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# Synthesis of Vinyl Sulfides and Vinylamines through Catalytic Intramolecular Hydroarylation in the Presence of $FeCl_3$ and AgOTf

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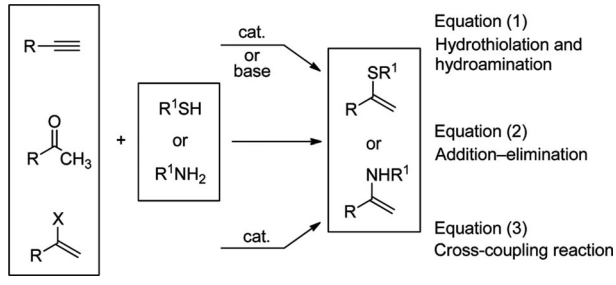
**Keywords:** Synthetic methods / Fused-ring systems / Cyclization / Iron / Substituent effects / Hydroarylation

A synthetic method was developed for the preparation of vinyl sulfides and vinylamines from arylalkynyl phenyl sulfides and sulfonamides. Under mild conditions, a catalytic intramolecular hydroarylation reaction was carried out in the presence of $FeCl_3$ and AgOTf (OTf = trifluoromethanesulfonate) in 1,2-dichloroethane. A variety of 1,2-dihydronaphthalenes, 2*H*-chromenes, and 1,2-dihydroquinolines containing a phenylsulfenyl or *N*-phenyl-*N*-tosyl group on the $sp^2$-hybridized benzylic carbon were prepared in good to excellent yields. The present method could be extended to the preparation of dihydropyrano[2,3-*g*]chromenes through a twofold Fe-catalyzed hydroarylation by a selective 6-*endo* mode.

## Introduction

Vinyl sulfides[1] and vinylamines[2] are important building blocks in organic synthesis and are present in many biologically and pharmaceutically active compounds.[3] Thus, the development of synthetic methods for these compounds is a significant goal. Transition-metal-catalyzed hydrothiolation[4] and hydroamination[5] reactions of alkynes are interesting methods for the synthesis of vinyl sulfides and vinylamines from the viewpoint of atom economy [see Scheme 1, Equation (1)]. Although sulfur compounds are often considered to be a poison to transition-metal catalysts, the hydrothiolation of alkynes has been reported to be catalyzed by Pd, Pt, Rh, Ni, Ir, and Au.[4] The hydroamination of alkynes is usually catalyzed by Ti, Zr, lanthanides, actinides, and late transition-metal catalysts such as Pd, Ru, Rh, Ag, and Au.[5] However, both the hydrothiolation and hydroamination of alkynes sometimes suffer from the issue of regioselectivity, which leads to the formation of undesired regioisomers. Vinyl sulfides and vinylamines can also be prepared from the reaction between carbonyl compounds and thiols or primary amines through an addition followed by an elimination reaction [see Scheme 1, Equation (2)].[6,7] In addition, the preparation of these compounds has been achieved through cross-coupling reactions of the corresponding electrophilic coupling partners such as vinyl halides and triflates with thiols or amines [see Scheme 1, Equation (3)].[8] Recently, the rare preparation of vinylamines through an intramolecular Brønsted acid-catalyzed hydroarylation was reported.[9] However, the hydroarylation of C-tethered arene-ynamides did not completely translate to N-tethered arene-ynamides.




Scheme 1. General synthetic methods towards vinyl sulfides and vinylamines.

During the past decades, iron has been one of the most useful metals in modern organic synthesis because of its lower toxicity and ease of accessibility.[10] Recently, we became interested in the transition-metal-catalyzed intramolecular hydroarylation reaction of arenes functionalized by alkynes.[11] Moreover, as part of a synthetic project, we needed to develop a simple route to cyclic vinyl sulfides and vinylamines through an intramolecular hydroarylation reaction. In this regard, we envisaged that by activating the triple bond, which has a sulfur or nitrogen on the sp-hybridized carbon, with an appropriate iron catalyst, the π system of the aryl group could initiate an intramolecular attack on the iron-activated alkyne to give cyclic vinyl sulfides and vinylamines. Herein, we describe an efficient synthetic method for the preparation of vinyl sulfides and vinylamines through a catalytic intramolecular hydroarylation

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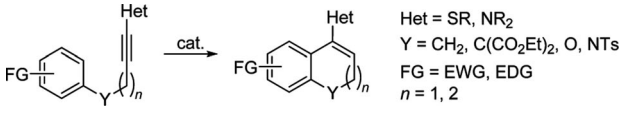
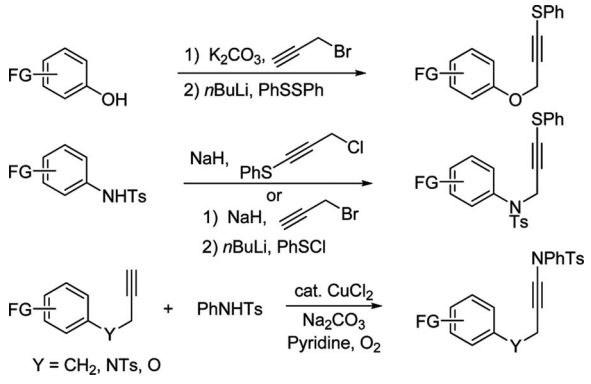
of arylalkynyl phenyl sulfides and sulfonamides in the presence of $FeCl_3$ and AgOTf (OTf = trifluoromethanesulfonate; see Scheme 2).




Scheme 2. Preparation of vinyl sulfides and vinylamines through catalytic intramolecular hydroarylation (Ts = *para*-toluenesulfonyl, FG = functional group, EWG = electron-withdrawing group, EDG = electron-donating group).

## Results and Discussion

First, a variety of functionalized arylalkynyl phenyl sulfides were prepared by treatment of phenol and *N*-phenyl sulfonamide derivatives with propargyl bromide followed by a reaction with phenyl disulfide or phenylsulfenyl chloride (see Scheme 3). Arylalkynyl phenyl sulfonamides were also produced by a Cu-catalyzed oxidative coupling reaction with 4-methyl-*N*-phenylbenzenesulfonamide in the presence of sodium carbonate and pyridine under oxygen.[12]

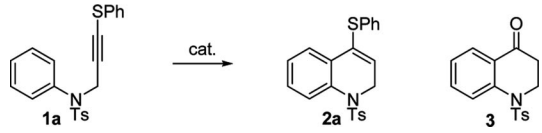



Scheme 3. Preparation of arylalkynyl phenyl sulfides and sulfonamides.

### Synthesis of Vinyl Sulfides from Arylalkynyl Phenyl Sulfides

To examine the feasibility of the intramolecular hydroarylation of arylalkynyl phenyl sulfide **1a**, the reaction was carried out with either $FeBr_2$, $FeCl_2$, or $Fe(acac)_3$ [5 mol-% each, (acac = acetylacetonate)] and heated to reflux in DCE (1,2-dichloroethane). In these cases, the reaction did not proceed, and most of **1a** was recovered unchanged (see Table 1, Entries 1, 2, and 3). However, when **1a** was treated with 5 mol-% $FeCl_3$ in various solvents such as toluene, acetonitrile, 1,4-dioxane, and DCE at 80 °C, the solvent of choice was DCE, although the formation of **3** was 19% yield (see Table 1, Entries 5–8). To conduct the hydroarylation reaction of **1a** more efficiently, we decided to use $FeCl_3$ activated with AgOTf.[13] Here, we found that the hydroarylation of **1a** proceeded intramolecularly under the catalytic conditions to provide **2a** selectively in 91% yield (DCE, 80 °C, 20 min) through a 6-*endo* mode, without the contamination from hydrolysis (see Table 1, Entry 9). A control experiment using 15 mol-% AgOTf in DCE at 80 °C for 6 h gave **2a** in 54% yield (see Table 1, Entry 10). However, formation of the hydrolyzed product **3** in 13% yield was inevitable. To check the possibility of catalysis by a protic acid,[9,14] we attempted the hydroarylation reaction in the presence of trifluoromethanesulfonic acid (5 mol-%) in DCE at 80 °C, which produced **2a** and **3** in 67 and 15% yields, respectively (see Table 1, Entry 11). These results indicate that using both $FeCl_3$ and AgOTf are essential for the catalytic system in this intramolecular hydroarylation reaction for the selective synthesis of cyclic vinyl sulfide **2a**.

Table 1. Optimization of preparation of vinyl sulfide through catalytic intramolecular hydroarylation.[a]



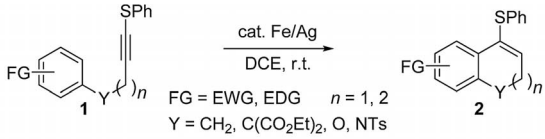

| Entry | Catalyst [mol-%] | Solvent | *t* [h] | % Yield[b] | | |
|---|---|---|---|---|---|---|
| | | | | **2a** | **3** | **1a** |
| 1 | $FeBr_2$ (5) | DCE | 6 | 0 | 0 | 96 |
| 2 | $FeCl_2$ (5) | DCE | 6 | 0 | 0 | 95 |
| 3 | $Fe(acac)_3$ (5) | DCE | 6 | 0 | 0 | 95 |
| 4 | $FeBr_3$ (5) | DCE | 6 | 40 | 0 | 47 |
| 5 | $FeCl_3$ (5) | toluene | 6 | 61 | 0 | 20 |
| 6 | $FeCl_3$ (5) | $CH_3CN$ | 1 | 60 | 0 | 28 |
| 7 | $FeCl_3$ (5) | dioxane | 6 | 0 | 0 | 94 |
| 8 | $FeCl_3$ (5) | DCE | 1 | 64 | 19 | 0 |
| 9 | $FeCl_3$ (5), AgOTf (15) | DCE | 0.3 | 91 | 0 | 0 |
| 10 | AgOTf (15) | DCE | 6 | 54 | 13 | 0 |
| 11 | TfOH (5) | DCE | 0.5 | 67 | 15 | 0 |

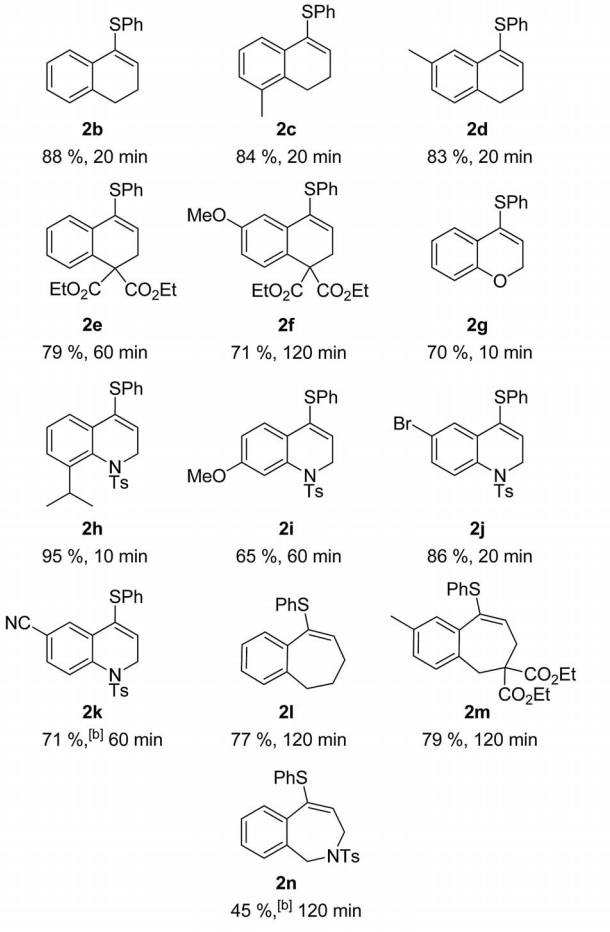
[a] Reactions were carried out at 80 °C. [b] Isolated yield.

To demonstrate the efficiency and scope of the present method, we applied this catalytic system to a wide range of arylalkynyl phenyl sulfides **1**, and the results are summarized in Scheme 4. The treatment of **1b** with 5 mol-% $FeCl_3$ and 15 mol-% AgOTf gave hydroarylated product **2b** selectively in 88% yield, without contamination from the α-tetralone. The reactions of **1c** and **1d**, substituted by a 2- or 4-methyl group on the aromatic ring, with the Fe catalyst afforded hydroarylated products **2c** and **2d** in 84 and 83% yield, respectively. Under the optimized reaction conditions, the diethyl malonate-tethered arylalkynyl phenyl sulfide **1e** underwent cyclization smoothly through a selective 6-*endo* mode to produce **2e** in 79% yield.

In contrast, an electron-rich aryl ring counter-intuitively depressed the transformation. Thus, the hydroarylation reaction of substrate **1f**, with an electron-donating 4-methoxy group, was slow and required a longer reaction time (120 min) to obtain the product in 71% yield. After 10 min in DCE at 25 °C, the exposure of oxygen-tethered **1g** to the Fe catalyst provided cyclic vinyl sulfide **2g** in 70% yield. Although the intramolecular hydroarylation of *N*-tosylamine-linked **1h** proceeded smoothly at 25 °C to afford cyclic vinyl sulfide **2h** (95%, 10 min), the hydroarylation of **1i** with a 3-methoxy group on the aromatic ring gave vinyl



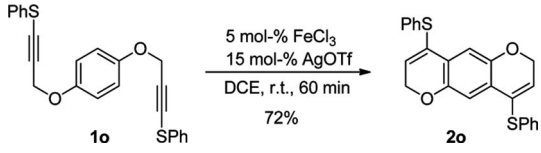




[a] Reactions were carried out with 5 mol-% $FeCl_3$ and 15 mol-% AgOTf in DCE at 25 °C. [b] The reaction was carried out at 80 °C.

Scheme 4. Synthesis of vinyl sulfides from arylalkynyl phenyl sulfides.[a]

sulfide **2i** in a lower yield (65%), even after a longer reaction time (60 min). These results indicate that the progress of the iron-catalyzed hydroarylation strongly depended on the electronic character of aryl ring, that is, the electron deficiency of the aryl ring accelerated the reaction. In the presence of an electron-withdrawing bromo group on aromatic ring, the reaction of **1j** with the Fe catalyst selectively provided, through a 6-*endo* mode, the desired cyclic vinyl sulfide **2j** in 86% yield. However, the hydroarylation of **1k**, containing an electron-withdrawing nitrile group on the aromatic ring, required a higher reaction temperature (80 °C) and afforded the desired cyclic vinyl sulfide **2k** in 71% yield, indicating that the iron catalyst could be forming a complex with the nitrile group. When **1l** was subjected to the optimized reaction conditions, the seven-membered cyclic vinyl sulfide **2l** was selectively obtained through an exclusive 7-*endo* mode in 77% yield. It was gratifying to obtain **2m** selectively in 79% yield, starting from diethyl malonate-tethered arylalkynyl phenyl sulfide **1m**. *N*-Tosylamine-linked alkynyl sulfide **1n** was compatible with the present reaction conditions, although the reaction required a higher temperature (80 °C) and gave a lower product yield (45%).

Next, a twofold intramolecular hydroarylation was briefly examined. When aryl bis(alkynyl phenyl sulfide) **1o** was subjected in one reaction vessel to 5 mol-% $FeCl_3$ and 15 mol-% AgOTf in DCE at 25 °C for 60 min, 2,7-dihydropyrano[2,3-*g*]chromene (**2o**) with a phenylsulfenyl group on the $sp^2$-hybridized benzylic carbon was isolated in 72% yield [see Equation (4)].



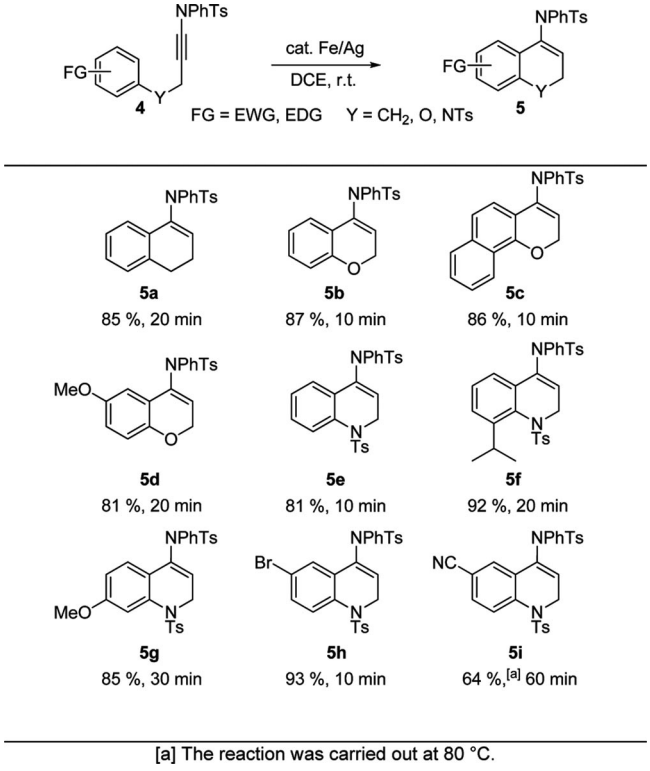

(4)

## Synthesis of Vinylamines from Arylalkynyl Phenyl Sulfonamides

On the basis of the catalytic hydroarylation of arylalkynyl phenyl sulfides, we next turned our attention to the hydroarylation of arylalkynyl phenyl sulfonamides (see Scheme 5). The treatment of **4a** with 5 mol-% $FeCl_3$ and 15 mol-% AgOTf in DCE at 25 °C for 20 min selectively provided hydroarylated product **5a** in 85% yield, without the contamination from the α-tetralone. When oxygen-tethered arylalkynyl phenyl sulfonamides **4b** and **4c** were subjected to the optimized reaction conditions, cyclic vinylamines **5b** and **5c** were selectively obtained in 87 and 86% yields, respectively, through a 6-*endo* mode. Although a longer reaction time was needed, the hydroarylation of arylalkynyl phenyl sulfonamide **4d**, with an electron-donating 4-methoxy group on the aromatic ring, proceeded smoothly to provide the corresponding cyclic vinylamine **5d** in 81% yield, albeit in a slightly lower yield than obtained for **5b** and **5c**. This tendency is similar to that observed in the catalytic hydroarylations of the arylalkynyl phenyl sulfides. Under the optimum reaction conditions, *N*-tosylamine-linked **4e** underwent a clean intramolecular hydroarylation to give cyclic vinylamine **5e** in 81% yield. The present method worked equally well with arylalkynyl phenyl sulfonamides **4f** and **4g**, containing an electron-donating 2-isopropyl or 3-methoxy group on the aromatic ring, to provide the selective formation of cyclic vinylamines **5f** and **5g** in 92 and 85% yields, respectively. The reaction of **4h**, with an electron-withdrawing bromo group, and the Fe catalyst afforded, through a 6-*endo* mode, the desired product **5h** in 93% yield. Because of the complexation of the nitrile group

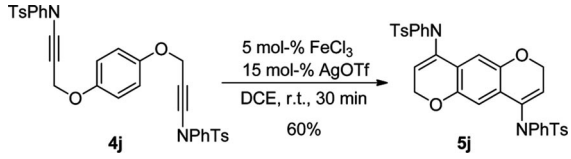
  

with the iron catalyst, arylalkynyl phenyl sulfonamide **4i**, with a nitrile group on the aromatic ring, required a longer reaction time and gentle heating to achieve completion.




Scheme 5. Synthesis of vinylamines from arylalkynyl sulfonamides.

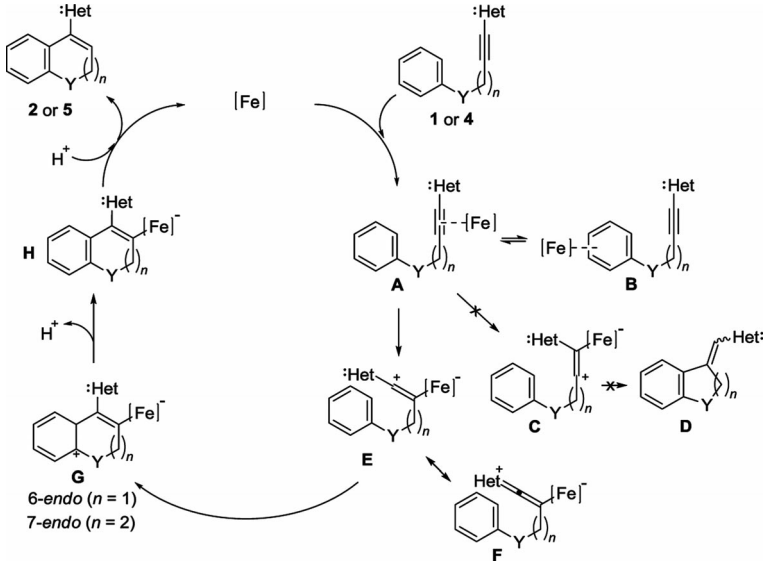
Likewise, a twofold intramolecular hydroarylation of arylalkynyl phenyl sulfonamide was attempted. When oxygen-tethered alkynyl sulfonamide **4j** was subjected in one pot to the standard conditions, bis(cyclic vinylamine) **5j** was produced in 60% yield [see Equation (5)].




(5)

## Mechanism

Although, at the present stage, the mechanism for the reaction has not been fully established, a possible reaction pathway is shown in Scheme 6. The coordination of the iron catalyst to the arylalkynyl phenyl sulfide (**1**) or sulfonamide (**4**) results in the formation of alkyne–iron complex **A** or arene–iron complex **B**. Moreover, the progress of the iron-catalyzed hydroarylation depended on the electronic character of the aromatic ring, that is, an electron-rich aromatic ring depressed the reaction. By considering these results, we envisage that the present hydroarylation might employ vinyl cationic intermediate **E**, which is generated in situ from **A** because of the π-electron delocalization occurring between the heteroatom and the conjugated alkyne as shown in alkynyl chromium–arene complexes.[15] An intramolecular hydroarylation through the addition of an aromatic C–H bond across a π bond might give intermediate **G**. Subsequent deprotonation of **G** followed by protodemetallation of **H** to release the iron catalyst back into the catalytic cycle might afford cyclic vinyl sulfide **2** or vinylamine **5**. The exclusive formation of **2** or **5** through a 6- or 7-*endo* mode rules out the formation of intermediate vinyl cation **C** in the catalytic cycle.




Scheme 6. Plausible mechanism for synthesis of vinyl sulfides and vinylamines through catalytic hydroarylation.

## Conclusions

In summary, we developed an efficient synthetic method for the preparation of cyclic vinyl sulfides and vinylamines containing 1,2-dihydronaphthalene, 2*H*-chromene, and 1,2-dihydroquinoline ring systems with a phenylsulfenyl or *N*-phenyl-*N*-tosyl group on the $sp^2$-hybridized benzylic carbon. The intramolecular hydroarylation of arylalkynyl phenyl sulfides and sulfonamides proceeded smoothly in a selective 6- or 7-*endo* mode in the presence of $FeCl_3$ and AgOTf. The present method could be further extended to the preparation of dihydropyrano[2,3-*g*]chromene derivatives through a twofold Fe-catalyzed hydroarylation by a selective 6-*endo* mode. Of special importance, the cationic iron catalyst permits the participation of electron-deficient aryl nucleophiles, which provide useful examples of hydroarylation.

## Experimental Section

**General Methods:** Many chemical reagents were purchased commercially and used without further purification. Analytical TLC was carried out with precoated plates and visualized by using UV light or staining with potassium permanganate. The $^1H$ and $^{13}C$ NMR spectroscopic data were recorded at 298 K with a 400 Fourier Transform NMR spectrometer. Chemical shifts were reported in $\delta$ (ppm), relative to the internal standard of TMS. The signals observed were described as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplets). The number of protons (n) for a given resonance was indicated as n H. Coupling constants were reported as *J* values in Hz. The $^{13}C$ NMR spectroscopic data were reported in $\delta$ (ppm), downfield from TMS and relative to the signal of $CDCl_3$ ($\delta$ = 77.00 ppm, triplet). Mass spectrometry was performed with a GC–HRMS spectrometer under electron impact (EI) ionization (magnetic sector/electric sector double-focusing mass analyzer). $FeCl_2$ (99.5%), $FeBr_2$ (98%), $Fe(acac)_2$ (99.9%), $Fe(OTf)_3$ (90%), $FeBr_3$ (98%), and $FeCl_3$ (98%) were used.

**Preparation of (3,4-Dihydronaphthalen-1-yl)(phenyl)sulfane:** A suspension of $FeCl_3$ (2.4 mg, $1.5 \times 10^{-2}$ mmol, 5 mol-%) and AgOTf (11.6 mg, $4.5 \times 10^{-2}$ mmol, 15 mol-%) in DCE (0.8 mL) was stirred at 25 °C for 5 min. Then, a solution of 4-methyl-*N*-phenyl-*N*-[3-(phenylthio)prop-2-ynyl]benzenesulfonamide (118.1 mg, 0.3 mmol) in DCE (0.7 mL) was added under nitrogen. After the reaction mixture was stirred at 80 °C for 20 min, it was quenched with water. The aqueous layer was extracted with dichloromethane (DCM, $2 \times 15$ mL), and the combined organic layers were washed with water and brine, filtered, and then dried under reduced pressure. Silica gel column chromatography (EtOAc/hexane, 1:15) gave 4-(phenylthio)-1-tosyl-1,2-dihydroquinoline (**2a**, 107.4 mg, 0.273 mmol, 91%).

**4-(Phenylthio)-1-tosyl-1,2-dihydroquinoline (2a):** Yellow solid, m.p. 75–80 °C. $R_f$ = 0.2 (EtOAc/hexane, 1:10). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.77 (dd, *J* = 1.1, 8.0 Hz, 1 H), 7.42–7.38 (m, 3 H), 7.34–7.30 (m, 1 H), 7.21–7.14 (m, 6 H), 6.87–6.84 (m, 2 H) 5.60 (t, *J* = 4.5 Hz, 1 H), 4.48 (d, *J* = 4.5 Hz, 2 H), 2.41 (s, 3 H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 143.6, 136.6, 135.3, 133.0, 131.3, 130.7, 129.4, 129.1, 128.8, 128.4, 127.7, 127.4, 126.9, 125.5, 125.2, 46.1, 21.6 ppm. IR (solid): $\tilde{\nu}$ = 3061, 1689, 1597, 1476, 1354, 1164, 1088 $cm^{-1}$. HRMS (EI): calcd. for $C_{22}H_{19}NO_2S_2$ 393.0857; found 393.0856.

**(3,4-Dihydronaphthalen-1-yl)(phenyl)sulfane (2b):**[8h] Colorless oil, $R_f$ = 0.3 (hexane). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.57 (d, *J* = 6.9 Hz, 2 H), 7.28–7.22 (m, 4 H), 7.14–7.10 (m, 4 H), 6.57 (t, *J* = 4.8 Hz, 1 H), 2.88 (t, *J* = 8.0 Hz, 2 H), 2.47–2.45 (m, 2 H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 143.2, 137.2, 133.9, 133.2, 129.1, 128.4, 128.1, 127.8, 127.7, 127.3, 127.1, 53.7, 29.4, 26.8 ppm. IR (film): $\tilde{\nu}$ = 3060, 2936, 1682, 1438, 1348, 1302, 1144, 1084, 1024, 739 $cm^{-1}$.

**5-Methyl-3,4-dihydronaphthalen-1-yl(phenyl)sulfane (2c):** Yellow oil, $R_f$ = 0.4 (hexane). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.48 (dd, *J* = 6.8, 1.9 Hz, 1 H), 7.24–7.16 (m, 4 H), 7.10–7.06 (m, 1 H), 7.03–6.97 (m, 2 H), 6.55 (t, *J* = 4.8 Hz, 1 H), 2.80 (t, *J* = 8.0 Hz, 2 H), 2.42 (td, *J* = 8.0, 4.8 Hz, 2 H), 2.29 (s, 3 H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 137.8, 137.3, 135.2, 135.1, 133.4, 131.0, 130.4, 129.3, 128.3, 126.4, 126.0, 123.8, 24.8, 23.9, 20.2 ppm. IR (film): $\tilde{\nu}$ = 2923, 2853, 1681, 1595, 1464, 1439, 1282, 1070, 897, 794, 742, 690, 632 $cm^{-1}$. HRMS (EI): calcd. for $C_{17}H_{16}S$ 252.0973; found 252.0970.

**(7-Methyl-3,4-dihydronaphthalen-1-yl)(phenyl)sulfane (2d):** Yellow oil, $R_f$ = 0.4 (hexane). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.41 (s, 1 H), 7.27–7.24 (m, 2 H), 7.19 (t, *J* = 7.6 Hz, 2 H), 7.12–7.07 (m, 1 H), 7.02 (d, *J* = 7.5 Hz, 1 H), 6.94 (d, *J* = 7.5 Hz, 1 H), 6.48 (t, *J* = 4.7 Hz, 1 H), 2.80 (t, *J* = 8.0 Hz, 2 H), 2.41–2.36 (m, 2 H), 2.21 (s, 3 H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 137.7, 137.0, 136.6, 133.8, 133.5, 131.0, 129.4, 128.8, 128.7, 127.8, 126.2, 126.17, 27.8, 25.4, 21.7 ppm. IR (film): $\tilde{\nu}$ = 2934, 1682, 1614, 1583, 1489, 1478, 1281, 1084, 813, 739, 690, 632 $cm^{-1}$. HRMS (EI): calcd. for $C_{17}H_{16}S$ 252.0973; found 252.0974.

**Diethyl 4-(Phenylthio)naphthalene-1,1(2*H*)-dicarboxylate (2e):** Yellow oil, $R_f$ = 0.3 (EtOAc/hexane, 1:20). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.67–7.65 (m, 1 H), 7.25–7.10 (m, 8 H), 6.50 (t, *J* = 4.7 Hz, 1 H), 4.32–4.22 (m, 4 H), 3.15 (d, *J* = 4.7 Hz, 2 H), 1.27 (t, *J* = 7.1 Hz, 6 H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 170.7, 135.8, 133.5, 132.8, 132.1, 130.9, 128.9, 128.4, 128.2, 128.1, 127.2, 125.9, 125.8, 62.1, 58.9, 31.9, 14.0 ppm. IR (film): $\tilde{\nu}$ = 3058, 2979, 1730, 1261, 1235, 1027, 738 $cm^{-1}$. HRMS (EI): calcd. for $C_{22}H_{22}O_4S$ 382.1239; found 382.1236.

**Diethyl 6-Methoxy-4-(phenylthio)naphthalene-1,1(2*H*)-dicarboxylate (2f):** Colorless oil, $R_f$ = 0.3 (EtOAc/hexane, 1:20). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.23 (d, *J* = 2.6 Hz, 1 H), 7.21–7.15 (m, 4 H), 7.13–7.08 (m, 2 H), 6.77 (dd, *J* = 8.5, 2.7 Hz, 1 H), 6.55 (t, *J* = 4.5 Hz, 1 H), 4.31–4.21 (m, 4 H), 3.67 (s, 3 H), 3.14 (d, *J* = 3.2 Hz, 2 H), 1.26 (t, *J* = 7.1 Hz, 6 H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 170.9, 159.4, 135.7, 134.2, 133.4, 130.9, 128.9, 128.4, 128.2, 125.9, 124.9, 113.6, 111.4, 62.0, 58.3, 55.2, 32.2, 14.0 ppm. IR (film): $\tilde{\nu}$ = 2981, 2938, 1731, 1488, 1291, 1235, 1178, 1049 $cm^{-1}$. HRMS (EI): calcd. for $C_{23}H_{24}O_5S$ 412.1344; found 412.1341.

**4-(Phenylthio)-2*H*-chromene (2g):** White solid, m.p. 125–128 °C. $R_f$ = 0.3 (EtOAc/hexane, 1:60). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.43–7.34 (m, 3 H), 7.30–7.20 (m, 4 H), 7.12 (m, 1 H), 6.84–6.81 (m, 2 H), 5.89 (t, *J* = 4.1 Hz, 1 H), 4.79 (d, *J* = 4.1 Hz, 2 H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 154.5, 133.9, 130.6, 130.1, 130.0, 129.4, 127.2, 125.4, 122.0, 121.7, 116.2, 66.1 ppm. IR (solid): $\tilde{\nu}$ = 1690, 1605, 1477, 1308, 1265, 1215, 1148, 1034, 737, 691 $cm^{-1}$. HRMS [FAB (fast atom bombardment)]: calcd. for $C_{15}H_{13}OS$ [M + H]$^+$ 241.0687; found 241.0689.

**8-Isopropyl-4-(phenylthio)-1-tosyl-1,2-dihydroquinoline (2h):** White solid, m.p. 140–145 °C. $R_f$ = 0.3 (EtOAc/hexane, 1:10). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.40 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.34–7.24 (m, 7 H), 7.19 (d, *J* = 8.2 Hz, 2 H), 7.07 (m, 2 H), 5.17 (dd, *J* = 18.2, 6.0 Hz, 1 H) 3.97–3.90 (m, 2 H), 2.46 (s, 3 H), 1.44 (d, *J* =

6.9 Hz, 3 H), 1.11 (d, $J$ = 6.9 Hz, 3 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 149.1, 144.0, 136.7, 133.5, 133.0, 132.6, 132.57, 131.0, 129.8, 129.6, 128.4, 128.2, 127.8, 124.9, 122.4, 47.3, 29.1, 26.4, 22.2, 22.1 ppm. IR (solid): $\tilde{\nu}$ = 2976, 1695, 1583, 1477, 1354, 1340, 1162, 1069, 818, 739, 706, 679 cm$^{-1}$. HRMS (EI): calcd. for $C_{25}H_{25}NO_2S_2$ 435.1327; found 435.1326.

**7-Methoxy-4-(phenylthio)-1-tosyl-1,2-dihydroquinoline (2i):** White solid, m.p. 140–145 °C. $R_f$ = 0.7 (EtOAc/hexane, 1:4). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.43 (d, $J$ = 8.3 Hz, 2 H), 7.36 (d, $J$ = 2.6 Hz, 1 H), 7.29 (d, $J$ = 8.6 Hz, 1 H), 7.20–7.14 (m, 5 H), 6.83–6.80 (m, 2 H), 6.69 (dd, $J$ = 8.8, 2.7 Hz, 1 H), 5.55 (t, $J$ = 4.5 Hz, 1 H), 4.47 (d, $J$ = 4.5 Hz, 2 H), 3.85 (s, 3 H), 2.41 (s, 3 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 159.7, 143.6, 136.74, 136.7, 133.5, 130.8, 130.3, 129.4, 129.0, 127.4, 126.9, 126.5, 123.1, 121.4, 112.9, 111.7, 55.6, 46.2, 21.6 ppm. IR (solid): $\tilde{\nu}$ = 2926, 1680, 1597, 1440, 1351, 1247, 1161, 1087, 1032, 813, 706, 659 cm$^{-1}$. HRMS (EI): calcd. for $C_{23}H_{21}NO_3S_2$ 423.0963; found 423.0963.

**6-Bromo-4-(phenylthio)-1-tosyl-1,2-dihydroquinoline (2j):** White solid, m.p. 138–142 °C. $R_f$ = 0.3 (EtOAc/hexane, 1:10). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.63 (d, $J$ = 8.6 Hz, 1 H), 7.55 (d, $J$ = 2.3 Hz, 1 H), 7.43–7.37 (m, 3 H), 7.23–7.17 (m, 5 H), 6.89–6.86 (m, 2 H), 5.55 (t, $J$ = 4.5 Hz, 1 H), 4.43 (d, $J$ = 4.5 Hz, 2 H), 2.42 (s, 3 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 144.3, 136.8, 134.7, 132.5, 132.1, 131.7, 131.2, 130.7, 130.0, 129.7, 128.9, 128.4, 128.1, 127.8, 126.4, 120.7, 46.4, 22.1 ppm. IR (solid): $\tilde{\nu}$ = 3062, 2923, 1589, 1474, 1382, 1230, 1158, 1087, 1008, 816, 683, 660 cm$^{-1}$. HRMS (EI): calcd. for $C_{22}H_{18}BrNO_2S_2$ 470.9962; found 470.9964.

**4-(Phenylthio)-1-tosyl-1,2-dihydroquinoline-6-carbonitrile (2k):** Yellow solid, m.p. 88–92 °C. $R_f$ = 0.3 (EtOAc/hexane, 1:4). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.88 (d, $J$ = 8.4 Hz, 1 H), 7.70 (d, $J$ = 1.9 Hz, 1 H), 7.56 (dd, $J$ = 8.4, 1.9 Hz, 1 H), 7.44 (d, $J$ = 8.3 Hz, 2 H), 7.27–7.16 (m, 5 H), 6.85–6.83 (m, 2 H), 5.81 (t, $J$ = 4.5 Hz, 1 H), 4.53 (d, $J$ = 4.5 Hz, 2 H), 2.44 (s, 3 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 144.8, 139.9, 136.7, 132.6, 132.4, 131.0, 130.5, 130.2, 129.8, 129.6, 129.4, 128.4, 128.1, 127.6, 127.3, 118.7, 110.3, 46.3, 22.1 ppm. IR (solid): $\tilde{\nu}$ = 3060, 2230, 1595, 1479, 1354, 1163, 1085, 814, 742, 670 cm$^{-1}$. HRMS (EI): calcd. for $C_{23}H_{18}N_2O_2S_2$ 418.0810; found 418.0813.

**(6,7-Dihydro-5*H*-benzo[7]annulen-9-yl)(phenyl)sulfane (2l):** Yellow solid, m.p. 64–66 °C. $R_f$ = 0.3 (hexane). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.65–7.63 (m, 1 H), 7.26–7.04 (m, 8 H), 6.61 (t, $J$ = 7.3 Hz, 1 H), 2.70 (t, $J$ = 7.0 Hz, 2 H), 2.22–2.18 (m, 2 H), 1.98–1.93 (m, 2 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 141.7, 138.4, 135.9, 135.3, 134.6, 129.6, 129.1, 128.8, 128.1, 127.5, 126.2, 126.1, 35.4, 32.7, 26.0 ppm. IR (solid): $\tilde{\nu}$ = 3059, 2931, 2855, 1681, 1163, 1582, 1478, 1438, 767, 748 cm$^{-1}$. HRMS (EI): calcd. for $C_{17}H_{16}S$ 252.0973; found 252.0972.

**Diethyl 2-Methyl-9-(phenylthio)-5*H*-benzo[7]annulene-6,6(7*H*)-dicarboxylate (2m):** Colorless oil, $R_f$ = 0.2 (EtOAc/hexane, 1:30). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.45 (s, 1 H), 7.29–7.27 (m, 2 H), 7.22–7.14 (m, 4 H), 6.97 (dd, $J$ = 7.7, 1.2 Hz, 1 H), 6.39 (t, $J$ = 7.3 Hz, 1 H), 4.23–4.16 (m, 4 H), 3.16 (s, 2 H), 2.40 (d, $J$ = 7.3 Hz, 2 H) 2.27 (s, 3 H), 1.26 (t, $J$ = 7.1 Hz, 6 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 171.4, 138.1, 137.8, 137.2, 135.2, 134.6, 131.2, 130.9, 130.2, 129.3, 129.2, 129.0, 127.2, 68.8, 64.0, 38.0, 32.3, 21.6, 14.5 ppm. IR (film): $\tilde{\nu}$ = 2979, 1731, 1439, 1267, 1211, 1074 cm$^{-1}$. HRMS (EI): calcd. for $C_{24}H_{26}O_4S$ 410.1552; found 410.1551.

**5-(Phenylthio)-2-tosyl-2,3-dihydro-1*H*-benzo[*c*]azepine (2n):** Brown solid, m.p. 78–82 °C. $R_f$ = 0.3 (DCM/EtOAc/hexane, 1:1:9). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.69 (d, $J$ = 8.3 Hz, 2 H), 7.65 (d, $J$ = 7.6 Hz, 1 H), 7.31–7.26 (m, 3 H), 7.24–7.15 (m, 7 H), 5.77 (t, $J$ = 7.4 Hz, 1 H), 4.19 (s, 2 H), 3.60 (d, $J$ = 7.4 Hz, 2 H), 2.44 (s, 3 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 143.4, 142.3, 137.7, 135.8, 133.8, 132.6, 130.1, 129.7, 129.2, 129.0, 128.5, 128.0, 127.96, 127.6, 122.6, 49.8, 43.9, 21.6 ppm. IR (solid): $\tilde{\nu}$ = 3061, 2923, 1336, 1157, 1091, 934, 814, 719, 690, 656 cm$^{-1}$. HRMS (EI): calcd. for $C_{23}H_{21}NO_2S_2$ 407.1014; found 407.1016.

**4,9-Bis(phenylthio)-2,7-dihydropyrano[2,3-*g*]chromene (2o):** White solid, m.p. 208–212 °C. $R_f$ = 0.7 (DCM/hexane, 1:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.38–7.25 (m, 10 H), 6.72 (s, 2 H), 6.22 (t, $J$ = 3.9 Hz, 2 H), 4.72 (d, $J$ = 3.9 Hz, 4 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 148.5, 133.6, 130.9, 129.9, 129.5, 127.5, 126.7, 123.0, 112.2, 65.9 ppm. IR (solid): $\tilde{\nu}$ = 3055, 2919, 1694, 1471, 1439, 1248, 1132, 1022, 745, 691, 632 cm$^{-1}$. HRMS (EI): calcd. for $C_{24}H_{18}O_2S_2$ 402.0748; found 402.0748.

***N*-(3,4-Dihydronaphthalen-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (5a):** Yellow solid, m.p. 150–154 °C. $R_f$ = 0.5 (EtOAc/hexane, 1:5). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.63 (d, $J$ = 8.2 Hz, 2 H), 7.56 (d, $J$ = 7.4 Hz, 1 H), 7.47–7.45 (m, 2 H), 7.30–7.05 (m, 8 H), 5.98 (t, $J$ = 4.6 Hz, 1 H), 2.76 (t, $J$ = 8.2 Hz, 2 H), 2.43–2.38 (m, 5 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 143.7, 140.5, 138.4, 137.7, 136.7, 132.8, 129.6, 129.2, 129.1, 128.1, 127.6, 127.2, 127.1, 126.8, 123.8, 27.3, 23.3, 21.8 ppm. IR (solid): $\tilde{\nu}$ = 2953, 2853, 1458, 1377, 1350, 1167, 1094, 962, 768, 691, 665, 619, 567 cm$^{-1}$. HRMS (FAB): calcd. for $C_{23}H_{22}NO_2S$ $[M + H]^+$ 376.1371; found 376.1371.

***N*-(2*H*-Chromen-4-yl)-4-methyl-*N*-phenylbenzenesulfonamide (5b):** Yellow solid, m.p. 153–158 °C. $R_f$ = 0.3 (EtOAc/hexane, 1:5). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.63 (d, $J$ = 8.7 Hz, 2 H), 7.44–7.42 (m, 2 H), 7.38–7.36 (m, 1 H), 7.31–7.22 (m, 5 H), 7.10–7.06 (m, 1 H), 6.86–6.82 (m, 1 H), 6.74 (d, $J$ = 8.2 Hz, 1 H), 5.75 (t, $J$ = 4.1 Hz, 1 H), 4.84 (d, $J$ = 4.1 Hz, 2 H), 2.41 (s, 3 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 155.5, 144.1, 139.6, 137.3, 135.8, 130.2, 129.8, 129.3, 128.1, 127.6, 127.4, 124.4, 121.7, 121.5, 121.4, 116.2, 65.4, 21.8 ppm. IR (solid): $\tilde{\nu}$ = 2953, 2853, 1456, 1377, 1348, 1304, 1223, 1167, 1090, 1065, 957, 756, 692, 660, 567 cm$^{-1}$. HRMS (FAB): calcd. for $C_{22}H_{20}NO_3S$ $[M + H]^+$ 378.1164; found 378.1164.

***N*-(2*H*-Benzo[*h*]chromen-4-yl)-4-methyl-*N*-phenylbenzenesulfonamide (5c):** White solid, m.p. 153–157 °C. $R_f$ = 0.3 (EtOAc/hexane, 1:4). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.06 (t, $J$ = 4.8 Hz, 1 H), 7.68–7.66 (m, 3 H), 7.50–7.45 (m, 3 H), 7.41–7.38 (m, 2 H), 7.32–7.18 (m, 6 H), 5.80 (t, $J$ = 4.1 Hz, 1 H), 5.02 (d, $J$ = 4.1 Hz, 2 H), 2.41 (s, 3 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 151.8, 144.1, 139.7, 137.4, 136.6, 134.8, 129.8, 129.3, 128.1, 127.8, 127.5, 127.3, 127.1, 125.8, 124.5, 122.0, 121.6, 120.9, 119.0, 116.1, 65.9, 21.8 ppm. IR (solid): $\tilde{\nu}$ = 2953, 2853, 1640, 1462, 1377, 1352, 1198, 1165, 1088, 1009, 962, 806, 692, 604, 556 cm$^{-1}$. HRMS (FAB): calcd. for $C_{26}H_{22}NO_3S$ $[M + H]^+$ 428.1320; found 428.1319.

***N*-(6-Methoxy-2*H*-chromen-4-yl)-4-methyl-*N*-phenylbenzenesulfonamide (5d):** White solid, m.p. 115–120 °C. $R_f$ = 0.3 (EtOAc/hexane, 1:5). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.63 (d, $J$ = 8.3 Hz, 2 H), 7.43 (d, $J$ = 7.1 Hz, 2 H), 7.31–7.20 (m, 5 H), 6.89 (d, $J$ = 2.9 Hz, 1 H), 6.68 (d, $J$ = 8.7 Hz, 1 H), 6.63 (dd, $J$ = 8.7, 2.9 Hz, 1 H), 5.82 (t, $J$ = 4.0 Hz, 1 H), 4.78 (d, $J$ = 4.0 Hz, 2 H), 3.67 (s, 3 H), 2.41 (s, 3 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 154.6, 149.7, 144.4, 139.9, 137.6, 136.0, 130.0, 129.5, 128.3, 127.9, 127.6, 122.4, 122.3, 117.1, 116.0, 109.6, 65.6, 56.0, 22.0 ppm. IR (solid): $\tilde{\nu}$ = 3064, 1595, 1578, 1429, 1354, 1208, 1165, 1092, 1062, 662 cm$^{-1}$. HRMS (FAB): calcd. for $C_{23}H_{22}NO_4S$ $[M + H]^+$ 408.1270; found 408.1267.

**4-Methyl-*N*-phenyl-*N*-(1-tosyl-1,2-dihydroquinolin-4-yl)benzenesulfonamide (5e):** White solid, m.p. 80–85 °C. $R_f$ = 0.3 (EtOAc/hexane,

1:4). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.73 (dd, $J$ = 8.0, 0.9 Hz, 1 H), 7.53 (dd, $J$ = 7.7, 1.4 Hz, 1 H), 7.44 (d, $J$ = 8.3 Hz, 2 H), 7.30–7.13 (m, 9 H), 6.97–6.95 (m, 2 H), 6.91 (t, $J$ = 8.1 Hz, 2 H), 5.73 (t, $J$ = 4.4 Hz, 1 H), 4.60 (s, 2 H), 2.42 (s, 3 H), 2.25 (s, 3 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 144.3, 143.7, 139.6, 137.4, 137.3, 137.1, 136.4, 129.9, 129.8, 129.5, 129.3, 128.2, 127.9, 127.8, 127.7, 127.3, 126.7, 125.0, 123.9, 45.5, 22.1, 22.0 ppm. IR (solid): $\tilde{\nu}$ = 2924, 2853, 2360, 1637, 1597, 1490, 1453, 1354, 1164, 1090, 1068, 814 cm$^{-1}$. HRMS (EI): calcd. for $C_{29}H_{26}N_2O_4S_2$ 530.1334; found 530.1334.

***N*-(8-Isopropyl-1-tosyl-1,2-dihydroquinolin-4-yl)-4-methyl-*N*-phenylbenzenesulfonamide (5f):** Yellow solid, m.p. 185–190 °C. $R_f$ = 0.5 (EtOAc/hexane, 1:3). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.55–7.53 (m, 1 H), 7.41 (d, $J$ = 8.2 Hz, 2 H), 7.36–7.30 (m, 4 H), 7.28–7.18 (m, 5 H), 7.07 (d, $J$ = 7.3 Hz, 2 H), 6.86 (d, $J$ = 7.8 Hz, 2 H), 5.73–5.71 (m, 1 H), 4.65 (dd, $J$ = 18.5, 5.9 Hz, 1 H), 4.14 (dd, $J$ = 18.5, 2.2 Hz, 1 H), 3.70 (sept, $J$ = 6.8 Hz, 1 H), 2.39 (s, 3 H), 2.23 (s, 3 H), 1.37 (d, $J$ = 6.8 Hz, 3 H), 1.08 (d, $J$ = 6.8 Hz, 3 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 147.0, 142.8, 142.3, 138.1, 137.1, 135.8, 135.6, 131.4, 128.8, 128.4, 128.3,127.9, 127.3, 126.9, 126.7, 126.6, 126.5, 124.1, 121.2, 44.6, 27.8, 24.9, 20.74, 20.7, 20.5 ppm. IR (solid): $\tilde{\nu}$ = 2926, 1726, 1344, 1158, 1109, 1088, 1068, 1030, 961, 819, 696, 668 cm$^{-1}$. HRMS (EI): calcd. for $C_{32}H_{32}N_2O_4S_2$ 572.1803; found 572.1806.

***N*-(7-Methoxy-1-tosyl-1,2-dihydroquinolin-4-yl)-4-methyl-*N*-phenylbenzenesulfonamide (5g):** White solid, m.p. 192–196 °C. $R_f$ = 0.4 (EtOAc/hexane, 1:3). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.44 (dd, $J$ = 8.3, 1.7 Hz, 3 H), 7.33–7.31 (m, 3 H), 7.22–7.12 (m, 5 H), 6.95 (d, $J$ = 7.9 Hz, 2 H), 6.91 (d, $J$ = 8.1 Hz, 2 H), 6.70 (dd, $J$ = 8.6, 2.5 Hz, 1 H), 5.58 (t, $J$ = 4.5 Hz, 1 H), 4.57 (s, 2 H), 3.79 (s, 3 H), 2.40 (s, 3 H), 2.24 (s, 3 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 160.4, 144.3, 143.8, 139.7, 137.8, 137.3, 137.2, 137.1, 129.9, 129.85, 129.3, 128.2, 127.8, 127.6, 127.3, 126.1, 120.7, 120.6, 112.6, 111.5, 56.0, 45.6, 22.1, 22.0 ppm. IR (solid): $\tilde{\nu}$ = 3661, 1607, 1492, 1344, 1157, 1089, 1062, 985, 918, 696, 671, 661 cm$^{-1}$. HRMS (EI): calcd. for $C_{30}H_{28}N_2O_5S_2$ 560.1440; found 560.1438.

***N*-(6-Bromo-1-tosyl-1,2-dihydroquinolin-4-yl)-4-methyl-*N*-phenylbenzenesulfonamide (5h):** White solid, m.p. 188–193 °C. $R_f$ = 0.3 (EtOAc/hexane, 1:5). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.60 (d, $J$ = 8.7 Hz, 1 H), 7.55 (s, 1 H), 7.42 (d, $J$ = 8.0 Hz, 2 H), 7.36 (d, $J$ = 8.5 Hz, 1 H), 7.30 (d, $J$ = 8.0 Hz, 2 H), 7.26–7.22 (m, 3 H), 7.18 (t, $J$ = 7.7 Hz, 2 H), 6.94 (d, $J$ = 8.0 Hz, 4 H), 5.79 (t, $J$ = 4.2 Hz, 1 H), 4.59 (s, 2 H), 2.42 (s, 3 H), 2.27 (s, 3 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 144.2, 143.6, 138.9, 136.5, 136.4, 136.0, 135.0, 131.9, 129.64, 129.6, 129.1, 127.8, 127.6, 127.5, 127.45, 127.4, 126.9, 125.0, 119.9, 45.0, 21.7, 21.6 ppm. IR (solid): $\tilde{\nu}$ = 3061, 1596, 1470, 1348, 1198, 1185, 1164, 1084, 1064, 949, 693, 659 cm$^{-1}$. HRMS (EI): calcd. for $C_{29}H_{25}BrN_2O_4S_2$ 608.0439; found 608.0439.

***N*-(6-Cyano-1-tosyl-1,2-dihydroquinolin-4-yl)-4-methyl-*N*-phenylbenzenesulfonamide (5i):** White solid, m.p. 135–138 °C. $R_f$ = 0.3 (EtOAc/hexane, 1:3). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.83 (d, $J$ = 8.5 Hz, 1 H), 7.69 (d, $J$ = 1.9 Hz, 1 H), 7.51 (dd, $J$ = 8.5, 1.9 Hz, 1 H), 7.43 (d, $J$ = 8.3 Hz, 2 H), 7.35 (d, $J$ = 8.3 Hz, 2 H), 7.25–7.19 (m, 5 H), 7.00 (t, $J$ = 8.0 Hz, 4 H), 5.88 (t, $J$ = 4.5 Hz, 1 H), 4.64 (s, 2 H), 2.44 (s, 3 H), 2.30 (s, 3 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 144.5, 144.2, 140.0, 138.7, 136.3, 136.1, 135.6, 132.5, 129.8, 129.7, 129.2, 128.2, 128.1, 127.8, 127.77, 127.3, 126.8, 125.8, 125.6, 118.2, 109.6, 45.0, 21.7, 21.6 ppm. IR (solid): $\tilde{\nu}$ = 2926, 2229, 1727, 1597, 1489, 1349, 1162, 1089, 1065, 696, 663, 629 cm$^{-1}$. HRMS (EI): calcd. for $C_{30}H_{25}N_3O_4S_2$ 555.1286; found 555.1289.

***N*,*N*′-(2,7-Dihydropyrano[2,3-*g*]chromen-4,9-diyl)bis(4-methyl-*N*-phenylbenzenesulfonamide) (5j):** Pale yellow solid, m.p. 279–283 °C. $R_f$ = 0.4 (DCM). $^1$H NMR (300 MHz, $[D_6]$DMSO): $\delta$ = 7.60 (d, $J$ = 8.3 Hz, 4 H), 7.40 (d, $J$ = 8.3 Hz, 4 H), 7.36 (d, $J$ = 6.9 Hz, 8 H), 7.32–7.26 (m, 2 H), 6.64 (s, 2 H), 5.99 (t, $J$ = 3.9 Hz, 2 H), 4.77 (d, $J$ = 3.9 Hz, 4 H), 2.39 (s, 6 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 149.8, 144.9, 140.2, 134.3, 130.7, 130.1, 128.4, 128.1, 127.3, 126.4, 125.7, 123.3, 111.5, 66.0, 21.8 ppm. IR (solid): $\tilde{\nu}$ = 2923, 2834, 1489, 1354, 1208, 1165, 695, 574 cm$^{-1}$. HRMS (FAB): calcd. for $C_{38}H_{32}N_2O_6S_2$ $[M + H]^+$ 677.1780; found 677.1777.

**Supporting Information** (see footnote on the first page of this article): $^1$H and $^{13}$C NMR spectra for the compounds synthesized.

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