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Metal-free catalyzed arylsulfonylation of chloroquinoline with sodium arylsulfinates under microwave irradiation

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Abstract: An efficient protocol for the synthesis of 2-arylsulfonyl quinolines has been developed via a metal-free catalyzed cross-coupling reaction of chloroquinoline with sodium arylsulfinates in moderate-to-good yields under microwave irradiation. The reactions proceed with a wide range of substrates with good functional group tolerance.

Keywords: 2-arylsulfonyl quinolone; chloroquinoline; metal-free catalysis; sodium arylsulfinates; sulfonylation.

1 Introduction

Heterocyclic aromatic sulfone is recognized as a crucial scaffold in natural products, pharmaceuticals, material sciences, and biologically active compounds [1–6]. In particular, quinoline sulfones exhibited antibacterial and antiproliferative activities [7, 8]. In the last decade, significant effort has been devoted to the synthesis of sulfonyl quinoline derivatives. Traditionally, quinoline sulfones can be synthesized by nucleophilic substitution of heteroaromatic halides with thiols to form thioethers, followed by oxidation to the corresponding sulfones [9]. However, low efficiency and redundant steps of these methodologies are prohibitive for general applications. Thus, the search for novel methods for the synthesis of sulfonyl quinolines has attracted considerable attention in medicinal and synthetic chemistry.

In the past few years, great efforts have been made to synthesize 2-sulfonyl quinoline scaffolds. Wu's group reported an efficient and concise protocol to synthesize sulfonylated quinoline *N*-oxides via C–H bond activation with aryl sulfonyl chlorides as the sulfonylation reagents [10]. Chen's group described a transition metal-free one-pot approach to selective synthesis of 2-sulfonyl quinolines via *H*-phosphite-mediated C–H activation [11]. He's and Xiang's groups independently developed the synthesis of 2-sulfonyl quinolines by the iodine- or iodide-induced 2-sulfonylation of quinoline *N*-oxides with sulfonyl hydrazides in the presence of *tert*-butyl hydroperoxide or hydrogen peroxide (H_2O_2) [12, 13]. Pan's group synthesized a variety of 2-sulfonyl quinoline derivatives via Cu-catalyzed C2-sulfonylation of quinoline *N*-oxides with sodium sulfinates in the presence of potassium persulfate ($K_2S_2O_8$) [14]. Zhao's and Yotphan's groups achieved the synthesis of 2-sulfonyl quinolines via iodine-mediated sulfonylation of quinoline *N*-oxides with sodium sulfinates [15, 16]. Although these reactions allowed the synthesis of the desired 2-sulfonylation of quinolines, these approaches suffered from a narrow range of substrates, long reaction times, air-sensitive reaction conditions, and required different oxidants and transition-metal catalysts. It is still highly desirable to develop new protocols that can tolerate a wide range of functional groups, short reaction times, metal-free, air-insensitive reaction conditions. Guided by the recent studies on using sodium arylsulfinate as a sulfonylation source, we decided to investigate the modular synthesis for arylsulfonylated quinolines based on transition-metal-free catalyzed arylsulfonylation of chloroquinoline. Herein, we disclose an efficient synthetic strategy for synthesizing a wide variety of sulfonylated quinoline derivatives by reacting chloroquinoline with sodium arylsulfinates under microwave irradiation (Scheme 1). Interestingly, other *N*-heteroaryl chlorine compounds also react smoothly with sodium arylsulfinates at these conditions. The advantages of our methodology include short reaction times, a broad range of substrates, and good functional group tolerance.

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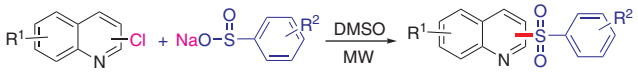
2 Results and discussion

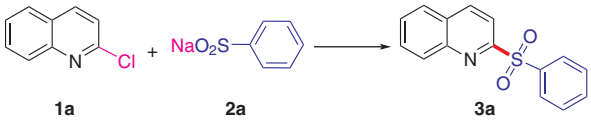
We initially chose 2-chloroquinoline (**1a**) as a model substrate for the reaction with sodium phenylsulfinate (**2a**) using dimethyl sulfoxide (DMSO) as solvent at 100°C for



Scheme 1: Synthesis of arylsulfonylated quinoline derivatives.

20 min under microwave irradiation. Much to our delight, the reaction proceeded to give access to the desired sulfonylation product **3aa**, albeit with a low yield (30%, Table 1, entry 1). The structure of **3aa** was verified by IR, NMR, and high-resolution mass spectra (HRMS) spectra. Inspired by this result, various solvents, such as CH_3CN, 1,4-dioxane, CH_3OH, 1,2-dichloroethane (DCE), THF, and H_2O, were screened, but they gave lower yields than DMSO (Table 1, entries 2–7). Thus DMSO proved to be definitely superior to the others. Rising the reaction temperature from 90 to 120°C showed a positive result, with the starting material consumed completely in 20 min and the yields improved up to 78%. However, a continued increase in temperature to 130°C had a negative impact on the reaction, and the yield decreased to 58%. Apparently, higher temperatures led to an increase in side reactions (Table 1, entries 1, 8–11). Additionally, the reaction time was also investigated, and 30 min proved to be ideal. If the time was prolonged, the yields did not improve (Table 1, entries 1, 12–15). The effects of various ratios of substrates were then probed and the ratio of **1a**–**2a** of 1:1.5 was found to be particularly effective for this sulfonylation (Table 1, entries 14, 16–17). The use of microwave irradiation is essential for this reaction, as no products formed in the absence of microwave irradiation even if the reaction time was prolonged to 5.0 h. After surveying a variety of solvents, temperature, reaction times, and the ratio of substrates, we found that the the ratio of substrates of 1:1.5 and DMSO as solvent at 120°C for 30 min were the optimal conditions for this transformation (Table 1, entry 14).

Table 1: Optimization of reaction conditions.[a]



1a 2a 3a

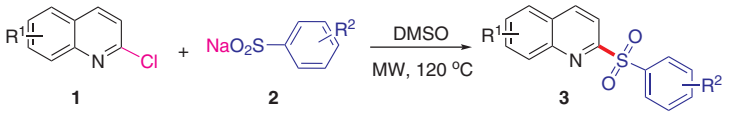
Entry	Solvent	Temp (°C)	Time (min)	Yield[b] (%)
1	DMSO	100	20	30
2	CH_3CN	100	20	21
3	1,4-Dioxane	100	20	18
4	CH_3OH	100	20	Trace
5	DCE	100	20	15
6	THF	100	20	12
7	H_2O	100	20	Trace
8	DMSO	90	20	10
9	DMSO	110	20	40
10	DMSO	120	20	78
11	DMSO	130	20	58
12	DMSO	120	5	10
13	DMSO	120	10	52
14	DMSO	120	30	88
15	DMSO	120	40	85
16[c]	DMSO	120	30	50
17[d]	DMSO	120	30	70

[a]Reaction conditions: 2-chloroquinoline **1a** (0.2 mmol, 32.6 mg), sodium phenylsulfinate **2a** (0.3 mmol, 49.2 mg), solvent (2.0 mL) under microwave irradiation. [b]Isolated yield. [c]The molar ratio of **1a**–**2a** is 1:1. [d]The molar ratio of **1a**–**2a** is 1:2.

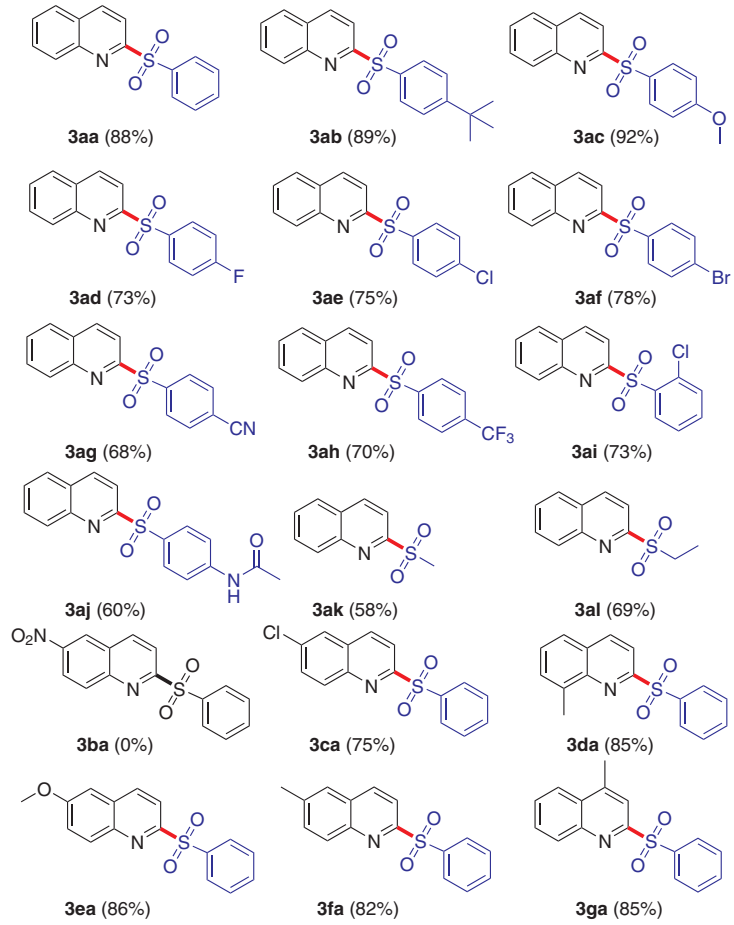
With the optimal reaction conditions in hand, we turned our attention to the substrates. Different sodium arylsulfinates were evaluated in the reaction with 2-chloroquinoline **1a** (Table 2). In addition, a series of functional groups on the phenyl ring of sodium arylsulfinates were tested. Both electron-donating and -withdrawing groups were well tolerated in this sulfonylation, affording the desired products in moderate-to-good yields (60–92%) (**3aa–3aj**). Generally, sodium arylsulfinates with electron-donating substituents (**3ab** and **3ac**) showed superior reaction efficiency as compared to those with electron-withdrawing ones (**3ad**–**3ai**). Fortunately, this protocol was tolerant of synthetically valuable functional groups on the phenyl moiety (in particular, chloro and bromo substituents), which gave an opportunity for further transformations (**3ae, 3af**). The sulfonylation process also occurred well with strongly electron-withdrawing –CN and $-CF_3$ groups at the sodium phenylsulfinates, affording the target compounds **3ag** and **3ah**, respectively. Reactions of sodium *o*- and *p*-chloro phenylsulfinate proceeded well, and nearly equal yields were achieved (**3ae** and **3ai**), suggesting that the steric effect of substituents on aromatic rings is negligible. Gratifyingly, when aliphatic sodium sulfinates were employed, the sulfonylation reaction also proceeded smoothly to provide the desired products (**3ak** and **3al**) with moderate yields (58% and 69%) under current conditions. The scope of chloroquinoline was also investigated. To our delight, the current catalytic system was suitable for a wide range of substituted chloroquinolines. No matter whether the quinoline ring is substituted with either electron-donating ($-CH_3$ and $-OCH_3$) or electron-withdrawing substituents (–Cl), all of them delivered the desired products in moderate-to-good yields (75–86%). Regrettably, when 2-chloro-6-nitroquinoline was employed, the desired product **3ba** did not form.

2-Chloroquinoline could react smoothly with sodium phenylsulfinate to obtain the desired product **3aa** in 88% yield. In order to investigate the effect of the position of the chloro substituent, we explored the phenylsulfonylation

Table 2: Synthesis of 2-(arylsulfonyl)quinoline derivatives from substituted 2-chloroquinolines and sodium arylsulfinates.[a,b]



1 2 3



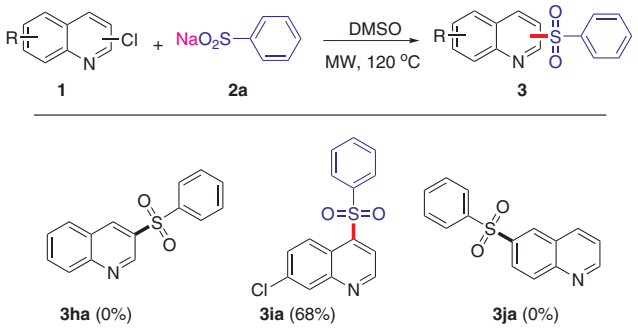
[a]Reaction conditions: substituted 2-chloroquinoline **1** (0.2 mmol), sodium sulfinates **2** (0.3 mmol), in 2.0 mL DMSO solvent, 120°C for 30 min under microwave irradiation. [b]Isolated yields.

of different chloroquinolines under the standard reaction conditions (Table 3). Unfortunately, when 3-chloroquinoline and 6-chloroquinoline were employed, the sulfonylation reactions did not occur and no products (**3ha** and **3ja**) were formed. To our satisfaction, 4,7-dichloroquinoline and 2,6-dichloroquinoline did react smoothly with sodium phenylsulfinate to provide the products (**3ia** and **3ca**) in 68% and 75% yields, respectively. These facts showed that the reactivity of 2-chloro and 4-chloroquinolines was higher than that of 3-chloro, 6-chloro, and 7-chloroquinolines.

The heterocyclic sulfone moiety has been proven to be useful building block in medicinal chemistry [17, 18]. In addition, heterocyclic sulfones are useful intermediates in organic synthesis [19, 20]. Recently, an efficient, concise, and transition metal-free synthesis of functionalized sulfonylated five-membered heterocyclic compounds via an S_NAr reaction has been developed using commercially available sodium sulfinates as sulfonylation reagents [21]. However, synthesis of six-membered heterocyclic sulfones containing multiple heteroatoms has hardly been studied [22–25]. Furthermore, the functionalized sulfonylated six-membered heterocyclic compounds containing one and two nitrogen heteroatoms were synthesized in good yields (75–86%) using the standard reaction conditions (Table 4).

To clarify the reaction mechanism, some control experiments were carried out (Scheme 2). When a radical

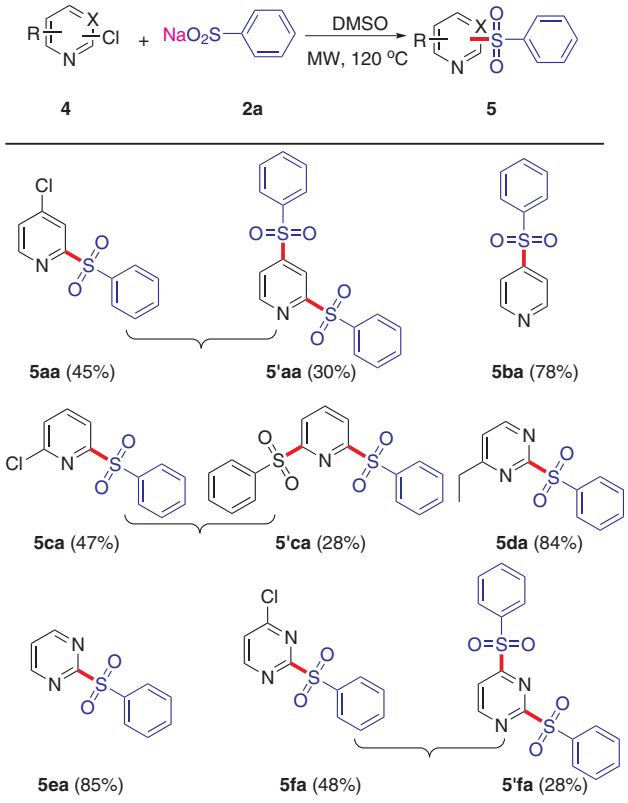
Table 3: The reaction of different chloroquinoline with sodium phenylsulfinate.[a,b]



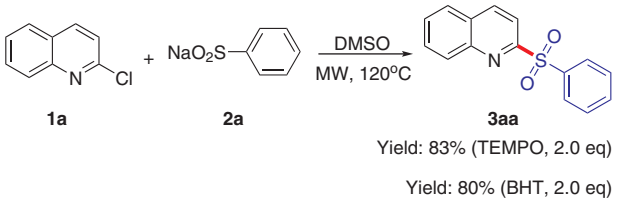
[a]Reaction conditions: substituted chloroquinoline **1** (0.2 mmol), sodium phenylsulfinates **2a** (0.3 mmol, 49.2 mg), in 2.0 mL DMSO solvent, 120°C for 30 min under microwave irradiation. [b]Isolated yields.

scavenger 2,2,6,6-tetramethylpiperidyl-1-oxyl or butylated hydroxytoluene was employed in the reaction of 2-chloroquinoline and sodium phenylsulfinate, the reaction still

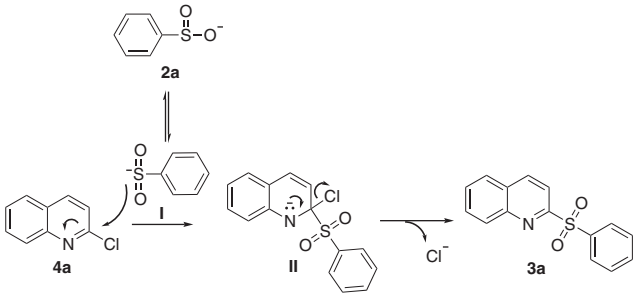
Table 4: The arylsulfonylation of six-membered *N*-heterocyclic compounds from heteroaryl halide with sodium phenylsulfinate.[a,b]



[a]Reaction conditions: six-membered *N*-heterocyclic compounds **4** (0.2 mmol), sodium phenylsulfinates **2a** (0.3 mmol, 49.2 mg), in 2.0 mL DMSO solvent, 120°C for 30 min under microwave irradiation. [b]Isolated yields.



Scheme 2: Control experiments.



Scheme 3: Proposed reaction mechanism.

proceeded well under the optimal conditions. The product **3aa** was obtained in 83% and 80% yields, respectively, which suggests that the reaction possibly involves a non-radical pathway.

With the above results and evidence given in the literature [21–25], an addition-elimination mechanism was proposed, as is shown in Scheme 3. Initially, sodium phenylsulfinate **2a** was transformed into phenysulfonyl anion **I** by isomerization. Then the addition of the nucleophilic anion **I** to the heteroaromatic electrophile **4a** generated the intermediate **II**, which was stabilized by resonance and the electron was dispersed into the phenyl ring. Finally, the intermediate **II** formed the desired product **3a** in a further elimination reaction.

3 Conclusion

In conclusion, an unexpected metal-free catalyzed arylsulfonylation reaction of chloroquinolines has been developed. This reaction is carried out under mild conditions, which provides an easy pathway for the preparation of bioactive 2-sulfonyl quinolines with sodium sulfinate as a sulfonyl precursor. The features such as a wide range of substrates, and functional group tolerance, short reaction times, and air-insensitive reaction conditions make the present method an attractive alternative for the preparation of 2-sulfonylquinolines. Furthermore, the arylsulfonylation derivatives of six-membered *N*-heterocycles have also been synthesized by the reaction of heteroaryl halide with sodium arylsulfinates.

4 Experimental section

4.1 General information

All substrates were purchased from J & K Scientific Ltd (Beijing, China), and were used without further purification. Column chromatography was performed using 300–400 mesh silica with the indicated solvent system according to standard techniques. A CEM Discover microwave reactor with an infrared pyrometer and pressure control system was used. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 400 MHz spectrometer. Chemical shifts for ^{1}H NMR spectra are recorded in parts per million with tetramethylsilane as a standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad), coupling constant in Hz, and integration. Chemical shifts for ^{13}C NMR spectra were recorded in parts per million with tetramethylsilane as a standard. Chemical shifts for ^{19}F NMR spectra were recorded in parts per million with CF_3COOH as an external standard. HRMS were obtained on a Thermo Scientific LTQ Orbitrap XL instrument using the electrospray ionization (ESI) technique. IR spectra were recorded on a Shimadazu IR-408 Fourier transform infrared spectrophotometer using a thin film supported on KBr pellets. Melting points were measured on XT4A microscopic apparatus and were uncorrected.

4.2 General experimental procedure for the synthesis of 2-arylsulfonyl quinolines (3) and six-membered N-heterocycles arylsulfonylated derivatives (5)

2-Chloroquinoline (substituted quinolines, and *N*-heteroaryl halide **4**) **1** (0.3 mmol), and sodium sulfinates **2** (0.45 mmol) in 3.0 mL DMSO were added to a 5.0 mL microwave reaction tube. The reactant mixture was heated at 120°C for 30 min under microwave irradiation. After completion of the reaction, the solvent was distilled under vacuum. Then, 10 mL ethyl acetate was added to the residuum, and 30 mL saturated sodium chloride solution washed three times. The organic phase was dried over anhydrous $NaSO_4$ and concentrated under vacuum. The crude product was purified by silica gel column chromatography to give the desired products **3** (or **5**) using ethyl acetate-petroleum ether (1:10–1:5) as eluant.

4.2.1 2-(Phenylsulfonyl)quinoline (3aa)

Light yellow solid; yield 47.3 mg (88%); m.p. 157–158°C (EtOAc) [lit. [14]: m.p. 164–165°C]. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.38$ (d, $J_{H-H} = 8.5$ Hz, 1H), 8.22 (d, $J_{H-H} = 8.5$ Hz, 1H), 8.18 (d, $J_{H-H} = 8.6$ Hz, 1H), 8.15 (d, $J_{H-H} = 8.6$ Hz, 2H), 7.88 (d, $J_{H-H} = 8.2$ Hz, 1H), 7.79 (t, $J_{H-H} = 7.2$ Hz, 1H), 7.66 (t, $J_{H-H} = 7.4$ Hz, 1H), 7.61 (t, $J_{H-H} = 7.2$ Hz, 1H), 7.54 (t, $J_{H-H} = 7.2$ Hz, 2H). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 158.1$, 147.4, 139.1, 138.7 (CH), 133.7 (CH), 131.0 (CH), 130.4 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.8, 127.7 (CH), 117.7 (CH). – IR (KBr): $\nu = 1587$, 1493, 1462, 1317, 1161, 1130, 758, 721, 644 cm^{-1}. – HRMS ((+)-ESI): $m/z = 270.0583$ (calcd. 270.0583 for $C_{15}H_{12}NO_2S$, $[M+H]^+$).

4.2.2 2-((4-(tert-Butyl)phenyl)sulfonyl)quinoline (3ab)

Light yellow solid; yield 57.8 mg (89%); m.p. 194–195°C (EtOAc) [lit. [14]: m.p. 197–198°C]. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.37$ (d, $J_{H-H} = 8.5$ Hz, 1H), 8.20 (d, $J_{H-H} = 8.5$ Hz, 2H), 8.06 (d, $J_{H-H} = 8.6$ Hz, 2H), 7.87 (d, $J_{H-H} = 8.2$ Hz, 1H), 7.79 (td, $J_{H-H} = 7.7$ Hz, $J_{H-H} = 1.4$ Hz, 1H), 7.65 (td, $J_{H-H} = 7.5$ Hz, $J_{H-H} = 1.0$ Hz, 1H), 7.54 (d, $J_{H-H} = 8.6$ Hz, 2H), 1.30 (s, 9H). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 158.4$, 157.7, 147.5, 138.6 (CH), 136.1, 130.9 (CH), 130.4 (CH), 129.1 (CH), 128.9, 128.8 (CH), 127.7 (CH), 126.1 (CH), 117.8 (CH), 35.2, 31.0 (CH_3). – IR (KBr): $\nu = 2956$, 2854, 1331, 1176, 1074, 764, 640 cm^{-1}. – HRMS ((+)-ESI): $m/z = 326.1209$ (calcd. 326.1209 for $C_{19}H_{20}NO_2S$, $[M+H]^+$).

4.2.3 2-((4-Methoxyphenyl)sulfonyl)quinoline (3ac)

White solid; yield 55.0 mg (92%); m.p. 133–134°C (EtOAc) [lit. [14]: m.p. 129–131°C]. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.35$ (d, $J_{H-H} = 8.6$ Hz, 1H), 8.17 (dd, $J_{H-H} = 8.5$ Hz, $J_{H-H} = 5.9$ Hz, 2H), 8.07 (d, $J_{H-H} = 8.9$ Hz, 2H), 7.86 (d, $J_{H-H} = 7.8$ Hz, 1H), 7.77 (t, $J_{H-H} = 7.6$ Hz, 1H), 7.64 (t, $J_{H-H} = 7.6$ Hz, 1H), 6.99 (d, $J_{H-H} = 8.9$ Hz, 2H), 3.84 (s, 3H). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 163.9$, 158.6, 147.4, 138.7 (CH), 131.2 (CH), 130.9 (CH), 130.4, 130.3 (CH), 129.0 (CH), 128.7, 127.7 (CH), 117.5 (CH), 114.4 (CH), 55.6 (CH_3). – IR (KBr): $\nu = 3037$, 2958, 1566, 1591, 1498, 1323, 1265, 1173, 1084, 795, 685 cm^{-1}. – HRMS ((+)-ESI): $m/z = 300.0684$ (calcd. 300.0689 for $C_{16}H_{14}NO_3S$, $[M+H]^+$).

4.2.4 2-((4-Fluorophenyl)sulfonyl)quinoline (3ad)

Light yellow solid; yield 41.9 mg (73%); m.p. 117–118°C (EtOAc) [lit. [14]: m.p. 120–122°C]. – ^{1}H NMR (400 MHz,

$CDCl_3$): δ = 8.40 (d, J_{H-H} = 8.6 Hz, 1H), 8.22–8.14 (m, 4H), 7.89 (d, J_{H-H} = 8.2 Hz, 2H), 7.80 (td, J_{H-H} = 7.0 Hz, J_{H-H} = 1.2 Hz, 1H), 7.67 (t, J_{H-H} = 7.2 Hz, 1H), 7.22 (t, J_{H-H} = 8.6 Hz, 2H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9 (d, J_{F-C} = 254.8 Hz), 157.9, 147.5, 138.8 (CH), 134.9, 132.0 (CH), 131.9 (CH), 131.1 (CH), 130.4 (CH), 129.3 (CH), 128.9, 127.7 (CH), 117.5 (CH), 116.4 (d, J_{F-C} = 22.5 Hz, CH). – ^{19}F NMR (376 MHz, $CDCl_3$): δ = –103.4. – IR (KBr): ν = 1591, 1487, 1333, 1244, 1173, 1130, 1084, 850, 679, 550 cm^{-1}. – HRMS ((+)-ESI): m/z = 288.0489 (calcd. 288.0489 for $C_{15}H_{11}FNO_2S$, $[M+H]^+$).

4.2.5 2-((4-Chlorophenyl)sulfonyl)quinoline (3ae)

Light yellow solid; yield 45.4 mg (75%); m.p. 131–132°C (EtOAc) [lit. [14]: m.p. 136–137°C]. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, J_{H-H} = 8.5 Hz, 1H), 8.21 (d, J_{H-H} = 8.5 Hz, 1H), 8.15 (d, J_{H-H} = 8.5 Hz, 1H), 8.08 (dd, J_{H-H} = 6.8 Hz, J_{H-H} = 1.9 Hz, 2H), 7.89 (d, J_{H-H} = 8.2 Hz, 1H), 7.80 (td, J_{H-H} = 8.4 Hz, J_{H-H} = 1.4 Hz, 1H), 7.67 (td, J_{H-H} = 8.0 Hz, J_{H-H} = 1.1 Hz, 1H), 7.51 (d, J_{H-H} = 6.8 Hz, 2H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 147.5, 140.6, 138.9 (CH), 137.5, 131.2 (CH), 130.6 (CH), 130.3 (CH), 129.4 (CH), 129.3 (CH), 128.9, 127.7 (CH), 117.5 (CH). – IR (KBr): ν =1581, 1319, 1161, 1134, 1084, 764, 652 cm^{-1}. – HRMS ((+)-ESI): m/z = 304.0190 (calcd. 304.0193 for $C_{15}H_{11}ClNO_2S$, $[M+H]^+$).

4.2.6 2-((4-Bromophenyl)sulfonyl)quinoline (3af)

Light yellow solid; yield 53.9 mg (78%); m.p. 141–142°C (EtOAc) [lit. [14]: m.p. 143–145°C]. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, J_{H-H} = 8.6 Hz, 1H), 8.20 (d, J_{H-H} = 8.6 Hz, 1H), 8.15 (d, J_{H-H} = 8.6 Hz, 1H), 8.00 (d, J_{H-H} = 8.6 Hz, 2H), 7.89 (d, J_{H-H} = 8.2 Hz, 1H), 7.80 (td, J_{H-H} = 7.0 Hz, J_{H-H} = 1.4 Hz, 1H), 7.69–7.67 (m, 3H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7, 147.5, 138.9 (CH), 138.0, 132.4 (CH), 131.2 (CH), 130.6 (CH), 130.3 (CH), 129.4, 129.3 (CH), 128.9, 127.7 (CH), 117.5 (CH). – IR (KBr): ν = 1566, 1331, 1132, 1003, 742, 646 cm^{-1}. – HRMS ((+)-ESI): m/z = 347.9686 (calcd. 347.9688 for $C_{15}H_{11}BrNO_2S$, $[M+H]^+$).

4.2.7 4-(Quinolin-2-ylsulfonyl)benzonitrile (3ag)

Light yellow solid; yield 39.9 mg (68%); m.p. 190–191°C (EtOAc). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, J_{H-H} = 8.5 Hz, 1H), 8.27 (d, J_{H-H} = 8.5 Hz, 2H), 8.23 (d, J_{H-H} = 8.5 Hz, 1H), 8.13 (d, J_{H-H} = 8.6 Hz, 1H), 7.91 (d, J_{H-H} = 8.3 Hz, 1H), 7.84 (d, J_{H-H} = 8.5 Hz, 2H), 7.72–7.68 (m, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0, 147.5, 143.2, 139.0 (CH), 132.7 (CH), 131.3 (CH), 130.3, 129.8 (CH), 129.6 (CH), 129.0, 127.8 (CH), 117.5 (CH), 117.2. – IR (KBr): ν = 2229, 1498, 1323, 1167, 1124, 1063, 829 cm^{-1}. – HRMS ((+)-ESI): m/z = 295.0538 (calcd. 295.0536 for $C_{16}H_{11}N_2O_2S$, $[M+H]^+$).

4.2.8 2-((4-(Trifluoromethyl)phenyl)sulfonyl)quinoline (3ah)

White solid; yield 47.2 mg (70%); m.p. 122–123°C (EtOAc) [lit. [14]: m.p. 128–129°C]. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (d, J_{H-H} = 8.6 Hz, 1H), 8.29 (d, J_{H-H} = 8.3 Hz, 2H), 8.24 (d, J_{H-H} = 8.5 Hz, 1H), 8.16 (d, J_{H-H} = 8.6 Hz, 1H), 7.91 (d, J_{H-H} = 8.2 Hz, 1H), 7.84–7.80 (m, 3H), 7.69 (td, J_{H-H} = 8.1 Hz, J_{H-H} = 1.0 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 147.5, 142.6, 139.0 (CH), 131.3 (CH), 130.3 (CH), 129.7 (CH), 129.5 (CH), 128.9, 127.7 (CH), 126.1 (q, J_{F-C} = 3.6 Hz), 117.5 (CH). ^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.2. – IR (KBr): ν = 1410, 1323, 1173, 1053, 706, 644 cm^{-1}. – HRMS ((+)-ESI): m/z = 338.0456 (calcd. 338.0457 for $C_{16}H_{11}F_3NO_2S$, $[M+H]^+$).

4.2.9 2-((2-Chlorophenyl)sulfonyl)quinoline (3ai)

Light yellow solid; yield 44.2 mg (73%); m.p. 165–166°C (EtOAc) [lit. [14]: m.p. 166–167°C]. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52–8.50 (m, 1H), 8.45 (d, J_{H-H} = 8.6 Hz, 1H), 8.34 (d, J_{H-H} = 8.6 Hz, 1H), 8.05 (d, J_{H-H} = 8.6 Hz, 1H), 7.92 (d, J_{H-H} = 8.5 Hz, 1H), 7.79–7.74 (m, 1H), 7.70–7.66 (m, 1H), 7.59–7.56 (m, 2H), 7.43–7.40 (m, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 147.2, 138.3 (CH), 136.7, 134.9 (CH), 133.1, 132.2 (CH), 131.5 (CH), 130.9 (CH), 130.3 (CH), 129.2 (CH), 129.0, 127.8 (CH), 127.2 (CH), 118.4 (CH). – IR (KBr): ν = 1572, 1448, 1309, 1157, 1039, 748, 559 cm^{-1}. – HRMS ((+)-ESI): m/z = 304.0197 (calcd. 304.0193 for $C_{15}H_{11}ClNO_2S$, $[M+H]^+$).

4.2.10 N-(4-(Quinolin-2-ylsulfonyl)phenyl)acetamide (3aj)

Colorless solid; yield 39.1 mg (60%); m.p. 220–221°C (EtOAc). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.45 (s, 1H), 8.72 (d, J_{H-H} = 8.6 Hz, 1H), 8.22 (d, J_{H-H} = 8.6 Hz, 1H), 8.11 (d, J_{H-H} = 8.2 Hz, 1H), 8.06 (d, J_{H-H} = 8.5 Hz, 1H), 7.99 (d, J_{H-H} = 8.7 Hz, 2H), 7.89–7.82 (m, 3H), 7.75 (t, J_{H-H} = 7.5 Hz, 1H), 2.07 (s, 3H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.7, 158.5, 146.9, 144.9, 140.3 (CH), 132.1 (CH), 132.0, 130.4 (CH), 129.8 (CH), 129.7 (CH), 128.9, 128.7 (CH), 119.2 (CH), 117.9 (CH), 24.6 (CH_3). – IR (KBr): ν = 3338, 3286, 1699, 1591, 1520, 1498, 1313, 1171, 1130, 1072, 719 cm^{-1}. – HRMS ((+)-ESI): m/z = 327.0795 (calcd. 327.0798 for $C_{17}H_{15}N_2O_3S$, $[M+H]^+$).

4.2.11 2-(Methylsulfonyl)quinoline (3ak)

Light yellow solid; yield 24.0 mg (58%); m.p. 98–99°C (EtOAc) [lit. [14]: m.p. 100–101°C]. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (d, $J_{H–H}$ = 8.5 Hz, 1H), 8.14 (d, $J_{H–H}$ = 8.5 Hz, 1H), 8.06 (d, $J_{H–H}$ = 8.5 Hz, 1H), 7.88 (d, $J_{H–H}$ = 8.2 Hz, 1H), 7.79 (t, $J_{H–H}$ = 8.0 Hz, 1H), 7.65 (t, $J_{H–H}$ = 7.7 Hz, 1H), 3.34 (s, 3H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 146.9, 139.0 (CH), 131.3 (CH), 130.0 (CH), 129.3 (CH), 129.1, 127.9 (CH), 116.2 (CH), 39.9 (CH_3). – IR (KBr): ν = 3014, 2931, 1581, 1498, 1304, 1171, 1130, 831, 769 cm^{-1}. – HRMS ((+)-ESI): m/z = 208.0431 (calcd. 208.0427 for $C_{10}H_{10}NO_2S$, $[M+H]^+$).

4.2.12 2-(Ethylsulfonyl)quinoline (3al)

Light yellow solid; yield 30.5 mg (69%); m.p. 104–105°C (EtOAc) [lit. [14]: m.p. 106–107°C]. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, $J_{H–H}$ = 8.5 Hz, 1H), 8.22 (d, $J_{H–H}$ = 8.5 Hz, 1H), 8.13 (d, $J_{H–H}$ = 8.5 Hz, 1H), 7.94 (d, $J_{H–H}$ = 8.2 Hz, 1H), 7.85 (td, $J_{H–H}$ = 6.9 Hz, $J_{H–H}$ = 1.2 Hz, 1H), 7.71 (t, $J_{H–H}$ = 7.1 Hz, 1H), 3.59 (q, $J_{H–H}$ = 7.5 Hz, 2H), 1.37 (t, $J_{H–H}$ = 7.5 Hz, 3H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.4, 147.2, 138.8 (CH), 131.2 (CH), 130.1 (CH), 129.2 (CH), 129.1, 127.9 (CH), 117.4, 46.4 (CH_2), 6.9 (CH_3). – IR (KBr): ν = 2927, 1581, 1498, 1313, 1149, 1130, 1099, 847, 764, 719 cm^{-1}. – HRMS ((+)-ESI): m/z = 222.0585 (calcd. 222.0583 for $C_{11}H_{12}NO_2S$, $[M+H]^+$).

4.2.13 6-Chloro-2-(phenylsulfonyl)quinoline (3ca)

Light yellow solid; yield 45.4 mg (75%); m.p. 161–162°C (EtOAc) [lit. [14]: m.p. 165–166°C]. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, $J_{H–H}$ = 8.6 Hz, 1H), 8.23 (d, $J_{H–H}$ = 8.6 Hz, 1H), 8.14–8.08 (m, 3H), 7.86 (d, $J_{H–H}$ = 2.2 Hz, 1H), 7.71 (dd, $J_{H–H}$ = 8.9 Hz, $J_{H–H}$ = 2.2 Hz, 1H), 7.62 (t, $J_{H–H}$ = 7.3 Hz, 1H), 7.55 (t, $J_{H–H}$ = 7.8 Hz, 2H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 145.8, 138.8, 137.8 (CH), 136.2, 135.3, 133.8 (CH), 132.1 (CH), 131.9 (CH), 129.2 (CH), 129.1 (CH), 126.4, 118.7 (CH). – IR (KBr): ν = 1493, 1437, 1327, 1161, 1136, 727, 679, 586 cm^{-1}. – HRMS ((+)-ESI): m/z = 304.0195 (calcd. 304.0194 for $C_{15}H_{11}ClNO_2S$, $[M+H]^+$).

4.2.14 8-Methyl-2-(phenylsulfonyl)quinoline (3da)

Light yellow solid; yield 48.1 mg (85%); m.p. 105–106°C (EtOAc) [lit. [13]: m.p. 106–107°C]. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, $J_{H–H}$ = 8.5 Hz, 1H), 8.22–8.17 (m, 3H), 7.69 (d, $J_{H–H}$ = 8.1 Hz, 1H), 7.63–7.50 (m, 5H), 2.65 (s, 3H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1, 146.3, 138.9, 138.7 (CH), 138.4, 133.6 (CH), 130.9 (CH), 129.4 (CH), 129.0 (CH), 128.9, 128.8 (CH), 125.5 (CH), 116.7 (CH), 17.4 (CH_3). – IR (KBr): ν = 3068, 2922, 1493, 1452, 1323, 1167, 1074, 731, 580 cm^{-1}. – HRMS ((+)-ESI): m/z = 284.0739 (calcd. 284.0740 for $C_{16}H_{14}NO_2S$, $[M+H]^+$).

4.2.15 6-Methoxy-2-(phenylsulfonyl)quinoline (3ea)

White solid; yield 51.4 mg (86%); m.p. 145–146°C (EtOAc) [lit. [13]: m.p. 147–149°C]. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, $J_{H–H}$ = 8.5 Hz, 1H), 8.17–8.11 (m, 3H), 8.06 (d, $J_{H–H}$ = 9.3 Hz, 1H), 7.61–7.57 (m, 1H), 7.54–7.51 (m, 2H), 7.42 (dd, $J_{H–H}$ = 9.3 Hz, $J_{H–H}$ = 2.8 Hz, 1H), 7.09 (d, $J_{H–H}$ = 2.8 Hz, 1H), 3.94 (s, 3H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 155.4, 143.7, 139.5, 136.8 (CH), 133.5 (CH), 131.8 (CH), 130.4, 129.0 (CH), 128.9 (CH), 124.3 (CH), 118.3 (CH), 104.6 (CH), 55.7 (CH_3). – IR (KBr): ν = 2925, 2844, 1618, 1500, 1321, 1173, 850, 604 cm^{-1}. – HRMS ((+)-ESI): m/z = 300.0685 (calcd. 300.0689 for $C_{16}H_{14}NO_3S$, $[M+H]^+$).

4.2.16 6-Methyl-2-(phenylsulfonyl)quinoline (3fa)

Yellow solid; yield 46.4 mg (82%); m.p. 149–150°C (EtOAc) [lit. [13]: m.p. 150–152°C]. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (d, $J_{H–H}$ = 8.5 Hz, 1H), 8.17–8.11 (m, 3H), 8.05 (d, $J_{H–H}$ = 8.5 Hz, 1H), 7.61–7.56 (m, 3H), 7.54–7.50 (m, 2H), 2.54 (s, 3H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1, 146.1, 139.7, 139.3, 137.8 (CH), 133.6 (CH), 133.4 (CH), 130.0 (CH), 129.0 (CH), 128.9 (CH), 126.4 (CH), 117.8 (CH), 21.8 (CH_3). – IR (KBr): ν = 2916, 2844, 1454, 1321, 1167, 1070, 600 cm^{-1}. – HRMS ((+)-ESI): m/z = 284.0733 (calcd. 284.0740 for $C_{16}H_{14}NO_2S$, $[M+H]^+$).

4.2.17 4-Methyl-2-(phenylsulfonyl)quinoline (3ga)

Light yellow solid; yield 48.1 mg (85%); m.p. 146–147°C (EtOAc) [lit. [13]: m.p. 145–146°C]. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16–8.12 (m, 3H), 8.04 (s, 1H), 7.99 (d, $J_{H–H}$ = 8.4 Hz, 1H), 7.74 (td, $J_{H–H}$ = 6.9 Hz, $J_{H–H}$ = 1.2 Hz, 1H), 7.64 (td, $J_{H–H}$ = 8.2 Hz, $J_{H–H}$ = 1.2 Hz, 1H), 7.60–7.56 (m, 1H), 7.51 (t, $J_{H–H}$ = 7.0 Hz, 2H), 2.77 (s, 3H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7, 148.0, 147.2, 139.2, 133.6 (CH), 131.0 (CH), 130.5 (CH), 129.0 (CH), 128.9 (CH), 128.7, 123.8 (CH), 118.1 (CH), 19.1 (CH_3). – IR (KBr): ν = 3072, 2922, 1570, 1437, 1321, 1161, 729, 621 cm^{-1}. – HRMS ((+)-ESI): m/z = 284.0739 (calcd. 284.0740 for $C_{16}H_{14}NO_2S$, $[M+H]^+$).

4.2.18 7-Chloro-4-(phenylsulfonyl)quinoline (3ia)

Colorless solid; yield 41.2 mg (68%); m.p. 170–171°C (EtOAc). – ^{1}H NMR (400 MHz, DMSO): δ = 9.24 (d, J_{H-H} = 4.4 Hz, 1H), 8.57 (d, J_{H-H} = 9.2 Hz, 1H), 8.26 (d, J_{H-H} = 4.5 Hz, 1H), 8.23 (d, J_{H-H} = 2.2 Hz, 1H), 8.06 (d, J_{H-H} = 8.8 Hz, 2H), 7.80 (dd, J_{H-H} = 9.2 Hz, J_{H-H} = 2.2 Hz, 1H), 7.73 (t, J_{H-H} = 7.4 Hz, 1H), 7.64 (t, J_{H-H} = 7.3 Hz, 2H). – ^{13}C NMR (100 MHz, DMSO): δ = 157.3 (CH), 154.2, 149.2, 144.4, 140.5, 139.8 (CH), 135.2 (CH), 134.9 (CH), 134.1 (CH), 132.9 (CH), 130.8 (CH), 127.3 (CH), 124.8. – IR (KBr): ν = 1485, 1433, 1315, 1151, 870 cm^{-1}. – HRMS ((+)-ESI): m/z = 304.0189 (calcd. 304.0194 for $C_{15}H_{11}ClNO_2S$, $[M+H]^+$).

4.2.19 4-Chloro-2-(phenylsulfonyl)pyridine (5aa)

Colorless solid; yield 22.7 mg (45%); m.p. 102–103°C (EtOAc). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (d, J_{H-H} = 5.1 Hz, 1H), 7.98 (d, J_{H-H} = 7.9 Hz, 2H), 7.82 (s, 1H), 7.70 (t, J_{H-H} = 5.1 Hz, 1H), 7.66 (d, J_{H-H} = 7.6 Hz, 1H), 7.58 (t, J_{H-H} = 7.6 Hz, 2H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8, 152.4, 151.2 (CH), 138.9, 134.5 (CH), 129.8 (CH), 128.2 (CH), 121.7 (CH), 119.5 (CH). – IR (KBr): ν = 1534, 1458, 1423, 1305, 1152, 879 cm^{-1}. – HRMS ((+)-ESI): m/z = 254.0038 (calcd. 254.0037 for $C_{11}H_9ClNO_2S$, $[M+H]^+$).

4.2.20 2,4-Bis(phenylsulfonyl)pyridine (5′aa)

Colorless solid; yield 21.5 mg (30%); m.p. 107–108°C (EtOAc). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.85 (d, J_{H-H} = 4.9 Hz, 1H), 8.61 (s, 1H), 8.05 (d, J_{H-H} = 8.0 Hz, 2H), 7.99 (d, J_{H-H} = 8.0 Hz, 2H), 7.94 (d, J_{H-H} = 4.9 Hz, 1H), 7.68–7.55 (m, 6H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.7, 152.5, 152.0 (CH), 138.6, 137.7, 134.8 (CH), 134.4 (CH), 130.0 (CH), 129.3 (CH), 129.2 (CH), 128.4 (CH), 123.9 (CH), 119.2 (CH). – IR (KBr): ν = 1526, 1450, 1417, 1321, 1143 cm^{-1}. – HRMS ((+)-ESI): m/z = 360.0362 (calcd. 360.0359 for $C_{17}H_{14}NO_4S_2$, $[M+H]^+$).

4.2.21 4-(Phenylsulfonyl)pyridine (5ba)

Colorless solid; yield 34.1 mg (78%); m.p. 128–129°C (EtOAc). – ^{1}H NMR (400 MHz, CDCl): δ = 8.84 (d, J_{H-H} = 5.7 Hz, 2H), 8.01 (d, J_{H-H} = 7.5 Hz, 2H), 7.82 (d, J_{H-H} = 5.8 Hz, 2H), 7.63 (t, J_{H-H} = 7.4 Hz, 1H), 7.55 (t, J_{H-H} = 7.7 Hz, 3H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.2 (CH), 149.6, 139.5, 134.2 (CH), 129.6 (CH), 128.0 (CH), 120.5 (CH). – IR (KBr): ν = 1553, 1437, 1420, 1322, 1134 cm^{-1}. – HRMS ((+)-ESI): m/z = 220.0430 (calcd. 220.0427 for $C_{11}H_{10}NO_2S$, $[M+H]^+$).

4.2.22 2-Chloro-6-(phenylsulfonyl)pyridine (5ca) [9]

Colorless solid; yield 23.7 mg (47%); m.p. 131–132°C (EtOAc). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J_{H-H} = 7.6 Hz, 1H), 8.07 (d, J_{H-H} = 8.0 Hz, 2H), 7.88 (t, J_{H-H} = 7.8 Hz, 1H), 7.64 (t, J_{H-H} = 7.1 Hz, 1H), 7.55 (t, J_{H-H} = 7.7 Hz, 2H), 7.47 (d, J_{H-H} = 8.0 Hz, 2H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 152.3, 140.4 (CH), 138.2, 134.1 (CH), 129.2 (CH), 129.1 (CH), 128.1 (CH), 120.6 (CH). – IR (KBr): ν = 1582, 1447, 1395, 1307, 1151, 1126, 1082 cm^{-1}. – HRMS ((+)-ESI): m/z = 254.0039 (calcd. 254.0037 for $C_{11}H_9ClNO_2S$, $[M+H]^+$).

4.2.23 2,6-Bis(phenylsulfonyl)pyridine (5′ca)

Colorless solid; yield 20.1 mg (28%); m.p. 178–179°C (EtOAc) [lit. [26] m.p. 178.1–180.4°C]. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, J_{H-H} = 7.9 Hz, 2H), 8.16 (d, J_{H-H} = 7.6 Hz, 1H), 7.91 (d, J_{H-H} = 8.1 Hz, 4H), 7.64 (t, J_{H-H} = 7.2 Hz, 2H), 7.49 (t, J_{H-H} = 7.7 Hz, 4H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 140.5 (CH), 137.4, 134.2 (CH), 129.4 (CH), 129.0 (CH), 124.1 (CH). – IR (KBr): ν = 1534, 1452, 1427, 1325, 1137, 1075 cm^{-1}. – HRMS ((+)-ESI): m/z = 360.0357 (calcd. 360.0359 for $C_{17}H_{14}NO_4S_2$, $[M+H]^+$).

4.2.24 5-Ethyl-2-(phenylsulfonyl)pyrimidine (5da)

Colorless liquid; yield 41.6 mg (84%); – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66 (s, 2H), 8.23 (d, J_{H-H} = 4.9 Hz, 1H), 8.06–8.04 (m, 2H), 7.62–7.58 (m, 1H), 7.52–7.48 (m, 2H), 2.67 (q, J_{H-H} = 7.6 Hz, 2H), 1.22 (t, J_{H-H} = 7.6 Hz, 3H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 157.9 (CH), 139.5, 137.8, 134.2 (CH), 129.3 (CH), 129.1 (CH), 23.5 (CH_2), 14.5 (CH_3). – IR (KBr): ν = 2974, 1937, 1556, 1396, 1325, 1134, 1078, 729 cm^{-1}. – HRMS ((+)-ESI): m/z = 249.0690 (calcd. 249.0692 for $C_{12}H_{13}N_2O_2S$, $[M+H]^+$).

4.2.25 2-(Phenylsulfonyl)pyrimidine (5ea)

Light yellow solid; yield 37.4 mg (85%); m.p. 117–118°C (EtOAc) [lit. [27]: m.p. 118–119°C]. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, J_{H-H} = 4.9 Hz, 2H), 8.02 (dd, J_{H-H} = 7.8 Hz, J_{H-H} = 1.4 Hz, 2H), 7.59 (t, J_{H-H} = 7.4 Hz, 1H), 7.50–7.45 (m, 3H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 158.8 (CH), 137.4, 134.4 (CH), 129.4 (CH), 129.2 (CH), 123.5 (CH). – IR (KBr): ν = 1576, 1446, 1385, 1317, 1203, 1146, 1084, 715, 602 cm^{-1}. – HRMS ((+)-ESI): m/z = 221.0381 (calcd. 221.0379 for $C_{10}H_9N_2O_2S$, $[M+H]^+$).

4.2.26 4-Chloro-2-(phenylsulfonyl)pyrimidine (5fa)

White solid; yield 24.3 mg (48%); m.p. 115–116°C (EtOAc). – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.95$ (d, $J_{H-H} = 4.9$ Hz, 1H), 8.08–8.05 (m, 3H), 7.74–7.70 (m, 1H), 7.63–7.59 (m, 2H). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 168.8$, 162.7 (CH), 162.1, 136.4, 135.0 (CH), 129.6 (CH), 129.5 (CH), 116.1 (CH). – IR (KBr): $\nu = 1545$, 1452, 1333, 1182, 1084, 727, 679 cm^{-1}. – HRMS ((+)-ESI): $m/z = 254.9992$ (calcd. 254.9990 for $C_{10}H_8ClN_2O_2S$, $[M+H]^+$).

4.2.27 2,4-Bis(phenylsulfonyl)pyrimidine (5′fa)

Light yellow solid; yield 20.1 mg (28%); m.p. 107–108°C (EtOAc). – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.24$ (d, $J_{H-H} = 4.9$ Hz, 1H), 8.23 (d, $J_{H-H} = 4.9$ Hz, 1H), 7.96 (dd, $J_{H-H} = 8.2$ Hz, $J_{H-H} = 0.9$ Hz, 2H), 7.89 (dd, $J_{H-H} = 8.2$ Hz, $J_{H-H} = 0.9$ Hz, 2H), 7.73–7.66 (m, 2H), 7.56–7.53 (m, 4H). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 167.9$, 167.0, 162.4 (CH), 136.2, 135.7, 135.1 (CH), 134.7 (CH), 129.8 (CH), 129.7 (CH), 129.4 (CH), 129.2 (CH), 119.3 (CH). – IR (KBr): $\nu = 1554$, 1535, 1323, 1157, 1090, 727, 685 cm^{-1}. – HRMS ((+)-ESI): $m/z = 361.0315$ (calcd. 361.0311 for $C_{16}H_{13}N_2O_4S_2$, $[M+H]^+$).

5 Supplementary information

The NMR spectra of **3aa**–**3ia**, **5aa**–**5′fa** are given as Supplementary Information available online (https://doi.org/10.1515/znb-2018-0007).

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Graphical synopsis

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