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S-Aryl Arenesulfonothioate and Copper Acetate Mediated Arylthiolation of 2-Aryl Pyridines and Heteroarenes

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ABSTRACT: Copper acetate mediated regioselective *ortho*-arylthiolation of 2-aryl pyridines has been accomplished for the first time using *S*-aryl arenesulfonothioate as the arythiolating agent. Reaction shows good functional group tolerance and gives thioarylated products in 67-89% yields. This reagent is a good alternative of the unpleasant smelling arylthiols. Experimental evidences suggest an unprecedented insertion of arylthio unit from both the parts of the reagent (SPh and *p*-TolSO_2) in the presence of copper acetate. Indoles and imidazopyridines also undergo facile reaction at C-3 position, and furnish thioarylated derivates in good yields.

INTRODUCTION

Aryl sulfides are ubiquitous structural motifs in numerous biologically active natural products, pharmaceuticals, materials etc. and have significant synthetic utility as building blocks of organosulfur compounds.[1] A few examples of biologically active arylthiolated molecules are shown in **figure 1.**

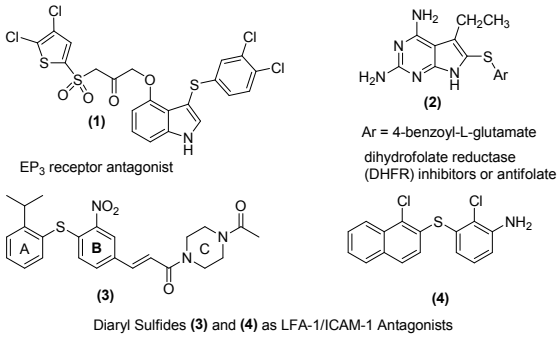
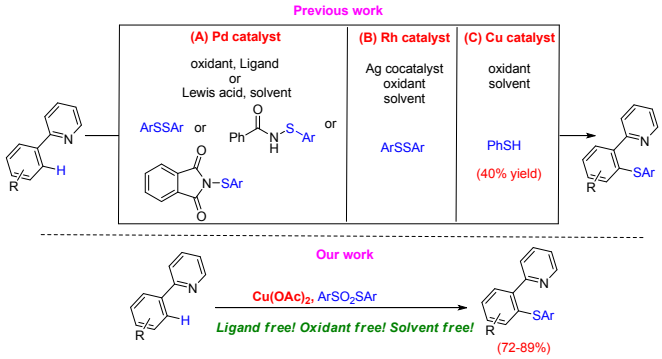


Figure 1. Selected examples of biologically active arylthiolated molecules

C-S bond formation, thus, holds immense importance from the perspective of organic synthesis. Traditional approach for synthesizing highly functionalized aryl sulfide scaffolds involves transition metal catalyzed cross-coupling of aryl halides with aryl thiols as coupling partners.[2] Though the reaction provides access to variety of aryl sulfides bearing various functional groups, need for pre-functionalizing arenes in the form of aryl halides limits its use. To overcome this challenge, chemistry involving C-H bond functionalization of arenes has been developed.[3] Since its inception, this area has grown exponentially as it provides the target molecules in a straightforward manner.

Functionalized pyridines find significant application in the synthesis of drugs, pharmaceuticals, herbicides and agrochemicals.[4] In this regard, pyridine as a directing group has been explored extensively for a variety of C-H functionalizations[5] such as alkylation, alkenylation, cyanation, carbonylation, acylation, amidation, trifluoromethylation, amination, azidation, nitration, halogenation, silylation and borylation. Generally, these reactions require toxic heavy metal salts or expensive transition metal catalysts such as Rh, Ru, Pt and Pd. Literature searches on pyridine directed arylthiolation on arene ring revealed only few reports where the reactions were accomplished using Pd and Rh metal catalysts (Scheme 1).[6]

Scheme 1: Various reagents for arylthiolation of 2-phenyl pyridines

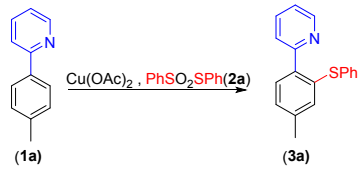


In Pd catalyzed arylthiolation of 2-arylpyridines, reagents such as diaryldisulfides,[6a,6b] *N*-arylthiobenzamides[6c] and *N*-(Arylthio)i(a)mides[6d] have been employed while Rh catalyzed arylthioation has been achieved only with diaryldisulfides[6e] as arylthiolating reagent. With an economical catalyst such as copper acetate, there is only one report on phenylthiolation of 2-phenyl pyridine by Yu and co-workers[7a] wherein through one example they have demonstrated synthesis of 2-(2-(phenylthio)phenyl)pyridine (40% yield) using foul smelling thiophenol as the thiolating reagent. With carbazole as substrate, $Cu(OAc)_2$ –promoted directed arylthiolation has been reported using diaryldisulfides with prolonged heating (48 h) at 160 °C.[7b] For methylthiolation, Qing and co-workers[8] disclosed a CuF_2–$K_2S_2O_8$ mediated reaction of 2-phenylpyridinesusing DMSO as the methylthiolating reagent. Though useful, the method employs harsh conditions, large excess of CuF_2 (4.0 equiv) and strong oxidant $K_2S_2O_8$ (2.0 equiv). Following this, in 2015, our group had demonstrated methylthiolation with DMSO under milder conditions using copper acetate (1.0 equiv) and air.[9] While these copper assisted reactions proceeded smoothly with dimethyl sulfoxide yielding methylthiolated products, the reactions failed to furnish the corresponding phenylthiolated derivatives with diphenyl sulfoxide. In view of the limited number of available arylthiolating reagents, there is a pressing need for developing efficient, cleaner and odourless arylthio transfer reagents. In a recent report, Wang *et al.* reported CuI catalyzed azide–alkyne cycloaddition (CuAAC) reaction using *S*-methyl benzenesulfonothioate as a methylthio group transfer reagent during one pot synthesis of 5-methylthiotriazoles.[10] The reagent enabled efficient thiomethylation with sulfinate as a leaving group. Following this, there was another report by Adimurthy *et al*. wherein they used *S*-arylsulfonothioate to achieve arylthiolation of activated C-H bond of heteroarenes with elimination of sulfinic acid as the leaving group.[11] However, use of this reagent in context of directing group assisted C-H bond arylthiolation does not exist. In view of the above literature and continuing our search towards copper assisted economic C-H functionalization pathways, we embarked upon the present study. We report for the first time the use of *S*-aryl arenesulfonothioate as an efficient and ordourless reagent for carrying out arylthiolation of *ortho* C-H bond of 2-aryl pyridines in the presence of copper acetate. The methodology also allows facile access to arylthioated indole and imidazopyridine derivatives.

RESULTS AND DISCUSSION

We initiated the work by using reaction conditions of Adimurthy's report for arylthiolation on 2-(*p*-tolyl)pyridine (**1a**) (1.0 equiv) with *S*-phenyl benzenesulfonothioate (**2a**) (1.5 equiv) and water as solvent at 120 °C. However, we could not observe any traces of desired product and decided to modify the reaction conditions. The same reaction was performed in presence of $Cu(OAc)_2$ under solvent free conditions. As desired, 2-(4-methyl-2-(phenylthio)phenyl)pyridine (**3a**) was obtained in 73% yield. Pleased with the finding, we decided to optimize the reaction further. Screening of solvents such as dioxane, toluene and chlorobenzene decreased the yield to 52%, 47% and 64% respectively (Table 1, entries 2-4). In polar solvents such as DMF, water and THF, either the product did not form or formed in trace amounts. Hence, neat conditions were used for further optimization. Replacing $Cu(OAc)_2$ with $Pd(OAc)_2$ or other copper catalysts such as $Cu(OTf)_2$, CuO and CuI (entry 5[b-e]) was detrimental for the reaction. The reaction quenched under oxidative conditions in presence of $K_2S_2O_8$ and O_2 (entry 6[f-g]), while the yield enhanced to 89% under inert atmosphere (entry 7). Decreasing the amount of $Cu(OAc)_2$ to 0.5 equiv and 0.75 equiv lowered the yield to 30% and 65% respectively, while increasing it to 1.5 equiv also gave reduced yield of 72% due to formation of side products (entry 8[i-k]). We noticed that decreasing the amount of $PhSO_2SPh$ to 1.0 equiv lowered the yield (entry 9). The reaction was monitored at different time intervals of 2 h, 4 h, 6 h, and gave the products in 35%, 71% and 89% yields respectively (entry 10[m-o]). Further, lowering the temperature to 100 °C or increasing it to140 °C resulted in reduced product yields (entry 11[p-q]).

Table 1. Optimization of the reaction conditions[a]



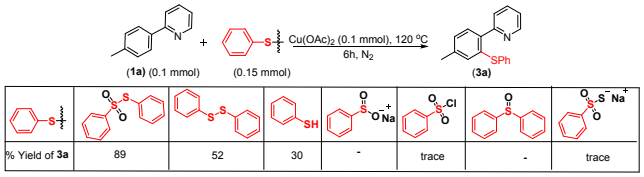
S. No.	Solvent	Time (h)	% Yield **3a**
1	-	12	73
2	Dioxane	12	52
3	Toluene	12	47
4	Chlorobenzene	12	64
5	-	12	(-)[b-d], trace[e]
6	-	12	(-)[f], (-)[g]
7	-	12	89[h]
8	-	12	30[i],65[j], 72[k]
9	-	12	72[l]
10	-	-	35[m],71[n], 89[o]
11	-	6	56[p], 62[q]

[a]Reaction conditions: 2-*p*tolPy (**1a**) (0.1 mmol, 1 equiv), $PhSO_2SPh$ (**2a**) (0.15 mmol, 1.5 equiv), $Cu(OAc)_2$ (0.1 mmol, 1equiv), 120 °C, 12h. [b]$Pd(OAc)_2$, [c]$Cu(OTf)_2$, [d]CuO, [e]CuI, [f]$K_2S_2O_8$, [g]O_2, [h]N_2, [i]0.5 equiv $Cu(OAc)_2$, [j]0.75 equiv $Cu(OAc)_2$, [k]1.5 equiv $Cu(OAc)_2$, [l]1.0 equiv $PhSO_2SPh$, [m]2 h, [n]4 h, [o]6 h, [p]100 °C, [q]140 °C.

A comparative analysis of **2a** with other known thiolating reagents such as PhSSPh, PhSH, $PhSO_2Na$, $PhSO_2Cl$, PhSOPh and $PhSO_2SNa$ was done as shown in table 2. It was found that under the optimized reaction conditions; only PhSSPh and

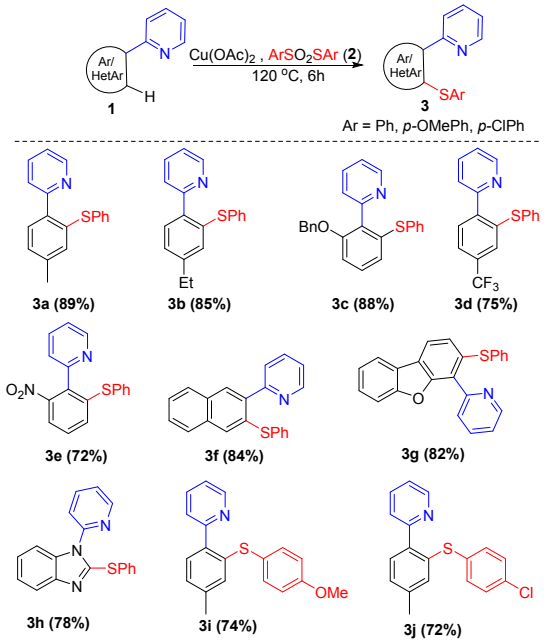
PhSH gave the phenylthiolated product **3a**, albeit in lower yields (52% and 30% respectively).

Table 2. Optimisation with different arylthiolating reagents



Convinced with the above findings, the scope of the reactionwas explored next. Various 2-phenypyridines substituted with electron donating as well as electron withdrawing groups were examined (Scheme 2).

Scheme 2. Substrate scope with 2-arylpyridines[a]

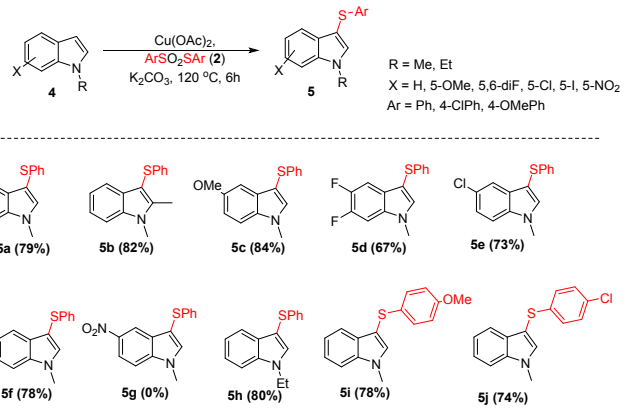


[a]Reaction conditions: 2-ArPy (0.25 mmol), $ArSO_2SAr$ (0.375 mmol), $Cu(OAc)_2$ (0.25 mmol), 120 °C, 6 h, N_2.

2-phenylpyridine substituted with 4-methyl, 4-ethyl and 2-benzyloxy substituents gave the phenylthiolated products **3a-3c** in 89%, 85% and 88% yields respectively. With electron withdrawing trifluoromethyl and nitro groups, the corresponding products **3d** and **3e** were obtained in slightly lower yields. The reaction was equally facile with 2-naphthylpyridine. Coupling occurred at the less hindered position to give the product **3f** selectively. 2-benzofuranyl pyridine (**1g**) and 2-benzimidazole pyridine (**1h**) yielded **3g** and **3h** in 82% and 78% yields respectively. Substitution in arylthiolating reagent at 4-position with electron donating methoxy group [*S*-(4-methoxyphenyl) 4-methoxybenzenesulfonothioate, (**2b**)], and electron withdrawing chloro group [*S*-(4-chlorophenyl) 4-chlorobenzenesulfonothioate, (**2c**)] furnished the corresponding arylthiolated products **3i** and **3j** in 74% and 72% yields respectively. The reaction was also carried out on gram-scale starting from 1.0 g of **1a**, and yielded **3a** in 78% yield (1.27 g). Notably, arylthiolation of 2-arylpyridines with sulfonothioate reagent is not only the first report of its kind but also provides a highly efficient and cost effective method by employing $Cu(OAc)_2$ instead of Pd or Rh reported previously with other arylthiolating reagents.

Copper catalyzed arylthioation of indoles[12] and imidazopyridines[13] with aryl iodides using unsymmetrical benzothiazolyl-containing disulfides, arene sulfinates, diaryldisulfides and sulfur powder has been reported previously. We decided to explore our condition for arylthiolation of *N*-methyl indole (**4a**) (Scheme 3). It was found that the reaction worked only in presence of K_2CO_3 and desired phenylthiolated product (**5a**) was formed in 79% yield. With 1,2-dimethyl-indole, 1,2-dimethyl-3-(phenylthio)-1*H*-indole (**5b**) was obtained confirming the position of phenylthioation at C-3. While electron donating methoxy group at 5-position of indole gave 5-methoxy-1-methyl-3-(phenylthio)-1*H*-indole (**5c**) in 84% yield; 5,6 difluoro substitution resulted in lower yield (67%) of product **5d**. 5-chloro and 5-iodo-substituted indole derivatives gave corresponding products **5e** and **5f** in moderate yields. Presence of nitro substituent resulted in complete inhibition of the reaction, and no product was formed. Changing *N*-methyl to *N*-ethyl indole did not affect the reaction, and **5h** was obtained in 80% yield. Arylthiolating reagents substituted with electron donating methoxy group (**2b**) and electron withdrawing chloro group (**2c**) at 4-position furnished the corresponding arylthiolated products **5i** and **5j** in 78% and 74% yields respectively.

Scheme 3. Arylthiolation of *N*-alkyl Indoles[a]

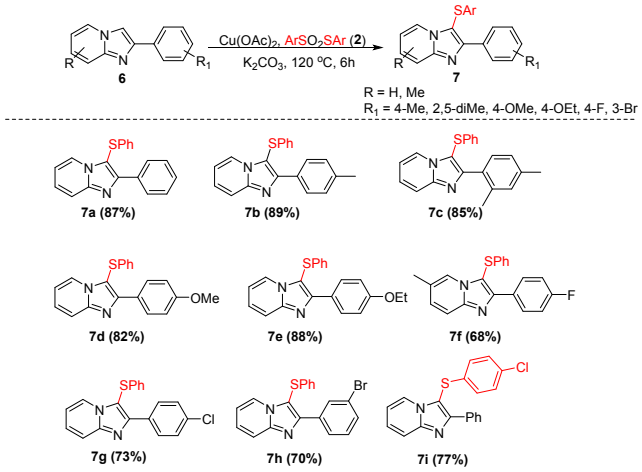


[a]Reaction conditions: *N*-alkyl Indole (0.25 mmol,1.0 equiv), $ArSO_2SAr$ (0.375 mmol, 1.5 equiv), $Cu(OAc)_2$ (0.25 mmol, 1.0 equiv), K_2CO_3 (0.25 mmol, 1.0 equiv) 120 °C, 6 h, N_2.

The reaction was further examined on 2-arylimidazopyridines (Scheme 4). Arylthiolation took place at C-3 position and arylthioated products **7a-7i** formed in moderate to good yields. Reaction of 2-phenylimidazo[1,2-a]pyridine (**6a**) afforded 2-phenyl-3-(phenylthio)imidazo[1,2-a]pyridine (**7a**) in 87% yield. Imidazopyridines substituted with 4-methyl, 2, 4 dimethyl, 4-methoxy and 4-ethoxy groups on 2-phenyl ring gave the corresponding products **7b-7e** in 82-89% yield. Notably, the yield of 2-(2,4-dimethylphenyl)-3-(phenylthio)imidazo[1,2-a]pyridine (**7c**) was not much effected by the steric effect of methyl group at *ortho* position in 2-(2,4-dimethylphenyl)imidazo[1,2-a]pyridine (**6c**). The halo substituted derivatives showed an electronic dependence, and gave the corresponding arylthioated products **7f, 7g** and

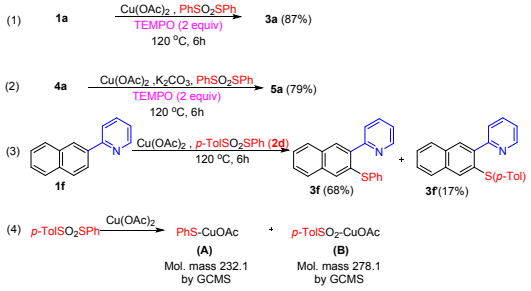
7h in 68%, 73% and 70% yields respectively due to electronic withdrawing effect of halo groups. 4-chloro substitution in arylthiolating reagent (**2c**) also yielded the product **7i** in 77% yield.

Scheme 4. Arylthiolation of 2-arylimidazopyridines[a]



[a]Reaction conditions: 2-arylimidazopyridine (0.25 mmol, 1.0 equiv), $ArSO_2SAr$ (0.375 mmol, 1.5 equiv), $Cu(OAc)_2$ (0.25 mmol, 1.0 equiv), K_2CO_3 (0.25 mmol, 1.0 equiv) 120 °C, 6 h, N_2.

Scheme 5. Control experiments



Some mechanistic studies were carried out to understand the reaction pathway. Reaction of **1a** as well as **4a** with **2a** in presence of 2.0 equivalents of TEMPO gave **3a** and **5a** in 87% and 79% yields respectively [**Scheme 5(1-2)**], ruling out the possibility of radical intermediates in the reaction. To check which part of the reagent was involved in delivering phenylthio group in the product, the reaction of 2-(naphthalen-2-yl)pyridine **(1f)** was carried out with mixed reagent, *S*-phenyl 4-methylbenzenesulfonothioate (**2d**). Interestingly, it was found that a mixture of arylthiolated products (**3f** and **3f'**) was obtained in the ratio 4:1, suggesting transfer of arylthio unit from both SPh and *p*-$TolSO_2$ motifs during the course of reaction [**Scheme 5(3)**]. The differential reactivity of the two can be explained in terms of the stability of their respective copper intermediates **A** and **B** as shown in **scheme 5 (4)**. Apparently, intermediate **A** is more reactive and undergoes faster kinetics owing to its lower stability than intermediate **B**, as indicated by their ratio in the GC-MS of the reaction mixture. Similar heterogeneity is reflected in the product distribution of **1f** with **3d**. (see the Supporting information). The transfer of both the thiol groups at the *ortho*-position albeit in differential reactivity was the rationale behind choosing symmetrical reagents to get one single compound in high yield. On the basis of these observations, a plausible mechanism has been proposed (see **Figure S1** in the Supporting information).

In summary, we report *S*-aryl arenesulfonothioate as an efficient, clean and ordourless reagent to achieve regioselective *ortho*-arylthiolation of 2-phenylpyridines in the presence of $Cu(OAc)_2$. This method shows high generality and selectivity, and yields only monoarylthiolated products in good yields. The conditions are quite versatile and allow access to C-3 arylthiolated indoles and imidazopyridines as well. Mechanistic investigations suggest involvement of both the thiol parts of the reagent in arylthio transfer after complexation with copper, though to different extents.

Experimental section

General Information

All reagents and solvents were of pure analytical grade. Thin layer chromatography (TLC) was performed on 60 F254 silica gel, pre-coated on aluminum plates and revealed with either a UV lamp (λ max= 254 nm) or iodine vapors. The products were purified by column chromatography on silica gel 230−400 mesh. ^1H, ^{19}F, and $^{13}C\{H\}$ NMR spectra were recorded on a 300 MHz (^1H 300 MHz,^{19}F 282 MHz,^{13}C 75 MHz) and 400 and 500 MHz spectrometer (^1H 400 MHz and 500 resp) using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are in δ (ppm) relative to TMS. The coupling constants (*J*) are in Hz. High resolution mass spectra (HRMS) were recorded on a mass spectrometer using electrospray ionization-time-of- flight (ESI-TOF) reflectron experiments.

All starting materials (**1**, **2**, **4** and **6**) are known compounds, and were synthesized using reported procedures. 2-aryl pyridines (**1a-1h**)[14], S-aryl arenethiosulfonates (**2a-2d**),[15] and *N*-protected indoles (**4a-4h**)[16] were synthesized following reported synthetic procedures. 2-arylimidazopyridines (**6a**, **6b**, **6g**)[17] and (**6c-6f**, **6h**)[18] were prepared using by two different methods reported previously.

General experimental procedure for arylthiolation of 2-arylpyridines (3a-3j)

2-arylpyridine (**1a**) (0.25 mmol, 1.0 equiv), *S*-phenyl benzenethiosulfonate (0.375 mmol, 1.5 equiv) and $Cu(OAc)_2$ (0.25 mmol, 1.0 equiv) were added in a 10 ml tube sealed with a Teflon-lined cap and flushed with nitrogen. The contents were heated for 6 h at 120 °C in oil bath. The reaction was monitored by TLC, after 6 h the reaction was completed. The contents were extracted with ethyl acetate, dried over anhydrous sodium sulfate, and concentrated at reduced pressure. The product was purified through the column chromatography on silica gel using hexane: EtOAc to give the corresponding arylthiolated products.

General experimental procedure for arylthiolation of *N*-alkyl indoles (5a-5j)

N-methylindole (**4a**) (0.25 mmol, 1.0 equiv), *S*-phenyl benzenethiosulfonate (0.375 mmol, 1.5 equiv), K_2CO_3 (0.25 mmol, 1.0 equiv) and $Cu(OAc)_2$ (0.25 mmol, 1.0 equiv) were added in a 10 mL tube sealed with a Teflon-lined cap and flushed with nitrogen. The contents were heated for 6 h at 120

°C in oil bath. The reaction was monitored by TLC, after 6 h the reaction was completed. The contents were extracted with ethyl acetate, dried over anhydrous sodium sulfate, and concentrated at reduced pressure. The product was purified through the column chromatography on silica gel using hexane: EtOAc to give the corresponding arylthiolated products.

General experimental procedure for arylthiolation of 2-arylimidazopyridines (7a-7h)

2-phenylimidazopyridine (**6a**) (0.25 mmol, 1.0 equiv), *S*-phenyl benzenethiosulfonate (0.375 mmol, 1.5 equiv), K_2CO_3 (0.25 mmol, 1.0 equiv) and $Cu(OAc)_2$ (0.25 mmol, 1.0 equiv) were added in a 10 mL tube sealed with a Teflon-lined cap and flushed with nitrogen. The contents were heated for 6 h at 120 °C in oil bath. The reaction was monitored by TLC, after 6 h the reaction was completed. The contents were extracted with ethyl acetate, dried over anhydrous sodium sulfate, and concentrated at reduced pressure. The product was purified through the column chromatography on silica gel using hexane: EtOAc to give the corresponding arylthiolated products.

Characterization data of synthesized compounds:

2-(4-methyl-2-(phenylthio)phenyl)pyridine (**3a**)**:**[19]

Isolated as colorless oil in Hexane/EtOAc (96/4), yield 89% (62 mg); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.67 (d, J = 5.0 Hz, 1H), 7.69-7.67 (m, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.28-7.26 (m, 2H), 7.25-7.23 (m, 2H), 7.21-7.18 (m, 2H), 7.14 (d, J = 8.0 Hz, 1H), 7.11 (s, 1H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 158.3, 149.0, 139.1, 139.0, 136.2, 135.8, 134.4, 132.6, 131.4, 130.4, 129.1, 128.0, 126.9, 124.3, 121.9, 21.1; MS (ESI) *m/z* 278 $[M+H]^+$; HRMS calcd. for $C_{18}H_{16}NS^+$ 278.0998; Found: 278.1002 $[M + H]^+$.

2-(4-ethyl-2-(phenylthio)phenyl)pyridine (**3b**)**:**[20]

Isolated as colorless oil in Hexane/EtOAc (96/4), Colorless oil, yield 85% (62 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.60-8.58 (m, 1H), 7.63-7.58 (m, 1H), 7.50-7.46 (m, 1H), 7.40 (d, J = 7.8 Hz, 1H), 7.21-7.18 (m, 3H), 7.17-7.16 (m, 1H), 7.15-7.14 (m, 1H), 7.14-7.12 (m, 1H), 7.11-7.10 (m, 1H), 7.08-7.06 (m, 1H), (q, J = 7.5 Hz, 2H), 1.09 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.3, 149.0, 145.3, 139.3, 136.3, 135.8, 134.3, 131.6, 131.3, 130.5, 129.1, 126.9, 126.8, 124.3, 121.9; MS (ESI) *m/z* 292 $[M+H]^+$; HRMS calcd. for $C_{19}H_{18}NS^+$ 292.1154; Found: 292.1141. $[M + H]^+$.

2-(2-(benzyloxy)-6-(phenylthio)phenyl)pyridine (**3c**):

New, Isolated as colorless oil in Hexane/EtOAc (94/6), yield 88% (81 mg), R_f = 0.68 (20% EtOAc/Hexane)^{1}H NMR (500 MHz, $CDCl_3$): δ 8.73 (d, J = 4.5 Hz, 1H), 7.73-7.69 (m, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.35-7.33 (m, 2H), 7.28-7.27 (m, 3H), 7.25-7.21 (m, 4H), 7.19-7.16 (m, 3H), 6.87 (d, J = 8.5 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 5.03 (s, 2H); ^{13}C{^{1}H} NMR(75 MHz, $CDCl_3$): δ 156.5, 155.7, 149.2, 138.1, 137.0, 135.8, 135.0, 132.7, 131.1, 129.4, 129.1, 128.3, 127.5, 127.4, 126.6, 125.9, 123.1, 122.2, 111.2, 70.5; MS (ESI) *m/z* 370 $[M+H]^+$; HRMS calcd. for $C_{24}H_{20}NOS^+$ 370.1260; Found: 370.1260. $[M + H]^+$.

2-(2-(phenylthio)-4-(trifluoromethyl)phenyl)pyridine (**3d**):[21]

Isolated as yellow solid in Hexane/EtOAc (95/5), yield 75% (62 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74-8.72 (m, 1H), 7.81-7.76 (m, 1H), 7.64-7.60 (m, 2H), 7.52-7.49 (m, 1H), 7.39-7.35 (m, 3H), 7.34-7.33 (m, 2H), 7.32-7.27 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 157.0, 149.3, 143.4, , 138.0, 136.3, 133.6, 133.1, 131.0 (q, J = 32.5 Hz), 130.6, 129.6, 128.3, 126.8 q (J = 3.8 Hz), 124.1, 123.7 (q, J = 270 Hz), 122.8 q (J = 3.8 Hz), 122.8; MS (ESI) *m/z* 332 $[M+H]^+$; HRMS calcd. for $C_{18}H_{13}F_3NS^+$ 332.0715; Found: 332.0717. $[M + H]^+$.

2-(2-nitro-6-(phenylthio)phenyl)pyridine (**3e**):

New, Isolated as colorless oil in Hexane/EtOAc (94/6), yield 72% (56 mg), R_f = 0.58 (20% EtOAc/Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63-8.62 (m, 1H), 7.76-7.69 (m, 2H), 7.42 (d, J = 8Hz, 1H), 7.33-7.29 (m, 4H), 7.28-7.27 (m, 2H), 7.19-7.17 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 154.11, 149.84, 141.15, 136.33, 134.0, 133.4, 133.88, 132.99, 132.55, 129.77, 129.04, 128.83, 124.72, 123.13, 121.67. MS (ESI) *m/z* 309 $[M+H]^+$; HRMS calcd. for $C_{17}H_{13}N_2O_2S^+$ 309.0692; Found: 309.0696. $[M + H]^+$.

2-(3-(phenylthio)naphthalen-2-yl)pyridine (**3f**):[19]

Isolated as colorless oil in Hexane/EtOAc (96/4), yield 84% (66 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.71 (d, J = 6.8 Hz, 1H), 8.0 (s, 1H), 7.86-7.83 (m, 1H), 7.76-7.70 (m, 2H), 7.66-7.64 (m, 2H), 7.48-7.44 (m, 2H), 7.33-7.32 (m, 1H), 7.30 (t, J = 2.1 Hz, 1H), 7.29-7.27 (m, 1H), 7.25-7.20 (m, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 158.3, 149.0, 139.2, 135.9, 135.6, 133.4, 133.2, 132.1, 132.0, 130.6, 130.0, 129.2, 128.0, 127.3, 127.0, 126.9, 126.4, 124.5, 122.2; MS (ESI) *m/z* 314 $[M+H]^+$; HRMS calcd.for $C_{21}H_{16}NS^+$ 314.0998; Found: 314.1000. $[M + H]^+$.

(2-(3-(phenylthio)naphthalen-2-yl)pyridine & 2-(3-(p-tolylthio)naphthalen-2-yl)pyridine) (**3f & 3f'**):

Isolated as colorless oil in Hexane/EtOAc (96/4), (yield) 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.705 (d, J = 4.0 Hz, 1H), 7.99 (s, 4H), 7.96 (s, 1H), 7.85-7.83 (m, 6H), 7.75-7.74 (m, 4H), 7.73-7.71 (m, 6H), 7.68-7.64 (m, 1H), 7.56 (s, 1H), 7.46-7.41 (m, 11H), 7.33-7.29 (m, 10H), 7.27-7.26 (m, 5H), 7.24-7.23 (m, 10H), 7.11 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 158.3, 158.2, 149.0, 139.2, 138.6, 137.9, 136.0, 135.9, 135.6, 133.4, 133.2, 133.16, 132.1, 132.0, 130.6, 130.1, 129.9, 129.6, 129.4, 129.2, 128.9, 128.0, 128.97, 127.3, 127.0, 126.9, 126.86, 126.7, 126.3, 126.0, 124.5, 122.2, 122.15, 21.2; MS (ESI) (**3f**) *m/z* 314 $[M+H]^+$; HRMS calcd.for $C_{21}H_{16}NS^+$ 314.0998; Found: 314.1000. $[M + H]^+$; MS (ESI) (**3f'**) *m/z* 328 $[M+H]^+$; HRMS calcd.for $C_{22}H_{18}NS^+$ 328.1154; Found: 328.1145. $[M + H]^+$.

2-(3-(phenylthio)dibenzo[b,d]furan-4-yl)pyridine (**3g**):

New, Isolated as colorless oil in Hexane/EtOAc (94/6), yield 82% (72 mg), R_f = 0.61 (20% EtOAc/Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74-8.73 (m, 1H), 7.83-7.81 (m, 1H), 7.75-7.71 (m, 2H), 7.61 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 8.4 Hz, 1H), 7.35-7.31(m, 1H), 7.26-7.19 (m, 5H), 7.19-7.11 (m, 3H); ^{13}C{^{1}H} NMR(75 MHz, $CDCl_3$): δ 156.6, 154.4, 153.7, 149.4, 136.2, 135.8, 135.0, 131.9, 129.2, 127.4, 127.3, 126.6, 126.3, 126.0, 123.9, 123.5, 123.0, 122.8, 120.7, 120.6, 112.0; MS (ESI) *m/z* 354 $[M+H]^+$; HRMS calcd.for $C_{23}H_{16}NOS^+$ 354.0947; Found: 354.0941. $[M + H]^+$.

2-(phenylthio)-1-(pyridin-2-yl)-1H-benzo[d]imidazole (**3h**):

New, Isolated as brown liquid in Hexane/EtOAc (94/6), yield 78% (59 mg), R_f = 0.63 (40% EtOAc/Hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66 (d, J = 4.5 Hz, 1H), 7.91 (t, J = 7.5 Hz, 1H), 7.72 (d, J =7.5 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.50-7.48 (m, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 6.5 Hz, 1H), 7.31-7.28 (m, 3H), 7.27-7.26 (m, 1H), 7.24-7.23 (m, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 149.5, 149.2, 143.5, 138.7, 135.7, 132.8, 130.8, 129.3, 128.5, 123.5, 123.2, 123.1, 120.2, 119.5, 110.5; MS (ESI) *m/z* 304 $[M+H]^+$; HRMS calcd.for $C_{18}H_{14}N_3S^+$ 304.0903; Found: 304.0916. $[M+H]^+$.

2-(2-((4-methoxyphenyl)thio)-4-methylphenyl)pyridine (**3i**):

New, Isolated as colorless oil in Hexane/EtOAc (96/4), yield 74% (57 mg), R_f = 0.61 (20% EtOAc/Hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.71-8.70 (m, 1H), 7.76-7.71 (m, 1H), 7.60-7.57 (m, 1H), 7.39-7.31 (m, 3H), 7.25-7.22 (m, 1H), 7.05-7.02 (m, 1H), 6.88-6.84 (m, 3H), 3.81 (s, 3H), 2.24 (s, 3H); ^{13}C{^{1}H} NMR(100 MHz, $CDCl_3$): δ 159.7, 158.4, 149.0, 138.8, 137.2, 137.0, 136.0, 135.6, 130.0, 129.6, 126.6, 125.0, 124.2, 122.0, 114.9, 55.3, 21.3; MS (ESI) *m/z* 308 $[M+H]^+$; HRMS calcd.for $C_{19}H_{18}NOS^+$ 308.1104; Found: 308.1117. $[M + H]^+$.

2-(2-((4-chlorophenyl) thio)-4-methylphenyl)pyridine (**3j**):

New, Isolated as colorless oil in Hexane/EtOAc (96/4), yield 72% (56 mg), R_f = 0.56 (10% EtOAc/Hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66 (d, J = 5.0 Hz, 1H), 7.71-7.68 (m, 1H), 7.53 (d, J = 7.5 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.24-7.21 (m, 2H), 7.19-7.17 (m, 3H), 7.167-7.15 (m, 1H), 7.10 (s, 1H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR(75 MHz, $CDCl_3$): δ 158.2, 149.0, 139.2, 135.9, 134.9, 133.9, 132.9, 132.6, 132.5, 132.2, 130.4, 129.2, 128.3, 124.2, 122.0, 21.5; MS (ESI) *m/z* 312 $[M+H]^+$; HRMS calcd.for $C_{18}H_{15}ClNS^+$ 312. 0608; Found: 312. 0620. $[M + H]^+$.

1-methyl-3-(phenylthio)-1H-indole (**5a**)**:**[22]

Isolated as colorless oil in Hexane/EtOAc (96/4), yield 79% (47 mg); ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.61 (d, J = 7.7 Hz, 1H), 7.38 (d, J = 8.1 Hz, 1H), 7.33-7.27 (m, 2H), 7.18-7.13 (m, 3H), 7.10-7.08 (m, 2H), 7.05-7.02 (m, 1H), 3.84 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.7, 137.6, 135.1, 129.9, 128.7, 125.7, 124.67, 122.6, 120.5, 119.8, 109.7, 100.6, 33.2. MS (ESI) *m/z* 262 $[M+Na]^+$; HRMS calcd.for $C_{15}H_{13}NNaS^+$ 262.0661; Found: 262.0655. $[M +Na]^+$.

1,2-dimethyl-3-(phenylthio)-1H-indole (**5b**)**:**[23]

Isolated as colorless oil in Hexane/EtOAc (96/4), yield 82% (52 mg);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.0 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.12-7.09 (m, 1H), 7.03-6.99 (m, 3H), 6.93-6.89 (m, 3H), 3.55 (m, 3H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR(75 MHz, $CDCl_3$): δ 143.0, 140.0, 137.2, 129.8, 128.8, 125.5, 124.5, 121.8, 120.5, 119.0, 109.2, 98.0, 30.4, 11.0; MS (ESI) *m/z* 253 $[M]^+$; HRMS calcd.for $C_{16}H_{15}NS^+$ 253.0920; Found: 253.0916. $[M]^+$.

5-methoxy-1-methyl-3-(phenylthio)-1H-indole (**5c**)**:**

New, Isolated as colorless oil in Hexane/EtOAc (95/5), yield 84% (56 mg), R_f = 0.42 (10% EtOAc/Hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.27 (m, 2H), 7.17-7.14 (m, 2H), 7.10-7.08 (m, 2H), 7.06-7.04 (m, 2H), 6.95-6.93 (m, 1H), 3.82 (s, 3H), 3.79 (s, 3H). ^{13}C{H} NMR (75 MHz, $CDCl_3$) δ 155.06, 139.82, 135.49, 132.67, 130.67, 128.67, 125.55, 124.60, 113.14, 110.63, 100.90, 99.66, 55.87, 33.31. MS (ESI) *m/z* 270 $[M+H]^+$; HRMS calcd.for $C_{16}H_{16}NOS^+$ 270.0947; Found: 270.0941. $[M + H]^+$.

5,6-difluoro-1-methyl-3-(phenylthio)-1H-indole (**5d**)**:**

New, Isolated as yellow oil in Hexane/EtOAc (96/4), yield 67% (46 mg), R_f = 0.62 (10% EtOAc/Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (s, 1H), 7.31-7.29 (m, 1H), 7.19-7.12 (m, 3H), 7.08-7.05 (m, 3H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR(75 MHz, $CDCl_3$) : δ 148.6 (dd, J = 241.1), 147.21 (dd, J = 238.6), 138.9 , 136.2 (d, J = 3.2 Hz), 132.6 (d, J = 10 Hz), 128.8, 125.8, 125.2 (J = 7.6 Hz), 125.0, 106.5 (J = 18.9 Hz), 101.2 , 98.0 (d, J = 20.5), 33.5; MS (ESI) *m/z* 276 $[M+H]^+$; HRMS calcd.for $C_{15}H_{12}F_2NS^+$ 276.0653; Found: 276.0648. $[M + H]^+$.

5-chloro-1-methyl-3-(phenylthio)-1H-indole (**5e**):[24]

Isolated as white solid in Hexane/EtOAc (96/4), yield 73% (49 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.57 (m, 1H), 7.35 (s, 1H), 7.30-7.28 (m, 1H), 7.25-7.24 (m, 1H), 7.22-7.19 (m, 1H), 7.16-7.15 (m, 2H), 7.08-7.04 (m, 2H), 3.84 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 139.2, 136.3, 136.0, 131.0, 128.8, 126.7, 125.8, 124.9, 123.0, 119.2, 110.9, 100.5, 33.4; MS (ESI) *m/z* 274 $[M+H]^+$; HRMS calcd.for $C_{15}H_{13}ClNS^+$ 274.0452; Found: 274.0457. $[M + H]^+$.

5-iodo-1-methyl-3-(phenylthio)-1H-indole (**5f**):[25]

Isolated as yellow oil in Hexane/EtOAc (96/4), yield 78% (71 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.54-7.51 (m, 1H), 7.25-7.24 (m, 1H), 7.19-7.12 (m, 3H), 7.08-7.05 (m, 3H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 139.2, 136.7, 135.8, 132.3, 131.1, 128.8, 128.5, 125.7, 124.9, 111.8, 100.1, 84.5, 33.3; MS (ESI) *m/z* 365 $[M+H]^+$;HRMS calcd.for $C_{15}H_{13}INS$ 365.9808; Found: 365.9801. $[M+H]^+$.

1-ethyl-3-(phenylthio)-1H-indole (**5h**):

Isolated as colorless oil in Hexane/EtOAc (96/4), yield 80% (51 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 7.6 Hz, 1H), 7.29-7.27 (m, 2H), 7.18-7.15 (m, 1H), 7.06-7.00 (m, 5H), 6.94-6.92 (m, 1H), 4.06 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 139.6, 136.5, 133.2, 129.8, 128.5, 125.5, 124.4, 122.3, 120.3, 119.7, 109.7, 100.3, 41.1, 15.2; MS (ESI) *m/z* 254 $[M+H]^+$; HRMS calcd.for $C_{16}H_{16}NS^+$ 254.0998; Found: 254.0992. $[M + H]^+$.

3-((4-methoxyphenyl)thio)-1-methyl-1H-indole (**5i**)**:**[26]

Isolated as white solid in Hexane/EtOAc (95/5), White solid, yield 78% (52 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (d, J = 7.8 Hz, 1H), 7.23 (s, 1H), 7.20-7.17 (m, 2H), 7.15-7.08 (m, 1H), 7.06-7.01 (m, 2H), 6.65-6.61 (m, 2H), 3.67 (s, 3H), 3.60 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.8, 137.5, 134.6, 130.0, 129.8, 128.4, 122.5, 120.4, 119.7, 114.5, 109.7, 102.3, 55.4, 33.1; MS (ESI) *m/z* 270 $[M+H]^+$; HRMS calcd.for $C_{16}H_{16}NOS^+$ 270.0947; Found: 270.0949. $[M + H]^+$.

3-((4-chlorophenyl)thio)-1-methyl-1H-indole (**5j**):[26]

Isolated as white solid in Hexane/EtOAc (96/4), yield 74% (51 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.31-7.23 (m, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 4.8 Hz, 2H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 138.3, 137.6, 135.1, 130.4, 129.6, 128.7, 127.0, 122.8, 120.7, 119.6, 109.9, 100.1, 33.2; MS (ESI) *m/z* 274 $[M+H]^+$; HRMS calcd.for $C_{15}H_{13}ClNS^+$ 274.0452; Found: 274.0457. $[M + H]^+$.

2-phenyl-3-(phenylthio)imidazo[1,2-a]pyridine (**7a**):[27]

Isolated as yellow solid in Hexane/EtOAc (88/12), yield 87% (66 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16-8.11 (m, 3H), 7.63 (d, J = 8Hz, 1H), 7.35-7.28 (m, 2H), 7.25 (d, J = 7.6 Hz, 1H), 7.22-7.18 (m, 1H), 7.15-7.07 (m, 2H), 7.03-7.00 (m, 1H), 6.90-6.88 (m, 2H), 6.73 (t, J = 6.8 Hz, 1H); ^{13}C{^{1}H} NMR(100 MHz, $CDCl_3$): δ 151.4, 147.1, 135.2, 133.2, 129.5, 128.7, 128.5, 126.8, 126.1, 125.6, 124.5, 117.6, 113.2, 106.7; MS (ESI) *m/z* 303 $[M+H]^+$; HRMS calcd.for $C_{19}H_{15}N_2S^+$ 303.0950; Found: 303.0942. $[M + H]^+$.

3-(phenylthio)-2-(p-tolyl)imidazo[1,2-a]pyridine (**7b**):[28]

Isolated as yellow solid in Hexane/EtOAc (88/12), yield 89% (70 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23-8.20 (m, 1H), 8.12 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 9.0 Hz, 1H), 7.29-7.26 (m, 1H), 7.24-7.19 (m, 2H), 7.16-7.14 (m, 2H), 7.11-7.06 (m, 1H), 6.97 (d, J = 7.8 Hz, 2H), 6.78 (t, J = 6.6 Hz, 1H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 151.5, 147.1, 138.6, 135.3, 130.5, 129.4, 129.2, 128.3, 126.6, 125.6, 124.5, 117.5, 113, 106.0, 21.4; MS (ESI) *m/z* 317 $[M+H]^+$; HRMS calcd.for $C_{20}H_{17}N_2S^+$ 317.1107; Found: 317.1103. $[M + H]^+$.

2-(2,4-dimethylphenyl)-3-(phenylthio)imidazo[1,2-a]pyridine (**7c**):

New, Isolated as yellow semisolid in Hexane/EtOAc (88/12), yield 85% (70 mg), R_f = 0.49 (30% EtOAc/Hexane), mp 87-89 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, J = 6.5 Hz, 1H), 7.72 (d, J = 9 Hz, 1H), 7.35-7.31 (m, 1H), 7.25 (s, 1H), 7.17 (t, J = 8.0 Hz, 2H), 7.11-7.09 (m, 2H), 7.00 (d, J = 8.00 Hz, 1H), 6.90-6.86 (m, 3H), 2.34 (s, 3H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.8, 146.9, 138.3, 137.3, 135.5, 131.2, 130.7, 130.1, 129.3, 126.2, 126.0, 125.9, 125.7, 124.6, 117.7, 112.9, 108.1, 21.3, 20.3; MS (ESI) *m/z* 331 $[M+H]^+$; HRMS calcd.for $C_{21}H_{19}N_2S^+$ 331.1263; Found: 331.1268. $[M + H]^+$.

2-(4-methoxyphenyl)-3-(phenylthio)imidazo[1,2-a]pyridine (**7d**):[28]

Isolated as brown semisolid in Hexane/EtOAc (85/15), yield 82% (68 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23-8.16 (m, 3H), 7.70 (d, J = 7.6 Hz, 1H), 7.31-7.29 (m, 1H), 7.18 (d, J = 5.2 Hz, 2H), 7.11 (s, 1H), 7.11-6.95 (m, 4H), 6.82 (s, 1H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.0, 151.4, 147.1, 135.4, 129.7, 129.4, 126.6, 126.0, 125.5, 124.4, 117.4, 113.9, 112.9, 105.5, 55.3; MS (ESI) *m/z* 333 $[M+H]^+$; HRMS calcd.for $C_{20}H_{17}N_2OS^+$ 333.1056; Found: 333.1071. $[M + H]^+$.

2-(4-ethoxyphenyl)-3-(phenylthio)imidazo[1,2-a]pyridine (**7e**)**:**

New, Isolated as yellow semisolid in Hexane/EtOAc (85/15), yield 88% (76 mg), R_f = 0.44 (30% EtOAc/Hexane), mp 94-96 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J = 6.5 Hz, 1H), 8.16 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 9.0 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.19 (t, J = 7.5 Hz, 2H), 7.12-7.10 (m, 1H), 6.99 (d, J = 7.5 Hz, 2H), 6.95 (d, J = 8.5 Hz, 2H), 6.82 (t, J = 7.0 Hz, 1H), 4.05 (q, J = 7.0 Hz, 2H), 1.40 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR(125 MHz, $CDCl_3$) : δ 159.4, 151.4, 147.1, 135.4, 129.7, 129.4, 126.6, 126.0, 125.8, 125.5, 124.4, 117.4, 114.4, 112.9, 105.2, 63.4, 14.9; MS (ESI) *m/z* 347 $[M+H]^+$; HRMS calcd.for $C_{21}H_{19}N_2OS^+$ 347.1213; Found: 347.1220. $[M + H]^+$.

2-(4-fluorophenyl)-6-methyl-3-(phenylthio)imidazo[1,2-a]pyridine (**7f**):

New, Isolated as pale yellow liquid in Hexane/EtOAc (85/15), yield 57% (86 mg), R_f = 0.59 (30% EtOAc/Hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18-8.13 (m, 3H), 7.48 (s, 1H), 7.23-7.20 (m, 2H), 7.15-7.09 (m, 3H), 6.99-6.97 (m, 2H), 6.72-6.71 (m, 1H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR(100 MHz, $CDCl_3$): δ 163.03 (d, J = 246.5 Hz), 150.5, 147.5, 138.0, 135.4, 130.1 (d, J = 8.1Hz), 129.7 (d, J = 3.32 Hz), 129.5, 126.1, 125.5, 123.7, 116.2, 115.7, 115.3 (d, J = 21.44 Hz), 105.2, 21.4; MS (ESI) *m/z* 335 $[M+H]^+$; HRMS calcd.for $C_{20}H_{16}FN_2S^+$ 335.1013; Found: 335.1020 $[M + H]^+$.

2-(4-chlorophenyl)-3-(phenylthio)imidazo[1,2-a]pyridine (**7g**):[29]

Isolated as white solid in Hexane/EtOAc (85/15), yield 73% (61 mg); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, J = 6.5 Hz, 1H), 8.17 (d, J = 8.5 Hz, 2H), 7.72 (d, J = 9.0 Hz, 1H), 7.40 (d, J = 8.5 Hz, 2H), 7.34 (t, J = 8.0 Hz, 1H), 7.21 (t, J = 8.0 Hz, 2H) 7.14 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 7.5 Hz, 2H), 6.88 (t, J = 7.0 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 150.2, 147.1, 134.9, 134.6, 131.9, 129.6, 129.5, 128.7, 127.0, 126.2, 125.6, 124.5, 117.7, 113.3, 106.5; MS (ESI) *m/z* 337 $[M+H]^+$; HRMS calcd.for $C_{19}H_{14}ClN_2S^+$ 337.0561; Found: 337.0560s $[M + H]^+$.

2-(3-bromophenyl)-3-(phenylthio)imidazo[1,2-a]pyridine (**7h**):[11]

Isolated as yellow semisolid in Hexane/EtOAc (85/15), yield 70% (67 mg); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (s, 1H), 8.29 (d, J = 7.0 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.38-7.35 (m, 1H), 7.30-7.27 (m, 1H), 7.23-7.20 (m, 2H), 7.16-7.14 (m, 1H), 6.99 (d, J = 7.5 Hz, 2H), 6.92-6.89 (m, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 149.6, 147.1, 135.4, 134.8, 131.5, 131.3, 129.9, 129.5, 127.0, 126.8, 126.3, 125.8, 124.6, 122.6, 117.8, 113.3, 107.1; MS (ESI) *m/z* 381 $[M+H]^+$; HRMS calcd.for $C_{19}H_{14}BrN_2S^+$ 381.0056; Found: 381.0050 $[M + H]^+$.

3-((4-chlorophenyl)thio)-2-phenylimidazo[1,2-a]pyridine (**7i**):[30]

Isolated as white solid in Hexane/EtOAc (88/12), yield 77% (65 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 6.8 Hz, 1H), 8.17 (d, J = 7.2 Hz, 2H), 7.73 (d, J = 9.2 Hz, 1H), 7.46-7.42 (m, 2H), 7.40-7.32 (m, 2H), 7.17 (d, J = 8.8 Hz, 2H), 6.92-6.86 (m, 3H); ^{13}C{^{1}H} NMR(100 MHz, $CDCl_3$): δ 151.7, 147.3, 133.8, 133.2, 132.1, 129.6, 128.8, 128.5, 128.4, 128.3, 126.9, 124.4, 117.8, 113.3, 105.7; MS (ESI) *m/z* 337 $[M+H]^+$; HRMS calcd.for $C_{19}H_{14}ClN_2S^+$ 337.0561; Found: 337.0567. $[M + H]^+$.

ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H NMR and ^{13}C NMR of all the synthesized compounds, GCMS spectra of intermediates **A** and **B,** and plausible reaction mechanism has been provided. The material is available free of charge on the ACS Publications website.

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