# Visible-Light-Induced Insertion of Sulfur Dioxide Mediated by Electron Donor–Acceptor Complex: Synthesis and Photophysical Properties of 3-Sulfonyl Indolizines

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This work investigates a light-driven 3-component sulfonylation reaction of indolizines without needing any external photocatalyst. The mechanistic investigations support the formation of an electron donor–acceptor (EDA) complex in situ. This transformation offers a mild and sustainable approach with high functional group tolerance for the synthesis of 3-sulfonylated indolizines. This compound class has valuable photophysical properties and represents promising candidates in various applications related to fluorescence.

## Introduction

First reported in 1890, pyrrolo[1,2-*a*]pyridine, better known as indolizine, is one of the five constitutive isomers of indole. It contains two condensed rings (5-membered and 6-membered rings) with a bridging nitrogen atom.[1] Many indolizine-based derivatives display a wide range of biological activities linked to fields that study cancer, HIV, viral, and inflammatory diseases.[2] Thanks to their 10 π-electron aromatic character, indolizines have recently attracted attention in fluorescence-related applications, including OLEDs, pH probes, and fluorescent bioprobes.[3] The most prominent example is the Seoul-Fluor, an indolizine-based fluorophore developed by Park et al. in 2011.[4] Interestingly, in 2020, Hosoya et al. described a 2-methoxyindolizine as an efficient photocleavable protecting group under red-light through a photooxidation process using a photosensitizer and singlet oxygen.[5] Such applications highlight the need to further explore the diversity of substituents that can be introduced on the different positions of the indolizine core.

A previously unexplored approach to analysing indolizine derivatives involves the use of sulfone groups, which are compelling groups with a strong electron-withdrawing character, H-bonding ability, and versatile chemical reactivity.[6] These qualities make the sulfone moiety a crucial group in a number of marketed pharmaceuticals and agrochemicals.[7] Sulfone-containing materials also display unique photophysical properties for OLED applications.[8] Introducing the sulfone moiety onto the indolizine ring offers an attractive approach for developing new indolizine derivatives with improved photophysical performance for various fluorescence-related applications.

The most common methods to prepare sulfonyl compounds rely on the transformations of sulfur-containing partners, including sulfides/sulfoxides, sulfonyl halides, and sulfonate salts. They are often tricky to prepare, have limited availability, and are associated with harsh reaction conditions or functional group incompatibilities.[9] In the last ten years, two significant advancements have been made in preparing sulfonyl compounds. The first involves a one-pot and multi-component approach involving two pre-activated sulfur-free partners and a $SO_2$ surrogate for directly introducing the sulfone moiety.[10] The second relies on the sustainable and environmentally-friendly visible-light photoredox catalysis that allows sulfonylation reactions.[11] The functionalization of the indolizine core, especially the more reactive C-3 position, has been the focus of intensive work with recent interest in photoredox catalysis. A small number of studies have presented examples related to visible-light-induced C—C or C—S bond formations.[12] However, the corresponding sulfonylation to synthesize sulfonyl indolizines remains to be discovered. The group of Oh described the only example of sulfonylation of indolizines in 2021 (Scheme 1a) and developed an electrochemical radical-radical cross-coupling

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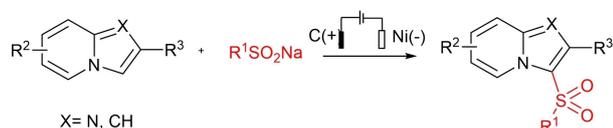91400, Orsay (France)
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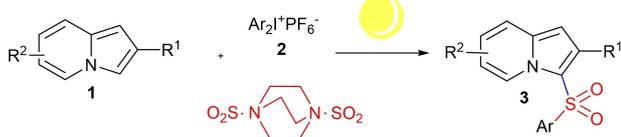Université Paris-Saclay
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**Scheme 1.** Strategies for C-3 sulfonylation of indolizines.



**Table 1.** Optimization of the sulfonylation reaction conditions of indolizines.

| Entry | Photocatalyst [5 mol %] | Solvent | Light | Time | Yield of 3a [a,b] |
|---|---|---|---|---|---|
| 1 | EosinY.Na$_2$ | DMSO | LED | 15 h | 25 %[c], [d] |
| 2 | EosinY.Na$_2$ | CH$_3$CN | LED | 48 h | NR[d] |
| 3 | EosinY.Na$_2$ | CH$_2$Cl$_2$ | LED | 90 h | NR[d] |
| 4 | fac((Ir(ppy))$_3$ | DMSO | LED | 15 h | 18 %[d] |
| 5 | fac((Ir(ppy))$_3$ | CH$_3$CN | 2*40 W | 15 h | 32 %[d] |
| 6 | fac((Ir(ppy))$_3$[e] | CH$_3$CN | 2*40 W | 15 h | 44 % |
| 7 | fac((Ir(ppy))$_3$[e] | CH$_3$CN | 2*10 W | 15 h | 50 % |
| 8 | – | CH$_3$CN | 2*10 W | 1 h | 52 % |
| 9 | – | CH$_2$Cl$_2$ | 2*10 W | 1 h | 46 % |
| 10 | – | AcOEt | 2*10 W | 1 h | 12 % |
| 11 | – | DMSO | 2*10 W | 1 h | 17 % |
| 12 | – | MeOH | 2*10 W | 1 h | NR |
| 13 | – | DMSO | 2*10 W | 15 h | 54 % |
| 14 | – | DMSO | 2*10 W | 15 h | 56 %[f] |
| 15 | – | DMSO | Sunlight | 15 h | 6 % |

[a] unless otherwise noted, reaction conditions are: 2-phenylindolizine **1a** (0.26 mmol), **2a** (1.5 eq), DABCO·(SO$_2$)$_2$ (2.0 eq), DMSO [0.1 M] at rt for indicated time, irradiation with indicated light, under argon. [b] Determined by $^1$H NMR based on **1a** using 1,3,5-trimethoxybenzene as internal standard. [c] Isolated yield based on **1a**. [d] reaction was performed at [0.04 M]. [e] 2 mol %. [f] **2a** (1.1 eq), DABCO·(SO$_2$)$_2$ (1.5 eq). NR = no reaction.

to access sulfonylated imidazopyridines and indolizines using sodium sulfonates as coupling partners.[13]

This article is a continuation of our research on C–H bond functionalization of nitrogen-containing heterocycles. It presents a straightforward protocol for the C–H bond sulfonylation of indolizines using (DABCO·(SO$_2$)$_2$) as a sulfur source under visible-light irradiation without the need of any catalyst. Our research also explores the photophysical properties of the new indolizine derivatives (Scheme 1b).

## Results and Discussion

We began our study by using the conditions previously developed in our group for the direct C–H bond sulfonylation of imidazoheterocycles.[14] We first initiated our reaction by mixing 2-phenylindolizine **1a** and diphenyl iodonium hexafluorophosphate **2a** as a coupling partner with 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (DABCO·(SO$_2$)$_2$ or DABSO) as a sulfur source in the presence of 5 mol% of the organic dye EosinY.Na$_2$ in DMSO upon green light irradiation. This reaction afforded the expected C-3 sulfonylated indolizine **3a** in a 25% yield along with unreacted starting material even after prolonged reaction time (up to 48 h, Table 1, entry 1). Other solvents, such as acetonitrile or dichloromethane, resulted in no conversion (Table 1, entries 2–3).

The use of metal complex photocatalyst such as fac((Ir(ppy))$_3$ (5 mol%) was able to catalyze the sulfonylation reaction under blue light irradiation but with uncomplete conversion, and the compound **3a** was isolated in an 18% yield after 15 h reaction time (entry 4). Switching from DMSO to acetonitrile led to an improvement of yield to 32% (entry 5). By decreasing the quantity of the catalyst while increasing the concentration of the reaction mixture, 3-sulfonylindolizine **3a** yield was increased up to 44% with complete conversion of the starting material **1a** (entry 6). Finally, the decrease of the lamp power (from 2*40 W to 2*10 W) allowed the formation of **3a** in 50% yield (entry 7). Surprisingly, a comparable yield of **3a** (52% vs. 50%) was obtained without any photoredox catalyst (entry 8). In

addition, the reaction time can be decreased from 15 h to one hour. Manolikakes et al. reported in 2018 the first examples of a radical-based incorporation of sulfur dioxide with diaryliodonium salts using visible-light as the sole energy source.[15] These conditions were efficiently applied for a 3-component synthesis of sulfonylated coumarins and later for the 3-sulfonylated oxindoles.[16] We also performed control experiments to verify the necessity of light for our reaction; we found that no product **3a** was formed without irradiation or in the dark. While a comparable yield of **3a** was obtained in dichloromethane (46%), the reaction in other solvents, such as AcOEt, and DMSO afforded the product in lower yields, 12% and 17%, respectively (entries 9–11). No conversion was observed in methanol (entry 12). During this optimization process, we found that the reaction mixture in DMSO was less sluggish, the crude was cleaner, and the purification step was more straightforward. Next, running the reaction in DMSO for a prolonged time (15 h) led to the expected compound **3a** with a 54% yield with a complete conversion of **1a** (entry 13). Decreasing the quantity of diphenyliodonium salt **2a** and DABCO·(SO$_2$)$_2$ to 1.1 equiv. and 1.5 eq, respectively led to a comparable yield of **3a** (56%, entry 14). Finally, exposure to sunlight for 15 h, compound **3a** was obtained in only 6% yield (entry 15).

Thus, the optimum conditions for this direct sulfonylation process were shown to be: 2-phenylindolizine **1a** (1 equiv.), diphenyliodonium salt **2a** (1.1 equiv.), and DABCO·(SO$_2$)$_2$

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(1.5 equiv.) in 0.1 M DMSO at room temperature for 15 h under blue light irradiation.

Using this optimized protocol, the reaction scope was explored with substituted indolizines **1** displaying various electronic properties. As shown in Scheme 2, the reaction conditions are compatible with a wide range of functionality, including electron-withdrawing (F, CN, and CF$_3$) and electron-donating (OCH$_3$ and N(CH$_3$)$_2$) groups located at the *ortho*-, *meta*-, or *para*-position of the C-2 phenyl ring. The corresponding sulfonylated indolizines **3a–h** were isolated in fair yields up to 65%. However, the yield dropped to 38% for compound **3h** with the dimethylamino substituent. The reaction was also scalable since the sulfonylated indolizine **3a** was obtained in 47% yield on a 1 mmol scale. In addition to a phenyl substituent on the C-2 position, 2-styrylindolizine and 2-thiophenylindolizine also proved to be reactive, providing the sulfonylated compounds **3i** and **3j** in 63% and 67% yield, respectively. Next, the reaction was shown to be sensitive to the nature and the position of the substituents on the pyridine moiety of the indolizine. Indeed, indolizine bearing a methoxy group at the C-7 position reacted smoothly with diphenyliodonium salt **2a** to yield the corresponding sulfonylated indolizine **3k** in 42% yield. The presence of a cyano group at the C-6 position was deleterious to the reaction outcome providing compound **3l** with 21% yield, along with unreacted starting material (~40% yield). Conversely, a methyl group on the C-8 position of the indolizine was well tolerated since sulfone **3m** was isolated in 65% yield.

An important goal of this work involves developing new indolizine derivatives with improved photophysical performance. To this end, we focused our efforts on combining substituents with opposite electronic properties rather than
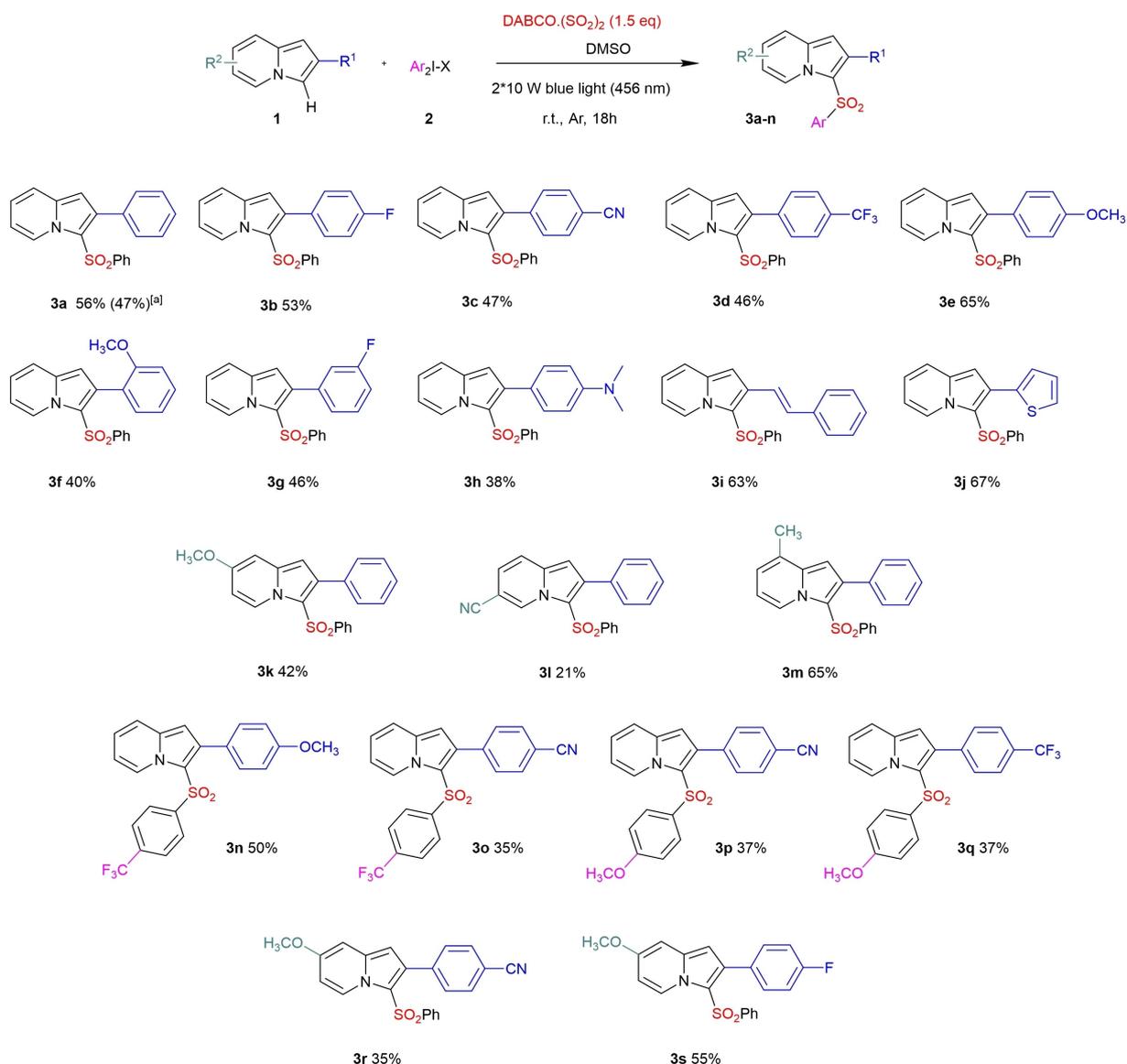


**Scheme 2.** Reaction scope regarding the diaryliodonium salts and/or the indolizines. Isolated yields obtained after purification see the experimental part. [a] Reaction run on a 1 mmol scale.

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preparing extensive numbers of substrates. It is well known that fluorescent properties can be enhanced using push-pull structures whose skeleton is composed of a conjugated π-electron system substituted by both an electron-withdrawing and an electron-donating groups.

We then chose to synthesize various push-pull sulfonylated indolizines. For this purpose, we used diaryliodonium hexafluorophosphate salts bearing either a trifluoro or a methoxy group in the *para*-position to react with indolizines bearing either a 4-methoxyphenyl, 4-cyanophenyl or 4-trifluoromethylphenyl on the C-2 position, which delivered the corresponding push-pull indolizines **3n**, **3p**, and **3q** in yield ranging from 37% to 50% yield. Although the yields are not very high, it is important to note that two C−S bonds are formed in one pot ($\approx$60–70 yield for each bond) using a mild, easy, and solely visible-light-driven process. Compound **3o** bearing two electron-withdrawing groups was also prepared with a comparable yield of 35%. The C-3 regioselectivity of the products was unambiguously confirmed by obtaining an X-ray crystal structure of the sulfonylated indolizine **3o** (Figure 1).[17]

Two more push-pull indolizines, **3r** and **3s**, possessing a methoxy group at the C-7 position and an electron-withdrawing group such as cyano and a fluorine atom at the C-2 position were prepared in 35% and 55% yield, respectively.

We first conducted some control experiments to gain insight into the reaction mechanism. The radical scavengers 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) were added separately in the standard conditions with indolizine **1a** and diphenyl iodonium hexafluorophosphate **2a**. No trace of **3a** was observed in the case of TEMPO, while a 30% yield of **3a** was obtained with BHT (Scheme S1 in the Supporting Information). Even though the reaction was not completely suppressed, all the results indicated a possible radical pathway. We also tried to characterize a possible electron-donor-acceptor (EDA) complex.[18] First, we recorded the UV-vis absorption spectra of the three reaction components: indolizine **1a**, diphenyliodonium hexafluorophosphate salt **2a**, and DABSO (Figure 2 up). A subsequent combination of a 1:1 mixture of **1a**+**2a** in DMSO did not show any change in the spectral region. However, when **1a** and DABSO were mixed, a slight increase in absorbance was observed (Figure 2 up), along with the appearance of the yellow colour of the mixture. More importantly, a clear and new absorption band was obtained upon adding of diphenyliodonium hexafluorophosphate salt **2a**, suggesting the
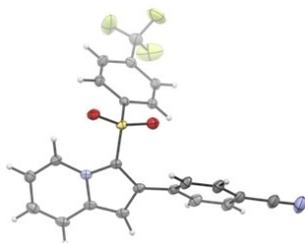


**Figure 2.** Up: UV-vis absoprtion spectra of **1a**, **2a**, DABSO, **1a**+**2a**, **1a**+DABSO, and **1a**+**2a**+DABSO in DMSO [0.05 M]. Down: photos of the reaction components and mixtures.

formation of a ternary EDA complex. This hypothesis was also seen by a drastic change in colour, going from colourless for all three reagents respectively to orange colour when mixed together. Unfortunately, ^{1}H NMR studies of the mixture **1a**, **2a**, and DABSO remained unchanged (Figure 2 down). However, data from previous studies allows us to propose a plausible mechanism involving an EDA ternary complex (Scheme 3).[19]

The reaction starts with the association of DABSO, diphenyliodonium hexafluorophosphate **2a**, and indolizine **1a** to form the charge-transfer complex. Upon irradiation, photoexcitation of the EDA complex triggers a single electron transfer (SET) to give the phenyl radical, $SO_2$, and the indolizine radical cation. The phenyl



**Figure 1.** Ortep diagram of **3o** with thermal ellipsoids drawn at the 50% probability level and hydrogen atoms with radius of arbitrary. Disorder of $CF_3$ group is not shown for clarity.
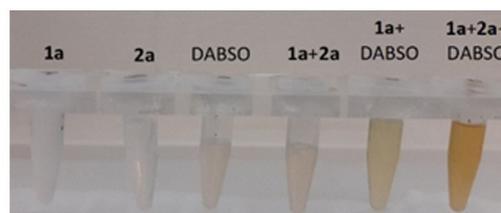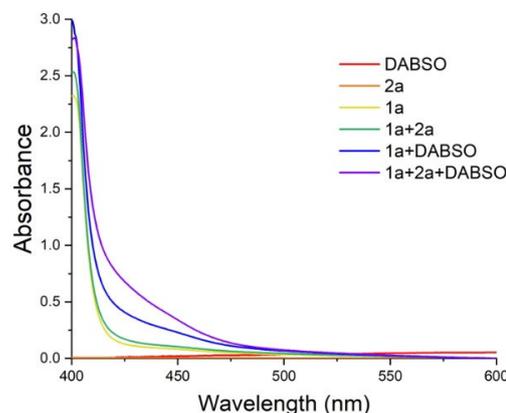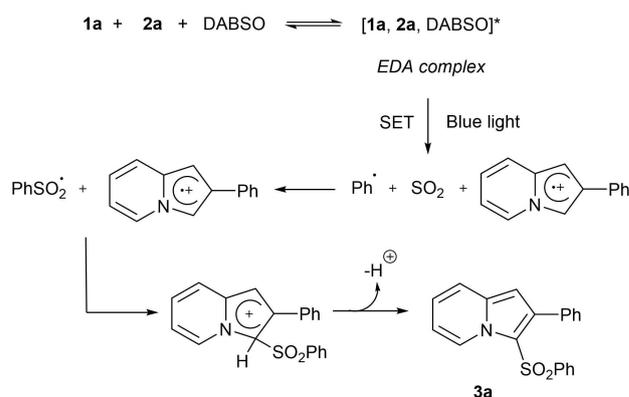


**Scheme 3.** Plausible mechanism for the photo-induced sulfonylation reaction of indolizines.

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radical is then rapidly trapped by sulfur dioxide. The resulting sulfonyl radical reacts regioselectively with the indolizine radical cation to afford the carbocation. Finally, re-aromatization occurs through proton loss resulting in the expected sulfonylated indolizine **3a**.

Table 2 summarizes the photophysical properties of the 14 sulfonylated indolizines **3a–e**, **3h–i**, **3k**, and **3n–s** in DMSO, highlighting the structure-properties' relationships (see also figure S7).

All the C-3 sulfonylated indolizines have a strong absorption band around 330–350 nm except **3h** and **3i** with $\lambda_{Abs} = 298$ nm and 306 nm, respectively. All compounds are fluorescent in DMSO with fluorescence quantum yields ranging from 0.8% to 58.2%. As expected, conjugation by a styryl group at the C-2 position gave the highest fluorescence quantum yield ($\phi_f = 58.2\%$ for **3i**). Indolizines **3c**, **3p**, **3q**, **3r** bearing at least one electron-withdrawing group at the para-position of the C-2 aryl and a methoxy group branched either on the aryl sulfonyl moiety or directly on the indolizine core at the C-7 position gave good fluorescence quantum yield ranging from 16.0% to 24.3%. Conversely, the inversion of the donor and acceptor groups on compound **3q** leads to the poorly fluorescent push-pull compound **3n**. Similarly, compound **3o** bearing an electron-withdrawing group on the

arylsulfonyl moiety showed a dramatic decrease in the fluorescence quantum yield ($\phi_f = 1.3\%$) compared to **3c** ($\phi_f = 23\%$). Most of the substituted indolizines emit in the blue window (450 to 485 nm), except compounds **3h**, **3n** and **3o** which are green emitters. Compounds **3h**, **3n**, and **3o** display also large Stokes shifts, up to 229 nm for the indolizine **3h** bearing a 4-dimethylaminophenyl at the C-2 position. A fluorosolvatochromic study has also been carried out on compounds having the highest Stokes shifts, including **3h**, **3i**, **3n**, **3o**, **3r**. No significant differences in the maximum emission wavelength were observed in various solvents of different polarity (Chloroform, DCM, DMF, EtOH, and Toluene, see Figure S8). In contrast, we observed a hypsochromic shift of the emission of compound **3h** after addition of TFA (Figure 3). Indeed, by reducing the donor character of the dimethylamino group; the protonation leads to the decrease of the push-pull character of indolizine **3h**.

The fluorescence lifetime ($\tau_f$) determinations of all compounds **3a–e**, **3h–i**, **3k**, and **3n–s**, were carried out, employing fluorescence resolved in time technique.[20] Compounds **3c**, **3i**, **3p**, **3q** and **3r** have the largest $\tau_f$. They also present the largest $\phi_f$. The $\tau_f$ values for these molecules range from 1.2 ns to 2.0 ns. Among them, **3p**, **3q** and **3r** are push-pull indolizines. However, the other compounds (i.e. **3a**, **3b**, **3d**, **3e**, **3k**, **3h**, **3n**, **3o** and **3s**) exhibited $\tau_f$ shorter than our experimental setup resolution, which allows us to determine $\tau_f$ longer than 0.6 ns.

The significative $\tau_f$ differences may be understood in view of radiative and nonradiative decay rates from excited states to the ground states.[21] These decay rates are influenced by the addition of electron-donating and electron-withdrawing groups, which impact the $\tau_f$.

**Table 2.** Photophysical properties of C-3 sulfonylated indolizines 3a–e, 3h–i, 3k, 3n–s measured in DMSO at [10-4 M] for the absorption and [10-6 M] for the fluorescence measurements.

| Compound | $\lambda_{Abs}$ (nm) | $\lambda_{em}$ (nm) | Stokes shift (nm) | $\phi_f$ (%) | $\tau_f$ (ns) |
|---|---|---|---|---|---|
| **3a** | 335 | 454 | 119 | 2.1 | <0.6 |
| **3b** | 336 | 456 | 120 | 2.0 | <0.6 |
| **3c** | 335 | 463 | 128 | 23.0 | $1.2 \pm 0.1$ |
| **3d** | 336 | 450 | 114 | 4.4 | <0.6 |
| **3e** | 334 | 452 | 118 | 2.5 | <0.6 |
| **3h** | 298 | 527 | 229 | 2.8 | <0.6 |
| **3i** | 306 | 458 | 152 | 58.2 | $2.7 \pm 0.3$ |
| **3k** | 341 | 473 | 132 | 1.2 | <0.6 |
| **3n** | 345 | 518 | 173 | 0.8 | <0.6 |
| **3o** | 347 | 521 | 174 | 1.3 | <0.6 |
| **3p** | 333 | 469 | 136 | 24.3 | $1.8 \pm 0.1$ |
| **3q** | 332 | 459 | 127 | 19.1 | $1.2 \pm 0.1$ |
| **3r** | 339 | 485 | 146 | 16.0 | $2.0 \pm 0.2$ |
| **3s** | 341 | 482 | 141 | 1.0 | <0.6 |

## Conclusions

This paper establishes a simple and convergent approach for accessing relevant fluorescent 3-sulfonylated indolizines from diaryliodonium salts and DABCO·(SO$_2$)$_2$ as a sulfonyl surrogate upon blue-light irradiation only, without the need of any photo-catalyst. This three-component sulfonylation reaction relies on the formation of a ternary electron donor-acceptor complex. This photo-induced process occurs smoothly at room temperature and shows a wide functional group tolerance. It allows the formation of a library of indolizines with distinct photophysical properties. Thus, the identification of the highly fluorescent compound **3i** demonstrates the promising potential of sulfonylated indolizines bearing a styryl group in the C-2 position as efficient fluorophores. Similarly, sulfonylated indolizines could lead to efficient fluorescent pH probes as demonstrated by the hypsochromic shift observed upon addition of TFA to compound **3h** bearing a dimethylamino group. The photophysical studies of these sulfonylated indolizines give structure-properties information that paves the way for the future design of new indolizine derivatives with even better photophysical performance.
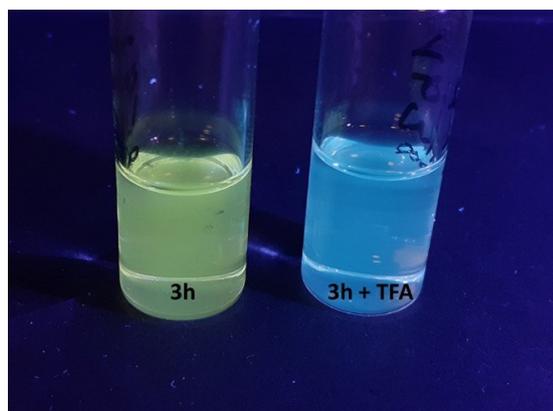


**Figure 3.** Colour changes of DMF solution of **3h** [65 μM] under irradiation at 370 nm and **3h** + 100 eq TFA.

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## Experimental Section

**General procedure for synthesis of 3-arylsulfonyl indolizines 3.**

To a tube under argon atmosphere were added 2-phenylindolizine **1** (0.26 mmol, 50 mg), diphenyliodonium hexafluorophosphate **2** (1.1 eq., 0.28 mmol, 121 mg), and DABCO·$(SO_2)_2$ (1.5 eq., 0.39 mmol, 93 mg) in anhydrous DMSO (2.6 mL). The reaction mixture was purged with argon. The tube was sealed, and the reaction mixture was stirred under blue light (2*10 W) at room temperature for 18 h. The mixture was extracted with AcOEt and washed with brine. The organic layer was dried with anhydrous $MgSO_4$ and the solvent evaporated under reduced pressure. The crude was purified by column chromatography with a gradient of cyclohexane to cyclohexane/EtOAc 30% to afford the sulfonylated product **3a** in 56% yield.

**2-Phenyl-3-(phenylsulfonyl)indolizine (3 a)**: greenish solid (48 mg, 56%), mp 103–104 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 9.13 (d, $J = 7.0$ Hz, 1H), 7.59 (d, $J = 7.5$ Hz, 2H), 7.50–7.40 (m, 7H), 7.35 - 7.30 (m, 2H), 7.05 (t, $J = 7.5$ Hz, 1H), 6.81 (td, $J = 7.0$ Hz, 1.0 Hz, 1H), 6.50 (s, 1H) ; $^{13}$C NMR (75 MHz, CDCl$_3$) δ 142.8 (Cq), 138.3 (Cq), 136.6 (Cq), 134.3 (Cq), 132.7 (CH), 130.6 (CH), 128.9 (CH), 128.0 (CH), 127.6 (CH), 126.2 (CH), 126.1 (CH), 122.8 (CH), 119.0 (CH), 114.8 (Cq), 113.2 (CH), 104.5 (CH) ; MS (ES+): $m/z$ (%) = 334.0 [M+H]$^+$; HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for $C_{20}H_{16}NO_2S^+$ 334.0896, found 334.0900. The characterization data are in agreement with the literature.[13]

## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

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

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[17] Deposition Number 2212137 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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