

Supporting Material for:

Copper (I) 3-methylsalicylate mediates the Chan-Lam *N*-arylation of heterocycles

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Experimental.

All commercial reagents were used without purification. Melting points were determined on a Mel-Temp 3.0 melting point apparatus, and are uncorrected. TLC analysis was carried out on silica gel 60 F254 precoated aluminum sheets using UV light for detection. ¹H NMR spectra were recorded on a 400 MHz spectrometer using the indicated solvents. High resolution mass spectra were obtained from the Georgia State University Mass Spectrometry Laboratory, Atlanta, GA.

General method of *N*-arylation.

A dry flask was charged with the nitrogen containing heterocycles (1 mmol), aryl boronic acids (2.2 mmol), potassium carbonate (2 mmol) and CuMeSal (0.015 mmol) then anhydrous methanol (10 ml) was added. The reaction

mixture was stirred at 65 °C, open to air, for 3 h (5 h in case of indole and benzimidazole), cooled to room temperature, filtered, and the precipitate was washed with methanol (2 ml), the filtrate was concentrated under vacuum, then stirred with ice water (30 ml) and extracted with ethyl acetate (3 × 50 ml), dried over sodium sulfate and the solvent was removed under reduced pressure. The residue was purified by chromatography or recrystallization as indicated with each compound.

1-(4-Nitrophenyl)-1*H*-imidazole. White solid (82%) (mp 200-201 °C, Lit¹. mp 201-203 °C (Purified by crystallization from ethyl acetate/ hexanes); ¹HNMR (CDCl₃): δ = 7.28 (br s, 1H), 7.40 (br s, 1H), 7.60 (d, *J* = 8.8 Hz, 2 H), 8.01 (br s, 1H), 8.40 (d, *J* = 8.8 Hz, 2 H).

1-(2-Nitrophenyl)-1*H*-imidazole. Yellow solid (35%) (mp 96-97 °C, Lit². mp 97-98 °C (Purified by crystallization from ethyl acetate/ hexanes); ¹HNMR (DMSO-*d*₆): δ = 7.13 (s, 1H), 7.44 (s, 1H), 7.70-7.76 (m, 2 H), 7.87-7.93 (m, 2H), 8.18 (d, *J* = 8 Hz, 1 H).

1-(4-cyanophenyl)-1*H*-imidazole. Yellow solid (77%) (mp 149-150) °C, Lit³. mp 143-145 °C (Purified by crystallization from ethyl acetate/ hexanes); ¹HNMR (DMSO-*d*₆): δ = 7.16 (br s, 1H), 7.92-7.94 (m, 3H), 8.20 (d, *J* = 8.4 Hz, 2 H), 8.46 (br s, 1H).

1-(4-Methoxyphenyl)-1*H*-imidazole ¹. Colorless oil (69%), (Purified by column chromatography using ethyl acetate/ hexanes); ¹HNMR (CDCl₃): δ = 3.85 (s, 3H), 6.80 (d, *J* = 8 Hz, 1 H), 6.97-6.99 (m, 3 H), 7.29 (d, *J* = 8 Hz, 2 H), 7.38 (br s, 1H), HRMS: *m/z* calculated for C₁₀H₁₀N₂O: 175.0871, found: 175.0871 (M⁺ +1).

1-(2-Methoxyphenyl)-1*H*-imidazole ⁴. Yellow solid (24 %), mp 39-41, (to our knowledge the mp is previously unreported) (Purified by crystallization from ethyl acetate/ hexanes); ¹HNMR (DMSO-*d*₆): δ = 3.84 (s, 3H), 6.86-6.88 (m, 1 H), 7.03 (br s, 2 H), 7.11 (d, *J* = 8 Hz, 1 H), 7.34-7.36 (m, 1H), 7.56 (d, *J* = 8 Hz, 1 H), 7.66 (s, 1 H).

1-Phenyl-1*H*-imidazole ¹. Yellow oil (71%), (Purified by column chromatography using ethyl acetate/ hexanes); ¹HNMR (CDCl₃): δ = 7.36 (d, *J* = 7.6 Hz, 2 H), 7.42-7.43 (m, 3 H), 7.49-7.51 (m, 3 H), HRMS: *m/z* calculated for C₉H₉N₂: 145.0766, found: 145.0766 (M⁺ +1).

1-(4-Nitrophenyl)-1*H*-pyrazole . White solid (78 %), mp 188-189 °C , Lit ⁵. mp 176-178 °C (Purified by crystallization from ethyl acetate/ hexanes); ¹HNMR (CDCl₃): δ = 6.75 (br s, 1H), 7.18 (br s, 1H), 7.90 (d, *J* = 8.8 Hz, 2 H), 8.05 (br s, 1H), 8.35 (d, *J* = 8.8 Hz, 2 H),

1-(4-Methoxyphenyl)-1H-pyrazole. Brown solid (74%), mp 38-40 °C, Lit¹ mp 33-35°C. (Purified by crystallization from ethyl acetate/ hexanes and then washing the residue with diethyl ether); ¹HNMR (CDCl₃): δ = 3.76 (s, 3H), 6.38 (br s, 1H), 6.91 (d, *J* = 8.4 Hz, 2 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 7.64 (br s, 1H), 7.78 (br s, 1H),

1-(4-Nitrophenyl)-1H-1,2,4-triazole. Yellow solid (84 %), mp 172-173 °C, Lit⁶. 170-173 °C. (Purified by crystallization from ethyl acetate/ hexanes); ¹HNMR (CDCl₃): δ = 7.90 (d, *J* = 8.8 Hz, 2 H), 8.06 (br s, 1H), 8.34 (d, *J* = 8.8 Hz, 2 H), 8.77 (br s, 1H).

1-(4-Methoxyphenyl)-1H-1,2,4-triazole. Yellow solid (77 %), mp 70-71 °C, Lit⁷. 71 °C. (Purified by crystallization from ethyl acetate/ hexanes and then washing the residue with diethyl ether); ¹HNMR (CDCl₃): δ = 3.75 (s, 3H), 6.99 (d, *J* = 8.8 Hz, 2 H), 7.55 (d, *J* = 8.8 Hz, 2 H), 8.05 (s, 1 H), 8.45 (s, 1H).

1-(4-Nitrophenyl)-1H-benzimidazole. White solid (75 %), mp 187-188 °C, Lit⁸. mp 181-183 °C (purified by crystallization from ethyl acetate/ hexanes); ¹HNMR (DMSO-*d*₆): δ = 7.37-7.40 (m, 2 H), 7.78 (d, *J* = 8 Hz, 1 H), 7.82 (d, *J* = 8 Hz, 1 H), 8.03 (d, *J* = 9.2 Hz, 2 H), 8.46 (d, *J* = 9.2 Hz, 2 H), 8.75 (s, 1 H).

1-(4-Methoxyphenyl)-1H-benzimidazole. White solid (65 %), mp 95-96°C, Lit². mp 99-100 °C (purified by crystallization from ethyl acetate/ hexanes); ¹HNMR (DMSO-*d*₆): δ = 3.86 (s, 3H), 7.16-7.18 (m, 2 H), 7.29-7.30, (m, 2H), 7.50 (br s, 1 H), 7.57 (d, *J* = 7.2 Hz, 2 H), 7.77 (br s, 1 H), 8.42 (s, 1 H).

1-(4-Nitrophenyl)-1H-indole. White solid (72 %), mp 129-130 °C, Lit⁹. mp 128-129 °C (Purified by crystallization from ethyl acetate/ hexanes); ¹HNMR (DMSO-*d*₆): δ = 6.38 (s, 1H), 7.22 (d, *J* = 7.6 Hz, 1 H), 7.29-7.30 (m, 2 H), 7.70 (d, *J* = 8 Hz, 1 H), 7.77 (d, *J* = 8 Hz, 1 H), 7.94 (d, *J* = 8.4 Hz, 2 H) 8.41 (d, *J* = 8.4 Hz, 2 H).

1-(4-Methoxyphenyl)-1H-indole. Yellow solid (67 %), mp 55-56 °C, Lit¹⁰. mp 56-57 °C (purified by crystallization from ethyl acetate/ hexanes); ¹HNMR (DMSO-*d*₆): δ = 3.72 (s, 3H), 6.30 (br s, 1H), 6.80 (d, *J* = 8.8 Hz, 2 H), 6.99-7.01 (m, 1 H), 7.06-7.08 (m, 1 H), 7.33 (br s, 1 H), 7.41 (d, *J* = 8 Hz, 1 H), 7.55 (d, *J* = 8 Hz, 1 H), 7.59 (d, *J* = 8.8 Hz, 2 H).

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