ACS Catalysis

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Trifluoromethylative Bifunctionalization of Alkenes via a Bibenzothiazole-Derived Photocatalyst under Both Visible- and Near-Infrared-Light Irradiation

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Cite This: *ACS Catal.* 2023, 13, 8119–8127 Read Online

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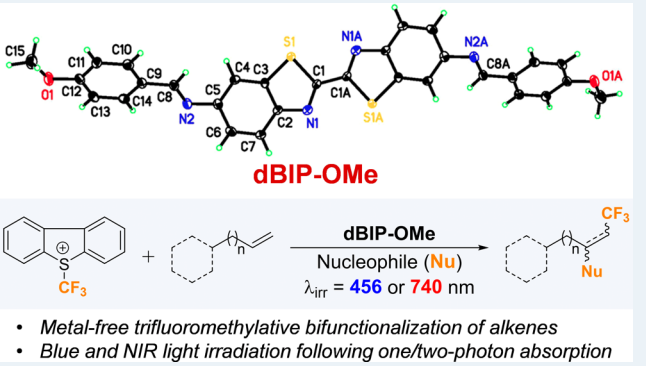
ABSTRACT: The incorporation of trifluoromethyl groups into organic molecules such as agrochemicals and pharmaceuticals has attracted a significant amount of interest because they will impact the binding ability, lipophilicity, metabolic stability, and chemical stability of the resulting molecules. Over the past few years, photocatalytic trifluoromethylation of aryl alkenes has been reported, which typically requires precious Ru/Ir-containing photocatalytic systems. Herein, we report a metal-free organic photocatalyst composed of a bibenzothiazole core and two imine-bridged methoxyphenyl substituents (**dBIP−OMe**), which is able to drive trifluoromethylative bifunctionalization of alkenes photocatalytically without the use of any sacrificial reagents. Mechanistic studies reveal two consecutive single-electron-transfer steps between the excited **dBIP−OMe***, the CF_3 precursor (Umemoto's reagent), and the alkene substrate. Substrate scope studies demonstrated that our trifluoromethylative bifunctionalization strategy using **dBIP−OMe** is applicable for both aryl and aliphatic alkenes. Furthermore, a variety of nucleophiles, such as H_2O, acetate, cyanide, azide, etc., can be readily incorporated into the carbocation intermediate once the foremost trifluoromethylation step is accomplished, substantially broadening the application scope of this photocatalytic method. Finally, taking advantage of the two-photon absorption capability of **dBIP−OMe** in the near-infrared region, we demonstrated that the hydroxytrifluoromethylation of styrene could be achieved using an inexpensive 740 nm LED as the sole light source.



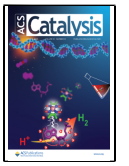
KEYWORDS: *organic photocatalysis, trifluoromethylation, alkene bifunctionalization, bibenzothiazole derivatives, two-photon absorption*

INTRODUCTION

Organic photocatalysis has enjoyed rapid developments over the past 15 years, and many thermocatalytically challenging reactions can now be readily achieved using photons as the sole energy input.[1] Thanks to their rich and robust photophysical properties, noble-metal-containing coordination complexes, such as $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridyl), $[Ir(ppy)_2(bpy)]^+$ (ppy = 2-phenylpyridine), and their close analogues have been the dominant photosensitizers in homogeneous organic photocatalysis.[2] However, considering the cost for large-scale applications, it is more desirable to replace those expensive Ru/Ir-based chromophores with more earth-abundant and inexpensive organic alternatives. Indeed, molecular organic photosensitizers have attracted growing recognition as promising candidates.[1c,3]

Among many types of organic transformations, trifluoromethylation of alkenes stands out as an appealing approach to introduce $-CF_3$ functional groups to existing molecular scaffolds. Because the incorporation of fluoromethyl groups (e.g., $-CF_3$) can influence the lipophilicity, binding selectivity, metabolism, and excretion properties of small molecules in the biological environment, the development of effective trifluoromethylation strategies is highly desirable for the development of pharmaceuticals and agrochemicals. The most common strategy is the generation and utilization of a trifluoromethyl radical ($^{\bullet}CF_3$) via either one-electron reduction of electrophilic trifluoromethylating reagents, such as CF_3I, CF_3Br, *N*-hydroxybenzimidoyl chloride trifluoroacetate, Umemoto's and Togni's reagents, or oxidation of CF_3SO_2Na, $AgCF_3$, and $CuCF_3$. Indeed, various thermocatalytic trifluoromethylation reactions mediated by transition-metal catalysts have been

Received: April 21, 2023
Revised: May 21, 2023
Published: June 2, 2023



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ACS Catal. 2023, 13, 8119–8127

reported (Figure 1A).[4,5] Nevertheless, stoichiometric amounts of redox reagents are usually required. For instance, Li et al.

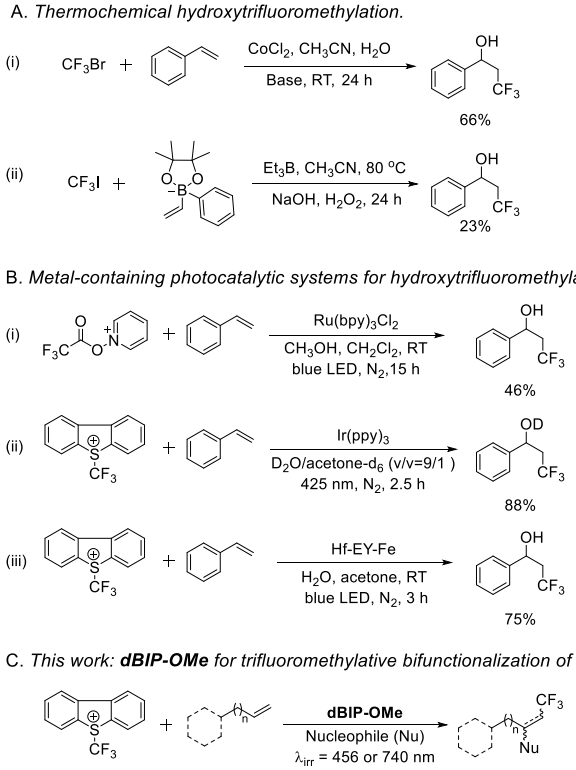

Figure 1. (A) Representative thermochemical hydroxytrifluoromethylation of styrene. (B) Selected photocatalytic hydroxytrifluoromethylation using metal-containing photocatalytic systems. (C) Photocatalytic trifluoromethylative bifunctionalization of alkenes using our organic photosensitizer **dBIP−OMe** under both visible and near-infrared-light irradiation.

recently reported the hydroxytrifluoromethylation of alkenes using CF_3Br and atmospheric O_2 mediated by cobalt-tertiary amine (Figure 1Ai).[6] Using Togni's reagent as a $^{\bullet}CF_3$ precursor, Kischkewitz et al. accomplished the synthesis of 3,3,3-trifluoro-1-phenylpropan-1-ol (after NaOOH oxidation) from vinyl phenyl piacoboronate in the presence of tetrabutylammonium iodide as an initiator (Figure 1Aii).[7] Encouraged by the competence of photoredox chemistry in producing alkyl radicals for various organic transformations,[8,9] photocatalytic trifluoromethylation of aryls and alkenes has also been explored, primarily using noble-metal-containing chromophores.[10] For instance, Koike, Akita,[11] McMillan, Stephenson,[11c] and others have systematically performed trifluoromethylation reactions using Ru/Ir-based photocatalysts (Figure 1Bi,ii). More recently, Lin et al. reported a bifunctional metal−organic layer consisting of eosin Y as the photosensitizer and Fe-TPY (TPY = 4′-(4-carboxyphenyl)-[2,2′:6′,2″-terpyridine]-5,5″-dicarboxylate) as the catalytic center to photocatalyze the hydroxytrifluoromethylation of alkenes (Figure 1Biii).[12]

Several organic photoredox catalysts composed of acridiniums, pyryliums, or phenoxazines have been recently reported for many organic transformations.[13] However, to the best of our knowledge, there is no metal-free photocatalytic system reported to drive the trifluoromethylative bifunctionalization of alkenes. In fact, given the radical nature of $^{\bullet}CF_3$, net redox neutral bifunctionalization of alkenes could be realized if the employed photocatalysts are equipped with both competent excited-state reduction power and sufficient ground-state oxidation power. Thus, in the presence of a suitable nucleophile, trifluoromethylative bifunctionalization of alkenes could be realized following two consecutive single-electron-transfer steps (Figure 1C). Herein, we report a novel bibenzothiazole-derived organic photocatalyst, **dBIP−OMe**, with adequate redox power, which is able to achieve trifluoromethylative bifunctionalization of both aryl and aliphatic alkenes under visible-light irradiation (λ_{irr} = 456 nm). The popular Umemoto's reagent was used as the CF_3 source, and no stoichiometric sacrificial reagents were required. Furthermore, taking advantage of its extended π-conjugation and quadrupolar intramolecular charge transfer, **dBIP−OMe** also possesses two-photon absorption capability and hence exhibits photoredox activity for the hydroxytrifluoromethylation of styrene under near-infrared-light irradiation (λ_{irr} = 740 nm).

RESULTS AND DISCUSSION

Following our recently reported strategy,[3c] the synthesis of **dBIP−OMe** began with commercially available benzothiazole.

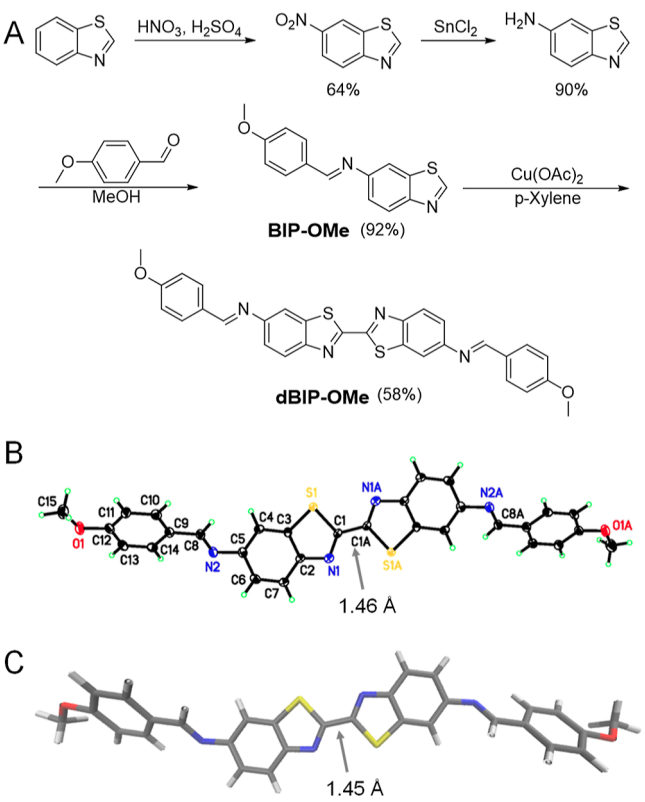

Figure 2. (A) Synthetic scheme of **dBIP−OMe** starting from benzothiazole. (B) Single-crystal structure of **dBIP-OMe** drawn at 50% probability as ellipsoids. The methoxyphenyl groups are rotated 47° relative to the coplanar benzothiazole groups; C1−C1A = 1.463(9) Å. (C) DFT-calculated structure of **dBIP−OMe** with the corresponding C−C = 1.45Å.

Consecutive nitration and reduction at the C-6 position of benzothiazole afforded 6-aminobenzothiazole in a high yield (Figure 2A). Subsequent condensation with 4-methoxybenzaldehyde resulted in the critical intermediate **BIP−OMe** with an

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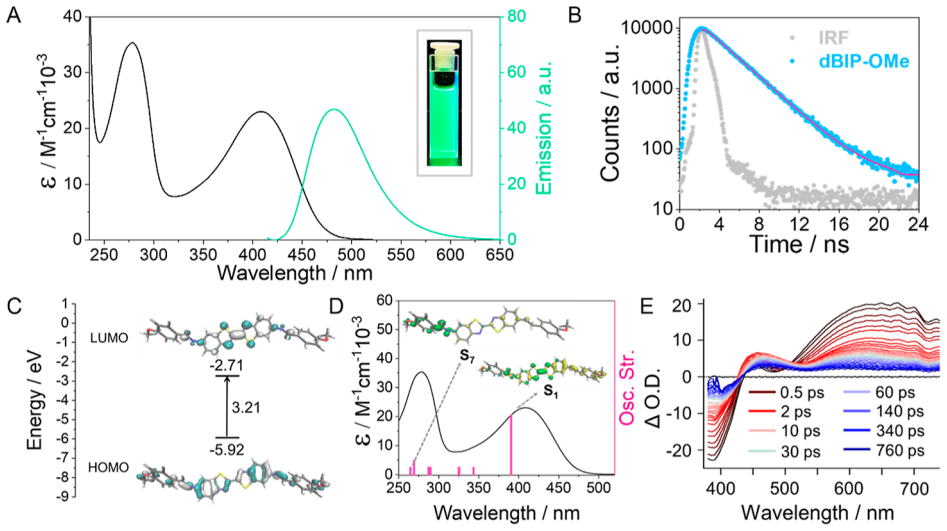

Figure 3. (A) Absorption and emission spectra of **dBIP−OMe** in CH_3CN. Inset: photograph of a 10 μM **dBIP−OMe** solution in CH_3CN. (B) Emission decay profile upon excitation at 405 nm. The "instrument response function" (IRF) was also included for comparison. (C) DFT-calculated frontier orbitals of **dBIP−OMe**. (D) Comparison between the TD-DFT-calculated singlet excited states and the experimental absorption spectrum with the EDDMs of S_1 and S_7 states (isovalue = 0.04; yellow and green indicate the electron density decrease and increase, respectively). (E) Femtosecond transient absorption spectra in CH_3CN upon excitation at 400 nm.

imine bridge. Finally, an oxidative Sonogashira homocoupling of **BIP−OMe** at its C-2 position resulted in the desired product **dBIP−OMe** in a decent yield of 58%. The synthetic details and the spectroscopic characterizations of **dBIP−OMe** and all the synthetic intermediates are included in the Supporting Information (Figures S1−S7). The single-crystal structure (CCDC 2249853, Figure 2B) of **dBIP−OMe** shows a coplanar arrangement of the two benzothiazole cores with a torsion angle of ∠S1−C1−C1A-S1A = 180°. Notably, the C1−C1A bond distance was 1.463(9) Å, shorter than a typical C−C single bond (~1.54 Å), inferring the effective π-conjugation between the two connected benzothiazole units. Density functional theory (DFT) calculations were also performed to obtain the optimized geometry of **dBIP−OMe**. As shown in Figure 2C, the most energetically favorable geometry adopted the S-trans configuration with a dihedral angle of 179.6° and a C−C bond length of 1.45 Å between the two benzothiazole units, perfectly matching the single-crystal structure displayed in Figures 2B and S9.

As shown in Figure 3A, **dBIP−OMe** exhibits two broad absorption bands in the UV−visible region, 279 nm (ε = 35,361 M^{-1} cm^{-1}) and 408 nm (ε = 23,034 M^{-1} cm^{-1}), and bright green emission with a maximum at 483 nm in CH_3CN. Its emission quantum yield was measured as 0.51, together with a lifetime of 2.9 ns (Figure 3B). Based on the DFT calculation, the highest occupied molecular orbital (HOMO, −5.92 eV) is distributed over the entire molecule with some degree of contribution from the terminal methoxyphenyl groups (Figure 3C), in agreement with their electron-donating character. In contrast, its lowest unoccupied molecular orbital (LUMO, −2.71 eV) is largely located at the central bibenzothiazole core, consistent with its electron-deficient nature. More DFT-calculated molecular orbitals are included in Figure S10. Furthermore, time-dependent DFT (TD-DFT) computations were carried out to shed light on its electronic transitions. The first singlet excited state (S_1) of **dBIP−OMe** was calculated at 390 nm (f = 3.12), and its electron density difference map (EDDM) indicated intramolecular charge transfer character, with the bibenzothiazole core serving as the electron acceptor (Figures 3D and S11). Another significant state was S_7 located at 269 nm (f = 0.40), characteristic of a $\pi\pi^*$ transition. Overall, these calculated excited-state transitions match the experimental absorption spectrum quite well.

To probe the early processes of **dBIP−OMe** upon excitation, its femtosecond transient absorption spectra upon excitation at 400 nm were also collected. As shown in Figure 3E, ground-state bleaching was observed between 380 and 440 nm. An excited-state absorption band was detected at 455 nm with another broader feature beyond 550 nm, which can be attributed to the excited-state absorption of those intramolecular charge transfer states.[14] Fitting the signals at 624 nm resulted in a fast internal conversion process (<1 ps) and a singlet excited-state lifetime >1 ns, in agreement with the measurement of its emission lifetime (2.9 ns).

Encouraged by the above photophysical properties, we next explored its application as an organic photocatalyst in photoredox reactions, such as trifluoromethylation of alkenes. Previous studies in this area mainly relied on noble-metal-containing (e.g., Ru and Ir) photosensitizers, while metal-free systems have rarely been reported. Because **dBIP−OMe** exhibits ground-state reduction and oxidation potentials at −1.16 and 0.93 V vs Ag/Ag^+, respectively, we were able to estimate its excited-state reduction potential at −1.64 V vs Ag/Ag^+ after considering its emission maximum. Such a large excited-state reduction potential makes it possible to reduce Umemoto's reagent to release a $^{\bullet}CF_3$ radical (Figures S12−S13). Indeed, when using **dBIP−OMe** as the photosensitizer and TEMPO as a radical scavenger, 456 nm irradiation of Umemoto's reagent resulted in the formation of a TEMPO-CF_3 adduct (Figures 4A and S14). In contrast, no such adduct was observed in the absence of **dBIP−OMe** (Figure S15).

After confirming that $^{\bullet}CF_3$ could be generated from Umemoto's reagent using **dBIP−OMe** as a photosensitizer, we subsequently decided to evaluate its applicability toward the photocatalytic trifluoromethylation of alkenes using styrene as a model substrate. Under the default condition of 0.2 mmol styrene, 1.1 equivalents of Umemoto's reagent, 5 mol %

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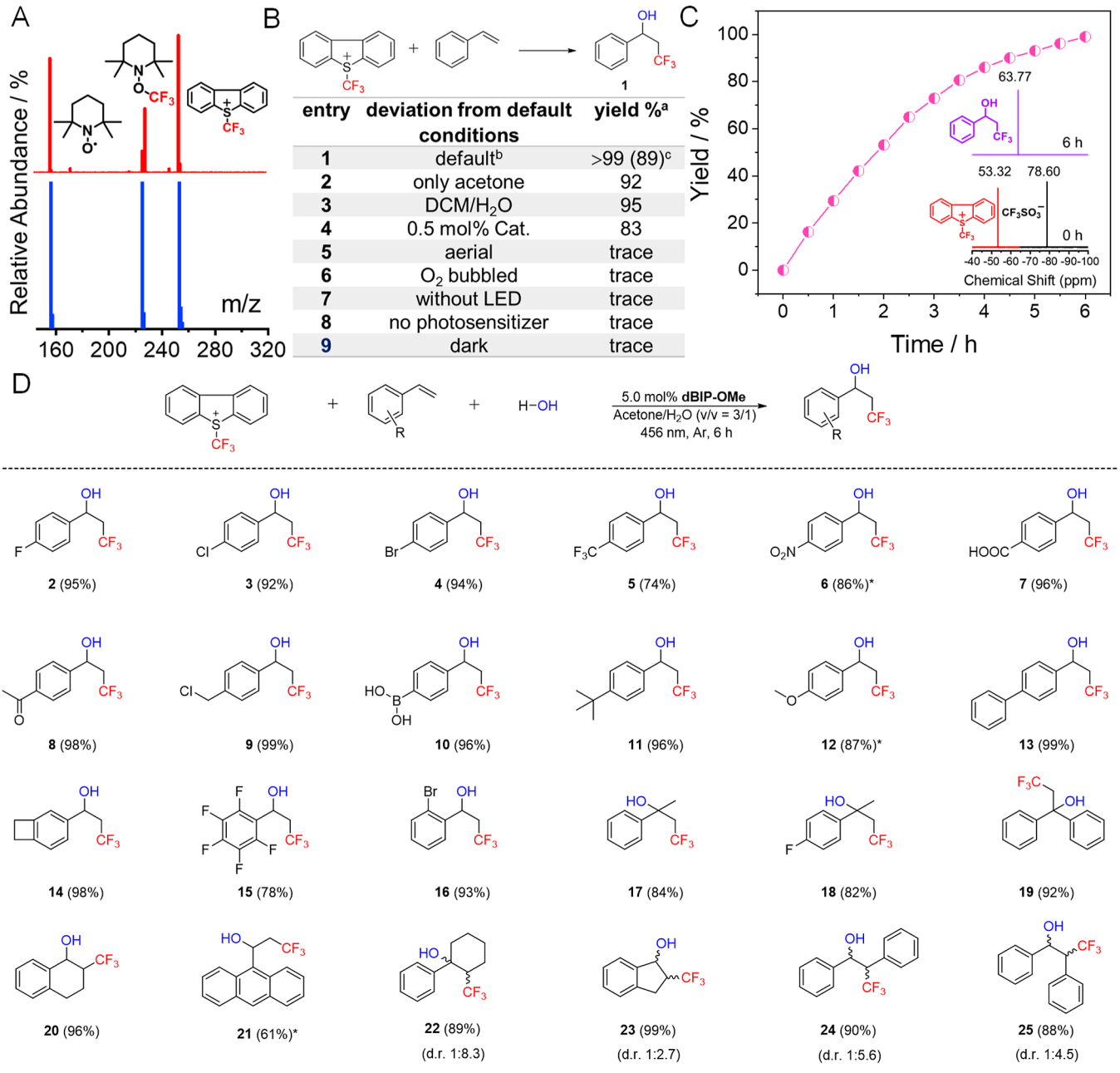

entry	deviation from default conditions	yield %[a]
1	default[b]	>99 (89)[c]
2	only acetone	92
3	DCM/H_2O	95
4	0.5 mol% Cat.	83
5	aerial	trace
6	O_2 bubbled	trace
7	without LED	trace
8	no photosensitizer	trace
9	dark	trace

Figure 4. (A) Mass spectra of TEMPO trapping experiments for the generation of the CF_3 radical during photocatalysis (theoretical: bottom, blue; experimental: top, red). (B) Control experiment results for the photocatalytic hydroxytrifluoromethylation of styrene under various conditions. [a]Yields were determined by ^{19}F NMR. [b]Default reaction conditions: styrene (0.2 mmol), Umemoto's reagent (1.1 equiv.), **dBIP−OMe** (5 mol %), 2 mL deaerated acetone/H_2O (v/v = 3/1), and irradiation at 456 nm for 6 h at room temperature. [c]Isolated yield. (C) Yield of the photocatalytic hydroxytrifluoromethylation of styrene over time. Inset: ^{19}F NMR spectra of the reaction solution before and after photocatalysis under the default condition. (D) Substrate scope studies of the photocatalytic hydroxytrifluoromethylation of styrene and its derivatives under the default condition with isolated yields shown in the parentheses (*^{19}F NMR yields).

dBIP−OMe, 2 mL of deaerated acetone/H_2O (v/v = 3/1), and irradiation at 456 nm for 6 h at room temperature, nearly quantitative conversion from styrene to 3,3,3-trifluoro-1-phenylpropan-1-ol (**1**) was obtained within 6 h (entry 1 in Figure 4B). The yield of **1** was slightly decreased to 92% when acetone was used as the sole solvent, probably because of the limited amount of water in acetone (entry 2). A high yield (95%) of **1** was obtained if the photocatalysis was carried out in a mixture of CH_2Cl_2/water (v/v = 3/1), even though CH_2Cl_2 and water are immiscible with each other (entry 3). If the **dBIP−OMe**'s amount was decreased to 0.5 mol %, a lower yield (83%) of **1** was obtained (entry 4), suggesting the importance of **dBIP−OMe** in facilitating this transformation. Other control experiments performed under either condition of being open to the atmosphere (entry 5), in O_2-saturated solution (entry 6), without 456 nm LED (entry 7), without **dBIP−OMe** (entry 8), or in the dark (entry 9) did not produce any desirable product (Figure S16), confirming the necessity of light, **dBIP−OMe**, and deaeration for the successful photocatalytic hydroxytrifluoromethylation of styrene. Figure 4C presents the increasing yield of **1** over the entire photocatalysis period under the default condition (Figure S17)

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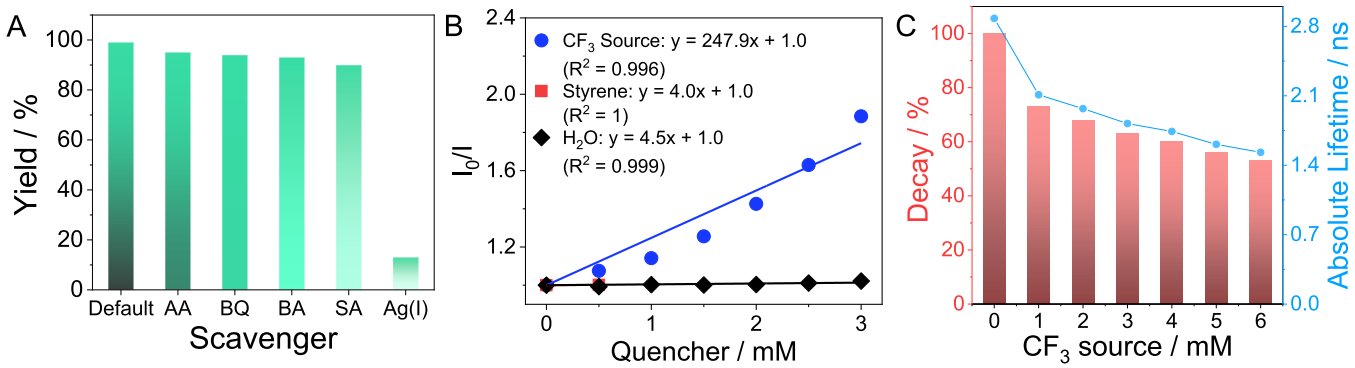

Figure 5. (A) Photocatalytic yields of styrene hydroxytrifluoromethylation obtained with or without scavengers. AA: L-ascorbic acid; BQ: benzoquinone; BA: benzoic acid; SA: sodium azide; Ag(I): $AgNO_3$. (B) Emission quenching of **dBIP−OMe** in the presence of Umemoto's reagent, styrene, and H_2O. (C) Emission lifetime decay of **dBIP−OMe** in the presence of Umemoto's reagent at different concentrations.

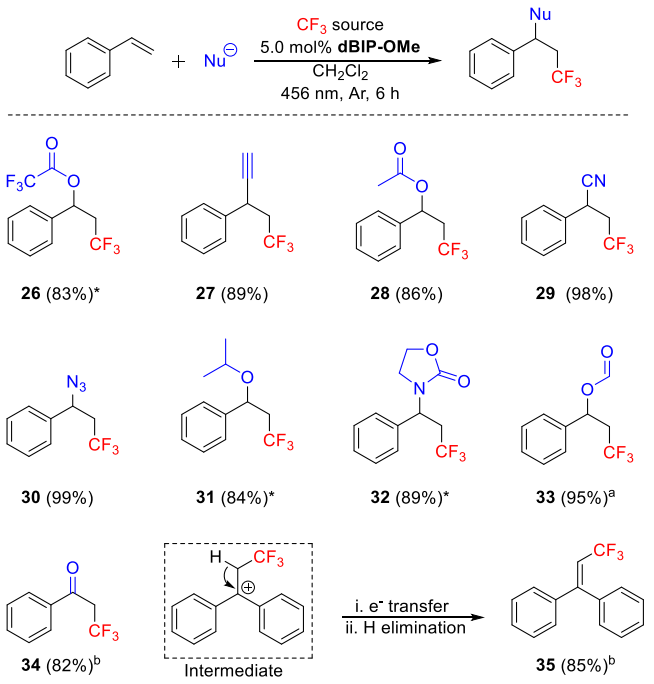

Figure 6. Photocatalytic trifluoromethylative bifunctionalization of aryl alkenes in the presence of different nucleophiles, with isolated yields shown in the parentheses (*^{19}F NMR yields). [a]DMF and [b]DMSO were used as solvents.

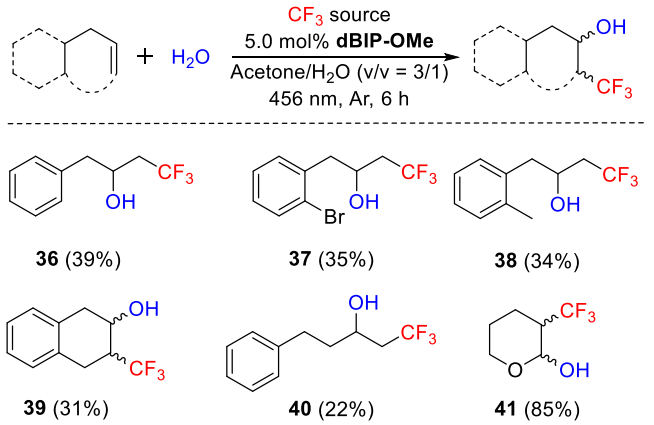

Figure 7. Photocatalytic hydroxytrifluoromethylation of aliphatic alkenes with isolated yields shown in parentheses.

together with the mass spectra (Figure 4C inset) of the reaction solution before and after the 6 h photocatalysis.

To expand the scope of aryl alkenes for photocatalytic hydroxytrifluoromethylation using **dBIP−OMe** as the sole photocatalyst, a variety of styrene derivatives were also subjected to the default photocatalytic condition (Figures S18−S100). As revealed in Figure 4D, substrates with halogen groups at the para position, including −F (**2**), −Cl (**3**), and −Br (**4**), all resulted in excellent yields of the desirable products (>92%). The strong electron-withdrawing groups of $-CF_3$ (**5**) and $-NO_2$ (**6**) led to lower yields at 74 and 86%, respectively. However, other mild electron-withdrawing substituents such as carboxylic acid (**7**), acetyl (**8**), methyl chloride (**9**), and boronic acid (**10**) all resulted in excellent yields above 95%. Similar high yields were obtained for those with electron-donating substituents at the para position, including *t*-butyl (**11**), methoxy (**12**), phenyl (**13**), and fused cyclobutene (**14**). However, 2,3,4,5,6-pentafluorostyrene (**15**) was photocatalytically transformed to the bifunctionalized product with a lower yield of 78%, while a decent yield (93%) could be achieved when 2-bromostyrene (**16**) was the substrate. The relatively lower yields of **17** (84%) and **18** (82%) could be ascribed to the steric hindrance resulting from the additional methyl groups at their benzyl positions. A similar effect, but to a lesser extent, could be observed for substrates like 1,1-diphenylethylene (**19**, 92%) and 1,2-dihydronaphthalene (**20**, 96%). Among the tested substrates, the lowest yield (61%) was from the photocatalytic conversion of vinylanthracene (**21**). On the other hand, a high diastereoselectivity of 1:8.3 (**22**, 89%) could be found using 1-phenyl-1-cyclohexene as substrate. In addition, indene could be converted to the desirable product (**23**) with a nearly quantitative yield (99%) and decent diastereoselectivity of 1:2.7. Similarly, photocatalytic hydroxytrifluoromethylation of both trans- and cis-stilbene proceeded smoothly with 1:5.6 (**24**, 90%) and 1:4.5 (**25**, 88%) diastereoselectivity, respectively, rivaling the reported photocatalytic performance of fac-$Ir(ppy)_3$ as the photocatalyst on the same substrates.[11c]

To assess the efficacy and stability of **dBIP−OMe** in photocatalysis, a series of irradiation "on/off" experiments of styrene hydroxytrifluoromethylation were performed. As depicted in Figure S101, the desired product yield increased during the light-on periods, whereas product formation ceased in the light-off phases (Figure S102). The product formation was resumed to increase when the irradiation was switched on, even after 6 h in the dark. No further increase in product yield

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ACS Catal. 2023, 13, 8119−8127

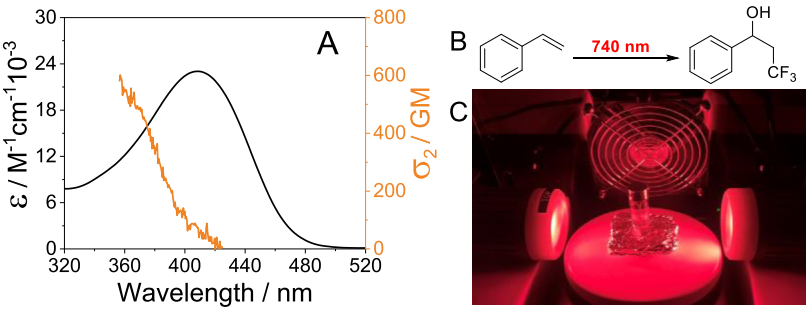
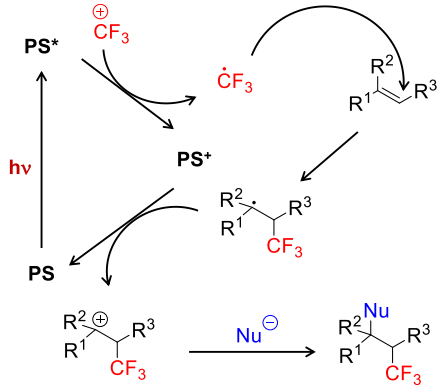


Figure 8. (A) Two-photon absorption spectrum of **dBIP−OMe** overlapped with its UV−vis absorption spectrum in CH_3CN. (B) Photocatalytic hydroxytrifluoromethylation of styrene upon 740 nm irradiation (equivalent to one-photon excitation at 370 nm) within 96 h following default reaction conditions as given in Figure 4B. (C) Typical photocatalysis setup under the irradiation of 740 nm LEDs.

Scheme 1. Proposed Photocatalytic Cycle of Trifluoromethylative Bifunctionalization of Alkenes Using dBIP−OMe (PS)



was detected if the reaction was kept in the dark for an additional 12 h. Furthermore, continuously irradiating **dBIP−OMe** at 456 nm for 24 h did not result in noticeable changes in its ^1H NMR spectra (Figure S103), further suggesting its excellent photostability for long-term applications.

Various scavengers were employed to probe the nature of this photocatalytic transformation. Figure 5A indicates that L-ascorbic acid, benzoquinone, benzoic acid, and sodium azide, which are scavengers targeting O_2, $O_2^{-\bullet}$, $OH^{-\bullet}$, and $^1O_2$, respectively, could not suppress the reaction yield. However, the addition of silver nitrate, an e^- scavenger, substantially decreased the product yield from 99% to 13% after 6 h of irradiation at 456 nm (Figure S104), consistent with previous reports that the photocatalytic hydroxytrifluoromethylation of styrene is initiated by an electron transfer step between the excited photocatalyst and Umemoto's reagent.[10] We carried out luminescence quenching experiments to further corroborate this conclusion. As plotted in Figure 5B, no appreciable luminescence change was observed upon the addition of styrene or H_2O. In striking contrast, the presence of Umemoto's reagent substantially quenched the luminescence intensity with a Stern−Volmer constant of 247.9 ± 19.5 M^{-1} (Figure S105). It can be concluded that the system is undergoing some combination of static and dynamic quenching, showing the characteristic upward curvature from mixed quenching. The excited-state lifetime derived from the emission decay fitting was also decreased from 2.9 ns to 1.5 ns in the presence of 6 mM Umemoto's reagent (Figure 5C).

In addition to hydroxytrifluoromethylation, we subsequently explored other nucleophiles to expand the scope of trifluoromethylative bifunctionalization of alkenes. As presented in Figure 6, when the photocatalysis was carried out in dry CH_2Cl_2, a variety of nucleophiles, including trifluoroacetate (**26**, 83%), ethynyl (**27**, 89%), acetate (**28**, 86%), cyanide (**29**, 98%), and azide (**30**, 99%), could all produce the desired bifunctionalized products with excellent to nearly quantitative yields. Moreover, insertion of an alkoxy functional group was also successfully achieved using isopropanol (**31**, 84%). Even a bulky nucleophile such as 3-(trimethylsilyl)oxazolidinone could furnish the incorporation of an oxazolidinone (**32**, 89%). Interestingly, DMF (**33**, 95%, Scheme S1) and DMSO (**34**, 82%, Scheme S2) were able to act as nucleophiles when used as solvents (Figures S106−S131). A different case was observed for 1,1-diphenylethylene. Instead of bifunctionalization, the primary product was (3,3,3-trifluoroprop-1-ene-1,1-diyl)dibenzene (**35**, 85%), probably due to steric hindrance, which prevents the subsequent nucleophilic attack after trifluoromethylation while instead being followed by a fast hydrogen elimination step.

Besides aryl alkenes, aliphatic alkenes could also be subjected to trifluoromethylative bifunctionalization using **dBIP−OMe** as the sole photocatalyst (Figures 7 and S132−S149). For instance, allylbenzene was converted to 4,4,4-trifluoro-1-phenylbutan-2-ol (**36**) with an isolated yield of 39%. The addition of electron-withdrawing (**37**, 35%) or -donating (**38**, 34%) substituents at the ortho position of allylbenzene did not result in apparent differences in the product yields. Moreover, 1,4-dihydronaphthalene and 4-phenyl-1-butene led to the corresponding hydroxytrifluoromethylated products in yields of 31% (**39**) and 22% (**40**), respectively. Finally, a decent yield of 85% could be achieved for 3-(trifluoromethyl)tetrahydro-2H-pyran-2-ol (**41**) when 3,4-dihydro-2H-pyran was used as the substrate. The depressed yields of **36-40** compared to the styrene derivatives **1-34**, along with the good yield of **41**, seem to indicate that the carbocation stability substantially impacts the photocatalytic yields.

Given the extended quadrupolar structure of **dBIP−OMe**, it was anticipated that it may also possess two-photon absorption (TPA) capability in the near-infrared region, as we recently observed for bibenzothiazole-derived chromophores.[3c] As shown in Figure 8A, the broadband two-photon absorption spectroscopy of **dBIP−OMe** measured by a pump−probe method in CH_3CN shows decent TPA cross-sections (200−600 GM) in the transition wavelength (i.e., one-photon equivalent) range of 350−380 nm. Hence, we performed photocatalytic hydroxytrifluoromethylation of styrene (Figure 8B) using inexpensive 740 nm LEDs instead of lasers, as the

https://doi.org/10.1021/acscatal.3c01812
ACS Catal. 2023, 13, 8119−8127

sole light source (Figure 8C). To our delight, a 45% yield of **1** could be obtained (Figure S150), confirming that **dBIP−OMe** could be suitably employed as a photoredox catalyst in the near-infrared region following the two-photon absorption strategy.

In line with all the above results, a plausible photocatalytic cycle is shown in Scheme 1. Upon 456 nm irradiation or two-photon excitation at 740 nm, the excited photocatalyst **dBIP−OMe*** is immediately formed, which will be oxidatively quenched by Umemoto's reagent to produce **dBIP−OMe**$^{+}$. The concomitantly generated $^{\bullet}CF_3$ radical from Umemoto's reagent will attack the C═C bond of an alkene substrate to result in a neutral alkyl radical intermediate, which can be oxidized by **dBIP−OMe**$^{+}$ to give a carbocation intermediate. A subsequent attack by a nucleophile at the carbocation will furnish the final three-component coupled product.

CONCLUSIONS

In summary, we have reported a novel organic photocatalyst, **dBIP−OMe,** composed of a bibenzothiazole core imine-bridged with two methoxyphenyl groups. Because of its competent redox power, **dBIP−OMe** is able to realize trifluoromethylative bifunctionalization of various alkenes under visible-light irradiation. Such a metal-free photocatalytic system is applicable to the incorporation of not only a CF_3 group but also many types of nucleophiles to both aryl and aliphatic alkenes. Furthermore, taking advantage of its π-extended quadrupolar structure, **dBIP−OMe** also possesses two-photon absorption capability in the near-infrared region. Hence, a 740 nm LED can be used to drive the hydroxytrifluoromethylation of styrene when **dBIP−OMe** is the sole photocatalyst, thus substantially expanding the wavelength range for important photoredox reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.3c01812.

Methods for the synthesis, characterization, and photophysical studies of **dBIP−OMe**; DFT, TDDFT, and EDDM calculation in detail; single-crystal X-ray diffraction data and cyclic voltammogram of **dBIP−OMe**; and photocatalysis and NMR spectra (including HSQC, HMBC, and COSY) of organic compounds involved in this study (PDF)

Crystal structure of dBIP-OMe (CIF)

Accession Codes

CCDC 2249853 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Y.S. acknowledges the support of the National Science Foundation (CHE-1955358), University of Cincinnati, and the Ohio Supercomputer Center. C.G.E. acknowledges support from the National Science Foundation (CHE-1905334). Funding for the D8 Venture diffractometer was through the NSF-MRI grant CHE-1625737.

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