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Cyclic Sulfoximine and Sulfonimidamide Derivatives by Copper-Catalyzed Cross-Coupling Reactions with Elemental Sulfur

Peng Wu,[a] Jas S. Ward,[b] Kari Rissanen,[b] and Carsten Bolm[a,*]

[a] Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, D-52074 Aachen, Germany
Phone: (+49)-241-8094675
E-mail: Carsten.Bolm@oc.RWTH-Aachen.de
[b] University of Jyvaskyla, Department of Chemistry, P.O. Box 35, Survontie 9B, FI-40014 Jyväskylä, Finland

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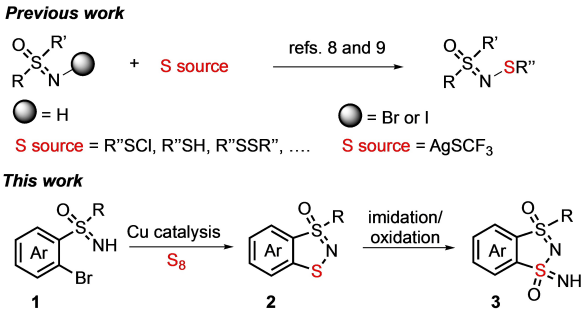
Abstract: Copper-catalyzed cross-coupling reactions of α-bromoaryl *N*H-sulfoximines with elemental sulfur lead to benzo[*d*][1,3,2]dithiazole-1-oxides, which represent a new class of three-dimensional heterocycles. The reactions proceed under mild conditions showing good functional group and heterocycle tolerance. By imination/oxidation, the initial cross-coupling products can be converted to unprecedented cyclic sulfonimidamides derivatives. Furthermore, a seven-membered heterocycle was obtained by a ruthenium-catalyzed ring-expansion with ethyl propiolate.

Keywords: copper catalysis; elemental sulfur; sulfoximines; sulfonimidamides; cross-coupling reactions

Sulfoximines have attracted considerable attention over the past several decades. As typical high oxidation state sulfur compounds, their molecular architectures offer attractive properties for drug and crop protection chemistry including metabolic stability, hydrogen-bond donor/acceptor capabilities, and structural diversity.[1] As response to the needs of organic synthesis and industrial applications, *N*-functionalizations of *N*H-sulfoximines have been greatly advanced.[2] In this context, the synthesis of three-dimensional heterocycles has become an important research area.[3] A high degree of saturation and the presence of stereogenic centers are important factors in the drug discovery process.[4] Synthesizing three-dimensional heterocycles with sulfur cores has been an ongoing research interest of our group, and we devised various protocols for accessing compounds such as benzothiazines and derivatives thereof,[5] benzo[*c*]isothiazole 2-oxides,[6] and other related compounds.[7] In this series, however, cyclic structures resulting from formal *N*-sulfenylations and ring closures are still lacking. This is surprising in light of the large number of recent straightforward methods for the generation of new N–S bonds from *N*H-sulfoximines with reagents such as RSCl, RSH, RSSR, and R′R″NSR.[8,9] In order to close this synthetic gap, we decided to focus on heterocycles **2** as molecular targets (Scheme 1). Considering substrate accessibility, 2-bromoaryl sulfoximines **1** were identified as attractive starting materials.[10] In addition, we envisaged avoiding the aforementioned toxic and odorous sulfur reagents and applying easy-to-use elemental sulfur (S_8) instead.[11] As the result of a long-lasting endeavor, we can now report a copper-catalyzed cross-coupling



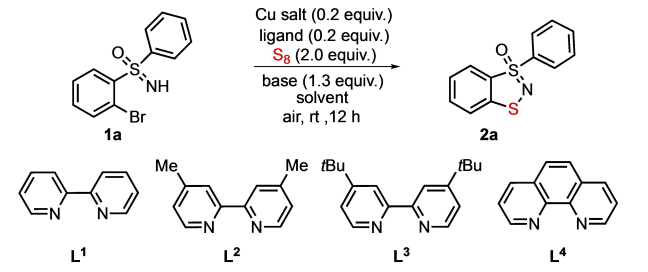
Scheme 1. *N*-Thiolations of sulfoximines.

reactions of *S*-2-bromophenyl *N*H-sulfoximines **1** with elemental sulfur under very mild reaction conditions leading to benzo[*d*][1,3,2]dithiazole1-oxides **2**, which can then be further converted into novel cyclic sulfonimidamides **3** by imination/oxidation protocols (Scheme 1).[12]

Preliminary studies had indicated that a combination of diaryl *N*H-sulfoximine **1a** and 2.0 equiv. of elemental sulfur led to heterocycle **2a** in 53% yield (as determined by NMR spectroscopy with CH_2Br_2 as internal standard) when a reagent mixture of 1.3 equiv. of K_2CO_3, 20 mol% of CuI, and 20 mol% of 2,2′-bipyridine (L^1) was applied in DMF at room temperature for 12 h (Table 1, entry 1). An inert atmosphere was not required. Encouraged by this result, a screening of the reaction conditions was initiated. The results are shown in Table 1. Changing the copper source from CuI to CuOAc or copper(I) thiophen-2-carboxylate (CuTc) proved unsuitable leading to **2a** in only trace quantities (Table 1, entries 2 and 3). While the solvents THF and DCE were inferior to DMF, the use of DMSO raised the yield of **2a** to 65% (Table 1, entries 1 and 4–6). With K_3PO_4, Cs_2CO_3, or Na_2CO_3 as the base in DMSO, the yield of **2a** dropped as compared to K_2CO_3 (Table 1, entries 7–9). Using substituted bipyridines L^2 (4,4′-dimethyl-2,2′-bipyridine) and L^3 (4,4′-di-*tert*-butyl-2,2′-bipyridine) instead of L^1 as ligand affected the yield of **2a** to a minor degree (Table 1, entries 10 and 11). Finally, the application of 1,10-phenanthroline (1,10-phen, L^4) proved beneficial leading to **2a** in 86% yield. Isolation by column chromatography gave **2a** in 81% yield (Table 1, entry 12). Without a ligand or reducing the amount of CuI from 20 mol% to 10 mol% afforded **2a** in yields of only 5% and 53%, respectively (Table 1, entries 13 and 14). Without a metal salt, no reaction occurred (Table 1, entry 15).

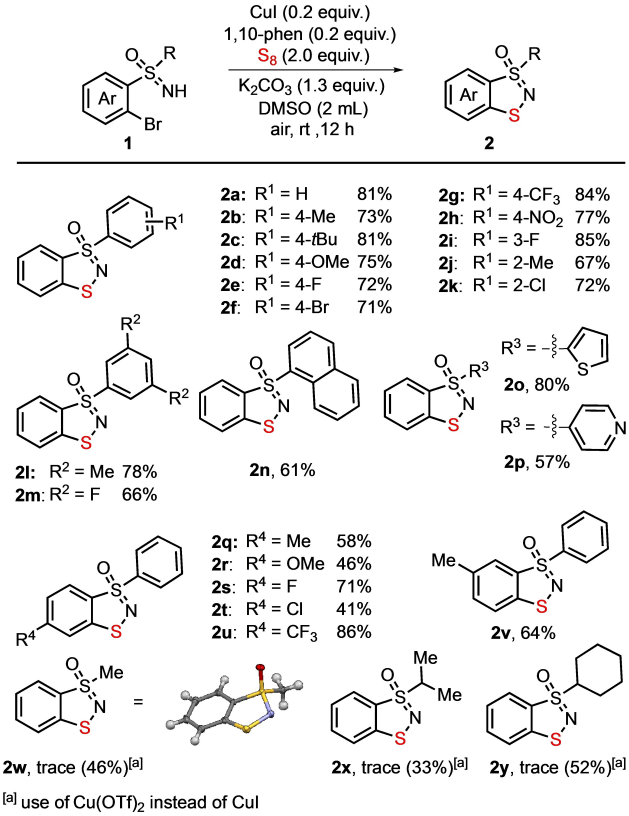
With the optimized reaction conditions in hand, the substrate scope was investigated. The results are shown in Scheme 2. In general, reactions with *S,S*-diaryl sulfoximines showed a broad functional group tolerance, and substrates with various substituents on the two arenes including methyl, methoxy, halo, trifluoromethyl, and nitro groups reacted well, providing the corresponding products **2a–v** in yields ranging from 41–86%. Neither electronic factors of the

Table 1. Optimization of reaction conditions.[a]



entry	Cu salt	ligand	base	solvent	yield[b]
1	CuI	L^1	K_2CO_3	DMF	53%
2	CuOAc	L^1	K_2CO_3	DMF	Trace
3	CuTc	L^1	K_2CO_3	DMF	Trace
4	CuI	L^1	K_2CO_3	THF	20%
5	CuI	L^1	K_2CO_3	DCE	Trace
6	CuI	L^1	K_2CO_3	DMSO	65%
7	CuI	L^1	K_3PO_4	DMSO	Trace
8	CuI	L^1	Cs_2CO_3	DMSO	Trace
9	CuI	L^1	Na_2CO_3	DMSO	46%
10	CuI	L^2	K_2CO_3	DMSO	68%
11	CuI	L^3	K_2CO_3	DMSO	63%
12	CuI	L^4	K_2CO_3	DMSO	86% (81%)[c]
13	CuI	–	K_2CO_3	DMSO	5%
14[d]	CuI	L^4	K_2CO_3	DMSO	53%
15	–	L^4	K_2CO_3	DMSO	0%

[a] Reaction conditions: **1a** (0.20 mmol), S_8 (12.8 mg, 0.40 mmol), base (0.26 mmol), Cu salt (0.04 mmol), and ligand (0.04 mmol) in the solvent (2.0 mL) at rt in air for 12 h.
[b] Determined by ^{1}H NMR analysis of the crude reaction mixture using CH_2Br_2 as the internal standard.
[c] In parentheses, yield of **2a** after isolation by column chromatography.
[d] Use of 10 mol% of CuI.



Scheme 2. Substrate scope (0.2 mmol scale) and X-ray crystal structure of **2w**.[14]

substituents nor their position on the arene had a clear effect. To highlight three particular aspects: First, also substrates with heteroarenes could be applied, as illustrated by the conversions of sulfoximines **1o** and **1p** with *S*-2-thienyl and *S*-4-pyridinyl substituents, respectively, which afforded **2o** and **2p** in 80% and 57% yield, respectively. Second, in the reaction of *S*-2-bromophenyl-*S*-2-chlorophenyl-sulfoximine (**1k**) a high halo selectivity was observed providing **2k** in 72% yield. Apparently, the bromo arene side reacted faster in the heterocycle formation leaving the C–Cl bond of the other arene intact. Third, as revealed in conversions of **1q–v** the reaction tolerated a wide range of substituents at the bromo-substituted arene, but the yields of the corresponding products (**2q–v**) varied significantly.

For example, while **1r** and **1t** bearing a methoxy and a chloro group at the *para* position gave **2r** and **2t** in only moderate yields (46% and 41%, respectively), analogously substituted **1s** and **1u** with a *para*-fluoro and a *para*-trifluoromethyl group led to **2s** and **2u** in higher yields of 71% and 86%, respectively. Noteworthy is also that in the reaction of dibromo derivative **1f** only cyclized **2f** and no other sulfide was observed (by LCMS analysis) revealing a high regioselectivity in the halo activation.

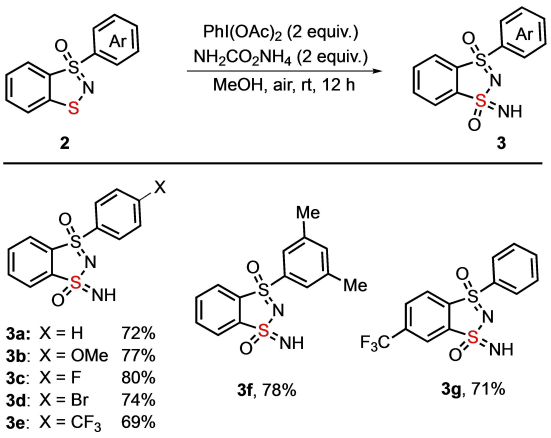
Reactions of *S*-alkyl-*S*-aryl sulfoximines proved more challenging due to a rapid decomposition of the starting materials under standard conditions. In this case, a change of the copper source offered a solution. Thus, applying $Cu(OTf)_2$ instead of CuI

gave 2-alkyl-substituted products **2w–y** in yields of 46% (**2w**), 33% (**2x**), and 52% (**2y**). The molecular structure of **2w** (Scheme 2) was confirmed by single-crystal X-ray analysis.[14] Performing the reactions of **1a** and **1f** on a 4 mmol scale led to 0.73 g of **2a** and 1.04 g of **2f** corresponding to yields of 74% and 80%, respectively.

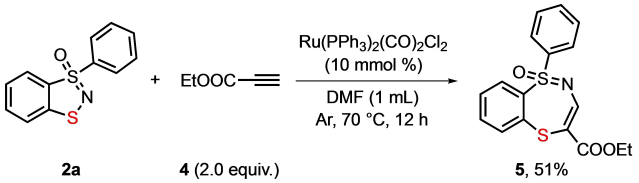
Imidation with or without subsequent oxidation of lower oxidation-state sulfur compounds in combination with a hypervalent iodine reagent and ammonium carbamate is a powerful strategy for the synthesis of sulfoximines and sulfonimidamides.[15]

Applying this approach here on compounds **2** led to cyclic sulfonimidamides **3** with structures reminiscent to saccharin and analogous aza bioisosteres (Scheme 3).[13,16] Thus, in a single step, products **3a–g** were obtained from the corresponding heterocycles **2** in yields ranging from 69% to 80% with d.r. values between 1:1 and 1:2. Significant substitution effects were not observed.

The synthetic potential of products **2** was further demonstrated by a ruthenium-catalyzed ring expansion reaction of **2a** with ethyl propiolate (**4**), which gave the seven-membered heterocycle **5** in 51% yield (Scheme 4).[17,18]



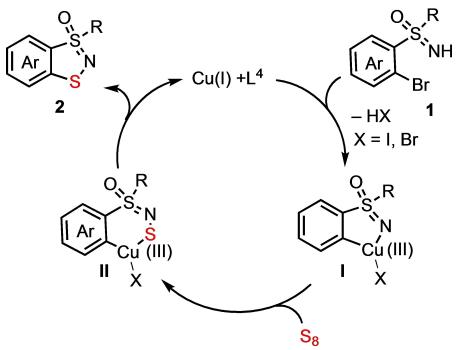
Scheme 3. Imination/oxidation reactions of **2** (0.2 mmol scale).



Scheme 4. Ring expansion of **2a** (0.1 mmol scale).

Based on the aforementioned experimental results and literature reports,[19] we propose a mechanistic pathway for the formation of heterocycles **2** as depicted in Scheme 5.[20] Starting from Cu(I), oxidative addition into the C–Br bond leads to a Cu(III) intermediate, which upon loss of HX provides copper-based heterocycle **I**. Sulfur insertion gives **II**. Finally, reductive elimination of **II** results in the formation of product **2** and regenerates the Cu(I) catalyst, which re-enters the catalytic cycle. Alternatively, a C–S bond could be formed first, which upon S–N coupling provides the product.[19]

In summary, we developed a copper-catalyzed cross-coupling reactions of α-bromoaryl *N*H-sulfoximines with elemental sulfur leading to



Scheme 5. Proposed mechanism.

benzo[*d*][1,3,2]dithiazole1-oxides. The transformations occur under mild reaction conditions (at room temperature in air), show good functional group tolerance, and lead to structurally interesting three-dimensional heterocycles. Through a combined imination/oxidation process the initial products can be converted into new heterocyclic sulfonimidamide derivatives. Alternatively, seven-membered heterocycles can be prepared by alkyne insertion into the S–N bond under ruthenium catalysis.

Experimental Section

General procedure for the preparation of cyclic sulfoximines derivatives. A mixture of sulfoximine **1** (0.20 mmol), S_8 (12.8 mg, 0.40 mmol, 2 equiv.), CuI (7.6 mg, 20 mol%), 1,10-phen (1,10-phenanthroline) (7.2 mg, 20 mol%), K_2CO_3 (35.9 mg, 0.26 mmol, 1.3 equiv.), and DMSO (2 mL) in a 10 mL sealed vial was stirred at room temperature for 12 h. Upon completion, ethyl acetate (10 mL) was added to dilute the mixture, which was then washed with an aqueous solution of ammonia (4 mL) and brine (10 mL). The organic layer was separated, dried over Mg_2SO_4 and evaporated under reduced pressure. The product was purified by flash column chromatography to give product **2**.

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References

[1] For recent overviews on the use of sulfoximines in medicinal and crop protection chemistry, see: a) U. Lücking, *Angew. Chem. Int. Ed.* **2013**, *52*, 9399–9408; *Angew. Chem.* **2013**, *125*, 9570–9580; b) M. Frings, C. Bolm, A. Blum, C. Gnamm, *Eur. J. Med. Chem.* **2017**, *126*, 225–245; c) U. Lücking, *Org. Chem. Front.* **2019**, *6*, 1319–1324; d) P. Mäder, L. Kattner, *J. Med. Chem.* **2020**, *63*, 14243–14275; e) Y. Han, K. Xing, J. Zhang, T. Tong, Y. Shi, H. Cao, H. Yu, Y. Zhang, D. Liu, L. Zhao, *Eur. J. Med. Chem.* **2021**, *209*, 112885; f) M. J. Tilby, M. C. Willis, *Expert Opin. Drug Discovery* **2021**, *16*, 1227–1231; g) U. Lücking, *Chem. Eur. J.* **2022**, *528*, e202201993; h) K. E. Arndt, D. C. Bland, N. M. Irvine, S. L. Powers, T. P. Martin, J. R. McConnell, D. E. Podhorez, J. M. Renga, R. Ross, G. A. Roth, B. D. Scherzer, T. W. Toyzan, *Org. Process Res. Dev.* **2015**, *19*, 454–462; i) T. C. Sparks, G. B. Watson, M. R. Loso, C. Geng, J. M. Babcock, J. D. Thomas, *Pest. Biochem. Phys.* **2013**, *107*, 1–7.

[2] For recent overviews on transformations of *N*H–sulfoximines, see: a) P. Ghosh, B. Ganguly, S. Das, *Asian J. Org. Chem.* **2020**, *9*, 2035–2082; b) W. Zheng, X. Chen, F. Chen, Z. He, Q. Zeng, *Chem. Rec.* **2021**, *21*, 396–416; c) M. Andresini, A. Tota, L. Degennaro, J. A. Bull, R. Luisi, *Chem. Eur. J.* **2021**, *27*, 17293–17321.

[3] a) F. Lovering, J. Bikker, C. Humblet, *J. Med. Chem.* **2009**, *52*, 6752–6756; b) F. Lovering, *MedChemComm.* **2013**, *4*, 515–519.

[4] a) P. Ertl, S. Jelfs, J. Muhlbacher, A. Schuffenhauer, P. Selzer, *J. Med. Chem.* **2006**, *49*, 4568–4573; b) W. R. Pitt, D. M. Parry, B. G. Perry, C. R. Groom, *J. Med. Chem.* **2009**, *52*, 2952–2963; c) F. W. Goldberg, J. G. Kettle, T. Kogej, M. W. D. Perry, N. P. Tomkinson, *Drug Discovery Today* **2015**, *20*, 11–17.

[5] a) W. Dong, L. Wang, K. Parthasarathy, F. Pan, C. Bolm, *Angew. Chem. Int. Ed.* **2013**, *52*, 11573–11576; *Angew. Chem.* **2013**, *125*, 11787–11790; b) Y. Cheng, C. Bolm, *Angew. Chem. Int. Ed.* **2015**, *54*, 12349–12352; *Angew. Chem.* **2015**, *127*, 12526–12529; c) L. Wang, D. L. Priebbenow, X. Y. Chen, F.-F. Pan, C. Bolm, *Eur. J. Org. Chem.* **2015**, 3338–3343; d) J. Wen, D. P. Tiwari, C. Bolm, *Org. Lett.* **2017**, *19*, 1706–1709; e) J.-H. Schöbel, P. Elbers, K.-N. Truong, K. Rissanen, C. Bolm, *Adv. Synth. Catal.* **2021**, *363*, 1322–13.

[6] a) P. Lamers, L. Buglioni, S. Koschmieder, N. Chatain, C. Bolm, *Adv. Synth. Catal.* **2016**, *358*, 3649–3653; b) P. Lamers, C. Bolm, *Org. Lett.* **2018**, *20*, 116–118; c) H. Yu, Z. Li, C. Bolm, *Angew. Chem. Int. Ed.* **2018**, *57*, 12053–12056; *Angew. Chem.* **2018**, *130*, 12229–12232.

[7] a) R. A. Bohmann, Y. Unoh, M. Miura, C. Bolm, *Chem. Eur. J.* **2016**, *22*, 6783–6786; b) H. Wang, M. Frings, C. Bolm, *Org. Lett.* **2016**, *18*, 2431–2434; c) Y. Cheng, W. Dong, H. Wang, C. Bolm, *Chem. Eur. J.* **2016**, *22*, 10821–10824; d) J. Wen, H. Cheng, G. Raabe, C. Bolm, *Org. Lett.* **2017**, *19*, 6020–6023; e) Y. Cheng, W. Dong, K. Parthasarathy, C. Bolm, *Org. Lett.* **2017**, *19*, 726–729; f) D. Zhang, H. Wang, H. Cheng, J. G. Hernández, C. Bolm, *Adv. Synth. Catal.* **2017**, *359*, 4274–4277; g) P. Shi, Y. Tu, C. Wang, D. Kong, D. Ma, C. Bolm, *Org. Lett.* **2020**, *22*, 8842–8845; h) R. Hommelsheim, H. M. Núñez Ponce, K.-N. Truong, K. Rissanen, C. Bolm, *Org. Lett.* **2021**, *23*, 3415–3420; i) D. Ma, D. Kong, C. Wang, K.-N. Truong, K. Rissanen, C. Bolm, *Org. Lett.* **2021**, *23*, 8287–8290.

[8] a) K. Akutagawa, N. Furukawa, S. Oae, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 518–524; b) Y. Peng, Y. Lin, R. Nie, Y. Zheng, Y. Liu, L. Guo, Y. Wu, *Eur. J. Org. Chem.* **2018**, 844–850; c) L. Yang, J. Feng, M. Qiao, Q. Zeng, *Org. Chem. Front.* **2018**, *5*, 24–28; d) H. Zhu, J.-T. Yu, J. Cheng, *Chem. Commun.* **2016**, *52*, 11908–11911; e) D. Kong, D. Ma, P. Wu, C. Bolm, *ACS Sustainable Chem. Eng.* **2022**, *10*, 2863–2867; f) Y. Lin, L. Ü. Guanghui, Y. Liu, Y. Zheng, R. Nie, L. Guo, Y. Wu, *Catal. Commun.* **2018**, *112*, 68–73; g) Y. Lin, Y. Liu, Y. Zheng, R. Nie, L. Guo, Y. Wu, *ACS Sustainable Chem. Eng.* **2018**, *6*, 13644–13649; h) H. Wang, D. Zhang, M. Cao, C. Bolm, *Synthesis* **2019**, *51*, 271–275.

[9] For *N*-trifluoromethylthiolations of sulfoximines, see: a) C. Bohnen, C. Bolm, *Org. Lett.* **2015**, *17*, 3011–3013;

b) N. Thota, P. Makam, K. K. Rajbongshi, S. Nagiah, N. S. Abdul, A. A. Chuturgoon, A. Kaushik, G. Lamichhane, A. M. Somboro, H. G. Kruger, T. Govender, T. Naicker, P. I. Arvidsson, *ACS Med. Chem. Lett.* **2019**, *10*, 1457–1461; c) A. Zupanc, M. Jereb, *J. Org. Chem.* **2021**, *86*, 5991–6000.

[10] For the synthesis and previous use of such compounds, see: a) M. Harmata, K. O. Rayanil, M. G. Gomes, P. Zheng, N. L. Calkins, S. Y. Kim, Y. Fan, V. Bumbu, D. R. Lee, S. Wacharasindhu, X. Hong, *Org. Lett.* **2005**, *7*, 143–145; b) H. Zhou, W. Chen, Z. Chen, *Org. Lett.* **2018**, *20*, 2590–2594; c) X. Chen, H. Zhou, Z. Chen, *Org. Chem. Front.* **2019**, *6*, 3415–3419; d) C. Wu, R. Huang, M. Zhang, Z. Chen, *J. Org. Chem.* **2020**, *85*, 841–850; e) A. Banerjeea, G. Panda, *Org. Biomol. Chem.* **2022**, *20*, 7112–7126.

[11] For overviews on the use of elemental sulfur in organic synthesis, see: a) T. B. Nguyen, *Adv. Synth. Catal.* **2017**, *359*, 1066–1130; b) T. Szabó, M. Milen, *Chem. Heterocylc. Comp.* **2019**, *55*, 126–128; c) S. Liu, G.-J. Deng, H. Huang, *Synlett* **2021**, *32*, 142–158; d) T. B. Nguyen, *Adv. Synth. Catal.* **2020**, *362*, 3448–3484.

[12] For reviews on metal-catalyzed cross-couplings providing sulfides, see: a) C. C. Eichman, J. P. Stambuli, *Molecules* **2011**, *16*, 590–608; b) F. Abedinifar, S. Bahadorikhalili, B. Larijani, M. Mahdavi, F. Verpoort, *Appl. Organomet. Chem.* **2022**, *36*, e6482.

[13] To the best of our knowledge, compound **3** are unprecedented. The closest analogs are molecules with $ArSO_2N–$ instead of Ar-SO(NH)N– units and $R{=}CF_3$. Those compounds have theoretically been investigated as CF_3 transfer agents, see: a) M. Li, X–S. Xue, J. Guo, Y. Wang, J.-P. Cheng, *J. Org. Chem.* **2016**, *81*, 3119–3126; b) M. Li, W. Wang, X.-S. Xue, J.-P. Cheng, *Asian J. Org. Chem.* **2017**, *6*, 235–240.

[14] For the X-ray of **2w** shown in Scheme , the thermal ellipsoids were set to the standard 50% probability level. CCDC 2225023 contains the supplementary crystallographic data for **2w**. 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.

[15] a) M. Zenzola, R. Doran, L. Degennaro, R. Luisi, J. A. Bull, *Angew. Chem. Int. Ed.* **2016**, *55*, 7203–7207; *Angew. Chem.* **2016**, *128*, 7319–7323; b) J.-F. Lohier, T. Glachet, H. Marzag, A.-C. Gaumont, V. Reboul, *Chem. Commun.* **2017**, *53*, 2064–2067; c) B. Verbelen, E. Siemes, A. Ehnbom, C. Rauber, K. Rissanen, D. Wöll, C. Bolm, *Org. Lett.* **2019**, *21*, 4293–4297; d) E. L. Briggs, A. Tota, M. Colella, L. Degennaro, R. Luisi, J. Bull, *Angew. Chem. Int. Ed.* **2019**, *58*, 14303–14310; *Angew. Chem.* **2019**, *131*, 14441–14448; e) F. Izzo, M. Schäfer, R. Stockman, U. Lücking, *Chem. Eur. J.* **2017**, *23*, 15189–15193; f) M. Ding, Z.-X. Zhang, T. Q. Davies, M. C. Willis, *Org. Lett.* **2022**, *24*, 1711–1715.

[16] Y. Chen, C.-J. Aurell, A. Pettersen, R. J. Lewis, M. A. Hayes, M. Lepistö, A. C. Jonson, H. Leek, *ACS Med. Chem. Lett.* **2017**, *8*, 672–677.

[17] For a related catalysis with acyclic sulfenamides, see: T. Kondo, A. Baba, Y. Nishi, T. Mitsudo, *Tetrahedron Lett.* **2004**, *45*, 1469–1471.

[18] Under the same conditions, dimethyl acetylendicarboxylate (DMAD) did not react with **2a**. The attempt to add DMAD to **2a** in the presence of CsF (25 mol%) in MeCN under argon at 60 °C for 6 h remained unsuccessful as well. For a guiding reference for the latter approach, see: C. Spitz, J.-F. Lohier, J. S. O. Santos, V. Reboul, P. Metzner, *J. Org. Chem.* **2009**, *74*, 3936–3939.

[19] a) B. S. Bhakuni, S. J. Balkrishna, A. Kumar, S. Kumar, *Tetrahedron Lett.* **2012**, *53*, 1354–1357; b) T. Li, L. Yang, K. Ni, Z. Shi, F. Li, D. Chen, *Org. Biomol. Chem.* **2016**, *14*, 6297–6303; c) J. Xiong, G. Zhong, Y. Liu, *Adv. Synth. Catal.* **2019**, *361*, 550–555; d) F.-J. Chen, G. Liao, X. Li, J. Wu, B.-F. Shi, *Org. Lett.* **2014**, *16*, 5644–5647.

[20] Radicals appear to be irrelevant here as suggested by a reaction of **1a** under standard conditions in the presence of 1 equiv. of TEMPO as radical trap. In this experiment, product **2a** was obtained in 74% yield after isolation by column chromatography. For details, see the Supporting Information.