

*Advanced*  
**Synthesis &  
Catalysis**

Supporting Information

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*Supporting Information for*

**An Efficient Method for the Selective Iridium-Catalyzed Monoalkylation of (Hetero)aromatic Amines with Primary Alcohols**

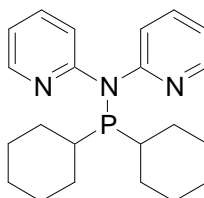
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## P,N-ligand synthesis

Py<sub>2</sub>NPPh<sub>2</sub> was prepared according to the literature procedure.

### Synthesis of Py<sub>2</sub>NPCy<sub>2</sub> (1b)



Di(2-pyridyl)amine (2.47 g, 14.4 mmol) was suspended in 50 mL hexane and the solution was cooled to -20 °C. Then *n*-BuLi (9.0 mL, 14.4 mmol) was added dropwise with a syringe. The reaction mixture was stirred at -20 °C for 30 min, allowed to warm to room temperature and stirred for 2 h. The reaction mixture was cooled to -20 °C and chlorodicyclohexylphosphine (3.18 mL, 14.4 mmol) added dropwise with a syringe. The yellow solution was then left to warm to room temperature and stirred overnight. The yellow suspension was filtered on a glass filter frit with a celite pad (3 cm) and washed with 100 mL pentane. The solvents were concentrated in vacuo to 10 mL and the product was left to crystallize at -20 °C. The supernatant solution was decanted, the solid washed with 3 mL cold pentane and subsequently dried in vacuo yielding Py<sub>2</sub>NPCy<sub>2</sub> as a beige solid (3.291 g, 64 %).

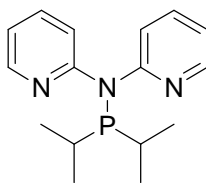
<sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 8.29 (ddd, *J* = 5.0, 2.1, 0.9 Hz, 2H), 7.53 (ddd, *J* = 8.5, 7.3, 2.1 Hz, 2H), 6.97 (d, *J* = 7.3 Hz, 2H), 6.91 (ddd, *J* = 7.2, 4.8, 0.9 Hz, 2H), 2.58-2.44 (m, 2H), 1.91-1.56 (m, 12H), 1.31-1.13 (m, 8H) ppm.

<sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 161.0 (d, *J* = 7.9 Hz), 148.5, 137.6, 118.9 (d, *J* = 7.8 Hz), 118.4, 38.0 (d, *J* = 16.6 Hz), 30.7 (d, *J* = 26.0 Hz), 28.9 (d, *J* = 9.4 Hz), 27.3 (d, *J* = 6.1 Hz), 27.3 (d, *J* = 28.7 Hz), 27.0 (d, *J* = 1.1 Hz) ppm.

<sup>31</sup>P-NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 77.8 ppm.

**Elemental analysis** found for C<sub>22</sub>H<sub>30</sub>N<sub>3</sub>P (calc.): C 72.06 (71.91), H 8.68 (8.23), N 11.44 (11.40).

### Synthesis of $\text{Py}_2\text{NPiPr}_2$ (1c)



Di(2-pyridyl)amine (2.57 g, 15.0 mmol) was suspended in 60 mL pentane/diethyl ether (2:1) and the solution was cooled to  $-20\text{ }^\circ\text{C}$ . Then *n*-BuLi (9.4 mL, 15.0 mmol) was added dropwise with a syringe. The reaction mixture was stirred at  $-20\text{ }^\circ\text{C}$  for 30 min, allowed to warm to room temperature and stirred for 2 h. The reaction mixture was cooled to  $-20\text{ }^\circ\text{C}$  and chlorodiisopropylphosphine (3.40 mL, 15.0 mmol) added dropwise with a syringe. The yellow solution was then left to warm to room temperature and stirred overnight. The yellow suspension was filtered on a glass filter frit with a celite pad (3 cm) and washed with 30 mL diethyl ether. The solvents were concentrated in vacuo, affording a red oil. 5 mL of a 1:1 hexane:diethyl ether mixture were added and the residue left to crystallize at  $-20\text{ }^\circ\text{C}$ . The supernatant solution was decanted and the solid subsequently dried in vacuo yielding  $\text{Py}_2\text{NPiPr}_2$  as an orange / red solid (3.017 g, 87 %).

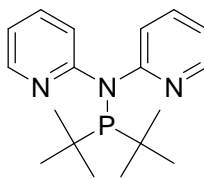
$^1\text{H-NMR}$  (300 MHz,  $\text{CD}_2\text{Cl}_2$ ): d = 8.28 (ddd,  $J = 5.0, 2.1, 0.9$  Hz, 2H), 7.54 (ddd,  $J = 8.9, 6.8, 1.9$  Hz, 2H), 6.99 (d,  $J = 8.2$  Hz, 2H), 6.92 (ddd,  $J = 7.2, 4.8, 0.9$  Hz, 2H), 2.78-2.62 (m, 2H), 1.13-1.00 (m, 12H) ppm.

$^{13}\text{C-NMR}$  (75 MHz,  $\text{CD}_2\text{Cl}_2$ ): d = 161.0 (d,  $J = 5.0$  Hz), 148.5, 137.6, 119.0 (d,  $J = 6.9$  Hz), 118.6, 27.8 (d,  $J = 15.8$  Hz), 20.6 (d,  $J = 11.4$  Hz), 20.1 (d,  $J = 29.7$  Hz) ppm.

$^{31}\text{P-NMR}$  (121 MHz,  $\text{CD}_2\text{Cl}_2$ ): d = 87.2 ppm.

**Elemental analysis** found for  $\text{C}_{16}\text{H}_{22}\text{N}_3\text{P}$  (calc.): C 67.05 (66.88), H 7.53 (7.72), N 14.54 (14.62).

## Synthesis of $\text{Py}_2\text{NPtBu}_2$ (**1d**)



Potassium hydride (0.48 g, 12.0 mmol) was suspended in 30 mL toluene and the solution was cooled to  $-40\text{ }^\circ\text{C}$ . Then di(2-pyridyl)amine (2.05 g, 12.0 mmol), dissolved in 30 mL toluene was added dropwise with a dropping funnel. The reaction mixture was stirred at  $-20\text{ }^\circ\text{C}$  for 30 min, allowed to warm to room temperature and stirred overnight. Then the reaction mixture was cooled to  $-20\text{ }^\circ\text{C}$  and chloro-di-tertbutylphosphine (2.3 mL, 12.0 mmol) was added dropwise with a syringe. The yellow solution was then stirred overnight at rt and subsequently heated to  $100\text{ }^\circ\text{C}$  for 4 days. The clear yellow solution was filtered on a glass filter frit with a celite pad (3 cm) and washed with 30 mL toluene. The solvent was removed in vacuo and the resulting brown oil left to crystallize at  $-20\text{ }^\circ\text{C}$ . The solid was dried in vacuo yielding  $\text{Py}_2\text{NPtBu}_2$  as a pale brown solid (3.301 g, 87 %).

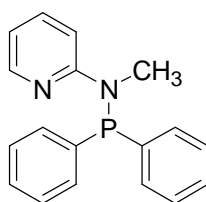
$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.35-8.25 (m, 2H), 7.58-7.33 (m, 3H), 6.99-6.79 (m, 2H), 6.75-6.58 (m, 1H), 1.22 (d,  $J$  = 13.2 Hz, 18H) ppm.

$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 163.8, 159.6, 148.3, 148.0, 137.5, 137.0, 120.3, 119.0, 118.9, 117.9, 36.7 (d,  $J$  = 30.6 Hz), 30.0 (d,  $J$  = 17.7 Hz) ppm.

$^{31}\text{P-NMR}$  (161 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 101.1 ppm.

**Elemental analysis** found for  $\text{C}_{18}\text{H}_{26}\text{N}_3\text{P}$  (calc.): C 68.39 (68.55), H 8.68 (8.31), N 13.37 (13.32).

## Synthesis of PyMeNPPh<sub>2</sub> (1e)



2-(Methylamino)pyridine (1.622 g, 15.0 mmol) was dissolved in 50 mL hexane / 30 mL diethyl ether and the solution was cooled to -30 °C. Then *n*-BuLi (9.4 mL, 15.0 mmol) was added dropwise with a syringe. The reaction mixture was stirred at -20 °C for 30 min, allowed to warm to room temperature and stirred for 2 h. The reaction mixture was cooled to -20 °C and chlorodiphenylphosphine (3.3 mL, 15.0 mmol) added dropwise with a syringe. The yellow solution was then left to warm to room temperature and stirred overnight. The yellow suspension was filtered on a glass filter frit with a celite pad (3 cm) and washed with 40 mL diethyl ether. The solvents were concentrated in vacuo until precipitation occurred and the solution was left to crystallize at -20 °C. The supernatant colored solution was decanted and the solid was then dried in vacuo yielding PyMeNPPh<sub>2</sub> as a beige solid (3.96 g, 90 %).

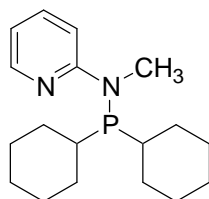
<sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 8.22 (ddd, *J* = 4.9, 2.0, 1.1 Hz, 1H), 7.54 (ddd, *J* = 8.8, 7.0, 1.9 Hz, 1H), 7.46-7.39 (m, 11H), 6.76 (ddd, *J* = 7.0, 4.9, 0.9 Hz, 1H), 2.92 (d, *J* = 1.5 Hz, 3H) ppm.

<sup>13</sup>C-NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 161.8 (d, *J* = 26.4 Hz), 148.1 (d, *J* = 1.6 Hz), 137.5 (d, *J* = 3.2 Hz), 137.4 (d, *J* = 15.3 Hz), 132.5 (d, *J* = 20.6 Hz), 129.5, 129.0 (d, *J* = 5.8 Hz), 115.1, 110.9 (d, *J* = 20.6 Hz), 34.7 (d, *J* = 8.4 Hz) ppm.

<sup>31</sup>P-NMR (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 51.9 ppm.

**Elemental analysis** found for C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>P (calc.): C 73.95 (73.96); H 5.78 (5.86); N 9.51 (9.58).

## Synthesis of PyMeNPCy<sub>2</sub> (1f)



Potassium hydride (0.601 g, 15.0 mmol) was suspended in 100 mL toluene, the solution cooled to -40 °C and 2-(methylamino)pyridine (1.622 g, 15.0 mmol) added dropwise with a syringe. The reaction mixture was stirred at -40 °C for 30 min, allowed to warm to room temperature and stirred for further 3 h until it became pale green. Then the reaction mixture was again cooled to -30 °C and chloro-dicyclohexylphosphine (3.49 g, 15.0 mmol) added dropwise with a syringe. The solution was stirred for further 30 min at -30 °C, the left to warm to rt and stirred overnight. The colorless but viscous solution was filtered on a glass filter frit with a celite pad (3 cm) and washed with 40 mL toluene. The solvent was removed in vacuo and the resulting colorless oil distilled under reduced pressure (0.06 mbar) at 180 °C to yield PyMeNPCy<sub>2</sub> as a colorless very viscous liquid (3.722 g, 82 %).

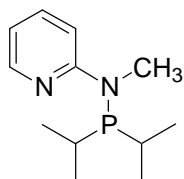
<sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 8.10 (d, *J* = 4.1 Hz, 1H), 7.55-7.44 (m, 1H), 7.38 (ddd, *J* = 8.9, 7.0, 2.1 Hz, 1H), 6.62-6.54 (m, 1H), 3.04 (d, *J* = 1.2 Hz, 3H), 1.96 (d, *J* = 10.8 Hz, 2H), 1.80-1.60 (m, 10H), 1.36-1.13 (m, 10H) ppm.

<sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 163.2 (d, *J* = 24.1 Hz), 147.7, 136.5, 113.7, 111.5 (d, *J* = 27.4 Hz), 37.0 (d, *J* = 15.6 Hz), 30.3 (d, *J* = 23.1 Hz), 29.6 (d, *J* = 8.5 Hz), 27.3 (d, *J* = 20.8 Hz), 27.2 (d, *J* = 26.4 Hz) ppm.

<sup>31</sup>P-NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 63.0 ppm.

**Elemental analysis** found for C<sub>18</sub>H<sub>29</sub>N<sub>2</sub>P (calc.): C 70.58 (71.02); H 9.52 (9.60); N 9.32 (9.20).

## Synthesis of PyMeNPiPr<sub>2</sub> (1g)



Potassium hydride (0.601 g, 15.0 mmol) was suspended in 100 mL toluene, the solution cooled to -40 °C and 2-(methylamino)pyridine (1.622 g, 15.0 mmol) added dropwise with a syringe. The reaction mixture was stirred at -40 °C for 30 min, allowed to warm to room temperature and stirred for further 3 h until it became pale green. Then the reaction mixture was again cooled to -30 °C and chloro-diisopropylphosphine (2.4 mL, 2.289 g, 15.0 mmol) added dropwise with a syringe. The solution was stirred for further 30 min at -30 °C, the left to warm to rt and stirred overnight. The solution was filtered on a glass filter frit with a celite pad (3 cm) and washed with 30 mL toluene. The solvents were removed in vacuo and the resulting colorless liquid distilled under reduced pressure (0.06 mbar) at 72 °C to yield PyMeNPiPr<sub>2</sub> as a pale yellow liquid (2.388 g, 71 %).

<sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 8.11 (d, *J* = 4.4 Hz, 1H), 7.52-7.44 (m, 1H), 7.40 (ddd, *J* = 8.7, 6.8, 2.1 Hz, 1H), 6.60 (ddd, *J* = 6.7, 5.2, 1.0 Hz, 1H), 3.04 (d, *J* = 1.8 Hz, 3H), 2.22-2.08 (m, 2H), 1.11 (dd, *J* = 16.8, 6.9 Hz, 6H), 0.99 (dd, *J* = 12.0, 7.0 Hz, 6H) ppm.

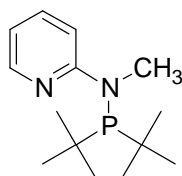
<sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 153.1 (d, *J* = 22.6 Hz), 147.7, 136.5, 113.9, 111.5 (d, *J* = 26.0 Hz), 26.8 (d, *J* = 15.5 Hz), 19.9, 19.6 (d, *J* = 17.7 Hz) ppm.

<sup>31</sup>P-NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 72.3 ppm.

**Elemental analysis** found for C<sub>12</sub>H<sub>21</sub>N<sub>2</sub>P (calc.): C 63.98 (64.26); H 9.56 (9.44); N 12.24 (12.49).



## Synthesis of PyMeNPtBu<sub>2</sub> (1h)



2-(Methylamino)pyridine (1.406 g, 13.0 mmol) was dissolved in 80 mL diethyl ether and the solution was cooled to -30 °C. Then *n*-BuLi (8.1 mL, 13.0 mmol) was added dropwise with a syringe. The reaction mixture was stirred at -30 °C for 30 min, allowed to warm to room temperature and stirred for 3 h. The reaction mixture was cooled to -20 °C and chlorodi-tert-butylphosphine (2.348 g, 13.0 mmol) added dropwise with a syringe. The yellow solution was then left to warm to room temperature and stirred overnight. The yellow suspension was filtered on a glass filter frit with a celite pad (3 cm) and washed with 40 mL diethyl ether. The solvents were concentrated in vacuo and the obtained yellow liquid was then distilled under reduced pressure (0.06 mbar) to yield PyMeNPtBu<sub>2</sub> as a yellow liquid (2.42 g, 73 %).

<sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 8.12 (dd, *J* = 4.9, 0.9 Hz, 1H), 7.72 (ddd, *J* = 8.7, 4.6, 0.7 Hz, 1H), 7.39 (ddd, *J* = 8.7, 6.8, 2.1 Hz, 1H), 6.64-6.56 (m, 1H), 3.27 (s, 3H), 1.24 (d, *J* = 12.6 Hz, 18H) ppm.

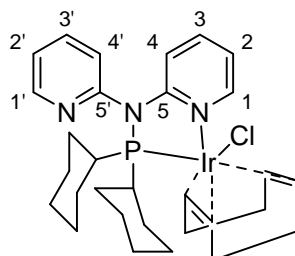
<sup>13</sup>C-NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 163.0 (d, *J* = 27.4 Hz), 147.0, 135.9 (d, *J* = 3.9 Hz), 113.4, 111.8 (d, *J* = 30.3 Hz), 36.9 (d, *J* = 8.4 Hz), 36.0 (d, *J* = 27.7 Hz), 29.8 (d, *J* = 17.1 Hz) ppm.

<sup>31</sup>P-NMR (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 86.1 ppm.

**Elemental analysis** found for C<sub>14</sub>H<sub>25</sub>N<sub>2</sub>P (calc.): C 66.15 (66.64); H 9.519 (9.99); N 11.21 (11.10).

## Complex Synthesis

### Preparation of [(Py<sub>2</sub>NPCy<sub>2</sub>)IrCl(cod)] (**2**)



[IrCl(cod)]<sub>2</sub> (0.134 g, 0.2 mmol) was dissolved in 15 mL CH<sub>2</sub>Cl<sub>2</sub> and subsequently a solution of Py<sub>2</sub>NPCy<sub>2</sub> (**1b**) (0.147 g, 0.4 mmol) in 5 mL CH<sub>2</sub>Cl<sub>2</sub> was added dropwise. A red solution was obtained and after 15 min the solvent was removed in vacuo, affording **2** as an orange solid in quantitative yields.

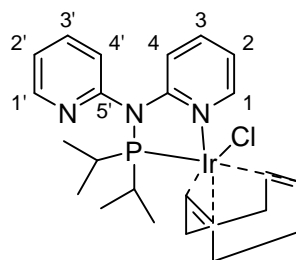
<sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 8.66 (d, *J* = 4.4 Hz, 1H, H<sup>1</sup>), 8.05 (d, *J* = 5.5 Hz, 1H, H<sup>1'</sup>), 7.91 (t, *J* = 7.7 Hz, 1H, H<sup>3</sup>), 7.47 (t, *J* = 7.7 Hz, 1H, H<sup>3'</sup>), 7.42 (dd, *J* = 6.6, 4.0 Hz, 1H, H<sup>2</sup>), 7.28 (d, *J* = 7.7 Hz, 1H, H<sup>4</sup>), 6.76 (t, *J* = 6.2 Hz, 1H, H<sup>2'</sup>), 6.24 (d, *J* = 8.8 Hz, 1H, H<sup>4'</sup>), 3.90 (s\_br, 4H, H<sub>CHcod</sub>), 2.71 (s\_br, 1H, H<sub>CHcyclohexyl</sub>), 2.39 (m, 4H, H<sub>CH<sub>2</sub>cod</sub>), 2.27 (s\_br, 1H, H<sub>CHcyclohexyl</sub>), 1.97-1.58 (m, 10H, H<sub>CH<sub>2</sub>cyclohexyl</sub> + 4H, H<sub>CH<sub>2</sub>cod</sub>), 1.45-0.9 (m, 10H, H<sub>CH<sub>2</sub>cyclohexyl</sub>) ppm.

<sup>13</sup>C-NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 164.9 (d, *J* = 15.1 Hz, C<sup>5</sup>), 154.3 (d, *J* = 6.0 Hz, C<sup>5'</sup>), 151.0 (s, C<sup>1</sup>), 148.5 (s, C<sup>1'</sup>), 139.9 (s, C<sup>3</sup>), 139.4 (s, C<sup>3'</sup>), 124.5 (s, C<sup>2</sup>), 124.2 (s, C<sup>4</sup>), 117.4 (s, C<sup>2'</sup>), 111.7 (d, *J* = 5.2 Hz, C<sup>4'</sup>), 67.3 (br, C<sub>CHcod</sub>), 66.0 (br, C<sub>CHcod</sub>), 42.1 (br, C<sub>CHcyclohexyl</sub>), 39.4 (br, C<sub>CHcyclohexyl</sub>), 33.4 (br, C<sub>CH<sub>2</sub>cod</sub>), 31.9 (br, C<sub>CH<sub>2</sub>cod</sub>), 28.0 (d, *J* = 5.0 Hz, C<sub>CH<sub>2</sub>cyclohexyl</sub>), 27.7 (d, *J* = 12.9 Hz, C<sub>CH<sub>2</sub>cyclohexyl</sub>), 27.5 (d, *J* = 11.3 Hz, C<sub>CH<sub>2</sub>cyclohexyl</sub>) 26.7 (s, C<sub>CH<sub>2</sub>cyclohexyl</sub>) ppm.

<sup>31</sup>P-NMR (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 103.6 ppm.

Elemental analysis found for C<sub>30</sub>H<sub>42</sub>ClIrN<sub>3</sub>P (calc.): C 51.72 (51.23); H 6.23 (6.02); N 5.68 (5.97).

### Preparation of [(Py<sub>2</sub>NP*i*Pr<sub>2</sub>)IrCl(cod)] (3)



[IrCl(cod)]<sub>2</sub> (0.269 g, 0.4 mmol) was dissolved in 15 mL CH<sub>2</sub>Cl<sub>2</sub> and subsequently a solution of Py<sub>2</sub>NP*i*Pr<sub>2</sub> (**1c**) (0.230 g, 0.8 mmol) in 5 mL CH<sub>2</sub>Cl<sub>2</sub> was added dropwise. A red solution was obtained and after 15 min the solvent was removed in vacuo, affording **3** as an orange solid in quantitative yields.

<sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 8.63 (d, *J* = 4.8 Hz, 1H, H<sup>1</sup>), 8.09 (d, *J* = 5.9 Hz, 1H, H<sup>1'</sup>), 7.89 (td, *J* = 7.8, 1.7 Hz, 1H, H<sup>3</sup>), 7.45 (t, *J* = 8.1 Hz, 1H, H<sup>3'</sup>), 7.39 (dd, *J* = 7.0, 5.1 Hz, 1H, H<sup>2</sup>), 7.29 (d, *J* = 7.7 Hz, 1H, H<sup>4</sup>), 6.74 (t, *J* = 6.6 Hz, 1H, H<sup>2'</sup>), 6.23 (d, *J* = 8.8 Hz, 1H, H<sup>4'</sup>), 3.85 (s\_br, 4H, H<sub>CHcod</sub>), 3.01 (s\_br, 1H, H<sub>CH*i*Pr</sub>), 2.55 (s\_br, 1H, H<sub>CH*i*Pr</sub>), 2.44-2.33 (m, 4H, H<sub>CH<sub>2</sub>cod</sub>), 1.91-1.81 (m, 4H, H<sub>CH<sub>2</sub>cod</sub>), 1.34-1.10 (m, 12H, H<sub>CH<sub>3</sub>*i*Pr</sub>) ppm.

<sup>13</sup>C-NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 164.5 (d, *J* = 15.8 Hz, C<sup>5</sup>), 154.3 (d, *J* = 5.8 Hz, C<sup>5'</sup>), 150.9 (s, C<sup>1</sup>), 148.7 (d, *J* = 1.3 Hz, C<sup>1'</sup>), 139.9 (s, C<sup>3</sup>), 139.1 (s, C<sup>3'</sup>), 124.4 (s, C<sup>2</sup>), 124.0 (s, C<sup>4</sup>), 117.3 (s, C<sup>2'</sup>), 111.4 (d, *J* = 5.2 Hz, C<sup>4'</sup>), 67.2 (br, C<sub>CHcod</sub>), 66.3 (br, C<sub>CHcod</sub>), 32.7 (br, C<sub>CH<sub>2</sub>cod</sub>), 28.9 (br, C<sub>CH*i*Pr</sub>), 18.2 (s, C<sub>CH<sub>3</sub>*i*Pr</sub>), 18.1 (s, C<sub>CH<sub>3</sub>*i*Pr</sub>), 17.6 (s, C<sub>CH<sub>3</sub>*i*Pr</sub>), 17.5 (s, C<sub>CH<sub>3</sub>*i*Pr</sub>) ppm.

<sup>31</sup>P-NMR (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>): d = 110.4 ppm.

Elemental analysis found for C<sub>24</sub>H<sub>34</sub>ClIrN<sub>3</sub>P x 0.5 CH<sub>2</sub>Cl<sub>2</sub> (calc.): C 44.41 (44.21); H 5.36 (5.30); N 6.05 (6.31).

## General procedure for screening reactions

In a pressure tube, stock solutions of  $[\text{IrCl}(\text{cod})]_2$  (80  $\mu\text{L}$ , 0.005 mmol, 0.0625 M in THF) and  $\text{Py}_2\text{NPiPr}_2$  (**1c**) (80  $\mu\text{L}$ , 0.01 mmol, 0.125 M in THF) were mixed. Then aniline (45.9  $\mu\text{L}$ , 0.50 mmol), benzyl alcohol (56.8  $\mu\text{L}$ , 0.55 mmol) and 1 mL diethylene glycol dimethyl ether (diglyme) as solvent were added. Last,  $\text{KO}^t\text{Bu}$  (0.56 g, 0.55 mmol) was dissolved in the reaction mixture and the pressure tube was fitted with a Teflon<sup>®</sup> cap and stirred at 110 °C for 24 h. The reaction mixture was cooled to room temperature. Then water (15 mL), diethyl ether (15 mL) and dodecane (56.8  $\mu\text{L}$ , 0.25 mmol) were added. After stirring, an aliquot of the organic phase was analyzed by gas chromatography.

## General procedure for the *N*-alkylation reactions

In a pressure tube, stock solutions of  $[\text{IrCl}(\text{cod})]_2$  (160  $\mu\text{L}$ , 0.01 mmol, 0.0625 M in THF) and  $\text{Py}_2\text{NPiPr}_2$  (**1c**) (160  $\mu\text{L}$ , 0.02 mmol, 0.125 M in THF) were mixed. Then the amine (1.00 equiv), the alcohol (1.10 equiv) and 1 mL diethylene glycol dimethyl ether (diglyme) as solvent were added. Last,  $\text{KO}^t\text{Bu}$  (1.10 equiv) was dissolved in the reaction mixture and the pressure tube was fitted with a Teflon<sup>®</sup> cap and stirred at 110 °C for 17 h. The reaction mixture was cooled to room temperature and all volatiles were removed in vacuo. Then water (40 mL) was added to the residue and extracted with diethyl ether (3 x 20 mL). The combined organic layers were washed with brine (15 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered and the solvent removed in vacuo. Finally, the residue was purified by column chromatography.

**Benzyl-phenyl-amine (Table 8, entry 1):**  $[\text{IrCl}(\text{cod})]_2$  (160  $\mu\text{L}$ , 0.01 mmol, 0.0625 M in THF),  $\text{Py}_2\text{NPiPr}_2$  (**1c**) (160  $\mu\text{L}$ , 0.02 mmol, 0.125 M in THF), aniline (90.9  $\mu\text{L}$ , 1.00 mmol), benzyl alcohol (113.6  $\mu\text{L}$ , 1.10 mmol),  $\text{KO}^t\text{Bu}$  (0.123 g, 1.10 mmol) and 1 mL diglyme. Purification by column chromatography (pentane: diethyl ether, 5:1) and gave 0.169 g (92%) benzyl-phenyl-amine as a yellow solid.

<sup>1</sup>**H-NMR** (400 MHz  $\text{CDCl}_3$ ):  $\delta$  = 7.37-7.24 (m, 5H), 7.16 (t,  $J$  = 8.4 Hz, 2H), 6.70 (t,  $J$  = 7.2 Hz, 1H), 6.63 (d,  $J$  = 5.9 Hz, 2H), 4.32 (s, 2H), 4.01 (s<sub>br</sub>, 1H) ppm.

<sup>13</sup>**C-NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.3, 139.6, 129.5, 128.9, 127.7, 127.5, 117.8, 113.1, 48.6 ppm.

**Benzyl-*m*-tolyl-amine (Table 8, entry 2):**  $[\text{IrCl}(\text{cod})]_2$  (160  $\mu\text{L}$ , 0.01 mmol, 0.0625 M in THF),  $\text{Py}_2\text{NPiPr}_2$  (**1c**) (160  $\mu\text{L}$ , 0.02 mmol, 0.125 M in THF), *m*-tolylamine (109  $\mu\text{L}$ ,

1.00 mmol), benzyl alcohol (113.6  $\mu$ L, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. Purification by column chromatography (pentane: diethyl ether, 5:1) afforded 0.182 g (92%) benzyl-*m*-tolyl-amine as a brown liquid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.43-7.32 (m, 5H), 7.11 (t,  $J$  = 7.6 Hz, 1H), 6.59 (d,  $J$  = 7.9 Hz, 1H), 6.51 (s, 1H), 6.49 (d,  $J$  = 8.4 Hz, 1H), 4.35 (s, 2H), 3.98 (s<sub>br</sub>, 1H), 2.32 (s, 3H) ppm.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 148.4, 139.7, 139.2, 129.3, 128.8, 127.7, 127.4, 118.7, 113.8, 110.1, 48.5, 21.8 ppm.

**Benzyl-(4-methoxy-phenyl)-amine (Table 8, entry 3):** [IrCl(cod)]<sub>2</sub> (160  $\mu$ L, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NPiPr<sub>2</sub> (**1c**) (160  $\mu$ L, 0.02 mmol, 0.125 M in THF), *p*-anisidine (0.123 g, 1.00 mmol), benzyl alcohol (113.6  $\mu$ L, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. Purification by column chromatography (pentane: diethyl ether, 5:1) afforded 0.208 g (98%) benzyl-(4-methoxy-phenyl)-amine as a yellow solid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.37-7.24 (m, 5H), 6.77 (dd,  $J$  = 9.2, 4.0 Hz, 2H), 6.61 (dd,  $J$  = 8.8, 4.8 Hz, 2H), 4.27 (s, 2H), 3.93 (s<sub>br</sub>, 1H), 3.73 (s, 3H) ppm.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 152.6, 142.3, 139.7, 128.8, 127.8, 127.4, 115.1, 114.6, 56.0, 49.6 ppm.

**Benzyl-(2-methoxy-phenyl)-amine (Table 8, entry 4):** [IrCl(cod)]<sub>2</sub> (160  $\mu$ L, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NPiPr<sub>2</sub> (**1c**) (160  $\mu$ L, 0.02 mmol, 0.125 M in THF), *o*-anisidine (112.8  $\mu$ L, 1.00 mmol), benzyl alcohol (113.6  $\mu$ L, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. Purification by column chromatography (pentane: diethyl ether, 20:1) afforded 0.169 g (79%) benzyl-(2-methoxy-phenyl)-amine as a brown liquid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.47-7.34 (m, 5H), 6.91 (t,  $J$  = 9.2 Hz, 1H), 6.86 (d,  $J$  = 3.9 Hz, 1H), 6.77 (t,  $J$  = 6.4 Hz, 1H), 6.68 (d,  $J$  = 7.2 Hz, 1H), 4.71 (s<sub>br</sub>, 1H), 4.42 (s, 2H), 3.90 (s, 3H) ppm.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 146.9, 139.7, 138.3, 128.7, 127.6, 127.2, 121.4, 116.8, 110.2, 109.5, 55.5, 48.2 ppm.

**Benzyl-(3-chloro-phenyl)-amine (Table 8, entry 5):** [IrCl(cod)]<sub>2</sub> (160  $\mu$ L, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NPiPr<sub>2</sub> (**1c**) (160  $\mu$ L, 0.02 mmol, 0.125 M in THF), 3-chloro-phenylamine (108.3  $\mu$ L, 1.00 mmol), benzyl alcohol (113.6  $\mu$ L, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g,

1.10 mmol) and 1 mL diglyme. Purification by column chromatography (pentane: diethyl ether, 5:1) afforded 0.209 g (96%) benzyl-(3-chloro-phenyl)-amine as a yellow liquid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): d = 7.27-7.17 (m, 4H), 6.97 (t, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 8.8 Hz, 1H), 6.50 (d, *J* = 1.6 Hz, 1H), 6.37 (dd, *J* = 10.4, 6.4 Hz, 1H), 4.17 (s, 2H), 3.97 (s\_br, 1H) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): d = 149.4, 138.9, 135.1, 130.4, 128.9, 127.6, 127.5, 117.5, 112.7, 111.3, 48.2 ppm.

**Benzyl-(4-trifluoromethyl-phenyl)-amine (Table 8, entry 6):** [IrCl(cod)]<sub>2</sub> (160 μL, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NPiPr<sub>2</sub> (**1c**) (160 μL, 0.02 mmol, 0.125 M in THF), 4-trifluoromethyl-phenylamine (124.3 μL, 1.00 mmol), benzyl alcohol (113.6 μL, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. **Reaction time: 3h!!** Purification by column chromatography (pentane: ethyl acetate, 5:1) afforded 0.169g (67 %) benzyl-(4-trifluoromethyl-phenyl)-amine as a brown solid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): d = 7.40 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 1.8 Hz, 2H), 7.35 (s, 2H), 7.32-7.28 (m, 1H), 6.63 (d, *J* = 8.8 Hz, 2H), 4.43-4.34 (m, 3H) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): d = 150.4, 138.4, 128.8, 127.5, 127.3, 126.6 (q, *J* = 3.9 Hz), 124.9 (q, *J* = 270.4 Hz), 119.0 (q, *J* = 23.5 Hz), 111.9, 44.8 ppm.

**4-Benzylamino-benzonitrile (Table 8, entry 7):** [IrCl(cod)]<sub>2</sub> (160 μL, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NPiPr<sub>2</sub> (**1c**) (160 μL, 0.02 mmol, 0.125 M in THF), 4-amino-benzonitrile (0.118 g, 1.00 mmol), benzyl alcohol (113.6 μL, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. **Reaction time: 20 min!!** Purification by column chromatography (pentane: diethyl ether, 1:1) afforded 0.144 g (69 %) 4-benzylamino-benzonitrile as a colorless solid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): d = 7.41-7.29 (m, 7H), 6.57 (d, *J* = 8.8 Hz, 2H), 4.59 (s\_br, 1H), 4.36 (d, *J* = 4.8 Hz, 2H) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): d = 151.3, 138.0, 133.9, 129.1, 127.9, 127.5, 120.6, 112.6, 47.7 ppm.

**Benzyl-biphenyl-2-yl-amine (Table 8, entry 8):** [IrCl(cod)]<sub>2</sub> (160 μL, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NPiPr<sub>2</sub> (**1c**) (160 μL, 0.02 mmol, 0.125 M in THF), biphenyl-2-ylamine (0.173 g, 1.00 mmol), benzyl alcohol (113.6 μL, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL

diglyme. Purification by column chromatography (pentane: diethyl ether, 30:1) afforded 0.238 g (92%) benzyl-biphenyl-2-yl-amine as a colorless solid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.48-7.38 (m, 5H), 7.35-7.23 (m, 5H), 7.18 (t, *J* = 8.8 Hz, 1H), 7.11 (dd, *J* = 9.2, 6.0 Hz, 1H), 6.77 (t, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 4.39 (s\_br, 1H), 4.32 (d, *J* = 4.0 Hz, 2H) ppm.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 145.0, 139.6, 139.6, 130.4, 129.6, 129.3, 129.2, 128.9, 128.8, 127.9, 127.5, 127.3, 117.5, 111.0, 48.4 ppm.

**Benzyl-pyridin-2-yl-amine (Table 8, entry 9):** [IrCl(cod)]<sub>2</sub> (160 μL, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NPiPr<sub>2</sub> (**1c**) (160 μL, 0.02 mmol, 0.125 M in THF), pyridin-2-ylamine (0.094 g, 1.00 mmol), benzyl alcohol (113.6 μL, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. Purification by column chromatography (pentane: diethyl ether, 5:1) afforded 0.171 g (93%) 2-benzyl-pyridin-2-yl-amine as a colorless solid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.09 (d, *J* = 4.4 Hz, 1H), 7.38 (t, *J* = 8.8 Hz, 1H), 7.34-7.25 (m, 5H), 6.57 (t, *J* = 6.0 Hz, 1H), 6.36 (d, *J* = 8.4 Hz, 1H), 4.79 (s\_br, 1H) ppm.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 158.8, 148.5, 139.4, 137.7, 128.9, 127.6, 127.5, 113.4, 107.0, 46.6 ppm.

**Benzyl-(4-methyl-pyridin-2-yl)-amine (Table 8, entry 10):** [IrCl(cod)]<sub>2</sub> (160 μL, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NPiPr<sub>2</sub> (**1c**) (160 μL, 0.02 mmol, 0.125 M in THF), 4-methyl-pyridin-2-yl amine (0.110 g, 1.00 mmol), benzyl alcohol (113.6 μL, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. Purification by column chromatography (diethyl ether) afforded 1.187 g (94%) benzyl-(4-methyl-pyridin-2-yl)-amine as a colorless solid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.96 (d, *J* = 5.9 Hz, 1H), 7.35-7.24 (m, 5H), 6.42 (d, *J* = 5.2 Hz, 1H), 6.19 (s, 1H), 4.78 (s\_br, 1H), 4.48 (d, *J* = 5.6 Hz, 2H), 2.19 (s, 3H) ppm.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.0, 148.8, 147.9, 139.5, 128.8, 127.6, 127.4, 115.0, 107.3, 46.6, 21.4 ppm.

**Benzyl-pyridin-3-yl-amine (Table 8, entry 11):** [IrCl(cod)]<sub>2</sub> (160 μL, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NPiPr<sub>2</sub> (**1c**) (160 μL, 0.02 mmol, 0.125 M in THF), pyridin-3-ylamine (0.097 g, 1.00 mmol), benzyl alcohol (113.6 μL, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. Purification by column chromatography (ethyl acetate) afforded 0.178 g (97%) benzyl-pyridin-3-yl-amine as a yellow solid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ = 8.5 (d, *J* = 2.8 Hz, 1H), 7.94 (d, *J* = 4.8 Hz, 1H), 7.34-7.26 (m, 5H), 7.4 (dd, *J* = 4.4, 3.9 Hz, 1H), 6.84 (dd, *J* = 10.4, 5.6 Hz, 1H), 4.32 (d, *J* = 4.4 Hz, 2H), 4.19 (s<sub>br</sub>, 1H) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): δ = 144.2, 139.1, 138.7, 136.4, 128.9, 127.7, 127.6, 123.9, 118.7, 48.0 ppm.

**(4-Methyl-benzyl)-pyridin-2-yl-amine (Table 9, entry 1):** [IrCl(cod)]<sub>2</sub> (160 μL, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NP*i*Pr<sub>2</sub> (**1c**) (160 μL, 0.02 mmol, 0.125 M in THF), pyridin-2-ylamine (0.095 g, 1.00 mmol), *p*-tolyl-methanol (0.137 g, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. Purification by column chromatography (diethyl ether) afforded 0.183 g (92%) (4-methyl-benzyl)-pyridin-2-yl-amine as a colorless solid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ = 8.09 (d, *J* = 4.8 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 1.2 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.58 (t, *J* = 6.4 Hz, 1H), 6.36 (d, *J* = 8.4 Hz, 1H), 4.85 (s<sub>br</sub>, 1H), 4.45 (d, *J* = 5.6 Hz, 2H), 2.34 (s, 3H) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): δ = 158.9, 148.4, 137.7, 137.1, 136.3, 129.5, 127.6, 113.3, 106.9, 46.3, 21.3 ppm.

**(4-Chloro-benzyl)-pyridin-2-yl-amine (Table 9, entry 2):** [IrCl(cod)]<sub>2</sub> (160 μL, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NP*i*Pr<sub>2</sub> (**1c**) (160 μL, 0.02 mmol, 0.125 M in THF), pyridin-2-ylamine (0.095 g, 1.00 mmol), (4-chloro-phenyl)-methanol (0.158 g, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. Purification by column chromatography (diethyl ether) afforded 0.207 g (97%) (4-chloro-benzyl)-pyridin-2-yl-amine as a colorless solid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ = 8.09 (d, *J* = 4.4 Hz, 1H), 7.40-7.27 (m, 5H), 6.58 (d, *J* = 7.2 Hz, 1H), 6.33 (d, *J* = 8.4 Hz, 1H), 4.87 (s<sub>br</sub>, 1H), 4.47 (d, *J* = 4.0 Hz, 2H) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): δ = 158.6, 148.6, 138.0, 137.7, 133.1, 129.0, 128.9, 113.6, 107.1, 45.7 ppm.

**(4-Methoxy-benzyl)-pyridin-2-yl-amine (Table 9, entry 3):** [IrCl(cod)]<sub>2</sub> (160 μL, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NP*i*Pr<sub>2</sub> (**1c**) (160 μL, 0.02 mmol, 0.125 M in THF), pyridin-2-ylamine (0.095 g, 1.00 mmol), (4-methoxy-phenyl)-methanol (0.154 g, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. Purification by column chromatography (diethyl ether) afforded 0.207 g (97%) (2-methoxy-benzyl)-pyridin-2-yl-amine as a colorless solid.



**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): d = 8.06 (d, *J* = 5.2 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 6.8 Hz, 2H), 6.55 (t, *J* = 6.8 Hz, 1H), 6.33 (d, *J* = 8.4 Hz, 1H), 4.84 (s\_br, 1H), 4.39 (d, *J* = 5.6 Hz, 2H), 3.76 (s, 3H) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): d = 159.0, 158.8, 148.4, 137.6, 131.4, 128.9, 114.2, 113.3, 107.0, 55.5, 46.0 ppm.

**(2-Methoxy-benzyl)-pyridin-2-yl-amine (Table 9, entry 4):** [IrCl(cod)]<sub>2</sub> (160 μL, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NPiPr<sub>2</sub> (**1c**) (160 μL, 0.02 mmol, 0.125 M in THF), pyridin-2-ylamine (0.095 g, 1.00 mmol), (2-methoxy-phenyl)-methanol (147.70 μL, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. Purification by column chromatography (diethyl ether) afforded 0.203 g (95%) (2-methoxy-benzyl)-pyridin-2-yl-amine as a colorless solid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): d = 8.08 (d, *J* = 5.6 Hz, 1H), 7.36 (dt, *J* = 8.4, 6.8 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.23 (dt, *J* = 8.6, 8.0 Hz, 1H), 6.86 (m, 2H), 6.53 (t, *J* = 6.0 Hz, 1H), 6.37 (d, *J* = 8.4 Hz, 1H), 4.95 (s\_br, 1H), 4.47 (d, *J* = 6.39, 2H), 3.84 (s, 3H) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): d = 159.1, 157.7, 148.4, 137.6, 128.9, 129.6, 127.3, 120.7, 113.0, 110.4, 106.9, 55.5, 41.9 ppm.

**Furan-2-ylmethyl-pyridin-2-yl-amine (Table 9, entry 5):** [IrCl(cod)]<sub>2</sub> (160 μL, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NPiPr<sub>2</sub> (**1c**) (160 μL, 0.02 mmol, 0.125 M in THF), pyridin-2-ylamine (0.095 g, 1.00 mmol), furan-2-yl-methanol (97.4 μL, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. Purification by column chromatography (pentane: diethyl ether, 1:1) afforded 0.123 g (71%) furan-2-ylmethyl-pyridin-2-yl-amine as a brown solid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): d = 8.09 (d, *J* = 5.6 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 1.0 Hz, 1H), 6.58 (t, *J* = 6.0 Hz, 1H), 6.14 (d, *J* = 8.4 Hz, 1H), 6.29 (t, *J* = 2.8 Hz, 1H), 6.21 (d, *J* = 3.2 Hz, 1H), 4.88 (s\_br, 1H), 4.49 (d, *J* = 5.6 Hz, 2H) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): d = 158.4, 152.8, 148.3, 142.1, 137.6, 113.6, 110.5, 107.5, 107.1, 39.5 ppm.

**Pyridin-2-yl-thiophen-2-ylmethyl-amine (Table 9, entry 6):** [IrCl(cod)]<sub>2</sub> (160 μL, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NPiPr<sub>2</sub> (**1c**) (160 μL, 0.02 mmol, 0.125 M in THF), pyridin-2-ylamine (0.095 g, 1.00 mmol), thiophen-2-yl-methanol (140.9 μL, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. Purification by column chromatography

(pentane: diethyl ether, 1:1) afforded 0.131 g (69%) pyridin-2-yl-tiophen-2-ylmethyl-amine as a colorless solid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): d = 8.11 (d, *J* = 5.2 Hz, 1H), 7.40 (t, *J* = 8.4, 1H), 7.18 (d, *J* = 6.4 Hz, 1H), 6.99 (d, *J* = 2.8 Hz, 1H), 6.94 (t, *J* = 3.4 Hz, 1H), 6.59 (t, *J* = 4.6 Hz, 1H), 6.41 (d, *J* = 8.4, 1H), 4.85 (s\_br, 1H), 4.68 (d, *J* = 5.6 Hz, 2H) ppm.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): d = 158.3, 148.4, 142.8, 137.6, 127.0, 125.4, 124.9, 113.7, 107.6, 41.5 ppm.

**Pyridin-2-yl-pyridin-2-ylmethyl-amine (Table 9, entry 7):** [IrCl(cod)]<sub>2</sub> (160 μL, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NPiPr<sub>2</sub> (**1c**) (160 μL, 0.02 mmol, 0.125 M in THF), pyridin-2-ylamine (0.095 g, 1.00 mmol), pyridin-2-yl-methanol (108.4 μL, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. Purification by column chromatography (pentane: diethyl ether: THF, 1:1:1) afforded 0.082 g (44%) pyridin-2-yl-pyridin-2-ylmethyl-amine as a colorless solid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): d = 8.53 (d, *J* = 4.8 Hz, 1H), 8.08 (d, *J* = 4.8 Hz, 1H), 7.59 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.35 (dt, *J* = 8.8, 1.6 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 5.2 Hz, 1H), 6.54 (t, *J* = 5.2 Hz, 1H), 6.42 (d, *J* = 8.4 Hz, 1H), 5.66 (s\_br, 1H), 4.62 (d, *J* = 5.2 Hz, 2H) ppm.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): d = 158.6, 158.3, 149.2, 148.3, 137.4, 136.8, 122.2, 121.8, 113.2, 107.9, 47.4 ppm.

**Butyl-pyridin-2-yl-amine (Table 9, entry 9):** [IrCl(cod)]<sub>2</sub> (160 μL, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NPiPr<sub>2</sub> (**1c**) (160 μL, 0.02 mmol, 0.125 M in THF), pyridin-2-ylamine (0.095 g, 1.00 mmol), butan-1-ol (102.54 μL, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. Purification by column chromatography (pentane: diethyl ether, 1:1) afforded 0.113 g (75%) butyl-pyridin-2-yl-amine as a colorless solid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): d = 8.04 (d, *J* = 4.0 Hz, 1H), 7.37 (dt, *J* = 8.4, 6.8 Hz, 1H), 6.51 (t, *J* = 6.0 Hz, 1H), 6.33 (d, *J* = 8.4 Hz, 1H); 4.52 (s\_br, 1H), 3.21 (q, *J* = 6.8 Hz, 2H), 1.61-1.53 (m, 2H), 1.42-1.38 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): d = 159.2, 148.4, 137.5, 112.7, 106.4, 42.2, 31.8, 20.4, 14.0 ppm.

**Octyl-pyridin-2-yl-amine (Table 9, entry 10):** [IrCl(cod)]<sub>2</sub> (160 μL, 0.01 mmol, 0.0625 M in THF), Py<sub>2</sub>NPiPr<sub>2</sub> (**1c**) (160 μL, 0.02 mmol, 0.125 M in THF), pyridin-2-ylamine (0.095 g,

1.00 mmol), octan-1-ol (175.0  $\mu$ L, 1.10 mmol), KO<sup>t</sup>Bu (0.123 g, 1.10 mmol) and 1 mL diglyme. Purification by column chromatography (pentane: diethyl ether, 1:1) afforded 0.149 g (72%) octyl-pyridin-2-yl-amine as a colorless solid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.04 (dd,  $J$  = 6.4, 4.0 Hz, 1H), 7.38 (dt,  $J$  = 7.2, 6.8 Hz, 1H), 6.52 (t,  $J$  = 4.8 Hz, 1H), 6.33 (d,  $J$  = 8.4 Hz, 1H), 4.48 (s<sub>br</sub>, 1H), 3.21 (q,  $J$  = 7.2 Hz, 2H), 1.59 (m, 2H), 1.36-1.24 (m, 10H), 0.85 (t,  $J$  = 6.8 Hz, 3H) ppm.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 159.2, 148.4, 137.6, 112.8, 106.5, 42.5, 32.0, 29.8, 29.6, 29.5, 27.3, 22.9, 14.3 ppm.