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Trifluoromethanesulfonyl azide as a bifunctional reagent for metal-free azidotrifluoromethylation of unactivated alkenes†

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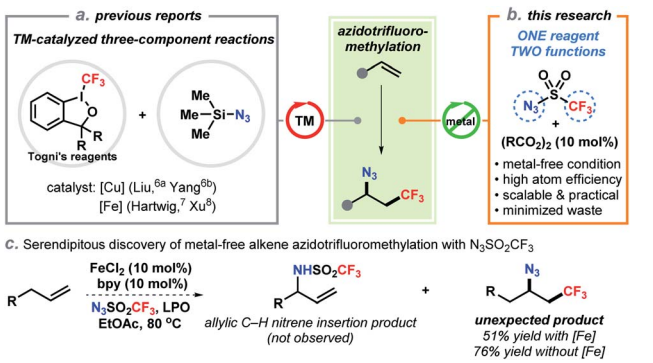
Vicinal trifluoromethyl azides have widespread applications in organic synthesis and drug development. However, their preparation is generally limited to transition-metal-catalyzed three-component reactions. We report here a simple and metal-free method that rapidly provides these building blocks from abundant alkenes and trifluoromethanesulfonyl azide ($N_3SO_2CF_3$). This unprecedented two-component reaction employs readily available $N_3SO_2CF_3$ as a bifunctional reagent to concurrently incorporate both CF_3 and N_3 groups, which avoids the use of their expensive and low atom economic precursors. A wide range of functional groups, including bio-relevant heterocycles and amino acids, were tolerated. Application of this method was further demonstrated by scale-up synthesis (5 mmol), product derivatization to CF_3-containing medicinal chemistry motifs, as well as late-stage modification of natural product and drug derivatives.

Introduction

The development of efficient synthetic methods, ideally those that convert chemical feedstocks into biologically important and complex structures, has significantly advanced drug discovery and development.[1] Direct difunctionalization of abundant alkenes is of fundamental importance to the synthesis of high-value molecules as evidenced by increasing research interests of the synthetic community in recent years.[2] Selective azidotrifluoromethylation of the carbon–carbon double bond enables to concomitantly assembly of two vicinal functional groups (N_3 and CF_3) in a single step. These structures have high biological significance due to the unique physical and electronic properties of the trifluoromethyl group.[3] On the other hand, the azide also serves as a handle for downstream derivatization to trifluoromethylated amines and heterocycles.[4] In particular, the well-established click chemistry of azides has empowered chemists to rapidly generate large libraries of CF_3-containing compounds for screening in drug discovery.[5]

To date, catalytic methods for efficient access to vicinal trifluoromethyl azides from alkenes are still limited. In 2014, Liu and co-workers pioneered the direct azidotrifluoromethylation of alkenes using copper catalysis (Scheme 1a).[6] In their report, Togni's reagent II and $TMSN_3$ were employed as the CF_3 and N_3 sources, respectively. Following this pattern, iron-catalyzed processes with extraordinary substrate scope were later reported by Hartwig[7] and Xu[8] (Scheme 1a). Other methods including oxidative radical relay[9] and photo–chemical reactions[10] were also successfully developed by a prudent choice of the precursors of CF_3 radical and azide. While these advances are invaluable, from a practical point of view, the requirement of transition-metal catalysts and expensive CF_3 sources (*e.g.*, Togni's reagents, Umemoto's reagent) has impeded their application especially for scale-up syntheses. Additionally, state-of-the-art approaches rely on the same three-component framework: addition of a CF_3 radical onto an alkene to form an alkyl radical or cation[11] and then trapped by a separate azide reagent, which generally constitutes a low level of mass



Scheme 1 Azidotrifluoromethylation of alkenes.

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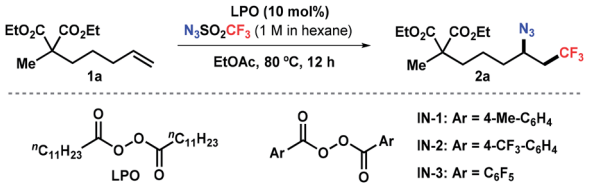
Table 1 Reaction optimization



Entry[a]	Deviation	2a[b] (%)
1	None	48
2	Dioxane, MeCN, DMF, or DCE instead of EtOAc	17–33
3	TBHP or DTBP instead of LPO	Trace
4	AIBN instead of LPO	20
5	**IN-1** instead of LPO	52
6	**IN-2** instead of LPO	50
7	**IN-3** instead of LPO	65
8	**IN-3** instead of LPO and with 2.5 equiv of $N_3SO_2CF_3$ (**standard conditions**)	86 (87)[c]
9	w/o initiator	N.R.

[a] Reaction conducted with **1a** (0.2 mmol), LPO (10 mol%), and $N_3SO_2CF_3$ (1.5 equiv., 1 M in hexane) in EtOAc (2 mL) at 80 °C for 12 h. [b] Determined by ^{19}F NMR of the crude reaction mixture using an internal standard. [c] Isolated yield. TBHP, *tert*-butyl hydroperoxide. DTBP, di-*tert*-butyl peroxide. AIBN, 2,2′-azobis(2-methylpropionitrile). N.R., no reaction.

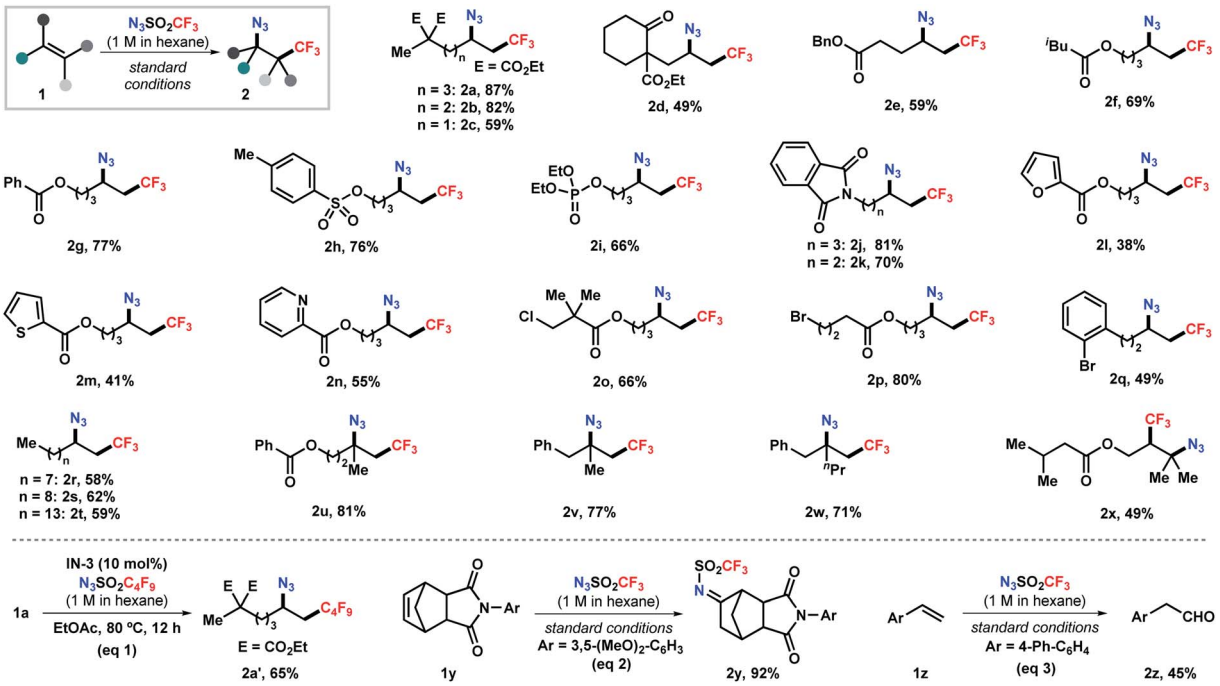
efficiency by producing stoichiometric side-products (*e.g.*, 2-iodobenzoic acid).[12] Therefore, the development of more environmentally benign and atom-economic alternatives is practically appealing and conceptually novel.

Trifluoromethanesulfonyl azide ($N_3SO_2CF_3$) is readily synthesized *in situ* by reacting trifluoromethanesulfonic anhydride with sodium azide in hexane (see ESI†). Although $N_3SO_2CF_3$ has been commonly used as a diazo- or trifluoromethanesulfonylamino-transfer reagent,[13] its ability to act as a radical precursor received little attention. The homolytic decomposition of $N_3SO_2CF_3$ to form a trifluoromethyl radical was first observed by Kamigata *et al.* in 1984.[14] In 2018, a significant work by the Studer group employed $N_3SO_2CF_3$ as an azide source for remote radical C–H azidation of amides by a fragmentation/1,5-HAT process.[15] Very recently, a notable radical 1,3-difunctionalization of allylboronic esters using $N_3SO_2CF_3$ was also reported by the same group.[16] These remarkable studies exemplified the potential utilization of $N_3SO_2CF_3$ as a bifunctional reagent.[17] Encouraged by this precedent and our serendipitous discovery (*vide infra*), we have developed a two-component azidotrifluoromethylation reaction of unactivated alkenes and $N_3SO_2CF_3$ (Scheme 1b). In this unprecedented strategy, $N_3SO_2CF_3$ serves as the sole precursor for both CF_3 and N_3 by releasing SO_2 gas, which therefore minimizes waste generation. This radical chain reaction is initiated by an acyl peroxide, avoids the use of transition-metal catalysts, tolerates a wide range of functional groups, and is amenable to late-stage modification of natural products and drug derivatives.

Results and discussion

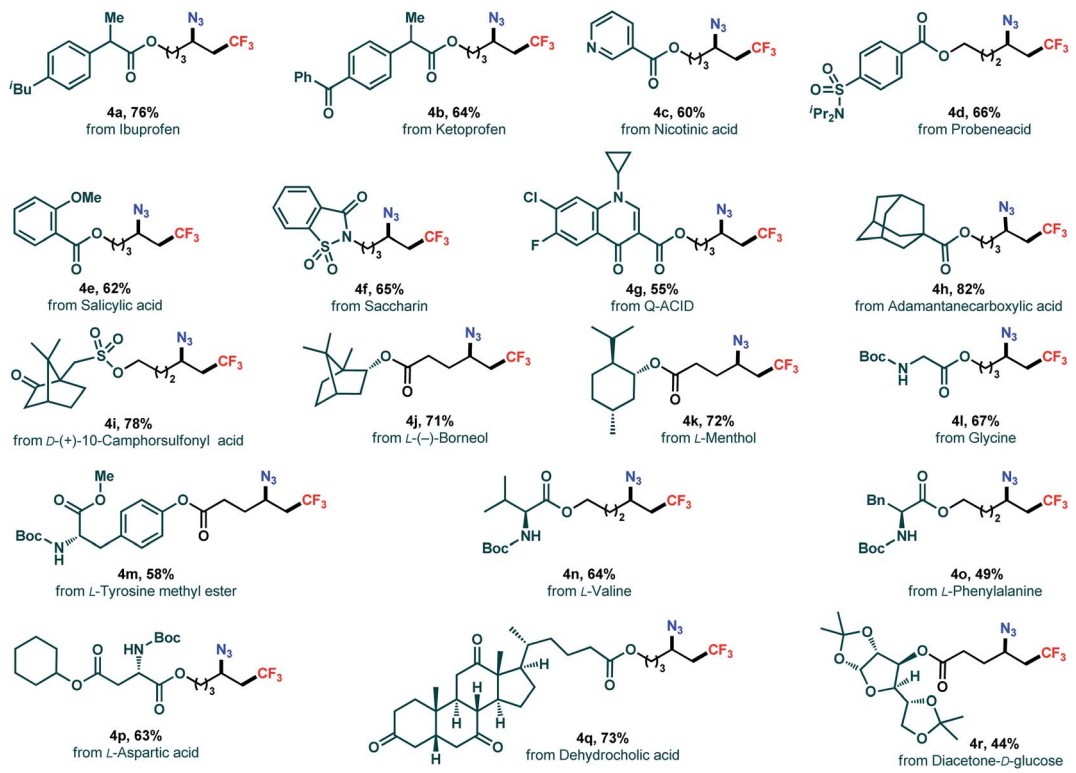
Our group has been interested in developing environmentally benign direct C–H amination methodologies.[18] In our efforts toward using trifluoromethanesulfonyl azide as a nitrene precursor for iron-catalyzed intermolecular allylic C–H amination, we unexpectedly observed azidotrifluoromethylation of the alkene (Scheme 1c). A control experiment disclosed that the reaction occurred without iron catalysts. Encouraged by this serendipity, we commenced the reaction optimization utilizing alkene **1a** as a model substrate as outlined in Table 1 (see Tables S1–S3 in ESI† for details). The desired product **2a** was obtained in 48% yield using 10 mol% of lauroyl peroxide (LPO) as a radical initiator and EtOAc as solvent (entry 1). Reactions in other solvents (*e.g.*, DCM, DMF, MeCN, entry 2 and Table S1†) were less effective. Varying the concentration of the reaction did not further improve the productivity. After surveying commonly used thermal radical initiators, such as organic peroxides and aliphatic azo compounds (entries 3–7), pentafluorobenzoyl peroxide (**IN-3**) emerged as the choice resulting in 65% yield of **2a** (entry 7). To our delight, an increased yield (87%) was obtained by using 2.5 equivalent of $N_3SO_2CF_3$ (entry 8). Unsurprisingly, radical initiators were indispensable and no desired product was detected in their absence (entry 9). It should be noted that $N_3SO_2CF_3$ should be handled with cautions, although its stock solution in hexane is fairly stable (see ESI†).

Next, we set out to explore the substrate scope of this reaction (Scheme 2). Aliphatic alkenes bearing a broad array of functional groups, such as ester, ketone, tosylate, phosphate, and phthalimide, were viable substrates under the standard conditions, delivering the corresponding products in moderate to good yields (**2a–2k**). Heterocycles relevant to medicinal chemistry, including furan, thiophene, and pyridine, were tolerated as well, albeit in moderate yields (**2l–2n**). The mild, base- and transition-metal-free reaction conditions also allowed the compatibility of chloride- and bromide-containing substrates with the halides unscathed (**2o–2q**). Moreover, abundant unsaturated hydrocarbons were efficiently converted



Scheme 2 Scope of the alkene azidotrifluoromethylation. Reactions conducted on a 0.2 mmol scale (except 0.4 mmol for **2e**) under the standard conditions (entry 8, Table 1).

into high-value bifunctionalized products in 58–62% yields (**2r–2t**). This simple process also pertains to sterically hindered alkenes. 1,1-Disubstituted alkenes were selectively transformed into the tertiary azides **2u–2w** in 71–81% yields. The reaction with 1,1,2-trisubstituted alkenes delivered the corresponding bifunctionalized product **2x** in moderate yield. This method

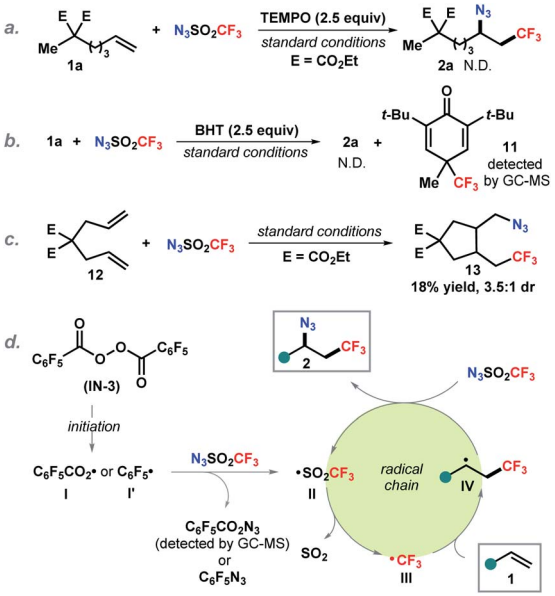


Scheme 3 Late-stage modification of drug and natural product derivatives. Reactions conducted on a 0.2 mmol scale under the standard conditions (entry 8, Table 1).

also enabled the efficient installation of perfluoroalkyl groups (*e.g.*, C_4F_9, eqn (1)), given the readily synthesis of the corresponding sulfonyl azides. Surprisingly, further expanding the scope to cyclic olefin **1y** and styrene **1z** unexpectively delivering imine **2y** and aldehyde **2z** in 92% and 45% yield, respectively (eqn (2) and (3)), which probably formed through a [3 + 2] cycloaddition pathway.[19] The reaction with vinyl ether resulted in a complex mixture.[19b] Attempts to employ acrylate or vinyl amide under the standard conditions failed to give any desired azidotrifluoromethylation product but led to polymerization of the substrates (Scheme S1 in ESI†).

The absence of transition metals and operationally simple procedure of this reaction offers a practical tool in late-stage modification of densely functionalized biologically relevant molecules(Scheme 3). Functionalization of a series of complex structures (**3a–3g**) derived from pharmaceuticals were successfully achieved in good yields (**4a–4g**). The alkenes synthesized from terpenes, norneol and menthol, reacted smoothly to the corresponding azidotrifluoromethylated products (**4j**, **4k**) in 71% and 72% yields, respectively. Remarkably, derivatives of amino acid including glycine (**4l**), tyrosine (**4m**), valine (**4n**), phenylalanine (**4o**), and aspartic acid (**4p**), were amenable as well to the reaction yielding the corresponding difunctionalized products smoothly. Moreover, a steroid example and a carbohydrate substrate were also included (**4q**, **4r**). Overall, these results showcased the broad applicability and usefulness of our chemistry.

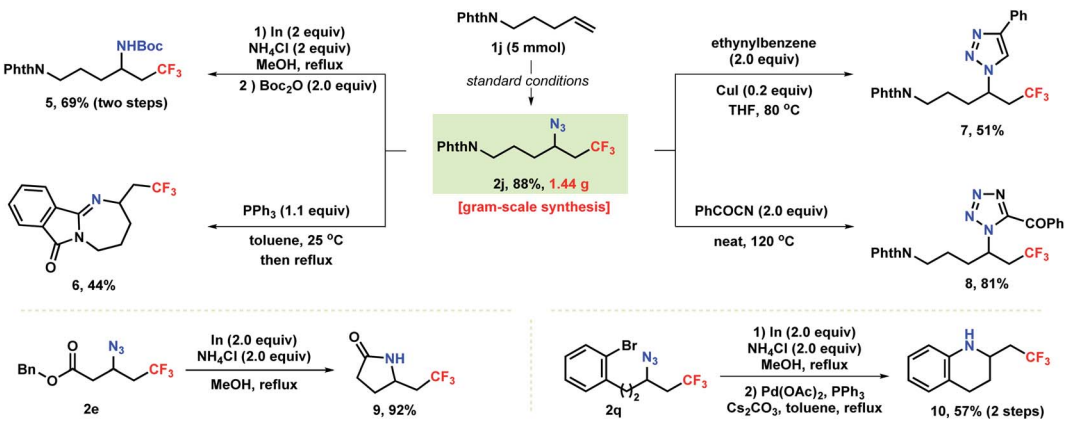
As shown in Scheme 4, the robustness of the reaction was demonstrated by a gram–scale reaction (5 mmol) under the standard conditions providing azidotrifluoromethylation product **2j** in 88% yield. The azide unit of the products accessed above can be conveniently converted into privileged medicinal chemistry motifs such as amines and heterocycles. Reduction of azide **2j** with In/NH_4Cl produced a vicinal trifluoromethylated primary amine **5** in 69% yield. Notably, treatment of **2j** with triphenylphosphine formed tetrahydro-1,3-diazepine **6** *via* a Staudinger reaction/aza-Wittig sequence. Moreover, [3 + 2] annulation of **2j** with ethynylbenzene and benzoyl cyanide resulted in the formation of CF_3-containing triazole **7** and tetrazole **8**, respectively. Additionally, selective reduction of an azide **2e** bearing a pendant ester group proceeded with concomitant aminolysis to provide γ-butyrolactam **9** in 92% yield. In a two-step protocol, reduction of azide **2q** to amine followed by subsequent cross-coupling delivered tetrahydroquinoline **10** in 57% overall yield.



Scheme 5 Mechanistic investigation.

Notably, all the trifluoromethyl-containing compounds accessed through these derivatizations are highly prevalent and commonly used in pharmaceuticals or as biological probes, demonstrating the ease of our chemistry in incorporating of trifluoromethyl group into these reminiscent motifs.

To gain mechanistic insight into this reaction, control experiments were carried out (Scheme 5). Addition of a radical scavenger TEMPO completely inhibited the reaction (Scheme 5a). Similarly, butylated hydroxytoluene (BHT) as an additive prevented the formation of the azidotrifluoromethylation product. The detection of trifluoromethyl adduct **11** by GC-MS (MS = 288.1) indicates that the trifluoromethyl radical is



Scheme 4 Synthetic application.

likely involved in this transformation (Scheme 5b). It is known that 5-hexenyl radical analogues undergo 5-*exo*-cyclization to the cyclopentylcarbinyl radical and are commonly employed as radical clocks.[20] The reaction with substituted 1,6-diene **12** delivered a cyclization product **13** which suggests that the addition of trifluoromethyl radical to the alkene forms an alkyl radical followed by 5-*exo*-cyclization (Scheme 5c). On the basis of the above observations and literature reports,[21] a putative radical chain pathway was illustrated as shown in Scheme 5d. First, thermal decomposition of the radical initiator **IN-3** produces an aryl carboxylic radical **I** or an aryl radical **I′**,[22] which reacts with trifluoromethanesulfonyl azide generating trifluoromethanesulfonyl radical **II**, following by SO_2 release to form the trifluoromethyl radical **III**.[23] Subsequent addition of **III** onto the alkene provides an alkyl radical **IV**. Finally, azidation of **IV** with $N_3SO_2CF_3$ yields the desired product **2** along with regeneration of the chain carrying radical **II**.

Conclusions

In summary, we have developed a transition-metal free azidotrifluoromethylation reaction of unactivated alkenes for the synthesis of vicinal trifluoromethyl azides. This unprecedented difunctionalization process employs trifluoromethanesulfonyl azide as the sole precursor for both CF_3 and N_3. The application was demonstrated by late-stage functionalization of complex bio-important molecules and converting the products into the corresponding CF_3-containing amine, lactam, and other privileged heterocycles. This study provides an atom economic, cost efficient, and operationally simple method for the synthesis of valuable vicinal difunctionalized structures from chemical feedstocks.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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