DOI: 10.1002/adsc.201600429
Advanced Synthesis & Catalysis

Copper(I) Bromide-Dimethyl Sulfide-Catalyzed Direct Sulfanylation of 4-Hydroxycoumarins and 4-Hydroxyquinolinones with Arylsulfonylhydrazides and Selective Fluorescence Switch-On Sensing of Cadmium(II) Ion in Water

Sanjay Paul,[a] Rajeev Shrestha,[a] T. N. J. I. Edison,[a] Yong Rok Lee,[a,*] and Sung Hong Kim[b]

[a] School of Chemical Engineering, Yeungnam University, Gyeongsan 712–749, Republic of Korea
Fax: (+82)-53–810–4631; phone: (+82)-53–810–2529; e-mail: yrlee@yu.ac.kr
[b] Analysis Research Division, Daegu Center, Korea; Basic Science Institute, Daegu 702-701, Republic of Korea

Received: April 22, 2016; Revised: July 12, 2016; Published online: ■■ ▮▮, 0000

Supporting information for this article can be found under: http://dx.doi.org/10.1002/adsc.201600429.

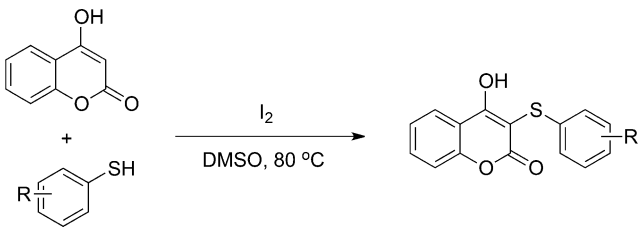
Abstract: An efficient protocol for the direct sulfanylation of various 4-hydroxycoumarins and 4-hydroxyquinolinones in good yield with arylsulfonylhydrazides as sulfanylating agents was developed *via* copper(I) bromide·dimethyl sulfide-catalyzed S–O, S–N bond cleavage and C–S cross-coupling reactions. A highly selective fluorescence turning-on sensing of cadmium(II) ions in water using the synthesized 3-sulfanyl-4-hydroxycoumarin derivative was also investigated.

Keywords: cadmium(II); cross-coupling; sulfanylation; 3-sulfanyl-4-hydroxycoumarins; 3-sulfanyl-4-hydroxyquinolinones; switch-on sensing

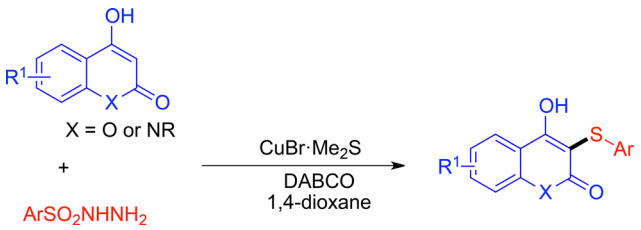
Molecules bearing a C–S bond are a privileged structural motif widely found in bioactive natural products,[1] pharmaceuticals,[2] and functional materials.[3] These sulfanylated coumarin and quinolinone derivatives have a wide range of biological and pharmacological activities, such as antifungal,[4] antibacterial,[5] antimicrobial,[6] and anti-HCV activities.[7] Because of their importance and usefulness, several synthetic approaches for the sulfanylation of 4-hydroxycoumarins and 4-hydroxyquinolinones have been developed by C–S bond formation between coumarins or quinolinones and sulfanylating reagents.[5,8] The representative approach for 3-sulfanylcoumarins or 3-sulfanylquinolinones includes the reaction of hydroxycoumarins and hydroxyquinolinones with the corresponding thiols and disulfides.[5] Recently, the Peddinti group reported an iodine-catalyzed method for the synthesis of 3-sulfanylcoumarin derivatives using aryl thiols as a sulfanylating agent (Scheme 1).[8] Traditionally, sulfanamides,[9] sulfanyl halides,[10] disulfides,[11] thiols,[5] and sulfanate esters[12] are used as the thiolating agent.

Although several synthetic methods for the sulfanylation of 4-hydroxycoumarins and 4-hydroxyquinolinones have been described, most of these synthetic protocols encounter drawbacks including harsh reaction conditions, especially the use of foul-smelling and volatile sulfanylating reagents such as thiols, disulfides, and thiolates. Therefore, more efficient and facile arsenals are still needed, which prompted this study to develop a new methodology relying on the characteristic reactivity of arylsulfonylhydrazides as a sulfanylating agent.

Recently, arylsulfonylhydrazides have been used widely as ideal and useful sulfanylation agents for C–S bond formation.[13] Copper-catalyzed direct C–H functionalization has attracted enormous attention over the past decade because of the high functional group compatibility of copper metal as well as the easy accessibility, and cost-effectiveness.[14] In this regard, sulfonyl hydrazides, a readily accessible synthetic intermediate, were used as the *in-situ* disulfide source for the copper-catalyzed C–S bond formation.



Scheme 1. Reported method for the sulfanylation of 4-hydroxycoumarin.

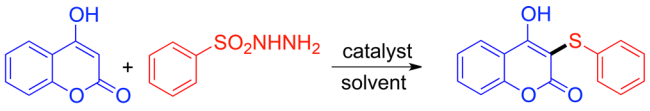


Scheme 2. Our protocol for the sulfanylation of 4-hydroxycoumarins and 4-hydroxyquinolinones.

To the best of the our knowledge, there are no reports on the CuBr·Me_2S-catalyzed sulfanylation of 4-hydroxycoumarins and 4-hydroxyquinolinones with arylsulfonylhydrazides. Herein, we describe the CuBr·Me_2S-catalyzed direct sulfanylation of 4-hydroxycoumarins and 4-hydroxyquinolinones for the synthesis of diverse 3-sulfanyl-4-hydroxycoumarins and 3-sulfanyl-4-hydroxyquinolinones (Scheme 2).

The direct coupling between 4-hydroxycoumarin (**1a**) and benzenesulfonylhydrazide (**2a**) using different catalysts and solvents was first examined (Table 1). The initial attempt in presence of 10 mol% Ag_2O, $Cu(OTf)_2$, or $Cu(OAc)_2$ catalyst and 1.0 equivalent of DABCO as the base additive did not provide the coupling product **3a** (entries 1–3). On the other hand, the reactions of **1a** with **2a** in the presence of 10 mol% of I_2, CuI, and CuBr afforded **3a** in 68, 65 and 70% yields, respectively (entries 4–6). The best result (88% yield) was achieved using 10 mol% of CuBr·Me_2S as a catalyst in combination with 1.0 equivalent of DABCO in refluxing 1,4-dioxane for 5 h (entry 7). The product **3a** was not detected in the absence of copper catalyst (entry 8). In the absence of the additive DABCO, the yield of **3a** was only 10% (entry 9). To improve the yield of this sulfanylation reaction, different base additives, such as DBU and Et_3N, were screened using the catalyst CuBr·Me_2S. With a combination of CuBr·Me_2S (10 mol%) and DBU (1.0 equiv.) or Et_3N (1.0 equiv.), the yield of **3a** decreased to 60 and 50% (entries 10 and 11), respectively. The product yield was not improved by increasing the catalyst loading to 15 mol% or decreasing it to 5 mol% (entries 12 and 13). In polar solvents, such as acetonitrile, DMSO, and DMF, **3a** was produced in 45, 58, and 66% yields, respectively, whereas in a nonpolar solvent, toluene, **3a** was obtained in only 10% yield (entries 14–17). The structure of **3a** was determined by an analysis of its spectral data and by a comparison with the reported values.[8]

Table 1. Optimization of reaction conditions for the synthesis of **3a**.[a]



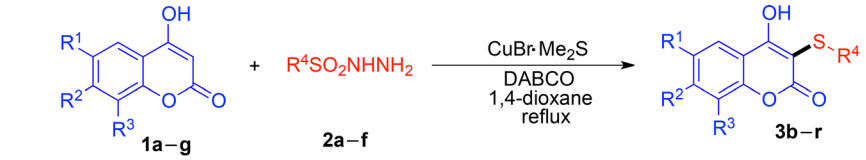
1a **2a** **3a**

Entry	Catalyst (mol%)	Additive	Solvent	Time [h]	Yield [%]
1	Ag_2O (10)	DABCO	1,4-dioxane	15	-
2	$Cu(OTf)_2$ (10)	DABCO	1,4-dioxane	15	-
3	$Cu(OAc)_2$ (10)	DABCO	1,4-dioxane	15	-
4	I_2 (10)	-	1,4-dioxane	10	68
5	CuI (10)	DABCO	1,4-dioxane	6	65
6	CuBr (10)	DABCO	1,4-dioxane	6	70
7	**CuBr·Me_2S (10)**	**DABCO**	**1,4-dioxane**	**5**	**88**
8	-	DABCO	1,4-dioxane	15	-
9	CuBr·Me_2S (10)	-	1,4-dioxane	15	10
10	CuBr·Me_2S (10)	DBU	1,4-dioxane	5	60
11	CuBr·Me_2S (10)	Et_3N	1,4-dioxane	5	50
12	CuBr·Me_2S (15)	DABCO	1,4-dioxane	5	88
13	CuBr·Me_2S (5)	DABCO	1,4-dioxane	6	60
14	CuBr·Me_2S (10)	DABCO	CH_3CN	8	45
15	CuBr·Me_2S (10)	DABCO	DMSO	8	58
16	CuBr·Me_2S (10)	DABCO	DMF	8	66
17	CuBr·Me_2S (10)	DABCO	toluene	8	10

[a] *Reaction conditions:* **1a** (1.0 mmol), **2a** (1.5 mmol), catalyst (mol%), and additive (1.0 equiv) in 5.0 mL of solvent, at 100 °C

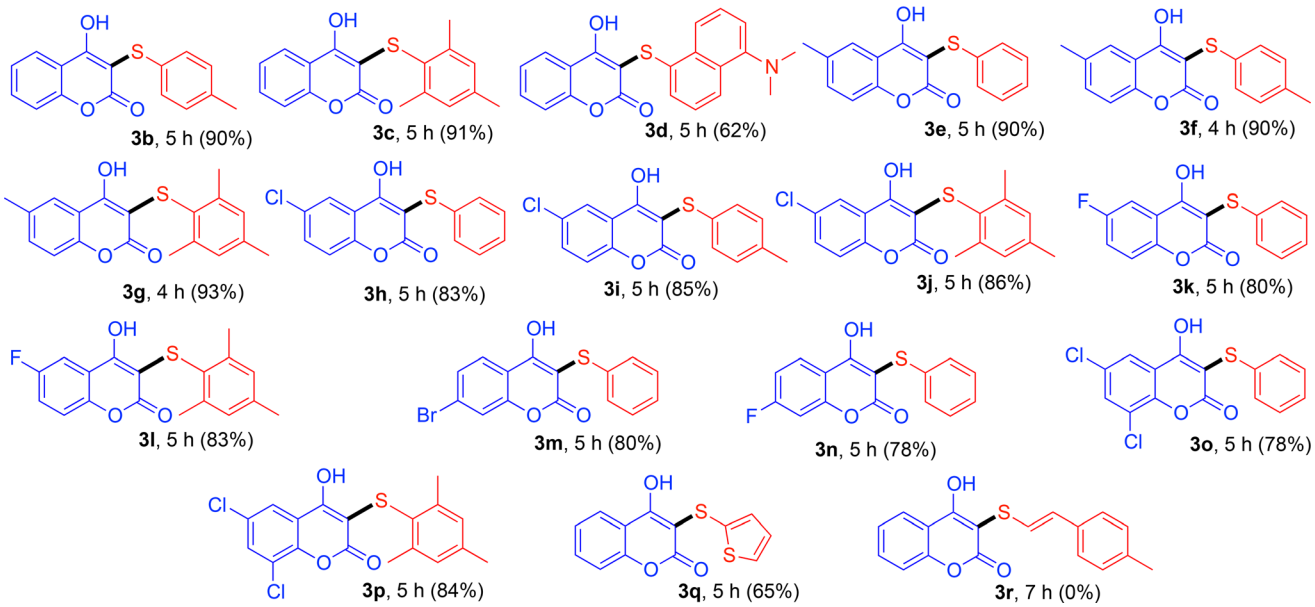
Under these optimized reaction conditions, the substrate scope was examined further using various 4-hydroxycoumarins **1a–1g** and sulfonyl hydrazides **2a–2f** (Table 2). Substituents, such as methyl, bromo, chloro, and fluoro on the benzene ring of coumarins were well tolerated, and several sulfonyl hydrazides bearing *p*-tolyl, mesityl, and 5-(dimethylamino)naphthalen-1-yl groups were coupled well with the corresponding 4-hydroxycoumarins to afford the desired products in good yield. For example, reactions of **1a** with **2b–d** for 5 h provided the desired products **3b–3d** in 90, 91, and 62% yields, respectively. The treatment of **1b** bearing an electron-donating methyl group at the 6-position on the benzene ring of 4-hydroxycoumarin with sulfonyl hydrazides **2a–2c** afforded **3e–3g** in 90–93% yield, whereas reactions of **1c–f** bearing electron-withdrawing groups, such as 6-Cl, 6-F, 7-Br, and 7-F, provided **3h–3n** in 78–86% yield. In the case of **1g** bearing two electron-withdrawing substituents on the benzene ring of hydroxycoumarin, the desired products **3o** and **3p** were isolated in 78 and 84% yields, respectively. To investigate the possibility of the use of heteroarylsulfonylhydrazide and alkenesulfonylhydrazide, additional reactions of thiophene-2-sulfonohydrazide (**2e**) and (*p*-tolyl)ethene-1-sulfonohydrazide (**2f**) were next carried out. Treatment of **1a** with **2e** in 1,4-dioxane at 100 °C for 5 h afforded the desired product **3q** in 65% yield, whereas that with **2f** did not provide the desired product **3r**. In this case, both starting materials **1a** and **2f** were recovered. In addition, reaction of 2*H*-chromen-2-one with benzenesulfonyl hydrazide in 1,4-dioxane at 100 °C for 12 h did not provide the desired product. In this reaction, benzenesulfonylhydrazide was decomposed, but unreacted 2*H*-chromen-2-one was recovered.

Table 2. CuBr·Me_2S-catalyzed synthesis of diverse 4-hydroxy-3-sulfanylcoumarin derivatives.[a]



1a R^1 = H, R^2 = H, R^3 = H
1b R^1 = Me, R^2 = H, R^3 = H
1c R^1 = Cl, R^2 = H, R^3 = H
1d R^1 = F, R^2 = H, R^3 = H
1e R^1 = H, R^2 = Br, R^3 = H
1f R^1 = H, R^2 = F, R^3 = H
1g R^1 = Cl, R^2 = H, R^3 = Cl

2a R^4 = phenyl
2b R^4 = *p*-tolyl
2c R^4 = mesityl
2d R^4 = 5-(dimethylamino)naphthalen-1-yl
2e R^4 = 2-thienyl
2f R^4 = 2-*p*-tolylethenyl



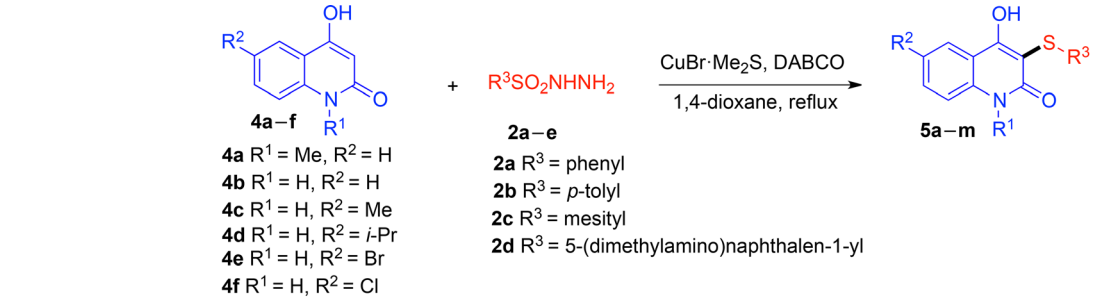
[a] *Reaction conditions:* 4-hydroxycoumarins (1.0 mmol), sulfonyl hydrazides (1.5 mmol), CuBr·Me_2S (10 mol%), and DABCO (1.0 equiv) in 5.0 mL of 1,4-dioxane, at 100 °C

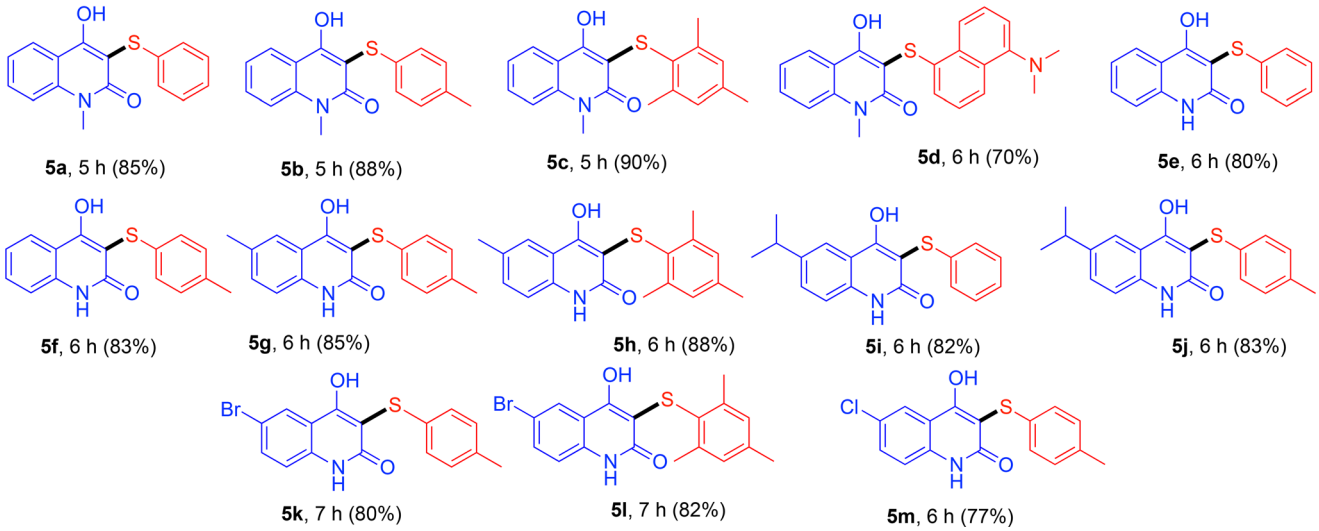
To further demonstrate the versatility of this sulfanylation, additional reactions of various 4-hydroxyquinolinones with arylsulfonylhydrazides were examined (Table 3). The reactions of 4-hydroxy-1-methylquinolone (**4a**) with **2a**–**2d** produced the desired products **5a**–**5d** in 70–90% yield, whereas those of **4b** with **2a** and **2b** afforded **5e** and **5f** in 80 and 83% yields, respectively. In addition, reactions of 4-hydroxyquinolinones **4c**–**4f** bearing electron-donating or electron-withdrawing groups on the aromatic ring were also successful. The reactions of **4c** and **4d** bearing electron-donating groups, such as 6-methyl or 6-isopropyl with **2a**–**2c** provided the desired products **5g**–**5j** in 82–88% yield, and those of **4e** and **4f** bearing electron-withdrawing groups, such as 6-bromo or 6-chloro with **2b** and **2c** afforded **5k**–**5m** in 80, 82, and 77% yields, respectively.

Some control experiments were next performed to obtain further insight into the mechanism of this sulfanylation reaction, as shown in Scheme 3. First, in the absence of 4-hydroxycoumarin or 4-hydroxyquinolinone, *S*-phenyl benzenesulfonothioate (**6**) and diphenyl disulfide (**7**) were isolated in 35 and 55% yield, respectively, under the standard reaction conditions [Eq. (1)]. On the other hand, upon refluxing with the arylsulfonylhydrazides for 24 h in 1,4-dioxane in the absence of copper(I) complex, neither **6** nor **7** were detected. Importantly, the reaction of **6** or **7** with 4-hydroxycoumarin provided the product **3a** in 80 and 82%, respectively, under optimized reaction conditions [Eqs. (2) and (3)]. These results clearly show that *S*-phenyl benzenesulfonothioate (**6**) or disulfide (**7**) might be an intermediate for this sulfanylation reaction. On the other hand, the effects of a radical scavenger were not observed when a reaction of **1a** with **2a** was attempted with the addition of TEMPO under the optimized conditions. This result excludes the possibility of a radical pathway [Eq. (4)].

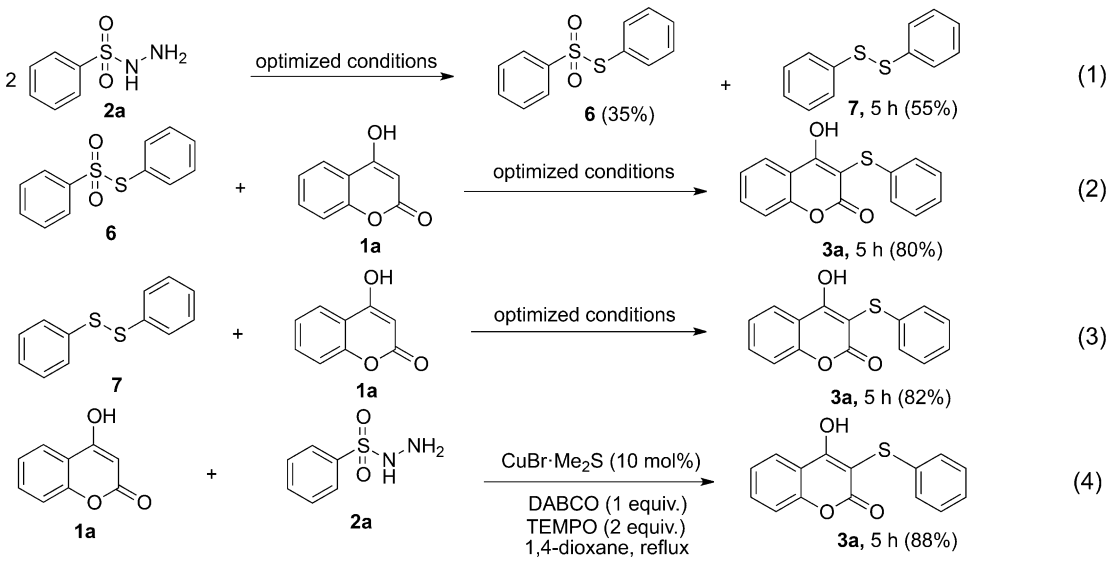
Based on previously reported studies and these experimental results, a plausible mechanistic pathway is

Table 3. CuBr·Me_2S-catalyzed synthesis of diverse 4-hydroxy-3-sulfanylquinolinone derivatives.[a]



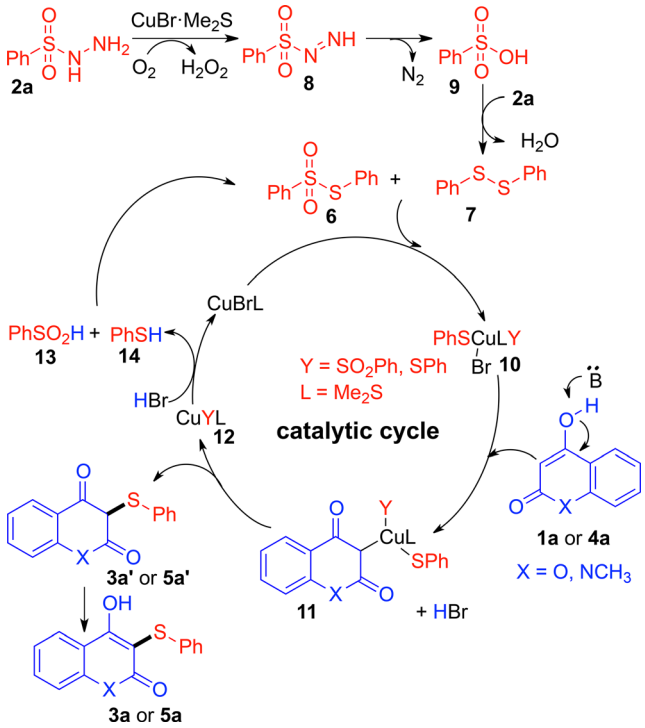


[a] *Reaction conditions:* 4-hydroxyquinolinones (1.0 mmol), sulfonyl hydrazides (1.5 mmol), CuBr·Me_2S (10 mol%), and DABCO (1.0 equiv) in 5.0 mL of 1,4-dioxane, at 100 °C



Scheme 3. Control experiments.

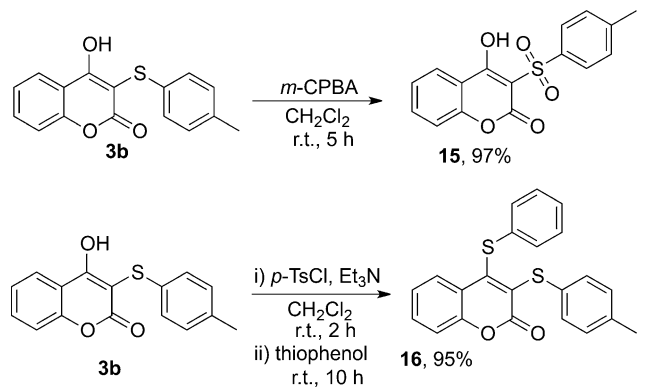
presented in Scheme 4 for the formation of **3a** and **5a** through the sulfanylation reaction.[13] The reaction is first initiated by Cu(I)-catalyzed aerobic oxidation to give intermediates thiosulfonate **6** and disulfide **7** via intermediates **8** and **9** through redox decomposition.[15] The copper catalyst then reacts with **6** or **7** to



Scheme 4. Proposed mechanism for the formation of **3a** or **5a**.

form copper(III) complex **10**, which undergoes DABCO-mediated transmetallation at the 3-position of 4-hydroxycoumarins or 4-hydroxyquinolinones to form another intermediate copper(III) complex **11**.[16] The reductive elimination of the copper(III) complex **11** gives **3a′** or **5a′** and copper (I) complex **12**. The exchange of copper(I) complex **12** with HBr leads to sulfinic acid **13** or thiol **14** and generates the copper (I) catalyst. Keto-enol tautomerzation of intermediate **3a′** or **5a′** leads to the final product **3a** or **5a**.

To explore the utility of the synthesized compounds, further conversion reactions were investigated (Scheme 5). For example, reaction of **3b** in the presence *m*-CPBA at room temperature for 5 h provided the pharmacologically interesting 4-hydroxy-3-tosyl-2*H*-chromen-2-one (**15**) in 97% yield.[5a] In addition, treatment of **3b** with *p*-TsCl and triethylamine followed by addition of thiophenol afforded 4-(phenylthio)-3-(*p*-tolylthio)-2*H*-chromen-2-one (**16**) in 95% yield, which shows that the synthesized sulfanyl derivatives can be effectively used for the conversion to various coumarin derivatives bearing two different sulfanyl groups at the 3- and 4-positions on the coumarin ring.



Scheme 5. The utility of the synthesized compound **3b**.

Several organic molecules have been successfully applied for the fluorescence sensing of various toxic metal ions such as Hg^{2+}, Pb^{2+}, Cd^{2+} and Cu^{2+}.[17a,18] Among these metal ions, Cd^{2+} is widely used in the field of electroplating, metallurgy and weapons industry. Therefore, the effluents of these industries contain high levels of Cd^{2+}, which lead to serious health issues such as renal dysfunction, calcium metabolism disorders, and prostate cancer.[17b] Hence, the detection and sensing of Cd^{2+} is significantly important.

In this regard, we have examined the fluorescence sensing ability of the synthesized compound **3f** in acetonitrile towards important metal ions in water. Figure 1a shows the fluorescence selectivity responses of **3f** towards many metal ions namely Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}. The results strongly suggested that **3f** is highly selective in sensing Cd^{2+} ions among other screened metal ions by fluorescence enhancement (Figure 1a).

Furthermore, the sensitivity of **3f** has also been tested towards different concentrations of Cd^{2+} ion in water as shown in Figure 1b. The maximum emission intensity (442 nm) was linearly fitted with various concentrations of Cd^{2+} ion (Figure 2a), which was identified from the linear correlation coefficient value ($R^2 = 0.99$).[17c] The detection limit of **3f** towards Cd^{2+} ion in water was found to be 6.29 μM. These results demonstrate that **3f** has highly efficient fluorescence selectivity and sensitivity towards Cd^{2+} ion. In addition, the results of Job's plot (Figure 2b) showed that at the maximum fluorescence intensity the binding ratio of Cd^{2+} ion and **3f** is 1:1. The enhanced fluorescence of **3f** (CHEF) can be attributed to the chelation between Cd^{2+} ion and the lone pair electrons of sulfur and oxygen (hydroxy group) along with the blocking of photoinduced electron transfer.[17d] In order to compare with the synthesized compound **3f**, we have tested the fluorescence sensing ability of commercially available 4-hydroxycoumarin, 4-hydroxyquinoline, and *p*-tolenesulfonylhydrazide, which did not show any fluorescence sensing properties for the detection of cadmium(II) ions.

In summary, we have disclosed a CuBr·Me_2S-catalyzed direct sulfanylation of 4-hydroxycoumarins and 4-hydroxyquinolinones to afford diverse 3-arylsulfanyl-4-hydroxycoumarins and 3-arylsulfanyl-4-hydroxyquinolinones in good yield. This protocol involves the

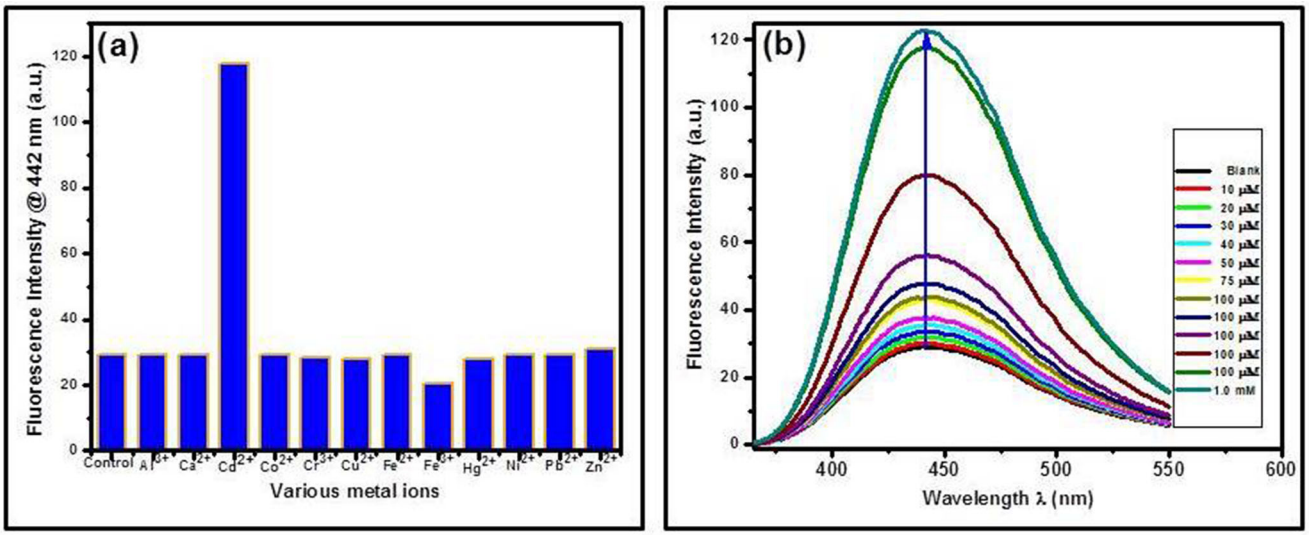


Figure 1. (a) The fluorescence response of **3f** (0.001 M) in the presence of various metal ions (500 μM) in water at excitation of 355 nm. (b) Fluorescence titration response of **3f** (0.001 M) in the presence of various concentrations of Cd^{2+} in water.

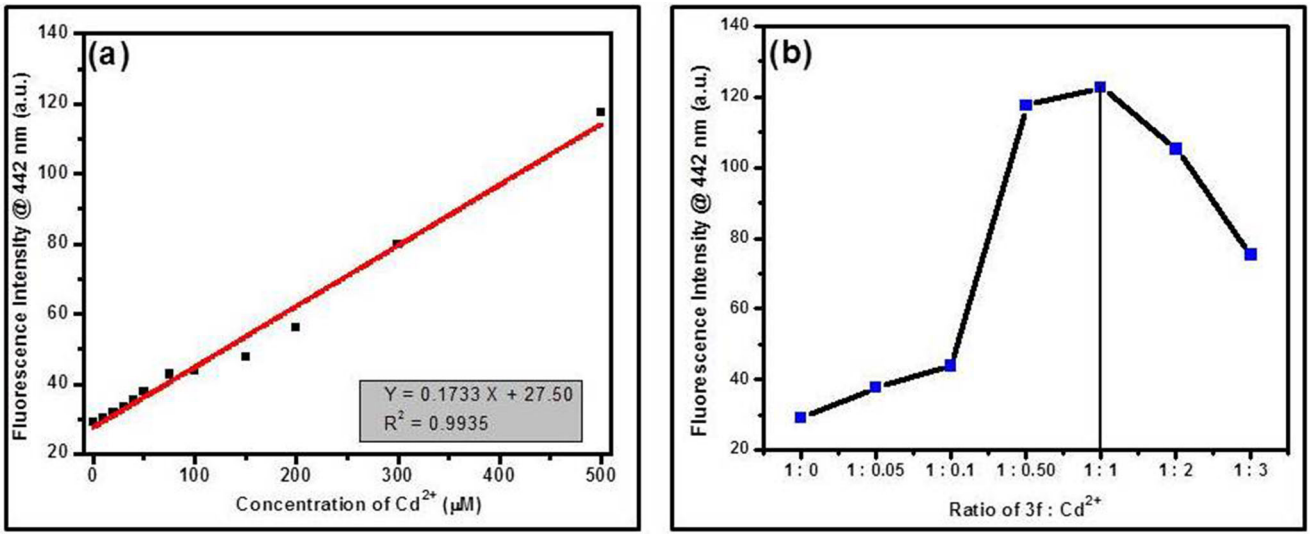


Figure 2. (a) Fluorescence intensity of **3f** at 442 nm as a function of Cd^{2+} ion (0–500 μM) concentration (b) Job's plot for **3f** and Cd^{2+} under different ratios.

copper-catalyzed S–O and S–N bond cleavage of sulfonyl hydrazides and the direct cross-coupling of various 4-hydroxycoumarins or 4-hydroxyquinolinones. This methodology offers a facile approach for direct C–S bond formation. In addition, the synthesized 3-arylsulfanyl-4-hydroxycoumarin displayed outstanding turn-on type fluorescence selectivity towards Cd^{2+} ions in water with a low detection limit and unique reversible function.

Experimental Section

General Procedure for the Synthesis of 3-Arylsulfanyl-4-hydroxycoumarin and 3-Arylsulfanyl-4-hydroxyquinolinone Derivatives (3 and 5)

A mixture of 4-hydroxycoumarin/4-hydroxyquinolinone (1.0 mmol), arylsulfonylhydrazide (1.5 mmol), CuBr·Me_2S (10 mol%) and DABCO (1.0 equiv.) was stirred in 5 mL 1,4-dioxane under refluxing conditions. The reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated under vacuum, and the residue was subjected to column chromatography using ethyl acetate in hexanes as the eluent to afford pure 3-arylsulfanyl-4-hydroxycoumar-

in (**3a**–**r**) and 3-arylsulfanyl-4-hydroxyquinolinone (**5a**–**m**) derivatives.

Acknowledgements

This study was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (NRF-2014R1A2A1A11052391) and the Nano Material Technology Development Program (2012M3A7B4049675).

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8 Copper(I) Bromide-Dimethyl Sulfide-Catalyzed Direct Sulfanylation of 4-Hydroxycoumarins and 4-Hydroxyquinolinones with Arylsulfonylhydrazides and Selective Fluorescence Switch-On Sensing of Cadmium(II) Ion in Water

Adv. Synth. Catal. **2016**, *358*, 1 – 8

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