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A Four-Component Reaction for the Synthesis of *β*-Quinoline Allylic Sulfones under Iron Catalysis

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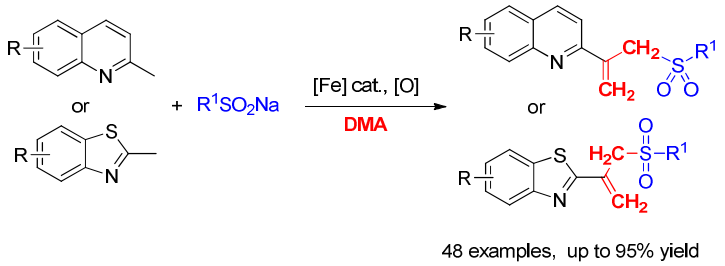


48 examples, up to 95% yield

ABSTRACT: An efficient strategy for the preparation of allylic sulfones has been developed. In this protocol, readily available 2-methylquinolines or 2-methylbenzothiazoles, sodium sulfinates and dimethylacetamide (DMA) were successfully assembled under user-friendly iron catalysis. And DMA provided two carbons as a dual synthon. A broad range of functionalized heterocyclic allylic sulfones were accessed with a wide functional group tolerance.

■ INTRODUCTION

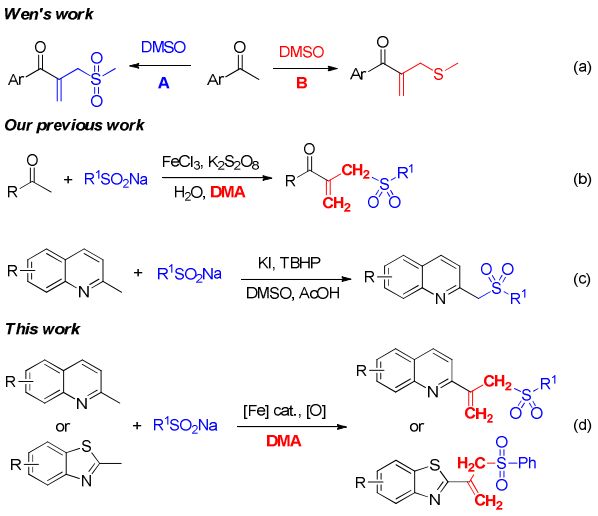
Quinoline derivatives widely exist in natural products, bioactive pharmaceutical drugs, and functional materials.[1] Among them, 2-alkenylquinoline regards as one of the typical molecular skeletons possessing significant bioactivities.[2] Moreover, quinoline compounds were also used as significant and versatile structural skeletal frameworks in molecular synthesis. As a result, direct quinoline functionalization has attracted considerable interest in organic

transformations. Alternatively, 2-methylquinolines frequently serve as a versatile nucleophilic coupling partner (*via* enamine intermediate), which undergoes nucleophilic addition reaction to construct the new C–C,[3] C–N,[4] C–O[5] bonds and among others.[6] For example, Huang and co-workers described an nucleophilic addition reaction between 2-alkyl azaarenes and the C=N double bonds of *N*-sulfonyl aldimines.[7] Very recently, significant progress has been made on the C(sp^3)–H bond functionalization of 2-alkyl azaarenes through oxidative cross dehydrogenative coupling (CDC).[8] Given the highly pharmaceutical and synthetic importance of quinolines and other azaarenes in chemistry, the development of environmentally friendly strategies for their direct functionalization is still highly desirable.

Multicomponent reactions (MCRs) have been established as a powerful methodology in molecular synthesis to show overall considerable atom- and step-economy.[9] Speciffically, many concise multicomponent approaches have been developed to construct C–S bond via the direct C(sp^3)–H bond functionalization.[10] In 2017, Wen and coworkers disclosed the chemoselective formation of allylic sulfones and allylic sulfides from methylketones with DMSO as multi-functional synthons, in which three molecules of DMSO were incorperated into the final products (Scheme 1a).[11] Recently, we reported on an iron-catalyzed three-component reaction with *N*,*N*-dimethylacetamide (DMA) as the dual carbon source and sodium sulfinates as the sulfone precursor to afford allylic sulfones (Scheme 1b).[12] As our continuing interest in C–H bond functionalization of methylquinolins including oxidative sulfonylation (Scheme 1c),[13] herein, we developed a simple and efficient three-component four-molecular approach for the synthesis of allylic sulfones bearing quinoline and benzothiazole motifs from readily available 2-methylheterocycles, sodium sulfinates, and

DMA (Scheme 1d). In this protocol, earth-abundant, cheap and low-toxic iron(III) chloride was used as the most effective catalyst and DMA provides two carbons (-CH_2- and =CH_2) as a dual synthon. Most importantly, this work provides a viable and sustainable access to highly functionalized quinolines and benzothiazoles.

Scheme 1. C-S Bond Formation via C(sp^3)–H Bond Functionalization.

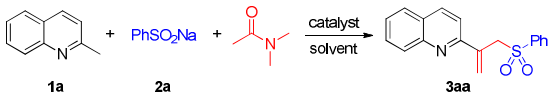


■ RESULTS AND DISCUSSION

Synthesis of *β*-Quinoline Allylic Sulfones. For the optimization of reaction conditions, we chosen 2-methylquinoline (**1a**) and sodium benzenesulfinate (**2a**) as starting materials (Table 1). To our pleasure, the corresponding product **3aa** was obtained in 52% yield when the reaction was carried out with $FeCl_3$ (10 mol%) and $K_2S_2O_8$ (3.5 equiv) in DMA at 110 °C for 14 h, while other metal salts such as $NiCl_2$ and $CuCl_2$ did not give the product (entries 1–3). Then, elevated or reduced reaction temperature could not enhance the transformation (entries 4–5). We also tried to modify the amount of the oxidant, in which 3.5 equiv of $K_2S_2O_8$ proved to be optimal (entries 6–8). To our delight, the reaction yield was significantly increased when

a mixture of DMA/H_2O (v/v = 10:1) was used as the solvent (entry 9). With this co-solvent system, some other iron catalysts such as $Fe(NO_3)_3$, $Fe(acac)_3$, $Fe(SO_4)_2$ •$7H_2O$ and $FeCl_2$ •$4H_2O$ provided lower yields (entries 10–13). The variation of the oxidant showed that $K_2S_2O_8$ was superior to $Na_2S_2O_8$, oxone and $K_2S_2O_5$ (entries 14–16). The addition of other protic solvents such as alcohol and CH_3COOH showed that H_2O gave the best result (entries 17–18). Decreasing or increasing the amount of H_2O did not enhance the reaction yields (entries 19–20). Moreover, the desired product was not observed when the reaction was carried out in the absence of the oxidant or iron catalyst (entries 21–22). Finally, air atmosphere found to be superior to oxygen and argon.

Table 1. Screening reaction Conditions[a]



entry	catalyst	oxidant	solvent	temperature (°C)	yield[b] (%)
1	$NiCl_2$	$K_2S_2O_8$	DMA	110	0
2	$CuCl_2$	$K_2S_2O_8$	DMA	110	trace
3	$FeCl_3$	$K_2S_2O_8$	DMA	110	52
4	$FeCl_3$	$K_2S_2O_8$	DMA	100	24
5	$FeCl_3$	$K_2S_2O_8$	DMA	120	36
6[c]	$FeCl_3$	$K_2S_2O_8$	DMA	110	42
7[d]	$FeCl_3$	$K_2S_2O_8$	DMA	110	35
8[e]	$FeCl_3$	$K_2S_2O_8$	DMA	110	43
9	$FeCl_3$	$K_2S_2O_8$	DMA:H_2O = 10:1	110	90

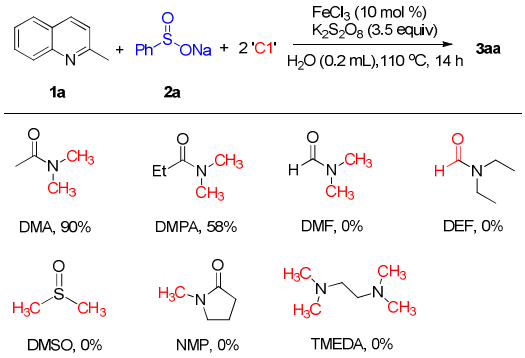
10	$Fe(NO_3)_3$	$K_2S_2O_8$	DMA:H_2O = 10:1	110	21
11	$Fe(acac)_3$	$K_2S_2O_8$	DMA:H_2O = 10:1	110	29
12	$FeSO_4 \cdot 7H_2O$	$K_2S_2O_8$	DMA:H_2O = 10:1	110	5
13	$FeCl_2 \cdot 4H_2O$	$K_2S_2O_8$	DMA:H_2O = 10:1	110	84
14	$FeCl_3$	$Na_2S_2O_8$	DMA:H_2O = 10:1	110	66
15	$FeCl_3$	Oxone	DMA:H_2O = 10:1	110	24
16	$FeCl_3$	$K_2S_2O_5$	DMA:H_2O = 10:1	110	8
17	$FeCl_3$	$K_2S_2O_8$	DMA:EtOH = 10:1	110	54
18	$FeCl_3$	$K_2S_2O_8$	DMA:AcOH = 10:1	110	45
19	$FeCl_3$	$K_2S_2O_8$	DMA:H_2O = 5:1	110	85
20	$FeCl_3$	$K_2S_2O_8$	DMA:H_2O = 20:1	110	77
21	$FeCl_3$	-	DMA:H_2O = 10:1	110	0
22	-	$K_2S_2O_8$	DMA:H_2O = 10:1	110	0
23[f]	$FeCl_3$	$K_2S_2O_8$	DMA:H_2O = 10:1	110	54
24[g]	$FeCl_3$	$K_2S_2O_8$	DMA:H_2O = 10:1	110	60

[a] Conditions: **1a** (0.2 mmol), **2a** (0.5 mmol), catalyst (10 mol %), oxidant (3.5 equiv), DMA (2.0 mL), 110 °C, 14 h, under air atmosphere. [b] Isolated yield based on **1a**. [c] $K_2S_2O_8$ (3.0 equiv). [d] $K_2S_2O_8$ (2.5 equiv). [e] **2a** (1.5 equiv). [f] O_2 atmosphere. [g] Ar atmosphere.

Besides the established DMA as the one carbon synthon, we screened other small molecular compounds which can provide carbon sources for the present four-component reaction (Scheme 2). When *N*,*N*-dimethylpropionamide (DMPA) was used, moderate yield of **3aa** was

observed, while other candidates of carbon sources such as *N*,*N*-dimethylformamide (DMF), *N*,*N*-diethylformamide (DEF), dimethyl sulfoxide (DMSO), *N*-methylpyrrolidone (NMP) and tetramethylethylenediamine (TMEDA) did not afford the desired products. These results show the unique feature of DMA in the reaction system.

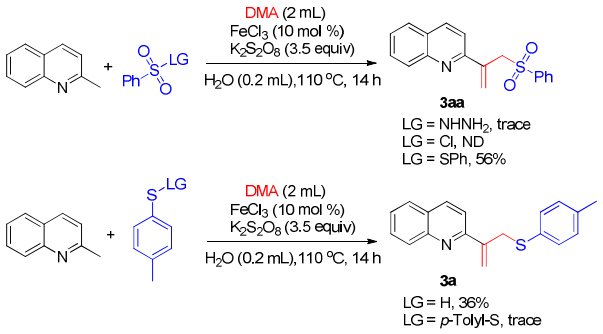
Scheme 2. One Carbon Synthons.[a]



[a] Conditions: **1a** (0.2 mmol), **2a** (0.5 mmol), $FeCl_3$ (10 mol %), $K_2S_2O_8$ (3.5 equiv), 'C1' (2.0 mL), 110 °C, 14 h, air atmosphere.

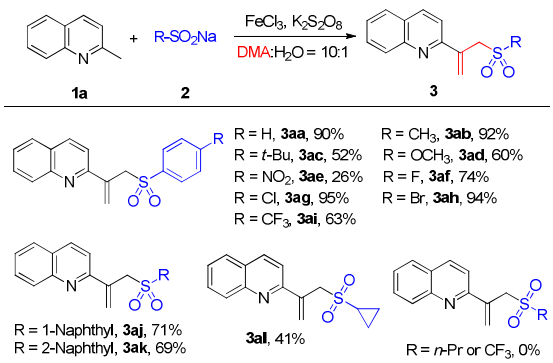
We also investigated other frequently employed sulfone sources for the formation of quinolinyl allylic sulfones (Scheme 3). Unexpectedly, the desired reaction did not occur with sulfonohydrazide and sulfonyl chloride, while modest yield of **3aa** was obtained when we use sulfonothioate instead of sodium benzenesulfinate. Notably, allylicthioether **3a** was formed when 4-methylbenzenethiol was subjected to the standard reaction conditions, while 1,2-di-*p*-tolyldisulfane could not afford the allylicthioether product.

Scheme 3. Other Sulfone Sources.



With the optimized reaction conditions established, a variety of sodium sulfinates were examined for the multi-component transformation (Scheme 4). Generally, a range of *para*-substituted phenyl sodium sulfinates reacted smoothly with **1a** to provide *β*-quinoline allylic sulfones (**3ab**–**3ai**) in moderate to high yields. A variety of functional groups on the benzene ring such as alkyl (**2b**–**2c**), methoxy (**2d**), nitro (**2e**), halo (**2f**–**2h**) and trifluoromethyl (**2i**) were all well tolerated. Notably, carbon–halogen bond cleavage of the substrates was not observed in the present system. The reaction yield decreased dramatically when sodium 4-nitrobenzenesulfinate (**2e**) was used as the substrate, probably because of the highly electron-withdrawing effect. Naphthylsulfinic acid sodium salts furnished the corresponding product **3aj** and **3ak** in 71% and 69% yield, respectively. To our delight, in addition to aromatic sodium sulfinates, relatively lower reactive cyclopropanesulfinate (**2l**) could also react with 2-methylquinoline, providing the desired products **3al** in 41% yield, while other aliphatic sodium sulfinates including sodium trifluoromethanesulfinate did not afford the corresponding products.

Scheme 4. Substrate Scope with Respect to Sodium Sulfinates.

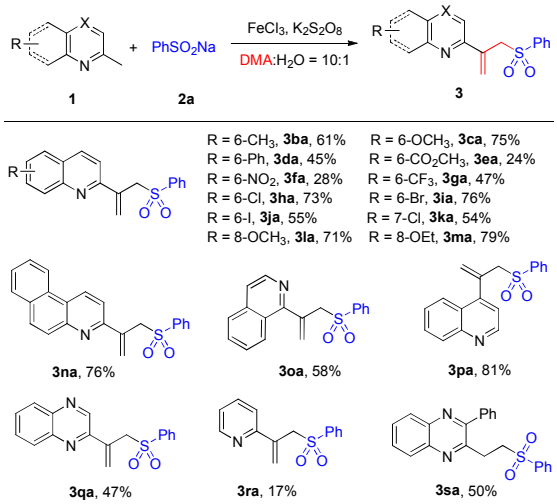


Reaction conditions: **1a** (0.2 mmol), **2** (0.5 mmol), $FeCl_3$ (10 mol %), $K_2S_2O_8$ (3.5 equiv), DMA (2.0 mL), H_2O (0.2 mL), 14 h, 110 ^oC, under air. Isolated yield based on **1a**.

To further explore the generality and limitations of the multi-component sulfonylation, other 2-methylazaarenes were treated with sodium benzenesulfinate **2a** (Scheme 5). Moderate yields were obtained for 2-methylquinolines with electron-donating groups such as methyl (**1b**), alkoxy (**1c**, **1l** and **1m**) and phenyl (**1d**) were presented at the C6 or C8-position. The quinolins bearing electron-withdrawing acetyl (**1e**), nitro (**1f**) and trifluoromethyl (**1g**) groups afforded the desired products in slightly lower yields. Notably, halogen substituted substrates reacted well under the optimized reaction conditions (**3ha**–**3ka**). The bulky 3-methylbenzo[*f*]quinoline (**1n**) also showed excellent reactivity. Apart from 2-methylquinolines, other methyl substituted quinolines such as 1-methylisoquinoline (**1o**), 4-methylquinoline (**1p**) and 2-methylquinoxaline (**1q**) could also be applied in this reaction system to provide the corresponding products in moderate to good yields. However, very low yield was obtained when using 2-methylpyridine (**1r**) as the substrate. Unexpectedly, 2-methyl-1,4-naphthyridine bearing a 3-phenyl group could not convert to the corresponding

product, and instead sulfonylmethylation product **3sa** was obtained.

Scheme 5. Substrate Scope with Respect to Methyl *aza*-Heterocycles.

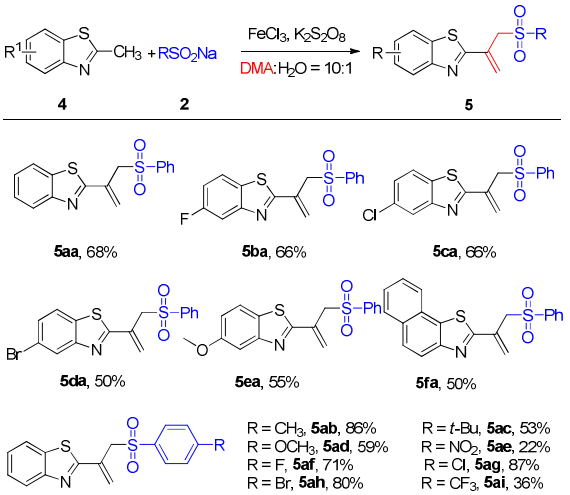


Reaction conditions: **1** (0.2 mmol), **2a** (0.5 mmol), $FeCl_3$ (10 mol %), $K_2S_2O_8$ (3.5 equiv), DMA (2.0 mL), H_2O (0.2 mL), 14 h, 110 ^oC, under air. Isolated yield based on **1**.

Benzothiazole and its derivatives are widespread in pharmaceuticals, functional materials and biological systems.[14] To our delight, 2-methylbenzothiazoles could also convert to the corresponding products with sodium sulfinates and DMA under the optimized reaction conditions (Scheme 6). The reaction of 2-methylbenzothiazole (**4a**) and sodium benzenesulfinate (**2a**) generated the corresponding 2-[3-(phenylsulfonyl)prop-1-en-2-yl]benzo[*d*]thiazole **5aa** in 68% isolated yield. The halo- and methoxyl-2-methylbenzothiazoles (**5ba–5ea**) were also smoothly reacted sodium benzenesulfinate (**2a**), affording the target products in moderate yields. The desired product **5fa** was obtained in 50% yield when 2-methylnaphtho[2,1-*d*]thiazole (**4f**) was used as the substrate. Furthermore, The reactions with sodium benzenesulfinates bearing

electron-donating groups substituents at the *para*-position proceeded smoothly to give the desired products (**5ab**–**5ad**). Lower yields were obtained when sodium 4-nitrobenzenesulfinate (**2e**) and sodium 4-(trifluoromethyl)benzenesulfinate (**2i**) were used as the substrates, probably because of the highly electron-withdrawing effect. Under the optimized conditions, halogen substituents were all well tolerated and afforded the desired products (**5af**–**5ah**) in good yields.

Scheme 6. Substrate Scope with Respect to 2-Methylbenzothiazoles.

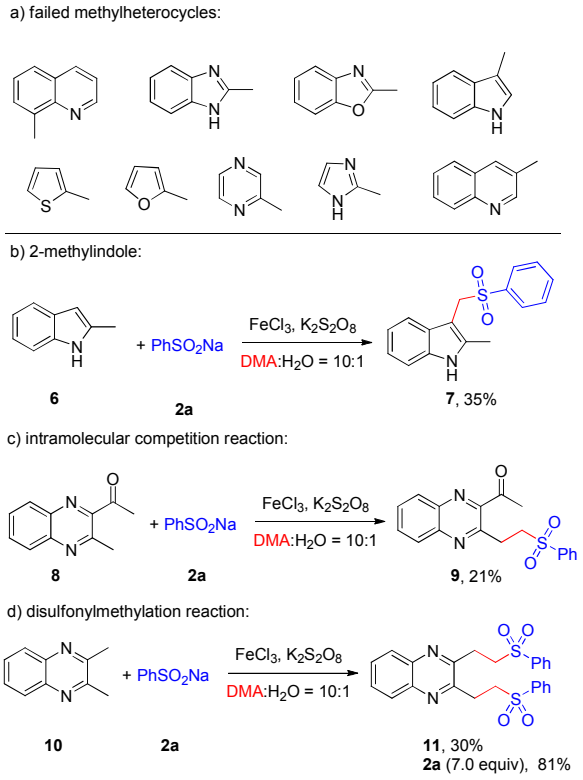


Reaction conditions: **4** (0.2 mmol), **2** (0.5 mmol), $FeCl_3$ (10 mol %), $K_2S_2O_8$ (3.5 equiv), DMA (2.0 mL), H_2O (0.2 mL), 14 h, 110 ^oC, under air. Isolated yield based on **4**.

The reaction convergence was reflected by the substrate limitations to above methyl *aza*-heterocycles. A range of other methylheterocycles such as 8-methylquinoline, 2-methylbenzo[*d*]imidazole, 2-methylbenzo[*d*]oxazole, 2-methylpyrazine, and so forth, failed to react with sodium sulfinates and DMA under the standard reaction conditions (Scheme 7a). When 2-methylindole was used, the sulfonylmethylation product **7** at C3-position of indole

was obtained in 35% yield (Scheme 7b). When the intramolecular competition reaction of 1-(3-methylquinoxalin-2-yl)ethanone **8** with **2a** was carried out under the standard reaction conditions, only the benzyl C–H sulfonylmethylation product **9** was obtained in 21% yield, while the α-methyl group to carbonyl did not participated (Scheme 7c).[12] Unexpectedly, the disulfonylmethylation product **11** was obtained when using 2,3-dimethylquinoxaline **10** as the substrate. To our delight, the reaction yield was significantly increased to 81% when 7.0 equiv. sodium benzenesulfinate (**2a**) was used. (Scheme 7d).

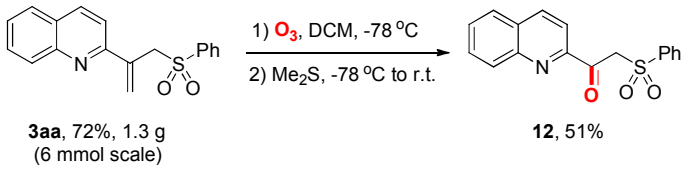
Scheme 7. Other Methylheterocycles.



The 2-(3-(phenylsulfonyl)prop-1-en-2-yl)quinoline product **3aa** was obtained in 72% yield in a gram-scale reaction. We further evaluated the ozonolysis reaction of **3aa**. When **3aa** was dissolved in CH_2Cl_2 and cooled to -78 ^{o}C, O_3 gas was bubbled into the mixture for 20 min.

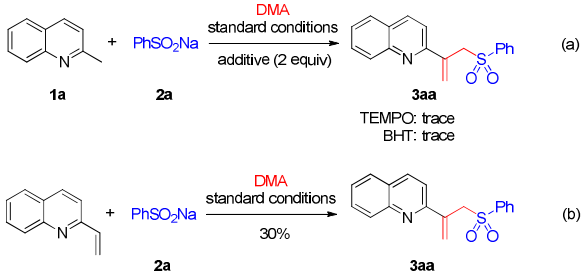
Then, The O_3 was removed by bubbled in N_2 (2 min), Me_2S was added dropwise. The mixture was stirred at -78 °C for about 10 min, then allowed to stir at r.t. 1 h. The product 2-(phenylsulfonyl)-1-(quinolin-2-yl)ethanone (**12**) was obtained in 49% yield (Scheme 8).

Scheme 8. Ozonolysis Reaction.



Mechanistically, the model reaction was significantly inhibited by the addition of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) or butylated hydroxytoluene (BHT) as a radical scavenger under the standard conditions (Scheme 9a). Hence, we speculate that the present multi-component reaction proceed through a radical process. Moreover, we employed 2-vinylquinoline as the starting material under the standard conditions, in which the corresponding product **3aa** was obtained in 30% yield (Scheme 9b).

Scheme 9. Control Experiments.



According to our previous work and related references,[12,15] a proposed mechanism is proposed in Figure 1. Initially, DMA was gradually oxidized to generate the iminium species **B** in the [Fe]/$K_2S_2O_8$-based system. 2-methylquinoline **1a** can be isomerized to **C** by the

Brønsted acid-promoted, and treatment of the iminium species **B** with intermediate **C** affords the intermediate product 2-vinylquinoline **1a'**. Then sodium benzenesulfinate **2a** with 2-vinylquinoline **1a'** undergoes Michael-type addition reaction to afford the anion intermediate **D**. Finally **D** and **B** undergoes nucleophilic addition reaction, followed by elimination methylamide to give the final product **3aa**.

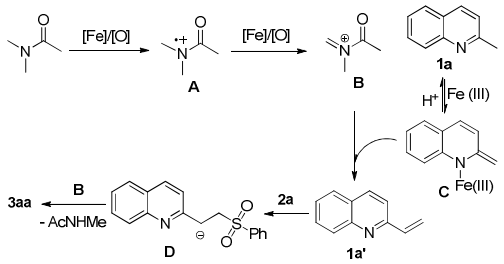


Figure 1. Possible reaction mechanism.

■ CONCLUSIONS

In summary, we have developed an iron-catalyzed oxidative benzylic C–H functionalization of 2-methylquinolines and 2-methylbenzothiazoles with sodium sulfinates and DMA under mild conditions. In this system, two carbon-carbon bonds and one carbon-sulfur bond were formed with high chemo-selectivity. Moreover, the broad functional group tolerance makes this method attractive for the synthesis of highly functionalized quinoline and benzothiazole derivatives.

■ EXPERIMENTAL SECTION

General Methods. All reactions were carried out under an atmosphere of air. Column chromatography was performed using silica gel 48-75 μm. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. Mass spectra were measured on Agilent 5975

GC-MS instrument (EI). HRMS was conducted using electrospraying ionization (ESI) and was performed on a Thermo Scientific LTQ Orbitrap XL. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature. Most reagents were obtained from commercial suppliers and used without further purification.

General Procedure for the Synthesis of 3 or 5. A 10 mL oven-dried reaction vessel was charged with $K_2S_2O_8$ (189.2 mg, 0.7 mmol), $FeCl_3$ (4.0 mg, 0.02 mmol), 2-methylquinoline (**1a**, 27.0 μL, 0.2 mmol), sodium benzenesulfinate (**2a**, 82.0 mg, 0.5 mmol), DMA (2.0 mL) and H_2O (0.2 mL) under air. The sealed reaction vessel was stirred at 110 ^{o}C for 14 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (3.0 mL) and washed with saturated sodium chloride solution. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to yield the desired product **3aa** as white solid (55.6 mg, 90% yield), mp = 92-95 ^{o}C.

2-[3-(Phenylsulfonyl)prop-1-en-2-yl]quinoline (3aa). White solid (55.6 mg, 90% yield), mp = 92-95 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.6 Hz, 1H), 7.80-7.75 (m, 3H), 7.70 (d, J = 8.1 Hz, 1H), 7.65-7.62 (m, 1H), 7.57 (d, J = 8.6 Hz, 1H), 7.49-7.45 (m, 1H), 7.23-7.17 (m, 3H), 6.18 (s, 1H), 5.88 (s, 1H), 4.87 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 146.7, 138.9, 137.1, 136.3, 132.9, 129.4, 128.5, 128.4, 127.2, 126.9, 126.6, 124.1, 117.6, 58.9. HRMS (ESI) calcd. for: $C_{18}H_{15}NO_2S^{+}$ $(M+H)^{+}$ 310.0896, found 310.0899.

2-(3-Tosylprop-1-en-2-yl)quinoline (3ab). White solid (59.5 mg, 92% yield), mp = 149-152 ^{o}C. ^{1}H

NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.6 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.65-7.57 (t, 4H), 7.49-7.45 (m, 1H), 6.93 (d, J = 8.0 Hz, 2H), 6.16 (s, 1H), 5.86 (s, 1H), 4.83 (s, 2H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 146.8, 144.0, 137.4, 136.2, 136.0, 129.5, 129.3, 129.0, 128.5, 127.1, 126.9, 126.7, 124.1, 117.9, 59.2, 21.2. HRMS (ESI) calcd. for: $C_{19}H_{18}NO_2S^+$ $(M+H)^+$ 324.1053, found 324.1055.

2-{3-[(4-tert-Butylphenyl)sulfonyl]prop-1-en-2-yl}quinoline (3ac). White solid. (38.0 mg, 52% yield), mp = 157-160 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.6 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.67-7.59 (m, 4H), 7.53 (d, J = 8.7 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 8.5 Hz, 2H), 6.19 (s, 1H), 5.94 (s, 1H), 4.85 (s, 2H), 0.97 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 154.5, 146.7, 137.3, 136.19, 135.6, 129.4, 128.5, 127.1, 126.8, 126.6, 125.2, 124.2, 117.6, 58.9, 34.7, 30.6. HRMS (ESI) calcd. for: $C_{22}H_{24}NO_2S^+$ $(M+H)^+$ 366.1522, found 366.1524.

2-{3-[(4-Methoxyphenyl)sulfonyl]prop-1-en-2-yl}quinoline (3ad). White solid (40.7 mg, 60% yield), mp = 151-154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.6 Hz, 1H), 7.81 (d, J = 7.5 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.65-7.63 (m, 3H), 7.57 (d, J = 8.7 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 6.57 (d, J = 8.7 Hz, 2H), 6.16 (s, 1H), 5.87 (s, 1H), 4.83 (s, 2H), 3.54 (d, J = 0.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 154.8, 146.7, 137.5, 136.3, 130.7, 130.4, 129.4, 127.2, 126.9, 126.6, 124.1, 117.9, 113.6, 59.4, 55.3. HRMS (ESI) calcd. for: $C_{19}H_{18}NO_3S^+$ $(M+H)^+$ 340.1002, found 340.1007.

2-{3-[(4-Nitrophenyl)sulfonyl]prop-1-en-2-yl}quinoline (3ae). Yellow solid (18.4 mg, 26% yield), mp = 200-203 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.6 Hz, 1H), 7.92-7.87 (m, 4H), 7.69 (d, J = 8.1 Hz, 1H), 7.62-7.60 (m, 3H), 7.48-7.4 (m, 1H), 6.27 (s, 1H), 6.01 (s, 1H), 4.92 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 149.8, 146.4, 144.7, 136.6, 130.0, 129.8, 128.9, 127.4, 127.2, 126.9, 124.8, 123.3, 117.5, 59.4. HRMS (ESI) calcd. for: $C_{18}H_{15}N_2O_4S^+$ $(M+H)^+$ 355.0747, found 355.0751.

2-{3-[(4-Fluorophenyl)sulfonyl]prop-1-en-2-yl}quinoline (3af). White solid (48.5 mg, 74% yield), mp = 222-225 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.6 Hz, 1H), 7.79-7.73 (m, 4H), 7.67-7.62 (t, 1H), 7.58 (d, J = 8.7 Hz, 1H), 7.51-7.46 (m, 1H), 6.87-6.77 (m, 2H), 6.20 (s, 1H), 5.91 (s, 1H), 4.86 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3 (d, J = 254.16 Hz), 154.3, 146.7, 137.1, 136.4, 136.0, 135.0, 131.4 (d, J = 9.52 Hz), 129.4 (d, J = 37.57 Hz), 127.2, 126.9, 126.8, 124.2, 117.5, 115.5 (d, J = 22.72 Hz), 59.0. HRMS (ESI) calcd. for: $C_{18}H_{15}FNO_2S^+$ $(M+H)^+$ 328.0802, found 328.0804.

2-{3-[(4-Chlorophenyl)sulfonyl]prop-1-en-2-yl}quinoline (3ag). White solid. (65.3 mg, 95% yield), mp = 251-254 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.6 Hz, 1H), 7.74 (d, J = 7.5 Hz, 2H), 7.70-7.65 (m, 3H), 7.59 (d, J = 8.7 Hz, 1H), 7.51 (dd, J_1 = 11.4, J_2 = 4.5 Hz, 1H), 7.11 (d, J = 8.6 Hz, 2H), 6.21 (s, 1H), 5.92 (s, 1H), 4.87 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 146.6, 139.8, 137.44, 137.42, 137.0, 136.5, 130.0, 129.7, 129.1, 128.6, 127.3, 126.9, 124.4, 117.6, 59.2. HRMS (ESI) calcd. for: $C_{18}H_{15}ClNO_2S^+$ $(M+H)^+$ 344.0507, found 344.0508.

2-{3-[(4-Bromophenyl)sulfonyl]prop-1-en-2-yl}quinoline (3ah). White solid. (73.0 mg, 94% yield), mp = 234-237 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.6 Hz, 1H), 7.73 (d, J = 8.7 Hz, 2H), 7.69-7.67 (m, 1H), 7.58-7.55 (m, 3H), 7.51-7.47 (m, 1H), 7.27-7.25 (m, 2H), 6.20 (s, 1H), 5.91 (s, 1H), 4.85 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 146.6, 138.0, 137.1, 136.5, 131.6, 130.0, 129.7, 129.2, 128.4, 127.3, 126.9, 124.4, 117.6, 59.3. HRMS (ESI) calcd. for: $C_{18}H_{15}BrNO_2S^+$ $(M+H)^+$ 388.0001, found 388.0004.

2-{3-[(4-(Trifluoromethyl)phenyl)sulfonyl]prop-1-en-2-yl}quinoline (3ai). White solid. (47.5 mg, 63% yield), mp = 249-251 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.7 Hz, 1H), 7.83 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.1 Hz, 1H), 7.64-7.58 (m, 2H), 7.55 (d, J = 8.7 Hz, 1H), 7.49-7.45 (m, 1H), 7.34 (d, J = 8.2 Hz, 2H), 6.22 (s, 1H), 5.96 (s, 1H), 4.89 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 146.4,

142.4, 136.9, 136.4, 134.4 (q, J = 3.69 Hz), 129.7, 129.2, 128.9, 127.2, 126.9, 126.8, 125.3 (q, J = 32.79 Hz), 124.5, 122.8 (q, J = 271.43 Hz), 117.4, 59.2. HRMS (ESI) calcd. for: $C_{19}H_{15}F_3NO_2S^+$ $(M+H)^+$ 378.0770, found 378.0773.

2-[3-(Naphthalen-1-ylsulfonyl)prop-1-en-2-yl]quinoline (3aj). White solid. (51.0 mg, 71% yield), mp = 203-206 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 8.7 Hz, 1H), 8.04 (dd, J_1 = 7.3, J_2 = 1.2 Hz, 1H), 7.87 (d, J = 8.6 Hz, 1H), 7.73-7.60 (m, 4H), 7.50-7.38 (m, 4H), 7.25-7.21 (m, 2H), 6.12 (s, 1H), 5.88 (s, 1H), 5.05 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 146.5, 137.2, 136.0, 134.6, 134.3, 133.8, 130.8, 129.2, 129.1, 128.7, 128.3, 127.0, 126.7, 126.6, 126.4, 124.8 124.1, 123.7, 117.7, 58.7. HRMS (ESI) calcd. for: $C_{22}H_{18}NO_2S^+$ $(M+H)^+$ 360.1053, found 360.1057.

2-[3-(Naphthalen-2-ylsulfonyl)prop-1-en-2-yl]quinoline (3ak). White solid. (49.6 mg, 69% yield), mp = 200-203 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.84 (s, 1H), 7.84 (m, 1H), 7.75-7.72 (m, 2H), 7.60-7.43 (m, 7H), 7.39-7.37(m, 1H), 6.16 (s, 1H), 5.90 (s, 1H), 4.95 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 146.5, 137.4, 136.1, 135.8, 134.8, 131.6, 130.3, 129.2, 129.1, 128.9, 128.7, 128.5, 127.5, 127.1, 127.0, 126.7, 126.4, 124.1, 123.2, 117.7, 59.4.HRMS (ESI) calcd. for: $C_{22}H_{18}NO_2S^+$ $(M+H)^+$ 360.1053, found 360.1054.

2-[3-(Cyclopropylsulfonyl)prop-1-en-2-yl]quinoline (3al). White solid (22.4 mg, 41% yield). mp = 131–134 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.7 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.7 Hz, 2H), 7.74-7.70 (m, 1H), 7.57-7.53 (m, 1H), 6.31 (s, 1H), 6.04 (s, 1H), 4.79 (s, 2H), 2.31-2.24 (m, 1H), 1.16-1.11 (m, 2H), 0.67-0.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 147.1, 137.1, 136.7, 129.9, 129.4, 127.5, 127.3, 126.9, 124.3, 117.7, 56.7, 29.9, 4.9. HRMS (ESI) calcd. for: $C_{15}H_{16}NO_2S^+$ $(M+H)^+$ 274.0896, found 274.0898.

6-Methyl-2-[3-(phenylsulfonyl)prop-1-en-2-yl]quinoline (3ba). White solid (39.5 mg, 61% yield), mp

= 153-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.89 (d, J = 8.6 Hz, 1H), 7.77-7.75 (m, 2H), 7.67 (d, J = 8.5 Hz, 1H), 7.53 (d, J = 8.6 Hz, 1H), 7.46-7.44 (m, 2H), 7.26-7.17 (m, 3H), 6.14 (s, 1H), 5.85 (s, 1H), 4.85 (s, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 153.8, 145.3, 138.9, 137.2, 136.6, 135.6, 132.9, 131.7, 129.1, 128.5, 128.3, 127.0, 126.1, 123.6, 117.6, 58.9, 21.6. HRMS (ESI) calcd. for: $C_{19}H_{18}NO_2S^+$ $(M+H)^+$ 324.1053, found 324.1057.

6-Methoxy-2-[3-(phenylsulfonyl)prop-1-en-2-yl]quinolone (3ca). White solid (50.9 mg, 75% yield), mp = 153-157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.6 Hz, 1H), 7.77-7.74 (m, 2H), 7.66 (d, J = 9.1 Hz, 1H), 7.53 (d, J = 8.7 Hz, 1H), 7.28-7.17 (m, 4H), 6.96 (d, J = 2.8 Hz, 1H), 6.12 (s, 1H), 5.81 (s, 1H), 4.84 (s, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 152.2, 142.7, 138.9, 137.0, 135.0, 132.9, 130.8, 128.5, 128.3, 127.9, 123.0, 122.0, 117.9, 104.8, 58.9, 55.5. HRMS (ESI) calcd. for: $C_{19}H_{18}NO_3S^+$ $(M+H)^+$ 340.1002, found 340.1003.

6-Phenyl-2-[3-(phenylsulfonyl)prop-1-en-2-yl]quinolone (3da). White solid (34.7 mg, 45% yield), mp = 157-160 °C. ^{1}H NMR (400 MHz, CDCl3) δ 8.03 (d, J = 8.6 Hz, 1H), 7.91-7.86 (m, 3H), 7.80-7.78 (m, 2H), 7.72-7.70 (m, 2H), 7.60 (d, J = 8.7 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.42 (dd, J = 4.8, 3.7 Hz, 1H), 7.26-7.22 (m, 3H), 6.19 (s, 1H), 5.88 (s, 1H), 4.88 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 146.1, 140.1, 139.3, 138.9, 137.1, 136.5, 133.0, 129.8, 129.1, 129.0, 128.6, 128.4, 127.8, 127.3, 127.1, 124.9, 124.1, 118.1, 58.9. HRMS (ESI) calcd. for: $C_{24}H_{20}NO_2S^+$ $(M+H)^+$ 386.1209, found 386.1212.

2-[3-(Phenylsulfonyl)prop-1-en-2-yl]quinoline-6-carboxylate (3ea). Yellow solid (17.6 mg, 24% yield), mp = 173-176 °C. ^{1}H NMR (400 MHz, CDCl3) δ 8.49-8.48 (m, 1H), 8.24-8.21 (m, 1H), 8.12 (d, J = 8.6 Hz, 1H), 7.87 (d, J = 8.7 Hz, 1H), 7.78-7.76 (m, 2H), 7.67 (d, J = 8.7 Hz, 1H), 7.26-7.20 (m, 3H), 6.26 (s, 1H), 5.96 (s, 1H), 4.87 (s, 2H), 4.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 156.8, 148.7, 139.0, 137.6, 137.0, 133.1, 130.3, 129.7, 129.1, 128.6, 128.5, 128.1, 126.1, 125.5, 118.5, 58.9,

52.5. HRMS (ESI) calcd. for: $C_{20}H_{18}NO_4S^+$ $(M+H)^+$ 368.0951, found 368.0954.

6-Nitro-2-[3-(phenylsulfonyl)prop-1-en-2-yl]quinolone (3fa). Yellow solid (19.8 mg, 28% yield), mp = 174-177 °C. ^{1}H NMR (400 MHz, CDCl3) δ 8.70 (d, J = 2.5 Hz, 1H), 8.42-8.40 (m, 1H), 8.22 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 9.2 Hz, 1H), 7.87-7.66 (m, 3H), 7.33-7.23 (m, 3H), 6.32 (s, 1H), 6.00 (s, 1H), 4.85 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 148.9, 145.5, 138.9, 138.1, 136.6, 133.3, 131.0, 128.59, 128.55, 126.7, 125.7, 124.0, 123.1, 119.6, 58.7. HRMS (ESI) calcd. for: $C_{18}H_{15}N_2O_4S^+$ $(M+H)^+$ 355.0747, found 355.0749.

2-[3-(Phenylsulfonyl)prop-1-en-2-yl]-6-(trifluoromethyl)quinoline (3ga). White solid (35.5 mg, 47% yield), mp = 135-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.7 Hz, 1H), 8.03 (s, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.82-7.77 (m, J = 8.3, 6.2, 1.8 Hz, 3H), 7.71 (d, J = 8.7 Hz, 1H), 7.31-7.22 (m, 3H), 6.26 (s, 1H), 5.95 (s, 1H), 4.85 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8 147.8, 138.9 137.1 136.8, 133.1, 130.6, 129.1, 128.2, 128.53, 128.49, 125.94 (q, J = 169.58 Hz), 125.90, 125.5, 125.1 (q, J = 2.78 Hz), 118.9, 58.8. HRMS (ESI) calcd. for: $C_{19}H_{15}F_3NO_2S^+$ $(M+H)^+$ 378.0770, found 378.0772.

6-Chloro-2-[3-(phenylsulfonyl)prop-1-en-2-yl]quinoline (3ha). White solid (50.3 mg, 73% yield), mp = 91-94 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.7 Hz, 1H), 7.78-7.69 (m, 4H), 7.62-7.55 (m, 2H), 7.28-7.20 (m, 3H), 6.19 (s, 1H), 5.89 (s, 1H), 4.83 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 145.1, 138.9, 136.8, 135.5, 133.1, 132.4, 131.0, 130.4, 128.5, 128.4, 127.5, 125.9, 124.7, 118.5, 58.8. HRMS (ESI) calcd. for: $C_{18}H_{15}ClNO_2S^+$ $(M+H)^+$ 344.0507, found 344.0509.

6-Bromo-2-[3-(phenylsulfonyl)prop-1-en-2-yl]quinoline (3ia). White solid (59.0 mg, 76% yield), mp = 195-198 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.7 Hz, 1H), 7.87 (d, J = 1.9 Hz, 1H), 7.77-7.75 (m, 2H), 7.71-7.65 (m, 2H), 7.61 (d, J = 8.7 Hz, 1H), 7.28-7.20 (m, 3H), 6.20 (s, 1H), 5.90 (s, 1H), 4.83 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 145.3, 138.9, 136.9, 135.4, 133.1, 133.0, 131.0,

129.3, 128.6, 128.5, 128.0, 124.8, 120.6, 118.6, 58.8. HRMS (ESI) calcd. for: for: $C_{18}H_{15}BrNO_2S^+$ $(M+H)^+$ 388.0001, found 388.0005.

6-Iodo-2-[3-(phenylsulfonyl)prop-1-en-2-yl]quinoline (3ja). White solid (47.9 mg, 55% yield), mp = 119-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 1.6 Hz, 1H), 7.95-7.87 (m, 2H), 7.79-7.77 (m, 2H), 7.62 (d, J = 8.7 Hz, 2H), 7.30-7.22 (m, 3H), 6.22 (s, 1H), 5.92 (s, 1H), 4.85 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 145.7, 138.9, 138.2, 136.9, 136.0, 135.1, 133.1, 131.1, 128.5, 128.4, 124.7, 118.3, 92.2, 58.8. HRMS (ESI) calcd. for: $C_{18}H_{15}INO_2S^+$ $(M+H)^+$ 435.9863, found 435.9864.

7-Chloro-2-[3-(phenylsulfonyl)prop-1-en-2-yl]quinoline (3ka). Yellow solid (37.1 mg, 54% yield), mp = 102-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.6 Hz, 1H), 7.78-7.76 (m, 3H), 7.65-7.58 (m, 2H), 7.43-7.40 (m, 1H), 7.30-7.22 (m, 3H), 6.20 (s, 1H), 5.89 (s, 1H), 4.82 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 147.1, 139.0, 136.9, 136.1, 135.2, 133.0, 128.47, 128.46, 128.4, 128.3, 127.6, 125.2, 124.8, 117.8, 58.9. HRMS (ESI) calcd. for: $C_{18}H_{15}ClNO_2S^+$ $(M+H)^+$ 344.0507, found 344.0508.

8-Methoxy-2-[3-(phenylsulfonyl)prop-1-en-2-yl]quinoline (3la). White solid (48.2 mg, 71% yield), mp = 138-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.6 Hz, 1H), 7.78-7.76 (m, 2H), 7.56 (d, J = 8.6 Hz, 1H), 7.42-7.38 (m, 1H), 7.29-7.27 (m, 1H), 7.20-7.13 (m, 3H), 6.99 (d, J = 7.7 Hz, 1H), 6.12 (s, 1H), 5.82 (s, 1H), 4.92 (s, 2H), 4.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 153.6, 138.72, 138.69, 137.3, 136.2, 132.7, 128.6, 128.11, 128.06, 126.9, 123.7, 119.1, 118.4, 108.1, 59.1, 55.9. HRMS (ESI) calcd. for: $C_{19}H_{18}NO_3S^+$ $(M+H)^+$ 340.1002, found 340.1003.

8-Ethoxy-2-[3-(phenylsulfonyl)prop-1-en-2-yl]quinoline (3ma). White solid (55.8 mg, 79% yield), mp = 105-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.7 Hz, 1H), 7.76-7.74 (m, 2H), 7.65 (d, J = 9.2 Hz, 1H), 7.51 (d, J = 8.7 Hz, 1H), 7.27-7.26 (m, 4H), 6.94 (d, J = 2.7 Hz, 1H), 6.10 (s, 1H), 5.80 (s, 1H), 4.84 (s, 2H), 4.11 (q, J = 7.0 Hz, 2H), 1.47 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

157.2, 152.1, 142.6, 138.9, 137.0, 135.0, 132.9, 130.7, 128.5, 128.3, 128.0, 122.9, 122.2, 117.8, 105. 5, 63.7, 58.9, 14.7. HRMS (ESI) calcd. for: $C_{20}H_{20}NO_3S^+$ $(M+H)^+$ 354.1158, found 354.1158.

3-[3-(Phenylsulfonyl)prop-1-en-2-yl]benzo[f]quinoline (3na). Yellow solid (54.6 mg, 76% yield), mp = 124-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 8.7 Hz, 1H), 8.49 (d, J = 7.8 Hz, 1H), 7.88-7.86 (m, 2H), 7.79-7.75 (m, 2H), 7.70-7.60 (m, 4H), 7.18-7.16 (m, 3H), 6.19 (s, 1H), 5.85 (s, 1H), 4.87 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 146.6, 138.8, 136.8, 133.0, 131.6, 131.0, 130.7, 129.2, 128.6, 128.5, 128.3, 128.0, 127.2, 127.0, 124.0, 123.8, 122.6, 117.7, 58.9. HRMS (ESI) calcd. for: $C_{22}H_{18}NO_2S^+$ $(M+H)^+$ 360.1053, found 360.1055.

1-[3-(Phenylsulfonyl)prop-1-en-2-yl]isoquinoline (3oa). White solid (35.9 mg, 58% yield), mp = 92-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32-8.30 (m, 2H), 7.76 (d, J = 8.2 Hz, 1H), 7.68-7.61 (m, 3H), 7.59-7.55 (m, 1H), 7.44 (d, J = 5.6 Hz, 1H), 7.31-7.27 (m, 1H), 7.15 (t, J = 7.8 Hz, 2H), 5.97 (s, 1H), 5.72 (s, 1H), 4.75 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 140.9, 138.6, 136.8, 134.4, 133.1, 130.1, 128.4, 128.0, 127.4, 127.3, 126.90, 126.87, 126.2, 120.2, 62.7. HRMS (ESI) calcd. for: $C_{18}H_{16}NO_2S^+$ $(M+H)^+$ 310.0896, found 310.0899.

4-[3-(Phenylsulfonyl)prop-1-en-2-yl]quinoline (3pa). Yellow oli (50.0 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 4.4 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.73-7.64 (m, 3H), 7.54-7.49 (m, 2H), 7.34 (t, J = 7.9 Hz, 2H), 7.07 (d, J = 4.4 Hz, 1H), 5.84 (s, 1H), 5.62 (s, 1H), 4.35 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 148.3, 146.3, 138.4, 133.7, 133.2, 130.0, 129.4, 128.9, 128.1, 127.2, 126.9, 125.5, 124.7, 119.9, 63.0. HRMS (ESI) calcd. for: $C_{18}H_{16}NO_2S^+$ $(M+H)^+$ 310.0896, found 310.0897.

2-[3-(Phenylsulfonyl)prop-1-en-2-yl]quinoxaline (3qa). White solid (29.2 mg, 47% yield), mp = 164-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.02-8.00 (m, 1H), 7.83-7.77 (m, 3H),

7.73-7.69 (m, 2H), 7.28-7.23 (m, 3H), 6.33 (s, 1H), 5.98 (s, 1H), 4.78 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 142.2, 141.0, 140.7, 138.6, 135.1, 133.3, 130.2, 130.0, 129.3, 128.8, 128.6, 128.5, 125.8, 58.5. HRMS (ESI) calcd. for: $C_{17}H_{15}N_2O_2S^+$ $(M+H)^+$ 311.0849, found 311.0850.

2-[3-(Phenylsulfonyl)prop-1-en-2-yl]pyridine (3ra). White solid (8.9 mg, 17% yield), mp = 133-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 3.8 Hz, 1H), 7.81-7.76 (m, 2H), 7.64 (m, 1H), 7.52-7.48 (m, 2H), 7.39 (t, J = 7.7 Hz, 2H), 7.14 (m, 1H), 6.03 (s, 1H), 5.63 (s, 1H), 4.66 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 148.4, 138.8, 136.6, 136.5, 133.3, 128.6, 123.3, 122.5, 120.3, 59.1. HRMS (ESI) calcd. for: $C_{14}H_{16}NO_2S^+$ $(M+H)^+$ 262.0896, found 262.0899.

2-Phenyl-3-[2-(phenylsulfonyl)ethyl]quinoxaline (3sa). Yellow solid (37.4 mg, 50% yield), mp = 122-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.09 (m, 1H), 7.97-7.95 (m, 1H), 7.80 (d, J = 7.4 Hz, 2H), 7.75-7.72 (m, 2H), 7.68-7.52 (m, 6H), 7.44 (t, J = 7.6 Hz, 2H), 3.83-3.80 (m, 2H), 3.53-3.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 150.7, 140.8, 140.7, 139.0, 137.8, 133.5, 129.90, 129.85, 129.3, 129.2, 129.1, 128.82, 128.78, 128.4, 128.0, 53.8, 28.9. HRMS (ESI) calcd. for: $C_{22}H_{19}N_2O_2S^+$ $(M+H)^+$ 375.1162, found 375.1165.

2-[3-(phenylsulfonyl)prop-1-en-2-yl]benzo[d]thiazole (5aa). White solid (42.9 mg, 68% yield), mp = 125-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.84 (m, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.42-7.30 (m, 5H), 6.20 (s, 1H), 5.93 (s, 1H), 4.64 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 154.1, 138.5, 133.6, 133.5, 131.8, 128.9, 128.73, 128.69, 127.6, 126.2, 122.4, 119.7, 58.9. HRMS (ESI) calcd. for: $C_{16}H_{14}NO_2S_2^+$ $(M+H)^+$ 316.0461, found 316.0466.

5-Fluoro-2-[3-(phenylsulfonyl)prop-1-en-2-yl]benzo[d]thiazole (5ba). White solid (44.0 mg, 66% yield), mp = 131-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.83 (m, 2H), 7.70-7.66 (m, 1H), 7.46-7.33 (m, 4H), 7.14-7.10 (m, 1H), 6.21 (s, 1H), 5.93 (s, 1H), 4.61 (s, 2H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 168.6, 162.8, 160.4, 153.8 (J = 12.0 Hz), 138.4, 133.5, 131.8, 130.08 (d, J = 1.9 Hz), 128.7, 127.3, 122.1(d, J = 8.89 Hz), 114.5 (d, J = 24.9 Hz), 109.4 (d, J = 23.4 Hz), 58.9. HRMS (ESI) calcd. for: $C_{16}H_{13}FNO_2S_2^+$ $(M+H)^+$ 334.0366, found 334.0368.

5-Chloro-2-[3-(phenylsulfonyl)prop-1-en-2-yl]benzo[d]thiazole (5ca). Yellow solid (44.0 mg, 63% yield), mp = 150-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.7 Hz, 2H), 7.76 (s, 1H), 7.68 (d, J = 8.6 Hz, 1H), 7.46-7.29 (m, 4H), 6.23 (s, 1H), 5.97 (s, 1H), 4.62 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 153.7, 138.4, 133.6, 133.0, 132.2, 131.7, 128.7, 127.6, 126.3, 123.1, 122.1, 58.9. HRMS (ESI) calcd. for: $C_{16}H_{13}ClNO_2S_2^+$ $(M+H)^+$ 350.0071, found 350.0073.

5-Bromo-2-[3-(phenylsulfonyl)prop-1-en-2-yl]benzo[d]thiazole (5da). Yellow solid (39.4 mg, 50% yield), mp = 146-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.85 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 8.4 Hz, 1H), 7.46-7.35 (m, 4H), 6.22 (s, 1H), 5.97 (s, 1H), 4.61 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 154.0, 138.4, 133.6, 133.5, 131.7, 128.9, 128.73, 128.68, 127.6, 126.2, 122.4, 119.7, 58.8. HRMS (ESI) calcd. for: $C_{16}H_{13}BrNO_2S_2^+$ $(M+H)^+$ 393.9566, found 393.9561.

5-Methoxy-2-[3-(phenylsulfonyl)prop-1-en-2-yl]benzo[d]thiazole(5ea). Yellow oil (38.0 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.85 (m, 2H), 7.61 (d, J = 8.8 Hz, 1H), 7.41-7.34 (m, 3H), 7.27 (m, 1H), 7.02-7.00 (m, 1H), 6.20 (s, 1H), 5.88 (s, 1H), 4.63 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 158.9, 154.0, 138.4, 133.5, 131.8, 128.73, 128.66, 126.6, 126.5, 121.6, 116.2, 105.5, 59.0, 55.6. HRMS (ESI) calcd. for: $C_{17}H_{16}NO_3S_2^+$ $(M+H)^+$ 346.0566, found 346.0569.

2-[3-(Phenylsulfonyl)prop-1-en-2-yl]naphtho[2,1-d]thiazole (5fa). White solid (36.5 mg, 50% yield), mp = 155-158 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 7.6 Hz, 2H), 7.76 (s, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.18 (t, J = 7.5 Hz, 2H), 7.11-7.10 (m, 1H), 6.24 (s, 1H), 5.96 (s, 1H), 4.77 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

165.1, 149.1, 138.5, 133.3, 132.2, 131.8, 131.5, 128.7, 128.5, 128.4, 128.0, 126.9, 126.7, 126.2, 125.7, 123.8, 118.6, 59.3. HRMS (ESI) calcd. for: $C_{20}H_{16}NO_2S_2^+$ $(M+H)^+$ 366.0617, found 366.0618.

2-(3-Tosylprop-1-en-2-yl)benzo[d]thiazole (5ab). White solid (55.9 mg, 86% yield), mp = 133-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (t, J = 6.2 Hz, 2H), 7.70 (d, J = 7.2 Hz, 2H), 7.41 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.07 (d, J = 7.6 Hz, 2H), 6.19 (d, J = 3.5 Hz, 1H), 5.93 (s, 1H), 4.60 (s, 2H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 152.9, 144.6, 135.5, 134.7, 132.2, 129.3, 128.7, 126.8, 126.1, 125.7, 123.3, 121.4, 59.3, 21.3. HRMS (ESI) calcd. for: $C_{17}H_{16}NO_2S_2^+$ $(M+H)^+$ 330.0617, found 330.0623.

2-(3-((4-(tert-Butyl)phenyl)sulfonyl)prop-1-en-2-yl)benzo[d]thiazole (5ac). Yellow solid (31.1 mg, 53% yield), mp = 128-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.71 (m, 4H), 7.38-7.29 (m, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.19 (s, 1H), 5.99 (s, 1H), 4.62 (s, 2H), 1.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 157.3, 152.8, 135.1 134.6, 132.2, 128.7, 126. 9, 126.1, 125.7, 125.5, 123.3, 121.3, 59.1, 34.8, 30.6. HRMS (ESI) calcd. for: $C_{20}H_{22}NO_2S_2^+$ $(M+H)^+$ 372.1087, found 372.1090.

2-{3-[(4-Methoxyphenyl)sulfonyl]prop-1-en-2-yl}benzo[d]thiazole (5ad). Yellow solid (41.0 mg, 59% yield), mp = 152-155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.42 (m, 4H), 7.42-7.32 (m, 2H), 6.72-6.70 (m, 2H), 6.19 (s, 1H), 5.92 (s, 1H), 4.59 (s, 2H), 3.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 163.5, 153.0, 134.7, 132.3, 130.9, 130.0, 126.8, 126.1, 125.7, 123.4, 121.3, 113.8, 59.5, 55.4. HRMS (ESI) calcd. for: $C_{17}H_{16}NO_3S_2^+$ $(M+H)^+$ 346.0566, found 346.0570.

2-{3-[(4-Nitrophenyl)sulfonyl]prop-1-en-2-yl}benzo[d]thiazole (5ae). Yellow solid (16.4 mg, 22% yield), mp = 181-184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.06 (m, 2H), 8.02-8.00 (m, 2H), 7.76-7.74 (m, 1H), 7.62-7.60 (m, 1H), 7.40-7.32 (m, 1H), 6.25 (s, 1H), 6.05 (s, 1H), 4.70 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 152.5, 150.5, 144.2, 134.4, 131.5, 130.3, 127.7, 126.6, 126.3, 123.6,

123.0, 121.6, 59.4. HRMS (ESI) calcd. for: $C_{16}H_{13}N_2O_4S_2^+$ $(M+H)^+$ 361.0307, found 361.0311.

2-{3-[(4-Fluorophenyl)sulfonyl]prop-1-en-2-yl}benzo[d]thiazole (5af). Yellow solid (47.6 mg, 71% yield), mp = 140-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.83 (m, 4H), 7.76 (t, J = 8.0 Hz, 2H), 7.44-7.34 (m, 4H), 6.97 (t, J = 8.5 Hz, 2H), 6.22 (s, 1H), 5.97 (s, 1H), 4.64 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.7 (J = 255 Hz), 152.9, 134.7, 132.0, 131.8, 131.7, 127.1, 126.4, 126.1, 123.3, 121.5, 116.0 (J = 22 Hz), 59.2. HRMS (ESI) calcd. for: $C_{16}H_{13}FNO_2S_2^+$ $(M+H)^+$ 334.0366, found 334.0369.

2-{3-[(4-Chlorophenyl)sulfonyl]prop-1-en-2-yl}benzo[d]thiazole (5ag). Yellow solid (60.4 mg, 87% yield), mp = 158-161 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (q, J = 8.3 Hz, 4H), 7.43 (t, J = 7.7 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.26 (d, J = 8.3 Hz, 2H), 6.22 (s, 1H), 5.97 (s, 1H), 4.63 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 152. 8, 140.4, 137.0, 134.6, 131.9, 130.2, 128.9, 127.1, 126.4, 126.1, 123.3, 121.4, 59.3. HRMS (ESI) calcd. for: $C_{16}H_{13}ClNO_2S_2^+$ $(M+H)^+$ 350.0071, found 350.0074.

2-{3-[(4-Bromophenyl)sulfonyl]prop-1-en-2-yl}benzo[d]thiazole (5ah). Yellow solid (63.1 mg, 80% yield), mp = 139-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.9 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.46-7.41 (m, 3H),, 7.37 (d, J = 7.7 Hz, 1H), 6.21 (s, 1H), 5.96 (s, 1H), 4.63 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 152.8, 137.5, 134.6, 131.9, 130.3, 129.1, 127.1, 126.4, 126.0, 123.3, 121.4, 59.3. HRMS (ESI) calcd. for: $C_{16}H_{13}BrNO_2S_2^+$ $(M+H)^+$ 393.9566, found 393.9569.

2-(3-((4-(Trifluoromethyl)phenyl)sulfonyl)prop-1-en-2-yl)benzo[d]thiazole (5ai). White solid (27.5 mg, 36% yield), mp = 163-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.1 Hz, 2H), 7.75-7.73 (m, 1H), 7.65-7.63 (m, 1H), 7.51 (d, J = 8.2 Hz, 2H), 7.41-7.32 (m, 2H), 6.23 (s, 1H), 6.01 (s, 1H), 4.67 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 152.6, 142.0, 135.0 (q, J = 33.0 Hz), 134.4, 131.7,

129.4, 127.4, 126.4, 126.1, 125.6 (q, J = 3.3 Hz), 123.1, 122.8 (q, J = 270.2 Hz), 121.4, 59.3. HRMS (ESI) calcd. for: $C_{17}H_{13}F_3NO_2S_2^+$ $(M+H)^+$ 384.0334, found 384.0337.

2-[3-(p-tolylthio)prop-1-en-2-yl]quinoline (3a). Yellow oil (21.0 mg, 36% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.08 (m, 2H), 7.79 (d, J = 8.0 Hz, 1H), 7.72-7.67 (m, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 5.88 (s, 1H), 5.51 (s, 1H), 4.31 (s, 2H), 2.30 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 147.6, 144.5, 136.4, 136.1, 132.8, 131.0, 129.8, 129.5, 129.4, 127.3, 126.4, 118.8, 118.4, 38.0, 21.0. HRMS (ESI) calcd. for: $C_{18}H_{16}NS^+$ $(M+H)^+$ 278.0998, found 278.1000.

2-Methyl-3-[(phenylsulfonyl)methyl]-1H-indole (7). Yellow oil (19.9 mg, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.65-7.63 (m, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.8 Hz, 2H), 7.22 (d, J = 8.1 Hz, 1H), 7.15 (d, J = 7.9 Hz, 1H), 7.10-7.06 (m, 1H), 6.99-6.94 (m, 1H), 4.47 (s, 2H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 135.9, 134.8, 133.4, 128.8, 128.7, 128.1, 121.6, 120.1, 117.9, 110.3, 99.2, 53.9, 11.4. HRMS (ESI) calcd. for: $C_{16}H_{15}NO_2SNa^+$ $(M+Na)^+$ 308.0716 found 308.0718.

1-{3-[2-(Phenylsulfonyl)ethyl]quinoxalin-2-yl}ethanone (9). White solid (14.3 mg, 21% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 7.6 Hz, 3H), 7.86-7.77 (m, 2H), 7.63-7.53 (m, 3H), 3.88-3.85 (m, 2H), 3.77-3.73 (m, 2H), 2.83 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 151.5, 146.4, 142.2, 139.7, 139.1, 133.6, 132.3, 130.2, 129.8, 129.2, 128.6, 128.2, 53.9, 29.6, 27.6. HRMS (ESI) calcd. for: $C_{18}H_{17}N_2O_3S^+$ $(M+H)^+$ 341.0954, found 341.0958.

2,3-Bis[2-(phenylsulfonyl)ethyl]quinoxaline (11). Yellow oil (28.0 mg, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.3 Hz, 4H), 7.87-7.84 (m, 2H), 7.67-7.60 (m, 4H), 7.55 (t, J = 7.5 Hz, 4H), 3.91-3.87 (m, 4H), 3.44-3.40 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 140.4, 139.1, 133. 8, 129.6, 129.4, 128.5, 128.0, 53.0, 27.1. HRMS (ESI) calcd. for: $C_{24}H_{23}N_2O_4S_2^+$ $(M+H)^+$ 467.1094,

found 467.1094.

2-(Phenylsulfonyl)-1-(quinolin-2-yl)ethanone (12). White solid (15.8 mg, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.5 Hz, 1H), 8.06 (dd, *J* = 8.4, 6.7 Hz, 2H), 8.08-8.04 (m, 2H), 7.96-7.94 (m, 2H),7.86 (d, *J* = 8.2 Hz, 1H), 7.79 (td, *J* = 7.0, 3.5 Hz, 1H), 7.69-7.65 (m, 1H), 7.56-7.52 (m, 1H), 7.49-7.45 (m, 2H), 5.36 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 151.3, 146.8, 139.6, 137.4, 133.8, 130.6, 130.3, 129.8, 129.4, 129.0, 128.5, 127.6, 118.1, 61.0. HRMS (ESI) calcd. for: $C_{17}H_{13}NO_3S^+$ $(M+Na)^+$ 334.0508, found 334.0511.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1020/acs.joc.0000000

Copies of ^{1}H and ^{13}C NMR spectra of the products (PDF)

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Notes

The authors declare no competing financial interest.

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