Supporting Information

Triazole-Based Monophosphine Ligands for Palladium Catalyzed Cross-Coupling Reactions of Aryl Chlorides

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General Methods. All reactions and manipulations were performed in a nitrogen-filled glove-box or under nitrogen using standard Schlenk techniques, unless otherwise noted. Column chromatography was performed using Sorbent silica gel 60 Å (230×450 mesh). Chemical shifts were reported in ppm downfield to tetramethylsilane with the solvent resonance as the internal standard. MS spectra were recorded on a KRATOS MS 9/50 mass spectrometer for LR-ESI and HR-ESI.

1,5-Diphenyl-1H-[1,2,3]triazole (6a). To a solution of EtMgBr in THF (1.0 M, 11.9 mL) was added phenylacetylene (1.3 mL, 11.9 mmol) at rt. The reaction mixture was heated to 50 °C for 15 min. After cooling the mixture to rt, a solution of phenylazide (1.41 g, 11.9 mmol) in THF (4 mL) was added. The resulting solution was stirred at rt for 30 min, and then heated to 50 °C for 1 h before quenching with saturated NH₄Cl (10 mL). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (10 mL × 3). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **6a** as a white solid (1.98 g, 75%). ¹H NMR (CDCl₃, 300 MHz) δ 7.86 (s, 1H), 7.44-7.30 (m, 8H), 7.23-7.20 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 137.6, 136.5, 133.4, 129.3, 129.2, 128.8, 128.5, 126.7, 125.1.

1-Phenyl-5-(1-naphthyl)-1H-[1,2,3]triazole (6b). To a solution of EtMgBr in THF (3.0 M, 2.5 mL) was added 1-naphthlyne (1.12 g, 7.36 mmol) at rt. The reaction mixture was heated to 50 °C for 15 min. After cooling the mixture to rt, a solution of phenylazide (0.88 g, 7.36 mmol) in THF (4 mL) was added. The resulting solution was stirred at rt for 30 min, and then heated to 50 °C for 1 h before quenching with saturated NH₄Cl (10 mL). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (10 mL × 3). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **6b** as a white solid (1.16 g, 58%). ¹H

NMR (CDCl₃, 360 MHz) δ 7.98 (s, 1H), 7.94 (t, J = 9.2 Hz, 3H), 7.67 (d, J = 8.3 Hz, 1H), 7.56-7.46 (m, 3H), 7.35-7.24 (m, 6H); ¹³C NMR (CDCl₃, 90 MHz) δ 136.6, 135.7, 135.4, 133.6, 131.7, 130.2, 129.2, 129.0, 128.8, 128.6, 127.2, 126.6, 125.1, 124.8, 124.6, 124.1; HRMS (ESI+) calcd. for C₁₈H₁₄N₃ (MH⁺) 272.1188, found 272.1182.

1-Phenyl-5-(2-methoxyphenyl)-1H-[1,2,3]triazole (6c). To a solution of EtMgBr in THF (3.0 M, 2.3 mL) was added 2-methoxyphenylacetylene (0.92 g, 6.96 mmol) at rt. The reaction mixture was heated to 50 °C for 15 min. After cooling the mixture to rt, a solution of phenylazide (0.83 g, 6.96 mmol) in THF (4 mL) was added. The resulting solution was stirred at rt for 30 min, and then heated to 50 °C for 1 h before quenching with saturated NH₄Cl (10 mL). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (10 mL $\times$ 3). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **6c** as a white solid (1.45 g, 83%). ¹H NMR (CDCl₃, 300 MHz) δ 7.85 (s, 1H), 7.44-7.33 (m, 6H), 7.01(t, J = 7.5 Hz, 1H), 6.87 (d, J = 8.3 Hz, 1H) 3.44 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 156.9, 138.1, 135.1, 134.9, 131.7, 131.4, 129.4, 129.0, 124.2, 121.2, 116.6, 111.8, 55.3; HRMS (ESI+) calcd. for C₁₅H₁₄N₃O (MH⁺) 252.1137, found 252.1127.

1-Phenyl-5-(2,N,N-dimethylphenyl)-1H-[1,2,3]triazole (6d). To a solution of EtMgBr in THF (3.0 M, 2.3 mL) was added 2-N,N-dimethylphenylacetylene (1.01 g, 6.96 mmol) at rt. The reaction mixture was heated to 50 °C for 15 min. After cooling the mixture to rt, a solution of phenylazide (0.83 g, 6.96 mmol) in THF (4 mL) was added. The resulting solution was stirred at rt for 30 min, and then heated to 50 °C for 1 h before quenching with saturated NH₄Cl (10 mL). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (10 mL $\times$ 3). The combined organic layers were dried over Na₂SO₄ and concentrated

under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **6d** as a yellow solid (1.12 g, 61%). ¹H NMR (300 MHz, CDCl₃) δ 7.87 (s, 1H), 7.25-7.35 (m, 7H), 7.02-7.05 (m, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 2.19 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 151.5, 137.8, 137.1, 133.6, 131.4, 130.6, 128.6, 128.2, 122.7, 119.8, 118.8, 41.9; HRMS (ESI+) calcd. for C₁₆H₁₇N₄ (MH⁺) 265.1453, found 265.1444.

1-Phenyl-5-(2,6-dimethoxyphenyl)-1H-[1,2,3]triazole (6e). To a solution of EtMgBr in THF (3.0 M, 2.3 mL) was added 2,6-dimethoxyphenylacetylene (0.95 g, 6.96 mmol) at rt. The reaction mixture was heated to 50 °C for 15 min. After cooling the mixture to rt, a solution of phenylazide (0.83 g, 6.96 mmol) in THF (4 mL) was added. The resulting solution was stirred at rt for 30 min, and then heated to 50 °C for 1 h before quenching with saturated NH₄Cl (10 mL). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (10 mL × 3). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **6e** as a white solid (1.39 g, 78%). ¹H NMR (300 MHz, CDCl₃) δ 7.76 (s, 1H), 7.27-7.33 (m, 6H), 6.49 (d, *J* = 8.4 Hz, 2H), 3.51 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 158.0, 137.7, 135.5, 131.5, 130.3, 128.6, 128.3, 123.3, 104.6, 103.7, 55.4; HRMS (ESI+) calcd. for C₁₆H₁₅N₃O₂Na (M + Na⁺) 304.1062, found 304.1063.

Phenyl-*p*-tolylamine (10a). ¹H NMR (CDCl₃, 400 MHz) δ 7.32 (t, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.10-7.06 (m, 4H), 6.97 (t, *J* = 7.2 Hz, 1H), 5.64 (br s, 1H), 2.39 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 143.9, 140.3, 130.9, 129.8, 129.3, 120.3, 118.9, 116.8, 20.7.

4-Methoxyphenyl-*p*-tolylamine (10b). ^1H NMR (300 MHz, CDCl_3) δ 7.05-7.27 (m, 4H), 6.87-6.90 (m, 4H), 5.43 (br s, 1H), 3.83 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 154.8, 142.4, 136.6, 129.8, 129.3, 121.1, 116.5, 114.6, 55.6, 20.5.

Diphenyl-*p*-tolylamine (10c). ^1H NMR (360 MHz, CDCl_3) δ 7.33-7.38 (m, 4H), 7.16-7.24 (m, 8H), 7.08-7.13 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (90 MHz, CDCl_3) δ 148.0, 145.2, 132.6, 129.9, 129.1, 124.9, 123.5, 122.2, 20.8.

Methylphenyl-*p*-tolylamine (10d). ^1H NMR (CDCl_3 , 400 MHz) δ 7.33-7.28 (m, 2H), 7.19 (d, $J = 8.2$ Hz, 2H), 7.10-7.05 (m, 2H), 7.02-6.98 (m, 2H), 6.97-6.92 (m, 1H), 3.36 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 149.3, 146.5, 132.0, 129.9, 129.0, 122.5, 119.7, 118.1, 40.3, 20.7.

4-*p*-Tolylmorpholine (10e). ^1H NMR (360 MHz, CDCl_3) δ 7.15 (d, $J = 8.2$ Hz, 2H), 6.89 (d, $J = 8.2$ Hz, 2H), 3.91 (t, $J = 4.6$ Hz, 4H), 3.15 (t, $J = 4.8$ Hz, 4H), 2.35 (s, 3H); ^{13}C NMR (90 MHz, CDCl_3) δ 149.1, 129.5, 129.3, 115.8, 66.8, 49.7, 20.3.

1-Methyl-4-*p*-tolylpiperazine (10f). ^1H NMR (360 MHz, CDCl_3) δ 7.09 (d, $J = 8.2$ Hz, 2H), 6.87 (d, $J = 8.2$ Hz, 2H), 3.18 (t, $J = 4.9$ Hz, 4H), 2.59 (t, $J = 5.0$ Hz, 4H), 2.36 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (90 MHz, CDCl_3) δ 149.3, 129.7, 129.2, 116.4, 55.2, 49.7, 46.2, 20.5.

Dibenzyl-*p*-tolylamine (10g). ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.51 (m, 10H), 7.17 (d, $J = 8.4$ Hz, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 4.78 (s, 4H),

2.43 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 147.8, 139.6, 130.5, 129.4, 127.6, 127.5, 126.5, 113.4, 55.1, 21.0.

Butyl-*p*-tolylamine (10h). ^1H NMR (300 MHz, CDCl_3) δ 7.07-7.10 (m, 2H), 6.60-6.65 (m, 2H), 3.46 (br s, 1H), 3.18 (t, $J = 4.0$ Hz, 2H), 2.34 (s, 3H), 1.65-1.71 (m, 2H), 1.48-1.56 (m, 2H), 1.06 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 146.2, 129.6, 126.1, 112.8, 44.0, 31.7, 20.3, 20.2, 13.8.

Phenyl-*o*-tolylamine (10i). ^1H NMR (CDCl_3 , 400 MHz) δ 7.30-7.23 (m, 4H), 7.18 (t, $J = 7.5$ Hz, 1H), 7.00-6.92 (m, 4H), 5.38 (br s, 1H), 2.28 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 143.9, 141.1, 130.9, 129.2, 128.3, 126.7, 122.0, 120.4, 118.8, 117.3, 17.8.

Diphenyl-*o*-tolylamine (10j). ^1H NMR (300 MHz, CDCl_3) δ 7.31-7.39 (m, 8H), 7.14-7.18 (m, 4H), 7.05-7.10 (m, 2H), 2.22 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 147.4, 145.3, 136.4, 131.6, 129.5, 129.0, 127.3, 126.0, 121.5, 121.3, 18.6.

(2,5-Dimethylphenyl)phenylamine (10k). ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.48 (m, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.11-7.15 (m, 3H), 6.99 (d, $J = 7.5$ Hz, 1H), 5.50 (br s, 1H), 2.49 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.1, 140.8, 136.3, 130.6, 129.2, 125.3, 122.8, 120.1, 119.6, 117.2, 21.0, 17.3.

(2,5-Dimethylphenyl)diphenylamine (10l). ^1H NMR (300 MHz, CDCl_3) δ 7.57-7.67 (m, 5H), 7.38-7.48 (m, 6H), 7.33-7.37 (m, 2H), 2.71 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 147.4, 145.0, 136.9, 133.2, 131.4, 130.0, 128.9, 126.9, 121.4, 121.2, 20.8, 18.1.

4-Methylbiphenyl (12a). ^1H NMR (CDCl_3 , 400 MHz) δ 7.67-7.64 (m, 2H), 7.59-7.55 (m, 2H), 7.51-7.47 (m, 2H), 7.41-7.37 (m, 1H), 7.32 (d, $J = 7.9$ Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 141.1, 138.3, 137.0, 129.5, 128.7, 127.0, 126.9, 21.1.

2-Methylbiphenyl (12b). ^1H NMR (CDCl_3 , 400 MHz) δ 7.54-7.50 (m, 2H), 7.45-7.41 (m, 3H), 7.38-7.34 (m, 4H), 2.39 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 141.95, 141.91, 135.3, 130.3, 129.8, 129.2, 128.0, 127.2, 126.7, 125.7, 20.4.

2,4-Dimethylbiphenyl (12c). ^1H NMR (CDCl_3 , 400 MHz) δ 7.50-7.46 (m, 2H), 7.42-7.40 (m, 3H), 7.25 (d, $J = 8.2$ Hz, 1H), 7.17-7.15 (m, 2H), 2.44 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 142.1, 141.7, 135.1, 132.1, 130.5, 130.2, 129.1, 128.0, 127.9, 126.6, 20.9, 19.9.

4-Methoxybiphenyl (12d). ^1H NMR (CDCl_3 , 400 MHz) δ 7.61-7.56 (m, 4H), 7.47-7.43 (m, 2H), 7.36-7.32 (m, 1H), 7.01 (dt, $J = 2.2, 8.8$ Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.1, 55.3.

4-Acetylbiphenyl (12e). ^1H NMR (CDCl_3 , 400 MHz) δ 8.04 (dd, $J = 1.6, 7.6$ Hz, 2H), 7.69 (dd, $J = 1.6, 6.9$ Hz, 2H), 7.65-7.62 (m, 2H), 7.50-7.41 (m, 3H), 2.64 (s, 3H); ^{13}C NMR (CDCl_3 , 90 MHz) δ 197.4, 145.4, 139.5, 135.6, 128.73, 128.67, 128.0, 127.0, 126.9, 26.4.

4-Nitrobiphenyl (12f). ^1H NMR (CDCl_3 , 400 MHz) δ 8.30 (dt, $J = 2.5, 9.3$ Hz, 2H), 7.74 (dt, $J = 2.0, 8.9$ Hz, 2H), 7.65-7.62 (m, 2H), 7.53-7.45 (m,

3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 147.5, 147.0, 138.7, 129.1, 128.9, 127.7, 127.3, 124.0.

4-Carbomethoxybiphenyl (12g). ^1H NMR (CDCl_3 , 400 MHz) δ 8.12 (dt, J = 1.8, 8.5 Hz, 2H), 7.69-7.62 (m, 4H), 7.50-7.46 (m, 2H), 7.43-7.39 (m, 1H), 3.95 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 166.9, 145.5, 139.9, 130.0, 128.9, 128.8, 128.1, 127.2, 127.0, 52.1.

4-Trifluoromethylbiphenyl (12h). ^1H NMR (CDCl_3 , 400 MHz) δ 7.72 (s, 4H), 7.66-7.60 (m, 2H), 7.54-7.41 (m, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 144.7, 139.8, 129.3 (q, J = 32.1 Hz), 129.0, 128.2, 127.4, 127.3, 125.7 (q, J = 3.7 Hz), 124.4 (q, J = 272 Hz).

2-Acetylbiphenyl (12i). ^1H NMR (CDCl_3 , 400 MHz) δ 7.58 (dd, J = 1.2, 7.6 Hz, 1H), 7.53 (dt, J = 1.4, 7.5 Hz, 1H), 7.47-7.35 (m, 7H), 2.03 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 204.7, 140.8, 140.6, 140.4, 130.6, 130.1, 128.8, 128.6, 127.79, 127.77, 127.4, 30.3.

2-Cyanobiphenyl (12j). ^1H NMR (CDCl_3 , 400 MHz) δ 7.77 (dd, J = 1.1, 7.7 Hz, 1H), 7.65 (dt, J = 1.3, 7.7 Hz, 1H), 7.59-7.57 (m, 2H), 7.53-7.44 (m, 5H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 145.3, 138.0, 133.6, 132.7, 130.0, 128.63, 128.60, 127.4, 118.6, 111.1.

2-Cyano-4'-methylbiphenyl (12k). ^1H NMR (CDCl_3 , 400 MHz) δ 7.76 (dd, J = 0.9, 7.8 Hz, 1H), 7.63 (dt, J = 1.3, 7.7 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.49 (d, J = 8.1 Hz, 2H), 7.42 (dt, J = 1.1, 7.6 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H),

2.43 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 145.4, 138.5, 135.1, 133.6, 132.7, 129.9, 129.3, 128.5, 127.2, 118.8, 111.0, 21.1.

2-Phenyl-pyridine (12l). ^1H NMR (CDCl_3 , 400 MHz) δ 8.71 (d, J = 4.8 Hz, 1H), 8.01 (d, J = 7.7 Hz, 2H), 7.72 (d, J = 3.3 Hz, 2H), 7.49 (t, J = 7.4 Hz, 2H), 7.42 (t, J = 7.3 Hz, 1H), 7.21 (dd, J = 4.5, 8.6 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 157.3, 149.5, 139.3, 136.6, 128.8, 128.6, 126.8, 122.0, 120.4.

2,5,2'-Trimethylbiphenyl (12m). ^1H NMR (CDCl_3 , 400 MHz) δ 7.25-7.18 (m, 3H), 7.13 (d, J = 7.7 Hz, 1H), 7.10-7.04 (m, 2H), 6.92 (s, 1H), 2.32 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 141.7, 141.4, 135.8, 134.9, 132.6, 129.9, 129.7, 129.6, 129.2, 127.8, 127.0, 125.5, 20.9, 19.8, 19.3.

2'-Methoxy-2,5-dimethylbiphenyl (12n). ^1H NMR (CDCl_3 , 400 MHz) δ 7.35 (ddd, J = 1.8, 7.5 8.2 Hz, 1H), 7.17 (dd, J = 1.6, 7.4 Hz, 2H), 7.09 (d, J = 7.7 Hz, 1H), 7.04 (d, J = 1.0 Hz, 1H), 7.01 (dd, J = 1.0, 7.4 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 3.77 (s, 3H), 2.36 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 156.5, 138.4, 134.7, 133.6, 130.93, 130.90, 130.6, 129.4, 128.4, 128.0, 120.4, 110.5, 55.3, 20.9, 19.4.

2'-Methoxy-2,6-dimethyl-biphenyl (12o). ^1H NMR (300 MHz, CDCl_3) δ 7.47-7.50 (m, 1H), 7.26-7.33 (m, 3H), 7.12-7.20 (m, 3H), 3.87 (s, 3H), 2.19 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 156.4, 138.1, 136.5, 130.6, 129.4, 128.3, 127.0, 126.9, 120.6, 110.7, 55.3, 20.4.

2,6,2'-Trimethyl-biphenyl (12p). ^1H NMR (300 MHz, CDCl_3) δ

7.39-7.45 (m, 3H), 7.26-7.36 (m, 3H), 7.17-7.20 (m, 1H), 2.15 (s, 3H), 2.13 (s, 6H);

^{13}C NMR (75 MHz, CDCl_3) δ 141.0, 140.5, 135.7, 135.5, 129.9, 128.8, 127.2, 127.0,

126.9, 126.0, 20.3, 19.4.