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Synthesis of 2-aryl-benzothiazoles via Ni-catalyzed coupling of benzothiazoles and aryl sulfamates

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Abstract: 2-Aryl-benzothiazoles have been successfully synthesized via a simple coupling reaction between benzothiazoles and aryl sulfamates using a nickel catalyst. The nickel catalyst is inexpensive, reusable and commercially available. In addition, the use of highly expensive palladium catalysts and unstable raw materials has been avoided. 2-Aryl-benzothiazoles bearing various substituents on the aryl groups were obtained in good yield.

Keywords: 2-Aryl-benzothiazoles, Aryl sulfamates, Coupling reaction

Introduction

2-Aryl-benzothiazoles are an important class of nitrogen-containing heterocyclic compounds, which are present in numerous natural products and synthetic compounds. Due to their biological and pharmacological properties, 2-aryl-benzothiazoles exhibit a wide range of biological activities, including insecticidal [1], antifungal [2], nematocidal [3], weed killing [2, 3], and plant growth regulation activities in agriculture [3]. In medicine, these compounds exhibit anti-tumor [4-7] and anti-bacterial activity [8, 9], and are also used in the treatment of Alzheimer's disease [10, 11]. Therefore, these compounds have received sustained attention from researchers in organic synthesis.

The conventional method used to prepare 2-aryl-benzothiazoles involves reacting 2-aminothiophenol with benzyl alcohol [12], benzylamine [13-16], benzonitrile [12, 17, 18] or aromatic aldehyde [19-27]. However, this approach is

disadvantageous because 2-aminothiophenol is extremely unstable in air and highly toxic. In addition, benzyl alcohol, benzylamine and aromatic aldehydes are also very reactive materials.

Recent studies have shown that novel synthetic methods which involve the direct coupling of benzothiazoles with arylating agents avoid the use of highly toxic and reactive materials. But, there are some disadvantages in these reports, such as using expensive palladium as a catalyst [28, 29], and the use of unstable aromatic iodides [29] or aromatic aldehydes [30] as raw materials.

In this work, inexpensive and commercially available nickel is used as a catalyst. In addition, inexpensive and stable aryl sulfamates are used as electrophiles. Moreover, the nickel catalyst can be recycled three times.

Results and discussion

Initially, the reaction of benzothiophene and *p*-toluenesulfonate was used to evaluate the catalytic activity of various nickel compounds (0.2 equivalent) using 1,10-phen-H₂O (1,10-phenanthroline·H₂O) as a co-catalyst. As listed in Table 1, the results showed that NiBr₂(DME) (DME = 1,2-dimethoxyethane) exhibited the best catalytic activity with 68% yield (Table 1, entry 4). When the co-catalyst was changed to an amino acid the reaction yielded little or no product. This means that NiBr₂ with 1,10-phen is a highly active catalyst. Moreover, it was easier to generate NiBr₂ with 1,10-phen ligands by replacing DME with 1,10-phen, rather than directly from 1,10-phen and NiBr₂. The yield was increased to 92% by increasing the amount of NiBr₂(DME) to 40 mol% (Table 1, entry 9).

After completion of the reaction, the reaction mixture was filtered, and the starting material and product were washed with diethyl ether. The catalyst residue was then charged with lithium *t*-butoxide, along with a small amount of 1,10-phenanthroline and used in the reaction again. Repeated use of the catalyst showed that it was active for three cycles (table 1, entry 14-16).

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Table 1. Synthesis of 2-(*p*-CH₃Ph)benzothiazoles by benzothiazoles with *p*-CH₃PhOSO₂NMe₂^{a,b}

Entry	Catalyst (mol%)	Ligand (mol%)	Yield/%
1	NiBr ₂ · 6H ₂ O (20)	1,10-phen · H ₂ O(20)	51
2	NiBr ₂ (20)	1,10-phen · H ₂ O(20)	50
3	Ni(COD) ₂ (20) ^e	1,10-phen · H ₂ O(20)	NR ^c
4	NiBr ₂ (DME) (20) ^d	1,10-phen · H ₂ O(20)	68
5	Ni(acac) ₂ (20) ^f	1,10-phen · H ₂ O(20)	10
6	NiCl ₂ · 6H ₂ O (20)	1,10-phen · H ₂ O(20)	45
7	NiBr ₂ (DME) (20)	1,10-phen(20)	31
8	NiBr ₂ (DME) (30)	1,10-phen · H ₂ O(30)	81
9	NiBr ₂ (DME) (40)	1,10-phen · H ₂ O(40)	92
10	NiBr ₂ (DME) (20)	-	NR ^c
11	NiBr ₂ (DME) (20)	L-proline	trace ^c
12	NiBr ₂ (DME) (20)	L-lysine	NR ^c
13	NiBr ₂ (DME) (20)	L-valine	trace ^c
14	NiBr ₂ (DME) (40) ^f	1,10-phen · H ₂ O(40)	90
15	NiBr ₂ (DME) (40) ^g	1,10-phen · H ₂ O(40)	89
16	NiBr ₂ (DME) (40) ^h	1,10-phen · H ₂ O(40)	85

a) Reaction conditions: benzothiazoles (0.1 mmol), *p*-CH₃PhOSO₂NMe₂ (0.1 mmol), ^tBuOLi(0.2 mmol), 1,10-phen · H₂O, NiBr₂(DME), dioxane (3 ml), 120 °C, N₂ atmosphere. b) Isolated yields. c) By ¹H NMR. d) DME = 1,2-dimethoxyethane. e) COD = 1,5-Cyclooctadiene. f) acac = acetylacetonate. g) Second recovered catalyst. h) Third recovered catalyst.

A wide variety of aryl sulfamates and benzothiazoles were investigated with regard to the effect on the yield of their corresponding 2-aryl-benzothiazole compounds. Table 2 shows that the reaction of various aryl sulfamates gave the desired products in high yield. The product yields obtained using aryl sulfamates bearing electron-donating groups were higher than those containing electron-withdrawing groups [*p*-N(CH₃)₂PhOSO₂NMe₂ (95%), *p*-CF₃PhOSO₂NMe₂ (85%)]. Sterically hindered aryl sulfamates gave higher product yields; the yield obtained using *o*-CH₃PhOSO₂NMe₂ is higher than its corresponding *m*- and *p*-derivatives. The product yield obtained using aryl sulfamates containing a naphthalene ring was the highest. This was attributed to the positively charged intermediate being stabilized by the electron-donating groups and large conjugated ring.

Conclusions

An inexpensive, reusable and commercially available nickel catalyst can be used to efficiently catalyze the coupling reaction between benzothiazoles and aryl sulfamates

Table 2. Synthesis of 2-arylbenzothiazoles from benzothiazoles with ArOSO₂NMe₂^{a,b}

a 92%	b 85%	c 95%

d 89%	e 93%	f 91%

g 90%	h 96%	i 94%

a) Reaction conditions: benzothiazoles (0.1 mmol), ArOSO₂NMe₂ (0.1 mmol), ^tBuOLi(0.2 mmol), 1,10-phen · H₂O(0.04 mmol), NiBr₂(DME)(0.04 mmol), dioxane (3 ml), 120 °C, N₂ atmosphere. b) Isolated yields.

to prepare a variety of 2-aryl-benzothiazole compounds. The aryl group in the aryl sulfamate starting material can contain electron-withdrawing groups (such as -C₆H₄CF₃, -C₆H₄OCH₃, and -C₆H₄Cl), electron-donating groups (such as -C₆H₄CH₃, and -C₆H₄N(CH₃)₂), or large conjugated rings (such as -C₁₀H₇). This method avoids the use of unstable and highly toxic 2-aminothiophenol, highly expensive palladium catalysts, and unstable aromatic iodine or aromatic aldehydes as starting materials. In future work, substituted benzothiazole compounds will be studied as raw materials.

Experimental

General procedure for the synthesis of 2-aryl-benzothiazole

A Schlenk tube was charged with the benzothiazole (0.10 mmol) and aryl sulfamate (0.10 mmol) [31], followed by lithium *t*-butoxide (0.20 mmol), nickel catalyst (0.4 equivalent), and co-catalyst (0.4 equivalent). The nitrogen atmosphere was replaced three times and 3 mL of dioxane was introduced to the reaction mixture. The Schlenk tube was placed into an oil bath and the reaction mixture was stirred at 120°C for 12 h. The reaction mixture was extracted with Et₂O. The combined organic phases were dried with anhydrous Na₂SO₄, filtered, concentrated under vacuum and the resulting residue purified by column chromatography on silica gel.

Catalyst recovery experiment

After completion of the catalytic reaction, the reaction mixture was filtered and the filter cake was washed three times with diethyl ether. The powder solid was charged with two equivalents of lithium *t*-butoxide and 0.4 equivalents of 1,10-phenanthroline and was used in the reaction again (table 1, entry 14-16).

Characterization Data of the Products:

2-*p*-Tolyl-benzothiazole (a) [17, 21, 32]

Yellow solid; 92% yield; mp 87–89°C. IR (KBr): 3081, 2957, 1449, 1431, 965, 840, 758, 450 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 8.06 (d, *J* = 8.0 Hz, 1 H), 7.98 (d, *J* = 7.9 Hz, 2 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 1 H), 7.36 (t, *J* = 8.2 Hz, 1 H), 7.28 (t, *J* = 8.5 Hz, 2 H), 2.40 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 168.1, 154.1, 141.2, 135.0, 131.1, 130.0, 127.4, 126.3, 125.3, 123.2, 121.4, 21.6. HRMS (EI): *m/z* [M]⁺ calcd for C₁₄H₁₁NS: 225.06; found: 225.09.

2-[4-(Trifluoromethyl)phenyl]-benzothiazole (b) [17, 33]

White solid; 85% yield; mp 160–163°C. IR (KBr): 3044, 1630, 1454, 1425, 1073, 976, 840, 761, 624, 450 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 8.20 (d, *J* = 7.9 Hz, 2 H), 8.10 (d, *J* = 7.9 Hz, 1 H), 7.91 (d, *J* = 7.9 Hz, 1 H), 7.74 (d, *J* = 7.9 Hz, 2 H), 7.50 (t, *J* = 7.9 Hz, 1 H), 7.43 (t, *J* = 7.9 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ = 165.8, 154.3, 135.9, 134.1, 130.3 (q, *J* = 31.3 Hz), 125.5, 126.5, 125.4 (q, *J* = 3.5 Hz), 122.9 (q, *J* = 270.9 Hz), 122.1, 120.0. HRMS (EI): *m/z* [M]⁺ calcd for C₁₄H₈F₃NS: 279.03; found: 279.08.

2-[4-(*N,N*-dimethyl)phenyl]-benzothiazole (c) [17, 34]

White solid; 95% yield; mp 167–169°C. IR (KBr): 3088, 2880, 1450, 1309, 1233, 1050, 965, 749, 715, 415. ¹H NMR (400 MHz, CDCl₃): δ = 7.96 (t, *J* = 7.5 Hz, 3 H), 7.89 (d, *J* = 7.8 Hz, 1 H), 7.50 (t, *J* = 7.5 Hz, 1 H), 7.38 (t, *J* = 7.4 Hz, 1 H),

6.75 (d, *J* = 8.7 Hz, 2 H), 3.00 (s, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ = 168.0, 158.7, 155.3, 136.5, 130.1, 127.4, 125.4, 123.5, 120.1, 118.2, 110.3, 39.5. HRMS (EI): *m/z* [M]⁺ calcd for C₁₅H₁₁N₂S: 254.09; found: 254.11.

2-(3-Methoxyphenyl) benzothiazole (d) [21, 35]

White solid; 89% yield; mp 88–90°C. IR (KBr): 3061, 2855, 1630, 1510, 1340, 887, 750, 711, 681 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 8.23 (d, *J* = 8.0, 1 H), 7.90 (d, *J* = 7.8 Hz, 1 H), 7.54 (t, *J* = 7.4, Hz, 1 H), 7.49 (d, *J* = 7.5, Hz, 1 H), 7.17 (t, *J* = 7.5, Hz, 1 H), 7.15–7.11 (m, 2 H), 6.96 (d, *J* = 7.4 Hz, 1 H), 3.55 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 160.1, 156.1, 152.9, 125.2, 120.5, 116.1, 123.9, 122.5, 119.6, 117.4, 109.3, 106.1, 101.2, 51.1. HRMS (EI): *m/z* [M]⁺ calcd for C₁₄H₁₁NOS: 241.06; found: 241.09.

2-(2-Methoxyphenyl) benzothiazole (e) [21]

White solid; 93% yield; mp 110–112°C. IR (KBr): 3055, 2850, 1628, 1520, 1361, 755, 723 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 8.45 (d, *J* = 7.9, 1 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.54 (t, *J* = 7.9 Hz, 1 H), 7.49 (d, *J* = 7.9 Hz, 1 H), 7.17 (t, *J* = 7.5, Hz, 1 H), 7.14–7.11 (m, 2 H), 7.06 (d, *J* = 7.4 Hz, 1 H), 6.96 (d, *J* = 7.9 Hz, 1 H), 3.45 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 161.1, 155.1, 153.9, 135.1, 131.1, 125.2, 124.9, 122.5, 120.5, 118.3, 108.8, 105.2, 103.1, 52.8. HRMS (EI): *m/z* [M]⁺ calcd for C₁₄H₁₁NOS: 241.06; found: 241.11.

2-(4-Methoxyphenyl)benzothiazole (f) [17, 35]

White solid; 91% yield; mp 123–125°C. IR (KBr): 3045, 2848, 1558, 1432, 1356, 1311, 1110, 748, 725. ¹H NMR (400 MHz, CDCl₃): δ = 8.14–8.11 (m, 3 H), 7.65 (d, *J* = 7.9 Hz, 1 H), 7.50 (t, *J* = 7.3 Hz, 1 H), 7.38 (t, *J* = 7.5 Hz, 1 H), 7.09 (d, *J* = 8.6 Hz, 2 H), 3.45 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 165.9, 159.7, 151.2, 130.5, 128.9, 124.3, 121.5, 120.4, 119.6, 117.8, 113.2, 53.4. HRMS (EI): *m/z* [M]⁺ calcd for C₁₄H₁₁NOS: 241.06; found: 241.09.

2-(4-Chlorophenyl)benzothiazole (g) [17, 34]

White solid; 90% yield; mp 116–118°C. IR (KBr): 3048, 2915, 1573, 1438, 1316, 1120, 759, 743. ^1H NMR (400 MHz, CDCl_3) δ = 8.19 (d, J = 8.1 Hz, 1H), 8.11 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.5, 155.0, 139.1, 134.2, 131.1, 128.9, 127.5, 126.1, 125.3, 120.3, 120.6. HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_{13}\text{H}_8\text{ClNS}$: 245.01; found: 245.05.

2-(Naphthalen-2-yl)benzothiazole (h) [21]

White solid; 96% yield; mp 128–130°C. IR (KBr): 3056, 2860, 1530, 1443, 1358, 1200, 1101, 1005, 958, 850, 751, 731 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 8.94 (d, J = 7.8 Hz, 1H), 8.19 (d, J = 7.8 Hz, 1H), 7.96 (t, J = 7.8 Hz, 1H), 7.87 (d, J = 7.8 Hz, 2H), 7.63 (t, J = 7.8 Hz, 1H), 7.60–7.58 (m, 3H), 7.41 (t, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ = 165.2, 153.1, 133.1, 132.5, 131.4, 130.2, 128.9, 127.5, 126.9, 126.5, 126.0, 125.7, 124.5, 124.0, 122.9, 122.1, 120.7. HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_{17}\text{H}_{11}\text{NS}$: 261.06; found: 261.06.

2-(Naphthalen-3-yl)benzothiazole (i) [17, 34]

White solid; 94% yield; mp 126–128 °C. IR (KBr): 3055, 2890, 1502, 1435, 1360, 1205, 998, 899, 758, 723. ^1H NMR (400 MHz, CDCl_3) δ 8.56 (s, 1H), 8.25 (d, J = 8.5 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.96–7.91 (m, 4H), 7.54–7.51 (m, 3H), 7.26 (t, J = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.1, 155.1, 136.2, 135.2, 131.0, 129.8, 128.0, 127.6, 126.6, 125.8, 123.1, 122.7, 122.0, 121.3, 120.5, 119.9, 119.0. HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_{17}\text{H}_{11}\text{NS}$: 261.06; found: 261.08.

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References

- [1] Sawada Y, Yanai T, Nakagawa H, Tsukamoto Y, Yokoi S, Yanagi M, et al. Synthesis and insecticidal activity of benzoheterocyclic analogues of N'-benzoyl-N-(tert-butyl) benzohydrazide: Part 1. Design of benzoheterocyclic analogues. *Pest Manag Sci.* 2003;59:25–35.
- [2] Wang H. R. L., Chen Yong, Liu Xinghai, Weng Jianquan, Synthesis and Herbicidal Activity of Novel N-Acyl-7-methoxybenzo[4,5]thiazolo[2,3-c][1,2,4]triazole-3(2H)-thione. *Youji Huaxue.* 2014;34:419–23.
- [3] Clifford DP, Edwards RV, Hewson RT. Synthesis and plant growth regulatory properties of substituted 2-(2,2,2-trichloroethylideneamino)phenols, 2-(trichloromethyl) benzoxazoles and benzothiazoles. *J Agric Food Chem.* 1981;29:640–3.
- [4] Mortimer CG, Wells G, Crochard JP, Stone EL, Bradshaw TD, Stevens MF, et al. Antitumor Benzothiazoles. 26. 2-(3,4-Dimethoxyphenyl)-5-fluorobenzothiazole (GW 610, NSC 721648), a Simple Fluorinated 2-Arylbenzothiazole, Shows Potent and Selective Inhibitory Activity against Lung, Colon, and Breast Cancer Cell Lines. *J Med Chem.* 2006;49:179–85.
- [5] Liebowitz MR, Salmán E, Mech A, Dunner D, Johnson AE, Akhtar J, et al. Ziprasidone monotherapy in bipolar II depression: an open trial. *J Affect Disord.* 2009;118:205–8.
- [6] Bourdet DL, Lee K, Thakker DR. Photoaffinity Labeling of the Anionic Sites in Caco-2 Cells Mediating Saturable Transport of Hydrophilic Cations Ranitidine and Famotidine. *J Med Chem.* 2004;47:2935–8.
- [7] Feng H, Ding J, Zhu D, Liu X, Xu X, Zhang Y, et al. Structural and Mechanistic Insights into NDM-1 Catalyzed Hydrolysis of Cephalosporins. *J Am Chem Soc.* 2014;136:14694–7.
- [8] Frost JM, Dart MJ, Tietje KR, Garrison TR, Grayson GK, Daza AV, et al. Indol-3-ylcycloalkyl Ketones: Effects of N1 Substituted Indole Side Chain Variations on CB2 Cannabinoid Receptor Activity. *J Med Chem.* 2010;53:295–315.
- [9] Chavan AS, Kharat AS, Bhosle MR, Mane RA. Baker's yeast catalyzed one-pot synthesis of bioactive 2-[benzylidene(or pyrazol-4-ylmethylene)hydrazono]-1,3-thiazolidin-4-one-5-yl-acetic acids. *Heterocycl Commun.* 2018;24:103–7.
- [10] Westwell AA. 2-Arylbenzothiazole as a Privileged Scaffold in Drug Discovery. *Curr Med Chem.* 2009;16:2430–40.
- [11] Geng J, Li M, Wu L, Ren J, Qu X. Liberation of Copper from Amyloid Plaques: Making a Risk Factor Useful for Alzheimer's Disease Treatment. *J Med Chem.* 2012;55:9146–55.
- [12] Kaldhi D, Vodnala N, Gujjarappa R, Nayak S, Ravichandiran V, Gupta S, et al. Organocatalytic oxidative synthesis of C2-functionalized benzoxazoles, naphthoxazoles, benzothiazoles and benzimidazoles. *Tetrahedron Lett.* 2019;60:223–9.

- [13] Nguyen TB, Ermolenko L, Dean WA, Al-Mourabit A. Benzazoles from Aliphatic Amines and o-Amino/Mercaptan/Hydroxyanilines: Elemental Sulfur as a Highly Efficient and Traceless Oxidizing Agent. *Org Lett*. 2012;14:5948–51.
- [14] Jin X, Liu Y, Lu Q, Yang D, Sun J, Qin S, et al. Formation of C=N bonds by the release of H₂: a new strategy for synthesis of imines and benzazoles. *Org Biomol Chem*. 2013;11:3776–80.
- [15] Naresh G, Kant R, Narender T. Molecular Iodine Promoted Divergent Synthesis of Benzimidazoles, Benzothiazoles, and 2-Benzyl-3-phenyl-3,4-dihydro-2H-benzo[e][1,2,4]thiadiazines. *J Org Chem*. 2014;79:3821–9.
- [16] Gopalaiah K, Chandrudu SN. Iron(II) bromide-catalyzed oxidative coupling of benzylamines with ortho-substituted anilines: synthesis of 1,3-benzazoles. *RSC Advances*. 2015;5:5015–23.
- [17] Sun Y, Jiang H, Wu W, Zeng W, Wu X. Copper-Catalyzed Synthesis of Substituted Benzothiazoles via Condensation of 2-Aminobenzenethiols with Nitriles. *Org Lett*. 2013;15:1598–601.
- [18] Li G, Jiang J, Zhang F, Xiao F, Deng GJ. Elemental sulfur mediated 2-substituted benzothiazole formation from 2-aminobenzenethiols and arylacetylenes or styrenes under metal-free conditions. *Org Biomol Chem*. 2017;15:10024–8.
- [19] Takashi Itoh KN. Michiko Miyazaki, and Akio Ohsawa, Scandium Triflate Catalyzed Formation of Benzothiazole from 2-Aminobenzenethiol and Formaldehyde in the Presence of Water. *Heterocycles*. 2000;52:1037–40.
- [20] Itoh T, Nagata K, Ishikawa H, Ohsawa A. Synthesis of 2-Arylbenthiazoles from 2-Aminobenzenethiol and Aryl Aldehydes Catalyzed by Scandium Triflate. *ChemInform*. 2004;35.
- [21] Ranu BC, Jana R, Dey SS. An Efficient and Green Synthesis of 2-Arylbenthiazoles in an Ionic Liquid, [pmlm]Br under Microwave Irradiation. *Chem Lett*. 2004;33:274–5.
- [22] Bahrami K, Khodaei MM, Naali F. Mild and Highly Efficient Method for the Synthesis of 2-Arylbenthiazoles and 2-Arylbenthiazoles. *J Org Chem*. 2008;73:6835–7.
- [23] Hui-Long X, Jiu-Xi C, Miao-Chang L, Dong-Jian Z, Jin-Chang D, Hua-Yue W. Trichloroisocyanuric Acid (TCCA) as a Mild and Efficient Catalyst for the Synthesis of 2-Arylbenthiazoles. *Chem Lett*. 2009;38:170–1.
- [24] Yu C, Lee K, You Y, Cho EJ. Synthesis of 2-Substituted Benzothiazoles by Visible Light-Driven Photoredox Catalysis. *Adv Synth Catal*. 2013;355:1471–6.
- [25] Li G, Xie H, Chen J, Guo Y, Deng GJ. Three-component synthesis of 2-heteroaryl-benzothiazoles under metal-free conditions. *Green Chem*. 2017;19:4043–7.
- [26] Gandhi D, Agarwal S. Urea nitrate catalyzed synthesis of 2-arylbenthiazoles using the grindstone technique. *Heterocycl Commun*. 2018;24:307–10.
- [27] Refat HM, Mohamed KS. Efficient and convenient synthesis of pyrido [2,1-b]benzothiazole, pyrimidopyrido[2,1-b] benzothiazole and benzothiazolo[3,2-a][1,8]naphthyridine derivatives. *Heterocycl Commun*. 2015;21.
- [28] Huang J, Chan J, Chen Y, Borths CJ, Faul MM. A Highly Efficient Palladium/Copper Cocatalytic System for Direct Arylation of Heteroarenes: An Unexpected Effect of Cu(Xantphos)I. *J Am Chem Soc*. 2010;132:3674–5.
- [29] Gu J, Cai C. Pd/Cu-cocatalyzed regioselective arylation of thiazole derivatives at 2-position under ligand-free conditions. *RSC Advances*. 2015;5:56311–5.
- [30] Liu S, Chen R, Guo X, Yang H, Deng G, Li CJ. Iron-catalyzed arylation of benzoazoles with aromatic aldehydes using oxygen as oxidant. *Green Chem*. 2012;14:1577.
- [31] Tao JL, Wang ZX. Pincer-Nickel-Catalyzed Cross-Coupling of Aryl Sulfamates with Arylzinc Chlorides. *Eur J Org Chem*. 2015;2015:6534–40.
- [32] Deng H, Li Z, Ke F, Zhou X. Cu-Catalyzed Three-Component Synthesis of Substituted Benzothiazoles in Water. *Chemistry*. 2012;18:4840–3.
- [33] Fan X, Wang Y, He Y, Zhang X, Wang J. Ru(III)-catalyzed oxidative reaction in ionic liquid: an efficient and practical route to 2-substituted benzothiazoles and their hybrids with pyrimidine nucleoside. *Tetrahedron Lett*. 2010;51:3493–6.
- [34] Ranjit S, Liu X. Direct Arylation of Benzothiazoles and Benzoxazoles with Aryl Boronic Acids. *Chemistry*. 2011;17:1105–8.
- [35] Zhang SL, Hu WY, Wang PP. An Iron and Copper System Catalyzed C–H Arylation of Azoles with Arylboronic Acids. *Synthesis*. 2014;47:42–8.