Direct arylation of benzoazoles with aldehydes utilizing metal-organic framework

Fe₃O(BDC)₃ as a recyclable heterogeneous catalyst

Son H. Doan, Khoa D. Nguyen, Tung T. Nguyen, Nam T. S. Phan*

Faculty of Chemical Engineering, HCMC University of Technology, VNU-HCM,

268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Viet Nam

*Email: ptsnam@hcmut.edu.vn

Ph: (+84 8) 38647256 ext. 5681 Fx: (+84 8) 38637504

Supporting Information

Materials and instrumentation

All reagents and starting materials were obtained commercially from Sigma-Aldrich and Merck, and were used as received without any further purification unless otherwise noted. Nitrogen physisorption measurements were conducted using a Micromeritics 2020 volumetric adsorption analyzer system. Samples were pretreated by heating under vacuum at 150 °C for 3 h. A Netzsch Thermoanalyzer STA 409 was used for thermogravimetric analysis (TGA) with a heating rate of 10 °C/min under a nitrogen atmosphere. X-ray powder diffraction (XRD) patterns were recorded using a Cu K α radiation source on a D8 Advance Bruker powder diffractometer. Scanning electron microscopy studies were conducted on a S4800 Scanning Electron Microscope (SEM). Transmission electron microscopy studies were performed using a JEOL JEM 1400 Transmission Electron Microscope (TEM) at 80 kV. The Fe₃O(BDC)₃ sample was dispersed on holey carbon grids for TEM observation. Elemental analysis with atomic

absorption spectrophotometry (AAS) was performed on an AA-6800 Shimadzu. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 instrument, with samples being dispersed on potassium bromide pallets.

Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μ m). The temperature program for GC analysis held samples at 120 °C for 1 min; heated them from 120 to 180 °C at 40 °C/min; held them at 180 °C for 1 min; heated them from 180 to 280 °C at 50 °C/min and held them at 280 °C for 3 min. Inlet and detector temperatures were set constant at 280 °C. Diphenyl ether was used as an internal standard to calculate GC yield. GC-MS analyses were performed using a Shimadzu GCMS-QP2010Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μ m). The temperature program for GC-MS analysis held samples at 50 °C for 2 min; heated samples from 50 to 280°C at 10 °C/min and held them at 280 °C for 10 min. Inlet temperature was set constant at 280 °C. MS spectra were compared with the spectra gathered in the NIST library. The ¹H NMR and ¹³C NMR were recorded on Bruker AV 500 spectrometers using residual solvent peak as a reference.

Synthesis of the metal-organic framework Fe₃O(BDC)₃

In a representative preparation, H_2BDC ($H_2BDC=1,4$ -benzenedicarboxylic acid; 0.199 g, 1.2 mmol), FeCl₃.6H₂O (0.325 g, 2.0 mmol) and were added to a mixture of ethanol (60

mL) and DMF (DMF = N,N° -dimethylformamide; 60 mL). The mixture was magnetically stirred for 30 min to dissolve the solids completely. The solution was equally added into eight 20-mL vials. The vials were securely covered and then heated at 85 °C for 48 h, forming the framework as light orange crystals. Subsequent to this period, the vials were cooled down to room temperature, and the crystals were collected by decantation. The as-synthesized framework was washed with DMF (3× 10 ml), and immersed in methanol (3× 10 ml). The framework crystals were then dried in a shlenkline under vacuum at 140 °C for 6 h, producing 0.318g of Fe₃O(BDC)₃ in the form of brick red crystals (47 % yield based on H₂BDC).



Fig. S1. X-ray powder diffractograms of the Fe₃O(BDC)₃.



Fig. S2. SEM micrograph of the Fe₃O(BDC)₃.



Fig. S3. TEM micrograph of the Fe₃O(BDC)₃.



Fig. S4. Pore size distribution of the $Fe_3O(BDC)_3$.



Fig. S5. Nitrogen adsorption/desorption isotherm of the Fe₃O(BDC)₃. Adsorption data are shown as closed triangles and desorption data as open triangles. Langmuir surface areas of 890 m²/g were recorded.



Fig. S6. TGA analysis of the Fe₃O(BDC)₃.



Fig. S7. FT-IR spectra of biphenyl-4,4'-dicarboxylic acid (a), and the Fe₃O(BDC)₃ (b).

Characterization of products

2-Phenylbenzothiazole (entry 1)

Prepared as shown in the general experimental procedure and purified on silica gel (petroleum ether/ethyl acetate = 98:2): white

solid, 90% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.12 – 8.10 (m, 3H), 7.90 (d, *J* = 9.5 Hz, 1H), 7.58 – 7.50 (m, 4H), 7.40 (t, *J* = 8.5 Hz, 1H). This compound is known.¹

2-(4-Methylphenyl)benzothiazole (entry 2)



Prepared as shown in the general experimental procedure and purified on silica gel (petroleum ether/ethyl acetate = 98:2):

¹ Liu, S; Chen, R.; Guo, X.; Yang, H.; Deng, G.; Li, C. J. Green Chem. 2012, 14, 1577.

white solid, 72% yield. ¹H-NMR (500 MHz, CDCl₃) δ 8.09 (d, *J* = 7.5 Hz, 2H), 8.00 (d, *J* = 5.5 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 9.5 Hz, 1H), 7.37 (t, *J* = 10 Hz 1H), 7.28 (d, *J* = 8.5 Hz, 2H), 2.43 (s, 3H). This compound is known.¹

2-(4-Methoxyphenyl)benzothiazole (entry 3)

Prepared as shown in the general experimental procedure and purified on silica gel (petroleum ether/ethyl acetate = 98:2): white solid, 84% yield. ¹H-NMR (500 MHz, CDCl₃) δ 8.01 – 8.08 (m, 3H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.49 (t, *J* = 9 Hz, 1H), 7.39 (t, *J* = 7 Hz, 1H), 7.00 (d, *J* = 9.5 Hz, 2H), 3.89 (s, 3H). This compound is known.¹

2-(4-Fluorophenyl)benzothiazole (entry 4)



Prepared as shown in the general experimental procedure and purified on silica gel (petroleum ether, then 5% ethyl acetate in

petroleum ether): light yellow solid, 81% yield. ¹H NMR (600 MHz, CDCl₃) δ 8.09 – 8.02 (m, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.15 (t, J = 8.5 Hz, 1H). ¹⁹F NMR (565 MHz, CDCl₃) δ -108.72 (dq, J = 8.4, 5.4 Hz). This compound is known.¹

2-(3-Methylphenyl)benzothiazole (entry 5)

Prepared as shown in the general experimental procedure and purified on silica gel (petroleum ether/ethyl acetate = 98:2): white solid, 71% yield. ¹H-NMR (500 MHz, CDCl₃) δ 8.08 (d, *J* = 11 Hz, 1H), 7.97 (s, 1H), 7.92 – 7.87 (m, 2H), 7.51 (t, *J* = 6.5 Hz, 1H), 7.41 (t, *J* = 9.5 Hz, 2H), 7.29 (d, *J* = 9.5 Hz, 1H), 2.469 (s, 3H). This compound is known.¹

2-(2-Methylphenyl)benzothiazole (entry 6)

Prepared as shown in the general experimental procedure and purified on silica gel (petroleum ether, then 5% ethyl acetate in petroleum ether): yellow oil, which slowly solidifies to light yellow solid, 55% yield. ¹H NMR (600 MHz, CDCl₃) δ 8.12 (d, J = 8.1 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.76 (d, J = 7.5 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.42 – 7.30 (m, 4H), 2.67 (s, 3H). This compound is known.²

2-(2-Hydroxylphenyl)benzothiazole (entry 7)

HO Prepared as shown in the general experimental procedure and purified on silica gel (petroleum ether, then 5% ethyl acetate in petroleum ether): off-white solid, 47% yield. ¹H NMR (400 MHz, CDCl₃) δ 12.54 (s, 1H), 7.99 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.70 (dd, J = 7.8, 1.5 Hz, 1H), 7.55 – 7.45 (m, 1H), 7.45 – 7.34 (m, 2H), 7.11 (dd, J = 8.3, 1.0 Hz, 1H), 7.01 – 6.92 (m, 1H). This compound is known.³

2-(1-Naphthyl)benzothiazole (entry 8)



Prepared as shown in the general experimental procedure and purified on silica gel (petroleum ether, then 2% ethyl acetate in petroleum ether): light yellow oil, 78% yield. ¹H NMR (400 MHz,

CDCl₃) δ 9.00 (d, J = 8.6 Hz, 1H), 8.25 (d, J = 8.2 Hz, 1H), 8.06 – 7.87 (m, 4H), 7.65 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.58 (dddd, J = 10.9, 7.4, 5.2, 3.0 Hz, 3H), 7.48 – 7.40 (m, 1H). This compound is known.²

2-(Furan-2-yl)benzothiazole (entry 9)

² Canivet, J.; Yamaguchi, J.; Ban, I.; Itami, K. Org. Lett. 2009, 11, 1733.

³ Noda, H.; Bode, J. W. J. Am. Chem. Soc. 2015, 137, 3958.



Prepared as shown in the general experimental procedure and purified on silica gel (petroleum ether/ethyl acetate = 98:2): white

solid, 62% yield. ¹H-NMR (500 MHz, CDCl₃) δ 8.09 (d, J = 6 Hz, 1H), 7.89 (d, J = 7 Hz, 1H), 7.60 (s, 1H), 7.50 (t, J = 6Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 9.5 Hz, 1H), 6.610 (s, 1H). This compound is known.¹

2-(Pyridin-2-yl)benzothiazole (entry 10)

Prepared as shown in the general experimental procedure and purified on silica gel (petroleum ether/ethyl acetate = 98:2): yellow solid, 80% yield. ¹H-NMR (500 MHz, CDCl₃) δ 8.74 – 8.70 (m, 1H), 8.29 (d, J = 9 Hz, 1H), 8.08 - 8.00 (m, 1H), 7.99 - 7.98 (m, 1H), 7.88 (t, J = 9 Hz, 1H), 7.40 (t, J = 8Hz, 1H), 7.38 - 7.31 (m, 2H). This compound is known.¹

5-Methyl-2-phenylbenzothiazole (entry 11)



Prepared as shown in the general experimental procedure and purified on silica gel (petroleum ether/ethyl acetate = 98:2): yellow solid, 71% yield. ¹H-NMR (500 MHz, CDCl₃) δ 8.13 – 8.08 (m, 2H), 7.99 (d, J = 7 Hz, 1H), 7.70 (s, 1H), 7.54 – 7.47 (m, 3H), 7.29 (d, J = 9.5 Hz, 1H), 2.51 (s, 3H). This compound is known.¹

5-Methoxy-2-phenylbenzothiazole (entry 12)



Prepared as shown in the general experimental procedure and purified on silica gel (petroleum ether/ethyl acetate = 98:2): yellow solid, 88% yield. ¹H-NMR (500 MHz, CDCl₃) δ 3.898 (s, 3H), 7.13 - 7.07 (m,

1H), 7.39 (s, 1H), 7.52 – 7.48 (m, 3H), 7.95 (d, J = 8.5 Hz, 1H), 8.07 – 8.02 (m, 2H). This compound is known.¹

5-Nitro-2-phenylbenzothiazole (entry 13)



Prepared as shown in the general experimental procedure and purified on silica gel (petroleum ether/ethyl acetate = 98:2):

yellow solid, 69% yield. ¹H-NMR (500 MHz, CDCl₃) δ 8.86 (s, 1H), 8.39 (d, J = 9 Hz,

1H), 8.14 – 8.11 (m, 3H), 7.65 – 7.58 (m, 3H). This compound is known.¹

4,5-Dimethyl-2-phenylthiazole (entry 14)



Prepared as shown in the general experimental procedure and purified on silica gel (petroleum ether, then 5% ethyl acetate in petroleum

ether): colorless liquid, 87% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.85 (m, 2H), 7.44 – 7.31 (m, 3H), 2.38 (s, 3H), 2.36 (s, 3H). This compound is known.⁴

⁴ Do, H. Q.; Daugulis, O. J. Am. Chem. Soc. 2007, 129, 12404.

































Fig. S8. MS analysis indicated the presence of S-2-formamidophenyl benzothioate with m/z = 257 as an intermediate in the reaction mixture.