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Sunlight Decatungstate Photoinduced Trifluoromethylations of (Hetero)aromatics and Electron-poor Olefins

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Tetrabutylammonium decatungstate has been exploited to photoinduce the trifluoromethylation of (hetero)aromatics and electron-poor olefins. The process made use of the cheap Langlois' reagent (CF_3SO_2Na) and occurred under sunlight irradiation in an acetonitrile/water mixture. The trifluoromethylation of (hetero)aromatics required the use of potassium persulfate as an additive and the mono- or bis-trifluoromethylated adducts were obtained, depending on the actual reaction conditions and the chosen substrate.

Trifluoromethylation reactions are highly important since the incorporation of a CF_3 moiety into a pharmacophore is often known to increase lipophilicity/bioavailability, resistance to oxidation, and activity.[1] Accordingly, trifluoromethylated compounds are playing an increasingly important role in different fields, particularly in medicinal chemistry, but also in materials science. Chart 1 gathers some examples of drugs containing the trifluomethylaryl core, including androgenic receptors (flutamide, nilutamide), antidepressants (fluoxetine) and antiarthritics (leflunomide, celocoxib). Accordingly, the introduction of a trifluoromethyl moiety in an organic compound is becoming a key issue in synthesis and different approaches have been recently developed to fulfill this goal.[2]
Several articles have been reported in recent years on the use of photoredox catalysis for the generation of the trifluoromethyl radical and the ensuing functionalization of organic compounds.[2,3] The strategy used is mainly that depicted in Scheme 1. The commonly used sources of $F_3C^{\bullet}$ are shown in Scheme 1a, including expensive Umemoto and Togni's reagents, along with cheaper CF_3I and CF_3SO_2Cl. The reductive cleavage of these reagents gave the $F_3C^{\bullet}$ radical that was used to functionalize alkenes (electron-deficient,[4] electron-rich[5] or styrene[6] derivatives), alkynes[7] and (hetero)aromatics[8] (Scheme 1b). In the case of alkenes and alkynes, the adduct radical (**A**) was in most cases oxidized by the oxidized form of the photocatalyst (PC_{OX}) and a cationic chemistry resulted. A radical homolytic aromatic substitution reaction (HAS) took place instead when using aromatic compounds (Scheme 1b).

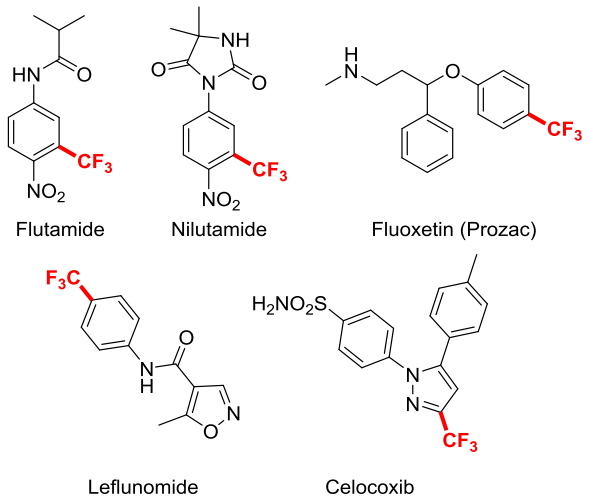

Chart 1

In search for a cheaper and easier to handle trifluoromethylating agent, sodium triflinate (CF_3SO_2Na, the Langlois' reagent)[9] was recently adopted.[4b,8a,10] The triflinate reagent has the unique feature to be oxidized rather than reduced from the excited photocatalyst (Scheme 1c). This calls for photocatalysts having a reduction potential in the excited state E^*_{RED} superior to the oxidation potential of the triflinate anion (E_{OX} = + 1.05 V *vs* SCE for potassium triflinate).[11] Albeit various photo(organo)catalysts were actually used for this purpose,[4b,8a,10] a robust, cheap and efficient alternative is desirable. We envisaged that tetrabutylammonium decatungstate (TBADT)[12-14] could be applied in this case as photoredox catalyst for the generation of the trifluoromethyl radical (Scheme 1c). In fact, TBADT was only sparsely used so far in the role of oxidant in the excited state[13,14] despite its E^*_{RED} is quite high (a value of + 2.44 V *vs* SCE was estimated)[15] and largely sufficient to promote the reaction even under sunlight irradiation.[12a]

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Electronic Supplementary Information (ESI) available: experimental details and copy of ^1H and ^{13}C NMR spectra of synthesized compounds. See DOI: 10.1039/x0xx00000x

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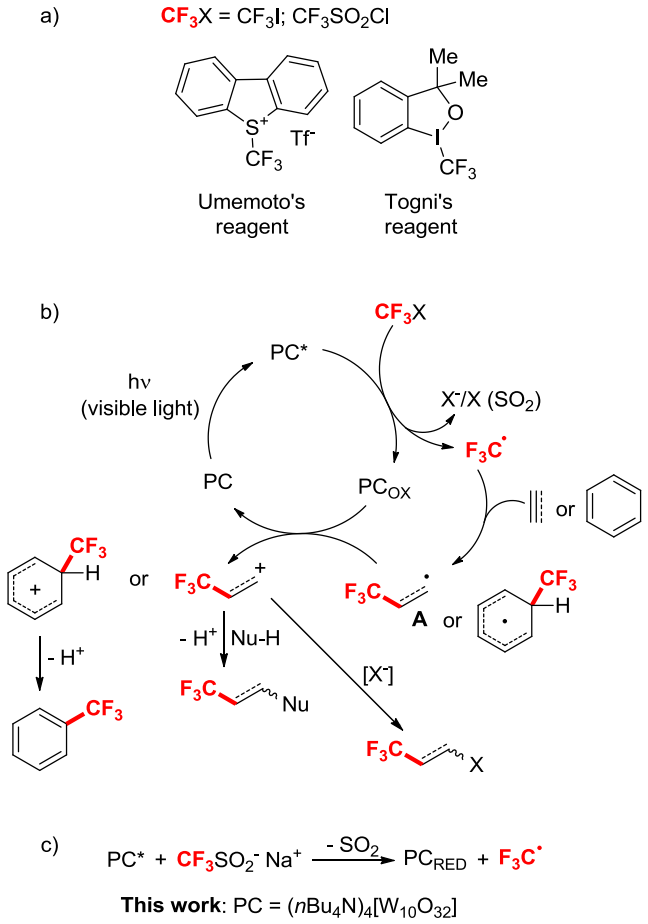
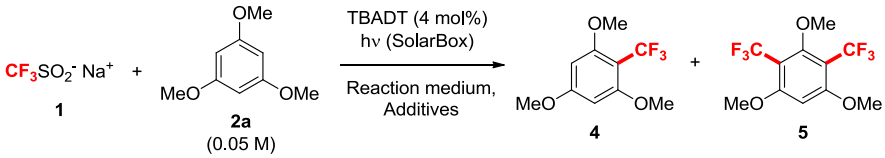


Scheme 1. Photocatalytic strategies for trifluoromethylation reactions.

At the beginning of our study, we focused the attention on the trifluoromethylation of 1,3,5-trimethoxybenzene (**2a**; see Table 1). Thus, when a 0.05 M solution of **2a** in the presence of sodium triflinate **1** and TBADT (4 mol%) in a MeCN/H_2O 5:1 mixture (to allow a complete solubility of the salt) was irradiated in a SolarBox equipped with a 1.5 kW Xenon lamp (500 W·m^{-2} light intensity) for 4 h, only traces of the expected product 1,3,5-trimethoxy-2-(trifluoromethyl)benzene **4** were observed by GC analysis (< 5% consumption of **2a**, entry 1). The addition of biphenyl (0.05 M) in the role of electron transfer agent did not have any appreciable effect (entry 2).[14a] By contrast, the addition of potassium persulfate (0.05 M) allowed to obtain a complete consumption of **2a**, with **4** formed in 57% yield according to GC analysis, along with traces of the bis-trifluoromethylated derivative 1,3,5-trimethoxy-2,4-bis(trifluoromethyl)benzene **5** (entry 3). The use of a larger amount of water (MeCN-H_2O 2:1), as well as the shift to aqueous/alcoholic media (MeOH-H_2O 5:1 or TFE-H_2O 5:1; TFE = 2,2,2-trifluoroethanol) was detrimental for the formation of **4** (entries 4-6). Substituting potassium persulfate with a different oxidant, such as hydrogen peroxide (from 1 to 6 equiv.) likewise gave a poor performance, both in terms of **2a** consumption and **4** formation (entries 7, 8). Blank experiments demonstrated that the reaction does not proceed when covering the reaction vessel with an aluminum foil (entry 9; temperature of the solution: 35 °C), albeit a significant consumption of **2a** (*ca.* 50%) occurred also in the absence of TBADT with a similar yield in terms of **4** (31% overall yield; 55% based on the consumption of starting **2a**; entry 10).

Table 1. Optimization of reaction conditions for the trifluoromethylation of **2a**.[a]



Entry	**1**, M	Reaction medium	Additives, M	Reaction Conditions	**2a** Consumption, %	Yield, %[b]	
						4	**5**
1	0.05	MeCN-H_2O 5/1	-	SolarBox, 4h	< 5	traces	-
2	0.05	MeCN-H_2O 5/1	Biphenyl, 0.05	SolarBox, 4h	< 5	traces	-
3	**0.05**	**MeCN-H_2O 5/1**	**$K_2S_2O_8$, 0.05**	**SolarBox, 4h**	100	**57**	**traces**
4	0.05	MeCN-H_2O 2/1	$K_2S_2O_8$, 0.05	SolarBox, 4h	77	35	-
5	0.05	MeOH-H_2O 5/1	$K_2S_2O_8$, 0.05	SolarBox, 4h	25	-	-
6	0.05	TFE-H_2O 5/1	$K_2S_2O_8$, 0.05	SolarBox, 4h	20	-	-
7	0.05	MeCN-H_2O 5/1	H_2O_2, 0.05	SolarBox, 4h	52	26	-
8	0.05	MeCN-H_2O 5/1	H_2O_2, 0.3	SolarBox, 4h	68	25	-
9[c]	0.05	MeCN-H_2O 5/1	$K_2S_2O_8$, 0.05	SolarBox, 4h	7	-	-
10[d]	0.05	MeCN-H_2O 5/1	$K_2S_2O_8$, 0.05	SolarBox, 4h	56	55	-
11	0.05	MeCN-H_2O 5/1	$K_2S_2O_8$, 0.05	Heating, 4h (50°C)	65	54	-
12	0.15	MeCN-H_2O 5/1	$K_2S_2O_8$, 0.1	SolarBox, 20h	100	24	44
13	**0.3**	**MeCN-H_2O 5/1**	**$K_2S_2O_8$, 0.1**	**SolarBox, 20h**	**100**	**traces**	**82**
14[d]	0.3	MeCN-H_2O 5/1	$K_2S_2O_8$, 0.1	SolarBox, 20h	100	7	56

[a] Reaction conditions: **1** (0.05-0.3 M, 0.25-1.5 mmol), **2a** (0.25 mmol), (n-$Bu_4N)_4[W_{10}O_{32}]$ (TBADT, 2·10^{-3} M, 4 mol%) in 5 mL of the chosen reaction medium. [b] Gas Chromatography (GC) yields referred to the consumption of the limiting reagent (**2a**), using biphenyl as standard (n-undecane for entry 2). [c] In the absence of light (the reaction mixture was covered with an aluminum foil, T = 35 °C). [d] No TBADT used, T = 48 °C.

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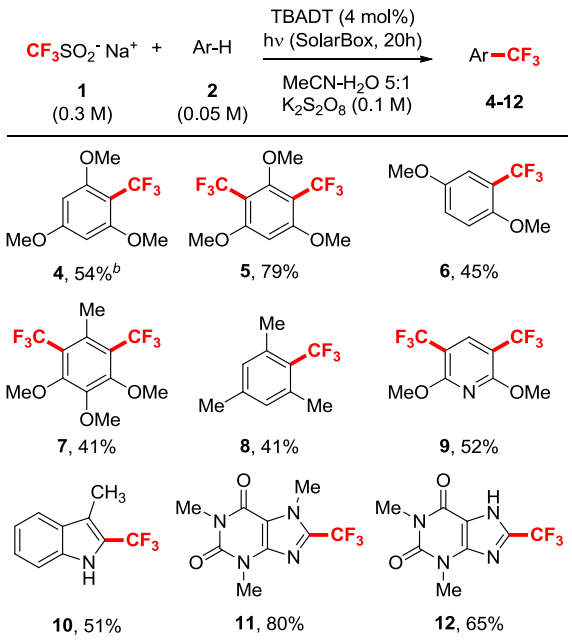
Since the temperature of the solution during irradiation was around 48 °C, we investigated the occurrence of the reaction also under thermal conditions. Thus, when the reaction was carried out on a heating plate at 50 °C, we observed a **2a** consumption of 65%, with **4** again formed in around 50% yield based on the consumption of the aromatic derivative (entry 11). We then surmised that, upon proper choice of the reaction conditions, we could drive the process towards the formation of **5**. Thus, when adopting a 3-fold amount of **1** in the presence of 2 equiv. of $K_2S_2O_8$, the reaction gave a mixture of **4** and **5** after irradiation for 20 h (entry 12). However, a clean reaction occurred when the excess of **1** was increased to 6 equiv., since **5** was formed in 82% GC yield (entry 13). When the reaction was repeated under the same conditions, but in the absence of TBADT, a complete consumption of **2a** was again observed, albeit a lower yield of **5** was obtained (56%, entry 14).

Thus, 1,3,5-trimethoxybenzene **2a** led to products **4** and **5** in 54 and 79% isolated yield, when subjected to the reaction conditions reported in entries 3 and 13, Table 1, respectively (Table 2). We then evaluated the scope of this trifluoromethylation procedure by subjecting different (hetero)aromatics to the optimized conditions reported in Table 1, entry 13, with the aim of maximizing the number of trifluoromethyl groups introduced in the final product.

Table 2. Trifluoromethylation of (hetero)aromatics.[a]



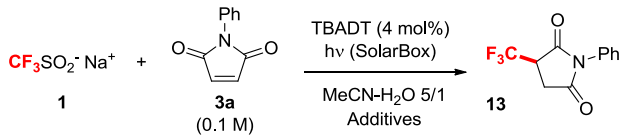
[a] Isolated yields after silica gel chromatography have been reported. [b] Reaction conditions: see entry 3, Table 1.

The trifluoromethylation of 1,4-dimethoxybenzene **2b** likewise proceeded smoothly to give product **6** in 45% yield. The presence of benzylic C-H bonds did not interfere with the desired reaction, as demonstrated by the formation of products **7** and **8** (both in 41% yield), from 3,4,5-trimethoxytoluene **2c** and mesitylene **2d**, respectively.

The reaction was next extended to heteroaromatic nuclei. The reaction of 2,6-dimethoxypyridine **2e** and 3-methylindole **2f** led to products **9** and **10** in *ca.* 50% isolated yield. Finally, the present protocol could be extended also to biologically relevant derivatives caffeine **2g** and theophylline **2h**, that were trifluoromethylated in the 8-position to give **11** and **12** in good yields (Table 2).

TBADT is widely used to perform radical conjugate addition reactions[12a] and we then evaluated whether electron-poor olefins could be trifluoromethylated as well. Optimization of the reaction conditions made use of *N*-phenyl maleimide **3a** (0.1 M), that was subjected to trifluoromethylation conditions in the presence of different amounts of **1** and TBADT (4 mol%) in a MeCN:H_2O 5/1 mixture (Table 3). Thus, the performance of the process increased when passing from 1.5 to 3 equiv. of **1**, albeit a further increase (5 equiv.) did not improve the reaction yield (entries 1-3).

Table 3. Optimization of reaction conditions for the trifluoromethylation of **5a**.[a]



Entry	**1**, M	Additives, M	Irradiation Conditions	**3a** Consumption, %	**13** Yield, %[b]
1	0.15	-	SolarBox, 20h	60	37
2	**0.3**	**-**	**SolarBox, 20h**	**100**	**42**
3	0.5	-	SolarBox, 20h	100	44
4	0.3	Biphenyl, 0.1	SolarBox, 20h	80	45
5	0.3	$K_2S_2O_8$, 0.15	SolarBox, 20h	95	22
6[c]	0.3	-	SolarBox, 20h	-	-
7[d]	0.3	-	SolarBox, 20h	9	-
8	0.3	-	Heating, 20h (50°C)	< 5	-

[a] Reaction conditions: **1** (0.15-0.5 M, 0.75-2.5 mmol), **3a** (0.5 mmol), $(n\text{-}Bu_4N)_4[W_{10}O_{32}]$ (TBADT, $4\cdot10^{-3}$ M, 4 mol%) in 5 mL of a MeCN-H_2O 5/1 mixture. [b] Gas Chromatography (GC) yields referred to the consumption of the limiting reagent (**3a**), using biphenyl as standard (*n*-undecane for entry 4). [c] In the absence of light, T = 35 °C. [d] No TBADT used, T = 48 °C.

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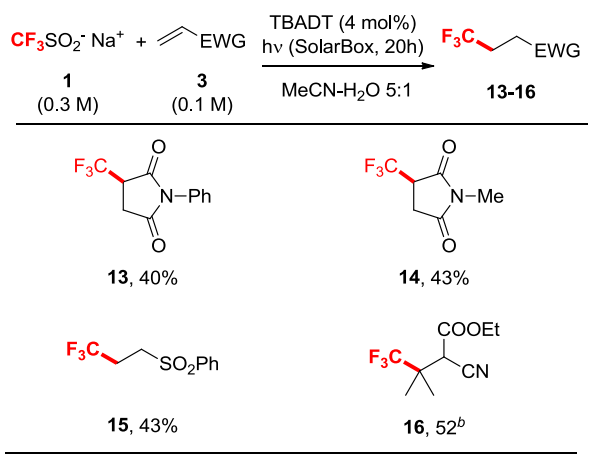
Table 4. Trifluoromethylation of electron-poor olefins.[a]

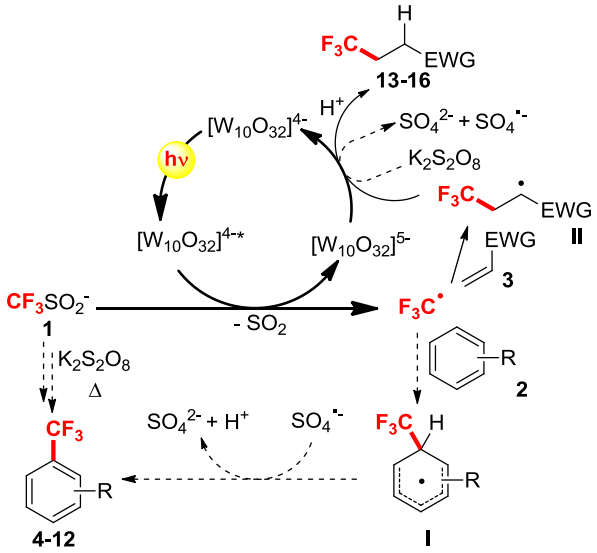


[a] Isolated yields after silica gel chromatography have been reported. [b] Yield based on 44% consumption of **3d**.

The role of additives was next tested and neither biphenyl (1 equiv.) nor potassium persulfate (1.5 equiv.) improved the performance of the reaction (entries 4, 5). Blank experiments finally demonstrated that the present trifluoromethylation requires both light and TBADT to occur (entries 6, 7). Contrary to the trifluoromethylation of aromatics, in this case thermal conditions were not effective in promoting the formation of product **13** (entry 8).

Thus, under the optimized conditions reported in entry 2, Table 3, the reaction of **3a** allowed to isolate the expected product *N*-phenyl 2-(trifluoromethyl)succinimide **13** in 40% yield after purification with column chromatography (Table 4). The process was next extended to *N*-methyl maleimide **3b**, leading to the formation of **14** in 43% isolated yield. Finally, the reaction was tested on acyclic substrates, such as phenyl vinyl sulfone **3c** and ethyl isopropylidene cyanoacetate **3d**. The former gave 3,3,3-trifluoropropyl phenyl sulfone **15** in 43% isolated yield, while the latter allowed to prepare product **16** containing a quaternary carbon, albeit only a partial consumption of the olefin (44%) was observed. Thus, **16** was obtained in 23% overall yield (52% based on the consumption of **3d**).

As depicted in Scheme 2, the strong oxidizing properties of the excited decatungstate anion are the key to the success of this reaction. Thus, upon excitation with solar light, $[W_{10}O_{32}]^{4-*}$ is capable of oxidizing the sulfinate anion, that then loses SO_2 to liberate the trifluoromethyl radical. This is a highly reactive intermediate, prone to add to the reaction partners present in solution, either an aromatic or an electron-poor olefin. As for aromatic derivatives, radical adducts **I** are formed, while the reduced form of the photocatalyst $[W_{10}O_{32}]^{5-}$ is restored to its original form by the persulfate anion through a single electron-transfer step.[16] This leads to the formation of sulfate radical $SO_4^{\bullet-}$ that is then involved in the oxidation of **I**, finally leading to the desired trifluoromethylated product. Likewise, bis-trifluoromethylated derivatives are formed in a similar way, when the original products undergo the same reaction sequence.



Scheme 2. Proposed reaction mechanism for the TBADT photoinduced trifluoromethylation of aromatics (dashed lines) and electron-poor olefins (solid lines); the steps in common to both mechanisms have been highlighted with a bold line.

Based on experimental evidences, we propose that the background reaction observed in the absence of the photocatalyst is due to thermal effects and is not related to direct absorption of light by the reagents (see Figure S1 in Electronic Supplementary Material with relevant UV-Vis spectra). This is also supported by the thermal experiments reported in Table 1 as well as by previous reports in the literature,[17] in nice agreement with the temperature registered inside the SolarBox during irradiation. Accordingly, the role of the photocatalyst here is to accelerate the reaction,[18] since only a partial consumption of substrate **2a** has been observed under thermal conditions (see also the kinetic profiles reported in Figure S2). At any rate, also under prolonged irradiation conditions, the presence of the photocatalyst allows to obtain a higher yield (compare the results of entries 13 and 14, Table 1). Another point is related to the formation of products either mono- (**4**, **6**, **8**, **10-12**) or bis-trifluoromethylated (**5**, **7**, **9**). In the case of **2a**, proper conditions were found to drive the process towards the clean formation of either of the trifluoromethylated derivatives. As a general trend, however, it is apparent that only markedly electron-rich nuclei (e.g. **2c** and **2e**) undergo a double trifluoromethylation process, while for the other substrates the clean introduction of a single CF_3-group occurred.

Turning to electron-poor olefins, a different reaction course is involved, since this is a redox-neutral process and does not require the use of any external oxidant. Thus, the photogenerated $F_3C^{\bullet}$ intermediate undergoes addition onto electron-poor olefins **3** to give radical adducts **II**, that finally lead to the desired products **13-16** upon back-electron transfer from the reduced photocatalyst and protonation.

In conclusion, we demonstrated here a new application of TBADT as photoredox catalyst in promoting trifluoromethylation reactions of (hetero)aromatics and electron-poor olefins under sunlight irradiation. The process is

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simple, versatile and occurs in a partial aqueous mixture, making use of the cheap Langlois' reagent as CF_3-source.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

We thank Luca Capaldo and Edoardo Torti (University of Pavia) for preliminary experiments. D.R. thanks the MIUR for financial support (SIR Project ''Organic Synthesis via Visible Light Photocatalytic Hydrogen Transfer''; Code: RBSI145Y9R).

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