Supplementary Information

Ethylene Glycol, an Efficient and Recoverable Medium for Copper-Catalyzed *N*-Arylation of Diazoles under Microwave Irradiation

Ali Sharifi*, Nima Ghonouei, and M. Saeed Abaee

Chemistry and Chemical Engineering Research Center of Iran, P.O.Box 14335-186 Tehran, Iran

General information

All reagents and solvents were commercially available and used as received. Progress of the reactions was monitored by TLC using silica gel coated plates and EtOAc/petroleum ether mixture (1:1) as the eluent. Microwave-assisted reactions were carried out in a Milestone Microsynth[®] instrument. Melting points are uncorrected and are obtained by Buchi Melting Point 530. ¹H NMR (500 MHz) spectra were obtained on a FT-NMR Bruker Ultra Shield[™] instrument as CDCl₃ solutions and the chemical shifts are expressed as δ units with Me₄Si as the internal standard. All products were known and their identity was confirmed by the comparison of their melting points, ¹H NMR, and ¹³C NMR data with those of authentic compounds available in the literature.

General procedure for microwave-assisted CuCl₂-catalyzed reactions of diazoles with aryl halides

A diazole derivative (2.0 mmol), CuCl₂ (0.1 mmol), and K₂CO₃ (3.0 mmol) were added to ethylene glycol (2.0 mL) and the mixture was stirred thoroughly. Then, the aryl halide (1.0 mmol) was added and the reaction vessel was capped. The reaction mixture was irradiated at 300 W in the microwave instrument for the time given in Table 2. After completion of the reaction, water (30.0 mL) was added to the mixture and the organic portion was extracted with ethyl

acetate (3×5.0 mL). The combined ethyl acetate layers were dried over Na₂SO₄ and evaporated under reduced pressure. The crude product was purified via a silica gel column using EtOAc/petroleum ether mixtures (1:1) as the eluent.

General procedure for recovering the reaction medium

After completion of the reaction, the reaction medium was extracted with portions of diethyl ether (three portions, 5 mL each). The immiscible ether layers were separated from EG, washed with water and brine, dried over Na₂SO₄, and evaporated under reduced pressure to give the crude product. The remaining EG layer was subjected concentration at reduced pressure using a rotary evaporator for 5 hours (at 60 °C). The recovered medium was reused in the next reaction, without addition any catalyst.

Characterization of the products (Table 2)

1-phenyl-1H-imidazole (1a): Colorless oil.^[1] ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 7.85 (s, 1H); 7.50 (m, 2H); 7.37 (m, 2H); 7.28 (s, 1H); 7.20 (s, 1H). ¹³C NMR (CDCl₃, 125MHz) δ (ppm) 137.7, 135.9, 130.7, 130.28, 127.8, 121.8, 118.6. The NMR data are in good agreement with those reported.^[1]

1-p-tolyl-1H-imidazole (1b): m.p: 45-47 °C (literture, 49-53 °C).^[2] ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 7.79 (s, 1H); 7.22 (m, 5H); 7.17 (s, 1H); 2.37 (s, 3H). ¹³C NMR (CDCl₃, 125MHz) δ (ppm) 137.7, 135.8, 135.4, 130.7, 130.4, 121.6, 118.6, 21.22. The ¹H NMR data are in good agreement with those reported.^[3]

1-(4-methoxyphenyl)-1H-imidazole (1c): m.p: 52-55 °C (literature, 57 °C).^[4] ¹H NMR (CDCl₃, 500 MHz) δ 7.80 (s, 1H); 7.26 (m, 1H); 7.12 (s, 1H); 7.11 (s, 1H); 6.86 (m, 1H); 6.81 (m, 2H); 3.74 (s, 3H). ¹³C NMR (CDCl₃, 125MHz) δ (ppm) 159.2, 136.0, 130.8, 130.0, 123.3, 119.0, 115.2, 55.8. The NMR data are in good agreement with those reported.^[3]

1-(3-methoxyphenyl)-1H-imidazole (1d): Colorless oil.^[5] ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 7.84 (s, 1H); 7.35 (t, *J* = 8.0 Hz, 1H); 7.26 (s, 1H); 7.18 (s, 1H); 6.95 (m 1H); 6.87 (m, 2H); 3.83 (s, 3H). ¹³C NMR (CDCl₃, 125MHz) δ (ppm) 161.0, 138.7, 135.9, 131.0, 130.6, 118.6, 113.9, 112.9, 108.0, 55.8. The NMR data are in good agreement with those reported.^[6]

1-(naphthalen-2-yl)-1H-imidazole (1e): m.p: 123-124 °C (literature, 122-124 °C).^[7] ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 8.00 (m, 2H), 7.92 (t, *J* = 7.7 Hz, 2H); 7.86 (m, 1H); 7.59 (m, 3H); 7.44 (s, 1H); 7.30 (s, 1H). ¹³C NMR (CDCl₃, 125MHz) δ (ppm) 136.2, 135.0, 133.9, 132.5, 131.0, 130.4, 128.3, 128.2, 127.7, 126.9, 120.5, 119.3, 118.8. The NMR data are in good agreement with those reported.^[8]

1-(4-phenyl-phenyl)-1H-imidazole (1f): m.p: 118-120 °C (literature, 122-124 °C).^[9] ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 7.94 (s, 1H); 7.37 (m, 2H); 7.65 (m, 2H); 7.50 (m, 4H); 7.44 (m, 1H); 7.36 (s, 1H), 7.28 (s, 1H). ¹³C NMR (CDCl₃, 125MHz) δ (ppm) 140.8, 140.1, 136.9, 136.0, 131.0, 129.4, 128.9, 128.2, 127.4, 122.0, 118.6. The NMR data are in good agreement with those reported.^[9]

1-(thiophen-2-yl)-1H-imidazole (1g): colorless oil.^[10] ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 7.74 (s, 1H); 7.13 (m, 3H); 6.98 (m, 2H). ¹³C NMR (CDCl₃, 125MHz) δ (ppm) 139.3, 137.3, 130.5, 126.7, 122.5, 120.6, 119.3. The NMR data are in good agreement with those reported.^[10]

1-phenyl-1H-pyrazole (1h): colorless oil.^[11] ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 7.97 (m, 1H); 7.78 (m, 1H); 7.74 (m, 2H); 7.49 (m, 2H); 7.31 (m, 1H). ¹³C NMR (CDCl₃, 125MHz) δ (ppm) 141.5, 140.6, 129.8, 127.2, 126.9, 119.6, 108.0. The NMR data are in good agreement with those reported.^[3]

1-p-tolyl-1H-pyrazole (1i): m.p: 28-30 °C (literature, 28-30°C).^[11] ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 7.91 (d, J = 2.4 Hz, 1H); 7.75 (m, 1H); 7.61 (d, J = 8.3 Hz, 2H); 7.28 (d, J = 8.4 Hz, 2H); 6.48 (m, 1H), 2.42 (s, 3H). ¹³C NMR (CDCl₃, 125MHz) δ (ppm) 141.2, 138.4, 136.6, 130.3, 127.1, 119.6, 107.7, 21.3. The ¹H NMR data are in good agreement with those reported.^[3]

1-(4-methoxyphenyl)-1H-pyrazole (1j): m.p: 30-33 °C (literature, 33-35).^[11] ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 7.86 (d, 1H, J = 2.4 Hz); 7.73 (m, 1H); 7.63 (m, 2H); 6.01 (m, 2H); 6.47 (t, 1H, J = 2.21 Hz); 3.86 (s, 3H). ¹³C NMR (CDCl₃, 125MHz) δ (ppm) 158.6, 140.9, 134.3, 127.2, 121.1, 115.0, 107.6, 55.8. The ¹H NMR data are in good agreement with those reported.^[3]

1-(3-methoxyphenyl)-1H-pyrazole (1k): colorless oil.^[11] ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 7.94 (m, 1H); 7.76 (m, 1H); 7.34 (m, 2H); 7.25 (m, 1H); 6.85 (m, 1H); 6.46 (m, 1H); 3.87 (s,

3H). ^{13}C NMR (CDCl_3 , 125MHz) δ (ppm) 160.9, 141.7, 141.4, 130.6, 127.4, 112.8, 111.5, 108.0, 105.5, 55.9. The ^1H NMR data are in good agreement with those reported.^[11]

1-phenyl-1H-benzo[d]imidazole (1l): m.p: 88-90 °C (literature, 94-95 °C).^[11] ^1H NMR (CDCl_3 , 500 MHz) δ (ppm) 8.13 (s, 1H); 7.92 (d, J = 8.0 Hz, 1H); 7.56 (m, 3H); 7.47 (m, 3H); 7.36 (m, 2H). ^{13}C NMR (CDCl_3 , 125MHz) δ (ppm) 144.5, 142.7, 136.7, 134.1, 130.4, 128.4, 124.4, 124.1, 123.2, 121.0, 111.0. The ^1H NMR data are in good agreement with those reported.^[3]

1-p-tolyl-1H-benzo[d]imidazole (1m): m.p: 51-53 °C (literature, 49-50 °C).^[12] ^1H NMR (CDCl_3 , 500 MHz) δ (ppm) 8.12 (s, 1H); 7.91 (m, 1H); 7.54 (m, 1H); 7.41 (m, 4H); 7.34 (m, 2H); 2.49 (s, 3H). ^{13}C NMR (CDCl_3 , 125MHz) δ (ppm) 144.4, 142.8, 138.5, 134.3, 134.2, 131.0, 124.4, 124.0, 123.0, 121.0, 111.0, 21.5. The ^1H NMR data are in good agreement with those reported.^[3]

1-(4-methoxyphenyl)-1H-benzo[d]imidazole (1n): m.p: 94-95 °C (literature, 95-96 °C).^[13] ^1H NMR (CDCl_3 , 500 MHz) δ (ppm) 8.08 (s, 1H); 7.90 (m, 1H); 7.48 (m, 1H); 7.41 (m, 2H); 7.34 (m, 2H); 7.09 (m, 2H); 3.90 (s, 3H). ^{13}C NMR (CDCl_3 , 125MHz) δ (ppm) 159.7, 153.4, 129.5, 126.0, 124.0, 123.0, 120.8, 116.0, 115.5, 115.0, 110.8, 56.1. The ^1H NMR data are in good agreement with those reported.^[3]

Copies of NMR spectra

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