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Oxidation Potential-Guided Electrochemical Radical–Radical Cross-Coupling Approaches to 3-Sulfonylated Imidazopyridines and Indolizines

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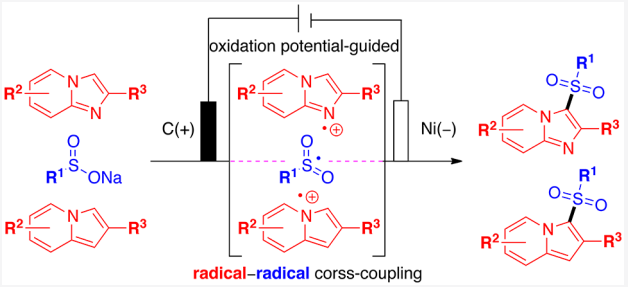
ABSTRACT: Oxidation potential-guided electrochemical radical–radical cross-coupling reactions between N-heteroarenes and sodium sulfinates have been established. Thus, simple cyclic voltammetry measurement of substrates predicts the likelihood of successful radical–radical coupling reactions, allowing the simple and direct synthetic access to 3-sulfonylated imidazopyridines and indolizines. The developed electrochemical radical–radical cross-coupling reactions to sulfonylated N-heteroarenes boast the green synthetic nature of the reactions that are oxidant- and metal-free.



INTRODUCTION

Direct installation of a sulfonyl group into heteroarenes allows rapid access to heteroarylsulfonyl derivatives with various biological activities as well as interesting photophysical properties.[1] While there exist considerable amounts of synthetic methods directed to the preparation of heteroarylsulfonyl derivatives,[2] the recent development of photoredox catalysis[3] and electrochemical synthesis[4] has opened up ample opportunity for greener and more efficient synthetic utilization of sulfonyl radicals.[5] In particular, the facile generation of sulfonyl radicals from sodium sulfinates under photoredox catalysis has been widely exploited in reactions with alkenes,[6] alkynes,[7] and arenes.[8] Even more, the necessity of photocatalyst and redox reagents can be eliminated in the electrochemical synthesis, where the direct anodic oxidation of sodium sulfinates to sulfonyl radicals can be performed (Scheme 1a). Thus, the sulfonyl radicals have been added to various radical acceptors such as alkenes,[9] alkynes,[10] and arenes[11] under the electrochemical conditions.[12] Since heteroarenes can be also anodically oxidized to radical cation species, the simple measurements of cyclic voltammetry of sodium sulfinates and heteroarenes can provide the total amount of voltage required for the electrochemical radical–radical cross-coupling processes.[13] Indeed, the previous works of the Li group[14] and the Waldvogel group[15] utilized the electrochemical radical–radical cross couplings between sodium sulfinates and aromatic compounds such as anilines and phenols. Our group also recently disclosed the electrochemical radical–radical cross-coupling of sulfonyl radicals and radical cationic species from sodium sulfinates and N-heteroaromatic 2*H*-indazoles, respectively.[16] Given that the simple measurement of cyclic voltammetry of substrates directly informs the likelihood of radical–radical cross-couplings of N-heteroarenes and sodium sulfinates, we envisaged the rapid synthetic access to N-heteroarylsulfonyl derivatives from the electrochemically generated sulfonyl radicals and radical cationic N-heteroaromatic species (Scheme 1b). Herein, we report the execution of such simple and direct electrochemical radical–radical cross-coupling strategies using imidazopyridines and indolizines through the identification of their close oxidation potentials to sodium sulfinates.

RESULTS AND DISCUSSION

While the iodine-mediated conversion of sodium sulfinates to the corresponding sulfonyl iodides has been used to effect the sulfonyl radical addition to imidazopyridines,[17] the feasibility of electrochemical cross-coupling between sodium sulfinates and heteroaromatic compounds was investigated by the cyclic voltammetry measurements of sodium *p*-toluenesulfinate **1a** and 2-(*p*-tolyl)imidazo[1,2-*a*]pyridine **2a** (Table 1). The oxidation potential measurement of sodium *p*-toluenesulfinate **1a** in a mixture of CH_3CN/H_2O indicated that **1a** started getting oxidized at around 1.2 V (blue curve), whereas the oxidation potential of the 2-(*p*-tolyl)imidazo[1,2-*a*]pyridine **2a** was around 1.5 V (red curve). The close oxidation potential between sodium *p*-toluenesulfinate **1a** and 2-(*p*-tolyl)imidazo[1,2-*a*]-pyridine **2a** was interpreted to be sufficient enough to induce the radical–radical cross-coupling reaction[18] and subsequently

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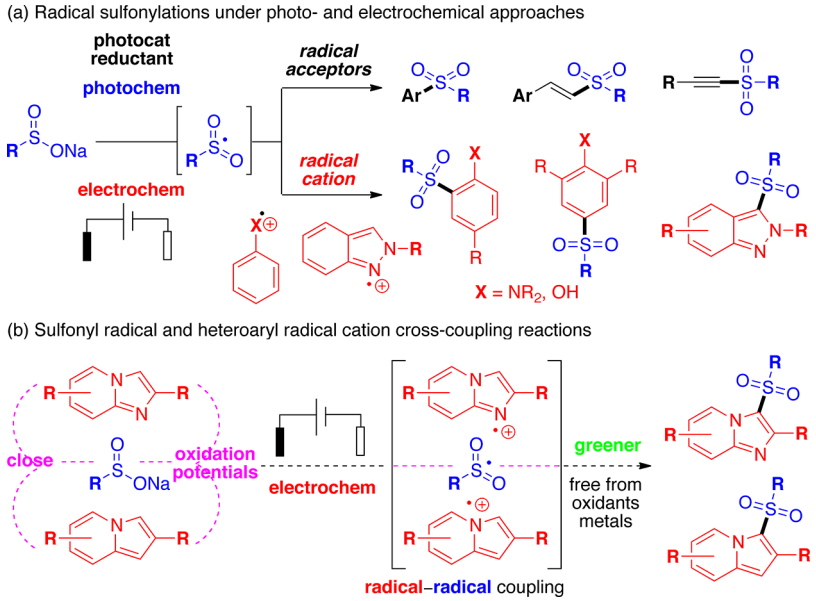
Scheme 1. Sulfonyl Radical Addition to Heteroarenes



explored under the electrochemical reaction conditions (Table 1). Thus, the use of a 3:1 mixture of **1a** and **2a** in an undivided cell with constant current conditions using a carbon rod anode and platinum plate cathode with the 7 mA current provided the desired 3-sulfonylated imidazopyridine **3a** in 92% yield in a 2.5:1 mixture of CH_3CN/H_2O with 0.4 M $LiClO_4$ (entry 1). The following control experiments further confirmed the optimal use of 3 equiv of sodium sulfinate **1a** (entries 2 and 3), the 7 mA current (entries 4 and 5), and the electrolyte concentration of 0.4 M (entries 6 and 7). A brief solvent screening also confirmed the optimal use of a 2.5:1 mixture of CH_3CN/H_2O (entries 8−11). The change of electrolyte to *n*-Bu_4ClO_4 and *n*-Bu_4BF_4 slightly lowered the isolated yields of **3a** to 70−76% (entries 12−13). A carbon rod anode and carbon rod cathode could be used, but that significantly lowered the yield of **3a** to 51% (entry 14); however, the reaction failed upon use of a platinum plate anode and platinum plate cathode (entry 15). The replacement of the platinum plate cathode with nickel plate cathode was possible, leading to 80% yield of **3a** (entry 16). No reaction occurred in the absence of applied current (entry 17).

The optimized electrochemical cross-coupling reaction conditions were applied to various phenylimidazo[1,2-*a*]-pyridines and sodium sulfinates, where the synthetically useful levels of chemical yields and functional tolerance were amply demonstrated (Scheme 2). In particular, the electronically as well as sterically varied phenylimidazo[1,2-*a*]pyridines could be utilized to give the desired products, **3a−3v**, where the majority of products were obtained in good to excellent yields except **3j**, **3k**, and **3n**. However, the utilization of 2-*tert*-butylimidazolpyridine **2w** was not successful under the optimized electrochemical conditions. The substrate scope of sodium sulfinates encompassed sodium phenylsulfinate derivatives **3w−3zc**, thiophenylsulfinate **3zd**, and alkylsulfinates **3ze−3zg**. With the recent electrochemical sulfenylation[19] and thiocyanation[20] of imidazopyridines, the current example marks the first electrochemical sulfonylation example of imidazopyridines.[21]

The oxidation potential of 2-phenylindolizine **4a** could not be measured in a mixture of CH_3CN and H_2O due to the low solubility of **4a**. Indeed, the electrochemical cross-coupling of 2-phenylindolizine **4a** in a mixture of CH_3CN/H_2O failed to give the desired product, 3-sulfonylated indolizine **5a**, due to the insufficient solubility of **4a**.[22] Thus, a brief survey of reaction solvents was conducted (Table 2, entries 1−6) and identified the optimal use of a 7:0.5 mixture of DMF/H_2O, providing the 3-sulfonylated indolizine **5a** in 75% yield (entry 3). The change of current to 4 or 10 mA slightly lowered the yields of **5a** to 57−59% (entries 7 and 8). Further control experiments were performed to verify the optimal amount of $LiClO_4$ (entries 9 and 10), the effect of other electrolytes (entries 11−14), and different cathode and anode combination (entries 15 and 16). In particular, the nickel plate cathode could be replaced with a platinum plate cathode without much influence to the yield of **5a** (entry 16). The requirement of 2 equiv of sodium *p*-toluenesulfinate **1a** (entry 3 vs entries 17 and 18) and the electric current (entry 19) for the current electrochemical radical−radical cross-coupling reaction was also confirmed.

Under the optimized reaction conditions using a mixture of DMF/H_2O, the oxidation potential of 2-phenylindolizine **4a** was not well-defined, ranging from 1.0 to 1.5 V, whereas sodium *p*-toluenesulfinate **1a** displayed two small bumps at 1.0 and 1.5 V (Scheme 3; **1a** in blue curve and **4a** in red curve with a maximum peak at 1.4 V), indicating the concurrent oxidation of **4a** to the corresponding radical cationic species as well as the generation of sulfonyl radicals from **1a**. The optimized electrochemical cross-coupling condition was further utilized for various indolizines and sodium sulfinates (Scheme 3). The presence of electron-withdrawing groups at the 4-position of phenyl substituents somewhat lowered the synthetic efficiency, where relatively low yields of the products (**5c**, **5f**, and **5g**) were observed. The biphenyl and furan moieties at the indolizine 2-position also provided the desired products **5m** and **5p** in 20−33% yields, possibly due to the poor solubility of the resulting products interfering the applied electric current. In general, the optimized electrochemical cross-coupling reaction conditions were applicable to various 2-aryl indolizine derivatives **5a−5s** in good yields. The substrate scope of sodium sulfinates was also investigated, and the desired 3-sulfonylated indolizines **5t−5ze** were readily obtained upon using 2−3 equiv of sodium sulfinates **1**. The current electrochemical coupling method could employ sodium heteroarylsulfinate and alkylsulfinates to give the desired

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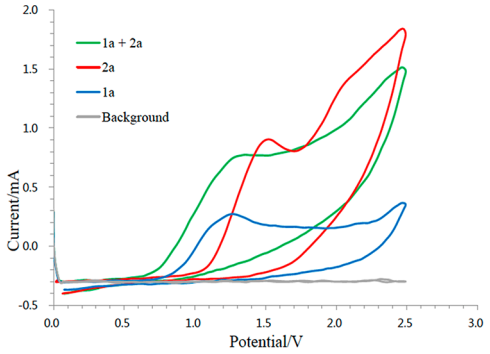
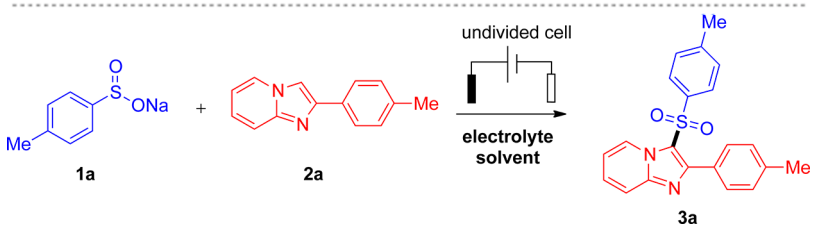
Table 1. Optimization of Electrochemical Cross-Coupling between Sodium Sulfinate and 2-Phenylimidazo[1,2-*a*]pyridine[a]





entry	(+)/(−) (mA)	electrolyte (M)	solvent	yield[b] (%)
1	C(+)−Pt(−) (7)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	92
2[c]	C(+)−Pt(−) (7)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	47
3[d]	C(+)−Pt(−) (7)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	63
4	C(+)−Pt(−) (4)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	49
5	C(+)−Pt(−) (10)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	70
6	C(+)−Pt(−) (7)	$LiClO_4$ (0.27)	CH_3CN/H_2O (2.5:1)	50
7	C(+)−Pt(−) (7)	$LiClO_4$ (0.53)	CH_3CN/H_2O (2.5:1)	68
8	C(+)−Pt(−) (7)	$LiClO_4$ (0.40)	CH_3OH/H_2O (2.5:1)	trace
9	C(+)−Pt(−) (7)	$LiClO_4$ (0.30)	DMF:H_2O (2.5:1)	trace
10	C(+)−Pt(−) (7)	$LiClO_4$ (0.50)	CH_3CN/H_2O (6:1)	61
11	C(+)−Pt(−) (7)	$LiClO_4$ (0.40)	CH_3CN/H_2O (4:3)	44
12	C(+)−Pt(−) (7)	*n*-Bu_4ClO_4 (0.40)	CH_3CN/H_2O (2.5:1)	70
13	C(+)−Pt(−) (7)	*n*-Bu_4BF_4 (0.40)	CH_3CN/H_2O (2.5:1)	76
14	C(+)−C(−) (7)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	51
15	Pt(+)−Pt(−) (7)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	trace
16	C(+)−Ni(−) (7)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	80
17[e]	C(+)−Ni(−) (0)	$LiClO_4$ (0.40)	CH_3CN/H_2O (2.5:1)	0

[a]Reaction using **1a** (0.6 mmol), **2a** (0.2 mmol), and electrolyte in solvent (M) in an undivided cell with constant current of 7 mA under argon for 2 h. [b]Isolated yield of **5a**. [c]Reaction using 1 equiv of **1a**. [d]Reaction using 2 equiv of **1a**. [e]No current.

products **5zb** and **5zd**−**5ze** without much compromise in yields. The current electrochemical synthesis of 3-sulfonylated indolizines represents the first direct sulfonylation of indolizines.[23]

The electrochemical radical generations from sodium *p*-toluenesulfinate **1a**, imidazolpyridine **2a**, and indolizine **4a** were validated by recording the electron paramagnetic resonance (EPR) spectra (Scheme 4). Thus, a spin-trapping agent, 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), was added to the electrochemical reaction conditions in the presence of each substrate. The observed *g* value of 2.004 corresponded to the [DMPO-**1a**] spin adduct with the hyperfine splitting constant (aN) of 14.35 G (Scheme 4a). The radical cationic species from the electrochemical oxidation of imidazolpyridine **2a** were also spin trapped by DMPO to give the [DMPO-**2a**] radical adduct with two different hyperfine splitting patterns, one resulting from the radical cationic species with a hyperfine splitting constant (aN) of 15.75 G and the other one from the radical cationic species with two hyperfine splitting constants (aN) of 14.00 G and (aH) of 14.2 G due to the presence of a β-hydrogen (Scheme 4b). Likewise, the formation of the [DMPO-**4a**] radical adduct was also observed from the electrochemical oxidation of indolizine **4a**, where the corresponding radical cationic species showed the hyperfine splitting constants (aN) of 15.07 G and (aH) of 25 G (Scheme 4c). The nonsymmetric line patterns and the different line width of the radical cationic adducts suggest their distinctive inductive effects in combination with conformational and intermolecular interactions.

The cyclic voltammetry measurement of substrates provides the predictive power for the successful electrochemical cross-coupling reactions. The oxidation potentials of imidazopyridines **2** with different electronic characters all fell around 1.5 V (Scheme 5a); thus, the unsuccessful radical−radical cross-coupling of imidazopyridine **2w** with an alkyl moiety was interpreted due to the short lifetime of the in situ generated radical cation species of **2w**. In addition, the oxidation potentials of indolizine derivatives **4** were around 1.4−1.5 V (Scheme 5b), except the indolizine **4m** with a biphenyl moiety at 1.2 V.

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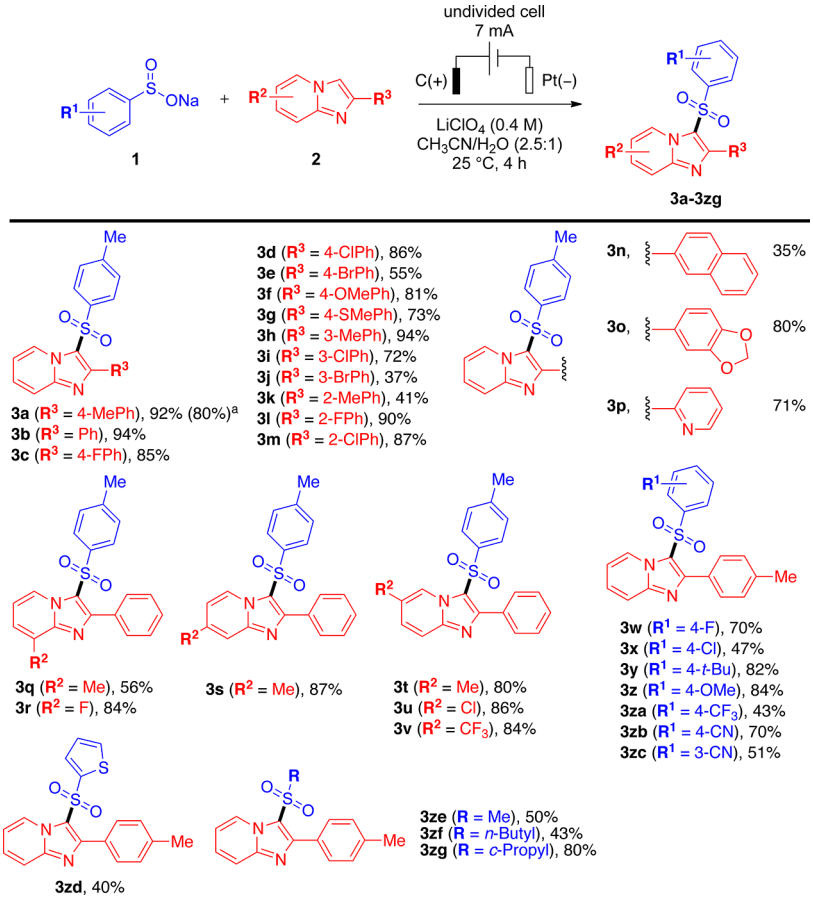
Scheme 2. Electrochemical Cross-Coupling between Sodium Sulfinates and Imidazopyridines



[a]Reaction on 1 mmol scale for 20 h.

However, the low yield observed for the indolizine **4m** was believed to originate from the poor solubility of **4m** and the corresponding product **5m**, but not due to a small oxidation potential difference to sodium sulfinates. As expected, the oxidation potentials of sodium sulfinates **1** in two different electrochemical conditions were also close to each other at around 1.0−1.2 V (Scheme 5c), except the sodium naphthalene-2-sulfinate **1k** that fell below 1.0 V in a mixture of CH_3CN/H_2O condition. Thus, the cyclic voltammetry measurements closely matched with the experimental results, suggesting that the indolizines **4** were better cross-coupling partners to the sodium naphthalene-2-sulfinate **1k** with their close oxidation potentials to each other, as opposed to imidazopyridines **2** with the oxidation potential difference of 0.5 V. Previously, the oxidation potential difference of 0.7 V between 2*H*-indazole and **1k** in CH_3CN/H_2O did not lead to the cross-coupled product.[16] The fact that the sodium naphthalene-2-sulfinate **1k** did not undergo the desired radical−radical cross-coupling reaction with the imidazopyridine **2a** in a mixture of CH_3CN/H_2O suggested that the close oxidation potential difference between two substrates is an important parameter for the proposed radical−radical cross-coupling reactions. The successful cross-coupling between the indolizine **4a** (the oxidation potential of around 1.4 V in DMF/H_2O) and the sodium naphthalene-2-sulfinate **1k** (the oxidation potential of 1.0 V in DMF/H_2O) further supports the predictive power of their oxidation potential-guided cross-coupling reactions. While more studies are needed to classify the nature of the radical species in the current electrochemical reaction conditions, the control experiments confirmed no reaction in the presence of a radical inhibitor, TEMPO. While the heteroarene radical cations from imidazopyridines and indolizines could not be captured by the known radical cation trapping agent, $P(OEt)_3$,[24] the EPR experiments clearly indicated the formation of DMPO−radical cation adducts. Thus, the heteroarene radical cations may have transient radical character,[25] whereas the sulfonyl radicals possess more likely the stable radical character. This interpretation may explain the excess use of sodium sulfinates **1** under the current electrochemical reaction conditions due to the radical−radical homocoupling pathway of sulfonyl radicals to α-disulfones that are known to undergo the homolytic dissociation to a variety of redox products.[26] Since the heteroarene radical cations from imidazopyridines and indolizines are believed to be generated in lower amounts relative to the sulfonyl radicals, the radical−radical homocoupling of the heteroarene radical cations may not represent the major pathway of imidazopyridines and indolizines under the current electrochemical reaction conditions. A mechanistic proposal based on the radical−radical cross-coupling is illustrated in Scheme 5d. Thus, while the different solvent systems are used due to the solubility issue, the anodic oxidation preference follows in the order of sodium sulfinate **1**, indolizine **4**, and imidazopyridine **2**. The preferential formation of the sulfonyl radical **A** and indolizine radical cation **B** under the electrochemical oxidation conditions in a DMF/H_2O mixture promotes the radical−radical cross-coupling reaction to give the 3-sulfonylated indolizines **5**.

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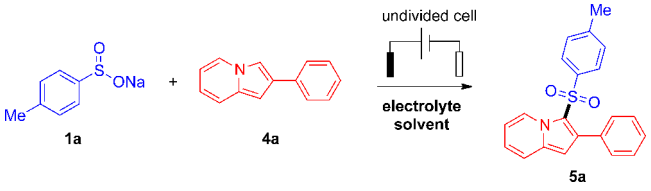
Table 2. Optimization of Electrochemical Cross-Coupling between Sodium Sulfinate and 2-Phenylindolizine[a]



entry	(+)/(−) (mA)	electrolyte (M)	solvent	yield[b] (%)
1	C(+)−Ni(−) (7)	$LiClO_4$ (0.40)	DMF	62
2	C(+)−Ni(−) (7)	$LiClO_4$ (0.40)	DMF/H_2O (7:1)	60
3	C(+)−Ni(−) (7)	$LiClO_4$ (0.40)	DMF/H_2O (7:0.5)	75
4	C(+)−Ni(−) (7)	$LiClO_4$ (0.40)	DMSO/H_2O (7:0.5)	0
5	C(+)−Ni(−) (7)	$LiClO_4$ (0.40)	EtOH/H_2O (7:0.5)	trace
6	C(+)−Ni(−) (7)	$LiClO_4$ (0.40)	CH_3CN/H_2O (7:0.5)	10
7	C(+)−Ni(−) (4)	$LiClO_4$ (0.40)	DMF/H_2O (7:0.5)	59
8	C(+)−Ni(−) (10)	$LiClO_4$ (0.40)	DMF/H_2O (7:0.5)	57
9	C(+)−Ni(−) (7)	$LiClO_4$ (0.30)	DMF/H_2O (7:0.5)	61
10	C(+)−Ni(−) (7)	$LiClO_4$ (0.50)	DMF/H_2O (7:0.5)	65
11	C(+)−Ni(−) (7)	NH_4I (0.40)	DMF/H_2O (7:0.5)	40
12	C(+)−Ni(−) (7)	*n*-Bu_4ClO_4 (0.40)	DMF/H_2O (7:0.5)	66
13	C(+)−Ni(−) (7)	*n*-Bu_4BF_4 (0.40)	DMF/H_2O (7:0.5)	49
14	C(+)−Ni(−) (7)	*n*-Bu_4I (0.40)	DMF/H_2O (7:0.5)	49
15	Pt(+)−Pt(−) (7)	$LiClO_4$ (0.40)	DMF/H_2O (7:0.5)	trace
16	C(+)−Pt(−) (7)	$LiClO_4$ (0.40)	DMF/H_2O (7:0.5)	71
17[c]	C(+)−Ni(−) (7)	$LiClO_4$ (0.40)	DMF/H_2O (7:0.5)	10
18[d]	C(+)−Ni(−) (7)	$LiClO_4$ (0.40)	DMF/H_2O (7:0.5)	69
19[e]	C(+)−Ni(−) (0)	$LiClO_4$ (0.40)	DMF/H_2O (7:0.5)	0

[a]Reaction using **1a** (0.4 mmol), **4a** (0.2 mmol), and electrolyte in solvent (M) in an undivided cell with constant current of 7 mA under argon for 2 h. [b]Isolated yield of **5a**. [c]Reaction using 1 equiv of **1a**. [d]Reaction using 3 equiv of **1a**. [e]No current.

Likewise, the sodium sulfinates **1** and the imidazopyridines **2** are anodically oxidized in a CH_3CN/H_2O mixture, paving a way to the cross-coupling reaction between the sulfonyl radical **A** and the imidazopyridine radical cation **C**. The cathodic reduction of protons to hydrogen gas balances the overall electrochemical reaction of sulfinates and heteroarenes.

CONCLUSION

In summary, we have developed the oxidation potential-guided radical−radical cross-coupling reactions for the sulfonylation of N-heterocycles. With the establishment of redox reagent-free and metal-free synthetic approaches to N-heteroaromatic compounds, the current cross-coupling strategy should be applicable for the introduction of various functional groups to heteroarenes via the electrochemical generation of radical species. We are currently working on the electrochemical functionalization of heterocyclic compounds, and our results will be reported in due course.

EXPERIMENTAL SECTION

Preparation and Characterization of Imidazo[1,2-*a*]-pyridines. Imidazo[1,2-*a*]pyridine starting materials were prepared on the basis of the literature procedure.[27] To a solution of CuI (0.25 mmol, 5 mol %), aminopyridine (5 mmol, 1 equiv), and acetophenone (10 mmol, 2 equiv) in DMF (5.0 mL) was added BF_3•Et_2O (0.1 mmol, 10 mol %) and the solution was stirred at 60 °C in an oil bath for 24 h under O_2 atmosphere. After the reaction was complete, the flask was cooled to room temperature and the reaction was quenched with saturated sodium carbonate solution (20 mL). The organic layer was extracted with dichloromethane (50 mL × 3), dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure, and the desired product was purified by column chromatograph on silica gel (20% ethyl acetate in hexanes).

*2-(p-Tolyl)imidazo[1,2-a]pyridine (**2a**).* (eluent: 4:1 hexanes/ethyl acetate). 933 mg (90%). The ^1H and ^{13}C NMR spectra for this compound were compared with the literature data.[27] ^1H NMR ($CDCl_3$, 600 MHz): δ 7.98−7.99 (m, 1H), 7.82 (d, 2H, J = 6.6 Hz), 7.72−7.83 (m, 1H), 7.98 (d, 1H, J = 9.0 H z), 7.21 (d, 2H, J = 6.6 Hz), 7.07−7.11 (m, 1H), 6.65−6.68 (m, 1H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 145.8, 145.6, 137.8, 130.9, 129.5, 126.0, 125.6, 124.5, 117.4, 112.3, 107.8, 21.3.

*2-Phenylimidazo[1,2-a]pyridine (**2b**).* (eluent: 4:1 hexanes/ethyl acetate). 596 mg (61%). The ^1H and ^{13}C NMR spectra for this compound were compared with the literature data.[27] ^1H NMR ($CDCl_3$, 600 MHz): δ 8.11 (d, 1H, J = 6.6 Hz), 7.96 (d, 2H, J = 7.2 Hz), 7.86 (s, 1H), 7.66 (d, 1H, J = 9.0 Hz), 7.44 (t, 2H, J = 7.8 Hz), 7.33 (t, 1H, J = 7.2 Hz), 7.18 (t, 1H, J = 7.8 Hz), 6.78 (t, 1H, J = 6.6 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 145.8, 145.7, 133.7, 128.8, 128.0, 126.1, 125.6, 124.7, 117.6, 112.5, 108.1.

*2-(4-Fluorophenyl)imidazo[1,2-a]pyridine (**2c**).* (eluent: 4:1 hexanes/ethyl acetate). 800 mg (75%). The ^1H and ^{13}C NMR spectra for this compound were compared with the literature data.[28] ^1H NMR ($CDCl_3$, 600 MHz): δ 8.00 (d, 1H, J = 7.2 Hz), 7.86−7.88 (m, 2H), 7.70 (s, 1H), 7.57 (d, 1H, J = 9.0 Hz), 7.06−7.12 (m, 3H), 6.69 (t, 1H, J = 6.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 162.7 (d, J = 245 Hz), 145.6, 144.8, 130.6, 127.7 (d, J = 8.5 H z), 125.6, 124.8, 117.4, 115.6 (d, J = 21.6 Hz), 112.5, 107.8.

*2-(4-Chlorophenyl)imidazo[1,2-a]pyridine (**2d**).* (eluent: 4:1 hexanes/ethyl acetate). 746 mg (65%). The ^1H and ^{13}C NMR spectra for this compound were compared with the literature data.[27] ^1H NMR ($CDCl_3$, 600 MHz): δ 8.01 (d, 1H, J = 6.6 Hz), 7.86−7.89 (m, 2H), 7.83 (s, 1H), 7.65 (d, 1H, J = 9.0 Hz), 7.37−7.39 (m, 2H), 7.19−7.22 (m, 1H), 6.80 (t, 1H, J = 6.6 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 145.7, 144.6, 133.7, 132.2, 128.9, 127.3, 125.7, 125.0, 117.5, 112.7, 108.2.

*2-(4-Bromophenyl)imidazo[1,2-a]pyridine (**2e**).* (eluent: 4:1 hexanes/ethyl acetate). 986 mg (72%). The ^1H and ^{13}C NMR spectra for this compound were compared with the literature data.[27] ^1H NMR ($CDCl_3$, 600 MHz): δ 8.08 (d, 1H, J = 6.6 Hz), 7.79−7.82 (m, 3H), 7.63 (d, 1H, J = 9.0 Hz), 7.52−7.54 (m, 2H), 7.17−7.20 (m, 1H), 6.78 (td, 1H, J = 6.6, 1.2 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 145.6, 144.5, 132.5, 131.9, 127.6, 125.7, 125.2, 122.0, 117.5, 112.8, 108.3.

*2-(4-Methoxyphenyl)imidazo[1,2-a]pyridine (**2f**).* (eluent: 4:1 hexanes/ethyl acetate). 803 mg (72%). The ^1H and ^{13}C NMR spectra for this compound were compared with the literature data.[27] ^1H NMR ($CDCl_3$, 600 MHz): δ 8.07 (d, 1H, J = 6.6 Hz), 7.88 (d, 2H, J = 8.4 Hz), 7.75 (s, 1H), 7.61 (d, 1H, J = 9.0 Hz), 7.14 (t, 1H, J = 7.2 Hz), 6.96 (d, 2H, J = 9.0 Hz), 6.73 (t, 1H, J = 7.2 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 159.6, 145.6(8), 145.6(0), 127.2, 126.4, 125.5, 124.6, 117.3, 114.2, 112.3, 107.3, 55.4.

*2-(4-(Methylthio)phenyl)imidazo[1,2-a]pyridine (**2g**).* (eluent: 4:1 hexanes/ethyl acetate). 767 mg (64%). The ^1H and ^{13}C NMR spectra for this compound were compared with the literature data.[27] ^1H NMR ($CDCl_3$, 600 MHz): δ 7.97 (d, 1H, J = 7.2 Hz), 7.80 (d, 2H, J = 7.2 H z),

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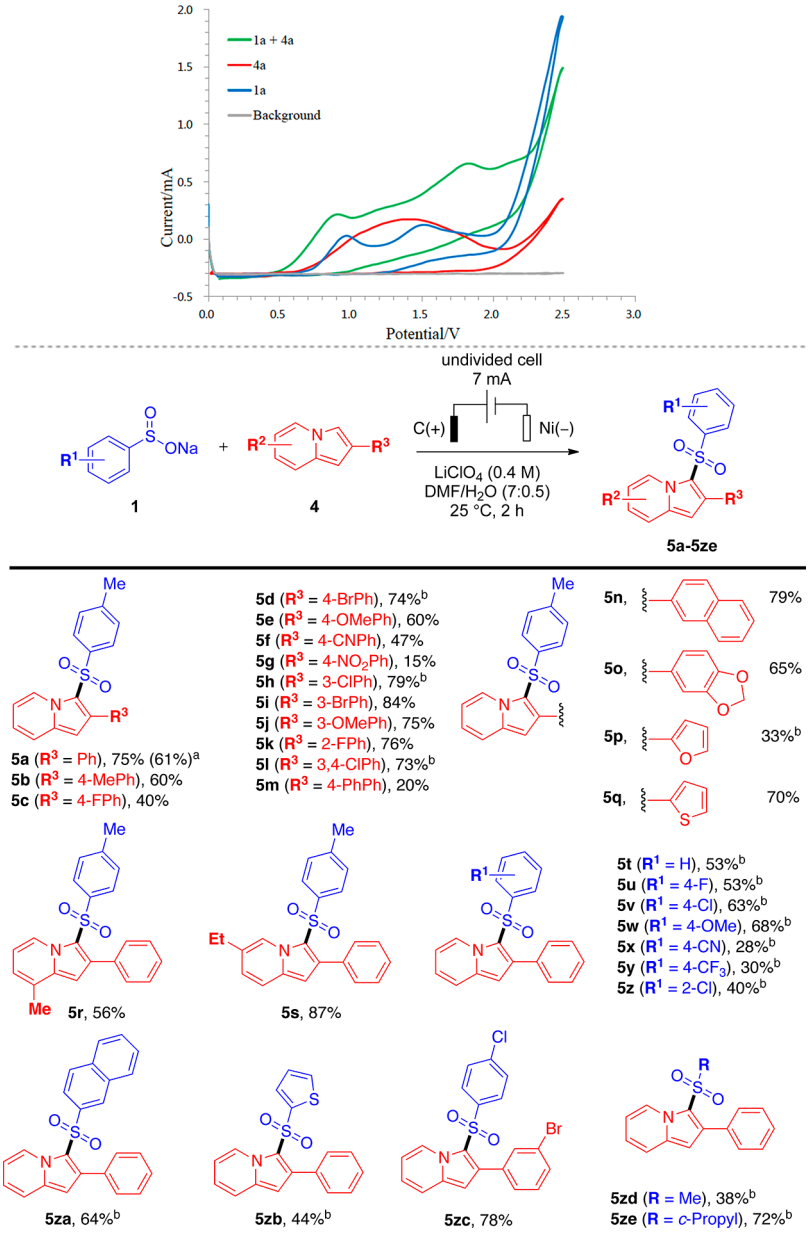
Scheme 3. Electrochemical Cross-Coupling between Sodium Sulfinates and Indolizines



[a]Reaction on 1 mmol scale for 10 h. [b]Reaction using 3 equiv of **1**.

7.69 (s, 1H), 7.55 (d, 1H, J = 9.0 Hz), 7.24 (d, 2H, J = 7.8 H z), 7.06–7.09 (m, 1H), 6.66 (t, 1H, J = 7.8 Hz), 2.54 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 145.6, 145.2, 138.2, 130.6, 126.7, 126.4, 125.6, 124.7, 117.3, 112.4, 107.9, 15.7.

*2-(m-Tolyl)imidazo[1,2-a]pyridine (**2h**).* (eluent: 4:1 hexanes/ethyl acetate). 788 mg (76%). The ^1H and ^{13}C NMR spectra for this compound were compared with the literature data.[29] ^1H NMR ($CDCl_3$, 600 MHz): δ 8.07 (d, 1H, J = 6.0 Hz), 7.82 (d, 2H, J = 7.8 Hz), 7.71 (d, 1H, J = 7.8 Hz), 7.62 (d, 1H, J = 9.0 Hz), 7.31 (t, 1H, J = 7.8 Hz), 7.13–7.16 (m, 2H), 6.74 (t, 1H, J = 6.0 Hz), 2.41 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 145.8, 145.6, 138.5, 133.5, 128.8, 128.6, 126.8, 125.6, 124.7, 123.1, 117.5, 112.4, 108.1, 21.5.

*2-(3-Chlorophenyl)imidazo[1,2-a]pyridine (**2i**).* (eluent: 4:1 hexanes/ethyl acetate). 598 mg (52%). The ^1H and ^{13}C NMR spectra for this compound were compared with the literature data.[29] ^1H NMR ($CDCl_3$, 600 MHz): δ 8.12–8.13 (m, 1H), 7.95–7.96 (m, 1H) 7.83–7.86 (m, 2H), 7.65–7.67 (m, 1H), 7.36 (t, 1H, J = 8.4 Hz), 7.30 (d, 1H, J = 7.2 Hz), 7.20–7.22 (m, 1H), 6.80–6.82 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 145.5, 134.8, 130.1, 128.1, 126.1(2C), 125.8, 125.4, 125.3, 124.2, 117.6, 112.9, 108.6.

*2-(3-Bromophenyl)imidazo[1,2-a]pyridine (**2j**).* (eluent: 4:1 hexanes/ethyl acetate). 952 mg (70%). The ^1H and ^{13}C NMR spectra for this compound were compared with the literature data.[30] ^1H NMR ($CDCl_3$, 600 MHz): δ 8.08–8.09 (m, 1H), 8.04 (d, 1H, J = 7.2 Hz), 7.80–7.83 (m, 1H), 7.77 (s, 1H), 7.58 (d, 1H, J = 9.0 H z), 7.39–7.41 (m, 1H), 7.24 (t, 1H, J = 8.4 Hz), 7.12–7.15 (m, 1H), 6.73 (td, 1H, J = 6.6, 1.2 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 145.6, 144.0, 135.9, 130.7, 130.2, 128.9, 125.7, 125.1, 124.5, 122.9, 117.4, 112.6, 108.6.

*2-(o-Tolyl)imidazo[1,2-a]pyridine (**2k**).* (eluent: 4:1 hexanes/ethyl acetate). 633 mg (61%). The ^1H and ^{13}C NMR spectra for this compound were compared with the literature data.[27] ^1H NMR ($CDCl_3$, 600 MHz): δ 7.88–7.90 (m, 2H), 7.53 (d, 1H, J = 9.0 Hz), 7.52 (s, 1H), 7.21–7.25 (m, 1H), 7.17–7.18 (m, 2H), 6.98–7.01 (m, 1H), 6.55 (t, 1H, J = 7.2 Hz), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 145.3, 144.7, 135.7, 133.4, 130.9, 129.7, 127.7, 126.0, 125.6, 124.5, 117.3, 112.1, 110.8, 21.6.

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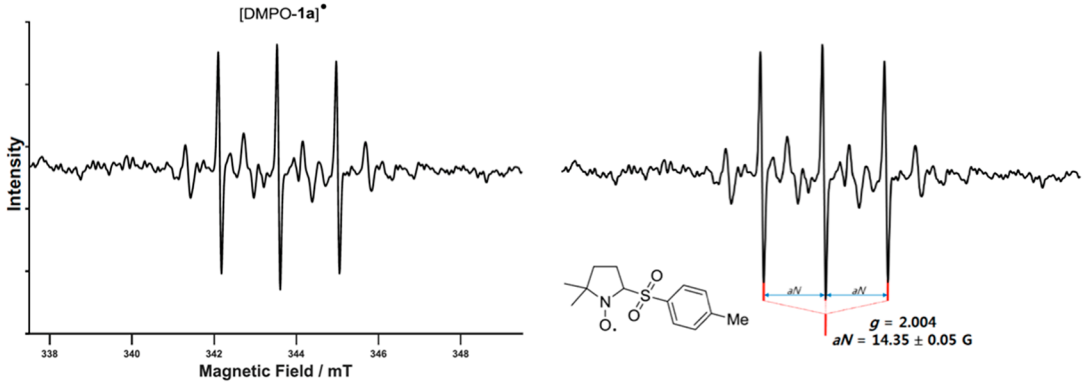
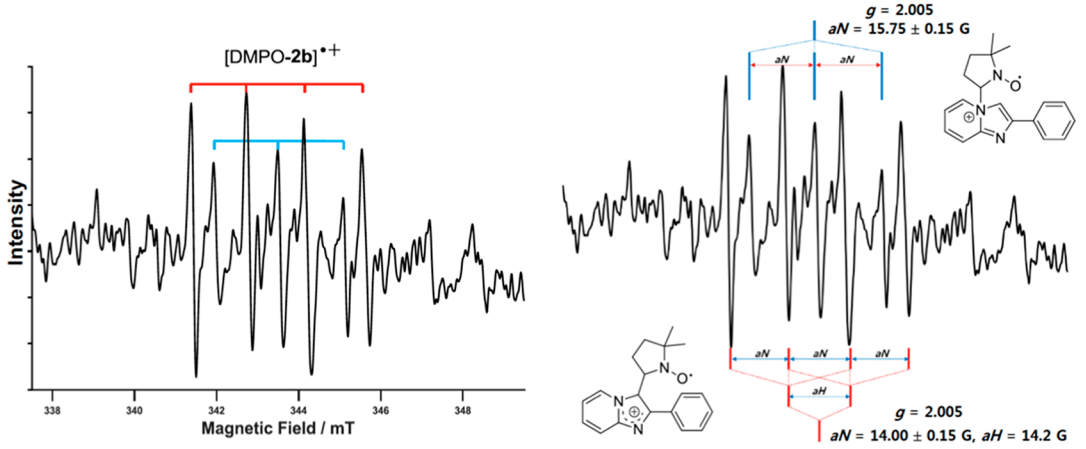
Scheme 4. Electron Paramagnetic Resonance Spectra of Electrochemically Generated Radical Species

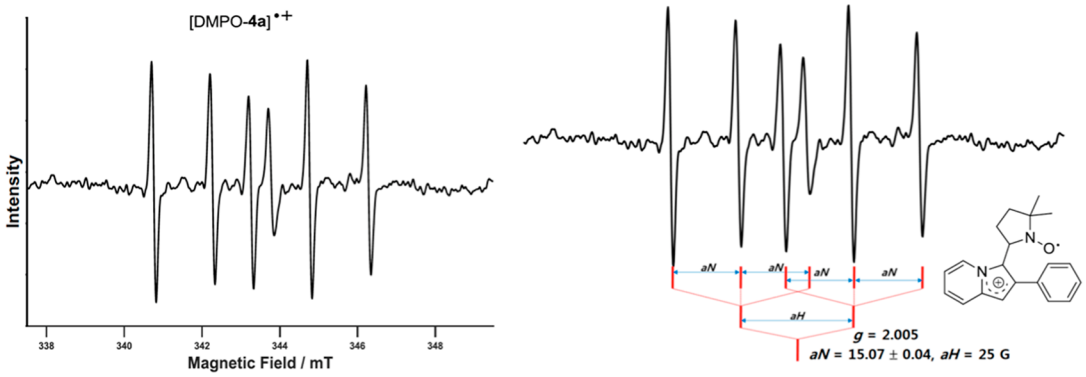
(a) EPR spectrum of [DMPO-**1a**] radical



(b) EPR spectrum of [DMPO-**2a**] radical cation



(c) EPR spectrum of [DMPO-**4a**] radical cation



2-(2-Fluorophenyl)imidazo[1,2-a]pyridine (***2l***). (eluent: 4:1 hexanes/ethyl acetate). 795 mg (75%). The ^{1}H and ^{13}C NMR spectra for this compound were compared with the literature data.[27] ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.32−8.36 (m, 1H), 8.01 (s,1H), 7.96 (s, 1H), 7.58 (d, 1H, J = 8.4 Hz), 7.21−7.23 (m, 2H), 7.08−7.11 (m, 2H), 6.58−6.66 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 160.4 (d, J = 248.5 Hz), 144.9, 139.2, 129.0 (d, J = 7.2 Hz), 129.9 (d, J = 4.3 Hz), 125.8, 125.0, 124.5 (d, J = 2.8 Hz), 121.6 (d, J = 12.9 H z), 117.5, 115.7 (d, J = 22.9 Hz), 112.5, 112.1 (d, J = 14.4 Hz).

2-(2-Chlorophenyl)imidazo[1,2-a]pyridine (***2m***). (eluent: 4:1 hexanes/ethyl acetate). 779 mg (68%). The ^{1}H and ^{13}C NMR spectra for this compound were compared with the literature data.[27] ^{1}H NMR

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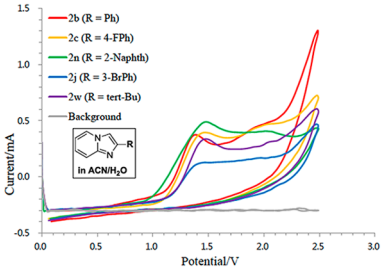
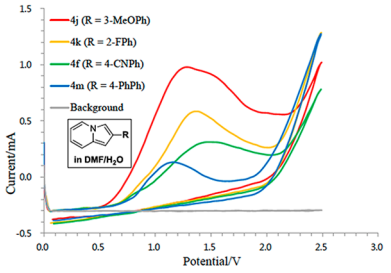
Scheme 5. Oxidation Potential-Guided Radical−Radical Cross-Coupling Strategy and Mechanistic Interpretation

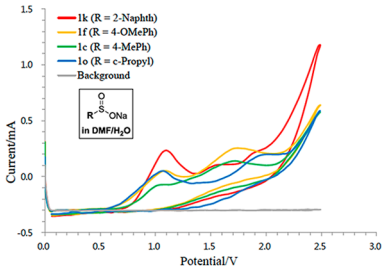
(a) Oxidation potentials of imidazopyridines **2**

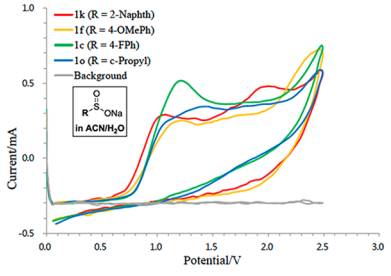


(b) Oxidation potentials of indolizines **4**

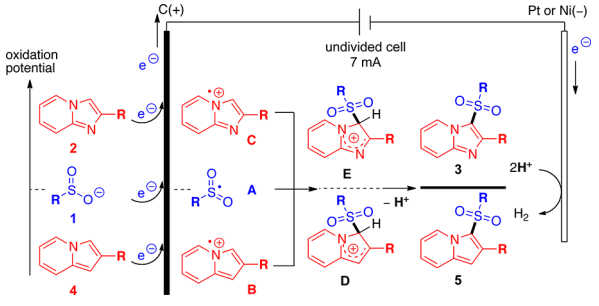


(c) Oxidation potentials of sodium sulfinates **1** in different solvents





(d) Proposed radical-radical coupling mechanism



(CDCl$_3$, 600 MHz): δ 8.22 (dd, 1H, J = 7.8, 1.8 Hz), 8.07 (s, 1H), 7.85 (d, 1H, J = 7.2 Hz), 7.46 (d, 1H, J = 9.0 Hz), 7.31 (d, 1H, J = 7.8 Hz), 7.23 (t, 1H, J = 7.8 Hz), 7.08 (td, 1H, J = 7.2, 1.8 Hz), 6.93−6.95 (m, 1H), 6.49 (t, 1H, J = 6.6 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$, 150 MHz): δ 144.3, 141.6, 132.3, 131.6, 130.9, 130.3, 128.5, 127.0, 125.7, 124.8, 117.3, 112.4, 112.3.

*2-(Naphthalen-2-yl)imidazo[1,2-a]pyridine (**2n**).* (eluent: 4:1 hexanes/ethyl acetate). 277 mg (23%). The ^{1}H and ^{13}C NMR spectra for this compound were compared with the literature data.[30] ^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.49 (s, 1H), 7.93−7.95 (m, 2H), 7.90 (d, 1H, J = 8.4 Hz), 7.83 (d, 1H, J = 8.4 Hz), 7.76−7.83 (m, 2H), 7.63 (d, 1H, J = 8.4 Hz), 7.43−7.48 (m, 2H), 7.08−7.11 (m, 1H), 6.64 (t, 1H, J = 7.2 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$, 150 MHz): δ 145.8, 145.6, 133.8, 133.2, 131.1, 128.4, 128.3, 127.7, 126.3, 126.0, 125.7, 124.9, 124.7, 124.2, 117.4, 112.4, 108.7.

*2-(Benzo[d][1,3]dioxol-5-yl)imidazo[1,2-a]pyridine (**2o**).* (eluent: 4:1 hexanes/ethyl acetate). 646 mg (54%). The ^{1}H and ^{13}C NMR spectra for this compound were compared with the literature data.[31] ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.98 (d, 1H, J = 6.0 Hz), 7.65 (s, 1H), 7.54 (d, 1H, J = 9.0 Hz), 7.39−7.43 (m, 2H), 7.07−7.11 (m, 1H), 6.83 (d, 1H, J = 8.4 Hz), 6.67 (t, 1H, J = 6.0 Hz), 5.94 (s, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$, 150 MHz): δ 148.1, 147.5, 145.6, 145.5, 128.1, 125.5, 124.6, 119.8, 117.2, 112.3, 108.6, 107.5, 106.6, 101.1.

*2-(Pyridin-2-yl)imidazo[1,2-a]pyridine (**2p**).* (eluent: 4:1 hexanes/ethyl acetate). 370 mg (38%). The ^{1}H and ^{13}C NMR spectra for this compound were compared with the literature data.[27] ^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.06 (d, 1H, J = 4.2 Hz), 8.25 (s, 1H), 8.19 (d, 1H, J = 8.4 Hz), 8.15 (d, 1H, J = 7.2 Hz), 7.77 (td, 1H, J = 7.2, 1.2 Hz), 7.64 (d, 1H, J = 9.0 Hz), 7.17−7.22 (m, 2H), 6.80 (t, 1H, J = 7.2 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$, 150 MHz): δ 152.9, 149.4 (2C), 145.6, 136.9, 126.0, 125.0, 122.7, 120.5, 117.9, 112.8, 110.9.

*8-Methyl-2-phenylimidazo[1,2-a]pyridine (**2q**).* (eluent: 4:1 hexanes/ethyl acetate). 428 mg (41%). The ^{1}H and ^{13}C NMR spectra for this compound were compared with the literature data.[27] ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.97 (d, 2H, J = 7.8 Hz), 7.77−7.82 (m, 1H), 7.67−7.69 (m, 1H), 7.42 (t, 2H, J = 7.8 Hz), 7.31 (t, 1H, J = 7.8 Hz), 6.86 (s, 1H), 6.53−6.55 (m, 1H), 2.65 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$, 150 MHz): δ 146.2, 145.1, 134.2, 128.7, 127.8, 127.4, 126.2, 123.5, 123.3, 112.3, 108.7, 17.2.

*8-Fluoro-2-phenylimidazo[1,2-a]pyridine (**2r**).* (eluent: 4:1 hexanes/ethyl acetate). 640 mg (60%). The ^{1}H and ^{13}C NMR spectra for this compound were compared with the literature data.[31] ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.98 (d, 2H, J = 7.8 Hz), 7.94 (d, 1H, J = 6.6 Hz), 7.91 (d, 1H, J = 3.0 H z), 7.43 (t, 2H, J = 7.8 Hz), 7.34 (t, 1H, J = 7.8 Hz), 6.87 (dd, 1H, J = 10.2, 7.8 Hz), 6.67−6.70 (m, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$, 150 MHz): δ 151.6 (d, J = 251.2 Hz), 146.2, 138.3 (d, J = 27.3 Hz), 133.1, 128.8, 128.3, 126.3, 122.0 (d, J = 4.3 Hz), 115.4 (d, J = 7.2 Hz), 109.5, 107.3 (d, J = 17.1 Hz).

*6-Methyl-2-phenylimidazo[1,2-a]pyridine (**2s**).* (eluent: 4:1 hexanes/ethyl acetate). 704 mg (68%). The ^{1}H and ^{13}C NMR spectra for this compound were compared with the literature data.[27] ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.91 (d, 2H, J = 7.4 Hz), 7.78 (s, 1H), 7.68 (s, 1H), 7.49 (d, 1H, J = 9.0 Hz), 7.40 (t, 2H, J = 7.4 Hz), 7.29 (t, 1H, J = 7.4 Hz), 6.96 (d, 1H, J = 9.0 Hz), 2.24 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$, 150 MHz): δ 145.2, 144.6, 133.7, 128.7, 128.1, 127.9, 125.9, 123.4, 122.2, 116.6, 107.9, 18.1.

*7-Methyl-2-phenylimidazo[1,2-a]pyridine (**2t**).* (eluent: 4:1 hexanes/ethyl acetate). 639 mg (61%). The ^{1}H and ^{13}C NMR spectra for this compound were compared with the literature data.[27] ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.79 (d, 2H, J = 7.2 Hz), 7.67 (d, 1H, J = 7.2 Hz), 7.49 (s, 1H), 7.27 (t, 2H, J = 7.2 Hz), 7.20 (s, 1H), 7.17 (t, 1H, J = 7.2 Hz), 6.33 (d, 1H, J = 7.2 Hz), 2.18 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$, 150 MHz): δ 146.1, 145.3, 135.5, 134.0, 128.7, 127.8, 125.9, 124.8, 115.7, 114.9, 107.6, 21.3.

*6-Chloro-2-phenylimidazo[1,2-a]pyridine (**2u**).* (eluent: 4:1 hexanes/ethyl acetate). 292 mg (26%). The ^{1}H and ^{13}C NMR spectra for this compound were compared with the literature data.[27] ^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.14 (d, 1H, J = 1.2 Hz), 7.91−7.93 (m, 2H), 7.80 (s, 1H), 7.58 (d, 1H, J = 9.6 H z), 7.43 (t, 2H, J = 7.8 Hz), 7.34 (t, 1H, J = 7.8 Hz), 7.13 (dd, 1H, J = 9.6, 2.4 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$, 150 MHz): δ 146.6, 143.9, 133.0, 128.9, 128.4, 126.3, 126.1, 123.4, 120.8, 117.7, 108.5.

*2-Phenyl-6-(trifluoromethyl)imidazo[1,2-a]pyridine (**2v**).* (eluent: 4:1 hexanes/ethyl acetate). 278 mg (21%). The ^{1}H and ^{13}C NMR

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spectra for this compound were compared with the literature data.[32] ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.53 (s, 1H), 7.96−7.98 (m, 3H), 7.83 (d, 1H, J = 9.6 Hz), 7.46 (t, 2H, J = 7.8 Hz), 7.34−7.39 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 142.6, 140.4, 127.8, 124.2, 124.0, 121.5, 119.9 (q, J = 5.7 Hz), 118.7 (q, J = 267 Hz), 116.2, 113.2, 112.4 (q, J = 34.3 Hz), 104.5.

*2-tert-Butylimidazo[1,2-a]pyridine (**2w**).* (eluent: 4:1 hexanes/ethyl acetate). 262 mg (30%). The ^{1}H and ^{13}C NMR spectra for this compound were compared with the literature data.[27] ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.84 (d, 1H, J = 6.6 Hz), 7.39 (d, 1H, J = 9.6 Hz), 7.15 (s, 1H), 6.89−6.92 (m, 1H), 6.48 (t, 1H, J = 7.2 Hz), 1.29 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 157.1, 144.8, 125.3, 123.7, 117.0, 111.5, 106.7, 32.2, 30.2.

General Procedure A for Electrochemical Sulfonylation of Imidazopyridines. An undivided cell equipped with a glassy carbon anode and a platinum cathode was connected to an ElectraSyn 2.0. A solution of imidazo[1,2-*a*]pyridine (**2**, 0.2 mmol), sodium sulfinate (**1**, 0.6 mmol), and $LiClO_4$ (320 mg, 0.42 M) in a mixture of CH_3CN and H_2O (7 mL, v/v = 2.5:1) was added to the undivided cell. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA under room temperature for 4 h. After the reaction was complete, the residue was diluted with EtOAc (10 mL), washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (EtOAc/Hex (v/v) = 2:5) to afford the desired product **3**.

For 1 mmol Scale Reaction. An undivided cell equipped with a glassy carbon anode and a platinum cathode was connected to an ElectraSyn 2.0. Sodium *p*-toluenesulfinate (**1a**, 3.0 mmol), 2-(*p*-tolyl)imidazo[1,2-*a*]pyridine (**2a**, 1.0 mmol), and $LiClO_4$ (1.6 g, 0.42 M) was dissolved in a mixture of CH_3CN and H_2O (21 mL, v/v = 2.5:1) and added to the undivided cell. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA under room temperature for 20 h. After the reaction was complete, the residue was diluted with EtOAc (50 mL), washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (EtOAc/Hex (v/v) = 2:5) to afford the desired product **3a** (290 mg, 80% yield).

Characterization of the Compounds in Scheme 2. *2-(p-Tolyl)-3-tosylimidazo[1,2-a]pyridine (**3a**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2a** (0.2 mmol). 67 mg (92%), white solid, mp 177.6−179.0 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.06 (d, 1H, J = 7.2 Hz), 7.69 (d, 1H, J = 9.0 Hz), 7.64 (d, 2H, J = 8.4 Hz), 7.52 (d, 2H, J = 8.4 Hz), 7.39−7.42 (m, 1H), 7.25 (d, 2H, J = 8. 4 Hz), 7.12 (d, 2H, J = 8.4 Hz), 7.01 (t, 1H, J = 7.2 Hz), 2.41 (s, 3H), 2.29 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 152.8, 146.5, 144.4, 139.4, 139.1, 130.5, 129.7 (2C), 129.6, 128.6, 126.8, 126.4, 117.8, 117.6, 114.6, 21.5(8), 21.5(5). IR (neat): 2866, 1638, 1466, 1321, 1144, 1084, 1004, 821, 762, 680 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{19}N_2O_2S$ $[M + H]^+$ 363.1162; Found 363.1159.

*2-Phenyl-3-tosylimidazo[1,2-a]pyridine (**3b**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2b** (0.2 mmol). The ^{1}H and ^{13}C NMR spectra for this compound were compared with the literature data.[17] 66 mg (94%); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.11 (d, 1H, J = 7.2 Hz), 7.71−7.74 (m, 3H), 7.52 (d, 2H, J = 7.8 Hz), 7.43−7.47 (m, 4H), 7.13 (d, 2H, J = 7.8 Hz), 7.05 (td, 1H, J = 7.2, 1.2 Hz), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 152.6, 146.5, 144.5, 139.1, 132.5, 130.6, 129.7, 129.4, 128.6, 127.8, 126.9. 126.4, 118.0, 117.9, 114.7, 21.5.

*2-(4-Fluorophenyl)-3-tosylimidazo[1,2-a]pyridine (**3c**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2c** (0.2 mmol). 62 mg (85%), white solid, mp 144.1−145.3 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.09 (d, 1H, J = 6.6 Hz), 7.74−7.77 (m, 2H), 7.70 (d, 1H, J = 9.0 Hz), 7.57 (d, 2H, J = 8.4 Hz), 7.44−7.47 (m, 1H), 7.12−7.16 (m, 4H), 7.05 (td, 1H, J = 6.6, 1.2 Hz), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 163.7 (d, J = 248.4, Hz), 151.6, 146.5, 144.6, 139.0, 132.6 (d, J = 8.7 Hz), 129.8, 128.7, 128.6, 126.9, 126.4, 117.9, 117.8, 115.0 (d, J = 21.6 Hz), 114.7, 21.6. ^{19}F NMR (564 MHz, $CDCl_3$): δ −111.6. IR (neat): 3131, 2927, 1600, 1466, 1317, 1222, 1138, 1084, 842, 810, 678 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{16}FN_2O_2S$ $[M + H]^+$ 367.0904; Found 367.0911.

*2-(4-Chlorophenyl)-3-tosylimidazo[1,2-a]pyridine (**3d**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2d** (0.2 mmol). 66 mg (86%), white solid, mp 167−169 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.06 (d, 1H, J = 6.6 Hz), 7.71 (d, 2H, J = 8.4 Hz), 7.68 (d, 1H, J = 9.0 Hz), 7.52 (d, 2H, J = 8.4 Hz), 7.41−7.45 (m, 3H), 7.14 (d, 2H, J = 8.4 Hz), 7.04 (t, 1H, J = 6.6 Hz), 2.31 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 151.4, 146.6, 144.7, 138.9, 135.6, 132.0, 131.2, 129.8, 128.7, 128.1, 126.8, 126.4, 118.0, 117.9, 114.8, 21.6. IR (neat): 3010, 2987, 1636, 1496, 1272, 1149, 836, 764, 676 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{16}ClN_2O_2S$ $[M + H]^+$ 383.0615; Found 383.0625.

*2-(4-Bromophenyl)-3-tosylimidazo[1,2-a]pyridine (**3e**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2e** (0.2 mmol). 47 mg (55%), white solid, mp 170.8−172.1 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.08 (d, 1H, J = 7.2 Hz), 7.70 (d, 1H, J = 9.0 Hz), 7.65 (d, 2H, J = 8.4 Hz), 7.59 (d, 2H, J = 8.4 Hz), 7.53 (d, 2H, J = 7.8 Hz), 7.44−7.47 (m, 1H), 7.16 (d, 2H, J = 7.8 Hz), 7.06 (td, 1H, J = 7.2, 1.2 Hz), 2.33 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 151.5, 146.6, 144.7, 138.9, 132.2, 131.6, 131.1, 129.8, 128.7, 126.8, 126.4, 124.1, 118.0, 117.9, 114.8, 21.6. IR (neat): 3093, 2931, 1640, 1599, 1496, 1461, 1319, 1144, 1086, 1008, 833, 747, 678 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{16}BrN_2O_2S$ $[M + H]^+$ 427.0110; Found 427.0106.

*2-(4-Methoxyphenyl)-3-tosylimidazo[1,2-a]pyridine (**3f**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2f** (0.2 mmol). 61 mg (81%), white solid, mp 151.1−152.3 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.08 (d, 1H, J = 6.6 Hz), 7.74 (d, 2H, J = 9.0 Hz), 7.70 (d, 1H, J = 9.0 Hz), 7.51 (d, 2H, J = 7.8 Hz), 7.41−7.44 (m, 1H), 7.13 (d, 2H, J = 7.8 Hz), 7.02 (t, 1H, J = 6.6 Hz), 6.98 (d, 2H, J = 9.0 Hz), 3.87 (s, 3H), 2.30 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 160.7, 152.5, 146.6, 144.4, 139.1, 132.1, 129.7, 128.7, 126.9, 126.3, 124.7, 117.7, 117.3, 114.6, 113.4, 55.4, 21.5. IR (neat): 3145, 2944, 2844, 1615, 1457, 1313, 1250, 1176, 1142, 1088, 1034, 812, 766, 676 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{19}N_2O_3S$ $[M + H]^+$ 379.1111; Found 379.1106.

*2-(4-(Methylthio)phenyl)-3-tosylimidazo[1,2-a]pyridine (**3g**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2g** (0.2 mmol). 58 mg (73%), white solid, mp 161.8−163.0 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.07 (d, 1H, J = 7.8 Hz), 7.69−7.72 (m, 3H), 7.52 (d, 2H, J = 7.8 Hz), 7.42−7.44 (m, 1H), 7.30 (d, 2H, J = 8.4 Hz), 7.14 (d, 2H, J = 8.4 Hz), 7.03 (td, 1H, J = 7.8, 1.2 Hz), 2.52 (s, 3H), 2.31 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 152.1, 146.5, 144.5, 140.6, 139.0, 131.0, 129.8, 128.9, 128.7, 126.8, 126.4, 125.3, 117.8, 117.6, 114.7, 21.6, 15.4. IR (neat): 3073, 2927, 1597, 1498, 1463, 1297, 1142, 1086, 823, 762, 682 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{19}N_2O_2S_2$ $[M + H]^+$ 395.0882; Found 395.0882.

*2-(m-Tolyl)-3-tosylimidazo[1,2-a]pyridine (**3h**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2h** (0.2 mmol). 68 mg (94%), white solid, mp 130.8−132.0 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.08 (d, 1H, J = 6.6 Hz), 7.69 (d, 1H, J = 9.0 Hz), 7.52−7.53 (m, 3H), 7.48 (s, 1H), 7.40−7.43 (m, 1H), 7.32 (t, 1H, J = 7.8 Hz), 7.25 (d, 1H, J = 7.2 Hz), 7.12 (d, 2H, J = 8.4 Hz), 7.02 (td, 1H, J = 7.8 Hz), 2.39 (s, 3H), 2.30 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 152.8, 146.5, 144.4, 139.1, 137.4, 132.4, 131.0, 130.1, 129.7, 127.6, 127.8, 127.7, 126.9, 126.5, 117.9, 117.8, 114.6, 21.5, 21.4. IR (neat): 3032, 2927, 1634, 1599, 1496, 1321, 1138, 1082, 874, 792, 684 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{19}N_2O_2S$ $[M + H]^+$ 363.1162; Found 363.1157.

*2-(3-Chlorophenyl)-3-tosylimidazo[1,2-a]pyridine (**3i**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2i** (0.2 mmol). Light yellow solid, 55 mg (72%), solid, mp 179.0−180.4 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.10 (d, 1H, J = 6.6 Hz), 7.71 (d, 1H, J = 9.0 Hz), 7.66−7.69 (m, 2H), 7.55 (d, 2H, J = 7.8 Hz), 7.43−7.48 (m, 2H), 7.39 (t, 1H, J = 7.8 Hz), 7.17 (d, 2H, J = 7.8 Hz), 7.07 (t, 1H, J = 6.6 Hz), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 150.8, 146.5, 144.8,

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138.8, 134.3, 133.8, 130.4, 129.8, 129.4, 129.1, 128.9, 128.8, 126.9, 126.5, 118.2, 118.1, 114.9, 21.6. IR (neat): 3091, 2929, 1597, 1492, 1461, 1319, 1144, 1084, 1008, 872, 818, 741, 678 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{16}ClN_2O_2S$ $[M + H]^+$ 383.0615; Found 383.0613.

*2-(3-Bromophenyl)-3-tosylimidazo[1,2-a]pyridine (**3j**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2j** (0.2 mmol). 32 mg (37%), white solid, mp 167.1−168.6 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.10 (d, 1H, J = 6.6 Hz), 7.81 (s, 1H), 7.72 (m, 2H), 7.59 (m, 1H), 7.55 (d, 2H, J = 8.4 Hz), 7.46−7.48 (m, 1H), 7.33 (t, 1H, J = 7.8 Hz), 7.18 (d, 2H, J = 8.4 Hz), 7.08 (td, 1H, J = 6.6, 1.2 Hz), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 150.7, 146.5, 144.8, 138.8, 134.5, 133.1, 132.4, 129.9, 129.4(4), 129.4(1), 128.8, 126.9, 126.5, 121.9, 118.3, 118.0, 114.9, 21.6. IR (neat): 2967, 2929, 1597, 1563, 1494, 1459, 1319, 1144, 1084, 816, 795, 676 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{16}BrN_2O_2S$ $[M + H]^+$ 427.0110; Found 427.0105.

*2-(o-Tolyl)-3-tosylimidazo[1,2-a]pyridine (**3k**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2k** (0.2 mmol). 30 mg (41%), white solid, mp 149.5−150.1 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.14 (d, 1H, J = 7.2 H), 7.72 (d, 1H, J = 9.0 Hz), 7.48 (d, 2H, J = 8.4 Hz), 7.45−7.47 (m, 1H), 7.33−7.36 (m, 1H), 7.23−7.25 (m, 3H), 7.14 (d, 2H, J = 8.4 Hz), 7.08 (t, 1H, J = 7.2 Hz), 2.34 (s, 3H), 2.02 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 151.3, 145.9, 144.6, 138.8, 137.6, 131.6, 130.7, 129.9, 129.7, 129.4, 128.7, 126.8(3), 126.9(1), 125.0, 119.1, 117.8, 114.9, 21.6, 20.0. IR (neat): 3071, 2927, 1600, 1487, 1463, 1325, 1146, 1088, 810, 762 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{19}N_2O_2S$ $[M + H]^+$ 363.1162; Found 363.1154.

*2-(2-Fluorophenyl)-3-tosylimidazo[1,2-a]pyridine (**3l**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2l** (0.2 mmol). 66 mg (90%), white solid, mp 126.4−127.3 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 8.88 (d, 1H, J = 6.6 Hz), 7.72 (d, 1H, J = 9.0 Hz), 7.65 (d, 2H, J = 8.4 Hz), 7.52 (td, 1H, J = 7.8, 1.8 Hz), 7.42−7.47 (m, 2H), 7.25 (t, 1H, J = 7.8 Hz), 7.20 (d, 2H, J = 8.4 Hz), 7.16 (t, 1H, J = 7.8 Hz), 7.04 (td, 1H, J = 6.6, 1.2 Hz), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 160.4 (d, J = 248.5 Hz), 146.6 (d, J = 5.7 Hz), 144.7, 138.5, 132.5, 131.3 (d, J = 8.7 Hz), 129.9, 128.6, 126.8, 126.3, 123.6(9), 123.6(7), 121.1 (d, J = 14.4 Hz), 119.2, 118.2, 115.5 (d, J = 21.6 Hz) 114.9, 21.6. ^{19}F NMR (564 MHz, $CDCl_3$): δ −112.8. IR (neat): 3054, 2929, 1625, 1599, 1494, 1463, 1325, 1226, 1144, 1086, 1008, 814, 754, 678 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{16}FN_2O_2S$ $[M + H]^+$ 367.0911; Found 367.0903.

*2-(2-Chlorophenyl)-3-tosylimidazo[1,2-a]pyridine (**3m**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2m** (0.2 mmol). 67 mg (87%), white solid, mp 167.0−168.1 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 8.99 (d, 1H, J = 7.2 Hz), 7.74 (d, 1H, J = 9.0 Hz), 7.62 (d, 2H, J = 7.8 Hz), 7.45−7.47 (m, 3H), 7.40−7.43 (m, 1H), 7.36 (td, 1H, J = 7.8, 1.2 Hz), 7.19 (d, 2H, J = 7.8 Hz), 7.08 (td, 1H, J = 7.2, 1.8 Hz), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 149.3, 146.3, 144.7, 138.4, 134.0, 132.7, 132.0, 130.5, 129.8, 129.3, 128.5, 127.0, 126.4 128.0, 119.2, 118.3, 114.9, 21.6. IR (neat): 3097, 1600, 1485, 1444, 1325, 1148, 1090, 769, 676 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{16}ClN_2O_2S$ $[M + H]^+$ 383.0615; Found 383.0617.

*2-(Naphthalen-2-yl)-3-tosylimidazo[1,2-a]pyridine (**3n**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2n** (0.2 mmol). 28 mg (35%), white solid, mp 187.8−189.5 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.14 (d, 1H, J = 7.8 Hz), 8.27 (s, 1H), 7.89−7.94 (m, 3H), 7.86 (dd, 1H, J = 8.4, 1.2 Hz), 7.76 (d, 1H, J = 9.0 Hz), 7.51−7.56 (m, 4H), 7.46−7.49 (m, 1H), 7.08 (d, 2H, J = 8.4 Hz), 7.06−7.08 (m, 1H), 2.28 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 152.5, 146.6, 144.5, 139.0, 133.7, 132.7, 130.6, 129.9, 129.7, 128.8, 128.7, 127.8, 127.7, 127.4, 126.9(9), 126.9(0), 126.5, 126.3, 118.1, 118.0, 114.7, 21.5. IR (neat): 3158, 3058, 2929, 1638, 1597, 1490, 1317, 1146, 1082, 831, 760, 684 cm^{-1}. HRMS (ESI): m/z calcd for $C_{24}H_{19}N_2O_2S$ $[M + H]^+$ 399.1161; Found 399.1160.

*2-(Benzo[d][1,3]dioxol-5-yl)-3-tosylimidazo[1,2-a]pyridine (**3o**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2o** (0.2 mmol). 63 mg (80%), white solid, mp 154.8−155.9 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.08 (d, 1H, J = 7.2 Hz), 7.68 (d, 1H, J = 9.0 Hz), 7.57 (d, 2H, J = 8.4 Hz), 7.42−7.45 (m, 1H), 7.25−7.30 (m, 2H), 7.16 (d, 2H, J = 8.4 Hz), 7.03 (td, 1H, J = 7.2, 1.2 Hz), 6.90 (d, 1H, J = 7.8 Hz), 6.03 (s, 2H), 2.33 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 152.3, 148.7, 147.2, 146.5, 144.5, 139.1, 129.7, 128.6, 126.9, 126.4, 126.3, 125.1, 117.8, 117.4, 114.6, 111.0, 107.9, 101.3, 21.6. IR (neat): 3144, 2905, 1632, 1600, 1486, 1373, 1321, 1299, 1241, 1155, 1038, 939, 857, 812, 769 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{17}N_2O_4S$ $[M + H]^+$ 393.0903; Found 393.0899.

*2-(Pyridin-2-yl)-3-tosylimidazo[1,2-a]pyridine (**3p**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2p** (0.2 mmol). 50 mg (71%), white solid, mp 113.9−115.1 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.04 (d, 1H, J = 7.2 Hz), 8.73 (d, 1H, J = 4.8 Hz), 7.98 (d, 2H, J = 8.4 Hz), 7.94 (d, 1H, J = 7.8 Hz), 7.82 (td, 1H, J = 7.8, 1.2 Hz), 7.72 (d, 1H, J = 9.0 Hz), 7.42−7.45 (m, 1H), 7.36 (dd, 1H, J = 7.8, 4.8 Hz), 7.25 (d, 2H, J = 8.4 Hz), 7.05 (td, 1H, J = 7.1, 1.2 Hz), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 151.6, 150.6, 148.9, 146.6, 144.5, 138.9, 136.2, 129.7, 128.5, 127.4, 126.8, 125.6, 123.8, 118.9, 118.4, 114.9, 21.6. IR (neat): 3138, 3047, 2924, 2860, 1679, 1638, 1595, 1487, 1373, 1326, 1250, 1149, 1082, 623, 741, 678 cm^{-1}. HRMS (ESI): m/z calcd for $C_{19}H_{16}N_3O_2S$ $[M + H]^+$ 350.0957; Found 350.0954.

*8-Methyl-2-phenyl-3-tosylimidazo[1,2-a]pyridine (**3q**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2q** (0.2 mmol). 40 mg (56%), white solid, mp 155.9−157.2 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 8.96 (d, 1H, J = 6.6 Hz), 7.71−7.72 (m, 2H), 7.51 (d, 2H, J = 9.0 Hz), 7.43−7.46 (m, 3H), 7.23 (d, 1H, J = 6.6 Hz), 7.13 (d, 2H, J = 7.8 Hz), 6.95 (t, 1H, J = 6.6 Hz), 2.63 (s, 3H), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 152.2, 146.8, 144.3, 139.2, 132.9, 130.6, 129.7, 129.2, 128.1, 127.8, 127.4, 126.5, 124.5, 118.1, 114.6, 21.5, 17.2. IR (neat): 3073, 3035, 2927, 1480, 1468, 1332, 1302, 1258, 1144, 1084, 756, 683 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{19}N_2O_2S$ $[M + H]^+$ 363.1161; Found 363.1155.

*8-Fluoro-2-phenyl-3-tosylimidazo[1,2-a]pyridine (**3r**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2r** (0.2 mmol). 62 mg (84%), white solid, mp 141.9−143.0 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 8.95 (d, 1H, J = 6.6 Hz), 7.73 (dd, 2H, J = 8.4, 1.2 Hz), 7.50 (d, 2H, J = 8.4 Hz), 7.43−7.47 (m, 3H), 7.13−7.16 (m, 3H), 6.98 (td, 1H, J = 7.8, 4.8 Hz), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 152.6, 151.2 (d, J = 254.1 Hz), 144.8, 139.2, (d, J = 27.3 Hz), 138.6, 132.2, 130.7, 129.8, 129.6, 127.8, 126.5, 123.2 (d, J = 5.7 Hz), 119.8, 113.7 (d, J = 5.7 Hz), 112.1 (d, J = 15.7 Hz), 21.6. ^{19}F NMR (564 MHz, $CDCl_3$): δ −127.6. IR (neat): 3061, 2929, 2857, 1600, 1561, 1468, 1308, 1267, 1144, 1080, 812, 766, 702 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{16}FN_2O_2S$ $[M + H]^+$ 367.0911; Found 367.0907.

*6-Methyl-2-phenyl-3-tosylimidazo[1,2-a]pyridine (**3s**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2s** (0.2 mmol). 63 mg (87%), white solid, mp 132.1−133.4 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 8.87 (s, 1H), 7.70−7.72 (m, 2H), 7.59 (d, 1H, J = 9.0 Hz), 7.51 (d, 2H, J = 8.4 Hz), 7.41−7.45 (m, 3H), 7.28 (dd, 1H, J = 9.0, 1.8 Hz), 7.12 (d, 2H, J = 8.4 Hz), 2.40 (s, 3H), 2.28 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 152.6, 145.6, 144.3, 139.2, 132.8, 131.5, 130.5, 129.7, 129.2, 127.8, 126.5, 124.6(9), 124.6(3), 117.3, 117.2, 21.5, 18.6. IR (neat): 2924, 1649, 1599, 1492, 1463, 1321, 1144, 1082, 1013, 820, 773 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{19}N_2O_2S$ $[M + H]^+$ 363.1162; Found 363.1159.

*7-Methyl-2-phenyl-3-tosylimidazo[1,2-a]pyridine (**3t**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2t** (0.2 mmol). 58 mg (80%), white solid, mp 138.1−138.7 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.06 (d, 1H, J = 6.6 Hz), 7.68 (d, 1H, J = 9.0 Hz), 7.64 (d, 2H, J = 7.8 Hz), 7.52 (d, 2H, J = 8.4 Hz), 7.39−7.43 (m, 1H), 7.25 (d, 2H, J = 7.8 Hz), 7.12 (d, 2H, J = 8.4 Hz), 7.01 (td, 1H, J = 7.2, 1.2 Hz), 2.41 (s, 3H),

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2.30 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 152.9, 146.4, 144.4, 139.4, 139.1, 130.5, 129.7, 129.6, 128.6, 128.5, 126.8, 126.4, 117.9, 117.5, 114.5, 21.6, 21.5. IR (neat): 2931, 1595, 1504, 1459, 1325, 1254, 1148, 1086, 810, 769, 681 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{19}N_2O_2S$ $[M + H]^+$ 363.1162; Found 363.1160.

*6-Chloro-2-phenyl-3-tosylimidazo[1,2-a]pyridine (**3u**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2u** (0.2 mmol). 66 mg (86%), white solid, mp 170.3−171.2 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.21 (s, 1H), 7.69−7.71 (m, 2H), 7.64 (d, 1H, J = 9.0 Hz), 7.49 (d, 2H, J = 8.4 Hz), 7.43−7.47 (m, 3H), 7.41 (dd, 1H, J = 9.6, 2.4 Hz), 7.14 (d, 2H, J = 8.4 Hz), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 153.1, 144.8(5), 144.8(1), 138.7, 132.2, 130.5, 129.8(9), 129.8(4), 129.6, 127.9, 126.5, 124.9, 123.0, 118.6, 118.2, 21.6. IR (neat): 3030, 1740, 1492, 1463, 1330, 1146, 1082, 820, 739 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{16}ClN_2O_2S$ $[M + H]^+$ 383.0615; Found 383.0615.

*2-Phenyl-3-tosyl-6-(trifluoromethyl)imidazo[1,2-a]pyridine (**3v**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1a** (0.6 mmol) and **2v** (0.2 mmol). 70 mg (84%), white solid, mp 166.7−168.1 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.55 (s, 1H), 7.81 (d, 1H, J = 9.6 Hz), 7.72 (d, 2H, J = 7.2 Hz), 7.59−7.60 (m, 1H), 7.45−7.51 (m, 5H), 7.14 (d, 2H, J = 7.2 Hz), 2.33 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 153.9, 146.2, 145.0, 138.4, 130.5, 129.8(9), 129.8(6), 129.0 (q, J = 278.5 Hz), 128.0, 126.5, 126.0 (q, J = 5.7 Hz), 124.4, 124.0, 122.2, 119.7, 119.2 (q, J = 34.5 Hz), 21.6. ^{19}F NMR (564 MHz, $CDCl_3$): δ −61.9. IR (neat): 3043, 2931, 1653, 1463, 1321, 1261, 1144, 1067, 1010, 948, 810, 684 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{16}F_3N_2O_2S$ $[M + H]^+$ 417.0879; Found 417.0876.

*3-((4-Fluorophenyl)sulfonyl)-2-(p-tolyl)imidazo[1,2-a]pyridine (**3w**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1c** (0.6 mmol) and **2a** (0.2 mmol). The ^1H and ^{13}C NMR spectra for this compound were compared with the literature data.[17] 51 mg (70%); ^1H NMR ($CDCl_3$, 600 MHz): δ 9.11 (d, 1H, J = 7.2 Hz), 7.72 (d, 1H, J = 9.0 Hz), 7.60−7.63 (m, 4H), 7.44−7.47 (m, 1H), 7.26 (d, 2H, J = 6.6 Hz), 7.06 (td, 1H, J = 6.6, 1.2 Hz), 6.98−7.01 (m, 2H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 165.4 (d, J = 254.2 Hz), 153.3, 146.7, 139.6, 138.1 (d, J = 2.8 Hz), 130.4, 129.5, 129.2 (d, J = 8.7 Hz), 128.7(6), 128.7(0), 126.8, 118.0, 117.1, 116.3 (d, J = 22.9 Hz), 114.7, 21.5.

*3-((4-Chlorophenyl)sulfonyl)-2-(p-tolyl)imidazo[1,2-a]pyridine (**3x**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1d** (0.6 mmol) and **2a** (0.2 mmol). 36 mg (47%), white solid, mp 142.5−144.3 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.04 (d, 1H, J = 6.6 Hz), 7.69 (d, 1H, J = 9.0 Hz), 7.57 (d, 2H, J = 8.4 Hz), 7.46 (d, 2H, J = 8.4 Hz), 7.42 (m, 1H), 7.18−7.24 (m, 4H), 7.01 (td, 1H, J = 6.6, 1.8 Hz), 2.37 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 153.6, 146.9, 140.5, 139.9, 139.7, 130.4, 129.5, 129.3, 128.8, 128.7, 127.8, 126.8, 118.1, 116.9, 114.7, 21.5. IR (neat): 3043, 2924, 1723, 1582, 1463, 1313, 1272, 1142, 1084, 1008, 818, 758 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{16}ClN_2O_2S$ $[M + H]^+$ 383.0616; Found 383.0612.

*3-((4-tert-Butylphenyl)sulfonyl)-2-(p-tolyl)imidazo[1,2-a]pyridine (**3y**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1e** (0.6 mmol) and **2a** (0.2 mmol). 64 mg (82%), white solid, mp 124.3−125.3 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.01 (d, 1H, J = 7.2 Hz), 7.70 (d, 1H, J = 9.0 Hz), 7.65 (d, 2H, J = 8.4 Hz), 7.58 (d, 2H, J = 9.0 Hz), 7.41−7.44 (m, 1H), 7.34 (d, 2H, J = 9.0 Hz), 7.25 (d, 2H, J = 8.4 Hz), 7.03 (td, 1H, J = 7.2, 1.2 Hz), 2.42 (s, 3H), 1.24 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 157.3, 152.9, 146.6, 139.3, 139.0, 130.5, 129.7, 128.6, 128.5, 126.9, 126.3, 126.1, 117.9, 117.6, 114.5, 36.2, 31.0, 21.5. IR (neat): 2967, 2873, 1595, 1498, 1463, 1326, 1149, 1110, 821, 758, 665 cm^{-1}. HRMS (ESI): m/z calcd for $C_{24}H_{25}N_2O_2S$ $[M + H]^+$ 405.1631; Found 405.1629.

*3-((4-Methoxyphenyl)sulfonyl)-2-(p-tolyl)imidazo[1,2-a]pyridine (**3z**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1f** (0.6 mmol) and **2a** (0.2 mmol). 64 mg (84%), white solid, mp 141.1−142.2 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.07 (d, 1H, J = 7.2 Hz), 7.73 (d, 1H, J = 8.4 Hz), 7.64 (d, 2H, J = 7.8 Hz), 7.56 (d, 2H, J = 9.0 Hz), 7.43 (dd, 1H, J = 8.4, 7.2 Hz), 7.25 (d, 2H, J = 7.8 Hz), 7.03 (dt, 1H, J = 7.2, 1.2 Hz), 6.78 (d, 2H, J = 9.0 Hz), 3.76 (s, 3H), 2.42 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 163.5, 152.2, 146.2, 139.5, 133.5, 130.5, 129.3, 128.7, 128.6, 126.8, 118.1, 117.8, 114.7, 114.6, 114.3, 55.6, 21.5. IR (neat): 3021, 2939, 2849, 1503, 1498, 1466, 1325, 1261, 1140, 1088, 803, 676 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{19}N_2O_3S$ $[M + H]^+$ 379.1110; Found 379.1103.

*2-(p-Tolyl)-3-((4-(trifluoromethyl)phenyl)sulfonyl)imidazo[1,2-a]pyridine (**3za**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1g** (0.6 mmol) and **2a** (0.2 mmol). 36 mg (43%), white solid, mp 149.5−150.1 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.12 (d, 1H, J = 7.2 Hz), 7.72 (d, 1H, J = 9.0 Hz), 7.70 (d, 2H, J = 7.8 Hz), 7.60 (d, 2H, J = 8.4 Hz), 7.57 (d, 2H, J = 8.4 Hz), 7.46−7.49 (m, 1H), 7.26 (d, 2H, J = 7.8 Hz), 7.08 (td, 1H, J = 7.2, 1.2 Hz), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 154.0, 147.0. 145.4, 139.9, 134.9 (q, J = 33.4 Hz), 130.5, 129.8, 129.1, 128.7, 126.8 (2C), 126.2 (q, J = 4.2 Hz), 123.0 (q, J = 271.5 Hz), 118.2, 116.4, 115.6, 21.5. ^{19}F NMR (564 MHz, $CDCl_3$): δ −63.1. IR (neat): 3050, 2927, 1496, 1463, 1321, 1131, 1062, 1008, 823, 711 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{16}F_3N_2O_2S$ $[M + H]^+$ 417.0879; Found 417.0876.

*4-((2-(p-Tolyl)imidazo[1,2-a]pyridin-3-yl)sulfonyl)benzonitrile (**3zb**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1h** (0.6 mmol) and **2a** (0.2 mmol). 52 mg (70%), white solid, mp 201.2−202.9 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.13 (d, 1H, J = 6.6 Hz), 7.73 (d, 1H, J = 9.0 Hz), 7.65 (d, 2H, J = 7.8 Hz), 7.58−7.61 (m, 4H), 7.48−7.51 (m, 1H), 7.27 (d, 2H, J = 7.8 Hz), 7.09 (td, 1H, J = 6.6, 1.2 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 154.4, 147.2, 146.0, 140.0, 132.8, 130.4, 129.3, 129.2, 128.3, 126.9(2C), 118.2, 117.1, 116.9, 115.9, 115.1, 21.5. IR (neat): 3157, 3050, 2232, 1613, 1495, 1442, 1323, 1267, 1146, 1084, 1008, 823, 762 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{16}N_3O_2S$ $[M + H]^+$ 374.0957; Found 374.0962.

*3-((2-(p-Tolyl)imidazo[1,2-a]pyridin-3-yl)sulfonyl)benzonitrile (**3zc**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1i** (0.6 mmol) and **2a** (0.2 mmol). 38 mg (51%), white solid, mp 162.0−162.7 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.17 (d, 1H, J = 7.8 Hz), 7.68−7.74 (m, 4H), 7.54 (d, 2H, J = 7.8 Hz), 7.49−7.52 (m, 1H), 7.41−7.45 (m, 1H), 7.27 (d, 2H, J = 7.8 Hz), 7.11 (td, 1H, J = 7.8, 1.2 Hz), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 154.2, 147.1, 143.5, 140.2, 136.2, 130.4, 130.2, 130.1, 130.0, 129.2, 129.1, 128.8, 127,0, 118.2, 116.8, 116.3, 115.1, 113.4, 21.5. IR (neat): 3157, 2924, 2238, 1496, 1461, 1330, 1296, 1138, 826, 762, 691 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{16}N_3O_2S$ $[M + H]^+$ 374.0957; Found 374.0952.

*3-(Thiophene-2-ylsulfonyl)-2-(p-tolyl)imidazo[1,2-a]pyridine (**3zd**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1l** (0.6 mmol) and **2a** (0.2 mmol). 28 mg (40%), white solid, mp 123.1−125.2 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.06 (d, 1H, J = 7.2 Hz), 7.76 (d, 1H, J = 9.0 Hz), 7.67 (d, 2H, J = 7.8 Hz), 7.47−7.51 (m, 3H), 7.27 (d, 2H, J = 7.8 Hz), 7.09 (t, 1H, J = 6.6 Hz), 6.95−6.96 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 152.9, 146.6, 143.4, 139.6, 133.1, 132.2, 130.4, 129.3, 128.9, 128.7, 127.6, 127.0, 117.9, 117.7, 114.8, 21.5. IR (neat): 2927, 1634, 1466, 1328, 1138, 1015, 823, 743, 678 cm^{-1}. HRMS (ESI): m/z calcd for $C_{18}H_{15}N_2O_2S_2$ $[M + H]^+$ 355.0569; Found 355.0565.

*3-(Methylsulfonyl)-2-(p-tolyl)imidazo[1,2-a]pyridine (**3ze**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1m** (0.6 mmol) and **2a** (0.2 mmol). 29 mg (50%), white solid, mp 205.5−206.2 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.01 (d, 1H, J = 7.2 Hz), 7.76−7.78 (m, 1H), 7.77 (d, 2H, J = 8.4 Hz), 7.47−7.50 (m, 1H), 7.29 (d, 2H, J = 8.4 Hz), 7.05 (td, 1H, J = 7.2, 1.2 Hz), 3.02 (s, 3H), 2.42 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 151.9, 146.4, 139.9, 130.2, 129.2, 129.1, 128.6, 127.2, 117.9, 116.9, 114.6, 44.9, 21.5. IR (neat): 3002, 2922, 1634, 1468, 1325, 1187, 961, 825, 758 cm^{-1}. HRMS (ESI): m/z calcd for $C_{15}H_{15}N_2O_2S$ $[M + H]^+$ 287.0848; Found 287.0849.

*3-(Butylsulfonyl)-2-(p-tolyl)imidazo[1,2-a]pyridine (**3zf**).* (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1n** (0.6 mmol) and **2a** (0.2 mmol). 28 mg (43%), white solid, mp 133.4−134.7 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.11

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(d, 1H, J = 7.2 Hz), 7.75−7.78 (m, 3H), 7.45−7.48 (m, 1H), 7.28 (d, 2H, J = 7.2 Hz), 7.03 (td, 1H, J = 7.2, 1.2 Hz), 3.00−3.03 (m, 2H), 2.41 (s, 3H), 1.49−1.54 (m, 2H), 1.22−1.24 (m, 2H), 0.75 (t, 3H, J = 7.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 152.5, 146.6, 139.7, 130.2, 129.4, 128.9, 128.5, 127.2, 117.9, 115.6, 114.5, 56.4, 24.3, 21.5, 21.2, 13.4. IR (neat): 2970, 2944, 2879, 1615, 1498, 1463, 1319, 1133, 1008, 827, 766, 667 cm^{-1}. HRMS (ESI): m/z calcd for $C_{18}H_{21}N_2O_2S$ $[M + H]^+$ 329.1318; Found 329.1314.

3-(Cyclopropylsulfonyl)-2-(p-tolyl)imidazo[1,2-a]pyridine (**3zg**). (eluent: 5:2 hexanes/ethyl acetate). The product was synthesized by the general procedure A using **1o** (0.6 mmol) and **2a** (0.2 mmol). 50 mg (80%), white solid, mp 194.7−195.7 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.08 (d, 1H, J = 6.6 Hz), 7.76 (d, 1H, J = 9.0 Hz), 7.73 (d, 2H, J = 8.4 Hz), 7.44−7.47 (m, 1H), 7.26 (d, 2H, J = 8.4 Hz), 7.02 (t, 1H, J = 6.6 Hz), 2.48 (m, 1H), 2.41 (s, 3H), 1.13−1.16 (m, 2H), 0.82−0.86 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 152.2, 146.3, 139.5, 130.3, 129.7, 128.8, 128.4, 127.1, 117.9, 117.5, 114.4, 34.3, 21.5, 5.4 (2C). IR (neat): 3090, 2927, 1641, 1470, 1321, 1302, 1243, 1133, 877, 825, 762, 706 cm^{-1}. HRMS (ESI): m/z calcd for $C_{17}H_{17}N_2O_2S$ $[M + H]^+$ 313.1005; Found 313.1004.

Preparation and Characterization of Indolizines. Step 1: *p*-Tolenesulfonic acid (1.0 mmol, 0.1 equiv) was added to a solution of ketone (10.0 mmol, 1.0 equiv) in ethyl acetate (10 mL) and stirred for 10 min under argon atmosphere. Then, *N*-bromosuccinimide (1.0 equiv) was added to this mixture. The reaction was stirred at room temperature with light exclusion for 24 h. After the reaction was complete, saturated sodium carbonate solution (10 mL) and brine (10 mL) were added to the reaction mixture. The aqueous layer was extracted with dichloromethane (20 mL × 3). The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The desired α-bromoketone intermediate was isolated by column chromatography on silica gel.

Step 2: The final indolizine products were synthesized by the literature method.[33] A solution of substituted pyridine (5.0 mmol, 1.0 equiv) and α-bromoketone (5.0 mmol, 1.0 equiv) in acetone (25 mL) was heated in an oil bath at 60 °C for 5 h. The intermediate was filtered using acetone, and solvent was removed under vacuum. Then, potassium carbonate (5.0 mmol, 1.0 equiv) was added to a solution of the residue in water (10 mL), and the mixture was heated at 60 °C for 5 h. The desired indolizine product was filtered and dried under vacuum.

2-Phenylindolizine (**4a**). 908 mg (94%). The ^1H and ^{13}C NMR spectra were compared with the literature data.[34] ^1H NMR (DMSO-d_6, 600 MHz): δ 8.13 (d, 1H, J = 6.6 Hz), 7.84 (s, 1H), 7.64 (d, 2H, J = 7.8 Hz), 7.33−7.36 (m, 3H), 7.18−7.20 (m, 1H), 6.68 (s, 1H), 6.62−6.65 (m, 1H), 6.46−6.47 (m, 1H). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 150 MHz): δ 135.5, 133.5, 129.2, 128.8, 126.9, 126.1(2C), 119.1, 118.0, 110.9, 110.3, 96.7. IR (neat): 3108, 3076, 3058, 3035, 1513, 1455, 1360, 907, 786, 728, 689 cm^{-1}. HRMS (ESI): m/z calcd for $C_{14}H_{12}N$ $[M + H]^+$ 194.0964; Found 194.0958.

2-(p-Tolyl)indolizine (**4b**). 601 mg (58%). The ^1H and ^{13}C NMR spectra were compared with the literature data.[34] ^1H NMR ($CDCl_3$, 600 MHz): δ 7.88 (s, 1H), 7.54−7.57 (m, 3H), 7.34 (d, 1H, J = 8.4 Hz), 7.21 (d, 2H, J = 7.8 Hz), 6.63−6.67 (m, 2H), 6.44−6.45 (m, 1H), 2.38 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 136.2, 133.6, 132.5, 129.5(2C), 126.1, 125.1, 119.0, 117.3, 110.4, 109.0, 96.6, 21.1. IR (neat): 3106, 3073, 3030, 2916, 2860, 1627, 1554, 1373, 1189, 827, 779, 725, 695 cm^{-1}. HRMS (ESI): m/z calcd for $C_{15}H_{14}N$ $[M + H]^+$ 208.1121; Found 208.1112.

2-(4-Fluorophenyl)indolizine (**4c**). 876 mg (83%). White solid, mp 222−224 °C. ^1H NMR (DMSO-d_6, 600 MHz): δ 8.13−8.15 (m, 1H), 7.83 (d, 1H, J = 4.8 Hz), 7.64−7.67 (m, 2H), 7.32−7.34 (m, 1H), 7.12−7.15 (m, 2H), 6.63−6.66 (m, 2H), 6.46−6.49 (m, 1H). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 150 MHz): δ 161.7 (d, J = 241.2 Hz), 133.7, 132.2, 128.1, 128.0 (d, J = 7.2 Hz), 126.1, 119.0, 118.0, 115.9 (d, J = 21.4 Hz), 110.9, 110.2, 96.8. ^{19}F NMR (564 MHz, DMSO-d_6): δ −116.4. IR (neat): 3112, 1550, 1517, 1373, 1297, 1146, 1097, 812, 730 cm^{-1}. HRMS (ESI): m/z calcd for $C_{14}H_{11}FN$ $[M + H]^+$ 212.0870; Found 212.0864.

2-(4-Bromophenyl)indolizine (**4d**). 626 mg (46%). The ^1H and ^{13}C NMR spectra were compared with the literature data.[34] ^1H NMR (DMSO-d_6, 600 MHz): δ 8.16 (d, 1H, J = 7.2 Hz), 7.92 (s, 1H), 7.61 (d, 2H, J = 7.8 Hz), 7.52 (d, 2H, J = 7.8 Hz), 7.35 (d, 1H, J = 9.0 H z), 6.71 (s, 1H), 6.64−6.67 (m, 1H), 6.50 (t, 1H, J = 7.2 Hz). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 150 MHz): δ 134.9, 133.6, 132.1, 128.1, 127.5, 126.2, 119.7, 119.2, 118.2, 111.1, 110.6, 96.7. IR (neat): 3108, 1545, 1455, 1371, 1299, 1146, 920, 773 cm^{-1}. HRMS (ESI): m/z calcd for $C_{14}H_{11}BrN$ $[M + H]^+$ 272.0069; Found 272.0059.

2-(4-Methoxyphenyl)indolizine (**4e**). 603 mg (54%). The ^1H and ^{13}C NMR spectra were compared with the literature data.[34] ^1H NMR (DMSO-d_6, 600 MHz): δ 8.10 (d, 1H, J = 6.6 Hz), 7.75 (s, 1H), 7.55 (d, 2H, J = 8.4 Hz), 7.30 (d, 1H, J = 9.0 Hz), 6.92 (d, 2H, J = 8.4 Hz), 6.61−6.63 (m, 2H), 6.43−6.45 (m, 1H), 3.75 (s, 3H). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 150 MHz): δ 158.9, 133.6, 129.0, 128.4, 127.4, 126.0, 118.9, 117.7, 115.0, 110.5, 109.7, 96.5, 55.8. IR (neat): 3117, 2967, 2842, 1628, 1580, 1513, 1487, 1427, 1243, 1148, 1032 cm^{-1}. HRMS (ESI): m/z calcd for $C_{15}H_{14}NO$ $[M + H]^+$ 224.1070; Found 224.1060.

4-(Indolizin-2-yl)benzonitrile (**4f**). 578 mg (53%). White solid, mp 215−217 °C. ^1H NMR (DMSO-d_6, 600 MHz): δ 8.18 (d, 1H, J = 6.6 Hz), 8.07 (d, 1H, J = 1.8 Hz), 7.84 (d, 2H, J = 7.8 Hz), 7.78 (d, 2H, J = 8.4 Hz), 7.37 (d, 1H, J = 9.0 Hz), 6.82 (s, 1H), 6.68 (dd, 1H, J = 9.0, 7.8 Hz), 6.53 (td, 1H, J = 6.6, 1.2 Hz). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 150 MHz): δ 140.3, 133.7, 133.3, 126.8, 126.6, 126.3, 119.7, 119.4, 118.6, 111.7, 111.6, 108.9, 97.1. IR (neat): 3112, 2228, 1610, 1550, 1423.8, 1302, 1222, 1148, 779, 738 cm^{-1}. HRMS (ESI): m/z calcd for $C_{15}H_{11}N_2$ $[M + H]^+$ 219.0917; Found 219.0909.

2-(4-Nitrophenyl)indolizine (**4g**). 727 mg (61%). Yellow solid, mp 204−206 °C. ^1H NMR (DMSO-d_6, 600 MHz): δ 8.19−8.21 (m, 3H), 8.13 (d, 1H, J = 7.2 Hz), 7.93 (d, 2H, J = 9.0 Hz), 7.39 (d, 1H, J = 9.0 Hz), 6.87 (s, 1H), 6.70 (dd, 1H, J = 9.0, 5.4 Hz), 6.55 (t, 1H, J = 7.2 Hz). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 150 MHz): δ 146.0, 142.5, 13.8, 126.6, 126.4, 126.3, 124.7 119.5, 118.8, 112.2, 111.8, 97.4. IR (neat): 3110, 1630, 1507, 1343, 1215, 1008, 855, 784, 700 cm^{-1}. HRMS (ESI): m/z calcd for $C_{14}H_{11}N_2O_2$ $[M + H]^+$ 239.0815; Found 239.0807.

2-(3-Chlorophenyl)indolizine (**4h**). 524 mg (46%). White solid, mp 153−155 °C. ^1H NMR (DMSO-d_6, 600 MHz): δ 8.15 (d, 1H, J = 6.6 Hz), 8.00 (s, 1H), 7.71 (t, 1H, J = 2.4 Hz), 7.63 (d, 1H, J = 8.4 Hz), 7.34−7.38 (m, 2H), 7.24 (dd, 1H, J = 7.2, 1.8 Hz), 6.71 (s, 1H), 6.66 (dd, 1H, J = 9.0, 5.4 Hz), 6.51 (td, 1H, J = 6.6, 1.2 Hz). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 150 MHz): δ 137.7, 134.1, 133.5, 131.1, 127.2, 126.6, 126.2, 125.6, 124.6, 119.2, 118.3, 111.2, 110.9, 96.8. IR (neat): 3110, 3010, 2987, 1630, 1513, 1425, 1295, 1148, 998, 771, 68 cm^{-1}. HRMS (ESI): m/z calcd forr $C_{14}H_{11}ClN$ $[M + H]^+$ 228.0575; Found 228.0569.

2-(3-Bromophenyl)indolizine (**4i**). 993 mg (73%). White solid, mp 164−166 °C. ^1H NMR (DMSO-d_6, 600 MHz): δ 8.15 (dd, 1H, J = 6.6, 1.2 Hz), 8.00 (d, 1H, J = 1.8 Hz), 7.84−7.85 (m, 1H), 7.66 (d, 1H, J = 7.2 Hz), 7.33−7.37 (m, 2H), 7.30 (t, 1H, J = 7.8 Hz), 6.76 (s, 1H), 6.66 (dd, 1H, J = 9.0, 6.0 Hz), 6.50 (td, 1H, J = 6.6, 1.2 Hz). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 150 MHz): δ 138.0, 133.5, 131.4, 129.5, 128.5, 127.1, 126.2, 125.0, 122.8, 119.2, 118.3, 111.2, 110.9, 96.8. IR (neat): 3110, 3071, 1597, 1559, 1455, 1369, 1252, 1144, 1073, 995, 767, 662 cm^{-1}. HRMS (ESI): m/z calcd for $C_{14}H_{11}BrN$ $[M + H]^+$ 272.0069; Found 272.0063.

2-(3-Methoxyphenyl)indolizine (**4j**). 770 mg (69%). White solid, mp 118−120 °C. ^1H NMR (DMSO-d_6, 600 MHz): δ 8.15 (d, 1H, J = 6.6 Hz), 7.93 (s, 1H), 7.33 (d, 1H, J = 9.0 Hz), 7.19−7.26 (m, 3H), 6.78 (d, 1H, J = 7.2 Hz), 6.72 (s, 1H), 6.63 (dd, 1H, J = 9.0, 7.2 Hz), 6.48 (t, 1H, J = 6.6 Hz), 3.76 (s, 3H). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 150 MHz): δ 160.2, 136.8, 133.3, 130.3, 128.6, 126.1, 119.1, 118.5, 118.0, 112.5, 111.5, 110.9, 110.6, 96.8, 55.5. IR (neat): 3108, 3075, 3004, 2944, 2842, 1589, 1511, 1461, 1325, 1258, 1148, 1039, 844, 734, 656 cm^{-1}. HRMS (ESI): m/z calcd for $C_{15}H_{14}NO$ $[M + H]^+$ 224.1070; Found 224.1061.

2-(2-Fluorophenyl)indolizine (**4k**). 549 mg (52%). White solid, mp 94−96 °C. ^1H NMR (DMSO-d_6, 600 MHz): δ 8.24 (d, 1H, J = 6.6 Hz), 7.95 (s, 1H), 7.77 (t, 1H, J = 7.2 Hz), 7.37 (d, 1H, J = 9.0 Hz), 7.19−7.25 (m, 3H), 6.77 (s, 1H), 6.66 (dd, 1H, J = 9.0, 6.6 Hz), 6.51 (t, 1H, J = 6.6 Hz). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 150 MHz): δ 159.8 (d, J = 245.5 Hz), 132.7, 129.4 (d, J = 4.4 Hz), 128.5 (d, J = 8.5 Hz), 126.2, 125.3,

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122.9 (d, J = 13.1 Hz), 122.1, 119.1, 118.2, 116.6 (d, J = 23.1 Hz), 112.6 (d, J = 10.5 Hz), 111.1, 98.0 (d, J = 2.8 Hz). ^{19}F NMR (564 MHz, DMSO-d_6): δ −115.0. IR (neat): 3155, 3060, 1580, 1511, 1459, 1302, 1248, 1144, 1053, 780, 657 cm^{-1}. HRMS (ESI): m/z calcd for $C_{14}H_{11}FN$ $[M + H]^+$ 212.0870; Found 212.0864.

*2-(3,4-Dichlorophenyl)indolizine (**4l**).* 917 mg (70%). Brown solid, mp 161−163 °C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ 8.12−8.13 (m, 1H), 7.94 (s, 1H), 7.85 (s, 1H), 7.60−7.62 (m, 1H), 7.53−7.55 (m, 1H), 7.33−7.35 (m, 1H), 6.72 (s, 1H), 6.65−6.67 (m, 1H), 6.50−6.51 (m, 1H). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 136.4, 133.5, 132.1, 131.4, 129.0, 127.6, 126.3, 126.1(2C), 119.3, 118.5, 111.4, 111.2, 96.9. IR (neat): 3110, 3071, 1634, 1595, 1505, 1449, 1360, 1213, 1129, 1026, 941, 775, 676 cm^{-1}. HRMS (ESI): m/z calcd for $C_{14}H_{10}Cl_2N$ $[M + H]^+$ 262.0185; Found 262.0180.

*2-([1,1′-Biphenyl]-4-yl)indolizine (**4m**).* 646 mg (48%). White solid, mp 305−307 °C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ 8.14−8.15 (m, 1H), 7.89−7.90 (m, 1H), 7.72−7.74 (m, 2H), 7.64−7.65 (m, 4H), 7.43−7.44 (m, 2H), 7.32−7.36 (m, 2H), 6.64−6.73 (m, 2H), 6.48−6.49 (m, 1H). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 140.7, 138.9, 134.9, 133.8, 129.3, 128.7, 127.6, 127.4, 126.8(9), 126.8(0), 126.1, 119.1, 117.9, 110.9, 110.5, 96.9. IR (neat): 3106, 3037, 1500, 1459, 1373, 1213, 1164, 1144, 782, 687 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{16}N$ $[M + H]^+$ 270.1277; Found 270.1267.

*2-(Naphthalen-2-yl)indolizine (**4n**).* 705 mg (58%). Light brown solid, mp 229−231 °C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ 8.15−8.17 (m, 2H), 7.99−8.01 (m, 1H), 7.83−7.90 (m, 4H), 7.38−7.47 (m, 3H), 6.83−6.85 (m, 1H), 6.65−6.67 (m, 1H), 6.50−6.52 (m, 1H). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 134.2, 133.8, 133.2, 132.6, 129.0, 128.6, 128.2, 128.0, 126.6, 126.2, 125.8, 125.3, 124.0, 119.1, 118.0, 110.9, 110.8, 97.1: IR (neat): 3106, 3052, 1630, 1513, 1459, 1323, 1248, 1142, 1047, 952, 779, 659 cm^{-1}. HRMS (ESI): m/z calcd for $C_{18}H_{14}N$ $[M + H]^+$ 244.1121; Found 244.1113.

*2-(Benzo[d][1,3]dioxol-5-yl)indolizine (**4o**).* 759 mg (64%). Yellow solid, mp 184−186 °C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ 8.12 (d, 1H, J = 6.6 Hz), 7.83 (d, 1H, J = 1.2 Hz), 7.30 (d, 1H, J = 9.0 Hz), 7.22−7.23 (m, 1H), 7.14 (dd, 1H, J = 7.8, 1.8 Hz), 6.89 (d, 1H, J = 8.3 Hz), 6.61−6.63 (m, 2H), 6.46 (td, 1H, J = 6.6, 1.8 Hz), 5.98 (s, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 148.3, 146.4, 133.3, 129.7, 128.7, 126.0, 119.4, 118.9, 117.9, 110.7, 110.0, 109.1, 106.7, 101.3, 96.6: IR (neat): 3106, 3052, 2901, 2784, 1513, 1479, 1451, 1367, 1241, 1149, 933, 777 cm^{-1}. HRMS (ESI): m/z calcd for $C_{15}H_{12}NO_2$ $[M + H]^+$ 238.0863; Found 238.0855.

*2-(Furan-2-yl)indolizine (**4p**).* 495 mg (54%). Brown solid, mp 134−136 °C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ 8.18 (d, 1H, J = 6.6 Hz), 7.78 (s, 1H), 7.60 (s, 1H), 7.33 (d, 1H, J = 9.0 Hz), 6.64−6.67 (m, 1H), 6.60−6.61 (m, 1H), 6.56 (s, 1H), 6.47−6.50 (m, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 150.8, 142.0, 133.1, 126.3, 119.9, 119.0, 118.3, 112.1, 111.0, 109.4, 105.0, 95.6: IR (neat): 3102, 2987, 1634, 1518, 1364, 1291, 1146, 948, 875, 773 cm^{-1}. HRMS (ESI): m/z calcd for $C_{12}H_{10}NO$ $[M + H]^+$ 184.0757; Found 184.0752.

*2-(Thiophene-2-yl)indolizine (**4q**).* 587 mg (59%). Brown solid, mp 165−167 °C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ 8.16 (d, 1H, J = 7.2 H z), 7.80 (s, 1H), 7.36 (d, 1H, J = 4.8 Hz), 7.32 (d, 1H, J = 9.0 Hz), 7.27 (dd, 1H, J = 3.6, 1.8 Hz), 7.03 (dd, 1H, J = 4.8, 3.6 Hz), 6.64−6.66 (m, 1H), 6.56 (s, 1H), 6.49 (td, 1H, J = 7.2, 1.2 Hz). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 138.7, 133.3, 128.5, 126.1, 124.3, 123.3, 122.9, 118.9, 118.4, 111.0, 110.0, 96.8: IR (neat): 3106, 3071, 2967, 1628, 1515, 1429, 1291, 1144, 998, 769, 728 cm^{-1}. HRMS (ESI): m/z calcd for $C_{12}H_{10}NS$ $[M + H]$+ 200.0529; Found 200.0524.

*8-Methyl-2-phenylindolizine (**4r**).* 466 mg (45%). White solid, mp 113−115 °C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ 8.04 (d, 1H, J = 6.6 Hz), 7.91 (d, 1H, J = 1.2 Hz), 7.68 (d, 2H, J = 7.2 Hz), 7.35 (t, 2H, J = 7.2 Hz), 7.19 (t, 1H, J = 6.6 Hz), 6.73 (s, 1H), 6.47 (d, 1H, J = 6.6 Hz), 6.43 (t, 1H, J = 7.2 Hz), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz): δ 135.5, 134.4, 129.3, 128.3, 127.7, 126.8, 126.0, 124.1, 117.0, 111.0, 110.8, 95.5, 18.2. IR (neat): 3112, 3039, 2976, 2916, 1511, 1433, 1304, 1222, 749, 689 cm^{-1}. HRMS (ESI): m/z calcd for $C_{15}H_{14}N$ $[M + H]^+$ 208.1121; Found 208.1116.

*6-Ethyl-2-phenylindolizine (**4s**).* 653 mg (59%). Yellow solid, mp 140−142 °C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ 7.97 (s, 1H), 7.83 (d, 1H, J = 1.2 Hz), 7.63 (d, 2H, J = 7.2 Hz), 7.33 (t, 2H, J = 7.2 Hz), 7.29 (d, 1H, J = 8.4 Hz), 7.17 (t, 1H, J = 7.2 Hz), 6.66 (s, 1H), 6.56 (dd, 1H, J = 9.0, 1.2 Hz), 2.46−2.47 (m, 2H), 1.15 (t, 3H, J = 7.8 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 135.6, 132.8, 129.0, 128.8, 126.4, 126.1, 121.9, 119.8, 118.7(2C), 109.1, 96.2, 25.9, 14.9. IR (neat): 2963, 2873, 1604, 1513, 1435, 1323, 1224, 849, 779 cm^{-1}. HRMS (ESI): m/z calcd for $C_{16}H_{16}N$ $[M + H]$+ 222.1277; Found 222.1272.

General Procedure B for Electrochemical Sulfonylation of Indolizines. An undivided cell equipped with a glassy carbon anode and a nickel cathode was connected to an ElectraSyn 2.0. A solution of 2-arylindolizine (**4**, 0.2 mmol), sodium sulfinate (**1**, 0.4 mmol), and $LiClO_4$ (320 mg, 0.40 M) in a mixture of DMF and H_2O (7.5 mL, v/v = 15:1) was added to the undivided cell. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA under room temperature for 2 h. After the reaction was complete, the residue was diluted with EtOAc (10 mL) and washed with water, dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash column chromatography (EtOAc/Hex = 1:10) to afford the desired product **5**.

1.0 mmol Scale. An undivided cell was set up with a glassy carbon anode and a nickel cathode and connected to an ElectraSyn 2.0. 2-Phenylindolizine (**4a**, 1.0 mmol), sodium *p*-toluenesulfinate (**1a**, 2.0 mmol), and $LiClO_4$ (1.6 g, 0.40 M) were dissolved in a mixture of DMF and H_2O (37.5 mL, v/v = 15:1) and added to the undivided cell. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA under room temperature for 10 h. After the reaction was complete, the residue was diluted with EtOAc (30 mL) and washed with water, dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash column chromatography (EtOAc/Hex = 1:10) to afford the product **5a** (212 mg, 61% yield).

Characterization of the Compounds in Scheme 3. *2-Phenyl-3-tosylindolizine (**5a**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.4 mmol) and **4a** (0.2 mmol). 52 mg (75%), greenish solid, mp 115.1−116.1 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.09 (d, 1H, J = 6.6 Hz), 7.46−7.48 (m, 4H), 7.44 (d, 1H, J = 9.0 H z), 7.39−7.41 (m, 3H), 7.11 (d, 2H, J = 7.8 H z), 7.01−7.04 (m, 1H), 6.79 (td, 1H, J = 6.6, 1.2 Hz), 6.48 (s, 1H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 143.5, 139.9, 138.0, 136.5, 134.4, 130.6, 129.5, 127.9, 127.5, 126.2, 126.1, 122.6, 118.9, 115.2, 113.0, 104.4, 21.5. IR (neat): 3062, 2927, 2858, 1599, 1505, 1448, 1377, 1313, 1146, 1082, 997, 743 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{18}NO_2S$ $[M + H]^+$ 348.1052; Found 348.1056.

*2-(p-Tolyl)-3-tosylindolizine (**5b**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.4 mmol) and **4b** (0.2 mmol). 43 mg (60%), greenish solid, mp 146.2−147.1 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.07 (d, 1H, J = 7.2 Hz), 7.50 (d, 2H, J = 8.4 Hz), 7.42 (d, 1H, J = 9.0 Hz), 7.39 (d, 2H, J = 8.4 Hz), 7.23 (d, 2H, J = 8.4 Hz), 7.12 (d, 2H, J = 8.4 Hz), 7.00−7.02 (m, 1H), 6.77 (td, 1H, J = 7.2, 1.2 Hz), 6.47 (s, 1H), 2.43 (s, 3H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 143.4, 139.9, 138.2, 137.6, 136.5, 131.4, 130.5, 129.5, 128.3, 126.2, 126.0, 122.5, 118.8, 115.1, 112.9, 104.4, 21.5, 21.4. IR (neat): 3039, 2922, 1599, 1505, 1375, 1300, 1148, 1086, 827, 784, 751 cm^{-1}. HRMS (ESI): m/z calcd for $C_{22}H_{20}NO_2S$ $[M + H]^+$ 362.1209; Found 362.1208.

*2-(4-Fluorophenyl)-3-tosylindolizine (**5c**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.4 mmol) and **4c** (0.2 mmol). 29 mg (40%), greenish solid, mp 121.5−123.1 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.08 (d, 1H, J = 7.2 Hz), 7.43−7.47 (m, 5H), 7.12 (d, 2H, J = 8.4 Hz), 7.07−7.11 (m, 2H), 7.04 (dd, 1H, J = 9.0, 6.6 Hz), 6.79 (td. 1H, J = 7.2, 1.2 Hz), 6.46 (s, 1H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 162.7 (d, J = 245.7, Hz), 143.6, 139.8, 136.9, 136.4, 132.3 (d, J = 8.5 Hz), 130.3, 129.5, 126.1, 126.0, 122.7, 118.9, 115.3, 114.5 (d, J = 21.6 Hz), 113.1, 104.3, 21.5. ^{19}F NMR (564 MHz, $CDCl_3$): δ −114.4. IR (neat): 3158, 2931, 1599, 1509, 1474, 1381, 1220, 1144, 1082, 838, 790, 676 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{17}FNO_2S$ $[M + H]^+$ 366.0959; Found 366.0957.

*2-(4-Bromophenyl)-3-tosylindolizine (**5d**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.6 mmol) and **4d** (0.2 mmol). 63 mg (74%), greenish solid, mp 169.9−170.6 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.07 (d, 1H, J =

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6.6 Hz), 7.53 (d, 2H, J = 8.4 Hz), 7.48 (d, 2H, J = 8.4 Hz), 7.43 (d, 1H, J = 9.0 Hz), 7.36 (d, 2H, J = 8.4 Hz), 7.13 (d, 2H, J = 8.4 Hz), 7.02−7.05 (m, 1H), 6.80 (td, 1H, J = 6.6, 1.2 Hz), 6.46 (s, 1H), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 143.7, 139.7, 136.6, 136.5, 133.4, 132.2, 130.7, 129.6, 126.1, 126.0, 122.8, 122.3, 118.9, 115.2, 113.3, 104.2, 21.5. IR (neat): 3157, 3058, 2929, 1502, 1463, 1313, 1276, 1189, 1082, 997, 834, 766, 670 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{17}BrNO_2S$ $[M + H]^+$ 426.0158; Found 426.0151.

*2-(4-Methoxyphenyl)-3-tosylindolizine (**5e**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.4 mmol) and **4e** (0.2 mmol). 45 mg (60%), greenish solid, mp 116.9−118.0 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.08 (d, 1H, J = 6.6 Hz), 7.47 (d, 2H, J = 7.8 Hz), 7.40−7.44 (m, 3H), 7.11 (d, 2H, J = 7.8 Hz), 7.00−7.02 (m, 1H), 6.94−6.96 (m, 2H), 6.76 (td, 1H, J = 6.6, 1.2 Hz), 6.45 (s, 1H), 3.87 (s, 3H), 2.30 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 159.5, 143.4, 140.0, 138.0, 136.5, 131.8, 129.5, 126.6, 126.1(8), 126.1(6), 122.6, 118.8, 115.0, 113.0, 112.9, 104.3, 55.3, 21.5. IR (neat): 2961, 2844, 1602, 1509, 1466, 1317, 1244, 1149, 1036, 801, 741 cm^{-1}. HRMS (ESI): m/z calcd for $C_{22}H_{20}NO_3S$ $[M + H]^+$ 378.1158; Found 378.1155.

*4-(3-Tosylindolizin-2-yl)benzonitrile (**5f**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.4 mmol) and **4f** (0.2 mmol). 35 mg (47%), greenish solid, mp 120.2−121.1 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.04 (d, 1H, J = 7.2 Hz), 7.69 (d, 2H, J = 8.4 Hz), 7.60 (d, 2H, J = 8.4 Hz), 7.46−7.48 (m, 3H), 7.15 (d, 2H, J = 8.4 Hz), 7.06−7.09 (m, 1H), 6.84 (td, 1H, J = 7.2, 1.2 Hz), 6.49 (s, 1H), 2.33 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 144.0, 139.5, 139.4, 136.6, 135.7, 131.4. 131.3, 129.7, 126.1, 125.9, 123.0, 119.1, 119.0, 115.3, 113.7, 111.6, 104.2, 21.5. IR (neat): 3125, 2929, 2232, 1612, 1502, 1317, 1274, 1149, 1084, 836, 812, 747 cm^{-1}. HRMS (ESI): m/z calcd for $C_{22}H_{17}N_2O_2S$ $[M + H]^+$ 373.1005; Found 373.1006.

*2-(4-Nitrophenyl)-3-tosylindolizine (**5g**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.4 mmol) and **4g** (0.2 mmol). 12 mg (15%), yellow solid, mp 167.6−168.1 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.04 (d, 1H, J = 6.6 Hz), 8.26−8.28 (m, 2H), 7.67 (d, 2H, J = 7.8 Hz), 7.47−7.49 (m, 3H), 7.16 (d, 2H, J = 8.4 Hz), 7.07−7.10 (m, 1H), 6.85 (td, 1H, J = 6.6, 1.2 Hz), 6.52 (s, 1H), 2.33 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 147.5, 144.1, 141.4, 139.4, 136.6, 135.3, 131.5, 129.7, 126.1, 124.9, 123.1, 122.7, 119.1, 115.5, 113.8, 104.2, 21.5. IR (neat): 3127, 2929, 2857, 1606, 1515, 1347, 1315, 1284, 1146, 1084, 857, 805, 743 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{17}N_2O_4S$ $[M + H]^+$ 393.0903; Found 393.0902.

*2-(3-Chlorophenyl)-3-tosylindolizine (**5h**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.6 mmol) and **4h** (0.2 mmol). 60 mg (79%), greenish solid, mp 113.0−113.7 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.08 (d, 1H, J = 6.6 Hz), 7.50 (d, 2H, J = 9.0 Hz), 7.45 (d, 1H, J = 9.0 Hz), 7.39−7.41 (m, 1H), 7.30−7.37 (m, 3H), 7.14 (d, 2H, J = 8.4 Hz), 7.03−7.06 (m, 1H), 6.81 (td, 1H, J = 6.6, 1.2 Hz), 6.47 (s, 1H), 2.33 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 143.8, 139.7, 136.4, 133.3, 130.3, 129.6, 129.0, 128.7(2C), 127.9, 126.2(2C), 126.0, 122.7, 119.0, 115.4, 113.3, 104.2, 21.5. IR (neat): 2931, 1600, 1563, 1502, 1317, 1285, 1149, 1082, 795, 739, 674 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{17}ClNO_2S$ $[M + H]^+$ 382.0663; Found 382.0661.

*2-(3-Bromophenyl)-3-tosylindolizine (**5i**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.4 mmol) and **4i** (0.2 mmol). 72 mg (84%), greenish solid, mp 131.6−132.4 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.10 (d, 1H, J = 6.6 Hz), 7.49−7.53 (m, 4H), 7.43−7.46 (m, 2H), 7.27 (t, 1H, J = 8.4 Hz), 7.15 (d, 2H, J = 8.4 Hz), 7.04 (dd, 1H, J = 9.0, 7.8 Hz), 6.81 (td, 1H, J = 6.6, 1.2 Hz), 6.46 (s, 1H), 2.33 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 143.8, 139.7, 136.5, 136.4, 136.0, 133.1, 130.8, 129.6, 129.5, 129.0, 126.2, 126.0, 122.7, 121.5, 119.0, 115.5, 113.3. 104.2, 21.5. IR (neat): 2967, 1373, 1328, 1280, 1153, 1082, 1004, 870, 762, 738 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{17}BrNO_2S$ $[M + H]^+$ 426.0158; Found 426.0153.

*2-(3-Methoxyphenyl)-3-tosylindolizine (**5j**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.4 mmol) and **4j** (0.2 mmol). 57 mg (75%), greenish solid, mp 108.6−109.5 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.11 (d, 1H, J = 7.2 Hz), 7.50 (d, 2H, J = 7.8 Hz), 7.43 (d, 1H, J = 9.0 Hz), 7.31 (t, 1H, J = 7.8 Hz), 7.11 (d, 2H, J = 8.4 Hz), 7.01−7.06 (m, 3H), 6.95 (dd, 1H, J = 8.4, 2.4 Hz), 6.79 (td, 1H, J = 7.2, 1.2 Hz), 6.49 (s, 1H), 3.84 (s, 3H), 2.31 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 158.7, 143.5, 139.9, 137.8, 136.4, 135.7, 129.5, 128.4, 126.3, 126.1, 123.1, 122.5, 118.9, 116.2, 115.3, 113.8, 113.0, 104.3, 55.3, 21.5. IR (neat): 3162, 2965, 2836, 1593, 1502, 1474, 1379, 1317, 1246, 1086, 792, 738, 663 cm^{-1}. HRMS (ESI): m/z calcd for $C_{22}H_{20}NO_3S$ $[M + H]^+$ 378.1158; Found 378.1154.

*2-(2-Fluorophenyl)-3-tosylindolizine (**5k**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.4 mmol) and **4k** (0.2 mmol). 56 mg (76%), greenish solid, mp 117.0−117.6 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 8.92 (d, 1H, J = 6.6 Hz), 7.60 (d, 2H, J = 8.4 H z), 7.38−7.46 (m, 3H), 7.21 (t, 1H, J = 7.8 Hz), 7.17 (d, 2H, J = 8.4 Hz), 7.14 (t, 1H, J = 8.4 Hz), 7.00−7.03 (m, 1H), 6.78 (td, 1H, J = 6.6, 1.2 Hz), 6.53 (s, 1H), 2.33 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 160.1 (d, J = 245.5 Hz), 143.7, 139.4, 136.4, 132.9, 130.5, 129.9 (d, J = 8.7 Hz), 129.6, 126.4, 125.6, 123.3 (d, J = 4.4 Hz), 122.4, 122.3, 119.1, 115.9, 115.2 (d, J = 21.6 Hz), 113.2, 104.5, 21.5. ^{19}F NMR (564 MHz, $CDCl_3$): δ −113.0. IR (neat): 3149, 2927, 1507, 1468, 1317, 11,44, 1082, 793, 743 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{17}FNO_2S$ $[M + H]^+$ 366.0959; Found 366.0950.

*2-(3,4-Dichlorophenyl)-3-tosylindolizine (**5l**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.6 mmol) and **4l** (0.2 mmol). 61 mg (73%), greenish solid, mp 132.3−133.4 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.05 (d, 1H, J = 6.6 Hz), 7.43−7.49 (m, 5H), 7.35 (dd, 1H, J = 7.8, 1.2 Hz), 7.15 (d, 2H, J = 7.8 Hz), 7.03−7.05 (m, 1H), 6.81 (td, 1H, J = 6.6, 1.2 Hz), 6.45 (s, 1H), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 143.9, 139.6, 136.4, 135.1, 134.4, 132.1(7), 132.1(1), 131.6, 130.1, 129.7, 129.5, 126.2, 125.9, 122.9, 119.0, 115.4, 113.5, 104.1, 21.5. IR (neat): 3155, 3058, 2927, 1502, 1449, 1381, 1280, 1254, 1151, 1041, 795, 747 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{16}Cl_2NO_2S$ $[M + H]^+$ 416.0273; Found 416.0267.

*2-([1,1′-Biphenyl]-4-yl)-3-tosylindolizine (**5m**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.4 mmol) and **4m** (0.2 mmol). 17 mg (20%), light green solid, mp 109.4−110.2 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.10 (d, 1H, J = 7.8 Hz), 7.68 (d, 2H, J = 6.6 Hz), 7.65 (d, 2H, J = 8.4 Hz), 7.57 (d, 2H, J = 8.4 Hz), 7.51 (d, 2H, J = 8.4 Hz), 7.44−7.49 (m, 3H), 7.37 (t, 1H, J = 7.8 Hz), 7.12 (d, 2H, J = 8.4 Hz), 7.02−7.05 (m, 1H), 6.80 (td, 1H, J = 7.8, 1.2 Hz), 6.53 (s, 1H), 2.31 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 143.5, 140.9, 140.6, 140.0, 137.7, 136.6, 133.4, 131.0, 130.4, 129.5, 128.8, 127.4, 127.2, 126.2(9), 126.2(4), 122.6, 118.9, 115.3, 113.0, 104.4, 21.4. IR (neat): 2922, 1599, 1507, 1468, 1317, 1149, 184, 844, 766 cm^{-1}. HRMS (ESI): m/z calcd for $C_{27}H_{22}NO_2S$ $[M + H]^+$ 424.1366; Found 424.1361.

*2-(Naphthalen-2-yl)-3-tosylindolizine (**5n**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.4 mmol) and **4n** (0.2 mmol). 63 mg (79%), greenish solid, mp 147.1−148.3 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.13 (d, 1H, J = 7.2 Hz), 7.87−7.90 (m, 4H), 7.66 (d, 1H, J = 7.8 Hz), 7.51−7.53 (m, 2H), 7.48 (d, 2H, J = 8.4 Hz), 7.46 (d, 1H, J = 9.0 Hz), 7.07 (d, 2H, J = 8.4 Hz), 7.03−7.06 (m, 1H), 6.81 (t, 1H, J = 7.2 Hz), 6.57 (s, 1H), 2.29 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 143.6, 139.9, 137.9, 136.5, 132.9, 132.8, 132.0, 129.5, 129.3, 129.0, 128.2, 127.8, 126.8, 126.2(9), 126.2(3), 126.1(7), 126.1(1), 122.6, 118.9, 115.5, 113.1, 104.6, 21.5. IR (neat): 3166, 3028, 1505, 1382, 1315, 1276, 1146, 1079, 792, 758 cm^{-1}. HRMS (ESI): m/z calcd for $C_{25}H_{20}NO_2S$ $[M + H]^+$ 398.1209; Found 398.1205.

*2-(Benzo[d][1,3]dioxol-5-yl)-3-tosylindolizine (**5o**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.4 mmol) and **4o** (0.2 mmol). 51 mg (65%), greenish solid, mp 125.4−126.3 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.06 (d, 1H, J = 6.6 Hz), 7.51 (d, 2H, J = 8.4 Hz), 7.41 (d, 1H, J = 9.0 Hz), 7.13 (d, 2H, J = 7.8 Hz), 7.00−7.02 (m, 1H), 6.97−6.98 (m, 1H), 6.92−6.94 (m, 1H), 6.85 (d, 1H, J = 7.2 Hz), 6.77 (dd, 1H, J = 6.6, 1.2

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Hz), 6.44 (s, 1H), 6.01 (s, 2H), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 147.5, 146.9, 143.5, 139.9, 137.7, 136.4, 129.5, 128.0, 126.3, 126.1, 124.2, 122.6, 118.8, 115.1, 113.0, 111.3, 107.5, 194.3, 101.1, 21.5. IR (neat): 2899, 2782, 1507, 1466, 1306, 1239, 1149, 1038, 939, 810, 784, 680 cm^{-1}. HRMS (ESI): m/z calcd for $C_{22}H_{18}NO_4S$ $[M + H]^+$ 392.0951; Found 392.0943.

*2-(Furan-2-yl)-3-tosylindolizine (**5p**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.6 mmol) and **4p** (0.2 mmol). 22 mg (33%), dark brown, sticky amorphous solid; ^1H NMR ($CDCl_3$, 600 MHz): δ 9.08 (d, 1H, J = 6.6 Hz), 7.73 (d, 2H, J = 7.8 Hz), 7.52 (d, 1H, J = 9.0 Hz), 7.42 (d, 1H, J = 9.0 Hz), 7.28 (d, 1H, J = 4.0 Hz), 7.18 (d, 2H, J = 7.8 Hz), 6.98−7.01 (m, 1H), 6.83 (s, 1H), 6.74 (td, 1H, J = 6.6, 1.2 Hz), 6.53 (dd, 1H, J = 4.2, 2.4 Hz), 2.33 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 147.1, 143.8, 142.7, 139.7, 136.8, 129.7, 126.5, 126.0 (2C), 122.7, 119.0, 113.2 (2C), 112.0, 111.9, 102.2, 21.5. IR (neat): 3129, 2927, 1634, 1599, 1509, 1317, 1148, 1082, 1015, 792, 736, 672 cm^{-1}. HRMS (ESI): m/z calcd for $C_{19}H_{16}NO_3S$ $[M + H]^+$ 338.0845; Found 338.0843.

*2-(Thiophene-2-yl)-3-tosylindolizine (**5q**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.4 mmol) and **4q** (0.2 mmol). 49 mg (70%), greenish solid, mp 84.5−85.8 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.14 (d, 1H, J = 7.2 Hz), 7.55 (d, 2H, J = 8.4 Hz), 7.49−7.50 (m, 1H), 7.38−7.41 (m, 2H), 7.12−7.14 (m, 3H), 7.00−7.03 (m, 1H), 6.78 (td, 1H, J = 7.2, 1.2 Hz), 6.58 (s, 1H), 2.31 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 143.7, 139.7, 136.4, 134.4, 129.8, 129.7, 129.5, 127.4, 126.6(2C), 126.1, 122.8, 118.8, 115.2, 113.3, 105.0, 21.5. IR (neat): 3108, 2924, 1595, 1505, 1358, 1317, 1271, 1149, 1108, 810, 717 cm^{-1}. HRMS (ESI): m/z calcd for $C_{19}H_{16}NO_2S_2$ $[M + H]^+$ 354.0617; Found 354.0612.

*8-Methyl-2-phenyl-3-tosylindolizine (**5r**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.4 mmol) and **4r** (0.2 mmol). 40 mg (56%), greenish solid, mp 94.4−95.9 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 8.97 (d, 1H, J = 7.2 Hz), 7.48−7.51 (m, 4H), 7.40−7.42 (m, 3H), 7.11 (d, 2H, J = 7.8 Hz), 6.83 (d, 1H, J = 6.6 Hz), 6.72 (t, 1H, J = 7.2 Hz), 6.48 (s, 1H), 2.41 (s, 3H), 2.31 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 143.4, 140.0, 137.6, 137.2, 134.6, 130.6, 129.5, 128.0, 127.8, 127.5, 126.2, 123.9, 121.8, 115.6, 113.1, 102.9, 21.5, 18.1. IR (neat): 3144, 3063, 2926, 1498, 1377, 1306, 1248, 1159, 1133, 1086, 911, 780 cm^{-1}. HRMS (ESI): m/z calcd for $C_{22}H_{20}NO_2S$ $[M + H]^+$ 362.1209; Found 362.1206.

*6-Ethyl-2-phenyl-3-tosylindolizine (**5s**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1a** (0.4 mmol) and **4s** (0.2 mmol). 65 mg (87%), brownish solid, mp 141.2−142.3 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 8.90 (s, 1H), 7.46−7.49 (m, 4H), 7.38−7.40 (m, 3H), 7.37 (d, 1H, J = 9.0 Hz), 7.11 (d, 2H, J = 7.8 Hz), 6.94 (dd, 1H, J = 9.0, 1.2 Hz), 6.43 (s, 1H), 2.65 (q, 2H, J = 7.2 Hz), 2.30 (s, 3H), 1.27 (t, 3H, J = 7.2 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 143.4, 139.9, 137.7, 135.5, 134.6, 130.6, 129.4, 129.0, 127.7, 127.4, 126.3, 124.8, 123.2, 118.4, 114.7, 104.0, 26.3, 21.5, 15.1. IR (neat): 2963, 2871, 1599, 1509, 1449, 1377, 1317, 1149, 1084, 808, 760, 700 cm^{-1}. HRMS (ESI): m/z calcd for $C_{23}H_{22}NO_2S$ $[M + H]^+$ 376.1365; Found 376.1363.

*2-Phenyl-3-(phenylsulfonyl)indolizine (**5t**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1b** (0.6 mmol) and **4a** (0.2 mmol). 35 mg (53%), greenish solid, mp 103.0−104.1 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.13 (d, 1H, J = 7.2 Hz), 7.58 (dd, 2H, J = 8.4, 1.2 Hz), 7.40−7.48 (m, 7H), 7.32 (t, 2H, J = 7.8 Hz), 7.03−7.05 (m, 1H), 6.80 (td, 1H, J = 7.2, 1.2 Hz), 6.49 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 142.8, 138.3, 126.6, 134.3, 132.7, 130.6, 128.8, 127.9, 127.5, 126.1(7), 126.1(3), 122.7, 118.9, 114.8, 113.1, 104.4. IR (neat): 3065, 3034, 2929, 1504, 1448, 1377, 1308, 1148, 1082, 997, 762, 730 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{16}NO_2S$ $[M + H]^+$ 3334.0896; Found 334.0889.

*3-((4-Fluorophenyl)sulfonyl)-2-phenylindolizine (**5u**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1c** (0.6 mmol) and **4a** (0.2 mmol). 37 mg (53%), greenish sticky solid; ^1H NMR ($CDCl_3$, 600 MHz): δ 9.12 (d, 1H, J = 6.6 Hz), 7.51−7.54 (m, 2H), 7.43−7.45 (m, 3H), 7.38−7.40 (m, 3H), 7.03−7.06 (m, 1H), 6.95 (t, 2H, J = 8.4 Hz), 6.80 (td, 1H, J = 6.6, 1.2 Hz), 6.48 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 165.1 (d, J = 254.2 Hz), 138.9, 138.2, 136.7, 134.1, 130.6, 128.9 (d, J = 8.5 Hz), 128.0, 127.6, 126.0, 122.8, 119.0, 116.0 (d, J = 22.9 Hz), 114.7, 113.3, 104.5. ^{19}F NMR (564 MHz, $CDCl_3$): δ −105.1. IR (neat): 3067, 2928, 2835, 1604, 1567, 1328, 1267, 1080, 766, 680 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{15}FNO_2S$ $[M + H]^+$ 352.0802; Found 352.0804.

*3-((4-Chlorophenyl)sulfonyl)-2-phenylindolizine (**5v**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1d** (0.6 mmol) and **4a** (0.2 mmol). 46 mg (63%), solid, mp 106.0−107.1 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.11 (d, 1H, J = 6.6 Hz), 7.39−7.46 (m, 8H), 7.24−7.26 (m, 2H), 7.04−7.07 (m, 1H), 6.81 (td, 1H, J = 6.6, 1.2 Hz), 6.48 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 141.3, 139.1, 138.4, 136.8, 134.1, 130.6, 129.1, 128.1, 127.6(3), 127.6(1), 126.1, 123.0, 119.0, 114.5, 113.3, 104.6. IR (neat): 3071, 2929, 1587, 1505, 1373, 1330, 1274, 1153, 1082, 1004, 803, 769 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{15}ClNO_2S$ $[M + H]^+$ 368.0507; Found 368.0504.

*3-((4-Methoxyphenyl)sulfonyl)-2-phenylindolizine (**5w**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1f** (0.6 mmol) and **4a** (0.2 mmol). 49 mg (68%), greenish solid, mp 112.7−113.8 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.09 (d, 1H, J = 6.6 Hz), 7.51−7.53 (m, 2H), 7.47−7.49 (m, 2H), 7.43 (d, 1H, J = 9.0 Hz), 7.38−7.40 (m, 3H), 7.01−7.04 (m, 1H), 6.76−6.80 (m, 3H), 6.48 (s, 1H), 3.76 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 163.0, 137.8, 136.4, 134.5, 134.4, 130.6, 128.4, 127.8, 127.5, 126.1, 122.5, 118.9, 115.5, 114.0, 113.0, 104.3, 55.6. IR (neat): 3075, 2931, 2858, 1593, 1496, 1310, 1254, 1135, 1082, 1019, 833, 741, 687 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{18}NO_3S$ $[M + H]^+$ 364.1001; Found 364.1001.

*4-((2-Phenylindolizin-3-yl)sulfonyl)benzonitrile (**5x**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1h** (0.6 mmol) and **4a** (0.2 mmol). 20 mg (28%), greenish solid, mp 120.2−121.1 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.18 (d, 1H, J = 6.6 Hz), 7.55−7.59 (m, 4H), 7.48 (d, 1H, J = 9.0 Hz), 7.39−7.43 (m, 5H), 7.10−7.13 (m, 1H), 6.87 (td, 1H, J = 6.6, 1.2 Hz), 6.51 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 146.8, 139.1, 137.4, 133.7, 132.6, 130.6, 128.3, 127.7, 126.6, 126.1, 123.6, 119.1, 117.4, 116.2, 113.7, 113.5, 105.0. IR (neat): 3125, 2929, 2232, 1612, 1502, 1317, 1274, 1149, 1084, 836, 812, 747 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{15}N_2O_2S$ $[M + H]^+$ 359.0849; Found 359.0847.

*2-Phenyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)indolizine (**5y**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1g** (0.6 mmol) and **4a** (0.2 mmol). 24 mg (30%), greenish solid, mp 138.9−139.9 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.17 (d, 1H, J = 6.6 Hz), 7.63 (d, 2H, J = 7.8 Hz), 7.55 (d, 2H, J = 8.4 Hz), 7.47 (d, 1H, J = 9.0 Hz), 7.39−7.487 (m, 5H), 7.08−7.11 (m, 1H), 6.86 (td, 1H, J = 6.6, 1.2 Hz), 6.51 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 146.2, 138.9, 137.1, 134.2 (q, J = 33.0 Hz), 133.9, 130.6, 128.2, 127.6, 126.6, 126.1, 125.9 (q, J = 3.4 Hz), 123.3, 123.2 (q, J = 270.0 Hz), 119.1, 113.9, 113.5, 104.8. ^{19}F NMR (564 MHz, $CDCl_3$): δ −63.0. IR (neat): 3067, 1507, 1379, 1321, 1153, 1131, 1062, 997, 853, 803, 762, 713 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{15}FNO_2S$ $[M + H]^+$ 402.0770; Found 402.0769.

*3-((2-Chlorophenyl)sulfonyl)-2-phenylindolizine (**5z**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1j** (0.6 mmol) and **4a** (0.2 mmol). 29 mg (40%), greenish solid, mp 147.7−148.7 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.27 (d, 1H, J = 7.2 Hz), 7.55 (d, 1H, J = 7.2 Hz), 7.48 (d, 1H, J = 9.0 Hz), 7.22−7.25 (m, 3H), 7.17−7.21 (m, 4H), 7.07−7.10 (m, 1H), 6.98 (td, 1H, J = 7.2, 1.8 Hz), 6.84 (t, 1H, J = 6.6 Hz), 6.48 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 140.0, 138.1, 136.4, 133.7, 133.3, 133.1 131.1, 130.3, 130.2, 127.7. 127.4, 126.9, 126.1, 122.8, 118.8, 113.6, 113.0, 104.0. IR (neat): 3155, 3058, 2927, 1502, 1449, 1381, 1313, 1280, 1254, 1151, 1105, 1041, 795, 747 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{15}ClNO_2S$ $[M + H]^+$ 368.0507; Found 368.0502.

*3-(Naphthalen-2-ylsulfonyl)-2-phenylindolizine (**5za**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1k** (0.6 mmol) and **4a** (0.2 mmol). 50 mg (64%), greenish solid, mp 91.7−92.6 °C. ^1H NMR ($CDCl_3$, 600 MHz):

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δ 9.22 (d, 1H, J = 6.6 Hz), 8.16 (d, 1H, J = 2.4 Hz), 7.79 (t, 2H, J = 8.4 Hz), 7.74 (d, 1H, J = 7.8 Hz), 7.51−7.58 (m, 2H), 7.46−7.48 (m, 3H), 7.42−7.44 (m, 1H), 7.38−7.41 (m, 3H), 7.02−7.05 (m, 1H), 6.81 (td, 1H, J = 6.6, 1.2 Hz), 6.49 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 139.5, 138.4, 136.7, 134.8, 134.3, 131.9, 130.7, 129.4, 129.2, 128.7, 128.0, 127.8, 127.5, 127.3, 126.2(2C), 122.8, 121.7, 118.9, 114.9, 113.2, 104.5. IR (neat): 3063, 2929, 2858, 1504, 1377, 1306, 1274, 1148, 1274, 1067, 795, 749, 685 cm^{-1}. HRMS (ESI): m/z calcd for $C_{24}H_{18}NO_2S$ $[M + H]^+$ 384.1052; Found 384,1054.

*2-Phenyl-3-(thiophene-2-ylsulfonyl)indolizine (**5zb**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1l** (0.6 mmol) and **4a** (0.2 mmol). 30 mg (44%), greenish solid, mp 149.1−149.6 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.06 (d, 1H, J = 6.6 Hz), 7.50−7.52 (m, 2H), 7.47 (d, 1H, J = 9.0 Hz), 7.40−7.44 (m, 4H), 7.39 (dd, 1H, J = 3.6, 1.2 Hz), 7.06−7.08 (m, 1H), 6.92 (dd, 1H, J = 4.2, 3.6 Hz), 6.84 (td, 1H, J = 6.6, 1.2 Hz), 6.52 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 144.6, 138.2, 136.8, 134.3, 132.1, 131.2, 130.5, 127.9, 127.5, 127.3, 126.2, 122.9, 118.9, 115.2, 113.2, 104.6. IR (neat): 3101, 3032, 1636, 1504, 1377, 1319, 1274, 1146, 1012, 762, 712 cm^{-1}. HRMS (ESI): m/z calcd for $C_{18}H_{14}NO_2S_2$ $[M + H]^+$ 340.0460; Found 340.0462.

*2-(3-Bromophenyl)-3-((4-chlorophenyl)sulfonyl)indolizine (**5zc**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1d** (0.4 mmol) and **4j** (0.2 mmol). 70 mg (78%), greenish solid, mp 131.6−132.4 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.09 (d, 1H, J = 6.6 Hz), 7.48−7.53 (m, 4H), 7.41−7.46 (m, 2H), 7.24−7.31 (m, 3H), 7.05−7.08 (m, 1H), 6.83 (td, 1H, J = 6.6, 1.2 Hz), 6.47 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 141.1, 139.4, 136.8, 136.5, 136.2, 133.1, 131.0, 129.4, 129.2, 129.1, 127.6, 126.0, 123.2, 121.6, 119.1, 114.7, 113.7, 104.5. IR (neat): 2967, 1373, 1328, 1280, 1153, 1082, 1004, 870, 762, 738 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{14}BrClNO_2S$ $[M + H]^+$ 445.9611; Found 445.9614.

*3-(Methylsulfonyl)-2-phenylindolizine (**5zd**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1m** (0.6 mmol) and **4a** (0.2 mmol). 21 mg (38%), greenish solid, mp 120.9−121.7 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.08−9.09 (m, 1H), 7.54−7.56 (m, 2H), 7.51 (d, 1H, J = 9.0 Hz), 7.39−7.44 (m, 3H), 7.06−7.09 (m, 1H), 6.82 (td, 1H, J = 7.2, 1.2 Hz), 6.55 (s, 1H), 2.94 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 137.3, 136.2, 134.1, 130.3, 128.1, 127.9, 126.2, 122.5, 119.0, 114.8, 113.1, 103.9, 45.0. IR (neat): 3123, 2927, 2857, 1505, 1451, 1312, 1146, 952, 760 cm^{-1}. HRMS (ESI): m/z calcd for $C_{15}H_{14}NO_2S$ $[M + H]^+$ 272.0739; Found 272.0734.

*3-(Cyclopropylsulfonyl)-2-phenylindolizine (**5ze**).* (eluent: 10:1 hexanes/ethyl acetate). The product was synthesized by the general procedure B using **1o** (0.6 mmol) and **4a** (0.2 mmol). 43 mg (72%), greenish solid, mp 120.9−121.7 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 9.09 (d, 1H, J = 7.2 H), 7.52−7.54 (m, 2H), 7.47 (d, 1H, J = 9.0 Hz), 7.36−7.41 (m, 3H), 7.04 (dd, 1H, J = 9.0, 7.8 Hz), 6.77 (td, 1H, J = 7.2, 1.2 Hz), 6.52 (s, 1H), 2.38−2.42 (m, 1H), 1.05−1.08 (m, 2H), 0.76−0.77 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 137.4, 136.1, 134.5, 130.5, 127.9, 127.6, 126.3, 122.3, 118.9, 115.5, 112.9, 104.0, 34.2, 5.1 (2C). IR (neat): 3157, 3058, 2929, 1502, 1463, 1313, 1276, 1189, 1082, 997, 834, 766, 670 cm^{-1}. HRMS (ESI): m/z calcd for $C_{17}H_{15}NO_2S$ $[M + H]^+$ 298.0896; Found 298.0893.

EPR Measurements. The EPR spectra were recorded on a Bruker EMX/plus CW EPR spectrometer with microwave tuned at 9.64 GHz, 3 mW of microwave power, 100 kHz modulation frequency, and 1 G modulation at room temperature. 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) was used for spin-trapping agent. For the formation of DMPO−**2a** adduct, imidazo[1,2-*a*]pyridine (**2a**, 0.1 mmol) and $LiClO_4$ (150 mg, 0.4 M) were dissolved in a mixture of CH_3CN and H_2O (3.5 mL, v/v = 2.5:1) under Ar atmosphere and an undivided cell with a glassy carbon anode and a platinum cathode was equipped in this solution. DMPO (20 μL) was then added to this solution, and the reaction mixture was electrolyzed at a constant current of 7 mA under room temperature using an ElectraSyn 2.0. After 30 min, the sample was taken by an EPR glass capillary and loaded to EPR spectrometer. DMPO−**1a** adduct was generated by the same procedure using sodium sulfinate (**1a**, 0.3 mmol), and the EPR sample was taken by an EPR glass capillary after 15 min. For the generation of DMPO−**4a** adduct, an undivided cell equipped with a glassy carbon anode and a nickel cathode was connected to an ElectraSyn 2.0. A solution of indolizine (**4a**, 0.1 mmol) and $LiClO_4$ (160 mg, 0.40 M) in a mixture of DMF and H_2O (3.75 mL, v/v = 15:1) was added to the undivided cell followed by the addition of DMPO (20 μL). The reaction mixture was stirred and electrolyzed at a constant current of 7 mA for 15 min at room temperature before the sample was taken by an EPR glass capillary for the EPR measurement.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00873.

Spectral data for all compounds (PDF)

FAIR data, including the primary NMR FID files, for compounds **2**−**5** (ZIP)

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Notes

The authors declare no competing financial interest.

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