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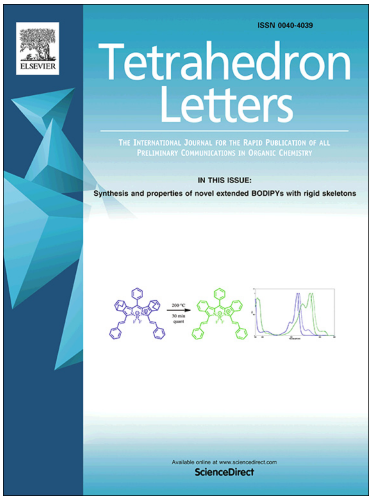

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Synthesis of Diaryl Sulfides through C-H Bond Functionalization of Arylamides with Cobalt Salt and Elemental Sulfur

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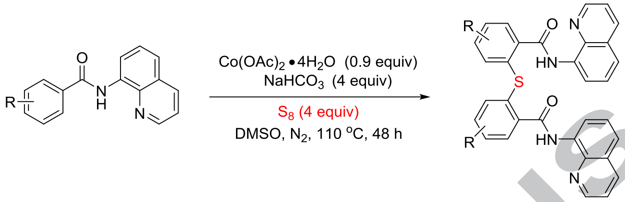

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Synthesis of diaryl sulfides through C–H bond functionalization of arylamides with cobalt salt and elemental sulfur

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ABSTRACT

A cobalt(II)-mediated, highly chemoselective thioarylation reaction of arylamides with elemental sulfur was reported. This reaction led to the formation of various symmetric diaryl sulfides in yields of up to 65% under mild reaction conditions. A cobalt-sulfur radical process was proposed based on preliminary results and mechanistic studies.

As some of the most important organic sulfur-containing compounds, diaryl sulfides have been considered to have an advantageous structure for use in many pharmaceuticals, biologically active natural products and advanced materials.[1] For example, the core structures of AZD4407 **1**, **2**, Zaltoprofen **3**, **4**, chlorpromazine hydrochloride **5** and quetiapine **6** are diaryl sulfides, that exhibit biological activities against cancer, HIV, inflammation, asthma, mood disorders and schizophrenia.[2]

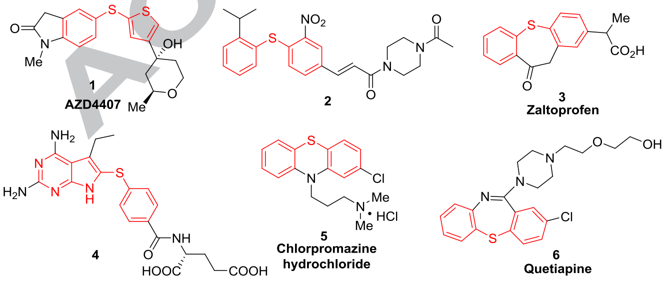

Figure 1. Diaryl sulfide-containing pharmaceuticals

Over the past few decades, significant progress has been made in transition-metal-catalyzed or transition-metal-mediated cross coupling of aryl halides and various sulfur-based partners to synthesize diaryl sulfide compounds.[3] Currently, transition-metal-catalyzed or transition-metal-mediated thioarylation of $C(sp^2)$–H bonds is becoming an increasingly attractive alternative for the formation of C–S bonds.[4] Numerous methods based on C–H functionalization have been developed to make various diaryl sulfides using Cu,[5] Fe,[6] Ni,[7] Pd,[8] Rh,[9] Ru[10] and Ag[11] metal sources and thiols and diaryl disulfides as sulfur reagents. However, the direct functionalization of $C(sp^2)$–H bonds to synthesize diaryl sulfides using cobalt salts has rarely been studied. Recently, Glorius and coworkers developed a thioarylation reaction of N-pyrimidyl indole via cobalt catalyzed $C(sp^2)$–H bond activation.[12] Herein, we report a cobalt(II)-mediated C–H functionalization of arylamides to prepare diaryl sulfides with elemental sulfur as a sulfur source.

This project was based on our initial work. During our studies on cobalt-mediated $C(sp^2)$–H functionalization of carboxamide **7a**, we isolated a dimerization product **9a** in 14% yield and two cobalt-amide complexes.[13] When the reaction was carried out under the conditions of $Co(OAc)_2{\cdot}4H_2O$ (2 equiv) and K_2CO_3 (2 equiv) in DMSO at 110 °Cfor 24 h, a very small amount of **8a** was obtained along with the production of **9a**. The main difference between **8a** and **9a** spectroscopically is seen in the HRMS data. We envisioned that the origin of the sulfur atom in the structure of **8a** might be the reduction of the solvent dimethyl sulfoxide. Once we added two equivalents of elemental sulfur into the reaction system,[14] the yield of **8a** increased to 34%, accompanied by **9a** and recovered **7a** in 4% and 24% yields, respectively (entry 1, Table 1). Then, we explored the effect of oxidants and bases on the reaction. The addition of an external

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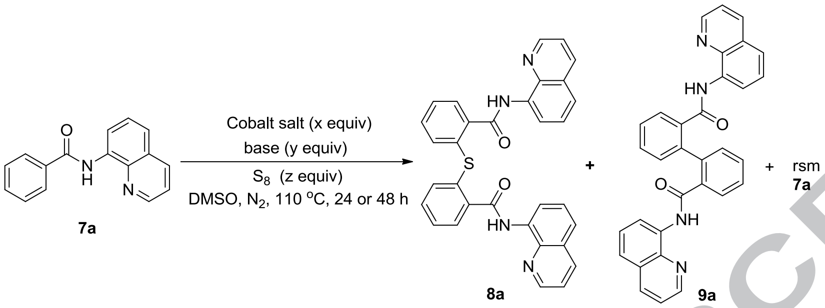
oxidant decreased the production of **8a** (details in the supporting information). $NaHCO_3$ has proven to be optimal (entries 2-6, Table 1). Among the several cobalt salts tested in the reaction, $Co(OAc)_2 \cdot 4H_2O$ gave the best yield (entries 7-11, Table 1). After extensive investigation of reaction conditions, including the loading of $Co(OAc)_2 \cdot 4H_2O$ and the ratio of $Co(OAc)_2 \cdot 4H_2O$/ $NaHCO_3/S_8$, the optimized conditions were determined to be a combination of $Co(OAc)_2 \cdot 4H_2O$ (0.9 equiv), $NaHCO_3$ (4 equiv) and S_8 (4 equiv) in DMSO at 110 °C under N_2 for 48 h, affording the desired product **8a** in 59% yield (entry 19, Table 1).[15]

Table 1. Optimization of the reaction conditions



Entry	Cobalt salt (equiv)	Base (equiv)	S_8 (equiv)	Yield [%]		
				8a	**9a**	rsm **7a**
1	$Co(OAc)_2 \cdot 4H_2O$/0.5	K_2CO_3/2	2	34	4	24
2	$Co(OAc)_2 \cdot 4H_2O$/0.5	Na_2CO_3/2	2	32	3	38
3	$Co(OAc)_2 \cdot 4H_2O$/0.5	K_3PO_4/2	2	17	0	74
4	$Co(OAc)_2 \cdot 4H_2O$/0.5	NaOH/2	2	21	0	67
5	$Co(OAc)_2 \cdot 4H_2O$/0.5	$KHCO_3$/2	2	27	0	50
6	$Co(OAc)_2 \cdot 4H_2O$/0.5	$NaHCO_3$/2	2	35	0	51
7	$Co(acac)_3$/0.5	$NaHCO_3$/2	2	6	0	86
8	$CoCl_2$/0.5	$NaHCO_3$/2	2	27	0	67
9	$CoBr_2$/0.5	$NaHCO_3$/2	2	21	0	73
10	CoI_2/0.5	$NaHCO_3$/2	2	27	0	68
11	$Co(OAc)_2 \cdot 4H_2O$/0.5	$NaHCO_3$/4	4	49	0	47
12	$Co(OAc)_2 \cdot 4H_2O$/0.1	$NaHCO_3$/4	4	16	0	82
13	$Co(OAc)_2 \cdot 4H_2O$/0.2	$NaHCO_3$/4	4	21	0	75
14	$Co(OAc)_2 \cdot 4H_2O$/0.3	$NaHCO_3$/4	4	32	0	58
15	$Co(OAc)_2 \cdot 4H_2O$/0.4	$NaHCO_3$/4	4	37	0	57
16	$Co(OAc)_2 \cdot 4H_2O$/0.6	$NaHCO_3$/4	4	50	0	47
17	$Co(OAc)_2 \cdot 4H_2O$/0.7	$NaHCO_3$/4	4	48	0	44
18	$Co(OAc)_2 \cdot 4H_2O$/0.8	$NaHCO_3$/4	4	46	0	33
19	$Co(OAc)_2 \cdot 4H_2O$/0.9	$NaHCO_3$/4	4	59	0	26
20	$Co(OAc)_2 \cdot 4H_2O$/1.0	$NaHCO_3$/4	4	40	0	21
21	$Co(OAc)_2 \cdot 4H_2O$/1.2	$NaHCO_3$/4	4	36	0	21
22	$Co(OAc)_2 \cdot 4H_2O$/0.9	$NaHCO_3$/1	4	24	0	60
23	$Co(OAc)_2 \cdot 4H_2O$/0.9	$NaHCO_3$/2	4	36	0	52
24	$Co(OAc)_2 \cdot 4H_2O$/0.9	$NaHCO_3$/3	4	52	0	40
25	$Co(OAc)_2 \cdot 4H_2O$/0.9	$NaHCO_3$/4	1	25	37	29
26	$Co(OAc)_2 \cdot 4H_2O$/0.9	$NaHCO_3$/4	2	38	11	30

With the optimal conditions known, we explored the substrate scope of the reaction. Generally, the efficiency of this cobalt-mediated thioarylation reaction of a $C(sp^2)$–H bond is limited (Table 2). A series of symmetric diaryl sulfides bearing electron-withdrawing or electron-donating groups on the benzene ring were obtained in moderate to low yields with some amount of starting materials recovered. It was found that the electronic properties and position of substituents on the benzene ring have a substantial effect on the production of the corresponding diaryl sulfides. For example, the yield of the *para*-methyl- substituted compound **8c** was higher than that of the more sterically-hindered *ortho*-methyl-substituted product **8b**. The production of the *para*-methoxy-substituted **8f** was two fold that of the *meta*-methoxy-substituted **8e**. Likely because of electronic and steric effects, *ortho*-methoxy-substituted **8d** was not formed. The electron-withdrawing groups, such as F, Cl, Br, I and CF_3 on the benzene ring made the reaction proceed more readily (e.g., **8g-8k** vs **8e**), and these groups also provided appropriate sites for further manipulation. Furthermore, thiophene substrates **7l** and **7m** underwent the thioarylation reaction of the $C(sp^2)$–H bond to afford diaryl sulfides **8l** and **8m** in 24% and 52% yields, respectively. Interestingly, more conjugated systems, such as the dibenzofuran substrate **7n,** provided a more structurally complicated product **8n** in 34% yield. The structures of the products were further confirmed by single-crystal X-ray diffraction of **8a**. The cross coupling of substrates **7e** and **7k** with elemental sulfur under standard conditions afforded heterocoupling product **8o** in 32% yield and homocoupling products **8e** and **8k** in 18% and 26% yields, respectively (eq. 1).

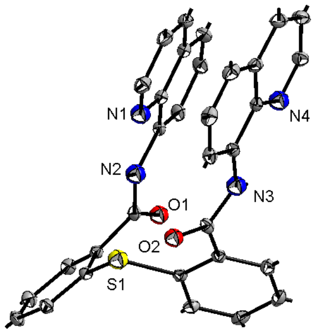
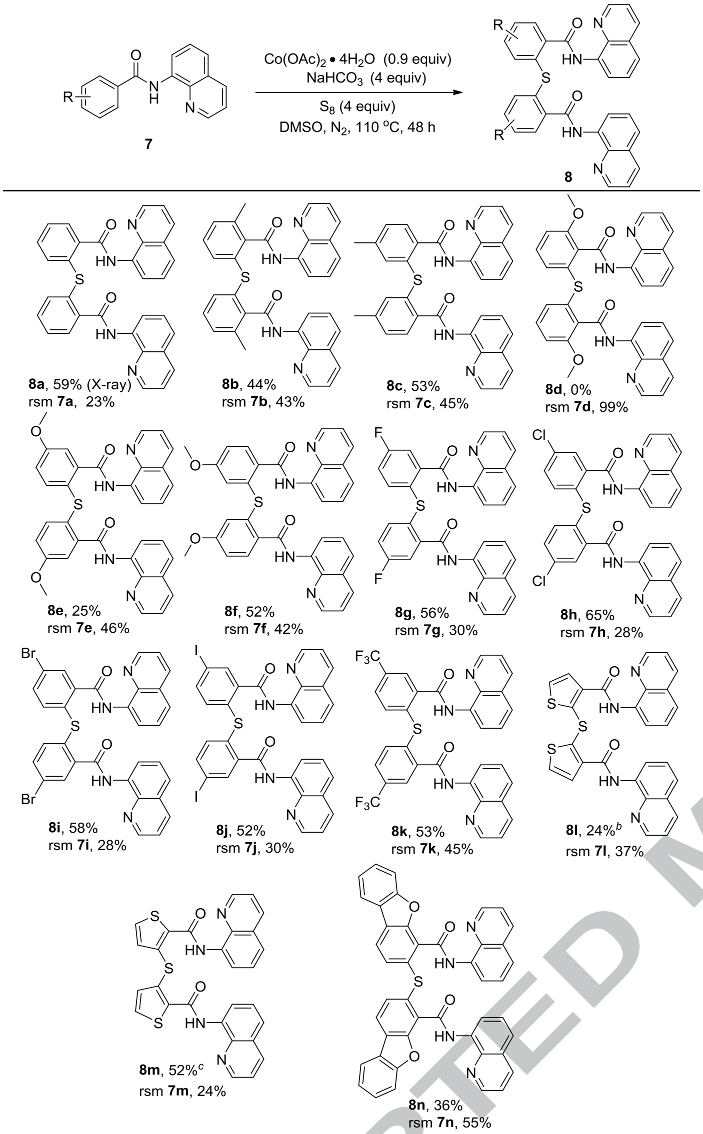


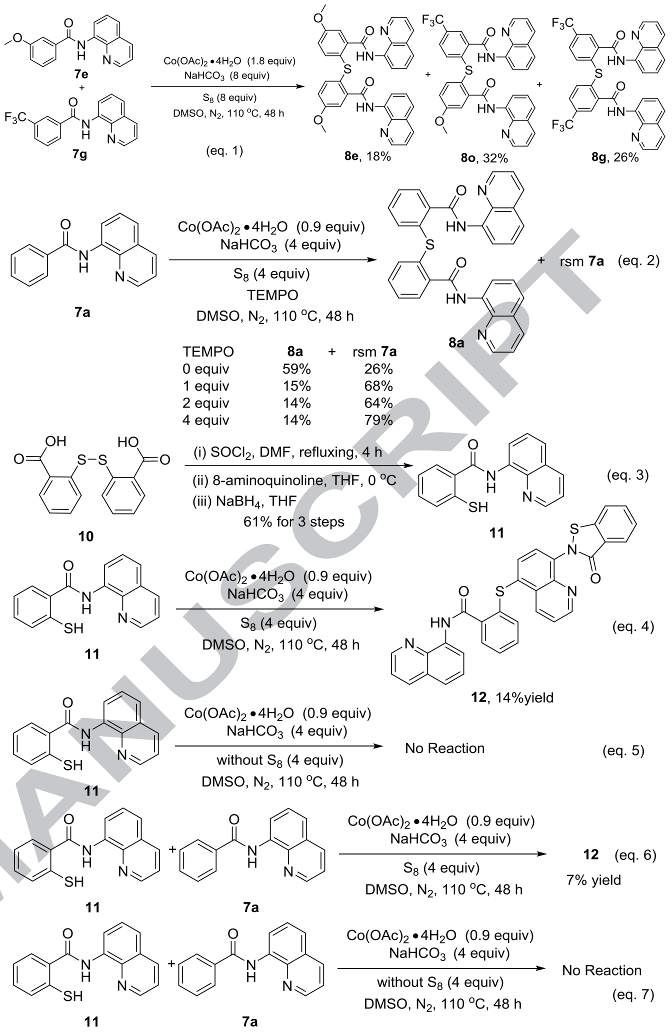
Figure 2. ORTEP Molecular Diagram of **8a**

Table 2. Substrate scope [a]



[a] Typical reaction conditions: substrate (0.10 mmol),Co(OAc)$_2$·4H$_2$O (0.09 mmol), NaHCO$_3$ (0.4 mmol), S$_8$ (0.4 mmol) in DMSO (2.0 mL) under Nitrogen at 110 °C for 48 h. Isolated yields. [b] Co(OAc)$_2$·4H$_2$O (0.06 mmol) was used. [c] Co(OAc)$_2$·4H$_2$O (0.06 mmol) and Na$_2$CO$_3$ (0.4 mmol) were used.

To determine the mechanism of this reaction, several control experiments were carried out (Scheme 1). First, the radical scavenger reagent TEMPO was subjected to standard reaction conditions. The production of **8a** was decreased to a low yield (eq. 2). Thiophenol substrate **11** was synthesized via three consequent steps from commercially available diaryl disulfide **10**.[16] Then, the cobalt-mediated thioarylation reaction was carried out under standard conditions with **11**. Interestingly, another type of diaryl sulfide, **12,** was formed in 14% yield, for which the coupling reaction occurred at the 5-position of the quinoline backbone (eq. 4). In contrast, the reaction did not occur in the absence of elemental sulfur. When equal amounts of **11** and **7a** were subjected to standard conditions, **12** was obtained in 7% yield along with a small amount of complicated mixtures (eq. 6). Similarly, the reaction did not proceed without elemental sulfur. These results indicated that this reaction probably experienced a free radical-involving process and that elemental sulfur had a key effect on the reaction.

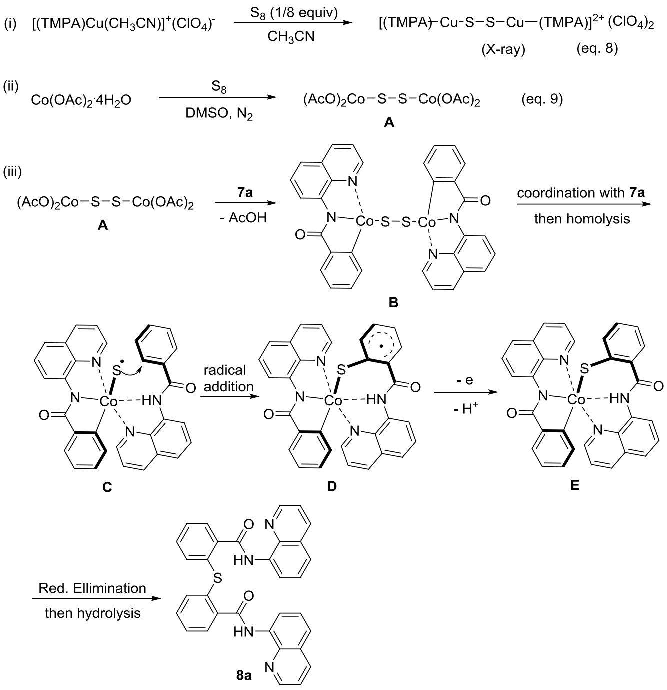


Scheme 1. Control experiments for mechanistic study

In 2003, Solomon and Karlin reported the synthesis of the copper-disulfide complex [(TMPA)Cu-S-S-Cu(TMPA)]$^{2+}$ from the reaction of [(TMPA)Cu^{I}(CH$_3$CN)]$^{+}$ with elemental sulfur.[17] The structure of the copper-disulfide complex was confirmed by single crystal X-ray diffraction (eq. 8). Inspired by this elegant work, we tried to isolate cobalt-disulfide complex A, but failed. In this period, we found that when S$_8$ was added to the solution of Co(OAc)$_2$ in DMSO at 110 °C under N$_2$, the color of the reaction mixture changed from purple to black, indicating that an oxidation reaction might happen to cobalt(II) salt.

Based on these results and literature work, a possible mechanism for this reaction is depicted in Scheme 2. Co(OAc)$_2$ is oxidized by elemental sulfur to form cobalt(III)-disulfide complex **A**, which undergoes ligand exchange with **7a** and then C(sp^2)–H bond activation to afford disulfide intermediate **B**. **B** coordinates with another molecule of **7a** and undergoes homolysis to form sulfur radical species **C**,[18] which provides **D** through a radical addition reaction. Rearomatization of **D** leads to the formation of **E**. **E** undergoes reductive elimination and hydrolysis to afford product **8a**.

In conclusion, we have studied the thioarylation reaction of arylamide via cobalt(II)-mediated C(sp^2)–H bond activation. This method provides a straightforward synthesis of symmetric diaryl sulfides with high chemoselectivity, albeit in moderate yields. Extensive investigation showed that the cooperation of three components (Co(OAc)$_2$, NaHCO$_3$ and elemental sulfur) is required for the reaction to occur. Based on preliminary results and mechanistic studies, this reaction is considered to involve a sulfur radical process.



Scheme 2. Possible mechanism

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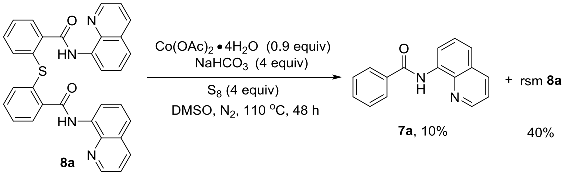
15. It was found that compound **8a** underwent decomposition back to the starting material **7a** under standard reaction conditions.



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Supplementary Material

Highlights

A cobalt(II)-mediated, highly chemoselective thioarylation reaction of arylamides with elemental sulfur was reported.
This reaction led to the formation of various symmetric diaryl sulfides in yields of up to 65% under mild reaction conditions.
A cobalt-sulfur radical process was proposed.

Graphical Abstract

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Synthesis of Diaryl Sulfides through C-H Bond Functionalization of Arylamides with Cobalt Salt and Elemental Sulfur

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Jian-Ye Li, Jun Huang, Shi-Jin Zhang, Chunna Yao, Wen-Wu Sun, Bin Liu, Yingbi Zhou and Bin Wu