Organic LETTERS

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Photoredox-Induced Three-Component Azido- and Aminotrifluoromethylation of Alkenes

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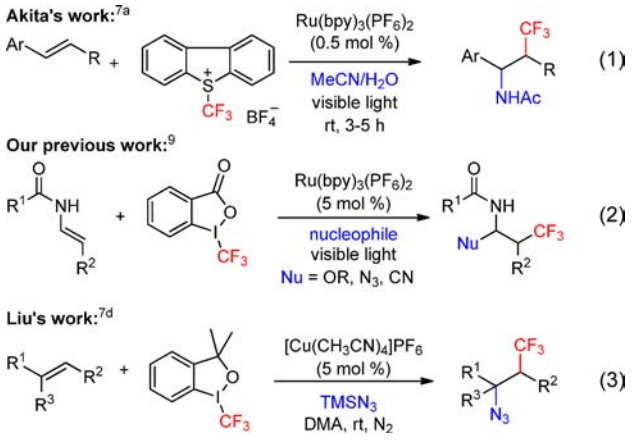
Supporting Information

ABSTRACT: We report herein a photoredox-catalyzed azidotrifluoromethylation of alkenes. Under the optimized conditions using $[Ru(bpy)_3(PF_6)_2]$ as the photocatalyst and Umemoto's reagent as the CF_3 source, a wide range of substituted styrenes as well as various activated and nonactivated alkenes can readily be difunctionalized, affording β-trifluoromethylated azides or amines in good yields.

The incorporation of a trifluoromethyl group into organic molecules can have a dramatic impact on the physical and chemical properties of bioactive compounds.[1] Undoubtedly, these features have stimulated the development of successful strategies for the efficient synthesis of functionalized trifluoromethylated compounds, and a large number of methods have been reported.[2] Among the contemporary methods, visible-light photoredox-mediated direct trifluoromethylation of alkenes has allowed major progress. The methods which consist of trapping the radical intermediate (or its corresponding oxidized electrophilic cation) with oxygen,[3] halogen,[4] carbon,[5] and hydrogen[6] nucleophiles are especially attractive and promising for structural diversity. However, the use of amines in such radical-cationic domino processes have been less studied,[7] due to their oxidation via the reductive quenching of photocatalysts.[8] To circumvent the problem, Akita et al. used acetonitrile as the nitrogen source and developed the first example of a photoredox-catalyzed aminotrifluoromethylation of styrenes yielding to CF_3-substituted amide products (Scheme 1, eq 1).[7a] Recently, our group reported the photocatalyzed azidotrifluoromethylation of enecarbamates,[9] allowing access to β-trifluoromethyl amines, which are important structural motifs in many bioactive compounds (Scheme 1, eq 2).[10] Very recently Liu et al.[7d] disclosed copper-catalyzed azidotrifluoromethylazidation of alkenes. Although the scope was impressive, few examples of β-substituted styrenes were described and the yields were quite moderate (33−45%, Scheme 1, eq 3). Despite these achievements, other methods to make diverse trifluoromethylated amines still need to be developed.

Scheme 1. Previous Work on Aminotrifluoromethylation



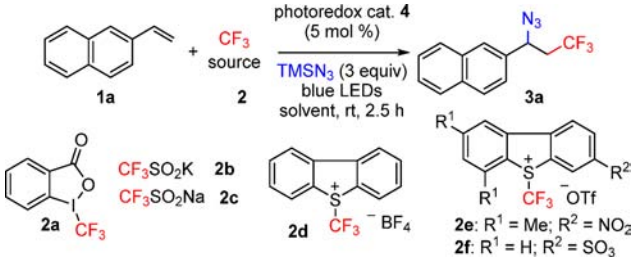
Based on our experience,[9,11,12] and considering the importance of the azide group as stable precursors of amines, we envisioned the generalization of this photoredox-catalyzed azidotrifluoromethylation reaction to standard alkenes. Herein we wish to report an efficient process giving rise to these key and original β-trifluoromethyl amines. Direct azido- and aminotrifluoromethylation of a wide range of C−C double bonds are described in this letter. Extension to more challenging and original primary amines[13] is furthermore presented.

On the basis of our previous work,[9] we initially attempted the trifluoromethylation of 2-vinylnaphthalene (**1a**) with Togni's reagent (**2a**)[14] in the presence of $Ru(bpy)_3(PF_6)_2$ photocatalyst **4a** and sodium azide (NaN_3) under visible light irradiation (blue LEDs). However, these conditions failed to give the desired trifluoromethylated product giving back mostly starting material. When azidotrimethylsilane ($TMSN_3$) was used in CH_2Cl_2, the reaction was sluggish and incomplete after 24 h, and the expected three-component trifluoromethylated alkyl azide **3a** was obtained in only 9% yield (Table 1, entry 1). These quite disappointing results were actually not so surprising considering the previous work devoted to this topic.[3−6,9] The photocatalytic trifluoromethylation process is a very efficient synthetic method but strongly depends on the substrates used. The choice of the CF_3 source must be adapted to the targeted system

Received: July 23, 2014
Published: August 7, 2014

dx.doi.org/10.1021/ol5021477 | Org. Lett. 2014, 16, 4340−4343

Table 1. Survey of Reaction Conditions for the Photocatalyzed Azidotrifluoromethylation of 1a[a]



entry	2	solvent	photoredox cat.	yield (%)[b]
1	**2a**	CH_2Cl_2	$Ru(bpy)_3(PF_6)_2$ (**4a**)	9
2	**2b**	CH_2Cl_2	**4a**	–[c]
3	**2c**	CH_2Cl_2	**4a**	–[c]
4	**2d**	CH_2Cl_2	**4a**	74
5	**2e**	CH_2Cl_2	**4a**	50
6	**2f**	CH_2Cl_2	**4a**	–[c]
7	**2d**	CH_2Cl_2	$Ru(bpy)_3Cl_2$ (**4b**)	68
8	**2d**	CH_2Cl_2	$Ir(ppy)_2(dtbbpy)(PF_6)$ (**4c**)	57
9	**2d**	CH_2Cl_2	$Ir(bpy)_3(PF_6)_3$ (**4d**)	–[c]
10	**2d**	CH_2Cl_2	$Ir(ppy)_3$ (**4e**)	38

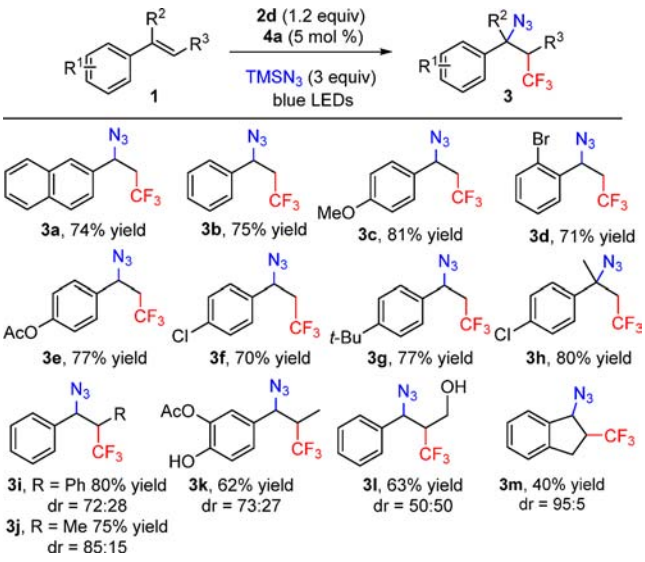
[a]General conditions: **1a** (0.10 mmol), CF_3 source (0.12 mmol), **4** (0.05 equiv) irradiated at rt for 2.5 h. [b]Yields referred to chromatographically pure product. [c]Reaction time: 24 h.

demonstrating the importance of this study. To increase the yield, various sources of the CF_3 radical were then tested. While no reaction took place with potassium or sodium trifluoromethanesulfinate **2b–c** (Langlois reagent), Umemoto's reagent **2d**[15] reacted very smoothly and afforded **3a** in 74% yield. Other substituted *S*-(trifluoromethyl)dibenzothiophenium salts **2e–f** were found to be less reactive than **2d** (yield <50%, entries 5–6). Different Ru and Ir photocatalysts **4b–e** (entries 7–10) as well as various solvents (see Supporting Information) were also screened. The best results were obtained using [$Ru(bpy)_3(PF_6)_2$] in CH_2Cl_2 (entry 4).

With the optimized reaction conditions in hand, the scope of this photoredox-catalyzed three-component azidotrifluoromethylation was studied (Scheme 2). Styrene derivatives **1a–g** bearing various substituents on the aromatic ring, including electron-withdrawing and -donationg groups, reacted smoothly and led to the corresponding trifluoromethylated azides **3a–g** in good yields (70–81%). 1,1-Disubstituted substrate **1h** was also compatible with this transformation, providing the desired β-CF_3 tertiary alkyl azide **3h** in 80% yield. Remarkably, internal alkenes **1i–l** were found to exhibit a similar reactivity compared to terminal alkenes. Thus, the corresponding adducts **3i–l** were obtained in 62–80% yield, with diastereomeric ratios from 50:50 to 85:15. This photocatalyzed transformation thus represents a complementary approach to the copper-catalyzed trifluoromethylazidation of alkenes.[7d] It is also worth noting that our methodology is compatible with a variety of functional groups, such as halogen, ester, phenol, and alcohol. Notably, the reaction of cinnamyl alcohol **1l**, having a primary hydroxy group, afforded compound **3l** in good yield without any oxytrifluoromethylation product.

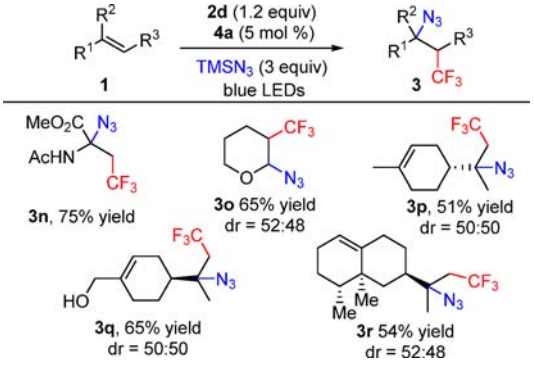
Extension of this novel multicomponent protocol to other alkenes was delightfully successful. Under the same conditions, activated alkenes such as methyl 2-acetamidoacrylate **1n** and dihydropyrane **1o** were suitable substrates for this azidotrifluoromethylation reaction and gave the corresponding trifluoromethylated azides **3n** and **3o** in good yields (Scheme 3). Interestingly, this transformation could also be broadened to

Scheme 2. Substrate Scope of the Azidotrifluoromethylation of Styrene Derivatives 1[a,b,c]



[a]Reaction conditions: styrene **1** (0.10 mmol), **2d** (0.12 mmol), **4a** (0.05 equiv), $TMSN_3$ (3 equiv), in CH_2Cl_2 (2.0 mL) irradiated at rt for 2.5 h. [b] Yields referred to chromatographically pure product. [c] dr determined by ^{19}F NMR analysis of crude mixtures.

Scheme 3. Substrate Scope of the Azidotrifluoromethylation of Alkenes 1[a,b,c]



[a]Reaction conditions: alkene **1** (0.10 mmol), **2d** (0.12 mmol), **4a** (0.05 equiv), $TMSN_3$ (3 equiv), in CH_2Cl_2 (2.0 mL) irradiated at rt for 2.5 h. [b] Yields referred to chromatographically pure product. [c] dr determined by ^{19}F-NMR analysis of crude mixtures.

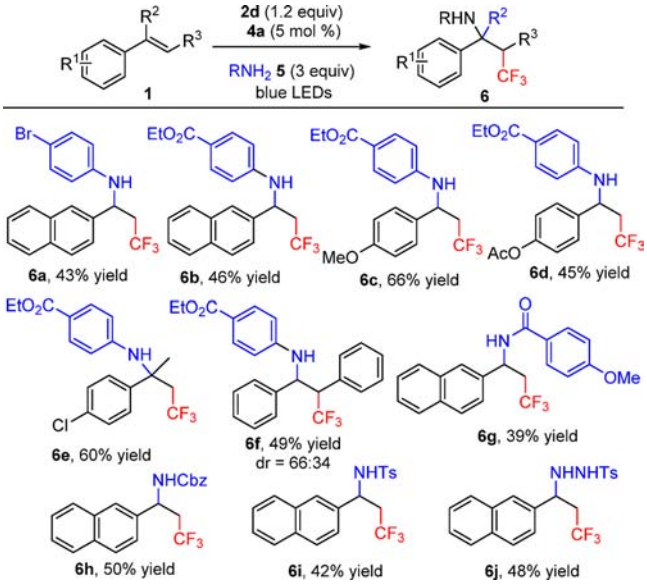
unactivated 1,1-disubstituted alkenes. In particular, terpene derivatives such as (*R*)-(+)-limonene **1p**, (*S*)-(−)-perillyl alcohol **1q**, and valencene **1r** reacted smoothly to furnish the expected tertiary alkyl azides **3p–r**.[16] Remarkably, the reaction was completely regioselective, without any trifluoromethylation of the trisubstituted C–C double bond.

Encouraged by these results, we next sought to extend the methodology to more challenging amines. Unfortunately, when $TMSN_3$ was replaced by a primary or a secondary amine such as *n*-butylamine or dimethylamine, the reaction mixture turned dark red, and no trifluoromethylated adduct was obtained. The same result was observed with easily oxidizable electron-rich *p*-anisidine. However, when anilines **5a–b** bearing electron-

dx.doi.org/10.1021/ol5021477 | Org. Lett. 2014, 16, 4340–4343

withdrawing groups were used under the same conditions, we were pleased to see that the reaction proceeded smoothly to give the corresponding β-trifluoromethylated amines **6a–b** in 43–46% yield (Scheme 4). To our delight, this reaction was extended

Scheme 4. Scope of the Aminotrifluoromethylation of Styrenes 1[a,b,c]

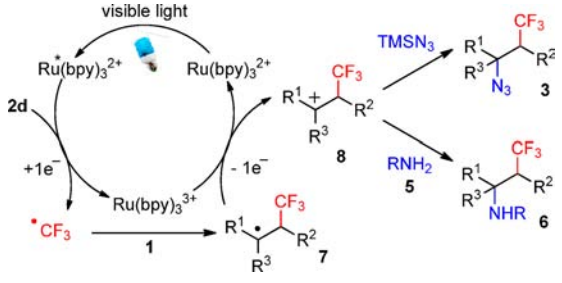


[a]Reaction conditions: styrene **1** (0.10 mmol), **2d** (0.12 mmol), **4a** (0.05 equiv), amine 5 (3 equiv), in CH_2Cl_2 (2.0 mL) irradiated at rt for 2.5 h. [b] Yields referred to chromatographically pure product. [c] dr determined by ^{19}F NMR analysis of crude mixtures.

to various α- or β-substituted styrenes bearing electron-withdrawing or -donating groups. These compounds were suitable partners for this reaction, leading to the expected β-trifluoromethylated anilines **6c–f** in up to 66% yield. We then turned our attention to other less oxidizable, albeit less nucleophilic, amine derivatives. To our delight, carbamates, amides, sulfonamides, and hydrazines were found to be effective nucleophilic partners in this photocatalyzed protocol, affording the desired compounds **6g–j** in up to 50% yield.

The following control experiments were carried out to gain some mechanistic insight. No reaction took place in the absence of irradiation and/or $[Ru(bpy)_3(PF_6)_2]$ **4a**. Moreover, the formation of **3** or **6** was inhibited in the presence of radical scavengers such as TEMPO, suggesting that a radical/cationic process is involved in this reaction. On the basis of the above results as well as other reports, a plausible reaction mechanism is shown in Scheme 5. First, irradiation with visible light excites

Scheme 5. Plausible Reaction Mechanism



$Ru(bpy)_3^{2+}$ into a strong reductant species $*Ru(bpy)_3^{2+}$, which performs a single electron transfer (SET) to generate $\cdot CF_3$ from Umemoto's reagent **2d**.[3a,6a,7a,17c] Subsequent regioselective addition of electrophilic $\cdot CF_3$ to alkene **1** leads to the radical species **7**, which can be further oxidized into cation **8** by SET from $Ru(bpy)_3^{3+}$.[18] Final nucleophilic trapping of this β-trifluoromethylated carbocation by $TMSN_3$ or amine **5** affords the corresponding trifluoromethylated adduct **3** or **6**. The high regioselectivity in such a radical to alkenes process is due to the stability of the alkyl radical and steric factors. Indeed, the radicals are very sensitive to steric factors, so they attack the least hindered carbon of the double bond. Additionally, the formation of a more stable benzylic radical or tertiary radical intermediate **7** than the primary one also plays an important role in the regioselectivity.

In conclusion, we have successfully developed a completely regioselective three-component azido- and aminotrifluoromethylation of alkenes using visible-light-driven photoredox catalyst $[Ru(bpy)_3(PF_6)_2]$ under mild conditions. This difunctionalization protocol enjoys a reasonably broad substrate scope and good functional group compatibility. Remarkably, terminal alkenes as well as internal alkenes are compatible with this completely regioselective radical/ionic process. Extension of this method to the preparation of other CF_3-containing scaffolds is currently underway in our laboratory and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and spectral data for all new compounds are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank ICSN and CNRS for financial support and doctoral fellowships to A.C.; G.D. thanks Labex Charmmmat for a postdoctoral fellowship.

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(16) Reaction of monosubstituted unactivated alkenes such as 1-octene led to the desired product only in poor yield (<20%).

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(18) Oxidation of **7** by Umemoto's reagent **2d** to regenerate $\cdot CF_3$ (radical chain propagation) was excluded, as the reaction requires continuous irradiation.