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Transition-metal- and oxidant-free three-component reaction of quinoline *N*-oxides, sodium metabisulfite and aryldiazonium tetrafluoroborates *via* a dual radical coupling process†

Guirong You,[a] Dan Xi,[b] Jian Sun,[a] Liqiang Hao[a] and Chengcai Xia *[a]

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A convenient and straightforward three-component transformation of quinoline *N*-oxides, sodium metabisulfite and aryldiazonium tetrafluoroborates has been developed, providing the target products in moderate to good yields. Compared with previous studies, the present methodology avoids the use of transition-metal catalysts and excess oxidants, providing a simple and practical alternative approach for the construction of 2-sulfonylquinolines. Control experiments indicate that a dual radical coupling process is responsible for this reaction.

Introduction

The heterocyclic aromatic sulfone skeleton has been recognized as an important building block in organic synthesis, medicinal chemistry, and advanced materials.[1] Traditional methods to prepare such compounds are nucleophilic substitution transformations of aryl halides with thiols, followed by the oxidation of the corresponding thioethers.[2] However, some aryl halides are not commercially available and are difficult to prepare. In addition, plenty of oxidants should be employed in the second step. Such problems violate the purpose of green chemistry. Therefore, it is necessary to develop simple and efficient approaches for the synthesis of heterocyclic aromatic sulfones from a synthetic practicality standpoint.[3]

Quinoline and its derivatives have received considerable attention, as these compounds exhibit numerous biological activities and pharmacological effects.[4] In this regard, the development of new approaches for the construction of quinoline-containing compounds is highly desired. In recent years, the C–H functionalization of quinoline *N*-oxides has been regarded as a powerful tool for direct modification at the C2 and C8 positions of quinoline and its derivatives, since such a strategy leads to high efficiency and good atom economy.[5] So far, a number of transformations have been reported, such as arylation,[6] alkylation,[7] alkenylation,[8] alkynylation,[9] acylation,[10] etherification,[11] esterification,[12] trifluoromethylation,[13] halogenation,[14] hydroxylation,[15] amination,[16] amidation,[17] azidation,[18] phosphorization,[19] and thioetherification.[20] Recently, the development of a two-component reaction for the construction of 2-sulfonylquinolines from quinoline *N*-oxides has also attracted much attention.[21] The main mechanism for such a transformation is nucleophilic addition, which has been well established.[21a–g] In sharp contrast, C2–H sulfonylation of quinoline *N*-oxides through a radical pathway continues to be scarce.[21h–j] In 2016, Pan, Han and co-workers reported the first example of copper-catalyzed C2-sulfonylation of quinoline *N*-oxides with sodium sulfinates through radical coupling (Scheme 1a).[21i] In 2018, He *et al.* achieved a $K_2S_2O_8$-mediated C2-sulfonylation of quinoline *N*-oxides with sodium sulfinates *via* a dual radical coupling process (Scheme 1a).[21j] Very recently, the same group demonstrated a visible-light-induced deoxygenative C2-sulfonylation of quinoline *N*-oxides with sulfinic acids (Scheme 1b).[21j] Despite these great advancements, such transformations required catalysts and excess oxidants, which failed to meet the principle of atom economy. Furthermore, the commonly employed sulfonylating reagents in previous studies were limited to benzene sulfonyl chloride, sodium benzenesulfinate, benzenesulfonyl hydrazide, and benzene sulfinic acid. Therefore, it is still meaningful to develop novel approaches for C2-sulfonylation of quinoline *N*-oxides by using other sulfone sources.

In recent years, great efforts have been devoted to the use of sulfur dioxide as a sulfone source for the synthesis of hetero-

[a]*Pharmacy College, Shandong First Medical University & Shandong Academy of Medical Sciences, Taian 271000, China. E-mail: xiachc@163.com*
[b]*Shandong Institute for Product Quality Inspection, Jinan 250102, China*

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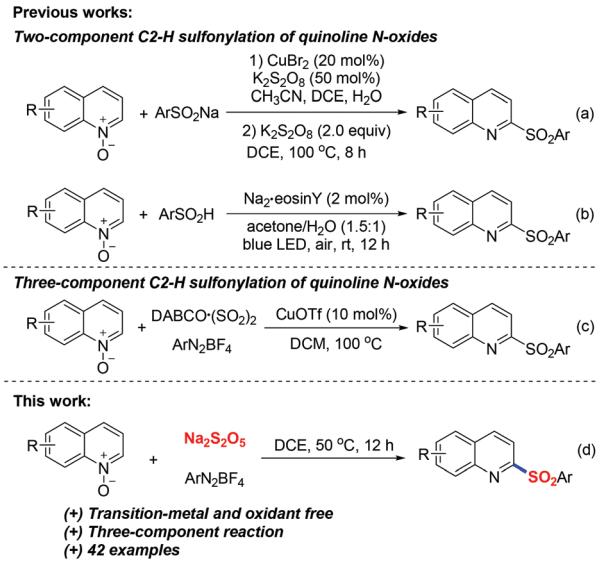


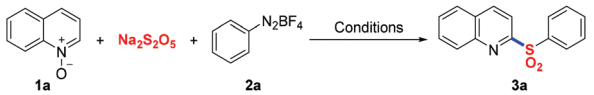
Scheme 1 Direct C2–H sulfonylation of quinoline *N*-oxides.

cyclic aromatic sulfones. Generally, DABCO·$(SO_2)_2$,[22] metabisulfites[23] and rongalite[24] were commonly used as the source of sulfur dioxide. More recently, Wang and coworkers reported the first example of three-component C2-sulfonylation of quinolone *N*-oxides with DABCO·$(SO_2)_2$ and phenyldiazonium tetrafluoroborates through a reductive elimination process (Scheme 1c).[22v] Although this work fills up the research gap, only 18 examples have been explored. Furthermore, the copper catalyst is toxic, and removal of trace amounts of copper residues from the products is quite costly and challenging, while crucial, especially in the pharmaceutical industry. To avoid the use of metal catalysts, the development of a transition-metal-free method is imperative. As part of our investigations devoted to the synthesis of nitrogen containing heterocyclic compounds,[25] herein, we report a transition-metal- and oxidant-free C2-sulfonylation of quinoline *N*-oxides with sodium metabisulfite and aryldiazonium tetrafluoroborates, providing a new methodology for the synthesis of 2-sulfonylquinolines (Scheme 1d).

Results and discussion

We first carried out the reaction of quinoline *N*-oxide (**1a**) with sodium metabisulfite, and phenyl diazonium tetrafluoroborate (**2a**) in CH_3CN at 30 °C for 12 hours, and the target product **3a** was obtained in 25% yield (Table 1, entry 1). Then, some other solvents such as dimethyl formamide (DMF), 1,4-dioxane, toluene, tetrahydrofuran (THF), H_2O, and 1,2-dichloroethane (DCE) were studied (Table 1, entries 2–7). The yield improved to 38% when the reaction was performed in 1,2-dichloroethane (DCE) (Table 1, entry 7). Subsequently, the amount of sodium metabisulfite was investigated, and the best result was obtained when 2.0 equivalents of sodium metabisulfite were employed (Table 1, entries 8–10). After this, the transformation

Table 1 Screening of reaction conditions[a]



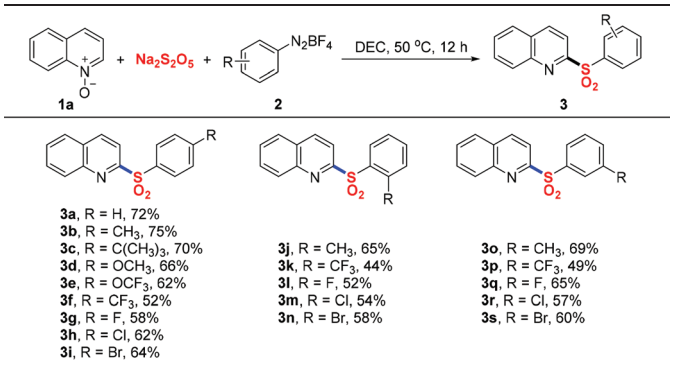
Entry	Solvent	$Na_2S_2O_5$ [*x* equiv.]	Temp. [°C]	Yield[b] [%]
1	CH_3CN	1.0	30	25
2	DMF	1.0	30	18
3	1,4-Dioxane	1.0	30	Trace
4	Toluene	1.0	30	Trace
5	THF	1.0	30	29
6	H_2O	1.0	30	Trace
7	DCE	1.0	30	38
8	DCE	1.5	30	49
9	DCE	2.0	30	58
10	DCE	2.5	30	57
11	DCE	2.0	50	71
12	DCE	2.0	80	69
13	DCE	2.0	rt	18
14[c]	DCE	2.0	50	53
15[d]	DCE	2.0	50	72
16[e]	DCE	2.0	50	Trace
17[f]	DCE	2.0	50	70
18[g]	DCE	2.0	50	21

[a] Reaction conditions: **1a** (0.2 mmol), $Na_2S_2O_5$ (*x* equiv.), **2a** (2.0 equiv.), solvent (2.0 mL), temp., N_2, 12 h. [b] Isolated yields. [c] **2a** (1.0 equiv.). [d] **2a** (1.5 equiv.). [e] Under air. [f] The reaction was performed for 24 h. [g] Used $K_2S_2O_5$ instead of $Na_2S_2O_5$.

was conducted at different reaction temperatures. It was found that the reaction was sensitive to the reaction temperature and a higher yield of 71% was obtained when the reaction was performed at 50 °C (Table 1, entries 11–13). To further improve the yield of the target product, the amount of phenyl diazonium tetrafluoroborate (**2a**) was also studied (Table 1, entries 14 and 15). However, no better result was obtained. It was worth noting that the yield of the target product showed no obvious change when the amount of phenyl diazonium tetrafluoroborate (**2a**) was reduced from 2.0 equivalents to 1.5 equivalents (Table 1, entry 15). No desired product was observed when the reaction was carried out under an air atmosphere (Table 1, entry 16). Further investigations on the reaction and sulfone source did not improve the product yield (Table 1, entries 17 and 18).

With the optimal reaction conditions in hand, we then explored the substrate scope of the three-component reaction. Firstly, aryldiazonium tetrafluoroborates with various substituent groups such as methyl, *tert*-butyl, methoxyl, trifluoromethoxy, trifluoromethyl and halo (F, Cl and Br) were tested under the standard conditions, giving the corresponding products in moderate to good yields (Table 2). According to the steric hindrance effect, the reactivities of aryldiazonium tetrafluoroborates bearing *para*-substituents were better than those bearing *meta*- and *ortho*-substituents. On the other hand, based on the electronic characteristics, aryldiazonium tetrafluoroborates bearing electron-donating groups (**3a–e**, **3j** and **3o**) reacted better than those bearing electron-withdrawing groups (**3f–i**, **3k–n** and **3p–s**). Unfortunately, pyridine *N*-oxide

Table 2 Substrate scope of aryldiazonium tetrafluoroborates[a,b]

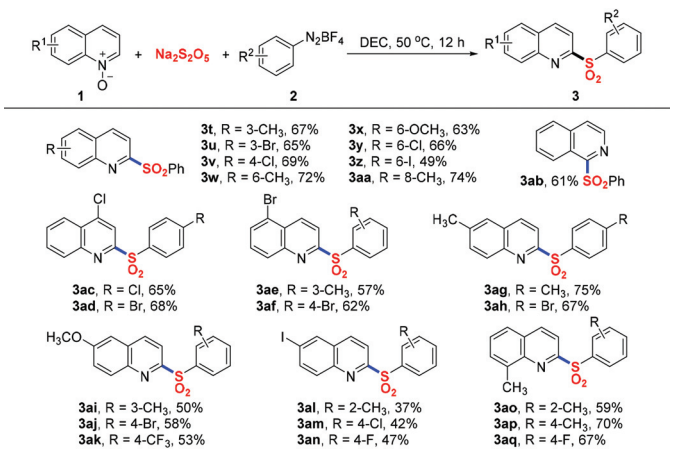


[a] Reaction conditions: **1a** (0.2 mmol), $Na_2S_2O_5$ (2.0 equiv.), **2** (1.5 equiv.), DCE (2.0 mL), 50 °C, N_2, 12 h. [b] Isolated yields.

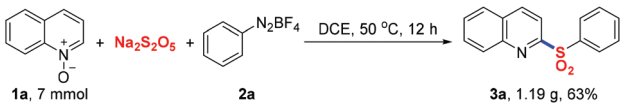
(**1j**) and quinoxaline *N*-oxide (**1k**) could not be converted into the corresponding product under the standard conditions (see the ESI†).

Next, the transformations of different aryldiazonium tetrafluoroborates with quinoline *N*-oxides bearing various synthetically useful functional groups were studied (Table 3). In general, all the substrates could be converted into the corresponding products smoothly. Quinoline *N*-oxides with common groups such as methyl ($-CH_3$) and methoxy ($-OCH_3$) were well compatible under the standard conditions, yielding the corresponding products (**3t**, **3w**, **3x**, **3aa**, **3ag–ak** and **3ao–aq**) in acceptable yields. Isoquinoline *N*-oxide was also tested under the standard conditions, and the product (**3ab**) was obtained in 61% yield. Halogen-containing substrates, which could be further functionalized, were also tolerated, giving the products (**3u**, **3v**, **3y**, **3z**, **3ac–af** and **3al–3an**) in 37–69% yields. It is worth mentioning that iodoquinoline *N*-oxides provided the corresponding products (**3z** and **3ak–am**) in lower yields than other substituted quinoline *N*-oxides. We suspected that the

Table 3 Substrate scope of quinoline *N*-oxides[a,b]



[a] Reaction conditions: **1** (0.2 mmol), $Na_2S_2O_5$ (2.0 equiv.), **2** (1.5 equiv.), DCE (2.0 mL), 50 °C, N_2, 12 h. [b] Isolated yields.

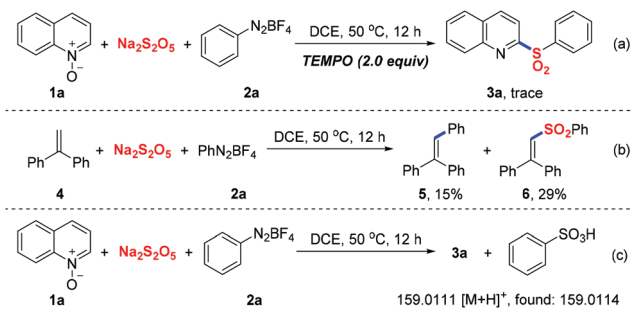


Scheme 2 Gram-scale synthesis.

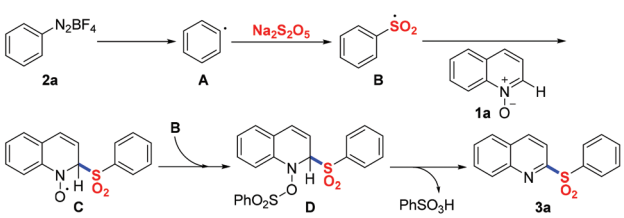
dehalogenation process of iodoquinoline *N*-oxides was responsible for this result. Furthermore, to demonstrate the application value of the transformation, a gram-scale synthesis of 2-(phenylsulfonyl)quinoline was carried out, giving the target product in 63% yield (Scheme 2).

To study the mechanism of the three-component reaction, some control experiments were conducted (Scheme 3). First of all, the transformation was completely suppressed by using TEMPO as the radical inhibitor (Scheme 3a). Further investigations found that triphenylethylene **5** and (2-(phenylsulfonyl) ethene-1,1-diyl)dibenzene **6** were obtained in 15% and 29% yields, respectively, by using 1,1-diphenylethylene as the radical trapping reagent. These results implied that a radical pathway was involved in this transformation (Scheme 3b). Meanwhile, the results of ^1H NMR and HRMS revealed that benzenesulfonic acid was generated during the transformation (Scheme 3c).

Based on the mechanism research in previous reports[21h–j,23] and the results of the above control experiments, a plausible mechanism was proposed for the three-component reaction (Scheme 4). Firstly, phenyldiazonium tetrafluoroborates underwent a decomposition process to generate phenyl radical **A**, which subsequently attacked $Na_2S_2O_5$ to give benzene sulfonyl radical **B**. Then, the benzene sulfonyl radical **B** reacted with quinoline *N*-oxide **1a** *via* a Minisci-like radical transformation



Scheme 3 Control experiments.



Scheme 4 Plausible mechanism.

to provide radical intermediate **C**. After another molecule of benzene sulfonyl radical **B** coupled with radical intermediate **C** to produce intermediate **D**, target product **3a** was obtained through an aromatization process with the release of benzenesulfonic acid.[21i]

Conclusions

In conclusion, we reported a novel and simple approach for the synthesis of 2-sulfonylquinolines from quinoline *N*-oxides, sodium metabisulfite, and aryldiazonium tetrafluoroborates under transition-metal- and oxidant-free conditions, giving the corresponding products in moderate to good yields. The control experiments revealed that a dual radical coupling process was responsible for this transformation.

Experimental section

General information

All commercial reagents were used as received. All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60–90 °C) and ethyl acetate. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Advance DRX-500 spectrometer at ambient temperature with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. All chemical shift values are quoted in ppm and coupling constants are quoted in Hz. Compounds for HRMS were analyzed by positive mode electrospray ionization (ESI) using an Agilent 6530 QTOF mass spectrometer.

General experimental procedure for synthesis of products 3

A solution of quinoline *N*-oxides **1** (0.2 mmol), sodium metabisulfite (2.0 equiv.), and aryldiazonium tetrafluoroborates **2** (1.5 equiv.) in DCE (2.0 mL) was stirred under a N_2 atmosphere at 50 °C for 12 hours. After the conversion was completed as indicated by TLC, the mixture was diluted with water and extracted with EA. The collected organic solvent was then evaporated under reduced pressure. The residue was purified directly by flash column chromatography (EA/PE, 1 : 5) to give products **3**.

General experimental procedure for gram-scale synthesis of product 3a

A solution of quinoline *N*-oxides **1a** (7.0 mmol), sodium metabisulfite (2.0 equiv.), and benzenediazonium tetrafluoroborates **2a** (1.5 equiv.) in DCE (30 mL) was stirred under a N_2 atmosphere at 50 °C for 12 hours. After the conversion was completed as indicated by TLC, the mixture was diluted with water and extracted with EA. The collected organic solvent was then evaporated under reduced pressure. The residue was purified directly by flash column chromatography (EA/PE, 1 : 5) to give product **3a**.

2-(Phenylsulfonyl)quinoline (3a).[21h] Obtained as a white solid, 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, J = 8.5 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 8.12–8.05 (m, 3H), 7.81 (d, J = 8.1 Hz, 1H), 7.72 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.62–7.57 (m, 1H), 7.54 (ddd, J = 6.6, 3.8, 1.2 Hz, 1H), 7.47 (dd, J = 10.4, 4.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.12, 146.46, 138.14, 137.70, 132.70, 129.97, 129.43, 128.20, 128.06, 128.05, 127.84, 126.68, 116.72.

2-Tosylquinoline (3b).[21h] Obtained as a white solid, 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, J = 8.5 Hz, 1H), 8.15 (dd, J = 12.7, 8.6 Hz, 2H), 8.00 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 1H), 7.78–7.71 (m, 1H), 7.62 (dd, J = 8.1, 7.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.17, 146.28, 143.73, 137.64, 134.99, 129.85, 129.19, 128.67, 128.03, 127.91, 127.65, 126.61, 116.55, 20.53.

2-((4-(*tert*-Butyl)phenyl)sulfonyl)quinoline (3c).[21h] Obtained as a white solid, 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, J = 2.5 Hz, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 2.4 Hz, 1H), 7.79 (t, J = 8.0 Hz, 3H), 7.76–7.69 (m, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.55 (d, J = 8.6 Hz, 2H), 1.34 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.97, 145.30, 144.25, 142.05, 130.68, 128.97, 128.18, 127.38, 127.04, 126.92, 126.88, 126.76, 125.48, 34.41, 29.96.

2-((4-Methoxyphenyl)sulfonyl)quinoline (3d).[21h] Obtained as a white solid, 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, J = 8.5 Hz, 1H), 8.21–8.14 (m, 2H), 8.07 (d, J = 8.9 Hz, 2H), 7.87 (d, J = 8.0 Hz, 1H), 7.77 (dd, J = 11.3, 4.0 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.91, 158.66, 147.44, 138.69, 131.31, 130.92, 130.50, 130.38, 129.07, 128.77, 127.70, 117.57, 114.41, 55.67.

2-((4-(Trifluoromethoxy)phenyl)sulfonyl)quinoline (3e).[21g] Obtained as a white solid, 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.22 (dd, J = 8.7, 6.7 Hz, 3H), 8.17 (d, J = 8.6 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.84–7.78 (m, 1H), 7.69 (t, J = 7.2 Hz, 1H), 7.36 (d, J = 8.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.72, 153.10, 147.50, 138.92, 137.27, 131.42, 131.19, 130.39, 129.42, 128.95, 127.77, 120.77, 120.19 (q, J = 259.6 Hz), 117.54.

2-((4-(Trifluoromethyl)phenyl)sulfonyl)quinoline (3f).[21h] Obtained as a white solid, 52% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, J = 8.5 Hz, 1H), 8.29 (d, J = 8.2 Hz, 2H), 8.24 (d, J = 8.5 Hz, 1H), 8.15 (d, J = 8.6 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.1 Hz, 3H), 7.69 (t, J = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.31, 146.47, 141.61, 137.98, 134.28 (q, J = 31.5 Hz), 130.25, 129.32, 128.70, 128.52, 127.96, 126.76, 125.14 (q, J = 3.8 Hz), 122.13 (q, J = 273.4 Hz), 116.55.

2-((4-Fluorophenyl)sulfonyl)quinoline (3g).[21h] Obtained as a white solid, 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, J = 8.5 Hz, 1H), 8.20 (d, J = 8.5 Hz, 1H), 8.18–8.12 (m, 3H), 7.88 (d, J = 8.1 Hz, 1H), 7.78 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.66 (ddd, J = 8.1, 7.0, 1.0 Hz, 1H), 7.20 (t, J = 8.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.86 (d, J = 257.0 Hz), 156.86, 146.35, 137.83, 133.93 (d, J = 3.8 Hz), 130.92 (d, J = 10.1 Hz), 130.06, 129.23, 128.26, 127.79, 126.70, 116.41, 115.37 (d, J = 22.7 Hz).

2-((4-Chlorophenyl)sulfonyl)quinoline (3h).[21h] Obtained as a white solid, 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, J = 8.5 Hz, 1H), 8.20 (d, J = 8.5 Hz, 1H), 8.15 (d, J = 8.6 Hz, 1H), 8.08 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.2 Hz, 1H), 7.80 (t, J = 7.7 Hz,

1H), 7.67 (t, J = 7.5 Hz, 1H), 7.51 (d, J = 8.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.80, 147.47, 140.60, 138.91, 137.52, 131.17, 130.59, 130.36, 129.44, 129.39, 128.91, 127.77, 117.52.

2-((4-Bromophenyl)sulfonyl)quinoline (3i).[21h] Obtained as a white solid, 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 8.5 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 8.08 (d, J = 8.6 Hz, 1H), 7.94 (d, J = 8.6 Hz, 2H), 7.82 (d, J = 8.0 Hz, 1H), 7.75–7.71 (m, 1H), 7.63–7.58 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.70, 146.44, 137.86, 137.01, 131.38, 130.14, 129.61, 129.33, 128.36, 128.22, 127.88, 126.73, 116.49.

2-(*o*-Tolylsulfonyl)quinoline (3j).[21g] Obtained as a white solid, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (d, J = 8.5 Hz, 1H), 8.32 (dd, J = 7.9, 1.2 Hz, 1H), 8.19 (d, J = 8.5 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.3 Hz, 1H), 7.78 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.67 (ddd, J = 8.1, 6.9, 1.1 Hz, 1H), 7.51 (td, J = 7.6, 1.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 1H), 7.26 (d, J = 5.7 Hz, 1H), 2.57 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.28, 147.22, 139.16, 138.60, 137.17, 133.91, 132.46, 130.96, 130.68, 130.46, 129.18, 128.92, 127.72, 126.41, 117.77, 20.74.

2-((2-(Trifluoromethyl)phenyl)sulfonyl)quinoline (3k). Obtained as a white solid, 44% yield. M.p. 117–118 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, J = 7.9 Hz, 1H), 8.35 (d, J = 8.6 Hz, 1H), 8.18 (d, J = 8.6 Hz, 1H), 7.89 (d, J = 8.6 Hz, 1H), 7.82 (dd, J = 14.4, 7.5 Hz, 2H), 7.77 (d, J = 6.8 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.67 (t, J = 7.0 Hz, 1H), 7.61–7.56 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.42, 145.98, 137.51, 135.99, 133.17, 132.79, 131.19, 129.86, 129.12, 128.37 (q, J = 34.0 Hz), 128.13, 127.94, 127.17 (q, J = 6.3 Hz), 126.79, 121.53 (q, J = 274.7 Hz), 115.97. HRMS (ESI) calculated for $C_{16}H_{10}F_3NO_2S^+$: 338.0457 $[M + H]^+$, found: 338.0459.

2-((2-Fluorophenyl)sulfonyl)quinoline (3l). Obtained as a white solid, 52% yield. M.p. 121–122 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, J = 8.6 Hz, 1H), 8.24 (d, J = 8.6 Hz, 1H), 8.22–8.18 (m, 1H), 8.04 (d, J = 8.6 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.70 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.63–7.58 (m, 1H), 7.55 (ddd, J = 7.5, 4.6, 2.1 Hz, 1H), 7.36–7.29 (m, 1H), 7.03 (t, J = 9.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.62 (d, J = 258.3 Hz), 156.58, 146.26, 137.71, 135.34 (d, J = 8.8 Hz), 130.13, 129.97, 129.36, 128.30, 128.15, 126.75, 126.13 (d, J = 13.9 Hz), 123.56 (d, J = 3.8 Hz), 116.89 (d, J = 2.5 Hz), 115.97 (d, J = 21.4 Hz). HRMS (ESI) calculated for $C_{15}H_{10}FNO_2S^+$: 288.0489 $[M + H]^+$, found: 288.0484.

2-((2-Chlorophenyl)sulfonyl)quinoline (3m).[21h] Obtained as a white solid, 54% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46–8.42 (m, 1H), 8.37 (d, J = 8.6 Hz, 1H), 8.27 (d, J = 8.6 Hz, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.71–7.67 (m, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.53–7.48 (m, 2H), 7.37–7.32 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.40, 146.22, 137.34, 135.75, 133.87, 132.09, 131.20, 130.52, 129.90, 129.31, 128.22, 128.02, 126.77, 126.17, 117.39.

2-((2-Bromophenyl)sulfonyl)quinoline (3n).[21f] Obtained as a white solid, 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (dd, J = 7.8, 1.5 Hz, 1H), 8.44 (d, J = 8.5 Hz, 1H), 8.35 (d, J = 8.6 Hz, 1H), 8.04 (d, J = 8.6 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.76 (dd, J = 11.3, 4.1 Hz, 1H), 7.69 (d, J = 7.1 Hz, 1H), 7.63 (t, J = 7.9 Hz, 2H), 7.49 (td, J = 7.7, 1.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.27, 148.81, 138.38, 138.28, 135.07, 134.86, 132.69, 130.93, 130.35, 129.25, 129.04, 129.01, 127.81, 127.77, 118.69.

2-(*m*-Tolylsulfonyl)quinoline (3o).[3e] Obtained as a white solid, 69% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, J = 8.5 Hz, 1H), 8.29 (t, J = 1.7 Hz, 1H), 8.22 (d, J = 8.5 Hz, 1H), 8.19 (d, J = 8.6 Hz, 1H), 8.10–8.08 (m, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.84–7.80 (m, 1H), 7.75–7.72 (m, 1H), 7.71–7.68 (m, 1H), 2.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.54, 145.49, 138.82, 136.89, 133.29, 131.86, 129.16, 128.42, 128.32, 127.42, 127.07, 126.94, 125.73, 125.25, 115.63, 20.83.

2-((3-(Trifluoromethyl)phenyl)sulfonyl)quinoline (3p). Obtained as a white solid, 49% yield. M.p. 109–110 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38–8.31 (m, 2H), 8.28 (d, J = 7.9 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H), 8.05 (d, J = 8.6 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.72 (ddd, J = 8.4, 7.0, 1.3 Hz, 1H), 7.64–7.57 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.35, 146.45, 139.25, 138.00, 131.47, 130.72 (q, J = 34.80 Hz), 130.24, 129.38 (q, J = 3.8 Hz), 129.29, 128.80, 128.49, 127.95, 126.76, 125.24 (q, J = 3.8 Hz), 1122.14 (q, J = 273.4 Hz), 116.46. HRMS (ESI) calculated for $C_{16}H_{10}F_3NO_2S^+$: 338.0457 $[M + H]^+$, found: 338.0451.

2-((3-Fluorophenyl)sulfonyl)quinoline (3q). Obtained as a white solid, 65% yield. M.p. 128–129 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 8.5 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 8.10 (d, J = 8.6 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.80–7.77 (m, 1H), 7.74 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.63–7.58 (m, 1H), 7.45 (td, J = 8.1, 5.2 Hz, 1H), 7.23 (td, J = 8.3, 1.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.35 (d, J = 253.3 Hz), 156.55, 146.47, 140.13 (d, J = 7.8 Hz), 137.87, 130.15, 129.82 (d, J = 7.8 Hz), 129.40, 128.41, 127.93, 126.73, 123.87 (d, J = 2.5 Hz), 120.00 (d, J = 21.4 Hz), 116.63, 115.41 (d, J = 21.4 Hz). HRMS (ESI) calculated for $C_{15}H_{10}FNO_2S^+$: 288.0489 $[M + H]^+$, found: 288.0481.

2-((3-Chlorophenyl)sulfonyl)quinoline (3r).[21h] Obtained as a white solid, 57% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, J = 8.5 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 8.11 (d, J = 8.6 Hz, 1H), 8.06 (t, J = 1.9 Hz, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.76–7.72 (m, 1H), 7.63–7.59 (m, 1H), 7.52–7.49 (m, 1H), 7.41 (t, J = 7.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.54, 146.48, 139.82, 137.89, 134.29, 132.86, 130.15, 129.42, 129.31, 128.41, 128.06, 127.94, 126.73, 126.24, 116.62.

2-((3-Bromophenyl)sulfonyl)quinoline (3s).[21g] Obtained as a white solid, 60% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, J = 8.5 Hz, 1H), 8.21 (t, J = 1.7 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 8.11 (d, J = 8.6 Hz, 1H), 8.03–8.00 (m, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.76–7.73 (m, 1H), 7.67–7.65 (m, 1H), 7.63–7.60 (m, 1H), 7.35 (t, J = 8.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.52, 146.48, 139.95, 137.90, 135.77, 130.85, 130.16, 129.53, 129.41, 128.42, 127.94, 126.73, 126.70, 122.02, 116.62.

3-Methyl-2-(phenylsulfonyl)quinoline (3t).[21c] Obtained as a white solid, 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, J = 4.0, 3.2 Hz, 3H), 7.88 (d, J = 8.5 Hz, 1H), 7.79–7.75 (m, 1H), 7.70–7.63 (m, 2H), 7.61–7.55 (m, 3H), 2.88 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.94, 144.67, 139.88, 138.79, 133.55, 129.97, 129.80, 129.49, 129.16, 129.03, 128.67, 128.59, 126.71, 18.80.

3-Bromo-2-(phenylsulfonyl)quinoline (3u). Obtained as a white solid, 65% yield. M.p. 132–133 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.13–8.06 (m, 2H), 7.93 (d, J = 8.4 Hz, 1H), 7.79–7.73 (m, 2H), 7.70–7.64 (m, 2H), 7.57 (t, J = 7.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.31, 143.36, 141.89, 136.91, 132.83, 130.07, 129.17, 129.07, 128.74, 128.52, 127.66, 125.49, 110.27. HRMS (ESI) calculated for $C_{15}H_{10}BrNO_2S^+$: 347.9689 $[M + H]^+$, found: 347.9682.

4-Chloro-2-(phenylsulfonyl)quinoline (3v). Obtained as a white solid, 69% yield. M.p. 162–163 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.27 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 8.5 Hz, 1H), 8.16–8.13 (m, 2H), 7.84 (t, J = 7.7 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.92, 147.14, 144.27, 137.62, 132.99, 130.80, 129.83, 129.21, 128.18, 128.14, 126.08, 123.21, 116.97. HRMS (ESI) calculated for $C_{15}H_{10}ClNO_2S^+$: 304.0194 $[M + H]^+$, found: 304.0191.

6-Methyl-2-(phenylsulfonyl)quinoline (3w). Obtained as a white solid, 72% yield. M.p. 130–131 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, J = 8.5 Hz, 1H), 8.18–8.10 (m, 3H), 8.05 (d, J = 8.5 Hz, 1H), 7.62–7.56 (m, 3H), 7.52 (t, J = 7.6 Hz, 2H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.09, 145.08, 138.68, 138.30, 136.80, 132.64, 132.58, 132.36, 128.98, 128.01, 127.91, 125.38, 116.77, 20.76. HRMS (ESI) calculated for $C_{16}H_{13}NO_2S^+$: 284.0740 $[M + H]^+$, found: 284.0734.

6-Methoxy-2-(phenylsulfonyl)quinoline (3x).[21c] Obtained as a white solid, 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 8.6 Hz, 1H), 8.15–8.09 (m, 3H), 8.03 (d, J = 9.3 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.40 (dd, J = 9.3, 2.7 Hz, 1H), 7.07 (d, J = 2.7 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.81, 154.34, 142.59, 138.47, 135.81, 132.50, 130.74, 129.39, 127.99, 127.78, 123.29, 117.23, 103.57, 54.69.

6-Chloro-2-(phenylsulfonyl)quinoline (3y).[21c] Obtained as a white solid, 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 8.6 Hz, 1H), 8.23 (d, J = 8.6 Hz, 1H), 8.17–8.11 (m, 2H), 8.10 (d, J = 9.1 Hz, 1H), 7.86 (d, J = 2.2 Hz, 1H), 7.71 (dd, J = 9.1, 2.3 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.40, 144.77, 137.81, 136.79, 134.32, 132.86, 131.09, 130.89, 128.35, 128.13, 128.08, 125.33, 117.63.

6-Iodo-2-(phenylsulfonyl)quinoline (3z). Obtained as a white solid, 49% yield. M.p. 142–143 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.6 Hz, 1H), 8.05 (dt, J = 9.0, 3.4 Hz, 3H), 7.96 (d, J = 9.3 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.33 (dd, J = 9.3, 2.7 Hz, 1H), 7.00 (d, J = 2.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.81, 153.34, 141.59, 137.47, 134.81, 131.50, 129.74, 128.39, 126.99, 126.78, 122.29, 116.23, 95.68. HRMS (ESI) calculated for $C_{15}H_{10}INO_2S^+$: 395.9550 $[M + H]^+$, found: 395.9555.

8-Methyl-2-(phenylsulfonyl)quinoline (3aa).[21c] Obtained as a white solid, 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 8.5 Hz, 1H), 8.24–8.14 (m, 3H), 7.68 (d, J = 8.1 Hz, 1H), 7.63–7.57 (m, 2H), 7.53 (dd, J = 16.2, 8.0 Hz, 3H), 2.65 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.05, 145.31, 137.84, 137.73, 137.34, 132.60, 129.88, 128.33, 127.94, 127.81, 127.77, 124.51, 115.66, 16.41.

1-(Phenylsulfonyl)isoquinoline (3ab).[21c] Obtained as a white solid, 61% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20–9.13 (m, 1H), 8.42 (d, J = 5.5 Hz, 1H), 8.14–8.05 (m, 2H), 7.93–7.87 (m, 1H), 7.82–7.73 (m, 3H), 7.64 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.07, 140.57, 139.13, 137.80, 133.71, 131.19, 129.30, 129.23, 128.91, 127.60, 125.30, 125.08, 124.38.

4-Chloro-2-((4-chlorophenyl)sulfonyl)quinoline (3ac). Obtained as a white solid, 65% yield. M.p. 176–177 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.27 (dd, J = 8.5, 0.9 Hz, 1H), 8.17 (d, J = 8.5 Hz, 1H), 8.08 (d, J = 8.7 Hz, 2H), 7.88–7.83 (m, 1H), 7.80–7.75 (m, 1H), 7.53 (d, J = 8.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.63, 148.15, 145.45, 140.94, 137.01, 131.98, 130.79, 130.69, 130.38, 129.55, 127.16, 124.29, 117.80. HRMS (ESI) calculated for $C_{15}H_9Cl_2NO_2S^+$: 337.9804 $[M + H]^+$, found: 337.9800.

2-((4-Bromophenyl)sulfonyl)-4-chloroquinoline (3ad). Obtained as a white solid, 68% yield. M.p. 186–187 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32–8.26 (m, 2H), 8.17 (d, J = 8.5 Hz, 1H), 8.08 (d, J = 8.7 Hz, 2H), 7.88–7.84 (m, 1H), 7.80–7.75 (m, 1H), 7.53 (d, J = 8.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.63, 148.16, 145.46, 140.94, 137.01, 131.97, 130.80, 130.69, 130.38, 129.56, 127.17, 124.30, 117.81. HRMS (ESI) calculated for $C_{15}H_9BrClNO_2S^+$: 381.9299 $[M + H]^+$, found: 381.9293.

5-Bromo-2-(*m*-tolylsulfonyl)quinoline (3ae). Obtained as a white solid, 57% yield. M.p. 176–177 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, J = 8.8 Hz, 1H), 8.33–8.27 (m, 1H), 8.16 (d, J = 8.6 Hz, 1H), 8.00–7.88 (m, 3H), 7.68–7.61 (m, 1H), 7.47–7.40 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.08, 148.17, 139.48, 138.65, 138.60, 134.78, 132.77, 131.17, 130.35, 129.33, 129.06, 128.36, 126.29, 121.88, 118.94, 21.34. HRMS (ESI) calculated for $C_{16}H_{12}BrNO_2S^+$: 361.9845 $[M + H]^+$, found: 361.9850.

5-Bromo-2-((4-bromophenyl)sulfonyl)quinoline (3af). Obtained as a white solid, 62% yield. M.p. 187–188 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (d, J = 8.8 Hz, 1H), 8.29 (d, J = 8.8 Hz, 1H), 8.12 (d, J = 8.6 Hz, 1H), 8.00 (d, J = 8.6 Hz, 2H), 7.97–7.92 (m, 1H), 7.69 (d, J = 8.6 Hz, 2H), 7.68–7.62 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.63, 148.13, 138.80, 137.69, 132.95, 132.50, 131.36, 130.71, 130.23, 129.51, 128.42, 121.93, 118.62. HRMS (ESI) calculated for $C_{15}H_9Br_2NO_2S^+$: 425.8794 $[M + H]^+$, found: 425.8797.

6-Methyl-2-tosylquinoline (3ag).[21c] Obtained as a white solid, 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, J = 8.5 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 8.01 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.9 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 2.55 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.45, 146.13, 144.67, 139.60, 137.78, 136.38, 133.33, 130.06, 129.75, 129.01, 128.93, 126.42, 117.78, 21.82, 21.66.

2-((4-Bromophenyl)sulfonyl)-6-methylquinoline (3ah).[21c] Obtained as a white solid, 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, J = 8.5 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 8.5 Hz, 1H), 8.00 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 9.0 Hz, 2H), 2.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.77, 146.14, 139.93, 138.30, 137.98, 133.58, 132.38, 130.57, 129.96, 129.10, 129.03, 126.49, 117.61, 21.85.

6-Methoxy-2-(*m*-tolylsulfonyl)quinoline (3ai). Obtained as a white solid, 50% yield. M.p. 195–196 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, J = 8.6 Hz, 1H), 8.15 (d, J = 8.6 Hz, 1H), 8.07 (d, J = 9.3 Hz, 1H), 7.92 (d, J = 8.9 Hz, 2H), 7.45–7.36 (m, 3H), 7.09 (d, J = 2.6 Hz, 1H), 3.94 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.85, 155.55, 143.69, 139.40, 139.31, 136.83, 134.39, 131.89, 130.45, 129.09, 128.94, 126.02, 124.29, 118.38, 104.62, 55.75, 21.33. HRMS (ESI) calculated for $C_{17}H_{15}NO_3S^+$: 314.0846 $[M + H]^+$, found: 314.0843.

2-((4-Bromophenyl)sulfonyl)-6-methoxyquinoline (3aj). Obtained as a white solid, 58% yield. M.p. 201–202 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, J = 8.6 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 9.3 Hz, 1H), 7.99 (d, J = 8.6 Hz, 2H), 7.67 (d, J = 8.6 Hz, 2H), 7.44 (dd, J = 9.3, 2.7 Hz, 1H), 7.10 (d, J = 2.7 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.00, 155.07, 143.71, 138.49, 136.93, 132.37, 131.82, 130.54, 130.48, 129.00, 124.53, 118.11, 104.61, 55.77. HRMS (ESI) calculated for $C_{16}H_{12}BrNO_3S^+$: 377.9794 $[M + H]^+$, found: 377.9796.

6-Methoxy-2-((4-(trifluoromethyl)phenyl)sulfonyl)quinoline (3ak). Obtained as a white solid, 53% yield. M.p. 190–191 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (dd, J = 8.2, 4.2 Hz, 3H), 8.18 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 9.3 Hz, 1H), 7.80 (d, J = 8.2 Hz, 2H), 7.47–7.41 (m, 1H), 7.10 (d, J = 2.2 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.12, 154.61, 143.75, 143.08, 137.01, 135.13 (q, J = 32.8 Hz), 131.80, 130.65, 129.53, 126.13 (q, J = 2.5 Hz), 124.67, 123.19 (q, J = 273.4 Hz), 118.21, 104.61, 55.79. HRMS (ESI) calculated for $C_{17}H_{12}F_3NO_3S^+$: 368.0563 $[M + H]^+$, found: 368.0560.

6-Iodo-2-(*o*-tolylsulfonyl)quinoline (3al). Obtained as a white solid, 37% yield. M.p. 149–150 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, J = 1.8 Hz, 1H), 8.25 (d, J = 8.6 Hz, 1H), 8.20 (d, J = 8.6 Hz, 1H), 8.03–7.98 (m, 3H), 7.87 (d, J = 9.0 Hz, 1H), 7.34 (d, J = 8.2 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.91, 146.34, 145.03, 139.80, 137.41, 136.49, 135.82, 131.77, 131.53, 130.42, 130.17, 129.85, 129.15, 118.47, 95.57, 21.69. HRMS (ESI) calculated for $C_{16}H_{12}INO_2S^+$: 409.9706 $[M + H]^+$, found: 409.9705.

2-((4-Chlorophenyl)sulfonyl)-6-iodoquinoline (3am). Obtained as a white solid, 42% yield. M.p. 152–153 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 1.8 Hz, 1H), 8.28 (d, J = 8.6 Hz, 1H), 8.21 (d, J = 8.6 Hz, 1H), 8.07 (d, J = 8.7 Hz, 2H), 8.03 (dd, J = 9.0, 1.9 Hz, 1H), 7.85 (d, J = 9.0 Hz, 1H), 7.52 (d, J = 8.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.07, 155.14, 143.78, 138.55, 136.99, 132.43, 131.89, 130.61, 130.55, 129.07, 124.59, 118.18, 95.57. HRMS (ESI) calculated for $C_{15}H_9ClINO_2S^+$: 408.0933 $[M + H]^+$, found: 408.0931.

2-((4-Fluorophenyl)sulfonyl)-6-iodoquinoline (3an). Obtained as a white solid, 47% yield. M.p. 141–142 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (dd, J = 10.2, 5.2 Hz, 2H), 8.21 (d, J = 8.6 Hz, 1H), 8.19–8.12 (m, 2H), 8.02 (dd, J = 9.0, 1.9 Hz, 1H), 7.85 (d, J = 9.0 Hz, 1H), 7.23 (t, J = 8.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.06 (d, J = 257.0 Hz), 158.50, 146.32, 139.99, 137.59, 136.56, 134.68, 132.10 (d, J = 8.8 Hz), 131.66, 130.22, 118.27, 116.53 (d, J = 22.7 Hz), 95.82. HRMS (ESI) calculated for $C_{15}H_9FINO_2S^+$: 413.9456 $[M + H]^+$, found: 413.9451.

8-Methyl-2-(*o*-tolylsulfonyl)quinoline (3ao). Obtained as a white solid, 59% yield. M.p. 132–133 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, J = 8.5 Hz, 1H), 8.27 (dd, J = 7.9, 0.9 Hz, 1H), 8.20 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 6.8 Hz, 1H), 7.55–7.49 (m, 2H), 7.41 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 2.65 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.30, 146.16, 139.58, 138.80, 138.50, 137.14, 133.77, 132.31, 130.96, 130.87, 129.02, 128.98, 126.27, 125.59, 116.91, 20.96, 17.44. HRMS (ESI) calculated for $C_{17}H_{15}NO_2S^+$: 298.0896 $[M + H]^+$, found: 298.0890.

8-Methyl-2-tosylquinoline (3ap). Obtained as a white solid, 70% yield. M.p. 125–126 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, J = 8.5 Hz, 1H), 8.20 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.1 Hz, 1H), 7.59 (d, J = 6.8 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 2.68 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.38, 146.44, 144.69, 138.72, 138.43, 136.00, 130.88, 129.52, 129.43, 128.92, 128.84, 125.56, 116.75, 21.68, 17.53. HRMS (ESI) calculated for $C_{17}H_{15}NO_2S^+$: 298.0896 $[M + H]^+$, found: 298.0888.

2-((4-Fluorophenyl)sulfonyl)-8-methylquinoline (3aq). Obtained as a white solid, 67% yield. M.p. 117–118 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, J = 8.5 Hz, 1H), 8.26–8.17 (m, 3H), 7.71 (d, J = 8.1 Hz, 1H), 7.61 (d, J = 7.0 Hz, 1H), 7.56–7.50 (m, 1H), 7.22 (dd, J = 20.7, 12.0 Hz, 2H), 2.65 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.99 (d, J = 257.0 Hz), 157.00, 148.29, 146.35, 138.92, 138.32, 132.32 (d, J = 10.1 Hz), 131.07, 129.10, 128.92, 125.63, 116.54, 116.15 (d, J = 22.7 Hz), 17.49. HRMS (ESI) calculated for $C_{16}H_{12}FNO_2S^+$: 302.0646 $[M + H]^+$, found: 302.0649.

Ethene-1,1,2-triyltribenzene (5).[26] Obtained as a yellow liquid, 18% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.27 (m, 8H), 7.23–7.18 (m, 2H), 7.15–7.09 (m, 3H), 7.04–7.01 (m, 2H), 6.97 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.45, 142.60, 140.37, 137.40, 130.40, 129.56, 128.64, 128.22, 128.18, 127.97, 127.62, 127.52, 127.42, 126.75.

(2-(Phenylsulfonyl)ethene-1,1-diyl)dibenzene (6).[27] Obtained as a yellow liquid, 29% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, J = 8.3, 1.1 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.38–7.31 (m, 4H), 7.27 (dd, J = 12.1, 7.6 Hz, 4H), 7.22–7.17 (m, 2H), 7.09–7.04 (m, 2H), 7.03 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.27, 141.49, 139.10, 135.50, 132.93, 130.41, 129.80, 128.94, 128.79, 128.75, 128.66, 128.26, 127.91, 127.65.

Conflicts of interest

There are no conflicts to declare.

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