Efficiency and Selectivity Aspects in the C–H Functionalization of Aliphatic Oxygen Heterocycles by Photocatalytic Hydrogen Atom Transfer

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Abstract The C–H to C–C conversion in aliphatic oxygen heterocycles (dioxolanes, 1,3-dioxane, or cyclic carbonates) by photocatalytic hydrogen atom transfer and subsequent trapping of the resulting radical with phenyl vinyl sulfone was investigated. The performance of three different photocatalysts, namely tetrabutylammonium decatungstate and the aromatic ketones thioxanthone and 9-fluorenone, was compared. The UV-light-absorbing decatungstate anion is more efficient and permits the use of a smaller excess of hydrogen donor than the aromatic ketones, although the ketones could be excited by visible light. Further intramolecular selectivity studies revealed that aromatic ketones afforded a higher proportion of functionalization at the acetalic versus the ethereal positions than did the decatungstate anion.

Key words photocatalysis, hydrogen atom transfer, oxygen heterocycles, chemoselectivity, radicals, C–C bond formation

Oxygen heterocycles are an important family of heterocyclic systems. These privileged structures are present in many naturally occurring compounds, notably carbohydrates and nucleosides among biomolecules, as well as in a plethora of compounds having pharmaceutical activities. According to a recent report, oxygenated derivatives are the second-most-common type of heterocycles present as a structural motif in pharmaceuticals approved by the US Food and Drug Administration. Interestingly, the majority (around 90%) of the encountered oxygen heterocycles are nonaromatic in character, with pyranoses, furanoses, macrolactones, morpholines, and dioxolanes occupying the first five positions in the ranking in terms of their relative abundance. Accordingly, the construction and functionalization of these scaffolds is an important topic for synthetic chemists. A classic example is the Paal–Knorr synthesis of furans, whereas more-recent strategies make extensive use of transition-metal catalysis. Interestingly, microwave-assisted protocols have also been developed.

An intriguing alternative is represented by photocatalytic strategies, in which a photoactive catalyst is responsible for light absorption and, once in its excited state, for the activation of the actual substrate of the process. This step leads to the formation of highly reactive intermediates, mostly open-shell radical ions or radicals, which, in turn, are responsible for the observed chemistry. In the particular case of aliphatic oxygen heterocycles, the photocatalytic approach opens the way to the direct functionalization of...
C–H bonds through a hydrogen atom transfer (HAT) step. Thus, a few photocatalysts or photogenerated HAT reagents are capable of directly cleaving C–H bonds in the starting material. Along this line, our group recently explored the use of the decatungstate anion, as its tetrabutylammonium salt ([Bu₄N]₄[W₁₀O₃₂]; TBADT) as a photocatalyst, thanks to the peculiar reactivity of its excited state, which has a partial alkoxy-radical character. Thus, TBADT smoothly promoted C–H to C–C conversions in various hydrogen donors, including tetrahydrofuran (THF), 1,4-dioxane, oxetanes, 1,3-benzodioxoles, and a few lactones, through trapping of the photogenerated radicals with electron-deficient olefins (α,β-unsaturated esters, ketones, nitriles, sulfones, etc.) in a conjugate radical addition process. Upon back-HAT, the resulting radical adduct finally led to the functionalized heterocycle, while the photocatalyst was restored to its original state. The reactions were routinely carried out under UV irradiation (λₜₐₓₑₛ = 310 or 366 nm), but solar radiation was also demonstrated to be a convenient choice.

In this work, we offer a direct comparison of the different reactivities shown by the decatungstate anion and by a selection of (visible-light absorbing) aromatic ketones in the functionalization through photocatalytic HAT of selected families of aliphatic oxygen heterocycles. Furthermore, we also investigated how the choice of the photocatalyst modifies the intramolecular chemoselectivity of the C–H cleavage step [Scheme 1(b)]. At the beginning, we performed an optimization of the reaction conditions by studying the addition of THF (1a) to phenyl vinyl sulfone (2), taken as a model trap and then used throughout the rest of the work, to give the adduct 3a in the presence of selected photocatalysts [Scheme 1(b)]. We had already investigated this reaction in the presence of TBADT (2 mol%), and we obtained 3a in 59% yield upon irradiation of a MeCN solution containing 1a (5 equiv) and 2 (0.1 M) for 24 hours with phosphor-coated lamps (12 × 15 W) that emitted radiation centered at 366 nm. Interestingly, the yield of 3a increased to 90% (as determined by GC analysis) when the irradiation was performed for 20 hours in a solar simulator equipped with a 1500 W xenon lamp (500 W·m⁻² light intensity; see Table 1, entry 1). When the reaction was performed on a 0.5 mmol scale, 3a was isolated in 86% yield after silica-gel chromatography. Next, we tested the aromatic ketones thioxanthone and 9-fluorenone as POCs under analogous reaction conditions. Thus, irradiation of a solution of 1a and 2 in the presence of thioxanthone (20 mol%) in dichloromethane (for reasons of solubility) under solar-simulated conditions led to a reasonable consumption of 2 (64%), with the formation of 3a in 88% yield based on the consumed 2 (56% overall yield; entry 2). In the presence of 9-fluorenone (20 mol%), the reaction gave poor results, and 3a was obtained in only 33% yield at 24% consumption of 2 (entry 3). Because they can absorb in the visible-light range [see Supporting Information (SI); Figure S1], aromatic ketones can also operate as POCs upon irradiation at λ > 400 nm. We therefore tested their reactivities upon irradiation with a 1 W violet LED (λ = 405 ± 5 nm; 130 W·m⁻² light intensity). With both POCs, product 3a was formed in a low yield and, again, with incomplete consumption of 2 (entries 4 and 5). In the attempt to improve both the yield and the conversion of the starting olefin, we decided to adopt a greater excess of the hydrogen donor (3 M; 30 equiv). Interestingly, in the case of thioxanthone, the desired adduct 3a was obtained in 87% isolated yield (entry 6), a similar value to what obtained with TBADT (entry 1). On the other hand, with 9-fluorenone, we failed to achieve complete consumption of 2, even after irradiation for 30 hours (entries 7 and 8). Importantly, in all cases, the reaction required both light and the presence of the chosen photocatalyst to proceed, as demonstrated by blank experiments (See SI; Table S1). With these preliminary results in hand, we extended the reaction to 2,2-dimethyl-1,3-dioxolane (1b). The reaction proceeded satisfactorily in the presence of TBADT, giving 3b in 55% iso-

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Other groups have exploited the similar HAT reactivity displayed by the excited states of aromatic ketones (e.g., benzophenone, 4-benzozopyridine, quinones, etc.) and by the dye eosin Y in a wide range of synthetically appealing processes, including C–C, C–N, and C–halogen bond-forming reactions, as well as in oxidations, among others. Indeed, a few of these photoorganocatalysts (POCs) have also been demonstrated to operate under visible-light irradiation.
lated yield with a complete consumption of 2 (entry 9). On the other hand, aromatic ketones gave unsatisfactory results, even when 1b was used in a large excess (50 equiv), and the yields were around 10% (entries 10 and 11). Finally, we tested the reactivity of a cyclic carbonate, namely ethylene carbonate (1c), as a hydrogen donor. In this case, the efficiency of the process dropped significantly, and 3c was obtained in only 57% isolated yield in the presence of TBADT and 50 equiv of 1c (entries 12–14), whereas both the investigated POCs failed to give the desired adduct 3c (entries 15 and 16).

**Table 1** Optimization of the Reaction Conditions, and Initial Experiments

<table>
<thead>
<tr>
<th>Entry</th>
<th>1 (M)</th>
<th>Conditionsb</th>
<th>Consumptionc (%) of 2</th>
<th>Yieldd (%) of 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>2 (0.1 M)</td>
<td>hν, 20 h, N2</td>
<td>100</td>
<td>90</td>
</tr>
<tr>
<td>1</td>
<td>1a (0.5)</td>
<td>TBADT (2 mol%), MeCN, SolarBox</td>
<td>100</td>
<td>90 (86)d</td>
</tr>
<tr>
<td>2</td>
<td>1a (0.5)</td>
<td>thioxanthone (20 mol%), CH2Cl2, SolarBox</td>
<td>64</td>
<td>88</td>
</tr>
<tr>
<td>3</td>
<td>1a (0.5)</td>
<td>9-fluorenone (20 mol%), MeCN, SolarBox</td>
<td>24</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>1a (0.5)</td>
<td>thioxanthone (20 mol%), CH2Cl2, LED</td>
<td>78</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>1a (0.5)</td>
<td>9-fluorenone (20 mol%), MeCN, LED</td>
<td>37</td>
<td>24</td>
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<tr>
<td>6</td>
<td>1a (3)</td>
<td>thioxanthone (20 mol%), CH2Cl2, LED</td>
<td>100</td>
<td>92 (87)d</td>
</tr>
<tr>
<td>7</td>
<td>1a (3)</td>
<td>9-fluorenone (20 mol%), MeCN, LED</td>
<td>78</td>
<td>71</td>
</tr>
<tr>
<td>8</td>
<td>1a (3)</td>
<td>9-fluorenone (20 mol%), MeCN, LEDe</td>
<td>85</td>
<td>74</td>
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To examine the possibility of performing selective C–H to C–C conversions, we then moved on to study a series of hydrogen donors containing various positions prone to functionalization, and the results are summarized in Table 2. We initially tested the reactivity of 1,3-dioxolane (1d) in the presence of the same photocatalysts as used above under conditions similar to those adopted for 1a and 1b. Thus, the use of TBADT gave a 42% overall yield of a 58:42 mixture of products 3d and 4d, resulting from the functionalization at the acetalic and ethereal positions, respectively (Table 2, entry 1).

**Table 2** Intramolecular selectivities in the C–H to C–C functionalization of aliphatic oxygen heterocycles

<table>
<thead>
<tr>
<th>Entry</th>
<th>1 (M)</th>
<th>Conditionsb</th>
<th>Consumptionc (%) of 2</th>
<th>Yieldd (%) of 3</th>
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</thead>
<tbody>
<tr>
<td>1d</td>
<td>2 (0.1 M)</td>
<td>hν, 20 h, N2</td>
<td>100</td>
<td>42d</td>
</tr>
<tr>
<td>1</td>
<td>1d (0.5)</td>
<td>TBADT (2 mol%), MeCN, SolarBox</td>
<td>100</td>
<td>42d</td>
</tr>
<tr>
<td>2</td>
<td>1d (5)</td>
<td>thioxanthone (20 mol%), CH2Cl2, LED</td>
<td>100</td>
<td>59d</td>
</tr>
<tr>
<td>3</td>
<td>1d (5)</td>
<td>9-fluorenone (20 mol%), MeCN, LED</td>
<td>55</td>
<td>33 (3d/4d = 90:10)d</td>
</tr>
<tr>
<td>4</td>
<td>1e (0.5)</td>
<td>TBADT (2 mol%), MeCN, SolarBox</td>
<td>100</td>
<td>3e</td>
</tr>
<tr>
<td>5</td>
<td>1e (5)</td>
<td>thioxanthone (20 mol%), CH2Cl2, LEDe</td>
<td>71</td>
<td>15</td>
</tr>
</tbody>
</table>

a Irradiations were carried out in Pyrex vials on a 0.1 mmol scale with MeCN (for TBADT or 9-fluorenone) or CH2Cl2 (for thioxanthone) as the solvent. Solutions were bubbled with N2 for 5 min before irradiation.

b SolarBox: irradiation was performed with a solar-light simulator equipped with a 1.5 kW Xe lamp (500 W·m–2 light intensity). LED: irradiation was performed with a 405 ± 5 nm LED (1 W; 130 W·m–2 light intensity).

c Except where otherwise noted, the consumption of 2 and the yield of 3 were determined by GC with dodecane (1 µl ml–1) as internal standard. Yields of 3 are expressed on the basis of the consumed 2 and can be interpreted as ‘selectivity’ values.

d Isolated yield from a reaction performed on a 0.5 mmol scale after chromatography (silica gel, cyclohexane–EtOAc).

e Irradiation for 30 h.

f n.d. = not detected.
Whereas the hydrogen donor was used in a fivefold excess in the case of TBADT, thioxanthone required the use of 50 equivalents of 1d, affording a 90:10 mixture of 3d and 4d in 59% overall yield upon irradiation for 30 h (Table 2, entry 2). A similar product ratio was consistently obtained when 9-fluorenone was used as the POC, although the desired adduct was formed in low yield and with a partial consumption of 2 (entry 3). Next, we moved to six-membered oxygen heterocycles, and we used 1,3-dioxane (1e) as the hydrogen donor. The reaction in the presence of TBADT afforded two different products, 3e (41% isolated yield) and 4e (27% isolated yield), resulting from the functionalization at the acetalic and ethereal positions, respectively (3e/4e = 60:40; entry 4). On the other hand, thioxanthone promoted the exclusive formation of 3f, albeit with a poor performance according to GC analysis, whereas 9-fluorenone only gave traces of the desired adduct 3g (entries 5 and 6). On changing to 2-methyl-1,3-dioxolane (1f), which has a tertiary acetalic position, the reaction in the presence of TBADT gave full consumption of 2 in the presence of only a threefold excess of 1f. Indeed, the functionalization at the acetalic position occurred exclusively, although the desired product 3f was accompanied by traces of compound 3g resulting from deprotection of the acetal group. Notably, the formation of this undesired byproduct could be suppressed by performing the reaction in the presence of a mild base (NaHCO₃, 1 equiv), giving product 3f as the only isolated adduct in 74% yield (entries 7 and 8). Thioxanthone or 9-fluorenone again required the use of a large excess of hydrogen donor (50 equiv). In the first case, 3f was formed in 35% yield along with 18% of 3g, whereas in the latter case, only traces of the adduct 3f were found by GC analysis (entries 9 and 10). In both cases, the addition of Cs₂CO₃ (1 equiv) pushed the reaction towards the formation of the desired adduct 3f (entries 11 and 12) while limiting the formation of 3g. Finally, functionalization of propylene carbonate 1g, in which 50 equivalents of 1g were used regardless of the chosen photocatalyst, led to selective formation of 3g in 49% isolated yield in the presence of TBADT (entry 13), whereas the aromatic ketones failed to give any trace of products (entries 14 and 15).

The results reported above show some interesting trends. TBADT consistently demonstrated superior reactivity to that of the POCs used, because the desired adducts were obtained in the presence of a lower catalyst loading (2 mol% versus 20 mol%) and a lower excess of the hydrogen donor (often 5-fold as against 50-fold). However, TBADT absorbs UV radiation exclusively, and it required the use of a solar-simulated light source, whereas the two POCs operated under irradiation by a violet light. Furthermore, thioxanthone was shown to be a superior photocatalyst to 9-fluorenone, as demonstrated by the higher conversions of the starting materials and the higher yields. All the photocatalysts showed a lower reactivity in the functionalization of 1b compared with that of 1a (with lower yields and/or a higher excess of hydrogen donor required). This might be due to steric effects connected with the presence of the two methyl groups at the acetalic position. Alternatively, it might be due to polar effects that disfavor the formation of the α-oxyalkyl radical intermediate in 1b with respect to 1a due to the presence of the electron-withdrawing β'-oxygen atom exerting a certain deactivating effect on HAT. Similarly, electronic effects played a role in the functionalization of cyclic carbonates (e.g., 1c), which required more-severe conditions (a greater excess of hydrogen donor) than in the case of 1a and 1b, and reacted only in the presence of TBADT, the tested ketones being ineffective in this process. The low reactivity observed in the case of the ketones might be related to the ππ* character of their lowest-lying

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Table 2 (continued)

<table>
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<tr>
<td>6</td>
<td>1e (5)</td>
<td>9-fluorenone (20 mol%) MeCN, LED[4]</td>
</tr>
<tr>
<td>7</td>
<td>1f (0.3)</td>
<td>TBADT (2 mol%) MeCN, SolarBox</td>
</tr>
<tr>
<td>8</td>
<td>1f (0.3)</td>
<td>TBADT (2 mol%) NaHCO₃ (1 equiv) MeCN, SolarBox</td>
</tr>
<tr>
<td>9</td>
<td>1f (5)</td>
<td>thioxanthone (20 mol%) CH₂Cl₂, LED</td>
</tr>
<tr>
<td>10</td>
<td>1f (5)</td>
<td>9-fluorenone (20 mol%) MeCN, LED</td>
</tr>
<tr>
<td>11</td>
<td>1f (5)</td>
<td>thioxanthone (20 mol%) Cs₂CO₃ (1 equiv) CH₂Cl₂, LED</td>
</tr>
<tr>
<td>12</td>
<td>1f (5)</td>
<td>9-fluorenone (20 mol%) MeCN, LED</td>
</tr>
<tr>
<td>13</td>
<td>1g (5)</td>
<td>TBADT (2 mol%) MeCN, SolarBox</td>
</tr>
<tr>
<td>14</td>
<td>1g (5)</td>
<td>thioxanthone (20 mol%) CH₂Cl₂, LED</td>
</tr>
<tr>
<td>15</td>
<td>1g (5)</td>
<td>9-fluorenone (20 mol%) MeCN, LED</td>
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</tbody>
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[a] See Table 1.
[b] The ratio of 3 to 4 was determined by 1H NMR (see SI).
[c] Irradiation for 30 h.
[d] Irradiation for 20 h, N₂O.
[e] Irradiation for 20 h.
[f] n.d. = not detected.

The results reported above show some interesting trends. TBADT consistently demonstrated superior reactivity to that of the POCs used, because the desired adducts were obtained in the presence of a lower catalyst loading (2 mol% versus 20 mol%) and a lower excess of the hydrogen donor (often 5-fold as against 50-fold). However, TBADT absorbs UV radiation exclusively, and it required the use of a solar-simulated light source, whereas the two POCs operated under irradiation by a violet light. Furthermore, thioxanthone was shown to be a superior photocatalyst to 9-fluorenone, as demonstrated by the higher conversions of the starting materials and the higher yields. All the photocatalysts showed a lower reactivity in the functionalization of 1b compared with that of 1a (with lower yields and/or a higher excess of hydrogen donor required). This might be due to steric effects connected with the presence of the two methyl groups at the acetalic position. Alternatively, it might be due to polar effects that disfavor the formation of the α-oxyalkyl radical intermediate in 1b with respect to 1a due to the presence of the electron-withdrawing β'-oxygen atom exerting a certain deactivating effect on HAT. Similarly, electronic effects played a role in the functionalization of cyclic carbonates (e.g., 1c), which required more-severe conditions (a greater excess of hydrogen donor) than in the case of 1a and 1b, and reacted only in the presence of TBADT, the tested ketones being ineffective in this process. The low reactivity observed in the case of the ketones might be related to the ππ* character of their lowest-lying
triplet excited states, responsible for the key HAT step (as opposed to the ππ* character of more-reactive ketones, such as benzophenone).25

Turning to the intramolecular selectivity aspect, we initially evaluated the competition between functionalization at the acetalic and the ethereal methylenic positions in 1d and 1e, where an α,α-dioxoyalkyl or an α-oxoalkyl radical is involved, respectively. With these substrates, products 3 were consistently formed in higher amounts than products 4. The choice of the photocatalyst, however, had an effect, as TBADT gave 3 and 4 in a ratio of about 3 (statistically corrected), whereas for the ketones this value was >18 (statistically corrected). Indeed, a clean reaction occurred in the case of 1e in the presence of thioxanthone, where 3e was the only product formed. In the particular case of the functionalization of 1,3-dioxolane (1d) promoted by (aromatic) ketones, similar trends have been reported in the literature. Whereas some reports indicated a completely selective functionalization at the acetalic position,16,17a–c in a couple of cases, a distribution of products similar to that found here was described, notably in the acetone-initiated alkylation of 1,3-dioxolane by terminal olefins.26 Interestingly, the same selectivity pattern found here for aromatic ketones has also been observed in the functionalization of 1d through HAT promoted by a photogenerated chlorine atom.11c On the other hand, the intramolecular competition between the functionalization at the acetalic versus the ethereal positions in the presence of TBADT has received limited attention.27 The different selectivity observed for the decatungstate anion compared with the tested POCs might be related to the different lifetimes of the relevant reactive states, where a short-lived species reacts with poor discrimination between the available sites. Indeed, whereas in the case of the decatungstate anion, the state responsible for the observed chemistry (named wo) has a lifetime of about 50–60 ns in acetonitrile,28 the triplet states of the ketones employed here show much longer lifetimes, of the order of microseconds,29a,c in turn leading to predominant or exclusive functionalization at the acetalic position.

The presence of a methyl group, however, dramatically changed the reaction outcome, as observed in the case of 1f. Thus, regardless of the choice of photocatalyst, the (tertiary) acetalic position was functionalized exclusively to give 3f in all cases. An undesired byproduct 3f was observed, presumably formed through spontaneous deprotection of the dioxolane moiety of product 3f. Its formation could, however, be suppressed by the addition of an (insoluble) inorganic base. Also, this agrees well with previous reports in which UV-light-induced, benzophenone-photosensitized, hydrogen abstraction from 2-alkyl-1,3-dioxolanes has been described as taking place at the 2-position exclusively.29 Finally, a similar selectivity towards the tertiary position was also observed in the case of propylene carbonate (1g), albeit only in the presence of TBADT. This is fully consistent with our previous investigation on lactones, where the presence of a tertiary position α to the oxygen atom drove the process toward exclusive functionalization of that position.30

In conclusion, the present work describes the different capabilities of selected HAT photocatalysts in promoting the functionalization of aliphatic oxygen heterocycles. We found that TBADT was the more reactive photocatalyst, requiring a lower loading and permitting the use of substrates in lower excesses than usually required for the aromatic ketones 9-fluorenone and thioxanthone. However, these ketones offer the possibility of performing more-selective reactions, as demonstrated in the reported examples of intramolecular selectivity.

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Supporting Information
Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1612079.

References and Notes


(21) C–H Functionalization of Aliphatic Oxygen Heterocycles: General Procedure

A solution of phenyl vinyl sulfone (2; 0.1 M), the chosen aliphatic heterocycle 1 (0.3–5 M), the photocatalyst (TBADT: 2 mol%; 9-fluorenethione or thioxanthone: 20 mol%), and the base (NaHCO₃ or Cs₂CO₃; 1 equiv, if required) in the chosen medium (MeCN or CH₂Cl₂) was purged with N₂ for 5 min then irradiated. The reaction course and the product distribution were monitored by GC analysis. The photolyzed solution was concentrated in vacuo, and the residue was purified by column chromatography (silica gel, cyclohexane–EtOAc) to give product(s) 3 and/or 4.

4-[2-(Phenylsulfonyl)ethyl]-1,3-dioxolan-2-one (3c)

Colorless oil; yield: 73 mg (57%). IR (neat): 2942, 1768, 1131 cm⁻¹. 1H NMR (CDCl₃, 300 MHz): δ = 7.95–7.90 (m, 2 H), 7.75–7.70 (m, 1 H), 7.65–7.60 (m, 2 H), 4.95–4.90 (m, 1 H), 4.65–4.50 (m, 1 H), 4.15–4.10 (m, 1 H), 3.35–3.20 (m, 2 H), 2.40–2.10 (m, 2 H). 13C NMR (CDCl₃, 75 MHz): δ = 154.4, 138.4, 134.2 (CH), 129.5 (CH), 127.9 (CH), 74.5 (CH), 68.8 (CH₂), 51.6 (CH₂), 27.3 (CH₃).


4-Methyl-4-[2-(phenylsulfonyl)ethyl]-1,3-dioxolan-2-one (3g)

White solid; yield: 66 mg (49%); mp 117–118 °C. IR (KBr): 2923, 1801, 1281, 1064 cm⁻¹. 1H NMR (CDCl₃, 300 MHz): δ = 7.95–7.90 (m, 2 H), 7.75–7.70 (m, 1 H), 7.65–7.60 (m, 2 H), 4.25–4.15 (m, 2 H), 3.25–3.20 (m, 2 H), 2.25–2.20 (m, 2 H), 1.15 (s, 3 H). 13C NMR (CDCl₃, 75 MHz): δ = 153.5, 138.4, 134.2 (CH), 129.5 (CH), 127.9 (CH), 81.5, 74.0 (CH), 50.7 (CH₂), 31.6 (CH₂), 24.2 (CH₃). Anal. Calcd for C₁₃H₁₆O₅S: C, 53.32; H, 5.22. Found: C, 53.3; H, 5.2.


(23) The decatungstate anion is known to be unstable under strongly basic conditions, although it tolerates the presence of NaHCO₃ as an insoluble base; see: Ravelli, D.; Albini, A.; Fagnoni, M. Chem. Eur. J. 2011, 17, 572.

(24) Similar behavior has recently been observed in the case of HAT from alkanols and alkanediols; see: Salamone, M.; Ortega, V. B.; Martin, T.; Bietti, M. J. Org. Chem. 2018, 83, 5539.


