OL Organic Letters

pubs.acs.org/OrgLett Letter

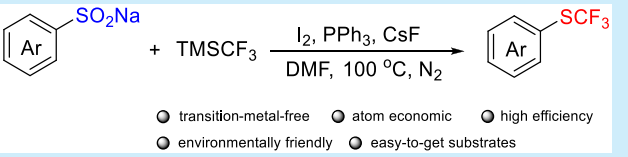
Transition-Metal-Free Synthesis of Aryl Trifluoromethyl Thioethers through Indirect Trifluoromethylthiolation of Sodium Arylsulfinate with $TMSCF_3$

Changge Zheng,* Chao Jiang, Shuai Huang, Kui Zhao, Yingying Fu, Mingyu Ma, and Jianquan Hong*

Cite This: https://doi.org/10.1021/acs.orglett.1c02656 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

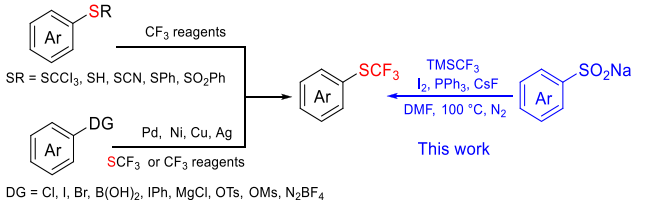
ABSTRACT: Herein, we report an indirect trifluoromethylthiolation of sodium arylsulfinates. This transition-metal-free reaction significantly provides an environmentally friendly and practical synthetic method for aryl trifluoromethyl thioethers using commercial Ruppert−Prakash reagent $TMSCF_3$. This approach is also a potential alternative to the current industrial production method owing to facile substrates, excellent functional group compatibility, and operational simplicity.



Downloaded via NANJING UNIV on September 1, 2021 at 13:14:26 (UTC).
See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

Fluorinated organic compounds have attracted significant interest in the fields of pharmaceutical,[1] agrochemical,[2] and material sciences.[3] As a consequence, the synthesis of the fluorinated compounds by different strategies has become a hot spot in modern organic chemistry.[4] Due to the improved lipophilicity and suppressed metabolic detoxification,[5] the trifluoromethylthio group (SCF_3) is highly valuable for its advantageous effects on the in vivo lifetime of a drug upon incorporation of SCF_3 into organic molecules. As early as 1960, the aryl trifluoromethyl thioethers ($ArSCF_3$) had been obtained through the hazardous chlorination of $ArSCH_3$ and the following Cl−F exchange of $ArSCCl_3$ with SbF_3.[6] Generally, there are two synthetic strategies for aryl trifluoromethyl thioethers,[7] direct and indirect insertions of the -SCF_3 group into organic molecules (Scheme 1). Although

Scheme 1. Synthetic Strategies of Aryl Trifluoromethyl Thioethers



$ArSCF_3$ can be obtained through the reaction between CF_3 sources and aryl substrates such as thiols,[8] thiocyanates,[9] disulfides,[10] and thiosulfinates,[11] the synthetic strategies have several disadvantages such as the foul-smelling odors and air sensitivity of thiols, the stoichiometric toxic byproducts from thiocyanates, and the atom economy of disulfides and thiosulfonates.

In 2011, direct trifluoromethylthiolation of the sulfur-free substrates was reported by Buchwald and co-workers[12] to drastically improve the reaction efficiency and operational safety through transition-metal-catalyzed/mediated reaction utilizing palladium,[12,13] nickel,[14] copper,[15] and silver[16] with $MSCF_3$ reagents. Despite SCF_3 sources being expensive, environmentally unfriendly, and instable, the synthetic strategy has aroused interest through direct introduction of the -SCF_3 group into the aromatic ring.[17]

Trifluoromethyltrimethylsilane ($TMSCF_3$), Ruppert−Prakash reagent, is most widely used as a trifluoromethyl nucleophile due to its commercial availability, bench stability, and operational convenience. The combination of $TMSCF_3$ with sulfur compounds, such as S_8,[18] CuSCN/NaSCN,[19] $Na_2S_2O_3$,[20] and DTSA,[21] has been also employed to introduce the -SCF_3 group into aromatic substrates. The reactions proceeded smoothly to generate the desired products with broad functional group tolerance, but these methods were still restricted by the starting substrates, transition-metal-catalyzed reagent, and/or toxic byproducts.

Inspired by the recent advance in the synthesis of thioether from sodium arylsulfinate,[22] aryl disulfides,[23] and ethyl arylsulfinates,[24] we have been trying to develop a green, economic, and efficient approach for the synthesis of aryl trifluoromethyl thioethers. Herein, the transition-metal-free reaction has been carried out using Ruppert−Prakash reagent and stable, environmentally friendly sodium arylsulfinate as starting substrates,[11] with high efficiency, excellent functional group compatibility, and operational simplicity.

Received: August 10, 2021

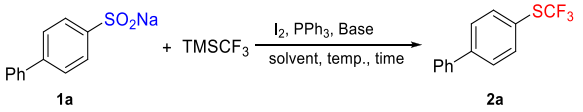
ACS Publications © XXXX American Chemical Society

We initiated our investigation using sodium 4-biphenylsulfinate **1a** as a model substrate, $TMSCF_3$ as the fluorinated reagent, and triphenylphosphine as the additive under a nitrogen atmosphere (Table 1). No desired product was found in DMSO at 100 °C in the absence of the oxidant iodine or an additive (Table 1, entry 1). To our delight, the desired product (**2a**) was favorably detected in 8% yield in the presence of I_2 at 100 °C, determined by ^{19}F NMR spectroscopy with 4,4′-difluorobiphenyl as the internal standard (entry 2). The addition of KF as an additive was beneficial for improving the reactivity, showing a slightly higher yield (entry 3). Compared with additives KF, K_3PO_4, CS_2CO_3, Na_2CO_3, K_2CO_3, and NaF (11−39%, entries 4−9, respectively), CsF is the best choice for the reaction, providing the desired product **2a** in the highest yield (68%, entry 10). The investigation of oxidant I_2 and PPh_3 revealed that the optimum molar ratio of I_2 to PPh_3 is 1 to 1.2 for the reaction in 83% yield (entry 12). Among the polar or less polar solvents (DMSO, DMAc, NMP, CH_3CN, toluene, and DMF, entries 12−17, respectively), the DMF solvent is the best reaction conditions to form the product in 12 h. Unfortunately, the desired product could not be obtained using H_2O as the solvent (entry 18). Although the reaction can also be performed at room temperature, a higher temperature of ≤100 °C is necessary for a high yield (Table 1, entry 19). The reaction yield decreases dramatically in the presence of air (entry 21).

With the optimal reaction conditions determined, the substrate scope of sodium arylsulfinate was explored. All monosubstituted sodium arylsulfinate substrates afforded the corresponding desired products in moderate to good yields (Scheme 2). With the electron-donating substituents on the aromatic ring such as aryl, alkyl, alkoxy, and methylthio, the sodium arylsulfinate salts were well tolerated under the reaction conditions to give the corresponding target products with moderate to good yields of 43−83% (**2a−2j**). With a halogen substituent on the aromatic ring such as Cl and Br, the sodium arylsulfinate substrates can tolerate the reaction system, providing the corresponding products in moderate yields (**2k** and **2l** in 34% and 44% yields, respectively). Remarkably, the iodo group in substrate **1m** can significantly survive the standard reaction conditions, affording the desired product **2m** in a moderate yield of 52%. Compared with the substrates with electron-donating substituents on the aromatic ring, the sodium arylsulfinates with electron-withdrawing substituents such as alkoxalyl, acetyl, cyano, and nitro (**2n−2v**) afforded the desired products in slightly lower yields of 47−67%. In comparison with the nitro substituent in the *para* (**2t**, 58%) and *meta* (**2u**, 52%) position, the slightly lower yield from sodium arylsulfinate with the nitro substituent in the *ortho* position (**2v**, 47%) indicated that steric effects have an important influence on the reaction system.

Similarly, the polysubstituted sodium arylsulfinates with more electron-donating substituents were well tolerated under the standard reaction conditions to give the desired products in higher yields than the corresponding monosubstituted sodium arylsulfinates (Scheme 3a). With two more methyl groups in the *meta* position on the aromatic ring, sodium 2,4,6-

Table 1. Optimization of the Reaction Conditions[a]

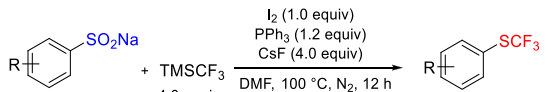


1a 2a

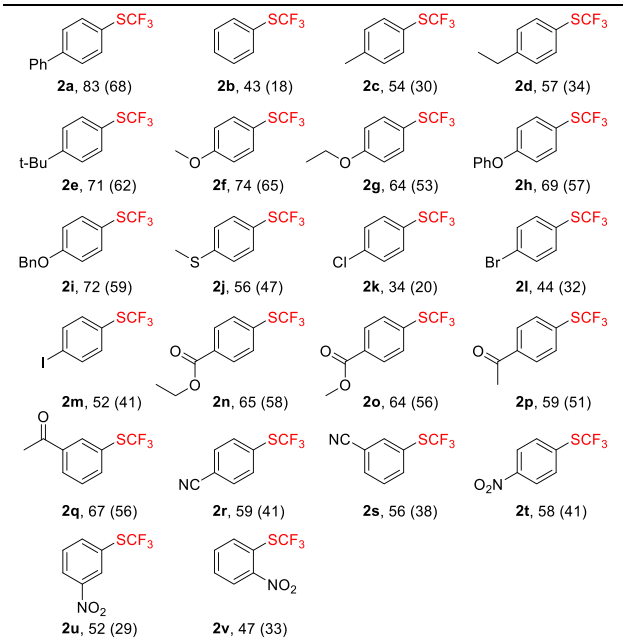
entry	I_2 (equiv)	PPh_3 (equiv)	additive	solvent	temp (°C)	time (h)	yield[b] (%)
1	–	1	–	DMSO	100	12	0
2	1	1	–	DMSO	100	12	8
3	1	1	KF	DMSO	100	12	11
4	1	1	KF	DMF	100	12	31
5	1	1	K_3PO_4	DMF	100	12	39
6	1	1	CS_2CO_3	DMF	100	12	30
7	1	1	Na_2CO_3	DMF	100	12	36
8	1	1	K_2CO_3	DMF	100	12	27
9	1	1	NaF	DMF	100	12	11
10	1	1	CsF	DMF	100	12	68
11	1	–	CsF	DMF	100	12	0
12	1	1.2	CsF	DMF	100	12	83
13	1	1.2	CsF	DMSO	100	12	30
14	1	1.2	CsF	DMAc	100	12	35
15	1	1.2	CsF	NMP	100	12	20
16	1	1.2	CsF	CH_3CN	100	12	49
17	1	1.2	CsF	toluene	100	12	19
18	1	1.2	CsF	H_2O	100	12	0
19	1	1.2	CsF	DMF	25	12	21
20	1	1.2	CsF	DMF	100	18	81
21[c]	1	1.2	CsF	DMF	100	12	59

[a]Reaction conditions: **1a** (0.10 mmol), $TMSCF_3$ (4.0 equiv), I_2, PPh_3, additive (4.0 equiv), 4,4′-difluorobiphenyl (0.1 mmol, internal standard), solvent (1.5 mL). [b]Yields determined by ^{19}F NMR spectroscopy based on **1a**. [c]Under air conditions.

Scheme 2. Transition-Metal-Free Indirect Trifluoromethylthiolation of Monosubstituted Sodium Arylsulfinate with $TMSCF_3$[a]



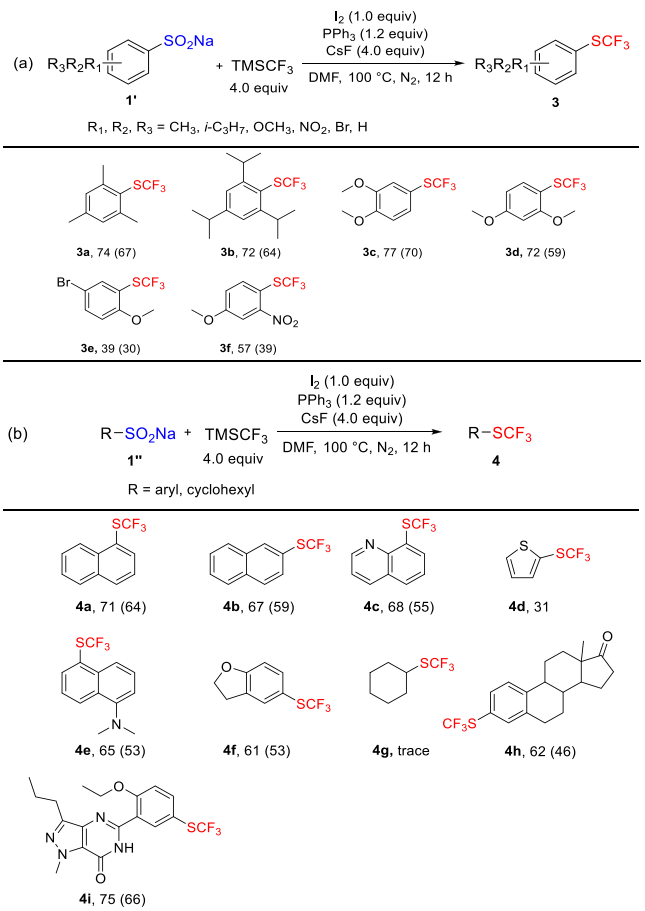
1 2



[a]Reaction yields were determined by ^{19}F NMR spectroscopy using 4,4′-difluorobiphenyl as the internal standard. Values in parentheses are isolated yields using column chromatography.

https://doi.org/10.1021/acs.orglett.1c02656
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 3. Transition-Metal-Free Indirect Trifluoromethylthiolation of Di- or Trisubstituted Sodium Arylsulfinates and Other Sodium Sulfinates with $TMSCF_3$[a]



[a]Reaction yields were determined by ^{19}F NMR spectroscopy using 4,4′-difluorobiphenyl as the internal standard. Values in parentheses are isolated yields using column chromatography.

trimethylbenzenesulfinate **1′a** afforded **3a** in a yield higher than that of sodium 4-methylbenzenesulfinate **1c** (**3a** to **2c**, 74% to 54%). Nevertheless, the polysubstituted sodium arylsulfinates with both electron-donating and electron-withdrawing substituents can tolerate the standard conditions, providing the target product in slightly higher or lower yield (**3f**, 57%) than the corresponding electron-withdrawing or electron-donating monosubstituted sodium arylsulfinate substrate (**2f** or **2v** in 74% or 47% yield, respectively). Overall, the electron-rich substrates always show relatively better reactivity than the electron deficient substrates.

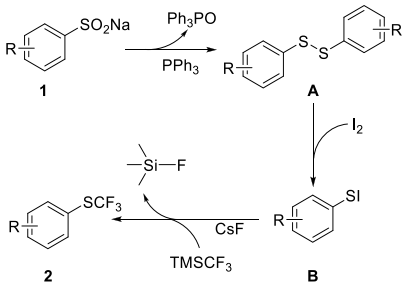
On the basis of the results presented above, the good substrate scope and functional group compatibility of this reaction, we next turned our attention to the polycyclic and heterocyclic sodium arylsulfinates bearing naphthaline, pyridine, and thiophene moieties. As shown in Scheme 3b, the transformation proceeded smoothly under the optimal conditions to give the corresponding target products in moderate to good yields in a range of 31−71% (**4a**−**4f**). Unfortunately, sodium acylsulfonate substrate **1″g** was not suitable under this reaction condition. Obviously, the conjugated structure of the substrates is the most important requirement for the reaction process.

Inspired by its applicability to various substrates, we further applied the synthetic method to more complex compounds, considering the potential pharmacological activity of these molecules after the insertion of the SCF_3 group. It was found that the synthetic method could be applied conveniently to the natural product and the drug to provide the corresponding trifluoromethylthiolated compounds (Scheme 3b). Estrone, a natural estrogenic hormone, could be easily transformed into the corresponding sulfinate to afford trifluoromethylthiolated estrone **4h** in 62% isolated yield, followed by the indirect trifluoromethylthiolation method. Trifluoromethylthio-modified sildenafil **4i** could be derived efficiently from benzenesulfonyl chloride, a pharmaceutical intermediate, through a similar transformation in 75% yield. The efficiency of this indirect trifluoromethylthiolation reaction was further demonstrated by running the transformation on a laboratory scale. For example, the reaction of **1a** with $TMSCF_3$ was carried out on a gram scale (7.2 mmol), and the transformation proceeded successfully to give the corresponding product **2a** (1.196 g, 65%) in good isolated yield (see the Supporting Information).

To gain insights into the reaction mechanism and to understand the role of each component in the transformation, the control experiments were performed using sodium 4-biphenylsulfinate **1a** as a model substrate (see the Supporting Information). In the absence of the oxidant iodine, the reaction of **1a** with $TMSCF_3$ cannot provide the target compound in the reaction system of PPh_3, CsF, and DMSO at 100 °C. In fact, sodium 4-biphenylsulfinate **1a** can transform into diphenyl disulfide intermediate **I** in DMSO at 100 °C in 81% isolated yield in the presence of reductant PPh_3. Indeed, 4,4′-dichlorodiphenyl disulfide has been isolated and identified as the main byproduct in the synthesis of 4-chlorophenyl trifluoromethyl thioether (see the Supporting Information). With oxidant I_2 and additive CsF, the reaction of diphenyl disulfide **I** with $TMSCF_3$ can give aryl trifluoromethyl thioether **2a** in DMSO at 100 °C in 75% yield, determined by ^{19}F NMR spectroscopy.

On the basis of the results presented above and previous relevant mechanistic studies,[25] a plausible reaction mechanism is proposed as shown in Scheme 4. Initially, the reduction of

Scheme 4. A Plausible Mechanism for Transition-Metal-Free Indirect Trifluoromethylthiolation



sodium arylsulfinate **1** by triphenylphosphine affords diphenyl disulfide **A**. Then, oxidation of **A** by iodine generates the active species ArSI **B**. Finally, attacked by CF_3^- generated from the reaction between $TMSCF_3$ and CsF, ArSI **B** was transformed into the target product aryl trifluoromethyl thioethers **2**.

In summary, we have developed a facile synthetic method for the aryl trifluoromethyl thioethers employing sodium arylsulfinate substrate and $TMSCF_3$. Through environmentally

https://doi.org/10.1021/acs.orglett.1c02656
Org. Lett. XXXX, XXX, XXX−XXX

friendly transition-metal-free reaction, the stable sodium arylsulfinates have been transformed efficiently into aryl trifluoromethyl thioethers via consecutive processes of the reduction of arylsulfinate by PPh_3, the subsequent oxidation by I_2, and then the construction of S−CF_3 bonds with $TMSCF_3$. This approach represents a new and efficient strategy for the synthesis of aryl trifluoromethyl thioethers with potential application in the fields of medicine, pesticides, and materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c02656.

Experimental procedures and spectroscopic characterization data and ^1H and ^{13}C NMR spectra of the new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Changge Zheng − *Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu 214122, P. R. China; School of Chemical Engineering, Xinjiang Agricultural University, Urumqi 830052 Xinjiang Uygur Autonomous Region, P. R. China;* orcid.org/0000-0001-7047-1594; Email: cgzheng@jiangnan.edu.cn

Jianquan Hong − *Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu 214122, P. R. China*; Email: hongjq@jiangnan.edu.cn

Authors

Chao Jiang − *Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu 214122, P. R. China*

Shuai Huang − *Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu 214122, P. R. China*

Kui Zhao − *Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu 214122, P. R. China*

Yingying Fu − *Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu 214122, P. R. China*

Mingyu Ma − *Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu 214122, P. R. China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.1c02656

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the financial support for this work from the National Natural Science Foundation of China (21971089, 21562041, and 21502070) and the Fundamental Research Funds for the Central Universities.

■ REFERENCES

(1) (a) Wang, J.; Sánchez-Roselló, M.; Aceña, J. L.; del Pozo, C.; Sorochinsky, A. E.; Fustero, S.; Soloshonok, V. A.; Liu, H. Fluorine in pharmaceutical industry: fluorine-containing drugs introduced to the market in the last decade (2001−2011). *Chem. Rev.* **2014**, *114*, 2432−2506. (b) Inoue, M.; Sumii, Y.; Shibata, N. Contribution of Organofluorine Compounds to Pharmaceuticals. *ACS Omega* **2020**, *5*, 10633−10640.

(2) (a) Fujiwara, T.; O'Hagan, D. Successful fluorine-containing herbicide agrochemicals. *J. Fluorine Chem.* **2014**, *167*, 16−29. (b) Ogawa, Y.; Tokunaga, E.; Kobayashi, O.; Hirai, K.; Shibata, N. Current contributions of organofluorine compounds to the agrochemical industry. *iScience* **2020**, *23*, 101467.

(3) (a) Zhang, Q.; Kelly, M. A.; Bauer, N.; You, W. The curious case of fluorination of conjugated polymers for solar cells. *Acc. Chem. Res.* **2017**, *50*, 2401−2409. (b) Yanai, H.; Hoshikawa, S.; Moriiwa, Y.; Shoji, A.; Yanagida, A.; Matsumoto, T. A fluorinated carbanionic substituent for improving water solubilityand lipophilicity of fluorescent dyes. *Angew. Chem., Int. Ed.* **2021**, *60*, 5168−5172.

(4) (a) Yang, X.-G.; Zheng, K.; Zhang, C. Electrophilic hypervalent trifluoromethylthio-iodine(III) reagent. *Org. Lett.* **2020**, *22*, 2026−2031. (b) Mykhailiuk, P. K. Fluorinated pyrazoles: from synthesis to applications. *Chem. Rev.* **2021**, *121*, 1670−1715.

(5) (a) Tlili, A.; Billard, T. Formation of C-SCF_3 bonds through direct trifluoromethylthiolation. *Angew. Chem., Int. Ed.* **2013**, *52*, 6818−6819. (b) Chachignon, H.; Cahard, D. State-of-the-Art in electrophilic trifluoromethylthiolation reagents. *Chin. J. Chem.* **2016**, *34*, 445−454.

(6) Nodiff, E. A.; Lipschutz, S.; Craig, P. N.; Gordon, M. Synthesis of Phenothiazines. III. Derivatives of Hydroxy- and Mercaptophenothiazines. *J. Org. Chem.* **1960**, *25*, 60−65.

(7) (a) Liang, T.; Neumann, C. N.; Ritter, T. Introduction of fluorine and fluorine-containing functional groups. *Angew. Chem., Int. Ed.* **2013**, *52*, 8214−8264. (b) Shao, X.; Xu, C.; Lu, L.; Shen, Q. Shelf-stable electrophilic reagents for trifluoromethylthiolation. *Acc. Chem. Res.* **2015**, *48*, 1227−1236. (c) Monfared, A.; Ebrahimiasl, S.; Babazadeh, M.; Arshadi, S.; Vessally, E. Recent advances in decarboxylative trifluoromethyl(thiol)ation of carboxylic acids. *J. Fluorine Chem.* **2019**, *220*, 24−34. (d) Hamzehloo, M.; Hosseinian, A.; Ebrahimiasl, S.; Monfared, A.; Vessally, E. Direct C-H trifluoromethylthiolation of (hetero)arenes: A review. *J. Fluorine Chem.* **2019**, *224*, 52−60. (e) Xie, G.-L.; Jia, S.-H.; Shen, X.; Behmagham, F. Recent trends in direct trifluoromethylthiolation of N−H bonds. *J. Fluorine Chem.* **2020**, *235*, 109524.

(8) (a) Xu, C.; Song, X.; Guo, J.; Chen, S.; Gao, J.; Jiang, J.; Gao, F.; Li, Y.; Wang, M. Synthesis of chloro(phenyl)trifluoromethyliodane and catalyst-free electrophilic trifluoromethylations. *Org. Lett.* **2018**, *20*, 3933−3937. (b) Kalim, J.; Duhail, T.; Le, T.-N.; Vanthuyne, N.; Anselmi, E.; Togni, A.; Magnier, E. Merging hypervalent iodine and sulfoximine chemistry: a new electrophilic trifluoromethylation reagent. *Chem. Sci.* **2019**, *10*, 10516−10523.

(9) Dyga, M.; Hayrapetyan, D.; Rit, R. K.; Goossen, L. J. Electrochemical ipso-thiocyanation of arylboron compounds. *Adv. Synth. Catal.* **2019**, *361*, 3548−3553.

(10) Geri, J. B.; Wade Wolfe, M. M.; Szymczak, N. K. Borazine-CF_3-adducts for rapid, room temperature, and broad scope trifluoromethylation. *Angew. Chem., Int. Ed.* **2018**, *57*, 1381−1385.

(11) Luo, Z.; Yang, X.; Tsui, G. C. Perfluoroalkylation of thiosulfonates: synthesis of perfluoroalkyl sulfides. *Org. Lett.* **2020**, *22*, 6155−6159.

(12) Teverovskiy, G.; Surry, D. S.; Buchwald, S. L. Pd-catalyzed synthesis of Ar-SCF_3 compounds under mild conditions. *Angew. Chem., Int. Ed.* **2011**, *50*, 7312−7314.

(13) (a) Xu, C.; Shen, Q. Palladium-catalyzed trifluoromethylthiolation of aryl C−H bonds. *Org. Lett.* **2014**, *16*, 2046−2049. (b) Uehling, M. R.; King, R. P.; Krska, S. W.; Cernak, T.; Buchwald,

S. L. Pharmaceutical diversification via palladium oxidative addition complexes. *Science* **2019**, *363*, 405−408.
(14) Kalvet, I.; Guo, Q.; Tizzard, G. J.; Schoenebeck, F. When weaker can be tougher: the role of oxidation state (I) in P- vs N-ligand-derived Ni-catalyzed trifluoromethylthiolation of aryl halides. *ACS Catal.* **2017**, *7*, 2126−2132.
(15) (a) Xu, J.; Mu, X.; Chen, P.; Ye, J.; Liu, G. Copper-catalyzed trifluoromethylthiolation of aryl halides with diverse directing groups. *Org. Lett.* **2014**, *16*, 3942−3945. (b) Zheng, C. G.; Liu, Y.; Hong, J. Q.; Huang, S.; Zhang, W.; Yang, Y. P.; Fang, G. Copper(I)-promoted trifluoromethylthiolation of arenediazonium salts with $AgSCF_3$. *Tetrahedron Lett.* **2019**, *60*, 1404−1407.
(16) (a) Liu, J.-B.; Xu, X.-H.; Chen, Z.-H.; Qing, F.-L. Direct dehydroxytrifluoromethylthiolation of alcohols using silver (I) trifluoromethanethiolate and tetra-*n*-butylammonium iodide. *Angew. Chem., Int. Ed.* **2015**, *54*, 897−900. (b) Li, M.; Petersen, J. L.; Hoover, J. M. Silver-mediated oxidative decarboxylative trifluoromethylthiolation of coumarin-3-carboxylic acids. *Org. Lett.* **2017**, *19*, 638−641.
(17) (a) Wang, D.; Carlton, C. G.; Tayu, M.; McDouall, J. J. W.; Perry, G. J. P.; Procter, D. J. Trifluoromethyl sulfoxides: reagents for metal-free C-H trifluoromethylthiolation. *Angew. Chem., Int. Ed.* **2020**, *59*, 15918−15922. (b) Kurose, R.; Nishii, Y.; Miura, M. Metal-free direct trifluoromethylthiolation of aromatic compounds using triptycenyl sulfide catalyst. *Org. Lett.* **2021**, *23*, 2380−2385.
(18) Chen, C.; Xie, Y.; Chu, L.; Wang, R.-W.; Zhang, X.; Qing, F.-L. Copper-catalyzed oxidative trifluoromethylthiolation of aryl boronic acids with $TMSCF_3$ and elemental sulfur. *Angew. Chem., Int. Ed.* **2012**, *51*, 2492−2495.
(19) Danoun, G.; Bayarmagnai, B.; Gruenberg, M. F.; Goossen, L. J. Sandmeyer trifluoromethylthiolation of arenediazonium salts with sodium thiocyanate and Ruppert-Prakash reagent. *Chem. Sci.* **2014**, *5*, 1312−1316.
(20) Zhong, W.; Liu, X. Copper-catalyzed synthesis of aryl and alkyl trifluoromethyl sulfides using CF_3SiMe_3 and $Na_2S_2O_3$ as -SCF_3 source. *Tetrahedron Lett.* **2014**, *55*, 4909−4911.
(21) Saravanan, P.; Anbarasan, P. An electrophilic trifluoromethylthiolation of silylenol ethers and β-naphthols with diethylaminosulfur trifluoride and (trifluoromethyl)trimethylsilane. *Adv. Synth. Catal.* **2018**, *360*, 2894−2899.
(22) (a) Lin, Y.-M.; Lu, G.-P.; Wang, G.-X.; Yi, W.-B. Odorless, regioselective synthesis of diaryl sulfides and α-thioaryl carbonyls from sodium arylsulfinates via a metal-free radical strategy in water. *Adv. Synth. Catal.* **2016**, *358*, 4100−4105. (b) Liu, Y.; Lam, L. Y.; Ye, J.; Blanchard, N.; Ma, C. DABCO-promoted diaryl thioether formation by metal-catalyzed coupling of sodium sulfinates and aryl iodides. *Adv. Synth. Catal.* **2020**, *362*, 2326−2331.
(23) (a) Wang, L.; Xie, Y.-B.; Huang, N.-Y.; Zhang, N.-N.; Li, D.-J.; Hu, Y.-L.; Liu, M.-G.; Li, D.-S. Disulfide-Directed C-H Hydroxylation for synthesis of sulfonyl diphenyl sulfides and 2-(phenylthio)phenols with oxygen as oxidant. *Adv. Synth. Catal.* **2017**, *359*, 779−785. (b) Wang, Y.; Deng, J.; Chen, J.; Cao, F.; Hou, Y.; Yang, Y.; Deng, X.; Yang, J.; Wu, L.; Shao, X.; Shi, T.; Wang, Z. Dechalcogenization of aryl dichalcogenides to synthesize aryl chalcogenides via copper catalysis. *ACS Catal.* **2020**, *10*, 2707−2712.
(24) Wei, Y.; He, J.; Liu, Y.; Xu, L.; Vaccaro, L.; Liu, P.; Gu, Y. Sulfenylation of arenes with ethyl arylsulfinates in water. *ACS Omega* **2020**, *5*, 18515−18526.
(25) (a) Kang, X.; Yan, R.; Yu, G.; Pang, X.; Liu, X.; Li, X.; Xiang, L.; Huang, G. Iodine-mediated thiolation of substituted naphthols/naphthylamines and arylsulfonyl hydrazides via C(sp^2)-H bond functionalization. *J. Org. Chem.* **2014**, *79*, 10605−10610. (b) Liu, C.-R.; Ding, L.-H. Byproduct promoted regioselective sulfenylation of indoles with sulfinic acids. *Org. Biomol. Chem.* **2015**, *13*, 2251−2254.

https://doi.org/10.1021/acs.orglett.1c02656
Org. Lett. XXXX, XXX, XXX−XXX