A practical approach for synthesis of 2-amino-benzoxazole in water

Ke Cao*, Jia-Ling Wang, and Lin-Hui Wang

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

E-mail: caoke@swust.edu.cn

Context

General information

Spectroscopic data for products

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

Experimental

General information:

The materials were used as purchased, and distilled water was used as water source. 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 ^{13}C 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-3d and 3f-3g

To a 10mL flask were sequentially added benzoxazole (60mg, 0.5mmol), amine (0.6mmol), H_2O (1mL), CuBr_2 (22.4mg, 0.1mmol), PPh_3 (26.2mg, 0.1mmol), $\text{K}_2\text{S}_2\text{O}_8$ (135mg, 0.5mmol) and AcOH (0.057mL, 1mmol) under air atmosphere. After the reaction mixture was stirred at 40°C until the substrate was consumed completely (6h), the reaction mixture was quenched with $\text{NaHSO}_3(\text{aq.})$ and cooled to room temperature. Then extracted with AcOEt (3x15mL), washed with $\text{NaHCO}_3(\text{aq.})$ (3x5mL), brine (3x10mL) and dried over anhydrous sodium sulfate. After evaporation of the solvent under vacuum, the residue was purified by column chromatography.

Compounds **3a-3g** 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.

Spectroscopic data for products

Yield: 75%, ^1H NMR(CDCl_3 , 400MHz, ppm): δ 7.39-7.37(d, J = 8Hz, 1H), 7.27-7.25(d, J = 8Hz, 1H), 7.19-7.15(dd, J = 8Hz, 1H), 7.06-7.01(dd, J = 8Hz, 1H), 3.82-3.79(m, 4H), 3.69-3.67(m, 4H); ^{13}C NMR(CDCl_3 , 100MHz, 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^+ , 83), 147(100), 119(17), 92(12).

Yield: 34%, ^1H NMR(CDCl_3 , 400MHz, ppm): δ 7.35-7.33(d, J = 8Hz, 1H), 7.24-7.22(d, J = 8Hz, 1H), 7.16-7.12(dd, J = 8Hz, 1H), 7.01-6.97(dd, J = 8Hz, 1H), 3.66-3.64(m, 4H), 1.68(brs, 6H); ^{13}C NMR(CDCl_3 , 100MHz, ppm): δ 161.6, 148.2, 141.6, 124.2, 120.8, 115.7, 108.7, 46.8, 25.2, 23.9; MS: m/z (%) 202(M^+ , 100), 134(64), 147(45), 173(33), 187(18).

Yield: 41%, ^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, 148.8, 143.4, 123.8, 120.0, 115.9, 108.5, 47.4, 25.5; MS: m/z (%) 188(M^+ , 100), 133(80), 160(65).

Yield: 15%, ^1H NMR(CDCl_3 , 400MHz, ppm): δ 7.55-7.53(d, J = 8Hz, 1H), 7.39-7.31(m, 6H), 7.28-7.24(dd, J = 8Hz, 1H), 7.15-7.11(dd, J = 8Hz, 1H), 4.86(s,

2H), 3.27(s, 3H); $^{13}\text{CNMR}(\text{CDCl}_3, 100\text{MHz}, \text{ppm})$: δ 161.7, 148.7, 143.1, 136.1, 128.6, 127.6, 127.5, 123.9, 120.3, 115.9, 108.6, 53.6, 35.0; MS: $m/z(\%)$ 238(M^+ , 100), 91(64), 223(59), 147(56).

Yield: 35%, $^1\text{HNMR}(\text{CDCl}_3, 400\text{MHz}, \text{ppm})$: δ 7.36-7.34(d, $J = 8\text{Hz}$, 1H), 7.24-7.22(d, $J = 8\text{Hz}$, 1H), 7.15-7.11(dd, $J = 8\text{Hz}$, 1H), 6.99-6.95(dd, $J = 8\text{Hz}$, 1H), 3.60-3.55(m, $J = 16, 8\text{Hz}$, 4H), 1.28-1.25(t, $J = 8\text{Hz}$, 6H); $^{13}\text{CNMR}(\text{CDCl}_3, 100\text{MHz}, \text{ppm})$: δ 161.9, 148.6, 143.0, 123.8, 120.0, 115.6, 108.5, 42.9, 13.4; MS: $m/z(\%)$ 190(M^+ , 55), 147(100), 161(44), 175(18).

Yield: 72%, $^1\text{HNMR}(\text{CDCl}_3, 400\text{MHz}, \text{ppm})$: δ 7.19(s, 1H), 7.14-7.12(d, $J = 8\text{Hz}$, 1H), 6.86-6.84(d, $J = 8\text{Hz}$, 1H), 3.82-3.80(m, 4H), 3.70-3.68(m, 4H), 2.39(s, 3H); $^{13}\text{CNMR}(\text{CDCl}_3, 100\text{MHz}, \text{ppm})$: δ 161.9, 146.6, 142.1, 133.9, 121.8, 116.7, 108.3, 66.2, 45.8, 21.5; MS: $m/z(\%)$ 218(M^+ , 100), 161(60), 149(22).

Yield: 52%, $^1\text{HNMR}(\text{CDCl}_3, 400\text{MHz}, \text{ppm})$: δ 7.34(s, 1H), 7.17-7.15(d, $J = 8\text{Hz}$, 1H), 7.02-6.99(d, $J = 8\text{Hz}$, 1H), 3.83-3.81(m, 4H), 3.71-3.69(m, 4H); $^{13}\text{CNMR}(\text{CDCl}_3, 100\text{MHz}, \text{ppm})$: δ 162.3, 147.1, 140.7, 129.6, 120.9, 116.5, 109.4, 66.1, 45.7; MS: $m/z(\%)$ 238(M^+ , 100), 181(58), 149(30).

Copies of $^1\text{HNMR}/^{13}\text{CNMR}$

WJ-3a

3a

7.39
7.39
7.37
7.37
7.27
7.25
7.19
7.19
7.17
7.17
7.15
7.15
7.06
7.05
7.04
7.03
7.02
7.01

3.82
3.81
3.79
3.69
3.68
3.67

1.35
1.32
1.30
1.26
0.99
0.98
0.92
0.90
0.88
0.87
0.86
0.85

WJ-3a

3a

— 161.64

— 148.44

— 141.93

— 124.21

— 121.12

— 116.29

— 108.86

77.21

77.00

76.79

— 66.09

— 45.73

WJ-3b

3b

7.35
7.35
7.33
7.33
7.26
7.24
7.24
7.22
7.22
7.16
7.16
7.14
7.14
7.12
7.12
7.01
7.01
6.99
6.99
6.97
6.97

3.66
3.64

1.68

0.07
-0.00

WJ-3b

3b

WJ-3c

3c

7.36
7.35
7.26
7.24
7.23
7.15
7.13
7.12
6.99
6.97
6.96

3.64

2.02

1.24

0.88

-0.01

WJ-3c

3c

—160.83

—148.89

—143.36

—123.77

—120.02

—115.86

—108.52

77.21

77.00

76.79

—47.36

—25.52

WJ-3d

7.55
7.53
7.39
7.38
7.37
7.36
7.35
7.34
7.31
7.28
7.26
7.24
7.15
7.13
7.11

4.86

3.27

1.25

0.07
-0.00

3d

WJ-3d

WJ-3e

3e

7.36
7.34
7.26
7.24
7.22
7.15
7.13
7.11
6.99
6.97
6.95

3.60
3.59
3.57
3.55

1.28
1.27
1.25

— 0.91

— 0.07
— -0.01

WJ-3e

3e

— 161.87

— 148.59

— 143.03

— 123.78

— 120.00

— 115.62

— 108.46

— 77.32

— 77.00

— 76.68

— 42.92

— 13.36

— 0.93

WJ-3f

3f

WJ-3f

3f

— 161.85 — 146.63 — 142.06 — 133.99 — 121.84 — 116.68 — 108.26 — 77.32
— 77.20 — 77.00 — 76.68 — 66.15 — 45.76 — 21.50

WJ-3g

3g

7.34
7.33
7.26
7.17
7.15
7.02
7.01
7.00
6.99

3.83
3.82
3.81
3.71
3.70
3.69

1.25
0.99
0.97
0.92
0.90
0.89
0.87

0.07
-0.01

WJ-3g

3g