有机化学 DOI: 10.6023/cjoc202206029 研究论文
Chinese Journal of Organic Chemistry ARTICLE

碘化钾催化无保护 8-氨基喹啉的选择性 C(5)-芳基硫醚化和 C(5),C(7)-双芳基硫醚化及吲哚 C(2),C(3)-双芳基硫醚化反应

吴豪志 罗 田 姜建文* 万结平*
(江西师范大学化学化工学院 南昌 330022)

摘要 报道了采用 2.5 mol%碘化钾为唯一催化剂, 无需任何过渡金属催条件下无保护 8-氨基喹啉的碳-氢甲芳基硫醚化反应. 有趣的是, 通过简单调控反应时间和介质可以实现选择性的 C(5)-芳基硫醚化和 C(5),C(7)-双芳基硫醚化. 在对二甲苯中反应 12 h 时为 C(5)-芳基硫醚化. 另一方面, 延长反应时间至 24 h 并更换反应介质为甲苯则选择性地发生 C(5),C(7)-双芳基硫醚化. 此外, 双芳基硫醚化反应可以扩展到吲哚类底物, 实现含 2,3-二芳基硫醚结构的吲哚合成.
关键词 碳-氢键官能化; 自由基; 8-氨基喹啉; 选择性; 芳基硫醚化

KI-Catalyzed Selective C(5)-Sulfenylation and C(5),C(7)-Disulfenylation of Unprotected 8-Aminoquinolines and the Indole C(2),C(3)-Disulfenylation

Wu, Haozhi Luo, Tian Jiang, Jianwen* Wan, Jieping*
(*College of Chemistry and Chemical Engineering*, *Jiangxi Normal University*, *Nanchang*, *330022*)

Abstract The aromatic C—H sulfenylation reactions of unprotected 8-aminoquinolines have been realized by employing KI as the only catalyst at 2.5 mol% loading without using any transition metal reagent. Interestingly, the selective C(5)-sulfenylation and C(5),C(7)-disulfenylation have been successfully achieved by simply controlling the reaction time. Reaction time of 12 h in *p*-xylene enables the C(5)-sulfenylation. On the other hand, prolonging the reaction time to 24 h and switching the reaction medium to toluene lead to the selective C(5),C(7)-double sulfenylation. Moreover, the double sulfenylation has been extended to the indole substrate for the selective synthesis of 2,3-disulfenyl indoles.
Keywords C—H functionalization; free radical; 8-aminoquinoline; selectivity; sulfenylation

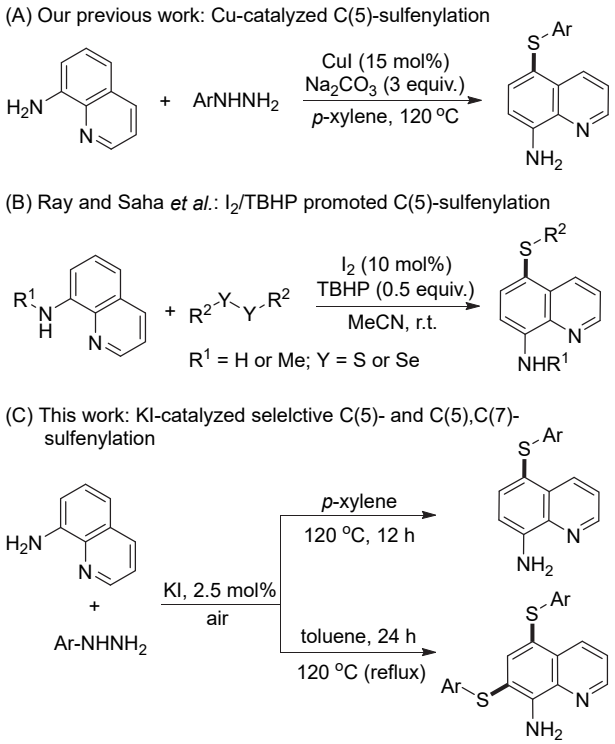
1 Introduction

Arene C—H bond activation or functionalization has evolved to unprecedentedly high level of application in academic research and industrial application.[1] Particularly, the catalytic processes for C—H bond functionalization without using precious or transition metal reagent have received tremendous attention and advances in recent years because of their incomparable advantages in: (i) atom economy associated with simple non-transition metal catalyst; (ii) free of trace heavy metal contamination in the synthesized products; (iii) broad application in the transformation of divergent stable C—H bonds.[2] As the prevalent and featured chemical structure in numerous functional molecules, the C—S bond has received particularly notable advances in the recent decade. A large variety of transition metal-free methods for the construction of new C—S bonds on the aryl-,[3] alkenyl-,[4] alkyl-[5] C—H bonds have been successfully realized.

On the other hand, the remote C(5)—H activation or functionalization on 8-aminoquinolines has been proved to be a highly useful tool for the generation of diversely functionalized quinoline derivatives.[6] The formation of new C—C,[7] C—halogen,[8] C—N,[9] C—O[10] and C—S[11] bonds by such transformation has been reported. Notably, the remote C(5)—H activation or functionalization forming new C—S bond occurs mainly in the form of sulfonation. The equivalent sulfenylation reactions, on the contrary, are much less available. In 2018, our group[12] reported the first example on the C(5)—H sulfenylation of unprotected

* Corresponding authors. E-mail: wanjieping@jxnu.edu.cn; jjw999@163.com
Received June 18, 2022; revised July 13, 2022; published online August 10, 2022.
Project supported by the National Natural Science Foundation of China (No. 22161022).
国家自然科学基金(No. 22161022)资助项目.

8-aminoquinolines by means of copper catalysis (Scheme 1A). Later, Ray and Saha *et al.*[13] reported the C(5)-sulfenylation/selenylation of unprotected 8-amino-quinolines via the catalysis of iodine in the presence of peroxide (TBHP) by employing disulfides/diselenides as reaction partners (Scheme 1B). However, the employment of transition metal catalyst or sensitive peroxide remains challenges for such reactions. In continuous to our sustaining interest in developing transition metal-free methods for the functionalization of C—H bonds,[14] we report herein another transition metal-free protocol for the sulfonyl hydrazine-based C(5)—H sulfenylation of unprotected 8-amino-quinolines with simple KI as catalyst at low loading. Moreover, the selective C(5),C(7)-disulfenylation could be achieved by modifying reaction medium and time (Scheme 1C). Under identical conditions, the 2,3-disulfenylation of indoles has also been efficiently reached with this sustainable catalytic method.

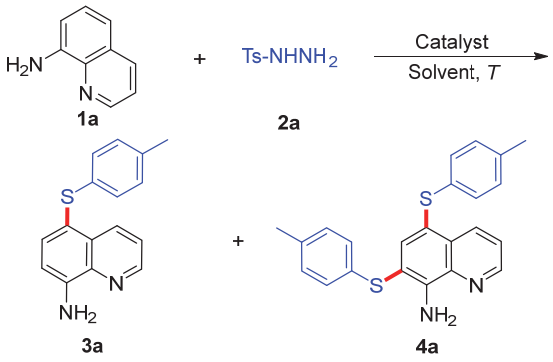


Scheme 1 Different methods for the C—H sulfenylation of 8-aminoquinolines

2 Results and discussion

Initially, the reaction between 8-aminoquinoline (**1a**) and tosyl hydrazine (**2a**) was run by utilizing different iodo-reagents, such as KI, tetrabutylammonium iodide (TBAI), I_2, *N*-iodo-succininide (NIS) or NaI as catalyst at 2.5 mmol% loading, and KI was found to be the most efficient catalyst for the synthesis of **3a** (Entries 1～5, Table 1). Increasing or reducing the KI loading did not give improved result (Entries 6, 7, Table 1). Varying reaction temperature was not favored, either (Entries 8, 9, Table 1). When the solvent was independently switched to toluene, *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), inferior yield of **3a** was observed (Entries 10～12, Table 1). However, the 5,7-disulfenylated product **4a** was provided with 47% yield in the entry using toluene as medium (Entry 10, Table 1). Modifying the concentration of the reaction system could increase the yield of **3a** to 60% by employing 3 mL of *p*-xylene (Entries 13～15, Table 1). Delightfully, the selective synthesis of disulfenylated product **4a** was realized with excellent yield of 84% by modifying the volume of toluene medium as well as prolonging the reaction time (Entries 16～19, Table 1), indicating the clear dynamic-dependent selectivity. A control experiment under argon in toluene provided no product **3a** or **4a**, proving the pivotal role of air to the sulfenylation

Table 1 Optimization study for the selective synthesis of **3a** and **4a**[a]



Entry	Catalyst	Solvent	Temp./℃	Yield[b]/%	
				3a	**4a**
1	KI	*p*-Xylene	120	36	0
2	TBAI	*p*-Xylene	120	36	0
3	I_2	*p*-Xylene	120	27	0
4	NIS	*p*-Xylene	120	33	0
5	NaI	*p*-Xylene	120	26	Trace
6[c]	KI	*p*-Xylene	120	32	0
7[d]	KI	*p*-Xylene	120	34	0
8	KI	*p*-Xylene	110	26	0
9	KI	*p*-Xylene	130	35	0
10	KI	Toluene	120	30	43
11	KI	DMF	120	25	0
12	KI	DMSO	120	0	0
13[e]	KI	*p*-Xylene	120	32	0
14[f]	KI	*p*-Xylene	120	60	Trace
15[g]	KI	*p*-Xylene	120	52	0
16[h]	KI	Toluene	120	Trace	57
17[h]	KI	Toluene	110	21	43
18[h,i]	KI	Toluene	120	Trace	74
19[h,j]	KI	Toluene	120	Trace	84
20[k]	KI	Toluene	120	0	0
21	—	Toluene	120	0	0

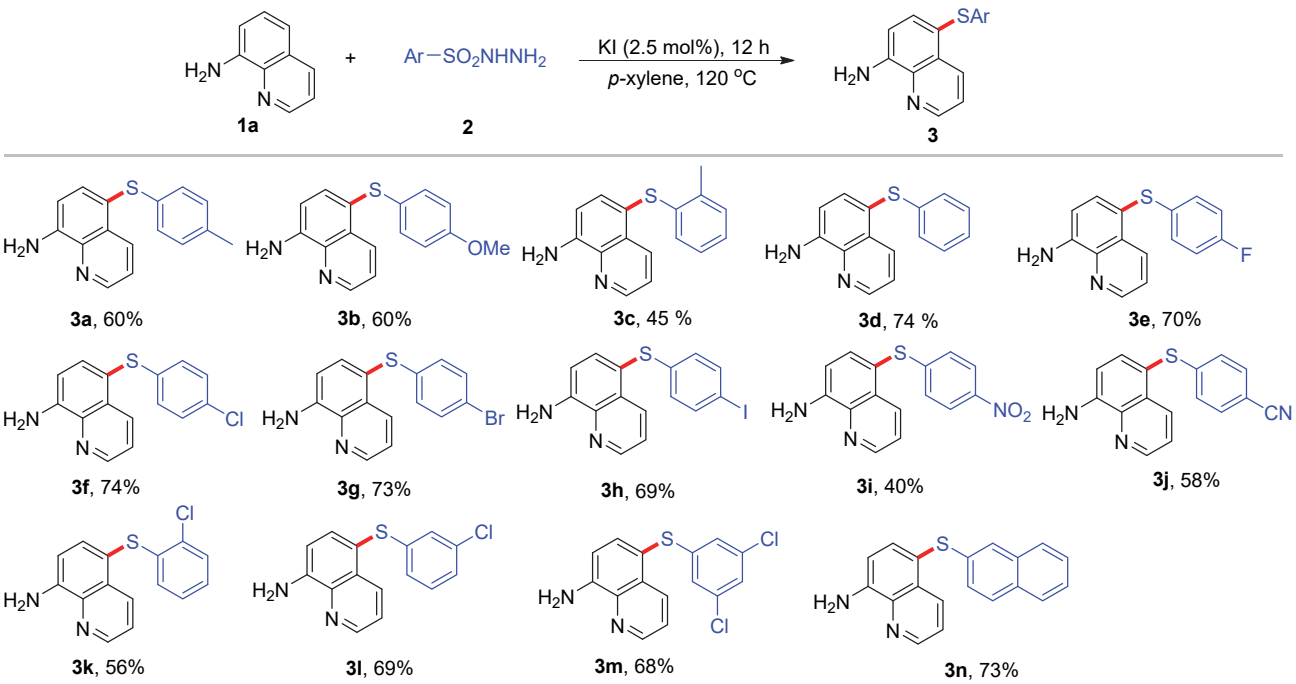
[a] Reaction condition: **1a** (0.5 mmol), **2a** (1 mmol), catalyst (0.0125 mmol), solvent (2.0 mL), stirred for 12 h under air atmosphere. The temperatures in the table were the outlet temperature set in the machine. [b] Isolated yield based on **1a**. [c] KI (0.010 mmol). [d] KI (0.025 mmol). [e] With 1.0 mL of *p*-xylene. [f] With 3.0 mL of *p*-xylene. [g] With 4.0 mL of *p*-xylene. [h] Stirred for 24 h. [i] With 0.3 mL of *p*-xylene. [j] With 0.5 mL of *p*-xylene.

reaction (Entry 20, Table 1). No product was formed in the absence of KI, either (Entry 21, Table 1).

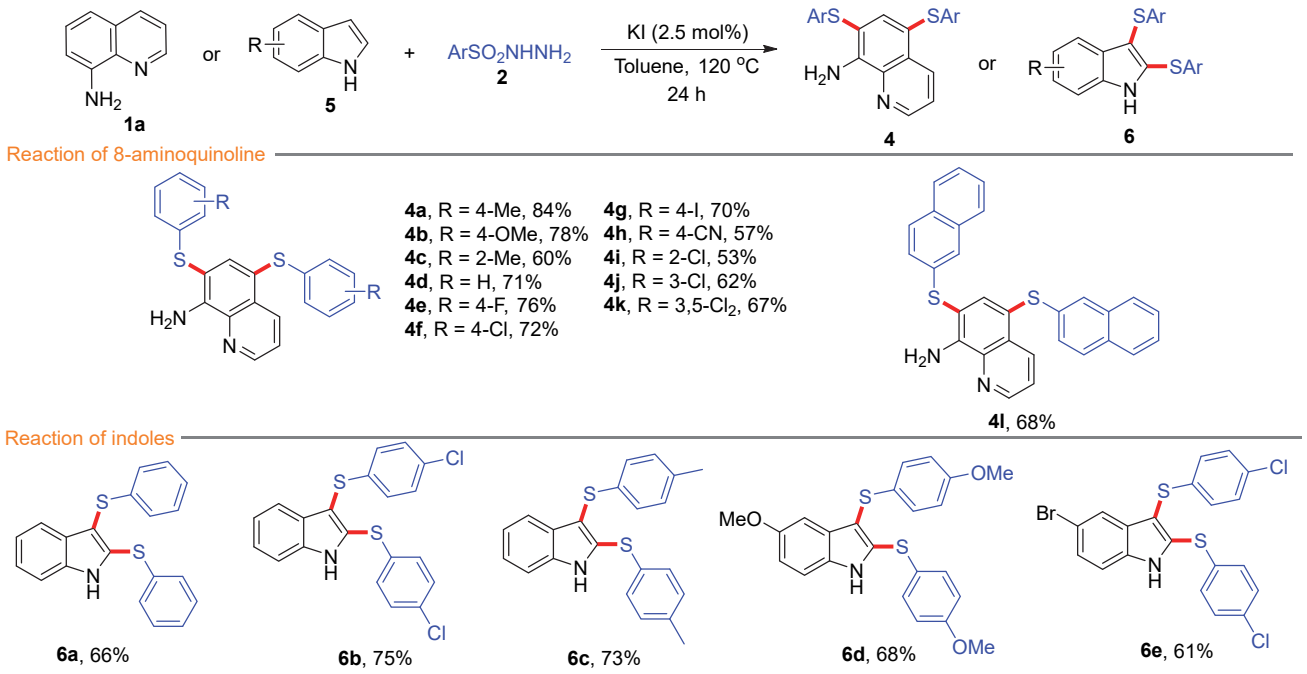
Following the works on optimization, the scope of the C(5)-sulfenylation reaction providing products **3** was investigated. The results employing different sulfonyl hydrazines were outlined in Scheme 2. The results indicated the satisfactory tolerance of sulfonyl hydrazines to the synthesis of 5-sulfenylated 8-aminoquinolines **3**. In the reactions using phenylsulfonyl hydrazines with *para*-substitution, the weak electron withdrawing group (EWG) functionalized sulfonyl hydrazines gave higher product yields than those reactions using electron donating group (EDG) functionalized phenyl sulfonyl hydrazines (**3a**～**3b** vs. **3e**～**3h**, Scheme 2). However, strong EWG such as nitro and cyano groups in the phenyl ring led to the corresponding products with even lower yield (**3i**～**3j**, Scheme 2), suggesting that the electronic effect of the aryl sulfonyl hydrazines was complex toward the single C—H sulfenylation reactions. More notably, the *ortho*- and *meta*-substituted phenyl sulfonyl hydrazines (**3k** and **3l**, Scheme 2) and disubstituted phenyl sulfonyl hydrazine (**3m**, Scheme 2) could also be practically used for the C(5)-sufenylation. As expected, fused aryl such as naphthyl functionalized sulfonyl hydrazine was also good substrate for the reaction (**3n**, Scheme 2). On the other hand, running the reaction of **1a** with methyl sulfonyl hydrazine under the current conditions didn't provide the expected 5-methylthioquinoline product. The reaction using simple quinoline without the 8-amino group to react with sulfonyl hydrazine **2a** could not provide the sulfenylated product, either.

Subsequently, the selective C(5),C(7)-disulfenylation on the 8-aminoquinolines was examined. As observed in the optimization study, prolonging the reaction time to 24 h in toluene was found to be broadly applicable for such disulfenylation reaction with various sulfonyl hydrazines (Scheme 3). Phenyl sulfonyl hydrazines, including those ones functionalized by both EDG and EWG, as well as naphthyl sulfonyl hydrazine were employed for the synthesis of disulfenyl 8-aminoquinolines **4** with moderate to excellent yields (**4a**～**4l**, Scheme 3). Besides the strong EWG substituted phenyl sulfonyl hydrazine (**4h**, Scheme 3), the EWG substituted phenyl sulfonyl hydrazines gave products with higher yield (**4a**～**4b**, **4e**～**4g** vs. **4i**～**4j**, Scheme 3). Interestingly, when indoles **5** were employed to react with hydrazines **2** under the standard reaction conditions, the selective disulfenylation at the C(2),C(3)-sites took place to afford disulfenyl indoles **6** with good results. Th reactions using unsubstituted phenyl sulfonyl hydrazine and indole (**6a**, Scheme 3), substituted phenyl sulfonyl hydrazines (**6b**～**6c**, Scheme 3), as well as substituted indoles (**6d**～**6e**, Scheme 3) were all well tolerated for the titled disulfenylation, disclosing expanded synthetic scope of this method to access diverse sulfenylated compounds.

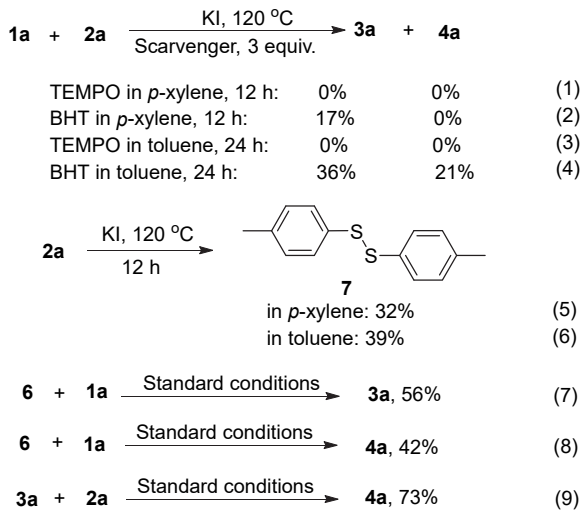
To gain information on reaction mechanism, a series of control experiments were run (Scheme 4). First, under corresponding standard reaction conditions for the single and double sulfenylation reactions, free radical scavenger such as 2,2,6,6-tetramethylpiperidinooxy (TEMPO) and 2,6-di-*t*-butyl-*p*-cresol (butylated hydroxytoluene) (BHT) were employed, respectively. The results showed that both TEMPO and BHT could evidently inhibit the single and double sulfenylation reactions (Eqs. 1～4), indicating the free radical reaction pathways in the reactions. The GC-MS analysis on the mixtures from the reactions in the presence of TEMPO or BHT didn't show the formation of



Scheme 2 Scope of the selective C(5)-sulfenylation



Scheme 3 Scope of the selective C(5),C(7)-disulfenylation of 8-aminoquinoline and C(2),C(3)-disulfenylation of indoles



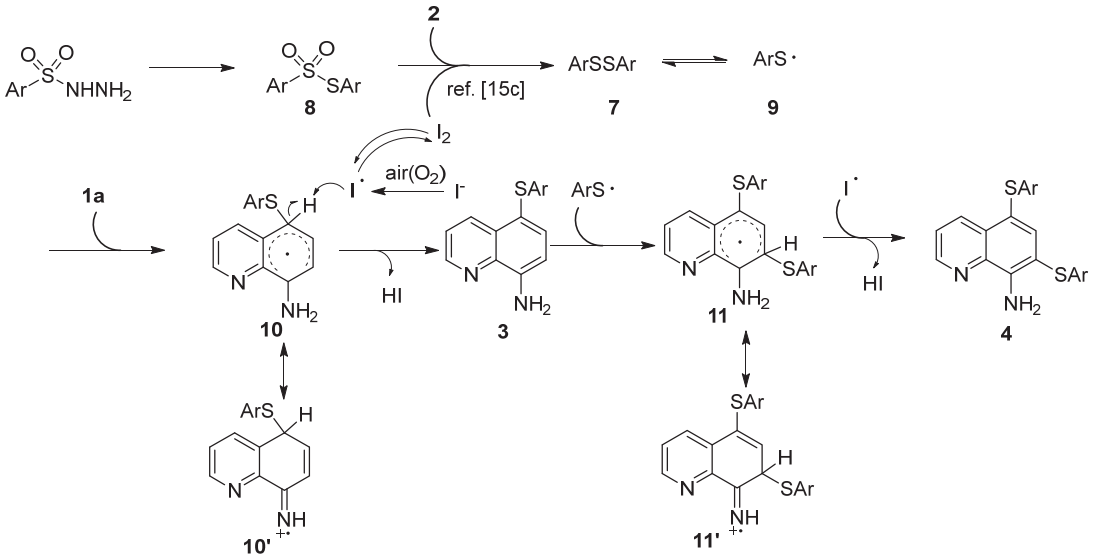
Scheme 4 Control experiments for mechanism study

the adduct resulting from sulfonyl free radical and scavenger, implying that the sulfenyl free radical might have been quickly captured by the quinoline substrate soon after its formation. In addition, subjecting sulfonyl hydrazine **2a** to both type of standard reaction conditions led to the formation of disulfide **7** with moderate yields (Eqs. 5, 6). Moreover, reacting **7** with 8-aminoquinoline **1a** could provide both C(5)-sulfenylated and C(5),C(7)-disulfenylated product with fine yields (Eqs. 7, 8), suggesting that disulfide might be a key intermediate for the titled reactions. Finally, employing C(5)-sulfenylated 8-aminoquinoline **3a** to react with sulfonyl hydrazine **2a** afforded disulfenylated product **4a** with high yield under the standard conditions for disulfenylation (Eq. 9), suggesting that the reaction sequence was C(5)-sulfenylation and C(7)-sulfenylation.

Based on the results from control experiments and related literatures on the C(5)—H functionalization of 8-aminoquinolines, a plausible reaction mechanism is proposed. As outlined in Scheme 5, the sulfonyl hydrazine may first undergo the homo-reductive coupling[15] to provide thiosulfonate **8**. The further reduction of **8** in the presence of iodine resulting from iodide oxidation leads to the generation of disulfide **7**.[15c] The homo-cleavage of the S—S bond in **7** affords sulfur free radical **9**. The fast addition of the sulfur free radical to the quinoline **1** in the C(5)-site takes place and produces free radical species **10**/**10'**. Meanwhile, the aerobic oxidation of the iodine anion provides iodine free radical which may capture the H atom in the fashion of free radical coupling to provide product **3** and HI. The HI would continue to catalyze the reaction by donating iodine anion. When the reaction time is prolonged, the further addition of sulfur free radical to the C(7) site of **3** occurs and yields free radical species **11**/**11'**. The analogous free radical coupling by releasing HI enables the selective synthesis of disulfenylated products **4**.

3 Conclusions

In conclusion, we have developed the transition metal-free C—H sulfenylation protocols of unprotected 8-aminoquinolines. The reactions are run in the presence of simple KI salt with low loading, and can selectively provide C(5)-sufenylated 8-aminoquinolines and C(5),C(7)-disulfenylated 8-aminoquinlines with generally good yields and substrate tolerance. Control experiments proves that the reactions proceed via free radical pathways. The transition metal-free, low cost KI catalyst as we ll as the simple operation associated with the present methods make them



Scheme 5 Proposed reaction mechanism

attractive in the synthesis of diverse sulfenyl quinolines and indoles.

4 Experimental section

4.1 General experimental information

All experiments were carried out under air atmosphere. All chemicals and solvents used in the experiments were obtained from commercial sources and used directly without further treatment. The ^{1}H NMR and ^{13}C NMR were recorded on a Brucker AVANCE 400 spectrometer by using $CDCl_3$ or DMSO-d_6 as solvent. The frequency for ^{1}H NMR and ^{13}C NMR test were 400 and 100 MHz, respectively. The chemical shifts were reported using tetramethylsilane (TMS) as internal standard. The high resolution mass spectrometry (HRMS) results were recorded under ESI model in a TripleTOF6600 mass spectrometer equipped with time of flight (TOF) analyzer.

4.2 General procedure for the synthesis of 3

To a 25 mL round-bottom flask equipped with condenser were added 8-aminoquinoline **1a** (0.5 mmol), sulfonyl hydrazine **2** (1.0 mmol), KI (0.0125 mmol), and *p*-xylene (3.0 mL). Then the resulting mixture was heated up to 120 ℃, and stirred at the same temperature for 12 h (thin-layer chromatography, TLC). After cooling down to room temperature, 5 mL of water was added, and the resulting mixture was extracted with ethyl acetate (8 mL×3). The organic phases were collected and washed with small amount of water for three times. After drying with anhydrous Na_2SO_4, the solid was filtered. The solvent was then removed under reduced pressure from the solution, and the resulting residue was subjected to flash silica gel column chromatography to provide pure products with the elution of mixed petroleum ether/dichloromethane (V∶V=2∶1).

5-(*p*-Tolylthio)quinolin-8-amine (**3a**):[12] 80.0 mg, 60% yield. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.76～8.72 (m, 1H), 8.60 (d, J=8.5 Hz, 1H), 7.71 (d, J=8.0 Hz, 1H), 7.40～7.36 (m, 1H), 6.96～6.88 (m, 5H), 5.15 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.4, 145.9, 138.9, 137.3, 135.8, 134.9, 134.8, 130.6, 129.6, 126.6, 122.3, 115.1, 109.5, 20.8.

5-((4-Methoxyphenyl)thio)quinolin-8-amine (**3b**):[12] 85.2 mg, 60% yield. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.65 (d, J=4.1 Hz, 1H), 8.54 (d, J=8.5 Hz, 1H), 7.58 (d, J=7.9 Hz, 1H), 7.31～7.27 (m, 1H), 6.95 (d, J=8.8 Hz, 2H), 6.78 (d, J=7.9 Hz, 1H), 6.63 (d, J=8.7 Hz, 2H), 4.67 (s, 2H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.0, 147.4, 145.6, 138.9, 136.5, 134.7, 130.3, 129.6, 129.1, 122.2, 116.4, 114.7, 109.5, 55.3.

5-(*o*-Tolylthio)quinolin-8-amine (**3c**):[12] 60.3 mg, 45% yield. Red soild, m.p. 83～84 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78～8.74 (m, 1H), 8.54～8.48 (m, 1H), 7.67 (d, J=7.9 Hz, 1H), 7.39～7.35 (m, 1H), 7.14 (d, J=7.4 Hz, 1H), 6.96 (t, J=7.4 Hz, 1H), 6.92 (d, J=7.9 Hz, 1H), 6.85 (t, J=7.6 Hz, 1H), 6.45 (d, J=7.8 Hz, 1H), 5.21 (s, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.5, 146.0, 138.9, 138.5, 137.5, 134.8, 134.6, 130.7, 129.9, 126.4, 125.7, 124.7, 122.4, 114.0, 109.7, 20.0.

5-(Phenylthio)quinolin-8-amine (**3d**):[12] 93.5 mg, 74% yield. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78～8.74 (m, 1H), 8.59 (d, J=8.5 Hz, 1H), 7.73 (d, J=7.9 Hz, 1H), 7.43～7.35 (m, 2H), 7.13 (t, J=7.6 Hz, 2H), 7.03 (t, J=7.3 Hz, 1H), 6.97 (d, J=8.0 Hz, 2H), 6.91 (d, J=7.9 Hz, 1H), 5.24 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.4, 146.1, 139.6, 138.8, 137.7, 134.9, 130.7, 128.8, 126.1, 124.9, 122.4, 114.14, 109.5.

5-((4-Fluorophenyl)thio)quinolin-8-amine (**3e**):[12] 95.0 mg, 70% yield. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78～8.72 (m, 1H), 8.59～8.53 (m, 1H), 7.72 (s, 1H), 7.42～7.37 (m, 1H), 7.01～6.93 (m, 2H), 6.91～6.82 (m, 3H), 5.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.0 (d, $^1J_{CF}$=243 Hz), 147.5, 146.2, 138.9, 137.4, 134.6, 134.4 (d, $^3J_{CF}$=4.0 Hz), 130.4, 128.1 (d, $^3J_{CF}$=7.0 Hz), 122.5, 115.9 (d, $^2J_{CF}$=22.0 Hz), 114.6, 109.4.

5-((4-Chlorophenyl)thio)quinolin-8-amine (**3f**):[12] 106.6 mg, 74% yield. Yellow solid, m.p. 124～125 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79～8.73 (m, 1H), 8.52 (d, J=8.5 Hz, 1H), 7.71 (d, J=7.9 Hz, 1H), 7.41～7.36 (m, 1H), 7.09 (d, J=8.5 Hz, 2H), 6.92～6.85 (m, 3H), 5.30 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6, 146.4, 138.9, 138.2, 137.8, 134.5, 130.7, 130.5, 128.9, 127.3, 122.6, 113.5, 109.4.

5-((4-Bromophenyl)thio)quinolin-8-amine (**3g**):[12] 120 mg, 73% yield. Yellow solid, m.p. 127～128 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.75 (d, J=3.1 Hz, 1H), 8.50 (d, J=8.5 Hz, 1H), 7.70 (d, J=7.9 Hz, 1H), 7.41～7.35 (m, 1H), 7.22 (d, J=8.3 Hz, 2H), 6.89 (d, J=7.9 Hz, 1H), 6.81 (d, J=8.3 Hz, 2H), 5.30 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6, 146.5, 139.0, 137.8, 134.4, 131.8, 130.5, 127.5, 122.6, 118.5, 113.3, 109.4.

5-((4-Iodophenyl)thio)quinolin-8-amine (**3h**): 119.9 mg, 69% yield. Yellow solid, m.p. 187～188 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.77～8.73 (m, 1H), 8.51～8.47 (m, 1H), 7.69 (d, J=7.9 Hz, 1H), 7.41～7.35 (m, 3H), 6.88 (d, J=7.9 Hz, 1H), 6.68 (d, J=8.4 Hz, 2H), 5.31 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6, 146.5, 140.0, 139.0, 137.9, 137.7, 134.4, 130.5, 127.8, 122.6, 113.0, 109.4, 89.2; HRMS (ESI) calcd for $C_{15}H_{12}IN_2S$ 378.9760 $[M+H]^+$, found 378.9776.

5-((4-Nitrophenyl)thio)quinolin-8-amine (**3i**):[12] 59.2 mg, 40% yield. Red solid, m.p. 88～89 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.82～8.77 (m, 1H), 8.47～8.41 (m, 1H), 7.97 (d, J=9.0 Hz, 2H), 7.73 (d, J=7.9 Hz, 1H), 7.45～7.40 (m, 1H), 7.02～6.90 (m, 3H), 5.44 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.0, 147.7, 147.1, 144.9, 138.7, 138.4, 134.2, 130.5, 125.1, 124.0, 122.9, 110.7, 109.5.

4-((8-Aminoquinolin-5-yl)thio)benzonitrile (**3j**):[12] 80.2 mg, 58% yield. Red solid, m.p. 178～179 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.81～8.78 (m, 1H), 8.48～8.44 (m, 1H), 7.73 (d, J=7.9 Hz, 1H), 7.45～7.41 (m, 1H), 7.38 (d, J=8.5 Hz, 2H), 6.98～6.93 (m, 3H), 5.37 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6, 147.3, 146.9, 138.6, 138.4, 134.4, 132.3, 130.6, 125.5, 122.8, 118.9, 110.9, 109.5, 107.9.

5-((2-Chlorophenyl)thio)quinolin-8-amine (**3k**):[12] 80.5 mg, 56% yield. Red solid, m.p. 128～129 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78～8.73 (m, 1H), 8.51～8.46 (m, 1H), 7.72 (d, J=7.9 Hz, 1H), 7.38～7.34 (m, 1H), 7.34～7.29 (m, 1H), 6.97～6.89 (m, 2H), 6.87～6.81 (m, 1H), 6.37～6.31 (m, 1H), 5.29 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.7, 146.7, 139.00, 138.9, 138.3, 134.5, 130.8, 130.2, 129.4, 127.0, 126.5, 125.5, 122.7, 112.2, 109.6.

5-((3-Chlorophenyl)thio)quinolin-8-amine (**3l**): 99.0 mg, 69% yield. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.80～8.75 (m, 1H), 8.57～8.51 (m, 1H), 7.73 (d, J=7.9 Hz, 1H), 7.44～7.39 (m, 1H), 7.07～6.99 (m, 2H), 6.96～6.89 (m, 2H), 6.83 (d, J=7.6 Hz, 1H), 5.35 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.5, 146.5, 141.9, 138.8, 138.1, 134.8, 134.6, 130.6, 129.8, 125.5, 125.1, 123.9, 122.6, 112.8, 109.5; HRMS (ESI) calcd for $C_{15}H_{12}ClN_2S$ 287.0404 $[M+H]^+$, found 287.0424.

5-((3,5-Dichlorophenyl)thio)quinolin-8-amine (**3m**): 109.3 mg, 68% yield. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.80～8.75 (m, 1H), 8.51～8.45 (m, 1H), 7.71 (d, J=7.9 Hz, 1H), 7.44～7.40 (m, 1H), 7.01 (s, 1H), 6.91 (d, J=7.9 Hz, 1H), 6.79 (d, J=1.5 Hz, 2H), 5.37 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.7, 146.9, 143.8, 138.9, 138.4, 135.3, 134.2, 130.5, 125.0, 123.6, 122.8, 111.5, 109.4; HRMS (ESI) calcd for $C_{15}H_{11}Cl_2N_2S$ 321.0015 $[M+H]^+$, found 321.0028.

5-(Naphthalen-1-ylthio)quinolin-8-amine (**3n**):[12] 110.4 mg, 73% yield. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.73～8.68 (m, 1H), 8.60～8.54 (m, 1H), 7.75 (d, J=7.9 Hz, 1H), 7.68～7.63 (m, 1H), 7.60 (s, 1H), 7.51～7.45 (m, 1H), 7.34～7.27 (m, 4H), 7.19～7.13 (m, 1H), 6.87 (d, J=7.9 Hz, 1H), 5.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6, 146.3, 139.0, 137.7, 137.2, 134.7, 133.8, 131.4, 130.7, 128.5, 127.7, 126.9, 126.5, 125.3, 124.9, 123.8, 122.5, 114.0, 109.6.

4.2 General procedure for the synthesis of **4** and **6**

To a round-bottom 25 mL flask equipped with condenser were added 8-aminoquinoline **1a** or indole **5** (0.5 mmol), sulfonyl hydrazine **2** (1.0 mmol), KI (0.0125 mmol), and toluene (0.5 mL). Then the resulting mixture was heated at 120 ℃ (reflux) and stirred at the same temperature for 12 h (TLC). After cooling down to room temperature, 5 mL of ethyl acetate was added. The solvent was then removed under reduced pressure from the solution, and the resulting residue was subjected to flash silica gel column chromatography to provide pure products with the elution of mixed petroleum ether/ethyl acetate (V∶V=100∶1).

5,7-Bis(*p*-tolylthio)quinolin-8-amine (**4a**):[16] 163.3 mg, 84% yield. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.70～8.67 (m, 1H), 8.57～8.53 (m, 1H), 7.94 (s, 1H), 7.35～7.31 (m, 1H), 7.06 (d, J=8.3 Hz, 2H), 7.00 (d, J=8.1 Hz, 2H), 6.92 (s, 4H), 5.96 (s, 2H), 2.24 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.8, 147.9, 143.4, 138.8, 135.9, 135.4, 135.1, 134.9, 132.5, 130.8, 130.0, 129.8, 127.6, 127.6, 126.9, 126.84, 123.0, 114.7, 109.6, 21.1, 21.0.

5,7-Bis((4-methoxyphenyl)thio)quinolin-8-amine (**4b**): 164.0 mg, 78% yield. White solid, m.p. 122～123 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.74～8.70 (m, 1H), 8.61～8.57 (m, 1H), 7.85 (s, 1H), 7.41～7.37 (m, 1H), 7.18 (d, J=8.8 Hz, 2H), 7.04 (d, J=8.8 Hz, 2H), 6.78 (d, J=8.8 Hz, 2H), 6.71 (d, J=8.8 Hz, 2H), 5.91 (s, 2H), 3.74 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.7, 158.1, 147.7, 147.6, 141.8, 138.7, 134.7, 130.3, 130.2, 129.4, 128.9, 126.2, 122.7, 116.1, 114.9, 114.7, 111.3, 55.4; HRMS (ESI) calcd for $C_{23}H_{21}N_2O_2S_2$ 421.1039 $[M+H]^+$, found 421.1052.

5,7-Bis(*o*-tolylthio)quinolin-8-amine (**4c**): 116.1 mg, 60% yield. Yellow solid, m.p. 106～107 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.68 (d, J=3.8 Hz, 1H), 8.43 (d, J=8.5 Hz, 1H), 7.75 (s, 1H), 7.35～7.31 (m, 1H), 7.09～7.03 (m, 2H), 6.97 (t, J=7.3 Hz, 1H), 6.93～6.86 (m, 2H), 6.81～6.73 (m, 2H), 6.44 (d, J=7.9 Hz, 1H), 5.89 (s, 2H), 2.37 (s,

3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.8, 147.9, 143.5, 138.7, 138.0, 135.9, 134.9, 134.8, 130.9, 130.5, 130.1, 126.7, 126.4, 126.3, 126.0, 125.8, 125.0, 123.0, 113.9, 108.8, 100.0, 20.2, 20.1; HRMS (ESI) calcd for $C_{23}H_{21}N_2S_2$ 389.1141 $[M+H]^+$, found 389.1156.

5,7-Bis(phenylthio)quinolin-8-amine (**4d**): 128.2 mg, 71% yield. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.73～8.70 (m, 1H), 8.57～8.53 (m, 1H), 7.97 (s, 1H), 7.38-7.35 (m, 1H), 7.18 (d, J=7.3 Hz, 2H), 7.15～7.08 (m, 5H), 7.04～6.98 (m, 3H), 6.01 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 147.9, 144.1, 139.1, 138.8, 136.1, 134.9, 131.1, 129.2, 129.0, 126.9, 126.3, 125.8, 125.2, 123.2, 113.9, 108.6; HRMS (ESI) calcd for $C_{21}H_{17}N_2S_2$ 361.0828 $[M+H]^+$, found 361.0845.

5,7-Bis((4-fluorophenyl)thio)quinolin-8-amine (**4e**): 151.0 mg, 76% yield. Yellow solid, m.p. 112～113 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79～8.75 (m, 1H), 8.59～8.54 (m, 1H), 7.91 (s, 1H), 7.48～7.43 (m, 1H), 7.18～7.12 (m, 2H), 7.03～6.98 (m, 2H), 6.94 (t, J=8.6 Hz, 2H), 6.87 (t, J=8.6 Hz, 2H), 6.02 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, $^1J_{CF}$=245.0 Hz), 161.1 (d, $^1J_{CF}$=244 Hz), 148.8, 147.9, 143.2, 138.6, 134.8, 133.7 (d, $^3J_{CF}$=4.0 Hz), 130.9 (d, $^3J_{CF}$=2 Hz), 130.7, 129.3 (d, $^3J_{CF}$=8 Hz), 128.6 (d, $^3J_{CF}$=7.0 Hz), 123.2, 116.2 (d, $^2J_{CF}$=22.0 Hz), 116.0 (d, $^2J_{CF}$=22.0 Hz), 114.7, 109.4; HRMS (ESI) calcd for $C_{21}H_{15}F_2N_2S_2$ 397.0639 $[M+H]^+$, found 397.0651.

5,7-Bis((4-chlorophenyl)thio)quinolin-8-amine (**4f**): 154.2 mg, 72% yield. Yellow solid, m.p. 122～123 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.60 (d, J=3.7 Hz, 1H), 8.37 (d, J=8.5 Hz, 1H), 7.80 (s, 1H), 7.29～7.25 (m, 1H), 7.02 (d, J=8.5 Hz, 2H), 6.98～6.90 (m, 4H), 6.78 (d, J=8.4 Hz, 2H), 5.92 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 148.1, 143.9, 138.8, 137.6, 134.6, 131.8, 131.1, 130.9, 129.3, 129.1, 128.1, 127.6, 123.4, 113.6, 108.0; HRMS (ESI) calcd for $C_{21}H_{15}Cl_2N_2S_2$ 429.0048 $[M+H]^+$, found 429.0059.

5,7-Bis((4-iodophenyl)thio)quinolin-8-amine (**4g**): 214.0 mg, 70% yield. Yellow solid, m.p. 167～168 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.80～8.77 (m, 1H), 8.51 (d, J=8.4 Hz, 1H), 7.92 (s, 1H), 7.52 (d, J=8.4 Hz, 2H), 7.48～7.43 (m, 3H), 6.86 (d, J=8.4 Hz, 2H), 6.72 (d, J=8.4 Hz, 2H), 6.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 148.1, 144.0, 139.2, 138.6, 138.1, 137.8, 136.2, 134.7, 130.9, 128.5, 128.0, 123.5, 113.2, 90.4, 89.6; HRMS (ESI) calcd for $C_{21}H_{15}I_2N_2S_2$ 612.8761 $[M+H]^+$, found 612.8746.

4,4'-((8-Aminoquinoline-5,7-diyl)bis(sulfanediyl))dibenzonitrile (**4h**): 116.8 mg, 57% yield. Yellow solid, m.p. 187～188 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.86～8.81 (m, 1H), 8.46 (d, J=8.4 Hz, 1H), 7.94 (s, 1H), 7.54～7.47 (m, 3H), 7.41 (d, J=8.2 Hz, 2H), 7.15 (d, J=8.2 Hz, 2H), 7.01 (d, J=8.2 Hz, 2H), 6.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.6, 148.5, 146.4, 144.5, 143.2, 138.6, 134.5, 132.6, 132.4, 131.2, 126.0, 125.7, 124.1, 118.7, 118.6, 111.5, 109.0, 108.4, 105.4; HRMS (ESI) calcd for $C_{23}H_{15}N_4S_2$ 411.0733 $[M+H]^+$, found 411.0742.

5,7-Bis((2-chlorophenyl)thio)quinolin-8-amine (**4i**): 113.6 mg, 53% yield. Yellow solid, m.p. 120～121 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.82～8.77 (m, 1H), 8.52 (d, J=8.5 Hz, 1H), 7.96 (s, 1H), 7.50～7.46 (m, 1H), 7.39～7.32 (m, 2H), 7.10～7.03 (m, 2H), 7.00 (t, J=7.8 Hz, 1H), 6.92 (t, J=7.6 Hz, 1H), 6.77～6.72 (m, 1H), 6.45 (d, J=7.9 Hz, 1H), 6.10 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.2, 148.2, 144.8, 138.8, 138.3, 135.1, 134.7, 131.6, 131.3, 130.5, 129.8, 129.5, 127.3, 127.0, 126.7, 126.7, 126.6, 125.8, 123.6, 112.5, 106.7; HRMS (ESI) calcd for $C_{21}H_{15}Cl_2N_2S_2$ 429.0048 $[M+H]^+$, found 429.0056.

5,7-Bis((3-chlorophenyl)thio)quinolin-8-amine (**4j**): 132.6 mg, 62% yield. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.81～8.77 (m, 1H), 8.57～8.53 (m, 1H), 7.95 (s, 1H), 7.50～7.45 (m, 1H), 7.17～7.12 (m, 1H), 7.11～7.05 (m, 3H), 7.04～6.98 (m, 2H), 6.96 (t, J=1.7 Hz, 1H), 6.88～6.84 (m, 1H), 6.10 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.8, 148.1, 144.5, 141.3, 138.6, 138.3, 135.1, 134.9, 134.7, 131.1, 130.2, 129.9, 126.2, 126.0, 125.8, 125.4, 124.6, 124.2, 123.6, 112.9, 107.3; HRMS (ESI) calcd for $C_{21}H_{15}Cl_2N_2S_2$ 429.0048 $[M+H]^+$, found 429.0058.

5,7-Bis((3,5-dichlorophenyl)thio)quinolin-8-amine (**4k**): 166.0 mg, 67% yield. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85～8.82 (m, 1H), 8.54～8.51 (m, 1H), 7.93 (s, 1H), 7.56～7.52 (m, 1H), 7.12 (t, J=1.7 Hz, 1H), 7.05 (t, J=1.7 Hz, 1H), 6.96 (d, J=1.7 Hz, 2H), 6.83 (d, J=1.7 Hz, 2H), 6.19 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.3, 148.2, 144.7, 142.8, 139.9, 138.5, 135.7, 135.5, 134.7, 131.3, 126.0, 125.4, 124.2, 124.0, 123.9, 111.9, 106.1; HRMS (ESI) calcd for $C_{21}H_{13}Cl_4N_2S_2$ 496.9269 $[M+H]^+$, found 496.9269.

5,7-Bis(naphthalen-2-ylthio)quinolin-8-amine (**4l**): 156.1 mg, 68% yield. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78～8.74 (m, 1H), 8.67～8.60 (m, 1H), 8.08 (s, 1H), 7.76～7.68 (m, 3H), 7.64～7.60 (m, 2H), 7.58 (s, 1H), 7.55～7.51 (m, 1H), 7.43～7.34 (m, 6H), 7.32～7.28 (m, 1H), 7.22～7.18 (m, 1H), 6.09 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.2, 147.9, 144.0, 138.7, 136.5, 135.0, 133.8, 133.8, 133.4, 131.8, 131.4, 131.0, 128.9, 128.5, 127.8, 127.7, 127.1, 127.0, 126.7, 126.5, 125.7, 125.5, 125.4, 125.12, 125.0, 124.3, 123.2, 114.0, 108.9; HRMS (ESI) calcd for $C_{29}H_{21}N_2S_2$ 461.1141 $[M+H]^+$, found 461.1145.

2,3-Bis(phenylthio)-1*H*-indole (**6a**)[17]: 110.2 mg, 66% yield. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (s, 1H), 7.58 (d, J=8.0 Hz, 1H), 7.30 (d, J=8.1 Hz, 1H), 7.26 ～7.19 (m, 6H), 7.16～7.09 (m, 5H), 7.04 (t, J=6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 136.9, 134.4, 133.6, 130.0, 129.8, 129.4, 128.7, 127.3, 126.7, 125.1, 123.9, 121.2, 119.9, 111.2, 109.2.

2,3-Bis((4-chlorophenyl)thio)-1*H*-indole (**6b**): 150.2 mg, 75% yield. White solid, m.p. 70～71 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (s, 1H), 7.46 (t, J=6.8 Hz, 1H), 7.20～7.14 (m, 2H), 7.04～6.93 (m, 7H), 6.88～6.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.9, 136.5, 133.4, 133.0, 132.9, 131.1, 130.7, 129.8, 129.5, 128.9, 128.0, 124.4, 121.6, 119.9, 111.5, 109.7; HRMS (ESI) calcd for $C_{20}H_{14}Cl_2NS_2$ 401.9939 $[M+H]^+$, found 401.9919.

2,3-Bis(*p*-tolylthio)-1*H*-indole (**6c**): 132.0 mg, 73% yield. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (s,

1H), 7.57 (d, J=7.9 Hz, 1H), 7.27 (d, J=8.1 Hz, 1H), 7.22 (d, J=7.9 Hz, 3H), 7.13 (d, J=7.6 Hz, 1H), 7.07 (d, J=8.0 Hz, 2H), 7.03 (d, J=8.1 Hz, 2H), 6.96 (d, J=8.1 Hz, 2H), 2.31 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.8, 136.8, 134.9, 134.6, 134.5, 130.8, 130.2, 130.1, 130.1, 129.5, 127.0, 123.5, 121.1, 119.7, 110.9, 108.3, 21.1, 20.9; HRMS (ESI) calcd for $C_{22}H_{20}NS_2$ 362.1032 $[M+H]^+$, found 362.1040.

5-Methoxy-2,3-bis((4-methoxyphenyl)thio)-1*H*-indole (**6d**): 144.3 mg, 68% yield. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02 (s, 1H), 7.23 (d, J=8.8 Hz, 2H), 7.06～7.02 (m, 3H), 6.94 (d, J=1.8 Hz, 1H), 6.72 (d, J=8.8 Hz, 3H), 6.64 (d, J=8.7 Hz, 2H), 3.70 (s, 3H), 3.69 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 157.9, 155.1, 135.9, 133.6, 131.5, 131.1, 129.0, 128.8, 123.5, 115.1, 114.5, 113.6, 111.7, 107.4, 100.8, 55.8, 55.4, 55.3; HRMS (ESI) calcd for $C_{23}H_{22}NO_3S_2$ 424.1036 $[M+H]^+$, found 424.1035.

5-Bromo-2,3-bis((4-chlorophenyl)thio)-1*H*-indole (**6e**): 146.0 mg, 61% yield. White solid, m.p. 113～114 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.47 (s, 1H), 7.48 (d, J=1.9 Hz, 1H), 7.37 (d, J=8.7 Hz, 1H), 7.32～7.28 (m, 1H), 7.27～7.23 (m, 2H), 7.15～7.10 (m, 4H), 6.91～6.87 (m, 2H); ^{13}C NMR (100 MHz, DMSO) δ: 137.0, 136.6, 135.0, 133.9, 132.3, 131.4, 130.7, 130.4, 129.8, 129.4, 127.9, 126.8, 121.2, 114.9, 114.2, 106.8; HRMS (ESI) calcd for $C_{20}H_{13}BrCl_2NS_2$479.9044 $[M+H]^+$, found 479.9054.

Supporting Information The NMR spectra of all products. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

References

[1] (a) Bisht, R.; Haldar, C.; Hassan, M. M. M.; Hoque, M. E.; Chaturvedi, J.; Chattopadhyay, B. *Chem. Soc. Rev.* **2022**, *51*, 5042.
(b) Liao, Y.; Liu, F.; Shi, Z.-J. *Chem. Commun.* **2021**, *57*, 13288.
(b) Ali, R.; Siddiqui, R. *Adv. Synth. Catal.* **2021**, *363*, 1290.
(d) Tian, S.; Luo, T.; Zhu, Y.; Wan, J.-P. *Chin. Chem. Lett.* **2020**, *31*, 3073.
(e) Zhao, B.; Liu, Y. *Synthesis* **2020**, *52*, 3211.
(f) Katariri, T.; Amao, Y. *Green Chem.* **2020**, *22*, 6682.

[2] (a) Chen, Y.; Wen, S.; Tian, Q.; Zhang, Y.; Cheng, G. *Org. Lett.* **2021**, *23*, 7905.
(b) Yu, Q.; Liu, Y.; Wan, J.-P. *Chin. Chem. Lett.* **2021**, *32*, 3514.
(c) Moseev, T. D.; Nikiforov, E. A.; Varaksin, M. V.; Charushin, V. N.; Chupakhin, O. N. *J. Org. Chem.* **2021**, *86*, 13702.
(d) Selmani, A.; Schoenebeck, F. *Org. Lett.* **2021**, *23*, 4779.
(e) Han, Q.-Q.; Chen, D.-M.; Wang, Z.-L.; Sun, Y.-Y.; Yang, S.-H.; Song, J.-C.; Dong, D.-Q. *Chin. Chem. Lett.* **2021**, *32*, 2559.
(f) Zhu, H.-L.; Zeng, F.-L.; Chen, X.-L.; Sun, K.; Li, H.-C.; Yuan, X.-Y.; Qu, L.-B.; Yu, B. *Org. Lett.* **2021**, *23*, 2976.
(g) Liu, D.; Zhang, Z.; Yu, J.; Chen, H.; Lin, X.; Li, M.; Wen, L.; Guo, W. *Org. Chem. Front.* **2022**, *9*, 2963.
(h) Wang, Z.-Q.; Hou, C.; Zhong, Y.-F.; Lu, Y.-X.; Mo, Z.-Y.; Pan, Y.-M.; Tang, H.-T. *Org. Lett.* **2019**, *21*, 9841.

[3] (a) Nandy, A.; Kazi, I.; Guha, S.; Sekar, G. *J. Org. Chem.* **2021**, *86*, 2570.
(b) Halimehjani, A. Z.; Shokrgozar, S.; Beier, P. *J. Org. Chem.* **2018**, *83*, 5778.
(c) Guo, W.-S.; Gong, H.; Zhang, Y.-A.; Wen, L.-R.; Li, M. *Org. Lett.* **2018**, *20*, 6394.
(d) Hazarika, S.; Barman, P. *ChemistrySelect* **2020**, *5*, 11583.
(e) Taninoto, K.; Ohkado, R.; Iida, H. *J. Org. Chem.* **2019**, *84*, 14980.
(f) Bai, F.; Zhang, S.; Wei, L.; Liu, Y. *Asian J. Org. Chem.* **2018**, *7*, 371.

[4] (a) Zhang, B.; Liu, D.; Sun, Y.; Zhang, Y.; Feng, J.; Yu, F. *Org. Lett.* **2021**, *23*, 3076.
(b) Deng, L.; Liu, Y. *ACS Omega* **2018**, *3*, 11890.
(c) Zhang, C.; Luo, J.; Zhang, J.; Chen, L.; Zhu, X.; Guo, M.; Shen, C.; Li, Z.; Wang, W. *Asian J. Org. Chem.* **2022**, *11*, e202200014.
(d) Zhang, T.; Yao, W.; Wan, J.-P.; Liu, Y. *Adv. Synth. Catal.* **2021**, *363*, 4811.
(e) Ali, D.; Panday, A. K.; Choudhury, L. H. *J. Org. Chem.* **2020**, *85*, 13610.
(e) Zeng, F.-L.; Zhu, H.-L.; Chen, X.-L.; Qu, L.-B.; Yu, B. *Green Chem.* **2021**, *23*, 3677.

[5] (a) Zhao, F.; Tan, Q.; Wang, D.; Chen, J.; Deng, G.-J. *Adv. Synth. Catal.* **2019**, *361*, 4075.
(b) Chen, L.; Xuchen, X.; Wang, F.; Yuang, Y.; Deng, G.; Liu, Y.; Liang, Y. *Org. Biomol. Chem.* **2021**, *19*, 10068.
(b) Tian, S.; Wang, C.; Xia, J.; Wan, J.-P.; Liu, Y. *Adv. Synth. Catal.* **2021**, *363*, 4627.
(c) Zhang, L.; Nagaraju, S.; Paplal, B.; Lin, Y.; Liu, S. *Eur. J. Org. Chem.* **2021**, 1365.
(d) Hu, B.; Zhang, Q.; Zhao, S.; Wang, Y.; Xu, L.; Yan, S.; Yu, F. *Adv. Synth. Catal.* **2019**, *361*, 49.

[6] (a) Xu, Z.; Yang, X.; Yin, S.; Qiu, R. *Top. Curr. Chem.* **2020**, *378*, 42.
(b) Khan, B.; Dutta, H. S.; Koley, D. *Asian J. Org. Chem.* **2018**, *7*, 1270.

[7] (a) Guo, X.; Li, P.; Wang, Q.; Wang, Q.; Wang, L. *Org. Chem. Front.* **2022**, *9*, 3192.
(b) Wu, W.; Wu, M.; Yoshikai, N. *Synthesis* **2021**, *53*, 3144.
(b) Zhang, Y.; Wen, C.; Li, J. *Org. Biomol. Chem.* **2018**, *16*, 1912.
(c) Mondal, S.; Hajra, A. *Org. Biomol. Chem.* **2018**, *16*, 2846.
(d) Zhao, L.; Li, P.; Xie, X.; Wang, L. *Org. Chem. Front.* **2018**, *5*, 1689.

[8] (a) Lin, X.; Zeng, C.; Liu, C.; Fang, Z.; Guo, K. *Org. Biomol. Chem.* **2021**, *19*, 1352.
(b) Wang, Y.; Wang, Y.; Jiang, K.; Zhang, Q.; Li, D. *Org. Biomol. Chem.* **2016**, *14*, 10180.
(c) Du, Y.; Liu, Y.; Wan, J.-P. *J. Org. Chem.* **2018**, *83*, 3403.
(d) Hou, J.; Wang, K.; Zhang, C.; Wei, T.; Bai, R.; Xie, Y. *Eur. J. Org. Chem.* **2020**, 6382.
(e) Li, Y.; Zhu, L.; Cao, X.; Au, C.-T.; Qiu, R.; Yin, S.-F. *Adv. Synth. Catal.* **2017**, *359*, 2864.

[9] (a) Dou, Y.; Xie, Z.; Sun, Z.; Fang, H.; Shen, C.; Zhang, P.; Zhu, Q. *ChemCatChem* **2016**, *8*, 3570.
(b) Sheng, L.; Shen, D.; Zhu, J.; Wu, G.; Fan, G.; Wu, X.; Du, K. *Tetrahedron* **2021**, *85*, 132033.
(c) Ji, D.; He, X.; Xu, Y.; Xu, Z.; Bian, Y.; Liu, W.; Zhu, Q.; Xu, Y. *Org. Lett.* **2016**, *18*, 4478.

[10] (a) Xia, C.; Wang, K.; Xu, J.; Shen, C.; Sun, D.; Li, H.; Wang, G.; Zhang, P. *Org. Biomol. Chem.* **2017**, *15*, 531.
(b) Wen, C.; Zhong, R.; Qin, Z.; Zhao, M.; Li, J. *Org. Biomol. Chem.* **2020**, *56*, 9529.
(c) Mondal, S.; Hajra, A. *J. Org. Chem.* **2018**, *83*, 11392.

[11] (a) Li, J.-M.; Weng, J.; Lu, G.; Chan, A. S. C. *Tetrahedron Lett.* **2016**, *57*, 2121.

(b) Chen, G.; Zhang, X.; Zeng, Z.; Peng, W.; Liang, Y.; Liu, J. *ChemistrySelect* **2017**, *2*, 1979.
(c) Liu, X.; Zhang, H.; Yang, F.; Wang, B. *Org. Biomol. Chem.* **2019**, *17*, 7564.
(d) Liang, S.; Manolikakes, G. M. *Adv. Synth. Catal.* **2016**, *358*, 2371.
[12] Yu, Q.; Yang, Y.; Wan, J.-P.; Liu, Y. *J. Org. Chem.* **2018**, *83*, 11385.
[13] Kumar, V.; Banert, K.; Ray, D.; Saha, B. *Org. Biomol. Chem.* **2019**, *17*, 10245.
[14] (a) Fu, L.; Wan, J.-P.; Zhou, Y.; Liu, Y. *Chem. Commun.* **2022**, *58*, 1808.
(b) Luo, T.; Wu, H.; Liao, L.-h.; Wan, J.-P.; Liu, Y. *J. Org. Chem.* **2021**, *86*, 15785.
(c) Luo, T.; Tian, S.; Wan, J.-P.; Liu, Y. *Curr. Org. Chem.* **2021**, *25*, 1180.
[15] (a) Pang, X.; Xiang, L.; Yang, X.; Yan, R. *Adv. Synth. Catal.* **2016**, *358*, 321.
(b) Yang, Y.; Zhang, S.; Tang, L.; Hu, Y.; Zha, Z.; Wang, Z. *Green Chem.* **2016**, *18*, 26093.
(c) Yang, F.-L.; Tian, S.-K. *Angew. Chem., Int. Ed.* **2013**, *52*, 4929.
[16] Lin, Y.-M.; Lu, G.-P.; Wang, G.-X.; Yi, W.-B. *Adv. Synth. Catal.* **2016**, *358*, 4100.
[17] Chen, L.; Pu, J.; Liu, P.; Dai, B. *J. Chem. Res.* **2018**, *42*, 456.

(Lu, Y.)

