A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition GDCh Chemie

www.angewandte.org

## Accepted Article

**Title:** Radical Fluorosulfonylation: Accessing Alkenyl Sulfonyl Fluorides from Alkenes

**Authors:** Saihu Liao, Xingliang Nie, Tianxiao Xu, Jinshuai Song, Anandkumar Devaraj, Bolun Zhang, and Yong Chen



**To be cited as:** *Angew. Chem. Int. Ed.* 10.1002/anie.202012229

**Link to VoR:** https://doi.org/10.1002/anie.202012229

WILEY-VCH

10.1002/anie.202012229

WILEY-VCH

COMMUNICATION

# Radical Fluorosulfonylation: Accessing Alkenyl Sulfonyl Fluorides from Alkenes

Xingliang Nie,[a] Tianxiao Xu,[a] Jinshuai Song,[b] Anandkumar Devaraj,[a] Bolun Zhang,[a] Yong Chen,[a] and Saihu Liao*[a,c]

[a] X. Nie, T. Xu, Dr. A. Devaraj, B. Zhang, Dr. Y. Chen, Prof. Dr. S. Liao
Key Laboratory of Molecule Synthesis and Function Discovery (Fujian Province University), State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University
Fuzhou 350108, China
E-mail: shliao@fzu.edu.cn
[b] Prof. Dr. J. Song
College of Chemistry and Molecular Engineering, Zhengzhou University
Zhengzhou 450001, China
[c] Prof. Dr. S. Liao
Beijing National Laboratory of Molecular Science (BNLMS)
Beijing 100190, China

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under https://xxxxxxxxxx..

**Abstract:** Sulfonyl fluorides have widespread applications in many fields. In particular, their unique biological activity has drawn considerable research interest in the context of chemical biology and drug discovery in the past years. Therefore, new and efficient methods for the synthesis of sulfonyl fluorides is highly in demand. In contrast to extensive studies on $FSO_2$+ type reagents, a radical fluorosulfonylation reaction with fluorosulfonyl radical ($FSO_2$•) remains elusive so far, probably due to its instability and difficulty in generation. Here, we report the development of the first radical fluorosulfonylation of alkenes based on $FSO_2$ radicals generated under photoredox conditions. This radical approach provides a new and general access to alkenyl sulfonyl fluorides, including structures that would otherwise be challenging to synthesize with previously established cross coupling methods. Moreover, further extention to the late-stage fluorosulfonylation of natural products is also demonstrated.

The development of effective methods for the introduction of functional groups or moieties is of central importance in modern organic synthesis. In the past decade, sulfonyl fluorides have drawn considerable research interests from different fields,[1] encompassing organic synthesis, materials science, drug discovery, etc.[2-6] Recently, Sulfur(VI) Fluoride Exchange (SuFEx) has been identified by Sharpless[1a] as the new generation of click chemistry. In particular, their unique proton-mediated reactivity-switch-on mechanism endows sulfonyl fluorides excellent site-specific targeting ability under complex biological contexts.[1,4-6] In fact, the past few years have witnessed a fast-growing research interest on the study of sulfonyl fluorides as selective warhead in chemical biology and drug discovery.[4-6] Consequently, the development of new and efficient synthetic methods to expand the scope of available sulfonyl fluorides is of great significance and highly desirable.[4,6,7]

Direct introduction of the $FSO_2$ group by using $FSO_2$-containing reagents[1,8,9] represents a concise and redox economic approach, in comparison with the conventional synthetic routes via chloride-fluoride exchange from sulfonyl chlorides which are often limited by their low stability and availability.[1] The known fluorosulfonylating reagents such as the widely used sulfuryl fluoride gas ($SO_2F_2$) and two newly developed reagents (FDIT[8a] and AISF[8b]) can be regarded as synthetic equivalents of the

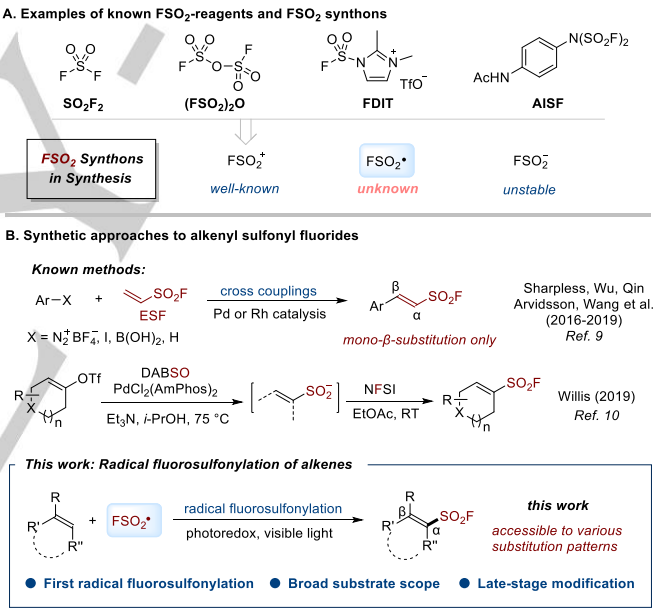



**Figure 1.** (A) Examples of known $FSO_2$- reagents and $FSO_2$ synthons in organic synthesis. (B) Methods for the synthesis of alkenyl sulfonyl fluorides. DABSO = 1,4-diazabicyclo[2.2.2]octane-bis(sulfur dioxide).

"$FSO_2$+" synthons. In contrast, fluorosulfonylation reaction with fluorosulfonyl radicals ($FSO_2$•), to the best of our known, remains elusive so far (Figure 1A). We thus questioned whether fluorosulfonyl radical ($FSO_2$•) can be readily generated and utilized in organic synthesis. In particular, a reactivity fundamentally different from its cationic counterpart ($FSO_2$+) can be expected, which could probably bring in the opportunity to overcome the challenging issues in sulfonyl fluoride synthesis.

Due to its instability and difficulty in generation, the $FSO_2$• has been regarded as a long-sought sulfur-centered radical.[11] Nonetheless, recently Zeng and Beckers observed the formation of this radical in the flash vacuum pyrolysis of fluorosulfonyl azides,[11a] which encouraged us to seek appropriate $FSO_2$• precursors to establish a radical fluorosulfonylation reaction. Here,

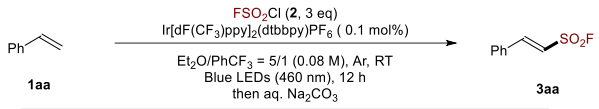
10.1002/anie.202012229

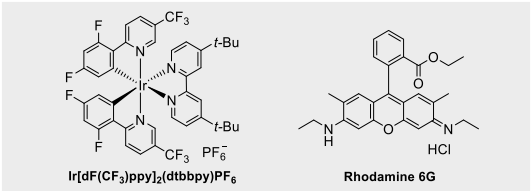
WILEY-VCH

COMMUNICATION

we report our efforts toward this goal, and the finding that $FSO_2$ radicals can be readily generated under photoredox conditions, which allowed for the development of the first radical fluorosulfonylation of alkenes. The significance and attractive biological properties of alkenyl sulfonyl fluorides have attracted considerable efforts to develop effective approaches to construct this class of molecules.[1,6,9,10] These methods work well, but are often fundamentally limited to certain type of substitutions.[9,10] For example, only β-mono-substitutions are accessible via the cross couplings of ArX with ethenesulfonyl fluoride (ESF) (Figure 1B).[9] Whereas, the present radical method represents a new approach for the synthesis of alkenyl sulfonyl fluorides, accessible to various substitution patterns, including structures (e.g. β-alkyl, tri-substituted ones) that would otherwise be challenging to synthesize with the known cross coupling methods.

**Table 1.** Reaction Conditions for Radical Fluorosulfonylation of Styrene.[a]



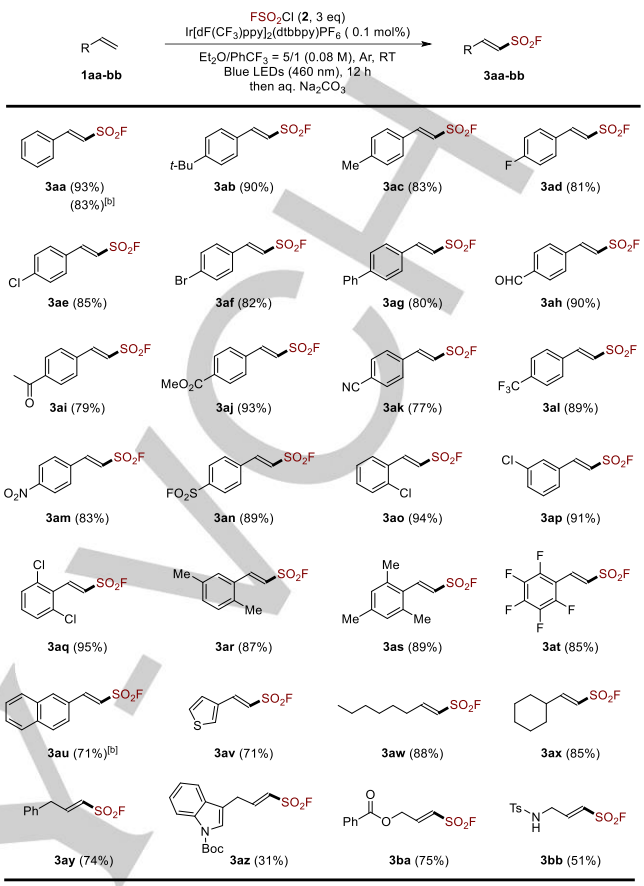

| Entry | Deviation from the standard conditions | Yield[b] |
|---|---|---|
| 1 | none | 96% |
| 2 | solvent: $PhCF_3$ instead of $Et_2O$ | 20% |
| 3 | 5 mol% of Rhodamine 6G instead of [Ir] | 85% |
| 4 | with 1 mol% [Ir] | 97% |
| 5 | no photocatalyst | 0% |
| 6 | in dark | <1% |

[a] On 0.2 mmol-scale. [b] Determined by $^{19}F$ NMR analysis.

We commenced our study with the screening of suitable $FSO_2$ radical precursors in the form of $FSO_2$–X that might be able to generate the $FSO_2$ radical under photoredox conditions.[12] Even though no desired product was observed in the reactions of styrene with a number of possible precursors including FDIT and fluorosulfates, we finally found sulfuryl chlorofluoride ($FSO_2Cl$),[13] could afford the desired radical fluorosulfonylation product, albeit in low yield. Surprisingly, a large amount of chlorinated by-products were detected by GC-MS analysis (for details, see Table S1). This may be ascribed to the strong electronegativity of fluorine, which make the chloride in $FSO_2Cl$ very electrophilic and its reactivity significant different from the corresponding alkyl or aryl sulfonyl chlorides ($RSO_2Cl$).[14] Nevertheless, upon further optimization (Table S1-3), we could finally achieve 96% $^{19}F$ NMR yield by using $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ ([Ir]) as photocatalyst under blue LEDs irradiation (product **3aa**, Table 1, entry 1). In addition, Rhodamine 6G, a cheap organic dye, can also promote the reaction (entry 3). Control experiments indicate that both the photocatalyst and light are crucial to the reaction (entry 5 & 6).

Having the optimized reaction conditions in hand, we next examined the generality of this transformation with different

**Table 2.** The Scope of Radical Fluorosulfonylation of Terminal Olefins.[a]




[a] On 0.2 mmol-scale. [b] With 5 mol% Rhodamine 6G as the photocatalyst. Ts = 4-toluenesulfonyl.

alkenes (Table 2). Remarkably, the reaction conditions are compatible with a wide range of functional groups such as aldehyde (**3ah**), ketone (**3ai**), ester (**3aj**), and nitro (**3am**). Further, multi-substituted ones (**3aq-3at**) also reacted well. Notably, bulky aryl (**3as**) can be well introduced to the β-position of product. The advantage of this radical method became manifested when applied to the synthesis of β-alkyl vinyl sulfonyl fluorides (**3aw-3bb**), which are challenging to synthesize via the Heck-type couplings with ESF, due to the potential β-H elimination in cases of alkyl substrates.[9a-c] Moreover, allylic arene (**3ay**), indole (**3az**), alcohol (**3ba**) and amine (**3bb**) can all be smoothly fluorosulfonylated with $FSO_2$ radicals.

The most prominent feature of this radical method could be that it allows for direct fluorosulfonylation of cyclic, di- and tri-substituted olefins to access multi-substituted vinyl sulfonyl fluorides, which are impossible to synthesize via cross couplings with ESF.[1d,9] As shown in Table 3A, α,β- and β,β-di-substituted, and also α,β,β-tri-substituted vinyl sulfonyl fluorides (**5a-5l**) can all be synthesized via this radical approach from the corresponding substituted olefins. Cyclic alkenyl sulfonyl fluorides (**5b-5g**) can be prepared from the corresponding cyclic alkenes (**4b-f**). It is worth mentioning that, for the synthesis of **5b**, no product was obtained via the palladium-catalyzed sulfur dioxide insertion/fluorination sequence from the corresponding alkenyl triflate.[10] The superiority of this radical approach was further demonstrated in the direct fluorosulfonylation of natural products. The C-C double bonds of different electronic nature in oleic ester (**4m**), cinnamate (**4n**), and chromene (**4o**) can all be

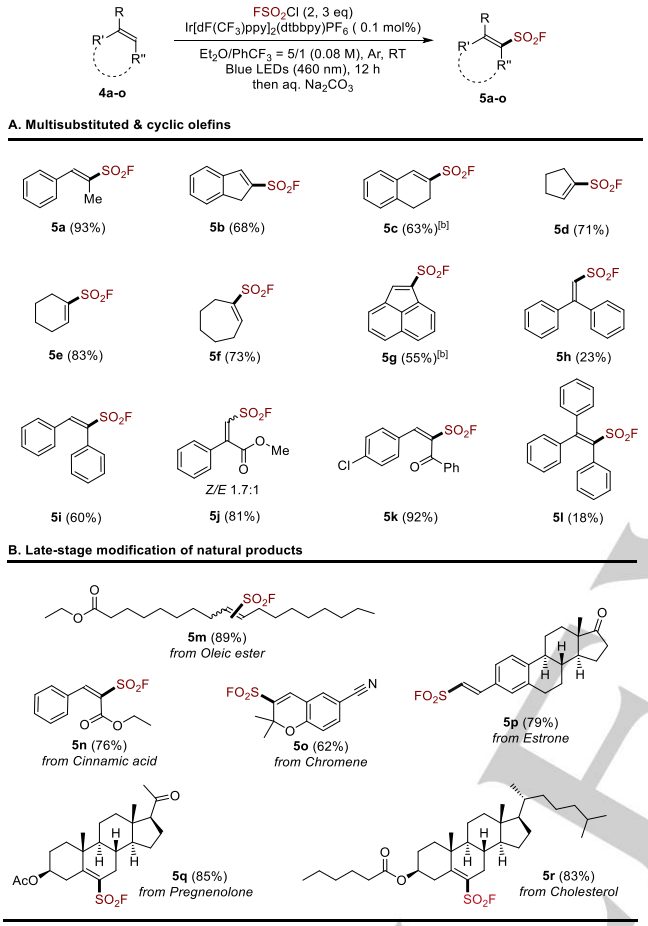
10.1002/anie.202012229

WILEY-VCH



functionalized to give the corresponding sulfonyl fluoride **5m-5o** in good to high yields. Moreover, direct fluorosulfonylation of Estrone-derived olefin (**4p**), Pregnenolone (**4q**), and Cholesterol (**4r**) is also feasible via this radical approach. The *Z*/*E*-configurations of **5a**, **5i**, **5k** and **5n** were assigned based on NMR analysis and density functional theory (DFT) calculation. The *E*-configuration of **5k** was further confirmed by its X-ray crystal structure (see SI for details).

**Table 3.** Extension to di-, tri-, Cyclic Olefins, and Late-stage Functionalization.[a]




[a] On 0.2 mmol scale. [b] With 5 mol% Rhodamine 6G as the photocatalyst.

Regarding the reaction mechanism, this radical fluorosulfonylation was found totally inhibited by the radical scavenger 2,2,6,6-tetramethylpiperidinooxy (TEMPO, Figure 2A, Eq. 1). A radical clock experiment was also performed with radical probe **6** under standard reaction conditions, which gave the ring-opened product **7** in 41% yield, suggesting an initial radical addition to the C-C double bond happened, followed by the ring-opening of the three-membered ring (Eq. 2). We also performed a DFT calculation on $FSO_2$• and compared its properties with the known radical of trifluoromethylsulfonyl ($CF_3SO_2$•). The $FSO_2$• has not only a more planar conformation but also a more positive sulfur center (NPA charge 1.930 vs 1.579 by natural bond orbital analysis) than $CF_3SO_2$• (Figure 2, B),[15] in consistence with the strong electronegativity of fluorine and the highly electrophilic nature of the chloride in $FSO_2Cl$ that led to the formation of chloride sideproducts. Accordingly, a possible reaction pathway is proposed in Figure 2B. The electron transfer from the excited iridium catalyst to chlorosulfonyl fluoride generates the fluorosulfonyl radicals, which subsequently add to the C-C double bond of olefin and form the key intermediate **Int-1**. This radical intermediate could attack $FSO_2Cl$ to give **Int-2** and initiate the chain pathway,[16] which is in line with the formation of chlorinated product **7** in the radical clock experiment (Eq. 2). Then, **Int-2** loses HCl, giving the desired conjugated product **3**.[17] Alternatively, a redox pathway via the oxidation of **Int-1** to **Int-1'** by $Ir^{IV}$ (**C**), followed by deprotonation, may be also involved to some extent.

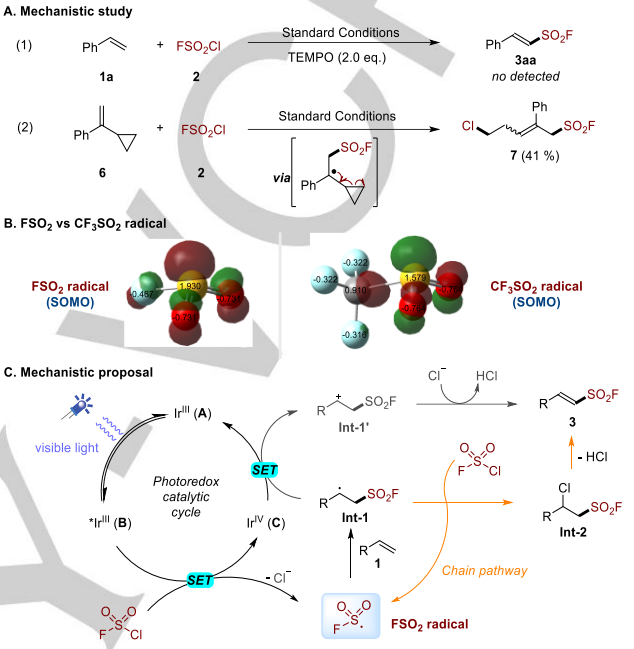



**Figure 2.** Mechanistic Study and Proposal.

In summary, fluorosulfonyl radical ($FSO_2$•) has been demonstrated as a feasible and useful synthon for introducing the sulfonyl fluoride group. Its addition activity toward C–C double enables the development of a general and facile approach for the synthesis of alkenyl sulfonyl fluorides. In particular, this radical fluorosulfonylation method allows for a convenient access to multi-substituted vinyl sulfonyl fluorides, which are challenging to synthesize via the known cross coupling methods with ESF. We anticipate that the first demonstration of the synthetic utility of $FSO_2$• here will encourage the engagement in the study of radical fluorosulfonylation in both synthetic methodology development and target synthesis of bioactive molecules in future.

## Acknowledgements

We gratefully acknowledge National Natural Science Foundation of China (Nr. 21602028), Beijing National Laboratory of Molecular Science (BNLMS), and Fuzhou University for the financial support.

**Keywords:** SuFEx • Sulfonyl Fluorides • Alkenes • Radical Reactions • Visible Light

[1] (a) J. Dong, L. Krasnova, M. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2014**, *53*, 9430–9448; *Angew. Chem.* **2014**, *126*, 9584–9603; (b) P. K. Chinthakindi, P. I. Arvidsson, *Eur. J. Org. Chem.* **2018**, 3648–3666; (c) L. Xu, J. Dong, *Chin. J. Chem.* **2020**, *38*, 414–419; (d) A. S. Barrow,

C. J. Smedley, Q. Zheng, S. Li, J. Dong, J. E. Moses, *Chem. Soc. Rev.* **2019**, *48*, 4731–4758.

[2] For selected recent reports, see: (a) G. Meng, T. Guo, T. Ma, J. Zhang, Y. Shen, K. B. Sharpless, J. Dong, *Nature* **2019**, *574*, 86–89; (b) C. J. Smedley, Q. Zheng, B. Gao, S. Li, A. Molino, H. M. Duivenvoorden, B. S. Parker, D. J. D. Wilson, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2019**, *58*, 4552–4556; *Angew. Chem.* **2019**, *131*, 4600–4604; (c) B. Moku, W. Y. Fang, J. Leng, L. Li, G. F. Zha, K. P. Rakesh, H. L. Qin, *iScience* **2019**, *21*, 695–705; (d) P. J. Foth, F. Gu, T. G. Bolduc, S. S. Kanani, G. M. Sammis, *Chem. Sci.* **2019**, *10*, 10331–10335; (e) M.-C. Giel, C. J. Smedley, E. R. R. Mackie, T. Guo, J. Dong, T. P. Soares da Costa, J. E. Moses, *Angew. Chem. Int. Ed.* **2020**, *59*, 1181–1186; *Angew. Chem.* **2020**, *132*, 1197–1202; (f) M. Mendel, I. Kalvet, D. Hupperich, G. Magnin, F. Schoenebeck, *Angew. Chem. Int. Ed.* **2020**, *59*, 2115–2119; *Angew. Chem.* **2020**, *132*, 2132–2136; (g) D. D. Liang, D. E. Streefkerk, D. Jordaan, J. Wagemakers, J. Baggerman, H. Zuilhof, *Angew. Chem. Int. Ed.* **2020**, *59*, 7494–7500; *Angew. Chem.* **2020**, *132*, 7564–7570; (h) S. Mahapatra, C. P. Woroch, T. W. Butler, S. N. Carneiro, S. C. Kwan, S. R. Khasnavis, J. Gu, J. K. Dutra, B. C. Vetelino, J. Bellenger, C. W. am Ende, N. D. Ball, *Org. Lett.* **2020**, *22*, 4389–4394.

[3] For selected reports, see: (a) J. Dong, K. B. Sharpless, L. Kwisnek, J. S. Oakdale, V. V. Fokin, *Angew. Chem. Int. Ed.* **2014**, *53*, 9466–9470; *Angew. Chem.* **2014**, *126*, 9620–9624; (b) B. Gao, L. Zhang, Q. Zheng, F. Zhou, L. M. Klivansky, J. Lu, Y. Liu, J. Dong, P. Wu, K. B. Sharpless, *Nat. Chem.* **2017**, *9*, 1083–1088; (c) T. Hmissa, X. Zhang, N. R. Dhumal, G. J. McManus, X. Zhou, H. B. Nulwala, A. Mirjafari, *Angew. Chem. Int. Ed.* **2018**, *57*, 16005–16009; *Angew. Chem.* **2018**, *130*, 16237–16241; (d) C. Yang, J. P. Flynn, J. Niu, *Angew. Chem. Int. Ed.* **2018**, *57*, 16194–16199; *Angew. Chem.* **2018**, *130*, 16426–16431.

[4] For reviews, see: (a) A. Narayanan, L. H Jones, *Chem. Sci.* **2015**, *6*, 2650–2659; (b) P. Martin-Gago, C. A. Olsen, *Angew. Chem. Int. Ed.* **2019**, *58*, 957–966; *Angew. Chem.* **2019**, *131*, 969–978.

[5] For selected recent reports, see: (a) Z. Liu, J. Li, S. Li, G. Li, K. B. Sharpless, P. Wu, *J. Am. Chem. Soc.* **2018**, *140*, 2919–2925; (b) R. Artschwager, D. J. Ward, S. Gannon, A. J. Brouwer, H. van de Langemheen, H. Kowalski, R. M. J. Liskamp, *J. Med. Chem.* **2018**, *61*, 5395–5411; (c) X. Yang, T. J. M. Michiels, C. de Jong, M. Soethoudt, N. Dekker, E. Gordon, M. van der Stelt, L. H. Heitman, D. van der Es, A. P. Ijzerman, *J. Med. Chem.* **2018**, *61*, 7892–7901; (d) H. Xu, F. Ma, N. Wang, W. Hou, H. Xiong, F. Lu, J. Li, S. Wang, P. Ma, G. Yang, R. A. Lerner, *Adv. Sci.* **2019**, *6*, 1901551; (e) C. Liu, Q. Zhou, Y. Li, L. V. Garner, S. P. Watkins, L. J. Carter, J. Smoot, A. C. Gregg, A. D. Daniels, S. Jervey, D. Albaiu, *ACS Cent. Sci.* **2020**, *6*, 315–331; (f) Q. Li, Q. Chen, P. C. Klauser, M. Li, F. Zheng, N. Wang, X. Li, Q. Zhang, X. Fu, Q. Wang, Y. Xu, L. Wang, *Cell* **2020**, *182*, 85–97.e16; (g) S. Kitamura, Q. Zheng, J. L. Woehl, A. Solania, E. Chen, N. Dillon, M. V. Hull, M. Kotaniguchi, J. R. Cappiello, S. Kitamura, V. Nizet, K. B. Sharpless, D. W. Wolan, *J. Am. Chem. Soc.* **2020**, *142*, 10899–10904.

[6] For selected reports, see: (a) C. Dubiella, H. Cui, M. Gersch, A. J. Brouwer, S. A. Sieber, A. Kruger, R. M. Liskamp, M. Groll, *Angew. Chem. Int. Ed.* **2014**, *53*, 11969–11973; *Angew. Chem.* **2014**, *126*, 12163–12167; (b) W. Chen, J. Dong, L. Plate, D. E. Mortenson, G. J. Brighty, S. Li, Y. Liu, A. Galmozzi, P. S. Lee, J. J. Hulce, B. F. Cravatt, E. Saez, E. T. Powers, I. A. Wilson, K. B. Sharpless, J. W. Kelly, *J. Am. Chem. Soc.* **2016**, *138*, 7353–7364; (c) Q. Zhao, X. Ouyang, X. Wan, K. S. Gajiwala, J. C. Kath, L. H. Jones, A. L. Burlingame, J. Taunton, *J. Am. Chem. Soc.* **2017**, *139*, 680–685; (d) D. E. Mortenson, G. J. Brighty, L. Plate, G. Bare, W. Chen, S. Li, H. Wang, B. F. Cravatt, S. Forli, E. T. Powers, K. B. Sharpless, I. A. Wilson, J. W. Kelly, *J. Am. Chem. Soc.* **2018**, *140*, 200–210; (e) N. Wang, B. Yang, C. Fu, H. Zhu, F. Zheng, T. Kobayashi, J. Liu, S. Li, C. Ma, P. G. Wang, Q. Wang, L. Wang, *J. Am. Chem. Soc.* **2018**, *140*, 4995–4999.

[7] (a) L. H. Jones, J. W. Kelly, *RSC Med. Chem.* **2020**, *11*, 10–17; (b) S. E. Dalton, S. Campos, *ChemBioChem* **2020**, *21*, 1080–1100.

[8] For selected recent papers, see: (a) T. Guo, G. Meng, X. Zhan, Q. Yang, T. Ma, L. Xu, K. B. Sharpless, J. Dong,. *Angew. Chem. Int. Ed.* **2018**, *57*, 2605–2610; *Angew. Chem.* **2018**, *130*, 2635–2640; (b) H. Zhou, P. Mukherjee, R. Liu, E. Evrard, D. Wang, J. M. Humphrey, T. W. Butler, L. R. Hoth, J. B. Sperry, S. K. Sakata, C. J. Helal, C. W. Am Ende, *Org. Lett.* **2018**, *20*, 812–815; (c) C. Lee, N. D. Ball, G. M. Sammis, *Chem. Commun.* **2019**, *55*, 14753–14756; (d) J. Chen, B.-q. Huang, Z.-q. Wang, X.-j. Zhang, M. Yan, *Org. Lett.* **2019**, *21*, 9742–9746; (e) C. J. Smedley, G. Li, A. S. Barrow, T. L. Gialelis, M. C. Giel, A. Ottonello, Y. Cheng, S. Kitamura, D. W. Wolan, K. B. Sharpless, J. E. Moses, *Angew. Chem. Int. Ed.* **2020**, *59*, 12460–12469; *Angew. Chem.* **2020**, *132*, 12560–12569; (f) Y. Liu, D. Yu, Y. Guo, J.-C. Xiao, Q.-Y. Chen, C. Liu, *Org. Lett.* **2020**, *22*, 2281–2286; (g) T. Zhong, M.-K. Pang, Z.-D. Chen, B. Zhang, J. Weng, G. Lu, *Org. Lett.* **2020**, *22*, 3072–3078.

[9] For selected examples, see: (a) H. L. Qin, Q. Zheng, G. A. Bare, P. Wu, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2016**, *55*, 14155–14158; *Angew. Chem.* **2016**, *128*, 14361–14364; (b) G. F. Zha, Q. Zheng, J. Leng, P. Wu, H. L. Qin, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2017**, *56*, 4849–4852; *Angew. Chem.* **2017**, *129*, 4927–4930; (c) P. K. Chinthakindi, K. B. Govender, A. S. Kumar, H. G. Kruger, T. Govender, T. Naicker, P. I. Arvidsson, *Org. Lett.* **2017**, *19*, 480–483; (d) C. Li, S.-M. Wang, H.-L. Qin, *Org. Lett.* **2018**, *20*, 4699–4703; (e) G. Ncube, M. P. Huestis, *Organometallics* **2019**, *38*, 76–80; (f) X. Y. Chen, Y. Wu, J. Zhou, P. Wang, J. Q. Yu, *Org. Lett.* **2019**, *21*, 1426–1429.

[10] T. S.-B. Lou, S. W. Bagley, M. C. Willis, *Angew. Chem. Int. Ed.* **2019**, *58*, 18859–18863; *Angew.Chem.* **2019**, *131*,19035–19039.

[11] (a) X. Q. Zeng, H. Beckers, H. Willner, *J. Am. Chem. Soc.* **2013**, *135*, 2096–2099. (b) Z. Li, *Chem. Phys. Lett.* **1997**, *269*, 128–137.

[12] For selected reviews, see: (a) J. Xuan, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2012**, *51*, 6828–6838; *Angew.Chem.* **2012**, *124*, 6934–6944; (b) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322–5363; (c) D. M. Schultz, T. P. Yoon, *Science* **2014**, *343*, 1239176.

[13] V. P. Reddy, D. R. Bellew, G. K. S. Prakash, *J. Fluorine Chem.* **1992**, *56*, 195–197.

[14] For examples, see: (a) A. Wimmer, B. König, *Beilstein J. Org. Chem.* **2018**, *14*, 54–83 (Review); (b) J. Zhu, W.-C. Yang, X.-D Wang, L. Wu, *Adv. Synth. Catal.* **2018**, 360, 386–400 (Review); (c) H. Li, C. Shan, C.-H. Tung, Z. Xu, *Chem. Sci.* **2017**, *8*, 2610–2615.

[15] F. De Vleeschouwer, V. Van Speybroeck, M. Waroquier, P. Geerlings, F. De Proft, *Org. Lett.* **2007**, *9*, 2721–2724.

[16] The quantum yield was measured to be ca. 18; for details, please see the Supporting Information.

[17] Dehydrochlorination can proceed in the absence of base; for details, please see the Supporting Information (Section 4).

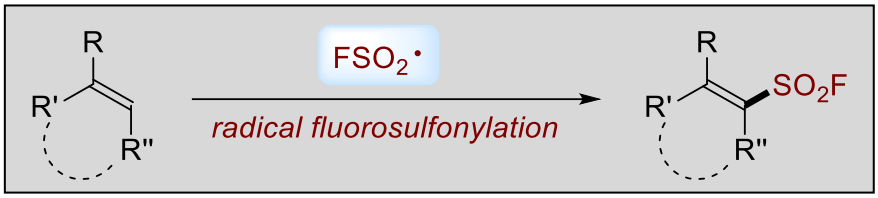
10.1002/anie.202012229





## Entry for the Table of Contents

Insert graphic for Table of Contents here.




Here demonstrates the generation of $FSO_2$ radicals under photoredox conditions, which led to the realization of radical fluorosulfonylation of alkenes. This method provides a new method for the synthesis of alkenyl sulfonyl fluorides, and allows for access to many structures that would otherwise be challenging to synthesize with known methods. Late-stage functionalization of natural products is also demonstrated.