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**Supporting Information**

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**Unparalleled Rates for the Activation of Aryl Chlorides.  
Coupling with Amines and Boronic Acids in Minutes at Room  
Temperature**

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**Supporting Information**

**General Methods.** Toluene and THF were distilled from sodium-benzophenone ketyl under nitrogen. Aryl halides except *t*-butyl *p*-chlorobenzoate<sup>[1]</sup> were purchased from commercial sources and were used without further purification. Amines were purchased from commercial sources and were distilled from CaH<sub>2</sub> under nitrogen before use with the exception of diphenylamine, which was used without further purification. NaOt-Bu was purchased from Aldrich and was stored in a nitrogen-filled dry box. {[P(*t*-Bu)<sub>3</sub>]PdBr}<sub>2</sub>,<sup>[2]</sup> Pd(dba)<sub>2</sub>,<sup>[3]</sup> Pd(cod)Br<sub>2</sub>,<sup>[4]</sup> and (1-adamantyl)P(*t*-Bu)<sub>2</sub><sup>[5]</sup> (= (1-Ad)P(*t*-Bu)<sub>2</sub>) were prepared by literature procedures.

**Representative procedure for the amination of aryl halides (Table 1, Entry 2).** In a drybox, a solution of **1a** (5 mg, 0.005 mmol) in THF (1 mL) was added to a stirred mixture of NaO-*t*Bu (144 mg, 1.50 mmol), *p*-chlorotoluene

(119  $\mu\text{L}$ , 1.00 mmol), and morpholine (92  $\mu\text{L}$ , 1.05 mmol) in 1 mL of THF. The vial was sealed with a Teflon-lined septum, capped, and removed from the drybox. After 15 min, water (ca. 1 mL) was added to the vial. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$ , and the organic layer was dried with  $\text{MgSO}_4$  and concentrated. The residue was purified by column chromatography to give 92% (164 mg) of a white solid.

#### **Spectroscopic Data of the Products in Table 1**

**Table 1, Entries 1,2.** The spectroscopic data of 4-*p*-tolyl-morpholine were identical to those published previously.<sup>[6]</sup>

**Table 1, Entry 3,4.** The spectroscopic data of 4-*o*-tolyl-morpholine were identical to those published previously.<sup>[7]</sup>

**Table 1, Entry 5.** The spectroscopic data of dibutyl-(4-methoxyphenyl)amine were similar to those published previously.<sup>[8]</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.93 (t, 6H, 7.4 Hz,  $\text{CH}_3$ ), 1.33 (sextet, 4H, 7.4 Hz,  $\text{CH}_2$ ), 1.47–1.56 (m, 4H,  $\text{CH}_2$ ), 3.17 (t, 4H, 7.6 Hz,  $\text{CH}_2$ ), 3.75 (s, 3H,  $\text{OCH}_3$ ), 6.64 (d, 2H, 7.4 Hz, Ar), 6.81 (d, 2H, 9.0 Hz, Ar);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.0 (s,  $\text{CH}_3$ ), 20.4 (s,  $\text{CH}_2$ ), 29.4 (s,  $\text{CH}_2$ ), 51.6 (s,  $\text{CH}_2$ ), 55.8 (s,  $\text{OCH}_3$ ), 114.2 (s, Ar), 114.8 (s, Ar), 143.3 (s, Ar), 150.9 (s, Ar).

**Table 1, Entry 6.** The spectroscopic data of 4-dibutylaminobenzonitrile were identical to those published previously.<sup>[9]</sup>

**Table 1, Entry 7.** The spectroscopic data of dibutyl(4-nitrophenyl)amine were identical to those published previously.<sup>[10]</sup>

**Table 1, Entry 8.** *tert*-Butyl 4-(*N,N*-dibutylamino)benzoate. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 0.95 (t, 6H, 7.2 Hz, CH<sub>3</sub>), 1.35 (sextet, 4H, 7.4 Hz, CH<sub>2</sub>), 1.52-1.62 (m, 4H, CH<sub>2</sub>), 1.56 (s, 9H, *t*Bu), 3.30 (t, 4H, 7.8 Hz, CH<sub>2</sub>), 6.56 (d, 2H, 9.0 Hz, Ar), 7.83 (d, 2H, 9.0 Hz, Ar); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 14.0 (s, CH<sub>3</sub>), 20.3 (s, CH<sub>2</sub>), 28.4 (s, *t*Bu), 29.3 (s, CH<sub>2</sub>), 50.7 (s, CH<sub>2</sub>), 79.5, 110.1 (s, Ar), 117.8 (s, Ar), 131.2 (s, Ar), 151.0 (s, Ar), 166.3 (s, CO); IR (neat) 1698 cm<sup>-1</sup>; 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, 74.78; H, 10.31; N, 4.55.

**Table 1, Entry 9.** The spectroscopic data of dibutyl(4-*tert*-butylphenyl)amine were identical to those published previously.<sup>[11]</sup>

**Table 1, Entry 10.** The spectroscopic data of (4-*tert*-butylphenyl)methylphenylamine were identical to those published previously.<sup>[12]</sup>

**Table 1, Entry 11,** (4-*tert*-Butylphenyl)diphenylamine. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,): δ = 1.31 (s, 9H, *t*Bu), 6.94-7.04 (m, 4H, Ar), 7.08 (d, 4H, Ar), 7.19-7.27 (m, 6H, Ar); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 31.4 (s, CH<sub>3</sub>), 34.3 (s, C *t*Bu), 122.3 (s, Ar), 123.8 (s, Ar), 124.0 (s, Ar), 126.2 (s, Ar), 129.1 (s, Ar), 145.0 (s, Ar), 145.7 (s, Ar), 148.0

(s, Ar). Anal. Calcd for  $C_{22}H_{23}N$ : C, 87.66; H, 7.69; N, 4.65. Found: C, 87.44; H, 7.70; N, 4.37.

**Table 1, Entries 12,13.** The spectroscopic data of (4-*tert*-butylphenyl)phenylamine were identical to those published previously.<sup>[13]</sup>

**Representative procedure for the Suzuki coupling of aryl halides (Table 2, Entry 1).** In a drybox, a solution of **1a** (5 mg, 0.005 mmol) in THF (1.5 mL) was added to a stirred mixture of KOH (168 mg, 3.0 mmol), phenylboronic acid (132 mg, 1.08 mmol), and *p*-bromotoluene (124  $\mu$ L, 1.00 mmol) in 1.5 mL of THF. The vial was sealed with a Teflon-lined septum, capped, and removed from the drybox. After 15 min, water (ca. 1 mL) was added to the vial. The mixture was extracted with  $CH_2Cl_2$ , and the organic layer was dried with  $MgSO_4$  and concentrated. The residue was purified by column chromatography to give 93% (156 mg) of an off-white solid.

**Spectroscopic Data of the Products in Table 2:**

**Table 2, Entry 1.** The spectroscopic data of 2-trifluoromethylbiphenyl were identical to those published previously.<sup>[14]</sup>

**Table 2, Entry 2.** The spectroscopic data of biphenyl-2-carbonitrile were identical to those published previously.<sup>[15]</sup>

**Table 2, Entry 3.** The spectroscopic data of 2-methoxybiphenyl were identical to those published previously.<sup>[16]</sup>

**Table 2, Entry 4.** The spectroscopic data of 4-methylbiphenyl were identical to those published previously.<sup>[17]</sup>

**Table 2, Entry 5.** The spectroscopic data of 2,6-dimethylbiphenyl were identical to those published previously.<sup>[16]</sup>

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