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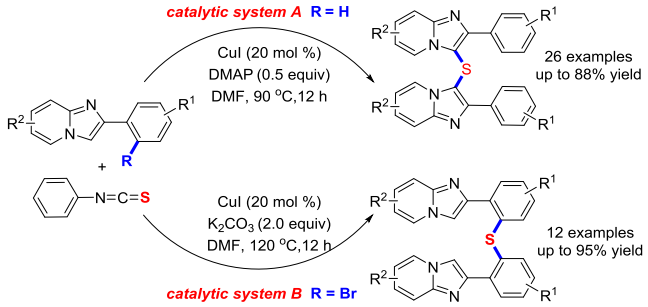
Supporting Information



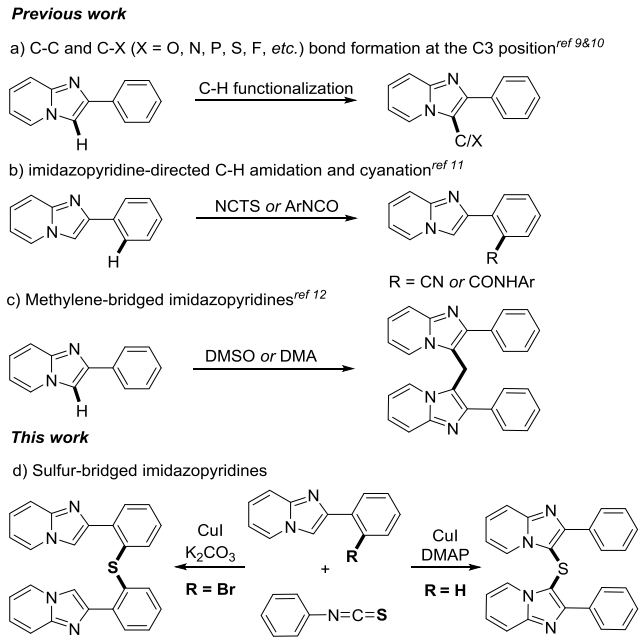
ABSTRACT: A copper(I)-catalyzed sulfur-bridged dimerization of imidazopyridines has been developed using isothiocyanate as the sulfur source. This method enables a switchable synthesis of bis(imidazo[1,2-*a*]pyridin-3-yl)sulfanes or bis(2-(imidazo[1,2-*a*]pyridin-2-yl)phenyl)sulfanes in the presence of DMAP or K_2CO_3 when different imidazopyridines were employed. Under the optimized conditions, a variety of sulfur-bridged imidazopyridines were obtained in good yields. Moreover, thiourea was proved to be the key intermediate under catalytic system A.

INTRODUCTION

The construction of C-S bonds is of fundamental research interest due to their wide applications in pharmaceuticals, organic syntheses, and materials science.[1] Accordingly, a wide range of protocols have been developed to introduce sulfur moiety onto target molecules.[2] Traditionally, the formation of C-S bonds usually involves cross-coupling between organic halides and thiols.[3] Recently, C-H functionalization has also emerged as a powerful strategy to construct C-S bonds, which is more atom economic and environmentally benign. In this context, various thiol surrogates, such as disulfide, thiols, sulfinic acids, arylsulfonyl chlorides, sulfonyl hydrazides, sodium sulfinates, and others, have been successfully utilized to access thioether derivatives.[4]

On the other hand, imidazo[1,2-*a*]pyridines have attracted considerable attention due to their significance in natural products, medicinal chemistry, and materials science.[5] Meanwhile, imidazo[1,2-*a*]pyridines have been utilized as abnormal *N*-heterocyclic carbene and pincer-type ligand precursors, which exhibited application in catalysis after coordinated with transition metals.[6] Consequently, great achievement has been made for the syntheses[7] and functionalizations[8] of imidazo[1,2-*a*]pyridine scaffold. Until now, direct C3 arylation, alkylation, carbonylation, amination, alkoxyla

Scheme 1. Functionalizations of imidazopyridines



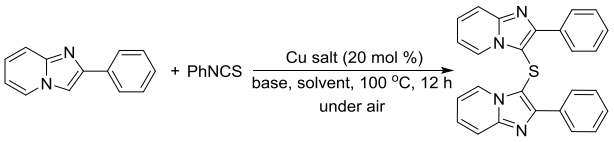
tion, halogenation, phosphonation, and thiolation have been well-developed to construct C-C[9] and C-X[10] (X = O, N, P, S, F, *etc.*) bonds (Scheme 1a). Meanwhile, imidazo[1,2-*a*]pyridine-directed C-H amidation and cyanation have also been developed (Scheme 1b).[11] Recently, DMA and DMSO have been utilized as the methylene sources to access bis(imidazo[1,2-*a*]pyridin-3-yl)methanes (Scheme 1c).[12] However, the methodology to access sulfur-bridged imidazopyridines is rather limited.[13] Considering the importance of sulfur-containing and bis(heteroaryl) compounds,[1,14] it is higher desirable to develop an environmentally benign strategy to prepare sulfur-bridged imidazopyridines.

As commercially available organic synthons, isothiocyanates have been utilized as thiocyanating agents[15] and are versatile synthetic intermediates for various heterocycles.[16,17] Meanwhile, the reaction involving cleavage of the C=S bond of isothiocyanates accompanied with formation of byproduct, such as CuS, Ag_2S, or H_2S, is reported.[18-20] As the continuation of our previous work in imidazopyridines,[9c,10f,h,11b,21] we herein reported a unique approach to access sulfur-bridged imidazopyridines utilizing CuI as the catalyst.[21] To the best of our knowledge, the employment of isothiocyanates as the sulfur source has not been reported.

RESULTS AND DISCUSSION

Our investigation was started with 2-phenylimidazo[1,2-*α*]pyridine **1a** (0.2 mmol), isothiocyanatobenzene **2** (0.3 mmol), CuI (20 mol%), and 1,10-phen (3 equiv) in DMF (2.5 mL). To our delight, the desired sulfur-bridged product **3a** was isolated in 29% yield at 100 °C for 12 h (Table 1, entry 1). Subsequently, various bases were screened, and DMAP was proved to be the best choice to afford **3a** in 64% yield (Table 1, entry 3). Next, the effect of different copper salts, such as CuCl, CuBr, and $CuBr_2$, were investigated, which all led to decreased yields (Table 1, entries 5-7). When DMF was replaced by other solvents, no improved result was obtained (Table 1, entries 8-10). In an attempt to improve reaction efficiency, reducing the usage amount of DMAP to 0.5 equivalent was beneficial, which provided **3a** in 71% yields (Table 1, entry 11). To further improve the outcome, the temperature range was modulated. Product **3a** was isolated in 88% yield at 90 °C (Table 1, entry 12), whereas decreased yield was observed at lower temperature (Table 1, entry 13). Moreover, when 10 mol% of copper salt was utilized, product **3a** was isolated in 26% yield (Table 1, entry 14). And **3a** could not be detected without CuI, indicating the necessity of copper salt (Table 1, entry 15). Finally, when the reaction was carried out under argon or oxygen atmosphere, decreased yields were observed. The structure of **3a** was further confirmed by X-ray diffraction (See the sup info).

Table 1. Optimization of reaction conditions[a]



1a 2 3a

Entry	catalyst	base	solvent	yield (%)[b]
1	CuI	1,10-phen	DMF	29
2	CuI	2,2'-bipyridine	DMF	59
3	CuI	DMAP	DMF	64
4	CuI	K_2CO_3	DMF	-
5	CuCl	DMAP	DMF	20
6	CuBr	DMAP	DMF	36
7	$CuBr_2$	DMAP	DMF	62
8	CuI	DMAP	DMA	44
9	CuI	DMAP	dioxane	55
10	CuI	DMAP	DMSO	20
11	CuI	DMAP (0.5 equiv)	DMF	71, 71[c]
12[c,d]	**CuI**	DMAP (0.5 equiv)	**DMF**	**88**
13[c,e]	CuI	DMAP (0.5 equiv)	DMF	75
14[cf]	CuI	DMAP (0.5 equiv)	DMF	26
15[c]	-	DMAP (0.5 equiv)	DMF	NR

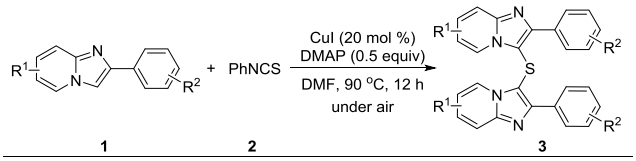
[a]Reaction Conditions: **1a** (0.2 mmol), **2** (0.3 mmol), Cu salt (20 mol %), base (3.0 equiv), solvent (2.5 mL), under air, T (°C), 12 h. [b]Isolated yields. [c]DMF (0.5 mL). [d]90 °C. [e]80 °C. [f]CuI (10 mol %).

With the optimized conditions in hand (Table 1, entry 12), the scope and generality of double C-H thiolation reaction was evaluated (Scheme 2). Initially, the substrate scope of 2-phenylimidazo[1,2-*α*]pyridines was investigated. It was found that Various substitutions at the *para*, *meta*, and *ortho* positions were well tolerated, affording the corresponding products **3a-m** in 37-88% yields. However, substrate bearing strong electron-withdrawing groups (NO_2 and CF_3) at the *para* position failed to yield the tar-

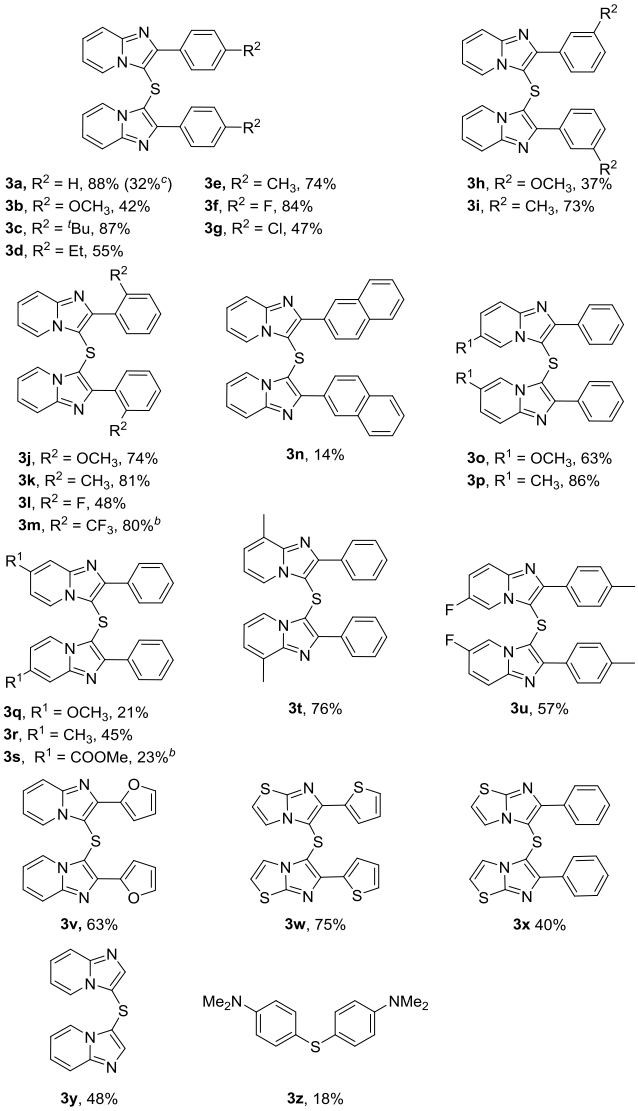
get products (not shown). When 2-naphthyl substituted substrates were employed, only 14% yield was achieved for **3n**. Subsequently, imidazopyridines bearing OCH_3, CH_3, F, or COOMe on the various positions of pyridine rings were also examined, which provided products **30-t** in 21-86% yields. Also, disubstituted imidazopyridine were employed to afford products **3u** in 57% yield. When 2-furanyl and 2-thienyl substituted imidazopyridines were utilized, **3v** and **3w** were isolated in 63% and 75% yields, respectively. Moreover, phenylimidazo[2,1-*b*] thiazole was also compatible to provide the sulfur-bridged product **3x** in 40% yield. Finally, when C2,C3-unsubstituted imidazopyridine was treated with PhNCS, only C3 sulfur-bridged product **3y** was obtained in 48% yield. Interestingly, when electron-rich aromatics *N*,*N*-dimethylaniline was utilized, the corresponding product **3z** was isolated in 18% yield.[22] Finally, a gram-scale experiment was conducted to evaluate the practical utility of the current protocol as a synthetic tool. Unfortunately, product **3a** was isolated in only 32% yield.

Unexpected, when 2-(2-bromophenyl)imidazo[1,2-*a*]pyridine **4a** was utilized as the coupling partners, bis(2-(imidazo[1,2-*a*]pyridin-2-yl)phenyl)sulfane **5a** was isolated in 19% yield (Table 2, entry 1). In the process to improve the yield of **5a**, various base and solvents were examined (see the sup info), which revealed that K_2CO_3 (2 equiv) and DMF (2.0 mL) are the best choice (Table 2, entry 6). When the temperature was increased to 120 °C, product **5a** was obtained in 89% yield (Table 2, entry 7). Further elevating temperature to 130 °C led to decreased yield (Table 2, entry 8). Moreover, when the Cu catalyst loading was decreased to 10 mol%, product **5a** was isolated in 76% yield (Table 2, entry 9). The struc ture of **5a** was further confirmed by X-ray diffraction (see the sup info).

Scheme 2. Substrate scope of imidazopyridines[a]

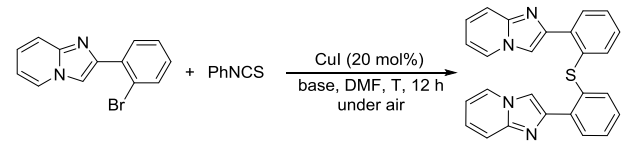


1 2 3



[a]Reaction Conditions: **1** (0.2 mmol), **2** (0.3 mmol), CuI (20 mol %), DMAP (0.5 equiv), DMF (0.5 mL), 90 °C, 12 h, under air. [b]24 h. [c]**1a** (1.2 g, 6 mmol), **2** (9 mmol).

Table 2. Optimization of reaction conditions[a]



4a 2 5a

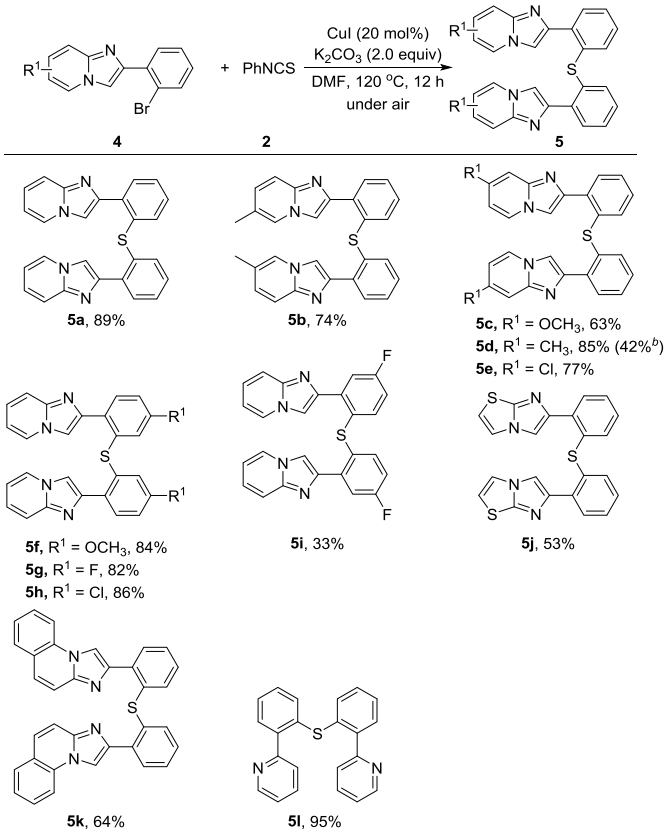
Entry	base	T (°C)	Yield (%)
1	DMAP	90	19
2	2,2'-bypr	90	-

3	K_2CO_3	90	24
4	Cs_2CO_3	90	17
5	K_2CO_3 (2 equiv)	90	34
6[c]	K_2CO_3 (2 equiv)	90	40
7[c]	**K_2CO_3 (2 equiv)**	**120**	**89**
8[c]	K_2CO_3 (2 equiv)	130	83
9[c,d]	K_2CO_3 (2 equiv)	120	76

[a]Reaction Conditions: 1a (0.2 mmol), 2 (0.3 mmol), CuI (20 mol%), base (0.5 equiv), DMF (0.5 mL), under air, T (°C), 12 h. [b]Isolated yields. [c]DMF (2.0 mL). [d]CuI (10 mol %).

Next, the substrate scope of 2-(2-bromophenyl)imidazo[1,2-*a*]pyridines **4** was investigated (Scheme 3). At first, imidazopyridines **4b**-**e** bearing OCH_3, CH_3, or Cl substituent on the C6 and C7 positions gave products **5b**-**e** in 63-85% yields, while substrates with strong electron-withdrawing groups such as C6-substituted CF_3 and C7-substituted NO_2 remained unreactive (not shown). Next, substitutions at the C2-benzene ring of imidazopyridines were examined, which gave *para*-substituted products **5f**-**h** in 82-86% yields. However, meta-substituted product **5i** was isolated in 33% yield. Also, imidazo-containing heterocycles pro

Scheme 3. Substrate scope of 2-(2-bromoaryl)imidazo[1,2-*a*]pyridines

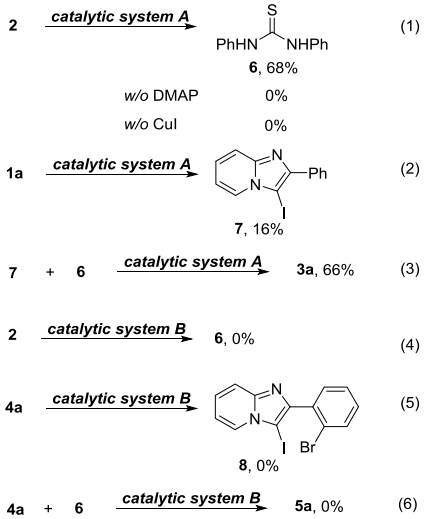


[a]Reaction Conditions: **4** (0.2 mmol), **2** (0.3 mmol), CuI (20 mol %), K_2CO_3 (2.0 equiv), DMF (2.0 mL), 120 °C, 12 h, under air. [c]**4d** (1.0 g, 4.6 mmol), **2** (0.90 g, 6.9 mmol).

ceeded smoothly to deliver product **5j** and **5k** in 53% and 64% yields. Finally, the catalytic system could be applied to 2-(2-bromophenyl)pyridine, which provide 5l in 95% yield. Other simple aryl bromides without a directing group, such as bromobenzene and 2-bromonaphthalene, failed to yield the desired products. We also tried to synthesize **5d** for a gram-scale production, which unfortunately gave the desired product in 42% yield.

To explore the reaction mechanism, a set of control experiments were carried out (Scheme 4). A symmetric thiourea **6** could be produced from isothiocyanatobenzene **2** under catalytic system A. Without DMAP or CuI, the thiourea intermediate **6** could not be detected (Scheme 4, eq 1). Meanwhile, iodo-substituted imidazopyridine **7** was isolated in 16% under catalytic system A (Scheme 4, eq 2). Moreover, coupling between **7** and **6** yielded the desired product **3a** in 66% yield (Scheme 4, eq 3). These results indicate that **6** and **7** are probably the key intermediate in the catalytic system A. By contrast, compound **6** and **8** could not be detected under catalytic system B (Scheme 4, eqs 4 and 5). Also, reaction between **4a** and **6** failed to give product **5a** under catalytic system B (Scheme 4, eq 6). These results indicate that formation of **5a** does not proceed through intermediate **6** and **8**.

Scheme 4. Mechanistic studies

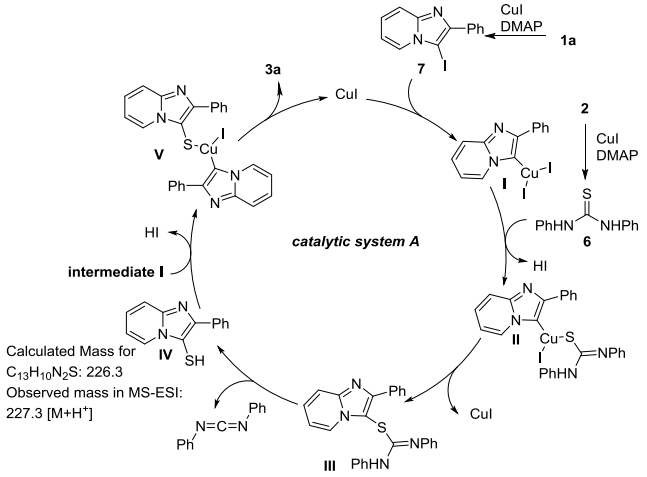


On the basis of above discussion and related reports,[18-20,23] a plausible mechanism was proposed for catalytic system A (Scheme 5). At first, Cu(I) underwent oxidative addition with iodo-substituted imidazopyridine **7** to yield Cu(III) intermediate **I**. Subsequently, the abstraction of a nitrogen proton from thiourea followed by nucleophilic substitution in the presence of DMAP gave Cu(III) intermediate **II**,[24] which underwent reductive elimination to provide CuI and intermediate **III.** Next, abstraction of a second proton generated diphenylmethanediimine and

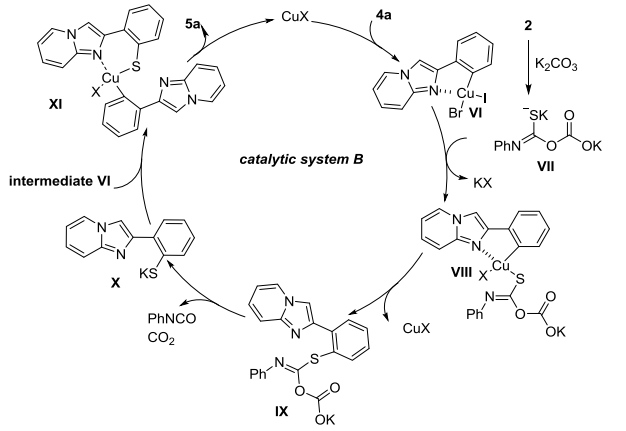
intermediate **IV**,[18c,19] which was confirmed by MS analysis (see the supporting information). Finally, nucleophilic attack of intermediate **I** by intermediate **IV** gave I^- and intermediate **V**, which underwent reductive elimination to deliver the final product **3a** and Cu(I) species.

On the other hand, catalytic system B also underwent similar reaction pathway (Scheme 6). Oxidative addition of Cu(I) with **4a** gave N1-chelated Cu(III) intermediate **VI**,[11] which reacted with **VII** species to yield intermediate **VIII**, which underwent reductive elimination to generated intermediate **IX** and CuX. After release of PhNCO and CO_2, intermediate **X** would be generated. Reaction between intermediates **X** and **VI** would afford Cu(III) intermediate **XI**, which underwent reductive elimination to deliver product **5a**, accompanied with the regeneration of Cu(I).

Scheme 5. Proposed catalytic cycles for catalytic system A



Scheme 6. Proposed catalytic cycles for catalytic system B



CONCLUSION

In conclusion, a novel CuI-catalyzed double thiolation of imidazopyridines using isothiocyanate as the sulfur source has been disclosed. This methodology could regioselective afford sulfur-bridged imidazopyridines via two proposed catalytic systems. Meanwhile, this protocol is featured with broad substrate scope, good functional group compatibility, and operational convenience. The discovery of isothiocyanate as sulfur source may promote the development of C-H thiolation.

EXPERIMENTAL SECTION

General Experimental Details. Unless otherwise mentioned, all materials were commercially obtained and used without further purification. All procedures were performed under the air atmosphere. Imidazo[1,2-*a*]pyridines **1**,[25] 2-(2-bromophenyl)imidazo[1,2-*a*]pyridines **4**,[26] and 2-(2-bromophenyl)pyridine[27] are known compounds and synthesized according to previously described methods. 1,3-diphenylthiourea **6**[28] and 3-iodo-2-phenylimidazo[1,2-*a*]pyridine **7**[29] are known compounds. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded at 400 MHz or 600 MHz, 100 MHz or 151 MHz, and 565 MHz respectively on a Bruker DPX instrument using Me_4Si as an internal standard. Chemical shift multiplicities are represented as follows: (s = singlet, d = doublet, t = triple, m = multiplet, dd = double doublet, td = triple doublet). Melting points were measured on a WC-1 instrument and uncorrected. New compounds for HRMS were tested on a Waters Q-Tof Micro MS/MS System ESI spectrometer.

Procedure for bis(2-phenylimidazo[1,2-*a*]pyridin-3-yl)sulfane (3a) synthesis. To a 10 mL sealed tube was added 2-phenylimidazo[1,2-*a*]pyridine **1a** (38.8 mg, 0.2 mmol), isothiocyanatobenzene **2** (40.5 mg, 0.3 mmol), CuI (7.6 mg, 20 mol %), and DMAP (12.2 mg, 0.5 equiv) in DMF (0.5 mL) under air. The reaction was heated at 90 °C for 12 h, and then cooled down to room temperature. Ethyl acetate (20 mL) was added and the mixture was extracted with water (2 × 10 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated. The residue was purified by preparative TLC on silica gel plates using petroleum ether/EtOAc = 2/1 as the eluent to give the corresponding product **3a**.

Procedure for bis(2-(imidazo[1,2-*a*]pyridin-2-yl)phenyl)sulfane (5a) synthesis. To a 10 mL sealed tube was added 2-(2-bromophenyl)imidazo[1,2-*a*]pyridine **4a** (54.4 mg, 0.2 mmol), isothiocyanatobenzene **2** (40.5 mg, 0.3 mmol), CuI (7.6 mg, 20 mol %), and K_2CO_3 (55.2 mg, 2.0 equiv) in DMF (2.0 mL) under air. The reaction was heated at 120 °C for 12 h, and then cooled down to room temperature. Ethyl acetate (20 mL) was added and the mixture was extracted with water (2 × 10 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated. The residue was purified by preparative TLC on silica gel plates using petroleum ether/EtOAc = 1/1 as the eluent to give the corresponding product **5a**.

Procedure for 1,3-diphenylthiourea (6) synthesis. To a 10 mL sealed tube was added isothiocyanatobenzene **2** (40.5 mg, 0.3 mmol), CuI (7.6 mg, 20 mol %), and DMAP (12.2 mg, 0.5 equiv) in DMF (0.5 mL) under air. The reaction was heated at 90 °C for 12 h, and then cooled down to

room temperature. Ethyl acetate (20 mL) was added and the mixture was extracted with water (2 × 10 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated. The residue was purified by preparative TLC on silica gel plates using petroleum ether/EtOAc = 2/1 as the eluent to give the corresponding product **6**.

Procedure for 3-iodo-2-phenylimidazo[1,2-a]pyridine (7) synthesis. To a 10 mL sealed tube was added 2-phenylimidazo[1,2-*a*]pyridine **1a** (38.8 mg, 0.2 mmol), CuI (7.6 mg, 20 mol %), and DMAP (0.5 equiv) in DMF (0.5 mL) under air. The reaction was heated at 90 °C for 12 h, and then cooled down to room temperature. Ethyl acetate (20 mL) was added and the mixture was extracted with water (2 × 10 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated. The residue was purified by preparative TLC on silica gel plates using petroleum ether/EtOAc = 2/1 as the eluent to give the corresponding product **7**.

*Bis(2-phenylimidazo[1,2-a]pyridin-3-yl)sulfane (**3a**)* purified by preparative TLC on silica gel with petroleum ether/EtOAc (2:1) as an eluent (R_f = 0.34); Light yellow solid (36.8 mg, 88% yield; 0.40 g, 32% yield for scale-up synthesis); mp 251 – 252 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.10 (m, 4H), 7.63 – 7.60 (m, 4H), 7.58 – 7.55 (m, 4H), 7.50 (d, *J* = 8.9 Hz, 2H), 7.11 – 7.07 (m, 2H), 6.34 (td, *J* = 6.9, 1.0 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.9, 146.6, 133.8, 129.6, 128.9, 128.6, 126.3, 125.4, 117.4, 112.6, 107.5. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{26}H_{18}N_4S^+$: 419.1325, Found: 419.1324.

*Bis(2-(4-methoxyphenyl)imidazo[1,2-a]pyridin-3-yl)sulfane (**3b**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (3:1) as an eluent (R_f = 0.23); Brown solid (20.0 mg, 42% yield); mp 224 – 225 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 9.0 Hz, 4H), 7.62 (d, *J* = 7.0 Hz, 2H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.16 – 7.11 (m, 4H), 7.11 – 7.07 (m, 2H), 6.40 (td, *J* = 6.8, 0.9 Hz, 2H), 3.96 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.2, 150.6, 146.5, 130.8, 126.3, 125.4, 117.2, 114.0, 112.5, 106.5, 55.5. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{28}H_{22}N_4O_2S^+$: 479.1536, Found: 479.1542.

*Bis(2-(4-(tert-butyl)phenyl)imidazo[1,2-a]pyridin-3-yl)sulfane (**3c**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.55); Light yellow solid (46.0 mg, 87% yield); mp 267 – 268 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 4H), 7.63 (d, *J* = 7.8 Hz, 4H), 7.54 (d, *J* = 6.5 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.27 (t, *J* = 6.5 Hz, 2H), 1.46 (s, 18H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.1, 150.9, 146.5, 130.9, 129.3, 126.2, 125.5, 125.4, 117.3, 112.3, 107.7, 34.9, 31.5. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{34}H_{34}N_4S^+$: 531.2577, Found: 531.2582.

*Bis(2-(4-ethylphenyl)imidazo[1,2-a]pyridin-3-yl)sulfane (**3d**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.25); Light yellow solid (26.0 mg, 55% yield); mp 209 – 210 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 4H), 7.58 (d, *J* = 6.9 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 4H), 7.10 – 7.06 (m, 2H), 6.32 (td, *J* = 6.8, 1.1 Hz, 2H), 2.82 (q, *J* = 7.7 Hz, 4H), 1.37 (t, *J* = 7.6 Hz, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 151.0, 146.5, 145.2, 131.2, 129.5, 128.1, 126.2, 125.46, 117.3, 112.4, 107.3, 28.9, 15.8. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{30}H_{26}N_4S^+$: 475.1951, Found: 475.1953.

*Bis(2-(p-tolyl)imidazo[1,2-a]pyridin-3-yl)sulfane (**3e**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (2:1) as an eluent (R_f = 0.22); Light yellow solid (33.1 mg, 74% yield); mp 263 – 264 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 4H), 7.60 (d, *J* = 6.9 Hz, 2H), 7.48 (t, *J* = 8.9 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 4H), 7.10 – 7.06 (m, 2H), 6.35 (td, *J* = 6.8, 0.9 Hz, 2H), 2.52 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.9, 146.5, 138.8, 130.9, 129.4, 129.3, 126.2, 125.4, 117.3, 112.5, 107.0, 21.5. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{28}H_{22}N_4S^+$: 447.1638, Found: 447.1642.

*Bis(2-(4-fluorophenyl)imidazo[1,2-a]pyridin-3-yl)sulfane (**3f**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.27); Light yellow solid (38 mg, 84% yield); mp 254 – 255 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.08 (m, 4H), 7.58 – 7.59 (m, 2H), 7.51 (d, *J* = 8.9 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.16 – 7.12 (m, 2H), 6.44 (td, *J* = 7.8, 1.0 Hz , 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.3 ($J_{C\text{-}F}$ = 247.6 Hz), 149.9, 146.5, 131.3 ($J_{C\text{-}F}$ = 247.6 Hz), 129.9 ($J_{C\text{-}F}$ = 3.3 Hz), 126.6, 125.1, 117.5, 115.7 ($J_{C\text{-}F}$ = 21.4 Hz), 112.8, 107.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.14. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{26}H_{16}F_2N_4S^+$: 455.1137, Found: 455.1138.

*Bis(2-(4-chlorophenyl)imidazo[1,2-a]pyridin-3-yl)sulfane. (**3g**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.28); Light yellow solid (23.1 mg, 47% yield); mp 296 – 297 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.06 (m, 4H), 7.62 – 7.57 (m, 6H), 7.51 (d, *J* = 9.0 Hz, 2H), 7.17 – 7.13 (m, 2H), 6.47 (td, *J* = 6.8, 1.0 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.8, 146.6, 135.1, 132.3, 130.7, 129.0, 126.7, 125.1, 117.6, 113.0, 107.1. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{26}H_{16}Cl_2N_4S$: 487.0545, Found: 487.0548.

*Bis(2-(3-methoxyphenyl)imidazo[1,2-a]pyridin-3-yl)sulfane. (**3h**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.25); Light yellow solid (17.9 mg, 37% yield); mp 153 – 154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 2H), 7.64 – 7.63 (m, 4H), 7.55 – 7.49 (m, 4H), 7.14 – 7.09 (m, 4H), 6.40 (td, *J* = 6.9, 1.0 Hz, 2H), 3.95 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.7, 150.7, 146.5, 135.08, 129.7, 126.5, 125.5, 122.0, 117.4, 115.3, 114.3, 112.7, 107.5, 55.5. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{28}H_{22}N_4O_2S^+$: 479.1536, Found: 479.1538.

*Bis(2-(m-tolyl)imidazo[1,2-a]pyridin-3-yl)sulfane (**3i**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.30); Light yellow solid (32.7 mg, 73% yield); mp 172 – 173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.89 (s, 2H), 7.58 (d, *J* = 6.8 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.12 – 7.07 (m, 2H), 6.36 (td, *J* = 6.9, 1.0 Hz, 2H), 2.52 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.0, 146.5, 138.3, 133.7, 130.1, 129.7, 128.5, 126.7, 126.3, 125.5, 117.3, 112.5,

107.4, 21.6. HRMS (positive ESI): [M + H]$^+$ Calcd. For $C_{28}H_{22}N_4S^+$: 447.1638, Found: 447.1641.

*Bis(2-(2-methoxyphenyl)imidazo[1,2-a]pyridin-3-yl)sulfane (**3j**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (3:1) as an eluent (R_f = 0.53); Light yellow solid (35.3 mg, 74% yield); mp 195 – 196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 8H), 7.19 – 7.08 (m, 6H), 6.45 – 6.41 (m, 2H), 3.84 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.5, 148.4, 146.4, 132.6, 130.6, 125.7, 124.9, 123.1, 120.6, 117.4, 112.2, 111.3, 109.9, 55.6. HRMS (positive ESI):[M + H]$^+$ Calcd. For $C_{28}H_{22}N_4O_2S^+$: 479.1536, Found: 479.1541.

*Bis(2-(o-tolyl)imidazo[1,2-a]pyridin-3-yl)sulfane (**3k**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.40); Light yellow solid (36 mg, 81% yield); mp 202 – 203 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, J = 8.6 Hz, 2H), 7.47 – 7.44 (m, 4H), 7.40 – 7.35 (m, 6H), 7.16 (t, J = 7.5 Hz, 2H), 6.45 (t, J = 6.7 Hz, 2H), 2.25 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.9, 146.2, 137.9, 133.4, 131.8, 130.5, 129.0, 126.1, 125.5, 124.9, 117.2, 112.5, 109.5, 20.3. HRMS (positive ESI): [M + H]$^+$ Calcd. For $C_{28}H_{22}N_4S^+$: 447.1638, Found: 447.1642.

*Bis(2-(2-fluorophenyl)imidazo[1,2-a]pyridin-3-yl)sulfane (**3l**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (2:1) as an eluent (R_f = 0.33); Light yellow solid (22.0 mg, 48% yield); mp 243 – 244 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (td, J = 7.4, 1.7 Hz, 2H), 7.60 – 7.51 (m, 6H), 7.40 – 7.33 (m, 4H), 7.17 – 7.13 (m, 2H), 6.47 (td, J = 6.9, 1.0 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.2 ($J_{C\text{-}F}$ = 250.1 Hz), 146.8, 146.2, 132.7, ($J_{C\text{-}F}$ = 2.4 Hz), 131.0 ($J_{C\text{-}F}$ = 8.2 Hz), 126.4, 124.6, 124.3, ($J_{C\text{-}F}$ = 3.6 Hz), 122.0 ($J_{C\text{-}F}$ = 13.9 Hz), 117.7, 116.3 ($J_{C\text{-}F}$ = 22.0 Hz), 112.8, 109.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.04. HRMS (positive ESI): [M + H]$^+$Calcd. For $C_{26}H_{16}F_2N_4S^+$: 455.1137, Found: 455.1142.

*Bis(2-(2-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridin-3-yl)sulfane (**3m**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (2:1) as an eluent (R_f = 0.25); Yellow solid (36.4 mg, 80% yield); mp 232 – 233 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.7 Hz, 2H), 7.62 (t, J = 7.5 Hz, 2H), 7.57 – 7.53 (m, 4H), 7.43 (d, J = 6.9 Hz, 2H), 7.32 (d, J = 7.5 Hz, 2H), 7.20 – 7.16 (m, 2H), 6.46 (td, J = 6.8, 0.9 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.2, 145.6, 133.2, 132.9, 131.2,130.4 ($J_{C\text{-}F}$ = 30.0 Hz), 129.0, 126.6($J_{C\text{-}F}$ = 5.2 Hz), 126.0, 124.1, 123.6 ($J_{C\text{-}F}$ = 274.7 Hz), 117.6, 112.7, 110.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.70. HRMS (positive ESI): [M + H]$^+$ Calcd. For $C_{28}H_{16}F_6N_4S^+$: 555.1073, Found: 555.1076.

*Bis(2-(naphthalen-2-yl)imidazo[1,2-a]pyridin-3-yl)sulfane (**3n**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.30); yellow solid (7.2 mg, 14% yield); mp 264 – 265 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 2H), 8.30 (dd, J = 8.5, 1.7 Hz, 2H), 8.10 (d, J = 8.5 Hz, 2H), 8.06 – 8.03 (m, 2H), 8.01 – 7.98 (m, 2H), 7.62 – 7.57 (m, 6H), 7.51 (d, J = 8.9 Hz, 2H), 7.08 – 7.03 (m, 2H), 6.16 (td, J = 6.9, 1.0 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.8, 146.7, 133.5, 133.3, 131.2, 128.9, 128.7, 128.3, 127.9, 126.9, 126.8, 126.6, 126.5, 125.3, 117.4, 112.7, 107.3. HRMS (positive ESI): [M + H]$^+$ Calcd. For $C_{34}H_{22}N_4S^+$: 519.1638, Found: 519.1643.

*Bis(6-methoxy-2-phenylimidazo[1,2-a]pyridin-3-yl)sulfane (**3o**)* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.42); Brown solid (30.0 mg, 63% yield); mp 264 – 265 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, J = 8.5, 1.3 Hz, 4H), 7.59 (t, J = 7.5, 4H), 7.47 – 7.41 (m, 6H), 6.90 (dd, J = 9.7, 2.5 Hz, 2H), 2.88 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.9, 149.1, 143.5, 134.0, 128.9, 128.8, 128.8, 122.1, 117.6, 106.6, 106.1, 54.8. HRMS (positive ESI): [M + H]$^+$ Calcd. For $C_{28}H_{22}N_4O_2S^+$: 479.1536, Found: 479.1537.

*Bis(6-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)sulfane (**3p**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.33); Light yellow solid (38.1 mg, 86% yield); mp 285 – 286 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.16 (m, 4H), 7.65 – 7.61 (m, 4H), 7.57 – 7.53 (m, 2H), 7.41 – 7.37 (m, 4H), 6.93 (dd, J = 9.1, 1.6 Hz, 2H), 1.74 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.3, 145.5, 134.1, 129.5, 129.4, 128.8, 123.7, 122.5, 116.5, 106.8, 17.8. HRMS (positive ESI): [M + H]$^+$ Calcd. For $C_{28}H_{22}N_4S$+: 447.1638, Found: 447.1640.

*Bis(7-methoxy-2-phenylimidazo[1,2-a]pyridin-3-yl)sulfane (**3q**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.39); Light yellow solid (27.3 mg, 57% yield); mp 272 – 273 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 – 8.49 (m, 4H), 7.60 – 7.57 (m, 4H), 7.47 – 7.41 (m, 6H), 6.89 (dd, J = 9.5, 2.4 Hz, 2H), 2.88 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.9, 149.1, 143.5, 134.0, 128.9, 128.8, 128.8, 122.1, 117.6, 106.6, 106.1, 54.8. HRMS (positive ESI): [M + H]$^+$ Calcd. For $C_{28}H_{22}N_4O_2S^+$: 479.1536, Found: 479.1537.

*Bis(7-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)sulfane (**3r**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.43); Yellow solid (20.0 mg, 45% yield); mp 197 – 198 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.09 (m, 4H), 7.63 – 7.59 (m, 4H), 7.56 – 7.52 (m, 2H), 7.40 (d, J = 7.0 Hz, 2H), 7.24 (s, 2H), 6.18 (dd, J = 7.0, 1.6 Hz, 2H), 2.26 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.7, 146.9, 137.7, 133.9, 129.5, 128.8, 128.6, 124.6, 115.9, 115.2, 106.8, 21.3. HRMS (positive ESI): [M + H]$^+$ Calcd. For $C_{28}H_{22}N_4S^+$: 447.1638, Found: 447.1641.

*Dimethyl 3,3′-thiobis(2-phenylimidazo[1,2-a]pyridine-7-carboxylate) (**3s**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.60); Light yellow solid (12.0 mg, 23% yield); mp 208 – 209 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.21 (m, 2H), 8.09 (dd, J = 8.2, 1.7 Hz, 4H), 7.67 – 7.62 (m, 6H), 7.54 (dd, J = 7.2, 0.7 Hz, 2H), 6.94 (dd, J = 7.1, 1.6 Hz, 2H), 3.90 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.2, 153.0, 145.6, 133.1, 129.6, 129.5, 128.9, 127.9, 124.9, 119.9, 111.9, 109.0, 52.7 HRMS (positive ESI): [M + H]$^+$ Calcd. For $C_{30}H_{22}N_4O_4S^+$: 535.1435, Found: 535.1440.

*Bis(8-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)sulfane (**3t**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.50); Brown solid (34 mg, 76% yield); mp 216 – 217 °C. ^{1}H NMR (400

MHz, $CDCl_3$) δ 8.09 – 8.07 (m, 4H), 7.62 – 7.58 (m, 4H), 7.55 – 7.51 (m, 2H), 7.41 (d, *J* = 6.7 Hz, 2H), 6.86 (d, *J* = 6.9 Hz, 2H), 6.25 (t, *J* = 6.9 Hz, 2H), 2.51 (s, 6H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 150.5, 146.8, 134.2, 129.8, 128.7, 128.5, 127.3, 125.1, 123.2, 112.5, 107.9, 16.7. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{28}H_{22}N_4S^+$: 447.1638, Found: 447.1642.

*Bis(6-fluoro-2-(p-tolyl)imidazo[1,2-a]pyridin-3-yl)sulfane (**3u**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.51); Light yellow solid (27.3 mg, 57% yield); mp 272 – 273 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.4 Hz, 4H), 7.46 – 7.39 (m, 8H), 7.00 (t, *J* = 7.9 Hz, 2H), 2.52 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.1 ($J_{C\text{-}F}$ = 238.9 Hz), 152.4 ($J_{C\text{-}F}$ = 2.4 Hz), 144.1, 139.4, 130.4, 129.4 ($J_{C\text{-}F}$ = 21.9 Hz), 118.2 ($J_{C\text{-}F}$ = 25.2 Hz), 117.6 ($J_{C\text{-}F}$ = 8.4 Hz), 112.8, 112.4, 108.9, 21.4.^{19}F NMR (376 MHz, $CDCl_3$) δ -138.14. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{28}H_{20}F_2N_4S^+$: 483.1450, Found: 483.1451.

*Bis(2-(furan-2-yl)imidazo[1,2-a]pyridin-3-yl)sulfane (**3v**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (3:1) as an eluent (R_f = 0.34); Light Brown solid (25.2 mg, 63% yield); mp 235 – 236 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 6.9 Hz, 2H), 7.72 (s, 2H), 7.54 (d, *J* = 9.1 Hz, 2H), 7.38 (d, *J* = 2.9 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 2H), 6.69 (s, 2H), 6.64 (t, *J* = 6.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.4, 147.0, 143.4, 141.8, 126.7, 125.0, 117.5, 113.3, 111.8, 110.7, 104.6. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{22}H_{14}N_4O_2S^+$: 399.0910, Found: 399.0913.

*Bis(2-(thiophen-2-yl)imidazo[1,2-a]pyridin-3-yl)sulfane (**3w**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.38); Light yellow solid (32.1 mg, 75% yield); mp 217 – 218 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 1.5 Hz, 2H), 7.93 (d, *J* = 6.7 Hz, 2H), 7.55 (d, *J* = 4.8 Hz, 2H), 7.52 (d, *J* = 8.9 Hz, 2H), 7.29 (s, 2H), 7.13 (t, *J* = 7.8 Hz, 2H), 6.54 (t, *J* = 6.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.8, 145.2, 136.5, 127.9, 127.4, 126.7, 125.2, 117.3, 113.2, 104.5. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{22}H_{14}N_4S_3^+$: 431.0453, Found: 431.0458.

*Bis(6-phenylimidazo[2,1-b]thiazol-5-yl)sulfane (**3x**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.55); Light yellow solid (17.0 mg, 40% yield); mp 228 – 229 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.05 (m, 4H), 7.56 – 7.53 (m, 4H), 7.49 – 7.45 (m, 2H), 6.51 (d, *J* = 4.5 Hz, 2H), 6.49 (dd, *J* = 4.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 151.4, 151.3, 133.6, 128.6, 128.6, 128.5, 118.4, 112.6, 109.5. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{22}H_{14}N_4S_3^+$: 431.0453, Found: 431.0456.

*Bis(imidazo[1,2-a]pyridin-3-yl)sulfane (**3y**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:3) as an eluent (R_f = 0.24); Light yellow solid (12.6 mg, 48% yield); mp 258 – 259 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.58 (d, *J* = 6.9 Hz, 2H), 7.99 (s, 2H), 7.62 (d, *J* = 9.0 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 2H), 6.97 (t, *J* = 6.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 147.6, 140.4, 126.0, 123.9, 118.2, 113.4, 109.7. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{14}H_{10}N_4S^+$: 267.0699, Found: 267.0700.

*Bis(2-(imidazo[1,2-a]pyridin-2-yl)phenyl)sulfane (**5a**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.21); Brown solid (37.3 mg, 89% yield); mp 165 – 166 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 7.9, 1.3 Hz, 2H), 8.06 (s, 2H), 8.01 (dd, *J* = 5.8, 0.9 Hz, 2H), 7.59 (dd, *J* = 9.2, 0.6 Hz, 2H), 7.36 (td, *J* = 7.8, 1.4 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.22 – 7.18 (m, 2H), 7.13 – 7.09 (m, 2H), 6.69 (td, *J* = 6.8, 1.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 144.6, 143.0, 135.3, 133.2, 132.7, 130.8, 128.5, 127.6, 125.9, 124.7, 117.4, 112.3, 112.3. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{26}H_{18}N_4S^+$: 419.1325, Found: 419.1330.

*Bis(2-(6-methylimidazo[1,2-a]pyridin-2-yl)phenyl)sulfane (**5b**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:2) as an eluent (R_f = 0.20); Light yellow solid (33.2 mg, 74% yield); mp 72 – 73 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.8 (dd, *J* = 7.8, 1.3 Hz, 2H), 7.98 (s, 2H), 7.79 (s, 2H), 7.50 (d, J = 9.2 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.29 – 7.27 (m, 2H), 7.22 – 7,17 (m, 2H), 6.98 (dd, *J* = 9.2, 1.5 Hz, 2H), 2.25 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.6, 142.6, 135.5, 133.0, 132.7, 130.7, 128.3, 127.9, 127.6, 123.6, 121.8, 116.6, 112.2, 18.1. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{28}H_{22}N_4S^+$: 447.1638, Found: 447.1643.

*Bis(2-(7-methoxyimidazo[1,2-a]pyridin-2-yl)phenyl)sulfane. (**5c**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:2) as an eluent (R_f = 0.21); Light yellow solid (30.0 mg, 63% yield); mp 85 – 86 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.9 Hz, 2H), 7.93 (s, 2H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.20 – 7.18 (m, 2H), 6.88 (s, 2H), 6.45 (dd, *J* = 7.4, 2.2 Hz, 2H), 3.84 (s, 6H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 158.0, 146.0, 142.4, 135.3, 132.9, 132.7, 130.5, 128.2, 127.6, 126.3, 111.3, 107.5, 94.4, 55.5. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{28}H_{22}N_4O_2S^+$: 479.1536, Found: 479.1541.

*Bis(2-(7-methylimidazo[1,2-a]pyridin-2-yl)phenyl)sulfane (**5d**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:2) as an eluent (R_f = 0.20); Light yellow solid (38.0 mg, 75% yield; 0.42 g, 42% yield for scale-up synthesis); mp 76 – 77 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.99 (s, 2H), 7.91 (d, *J* = 6.9, 2H), 7.37 – 7.33 (m, 4H), 7.29 – 7.26 (m, 2H), 7.21 – 7.17 (m, 2H), 6.55 (dd, *J* = 6.9, 1.5 Hz, 2H), 2.37 (s, 6H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 145.0, 142.6, 135.6, 135.5, 133.1, 132.7, 130.7, 128.3, 127.6, 125.1, 115.7, 114.9, 111.8, 21.4. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{28}H_{22}N_4S^+$: 447.1638, Found: 447.1644.

*Bis(2-(7-chloroimidazo[1,2-a]pyridin-2-yl)phenyl)sulfane (**5e**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (3:1) as an eluent (R_f = 0.30); Brown solid (37.2 mg, 77% yield); mp 203 – 204 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.8 Hz, 2H), 8.10 (s, 2H), 8.00 (s, 2H), 7.56 (d, *J* = 9.5 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 9.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 144.0, 142.9, 134.9, 133.2, 132.9, 130.8, 128.8, 127.8, 126.2, 123.6, 120.5, 117.8, 112.7. HRMS (positive ESI): $[M + H]^+$ Calcd. For $C_{26}H_{16}Cl_2N_4S^+$: 487.0545, Found: 487.0550.

*bis(2-(imidazo[1,2-a]pyridin-2-yl)-5-methoxyphenyl)sulfane.(**5f**)* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.21); Light yellow solid (40.0 mg, 84% yield); mp 196 – 197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.9, Hz, 2H), 8.02 – 8.00 (m, 4H), 7.59 (d, J = 9.1 Hz, 2H), 7.14 – 7.09 (m, 2H), 6.92 (dt, J = 8.6, 2.6 Hz, 2H), 6.85 (d, J = 2.6 Hz, 2H), 6.69 (td, J = 7.5, 0.7 Hz, 2H), 3.71 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.5, 144.5, 142.9, 133.9, 131.9, 128.0, 125.8, 124.6, 117.6, 117.2, 113.7, 112.1, 111.6, 55.3. HRMS (positive ESI): [M + H]$^+$ Calcd. For $C_{28}H_{22}N_4O_2S^+$: 479.1536, Found: 479.1548.

*bis(5-fluoro-2-(imidazo[1,2-a]pyridin-2-yl)phenyl)sulfane.(**5g**)* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.20); Light yellow solid (37.0 mg, 82% yield); mp 139 – 140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 8.4, 6.1 Hz, 2H), 8.05 (d, J = 6.58 Hz, 2H), 8.00 (s, 2H), 7.60 (d, J = 9.3 Hz, 2H), 7.16 (ddd, J = 7.9, 6.7, 1.0 Hz, 2H), 7.00 (td, J = 9.1, 2.6 Hz, 2H), 7.00 (dd, J = 9.1, 2.6 Hz, 2H), 6.76 – 6.63 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.3 ($J_{C\text{-}F}$ = 247.8 Hz), 144.6, 142.1, 134.5 ($J_{C\text{-}F}$ = 7.3 Hz), 132.5 ($J_{C\text{-}F}$ = 8.7 Hz), 131.6 ($J_{C\text{-}F}$ = 3.1 Hz), 125.9, 124.9, 119.1 ($J_{C\text{-}F}$ = 23.8 Hz), 117.4, 115.2 ($J_{C\text{-}F}$ = 21.5 Hz), 112.5, 111.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.73. HRMS (positive ESI): [M + H]$^+$ Calcd. For $C_{26}H_{16}F_2N_4S^+$: 455.1137, Found: 455.1147.

*bis(5-chloro-2-(imidazo[1,2-a]pyridin-2-yl)phenyl)sulfane.(**5h**)* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.25); Light yellow solid (42.0 mg, 86% yield); mp 213 – 214 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, J = 8.4 Hz, 2H), 8.05 – 8.04 (m, 4H), 7.60 (t, J = 9.1 Hz, 2H), 7.35 (dd, J = 8.4, 2.1 Hz, 2H), 7.25 (d, J = 2.1, 2H), 7.18 – 7.14 (m, 2H), 6.74 (td, J = 6.8, 0.9 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.7, 141.9, 134.2, 134.0, 133.9, 132.0, 128.2, 125.9, 125.1, 117.5, 112.5, 112.3. HRMS (positive ESI): [M + H]$^+$ Calcd. For $C_{26}H_{16}Cl_2N_4S^+$: 487.0545, Found: 487.0551.

*bis(4-fluoro-2-(imidazo[1,2-a]pyridin-2-yl)phenyl)sulfane.(**5i**)* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.31); Light yellow solid (15.0 mg, 33% yield); mp 202 – 203 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 2H), 8.05 (d, J = 6.7 Hz, 2H), 7.96 (dd, J = 10.2, 2.9 Hz, 2H), 7.61 (d, J = 9.3, 2H), 7.27 – 7.22 (m, 2H), 7.20 – 7.15 (m, 2H), 6.93 (td, J = 7.8, 2,9 Hz, 2H), 6.75 (td, J = 6.7, 0.8 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ 162.3 ($J_{C\text{-}F}$ = 249.2 Hz), 144.6, 141.9, 137.4 ($J_{C\text{-}F}$ = 8.6 Hz), 134.5 ($J_{C\text{-}F}$ = 7.7 Hz), 128.0 ($J_{C\text{-}F}$ = 3.0 Hz), 126.0, 125.2, 117.5, 117.4($J_{C\text{-}F}$ = 24.0 Hz), 115.7 ($J_{C\text{-}F}$ = 22.0 Hz), 112.6, 112.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.07. HRMS (positive ESI): [M + H]$^+$ Calcd. For $C_{26}H_{16}F_2N_4S^+$: 455.1137, Found: 455.1148.

*Bis(2-(imidazo[2,1-b]thiazol-6-yl)phenyl)sulfane (**5j**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:2) as an eluent (R_f = 0.25); Light yellow solid (23.0 mg, 53% yield); mp 230 – 231 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (dd, J = 7.8, 1.0 Hz, 2H), 7.97 (s, 2H), 7.37 (d, J = 4.3 Hz, 2H), 7.35 – 7.33 (m, 2H), 7.25 – 7.24 (m, 2H), 7.19 – 7.16 (m, 2H), 6.79 (d, J = 4.5 Hz, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 149.2, 144.9, 135.5, 132.6, 132.2, 130.1, 128.0, 127.6, 118.7, 112.5, 112.4. HRMS (positive ESI): [M + H]$^+$ Calcd. For $C_{22}H_{14}N_4S_3^+$: 431.0453, Found: 431.0454.

*Bis(2-(imidazo[1,2-b]quinolin-2-yl)phenyl)sulfane (**5k**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:2) as an eluent (R_f = 0.48); Brown solid (33.2 mg, 64% yield); mp 209 – 210 °C. ^{1}H NMR (600 MHz, CDCl3) δ 8.57 (s, 2H), 8.27 (d, J = 7.0 Hz, 2H), 7.74 (d, J = 7.9 Hz, 2H), 7.70 (d, J = 7.5 Hz, 2H), 7.54 (d, J = 8.9 Hz, 2H), 7.49 (t, J = 7.2 Hz, 2H), 7.44 (d, J = 9.4 Hz, 2H), 7.39 – 7.35 (m, 6H), 7.24 (d, J = 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.0, 142.1, 135.2, 133.0, 132.8, 132.6, 130.6, 128.9, 128.8, 128.3, 127.8, 126.4, 124.6, 123.3, 116.9, 115.4, 111.2. HRMS (positive ESI): [M + H]$^+$ Calcd. For $C_{34}H_{22}N_4S^+$: 519.1638, Found: 519.1643.

*Bis(2-(pyridin-2-yl)phenyl)sulfane. (**5l**).* purified by preparative TLC on silica gel with petroleum ether/EtOAc (1:1) as an eluent (R_f = 0.43); Light yellow solid (32.4 mg, 95% yield); mp 77 – 78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.57 (m, 2H), 7.54 (td, J = 7.7, 1.8 Hz, 2H), 7.45 (dd, J = 7.5, 1.7 Hz, 2H), 7.40 (d, J = 7.8 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.24 – 7.17 (m, 4H), 7.13 – 7.09 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.0, 149.0, 142.0, 135.7, 135.1, 132.9, 130.4, 129.0, 127.1, 124.1, 121.9. HRMS (positive ESI): [M + H]$^+$ Calcd. For $C_{22}H_{16}N_2S^+$: 341.1107, Found: 341.1111.

*1,3-Diphenylthiourea (**6**).* White solid (23.4 mg, 68%). ^{1}H NMR (600 MHz, DMSO) δ 9.27 (d, J = 9.3 Hz, 2H), 7.47 (d, J = 7.6 Hz, 4H), 7.27 (t, J = 7.6 Hz, 4H), 6.95 (td, J = 7.3, 0.8 Hz, 2H).^{13}C{^{1}H} NMR (101 MHz, DMSO) δ 152.5, 139.7, 128.7, 121.8, 118.2.

*3-Iodo-2-phenylimidazo[1,2-a]pyridine (**7**).* Yellow solid (10.4 mg, 16%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, J = 6.9 Hz, 1H), 8.07 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 9.0 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.26 – 7.23 (m, 1H), 6.90 (t, J = 6.9 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 148.2, 148.1, 133.6, 128.6, 128.4, 128.4, 126.5, 125.5, 117.6, 113.2, 59.5.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and spectra data for **3** and **5** (PDF)

Singly-crystal X-ray diffraction data for compounds **3a** and **5a** (CIF)

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Notes

The authors declare no competing financial interest.

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