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Photocatalysis

Exploiting *trans*-Sulfinylation for the Synthesis of Diverse *N*-Alkyl Sulfinamides via Decarboxylative Sulfinamidation

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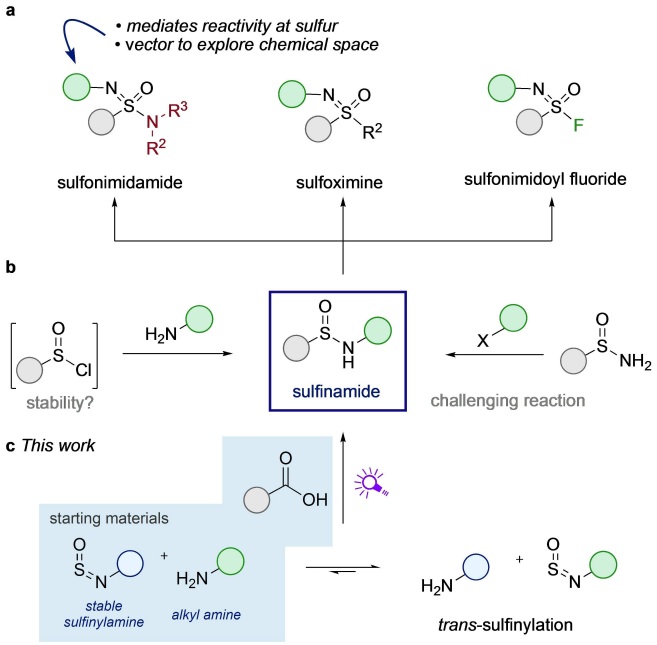
Abstract: Combining simple amines with the bench-stable sulfinylamine Tr-NSO allows in situ preparation of reactive alkyl sulfinylamines, which when combined with alkyl radicals generated by photocatalytic decarboxylation, provides N-alkyl sulfinamides. The reactions are broad in scope and tolerate a wide variety of functional groups on both the acid and amine components. The sulfinamide products are used to prepare a selection of challenging S(VI) products. The method provides a convenient way to use reactive and unstable alkyl sulfinylamines.

Aza-sulfur(VI) functional groups such as sulfonimidamides, sulfoximines and sulfonimidoyl fluorides are increasingly popular motifs in medicinal chemistry, and have been shown to display broad biological function.[1] Many factors contribute to the desirability of these groups, including their 3D-character, favorable polarity, and their H-bond donor/acceptor capabilities. In addition, variation of the substituent attached to the imidic N-atom, present in all of these functional groups, can be used to fine-tune reactivity, for example by electronic or steric control, or to provide a new vector to explore 'chemical space' (Scheme 1a).[2] The oxidative functionalization of sulfinamides is a common and useful method for the preparation of many aza-S(VI) functional groups; in these approaches the imidic N-substituent is derived from the N-substituent on the starting sulfinamides (Scheme 1b).[3,4] Consequently, methods for the preparation of diverse N-functionalized sulfinamides are



Scheme 1. a + b) Aza-sulfur(VI) functional groups, and their synthesis from sulfinamides. c) *This work: trans*-sulfinylation route to N-alkyl sulfinamides.

valuable to synthetic organic chemists,[5] and common methods for their preparation include the reaction of amines with S(IV) electrophiles,[6] although these electrophilic species are often unstable, or via the N-functionalization of primary sulfinamides, which are also non-trivial transformations.[5,7] An attractive alternative would be to incorporate the key N-substituents early in the synthesis, and would ideally use simple readily available and structurally-diverse starting materials. In this Communication we disclose such a method, which proceeds via a *trans*-sulfinylation process, and which uses alkyl carboxylic acids, amines, and a commercial, bench-stable sulfinylamine as the substrates (Scheme 1c).

We recently reported the synthesis of sulfinamides from structurally diverse alkyl carboxylic acids. The reactions are acridine-catalyzed, and proceed by a proton-coupled electron transfer (PCET) mechanism that facilitates the visible light-mediated radical addition to sulfinylamine reagents;[8] Larionov has also developed closely related chemistry (Scheme 2a).[9] Our prior work focused on the use of bench-stable sulfinylamine reagents, such as Tr-NSO, *t*-Oct-NSO

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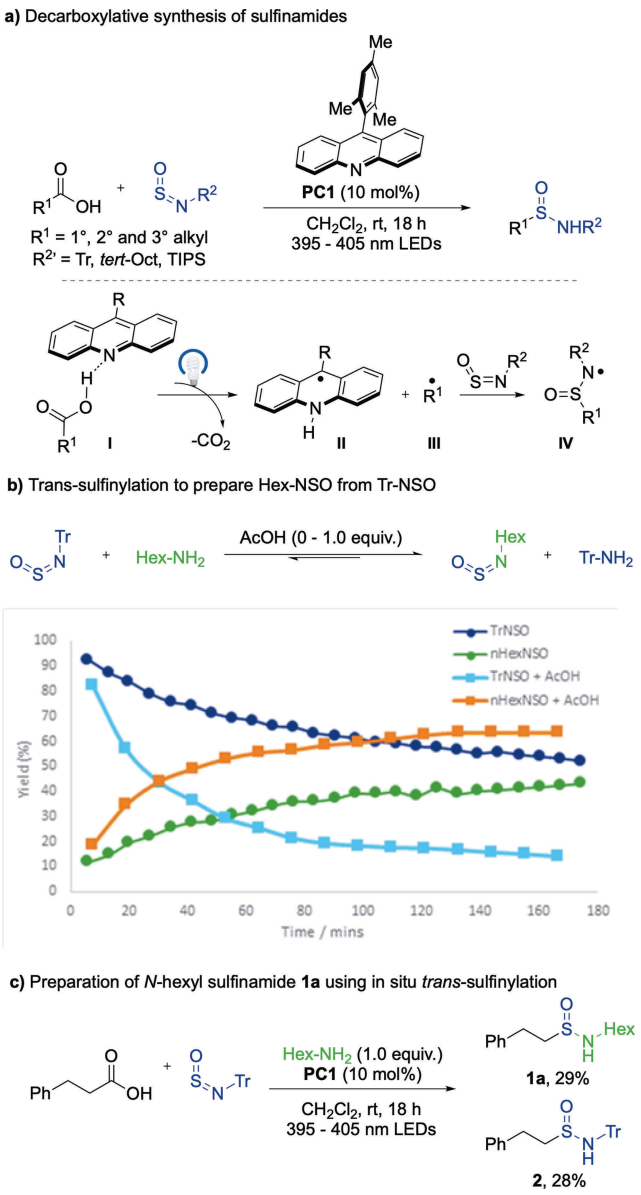
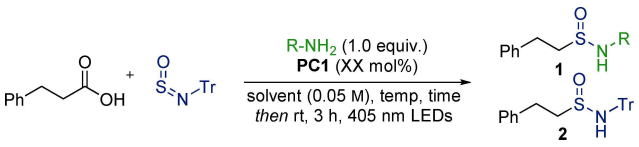


Scheme 2. a) Prior decarboxylative sulfination chemistry, together with mechanistic detail; b) Acid catalyzed *trans*-sulfinylation with Tr-NSO; and c) decarboxylative *trans*-sulfinylation proof-of-concept.

and TIPS-NSO (Tr = triphenylmethyl; TIPS = triisopropylsilyl).[8,10] Whilst the resulting sulfinamide products could hypothetically provide alternative N-functionalised molecules by a deprotection-functionalization sequence, this would be a multi-step procedure.[5] Application of the decarboxylative process to diverse N-alkyl sulfinylamine reagents would provide a more direct route to the corresponding N-alkyl sulfinamides. Although 'non-deprotectable' sulfinylamine reagents have been used in syntheses, these reagents generally feature N-aryl substituents,[11] with the use of simple N-alkyl examples being rare. The reason for this is that simple N-alkyl sulfinylamines are prone to rapid hydrolysis, making their preparation and isolation impractical.[12] Indeed, sulfinylamines derived from low molecular weight amines, such as methyl and propyl amines, are gaseous reagents,[13] providing a further challenge to their use. To avoid these issues, we turned our attention to the in situ preparation of N-alkyl sulfinylamine reagents, exploiting a *trans*-sulfinylation process.

Trans-sulfinylation is the transfer of the sulfinylamine functional group from one amine to another, with the position of the resulting equilibrium dependent on the pK_a of the two amines (Scheme 2b).[12a,b] We reasoned that using a bench-stable sulfinylamine such as Tr-NSO as the starting sulfinylamine should allow the in situ formation of reactive alkyl-amine derived reagents.[10a] Preliminary studies established that the addition of one equivalent of *n*-hexylamine to a solution of Tr-NSO in benzene resulted in a 4:1 mixture of *n*-Hex-NSO and Tr-NSO, and that the rate of equilibration was accelerated by the addition of acetic acid (Scheme 2b). Although alternative sulfinylamine substrates were explored, they were either less efficient, or offered poor bench-stability (see Supporting Information for details). In a proof-of-concept experiment, the addition of an equivalent of hexylamine to our earlier reported decarboxylative synthesis of sulfinamides delivered *n*-hexyl sulfinamide **1a** in 29 % yield, along with the *N*-trityl sulfinamide **2** in 28 % yield (Scheme 2c).

With proof-of-concept established, we embarked on an optimization study. Some improvement in yield was obtained when using an increased catalyst loading of 20 mol % (Scheme 3, entry 2), and further improvement was observed when using more powerful LEDs (18 W *vs* 10 W, entry 3),[14] although substantial amounts of the *N*-trityl side-product **2** were still obtained. The ratio of the two products could be improved by allowing the *trans*-sulfinylation to reach equilibrium prior to radical generation, and an improved yield of 69 % of sulfinamide **1a** was obtained by stirring the



Entry	R	PC1 loading (mol%)	Solvent	Pre-equilibrium Time (mins)	Pre-equilibrium Temp. (°C)	Yield (%) 1	Yield (%) 2
1[a]	Hex	10	CH_2Cl_2	-	-	29	28
2[a]	Hex	20	CH_2Cl_2	-	-	44	27
3[b]	Hex	20	CH_2Cl_2	-	-	53	28
4[b]	Hex	20	CH_2Cl_2	120	20	69	6
5[b]	Hex	20	CH_2Cl_2	30	40	74	4
6[b]	Hex	20	CH_2Cl_2	30	60	74	2
7[b]	Hex	20	MeCN	30	40	75	2
8[b]	*i*-Pr	20	CH_2Cl_2	30	40	22	50
9[b]	*i*-Pr	20	CH_2Cl_2	30	60	55	19
10[b]	*i*-Pr	20	MeCN	30	60	59	15
11[b]	*i*-Pr	20	MeCN	60	60	66	11

Scheme 3. Selected optimization data. [a] Using 10 W 395–405 nm LED strips wrapped inside a crystallising dish. [b] Using a HepatoChem EvoluChem™ 405PF 18 W 405 nm LED spotlight (See Figure S2). Yields determined by HPLC analysis using 1,3,5-triisopropylbenzene as internal standard.

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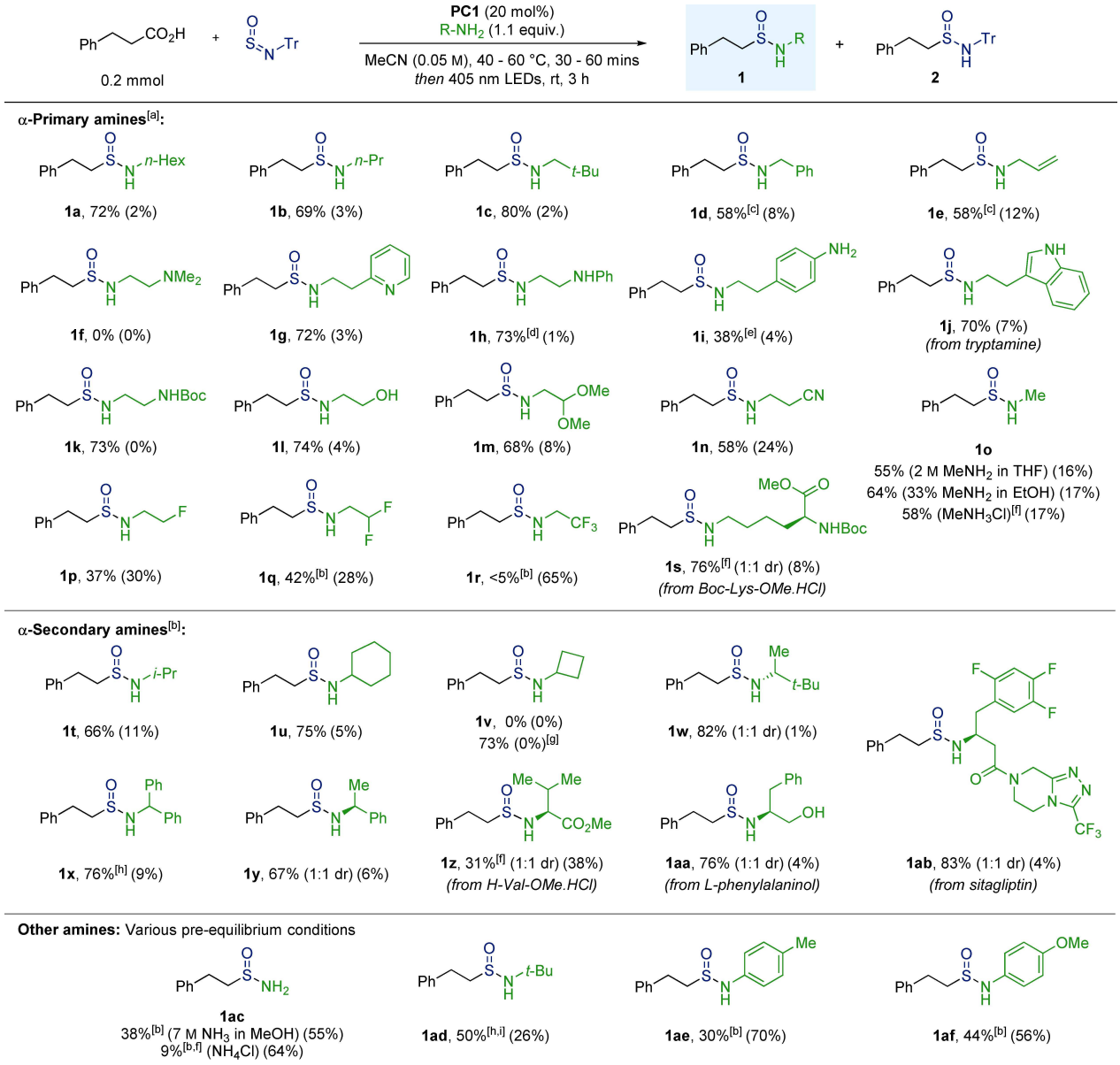
reaction mixture for 2 h at rt prior to irradiation (entry 4). Heating the reaction mixture to 40 °C for 30 mins provided a further increase in yield (entry 5), although temperatures higher than this were not beneficial (entry 6). MeCN was also a suitable solvent for the reaction (entry 7). We then explored a more hindered amine component, and found that using isopropylamine delivered N-isopropyl sulfinamide **1t** in a poor 22 % yield, alongside N-trityl sulfinamide **2** in 50 % yield (entry 8). The yield of sulfinamide **1t** could be improved to 55 % using a higher pre-equilibrium temperature of 60 °C for 30 mins (entry 9). Using MeCN as solvent offered a slight improvement to 59 % (entry 10), and incorporating a longer 1 h pre-equilibrium at 60 °C delivered sulfinamide **1t** in 66 %, with only 11 % of the unwanted N–Tr sulfinamide being formed (entry 11). Thus, the final optimized conditions involved a pre-equilibrium of 30 mins at 40 °C for α-primary amines, and 1 h at 60 °C for α-secondary amines, both using MeCN as the solvent, before illumination at 405 nm in the presence of the acridine catalyst **PC1**[15] at rt for 3 hours.

With optimized conditions in hand, we then evaluated the reaction scope with respect to the amine component, using hydrocinnamic acid as the carboxylic acid (Scheme 4). The reaction tolerated a broad selection of primary amine substrates, providing good yields irrespective of steric environment, as demonstrated by linear (**1a** and **1b**), as well



Scheme 4. Primary amine scope. Isolated Yields. [a] 40 °C, 30 mins pre-equilibrium. [b] 60 °C, 1 h pre-equilibrium. [c] CH_2Cl_2 used as solvent. [d] 5 h irradiation. [e] 40 °C, 18 h pre-equilibrium. [f] From HCl salt, added NEt_3 (1.1 equiv.). [g] CuBr (10 mol %) added. [h] DCE used as solvent. [h] 80 °C, 18 h pre-equilibrium. Yield of **2** in parentheses, calculated by HPLC analysis using 1,3,5-triisopropylbenzene as internal standard. Using a HepatoChem EvoluChem™ 405PF 18 W 405 nm LED spotlight (See Figure S2).

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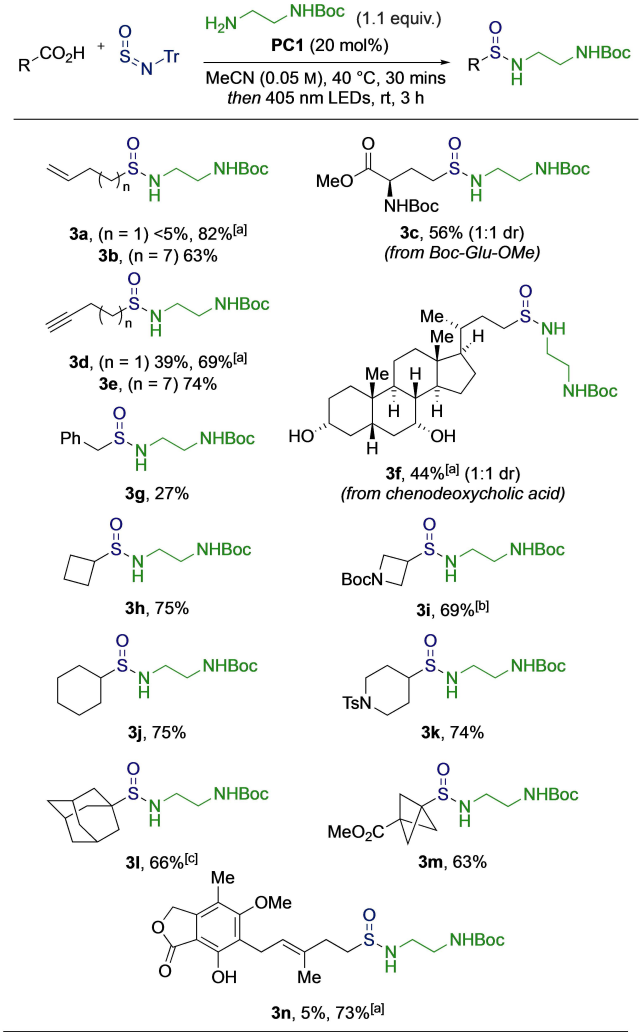
as more hindered β-tertiary examples (**1c**). No desired product was obtained with benzylamine or allylamine using acetonitrile as solvent; however, switching to dichloromethane delivered the N-benzyl and N-allyl products **1d** and **1e** in good yields. Substrate **1f** containing a tertiary amine gave no conversion, likely due to deprotonation of the carboxylic acid; this is consistent with earlier reports of organic bases suppressing acridine-catalyzed decarboxylation.[16] However, less-basic N-functionalities such as pyridine (**1g**), anilines (**1h** and **1i**), and indole (**1j**) could be included, to give the sulfinamide products in moderate to excellent yields. The reaction was found to be tolerant of a broad selection of other functional groups, including carbamates (**1k**), alcohols (**1l**), acetals (**1m**), nitriles (**1n**), methyl esters (**1s**) and fluorinated alkyl substituents (**1p** and **1q**). Sulfinamide products derived from amines bearing electron-withdrawing functional groups, such as nitrile (**1n**) or fluorides (**1p** and **1q**), were obtained in moderate yields, and in the case of trifluoroethylamine, could not be isolated (**1r**). The trityl side-product **2** was obtained in higher yields for these examples. Presumably, the electron-withdrawing groups decrease the basicity of these amines, lowering the extent to which the *trans*-sulfinylation equilibrium favours their corresponding sulfinylamines.[12a,b] The *trans*-sulfinylation protocol could also be used with volatile amines, and good yields were obtained using methylamine either as a solution in THF/ethanol, or as the hydrochloride salt with addition of 1 equivalent of NEt_3, providing *N*-methyl sulfinamide **1o**. Primary sulfinamide **1ac** was also accessible when using ammonia or ammonium chloride, albeit in only moderate yields, via the formation of thionylimide (HNSO) in situ.

A selection of *α*-secondary amines were also explored using 1 h of pre-equilibrium at 60 °C, and we were able to demonstrate that both cyclic and acyclic alkyl groups were tolerated (**1t** and **1u**). Using cylobutylamine as a substrate was initially challenging, with the standard conditions delivering no product; however, the addition of CuBr (10 mol %) to the reaction allowed the corresponding sulfinamide (**1v**) to be obtained in good yield (73 %). Larionov has described the use of Cu(I) as a co-catalyst in their decarboxylative sulfinamidation chemistry, with the Cu reported to stabilize the proposed N-centered radical intermediates formed after addition to the sulfinylamine reagents (see intermediate **IV** in Scheme 2a).[9] In our hands, the effect of added CuBr could be dramatic, as in the case with cyclobutylamine, however, for standard substrates there was little benefit. Using cyclopropylamine was not successful, presumably due to ring-opening from the corresponding N-radical intermediate (such as **IV**), and in this case the addition of CuBr had no effect.[17] The use of sterically demanding amines to provide congested sulfinamide products (**1w**–**1y**) worked well, and prolonged heating in DCE at a higher temperature of 80 °C allowed the reaction with *tert*-butylamine to proceed, providing the sulfinamide (**1ad**) in 50 % yield. The reaction could be applied to biologically relevant amines, including H–Val–OMe, phenylalaninol, and the drug molecule sitagliptin, giving moderate to excellent yields of the corresponding sulfinamide products (**1z**, **1aa**, **1ab**). Finally, we showed that anilines could also be used in the *trans*-sulfinylation reaction with Tr-NSO to give the corresponding N-aryl sulfinamides in moderate yields (**1ae** and **1af**).

The scope of the reaction with respect to carboxylic acids was then investigated, with *N*-Boc-ethylenediamine used as the amine component (Scheme 5). When assessing primary alkyl carboxylic substrates we found that alkene and alkyne-containing sulfinamides **3a** and **3d** were obtained in poor yields, which we hypothesised was due to cyclisation of the sulfonimidoyl radical intermediates (such as **IV** in Scheme 2a) competing with the HAT. Accordingly, using substrates with longer alkyl tethers slowed cyclisation and allowed the sulfinamides (**3b** and **3e**) to be obtained in good yields. Alternatively, the addition CuBr (10 mol %) was again found to be beneficial, delivering sulfinamides **3a** and **3d** in 82 % and 69 % yield, respectively. We were able to use biologically-relevant carboxylic acid substrates, including the amino acid Boc-Glu-OMe, the steroid natural product



Scheme 5. Carboxylic acid scope. [a] CuBr (10 mol %) added. [b] CH_2Cl_2 used as solvent. [c] MeCN : CH_2Cl_2 (1 : 1) used as solvent. Isolated yields. Using a HepatoChem EvoluChem™ 405PF 18 W 405 nm LED spotlight (See Figure S2).

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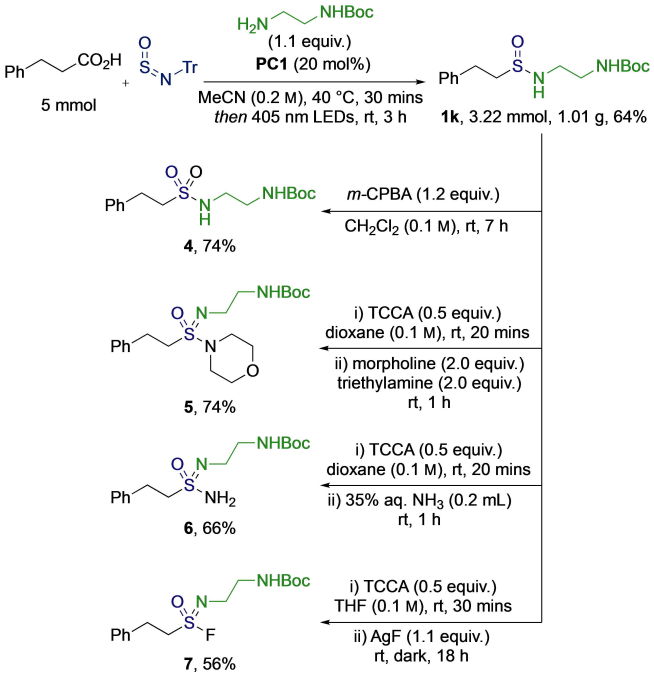
chenodeoxycholic acid, and the medicinal agent mycophenolic acid (with addition of CuBr), giving the complex sulfinamides (**3c**, **3f** and **3n**) in moderate yields. Although the reaction proceeded using phenylacetic acid, the diminished yield of sulfinamide **3g** was likely due to dimerization of the intermediate (stable) benzylic radical. Secondary carboxylic acids provided good to excellent yields of the corresponding cyclobutane (**3h**), azetidine (**3i**), cyclohexane (**3j**), and piperidine (**3k**) sulfinamides. Tertiary alkyl carboxylic acids also gave good yields of the desired adamantane (**3l**) and bicyclopentane (**3m**) sulfinamide products. With the breadth of the methodology's scope established, we wished to demonstrate its scalability. To achieve this, the reaction was carried out at a higher concentration of 0.2 M, and we were then able to prepare sulfinamide **1k** on a 5 mmol scale, with only a small drop in yield to 64 % (Scheme 6).

With over 1 g of sulfinamide **1k** in hand, we explored its utility in the synthesis of a selection of challenging S(VI) motifs (Scheme 6). Oxidation at sulfur using *m*-CPBA provided sulfonamide **4** in 74 % yield. Oxidative chlorination using TCCA followed by addition of morpholine or ammonia gave sulfonimidamide products **5** and **6** in 74 % and 66 % yields, respectively. Finally, oxidative chlorination followed by addition of silver(I) fluoride provided access to synthetically useful sulfonimidoyl fluorides,[18] with fluoride **7** being isolated in 56 % yield.

In conclusion, we have developed a novel photocatalytic method to prepare a broad selection of N-alkyl sulfinamide products using structurally diverse primary amines and carboxylic acids as substrates. The methodology has been shown to be both readily scalable and conveniently applied to the preparation of a selection of challenging S(VI) products. This chemistry introduces *trans*-sulfinylation as a useful synthetic method, and uses Tr-NSO and primary amines to prepare the key sulfinylamine reagents in situ, which then intercept alkyl radicals derived from the carboxylic acids. Given the potential diverse applications of sulfinylamines, we anticipate that *trans*-sulfinylation will be widely adopted as a useful synthetic tool.



Scheme 6. Scale-up and preparation of S(VI) motifs.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: sulfinylamine · sulfinamide · amine · synthetic methods · photochemistry

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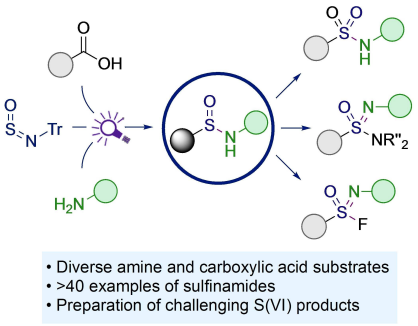
Photocatalysis

J. A. Andrews, R. G. Woodger, C. F. Palmer, D. L. Poole, M. C. Willis* — **e202407970**

Exploiting *trans*-Sulfinylation for the Synthesis of Diverse *N*-Alkyl Sulfinamides via Decarboxylative Sulfinamidation



- Diverse amine and carboxylic acid substrates
- >40 examples of sulfinamides
- Preparation of challenging S(VI) products

Trans-sulfinylation enables the generation of hydrolytically-sensitive alkyl sulfinylamines in situ from Tr-NSO and primary amines. We exploit this process alongside alkyl radical generation from carboxylic acids using acridine photocatalysis to prepare a broad selection of N-alkyl sulfinamides from structurally diverse and readily available feedstocks.

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