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# A Catalyst-Free Benzylic C−H Bond Olefination of Azaarenes for Direct Mannich-like Reactions

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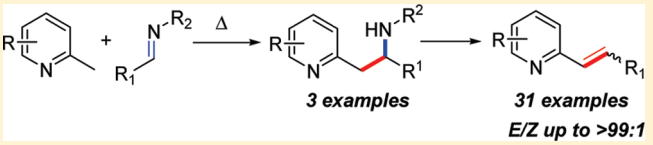
Supporting Information

**ABSTRACT:** A highly efficient synthesis of *trans*-alkenylazaarene under catalyst-free conditions was developed via the addition of methylazaarenes to *N*-sulfonyl aldimines and a subsequent C−N elimination in situ. A one-pot procedure for this addition−elimination was also developed. The reaction could tolerate a broad substrate scope and give the corresponding alkenylazaarenes in high yields.




Transition-metal-catalyzed $sp^3$ C−H bond functionalizations have emerged as important methods for C−C bond formation in synthetic organic chemistry.[1,2] Although many excellent results have been reported, the functionalization of a methyl group directly attached to an aromatic ring remains limited.[3] Recently, Huang and Rueping reported the palladium or Lewis acid catalyzed benzylic addition of 2-methylazaarenes to *N*-sulfonyl aldimines (Scheme 1A).[4] Concurrently, Kanai and Matsunaga reported a Lewis acid catalyzed benzylic C−H bond functionalization of alkyl-substituted azaarenes.[5] In their report, a mechanism via premetalation of the 2-methyl group was proposed. In our study about the addition of 2-methylazaarenes to *N*-sulfonyl aldimines, we found that no addition product **4** was observed, but elimination products **3** were obtained in the absence of metal (Scheme 1B).[6]

2-Alkenylazaarenes **3** can be used as antagonist, antiproliferative, antiviral, and antimicrobial agents because of their important biological activities.[7] Although the aldol reactions of 2-methyl azaarenes were directly used to synthesize alkenylazaarenes in the presence of strong acid or base,[8] only low *E*/*Z* selectivity was obtained. Herein, we report a highly efficient and stereoselective synthesis of alkenylazaarenes through the addition of methylazaarenes to *N*-sulfonyl aldimines and a subsequent C−N elimination in situ without any metal catalyst or other additives. Moreover, a one-pot procedure based on *p*-toluenesulfonamide was developed to simplify this tedious addition−elimination.

Initially, the reaction of 2-methylquinoline (**1a**) with *N*-tosyl aldimine (**2a**) was chosen as a model reaction to optimize reaction conditions. Solvent polarity had no effect on the *E*/*Z* ratio (Table 1, entries 1−4). However, the less polar solvent (toluene) gave the highest yield (Table 1, entry 4). The optimal temperature was found to be 120 °C (Table 1, entries 4−6). Subsequently, when various Lewis acids were added, the reactions resulted in lower yields and poor selectivities of *E*/*Z* (Table 1, entries 7−15). When a base was added, no desired product was observed because *N*-tosyl aldimine was hydrolyzed to generate the corresponding aldehyde (Table 1, entries 16 and 17). In addition, reducing the amount of 2-methylquinoline incurred a decrease in the reaction yields (Table 1, entries 18 and 19). Therefore, the optimal conditions are those described in entry 4.

Under the optimized reaction conditions, the scope of the reaction substrates was investigated. As shown in Table 2, various *N*-tosyl aldimines **2a**−**2u** were employed in this reaction. No electronic effect was observed when different substituents were located on the phenyl ring of aromatic aldimines. Both electron-withdrawing and electron-donating substituents were tolerated in this reaction (Table 2, entries 5, 7, 11−14). There seems to be some steric effect in this reaction because $R^1$ bearing a substituent at *ortho*-position gave a lower yield in comparison with the $R^1$ bearing a substituent at *para*-position (Table 2, entries 2, 4−10). The reactions of ring-fused, heterocyclic, and styryl aldimines also gave the corresponding products in satisfactory yields (Table 2, entries 15−17 and 19), except for 2-pyridyl aldimine (Table 2, entry 18). To our delight, aliphatic tosyl aldimines can also be the substrates in this reaction despite slightly lower yields (Table 2, entries 20 and 21). It was noted that in every case an excellent stereoselctivity can be obtained.

Subsequently, various $R^2$ substitutents on *N*-sulfonyl aldimines were also examined when $R^1$ was fixed as a phenyl group. When different sulfonyl groups were used as the N-protecting groups, the reaction can give desired product **3aa** in 84−98% yield (Table 3, entries 1−8). It was noteworthy that aldimine bearing a *m*-nitrobenzenesulfonyl group as an N-protecting group resulted in the highest yield (Table 3, entry 2). These results indicated that the stronger the electron-withdrawing capability of $R^2$, the higher the reactivity or the eletrophilicity of $sp^2$ carbon of aldimine. Subsequently, only a 10% yield of **3aa** was obtained with benzyl (Bn) as an N-protecting group

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**Scheme 1. Benzylic C−H Bond Transformations**

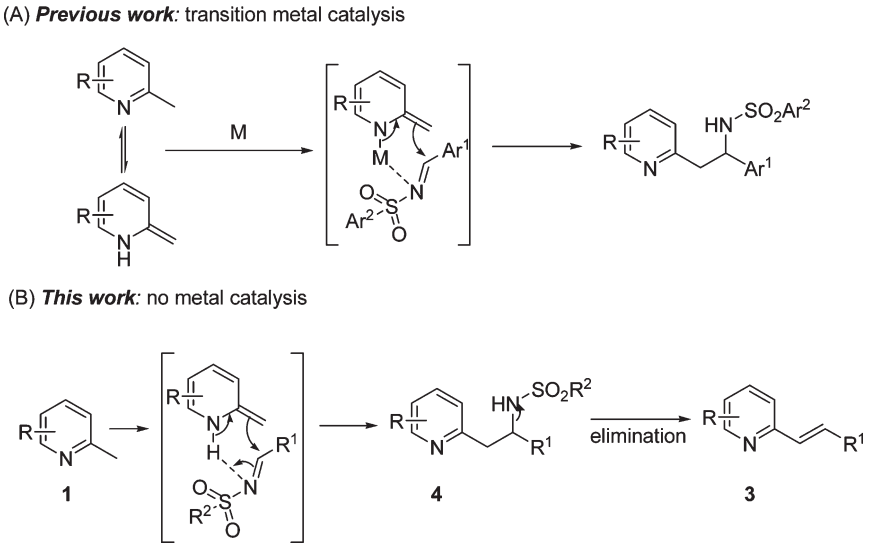
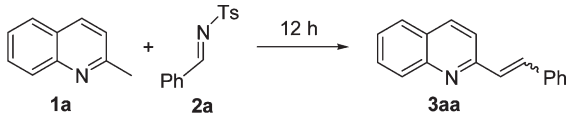



**Table 1. Optimization of Reaction Conditions**[a]

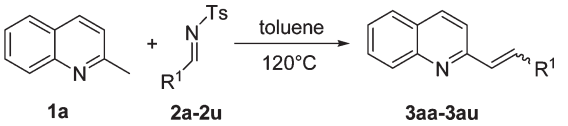



| entry | solvent | additive | temp (°C) | yield (%)[b] | *E*/*Z*[c] |
|---|---|---|---|---|---|
| 1 | THF | | 70 | 36 | >99:1 |
| 2 | DMF | | 120 | 66 | >99:1 |
| 3 | DMSO | | 120 | 72 | >99:1 |
| 4 | tol. | | 120 | 92 | >99:1 |
| 5 | tol. | | 140 | 92 | >99:1 |
| 6 | tol. | | 80 | 57 | >99:1 |
| 7 | tol. | $Cu(OAc)_2$ | 120 | 54 | 95:5 |
| 8 | tol. | $CuCl_2$ | 120 | 48 | 87:13 |
| 9 | tol. | $CuBr_2$ | 120 | 48 | 80:20 |
| 10 | tol. | $Cu(OTf)_2$ | 120 | 69 | 70:30 |
| 11[d] | tol. | $CuBr_2$ + $Cu(OTf)_2$ | 120 | 80 | 30:70 |
| 12 | tol. | CuBr | 120 | 79 | >99:1 |
| 13 | tol. | CuI | 120 | 90 | >99:1 |
| 14 | tol. | $FeCl_3$ | 120 | 27 | 83:17 |
| 15 | tol. | $ZnCl_2$ | 120 | 52 | 90:10 |
| 16 | tol. | $Cs_2CO_3$ | 120 | 0 | |
| 17 | tol. | *t*BuOK | 120 | 0 | |
| 18[e] | tol. | | 120 | 86 | >99:1 |
| 19[f] | tol. | | 120 | 90 | >99:1 |

[a] Reaction conditions: **1a** (0.6 mmol), **2a** (0.3 mmol), and additive (0.1 equiv) in solvent (0.5 mL) were refluxed for 12 h under $N_2$. [b] Isolated yields. [c] Determined by GC-MS on the basis of peak areas. [d] $CuBr_2$ (5 mol %) and $Cu(OTf)_2$ (5 mol %) were added in a 1:1 ratio. [e] **1a** (0.3 mmol) was used. [f] **1a** (0.45 mmol) was used.

(Table 3, entry 9). In addition, when phenyl and butylcarbonyl (Boc) were employed as N-protecting groups, no product was obtained (Table 3, entries 10 and 11).

**Table 2. Substrate Scope of Various *N*-Tosyl Aldimines**[a]




| entry | $R^1$ | product | yield (%)[b] | *E*/*Z*[c] |
|---|---|---|---|---|
| 1 | Ph | **3aa** | 92 | >99:1 |
| 2 | 4-Cl-Ph | **3ab** | 90(92[d]) | >99:1 |
| 3 | 3-Cl-Ph | **3ac** | 90 | >99:1 |
| 4 | 2-Cl-Ph | **3ad** | 86 | >99:1 |
| 5 | 4-$CF_3$-Ph | **3ae** | 94(96[d]) | >99:1 |
| 6 | 2-$CF_3$-Ph | **3af** | 80(85[d]) | >99:1 |
| 7 | 4-$NO_2$-Ph | **3ag** | 94 | >99:1 |
| 8 | 2-$NO_2$-Ph | **3ah** | 90 | >99:1 |
| 9 | 4-OMe-Ph | **3ai** | 87 | >99:1 |
| 10 | 2-OMe-Ph | **3aj** | 76(80[d]) | >99:1 |
| 11 | 2,4-di-OMe-Ph | **3ak** | 96 | 95:5 |
| 12 | 4-Me-Ph | **3al** | 97 | >99:1 |
| 13 | 3-Me-Ph | **3am** | 96 | >99:1 |
| 14 | 2-Me-Ph | **3an** | 97 | >99:1 |
| 15 | 1-naphthyl | **3ao** | 91 | >99:1 |
| 16 | 2-furyl | **3ap** | 79(84[d]) | >99:1 |
| 17 | 2-thienyl | **3aq** | 70(85[d]) | 99:1 |
| 18 | 2-pyridyl | **3ar** | trace[e] | |
| 19 | PhCH=CH | **3as** | 90 | 93:7 |
| 20 | cyclohexyl | **3at** | 71 | 99:1 |
| 21 | *i*-$C_4H_9$ | **3au** | 78 | >99:1 |

[a] Reaction conditions: **1a** (0.6 mmol) and **2** (0.3 mmol) in toluene (0.5 mL) were refluxed at 120 °C for 12 h under $N_2$. [b] Isolated yields. [c] Determined by $^1H$ NMR on the basis of peak areas. [d] The system was heated in mesitylene (0.5 mL) at 140 °C. [e] Unknown complex mixture.

Next, the generality of methylazaarenes was investigated in this reaction. When methylazaarenes (**1b**−**1i** and **1m**) were


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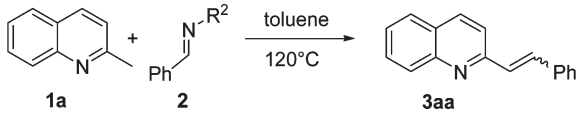
**Table 3. Substrate Scope of Aldimines with Different N-Protecting Groups**[a]




| entry | $R^2$ | yield (%)[b] | $E/Z$[c] |
|---|---|---|---|
| 1 | *o*-toluenesulfonyl | 92 | >99:1 |
| 2 | *m*-nitrobenzenesulfonyl | 98 | >99:1 |
| 3 | *p*-methoxybenzenesulfonyl | 88 | >99:1 |
| 4 | benzenesulfonyl | 90 | >99:1 |
| 5 | 2-mesitylenesulfonyl | 86 | >99:1 |
| 6 | 2-naphthalenesulfonyl | 89 | >99:1 |
| 7 | methanesulfonyl | 87 | >99:1 |
| 8 | 1-hexadecanesulfonyl | 84 | >99:1 |
| 9 | Bn | 10 | 90:10 |
| 10 | Ph | 0 | |
| 11 | Boc | 0 | |

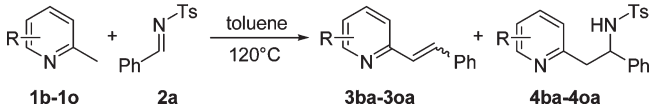
[a] Reaction conditions: **1a** (0.6 mmol) and **2** (0.3 mmol) in toluene (0.5 mL) were refluxed at 120 °C for 12 h under $N_2$. [b] Isolated yields. [c] Determined by $^1$H NMR on the basis of peak areas.

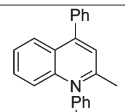
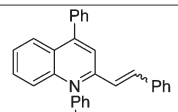
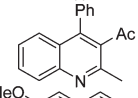
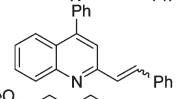
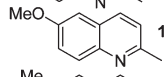
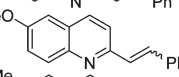
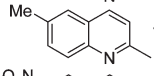
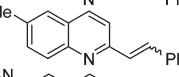
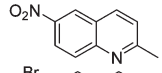
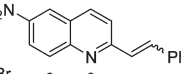
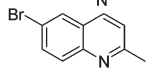
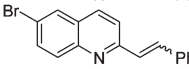
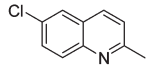
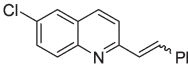
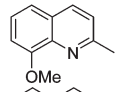
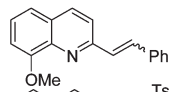
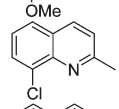
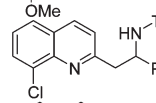
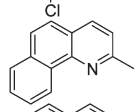
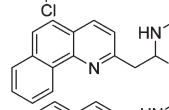
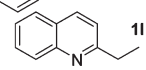
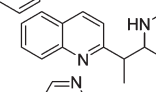
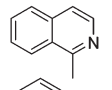
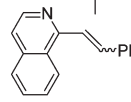
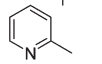
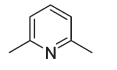
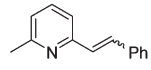
employed in the reaction, the corresponding products (**3ba-3ia** and **3ma**) were obtained in 77−90% yield with high stereoselectivities (Table 4, entries 1−8 and 12). However, when **1j**−**1l** were used as the substrates, only addition products (**4ja-4la**) were obtained (Table 4, entries 9−11). In addition, 2,6-lutidine (**1o**) also gave the desired product **3oa** in 35% yield, while 2-methylpyridine (**1n**) did not give any product (Table 4, entries 13−14). This can be perhaps ascribed to the electronic effect of the methyl group on the pyridyl ring.

In order to improve atom economy and enhance the reaction efficiency, we developed a one-pot procedure for this reaction. When the reaction mixture of 2-methylquinoline, benzaldehyde, and *p*-toluenesulfonamide with a ratio of 1:1:1 was heated either under nitrogen atmosphere or open to air for 12 h, the product **3aa** can be obtained with 93 and 83% isolated yield respectively (Table 5, entries 1 and 3). With this procedure, the tedious isolation of *N*-tosyl aldimines is avoided. The yield was not increased by increasing the amount of 2-methylquinoline (Table 5, entry 2). Reducing the amount of *p*-toluenesulfonamide to 0.5 equiv incurred a lower reaction yield of 86% (Table 5, entry 4). Further reducing the amount of *p*-toluenesulfonamide to 0.2 equiv, the reaction yield was slightly decreased (Table 5, entry 5). The reaction hardly proceeded in the absence of *p*-toluenesulfonamide (Table 5, entry 6). It was noted that sulfonamide possibly plays the role of a catalyst in this condensation of aldehydes. Moreover, other aldehydes and azaarenes can also give the olefination products with moderate to good yield under these one-pot conditions (Table 5, entries 7−17) .

To get insight into the mechanism of this reaction, several control experiments were performed. The intermediate **4aa** could be synthesized according to the literature and then converted to C−C cleavage product **1a** and C−N cleavage product **3aa**. In addition, **4ja** could also give similar products in mesitylene at a higher temperature (Scheme 2). This indicates that **4** should be the intermediate of reaction, and the addition step may be reversible.

**Table 4. Substrate Scope of Various Methylazaarenes**[a]




| entry | substrate | product | yield(%)[b] | E/Z[c] |
|---|---|---|---|---|
| 1 |  **1b** |  | 91 | 92:8 |
| 2 |  **1c** |  | 80 | >99:1 |
| 3 |  **1d** |  | 77 | >99:1 |
| 4 |  **1e** |  | 84 | >99:1 |
| 5 |  **1f** |  | 88 | >99:1 |
| 6 |  **1g** |  | 83 | >99:1 |
| 7 |  **1h** |  | 86 | 91:9 |
| 8 |  **1i** |  | 90 | >99:1 |
| 9 |  **1j** |  | 82 | — |
| 10 |  **1k** |  | 60 | — |
| 11 |  **1l** |  | 70[d] | — |
| 12 |  **1m** |  | 78 | >99:1 |
| 13 |  **1n** | — | — | — |
| 14 |  **1o** |  | 35 | >99:1 |

[a] Reaction conditions: **1** (0.6 mmol) and **2a** (0.3 mmol) in toluene (0.5 mL) were refluxed at 120 °C for 12 h under $N_2$. [b] Isolated yields. [c] Determined by $^1$H NMR on the basis of peak areas. [d] dr = 1.8:1.

On the basis of the above experimental results, a plausible reaction pathway is proposed in Scheme 3. First, *N*-tosyl aldimine (**2a**) was formed from benzaldehyde and *p*-toluenesulfonamide in situ. Subsequently, the enamine intermediate **5**, which was generated via the requisite disruption of aromaticity of **1a**, cooperated with **2a** to form the cyclic transition state **6**. Then intermediate **4aa** was generated via a hydrogen transfer. Finally, the stable *trans*-2-styrylquinoline (**3aa**) was obtained through the elimination of **4aa** in situ (Scheme 3), regenerating *p*-toluenesulfonamide.

In conclusion, we have developed a highly efficient synthesis of *trans*-alkenylazaarenes under catalyst-free conditions. The one-pot procedure realizes successfully the condensation of aldehydes and methylazaarenes with the use of an organocatalyst,


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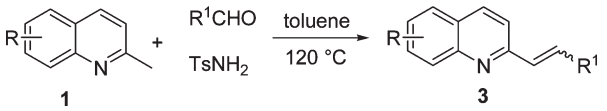
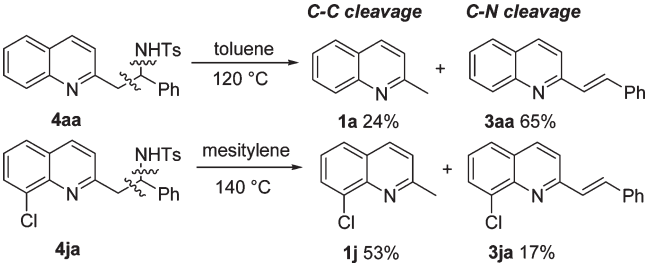
**Table 5. One-Pot Synthesis of 3**[a]




| entry | R | $R^1$ | product | yield (%)[b] | $E/Z$[c] |
|---|---|---|---|---|---|
| 1 | H | Ph | **3aa** | 93 | >99:1 |
| 2[d] | H | Ph | **3aa** | 93 | >99:1 |
| 3[e] | H | Ph | **3aa** | 83 | >99:1 |
| 4[f] | H | Ph | **3aa** | 86 | >99:1 |
| 5[g] | H | Ph | **3aa** | 85 | >99:1 |
| 6[h] | H | Ph | **3aa** | n.d. | |
| 7 | H | 4-Cl-Ph | **3ab** | 95(90[g]) | >99:1 |
| 8 | H | 4-$NO_2$-Ph | **3ag** | 90(84) | >99:1 |
| 9 | H | 4-OMe-Ph | **3ai** | 94(87) | >99:1 |
| 10 | H | 4-Me-Ph | **3al** | 98(90) | >99:1 |
| 11 | H | 2-pyridyl | **3ar** | 81(75) | >99:1 |
| 12 | H | cyclohexyl | **3at** | 50(45) | >99:1 |
| 13 | H | $i$-$C_4H_9$ | **3au** | 60(50) | >99:1 |
| 14 | 6-OMe | Ph | **3da** | 90(83) | >99:1 |
| 15 | 6-Me | Ph | **3ea** | 92(85) | >99:1 |
| 16 | 6-Br | Ph | **3ga** | 94(86) | >99:1 |
| 17 | 6-Cl | Ph | **3ha** | 92(87) | >99:1 |

[a] Reaction conditions: **1** (0.3 mmol), aldehyde (0.3 mmol), and *p*-toluenesulfonamide (0.3 mmol) in toluene (0.5 mL) were refluxed at 120 °C for 12 h under $N_2$. [b] Isolated yields. [c] Determined by $^1$H NMR on the basis of peak areas. [d] 2 equiv of **1a** was used. [e] Under air. [f] 0.5 equiv of *p*-toluenesulfonamide was used. [g] 0.2 equiv of *p*-toluenesulfonamide was used. [h] In the absence of *p*-toluenesulfonamide.

**Scheme 2. Control Experiments**




tosylamine. Further investigations of the mechanism and the application of the reaction are currently underway in our laboratory.

## EXPERIMENTAL SECTION

**General Procedure for the Synthesis of Alkenylazaarene.** A solution of **1a** (81 μL, 0.6 mmol) and **2a** (77.7 mg, 0.3 mmol) in toluene (0.5 mL) was refluxed at 120 °C for 12 h in a reaction tube under $N_2$. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure. Then the concentrate was purified by column chromatography on silica gel, affording **3aa** as a white solid (64 mg, 92% yield).

**General Procedure for the Synthesis of *N*-Sulfonyl Aldimines.**[9] Benzaldehyde (2.12 g, 20 mmol), *p*-toluenesulfonamide (3.42 g, 20 mmol), and $Si(OEt)_4$ (4.7 mL, 21 mmol) were placed in a flask and heated at 120 °C for 12 h . After cooling, the mixture was crystallized with ethyl acetate and petroleum ether. The resulting solid was collected by filtration and then dried in a vacuum, giving **2a** as a white solid (3 g, 58% yield).

**General Procedure for the Synthesis of Methylazaarenes.** *Synthesis of* ***1b***. The mixture of *o*-aminobenzophenone (394 mg, 2 mmol) and acetone (0.5 mL) in 20% KOH ethanol solution (10 mL) was refluxed overnight at 80 °C. Then the reaction mixture was quenched with hydrochloric acid (1 M) and extracted three times with EtOAc (3 × 20 mL). The combined organic layers were washed with brine once and dried over $Na_2SO_4$. The organic phase was concentrated in a vacuum and purified by chromatographic column over silica gel, giving 2-methyl-4-phenylquinoline (**1b**) as a light yellow solid.

*Synthesis of* ***1c***.[10] The mixture of *o*-aminobenzophenone (394 mg, 2 mmol), acetylacetone (240 mg, 2.4 mmol), and a grain of $I_2$ in EtOH (5 mL) was stirred overnight at room temperature. Then the mixture was quenched with water (15 mL) and extracted with EtOAc (3 × 20 mL). The organic phase was dried over $Na_2SO_4$ and purified by column chromatography on silica gel, giving 2-methyl-3-acetyl-4-phenylquinoline (**1c**) as a white solid.

*Synthesis of* ***1d***-***1j***.[11] Aniline (2 mmol) was added into a solution of phosphotungstic acid (2 mmol) in water (10 mL). To this was added crotonaldehyde (3 mmol) in toluene (15 mL), and the mixture was heated at 100 °C for 6 h. After cooling to room temperature, the mixture was basified by sodium hydroxide solution and extracted three times with EtOAc (3 × 25 mL). The combined organic layers were dried over $Na_2SO_4$, concentrated, and purified by column chromatography on silica gel.

*Synthesis of* ***1k***.[12] A solution of Sulfo-mix (5.85 g), $FeSO_4 \cdot 7H_2O$ (140 mg), $H_3BO_3$ (240 mg), water (5 mL), and 1-naphthylamine (572 mg, 4 mmol) was warmed to 110 °C, and crotonaldehyde (350 mg, 5 mmol) was added dropwise over 30 min. The reaction mixture was heated at 130 °C for 5 h. The cooled solution was basified with aqueous 20% NaOH and extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were washed with brine and dried over $Na_2SO_4$. The organic phase was concentrated in a vacuum and purified by chromatographic column over silica gel, giving 2-methylbenzo[*h*]quinoline (**1k**) as a yellow solid.

*Synthesis of the Intermediate* ***4aa***.[4] Under $N_2$, $Pd(OAc)_2$ (6.8 mg, 5 mol %), 1,10-phenanthroline (5.4 mg, 5 mol %), and dry $CH_2Cl_2$ (2 mL) were added to a tube. The mixture was kept stirring at room temperature for 0.5 h. After evaporating $CH_2Cl_2$, the mixture of **1a** (1.5 mmol) and **2a** (0.6 mmol) in dry THF (3 mL) was heated at 120 °C for 24 h. After the completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel, giving **4aa** as a white solid (145 mg, 60% yield).

**Characterization Data for the Products.** *(E)-2-Styrylquinoline (**3aa**).*[13] White solid (*E*:*Z* > 99:1, 92% yield): mp 98−100 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 8.14−8.07 (m, 2H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.74−7.63 (m, 5H), 7.52−7.30 (m, 5H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 156.0, 148.3, 136.6, 136.4, 134.5, 129.8, 129.3, 129.1, 128.8, 128.7, 127.6, 127.4, 126.2, 119.3. HRMS calcd for $C_{17}H_{13}N$: 231.1048. Found: 231.1045.

*(E)-2-(4-Chlorostyryl)quinoline (**3ab**).*[14] White solid (*E*:*Z* > 99:1, 90% yield): mp 143−145 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.75−7.62 (m, 3H), 7.59−7.48 (m, 3H), 7.41−7.35 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 155.6, 148.3, 136.5, 135.1, 134.4, 133.1, 129.9, 129.5, 129.3, 129.1, 128.5, 127.6, 127.5, 126.4, 119.4. HRMS calcd for $C_{17}H_{12}ClN$: 265.0658. Found: 265.0660.

*(E)-2-(3-Chlorostyryl)quinoline (**3ac**).*[6] White solid (*E*:*Z* > 99:1, 90% yield): mp 97−99 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 8.15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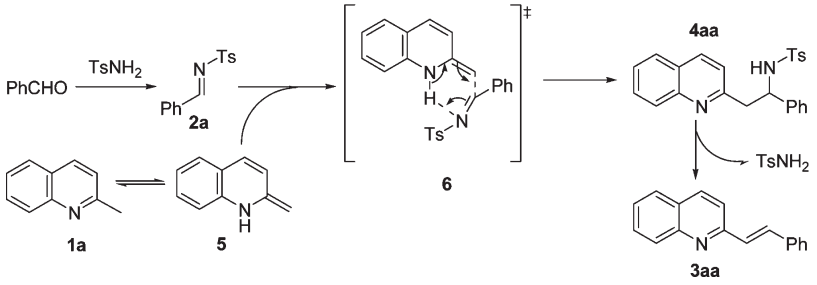
**Scheme 3. Plausible Reaction Pathway**




(d, $J$ = 8.4 Hz, 1H), 8.10 (d, $J$ = 8.7 Hz, 1H), 7.79 (d, $J$ = 8.1 Hz, 1H), 7.75−7.62 (m, 4H), 7.54−7.49 (m, 2H), 7.44−7.27 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 155.4, 148.3, 138.5, 136.5, 134.8, 132.9, 131.0, 130.3, 130.1, 129.9, 129.3, 128.5, 127.6, 127.2, 126.5, 125.5, 119.5. HRMS calcd for $C_{17}H_{12}ClN$: 265.0658. Found: 265.0655.

*(E)-2-(2-Chlorostyryl)quinoline (**3ad**).*[15] Light yellow solid ($E$:$Z$ > 99:1, 86% yield): mp 78−80 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.16−8.00 (m, 3H), 7.84−7.68 (m, 4H), 7.53−7.39 (m, 3H), 7.33−7.21 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 155.7, 148.2, 136.5, 134.6, 134.1, 131.7, 130.3, 130.0, 129.8, 129.5, 129.3, 127.6, 127.5, 127.1, 127.0, 127.0, 119.0. HRMS calcd for $C_{17}H_{12}ClN$: 265.0658. Found: 265.0659.

*(E)-2-(4-(Trifluoromethyl)styryl)quinoline (**3ae**).* White solid ($E$:$Z$ > 99:1, 94% yield): mp 124−126 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.17 (d, $J$ = 8.7 Hz, 1H), 8.11 (d, $J$ = 8.4 Hz, 1H), 7.81 (d, $J$ = 8.1 Hz, 1H), 7.76−7.63 (m, 7H), 7.56−7.45 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 155.2, 148.3, 140.0, 136.5, 132.6, 131.3, 130.3, 130.0, 129.3, 127.6, 127.3, 126.6, 126.0, 125.8, 125.7, 119.5. HRMS calcd for $C_{18}H_{12}F_3N$: 299.0922. Found: 299.0925.

*(E)-2-(2-(Trifluoromethyl)styryl)quinoline (**3af**).* White solid ($E$:$Z$ > 99:1, 80% yield): mp 93−95 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.18 (d, $J$ = 8.7 Hz, 1H), 8.12 (d, $J$ = 8.4 Hz, 1H), 8.02−7.91 (m, 2H), 7.81 (d, $J$ = 8.1 Hz, 1H), 7.77−7.72 (m, 3H), 7.70−7.40 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 155.6, 148.3, 136.6, 133.4, 132.2, 130.0, 129.95, 129.5, 128.2, 127.6, 127.5, 126.7, 126.3, 126.24, 126.17, 126.1, 126.0, 122.7, 118.9. HRMS calcd for $C_{18}H_{12}F_3N$: 299.0922. Found: 299.0918.

*(E)-2-(4-Nitrostyryl)quinoline (**3ag**).*[16] Light yellow solid ($E$:$Z$ > 99:1, 94% yield): mp 170−172 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.26 (d, $J$ = 9.0 Hz, 2H), 8.20 (d, $J$ = 8.4 Hz, 1H), 8.12 (d, $J$ = 8.4 Hz, 1H), 7.84−7.72 (m, 5H), 7.68 (d, $J$ = 8.4 Hz, 1H), 7.41−7.35 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 154.7, 148.3, 147.5, 143.0, 136.8, 133.2, 131.8, 131.0, 130.2, 129.4, 128.9, 127.7, 126.9, 124.2, 119.8. HRMS calcd for $C_{17}H_{12}N_2O_2$: 276.0899. Found: 276.0904.

*(E)-2-(2-Nitrostyryl)quinoline (**3ah**).*[13] Light yellow solid ($E$:$Z$ > 99:1, 90% yield): mp 102−104 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.18 (d, $J$ = 8.7 Hz, 1H), 8.14−8.08 (m, 2H), 8.02 (d, $J$ = 8.1 Hz, 1H), 7.89 (d, $J$ = 7.8 Hz, 1H), 7.83−7.68 (m, 3H), 7.65 (d, $J$ = 7.8 Hz, 1H), 7.64−7.47 (m, 2H), 7.42 (d, $J$ = 16.2 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 155.2, 148.3, 148.2, 136.7, 134.3, 133.4, 132.4, 130.0, 129.5, 129.2, 128.9, 128.6, 127.6, 126.8, 124.9, 119.1. HRMS calcd for $C_{17}H_{12}N_2O_2$: 276.0899. Found: 276.0901.

*(E)-2-(4-Methoxystyryl)quinoline (**3ai**).*[17] Light yellow solid ($E$:$Z$ > 99:1, 87% yield): mp 125−127 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.12−8.06 (m, 2H), 7.77 (d, $J$ = 8.1 Hz, 1H), 7.70−7.57 (m, 5H), 7.50−7.45 (t, 1H), 7.29 (d, $J$ = 16.5 Hz, 1H), 6.93 (d, $J$ = 8.9 Hz, 2H), 3.84 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 160.2, 156.4, 148.3, 136.3, 134.2, 130.7, 129.8, 129.4, 129.1, 128.7, 127.6, 127.3, 126.9, 126.4, 126.0, 119.2, 114.3, 55.4. HRMS calcd for $C_{18}H_{15}NO$: 261.1154. Found: 261.1155.

*(E)-2-(2-Methoxystyryl)quinoline (**3aj**).* Yellow oil ($E$:$Z$ > 99:1, 76% yield): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.14−8.09 (m, 2H), 8.03 (d, $J$ = 16.8 Hz, 1H), 7.79−7.67 (m, 4H), 7.52−7.46 (m, 2H), 7.32−7.25 (m, 1H), 7.03−6.92 (m, 2H), 3.93 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 157.5, 156.8, 148.2, 136.3, 129.9, 129.7, 129.54, 129.5, 129.2, 127.5, 127.3, 126.1, 125.5, 120.9, 119.1, 111.1, 55.6. HRMS calcd for $C_{18}H_{15}NO$: 261.1154. Found: 261.1156.

*(E)-2-(2,4-Dimethoxystyryl)quinoline (**3ak**).* Bright yellow oil ($E$:$Z$ = 95:5, 96% yield): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.11−8.07 (m, 2H), 7.93 (d, $J$ = 16.8 Hz, 1H), 7.82−7.63 (m, 4H), 7.50−7.26 (m, 2H), 7.32−7.25 (m, 1H), 6.58−6.48 (m, 2H), 3.91 (s, 3H), 3.85 (s, 3H), 3.81 (s, 0.13H), 3.79 (s, 0.13H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 161.4, 158.7, 157.1, 148.1, 136.1, 129.55, 129.5, 129.4, 128.8, 128.2, 127.5, 127.0, 126.3, 125.8, 118.8, 118.5, 105.2, 98.4, 55.5, 55.4. HRMS calcd for $C_{19}H_{17}NO_2$: 291.1259. Found: 291.1255.

*(E)-2-(4-Methylstyryl)quinoline (**3al**).*[6] White solid ($E$:$Z$ > 99:1, 97% yield): mp 140−142 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.14−8.07 (m, 2H), 7.78 (d, $J$ = 8.1 Hz, 1H), 7.73−7.63 (m, 3H), 7.56−7.46 (m, 3H), 7.38 (d, $J$ = 16.5 Hz, 1H), 7.26−7.19 (m, 2H), 2.38 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 156.2, 148.3, 138.8, 136.3, 134.5, 133.8, 131.0, 129.7, 129.6, 129.2, 128.0, 127.5, 127.3, 126.1, 119.2, 21.4. HRMS calcd for $C_{18}H_{15}N$: 245.1204. Found: 245.1208.

*(E)-2-(3-Methylstyryl)quinoline (**3am**).* White solid ($E$:$Z$ > 99:1, 96% yield): mp 71−73 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.12−8.06 (m, 2H), 7.77 (d, $J$ = 8.1 Hz, 1H), 7.73−7.62 (m, 3H), 7.51−7.37 (m, 4H), 7.32−7.24 (m, 1H), 7.03−6.92 (d, $J$ = 7.2 Hz, 1H), 2.39 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 156.1, 148.3, 138.4, 136.5, 136.3, 134.6, 129.7, 129.5, 129.2, 128.9, 128.7, 128.0, 127.5, 127.4, 126.1, 124.5, 119.2, 21.5. HRMS calcd for $C_{18}H_{15}N$: 245.1204. Found: 245.1205.

*(E)-2-(2-Methylstyryl)quinoline (**3an**).* Colorless oil ($E$:$Z$ > 99:1, 97% yield): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.13−8.09 (m, 2H), 7.94 (d, $J$ = 16.2 Hz, 1H), 7.79−7.64 (m, 4H), 7.51−7.45 (m, 1H), 7.32 (d, $J$ = 16.2 Hz, 1H), 7.26−7.20 (m, 3H), 2.51 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 156.2, 148.3, 136.6, 136.4, 135.6, 132.2, 130.7, 130.2, 129.8, 129.3, 128.6, 127.6, 127.4, 126.4, 126.2, 125.9, 119.4, 20.1. HRMS calcd for $C_{18}H_{15}N$: 245.1204. Found: 245.1201.

*(E)-2-(2-(Naphthalen-1-yl)vinyl)quinoline (**3ao**).*[6] Yellow solid ($E$:$Z$ > 99:1, 91% yield): mp 103−105 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.53 (d, $J$ = 16.2 Hz, 1H), 8.34 (d, $J$ = 8.4 Hz, 1H), 8.16 (t, $J$ = 8.1 Hz, 2H), 7.93−7.70 (m, 6H), 7.59−7.46 (m, 5H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 156.0, 148.3, 136.4, 134.0, 133.8, 131.7, 131.5, 131.4, 129.8, 129.3, 129.0, 128.7, 127.6, 127.4, 126.4, 126.3, 126.0, 125.7, 124.2, 123.8, 119.6. HRMS calcd for $C_{21}H_{15}N$: 281.1204. Found: 281.1202.

*(E)-2-(2-(Furan-2-yl)vinyl)quinoline (**3ap**).*[6] Yellow oil ($E$:$Z$ > 99:1, 79% yield): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.10 (dd, $J_1$ = 8.4 Hz, $J_2$ = 3.3 Hz, 2H), 7.78−7.67 (m, 2H), 7.61−7.45 (m, 4H), 7.29 (d, $J$ = 16.2 Hz, 1H), 6.56 (d, $J$ = 3 Hz, 1H), 6.47 (dd, $J_1$ = 9.0 Hz, $J_2$ = 1.8 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 155.7, 153.0, 148.3, 143.3, 136.54, 136.49, 129.9, 129.2, 127.6, 127.4, 126.8, 126.2, 122.0, 120.0, 112.1, 111.4, 111.3. HRMS calcd for $C_{15}H_{11}NO$: 221.0841. Found: 221.0843.

*(E)-2-(2-(Thiophen-2-yl)vinyl)quinoline (**3aq**).* Light yellow solid ($E$:$Z$ = 99:1, 70% yield): mp 89−91 °C; $^1$H NMR (300 MHz, $CDCl_3$)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δ 8.10 (t, $J$ = 8.1 Hz, 2H), 7.86 (d, $J$ = 15.9 Hz, 1H), 7.77 (d, $J$ = 8.1 Hz, 1H), 7.70 (t, $J$ = 7.8 Hz, 1H), 7.58 (d, $J$ = 8.7, 1H), 7.52−7.46 (m, 1H), 7.31−7.19 (m, 3H), 7.05 (t, $J$ = 4.2 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 155.7, 148.4, 142.2, 136.51, 136.46, 129.93, 129.89, 129.2, 128.25, 128.16, 127.9, 127.6, 127.5, 127.4, 126.24, 126.22, 126.15, 119.5. HRMS calcd for $C_{15}H_{11}NS$: 237.0612. Found: 237.0610.

*(E)-2-(2-(Pyridin-2-yl)vinyl)quinoline* (***3ar***). Light yellow solid ($E$:$Z$ > 99:1, 81% yield): mp 95−97 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.65 (dq, $J_1$ = 4.8 Hz, $J_2$ = 0.8 Hz, 1H), 8.12 (dd, $J_1$ = 11.6 Hz, $J_2$ = 8.8 Hz, 2H), 7.83 (d, $J$ = 6.0 Hz, 2H), 7.80−7.77 (m, 1H), 7.73−7.65 (m, 3H), 7.58−7.55 (m, 1H), 7.53−7.48 (m, 1H), 6.97 (d, $J_1$ = 7.6 Hz, 1H, $J_2$ = 4.8 Hz, $J_3$ = 1.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.4, 155.2, 149.9, 148.4, 136.7, 136.6, 133.9, 132.7, 129.9, 129.5, 127.7, 127.6, 126.5, 122.92, 122.87, 120.43. HRMS calcd for $C_{16}H_{12}N_2$: 232.1000. Found: 232.1005.

*2-((1E,3E)-4-Phenylbuta-1,3-dienyl)quinoline* (***3as***).[6] Light yellow solid ($E$:$Z$ = 93:7, 90% yield): mp 117−119 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.11−8.06 (m, 2H), 7.77−7.66 (m, 2H), 7.58−7.46 (m, 5H), 7.40−7.25 (m, 3H), 7.10−7.02 (dd, $J_1$ = 15.6 Hz, $J_2$ = 10.8 Hz, 1H), 6.97 (d, $J$ = 15.6 Hz, 1H), 6.86 (d, $J$ = 15.6 Hz, 1H), 6.59 (d, 0.16H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.0, 148.2, 138.0, 137.5, 137.1, 136.5, 136.3, 136.1, 135.6, 135.3, 132.7, 130.0, 129.71, 129.68, 129.2, 128.88, 128.81, 128.7, 128.3, 128.2, 127.61, 127.55, 127.4, 127.1, 126.93, 126.87, 126.7, 126.35, 126.32, 123.1, 119.5. HRMS calcd for $C_{19}H_{15}N$: 257.1204. Found: 257.1205.

*(E)-2-(2-Cyclohexylvinyl)quinoline* (***3at***). Light yellow oil ($E$:$Z$ = 99:1, 71% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 8.04 (dd, $J_1$ = 8.1 Hz, $J_2$ = 5.6 Hz, 2H), 7.74 (d, $J$ = 8.1 Hz, 1H), 7.69−7.63 (m, 1H), 7.53 (d, $J$ = 8.9 Hz, 1H), 7.48−7.42 (m, 1H), 6.78 (dd, $J_1$ = 16.2 Hz, $J_2$ = 6.3 Hz, 1H), 6.68 (d, $J$ = 16.2 Hz, 1H), 2.30−2.21 (m, 1H), 1.91−1.68 (m, 4H), 1.43−1.19 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 156.9, 148.2, 143.6, 136.3, 129.6, 129.2, 128.8, 127.5, 127.3, 125.9, 118.9, 41.3, 37.7, 26.3, 26.2, 25.9. HRMS calcd for $C_{17}H_{19}N$: 237.1517. Found: 237.1514.

*(E)-2-(4-Methylpent-1-enyl)quinoline* (***3au***). Light yellow oil ($E$:$Z$ > 99:1, 78% yield): $^1$H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, $J_1$ = 8.4 Hz, $J_2$ = 3.6 Hz, 2H), 7.74 (dd, $J_1$ = 8.4 Hz, $J_2$ = 1.2 Hz, 1H), 7.69−7.64 (m, 1H), 7.53 (d, $J$ = 8.8 Hz, 1H), 7.48−7.43 (m, 1H), 6.83−6.77 (m, 1H), 6.72 (d, $J$ = 16.0 Hz, 1H), 2.25−2.20 (m, 2H), 1.90−1.70 (m, 1H), 0.99 (d, $J$ = 6.8 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.5, 148.1, 137.0, 136.3, 132.2, 129.7, 129.2, 127.5, 127.3, 126.0, 118.8, 42.6, 28.5, 22.6. HRMS calcd for $C_{15}H_{17}N$: 211.1361. Found: 211.1364.

*(E)-4-Phenyl-2-styrylquinoline* (***3ba***). White solid ($E$:$Z$ = 92:8, 91% yield): mp 145−147 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, $J$ = 8.4 Hz, 1H), 7.86 (dd, $J_1$ = 8.4 Hz, $J_2$ = 0.8 Hz, 1H), 7.74−7.62 (m, 5H), 7.56−7.32 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.5, 149.2, 138.4, 136.6, 135.0, 129.9, 129.7, 129.5, 129.4, 129.0, 128.9, 128.8, 128.63, 128.55, 128.4, 128.1, 127.5, 126.5, 126.2, 125.9, 125.8, 119.6. HRMS calcd for $C_{23}H_{17}N$: 307.1361. Found: 307.1365.

*(E)-1-(4-Phenyl-2-styrylquinolin-3-yl)ethanone* (***3ca***). White solid ($E$:$Z$ > 99:1, 80% yield): mp 189−191 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, $J$ = 8.4 Hz, 1H), 8.10 (d, $J$ = 15.6 Hz, 1H), 7.76−7.71 (m, 1H), 7.63−7.53 (m, 3H), 7.53−7.50 (m, 3H), 7.46−7.31 (m, 6H), 7.22 (d, $J$ = 15.6 Hz, 1H), 2.09 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 205.8, 150.3, 148.0, 144.6, 137.1, 136.6, 135.3, 134.7, 130.5, 130.2, 129.6, 129.04, 128.96, 128.8, 127.8, 126.9, 126.3, 125.7, 124.1, 33.0. HRMS calcd for $C_{25}H_{19}NO$: 349.1467. Found: 349.1466.

*(E)-6-Methoxy-2-styrylquinoline* (***3da***).[6] White solid ($E$:$Z$ > 99:1, 77% yield): mp 149−151 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, $J$ = 8.8 Hz, 2H), 7.63−7.58 (m, 4H), 7.40−7.28 (m, 5H), 7.03 (d, $J$ = 2.8 Hz, 1H), 3.91 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.8, 153.8, 144.2, 136.8, 135.3, 133.5, 130.6, 129.0, 128.9, 128.5, 128.4, 127.3, 122.5, 119.6, 105.4, 55.7. HRMS calcd for $C_{18}H_{15}NO$: 261.1154. Found: 261.1155.

*(E)-6-Methyl-2-styrylquinoline* (***3ea***).[13] White solid ($E$:$Z$ > 99:1, 84% yield): mp 136−138 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.03−7.98 (m, 2H), 7.68−7.60 (m, 4H), 7.55−7.52 (m, 2H), 7.43−7.38 (m, 3H), 7.34−7.30 (m, 1H), 2.53 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.2, 145.8, 135.7, 135.2, 134.8, 133.1, 131.2, 128.1, 127.92, 127.89, 127.6, 126.5, 126.3, 125.6, 118.3, 20.7. HRMS calcd for $C_{18}H_{15}N$: 245.1204. Found: 245.1206.

*(E)-6-Nitro-2-styrylquinoline* (***3fa***). Yellow solid ($E$:$Z$ > 99:1, 88% yield): mp 192−194 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, $J$ = 2.4 Hz, 1H), 8.46 (dd, $J_1$ = 9.2 Hz, $J_2$ = 2.8 Hz, 1H), 8.28 (d, $J$ = 8.4 Hz, 1H), 8.18 (d, $J$ = 9.2 Hz, 1H), 7.84 (d, $J$ = 16.0 Hz, 1H), 7.77 (d, $J$ = 8.8 Hz, 1H), 7.67−7.64 (m, 2H), 7.45−7.35 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.4, 150.5, 145.2, 138.2, 137.4, 136.0, 130.8, 129.6, 129.1, 127.85, 127.78, 126.1, 124.4, 123.5, 121.5. HRMS calcd for $C_{17}H_{12}N_2O_2$: 276.0899. Found: 276.0896.

*(E)-6-Bromo-2-styrylquinoline* (***3ga***).[13] White solid ($E$:$Z$ > 99:1, 83% yield): mp 168−170 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, $J$ = 8.8 Hz, 1H), 7.97−7.92 (m, 2H), 7.78−7.62 (m, 5H), 7.42−7.31 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.4, 146.8, 136.4, 135.6, 135.4, 133.4, 130.9, 129.7, 129.03, 128.98, 128.5, 128.4, 127.5, 120.3, 120.1. HRMS calcd for $C_{17}H_{12}BrN$: 309.0153. Found: 309.0152.

*(E)-6-Chloro-2-styrylquinoline* (***3ha***).[13] White solid ($E$:$Z$ = 91:9, 86% yield): mp 156−158 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, $J_1$ = 8.4 Hz, $J_2$ = 3.2 Hz, 2H), 7.76−7.62 (m, 6H), 7.43−7.26 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.3, 146.6, 136.5, 135.7, 135.3, 132.0, 130.9, 130.8, 129.2, 129.01, 128.98, 128.52, 128.45, 128.2, 128.0, 127.5, 126.4, 123.1, 120.3. HRMS calcd for $C_{17}H_{12}ClN$: 265.0658. Found: 265.0665.

*(E)-8-Methoxy-2-styrylquinoline* (***3ia***).[6] Colorless oil ($E$:$Z$ > 99:1, 90% yield): $^1$H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, $J$ = 4.4 Hz, 1H), 7.74 (d, $J$ = 8.4 Hz, 1H), 7.64−7.51 (m, 4H), 7.43−7.30 (m, 5H), 7.04 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz, 1H), 4.10 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.27, 155.25, 140.1, 136.7, 136.4, 134.1, 129.7, 128.9, 128.6, 128.5, 127.3, 126.5, 119.5, 119.3, 108.1, 56.2. HRMS calcd for $C_{18}H_{15}NO$: 261.1154. Found: 261.1150.

*N-(2-(8-Chloroquinolin-2-yl)-1-phenylethyl)-4-methylbenzenesulfonamide* (***4ja***).[18] White solid (82% yield): mp 169−171 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, $J$ = 6.0 Hz, 1H), 7.94 (d, $J$ = 8.4 Hz, 1H), 7.86 (dd, $J_1$ = 7.2 Hz, $J_2$ = 1.2 Hz, 1H), 7.66 (dd, $J_1$ = 8.4 Hz, $J_2$ = 1.2 Hz, 1H), 7.54 (d, $J$ = 8.4 Hz, 2H), 7.45 (t, $J$ = 8.0 Hz, 1H), 7.22−7.19 (m, 2H), 7.14−7.09 (m, 3H), 7.04 (d, $J$ = 8.0 Hz, 1H), 6.93 (d, $J$ = 8.4 Hz, 2H), 4.86 (m, 1H), 3.35−3.30 (m, 1H), 3.27−3.20 (m, 1H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.4, 143.4, 142.5, 141.1, 138.1, 137.4, 133.3, 130.0, 129.1, 128.3, 128.1, 127.2, 127.0, 126.9, 126.7, 126.5, 123.1, 57.3, 43.8, 21.5. HRMS calcd for $C_{24}H_{21}ClN_2O_2S$: 436.1012. Found: 436.1018. Crystal Data for **4ja**. Empirical formula: $C_{24}H_{21}ClN_2O_2S$, MW = 436.94, $T$ = 293(2) K, $\lambda$ = 0.71073 Å, tetragonal, $P42/n$, $a$ = 22.6880 (5) Å, $b$ = 22.6880 (5) Å, $c$ = 8.4809 (3) Å, α = 90.00°, β = 90.00°, γ = 90.00°, $V$ = 4365.5 (2) Å$^3$, $Z$ = 8, $D_{calcd}$ = 1.330 mg/m$^3$, $F$(000) = 1824. Crystal size 0.36 × 0.32 × 0.26 mm, independent reflections 3836 [$R$(int) = 0.0310], reflections collected 13919, refinement method, full-matrix least-squares on $F^2$, goodness-of-fit on $F^2$ 1.069, final $R$ indices [$I$ > 2σ($I$)] $R_1$ = 0.0541, $wR_2$ = 0.1708, $R$ indices (all data) $R_1$ = 0.0824, $wR_2$ = 0.1838, Largest diff. peak and hole 1.557 and −0.232 e·Å$^{-3}$.

*N-(2-(Benzo[h]quinolin-2-yl)-1-phenylethyl)-4-methylbenzenesulfonamide* (***4ka***). Light yellow solid (60% yield): mp 124−126 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.26 (d, $J$ = 7.2 Hz, 1H), 7.94−7.92 (m, 2H), 7.86−7.72 (m, 3H), 7.59 (d, $J$ = 8.8 Hz, 1H), 7.47 (s, 1H), 7.32−7.17 (m, 7H), 7.09 (d, $J$ = 8.0 Hz, 1H), 6.70 (d, $J$ = 8.0 Hz, 1H), 4.80−4.70 (m, 1H), 3.30−3.20 (m, 2H), 2.13 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.7, 145.7, 142.5, 141.6, 137.2, 136.8, 133.9, 131.0, 129.0, 128.7, 128.5, 128.1, 127.8, 127.7, 127.4, 126.9, 126.8, 125.1, 125.0, 124.4, 122.5, 58.1, 44.9, 21.4. HRMS calcd for $C_{28}H_{24}N_2O_2S$: 452.1558. Found: 452.1565.

*4-Methyl-N-(1-phenyl-2-(quinolin-2-yl)propyl)benzenesulfonamide* (***4la***).[4] Light yellow oil (dr = 1.8:1, 70% yield): $^1$H NMR (400 MHz,

$CDCl_3$) $\delta$ 8.09 (d, $J$ = 8.4 Hz, 1.56H), 7.88 (dd, $J_1$ = 8.4 Hz, $J_2$ = 5.6 Hz, 1.56H), 7.75−7.70 (m, 3.12H), 7.54−7.51 (m, 1.56H), 7.47 (d, $J$ = 6.8 Hz, 1.0H), 7.39 (d, $J$ = 8.0 Hz, 2.0H), 7.28−7.24 (m, 1.4), 7.15−7.13 (m, 3.5H), 7.07−7.01 (m, 5H), 6.97−6.89 (m, 3.6H), 6.70 (d, $J$ = 8.0 Hz, 1.12H), 4.62 (t, $J$ = 6.0 Hz, 1.0H), 4.54 (t, $J$ = 4.4 Hz, 0.56H), 3.34−3.32 (m, 1.56H), 2.25 (s, 3.0H), 2.17 (s, 1.68H), 1.29 (d, $J$ = 6.8 Hz, 3.0H), 1.25 (d, $J$ = 7.2 Hz, 1.68H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.0, 162.4, 147.3, 147.0, 142.5, 142.4, 140.9, 139.7, 138.1, 137.0, 136.8, 136.6, 129.9, 129.86, 129.7, 129.2, 129.0, 128.94, 128.89, 128.1, 128.0, 127.6, 127.5, 127.2, 127.1, 127.07, 127.02, 126.9, 126.8, 126.5, 126.47, 126.4, 121.2, 120.8, 62.9, 61.8, 47.5, 46.6, 21.42, 21.36, 19.2, 14.3. HRMS calcd for $C_{25}H_{24}N_2O_2S$: 416.1558. Found: 416.1555.

*(E)-1-Styrylisoquinoline (**3ma**).* White solid ($E$:$Z$ > 99:1, 78% yield): mp 116−118 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.55 (d, $J$ = 5.6 Hz, 1H), 8.35 (d, $J$ = 8.0 Hz, 1H), 7.99 (s, 2H), 7.81 (d, $J$ = 8.0 Hz, 1H), 7.71−7.58 (m, 4H), 7.55 (d, $J$ = 5.6 Hz, 1H), 7.43−7.38 (m, 2H), 7.35−7.30 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 154.6, 142.5, 137.0, 136.9, 136.1, 130.0, 128.9, 128.7, 127.6, 127.4, 127.3, 126.9, 124.6, 122.9, 120.0. HRMS calcd for $C_{17}H_{13}N$: 231.1048. Found: 231.1053.

*(E)-2-Methyl-6-styrypyridine (**3oa**).*[6] Yellow oil ($E$:$Z$ > 99:1, 35% yield): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.60−7.53 (m, 4H), 7.39−7.34 (m, 2H), 7.31−7.28 (m, 1H), 7.25 (d, $J$ = 8.4 Hz, 1H), 7.18 (d, $J$ = 16.0 Hz, 1H), 7.02 (d, $J$ = 7.6 Hz, 1H), 2.59 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 158.4, 155.2, 136.9, 132.7, 129.1, 128.8, 128.44, 128.35, 127.2, 127.3, 121.9, 118.9, 24.7. HRMS calcd for $C_{14}H_{13}N$: 195.1048. Found: 195.1045.

## ■ ASSOCIATED CONTENT

**Supporting Information.** $^1$H and $^{13}$C NMR spectra and crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) CCDC-790188 contains the supplementary crystallographic data for **4ja**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.