**Supporting Information**

**TiO2-ZrO2 composite: Synthesis, characterization and its application as a facile, expeditious and recyclable catalyst for the synthesis of 2-aryl substituted benzoxazole derivatives**

Mahadeo R. Patil, Jayesh T. Bhanushali, Bhari Mallanna Nagaraja, Rangappa S. Keri

***Spectral data of the synthesized compounds***

***2-Phenylbenzo[d]oxazole* (3a)**: White solid, *R*f=0.70 (SiO2; hexane, 100); Mp 99-102°C (lit. Mp 98-100) [1]; 1H NMR (CDCl3, 400 MHz, δ ppm): 8.31-8.27 (m, 2H, Ar), 7.79-7.76 (m, 1H, Ar), 7.37-7.32 (m, 2H, Ar), 7.62-7.49 (m, 4H, Ar); 13C NMR (CDCl3, 75 MHz, δ ppm): 163.4 (C-2), 150.7 (C-3a), 142.1 (C-7a), 130.9 (C-2′), 129.8 (C-4′& C-6′), 127.9 (C-5′), 127.6 (C-1′& C-3′), 125.4 (C-6), 125.1 (C-5), 120.6 (C-7), 110 (C-4); MS (ESI, m/z): 196.23 ([M+H]+, 100).

***2-(4-Hydroxy)benzo[d]oxazole* (3b)**: Yellow solid, *R*f=0.61 (SiO2; EtOAc/*n*-hexane, 1:10); Mp 286-288°C (lit. Mp 287-289) [2] ; 1H NMR (CDCl3, 400 MHz, δ ppm): 8.61 (bs, 1H, OH), 7.69 (d, *J=*8.2Hz, 2H, Ar), 7.65 (d, *J=*8.3Hz, 1H, Ar), 7.14 (m, 1H, Ar), 6.98-6.87 (m, 4H, Ar), 6.85 (t, *J=*8.4Hz, 1H, Ar); 13C NMR (CDCl3, 75 MHz, δ ppm): 160.6 (C-2), 156.1 (C-5′), 152.2 (C-3a), 140.7 (C-7a), 130.9 (C-2), 128.8 (C-6), 121.9 (C-5), 120.7 (C-7), 116.5 (C-1′& C-3′), 114.2 (C-4′& C-6′), 110.6 (C-4); MS (ESI, m/z): 211 ([M+H]+, 100%).

***2-(4-Nitro)benzo[d]oxazole* (3c)**: Yellow solid, *R*f=0.41 (SiO2; EtOAc/*n*-hexane, 1:9); Mp 263-266°C (lit. Mp 264-265) [3]; 1H NMR (CDCl3, 400 MHz, δ ppm): 8.46 (d, *J*=8.3Hz, 2H, Ar), 8.41 (d, *J*=8.3Hz, 2H,Ar), 7.87 (d, *J*=6.9Hz, 1H, Ar),7.67 (d, *J*=7.2Hz, 1H, Ar),7.46*-*7.42 (m, 2H, Ar); 13C NMR (CDCl3, 75 MHz, δ ppm): 163.4 (C-2), 150.6 (C-3a), 148.5 (C-5′), 141.3 (C-7a), 136.8 (C-2′), 129.9 (C-4′), 129.5 (C-1′& C-3′), 128.4 (C-4′& C-6′) 126.7 (C-6), 125.2 (C-5), 121.1 (C-7), 110.8 (C-4); MS (ESI, m/z): 240 ([M+H]+, 100%).

***2-(2-Hydroxy)benzo[d]oxazole* (3d):** White solid, *R*f=0.61 (SiO2; EtOAc/*n*-hexane, 1:20); Mp 120-124°C (lit. Mp 122-124) [3]; 1H NMR (CDCl3, 400 MHz, δ ppm): 8.34 (bs, 1H, OH), 7.42 (t, *J=*8.48Hz, 2H, Ar), 7.26-7.20 (m, 1H, Ar), 7.14 (m, 1H, Ar), 7.10-6.98 (m, 4H, Ar); 13C NMR (CDCl3, 75 MHz, δ ppm): 161.2 (C-2), 157.2 (C-1′), 150.4 (C-3a), 142.3 (C-7a), 132,8 (C-3′), 130.5 (C-5′), 125,1 (C-6), 124.4 (C-4′), 123.7 (C-5), 118.6 (C-6′), 117 (C-7), 113.3 (C-2′), 110.9(C-4); MS (ESI, m/z) : 211.10 ([M+H]+, 100%).

***2-(3-Nitro)benzo[d]oxazole* (3e):** Yellow solid, *R*f=0.44 (SiO2; EtOAc/*n*-hexane, 1:9); Mp 208-211°C (lit. Mp. 211-212) [3]; 1H NMR (CDCl3, 400 MHz, δ ppm): 8.96-8.94 (t, *J*=1.8Hz, 1H, Ar), 8.58-8.54 (dd, *J*=7.9, 1.7Hz, 1H, Ar), 8.28-8.24 (m, 1H, Ar), 7.67-7.63 (t, *J*=7.7 Hz,1H, Ar), 7.75-7.64 (m, 1H, Ar),7.43-7.38 (m, 2H, Ar); 13C NMR (CDCl3, 75 MHz, δ ppm): 161.3 (C-2), 151.8 (C-3a), 149.5 (C-6′), 142.3 (C-7a), 132.6 (C-3′), 130.4 (C-4′), 129.5(C-2′), 126.4 (C-6), 125.5 (C-5′), 125.3 (C-5), 122.2 (C-1), 120.9 (C-7), 111.1 (C-4): MS (ESI, m/z): 240 ([M+H]+, 100%), 194 (50).

***2-(3-Hydroxy)benzo[d]oxazole* (3f):** Yellow solid, *R*f=0.42 (SiO2; EtOAc/*n*-hexane, 1:10); Mp 235-238°C (lit. Mp. 237-238) [3]; 1H NMR (CDCl3, 400 MHz, δ ppm): 8.57 (bs, 1H, OH), 7.66 (d, *J=*8.2Hz, 2H, Ar), 7.64 (d, *J=*8.1Hz,1H, Ar), 7.18 (m, 1H, Ar), 6.99-6.88 (m, 4H, Ar), 6.78 (t, *J=*8.3Hz, 1H, Ar); 13C NMR (CDCl3, 75 MHz, δ ppm): 160.6 (C-2), 155.6 (C-6′), 151.8 (C-3a), 141.2 (C-7a), 130.7 (C-4′), 127.86 (C-2′), 123.1 (C-6), 121.8 (C-5), 120.7 (C-3′), 118.6 (C-7), 116.5 (C-5′), 113.9 (C-1′), 110.9 (C-4); MS (ESI, m/z): 211 ([M+H]+, 100%).

***2-(p-Tolyl)benzo[d]oxazole* (3g):** White solid, *R*f=0.39 (SiO2; EtOAc/*n*-hexane, 1:99); Mp 110-113°C (lit. Mp 112-113) [3]; 1H NMR (CDCl3, 400 MHz, δ ppm): 8.21 (m, 2H, Ar), 7.78-7.73 (m, 2H, Ar), 7.39-7.31 (m, 4H, Ar), 2.49 (s, 3H, CH3); 13C NMR (CDCl3, 75MHz,δ ppm): 161.3 (C-2), 150.4 (C-3a), 142.8 (C-7a), 142.6 (C-5′), 129.8 (C-2′), 127.5 (C-1′& C-3′), 124.4 (C-4′& C-6′), 123.7 (C-6), 123.00 (C-5), 119.6 (C-7), 110.8 (C-4a), 21.2 (C of CH3); (MS, m/z) 210.0865([M+H]+, 100%).

***2-(4-Chlorophenyl)benzo[d]oxazole* (3h):** White solid, *R*f=0.63 (SiO2; EtOAc/*n*-hexane, 1:20); Mp 146-149°C (lit. Mp 147-149) [3]; 1H NMR (CDCl3, 400 MHz, δ ppm): 8.18-8.10 (m, 2H, Ar),7.78-7.69 (m, 2H, Ar),7.52-7.48 (m, 2H, Ar), 7.41-7.36 (m, 2H, Ar); 13C NMR (CDCl3, 75 MHz, δ ppm): 162.5 (C-2), 151.1 (C-3a), 141.7 (C-7a), 138.2 (C-5′), 129.8 (C-4′& C-6′), 128.5 (C-1′& C-3′), 124.5 (C-2′), 124.9 (C-6), 124.5 (C-5), 119.9 (C-7), 110.4 (C-4); MS (ESI, m/z) 230.12 ([M+H]+, 100%).

***2-(4-Flurophenyl)benzo[d]oxazole* (3i):** Viscous liquid, *R*f=0.51 (SiO2; EtOAc/*n*-hexane, 1:20); 1H NMR (CDCl3, 400 MHz, δ ppm): 8.30-8.24 (m, 2H, Ar), 7.77-7.73 (m, 2H, Ar), 7.38-7.33 (m, 2H, Ar), 7.26-7.22 (m, 2H, Ar); 13C NMR (CDCl3, 75 MHz, δ ppm) 163.9 (C-5′), 162.3 (C-2), 150.6 (C-3a), 142.5 (C-7a), 130.1 (C-1′), 129.8 (C-3′), 125.1 (C-2′), 124.8 (C-6), 123.6 (C-5), 119.9 (C-7), 116.4 (C-4′), 116.3 (C-6′), 110.8 (C-4); MS (ESI, m/z): 214 ([M+H]+, 100%).

***2-(3-Chlorophenyl)benzo[d]oxazole* (3j):** White solid, *R*f=0.63 (SiO2; EtOAc/*n*-hexane, 1:20); Mp 130-132°C (lit. Mp 131-133) [4]; 1H NMR (CDCl3, 400 MHz, δ ppm): 8.10 (s, 1H), 8.10-7.99 (m, 1H, Ar), 7.77-7.72 (m, 1H, Ar), 7.68-7.59 (m, 1H, Ar), 7.53-7.47 (m, 2H, Ar), 7.38-7.34 (m, 2H, Ar); 13C NMR (CDCl3, 75 MHz, δ ppm): 161.6 (C-2), 150.3 (C-3a), 141.7 (C-7a), 129.8 (C-4′), 127.7 (C-5′), 126.9 (C-1′), 126.4 (C-3′), 124.9 (C-6), 124.5 (C-5), 120.1 (C-7a), 110.7 (C-4); MS (ESI, m*/z*): 230.13 [M+H]+.

***2-(3-Bromo)benzo[d]oxazole* (3k):** White solid, *R*f=0.53 (SiO2; EtOAc/*n*-hexane, 1:25); Mp 261-263°C (lit. Mp 264-265) [3]; 1H NMR (CDCl3, 400 MHz, δ ppm): 8.46 (t, *J*=1.9Hz, 1H, Ar), 8.24-8.18 (m, 1H, Ar), 7.78-7.75 (m, 1H, Ar), 7.69-7.65 (m, 1H, Ar), 7.60-7.56 (m, 1H, Ar), 7.41-7.36 (m, 3H, Ar); 13C NMR (CDCl3, 75 MHz, δ ppm): 162.3 (C-2), 151.4 (C-3a), 142.4 (C-7a), 134.8 (C-1′) , 131.8 (C-4′), 129.6 (C-2′), 126.00 (C-5′) 125.4 (C-3′), 124.6 (C-6), 123.5 (C-5), 120.7 (C-7), 110.7 (C-4); MS (ESI, m/z): 275.10 ([M+H]+, 100 %).

***2-(4-Methoxyphenyl)benzo[d]oxazole*(3l):** Yellow solid, *R*f=0.64 (SiO2; EtOAc/*n*-hexane, 1:50); Mp 98-101°C (lit. Mp 97-99) [4];1H NMR (CDCl3, 400 MHz, δ ppm): 7.73-7.69 (m, 2H, Ar), 7.54-7.51 (m, 1H, Ar), 7.39-7.34 (m, 2H, Ar), 7.14 (d, *J*=8.7 Hz, 2H, Ar), 3.85 (s, 3H); 13C NMR (CDCl3, 75 MHz, δ ppm): 162.7 (C-2), 162.1 (C-5′), 150.2 (C-3a), 142.7 (C-7a), 128.9 (C-2′), 124.8 (C-6), 124.5 (C-5), 119.9 (C-1′& C-3′), 119.3 (C-7), 113.7 (C-4′& C-6′), 110.8 (C-4), 55.3 (C of OCH3); MS (ESI, m/z) : 226.10 ([M+H]+, 100), 182 (34.4), 210 (38.6).

***2-(3-Methoxy)benzo[d]oxazole* (3m):** Yellow solid, *R*f=0.62 (SiO2; EtOAc/*n*-hexane,1:50); Mp 71-73°C (lit. Mp 72-74) [1]; 1H NMR (CDCl3, 400 MHz, δ ppm): 7.87 (d, *J*=7.2 Hz,1H, Ar), 7.79-7.76 (m, 2H, Ar), 7.63-7.59 (m, 1H, Ar),7.52 (t, *J*=7.9Hz, 1H, Ar), 7.39-7.35 (m, 2H, Ar), 7.14 (d, *J*=8.3 Hz, 1H, Ar), 3.83 (s, 3H, CH3); 13C NMR (CDCl3, 75 MHz, δ ppm): 162.8 (C-2), 161.5 (C-6′), 151.2 (C-3a), 141.7 (C-7a), 129.8 (C-4′), 128.65 (C-2′), 125.6 (C-6), 124.7 (C-5), 120.4 (C-3′), 119.2 (C-7), 113.5 (C-5′) 112.1 (C-1′), 110.7 (C-4), 54.8 (C of OCH3); MS (ESI, m/z) : 226.10 ([M+H]+, 100%).

***2-(Furan-2-yl)benzo[d]oxazole* (3n):** White solid, *R*f=0.73 (SiO2; EtOAc/*n*-hexane, 1:25); Mp 78-82°C (lit. Mp. 80-82) [1]; 1H NMR (CDCl3, 400 MHz, δ ppm): 7.78-7.75 (m, 1H, Ar), 7.70-7.68 (m, 1H, Ar), 7.65-7.59 (m, 1H, Ar), 7.49-7.45 (m, 2H, Ar), 7.39 (d, *J*=3.1Hz, 1H, Ar), 6.67 (dd, *J*=3.3, 2.0Hz, 1H, Ar); 13C NMR (CDCl3, 75 MHz, δ ppm): 160.2 (C-2), 149.8 (C-3a), 142.2 (C-7a), 130.1 (C-2′), 127.6 (C-3′), 127.2 (C-4′), 126.7 (C-5′), 125.3 (C-6), 124.7 (C-5), 120.5 (C-7), 110.6 (C-4); MS (ESI, m/z) : 187 ([M+H]+, 100).

***2-(Thiophen-2-yl)benzo[d]oxazole* (3o):** White solid, *R*f=0.61 (SiO2; EtOAc/*n*-hexane, 1:10); Mp 80-83°C (lit. Mp 82-84) [1]; 1H NMR (CDCl3, 400 MHz, δ ppm): 8.15 (dd, *J*=3.2, 1.4Hz, 1H, Ar), 7.73 (dd, *J*=4.5, 1,2Hz, 1H, Ar), 7.78-7.75 (m, 1H, Ar), 7.57-7.52 (m, 1H, Ar), 7.49-7.45 (m, 1H, Ar), 7.41-7.37 (m, 2H, Ar); 13C NMR (CDCl3, 75 MHz, δ ppm): 160.3 (C-2), 149.8 (C-3a), 142.3 (C-7a), 129.6 (C-2′), 127.7 (C-3′), 127.2 (C-4′), 126.3 (C-5′), 125.7 (C-6), 124.8 (C-5), 120.6 (C-7), 110.7 (C-4); MS (ESI, m/z): 202.10 ([M+H]+, 100 %).

***2-(4-Bromo)benzo[d]oxazole* (3p):** White solid, *R*f=0.55 (SiO2; EtOAc/*n*-hexane, 1:20); Mp 156-159°C (lit. Mp 156-157) [3]; 1H NMR (CDCl3, 400 MHz, δ ppm): 8.16-8.12 (m, 2H, Ar), 7.77-7.73 (m, 1H, Ar), 7.68-7.65 (m, 2H, Ar), 7.54-7.51 (m, 1H, Ar), 7.40-7.36 (m, 2H, Ar); 13C NMR (CDCl3, 75 MHz, δ ppm): 161.6 (C-2), 149.9 (C-3a), 142.7 (C-7a), 131.8 (C-4′&C-6′), 129.5 (C-1′& C-3′), 126.2 (C-2′), 125.8 (C-6), 125.4 (C-5′), 124.7 (C-5), 120.7 (C-7), 110.6 (C-4); MS (ESI, m/z): 275.10 ([M+H]+, 100 %).

***6-methyl-2-benzo[d]oxazole* (3q):** White solid, *R*f=0.51(SiO2; EtOAc/*n*-hexane, 1:10); Mp 94-97°C (lit. Mp 95) [3]; 1H NMR (CDCl3, 400 MHz, δ ppm): 8.37-8.26 (m, 2H, Ar), 7.77 (d, *J*=8.3Hz, 1H, Ar), 7.64-7.57(m, 3H, Ar), 7.38 (m, 1H, Ar), 7.19 (m, 1H, Ar), 2.57(s, 3H, CH3); MS (ESI, *m/z*): 210.14 ([M+H]+, 100 %).

**References**

[1] H. Naeimi, S. Rahmatinejad, Z. S. Nazifi, J. Taiwan Inst. Chem. Eng. 56 (2016) 1.

[2] M. Kodomari, Y. Tamaru, T. Aoyama, Synth. Commun. 34 (2004) 3029.

[3] Y. Lio, D. Mao, S. Lou, J. Qianand, Z. Xu, J. Zhejiang. Univ. Sci. B. 10 (2009) 472.

[4] K. Ravi Kumar, P.V.V.Satyanarayana, B. Srinivasa Reddy, Der Pharma. Chemica. 4 (2012) 761.