Arylation of Diarylamines Catalyzed by Ni(II)–PPh₃ System

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Supporting Information

General Considerations. All reactions were carried out under a nitrogen atmosphere in oven-dried glassware. THF, ether and toluene were dried over Na/benzophenone and distilled before use. Ethyl bromide was distilled from CaH₂. Magnesium powder (99.5%), diarylamines (>98%), aryl halides (>98%), triphenylphosphine (99%), 1,5-cyclooctadiene (COD, 99%) and triethylphosphite (98%) were commercially available and used without further purification. The Ni pre-catalysts were synthesized according to the known common procedure. All yields refer to the isolated yields (average of two run) of compounds estimated to be >95% pure as determined by ¹H NMR.

General Procedure: To an oven-dried 100-mL three-necked flask charged with pre-prepared ethylmagnesium bromide (13.5 mmol in 5 mL THF) was added dropwise under nitrogen at room temperature a solution of the diarylamine (12.5 mmol in 5 mL of THF). Then the solvent THF in the mixture was utterly removed on vacuum and replaced under nitrogen with dried toluene (20 mL). After successive addition of NiCl₂(PPh₃)₂ (5 mol%, relative to the amount of the used aryl halide), PPh₃ (10 mol%) and the aryl halide (10.0 mmol), the reaction mixture was heated at 80–100 °C for 3–5 hours (at 100 °C for 5 h for aryl bromides and at 80 °C for 3 h for aryl iodides), and then was cooled to room temperature, quenched with H₂O (20 mL), and filtered through a pad of silica. The organic layer was separated, and the aqueous phase extracted with ether (50 mL×2), and then the combined organic phase was dried over anhydrous Na₂SO₄ and filtered. The obtained filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (60–90 °C petroleum ether) to give the desired product.

Varied Procedure for General Procedure at the Use of a Co-solvent of THF-Toluene: To an oven-dried 100-mL three-necked flask charged with pre-prepared ethylmagnesium bromide (13.5 mmol in 5 mL THF) was added dropwise under nitrogen at room temperature a solution of the diarylamine (12.5 mmol in 3 mL of THF). Then 24 mL dried toluene was added. After successive addition of NiCl₂(PPh₃)₂ (5 mol%, relative to the amount of the used aryl halide), PPh₃ (10 mol%) and the aryl halide (10.0 mmol), the reaction mixture was heated at 80–90 °C for 3–5 hours (at 90 °C for 5 h for aryl bromides and at 80 °C for 3 h for aryl iodides), and then was cooled to room temperature. Workup proceeded as before.

Triphenylamine. According to the general procedure, ethylmagnesium bromide (13.5 mmol in 5 mL THF), diphenylamine (2.11 g, 12.5 mmol), bromobenzene (1.57 g, 10 mmol), NiCl₂(PPh₃)₂ (0.33 g, 5 mol%) and PPh₃ (0.26 g, 10 mol%) was transformed into the product (entry 1) as white solid (2.20 g, 90%); mp 127–128 °C (lit.¹ mp 127 °C). EI-MS: m/z 245 (M⁺, 100%). ¹H NMR (CDCl₃, 300 MHz): 7.01 (t, *J* = 7.2 Hz, 3 H), 7.09 (d, *J* = 7.8 Hz, 6 H), 7.20–7.30 (m, 6 H). CAS Registry No.: 603-34-9.

A similar reaction using iodobenzene (2.04 g, 10 mmol) afforded the product (entry 7) (2.36 g, 96%).

According to the varied procedure, ethylmagnesium bromide (13.5 mmol in 5 mL THF), diphenylamine (2.11 g, 12.5 mmol), bromobenzene (1.57 g, 10 mmol), NiCl₂(PPh₃)₂ (0.33 g, 5 mol%) and PPh₃ (0.26 g, 10 mol%) was transformed into the product (entry 1) as white solid

(2.15 g, 88%).

A similar reaction using iodobenzene (2.04 g, 10 mmol) afforded the product (entry 7)(2.34g, 96%).

Diphenyl(*o*-tolyl)amine. According to the general procedure, ethylmagnesium bromide (13.5 mmol in 5 mL THF), diphenylamine (2.11 g, 12.5 mmol), *o*-bromotoluene (1.71 g, 10 mmol), NiCl₂(PPh₃)₂ (0.33 g, 5 mol%) and PPh₃ (0.26 g, 10 mol%) was transformed into the product (entry 2) as white solid (2.35 g, 91%): mp 55–56 °C (lit.² mp 56–58 °C). EI-MS: m/z 259 (M⁺, 100%). ¹H NMR (CDCl₃, 300 MHz): 2.04 (s, 3 H), 6.93 (t, *J* = 7.5 Hz, 3 H), 6.98 (d, *J* = 7.8 Hz, 4 H), 7.10–7.25 (m, 8 H). CAS Registry No.: 4316-55-6.

Diphenyl(*m*-tolyl)amine. According to the general procedure, ethylmagnesium bromide (13.5 mmol in 5 mL THF), diphenylamine (2.11 g, 12.5 mmol), *m*-bromotoluene (1.71 g, 10 mmol), NiCl₂(PPh₃)₂ (0.33 g, 5 mol%) and PPh₃ (0.26 g, 10 mol%) was transformed into the product (entry 3) as white solid (1.99 g, 77%): mp 69–71 °C (lit.³ mp 69.5–70.5 °C). EI-MS: m/z 259 (M⁺, 100%). ¹H NMR (CDCl₃, 400 MHz): 2.28 (s, 3 H), 6.85 (d, *J* = 7.6 Hz, 1 H), 6.90 (d, *J* = 8.0 Hz, 1 H), 6.94 (s, 1 H), 7.01 (t, *J* = 7.2 Hz, 2 H), 7.09 (d, *J* = 7.6 Hz, 4 H), 7.15 (t, *J* = 7.6 Hz, 1 H), 7.26 (t, *J* = 7.6 Hz, 4 H). CAS Registry No.: 4316-54-5.

Diphenyl(*p*-tolyl)amine. According to the general procedure, ethylmagnesium bromide (13.5 mmol in 5 mL THF), diphenylamine (2.11 g, 12.5 mmol), *p*-bromotoluene (1.71g, 10 mmol), NiCl₂(PPh₃)₂ (0.33 g, 5 mol%) and PPh₃ (0.26 g, 10 mol%) was transformed into the product (entry 4) as white solid (1.83 g, 71%): mp 69–70 °C (lit.⁴ mp 68.8 °C). EI-MS: m/z 259 (M⁺, 100%). ¹H NMR (CDCl₃, 400 MHz): 2.38 (s, 3 H), 7.03 (t, *J* = 7.4 Hz, 2 H), 7.06 (d, *J* = 8.8 Hz, 2 H), 7.10–7.15(m, 6 H), 7.28 (t, *J* = 8.2 Hz, 4H). CAS Registry No.: 4316-53-4.

A similar reaction using *p*-iodotoluene (2.18 g, 10 mmol) afforded the product (entry 8) (2.29 g, 88%).

According to the varied procedure, ethylmagnesium bromide (13.5 mmol in 5 mL THF), diphenylamine (2.11 g, 12.5 mmol), *p*-bromotoluene (1.71g, 10 mmol), NiCl₂(PPh₃)₂ (0.33 g, 5 mol%) and PPh₃ (0.26 g, 10 mol%) was transformed into the product (entry 4) as white solid (1.73 g, 67%).

Diphenyl(1-naphthyl)amine. According to the general procedure, ethylmagnesium bromide (13.5 mmol in 5 mL THF), diphenylamine (2.11 g, 12.5 mmol), α -bromonaphthene (2.07 g, 10 mmol), NiCl₂(PPh₃)₂ (0.33 g, 5 mol%) and PPh₃ (0.26 g, 10 mol%) was transformed into the product (chromatographed on neutral aluminum oxide with 60–90 °C petroleum ether and recrystallized from ethanol) (entry 5) as white solid (2.68g, 91%): mp 136–137 °C (lit.⁵ mp 137.5–138.5 °C). EI-MS: m/z 295 (M⁺, 100%). ¹H NMR (CDCl₃, 300 MHz): 6.92 (t, *J* = 7.2 Hz, 2 H), 7.02 (d, *J* = 10.8 Hz, 4 H), 7.19 (t, *J* = 7.7 Hz, 4 H), 7.31–7.49 (m, 4 H), 7.76 (d, *J* = 8.1 Hz, 1 H), 7.87 (d, *J* = 9.3 Hz, 1 H), 7.93 (d, *J* = 8.4 Hz, 1 H). CAS Registry No.: 61231-45-6.

A similar reaction using iodobenzene (2.04 g, 10 mmol) and N-phenyl-1-naphthylamine (2.74 g, 12.5 mmol) afforded the product (entry 13) (0.38 g, 13%).

(4-Chlorophenyl)diphenylamine. According to the general procedure, ethylmagnesium bromide (54 mmol in 20 mL THF), diphenylamine (8.46 g, 50 mmol), 4-bromo-1-chlorobenzene (7.66 g, 40 mmol), NiCl₂(PPh₃)₂ (1.32 g, 5 mol%) and PPh₃ (1.04 g, 10 mol%) was transformed into the product (entry 6) as white solid (8.15 g, 73%): mp 102–104 °C (lit.⁶ mp 103–104.5 °C). EI-MS: m/z 279 (M⁺, 100%), 281 (M⁺+2, 34%). ¹H NMR (CDCl₃, 400 MHz): 6.99 (d, *J* = 8.8 Hz, 2 H), 7.02 (t, *J* = 7.2 Hz, 2 H), 7.05 (d, *J* = 8.4 Hz, 4 H), 7.17 (d, *J* = 8.8 Hz, 2 H), 7.24 (t, *J* = 7.8 Hz, 4H). CAS Registry No.: 4316-56-7.

(4-Methoxyphenyl)diphenylamine. According to the general procedure, ethylmagnesium bromide (13.5 mmol in 5 mL THF), diphenylamine (2.11 g, 12.5 mmol), 4-iodoanisole (2.34 g, 10 mmol), NiCl₂(PPh₃)₂ (0.33 g, 5 mol%) and PPh₃ (0.26 g, 10 mol%) was transformed into

the product (chromatographed with 2% ethyl acetate in hexane) (entry 9) as white solid (2.15 g, 78%): mp 98–100 °C (lit.⁷ mp 102 °C). EI-MS: m/z 275(M⁺, 100%). ¹H NMR (CDCl₃, 300 MHz): 3.80 (s, 3 H), 6.84 (d, *J* = 8.7 Hz, 2 H), 6.94 (t, *J* = 7.2 Hz, 2 H), 7.00–7.10 (m, 6 H), 7.21 (t, *J* = 7.6 Hz, 4 H). CAS Registry No.: 4316-51-2.

Di(*p*-tolyl)phenylamine. According to the general procedure, ethylmagnesium bromide (13.5 mmol in 5 mL THF), 4,4'-dimethyldiphenylamine (2.47 g, 12.5 mmol), bromobenzene (1.57 g, 10 mmol), NiCl₂(PPh₃)₂ (0.33 g, 5 mol%) and PPh₃ (0.26 g, 10 mol%) was transformed into the product (entry 10) as white solid (2.08 g, 76%): mp 105–107 °C (lit.⁵ mp 107–108 °C). EI-MS: m/z 273 (M⁺, 100%). ¹H NMR (CDCl₃, 300 MHz): 2.30 (s, 6 H), 6.90–7.09 (m, 11 H), 7.19 (t, *J* = 7.7 Hz, 2 H). CAS Registry No.: 20440-95-3.

A similar reaction using iodobenzene (2.04 g, 10 mmol) afforded the product (entry 11) (2.33 g, 84%).

Diphenyl(2-naphthyl)amine. According to the general procedure, ethylmagnesium bromide (54 mmol in 20 mL THF), N-phenyl-2-naphthylamine (10.96 g, 50 mmol), iodobenzene (8.16 g, 40 mmol), NiCl₂(PPh₃)₂ (1.32 g, 5 mol%) and PPh₃ (1.04 g, 10 mol%) was transformed into the product (chromatographed on neutral aluminum oxide with 60–90 °C petroleum ether, and recrystallized from ethanol) (entry 10) as white solid (6.85 g, 58%): mp 118–120 °C (lit.⁵ mp 120–121 °C). EI-MS: m/z 295(M⁺, 100%); ¹H NMR (CDCl₃, 400 MHz): 7.05 (t, *J* = 7.4 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 4 H), 7.24–7.44 (m, 8 H), 7.59 (d, *J* = 8.0 Hz, 1 H), 7.02 (d, *J* = 8.8 Hz, 1 H), 7.75 (d, *J* = 7.6 Hz, 1 H).

N,N,N',N'-tetraphenyl-1,1'-biphenyl-4,4'-diamine (TPB). According to the general procedure, ethylmagnesium bromide (24 mmol in 10 mL of THF), diphenylamine (3.73 g, 22 mmol, in 10 mL of THF), 4,4'-diiodo-biphenyl (4.06 g, 10 mmol), NiCl₂(PPh₃)₂ (0.65 g, 10 mol%) and PPh₃ (0.53 g, 20 mol%) was transformed into the product (recrystallized from toluene and 60–90 °C petroleum ether) (entry 14) as pale yellow solid (3.78 g, 77%): mp 224–225 °C (lit.⁵ mp 224–225 °C). EI-MS: m/z 488 (M⁺, 100%). ¹H NMR (CDCl₃, 400 MHz): 7.03 (t, *J* = 7.2 Hz, 4 H), 7.10–7.15 (m, 12 H), 7.27 (t, *J* = 7.8 Hz, 8 H), 7.45 (d, *J* = 8.8 Hz, 4 H). CAS Registry No.: 15546-43-7.

N,N,N',N'-tetraphenyl-1,4-phenylenediamine (DDP). According to the general procedure, ethylmagnesium bromide (24 mmol in 10 mL of THF), diphenylamine (3.73 g, 22 mmol, in 10 mL of THF), *p*-dibromobenzene (2.36 g, 10 mmol), NiCl₂(PPh₃)₂ (0.65 g, 10 mol%) and PPh₃ (0.53 g, 20 mol%) was transformed into the product (chromatographed with 30% toluene in hexane, and recrystallized from ethyl acetate) (entry 15) as white solid (2.64 g, 64%): mp 202–204 °C (lit.⁸ mp 201 °C). EI-MS: m/z 412 (M⁺, 100%). ¹H NMR (C₆D₆, 300 MHz): 6.86 (t, *J* = 7.1 Hz, 4 H), 7.0 (s, 4 H), 7.08 (t, *J* = 7.7 Hz, 8 H), 7.16 (d, *J* = 8.1 Hz, 8 H). CAS Registry No.: 14118-16-2.

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