Organic LETTERS

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

Selective Synthesis of Diaryl Sulfoxides and *m*-Arylthio Sulfones from Arylsulfinic Acids and Arenes via BF_3-Promoted C−S Bond Formation

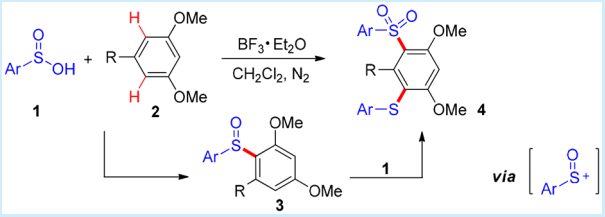
Wei Shi,[†] Tao Miao,*[,†] Yang Li,[†] Pinhua Li,[†] and Lei Wang*[,†,‡]

[†]Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P. R. China

[‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032, P. R. China

Supporting Information

ABSTRACT: A novel and efficient method for selective synthesis of diaryl sulfoxides and *m*-arylthio sulfones has been achieved from readily available arylsulfinic acids and arenes via an unusual sulfinyl cation, providing a range of structurally diverse products in good to excellent yields under mild conditions. Notably, mechanistic investigations suggested *m*-arylthio sulfones were generated from diaryl sulfoxides and sulfinyl cation by a sequence of redox reaction and electrophilic aromatic substitution process.



Organosulfur compounds, such as thioethers, sulfoxides, and sulfones, play an important role in organic chemistry. They are versatile building blocks in organic synthesis and frequently present in biologically active molecules, agrochemicals, and functional materials.[1] For instance, the pyrazolotriazine derivative (**I**) shows potent antihyperuricemia properties,[1f] and arylthio sulfone (**II**) is a novel and promising inhibitor of the annexin A2-S100A10 protein interaction (Figure 1).[1g] In the past few years,

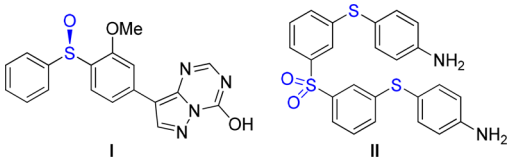
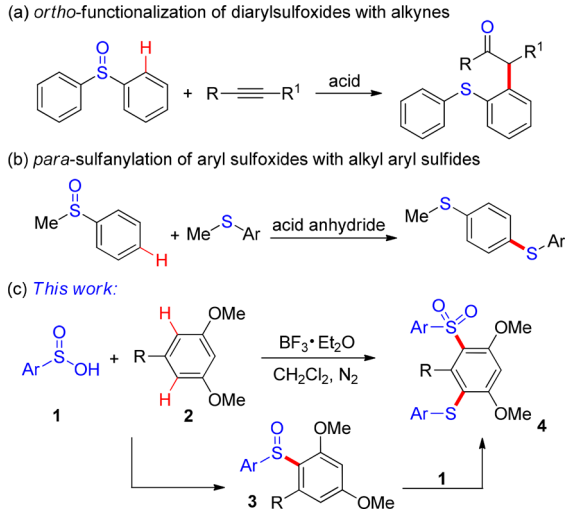


Figure 1. Biologically active molecules.

considerable efforts have been directed toward the incorporation of sulfur-containing substituents into organic frameworks, and various methodologies including sulfonylation of arenes, addition reactions of thiyl and sulfonyl radicals to double or triple bonds, and transition-metal-catalyzed C−S coupling reactions have been developed to access these important families of target molecules.[2] Some of these methods are popular and attractive for construction of C−S bonds on aromatic molecules, while they mainly suffer from limitations due to the harsh reaction conditions or multistep strategies required. Therefore, the development of a direct, efficient, and general protocol for formation of C−S bonds, by which structurally diverse sulfur-containing compounds could be selectively prepared from readily available starting materials, would be highly desirable.

As a subclass of organosulfur compounds, aryl sulfoxides not only constitute a core structure of a variety of pharmaceuticals and drug candidates but also contain a fundamental functional sulfoxide group, which renders them ligands for metal catalysts, organocatalysis, and useful synthetic reagents.[3] For example, Maulide and co-workers described a Brønsted acid catalyzed redox arylation of alkynes with aryl sulfoxides via [3,3] sigmatropic rearrangement, an easy approach to functionalize selectively the *ortho*-position of aryl sulfides (Scheme 1a).[4] Recently, the Yorimitsu group reported a regioselective C−H sulfanylation of aryl sulfoxides with alkyl aryl sulfides through Pummerer-type activation (Scheme 1b).[5] Despite long-standing biological and synthetic interest, direct access to this

Scheme 1. Synthetic Applications of Aryl Sulfoxides



Received: May 29, 2018

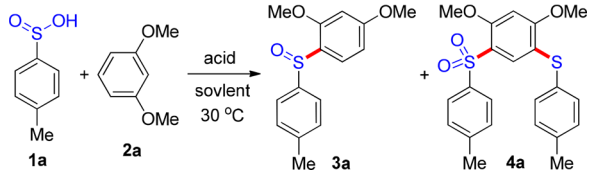
DOI: 10.1021/acs.orglett.8b01681
Org. Lett. XXXX, XXX, XXX−XXX

important class of compounds remains a challenge. Arylsulfinic acids or salts are stable and readily accessible starting materials for the preparation of a wide range of organic molecules, especially for various functionalized arylsulfones via sulfonyl anion or radical.[6,7] However, examples of arylsulfinic acids serving as precursors for unusual sulfinyl cations for the construction of C−S bonds are scarce.[8] In 1996, the Tsuchida group first realized direct synthesis of aryl sulfoxides from sulfinic acid, yet the narrow scope of substrates limited the further synthetic application.[8a] Until now, no example has been reported to prepare *m*-arylthio sulfones from sulfinic acids via sulfinyl cation. In continuation of our work on application of arylsulfinic acids in organic reactions, herein, we disclose a BF_3-promoted C−S bond formation for selective synthesis of diaryl sulfoxides and *m*-arylthio sulfones from arylsulfinic acids and arenes under mild conditions (Scheme 1c).

In our initial study, *p*-tolylsulfinic acid (**1a**) and 1,3-dimethoxybenzene (**2a**) were chosen as the model substrates to optimize the reaction conditions. First, the model reaction of **1a** with **2a** was carried out in CH_2Cl_2, and the corresponding product 1,3-dimethoxy-5-(*p*-tolylsulfinyl)-benzene (**3a**) was obtained in 30% yield (Table 1, entry 1). Much to our pleasure, 67% yield of **3a** was achieved when 1.2 equiv of trifluoroacetic acid (TFA) was added to the reaction (Table 1, entry 2). Further exploration of a variety of commercially available acids indicated that $BF_3{\cdot}Et_2O$ shows the best efficiency as an 87% yield of **3a** was achieved (Table 1, entry 3). Importantly, no regioisomer of **3a** was observed in the reaction. Other acids including AcOH, TsOH, H_2SO_4, HCl and H_3PO_4 were less effective and gave the inferior results (Table 1, entries 4−8). Next, the effect of the solvent on the model reaction was investigated. When the model reaction was carried out in $CHCl_3$, DCE, toluene, or CH_3CN, **3a** was produced in 54−78% yields (Table 1, entries 9−12). However, THF, 1,4-dioxane, and DMSO were not suitable solvents, and the model reaction was prohibited completely (Table 1, entries 13−15). Surprisingly, (2,4-dimethoxy-5-tosylphenyl)(*p*-tolyl)-sulfane **4a** was isolated in 15% yield along with **3a** in 60% yield under N_2 atmosphere (Table 1, entry 16). The use of an increased amount of *p*-tolylsulfinic acid (**1a**) and elevated reaction temperature to 80 °C, to our delight, allowed the reaction of **1a** and **2a** to proceed well and generate **4a** in 75% yield in 2.5 h (Table 1, entry 17). Subsequently, several solvents and TFA were also examined under N_2 atmosphere and led to the formation of product (**4a**) in 30−53% yields (Table 1, entries 18−21).

With the optimized conditions in hand, we examined the substrate scope of arylsulfinic acids and electron-rich arenes, and the results are summarized in Scheme 2. As expected, a variety of substituted arylsulfinic acids underwent the reactions with 1,3-dimethoxybenzene (**2a**) smoothly under the standard conditions. Importantly, the reaction was not sensitive to the

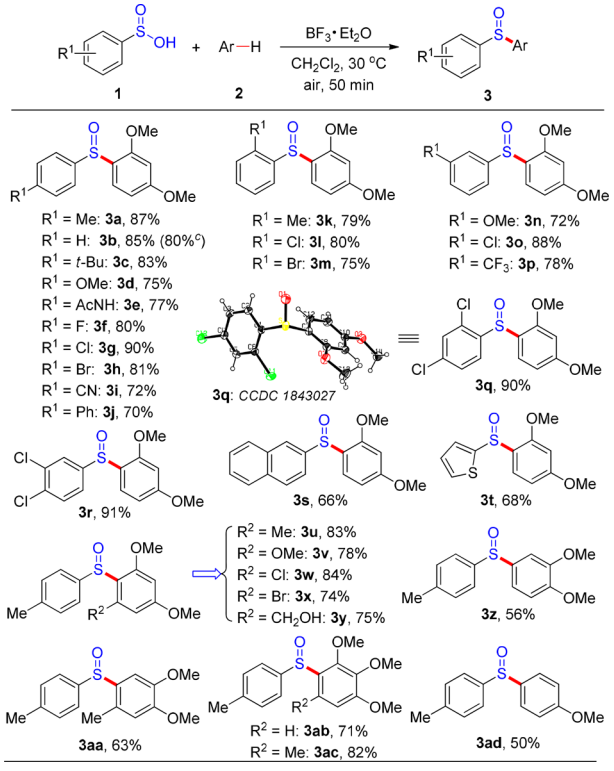
Table 1. Optimization of the Reaction Conditions[a,b]



entry	acid	solvent	yield[b] (%) 3a	4a
1		CH_2Cl_2	30	0
2	TFA	CH_2Cl_2	67	0
3	$BF_3{\cdot}Et_2O$	CH_2Cl_2	**87**	**<5**
4	AcOH	CH_2Cl_2	0	0
5	TsOH	CH_2Cl_2	18	0
6	H_2SO_4	CH_2Cl_2	12	0
7	HCl	CH_2Cl_2	0	0
8	H_3PO_4	CH_2Cl_2	15	0
9	$BF_3{\cdot}Et_2O$	$CHCl_3$	78	<5
10	$BF_3{\cdot}Et_2O$	DCE	71	<5
11	$BF_3{\cdot}Et_2O$	toluene	60	0
12	$BF_3{\cdot}Et_2O$	CH_3CN	54	0
13	$BF_3{\cdot}Et_2O$	THF	0	0
14	$BF_3{\cdot}Et_2O$	dioxane	0	0
15	$BF_3{\cdot}Et_2O$	DMSO	0	0
16[c]	$BF_3{\cdot}Et_2O$	CH_2Cl_2	60	15
17[c,d]	$BF_3{\cdot}Et_2O$	CH_2Cl_2	**<5**	**75**
18[c,e]	TFA	CH_2Cl_2	15	45
19[c,d]	$BF_3{\cdot}Et_2O$	$CHCl_3$	0	53
20[c,d]	$BF_3{\cdot}Et_2O$	DCE	0	48
21[c,d]	$BF_3{\cdot}Et_2O$	CH_3CN	11	30

[a]Reaction conditions: *p*-toluenesulfinic acid (**1a**, 0.375 mmol), 1,3-dimethoxybenzene (**2a**, 0.25 mmol), acid (1.2 equiv), and solvent (2.0 mL), in air at 30 °C for 50 min. [b]Isolated yield based on **2a**. [c]Under N_2 atmosphere. [d]*p*-Toluenesulfinic acid (**1a**, 0.75 mmol) and $BF_3{\cdot}Et_2O$ (2.0 equiv) were used, at 80 °C for 2.5 h [e]*p*-Toluenesulfinic acid (**1a**, 0.75 mmol) and TFA (2.0 equiv) were used at 80 °C for 2.5 h.

Scheme 2. Scope of Sulfinic Acids and Arenes[a,b]



[a]Reaction conditions: arylsulfinic acid (**1**, 0.375 mmol), arene (**2**, 0.25 mmol), $BF_3{\cdot}Et_2O$ (1.2 equiv), and CH_2Cl_2 (2.0 mL), in air at 30 °C for 50 min. [b]Isolated yield based on **2**. [c]The reaction is performed on a 5 mmol scale.

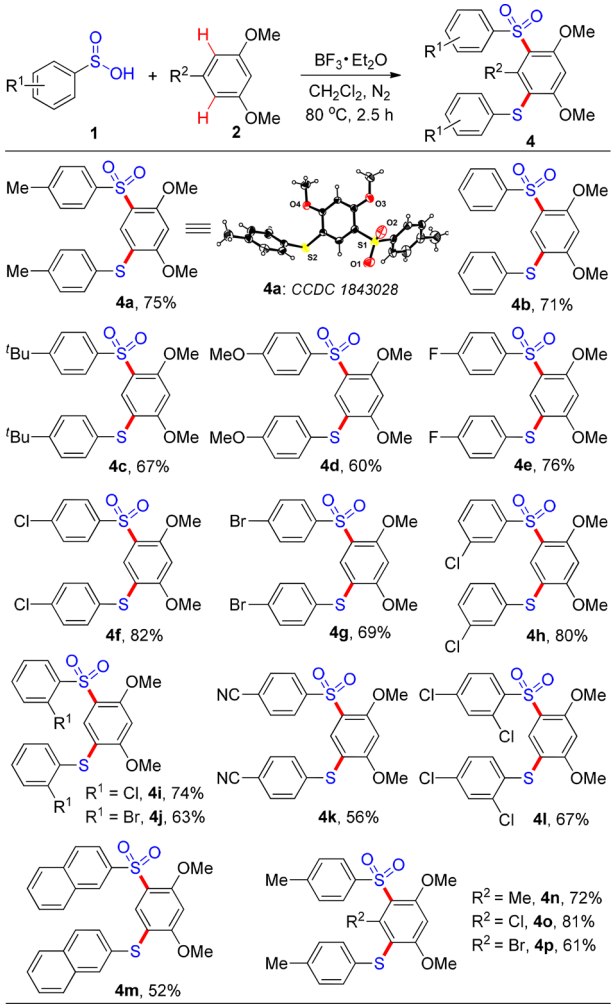
DOI: 10.1021/acs.orglett.8b01681
Org. Lett. XXXX, XXX, XXX−XXX

electronic nature of the substituents on the phenyl rings, and both electron-withdrawing groups including F, Cl, Br, CN, and CF_3 and electron-donating groups such as Me-, *t*-Bu-, and OMe-substituted substrates worked well to deliver the desired products in good to excellent yields. It was found that there is no obvious *ortho*-position effect in the reaction of *ortho*-substituted arylsulfinic acids with **2a**, leading to the desired products **3k**−**m** in 75−80% yields. It should be noted that arylsulfinic acid bearing a trifluoromethyl group (CF_3), as a useful structural motif in biologically active molecules,[9] reacted with **2a** to generate the corresponding product **3p** in good yield. In the other cases, disubstituted arylsulfinic acids also showed higher reactivity, affording products **3q** and **3r** in excellent yields. The structure of product **3q** was further characterized by X-ray crystallographic analysis. Furthermore, good yields were obtained with the bulkier 1,1′-biphenyl- and 2-naphthylsulfinic acid as coupling partners. In particular, heterocyclic sulfinic acid, as exemplified by 2-thiophenesulfinic acid, was also well tolerated in this protocol and gave the desired product **3t** in 68% yield. Subsequently, we turned our attention toward various electron-rich arenes. The reactions of a number of arenes with *p*-tolylsulfinic acid (**1a**) were examined in the presence of $BF_3{\cdot}Et_2O$, providing the corresponding products (**3u**−**ad**) in good yields. It was observed that *m*-dimethoxybenzene derivatives possessing a moderately electron-withdrawing substituent such as Cl or Br on the aromatic rings gave the products **3w** and **3x** in comparable yields in comparison with those bearing an electron-donating substituent such as Me or MeO (**3u** or **3v**). Notably, (3,5-dimethoxyphenyl)methanol proved to be a suitable nucleophile, and selectively generated product **3y** in 75% yield. Moreover, reactions of *o*-dimethoxybenzenes and *p*-tolylsulfinic acid were performed under the optimal conditions, leading to the expected products **3z** and **3aa** exclusively in 56% and 63% yields, respectively. 1,2,3-Trimethoxybenzenes could also be transformed into the diaryl sulfoxides (**3ab** and **3ac**) in good yields. In addition, when anisole was reacted with *p*-toluenesulfinic acid under optimized conditions, the reaction also proceeded smoothly to give the desired product **3ad** in 50% yield. However, no product was obtained when toluene and benzene were used as arene sources.

Direct incorporation of two different sulfur-containing substituents into arenes for the synthesis of *m*-sulfanylsulfone derivatives is always a challenge due to selective construction of two C−S bonds from two different sulfur-containing precursors in one pot and reaction regioselectivity. In our reaction system, we found that various 2,4-dimethoxy-5-(arylsulfonyl)phenyl)arylsulfane derivatives could be smoothly generated by increasing amount of sulfinic acid and $BF_3{\cdot}Et_2O$ (Scheme 3). It is important to note that different functional groups such as cyano, halides, etc. could be tolerated on the aryl rings of sulfinic acids, which will permit the products to be further functionalized in sequence step. Furthermore, the reaction was not sensitive to steric effects, and sterically hindered substituted 1,3-dimethoxybenzenes derivatives also selectively furnished products **4n**−**p** in good yields.

Arylsulfoxide plays a vital role in redox arylation of alkynes both as the oxidant and arylating agent for the synthesis of *ortho*-functionalized arylsulfides.[4,10] These studies prompted us to make a further transformation for the generation of *m*-arylthio sulfones. To our delight, desired product (2,4-dimethoxy-5-tosylphenyl)(*p*-tolyl)sulfane **4a** was obtained in good yield when 2,4-dimethoxy-1-(*p*-tolylsulfinyl)benzene **3a**

Scheme 3. One-Pot Synthesis of *m*-Arylthio Sulfones from Arylsulfinic Acids and Arenes[a,b]



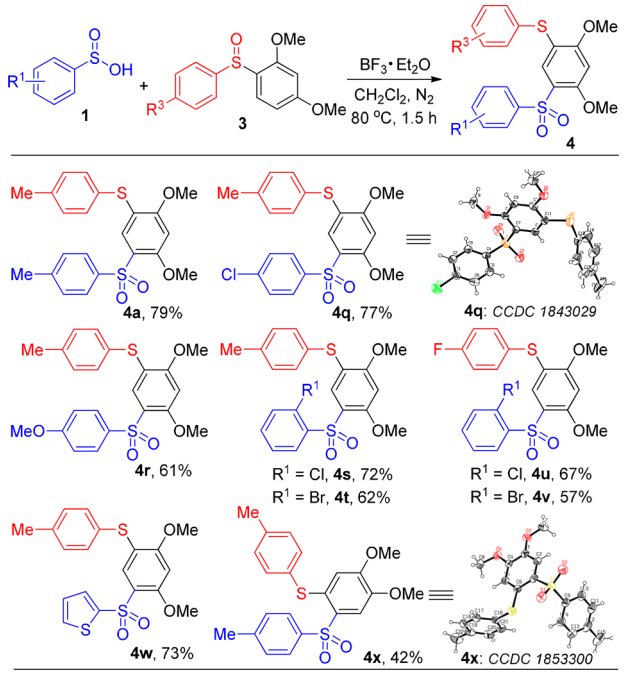
[a]Reaction conditions: arylsulfinic acid (**1**, 0.75 mmol), arene (**2**, 0.25 mmol), $BF_3{\cdot}Et_2O$ (2.0 equiv), and CH_2Cl_2 (2.0 mL) under N_2 atmosphere at 80 °C for 2.5 h. [b]Isolated yield based on **2**.

reacted with **1a**, which indicated that **3a** was an indispensable intermediate for the generation of **4a** from **1a** and **2a** in one pot. Importantly, the reaction of **3a** and *p*-chlorophenylsulfinic acid selectively led to the formation of **4q** in 77% yield. Particularly noteworthy is the mild nature of sulfoxide as oxidant and the extremely high efficiency for the formation of *m*-arylthio sulfones **4**. Furthermore, the strongly regioselective preference for transferring the most electron-rich aryl moiety during the crucial C−S bond-forming event supported electrophilic aromatic substitution process. In an attempt to further explore its synthetic utility, several aryl sulfoxides were conducted to react with arylsulfinic acids with different electronic properties, and the corresponding products were obtained in moderate to good yields. When (3,4-dimethoxy-5-tosylphenyl)(*p*-tolyl)sulfane **3z** reacted with **1a**, *o*-arylthio sulfone **4x** was selectively formed in 42% yield. The structures of **4q** and **4x** were confirmed by single-crystal X-ray diffraction (Scheme 4).

Based our observations on and previous reports,[4,8,10] we assumed a proposed reaction pathway for the formation of products **3** and **4**, which is in agreement with an electrophilic aromatic substitution process (Scheme 5). First, sulfinyl cation

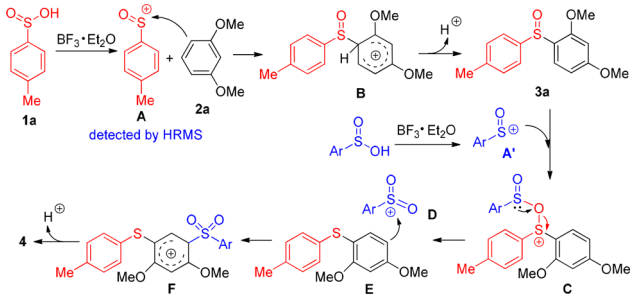
DOI: 10.1021/acs.orglett.8b01681
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 4. Synthesis of *m*-Arylthio Sulfones from Aryl Sulfoxides and Arylsulfinic Acids[a,b]



[a]Reaction conditions: arylsulfinic acid (**1**, 0.5 mmol), arylsulfoxide (**3**, 0.25 mmol), BF_3·Et_2O (1.0 equiv), and CH_2Cl_2 (2.0 mL) under N_2 atmosphere at 80 °C for 1.5 h. [b]Isolated yield based on **3**.

Scheme 5. Proposed Pathway for the Formation of 3 and 4



A was formed from arylsulfinic acid (**1a**) in the presence of BF_3 and detected by HRMS (SI). Then the intermediate **B** could be produced by a direct electrophilic substitution of **2a** to afford product **3a** by loss of a proton from **B**. Subsequently, the reaction of arylsulfoxide **3a** with in situ generated arylsulfinyl cation **A′** would lead to **C**, which underwent a redox reaction to afford sulfonyl cation **D** and intermediate **E**. Thereafter, an electrophilic aromatic substitution of **E** with sulfonyl cation **D** selectively generated **F**. Final, deprotonation from **F** produced *m*-arylthio sulfone **4**.

In summary, we have developed a novel and effective approach for selectively preparing diverse diaryl sulfoxides and *m*-arylthio sulfones from arylsulfinic acids and arenes via an unusual sulfinyl cation. The method proceeds under mild reaction conditions and produces a wide range of diaryl sulfoxides and *m*-arylthio sulfones in good yields with good functional group tolerance. In particular, the reaction enables the generation of two different sulfur-containing groups at the aromatic rings with high regioselectivity in one pot. Notably, the two regiocontrolled C–S bond formations have been realized by a mechanism involving a sequence of redox reaction and electrophilic aromatic substitution directed by a temporary and removable tether between the sulfinyl group and the sulfinyl cation. Further creation of more interesting sulfur-containing compounds as well as asymmetric arylthiosulfone synthesis via this strategy is currently underway.

■ ASSOCIATED CONTENT

Supporting Information

Full experimental details and characterization data for all products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01681.

Full experimental details and characterization data for all products (PDF)

Accession Codes

CCDC 1843027–1843029 and 1853300 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: taomiaochem@163.com.
*E-mail: leiwang88@hotmail.com.

ORCID

Lei Wang: 0000-0001-6580-7671

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the National Natural Science Foundation of China (21772062, 21602072, 21572078) and the National Science Foundation of Anhui Education Department (KJ2016A643) for financial support of this work.

■ REFERENCES

(1) (a) Kharasch, N. *The Chemistry of Organic Sulfur Compounds*; Pergamon: London, 1996. (b) Patai, S.; Rappoport, Z.; Stirling, C. *Sulphones and Sulfoxides*; John Wiley & Sons, Ltd: Chichester, 1988. (c) Damani, L. A. *Sulfur-Containing Drugs and Related Organic Compounds: Chemistry, Biochemistry, and Toxicology*; Ellis Horwood, Ltd.: Chichester, U.K., 1989; Vol. *1*, Part B. (d) Simpkins, N. S. *Sulfones in Organic Synthesis*; Pergamon Press: Oxford, 1993. (e) Feng, M.; Tang, B.; Liang, S. H.; Jiang, X. *Curr. Top. Med. Chem.* **2016**, *16*, 1200. (f) Naito, S.; Nishimura, M. *Xenobiotica* **2002**, *32*, 491. (g) Reddy, T. R. K.; Li, C.; Guo, X.; Myrvang, H. K.; Fischer, P. M.; Dekker, L. V. *J. Med. Chem.* **2011**, *54*, 2080. (h) Dini, I.; Tenore, G. C.; Dini, A. *J. Nat. Prod.* **2008**, *71*, 2036. (i) Kim, S.; Kubec, R.; Musah, R. A. *J. Ethnopharmacol.* **2006**, *104*, 188.

(2) (a) Castarlenas, R.; Di Giuseppe, A.; Pérez-Torrente, J. J.; Oro, L. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 211. (b) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596. (c) Hartwig, J. F. *Nature* **2008**, *455*, 314. (d) Kubas, G. J. *Acc. Chem. Res.* **1994**, *27*, 183. (e) Kar, A.; Sayyed, I. A.; Lo, W. F.; Kaiser, H. M.; Beller, M.; Tse, M. K. *Org. Lett.* **2007**, *9*, 3405. (f) Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Parisi, L. M.; Bernini, R. *J. Org. Chem.* **2004**, *69*, 5608. (g) Baskin, J. M.; Wang, Z. *Org. Lett.* **2002**, *4*, 4423. (h) Umierski, N.; Manolikakes, G. *Org. Lett.* **2013**, *15*, 188. (i) Liu, N.-W.; Liang, S.; Manolikakes, G. *Synthesis* **2016**, *48*, 1939. (j) Shaaban, S.; Liang, S.; Liu, N.-W.;

DOI: 10.1021/acs.orglett.8b01681
Org. Lett. XXXX, XXX, XXX–XXX

Manolikakes, G. *Org. Biomol. Chem.* **2017**, *15*, 1947. (k) Rao, W.-H.; Zhan, B.-B.; Chen, K.; Ling, P.-X.; Zhang, Z.-Z.; Shi, B.-F. *Org. Lett.* **2015**, *17*, 3552. (l) Wang, P.; Tang, S.; Huang, P.; Lei, A. *Angew. Chem., Int. Ed.* **2017**, *56*, 3009. (m) Huang, Z.; Zhang, D.; Qi, X.; Yan, Z.; Wang, M.; Yan, H.; Lei, A. *Org. Lett.* **2016**, *18*, 2351. (n) Ke, F.; Qu, Y.; Jiang, Z.; Li, Z.; Wu, D.; Zhou, X. *Org. Lett.* **2011**, *13*, 454. (o) Zhang, G.; Liu, C.; Yi, H.; Meng, Q.; Bian, C.; Chen, H.; Jian, J.-X.; Wu, L.-Z.; Lei, A. *J. Am. Chem. Soc.* **2015**, *137*, 9273. (p) Liu, C.; Szostak, M. *Chem. Commun.* **2018**, *54*, 2130. (q) Jouffroy, M.; Kelly, C. B.; Molander, G. A. *Org. Lett.* **2016**, *18*, 876. (r) Farmer, J. L.; Pompeo, M.; Lough, A. J.; Organ, M. G. *Chem. - Eur. J.* **2014**, *20*, 15790.

(3) For selected reviews, see: (a) Fernandez, I.; Khiar, N. *Chem. Rev.* **2003**, *103*, 3651. (b) Mellah, M.; Voituriez, A.; Schulz, E. *Chem. Rev.* **2007**, *107*, 5133. (c) Wojaczyńska, E.; Wojaczyński, J. *Chem. Rev.* **2010**, *110*, 4303. (d) Yorimitsu, H. *Chem. Rec.* **2017**, *17*, 1156. (e) Pulis, A. P.; Procter, D. J. *Angew. Chem., Int. Ed.* **2016**, *55*, 9842.

(4) (a) Peng, B.; Huang, X.; Xie, L.-G.; Maulide, N. *Angew. Chem., Int. Ed.* **2014**, *53*, 8718. (b) Peng, B.; Geerdink, D.; Farès, C.; Maulide, N. *Angew. Chem., Int. Ed.* **2014**, *53*, 5462. (c) Kaiser, D.; Veiros, L. F.; Maulide, N. *Chem. - Eur. J.* **2016**, *22*, 4727. (d) Cuenca, A. B.; Montserrat, S.; Hossain, K. M.; Mancha, G.; Lledós, A.; Medio-Simón, M.; Ujaque, G.; Asensio, G. *Org. Lett.* **2009**, *11*, 4906. (e) Shapiro, N. D.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 4160. (f) Stopka, T.; Niggemann, M.; Maulide, N. *Angew. Chem., Int. Ed.* **2017**, *56*, 13270.

(5) Kawashima, H.; Yanagi, T.; Wu, C.-C.; Nogi, K.; Yorimitsu, H. *Org. Lett.* **2017**, *19*, 4552.

(6) For selected examples, see: (a) Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Parisi, L. M. *Org. Lett.* **2002**, *4*, 4719. (b) Baskin, J. M.; Wang, Z. Y. *Org. Lett.* **2002**, *4*, 4423. (c) Zhu, W.; Ma, D. *J. Org. Chem.* **2005**, *70*, 2696. (d) Liu, C.; Li, M.; Cheng, D.; Yang, C.; Tian, S. *Org. Lett.* **2009**, *11*, 2543. (e) Reddy, M.; Reddy, P.; Sreedhar, B. *Adv. Synth. Catal.* **2010**, *352*, 1861. (f) Ueda, M.; Hartwig, J. F. *Org. Lett.* **2010**, *12*, 92. (g) Maloney, K.; Kuethe, J.; Linn, K. *Org. Lett.* **2011**, *13*, 102. (h) Kar, A.; Sayyed, I. A.; Lo, W. F.; Kaiser, H. M.; Beller, M.; Tse, M. K. *Org. Lett.* **2007**, *9*, 3405. (i) Yang, H.; Li, Y.; Jiang, M.; Wang, J.; Fu, H. *Chem. - Eur. J.* **2011**, *17*, 5652.

(7) For selected examples, see: (a) Lu, Q.; Zhang, J.; Zhao, G.; Qi, Y.; Wang, H.; Lei, A. *J. Am. Chem. Soc.* **2013**, *135*, 11481. (b) Xiao, F.; Chen, H.; Xie, H.; Chen, S.; Yang, L.; Deng, G.-J. *Org. Lett.* **2014**, *16*, 50. (c) Wei, W.; Wen, J.; Yang, D.; Du, J.; You, J.; Wang, H. *Green Chem.* **2014**, *16*, 2988. (d) Yang, W.; Yang, S.; Li, P.; Wang, L. *Chem. Commun.* **2015**, *51*, 7520. (e) Tang, S.; Wu, Y.; Liao, W.; Bai, R.; Liu, C.; Lei, A. *Chem. Commun.* **2014**, *50*, 4496. (f) Xia, D.; Miao, T.; Li, Y.; Wang, L. *Chem. Commun.* **2016**, *52*, 11559.

(8) (a) Yamamoto, K.; Miyatake, K.; Nishimura, Y.; Tsuchida, E. *Chem. Commun.* **1996**, 2099. (b) Miao, T.; Li, P.; Zhang, Y.; Wang, L. *Org. Lett.* **2015**, *17*, 832.

(9) (a) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, *37*, 320. (b) Hagmann, W. K. *J. Med. Chem.* **2008**, *51*, 4359.

(10) (a) Colomer, I.; Velado, M.; Pradilla, R. F.; Viso, A. *Chem. Rev.* **2017**, *117*, 14201. (b) Yuste, F.; Linares, A. H.; Mastranzo, V. M.; Ortiz, B.; Sánchez-Obregón, R.; Fraile, A.; Ruano, J. L. G. *J. Org. Chem.* **2011**, *76*, 4635.

DOI: 10.1021/acs.orglett.8b01681
Org. Lett. XXXX, XXX, XXX−XXX