Organic Letters
Letter
pubs.acs.org/OrgLett

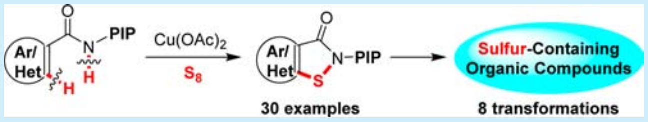
Cu(II)-Mediated C−S/N−S Bond Formation via C−H Activation: Access to Benzoisothiazolones Using Elemental Sulfur

Fa-Jie Chen,[†] Gang Liao,[†] Xin Li,[†] Jun Wu,*[,†] and Bing-Feng Shi*[,†,‡]

[†]Department of Chemistry, Zhejiang University, Hangzhou 310027, China

[‡]State Key Laboratory of Bioorganic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

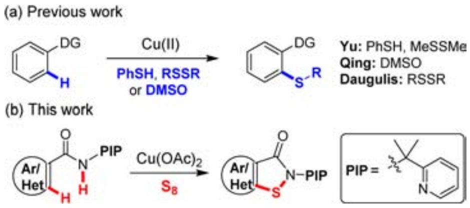
S Supporting Information



ABSTRACT: A copper-mediated C−S/N−S bond−forming reaction via C−H activation that uses elemental sulfur has been developed. The addition of TBAI was found to be crucial for the success of this transformation. The method is scalable, shows excellent functional group tolerance, and is compatible with heterocycle substrates, providing efficient and practical access to benzoisothiazolones. The direct diversification of the benzoisothiazolone products into a variety of sulfur-containing compounds is also demonstrated.

In recent years, copper-catalyzed/mediated functionalization of C−H bonds to form C−C, C−N, and C−O bonds has attracted significant attention.[1,2] In contrast, copper-catalyzed direct C−S bond formation has remained relatively undeveloped.[3−8] This could be due to catalyst poisoning by sulfur species or the susceptibility of sulfur toward oxidative decomposition or oligomerization.[3] So far, only a few examples of sulfenylation of unactivated arene C−H bonds have been reported.[6−8] In 2006, Yu reported the first copper-mediated C−H thioetherification of 2-phenylpyridine substrates with PhSH and MeSSMe as the sulfur sources in moderate yields.[6] Qing reported a copper-mediated methylthiolation of arylpyridines using DMSO as the sulfur source.[7] In 2012, the Daugulis group reported a copper-promoted sulfenylation of benzoic acid derivatives with disulfides employing a removable 8-aminoquinoline directing group (Scheme 1a).[8] These established sulfenylation methods, however, suffer from some limitations, including restricted substrate scope; the use of odorous sulfur sources, such as thiols and disulfides; and the formation of undesired toxic byproducts. Thus, identifying a generally useful and operationally convenient sulfur source is crucial for expanding the practical utility of this class of reactions. Elemental sulfur (S_8) is inexpensive, readily available, and nonodorous.[9] Therefore, the use of elemental sulfur as a sulfur source in copper-catalyzed sulfenylation of unactivated C−H bonds is an appealing transformation but has not been reported to the best of our knowledge.

Scheme 1. Copper-Mediated C−H Activation/C−S Bond Formation



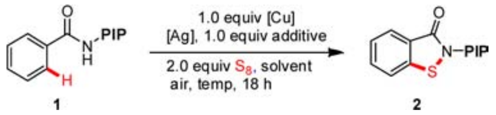
Benzoisothiazolones are well-known five-membered sulfur- and nitrogen-containing heterocycles that are ubiquitous in agrochemicals and pharmaceuticals. It has been shown that certain benzoisothiazolones and their derivatives possess anti-HIV and antifungal activities.[10] In view of their biological and synthetic importance, a number of methods have been developed to access these compounds.[11] However, these procedures generally require multiple synthetic steps and/or use highly toxic and corrosive reagents. Therefore, the development of an efficient and environmentally benign protocol, by which a diverse library of benzoisothiazolones could be prepared from readily available starting materials, would be highly desirable.

Herein, we report the first example of copper-mediated C−S/N−S bonds formation via C−H activation that uses elemental sulfur (Scheme 1b). This protocol uses readily available benzamide starting materials and provides a straightforward means of preparing a variety of benzoisothiazolones. We have also demonstrated that the corresponding benzoisothiazolones are versatile intermediates for the synthesis of aryl sulfides, aryl sulfoxides, saccharins, and other sulfur-containing organic compounds.

As part of our ongoing research in developing novel C−H functionalization reactions for the synthesis of heterocycles,[12] we became interested in the use of our newly developed bidentate directing group derived from (pyridin-2-yl)isopropylamine (PIP-amine) for such transformations.[13−15] Therefore, we commenced our studies by attempting to couple benzamide **1** with S_8 in the presence of $Cu(OAc)_2$ and Ag_2CO_3 under aerobic conditions. Gratifyingly, the desired product **2** was obtained in 10% yield in DMF (Table 1, entry 1). TBAI is commonly employed as an efficient additive in C−S bond-forming

Received: September 15, 2014
Published: October 17, 2014

Table 1. Optimization of the Reaction Conditions[a]



entry	[Cu]	[Ag] (equiv)	additive	temp (°C)	solvent	yield (%)[b]
1	$Cu(OAc)_2$	Ag_2CO_3 (2.0)	—	100	DMF	10
2	$Cu(OAc)_2$	Ag_2CO_3 (2.0)	TBAI	100	DMF	13
3	$Cu(OAc)_2$	—	TBAI	100	DMF	11
4	$Cu(OAc)_2$	Ag_2O (2.0)	TBAI	100	DMF	25
5	$Cu(OAc)_2$	Ag_2O (2.0)	TBAB	100	DMF	20
6	CuBr	Ag_2O (2.0)	TBAI	100	DMF	21
7	$CuCl_2$	Ag_2O (2.0)	TBAI	100	DMF	18
8	CuCl	Ag_2O (2.0)	TBAI	100	DMF	25
9	$Cu(OAc)_2·H_2O$	Ag_2O (2.0)	TBAI	100	DMF	29
10	—	Ag_2O (2.0)	TBAI	100	DMF	0
11	$Cu(OAc)_2·H_2O$	Ag_2O (2.0)	TBAI	100	CH_2Cl_2	59
12[b]	$Cu(OAc)_2·H_2O$	Ag_2O (2.0)	TBAI	100	CH_2Cl_2	15
13[c]	$Cu(OAc)_2·H_2O$	Ag_2O (2.0)	TBAI	100	CH_2Cl_2	66
14[c]	$Cu(OAc)_2·H_2O$	Ag_2O (2.5)	TBAI	100	CH_2Cl_2	71
15[c]	**$Cu(OAc)_2·H_2O$**	Ag_2O (2.5)	**TBAI**	**90**	**CH_2Cl_2**	**89**
16[c]	$Cu(OAc)_2·H_2O$	Ag_2O (2.5)	—	90	CH_2Cl_2	0
17[c]	$Cu(OAc)_2·H_2O$	—	TBAI	90	CH_2Cl_2	10
18[c]	$Cu(OAc)_2·H_2O$	Ag_2O (0.5)	TBAI	90	CH_2Cl_2	41
19[c]	$Cu(OAc)_2·H_2O$	Ag_2O (1.0)	TBAI	90	CH_2Cl_2	52
20[c]	$Cu(OAc)_2·H_2O$	Ag_2O (1.5)	TBAI	90	CH_2Cl_2	64

[a] Isolated yield on 0.2 mmol scale in 2.0 mL of solvent unless otherwise noted. PIP = (pyridin-2-yl)isopropyl. [b] 0.2 equiv of $Cu(OAc)_2·H_2O$ was used. [c] 1.0 mL of CH_2Cl_2 was used.

reactions.[3e,5d] Indeed, in the present reaction, the addition of 1 equiv of TBAI slightly improved the yield of **2** (entry 2). The desired product was obtained in 11% yield in the absence of silver salt (entry 3), while the use of Ag_2O led to modest improvement (25%, entry 4). $Cu(OAc)_2·H_2O$ proved to be the best promoter among various copper sources that were examined (entries 6–9). No desired product was observed in the absence of copper salt (entry 10). The yield improved to 59% when the reaction was conducted in CH_2Cl_2 (entry 11). After further screening the desired product **2** could be obtained in 89% yield under the following optimized conditions: 1.0 equiv of $Cu(OAc)_2·H_2O$, 2.5 equiv of Ag_2O, 2.0 equiv of S_8 and 1.0 equiv of TBAI in CH_2Cl_2 (0.2 M) under air at 90 °C for 18 h (entry 15). Both TBAI and Ag_2O are crucial for the efficiency of this transformation (entries 16–20). The connectivity of benzoisothiazolone **2** was confirmed by single-crystal X-ray diffraction (Figure S1, Supporting Information).

After identifying the optimized conditions, we next explored the substrate scope of this transformation. Both electron-rich and -deficient benzamides proceeded well to afford substituted benzoisothiazolones in moderate to high yields (Figure 1). Trifluoromethyl substituents in the *ortho*, *meta*, and *para* positions gave the desired products in high yields (**3**–**5**). Generally, substrates bearing electron-withdrawing groups ($-CF_3$, **5**; $-CO_2Me$, **9**; $-CN$, **10**; and $-NO_2$, **11**) gave higher yields than those bearing electron-donating groups (−OMe, **6**; −Me, **7**; and −OAc, **8**). This qualitative trend suggests the electrophilic aromatic substitution (S_EAr) pathway was unlikely to be operative. It is worth noting that all halides, fluoride, chloride, bromide, and iodide, remained intact under the standard reaction conditions, affording the desired products in moderate to high yields (**12**–**16**). *m*-Alkoxy substrate partially led to the sulfenylation adjacent to oxygen (**19b**), possibly indicating that coordination of the alkoxy substituent stabilizes the aryl–copper intermediates.

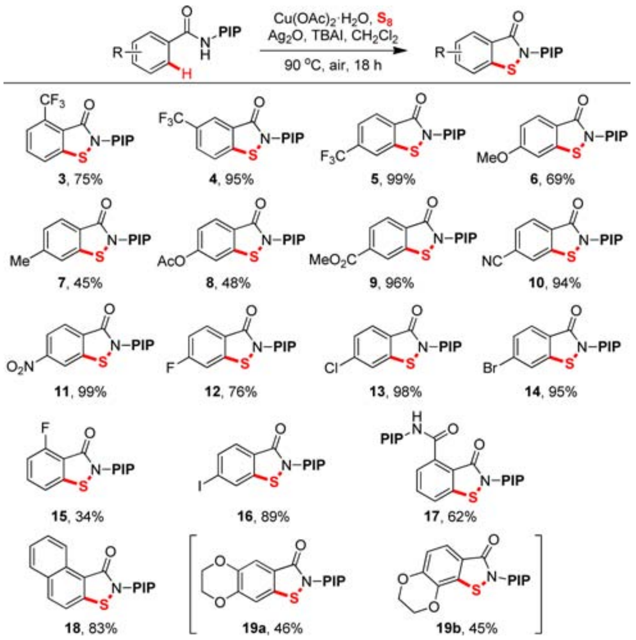


Figure 1. Benzamide substrate scope. Reaction conditions: substrate (0.2 mmol), $Cu(OAc)_2·H_2O$ (0.2 mmol), Ag_2O (0.5 mmol), S_8 (0.4 mmol), and TBAI (0.2 mmol) in CH_2Cl_2 (1.0 mL) under air at 90 °C for 18 h. Isolated yield.

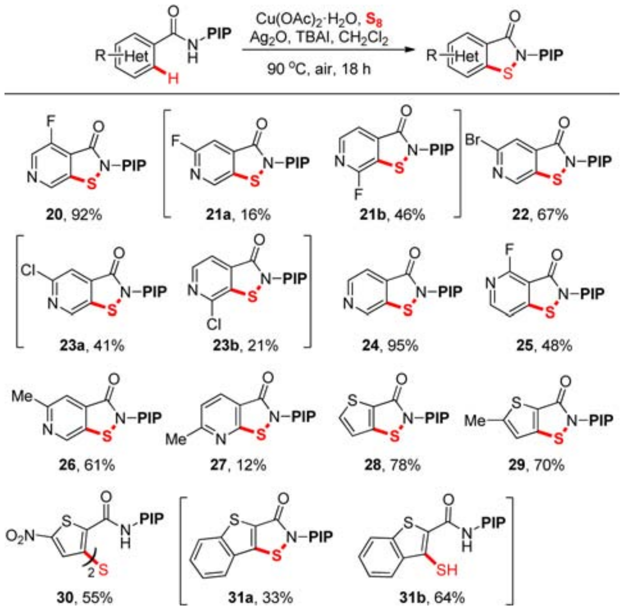
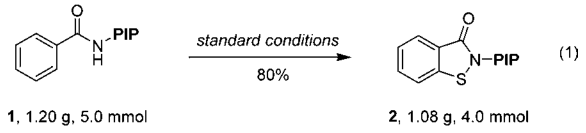


Figure 2. Scope of heteraryl benzamide. Reaction conditions: substrate (0.2 mmol), $Cu(OAc)_2·H_2O$ (0.2 mmol), Ag_2O (0.5 mmol), S_8 (0.4 mmol), and TBAI (0.2 mmol) in CH_2Cl_2 (1.0 mL) under air at 90 °C for 18 h. Isolated yield.

In light of the biological importance of the heteroaryl-fused isothiazolones, we further investigated the compatibility of this protocol with heterocyles (Figure 2). Gratifyingly, a wide range of heterocycles including pyridines, thiophenes and benzothiophenes, were all tolerated under the reaction conditions, furnishing the heteroaryl-fused isothiazolones in good yields. Notably, 2-fluoroisonicotinamide reacted at the kinetically more acidic C–H bond (**21b**). This observation can be rationalized by invoking a concerted metalation/deprotonation (CMD) pathway. 5-Nitrothiophene-2-PIP-carboxamide gave thioether **30**, presumably due to the presence of a strong electron-withdrawing group. Interestingly, benzothiophene-2-PIP-carboxamide predominantly gave the free thiol product **31b** in 64% yield.

To demonstrate the synthetic utility of this method, the reaction was performed on 5 mmol scale, producing benzoisothiazolone **2** in 80% yield (eq 1, 1.08 g).



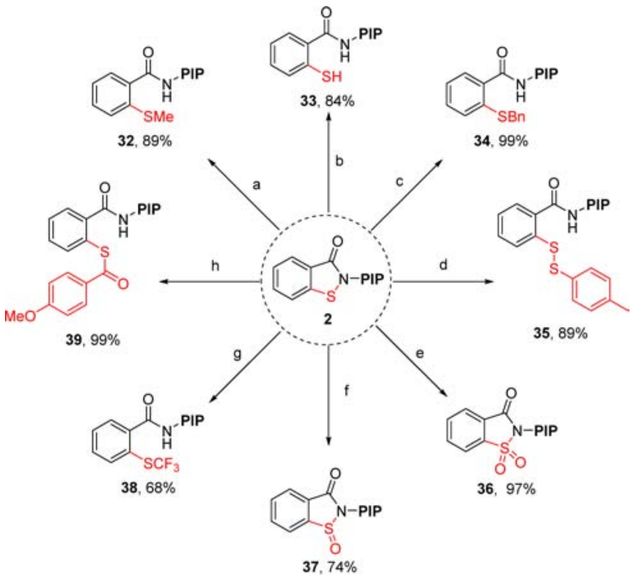
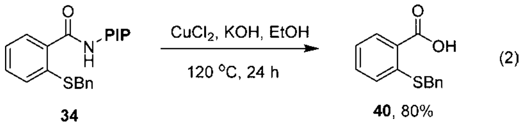


Figure 3. Versatile transformations of benzoisothiazolone **2** to various sulfur-containing compounds. Conditions: (a) MeMgBr, THF, rt, 2 h; (b) $NaBH_4$, EtOH, 0 °C to rt, overnight; (c) $NaBH_4$, EtOH, 0 °C to rt, 30 min; then BnBr, Et_3N, overnight; (d) 4-methylbenzenethiol, CH_2Cl_2, rt, 12 h; (e) H_5IO_6, CrO_3 (cat.), CH_3CN, rt, 3 h; (f) 2,4,6-trichloro-1,3,5-triazine, 30% H_2O_2, CH_3CN, rt, 1 h; (g) $TMSCF_3$, KF, DMF, 80 °C, overnight; (h) $NaBH_4$, EtOH, 0 °C to rt, 30 min; then *p*-MeOPhCOCl, overnight.

The synthetic versatility of the products can be exploited through the diverse transformations shown in Figure 3, allowing access to various sulfur-containing compounds. Treatment of benzoisothiazolone **2** with MeMgBr gave thioether **32** in 89% yield.[16] Reduction of **2** by $NaBH_4$ gave thiophenol **33** in 84% yield. Oxidation of **2** with 30% H_2O_2 in the presence of 2,4,6-trichloro-1,3,5-triazine selectively afforded sulfoxide **37** in 74% yield.[17] Saccharin derivative **36** was obtained in 97% yield by the oxidation of **2** with H_5IO_6 in the presence of catalytic CrO_3.[18] Notably, trifluoromethylthiolation product **38** was obtained in 68% yield when **2** was reacted with Ruppert's reagent and KF, providing a new route to aryl trifluoromethylthioarenes. Other sulfur-containing compounds, such as benzyl thioether **34**, disulfide **35**, and thioester **39** could also be produced by the transformation of benzoisothiazolone **2**. Although the PIP group could not be directly cleaved from the benzoisothiazolone products, it can be easily removed from sulfur-containing benzamides, such as **34**, by treatment with KOH and $CuCl_2$ in EtOH (eq 2).



To gain further insight into the reaction mechanism, additional experiments were conducted (Figure S3, Supporting Information). An intermolecular competition experiment between **5s** and **7s** revealed that electron-deficient arenes reacted with higher relative rates (Figure S3a, Supporting Information). Addition of 1 equiv of radical scavengers, such as TEMPO and 1,1-diphenylethylene, did not inhibit the reaction (Figure S3b, Supporting Information). Addition of 1 equiv hydroquinone substantially reduced the yield but still did not completely suppress the reaction. These experiments suggest that the transformation does not proceed via radical intermediates. The intermolecular KIE between **1** and ***d*$_4$-1** gave a value of 2.6, indicating that C−H cleavage could potentially be the rate-limiting step (Figure S3c, Supporting Information). Although the exact role of TBAI is unclear at this point, we speculated that TBAI could play a role as a S_8 activator and increase the solubility of sulfur in dichloromethane.[5d,19]

On the basis of these mechanistic studies and earlier precedents,[20,21] a plausible mechanism appears to involve Cu(II)-mediated, disproportionative C−H activation followed by sulfur-atom transfer to form Cu(III) intermediate B.[22,23] Subsequent N−S reductive elimination leads to benzoisothiazolone **2** and Cu(OAc) (Figure 4).[21] Finally, Cu(OAc) is oxidized by Ag_2O/air to regenerate Cu(II), which would finish the catalytic cycle. A detailed mechanism remained to be elucidated.[24]

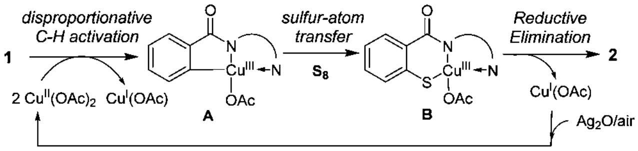


Figure 4. Plausible reaction mechanism.

In conclusion, we have developed the first copper-mediated C−S/N−S bond-forming reaction via C−H activation that uses elemental sulfur as the sulfur source. The presence of a stoichiometric amount of TBAI is crucial for the success of this transformation. This reaction is scalable and tolerates a wide range of functional groups, providing an efficient means of accessing biologically important benzoisothiazolones. In addition, heterocyclic substrates are compatible with this protocol, which allows synthesis of a variety of unique heteroaryl-fused isothiazolones. The versatility of the benzoisothiazolone moiety renders this protocol highly attractive for both synthetic and medicinal chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, spectral data for all new compounds, and X-ray data for **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: wujunwu@zju.edu.cn.
*E-mail: bfshi@zju.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the National Basic Research Program of China (2015CB856600), the NSFC (21422206, 21272206), the Fundamental Research Funds for the Central Universities (2014QNA3008), Qianjiang Project (2013R10033), and Special Fund for Agro-Scientific Research in the Public Interest of China (201403030) is gratefully acknowledged. We thank Dr. Keary M. Engle (California Institute of Technology) for helpful suggestions and comments.

■ REFERENCES

(1) Selected reviews on copper-catalyzed C−H activation: (a) Allen, S. E.; Walvoord, R. R.; Padilla-Salinas, R.; Kozlowski, M. C. *Chem. Rev.* **2013**, *113*, 6234. (b) Zhang, C.; Tang, C.; Jiao, N. *Chem. Soc. Rev.* **2012**, *41*, 3464. (c) Wendlandt, A. E.; Suess, A. M.; Stahl, S. S. *Angew. Chem., Int. Ed.* **2011**, *50*, 11062. (d) Daugulis, O.; Do, H.-Q.; Shabashov, D. *Acc. Chem. Res.* **2009**, *42*, 1074.

(2) Selected examples on copper-catalyzed C−H functionalization. C−N: (a) Uemura, T.; Imoto, S.; Chatani, N. *Chem. Lett.* **2006**, *35*, 842. (b) Wang, H.; Wang, Y.; Peng, C.; Zhang, J.; Zhu, Q. *J. Am. Chem. Soc.* **2010**, *132*, 13217. (c) Tran, L. D.; Roane, J.; Daugulis, O. *Angew. Chem., Int. Ed.* **2013**, *52*, 6043. (d) Shang, M.; Sun, S.-Z.; Dai, H.-X.; Yu, J.-Q. *J. Am. Chem. Soc.* **2014**, *136*, 3354. C−O: (e) Suess, A. M.; Ertem, M. Z.; Cramer, C. J.; Stahl, S. S. *J. Am. Chem. Soc.* **2013**, *135*, 9797. (f) Roane, J.; Daugulis, O. *Org. Lett.* **2013**, *15*, 5842. (g) Liu, Q.; Wu, P.; Yang, Y.; Zeng, Z.; Liu, J.; Yi, H.; Lei, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 4666. C−C: (h) Nishino, M.; Hirano, K.; Satoh, T.; Miura, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 4457. (i) Zhao, X.; Wu, G.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2011**, *133*, 3296. (j) Wei, Y.; Zhao, H.; Kan, J.; Su, W.; Hong, M. *J. Am. Chem. Soc.* **2010**, *132*, 2522.

(3) Selected reviews on C−S bond formation: (a) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596. (b) Kondo, T.; Mitsudo, T.-A. *Chem. Rev.* **2000**, *100*, 3205. (c) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147.

(4) Cu-catalyzed intramolecular C−S bond formation: Banerjee, A.; Santra, S. K.; Rout, S. K.; Patel, B. K. *Tetrahedron* **2013**, *69*, 9096.

(5) Cu-catalyzed C−H activation/C−S bond formation of activated C−H bonds: (a) Fukuzawa, S.; Shimizu, E.; Atsuumi, Y.; Haga, M.; Ogata, K. *Tetrahedron Lett.* **2009**, *50*, 2374. (b) Zhang, S.; Qian, P.; Zhang, M.; Hu, M.; Cheng, J. *J. Org. Chem.* **2010**, *75*, 6732. (c) Ranjit, S.; Lee, R.; Heryadi, D.; Shen, C.; Wu, J.; Zhang, P.; Huang, K.-W.; Liu, X. *J. Org. Chem.* **2011**, *76*, 8999. (d) Chen, C.; Xu, X.-H.; Yang, B.; Qing, F.-L. *Org. Lett.* **2014**, *16*, 3372. (e) Li, X.; Xu, Y.; Wu, W.; Jiang, C.; Qi, C.; Jiang, H. *Chem.—Eur. J.* **2014**, *20*, 7911.

(6) Chen, X.; Hao, X.-S.; Goodhue, C. E.; Yu, J.-Q. *J. Am. Chem. Soc.* **2006**, *128*, 6790.

(7) Chu, L.; Yue, X.; Qing, F.-L. *Org. Lett.* **2010**, *12*, 1644.

(8) Tran, L. D.; Popov, I.; Daugulis, O. *J. Am. Chem. Soc.* **2012**, *134*, 18237.

(9) For recent examples of C−S bond formation with elemental sulfur, see: (a) Popov, I.; Do, H.-Q.; Daugulis, O. *J. Org. Chem.* **2009**, *74*, 8309. (b) Chen, C.; Chu, L.; Qing, F.-L. *J. Am. Chem. Soc.* **2012**, *134*, 12454. (c) Weng, Z.; He, W.; Chen, C.; Lee, R.; Tan, D.; Lai, Z.; Kong, D.; Yuan, Y.; Huang, K.-W. *Angew. Chem., Int. Ed.* **2013**, *52*, 1548. (d) Paul, R.; Punniyamurthy, T. *RSC Adv.* **2012**, *2*, 7057 and references cited therein.

(10) Turpin, J. A.; Song, Y.; Inman, J. K.; Huang, M.; Wallqvist, A.; Maynard, A.; Covell, D. G.; Rice, W. G.; Appella, E. *J. Med. Chem.* **1998**, *42*, 67.

(11) (a) Henke, A.; Srogl, J. *Chem. Commun.* **2010**, *46*, 6819. (b) Henke, A.; Srogl, J. *J. Org. Chem.* **2008**, *73*, 7783.

(12) (a) Zhou, J.; Li, B.; Hu, F.; Shi, B.-F. *Org. Lett.* **2013**, *15*, 3460. (b) Zhou, J.; Li, B.; Qian, Z.-C.; Shi, B.-F. *Adv. Synth. Catal.* **2014**, *356*, 1038.

(13) (a) Li, X.; Liu, Y.-H.; Gu, W.-J.; Li, B.; Chen, F.-J.; Shi, B.-F. *Org. Lett.* **2014**, *16*, 3904. (b) Zhang, Q.; Yin, X.-S.; Zhao, S.; Fang, S.-L.; Shi, B.-F. *Chem. Commun.* **2014**, *50*, 8353. (c) Zhang, Q.; Chen, K.; Rao, W.; Zhang, Y.; Chen, F.-J.; Shi, B.-F. *Angew. Chem., Int. Ed.* **2013**, *52*, 13588. (d) Chen, F.-J.; Zhao, S.; Hu, F.; Chen, K.; Zhang, Q.; Zhang, S.-Q.; Shi, B.-F. *Chem. Sci.* **2013**, *4*, 4187.

(14) For pioneering work on the use of bidentate auxiliaries, see: (a) Zaitsev, V. G.; Shabashov, D.; Daugulis, O. *J. Am. Chem. Soc.* **2005**, *127*, 13154. (b) Shabashov, D.; Daugulis, O. *J. Am. Chem. Soc.* **2010**, *132*, 3965.

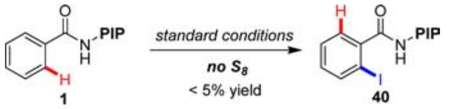
(15) For reviews: (a) Rouquet, G.; Chatani, N. *Angew. Chem., Int. Ed.* **2013**, *52*, 11726. (b) Corbet, M.; Campo, F. D. *Angew. Chem., Int. Ed.* **2013**, *52*, 9896.

(16) Bao, M.; Shimizu, M.; Shimada, S.; Inoue, J.; Konakahara, T. *Tetrahedron* **2004**, *60*, 11359.

(17) Bahrami, K.; Khodaei, M. M.; Sohrabnezhad, S. *Tetrahedron Lett.* **2011**, *52*, 6420.

(18) Xu, L.; Cheng, J.; Trudell, M. L. *J. Org. Chem.* **2003**, *68*, 5388.

(19) TBAI is not merely act as an iodine source for C−H iodination and an iodination/sulfenylation pathway is unlikely, since trace amounts of iodination product **40** were observed in the absence of elemental sulfur, and **2** could be obtained in 10% yield in DMF without TBAI (Table 1, entry 1). See the Supporting Information for detailed studies (Figure S2).



(20) (a) King, A. E.; Huffman, L. M.; Casitas, A.; Costas, M.; Ribas, X.; Stahl, S. S. *J. Am. Chem. Soc.* **2010**, *132*, 12068. (b) Huffman, L. M.; Stahl, S. S. *J. Am. Chem. Soc.* **2008**, *130*, 9196. (c) Wang, Z.-L.; Zhao, L.; Wang, M.-X. *Org. Lett.* **2011**, *13*, 6560. (d) Zhang, H.; Yao, B.; Zhao, L.; Wang, D.-X.; Xu, B.-Q.; Wang, M.-X. *J. Am. Chem. Soc.* **2014**, *136*, 6326.

(21) For mechanistic studies of C−S bond formation mediated by a Cu(I)/Cu(III) redox cycle, see: Font, M.; Parella, T.; Costas, M.; Ribas, X. *Organometallics* **2012**, *31*, 7976.

(22) A similar sulfur-atom transfer from elemental sulfur to nickel−carbon bonds has been reported; see: Han, R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1998**, *120*, 7657.

(23) An early study of the reaction of elemental sulfur with copper(I) has been reported; see: Helton, M. E.; Chen, P.; Paul, P. P.; Tyeklár, Z.; Sommer, R. D.; Zakharov, L. N.; Rheingold, A. L.; Solomon, E. I.; Karlin, K. D. *J. Am. Chem. Soc.* **2003**, *125*, 1160.

(24) A possible pathway involving C−S bond formation followed by N−S bond formation via oxidative dehydrogenative cyclization cannot be ruled out; see: (a) Correa, A.; Tellitu, I.; Domínguez, E.; SanMartin, R. *Org. Lett.* **2006**, *8*, 4811. (b) Wang, Z.; Kuninobu, Y.; Kanai, M. *J. Org. Chem.* **2013**, *78*, 7337.