquid.

***o*-Toluidine (Table 2, entry 5).** 2-Bromotoluene (0.171 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00 × 10^{-2} mmol), and $LiNH_2$ (0.230 g, 10.0 mmol) in 20.0 mL DME gave 89.5 mg (86%) of *o*-toluidine as a colorless liquid.

***o*-Toluidine (Table 2, entry 6).** 2-Iodotoluene (0.217 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00 × 10^{-2} mmol), and $LiNH_2$ (0.230 g, 10.0 mmol) in 20.0 mL DME gave 86.8 mg (81%) of *o*-toluidine as a colorless liquid.

2-Aminobiphenyl (Table 2, entry 7). 2-Bromobiphenyl (0.233 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00 × 10^{-2} mmol), and $LiNH_2$ (0.230 g, 10.0 mmol) in 20.0 mL DME gave 0.129 g (76%) of 2-Aminobiphenyl as a solid.

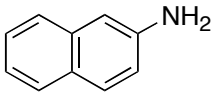
2-*iso*-Propylaniline (Table 2, entry 8). 1-Bromo-2-*iso*-propylbenzene (0.199 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00 × 10^{-2} mmol), and $LiNH_2$ (0.230 g, 10.0 mmol) in 2.0 mL DME gave 0.109 g (81%) of 2-*iso*-Propylaniline as a solid.

4-Amino-*iso*-quinoline (Table 2, entry 9). 4-Bromo-*iso*-quinoline (0.208 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00 × 10^{-2} mmol), and $LiNH_2$ (0.230 g, 10.0 mmol) in 20.0 mL DME gave 0.118 g (82%) of 4-Amino-*iso*-quinoline as a solid.

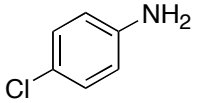
5-Amino-*iso*-quinoline (Table 2, entry 10). 5-Bromo-*iso*-quinoline (0.208 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00 × 10^{-2} mmol), and $LiNH_2$ (0.230 g, 10.0 mmol) in 2.0 mL DME gave 0.114 g (79%) of 5-Amino-*iso*-quinoline as a solid.

1-Aminonaphthalene (Table 2, entry 11). 1-Bromonapthathene (0.207 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00×10^{-2} mmol), and $LiNH_2$ (0.230 g, 10.0 mmol) in 4.0 mL DME gave 0.128 g (89%) of 1-Aminonaphthalene as a solid.

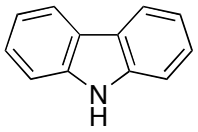
2-Aminonaphthalene (Table 2, entry 12). 2-Bromonapthathene (0.207 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00×10^{-2} mmol), and $LiNH_2$ (0.230 g, 10.0 mmol) in 4.0 mL DME gave 0.100 g (69%) of 1-Aminonaphthalene as a solid (hexane/ethyl acetate: 70/30). ^{1}H NMR ($CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 1 H), 7.63 (d, *J* = 8.4 Hz, 1 H), 7.57 (d, *J* = 8.0 Hz, 1 H), 7.35 (td, *J* = 7.2, 1.2 Hz, 1 H), 7.21 (td, *J* = 7.2, 1.6 Hz, 1 H), 6.93 (s, 1 H), 6.90 (dd, *J* = 8.4, 2.0 Hz, 1 H), 3.76 (s, br, 2 H); ^{13}C NMR ($CDCl_3$) δ 144.05, 134.83, 129.12, 127.86, 127.65, 126.27, 125.73, 122.38, 118.17, 108.48.



1-Amino-4-chlorobenzene (Table 2, entry 13). 1-Bromo-4-chlorobenzene (0.207 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00×10^{-2} mmol), and $LiNH_2$ (0.230 g, 10.0 mmol) in 2.0 mL DME gave 86.7 mg (68%) of 1-Amino-4-chlorobenzene as a solid (hexane/ethyl acetate: 70/30). ^{1}H NMR ($CDCl_3$) δ 7.08 (d, *J* = 8.4 Hz, 2 H), 6.58 (d, *J* = 8.8 Hz, 2 H), 3.63 (s, br, 2 H); ^{13}C NMR ($CDCl_3$) δ 144.90, 129.05, 123.05, 116.17.



Carbazole (Table 2, entry 14). 2,2'-Dibromobiphenyl (0.207 g, 1.00 mmol), (CyPF-*t*-Bu)$PdCl_2$ (7.30 mg, 1.00×10^{-2} mmol), and $LiNH_2$ (0.230 g, 10.0 mmol) in 2.0 mL DME gave 0.107 g (64%) of Carbazole as a solid (hexane/ethyl acetate: 70/30). ^{1}H NMR ($CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2 H), 7.99 (s, br, 1 H), 7.39-7.44 (m, 4 H), 7.21-7.27 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 139.43, 125.81, 123.31, 120.31, 119.41, 110.54.



Procedure for Large-Scale Catalytic Amination of 1-Bromo-2-*iso*-propyl benzene with Lithium Amide (CyPF-*t*-Bu)$PdCl_2$ (73.0 mg, 100 mmol), $LiNH_2$ (2.30 g, 100 mmol) and 1-Bromo-2-*iso*-propylbenzene (1.99 g, 100 mmol) were weighed into a 100 mL round bottom flask with a stirring bar. DME (20.0 mL) was then added. The flask was sealed with a cap and wrapped tightly with electrical tape. The reaction mixture was stirred for 24 h at 90 °C. The reaction mixture was allowed to cool to room temperature before pouring into ice water (50.0 mL). To this mixture was added aqueous HCl (100 mL, 1.0 M). The mixture was stirred at room temperature for 5 min and was then neutralized with a saturated solution of $NaHCO_3$ (50.0 mL). After extraction with CH_2Cl_2 (3 × 50.0 mL), the organic layer was separated and dried over $MgSO_4$. The solvent was

evaporated, and the crude product isolated by column chromatography, eluting with hexane/ethyl acetate (70/30) to give 1.11 g (82%) of 2-*iso*-propylaniline as a solid.

Preparation of (CyPF-*t*-Bu)Pd(4-MeOPh)(Br) 1. CyPF-t-Bu (0.277g, 0.500 mmol) in 2.0 mL benzene was added to a mixture of $Pd[P(o\text{-}Tol)_3]_2$ (0.357 g, 0.500 mmol) and 4-bromoanisole (0.467 g, 5.00 mmol) in 20 ml benzene. The mixture was allowed to stir at room temperature for 30 min. The resulting red solution was filtered, and the solvent was evaporated under vacuum. The residue was redissolved in 2 mL THF. The THF solution was layered with pentane and cooled at -10 °C. The product was deposited as red crystals. The crystals were filtered and washed with pentane and dried under vacuum to give 356 mg (84%) of a single isomer of the product. ^{1}H NMR ($CDCl_3$) δ 0.80-2.80 (m, 22 Cy H), 1.16 (d, J = 12.8 Hz, 9 H), 1.66 (d, J = 11.6 Hz, 9 H), 1.80-1.84 (m, 4 H from THF), 1.96 (t, J = 7.6 Hz, 3 H), 3.17 (dq, J = 6.0, 5.6 Hz, 1 H), 3.74 (s, 3 H), 3.71-3.76 (m, 4 H from THF), 4.23 (s, 5 H), 4.30 (t, J = 2.4 Hz, 1 H), 4.49 (s, br, 1 H), 4.85 (s, br, 1 H), 6.55 (d, J = 7.2 Hz, 1 H), 6.77 (d, J = 6.8 Hz, 1 H), 7.10-7.25 (s, br, 1 H), 7.25-7.40 (s, br, 1 H); ^{31}P {^{1}H] NMR (CH_2Cl_2, -30 °C) 72.83 (d, J = 34.5 Hz), 18.08 (d, J = 34.8 Hz); Anal. Calcd. For $C_{43}H_{67}BrFeO_2P_2Pd$•THF: C, 56.13; H, 7.34. Found: C, 56.35; H, 7.65.

Stoichiometric reactions of (CyPF-*t*-Bu)Pd (4-MeOPh)(Br)[8] (1) with ammonia and NaO*t*Bu. (CyPF-*t*-Bu)Pd(4-MeOPh)(Br) (8.2 mg, 1.0×10^{-3} mmol), NaO*t*Bu (1.0 mg, 1.0×10^{-3} mmol) and P(Ph-d_5)$_3$ (2.7 mg, 2.0×10^{-3} mmol) were dissolved 0.5 mL C_6D_6 containing 1,3,5-trimethoxybenzene (0.29 mg, 1.7×10^{-3} mmol). A ^{1}H NMR spectrum was recorded. NH_3 (5.0 cm^3 at 0.1 atm pressure) was added by vacuum transfer. The tube was sealed and heated at 90 °C in a oil bath. ^{31}P{^{1}H} NMR spectrometry showed the disappearance of the starting material and the formation of (CyPF-*t*-Bu)Pd P(Ph-d_5)$_3$. A ^{1}H NMR spectrum was recorded, and the yield of 4-*tert*-butylaniline and di(4-*tert*-butylphenyl)amine was determined by the integrating the aromatic C-H resonances of amines vs. the internal standard.

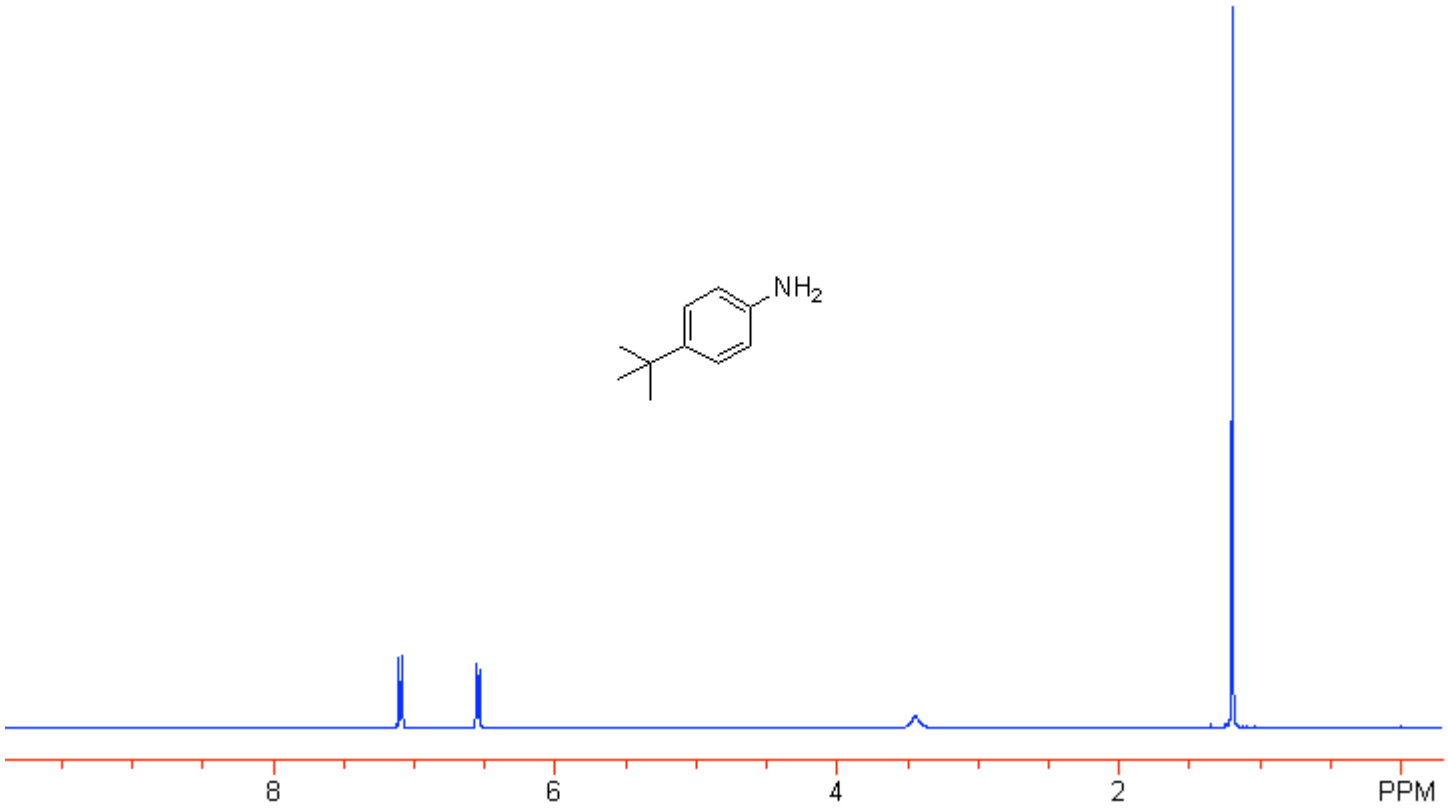
Preparation of [(CyPF-*t*-Bu)Pd(4-MeOPh)(NH_3)]OTf (2). (CyPF-*t*-Bu)Pd(4-MeOPh)(Br) **1** (220 mg, 25.9 mmol) was dissolved in 5 mL of CH_2Cl_2 in a reaction tube sealed to a high vacuum valve. 50 cm^3 of ammonia at 0.3 atm pressure was condensed into the reaction tube by vacuum transfer. The tube was brought into the dry box AgOTf (66.0mg, 25.9 mmol) was added. The solution turned cloudy immediately. After stirring at room temperature for 30 min, the solution was carefully decanted and filtered through a plug of Celite. The resulting solution was evaporated to approximately 1/10th of the original volume. The solution was layered with toluene and allowed to stand at -35 ºC overnight. The product was isolated as a pale yellow powder. Crystals suitable for X-ray diffraction was obtained by slow crystallization of a toluene solution of the complex at room temperature. ^{1}H NMR (THF-d_8, -30 °C) δ 7.48-7.56 (m, 1 H), 7.05-7.22 (m, 1 H), 7.05-7.22 (m, from toluene), 6.80-6.90 (m, 1 H), 6.65-6.69 (m, 1 H), 5.07 (s, br, 0.74 H, major), 4.96 (s, br, 0.20 H from minor), 4.83 (s, br, 0.78 H from major), 4,68 (s, br, 0.27 H from minor), 4.63 (s, br, 1 H), 4.27 (s, 1 H from minor), 4.36 (s, 4 H from major), 3.70 (s, 3 H), 3.57-3.61 (m, 2.7 H from THF), 3.22-3.32 (m, 0.77 H from major), 3.06 (s, br, 0.21 H from minor), 2.94 (s, br, 0.62 H from minor), 2.74 (s, b, 2.37 H from major), 2.31 (s, 2.39 H from toluene), 2.03 (t, J = 7.6 Hz, 3 H), 1.56 (d, J = 11.6 Hz, 9 H), 1.05 (d, J = 11.6 Hz, 9 H), 0.80-2.50 (m, 22 Cy H); ^{31}P{^{1}H] NMR (THF-d_8, -30 °C) 70.96 (d, J = 29.1 Hz, major), 68.74 (d, J = 27.5 Hz, minor), 25.82 (d, J = 27.5 Hz, minor), 20.12 (d, J =

29.1 Hz, major). IR: $\nu(NH_3)$ 3088, 3172, 3255, 3321, 3364 cm^{-1}. Anal. Calcd. For $C_{40}H_{62}F_3FeNO_4P_2Pd$•0.8 equiv. of toluene: C, 54.34; H, 6.83; N, 1.39. Found: C, 54.16; H, 6.50; N, 1.32.

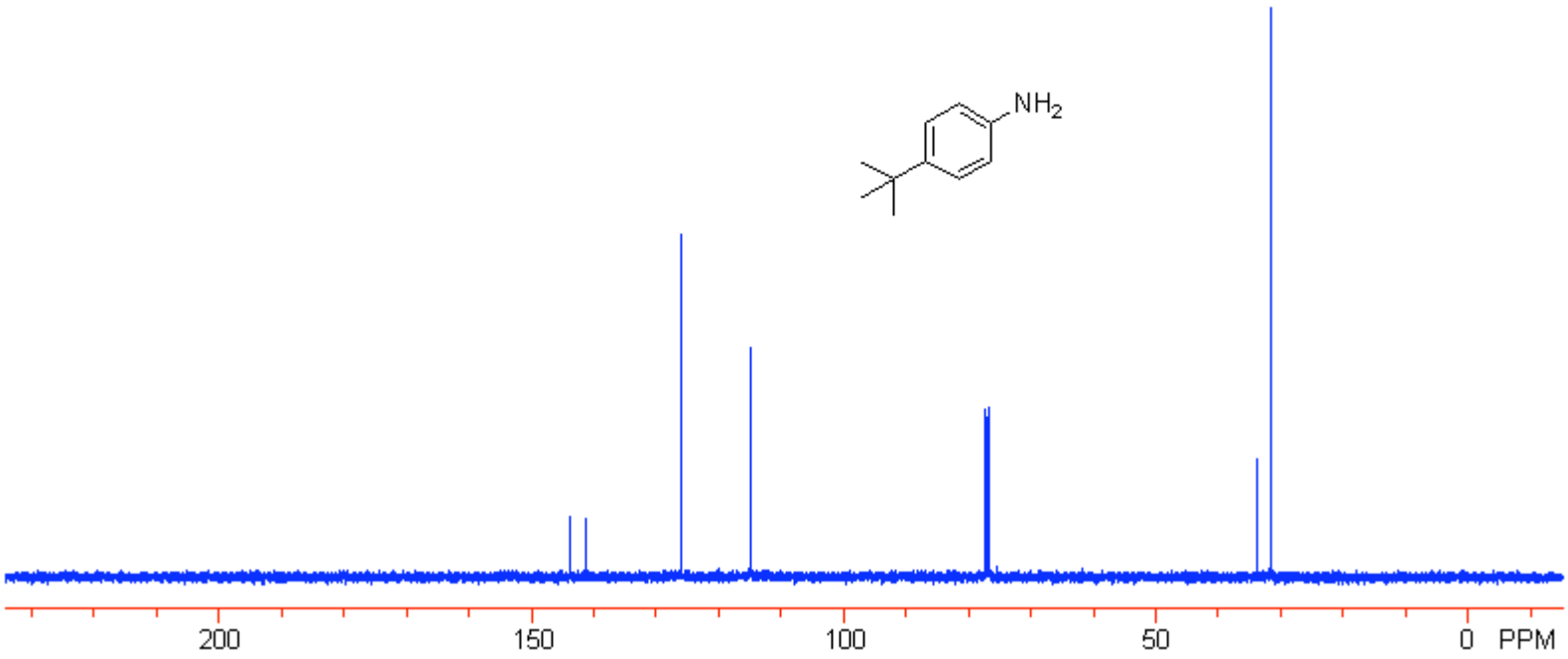
Preparation of (CyPF-*t*-Bu)Pd(4-MeOPh)(NH_2) (3). [(CyPF-*t*-Bu)Pd(4-MeOPh)(NH_3)]OTf (147 mg, 0.150 mmol) was dissolved in 5 mL of THF. $KN(SiMe_3)_2$ (33.0 mg, 0.160 mmol) was added to the stirred solution as a solid. The reaction was allowed to stir at room temperature for 30 min, and it turned to a slightly pale yellow-green color. The solvent was evaporated under vacuum. The resulting solid was dissolved in 3 mL benzene. The benzene solution was filtered through a plug of Celite, and benzene was evaporated under vacuum. The solid was dissolved in 1 mL THF and was layered with pentane. Pure yellow crystals (47.0 mg, 40 %) were obtained by cooling the layered solution at -35 ºC for two days. ^{1}H NMR (C_6D_6) δ 7.88 (br, 1 H), 7.64 (br, 1 H), 7.04 (d, *J* = 7.2 Hz, 1 H), 6.94 (d, *J* = 6.0 Hz, 1 H), 4.56 (s, br, 1 H), 4.06 (s, br, 1 H), 4.01 (s, 6 H), 3.55-3.57 (m, 0.4 H from THF), 3.48 (s, 3 H), 3.00-3.10 (m, 1 H), 1.69 (t, *J* = 6.8 Hz, 3 H), 1.56 (d, *J* = 10.8 Hz, 9 H), 1.30 (d, *J* = 12.8 Hz, 9 H), 0.80-2.5 (m, 22 Cy H), 0.47 (s, br, 2 H); ^{31}P {^{1}H] NMR (THF-*d8*, -30 °C) 65.03 (d, *J* = 31.9 Hz, major), 64.74 (d, *J* = 30.1 Hz, minor), 17.98 (d, *J* = 30.8 Hz, minor), 11.45 (d, *J* = 30.8 Hz, major). IR: $\nu(NH_2)$ 3278, 3356 cm^{-1}. Suitable elemental analysis was not obtained because the compound decomposes at room temperature as a solid over a 12-24 h time period.

Reductive elimination reaction from (CyPF-*t*-Bu)Pd(4-MeOPh)(NH_2) 3. (CyPF-*t*-Bu)Pd(4-MeOPh)(NH_2) (8.2 mg, 1.0 × 10^{-3} mmol)and P(Ph-d_5)$_3$ (2.7 mg, 2.0 × 10^{-3} mmol) were dissolved 0.5 mL C_6D_6 containing 1,3,5-trimethoxybenzene (0.29 mg, 1.7 × 10^{-3} mmol). A ^{1}H NMR spectrum was recorded. The tube was sealed and heated at 90 °C in a oil bath. ^{31}P{^{1}H} NMR spectrometry showed the disappearance of the starting material and the formation of (CyPF-*t*-Bu)PdP(Ph-d_5)$_3$. A ^{1}H NMR spectrum was recorded, and the yield of 4-*tert*-butylaniline and di(4-*tert*-butylphenyl)amine was determined by integrating the aromatic C-H resonances of amines vs. the internal standard.

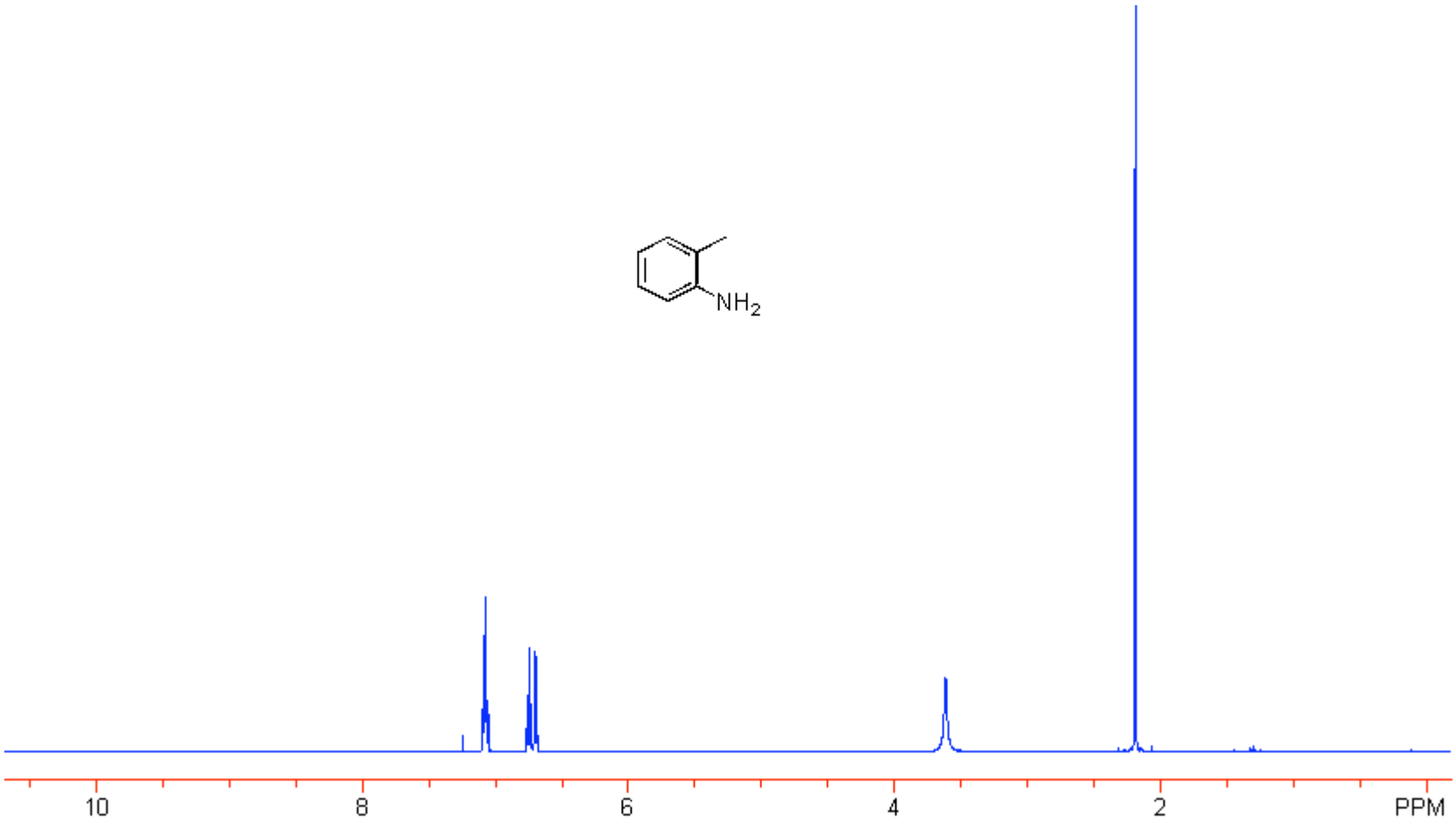
4-*tert*-butylaniline (Table 1and Table 2, entry 1)



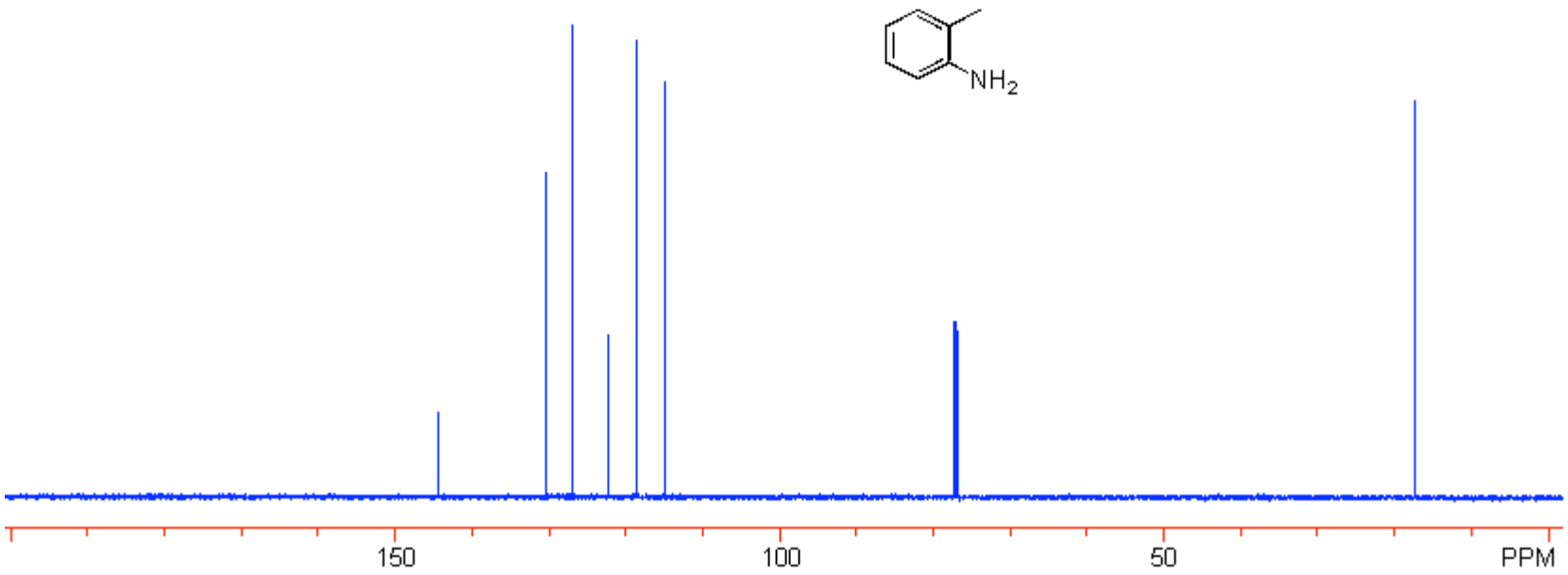
4-*tert*-butylaniline (Table 1and Table 2, entry 1)



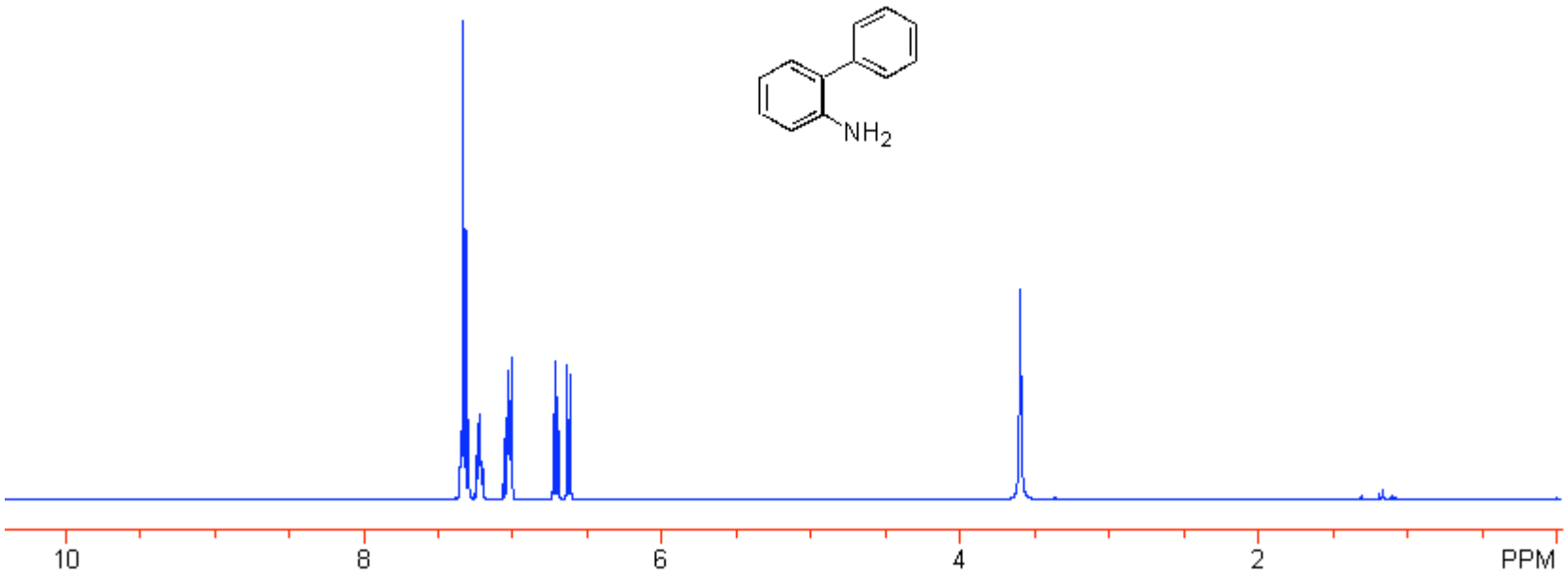
_o_-Toluidine (Table 1, 3-5, Table 2, 4-6)



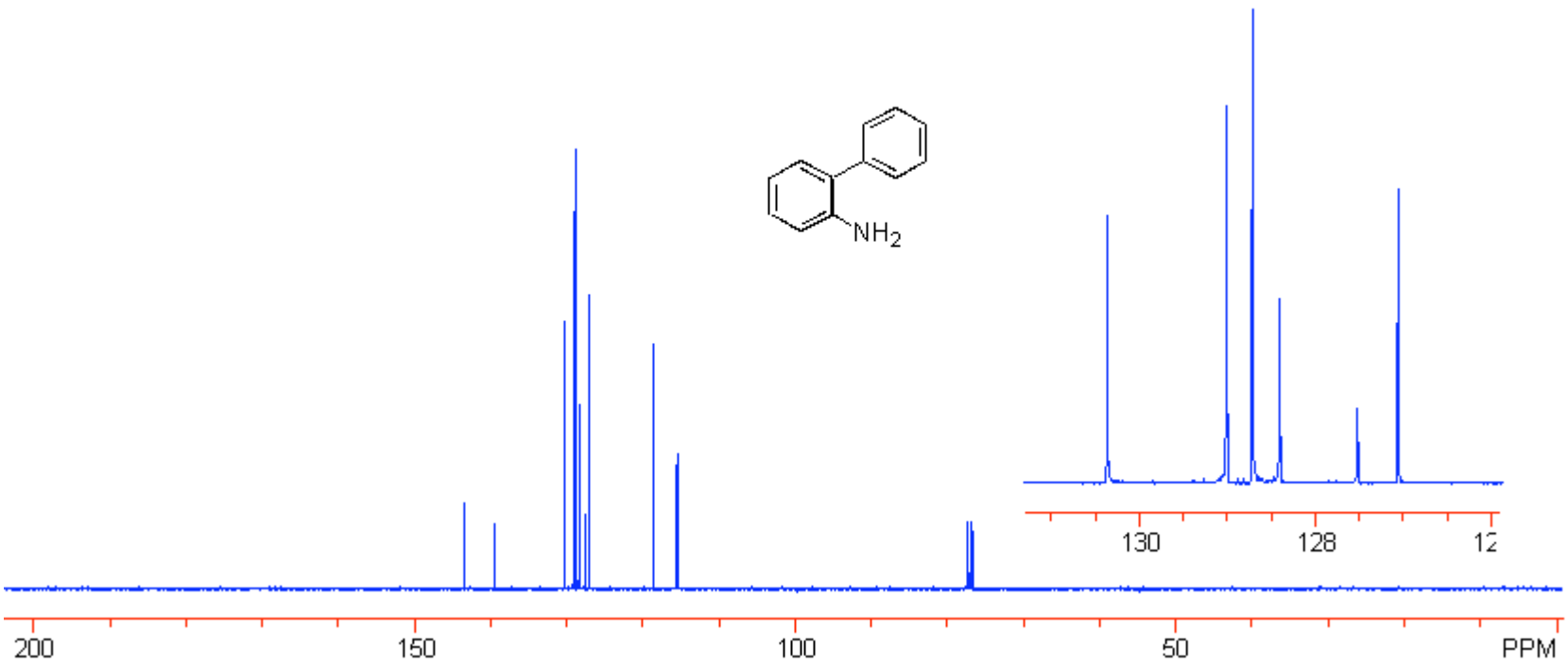
o-Toluidine (Table 1, 3-5, Table 2, 4-6)



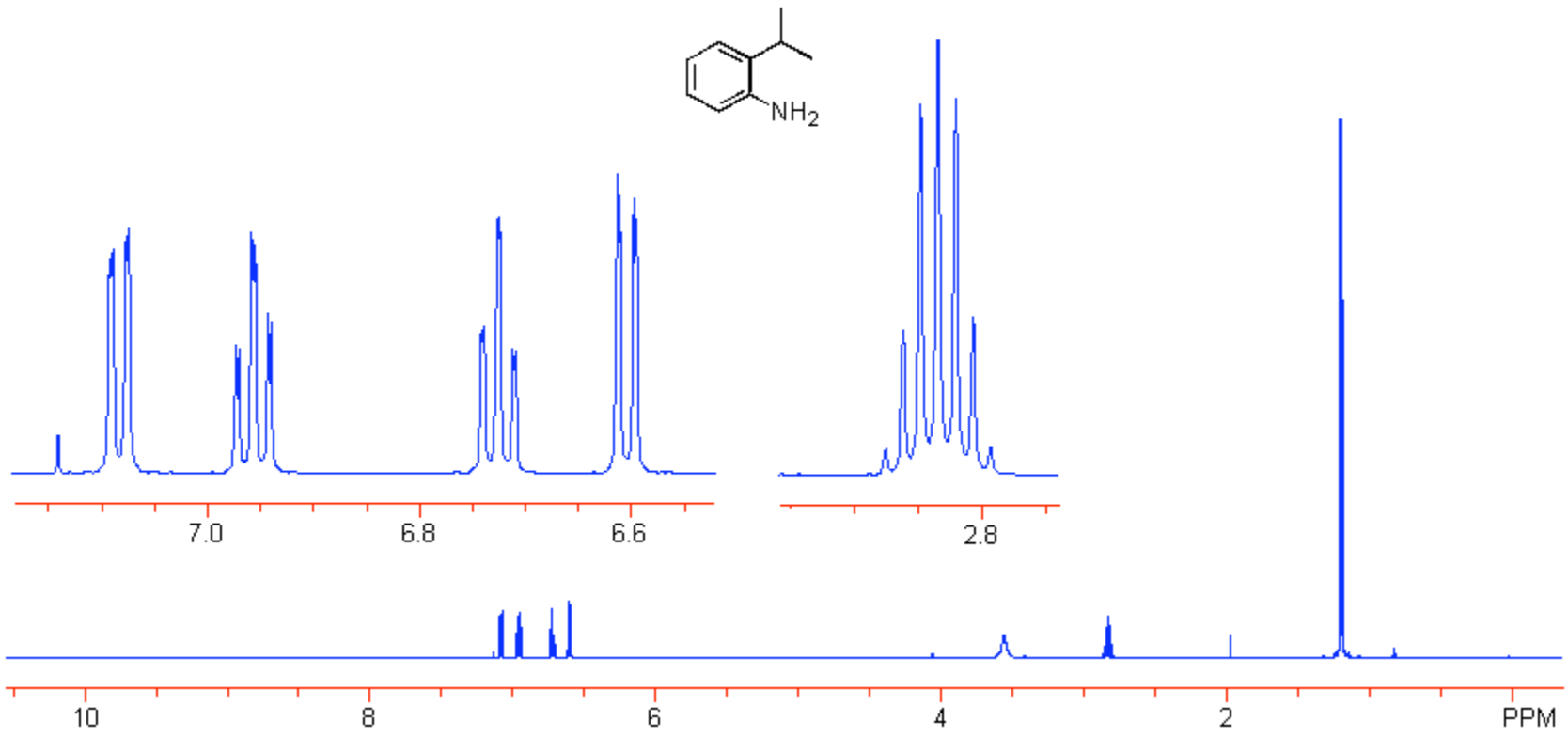
2-*iso*-Propylaniline (Table 1and 2, entry 7)



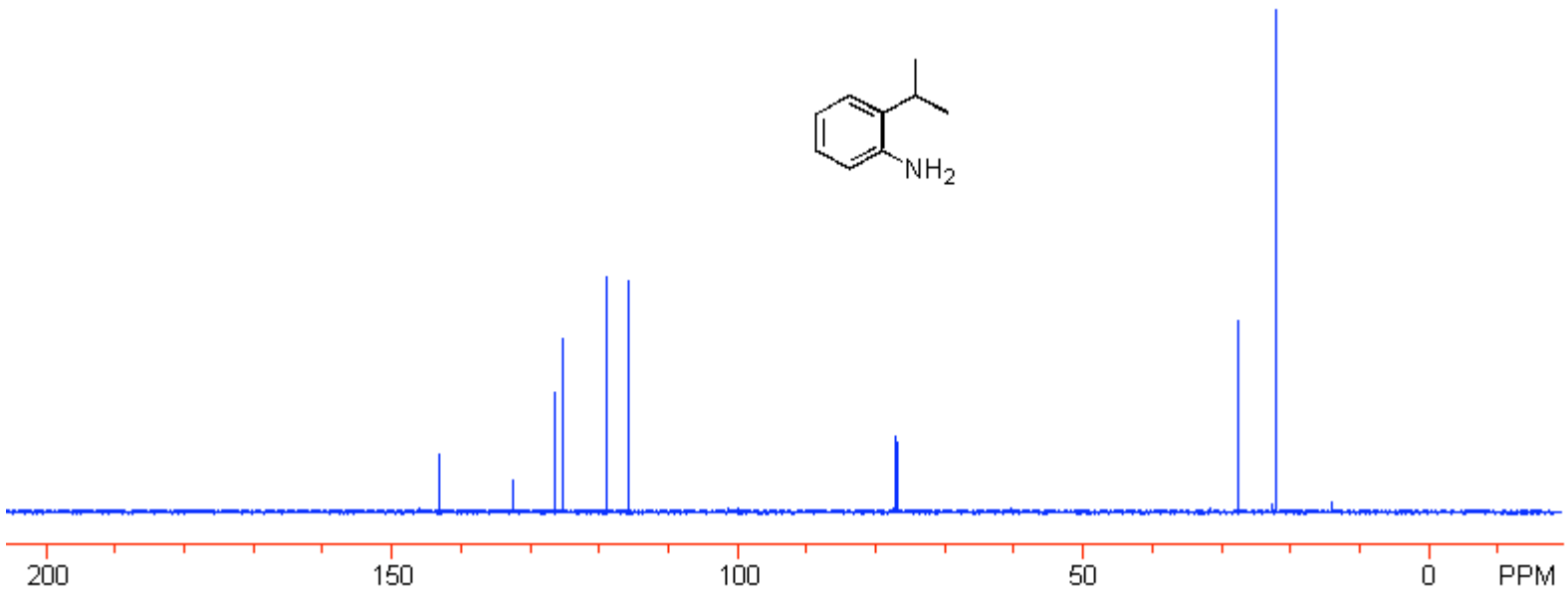
2-*iso*-Propylaniline (Table 1and 2, entry 7)



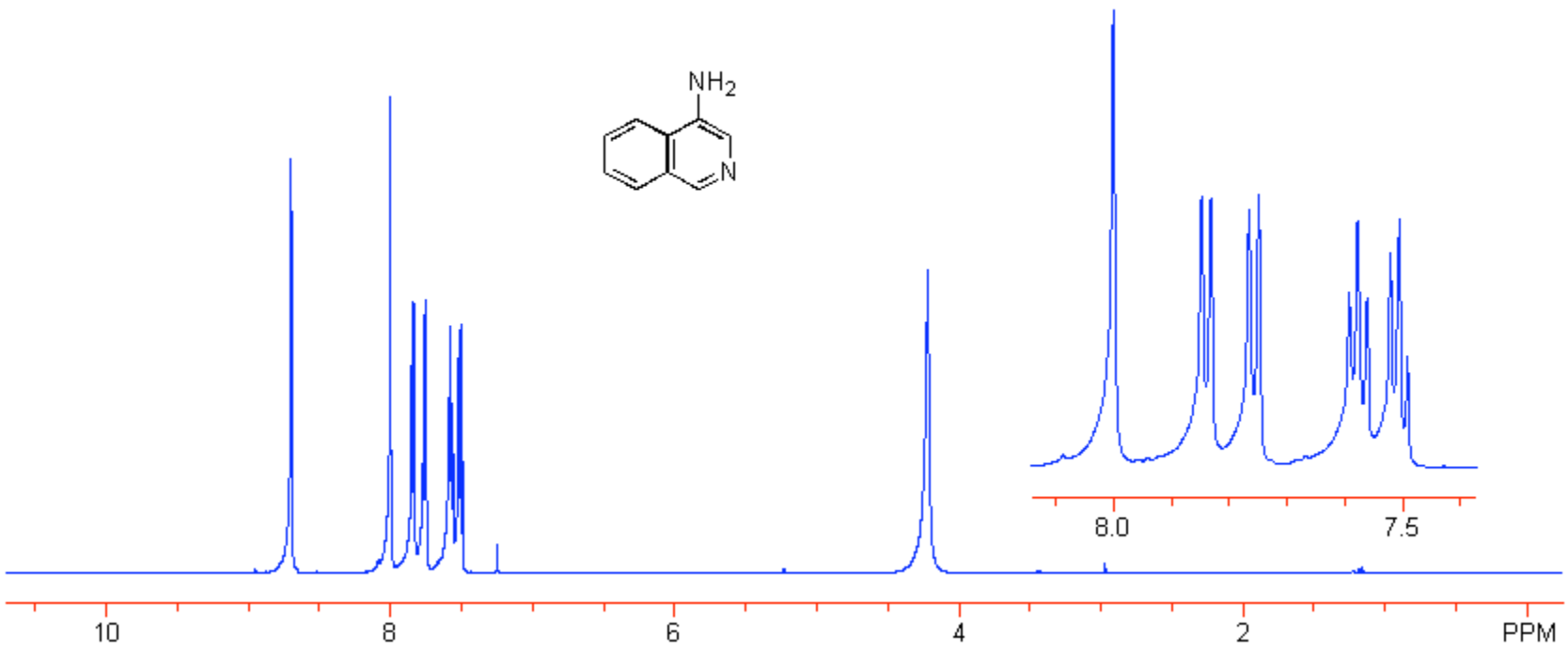
2-*iso*-Propylaniline (Table 1, entry 7; Table 2, 8)



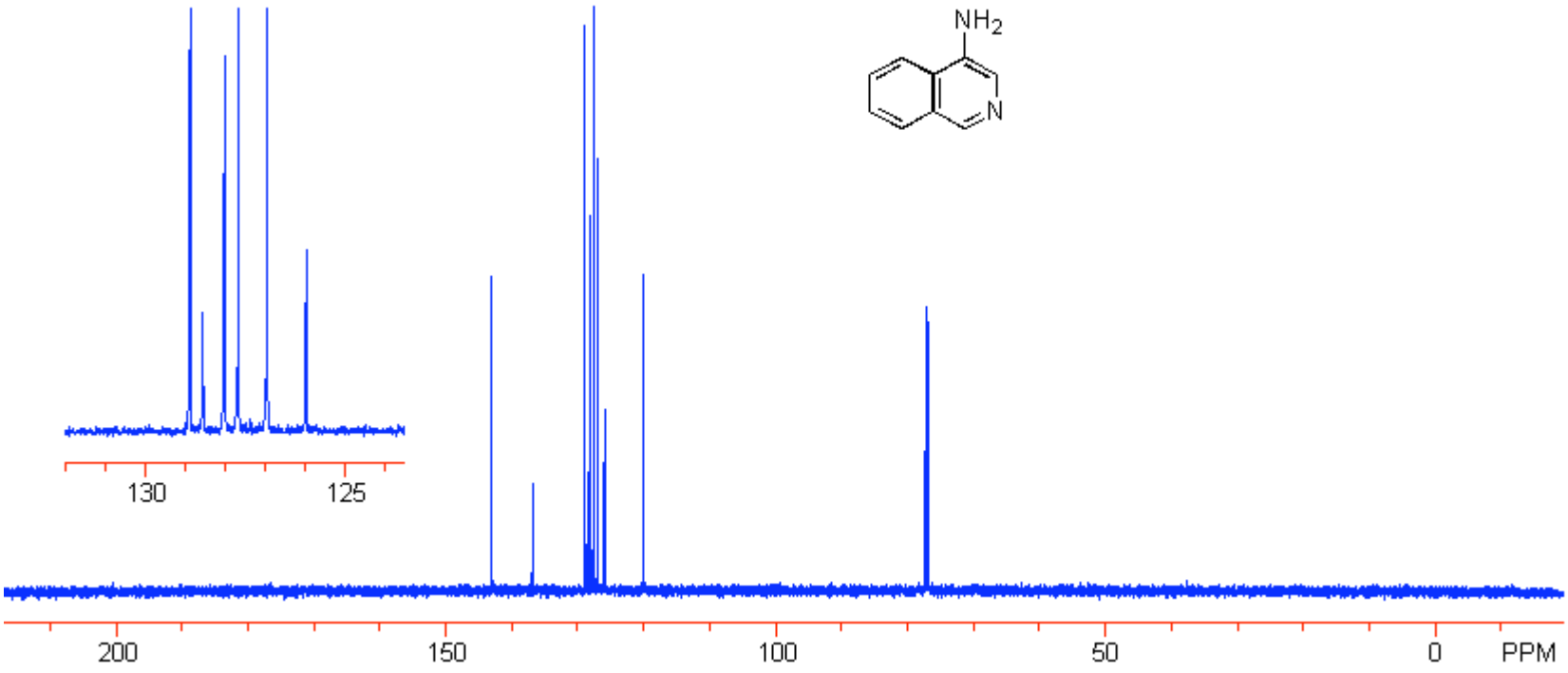
2-*iso*-Propylaniline (Table 1, entry 7; Table 2, 8)



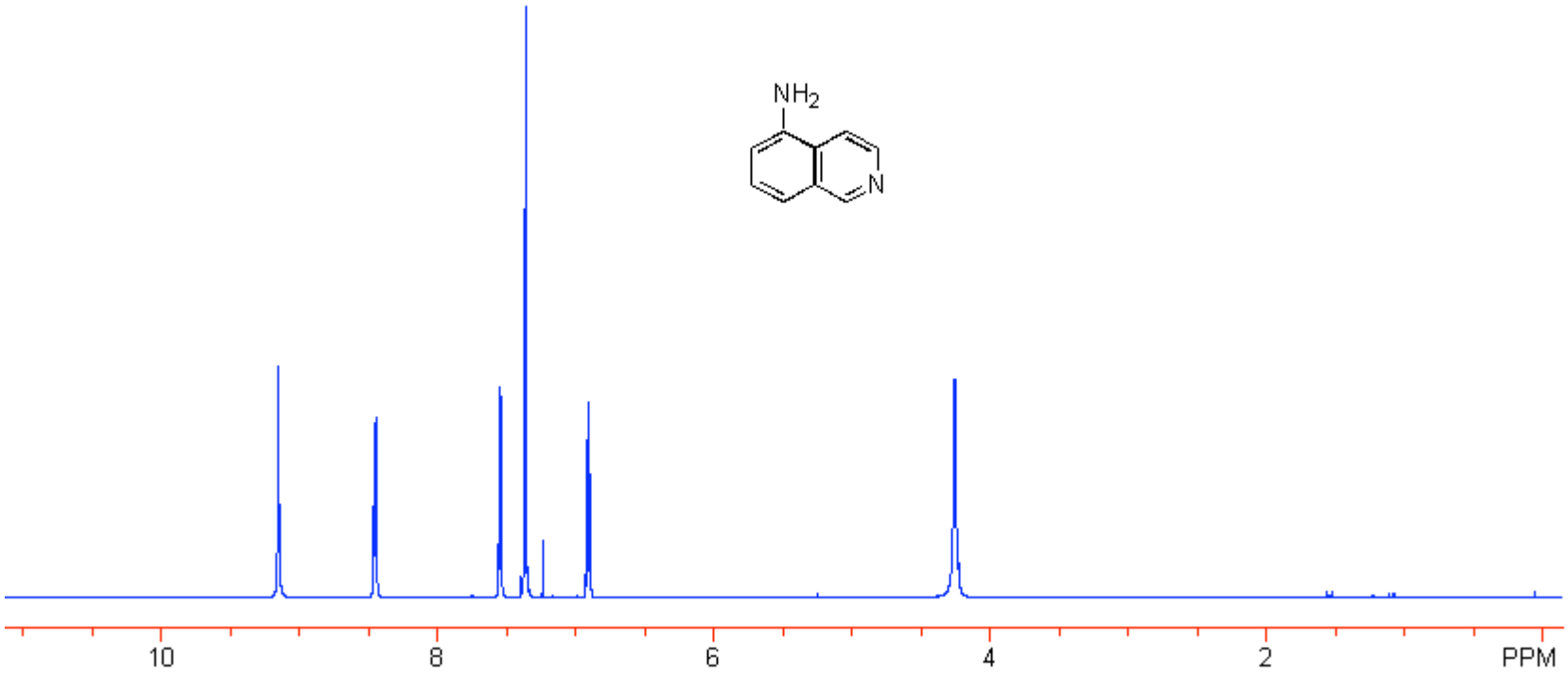
4-Amino-*iso*-quinoline (Table 1, entry 8; Table 2, entry 9)



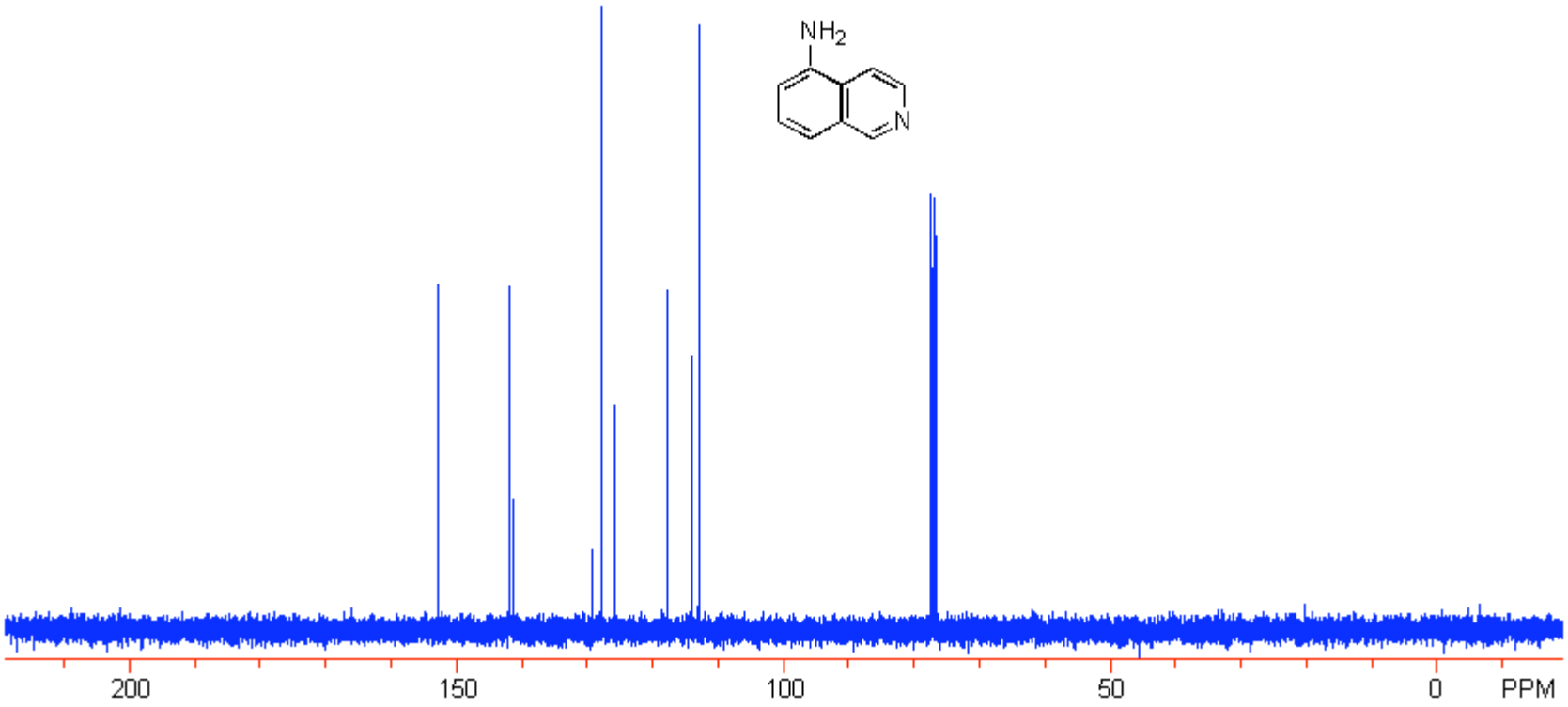
4-Amino-*iso*-quinoline (Table 1, entry 8; Table 2, entry 9)



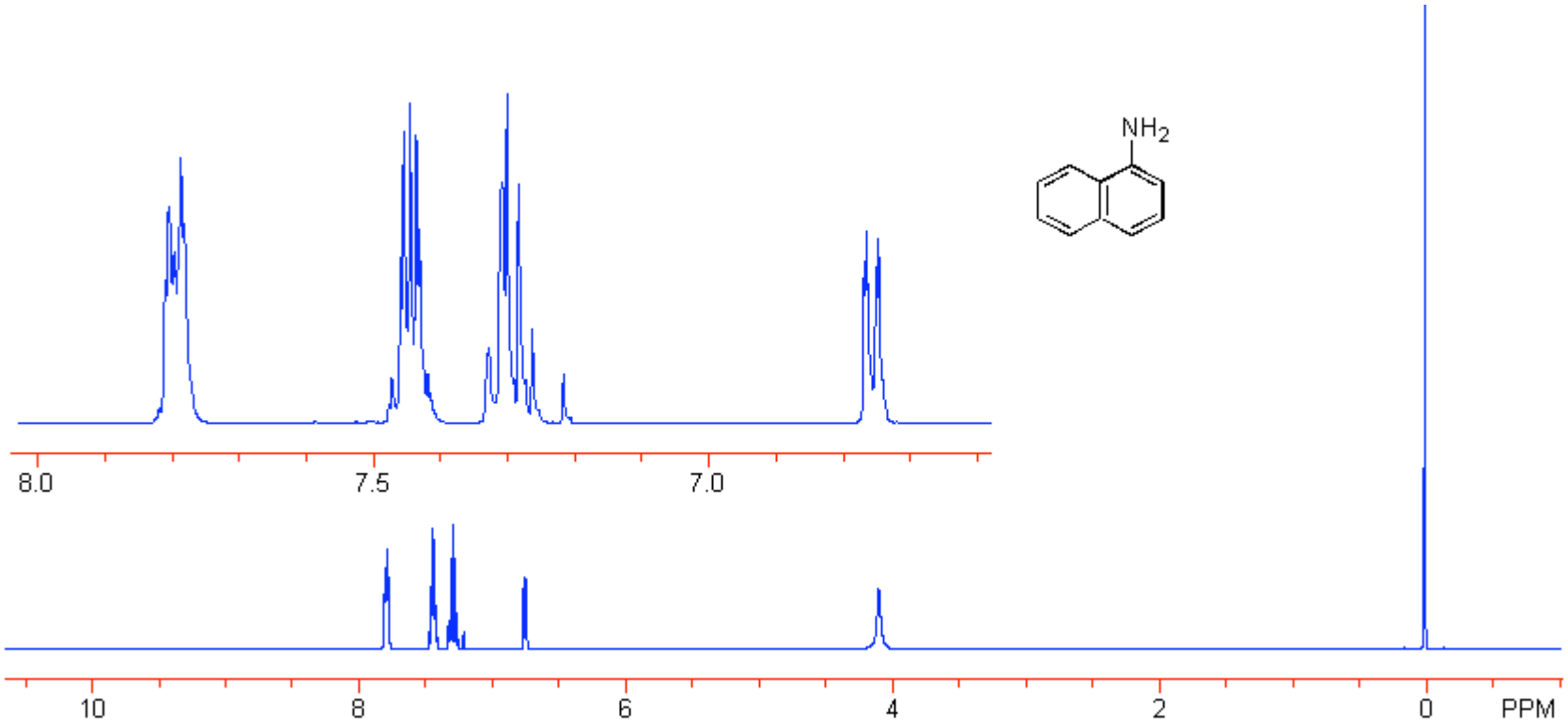
5-Amino-*iso*-quinoline (Table 1, entry 9; Table 2, entry 10)



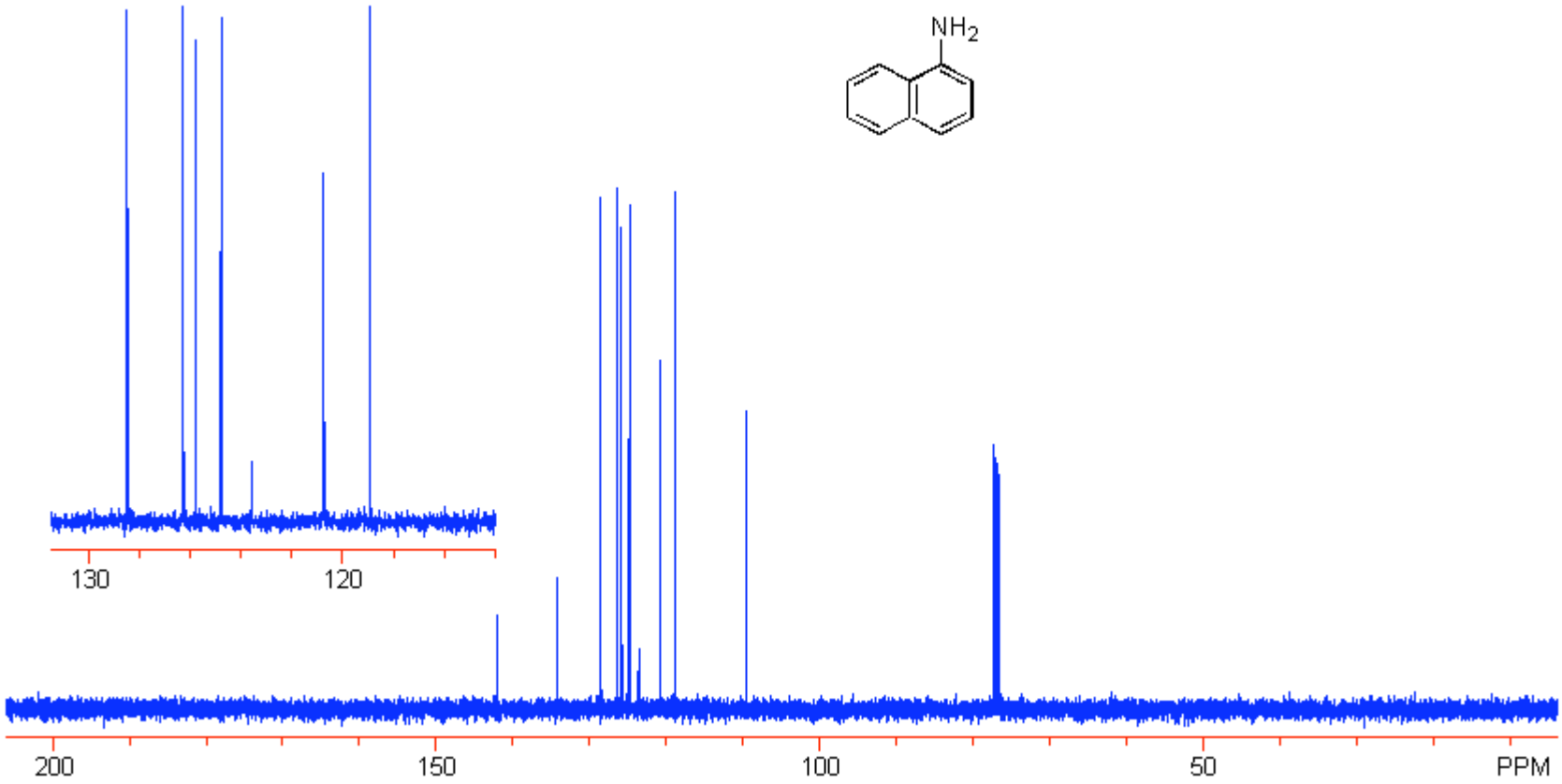
5-Amino-*iso*-quinoline (Table 1, entry 9; Table 2, entry 10)



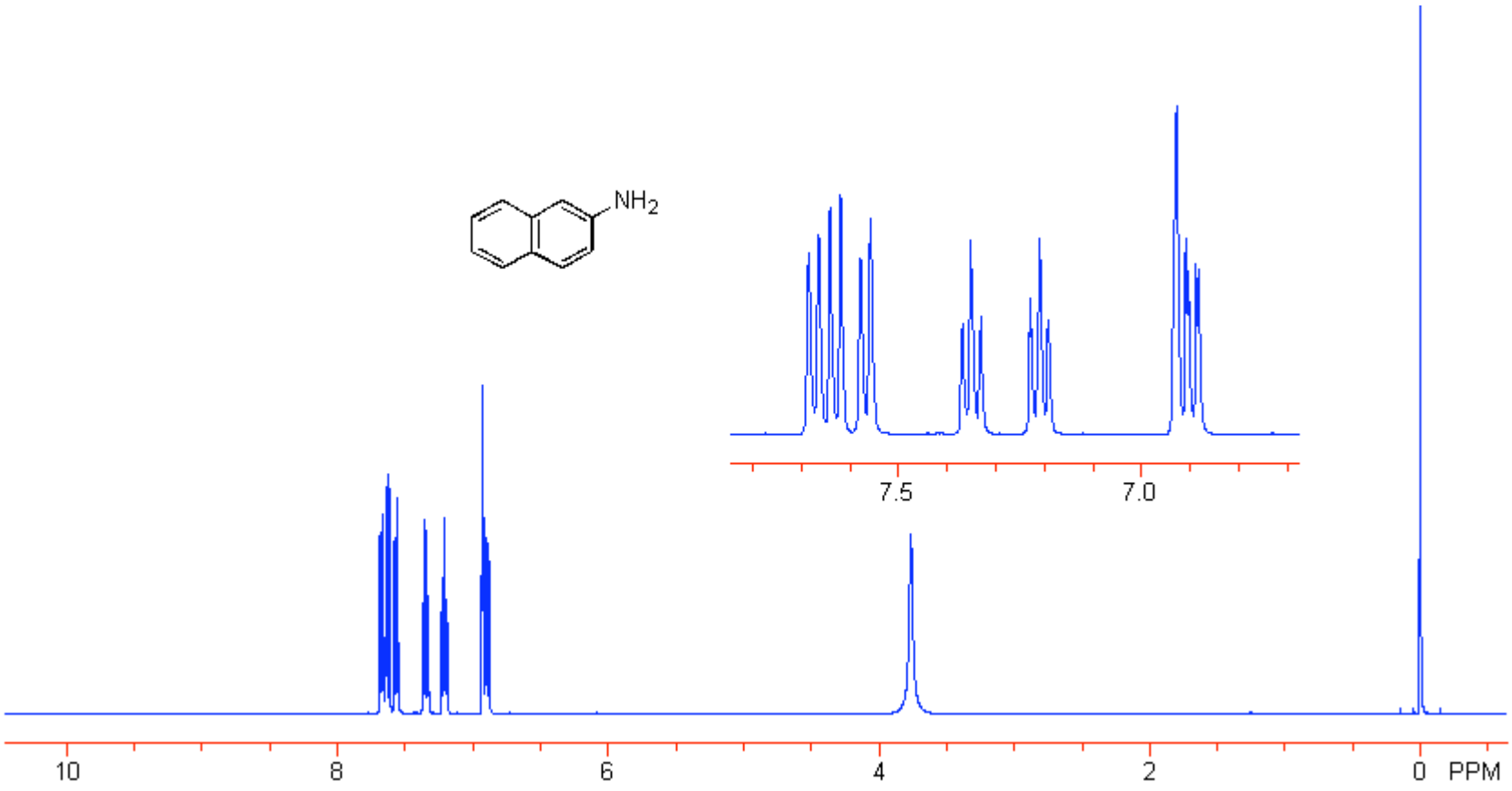
1-Aminonaphthalene (Table 1, entry 10; Table 2, 11)



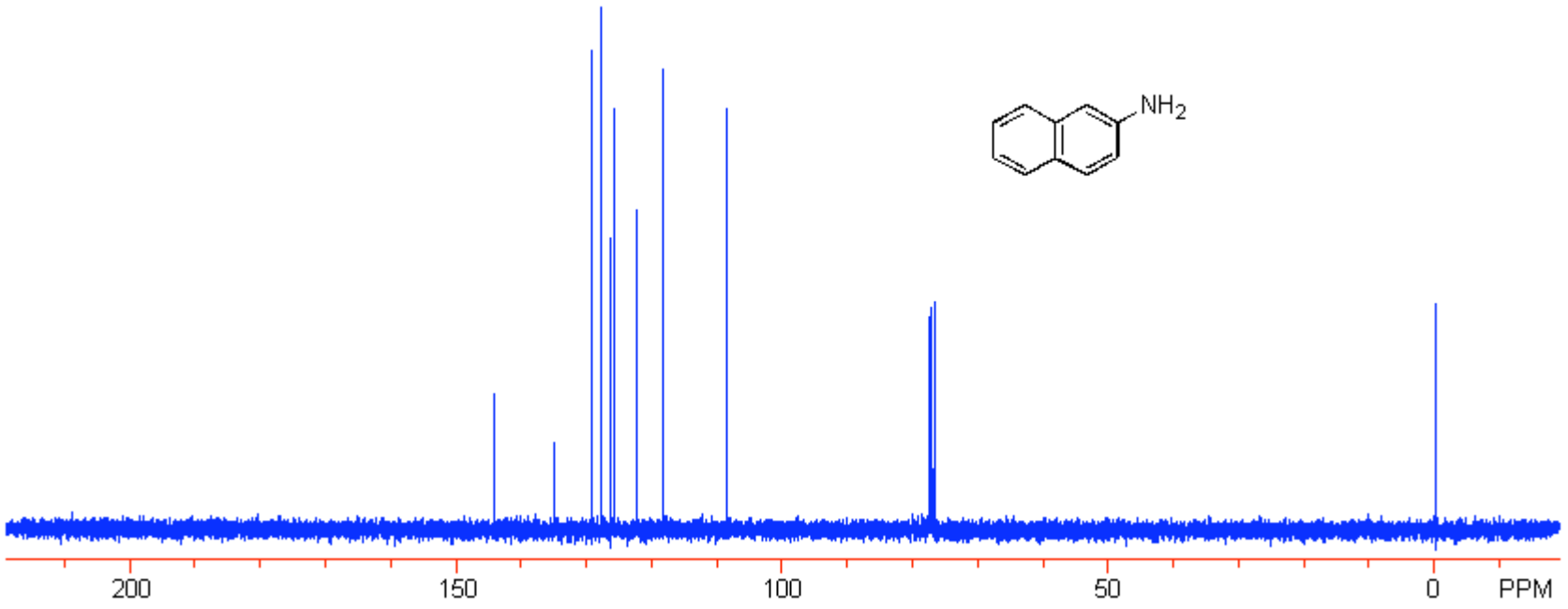
1-Aminonaphthalene (Table 1, entry 10; Table 2, 11)



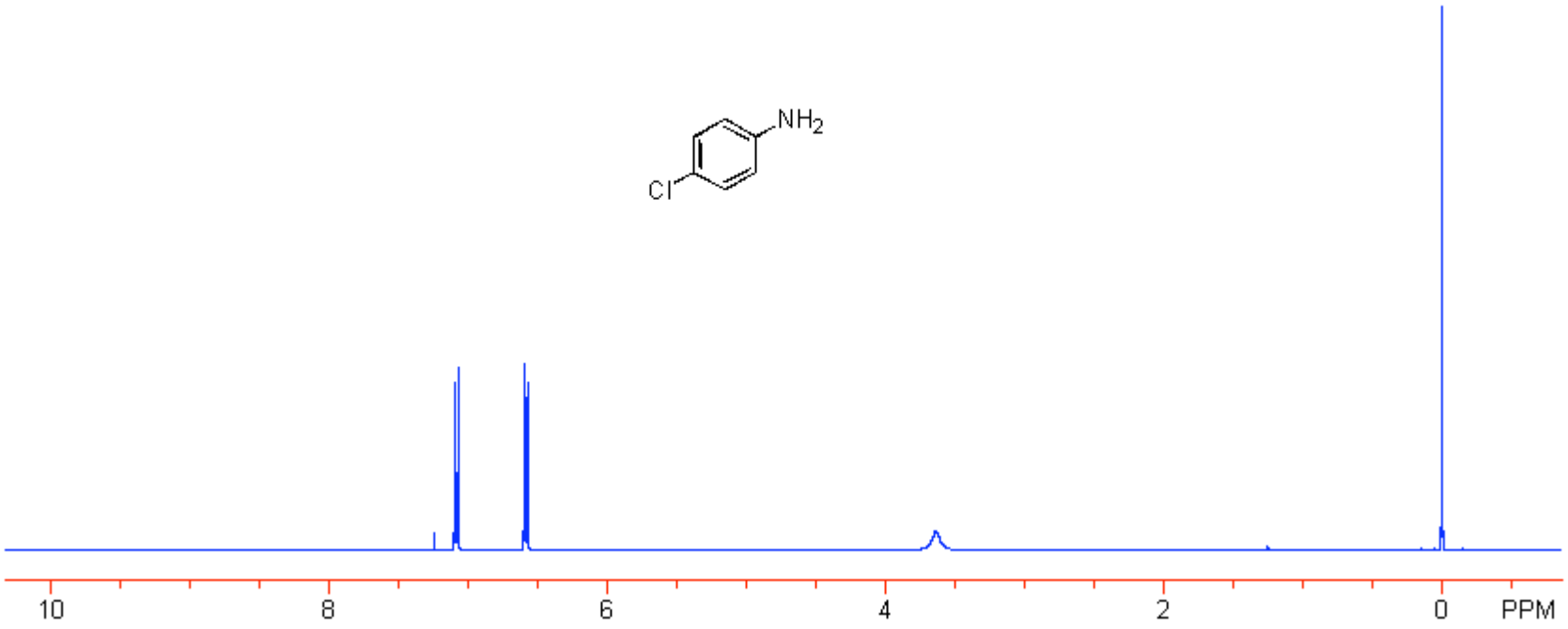
2-Aminonaphthalene (Table 2, entry 12)



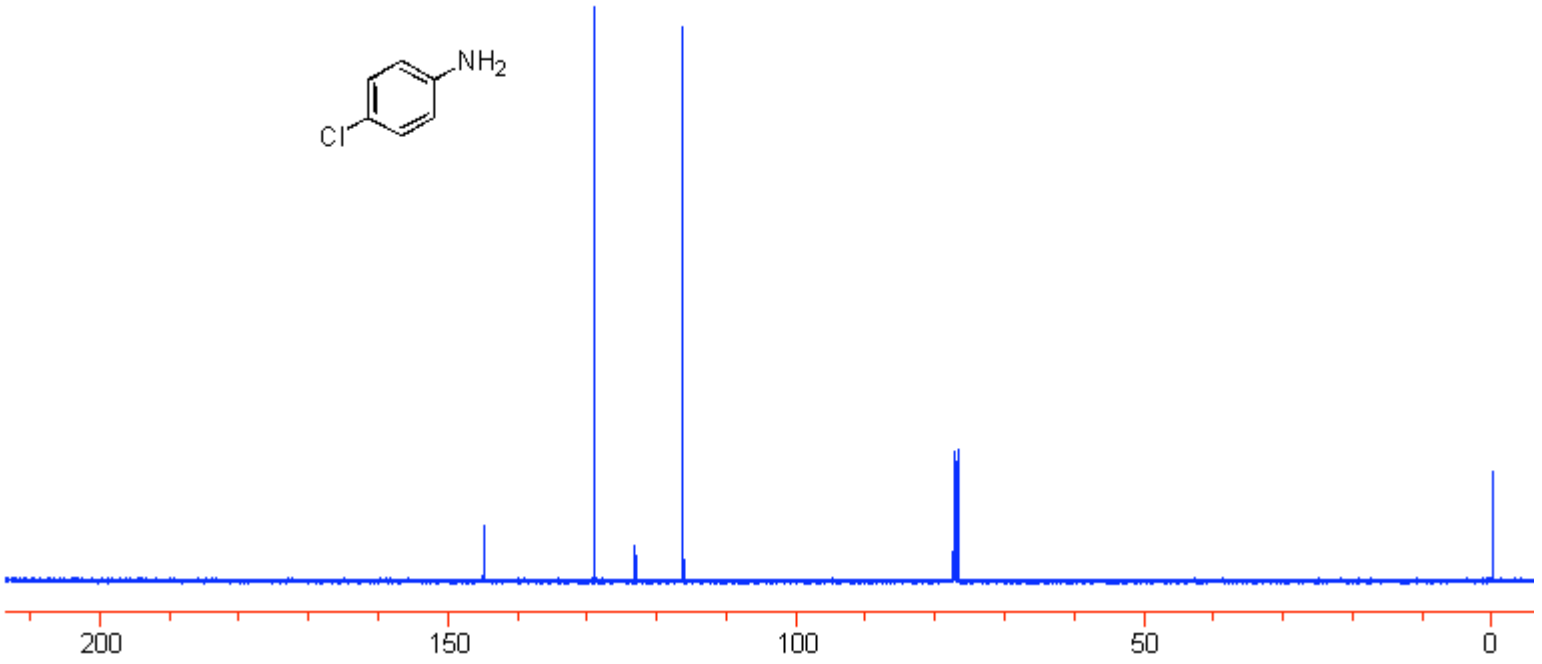
2-Aminonaphthalene (Table 2, entry 12)



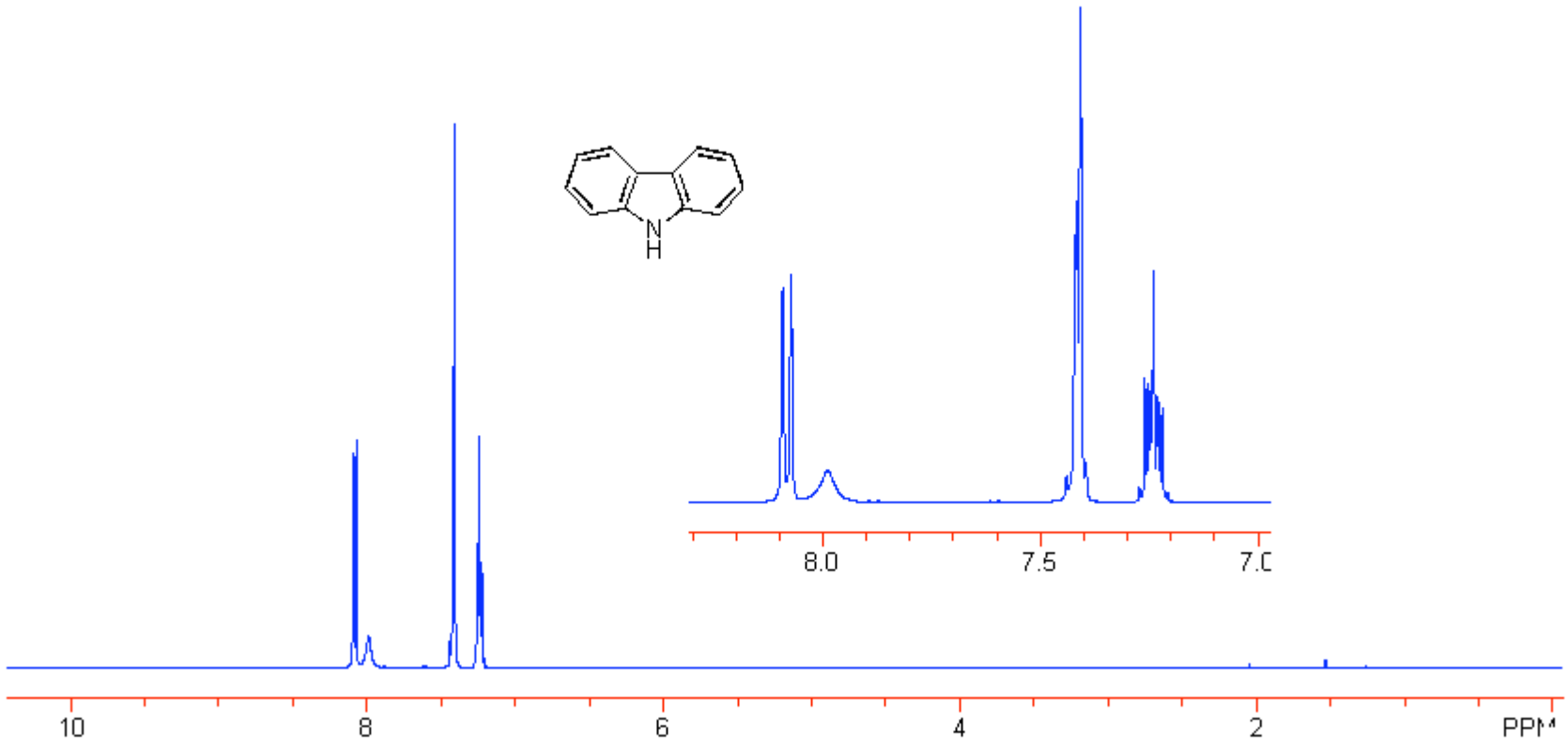
1-Amino-4-chlorobenzene (Table 2, entry 13)



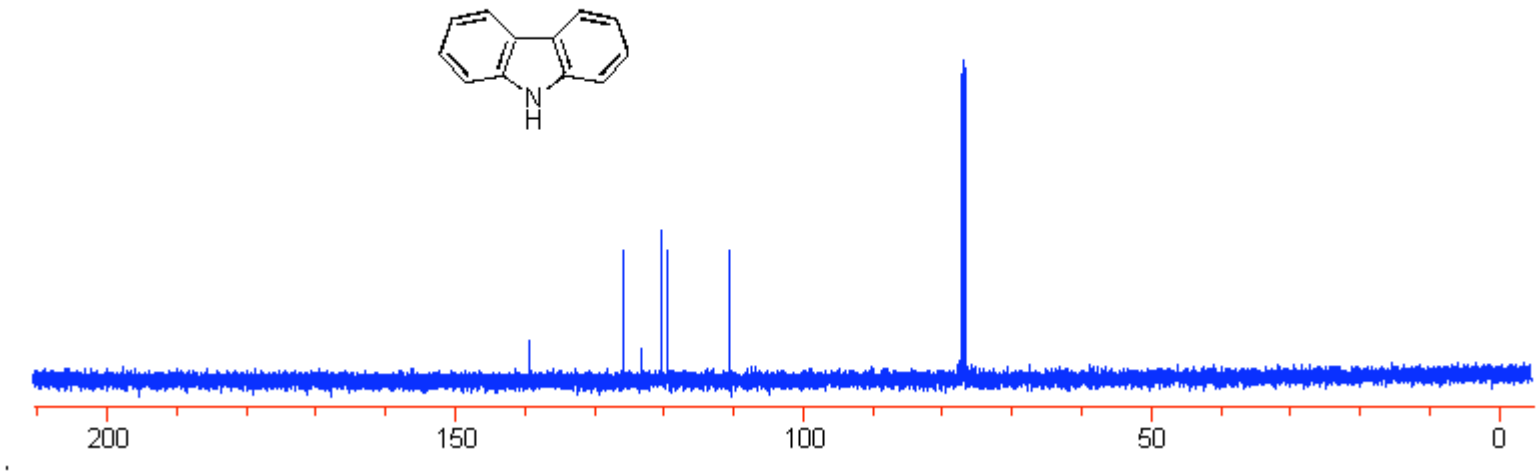
1-Amino-4-chlorobenzene (Table 2, entry 13)



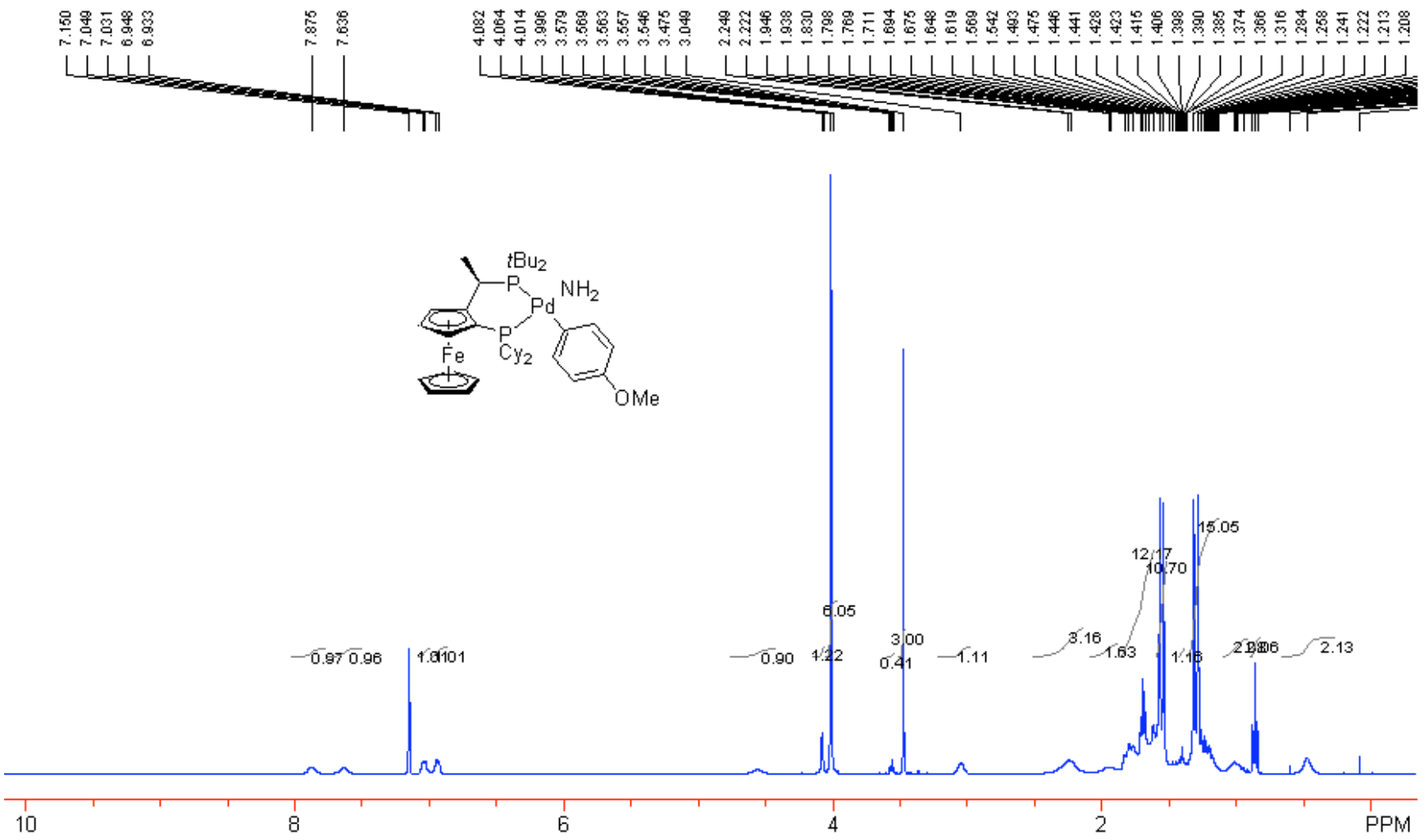
Carbazole (Table 2, entry 14)



Carbazole (Table 2, entry 14)



(CyPF-*t*-Bu)Pd(4-MeOPh)(NH_2) (3)



(CyPF-*t*-Bu)Pd(4-MeOPh)(NH_2) (3)