Supporting information

A Ligand-free Copper(1) catalysed intramolecular N-arylation of diazoaminobenzenes in PEG-water : an expeditious protocol towards regiospecific 1-aryl benzotriazoles

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1. Materials and Methods

All solvents were dried by standard methods. Unless otherwise specified, chemicals were purchased from commercial suppliers and used without further purification. Some of 2-halo anilines were prepared using some reported methods^{1,2}. Column chromatography was performed on silica gel (60-120 mesh). TLC was done on glass sheets pre-coated with silica gel (with binder, 300 mesh, Merck). The ¹H- and ¹³C-NMR spectra were taken in CDCl₃ with TMS as an internal reference. The chemical shifts were reported as δ values (ppm) relative to TMS. IR spectra were recorded in KBr pellets. Compounds 2a³, 2b³, 2c³, 2m⁴, 2n⁵, 2r⁶, 2s⁶ are known in the literature and thus spectroscopic data elemental analysis data and ¹³C NMR spectra are not given (only ¹H NMR are given).

2. Synthesis of diazoaminobenzenes

Diazoaminobenzenes were prepared using a reported procedure¹ with some modification. In a 20 mL Erlenmayer flask, 2-halo aniline (7 mmol), concentrated hydrochloric acid (1 mL) and 4 mL of water were stirred for 10 min. After adding 2 g of crushed ice into it, 7 mmol of sodium nitrite in 1 mL of cold water was added dropwise for 5 min. maintaining 0-5 °C of temperature with constant stirring. It was then allowed to stand for another 15 min. 7 mmol of aniline or substituted aniline was then added into it with constant stirring maintaining 0-5 °C of temperature. After 5 min, 1 g of crystalline sodium acetate in 2 mL of cold water was added drop wise for five min with constant stirring. A yellow precipitate begins to form immediately. It was stirred for another 45 min. maintaining a temperature not above 20 °C. The precipitate was filtered and recrystallized from petroleum ether (boiling range 60-80 °C).



3. Analytical data of compounds

Compound 2a:



Characteristic: Pale yellow solid (Reaction time 2.5 h, isolated yield 92 %)

¹H NMR (300 MHz, CDCl₃): δ 7.42 (1H, t, J = 7.6 Hz), 7.68 - 7.46 (4H, m), 7.74 (1H, d, J=8.3 Hz), 7.76 (2H, d, J = 7.6 Hz), 8.14 (1H, d, J = 8.3Hz). **Compound 2b:**



Characteristic: Pale yellow crystalline solid (Reaction time 2.5 h, isolated yield 92 %) ¹H NMR (300 MHz, CDCl₃): δ 2.42 (3H, s), 7.42 – 7.32 (3H, m), 7.49 (1H, t, J = 7.6 Hz), 7.62 (2H, d, J = 7.6 Hz), 7.68 (1H, d, J = 8.3 Hz) 8.11 (1H, d, J = 8.3Hz). **Compound 2c:**



Characteristic: light red crystalline solid (Reaction time 3.0 h, isolated yield 90 %) ¹H NMR (300 MHz, CDCl₃): δ 7.37 (1H, d, J = 8.1 Hz), 7.60 - 7.40 (5H, m), 7.84 (1H, d, J=8.1 Hz), 8.16 (1H, d, J = 8.1Hz).

Compound 2d:



Characteristic: White crystalline solid (Reaction time 2.5 h, isolated yield 92 %)

Compound 2e:



Characteristic: Yellow crystalline solid (Reaction time 3 h, isolated yield 89 %) **Melting point:** 180 – 182 °C (EtOAc)

¹H NMR (300 MHz, CDCl₃): δ 7.52 (1H, t, J=7.8Hz), 7.67 (1H, t, J=8.1Hz), 7.85 (2H, t, J=8.4 Hz), 8.21 (1H, d, J=8.1 Hz), 8.25 (1H, dd, J=8.1 and 0.6 Hz), 8.38 (1H, d, J=7.8 Hz), 8.72 (1H, s).

¹³C NMR (75 MHz, CDCl₃): δ 109.8, 117.0, 120.8, 122.9, 125.0, 128.0, 129.4, 131.0, 131.8, 138.0, 146.7, 149.0.

EI-MS (m/z): 240 (M⁺), 209, 208, 207, 191, 133.

IR (KBr, cm⁻¹): 740, 1049, 1089, 1182, 1242, 1346, 1529, 2374, 2866, 2922, 3090 cm⁻¹. Elemental Analysis calculated for $C_{12}H_8N_4O_2$: C 60.00, H 3.36, N 23.32; Found: C 59.92, H 3.38, N 23.38 %.

Compound 2f:



Characteristic: White solid (Reaction time 3 h, isolated yield 90 %) **Melting point:** 110 – 112 °C (EtOAc)

¹H NMR (300 MHz, CDCl₃): δ 7.40 (1H, d, J=8.1 Hz), 7.46 (1H, dt, J=7.5 and 1.5 Hz), 7.62-7.49 (4H, m), 8.17 (1H, d, J=8.4Hz).

¹³C NMR (75 MHz, CDCl₃): δ 110.3, 120.3, 124.4, 128.4, 129.2, 129.3, 131.2, 131.7, 133.4, 133.6, 134.9, 145.6.

EI-MS (m/z): 263 (M⁺), 237, 235, 202, 200, 164.

IR (KBr, cm⁻¹): 733, 811, 998, 1038, 1101, 1287, 1422, 1481, 1580, 2280, 2372, 3090 cm⁻¹.

Elemental Analysis calculated for $C_{12}H_7N_3Cl_2$: C 54.57, H 2.67, N 15.91; Found: C 54.50, H 2.70, N 15.95 % .

Compound 2g:



Characteristic: White solid (Reaction time 2.5 h, isolated yield 92 %) **Melting point:** 128 – 130 °C (EtOAc) ¹H NMR (300 MHz, CDCl₃): δ 2.33 (3H, s), 7.05 (1H, d, J= 7.2Hz), 7.26 (1H, s), 7.36 (2H, d, J= 9.0 Hz), 7.51 (2H, d, J=8.7Hz), 7.79 (1H, d, J= 8.7Hz). ¹³C NMR (75 MHz, CDCl₃): δ 22.1, 109.3, 119.8, 124.0, 126.7, 130.0, 134.2, 135.6, 139.3. EI-MS (m/z): 243 (M⁺), 216, 214, 180. IR (KBr, cm⁻¹): 810, 1063, 1499, 1613, 2373, 2917, 3063 cm⁻¹. Elemental Analysis calculated for C₁₃H₁₀N₃Cl : C 64.07, H 4.14, N 17.24; Found: C 64.05, H 4.13, N 17.27 %.

Compound 2h:

Characteristic: White solid (Reaction time 3 h, isolated yield 91 %)

Melting point: 132 °C (EtOAc)

¹H NMR (300 MHz, CDCl₃): δ 2.53 (3H, s), 7.36-7.22 (2H, m), 7.62-7.50 (3H, m), 8.09 (1H, s).

¹³C NMR (75 MHz, CDCl₃): δ 22.0, 109.5, 119.7, 126.6, 129.2, 129.5, 131.1, 131.7, 133.5, 135.2, 139.4.

EI-MS (m/z): 277 (M⁺), 250, 248, 216, 214.

IR (KBr, cm⁻¹): 800, 1041, 1482, 1581, 2373, 2924, 3077 cm⁻¹.

Elemental Analysis calculated for $C_{13}H_{10}N_3Cl_2$: C 56.14, H 3.26, N 15.11; Found: C 56.07, H 3.28, N 15.16 %.

Compound 2i:



Characteristic: White solid (Reaction time 6 h, isolated yield 91 %) **Melting point:** 154 - 156 °C (EtOAc)

¹H NMR (300 MHz, CDCl₃): δ 7.34 (1H, d, J= 8.7 Hz), 7.63-7.50 (4H, m), 8.15 (1H, d, J= 1.2Hz).

¹³C NMR (75 MHz, CDCl₃): δ 111.4, 119.7, 129.2, 129.2, 129.4, 130.5, 131.5, 131.8, 132.2, 133.8, 134.5, 146.3.

EI-MS (m/z): 297 (M⁺), 269, 234, 198, 164.

IR (KBr, cm⁻¹): 816, 1045, 1102, 1210, 1290, 1422, 1479, 1579, 1736, 2373, 3091 cm⁻¹. Elemental Analysis calculated for $C_{12}H_6N_3Cl_3$: C 48.28, H 2.03, N 14.07; Found: C 48.20, H 2.08, N 14.10 %.

Compound 2j:

Characteristic: Yellow solid (Reaction time 6.5 h, isolated yield 84 %) **Melting point:** 182 -184 °C (EtOAc)

¹H NMR (300 MHz, CDCl₃): δ 7.62 (1H, dd, J= 8.7and 1.5Hz), 7.78 (1H, d, J=8.7Hz), 8.05 (2H, d, J= 9.0Hz), 8.18 (1H, br.d, J=0.9Hz), 8.52 (2H, d, J= 9.0Hz).

¹³C NMR (75 MHz, CDCl₃): δ 111.0, 120.3, 122.4, 125.7, 130.1, 130.4, 131.1, 141.5, 147.2, 147.6.

EI-MS (m/z): 274 (M⁺), 229, 207, 202, 200, 165, 164.

IR (KBr, cm⁻¹): 816, 1045, 1102, 1210, 1290, 1422, 1479, 1579, 1736, 2373, 3091 cm⁻¹. Elemental Analysis calculated for $C_{12}H_7N_4O_2Cl$: C 52.47, H 2.57, N 20.40; Found: C 52.39, H 2.61, N 20.44 %.

Compound 2k:

NO₂ **Characteristic:** Yellow solid (Reaction time 6 h, isolated yield 84 %) **Melting point:** 184 – 186 °C (EtOAc) ¹H NMR (300 MHz, CDCl₃): δ 7.62 (1H, dd, J=9.0 and 1.8 Hz), 7.76 (1H, d, J= 8.7 Hz), 7.86 (1H, t, J= 8.4 Hz), 8.18 (1H, br.t, J= 0.9 Hz), 8.21 (1H, td, J= 8.1 and 1.2Hz), 8.40 (1H, td, J= 8.4 and 1.2 Hz), 8.68 (1H, t, J= 1.8 Hz). ¹³C NMR (75 MHz, CDCl₃): δ 110.8, 117.1, 120.2, 123.3, 128.0, 130.0, 130.5, 130.9, 131.2, 137.6, 147.4, 149.1. EI-MS (m/z): 274 (M⁺), 229, 202, 200, 199, 174, 165, 164. IR (KBr, cm⁻¹): 810, 1062, 1349, 1535, 2375, 3093.cm⁻¹.

Elemental Analysis calculated for $C_{12}H_7N_4O_2Cl$: C 52.47, H 2.57, N 20.40; Found: C 52.39, H 2.60, N 20.45 %.

Compound 21:

Characteristic: Yellow solid (Reaction time 6 h, isolated yield 82 %) **Melting point:** 152 – 154 °C (EtOAc) ¹H NMR (300 MHz, CDCl₃): δ 7.39 (1H, d, J= 8.4 Hz), 7.46 (1H, d, J= 7.5Hz), 7.61-7.49 (4H, m), 8.15 (1H, d, J= 8.4Hz). ¹³C NMR (75 MHz, CDCl₃): δ 110.3, 120.1, 124.3, 128.3, 129.0, 129.2, 131.1, 131.6, 133.3, 133.4, 134.8, 145.7. EI-MS (m/z): 274 (M⁺), 246, 229, 200, 174, 164. IR (KBr, cm⁻¹): 732, 998, 1038, 1099, 1286, 1422, 1480, 1581, 1903, 3090 cm⁻¹. Elemental Analysis calculated for $C_{12}H_7N_4O_2Cl$: C 52.47, H 2.57, N 20.40; Found: C 52.38, H 2.61, N 20.45 %

Compound 2m: (Reaction time 2.5 h, isolated yield 92 %)

Characteristic: Pale yellow crystalline solid

¹H NMR (300 MHz, CDCl₃): δ 2.48 (3H, s), 7.40 (3H, two doublets merged together as a triplet, J = 8.3 and 8.6 Hz), 7.61 (2H, d, J = 8.3 Hz), 7.71 (1H, d, J = 1.5 Hz), 8.05 (1H, d, J = 8.6Hz).

Compound 2n: (Reaction time 3 h, isolated yield 82 %)

Characteristic: White solid

¹H NMR (300 MHz, CDCl₃): δ 7.49 (1H, t, J = 7.6 Hz), 7.62 (1H, t, J = 7.7 Hz), 7.68 (1H, t, J = 7.7 Hz), 7.82 (2H, br.d, J = 8.2 Hz), 7.97 (1H, d, J = 8.0 Hz), 8.19 (1H, d, J = 8.5 Hz), 8.24 (1H, d, J = 8.5 Hz), 8.54 (1H, d, J = 1.8 Hz), 9.41 (1H, s).

Compound 2o:

Characteristic: White solid (Reaction time 6.5 h, isolated yield 88 %) **Melting point:** 186 – 188 °C (EtOAc)

¹H NMR (300 MHz, CDCl₃): δ 7.76 (1H, d, J = 9.0 Hz), 7.78 – 7.67 (2H, m), 7.87 (1H, dt, J= 1.2 and 8.4 Hz), 7.99 (1H, d, J = 8.1 Hz), 8.19 (1H, d, J = 1.5 Hz), 8.25 (1H, d, J = 8.4 Hz), 8.53 (1H, d, J = 2.1Hz), 9.37 (1H, d, J = 2.7 Hz).

¹³C NMR (75 MHz, CDCl₃): δ 110.8, 120.0, 127.5, 128.1, 128.3, 128.5, 129.7, 129.8, 130.2, 130.7, 130.8, 131.1, 144.7, 147.2, 147.8.

EI-MS (m/z): 280 (M⁺), 252, 217, 190.

IR (KBr, cm⁻¹): 743, 812, 865, 1073, 1202, 1280, 1480, 1598, 2362, 3091cm⁻¹.

Elemental Analysis calculated for $C_{15}H_9N_4Cl$: C 64.18, H 3.23, N 19.96; Found: C 64.10, H 3.28, N 19.99 %.

Compound 2p:

Characteristic: White solid (Reaction time 3 h, isolated yield 90 %) **Melting point:** 122- 124 °C (EtOAc) ¹H NMR (300 MHz, CDCl₃): δ 2.57 (3H, s), 7.29 (1H, d, J = 7.2 Hz), 7.58 (1H, s), 7.67 (1H, t, J = 7.8Hz), 7.82 (1H, t, J = 7.8 Hz), 7.97 (1H, d, J = 8.1 Hz), 8.04 (1H, d, J = 8.7 Hz), 8.22 (1H, d, J= 8.7 Hz), 8.50 (1H, d, J = 1.2 Hz), 9.39 (1H, s). ¹⁹C NMR (75 MHz, CDCl₃): δ 22.0, 109.0, 119.9, 126.9, 127.5, 128.0, 129.5, 130.3, 130.6, 132.7, 139.7, 144.9, 145.1, 147.4. EI-MS (m/z): 260 (M⁺), 244, 223, 209, 192. IR (KBr, cm⁻¹): 1056, 1286, 1470, 1498, 1605, 2376, 2917, 3054 cm⁻¹. Elemental Analysis calculated for C₁₆H₁₂N₄: C 73.83, H 4.65, N 21.52; Found: C 73.78, H 4.66, N 21.56 %.

Compound 2q:

Characteristic: White solid (Reaction time 3 h, isolated yield 75 %) **Melting point:** 226 – 228 °C (EtOAc)

¹H NMR (300 MHz, CDCl₃): δ 7.30 – 7.23 (1H, m), 7.56 (1H, dt, J = 1.5 and 7.5 Hz), 7.63 (1H, dd, J = 1.4 and 7.5 Hz), 7.75-7.66 (4H, m), 7.84 (1H, d, J = 9.4 Hz), 8.04 (1H, dd, J = 1.5 and 8.0 Hz), 8.86 (1H, d, J = 3.0 Hz).

¹³C NMR (75 MHz, CDCl₃): δ 120.2, 120.4, 121.6, 125.1, 128.8, 129.4, 130.3, 130.6, 132.1, 133.9, 138.6, 141.5, 142.7, 148.6, 149.8.

EI-MS (m/z): 246 (M⁺), 225, 205, 168, 156.

IR (KBr, cm⁻¹): 769, 1058, 1097, 1312, 1356, 1409, 1445, 1494, 1588, 2373, 3055 cm⁻¹. Elemental Analysis calculated for $C_{15}H_{10}N_4$: C 73.16, H 4.09, N 22.75; Found: C 73.11, H 4.11, N 22.78 %.

Compound 2r: (Reaction time 6 h, isolated yield 86 %)

Characteristic: Pale yellow crystalline solid

¹H NMR (300 MHz, CDCl₃): δ 2.42 (3H, s), 7.40 – 7.35 (3H, m), 8.09 (2H, d, J = 8.4 Hz), 8.41 (1H, dd, J = 8.4 and 1.5Hz), 8.71 (1H, dd, J = 4.5 and 1.5 Hz).

Compound 2s: (Reaction time 6 h, isolated yield 88 %)

Characteristic: Pale white crystalline solid ¹H NMR (300 MHz, CDCl₃): δ 7.43 – 7.38 (1H, m), 7.52 (2H, d, J = 9.0 Hz), 8.27 (2H, d, J = 9.0 Hz), 8.43 (1H, d, J = 8.1Hz), 8.73 (1H, d, J = 4.2 Hz). **Compound 2t:**

Characteristic: White crystalline solid (Reaction time 6 h, isolated yield 88 %) **Melting point:** 146-148 °C (EtOAc) ¹H NMR (300 MHz, CDCl₃): δ 7.44-7.39 (1H, m), 7.51-7.47 (1H, m), 7.61-7.55 (2H, m), 8.46 (1H, d, J = 8.4 Hz), 8.70 (1H, d, J = 4.5 Hz). ¹³C NMR (75 MHz, CDCl₃): δ 120.3, 129.1, 129.2, 130.0, 131.4, 131.6, 133.3, 133.5, 136.5, 146.2, 151.2. EI-MS (m/z): 264 (M⁺), 238, 236, 201, 174, 166. IR (KBr, cm-1): 786, 1049, 1248, 1407, 1495, 1565, 2345, 3044 cm⁻¹. Elemental Analysis calculated for C11H6N₄Cl₂ : C 49.84, H 2.28, N 21.13; Found: C 49.80, H 2.30, N 21.15 %. **Compound 2u:**

Characteristic: yellow crystalline solid (Reaction time 6.5 h, isolated yield 75 %) **Melting point:** 178 – 180 °C (EtOAc) **Compound 2v:**

Characteristic: White crystalline solid (Reaction time 6.5 h, isolated yield 84 %) **Melting point:** 152 - 154 °C (EtOAc)

¹H NMR (300 MHz, CDCl₃): δ 7.56-7.44 (2H, m), 7.99 (1H, dd, J = 8.1 and 1.5 Hz), 8.51(1H, dd, J = 8.5 and 1.5 Hz), 8.80 - 8.63 (2H, m).

¹³C NMR (75 MHz, CDCl₃): δ 120.5, 123.1, 129.2, 130.1, 136.7, 137.6, 146.3, 148.6, 151.0, 151.4.

EI-MS (m/z): 231 (M⁺), 205, 203, 176, 168.

IR (KBr, cm-1): 773, 811, 1046, 1237, 1406, 1479, 1588, 2374, 3070 cm⁻¹.

Elemental Analysis calculated for $C_{10}H_6N_5Cl$: C 51.85, H 2.61, N 30.23; Found: C 51.80, H 2.63, N 30.26 %.

Compound 2w:

H₃C

Characteristic: Off white solid (Reaction time 3 h, isolated yield 85%) **Melting point:** 126 - 128 °C (EtOAc)

¹H NMR (300 MHz, CDCl₃): δ 2.40 (3H, s), 5.74 (2H, s), 7.13 – 7.09 (2H, m), 7.31 – 7.26 (5H, m), 7.88 (1H, d, J= 8.4 Hz).

¹³C NMR (75 MHz, CDCl₃): δ 22.0, 52.0, 108.9, 119.3, 126.4, 127.5, 128.4, 129.0, 133.3, 134.9, 138.2, 144.7.

EI-MS (m/z): 223 (M⁺), 208, 162.

IR (KBr, cm-1): 708, 1221, 1450, 1618, 2375, 2921, 3032 cm⁻¹.

Elemental Analysis calculated for C14H13N3 : C 75.31, H 5.87, N 18.82; Found: C 75.18, H 5.95, N 18.87 %

Compound 2x:

Br ĊH₃

Characteristic: White solid (Reaction time 3 h, isolated yield 92 %) **Melting point:** 140 - 142 °C (EtOAc) ¹H NMR (300 MHz, CDCl₃): δ 2.53 (3H, s), 7.18 (1H, s), 7.27 (1H, d, J= 8.4 Hz), 7.62 – 7.49 (3H, m), 8.03 (1H, d, J= 8.4 Hz). ¹³C NMR (75 MHz, CDCl₃): δ 21.9, 109.4, 119.5, 126.6, 129.0, 129.3, 131.0, 131.6, 133.4, 134.0, 134.9, 139.3. EI-MS (m/z): 322 (M⁺+1), 290, 266, 207, 166. IR (KBr, cm-1): 799, 1040, 1481, 1580, 2340, 3075 cm⁻¹. Elemental Analysis calculated for C13H9N₃BrCl : C 48.40, H 2.81, N 13.03; Found: C 48.36, H 2.82, N 13.06 %

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