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\(^1 \) were purchased from commercial sources and were used without further purification. Amines were purchased from commercial sources and were distilled from CaH\(_2\) under nitrogen before use with the exception of diphenylamine, which was used without further purification. NaO\( t \)-Bu was purchased from Aldrich and was stored in a nitrogen-filled dry box. \([\text{P}(t-Bu)_3]\text{PdBr}_2\),\(^2\) Pd(dba)\(_2\),\(^3\) Pd(cod)Br\(_2\),\(^4\) and \( (1\text{-adamantyl})\text{P}(t-Bu)_2\)\(^5\) (= \( (1\text{-Ad})\text{P}(t-Bu)_2\)) 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 L, 1.00 mmol), and morpholine (92 \mu 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 CH$_2$Cl$_2$, and the organic layer was dried with 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-\textit{p}-tolyl-morpholine were identical to those published previously.$^6$

**Table 1, Entry 3,4.** The spectroscopic data of 4-\textit{o}-tolyl-morpholine were identical to those published previously.$^7$

**Table 1, Entry 5.** The spectroscopic data of dibutyl-(4-methoxyphenyl)amine were similar to those published previously.$^8$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.93 (t, 6H, 7.4 Hz, CH$_3$), 1.33 (sextet, 4H, 7.4 Hz, CH$_2$), 1.47-1.56 (m, 4H, CH$_2$), 3.17 (t, 4H, 7.6 Hz, CH$_2$), 3.75 (s, 3H, OCH$_3$), 6.64 (d, 2H, 7.4 Hz, Ar), 6.81 (d, 2H, 9.0 Hz, Ar); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 14.0 (s, CH$_3$), 20.4 (s, CH$_2$), 29.4 (s, CH$_2$), 51.6 (s, CH$_3$), 55.8 (s, 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.$^9$
Table 1, Entry 7. The spectroscopic data of dibutyl(4-nitrophenyl)amine were identical to those published previously.\textsuperscript{10}

Table 1, Entry 8. tert-Butyl 4-(N,N-dibutylamino)benzoate. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 0.95\) (t, 6H, 7.2 Hz, CH\textsubscript{3}), 1.35 (sextet, 4H, 7.4 Hz, CH\textsubscript{2}), 1.52-1.62 (m, 4H, CH\textsubscript{2}), 1.56 (s, 9H, tBu), 3.30 (t, 4H, 7.8 Hz, CH\textsubscript{2}), 6.56 (d, 2H, 9.0 Hz, Ar), 7.83 (d, 2H, 9.0 Hz, Ar); \textsuperscript{13}C \{\textsuperscript{1}H\} NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 14.0\) (s, CH\textsubscript{3}), 20.3 (s, CH\textsubscript{2}), 28.4 (s, tBu), 29.3 (s, CH\textsubscript{2}), 50.7 (s, CH\textsubscript{2}), 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\textsuperscript{-1}; Anal. Calcd for C\textsubscript{19}H\textsubscript{31}NO\textsubscript{2}: 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.\textsuperscript{11}

Table 1, Entry 10. The spectroscopic data of (4-tert-butylphenyl)methylphenylamine were identical to those published previously.\textsuperscript{12}

Table 1, Entry 11. (4-tert-Butylphenyl)diphenylamine. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 1.31\) (s, 9H, tBu), 6.94-7.04 (m, 4H, Ar), 7.08 (d, 4H, Ar), 7.19-7.27 (m, 6H, Ar); \textsuperscript{13}C \{\textsuperscript{1}H\} NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 31.4\) (s, CH\textsubscript{3}), 34.3 (s, C tBu), 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.\(^{[13]}\)

**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 µL, 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$_2$Cl$_2$, 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.\(^{[14]}\)

**Table 2, Entry 2.** The spectroscopic data of biphenyl-2-carbonitrile were identical to those published previously.\(^{[15]}\)
Table 2, Entry 3. The spectroscopic data of 2-methoxybiphenyl were identical to those published previously.[16]

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

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

References:


