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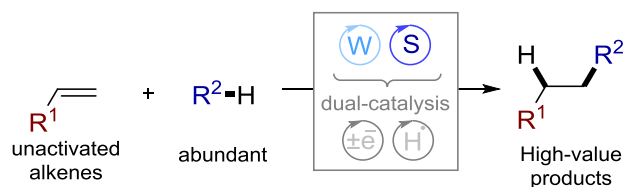
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# Visible-Light Decatungstate/Disulfide Dual Catalysis for the Hydrofunctionalization of Styrenes

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**KEYWORDS :** Radicals, Photocatalysis, Dual catalysis, Hydrofunctionalization



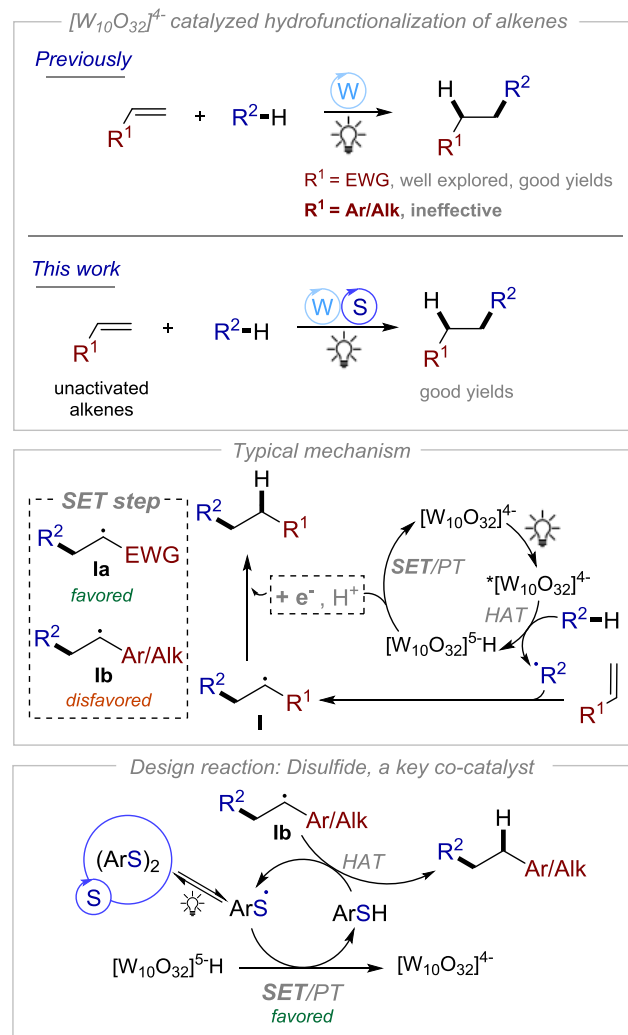
□ Various hydrofunctionalizations □ Broad scope & FG tolerance

**ABSTRACT:** We describe an efficient photoredox system, relying on decatungstate/disulfide catalysts, for the hydrofunctionalization of styrenes. In this methodology the use of disulfide as co-catalyst was shown to be crucial for the reaction efficiency. This photoredox system was employed for the hydro-carbamoylation, -acylation, -alkylation and -silylation of styrenes, giving access to a large variety of useful building blocks and high-value molecules such as amides and unsymmetrical ketones from simple starting materials.

Unactivated alkenes are ubiquitous reagents in organic chemistry as they are inexpensive, stable and readily available. As a consequence, they have been intensively used as starting materials in a plethora of organic transformations.<sup>1</sup> Among them, the hydrofunctionalization of unactivated alkenes has been recognized as a valuable method to construct complex molecules but, above all, to introduce functional groups with full atom efficiency.<sup>2,3</sup> This transformation is still at the center of modern research as illustrated, for instance, by the recent developments on the photocatalyzed hydroaminations<sup>4,5</sup> and hydroalkoxylations.<sup>4,6</sup> In this field, the photocatalytic hydrocarboxylation of unactivated alkenes has been so far underexplored. On the other hand, *CH*-functionalization has become a powerful strategy for the construction of high-value molecules from readily available starting materials.<sup>7</sup> The hydrogen atom transfer (HAT) reactions promoted by a photocatalyst have appeared as a promising alternative to the traditional transition metal-catalyzed *CH*-activation which usually required the use of directing groups. For instance, the decatungstate photocatalyst,<sup>8</sup> which has been democratized by Fagnoni/Albini<sup>9a-d</sup> and recently used by the MacMillan<sup>9e-f</sup> and Noël<sup>9g</sup> groups, proved to be effective for the generation of various radical species through direct HAT.<sup>9h</sup> The radical intermediate can then be involved in various transformations such as the hydrocarboxylation of alkenes. While the decatungstate photocatalyzed hydrocarboxylation was found to be efficient with activated alkenes (Michael acceptor),<sup>9a-d</sup> the reaction mainly afforded poor conversions or led to product mixtures in the presence of unactivated alkenes (Figure 1).<sup>10</sup> The typical mechanism<sup>8</sup> for the photocatalyzed hydrocarboxylation using decatungstate photocatalyst would

start with the photoexcitation of the decatungstate ( $[W_{10}O_{32}]^{4+}$ ) (Figure 1). The excited complex ( $^*[W_{10}O_{32}]^{4+}$ ) would abstract a hydrogen atom from the substrate ( $R^2H$ ) leading to the generation of the reduced form of decatungstate catalyst ( $[W_{10}O_{32}]^{5-}H$ ) and a radical species ( $\dot{R}^2$ ). The latter would then react with alkenes, forming the radical intermediate (**I**). Finally, the catalytic cycle would be closed through the consecutive single electron transfer/proton transfer (SET/PT) steps from the reduced decatungstate ( $[W_{10}O_{32}]^{5-}H$ ) to the intermediate **I**, delivering the hydro-functionalized product (Figure 1). Considering the mechanism, we wondered why unactivated alkenes reacted so differently from their activated counterparts. The most likely explanation is the difference of the reduction potential between the intermediates **Ia** (activated alkene) and **Ib** (unactivated alkene). Indeed, SET reduction between the reduced decatungstate  $[W_{10}O_{32}]^{5-}H$  ( $E_{1/2}^{red}([W_{10}O_{32}]^{4+}/[W_{10}O_{32}]^{5-}H) = -0.96$  V vs Ag/Ag<sup>+</sup> in acetonitrile),<sup>11</sup> is thermodynamically favored with the intermediates **Ia** ( $E_{1/2}^{red} = -0.66$  V vs SCE in acetonitrile, for  $\dot{C}H_2(CH_3)CO_2Et / \dot{C}H_2(CH_3)CO_2Et$ ),<sup>12</sup> while the latter is disfavored with the intermediates **Ib** ( $E_{1/2}^{red} = -1.43$  V vs SCE in acetonitrile, for  $\dot{C}H_2Ph / \dot{C}H_2Ph$ ).<sup>13</sup> To overcome this limitation, we envisaged to develop a process that would unlock such reactivity by using disulfides as co-catalysts. Indeed, given that organic disulfides form the corresponding thiyl radical species under light irradiation,<sup>14</sup> and that such radicals can be easily reduced ( $E_{1/2}^{red} = +0.16$  V vs SCE, for  $\dot{S}Ph / \dot{S}Ph$ ),<sup>15</sup> we considered to use them as co-catalysts acting as both electron mediators and hydrogen donors, through the *in-situ* formation of thiols (Figure 1).<sup>4</sup> *In-situ* formed thiols might also be advantageous, as they can act as a polarity-reversal catalyst, enabling radical-

chain propagation by suppressing polarity-mismatching in the HAT processes. Seminal work from Roberts and co-workers demonstrated that the radical hydroacylation of aliphatic alkenes with aldehydes is sluggish in the absence of thiol, while the reaction in presence of catalytic amount of thiol is impressively effective.<sup>3a</sup> Herein, we describe preliminary results demonstrating that the use of disulfides is crucial for achieving the decatungstate-mediated hydrofunctionalization of styrenes under light irradiation.



**Figure 1.** Decatungstate-photocatalyzed hydrofunctionalization of alkenes

Our starting investigations focused on the hydrocarbamylation of styrene **1a** with formamide **2a** catalyzed by TBADT photocatalyst (tetra-*n*-butylammonium decatungstate) (Table 1).<sup>16</sup> The first experiment was conducted in acetonitrile without disulfide, 1 mol% of TBADT and as expected no reaction was observed (Table 1, entry 1). Remarkably, the addition of 10 mol% of phenyl disulfide to the previous reaction conditions switched on the reactivity, allowing the formation the product **3a** in moderate yield (Table 1, entry 2). The use of thiophenol instead of the phenyl disulfide allowed the formation of **3a**, albeit in lower yield. (Table 1, entry 3). Best results upon optimization, were obtained with (MeOpPhS)<sub>2</sub> affording the product **3a** in 75% NMR yield, and 59% isolated yield (Table 1, entry 4).<sup>17</sup> Control experiments showed that the photocatalyst and the light irradiation are both

required for the reaction efficiency (Table 1, entries 5–6).<sup>18</sup> Finally, the change of light source, the increase of the catalytic loading, or the change of stoichiometric ratio did not lead to further improvement (Table 1, entries 7-9). It is important to mention that a larger quantity of the thiol-ene reaction product was observed with the use of thiol species. The use of disulfides seems to prevent the thiol-ene side reaction, likely by maintaining a lower concentration of thiyl radical in the media than when thiols are employed.

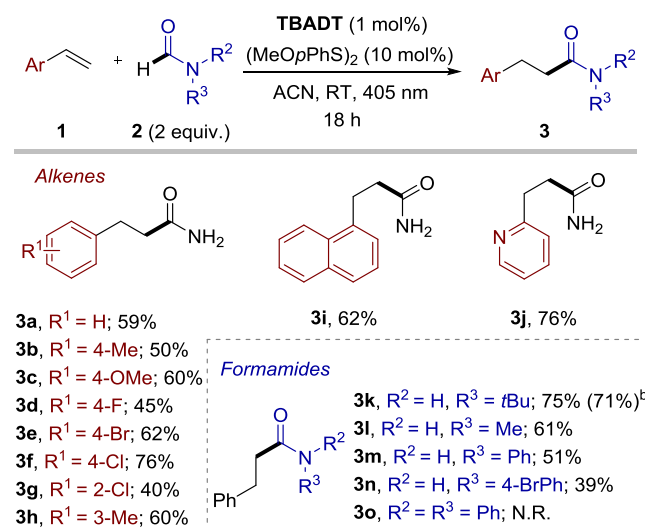
**Table 1.** Optimization of the hydrocarbamylation reaction

**1a** + **2a** (2 equiv.)  $\xrightarrow[18\text{ h}]{1\text{ mol\% TBADT, } 10\text{ mol\% (MeOpPhS)}_2, \text{ACN, RT, } 405\text{ nm}}$  **3a**

Entry	Deviation from standard conditions	Yield <b>3a</b> (%) <sup>a</sup>
1	w/o (MeOpPhS) <sub>2</sub>	N.R.
2	(PhS) <sub>2</sub> instead of (MeOpPhS) <sub>2</sub>	57
3	PhSH <sup>b</sup> instead of (MeOpPhS) <sub>2</sub>	42 <sup>c</sup>
4	none	75 (59) <sup>d</sup>
5	w/o light	N.R.
6	w/o TBADT	N.R.
7	365 nm instead of 405 nm	70
8	3 mol% TBADT	70
9	<b>1a</b> (2 equiv.), <b>2a</b> (1 equiv.)	49

Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol) in ACN (0.6 mL). <sup>a</sup>Yields were determined by <sup>1</sup>H NMR using trichloroethylene as an internal standard. <sup>b</sup>20 mol%. <sup>c</sup>Around 10% thiol-ene product was detected. <sup>d</sup>Isolated yield. TBADT = Tetra-*n*-butylammonium decatungstate. N.R. = no reaction, the starting materials were fully recovered.

**Scheme 1.** Scope of the hydrocarbamylation of alkenes<sup>a</sup>

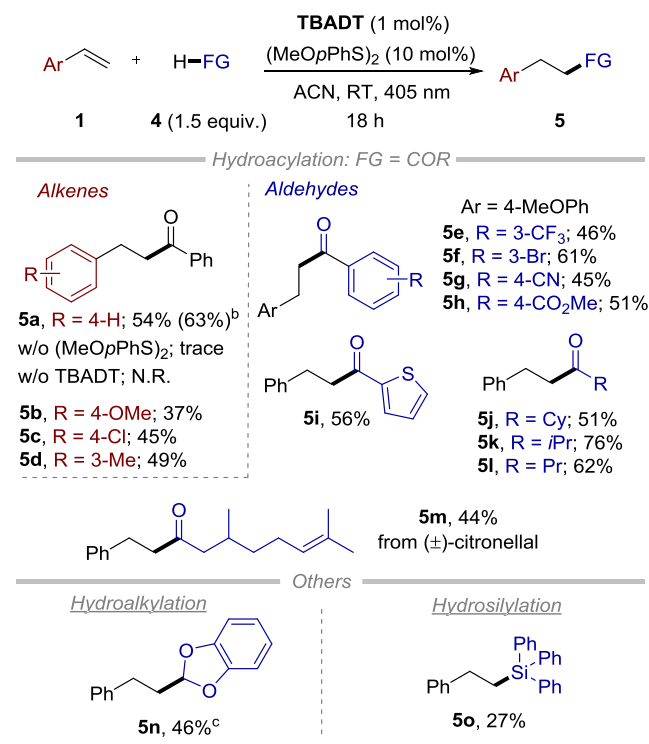


<sup>a</sup>Reaction conditions: **1** (0.5 mmol), **2** (1 mmol), TBADT (1 mol%), (MeOpPhS)<sub>2</sub> (10 mol%) in ACN (1 mL). Yields refer to isolated products. <sup>b</sup>5 mmol scale, 48 h.

With the optimized conditions in hand, we then explored the scope of the TBADT/disulfide photocatalyzed hydrocarbomoylation of styrene derivatives (Scheme 1). The reaction furnished the primary amide derivatives **3** in moderate to good yields, regardless of the electronic nature and the position of the aromatic substituents (**3a-3h**). Naphthyl and pyridinyl<sup>19</sup> aromatic patterns (**3i-j**), proved to be suitable substrates for the transformation. Attempts for the hydrocarbomoylation of aliphatic vinyl compounds failed. Then, we investigated the reaction with formamide derivatives bearing *N*- or *N,N*-substituents.<sup>20</sup> The reaction proceeded efficiently with *N*-alkyl and -aryl formamides affording the corresponding amides (**3k-3n**) in moderate to good yields. The reaction proved to be suitable for scale-up experimentation (5 mmol), delivering the product **3k** in a similar yield compared to the small scale. However, the reaction was ineffective with the *N,N*-diphenylformamide (**2o**), and no reaction occurred. Finally, the hydrocarbomoylation reaction tolerates a wide range of functional groups, including alkyl, ether, naphthyl, pyridinyl, halide (F, Cl, Br), thus offering opportunities for further diversification.

Next, we studied without further optimization other hydrocarbonations with a particular focus on the hydroacylation process (Scheme 2), as photo-mediated hydroacylations are extremely scarce in the literature.<sup>21</sup> We were pleased to observe that the reaction proceeded well with styrene **1a** and benzaldehyde **4a**, affording the ketone **5a** in moderate yield. With these substrates, the control experiments demonstrated that the disulfide and the TBADT catalysts<sup>18</sup> were crucial to the reaction efficiency (Scheme 2). We also demonstrated the robustness of our method by performing the reaction on a semi-preparative 5 mmol scale, which pleasingly, delivered the product **5a** with similar yields.

**Scheme 2.** Other hydrofunctionalizations of alkenes<sup>a</sup>

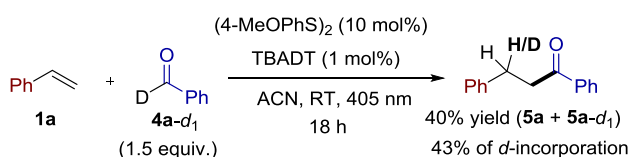


<sup>a</sup>Reaction conditions: **1** (0.5 mmol), **4** (0.75 mmol), TBADT (1 mol%), (MeOpPhS)<sub>2</sub> (10 mol%) in ACN (1 mL). Yields refer to isolated products. <sup>b</sup>5 mmol scale, 48 h. <sup>c</sup><sup>1</sup>H NMR yield is given as the product was inseparable from the disulfide catalyst.

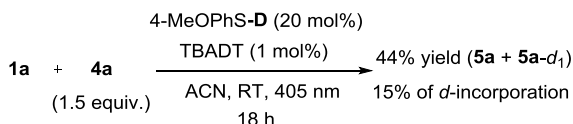
Then, we explored the scope of the hydroacylation reactions with various alkenes and aldehydes. All the unsymmetrical ketones **5** were obtained in moderate to good yields, and a large variety of functional groups was tolerated including halides, esters, and nitriles (Scheme 2). Aliphatic aldehydes were also suitable reagents in the reaction, leading to the formation of the corresponding dialkyl ketones (**5j-5l**) in moderate to good yields (Scheme 2). To demonstrate the utility of our methodology, the late-stage functionalization of the (±)-citronellal with the styrene **1a** was carried out. Pleasingly, the reaction afforded the product **5m** in moderate yield (Scheme 2). Then, the hydroalkylation and the hydrosilylation of styrene **1a** were explored, respectively with 1,3-benzodioxole (**4n**) and triphenylsilane (**4o**), leading to the formation of the expected products (**5n-5o**), albeit in modest yields (Scheme 2).<sup>22</sup> Finally, we turned our attention to the elucidation of the reaction mechanism. The control experiments carried out previously (Table 1 & Scheme 2) allowed us to rule out potential mechanistic routes. Indeed, the reactions performed without the disulfide catalyst were ineffective. This result tends to prove that the direct hydrogen back donation from [W<sub>10</sub>O<sub>32</sub>]<sup>5-</sup>H to the intermediate **1b** is not possible (Figure 1). Meanwhile, the result seems to indicate that the TBADT acts as a catalyst and not as an initiator. Therefore, a radical chain propagation might be excluded. When the reaction was performed only with disulfide catalyst, the reactivity was completely shut down, suggesting that the success of the reaction is unlikely due to the polarity-reversal catalysis, in which the thiyl radical (<sup>•</sup>SAr) would perform HAT on starting materials **2** or **4**.<sup>3,18</sup> To get additional insights, experiments were carried out without the TBADT catalyst in the presence of a radical initiator ((BzO)<sub>2</sub>) (see SI for more details). These reactions did not lead to the formation of **5a**, confirming that the thiyl radical is not a polarity reversal catalyst in our reaction. These results are in accordance with previous work,<sup>3a</sup> which have demonstrated that aryl thiyl radicals (<sup>•</sup>SAr) were not suitable to abstract hydrogen from aldehydes. Finally, to gain further insight into the operating mechanism, experiments in the presence of radical scavengers and deuterium labeling experiments were performed (Scheme 3). The hydroacylation reaction of **1a** with the benzaldehyde **4a** was thus repeated in the presence of the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO; 1.5 equiv). Interestingly, formation of coupling product **5a** was completely inhibited. However, no TEMPO-adduct was observed (see SI for more details). The reaction was also conducted in the presence of galvinoxyl (1.5 equiv), which again switched off the reactivity (see SI for more details).

**Scheme 3.** Deuterium labeling experiments<sup>a</sup>

a) Reaction with (4-MeOPhS)<sub>2</sub> and 4a-d<sub>1</sub>



b) Reaction with 4-MeOPhSD



<sup>a</sup>Yields were determined by <sup>1</sup>H NMR using trichloroethylene as an internal standard.

Then, we performed deuterium labeling experiments (Scheme 3). First, the reaction was carried out in presence of the compound 4a-d<sub>1</sub> under standard reaction conditions (Scheme 3a). We were pleased to observe 43% of deuterium incorporation at benzylic position, suggesting that the disulfide species is involved in the deuterium transfer from the benzaldehyde 4a-d<sub>1</sub> to the compound 5a-d<sub>1</sub>, likely through the *in-situ* generation of thiol (see SI for more details). To confirm the hypothesis, we considered to perform the reaction with the benzaldehyde 4a, and to replace the disulfide species by its deuterated thiol counterpart (4-MeOPhSD; 20 mol%). Under these conditions, we observed 15% of deuterium incorporation, demonstrating that the thiol species is a putative intermediate in the mechanism (Scheme 3b & Figure 1). Those experiments are in accordance with the dual role of the disulfide catalyst as both an electron mediator and a hydrogen donor (Figure 1).

In summary, we have demonstrated that the use of the disulfide/TBADT dual catalysis can unlock various hydrofunctionalization reactions of unactivated alkenes. This catalytic system allowed the formation of high-value molecules such as amides and unsymmetrical ketones from abundant starting materials. Preliminary mechanistic studies tend to prove that the disulfide catalyst acts as an electron mediator and a hydrogen donor. We are conducting ongoing studies to further understand and exploit this dual catalytic system in other radical processes.

## ASSOCIATED CONTENT

### Supporting Information.

The Supporting Information is available free of charge at URL Detailed experimental procedures and characterization data for compounds (PDF)

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