Lewis-Acid Acceleration of C-N Bond-Forming Reductive Elimination from Heteroarylpalladium Complexes and Catalytic Amidation of Heteroaryl Bromides

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Supporting Information

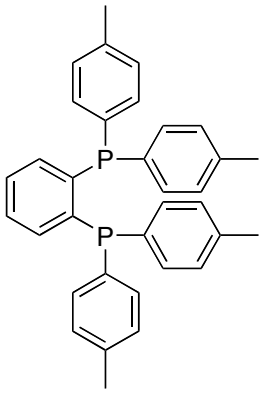
General Methods. Unless otherwise noted, all manipulation were conducted under an inert atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 or 500 MHz Spectrometer, and ^{31}P $\{^{1}H\}$ NMR spectra were recorded on a General Electric QE 300 MHz spectrometer with tetramethylsilane 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.

Unless specified otherwise, all reagents were purchased from commercial suppliers and used without further purification. $[PdBr(R)(PPh_3)_2]$[1] (R = C_5H_4N-C^3, C_5H_4N-C^4), $[PdBr(R)(PPh_3)]_2$ (R = C_5H_4N-C^3), and [Pd(DPPBz)(*p*-Tol)(Br)] (**4**)[2] were prepared by literature procedures. Potassium amides were prepared by the addition of one equivalent of the corresponding amine to a suspension of one equivalent of KH in benzene. Potassium amidates were prepared by the addition of one equivalent of the corresponding amide to a suspension of one equivalent of KH in THF.

Preparation of Tol-DPPBz. Into to a Schlenk flask was placed $Pd(OAc)_2$ (110 mg, 0.500 mmol), 1-bromo-2-iodobenzene (2.83 g, 10.0 mmol) and di-*p*-tolphosphine (2.14 g, 10.0 mmol). The flask was sealed with a septum and then evacuated and filled with nitrogen three times. Triethyl amine (7.00 mL, 50.0 mmol) and acetonitrile (20.0 mL) was then added. The reaction mixture was stirred for 12 h at 100 °C. The reaction mixture was allowed to cool to room temperature before filtered through a short plug of Celite. The solvent was evaporated, and the crude product isolated by silica gel chromatography eluting with hexane/ethyl acetate (95/5) to give 3.50 g (95%) of the product as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.45-7.50 (m, 1 H), 7.05-7.10 (m, 10 H), 6.65-6.70 (m, 1 H); ^{31}P $\{^{1}H\}$ NMR (CD_2Cl_2) δ -6.34 (s).

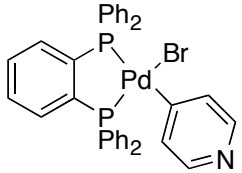
An ether solution of *p*-tolylmagnesium chloride (100 mL, 0.5 M, 100 mmol) was added dropwise to a cold solution (-78 ºC) of Me_2NPCl_2 (7.30 g, 50.0 mmol) and pyridine (20.0 mL, 250 mmol) in dry ether. The reaction mixture was stirred for 2 h at room temperature and heated to reflux for additional 2 hr. The solution was cooled to room temperature and HCl in ether (30.0 mL, 2.00 M in diethyl ether) was added dropwise. The mixture was stirred for additional 10 hr at room temperature. The mixture consisted two layers. The upper layer was collected and concentrated under reduced pressure to give 4.50 g of the crude $(p\text{-tolyl})_2PCl$. The crude product was used directly without further purification.

A solution of 1-bromo-2-(di-*p*-tolylphenyl)phosphinobenzene 3.69 g, 10.0 mmol) in THF (50.0 mL) was cooled to -78 ºC and *n*BuLi (7.00 mL, 1.60 M, 11.2 mmol) was added dropwise. The solution was stirred at -78 ºC for 1 hr and chloro-di-*p*-tolylphosphine (2.80g, 11.0 mmol) in 10.0 diethyl ether was added dropwise. The solution was allowed to warm to room temperature and stir for 2 h. CH_2Cl_2 (50.0 mL) was then added to the solution. The organic layer was washed with water and saturated sodium chloride and then dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography, eluting with hexane/ethyl acetate (80/20) to give 3.50 g (70%) of the desired Tol-DPPBz as a white solid. ^{1}H NMR (CD_2Cl_2) δ 7.21 (dd, J = 6.0, 3.0 Hz, 2 H), 6.96-7.05 (m, 18 H), 2.29 (s, 12 H); ^{31}P $\{^{1}H\}$ NMR (CD_2Cl_2) δ -15.42. Anal. Calcd. For $C_{34}H_{32}P_2$: C, 81.26; H, 6.42. Found: C, 81.11; H, 6.22.

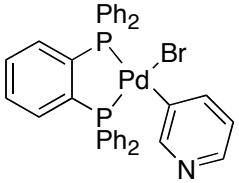


General Procedure for the Synthesis of [Pd(DPPBz)(Ar)(Br)], Ar = C_5H_4N-C^3, C_5H_4N-C^4. A solution of 1,2-bis(diphenylphosphino)benzene (97.0 mg, 0.220 mmol) in benzene (5.00 mL) was added dropwise to a stirred mixture of $[Pd(PPh_3)_2(Ar)(Br)]$ (157 mg, 0.200 mmol) in benzene (10.0 mL). The mixtures changed from cloudy white to clear immediately and became cloudy white again after 5 min. The mixture was stirred at room temperature for 5 h. The white solid was filtered, washed with pentane and used without further purification.

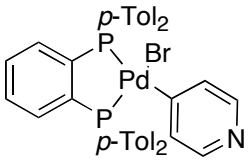
[Pd(DPPBz)(C_5H_4N-C^4)(Br)] (1). The general procedure was followed and gave 101 mg (84%) of the product. ^{1}H NMR (CD_2Cl_2) δ 7.61-7.68 (m, 7 H), 7.37-7.54 (m, 11 H), 7.24-7.27 (m, 8 H), 6.89-6.93 (m, 2 H); ^{31}P {^{1}H} NMR (CD_2Cl_2) δ 54.2 (d, J = 26 Hz), 44.7 (d, J = 26 Hz). Anal. Calcd. For $C_{35}H_{28}BrNP_2Pd$: C, 59.13; H, 3.97; N, 1.97. Found: C, 59.14; H, 3.70; N, 1.84.



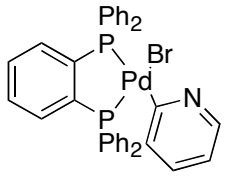
[Pd(DPPBz)(C_5H_4N-C^3)(Br)] (2). The general procedure was followed and gave 146 mg (90%) of the product. ^{1}H NMR (CD_2Cl_2) δ 7.90-8.06 (m, 1 H), 7.84-7.86 (m, 1 H), 7.56-7.64 (m, 5 H), 7.37-7.56 (m, 11 H), 7.24-7.27 (m, 8 H), 7.07-7.11 (m, 1 H), 6.59 (t, J = 4.8 Hz, 1 H); ^{31}P {^{1}H} NMR (THF) δ 55.4 (d, J = 26 Hz), 44.5 (d, J = 26 Hz). Anal. Calcd. For $C_{35}H_{28}BrNP_2Pd$: C, 59.13; H, 3.97; N, 1.97. Found: C, 58.94; H, 3.91; N, 2.04.



[Pd(DTPBz)(C_5H_4N-C^4)(Br)] (5). The general procedure was followed and gave 130 mg (85%) of the product. ^{1}H NMR (CD_2Cl_2) δ 7.67 (t, J = 4.0 Hz, 2H), 7.56 (t, J = 7.0 Hz, 1 H), 7.37-7.47 (m, 7 H), 7.11-7.12 (m, 4 H), 7.08 (d, J = 8.0 Hz, 2 H), 7.05 (d, J = 8.0 Hz, 2 H), 6.99-7.01 (m, 4 H), 6.95 (td, J = 6.0, 2.0 Hz, 2 H); ^{31}P {^{1}H} NMR (CD_2Cl_2) δ 53.0 (d, J = 28 Hz), 44.1 (d, J = 28 Hz).

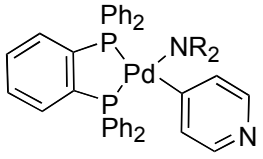


Synthesis of [Pd(DPPBz)(C_5H_4N-C^2)(Br)] (3). A mixture of 1,2-bis(diphenylphosphino)benzene (188 mg, 0.440 mmol) and $[PdBr(R)(PPh_3)]_2$ (R = C_5H_4N-C^3) (211 mg, 0.200 mmol) in toluene (20.0 mL) was heated at 90 °C for 10 h. When the reaction was complete, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy, the reaction mixture was filtered through a medium fritted funnel containing Celite. The resulting solution was cooled to room temperature. Addition of pentane led to precipitation of 140 mg (98% yield) of the product as a white solid. The solid was filtered, washed with pentane and used without further purification. ^1H NMR (CD_2Cl_2) δ 8.04 (d, *J* = 4.8 Hz, 1 H), 7.57-7.62 (m, 5 H), 7.44-7.55 (m, 3 H), 7.28-7.43 (m, 12 H), 7.20-7.24 (m, 4 H), 6.84-6.86 (m, 2 H), 6.49-6,51 (m, 1 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 49.4 (d, *J* = 32 Hz), 39.9 (d, *J* = 32 Hz). Anal. Calcd. For $C_{35}H_{28}BrNP_2Pd$: C, 59.13; H, 3.97; N, 1.97. Found: C, 59.21; H, 3.84; N, 1.92.



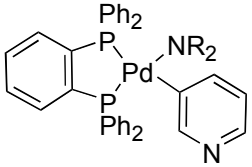
Synthesis of Palladium Amides. Representative Procedure.

[Pd(DPPBz)(C_5H_4N-C^4)($N(C_6H_4$-4-*t*-$Bu)_2$)] (6). $KN(C_6H_4$-4-*t*-Bu_2 (33.6 mg, 0.110 mmol) in 2.0 mL of THF was added dropwise to a suspension of [Pd(DPPBz)(C_5H_4N-C^4)(Br)] (71.2 mg, 0.100 mmol) in 10.0 mL of THF in a 20 mL vial. The color of the mixture changed from colorless to deep red immediately. The mixture was allowed to stir for 10 min. When the reaction was complete, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy, the deep red solution was filtered through Celite to remove the solid. The solvent was evaporated, and toluene (1.0 ml) was added. The red crystalline product was obtained in 89% (81.0 mg) yield by layering the toluene solution with pentane and cooling at -35 °C. ^1H NMR (C_6D_6) δ 8.03-8.06 (m, 2 H), 7.46-7.51 (m, 4 H), 7.35-7.40 (m, 8 H), 7.25-7.28 (m, 2 H), 6.89-7.04 (m, 18 H), 6.80-6.89 (m, 2 H), 1.28 (s, 18 H); $^{31}P\{^1H\}$ NMR (THF) δ 51.6 (d, *J* = 25 Hz), 37.4 (d, *J* = 25 Hz). Anal. Calcd. For $C_{55}H_{54}N_2P_2Pd$: C, 72.48; H, 5.97; N, 3.07. Found: C, 72.23; H, 5.83; N, 2.96.



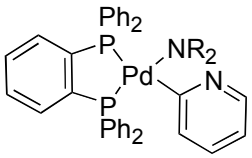
R = *p*-*t*-BuC_6H_4

[Pd(DPPBz)(C_5H_4N-C^3)($N(C_6H_4$-4-*t*-$Bu)_2$)] (7). The general procedure was followed, and crystallization from THF layered with pentane at -35 °C gave 73 mg (80%) of the product. ^1H NMR (C_6D_6) δ 8.75-8.77 (m, 1 H), 8.14 (dt, *J* = 4.4, 1.2 Hz, 1 H), 7.32-7.48 (m, 14 H), 7.12-7.27 (m, 2 H), 6.87-7.00 (m, 15 H), 6.79-6.81 (m, 2 H), 6.45 (dt, *J* = 7.2, 1.2 Hz, 1 H), 1.31 (s, 18 H); $^{31}P\{^1H\}$ NMR (THF) δ 52.0 (d, *J* = 24 Hz), 37.7 (d, *J* = 24 Hz). Anal. Calcd. For $C_{55}H_{54}N_2P_2Pd$: C, 72.48; H, 5.97; N, 3.07. Found: C, 72.23; H, 5.88; N, 2.91.



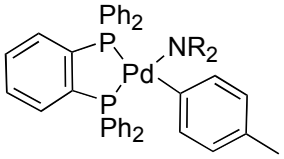
R = *p*-*t*-BuC_6H_4

[Pd(DPPBz)(C_5H_4N-C^2)($N(C_6H_4$-4-*t*-Bu)$_2$)] (8). The general procedure was followed, and crystallization from THF layered with pentane at -35 °C gave 65 mg (71%) of the product. ^{1}H NMR (C_6D_6) δ 8.20 (dd, *J* = 4.8, 1.6 Hz, 1 H), 8.70-8.72 (m, 4 H), 8.14 (dt, *J* = 8.4 Hz, 4 H), 7.47 (dd, *J* = 8.0, 3.4 Hz, 1 H), 7.21-7.36 (m, 6 H), 7.09 (d, *J* = 8.4 Hz, 4 H), 6.89-6.96 (m, 12 H), 6.81-6.85 (m, 2 H), 6.52-6.58 (m, 1 H), 6.23 (t, *J* = 6.4 Hz, 1 H), 1.34 (s, 18 H); ^{31}P {^{1}H} NMR (THF) δ 44.1 (d, *J* = 24 Hz), 32.2 (d, *J* = 24 Hz). Anal. Calcd. For $C_{55}H_{54}N_2P_2Pd$: C, 72.48; H, 5.97; N, 3.07. Found: C, 72.21; H, 5.88; N, 2.80.



R = *p*-*t*-BuC_6H_4

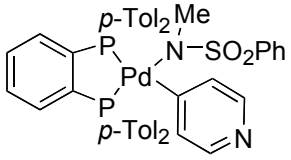
[Pd(DPPBz)(C_6H_4-4-M*e*)($N(C_6H_4$-4-*t*-Bu)$_2$)] (9). The general procedure was followed, and crystallization from toluene layered with pentane at -35 °C gave 69 mg (75%) of the product. ^{1}H NMR (THF-d_8) δ 7.68-7.72 (m, 1 H), 7.51-7.57 (m, 3 H), 7.26-7.44 (m, 15 H), 7.15-7.20 (m, 5 H), 6.86 (dt, *J* = 9.2, 2.4 Hz, 4 H), 6.66-6.69 (m, 2 H), 6.67 (d, *J* = 8.8 Hz, 4 H), 6.25 (dd, J = 8.0, 2.0 Hz, 2 H), 1.94 (s, 3 H), 1.18 (s, 18 H); ^{31}P {^{1}H} NMR (THF) δ 43.3 (d, *J* = 22 Hz), 28.5 (d, *J* = 21 Hz). Anal. Calcd. For $C_{57}H_{57}NP_2Pd$: C, 74.06; H, 6.21; N, 1.52. Found: C, 74.36; H, 5.93; N, 1.46.



R = *p*-*t*-BuC_6H_4

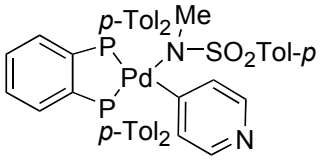
Synthesis of Palladium Amideates.

Synthesis of [Pd(DTPBz)(C^4-C_5H_4N)(N(Me)(SO_2Ph))] (10). [Pd(DTPBz)(C_5H_4N-C^4)(Br)] **(5)** (76.8 mg, 0.100 mmol) and KN(Me)(SO_2Ph) (35 mg, 0.167 mmol) were placed in a 20 mL vial. Dichloromethane (5 mL) was added, and the mixture was stirred at room temperature for 2 h. The solvent was removed in vacuum. THF (10 mL) was added, and the resulting solution was filtered through Celite. The Celite was washed with 6 mL of THF, and the volume was reduced under vacuum to 1.0 mL. The white crystalline product was obtained in 72% (68.0 mg) yield by layering the toluene solution with pentane and cooling at -35 °C. ^{1}H NMR (C_6D_6) δ 8.14 (t, *J* = 4.0 Hz, 2 H), 7.92 (d, *J* = 8.0 Hz, 2 H), 7.90 (d, *J* = 8.0 Hz, 2 H), 7.66 (d, *J* = 8.5 Hz, 2 H), 7.38-7.46 (m, 7 H), 7.30-7.32 (m, 1 H), 6.99 (d, *J* = 8.0 Hz, 4 H), 6.81-6.93 (m, 4 H), 6.75 (d, *J* = 8.0 Hz, 4 H), 2.60 (d, *J* = 3.0 Hz, 3 H), 1.96 (s, 6 H), 1.89 (s, 6 H); ^{31}P {^{1}H} NMR (CH_2Cl_2) δ 51.2 (d, *J* = 27 Hz), 39.1 (d, *J* = 27 Hz).

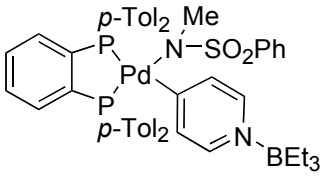


Synthesis of [Pd(DTPBz)(C^4-C_5H_4N)(N(Me)(SO_2Tol-*p*))] (11). [Pd(DTPBz)(C_5H_4N-C^4)(Br)] **(5)** (76.8 mg, 0.100 mmol) and KN(Me)(SO_2Tol-*p*) (35 mg, 0.167 mmol) were placed in a 20 mL vial. Dichloromethane (5 mL) was added, and the mixture was stirred at room temperature for 0.5 h. The solvent was removed in vacuum. THF (10 mL) was added, and the resulting solution was filtered through Celite. The Celite was washed with 6 mL of THF, and the volume was reduced under vacuum to 1.0 mL. The white crystalline

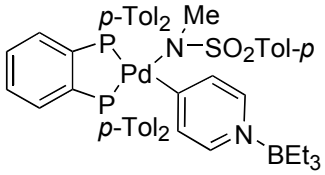
product was obtained in 85% (74.0 mg) yield by layering the THF solution with pentane and cooling at -35 ºC. ^{1}H NMR (C_6D_6) δ 8.32 (t, *J* = 4.4 Hz, 2 H), 8.11 (d, *J* = 8.0 Hz, 2 H), 8.08 (d, *J* = 8.0 Hz, 2 H), 7.73 (d, *J* = 8.4 Hz, 2 H), 7.59-7.62 (m, 3 H), 7.58 (d, *J* = 8.0 Hz, 2 H), 7.55 (d, *J* = 8.0 Hz, 2 H), 7.47(t, *J* = 7.6 Hz, 1 H), 7.16 (d, *J* = 6.8 Hz, 4 H), 6.94-6.99 (m, 2 H), 6.90 (d, *J* = 6.4 Hz, 4 H), 6.89 (d, *J* = 7.2 Hz, 2 H), 2.60 (d, *J* = 2.5 Hz, 3 H), 1.96 (s, 6 H), 1.89 (s, 6 H), 1.85 (s, 3 H); ^{31}P {^{1}H} NMR (CH_2Cl_2) δ 51.2 (d, *J* = 27 Hz), 39.1 (d, *J* = 27 Hz). Anal. Calcd. For $C_{47}H_{46}BN_2O_2P_2PdS$: C, 64.79; H, 5.32; N, 3.22. Found: C, 64.85; H, 5.64; N, 2.92.



Synthesis of [Pd(DTPBz)(C^4-C$_5$H$_4$N-BEt$_3$)(N(Me)(SO$_2$Ph))] (12). [Pd(DTPBz)(C^4-C$_5$H$_4$N)(N(Me)(SO$_2$Ph))] (77 mg, 0.10 mmol) was dissolved in 3 mL of THF. A 1.0 M solution of triethylborane in hexane (100 μL) was added. The color of the solution gradually changed from pale yellow to pale pink. After 0.5 h, the solution was filtered through a short plug of Celite, and the volume was reduced under vacuum to 1.0 mL. The white crystalline product was obtained in 80% (66.0 mg) yield by layering the THF solution with pentane and cooling at -35 ºC. ^{1}H NMR (C_6D_6) δ 7.87 (d, *J* = 8.0 Hz, 2 H), 7.84 (d, *J* = 8.0 Hz, 2 H), 7.70 (d, *J* = 4.5 Hz, 2 H), 7.61 (d, *J* = 7.0 Hz, 2 H), 7.42 (t, *J* = 6.5 Hz, 2 H), 7.47-7.55 (m, 1 H), 7.37 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.22-7.25 (m, 1 H), 6.96-6.99 (m, 2 H), 6.97 (d, *J* = 7.5 Hz, 4 H), 6.88 (t, *J* = 7.5 Hz, 1 H), 6.78-6.85 (m, 6 H), 2.41 (d, *J* = 3.0 Hz, 3 H), 1.93 (s, 6 H), 1.91 (s, 6 H), 1.09 (t, *J* = 7.5 Hz, 9 H), 0.87 (q, *J* = 7.5 Hz, 6 H); ^{31}P {^{1}H} NMR (THF) δ 50.0 (d, *J* = 27 Hz), 36.7 (d, *J* = 27 Hz). ^{11}B NMR (C_6D_6) δ 1.0. Anal. Calcd. For $C_{52}H_{59}BN_2O_2P_2PdS$: C, 65.38; H, 6.23; N, 2.93. Found: C, 65.55; H, 6.51; N, 2.71.



Synthesis of [Pd(DTPBz)(C^4-C$_5$H$_4$N-BEt$_3$)(N(Me)(SO$_2$Tol-*p*))] (13). [Pd(DTPBz)(C^4-C$_5$H$_4$N)(N(Me)(SO$_2$Tol-*p*))] (87 mg, 0.10 mmol) was dissolved in 3 mL of THF. A 1.0 M solution of triethylborane in hexane (100 μL) was added. The color of the solution gradually changed from pale yellow to pale pink. After 0.5 h, the solution was filtered through a short plug of Celite, and the volume was reduced under vacuum to 1.0 mL. The white crystalline product was obtained in 89% (81.0 mg) yield by layering the THF solution with pentane and cooling at -35 ºC. ^{1}H NMR (C_6D_6) δ 7.98 (d, *J* = 8.5 Hz, 2 H), 7.96 (d, *J* = 8.0 Hz, 2 H), 7.80 (dd, *J* = 6.0, 2.0 Hz, 2 H), 7.64 (d, *J* = 8.5 Hz, 2 H), 7.54 (t, *J* = 6.0 Hz, 2 H), 7.47-7.55 (m, 2 H), 7.48 (d, *J* = 8.0 Hz, 2 H), 7.46 (d, *J* = 8.0 Hz, 2 H), 7.34-7.38 (m, 1 H), 7.09 (dd, *J* = 8.0, 1.5 Hz, 4 H), 6.94 (dd, *J* = 4.5, 3.0 Hz, 1 H), 6.86-6.92 (m, 6 H), 2.53 (d, *J* = 3.0 Hz, 3 H), 2.02 (s, 6 H), 1.99 (s, 6 H), 1.98 (s, 3 H), 1.17 (t, *J* = 7.5 Hz, 9 H), 0.95 (q, *J* = 7.5 Hz, 6 H); ^{31}P {^{1}H} NMR (THF) δ 53.1 (d, *J* = 26 Hz), 40.2 (d, *J* = 26 Hz). ^{11}B NMR (C_6D_6) δ -0.01. Anal. Calcd. For $C_{53}H_{61}BN_2O_2P_2PdS$: C, 65.67; H, 6.34; N, 2.89. Found: C, 65.47; H, 6.28; N, 2.77.



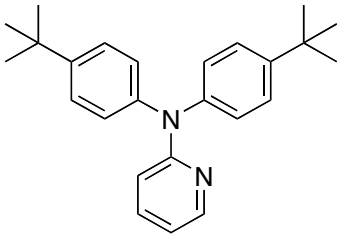
Reductive Elimination Reactions. A typical procedure is provided for reaction of [Pd(DPPBz)(C_5H_4N-C^2)(N(C_6H_4-4-*t*-Bu)$_2$)] complex **8**. Into an NMR tube with a Teflon-lined screw-cap was placed 0.5 ml of a C_6D_6 solution containing complex **8** (9.0 mg, 0.010 mmol), PPh_3 (39.4 mg, 0.150 mmol), and trimethoxybenzene (10 μL, 0.5 M in C_6D_6). A ^{1}H NMR spectrum was obtained of this initial mixture. The tube was then placed in an oil bath at 70 ºC for 5 h, after which time ^{1}H NMR spectroscopy showed the formation of reductive elimination product in 95% yield. The yield of reductive elimination product was determined by integrating the methyl resonances of the palladium complex and the methyl protons of the triarylamine with respect to the internal standard. Yields for reactions of the other amido and sulfonamido complexes are provided in the tables of the body of the paper.

Measurement of the Rate Constants for Reductive Elimination in the Presence of Lewis Acids: Representative Procedure for Isolated Complex with Lewis Acid. Into an NMR tube with a Teflon-lined screw-cap was placed 0.5 ml of a toluene-d_8 solution containing complex **13** (9.7 mg, 0.010 mmol), P(Ph-d_5)$_3$ (27 mg, 0.10 mmol), and trimethoxybenzene (10 μL, 0.5 M in toluene-d_8). The sample was heated at 90 ºC, and ^{1}H NMR spectra were obtained every 5 min for at least 5 half-lives by an automated acquisition program.

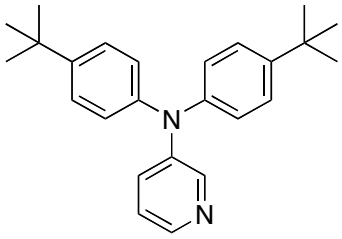
Representative Procedure for Reductive Eliminations with Added Lewis Acid. Into an NMR tube with a Teflon-lined screw-cap was placed 0.5 ml of a toluene-d_8 solution containing complex **11** (9.0 mg, 0.010 mmol) and BPh_3 (1.5 mg, 0.010 mmol). The solid gradually dissolved to give a clear pale pink solution. P(Ph-d_5)$_3$ (27 mg, 0.10 mmol), and trimethoxybenzene (10 μL, 0.5 M in toluene-d_8) were then added. The sample was heated at 70 ºC, and ^{1}H NMR spectra were obtained every 5 min for at least 5 half-lives by an automated acquisition program.

Independent Synthesis of the Products from Reductive Elimination.
General Procedure for the Preparation of 2-(Di-*p*-*t*-butylphenylamino)pyridine. A typical procedure is given for the preparation of *N*,*N*-di-*p*-*t*-butylphenyl-amino-2-pyridine.

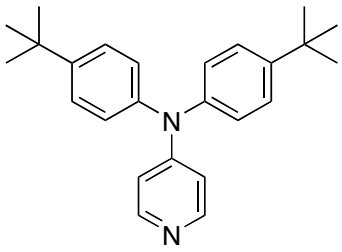
2-(Di-*p*-*t*-butylphenylamino)pyridine. Into a 20 mL Schlenk tube was placed Pd(dba)$_2$ (12 mg, 0. 020 mmol), BINAP (25 mg, 0.040 mmol), NaO*t*Bu (58 mg, 0.60 mmol), and di-*p*-*t*-butylphenylamine (169 mg, 0.600 mmol). The tube was sealed with septum and then evacuated and filled with nitrogen three times. 2-Bromopyridine (79.0 mg, 0.500 mmol) and toluene (10 mL) were then added. The reaction mixture was stirred for 12 h at 70 °C. The reaction mixture was allowed to cool to room temperature before filtered through a short plug of Celite. The solvent was evaporated, and the crude product isolated by eluting with hexane/ethyl acetate (95/5) to give 155 mg (87%) of the product as a white solid. ^{1}H NMR (C_6D_6) δ 8.20 (d, *J* = 4.8 Hz, 1 H), 7.24 (d, *J* = 8.8 Hz, 4 H), 7.20 (d, *J* = 8.4 Hz, 4 H), 6.97 (ddd, *J* = 8.0, 7.2, 2.0 Hz, 1 H), 6.69 (d, *J* = 8.4 Hz, 1 H), 6.39 (dd, *J* = 7.2, 4.8 Hz, 1 H), 1.20 (s, 18 H); ^{13}C NMR (C_6D_6) δ 159.57, 148.45, 147.18, 144.18, 136.88, 126.81, 126.40, 115.50, 112.65, 34.34, 31.46. Anal. Calcd. For $C_{25}H_{30}N_2$: C, 83.75; H, 8.43; N, 7.81. Found: C, 83.68; H, 8.47; N, 7.58.



3-(Di-*p*-*t*-butylphenylamino)pyridine. The general procedure was followed to give 128 mg (72%) of the product. ^{1}H NMR (C_6D_6) δ 8.72 (d, *J* = 2.4 Hz, 1 H), 8.24 (dd, *J* = 4.8, 1.2 Hz, 1 H), 7.14 (d, *J* = 8.4 Hz, 4 H), 7.10-7.13 (m, 1 H), 7.02 (d, *J* = 8.4 Hz, 4 H), 6.65 (dd, *J* = 8.4, 4.8 Hz, 1 H), 1.21 (s, 18 H); ^{13}C NMR (C_6D_6) δ 146.43, 145.24, 144.95, 144.84, 142.99, 128.53, 126.70, 124.58, 123.48, 34.28, 31.45. Anal. Calcd. For $C_{25}H_{30}N_2$: C, 83.75; H, 8.43; N, 7.81. Found: C, 83.69; H, 8.46; N, 7.58.

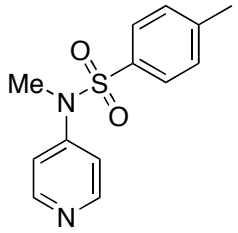


4-(Di-*p*-*t*-butylphenylamino)pyridine. The general procedure was followed to give 135mg (76%) of the product. ^{1}H NMR ($CDCl_3$) δ 8.17 (dd, *J* = 6.0, 1.5 Hz, 2 H), 7. (d, *J* = 7.2, Hz, 4 H), 7.10 (d, *J* = 7.2 Hz, 4 H), 6.67 (dd, *J* = 4.5, 1.5 Hz, 2 H), 1.30 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 153.84, 150.0, 148.49, 142.33, 126.57, 126.24, 111.94, 34.45, 31.31. Anal. Calcd. For $C_{25}H_{30}N_2$: C, 83.75; H, 8.43; N, 7.81. Found: C, 83.56; H, 8.63; N, 7.68.

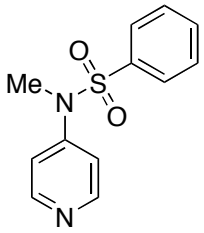


General Procedure for the Preparation of *N*-4-Pyridyl-*N*-Methylsulfonamine. A typical procedure is given for the preparation of *N*-4-Pyridyl-*N*-Methyl-p-tolylsulfonylamine.

***N*-4-Pyridyl-*N*-Methyl-*p*-toluenesulfonamine.** Into a small round bottom flask was placed 4-(dimethylamino)pyridine (10 mg, 0. 082 mmol), 4-(methylamino)pyridine (108 mg, 1.00 mmol) and *p*-toluenesulfonyl chloride (191 mg, 1.00 mmol). Pyridine (2.0 mL) was then added. The reaction mixture was stirred for 18 h at 60 °C. The reaction mixture was allowed to cool to room temperature before the solvent was evaporated. The crude product was isolated by silica gel chromatography eluting with ethyl acetate to give 236 mg (90%) of the product as a pale yellow liquid. ^{1}H NMR (C_6D_6) δ 8.49 (d, *J* = 4.3 Hz, 2 H), 7.44 (d, *J* = 7.5 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 7.14 (dd, *J* = 4.5, 1.5 Hz, 2 H), 3.20 (s, 3 H), 2.38 (s, 3 H). ^{13}C NMR ($CDCl_3$) δ 150.20, 148.58, 144.18, 133.05, 129.49, 127.10, 117.64, 36.06, 21.24. Anal. Calcd. For $C_{10}H_{14}N_2O_2S$: C, 59.52; H, 5.38; N, 10.68. Found: C, 59.29; H, 5.54; N, 10.45.

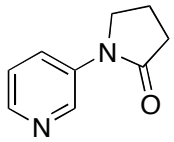


***N*-4-Pyridyl-*N*-Methyl-benzenesulfonamine.** The general procedure was followed to give 211 mg (85%) of the product as a pale yellow liquid ^{1}H NMR ($CDCl_3$) δ 8.49 (dd, *J* = 5.0, 1.5 Hz, 2 H), 7.55-7.60 (m, 3 H), 7.44 (t, *J* = 7.5 Hz, 2 H), 7.13 (dd, *J* = 5.0, 1.5 Hz, 2 H), 3.21 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 150.58, 148.75, 136.26, 133.40, 129.09, 127.36, 118.53, 36.38. Anal. Calcd. For $C_{12}H_{12}N_2O_2S$: C, 58.05; H, 4.37; N, 11.28. Found: C, 58.42; H, 4.77; N, 10.94.

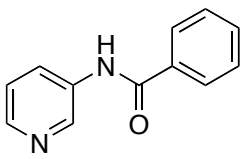


General Procedure for the Palladium-Catalyzed Amidation of Heteroaryl Halides in the Presence of Lewis Acids. A typical procedure is given for the preparation of *N*-3-pyridyl-pyrrolidinone.

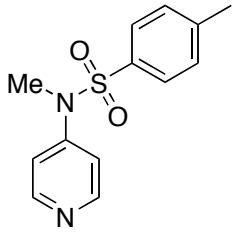
***N*-3-Pyridyl-pyrrolidinone.** A 1.0 M solution of BEt_3 in hexane (1.0 mL, 1.0 mmol) was added dropwise to a solution of 3-bromopyridine (158 mg, 1.00 mmol) in diethyl ether (2.0 mL). The mixture was stirred for 2 h at room temperature. The solvent was then evaporated under vacuum. Toluene (1.0 mL) was added. The toluene solution was added to a vial placed $Pd(dba)_2$ (11.6 mg, 0.020 mmol), Xantphos (11.8 mg, 0.020 mmol), K_3PO_4 (254 mg, 1.20 mmol), pyrrolidinone (102 mg, 1.20 mmol). The vial was sealed with a cap containing a PTFE septum, and the mixture was stirred at 110 °C for 24 h until the 3-bromopyridine was consumed, as determined by GC/MS. The reaction mixture was allowed to cool to room temperature. After filtration and evaporation of the solvent, the residue was purified by chromatography on silica gel (ethyl acetate/methanol = 90/10) to give 136 mg (84%) of *N*-3-pyridyl-pyrrolidinone as a white solid. ^{1}H NMR ($CDCl_3$) δ 8.64 (d, *J* = 2.5 Hz, 1 H), 8.29 (dd, *J* = 5.0, 1.5 Hz, 1 H), 7.42 (ddd, *J* = 8.5, 2.5, 1.5 Hz, 1 H), 7.20 (dd, *J* = 8.5, 5.0 Hz, 1 H), 3.80 (t, *J* = 7.5 Hz, 2 H), 2.53 (t, *J* = 7.5 Hz, 2 H), 2.12 (quint, *J* = 7.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 174.62, 145.14, 145.36, 135.86, 126.67, 123.20, 47.71, 32.12, 17.80.



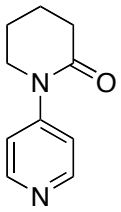
***N*-3-Pyridylbenzamide.** The general procedure, eluting with ethyl acetate/methanol = 90/10, gave 147 mg (74%) of the product as a pale yellow liquid ^{1}H NMR (DMSO-*d6*) δ 10.46 (s, 1 H), 8.93 (s, 1 H), 8.30 (d, *J* = 1.5 Hz, 1 H), 8.19 (d, *J* = 7.5 Hz, 1 H), 7.96 (d, *J* = 8.0 Hz, 2 H), 7.59 (d, *J* = 7.0 Hz, 1 H), 7.53 (t, *J* = 7.5 Hz, 2 H), 7.37 (dd, *J* = 8.0, 4.5 Hz, 1 H); ^{13}C NMR (DMSO-*d6*) δ 166.03, 144.65, 142.04, 135.89, 134.41, 131.97, 128.55, 127.80, 127.35, 123.61.



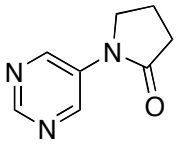
***N*-4-Pyridyl-*N*-Methyl-benzenesulfonamine.** The general procedure, eluting with ethyl acetate, gave 239 mg (91%) of the product as a pale yellow liquid. ^{1}H NMR (C_6D_6) δ 8.49 (d, *J* = 4.3 Hz, 2 H), 7.44 (d, *J* = 7.5 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 7.14 (dd, *J* = 4.5, 1.5 Hz, 2 H), 3.20 (s, 3 H), 2.38 (s, 3 H). ^{13}C NMR ($CDCl_3$) δ 150.20, 148.58, 144.18, 133.05, 129.49, 127.10, 117.64, 36.06, 21.24. Anal. Calcd. For $C_{10}H_{14}N_2O_2S$: C, 59.52; H, 5.38; N, 10.68. Found: C, 59.29; H, 5.54; N, 10.45.



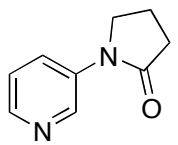
***N*-4-Pyridyl-valerolactam.** The general procedure, eluting with ethyl acetate/methanol = 80/20, gave 155 mg (88%) of the product as a white solid. ^{1}H NMR ($CDCl_3$) δ 8.56 (d, *J* = 5.0 Hz, 2 H), 7.29 (d, *J* = 5.0 Hz, 2 H), 3.68 (t, *J* = 6.0 Hz, 2 H), 2.57 (t, *J* = 6.5 Hz, 2 H), 1.89-1.98 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 170.15, 150.45, 150.08, 118.93, 49.82, 33.24, 23.21, 21.04. Anal. Calcd. For $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.90. Found: C, 67.88; H, 6.82; N, 15.88.



***N*-3-Pyrimidinyl-pyrrolidinone.** Following the above procedure (ethyl acetate/methanol = 90/10) to give 92 mg (57%) of the product as a white sold. ^{1}H NMR ($CDCl_3$) δ 9.04 (s, 2 H), 8.91 (s, 1 H), 3.83 (t, *J* = 7.0 Hz, 2 H), 2.58 (t, *J* = 8.0 Hz, 2 H), 2.12 (quint, *J* = 7.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 174.87, 153.79, 146.70, 134.49, 46.77, 31.71, 17.97. Anal. Calcd. For $C_8H_9N_3O$: C, 58.88; H, 5.56; N, 25.75. Found: C, 59.16; H, 5.41; N, 25.48.



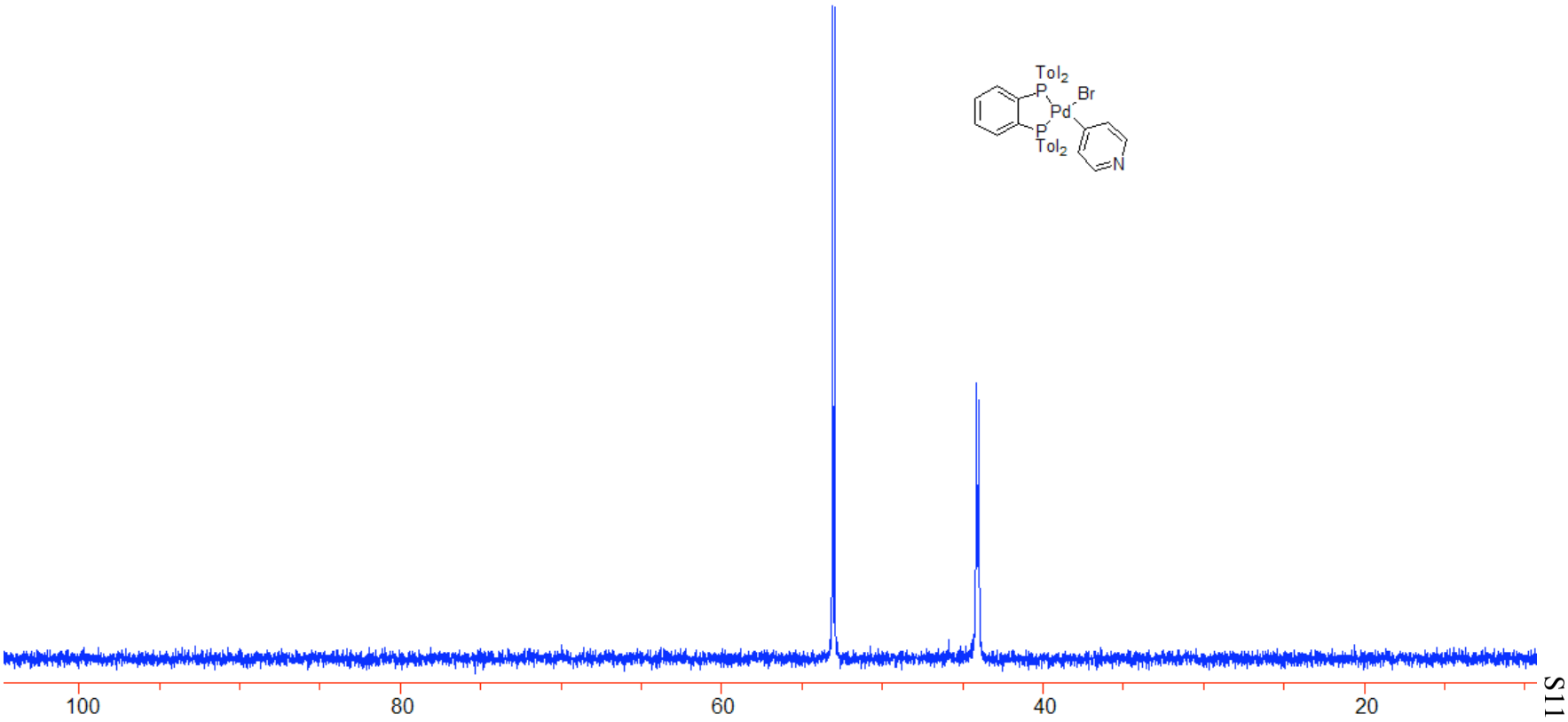
Procedure for the Palladium-Catalyzed Amidation of Heteroaryl Halides in the Presence of Catalytic Amount of the Lewis Acids. Into a vial was added 3-bromopyridine (0.126 mg, 0.800 mmol) and 3-bromopyridine triethylborane complex (52.0 mg, 0.200 mmol) and pyrrolidinone (102 mg, 1.20 mmol). $Pd(dba)_2$ (11.6 mg, 0.020 mmol), Xantphos (11.8 mg, 0.020 mmol), K_3PO_4 (254 mg, 1.20 mmol) were then added, followed by toluene (1.0 ml) and the stirring bar. The vial was sealed with a cap containing a PTFE septum, and the mixture was stirred at 110 °C for 1.5 h until the 3-bromopyridine was consumed, as determined by GC/MS. The reaction mixture was allowed to cool to room temperature. After filtration and evaporation of the solvent, the residue was purified by chromatography on silica gel (ethyl acetate/methanol = 90/10) to give 133 mg (83%) of *N*-3-pyridyl-pyrrolidinone as a white solid.



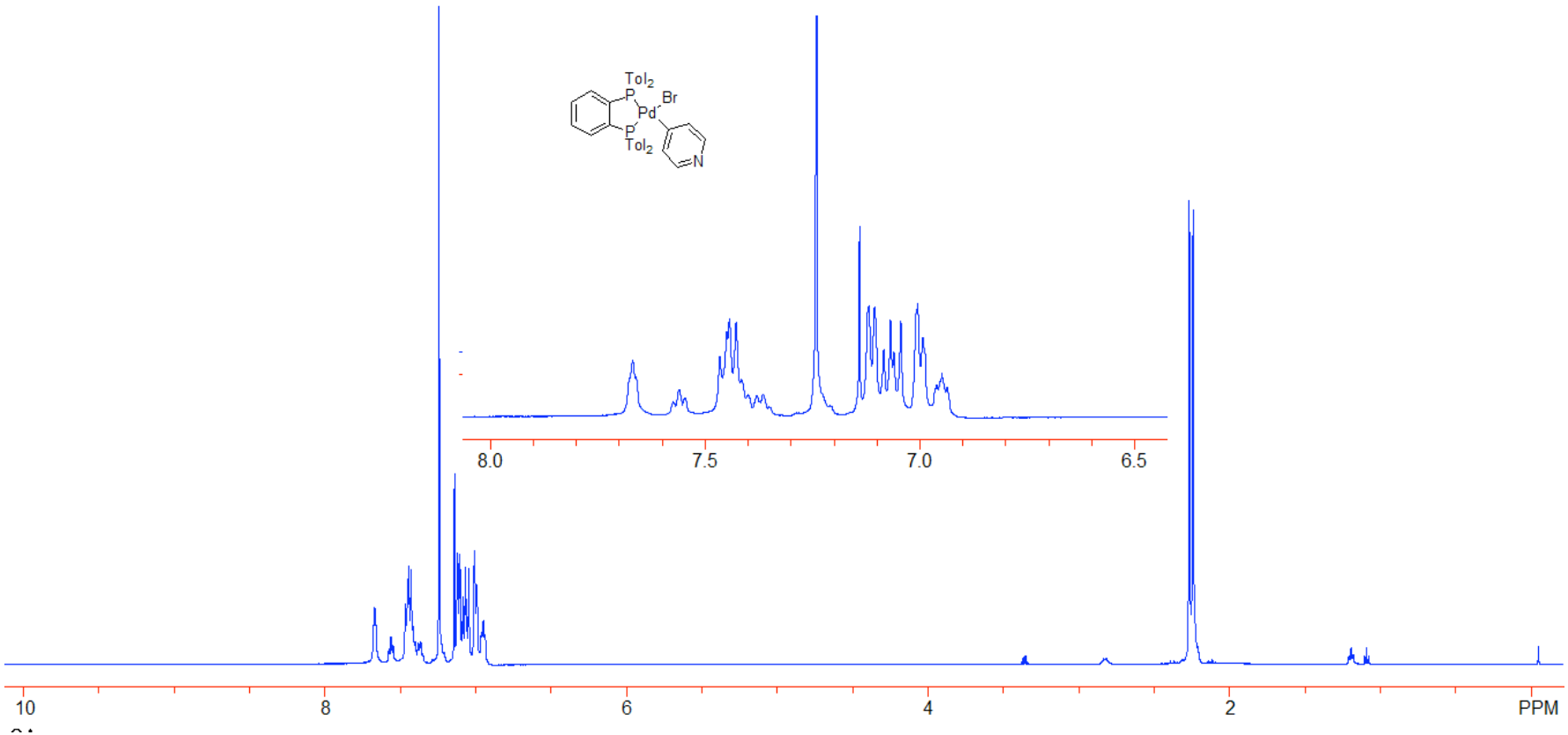
References:

1. (a) Isobe, K.; Nanjo, K.; Nakamura, Y.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2141.
   (b) Isobe, K.; Nanjo, K.; Nakamura, Y.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1986**, *60*, 149.
2. Culkin, D. A.; Hartwig, J. F. *Organometallics* **2004**. *23,* 3398-3416.

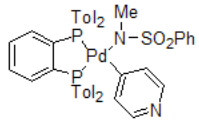
[Pd(DTPBz)(C_5H_4N-C^4)(Br)] (5)

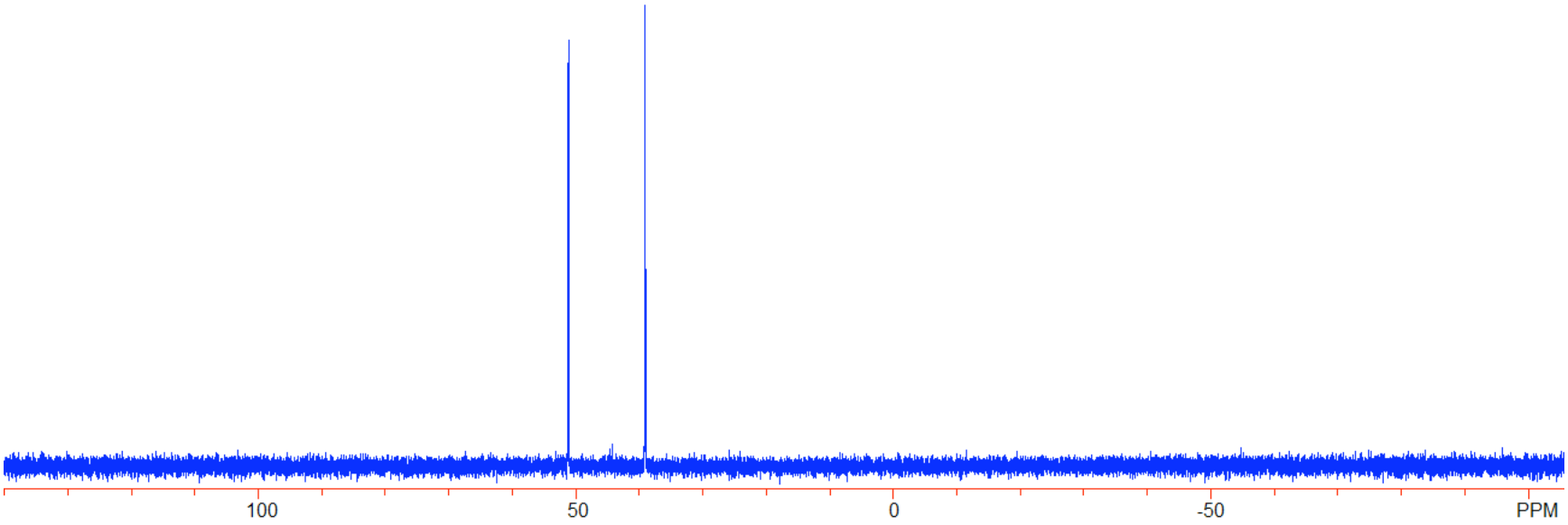


[Pd(DTPBz)(C_5H_4N-C^4)(Br)] (5)

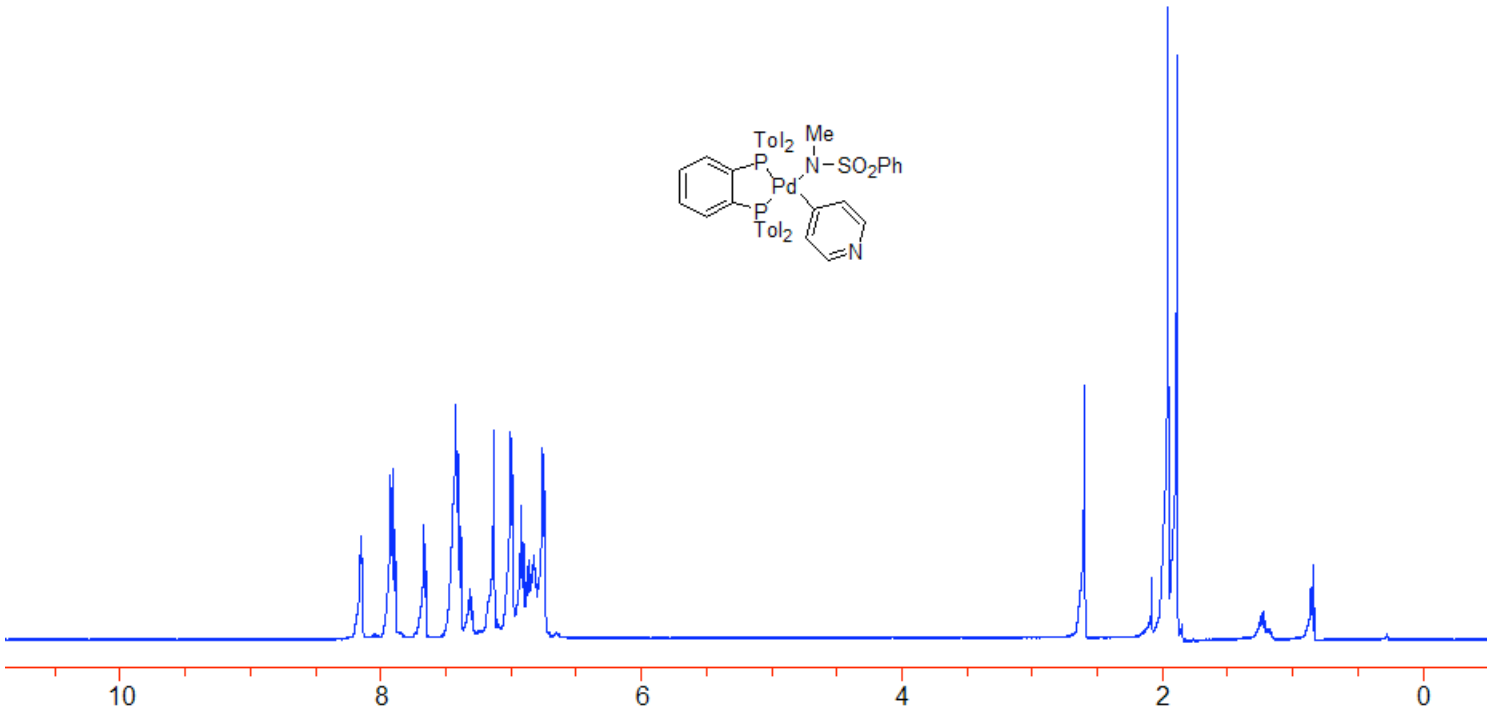


[Pd(DTPBz)(C^4-C_5H_4N)(N(Me)(SO_2Ph))] (10)

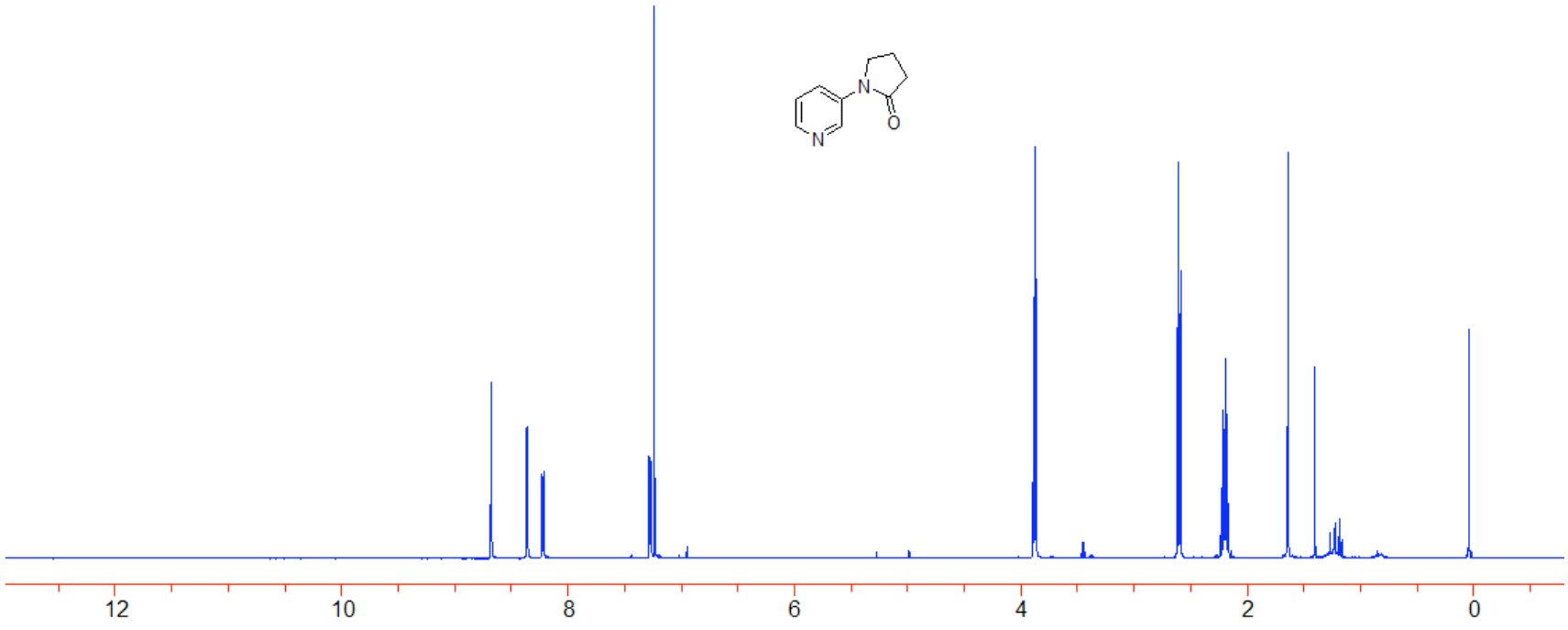




[Pd(DTPBz)(C^4-C_5H_4N)(N(Me)(SO_2Ph))] (10)



_N_-3-Pyridyl-pyrrolidinone



N-3-Pyridyl-pyrrolidinone