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Photocatalytic Dual-Defluorination Thiolation of Trifluoromethyl Hydrazones

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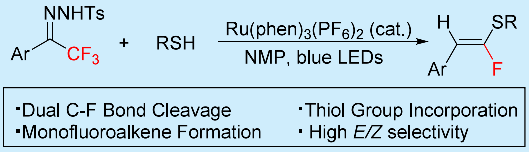
ABSTRACT: The defluorination of trifluoromethyl groups typically involves breaking one or all three C−F bonds, while selectively cleaving exactly two C−F bonds presents a considerable challenge. In this work, we present a method for the sequential defluorination of trifluoromethyl hydrazones under photocatalytic conditions, which involves the specific breakage of two C−F bonds followed by thiolation to yield monofluorinated alkenes containing a thiol group. Transforming trifluoromethyl-containing polyfluoroalkyl substances into fluorinated non-PFAS compounds holds potential practical implications.



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Fluorine exhibits unique electronic properties, such as a small atomic radius and low polarizability, which allow fluorinated groups to enhance the physicochemical properties of organic molecules, such as improving the metabolic stability and lipophilicity of drug molecules.[1] This enhancement has made the development of methods for incorporating fluorinated groups into molecular structures a critical focus in organofluorine chemistry.[2] On the other hand, the widespread use of well-established compounds containing perfluoroalkyl groups has led to significant environmental concerns. The European Union's increasing regulatory restrictions on PFAS (per- and poly fluoroalkyl-containing substances) highlight the challenges in managing and disposing of these compounds.[3] Developing a method to selectively defluorinate molecules containing perfluoroalkyl groups could yield unique fluorinated molecules. Such an achievement would not only mark a significant advancement in the synthesis of fluorinated compounds but also contribute to mitigating the environmental pressures associated with the accumulation of PFAS. Given the inclusion of CF_3-containing compounds within the category of PFAS,[3a] the defluorinative functionalization of the CF_3 moiety has garnered considerable attention,[4] as it can transform these substances into valuable non-PFAS alternatives. However, most research efforts focus on manipulating either a single C−F bond or all three C−F bonds within the CF_3 group.[4] Selectively breaking two C−F bonds for functionalization presents a significant challenge, as the strength of the C−F bond decreases with progressive defluorination,[5] often resulting in complete defluorination rather than the desired selective modification (Scheme 1A).

Limited research has been conducted on the functionalization of CF_3 groups through the cleavage of two C−F bonds. Typically, the methods employed involve the use of reactive substrates, including CF_3-alkenes,[6] CF_3CH_2−ketones,[7] and Ar−CHBr-CF_3 compounds[8] (Scheme 1B, eq a). CF_3-alkenes are susceptible to nucleophilic or radical attack, leading to the formation of a carbanion that readily undergoes β-fluoride elimination, which is similar to an S_N2' process.[6] The CH_2 segment in CF_3CH_2−ketones exhibits notable acidity, allowing for facile deprotonation and subsequent β-fluoride elimination.[7] In the case of Ar−CHBr-CF_3, the C−Br bond's high reactivity facilitates the oxidation of a transition metal, forming a Br-[M]-C−CF_3intermediate that is predisposed to β-fluoride elimination.[8] All of these elimination processes can easily cleave a C−F bond, which is a traditional approach for breaking such bonds and not particularly challenging in the chemistry of C−F bond functionalization. Recently, Wang, Houk, and co-workers reported a dihydrodefluorination of trifluoroacetamides by selectively breaking two C−F bonds (Scheme 1B, eq b1).[9] The key to this method lies in a two-stage process, where each stage involves a spin-center shift step to achieve controlled C−F bond cleavage. This strategy not only effectively prevents overdefluorination but also enables the rapid and efficient synthesis of highly functionalized monofluorinated products from inexpensive CF_3 sources. Additionally, CF_3-diazo compounds have been shown to undergo dual C−F bond cleavages.[10] Zhou's group described a Rh(III)-catalyzed defluorinative [4 + 2] annulation for synthesizing 1,3,4-substituted isoquinolines (Scheme 1B, b2).[10a] Similarly, Li and co-workers reported a Ru-catalyzed redox-neutral [4 + 2] cyclization of 2-arylbenzimidazoles with α-trifluoromethyl-α-diazoketones via sequential C−H activation and defluorinative annulation (Scheme 1B, b3).[10b]

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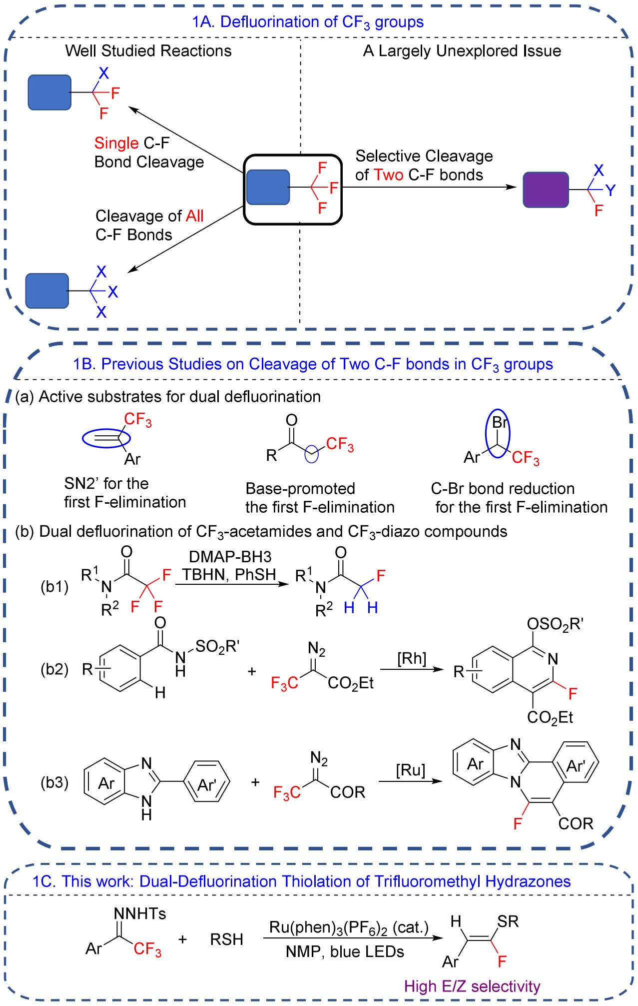
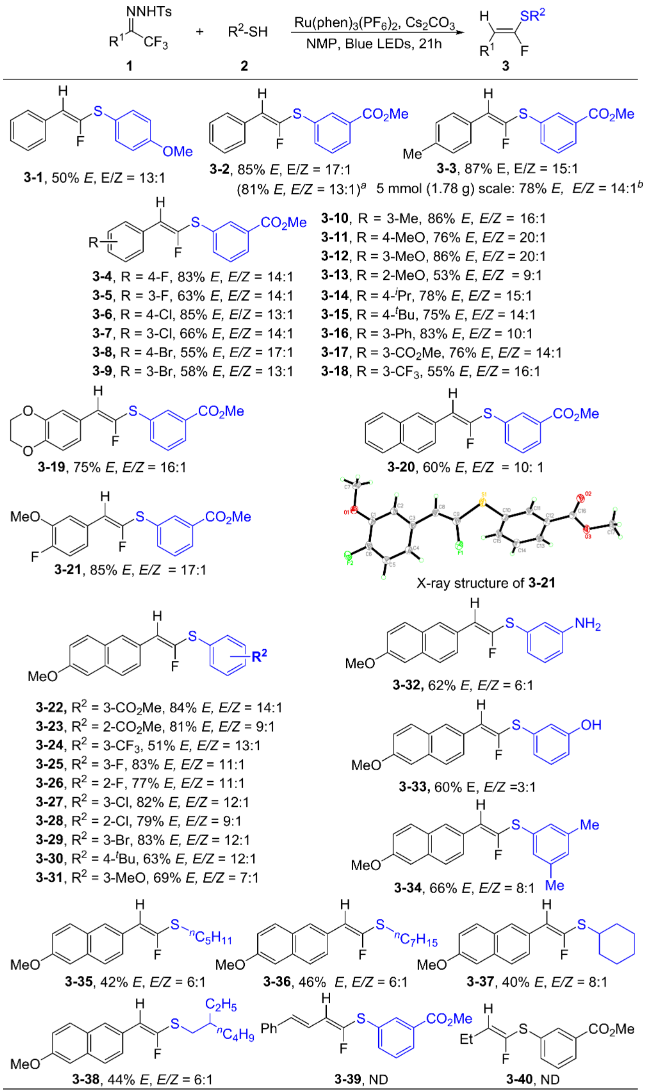
Scheme 1. Functionalizations of C−F Bonds in CF_3 Groups



Scheme 2. Substrate Scope of the Photocatalyzed Dual-Defluorination Thiolation of Trifluoromethyl Hydrazones[c]



[a] The reaction was performed under air atmosphere; the yield and the *E*/*Z* ratio were determined by ^{19}F NMR spectroscopy. [b] The reaction was performed on a 5 mmol (1.78 g) scale of the substrate. The yield and the *E*/*Z* ratio were determined by ^{19}F NMR spectroscopy. [c] Reaction conditions: **1** (0.2 mmol, 1 equiv), **2** (0.4 mmol, 2 equiv), Cs_2CO_3 (0.4 mmol, 2 equiv), and $Ru(phen)_3(PF_6)_2$ (2 mol %) in NMP (2 mL) under 465 nm blue LED irradiation for 21 h at rt under a N_2 atmosphere. Isolated yields are shown. The *E*/*Z* ratios were determined by analyzing the reaction mixtures using ^{19}F NMR spectroscopy.

We have been interested in the introduction of fluorinated groups into organic molecules, typically relying on the use of fluorinated reagents.[11] Recently, we explored the synthetic potential of CF_3-hydrazones, which are widely used as CF_3-carbene precursors.[12] Surprisingly, we discovered that CF_3-hydrazones can readily undergo double C−F bond cleavage followed by thiolation to yield monofluoroalkenes under photocatalytic conditions (Scheme 1C). This protocol efficiently incorporates a thiol group and constructs monofluoroolefins with high *E*/*Z* selectivity. Mechanistic studies reveal that the high *E* selectivity is attributed to visible light irradiation.

Photocatalysis has emerged as a potent methodology in the realm of organic synthesis.[13] Following a systematic screening of the photocatalytic dual-defluorinative thiolation of a trifluoromethyl hydrazone with thiols (see Supporting Information), optimal reaction conditions were established. With the optimal reaction conditions established, we proceeded to explore the substrate scope for the photocatalytic dual-defluorination thiolation of trifluoromethyl hydrazones.

As illustrated in Scheme 2, this protocol demonstrates broad applicability across a diverse array of trifluoromethyl hydrazones and thiols. Notably, when employing thiols containing a 3-CO_2Me group, the reactions delivered the desired products with high *E*/*Z* selectivity and in moderate to good yields (**3−2** to **3−21**). The electronic nature of the substituents on CF_3-hydrazones did not significantly influence the *E*/*Z* ratio; whether the hydrazones were electron-withdrawing, electron-neutral, or electron-donating, the preference for *E*-olefins as the major products remained consistent. However, it was observed that electron-withdrawing groups on the hydrazone substrates tended to result in slightly diminished yields. The structure of product **3−21** was confirmed by X-ray diffraction analysis.[14] Besides 3-CO_2Me phenyl thiol, other aryl thiols also showed reactivity in this process (**3−23** to **3−34**). Notably, free amino and hydroxyl groups (**3−32** and **3−33**) can be tolerated under these conditions, which may allow for convenient structural

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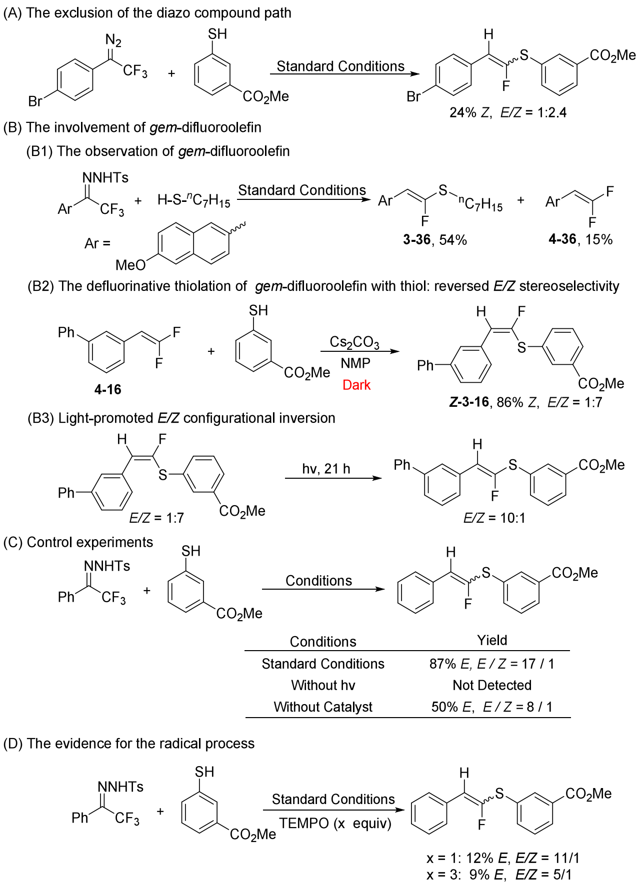
modifications. Alkyl thiols are also reactive, although they resulted in lower yields and *E*/*Z* ratios (**3–35** to **3–38**). In contrast, alkenyl hydrazones were unreactive toward this process, with no desired product formation observed (**3–39**). Alkyl hydrazones cannot be converted into desired products (**3–40**). Even when the reaction was performed under an air atmosphere, it still proceeded smoothly, albeit with a lower yield and reduced *E*/*Z* selectivity (**3–2**). This indicates that while nitrogen protection optimizes the reaction outcome, it is not strictly necessary for the reaction to proceed. Upon scaling up to a gram scale, a good yield and excellent *E*/*Z* selectivity were still achieved (**3–3**), further demonstrating the robustness and versatility of this approach. Replacing the CF_3 group with the HCF_2 group has the potential to produce a thiol-containing alkene without a fluorine substituent. However, using HCF_2-hydrazone, derived from $PhCOCF_2H$ ketone, as the substrate in a reaction with $3\text{-}MeO_2CC_6H_4SH$ thiol, resulted in a complex mixture, and the formation of the desired thiol-containing alkene was not clearly observed.

This dual-defluorination thiolation protocol not only achieves the challenging task of sequentially cleaving two strong C–F bonds but also introduces another functional group, representing a significant discovery in organofluorine chemistry. Additionally, from a synthetic standpoint, this protocol offers an efficient route for obtaining thiol-containing monofluoroolefins, the synthesis of which has received increasing attention due to their potential uses in biological chemistry.[15] For example, Yang, Xia, and co-workers reported an efficient photocatalytic thiolation of *gem*-difluoroolefins with thiols, which suffers from low *E*/*Z* selectivity.[15e] The Shi group described visible-light-promoted thiolation of *gem*-difluoroolefins with sodium sulfinates, primarily producing *E*-olefins.[15g] Recently, the Xue group introduced a thiolation via convergent paired electrolysis, mainly yielding *Z*-olefins.[15h] Despite their efficiency, all of these methods use non-PFAS compounds such as *gem*-difluoroolefins as starting materials. In contrast, our approach begins with CF_3-containing compounds, which are classified as PFAS and are known for their environmental concerns.[3a] By transforming these PFAS materials into valuable non-PFAS products, we not only expand synthetic possibilities but also address environmental challenges. This conversion of PFAS into useful non-PFAS compounds offers several advantages, including enhanced synthetic versatility and a reduction in environmental impact. The ability to sequentially break two C–F bonds and convert PFAS into useful non-PFAS compounds makes our strategy particularly attractive.

It is widely recognized that hydrazones typically act as precursors to diazo compounds.[12a,16] We then explored the possibility that diazo compounds might be the actual reactive intermediates in the dual-defluorination thiolation reaction. However, the reaction using a diazo compound directly as the substrate resulted in low yields and exhibited reversed *E*/*Z* selectivity (Scheme 3, eq A), suggesting that the diazo pathway is not the primary route for this transformation. Upon observing low yields of the desired monofluoroolefin, the presence of *gem*-difluoroolefin (**4–36**) in the reaction mixture was noted (eq B1). While *gem*-difluoroolefins were rarely observed during most cases of substrate scope exploration, their appearance led us to hypothesize that *gem*-difluoroolefin may play a role in the transformation. Under basic conditions without light irradiation, *gem*-difluoroolefin can react with the thiol to yield a monofluoroolefin in high yields, exhibiting surprisingly reversed *E*/*Z* selectivity (eq B2). Notably, the *E*/*Z* mixture, initially dominated by the *Z* isomer, could undergo configurational inversion under hv irradiation to predominantly form the *E* isomer (eq B3), which aligns with the primary product configuration observed under standard reaction conditions. These findings show that *gem*-difluoroolefin plays a critical role as an intermediate, with its formation and subsequent reactions with thiols being pivotal steps in the process. Control experiments were also conducted (eq C). Light irradiation is essential for this dual-defluorination thiolation, as no product forms in its absence. While the desired product can still be obtained without a photocatalyst, it resulted in a dramatically lower yield and poor *E*/*Z* selectivity (eq C). The conversion observed without a photocatalyst is likely due to hv light irradiation facilitating the generation of RS· radicals from thiols, thereby enabling the necessary transformations. The presence of a radical scavenger, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), led to the almost complete inhibition of the desired reaction, indicating that a radical process is operative (eq D).

Scheme 3. Experimental Evidence[a]

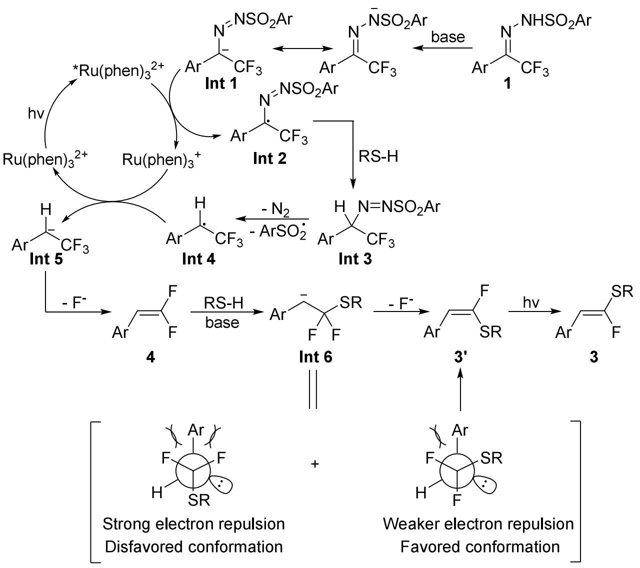


Conditions	Yield
Standard Conditions	87% *E*, *E* / *Z* = 17 / 1
Without hv	Not Detected
Without Catalyst	50% *E*, *E* / *Z* = 8 / 1

[a] All yields and *E*/*Z* values were determined by ^{19}F NMR spectroscopy.

Based on the above results, we propose the reaction mechanism shown in Scheme 4. Hydrazone (**1**) is easily deprotonated by a base to form carbanion (**Int 1**), which is then oxidized by the photoexcited complex $[{}^*Ru(phen)_3{}^{2+}]$ to form radical **Int 2**. This radical readily abstracts a hydrogen from the hydrogen source, a thiol, to provide diazo compound **Int 3**. **Int 3** is unstable and readily decomposes to release nitrogen gas and form radical **Int 4**. **Int 4** is then reduced by

Scheme 4. Proposed Reaction Mechanism



the in situ generated [Ru(phen)$_3^+$] to give anion **Int 5**. *β*-fluoride elimination of this anion delivers *gem*-difluoroolefins **4**.[17] *gem*-Difluoroolefin **4** is reactive toward thiols under basic conditions and their reaction yields anions **Int 6**. In this intermediate, two conformations exist. One suffers from strong electronic repulsion between the two fluorine atoms and the aromatic rings, making it disfavored. The other conformation experiences less electronic repulsion and thus becomes favored.[15g] *β*-fluoride elimination from this favored conformation affords *Z*-isomer **3′**, which is thermodynamically unstable. This isomer undergoes *E*/*Z* configurational inversion under hv irradiation to give thermodynamically stable *E*-isomer **3**. Further mechanistic studies supporting the proposed reaction pathway, including evidence against *β*-fluoride elimination from **Int1**, fluorescence quenching experiments, and indirect support for the formation of **Int3**, are provided in the Supporting Information.

In summary, we have developed an efficient photocatalytic dual-defluorination thiolation of hydrazones with thiols to provide thiol-containing monofluoroolefins with yields and *E*/*Z* selectivities up to high levels. The sequential cleavage of two C−F bonds and the incorporation of new functionality represent a significant advancement in organofluorine chemistry. Notably, the protocol also demonstrates the potential to convert PFAS into useful non-PFAS derivatives, highlighting its practical value. Our approach thus opens new avenues for the synthesis of functionalized fluorinated molecules with broad applications.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.5c01492.

Experimental procedures, analytical data, crystal structure, and NMR spectra of synthesized compounds (PDF)

Accession Codes

Deposition Number 2408193 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Xiao, J.-C.; Lu, S.-F.; Lin, J.-H. *Fluorine-Containing Drugs*; Chemical Industry Press: Beijing, 2022. (b) Xiao, J.-C.; Xu, T.-M.; Lin, J.-H.; Chen, H.-B. *Fluorine-Containing Pesticides*; Chemical Industry Press: Beijing, 2024. (c) Kirsch, P. *Modern Fluoroorganic Chemistry: Synthesis, Reactivity, Applications*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2013; pp 299−350. (d) Muller, K.; Faeh, C.; Diederich, F. Fluorine in pharmaceuticals: looking beyond intuition. *Science* **2007**, *317*, 1881−1886. (e) Meanwell, N. A. Fluorine and Fluorinated Motifs in the Design and Application of Bioisosteres for Drug Design. *J. Med. Chem.* **2018**, *61*, 5822−5880.

(2) (a) Hu, J.; Zhang, W.; Wang, F. Selective difluoromethylation and monofluoromethylation reactions. *Chem. Commun.* **2009**, 7465−7478. (b) Furuya, T.; Kamlet, A. S.; Ritter, T. Catalysis for

fluorination and trifluoromethylation. *Nature* **2011**, *473*, 470−477. (c) Campbell, M. G.; Ritter, T. Modern Carbon-Fluorine Bond Forming Reactions for Aryl Fluoride Synthesis. *Chem. Rev.* **2015**, *115*, 612−633. (d) Preshlock, S.; Tredwell, M.; Gouverneur, V. 18F-Labeling of Arenes and Heteroarenes for Applications in Positron Emission Tomography. *Chem. Rev.* **2016**, *116*, 719−766. (e) Britton, R.; Gouverneur, V.; Lin, J.-H.; Meanwell, M.; Ni, C.; Pupo, G.; Xiao, J.-C.; Hu, J. Contemporary synthetic strategies in organofluorine chemistry. *Nat. Rev. Methods Primers* **2021**, *1*, 47.

(3) (a) OECD. *Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances*; Series on Risk Management; OECD Publishing: Paris, 2021. DOI: 10.1787/e458e796-en (b) Wang, Z.; Buser, A. M.; Cousins, I. T.; Demattio, S.; Drost, W.; Johansson, O.; Ohno, K.; Patlewicz, G.; Richard, A. M.; Walker, G. W.; et al. A New OECD Definition for Per- and Polyfluoroalkyl Substances. *Environ. Sci. Technol.* **2021**, *55*, 15575−15578. (c) Sharma, N.; Kumar, V.; Sugumar, V.; Umesh, M.; Sondhi, S.; Chakraborty, P.; Kaur, K.; Thomas, J.; Kamaraj, C.; Maitra, S. S. A comprehensive review on the need for integrated strategies and process modifications for per- and polyfluoroalkyl substances (PFAS) removal: Current insights and future prospects. *Case Stud. Chem. Environ. Eng.* **2024**, *9*, 100623.

(4) (a) Xu, W.; Zhang, Q.; Shao, Q.; Xia, C.; Wu, M. Photocatalytic C-F Bond Activation of Fluoroarenes, gem-Difluoroalkenes and Trifluoromethylarenes. *Asian J. Org. Chem.* **2021**, *10*, 2454−2472. (b) Gong, X.; Zhou, Q.; Yan, G. Recent advances in C-F bond activation of trifluoromethylated carbonyl compounds and derivatives. *Org. Biomol. Chem.* **2022**, *20*, 5365−5376. (c) Simur, T. T.; Ye, T.; Yu, Y.-J.; Zhang, F.-L.; Wang, Y.-F. C-F bond functionalizations of trifluoromethyl groups via radical intermediates. *Chin. Chem. Lett.* **2022**, *33*, 1193−1198. (d) Zhao, F.; Zhou, W.; Zuo, Z. Recent Advances in the Synthesis of Difluorinated Architectures from Trifluoromethyl Groups. *Adv. Synth. Catal.* **2022**, *364*, 234−267. (e) Hooker, L. V.; Bandar, J. S. Synthetic Advantages of Defluorinative C-F Bond Functionalization. *Angew. Chem., Int. Ed.* **2023**, *62*, e202308880. (f) Liu, J.-W.; Li, S.-Y.; Xu, J.; Xu, H.-J. Recent Advance in the C-F Bond Functionalization of Trifluoromethyl Aromatic and Carbonyl Compounds. *ChemCatChem.* **2024**, *16*, e202301504. (g) Wang, F.; Wang, Q.; Wang, L. Visible light induced selective cleavage of single C(sp^3)-F bond in trifluoromethyl groups containing compounds. *Tetrahedron* **2024**, *163*, 134155. (h) Lye, K.; Young, R. D. A review of frustrated Lewis pair enabled monoselective C-F bond activation. *Chem. Sci.* **2024**, *15*, 2712−2724.

(5) Ai, H.-J.; Ma, X.; Song, Q.; Wu, X.-F. C-F bond activation under transition-metal-free conditions. *Sci. China: Chem.* **2021**, *64*, 1630−1659.

(6) (a) Yang, J.; Mao, A.; Yue, Z.; Zhu, W.; Luo, X.; Zhu, C.; Xiao, Y.; Zhang, J. A simple base-mediated synthesis of diverse functionalized ring-fluorinated 4H-pyrans via double direct C−F substitutions. *Chem. Commun.* **2015**, *51*, 8326−8329. (b) Yang, J.; Zhou, X.; Zeng, Y.; Huang, C.; Xiao, Y.; Zhang, J. Synthesis of 2-fluoro-2-pyrrolines via tandem reaction of α-trifluoromethyl-α,β-unsaturated carbonyl compounds with N-tosylated 2-aminomalonates. *Chem. Commun.* **2016**, *52*, 4922−4925. (c) Fuchibe, K.; Takahashi, M.; Ichikawa, J. Substitution of Two Fluorine Atoms in a Trifluoromethyl Group: Regioselective Synthesis of 3-Fluoropyrazoles. *Angew. Chem., Int. Ed.* **2012**, *51*, 12059−12062. (d) Li, L.; Xiao, T.; Chen, H.; Zhou, L. Visible-Light-Mediated Two-Fold Unsymmetrical C(sp^3)−H Functionalization and Double C−F Substitution. *Chem. Eur. J.l* **2017**, *23*, 2249−2254. (e) Chen, H.; He, Y.; Zhou, L. A photocatalytic decarboxylative/defluorinative [4 + 3] annulation of o-hydroxyphenylacetic acids and trifluoromethyl alkenes: synthesis of fluorinated dihydrobenzoxepines. *Org. Chem. Front.* **2018**, *5*, 3240−3244. (f) Poutrel, P.; Pannecoucke, X.; Jubault, P.; Poisson, T. Stereoselective Synthesis of Terminal Monofluoroalkenes from Trifluoromethylated Alkenes. *Org. Lett.* **2020**, *22*, 4858−4863.

(7) (a) Xu, L.; Zhang, Q.; Xie, Q.; Huang, B.; Dai, J.-J.; Xu, J.; Xu, H.-J. Pd-catalyzed defluorination/arylation of α-trifluoromethyl ketones via consecutive β-F elimination and C−F bond activation. *Chem. Commun.* **2018**, *54*, 4406−4409. (b) Adam, A. T.; Fronczek, F. R.; Colby, D. A. Synthesis of β-Fluoro-α,β-Unsaturated Amides from the Fragmentation of Morpholine 3,3,3-Trifluoropropanamide by Grignard Reagents. *Org. Lett.* **2020**, *22*, 2630−2633.

(8) He, S.-Y.; Zhang, X.-G. Palladium-catalyzed selective defluorinative sulfenylation for the synthesis of fluorovinylthioethers. *Org. Chem. Front.* **2020**, *7*, 3174−3178.

(9) Yu, Y.-J.; Zhang, F.-L.; Peng, T.-Y.; Wang, C.-L.; Cheng, J.; Chen, C.; Houk, K. N.; Wang, Y.-F. Sequential C−F bond functionalizations of trifluoroacetamides and acetates via spin-center shifts. *Science* **2021**, *371*, 1232−1240.

(10) (a) Li, H.; Mei, M.; Zhou, L. Rh(III)-Catalyzed Defluorinative [4 + 2] Annulation of N-Sulfonylarylamides with Ethyl 2-Diazo-3,3,3-trifluoropropanoate: Synthesis of 1,3,4-Functionalized Isoquinolines. *Org. Lett.* **2022**, *24*, 8969−8974. (b) Dong, Z.; Zhang, H.; Wang, B.; Li, B. Cascade C−H Activation and Defluorinative Annulation of 2-Arylbenzimidazoles with α-Trifluoromethyl-α-diazoketones: Modular Assembly of 6-Fluorobenzimidazo[2,1-a]isoquinolines. *Org. Lett.* **2023**, *25*, 4770−4775.

(11) Lin, J.-H.; Xiao, J.-C. Fluorinated Ylides/Carbenes and Related Intermediates from Phosphonium/Sulfonium Salts. *Acc. Chem. Res.* **2020**, *53*, 1498−1510.

(12) (a) Xiao, Q.; Zhang, Y.; Wang, J. Diazo compounds and N-tosylhydrazones: novel cross-coupling partners in transition-metal-catalyzed reactions. *Acc. Chem. Res.* **2013**, *46*, 236−247. (b) Liu, Z.; Sivaguru, P.; Zanoni, G.; Bi, X. N-Triftosylhydrazones: A New Chapter for Diazo-Based Carbene Chemistry. *Acc. Chem. Res.* **2022**, *55*, 1763−1781.

(13) (a) Yoon, T. P.; Ischay, M. A.; Du, J. Visible light photocatalysis as a greener approach to photochemical synthesis. *Nat. Chem.* **2010**, *2*, 527−532. (b) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. Visible light photoredox catalysis with transition metal complexes: applications in organic synthesis. *Chem. Rev.* **2013**, *113*, 5322−5363. (c) Schultz, D. M.; Yoon, T. P. Solar Synthesis: Prospects in Visible Light Photocatalysis. *Science* **2014**, *343*, 985. (d) Meggers, E. Asymmetric catalysis activated by visible light. *Chem. Commun.* **2015**, *51*, 3290−3301. (e) Marzo, L.; Pagire, S. K.; Reiser, O.; Koenig, B. Visible-Light Photocatalysis: Does It Make a Difference in Organic Synthesis? *Angew. Chem., Int. Ed.* **2018**, *57*, 10034−10072. (f) Huang, X.; Meggers, E. Asymmetric photocatalysis with bis-cyclometalated rhodium complexes. *Acc. Chem. Res.* **2019**, *52*, 833−847.

(14) CCDC 2408193 contains the supplementary crystallographic data of compound **3−21**.

(15) (a) Sacasa, P. R.; Zayas, J.; Wnuk, S. F. Radical-mediated thiodesulfonylation of the vinyl sulfones: access to (α-fluoro)vinyl sulfides. *Tetrahedron Lett.* **2009**, *50*, 5424−5427. (b) Bello, D.; O'Hagan, D. Lewis acid-promoted hydrofluorination of alkynyl sulfides to generate α-fluorovinyl thioethers. *Beilstein J. Org. Chem.* **2015**, *11*, 1902−1909. (c) Huang, T.; Zhao, X.; Ji, X.; Wu, W.; Cao, S. Synthesis of fluorovinyl pyrazolyl (thio)ethers by the reaction of gem-difluoroalkenes with pyrazolin-5-ones (thiones). *J. Fluorine Chem.* **2016**, *182*, 61−68. (d) Cong, Z.-S.; Li, Y.-G.; Chen, L.; Xing, F.; Du, G.-F.; Gu, C.-Z.; He, L. N-Heterocyclic carbene-catalyzed stereoselective construction of olefinic carbon−sulfur bonds via cross-coupling reaction of gem-difluoroalkenes and thiols. *Org. Biomol. Chem.* **2017**, *15*, 3863−3868. (e) Wang, J.; Huang, B.; Yang, C.; Xia, W. Visible-light-mediated defluorinative cross-coupling of gem-difluoroalkenes with thiols. *Chem. Commun.* **2019**, *55*, 11103−11106. (f) Li, J.; Rao, W.; Wang, S.-Y.; Ji, S.-J. Nickel-Catalyzed Defluorinative Reductive Cross-Coupling Reaction of gem-Difluoroalkenes with Thiosulfonate or Selenium Sulfonate. *J. Org. Chem.* **2019**, *84*, 11542−11552. (g) Li, Y.; Li, X.; Li, X.; Shi, D. Visible-light-promoted E-selective synthesis of alpha-fluoro-beta-arylalkenyl sulfides via the deoxygenation/isomerization process. *Chem. Commun.* **2021**, *57*, 2152−2155. (h) Pan, Z.; Wang, X.; Zhao, S.; Deng, H.; Ma, M.; Xue, F. Defluorinative Thiolation of gem-Difluoroalkenes by Convergent Paired Electrolysis. *Org. Lett.* **2023**, *25*, 6143−6148.

(16) Barluenga, J.; Moriel, P.; Valdés, C.; Aznar, F. N-Tosylhydrazones as Reagents for Cross-Coupling Reactions: A

Route to Polysubstituted Olefins. *Angew. Chem., Int. Ed.* **2007**, *46*, 5587−5590.

(17) (a) Wang, S.; Cheng, B.-Y.; Sršen, M.; König, B. Umpolung Difunctionalization of Carbonyls via Visible-Light Photoredox Catalytic Radical-Carbanion Relay. *J. Am. Chem. Soc.* **2020**, *142*, 7524−7531. (b) Ranjan, P.; Pillitteri, S.; Coppola, G.; Oliva, M.; Van der Eycken, E. V.; Sharma, U. K. Unlocking the Accessibility of Alkyl Radicals from Boronic Acids through Solvent-Assisted Organophotoredox Activation. *ACS Catal.* **2021**, *11*, 10862−10870. (c) Yue, F.; Ma, H.; Song, H.; Liu, Y.; Dong, J.; Wang, Q. Alkylboronic acids as alkylating agents: photoredox-catalyzed alkylation reactions assisted by K_3PO_4. *Chem. Sci.* **2022**, *13*, 13466−13474.