The difluoromethylthio group, as a member of the fluoroalkyl family, has been receiving growing attention from both academia and industry. This is not only because it incorporates two instrumental elements, sulfur and fluorine, into one functionality, but also due to its unique properties. Direct introduction of a difluoromethylthio group (−SCF₂H) to arenes represents an efficient route to access a valuable catalogue of organosulfurines; however, to realize this transformation under metal-free and mild conditions still remains challenging and rarely reported. Herein, a metal-catalyst-free and redox-neutral innate difluoromethylthiolation method with a shelf-stable and readily available reagent, PhSO₂SCF₂H, under visible light irradiation is described. This light-mediated protocol successfully converts a broad spectrum of arenes and heteroarenes to difluoromethylthioethers in the absence of noble metals and stoichiometric amounts of additives.

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Despite the intriguing pharmaceutical potential exhibited by difluoromethylthioethers, their widespread application remains limited possibly owing to a lack of efficient preparative methods. Classical and commonly used approaches to synthesize difluoromethylthioethers employ the nucleophilic attack of an appropriate thiolate (RSH) to some “CF₃” species, typically a difluoromethyl carbene (:CF₂), to some “CF₃” species, typically a difluoromethyl carbene (:CF₂), treated as the most preferable structure. A complementary but less common approach to assemble −SCF₂H is difluoromethylation of disulfides using nucleophilic difluoromethyl sources (e.g., activated TMSCF₂H). A major step forward to expand the substrate scope was made by the Goolen group who described a stepwise synthetic route involving preformed thiocyanates and the subsequent copper-mediated Langlois type nucleophilic substitution by TMSCF₂H (Scheme 1b). Nevertheless, these indirect methods still suffer from a limited substrate scope. In addition, they usually necessitate strong bases, harsh thermal conditions and environmentally unfriendly reagents to generate reactive thiocyanates and “CF₃” species.

To address these issues, a key contribution was made by Shen and his co-workers who delineated the first nucleophilic difluoromethylthiolating reagent 1, [[SIPr]Ag(SCF₂H)] (Scheme 1b). In the presence of transition metals (M = Pd, Cu), this complex could couple with diverse aryl and heteroaryl halides.
triflates and diazoniun compounds to prepare difluoromethylthioethers. Complementarily, the same group debuted an electrophilic difluoromethylthiolating reagent \( \text{2} \), which could undergo a Friedel–Craft type \( 
abla \text{C} = \text{C} \) difluoromethylthiolation on various N-heteroarenes. Shortly after, Shibata et al. uncovered a hypervalent difluoromethanesulfoniliodonium ylide reagent \( \text{3} \), which efficiently difluoromethylthiolated N-heterocycles under copper catalysis. Moreover, the Billard, Besset and Shen groups independently synthesized an electrophilic \( \text{SCF}_2 \text{FG} \) group transfer reagents (\( \text{FG} = \text{PhSO}_2 \), PO(\text{OEt})_3 and \( \text{CO}_2\text{Et} \) respectively), although a separate reductive workup was necessary to give difluoromethylthioethers. Inspired by these elegant examples, other difluoromethylthiolating systems were unveiled.

Alternatively, difluoromethylthiolation could be operated in a radical pathway. \( \text{S} \)-(Difluoromethyl)benzenesulfonithioate, \( \text{PhSO}_2\text{SCF}_2\text{H} \), invented in 2016 by Shen et al., was revealed as an effective difluoromethylthiolating reagent (Scheme 1c). Mechanistically, it was proposed to execute as a radical acceptor and combine with the alkyl or aryl radicals generated from the Ag/persulfate-involved oxidation event. This reactivity was further elaborated in two recent studies on the ring-opening difluoromethylthiolation of cycloalkanols and the preparation of difluoromethylthioethers by using aldehydes as acyl radical precursors.

Promising though these strategies are, the main drawbacks lie in their requirement of relatively high thermal energy (ranging from 50 to 120 °C), or involvement of precious metal catalysts and stoichiometric amounts of additives. In the case of \( \text{SCF}_2\text{FG} \) group transfer, additional steps were required to furnish the final thioether products. Clearly, a more sustainable synthetic protocol that features mild conditions and step economy is highly desired.

In 2017, our group disclosed a radical trifluoromethylation reaction on arenes with a novel sulfone reagent \( \text{6} \) (Scheme 2a).

With light irradiation, \( \text{6} \) engenders two twin radicals \( \text{via} \) Norrish type 1 cleavage as the sulfinyl radical fragments further to produce the CF\(_3\) radical and implements trifluoromethylation. The success of this chemistry lies in the judicious design of the reagent structure. In the so-called “dummy group” strategy, the undesirable radical produced by homolysis of \( \text{6} \) is diminished in reactivity by the “captodative effect” as well as steric.

Inspired by this work, we would like to apply a similar strategy and achieve a rarely known direct radical difluoromethylthiolation (Scheme 2b). A key component of this project is to explore and identify a suitable \( \text{SCF}_2\text{H} \) radical precursor. After a careful examination of the literature, we consider that the thiosulfinate reagent, \( \text{PhSO}_2\text{SCF}_2\text{H} \), might be applicable, although it was documented to be a radical acceptor as its principle utility. We proposed that the homolytic fragmentation of \( \text{PhSO}_2\text{SCF}_2\text{H} \) with a suitable light source is feasible due to the well-studied propensity of homolysis of the S–S bond and the stabilization of the resulting sulfonyl radical exerted by the resonance effect of the phenyl group. The stabilization of the dummy radical is beneficial in two ways: (1) it facilitates homolytic bond scission and allows the accumulation of \( \text{SCF}_2\text{H} \) radicals; (2) it is expected to cause less competition toward the targeted reaction pathway. Radical addition of the desired \( \text{SCF}_2\text{H} \) radical will furnish the target product.

As a part of our interest in photo-induced fluorine chemistry, we wish to document a photo-induced metal-free aromatic difluoromethylthiolation protocol with \( \text{PhSO}_2\text{SCF}_2\text{H} \), wherein \( \text{PhSO}_2\text{SCF}_2\text{H} \) was utilized as a difluoromethylthyl radical source. To the best of our knowledge, direct aromatic difluoromethylthiolation realized by radical attack of \( \text{SCF}_2\text{H} \) radical on arenes remained unexplored.

To commence the study, N-methylindole \( \text{1a} \) was chosen as a model substrate and treated with difluoromethylthiolating sources in CH\(_2\)CN under an inert atmosphere based on some literature parallels on difluoromethylthiolation (see ESI† for full details). Although no desired product was detected when using BnSCF\(_2\text{H} \), the reaction with \( \text{PhSO}_2\text{SCF}_2\text{H} \) proceeded as expected and upon 16 hours of UV irradiation, 20% yield of the desired product was obtained (Table 1, entries 1 and 2). Using compact fluorescence lamps (CFL) as a light source gave 64% yield of the target compound (entry 3). Fortunately, prolonging the reaction time enabled the consumption of unreacted substrates and increased the yield to 80% (entry 4). The
The essential role played by light was illustrated by the control experiment as the dark condition disabled the reaction completely (entry 5 and see ESI† for details on control experiments). Recent work by our group revealed the unique properties of NaI, e.g., high reducing ability along with low nucleophilicity, which were helpful in radical generation. Therefore, we expected the SCF₂H radical generation would be accelerated by a complementary reductive pathway. Gratifyingly, catalytic incubation of iodide gave similarly good yield in a shortened reaction time (entries 6–8). Among the tested iodides, tetrabutylammonium iodide (TBAI) offered the highest yield (entry 8). Further increment of TBAI loading could promote the reaction to be quantitative (entry 9). Conforming to other electrophilic difluoromethylthiolation studies, 1a as a limiting reagent would be more profitable as an excess of difluoromethylthiolating reagent is crucial to maintain a decent level of active difluoromethylthiolating species (entries 10 and 11).

With the optimal conditions identified, the generality of this method was examined (Scheme 3). Initially, the functional group tolerance of different indoles was investigated. In general, indoles bearing substituents with different electronic and steric properties at various sites are compatible with the optimal conditions. Reaction rates of substrates with electron-donating groups were higher than those with electron-withdrawing groups. Satisfactorily, quantitative yield was obtained for non-substituted indole (2b). Product formation was not

### Table 1  Selected results of evaluation under various conditions

| entry  | 1a | additive(equiv) | time | yield |
|--------|----|----------------|------|-------|
| 1      | 1:2| -              | 16 h | NR    |
| 2      | 1:2| -              | 16 h | 20%   |
| 3      | 1:2| -              | 16 h | 64%   |
| 4      | 1:2| -              | 48 h | 80%   |
| 5      | 1:2| -              | 16 h | NR    |
| 6      | 1:2| NaI (5 mol%)   | 16 h | 80%   |
| 7      | 1:2| KI (5 mol%)    | 16 h | 80%   |
| 8      | 1:2| TBAI (5 mol%)  | 16 h | 86%   |
| 9      | 1:2| TBAI (20 mol%) | 16 h | 99%   |
| 10     | 1:1| TBAI (20 mol%) | 16 h | 65%   |
| 11     | 2:1| TBAI (20 mol%) | 16 h | 80%   |

a Abbreviations: CFL, compact fluorescent lamp; rt, room temperature; TBAI, tetrabutylammonium iodide; NR, no reaction. All reactions were conducted with 0.10 mmol 1a, 0.20 mmol PhSO₂SCF₂H, 0.020 mmol TBAI in 1.0 mL CH₃CN under argon with irradiation of two 40 W CFL unless otherwise noted. The yield was determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. BNSCF₂H as the difluoromethylthiolating source. Six 254 nm 2.5 W UV lamps (photo-box). In the dark.

Scheme 3  Scope of arenes. Method A: arene (0.10 mmol), PhSO₂SCF₂H (0.20 mmol), TBAI (0.020 mmol) in 1.0 mL CH₃CN under argon for CFL irradiation at rt for 16 h. Method B: arene (0.10 mmol), PhSO₂SCF₂H (0.20 mmol) in 1.0 mL CH₃CN under argon for CFL irradiation at rt for 48 h. The yields in the parentheses refer to the isolated ones unless otherwise specified. Volatility resulted in the low isolated yield of 17b and 18b.

Reaction performed on the 0.40 mmol scale. The reactions were performed for 24 h. The reactions were performed for 48 h. 4 equiv PhSO₂SCF₂H were used. Yields are quantified by GC-MS due to the volatility of target compounds.
affected by the methyl group at the C-5 or C-7 position (3b and 4b). Even in the presence of a phenyl group at the C-2 position, a decent yield can also be achieved (5b). Notably, the reaction proceeded smoothly in indole tethering a phenolic proton (6b). Methoxylated indoles could result in 98% and 78% of desired products respectively (7b and 8b). Indole derivatives bearing the chloro, bromo and boryl groups resulted in good to excellent yields of products, which allow further cross coupling to achieve more complex settings (9b to 11b). Unexpectantly, regioisomers were isolated for substrates with an ester group (12b and 12b'). Then we moved the focus to a class of closely related N-heterocycles, pyrroles. Pyrroles with phenyl, methyl, benzyl, dimethylamino and carbonato groups all gave around 70% of target difluormethylthioethers (13b to 17b). Of note is the substrate bearing a double bond, which is known to be reactive toward PhSO2SCF2H. Gratifyingly, the Csp2-fluoromethylthiolation product was selectively obtained (18b).

Other heteroarrows, e.g., azaindole, pyrazole, isoxazole, and chromone, which are pharmaceutically important scaffolds, were also effective (19b to 22b). Notably, this protocol was viable for thiophene, which was generally unreactive in other difluoromethylthiolating recipes (23b).16,20 Finally, the versatility of this method on some arenes was explored. 1,3,5-Trimethoxybenzene was difluoromethylthiolated successfully (24b). As this method was proved adaptable to phenolic protons, installing –SCF2H on phenol (25b) and resorcinol derivatives (26b and 27b) was efficient. Aniline and sulfide underwent difluoromethylthiolation smoothly as well, resulting in good yields (28b and 29b).

Generally, high regioselectivity was observed for this difluoromethylthiolation reaction, which was a combined effect of electronics and steric. In most cases, the site of the highest electron density was difluoromethylated, e.g., C-2 in indoles and C-1 in pyrroles. When multiple sites of similar electron richness were available, the reaction occurred at the sterically less hindered Csp2-fluoromethylthiolation product was rarely detected during our scope exploration (see ESI† for details of mono-/difunctionalization and regioselectivity issues).

Knowing that the difluoromethylsulfoxides and difluoromethylsulfoxides28 are valuable entities in medicinal chemistry, we were encouraged to alter the oxidation state of sulfur in –SCF2H. As expected, the oxidation of difluoromethylthioethers could be accomplished in a controlled manner under different oxidizing conditions (Scheme 4a). Besides, the versatility of this photochemical strategy was extended to produce other synthetically useful thyl radicals. Under the optimal conditions, phenylthioether (30b) and naphthylthioether (31b) were furnished smoothly. However, alkylthiolation (32b) was undermined by the homocoupling event of alkylthyl radicals. Moreover, 33a was subjected to a gram-scale experiment to demonstrate the practicability of this method (Scheme 4c). We were pleased to see that the reaction proceeded smoothly and a good yield of the desired product was obtained (33b).

Although the underlying mechanism remained obscure at this stage, our preliminary study hints at the radical nature of this reaction as designed. The presence of various radical quenchers significantly impacted the desired reactivity (Scheme 5, eqn (1) and (2)). When diallylmalonate (34a) was employed as the radical clock-type trapper, a cyclization adduct (34b) with PhSO2SCF2H was observed irrespective of the presence of 1a (eqn (2) and (3)). This result, to a degree, supports our postulation of the radical mechanism.

Based on the previous literature26,22 and the above-mentioned experiments (see ESI† for details that rationalized the intermediacy of the proposed radical and the by-product formation), we envisioned that a radical-involved mechanism was operative. Under light irradiation, a difluoromethylthyl radical resulted from either the homolysis of PhSO2SCF2H or the photo-induced electron transfer (PET) event between PhSO2SCF2H and iodide. Subsequently, the action of SCF2H radical on arenes was followed by hydrogen atom abstraction by phenylsulfonium (radical) to furnish the target compound. The resulting phenylsulfinic acid was unstable and further transformed into thiosulfonate.29

Scheme 4 Application. (a) Controlled oxidation of thiocethers to corresponding sulfoxides and sulfones; (b) modified reagents to afford arythiolation products; (c) scaled-up experiments.

Scheme 5 Mechanistic study. (a) Termination of the desired reactivity in the presence of radical trappers; (b) plausible mechanism.
Conclusions

In summary, we have developed a metal-catalyst-free aromatic difluoromethylthiolation reaction at room temperature enabled by visible light. This operationally simple strategy features the synthesis of a series of difluoromethioethers under mild conditions, which are a class of compounds with high medicinal value. These difluoromethylthioethers could be readily diversified into corresponding sulfones and sulfoxides. Moreover, this “dummy group” strategy holds great potential for achieving other types of radical thiolations by simply switching the functionalities tethered on thiosulfonate reagents. Details of mechanistic insight remain to be explored and we are dedicated to introducing fluoride-containing functional groups on arenes with similar strategies.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1. (a) F. Leroux, P. Jeschke and M. Schlosser, Chem. Rev., 2005, 105, 827–856; (b) B. Manteau, S. Pazenok, J.-P. Voris and F. R. Leroux, J. Fluorine Chem., 2010, 131, 140–158; (c) C. Ni, M. Hu and J. Hu, Chem. Rev., 2014, 115, 765–825; (d) X.-H. Xu, K. Matsuzaki and N. Shibata, Chem. Rev., 2014, 115, 731–764.

2. (a) T. Fujita, J. Iwasa and C. Hansch, J. Am. Chem. Soc., 1964, 86, 5175–5180; (b) I. Rico and C. Wakselhan, Tetrahedron Lett., 1981, 22, 323–326.

3. (a) B. Bayarmagnai, C. Matheis, K. Jouvin and L. J. Goossen, Angew. Chem., Int. Ed., 2015, 54, 5753–5756; (b) Y. Zafrani, D. Yeftet, G. Sod-Moriah, A. Berliner, D. Amir, D. Marciano, E. Gershonov and S. Sapfher, J. Med. Chem., 2017, 60, 797–804.

4. S. Okui, N. Kyomura, T. Fukushima, K. Okano, L. He and A. Miyauchi, US Pat., 7 371 768, 2008.

5. K. Morita, K. Ide, Y. Hayase, T. Takahashi and Y. Hayashi, Agric. Biol. Chem., 1987, 51, 1339–1343.

6. L. Yagupolskii, I. Maletina, K. Petko, D. Fedyuk, R. Handrock, S. Shavaran, B. Klebanov and S. Herzig, J. Fluorine Chem., 2001, 109, 87–94.

7. Z. Huang, O. Matsubara, S. Jia, E. Tokunaga and N. Shibata, Org. Lett., 2017, 19, 934–937.

8. H.-Y. Xiong, X. Panneeoucke and T. Besset, Chem.–Eur. J., 2016, 22, 16734–16749.

9. Selected examples for difluoromethylthiolation by reacting thiolates with “CF₂” species other than CF₂ difluorocarbene: (a) W. Zhang, J. Zhu and J. Hu, Tetrahedron Lett., 2008, 49, 5006–5008; (b) G. S. Prakash, Z. Zhang, F. Wang, C. Ni and G. A. Olah, J. Fluorine Chem., 2011, 132, 792–798; (c) Y. Fujiwara, J. A. Dixon, R. A. Rodriguez, R. D. Baxter, D. D. Dixon, M. R. Collins, D. G. Blackmond and P. S. Baran, J. Am. Chem. Soc., 2012, 134, 1494–1497.

10. Selected examples for difluoromethylthiolation by reacting thiolates with :CF₂ difluorocarbene: (a) B. R. Langlois, J. Fluorine Chem., 1988, 41, 247–261; (b) Q.-Y. Chen and S.-W. Wu, J. Fluorine Chem., 1989, 44, 433–440; (c) P. Deprez and J.-P. Vevert, J. Fluorine Chem., 1996, 80, 159–162; (d) W. Zhang, F. Wang and J. Hu, Org. Lett., 2009, 11, 2109–2112; (e) Y. Zafrani, G. Sod-Moriah and Y. Segall, Tetrahedron, 2009, 65, 5278–5283; (f) F. Wang, W. Huang and J. Hu, Chin. J. Chem., 2011, 29, 2717–2721; (g) L. Li, F. Wang, C. Ni and J. Hu, Angew. Chem., 2013, 125, 12616–12620; (h) P. S. Fier and J. F. Hartwig, Angew. Chem., 2013, 125, 2146–2149; (i) C. S. Thomeson and W. R. Dolbier Jr. J. Org. Chem., 2013, 78, 8904–8908; (j) K. Fuchibe, M. Bando, R. Takayama and J. Ichikawa, J. Fluorine Chem., 2015, 171, 133–138; (k) J. Yu, J.-H. Lin and J.-C. Xiao, Angew. Chem., Int. Ed., 2017, 56, 16669–16673; (l) V. P. Mehta and M. F. Greaney, Org. Lett., 2013, 15, 5036–5039; (m) T. Ding, L. Jiang and W. Yi, Org. Lett., 2017, 20, 170–173.

11. Selected examples for difluoromethylthiolation by reacting thiolates with CF₂H species other than CF₂H: (a) J. L. Howard, C. Schotten, S. T. Alston and D. L. Browne, Chem. Commun., 2016, 52, 8448–8451; (b) J.-B. Han, H.-L. Qin, S.-H. Ye, L. Zhu and C.-P. Zhang, J. Org. Chem., 2016, 81, 2506–2512; (c) Y.-m. Lin, W.-b. Yi, W.-z. Shen and G.-p. Lu, Org. Lett., 2016, 18, 592–595.

12. K. Jouvin, C. Matheis and L. J. Goossen, Chem.–Eur. J., 2015, 21, 14324–14327.

13. (a) J. Wu, Y. Gu, X. Leng and Q. Shen, Angew. Chem., Int. Ed., 2015, 54, 7648–7652; (b) J. Wu, Y. Liu, C. Lu and Q. Shen, Chem. Sci., 2016, 7, 3757–3762.

14. (a) D. Zhu, Y. Gu, L. Lu and Q. Shen, J. Am. Chem. Soc., 2015, 137, 10547–10553; (b) D. Zhu, X. Hong, D. Li, L. Lu and Q. Shen, Org. Process Res. Dev., 2017, 21, 1383–1387.

15. S. Arimori, O. Matsubara, M. Takada, N. Shibata and M. Shiro, R. Soc. Open Sci., 2016, 3, 160102–160110.

16. E. Ismalaj, D. Le Bars and T. Billard, Angew. Chem., Int. Ed., 2016, 55, 4790–4793.

17. H.-Y. Xiong, A. Bayle, X. Panneeoucke and T. Besset, Angew. Chem., Int. Ed., 2016, 55, 13490–13494.

18. F. Shen, P. Zhang, L. Lu and Q. Shen, Org. Lett., 2017, 19, 1032–1035.

19. (a) X. Zhao, A. Wei, T. Li, Z. Su, J. Chen and K. Lu, Org. Chem. Front., 2017, 4, 232–235; (b) Q. Yan, L. Q. Jiang, W. B. Yi,
Q. R. Liu and W. Zhang, *Adv. Synth. Catal.*, 2017, **359**, 2471–2480.
20 D. Zhu, X. Shao, X. Hong, L. Lu and Q. Shen, *Angew. Chem., Int. Ed.*, 2016, **55**, 15807–15811.
21 B. Xu, D. Wang, Y. Hu and Q. Shen, *Org. Chem. Front.*, 2018, **5**, 1462–1465.
22 (a) S.-H. Guo, X.-L. Zhang, G.-F. Pan, X.-Q. Zhu, Y.-R. Gao and Y.-Q. Wang, *Angew. Chem., Int. Ed.*, 2017, **57**, 1663–1667; (b) S. H. Guo, M. Y. Wang, G. F. Pan, X. Q. Zhu, Y. R. Gao and Y.-Q. Wang, *Adv. Synth. Catal.*, 2018, **360**, 1861–1869; (c) B. Xu, D. Li, L. Lu, D.-C. Wang, Y. Hu and Q. Shen, *Org. Chem. Front.*, 2018, DOI: 10.1039/c8qo00327k.
23 P. Liu, W. Liu and C.-J. Li, *J. Am. Chem. Soc.*, 2017, **139**, 14315–14321.
24 H. G. Viehe, Z. Janousek, R. Merenyi and L. Stella, *Acc. Chem. Res.*, 1985, **18**, 148–154.
25 (a) W. E. Lyons, *Nature*, 1948, **162**, 1004; (b) O. Curcuruto, J. Winders, D. Franchi and M. Hamdan, *Rapid Commun. Mass Spectrom.*, 1993, **7**, 670–672.
26 F. Freeman and C. N. Angeletakis, *J. Am. Chem. Soc.*, 1983, **105**, 4039–4049.
27 (a) L. Li, W. Liu, H. Zeng, X. Mu, G. Cosa, Z. Mi and C. J. Li, *J. Am. Chem. Soc.*, 2015, **137**, 8328–8331; (b) L. Li, W. Liu, X. Mu, Z. Mi and C. J. Li, *Nat. Protoc.*, 2016, **11**, 1948–1954; (c) W. Liu, X. Yang, Y. Gao and C.-J. Li, *J. Am. Chem. Soc.*, 2017, **139**, 8621–8627.
28 (a) C. Rosinger, S. Shirakura, E. Hacker, Y. Sato, S. Heibges and S. Nakamura, *Julius-Kühn-Archiv*, 2012, **2**, 544–548; (b) T. Yoshimura, T. Ikeuchi, S. Ohno, S. Asakura and Y. Hamada, *J. Pestic. Sci.*, 2013, **38**, 171–172.
29 C. J. M. Stirling, in *The chemistry of sulphinic acids, esters and their derivatives*, ed. S. Patai, John Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapore, 1990, ch. 1, pp. 1–7.