Organic & Biomolecular Chemistry

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2021, **19**, 2941

5-(Diarylimino)- and 5-(sulfoximido) dibenzothiophenium triflates: syntheses and applications as electrophilic aminating reagents†

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Received 15th February 2021,
Accepted 8th March 2021

DOI: 10.1039/d1ob00285f

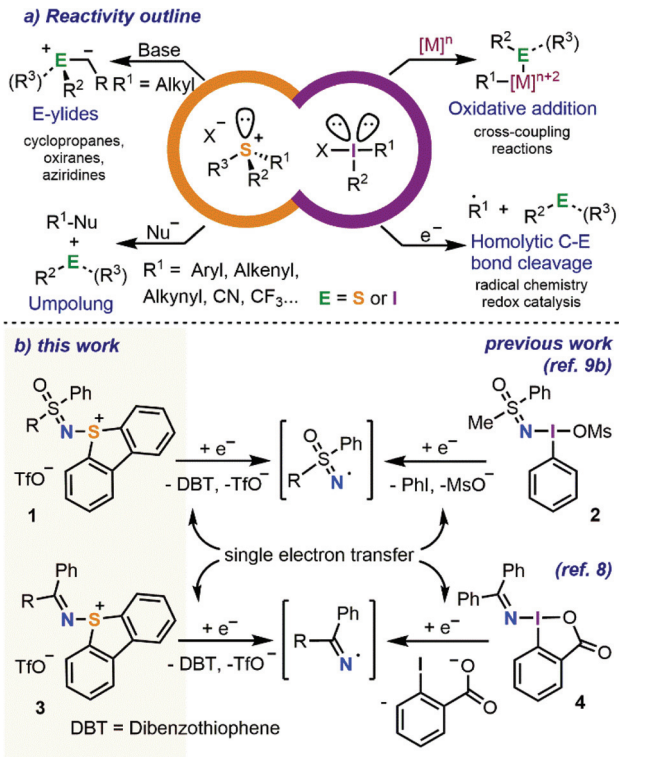
rsc.li/obc

The one-pot synthesis of well-defined 5-(diarylimino) and 5-(sulfoximido)dibenzothiophenium triflates, respectively from diarylimines or sulfoximines, is reported and the structures of a series of these compounds are elucidated by X-ray crystallography. In analogy to their hypervalent I(III) analogues, the iminoyl and sulfoximidoyl groups of these compounds can be selectively transferred to organic substrates. Specifically, the uncatalyzed imination of thiols or sulfinates proceeds with good yields, while under the mild reaction conditions offered by visible light photoredox catalysis, the radical amination of hydrazones or the sulfoximidation of benzylic, allylic and propargylic C–H bonds takes place satisfactorily.

Introduction

The reactivity of *S*-(aryl/alkyl) sulfonium salts shows many similarities with that of hypervalent I(III) reagents of an analogue substitution pattern.[1] Both types of compounds do react with low valent metals such as Ni(0) or Pd(0) *via* oxidative addition at the C–S or C–I bond, respectively, making these compounds suitable partners for cross coupling reactions.[2] In addition, the highly electrophilic nature of the central heteroatom in these species facilitates one-electron reduction of both sulfonium salts and hypervalent I(III) reagents, which ultimately leads to the homolytic fragmentation of one of the C–E (E = heteroatom) bonds and generates a carbon-centred radical.[3] This fragmentation pattern paves the way to the use of both compounds as radical precursors; however, the synthetic utility of this methodology can only be fully exploited if the chemoselective cleavage of only one of the C–E bonds is achieved.[4] Finally, the uncatalyzed reaction of both species with suitable nucleophiles is also possible. This last process can be seen as an attack of the nucleophile on the central heteroatom followed by reductive elimination of a Nu–R moiety (Scheme 1a).[5]

Much more obscure is the chemistry of sulfonium salts bearing nitrogen-based substituents. Specifically, while many hypervalent iodine reagents containing transferable nitrogen functional groups such as azido,[6] phthalimido,[7] diarylimino,[8] or sulfoximido are available,[9] only a few *S*-analogues of these compounds have been reported to date and the studies regard-



Scheme 1 Reactivity overview and previous and current work on the use of hypervalent iodine and sulfonium salts as electrophilic sulfoximide/imine transfer reagents.

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† Electronic supplementary information (ESI) available. CCDC 2062172–2062181; 2063032–2063039. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1ob00285f

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ing their reactivity are even more scarce.[10] We speculated however that they should also share similarities with their iodine counterparts and hypothesized that imino- and sulfoximido-substituted sulfonium salts might potentially function as electrophilic aminating reagents or efficient sources of imine/sulfoximide radicals (Scheme 1b).

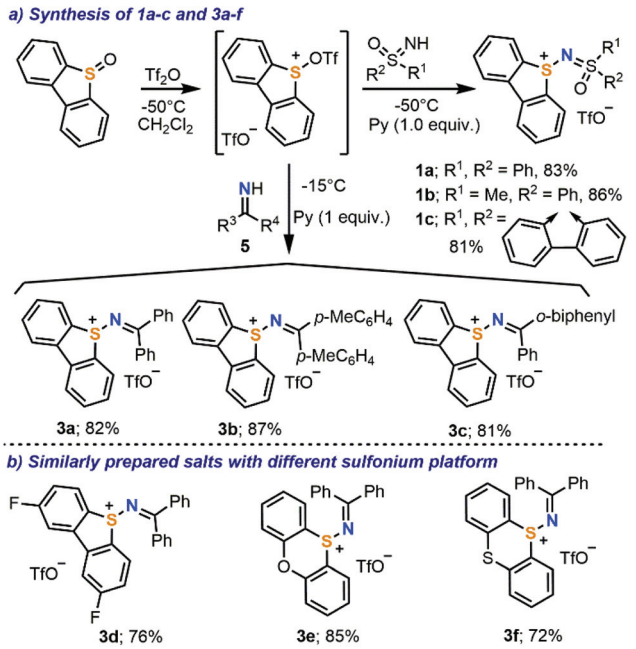
With this idea in mind, we report herein the multigram-scale syntheses of a series of sulfonium salts containing sulfoximido **1** and diarylimino **3** functional groups and preliminarily evaluate their use in the electrophilic amination of thiols and organic sulfonites. The generation of sulfoximidoyl and iminyl radicals from the same reagents under photochemical conditions and their subsequent reaction with hydrazones and benzylic C–H bonds to deliver *N*-(amino)amidines and *N*-benzylic sulfoximides, respectively, are also studied.

Results and discussion

Synthesis and structure of *S*-imino- and *S*-sulfoximido-substituted sulfonium salts

Our initial efforts focused on the synthesis of the parent sulfonium salts **1**, which have a sulfoximidoyl moiety attached to the dibenzothiophene platform (Scheme 2). While the preparation of structurally analogous sulfonium salts has been described by the reaction of *N*-halosulfilimines with dialkyl/arylsulfides,[10e,11] we decided to explore alternative methods, which employ less elaborated starting materials and minimize the number of synthetic steps. Hence, the direct reaction of diphenylsulfoximide with Tf_2O-activated dibenzothiophene *S*-oxide was evaluated.[12] Gratifyingly, the desired reaction took place at −50 °C in the presence of pyridine as a base, affording **1a** as a beige crystalline solid in 83% yield. Scaling the reaction up to multigram quantities is possible without a drop in the isolated yield (see the ESI for details†). This simple synthetic protocol seems to be general and it has been successfully extended to the preparation of sulfonium salts **1b** and **1c**, containing two different sulfoximidoyl moieties (Scheme 2a). Following a very similar methodology, but just replacing the sulfoximide with benzophenone imines **5**, one obtains diarylimino-substituted sulfonium salts **3a–c**. Compounds **3d–f**, which employ 2,8-difluorodibenzothiophene, phenoxathiin and thianthrene units as sulfonium platforms, are also prepared from the respective sulfoxides through the same route.

X-ray diffraction analysis of single crystals of **1a–c** and **3a–f** confirmed the expected connectivity of the newly prepared compounds (see Fig. 1 for the structures of **1b**, **1c**, **3a** and **3e** and the ESI for the others†). In **1c**, the sulfur atom from the dibenzothiophenium unit (S1) remains in the plane defined by that heterocycle and adopts a trigonal-pyramidal bond geometry, the sum of the bond angles around S1 being 304.6°. The S1–N1 bond distance of 1.652(1) Å falls in between the ranges for S–N single bonds and double bonds, while the N1–S2 length for the sulfoximide moiety (1.597(1) Å) gets closer to the typical $S{=}N_{(sp^2)}$ double bond distance of neutral sulfoximides (1.517 Å).[13] Although the general bonding situation in **3a** is relatively similar to that in **1c**, two differences are of note. An S1–N1 bond distance of 1.705(1) Å was determined, which more clearly indicates that a single bond connects both atoms. Moreover, in **3a**, the sum of the bond angles around S1 decreases to 297.9°. Both facts can be attributed to the lack of significant π-interaction between S1 and N1 in this molecule; this is also confirmed by the N1–C13 bond distance, 1.304(2)



Scheme 2 Synthesis of target sulfonium salts and scope of the transformation.

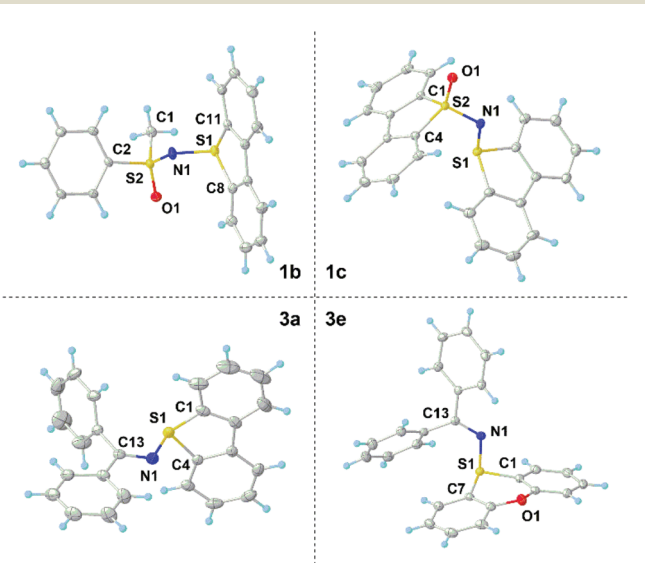


Fig. 1 Molecular structures of compounds **1b** (top left), **1c** (top right), **3a** (bottom left) and **3e** (bottom right) in the solid state. Anisotropic displacement shown at the 50% probability level; triflate anions and hydrogen atoms are omitted for clarity.[14]

Å, which is just slightly longer than the typical one for C=N double bonds in imines (1.297 Å).[13]

In an attempt to better understand the bonding situation just described, the geometry of each compound was optimized at the PBE/def2TZVP/univ-JFIT level of theory and an IBO (Intrinsic Bond Orbital) analysis was carried out for **1c** and **3a** (see Fig. 2 for the most important IBOs and the ESI for full details†). In line with our interpretation of the crystallographic data, a weak π-interaction (**2e**; **3c**) is detected between the central nitrogen and the two flanking sulfur atoms in **1c**, which may account for the reduced bond length in between these atoms. Conversely, in **3a** the bond situation is better represented by a clear C=N π-bond. Non-shared electron pairs are found at S1 and N1 in both compounds.

Along these lines, natural population analysis (B3LYP/6-31G*) in **1c** and **3a** indicates that the sulfur atoms belonging to the dibenzothiophene unit (S1) bear an entire positive charge in both compounds (+1.050*e*, **1c**, and +1.021*e*, **3a**, respectively), while the nitrogen atoms significantly differentiate from each other. N1 bears a negative charge in **1c** (−1.060*e*) while this atom is only partially charged in **3a** (−0.613*e*). Wiberg bond indices for the S1–N1 interaction are 1.023 and 0.966 for **1c** and **3a**, respectively, 1.043 for N1–S2 in **1c** and 1.672 for the N1=C13 bond in **3a**. This analysis, together with the X-ray structures, points to a slightly stronger S1–N1 interaction in **1c** than in **3a**.

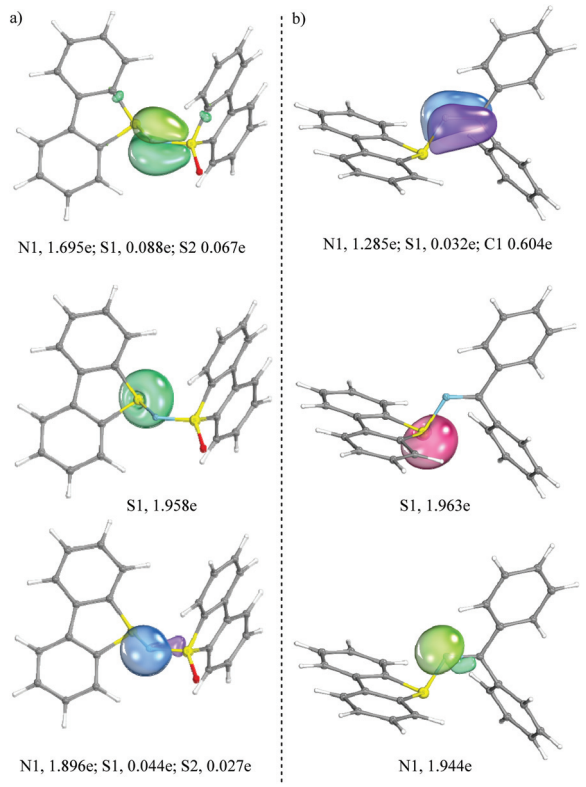


Fig. 2 Selected IBO plots for complexes **1c** (a) and **3a** (b); assigned partial charges for the given IBOs to the individual atoms. Threshold value for printing: 80.

Inspection of the frontier orbitals reveals that in both **1c** and **3a** the very low-lying LUMO+1 largely corresponds to a mixture between the π*-system of the dibenzothiophene platform and the σ*(S1–N1) bond (see the ESI†). This distribution of orbital coefficients suggests that any donation of electron density to this orbital weakens the S1–N1 bond. Hence, one might expect that the amination of appropriately selected nucleophiles might occur *via* the formation of a sulfurane intermediate and subsequent reductive elimination from the S-center. In addition, single electron transfer to **1** or **3** should deliver dibenzothiophene and N-center radicals, as in the case of the analogous I(III)-compounds.[8,9]

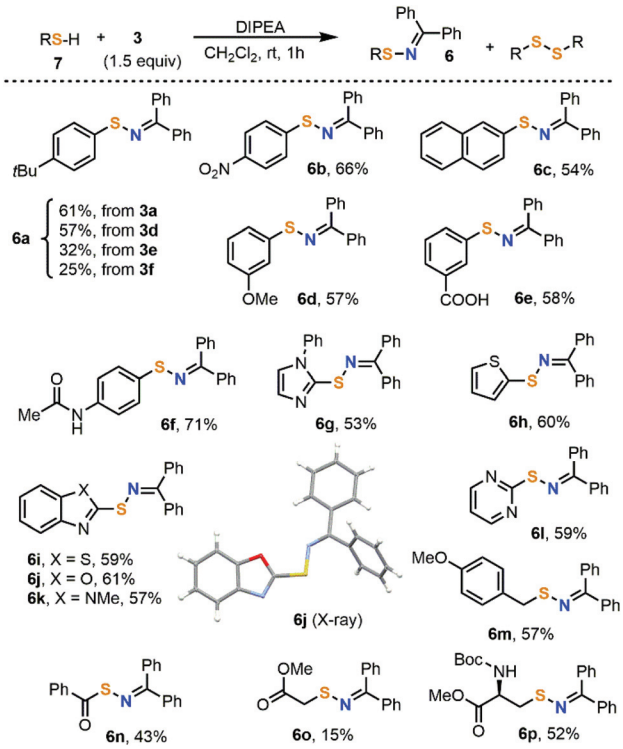
Reactivity studies

Once compounds **1a–c** and **3a–f** were completely characterized, their potential as electrophilic amination reagents was preliminarily examined. Our study started with an attempt to prepare sulfenylimines **6** by direct reaction of **3a–f** with thiols under mildly basic conditions. While several methods are already available for the synthesis of these products,[15] to the best of our knowledge, the disconnection approach we report here is new. Moreover, most protocols start from disulfides, and the only one described employing thiol substrates requires metal catalysis.[16] This could be attributed to the facile oxidation of thiols, resulting in undesired products.

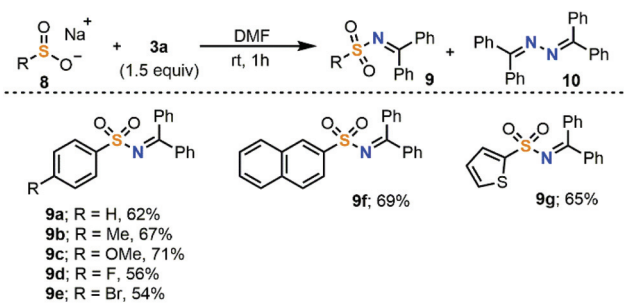
4-(*t*-Butyl)benzenethiol **7a** was initially used as a model substrate (Scheme 3). Treatment of that thiol with salts **3a,d–f** smoothly afforded the desired sulfenylimine **6a**, with reagent **3a** being the one that delivered the desired product with better yields. Employing **3a**, the reaction indistinctly works with electron-rich or electron-poor thiols, albeit all yields are moderate. On the other hand, the functional group tolerance of the transformation is quite broad; ether, ester, amide and nitro groups as well as a range of heterocycles did not disturb. As a side reaction, the formation of 5–10% of the corresponding disulfide was systematically observed in all experiments. When TEMPO (1.0 equiv.) was added to the imination reaction, the formation of **6a** was completely suppressed. It seems therefore reasonable to believe that this reaction takes place *via* one-electron oxidation of the thiolate by **3a** followed by coupling of the iminyl and thiyl radicals.

The electrophilic amination could also be extended to sulfinates **8** to obtain sulfonamides **9**. In this case, bisimine **10** is often observed as a homocoupled side product. Moreover, the addition of TEMPO (1.0 equiv.) to the reaction mixture significantly reduced the isolated yield of **9b** (23%). For these reasons we also believe that the aryl sulfinate salts, which have low oxidation potentials ($E_{1/2}$ = −0.37 V *vs.* SCE for sodium phenylsulfinate), undergo SET oxidation in the presence of **3a** ($E_{1/2}$ = −0.46 V *vs.* SCE) to furnish sulfonyl and iminyl radicals, which recombine to form **9** and small amounts of **10** (Scheme 4).[17]

After this initial contact with the reactivity of salts with the general formula of **3**, and given the number of precedents in which sulfonium salts are reduced *via* single electron transfer under photochemical conditions to produce radicals of

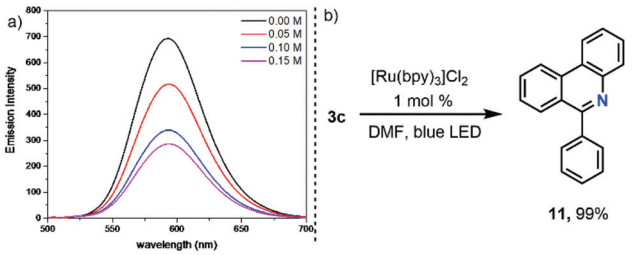


Scheme 3 Substrate scope of the electrophilic amination of thiols. The reaction was conducted at room temperature. Unless specified, all reactions were performed using reagent **3a** (1.5 equiv.). All reactions were quenched after 1 h and yields are of the isolated products.



Scheme 4 Substrate scope of the electrophilic amination of sodium sulfinates with **3a**. All reactions were conducted at room temperature and quenched after 1 h. Yields are of isolated products.

different nature,[2] it was hypothesized that under these soft activation conditions, **3a** also might be able to generate iminyl radicals. An experiment often used to determine the feasibility of that process consists of the evaluation of fluorescence intensity quenching of the photoexcited state of a photocatalyst (Stern–Volmer) in the presence of the desired substrate. In fact, this analysis revealed an effective oxidative quenching of the photoexcited Ru catalyst ($E_{1/2}^{(II)*/(III)} = -0.81$ V *vs.* SCE) in the presence of **3a** ($E_{red} = -0.46$ V *vs.* SCE). The formation of the envisaged iminyl radical was subsequently evidenced by a radical scavenger experiment. Hence, irradiation of **3c**, bearing



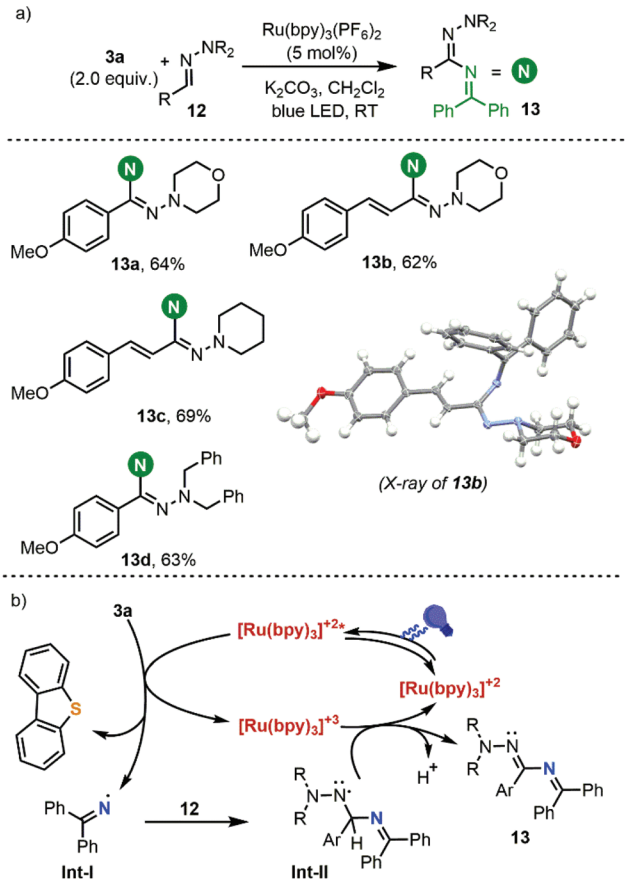
Scheme 5 (a) Stern–Volmer plot of photocatalyst luminescence quenching by **3a** and (b) intramolecular radical trap experiment employing substrate **3c**.

an *o*-biphenyl substituent, in the presence of $[Ru(bpy)_3]Cl_2$ (1 mol%) quantitatively afforded the product of radical trapping, phenanthridine **11** (Scheme 5).[18]

Having established the conditions to form iminyl radicals from **3a**, we set about determining the potential of this photocatalytic system on the C(sp^2)–H amination of aldehyde-derived hydrazones **12** into hydrazonamides **13**, which would represent the most step-economical method to carry out this transformation.[19] We were pleased to see that the desired transformation actually proceeded, leading to the formation of C(sp^2)–H aminated products; the yields however are moderate and they drop dramatically if the hydrazones used as substrates are not derived from electron-rich aromatic aldehydes (Scheme 6).

Based on these results and literature precedents, we proposed the reaction pathway shown in Scheme 6b. Initial irradiation of $[Ru(bpy)_3]^{2+}$ generates photoexcited $([Ru(bpy)_3]^{2+})^*$, which reduces reagent **3a** *via* single-electron transfer and generates the transient iminyl radical (**Int-I**) *via* homolytic S–N bond cleavage. Addition of the N-centered radical to the azomethine carbon of **12** delivers an aminyl radical intermediate (**Int-II**), which is stabilized by the adjacent N atom. At this stage, **Int-II** can be oxidized by $[Ru(bpy)_3]^{3+}$ ($E_{1/2}^{(III)/(II)} = 1.29$ V *vs.* SCE) to produce a diazenium cation with regeneration of the photocatalyst, followed by deprotonation to deliver **13**.[20] Alternatively, deprotonation of **Int-II** may occur first leading to the formation of the corresponding radical anion, which would undergo oxidation to **13**.[21]

Finally, we also checked the reactivity of salt **1a** in the sulfoximidation of benzylic C–H bonds. A closely related transformation to this one has been already described by Bolm and co-workers, also under photochemical conditions, but employing hypervalent I(III) reagent **2**.[9c] These authors report the formation of the desired sulfoximides in moderate to good yields. Mechanistic studies suggest the formation of a sulfoximidoyl radical as a key intermediate, which is able to abstract a benzylic hydrogen atom from the substrate delivering the N–H sulfoximine and a benzyl radical. Oxidation of this radical by the oxidized photocatalyst delivers a benzylic carbocation, which reacts with the sulfoximine to afford the *N*-functionalized products. Hence, if sulfoximidoyl radicals could be generated from sulfonium salts **1a–c**, then, similar reactivity could be expected.



Scheme 6 (a) Synthesis of hydrazonamides **13** and (b) plausible reaction mechanism.

We initially evaluated this possibility by cyclic voltammetry. These experiments showed an irreversible reduction with E_{red} = −0.462 V and −0.606 V *vs.* SCE for **1a** and **1c**, respectively; values that are considerably less negative than that determined for the photoexcited state of $[Ru(bpy)_3][PF_6]$ ($E_{1/2}^{(II)*/(III)} = -0.81$ V *vs.* SCE) indicate the feasibility of the necessary SET event. Moreover, a Stern–Volmer experiment confirms that **1c** effectively quenches the excited state of $[Ru(bpy)_3][PF_6]$ (Fig. 3a). A final confirmation of the generation of sulfoximidoyl radicals by one-electron reduction of **1a** was provided by the reaction of that compound with Cp_2Co (E_{red} =

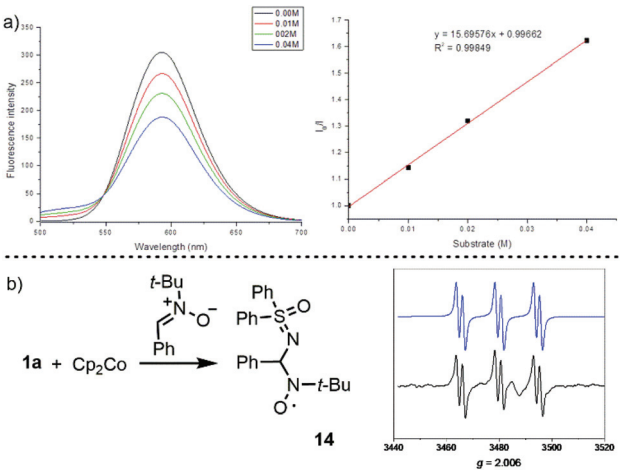
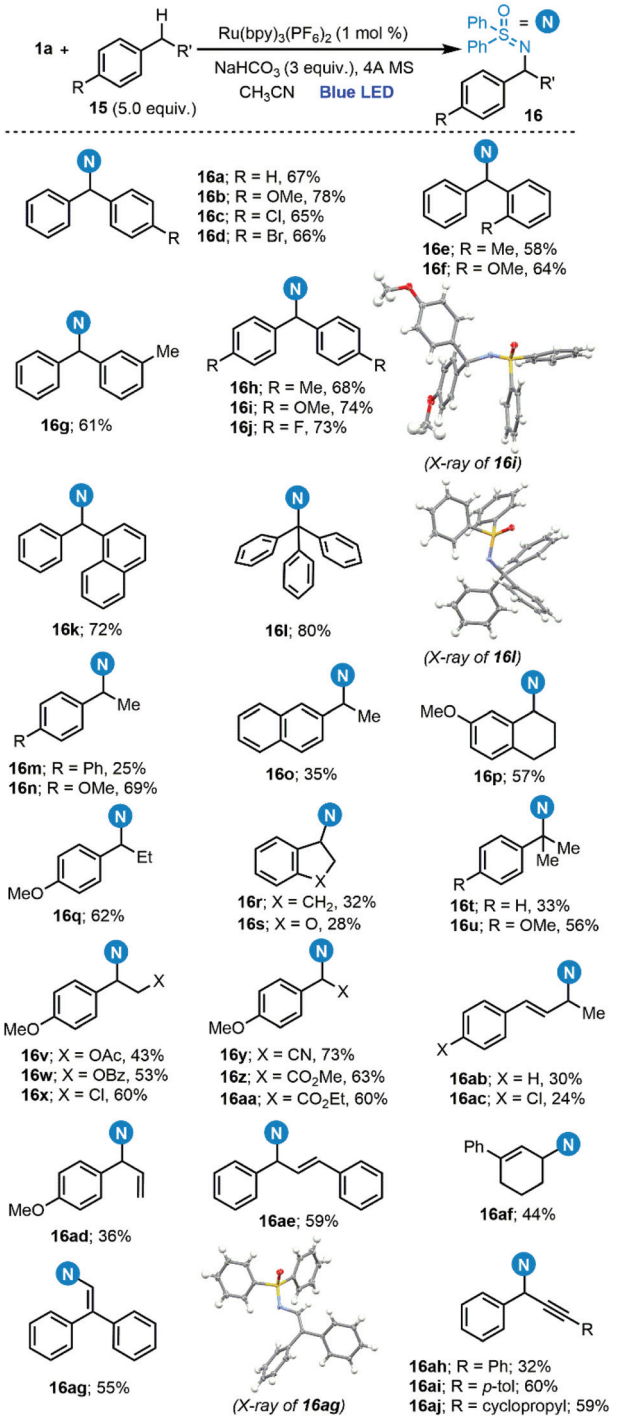


Fig. 3 Mechanistic studies: (a) Stern–Volmer plot of photocatalyst luminescence quenching by **1a** and (b) simulated (blue) and experimental (black) EPR spectra of **14**.



Scheme 7 Reaction scope for the sulfoximidation of benzylic C–H bonds.

−0.93 *vs.* SCE) in the presence of *N*-(*t*-butyl)phenylnitrone (PBN) as a radical trap. The EPR spectrum of the reaction mixture shows a well-resolved splitting as a result of hyperfine coupling with a N- and a H-atom (a_N = 14.61; a_H = 2.22 G), a pattern that fits with that expected for radical **14**.

Once the generation of the desired sulfoximidoyl radical was confirmed, the amination of benzylic C–H bonds was evaluated. In fact, we could perform this reaction with a scope very similar to that reported by Bolm,[9c] which includes not only benzylic positions **16a–aa**, but also allylic **16ab–ag** and propargylic ones **16ah–aj** (Scheme 7).[22] A light on/off experiment confirmed the necessity of continuous irradiation for the reaction to proceed, and the quantum yield of the reaction to form **16a** (Φ = 0.044) indicates that a radical chain process cannot be a predominant pathway.

Conclusions

In summary, we report herein the straightforward syntheses of sulfonium salts containing imino and sulfoximido substituents and demonstrated that under photochemical conditions, these compounds are effective sources of iminyl and sulfoximidoyl radicals, respectively, which can be subsequently employed in the imination of hydrazones or the sulfoximidation of benzylic C–H positions. The straightforward synthesis, easy handling and safe profile of compounds **1** and **3** confirm these sulfonium salts as convenient surrogates of iodonium salts of analogue structure and reactivity.

Experimental section

Synthesis of 1a

Triflic anhydride (1.4 g, 5.0 mmol, 1.0 equiv.) was dropwise added to a solution of dibenzothiophene-*S*-oxide (1.00 g, 5.0 mmol) in dry DCM (40 mL) at −50 °C. After stirring the resulting mixture for 1 hour, pyridine (403 μL, 5.0 mmol) and diphenylsulfoximide (1.09 g, 5.0 mmol) dissolved in DCM (10 mL) were sequentially added dropwise, and the mixture was further stirred at −50 °C for 6 additional hours. Then, the cooling system was removed, and the obtained solution was allowed to reach room temperature. After this, an aqueous K_2CO_3 solution was added, upon which the phases separated and the organic one was dried with anhydrous $MgSO_4$ and evaporated *in vacuo*. The thus obtained residue was washed with dry Et_2O (3×) and finally dried under vacuum to deliver **1a** as a beige solid (2.28 g, 83%). ^{1}H NMR (400 MHz, CD_3CN) δ = 8.15–8.06 (m, 2H), 8.04–7.95 (m, 6H), 7.89–7.77 (m, 4H), 7.74–7.55 (m, 6H). ^{13}C NMR (101 MHz, CD_3CN) δ = 138.6, 136.6, 135.8, 135.2, 133.6, 131.2, 130.6, 128.7, 128.0, 124.0, 121.2 (q, J = 321.0 Hz); IR (neat): 3566, 3088, 1709, 1577, 1448, 1362, 1258, 1224, 1152, 1088, 1029, 1005, 969, 758, 738, 707, 685, 637, 613, 589, 573, 541, 518, 422 cm^{-1}. HRMS calculated *m*/*z* for $C_{24}H_{18}NOS_2^+$ $[M\text{-}TfO]^+$: 400.0824, found 400.0831. Mp: 152–153 °C.

Synthesis of 3a

Triflic acid anhydride (0.62 g, 2.2 mmol, 1.1 equiv.) was slowly added at −50 °C to a suspension of dibenzothiophene-*S*-oxide (0.40 g, 2.0 mmol, 1.0 equiv.) in dry dichloromethane (16 mL). After stirring the reaction mixture for 30 min at that temperature, pyridine (0.17 g, 2.2 mmol, 1.1 equiv.) and benzophenone imine (0.39 g, 2.2 mmol, 1.1 equiv.) were added as a solution in dichloromethane (3 mL). After this, the reaction mixture was slowly warmed to −15 °C and stirred for another 6 h at the same temperature. Then the resulting mixture was washed with aq. K_2CO_3 and extracted with dichloromethane. The solvent was evaporated *in vacuo* and the residue was washed with dry Et_2O (2 × 10 mL) and dried *in vacuo* to obtain the desired product as a pale-yellow solid (0.84 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (d, J = 7.8 Hz, 2H), 7.88 (d, J = 7.3 Hz, 2H), 7.84–7.75 (m, 5H), 7.68 (d, J = 8.0 Hz, 2H), 7.57–7.53 (m, 5H), 7.35 (t, J = 7.8 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 190.7, 139.5, 135.9, 135.5, 135.3, 134.6, 132.9, 132.5, 131.6, 131.3, 130.4, 129.7, 129.0, 128.9, 124.1, 121.0 (q, J = 322.2 Hz) ppm; ^{19}F NMR (377 MHz, $CDCl_3$) δ = −78.11 ppm; IR (ATR): 3061, 1710, 1657, 1582, 1526, 1482, 1446, 1259, 1223, 1155, 1029, 999, 955, 761, 707, 637, 572, 517 cm^{-1}; HRMS calculated *m*/*z* for $C_{25}H_{18}NS^+$ $[M\text{-}OTf]^+$: 364.1154, found 364.1156; Mp: 122–123 °C.

Author contributions

Zhen Li synthesized compounds **1a–c** and studied their reactivity, Gonela Vijaykumar synthesized **3a–f** and studied their reactivity, Xiangdong Li performed the mechanistic studies, Christopher Golz performed the calculations and determined the X-ray structures, and Manuel Alcarazo supervised the project and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Support from the European Research Council (ERC CoG 771295) and the DFG (INST 186/1237-1 and INST 186/1324-1) is gratefully acknowledged. We also thank Mr M. Simon for assistance with preparative HPLC and Dr S. I. Kozhushkov for proof checking this manuscript.

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