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Supporting Information

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A Highly Active Catalyst for Suzuki-Miyaura Cross-Coupling Reactions of Heteroaryl Compounds**

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Experimental Details

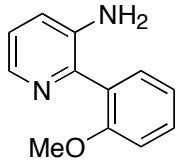
Reagents. All reactions were carried out under an argon atmosphere. $Pd(OAc)_2$ and Pd_2dba_3 were obtained from Englehard and used without further purification. n-Butanol (HPLC grade) was purchased from Alfa Aesar. *Sec*-Butanol (anhydrous) and acetonitrile (anhydrous) were purchased from Aldrich. Commercially available materials were used without further purification unless otherwise noted. SPhos **1** and XPhos **2** were synthesized in our laboratories, but are commercially available from Aldrich Chemical Co. or Strem Chemicals, Inc. Aryl halides were purchased from Aldrich Chemical Co. Liquid aryl bromides were purified through a pad of basic alumina prior to use. Boron reagents were purchased from Aldrich or Frontier Scientific. Anhydrous granular potassium phosphate and potassium carbonate were purchased from Mallinckrodt Chemicals and ground with a mortar and pestle and stored in a bench-top dessicator.

Analytical Methods. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis. Several elemental analysis are pending: copies of ^{1}H NMR spectra are included for those examples. Known compounds were characterized by ^{1}H NMR and melting points (for solids) and compared to their literature values. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz or Bruker 400 MHz. Infrared spectra were recorded on a Perkin-Elmer Model 2000 FT-IR using NaCl plates (thin film). Elemental analyses were preformed by Atlantic Microlabs Inc., Norcros, GA. All ^{1}H NMR experiments are reported in ≥ units, parts per million (ppm) downfield of TMS and were measured relative to the signals for the residual benzene (7.16 ppm), chloroform (7.26 ppm), dimethylsulfoxide (2.50 ppm) or methanol (3.31 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual chloroform (77 ppm), dimethylsulfoxide (39.5 ppm) or methanol (49 ppm) and were obtained with ^{1}H decoupling. Melting points were obtained on a Mel-Temp capillary melting point apparatus. Gas chromatographic analyses were preformed on Hewlett-Packard 6890 gas chromatography instrument with a FID detector using 25m x 0.20 mm capillary column with cross-linked methyl siloxane as a stationary phase.

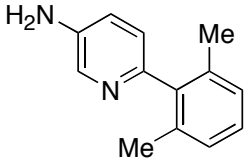
The yields in tables 1-3 refer to isolated yields (average of two runs) of compounds estimated to be ≥ 95% pure as determined by ^{1}H NMR and GC analysis and/or combustion analysis.

Table 1: General Procedure A for Suzuki-Miyaura coupling. A disposable tube with a screw cap, Teflon septum and stir bar was charged with $Pd(OAc)_2$ (2.2 mg, 0.010 mmol, 1 mol %), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (8.3 mg, 0.0200 mmol, 2 mol %), aryl halide (1.00 mmol), boronic acid (1.20-1.50 mmol) and K_2CO_3 (276-690 mg, 2.00-5.00 mmol). The tube was evacuated and back-filled with argon (this was repeated two additional times). The solvent/solvents were added (when degassed water was used, it was sonicated under vacuum for 2 min. prior to addition) and the reaction mixture was allowed to stir at the noted temperature for the indicated period of time. After cooling to room temperature, the products were extracted from the water layer with diethyl ether or ethyl acetate, dried over $MgSO_4$, filtered through celite and concentrated to dryness and

purified by column chromatography on silica gel (eluting with hexanes/ethyl acetate mixtures).

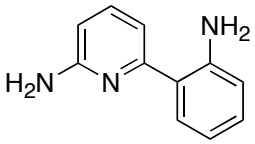


2-(2-Methoxy-phenyl)-pyridin-3-ylamine (Table 1, Entry 1). The general procedure was used with 3-amino-2-chloro-pyridine (128 mg, 1.00 mmol), 2-methoxyphenylboronic acid (225 mg, 1.50 mmol), $Pd(OAc)_2$ (2.3 mg, 0.010 mmol, 1 mol %), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (8.3 mg, 0.020 mmol, 2 mol %), K_2CO_3 (414 mg, 3.00 mmol), water (1.0 mL), acetonitrile (1.5 mL), 12 h, 100 °C. The product was purified by column chromatography on silica gel (eluting with ethyl acetate) to provide the title compound as a light yellow solid (177 mg, 95%). Mp = 97-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12 (dd, J = 1.2 Hz, J = 4.4 Hz, 1H), 7.36-7.40 (m, 2H), 7.04-7.09 (m, 2H), 6.99-7.01 (m, 2H), 3.79 (s, 3H), 3.76 (br-s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.6, 144.1, 141.2, 139.8, 131.7, 129.9, 127.8, 123.1, 122.5, 121.5, 111.4, 55.9. IR (neat, cm^{-1}): 3452, 3325, 3200, 3056, 3009, 2964, 2934, 2836, 1632, 1600, 1580, 1494, 1456, 1310, 1273, 1238, 1179, 1140, 1123, 1070, 1052, 1018, 796, 755. Anal. Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04. Found: C, 71.67; H, 6.10.

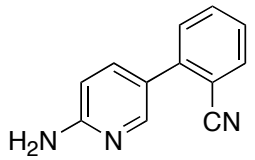


6-(2,6-Dimethyl-phenyl)-pyridin-3-ylamine (Table 1, Entry 2). The general procedure was used with 3-amino-6-chloro-pyridine (128 mg, 1.00 mmol), 2,6-dimethylphenylboronic acid (300 mg, 2.00 mmol), $Pd(OAc)_2$ (4.6 mg, 0.020 mmol, 2 mol %), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (16.8 mg, 0.040 mmol, 4 mol %), K_2CO_3 (414 mg, 3.00 mmol), water (1.0 mL), acetonitrile (1.5 mL), 14 h, 100 °C. The product was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes, 9:1) to provide the title compound as a light beige solid (163 mg, 82%). Mp = 129-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (d, J = 2.8 Hz, 1H), 7.15 (m, 1H), 6.99-7.08 (m, 4H), 3.72 (br-s, 2H), 2.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.9, 140.9, 140.6, 137.2, 136.6, 127.6,

127.5, 124.5, 122.2, 20.4. IR (neat, cm^{-1}): 3446, 3322, 3194, 1631, 1596, 1565, 1494, 1466, 1407, 1297, 838, 772.

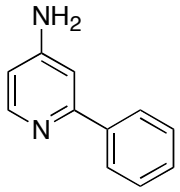


6-(2-Amino-phenyl)-pyridin-2-ylamine (Table 1, Entry 3). The general procedure was used with 2-amino-6-chloropyridine (128 mg, 1.00 mmol), 2-amino-phenylboronic acid (205 mg, 1.50 mmol), $Pd(OAc)_2$ (2.3 mg, 0.010 mmol, 1.0 mol %), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (8.3 mg, 0.020 mmol, 2 mol %), K_2CO_3 (414 mg, 3.00 mmol), water (2.0 mL), acetonitrile (2.0 mL), 10 h, 100 °C. The product was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes, 4:1) to provide the title compound as a light brown solid (177 mg, 95%). Mp = 119-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (t, J = 7.6 Hz, 1H), 7.44 (dd, J = 1.6 Hz, J = 8.0 Hz, 1H), 7.14 (td, J = 1.6 Hz, J = 8.4 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.73-7.79 (m, 2H), 6.42 (d, J = 8.0 Hz, 1H), 5.41 (br-s, 2H), 4.30 (br-s, 2H).). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.0, 157.1, 145.9, 138.9, 129.7, 129.6, 123.4, 117.9, 117.1, 113.1, 106.2. IR (neat, cm^{-1}): 3429, 3371, 3194, 1652, 1597, 1563, 1467, 1453, 1420, 1269, 759.

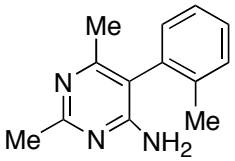


2-(6-Amino-pyridin-3-yl)-benzonitrile (Table 1, Entry 4). The general procedure was used with 2-amino-5-chloro-pyridine (64 mg, 0.500 mmol), 2-cyanophenylboronic acid (110 mg, 0.750 mmol), $Pd(OAc)_2$ (2.3 mg, 0.010 mmol, 2 mol %), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (8.3 mg, 0.020 mmol, 4 mol %), K_3PO_4 (212 mg, 1.00 mmol), 1,4-dioxane (2.5 mL), 14 h, 100 °C. The product was purified by column chromatography on silica gel (eluting with ethyl acetate) to provide the title compound as a white solid (77 mg, 79%). Mp = 144-145 °C ^{1}H NMR (400 MHz, $CDCl_3$/d^4-MeOH) δ: 8.08 (d, J = 2.0 Hz, 1H), 7.73 (dd, J = 0.8 Hz, J = 7.6 Hz, 1H), 7.64 (m, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.42 (td, J = 0.8 Hz, J = 7.6 Hz, 1H), 6.65 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.4,

147.7, 143.4, 139.3, 134.7, 134.3, 130.5, 128.4, 124.2, 119.6, 111.4, 109.7. IR (neat, cm^{-1}): 3450, 3362, 2224, 1624, 1510, 1480, 1440, 1393, 823, 762.

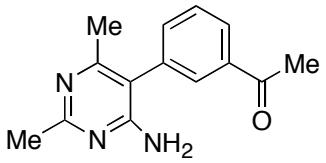


2-Phenyl-pyridin-4-ylamine (Table 1, Entry 5). The general procedure was used with 4-amino-2-chloropyridine (129 mg, 1.00 mmol), phenylboronic acid (181 mg, 1.50 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 0.5 mol %), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (4.1 mg, 0.010 mmol, 1 mol %), K_2CO_3 (414 mg, 3.00 mmol), water (1.0 mL), acetonitrile (1.5 mL), 13 h, 100 °C. The product was purified by column chromatography on silica gel (eluting with methanol/ethyl acetate, 0.3:9.7) to provide the title compound as a light beige solid (158 mg, 92%). Mp = 123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (d, J = 5.6 Hz, 1H), 7.91 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.2 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 6.96 (d, J = 2.4 Hz, 1H), 6.50 (dd, J = 2.4 Hz, J = 5.6 Hz, 1H), 4.22 (br-s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.4, 153.7, 150.2, 139.9, 128.9, 128.7, 127.0, 108.5, 106.7. *Tetrahedron Lett. 2005 46, 3573.*

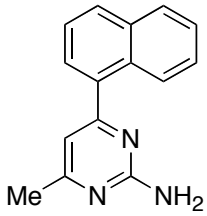


2,6-Dimethyl-5-*o*-tolyl-pyrimidin-4-ylamine (Table 1, Entry 6). The general procedure was used with 5-Chloro-2,6-dimethyl-pyrimidin-4-ylamine (156 mg, 1.00 mmol), 2-methylphenylboronic acid (203 mg, 1.50 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 2 mol %), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (16.4 mg, 0.040 mmol, 4 mol %), K_2CO_3 (552 mg, 4.00 mmol), water (2.0 mL), acetonitrile (2.0 mL), 16 h, 100 °C. The product was purified by column chromatography on silica gel (eluting with methanol/ethyl acetate, 0.5:9.5) to provide the title compound as a light yellow solid (207 mg, 97%). Mp = 204-205 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29-7.34 (m, 3H), 7.11 (d, J = 8.4 Hz, 1H), 4.55 (br-s, 2H), 2.55 (s, 3H), 2.11 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.9, 162.7,

161.1, 137.3, 133.8, 130.9, 130.0, 128.8, 113.7, 25.8, 22.0, 19.4. IR (neat, cm^{-1}): 3382, 3303, 3174, 2919, 2543, 2487, 2352, 1635, 1562, 1420, 998, 761.

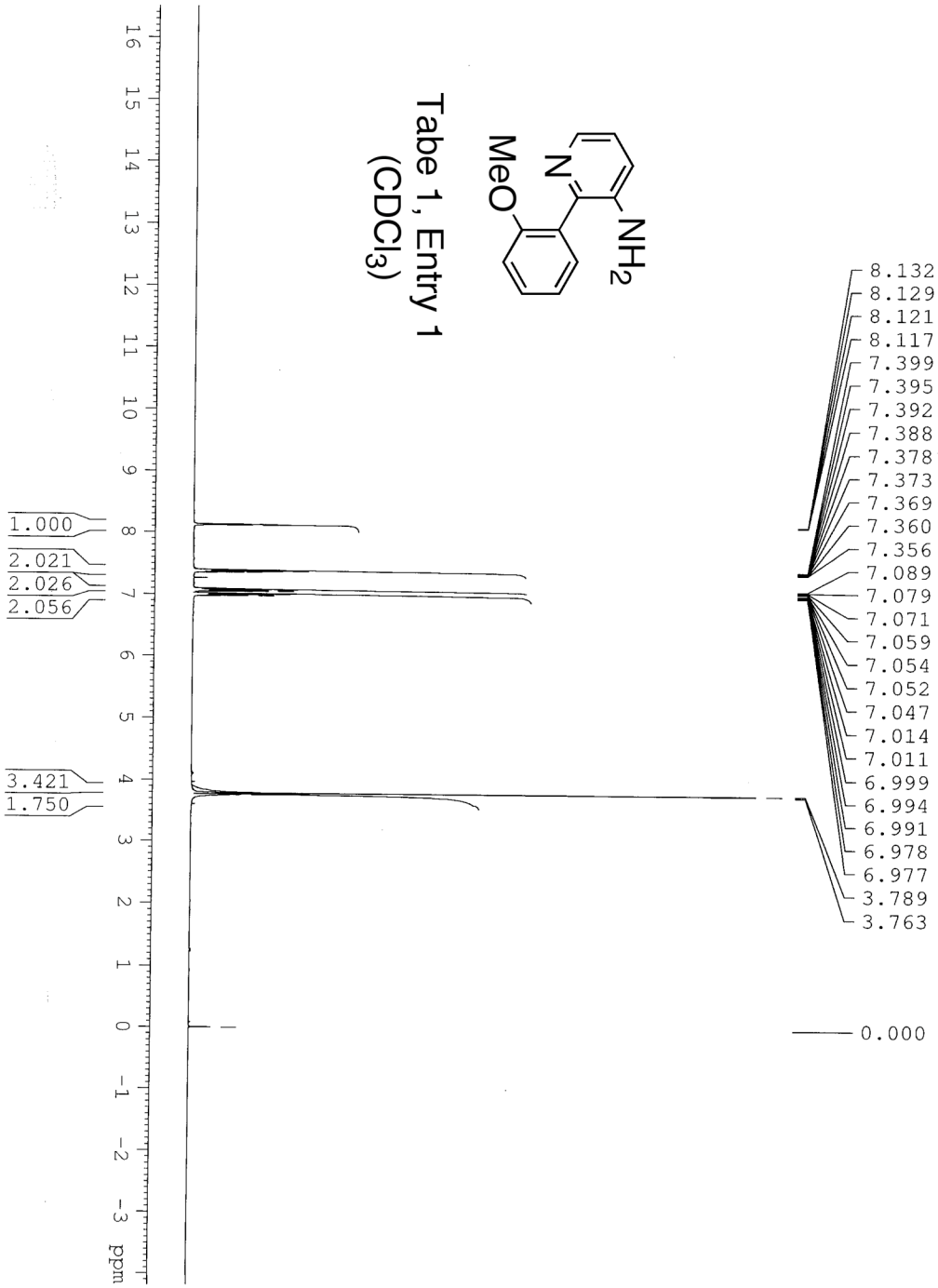


1-[3-(4-Amino-2,6-dimethyl-pyrimidin-5-yl)-phenyl]-ethanone (Table 1, Entry 7). The general procedure was used with 5-Chloro-2,6-dimethyl-pyrimidin-4-ylamine (156 mg, 1.00 mmol), 3-acetylphenylboronic acid (246 mg, 1.50 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 1 mol %), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (8.3 mg, 0.020 mmol, 2 mol %), K_2CO_3 (414 mg, 3.00 mmol), water (1.5 mL), acetonitrile (2.0 mL), 10 h, 100 °C. The product was purified by column chromatography on silica gel (eluting with methanol/ethyl acetate, 0.1:9.9) to provide the title compound as a white solid (231 mg, 96%). Mp = 197-198 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (dt, J = 7.6 Hz, J = 1.2 Hz, 1H), 7.87 (t, J = 1.6 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.47 (dt, J = 7.6 Hz, J = 1.6 Hz, 1H), 4.69 (br-s, 2H), 2.64 (s, 3H), 2.54 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.7, 166.2, 162.8, 161.1, 138.4, 135.6, 134.7, 130.0, 129.7, 128.3, 113.6, 26.9, 25.8, 22.4. IR (neat, cm^{-1}): 3416, 3309, 3157, 1678, 1646, 1560, 1465, 1422, 1370, 1358, 1290, 1227.



4-Methyl-6-naphthalen-1-yl-pyrimidin-2-ylamine (Table 1, Entry 8). The general procedure was used with 2-amino-4-chloro-6-methylpyrimidine (144 mg, 1.00 mmol), 1-naphthylboronic acid (258 mg, 1.50 mmol), $Pd(OAc)_2$ (4.6 mg, 0.020 mmol, 2 mol %), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (16.8 mg, 0.040 mmol, 4 mol %), K_3PO_4 (424 mg, 2.00 mmol), 1,4-dioxane (3.0 mL), 14 h, 100 °C. The product was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes, 4:1) to provide the title compound as a white solid (218 mg, 92%). Mp = 157 °C (lit. = 158-161 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15-8.17 (m, 1H), 7.89-7.94 (m, 2H), 7.50-7.61 (m, 4H), 6.80 (s, 1H), 5.17 (br-s, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.5, 167.7, 163.2, 136.8,

133.9, 130.7, 129.7, 128.5, 127.0, 126.8, 126.2, 125.6, 125.3, 111.9, 24.2. *Collect. Czech. Commun. 26, 1961, 2865.*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N
NH2
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8.129
8.121
8.117
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7.395
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7.388
7.378
7.373
7.369
7.360
7.356
7.089
7.079
7.071
7.059
7.054
7.052
7.047
7.014
7.011
6.999
6.994
6.991
6.978
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2.026
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ppm

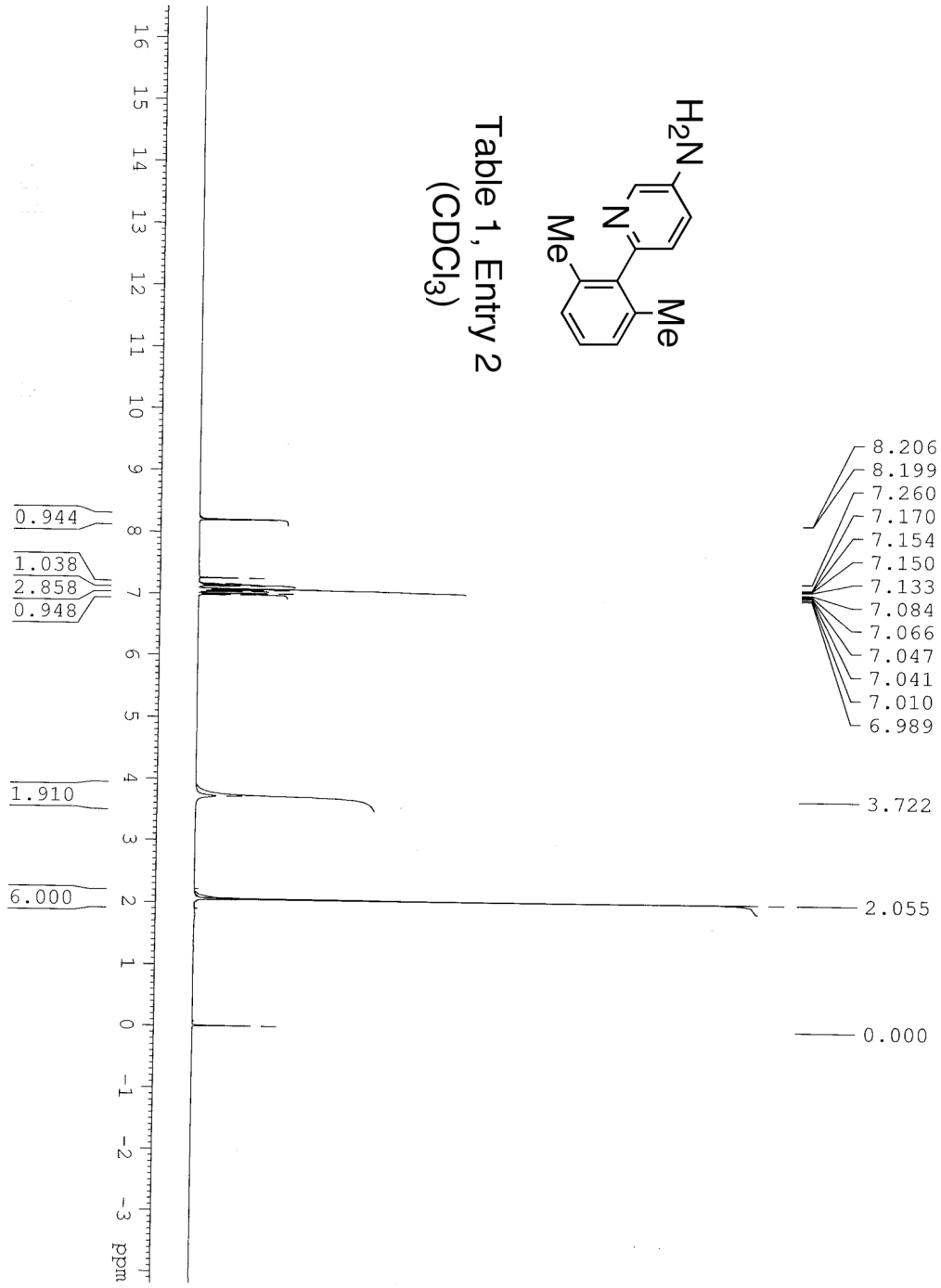
Table 1, Entry 2
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N
Me
Me
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7.170
7.154
7.150
7.133
7.084
7.066
7.047
7.041
7.010
6.989
3.722
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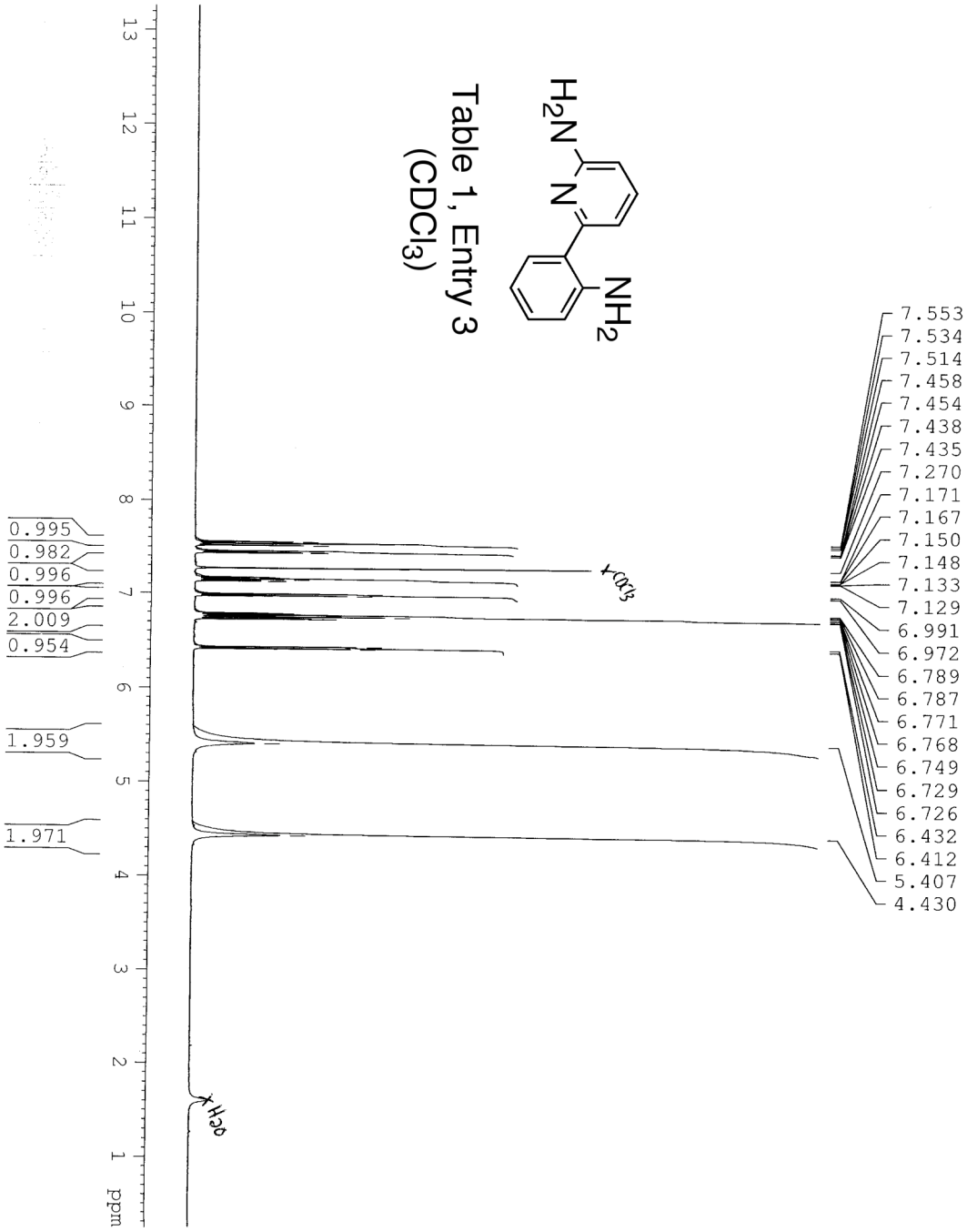
Table 1, Entry 3
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H2N
N
NH2
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7.454
7.438
7.435
7.270
7.171
7.167
7.150
7.148
7.133
7.129
6.991
6.972
6.789
6.787
6.771
6.768
6.749
6.729
6.726
6.432
6.412
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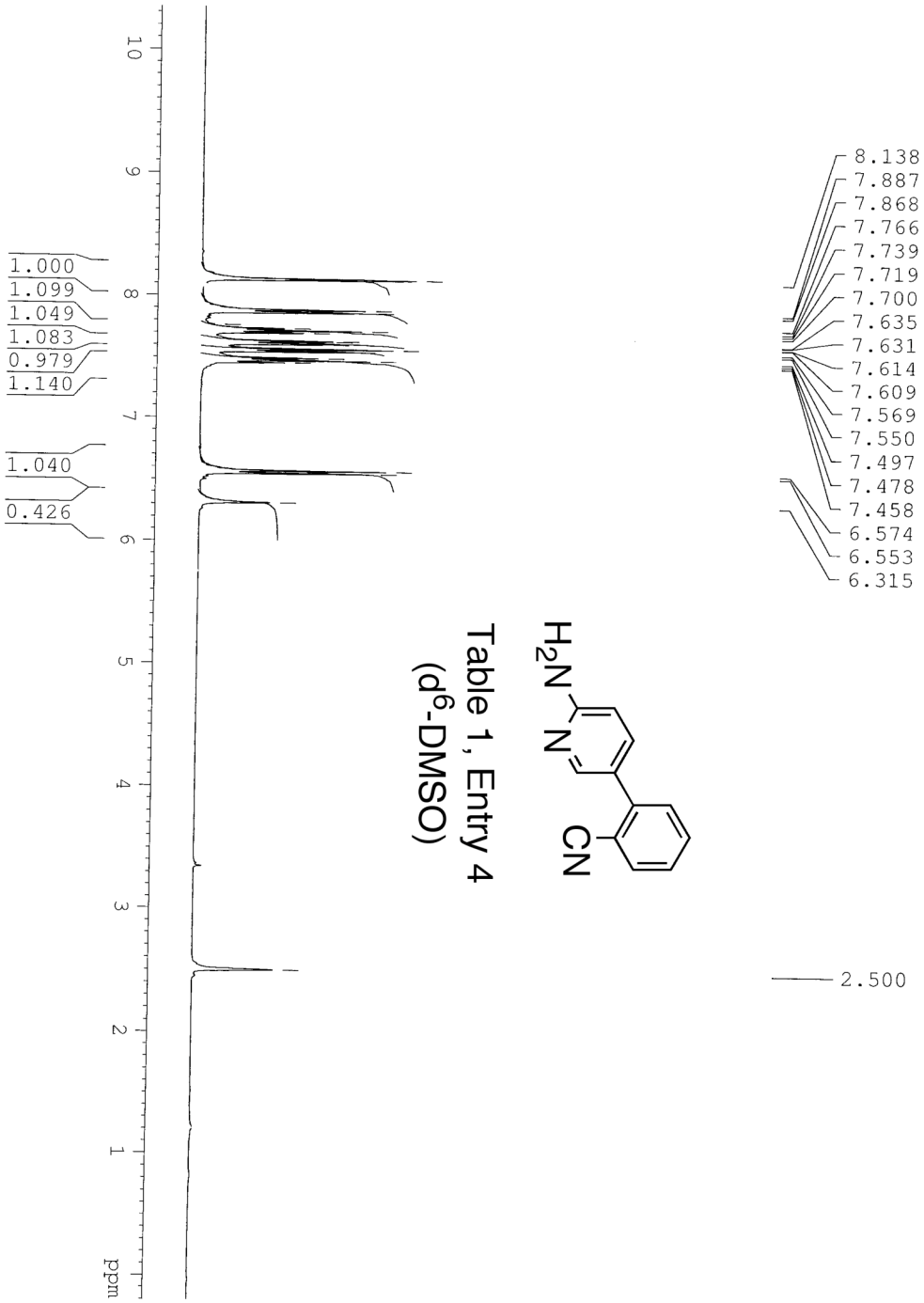
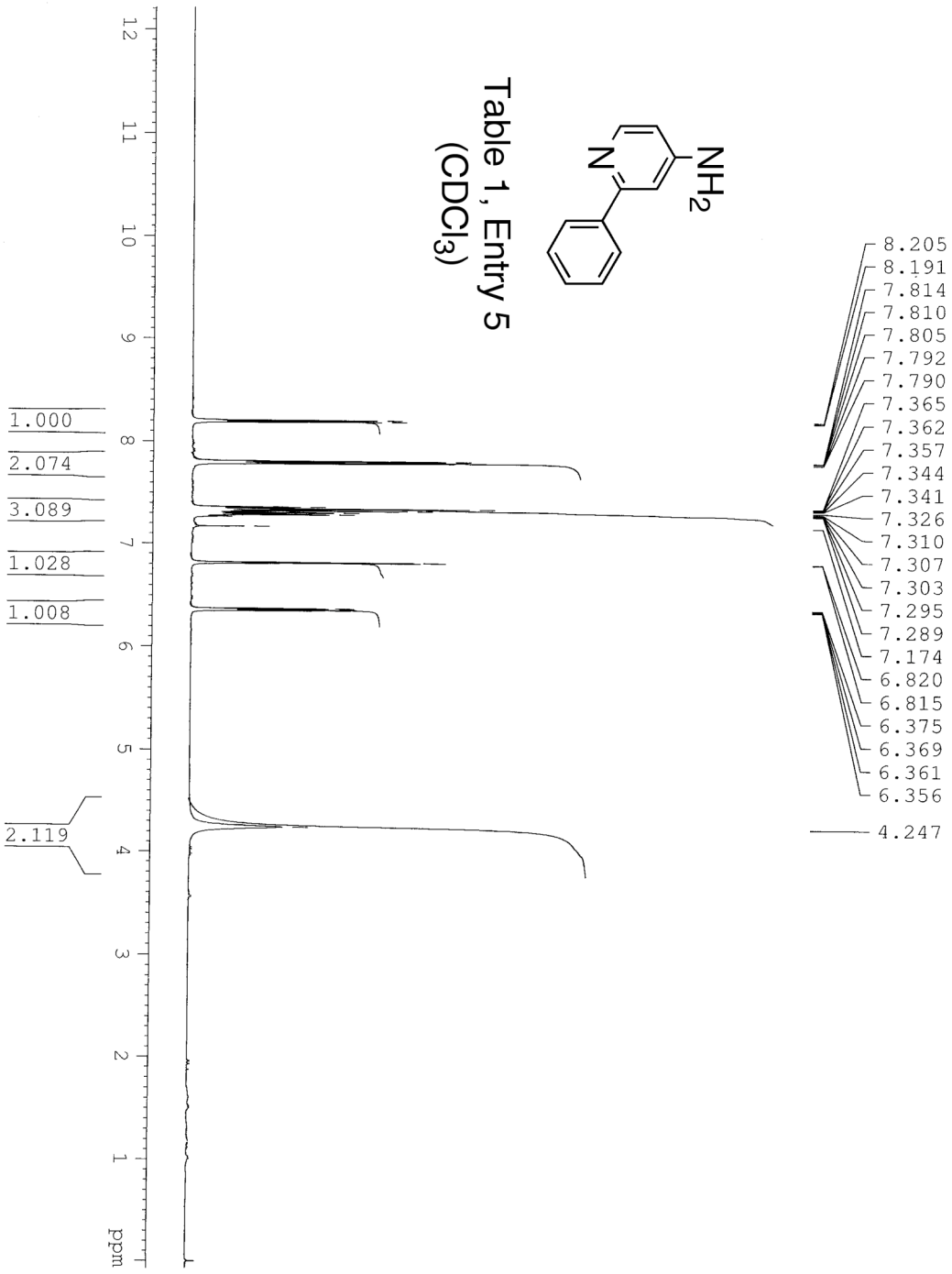


Table 1, Entry 4 (d^6-DMSO)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NH2
N
8.205
8.191
7.814
7.810
7.805
7.792
7.790
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7.362
7.357
7.344
7.341
7.326
7.310
7.307
7.303
7.295
7.289
7.174
6.820
6.815
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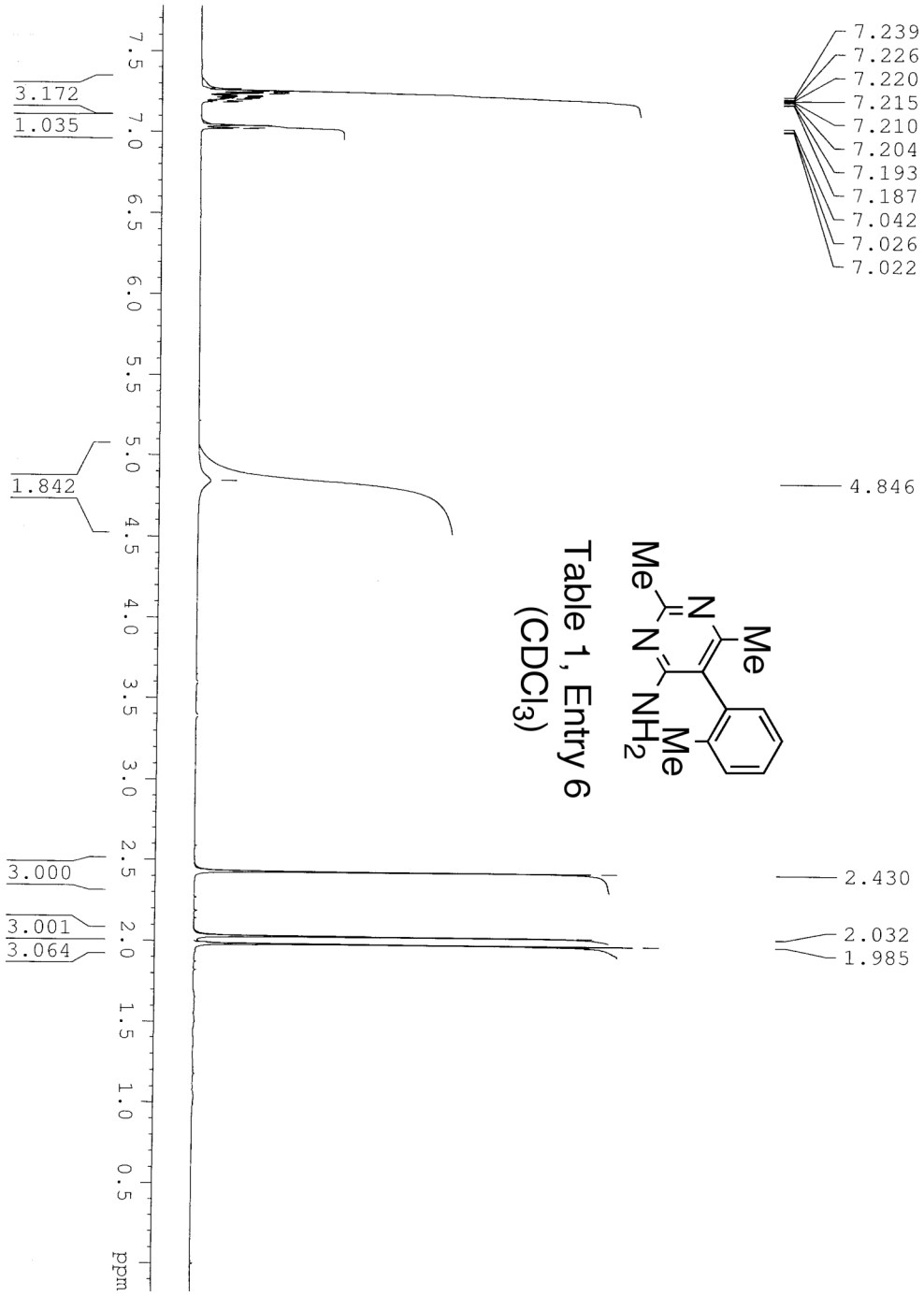
2.119
ppm


7.239
7.226
7.220
7.215
7.210
7.204
7.193
7.187
7.042
7.026
7.022
4.846
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2.032
1.985
3.172
1.035
1.842
3.000
3.001
3.064
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
Table 1, Entry 6
(CDCl3)
Me
N
Me
N
NH2
Me

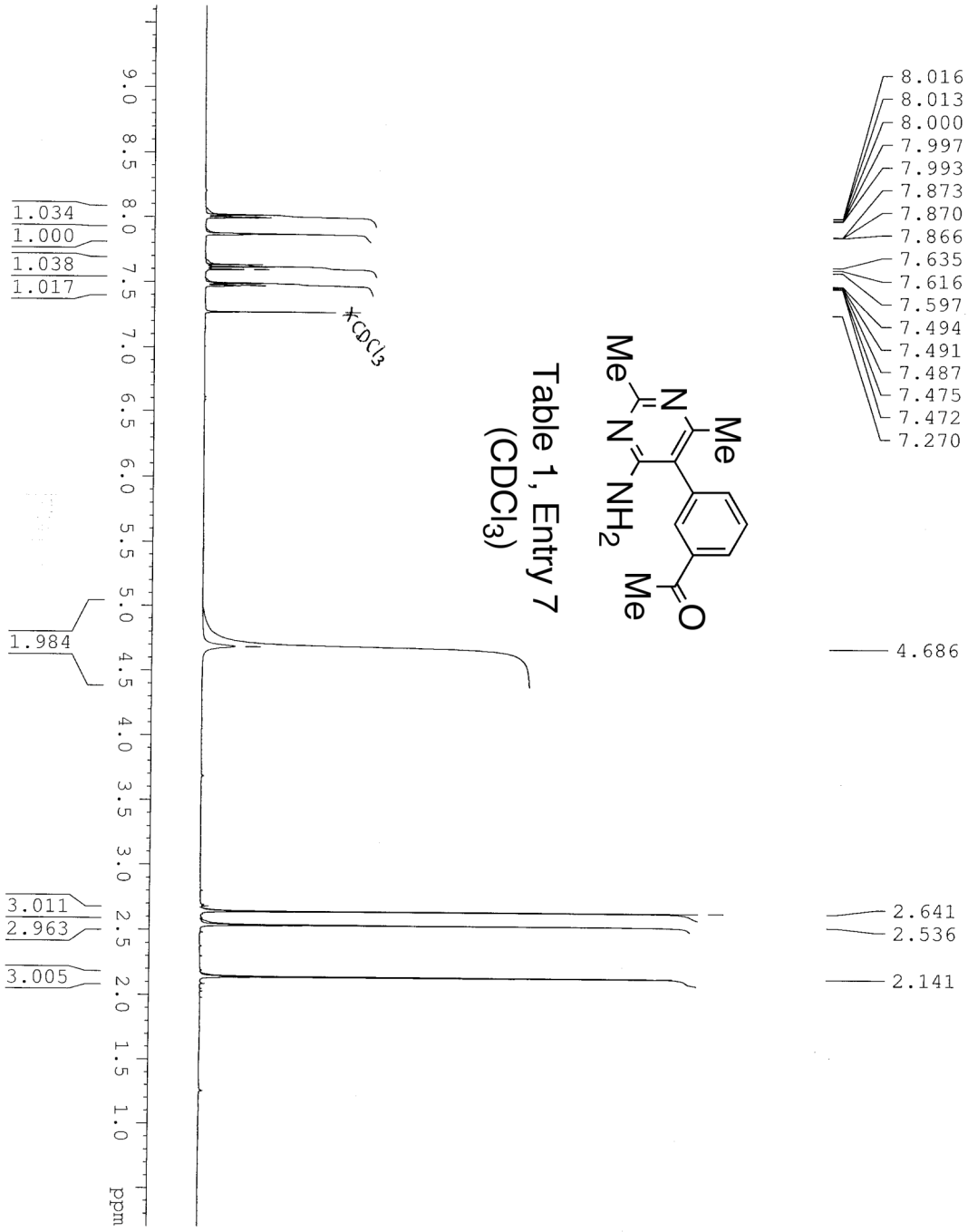
Table 1, Entry 7
(CDCl3)
Me
N
Me
N
NH2
Me
O
*CDCl3
8.016
8.013
8.000
7.997
7.993
7.873
7.870
7.866
7.635
7.616
7.597
7.494
7.491
7.487
7.475
7.472
7.270
4.686
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1.017
1.984
3.011
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3.005
ppm

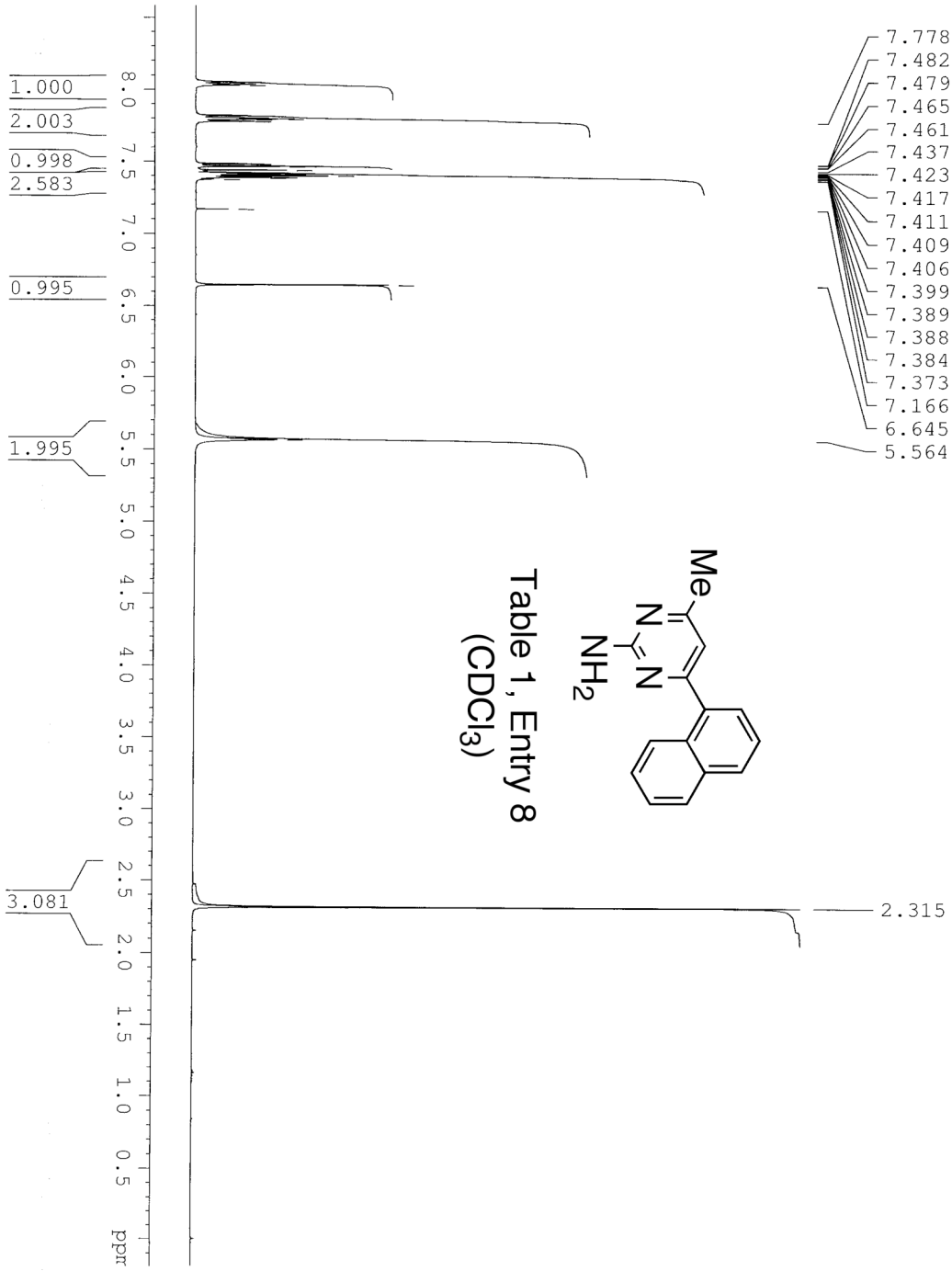
Table 1, Entry 8
(CDCl3)
Me
N
N
NH2
7.778
7.482
7.479
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7.461
7.437
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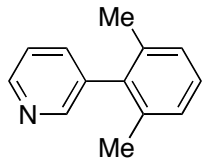
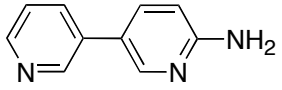
7.417
7.411
7.409
7.406
7.399
7.389
7.388
7.384
7.373
7.166
6.645
5.564
2.315
1.000
2.003
0.998
2.583
0.995
1.995
3.081
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

Table 2: General Procedure B for Suzuki-Miyaura Couplings of Pyridine Boronic Acids.

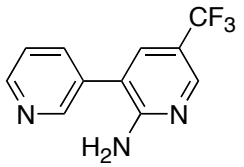
An-oven dried Schlenk tube was charged with $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), ligand (0.01 mmol), pyridine boronic acid (46.1 mg, 0.375 mmol) and powdered, anhydrous K_3PO_4 (106 mg, 0.50 mmol). The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with argon (this sequence was carried out two times). *n*Butanol (0.50 mL) was added via syringe, through the septum, followed by the addition of the aryl halide (0.25 mmol) in a like manner (aryl halides that were solid were added with other reagents before evacuation). The septum was then replaced with a Teflon screwcap and the Schlenk tube was sealed. The reaction mixture was heated to 100 °C until aryl halide had been completely consumed as determined by gas chromatography. At this point the reaction mixture was allowed to cool to room temperature. The reaction solution was then filtered through a thin pad of silica gel (eluting with ethyl acetate) and the eluent was concentrated under reduced pressure. The crude material so obtained was purified via flash chromatography on silica gel.



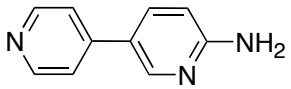
3-(2,6-Dimethyl-phenyl)-pyridine (Table 2, entry 1). Following general procedure B, a mixture of 2-chloro-m-xylene (33.1 μL, 0.25 mmol), 3-pyridine boronic acid (46.1 mg, 0.375 mmol), K_3PO_4 (106 mg, 0.50 mmol), Pd_2dba_3 (2.3 mg, 0.0025 mmol) and XPhos (4.8 mg, 0.01 mmol) was heated to 100 °C in butanol with stirring for 18 hours. The crude product was purified via flash column chromatography on silica gel (15% EtOAc/Hexanes) to provide the title compound in an 81% yield (37 mg) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) ≥: 8.60 (dd, J = 5,1 Hz, 1H), 8.44 (d, J = 2Hz, 1H), 7.51 (dt, J = 8,2 Hz, 1H) 7.37 (dd, J = 8,5 Hz, 1H) 7.21 (dd, J = 8,7 Hz, 1H), 7.13 (d, J = 7Hz, 2H), 2.03 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) ≥: 150.0, 148.1, 137.8, 136.7, 136.3, 127.8, 127.5, 123.3, 20.9. IR (neat, cm^{-1}): 3023, 2921, 1653, 1565, 1463, 1406.



[3,3']Bipyridinyl-6-ylamine (Table 2, entry 2). Following general procedure B, a mixture of 2-amino-5-chloropyridine (32.1 mg, 0.25 mmol), 3-pyridine boronic acid (46.1 mg, 0.375 mmol), K_3PO_4 (106 mg, 0.50 mmol), Pd_2dba_3 (2.3 mg, 0.0025 mmol) and XPhos (4.8 mg, 0.01 mmol) was heated to 120 °C in butanol with stirring for 24 hours. The crude product was purified via flash column chromatography on silica gel (10% Methanol/EtOAc) to provide the title compound in a 95% yield (40 mg) as a yellow solid, mp 134-136 °C. ^{1}H NMR (300 MHz, DMSO) ≥: 8.63 (t, J = 1Hz, 1H), 8.60 (dt, J = 5,1 Hz, 1H), 8.31 (t, J = 1Hz, 1H), 7.88 (dt, J = 8,1 Hz, 1H), 7.61 (s, 1H), 7.48 (dd, J = 8,5Hz, 1H), 6.62 (bs, 2H). ^{13}C NMR (75 MHz, DMSO) ≥: 159.5, 149.3, 148.9, 145.4, 136.4, 134.6, 132.5, 123.9, 116.7. IR (neat, cm^{-1}): 3328, 3198, 1624, 1511, 1474, 1425, 1384.

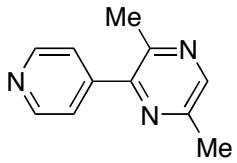


5-Trifluoromethyl-[3,3']bipyridinyl-2-ylamine (Table 2, entry 3). Following general procedure B, a mixture of 2-amino-3-chloro-5-trifluoromethylpyridine (49.1 mg, 0.25 mmol), 3-pyridine boronic acid (46.1 mg, 0.375 mmol), K_3PO_4 (106 mg, 0.50 mmol), Pd_2dba_3 (2.3 mg, 0.0025 mmol) and XPhos (4.8 mg, 0.01 mmol) was heated to 120 °C in butanol with stirring for 24 hours. The crude product was purified via flash column chromatography on silica gel (10% Methanol/EtOAc) to provide the title compound in a 95% yield (57 mg) as a white solid, mp 167-169 °C. ^{1}H NMR (300 MHz, DMSO) ≥: 8.63 (t, J = 1 Hz, 1H), 8.60 (dt, J = 5,2 Hz, 1H), 8.31 (t, J = 1 Hz, 1H), 7.88 (dt, J = 8,2 Hz, 1H), 7.60 (d, J = 2 Hz, 1H), 7.48 (dd, J = 8,5 Hz, 1H), 6.62 (bs, 1H). ^{13}C NMR (75 MHz, CD_3OD) ≥: 160.9, 150.2, 150.0, 146.7, 146.6, 138.8, 136.6, 136.5, 134.9, 125.8, 119.0. IR (neat, cm^{-1}): 3407, 2254, 2128, 1649, 1269, 1049, 1025, 1003.

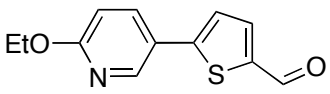


[3,4']Bipyridinyl-6-ylamine (Table 2, entry 4). Following general procedure B, a mixture of 2-amino-5-chloropyridine (32.1 mg, 0.25 mmol), 4-pyridine boronic acid (46.1 mg, 0.375 mmol), K_3PO_4 (106 mg, 0.50 mmol), Pd_2dba_3 (2.3 mg, 0.0025 mmol) and XPhos (4.8 mg,

0.01 mmol) was heated to 120 °C in butanol with stirring for 24 hours. The crude product was purified via flash column chromatography on silica gel (10% Methanol/EtOAc) to provide the title compound in a 95% yield (40 mg) as a yellow solid, mp 171-173 °C. ^{1}H NMR (300 MHz, $CDCl_3$) ≥: 8.43 (d, J = 6Hz, 2H), 8.29 (d, J = 2 Hz, 1H), 7.80 (dd, J = 8,3 Hz, 1H), 7.55 (d, J = 6 Hz, 2H), 6.63 (d, J = 8 Hz, 1H), 4.90 (bs, 2H). ^{13}C NMR (75 MHz, CD_3OD) ≥: 161.8, 151.3, 150.6, 148.1, 147.0, 137.6, 123.3, 123.1, 121.6, 110.5. IR (neat, cm^{-1}): 3428, 2925, 2856, 1633, 1519, 1488, 1394, 1221. Anal. Calcd. for $C_{10}H_9N_3$: C, 70.16; H, 5.30. Found C, 70.00; H, 5.49.

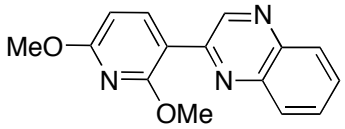


2,5-Dimethyl-3-pyridin-4-yl-pyrazine (Table 2, entry 5). Following general procedure B, a mixture of 3-chloro-2,5-dimethylpyrazine (30.2 μL, 0.25 mmol), 4-pyridine boronic acid (46.1 mg, 0.375 mmol), K_3PO_4 (106 mg, 0.50 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) and SPhos (4.1 mg, 0.01 mmol) was heated to 100 °C in butanol with stirring for 12 hours.. The crude product was purified via flash column chromatography on silica gel (20% EtOAc/Hexanes) to provide the title compound in a 83% yield (39 mg) as a yellow solid, mp 56-58 °C. ^{1}H NMR (300 MHz, $CDCl_3$) ≥: 8.73 (d, J = 4Hz, 2H), 8.39 (s, 1H), 7.49 (d, J = 4Hz, 2H), 2.58 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) ≥: 150.8, 149.9, 148.1, 146.4, 143.1, 130.5, 123.5, 22.3, 21.1. IR (neat, cm^{-1}): 2925, 2857, 1724, 1598, 1449, 1404, 1370. Anal. Calcd. for $C_{11}H_{11}N_3$: C, 71.33; H, 5.99. Found C, 71.22; H, 6.16.

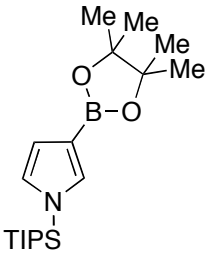


5-(6-Ethoxy-pyridin-3-yl)-thiophene-2-carbaldehyde (Table 2, entry 6). Following general procedure B, a mixture of 5-chloro-2-thiophenecarbaldehyde (26.6 μL, 0.25 mmol), 2-ethoxy-5-pyridine boronic acid (62.6 mg, 0.375 mmol), K_3PO_4 (106 mg, 0.50 mmol), Pd_2dba_3 (2.3 mg, 0.0025 mmol) and XPhos (4.8 mg, 0.01 mmol) was heated to 100 °C in tert-amyl alcohol with stirring for 12 hours. The crude product was purified via flash column chromatography on silica gel (15% EtOAc/Hexanes) to provide the title compound in a 91%

yield (53 mg) as a orange solid, mp 62-64 °C. ^{1}H NMR (300 MHz, $CDCl_3$) ≥: 9.83 (s, 1H), 8.43 (d, J = 3 Hz, 1H), 7.76 (dd, J = 8,2 Hz, 1H), 7.68 (t, J = 2 Hz, 1H), 7.26 (d, J = 4 Hz, 1H), 6.73 (d, J = 8 Hz, 1H), 4.35 (q, J = 7 Hz, 2H), 1.37 (t, J = 7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) ≥: 182.5, 164.4, 150.8, 144.7, 142.1, 137.5, 136.4, 123.5, 122.4, 111.4, 62.2, 14.5. IR (neat, cm^{-1}): 2977, 2900, 1598, 1564, 1446, 1381, 1287, 1236, 1064. Anal. Calcd. for $C_{12}H_{11}NO_2S$: C, 61.78; H, 4.75. Found C, 61.78; H, 4.91.



2-(2,6-Dimethoxy-pyridin-3-yl)-quinoxaline (Table 2, entry 7). Following general procedure B, a mixture of 2-chloroquinozaline (41.2 mg, 0.25 mmol), 2,6-dimethoxy-5-pyridine boronic acid (68.6 mg, 0.375 mmol), K_3PO_4 (106 mg, 0.50 mmol), Pd_2dba_3 (2.3 mg, 0.0025 mmol) and XPhos (4.8 mg, 0.01 mmol) was heated to 100 °C in tert-amyl alcohol with stirring for 12 hours. The crude product was purified via recrystallization (Hexanes) to provide the title compound in a 91% yield (61 mg) as a yellow solid, mp 95-96 °C.. ^{1}H NMR (300 MHz, $CDCl_3$) ≥: 9.48 (s, 1H), 8.37 (d, J = 8 Hz, 1H), 8.07 (d, J = 8 Hz, 2H), 7.67-7.73 (m, 2H), 6.51 (d, J = 8 Hz, 1H), 4.07 (s, 3H), 3.99 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) ≥: 164.1, 160.4, 150.3, 146.4, 142.7, 142.4, 140.7, 129.7, 129.1, 129.0, 128.9, 111.6, 102.8, 53.8, 53.6. IR (neat, cm^{-1}): 2947, 1600, 1578, 1483, 1383, 1305, 1267, 1226, 1030, 1014.



3-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-1-(triisopropyl-silanyl)-1*H*-pyrrole, A. An oven dried Schlenk tube was charged with $PdCl_2(CH_3CN)_2$ (59 mg, 3.0 mol%) and SPhos (278 mg, 9.0 mol%). The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with argon (this sequence was carried out two times). Toluene (10 mL) was added via syringe, through the septum, followed by the addition of 3-bromo-1-

(triisopropyl-silanyl)-1*H*-pyrrole[1] (2.27 g, 7.52 mmol), pinacol borane (1.15 g, 1.31 mL, 9.02 mmol) and triethylamine (2.64 mL, 18.8 mmol). Additional toluene (4 mL) was then added and the vessel was sealed with a Teflon screwcap. The reaction mixture was heated to 90 °C and stirred for 18 hours. At this point the reaction mixture was allowed to cool to room temperature. The solution was then filtered though a thin pad of silica gel (eluting with ethyl acetate) and the eluent was concentrated under reduced pressure. The crude product was purified via flash column chromatography on silica gel (5% EtOAc/Hexanes) to provide the title compound in a 85% yield (2.25 g) as a light yellow solid, m.p. 59 °C. ^{1}H NMR (300 MHz, $CDCl_3$) ≥: 7.24 (dd, J = 2,1 Hz, 1H), 6.81 (dd, J= 3,2 Hz, 1H) 6.63 (dd, J = 3,1 Hz, 1H), 7.00 (dd, J = 7,1 Hz, 1H), 1.46 (sept, J = 7 Hz, 3H), 1.33 (s, 12H), 1.09 (d, J= 7 Hz, 18H).^{13}C NMR (75 MHz, $CDCl_3$) ≥: 133.6, 124.9, 115.6, 110.0, 82.6, 24.8, 17.7, 11.6. IR (neat, cm^{-1}): 2949, 2873, 1540, 1466, 1381, 1296, 1142. Anal. Calcd. for $C_{19}H_{36}BNO_2Si$: C, 65.31; H, 10.39. Found C, 65.32; H, 10.30.

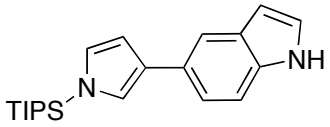
Table 3: General Procedure C for Suzuki-Miyaura Couplings of A.

An-oven dried Schlenk tube was charged with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), SPhos (4.1 mg, 0.01 mmol), **A** (131 mg, 0.375 mmol) and powdered, anhydrous K_3PO_4 (106 mg, 0.50 mmol). The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with argon (this sequence was carried out two times). *n*Butanol (0.45 mL) and water (0.05 mL) were added via syringe, through the septum, followed by the addition of the aryl halide (0.25 mmol) in a like manner (aryl halides that were solid were added with other reagents before evacuation). The septum was then replaced with a Teflon screwcap and the Schlenk tube was sealed. The reaction mixture was heated to 100 °C until aryl halide had been completely consumed as determined by gas chromatography. At this point the reaction mixture was allowed to cool to room temperature. The reaction solution was then filtered through a thin pad of silica gel (eluting with ethyl acetate) and the eluent was concentrated under reduced pressure. The crude material so obtained was purified via flash chromatography on silica gel.

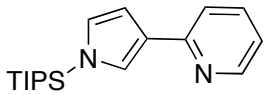
[1] Alzarez, A.; Guzmen, A.; Ruiz, A.; Velards, E.; Muchowski, J. *J. Org. Chem*. **1992**, *57*, 1653-1656.

Table 3: General Procedure D for Suzuki-Miyaura Couplings of E at Low Catalyst Loadings.

Procedure C was followed with the following changes: A separate vial was initially charged with $Pd(OAc)_2$ (1.0 mol%) and SPhos (2.0 mol%). The vial was sealed with Teflon coated screwcap, a needle was inserted through the cap and the vial was then evacuated and backfilled with argon. *n*Butanol (1 mL) was added and the mixture as briefly heated. 250 μL of this solution (0.25% Pd, 0.50% SPhos) was then added to the Schlenk flask containing the base and boronic acid. 200 μL of butanol and 50 μL of water were added in the final solvent addition. The temperature was raised to 100 °C.

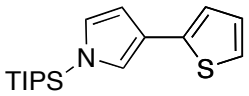


5-[1-(Triisopropyl-silanyl)-1*H*-pyrrol-3-yl]-1*H*-indole (Table 3, entry 1). Following general procedure D, a mixture of 5-bromoindole (49 mg, 0.25 mmol), **A** (131 mg, 0.375 mmol), K_3PO_4 (106 mg, 0.50 mmol), $Pd(OAc)_2$ (0.25 mol%) and SPhos (0.50 mol%) was heated to 100 °C in 2.5:1 *n*-butanol/water with stirring for two hours. The crude product was purified via flash column chromatography on silica gel (10% EtOAc/Hexanes) to provide the title compound in a 97% yield (82 mg) as a red oil. ^{1}H NMR (300 MHz, $CDCl_3$) ≥: 8.01 (bs, 1H), 7.82 (d, J= 1 Hz, 1H) 7.46 (dd, J = 8,1 Hz, 1H), 7.36 (d, J = 8 Hz, 1H), 7.16 (t, J = 3 Hz, 1H), 7.10 (t, J = 1 Hz, 1H), 6.86 (t, J = 2 Hz, 1H), 6.71 (dd, J = 2,1 Hz, 1H), 6.56 (m, 1H), 1.55 (sept, J = 7 Hz), 1.20 (d, J= 7 Hz, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) ≥: 134.4, 128.3, 128.1, 127.8, 125.0, 124.3, 120.3, 120.0, 116.8, 111.0, 108.8, 102.5, 17.8, 11.7. IR (neat, cm^{-1}): 3481, 3400, 2949, 2867, 1709, 1467, 1327, 1119.



2-[1-(Triisopropyl-silanyl)-1*H*-pyrrol-3-yl]-pyridine (Table 3, entry 2). Following general procedure D, a mixture of 2-bromopyridine (23.8 μL, 0.25 mmol), **A** (131 mg, 0.375 mmol),

K_3PO_4 (106 mg, 0.50 mmol), $Pd(OAc)_2$ (0.25 mol%) and SPhos (0.50 mol%) was heated to 100 °C in 2.5:1 *n*-butanol/water with stirring for two hours. The crude product was purified via flash column chromatography on silica gel (10% EtOAc/Hexane) to provide the title compound in a 91% yield (68 mg) as a white solid, mp 74-75 °C. ^{1}H NMR (300 MHz, $CDCl_3$) ≥: 8.52-8.55 (ddd, J = 7,2,1 Hz, 1H), 7.56-7.61 (m, 1H), 7.48 (dt, J = 7,1 Hz, 1H), 7.43 (t, J = 1 Hz, 1H), 7.00 (ddd, J = 7,5,1 Hz, 1H), 6.80 (ddd, J = 8,3,1 Hz, 1H), 1.55 (sept, J = 7 Hz, 3H), 1.10 (d, J= 7 Hz, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) ≥: 154.7, 149.2, 136.2, 127.0, 125.4, 123.3, 120.0, 119.2, 108.9, 17.8, 11.6. IR (neat, cm^{-1}): 2946, 2867, 1635, 1591, 1541, 1488, 1464, 1429, 1145, 1082. Anal. Calcd. for $C_{18}H_{28}N_2Si$: C, 71.94; H, 9.39. Found C, 72.07; H, 9.35.

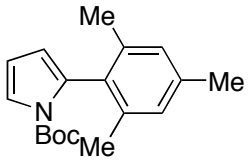


3-Thiophen-2-yl-1-(triisopropyl-silanyl)-1*H*-pyrrole (Table 3, entry 3). Following general procedure D, a mixture of 2-bromothiophene (0.25 mmol, 24.2 μL), **A** (131 mg, 0.375 mmol), K_3PO_4 (106 mg, 0.50 mmol), $Pd(OAc)_2$ (0.25 mol%) and SPhos (0.50 mol%) was heated to 100 °C in 2.5:1 *n*-butanol/water with stirring for two hours. The crude product was purified via flash column chromatography on silica gel (5% EtOAc/Hexanes) to provide the title compound in 99% yield (75 mg) as a red oil. ^{1}H NMR (300 MHz, $CDCl_3$) ≥: 7.04-7.08 (ddd, J = 5,5,1 Hz, 1H), 6.96-7.00 (m, 1H) 6.81 (t, J = 2 Hz, 1H), 6.76 (dd, J = 3,2 Hz, 1H), 6.51 (dd, J = 3,2 Hz, 1H), 6.32 (t, J = 2 Hz, 1H), 1.49 (sept, J = 7 Hz, 3H), 1.15 (d, J = 7 Hz, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) ≥: 139.7, 127.4, 125.1, 121.4, 120.8, 120.7, 120.5, 109.2, 17.8, 11.6. IR (neat, cm^{-1}): 2949, 2867, 1706, 1462, 1112. Anal. Calcd. for $C_{17}H_{27}NSSi$: C, 65.45; H, 8.24. Found C, 65.43; H, 8.77.

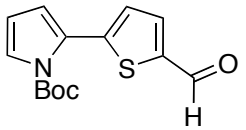
Table 3: General Procedure E for Suzuki-Miyaura Couplings of *N*-(*t*-butoxycarbonyl)-pyrrole-2-boronic acid.

An-oven dried Schlenk tube was charged with $Pd(OAc)_2$ (1.1 mg, 2.0 mol%), SPhos (4.1 mg, 4.0 mol%), *N*-(*t*-butoxycarbonyl)-pyrrole-2-boronic acid (79.1 mg, 0.375 mmol) and powdered, anhydrous K_3PO_4 (106 mg, 0.50 mmol). The Schlenk tube was capped with a

rubber septum and then evacuated and backfilled with argon (this sequence was carried out two times). *n*Butanol (0.5 mL) were added via syringe, through the septum, followed by the addition of the aryl halide (0.25 mmol) in a like manner (aryl halides that were solid were added with other reagents before evacuation). The septum was then replaced with a Teflon screwcap and the Schlenk tube was sealed. The reaction mixture was heated to 100 °C until aryl halide had been completely consumed as determined by gas chromatography. At this point the reaction mixture was allowed to cool to room temperature. The reaction solution was then filtered through a thin pad of silica gel (eluting with ethyl acetate) and the eluent was concentrated under reduced pressure. The crude material so obtained was purified via flash chromatography on silica gel.

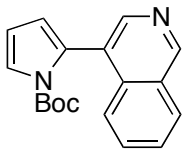


2-(2,4,6-Trimethyl-phenyl)-pyrrole-1-carboxylic acid *tert*-butyl ester (Table 3, entry 4). Following general procedure E, a mixture of 2-bromomesitylene (38.3 μL, 0.25 mmol), *N*-(*t*-butoxycarbonyl)-pyrrole-2-boronic acid (79.1 mg, 0.375 mmol), K_3PO_4 (106 mg, 0.50 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) and SPhos (4.1 mg, 0.01 mmol) was heated to 100 °C in *n*-butanol with stirring for five hours. The crude product was purified via flash column chromatography on silica gel (5% EtOAc/Hexanes) to provide the title compound in a 89% yield (63 mg) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) ≥: 7.39 (dd, J = 3, 1H), 6.87 (s, 2H) 6.27 (t, J = 3 Hz, 1H), 5.99 (dd, J = 3 Hz, 1H), 2.30 (s, 3H), 2.02 (s, 6H), 1.21 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) ≥: 149.4, 137.8, 137.1, 131.9, 131.8, 127.5, 130.8, 113.1, 110.6, 82.7, 27.3, 21.1, 20.2. IR (neat, cm^{-1}): 2979, 1733, 1339. Anal. Calcd. for $C_{18}H_{23}NO_2$: C, 75.8; H, 8.1. Found C, 75.82; H, 8.25.



2-(5-Formyl-thiophen-2-yl)-pyrrole-1-carboxylic acid *tert*-butyl ester (Table 3, entry 5). Following general procedure E, a mixture of 5-chlorothiophene-2-carbaldehyde (26.6 μL, 0.25 mmol), *N*-(*t*-butoxycarbonyl)-pyrrole-2-boronic acid (79.1 mg, 0.375 mmol), K_3PO_4

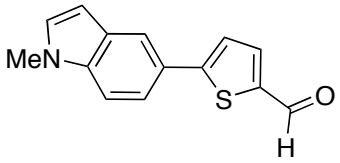
(106 mg, 0.50 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) and SPhos (4.1 mg, 0.01 mmol) was heated to 100 °C in *n*-butanol with stirring for three hours. The crude product was purified via flash column chromatography on silica gel (10% EtOAc/Hexanes) to provide the title compound in a 77% yield (53 mg) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) ≥: 9.87 (s, 1H), 7.67 (d, J = 4 Hz, 1H), 7.40 (dd, J = 4, 2 Hz, 1H), 7.19 (d, J = 4 Hz, 1H), 6.44 (dd, J = 3,2 Hz, 1H), 6.24 (t, J = 3Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) ≥: 183.6, 149.3, 145.8, 143.3, 136.7, 129.1, 126.8, 125.3, 118.7, 111.8, 85.4, 28.4. IR (neat, cm^{-1}): 2979, 1745, 1664, 1475, 1431, 1337, 1317, 1139.



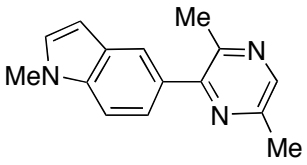
2-Isoquinolin-4-yl-pyrrole-1-carboxylic acid *tert*-butyl ester (Table 3, entry 6). Following general procedure E, a mixture of 4-bromoisoquinoline (52 mg, 0.25 mmol), *N*-(*t*-butoxycarbonyl)-pyrrole-2-boronic acid (79.1 mg, 0.375 mmol), K_3PO_4 (106 mg, 0.50 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) and SPhos (4.1 mg, 0.01 mmol) was heated to 100 °C in *n*-butanol with stirring for five hours. The crude product was purified via flash column chromatography on silica gel (10% EtOAc/Hexanes) to provide the title compound in a 95% yield (70 mg) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) ≥: 9.23 (s, 1H), 8.47 (s, 1H) 8.00 (dd, J = 7,2 Hz, 1H), 7.54-7.67 (m, 4H), 6.37 (t, J = 3 Hz, 1H), 6.33 (dd, J = 3,2 Hz, 1H), 0.90 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) ≥: 148.4, 147.9, 137.0, 134.4, 132.4, 131.2, 126.8, 123.5, 123.4, 119.4, 115.7, 107.3, 83.9, 28.2. IR (neat, cm^{-1}): 2979, 1733, 1462, 1370. Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16. Found C, 73.19; H, 6.21.

Table 3: General Procedure F for Suzuki-Miyaura Couplings of Indole Boronic Acids. An-oven dried Schlenk tube was charged with $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), ligand (0.01 mmol), indole boronic acid (0.375 mmol) and powdered, anhydrous K_3PO_4 (106 mg, 0.50 mmol). The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with argon (this sequence was carried out two times). *n*Butanol (0.50 mL) was added via syringe, through the septum, followed by the addition of the aryl halide (0.25 mmol) in a like manner (aryl halides that were solid were added with other reagents before

evacuation). The septum was then replaced with a Teflon screwcap and the Schlenk tube was sealed. The reaction mixture was heated to 100 °C until aryl halide had been completely consumed as determined by gas chromatography. At this point the reaction mixture was allowed to cool to room temperature. The reaction solution was then filtered through a thin pad of silica gel (eluting with ethyl acetate) and the eluent was concentrated under reduced pressure. The crude material so obtained was purified via flash chromatography on silica gel.

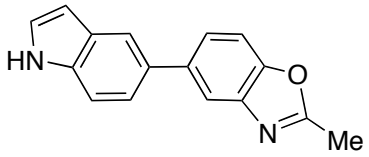


5-(1-Methyl-1*H*-indol-5-yl)-thiophene-2-carbaldehyde (Table 3, entry 7). Following general procedure F, a mixture of 5-chloro-2-thiophenecarbaldehyde (26.6 μL, 0.25 mmol), 1-methyl-5-indole boronic acid (65.3 mg, 0.375 mmol), K_3PO_4 (106 mg, 0.50 mmol), $Pd(OAc)_2$ (0.25 mol%) and SPhos (0.50 mol%) was heated to 100 °C in butanol with stirring for 12 hours. The crude product was purified via flash column chromatography on silica gel (10% EtOAc/Hexanes) to provide the title compound in a 96% yield (57 mg) as a yellow solid, mp 138-140 °C. ^{1}H NMR (300 MHz, $CDCl_3$) ≥: 9.87 (s, 1H), 7.96 (d, J = 2 Hz, 1H), 7.74 (d, J = 4 Hz, 1H), 7.56 (dd, J = 8,2 Hz, 1H), 7.39 (d, J = 4 Hz, 1H), 7.35 (d, J = 8 Hz, 1H), 7.10 (d, J = 3 Hz, 1H), 6.55 (d, J = 3Hz, 1H), 2.68 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) ≥: 182.7, 156.9, 141.1, 137.9, 137.3, 130.3, 128.8, 124.6, 122.8, 120.5, 119.3, 109.9, 101.8, 33.0. IR (neat, cm^{-1}): 3020, 2854, 1741, 1659, 1607, 1512, 1446, 1377, 1231, 1056.

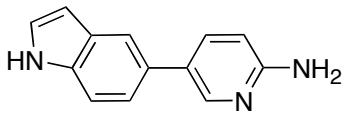


5-(3,6-Dimethyl-pyrazin-2-yl)-1-methyl-1*H*-indole (Table 3, entry 8). Following general procedure F, a mixture of 3-chloro-2,5-dimethylpyrazine (30.2 μL, 0.25 mmol), 1-methyl-5-indole boronic acid (65.3 mg, 0.375 mmol), K_3PO_4 (106 mg, 0.50 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) and SPhos (4.1 mg, 0.01 mmol) was heated to 100 °C in butanol with stirring for 12 hours. The crude product was purified via flash column chromatography on silica gel (25% EtOAc/Hexanes) to provide the title compound in a 90% yield (53 mg) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) ≥: 8.29 (s, 1H), 7.82 (s, 1H), 7.43 (t, J = 8 Hz, 1H), 7.40 (t, J = 8 Hz, 1H), 7.10 (d, J = 3 Hz, 1H), 6.54 (d, J = 3 Hz, 1H), 3.83 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) ≥: 154.1, 150.0, 148.3, 136.6, 130.1, 129.6, 128.3, 122.6, 121.7, 109.1, 101.5, 32.9, 22.9, 21.2. IR (neat, cm^{-1}): 3099, 2959, 1923, 2824, 1617, 1514, 1449, 1426, 1331, 1245, 1150, 1105.

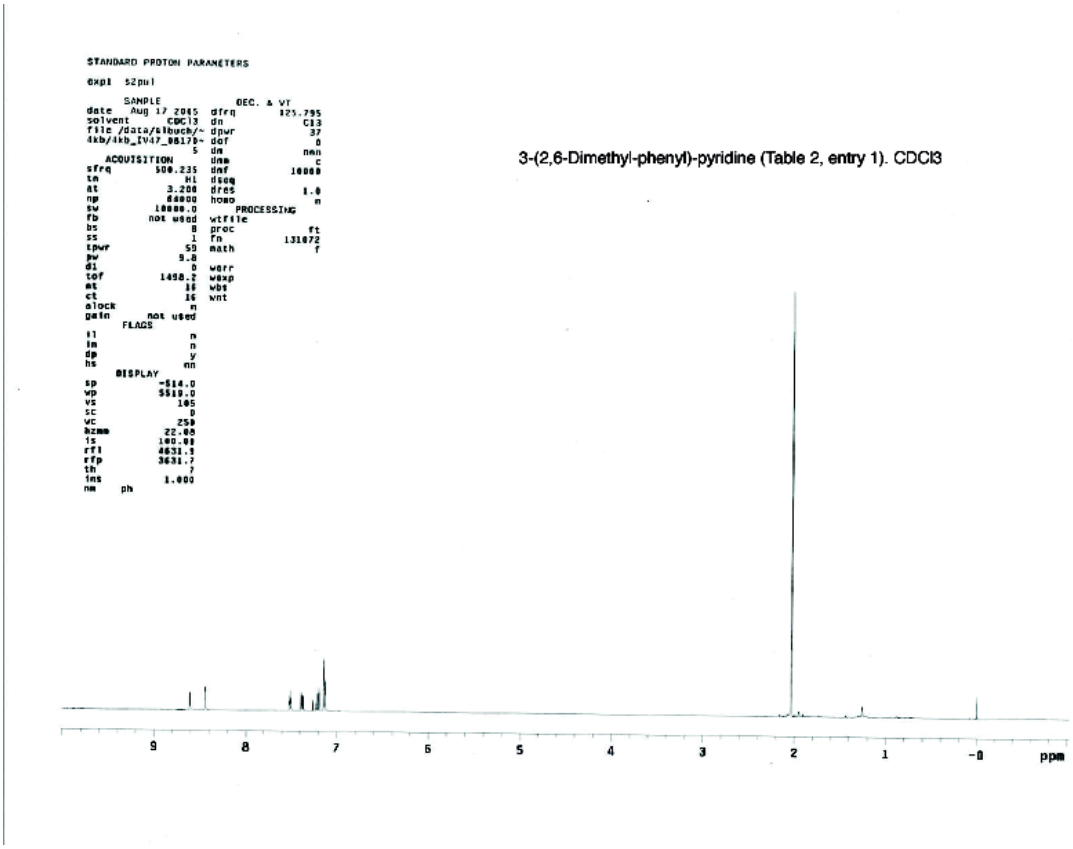


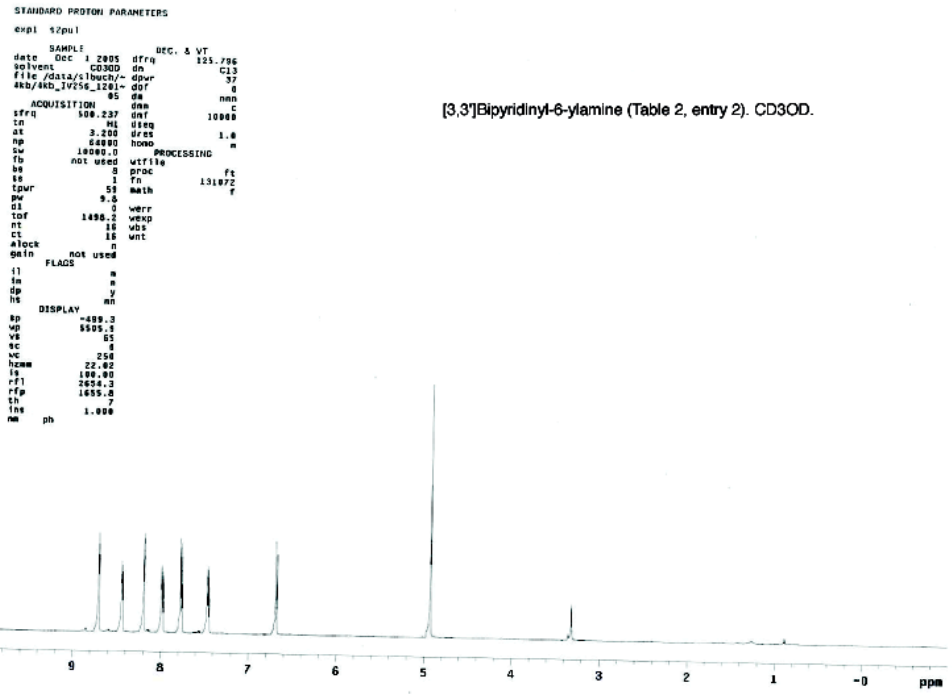
5-(1*H*-Indol-5-yl)-2-methyl-benzooxazole (Table 3, entry 9). Following general procedure F, a mixture of 5-chloro-2-methylbenzoxazole (41.8 mg, 0.25 mmol), 5-indole boronic acid (60.4 mg, 0.375 mmol), K_3PO_4 (106 mg, 0.50 mmol), Pd_2dba_3 (2.3 mg, 0.0025 mmol) and XPhos (4.8 mg, 0.01 mmol) was heated to 120 °C in butanol with stirring for 18 hours. The crude product was purified via flash column chromatography on deactivated silica gel (10% Triethylamine/Hexanes) and eluent (40% EtOAc/Hexanes) to provide the title compound in a 91% yield (56 mg) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$) ≥: 8.35 (bs, 1H), 7.90 (d, J = 1 Hz, 1H), 7.87 (d, J = 1Hz, 1H), 7.60 (dd, J = 8,2 Hz, 1H), 7.53 (dd, J = 8,1 Hz, 1H), 7.47 (d, J = 1 Hz, 1H), 7.46 (d, J = 1Hz, 1H), 7.26 (t, J = 3 Hz, 1H), 6.63 (t, J = 3 Hz, 1H), 2.68 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) ≥: 164.3, 150.0, 142.0, 139.4, 135.2, 133.2, 128.4, 124.9, 124.3, 122.1, 119.5, 118.0, 111.3, 110.0, 102.9, 14.6. IR (neat, cm^{-1}): 3411, 3238, 2963, 2929, 1577, 1458, 1275.



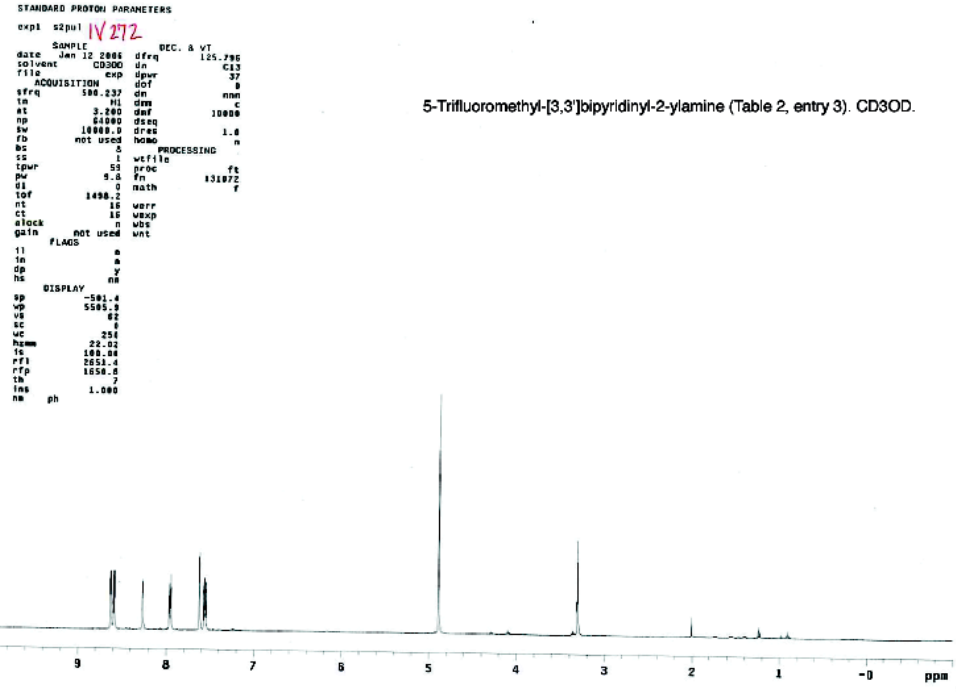
5-(1*H*-Indol-5-yl)-pyridin-2-ylamine (Table 3, entry 9). Following general procedure F, a mixture of 2-amino-5-chloropyridine (32.1 mg, 0.25 mmol), 5-indole boronic acid (60.4 mg, 0.375 mmol), K_3PO_4 (106 mg, 0.50 mmol), Pd_2dba_3 (2.3 mg, 0.0025 mmol) and XPhos (4.8 mg, 0.01 mmol) was heated to 120 °C in butanol with stirring for 18 hours. The crude product was purified via flash column chromatography on silica gel (EtOAc) to provide the

title compound in a 77% yield (40 mg) as a red oil. ^{1}H NMR (300 MHz, CD_3OD) ≥: 8.14 (dd, J = 2,1 Hz, 1H), 7.77 (dd, J = 8,3 Hz, 1H), 7.67 (dd, J = 2,1 Hz, 1H), 7.41 (dt, J = 8,1 Hz, 1H), 7.26 (dd, J = 8,1 Hz, 1H), 7.24 (d, J = 3 Hz, 1H), 6.67 (dd, J = 8,1 Hz, 1H), 6.46 (dd, J = 3,1 Hz, 1H). ^{13}C NMR (75 MHz, CD_3CN) ≥: 159.0, 147.0, 137.2, 136.2, 130.9, 129.6, 128.6, 126.5, 121.3, 118.5, 112.6, 109.0, 102.7. IR (neat, cm^{-1}): 3394, 3025, 2924, 2532, 1620, 1499, 1468, 1389, 1316.

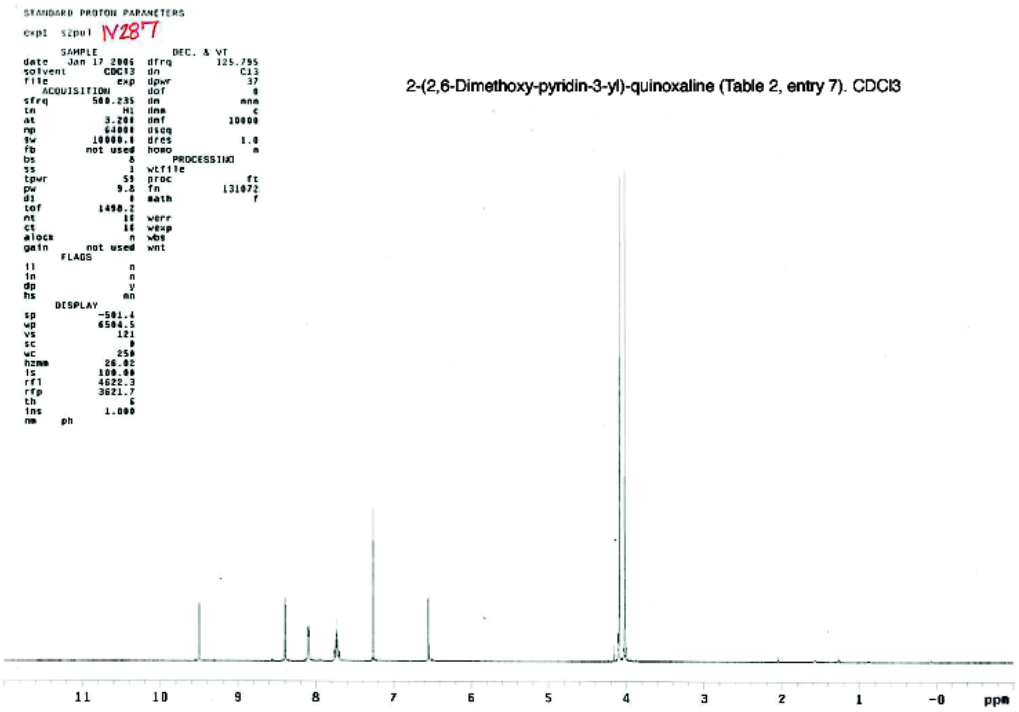




[3,3']Bipyridinyl-6-ylamine (Table 2, entry 2). CD3OD.



5-Trifluoromethyl-[3,3']bipyridinyl-2-ylamine (Table 2, entry 3). CD3OD.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homo n
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math f
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wexp
wbs
wnt
2-(2,6-Dimethoxy-pyridin-3-yl)-quinoxaline (Table 2, entry 7). CDCl3
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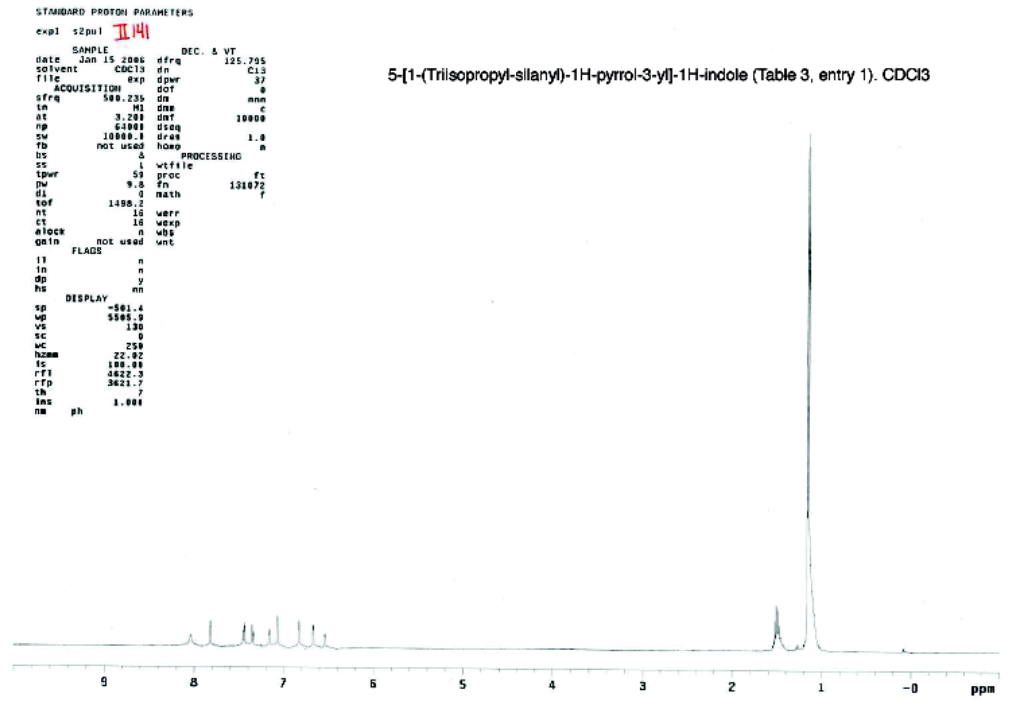
10
9
8
7
6
5
4
3
2
1
-0
ppm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in n
dp y
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5
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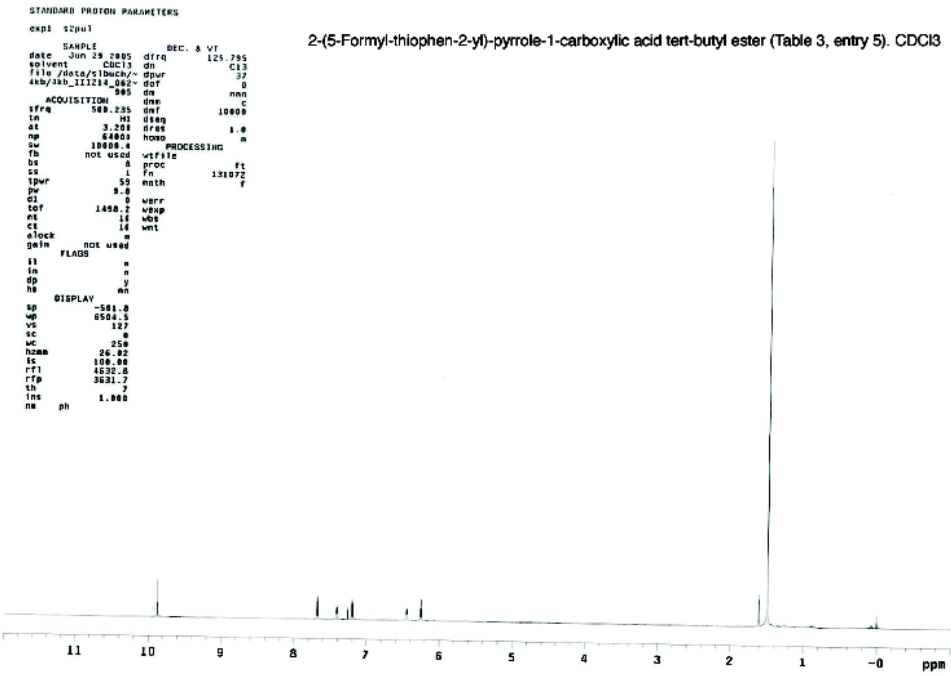
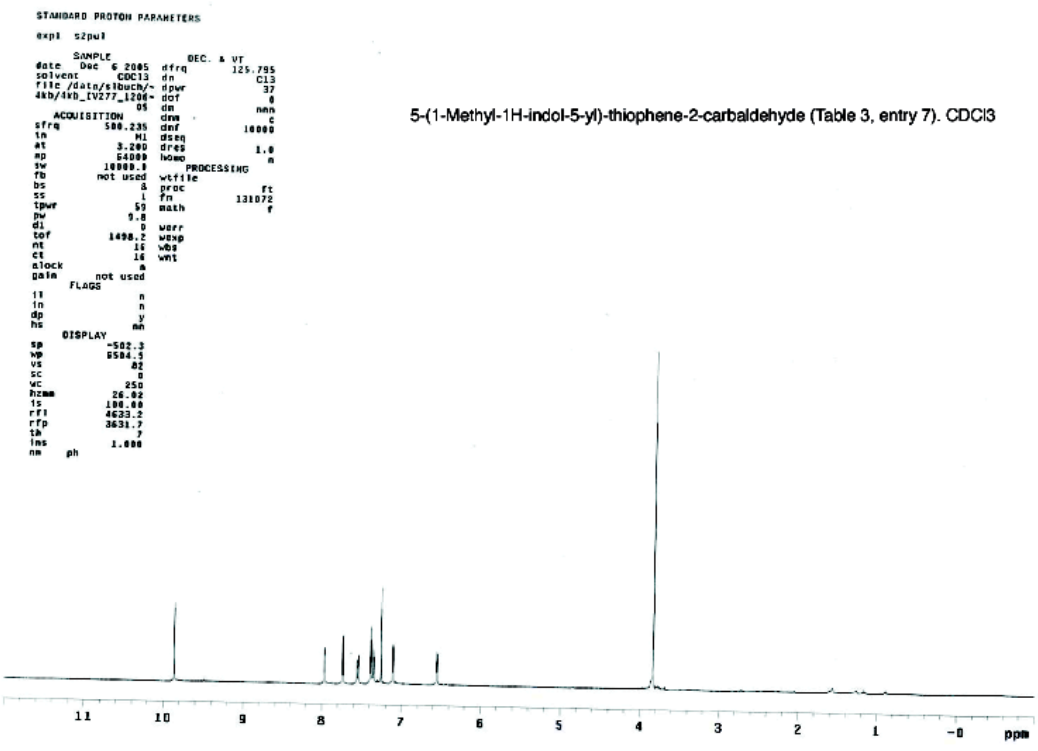


2-(5-Formyl-thiophen-2-yl)-pyrrole-1-carboxylic acid tert-butyl ester (Table 3, entry 5). CDCl3



5-(1-Methyl-1H-indol-5-yl)-thiophene-2-carbaldehyde (Table 3, entry 7). CDCl3

STANDARD PROTON PARAMETERS

expl s2pul

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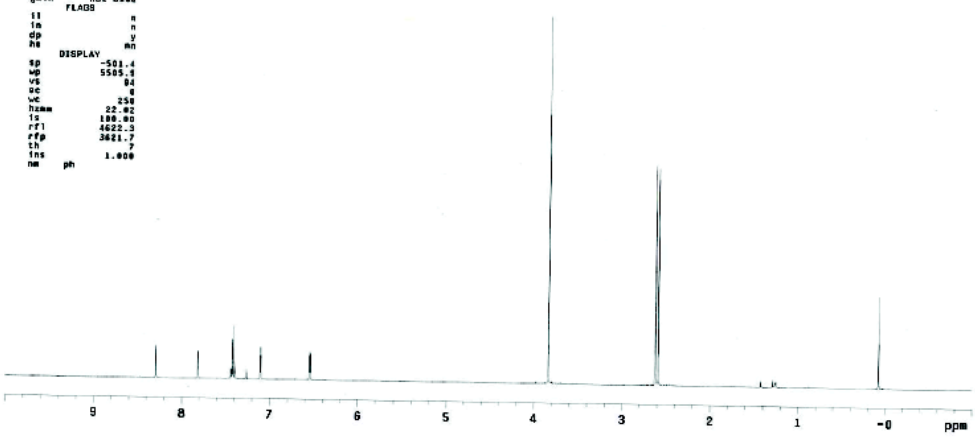
5-(3,6-Dimethyl-pyrazin-2-yl)-1-methyl-1H-indole (Table 3, entry 8). CDCl3



STANDARD PROTON PARAMETERS

expl s2pul IV88

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tof	1498.2		
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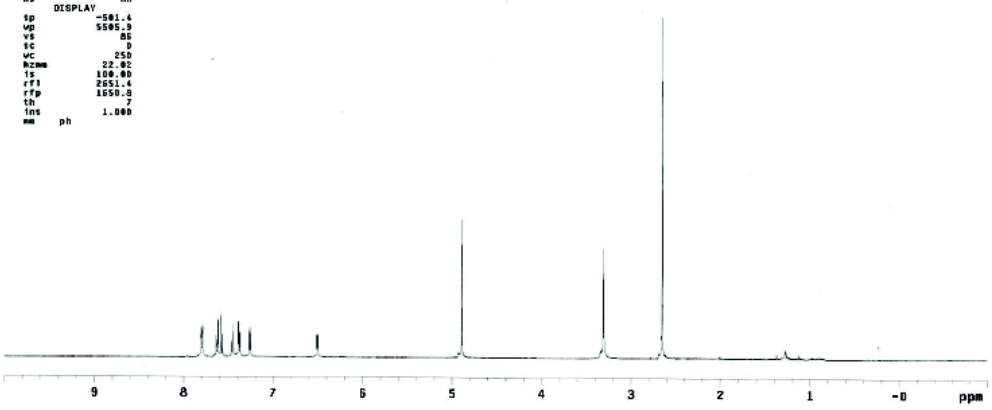
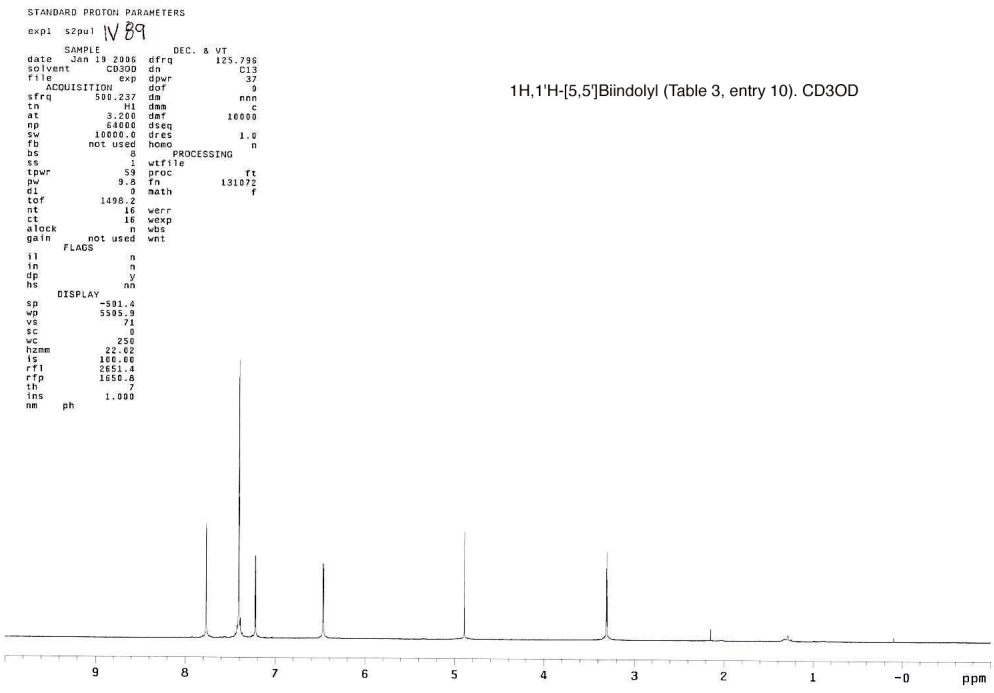
ins	1.000		
nm	ph		

5-(1H-Indol-5-yl)-2-methyl-benzooxazole (Table 3, entry 9). CD3OD





1H,1'H-[5,5']Biindolyl (Table 3, entry 10). CD3OD