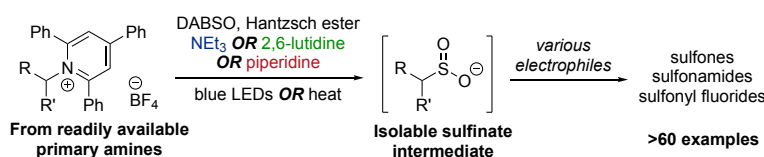


# Sulfinates from Amines: A Radical Approach to Alkyl Sulfonyl Derivatives via Donor-Acceptor Activation of Pyridinium Salts.

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Supporting Information Placeholder



**ABSTRACT:** Synthetically versatile alkyl sulfinates can be prepared from readily available amines, using Katritzky pyridinium salt intermediates. In a catalyst-free procedure, primary, secondary and benzylic alkyl radicals are generated by photo- or thermally-induced single-electron transfer (SET) from an electron donor-acceptor (EDA) complex, and trapped by SO<sub>2</sub> to generate sulfonyl radicals. Hydrogen atom transfer (HAT) from Hantzsch ester gives alkyl sulfinate products, which are used to prepare a selection of medicinal chemistry relevant sulfonyl-containing motifs.

Sulfinate salts are versatile intermediates used in the synthesis of a variety of sulfonyl-derived functional groups<sup>1</sup> that are frequently found in agrochemicals<sup>2</sup> and pharmaceuticals.<sup>3</sup> Bench-stable SO<sub>2</sub> surrogates, such as the amine-SO<sub>2</sub> Lewis adduct DABSO (DABCO·(SO<sub>2</sub>)<sub>2</sub>),<sup>4</sup> or inorganic metal bisulfites, such as K<sub>2</sub>S<sub>2</sub>O<sub>5</sub>,<sup>5</sup> used in combination with metal catalysts,<sup>6</sup> organometallic reagents,<sup>4b,7</sup> or reactive intermediates, have made a tremendous impact on the synthesis of aryl sulfinates. However, applications to the preparation of alkyl sulfinates are more limited. As a result, long reaction sequences, often using thiol or sulfonyl chloride building blocks, that require the manipulation of oxidation states, are frequently needed for the synthesis of these alkyl variants.<sup>8</sup> Sulfinate transfer agents, such as sodium 3-methoxy-3-oxopropane-1-sulfinate (SMOPS),<sup>9</sup> which use alkyl halides as the substrates,<sup>10</sup> offer an alternative approach.

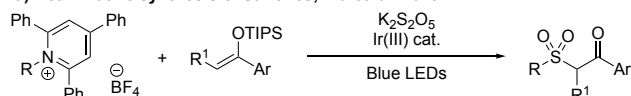
Recently, the radical acceptor properties of SO<sub>2</sub> have been exploited,<sup>11</sup> and radicals generated from a range of precursors, including alkyl halides,<sup>12</sup> and alkyl potassium trifluoroborates,<sup>13</sup> and others<sup>14,15,16</sup> have all been employed.<sup>11a, 11b</sup> However, the selection of radical traps that can be used in these methods is restrictive. Decarboxylative strategies for the synthesis of alkyl sulfinates have been reported. Jiang and co-workers used sodium dithionite as the SO<sub>2</sub> source and reductant to generate alkyl sulfinates from activated esters in a sulfone synthesis,<sup>17</sup> although no primary non-benzylic substrates were included. Larionov has reported the synthesis of alkyl sulfonamides from carboxylic acids,<sup>18</sup> and a recent report has shown that decatungstate photocatalysis can achieve C-H bond sulfination.<sup>19</sup>

2,4,6-Trisubstituted pyridinium (Katritzky) salts, studied by Katritzky and co-workers since the 1970s,<sup>20</sup> have recently seen a surge in interest, and have been used as radical precursors, generating alkyl radicals under mild conditions by single-electron reduction.<sup>21</sup> This has resulted in several new deaminative transformations using metal<sup>22</sup> or photoredox catalysis,<sup>23</sup> as well as catalyst-free procedures.<sup>24</sup> Wu and co-workers have used Katritzky salts and photoredox catalysis to generate alkyl radicals,<sup>23a</sup> which, following addition to SO<sub>2</sub> and trapping with enol ethers, provides alkyl sulfones (Scheme 1a); a related process using alkenyl boronic acids as traps is also known.<sup>25</sup> Importantly, access to what are arguably the most useful sulfonyl derivatives – sulfinate salts – from Katritzky salts, has not been achieved.

Recently, single electron transfer (SET) from electron donor-acceptor (EDA) complexes has emerged as an effective catalyst-free strategy for radical generation from Katritzky salts. Complexation of electron donors such as bis(catecholato)diboron, or amines, followed by photo- or thermally-induced SET, has been used in various deaminative functionalisations.<sup>26</sup> Notably, Aggarwal used Hantzsch ester as an electron-donor for the photoinduced generation of alkyl radicals. Alkylation (Giese) and allylation products were then obtained following a further hydrogen atom transfer (HAT) from Hantzsch ester (Scheme 1b).<sup>26e</sup> Inspired by the contributions from Aggarwal and Wu,<sup>23a, 26e</sup> we conceived a route to alkyl sulfinates that exploited HAT from Hantzsch ester to sulfonyl radicals using Katritzky salts. Subsequent in situ reaction with electrophiles would provide access to diverse sulfonyl-derived products from readily available alkyl amines in a simple, catalyst-free procedure (Scheme 1c).

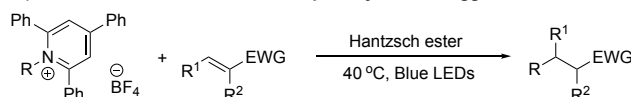
**Scheme 1. a) Photoredox-catalysed deaminative synthesis of sulfones. b) Catalyst-free photoinduced deaminative functionalisation. c) This work: Catalyst-free deaminative synthesis of alkyl sulfonates.**

**a) Deaminative synthesis of sulfones, Wu et. al. 2019**



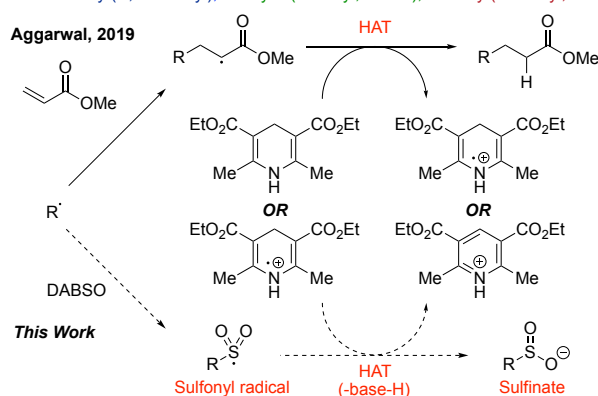
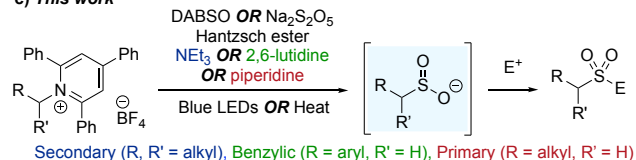
- Expensive Ir(III) photocatalyst
- Electrophile limited to silyl enol ethers, limiting scope of sulfone products
- No access to other sulfonyl-derivatives (sulfonates not available)

**b) Deaminative functionalisations of primary amines, Aggarwal et. al. 2019**



- Application to multiple reaction classes
- Moderate yields for benzylic and primary substrates
- Elevated temperatures and light required for primary substrates

**c) This work**

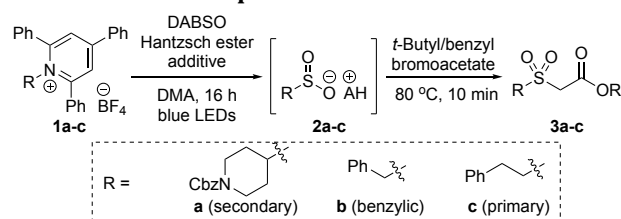


- Catalyst-free route to sulfonyl-derivatives from readily available amines
- Good yields for secondary, primary and benzylic substrates
- Photo- or thermally-induced radical generation

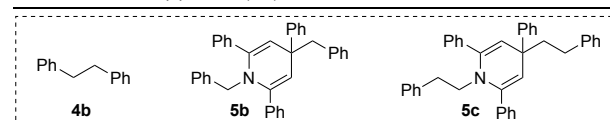
We selected secondary Katritzky salt **1a** as a model substrate, and used modified conditions from Aggarwal as a starting point,<sup>26e</sup> with DABSO as the SO<sub>2</sub> source, and Et<sub>3</sub>N to form the ammonium sulfonate salt **2a**. (Scheme 2). We were pleased to observe sulfonate in the reaction mixture, and following alkylation with *t*-butyl bromoacetate, sulfone **3a** was obtained in 39% yield (entry 1). The equivalents of Hantzsch ester could be lowered (entry 2). Et<sub>3</sub>N was found to be essential (entries 3 and 4), demonstrating the importance of ternary EDA complex formation.<sup>26e</sup> The reaction temperature could also be reduced to ambient (~30 °C) without reducing yields (entry 5). Removing Hantzsch ester substantially reduced the yield (entry 6). Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> could be used as an SO<sub>2</sub> surrogate but gave a lower yield (entry 7). Only trace product was observed without blue LEDs, but increasing the temperature to 60 °C in the dark restored reactivity, giving a yield of 80% (entries 8 and 9). We then moved to evaluate benzylic substrate **1b**, and a low yield of 28% was obtained using the optimized conditions for the secondary substrate (entry 10), with significant amounts of homocoupling product **4b** and adduct **5b** being observed. Removing Et<sub>3</sub>N was detrimental, but replacing it with 2,6-

lutidine gave a yield of 82% (entries 11 and 12). Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> could be used with or without 2,6-lutidine, to provide sulfone **2b** in 67% and 70% yields, respectively (entries 13 and 14). Reaction in the dark at 40 °C was also effective (entries 15 and 16). Higher reaction temperatures were needed when the primary amine-derived substrate **1c** was used (entries 17 and 18).<sup>26e</sup> As noted by Glorius, the addition of piperidine gave a significantly improved yield, and an increase in temperature to 80 °C gave a further increase to 74% (entries 19 and 20).<sup>26d</sup> Reaction in the dark at 90 °C delivered a 82% yield, and Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> was also found to be compatible (entries 21-23).

**Scheme 2. Selected optimization studies. <sup>a</sup>**



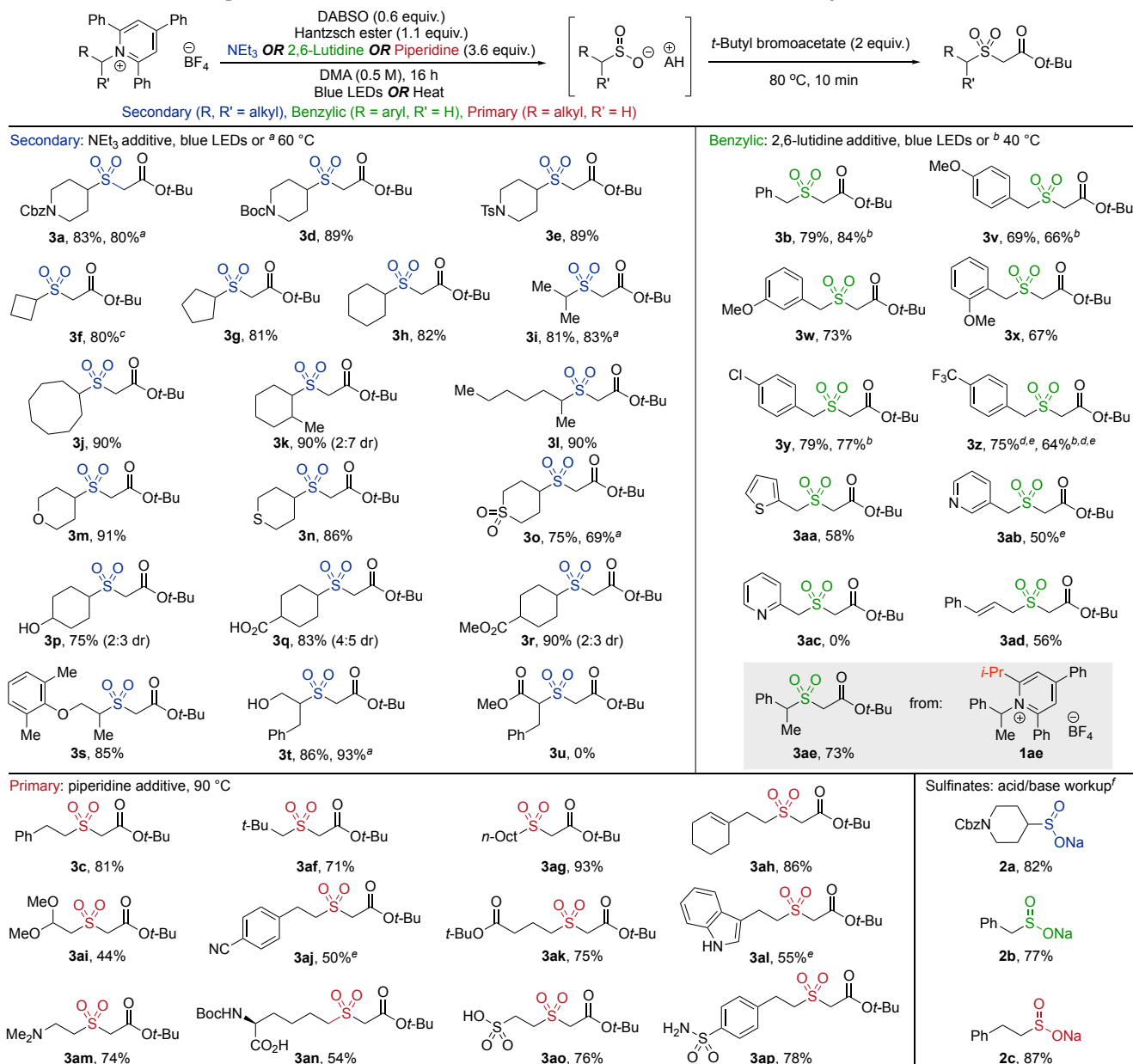
Entry	R	R'	Additive (equiv.)	Temp. (°C)	Modifications	Yield of 3 (%)
1	a	<i>t</i> -Bu	Et <sub>3</sub> N (1.2)	~40	Hantzsch ester (3.0 equiv.)	39
2	a	<i>t</i> -Bu	Et <sub>3</sub> N (1.2)	~40	-	46
3	a	<i>t</i> -Bu	none	~40	-	0
4	a	<i>t</i> -Bu	Et <sub>3</sub> N (3.6)	~40	-	78
5	a	<i>t</i> -Bu	Et <sub>3</sub> N (3.6)	~30	-	82
6	a	<i>t</i> -Bu	Et <sub>3</sub> N (3.6)	~30	no Hantzsch ester	0
7	a	<i>t</i> -Bu	Et <sub>3</sub> N (3.6)	~30	Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> (1.2 equiv.)	62
8	a	<i>t</i> -Bu	Et <sub>3</sub> N (3.6)	30	no light	trace
9	a	<i>t</i> -Bu	Et <sub>3</sub> N (3.6)	60	no light	80
10	b	<i>t</i> -Bu	Et <sub>3</sub> N (3.6)	~30	-	28
11	b	<i>t</i> -Bu	2,6-lutidine (3.6)	~30	-	82
12	b	<i>t</i> -Bu	none	~30	-	9
13	b	<i>t</i> -Bu	2,6-lutidine (3.6)	~30	Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> (1.2 equiv.)	67
14	b	<i>t</i> -Bu	none	~30	Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> (1.2 equiv.)	70
15	b	<i>t</i> -Bu	2,6-lutidine (3.6)	30	no light	54
16	b	<i>t</i> -Bu	2,6-lutidine (3.6)	40	no light	84
17	c	Bn	Et <sub>3</sub> N (3.6)	~30	-	0
18	c	Bn	Et <sub>3</sub> N (3.6)	~60	-	trace
19	c	Bn	piperidine (3.6)	~60	-	57
20	c	Bn	piperidine (3.6)	~80	-	74
21	c	Bn	piperidine (3.6)	80	no light	67
22	c	Bn	piperidine (3.6)	90	no light	82
23	c	Bn	piperidine (3.6)	90	Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> (1.2 equiv.), no light	69



<sup>a</sup> Reaction conditions: (step 1) **1a-c** (1 equiv.), DABSO (0.6 equiv.), additive (3.6 equiv.), Hantzsch ester (1.1 equiv.), DMA [0.5 M], blue LEDs, 16 h; (step 2) *t*-butylbromoacetate (2.0 equiv.), 80 °C, 10 min. Yields calculated from HPLC analysis using 1,3,5-triisopropylbenzene as internal standard.

We next examined the scope of the reaction (Scheme 3). In general, a broad range of secondary and benzylic substrates reacted efficiently in both photo- and thermally-induced reactions. The scope of primary substrates was explored using thermal conditions only. Varied steric properties were tolerated in both cyclic and acyclic secondary substrates (**3a-j**), including sterically demanding examples (**3k**). Steric hindrance was also tolerated in primary substrates (**3af**).

### Scheme 3. Reaction scope for the formation of functionalized sulfones from Katritzky salts.



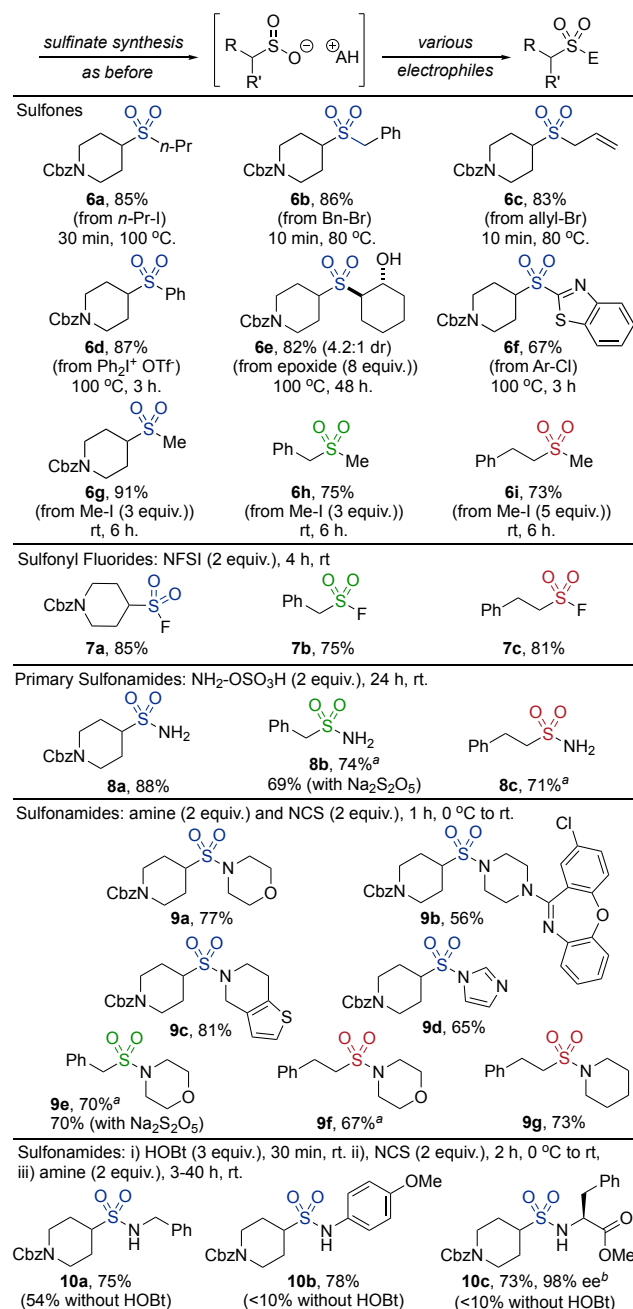
<sup>a</sup> Step 1: 60 °C without LEDs. <sup>b</sup> Step 1: 40 °C without LEDs. <sup>c</sup> Step 1: 90 °C with piperidine (3.6 equiv.) instead of NEt<sub>3</sub>. <sup>d</sup> Step 1: 8 h reaction time. <sup>e</sup> Step 2: rt, 5 h. <sup>f</sup> After step 1: acidify using 2 M H<sub>3</sub>PO<sub>4</sub>, extract (Na<sub>2</sub>CO<sub>3</sub>). All reactions on 0.2 mmol scale, isolated yields.

Varied functional groups were tolerated under the reaction conditions, including unprotected alcohols (**3p**, **3t**), ethers (**3m**, **3s**, **3v-3x**), acetals (**3aj**), carboxylic acids (**3q**, **3an**), esters (**3r**, **3ak**), nitriles (**3aj**), thioethers (**3n**), sulfones (**3o**), sulfonic acids (**3ao**), sulfonamides (**3e**, **3ap**), tertiary amines (**3am**), and carbamates (**3a**, **3d**). Substrates with the sulfone positioned alpha to strong electron-withdrawing groups, such as 2-pyridine (**3ac**) and ester (**3u**), were unsuccessful due to the loss of SO<sub>2</sub> from the intermediate sulfonates. However, moderate electron-withdrawing groups, such as *p*-trifluoromethylphenyl (**3z**), were tolerated, giving good yields. Alkenes (**3ad**, **3ah**) and a selection of heterocycles (**3aa**, **3ab**, **3al**) were also tolerated. The 2,4,6-triphenyl Katritzky salt needed to deliver secondary benzylic sulfone **3ae** was unstable. However, the 2-isopropyl analogue **1ae**, previously reported by Katritzky,<sup>27</sup> could be prepared and generated sulfone **3ae** in 73% yield.

Sulfinate salts could also be isolated; sodium sulfonates **2a-c** could be obtained in excellent yields following simple acidification and extraction using aq. Na<sub>2</sub>CO<sub>3</sub> solution.

Alternative derivatization reactions were also possible (Scheme 4). Variation of the carbon-electrophile allowed access to unsymmetrical sulfones, with alkyl (**6a-c**, **6h-i**) and heteroaryl halides (**6f**), diaryliodonium salts (**6d**) and epoxides (**6e**) all being used, providing structurally diverse products. Sulfonyl fluorides were also synthesised in excellent yields, with examples **7a-c** being prepared using *N*-fluorobenzenesulfonamide (NFSI) as the electrophile.

## Scheme 4. Functionalization of sulfonates.



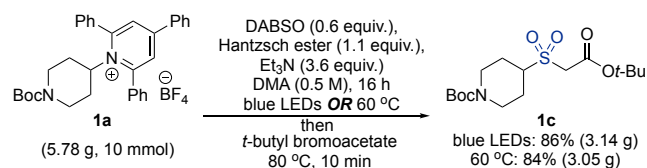
<sup>a</sup> After step 1: acidify using 2 M aq. H<sub>3</sub>PO<sub>4</sub>, extract using DCM × 3, combine organic phases and add DIPEA. <sup>b</sup> Stir HCl salt with DIPEA in DMA for 30 min before addition to reaction mixture. All reactions on 0.2 mmol scale, isolated yields.

Given the high value placed on sulfonamides in medicinal chemistry, we have developed conditions that allow the preparation of primary, secondary and tertiary variants: Primary sulfonamides **8a–c** were obtained by reaction with hydroxylamine-*O*-sulfonic acid; tertiary sulfonamides could be obtained by way of the intermediate sulfonyl chloride, with examples **9a–g**; and finally, the use of primary amines required the addition of HOBt to promote sulfonamide formation (**10a–c**).<sup>28</sup>

Pleasingly, the reactions could be conducted on multigram scale (10 mmol) using either photochemical or thermal

conditions (Scheme 5). For example, sulfone **1c** was isolated in 86% and 84% yields, using blue LEDs and heating to 60 °C, respectively.

## Scheme 5. 10 mmol scale reactions.



Experiments to probe the mechanism, including the use of TEMPO as a radical trap, and formation of EDA complexes, are included in the Supporting Information.

In summary, we have reported, for the first time, a general, scalable synthesis of alkyl sulfonates from readily available primary amines via Katritzky pyridinium salt intermediates. Alkyl radicals are generated by photo- or thermally-induced SET from EDA complexes, and the capture of SO<sub>2</sub> and subsequent HAT gives alkyl sulfonate products. The versatility of the alkyl sulfonate intermediates is demonstrated through the synthesis of >60 examples of sulfones, sulfonamides and sulfonyl fluorides, using one-pot procedures.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and supporting characterization data and spectra (PDF).

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