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Molecular iodine enabled generation of iminyl radicals from oximes: A facile route to imidazo[1,2-*a*]pyridines and its regioselective C-3 sulfenylated products from simple pyridines

Deepak Singh, Soumyadeep Roy Chowdhury, Shyamal Pramanik, Soumitra Maity*

Department of Chemistry, Indian Institute of Technology (ISM), Dhanbad, JH, 826004, India

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ABSTRACT

An iodine promoted simple and environment friendly protocol has been developed to access imidazo [1,2-*a*]pyridines from unfunctionalized pyridines and oxime esters. This straightforward method efficiently converts the substrates into corresponding products affording moderate to good yields with large functional group tolerance. Additionally extensive investigation revealed that regioselective domino C-3 methyl sulfenylated imidazo[1,2-*a*]pyridines were also accessible first time from pyridines and oxime esters in DMSO solvent. The reaction operates through metal-free generation of iminyl radicals from easily accessible oxime esters, to build up the second heterocyclic ring on pyridines.

1. Introduction

Imidazo-pyridine is an important class of nitrogen-bridgehead heterocycles frequently found in many biologically active compounds [1]. Among them, imidazo[1,2-*a*]pyridines (IPs) display very interesting biological activities such as antifungal, anti-inflammatory, antitumor, antiviral, antiprotozoal, antibacterial, and antipyretic [2].Importantly, IPs constitutethe key structure of many marketed drugs, like Zolpidem, Zolimidine, Alpidem, Saripidem, Necopidem and Olprinone [3]. Furthermore, their unique photo-physical properties make them useful in material and allied sciences [4].Accordingly, various efficient strategies to imidazo[1,2-*a*]pyridines have been developed [5]. Conventional synthesis of IPs mainly rely on reaction of functionalized pyridine derivatives, usually 2-amino pyridines [6] with variety of coupling partners including ketones [6a-e], isonitriles [6f-g],α-halocarbonyls [6h-j] or olefins [6k-n] under condensation and/or oxidative conditions. A straight forward route to access IPs from unfunctionalized pyridines are quite rare and only a few reports are there in literature (Scheme 1a) [7]. Fabio et al. [7a] reported a novel thermal synthesis of IPs derivatives from pyridines and 1,2-diaza-1,3-dienes. Lee et al. [7b] described a Cu-catalyzed formal aza-[3 + 2] cycloaddition reaction of pyridine derivatives with highly functionalized α-diazo oxime ethers. Recently Adimurthy [7c] and Huang [7d] independently utilized vinyl azides and enamides as the nitrogen source to construct imidazo[1,2-*a*]pyridine frameworks on pyridine ring by copper catalysis. Moreover, Litvinov et al. reported [7i] a base induced cyclization protocol to IPs from *p*-bromophenacyl bromide and pyridines under heating conditions. However, all of these methods are suffer with the limited accessibility of the highly functionalized coupling partners: 1,2-diaza-1,3-dienes, α-diazo oxime ethers, vinyl azides and enamides which restrict the synthetic versatility of IPs. In addition, the success of these methods are majorly depending on the effective use of copper catalysts with additives and/or solvent. Consequently, a simple and easily available versatile coupling partner which overcomes the above limitations certainly advances the synthesis of IPs from pyridines.

Owing to cheap and readily accessible with versatility, oximes are widely used in chemical industry and academia as starting materials [8]. Recently, the development of transition metal catalysis has further expanded the scope of this substrate in organic synthesis [9]. Particularly, reductive cleavage of N–O bond of ketoximes provides a unique structural skeleton 'N–C–C' which could be fused with diverse partners to construct azaheterocycles [10]. In fact, this strategy had been established in the synthesis of

* Corresponding author.
E-mail address: smaity@iitism.ac.in (S. Maity).

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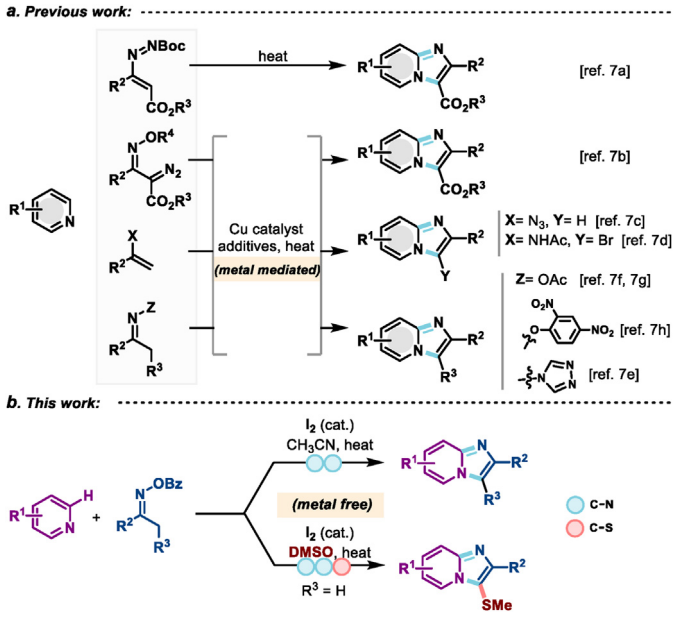


Scheme 1. IPs synthesis from unfunctionalized pyridines.

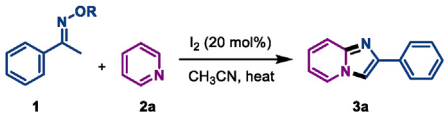
various fused nitrogen heterocycles including imidazo[1,2-*a*]pyridines[7f-h] and others [11]. However, in this reaction the reactive iminyl radical was generated from ketoxime by exposure of metal catalyst with additives that introduce toxic waste to the environment. So a metal-free method could render a modified better technique to access these targeted heterocycles under environment benign conditions [12].

In recent years, molecular iodine has emerged as a flexible and environmentally benign reagent for various organic transformations [13]. Furthermore, the discovery of complementary redox-reactivity of iodine in transition metal-catalyzed coupling reactions has opened a new opportunity to test radical reactions [14]. Within this context, seminal iodine-catalyzed redox reaction of oxime esters were explored by Deng [15a-b] and Gao [15c]. Inspired by these works [15] we hypothesized that iminyl radical generated from oxime esters by iodine might couple with pyridine generating IPs under metal-free conditions (Scheme 1b). As a part of our ongoing research on sustainable methods development [16], herein we report for the first time a simple molecular iodine-catalyzed synthesis of imidazo[1,2-*a*]pyridines by the intermolecular oxidative coupling of ketoxime and pyridines under metal and additive-free conditions. Additionally, regioselective C-3 methylsulphenated IPs were also synthesized by applying the same protocol using DMSO as methylthiolated source through a domino process.

2. Results and discussion

To investigate the finest starting material, we started with acetophenone oxime with unfunctionalized pyridine (**2a**) in presence of 20 mol% molecular iodine under 110 ^{O}C of temperature for 6 h. Initially, acetonitrile was selected as a solvent and in this case, a promising 22% yield of the desired product was observed (Table 1, entry 1). Protecting the free oxime-hydroxyl group certainly improved the yield of **3a** and the best yield was achieved with the benzoyl derivative (entries 2–4). The use of sulfonyl groups such as mesyl or tosyl derivatives of oxime converts the starting material to amide through Beckmann Rearrangement [17] and no IP product was formed (entries 5–6).

Table 1
Screening of protecting groups.[a].



Entry	R	Yield[a] (%)	Entry	R	Yield (%)
1.	H	22	**4.**	**Bz**	**38**
2.	Ac	26	5.	Ts	N.R
3.	Boc	24	6.	Ms	N.R

[a] Unless otherwise noted, all reactions were carried out with: **1** (0.5 mmol), **2a** (0.2 mmol), catalyst (20 mol %), solvent (acetonitrile) (2 mL) at heating (110 ^{O}C) in a reaction tube for 6 h in air.

After defining benzoyl as the optimal protecting group, we set out to find the optimized reaction condition (Table 2). Accepting the initial result from Table 1, we went ahead to fix other reaction parameters for improving yield. Varying the solvent from polar aprotic DMF to other common solvents like nitromethane, NMP, HFIP, and MeOH (entries 1–6) hardly provided the desired imidazo [1,2-*a*]pyridine. Moreover, acetonitrile was appeared to be

the best one compared to other productive solvents, chlorobenzene, and toluene (entries 7–8). Next increasing the equivalency of iodine from 20 mol% to 50 mol%, boosted up the reaction yield up to 48% (entry 9) and became consistent with further raising the equivalency of iodine. It is noticeable that a maximum yield of 62% (entry 10) was obtained when the temperature was raised to 140 °C and beyond the optimal temperature, the yield decreased gradually. At this point excess loading of iodine didn't help to improve the yield of **3a** (entry 11). Furthermore, the reaction got completely inhibited below the minimum temperature of 100 °C

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

Entry	Catalyst (mol%)	Solvent	Temp (°C)	Yield (%)[b]
1	I_2 (20)	MeCN	110	38
2	I_2 (20)	DMF	110	Trace
3	I_2 (20)	$MeNO_2$	110	n.r.
4	I_2 (20)	NMP	110	n.r
5	I_2 (20)	HFIP	110	n.r.
6	I_2 (20)	MeOH	110	n.r.
7	I_2 (20)	PhCl	110	23
8	I_2 (20)	toluene	110	20
9	I_2 (50)	MeCN	110	48
10	**I_2 (50)**	**MeCN**	**140**	**62**
11	I_2 (100)	MeCN	140	15
12	I_2 (50)	MeCN	100	n.r.
13	TBAI(50)	MeCN	140	n.r
14	KI(50)	MeCN	140	n.r.
15	$PhI(OAc)_2$ (100)	MeCN	140	trace
16[c]	–	MeCN	140	n.r.
17[d]	I_2 (50)	MeCN	140	n.r.
18[e]	I_2 (50)	MeCN	140	36

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.2 mmol), I_2 (x mmol), solvent (2 mL) for 6 h in air.
[b] Isolated yields after column chromatography; n.r. = no reaction.
[c] In the absence of I_2.
[d] Degassed condition under argon.
[e] With oxygen balloon.

(entry 12). Other iodine sources (KI, TBAI, and PIDA) were also studied, but didn't found any better result (entries 13–15). When the reaction was carried out in the absence of iodine the reaction scope completely withheld (entry 16). This suggests that molecular iodine is one of the essential element for the reaction. Controlled experiment revealed that replacing aerobic reaction atmosphere with argon completely prohibited the reaction scope (entry 17). On the other hand, using a fully oxygenated reaction atmosphere displayed significantly lower yield (entry 18) probably due to the damage of substrates through aerial oxidation at elevated temperature. Considering Oxime ester as a limiting substrate, further increment of the concentration of pyridine did not help to get better yields (for details see SI).

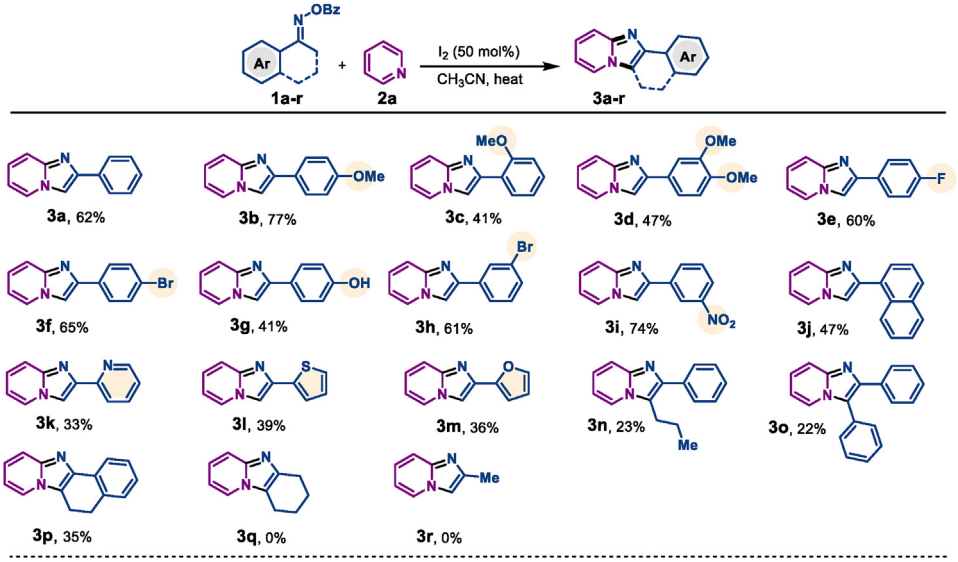
Now, with the optimized reaction condition in hand we moved to investigate the substrate scope and generality of the aforementioned process. A large variety of oxime esters derived from aryl methyl ketones smoothly participated in the reaction with good to moderate yields (Table 3). This iodine catalyzed reaction permits a broad spectrum of functional group tolerance and making it quite a general process. Aryl methyl ketoxime esters bearing highly electron-donating 4-methoxy (**3b**) and prominent electron-withdrawing groups like 4-Fluoro (**3e**) or 3-nitro (**3i**) on the aryl rings, comfortably participated with good yields making the reaction quite insensitive towards the electronic effects. Whereas other aryl methyl ketoxime benzoate incorporated with bromine, hydroxyl groups (**3f**-**3h**) substituted in aryl rings, all reacted smoothly to produce corresponding IPs. Oxime esters containing -*ortho* or -*meta* substituted aryl ring, possess significantly lower yields with respect to -*para* substituted aryl counterparts (**3c**, **3d** *vs* **3b**). Moreover, sterically bulky oxime esters derived from 1-naphthyl methyl ketone (**3j**) and 1-tetralone (**3p**) can also be well accommodated into the protocol albeit with lower yields. This indicates steric hindrance plays a negative impact on the transition state of the reaction. Oxime esters derived from pyridine-2-yl, thiophen-2-yl and furan-2-yl ketones were also productive, leading to the products (**3k**-**3m**) in lower yield respectively. Pleasingly aryl ketoxime benzoates prepared from 2-substituted acetophenone derivatives such as valerophenone and deoxybenzoin afforded the final products **3n**-**3o** respectively, in marginal yields. Unfortunately, oxime esters derived from alkyl ketones such as cyclohexanone and acetone were not amenable to this condition (**3q**-**3r**).

Next, we tried to explore the scope of substituted pyridines (Table 4). Generally, it was found that the substituted pyridine derivatives displayed lower yields compared to pyridine. Interestingly pyridines substituted with electron rich methyl (**4a**, **4b,** and **4f**) and electron deficient fluoro, cyano groups (**4c**, **4d**) reacted similarly affording corresponding IPs in moderate yields [18a]. Moreover, C-2 substituted pyridine (**4e**) which was sterically less reactive, also found no problem to participate in this process albeit with a lower yield. Lastly, pyridines, fused with aromatic rings such as quinoline (**4g**) and isoquinoline (**4h**) underwent fair involvement in this method affording moderate yields [18b].

Inducting sulfenyl substructures into aromatic or heteroaromatic rings is considered to be a fundamental and formidable area of research interest for synthetic chemists in recent years. This process gives a clear-cut route to synthesize thioethers which sometimes exhibit useful physicochemical properties amenable for biological and material applications [19]. Some of the very important pharmaceutical entities come from the aforementioned thioethers family [20]. Although significant attempts had been made for the C-3 sulfenylation of imidazo[1, 2-*a*]pyridines [21], but their regioselective C-3 methylsulfenylation is quite less [22]. Moreover, the majority of these methods are primarily focussing on C-3 functionalization of IPs in a stepwise process. On the other hand, direct access of the C-3 functionalized IPs from unfunctionalized pyridines through a single step domino process is completely unexplored. During our course of solvent optimization studies in IPs synthesis, C-3 methylsulfenated IP (**5a**) was isolated in moderate yields when DMSO was used as solvent unaffecting other reaction parameters. In this context, we are reporting an iodine-mediated environment-friendly direct method to access regioselective C-3 methylsulfenylated imidazo[1,2-*a*]pyridine where DMSO is employed as methyl thiolating agent as well as solvent.

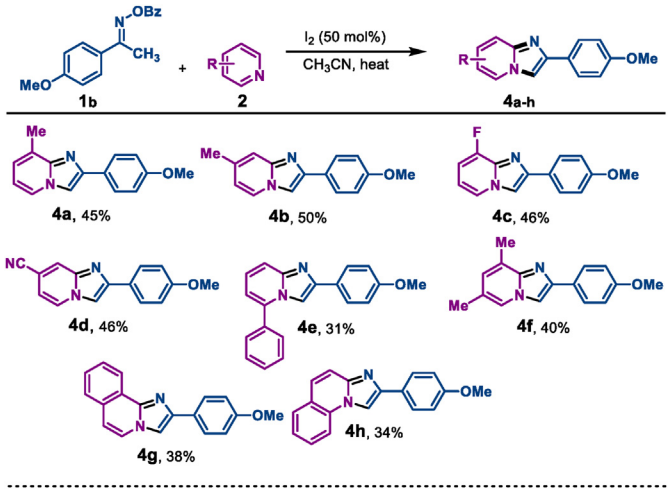
Furthermore, to check the substrate scope a showcase of structurally diverse methylsulphanylated IPs were prepared from corresponding oxime esters and pyridines (Table 5). To our delight

Table 3
Scope of Oxime esters:[a,b].



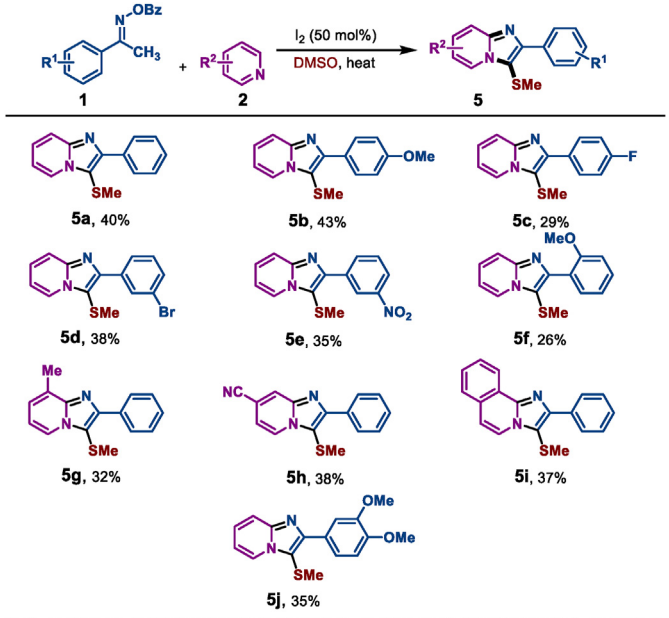
[a] Reaction Conditions, unless otherwise noted: 1 (0.5 mmol), 2a (0.2 mmol), I2 (0.1 mmol), acetonitrile (2 mL), heated under 140 °C for 6 hrs in air.
[b] isolated yields.

Table 4
Scope of pyridine derivatives.[a,b].



[a] Reaction Conditions:**1b** (0.5 mmol), **2** (0.2 mmol), I2 (0.1 mmol), acetonitrile (2 mL), heated under 140 °C for 6 hrs in air.
[b] Isolated yields after column chromatography.

Table 5
Substrate scope of 3-sulfenylimidazopyridines synthesis.[a,b].

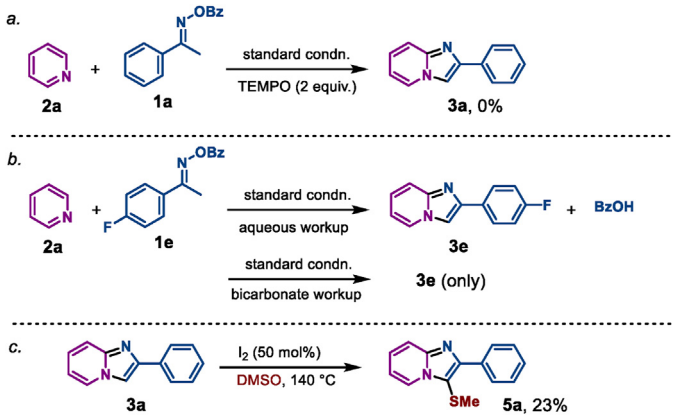


[a] Reaction Conditions: **1** (0.5 mmol), **2** (0.2 mmol), I2 (0.1 mmol), DMSO (2 mL), heated under 140 °C for 6 hrs in air.
[b] Isolated yields after column chromatography

aryl methyl oxime esters bearing electron rich, and electron deficient aryl rings (**5b**-**f**, **j**), all participated in the reaction but with lower yields. Furthermore, substituted pyridines were also accommodated into the target methylsulfanylated products (**5g**-**i**).

To gain a better inside into the mechanism we have done a series of controlled experiments. Previously it was evident that without aerial oxygen or iodine the reaction got completely inhibited (Table 1, entries 16–17). After that when TEMPO was introduced to the reaction mixture under optimum reaction conditions, it failed to provide the desired product. This observation indicated that a radical process might be involved in the present transformation (Scheme 2a). Furthermore, it was observed that benzoyl protecting group of oxime ester was ended up with benzoic acid, as evident from the ^{1}H NMR spectra of bicarbonate unwashed reaction mixture of **2a** and **1e** (Scheme 2b) [23]. To further understand the thiolation reaction mechanism, the reaction of 2-phenylimidazo [1,2-*a*]pyridine (**3a**) was performed with iodine in DMSO, which gave

expected 3-methylthioimidazo[1,2-*a*]pyridine (**5a**) in 23% yield (Scheme 5c) [22b-c]. This result provides information that thiolation might be taken place after formation of parent imidazo[1,2-*a*] pyridine ring.

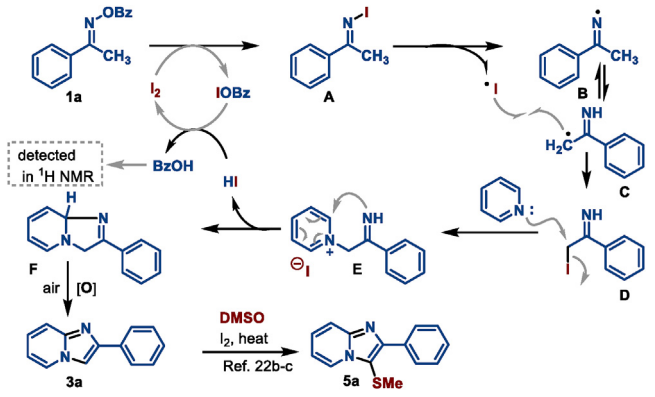


Scheme 2. Mechanistic studies.

Although the mechanism involved here is not clear at present, a plausible route for the progress of the reaction was depicted based on the above mechanistic studies and previous reports (Scheme 3) [13a,15]. First, oxime ester **1a** undergoes reductive cleavage to iminyl radical **B**, where molecular iodine promotes the N—O bond reduction of oxime[13a], [15b-c] through intermediate **A**. In this process, hypervalent iodine species (I^+) IOBz liberated as the initial by-product. After isomerization, **B** readily transforms to α-carbon radical **C** which later undergoes coupling with Iodine radical to produce **D** as intermediate. Next, pyridine present in the reaction mixture offers a nucleophilic substitution to generate iminium intermediate **E**, which readily participates in electrocyclisation to afford **F**. In this case liberated hydrogen iodide oxidizes the hypervalent iodine species to benzoic acid. Finally, the intermediate **F** aromatizes through aerial oxidation to imidazopyridine **3a**. The later investigation suggested that the action of iodine and DMSO under elevated temperature converted **3a** into its C-3 methylsulfenylated imidazo[1,2-*a*]pyridine **5a** [22b-c].

3. Conclusion

In conclusion, we have disclosed a simple and metal-free approach to deliver pharmaceutically active Imidazo[1,2-α]pyridine from cheap and easily accessible starting material like oxime ester with pyridine. Moreover, molecular iodine is employed here as an environmentally friendly catalyst. In this case, iodine triggers cleavage of N—O bond of oxime esters to generate reactive iminyl radicals which regioselectively coupled with pyridines ended up the Imidazo[1,2-*a*]pyridines as a value-added product. Importantly, further extension of this strategy to obtain regioselective C-3 methylthiolated imidazopyridines in DMSO solvent through a single step domino process makes this process attractive for diversified synthesis. Overall this effort provided a rare and extended case study to explore the role of iodine in the oxidative coupling reaction to provide Imidazo[1,2-*a*]pyridine and it's regioselective C-3 methylthiolated functionalization.



Scheme 3. Plausible reaction mechanism.

4. Experimental section

4.1. General information

All commercially available chemicals and reagents were used without any further purification unless otherwise stated. All reactions were carried out in oven-dried glassware under argon or nitrogen atmosphere with freshly distilled anhydrous solvents [24]. The progress of the reaction was monitored by thin layer chromatography (TLC) using silica gel Aluminium Sheet (Merck, TLC Silica gel 60 F254). All compounds were purified through column chromatography using silica gel (230—400 mesh). Nuclear magnetic resonance spectra were recorded on Bruker Avance III HD 400 instrument. Chemical shifts (δ) are quoted in ppm relative to residual solvent signals, $CDCl_3$ referenced at δ 7.26 ppm for 1H and 77.16 ppm for 13C. TMS are used as internal standard and Coupling constants (J) are quoted in hertz (Hz). Multiplicity is reported with the following abbreviations: s = sin-glet, d = doublet, t = triplet, q = quartet, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets. HRMS were recorded using (ESI) mass spectrometer. Melting points (°C) are uncorrected.

4.2. General procedure for molecular iodine promoted synthesis of imidazo[1, 2-a]pyridine

To an oven-dried pressure tube equipped with a magnetic stir bar was charged with molecular iodine (0.1 mmol), corresponding oxime ester (0.5 mmol), pyridine (0.2 mmol) derivatives and 2 mL of dry acetonitrile. After mixing the reaction components by shaking, the tube was sealed with an airtight screw cap. After that, the reaction mixture was stirred at 140 °C temperature in oil bath for 6 h. The completion of the reaction was confirmed by TLC. Then the crude reaction mixture was washed with saturated sodium thiosulphate solution (5 mL) and saturated sodium bicarbonate solution (5 mL). The resulting mixture was extracted with ethyl acetate (3 × 6 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Then the mixture was concentrated in a rotary evaporator and the residue was purified by silica gel column chromatography with a plug of neutral alumina to the top of the column to afford the desired imidazo[1,2-*a*]pyridine as a key product.

4.3. General procedure for molecular iodine promoted synthesis of C-3 methylsulfenylated imidazo[1,2-a]pyridine

To an oven-dried pressure tube equipped with a magnetic stir bar was charged with molecular iodine (0.1 mmol), corresponding oxime ester (0.5 mmol), pyridine (0.2 mmol) derivatives and 2 mL of dry DMSO. After mixing the reaction components by shaking, the tube was sealed with an airtight screw cap. After that, the reaction mixture was stirred at 140 °C temperature in a preheated oil bath for 6 h. The completion of the reaction was confirmed by TLC. After that, the crude reaction mixture was washed with both saturated sodium thiosulphate solution (5 mL) and saturated sodium bicarbonate solution (5 mL). The resulting mixture was extracted with ethyl acetate (3 × 6 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Then the mixture was

concentrated in a rotary evaporator and the residue was purified by silica gel column chromatography with a plug of neutral alumina to the top of the column to afford the desired 3-methylthiolated imidazo[1,2-*a*]pyridine product.

4.4. Characterization data of products

2-phenylimidazo[1,2-*a*]pyridine (Tables 3 and 3a) [7f]. Light yellow Solid; mp 135–137 °C; 62% yield (24 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, J = 6.8 Hz, 1H), 7.96 (d, J = 7.4 Hz, 2H), 7.85 (s, 1H), 7.63 (d, J = 9.1 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.18–7.13 (m, 1H), 6.76 (t, J = 6.6 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 145.9, 145.8, 133.8, 128.9, 128.1, 126.2, 125.7, 124.8, 117.6, 112.6, 108.2.

2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine (Tables 3 and 3b) [7f]. Yellowish solid; mp 133–135 °C; 77% yield (34 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (dt, J = 6.8, 1.2 Hz, 1H), 7.90–7.86 (m, 2H), 7.75 (s, 1H), 7.60 (d, J = 9.6 Hz, 1H), 7.13 (ddd, J = 9.2, 6.8, 1.2 Hz, 1H), 6.98–6.94 (m, 2H), 6.73 (td, J = 6.8, 1.1 Hz, 1H), 3.84 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 159.7, 145.8, 145.7, 127.4, 126.6, 125.6, 124.6, 117.4, 114.2, 112.3, 107.3, 55.4.

2-(2-methoxyphenyl)imidazo[1,2-*a*]pyridine (Table 3 **and 3c)** [7f]. Light yellow Solid; mp 94–96 °C; 41% yield (18 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 2:3 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.41 (dd, J = 7.7, 1.8 Hz, 1H), 8.18 (s, 1H), 8.10 (d, J = 6.8 Hz, 1H), 7.61 (dd, J = 9.2, 0.7 Hz, 1H), 7.31 (ddd, J = 8.2, 7.4, 1.9 Hz, 1H), 7.15–7.09 (m, 2H), 7.00 (dd, J = 8.3, 0.6 Hz, 1H), 6.72 (td, J = 6.8, 0.9 Hz, 1H), 3.98 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 156.8, 144.5, 141.2, 128.9, 128.7, 125.7, 124.6, 122.4, 121.1, 117.3, 112.6, 112.1, 110.9, 55.5.

2-(3,4-dimethoxyphenyl)imidazo[1,2-*a*]pyridine (Tables 3 and 3d**).** [7g] Yellow Solid; mp 104–106 °C; 47% yield (24 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 1:1 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09 (d, J = 6.7 Hz, 1H), 7.79 (s, 1H), 7.61 (d, J = 9.1 Hz, 1H), 7.57 (d, J = 1.7 Hz, 1H), 7.44 (dd, J = 8.3, 1.8 Hz, 1H), 7.15 (t, J = 8.2 Hz, 1H), 6.92 (d, J = 8.3 Hz, 1H), 6.75 (t, J = 6.7 Hz, 1H), 3.99 (s, 3H), 3.92 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 149.3, 149.1, 145.8, 145.6, 126.9, 125.6, 124.7, 118.6, 117.4, 112.5, 111.4, 109.3, 107.6, 56.1, 56.0.

2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine (Tables 3 and 3e**).** [7f] Brown yellow Solid; mp 156–158 °C; 60% yield (25 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, J = 6.7 Hz, 1H), 7.93–7.90 (m, 2H), 7.79 (s, 1H), 7.62 (d, J = 9.1 Hz, 1H), 7.19–7.15 (m, 1H), 7.12 (t, J = 8.7 Hz, 2H), 6.77 (t, J = 6.7 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 162.9 (d, J = 247.4 Hz), 145.8, 145.0, 130.0, 127.9 (d, J = 8.5 Hz), 125.7, 125.0, 117.6, 115.8 (d, J = 22.0 Hz), 112.7, 107.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): −114.1 (s, 1F).

2-(4-bromophenyl)imidazo[1,2-*a*]pyridine (Tables 3 and 3f**).** [7f] Yellow Solid; mp 210–212 °C; 65% yield (35 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (dt, J = 6.8, 1.1 Hz, 1H), 7.83–7.82 (m, 2H), 7.80 (d, J = 1.9 Hz, 1H), 7.62–7.60 (m, 1H), 7.56–7.53 (m, 2H), 7.18 (ddd, J = 8.9, 6.8, 1.2 Hz, 1H), 6.78 (td, J = 6.8, 0.9 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 145.8, 144.7, 132.8, 131.9, 127.6, 125.7, 125.1, 122.0, 117.6, 112.8, 108.4.

4-(imidazo[1,2-*a*]pyridin-2-yl)phenol (Tables 3 and 3g**).** [22b] Brown Solid; mp 142–144 °C; 41% yield (17 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 1:1 (v/v)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.54 (s, 1H), 8.48 (dt, J = 6.8, 1.1 Hz, 1H), 8.21 (s, 1H), 7.77 (d, J = 8.6 Hz, 2H), 7.53–7.51 (m, 1H), 7.20 (ddd, J = 9.2, 6.7, 1.2 Hz, 1H), 6.86 (dd, J = 6.8, 1.0 Hz, 1H), 6.82 (d, J = 8.7 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ (ppm): 157.3, 144.9, 144.6, 126.1, 126.6, 124.9, 124.5, 116.3, 115.5, 111.9, 107.5.

2-(3-bromophenyl)imidazo[1,2-*a*]pyridine (Tables 3 and 3h**).** [7f] Light yellow Solid; mp 129–131 °C; 61% yield (33 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12–8.09 (m, 2H), 7.87–7.84 (m, 2H), 7.63–7.61 (m, 1H), 7.44 (ddd, J = 8.3, 1.8, 1.0 Hz, 1H), 7.29 (t, J = 7.9 Hz, 1H), 7.18 (ddd, J = 9.1, 6.8, 1.3 Hz, 1H), 6.78 (td, J = 6.8, 1.0 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 145.8, 144.3, 135.9, 130.9, 130.4, 129.1, 125.8, 125.2, 124.6, 123.1, 117.7, 112.8, 108.6.

2-(3-nitrophenyl)imidazo[1,2-*a*]pyridine (Tables 3 and 3i**).** [7h] Yellow Solid; mp 201–202 °C; 74% yield (35 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.78 (s, 1H), 8.35 (d, J = 7.7 Hz, 1H), 8.19 (d, J = 7.0 Hz, 2H), 8.01 (s, 1H), 7.68 (d, J = 9.1 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.27 (dd, J = 15.4, 7.7 Hz, 1H), 6.87 (t, J = 6.7 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 147.8, 145.0, 142.5, 134.8, 130.9, 128.8, 125.0, 124.6, 121.6, 119.9, 116.9, 112.2, 108.2.

2-(naphthalen-1-yl)imidazo[1,2-*a*]pyridine (Tables 3 and 3j**).** [7f] Light yellow Solid; mp 158–160 °C; 47% yield (23 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.63–8.61 (m, 1H), 8.14 (dt, J = 6.8, 1.1 Hz, 1H), 7.92–7.87 (m, 2H), 7.83 (dd, J = 6.7, 1.4 Hz, 2H), 7.71 (d, J = 9.5 Hz, 1H), 7.57–7.55 (m, 1H), 7.53–7.50 (m, 2H), 7.20 (ddd, J = 9.1, 6.7, 1.2 Hz, 1H), 6.79 (td, J = 6.8, 0.9 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 145.5, 145.3, 134.0, 131.9, 131.6, 128.5, 128.4, 127.8, 126.5, 126.0, 125.9, 125.6, 125.5, 124.7, 117.8, 112.5, 111.3.

2-(pyridin-2-yl)imidazo[1,2-*a*]pyridine (Tables 3 and 3k**).** [25] Brown yellow Solid; mp 135–137 °C; 33% yield (13 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.62–8.60 (m, 1H), 8.24 (s, 1H), 8.18 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 6.8 Hz, 1H), 7.77 (td, J = 7.8, 1.8 Hz, 1H), 7.65–7.62 (m, 1H), 7.23–7.15 (m, 2H), 6.78 (td, J = 6.8, 0.8 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 152.7, 149.4, 137.2, 130.0, 128.4, 126.2, 125.4, 122.9, 120.8, 117.8, 113.0, 111.1.

2-(thiophen-2-yl)imidazo[1,2-*a*]pyridine Tables 3 **and 3l).** [7f] Yellowish Solid; mp 136–138 °C; 39% yield (16 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 2:8 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (dd, J = 6.8, 0.8 Hz, 1H), 7.74 (s, 1H), 7.59 (d, J = 9.2 Hz, 1H), 7.46 (d, J = 3.5 Hz, 1H), 7.29 (d, J = 5.0 Hz, 1H), 7.17–7.12 (m, 1H), 7.08 (dd, J = 5.0, 3.7 Hz, 1H), 6.75 (t, J = 6.7 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 145.5, 140.8, 137.5, 127.9, 125.5, 125.1, 125.0, 123.8, 117.3, 112.7, 107.5.

2-(furan-2-yl)imidazo[1,2-*a*]pyridine (Tables 3 **and 3m).** [7f] Brown black Solid; mp 88–90 °C; 36% yield (13 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 2:8 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11 (d, J = 6.8 Hz, 1H), 7.80 (s, 1H), 7.61–7.59 (m, 1H), 7.48–7.47 (m, 1H), 7.18 (ddd, J = 9.1, 6.8, 1.3 Hz, 1H), 6.89 (d, J = 3.4 Hz, 1H), 6.79 (td, J = 6.8, 1.0 Hz, 1H), 6.51 (dd, J = 3.3, 1.8 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 149.6, 145.7, 142.2, 137.9, 125.8, 125.2, 117.4, 112.7, 111.7, 108.0, 106.9.

2-phenyl-3-propylimidazo[1,2-*a*]pyridine (Tables 3 **and 3n).** [26] Pale yellow oil; 23% yield (11 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (d, J = 6.9 Hz, 1H), 7.78 (dd, J = 8.3, 1.0 Hz, 2H), 7.64 (d, J = 8.9 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.37–7.33 (m, 1H), 7.16 (ddd, J = 9.1, 6.8, 1.3 Hz, 1H), 6.81 (td, J = 6.8, 1.2 Hz, 1H), 3.06–3.02 (m, 2H), 1.76 (dd, J = 15.6, 7.6 Hz, 2H), 1.05 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 144.5, 142.4, 135.0, 128.6, 128.3, 127.5, 123.6, 123.1, 120.8, 117.7, 112.1, 25.9, 21.2, 14.3.

2,3-diphenylimidazo[1,2-*a*]pyridine (Tables 3 **and 3o).** [7f] Light yellow solid; mp 149–151 °C; 22% yield (12 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (d, J = 6.9 Hz, 1H), 7.71–7.65 (m, 3H), 7.55–7.45 (m, 5H), 7.31–7.27 (m, 3H), 7.25–7.19 (m, 1H), 6.75 (td, J = 6.8, 0.9 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 144.1,

142.6, 134.3, 130.9, 130.1, 129.7, 129.0, 128.4, 128.2, 127.6, 124.8, 123.4, 121.2, 117.7, 112.4.

5,6-dihydronaphtho[1′,2':4,5]imidazo[1,2-*a*]pyridine (Tables 3 and 3p). [27] Brown yellow Solid; mp 147–149 °C; 35% yield (15 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98 (dd, J = 7.7, 0.7 Hz, 1H), 7.86 (dt, J = 6.8, 1.2 Hz, 1H), 7.63 (dt, J = 9.3, 0.9 Hz, 1H), 7.31 (td, J = 7.3, 1.4 Hz, 1H), 7.24–7.17 (m, 2H), 7.13 (ddd, J = 8.9, 6.8, 1.2 Hz, 1H), 6.80 (td, J = 6.8, 1.0 Hz, 1H), 3.21 (t, J = 7.8 Hz, 2H), 7.10–7.06 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 145.9, 140.7, 135.0, 131.4, 128.2, 127.4, 127.3, 123.6, 122.9, 122.6, 119.8, 117.6, 112.3, 28.8, 19.1.

2-(4-methoxyphenyl)-8-methylimidazo[1,2-*a*]pyridine (Tables 4 and 4a). [6l] Brown yellow Solid; mp 130–132 °C; 45% yield (21 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 (d, J = 6.6 Hz, 1H), 7.89 (d, J = 8.8 Hz, 2H), 7.74 (s, 1H), 6.97 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 6.9 Hz, 1H), 6.66 (t, J = 6.8 Hz, 1H), 3.85 (s, 3H), 2.65 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 159.5, 146.2, 145.2, 127.5, 127.4, 126.9, 123.4, 123.3, 114.2, 112.3, 107.9, 55.4, 17.3.

2-(4-methoxyphenyl)-7-methylimidazo[1,2-*a*]pyridine (Tables 4 and 4b). [6a] Pale yellow Solid; mp 140–141 °C; 50% yield (24 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 (d, J = 6.9 Hz, 1H), 7.86 (d, J = 8.8 Hz, 2H), 7.68 (s, 1H), 7.36 (s, 1H), 6.96 (d, J = 8.9 Hz, 2H), 6.58 (dd, J = 6.9, 1.5 Hz, 1H), 3.84 (s, 3H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 159.6, 146.2, 145.5, 135.5, 127.4, 126.8, 124.8, 115.8, 115.0, 114.2, 106.7, 55.4, 21.5.

8-fluoro-2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine (Tables 4 and 4c). Brown yellow Solid; mp 143–145 °C; 46% yield (22 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93–7.90 (m, 3H), 7.83 (d, J = 3.1 Hz, 1H), 6.97 (d, J = 8.9 Hz, 2H), 6.88–6.84 (m, 1H), 6.70–6.66 (m, 1H), 3.85 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 159.9, 151.6 (d, J = 253.0 Hz), 146.3, 127.7, 126.0, 121.9, 114.3, 111.4 (d, J = 7.1 Hz), 108.7, 107.1 (d, J = 17.1 Hz), 55.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): −129.8 (s, 1F). HRMS (ESI) m/z calcd for $C_{14}H_{12}FN_2O$ $[M+H]^+$: 243.0934; found: 243.0928.

2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine-7-carbonitrile (Tables 4 and 4d). Brown Solid; mp 157–159 °C; 46% yield (23 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19–8.17 (m, 1H), 7.98 (s, 1H), 7.90 (d, J = 4.7 Hz, 2H), 7.87 (s, 1H), 6.99 (d, J = 8.8 Hz, 2H), 6.92 (dd, J = 6.9, 1.5 Hz, 1H), 3.86 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 160.5, 149.2, 143.6, 127.8, 126.1, 125.3, 123.3, 117.9, 114.5, 112.8, 109.6, 106.9, 55.5; HRMS (ESI) m/z calcd for $C_{15}H_{12}N_3O$ $[M+H]^+$: 250.0980; found: 250.0975.

2-(4-methoxyphenyl)-5-phenylimidazo[1,2-*a*]pyridine (Tables 4 and 4e). Brownish gummy; 31% yield (19 mg); R_f value = 0.5 [EtOAc: Petroleum ether = 3:7 (v/v)].^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 (s, 1H), 7.84 (d, J = 2.6 Hz, 2H), 7.68–7.63 (m, 3H), 7.60–7.54 (m, 3H), 7.26 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 8.9 Hz, 2H), 6.74–6.72 (m, 1H), 3.84 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 159.7, 146.5, 145.6, 138.2, 134.7, 129.9, 129.4, 128.4, 127.5, 126.6, 125.1, 116.1, 114.2, 112.8, 105.9, 55.4; HRMS (ESI) m/z calcd for $C_{20}H_{17}N_2O$ $[M+H]^+$: 301.1341; found: 301.1338.

2-(4-methoxyphenyl)-6,8-dimethylimidazo[1,2-*a*]pyridine (Tables 4 and 4f). Brown yellow Solid; mp 147–149 °C; 40% yield (20 mg); R_f value = 0.4 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.87 (d, J = 8.8 Hz, 2H), 7.73 (s, 1H), 7.64 (s, 1H), 6.95 (d, J = 8.8 Hz, 2H), 6.79 (s, 1H), 3.84 (s, 3H), 2.61 (s, 3H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 159.4, 145.2, 144.9, 127.4, 127.1, 126.6, 126.5, 121.7, 121.2, 114.1, 107.6, 55.4, 18.2, 17.1; HRMS (ESI) m/z calcd for $C_{16}H_{17}N_2O$ $[M+H]^+$: 253.1341; found: 253.1335.

2-(4-methoxyphenyl)imidazo[2,1-*a*]isoquinoline (Table 4 4g). [7f] Brown yellow Solid; mp 175–177 °C; 38% yield (21 mg); R_f value = 0.5 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.72 (d, J = 7.9 Hz, 1H), 7.93 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 7.1 Hz, 1H), 7.71 (s, 1H), 7.68 (d, J = 7.9 Hz, 1H), 7.65–7.61 (m, 1H), 7.57–7.53 (m, 1H), 7.01–6.98 (m, 3H), 3.86 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 159.3, 143.9, 143.2, 129.5, 128.7, 128.5, 128.0, 127.2, 127.0, 123.8, 123.5, 123.0, 114.2, 112.9, 109.0, 55.4.

2-(4-methoxyphenyl)imidazo[1,2-*a*]quinoline (Tables 4 and 4h). [28] Brownish gummy; 34% yield (19 mg); R_f value = 0.5 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.22 (s, 1H), 7.95–7.91 (m, 3H), 7.79 (dd, J = 7.9, 1.2 Hz, 1H), 7.63 (ddd, J = 8.5, 7.4, 1.4 Hz, 1H), 7.58 (d, J = 9.5 Hz, 1H), 7.50 (d, J = 9.4 Hz, 1H), 7.45 (dd, J = 10.9, 3.9 Hz, 1H), 6.99 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 159.6, 144.1, 144.2, 132.6, 129.3, 128.9, 127.2, 126.7, 126.2, 124.7, 123.5, 117.1, 115.2, 114.3, 105.9, 55.5.

3-(methylthio)-2-phenylimidazo[1,2-*a*]pyridine (Tables 5 and 5a). [22b] Brown yellow Solid; mp 65–67 °C; 40% yield (19 mg); R_f value = 0.5 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.49–8.46 (m, 1H), 8.28 (dd, J = 8.2, 1.0 Hz, 2H), 7.68 (dt, J = 9.3, 1.0 Hz, 1H), 7.50–7.46 (m, 2H), 7.41–7.36 (m, 1H), 7.31–7.26 (m, 1H), 6.93 (td, J = 6.8, 1.2 Hz, 1H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 148.9, 146.4, 133.9, 128.5, 128.4, 128.3, 126.1, 124.4, 117.7, 112.9, 111.5 18.3.

2-(4-methoxyphenyl)-3-(methylthio)imidazo[1,2-*a*]pyridine(Tables 5 and 5b). [22b] Brown yellow oil; 43% yield (23 mg); R_f value = 0.4 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.46 (d, J = 6.8 Hz, 1H), 8.25 (d, J = 8.9 Hz, 2H), 7.64 (d, J = 8.9 Hz, 1H), 7.27 (ddd, J = 8.3, 5.3, 1.2 Hz, 1H), 7.02 (d, J = 8.8 Hz, 2H), 6.91 (td, J = 6.8, 0.7 Hz, 1H), 3.87 (s, 3H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 159.9, 148.9, 146.5, 129.7, 126.6, 125.9, 124.3, 117.6, 113.1, 112.7, 110.6, 55.4, 18.3.

2-(4-fluorophenyl)-3-(methylthio)imidazo[1,2-*a*]pyridine (Tables 5 and 5c) [22b] Brown yellow Solid; mp 88–90 °C; 29% yield (15 mg); R_f value = 0.7 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.47–8.45 (m, 1H), 8.30–8.26 (m, 2H), 7.65 (dd, J = 8.9, 0.9 Hz, 1H), 7.29 (ddd, J = 9.0, 6.8, 1.3 Hz, 1H), 7.16 (t, J = 8.8 Hz, 2H), 6.93 (td, J = 6.8, 0.9 Hz, 1H), 2.24 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 163.0 (d, J = 247.9 Hz), 148.1, 146.5, 130.2 (d, J = 7.5 Hz), 126.2, 124.4, 117.7, 115.5 (d, J = 21.9 Hz), 112.9, 111.2, 18.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): −113.48 (s, 1F).

2-(3-bromophenyl)-3-(methylthio)imidazo[1,2-*a*]pyridine (Tables 5 and 5d). Brown yellow Solid; mp 88–90 °C; 38% yield (24 mg); R_f value = 0.6 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.47 (d, J = 6.8 Hz, 2H), 8.25 (d, J = 7.8 Hz, 1H), 7.65 (d, J = 9.0 Hz, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.35–7.28 (m, 2H), 6.95 (t, J = 6.8 Hz, 1H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 147.3, 146.5, 136.0, 131.3, 131.2, 130.0, 126.8, 126.4, 124.4, 122.7, 117.8, 113.1, 112.1, 18.3; HRMS (ESI) m/z calcd for $C_{14}H_{12}BrN_2S$ $[M+H]^+$: 318.9905; found: 318.9909.

3-(methylthio)-2-(3-nitrophenyl)imidazo[1,2-*a*]pyridine (Tables 5 and 5e). Brown yellow Solid; mp 126–128 °C; 35% yield (20 mg); R_f value = 0.6 [EtOAc: Petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.22 (t, J = 1.9 Hz, 1H), 8.65 (d, J = 7.8 Hz, 1H), 8.49 (d, J = 6.9 Hz, 1H), 8.21 (ddd, J = 7.8, 2.1, 0.8 Hz, 1H), 7.68–7.61 (m, 2H), 7.37–7.31 (m, 1H), 6.99 (td, J = 6.8, 0.9 Hz, 1H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 148.6, 146.6, 146.3, 135.8, 134.0, 129.4, 126.8, 124.5, 123.1, 122.9, 118.0, 113.4, 112.6, 18.3; HRMS (ESI) m/z calcd for $C_{14}H_{12}N_3O_2S$ $[M+H]^+$: 286.0650; found: 286.0652.

2-(2-methoxyphenyl)-3-(methylthio)imidazo[1,2-*a*]pyridine (Tables 5 and 5f). Brown yellow oil; 26% yield (14 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 2:3 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$)

δ (ppm)): 8.42 (d, J = 6.8 Hz, 1H), 7.72 (d, J = 9.1 Hz, 1H), 7.50 (dd, J = 7.5, 1.7 Hz, 1H), 7.43–7.39 (m, 1H), 7.30–7.26 (m, 1H), 7.08–7.02 (m, 2H), 6.94 (td, J = 6.8, 1.0 Hz, 1H), 3.83 (s, 3H), 2.20 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 157.6, 148.3, 146.5, 132.3, 130.0, 128.3, 125.5, 124.3, 123.3, 120.5, 118.0, 112.8, 111.2, 55.7, 17.9; HRMS (ESI) m/z calcd for $C_{15}H_{15}N_2OS$ $[M+H]^+$: 271.0905; found: 271.0910.

8-methyl-3-(methylthio)-2-phenylimidazo[1,2-*a*]pyridine (Tables 5 and 5g). [22b] Brown yellow Solid; mp 103–105 °C; 32% yield (16 mg); R_f value = 0.5 [EtOAc: Petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.35 (d, J = 6.7 Hz, 1H), 8.27 (dd, J = 8.3, 1.3 Hz, 2H), 7.48 (dd, J = 8.1, 7.0 Hz, 2H), 7.38 (dd, J = 11.7, 4.4 Hz, 1H), 7.09–7.07 (m, 1H), 6.85 (t, J = 6.8 Hz, 1H), 2.67 (s, 3H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 148.7, 146.8, 134.3, 128.6, 128.5, 128.2, 127.8, 124.8, 122.2, 112.8, 111.8, 18.4, 16.9.

3-(methylthio)-2-phenylimidazo[1,2-*a*]pyridine-7-carbonitrile (Tables 5 and 5h). Brown yellow Solid; mp 128–130 °C; 38% yield (20 mg); R_f value = 0.6 [EtOAc: Petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.56–8.54 (m, 1H), 8.28 (dd, J = 8.4, 1.2 Hz, 2H), 8.03 (d, J = 1.1 Hz, 1H), 7.52–7.48 (m, 2H), 7.45–7.41 (m, 1H), 7.07 (dd, J = 7.0, 1.5 Hz, 1H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 151.5, 144.2, 132.9, 129.2, 128.7, 128.4, 125.2, 123.5, 117.6, 114.9, 113.1, 108.5, 18.1; HRMS (ESI) m/z calcd for $C_{15}H_{12}N_3S$ $[M+H]^+$: 266.0752; found: 266.0755.

3-(methylthio)-2-phenylimidazo[2,1-*a*]isoquinoline (Tables 5 and 5i). Brown yellow Solid; mp 83–85 °C; 37% yield (21 mg); R_f value = 0.7 [EtOAc: Petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.76 (dd, J = 7.8, 1.1 Hz, 1H), 8.38–8.36 (m, 2H), 8.27 (d, J = 7.3 Hz, 1H), 7.73–7.71 (m, 1H), 7.67–7.63 (m, 1H), 7.61–7.57 (m, 1H), 7.54–7.50 (m, 2H), 7.42–7.38 (m, 1H), 7.14 (d, J = 7.3 Hz, 1H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 152.7, 147.3, 144.2, 134.2, 130.2, 128.7, 128.5, 128.2, 128.1, 127.0, 123.8, 123.6, 121.2, 113.6, 113.3, 18.1; HRMS (ESI) m/z calcd for $C_{18}H_{15}N_2S$ $[M+H]^+$: 291.0956; found: 291.0959.

2-(3,4-dimethoxyphenyl)-3-(methylthio)imidazo[1,2-*a*]pyridine (Tables 5 and 5j). Yellow low melting Solid; 35% yield (21 mg); R_f value = 0.3 [EtOAc: Petroleum ether = 2:3 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.47 (dd, J = 6.8, 0.9 Hz, 1H), 7.94–7.92 (m, 2H), 7.65 (dd, J = 10.0, 0.9 Hz, 1H), 7.30–7.27 (m, 1H), 6.98 (d, J = 8.1 Hz, 1H), 6.92 (td, J = 6.8, 0.9 Hz, 1H), 4.00 (s, 3H), 3.94 (s, 3H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 149.4, 148.1, 148.7, 146.4, 126.8, 126.0, 124.3, 121.0, 117.5, 112.8, 111.5, 111.1, 110.7, 56.1, 56.0, 18.2; HRMS (ESI) m/z calcd for $C_{16}H_{17}N_2O_2S$ $[M+H]^+$: 301.1011; found: 301.1010.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132125.

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