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Supporting Information

Highly active recyclable heterogeneous Pd/ZnO nanoparticles catalyst: Sustainable developments for the C-O and C-N bond cross-coupling reactions of aryl halides under ligand-free condition

Mona Hosseini-Sarvari,[a,*] Zahra Razmi

[a] *Department of Chemistry, College of Science, Shiraz University, Shiraz 71454, I. R. Iran*

Contents

1. General Experimental:

The amount of palladium nanoparticles supported on ZnO was measured by ICP analyzer (Varian, Vista-pro) and atomic absorption spectroscopy. The distribution morphology of the product was analyzed by Leica Cambridge, models 360, version V03.03 scanning electron microscope (SEM) and the size of the nano particles was confirmed by a Philips CM10 TEM instrument. X-ray photoelectron spectroscopy (XPS) measurements were conducted with a XR3E2 (VG Microtech) twin anode X-ray source using AlKα=1486.6 eV). The specific surface areas (SSA_{BET}; (m^2 /g)) of the nanopowders were determined with the nitrogen adsorption measurement applying the BET method at 77 K (BELsorp-mini II). A lab-made thermogravimetric analyzer (TGA) was also adopted for studying both the interaction behavior of CO (Linde, 99.99%) as a selective probe molecule with palladium nanoparticles and thermal stability of Pd-supported ZnO nanoparticles after interacted with CO molecules. ^{1}H and ^{13}CNMR spectra were obtained on a Bruker DPX 250 MHz instrument. Elemental analyses were performed using C, H, and N elemental analyzer.

2. Synthesis of nano Pd/ZnO

Pd/ZnO nanoparticles catalyst was prepared by co-precipitation (CP) method. $Zn(NO_3)_2.6H_2O$ (0.267 g, 0.897 mmol), was dissolved in 25 mL distilled water to

obtain a certain concentration solutions. Also $Pd(NO_3)_2.2H_2O$ (0.0266 g, 0.099 mmol) was dissolved in 25 mL distilled water and sonicated to obtain a uniform solutions. Then the corresponding mixed nitrate solutions of palladium and zinc were precipitated with 1M sodium carbonate solution at room temperature to produce a final pH of 8. After aging for 2 h at 70-80 °C, the precipitates were filtered, washed several times with distilled water, dried at 80 °C overnight and then calcined at 723 K for 2 h. Palladium coating was 9.84 wt% as measured by ICP.

3. Synthesis of nanoZnO

ZnO nanoparticles catalyst was prepared by co-precipitation (CP) method. $Zn(NO_3)_2.6H_2O$ (0.267 g, 0.897 mmol), was dissolved in 25 mL distilled water to obtain a certain concentration solutions. Then the corresponding nitrate solution of zinc was precipitated with 1M sodium carbonate solution at room temperature to produce a final pH of 8. After aging for 2 h at 70-80 °C, the precipitate was filtered, washed several times with distilled water, dried at 80 °C overnight and then calcined at 723 K for 2 h.

4. General procedure for *O*-arylation reaction

In the typical procedure *O*-arylation coupling reaction, a mixture of arylhalide

(1mmol), phenol (1 mmol), K_2CO_3 (1 mmol), and Pd/ZnO nanoparticles (0.005 g, which contains 462×10^{-8} mol% of Pd which was determined by ICP) at 120 °C was placed in a round bottom flask. The progress of reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted with ethyl acetate (5 mL) and then centrifuged to separate the catalyst. The solvent was removed under reduced pressure to get the crude product. The crude product was purified by column chromatography to afford the pure product.

5. General procedure for *N*-arylation reaction

A mixture of arylhalide (1mmol), *N*-H heterocycle (1.0 mmol), K_2CO_3 (1 mmol), DMF (1 mL), and Pd/ZnO nanoparticles (0.003 g, which contains 277×10^{-8} mol% of Pd which was determined by ICP) at 120 ˚C was placed in a round bottom flask. Progress of the reaction was monitored by TLC. After the reaction was finished, it was cooled to the room temperature, and DMF was removed under reduced pressure. The residue was diluted with ethyl acetate (5 mL), and centrifuged to separate the catalyst. The centrifugate was washed with water (2×5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. Further purification was achieved by column chromatography.

6. Characterization of the products

Oxydibenzene (Table 5, entry 1). ^{1}H NMR (250 MHz, $CDCl_3$): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.94–7.11 (m, 6H), 7.29–7.35 (m, 4H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 118.9, 123.2, 129.7, 157.2; Anal. Calcd. for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.69; H, 5.92.

1-phenoxynaphthalene (Table 5, entry 2). ^{1}HNMR (250 MHz, $CDCl_3$) δ = 6.87–7.9 (m, 4H), 7.21– 7.34 (m, 3H), 7.40–7.48 (m, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 8.14 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 113.3, 118.4, 118.10, 122.5, 123.1, 123.2, 125.5, 125.7, 126.6, 127.8, 128.1, 129.9, 135.1, 153.1, 157.7; Anal. Calcd. for $C_{16}H_{12}O$: C, 87.25; H, 5.49. Found: C, 87.25; H, 5.49.

2-phenoxynaphthalene (Table 5, entry 3). ^{1}HNMR (250 MHz, $CDCl_3$) δ = 6.94–7.08 (m, 3H), 7.12–7.38 (m, 6H), 7.60–7.80 (m, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 114.1, 119.1, 120.0, 123.5, 124.7, 126.5, 127.1, 127.8, 129.9, 129.9, 130.2, 134.4, 155.1, 157.2; Anal. Calcd. For $C_{16}H_{12}O$: C, 87.25; H, 5.49. Found: C, 87.25; H, 5.48.

1-Bromo-4-phenoxybenzene (Table 5, entry 4). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 6.82–7.02 (m, 4H), 7.09 (m, 1H), 7.27–7.43 (m, 4H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 115.6, 119.0, 120.4, 123.7, 129.9, 132.6, 156.5, 156.7; Anal. Calcd. for $C_{12}H_9BrO$: C, 57.86; H, 3.64; Br, 32.08. Found: C, 57.87; H, 3.64; Br, 32.06.

1-Chloro-4-phenoxybenzene (Table 5, entry 5). ^{1}H NMR (250 MHz, $CDCl_3$) δ =

6.86–6.96 (m, 4H), 7.07–7.11 (m, 1H), 7.21–7.30 (m, 4H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 118.9, 119.9, 123.5, 128.1, 129.6, 129.8, 155.9, 156.8; Anal. Calcd. for $C_{12}H_9ClO$: C, 70.43; H, 4.43; Cl, 17.32. Found: C, 70.42; H, 4.43; Cl, 17.31.

1-Methoxy-4-phenoxybenzene (Table 5, entry 6). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 3.78 (s, 3H), 6.87–7.02 (m, 6H), 7.25–7.31 (m, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 55.6, 114.8, 117.5, 120.8, 122.4, 129.5, 150.0, 155.8, 158.5; Anal. Calcd. For $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.98; H, 6.03.

1-Ethyl-2-phenoxybenzene (Table 5, entry 7). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 1.19 (t, *J* = 7.75 Hz, 3H), 2.64 (q, *J* = 7.25 Hz, 2H), 6.83–6.92 (m, 3H), 7.03–7.13 (m, 3H), 7.23–7.29 (m, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.4, 23.2, 117.4, 119.7, 122.3, 124.0, 127.0, 129.6, 129.7, 135.8, 154.1, 158.1; Anal. Calcd. For $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.81; H, 7.10.

1-Ethyl-3-phenoxybenzene (Table 5, entry 8). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 1.11 (t, *J* = 7.5Hz, 3H), 2.51 (q, *J* = 7.5 Hz, 2H), 6.77–6.92 (m, 5H), 7.18–7.24 (m, 4H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 15.4, 28.7, 116.1, 118.5, 118.8, 122.8, 123.0, 129.5, 129.7, 146.3, 157.2, 157.4; Anal. Calcd. For $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.82; H, 7.12.

1-Nitro-4-phenoxybenzene (Table 5, entry 9). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.00 (d, *J* = 9.25 Hz, 2H), 7.09 (d, *J* = 9.5 Hz, 2H), 7.25 (t, *J* = 7.25 Hz, 1H), 7.40-7.46 (m, 2H), 8.19 (d, *J* = 9.25 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 117.0,

120.5, 125.4, 125.9, 130.3, 142.5, 154.6, 163.3; Anal. Calcd. For $C_{12}H_9NO_3$: C, 66.97; H, 4.22; N, 6.51. Found: C, 66.97; H, 4.22; N, 6.50.

1-Benzyl-2-phenoxybenzene (Table 5, entry 10). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 3.96 (s, 2H), 6.85–7.03 (m, 5H), 7.11–7.23 (m, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 35.9, 117.8, 119.4, 122.6, 123.8, 125.9, 127.5, 128.2, 128.9, 129.5, 130.9, 132.7, 140.4, 154.4, 157.6; Anal. Calcd. For $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.66; H, 6.20.

1-Benzyl-4-phenoxybenzene (Table 5, entry 11). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 3.95 (s, 2H), 6.96-7.23 (m, 14H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 41.1, 118.6, 119.0, 122.9, 126.1, 128.4, 128.8, 129.6, 130.1, 136.0, 141.7, 155.3, 159.4; Anal. Calcd. For $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: 87.66; H, 6.19.

1-Methyl-4-phenoxybenzene (Table 5, entry 15). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 2.34 (s, 3H), 6.93 (d, *J* = 6.25, 2H), 6.99 (d, *J* = 6.25 Hz, 2H), 7.07–7.17 (m, 3H), 7.25–7.35 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.7, 118.3, 119.1, 122.7, 129.6, 130.2, 132.9, 154.7, 157.8; Anal. Calcd. For $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.75; H, 6.56.

1,4-Diphenoxybenzene (Table 5, entry 16). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 6.90-6.93 (m, 10H), 7.21–7.27 (m, 4H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 118.2, 120.4, 123.0, 129.7, 152.6, 157.7; Anal. Calcd. For $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.42; H, 5.37.

Dibenzodioxin (Table 5, entry 17). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 6.86–6.87 (m, 8H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 116.3, 123.7, 142.1; Anal. Calcd. For $C_{12}H_8O_2$: C, 78.25; H, 4.38. Found: C, 78.25; H, 4.39.

4-Phenoxybenzonitrile (Table 5, entry 21). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 6.82 (d, *J* = 7.75 Hz, 2H), 6.91 (d, *J* = 7.72 Hz, 2H), 7.00 (t, *J* = 7.72 Hz, 1H), 7.30 (d, *J*= 8.1 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H); ^{13}CNMR (62.9 MHz, $CDCl_3$) δ = 105.5, 117.8, 118.6, 120.2, 125.0 , 130.1, 134.0, 154.6, 161.5; Anal. Calcd. For $C_{13}H_9NO$: C, 79.98; H, 4.65; N, 7.17. Found: C, 79.97; H, 4.66; N, 7.16.

4-(*P*-tolyloxy)benzonitrile (Table 5, entry 23). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 2.40 (s, 3H), 6.87 (m, 4H), 7.20 (d, *J* = 8.0, 2H), 7.60 (d, *J* = 8.7, 2H); ^{13}CNMR (62.9 MHz, $CDCl_3$) δ = 20.6, 105.2, 117.4, 118.7, 120.2, 130.6, 133.9, 134.7, 152.1, 161.7; Anal. Calcd. For $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.37; H, 5.30; N, 6.69.

2-Phenoxypyridine (Table 5, entry 25). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 6.90 (d, *J* = 8.2 Hz, 1H), 6.98–7.13 (m, 3H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 4.1 Hz, 2H), 7.67 (t, *J* = 8.7 Hz, 1H), 8.15 (d, *J* = 6.3 Hz, 1H); ^{13}CNMR (62.9 MHz, $CDCl_3$) δ = 163.8, 154.2, 147.8, 139.4, 129.7, 124.7, 121.2, 118.4, 111.5; Anal. Calcd. For $C_{11}H_9NO$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.17; H, 5.29; N, 8.16.

1-(4-Phenoxyphenyl)ethanone (Table 5, entry 26). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 2.57 (s, 3H), 6.99 (d, *J* = 9.0 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 7.16–7.22 (m,

1H), 7.35–7.42 (m, 2H), 7.93 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 26.4, 117.2, 120.1, 124.6, 130.0, 130.5, 131.8. 155.4, 161.9, 196.7; Anal. Calcd. For $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.22; H, 5.70.

1-Phenyl-1*H*-pyrrole (Table 6, entry 1). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 6.34 (d, *J* = 2.25 Hz, 2H), 7.08 (d, *J* = 2.25 Hz, 2H), 7.21–7.24 (m, 1H), 7.37–7.42 (m, 4H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 110.3, 119.3, 120.5, 125.6, 129.5, 141.1; Anal. Calcd. For $C_{10}H_9N$: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.88; H, 6.34; N, 9.77.

1-Phenyl-1*H*-benzoimidazole (Table 6, entry 2). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.30–7.53 (m, 8H), 7.81–7.88 (m, 1H), 8.10 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 110.4, 120.5, 122.7, 123.6, 124.0, 128.0, 130.0, 133.6, 136.3, 142.2, 144.0; Anal. Calcd. For $C_{13}H_{10}N_2$: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.39; H, 5.18; N, 14.41.

1-Phenyl-1*H*-indole (Table 6, entry 3). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 6.70 (d, *J* = 2.25 Hz, 1H), 7.14–7.21 (m, 2H), 7.30–7.34 (m, 2H), 7.48–7.49 (m, 4H), 7.55 (d, *J* = 8.50 Hz, 1H), 7.68 (d, *J* = 6.75 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 103.5, 110.4, 120.3, 121.0, 122.3, 124.3, 126.4, 127.9, 129.2, 129.5, 135.8, 139.7; Anal. Calcd. For $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.01; H, 5.73; N, 7.25.

1-Phenyl-1*H*-1,2,4-triazole (Table 6, entry 4). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.40–7.51 (m, 3H), 7.66–7.70 (m, 2H), 8.11 (s, 1H), 8.56 (s, 1H); ^{13}C NMR (62.9

MHz, $CDCl_3$): δ = 120.0, 128.2, 129.8, 131.5, 140.8, 152.6; Anal. Calcd. For $C_8H_7N_3$: C, 66.19; H, 4.86; N, 28.95. Found: C, 66.20; H, 4.86; N, 28.94.

1-Phenyl-1*H*-imidazole (Table 6, entry 5). ^1H NMR (250 MHz, $CDCl_3$) δ = 7.19–7.38 (m, 7H), 7.80 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 118.2, 121.4, 127.4, 129.8, 130.3, 135.5, 137.2; Anal. Calcd. For $C_9H_8N_2$: C, 74.98; H, 5.59; N, 19.43. Found: C, 74.98; H, 5.59; N, 19.42.

1-(*P*-tolyl)-1*H*-pyrrole (Table 6, entry 6). ^1H NMR (250 MHz, $CDCl_3$) δ = 2.33 (s, 3H), 6.31 (brs, 2H), 7.00 (brs, 2H), 7.20 (d, *J* = 8.40 Hz, 2H), 7.27 (d, *J* = 8.10 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.7, 110.0, 119.1, 120.3, 130.1, 135.2, 138.1; Anal. Calcd. For $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.04; H, 7.06; N, 8.91.

1-(4-Methoxyphenyl)-1*H*-indole (Table 6, entry 7). ^1H NMR (250 MHz, $CDCl_3$) δ = 3.82 (s, 3H), 6.63 (d, *J* = 3.25 Hz, 1H), 6.62–7.00 (m, 2H), 7.13–7.25 (m, 3H), 7.34–7.39 (m, 2H), 7.44 (d, *J* = 9.25 Hz, 1H), 7.67 (d, *J* = 6.75 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 55.5, 102.8, 110.3, 114.6, 120.0, 120.9, 122.1, 125.9, 128.2, 128.9, 132.7, 136.2, 158.1; Anal. Calcd. For $C_{15}H_{13}NO$: 80.69; H, 5.87; N, 6.27. Found: C, 80.68; H, 5.87; N, 6.27.

1-(4-Methoxyphenyl)-1*H*-benzoimidazole (Table 6, entry 8). ^1H NMR (250 MHz, $CDCl_3$) δ = 3.82 (s, 3H), 7.12–7.17 (m, 2H), 7.20–7.30 (m, 2H), 7.50–7.53 (m, 1H), 7.55–7.75 (m, 2H), 7.70–7.77 (m, 1H), 8.45 (s, 1H); ^{13}C NMR (62.9

MHz, $CDCl_3$): δ = 55.6, 110.3, 115.1, 120.4, 122.6, 123.5, 125.7, 129.1, 134.2, 142.5, 143.7, 159.3; Anal. Calcd. For $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.49. Found: C, 74.98; H, 5.38; N, 12.48.

1-(*P*-tolyl)-1*H*-1,2,4-triazole (Table 6, entry 9)**.** ^{1}H NMR (250 MHz, $CDCl_3$) δ = 2.40 (s, 3H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 8.10. (s, 1H), 8.53 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.0, 119.7, 130.0, 134.6, 138.2, 140.4, 152.1; Anal. Calcd. For $C_9H_9N_3$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.91; H, 5.70; N, 26.40.

4-(1*H*-1,2,4-Triazol-1-yl)aniline (Table 6, entry 10). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 3.90 (brs, 2H), 6.75 (d, *J* = 8.75 Hz, 2H), 7.40 (d, *J* = 8.75 Hz, 2H), 8.05 (s, 1H), 8.39 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 122.0, 128.5, 140.6, 146.7, 152.1; Anal. Calcd. For $C_8H_8N_4$: C, 59.99; H, 5.03; N, 34.98. Found: C, 59.99; H, 5.04; N, 34.97.

1-(4-Nitrophenyl)-1*H*-pyrrole (Table 6, entry 11). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 6.40 (m, 2H), 7.15 (m, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 8.30 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 112.4, 119.0, 119.3, 125.4, 144.6, 145.1; Anal. Calcd. For $C_{10}H_8N_2O_2$: C, 63.82; H, 4.28; N, 14.89. Found: C, C, 63.82; H, 4.27; N, 14.88.

1-(4-Nitrophenyl)-1*H*-benzoimidazole (Table 6, entry 12). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.30–7.40 (m, 2H), 7.75–7.80 (m, 2H), 8.00–8.07 (m, 2H), 8.42–8.47

(m, 2H), 8.72 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 111.5, 120.6, 123.7, 124.1, 124.4, 126.0, 132.9, 141.9, 143.7, 144.6, 146.1; Anal. Calcd. For $C_{13}H_9N_3O_2$: C, 65.27; H, 3.79; N, 17.56. Found: C, 65.27; H, 3.78; N, 17.55.

1-(4-Fluorophenyl)-1*H*-benzoimidazole (Table 6, entry 13). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.08–7.30 (m, 4H), 7.29–7.33 (m, 3H), 7.72–7.75 (m, 1H), 7.93 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 110.1, 116.8, 120.2, 122.8, 123.7, 126.4, 132.5, 133.3, 141.0, 142.8, 161.9 (*J* = 249 Hz); Anal. Calcd. For $C_{13}H_9FN_2$: C, 73.57; H, 4.27; F, 8.95; N, 13.20. Found: C, 73.57; H, 4.27; F, 8.94, N, 13.20.

162.0 (d, *J* = 248.53 Hz), 143.9, 142.3, 133.9, 132.4, 126.1 (d, *J* = 8.67 Hz), 123.9, 122.9, 120.7, 117.1 (d, *J* = 23.12 Hz), 110.27.

1-(4-Nitrophenyl)-1*H*-indole (Table 6, entry 14). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 6.80 (d, *J* = 3.2 Hz, 1H), 7.15–7.25 (m, 2H), 7.66–7.74 (m, 2H), 7.77–7.80 (d, *J* = 3.3 Hz, 1H), 7.85–7.91 (d, *J* = 9.0 Hz, 2H), 8.36–8.40 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 106.2, 111.3, 121.7, 123.8, 123.7, 125.8, 128.6, 130.4, 135.0, 144.7, 145.0; Anal. Calcd. For $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23; N, 11.76. Found: 70.58; H, 4.22; N, 11.75.

1-(4-Nitrophenyl)-1*H*-1,2,4-triazole (Table 6, entry 15). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 9.0 Hz, 2H), 8.18 (s, 1H), 8.41 (d, *J* = 9.0 Hz, 2H), 8.70 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 124.8, 130.2, 130.3, 138.6, 147.7, 154.8; Anal. Calcd. For $C_8H_6N_4O_2$: C, 50.53; H, 3.18; N, 29.46. Found: 50.53; H, 3.18; N,

29.45.

1-(4-Fluorophenyl)-1*H*-pyrrole (Table 6, entry 16). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.33 (d, *J* = 8.75 Hz, 2H), 7.12 (d, *J* = 8.75 Hz, 2H), 7.01 (d, *J* = 2.25 Hz, 2H), 6.34 (d, *J* = 2.25 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 110.4, 116.4, 119.6, 122.3, 137.7, 159.4 (*J* = 397 Hz); Anal. Calcd. For $C_{10}H_8FN$: C, 74.52; H, 5.00; F, 11.79; N, 8.69. Found: C, 74.52; H, 5.01; F, 11.78; N, 8.68.

1-(4-Fluorophenyl)-1*H*-1,2,4-triazole (Table 6, entry 18). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.18 (d, *J* = 8.0 Hz, 2H), 7.65 (m, 2H), 8.11 (s, 1H), 8.50 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 115.7, 126.1, 136.8 (*J* = 197.0 Hz), 143.2, 160.2, 163.0; Anal. Calcd. For $C_8H_6FN_3$: C, 58.89; H, 3.71; F, 11.64; N, 25.76. Found: C, 58.89; H, 3.70; F, 11.63; N, 25.76.

1-(4-Fluorophenyl)-1*H*-imidazole (Table 6, entry 19). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.14–7.20 (m, 4H), 7.30–7.35 (m, 2H), 7.74 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 116.5, 118.4, 123.4, 130.1, 134.7 (*J* = 194.0 Hz), 160.0, 162.7; Anal. Calcd. For $C_9H_7FN_2$: C, 66.66; H, 4.35; F, 11.72; N, 17.27. Found: C, 66.67; H, 4.35; F, 11.71; N, 17.25.

4-(1*H*-pyrrol-1-yl)benzonitrile (Table 6, entry 20). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 6.42 (s, 2H), 7.15 (s, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 108.1, 111.7, 118.1, 118.5, 119.3, 133.3, 143.2; Anal. Calcd. For $C_{11}H_8N_2$: C, 78.55; H, 4.79; N, 16.66. Found: C, 78.56; H, 4.79;

N, 16.65.

4-(1*H*-Benzo[*d*]imidazol-1-yl)benzonitrile (Table 6, entry 22). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.32–7.39 (m, 2H), 7.55–7.68 (m, 3H), 7.81–7.89 (m, 3H), 8.13 (d, *J* = 9.25 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 110.2, 111.3, 117.9, 120.9, 123.5, 123.8, 124.3, 132.6, 134.1, 139.9, 141.6, 144.2; Anal. Calcd. For $C_{14}H_9N_3$: C, 76.70; H, 4.14; N, 19.17. Found: C, 76.70; H, 4.15; N, 19.17.