Chinese Journal of Catalysis 38 (2017) 1842–1850

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/chnjc

Article

Copper-catalyzed amination of phenylboronic acids with benzofurazan 1-oxides

Manman Wang [a], Yunyun Li [b], Fen Wang [b,#], Xingwei Li [a,b,*]

[a] *Henan Key Laboratory of Organic Functional Molecule and Drug Innovation, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, Henan, China*

[b] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China*

ARTICLE INFO

Article history:
Received 26 June 2017
Accepted 7 August 2017
Published 5 November 2017

Keywords:
C–N coupling
Arylboronic acid
Benzofurazan 1-oxide
Redox-neutral
Bifunctional

ABSTRACT

CuCl/Phen can catalyze the C–N coupling between arylboronic acid and benzofurazan 1-oxide. This reaction occurred under mild and redox-neutral conditions with benzofurazan 1-oxide as an aminating reagent via ring scission, leading to a bifunctionalized aminonitrobenzene.

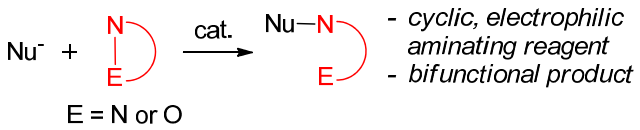
1. Introduction

The C–N bond is a key linkage in most pharmaceuticals and organic functional molecules [1–6]. Traditional methods to construct C–N bonds include the Goldberg reaction [5–11], the Buchwald-Hartwig coupling [12–16], the Chan-Lam coupling [17–24], and C–H activation-amination/amidation [25–45]. Although very efficient, these methods either require the employment of functionalized arenes [46], functionalized aminating reagents [47–53], or oxidative conditions [54]. From the redox-economy aspect, the amination reaction is ideally performed under redox-neutral conditions. Moreover, it is ideal that this process allows the introduction of an amine group simultaneously with another functional group. The most straightforward strategy to realize this is probably the employment of an azacycle (Scheme 1). Upon cleavage of N–E bond, both the N and the E atoms can be incorporated, especially under redox-neutral conditions. Indeed, this difunctionalization process has been recently realized by us and others in C–H activation chemistry using anthranils [50,55–58] and azabenzonorbornadienes [59].

Although appealing, difunctionalization via scission of an azacycle requires overcome of unfavorable thermodynamics associated with scission of unstrained rings. In this respect and as a continuation of our interest in amination of nucleophiles [50,55,59], we reasoned that benzofurazan 1-oxide may function as an aminating reagent because it is known to undergo ring scission to give an *ortho* dinitrosobenzene [60,61]. On the other hand, although simple amination of phenyboronic acid has been reported using nitrosobenzene [62], either a stoichi-

* Corresponding author. Tel: +86-411-84379089; E-mail: xwli@dicp.ac.cn
# Corresponding author. E-mail: wangfen@dicp.ac.cn

This work was supported by the National Natural Science Foundation of China (21525208 and 21472186) and Research Fund from Henan Normal University (5101034011009).
DOI: 10.1016/S1872-2067(17)62914-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 11, November 2017



Scheme 1. Amination leading to bifuncationality.

ometric amount of copper salt or terminal reducing reagent is necessary. We now report copper-catalyzed amination of phenyboronic acid using benzofurazan 1-oxide, leading to difunctionalization under mild and redox-neutral conditions.

2. Experimental

2.1. General

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All the reactions were carried out under nitrogen atmosphere using standard Schlenk technique. The ^{1}H NMR spectra were recorded on a 400 or 600 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 100 or 150 MHz. The ^{19}F NMR spectra were recorded at 565 MHz. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), m (multiplet), br s (broad singlet), etc. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale. High resolution mass spectra were obtained on an Agilent Q-TOF 6540 spectrometer. Column chromatography was performed on silica gel (300–400 mesh) using ethyl acetate (EA)/petroleum ether (PE).

The [*c*][1,2,5]oxadiazole 1-oxide **1a**, **1b** and **1h** were obtained from commercial sources. The others were prepared following a published procedure [63]. Compounds **6** and **7** were prepared according to the literature report [64,65].

2.2. General procedure for the synthesis of compounds *3* and *3'*

Benzofuroxan (0.2 mmol), phenylboronic acid (0.6 mmol), CuCl (10 mol%), 1,10-phen (10 mol%) and Na_2CO_3 (2 equiv.) were charged into a Schlenk tube, to which was added anhydrous 1,4-dioxane (2 ml) under N_2 atmosphere. The reaction mixture was stirred at 60 °C for 12 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the product.

2.3. Spectral data for products

3aa. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (br s, 1H), 8.12 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.31–7.25 (m, 1H), 7.22–7.12 (m, 4H), 6.70 –6.67 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 138.7, 135.7, 133.2, 129.8, 126.7, 125.7, 124.4, 117.5, 116.1. HRMS calc. for $C_{12}H_{11}N_2O_2^+$ $(M + H)^+$: 215.0815; found: 215.0818.

3ab. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (br s, 1H), 8.09 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.26–7.22 (m, 1H), 7.13 (m, 2H), 7.09–7.03 (m, 3H), 6.66–6.61 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 135.9, 135.7, 135.7, 132.8, 130.3, 126.6, 124.8, 117.1, 116.0, 21.0. HRMS calc. for $C_{13}H_{13}N_2O_2^+$ $(M + H)^+$: 229.0972; found: 229.0974.

3ac. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (br s, 1H), 8.10 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.38–7.31 (m, 2H), 7.36–7.32 (m, 1H), 7.12–7.10 (m, 3H), 6.66–6.62 (m, 1H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 143.6, 135.9, 135.7, 132.9, 126.7, 126.6, 124.3, 117.2, 116.1, 34.6, 31.4. HRMS calc. for $C_{16}H_{19}N_2O_2^+$ $(M + H)^+$: 271.1441; found: 271.1443.

3ad. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (br s, 1H), 8.11 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.32–7.24 (m, 1H), 7.22–7.12 (m, 2H), 7.08–6.99 (m, 2H), 6.96 (d, *J* = 8.6 Hz, 1H), 6.73–6.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6 (d, *J* = 245.8 Hz), 143.6, 135.8, 134.6 (d, *J* = 3.0 Hz), 133.0, 127.0 (d, *J* = 8.3 Hz), 126.7, 117.5, 116.6 (d, *J* = 22.5 Hz), 115.7. HRMS calc. for $C_{12}H_{10}FN_2O_2^+$ $(M + H)^+$: 233.0721; found: 233.0725.

3ae. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (br s, 1H), 8.11 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.32–7.28 (m, 3H), 7.15–7.12 (m, 2H), 7.09 (dd, *J* = 8.6, 1.0 Hz, 1H), 6.74–6.70 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 137.4, 135.8, 133.5, 130.8, 129.9, 126.8, 125.5, 118.0, 115.9. HRMS calc. for $C_{12}H_{10}ClN_2O_2^+$ $(M + H)^+$: 249.0425; found: 249.0428.

3af. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (br s, 1H), 8.20 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.57–7.47 (m, 2H), 7.43–7.35 (m, 1H), 7.24–7.11 (m, 3H), 6.83–6.79 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 138.0, 135.8, 133.6, 132.8, 126.8, 125.7, 118.4, 118.1, 116.0. HRMS calc. for $C_{12}H_{10}BrN_2O_2^+$ $(M + H)^+$: 292.9920; found: 292.9922.

3ag. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (br s, 1H), 8.20 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.77–7.67 (m, 2H), 7.43–7.35 (m, 1H), 7.22 (dd, *J* = 8.6, 0.8 Hz, 1H), 7.05–7.03 (m, 2H), 6.84–6.80 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 138.8, 138.7, 135.8, 133.8, 126.8, 125.8, 118.2, 116.1, 89.0. HRMS calc. for $C_{12}H_{10}IN_2O_2^+$ $(M + H)^+$: 340.9781; found: 340.9785.

3ah. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (br s, 1H), 8.23 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.67–7.62 (m, 4H), 7.50–7.46 (m, 2H), 7.44–7.38 (m, 2H), 7.36–7.32 (m, 3H), 6.83– 6.79 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 140.2, 138.4, 138.0, 135.8, 133.4, 128.9, 128.4, 127.5, 126.9, 126.8, 124.4, 117.7, 116.3. HRMS calc. for $C_{18}H_{15}N_2O_2^+$ $(M + H)^+$: 291.1128; found: 291.1131.

3ai. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (br s, 1H), 8.20 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.40–7.34 (m, 1H), 7.31–7.26 (m, 2H), 7.19 (d, *J* = 8.6 Hz, 1H), 7.17–7.11 (m, 2H), 6.82–6.74 (m, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 148.2, 143.1, 136.3, 135.8, 133.2, 126.7, 125.6, 122.9, 117.7, 116.0, 21.1. HRMS calc. for $C_{14}H_{13}N_2O_4^+$ $(M + H)^+$: 273.0870; found: 273.0874.

3aj. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (br s, 1H), 8.20 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.50–7.40 (m, 4H), 7.39–7.30 (m, 2H), 7.22–7.19 (m, 2H), 7.10–7.01 (m, 3H), 6.77–6.67 (m, 1H), 5.11 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 144.4, 136.8, 135.8, 132.5, 131.5, 128.7, 128.2, 127.5, 127.0, 126.6, 116.9, 116.0, 115.8, 70.4. HRMS calc. for $C_{19}H_{17}N_2O_3^+$ $(M + H)^+$: 321.1234; found: 321.1236.