Copper catalyzed aerobic oxidation for the amination of benzoxazole under air

Ke Cao*, Jia-Ling Wang,[†] Lin-Hui Wang,[†] Yuan-Yuan Li,[†] Xing-Hua Yu, Yawen Huang, Junxiao Yang and Guanjin Chang

School of Materials Science and Engineering & State Key Laboratory Cultivation Base for Nonmetal Composite and Functional Materials, Southwest University of Science and Technology, Mianyang, 621010, P. R. China

[†] The three juniors are contributed equally to this work

E-mail: caoke@swust.edu.cn

Context

General information

Spectroscopic data for products

Copies of ¹HNMR/¹³CNMR

Experimental

General information:

The materials were used as purchased, and the CH₃CN was dried and distilled over P₂O₅ before use. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200-300 meshes) is used for column chromatography, and the distillation range of petroleum ether is 60-90°C. ¹H and ¹³C NMR spectra were recorded on the 600MHz or 400MHz instruments, and spectral data are reported in ppm relative to tetramethylsilane (TMS) as internal standard. MS were measured on spectrometer by direct inlet at 70 eV, and signals were given in m/z with relative intensity (%) in brackets.

General procedure for synthesis of 3a-3j

To a 10mL flask were sequentially added CH₃CN (2mL), benzoxazole (60mg, 0.5mmol), amine (0.052mL, 0.6mmol), CuBr₂ (11.2mg, 0.05mmol) and AcOH (0.057mL, 1mmol) under air atmosphere. After the reaction mixture was stirred at 50°C until the substrate was consumed completely (12h), the reaction mixture was cooled to room temperature and filtered through a short silica gel column using AcOEt as eluent. After evaporation of the solvent, the residue was purified by flash chromatography (petroleum ether/AcOEt = 4:1).

Compounds **3a-3j** are known in literature, and the reference are listed as below:

1. Cho, S. H.; Kim, J. Y.; Lee, S. Y.; Chang, S. *Angew. Chem. Int. Ed.* **2009**, *48*, 9127-9130;
2. Kim, J. Y.; Cho, S. H.; Joseph, J.; Chang, S. *Angew. Chem. Int. Ed.* **2010**, *49*, 9899-9903;
3. Wang, J.; Hou, J.-T.; Wen, J.; Zhang, J.; Yu, X.-Q. *Chem. Commun.* **2011**, *47*, 3652-3654;
4. Li, Y.; Xie, Y.; Zhang, R.; Jin, K.; Wang, X.; Duan, C. *J. Org. Chem.* **2011**, *76*, 5444-5449.

Yield: 81%, ^1H NMR(CDCl_3 , 600MHz, *ppm*): δ 7.38-7.37(d, J = 6Hz, 1H), 7.27-7.26(d, J = 6Hz, 1H), 7.19-7.16(dd, J = 6Hz, 1H), 7.05-7.03(dd, J = 6Hz, 1H), 3.82(brs, 4H), 3.70(brs, 4H); ^{13}C NMR(CDCl_3 , 125MHz, *ppm*): δ 161.6, 148.4, 141.9, 124.2, 121.1, 116.3, 108.9, 66.1, 45.7; MS: *m/z*(%) 204(M^+ , 85), 147(100), 119(15), 92(12).

Yield: 95%, ^1H NMR(CDCl_3 , 600MHz, *ppm*): δ 7.39-7.38(d, J = 6Hz, 1H), 7.25-7.24(d, J = 6Hz, 1H), 7.18-7.16(dd, J = 6Hz, 1H), 7.03-7.01(dd, J = 6Hz, 1H), 3.70(brs, 4H), 1.69(brs, 6H); ^{13}C NMR(CDCl_3 , 125MHz, *ppm*): δ 161.6, 148.2, 141.6, 124.1, 120.9, 115.6, 108.7, 46.9, 25.2, 23.8; MS: *m/z*(%) 202(M^+ , 100), 134(67), 147(41), 173(35), 187(19).

Yield: 31%, ^1H NMR(CDCl_3 , 600MHz, *ppm*): δ 7.36-7.35(d, J = 6Hz, 1H), 7.24-7.23(d, J = 6Hz, 1H), 7.15-7.12(dd, J = 6Hz, 1H), 6.99-6.96(dd, J = 6Hz, 1H), 3.64(brs, 4H), 2.02(brs, 4H); ^{13}C NMR(CDCl_3 , 125MHz, *ppm*): δ 160.8, 148.9, 143.4, 123.8, 120.0, 115.9, 108.5, 47.4, 25.5; MS: *m/z*(%) 188(M^+ , 100), 133(82), 160(64).

Yield: 92%, ^1H NMR(CDCl_3 , 600MHz, *ppm*): δ 7.39-7.38(d, J = 6Hz, 1H), 7.28-7.27(d, J = 6Hz, 1H), 7.24-7.15(m, 5H), 7.03-7.00(dd, J = 6Hz, 1H), 4.84(s, 2H), 3.94-3.92(t, J = 6Hz, 2H), 2.99-2.97(t, J = 6Hz, 2H); ^{13}C NMR(CDCl_3 , 125MHz, *ppm*): δ 161.9, 148.7, 142.9, 133.9, 132.2, 128.7, 126.7, 126.5, 126.3, 123.9, 120.5, 116.1, 108.7, 47.1, 43.0, 28.4; MS: m/z (%) 250(M^+ , 100), 117(64), 149(42), 235(18).

Yield: 65%, ^1H NMR(CDCl_3 , 400MHz, *ppm*): δ 7.36-7.34(d, J = 8Hz, 1H), 7.24-7.22(d, J = 8Hz, 1H), 7.15-7.11(dd, J = 8Hz, 1H), 6.99-6.95(dd, J = 8Hz, 1H), 3.61-3.55(m, J = 16, 8Hz, 4H), 1.28-1.25(t, J = 8Hz, 6H); ^{13}C NMR(CDCl_3 , 100MHz, *ppm*): δ 161.9, 148.6, 143.0, 123.8, 120.0, 115.6, 108.5, 42.9, 13.4; MS: m/z (%) 190(M^+ , 57), 147(100), 161(44), 175(19).

Yield: 75%, ^1H NMR(CDCl_3 , 400MHz, *ppm*): δ 7.56-7.54(d, J = 8Hz, 1H), 7.40-7.32(m, 6H), 7.29-7.25(dd, J = 8Hz, 1H), 7.16-7.12(dd, J = 8Hz, 1H), 4.86(s, 2H), 3.28(s, 3H); ^{13}C NMR(CDCl_3 , 100MHz, *ppm*): δ 161.2, 147.6, 144.8, 134.8, 129.0, 128.3, 127.9, 125.1, 122.1, 115.5, 109.3, 54.4, 35.9; MS: m/z (%) 238(M^+ , 100), 91(67), 223(59), 147(54).

Yield: 37%, ^1H NMR(CDCl_3 , 600MHz, *ppm*): δ 7.42-7.41(d, J = 6Hz, 1H), 7.28-7.27(d, J = 6Hz, 1H), 7.18-7.16(dd, J = 6Hz, 1H), 7.03-7.01(dd, J = 6Hz, 1H), 4.27(m, 2H), 1.40-1.39(d, J = 6Hz, 12H); ^{13}C NMR(CDCl_3 , 125MHz, *ppm*): δ 161.4, 147.9, 141.1, 124.1, 120.4, 115.4, 108.5, 48.1, 20.7; MS: $m/z(\%)$ 218(M^+ , 59), 161(100), 134(56), 175(41), 133(18).

Yield: 95%, ^1H NMR(CDCl_3 , 600MHz, *ppm*): δ 7.16 (s, 1H), 7.11-7.10(d, J = 6Hz, 1H), 6.80-6.79(dd, J = 6Hz, 1H), 3.64(brs, 4H), 2.39(s, 3H), 1.66(brs, 6H); ^{13}C NMR(CDCl_3 , 125MHz, *ppm*): δ 162.4, 146.7, 143.3, 133.2, 120.8, 116.2, 107.7, 46.4, 25.1, 23.9, 21.4; MS: $m/z(\%)$ 216(M^+ , 100), 148(44), 161(21), 187(20).

Copies of ^1H NMR/ ^{13}C NMR

WLH-3a

WLH-3a

WLH-3b

WLH-3b

WLH-3c

WLH-3c

WLH-3d

WLH-3d

WLH-3e

WLH-3e

WLH-3f

WLH-3f

WLH-3g

WLH-3g

WLH-3j

WLH-3j