Supporting Information

Direct Pd-Catalyzed Arylation of 1,2,3-Triazoles

Stepan N. Chuprakov, Natalia Chernyak, Alexander S. Dudnik, and Vladimir Gevorgyan*

Department of Chemistry, University of Illinois at Chicago,

845 West Taylor Street, Chicago, Illinois 60607-7061

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General Information

All experiments were conducted under inert atmosphere. NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) or DPX-400 (400 MHz) instruments. (+) and (-) represent positive and negative intensities of signals in ^{13}C DEPT-135 experiments. GC/MS analysis was performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Silicycle Silia-P Flash silica gel (40-63 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. Anhydrous solvents were purchased from Aldrich and stored over calcium hydride. Alkynes, azides, and Pd-catalysts were commercially available and purchased from Aldrich, Strem Chemicals Inc., Alfa Aesar, or Acros Organics, or synthesized via known literature procedures.

Starting Materials

1,4-Disubstituted 1,2,3-triazoles **1a-h** were prepared via standard Cu-catalyzed azide-alkyne cycloaddition¹ (CuAAC), 1,5-disubstituted triazoles **4a-b** were obtained through Ru-catalyzed cycloaddition procedure², while triazole **1i** was prepared through BSA-mediated benzylation of commercially available 1*H*-1,2,3-triazole as described below.

1-Benzyl-1*H*-1,2,3-triazole (1i). To a stirred solution of 1*H*-1,2,3-triazole (0.50 g, 0.42 ml, 0.0072 mol) and benzyl bromide (1.36 g, 0.95 ml, 0.0080 mol) in 15 ml of 1-methyl-2-pyrrolidinone (NMP) 1.95 ml (1.62 g, 0.0080 mol) of N,O-bis(trimethylsilyl)acetamide (BSA) was added slowly. The resulting yellowish solution was stirred overnight at 100°C, quenched with 30 ml of water, and extracted with dichloromethane (2 X 50 ml). Combined organic fractions were washed thoroughly with water and brine and dried over anhydrous sodium sulfate. Flash chromatography afforded 0.775 g (4.87 mmol, 67%) of 1-benzyl-1*H*-1,2,3-triazole (**1i**) as yellowish solid.

1i: ^1H NMR (500 MHz, CDCl_3) δ ppm 7.67 (s, 1 H), 7.47 (d, $J=0.73$ Hz, 1 H), 7.28 - 7.39 (m, 3 H), 7.23 (s, 2 H), 5.53 (d, $J=2.38$ Hz, 2 H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 134.7, 134.2 (+), 129.1 (+), 128.7 (+), 128.0 (+), 123.4 (+), 53.9 (-); LR EI MS m/z 159.1 (M^+).

¹ Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2002**, *41*, 2596.

² Sharpless et al. *J. Am. Chem. Soc.* **2005**, *127*, 15998.

Pd-catalyzed Arylation of 1,2,3-Triazoles

Typical Preparative Procedure. To an oven dried 3 ml Wheaton vial equipped with mini-inert valve were added 1-heptyl-4-phenyl-1*H*-1,2,3-triazole (**1a**) (0.122 g, 0.5 mmol), Pd(Ph₃P)₂Cl₂ (18 mg, 0.025 mmol), and tetrabutylammonium acetate (0.302 g, 1.0 mmol) under N₂ atmosphere. One ml of NMP was then added, followed by bromobenzene (0.118 g, 0.080 ml, 0.75mmol), and the reaction mixture was stirred at 100°C for 2h, when judged complete by GC/MS analysis. The reaction mixture was diluted with ethyl acetate (20 ml), washed twice with 10 ml portions of water and brine, dried over anhydrous sodium sulfate. The solvents were removed and the residue was purified via flash Silica chromatography (1:4 EtOAc/Hexanes) to afford 0.154 g (0.48 mmol, 96%) of 1-heptyl-4,5-diphenyl-1*H*-1,2,3-triazole (**2a**) as yellowish oil, which crystallized upon storage.

2a: ¹H NMR (500 MHz, CDCl₃) δ ppm 7.42 - 7.64 (m, 5 H), 7.30 - 7.39 (m, 2 H), 7.19 - 7.29 (m, 3 H), 4.20 (s, 2 H), 1.78 (s, 2 H), 1.04 - 1.39 (m, 8 H), 0.84 (t, *J*=7.06 Hz, 3 H); ¹³C NMR (126 MHz, CDCl₃) δ ppm 144.2, 133.6, 131.1, 130.0 (+), 129.6 (+), 129.3 (+), 128.4 (+), 128.3, 127.6 (+), 126.8 (+), 48.3 (-), 31.5 (-), 30.1 (-), 28.5 (-), 26.4 (-), 22.5 (-), 14.0 (+); LR EI MS *m/z* 319.3 (M⁺); HR EI MS *m/z* 319.2045, Calcd for C₂₁H₂₅N₃ 319.20485.

1-Heptyl-5-(4-methoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole (**2b**)

2b: ¹H NMR (500 MHz, CDCl₃) δ ppm 7.49 - 7.63 (m, 2 H), 7.19 - 7.35 (m, 5 H), 7.03 (s, 2 H), 4.18 (t, *J*=7.43 Hz, 2 H), 3.89 (s, 3 H), 1.78 (s, 2 H), 1.11 - 1.33 (m, 8 H), 0.85 (t, *J*=6.97 Hz, 3 H); ¹³C NMR (126 MHz, CDCl₃) δ ppm 160.5, 144.1, 133.5, 131.3 (+), 128.4 (+), 127.5 (+), 126.7 (+), 120.1, 114.8 (s), 55.4 (+), 48.2 (-), 31.5 (-), 30.1 (-), 28.6 (-), 26.4 (-), 22.5 (-), 14.0 (+); LR EI MS *m/z* 349.3 (M⁺); HR EI MS *m/z* 349.2140, Calcd for C₂₂H₂₇N₃O 349.21541.

1-Heptyl-5-(4-nitrophenyl)-4-phenyl-1*H*-1,2,3-triazole (**2c**)

2c: ¹H NMR (500 MHz, CDCl₃) δ ppm 8.31 - 8.45 (m, 2 H), 7.50 - 7.61 (m, 2 H), 7.41 - 7.50 (m, 2 H), 7.27 - 7.34 (m, 3 H), 4.24 (s, 2 H), 1.72 - 1.92 (m, 2 H), 1.10 - 1.33 (m, 8 H), 0.84 (s, 3 H); ¹³C NMR (126 MHz, CDCl₃) δ ppm 148.5, 145.0, 135.0, 131.5, 131.1 (+), 130.1, 128.7 (+), 128.2 (+), 127.1 (+), 126.1, 124.5 (+), 115.9, 48.7 (-), 31.5 (-), 30.1 (-), 28.5 (-), 26.4 (-), 22.5 (-), 14.0 (+); LR EI MS *m/z* 364.3 (M⁺); HR EI MS *m/z* 364.18851, Calcd for C₂₁H₂₄N₄O₂ 364.18993.

1-Heptyl-5-(2-naphthyl)-4-phenyl-1*H*-1,2,3-triazole (2d)

2d: ^1H NMR (500 MHz, CDCl_3) δ ppm 7.97 (s, 2 H), 7.87 (s, 2 H), 7.51 - 7.70 (m, 4 H), 7.38 (dd, $J=8.34, 1.74$ Hz, 1 H), 7.16 - 7.26 (m, 3 H), 4.25 (t, $J=7.43$ Hz, 2 H), 1.71 - 1.92 (m, 2 H), 1.06 - 1.35 (m, 8 H), 0.80 (s, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 144.3, 133.6, 133.4, 133.3, 131.1, 129.7 (+), 129.3 (+), 128.5 (+), 128.3 (+), 128.0 (+), 127.6 (+), 127.4 (+), 127.0 (+), 126.9 (+), 126.8 (+), 125.7, 48.4 (-), 31.5 (-), 30.1 (-), 28.5 (-), 26.4 (-), 22.5 (-), 14.0 (+); LR EI MS m/z 369.3 (M^+); HR EI MS m/z 369.22148, Calcd for $\text{C}_{25}\text{H}_{27}\text{N}_3$ 369.22050.

1-Benzyl-5-(1-naphthyl)-4-phenyl-1*H*-1,2,3-triazole (2e)

2e: ^1H NMR (500 MHz, CDCl_3) δ ppm 8.02 (d, $J=8.07$ Hz, 1 H), 7.94 (d, $J=8.25$ Hz, 1 H), 7.39 - 7.59 (m, 4 H), 6.96 - 7.38 (m, 9 H), 6.81 (d, $J=7.70$ Hz, 2 H), 5.39 (d, $J=15.04$ Hz, 1 H), 5.10 (d, $J=15.04$ Hz, 1 H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 145.5, 134.8, 133.6, 131.9, 130.9, 130.4 (+), 129.2 (+), 128.5 (+), 128.4 (+), 128.0 (+), 127.8 (+), 127.6 (+), 127.4 (+), 126.7 (+), 126.1 (+), 125.4 (+), 125.3, 124.6 (+), 52.4 (-); LR EI MS m/z 361.2 (M^+); HR EI MS m/z 361.1570, Calcd for $\text{C}_{25}\text{H}_{19}\text{N}_3$ 361.15790.

***N*-[4-(1-Benzyl-4-phenyl-1*H*-1,2,3-triazol-5-yl)phenyl]-*N,N*-dimethylamine (2f)**

2f: ^1H NMR (500 MHz, CDCl_3) δ ppm 7.56 - 7.72 (m, 2 H), 7.16 - 7.36 (m, 6 H), 7.10 (s, 2 H), 6.95 - 7.05 (m, 2 H), 6.71 (d, $J=8.62$ Hz, 2 H), 5.40 (s, 2 H), 3.03 (s, 6 H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 150.8, 144.1, 135.9, 134.6, 131.5, 130.9 (+), 128.6 (+), 128.3 (+), 128.0 (+), 127.5 (+), 127.4 (+), 126.6 (+), 112.3 (+), 51.6 (-), 40.3 (+); m.p. 162°C (hexanes/dichloromethane); LR EI MS m/z 354.3 (M^+); Found: C 77.56, H 6.31; Calcd for $\text{C}_{23}\text{H}_{22}\text{N}$ C 77.94, H 6.26.

3-(1-Benzyl-4-phenyl-1*H*-1,2,3-triazol-5-yl)pyridine (2g)

2g: ^1H NMR (500 MHz, CDCl_3) δ ppm 8.71 (dd, $J=4.77, 1.65$ Hz, 1 H), 8.41 (dd, $J=2.02, 0.73$ Hz, 1 H), 7.46 - 7.55 (m, 2 H), 7.36 - 7.43 (m, 1 H), 7.18 - 7.36 (m, 7 H), 6.95 - 7.07 (m, 2 H), 5.45 (s, 2 H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 150.8 (+), 150.5 (+), 150.4 (+), 145.7, 137.6 (+), 134.9, 130.5, 130.3, 128.9 (+), 128.6 (+), 128.5 (+), 128.1 (+), 127.3 (+), 126.9 (+), 124.5, 123.7 (+),

52.5 (-); LR EI MS m/z 312.2 (M^+); HR EI MS m/z 312.13708, Calcd for $C_{20}H_{16}N_4$ 312.13750.

Ethyl 1-heptyl-5-[4-(trifluoromethyl)phenyl]-1*H*-1,2,3-triazole-4-carboxylate (2h)

2h: 1H NMR (500 MHz, $CDCl_3$) δ ppm 7.80 (d, $J=8.07$ Hz, 2 H), 7.51 (d, $J=7.89$ Hz, 2 H), 4.31 (q, $J=7.15$ Hz, 2 H), 4.22 (t, $J=7.34$ Hz, 2 H), 1.66 - 1.87 (m, 2 H), 1.10 - 1.35 (m, 11 H), 0.84 (t, $J=7.06$ Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 160.8, 139.6, 137.1, 132.2 (q, $J_{FC} = 32.36$ Hz), 130.3 (+), 130.2, 125.7 (+, q, $J_{FC} = 2.77$ Hz), 123.6 (q, $J_{FC} = 272.81$ Hz), 61.2 (-), 48.7 (-), 31.4 (-), 30.0 (-), 28.4 (-), 26.2 (-), 22.4 (-), 14.1 (+), 13.9 (+).

Ethyl 5-[4-(ethoxycarbonyl)phenyl]-1-(4-methylphenyl)-1*H*-1,2,3-triazole-4-carboxylate (2i)

2i: 1H NMR (500 MHz, $CDCl_3$) δ ppm 8.04 (s, 2 H), 7.38 (s, 2 H), 7.15 (s, 4 H), 4.20 - 4.56 (m, 4 H), 2.36 (s, 3 H), 1.17 - 1.61 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 165.8, 160.8, 140.1, 139.8, 137.2, 133.1, 131.7, 130.4 (+), 130.0 (+), 129.4 (+), 125.0 (+), 61.3 (-), 21.2 (+), 14.3 (+), 14.2 (+); m.p. 105-106°C (hexanes/dichloromethane); LR EI MS m/z 379.2 (M^+); Found: C 66.46, H 5.60; Calcd for $C_{21}H_{21}N_3O_4$ C 66.48, H 5.58.

5-(4-Methoxyphenyl)-4-(4-methylphenyl)-1-phenyl-1*H*-1,2,3-triazole (2j)

2j: 1H NMR (400 MHz, $CDCl_3$) δ ppm 7.51 (s, 2 H), 7.27 - 7.44 (m, 5 H), 7.12 (s, 4 H), 6.87 (d, $J=8.62$ Hz, 2 H), 3.82 (s, 3 H), 2.34 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 160.2, 144.7, 137.6, 136.7, 133.2, 131.5 (+), 129.2 (+), 129.1 (+), 128.8 (+), 128.1, 127.2 (+), 125.2 (+), 119.7, 114.5 (+), 55.3 (+), 21.3 (+); m.p. 177°C (hexanes/dichloromethane); LR EI MS m/z 341.2 (M^+); Found: C 77.38, H 5.68; Calcd for $C_{22}H_{19}N_3O$ C 77.40, H 5.61.

1-[1-Benzyl-5-(3-methylphenyl)-1*H*-1,2,3-triazol-4-yl]ethanol (2k)

2k: 1H NMR (500 MHz, $CDCl_3$) δ ppm 7.10 - 7.53 (m, 5 H), 6.82 - 7.11 (m, 4 H), 5.37 (d, $J=1.10$ Hz, 2 H), 4.86 (q, $J=6.60$ Hz, 1 H), 2.98 (s, 1 H), 2.31 (s, 3 H), 1.52 (d, $J=6.60$ Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 148.4, 138.7, 135.4, 134.4, 130.5 (+), 130.4 (+), 128.7 (+), 128.7 (+),

128.1 (+), 127.5 (+), 127.0 (+), 126.7, 62.6 (+), 52.0 (-), 23.3 (+), 21.3 (+); LR EI MS m/z 293.3 (M^+).

1-Heptyl-4-(4-methoxyphenyl)-5-phenyl-1*H*-1,2,3-triazole (2l)

2l: ^1H NMR (400 MHz, CDCl_3) δ ppm 7.93 (s, 2 H), 7.61 (s, 2 H), 7.48 - 7.58 (m, 3 H), 7.27 - 7.40 (m, 2 H), 4.33 (q, $J=7.11$ Hz, 2 H), 4.20 (t, $J=7.38$ Hz, 2 H), 1.71 - 1.86 (m, 2 H), 1.36 (t, $J=7.16$ Hz, 3 H), 1.08 - 1.29 (m, 8 H), 0.83 (t, $J=6.87$ Hz, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 166.4, 143.2, 135.4, 134.5, 129.9 (+), 129.9 (+), 129.7 (+), 129.5 (+), 129.3, 127.9, 126.4 (+), 60.9 (-), 48.3 (-), 31.5 (-), 30.1 (-), 28.5 (-), 26.4 (-), 22.5 (-), 14.3 (+), 14.0 (+); m.p. 78-79°C (hexanes); LR EI MS m/z 391.3 (M^+); Found: C 73.44, H 7.32; Calcd for $\text{C}_{24}\text{H}_{29}\text{N}_3\text{O}_2$ C 73.63, H 7.47.

Ethyl 4-(1-heptyl-5-phenyl-1*H*-1,2,3-triazol-4-yl)benzoate (2m)

2m: ^1H NMR (400 MHz, CDCl_3) δ ppm 7.40 - 7.61 (m, 5 H), 7.32 (s, 2 H), 6.80 (s, 2 H), 4.18 (t, $J=7.38$ Hz, 2 H), 3.77 (s, 3 H), 1.70 - 1.84 (m, 2 H), 1.08 - 1.36 (m, 8 H), 0.84 (t, $J=6.87$ Hz, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 159.1, 144.1, 132.9, 130.0 (+), 129.5 (+), 129.3 (+), 128.5, 128.0 (+), 123.7, 113.9 (+), 55.2 (+), 48.3 (-), 31.5 (-), 30.1 (-), 28.5 (-), 26.4 (-), 22.5 (-), 14.0 (+); LR EI MS m/z 349.3 (M^+); HR EI MS m/z 349.2144, Calcd for $\text{C}_{22}\text{H}_{27}\text{N}_3\text{O}$ 349.21541.

5-Butyl-1-heptyl-4-phenyl-1*H*-1,2,3-triazole (2n)

2n: ^1H NMR (500 MHz, CDCl_3) δ ppm 7.61 - 7.79 (m, 2 H), 7.39 - 7.50 (m, 2 H), 7.30 - 7.38 (m, 1 H), 4.26 (s, 2 H), 2.82 (s, 2 H), 1.87 - 2.03 (m, 2 H), 1.50 - 1.67 (m, 2 H), 1.19 - 1.49 (m, 10 H), 0.79 - 1.05 (m, 6 H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 144.1, 133.1, 132.0, 128.6 (+), 127.5 (+), 127.1 (+), 48.0 (-), 31.6 (-), 31.1 (-), 30.4 (-), 28.8 (-), 26.7 (-), 22.9 (-), 22.6 (-), 22.6 (-), 14.0 (+), 13.6 (+); LR EI MS m/z 299.3 (M^+).

1-Benzyl-5-phenyl-1*H*-1,2,3-triazole (3a)

3a: ^1H NMR (500 MHz, CDCl_3) δ ppm 7.74 (s, 1 H), 7.35 - 7.53 (m, 3 H), 7.19 - 7.36 (m, 5 H), 7.08 (s, 2 H), 5.55 (s, 2 H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 138.2, 135.5 (+), 133.3 (+), 133.3, 129.5 (+), 128.9 (+), 128.9 (+), 128.8 (+), 128.2 (+), 127.2 (+), 126.9, 51.8 (-); LR EI MS m/z 235.1 (M^+).

1-Benzyl-5-(4-methoxyphenyl)-1*H*-1,2,3-triazole (3b)

3b: ^1H NMR (400 MHz, CDCl_3) δ ppm 7.69 (s, 1 H), 7.19 - 7.36 (m, 3 H), 7.12 - 7.21 (m, 2 H), 7.08 (s, 2 H), 6.89 - 6.95 (m, 2 H), 5.52 (s, 2 H), 3.83 (s, 3 H); ^{13}C NMR (101 MHz, CDCl_3) δ ppm 160.5, 138.0, 135.7, 133.1 (+), 130.2 (+), 128.8 (+), 128.1 (+), 127.1 (+), 118.9, 114.4 (+), 55.4 (+), 51.7 (-); LR EI MS m/z 265.1 (M^+); HR EI MS m/z 265.12107, Calcd for $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}$ 265.12151.

***N*-[4-(1-Benzyl-1*H*-1,2,3-triazol-5-yl)phenyl]-*N,N*-dimethylamine (3c)**

3c: ^1H NMR (400 MHz, CDCl_3) δ ppm 7.67 (s, 1 H), 7.28 (s, 3 H), 7.12 (s, 4 H), 6.69 (s, 2 H), 5.53 (s, 2 H), 2.99 (s, 6 H); ^{13}C NMR (101 MHz, CDCl_3) δ ppm 150.9, 138.7, 136.0, 132.6 (+), 129.7 (+), 128.8 (+), 128.0 (+), 127.1 (+), 113.7, 112.1 (+), 51.5 (-), 40.2 (+); m.p. 132°C (hexanes/dichloromethane); LR EI MS m/z 278.2 (M^+).

1-Benzyl-5-(2-naphthyl)-1*H*-1,2,3-triazole (3d)

3d: ^1H NMR (500 MHz, CDCl_3) δ ppm 7.86 - 7.94 (m, 2 H), 7.85 (s, 1 H), 7.76 (s, 1 H), 7.72 (d, $J=0.73$ Hz, 1 H), 7.49 - 7.63 (m, 2 H), 7.32 - 7.39 (m, 1 H), 7.27 - 7.33 (m, 3 H), 7.08 - 7.20 (m, 2 H), 5.61 (s, 2 H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 138.3, 135.6, 133.5 (s), 133.3, 132.9, 128.9 (s), 128.8 (s), 128.7 (s), 128.2 (s), 128.2 (s), 127.8 (s), 127.3 (s), 127.2 (s), 127.0 (s), 125.9 (s), 124.1, 52.0 (s); LR EI MS m/z 285.2 (M^+).

Ethyl 4-(1-benzyl-1*H*-1,2,3-triazol-5-yl)benzoate (3e)

3e: ^1H NMR (500 MHz, CDCl_3) δ ppm 7.91 - 8.31 (m, 2 H), 7.79 (s, 1 H), 7.15 - 7.55 (m, 5 H), 7.06 (dd, $J=6.60, 2.57$ Hz, 2 H), 5.57 (s, 2 H), 4.40 (q, $J=7.15$ Hz, 2 H), 1.40 (t, $J=7.15$ Hz, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 165.7, 137.2, 135.2, 133.7 (+), 131.4, 131.2, 130.1 (+), 128.9 (+), 128.8 (+), 128.3 (+), 127.1 (+), 61.4 (-), 52.1 (-), 14.3 (+); LR EI MS m/z 307.2 (M^+).

1-Benzyl-5-[4-(trifluoromethyl)phenyl]-1*H*-1,2,3-triazole (3f)

3f: ^1H NMR (500 MHz, CDCl_3) δ ppm 7.79 (s, 1 H), 7.67 (s, 2 H), 7.37 (s, 2 H), 7.22 - 7.34 (m, 3 H), 7.06 (s, 2 H), 5.56 (s, 2 H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 136.8, 135.1, 133.7 (+), 131.6 (q, $J_{\text{FC}} = 33.29$ Hz), 130.6, 129.3 (+), 129.0 (+), 128.4 (+), 127.0 (+), 125.9 (+, q, $J_{\text{FC}} = 2.77$ Hz), 123.7 (q, $J_{\text{FC}} = 272.81$ Hz), 52.1 (-); LR EI MS m/z 303.2 (M^+).

Mechanistic Studies

4-(4-Methylphenyl)-1-phenyl-1*H*-1,2,3-triazole-*d*₁ (1e-*d*). To a stirred solution of 4-(4-methylphenyl)-1-phenyl-1*H*-1,2,3-triazole (**1e**) (0.235 g, 1 mmol) in 10 ml of dry THF, *n*-BuLi (0.460 ml of 2.61M in hexanes, 1.2 mmol) was added dropwise over a period of 5 min at -78°C . The reaction mixture was stirred for 30 min, then deuterium oxide (0.270 ml, 0.301 g, 15 mmol) was added and the reaction mixture was allowed to warm up to room temperature over 1h period and filtered through a short path of Silica (eluted with 100 ml of dichloromethane/ethyl acetate 1:1 mixture). Removal of all solvents afforded 0.235 g (1 mmol, >99%) of 4-(4-methylphenyl)-1-phenyl-1*H*-1,2,3-triazole-*d*₁ (**1e-*d***) as white solid. Deuterium purity measured by ^1H NMR was >99%.

1e-*d*: ^1H NMR (500 MHz, CDCl_3) δ ppm 7.69 - 7.91 (m, 4 H), 7.49 - 7.60 (m, 2 H), 7.39 - 7.48 (m, 1 H), 7.20 - 7.34 (m, 2 H), 2.40 (s, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 148.4, 138.3, 137.1, 129.8 (+), 129.6 (+), 128.7 (+), 127.4, 125.8 (+), 120.5 (+), 21.3 (+); ^2H NMR (77 MHz, CHCl_3) δ ppm 8.23 (s, 1 D); m.p. 156°C ; LR EI MS m/z 236.2 (M^+).

Deuterium scrambling experiment. To an oven dried 1 ml Wheaton vial equipped with mini-inert valve were added 4-(4-methylphenyl)-1-phenyl-1*H*-1,2,3-triazole-*d*₁ (**1e-*d***) (0.024 g, 0.1 mmol), $\text{Pd}(\text{Ph}_3\text{P})_2\text{Cl}_2$ (3.6 mg, 0.005 mmol) and tetrabutylammonium acetate (0.060 g, 0.2 mmol) under N_2 atmosphere. NMP (0.2 ml) was then added followed by 1-bromo-4-methoxybenzene (0.028 g, 0.019 mmol), and the reaction mixture was stirred at 100°C until judged ~50% complete by quantitative GC/MS analysis. The reaction mixture was diluted with ethyl acetate (2 ml) and filtered through a short Silica path (dichloromethane/ethyl acetate 1:1 mixture used as eluent). The solvents were removed, and the residue was analyzed by ^1H NMR. Analysis showed that initial >99% deuterium incorporation in starting material was retained.

KIE measurements were done as following. To five oven dried 3 ml Wheaton vials equipped with mini-inert valve were added **1e** and **1e-d** (0.024 g, 0.1 mmol each), Pd(Ph₃P)₂Cl₂ (7.2 mg, 0.010 mmol), and tetrabutylammonium acetate (0.121 g, 0.4 mmol) under N₂ atmosphere. NMP (0.4 ml) was then added to each of five vials followed by 1-bromo-4-methoxybenzene (0.056 g, 0.038 ml, 0.3mmol), and the reaction mixtures were stirred at 100°C until judged ~25-30% complete by quantitative GC/MS analysis. The reaction mixtures were diluted with ethyl acetate (1 ml) and filtered through short Silica path (dichloromethane/ethyl acetate 1:1 mixture used as eluent). The solvents were removed, and the residues were analyzed by ¹H NMR using dibromomethane as an internal standard. Data are summarized in Table 1.

Table 1

#	k_H/k_D	k_H/k_D mean value
1	1.1	
2	0.9	
3	1.0	1.0 ± 0.1
4	1.1	
5	1.5 (excluded value)	

Relative rates of reactivity were measured within competition experiments between compounds **1g** and **1a**, and **1h** and **1a**. A set of three parallel experiments was done for each pair. To an oven dried 3 ml Wheaton vial equipped with mini-inert valve were added triazoles (0.1 mmol of each), Pd(Ph₃P)₂Cl₂ (7.2 mg, 0.010 mmol) and tetrabutylammonium acetate (0.120 g, 0.4 mmol) under N₂ atmosphere. NMP (0.4 ml) was then added followed by bromobenzene (0.47 g, 0.032 ml, 0.3 mmol) and the reaction mixture was stirred at 100°C until judged ~25-30% complete by quantitative GC/MS analysis. Molar ratios of products formed and, consequently, relative rates of reactivity were obtained from quantitative GC integration. Data and results are summarized in Table 2.

Table 2

#	k_H/k_{OMe}		k_H/k_{CO_2Et}	
1	0.80		1.00	
2	0.78	0.79 ± 0.01	0.98	0.99 ± 0.01
3	0.78		1.00	

Additionally, arylation of compound **1i** with bromobenzene was tested (**a**) in the presence of 1 molar equivalent of copper(I)iodide to evaluate a potential acceleration of reaction and/or change in regioselectivity of arylation; (**b**) in the presence of 3 molar equivalents of potassium formate in an attempt to trap Heck-type intermediate. Reactions were run in parallel with “blank” (no additive) experiment and monitored by GC/MS.

Results:

- (a) Neither rate of the arylation, nor regioselectivity outcome differed from “blank” (copper-free) experiment;
- (b) No reaction was observed in a presence of hydride source.