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Concise Approach to Benzisothiazol-3(2*H*)-one via Copper-Catalyzed Tandem Reaction of *o*-Bromobenzamide and Potassium Thiocyanate in Water

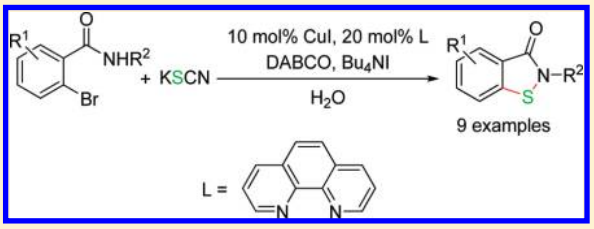
Fei Wang,[†] Chao Chen,*[,†] Geng Deng,[†] and Chanjuan Xi*[,†,‡]

[†]Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, China

[‡]State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

Supporting Information

ABSTRACT: A concise approach to various benzisothiazol-3(2*H*)-one derivatives has been developed by copper-catalyzed the reaction of *o*-bromobenzamide derivatives with potassium thiocyanate (KSCN) in water. The reaction proceeds via a tandem reaction with S−C bond and S−N bond formation.



Benzisothiazol-3(2*H*)-ones are widely used as pharmaceutical agents because of their fungistatic, antimicrobial, and antipsychotic activities.[1] Recently, benzisothiazol-3(2*H*)-one derivatives were discovered to be a potentially antithrombotic agent that could be developed into a drug for the first-phase aggregation ex vivo in man.[2] The traditional approaches to benzisothiazol-3(2*H*)-ones generally converged on the reaction of 2,2′-dithiosalicylic acids with amines[2,3] or amination of 2-mercaptobenzoate.[4] Although these protocols provided powerful access to benzisothiazol-3(2*H*)-ones, they often suffered limitations in scope and generality. Furthermore, some protocols proceeded via a multistep process with harsh reaction conditions and low yields. Because of the powerful requirement of benzisothiazol-3(2*H*)-ones in medicament, development of more practical methods to synthesize benzoisothiazol-3(2*H*)-ones from easily available materials is highly desirable.

Recently, one-pot strategy for the synthesis of various useful heterocyclic compounds based on the copper-catalyzed C-X (X = N, O, and S) bond formation have been studied.[5−7] For example, aminobenzothiazoles could be efficiently formed via a copper(I)-catalyzed one-pot cascade process of *o*-haloanilines with isothiocyanates.[7e,f] More recently, benzothiazole derivatives could be prepared via a copper-catalyzed three-component reaction of *o*-haloanilines, carbon disulfide, and nucleophiles.[7k] Although the chemistry of Cu-catalyzed C−N, C−O and C−S bond formations for the preparation of heterocyclic compounds is well explored, the reaction involving S−N bond formation is rare in the formation of heterocyclic compounds.[8] Furthermore, the use of water as solvent in organic reactions has attracted much attention in recent years because of its low cost, nontoxicity, safety, and environmental friendliness compared with organic solvents.[9] As part of an ongoing program in our laboratory to systematically synthesize a variety of heterocyclic compounds action in a one-pot strategy, we herein report the first example of synthesizing benzisothiazol-3(2*H*)-ones via copper-catalyzed tandem reaction of *o*-bromobenzamides and potassium thiocyanate (KSCN) under the water as solvent. This reaction includes new C−S bond and N−S bond formation in one pot.

In the preliminary experiment, we used *o*-bromobenzamide **1a** and potassium thiocyanate as the starting material and Cs_2CO_3 as a base in DMF at 140 °C, and the reaction did not proceed after 48 h (Table 1, entry 1). Then several bases were screened under the same reaction conditions. Clearly, inorganic bases such as Cs_2CO_3, K_3PO_4, and ^{t}BuONa were ineffective for this reaction (entries 1−3). Organic bases such as Et_3N and 1,4-diazabicyclo[2.2.2]octane (DABCO) could promote the reaction, and benzisothiazol-3(2*H*)-one **3a** was observed (entries 4 and 5). When 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was used as a base, the reaction did not proceed (entry 6). A range of ligands including *N*,*N*′-dimethylethylenediamine (DMEDA), tetramethylethylenediamine (TMEDA), 2,2-bipyridine, and 1,10-phenanthroline were screened (entries 7−10), and 1,10-phenanthroline was found to gave the best result (entry 10). We then examined the effect of different solvents, such as toluene, dimethyl sulfoxide (DMSO), MeCN, MeOH, and H_2O (entries 10−15). Of the solvents tested, water improved the yield to 41% (entry 15). In order to further improve the yield, a phase-transfer catalyst such as Bu_4NI was added in the reaction. To our delight, a satisfactory yield could be obtained when Bu_4NI was used as an additive in the reaction system (entry 16). The reaction also depended on the reaction temperature (entries 16 and 17). When the reaction temperature was decreased to 120 °C, the yield of product was decreased to 48% (entry 17). On the other hand, without use of CuI, the reaction did not proceed (entry 18). Furthermore, CuI

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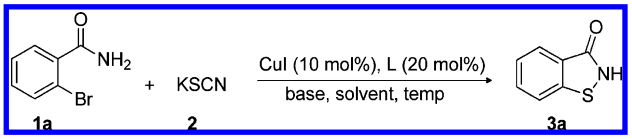
Table 1. Optimization between *o*-Bromobenzamide and Potassium Thiocyanate[a]



entry	base	ligand	solvent	temp (°C)	yield[b] (%)
1	Cs_2CO_3		DMF	140	trace
2	^{t}BuONa		DMF	140	trace
3	K_3PO_4		DMF	140	trace
4	Et_3N		DMF	140	15
5	DABCO		DMF	140	22
6	DBU		DMF	140	trace
7	DABCO	DMEDA	DMF	140	25
8	DABCO	TMEDA	DMF	140	30
9	DABCO	2,2′-bipyridine	DMF	140	35
10	DABCO	1,10-phenanthroline	DMF	140	37
11	DABCO	1,10-phenanthroline	toluene	140	22
12	DABCO	1,10-phenanthroline	DMSO	140	27
13	DABCO	1,10-phenanthroline	MeCN	140	30
14	DABCO	1,10-phenanthroline	MeOH	140	15
15	DABCO	1,10-phenanthroline	H_2O	140	41
16[c]	DABCO	1,10-phenanthroline	H_2O	140	60
17[c]	DABCO	1,10-phenanthroline	H_2O	120	48
18[d]	DABCO	1,10-phenanthroline	H_2O	140	NR
19[e]	DABCO	1,10-phenanthroline	H_2O	140	42
20[f]	DABCO	1,10-phenanthroline	H_2O	140	34
21[g]	DABCO	1,10-phenanthroline	H_2O	140	50
22[h]	DABCO	1,10-phenanthroline	H_2O	140	38

[a]Unless otherwise noted, the reactions were performed in a sealed tube with **1a** (0.5 mmol), **2** (1.0 mmol), base (1.0 mmol), CuI (10 mol %), and ligand (20 mol %) in solvent (1.0 mL) for 48 h. [b]Isolated yield. [c]Bu_4NI (20 mol %) was added. [d]Without CuI. [e]CuBr was added instead of CuI. [f]CuCl was added instead of CuI. [g]$CuCl_2$ was added instead of CuI. [h]$Cu(OAc)_2$ was added instead of CuI.

proved to be best choice among the screened copper salts under the reaction conditions (entries 16 and 19−22).

To our delight, the crystal of **3a** was suitable for single-crystal analysis, and its structure was fully characterized by X-ray diffraction analysis.[10] The structure of **3a** clearly shows the formation of the benzisothiazol-3(2*H*)-one skeleton, in which the C−S and S−N bond were formed within the five-membered ring.

On the basis of these results, the optimal reaction conditions involved the following parameters: CuI as a precatalyst, 1,10-phenanthroline as a ligand, DABCO as a base, Bu_4NI as an additive, and H_2O as a solvent with a reaction temperature of 140 °C. Under these optimized conditions, a study on the substrate scope was carried out, and the results are summarized in Table 2. First, we used *o*-bromobenzamide derivatives **1** to react with potassium thiocyanate **2**. The methyl group and fluoro atom on the benzene ring performed well (entries 2 and 3). Nitro-substituted *o*-bromobenzamide showed a lower yield (entry 4). Then different *N*-substituted *o*-bromobenzamide derivatives were applied under the optimized conditions. The behaviors of benzisothiazol-3(2*H*)-ones in fungistatic, antimicrobial, and antipsychotic bioactivities could be improved through the use of various *N*-substituents,[1,2] and our current work provides an easy-access procedure for the *N*-substituted benzisothiazol-3(2*H*)-ones. It is noteworthy that in this case a higher temperature (160 °C) was required to complete the reaction. For example, when *N*-methyl-2-bromobenzamide **1e** was treated with potassium thiocyanate at 160 °C, the desired product was obtained in 62% yield (entry 5). Other substrates such as ethyl- or *n*-butyl-substituted 2-bromobenzamide with potassium thiocyanate also proceeded in moderate yields (entries 6 and 7). When substrates **1h** and **1i** were employed in the reaction, the desired product **3h** and **3i** also formed in good yields, respectively (entries 8 and 9). When 2-bromo-*N*-phenylbenzamide **1j** was treated with potassium thiocyanate under the optimized conditions, the 2,2′-thiobis(*N*-phenylbenzamide) **4** was obtained under the reaction conditions in 35% yield without ring closure (entry 10).[11] This result may be attributed to the weaker nucleophilicity of nitrogen in aromatic amines.

On the basis of the above observations and reported literature,[12,13] a plausible reaction mechanism was proposed as shown in Scheme 1. The first step involves oxidative addition of CuI catalyst into the *o*-bromobenzamide and ligand exchange between Br^- and ^-SCN to form intermediate **I**. Reductive elimination then gives the aryl thiocyanate (**II**), which undergoes an intramolecularly nucleophilic substitution reaction[13] to afford compound **3**. The ^-CN group is hydrolyzed by a base under the reaction conditions.[11]

In summary, a novel method to prepare benzisothiazol-3(2*H*)-ones has been presented based on the copper-catalyzed reaction of *o*-halobenzamides with potassium thiocyanate (KSCN) in water. The reaction proceeds via a tandem reaction with S−C bond and S−N bond formation. Further application of this method to prepare other cyclic sulfur-containing heterocycles is under investigation in our laboratory

EXPERIMENTAL SECTION

Unless otherwise indicated, all materials were obtained from commercial sources and used as received. Column chromatography

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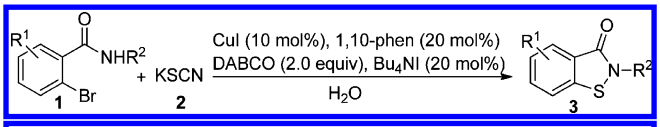
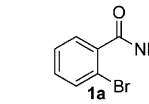
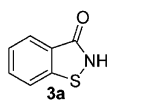
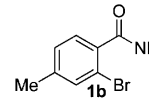
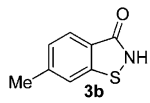
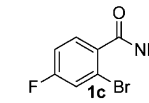
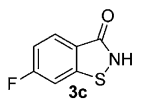
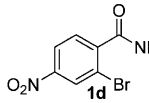
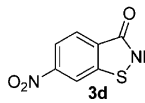
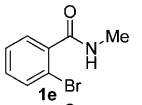
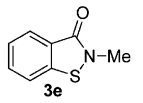
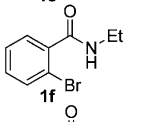
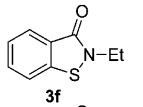
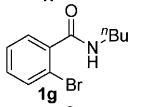
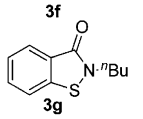
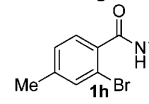
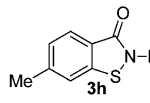
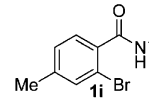
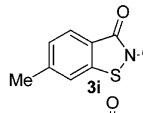
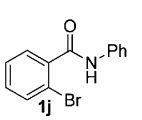
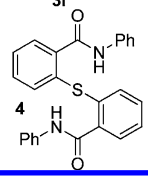
Table 2. CuI-catalyzed One-Pot Reactions of *o*-Bromobenzamides 1 with KSCN[a]



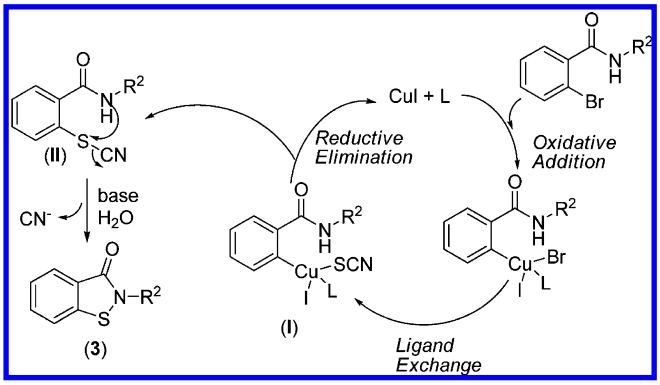
entry	substrate 1	temp (°C)	time (h)	product	yield (%)[c]
1	 1a	140	48	 3a	60
2	 1b	140	48	 3b	48
3	 1c	140	48	 3c	52
4	 1d	140	48	 3d	35
5	 1e	160	48	 3e	62
6	 1f	160	48	 3f	45
7	 1g	160	48	 3g	55
8	 1h	160	72	 3h	45
9	 1i	160	48	 3i	50
10[b]	 1j	160	72	 4	35

[a]Unless otherwise noted, the reactions were performed in a sealed tube with **1** (0.5 mmol), **2** (1.0 mmol), DABCO (1.0 mmol), CuI (10 mol %), ligand (20 mol %), and Bu_4NI (20 mol %) in H_2O (1 mL). [b]2,2′-Thiobis(*N*-phenylbenzamide) **4** was obtained under the reaction conditions without ring closure. [c]Isolated yields.

was performed on silica gel. ^1H NMR and ^{13}C NMR spectra were recorded on a 300 or 600 MHz spectrometer at ambient temperature with DMSO-d_6 or methanol-d_4 as the solvent. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of DMSO (2.50) or methanol (3.31), to the carbon resonance of DMSO-d_6 (39.52) or methanol-d_4 (39.00). Coupling constants (J) are given in hertz (Hz). The terms m, t, d, and s refer to multiplet, triplet, doublet, and singlet. The melting points were measured on an X-4 digital melting point apparatus and are uncorrected. Mass spectra were obtained using an ion-trap mass spectrometer in positive mode. IR spectra were recorded on AVATAR 360 FT-IR.

General Procedure for the Synthesis of Benzisothiazol-3(2*H*)-one. A sealed tube was charged with the mixture of *o*-halobenzamide **1** (0.5 mmol), potassium thiocyanate **2** (1.0 mmol),

Scheme 1. Proposed Reaction Pathway



CuI (0.05 mmol), 1,10-phenanthroline (0.1 mmol), DABCO (1.0 mmol), and Bu_4NI (0.1 mmol) and then stirred in H_2O (1 mL) at room temperature under nitrogen atmosphere. Half an hour later, the tube was sealed, and the mixture was allowed to stir at 140−160 °C for the indicated time. After completion of the reaction, the mixture was cooled to room temperature, and then H_2O (5 mL) was added and the mixture extracted with EtOAc (5 mL × 3) and dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel (petroleum ether/ethyl acetate = 2/1) provided the corresponding product **3**.

Benzisothiazol-3(2*H*)-one (3a).[3d] White solid, 45 mg (60% yield). Mp: 150−151 °C (lit.[3d] mp 157−158 °C). ^1H NMR (DMSO-d_6, 300 MHz): δ 7.41−7.44 (m, 1H), 7.59−7.62 (m, 1H), 7.87−7.98 (m, 2H), 11.42 (brs, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 121.6, 124.3, 124.8, 125.0, 130.2, 147.4, 165.0. IR (KBr) ν_{max}: 3462, 2921, 1638, 1591, 742, 605 cm^{-1}. ESI-MS: $[M + H]^+$ m/z 152.2.

6-Methylbenzisothiazol-3(2*H*)-one (3b). White solid, 39 mg (48% yield). Mp: 198−200 °C. ^1H NMR (DMSO-d_6, 300 MHz): δ 2.43 (s, 3H), 7.24 (d, J_{H-H} = 8.2 Hz, 1H), 7.72−7.76 (m, 2H), 11.19 (brs, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 21.3, 121.0, 122.6, 124.0, 126.6, 140.6, 147.4, 164.9. IR (KBr) ν_{max}: 3461, 2913, 1627, 1514, 761, 600 cm^{-1}. ESI-MS: $[M + H]^+$ m/z 166.3. HRMS calcd for C_8H_7NOS: 166.0321 $(M + H)^+$, found 166.0324.

6-Fluorobenzisothiazol-3(2*H*)-one (3c). White solid, 44 mg (52% yield). Mp: 213-215 °C. ^1H NMR (DMSO-d_6, 600 MHz): δ 7.27−7.30 (m, 1H), 7.87−7.91 (m, 2H), 11.56 (brs, 1H). ^{13}C NMR (DMSO-d_6, 150 MHz): δ 108.3 (d, J_{F-C} = 27.3 Hz), 114.4 (d, J_{F-C} = 24.4 Hz), 122.2, 126.7 (d, J_{F-C} = 10.0 Hz), 150.0, 163.8 (J_{F-C} = 245.6 Hz), 164.6. IR (KBr) ν_{max}: 3457, 3069, 1642, 1465, 754, 605 cm^{-1}. ESI-MS: $[M + H]^+$ m/z 170.2. HRMS calcd for C_7H_4FNOS: 170.0070 $(M + H)^+$, found 170.0067.

6-Nitrobenzisothiazol-3(2*H*)-one (3d).[4d] Light yellow solid, 34 mg (35% yield). Mp: 272−274 °C (lit.[4d] mp 275−280 °C). ^1H NMR (DMSO-d_6, 300 MHz): δ 8.07 (d, J_{H-H} = 8.9 Hz, 1H), 8.19 (d, J_{H-H} = 8.9 Hz, 1H), 9.06 (s, 1H), 12.44 (brs, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 118.0, 119.6, 124.9, 128.5, 148.0, 148.4, 163.3. IR (KBr) ν_{max}: 3464, 3093, 1643, 1339, 721, 608 cm^{-1}. ESI-MS: $[M + H]^+$ m/z 197.2.

2-Methylbenzisothiazol-3(2*H*)-one (3e).[4c] White solid, 51 mg (62% yield). Mp: 46−47 °C (lit.[4c] mp 50−51 °C). ^1H NMR (methanol-d_4, 300 MHz): δ 3.43 (s, 3H), 7.40−7.46 (m, 1H), 7.62−7.68 (m, 1H), 7.76 (d, J_{H-H} = 8.2 Hz, 1H), 7.92 (d, J_{H-H} = 8.2 Hz, 1H). ^{13}C NMR (methanol-d_4, 75 MHz): δ 30.7, 122.1, 125.2, 126.7, 126.8, 133.2, 142.1, 167.3; IR (KBr) ν_{max}: 3065, 1640, 1337, 740, 667 cm^{-1}. ESI-MS: $[M + H]^+$ m/z 166.2.

2-Ethylbenzisothiazol-3(2*H*)-one (3f).[14] Colorless oil, 40 mg (45% yield). ^1H NMR (methanol-d_4, 300 MHz): δ 1.35 (t, J_{H-H} = 7.2 Hz, 3H), 3.94 (q, J_{H-H} = 7.2 Hz, 2H), 7.42−7.47 (m, 1H), 7.64−7.69 (m, 1H), 7.78 (d, J_{H-H} = 8.2 Hz, 1H), 7.93 (d, J_{H-H} = 7.9 Hz, 1H). ^{13}C NMR (methanol-d_4, 75 MHz): δ 14.9, 40.2, 122.2, 125.7, 126.8, 126.8, 133.2, 142.2, 166.8. IR (KBr) ν_{max}: 2975, 1652, 1447, 741, 673 cm^{-1}. ESI-MS: $[M + H]^+$ m/z 180.1.

2-Butylbenzisothiazol-3(2*H*)-one (3g).[3c] Colorless oil, 57 mg (55% yield). ^1H NMR (methanol-d_4, 300 MHz): δ 0.96 (t, J_{H-H} = 7.6

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Hz, 3H), 1.34−1.41 (m, 2H), 1.69−1.76 (m, 2H), 3.90 (t, J_{H-H} = 7.2 Hz, 2H), 7.42−7.47 (m, 1H), 7.63−7.68 (m, 1H), 7.77 (d, J_{H-H} = 8.2 Hz, 1H), 7.93 (d, J_{H-H} = 7.9 Hz, 1H). ^{13}C NMR (methanol-d_4, 75 MHz): δ 13.9, 20.7, 32.6, 44.7, 122.1, 125.6, 126.8, 126.9, 133.2, 142.2, 167.1. IR (KBr) ν_{max}: 2958, 1662, 1447, 740, 674 cm^{-1}. ESI-MS: $[M + H]^+$ m/z 208.3.

2,6-Dimethylbenzisothiazol-3(2*H*)-one (3h). White solid, 38 mg (45% yield). Mp: 79−80 °C. ^{1}H NMR (methanol-d_4, 300 MHz): δ 2.46 (s, 3H), 3.40 (s, 3H), 7.25 (d, J_{H-H} = 8.2 Hz, 1H), 7.53 (s, 1H), 7.79 (d, J_{H-H} = 7.9 Hz, 1H). ^{13}C NMR (methanol-d_4, 75 MHz): δ 21.9, 30.7, 121.7, 122.9, 126.5, 128.4, 142.4, 144.5, 167.4. IR (KBr) ν_{max}: 2923, 1642, 1331, 754, 669 cm^{-1}. ESI-MS: $[M + H]^+$ m/z 180.1. HRMS calcd for C_9H_9NOS: 180.0478 $(M + H)^+$, found 180.0480.

2-Butyl-6-methylbenzisothiazol-3(2*H*)-one (3i). Colorless oil, 55 mg (50% yield). ^{1}H NMR (methanol-d_4, 300 MHz): δ 0.95 (t, J_{H-H} = 7.2 Hz, 3H), 1.33−1.41 (m, 2H), 1.67−1.75 (m, 2H), 2.46 (s, 3H), 3.87 (t, J_{H-H} = 6.9 Hz, 2H), 7.26 (d, J_{H-H} = 8.2 Hz, 1H), 7.55 (s, 1H), 7.80 (d, J_{H-H} = 8.2 Hz, 1H). ^{13}C NMR (methanol-d_4, 75 MHz): δ 13.9, 20.7, 21.9, 32.6, 44.6, 121.8, 123.3, 126.6, 128.4, 142.5, 144.5, 167.1. IR (KBr) ν_{max}: 2959, 1662, 1457, 760, 671 cm^{-1}. ESI-MS: $[M + H]^+$ m/z 222.1. HRMS calcd for $C_{12}H_{15}NOS$: 222.0947 $(M + H)^+$, found 222.0949.

2,2′-Thiobis(*N*-phenylbenzamide) (4). Light yellow solid, 37 mg (35% yield). Mp: 219−220 °C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 7.06−7.11 (m, 2H), 7.25−7.32 (m, 6H), 7.35−7.42 (m, 4H), 7.59−7.62 (m, 4H), 7.70 (d, J_{H-H} = 7.9 Hz, 2H), 10.45 (s, 2H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 119.7, 123.7, 127.3, 127.9, 128.7, 130.6, 132.6, 134.2, 139.0, 139.3, 166.3. IR (KBr) ν_{max}: 3054, 1649, 1437, 751, 688 cm^{-1}. ESI-MS: $[M + Na]^+$ m/z 447.3. HRMS calcd for $C_{26}H_{20}N_2O_2S$: 447.1138 $(M + Na)^+$, found 447.1140.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR and ^{13}C NMR spectra for compounds **3a**−**i** and **4** and X-ray data for **3a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: (C.C.) chenchao01@mails.tsinghua.edu.cn; (C.X.) cjxi@tsinghua.edu.cn.

Notes

The authors declare no competing financial interest.

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