

## Supporting Information

### Palladium-Catalyzed Amination of Aryl and Heteroaryl Tosylates at Room Temperature

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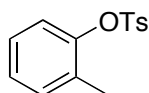
**General Conderations.** Unless otherwise noted, all manipulation was conducted inside an inert atmosphere glovebox.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX 400 or 500 MHz Spectrometer and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a General Electric QE 300 MHz spectrometer with tetramethylsilane or residual protiated solvent as a reference. All  $^{31}\text{P}\{^1\text{H}\}$  NMR chemical shifts are reported in parts per million relative to an 85%  $\text{H}_3\text{PO}_4$  external standard. Shifts downfield of the standard are reported as positive. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA or Robertson Microlab, Inc., Madison, NJ. GC and GC/MS analyses were conducted with an HP-1 methyl silicone column. CyPF-*t*-Bu (1-dicyclohexylphosphino-2-di-*t*-butylphosphinoethylferrocene) was obtained from Solvias AG and Strem Chemicals and used without further purification. All other chemicals were used as received from commercial sources.

**Practical synthesis of Pd[P(*o*-tol) $_3$ ] $_2$  (**2**).<sup>1</sup>** A suspension of Pd(dba) $_2$  (400 mg, 0.696 mmol) and P(*o*-tol) $_3$  (423 mg, 1.39 mmol) in anhydrous DMF (56 mL) was stirred at room temperature for 1 h. The resulting greyish-yellow precipitate including Pd-black was collected by filtration and washed with small volume of ether. To remove the Pd-black, the precipitate was dissolved in THF (140 mL), and then filtered through Celite. The solvent was removed under reduced pressure to afford the titled compound in 95% yield (472 mg) as a yellow powder.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  7.03-7.05 (m, 18 H), 6.80-6.83 (m, 6 H), 2.97 (s, 18 H);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  -6.97 (s).

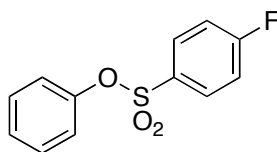
**Synthesis of Pd(CyPF-*t*-Bu)[P(*o*-tol) $_3$ ] (**1**).<sup>2</sup>** A solution of CyPF-*t*-Bu (2.8 mg, 0.005 mmol) and **2** (3.6 mg, 0.005 mmol) in 0.5 mL of toluene was stirred at room temperature for 5 min. The solution was transferred to an NMR sample tube and was characterized by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy.  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta$  69.39 (t,  $J = 88.6$  Hz), 21.87 (br), 11.35 (br).

**Preparation of solid admixture of **2** and **3**.** Pd[P(*o*-tol) $_3$ ] $_2$  (21.5 mg, 0.03 mmol) and CyPF-*t*-Bu (16.6 mg, 0.03 mmol) was put in a 4 ml vial and stirred to combine

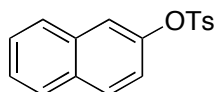
manually using micro-spatula to give the titled compound as a light yellow powder. This powder (effective molecular weight: 1269 gmol<sup>-1</sup>) was stored in air for at least 48 h with no loss of activity and was tested as the pre-catalyst for the reaction as shown in Table 1, entry 1 to give 95% of the coupled product.



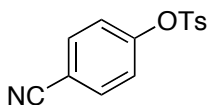
**2-Methylphenyl *p*-toluenesulfonate**<sup>3</sup>: **General procedure A for preparation of aryl tosylates.** According to literature procedure,<sup>4</sup> to a solution of *o*-cresol (1.62 g, 15 mmol) in pyridine (15 mL), TsCl (3.42 g, 18 mmol) was added portionwise under air atmosphere and the whole mixture was stirred at 45 °C for 15 h. After cooling to room temperature, 20 mL of water was added to the mixture and then stirred for 3 h. This mixture was diluted with benzene (200 mL) and washed with water, 10% aqueous HCl (x 2), saturated aqueous NaHCO<sub>3</sub>, brine and then dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, solvent was evaporated in vacuo to give white solid. Recrystallization from hexane and ethyl acetate gave 3.38 g (86%) of the titled compound as colorless needles. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.74 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 6.97-7.16 (m, 4 H), 2.46 (s, 3 H), 2.07 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 148.34, 145.29, 145.08, 133.18, 131.56, 129.78, 128.41, 126.96, 126.89, 122.31, 21.69, 16.25.



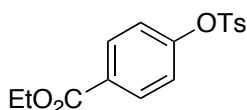
**Phenyl *p*-fluorobenzenesulfonate**<sup>5</sup> The general procedure A conducted with phenol (1.88 g, 20 mmol) and *p*-fluorobenzenesulfonyl chloride (4.66 g, 24 mmol) gave 4.65 g (92%) of the titled compound as a colorless liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.83-7.86 (m, 2 H), 7.25-7.32 (m, 3 H), 7.18-7.22 (m, 2 H), 6.99 (d, *J* = 8.0 Hz, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 166.93, 164.88, 149.37, 131.30 (d, *J* = 38.5 Hz), 129.66, 127.25, 122.21, 116.46 (d, *J* = 91.0 Hz).



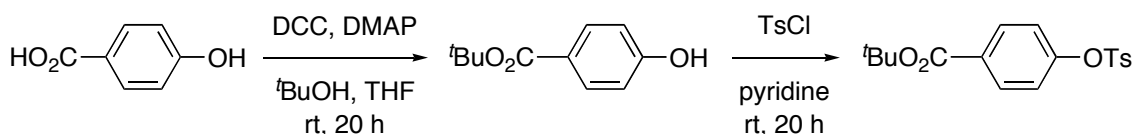
**2-Naphthyl *p*-toluenesulfonate**<sup>6</sup> The general procedure A conducted with 2-naphthol (2.88 g, 20 mmol) and TsCl (4.55 g, 24 mmol) gave 5.42 g (91%) of the titled compound as colorless needles. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.72-7.82 (m, 5 H), 7.47-7.50 (m, 3 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.09 (dd, *J* = 2.5, 9.0 Hz, 1H), 2.44 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 147.16, 145.38, 133.40, 132.36, 131.84, 129.75, 129.73, 128.53, 127.85, 127.72, 126.82, 126.35, 121.15, 119.94, 21.65.



**4-Cyanophenyl *p*-toluenesulfonate.**<sup>6</sup> The general procedure A conducted with 4-cyanophenol (1.79 g, 15 mmol) and TsCl (3.42 g, 18 mmol) gave 3.72 g (91%) of the titled compound as colorless needles. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.71 (d, *J* = 10.0 Hz, 2 H), 7.62 (d, *J* = 5.0 Hz, 2 H), 7.35 (d, *J* = 5.0 Hz, 2 H), 7.13 (d, *J* = 10.0 Hz, 2H), 2.47 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 152.51, 146.11, 133.87, 131.71, 130.03, 128.42, 123.42, 117.71, 111.14, 21.70.



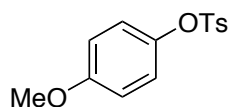
**Ethyl 4-[[4-(4-methylphenyl)sulfonyl]oxy]benzoate.**<sup>7</sup> The general procedure A conducted with ethyl 4-hydroxybenzoate (2.49 g, 15 mmol) and TsCl (3.42 g, 18 mmol) gave 4.53 g (94%) of the titled compound as colorless needles. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.97 (d, *J* = 8.5 Hz, 2 H), 7.69 (d, *J* = 8.5 Hz, 2 H), 7.31 (d, *J* = 8.5 Hz, 2 H), 7.05 (d, *J* = 8.5 Hz, 2H), 4.35 (q, *J* = 7.0 Hz, 2 H), 2.44 (s, 3 H), 1.37 (t, *J* = 7.0 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 165.46, 152.83, 145.68, 132.00, 131.21, 129.85, 129.22, 128.47, 122.27, 61.26, 21.67, 14.25.



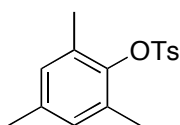
**4-Hydroxybenzoic acid *tert*-butyl ester.**<sup>8</sup> According to literature procedure,<sup>8</sup> to a solution of 4-hydroxybenzoic acid (3.0 g, 21.74 mmol), DMAP (103 mg, 0.84 mmol) and *t*BuOH (60 ml) in dry THF (90 ml) under nitrogen atmosphere, a solution of DCC (6.72 g, 32.61 mmol) in dry THF (30 ml) was added dropwise for 30 min. The reaction mixture was stirred at room temperature for 20 h. The residue mixture was filtered and evaporated in *vacuo*. The filtrate was diluted with AcOEt (50 ml) and washed with saturated aqueous NaHCO<sub>3</sub> (×2), brine and then dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, solvent was evaporated in *vacuo* to give pale yellow solid. The crude mixture was purified by flash chromatography (hexane to hexane/ethyl acetate (10/3)) to give 2.38 g (56%) of the titled compound as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.89 (d, *J* = 8.8 Hz, 2 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 6.30 (s, br, 1 H), 1.58 (s, 9 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 165.97, 159.58, 131.61, 124.10, 114.95, 80.95, 28.24.

***tert*-Butyl 4-[[4-(4-methylphenyl)sulfonyl]oxy]benzoate.** The general procedure A conducted with 4-hydroxybenzoic acid *tert*-butyl ester (2.35 g, 12 mmol) and TsCl (2.74 g, 14.4 mmol) gave 3.16 g (76%) of the titled compound as a white powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.91 (d, *J* = 9.0 Hz, 2 H), 7.70 (d, *J* = 8.5 Hz, 2 H), 7.31 (d, *J* = 8.5 Hz, 2 H), 7.02 (d, *J* = 9.0 Hz, 2H), 2.45 (s, 3 H), 1.57 (s, 9 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 164.58,

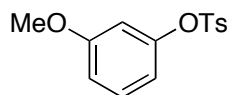
152.57, 145.61, 132.06, 131.04, 130.73, 129.83, 128.47, 122.06, 81.51, 28.09, 21.72; Anal. Calcd. For C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>S: C, 62.05; H, 5.79. Found: C, 62.01; H, 5.72.



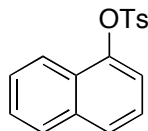
**4-Methoxyphenyl *p*-toluenesulfonate.**<sup>9</sup> The general procedure A conducted with 4-methoxyphenol (1.86 g, 15 mmol) and TsCl (3.42 g, 18 mmol) gave 3.78 g (90%) of the titled compound as colorless needles. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.68 (d, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 6.87 (d, *J* = 8.0 Hz, 2 H), 6.76 (d, *J* = 8.0 Hz, 2 H), 3.76 (s, 3 H), 2.45 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 158.16, 145.24, 143.04, 132.27, 129.69, 128.55, 123.34, 114.41, 55.50, 21.66.



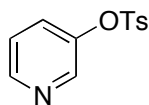
**2,4,6-Trimethylphenyl *p*-toluenesulfonate.**<sup>10</sup> The general procedure A conducted with 2,4,6-trimethylphenol (2.04 g, 15 mmol) and TsCl (3.42 g, 18 mmol) gave 4.12 g (95%) of the titled compound as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.85 (d, *J* = 8.4 Hz, 2 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 6.83 (s, 2 H), 2.47 (s, 3 H), 2.25 (s, 3 H), 2.07 (s, 6 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 145.38, 145.04, 136.28, 134.45, 131.75, 129.82, 129.80, 128.10, 21.67, 20.65, 17.16.



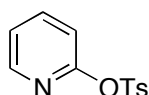
**3-Methoxyphenyl *p*-toluenesulfonate.**<sup>11</sup> The general procedure A conducted with 3-methoxyphenol (1.86 g, 15 mmol) and TsCl (3.42 g, 18 mmol) gave 4.01 g (96%) of the titled compound as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.72 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.16 (t, *J* = 8.0 Hz, 1 H), 6.77-6.80 (m, 1H), 6.52-6.56 (m, 2H), 3.72 (s, 3 H), 2.45 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 160.36, 150.45, 145.33, 132.37, 129.84, 129.70, 128.50, 114.28, 113.01, 108.19, 55.37, 21.64.



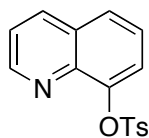
**1-Naphthyl *p*-toluenesulfonate.**<sup>12</sup> The general procedure A conducted with 1-naphthol (2.88 g, 20 mmol) and TsCl (4.55 g, 24 mmol) gave 5.66 g (83%) of the titled compound as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.91 (d, *J* = 8.0 Hz, 1 H), 7.73-7.82 (m, 4 H), 7.41-7.49 (m, 2 H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 1 H), 2.42 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 145.76, 145.40, 134.69, 132.74, 129.78, 128.48, 127.67, 127.28, 127.07, 126.69, 126.67, 125.09, 121.77, 118.38, 21.65.



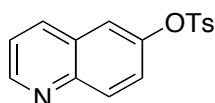
**3-Pyridyl *p*-toluenesulfonate.**<sup>13</sup> **General procedure B for preparation of heteroaryl tosylates.** To a solution of 3-hydroxypyridine (1.43 g, 15 mmol) in pyridine (15 mL), TsCl (3.42 g, 18 mmol) was added portionwise under air atmosphere and the whole mixture was stirred at 45 °C for 24 h. After cooling to room temperature, 20 mL of water was added to the mixture and then stirred for 3 h. This mixture was diluted with benzene (200 mL) and washed with 10% aqueous NaOH (x 2), water and brine and then dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, solvent was evaporated in vacuo to give pale yellow oil. Silica gel column chromatography (hexane/ethyl acetate = 2/1) gave 3.50 g (94%) of the titled compound as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.50 (d, *J* = 5.0 Hz, 1 H), 8.14 (d, *J* = 2.5 Hz, 1 H), 7.70 (d, *J* = 8.0 Hz, 2 H), 7.47 (ddd, *J* = 2.5, 5.0, 8.5 Hz, 1 H), 7.28-7.34 (m, 3 H), 2.45 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 148.23, 146.45, 146.01, 144.00, 131.59, 130.22, 130.02, 128.51, 124.18, 21.70.



**2-Pyridyl *p*-toluenesulfonate.**<sup>13</sup> The general procedure B conducted with 2-hydroxypyridine (1.43 g, 15 mmol) and TsCl (3.42 g, 18 mmol) gave 3.59 g (96%) of the titled compound as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.25 (d, *J* = 7.0 Hz, 1 H), 7.88 (d, *J* = 8.5 Hz, 2 H), 7.76 (ddd, *J* = 2.0, 7.0, 8.0 Hz, 1 H), 7.34 (d, *J* = 8.5 Hz, 2 H), 7.21 (m, 1 H), 7.11 (d, *J* = 8.0 Hz, 1 H), 2.44 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 156.97, 148.31, 145.29, 140.07, 133.63, 129.69, 128.57, 122.61, 115.94, 21.68.

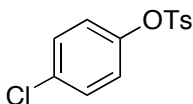


**8-Quinolinyl *p*-toluenesulfonate.**<sup>13</sup> The general procedure B conducted with 8-hydroxyquinoline (2.18 g, 15 mmol) and TsCl (3.42 g, 18 mmol) gave 4.29 g (96%) of the titled compound as colorless crystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.82 (d, *J* = 2.0, 4.0 Hz, 1 H), 8.13 (dd, *J* = 2.0, 8.5 Hz, 1 H), 7.87 (d, *J* = 8.0 Hz, 2 H), 7.74 (dd, *J* = 1.0, 8.0 Hz, 1 H), 7.59 (d, *J* = 1.0, 7.5 Hz, 1 H), 7.49 (t, *J* = 7.5, 8.0 Hz, 1 H), 7.39 (dd, *J* = 4.0, 8.5 Hz, 1 H), 7.25 (d, *J* = 8.0 Hz, 2 H), 2.40 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 150.78, 145.52, 145.00, 141.60, 135.67, 133.15, 129.59, 129.41, 128.74, 126.96, 125.96, 122.46, 121.82, 21.61.

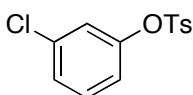


**6-Quinolinyl *p*-toluenesulfonate.**<sup>13</sup> The general procedure B conducted with 6-hydroxyquinoline (2.18 g, 15 mmol) and TsCl (3.42 g, 18 mmol) gave 4.12 g (92%)

of the titled compound as light brown needles.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.92 (dd,  $J = 1.5, 4.0$  Hz, 1 H), 8.10 (d,  $J = 8.5$  Hz, 1 H), 8.01 (d,  $J = 9.5$  Hz, 1 H), 7.73 (d,  $J = 8.0$  Hz, 2 H), 7.56 (d,  $J = 2.5$  Hz, 1 H), 7.43 (dd,  $J = 4.0, 8.5$  Hz, 1 H), 7.31 (d,  $J = 8.0$  Hz, 2 H), 7.25 (dd,  $J = 2.5, 9.5$  Hz, 1 H), 2.45 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  150.89, 147.21, 146.61, 145.65, 135.99, 132.11, 131.40, 129.86, 128.49, 128.30, 124.60, 121.83, 119.95, 21.67.



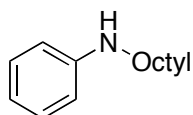
**4-Chlorophenyl *p*-toluenesulfonate.**<sup>14</sup> The general procedure A conducted with 4-chlorophenol (2.56 g, 20 mmol) and TsCl (4.56 g, 24 mmol) gave 3.41 g (61%) of the titled compound as colorless needles.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 8.5$  Hz, 2 H), 7.32 (d,  $J = 8.0$  Hz, 2 H), 7.24 (d,  $J = 8.5$  Hz, 2 H), 6.92 (d,  $J = 8.0$  Hz, 2 H), 2.45 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  147.99, 145.61, 132.74, 131.96, 129.83, 129.68, 128.50, 123.75, 21.71.



**3-Chlorophenyl *p*-toluenesulfonate.**<sup>7</sup> The general procedure A conducted with 3-chlorophenol (2.56 g, 20 mmol) and TsCl (4.56 g, 24 mmol) gave 3.59 g (64%) of the titled compound as colorless needles.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J = 8.5$  Hz, 2 H), 7.33 (d,  $J = 8.5$  Hz, 2 H), 7.20-7.24 (m, 2 H), 7.02 (d,  $J = 2.0$  Hz, 1 H), 6.89 (dt,  $J = 2.0, 7.0$  Hz, 1 H), 2.46 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  149.85, 145.70, 134.79, 131.97, 130.28, 129.85, 128.46, 127.40, 122.97, 120.66, 21.72.

**General Procedure C for Catalytic Amination of Aryl and heteroaryl Tosylates.** The reaction conditions and average yields for each reaction are shown in Table 1. A typical procedure is given for the entry 1 in Table 1.

**Stock Solution A ( $1.0 \times 10^{-2}$  M):** Under nitrogen filled grove-box, toluene (1.0 mL) was added to the mixture of  $\text{Pd}[\text{P}(o\text{-tol})_3]_2$  (7.2 mg,  $1.0 \times 10^{-2}$  mmol) and  $\text{CyPF-}t\text{-Bu}$  (5.5 mg,  $1.0 \times 10^{-2}$  mmol). The resulting yellow colored solution was stirred at room temperature for one minute before using.



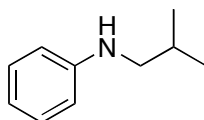
***N*-Phenyl octylamine**<sup>15</sup> (entries 1 and 2). A solution of  $\text{Pd}[\text{P}(o\text{-tol})_3]_2$  and  $\text{CyPF-}t\text{-Bu}$  (100  $\mu\text{L}$  from stock solution A,  $1.0 \times 10^{-3}$  mmol) was added to a 4 mL vial containing phenyl tosylate (0.248 g, 1.00 mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) in 1.0 mL of toluene. Octylamine (0.155 g, 1.20 mmol) was then added by syringe. The vial was sealed with a cap containing a PTFE septum, and the reaction mixture was stirred at room temperature until phenyl tosylate was consumed, as determined by GC. The reaction mixture was filtered through Celite and concentrated to afford a pale

yellow liquid. The crude mixture was purified by flash chromatography (hexane/ethyl acetate, 10/1) to give 0.193 g (94%) of the titled compound as a colorless liquid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.09 (tt,  $J = 2.0, 7.2$  Hz, 2 H), 6.60 (tt,  $J = 1.0, 7.2$  Hz, 1 H), 6.50 (dd,  $J = 2.0, 7.2$  Hz, 2 H), 3.47 (s, br, 1 H), 3.00 (t,  $J = 7.2$  Hz, 2 H), 1.52 (quint,  $J = 7.2$  Hz, 2 H), 1.21-1.32 (m, 10 H), 0.82 (t,  $J = 6.8$  Hz, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  148.45, 129.11, 116.94, 112.57, 43.90, 31.79, 29.51, 29.39, 29.23, 27.14, 22.62, 14.07.

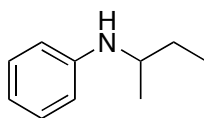
***N*-Phenyl-octylamine<sup>15</sup> (entry 3).** The general procedure C conducted with phenyl triflate (0.226 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol),  $\text{Pd}[\text{P}(o\text{-tol})_3]_2$  and CyPF-*t*-Bu (100  $\mu\text{L}$  from stock solution A,  $1.0 \times 10^{-3}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.059 g (29%) of the titled compound as a colorless liquid.

**(entry 4).** The general procedure C conducted with phenyl mesylate (0.172 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol),  $\text{Pd}[\text{P}(o\text{-tol})_3]_2$  and CyPF-*t*-Bu (100  $\mu\text{L}$  from stock solution A,  $1.0 \times 10^{-3}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave no coupled product judged by GC/MS analysis.

***N*-Phenyl-octylamine<sup>15</sup> (entry 5).** The general procedure C conducted with phenyl *p*-fluorobenzenesulfonate (0.252 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol),  $\text{Pd}[\text{P}(o\text{-tol})_3]_2$  and CyPF-*t*-Bu (100  $\mu\text{L}$  from stock solution A,  $1.0 \times 10^{-3}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.156 g (76%) of the titled compound as a colorless liquid.

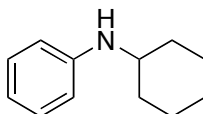


***N*-(*iso*-Butyl)aniline<sup>16</sup> (entry 6).** The general procedure C conducted with phenyl tosylate (0.248 g, 1.00 mmol), *iso*-butylamine (87.8 mg, 1.20 mmol),  $\text{Pd}[\text{P}(o\text{-tol})_3]_2$  and CyPF-*t*-Bu (100  $\mu\text{L}$  from stock solution A,  $1.0 \times 10^{-3}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.129 g (87%) of the titled compound as a colorless liquid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.18 (tt,  $J = 2.0, 7.2$  Hz, 2 H), 6.68 (t,  $J = 7.2$  Hz, 1 H), 6.61 (dd,  $J = 2.0, 7.2$  Hz, 2 H), 3.71 (s, br, 1 H), 2.94 (d,  $J = 6.8$  Hz, 2 H), 1.89 (nonet,  $J = 6.8$  Hz, 1 H), 0.99 (d,  $J = 6.8$  Hz, 6 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  148.55, 129.19, 116.91, 112.59, 51.73, 27.95, 20.43.

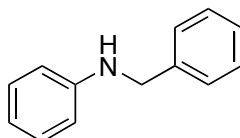


***N*-(*sec*-Butyl)aniline<sup>17</sup> (entry 7).** The general procedure C conducted with phenyl tosylate (0.248 g, 1.00 mmol), *sec*-butylamine (87.8 mg, 1.20 mmol),  $\text{Pd}[\text{P}(o\text{-tol})_3]_2$  (1.4 mg,  $2.0 \times 10^{-3}$  mmol), CyPF-*t*-Bu (1.1 mg,  $2.0 \times 10^{-3}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.124 g (83%) of the titled compound as a colorless liquid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.13 (tt,  $J = 2.0, 7.2$  Hz, 2 H), 6.66 (tt,  $J = 1.0, 7.2$  Hz, 1 H), 6.58 (dd,  $J = 2.0, 7.2$  Hz, 2 H), 3.46 (s, br, 1 H), 1.41-1.66 (m, 3 H), 1.17 (d,  $J = 6.4$  Hz, 3 H), 0.96 (t,  $J = 7.6$  Hz, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  147.65, 129.19, 116.65, 113.00, 49.63,

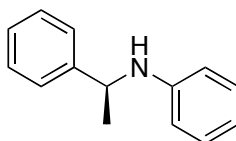
29.51, 20.11, 10.28.



***N*-cyclohexylaniline<sup>18</sup> (entry 8).** The general procedure C conducted with phenyl tosylate (0.248 g, 1.00 mmol), cyclohexylamine (0.119 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> and CyPF-*t*-Bu (100  $\mu$ L from stock solution A,  $1.0 \times 10^{-3}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.126 g (72%) of the titled compound as a colorless liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.05 (t,  $J = 7.6$  Hz, 2 H), 6.56 (td,  $J = 1.2, 7.2$  Hz, 1 H), 6.48 (dd,  $J = 0.8, 7.6$  Hz, 2 H), 3.38 (s, br, 1 H), 3.11-3.18 (m, 1 H), 1.94-1.97 (m, 2 H), 1.66 (dt,  $J = 4.0, 13.2$  Hz, 2 H), 1.55 (dt,  $J = 3.6, 12.0$  Hz, 1 H), 1.22-1.32 (m, 2 H), 0.99-1.18 (m, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  147.38, 129.23, 116.77, 113.08, 51.61, 33.42, 25.88, 24.97.



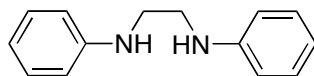
***N*-(Phenyl)benzylamine<sup>18</sup> (entry 9).** The general procedure C conducted with phenyl tosylate (0.248 g, 1.00 mmol), benzylamine (0.129 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> and CyPF-*t*-Bu (100  $\mu$ L from stock solution A,  $1.0 \times 10^{-3}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.165 g (90%) of the titled compound as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.49 (d,  $J = 6.0$  Hz, 2 H), 7.46 (d,  $J = 7.2$  Hz, 2 H), 7.38-7.41 (m, 1 H), 7.30 (t,  $J = 7.2$  Hz, 2 H), 6.86 (td,  $J = 1.2, 7.2$  Hz, 1 H), 6.74 (dd,  $J = 1.2, 7.6$  Hz, 2 H), 4.42 (s, 2 H), 4.09 (s, br, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  148.04, 139.36, 129.15, 128.51, 127.37, 127.09, 117.41, 112.73, 48.13.



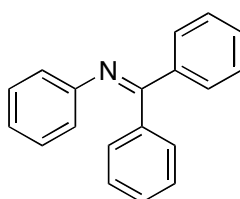
**(*S*)-*N*-(1-Phenylethyl)aniline<sup>19</sup> (entry 10).** The general procedure C conducted with phenyl tosylate (0.248 g, 1.00 mmol), *L*-(-)- $\alpha$ -methylbenzylamine (0.145 g, 1.20 mmol, 99% ee), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (7.2 mg,  $1.0 \times 10^{-2}$  mmol), CyPF-*t*-Bu (5.5 mg,  $1.0 \times 10^{-2}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.188 g (95%, 99% ee) of the titled compound as a colorless liquid. Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, 256 nm, 0.5 ml/min, hexane/2-propanol (98:2)).  $t_R = 18.3$  min (*S*) major, 23.3 min (*R*) minor. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.36 (d,  $J = 7.0$  Hz, 2 H), 7.31 (t,  $J = 7.5$  Hz, 2 H), 7.22 (t,  $J = 7.0$  Hz, 1 H), 7.08 (dd,  $J = 7.5, 8.5$  Hz, 2 H), 6.63 (t,  $J = 7.5$  Hz, 1 H), 6.50 (d,  $J = 8.5$  Hz, 2 H), 4.48 (q,  $J = 6.5$  Hz, 1 H), 4.01 (s, br, 1 H), 1.51 (d,  $J = 6.5$  Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  147.24, 145.19, 129.06, 128.60, 126.82, 125.80, 117.18, 113.24, 53.42, 25.01. The absolute configuration was determined by comparison with



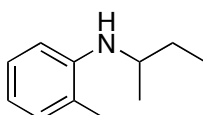
the reported analytical data.<sup>19</sup>



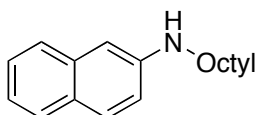
***N,N'*-Diphenylethylenediamine<sup>20</sup> (entry 11).** The general procedure C conducted with phenyl tosylate (0.248 g, 1.00 mmol), *N*-phenylethylenediamine (204 mg, 1.50 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (3.6 mg, 5.0 × 10<sup>-3</sup> mmol), CyPF-*t*-Bu (2.8 mg, 5.0 × 10<sup>-3</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.202 g (96%) of the titled compound as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.21 (t, *J* = 7.5 Hz, 4 H), 6.75 (t, *J* = 7.5 Hz, 2 H), 6.67 (d, *J* = 8.5 Hz, 4 H), 3.87 (s, br, 2 H), 3.41 (s, 4 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 147.99, 129.32, 117.81, 113.00, 43.26.



***N*-Phenylbenzophenone imine (entry 12).** The general procedure C conducted with phenyl tosylate (0.248 g, 1.00 mmol), benzophenone imine (0.217 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> and CyPF-*t*-Bu (100 μL from stock solution A, 1.0 × 10<sup>-3</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.234 g (91%) of the titled compound as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.67 (dt, *J* = 2.0, 8.0 Hz, 2 H), 7.38 (tt, *J* = 1.5, 7.2 Hz, 1 H), 7.31 (t, *J* = 7.5 Hz, 2 H), 7.14-7.20 (m, 3 H), 7.02-7.07 (m, 4 H), 6.83 (tt, *J* = 1.0, 7.2 Hz, 1 H), 6.64 (dd, *J* = 1.0, 8.5 Hz, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 168.18, 151.21, 139.65, 136.19, 130.67, 129.48, 129.29, 128.51, 128.43, 128.16, 127.85, 123.10, 120.90; Anal. Calcd. For C<sub>19</sub>H<sub>15</sub>N: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.68; H, 5.86; N, 5.44.

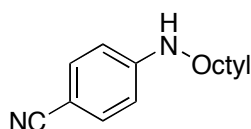


**2-Methyl-*N*-(1-methylpropyl)benzenamine<sup>21</sup> (entry 13).** The general procedure C conducted with 2-methylphenyl tosylate (0.262 g, 1.00 mmol), *sec*-butylamine (87.6 mg, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (1.4 mg, 2.0 × 10<sup>-3</sup> mmol), CyPF-*t*-Bu (1.1 mg, 2.0 × 10<sup>-3</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.162 g (99%) of the titled compound as a colorless liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.12 (t, *J* = 6.8 Hz, 1 H), 7.06 (d, *J* = 6.8 Hz, 1 H), 6.62 (t, *J* = 6.8 Hz, 2 H), 3.42-3.50 (m, 1 H), 3.32 (s, br, 1 H), 2.13 (s, 3 H), 1.46-1.70 (m, 2 H), 1.21 (d, *J* = 6.4 Hz, 3 H), 0.97 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 145.52, 130.19, 127.06, 121.56, 116.16, 110.02, 49.52, 29.62, 20.39, 17.51, 10.30.

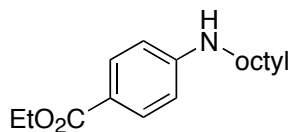


***N*-octyl-2-naphthylamine<sup>22</sup> (entry 14).** The general procedure C conducted with 2-naphthyl tosylate (0.298 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> and CyPF-*t*-Bu (50 μL from stock solution A, 5.0 × 10<sup>-4</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.247 g (97%) of the titled compound as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.67 (d, *J* = 7.5 Hz, 1 H), 7.62 (d, *J* = 8.5 Hz, 2 H), 7.36 (dt, *J* = 1.0, 8.5 Hz, 1 H), 7.19 (dt, *J* = 1.0, 7.5 Hz, 1 H), 6.88 (dd, *J* = 2.5, 8.5 Hz, 1 H), 6.80 (d, *J* = 2.5 Hz, 1 H), 3.78 (s, br, 1 H), 3.21 (t, *J* = 7.0 Hz, 2 H), 1.69 (quint, *J* = 7.0 Hz, 2 H), 1.27-1.48 (m, 10 H), 0.90 (t, *J* = 7.0 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 146.09, 135.29, 128.85, 127.63, 127.41, 126.27, 125.87, 121.81, 118.00, 104.24, 44.06, 31.82, 29.41, 29.38, 29.26, 27.22, 22.64, 14.08.

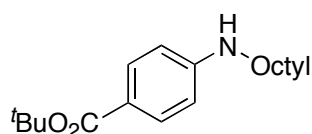
***N*-octyl-2-naphthylamine<sup>22</sup> (entry 15).** The general procedure C conducted with 2-naphthyl tosylate (0.298 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> and CyPF-*t*-Bu (10 μL from stock solution A, 1.0 × 10<sup>-4</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.214 g (84%) of the titled compound as a white solid.



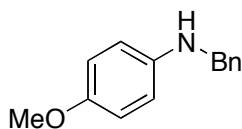
***N*-(4-Cyanophenyl)-octylamine (entry 16).** The general procedure C conducted with 4-cyanophenyl tosylate (0.273 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (3.6 mg, 5.0 × 10<sup>-3</sup> mmol), CyPF-*t*-Bu (2.8 mg, 5.0 × 10<sup>-3</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.228 g (99%) of the titled compound as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.42 (d, *J* = 8.8 Hz, 2 H), 6.58 (d, *J* = 8.8 Hz, 2 H), 4.38 (s, 1 H), 3.16 (q, *J* = 7.0 Hz, 2 H), 1.62-1.69 (m, 2 H), 1.31-1.42 (m, 10 H), 0.92 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 151.46, 133.63, 120.59, 111.96, 98.12, 43.14, 31.70, 29.22, 29.13, 29.05, 26.94, 22.55, 14.00; Anal. Calcd. For C<sub>15</sub>H<sub>22</sub>N<sub>2</sub>: C, 78.21; H, 9.63; N, 12.16. Found: C, 78.23; H, 9.63; N, 12.16.



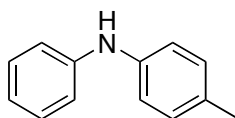
**4-Octylaminobenzoic acid ethyl ether<sup>23</sup> (entry 17).** The general procedure C conducted with ethyl 4-[(4-methylphenyl)sulfonyl]oxybenzoate (0.320 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (7.2 mg, 1.0 × 10<sup>-2</sup> mmol), CyPF-*t*-Bu (5.5 mg, 1.0 × 10<sup>-2</sup> mmol) and potassium phosphate (0.297 g, 1.40 mmol) gave 0.276 g (99%) of the titled compound as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.86 (d, *J* = 9.0 Hz, 2 H), 6.53 (d, *J* = 9.0 Hz, 2 H), 4.31 (q, *J* = 7.0 Hz, 2 H), 4.08 (s, br, 1H), 3.15 (dd, *J* = 5.0, 7.0 Hz, 2 H), 1.62 (quint, *J* = 7.5 Hz, 2 H), 1.26-1.42 (m, 13 H), 0.88 (t, *J* = 6.5 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 166.89, 152.04, 131.43, 118.44, 111.25, 60.12, 43.38, 31.74, 29.34, 29.32, 29.22, 27.06, 22.58, 14.45, 14.08.



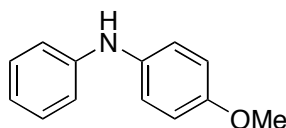
**4-Octylaminobenzoic acid *tert*-butyl ether (entry 18).** The general procedure C conducted with *tert*-butyl 4-[[[(4-methylphenyl)sulfonyl]oxy]benzoate (0.348 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (7.2 mg, 1.0 × 10<sup>-2</sup> mmol), CyPF-*t*-Bu (5.5 mg, 1.0 × 10<sup>-2</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.268 g (88%) of the titled compound as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.81 (d, *J* = 9.0 Hz, 2 H), 6.52 (d, *J* = 9.0 Hz, 2 H), 4.04 (s, br, 1H), 3.14 (dd, *J* = 5.5, 6.5 Hz, 2 H), 1.62 (quint, *J* = 7.0 Hz, 2 H), 1.56 (s, 9 H), 1.27-1.40 (m, 10 H), 0.88 (t, *J* = 6.5 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 166.03, 151.75, 131.29, 119.93, 111.17, 79.72, 43.41, 31.78, 29.34, 29.31, 29.22, 28.32, 27.06, 22.63, 14.09; Anal. Calcd. For C<sub>19</sub>H<sub>31</sub>NO<sub>2</sub>: C, 74.71; H, 10.23; N, 4.59. Found: C, 74.54; H, 10.45; N, 4.69.



***N*-(Benzylamino)-*p*-anisidine<sup>18</sup> (entry 19).** The general procedure C conducted with 4-methoxyphenyl tosylate (0.278 g, 1.00 mmol), benzylamine (0.128 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (3.6 mg, 5.0 × 10<sup>-3</sup> mmol), CyPF-*t*-Bu (2.8 mg, 5.0 × 10<sup>-3</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.185 g (87%) of the titled compound as a pale yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.33-7.46 (m, 5 H), 6.86 (d, *J* = 9.0 Hz, 2 H), 6.67 (d, *J* = 8.8 Hz, 2 H), 4.33 (s, 2 H), 3.85 (s, br, 1 H), 3.80 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 151.94, 142.28, 139.56, 128.42, 127.36, 126.98, 114.70, 113.90, 55.56, 48.97.

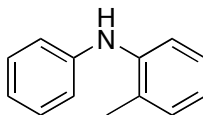


***N*-Phenyl-*p*-toluidine<sup>24</sup> (entry 20).** The general procedure C conducted with phenyl tosylate (0.248 g, 1.00 mmol), *p*-toluidine (0.128 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> and CyPF-*t*-Bu (100 μL from stock solution A, 1.0 × 10<sup>-3</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.159 g (87%) of the titled compound as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.28 (t, *J* = 8.4 Hz, 2 H), 7.13(d, *J* = 8.0 Hz, 2 H), 7.03-7.06 (m, 4 H), 6.92 (t, *J* = 7.2 Hz, 1 H), 5.62 (s, br, 1 H), 2.35 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 143.84, 140.18, 130.83, 129.79, 129.24, 120.21, 118.82, 116.76, 20.65.

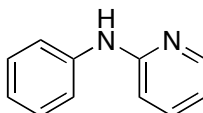


***N*-Phenyl-*p*-anisidine<sup>25</sup> (entry 21).** The general procedure C conducted with phenyl tosylate (0.248 g, 1.00 mmol), *p*-anisidine (0.148 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> and CyPF-*t*-Bu (100 μL from stock solution A, 1.0 × 10<sup>-3</sup> mmol) and sodium *tert*-butoxide

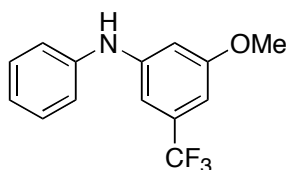
(0.135 g, 1.40 mmol) gave 0.154 g (77%) of the titled compound as a white solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.22 (dt,  $J = 1.5, 9.0$  Hz, 2 H), 7.08 (d,  $J = 9.0$  Hz, 2 H), 6.91 (dd,  $J = 1.5, 9.0$  Hz, 2 H), 6.87 (d,  $J = 9.0$  Hz, 2 H), 6.84 (t,  $J = 9.0$  Hz, 1 H), 5.50 (s, br, 1 H), 3.81 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  155.22, 145.12, 135.67, 129.28, 122.15, 119.50, 115.57, 114.61, 55.50.



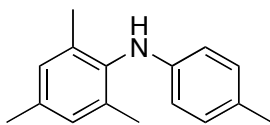
**N-Phenyl-*o*-toluidine**<sup>26</sup> (entry 22). The general procedure C conducted with phenyl tosylate (0.248 g, 1.00 mmol), *o*-toluidine (0.128 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (1.4 mg,  $2.0 \times 10^{-3}$  mmol), CyPF-*t*-Bu (1.1 mg,  $2.0 \times 10^{-3}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.137 g (75%) of the titled compound as a yellow liquid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.33-7.36 (m, 3 H), 7.30 (d,  $J = 7.5$  Hz, 1 H), 7.24 (t,  $J = 7.5$  Hz, 1 H), 6.98-7.06 (m, 4 H), 5.45 (s, br, 1 H), 2.34 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  143.90, 141.14, 130.89, 129.25, 128.24, 126.71, 121.93, 120.38, 118.72, 117.36, 17.80.



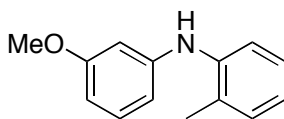
**N-Phenyl-2-pyridinamine**<sup>27</sup> (entry 23). The general procedure C conducted with phenyl tosylate (0.248 g, 1.00 mmol), 2-aminopyridine (0.113 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (7.2 mg,  $1.0 \times 10^{-2}$  mmol), CyPF-*t*-Bu (5.5 mg,  $1.0 \times 10^{-2}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.121 g (71%) of the titled compound as a white solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.21 (dd,  $J = 1.0, 5.0$  Hz, 1 H), 7.49 (t,  $J = 7.5$  Hz, 1 H), 7.29-7.37 (m, 4 H), 7.01-7.09 (m, 2 H), 6.90 (d,  $J = 8.5$  Hz, 1 H), 6.73 (t,  $J = 6.0$  Hz, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  156.12, 148.39, 140.53, 137.68, 129.27, 122.76, 120.38, 114.92, 108.12.



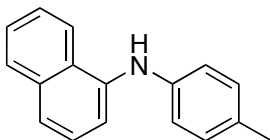
**3-Methoxy-*N*-phenyl-5-(trifluoromethyl)benzenamine** (entry 24). The general procedure C conducted with phenyl tosylate (0.248 g, 1.00 mmol), 3-methoxy-5-(trifluoromethyl)aniline (0.229 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (14.3 mg,  $2.0 \times 10^{-2}$  mmol), CyPF-*t*-Bu (11.1 mg,  $2.0 \times 10^{-2}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.236 g (88%) of the titled compound as a pale yellow liquid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.33 (t,  $J = 7.2$  Hz, 2 H), 7.12 (d,  $J = 7.2$  Hz, 2 H), 7.04 (t,  $J = 7.2$  Hz, 1 H), 6.86 (s, br, 1 H), 6.74 (t,  $J = 2.0$  Hz, 1 H), 6.67 (s, br, 1 H), 5.83 (s, br, 1 H), 3.81 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  160.86, 145.36, 141.51, 132.70, 132.38, 129.54, 122.47, 119.39, 106.03 (q,  $J = 18.4$  Hz), 105.07, 102.26 (q,  $J = 15.2$  Hz), 55.45; Anal. Calcd. For  $\text{C}_{14}\text{H}_{12}\text{F}_3\text{NO}$ : C, 62.92; H, 4.53; N, 5.24. Found: C, 62.53; H, 4.22; N, 5.21.



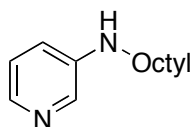
**2,4,6-Trimethyl-N-(4-methylphenyl)benzenamine<sup>28</sup> (entry 25).** The general procedure C conducted with 2,4,6-trimethylphenyl tosylate (0.290 g, 1.00 mmol), *p*-toluidine (0.128 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> and CyPF-*t*-Bu (100 μL from stock solution A, 1.0 × 10<sup>-3</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.223 g (99%) of the titled compound as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.99 (d, *J* = 8.5 Hz, 2 H), 6.97 (s, 2 H), 6.45 (d, *J* = 8.5 Hz, 2 H), 5.04 (s, br, 1 H), 2.34 (s, 3 H), 2.27 (s, 3 H), 2.20 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 144.24, 135.94, 135.62, 135.04, 129.71, 129.18, 127.08, 113.42, 20.85, 20.39, 18.19.



**N-(3-Methoxyphenyl)-2-methylbenzenamine<sup>26</sup> (entry 26).** The general procedure C conducted with 2-methoxyphenyl tosylate (0.278 g, 1.00 mmol), *o*-toluidine (0.128 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (1.4 mg, 2.0 × 10<sup>-3</sup> mmol), CyPF-*t*-Bu (1.1 mg, 2.0 × 10<sup>-3</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.148 g (70%) of the titled compound as a pale yellow liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.31 (d, *J* = 8.0 Hz, 1 H), 7.24 (d, *J* = 7.5 Hz, 1 H), 7.19 (t, *J* = 8.0 Hz, 2 H), 6.99 (t, *J* = 7.5 Hz, 1 H), 6.59 (dd, *J* = 2.0, 8.0 Hz, 1 H), 6.55 (t, *J* = 2.0 Hz, 1 H), 6.50 (dd, *J* = 2.5, 8.0 Hz, 1 H), 5.43 (s, br, 1 H), 3.80 (s, 3 H), 2.29 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 160.66, 145.72, 140.70, 130.90, 129.99, 128.80, 126.71, 122.29, 119.61, 109.72, 105.47, 102.78, 55.09, 18.01.

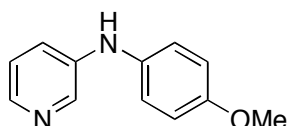


**N-(4-Methylphenyl)-1-naphthylamine<sup>29</sup> (entry 27).** The general procedure C conducted with 1-naphthyl tosylate (0.298 g, 1.00 mmol), *p*-toluidine (0.128 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (1.4 mg, 2.0 × 10<sup>-3</sup> mmol), CyPF-*t*-Bu (1.1 mg, 2.0 × 10<sup>-3</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.234 g (96%) of the titled compound as a pale yellow liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.02 (d, *J* = 7.5 Hz, 1 H), 7.86 (d, *J* = 7.5 Hz, 1 H), 7.46-7.53 (m, 3 H), 7.37 (t, *J* = 8.0 Hz, 1 H), 7.29 (d, *J* = 7.0 Hz, 1 H), 7.10 (d, *J* = 8.5 Hz, 2 H), 6.96 (d, *J* = 8.5 Hz, 2 H), 5.91 (s, br, 1 H), 2.32 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 141.73, 139.57, 134.63, 130.37, 129.84, 128.50, 127.00, 126.05, 126.00, 125.45, 122.00, 121.51, 118.46, 114.05, 20.61.

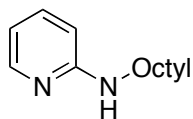


**N-octyl-3-aminopyridine<sup>30</sup> (entry 28).** The general procedure C conducted with

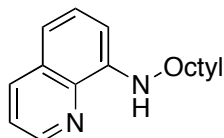
3-pyridyl tosylate (0.249 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (3.6 mg, 5.0 × 10<sup>-3</sup> mmol), CyPF-*t*-Bu (2.8 mg, 5.0 × 10<sup>-3</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.185 g (90%) of the titled compound as a yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.02 (d, *J* = 2.8 Hz, 1 H), 7.93 (dd, *J* = 1.6, 4.4 Hz, 1 H), 7.07 (dd, *J* = 4.6, 8.4 Hz, 1 H), 6.86 (ddd, *J* = 1.6, 3.2, 8.8 Hz, 1 H), 3.72 (s, br, 1 H), 3.11 (t, *J* = 7.2 Hz, 2 H), 1.63 (quint, *J* = 7.2 Hz, 2 H), 1.26-1.42 (m, 10 H), 0.89 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 144.37, 138.0, 135.69, 123.49, 118.01, 43.35, 31.63, 29.19, 29.16, 29.06, 26.92, 22.47, 13.9.



***N*-3-pyridyl-*p*-anisidine<sup>30</sup> (entry 29).** The general procedure C conducted with 3-pyridyl tosylate (0.249 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (7.2 mg, 1.0 × 10<sup>-2</sup> mmol), CyPF-*t*-Bu (5.5 mg, 1.0 × 10<sup>-2</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.126 g (63%) of the titled compound as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.22 (d, *J* = 2.8 Hz, 1 H), 8.03 (dd, *J* = 1.0, 4.4 Hz, 1 H), 7.18 (ddd, *J* = 1.4, 2.4, 8.0 Hz, 1 H), 7.05-7.09 (m, 1 H), 7.05 (d, *J* = 8.8 Hz, 2 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 5.84 (s, br, 1 H), 3.77 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 155.73, 141.70, 140.33, 138.17, 134.32, 123.64, 122.55, 121.02, 114.74, 55.49.

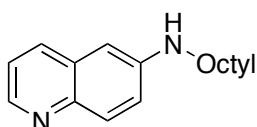


***N*-octyl-2-aminopyridine<sup>30</sup> (entry 30).** The general procedure C conducted with 2-pyridyl tosylate (0.249 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (7.2 mg, 1.0 × 10<sup>-2</sup> mmol), CyPF-*t*-Bu (5.5 mg, 1.0 × 10<sup>-2</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.164 g (80%) of the titled compound as a yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.07 (d, *J* = 4.8 Hz, 1 H), 7.42 (dd, *J* = 7.2, 8.6 Hz, 1 H), 6.38 (d, *J* = 8.4 Hz, 1 H), 6.55 (dd, *J* = 4.8, 7.0 Hz, 1 H), 4.55 (s, br, 1 H), 3.24 (q, *J* = 6.8 Hz, 2 H), 1.62 (quint, *J* = 7.2 Hz, 2 H), 1.20-1.42 (m, 10 H), 0.89 (t, *J* = 6.8 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 158.88, 148.14, 137.19, 12.32, 106.1, 42.32, 31.68, 29.59, 29.42, 29.24, 27.11, 22.51, 13.95.

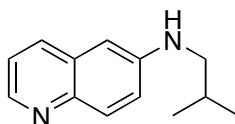


***N*-octyl-8-quinolinamine (entry 31).** The general procedure C conducted with 8-quinolinyl tosylate (0.299 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (7.2 mg, 1.0 × 10<sup>-2</sup> mmol), CyPF-*t*-Bu (5.5 mg, 1.0 × 10<sup>-2</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.210 g (82%) of the titled compound as a yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.71 (dd, *J* = 1.2, 4.4 Hz, 1 H), 8.05 (dd, *J* = 1.6,

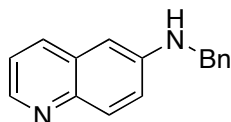
8.4 Hz, 1 H), 7.34-7.41 (m, 2 H), 7.03 (dd,  $J = 1.2, 8.4$  Hz, 1 H), 6.66 (d,  $J = 7.6$  Hz, 1 H), 6.11 (s, br, 1 H), 3.30 (q,  $J = 6.8$  Hz, 2 H), 1.79 (quint,  $J = 7.6$  Hz, 2 H), 1.30-1.51 (m, 10 H), 0.89 (t,  $J = 6.8$  Hz, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  146.70, 144.95, 138.10, 135.97, 128.63, 127.81, 121.30, 113.38, 104.39, 43.42, 31.84, 29.46, 29.27, 27.35, 22.66, 14.11; Anal. Calcd. For  $\text{C}_{17}\text{H}_{24}\text{N}_2$ : C, 79.64; H, 9.44; N, 10.93. Found: C, 79.22; H, 9.51; N, 10.56.



**N-Octyl-6-quinolinamine (entry 32).** The general procedure C conducted with 6-quinolinyl tosylate (0.299 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol),  $\text{Pd}[\text{P}(o\text{-tol})_3]_2$  (1.4 mg,  $2.0 \times 10^{-3}$  mmol),  $\text{CyPF-}t\text{-Bu}$  (1.1 mg,  $2.0 \times 10^{-3}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.233 g (91%) of the titled compound as a yellow solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.59 (dd,  $J = 1.5, 4.0$  Hz, 1 H), 7.90 (d,  $J = 8.0$  Hz, 1 H), 7.85 (d,  $J = 9.0$  Hz, 1 H), 7.23 (q,  $J = 4.0$  Hz, 1 H), 7.06 (dd,  $J = 2.5, 9.0$  Hz, 1 H), 6.66 (d,  $J = 2.5$  Hz, 1 H), 3.98 (s, br, 1 H), 3.18 (q,  $J = 7.5$  Hz, 2 H), 1.67 (quint,  $J = 7.0$  Hz, 2 H), 1.23-1.45 (m, 10 H), 0.88 (t,  $J = 7.0$  Hz, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  146.34, 145.90, 143.06, 133.67, 130.17, 130.09, 121.36, 121.28, 102.55, 43.86, 31.74, 29.32, 29.18, 27.13, 22.58, 14.03; Anal. Calcd. For  $\text{C}_{17}\text{H}_{24}\text{N}_2$ : C, 79.64; H, 9.44; N, 10.93. Found: C, 79.87; H, 9.66; N, 10.96.

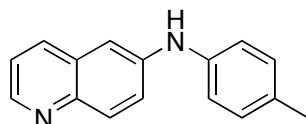


**N-(2-methylphenyl)-6-quinolinamine (entry 33).** The general procedure C conducted with 6-quinolinyl tosylate (0.299 g, 1.00 mmol), *iso*-butylamine (87.6 mg, 1.20 mmol),  $\text{Pd}[\text{P}(o\text{-tol})_3]_2$  (1.4 mg,  $2.0 \times 10^{-3}$  mmol),  $\text{CyPF-}t\text{-Bu}$  (1.1 mg,  $2.0 \times 10^{-3}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.194 g (97%) of the titled compound as a yellow solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.58 (dd,  $J = 1.6, 2.8$  Hz, 1 H), 7.89 (d,  $J = 8.4$  Hz, 1 H), 7.85 (d,  $J = 9.2$  Hz, 1 H), 7.23 (ddd,  $J = 1.6, 4.0, 8.4$  Hz, 1 H), 7.07 (ddd,  $J = 1.6, 2.8, 9.2$  Hz, 1 H), 6.65 (s, 1 H), 4.08 (s, br, 1 H), 3.02 (t,  $J = 5.6$  Hz, 2 H), 1.90-2.01 (m, 1 H), 1.02 (dd,  $J = 1.6, 6.8$  Hz, 6 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  146.35, 145.84, 142.98, 133.62, 130.14, 130.08, 121.33, 121.27, 102.51, 51.63, 27.80, 20.48; Anal. Calcd. For  $\text{C}_{13}\text{H}_{16}\text{N}_2$ : C, 77.96; H, 8.05; N, 13.99. Found: C, 77.97; H, 8.20; N, 13.86.

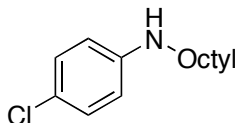


**N-Benzyl-6-quinolinamine (entry 34).** The general procedure C conducted with 6-quinolinyl tosylate (0.299 g, 1.00 mmol), benzylamine (0.128 g, 1.20 mmol),  $\text{Pd}[\text{P}(o\text{-tol})_3]_2$  (1.4 mg,  $2.0 \times 10^{-3}$  mmol),  $\text{CyPF-}t\text{-Bu}$  (1.1 mg,  $2.0 \times 10^{-3}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.204 g (87%) of the titled compound

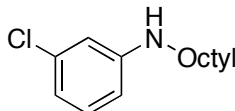
as a yellow solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.61 (dd,  $J = 2.4, 4.4$  Hz, 1 H), 7.89 (d,  $J = 8.8$  Hz, 1 H), 7.88 (d,  $J = 8.0$  Hz, 1 H), 7.35-7.42 (m, 3 H), 7.31 (t,  $J = 4.4$  Hz, 1 H), 7.24 (dd,  $J = 4.4, 8.8$  Hz, 1 H), 7.13 (dd,  $J = 2.8, 8.8$  Hz, 1 H), 6.71 (d,  $J = 2.4$  Hz, 1 H), 4.43 (s, 2 H), 2.38 (s, br, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  146.18, 145.89, 143.18, 138.60, 133.82, 130.21, 130.13, 128.69, 127.44, 127.38, 121.31, 121.25, 103.15, 48.15; Anal. Calcd. For  $\text{C}_{16}\text{H}_{14}\text{N}_2$ : C, 82.02; H, 6.02; N, 11.96. Found: C, 81.94; H, 5.85; N, 11.83.



***N*-6-quinolinyl-*p*-toluidine<sup>31</sup> (entry 35).** The general procedure C conducted with 6-quinolinyl tosylate (0.299 g, 1.00 mmol), *p*-toluidine (0.128 g, 1.20 mmol),  $\text{Pd}[\text{P}(o\text{-tol})_3]_2$  (7.2 mg,  $1.0 \times 10^{-2}$  mmol), CyPF-*t*-Bu (5.5 mg,  $1.0 \times 10^{-2}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.183 g (78%) of the titled compound as a yellow solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.69 (dd,  $J = 1.5, 4.0$  Hz, 1 H), 7.96 (d,  $J = 9.0$  Hz, 1 H), 7.91 (d,  $J = 8.0$  Hz, 1 H), 7.37 (dd,  $J = 2.5, 9.0$  Hz, 1 H), 7.28 (dd,  $J = 4.0, 8.0$  Hz, 7.26 (d,  $J = 2.5$  Hz, 1 H), 7.17 (d,  $J = 8.0$  Hz, 2 H), 7.13 (d,  $J = 8.0$  Hz, 2 H), 5.95 (s, br, 1 H), 2.35 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  147.29, 144.10, 142.44, 139.26, 134.19, 132.22, 130.52, 130.02, 129.61, 122.61, 121.44, 120.14, 108.12, 20.60.



***N*-(4-Chlorophenyl)octylamine<sup>32</sup> (eq 2).** The general procedure C conducted with 4-chlorophenyl *p*-toluenesulfonate (0.282 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol),  $\text{Pd}[\text{P}(o\text{-tol})_3]_2$  (3.6 mg,  $5.0 \times 10^{-3}$  mmol), CyPF-*t*-Bu (2.8 mg,  $5.0 \times 10^{-3}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.227 g (95%) of the titled compound as a colorless liquid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.11 (d,  $J = 9.0$  Hz, 2 H), 6.52 (d,  $J = 9.0$  Hz, 2 H), 3.61 (s, br, 1H), 3.07 (t,  $J = 7.0$  Hz, 2 H), 1.61 (quint,  $J = 7.5$  Hz, 2 H), 1.29-1.41 (m, 10 H), 0.90 (t,  $J = 7.0$  Hz, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  147.04, 128.96, 121.50, 113.64, 44.08, 31.80, 29.41, 29.37, 29.23, 27.11, 22.64, 14.08.

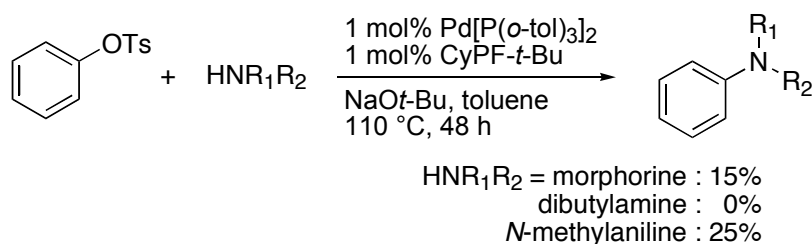


***N*-(3-Chlorophenyl)octylamine (eq 2).** The general procedure C conducted with 3-chlorophenyl *p*-toluenesulfonate (0.282 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol),  $\text{Pd}[\text{P}(o\text{-tol})_3]_2$  (3.6 mg,  $5.0 \times 10^{-3}$  mmol), CyPF-*t*-Bu (2.8 mg,  $5.0 \times 10^{-3}$  mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.229 g (96%) of the titled compound as a colorless liquid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.06 (t,  $J = 8.0$  Hz, 1 H), 6.65 (ddd,  $J = 0.8, 1.6, 8.0$  Hz, 1 H), 6.57 (t,  $J = 1.6$  Hz, 1 H), 6.46 (dd,  $J = 2.4, 8.0$  Hz, 1 H), 3.70 (s, br, 1H), 3.08 (dd,  $J = 4.0, 6.8$  Hz, 2 H), 1.61 (quint,  $J = 7.6$  Hz, 2 H), 1.27-1.34 (m, 10 H), 0.90 (t,  $J = 6.8$  Hz, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  149.59, 134.96, 130.07, 116.76,

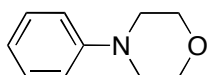


112.09, 110.98, 43.77, 31.80, 29.36, 29.23, 27.09, 22.64, 14.08 (one peak was overlapped) ; Anal. Calcd. For C<sub>14</sub>H<sub>22</sub>NCl: C, 70.13; H, 9.25; N, 5.84. Found: C, 70.39; H, 9.55; N, 5.92.

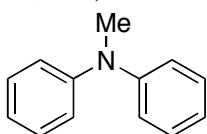
**Scheme S1.** Coupling of Aryl Tosylates with Secondary Alkylamines and Arylamines Catalyzed by Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> and CyPF-*t*-Bu (1:1)<sup>a</sup>



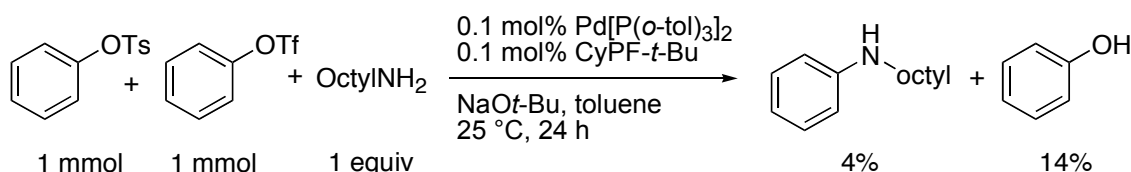
<sup>a</sup> Reactions conducted with a 1:1 ratio of metal to ligand 1 mmol ArOTs, 1.2 equiv amine, and 1.4 equiv NaOt-Bu in 1 mL toluene.



**4-Phenylmorpholine.**<sup>33</sup> The general procedure C conducted with phenyl *p*-toluenesulfonate (0.248 g, 1.00 mmol), morpholine (0.104 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (7.2 mg, 1.0 × 10<sup>-2</sup> mmol), CyPF-*t*-Bu (5.5 mg, 1.0 × 10<sup>-2</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.047 g (15%) of the titled compound as a pale yellow liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.26-7.29 (m, 2 H), 6.81-6.94 (m, 3 H), 3.88 (t, *J* = 5.0 Hz, 4 H), 3.17 (t, *J* = 5.0 Hz, 4 H).



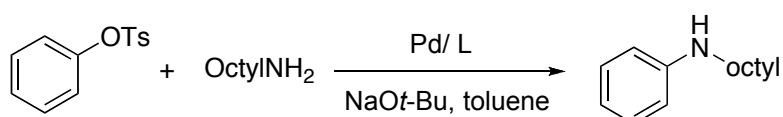
***N*-Methyldiphenylamine.**<sup>30</sup> The general procedure C conducted with phenyl *p*-toluenesulfonate (0.248 g, 1.00 mmol), *N*-methylaniline (0.128 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (7.2 mg, 1.0 × 10<sup>-2</sup> mmol), CyPF-*t*-Bu (5.5 mg, 1.0 × 10<sup>-2</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.045 g (25%) of the titled compound as a pale yellow liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.31 (t, *J* = 8.5 Hz, 4 H), 7.06 (dd, *J* = 1.0, 8.5 Hz, 4 H), 6.99 (tt, *J* = 1.0, 8.5 Hz, 2 H), 3.35 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 148.97, 129.16, 121.21, 120.39, 40.18.



***N*-Phenyloctylamine.**<sup>15</sup> The general procedure C conducted with phenyl *p*-toluenesulfonate (0.248 g, 1.00 mmol), phenyl triflate (0.226 g, 1.00 mmol),

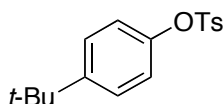
octylamine (0.129 g, 1.00 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> and CyPF-*t*-Bu (100 μL from stock solution **A**, 1.0 × 10<sup>-3</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 4% of the titled compound and 14% of phenol. Yields were determined by GC using dodecane as an internal standard.

**Table S1.** Comparison of the Activity of CyPF-*t*-Bu, Q-phos, X-phos, SIPr, DPPF, and BINAP with Low Loading of Pd Precatalyst for the Reactions of Aryl Tosylate with Primary Alkylamine<sup>a</sup>

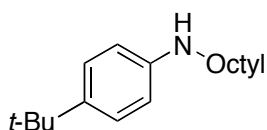


entry	precatalyst (0.1 mol %)	ligand (mol %)	temp (°C)	time (h)	yield <sup>b</sup> (%)
1	Pd[P( <i>o</i> -tol) <sub>3</sub> ] <sub>2</sub>	CyPF- <i>t</i> -Bu, 0.1	25	24	94
2	Pd(dba) <sub>2</sub>	CyPF- <i>t</i> -Bu, 0.1	25	48	0
3	Pd(OAc) <sub>2</sub>	CyPF- <i>t</i> -Bu, 0.1	25	48	6 <sup>c</sup>
4	PdCl <sub>2</sub> (CyPF- <i>t</i> -Bu)		25	48	65
5	Pd[P( <i>o</i> -tol) <sub>3</sub> ] <sub>2</sub>	Q-phos, 0.25	110	24	0
6	Pd(dba) <sub>2</sub>	Q-phos, 0.25	110	24	0
7	Pd(OAc) <sub>2</sub>	Q-phos, 0.25	110	24	0
8	Pd[P( <i>o</i> -tol) <sub>3</sub> ] <sub>2</sub>	X-phos, 0.25	110	24	0
9	Pd(dba) <sub>2</sub>	X-phos, 0.25	110	24	0
10	Pd(OAc) <sub>2</sub>	X-phos, 0.25	110	24	4 <sup>c</sup>
11	Pd[P( <i>o</i> -tol) <sub>3</sub> ] <sub>2</sub>	SIPr, 0.25	110	24	0
12	Pd(dba) <sub>2</sub>	SIPr, 0.25	110	24	0
13	Pd(OAc) <sub>2</sub>	SIPr, 0.25	110	24	0
14	Pd[P( <i>o</i> -tol) <sub>3</sub> ] <sub>2</sub>	DPPF, 0.1	110	24	0
15	Pd(dba) <sub>2</sub>	DPPF, 0.1	110	24	0
16	Pd(OAc) <sub>2</sub>	DPPF, 0.1	110	24	0
17	Pd[P( <i>o</i> -tol) <sub>3</sub> ] <sub>2</sub>	BINAP, 0.1	110	24	0
18	Pd(dba) <sub>2</sub>	BINAP, 0.1	110	24	0
19	Pd(OAc) <sub>2</sub>	BINAP, 0.1	110	24	0
20	Pd(OAc) <sub>2</sub> (2 mol %)	X-phos, 5.0	110	18	72

<sup>a</sup> Reactions conducted with 1 mmol ArOTs, 1.2 equiv amine, and 1.4 equiv NaOt-Bu in 1 mL toluene. <sup>b</sup> Isolated yield. <sup>c</sup> Yield was determined by GC using dodecane as an internal standard.



**4-*tert*-Butylphenyl *p*-toluenesulfonate.**<sup>35</sup> The general procedure A conducted with 4-*tert*-butylphenol (3.0 g, 20 mmol) and TsCl (4.56 g, 24 mmol) gave 4.50 g (81%) of the titled compound as colorless plates. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.72 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 8.8 Hz, 2 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 2.46 (s, 3 H), 1.27 (s, 9 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 150.06, 147.28, 145.18, 132.65, 129.69, 128.46, 126.46, 121.66, 34.48, 31.25, 21.66.



**4-tert-Butyl-N-octylaniline (Scheme S2, condition A).** The general procedure C conducted with 4-*tert*-butylphenyl tosylate (0.304 g, 1.00 mmol), octylamine (0.155 g, 1.20 mmol), Pd[P(*o*-tol)<sub>3</sub>]<sub>2</sub> (1.4 mg, 2.0 × 10<sup>-3</sup> mmol), CyPF-*t*-Bu (1.1 mg, 2.0 × 10<sup>-3</sup> mmol) and sodium *tert*-butoxide (0.135 g, 1.40 mmol) gave 0.251 g (96%) of the titled compound as a colorless liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.25 (d, *J* = 8.4 Hz, 2 H), 6.61 (d, *J* = 8.4 Hz, 2 H), 3.54 (s, b, 1 H), 3.13 (t, *J* = 7.2 Hz, 2 H), 1.65 (quint, *J* = 7.2 Hz, 2 H), 1.33-1.48 (m, 10 H), 0.94 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 146.18, 139.73, 125.93, 112.35, 44.18, 33.77, 31.81, 31.53, 29.64, 29.41, 29.27, 27.18, 22.64, 14.09; Anal. Calcd. For C<sub>18</sub>H<sub>31</sub>N: C, 82.69; H, 11.95; N, 5.36. Found: C, 82.77; H, 12.35; N, 5.77.

**4-tert-Butyl-N-octylaniline (Scheme S2, condition B).** The general procedure C conducted with 4-*tert*-butylphenyl tosylate (0.152 g, 0.50 mmol), octylamine (0.097 g, 0.75 mmol), Pd(OAc)<sub>2</sub> (2.3 mg, 1.0 × 10<sup>-2</sup> mmol), X-phos (11.9 mg, 2.5 × 10<sup>-2</sup> mmol) and Cs<sub>2</sub>CO<sub>3</sub> (0.408 g, 1.25 mmol) in toluene/*t*-BuOH (5/1, 1.2 mL) gave 0.102 g (78%) of the titled compound as a colorless liquid.

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