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*Very Important Publication*

# Visible-Light Photoredox-Catalyzed Aminosulfonylation of Diaryliodonium Salts with Sulfur Dioxide and Hydrazines

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**Abstract:** A photoredox-catalyzed three-component synthesis of *N*-aminosulfonamides starting from diaryliodonium salts, hydrazines and sulfur dioxide is reported. This reaction proceeds under mild conditions at room temperature and is driven by visible light. A simple bisulfite salt can be used as a readily available and easy-to-handle sulfur dioxide source. Mechanistic studies support a catalytic photoredox pathway with the diaryliodonium salt as convenient source for aryl radicals.

**Keywords:** aminosulfonylation; diaryliodonium salts; organic photoredox catalysis; sulfur dioxide; three-component reaction

## Introduction

The sulfonamide group is a frequent motif in biologically active molecules,[1] including top selling drugs such as Rosuvastin,[2] Sildenafil[3] and Celecoxib[4] (Figure 1). Indeed, the history of sulfonamide-based drugs dates back over 100 years to the synthesis of the antibacterial Sulfanilamide[5] (Figure 1), which marked the beginning of the so-called antibiotic revolution.[6]

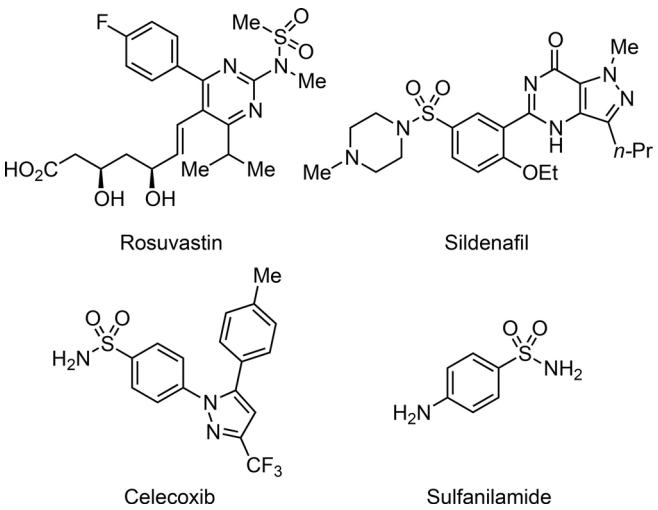
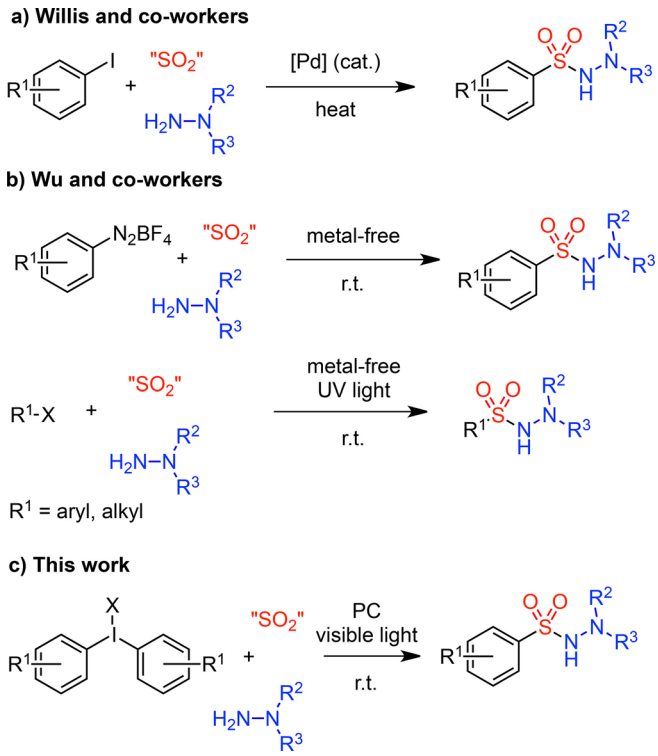



**Figure 1.** Drugs containing a sulfonamide moiety.

The most common approach for the synthesis of this important compound class is the reaction of a sulfonyl chloride with an amine.[7,8] In general, this is a very efficient and also easy to perform reaction. However, access to the sulfonyl chloride starting materials can be limited. Traditional methods for the preparation of sulfonyl chlorides, such as electrophilic aromatic substitution with chlorosulfonic acid[7,9] or oxidative chlorination of thiols,[10] are limited due to the harsh reaction conditions and regioselectivity issues.

In 2010 Willis and co-workers reported a conceptually different approach for the synthesis of the C–$SO_2$–N motif. The palladium-catalyzed three-component coupling of aryl iodides with hydrazines and the 1,4-diazabicyclo[2.2.2]octane·bis(sulfur dioxide) adduct [DABCO·$(SO_2)_2$] as convenient sulfur dioxide source directly furnishes *N*-aminosulfonamides (Scheme 1a).[11] Since this pioneering study, various methods for the incorporation of sulfur dioxide into small organic molecules have been reported using bench-stable sulfur dioxide surrogates.[12–16] Recently the group of Wu described two metal-free three-component reactions for the synthesis of *N*-aminosulfonamides based on DABCO·$(SO_2)_2$ as sulfur dioxide source and *in situ* generated carbon-centered radicals.[14,16] The radicals were either generated directly from aryldiazonium salts or through the photolysis of aryl or alkyl halides with UV light (Scheme 1b). Although these methods allow the synthesis of *N*-amino-




**Scheme 1.** Three-component synthesis of *N*-aminosulfonamides with sulfur dioxide surrogates.

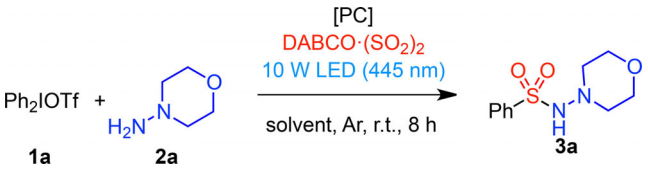
sulfonamides without the use of an expensive catalyst, they are limited either by safety issues associated with unstable diazonium salts or the need of special equipment and potential side reactions connected with the use of high-energy ultraviolet light. In the last years visible light-mediated photoredox catalysis has emerged as a powerful tool in organic synthesis.[17] Numerous examples have shown that it is possible to generate aryl or alkyl radicals from various starting materials under very mild conditions with visible light in the presence of a suitable catalyst. Amongst these different radical precursors, diaryliodonium salts play a prominent role, due to an intriguing combination of availability, stability and reactivity.[18–20] In our ongoing research program on the synthesis of sulfones and sulfonamides,[21] we could show that diaryliodonium salts are versatile building blocks for the synthesis of sulfones. Inspired by the reports on radical-based aminosulfonamide synthesis, we envisioned that diaryliodonium salts could be employed as radical precursors in aminosulfonylation reactions.

Herein we wish to report our studies towards a visible-light photoredox-catalyzed, three-component synthesis of *N*-aminosulfonamides starting from diaryliodonium salts, hydrazines and different sulfur dioxide sources (Scheme 1c).

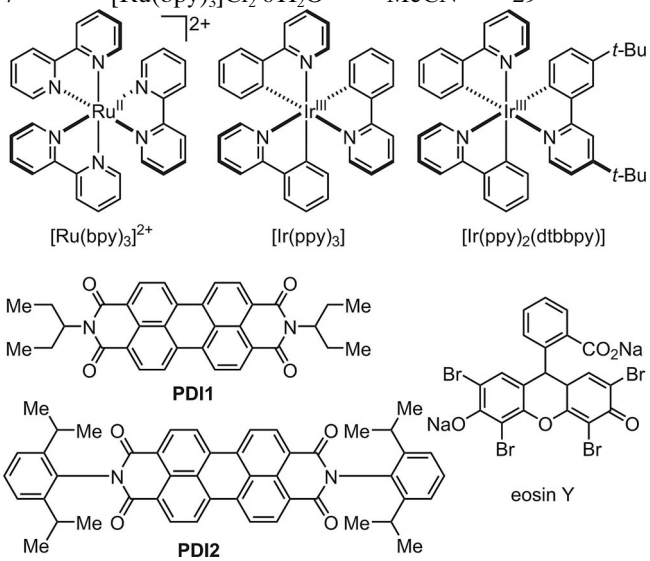
## Results and Discussion

We started our investigations with the reaction of diphenyliodonium triflate (**1a**) with 4-aminomorpholine (**2a**) and DABCO·$(SO_2)_2$ as sulfur dioxide source in in acetonitrile (Table 1). Initially, the efficiency of different photoredox catalysts (PC) was evaluated. Several common metal complexes, such as $Ru(bpy)_3Cl_2·6H_2O$, $Ir(ppy)_3$ and $[Ir(ppy)_2(dtbbpy)]PF_6$ could catalyze the desired transformation upon irradiation with visible light (10 W LED) and aminosulfonamide **3a** was isolated in 50–67 % yield (entries 1–3). To our delight, also the readily available organic dyes eosin Y and perylenediimides **PDI1** and **PDI2**, were suitable photoredox catalysts, furnishing aminosulfonamide **3a** in

**Table 1.** Initial catalyst screening of the photoredox catalysts.[a]




| Entry | [PC] | Solvent | Yield [%] |
|---|---|---|---|
| 1 | $[Ru(bpy)_3]Cl_2·6H_2O$ | MeCN | 50 |
| 2 | $[Ir(ppy)_3]$ | MeCN | 67 |
| 3 | $[Ir(ppy)_2(dtbbpy)]PF_6$ | MeCN | 56 |
| 4[b] | eosin Y | MeCN | 53 |
| 5[c] | **PDI1** | MeCN | 63 |
| 6[c] | **PDI2** | MeCN | 62 |
| 7[d] | $[Ru(bpy)_3]Cl_2·6H_2O$ | MeCN | 29 |

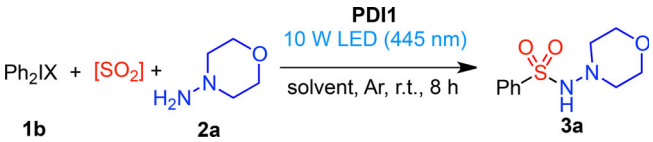



[a] *Reaction conditions:* $Ph_2IOTf$ (**1a**, 0.3 mmol), 4-aminomorpholine (**2a**, 0.36 mmol), DABCO·$(SO_2)_2$ (0.18 mmol), 10 W LED (445 nm), photocatalyst (1 mol%), solvent (2 mL), argon, room temperature.
[b] Irradiation at 530 nm was used.
[c] With 2 mol% of the photocatalyst.
[d] A 35 W halogen lamp was used.

53–66% yield. Best result were obtained either with the very expensive iridium complex $Ir(ppy)_3$ or with the perylene dyes **PDI1** and **PDI2** (entries 4–6). Unfortunately, use of cheaper household halogen lamps furnished only a 29% yield (entry 7). Since only **PDI1** is commercially available for a reasonable price,[22] this organic dye was selected as photoredox catalyst for further studies.

Screening of solvents showed that the reaction proceeds more efficiently in a 1:1 mixture of acetonitrile and dimethyl sulfoxide, presumably due to the low solubility of the catalyst **PDI1** in acetonitrile (Table 2, entry 1). Dimethyl sulfoxide alone or dimethylformamide[23] proved to be to be less efficient solvents (entries 2 and 3). Good yields were also obtained in an acetonitrile-dichloroethane mixture (entry 4). Substitution of DABCO·$(SO_2)_2$ with DMAP·$SO_2$, another solid $SO_2$-amine adduct, afforded product **3a** in only 57% yield (entry 5). It has been shown that simple sulfite salts, such as potassium metabisulfite, can be used as the sulfur dioxide source in aminosulfonylation reactions.[13,24,25] Replacing DABCO·$(SO_2)_2$ with

**Table 2.** Optimization of the reaction.[a]




| Entry | X | [$SO_2$] | Solvent | Yield [%] |
|---|---|---|---|---|
| 1 | OTf | DABCO·$(SO_2)_2$ | MeCN | 63 |
| 2 | OTf | DABCO·$(SO_2)_2$ | MeCN/DMSO (1:1) | 72 |
| 3 | OTf | DABCO·$(SO_2)_2$ | DMSO | 66 |
| 4 | OTf | DABCO·$(SO_2)_2$ | DMF | 56 |
| 5 | OTf | DABCO·$(SO_2)_2$ | MeCN/DCE (1:1) | 72 |
| 6[b] | OTf | $K_2S_2O_5$ | MeCN/DMSO (1:1) | 20 |
| 7[b,c] | OTf | $K_2S_2O_5$/TFA | MeCN/DMSO (1:1) | 74 |
| 8[b,c] | OTf | $Na_2S_2O_5$/TFA | MeCN/DMSO (1:1) | 70 |
| 9[e] | OTf | DMAP·$(SO_2)$ | MeCN/DMSO (1:1) | 57 |
| 10[c,d] | OTf | $K_2S_2O_5$/TFA | MeCN/DMSO (1:1) | 71 |
| 11[c,d] | Cl | $K_2S_2O_5$/TFA | MeCN/DMSO (1:1) | 76 |
| 12[c,d] | $PF_6$ | $K_2S_2O_5$/TFA | MeCN/DMSO (1:1) | 75 |
| 13[c,d] | $BF_4$ | $K_2S_2O_5$/TFA | MeCN/DMSO (1:1) | 76 |
| 14[c,d] | OTs | $K_2S_2O_5$/TFA | MeCN/DMSO (1:1) | 65 |
| 15[c,d,f] | OTf | $K_2S_2O_5$/TFA | MeCN/DMSO (1:1) | 71 |
| 16[c,d,g] | OTf | $K_2S_2O_5$/TFA | MeCN/DMSO (1:1) | 75 |

[a] *Reaction conditions:* $Ph_2IX$ (**1b**, 0.3 mmol), $SO_2$ source (0.18 mmol), 4-aminomorpholine (**2a**, 0.36 mmol), **PDI1** (2 mol%), 10 W LED (445 nm), solvent (2 mL), argon, room temperature.
[b] With 2 equiv. of $K_2S_2O_5$ or $Na_2S_2O_5$.
[c] With 1 equiv. of TFA.
[d] With 0.6 equiv. of $K_2S_2O_5$.
[e] With 1.2 equiv. of DMAP·$SO_2$
[f] With 4 h of irradiation.
[g] With 1 h of irradiation.

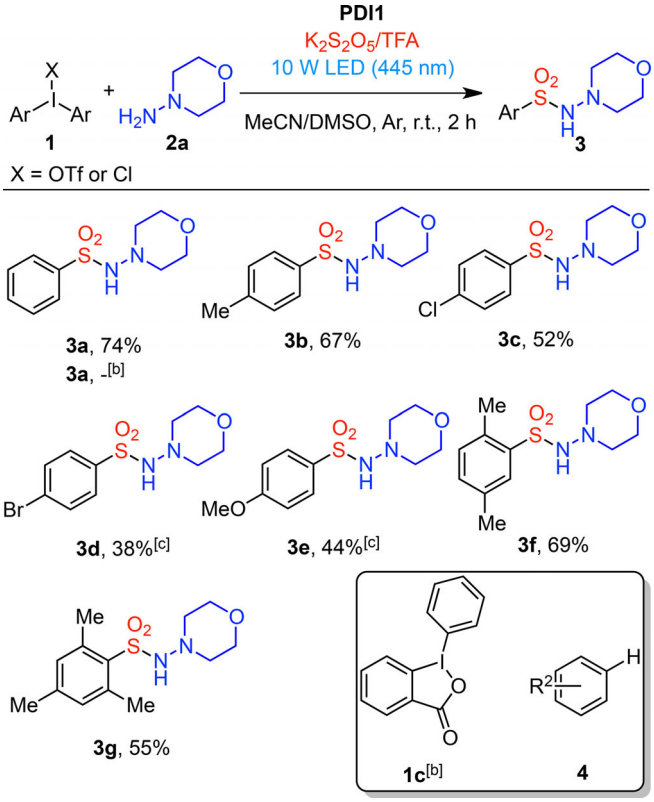
2 equivalents of $K_2S_2O_5$ in our photoredox-catalyzed transformation led to a decreased yield of 20% (entry 6). However, this yield could be improved to 74% by the simple addition of stoichiometric amounts of an acid, such as trifluoroacetic acid (TFA) (entry 6). In a similar manner aminosulfonamide **3a** could be synthesized in 70% yield using $Na_2S_2O_5$ together with TFA as sulfur dioxide source (entry 7). These results show that it is possible to generate a controlled amount of sulfur dioxide *in situ* by the acid-mediated decomposition of metabisulfite salts.[26] Due to the ease of this process and the availability and price of metabisulfite salts, the combination of $K_2S_2O_5$ and TFA was chosen as sulfur dioxide source for all further transformations. No influence of the diphenyliodonium counterion on the reaction was observed (entries 10–14). The entire transformation proceeds very rapidly and full conversion was observed after only 1 h (entries 15 and 16).

With the optimized conditions at hand, we examined the scope of this three-component process (Table 3). Various symmetrical diaryliodonium salts **1** were reacted with 4-aminomorpholine **2a** and sulfur dioxide generated from $K_2S_2O_5$ in the presence of 2 mol% **PDI1** upon irradiation with blue light (445 nm). Aminosulfonamides **3a–3g** were isolated in moderate to good yields. In the case of low yields, considerable amounts of arenes of type **4**, presumably formed *via* reduction of the iodonium salts, could be detected in the crude reaction by NMR.[27] Reactions with other hypervalent iodine species, such as benzoiodooxolone **1c** were unsuccessful.

Next, reactions with different hydrazines were explored (Table 4). Whereas most hydrazines afforded the aminosulfonylated products **3a** and **3h–3n** in moderate to good yields, in one case very low yield were obtained. Most strikingly the reaction of *N*-aminopiperidine **2b** furnished the product **3h** in only 23% yield. All attempts to improve the yield, such as vigorous repurification of the hydrazine, changes in the reaction stoichiometry or slow addition of one component, did not affect the yield significantly. Examination of the reaction mixture revealed the formation of considerable amounts of reduced side products of type **4**.[27] This indicates that a small change in the structure of the hydrazine component can affect the ratio of the side product formation tremendously. Unfortunately, reaction with simple amines, such as aniline did not afford the desired sulfonamide (**3o**).

Unsymmetrical iodonium salts ($Ar^1 \neq Ar^2$) can transfer one of the two aryl moieties with a high degree of selectivity. In general, the chemoselectivity of the aryl transfer reaction is influenced by the electronic and steric properties of the diaryliodonium salt and the reaction conditions (metal-free *vs.* metal-catalyzed).[28] The use of unsymmetrical salts has several advantages. Such iodonium salts are readily accessible

**Table 3.** Substrate scope.[a]

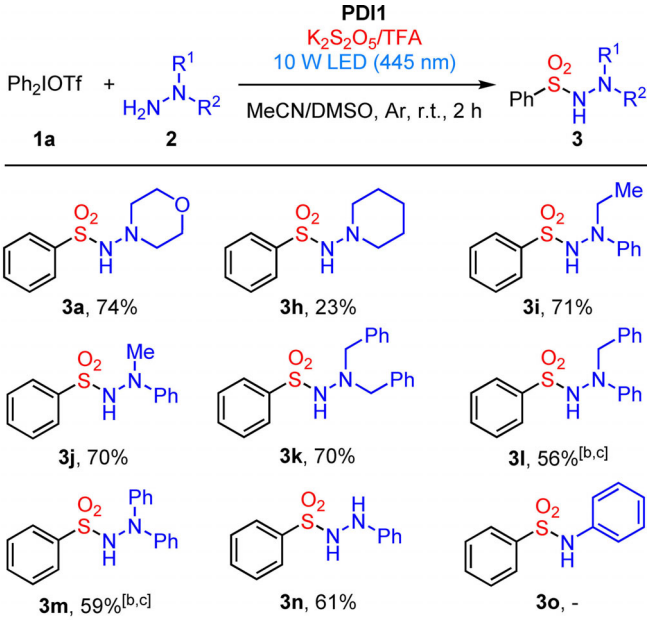



[a] *Reaction conditions:* $Ar_2IOTf$ (**1**, 0.3 mmol), $K_2S_2O_5$ (0.18 mmol), TFA (0.3 mmol), 4-aminomorpholine (**2a**, 0.36 mmol), **PDI1** (2 mol%), 10 W LED (445 nm), DMSO/MeCN (1:1, 2 mL), argon, room temperature, 2 h.

[b] The corresponding mono hydrate of benzoiodooxolone **1c** was used.

[c] The corresponding iodonium chloride salt was used.

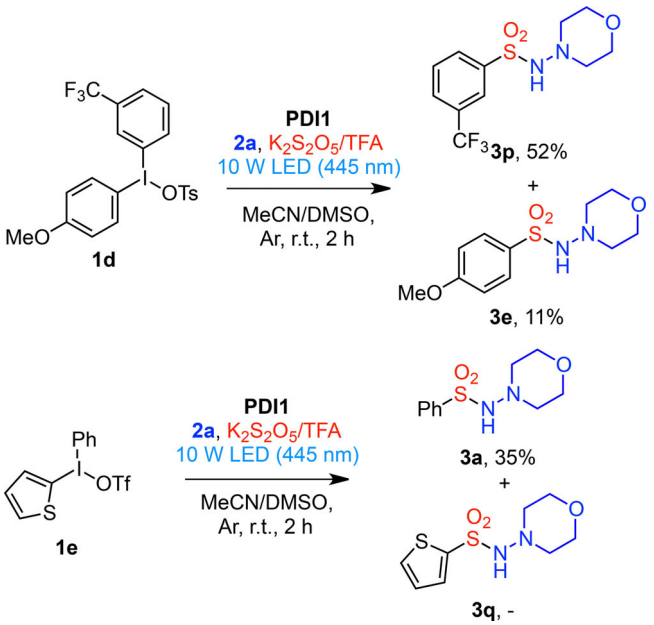
**Table 4.** Substrate scope.[a]




[a] *Reaction conditions:* $Ph_2IOTf$ (**1a**, 0.3 mmol), $K_2S_2O_5$ (0.18 mmol), TFA (0.3 mmol), hydrazine (**2**, 0.36 mmol), **PDI1** (2 mol%), 10 W LED (445 nm), DMSO/MeCN (1:1, 2 mL), argon, room temperature, 2 h.

[b] The corresponding hydrochloride hydrazine adduct was used.

[c] Without TFA addition.

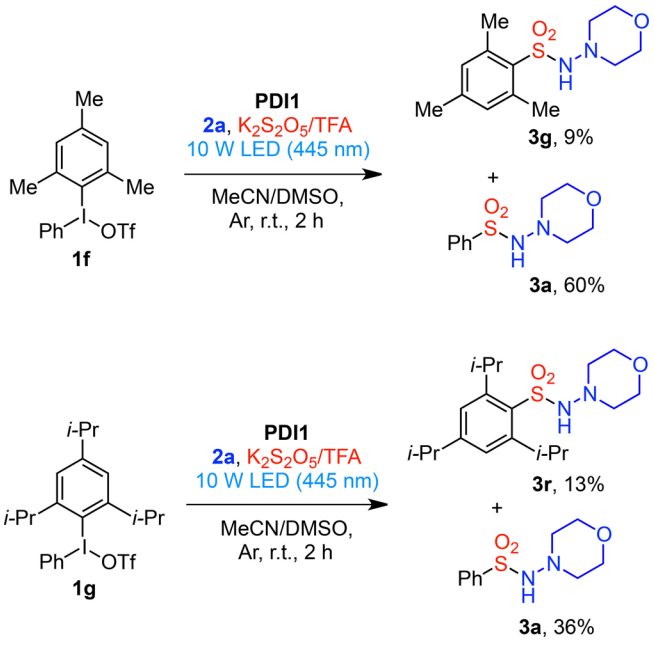



**Scheme 2.** Selectivity studies with electronically differentiated diaryliodonium salts.

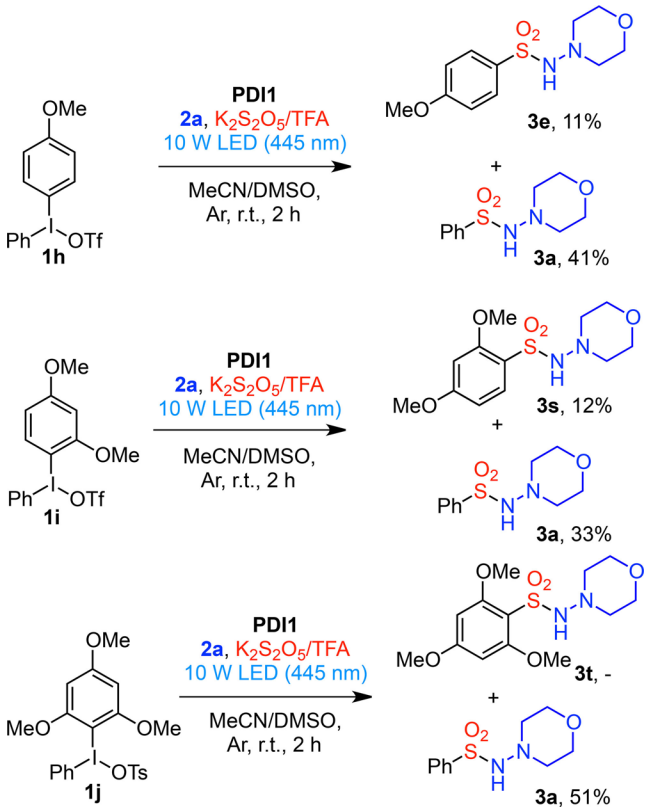
with a greater structural variety and the selective transfer of the desired aryl moiety over a "dummy ligand" avoids the waste of an expensive aryl iodides. Therefore, we performed a series of experiments in order to investigate a potential chemoselective aryl transfer in photoredox-catalyzed transformations. Firstly, reactions with electronically-differentiated systems were carried out. In the case of diaryliododnium salt **1d**, a selective transfer of the electron-poor trifluoromethylphenyl group over the electron-rich methoxybenzene moiety was observed (Scheme 2). In a similar manner, the reaction of phenylthienyliodonium triflate **1e** led to a selective transfer of the phenyl group over the electron-rich thiophene moiety albeit with a low overall yield of 35%.

Next, experiments with sterically-differentiated iodonium salts were performed (Scheme 3). The reaction of mesitylphenyliodonium triflate **1f** led to a selective transfer of the sterically less shielded phenyl moiety. Interestingly, the reaction of **1g**, bearing the sterically more demanding trisisopropylphenyl group, did proceed less efficiently and with a lower degree of selectivity.

The group of Olofsson has shown that di- or trimethoxyaryl groups are convenient dummy ligands for




**Scheme 3.** Selectivity studies with sterically differentiated diaryliodonium salts.

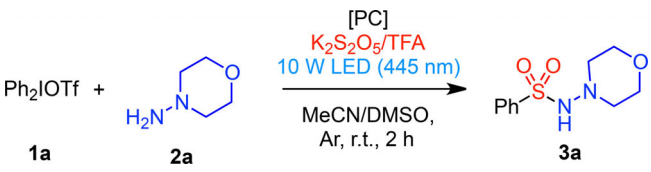



**Scheme 4.** Selectivity studies with sterically differentiated diaryliodonium salts.

a chemoselective aryl transfer with a wide variety of different nucleophiles.[28] Therefore, we examined the behavior the three mono, di- and trimethoxybenzene-derived iodonium salts **1h**–**1j** under our reaction conditions (Scheme 4). As expected a very low selectivity of 2.7:1 was observed in the case of monomethoxybenzene derivative **1h**. Introduction of a second methoxy substituent did not lead to a significant improvement of the selectivity. However, the reaction with trimethoxybenzene-derived iodonium salt **1j** afforded *N*-morpholinobenzenesulfonamide **3a** in 51% yield with a completely chemoselective transfer of the phenyl group. These results show that a selective transfer of one aryl moiety from unsymmetrical diaryliodonium salts is possible under photoredox catalysis. The selectivity of this transformation is affected by electronic and steric properties of both aryl residues. In general, selectivities are not as high as from other reported reactions with unsymmetrical substituted salts. Only in the cases of trimethoxybenzene derivative **1j** and the thiophene-based salt **1e**, complete chemoselectivity was observed. Our preliminary investigations also show that the overall efficiency of the photoredox catalyzed three-component reaction is affected by the steric properties of the iodonium salt. Steric shielding in the *ortho*-positions leads to a decrease in yield. Reaction with styryl(phenyl)iodonium tetrafluoroborate resulted in a complex mixture.

In order to gain further insights into the reaction mechanism a series of control experiments was performed. Reaction in the absence of light did not afford the desired product at all (Table 5, entry 1).

**Table 5.** Control experiments.[a]




| Entry | [PC] | Variation | Yield [%] |
|---|---|---|---|
| 1 | **PDI1** | dark | – |
| 2 | **PDI1** | TEMPO (1.0 equiv.) | – |
| 3 | – | – | 18 |
| 4 | **PDI1** | dark, 60 °C | 11 |
| 5 | – | dark, 60 °C | 35 |
| 6 | **PDI1** | – | 72 |
| 7 | – | benzophenone | 15 |

[a] *Reaction conditions:* $Ph_2IOTf$ (**1a**, 0.3 mmol), $K_2S_2O_5$ (0.18 mmol), TFA (0.3 mmol), 4-aminomorpholine (**2a**, 0.36 mmol), photocatalyst (2 mol%), 10 W LED (445 nm), DMSO/MeCN (1:1, 2 mL), argon, room temperature, 2 h.

Addition of radical scavengers, such as (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), shut down the reaction completely (entry 2). Interestingly, irradiation with blue LEDs in the absence of a photoredox catalyst delivered the expected product, albeit in

a very low yield (entry 3). In a similar manner, heating the reaction mixture in the dark to 60 °C either in the presence or the absence of **PDI1** furnished the expected product in 11 or 35% yield after 2 h (entries 4 and 5). Full conversion of the iodonium salts was observed after 2 h by $^1$H NMR and prolonged heating did not improve the yield. Indeed iodonium salts are known to react either under thermal conditions[29] or under irradiation with visible light through the formation of a charge-transfer complex.[19,30] However, only the use of a photoredox catalyst in combination with irradiation delivered the *N*-aminosulfonamide **3a** in a synthetically useful yield (entry 6). Addition of organic photoinitiators, such as benzophenone, did not promote the reaction (entry 7).

Next the UV/Vis-spectra of all three components as well as UV/Vis-spectra of 1:1 mixtures of two components were recorded (Figure 2). Hydrazine **2a**, sulfur dioxide and diphenyliodonium hexafluorophosphate **1k**[31] show no absorbance between 400 and 500 nm. In the case of the 1:1 mixtures of hydrazine **2a** with either sulfur dioxide or the iodonium salt **1k**, a small, but presumably negligible increase of the absorbance between 400 and 450 nm was observed. The mixture of all three components showed an insignificantly higher absorbance than the corresponding two component mixtures. Contrary to the work of Chatani, no charge-transfer complex between the iodonium salt and a second component could be observed.[19]

Subsequently, determination of the quantum yield Φ using the well-established chemical actinomer potassium ferrioxalate[32] afforded a Φ value of 0.26–0.29 (Scheme 5). This suggests that a photocatalytic pathway is operative and radical chain propagation can be neglected as a dominant pathway.

Stern–Volmer fluorescence quenching studies with **PDI1** revealed a significant quenching in the presence of the hydrazine (Figure 3). Interestingly, no change

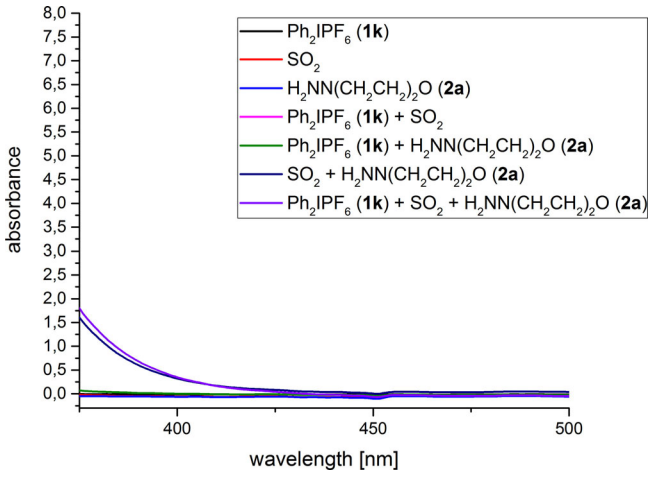
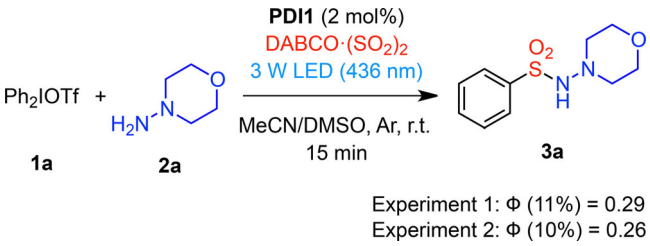



**Figure 2.** UV/Vis-spectra of $Ph_2IPF_6$ (**1k**), $SO_2$ and 4-aminomorpholine (**2a**).




**Scheme 5.** Quantum yield determination.

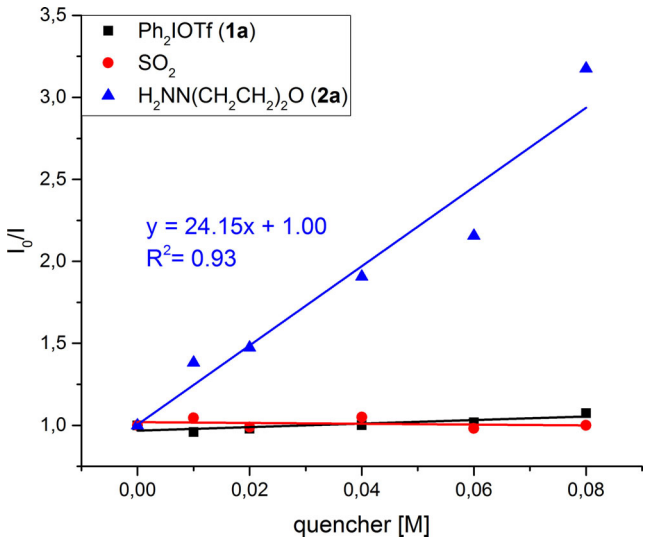
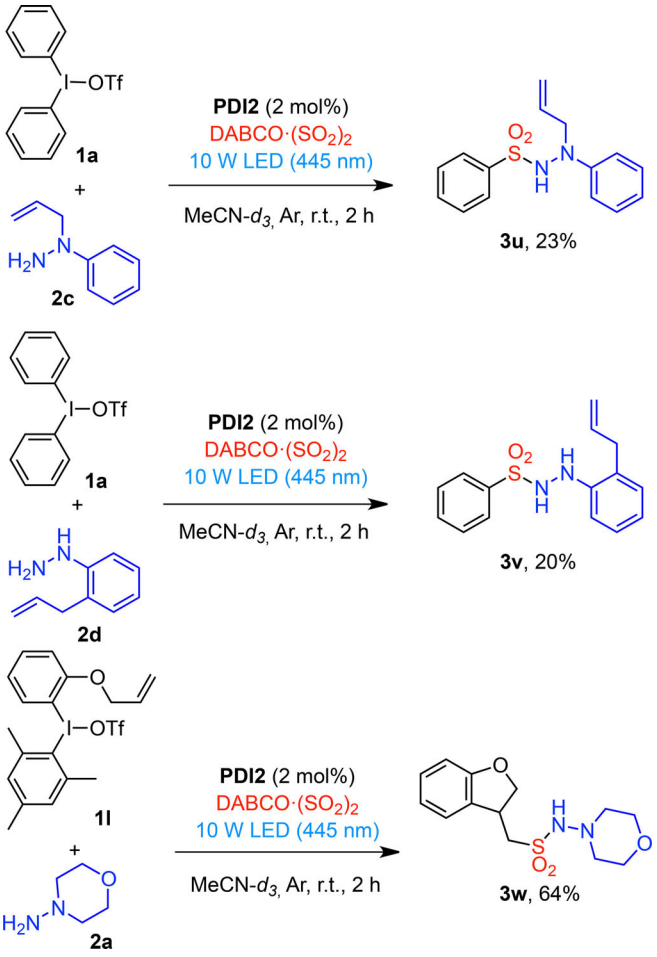


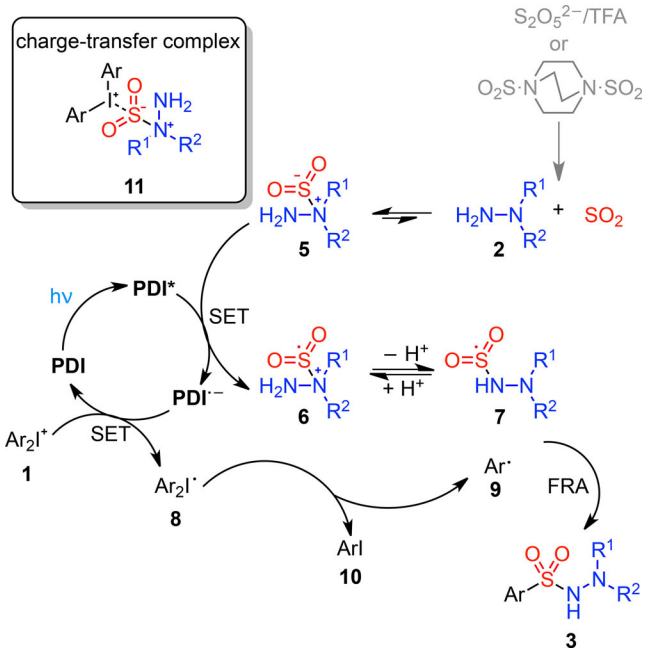

**Figure 3.** Stern–Volmer plots.

in emission was observed in the presence of the iodonium salt or sulfur dioxide. These results indicate that the catalytic cycle starts with a reductive quenching cycle, wherein the excited state of the photoredox catalysts oxidizes the hydrazine.

Finally, a series of control experiments with the radical clocks **2c**, **2d** and **1l** was performed (Scheme 6). Formation of the cyclized product **3w** was observed only in the case of the iodonium-based radical clock **1l**. Reaction of the allylhydrazines **2c** and **2d** furnished the linear products **3u** and **3v** in 23 and 20% yields. In all cases only unreacted starting materials or reduction products of type **4** and no other side-products were observed in the crude reaction mixture by $^1$H NMR.[33] These findings suggest that, as originally envisioned, aryl-based radicals are formed from the iodonium salt. Although, as shown above, an initial electron-transfer to the hydrazine should take place, no cyclization occurs on the hydrazines **2c** and **2d**. There are two possible reasons for this observation. Either the formed radical is very unstable and reacts rapidly without cyclization or a stable intermediate is formed, which is not prone to undergo an addition to the double bond.




**Scheme 6.** Radical clock experiments.




**Scheme 7.** Proposed mechanism.

Based on these results, we propose the following mechanism (Scheme 7). The hydrazine and sulfur dioxide, either generated *in situ* from the acid-mediated decomposition of a bisulfite salt or delivered in the form of the sulfur dioxide surrogate DABCO·$(SO_2)_2$, from a stable hydrazine-sulfur dioxide adduct **5**[14,15,24,34] Irradiation of the photoredox catalyst **PDI** affords the photoexcited **PDI***. Reductive quenching of **PDI*** with the hydrazine-sulfur dioxide complex **5** furnishes the radical cation **6** and the reduced catalyst **PDI**$^{\cdot-}$. Deprotonation of intermediate **6** affords radical adduct **7**. One could also envision similar electron and proton-transfer processes solely with the hydrazine **2** or a dissociation of the adducts **5** or **6** into hydrazine-based radicals and free sulfur dioxide.

However, such a formation of the stable, sulfonyl-type radicals[35] could explain the lack of cyclization in the case of hydrazines **2c** and **2d**. Electron-transfer from **PDI**$^{\cdot-}$ onto diaryliodonium salt **1** gives the reduced species **8** and the regenerated catalyst **PDI** in its ground state. Fragmentation of **8** affords an aryl radical **9**, which can undergo a radical cyclization in the case of substrate **1l**, and form aryl iodide **10** as by-product. Free-radical addition (FRA) of **9** with the sulfur dioxide-hydrazine adduct **7** furnishes the final product **3**.

In principle, one could speculate on the formation of a distinct charge-transfer complex **11** between the iodonium salt **1**, sulfur dioxide and the hydrazine **2**. Such a complex might be able to absorb visible light directly[36] or undergo a thermal reaction.[37] However, we were unable to detect such an intermediate.

## Conclusions

In summary, we have reported a visible-light photoredox-catalyzed three-component aminosulfonylation reaction of diaryliodonium salts with sulfur dioxide and hydrazines. This novel method enables the synthesis of *N*-aminosulfonamides in moderate to good yields under mild conditions using visible light as driving source of the reaction. Commercially available perylene dyes serve as efficient organic photoredox catalysts. Sulfur dioxide can be either employed as the solid amine complex DABCO·$(SO_2)_2$ or generated *in situ via* acid-mediated decomposition of bisulfite salts. Reactions with unsymmetrical diaryliodonium salts can lead to a highly selective transfer of one aryl moiety. Selectivity studies revealed that for reported three-component reaction best selectivities can be obtained with trimethoxybenzene as dummy ligands. A plausible photocatalytic reaction mechanism, based on a series of control experiments, is proposed.

## Experimental Section

### Typical Procedure for the Synthesis of Aryl *N*-aminosulfonamides with $K_2S_2O_5$/TFA

A 10-mL tube was charged with a stirring bar, diaryliodonium salt (1 equiv., 0.3 mmol), $K_2S_2O_5$ (40 mg, 0.60 equiv., 0.18 mmol), hydrazine (1.2 equiv., 0.36 mmol), photocatalyst (1–2 mol%) and a 1:1 mixture of MeCN and DMSO (0.15 M referring to diaryliodonium salt, 2 mL, 1:1) (if a hydrazine hydrochloride adduct was use, TFA could be omitted and the reaction was not cooled to 0 °C). The tube was closed with a rubber septum, cooled to 0 °C, TFA (23 μL, 34 mg, 1.0 equiv., 0.3 mmol) was added slowly and the resulting reaction mixture was warmed up to room temperature. After 5 min of argon sparging, the resulting reaction mixture was irradiated (445 nm, 10 W) for 2 h at ambient temperature. After the completion of the reaction, the mixture was diluted with $H_2O$ (15 mL). The aqueous layer was extracted with EtOAc (3×20 mL). The combined organic phases were washed with saturated aqueous NaCl (25 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. Purification of the crude residue by column chromatography (*n*-hexane/EtOAc) afforded the analytically pure product.

***N*-Morpholinobenzenesulfonamide (3a):** Prepared from $Ph_2IOTf$ (**1a**, 129 mg), 4-aminomorpholine (**2a**, 35 μL, 37 mg) and **PDI1** (3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 9:1→7:3) afforded **3a** as an off-white solid; yield: 54 mg (74%). Analytical data are consistent with the literature values.[14] $R_f$ = 0.34 (*n*-hexane/EtOAc 7:3); mp 23.9 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$ = 8.01–7.93 (m, 2H), 7.65–7.59 (m, 1H), 7.56–7.50 (m, 2H), 5.41 (s, 1H), 3.60 (t, $J$ = 5.0 Hz, 4H), 2.61 (t, $J$ = 5.0 Hz, 4H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$ = 138.7, 133.3, 129.0, 128.3, 66.8, 56.9; MS (ESI): $m/z$ = 243.07, calcd. for $C_{10}H_{15}N_2O_3S$ $[M+H]^+$: 243.08.

**4-Methyl-*N*-morpholinobenzenesulfonamide (3b):** Prepared from $(p\text{-Tol})_2IOTf$ (**1m**, 137 mg), 4-aminomorpholine (**2a**, 35 μL, 37 mg), **PDI1** (3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 9:1→7:3) afforded **3b** as an off-white solid; yield: 52 mg (68%). Analytical data are consistent with the literature values.[14] $R_f$ = 0.34 (*n*-hexane/EtOAc 7:3); mp 151.1 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$ = 7.84 (d, $J$ = 8.3 Hz, 2H), 7.31 (d, $J$ = 8.3 Hz, 2H), 5.51 (s, 1H), 3.60 (t, $J$ = 5.0 Hz, 4H), 2.62 (t, $J$ = 5.0 Hz, 4H), 2.43 (s, 3H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$ = 144.2, 135.8, 129.6, 128.3, 66.8, 56.9, 21.8; MS (ESI): $m/z$ = 257.11, calcd. for $C_{11}H_{17}N_2O_3S$ $[M+H]^+$: 257.10.

**4-Chloro-*N*-morpholinobenzenesulfonamide (3c):** Prepared from $(p\text{-}ClC_6H_4)_2IOTf$ (149 mg), 4-aminomorpholine (**2a**, 35 μL, 37 mg) and **PDI1** (3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 9:1→7:3) afforded **3c** as an off-white solid; yield: 43 mg (52%). Analytical data are consistent with the literature values.[14] $R_f$ = 0.34 (*n*-hexane/EtOAc 7:3); mp 163.7 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$ = 7.96–7.81 (m, 2H), 7.60–7.48 (m, 2H), 5.55 (s, 1H), 3.62 (t, $J$ = 5.0 Hz, 4H), 2.64 (t, $J$ = 5.0 Hz, 4H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$ = 139.9, 137.2,3, 129.7, 129.3, 66.8, 56.9; MS (ESI): $m/z$ = 274.96, calcd. for $C_{10}H_{12}ClN_2O_3S$ $[M-H]^-$: 275.03.

**4-Bromo-*N*-morpholinobenzenesulfonamide (3d):** Prepared from $(4\text{-bromophenyl})_2ICl$ (142 mg), 4-aminomorpholine (**2a**, 35 μL, 37 mg), **PDI1** (3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 9:1→7:3) afforded **3d** as an off-white solid; yield: 36 mg (38%). Analytical data are consistent with the literature values.[14] $R_f$ = 0.36 (*n*-hexane/EtOAc 7:3); mp 159.1 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$ = 7.86–7.81 (m, 2H), 7.69–7.64 (m, 2H), 5.38 (m, 1H), 3.62 (t, $J$ = 5.0 Hz, 4H), 2.64 (t, $J$ = 5.0 Hz, 4H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$ = 137.8, 132.3, 129.8, 128.5, 66.8, 57.0; MS (ESI): $m/z$ = 320.98, calcd. for $C_{10}H_{14}BrN_2O_3S_1$ $[M+H]^+$: 320.99.

**4-Methoxy-*N*-morpholinobenzenesulfonamide (3e):** Prepared from $(4\text{-methoxyphenyl})_2ICl$ (112.99 mg), 4-aminomorpholine (**2a**, 35 μL, 37 mg) and **PDI1** (3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 9:1→7:3) afforded **3e** as an off-white solid; yield: 36 mg (44%). Analytical data are consistent with the literature values.[14] $R_f$ = 0.33 (*n*-hexane/EtOAc 7:3); mp 163.9 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$ = 7.91–7.86 (m, 2H), 7.01–6.95 (m, 2H), 5.40 (s, 1H), 3.88 (s, 3H), 3.64–3.56 (t, $J$ = 5.0 Hz, 4H), 2.62 (t, $J$ = 5.0 Hz, 4H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$ = 163.4, 130.5, 130.2, 114.1, 66.8, 56.9, 55.8; MS (ESI): $m/z$ = 273.11, calcd. for $C_{11}H_{17}N_2O_4S$ $[M+H]^+$: 273.09.

**2,5-Dimethyl-*N*-morpholinobenzenesulfonamide (3f):** Prepared from $(2,5\text{-dimethylphenyl})_2IOTf$ (146 mg), 4-aminomorpholine (**2a**, 35 μL, 37 mg) and **PDI1** (3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 9:1→7:3) afforded **3f** as an off-white solid; yield: 57 mg (70%). $R_f$ = 0.14 (*n*-hexane/EtOAc 4:1); mp 128.8 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$ = 7.88–7.97 (m, 1H), 7.29–7.26 (m, 1H), 7.18 (d, $J$ = 7.5 Hz, 1H), 5.35 (s, 1H), 3.59 (t, $J$ = 5.0 Hz, 4H), 2.65 (t, $J$ = 5.0 Hz, 4H), 2.64 (s, 3H), 2.39 (s, 3H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$ = 136.3, 136.2, 134.9, 134.1, 132.4, 131.4, 66.7, 57.0, 20.9, 20.4; MS (ESI): $m/z$ = 269.09, calcd. for $C_{12}H_{17}N_2O_3S_1$ $[M-H]^-$: 269.10; HR-MS: $m/z$ = 271.1115, calcd. for $C_{12}H_{19}N_2O_3S_1$ $[M+H]^+$: 271.1111; IR: $\nu$ = 3217 (m), 2924 (m), 2862 (m), 1727 (w), 1507 (w), 1493 (m), 1472 (m), 1428 (m), 1392 (m), 1368 (w), 1327 (s), 1156 (s), 1109 (s), 1063 (m), 867 (s), 828 (m), 849 (m), 828 (s), 816 (s), 706 (m), 698 (s), 603 (s), 583 (s), 499 (s), 491 $cm^{-1}$ (s).

**2,4,6-Trimethyl-*N*-morpholinobenzenesulfonamide (3g):** Prepared from $Mes_2IOTf$ (154 mg), 4-aminomorpholine (**2a**, 35 μL, 37 mg) and **PDI1** (3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 9:1→7:3) afforded **3g** as an off-white solid; yield: 47 mg (55%). Analytical data are consistent with the literature values.[14] $R_f$ = 0.17 (*n*-hexane/EtOAc 4:1); mp 163.4 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$ = 6.95 (s, 2H), 5.42 (s, 1H), 3.57 (t, $J$ = 5.0 Hz, 4H), 2.68 (s, 6H), 2.65 (t, $J$ = 5.0 Hz, 4H), 2.30 (s, 3H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$ = 142.9, 140.6, 132.6, 131.8, 67.0, 56.8, 23.3, 21.2; MS (ESI): $m/z$ = 285.12, calcd. for $C_{13}H_{21}N_2O_3S$ $[M+H]^+$: 285.13.

***N*-(Piperidin-1-yl)benzenesulfonamide (3h):** Prepared from $Ph_2IOTf$ (**1a**, 129 mg), 1-aminopiperidine (**2b**, 39 μL,

36 mg) and **PDI1** (3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 50:1→7:3) afforded **3h** as an off-white solid; yield: 17 mg (23%). Analytical data are consistent with the literature values.[16] $R_f$=0.4 (*n*-hexane/EtOAc 4:1); mp 100.7 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$=8.02–7.92 (m, 2H), 7.61–7.57 (m, 1H), 7.53–7.49 (m, 2H), 5.30 (s, 1H), 2.58–2.48 (m, 4H), 1.50 (quint., $J$=5.8 Hz, 4H), 1.33–1.26 (m, 2H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$=138.9, 133.0, 128.8, 128.3, 58.0, 25.8, 23.2; MS (ESI): $m/z$=241.07, calcd. for $C_{11}H_{17}N_2O_2S_1$ $[M+H]^+$: 241.10.

***N′*-Ethyl-*N′*-phenylbenzenesulfonohydrazide (3i):** Prepared from $Ph_2IOTf$ (**1a**, 129.05 mg), 1-ethyl-1-phenylhydrazine (48 µl, 49 mg) and **PDI1** (3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 20:1→7:3) afforded **3i** as an off-white solid; yield: 58 mg (71%). Analytical data are consistent with the literature values.[14] $R_f$=0.63 (*n*-hexane/EtOAc 7:3); mp 95.7 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$=7.94–7.90 (m, 2H), 7.58–7.52 (m, 1H), 7.47–7.43 (m, 2H), 7.15–7.09 (m, 2H), 6.84–6.80 (m, 1H), 6.78–6.74 (m, 2H), 6.30 (s, 1H), 3.45 (m, 2H), 1.02 (t, $J$=7.0 Hz, 3H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$=147.7, 138.8, 133.4, 129.1, 129.1, 128.2, 121.0, 115.1, 49.3, 9.5; MS (ESI): $m/z$=299.11, calcd. for $C_{14}H_{16}N_2NaO_2S_1$ $[M+Na]^+$: 299.08.

***N′*-Methyl-*N′*-phenylbenzenesulfonohydrazide (3j):** Prepared from $Ph_2IOTf$ (**1a**, 129 mg), 1-methyl-1-phenylhydrazine (42 µL, 44 mg) and **PDI1** (3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 20:1→7:3) afforded **3j** as an off-white solid; yield: 51 mg (70%). Analytical data are consistent with the literature values.[14] $R_f$=0.50 (*n*-hexane/EtOAc 7:3); mp 127.7 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$=7.98–7.93 (m, 2H), 7.62–7.57 (m, 1H), 7.53–7.48 (m, 2H), 7.18–7.12 (m, 2H), 6.88–6.84 (m, 1H), 6.83–6.80 (m, 2H), 6.10 (s, 1H), 3.00 (s, 3H); $^{13}$C NMR (125.77 MHz, $CDCl_3$):$\delta$=149.7, 138.7, 133.5, 129.3, 129.1, 128.3, 121.2, 114.4, 43.0; MS (ESI): $m/z$=285.09, calcd. for $C_{13}H_{14}N_2NaO_2S_1$ $[M+Na]^+$: 285.07.

***N′*,*N′*-Dibenzylbenzenesulfonohydrazide (3k):** Prepared from $Ph_2IOTf$ (**1a**, 129 mg), 1-benzyl-1-phenylhydrazine hydrochloride (76 mg) and **PDI1** (3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 50:1→1:1) afforded **3k** as an off-white solid; yield: 74 mg (70%). Analytical data are consistent with the literature values.[38] $R_f$=0.38 (*n*-hexane/EtOAc 4:1); mp 133.3 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$=7.87–7.81 (m, 2H), 7.53–7.49 (m, 1H), 7.43–7.38 (m, 2H), 7.29–7.24 (m, 6H), 7.19–7.15 (m, 4H), 5.55 (s, 1H), 3.72 (s, 4H); $^{13}$C NMR (125.77 MHz, $CDCl_3$) $\delta$ 138.6, 134.9, 133.0, 129.9, 128.9, 128.6, 128.3, 127.9, 59.9; MS (ESI): $m/z$=353.09, calcd. for $C_{20}H_{21}N_2O_2S_1$ $[M+H]^+$: 353.13.

**2-Benzyl-2-phenyl-1-(phenylsulfonyl)hydrazine-1-ide (3l):** Prepared from $Ph_2IOTf$ (**1a**, 129 mg), 1-benzyl-1-phenylhydrazine hydrochloride (85 mg) and **PDI1** (3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 50:1→7:3) afforded **3l** as an off-white solid; yield: 57 mg (59%). Analytical data are consistent with the literature values.[14] $R_f$=0.68 (*n*-hexane/EtOAc 7:3); mp 118.7 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$=7.94–7.90 (m, 2H), 7.58–7.54 (m, 1H), 7.48–7.44 (m, 2H), 7.27–7.24 (m, 3H), 7.16–7.12 (m, 2H), 7.04–7.01 (m, 2H), 6.91–6.88 (m, 2H), 6.87–6.83 (m, 1H), 6.21 (s, 1H), 4.55 (s, 2H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$=148.8, 139.0, 134.4, 133.4, 129.2, 129.1, 129.0, 128.5, 128.2, 128.2, 121.2, 115.5, 58.2; MS (ESI): $m/z$=339.10, calcd. for $C_{19}H_{19}N_2O_2S_1$ $[M+H]^+$: 339.12.

***N′*,*N′*-Diphenylbenzenesulfonohydrazide (3m):** Prepared from $Ph_2IOTf$ (**1a**, 129 mg), 1,2-diphenylhydrazine hydrochloride (79 mg) and **PDI1** (3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 20:1→4:1) afforded **3m** as an off-white solid; yield: 57 mg (59%). Analytical data are consistent with the literature values.[14] $R_f$=0.3 (*n*-hexane/EtOAc 9:1); mp 159.8 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$=7.79–7.75 (m, 2H), 7.48–7.43 (m, 1H), 7.34–7.30 (m, 2H), 7.19–7.13 (m, 4H), 7.02–6.98 (m, 1H), 6.97–6.94 (m, 4H), 6.81 (s, 1H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$=146.9, 138.7, 133.2, 129.2, 128.9, 128.4, 124.2, 120.8; MS (ESI): $m/z$=325.10, calcd. for $C_{18}H_{17}N_2O_2S_1$ $[M+H]^+$: 325.10.

***N′*-Phenylbenzenesulfonohydrazide (3n):** Prepared from $Ph_2IOTf$ (**1a**, 129 mg), phenylhydrazine (35 µL, 39 mg) and **PDI1** (3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 20:1→7:3) afforded **3n** as an off-white solid; yield: 57 mg (59%). Analytical data are consistent with the literature values.[39] $R_f$=0.12 (*n*-hexane/EtOAc 9:1); mp =137.9 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$=7.92–7.86 (m, 2H), 7.57 (tt, $J$=7.5, 1.4 Hz, 1H), 7.46–7.44 (m, 2H), 7.12–7.07 (m, 2H), 6.85–6.77 (m, 1H), 6.74–6.66 (m, 2H), 6.26 (s, 1H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$=146.1, 138.1, 133.6, 129.2, 129.2, 128.3, 121.5, 113.6; MS (ESI): $m/z$=249.14, calcd. for $C_{12}H_{13}N_2O_2S_1$ $[M+H]^+$: 249.07; IR: $\nu$=3661 (w), 3328 (w), 3262 (m), 2981 (m), 2889 (w), 1603 (m), 1496 (m), 1445 (m), 1328 (s), 1312 (m), 1254 (m), 1178 (m), 1155 (s), 1087 (m), 1073 (m), 1023 (m), 998 (w), 887 (m), 754 (s), 729 (s), 686 (s), 617 (m), 563 (s), 498 $cm^{-1}$ (s).

***N*-Morpholino-3-(trifluoromethyl)benzenesulfonamide (3p):** Prepared from (4-methoxyphenyl)-(3-trifluoromethylphenyl)iodonium tosylate (**1d**, 165 mg), 4-aminomorpholine (**2a**, 35 µL, 37 mg) and **PDI1** (3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 20:1→7:3) afforded **3p** as an off-white solid; yield: 48 mg (52%). $R_f$=0.50 (*n*-hexane/EtOAc 1:1); mp 110.8 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$=8.27 (s, 1H), 8.17 (d, $J$=8.0 Hz, 1H), 7.88 (d, $J$=8.0 Hz, 1H), 7.69 (t, $J$=8.0 Hz, 1H), 5.52 (s, 1H), 3.62 (t, $J$=4.8 Hz, 4H), 2.64 (t, $J$=4.8 Hz, 4H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$=139.9, 131.8 (q, $J$=34.0 Hz), 131.3, 129.9 (q, $J$=3.1 Hz), 129.8, 125.5 (q, $J$=3.8 Hz), 122.2, 66.7, 57.0; $^{19}$F NMR (470.64 MHz, $CDCl_3$): $\delta$=−62.8; MS (ESI): $m/z$=309.02, calcd. for $C_{11}H_{12}F_3N_2O_3S_1$ $[M-H]^-$:309.05; HR-MS: $m/z$=311.06816, calcd. for $C_{11}H_{14}F_3N_2O_3S_1$ $[M+H]^+$: 311.06717; IR: $\nu$=3217 (m), 2981 (s), 2971 (s), 2925 (m), 2865 (w), 1607 (w), 1507 (w), 1461 (w), 1324 (m), 1309 (w), 1282 (m), 1264 (m), 1164 (s), 1112 (s), 1088 (s), 1067 (s), 1031 (w), 940 (w), 868 (m), 724 (s), 662 (s), 653 (s), 635 (s), 486 $cm^{-1}$ (s).

**2,4,6-Triisopropyl-*N*-morpholinobenzenesulfonamide (3r):** Prepared from triisopropylphenyliodonium triflate (**1g**, 167 mg), 4-aminomorpholine (**2a**, 35 µL, 37 mg) and **PDI1**

(3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 20:1→1:1) afforded **3p** as an off-white solid; yield: 14 mg (13%). $R_f$=0.04 (*n*-hexane/EtOAc 9:1); mp 139.9 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$=7.15 (s, 2H), 5.30 (s, 1H), 4.20 (hept, $J$=7.4 Hz, 2H), 3.63 (t, $J$=4.5 Hz, 4H), 2.90 (hept, $J$=7.0 Hz, 1H), 2.79–2.73 (m, 4H), 1.28 (d, $J$=6.5 Hz, 12H), 1.26 (d, $J$=7.0 Hz, 6H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$=153.3, 151.8, 131.5, 123.8, 66.9, 57.1, 34.3, 30.0, 25.1, 23.7; MS (ESI): $m/z$=369.18, calcd. for $C_{19}H_{33}N_2O_3S_1$ $[M+H]^+$: 369.22; HR-MS: $m/z$=369.22068, calcd. for $C_{19}H_{33}N_2O_3S_1$ $[M+H]^+$: 369.22064; IR: $\nu$=3660 (w), 3132 (w), 2971 (s), 2981 (s), 2893 (m), 1600 (w), 1457 (m), 1425 (w), 1383 (m), 1323 (m), 1268 (m), 1193 (w), 1164 (s), 1155 (s), 1105 (s), 941 (m), 906 (w), 881 (m), 811 (s), 759 (w), 659 (s) 650 (m), 584 (m), 563 (s), 527 cm$^{-1}$ (m).

**2,4-Dimethoxy-*N*-morpholinobenzenesulfonamide (3s):** Prepared from (2,4-dimethoxyphenyl)phenyliodonium triflate (**1i**, 147 mg), 4-aminomorpholine (**2a**, 35 µL, 37 mg) and **PDI1** (3 mg, 2 mol%) according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 50:1→1:1) afforded **3s** as an off-white solid; yield: 14 mg (13%). $R_f$=0.1 (-*h*exane/EtOAc 1:1); mp 141.3 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$=7.92 (d, $J$=8.5 Hz, 1H), 6.58 (dd, $J$=8.8, 2.3 Hz, 1H), 6.51 (d, $J$=2.5 Hz, 1H), 5.82 (s, 1H), 3.95 (s, 3H), 3.87 (s, $J$=4.5 Hz, 3H), 3.58 (t, $J$=4.5 Hz, 3H), 2.67 (t, $J$=4.8 Hz, 3H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$=165.3, 157.8, 133.7, 119.2, 104.7, 99.7, 66.7, 56.7, 56.5, 55.9; MS (ESI): $m/z$=303.15, calcd. for $C_{12}H_{19}N_2O_5S_1$ $[M+H]^+$: 303.10; HR-MS: $m/z$=341.05746, calcd. for $C_{12}H_{18}N_2O_3S_1K_1$ $[M+K]^+$: 341.05680; IR: $\nu$=2955 (w), 2920 (s), 2851 (m), 1595 (w), 1578 (w), 1457 (m), 1314 (w), 1289 (w), 1261 (w), 1211 (s), 1159 (s), 1094 (m), 1075 (s), 1015 (s), 921 (w), 866 (w), 837 (w), 810 (w), 732 (w), 682 (m), 643 (w), 558 (s), 519 (m), 503 (m), 464 cm$^{-1}$ (w).

***N'*-*Allyl*-*N'*-phenylbenzenesulfonohydrazide (3u):** Prepared from $Ph_2IOTf$ (**1a**, 129.05 mg), DABCO·$(SO_2)_2$ (43 mg), *N*-(2-allylphenyl)hydrazine (**2c**, 53.35 mg) and **PDI2** (4.27 mg, 2 mol%) in 2 mL MeCN-$d_3$ according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 50:1→7:3) afforded **3u** as an off-white oil; yield: 17 mg (20%). $R_f$=0.1 (*n*-hexane/EtOAc 4:1); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$=7.95 (d, $J$=8.0 Hz, 2H), 7.58 (t, $J$=7.5 Hz, 1H), 7.49 (t, $J$=7.8 Hz, 2H), 7.15 (t, $J$=7.8 Hz, 2H), 6.89 (d, $J$=8.5 Hz, 2H), 6.84 (t, $J$=7.3 Hz, 1H), 6.35 (s, 1H), 5.65 (ddt, $J$=16.8, 10.5, 6.3 Hz, 1H), 5.27 (d, $J$=10.0 Hz, 1H), 5.15 (d, $J$=17.0 Hz, 1H), 3.90 (br s, 2H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$=148.4, 138.8, 133.5, 129.9, 129.2, 129.1, 128.3, 121.3, 121.3, 115.3, 56.7; MS (ESI): $m/z$=289.12, calcd. for $C_{15}H_{17}N_2O_2S_1$ $[M+H]^+$: 289.10; HR-MS: $m/z$= 289.10075, calcd. for $C_{15}H_{17}N_2O_2S_1$ $[M+H]^+$: 289.10053; IR: $\nu$=3234 (w), 3064 (w), 1643 (w), 1598 (m), 1497 (m), 1448 (m), 1419 (w), 1328 (s), 1309 (m), 1216 (w), 1156 (s), 1091 (s), 1072 (w), 1036 (w), 1024 (w), 990 (m), 924 (m), 879 (m), 749 (s), 718 (s), 686 (s), 583 (s), 543 (s), 479 (m), 463 cm$^{-1}$ (m).

***N'*-(2-Allylphenyl)benzenesulfonohydrazide (3v):** Prepared from $Ph_2IOTf$ (**1a**, 129.05 mg), DABCO·$(SO_2)_2$ (43 mg), *N*-allyl-*N*-phenylhydrazine (**2d**, 53.35 mg) and **PDI2** (4.27 mg, 2 mol%) in 2 mL MeCN-$d_3$ according to the typical procedure. Purification by column chromatography (*n*-hexane/EtOAc 50:1→7:3) afforded **3v** as an off-white oil; yield: 20 mg (23%). $R_f$=0.46 (*n*-hexane/EtOAc 7:3); $^1$H NMR (250.13 MHz, $CD_3CN$): $\delta$=7.95–7.81 (m, 2H), 7.72–7.65 (m, 1H), 7.64–7.52 (m, 2H), 7.31 (s, 1H), 7.15–6.97 (m, 3H), 6.83–6.75 (m, 1H), 5.92–5.75 (m, 2H), 4.98 (dq, $J$=10.0, 1.5 Hz, 1H), 4.86 (dq, $J$=17.3, 1.8 Hz, 1H), 3.20–3.14 (m, 2H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$=144.2, 138.0, 135.7, 133.6, 130.2, 129.2, 128.3, 127.6, 123.6, 121.2, 116.8, 36.3; MS (ESI): $m/z$=311.11, calcd. for $C_{15}H_{16}N_2NaO_2S_1$ $[M+Na]^+$: 311.08; HR-MS: $m/z$=271.10062, calcd. for $C_{15}H_{17}N_2O_2S_1$ $[M+H]^+$: 271.10053; IR: $\nu$=3246 (w), 2922 (w), 1603 (w), 1588 (w), 1521 (w), 1476 (w), 1458 (m), 1447 (m), 1328 (m), 1293 (w), 1261 (w), 1159 (s), 1124 (m), 1091 (m), 1071 (w), 1016 (w), 997 (w), 907 (w), 744 (s), 722 (s), 683 (s), 611 (m), 583 (s), 546 (s), 463 cm$^{-1}$ (s).

**1-(2,3-Dihydrobenzofuran-3-yl)-*N*-morpholinomethanesulfonamide (3w):** Prepared from (2-allyloxylphenyl)(Mes)$IPF_6$ (**1l**, 157.27 mg), DABCO·$(SO_2)_2$ (43 mg), 4-aminomorpholine (**2a**, 34.69 µL, 36.77 mg) **PDI2** (4.27 mg, 2 mol%) in 2 mL MeCN-$d_3$ according to the typical procedure. After 2 h of irradiation 0.1 mL of the reaction mixture was diluted with 0.4 mL of MeCN-$d_3$ for the crude $^1$H NMR. Purification by column chromatography (*n*-hexane/EtOAc 50:1→1:1) afforded **3w** as an off-white solid; yield: 58 mg (68%). Analytical data are consistent with the literature values.[14] $R_f$=0.1 (*n*-hexane/EtOAc 7:3); mp 145.0 °C (decomp., DCM); $^1$H NMR (500.18 MHz, $CDCl_3$): $\delta$=7.21–7.17 (m, 2H), 6.91 (t, $J$=7.5 Hz, 1H), 6.84 (d, $J$=8.5 Hz, 1H), 5.23 (s, 1H), 4.75 (t, $J$=9.3 Hz, 1H), 4.61 (dd, $J$=9.5, 6.0 Hz, 1H), 4.08–3.99 (m, 1H), 3.77 (t, $J$=5.0 Hz, 4H), 3.60 (dd, $J$=14.3, 3.3 Hz, 1H), 3.34 (dd, $J$=14.5, 10.8 Hz, 1H), 2.96–2.83 (m, 4H); $^{13}$C NMR (125.77 MHz, $CDCl_3$): $\delta$=159.9, 129.6, 127.1, 124.3, 121.1, 110.3, 76.1, 66.7, 57.7, 54.4, 37.6; MS (ESI): $m/z$=299.08, calcd. for $C_{13}H_{19}N_2O_4S_1$ $[M+H]^+$: 299.11.

Additional experimental details and data can be found in the Supporting Information along with copies of NMR spectra and UV-vis spectra.

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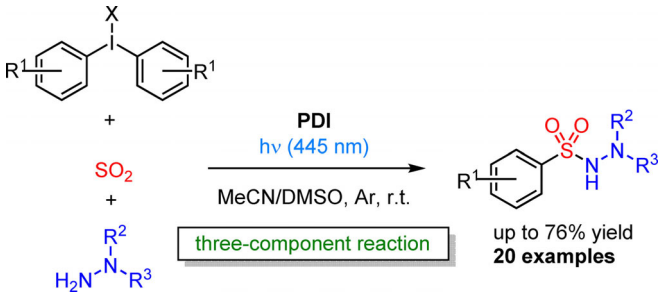


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