Supporting information

Copper-Catalyzed Arylation of Amines Using Diphenyl Pyrrolidine-2-Phosphonate as the New Ligand

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General experimental procedures

All reactions were carried out under nitrogen atmosphere. DMF was freshly distilled from CaH_2 . Proton and carbon magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded with tetramethylsilane or solvent resonance as the internal standard (^1H NMR: TMS at 0.00 ppm, CDCl_3 at 7.24 ppm; ^{13}C NMR: CDCl_3 at 77.0 ppm).

Synthesis for diphenyl pyrrolidine-2-phosphonate hydrochloride (DPP): This compound was synthesized through reaction of 1-pyrroline trimer¹ and diphenyl phosphite. A mixture of 1-pyrroline trimer (15 mmol, 3.11 g) and diphenyl phosphite (45 mmol, 10.53 g) was heated under nitrogen atmosphere to give the crude diphenyl pyrrolidine-2-phosphonate which was dissolved in 100 mL of dry diethyl ether, the resulting solution was filtered, and the filtrate was saturated with dry HCl gas. The precipitated diphenyl pyrrolidine-2-phosphonate hydrochloride was collected by filtration, washed with ether, and recrystallized from acetone² to give the pure product as a white solid.

Diphenyl pyrrolidine-2-phosphonate Hydrochloride (1).² White powder, yield 32%. mp 145-148 °C (lit.² 146-148 °C). ^{31}P NMR (D_2O , 121 MHz) δ 14.00. ^1H NMR (D_2O , 300 MHz) δ 7.32 (t, J = 7.57 Hz, 4H), 7.21 (t, J = 7.57 Hz, 2H), 7.07 (d, J = 7.22 Hz, 4H), 4.29-4.33 (m, 1H), 3.42-3.46 (m, 2H), 2.07-2.48 (m, 4H). ^{13}C NMR (D_2O , 75 MHz) δ 149.4, 130.1, 120.8, 115.6, 54.0, 51.9, 26.8, 24.3. HR-ESI-MS $[\text{M}+\text{H}]^+$ m/z Calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_3\text{P}$: 304.1103. Found: 304.1110.

Diphenylamine (3a).³ White solid, yield 57%. mp 52-53 °C (lit.^{3b} 54 °C). ¹H NMR (CDCl₃, 300 MHz) δ 7.24-7.29 (m, 4H), 7.08 (d, 4H, J = 7.57 Hz), 6.93 (t, 2H, J = 7.22 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ 143.1, 129.4, 121.2, 118.0. Positive ion ESI-MS [M+H]⁺ m/z 170.3. HR-EI-MS M⁺ m/z Calcd for C₁₂H₁₁N: 169.0891. Found: 169.0885.

N-(2-nitrophenyl)benzenamine (3b).⁴ Yellow powder, yield 75%. mp 72-74 °C (lit.^{4b} 75.5 °C). ¹H NMR (CDCl₃, 300 MHz) δ 9.50 (s, br, 1H), 8.21 (dd, 1H, J = 7.22, 1.38 Hz), 7.35-7.45 (m, 3H), 7.21-7.29 (m, 4H), 6.78 (t, 1H, J = 6.88 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ 143.1, 138.7, 135.6, 133.2, 129.7, 126.6, 125.6, 124.4, 117.5, 116.0. HR-EI-MS M⁺ m/z Calcd for C₁₂H₁₀NO₃: 214.0742. Found: 214.0749.

N-(3-nitrophenyl)benzenamine (3c).⁵ White solid, yield 73%. mp 85-87 °C (lit.⁵ 89 °C). ¹H NMR (CDCl₃, 300 MHz) δ 7.84 (s, 1H), 7.69 (d, 1H, J = 7.84 Hz), 7.29-7.38 (m, 4H), 7.14 (d, 2H, J = 8.25 Hz), 7.08 (t, 1H, J = 7.57 Hz), 5.90 (s, br, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ 145.2, 141.0, 140.0, 130.1, 129.8, 123.3, 121.9, 120.0, 114.8, 110.4. HR-EI-MS M⁺ m/z Calcd for C₁₂H₁₀N₂O₂: 214.0742. Found: 214.0747.

***N*-(4-nitrophenyl)benzenamine (3d).**⁵ Yellow powder, yield 71%. mp 132-135 °C (lit.⁵ 131 °C). ¹H NMR (CDCl₃, 300 MHz) δ 8.12 (d, 2H, J = 9.27 Hz), 7.39 (t, 2H, J = 7.56 Hz), 7.16-7.22 (m, 3H), 6.94 (d, 2H, J = 9.27 Hz), 6.37 (s, br, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ 150.3, 139.8, 139.6, 129.8, 126.3, 124.8, 122.0, 113.8. HR-EI-MS M⁺ m/z Calcd for C₁₂H₁₀N₂O₂: 214.0742. Found: 214.0746.

methyl 2-(phenylamino)benzoate (3e).⁴ White solid, yield 70%. mp 54-56 °C (lit.^{4a} 52-54 °C). ¹H NMR (CDCl₃, 600 MHz) δ 9.46 (br, 1H), 7.95 (dd, 1H, J = 8.25, 1.37 Hz), 7.33 (t, 2H, J = 7.91 Hz), 7.29 (td, 1H, J = 6.87, 1.37 Hz), 7.23-7.25 (m, 3H), 7.08 (t, 1H, J = 7.56 Hz), 6.71 (t, 1H, J = 7.56 Hz), 3.88 (s, 3H). ¹³C NMR (CDCl₃, 150 MHz) δ 169.0, 148.0, 140.9, 134.2, 131.7, 129.5, 123.7, 122.6, 117.2, 114.1, 112.0, 51.9. HR-EI-MS M⁺ m/z Calcd for C₁₄H₁₃NO₂: 227.0946. Found: 227.0952.

1-(4-phenylamino)phenyl ethanone (3f).⁶ White solid, yield 65%. mp 105-106 °C (lit.⁶ 106 °C). ¹H NMR (CDCl₃, 300 MHz) δ 7.79 (dd, 1H, J = 8.94, 1.72 Hz), 7.32 (m, 3H), 7.14 (d, 4H), 6.98 (dd, 1H, J = 8.60, 1.72 Hz), 2.52 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ 196.5, 152.1, 146.4, 129.9, 129.6, 125.9, 124.6, 119.6, 26.2. HR-EI-MS M⁺ m/z Calcd for C₁₄H₁₃NO: 211.0997. Found: 211.0992.

***N*-(2-methoxyphenyl)benzenamine (3g).**³ Yellow oil, yield 60%. ¹H NMR (CDCl₃, 300 MHz) δ 7.23 -7.28 (m, 3H), 7.13 (d, 2H, J = 7.91 Hz), 6.92 (t, 1H, J = 7.40 Hz), 6.84-6.53 (m, 3H), 6.14 (s, br, 1H), 3.85 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ 148.4, 142.9, 133.1, 129.4, 121.3, 120.9, 120.0, 118.7, 114.8, 110.7, 55.7. HR-EI-MS M⁺ m/z Calcd for C₁₃H₁₃NO: 199.0997. Found: 199.0990.

4-methoxy-*N*-(2-nitrophenyl)benzenamine (3h).⁷ Yellow solid, yield 70%. mp 87-88 °C (lit.⁷ 87-88 °C). ¹H NMR (CDCl₃, 300 MHz) δ 9.41 (s, br, 1H), 8.19 (d, 1H, J = 8.60 Hz), 7.32 (t, 1H, J = 7.91 Hz), 7.20 (d, 2H, J = 8.60 Hz), 7.00 (d, 1H, J = 8.94 Hz), 6.96 (dd, 2H, J = 8.60, 1.72 Hz), 6.71 (t, 1H, J = 7.74 Hz), 3.84 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ 157.9, 144.5, 135.7, 132.4, 131.2, 127.1, 126.6, 116.8, 115.7, 114.9, 55.5. HR-EI-MS M⁺ m/z Calcd for C₁₃H₁₂N₂O₃: 244.0848. Found: 244.0842.

***N*-(2,6-dimethylphenyl)-3-nitrobenzenamine (3i).**⁸ Yellow solid, yield 62%. mp 79-83 °C. ¹H NMR (CDCl₃, 300 MHz) δ 7.71 (d, 1H, J = 8.58 Hz), 7.21 (s, 1H), 6.99-7.08 (m, 5H), 6.40 (s, 1H), 1.98 (s, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ 158.9, 141.3, 137.6, 129.3, 128.6, 128.0, 125.6, 124.5, 124.3, 113.6, 18.3. HR-EI-MS M⁺ m/z Calcd for C₁₄H₁₄N₂O₂: 242.1055. Found: 242.1051.

***N*-(2,6-dimethylphenyl)benzenamine (3j).**⁸ Slight yellow oil, yield 66%. ¹H NMR (CDCl₃, 300 MHz) δ 7.27 (t, 2H, J = 8.08 Hz), 7.01-7.17 (m, 3H), 6.90 (d, 2H, J = 7.91Hz), 6.74 (t, 1H, J = 7.22 Hz), 2.21 (s, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ 146.3, 136.0, 129.6, 129.3, 128.6, 118.3, 117.7, 113.6, 18.5. HR-EI-MS M⁺ m/z Calcd for C₁₄H₁₅N: 197.1204. Found: 197.1211.

1-(4-(4-bromophenylamino)phenyl)ethanone (3k).⁹ White solid, yield 73%. mp 114-116 °C (lit.⁹ 114-116 °C). ¹H NMR (CDCl₃, 300 MHz) δ 7.82 (d, 2H, J = 8.60 Hz), 7.60 (d, 2H, J = 8.60Hz), 7.42 (d, 2H, J = 8.94Hz), 7.02 (d, 2H, J = 8.94 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ 196.6, 145.4, 138.8, 132.9, 131.0, 130.1, 127.1, 121.0, 117.7, 26.4. HR-EI-MS M⁺ m/z Calcd for C₁₄H₁₂BrNO: 289.0102. Found: 289.0109.

4-bromo-N-methyl-N-phenylbenzenamine (3l).¹⁰ Yellow oil, yield 60%. ¹H NMR (CDCl₃, 300 MHz) δ 7.41 (d, 2H, J = 8.94), 7.33 (dd, 2H, J = 7.89, 7.56 Hz), 7.11 (t, 1H, J = 7.56 Hz), 6.99 (d, 2H, J = 7.89 Hz), 6.87 (d, 2H, J = 8.94 Hz), 2.85 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ 156.7, 138.8, 132.8, 130.0, 120.9, 120.5, 119.1, 115.7, 41.8. HR-EI-MS M⁺ m/z Calcd for C₁₃H₁₂BrN: 261.0153. Found: 261.0149.

3m

4-phenylmorpholine (3m).⁴ White solid, yield 78%. mp 51-54 °C (lit.^{4c} 54 °C). ¹H NMR (CDCl₃, 300 MHz) δ 7.29 (t, 2H, J = 7.89 Hz), 6.88-6.96 (m, 3H), 3.88 (t, 4H, J = 4.83 Hz), 3.167 (t, 4H, J = 4.83 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ 151.2, 129.3, 120.7, 116.0, 67.0, 49.6. HR-EI-MS M⁺ m/z Calcd for C₁₀H₁₃NO: 163.0997. Found: 163.0991.

3n

4-(4-methoxyphenyl)morpholine (3n).⁸ White solid, yield 75%. mp 72-74 °C (lit.^{8b} 75 °C). ¹H NMR(CDCl₃, 300 MHz) δ 6.90 (d, 2H, J = 9.29 Hz), 6.85 (d, 2H, J = 9.29 Hz), 3.86 (t, 4H, J = 4.82 Hz), 3.77 (s, 3H), 3.06 (t, 4H, J = 4.82 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ 154.1, 145.7, 117.9, 114.6, 67.1, 55.7, 50.9. HR-EI-MS M⁺ m/z Calcd for C₁₁H₁₅NO₂: 193.1103. Found: 193.1108.

3o

N-dodecylbenzenamine (3o).¹¹ Milk-white oil, yield 73%. ¹H NMR (CDCl₃, 300 MHz) δ 7.18 (t, 2H, J = 7.54 Hz), 6.70 (t, 1H, J = 7.20 Hz), 6.62 (d, 2H, J = 7.89 Hz), 3.11 (t, 2H, J = 7.03 Hz), 1.67-1.65 (m, 2H), 1.29 (m, 18H), 0.91 (t, 3H, J = 6.00 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ 148.7, 129.3, 117.2, 112.8, 44.1, 32.1, 29.71, 29.6, 29.5, 27.3, 22.8, 14.2. HR-EI-MS M⁺ m/z Calcd for C₁₈H₃₁N: 261.2457. Found: 261.2452.

3p

N-cyclohexylbenzenamine (3p).¹² Colorless oil, yield 84%. ¹H NMR (CDCl₃, 300 MHz) δ 7.16 (t, 2H, J = 7.74 Hz), 6.67 (t, 1H, J = 7.57 Hz), 6.61 (d, 2H, J = 7.91 Hz), 3.75 (s, br, 1H), 3.25-3.28 (m, 1H), 2.03 -2.08 (m, 2H), 1.74-1.79 (m, 2H), 1.63-1.67 (m, 1H), 1.13-1.42 (m, 5H). ¹³C NMR (CDCl₃, 75 MHz) δ 147.1, 129.4, 117.2, 113.5, 52.1, 33.5, 26.0, 25.1. HR-EI-MS M⁺ m/z Calcd for C₁₂H₁₇N: 175.1361. Found: 175.1367.

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single_pulse_decoupled gated NOE

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rhb-050609-Ligand-C-single pulse_dec-2.jdr
single pulse decoupled gated NOE

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rlh-050607-4_aminophacetone-II-single_pulse-4.jdr
single_pulse

3f