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Three-component C-H bond sulfonylation of imidazoheterocycles via visible-light organophotoredox catalysis.

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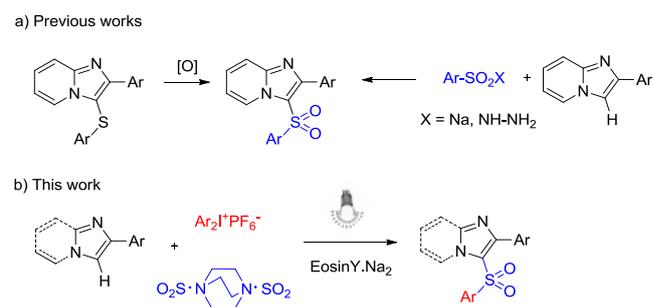
Abstract: The first entirely visible-light photoredox catalyzed sulfonylation of imidazoheterocycles has been developed. This transformation demonstrates an efficient C-H functionalization for the straightforward synthesis of novel C-3 sulfonylated imidazoheterocycles from various imidazopyridines and diaryliodonium salts with different electronic and steric properties and easy handled DABCO-bis(sulfur dioxide). The reaction proceeds in moderate to good yields under mild conditions at room temperature using the inexpensive organophotocatalyst EosinY and shows a high functional group tolerance (37 examples).

The sulfone moiety is a cornerstone of chemistry.^[1] Indeed, the widespread and modifiable chemical reactivity of sulfones has earned them the nickname “*Chemical Chameleons*”.^[2] Besides their renown as versatile intermediates in organic reactions, their physico-chemical and coordination properties also contribute to various applications in the field of pharmaceuticals,^[3] agrochemicals^[4] and materials^[5] thanks to sulfone-containing architectures. Considering this major double role, countless methods have been developed for the introduction of the sulfone moiety. Prevalent approaches such as oxidation, Friedel-Crafts type sulfonylation, radical additions of unsaturated compounds, and transition-metal catalyzed cross-couplings are all based on transformations of sulfur-containing partners including sulfides/sulfoxides, sulfonyl halides and sulfonate salts.^[6] More recently, a multicomponent reaction involving two pre-activated sulfur-free partners and SO₂ has emerged as an appealing route for the direct introduction of the sulfone moiety.^{[7],[8]} The importance of this approach relies on the development of bench-stable and easy handled SO₂ surrogates which circumvent the toxicity and the drawbacks associated with handling gaseous sulfur dioxide.^[9] In the omnipresent field of C-H bond functionalization, sulfonylation has also become a subject of significant work with achievements made using one sulfur partner often sulfonates or sulfonyl halides.^[10] In contrast, combining C-H bond sulfonylation and direct incorporation of SO₂ in a three-component approach still remains rare despite its advantage in terms of atom-economy and convergence.^[11]

In the past decade, sustainable and environmentally-friendly visible-light photoredox catalysis has been successfully applied to C-H bond functionalization including a few examples of sulfonylation.^[12] Indeed, Reiser *et al.* developed a photocatalytic sulfonylation of heteroarenes including pyrrole, indole and

thiophene using aryl sulfonyl chlorides as the sulfur-containing partner.^[13] Clearly, the use of abundant and renewable light sources, the availability and simplicity of reactions and the mild conditions involved are key advantages for this methodology over classical transition metal-catalyzed procedures. In addition, high functional group tolerance and the diversity of possible chemical reactions all promote visible-light photoredox catalysis as a powerful tool in organic synthesis.^[14]

Among the four imidazopyridine isomers, imidazo[1,2-*a*]pyridine is the most common through its wide variety of biological activities.^[15] This scaffold is a key element in a number of prominent marketed pharmaceuticals such as Zolpidem and Alpidem, used worldwide for the treatment of insomnia and associated sleeping disorders.^[16] Therefore, it is not surprising to note that C-H bond functionalization of the imidazo[1,2-*a*]pyridine core has been the focus of intensive work^[17] with recent interest in visible-light photoredox catalysis concentrating on the formation of C-C, C-O, C-N and C-S bonds.^[18] However, the corresponding sulfonylation reaction to synthesize sulfonyl imidazoheterocycles remains heretofore unknown.



Scheme 1. Main strategies for C-3 sulfonylation of imidazoheterocycles.

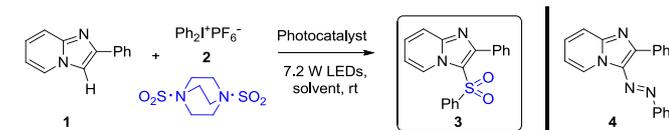
In general usage, the oxidation of 3-sulfonylimidazoheterocycles is the most common method to introduce the sulfone moiety (Scheme 1, eq a). However, the use of an oxidant and high temperatures can lead to functional group incompatibility and toxicity issues. In this context, in 2018, Zhu and Shao developed a more straightforward sulfonylation approach mediated by iodine and involving the use of aryl sodium sulfinates as the sulfone source at 100°C.^[19] Concurrently, Huang and Lei also

reported a metal-free procedure of C-H bond sulfonylation of heteroarenes, including a single example of 2-phenylimidazo[1,2-a]pyridine, with arylsulfonyl hydrazides under electrochemical oxidative conditions (Scheme 1, eq a).^[20] In this context, the sulfonylation of imidazoheterocycles remains largely unexplored despite the relevance of the sulfone moiety and these nitrogen-containing heterocycles.

Our efforts to enlarge straightforward but also green and sustainable approaches for the functionalization of heterocycles, prompted us to develop a multicomponent approach for the direct insertion of sulfur dioxide via C-H bond sulfonylation of imidazoheterocycles via organophotoredox catalysis (Scheme 1, eq b).

Initially, we screened various ruthenium and iridium polypyridyl complexes or organic dyes as photoredox catalysts and solvents, using 2-phenylimidazo[1,2-a]pyridine **1** and a phenyl diazonium salt as coupling partners in the presence of 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (DABCO·(SO₂)₂) as sulfur source, as popularized by Willis *et al.*, under light irradiation at room temperature (not shown).^[9a, 9b] In the best case scenario, only traces of the expected sulfonylated compound **3** was observed. Instead, the diazenylimidazo[1,2-a]pyridine **4** was isolated as the major product in an average yield of 70%. Indeed, this result was in total accordance with a recent study, which reports exclusively azoylation of imidazo[1,2-a]pyridine derivatives under free-photocatalyst conditions using aryl diazonium salt.^[21] Subsequently, we decided to switch from diazonium salts to diaryliodonium salts which are valuable coupling partners in photoredox-catalyzed three-component synthesis of aminosulfonamides as demonstrated by Manolikakes *et al.* and others.^[22] Diaryliodonium salts are air- and moisture-stable, easy-to-make compounds that have proved to be mild, and environmentally friendly. Thanks to these versatile properties, they are now used in various organic transformations including radical-based processes.^{[23],[24]}

Table 1. Optimization of the sulfonylation reaction conditions.



| Entry | Photocatalyst (5 mol%) | Solvent | Light | Yield 3 ^[a, b] |
|-------|--|--------------------|-------|----------------------------------|
| 1 | Fac(Ir(ppy) ₃) | CH ₃ CN | Blue | NR |
| 2 | Ru(bpy) ₃ (PF ₆) ₂ | CH ₃ CN | Blue | NR |
| 3 | EosinY.Na ₂ | CH ₃ CN | Green | NR |
| 4 | EosinY.Na ₂ | DMSO | Green | 55% (53%) ^[c] |
| 5 | Fluorescein | DMSO | Green | NR |
| 6 | Eosin B | DMSO | Green | NR |
| 7 | Rose Bengal | DMSO | Green | 45% |
| 8 | Rhodamine 6G | DMSO | Green | NR |
| 9 | EosinY.Na ₂ | DMSO | Blue | 50% |
| 10 | EosinY.Na ₂ (10 mol%) | DMSO | Green | 44% |

| | | | | |
|----|--|------|-------|-----|
| 11 | EosinY.Na ₂ (3 mol%) | DMSO | Green | 40% |
| 12 | EosinY.Na ₂ ^[d] | DMSO | Green | 45% |
| 13 | EosinY. Na ₂ ^[e] | DMSO | Green | 31% |

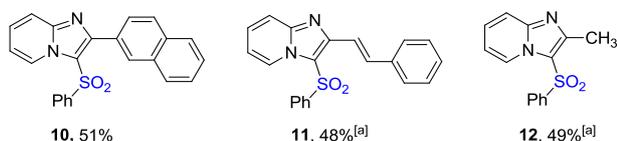
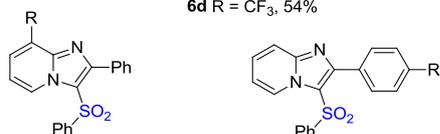
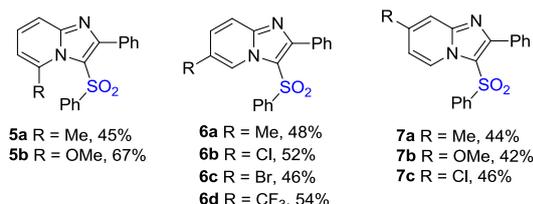
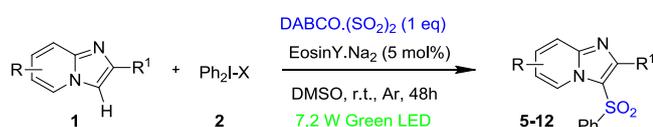
[a] Unless otherwise noted, reaction conditions are: 2-phenylimidazo[1,2-a]pyridine **1** (0.257 mmol), **2** (1.5 eq), DABCO·(SO₂)₂ (2 eq), photocatalyst (5 mol%), DMSO [0,08 M] at rt for 24 hours, irradiation with green LED (7.2 W), under argon. [b] Isolated yields. [c] 1 eq of DABCO·(SO₂)₂ was used for 48h. [d] diphenyliodonium triflate. [e] Sodium metabisulfite Na₂S₂O₅ was used as sulfur dioxide surrogate. NR = no reaction.

Our first attempts using diphenyl iodonium hexafluorophosphate **2** as coupling partner with DABCO·(SO₂)₂ as the sulfur dioxide surrogate in the presence of 5 mol% of iridium or ruthenium complexes in acetonitrile led to no discernable reaction even after prolonged reaction times (Table 1, entries 1-2). However, the use of organic photoredox catalyst EosinY.Na₂ in DMSO as solvent was the most effective combination with complete conversion of the starting material **1** and 55% yield of the desired C-3 sulfonylated imidazopyridine **3** within 24h (Table 1, entries 3-4). Following this preliminary result, control experiments were performed. No product **3** was formed upon irradiation with green light in the absence of photoredox catalyst. Similarly, reaction in the dark and in the presence of the organic dye EosinY.Na₂ gave also a negative result which confirmed the relevance of the combination of light and photocatalyst for a successful reaction outcome. It also appears that the reaction was sensitive to air leading to variable yields. Therefore, purging the reaction mixture with argon prior irradiation was required to reliably reproduce the desired sulfonylation process. Subsequent screening of xanthene-derivative photocatalysts including fluorescein, Eosin B, rhodamine 6G and rose bengal gave no improvement of yields with only 45% for the latter (entries 5-8). When turning the light source from green to blue LEDs, sulfone **3** was obtained in a slightly lower yield (50%, entry 9). The photocatalyst loading was also evaluated. With the goal of speeding up the reaction, the loading was raised to 10 mol% of EosinY.Na₂ but showed a lower catalytic activity furnishing **3** in 44% yield (entry 10). On reducing the photocatalyst loading to 3 mol%, an even lower yield of **3** was obtained (40%, entry 11). The nature of the iodonium salt counterion also had little effect on the reaction outcome as the corresponding triflate salt of **2** afforded sulfone **3** in 45% yield (entry 12). Inorganic sulfite salts are also well-developed sources for delivery sulfur dioxide.^[9c, 9d] When DABCO·(SO₂)₂ was replaced with sodium metabisulfite Na₂S₂O₅, the yield of the sulfonylation process dropped to 31% probably due to solubility issues (entry 13). Surprisingly, DMSO proved to be the only effective solvent as reaction in other polar solvents such as DMF, CH₃CN, MeOH, dioxane and in THF and CH₂Cl₂ resulted in no conversion.

Ultimately, the yield of the sulfonylation process could not be improved beyond 55% yield despite complete conversion of the starting material **1**. Indeed, along with the expected compound **3**, we were able to isolate varying amounts of two side-products (15-20% yield). The first was characterized as the C-3 bromination product of 2-phenylimidazo[1,2-a]pyridine **1**. Recently, Xia *et al.* showed that EosinY can serve as a bromine source in combination with Selectfluor. We conclude that the generation of DABCO upon releasing the sulfur dioxide could activate the cleavage of the C-Br bond of EosinY in a similar

way to Selectfluor.^[25] The second side-product arises from the C-3 formylation of the 2-phenylimidazo[1,2-*a*]pyridine using DMSO as the carbon source of the formyl moiety.^[26] In addition, the stability of the sulfone **3** was also studied. After 24h under green light irradiation in DMSO, 82% of **3** were recovered and only 60% when the sulfone **3** was placed under our reaction conditions.

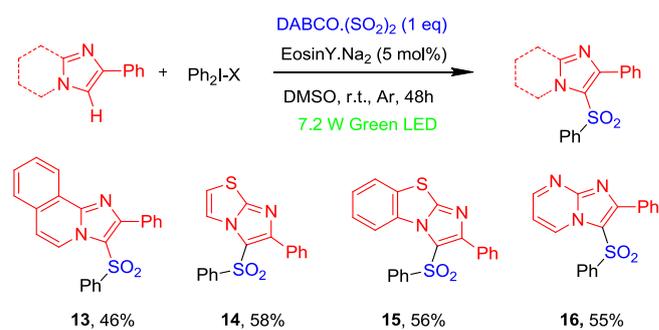
Finally, a comparable yield of **3** (53% versus 55%) was obtained with only 1 eq of DABCO•(SO₂)₂ after 48h reaction time (Table 1, entry 4). The reaction mixture was also less sluggish and the crude was cleaner. Thus, the optimum conditions for our three-component sulfonylation process with 2-phenylimidazo[1,2-*a*]pyridine **1** (1 eq), diphenyliodonium salt (1.5 eq) and DABCO•(SO₂)₂ (1 eq) were shown to be EosinY.Na₂ (5 mol%), in DMSO at room temperature for 48h under green light irradiation.



Scheme 2. Regioselective sulfonylation of various imidazo[1,2-*a*]pyridines under visible-light. [a] 72h reaction time.

Next, the reaction scope was explored with various substituted imidazo[1,2-*a*]pyridines **1** using this optimized protocol. As shown in scheme 2, it is clear that the reaction conditions are compatible with a wide range of functionality including electron-donating and electron-withdrawing groups. Overall, the nature and the position of the substituents on the pyridine moiety of the imidazo[1,2-*a*]pyridine showed minimal effects on the photoredox sulfonylation process furnishing the C-3 sulfonated compounds in moderate to good yields. Although full conversion of the starting material was observed in all cases as for 2-phenylimidazo[1,2-*a*]pyridine **1**, yields did not exceed at best 67% with an average of 50%. Bearing in mind that two C-S bonds are formed in one pot (~70% yield for each bond), this

mild and easy handling visible-light sulfonylation can be considered as a quite efficient and valuable process. Unexpectedly, substrates possessing 5-substituent groups were successfully sulfonylated selectively at the C-3 position delivering sulfones **5a** and **5b** in 45 and 67% yield respectively dismissing any potential steric issues. Halogens, such as fluorine, chlorine and bromine, survived the reaction conditions enabling further functionalization, as the corresponding sulfones **6b-c**, **7c**, **8c-e** and **9c-d** were delivered in yields ranging from 42 to 58% depending on the halogen position on the heterocycle. Similarly, electron-withdrawing-substituents such as trifluoro, nitro and cyano groups, whether on the heterocyclic platform or on the 2-phenyl ring, were also well tolerated providing the expected sulfones **6d**, **8f**, **8g**, **9f** and **9g** in moderate yields (42 to 55%). Finally, imidazo[1,2-*a*]pyridine bearing a naphthyl substituent on the C-2 position led to **10** in a yield of 51%. In addition to an aryl substituent on the C-2 position, 2-styrylimidazo[1,2-*a*]pyridine or 2-methylimidazo[1,2-*a*]pyridine also proved reactive, providing the sulfonylated compounds **11** and **12** in 48% and 49% yield respectively. By contrast, unsubstituted imidazo[1,2-*a*]pyridine was totally unreactive under the standard conditions (not shown).



Scheme 3. Scope of the photocatalyzed sulfonylation reaction with respect to imidazoheterocycles.

These new reaction conditions were also further applied to related imidazoheterocycles of importance in medicinal chemistry, to assess the scope of this visible light photoredox catalyzed sulfonylation (Scheme 3). Most were found to be suitable substrates giving full conversion of the starting material along with slightly higher yields as compared with 2-phenylimidazo[1,2-*a*]pyridine **1**. Indeed, 2-phenylimidazo[2,1-*a*]isoquinoline and 6-phenylimidazo[2,1-*b*]thiazole reacted smoothly to give sulfonated compounds **13** and **14** in 46 and 58% yields respectively. As expected, the benzo[*d*]imidazo[2,1-*b*]thiazole survived these conditions delivering the corresponding sulfone **15** in 56% yield. Remarkably, 2-phenylimidazo[1,2-*a*]pyrimidine was also regioselectively sulfonylated at the C-3 position in good yield (Scheme 3, **16**, 55%). By contrast, the 2-phenylimidazo[1,2-*a*]pyrazine was not reactive under these conditions (not shown).



Scheme 4. Scope using various diaryliodonium salts.

We also examined the reactivity of different symmetrical diaryliodonium salts in this photoredox sulfonylation process (Scheme 4). Various substituents in the *para*-position were well tolerated delivering the corresponding sulfonylated imidazo[1,2-*a*]pyridines **17a-e** in 40 to 51 % yield. Moreover, the diphenyliodonium counterion displays no significant influence on the outcome of the reaction, the isolated yields being in the same range of values.

To gain some insight into the reaction mechanism, a few control experiments were conducted on the model reaction (**1** to **3**). In addition to basic reactions proving the need of light and organic photoredox catalyst (cf *vide supra*), the radical scavengers 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) were separately added in the standard conditions with 2-phenylimidazo[1,2-*a*]pyridine **1** and diphenyl iodonium hexafluorophosphate **2**. In both cases, no trace of compound **3** was observed suggesting a radical reaction pathway. In addition, Stern-Volmer fluorescence quenching experiments with EosinY.Na₂ were performed (see supporting information for more details). While no change in emission was observed with imidazo[1,2-*a*]pyridine **1** or DABCO•(SO₂)₂, only diphenyl iodonium hexafluorophosphate **2** efficiently quenched the excited photocatalyst Eosin Y* (figure 1). This result indicates that the catalytic cycle would start with an oxidative quenching. Indeed, this hypothesis is also strengthened by the thermodynamically feasibility of the process with respect to the well-known redox potentials of diaryl iodonium salts ($E_{1/2} = -0,5$ V versus SCE) and excited state Eosin Y* ($E_{1/2} = -1,1$ V versus SCE).^[27]

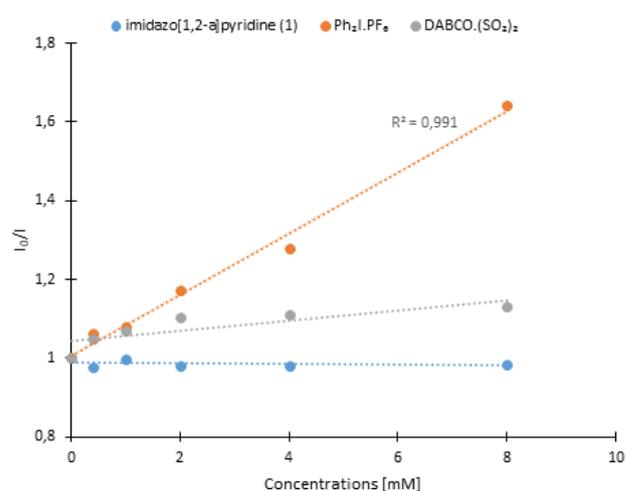
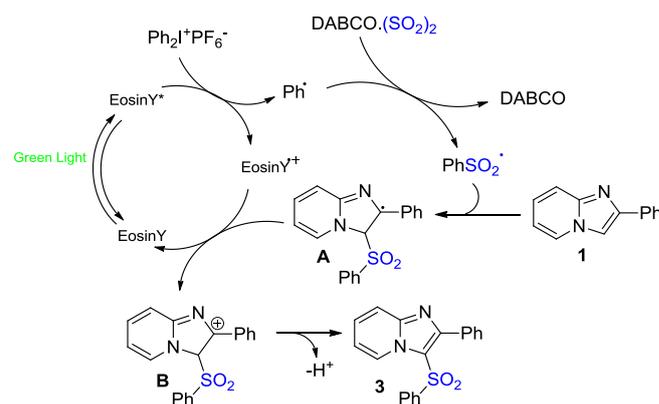


Figure 1. Stern-volmer plots.

On the basis of the above preliminary results and by reference to abundant literature studies, a plausible mechanism involving an oxidative quenching cycle can be proposed.^[28] Initially, upon green light irradiation, EosinY undergoes excitation to generate Eosin Y* which then undergo a single electron transfer to the diphenyl iodonium salt giving the radical cation Eosin Y^{•+} and the phenyl radical Ph[•]. This is then rapidly trapped by SO₂ generated from DABCO•(SO₂)₂. The resulting sulfonyl radical reacts regioselectively with 2-phenylimidazo[1,2-*a*]pyridine **1** to afford the radical intermediate **A**. The catalytic cycle is further closed by an electron transfer to the oxidant Eosin Y^{•+} from **A**, which is then transformed into carbocation **B**, and that regenerates Eosin Y. Finally, re-aromatization occurs through proton loss resulting in the expected sulfone **3**.



Scheme 5. Proposed mechanism for the photocatalyzed sulfonylation reaction of imidazoheterocycles.

In summary, we have developed conditions for a three-component reaction that enables the first entirely visible-light photoredox catalyzed sulfonylation of imidazoheterocycles. With a diaryliodonium salt as coupling partner, DABCO•(SO₂)₂ as sulfur dioxide surrogate and EosinY.Na₂ in DMSO, this reaction provides a straightforward entry to diverse and novel C-3 sulfonylated imidazoheterocycles in moderate to good yields.

Process efficiency is high, given that two new C-S bonds are formed concurrently with an average of 70 %yield for each bond. The reaction takes place smoothly at room temperature and shows a wide functional group tolerance. This transformation overcomes significant drawbacks of existing methods and opens new possibilities for the sustainable synthesis of sulfones in the field of heterocyclic chemistry.

Experimental section

General information: Commercially available reagents and solvents were used without further purification. Yields refer to isolated and purified products. Reactions were monitored by Thin Layer Chromatography (TLC) carried out on 60F-254 silica gel plates and visualized under UV light at 254 and 365 nm. Column chromatography was performed on a CombiFlash Companion using pre-packed silica 60 columns. Chemical shifts (δ) of ^1H and ^{13}C NMR are reported in ppm and residual non deuterated solvents were used as references. Multiplicities are designated by the following abbreviations: s = singlet, d = doublet, t = triplet, q = quadruplet, bs = broad singlet, bd = broad doublet, bt = broad triplet, m = multiplet. Melting points were measured with a Stuart SMP30. High-resolution mass spectra (HRMS) were measured by a TOF spectrometer, using electrospray ionization (ESI) or atmospheric pressure photoionization (APPI) method. LCMS were performed on a Waters spectrometer using Phenomenex LunaOmega 3 μm Polar C18 100A column. MS were determined on a Waters micromass ZQ spectrometer using electrospray ionization (ESI). IR spectra were recorded on a FT/IR-4100 Spectrometer. Irradiation experiments were performed using a commercially available 7.2W LED. The light source was placed 5 cm away from the sealed tube. No cooling system was used and the temperature measured inside the vessel was not above 30 °C. Substituted imidazo[1,2-a]pyridines were synthesized according to literature from condensation of the corresponding α -bromoketones and 2-aminopyridines in refluxing EtOH with NaHCO_3 .^[29] 2-styrylimidazo[1,2-a]pyridine was synthesized using a protocol described by Mohan et al.^[30] Substituted diphenyliodonium salts are synthesized according to the literature.^[23a]

General procedure: To a sealed tube under argon atmosphere were added imidazo[1,2-a]pyridine **1** (0.257 mmol, 50 mg), diphenyliodonium hexafluorophosphate **2** (0.368 mmol, 164 mg), DABCO $\cdot(\text{SO}_2)_2$ (0.257 mmol, 62 mg) and Eosin Y (0.012 mmol, 8.9 mg) in anhydrous DMSO. The reaction mixture was purge with argon. The tube was sealed and the reaction mixture was stirred under green light at room temperature for 48h. The mixture was extracted with AcOEt and washed with brine. The organic layer was dried with anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude was purified by chromatography with a gradient of cyclohexane to cyclohexane/EtOAc 30 % to afford the sulfonylated product **3** in 55 % yield.

2-phenyl-3-(phenylsulfonyl)imidazo[1,2-a]pyridine (3)^[19]: Yellow solid (47 mg, 55% yield); m.p. 122-123°C; IR: 1640 (C=N, m), 1480, 1460, 1440 (C-C, m), 1340, 1150 (SO_2 , s); ^1H NMR (300 MHz, CDCl_3): δ = 9.14 (d, J = 7.0 Hz, 1H), 7.77 – 7.69 (m, 3H), 7.63 (d, J = 7.5 Hz, 2H), 7.54 – 7.40 (m, 5H), 7.35

(t, J = 7.5 Hz, 2H), 7.07 (td, J = 7.0, 1.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 153.2, 146.8, 142.0, 133.4, 132.7, 130.6, 129.5, 129.2, 128.7, 127.9, 126.9, 126.4, 118.1, 117.5, 114.8. MS (ES^+): m/z (%) = 335.3 (100) $[\text{M} + \text{H}]^+$; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}_2\text{S}$: 335.0849, found 335.0855.

5-methyl-2-phenyl-3-(phenylsulfonyl)imidazo[1,2-a]pyridine (5a): Yellow solid (38 mg, 45% yield); m.p. 195-196°C; IR: 1625 (C=N, m), 1500, 1440 (C-C, m), 1310, 1160 (SO_2 , s); ^1H NMR (300 MHz, CDCl_3): δ = 7.67 – 7.60 (m, 3H), 7.54 – 7.51 (m, 2H), 7.49 – 7.35 (m, 2H), 7.34 – 7.22 (m, 5H), 6.86 (d, J = 7.0 Hz, 1H), 2.94 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ = 156.4, 149.3, 143.3, 140.9, 134.0, 132.9, 130.3, 129.6, 129.2, 128.7, 127.9, 127.2, 118.6, 116.8, 115.6, 23.6; MS (ES^+): m/z (%) = 349.3 (100) $[\text{M} + \text{H}]^+$; HRMS (ESI-TOF): m/z $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_2\text{S}$: 349.1011, found 349.1002.

5-methoxy-2-phenyl-3-(phenylsulfonyl)imidazo[1,2-a]pyridine (5b): White solid (54.2 mg, 67%); m.p. 183-184; IR: 1630 (C=N, m), 1540, 1500 (C-O, s), 1460, 1440 (C-C, m), 1310, 1140 (SO_2 , s); ^1H NMR (300 MHz, CDCl_3): δ = 7.93 (dd, J = 7.5, 2.0 Hz, 2H), 7.78 – 7.75 (m, 2H), 7.61 – 7.48 (m, 3H), 7.48 – 7.32 (m, 5H), 6.16 (dd, J = 7.5, 1.0 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ = 156.8, 151.8, 148.9, 144.9, 134.3, 132.3, 130.9, 130.3, 129.1, 128.9, 127.7, 125.7, 116.2, 110.1, 92.1, 56.2; MS (ES^+): m/z (%) = 365.2 (100) $[\text{M} + \text{H}]^+$; HRMS (ESI-TOF): m/z $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_3\text{S}$: 365.0960, found 365.0948.

6-methyl-2-phenyl-3-(phenylsulfonyl)imidazo[1,2-a]pyridine (6a)^[19]: Yellow solid (40 mg, 48% yield); m.p. 139-140°C; ^1H NMR (300 MHz, CDCl_3): δ = 8.92 (s, 1H), 7.70 (m, 2H), 7.66 – 7.52 (m, 3H), 7.54 – 7.40 (m, 4H), 7.38 – 7.28 (m, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ = 153.0, 145.8, 14.16, 133.3, 132.8, 131.7, 130.5, 129.3, 129.1, 127.8, 126.3, 124.8, 124.6, 117.3, 117.0, 18.7; MS (ES^+): m/z (%) = 348.9 (100) $[\text{M} + \text{H}]^+$; HRMS (ESI-TOF): m/z $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_2\text{S}$: 349.1011, found 349.1002.

6-Chloro-2-phenyl-3-(phenylsulfonyl)imidazo[1,2-a]pyridine (6b)^[19]: Orange solid (32 mg, 40%); m.p. 149-150°C; IR: 1630 (C=N, m), 1480, 1460, 1440 (C-C, m), 1320, 1160 (SO_2 , s); ^1H NMR (300 MHz, CDCl_3): δ = 9.25 (d, J = 1.0 Hz, 1H), 7.69 (dd, J = 12.5, 5.0 Hz, 3H), 7.61 (d, J = 7.5 Hz, 2H), 7.46 (m, 5H), 7.36 (t, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ = 153.4, 145.0, 141.6, 133.6, 132.1, 130.4, 130.0, 129.6, 129.2, 127.9, 126.4, 124.9, 123.1, 118.3. HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{19}\text{H}_{14}\text{ClN}_2\text{O}_2\text{S}$: 369.0459, found 369.0451.

6-Bromo-2-phenyl-3-(phenylsulfonyl)imidazo[1,2-a]pyridine (6c)^[19]: Yellow solid (35 mg, 46%); m.p. 153-154°C; ^1H NMR (300 MHz, CDCl_3): δ = 9.34 (s, 1H), 7.69 (dd, J = 7.5, 1.5 Hz, 2H), 7.61 (dd, J = 8.5, 3.0 Hz, 3H), 7.53 (dd, J = 9.5, 1.5 Hz, 5H), 7.36 (t, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ = 153.3, 145.0, 141.6, 133.6, 132.1, 132.1, 130.4, 129.6, 129.1, 127.9, 127.0, 126.4, 118.5, 118.1, 109.6; MS (ES^+): m/z (%) = 415.1 (100) $[\text{M} + \text{H}]^+$; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{19}\text{H}_{14}\text{BrN}_2\text{O}_2\text{S}$: 412.9954, found 412.9951.

2-Phenyl-3-(phenylsulfonyl)-6-(trifluoromethyl)imidazo[1,2-a]pyridine (6d)^[19]: Beige solid (34 mg, 54%); m.p. 146-147°C;

¹H NMR (300 MHz, CDCl₃): δ = 9.58 (s, 1H), 7.83 (d, *J* = 9.5 Hz, 1H), 7.72 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.62 (dd, *J* = 7.5, 4.5 Hz, 3H), 7.54 – 7.42 (m, 4H), 7.35 (t, *J* = 7.5 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ = 154.3, 146.4, 141.3, 133.8, 131.8, 130.5, 129.9, 129.2, 128.0, 126.6, 126.0 (q, *J* = 5.6 Hz), 124.5 (q, *J* = 2.6 Hz), 123.1 (q, *J* = 272 Hz), 119.2, 118.8, 107.2; MS (ES⁺): *m/z* (%) = 403.3 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₂₀H₁₄F₃N₂O₂S: 403.0723, found 403.0725.

7-Methyl-2-phenyl-3-(phenylsulfonyl)imidazo[1,2-*a*]pyridine (7a)^[19]: Yellow solid (37 mg, 44%); m.p. 156-157°C; ¹H NMR (300 MHz, CDCl₃): δ = 8.98 (d, *J* = 7.0 Hz, 1H), 7.73 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.66 – 7.56 (m, 2H), 7.50 – 7.40 (m, 5H), 7.33 (t, *J* = 7.5 Hz, 2H), 6.88 (dd, *J* = 7.0, 1.5 Hz, 1H), 2.45 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 153.3, 147.2, 142.1, 140.2, 133.2, 132.7, 130.5, 129.3, 129.0, 127.8, 126.2, 126.0, 117.2, 116.7, 116.5, 21.4; MS (ES⁺): *m/z* (%) = 349.2 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₂₀H₁₇N₂O₂S: 349.1005, found 349.1006.

7-methoxy-2-phenyl-3-(phenylsulfonyl)imidazo[1,2-*a*]pyridine (7b)^[19]: White solid (34 mg, 42% yield); m.p. 172-173°C; ¹H NMR (300 MHz, CDCl₃): δ 8.91 (d, *J* = 7.5 Hz, 1H), 7.75 - 7.72 (m, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.49 – 7.38 (m, 4H), 7.32 (t, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 2.5 Hz, 1H), 6.72 (dd, *J* = 7.5, 2.5 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 160.5, 153.7, 148.9, 142.4, 133.2, 132.7, 130.5, 129.4, 129.1, 127.9, 127.3, 126.2, 116.2, 109.2, 95.6, 77.6, 77.2, 76.7, 55.9; MS (ES⁺): *m/z* (%) = 365.2 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₂₀H₁₇N₂O₃S: 365.0960, found 365.0945.

7-Chloro-2-phenyl-3-(phenylsulfonyl)imidazo[1,2-*a*]pyridine (7c)^[19]: Beige solid (42 mg, 52%); m.p. 145-146°C; IR: 1610 (C=N, m), 1480, 1460, 1440 (C-C, m), 1340, 1150 (SO₂, s); ¹H NMR (300 MHz, CDCl₃): δ = 9.09 (d, *J* = 7.5 Hz, 1H), 7.71 (m, 3H), 7.59 (bd, *J* = 8 Hz, 2H), 7.53 – 7.41 (m, 4H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.05 (dd, *J* = 7.5, 2.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 153.8, 146.6, 141.7, 135.5, 133.6, 132.1, 130.5, 129.7, 129.1, 127.9, 127.2, 126.4, 117.9, 116.9, 116.2; MS (ES⁺): *m/z* (%) = 369.2 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₁₉H₁₄ClN₂O₂S: 369.0459, found 369.0451.

8-Methyl-2-phenyl-3-(phenylsulfonyl)imidazo[1,2-*a*]pyridine (8a)^[19]: Yellow solid (37.6 mg, 45% yield); m.p. 118-119°C; ¹H NMR (300 MHz, CDCl₃): δ = 8.98 (d, *J* = 7.0 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.67 – 7.59 (d, *J* = 7.5 Hz, 2H), 7.50 – 7.41 (m, 4H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.0 Hz, 1H), 2.64 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ = 152.7, 147.0, 142.1, 133.3, 133.0, 130.7, 129.3, 129.1, 128.2, 127.9, 127.5, 126.4, 124.5, 117.8, 114.7, 17.2; MS (ES⁺): *m/z* (%) = 349.1 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₂₀H₁₇N₂O₂S: 349.1011, found 349.0995

8-methoxy-2-phenyl-3-(phenylsulfonyl)imidazo[1,2-*a*]pyridine (8b)^[19]: Yellow solid (41 mg, 50% yield); m.p. 123-124°C; ¹H NMR (300 MHz, CDCl₃): δ 8.72 (d, *J* = 7.0 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.62 (d, *J* = 7.7 Hz, 2H), 7.49 – 7.36 (m, 4H), 7.32 (t, *J* = 7.5 Hz, 2H), 6.94 (t, *J* = 7.0 Hz, 1H), 6.72 (d, *J* = 7.5 Hz, 1H), 4.00 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 152.2, 148.9, 141.8, 141.0, 133.4, 132.6, 130.7, 129.2, 129.1, 127.6, 126.3, 119.2, 118.5, 114.7, 104.8, 56.2; MS (ES⁺): *m/z* (%) =

365.1 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₂₀H₁₇N₂O₃S: 365.0960, found 365.0950.

8-chloro-2-phenyl-3-(phenylsulfonyl)imidazo[1,2-*a*]pyridine (8c)^[19]: Beige solid (47 mg, 58% yield); m.p. 167-168°C; ¹H NMR (300 MHz, CDCl₃): δ = 9.11 (d, *J* = 7.0 Hz, 1H), 7.71 (m, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.54 - 7.41 (m, 5H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.01 (t, *J* = 7.5 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 153.3, 144.1, 141.6, 133.7, 132.2, 130.7, 129.6, 129.2, 127.9, 127.5, 126.5, 125.6, 124.0, 119.4, 114.4; MS (ES⁺): *m/z* (%) = 369.0 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₁₉H₁₄ClN₂O₂S: 369.0465, found 369.0454.

8-bromo-2-phenyl-3-(phenylsulfonyl)imidazo[1,2-*a*]pyridine (8d): Yellow solid (34 mg, 45% yield); m.p. 185-186°C; IR: 1580 (C=N, m), 1480, 1460, 1440 (C-C, m), 1320, 1140 (SO₂, s); ¹H NMR (300 MHz, CDCl₃): δ = 9.15 (d, *J* = 7.0 Hz, 1H), 7.71 (m, 3H), 7.63 – 7.54 (m, 2H), 7.53 – 7.40 (m, 4H), 7.33 (t, *J* = 7.5 Hz, 2H), 6.94 (t, *J* = 7.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 153.3, 144.6, 141.6, 133.7, 131.0, 130.8, 129.6, 129.2, 127.9, 126.5, 126.2, 119.5, 114.7, 112.1. MS (ES⁺): *m/z* (%) = 415.1 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₁₉H₁₄BrN₂O₂S: 412.9959, found 412.9953.

8-Fluoro-2-phenyl-3-(phenylsulfonyl)imidazo[1,2-*a*]pyridine (8e): Beige solid (78 mg, 42%); m.p. 100-101°C; IR: 1560 (C=N, m), 1500, 1460, 1440 (C-C, m), 1320 (SO₂, s), 1260 (C-F, s), 1140 (SO₂, s); ¹H NMR (300 MHz, CDCl₃): δ = 8.99 (d, *J* = 7.0 Hz, 1H), 7.73 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.65 – 7.58 (m, 2H), 7.54 – 7.40 (m, 4H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.18 (bt, 1H), 7.00 (td, *J* = 7.5, 5.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 152.96, 151.23 (d, *J* = 256.1 Hz), 141.5, 139.3 (d, *J* = 27.5 Hz), 133.6, 132.0, 130.6, 129.6, 129.1, 127.9, 126.5, 123.2 (d, *J* = 5.5 Hz), 119.4, 113.8 (d, *J* = 6.4 Hz), 111.7 (d, *J* = 15.7 Hz); MS (ES⁺): *m/z* (%) = 353.1 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₁₉H₁₃FN₂O₂S: 353.0755, found 353.0772.

8-trifluoromethyl-2-phenyl-3-(phenylsulfonyl)imidazo[1,2-*a*]pyridine (8f): Yellow solid (37 mg, 48%); m.p. 202-203°C; IR: 1625 (C=N, m), 1460, 1440 (C-C, m), 1320, 1145 (SO₂, s); ¹H NMR (300 MHz, CDCl₃): δ = 9.36 (d, *J* = 7.0 Hz, 1H), 7.79 (d, *J* = 7.0 Hz, 1H), 7.72 (dd, *J* = 7.5 Hz, 1.5 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.52-7.42 (m, 4H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.14 (t, *J* = 7.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 153.6, 142.3, 141.4, 133.7, 131.9, 130.8, 130.1, 129.7, 129.2, 127.9, 126.6 (q, *J* = 5.0 Hz), 126.5, 122.3 (q, *J* = 272.6 Hz), 119.9 (q, *J* = 34.5 Hz), 116.8, 113.0; MS (ES⁺): *m/z* (%) = 403.3 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₂₀H₁₃F₃N₂O₂S: 403.0723, found 403.0725.

2-phenyl-3-(phenylsulfonyl)imidazo[1,2-*a*]pyridine-8-carbonitrile (8g): Yellow solid (34.2 mg, 42% yield); m.p. 201-202°C; IR: 2240 (C≡N, w), 1620 (C=N, w), 1480, 1460, 1440 (C-C, m), 1320, 1140 (SO₂, s); ¹H NMR (300 MHz, CDCl₃): δ = 9.40 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.88 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.79 – 7.67 (m, 2H), 7.61 – 7.53 (m, 2H), 7.52 – 7.38 (m, 4H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 154.1, 144.4, 141.3, 134.8, 134.0, 131.5, 131.0, 130.8, 130.1, 129.3, 128.1, 126.6, 119.7, 114.1, 113.8, 103.4; MS (ES⁺): *m/z* (%) = 360.3 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₂₀H₁₄N₃O₂S: 360.0807 found 360.0802.

3-(phenylsulfonyl)-2-(p-tolyl)imidazo[1,2-a]pyridine (9a)^[19]: Yellow solid (44 mg, 53% yield); m.p. 166-167°C; ¹H NMR (300 MHz, CDCl₃): δ = 9.10 (d, *J* = 7.0 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 4H), 7.52 – 7.39 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.03 (td, *J* = 7.0, 1.0 Hz, 1H), 2.43 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ = 153.4, 146.8, 142.1, 139.5, 133.4, 130.5, 129.7, 129.2, 128.7, 126.9, 126.4, 118.0, 117.2, 114.6, 21.6; MS (ES⁺): *m/z* (%) = 349.1 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₂₀H₁₇N₂O₂S: 349.1011, found 349.0996.

2-(4-Methoxyphenyl)-3-(phenylsulfonyl)imidazo[1,2-a]pyridine (9b)^[19]: Brown solid (33 mg, 41%); m.p. 127-128°C; ¹H NMR (300 MHz, CDCl₃): δ = 9.12 (d, *J* = 7.0 Hz, 1H), 7.72 (m, 3H), 7.67 – 7.61 (m, 2H), 7.54 – 7.40 (m, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.04 (t, *J* = 7.0 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 160.7, 153.1, 146.7, 142.1, 133.3, 132.0, 129.1, 128.6, 126.9, 126.2, 124.9, 117.9, 116.8, 114.5, 113.3, 55.3; MS (ES⁺): *m/z* (%) = 365.3 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₂₀H₁₇N₂O₃S 365.0954, found 365.0966.

2-(4-chlorophenyl)-3-(phenylsulfonyl)imidazo[1,2-a]pyridine (9c)^[19]: Yellow solid (39.5 mg, 49% yield); m.p. 185-186°C; ¹H NMR (300 MHz, CDCl₃): δ = 9.11 (d, *J* = 7.0 Hz, 1H), 7.73 - 7.70 (m, 3H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.54 – 7.30 (m, 6H), 7.07 (td, *J* = 7.0, 1.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 151.9, 146.8, 141.9, 135.8, 133.6, 132.0, 131.1, 129.3, 128.9, 128.2, 126.9, 126.3, 118.1, 117.6, 115.0; MS (ES⁺): *m/z* (%) = 369.3 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₁₉H₁₄ClN₂O₂S: 369.0465, found 369.0464

2-(4-fluorophenyl)-3-(phenylsulfonyl)imidazo[1,2-a]pyridine (9d)^[19]: Yellow solid (40.6 mg, 49% yield); m.p. 114-115°C; ¹H NMR (300 MHz, CDCl₃): δ = 9.11 (d, *J* = 7.0 Hz, 1H), 7.79 – 7.65 (m, 3H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.49 (d, *J* = 7.0 Hz, 1H), 7.44 (d, *J* = 7.0 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.14 (t, *J* = 9.0 Hz, 2H), 7.06 (td, *J* = 7.0, 1.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 163.7 (d, *J*_{C-F} = 249.2 Hz), 152.1, 146.8, 141.9, 133.6, 132.6 (d, *J*_{C-F} = 8.5 Hz), 129.2, 128.9, 128.73 (d, *J*_{C-F} = 3.3 Hz), 126.9, 126.3, 118.1, 117.5, 115.0 (d, *J*_{C-F} = 21.8 Hz). MS (ES⁺): *m/z* (%) = 353.2 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₁₉H₁₄FN₂O₂S: 353.0760, found 353.0752.

3-(phenylsulfonyl)-2-(4-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (9e)^[19]: Yellow solid (35 mg, 46% yield); m.p. 173-174°C; ¹H NMR (300 MHz, CDCl₃): δ = 9.10 (d, *J* = 7.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.77 – 7.69 (m, 3H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.53 – 7.46 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.09 (td, *J* = 7.0, 1.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 151.3, 146.8, 141.6, 136.3, 133.7, 131.3 (q, *J*_{C-F} = 32.5 Hz), 131.0, 129.3, 129.0, 126.8, 126.3, 124.8 (q, *J*_{C-F} = 3.5 Hz), 124.1 (q, *J*_{C-F} = 270 Hz), 118.2, 117.9, 115.1; MS (ES⁺): *m/z* (%) = 403.1 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₂₀H₁₄F₃N₂O₂S: 403.0728, found 403.0709.

4-(3-(phenylsulfonyl)imidazo[1,2-a]pyridin-2-yl)benzotrile (9f): Yellow solid (45 mg, 55% yield); m.p. 185-186°C; IR: 2220 (C≡N, m), 1620 (C=N, m), 1480, 1460, 1440 (C-C, m), 1320, 1150 (SO₂, s); ¹H NMR (300 MHz, CDCl₃): δ = 9.08 (d, *J* = 7.0 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.81 – 7.69 (m, 3H), 7.64 (d, *J*

= 7.5 Hz, 2H), 7.54 - 7.48 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 7.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 150.7, 146.9, 141.6, 137.3, 133.9, 131.7, 131.4, 129.4, 129.2, 126.8, 126.3, 118.8, 118.4, 115.4, 113.1, 77.6, 77.2, 76.7; MS (ES⁺): *m/z* (%) = 360.2 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₂₀H₁₄N₃O₂S: 360.080 found 360.0802.

2-(4-nitrophenyl)-3-(phenylsulfonyl)imidazo[1,2-a]pyridine (9g): Red- Brown solid (41 mg, 52% yield); m.p. 186-187°C; IR: 1600 (C=N, m), 1520 (NO₂, s), 1480, 1460, 1440 (C-C, w), 1340 (NO₂, s), 1320, 1150 (SO₂, s); ¹H NMR (300 MHz, CDCl₃): δ = 9.09 (d, *J* = 7.0 Hz, 1H), 8.33 (d, *J* = 9.0 Hz, 2H), 7.98 (d, *J* = 9.0 Hz, 2H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 2H), 7.60 – 7.46 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.13 (td, *J* = 7.0, 1.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 150.3, 148.4, 146.9, 141.5, 139.1, 133.9, 131.8, 129.5, 129.3, 126.8, 126.3, 123.0, 118.4, 118.3, 115.5; MS (ES⁺): *m/z* (%) = 380.2 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₁₉H₁₄N₃O₄S: 380.0705, found 380.0698.

2-(Naphthalen-2-yl)-3-(phenylsulfonyl)imidazo[1,2-a]pyridine (10)^[19]: Orange solid (41 mg, 51% yield); m.p. 127-128°C; ¹H NMR (300 MHz, CDCl₃): δ = 9.18 (d, *J* = 7.0 Hz, 1H), 8.27 (s, 1H), 8.01 – 7.81 (m, 4H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.59 – 7.39 (m, 5H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 6.5 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 153.1, 146.8, 142.0, 133.7, 133.4, 132.7, 130.6, 130.0, 129.1, 128.8, 128.7, 127.7, 127.7, 127.4, 126.9, 126.9, 126.4, 126.3, 118.1, 117.7, 114.7; MS (ES⁺): *m/z* (%) = 385.3 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₂₃H₁₇N₂O₂S: 385.1005, found 385.0993.

(E)-3-(phenylsulfonyl)-2-styrylimidazo[1,2-a]pyridine (11): Yellow solid (39 mg, 48% yield); m.p. 179-181°C; IR: 1625 (C=N, m), 1460, 1440 (C-C, m), 1320, 1145 (SO₂, s); ¹H NMR (300 MHz, CDCl₃): δ = 8.84 (d, *J* = 7.0 Hz, 1H), 8.04 (d, *J* = 16.0 Hz, 1H), 7.96 (d, *J* = 7.0 Hz, 2H), 7.88 (d, *J* = 16.0 Hz, 1H), 7.71 - 7.64 (m, 3H), 7.58 – 7.31 (m, 7H), 6.96 (td, *J* = 7.0, 1.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 149.5, 147.4, 141.9, 136.6, 136.5, 133.7, 129.6, 129.1, 129.0, 128.9, 127.7, 126.5, 126.1, 117.6, 117.5, 116.6, 114.3; MS (ES⁺): *m/z* (%) = 361.1 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₂₁H₁₇N₂O₂S: 361.1011, found 361.1023

2-methyl-3-(phenylsulfonyl)imidazo[1,2-a]pyridine (12): Yellow solid (40 mg, 49% yield); mp 121-122°C; IR: 1620 (C=N, w), 1480, 1440 (C-C, m), 1315, 1140 (SO₂, s); ¹H NMR (300 MHz, CDCl₃): δ = 8.83 (d, *J* = 7.0 Hz, 1H), 7.94 (d, *J* = 7.0 Hz, 2H), 7.53 (m, 4H), 7.43 – 7.32 (td, *J* = 7.0, 1.0 Hz, 1H), 6.97 (td, *J* = 7.0, 1.0 Hz, 1H), 2.79 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 151.5, 146.7, 142.2, 133.6, 129.5, 128.4, 126.2, 126.0, 117.4, 117.0, 114.4, 15.5; MS (ES⁺): *m/z* (%) = 273.2 (100) [M + H]⁺; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd. for C₁₄H₁₃N₂O₂S: 273.0698, found 0694.

2-phenyl-3-(phenylsulfonyl)imidazo[2,1-a]isoquinoline (13): Yellow solid (36 mg, 46%); m.p. 205-206°C; IR: 1625 (C=N, m), 1460, 1440 (C-C, m), 1325, 1145 (SO₂, s); ¹H NMR (300 MHz, CDCl₃): δ = 8.92 (d, *J* = 7.5 Hz, 1H), 8.77 – 8.66 (m, 1H), 7.79-7.76 (m, 3H), 7.71 – 7.62 (m, 4H), 7.47 (m, 4H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ =

151.5, 145.0, 142.1, 133.3, 132.7, 130.7, 130.4, 130.1, 129.3, 129.1, 128.7, 127.9, 126.9, 126.4, 124.5, 122.9, 122.8, 119.4, 115.0; MS (ES⁺) : m/z (%) = 385.3 (100) [M + H]⁺; HRMS (ESI-TOF) m/z [M + H]⁺ calcd. for C₂₃H₁₆N₂O₂S: 385.1005, found 385.1016.

6-Phenyl-5-(phenylsulfonyl)imidazo[2,1-b]thiazole (14)^[19]: Yellow oil (49 mg, 58%); ¹H NMR (300 MHz, CDCl₃): δ = 8.23 (d, J = 4.5 Hz, 1H), 7.76 (dd, J = 6.5, 3.0 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.53 – 7.38 (m, 4H), 7.33 (t, J = 7.5 Hz, 2H), 7.04 (d, J = 4.5 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 153.3, 152.7, 141.9, 133.4, 132.2, 129.9, 129.4, 129.1, 128.1, 126.4, 120.7, 120.6, 114.4; MS (ES⁺) : m/z (%) = 341.2 (100) [M + H]⁺; HRMS (ESI-TOF) m/z [M + H]⁺ calcd. for C₁₇H₁₃N₂O₂S₂: 341.0413, found 341.0424.

2-Phenyl-3-(phenylsulfonyl)benzo[d]imidazo[2,1-b]thiazole (15)^[19]: Yellow solid (44 mg, 56%); m.p. 175-176°C; ¹H NMR (300 MHz, CDCl₃): δ = 8.80 (d, J = 8.5 Hz, 1H), 7.85 – 7.59 (m, 5H), 7.55 – 7.31 (m, 9H); ¹³C NMR (75 MHz, CDCl₃): δ = 156.0, 152.8, 142.0, 133.3, 133.2, 132.6, 130.5, 129.9, 129.4, 129.2, 127.7, 127.0, 126.7, 125.8, 124.1, 122.3, 117.3; MS (ES⁺) : m/z (%) = 391.2 (100) [M + H]⁺; HRMS (ESI-TOF) m/z [M + H]⁺ calcd. for C₂₁H₁₅N₂O₂S₂: 391.0569, found 391.0585.

2-phenyl-3-(phenylsulfonyl)imidazo[1,2-a]pyrimidine (16): Yellow solid (47 mg, 55%); m.p. 56-60°C; IR: 1630 (C=N, m), 1480, 1460, 1440 (C-C, m), 1340, 1160 (SO₂, s); ¹H NMR (300 MHz, CDCl₃): δ = 9.51 (dd, J = 7.0, 2.0 Hz, 1H), 8.77 (dd, J = 4.0, 2.0 Hz, 1H), 7.80 (dd, J = 7.5, 1.5 Hz, 2H), 7.56 (dd, J = 8.5, 1.5 Hz, 2H), 7.52 – 7.39 (m, 4H), 7.33 (t, J = 7.5 Hz, 2H), 7.15 (dd, J = 7.0, 4.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 154.4, 153.4, 149.1, 141.6, 135.1, 133.9, 131.8, 130.8, 130.0, 129.2, 126.5, 116.6, 110.8; MS (ES⁺) : m/z (%) = 336.1 (100) [M + H]⁺; HRMS (ESI-TOF) m/z [M + H]⁺ calcd. for C₁₉H₁₆N₃O₂S: 335.0728, found 335.0728.

2-phenyl-3-tosylimidazo[1,2-a]pyridine (17a)^[19]: Yellow solid (41 mg, 46% yield); m.p. 130-131°C; ¹H NMR (300 MHz, CDCl₃): δ = 9.11 (d, J = 7.0 Hz, 1H), 7.75 - 7.69 (m, 3H), 7.52 (d, J = 8.5 Hz, 2H), 7.47 - 7.42 (m, 4H), 7.14 (d, J = 8.0 Hz, 2H), 7.05 (t, J = 7.0 Hz, 1H), 2.32 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 152.9, 146.7, 144.5, 139.2, 132.8, 130.6, 129.8, 129.4, 128.5, 127.9, 126.9, 126.5, 118.1, 117.9, 114.7, 21.6; MS (ES⁺) : m/z (%) = 349.2 (100) [M + H]⁺; HRMS (ESI-TOF) m/z [M + H]⁺ calcd. for C₂₀H₁₇N₂O₂S: 349.1010, found 349.0998.

3-((4-tertbutylphenyl)sulfonyl)-2-phenylimidazo[1,2-a]pyridine (17b): Yellow solid (43 mg, 43%); m.p. 144-145°C; IR: 1625 (C=N, m), 1480, 1460, 1440 (C-C, m), 1320, 1160 (SO₂, s); ¹H NMR (300 MHz, CDCl₃): δ = 9.13 (d, J = 7.0 Hz, 1H), 7.83 – 7.65 (m, 3H), 7.57 (d, J = 8.5 Hz, 2H), 7.46 (dd, J = 5.0, 1.5 Hz, 4H), 7.35 (d, J = 8.5 Hz, 2H), 7.05 (td, J = 7.0, 1.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 157.3, 152.8, 146.6, 138.9, 132.7, 130.5, 129.3, 127.8, 126.9, 126.3, 126.1, 118.0, 117.9, 114.6, 35.2, 31.0; MS (ES⁺) : m/z (%) = 391.0 (100) [M + H]⁺; HRMS (ESI-TOF) m/z [M + H]⁺ calcd. for C₂₃H₂₂N₂O₂S: 391.1475, found 391.1489.

3-((4-bromophenyl)sulfonyl)-2-phenylimidazo[1,2-a]pyridine (17c): Yellow solid (51 mg, 48%); m.p. 146-147°C; IR: 1560

(C=N, m), 1480, 1460, 1440 (C-C, m), 1320, 1140 (SO₂, s); ¹H NMR (300 MHz, CDCl₃): δ = 9.12 (d, J = 7.0 Hz, 1H), 7.74 - 7.69 (m, 3H), 7.59 – 7.36 (m, 8H), 7.08 (t, J = 7.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 153.5, 146.9, 141.0, 132.5, 132.0, 130.6, 129.6, 128.9, 128.6, 128.0, 127.9, 126.9, 118.2, 117.2, 115.0; MS (ES⁺) : m/z (%) = 415.1 (100) [M + H]⁺; HRMS (ESI-TOF) m/z [M + H]⁺ calcd. for C₁₉H₁₄BrN₂O₂S: 412.9959, found 412.9953.

3-((4-Fluorophenyl)sulfonyl)-2-phenylimidazo[1,2-a]pyridine (17d)^[19]: Orange solid (46 mg, 51%); m.p. 130-131°C; ¹H NMR (300 MHz, CDCl₃): δ = 9.14 (d, J = 7.0 Hz, 1H), 7.86 – 7.67 (m, 3H), 7.68 – 7.55 (m, 2H), 7.52 – 7.38 (m, 4H), 7.08 (td, J = 7.0, 1.0 Hz, 1H), 7.04 – 6.94 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ = 165.44 (d, J = 256.3 Hz), 153.1, 146.7, 138.0 (d, J = 3.2 Hz), 132.5, 130.5, 129.5, 129.2 (d, J = 9.6 Hz), 128.7, 127.9, 126.8, 118.1, 117.4, 116.3 (d, J = 22.7 Hz), 114.8; MS (ES⁺) : m/z (%) = 353.0 (100) [M + H]⁺; HRMS (ESI-TOF) m/z [M + H]⁺ calcd. for C₁₉H₁₄FN₂O₂S: 353.0755, found 353.0758.

2-Phenyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)imidazo[1,2-a]pyridine (17e): Yellow solid (41 mg, 40%); m.p. 126-127°C; ¹H NMR (300 MHz, CDCl₃): δ = 9.17 (d, J = 7.0 Hz, 1H), 7.79 – 7.65 (m, 5H), 7.58 (d, J = 8.5 Hz, 2H), 7.54 – 7.42 (m, 4H), 7.11 (td, J = 7.0, 1.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 153.9, 147.0, 145.4, 134.9 (q, J = 33.2 Hz), 132.3, 130.5, 129.7, 129.1, 128.0, 126.8, 126.2 (q, J = 3.7 Hz), 123.0 (q, J = 273.1 Hz), 118.2, 116.6, 115.1; MS (ES⁺) : m/z (%) = 402.9 (100) [M + H]⁺; HRMS (ESI-TOF) m/z [M + H]⁺ calcd. for C₂₀H₁₄F₃N₂O₂S: 403.0723, found 403.0716.

Acknowledgements

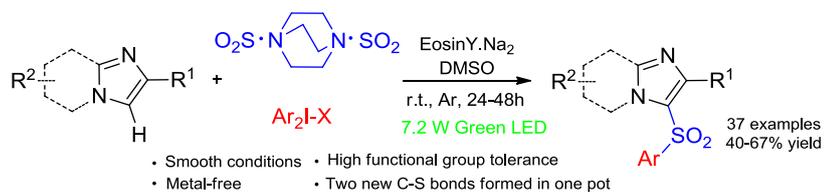
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Keywords: imidazoheterocycles • sulfones • sulfur dioxide • photoredox catalysis • diaryliodonium salts

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The first examples of visible-light induced direct sulfur dioxide insertion on imidazoheterocycles have been developed using an organic photoredox catalyst at room temperature and $\text{DABCO}\cdot(\text{SO}_2)_2$. The formation of 2 new C-S bonds, without further pre-functionalization, in metal-free and mild conditions render this three-component approach sustainable and green and led to novel and valuable C-3 sulfonlated imidazoheterocycles in moderate to good yields.