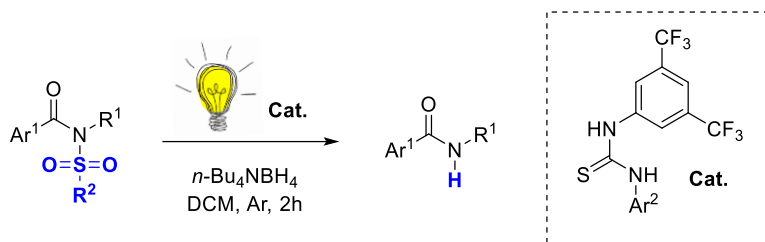# Light-driven reductive cleavage of sulfonamides promoted by thiourea organophotosensitizers

Jules Brom,[a] Antoine Maruani,[a] Laurent Micouin [a,] and Erica Benedetti [a,*]

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ABSTRACT: We have developed a practical method to perform the reductive photocleavage of sulfonamides using thioureas as organophotocatalysts. This transformation, which tolerates a variety of substrates, occurs under mild reaction conditions in the presence of tetrabutylammonium borohydride as a reducing agent. Experimental and theoretical mechanistic investigations complete the study, shedding light on the nature of the active species involved in the photocatalytic process.

Introduction

Sulfonamides can be considered as useful amine protecting groups due to their advantageous properties including ease of introduction, general inertia to acids, bases, electrophiles, or mild reducing agents, and stability under oxidizing conditions.[1] In addition, some of these derivatives, incorporating for example benzenesulfonyl or *p*-toluenesulfonyl moieties, can easily crystalize, a characteristic that may simplify products purification.[1] As of today, the main drawback limiting the potential widespread use of sulfonamides in organic synthesis is the difficult cleavage of these functions, which can require quite harsh reaction conditions.[1-17] Indeed, classical deprotection of *N*-sulfonyl protected compounds usually involve treatments with strong acids, bases or reducing agents such as HBr,[2-4] NaOH or KOH in MeOH,[5,6] or sodium naphthalene.[7] Electrochemical methods have also been described over the years,[8-11] together with different procedures relaying on SmI2-promoted electron transfer cleavage.[12-17]

Recently, the advent of photocatalysis has opened up new possibilities for performing light-driven desulfonylation reactions under milder conditions. However, most of the processes described up to now require stoichiometric amounts of various reagents.[18] Only few catalytic approaches have proven to be successful

to date.[19-21] These include the use of transition metal photocatalysts in combination with Hantzsch esters (Scheme 1),[19] benzimidazolium aryloxide betaines in the presence of hydride donors (Scheme 1),[20] or extremely potent acridine radical photoreductants (Scheme 1).[21] Herein, we describe a convenient and practical alternative to these methods, which encompasses the employment of expensive or hard-to-prepare photocatalysts. Our approach exploits the scarcely investigated organophotocatalytic activity of thioureas (Scheme 1) and allows the efficient cleavage of N-S bonds under mild reaction conditions.
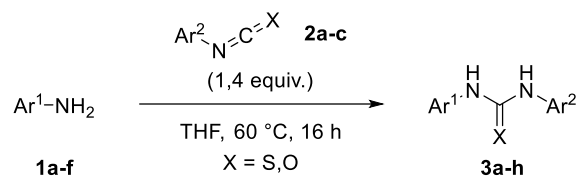
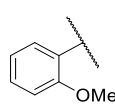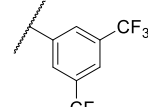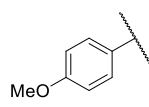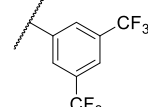**Scheme 1. Photocatalytic desulfonylation reactions**
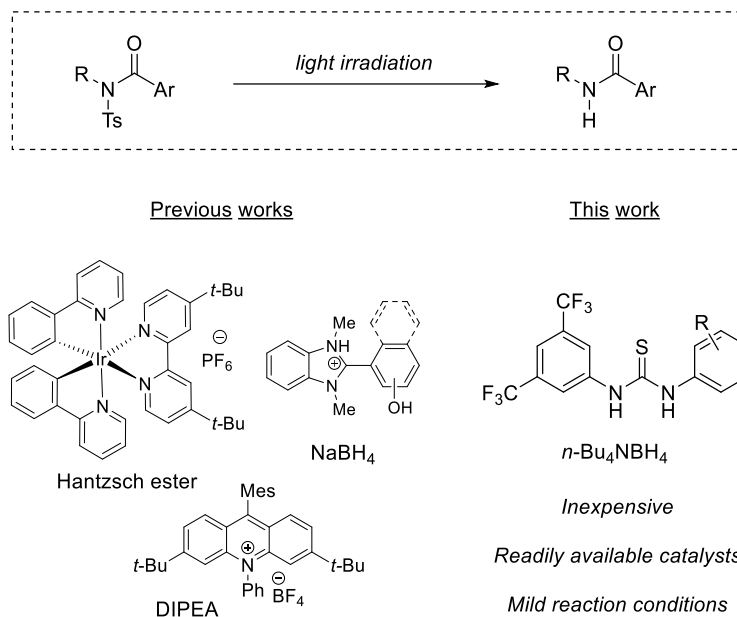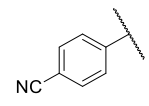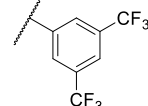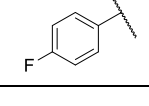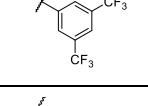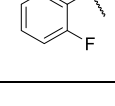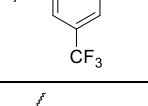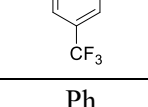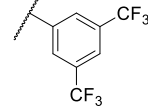
Thioureas have been extensively employed in organocatalysis to promote a variety of transformations.[22-24] Only recently, however, the ability of these molecules to act as photocatalysts has been reported in the literature. In fact, Schreiner's catalyst has proven capable of promoting the formation of acetals under light irradiation.[25] Thioureas have also played the role of photosensitizers in light-enabled [2+2] or [4+2] cycloadditions.[26] Taking into consideration these interesting examples, we envisaged the possibility to employ such molecules to promote different light-driven reactions. Herein, we describe the use of these compounds to achieve the reductive photocleavage of sulfonamides.

Results and discussion

We began our investigations by synthesizing various thioureas (**3a-g**, Table 1) *via* the condensation of commercially available anilines with isothiocyanates. This well-known one step reaction proceeded smoothly to form the expected compounds in 95% to quantitative yields (Table 1). Following a similar procedure, a urea derivative (**3h**, Table 1) was also prepared in 98% yield by reacting aniline with 3,5-bis(trifluoromethyl)phenyl isocyanate.

Table 1. Synthesis of the thiourea photocatalysts

Product	Ar¹	Ar²	X	Yield (%)
3a	(2-OMe-phenyl)	(3,5-(CF₃)₂-phenyl)	S	99
3b	(4-MeO-phenyl)	(3,5-(CF₃)₂-phenyl)	S	99
3c	(4-NC-phenyl)	(3,5-(CF₃)₂-phenyl)	S	99
3d	(4-F-phenyl)	(3,5-(CF₃)₂-phenyl)	S	99
3e	(2-F-phenyl)	(3,5-(CF₃)₂-phenyl)	S	95
3f	Ph	(3,5-(CF₃)₂-phenyl)	S	97
3g	Ph	Ph	S	95
3h	Ph	(3,5-(CF₃)₂-phenyl)	O	98

We next set out to study the ability of catalysts **3a-h** to promote the photocleavage of N–S bonds under mild reducing conditions. To this end, we synthesized an *N*-sulfonylated model compound (**4a**, Table 2) starting from benzylamine and following a two-step procedure which involves first a tosylation and then a benzoylation reaction.[20] Having the model substrate in hand, we turned our attention to the optimization of the reaction conditions. We first tested the photodesulfonylation under light irradiation at 350 nm in the presence of catalyst **3a** (15 mol%) with NaBH₄ as the reducing agent and DMSO as the solvent.[27] Under these conditions, the formation of the expected product **5a** could be detected by proton NMR of

the crude reaction mixture, but the reaction reached only 46% conversion after irradiation for 2 h (Table 2, entry 1). A longer reaction time was required to achieve total conversion (18 h, Table 2, entry 1). Different reducing agents, namely NaBH(OAc)$_3$ and n-Bu$_4$NBH$_4$, were also tested but moderate conversions were again attained in 2 h (Table 2, entries 3 and 4). We next screened different solvents, and we were pleased to observe that the reaction proceeded smoothly in DCM when using n-Bu$_4$NBH$_4$ as the reducing agent. In this case, total conversion could be reached after irradiating for short reaction times (2h, Table 2, entry 5). Note that other reducing agents (*i.e.* NaBH$_4$ or NaBH(OAc)$_3$) failed to react in DCM due to their known poor solubility in this common organic solvent. A lower catalytic loading (5 mol%) could be employed to promote the deprotection of **4a**, without any loss in efficiency (Table 2, entry 6).

Table 2. Optimization of the reaction conditions
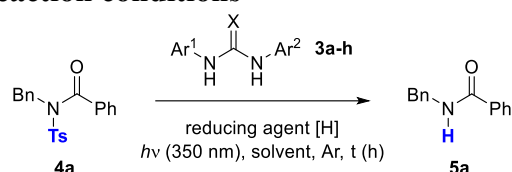
Entry	Cat. (mol %)	Solvent	[H]	t (h)	Conv. (%)[c]
1[a]	**3a** (15)	DMSO	NaBH$_4$	2	46
2[a]	**3a** (15)	DMSO	NaBH$_4$	18	>99
3[a]	**3a** (15)	DMSO	NaBH(OAc)$_3$	2	32
4[a]	**3a** (15)	DMSO	n-Bu$_4$NBH$_4$	2	44
5[a]	**3a** (15)	DCM	n-Bu$_4$NBH$_4$	2	>99
6[a]	**3a** (5)	DCM	n-Bu$_4$NBH$_4$	2	>99
7[a]	/	DCM	n-Bu$_4$NBH$_4$	2	/
8[a]	**3a** (15)	DCM	/	2	/
9[b]	**3a** (15)	DCM	n-Bu$_4$NBH$_4$	2	/
10[a]	**3b** (5)	DCM	n-Bu$_4$NBH$_4$	2	>99
11[a]	**3c** (5)	DCM	n-Bu$_4$NBH$_4$	2	>99
12[a]	**3d** (5)	DCM	n-Bu$_4$NBH$_4$	2	>99
13[a]	**3e** (5)	DCM	n-Bu$_4$NBH$_4$	2	>99
14[a]	**3f** (15)	DCM	n-Bu$_4$NBH$_4$	2	>99
15[a]	**3g** (15)	DCM	n-Bu$_4$NBH$_4$	2	/
16[a]	**3h** (15)	DCM	n-Bu$_4$NBH$_4$	2	/
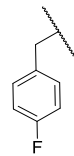
[a] Reaction performed in a Rayonet photochemical reactor equipped with 350 nm lamps (T = 29 °C, c = 0.05 M). [b] Reaction performed in dark (T = 25 °C, c = 0.05 M). [c] Determined by 1H NMR of the crude reaction mixture.

Control reactions were then performed and proved the utility of all reaction partners as compound **4a** did not undergo the photodeprotection in the absence of the catalyst or the hydride source (Table 2, entries 7 and 8). Light irradiation was also essential for the reaction to work, as no product **5a** was formed in the dark (Table 2, entry 9). The ability of catalysts **3b-h** to promote the photocleavage was investigated next (Table 2, entries 10–16). Most of the synthesized thioureas resulted to be efficient photocatalysts in this transformation, also a higher catalytic loading (15 mol%) was required to achieve complete conversion in the presence of catalyst **3f** (Table 2, entry 14). However, the presence of at least one strong electron-withdrawing aromatic moiety on the compounds, and in particular the 3,5-bis(trifluoromethyl)phenyl group, turned out to be important to ensure a good catalytic activity. Indeed, no conversion of sulfonamide **4a** into the corresponding product **5a** was observed in the presence of thiourea **3g**, showing two phenyl substituents (Table 2, entry 15). Urea **3h** also failed to promote the photodeprotection (Table 2, entry 16). These results are probably due to the poor ability of compounds **3g** and **3h** to absorb light at 350 nm (see the SI for more details).

The scope of the photodeprotection was then investigated using thiourea **3a** (5 mol%) as the catalyst (Table 3). Different sulfonyl groups (Ts, SO$_2$Ph, SO$_2$Mes) could be easily cleaved under the optimized reaction conditions to afford the deprotected products **5a** in excellent yields (Table 3, entries 1–3). A mesyl group was also successfully removed to afford product **5a** in 77% yield (Table 3, entry 4). Various substituents were tolerated on the starting materials, including differently substituted (hetero)aromatic groups and alkyl chains (Table 3, entries 5–9). However, the presence of an aroyl moiety on the substrates was require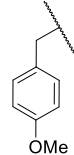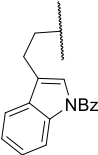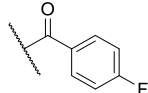d for the reaction to work (Table 3, entries 1–11). Boc- or Me-substituted sulfonamides indeed proved to be unreactive, as only the starting material was recovered after the reaction (Table 3, entries 12 and 13). A secondary tosylamide did not undergo photodesulfonylation under these conditions (Table 3, entry 15). Moreover, decomposition of the starting material was observed in the presence of an acetyl moiety (Table 3, entry 14). Note that, starting from precursors **4a-d** and **4f,** quantitative yields of products **5a**, and **5c** could be obtained by increasing the catalytic charge to 15 mol%.

Table 3. Scope of the photodeprotection
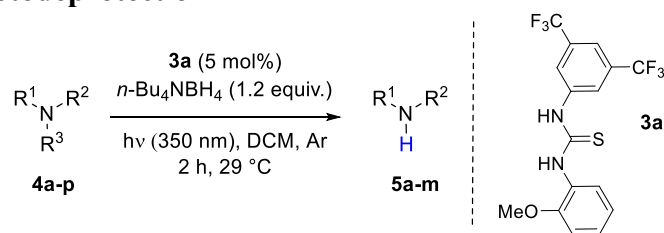
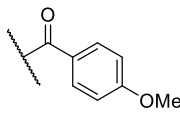| Entry	SM	R^1	R^2	R^3	P[a]	%[b]
1	**4a**	Bn	COPh	Ts	**5a**	76
2	**4b**	Bn	COPh	SO$_2$Ph	**5a**	73
3	**4c**	Bn	COPh	SO$_2$Mes	**5a**	78
4	**4d**	Bn	COPh	Ms	**5a**	77
5	**4e**	Ph–CH(Me)–	COPh	Ts	**5b**	71
6	**4f**	(4-F-phenethyl)	COPh	Ts	**5c**	74
7[c]	**4g**	(4-OMe-phenethyl)	COPh	Ts	**5d**	82
8[c]	**4h**	(indol-3-yl, NBz)	COPh	Ts	**5e**	70
9[c]	**4i**	Me	COPh	Ts	**5f**	69
10[c]	**4j**	Bn	CO-C$_6$H$_4$-F	Ts	**5g**	60
11[c]	**4k**	Bn	CO-C$_6$H$_4$-OMe	Ts	**5h**	44
12	**4l**	Bn	Boc	Ts	**5i**	/[d]
13	**4m**	Bn	Me	Ts	**5j**	/[d]
14	**4n**	Bn	COMe	Ts	**5k**	/[e]
15	**4o**	Bn	H	Ts	**5l**	/[d]

[a] Reaction performed in a Rayonet photochemical reactor equipped with 350 nm lamps (T = 29 °C, c = 0.05 M). [b] Isolated yields. [c] 15 mol % of catalyst **3a** were employed to promote the transformation. [d] The starting material was recovered after the reaction. [e] Decomposition of the starting material vas observed.

Based on these observations, we anticipated the possibility to achieve the chemoselective cleavage of differently substituted sulfonamides. We therefore synthesized compound **4p**, incorporating two diverse tosylamide moieties. This substrate underwent the reductive cleavage smoothly to deliver the mono-deprotected product **5m** in 81% yield (Scheme 2a). Base-sensitive stereogenic centers did not racemize

under the optimized reaction conditions, as product (*S*)-**5e** was isolated in 71% yield and 99% *ee* (Scheme 2b).

Scheme 2. Selectivity of desulfonylation reactions

a)

3a (5 mol%)
n-Bu₄NBH₄ (1.2 equiv.)
→
hν (350 nm), DCM
Ar, 2 h, 29 °C

4p

5m (81%)

b)

3a (5 mol%)
n-Bu₄NBH₄ (1.2 equiv.)
→
hν (350 nm), DCM
Ar, 2 h, 29 °C

(*S*)-**4e** (99% *ee*)

(*S*)-**5e** (71%; 99% *ee*)
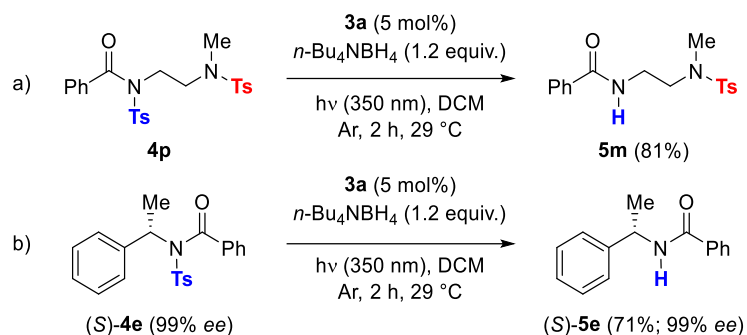
We finally wished to gain some insight into the mechanism of the reaction promoted by thioureas. Taking into account the previously described methods for the photodeprotection of sulfonamides, two different modes of activation could be envisaged, involving either an energy transfer or an electron transfer from the catalyst to the reaction substrates. The observed photocleavage of sulfonamides was thought to more likely occur via an energy transfer pathway based on previously reported studies,[25,26] and experimental evidences. Involvement of triplet-excited states in the photodeprotection was highlighted when performing the reaction under an oxygen atmosphere (Scheme 3a), or in the presence of 3,3,4,4-tetramethyl 1,2-diazetine-1,1-dioxide (TMDD),[28] a well-known triplet-energy quencher (Scheme 3b). The possibility for the photocleavage to occur through a self-sustaining radical process was excluded for the fact that the reaction stops as soon as the light irradiation is turned off.

Based on these results, a plausible mechanism was proposed for this transformation (Scheme 4). The thiourea photosensitizer absorbs light at 350 nm and transfers the energy to the reaction substrate from its triplet-excited state. The formation of an EDA complex at this stage was excluded by UV–vis analysis of **4a** in the presence of increasing quantities of catalysts **3a** (see the SI for more details).

Scheme 3. Triplet-state quenching experiments

a)

3a (5 mol%)
n-Bu₄NBH₄ (1.2 equiv.)
⟶✗
hν (350 nm), DCM
O_2, 2 h, 29 °C

4a

5a (not observed)

b)

3a (5 mol%)
TMDD (0.2 mol%)
n-Bu₄NBH₄ (1.2 equiv.)
⟶
hν (350 nm), DCM
Ar, 2 h, 29 °C

4a

5a (7%)

TMDD
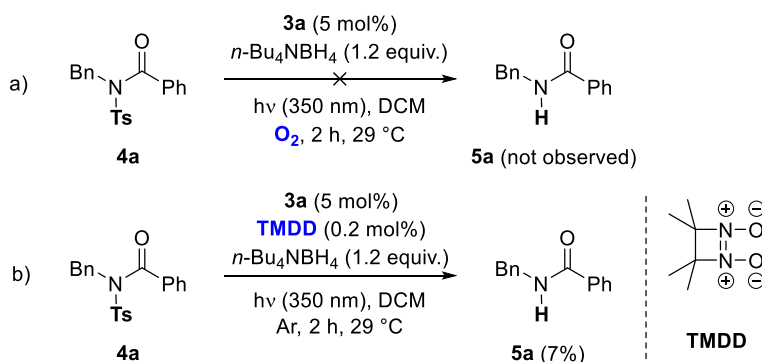
The excited sulfonamide then reacts with BH_4^- to generate a carbon centered ketyl radical).[29] The formation of such reaction intermediate was previously proposed for analogous electrochemical transformations,[12] and is supported by the fact that the reaction does not occur in the absence of a benzoyl moiety on the starting material. This key radical species undergoes an homolytic cleavage of its N–S bond to generate the deprotected amide (after tautomerism), and an aromatic sulphonyl radical than can evolve by either desulfonylation and/or reaction with $BH_3^{\bullet-}$.[30]

Scheme 4. Proposed mechanism
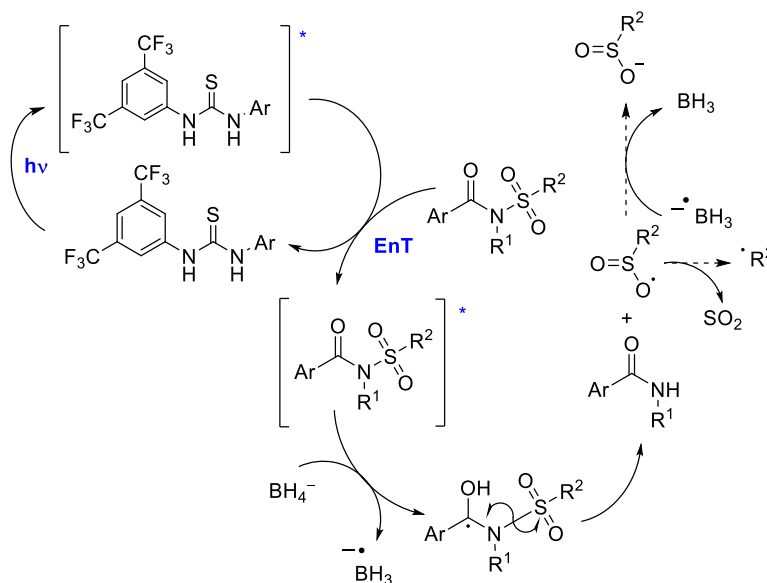
Theoretical investigations were also performed to obtain a better understanding of this novel reaction. Initially, in order to explore the spectral characteristics and energy data of the catalyst from a theoretical perspective, TD-DFT calculations were used to calculate the excited state of **3f**. Based on the calculation results and following a natural transition orbital analysis (NTO), we have drawn a graph of the energy that yields the excited sulfonamides; see Scheme 5 for details. The thiourea needs 4.04 eV to transition from the ground state, S0 to S1 (see ESI for details). This π to π^* transition has a 58% chance of the electron moving from the highest occupied natural transition orbitals (HONTOs) to the lowest unoccupied natural transition orbital (LUNTO). The energy corresponding to the T1 state of **3f** is 3.45 eV and the corresponding one for **4a** is 3.32 eV ($\Delta E = 9.61$ kcal/mol). More detailed calculation data are listed in the ESI (Table S1).

Next, to gain information about the energy transfer mechanism as well as the nature of the N–S bond cleavage, DFT and TD-DFT calculations using CAM-B3LYP/6-31++G(d,p) were conducted on the ground and triplet excited states of the substrates. The results are summarized in Scheme 6.

Scheme 5. Diagram of 3f orbital transitions.

π → π* (HONTO-LUNTO) 58%
n → π* (HONTO-1→LUNTO+1) 28%
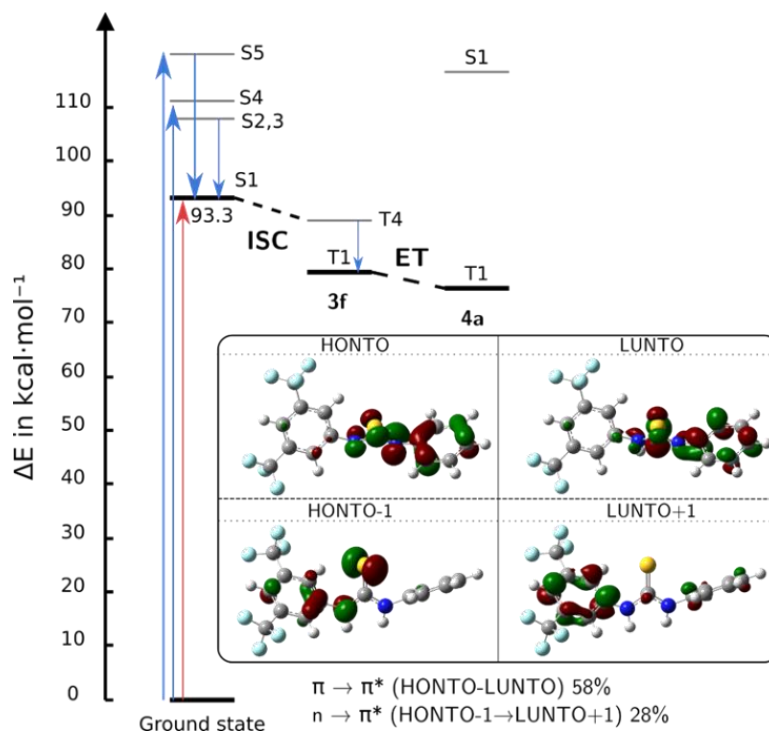
Scheme 6. Computationally established mechanism of the reaction and its corresponding free energy profile
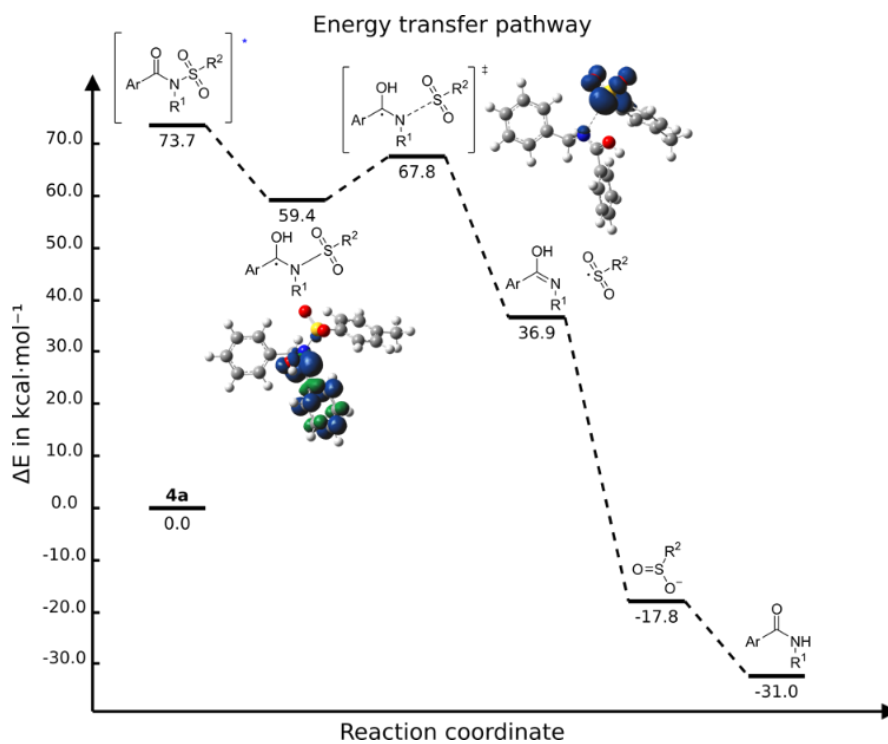
Following a proton-coupled electron transfer, the cleavage proceeds *via* a TS with an elongated N–S bond (+0.2 Å, see ESI for details) and an activation barrier $\Delta G^{\ddagger} = 8.4$ kcal/mol. The small energy barrier for the N–S cleavage suggests that rapid dissociation to form two fragments takes place prior to the conformational change observed for the amide. The calculated spin density shows a shift from the benzylic carbon to the sulfur atom prior to dissociation (see Scheme 6 and Figure S1). All these theoretical evidences are in agreement with the proposed mechanism.

CONCLUSIONS

We have developed a mild photodesulfonylation of sulfonamides. This light-driven reductive cleavage of N−S bonds is promoted by readily available thiourea organophotosensitizers. The reaction tolerates different substituents on the starting materials, and various sulfonyl groups can be easily cleaved under the optimized reaction conditions. Experimental mechanistical investigations and theoretical calculations suggest that this reaction occurs through energy transfer from the excited thiourea catalyst to the reaction substrates.

EXPERIMENTAL SECTION

General Remarks. All reactions were carried out under inert atmosphere (in oven-dried glassware, using dry solvents), unless otherwise specified. All commercially available compounds were purchased from Merck, Fisher Scientific or TCI chemicals and used as received. Analytical thin layer chromatography (TLC) was performed on silica gel plates (Merck 60F254) visualized with a UV lamp (254 nm). Flash chromatography was performed on silica gel (60-230 mesh) unless otherwise specified. Organic extracts were dried over anhydrous $MgSO_4$. NMR spectra (^1H and $^{13}C\{^1H\}$) were recorded on Bruker Avancell 500 spectrometer, at 500 MHz (H value) in $CDCl_3$ or DMSO-d_6. Spectra were referenced to residual chloroform (7.26 ppm, ^1H; 77.0 ppm, $^{13}C\{^1H\}$) or dimethyl sulfoxide (2.50 ppm, ^1H; 39.52 ppm, $^{13}C\{^1H\}$). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet or overlap of nonequivalent resonances), dd (doublet of doublet), td (triplet of doublet), and br (broad signal). Coupling constants, *J*, are reported in hertz (Hz). DEPT-135 experiments were used to assign ^{13}C NMR spectra. All NMR spectra were obtained at 300K unless otherwise specified. IR spectra were obtained using a spectrum one FT-IR spectrometer (Perkin Elmer). High Resolution mass spectra were recorded on a ThermoFischer Exactive Orbitrap spectrometer. HPLC analyses were performed on a Shimadzu chromatograph equipped with a diode array UV/VIS detector. Optical rotations (α_D) were measured on a Perkin Elmer polarimeter (model 341) at 20 °C.

Representative Procedure for the synthesis of the photocatalysts: Synthesis of Compound 3a.

A microwave vial was charged with *o*-anisidine (**1a**, 1 eq., 0.09 mL, 0.81 mmol) under an argon atmosphere. Dry THF (5 mL) was then added, and the resulting mixture was stirred at RT for 5 min. 3,5-bis(trifluoromethyl)phenyl isothiocyanate (**2a**, 1.4 eq., 0.210 mL, 1.14 mmol) was finally added. The tube was sealed, then evacuated and refilled with argon three times. The reaction was heated at 60 °C and stirred for 16 h. The mixture was then cooled back to RT and evaporated under reduced pressure. The crude product was purified by trituration using cyclohexane as the solvent, yielding the pure thiourea **3a** as an off-white solid (311 mg, 0.79 mmol, 97 %). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.98 (s, 1H), 7.96 (s, 2H), 7.87 (s, 1H), 7.69 (s, 1H), 7.59 (d, J = 6.7 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.04 (dd, J = 12.9, 8.0 Hz, 2H), 3.89 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 179.4 (C), 152.4 (C), 139.5 (C), 132.2 (q, J = 33.8 Hz, 2C), 128.5 (CH), 125.1 (CH), 124.8 (C), 124.2 (br m, 2CH), 122.9 (q, J = 273.0 Hz, 2C), 121.3 (CH), 119.3 (m, CH), 112.0 (CH), 55.8 (CH$_3$) ppm. ^{19}F NMR (471 MHz, DMSO-d_6): δ −61.6 (6F) ppm. IR (neat): ν 3629, 3012, 1737, 1530, 1510, 1375, 1284, 1180, 1128, 1118, 1022, 949, 892, 758 cm^{-1}. HRMS (ESI-Orbitrap) : *m/z* [M+H$^+$] calcd for C$_{16}$H$_{13}$F$_6$N$_2$OS : 395.0647; found : 395.0638.

Compound 3b. According to the representative procedure, starting from *p*-anisidine (**1b**, 1 eq., 0.094 mL, 0.81 mmol) and 3,5-bis(trifluoromethyl)phenyl isothiocyanate (**2a**, 1.4 eq., 0.208 mL, 1.14 mmol); trituration gave compound **3b** (304 mg, 0.77 mmol, 95 %) as a purple solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.14 (s, 1H), 10.03 (s, 1H), 8.25 (s, 2H), 7.78 (s, 1H), 7.31 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 179.9 (C), 157.1 (C), 142.0 (C), 131.2 (C), 129.9 (q, J = 32.8 Hz, 2C), 126.3 (2CH), 123.5 (2CH), 123.2 (q, J = 272.7 Hz, 2C), 116.6 (CH), 114.0 (2CH), 55.3 (CH$_3$) ppm. ^{19}F NMR (471 MHz, DMSO-d_6): δ −61.6 (6F) ppm. Spectroscopic data were consistent with the literature data for this compound.[31]

Compound 3c. According to the representative procedure, starting from 4-aminobenzonitrile (**1c**, 1 eq., 100 mg, 0.85 mmol) and 3,5-bis(trifluoromethyl)phenyl isothiocyanate (**2a**, 1.4 eq., 0.208 mL, 1.14 mmol); trituration gave compound **3c** (326mg, 0.84 mmol, 99 %) as an off-white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.62 (s, 1H), 10.52 (s, 1H), 8.24 (s, 2H), 7.89 – 7.76 (m, 3H), 7.73 (d, J = 8.8 Hz, 2H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 179.9 (C), 143.3 (C), 141.4 (C), 132.9 (2CH), 130.2 (q, J = 32.9 Hz, 2C), 123.7 (CH), 123.2 (q, J = 272.7 Hz, 2C), 123.0 (2CH), 119.0 (C), 117.4 (2CH), 106.2 (C) ppm. ^{19}F NMR (471 MHz, DMSO-d_6): δ −61.5 (6F) ppm. Spectroscopic data were consistent with the literature data for this compound.[32]

Compound 3d. According to the representative procedure, starting from *p*-fluoroaniline (**1d**, 1 eq., 0.086 mL, 0.9 mmol) and 3,5-bis(trifluoromethyl)phenyl isothiocyanate (**2a**, 1.4 eq., 0.23 mL, 1.26 mmol); trituration gave compound **3d** (341mg, 0.89 mmol, 99 %) as a purple solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.23 (s, 1H), 10.17 (s, 1H), 8.25 (s, 2H), 7.79 (s, 1H), 7.52 – 7.41 (m, 2H), 7.28 – 7.15 (m, 2H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 180.2 (C), 159.6 (d, J = 242.4 Hz, C), 141.8 (C), 134.9 (C), 130.0 (q, J = 32.9 Hz, 2C), 126.6 (2CH), 123.6 (d, J = 8.4 Hz, 2CH), 123.2 (q, J = 272.8 Hz, 2C), 116.9 (CH), 115.4 (d, J = 22.6 Hz, 2CH) ppm. ^{19}F NMR (471 MHz, DMSO-d_6): δ −61.6 (6F), - 117.0 (F) ppm. IR (neat): ν 3629, 3035, 1548, 1508, 1384, 1278, 1232, 1167, 1139, 981, 887, 840 cm^{-1}. HRMS (ESI-Orbitrap) : *m/z* [M-H$^+$] calcd for C$_{15}$H$_8$F$_7$N$_2$S : 381.0302; found : 381.0300.

Compound 3e. According to the representative procedure, starting from 2-fluoroaniline (**1e**, 1 eq., 0.087 mL, 0.9 mmol) and 3,5-bis(trifluoromethyl)phenyl isothiocyanate (**2a**, 1.4 eq., 0.23 mL, 1.26 mmol); trituration gave compound **3e** (341 mg, 0.89 mmol, 99 %) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.37 (s, 1H), 9.99 (s, 1H), 8.29 (s, 2H), 7.82 (s, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.37 – 7.27 (m, 2H), 7.26 – 7.17 (m, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 181.0 (C), 156.6 (d, J = 246.9 Hz, C), 141.7 (C), 130.1 (q, J = 32.9 Hz, 2C), 128.8 (C), 128.1 (d, J = 7.7 Hz, CH), 126.3 (d, J = 12.0 Hz, CH), 124.4 (CH), 123.3 (2CH), 123.2 (q, J = 272.7 Hz, 2C), 117.0 (CH), 116.0 (d, J = 19.9 Hz, CH) ppm. ^{19}F NMR (471 MHz, DMSO-d_6): δ −61.5 (6F), −121.4 (F) ppm. IR (neat): ν 3629, 3015, 1738, 1549, 1383, 1279, 1168, 1131, 981, 890, 746 cm^{-1}. HRMS (ESI-Orbitrap) : *m/z* [M-H$^+$] calcd for C$_{15}$H$_{10}$F$_7$N$_2$S : 383.0447; found : 381.0439.

Compound 3f. According to the representative procedure, starting from aniline (**1f**, 1 eq., 0.098 mL, 1.074 mmol) and 3,5-bis(trifluoromethyl)phenyl isothiocyanate (**2a**, 1.4 eq., 0.27 mL, 1.503 mmol); trituration gave compound **3f** (387 mg, 1.063 mmol, 99 %) as an off-white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.29 (s, 1H), 10.21 (s, 1H), 8.27 (s, 2H), 7.79 (s, 1H), 7.47 (d, J = 7.7 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) : δ 179.8 (C), 141.9 (C), 138.6 (C), 130.0 (q, J = 32.9 Hz, 2C), 128.7 (2CH), 125.2 (CH), 124.0 (2CH), 123.4 (2CH), 123.2 (q, J = 272.7 Hz, 2C), 116.8 (CH) ppm. ^{19}F NMR (471 MHz, DMSO-d_6) : δ −61.6 (6F) ppm. Spectroscopic data were consistent with the literature data for this compound.[33]

Compound 3g. According to the representative procedure, starting from aniline (**1f**, 1 eq., 0.098 mL, 1.074 mmol) and phenyl isothiocyanate (**2b**, 1.4 eq., 0.18 mL, 1.503 mmol); trituration gave compound **3g** (233 mg, 1.02 mmol, 95 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 14.52 (s, 2H), 12.21 (d, J = 7.5 Hz, 4H), 12.11 – 12.06 (m, 4H), 11.88 (t, J = 7.4 Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 179.9 (C),

139.6 (2C), 128.7 (4CH), 124.8 (2CH), 124.1 (4CH) ppm. Spectroscopic data were consistent with the literature data for this compound.[34]

Compound 3h. According to the representative procedure, starting from aniline (**1f**, 1 eq., 0.098 mL, 1.074 mmol) and 1-isocyanato-3,5-bis(trifluoromethyl)benzene (**2c**, 1.4 eq., 0.26 mL, 1.503 mmol); trituration gave compound **3h** (367 mg, 1.052 mmol, 98 %) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.37 (s, 1H), 8.96 (s, 1H), 8.13 (s, 2H), 7.63 (s, 1H), 7.51 – 7.44 (m, 2H), 7.34 – 7.26 (m, 2H), 7.05 – 6.98 (m, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 152.4 (C), 141.9 (C), 139.0 (C), 130.7 (q, J = 32.6 Hz, 2C), 128.8 (2CH), 123.3 (q, J = 272.8 Hz, 2C), 122.5 (CH), 118.9 (2CH), 118.0 (2CH), 114.3 (CH) ppm. ^{19}F NMR (471 MHz, DMSO-d_6): δ −63.1 (6F) ppm. Spectroscopic data were consistent with the literature data for this compound.[33]

Representative Procedure for the tosylation reactions: Synthesis of Compound 4o

A flame-dried vial was charged with benzylamine (1 eq., 0.408 mL, 3.73 mmol), triethylamine (1.5 eq., 0.78 mL, 5.6 mmol) and DCM (30 mL) under an argon atmosphere. Tosyl chloride (1.1 eq., 783 mg, 4.106 mmol) was then added, and the resulting mixture was stirred at RT overnight. Water was then added, the immiscible phases were separated, and the aqueous layer was extracted with DCM (3x). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography using EtOAc/Cy (1:9) as the eluent to afford compound **4o** (966 mg, 3.7 mmol, 99 %) as a pinkish solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.76 (d, J = 7.4 Hz, 2H), 7.33 – 7.26 (m, 5H), 7.19 (d, J = 7.4 Hz, 2H), 4.59 (br s, 1H), 4.13 (d, J = 6.2 Hz, 2H), 2.44 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 143.6 (C), 136.9 (C), 136.3 (C), 129.8 (2CH), 128.7 (2CH), 128.0 (CH), 127.9 (2CH), 127.2 (2CH), 47.3 (CH$_2$), 21.5 (CH$_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[35]

Compound S1. According to the representative procedure, starting from benzylamine (1 eq., 400 mg, 0.408 mL, 3.73 mmol) and benzenesulfonyl chloride (1.1 eq., 725 mg, 0.52 mL, 4.106 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **S1** (914 mg, 3.7 mmol, 99 %) as an amorphous white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.87 (d, J = 7.7 Hz, 2H), 7.58 (t, J = 7.0 Hz, 1H), 7.51 (m, 2H), 7.34 – 7.25 (m, 3H), 7.18 (d, J = 6.9 Hz, 2H), 4.86 – 4.58 (m, 1H), 4.14 (d, J = 6.0 Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 140.0 (C), 136.2 (C), 132.9 (CH), 129.3 (2CH), 128.9 (2CH), 128.1 (CH), 128.0 (2CH), 127.2 (2CH), 47.4 (CH$_2$) ppm. Spectroscopic data were consistent with the literature data for this compound.[36]

Compound S2. According to the representative procedure, starting from benzylamine (1 eq., 300 mg, 0.306 mL, 2.8 mmol) and 2-mesitylenesulfonyl chloride (1.1 eq., 674 mg, 3.08 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **S2** (717 mg, 2.48 mmol, 89 %) as an amorphous white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.29 – 7.22 (m, 3H), 7.20 – 7.14 (m, 2H), 6.96 (s, 2H), 4.72 (t, J = 5.9 Hz, 1H), 4.07 (d, J = 6.2 Hz, 2H), 2.64 (s, 6H), 2.31 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 141.8 (C), 138.6 (2C), 135.8 (C), 132.9 (C), 131.5 (2CH), 128.1 (2CH), 127.4 (3CH), 46.3 (CH$_2$), 22.4 (2CH$_3$), 20.4 (CH$_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[37]

Compound S3. According to the representative procedure, starting from benzylamine (1 eq., 0.26 mL, 2.3 mmol) and mesyl chloride (1.1 eq., 0.20 mL, 2.6 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **S3** (300 mg, 1.62 mmol, 69 %) as a colourless oil. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.37 – 7.23 (m, 5H), 4.57 (s, 1H), 4.26 (d, J = 6.0 Hz, 2H), 2.81 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 136.6 (C), 129.0 (2CH), 128.2 (CH), 127.9 (2CH), 47.3 (CH$_2$), 41.2 (CH$_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[38]

Compound (±)-S4. According to the representative procedure, starting from DL-alpha-methylbenzylamine (1 eq., 0.213 mL, 1.65 mmol) and tosyl chloride (1 eq., 314 mg, 1.65 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound (±)-**S4** (448 mg, 1.63 mmol, 99 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.62 (d, J = 8.3 Hz, 2H), 7.19 (m, 5H), 7.12 – 7.07 (m, 2H), 5.06 – 4.76 (br m, 1H), 4.46 (p, J = 6.9 Hz, 1H), 2.38 (s, 3H), 1.42 (d, J = 6.9 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 143.3 (C), 142.1 (C), 137.7 (C), 129.6 (2CH), 128.7 (2CH), 127.6 (CH), 127.2 (2CH), 126.2 (2CH), 53.7 (CH), 23.7 (CH$_3$), 21.6 (CH$_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[39]

Compound (S)-S4. According to the representative procedure, starting from (L)-(-)-1-phenylethylamine (1 eq., 0.158 mL, 1.24 mmol) and tosyl chloride (1 eq., 236 mg, 1.24 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9 to 2:8) gave compound (S)-**S4** (327 mg, 1.19 mmol, 96 %) as a white solid. Spectroscopic data were identical to those of compound (±)-**S4**. $[\alpha]_D^{20}$ −80 (c 0.3, CHCl$_3$).

Compound S5. According to the representative procedure, starting from 4-fluorobenzylamine (1 eq., 0.18 mL, 1.6 mmol) and tosyl chloride (1.1 eq., 335 mg, 1.76 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **S5** (442 mg, 1.58 mmol, 99 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.73 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 7.16 (dd, J = 8.3, 5.5 Hz, 2H), 6.95 (t, J = 8.5 Hz, 2H), 4.86 (s, J = 40.1 Hz, 1H), 4.08 (d, J = 6.2 Hz, 2H), 2.43 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 162.5 (d, J = 246.6 Hz, C), 143.8 (C), 136.9 (C), 132.2 (d, J = 2.9 Hz, C), 129.9 (2CH), 129.7 (d, J = 8.3 Hz, 2CH), 127.3 (2CH), 115.7 (d, J = 21.5 Hz, 2CH), 46.7 (CH$_2$), 21.7 (CH$_3$) ppm. ^{19}F NMR

(471 MHz, CDCl₃): δ - 114.3 (F) ppm. Spectroscopic data were consistent with the literature data for this compound.[40]

Compound S6. According to the representative procedure, starting from 4-methoxybenzylamine (1 eq., 0.19 mL, 1.46 mmol) and tosyl chloride (1.1 eq., 306 mg, 1.604 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **S6** (421 mg, 1.44 mmol, 99 %) as a white solid. ^{1}H NMR (500 MHz, CDCl₃): δ 7.76 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.6 Hz, 2H), 6.82 – 6.78 (m, 2H), 4.54 (t, J = 5.8 Hz, 1H), 4.05 (d, J = 6.1 Hz, 2H), 3.78 (s, 3H), 2.44 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl₃ : δ 159.3 (C), 143.5 (C), 136.8 (C), 129.7 (2CH), 129.3 (2CH), 128.2 (C), 127.2 (2CH), 114.1 (2CH), 55.3 (CH₃), 46.8 (CH₂), 21.6 (CH₃) ppm. Spectroscopic data were consistent with the literature data for this compound.[36]

Compound S7. According to the representative procedure, starting from tryptamine (1 eq., 250 mg, 1.56 mmol) and tosyl chloride (1.1 eq., 327 mg, 1.72 mmol); flash chromatography on silica gel (EtOAc/Cy, 3:7) gave compound **S7** (380 mg, 1.209 mmol, 77 %) as a pinkish solid. ^{1}H NMR (500 MHz, CDCl₃): δ 8.06 (s, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.24 – 7.16 (m, 3H), 7.09 – 7.03 (m, 1H), 6.97 (d, J = 2.2 Hz, 1H), 4.42 (t, J = 6.0 Hz, 1H), 3.27 (q, J = 6.5 Hz, 2H), 2.93 (t, J = 6.6 Hz, 2H), 2.40 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl₃): δ 143.3 (C), 136.7 (C), 136.4 (C), 129.6 (2CH), 127.0 (2CH), 126.8 (C), 122.6 (CH), 122.3 (CH), 119.5 (CH), 118.5 (CH), 111.6 (C), 111.3 (CH), 43.0 (CH₂), 25.5 (CH₂), 21.5 (CH₃) ppm. Spectroscopic data were consistent with the literature data for this compound.[41]

Compound S8. According to the representative procedure, starting from methylamine (33 wt. % in absolute ethanol, 1 eq., 300 mg, 3.19 mmol) and tosyl chloride (1.1 eq., 668 mg, 3.51 mmol); compound **S8** (300 mg, 1.62 mmol, 51 %) was isolated as a white solid. ^{1}H NMR (500 MHz, CDCl₃): δ 7.82 – 7.70 (m, 2H), 7.36 – 7.26 (m, 2H), 4.51 (s, 1H), 2.64 (s, 3H), 2.43 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl₃): δ 143.6 (C), 135.8 (C), 129.8 (2CH), 127.3 (2CH), 29.4 (CH₃), 21.6 (CH₃) ppm. Spectroscopic data were consistent with the literature data for this compound.[42]

Compound S9. According to the representative procedure, starting from N-methylethylenediamine (1 eq., 0.12 mL, 1.35 mmol) and tosyl chloride (2 eq., 728 mg, 2.70 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:1) gave compound **S9** (226 mg, 0.59 mmol, 44 %) as a white solid. ^{1}H NMR (500 MHz, CDCl₃): 7.77 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 8.2 Hz, 2H), 7.32 (t, J = 8.3 Hz, 4H), 4.94 (dd, J = 14.3, 5.8 Hz, 1H), 3.13 (q, J = 5.8 Hz, 2H), 3.03 (t, J = 5.8 Hz, 2H), 2.65 (s, 3H), 2.44 (s, 3H), 2.42 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl₃): δ 143.9 (C), 143.6 (C), 136.6 (C), 133.7 (C), 129.9 (2CH), 129.8 (2CH), 127.4 (2CH), 127.2 (2CH), 49.8 (CH₂), 41.4 (CH₂), 36.1 (CH₃), 21.6 (2CH₃) ppm. IR (neat) : ν 3308,

2882, 2254, 1598, 1453, 1333, 1159, 1090, 1048, 906, 730 cm^{-1}. HRMS (ESI-Orbitrap) : m/z [M-H$^+$] calcd for C$_{17}$H$_{21}$N$_2$O$_4$S$_2$: 381.0948; found : 381.0954.

Representative Procedure for the acylation reactions: Synthesis of Compound 4a.

A round-bottomed flask containing N-benzyl-4-methylbenzene-1-sulfonamide (**4o**, 1 eq., 1.05 g, 4.02 mmol), DMAP (0.1 eq., 49 mg, 0.402 mmol) and triethylamine (1.5 eq., 0.84 mL, 6.03 mmol) dissolved in DCM (30 mL), was cooled to 0 °C. Benzoyl chloride (1.5 eq., 0.7 mL, 6.03 mmol) was then added dropwise. The reaction was warmed up to RT and stirred overnight. Water was then added, the immiscible phases were separated, and the aqueous layer was extracted with DCM (3x). The combined organic layers were dried over MgSO$_4$ and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography using EtOAc/Cy (1:9) as the eluent to afford compound **4a** (1.14 g, 3.13 mmol, 78 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.58 (d, J = 8.3 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.33 (t, J = 7.7 Hz, 2H), 7.26 – 7.18 (m, 7H), 4.98 (s, 2H), 2.41 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 171.6 (C), 144.7 (C), 136.3 (C), 136.0 (C), 135.0 (C), 131.7 (CH), 129.4 (2CH), 128.6 (2CH), 128.5 (2CH), 128.3 (2CH), 128.2 (2CH), 128.0 (2CH), 127.8 (CH), 51.2 (CH$_2$), 21.6 (CH$_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[19]

Compound 4b. According to the representative procedure, starting from N-benzylbenzenesulfonamide (**S1**, 1 eq., 980 mg, 3.96 mmol) and benzoyl chloride (1.5 eq., 0.69 mL, 5.94 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4b** (1.3 g, 3.69 mmol, 93 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.76 – 7.70 (m, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.51 – 7.41 (m, 5H), 7.37 – 7.34 (m, 2H), 7.29 – 7.24 (m, 3H), 7.23 – 7.19 (m, 2H), 5.03 (s, 2H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 171.5 (C), 138.8 (C), 136.0 (C), 134.7 (C), 133.6 (CH), 131.8 (CH), 128.7 (2CH), 128.6 (2CH), 128.4 (3CH), 128.2 (2CH), 127.9 (2CH), 127.8 (2CH), 51.3 (CH$_2$) ppm. Spectroscopic data were consistent with the literature data for this compound.[43]

Compound 4c. According to the representative procedure, starting from *N*-benzyl-2,4,6-trimethylbenzene-1-sulfonamide (**S2**, 1 eq., 150 mg, 0.52 mmol) and benzoyl chloride (1.5 eq., 0.09 mL, 0.78 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4c** (122 mg, 0.31 mmol, 60 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.41 – 7.36 (m, 1H), 7.35 – 7.21 (m, 9H), 6.93 (s, 2H), 5.02 (s, 2H), 2.62 (s, 6H), 2.29 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 171.3 (C), 143.7 (C), 140.4 (2C), 136.5 (C), 135.2 (C), 133.0 (C), 132.1 (2CH), 131.1 (CH), 128.6 (2CH), 128.1 (2CH), 127.8 (2CH), 127.7 (CH), 127.4 (2CH), 50.2 (CH$_2$), 22.4 (2CH$_3$), 21.0 (CH$_3$) ppm. IR (neat): ν 2977, 2255, 1681, 1603, 1344, 1278, 1165, 1056, 911, 733 cm^{-1}. HRMS (ESI-Orbitrap): m/z [M+H$^+$] calcd for C$_{23}$H$_{24}$NO$_3$S: 394.1471; found : 394.1467.

Compound 4d. According to the representative procedure, starting from *N*-benzylmethanesulfonamide (**S3**, 1 eq., 150 mg, 0.81 mmol) and benzoyl chloride (1.5 eq., 0.14 mL, 1.22 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9 to 2:8) gave compound **4d** (222 mg, 0.77 mmol, 95 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.70 – 7.60 (m, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.38 – 7.27 (m, 3H), 7.21 – 7.11 (m, 2H), 4.99 (s, 2H), 3.04 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 172.6 (C), 135.6 (C), 133.8 (C), 132.3 (CH), 129.0 (2CH), 128.9 (2CH), 128.4 (3CH), 128.1 (2CH), 52.2 (CH$_2$), 42.9 (CH$_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[14]

Compound (±)-4e. According to the representative procedure, starting from 4-methyl-*N*-(1-phenylethyl)benzene-1-sulfonamide ((±)-**S4**, 1 eq., 448 mg, 1.63 mmol) and benzoyl chloride (1.5 eq., 0.28 mL, 2.44 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound (±)-**4e** (600 mg, 1.58 mmol, 97 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.51 (d, J = 8.3 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.34 – 7.24 (m, 9H), 7.19 (d, J = 8.1 Hz, 2H), 5.48 (q, J = 7.0 Hz, 1H), 2.41 (s, 3H), 1.91 (d, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 172.3 (C), 144.6 (C), 139.3 (C), 136.6 (C), 136.3 (C), 131.4 (CH), 129.4 (2CH), 128.9 (2CH), 128.4 (2CH), 128.2 (2CH), 127.9 (2CH), 127.8 (2CH), 127.8 (CH), 58.7 (CH), 21.8 (CH$_3$), 18.6 (CH$_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[16]

Compound (S)-4e. According to the representative procedure, starting from 4-methyl-*N*-(1-phenylethyl)benzene-1-sulfonamide (*S*-**S4**, 1 eq., 100 mg, 0.36 mmol) and benzoyl chloride (1.5 eq., 0.06mL, 0.54 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound (S)-**4e** (74 mg, 0.20 mmol, 54 %) as a white solid. Spectroscopic data were identical to those of compound (±)-**4e**. [α]$_D^{20}$ −64 (c 0.25, CHCl$_3$).

Compound 4f. According to the representative procedure, starting from *N*-[(4-fluorophenyl)methyl]-4-methylbenzene-1-sulfonamide (**S5**, 1 eq., 200 mg, 0.72 mmol) and benzoyl chloride (1.5 eq., 0.12 mL, 1.074 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4f** (273 mg, 0.71 mmol, 99 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.57 (d, J = 8.3 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.34 (t, J = 7.7 Hz, 2H), 7.25 – 7.19 (m, 4H), 6.95 (t, J = 8.7 Hz, 2H), 4.94 (s, 2H), 2.42 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 171.5 (C), 162.4 (d, J = 246.7 Hz, C), 144.8 (C), 135.9 (C), 135.0 (C), 132.0 (d, J = 3.1 Hz, C), 131.8 (CH), 130.0 (d, J = 8.2 Hz, 2CH), 129.5 (2CH), 128.4 (2CH), 128.3 (2CH), 128.2 (2CH), 115.5 (d, J = 21.6 Hz, 2CH), 50.3 (CH$_2$), 21.6 (CH$_3$) ppm. ^{19}F NMR (471 MHz, DMSO): δ - 114.24 (F) ppm. Spectroscopic data were consistent with the literature data for this compound.[16]

Compound 4g. According to the representative procedure, starting from *N*-[(4-methoxyphenyl)methyl]-4-methylbenzene-1-sulfonamide (**S6**, 1 eq., 200 mg, 0.67 mmol) and benzoyl chloride (1.5 eq., 0.17 mL, 1.43 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4g** (255.17 mg, 0.65 mmol, 94 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.58 (d, J = 8.3 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.34 (t, J = 7.7 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.7 Hz, 2H), 6.78 (d, J = 8.7 Hz, 2H), 4.92 (s, 2H), 3.78 (s, 3H), 2.41 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 171.6 (C), 159.2 (C), 144.6 (C), 136.0 (C), 135.0 (C), 131.7 (CH), 129.5 (2CH), 129.4 (2CH), 128.4 (2CH), 128.3 (2CH), 128.2 (CH), 128.2 (2CH), 113.9 (2CH), 55.3 (CH$_3$), 50.7 (CH$_2$), 21.6 (CH$_3$) ppm. IR (neat) : ν 2981, 1686, 1613, 1598, 1514, 1447, 1357, 1249, 1167, 1087, 1033, 955, 814, 731 cm^{-1}. HRMS (ESI-Orbitrap): *m/z* [M+H$^+$] calcd for C$_{22}$H$_{22}$NO$_4$S: 396.1264; found : 396.1257.

Compound 4h. According to the representative procedure, starting from *N*-[2-(1H-indol-3-yl)ethyl]-4-methylbenzene-1-sulfonamide (**S7**, 1 eq., 200 mg, 0.64 mmol) and benzoyl chloride (1.5 eq., 0.11 mL, 0.95 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4h** (158 mg, 0.302 mmol, 48 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.37 (d, J = 8.3 Hz, 1H), 7.75 – 7.67 (m, 4H), 7.63 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.5 Hz, 2H), 7.40 (qd, J = 5.6, 2.7 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.25 – 7.17 (m, 8H), 7.04 (s, 1H), 4.17 – 4.04 (m, 2H), 3.14 – 2.99 (m, 2H), 2.39 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 171.4 (C), 168.4 (C), 144.9 (C), 136.3 (C), 136.0 (C), 134.8 (C), 134.5 (C), 131.9 (CH), 131.4 (CH), 130.4 (C), 129.5 (2CH), 129.2 (2CH), 128.7 (2CH), 128.4 (2CH), 128.1 (2CH), 127.7 (2CH), 125.8 (CH), 125.2 (CH), 123.9 (CH), 118.6 (CH), 117.5 (C), 116.6 (CH), 47.6 (CH$_2$), 25.6 (CH$_2$), 21.6 (CH$_3$) ppm. IR (neat): ν 2924, 2255, 1683, 1600, 1453, 1376, 1356, 1167, 910, 732 cm^{-1}. HRMS (ESI-Orbitrap): *m/z* [M+H$^+$] calcd for C$_{31}$H$_{27}$N$_2$O$_4$S: 523.1686; found : 523.1678.

Compound 4i. According to the representative procedure, starting from *N*-methyl-p-toluenesulfonamide (**S8**, 1 eq., 150 mg, 0.81 mmol) and benzoyl chloride (1.5 eq., 0.14 mL, 1.22 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4i** (242 mg, 0.81 mmol, quantitative) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$ δ 7.84 (d, J = 8.3 Hz, 2H), 7.68 – 7.48 (m, 3H), 7.41 (dd, J = 10.8, 4.5 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 3.28 (s, 3H), 2.44 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 171.5 (C), 144.9 (C), 135.1 (C), 134.4 (C), 132.0 (CH), 129.6 (2CH), 128.5 (2CH), 128.4 (2CH), 128.3 (2CH), 35.6 (CH$_3$), 21.7 (CH$_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[44]

Compound 4j. According to the representative procedure, starting from *N*-benzyl-4-methylbenzene-1-sulfonamide (**4o**, 1 eq., 150 mg, 0.57 mmol) and 4-fluorobenzoyl chloride (1.5 eq., 0.10 mL, 0.86 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4j** (226 mg, 0.57 mmol, quantitative)

as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.58 (d, J = 8.4 Hz, 2H), 7.56 – 7.45 (m, 2H), 7.35 – 7.16 (m, 7H), 7.09 – 6.94 (m, 2H), 4.92 (s, 2H), 2.42 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 170.6 (C), 164.8 (d, J = 253.5 Hz, C), 144.8 (C), 136.0 (C), 135.6 (C), 131.2 (d, J = 3.4 Hz, C), 131.1 (d, J = 9.1 Hz, 2CH), 129.5 (2CH), 128.6 (2CH), 128.3 (2CH), 128.0 (2CH), 127.8 (CH), 115.3 (d, J = 22.1 Hz, 2CH), 51.1 (CH$_2$), 21.6 (CH$_3$) ppm. ^{19}F NMR (471 MHz, CDCl$_3$): δ - 106.3 (F) ppm. Spectroscopic data were consistent with the literature data for this compound.[16]

Compound 4k. According to the representative procedure, starting from *N*-benzyl-4-methylbenzene-1-sulfonamide (**4o**, 1 eq., 150 mg, 0.57 mmol) and 4-methoxybenzoyl chloride (1.5 eq., 0.12 mL, 0.86 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4k** (182 mg, 0.46 mmol, 80 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.62 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.9 Hz, 2H), 7.25 – 7.19 (m, 7H), 6.85 (d, J = 8.9 Hz, 2H), 4.89 (s, 2H), 3.83 (s, 3H), 2.42 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 171.3 (C), 162.9 (C), 144.5 (C), 136.1 (C), 135.8 (C), 131.3 (2CH), 129.5 (2CH), 128.5 (2CH), 128.4 (2CH), 128.1 (2CH), 127.7 (CH), 127.2 (C), 113.5 (2CH), 55.4 (CH$_3$), 51.4 (CH$_2$), 21.6 (CH$_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[45]

Synthesis of Compound 4l. A round-bottomed flask containing *N*-benzyl-4-methylbenzene-1-sulfonamide (**4o**, 1 eq., 150 mg, 0.57 mmol), and DMAP (0.1 eq., 7 mg, 0.057 mmol), dissolved in THF (5 mL), was cooled to 0 °C. Boc$_2$O (1.5 eq., 0.18 mL, 0.86 mmol) was then added. The reaction was warmed up to RT and stirred overnight. Water was then added, and the resulting aqueous mixture was extracted with DCM (3x). The combined organic layers were dried over MgSO$_4$ and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography eluent: EtOAc/Cyclohexane 1:9) to afford compound **4l** (124 mg, 0.34 mmol, 60 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.59 – 7.53 (m, 2H), 7.43 – 7.38 (m, 2H), 7.37 – 7.27 (m, 3H), 7.21 (d, J = 8.0 Hz, 2H), 5.04 (s, 2H), 2.41 (s, 3H), 1.31 (s, 9H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 151.1 (C), 144.1 (C), 137.4 (C), 137.1 (C), 129.1 (2CH), 128.5 (2CH), 128.2 (2CH), 128.1 (2CH), 127.7 (CH), 84.5 (C), 49.7 (CH$_2$), 27.9 (3CH$_3$), 21.6 (CH$_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[46]

Synthesis of Compound 4m. A round-bottomed flask *N*-benzyl-4-methylbenzene-1-sulfonamide (**4o**, 1 eq., 100 mg, 0.38 mmol), K$_2$CO$_3$ (6 eq., 317 mg, 2.3 mmol), and DMF (5 mL), was cooled to 0 °C. MeI (1.5 eq., 0.04 mL, 0.57 mmol) was then added. The reaction was warmed up to RT and stirred overnight. Water was then added, and the resulting aqueous mixture was extracted with DCM (3x). The combined organic layers were dried over MgSO$_4$ and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography eluent: EtOAc/Cyclohexane 1:9) to afford compound **4m** (104 mg, 0.38 mmol, quantitative yield) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.73 (d, J = 8.2 Hz, 2H),

7.36 (m, 3H), 7.35 – 7.28 (m, 4H), 4.12 (s, 2H), 2.58 (s, 3H), 2.46 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 143.5 (C), 135.7 (C), 134.2 (C), 129.8 (2CH), 128.6 (2CH), 128.4 (2CH), 127.9 (CH), 127.5 (2CH), 54.1 (CH$_2$), 34.3 (CH$_3$), 21.6 (CH$_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[21]

Compound 4n. According to the representative procedure, starting from *N*-benzyl-4-methylbenzene-1-sulfonamide (**4o**, 1 eq., 150 mg, 0.57 mmol) and acetyl chloride (1.5 eq., 0.06 mL, 0.86 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **4n** (168 mg, 0.55 mmol, 96 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.61 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 7.3 Hz, 2H), 7.35 – 7.23 (m, 5H), 5.08 (s, 2H), 2.42 (s, 3H), 2.29 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 170.4 (C), 144.9 (C), 136.7 (C), 136.5 (C), 129.8 (2CH), 128.6 (2CH), 128.0 (2CH), 127.8 (3CH), 49.5 (CH$_2$), 24.9 (CH$_3$), 21.6 (CH$_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[47]

Compound 4p. According to the representative procedure, starting from *N*,4-dimethyl-*N*-(2-((4-methylphenyl)sulfonamido)ethyl)benzenesulfonamide (**S9**, 1 eq., 150 mg, 0.26 mmol) and benzoyl chloride (1.5 eq., 0.05 mL, 0.39 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **4o** (126 mg, 0.26 mmol, quantitative yield) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 4H), 4.03 (t, *J* = 6.5 Hz, 2H), 3.25 (t, *J* = 6.5 Hz, 2H), 2.74 (s, 3H), 2.43 (s, 3H), 2.43 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 171.5 (C), 145.1 (C), 143.6 (C), 135.6 (C), 134.8 (C), 134.1 (C), 131.6 (CH), 129.8 (2CH), 129.7 (2CH), 128.5 (2CH), 128.2 (4CH), 127.4 (2CH), 49.6 (CH$_2$), 45.3 (CH$_2$), 36.0 (CH$_3$), 21.7 (CH$_3$), 21.6 (CH$_3$) ppm. IR (neat) : ν 3068, 2980, 1688, 1598, 1345, 1163, 1089, 910, 731 cm^{-1}. HRMS (ESI-Orbitrap): *m/z* [M+H$^+$] calcd for C$_{24}$H$_{27}$N$_2$O$_5$S$_2$: 487.1356; found : 487.1343.

Representative Procedure for the photocleavage reactions: Synthesis of Compound 5a (Table 3, entry 1).

A flame dried vial was charged with *N*-benzyl-*N*-(4-methylbenzenesulfonyl)benzamide (**4a**, 1 eq., 20 mg, 0.05 mmol), tetrabutylammonium borohydride (1.2 eq., 17 mg, 0.07 mmol) and photocatalyst **3a** (0.05 eq., 1 mg, 0.003 mmol) under an argon atmosphere. Dry DCM was then added, and the resulting mixture (0.05 M) was stirred at RT for 5 min. The tube was then sealed and evacuated and refilled with argon three times. The reaction was irradiated in a Rayonet chamber for 2 h (hν = 350 mn). H$_2$O was then added, and the immiscible phases were separated. The aqueous layer was extracted with DCM (3x). The combined organic layers were dried over MgSO$_4$, then concentrated under reduced pressure. The resulting crude residue was purified by silica gel column chromatography using EtOAc/Cy as the eluent (2:8) to afford the compound **5a** (9 mg, 0.14 mmol, 76 %). As an off-white solid.

Compound 5a (Table 3, entry 2). According to the representative procedure, starting from *N*-(benzenesulfonyl)-*N*-benzylbenzamide (**4b**, 1 eq., 50 mg, 0.14 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **5a** (22 mg, 0.10 mmol, 73 %) as an off-white solid.

Compound 5a (Table 3, entry 3). According to the representative procedure, starting from *N*-benzyl-*N*-(2,4,6-trimethylbenzenesulfonyl)benzamide (**4c**, 1 eq., 50 mg, 0.13 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **5a** (21 mg, 0.10 mmol, 78 %) as an off-white solid.

Compound 5a (Table 3, entry 4). According to the representative procedure, starting from *N*-benzyl-*N*-(methylsulfonyl)benzamide (**4d**, 1 eq., 50 mg, 0.17 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **5a** (28 mg, 0.13 mmol, 77 %) as an off-white solid.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.82 – 7.76 (m, 2H), 7.54 – 7.47 (m, 1H), 7.43 (m, 2H), 7.36 (d, J = 4.5 Hz, 4H), 7.30 (dq, J = 8.7, 4.2 Hz, 1H), 6.39 (br, s, 1H), 4.66 (d, J = 5.7 Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 167.4 (C), 138.1 (C), 134.4 (C), 131. (CH), 128.8 (2CH), 128.6 (2CH), 128.0 (2CH), 127.7 (CH), 126.9 (2CH), 44.2 (CH$_2$) ppm. Spectroscopic data were consistent with the literature data for this compound.[48]

Compound (±)-5b (Table 3, entry 5). According to the representative procedure, starting from *N*-(4-methylbenzenesulfonyl)-*N*-(1-phenylethyl)benzamide ((±)-**4e**, 1 eq., 50 mg, 0.13 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound (±)-**5b** (29 mg, 0.14 mmol, 71 %) as an off-white solid.

Compound (S)-5b. According to the representative procedure, starting from *N*-(4-methylbenzenesulfonyl)-*N*-(1-phenylethyl)benzamide ((S)-**4e**, 1 eq., 50 mg, 0.13 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound (S)-**5b** (28 mg, 0.24 mmol, 70 %) as an off-white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.76 (dd, J = 5.2, 3.4 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.32 (m, 5H), 7.31 – 7.24 (m, 2H), 6.33 (br s, 1H), 5.34 (p, J = 7.0 Hz, 1H), 1.61 (d, J = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 166.6 (C), 143.0 (C), 134.5 (C), 131.5 (CH), 128.7 (2CH), 128.6 (2CH), 127.5 (CH), 126.9 (2CH), 126.2 (2CH), 49.2 (CH), 21.7 (CH$_3$). Spectroscopic data were consistent with the literature data for these compounds.[19]

Compound 5c (Table 3, entry 6). According to the representative procedure, starting from *N*-[(4-fluorophenyl)methyl]-*N*-(4-methylbenzenesulfonyl)benzamide (**4f**, 1 eq., 50 mg, 0.13 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **5c** (29 mg, 0.14 mmol, 74 %) as an off-white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.82 – 7.76 (m, 2H), 7.51 (m, 1H), 7.44 (m, 2H), 7.37 – 7.31 (m, 2H), 7.07 – 7.01 (m, 2H), 6.40 (s, 1H), 4.63 (d, J = 5.7 Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ

167.3 (C), 162.3 (d, $J = 245.9$ Hz, C), 134.2 (C), 134.0 (d, $J = 3.3$ Hz, C), 131.7 (CH), 129.6 (d, $J = 8.2$ Hz, 2CH), 128.7 (2CH), 126.9 (2CH), 115.6 (d, $J = 21.4$ Hz, 2CH), 43.4 (CH$_2$) ppm. ^{19}F NMR (471 MHz, CDCl$_3$): δ - 114.8 (F) ppm. Spectroscopic data were consistent with the literature data for this compound.[49]

Compound 5d (Table 3, entry 7). According to the representative procedure, starting from *N*-[(4-methoxyphenyl)methyl]-*N*-(4-methylbenzenesulfonyl)benzamide (**4g**, 1 eq., 50 mg, 0.13 mmol) and photocatalyst **3a** (0.15 eq., 8 mg, 0.019 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **5d** (25 mg, 0.104 mmol, 82 %) as an off-white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.81 – 7.76 (m, 2H), 7.53 – 7.48 (m, 1H), 7.46 – 7.40 (m, 2H), 7.32 – 7.27 (m, 2H), 6.92 – 6.86 (m, 2H), 6.31 (s, 1H), 4.59 (d, $J = 5.5$ Hz, 2H), 3.81 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 167.2 (C), 159.1 (C), 134.4 (C), 131.5 (CH), 130.2 (C), 129.4 (2CH), 128.6 (2CH), 126.9 (2CH), 114.2 (2CH), 55.3 (CH$_3$), 43.7 (CH$_2$) ppm. Spectroscopic data were consistent with the literature data for this compound.[49]

Compound 5e (Table 3, entry 8). According to the representative procedure, starting from *N*-[2-(1-benzoyl-1H-indol-3-yl)ethyl]-*N*-(4-methylbenzenesulfonyl)benz-amide (**4h**, 1 eq., 50 mg, 0.096 mmol) and photocatalyst **3a** (0.15 eq., 6 mg, 0.014 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **5e** (25 mg, 0.067 mmol, 70 %) as an off-white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.41 (d, $J = 8.2$ Hz, 1H), 7.67 (t, $J = 6.4$ Hz, 4H), 7.64 (d, $J = 7.7$ Hz, 1H), 7.58 (t, $J = 7.5$ Hz, 1H), 7.54 – 7.37 (m, 6H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.15 (s, $J = 8.8$ Hz, 1H), 6.26 (s, 1H), 3.77 (q, $J = 6.8$ Hz, 2H), 3.03 (t, $J = 6.8$ Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 168.3 (C), 167.3 (C), 136.3 (C), 134.3 (C), 134.2 (C), 131.7 (CH), 131.4 (CH), 130.5 (C), 128.8 (2CH), 128.5 (2CH), 128.4 (2CH), 126.6 (2CH), 125.2 (CH), 124.8 (CH), 123.8 (CH), 118.9 (C), 118.8 (CH), 116.5 (CH), 39.4 (CH$_2$), 25.0 (CH$_2$) ppm. IR (neat): ν 3346, 3066, 2930, 2489, 1679, 1644, 1537, 1453, 1378, 1357, 908, 712 cm^{-1}. HRMS (ESI-Orbitrap) : *m/z* [M+H$^+$] calcd for C$_{24}$H$_{21}$N$_2$O$_2$: 369.1598; found : 369.1594.

Compound 5f (Table 3, entry 9). According to the representative procedure, starting from *N*-methyl-*N*-tosylbenzamide (**4i**, 1 eq., 50 mg, 0.17 mmol) and photocatalyst **3a** (0.15 eq., 10 mg, 0.026 mmol); flash chromatography on silica gel (EtOAc/Cy, 3:7) gave compound **5f** (16 mg, 0.12 mmol, 69 %) as an off-white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.75 (dd, $J = 5.2, 3.2$ Hz, 2H), 7.53 – 7.46 (m, 1H), 7.46 – 7.38 (m, 2H), 6.11 (s, 1H), 3.02 (d, $J = 4.9$ Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 168.3 (C), 134.7 (C), 131.4 (CH), 128.6 (2CH), 126.8 (2CH), 26.9 (CH$_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[50]

Compound 5g (Table 3, entry 10). According to the representative procedure, starting from *N*-benzyl-4-fluoro-*N*-(4-methylbenzenesulfonyl)benzamide (**4j**, 1 eq., 50 mg, 0.13 mmol) and photocatalyst **3a** (0.15 eq., 8 mg, 0.02 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **5g** (18 mg,

0.078 mmol, 60%) as an off-white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.84 – 7.77 (m, 2H), 7.39 – 7.33 (m, 4H), 7.34 – 7.29 (m, 1H), 7.14 – 7.08 (m, 2H), 6.36 (s, 1H), 4.64 (d, J = 5.6 Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 163.7 (C), 162.7 (d, J = 252.0 Hz, C), 135.9 (C), 128.4 (d, J = 3.3 Hz, C), 127.2 (d, J = 8.9 Hz, 2CH), 126.8 (2CH), 125.9 (2CH), 125.7 (CH), 113.6 (d, J = 21.9 Hz, 2CH), 42.2 (CH$_2$) ppm. ^{19}F NMR (471 MHz, CDCl$_3$): δ - 108.1 (F) ppm. Spectroscopic data were consistent with the literature data for this compound.[51]

*Compound **5h** (Table 3, entry 11).* According to the representative procedure, starting from *N*-benzyl-4-methoxy-*N*-(4-methylbenzenesulfonyl)benzamide (**4k**, 1 eq., 30 mg, 0.076 mmol) and photocatalyst **3a** (0.15 eq., 4 mg, 0.011 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **5h** (8 mg, 0.033 mmol, 44 %) as an off-white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.76 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 4.3 Hz, 4H), 7.33 – 7.29 (m, 1H), 6.92 (d, J = 8.7 Hz, 2H), 6.31 (s, 1H), 4.65 (d, J = 5.6 Hz, 2H), 3.85 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 166.9 (C), 162.2 (C), 138.4 (C), 128.8 (2CH), 128.8 (2CH), 128.0 (2CH), 127.6 (CH), 126.6 (C), 113.8 (2CH), 55.4 (CH$_3$), 44.1 (CH$_2$) ppm. Spectroscopic data were consistent with the literature data for this compound.[52]

*Compound **5m**.* According to the representative procedure, starting from *N*,4-dimethyl-N-(2-((4-methylphenyl)sulfonamido)ethyl)benzenesulfonamide (**4o**, 1 eq., 20 mg, 0.041 mmol); flash chromatography on silica gel (EtOAc/Cy, 3:7) gave compound **5m** (11 mg, 0.033 mmol, 81 %) as an off-white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.87 – 7.82 (m, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 6.93 (s, 1H), 3.62 (dd, J = 11.0, 5.2 Hz, 2H), 3.26 – 3.20 (m, 2H), 2.84 (s, 3H), 2.43 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 166.7 (C), 142.8 (C), 133.2 (C), 133.0 (C), 130.5 (CH), 128.9 (2CH), 127.6 (2CH), 126.3 (2CH), 126.0 (2CH), 48.3 (CH$_2$), 36.9 (CH$_2$), 34.7 (CH$_3$), 20.5 (CH$_3$) ppm. IR (neat): ν 3383, 2885, 2253, 1649, 1537, 1336, 1160, 906, 730 cm^{-1}. HRMS (ESI-Orbitrap) : *m/z* [M+H$^+$] calcd for C$_{17}$H$_{21}$N$_2$O$_3$S: 333.1267; found : 333.1256.

ASSOCIATED CONTENT

Supporting Information

UV-vis absorption of compounds **3a-h** and **4a-n**, cyclic voltammetry, details on the photochemical apparatus and triplet quenching experiments, theoretical data, copies of ^{1}H NMR and ^{13}C NMR spectra (PDF).

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The manuscript was written through contributions of all authors.

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