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Co-Catalyzed Intramolecular S-N Bond Formation in Water for 1,2-Benzisothiazol-3(*2H*)-ones and 1,2,4-Thiadiazoles Synthesis

Liting Yang, Lijuan Song, Shanyu Tang, Longjia Li, Heng Li, Bingxin Yuan,* and Guanyu Yang*[a][+]

Abstract: An efficient and versatile Co-catalyzed intramolecular S-N bond formation in water to synthesize 1,2-benzisothiazol-3(*2H*)-one and 1,2,4-thiadiazoles derivatives in good to excellent yields was developed. The transformation showed great tolerance with a broad range of substituents. The mother liquor was able to be recycled 6 times with minor loss in product yield.

Introduction

1,2-Benzisothiazol-3(*2H*)-one (BIT) derivatives, a significant class of heterocyclic compounds, have attracted wide attention and play important roles in drug discovery, agriculture, food science and industrial settings.[1] Since the first synthesis by Mckibben and McClelland in 1923,[2] 1,2-benzisothiazol-3(*2H*)-ones were discovered to show broad spectrum bioactivity, such as antibacterial,[3] fungistatic,[4] antipsychotic,[5] antiviral,[6] antithrombotic[7] and analgesic[8]. Nowadays, it's widely used as a preservative in numerous daily products, such as paints, cleaning detergents, leather processing, pesticides and gas preservation.[9] A study in 2014 declared that BIT was found in 96% of the paints from five European countries.[10] Furthermore, it has been reported that some certain derivatives could process anti-HIV activity.[11]

Owing to BITs' excellent performance in pharmathutical science, a number of synthetic routes have been disclosed in literatures, as summarized in Figure 1. Reaction pathways involving intramolecular cyclization starts from N-substituted sulfonamides,[12] 2,2-dithiodibenzoate,[13] N-substituted thiosalicylate,[14] and sulfinyl substituted carboxamides[15] with H_2O_2, hypervalent iodine reagent, $(Cl_3COO)_2O$ or O_2 as the oxidizer. The conventional strategies accomplish the synthesis of 1,2-Benzisothiazol-3(*2H*)-ones via intermolecular cyclization by: 1) introducing sulfur reagents(S_8, CS_2, KSCN) into substrates including 2-halobenzamides (CuHal as catalyst)[16] and benzamide ($Cu(OAc)_2$ as catalyst);[17] 2)introducing nitrogen reagents (azide, primary amines) into substrates including 2-mercaptobenzoic acid,[18] 2,2'-dithiodibenzoate,[19] 3*H*-1,2-benzodithiol-3-one-1-oxide,[20] and 1,3-benzoxathiin-4-one 1-oxide.[21] Despite these great advances, the shortcomings are apparent, such as toxic waste, extra additives or bases, screening a large variety of ligands, tedious work-up procedures, and long reaction hours. More importantly, among all the methods mentioned above, there are just a few catalytic transformations and copper catalyst is the only catalyst specie that has been investigated. Besides, strong organic and inorganic oxidizers were used in most cases, except molecular oxygen was adopted as the oxidant in one single report.[14b] All reactions were carried out in organic solvents. From the environmental and industrial points of view, the development of a green and versatile catalytic method for the synthesis of 1,2-benzisothiazol-3(*2H*)-one compounds still remains a challenge and is highly desired.

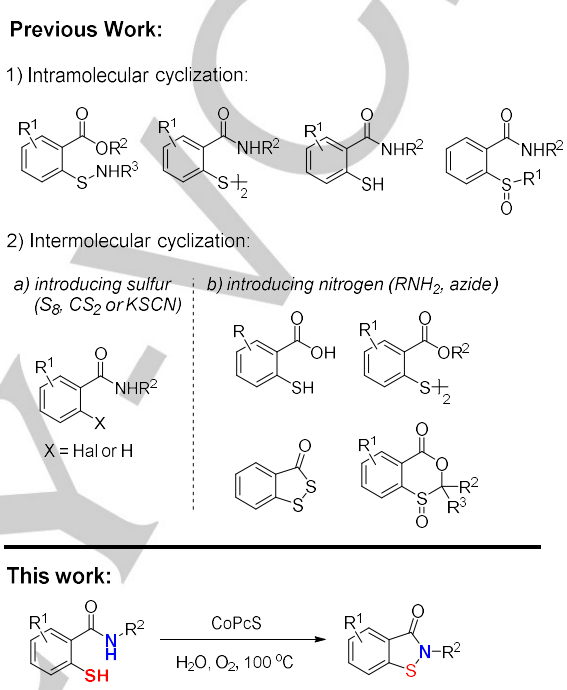

Figure 1. Previous and present methods to synthesize 1,2-benzisothiazol-3(*2H*)-one derivatives.

Recently, we reported the Co-catalyzed aerobic oxidation of thiols with amines to synthesize sulfenamides.[22] Tetra-substituted sulfonated cobalt phthalocyanine (CoPcS) showed great catalytic ability to construct S-N bond with molecular oxygen as the environment friendly oxidant and water as the ideal green chemistry solvent. Inspired by that and our continuous interest in green synthesis,[23] we intend to expend

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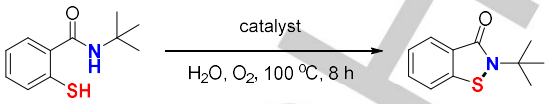
this methodology to the synthesis of 1,2-benzisothiazol-3(*2H*)-ones. Herein, we report the first example of Co-catalyzed aerobic oxidation of N-substituted thiosalicylate to form benzoisothiazolones in water (Figure 1).

Results and Discussion

Initially, we attempted the intramolecular coupling of N-(*t*-butyl)-2-mercaptobenzamide **1a** to produce the corresponding benzoisothiazolone **2a** with the similar procedure [22] as we reported, in which 1 atm O_2 was used as the oxidizing agent, and water as the solvent. The attempt to use $Co(OAc)_2 \cdot 2H_2O$ as catalyst only furnished the product in 23% yield (Table 1, Entry 1). $Cu(acac)_2$ gave the best results among the metal-acac complexes (Entry 2-4). By changing the ligand to phthalocyanine-tetra-sodium sulfonate (PcS), the catalytic performance was improved markedly owing to higher solubility of MPcS in water (Entry 5, 6). However, the replacement of sulfonate groups by carbonate lowered the product yield to 62% (Entry 7). $Na[Co(EDTA)] \cdot 2H_2O$ only led to trace amount of product. Additionally, the elimination of CoPcS resulted in no product (Entry 10). These results illustrate the necessity of CoPcS as the catalyst. The reaction was examined under different temperatures. Either decreasing the equivlant of CoPcS (Entry 11, 12) or the reaction temperature (Entry 5) led to lower

Table 1. Optimization of reaction conditions. [a]

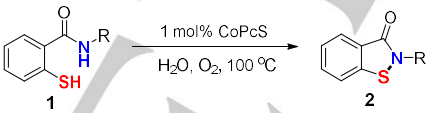


1a **2a**

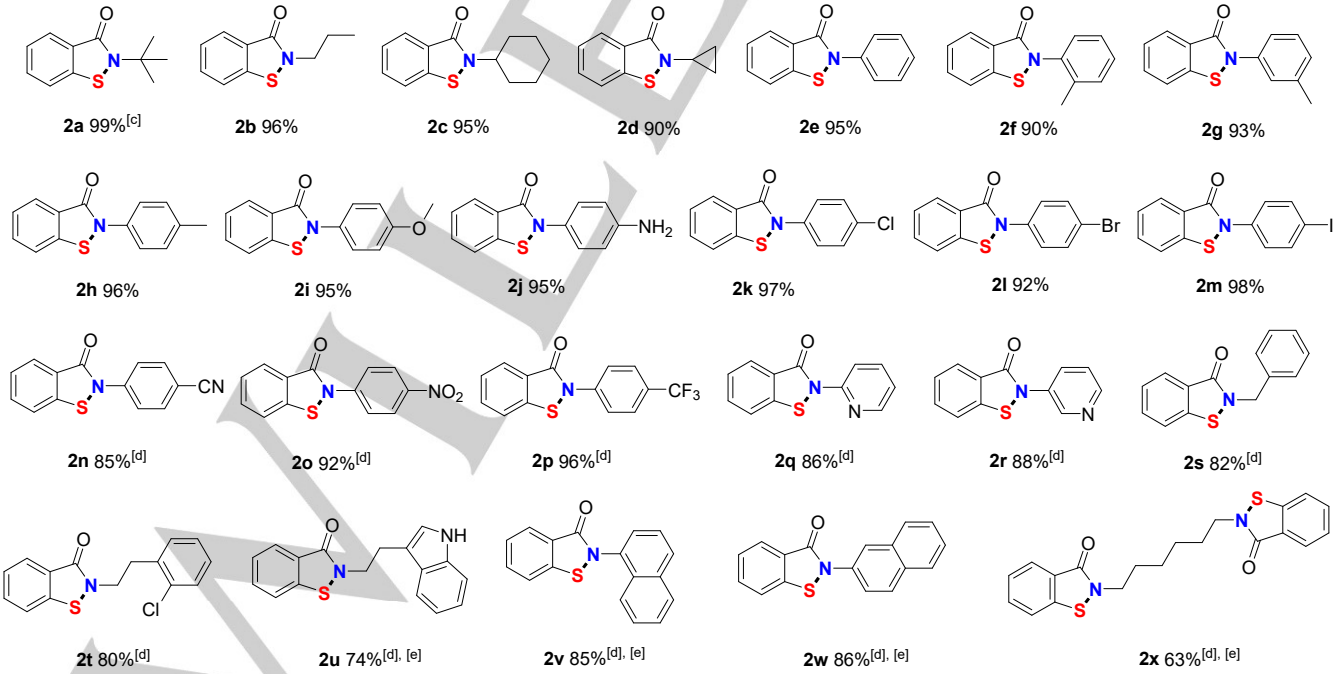
Entry	Catalyst	Yield(%)[b]
1	$Co(OAc)_2 \cdot 2H_2O$	23
2	$Co(acac)_2$	29
3	$Mn(acac)_2$	18
4	$Cu(acac)_2$	46
5	CoPcS	99(82[c])
6	CuPcS	78
7	CoPcC	62
8	CoPc	Trace
9	$Na[Co(EDTA)] \cdot 2H_2O$	Trace
10	–	0
11	0.5 mol% CoPcS	49
12	0.1 mol% CoPcS	10
13[d]	CoPcS	59

[a] Reaction conditions: **1a** (0.2 mmol), catalyst (1 mol %), 2 mL H_2O, 1 atm O_2, 100 °C, 8 h. [b] Isolated yield. [c] 80 °C. [d] In air.

Table 2. Synthesis of 1,2-Benzisothiazol-3(2H)-one derivatives.[a], [b]



1 2

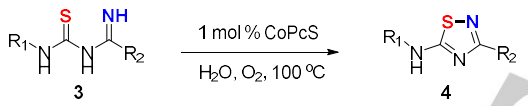


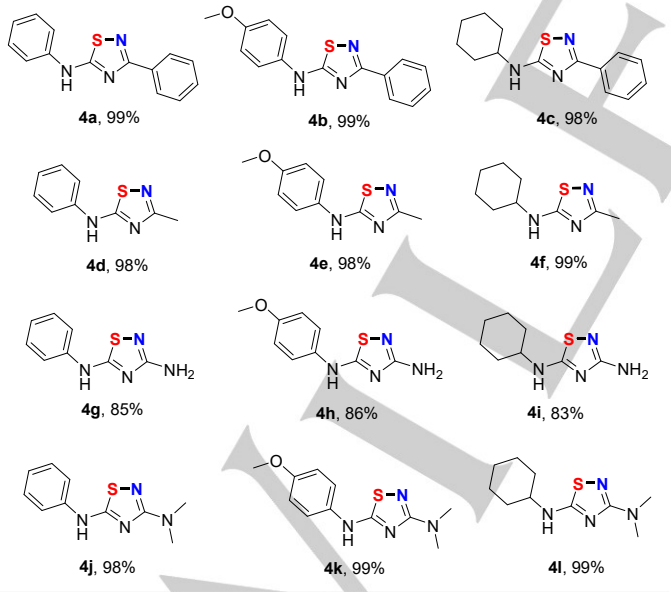
[a] Reaction conditions: **1** (0.5 mmol), CoPcS (1 mol %), 1 atm O_2, 5 mL H_2O, 100 °C, 12 h. [b] Isolated yield. [c] 8 h. [d] 24 h. [e] 0.3 Mpa O_2.

yields of **2a**. The replacement of 1 atm O_2 by air atmosphere lowered the yield to 59%.

With the optimal reaction conditions in hand, we continued to screen the reaction scope of the CoPcS-catalyzed intramolecular cyclization to synthesize a variety of *N*-substituted 1,2-benzisothiazol-3(*2H*)-one derivatives (Table 2). To be noted, substrate **1a** was found to be more reactive and the reaction could complete in 8 h under 1 atm O_2, however, for other substrates **1b-m**, the reaction time was extended to 12 h under the same conditions. In general, all *N*-substituted alkyl and aryl groups were well tolerated and furnished the desired 1,2-benzisothiazol-3(*2H*)-ones **2a-x** in excellent yields. The reaction was not affected by electron-donating groups, such as methyl (**2f-h**), methoxyl (**2i**), amino (**2j**), or electron-withdrawing groups, such as halogen (**2k-m**), nitrile (**2n**), nitro (**2o**), trifluoromethyl (**2p**), on the benzene ring. In addition, mercaptobenzamide **1f-h** bearing a methyl group at *ortho*-, *meta*- or *para*-position gave the desired compounds **2f-h** in similar yields. Substrates with pyridyl, naphthyl, benzyl groups, 1-(2-chlorophenyl)ethyl, and 2-(*1H*-indol-3-yl)ethyl groups on the nitrogen atom afforded the desired products in good to modest yields (**2q-w**). The product **2x** with two 1,2-benzisothiazol-3(*2H*)-one units was produced in 63% yield.

Table 3. Synthesis of Substituted 1,2,4-Thiadiazoles. [a], [b]

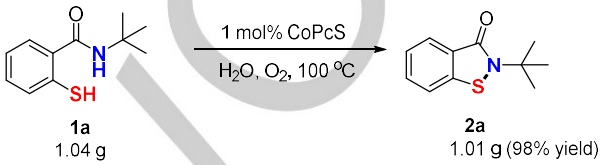




[a] Reaction conditions: 3 (0.5 mmol), catalyst (1 mol %), 5 mL H_2O, 1 atm O_2, 100 °C, 10 h. [b] Isolated yield.

Encouraged by the successful results, the reaction versatility of intramolecular oxidative coupling of S-H/N-H was further studied to synthesize 3-substituted 5-amino-1,2,4-thiadiazoles (Table 3). 1,2,4-Thiadiazole derivatives also are important sulfur-containing heterocylclic moieties with various biological and pharmaceutical properties.[24] 3-Aryl, alkyl, and *N*,*N*-dimethylamino substituted 5-amino-1,2,4-thiadiazoles under the optimal reaction conditions in quantitive yields, while the amion group led to good yields. *N*-substituents of 3-substituted 1,2,4-thiadiazoles showed no significant effect on the reaction.

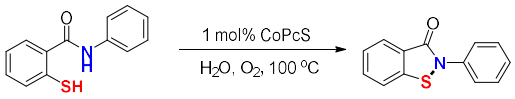
To demonstrate the synthetic value of this protocol, a gram-scale reaction of **1a** was performed (Scheme 1). This reaction could generate the desired product in an isolated yield of 98%.



Scheme 1. The gram scale reaction.

With water as solvent, the work-up procedure for some certain products was quite handy and convenient. Once completed, the reaction mixture could be simply filtered and washed by H_2O to give pure desired products, implying promising application of this synthetic strategy in chemical manufacturing and commercialization. Since there was nearly no byproduct, the mother liquor containing CoPcS should be able to be recycled. Therefore, the circulation of the mother liquor was performed based on the substrate **1e** (Table 4). The results showed that the mother liquor could be circulated up to 6 times with a minor loss in product yield.

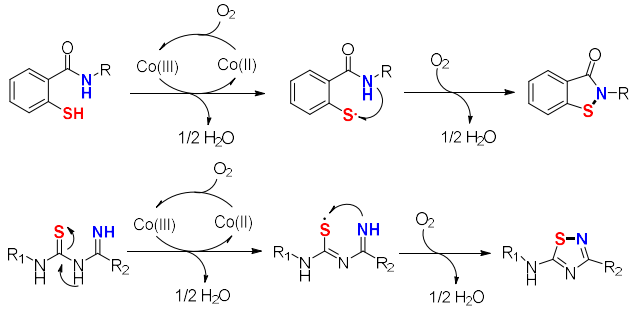
Table 4. The circulation of mother liquor for the synthesis of 1,2-benzisothiazol-3(*2H*)-one **2e**. [a],



Time	Yield(%)[b]
1	94
2	92
3	89
4	85
5	81
6	76

[a] Reaction conditions: **1e** (1 mmol), catalyst (1 mol %), 10 mL H_2O, 1 atm O_2, 100 °C, 12 h. [b] Isolated yield.

On the basis of our earlier study of aerobic dehydrogenative coupling of intermolecular S-H/N-H, the reaction mechanism is proposed as shown in Scheme 2. The interaction of CoPcS by molecular oxygen generates Co(III) complex, which is able to oxidize the thiyl group and result in the corresponding thiyl radical. The nucleophilic attack on the sulfur atom by N-H with the removal of H furnished the desired product.



Scheme 2. Proposed Reaction Mechanism.

Conclusions

Conclusively, we have developed a versatile and green tool for the synthesis of benzisothiazol-3(*2H*)-ones and 3-substituted 5-amino-1,2,4-thiadiazoles. The protocol applied molecular oxygen as the sole oxidant and avoids the usage of excess additives or base. Water as solvent enables simple product purification and mother liquor circulation. Such efficient and benign method for working with chemical processes and product addresses the challenges in green chemistry.

Experimental Section

General Information.

All materials and catalysts were purchased from general merchant. ^{1}H NMR and ^{13}C NMR spectra were recorded at a Bruker Avance III HD spectrometer (Bremen, Germany) at 600 MHz (400 MHz) for ^{1}H NMR and 150 MHz (100 MHz) for ^{13}CNMR with $CDCl_3$ or DMSO-d_6 as the solvent and TMS as the internal standard. High-resolution mass spectra (HRMS) were measured with an Agilent 1290-6540 Q-TOF (Santa Clara, CA). Low resolution mass spectra (LRMS) were recorded under electron ionization (EI) conditions using a Shimadzu GCMS-QP2010 Plus mass spectrometer (Kyoto, Japan). Infrared (IR) spectra were recorded on a PerkinElmer Spectrum Two FT-IR spectrophotometer and are reported as wave number (cm^{-1}) (Massachusetts, USA).The melting points of the products were determined using an X-4 micromelting point apparatus (Beijing, China).

Preparation of Substrates.

*General Procedure A for the substrates **1***: To a cooled (0 °C) solution of amine (4.6 mmol) in CH_2Cl_2 (12 mL) was added a solution of $AlMe_3$ in toluene (1.6 M, 2.9 mL, 4.6 mmol). The reaction mixture was warmed to room temperature and continued to stir for 30 min until the gas evolution ceased. Then, methyl thiosalicylate (0.31 mL, 2.3 mmol) was added and the solution was refluxed for 12 h. The reaction mixture was cooled in an ice bath, and aq HCl (5%, 12 mL) was added carefully. The solution was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic extracts were washed with a saturated aq solution of $NaHCO_3$ (20 mL) and brine (20 mL) consequently. Then, the organic layer was dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under vacuum, the residue was purified by using column chromatography to afford the substrates **1**.

*General Procedure B for the substrates **3a-f***: A mixture of an amidine salt (2.0 mmol), the corresponding isothiocyanate (2.2 mmol), and K_2CO_3 (414 mg, 3.0 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 12 h, then quenched with H_2O (10 mL), and extracted with CH_2Cl_2 (15 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified through silica gel column chromatography to afford the substrates **3a-f**.

*General Procedure C for the substrates **3g-l***: A mixture of an guanidine salt (2.4 mmol), the corresponding isothiocyanate (2.0 mmol), and K_2CO_3 (553 mg, 4.0 mmol) in EtOH (10 mL) was stirred at 70 °C for 3 h, and then concentrated under reduced pressure. The resulting residue was treated with H_2O (15 mL) and extracted with EtOAc (15 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified through silica gel column chromatography to afford the substrates **3g-l**.

General procedure for the synthesis of product 2 and 4.

A 25 mL Schlenk tube was charged with **1** or **3** (0.5 mmol), CoPcS (4.5 mg, 0.005 mmol), H_2O (5 mL), and 1 atm O_2, and then the resulting mixture was stirred at 100 °C for 8 h (for **3**, 10 h was required). The reaction mixture was extracted with ethyl acetate (3 × 10 mL) and then dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was subjected to flash column chromatography on silica gel to give the products **2** or **4**.

The procedure for gram scale reaction.

A 100 mL Schlenk tube was charged with **1a** (1.04 g, 5.0 mmol), CoPcS (45 mg, 0.05 mmol), H_2O (50 mL), and 1 atm O_2, and then the resulting mixture was stirred at 100 °C for 18 h. The reaction mixture was extracted with ethyl acetate (3 × 10 mL) and then dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was subjected to flash column chromatography on silica gel to give the products **2a.**

The procedure for recycling of mother liquor.

A 50 mL Schlenk tube was charged with 2-mercapto- *N*-phenyl benzamide (0.23 g, 1 mmol), CoPcS (8.9 mg, 1 mol %), H_2O (10 mL), and 1 atm O_2, and then the resulting mixture was stirred at 100 °C. After 12 h, the reaction mixture was filtered. The filter cake was dried and the desired product **2e** was obtained, giving the yield up to 94%. The filtrate was reused directly as the solvent in the next run in which 2-mercapto-*N*-phenylbenzamide (1 mmol) was added. The results are presented in **Table 4.** We carried out the oxidation process successfully in 6 runs, with the yields varying as follow: 94%, 92%, 89%, 85%, 81%, 76%.

Acknowledgments

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Keywords: Benzisothiazol-3(*2H*)-one • 1,2,4-Thiadiazole • Aqueous reaction • Homogeneous catalysis • Oxidation • Radical reaction •

[1] a) L. Craine, M. Raban, *Chem. Rev.* **1989,** *89*, 689-712; b) A. G. Romero, W. H. Darlington, M. F. Piercey, R. A. Lahti, *Bioorg. Med. Chem. Lett.* **1992,** *2*, 1703-1706; c) K. D. Combrink, H. B. Gülgeze, N. A. Meanwell, B. C. Pearce, P. Zulan, G. S. Bisacchi, D. G. M. Roberts, P. Stanley, S. M. Seiler, *J. Med. Chem.* **1998,** *41*, 4854-4860.

[2] M. McKibben, E. W. McClelland, *J. Chem. Soc., Trans.* **1923,** *123*, 170-173.

[3] a) P. Zoumpoulakis, C. Camoutsis, G. Pairas, M. Soković, J. Glamočlija, C. Potamitis, A. Pitsas, *Bioorg. Med. Chem.* **2012,** *20*, 1569-1583; b) P. Borgna, M. L. Carmellino, M. Natangelo, G. Pagani, F. Pastoni, M. Pregnolato, M. Terreni, *Eur. J. Med. Chem.* **1996,** *31*, 919-925; c) M. L. Carmellino, G. Pagani, M. Pregnolato, M. Terreni, F. Pastoni, *Eur. J. Med. Chem.* **1994,** *29*, 743-751.

[4] D. Dou, D. Alex, B. Du, K.-C. Tiew, S. Aravapalli, S. R. Mandadapu, R. Calderone, W. C. Groutas, *Bioorg. Med. Chem.* **2011,** *19*, 5782-5787.

[5] M. H. Norman, J. L. Kelley, E. B. Hollingsworth, *J. Med. Chem.* **1993,** *36*, 3417-3423.

[6] a) K.-C. Tiew, D. Dou, T. Teramoto, H. Lai, K. R. Alliston, G. H. Lushington, R. Padmanabhan, W. C. Groutas, *Bioorg. Med. Chem.* **2012,** *20*, 1213-1221; b) H. Lai, D. Dou, S. Aravapalli, T. Teramoto, G. H. Lushington, T. M. Mwania, K. R. Alliston, D. M. Eichhorn, R. Padmanabhan, W. C. Groutas, *Bioorg. Med. Chem.* **2013,** *21*, 102-113.

[7] K. H. Baggaley, P. D. English, L. J. A. Jennings, B. Morgan, B. Nunn, A. W. R. Tyrrell, *J. Med. Chem.* **1985,** *28*, 1661-1667.

[8] W. L. Jorgensen, A. Trofimov, X. Du, A. A. Hare, L. Leng, R. Bucala, *Bioorg. Med. Chem. Lett.* **2011,** *21*, 4545-4549.

[9] a) K. V. Thomas, *Biofouling* **2001,** *17*, 73-86; b) I. Gubelmann-Bonneau, F. Pfammatter, C. Schlatter, M. Vogt, Pesticidal compositions. Google Patents: **2002**; c) A. Brand, J. Leitermann, R. Nyssen, K. Schubert, E. Schuffenhauer, K. Wieser, H. Wigger, Aqueous pigment preparations. Google Patents: **1999**; d) R. E. Smith, E. S. Bensaid, Antimicrobial mixtures of 1,3-bis(hydroxymethyl)-5,5-dimethylhydantoin and 1,2-benzisothiazolin-3-one. Google Patents: **2000**.

[10] J. F. Schwensen, M. D. Lundov, R. Bossi, P. Banerjee, E. Gimenez-Arnau, J.-P. Lepoittevin, C. Lidén, W. Uter, K. Yazar, I. R. White, J. D. Johansen, *Contact Dermatitis* **2015,** *72*, 127-138.

[11] W. G. Rice, J. G. Supko, L. Malspeis, R. W. Buckheit, D. Clanton, M. Bu, L. Graham, C. A. Schaeffer, J. A. Turpin, J. Domagala, R. Gogliotti, J. P. Bader, S. M. Halliday, L. Coren, R. C. Sowder, L. O. Arthur, L. E. Henderson, *Science* **1995,** *270*, 1194-1197.

[12] a) M. Shimizu, Y. Sugano, T. Konakahara, Y. Gama, I. Shibuya, *Tetrahedron* **2002,** *58*, 3779-3783; b) J. C. Grivas, *J. Org. Chem.* **1975,** *40*, 2029-2032.

[13] a) T. Sano, T. Takagi, Y. Gama, I. Shibuya, M. Shimizu, *Synthesis* **2004,** *2004*, 1585-1588; b) A. Henke, J. Srogl, *Chem. Commun.* **2010,** *46*, 6819-6821.

[14] a) A. Correa, I. Tellitu, E. Domínguez, R. SanMartin, *Org. Lett.* **2006,** *8*, 4811-4813; b) Z. Wang, Y. Kuninobu, M. Kanai, *J. Org. Chem.* **2013,** *78*, 7337-7342.

[15] S. W. Wright, M. M. Abelman, L. L. Bostrom, R. L. Corbett, *Tetrahedron Lett.* **1992,** *33*, 153-156.

[16] a) V. Krasikova, M. Katkevics, *Chem. Heterocycl. Com*$^{+}$. **2013,** *48*, 1684-1690; b) B. S. Bhakuni, S. J. Balkrishna, A. Kumar, S. Kumar, *Tetrahedron Lett.* **2012,** *53*, 1354-1357; c) F. Wang, C. Chen, G. Deng, C. Xi, *J. Org. Chem.* **2012,** *77*, 4148-4151; d) T. Li, L. Yang, K. Ni, Z. Shi, F. Li, D. Chen, *Org. Biomol. Chem.* **2016,** *14*, 6297-6303; e) R. Paul, T. Punniyamurthy, *RSC Adv.* **2012,** *2*, 7057-7060.

[17] F.-J. Chen, G. Liao, X. Li, J. Wu, B.-F. Shi, *Org. Lett.* **2014,** *16*, 5644-5647.

[18] T. Chiyoda, K. Iida, K. Takatori, M. Kajiwara, *Synlett* **2000,** *2000*, 1427-1428.

[19] a) J. P. Yevich, J. S. New, D. W. Smith, W. G. Lobeck, J. D. Catt, J. L. Minielli, M. S. Eison, D. P. Taylor, L. A. Riblet, D. L. Temple, *J. Med. Chem.* **1986,** *29*, 359-369; b) C. K. Jin, J.-K. Moon, W. S. Lee, K. S. Nam, *Synlett* **2003,** *2003*, 1967-1968; c) P. Gopinath, K. Ramalingam, K. M. Muraleedharan, D. Karunagaran, *MedChemComm* **2013,** *4*, 749-752; d) A. Siegemund, K. Taubert, B. Schulze, *Sulfur Rep.* **2002,** *23*, 279-319; e) E. W. McClelland, A. J. Gait, *J. Chem. Soc.* **1926,** *129*, 921-925.

[20] W. Kim, J. Dannaldson, K. S. Gates, *Tetrahedron Lett.* **1996,** *37*, 5337-5340.

[21] M. Shimizu, T. Shimazaki, T. Yoshida, W. Ando, T. Konakahara, *Tetrahedron* **2012,** *68*, 3932-3936.

[22] Y. Dou, X. Huang, H. Wang, L. Yang, H. Li, B. Yuan, G. Yang, *Green Chem.* **2017,** *19*, 2491-2495.

[23] a) L. Yang, S. Li, Y. Dou, S. Zhen, H. Li, P. Zhang, B. Yuan, G. Yang, *Asian J. Org. Chem.* **2017,** *6*, 265-268; b) X. Huang, Y. Chen, S. Zhen, L. Song, M. Gao, P. Zhang, H. Li, B. Yuan, G. Yang, *J. Org. Chem.* **2018,** *83*, 7331-7340; c) Y. Zong, L. Yang, S. Tang, L. Li, W. Wang, B. Yuan, G. Yang, *Catalysts* **2018,** *8*, 48-57; d) Y. Dou, X. Huang, H. Wang, L. Yang, H. Li, B. Yuan, G. Yang, *Green Chem.* **2017,** *19*, 2491-2495; e) Y. Dou, L. Yang, L. Zhang, P. Zhang, H. Li, G. Yang, *RSC Adv.* **2016,** *6*, 100632-100635; f) L. Zhang, X. Huang, S. Zhen, J. Zhao, H. Li, B. Yuan, G. Yang, *Org. Biomol. Chem.* **2017,** *15*, 6306-6309.

[24] a) T. Tim Fat, L.-T. Regis, L. Wanren, S. Michael, K. Khashayar, *Mini-Rev. Med. Chem.* **2005,** *5*, 367-379; b) L. M. T. Frija, A. J. L. Pombeiro, M. N. Kopylovich, *Eur. J. Org. Chem.* **2017,** *2017*, 2670-2682; c) K. M. Dawood, T. A. Farghaly, *Expert Opin. Ther. Pat.* **2017,** *27*, 477-505; d) Y. Li, J. Geng, Y. Liu, S. Yu, G. Zhao, *ChemMedChem* **2013,** *8*, 27-41; e) K. Martin, V. Jarmila, *Curr. Top. Med. Chem.* **2016,** *16*, 2921-2952.

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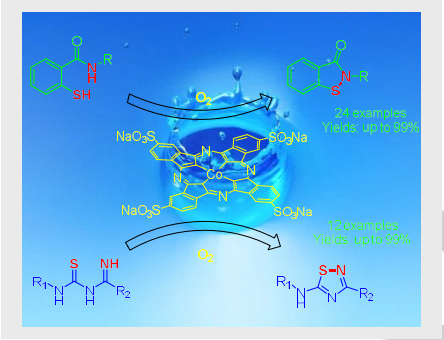
Sustainable synthesis of 1,2-benzisothiazol-3(*2H*)-ones and 1,2,4-thiadiazoles via intramolecular S-N bond formation were realized in aqueous media with good to excellent yields, which used tetra-sulfonated cobalt phthalocyanine as a catalyst and molecular oxygen as the environment friendly oxidant.



Sustainable Methodology

Liting Yang, Lijuan Song, Shanyu Tang, Longjia Li, Heng Li, Bingxin Yuan, and Guanyu Yang**

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Co-Catalyzed Intramolecular S-N Bond Formation in Water for 1,2-Benzisothiazol-3(*2H*)-ones and 1,2,4-Thiadiazoles Synthesis

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Sustainable Methodology