Aqueous Hydroxide as a Base for Palladium Catalyzed Amination of Aryl Chlorides and Bromides

Ryoichi Kuwano, Masaru Utsunomiya, John F. Hartwig*

*Department of Chemistry, Yale University P.O. Box 208107
New Haven, Connecticut 06520-8107*

Supporting Information

General Procedure for the Reactions of Liquid Aryl Halides with Amines Using KOH Powder (Method A). In a drybox, aryl halide (1.0 mmol) and amine (1.05 mmol) were added to a suspension of Pd[P(*t*-Bu)₃]₂ (5.1 mg, 10.0 μmol), cetyltrimethylammonium bromide (1.8 mg, 5.0 μmol), and KOH powder (84 mg, 1.5 mmol) in toluene (1.0 ml) in a screw-capped vial. A small stirbar was added, and the vial was sealed with a cap containing a PTFE septum and removed from the drybox. Water (27 μl, 1.5 mmol) was added to the mixture by syringe. The reaction mixture was then stirred *vigorously* at 90 °C. The reaction was monitored by GC. After the reaction, the mixture was absorbed onto the silica gel and purified by flash column chromatography on silica gel to give desired aryl amine.

General Procedure for the Reactions of Liquid Aryl Halides with Diphenylamine Using KOH Powder (Method B). In a drybox, aryl halide (1.0 mmol) was added to a suspension of Pd[P(*t*-Bu)₃]₂ (5.1 mg, 10.0 μmol), cetyltrimethylammonium bromide (1.8 mg, 5.0 μmol), KOH powder (84 mg, 1.5 mmol), and diphenylamine (178 mg, 1.05 mmol) in toluene (1.0 ml) in a screw-capped vial. A small stirbar was added, and the vial was sealed with a cap containing a PTFE septum and removed from the drybox. Water (27 μl, 1.5 mmol) was added to the mixture by syringe. The reaction mixture was then stirred *vigorously* at 90 °C. The reaction was monitored by GC. After the reaction, the mixture was absorbed onto the silica gel and purified by flash column chromatography on silica gel to give desired aryl amine.

General Procedure for the Reactions of Solid Aryl Halides with Liquid Amine Using KOH Powder (Method C). In a drybox, amine (1.05 mmol) was added to a suspension of Pd[P(*t*-Bu)₃]₂ (5.1 mg, 10.0 μmol), cetyltrimethylammonium bromide (1.8 mg, 5.0 μmol), KOH powder (84 mg, 1.5 mmol), and aryl halide (1.0 mmol) in toluene (1.0 ml) in a screw-capped vial. A small stirbar was added, and the vial was sealed with a cap containing a PTFE septum and removed from the drybox. Water (27 μl, 1.5 mmol) was added to the mixture by syringe. The reaction mixture was then stirred *vigorously* at 90 °C. The reaction was monitored by GC. After the reaction, the mixture was absorbed onto the silica gel and purified by flash column chromatography on silica gel to give desired aryl amine.

General Procedure for the Reactions of Aryl Chlorides with Amines Using KOH Water Solution (Method D). In a drybox, aryl chloride (0.8 mmol) and amine (0.84 mmol) were

added to a suspension of Pd[P(*t*-Bu)₃]₂ (4.1 mg, 8.0 μmol) and cetyltrimethylammonium bromide (1.5 mg, 4.0 μmol) in toluene (0.8 ml) in a screw-capped vial. A small stirbar was added, and the vial was sealed with a cap containing a PTFE septum before removing it from the drybox. KOH (45 wt% in water, 150 μl, KOH 1.2 mmol, H₂O 4.57 mmol) was added to the mixture by syringe. The reaction mixture was then stirred *vigorously* at 90 °C. The reaction was monitored by GC. After the reaction, the mixture was absorbed onto the silica gel and purified by flash column chromatography on silica gel to give desired aryl amine.

General Procedure for the Reactions of Aryl Chlorides with Amines Using NaOH Water Solution (Method E). In a drybox, aryl chloride (0.8 mmol) and amine (0.84 mmol) were added to a suspension of Pd[P(*t*-Bu)₃]₂ (4.1 mg, 8.0 μmol) and cetyltrimethylammonium bromide (1.5 mg, 4.0 μmol) in toluene (0.8 ml) in a screw-capped vial. A small stirbar was added, and the vial was sealed with a cap containing a PTFE septum before removing it from the drybox. NaOH (50 wt% water solution, 96 μl, NaOH 1.2 mmol, H₂O 2.65 mmol) was added to the mixture by syringe. The reaction mixture was then stirred *vigorously* at 90 °C. The reaction was monitored by GC. After the reaction, the mixture was absorbed onto the silica gel and purified by flash column chromatography on silica gel to give desired aryl amine.

***N,N*-Dibutyltoluidine¹ (Table 3, Entry 1).** Method A of the general procedure was followed with *p*-chlorotoluene (128 mg, 1.01 mmol) and dibutylamine (134 mg, 1.04 mmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (200 mg, 91%) as colorless oil: ¹H NMR (400 MHz, CDCl₃, TMS) δ 0.94 (t, *J* = 7.4 Hz, 6H), 1.33 (sextet, *J* = 7.6 Hz, 4H), 1.54 (quintet, *J* = 7.6 Hz, 4H), 2.23 (s, 3H), 3.22 (t, *J* = 7.6 Hz, 4H), 6.57 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 14.0, 20.1, 20.4, 29.4, 51.0, 112.1, 124.3, 129.7, 146.1.

***N*-(4-Methylphenyl)morpholine² (Table 3, Entry 2).** Method A of the general procedure was followed with *p*-chlorotoluene (127 mg, 1.00 mmol) and morpholine (92 mg, 1.06 mmol). The reaction mixture was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give the desired product (160 mg, 90%) as a white solid: ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.28 (s, 3H), 3.10 (t, *J* = 4.8 Hz, 4H), 3.86 (t, *J* = 4.8 Hz, 4H), 6.83 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 20.4, 49.9, 67.0, 116.0, 129.6, 129.7, 149.2.

***N*-Methy-*N*-phenyl-*p*-toluidine³ (Table 3, Entry 3).** Method A of the general procedure was followed with *p*-chlorotoluene (127 mg, 1.00 mmol) and *N*-methylaniline (116 mg, 1.08 mmol). The reaction mixture was purified by flash column chromatography on silica gel (1% EtOAc in hexanes) to give the desired product (195 mg, 99%) as colorless oil: ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.32 (s, 3H), 3.28 (s, 3H), 6.86 (t, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.19–7.26 (m, 2H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 20.7, 40.3, 118.1, 119.6, 122.5, 129.0, 129.9, 132.1, 146.5, 149.3.

***N,N*-Diphenyl-*p*-toluidine⁴ (Table 3, Entry 4).** Method B of the general procedure was followed with *p*-chlorotoluene (128 mg, 1.01 mmol) and diphenylamine (177 mg, 1.05 mmol). The reaction mixture was purified by flash column chromatography on silica gel (hexanes) to give the desired

product (214 mg, 82%) as a white solid: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.31 (s, 3H), 6.96 (t, J = 7.2 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 7.03–7.09 (m, 6H), 7.21 (t, J = 7.8 Hz, 4H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 20.8, 122.2, 123.6, 124.9, 129.1, 129.9, 132.7, 145.2, 148.0.

***N*-Phenyl-*p*-toluidine⁵ (Table 3, Entry 5).** Method A of the general procedure was followed with *p*-chlorotoluene (126 mg, 1.00 mmol) and aniline (98 mg, 1.05 mmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (167 mg, 91%) as a white solid: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.30 (s, 3H), 5.62 (br s, 1H), 6.88 (t, J = 7.0 Hz, 1H), 6.96–7.05 (m, 4H), 7.09 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 20.7, 116.8, 118.9, 120.3, 129.3, 129.8, 130.9, 140.2, 143.9.

***N*-Hexyl-*p*-toluidine³ (Table 3, Entry 6).** Method A of the general procedure was followed with *p*-chlorotoluene (128 mg, 1.01 mmol), hexylamine (202 mg, 2.00 mmol), $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$ (25.6 mg, 50 μmol), and cetyltrimethylammonium bromide (9.1 mg, 25 μmol). The reaction mixture was purified by flash column chromatography on silica gel (1% EtOAc in hexanes) to give 151 mg of a mixture of desired *N*-hexyl-*p*-toluidine (62% estimated by ^1H NMR) and *N*-hexyldi(*p*-tolyl)amine (22% estimated by ^1H NMR) as a white solid. Pure *N*-hexyl-*p*-toluidine for NMR analysis (14 mg) could be obtained as a white solid by collecting pure fractions in the flash column chromatography. *N*-Hexyl-*p*-toluidine: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 0.89 (t, J = 6.8 Hz, 3H), 1.25–1.43 (m, 6H), 1.60 (quintet, J = 7.2 Hz, 2H), 2.23 (s, 3H), 3.07 (t, J = 7.2 Hz, 2H), 3.45 (br s, 1H), 6.53 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 14.0, 20.4, 22.6, 26.9, 29.6, 31.7, 44.4, 112.9, 126.2, 129.7, 146.3.

***N*-(2-Methylphenyl)morpholine² (Table 3, Entry 7).** Method A of the general procedure was followed with *o*-chlorotoluene (126 mg, 0.99 mmol) and morpholine (91 mg, 1.05 mmol). The reaction mixture was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give the desired product (149 mg, 84%) as colorless oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.32 (s, 3H), 2.91 (t, J = 4.6 Hz, 4H), 3.85 (t, J = 4.6 Hz, 4H), 6.97–7.04 (m, 2H), 7.15–7.21 (m, 2H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 17.9, 52.2, 67.4, 118.9, 123.3, 126.6, 131.1, 132.6, 151.2.

***N,N*-Diphenyl-*o*-toluidine⁶ (Table 3, Entry 8).** Method B of the general procedure was followed with *o*-chlorotoluene (125 mg, 0.99 mmol) and diphenylamine (177 mg, 1.04 mmol). The reaction mixture was purified by flash column chromatography on silica gel (hexanes) to give the desired product (226 mg, 88%) as a white solid: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.03 (s, 3H), 6.91 (t, J = 7.2 Hz, 2H), 6.96 (d, J = 8.6 Hz, 4H), 7.10–7.26 (m, 8H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 18.6, 121.3, 121.5, 126.0, 127.3, 129.0, 129.6, 131.7, 136.5, 145.3, 147.4.

***N*-Phenyl-*o*-toluidine⁷ (Table 3, Entry 9).** Method A of the general procedure was followed with *o*-chlorotoluene (127 mg, 1.00 mmol) and aniline (97 mg, 1.04 mmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (165 mg, 90%) as colorless oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.25 (s, 3H), 5.38 (br s, 1H), 6.87–6.98 (m, 4H), 7.13 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.21–7.28 (m, 3H);

^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 17.9, 117.4, 118.7, 120.4, 121.9, 126.7, 128.2, 129.3, 130.9, 141.1, 143.9.

***N*-Hexyl-*o*-toluidine** (Table 3, Entry 10). Method A of the general procedure was followed with *o*-chlorotoluene (127 mg, 1.00 mmol), hexylamine (122 mg, 1.20 mmol), $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$ (10.2 mg, 20 μmol), and cetyltrimethylammonium bromide (3.6 mg, 10 μmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (192 mg, 95%) as colorless oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 0.90 (t, J = 7.0 Hz, 3H), 1.38–1.47 (m, 6H), 1.66 (quintet, J = 7.4 Hz, 2H), 2.13 (s, 3H), 3.14 (t, J = 7.0 Hz, 2H), 3.43 (br s, 1H), 6.59–6.67 (m, 2H), 7.05 (d, J = 7.2 Hz, 1H), 7.12 (dt, J = 1.0, 7.7 Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 14.0, 17.5, 22.6, 26.9, 29.5, 31.6, 43.9, 109.5, 116.5, 121.6, 127.1, 130.0, 146.4; IR (neat) 3431 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{N}$: C, 81.61; H, 11.06; N, 7.32. Found: C, 81.32; H, 11.06; N, 7.46.

***N*-Methyl-*N*-phenyl-*p*-anisidine**⁸ (Table 3, Entry 11). Method A of the general procedure was followed with *p*-chloroanisole (144 mg, 1.01 mmol) and *N*-methylaniline (111 mg, 1.03 mmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (197 mg, 92%) as colorless oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 3.25 (s, 3H), 3.81 (s, 3H), 6.75–6.81 (m, 3H), 6.89 (d, J = 9.0 Hz, 2H), 7.09 (d, J = 9.0 Hz, 2H), 7.19 (dd, J = 7.4, 8.6 Hz, 2H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 40.4, 55.5, 114.7, 115.6, 118.3, 126.2, 128.9, 142.2, 149.7, 156.2.

***N,N*-Dibutyl-4-nitroaniline**⁹ (Table 3, Entry 12). Method C of the general procedure was followed with 1-chloro-4-nitrobenzene (157 mg, 1.00 mmol) and dibutylamine (135 mg, 1.04 mmol). The reaction mixture was purified by flash column chromatography on silica gel (10% EtOAc in hexanes) to give the desired product (233 mg, 93%) as orange oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 0.98 (t, J = 7.4 Hz, 6H), 1.38 (sextet, J = 7.4 Hz, 4H), 1.56–1.65 (m, 4H), 3.36 (t, J = 7.8 Hz, 4H), 6.54 (d, J = 9.4 Hz, 2H), 8.09 (d, J = 9.4 Hz, 2H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 13.9, 20.2, 29.1, 51.0, 109.9, 126.4, 136.1, 152.5.

***N*-(4-Nitrophenyl)morpholine**¹⁰ (Table 3, Entry 13). Method C of the general procedure was followed with 1-chloro-4-nitrobenzene (158 mg, 1.00 mmol) and morpholine (92 mg, 1.06 mmol). The reaction mixture was purified by flash column chromatography on silica gel (50% EtOAc in hexanes) to give the desired product (196 mg, 94%) as an orange solid: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 3.38 (t, J = 5.0 Hz, 4H), 3.87 (t, J = 5.0 Hz, 4H), 6.84 (d, J = 9.2 Hz, 2H), 8.14 (d, J = 9.2 Hz, 2H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 47.1, 66.3, 112.6, 125.9, 138.9, 155.0.

***N*-Methyl-4-nitro-*N*-phenylaniline**¹¹ (Table 3, Entry 14). Method C of the general procedure was followed with 1-chloro-4-nitrobenzene (158 mg, 1.00 mmol) and *N*-methylaniline (116 mg, 1.08 mmol). The reaction mixture was purified by flash column chromatography on silica gel (10% EtOAc in hexanes) to give the desired product (228 mg, >99%) as orange oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 3.41 (s, 3H), 6.67 (d, J = 9.2 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 8.06 (d, J = 9.2 Hz, 2H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 40.5, 112.3, 125.8, 126.7, 126.8, 130.2, 138.0, 146.3, 153.7.

4-Nitro-*N,N*-diphenylaniline¹² (Table 3, Entry 15). In a drybox, toluene (1.0 ml) was added to a mixture of Pd[P(*t*-Bu)₃]₂ (5.1 mg, 10.0 μmol), cetyltrimethylammonium bromide (1.8 mg, 5.0 μmol), KOH powder (84 mg, 1.5 mmol), 1-chloro-4-nitrobenzene (167 mg, 1.06 mmol), and diphenylamine (170 mg, 1.00 mmol) in a screw-capped vial. A small stirbar was added, and the vial was sealed with a cap containing a PTFE septum and removed from the drybox. Water (27 μl, 1.5 mmol) was added to the mixture by syringe. The reaction mixture was then stirred *vigorously* at 90 °C. After 6 h, the mixture was absorbed onto the silica gel and purified by flash column chromatography on silica gel (10% EtOAc in hexanes) to give the desired product (285 mg, 98% based on diphenylamine) as an orange solid: ¹H NMR (400 MHz, CDCl₃, TMS) δ 6.92 (d, *J* = 9.4 Hz, 2H), 7.06–7.24 (m, 6H), 7.37 (t, *J* = 7.8 Hz, 4H), 8.04 (d, *J* = 9.4 Hz, 2H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 118.1, 125.4, 125.7, 126.5, 129.9, 140.1, 145.6, 153.4.

4-Nitro-*N*-phenylaniline¹³ (Table 3, Entry 16). Method C of the general procedure was followed with 1-chloro-4-nitrobenzene (157 mg, 1.00 mmol) and aniline (98 mg, 1.05 mmol). The reaction mixture was purified by flash column chromatography on silica gel (20% EtOAc in hexanes) to give the desired product (206 mg, 96%) as an orange solid: ¹H NMR (400 MHz, CDCl₃, TMS) δ 6.26 (br s, 1H), 6.94 (d, *J* = 9.4 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 8.13 (d, *J* = 9.4 Hz, 2H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 113.6, 121.9, 124.6, 126.2, 129.7, 139.4, 139.7, 150.1.

Methyl 4-(*N*-phenylamino)benzoate¹⁴ (Table 3, Entry 17). Method C of the general procedure was followed with methyl 4-chlorobenzoate (170 mg, 1.00 mmol) and aniline (99 mg, 1.06 mmol). The reaction mixture was purified by flash column chromatography on silica gel (20% EtOAc in hexanes) to give the desired product (209 mg, 92%) as a white solid: ¹H NMR (400 MHz, CDCl₃, TMS) δ 3.87 (s, 3H), 6.05 (br s, 1H), 6.99 (d, *J* = 9.0 Hz, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 9.0 Hz, 2H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 51.7, 114.5, 120.4, 121.0, 123.1, 129.5, 131.5, 140.8, 148.0, 166.9.

***tert*-Butyl 4-(*N,N*-dibutylamino)benzoate** (Table 3, Entry 18). Method A of the general procedure was followed with *tert*-butyl 4-chlorobenzoate (211 mg, 0.99 mmol) and dibutylamine (135 mg, 1.04 mmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (298 mg, 98%) as colorless oil: ¹H NMR (400 MHz, CDCl₃, TMS) δ 0.95 (t, *J* = 7.2 Hz, 6H), 1.35 (sextet, *J* = 7.4 Hz, 4H), 1.52–1.62 (m, 4H), 1.56 (s, 9H), 3.30 (t, *J* = 7.8 Hz, 4H), 6.56 (d, *J* = 9.0 Hz, 2H), 7.83 (d, *J* = 9.0 Hz, 2H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 14.0, 20.3, 28.4, 29.3, 50.7, 79.5, 110.1, 117.8, 131.2, 151.0, 166.3; IR (neat) 1698 cm⁻¹; Anal. Calcd for C₁₉H₃₁NO₂: C, 74.71; H, 10.23; N, 4.59. Found: C, 74.78; H, 10.31; N, 4.55.

***tert*-Butyl 4-(*N,N*-diphenylamino)benzoate** (Table 3, Entry 19). Method B of the general procedure was followed with *tert*-butyl 4-chlorobenzoate (216 mg, 1.02 mmol) and diphenylamine (178 mg, 1.05 mmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (352 mg, >99%) as a white solid: mp 132–133 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.57 (s, 9H), 6.99 (d, *J* = 9.0 Hz, 2H), 7.07–7.14 (m, 6H), 7.29 (t, *J* = 7.8 Hz, 4H), 7.82 (d, *J* = 9.0 Hz, 2H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 28.2, 80.4, 120.4,

124.1, 124.3, 125.5, 129.5, 130.6, 146.8, 151.6, 165.6; IR (KBr disk) 1696 cm^{-1} ; Anal. Calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_2$: C, 79.97; H, 6.71; N, 4.05. Found: C, 79.97; H, 6.71; N, 4.06.

***tert*-Butyl 4-(*N*-phenylamino)benzoate (Table 3, Entry 20).** Method A of the general procedure was followed with *tert*-butyl 4-chlorobenzoate (216 mg, 1.02 mmol) and aniline (98 mg, 1.05 mmol). The reaction mixture was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give the desired product (252 mg, 92%) as a white solid: mp 114–115 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.58 (s, 9H), 6.00 (br s, 1H), 6.98 (d, J = 8.8 Hz, 2H), 7.04 (t, J = 7.4 Hz, 1H), 7.16 (d, J = 8.6 Hz, 2H), 7.32 (dd, J = 7.4, 8.6 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 28.3, 80.2, 114.7, 120.0, 122.8, 123.2, 129.4, 131.2, 141.1, 147.4, 165.7; IR (KBr disk) 3320, 1678 cm^{-1} ; Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.88; H, 7.16; N, 5.24.

***N*-(4-Acetylphenyl)morpholine¹⁵ (Table 3, Entry 21).** Method A of the general procedure was followed with 4-chloroacetophenone (153 mg, 0.99 mmol) and morpholine (91 mg, 1.04 mmol). The reaction mixture was purified by flash column chromatography on silica gel. Bis(4-acetylphenyl)methane (**4**) (6 mg, 8%) was eluted with 20% EtOAc in hexanes, and desired *N*-(4-acetylphenyl)morpholine (171 mg, 84%) was eluted with 50% EtOAc in hexanes. *N*-(4-acetylphenyl)morpholine: pale yellow solid; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.53 (s, 3H), 3.31 (t, J = 5.0 Hz, 4H), 3.86 (t, J = 5.0 Hz, 4H), 6.87 (d, J = 9.0 Hz, 2H), 7.90 (d, J = 9.0 Hz, 2H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 26.2, 47.5, 66.5, 113.2, 128.1, 130.3, 154.2, 196.5. **4**:¹⁶ yellow solid; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.58 (s, 6H), 4.09 (s, 2H), 7.27 (d, J = 8.4 Hz, 4H), 7.90 (d, J = 8.4 Hz, 4H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 26.6, 41.8, 128.8, 129.1, 135.5, 145.6, 197.7.

4-(*N*-Phenylamino)acetophenone¹⁷ (Table 3, Entry 22). Method A of the general procedure was followed with 4-chloroacetophenone (156 mg, 1.01 mmol) and aniline (97 mg, 1.04 mmol). The reaction mixture was purified by flash column chromatography on silica gel (20% EtOAc in hexanes) to give the desired product (185 mg, 87%) as a pale yellow solid: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.54 (s, 3H), 6.12 (br s, 1H), 7.00 (d, J = 8.8 Hz, 2H), 7.09 (t, J = 7.4 Hz, 1H), 7.19 (d, J = 8.4 Hz, 2H), 7.35 (dd, J = 7.4, 8.4 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 26.2, 114.4, 120.6, 123.3, 129.0, 129.5, 130.6, 140.5, 148.3, 196.4.

4-(*N*-Phenylamino)benzonitrile¹⁸ (Table 3, Entry 23). Method C of the general procedure was followed with *p*-chlorobenzonitrile (137 mg, 1.00 mmol) and aniline (99 mg, 1.07 mmol). The reaction mixture was purified by flash column chromatography on silica gel (20% EtOAc in hexanes) to give the desired product (168 mg, 86%) as a white solid: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 6.07 (br s, 1H), 6.97 (d, J = 8.8 Hz, 2H), 7.12 (t, J = 7.4 Hz, 1H), 7.17 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 8.0 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 101.5, 114.9, 119.9, 121.2, 124.0, 129.6, 133.8, 139.9, 148.0.

***N,N*-Dibutylaniline¹⁹ (Table 4, Entry 1).** Method A of the general procedure was followed with bromobenzene (157 mg, 1.00 mmol) and dibutylamine (136 mg, 1.05 mmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (189 mg, 92%) as a colorless oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 0.95 (t, J = 7.2

Hz, 6H), 1.35 (sextet, $J = 7.5$ Hz, 4H), 1.51–1.61 (m, 4H), 3.25 (t, $J = 7.6$ Hz, 4H), 6.59–6.66 (m, 3H), 7.19 (dd, $J = 7.6, 8.8$ Hz, 2H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 14.0, 20.4, 29.4, 50.7, 111.6, 115.0, 129.2, 148.1.

***N*-Phenylmorpholine² (Table 4, Entry 2).** Method A of the general procedure was followed with bromobenzene (157 mg, 1.00 mmol) and morpholine (92 mg, 1.05 mmol). The reaction mixture was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give the desired product (156 mg, 95%) as a white solid: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 3.16 (t, $J = 4.8$ Hz, 4H), 3.87 (t, $J = 4.8$ Hz, 4H), 6.89 (t, $J = 7.4$ Hz, 1H), 6.92 (d, $J = 8.2$ Hz, 2H), 7.28 (dd, $J = 7.4, 8.2$ Hz, 2H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 49.3, 66.9, 115.7, 120.0, 129.2, 151.2.

***N*-Methyldiphenylamine²⁰ (Table 4, Entry 3).** Method A of the general procedure was followed with bromobenzene (157 mg, 1.00 mmol) and *N*-methylaniline (113 mg, 1.05 mmol). The reaction mixture was purified by flash column chromatography on silica gel (1% EtOAc in hexanes) to give the product (173 mg, 94%) as a colorless oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 3.31 (s, 3H), 6.95 (tt, $J = 1.2, 7.2$ Hz, 2H), 7.02 (dd, $J = 1.2, 8.8$ Hz, 4H), 7.27 (dd, $J = 7.2, 8.8$ Hz, 4H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 40.2, 120.4, 121.2, 129.1, 149.0.

Triphenylamine²¹ (Table 4, Entry 4). Method B of the general procedure was followed with bromobenzene (157 mg, 1.00 mmol) and diphenylamine (177 mg, 1.05 mmol). The reaction mixture was purified by flash column chromatography on silica gel (hexanes) to give the desired product (236 mg, 96%) as a white solid: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.00 (t, $J = 7.2$ Hz, 3H), 7.08 (d, $J = 8.8$ Hz, 6H), 7.24 (dd, $J = 7.2, 8.8$ Hz, 6H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 122.6, 124.1, 129.2, 147.8.

Diphenylamine²² (Table 4, Entry 5). Method A of the general procedure was followed with bromobenzene (157 mg, 1.00 mmol) and aniline (98 mg, 1.05 mmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (159 mg, 94%) as a white solid: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 5.68 (br s, 1H), 6.92 (t, $J = 7.4$ Hz, 2H), 7.08 (d, $J = 7.8$ Hz, 4H), 7.26 (t, $J = 7.6$ Hz, 4H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 117.7, 120.9, 129.3, 143.0.

***N*-Hexylaniline²³ (Table 4, Entry 6).** Method A of the general procedure was followed with bromobenzene (156 mg, 1.00 mmol), hexylamine (304 mg, 3.00 mmol), $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$ (10.2 mg, 20 μmol), and cetyltrimethylammonium bromide (3.6 mg, 10 μmol). The reaction mixture was purified by flash column chromatography on silica gel. *N*-Hexyldiphenylamine (8 mg, 6%) was eluted with 1% EtOAc in hexanes, and desired *N*-hexylaniline (140 mg, 79%) was eluted with 2% EtOAc in hexanes. *N*-Hexylaniline: colorless oil; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 0.90 (t, $J = 7.0$ Hz, 3H), 1.27–1.44 (m, 6H), 1.61 (quintet, $J = 7.2$ Hz, 2H), 3.10 (t, $J = 7.2$ Hz, 2H), 3.59 (br s, 1H), 6.60 (dd, $J = 0.9, 8.6$ Hz, 2H), 6.68 (tt, $J = 0.9, 7.2$ Hz, 1H), 7.17 (dd, $J = 7.2, 8.6$ Hz, 2H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 14.1, 22.6, 26.9, 29.5, 31.6, 44.0, 112.6, 117.0, 129.2, 148.5. *N*-Hexyldiphenylamine: colorless oil; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 0.87 (t, $J = 6.6$ Hz, 3H), 1.23–1.38 (m, 6H), 1.65 (quintet, $J = 7.6$ Hz, 2H), 3.67 (t, $J = 7.6$ Hz, 2H), 6.93 (dt, $J = 0.9, 7.4$ Hz, 2H), 6.98 (d, $J = 8.0$ Hz,

4H), 7.25 (t, $J = 7.6$ Hz, 4H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 14.0, 22.7, 26.7, 27.4, 31.6, 52.4, 120.8, 121.0, 129.2, 148.0.

***N,N*-Diphenyl-*o*-toluidine**⁶ (Table 4, Entry 7). Method B of the general procedure was followed with *o*-bromotoluene (171 mg, 1.00 mmol) and diphenylamine (178 mg, 1.05 mmol). The reaction mixture was purified by flash column chromatography on silica gel (hexanes) to give the desired product (237 mg, 92%) as a white solid.

***N*-Phenyl-*o*-toluidine**⁷ (Table 4, Entry 8). Method A of the general procedure was followed with *o*-bromotoluene (171 mg, 1.00 mmol) and aniline (97 mg, 1.04 mmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (178 mg, 97%) as colorless oil.

2,6-Dimethyl-*N*-phenylaniline²⁴ (Table 4, Entry 9). Method A of the general procedure was followed with 1-bromo-2,6-dimethylbenzene (187 mg, 1.01 mmol) and aniline (99 mg, 1.06 mmol). The reaction mixture was purified by flash column chromatography on silica gel (1% EtOAc in hexanes) to give the desired product (193 mg, 98%) as colorless oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.21 (s, 6H), 5.17 (br s, 1H), 6.50 (d, $J = 8.8$ Hz, 2H), 6.74 (tt, $J = 0.9, 7.4$ Hz, 1H), 7.05–7.18 (m, 5H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 18.4, 113.5, 118.1, 125.7, 128.5, 129.2, 135.9, 138.2, 146.2.

***N,N*-Dibutyl-*p*-anisidine**¹ (Table 4, Entry 10). Method A of the general procedure was followed with *p*-bromoanisole (188 mg, 1.01 mmol) and dibutylamine (136 mg, 1.05 mmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (193 mg, 81%) as a colorless oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 0.93 (t, $J = 7.4$ Hz, 6H), 1.33 (sextet, $J = 7.4$ Hz, 4H), 1.47–1.56 (m, 4H), 3.17 (t, $J = 7.6$ Hz, 4H), 3.75 (s, 3H), 6.64 (d, $J = 9.0$ Hz, 2H), 6.81 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 20.4, 29.4, 51.6, 55.8, 114.2, 114.8, 143.3, 150.9.

***N*-(4-Methoxyphenyl)morpholine**² (Table 4, Entry 11). Method A of the general procedure was followed with *p*-bromoanisole (192 mg, 1.03 mmol) and morpholine (92 mg, 1.06 mmol). The reaction mixture was purified by flash column chromatography on silica gel (20% EtOAc in hexanes) to give the desired product (202 mg, >99%) as a white solid: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 3.06 (t, $J = 4.6$ Hz, 4H), 3.78 (s, 3H), 3.86 (t, $J = 4.6$ Hz, 4H), 6.83–6.92 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 50.8, 55.5, 67.0, 114.5, 117.8, 145.6, 153.9.

***N*-Methyl-*N*-phenyl-*p*-anisidine**⁸ (Table 4, Entry 12). Method A of the general procedure was followed with *p*-bromoanisole (187 mg, 1.00 mmol) and *N*-methylaniline (113 mg, 1.05 mmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (199 mg, 93%) as a colorless oil.

***N,N*-Diphenyl-*p*-anisidine**²¹ (Table 4, Entry 13). Method B of the general procedure was followed with *p*-bromoanisole (186 mg, 1.00 mmol) and diphenylamine (177 mg, 1.04 mmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (272 mg, 99%) as a white solid: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 3.80 (s, 3H), 6.84 (d, $J = 9.0$ Hz, 2H), 6.94 (t, $J = 7.6$ Hz, 2H), 7.03 (d, $J = 8.4$ Hz, 4H), 7.07 (d, $J = 9.0$ Hz,

2H), 7.21 (dd, $J = 7.6, 8.4$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.5, 114.7, 121.8, 122.8, 127.3, 129.0, 140.7, 148.1, 156.1.

***N*-Phenyl-*p*-anisidine**²⁵ (Table 4, Entry 14). Method A of the general procedure was followed with *p*-bromoanisole (192 mg, 1.03 mmol) and aniline (99 mg, 1.06 mmol). The reaction mixture was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give the desired product (184 mg, 90%) as a white solid: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 3.80 (s, 3H), 5.50 (br s, 1H), 6.80–6.89 (m, 3H), 6.91 (d, $J = 8.4$ Hz, 2H), 7.07 (d, $J = 8.4$ Hz, 2H), 7.21 (dd, $J = 7.4, 8.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.6, 114.6, 115.6, 119.5, 122.2, 129.3, 135.6, 145.1, 155.2.

Methyl 4-(*N*-phenylamino)benzoate¹⁴ (Table 4, Entry 15). Method C of the general procedure was followed with methyl *p*-bromobenzoate (170 mg, 1.00 mmol) and aniline (99 mg, 1.06 mmol). The reaction mixture was purified by flash column chromatography on silica gel (20% EtOAc in hexanes) to give the desired product (209 mg, 92%) as a white solid.

4-(*N*-Phenylamino)benzonitrile¹⁸ (Table 4, Entry 16). Method C of the general procedure was followed with *p*-bromobenzonitrile (182 mg, 1.00 mmol) and aniline (99 mg, 1.06 mmol). The reaction mixture was purified by flash column chromatography on silica gel (20% EtOAc in hexanes) to give the desired product (135 mg, 70%) as a white solid.

***N,N*-Dibutyltoluidine**¹ (Table 5, Entry 1). Method D of the general procedure was followed with *p*-chlorotoluene (100 mg, 0.79 mmol) and dibutylamine (108 mg, 0.804 mmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (141 mg, 81%) as colorless oil.

***N,N*-Dibutyltoluidine**¹ (Table 5, Entry 2). Method E of the general procedure was followed with *p*-chlorotoluene (102 mg, 0.80 mmol) and dibutylamine (108 mg, 0.804 mmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (145 mg, 82%) as colorless oil.

***N*-Hexyl-*o*-toluidine** (Table 5, Entry 3). Method D of the general procedure was followed with *o*-chlorotoluene (100 mg, 0.79 mmol), hexylamine (96 mg, 0.95 mmol), $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$ (8.2 mg, 16 μmol), and cetyltrimethylammonium bromide (2.9 mg, 8 μmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (138 mg, 91%) as colorless oil.

***N*-Hexyl-*o*-toluidine** (Table 5, Entry 4). Method E of the general procedure was followed with *o*-chlorotoluene (108 mg, 0.86 mmol), hexylamine (104 mg, 1.00 mmol), $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$ (8.2 mg, 16 μmol), and cetyltrimethylammonium bromide (2.9 mg, 8 μmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (151 mg, 92%) as colorless oil.

***N*-Methyl-*N*-phenyl-*p*-anisidine**⁸ (Table 5, Entry 5). Method D of the general procedure was followed with *p*-chloroanisole (114 mg, 0.80 mmol) and *N*-methylaniline (90 mg, 0.84 mmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (156 mg, 92%) as colorless oil.

***N*-Methyl-*N*-phenyl-*p*-anisidine⁸ (Table 5, Entry 6).** Method E of the general procedure was followed with *p*-chloroanisole (114 mg, 0.80 mmol) and *N*-methylaniline (90 mg, 0.84 mmol). The reaction mixture was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give the desired product (157 mg, 92%) as colorless oil.

***N,N*-Dibutyl-4-nitroaniline⁹ (Table 5, Entry 7).** Method D of the general procedure was followed with 1-chloro-4-nitrobenzene (158 mg, 1.00 mmol), dibutylamine (136 mg, 1.04 mmol), Pd[P(*t*-Bu)₃]₂ (5.1 mg, 10 μmol), cetyltrimethylammonium bromide (1.8 mg, 5 μmol), KOH 45wt% water solution (191 μl, KOH 1.5 mmol, H₂O 5.8 mmol) and toluene (1 ml). The reaction mixture was purified by flash column chromatography on silica gel (10% EtOAc in hexanes) to give the desired product (247 mg, 97%) as orange oil.

***N,N*-Dibutyl-4-nitroaniline⁹ (Table 5, Entry 8).** Method E of the general procedure was followed with 1-chloro-4-nitrobenzene (157 mg, 1.00 mmol), dibutylamine (136 mg, 1.04 mmol), Pd[P(*t*-Bu)₃]₂ (5.1 mg, 10 μmol), cetyltrimethylammonium bromide (1.8 mg, 5 μmol), KOH 45wt% water solution (111 μl, NaOH 1.5 mmol, H₂O 3.3 mmol) and toluene (1 ml). The reaction mixture was purified by flash column chromatography on silica gel (10% EtOAc in hexanes) to give the desired product (239 mg, 93%) as orange oil.

Methyl 4-(*N,N*-Diphenylamino)benzoate¹⁴ (Table 5, Entry 9). Method D of the general procedure was followed with methyl 4-chlorobenzoate (135 mg, 0.79 mmol) and *N*-Phenylaniline (140 mg, 0.84 mmol). The reaction mixture was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give the desired product (233 mg, 97%) as a white solid: ¹H NMR (400 MHz, CDCl₃, TMS) δ 3.86 (s, 3H), 6.98 (d, *J* = 8.9 Hz, 2H), 7.08 - 7.15 (m, 6H), 7.29 (t, *J* = 7.6 Hz, 4H), 7.85 (d, *J* = 8.9 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 51.7, 120.0, 122.1, 124.4, 125.7, 129.5, 130.8, 146.6, 151.9, 166.7.

Methyl 4-(*N,N*-Diphenylamino)benzoate¹⁴ (Table 5, Entry 10). Method E of the general procedure was followed with methyl 4-chlorobenzoate (135 mg, 0.79 mmol) and *N*-Phenylaniline (140 mg, 0.84 mmol). The reaction mixture was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give the desired product (217 mg, 90%) as a white solid.

Methyl 4-(*N*-phenylamino)benzoate²⁶ (Table 5, Entry 11). Method E of the general procedure was followed with methyl 4-chlorobenzoate (88 mg, 0.51 mmol), aniline (50 mg, 0.54 mmol), Pd[P(*t*-Bu)₃]₂ (2.6 mg, 5 μmol), cetyltrimethylammonium bromide (0.9 mg, 3 μmol), NaOH 50wt% water solution (62 μl, NaOH 0.77 mmol, H₂O 1.7 mmol) and toluene 0.5 mL. The reaction mixture was purified by flash column chromatography on silica gel (20% EtOAc in hexanes) to give the desired product (105 mg, 90%) as a white solid.

***N*-(4-Acetylphenyl)morpholine¹⁵ (Table 5, Entry 12).** Method D of the general procedure was followed with methyl 4-chlorobenzoate (105 mg, 0.68 mmol), morpholine (62 mg, 0.72 mmol), Pd[P(*t*-Bu)₃]₂ (3.6 mg, 7 μmol), cetyltrimethylammonium bromide (1.3 mg, 4 μmol), KOH 45wt% water solution (127 μl, KOH 1.0 mmol, H₂O 3.9 mmol) and toluene (0.7 ml). The reaction mixture was purified by flash column chromatography on silica gel (50% EtOAc in hexanes) to give the desired product (115 mg, 86%) as pale yellow solid.

***N*-(4-Acetylphenyl)morpholine¹⁵ (Table 5, Entry 13).** Method E of the general procedure was followed with methyl 4-chlorobenzoate (123 mg, 0.80 mmol), and morpholine (73 mg, 0.84 mmol). The reaction mixture was purified by flash column chromatography on silica gel (50% EtOAc in hexanes) to give the desired product (130 mg, 84%) as pale yellow solid.

References:

- 1) Watanabe, Y.; Tsuji, Y.; Ige, H.; Ohsugi, Y.; Ohta, T. *J. Org. Chem.* **1984**, *49*, 3359–3363.
- 2) Tsuji, Y.; Huh, K. T.; Ohsugi, Y.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 1365–1370.
- 3) Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 1133–1135.
- 4) Marsden, R. J. B. *J. Chem. Soc.* **1937**, 627.
- 5) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217–7218.
- 6) Nelson, R. F.; Adams, R. N. *J. Am. Chem. Soc.* **1968**, *90*, 3925–3930.
- 7) Ullmann, F. *Ann. Chem.* **1907**, *355*, 312–358.
- 8) Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6054–6058.
- 9) Mansour, G.; Creedon, W.; Dorrestein, P. C.; Maxka, J.; MacDonald, J. C.; Helburn, R. *J. Org. Chem.* **2001**, *66*, 4050–4054.
- 10) Kremer, C. B.; Meltsner, M.; Greenstein, L. *J. Am. Chem. Soc.* **1939**, *61*, 2552.
- 11) Pachter, I. J.; Kloetzel, M. C. *J. Am. Chem. Soc.* **1952**, *74*, 1321–1322.
- 12) Herz, R. *Ber.* **1890**, *23*, 2536–2542.
- 13) Goldberg, I. *Ber.* **1907**, *40*, 4541–4546.
- 14) Gilman, H.; Brown, G. F. *J. Am. Chem. Soc.* **1940**, *62*, 3208–3210.
- 15) Kotsuki, H.; Kobayashi, S.; Matsumoto, K.; Suenaga, H.; Nishizawa, H. *Synthesis* **1990**, 1147–1148.
- 16) Nelen, M. I.; Eliseev, A. V. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1359–1364.
- 17) Itier, J.; Casadevall, A. *Bull. Soc. Chim. Fr.* **1969**, *7*, 2342.
- 18) Takeuchi, H.; Takano, K. *J. Chem. Soc., Perkin Trans. 1* **1986**, 611–618.
- 19) Watanabe, Y.; Suzuki, N.; Tsuji, Y.; Shim, S. C.; Mitsudo, T.-a. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1116–1120.
- 20) Ishikawa, T.; Uedo, E.; Tani, R.; Saito, S. *J. Org. Chem.* **2001**, *66*, 186–191.
- 21) Paine, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1496–1502.
- 22) Gaylord, N. G. *J. Org. Chem.* **1960**, *25*, 1874–1876.
- 23) Hickinbottom, W. J. *J. Chem. Soc.* **1937**, 1119–1125.
- 24) Freeman, H. S.; Butler, J. R.; Freedman, L. D. *J. Org. Chem.* **1978**, *43*, 4975–4978.
- 25) Willstatter, R.; Kubli, H. *Ber.* **1909**, *42*, 4135–4151.
- 26) Creason, S. C.; Wheeler, J.; Nelson, R. F. *J. Org. Chem.* **1972**, *37*, 4440–4446.