Pure Appl. Chem.; doi:10.1351/PAC-CON-10-07-04

Supplementary Information

Chlorine-Free Copper-Catalyzed Oxidative Synthesis of 1,3,4-Oxadiazoles with Molecular Oxygen as the Sole Oxidant

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List of Contents

A. General method----------S2

B. General procedure----------S2

C. Analytical data for 2a-2n----------S2

D. References ----------S7

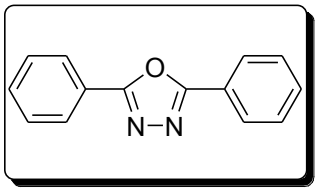
A. General method

^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). GC–MS was obtained using electron ionization. TLC was performed by using commercially prepared 100–400 mesh silica gel plates (GF_{254}) and visualization was effected at 254 nm.

B. General Procedure

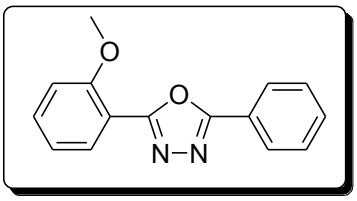
To the mixture of **1** (0.5 mmol), $Cu(OAc)_2$ (0.05 mol, 9.1 mg), DABCO (0.15 mmol, 168 mg) in 2 mL DMF as the solvent. Then the mixture was stirred at 80 ^{o}C for 12 h under 1 atm O_2. After completion, the reaction mixture was washed by saturated NaCl aqueous solution (2×10 mL) and then extracted with ethyl acetate (3×10 mL), and the organic layer was combined, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure, and the residue was purified by preparative TLC (GF_{254}) with petroleum ether/ethyl acetate (50:1 to 20:1) to give the desired products **2**.

C. Analytical data for 2a-2n



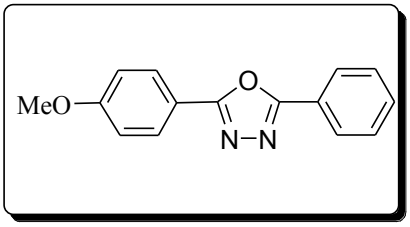
2,5-Diphenyl-1,3,4-oxadiazole (2a)[1]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.14-8.16 (m, 4 H), 7.54-7.56 (m, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 124.0, 127.0, 129.1, 131.8, 164.6 ppm. MS (EI) m/z: 28, 32, 40, 44, 51, 63, 77, 89, 105, 165, 180, 222.



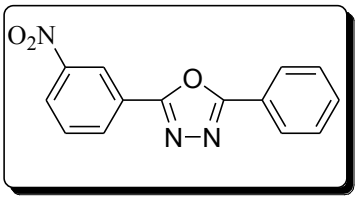
2-(2-Methoxyphenyl)-5-phenyl-1,3,4-oxadiazole (2b)[2]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.99(s, 3 H), 7.07-7.11 (m, 2 H), 7.50-7.52 (m, 4 H), 8.00-8.02 (d, *J* = 7.6 Hz, 1 H),8.12-8.14 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 56.1, 112.0,113.1, 120.8, 124.2, 127.0, 127.1, 128.3, 129.0, 129.5, 133.1, 136.3, 158.0, 171.7 ppm. MS (EI) m/z: 28, 39, 51, 65, 77, 89, 92, 105, 135, 181, 252.



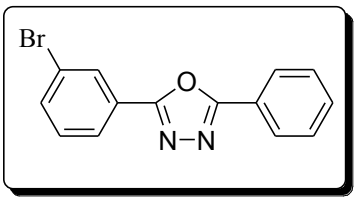
2-(4-Methoxyphenyl)-5-phenyl-1,3,4-oxadiazole (2c)[2]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.86 (s, 3H), 7.00-7.02 (d, *J* = 8.0Hz, 2H), 7.50-7.51 (m, 3H), 8.04-8.11 (m, *J* = 28.0 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.7, 55.5, 114.5, 116.4, 124.1, 126.8, 128.7, 131.5, 132.0, 162.4 ppm. MS (EI) m/z: 28, 39, 50, 51, 63, 64, 65, 77, 89, 92, 105, 135, 181, 252.



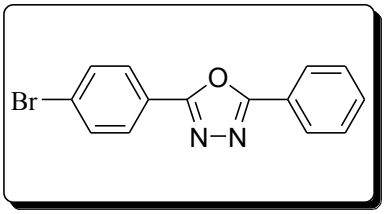
2-(3-Nitrophenyl)-5-phenyl-1,3,4-oxadiazole (2d)[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52-7.57 (m, 3 H), 7.73-7.77 (t, *J*=8.0 Hz, 1 H), 8.12-8.14 (d, *J* = 7.6 Hz, 2 H), 8.37-8.39 (d, *J* = 8.0 Hz,1 H), 8.47-8.49 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 121.7, 123.3, 125.6, 126.1, 127.1, 129.2, 130.5, 132.3, 132.5, 134.2, 148.7 ppm. MS (EI) m/z: 28, 32, 51, 63, 75, 76, 77, 92, 105, 120, 150, 164, 180, 237, 267.



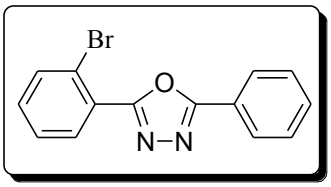
2-(3-Bromophenyl)-5-phenyl-1,3,4-oxadiazole (2e)[4]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.45 (t, *J* = 16 Hz, 1 H), 7.54-7.60 (m, 3 H), 7.68-7.70 (d, *J* = 8.0 Hz, 1 H), 8.09-8.11-6.19 (d, *J* = 8.0 Hz 1H), 8.15-8.16 (d, *J* = 6.4 Hz, 2 H), 8.29 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 123.15, 123.7, 125.5, 125.8, 127.1, 129.2, 129.8, 130.7, 132.0, 134.7, 163.7, 166.1 ppm. MS (EI) m/z: 28, 32, 51, 63, 76, 77, 90, 105, 155, 157, 165, 166, 183, 185, 300.



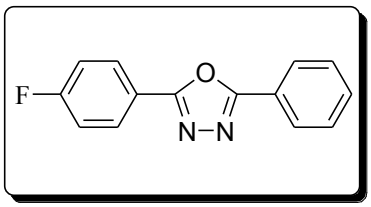
2-(4-Bromophenyl)-5-phenyl-1,3,4-oxadiazole (2f)[5]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50-7.57 (m, 3 H), 7.65-7.67 (d, *J* = 8.0 Hz, 2 H), 7.98-8.00 (d, *J* =8.0 Hz, 2 H), 8.10-8.12 (d, *J* = 7.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.8, 123.7, 127.0, 128.3, 129.1, 131.9, 132.4, 163.8, 164.7 ppm. MS (EI) m/z: 28, 32, 40, 51, 63, 75, 105, 155, 165, 183, 185, 300.



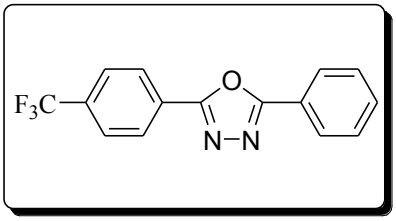
2-(2-Bromophenyl)-5-phenyl-1,3,4-oxadiazole (2g)[6]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.55 (m, 5 H), 7.76-7.78 (d, *J* = 8.0 Hz, 1 H), 8.05-8.07 (d, *J* = 7.6 Hz, 1 H), 8.15-8.16 (d, *J* = 6.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 121.5, 123.8, 125.3, 127.1, 127.7, 131.7, 131.9, 132.5, 134.6, 164.7 ppm. MS (EI) m/z: 28, 32, 51, 63, 77, 91, 105, 157, 165, 183, 185, 300.



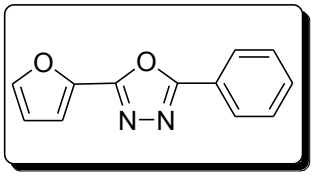
2-(4-Fluorophenyl)-5-phenyl-1,3,4-oxadiazole (2h)[7]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.18-7.22 (m, 2 H), 7.51-7.52 (m, 3 H), 8.10-8.11 (m, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 116.3, 116.5, 120.3, 123.8, 126.9, 129.1, 129.2, 131.8, 163.5, 166.0 ppm. MS (EI) m/z: 28, 32, 51, 63, 77, 91, 105, 123, 164, 240.



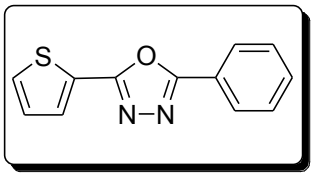
2-Phenyl-5-[4-(trifluoromethyl)phenyl]-1,3,4-oxadiazole (2i)[8]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53-7.55 (m, 3 H), 7.78-7.80 (d, *J* = 8.0 Hz, 3 H), 8.12-8.14 (d, *J* = 8.0 Hz, 2 H), 8.24-8.26 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.2, 123.6, 125.0, 126.1, 127.0, 127.1, 127.2, 129.2, 132.1, 132.8, 133.1, 133.5, 133.8, 165.2, 165.4 ppm. MS (EI) m/z: 28, 32, 39, 51, 63, 75, 77, 89, 95, 105, 145, 165, 173, 233, 290.



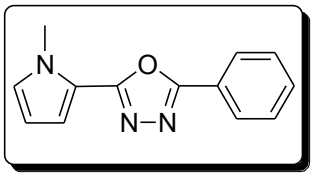
2-(2-Furanyl)-5-phenyl-1,3,4-oxadiazole (2j)[9]

^{1}H NMR ($(CD_3)_2CO$, 400 MHz) δ 6.78-6.79 (m, 1 H), 7.37-7.38 (d, *J* = 3.2 Hz, 1 H), 7.62-7.64 (m, 3 H), 7.94 (s, 1 H), 8.12-8.14 (m, 2 H); ^{13}C NMR ($(CD_3)_2CO$, 100 MHz) δ 113.3, 115.0,124.7, 127.6, 130.2, 132.8, 140.5, 147.3, 158.2, 164.6 ppm. MS (EI) m/z: 28, 32, 39, 51,63, 77, 95, 102, 105, 128, 156, 212.



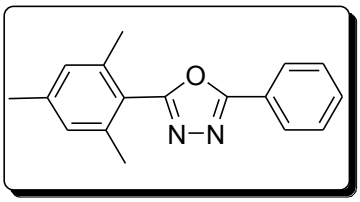
2-(2-Thienyl)-5-phenyl-1,3,4-oxadiazole (2k)[2]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19-7.21 (t, *J* = 4.4 Hz, 1 H), 7.53-7.60 (m, 4 H), 7.84-7.85 (d, *J* =3.6 Hz, 1 H), 8.12-8.13 (d, *J* = 3.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 123.7, 125.3, 127.0, 128.2, 129.1, 129.8, 130.2, 131.8, 160.8, 164.1 ppm. MS (EI) m/z: 28, 32, 39, 51,63, 77, 95, 105, 144, 170, 228.



2-(1-Methyl-1H-pyrrol-2-yl)-5-phenyl-1,3,4-oxadiazole (2l)

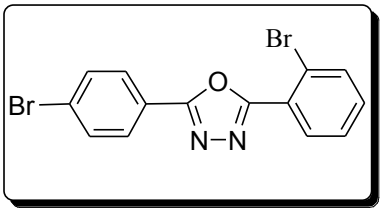
^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.10 (s, 3H), 6.25-6.26 (m, 1H), 6.87 (s, 1 H), 6.94-6.95 (d, *J* = 4.0 Hz, 2H), 7.50-7.53 (m, 3H), 8.10-8.11 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 37.1, 109.0, 114.2, 124.0, 126.8, 128.4, 129.0, 190.0, 159.5, 162.7 ppm. MS (EI) m/z: 28, 32, 39, 51, 63, 77, 95, 105, 164, 211, 225.



2-Mesityl-5-phenyl-1,3,4-oxadiazole (2m)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32-2.36 (m, 9 H), 7.00 (s, 2 H), 7.53-7.54 (m, 2 H), 8.10-8.12 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.5, 21.3, 29.7, 121.1,

124.1, 126.9, 128.9, 129.1, 130.1, 131.7, 138.8, 141.1, 163.3 ppm. MS (EI) m/z: 28, 32, 39, 51, 63, 76, 95, 106, 164, 250, 264.



5-(2-Bromophenyl)-2-(4-bromophenyl)-1,3,4-oxadiazole (2n)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32-2.36 (m, 9 H), 7.00 (s, 2 H), 7.53-7.54 (m, 2 H), 8.10-8.12 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.5, 21.3, 29.7, 121.1, 124.1, 126.9, 128.9, 129.1, 130.1, 131.7, 138.8, 141.1, ppm. MS (EI) m/z: 28, 50, 75, 104, 143, 155, 157, 183, 243, 273, 326, 377.

D. References

(1) Ivanishko, I. S.; Borovkov, V. I. *J. Phy. Chem. B.* **2010**, *114*, 9812-9819.
(2) Stabile, P.; Lamonica, A.; Ribecai, A.; Castoldi, D.; Guercio, G.; Curcuruto, O. *Tetrahedron Lett.* **2010**, *51*, 4801-4805.
(3) Dobrota, C.; Paraschivescu, C. C.; Dumitru, I.; Matache, M.; Baciu, I.; Ruta, L. L. *Tetrahedron Lett.* **2009**, *50*, 1886-1888.
(4) Dailey, S.; Feast, W. J.; Peace, R. J.; Sage, I. C.; Till, S.; Wood, E. L. *J. Mater. Chem.* **2001**, *11*, 2238-2243.
(5) Fang, Y. K.; Liu, C. L.; Chen, W. C. *J. Mater. Chem.* **2011**, *21*, 4778-4786.
(6) Iqbal, R.; Zareef, M.; Ahmed, S.; Zaidi, J. H.; Khan, K. M.; Arfan, M.; Shafique, M.; Shahzad, S. A. *J. Chem. Soc. Pakistan.* **2006**, *28*, 165-168.
(7) Kawano, T.; Yoshizumi, T.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2009**, *11*, 3072-3075.
(8) Hachiya, H.; Hirano, K.; Satoh, T.; Miura, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 2202-2205.
(9) Isobe, T.; Ishikawa, T. *J. Org. Chem.* **1999**, *64*, 6989-6992.