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Iodine-Mediated One-Pot Synthesis of Imidazo[1,5-*a*]Pyridines

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Abstract: In this report, we developed an efficient one-pot method for the synthesis of 3-phenyl-1-(phenylthio)imidazo[1,5-*a*]pyridine analogs starting from 2-aminomethylpyridines, benzaldehydes, and sodium benzenesulfinates, which constructed C-N and C-S bonds simultaneously. The method features mild reaction conditions, a wide range of substrates, high atom utilization, and convenient and easily accessible starting materials.

Keywords: 2-aminomethylpyridine; benzaldehyde; cyclization; sodium benzenesulfinate; iodine

1. Introduction

As an important nitrogen-containing heterocyclic compound, imidazo[1,5-*a*]pyridine has a wide range of applications in various fields, especially in medicinal chemistry [1–7]. For example, imidazo[1,5-*a*]pyridine derivative (Figure 1a) shows good anti-inflammatory effects as NIK inhibitors [8], compound b (Figure 1b) demonstrates excellent anti-cancer activity in biomedical fields [9], and compound c (Figure 1c) shows good antitumor activity in vivo and vitro [10]. In addition, compound d (Figure 1d) shows promising results in treating brain injury, such as Alzheimer's disease [11].

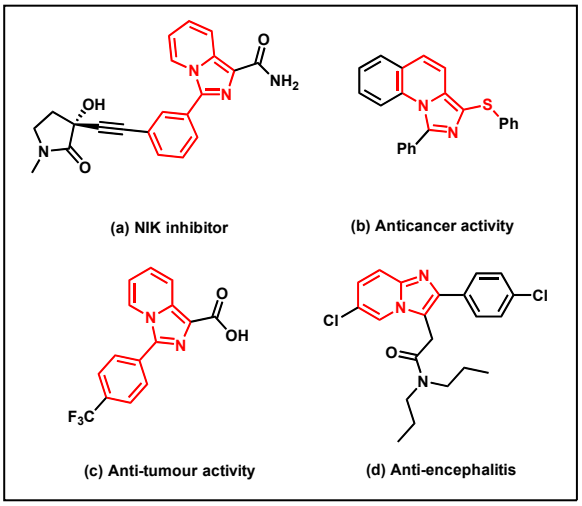

Figure 1. Imidazopyridine-based drugs and biologically relevant molecules.

Imidazo[1,5-*a*]pyridine is considered to be a special backbone with a wide range of applications in medicine and chemistry [12–14], and efforts have been made to modify this skeleton over the past years [15,16]. In recent years, sulfur-containing compounds have also attracted significant attention due to their widespread presence in various natural

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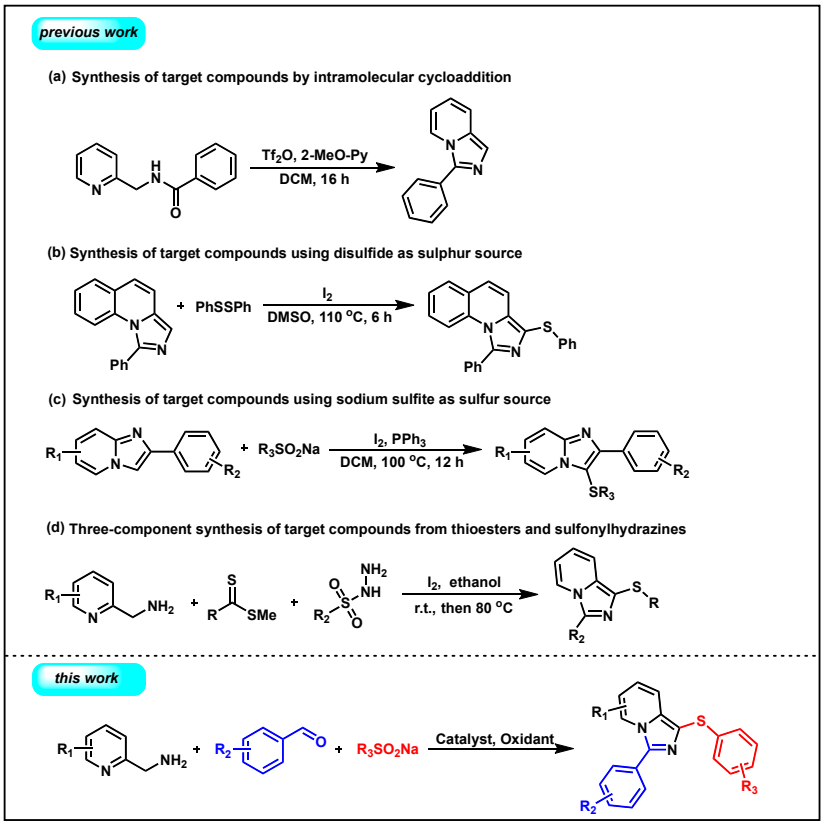
Citation: Huang, L.; Liu, Y.; Guan, Z.; Dong, Z. Iodine-Mediated One-Pot Synthesis of Imidazo[1,5-*a*]Pyridines. *Catalysts* **2024**, *14*, 601. https://doi.org/10.3390/catal14090601

Academic Editor: Fabio Ragaini

Received: 14 August 2024
Revised: 30 August 2024
Accepted: 3 September 2024
Published: 6 September 2024

products and drugs [17]. Therefore, the modification of imidazopyridine by the construction of C(sp^2)–S bonds is highly desirable [18–27]. Conventional methods for the synthesis of imidazo[1,5-*a*]pyridines are generated by cyclic dehydration or arylation reactions initiated by using trifluoromethic anhydride (Tf_2O) and 2-methoxypyridine (2-MeO-Py) (Scheme 1a) [28]. In recent years, relevant literature reports have been published on the synthesis of 3-sulfinylimidazo[1,5-*a*]quinoline derivatives using iodine-catalyzed imidazo[1,5-*a*]quinolines and disulfides as sulfinylation reagents (Scheme 1b). [9] In 2018, Song's group used sodium sulfite as the sulfur source to prepare 3-sulfinylimidazolo [1,2-a] pyridine derivatives under high temperatures (Scheme 1c) [29]. Similarly, 3-sulfinylimidazo[1,5-*a*]pyridine can also be synthesized by C–H functionalization using disulfide esters, 2-methylaminopyridine, and sulfonylhydrazine (Scheme 1d) [30]. These methods are important for the C–S modification of imidazo[1,5-*a*]pyridines, while they still suffer from safety issues, harsh reaction conditions, long reaction time, the use of toxic starting materials, and expensive substrates.



Scheme 1. Strategies for the synthesis of imidazo[1,5-*a*]pyridines and 3-sulfinylimidazo[1,5-*a*]pyridines.

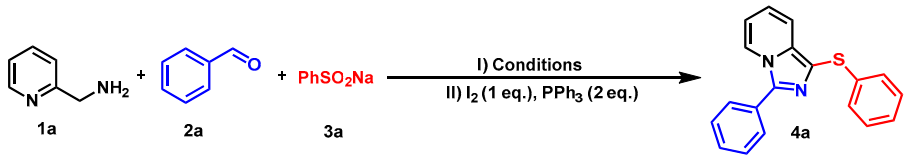
Inspired by our longstanding interest in organosulfur chemistry [31–36], we would like to report an efficient method for the synthesis of 3-phenyl-1-(phenylthio)imidazo[1,5-*a*]pyridine by using sodium benzenesulfinates, 2-aminomethylpyridines, and benzaldehydes as starting materials, which might pave an alternative way for the preparation of this important backbone (Scheme 1, this work).

2. Results and Discussion

Initially, 2-aminomethylpyridine (**1a**), benzaldehyde (**2a**), and sodium benzenesulfinate (**3a**) were chosen as starting materials for the synthesis of 3-phenyl-1-(phenylthio)imidazo-[1,5-*a*]pyridine analogs, and the reaction conditions are summarized in Table 1. Since the second step of the reaction using sodium benzenesulfinate is essentially quantitative in yields, we mainly focused on the optimization in the first step. Inspired by the previous literature, we used TBHP (*tert*-Butyl hydroperoxide) as the oxidant, I_2 as the catalyst, and DMF (*N*,*N*-

Dimethylformamide) as the solvent at a temperature of 70 °C, obtaining the target compound **4a** with a 60% yield (entry 1). Firstly, a variety of oxidants (*m*-CPBA (3-Chloroperoxybenzoic acid), IBX (2-Iodoxybenzoic acid), PIDA (Iodobenzene diacetate), and $K_2S_2O_8$) were screened, and it was found that TBHP was the best oxidant. The reaction did not occur without the addition of oxidants (entries 2–6). Furthermore, when the catalyst was replaced with NaI or NIS, it had a negative impact on the results (entries 8–9). Additionally, a series of solvents such as DCM (Dichloromethane), Et_2O (Diethyl ether), EtOH (Ethanol), and 1,4-Dioxane were screened, and the best results were obtained with DMF (entries 10–13). Moreover, further optimization on the reaction temperature showed that 100 °C was the best, giving the target product with a 70% yield (entry 16). Subsequently, the oxidant loading was optimized, and the results showed that the optimal oxidant loading was 1.0 equiv. (entries 18–19). Finally, the screening on the ratio (entries 16, 20-21) of **1a** and **2a** showed that the best one is **1a**:**2a**=2:1. Therefore, the optimal reaction conditions are summarized in entry 16.

Table 1. Optimization of the reaction conditions [a,b].



Entry	Oxidant	Catalyst	Solvent	T (°C)	Yield (%) [b]
1	TBHP	I_2	DMF	70	60
2	*m*-CPBA	I_2	DMF	70	45
3	IBX	I_2	DMF	70	38
4	PIDA	I_2	DMF	70	trace
5	$K_2S_2O_8$	I_2	DMF	70	35
6	-	I_2	DMF	70	N.R.
7	TBHP	-	DMF	70	N.R.
8	TBHP	NaI	DMF	70	28
9	TBHP	NIS	DMF	70	21
10	TBHP	I_2	DCM	70	54
11	TBHP	I_2	Et_2O	70	26
12	TBHP	I_2	EtOH	70	34
13	TBHP	I_2	1,4-Dioxane	70	40
14	TBHP	I_2	DMF	80	54
15	TBHP	I_2	DMF	90	60
16	TBHP	I_2	DMF	100	70
17	TBHP	I_2	DMF	110	42
18 [c]	TBHP	I_2	DMF	100	64
19 [d]	TBHP	I_2	DMF	100	56
20 [e]	TBHP	I_2	DMF	100	57
21 [f]	TBHP	I_2	DMF	100	50

[a] Reaction conditions: **1a** (1 mmol), **2a** (0.5 mmol), **3a** (1 mmol), catalyst (20 mol%), oxidant (0.5 mmol), solvent (2 mL). The mixture in the sealed tube was stirred at 100 °C for 2 h in the first step and was stirred for 2 h in the second step. [b] Isolated yield. [c] Oxidant loading (1.5 equiv.). [d] Oxidant loading (2 equiv.). [e] **1a** (0.5 mmol), **2a** (0.5 mmol). [f] **1a** (1.5 mmol), **2a** (0.5 mmol).

Based on the above optimal reaction conditions, the substrate range of substituted benzaldehyde **1a** and sodium sulfite **3a** was explored (Figure 2). Firstly, aryl aldehydes containing electron-withdrawing groups (–Cl, –Br, $–NO_2$) were used to carry out the reaction in moderate to good yields (**4e**–**4g**). When changing the position of chlorine, the yields were significantly reduced, such as **4h** and **4i**, which may be due to the influence of steric hindrance. In addition, the yield of the substrate containing electron-donating groups ($–CH_3$, $–^tBu$, –Ph) decreased considerably (**4b**–**4d**). To our delight, when naphthalene formaldehyde, pyridine formaldehyde, and thiophene formaldehyde were used, the corresponding target compounds were obtained smoothly (**4m**–**4o**). In addition, the

substrate range of sodium benzenesulfinates was also surveyed. The experimental results showed that the target compounds bearing Me–, Cl–, and F– were obtained in moderate to good yields (**4j**–**4l**). Unfortunately, no target compounds were obtained when sodium alkylsulfinate was tested. Subsequently, the target compounds (**4p**–**4za**) were obtained in high yield when the substituents on the benzene ring of aryl aldehydes and sodium benzenesulfinates were adjusted simultaneously.

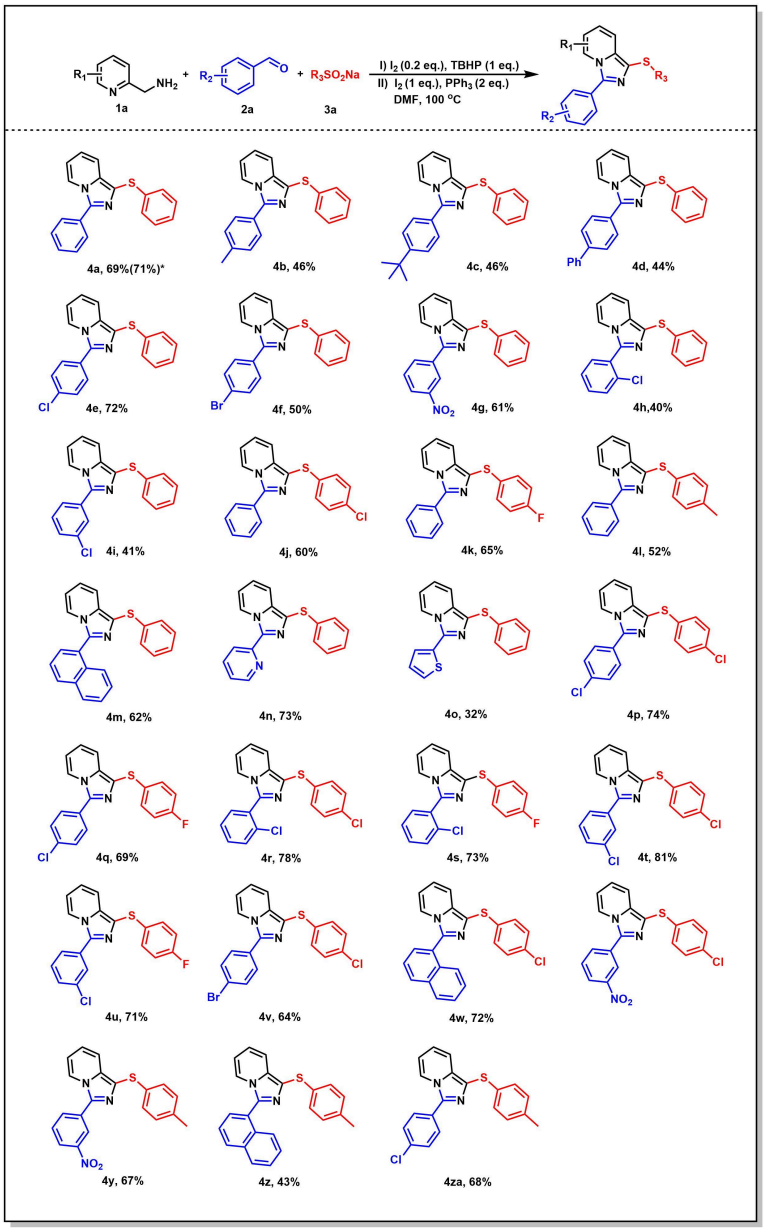
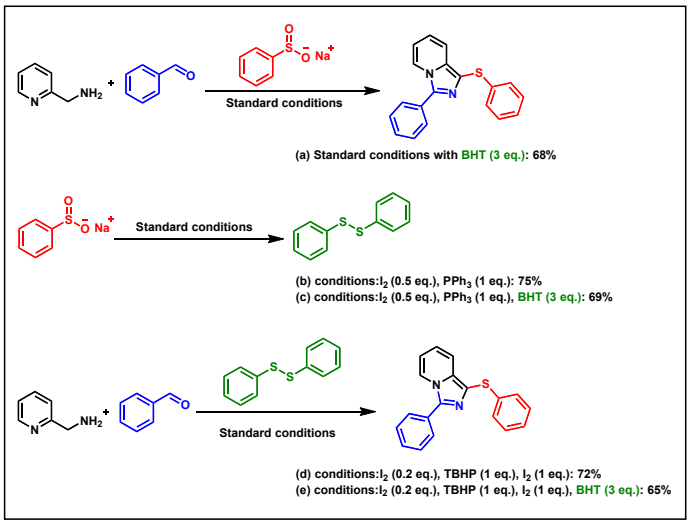


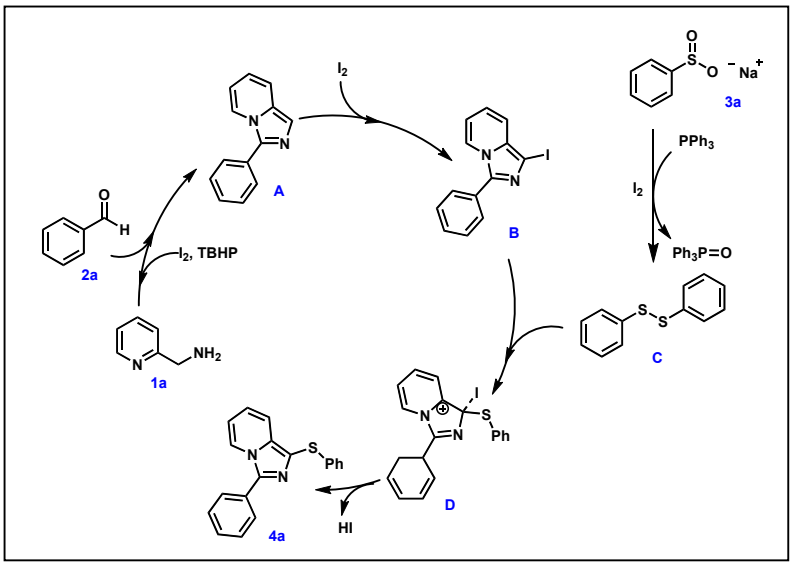
Figure 2. Substrate scope for various benzaldehydes and sodium benzenesulfinates. Reaction conditions: **1a** (1 mmol), **2a** (0.5 mmol), **3a** (1 mmol), I_2 (0.1 mmol), TBHP (0.5 mmol), DMF (2 mL). The mixture in the sealed tube was stirred at 100 °C for 2 h in the first step and was stirred for 2 h in the second step. Isolated yield. * For a scaled-up reaction, **1a** (20 mmol, 2.16 g), **2a** (10 mmol, 1.06 g), iodine (2 mmol, 0.5 g) in DMF (30 mL) were added into the reaction tube, then TBHP (10 mmol, 1.29 g) was added, and the mixture was stirred at 100 °C for 2 h. Then, **3a** (20 mmol, 3.28 g), iodine (10 mmol, 2.54 g), PPh_3 (Triphenylphosphine) (20 mmol, 5.25 g) was added, and the mixture was stirred at 100 °C and monitored by TLC (Thin Layer Chromatography) until the starting material (**1a** or **2a**) was consumed. The crude product was purified by column chromatography to give **4a** (71%, 2.15 g).

To explore the reaction mechanism, some control experiments were performed. Initially, 3 equiv. of BHT (2,6-di-*tert*-butyl-4-methylphenol) was added to the reaction system under standard conditions, giving the target product **4a** in a 68% yield (Scheme 2a). This indicated that a radical pathway was excluded. Furthermore, sodium benzenesulfinate (**3a**) could be converted to diphenyl disulfide in 75% in the presence of triphenylphosphine and iodine (Scheme 2b). Interestingly, the yield of diphenyl disulfide remained basically unchanged when 3 equiv. of BHT was added under these conditions. Finally, the target product **4a** could be obtained by using diphenyl disulfide in the presence of iodine, giving the target product in 72% yield (Scheme 2c). The product yield remained essentially unchanged even with the addition of 3 equiv. of BHT (Scheme 2d).



Scheme 2. Control experiments.

Based on the results of control experiments and related literature [37–40], we proposed a possible mechanism for the model reaction (Scheme 3). Initially, 2-aminomethylpyridine (**1a**) and benzaldehyde (**2a**) reacted with iodine/TBHP to form intermediate **A**. Subsequently, **A** reacted with I_2 to produce intermediate **B**. Meanwhile, sodium benzenesulfinate (**3a**) generated diphenyl disulfide **C** in the presence of PPh_3 and I_2. Thus, **B** reacted with diphenyl disulfide **C** to form intermediate **D**, which gave the target product **4a** via the removal of HI.



Scheme 3. Plausible reaction mechanism.

3. Experimental Section

General Information. See the details in the Supplementary Materials.

General procedure for the synthesis of 3-sulfinylimidazo[1,5-*a*]pyridines.

A mixture of pyridin-2-ylmethanamine (**1a**, 1 mmol), benzaldehyde (**2a**, 0.5 mmol), and iodine (0.1 mmol) in DMF (3 mL) was added into the reaction tube, then TBHP (1.0 eq., based on **2a**) was added, and the mixture was stirred at 100 °C for 2 h. Then, sodium benzenesulfinate (**3a**, 1 mmol), iodine (0.5 mmol), and PPh_3 (2.0 eq., based on **2a**) were added, and the mixture was stirred at 100 °C and monitored by TLC until the starting material (**1a** or **2a**) was consumed. The reaction was then quenched with saturated $Na_2S_2O_3$ solution (about 5 mL), and extracted with ethyl acetate. The original solution was dried with anhydrous Na_2SO_4 and evaporated in vacuo. The crude product was purified by column chromatography to give **4a**.

3-phenyl-1-(phenylthio)imidazo[1,5-*a*]pyridine (4a): 104 mg (yield: 69%), a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.32 (d, *J* = 7.2 Hz, 1H), 7.85–7.83 (m, 2H), 7.65 (d, *J* = 9.1 Hz, 1H), 7.55–7.51 (m, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.23–7.17 (m, 4H), 7.09 (t, *J* = 6.9 Hz, 1H), 6.87 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.67 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 139.3, 138.4, 135.1, 129.5, 129.2, 129.0, 128.8, 128.3, 127.1, 125.5, 122.1, 121.1, 120.1, 118.5, 113.9. HRMS (ESI) m/z [$(M + H)^+$] Calcd for $C_{19}H_{15}N_2S^+$ (303.0950), found 303.0953.

1-(phenylthio)-3-(p-tolyl)imidazo[1,5-*a*]pyridine (4b)*:* 72 mg (yield: 46%), a white solid. M.P.: 142-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.29 (d, *J* = 7.2 Hz, 1H), 7.74–7.72 (m, 2H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.35–7.33 (m, 2H), 7.23–7.16 (m, 4H), 7.08 (t, *J* = 7.0 Hz, 1H), 6.85 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.65 (t, *J* = 6.8 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 139.5, 139.3, 138.4, 135.0, 129.7, 128.8, 128.2, 127.1, 126.6, 125.5, 122.2, 121.0, 119.7, 118.5, 113.8, 21.5. HRMS (ESI) m/z [$(M + H)^+$] Calcd for $C_{20}H_{17}N_2S^+$ (317.1107), found 317.1104.

3-(4-(tert-butyl)phenyl)-1-(phenylthio)imidazo[1,5-*a*]pyridine (4c)*:* 82 mg (yield: 46%), a green solid. M.P.: 140-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31 (d, *J* = 7.2 Hz, 1H), 7.79–7.77 (m, 2H), 7.62 (d, *J* = 9.2 Hz, 1H), 7.56–7.54 (m, 2H), 7.23–7.16 (m, 4H), 7.07 (t, *J* = 7.1 Hz, 1H), 6.82 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.62 (t, *J* = 6.8 Hz, 1H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 152.4, 139.5, 138.5, 135.0, 128.8, 128.0, 127.0, 126.7, 126.0, 125.5, 122.2, 121.0, 119.8, 118.4, 113.7, 34.9, 31.3. HRMS (ESI) m/z [$(M + H)^+$] Calcd for $C_{23}H_{23}N_2S^+$ (359.1576), found 359.1572.

3-([1,1′-biphenyl]-4-yl)-1-(phenylthio)imidazo[1,5-*a*]pyridine (4d)*:* 84 mg (yield: 44%), a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.39 (d, *J* = 7.3 Hz, 1H), 7.96 (s, 1H), 7.94 (s, 1H), 7.80 (s, 1H), 7.77 (s, 1H), 7.70–7.67 (m, 3H), 7.52–7.48 (m, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.28–7.20 (m, 4H), 7.12 (t, *J* = 7.1 Hz, 1H), 6.90 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.71 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.8, 140.3, 139.0, 138.4, 135.2, 129.0, 128.9, 128.6, 128.4, 127.8, 127.7, 127.1, 127.1, 125.6, 122.2, 121.2, 120.3, 118.5, 114.0. HRMS (ESI) m/z [$(M + H)^+$] Calcd for $C_{25}H_{19}N_2S^+$ (379.1263), found 379.1260.

3-(4-chlorophenyl)-1-(phenylthio)imidazo[1,5-*a*]pyridine (4e)*:* 121 mg (yield: 72%), a yellow solid. M.P.: 104–1110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.25 (d, *J* = 7.2 Hz, 1H), 7.79 (s, 1H), 7.77 (s, 1H), 7.65 (d, *J* = 9.1 Hz, 1H), 7.50 (s, 1H), 7.48 (s, 1H), 7.22–7.17 (m, 4H), 7.09 (t, *J* = 6.7 Hz, 1H), 6.88 (dd, *J* = 9.2, 6.5 Hz, 1H), 6.69 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 138.1, 135.3, 135.0, 129.4, 129.3, 128.9, 128.0, 127.2, 125.6, 122.4, 121.9, 121.3, 120.5, 118.6, 114.3. HRMS (ESI) m/z [$(M + H)^+$] Calcd for $C_{19}H_{14}ClN_2S^+$ (337.0561), found 337.0565.

3-(4-bromophenyl)-1-(phenylthio)imidazo[1,5-*a*]pyridine (4f)*:* 95 mg (yield: 50%), a yellow solid. M.P.: 118–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.25 (d, *J* = 7.2 Hz, 1H), 7.73–7.70 (m, 2H), 7.65–7.73 (m, 3H), 7.22–7.16 (m, 4H), 7.09 (t, *J* = 6.7 Hz, 1H), 6.88 (dd, *J* = 9.0, 6.6 Hz, 1H), 6.69 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 138.1, 135.3, 132.3, 129.6, 128.9, 128.5, 127.2, 125.6, 123.2, 121.9, 121.3, 120.6, 118.6, 114.3. HRMS (ESI) m/z [$(M + H)^+$] Calcd for $C_{19}H_{13}BrN_2S^+$ (381.0056), found 381.0053.

3-(3-nitrophenyl)-1-(phenylthio)imidazo[1,5-*a*]pyridine (4g)*:* 105 mg (yield: 61%), a yellow solid. M.P.: 116–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.70 (s, 1H), 8.34 (d, *J* = 7.5 Hz, 1H), 8.27–8.21 (m, 2H), 7.72–7.68 (m, 2H), 7.22–7.16 (m, 4H), 7.09 (t, *J* = 6.6 Hz, 1H), 6.95 (dd, *J* = 8.9, 6.7 Hz, 1H), 6.79 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.6, 137.8, 136.6, 135.7, 134.0, 131.3, 130.3, 128.9, 127.3, 125.8, 123.5, 122.3, 121.9, 121.6, 121.5, 118.7, 115.1. HRMS (ESI) m/z [$(M + H)^+$] Calcd for $C_{19}H_{14}N_3O_2S^+$ (348.0801), found 348.0805.

3-(2-chlorophenyl)-1-(phenylthio)imidazo[1,5-*a*]pyridine (4h)*:* 67 mg (yield: 40%), a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69–7.65 (m, 3H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.48–7.40 (m, 2H), 7.20–7.19 (m, 4H), 7.11–7.06 (m, 1H), 6.92 (dd, *J* = 9.9, 6.6 Hz, 1H), 6.69 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 138.5, 136.9, 134.7, 134.3, 133.4, 131.1, 130.0, 128.8, 128.8, 127.3, 127.0, 125.5, 122.9, 121.3, 119.6, 118.1, 113.5. HRMS (ESI) m/z [$(M + H)^+$] Calcd for $C_{19}H_{14}ClN_2S^+$ (337.0561), found 337.0564.

3-(3-chlorophenyl)-1-(phenylthio)imidazo[1,5-*a*]pyridine (4i)*:* 69 mg (yield: 41%), a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.32 (d, *J* = 7.2 Hz, 1H), 7.86 (s, 1H), 7.74 (d, *J* = 7.3 Hz, 1H), 7.68 (d, *J* = 9.2 Hz, 1H), 7.49–7.44 (m, 2H), 7.24–7.17 (m, 4H), 7.12–7.08 (m, 1H), 6.91 (dd, *J* = 9.1, 6.4 Hz, 1H), 6.74 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 137.9, 137.7, 135.3, 135.1, 131.0, 130.3, 129.3, 128.9, 128.2, 127.4, 126.2, 125.7, 121.9, 121.5, 118.7, 114.5. HRMS (ESI) m/z [$(M + H)^+$] Calcd for $C_{19}H_{14}ClN_2S^+$ (337.0561), found 337.0565.

1-((4-chlorophenyl)thio)-3-phenylimidazo[1,5-*a*]pyridine (4j)*:* 101 mg (yield: 60%), a white solid. M.P.: 104–110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.32 (d, *J* = 7.3 Hz, 1H), 7.84–7.82 (m, 2H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.56–7.52 (m, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.15 (s, 4H), 6.90 (dd, *J* = 9.1, 6.4 Hz, 1H), 6.69 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 139.4, 136.9, 135.0, 131.5, 129.3, 129.1, 128.9, 128.5, 128.3, 122.2, 121.5, 119.5, 118.3, 114.1. HRMS (ESI) m/z [$(M + H)^+$] Calcd for $C_{19}H_{14}ClN_2S^+$ (337.0561), found 337.0563.

1-((4-fluorophenyl)thio)-3-phenylimidazo[1,5-*a*]pyridine (4k)*:* 104 mg (yield: 65%), a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.32 (d, *J* = 7.2 Hz, 1H), 7.85–7.83 (m, 2H), 7.67 (d, *J* = 9.2 Hz, 1H), 7.56–7.52 (m, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.28–7.25 (m, 2H), 6.94–6.87 (m, 3H), 6.68 (t, *J* = 6.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.4 [d, *J*(C–F) = 244.0 Hz], 139.3, 134.9, 133.2, 129.5, 129.5 [d, *J*(C-F) = 8.0 Hz], 129.2, 129.1, 128.3, 122.1, 121.3, 120.5, 118.3, 115.9 [d, *J*(C-F) = 21.0 Hz], 113.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ –117.0. HRMS (ESI) m/z [$(M + H)^+$] Calcd for $C_{19}H_{14}FN_2S^+$ (321.0856), found 321.0853.

3-phenyl-1-(p-tolylthio)imidazo[1,5-*a*]pyridine (4l)*:* 82 mg (yield: 52%), a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.29 (d, *J* = 7.2 Hz, 1H), 7.84–7.82 (m, 2H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.54–7.50 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.18–7.16 (m, 2H), 7.02–7.00 (m, 2H), 6.84 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.64 (t, *J* = 6.8 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 139.1, 136.5, 135.5, 134.8, 134.6, 129.6, 129.6, 129.1, 129.0, 128.3, 127.8, 122.0, 121.0, 118.5, 113.9, 21.0. HRMS (ESI) m/z [$(M + H)^+$] Calcd for $C_{20}H_{17}N_2S^+$ (317.1107), found 317.1104.

3-(naphthalen-1-yl)-1-(phenylthio)imidazo[1,5-*a*]pyridine (4m)*:* 109 mg (yield: 62%), a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.01 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 7.1 Hz, 1H), 7.74–7.70 (m, 3H), 7.63–7.59 (m, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.31–7.29 (m, 2H), 7.24–7.20 (m, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.89 (dd, *J* = 9.6, 6.4 Hz, 1H), 6.58–6.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 138.6, 138.1, 134.7, 134.0, 131.8, 130.3, 129.0, 128.9, 128.7, 127.2, 126.6, 126.5, 125.5, 125.4, 125.3, 122.5, 121.3, 119.8, 118.3, 113.5. HRMS (ESI) m/z [$(M + H)^+$] Calcd for $C_{23}H_{17}N_2S^+$ (353.1107), found 353.1104.

1-(phenylthio)-3-(pyridin-2-yl)imidazo[1,5-*a*]pyridine (4n):. 110 mg (yield: 73%), a white solid. M.P.: 100-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.00 (d, *J* = 7.3 Hz, 1H), 8.61 (d, *J* = 4.0 Hz, 1H), 8.43 (d, *J* = 8.1 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 9.1 Hz, 1H), 7.20–7.15 (m, 5H), 7.09–7.0 (m, 1H), 6.93 (dd, *J* = 9.0, 6.5 Hz, 1H), 6.76 (t, *J* = 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.6, 148.1, 138.3, 136.6, 136.4, 136.3, 128.9,

126.9, 126.8, 125.5, 122.4, 122.2, 120.3, 117.6, 114.2. HRMS (ESI) m/z [(M + H)$^+$] Calcd for $C_{18}H_{14}N_3S^+$ (304.0903), found 304.0906.

1-(phenylthio)-3-(thiophen-2-yl)imidazo[1,5-*a*]pyridine (4o)*:* 49 mg (yield: 32%), a yellow solid. M.P.: 112–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.40 (d, *J* = 7.2 Hz, 1H), 7.65 (d, *J* = 9.1 Hz, 1H), 7.60 (d, *J* = 3.7 Hz, 1H), 7.45 (d, *J* = 5.1 Hz, 1H), 7.21–7.16 (m, 5H), 7.10–7.07 (m, 1H), 6.89 (dd, *J* = 9.1, 6.4 Hz, 1H), 6.76 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 138.2, 135.1, 134.0, 131.5, 128.8, 127.7, 127.1, 126.6, 125.8, 125.6, 122.4, 121.1, 120.5, 118.5, 114.4. HRMS (ESI) m/z [(M + H)$^+$] Calcd for $C_{17}H_{13}N_2S_2^+$ (309.0515), found 309.0518.

3-(4-chlorophenyl)-1-((4-chlorophenyl)thio)imidazo[1,5-*a*]pyridine (4p)*:* 138 mg (yield: 74%), a yellow solid. M.P.: 140–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.26 (d, *J* = 7.3 Hz, 1H), 7.78–7.76 (m, 2H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.51–7.49 (m, 2H), 7.14 (s, 4H), 6.91 (dd, *J* = 9.2, 6.5 Hz, 1H), 6.71 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 138.3, 136.7, 135.3, 135.2, 131.5, 129.4, 129.4, 128.9, 128.5, 127.9, 121.9, 121.6, 112.0, 118.4, 114.3. HRMS (ESI) m/z [(M + H)$^+$] Calcd for $C_{19}H_{13}C_{l2}N_2S^+$ (371.0171), found 371.0175.

3-(4-chlorophenyl)-1-((4-fluorophenyl)thio)imidazo[1,5-*a*]pyridine (4q)*:* 122 mg (yield: 69%), a white oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.27 (d, *J* = 7.2 Hz, 1H), 7.81 (s, 1H), 7.79 (s, 1H), 7.69 (d, *J* = 9.2 Hz, 1H), 7.54 (s, 1H), 7.52 (s, 1H), 7.29–7.25 (m, 2H), 6.95 –6.91 (m, 3H), 6.73 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.5 [d, *J*(C-F) = 244.0 Hz], 138.1, 135.2, 135.0, 132.9, 129.7 [d, *J*(C-F) = 7.0 Hz], 129.5, 129.4, 127.8, 121.9, 121.5, 120.9, 118.5, 115.9 [d, *J*(C-F) = 22.0 Hz], 114.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -116.7. HRMS (ESI) m/z [(M + H)$^+$] Calcd for $C_{19}H_{13}ClFN_2S^+$ (355.0467), found 355.0465.

3-(2-chlorophenyl)-1-((4-chlorophenyl)thio)imidazo[1,5-*a*]pyridine (4r)*:* 145 mg (yield: 78%), a yellow solid. M.P.: 150–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69–7.64 (m, 3H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.49–7.40 (m, 2H), 7.15–7.12 (m, 4H), 6.94 (dd, *J* = 9.1, 6.5 Hz, 1H), 6.70 (t, *J* = 6.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 137.1, 134.7, 134.3, 133.3, 131.4, 131.3, 130.0, 128.9, 128.6, 128.3, 127.3, 123.0, 121.7, 119.1, 117.9, 113.6. HRMS (ESI) m/z [(M + H)$^+$] Calcd for $C_{19}H_{13}Cl_2N_2S^+$ (371.0171), found 371.0174.

3-(2-chlorophenyl)-1-((4-fluorophenyl)thio)imidazo[1,5-*a*]pyridine (4s)*:* 130 mg (yield: 73%), a white solid. M.P.: 80–92°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.68–7.62 (m, 3H), 7.54 (s, 1H), 7.53 (s, 1H), 7.47–7.39 (m, 2H), 7.24 -7.21 (m, 2H), 6.94–6.87 (m, 3H), 6.69–6.66 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.4 [d, *J*(C–F) = 244.0 Hz], 136.9, 134.5, 134.3, 133.3, 131.2, 130.0, 129.3 [d, *J*(C–F) = 8.0 Hz], 128.7, 127.3, 122.9, 121.5, 120.0, 118.0, 115.9 [d, *J*(C–F) = 22.0 Hz], 113.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ –117.1. HRMS (ESI) m/z [(M + H)$^+$] Calcd for $C_{19}H_{13}ClFN_2S^+$ (355.0467), found 355.0464.

3-(3-chlorophenyl)-1-((4-chlorophenyl)thio)imidazo[1,5-*a*]pyridine(4t)*:* 150 mg (yield: 81%), a yellow solid. M.P.: 98–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.30 (d, *J* = 7.2 Hz, 1H), 7.84 (s, 1H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.48–7.41 (m, 2H), 7.17–7.12 (m, 4H), 6.92 (dd, *J* = 9.2, 6.5 Hz, 1H), 6.73 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 137.9, 136.7, 135.4, 135.1, 131.6, 131.1, 130.4, 129.3, 128.9, 128.5, 128.2, 126.1, 122.0, 121.8, 120.2, 118.4, 114.5. HRMS (ESI) m/z [(M + H)$^+$] Calcd for $C_{19}H_{13}Cl_2N_2S^+$ (371.0171), found 371.0175.y6

3-(3-chlorophenyl)-1-((4-fluorophenyl)thio)imidazo[1,5-*a*]pyridine (4u)*:* 126 mg (yield: 71%), a yellow solid. M.P.: 98–100°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.30 (d, *J* = 7.3 Hz, 1H), 7.85 (s, 1H), 7.74–7.67 (m, 2H), 7.49–7.42 (m, 2H), 7.27–7.24 (m, 2H), 6.95–6.89 (m, 3H), 6.74 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.5 [d, *J*(C-F) = 243.0 Hz], 137.7, 135.1, 132.9, 131.1, 130.3, 129.7 [d, *J*(C-F) = 8.0 Hz], 129.3, 128.2, 126.1, 121.9, 121.6, 121.1, 118.5, 115.9 [d, *J*(C–F) = 23.0 Hz], 114.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ –116.7. HRMS (ESI) m/z [(M + H)$^+$] Calcd for $C_{19}H_{13}ClFN_2S^+$ (355.0467), found 355.0463.

3-(4-bromophenyl)-1-((4-chlorophenyl)thio)imidazo[1,5-*a*]pyridine (4v)*:* 133 mg (yield: 64%), a white solid. M.P.:150–156°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.26 (d, *J* = 7.2 Hz, 1H), 7.72 (s, 1H), 7.70 (s, 1H), 7.66–7.62 (m, 3H), 7.14 (s, 4H), 6.91 (dd, *J* = 9.2, 6.5 Hz, 1H), 6.71 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 138.3, 136.7, 135.3,

132.3, 131.5, 129.6, 128.9, 128.5, 128.3, 123.4, 121.9, 121.6, 120.0, 118.4, 114.4. HRMS (ESI) m/z [(M + H)$^+$] Calcd for $C_{19}H_{13}BrClN_2S^+$ (414.9666), found 414.9669.

1-((4-chlorophenyl)thio)-3-(naphthalen-1-yl)imidazo[1,5-*a*]pyridine (4w): 140 mg (yield: 72%), a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 7.1 Hz, 1H), 7.73–7.67 (m, 3H), 7.64–7.60 (m, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.50–7.46 (m, 1H), 7.24–7.17 (m, 4H), 6.92 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.59 (t, *J* = 6.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 138.3, 137.0, 134.7, 134.0, 131.7, 131.5, 130.4, 129.0, 128.9, 128.7, 128.6, 127.3, 126.5, 126.3, 125.3, 125.3, 122.6, 121.6, 119.3, 118.1, 113.6. HRMS (ESI) m/z [(M + H)$^+$] Calcd for $C_{23}H_{16}ClN_2S^+$ (387.0717), found 387.0720.

1-((4-chlorophenyl)thio)-3-(3-nitrophenyl)imidazo[1,5-a]pyridine (4x): 144 mg (yield: 75%), a yellow solid. M.P.:140–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.68 (s, 1H), 8.34 (d, *J* = 7.2 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 7.72–7.65 (m, 2H), 7.13 (s, 4H), 6.97 (dd, *J* = 9.2, 6.5 Hz, 1H), 6.81 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.6, 136.7, 136.4, 135.7, 134.0, 131.7, 131.2, 130.3, 129.0, 128.6, 123.6, 122.4, 122.2, 121.7, 120.9, 118.5, 115.1. HRMS (ESI) m/z [(M + H)$^+$] Calcd for $C_{19}H_{13}ClN_3O_2S^+$ (382.0412), found 382.0416.

3-(3-nitrophenyl)-1-(p-tolylthio)imidazo[1,5-*a*]pyridine (4y): 120 mg (yield: 67%), a yellow solid. M.P.:140–144°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.70 (s, 1H), 8.33 (d, *J* = 7.2 Hz, 1H), 8.28–7.26 (m, 2H), 7.71–7.68 (m, 2H), 7.18 (s, 1H), 7.16 (s, 1H), 7.02–7.01 (m, 2H), 6.94 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.78 (t, *J* = 6.8 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.6, 136.3, 135.9, 135.4, 134.0, 133.9, 131.3, 130.2, 129.7, 128.1, 123.4, 122.5, 122.3, 121.7, 121.5, 118.8, 115.0, 21.0. HRMS (ESI) m/z [(M + H)$^+$] Calcd for $C_{20}H_{16}N_3O_2S^+$ (362.0958), found 362.0955.

3-(naphthalen-1-yl)-1-(p-tolylthio)imidazo[1,5-*a*]pyridine (4z): 78 mg (yield: 43%), a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 7.1 Hz, 1H), 7.75–7.71 (m, 3H), 7.65–7.61 (m, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.28 (s,1H), 7.26 (s,1H), 7.08 (s, 1H), 7.06 (s, 1H), 6.90 (dd, *J* = 9.1, 6.3 Hz, 1H), 6.59–6.56 (m, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 137.8, 135.6, 134.7, 134.4, 134.0, 131.7, 130.3, 129.6, 129.0, 128.7, 128.0, 127.2, 126.5, 126.4, 125.4, 125.3, 122.5, 121.1, 120.7, 118.4, 113.5, 21.0. HRMS (ESI) m/z [(M + H)$^+$] Calcd for $C_{24}H_{19}N_2S^+$ (367.1263), found 367.1266.

3-(4-chlorophenyl)-1-(p-tolylthio)imidazo[1,5-*a*]pyridine (4za): 120 mg (yield: 68%), a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.22 (d, *J* = 7.3 Hz, 1H), 7.77 (m, 1H), 7.75 (m, 1H), 7.64 (d, *J* = 9.1 Hz, 1H), 7.48 (s, 1H), 7.46 (s, 1H), 7.16 (s, 1H), 7.14 (s, 1H),, 7.01 (s, 1H), 6.99 (s, 1H), 6.85 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.66 (t, *J* = 6.8 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 137.9, 135.7, 135.0, 134.9, 134.4, 129.6, 129.4, 129.3, 128.1, 127.8, 121.8, 121.4, 121.1, 118.6, 114.2, 21.0. HRMS (ESI) m/z [(M + H)$^+$] Calcd for $C_{20}H_{16}ClN_2S^+$ (351.0717), found 351.0714.

4. Conclusions

In conclusion, we developed a one-pot strategy for the efficient synthesis of sulfinylimidazo[1,5-*a*]pyridine derivatives starting from 2-aminomethylpyridines, benzaldehydes, and sodium benzenesulfinates, which constructed C–N and C–S bonds simultaneously. The method is characterized by a short reaction time, mild reaction conditions, high atom efficiency, and good yields. This method demonstrates significant potential for the preparation of a variety of biologically or pharmaceutically active compounds.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal14090601/s1, General Information, Typical procedure, NMR spectra of all of the products.

Author Contributions: Conceptualization, Z.D. and Z.G.; methodology, L.H.; writing—original draft preparation, L.H.; writing—review and editing, Y.L.; supervision, Z.D.; project administration, Z.D. All authors have read and agreed to the published version of the manuscript.

Funding: The financial support from the National Natural Science Foundation of China (22401223), the Natural Science Foundation of Hubei Province (2024AFB315), the Open Research Fund of School of Chemistry and Chemical Engineering, Henan Normal University (2020ZD02), the Open and Innovation Fund of Hubei Three Gorges Laboratory (SC240004), Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province (CSPC202306), Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology (BM2012110), and Knowledge Innovation Program of Wuhan -Basic Research (2023020201010142) is greatly appreciated.

Data Availability Statement: The data supporting this article have been included as part of the Supplementary Materials.

Acknowledgments: L. H. is thankful for the support of Postgraduate Innovation Foundation from Wuhan Institute of Technology.

Conflicts of Interest: The authors declare no conflicts of interest.

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