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Note

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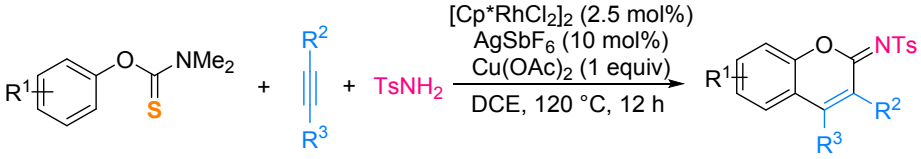
Multicomponent Synthesis of Iminocoumarins *via* Rhodium-Catalyzed C−H Bond Activation

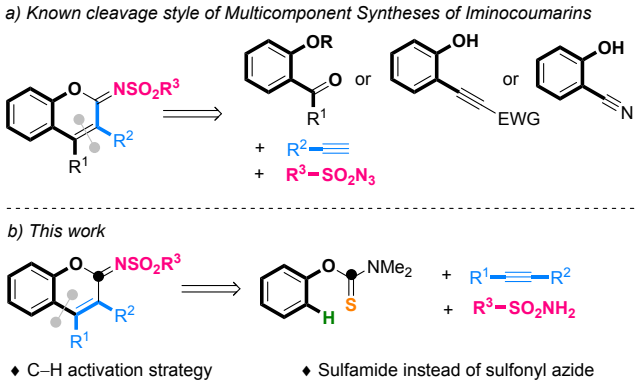
Zhan Chen, Shengnan Jin, Wenyao Jiang, Feimin Zhu, Yuqi Chen, and Yingwei Zhao*

College of Chemical Engineering, Huaqiao University, 668 Jimei Boulevard, Xiamen 361021, P. R. China



ABSTRACT: We herein establish a multicomponent annulation method for the synthesis of valuable iminocoumarins using aryl thiocarbamates, internal alkynes, and sulfonamides as starting materials which are safe and readily available. The key step is a Rh-catalyzed and sulfur-directed C−H bond activation. Preliminary mechanistic investigations suggested that the nucleophilic attack of sulfonamide onto an active iminium cation finally completes the imine segment.

Coumarins and their derivatives are known important molecules with widespread applications in medicine, perfumery, and material chemistry.[1] The iminocoumarins have attracted considerable attentions own to their interesting biomedical features including antagonistic,[2] antitumor,[3] anti-HIV[4] and lipoxygenase inhibitory[5] activities. In recent years, iminocoumarins are also found to be efficient fluorescent dyes[6] and fluorescence probes.[7] Along with the increasing studies spread out on various domains, the methods for the construction of iminocoumarins are improving. Traditional Knoevenagel condensation suffers from the drawbacks of harsh condition and limited substrate scope.[6a, 8] Another strategy refers to the modification of coumarin framework which requires the pre-activation of carbonyl group, usually by transformation to more reactive thiocarbonyl by Lawesson's reagent.[5, 9] Multicomponent reaction is a powerful tool to construct complex functional molecules from simple substrates in one pot.[10] In 2006, Wang and co-workers pioneered a general and efficient copper-catalyzed three component cyclization of a sulfonyl azide, a terminal alkyne, and a salicylaldehyde or 2-hydroxylacetophenone to afford the iminocoumarin skeleton.[11] Following this strategy, a variety of analogous reactions were developed for the preparation of functionalized iminocoumarins by using other phenol derivatives instead of salicylaldehyde or 2-hydroxylacetophenone (Scheme 1a).[2, 12]



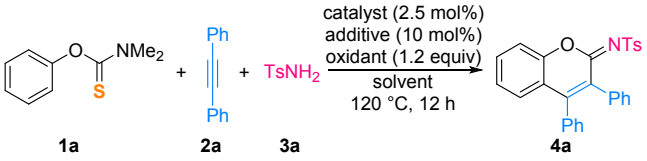
Scheme 1. Synthetic strategies for iminocoumarins

In recent years, transition-metal-catalyzed C−H bond activation has been regarded as an emerging weapon to provide novel solutions for the problems in organic synthesis.[13] It has also been successfully applied in annulation of multiple unreactive substrates via metallacyclic intermediates to construct heterocycles.[14] We and Satoh group have independently developed a Rh-catalyzed oxidative annulation protocol to construct coumarins[15] via a thiocarbamate group directed C−H activation.[16] The final step to finish coumarin's lactone skeleton is the nucleophilic attack of acetic anion on the highly reactive iminium cation in the structure of rhodacycle intermediate. This reactivity of such intermediates may allow the nucleophilic attack by amines to afford iminocoumarin, while the direct attack and condensation of an amine with the carbonyl group of coumarin has rarely been seen. In this work, we proved that this strategy

could be used to disconnect iminocoumarin structure into an aryl thiocarbamate which can be readily prepared from phenol, an internal alkyne, and a sulfonamide instead of sulfonyl azide as the nucleophile and imine source, which is safe and widely available (Scheme 1b).

We began with this program by utilizing *O*-phenyl *N*,*N*-dimethylthiocarbamate (**1a**), diphenylacetylene (**2a**) and *p*-toluenesulfonamide (**3a**) as the model substrates (Table 1). Exposure of them to the catalyst $[Cp^*RhCl_2]_2$, the additive $AgSbF_6$ and the oxidant $Cu(OAc)_2$ in *tert*-amyl alcohol afforded the desired iminocoumarin (**4a**) in a moderate 37% yield (entry 1). Next, we screened various common solvents. To our delight, the use of 1,2-dichloroethane (DCE) led to 84% yield of the product (entry 3). Other polar aprotic solvents also resulted in good yields except for DMF. We then studied the effect of different silver salts. It was found that $AgNTf_2$ also exhibited comparative efficiency, while AgOTf unexpectedly inhibited the reaction completely (entries 7 and 8). A moderate yield could also be obtained in the absence of a silver salt (entry 9). Examination of the oxidants revealed that stoichiometric amount of AgOAc and $Cu(OAc)_2{\cdot}5H_2O$ were also efficient oxidants compared to $Cu(OAc)_2$, albeit in diminishment of the yield (entries 10 and 11). Control experiments showed that both Rh catalyst and the oxidant are indispensable for this reaction (entries 12 and 13). Still good yield was obtained when the catalyst loading was lowered to 1 mol % (entry 14). Finally, the effect of reaction temperature was studied and it was shown that further increasing to 130 °C did not lead to an improvement on the product yield (entry 15).

Table 1 Optimization of the reaction conditions [a]

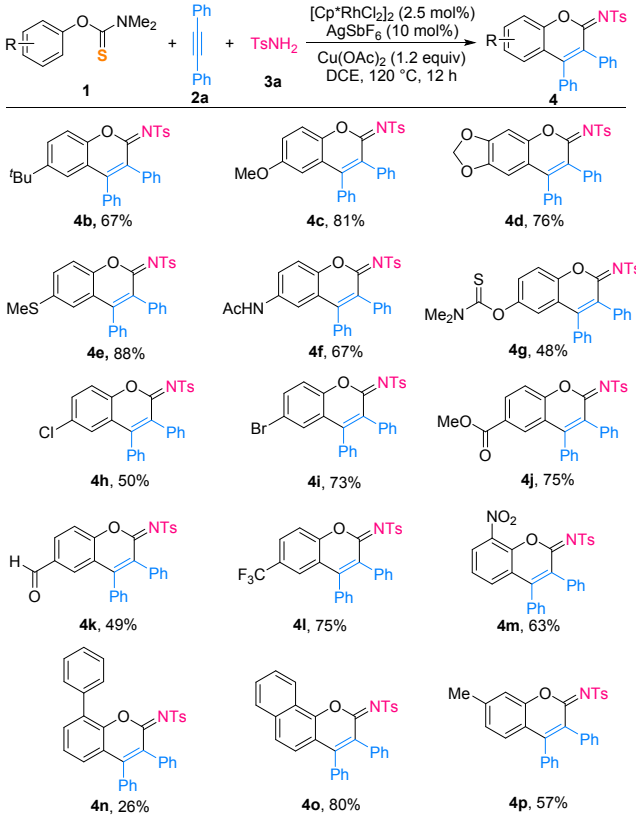


1a 2a 3a 4a

Entry	Catalyst	Additive	Oxidant	Solvent	Yield (%)
1	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$	*t*-AmOH	37
2	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$	THF	69
3	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$	DCE	84
4	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$	DMF	10
5	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$	acetone	76
6	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$	MeCN	77
7	$[Cp^*RhCl_2]_2$	$AgNTf_2$	$Cu(OAc)_2$	DCE	80
8	$[Cp^*RhCl_2]_2$	AgOTf	$Cu(OAc)_2$	DCE	0
9	$[Cp^*RhCl_2]_2$	-	$Cu(OAc)_2$	DCE	58
10	$[Cp^*RhCl_2]_2$	-	AgOAc	DCE	52
11	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}5H_2O$	DCE	45
12	$[Cp^*RhCl_2]_2$	$AgSbF_6$	-	DCE	0
13	-	$AgSbF_6$	$Cu(OAc)_2$	DCE	0
14 [b]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$	DCE	79
15 [c]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$	DCE	77

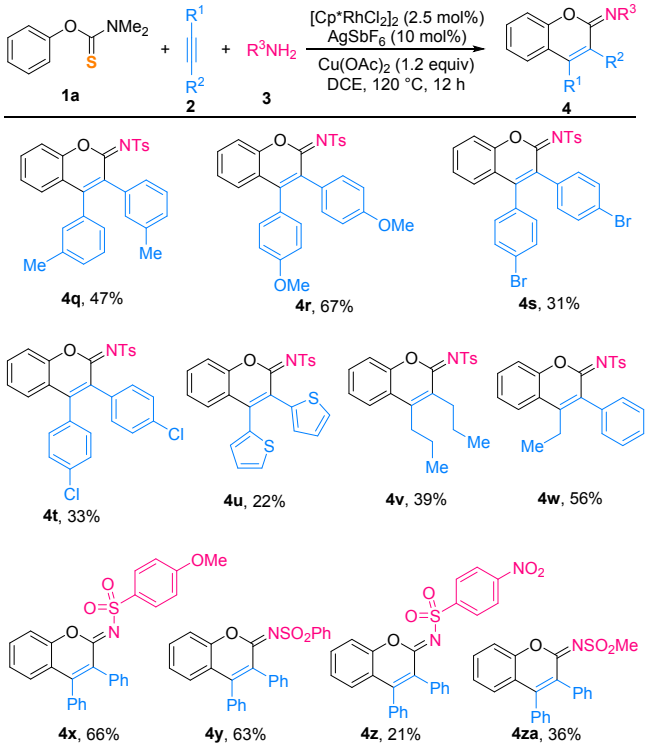
[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.3 mmol), **3a** (0.25 mmol), catalyst (0.00625 mmol), additive (0.025 mmol), oxidant (0.3 mmol), solvent (1 mL). All the reactions were performed in sealed tubes under air atmosphere at 120 °C for 12 h. [b] 1 mol% of $[Cp^*RhCl_2]_2$ and 4 mol% of $AgSbF_6$ were used. [c] 130 °C.

With the optimal condition in hand, we then examined the scope and limitations of the multicomponent annulation reaction by changing the electronic and steric nature of the aryl thiocarbamates (Scheme 2). The investigation of their reactivity in annulation with diphenylacetylene (**2a**) and *p*-toluenesulfonamide (**3a**) revealed that both electron donating (alkyl, alkoxy, methylthio, acetamido) and electron withdrawing (halogen, methoxycarbonyl, formyl, trifluoromethyl) substituents at the *para* position of the corresponding aryl thiocarbamate resulted in satisfactory yields of the iminocoumarin products (**4b** – **4l**). It is worth noting that the existence of the known directing group acetamido did not interfere with this reaction (**4f**), showing the stronger coordination ability of thiocarbonyl. The hydroquinone derived dithiocarbamate only led to mono-cyclization product (**4g**), even when exposed to large excess of **2a** and **3a**. The structure of **4i** was unambiguously confirmed by X-ray single crystal diffraction analysis (See Supporting Information).[17] Examination of steric effect was then performed through placing a substituent at the *ortho* position. Desired nitro substituted iminocoumarin **4m** and 1-naphthol derivative **4o** formed smoothly. The phenyl group at the *ortho* position of phenyl thiocarbamate exhibited significant steric effect for the reaction, resulting in a low yield for **4n**. When *meta*-methyl substituted thiocarbamate was submitted to this reaction, iminocoumarin **4p** was detected as the only product in 57% yield. The same selectivity was obtained for the benzodioxole derived product **4d**.



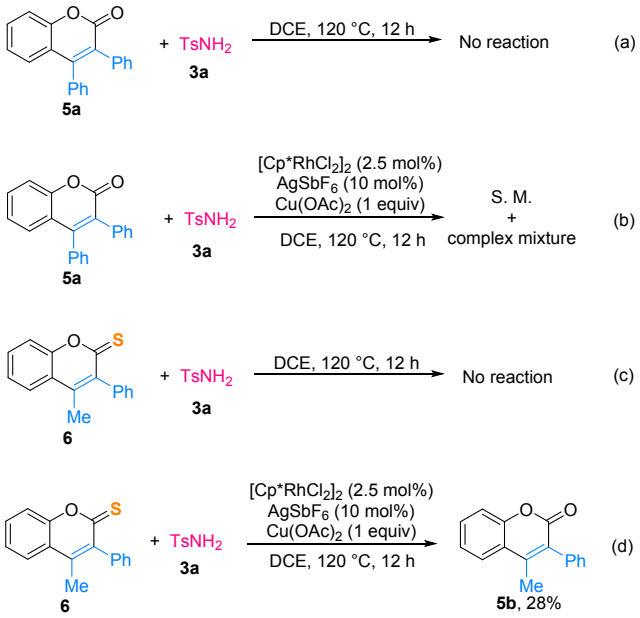
Scheme 2 Scope of aryl thiocarbamates

Next, the effects of changing the substituent on the diphenylacetylene (**2**) and sulfonamide (**3**) were surveyed (Scheme 3). It was found that electron-donating substituents were well tolerated at the 3-position or 4-position to provide iminocoumarins **4q** and **4r** in moderate to good yield respectively. The electro-withdrawing Br and Cl group at 4-position were also tolerated, albeit the yields were attenuated (**4s** and **4t**). The thienyl-substituted alkyne led to corresponding product **4u** in low yield probably because of the instability of thiophene ring. The present reaction was also successfully extended to aliphatic alkyne. The expected iminocoumarin **4v** was obtained from the reaction of **1a**, **3a** and 4-octyne in 39% yield. The unsymmetric 1-phenyl-1-butyne led to **4w** (the structure was confirmed by the NOESY spectrum, see Supporting Information) as the sole product, which is attributed to the steric effect.[18] The reaction using terminal alkynes such as phenylacetylene did not proceed, probably because of the formation of alkynyl copper species. Benzensulfonamide and 4-methoxy benzensulfonamide led to the corresponding products in comparative good yields (**4x** and **4y**), while 4-nitro benzensulfonamide gave low yield of **4z**, probably due to its low nucleophilicity. Finally, aliphatic-substituted sulfonamide was also reactive in this transformation (**4za**). However, the utilization of other kinds of amine or amide compounds failed to afford corresponding iminocoumarin products.



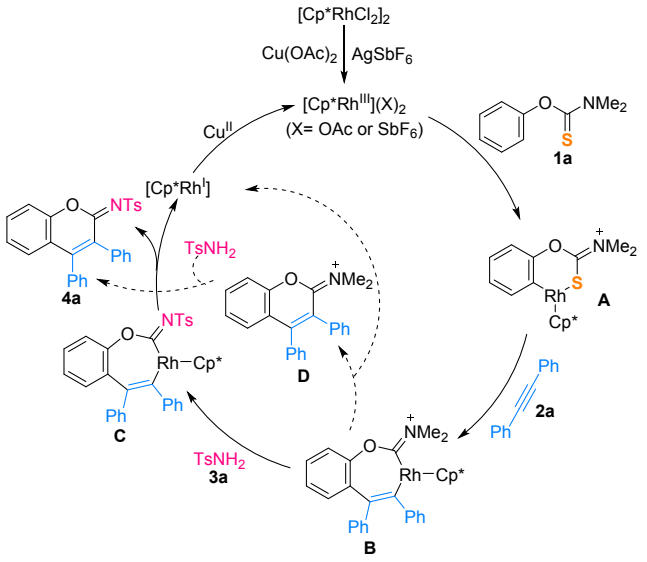
Scheme 3 Scope of alkynes and amines

To gain insights into the sequence of the multiple step reactions, 3,4-diphenyl coumarin (**5a**) and *p*-toluenesulfonamide (**3a**) were heated together or exposed to the standard reaction conditions. The corresponding iminocoumarin (**4a**) was not detected (Scheme 4a and 4b). This result implied that the C=N double bond was not generated from the direct carbonyl-amine condensation. The reactivity of thiocarbonyl is known to be much higher in comparison with carbonyl.[19] Thiocoumarins can readily react with hydrazine[5] or hydroxylamine[7b] to afford iminocoumarin analogues. However, heating thiocoumarin **6** with *p*-toluenesulfonamide **3a** in DCE led to no reaction (Scheme 4c). It might be resulted from the low nucleophilicity of sulfonamide. When the reaction was performed under the standard Rh/Ag/Cu system, a S to O exchange product coumarin **5b** was isolated in 28% yield accompany with only trace amount of corresponding iminocoumarin which was detected by LC-MS (Scheme 4d). These results showed that thiocoumarin could not be the intermediate of this reaction and desulfurization might take place before the nucleophilic attack by sulfonamide.



Scheme 4 The reaction of coumarin or thiocoumarin with *p*-toluenesulfonamide

Based on the above results as well as the previous mechanistic studies, we proposed the following catalytic cycle as illustrated in Scheme 5. Initially, the reactive cationic Rh^{III} complex is generated in the presence of $AgSbF_6$ and/or $Cu(OAc)_2$. Directed by polarized thiocarbamate group, the *ortho* C−H bond activation is realized to form a six-membered rhodacyclic complex **A**. Next, alkyne insertion and desulfurization take place to give the seven-membered rhodacycle **B** containing an iminium cation. It is unclear which step occurs prior. The nucleophilic attack by sulfonamide affords the more thermodynamically stable imine intermediate **C**, followed by reductive elimination to release the iminocoumarin **4a** and a Rh^{I} species which is then oxidized by Cu^{II} to complete the catalytic cycle. Alternatively, the reductive elimination of **B** releases the reactive iminium intermediate **D** which is attacked by sulfonamide to afford the iminocoumarin product (shown in dashed arrows).



Scheme 5 Proposed mechanism

In conclusion, we have developed a novel synthetic method to access iminocoumarin via multicomponent reaction of an aryl thiocarbamate, an internal alkyne, and a sulfonamide. All these starting materials are safe and readily available. This process exploits a Rh-catalyzed and thiocarbamate-directed C−H bond activation as the key step. Currently, we are working toward utilizing this method to prepare potentially bioactive and fluorescent molecules containing iminocoumarin skeleton.

Experimental Section

NMR spectra were recorded on BRUKER Avence III 500MHz spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (J) were reported in Hz and referred to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker Micro TOF-QII mass instrument (ESI).

All the aryl thiocarbamates are known products which were synthesized according to reported methods.[20] The internal alkynes were also prepared following the method described in known literature.[21] Other reagents used were purchased from Alfa Aesar or J&K.

In a typical reaction of Rh catalyzed oxidative annulation to access iminocoumarin, aryl thiocarbamate **1** (0.25 mmol), internal alkyne **2** (0.3 mmol), the sulfonamide **3** (0.25 mmol), $[Cp^*RhCl_2]_2$ (0.00625 mmol, 3.8 mg), $AgSbF_6$ (0.025 mmol, 6.4 mg), $Cu(OAc)_2$ (0.3 mmol, 54.5 mg), and 1,2-dichloroethane (1 mL) were added to a 25 mL dried Young-type tube under air atmosphere. Then it was sealed and heated with stirring at 120 °C in oil bath for 12 h. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate/petroleum ether (1:10 to 1:5 for each case) to give the corresponding product **4**.

(*Z*)-*N*-(3,4-diphenyl-2*H*-chromen-2-ylidene)-4-methylbenzenesulfonamide (4a) was obtained as a white powder (94.0 mg, 84%). M. P. 228 – 230 °C; IR (KBr, cm-1): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.52 (m, 2H), 7.28 – 7.22 (m, 7H), 7.14 – 7.13 (m, 3H), 7.08 – 7.04 (m, 4H), 2.38 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.5, 152.2, 151.1, 142.7, 139.6, 134.1, 133.4, 131.9, 130.7, 129.3, 129.1, 128.5, 128.3, 127.9, 127.7, 127.6, 127.1, 125.3, 120.7, 116.8, 21.5. IR (KBr, cm^{-1}): 3448, 3058, 2923, 1619, 1547, 1450, 1317, 1162, 1152, 871, 769, 758, 743, 694, 665, 570, 544; HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{22}NO_3S$ ($M+H^+$): 452.1315, found 452.1318.

(*Z*)-*N*-(6-(*tert*-butyl)-3,4-diphenyl-2*H*-chromen-2-ylidene)-4-methylbenzenesulfonamide (4b) was obtained as a white powder (72.1 mg, 67%). M. P. 204 – 209 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.61 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.28 – 7.18 (m, 5H), 7.14 (d, *J* = 1.2 Hz, 1H), 7.14 – 7.13 (m, 3H), 7.07 – 7.04 (m, 4H), 2.38 (s, 3H), 1.20 (s, 9H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.8, 151.5, 150.3, 148.5, 142.6, 139.7, 134.2, 133.6, 130.7, 129.5, 129.3, 129.0, 128.5, 128.2, 128.2, 127.5, 127.1, 124.0, 120.0, 116.3, 34.7, 31.2, 21.5; IR (KBr, cm^{-1}): 3439, 3055, 2967, 1618, 1537, 1323, 1086, 157, 1086, 764, 682, 665, 603, 569, 556, 549; HRMS (ESI, *m*/*z*) calcd for $C_{32}H_{30}NO_3S$($M+H^+$): 508.1941, found 508.1941.

(*Z*)-*N*-(6-methoxy-3,4-diphenyl-2*H*-chromen-2-ylidene)-4-methylbenzenesulfonamide (4c) was obtained as a white powder (58.0 mg, 81%). M. P. 203 – 208 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 6.7, 1.6 Hz, 2H), 7.48 (d, *J* = 9.1 Hz, 1H), 7.28 – 7.26 (m, 4H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.15 – 7.13 (m, 4H), 7.07 – 7.04 (m, 4H), 6.63 (d, *J* = 2.9 Hz, 1H), 3.68 (s, 3H), 2.38 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.7, 156.6, 146.8, 142.6, 139.7, 134.1, 133.5, 130.6, 129.2, 129.1, 128.5, 128.3, 127.6, 127.6, 127.0, 121.4, 118.9, 117.8, 110.7, 55.7, 21.5; IR (KBr, cm^{-1}): 3436, 2923, 2851, 1621, 1548, 1445, 1310, 1290, 1269, 1153, 1088, 775, 699, 681, 599, 552; HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{24}NO_4S$ ($M+H^+$): 482.1421, found 482.1422.

(*Z*)-*N*-(7,8-diphenyl-6*H*-[1,3]dioxolo[4,5-g]chromen-6-ylidene)-4-methylbenzenesulfonamide (4d) was obtained as a white powder (94.0 mg, 76%). M. P. 232 – 235 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.19 – 7.15 (m, 3H), 7.12 – 7.10 (m, 3H), 7.05 – 7.00 (m, 6H), 5.75 (s, 2H), 2.37 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.2, 147.9, 146.5, 145.1, 144.3, 142.7, 139.6, 135.3, 133.0, 130.7, 129.1, 128.7, 128.2, 127.5, 127.4, 127.0, 111.1, 108.9, 106.7, 102.3, 21.5; IR (KBr, cm^{-1}): 3439, 3063, 2902, 1642, 1558, 1451, 1306, 1232, 1146, 1071, 908, 815, 777, 695, 659, 548; HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{22}NO_5S$($M+H^+$): 496.1213, found 496.1213.

(*Z*)-4-methyl-*N*-(6-(methylthio)-3,4-diphenyl-2*H*-chromen-2-ylidene)benzenesulfonamide (4e) was obtained as a white powder (109.2 mg, 88%). M. P. 201 – 207 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.29 – 7.26 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.12 (m, 3H), 7.07 – 7.02 (m, 5H), 2.38 (s, 3H), 2.36 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.3, 150.5, 150.2, 142.8, 139.6, 135.9, 133.8, 133.3, 130.6, 130.4, 129.2, 129.1, 128.7, 128.3, 127.7, 127.6, 127.0, 125.2, 121.2, 117.3, 21.5, 16.4; IR (KBr, cm^{-1}): 3429, 2919, 1608, 1560, 1443, 1309, 1275, 1207, 1146, 1089, 960, 780, 698, 672, 592, 547; HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{24}NO_3S_2$ ($M+H^+$): 498.1192, found 498.1193.

(*Z*)-*N*-(3,4-diphenyl-2-(tosylimino)-2*H*-chromen-6-yl)acetamide (4f) was obtained as a white powder (85.0 mg,

67%). M. P. 143 – 146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.70 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.52 (d, *J* = 2.5 Hz, 1H), 7.27 – 7.22 (m, 6H), 7.13 – 7.11 (m, 3H), 7.02 – 6.98 (m, 4H), 2.39 (s, 3H), 2.01 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.9, 158.7, 151.4, 148.1, 143.0, 139.3, 135.9, 133.7, 133.3, 130.6, 129.2, 128.8, 128.5, 128.3, 127.7, 127.6, 126.9, 123.8, 120.8, 118.0, 116.9, 24.3, 21.5; IR (KBr, cm^{-1}): 3346, 3062, 2924, 1695, 1554, 1414, 1278, 1150, 1088, 937, 814, 779, 699, 539; HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{25}N_2O_4S$ ($M+H^+$): 509.1530, found 509.1530.

(*Z*)-*O*-(3,4-diphenyl-2-(tosylimino)-2*H*-chromen-6-yl) dimethylcarbamothioate (4g) as a white powder (66.1 mg, 48%). M. P. 204 – 213 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 9.0 Hz, 1H), 7.32 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.28 – 7.23 (m, 5H), 7.14 – 7.13 (m, 3H), 7.07 – 7.04 (m, 4H), 6.93 (d, *J* = 2.7 Hz, 1H), 3.03 (s, 3H), 2.95 (s, 3H), 2.39 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.3, 154.4, 150.6, 149.3, 148.3, 142.9, 139.4, 133.8, 133.3, 130.6, 129.3, 129.1, 129.0, 128.6, 128.4, 127.7, 127.6, 127.1, 126.1, 121.2, 120.3, 117.5, 36.8, 36.5, 21.5; IR (KBr, cm^{-1}): 3435, 2956, 2922, 1727, 1625, 1557, 1444, 1390, 1263, 1154, 1090, 825, 779, 698, 547; HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{27}N_2O_4S_2$ ($M+H^+$): 555.1407, found 555.1410.

(*Z*)-*N*-(6-chloro-3,4-diphenyl-2*H*-chromen-2-ylidene)-4-methylbenzenesulfonamide (4h) was obtained as a white powder (60.3 mg, 50%). M. P. 231 – 239 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.48 (m, 2H), 7.30 – 7.29 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 1.9 Hz, 1H), 7.14 – 7.13 (m, 3H), 7.05 – 7.04 (m, 4H), 2.38 (s, 2H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.9, 150.5, 149.8, 142.8, 139.4, 133.5, 133.1, 131.8, 130.9, 130.5, 129.6, 129.2, 129.1, 128.8, 128.5, 127.9, 127.6, 127.1, 126.9, 122.0, 118.3, 21.5; IR (KBr, cm^{-1}): 3437, 3058, 2921, 1618, 1568, 1312, 1262, 1147, 1089, 960, 814, 766, 699, 673, 595, 545; HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{21}ClNO_3S$ ($M+H^+$): 486.0925, found 486.0926.

(*Z*)-*N*-(6-bromo-3,4-diphenyl-2*H*-chromen-2-ylidene)-4-methylbenzenesulfonamide (4i) was obtained as a white powder (96.0 mg, 73%). The single crystal was prepared by recrystallization of the crude product in ethyl acetate/petroleum ether at –20 °C. M. P. 238 – 243 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 6.7, 1.7 Hz, 2H), 7.66 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.32 – 7.29 (m, 4H), 7.23 (d, *J* = 8.0 Hz, 2H); 7.14 – 7.12 (m, 3H); 7.06 – 7.02 (m, 4H), 2.38 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz , $CDCl_3$) δ 157.8, 151.0, 149.7, 142.9, 139.4, 134.6, 133.4, 133.0, 130.5, 130.1, 129.6, 129.2, 129.1, 128.8, 128.5, 127.9, 127.6, 126.9, 122.4, 118.5, 118.3, 21.3; IR (KBr, cm^{-1}): 3435, 3060, 1615, 1564, 1443, 1399, 1312, 1263, 1203, 1146, 1089, 957, 891, 814, 777, 699, 670, 588, 544; HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{21}BrNO_3S$ ($M+H^+$): 530.0420, found 530.0420.

Methyl-(*Z*)-3,4-diphenyl-2-(tosylimino)-2*H*-chromene-6-carboxylate (4j) was obtained as a white powder (50.4 mg, 75%). M. P. 204 – 209 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.93 (d, *J* = 2.0 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.31 – 7.29 (m, 3H), 7.26 – 7.23 (m, 2H), 7.15 – 7.13 (m, 3H), 7.07 – 7.04 (m, 4H), 3.86 (s, 3H), 2.38 (s, 3H).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.5, 157.7, 154.6, 150.5, 142.9, 139.4, 133.5, 133.1, 132.7, 130.6, 129.8, 129.3, 129.3, 129.2, 128.9, 128.5, 127.8, 127.6, 127.4, 127.0, 120.6, 117.1, 52.5, 21.5; IR (KBr, cm^{-1}): 3424, 3052, 2950, 1720, 1552, 1412, 1371, 1312, 1256, 1206, 1165, 1090, 909, 775, 702, 671, 593, 545; HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{24}NO_5S$ ($M+H^+$): 510.1370, found 510.1370.

(*Z*)-*N*-(6-formyl-3,4-diphenyl-2*H*-chromen-2-ylidene)-4-methylbenzenesulfonamide (4k) was obtained as a white powder (58.2 mg, 49%). M. P. 223 – 227 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.09 (dd, *J* = 5.6, 1.9 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 1.9 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.33 – 7.32 (m, 3H), 7.26 – 7.24 (m, 2H), 7.16 – 7.14 (m, 3H), 7.08 – 7.06 (m, 4H), 2.39 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 190.0, 157.5, 155.4, 150.2, 143.1, 139.2, 133.4, 133.3, 132.9, 131.9, 130.5, 130.4, 129.7, 129.2, 129.2, 129.0, 128.6, 128.0, 127.7, 126.9, 121.3, 118.0, 21.5; IR (KBr, cm^{-1}): 3437, 3059, 2841, 1705, 1552, 1445, 1315, 1157, 1087, 934, 819, 771, 741, 701, 671, 545; HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{22}NO_4S$ ($M+H^+$): 480.1264, found 480.1264.

(*Z*)-*N*-(3,4-diphenyl-6-(trifluoromethyl)-2*H*-chromen-2-ylidene)-4-methylbenzenesulfonamide (4l) was obtained as a white powder (97.0 mg, 75%). M. P. 214 – 219 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 3H), 7.66 (d, *J* = 8.6 Hz, 1H), 7.48 (d, *J* = 1.5 Hz, 1H), 7.32 – 7.31 (m, 3H), 7.26 – 7.23 (m, 2H), 7.15 – 7.14 (m, 3H), 7.07 – 7.04 (m, 4H), 2.38 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.5, 153.7, 149.9, 143.0, 139.3, 133.2, 132.9, 130.5, 130.0, 129.2 (d, J_{CF} = 6.8 Hz), 129.0, 128.6, 128.4 (d, J_{CF} = 12.9 Hz), 128.1 (q, J_{CF} = 200.5 Hz), 128.0, 127.7, 126.9, 125.2, 125.2, 124.4, 121.0, 117.7, 21.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.1; IR (KBr, cm^{-1}): 3425, 3058, 2917, 1710, 1590, 1358, 1262, 1147, 1089, 960, 814, 766, 688, 673, 595, 545; HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{21}F_3NO_3S$ ($M+H^+$): 520.1189, found 520.1189.

(*Z*)-4-methyl-*N*-(8-nitro-3,4-diphenyl-2*H*-chromen-2-ylidene)benzenesulfonamide (4m) was obtained as a white powder (78.0 mg, 63%). M. P. 205 – 208 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.45 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.33 – 7.31 (m, 4H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.14 (m, 3H), 7.06 – 7.03 (m, 4H), 2.37 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.5, 149.3, 144.3, 143.0, 139.0, 138.2, 133.4, 132.3, 132.2, 130.4, 130.3, 129.2, 129.2, 129.0, 128.6, 128.1, 127.7, 126.8, 126.8, 124.5, 122.9, 21.5; IR (KBr, cm^{-1}): 3437, 3064, 1625, 1584, 1455, 1454, 1317, 1244, 1170, 1089, 864, 779, 692, 568; HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{21}N_2O_5S$ ($M+H^+$): 497.1166, found 497.1168.

(*Z*)-4-methyl-*N*-(3,4,8-triphenyl-2*H*-chromen-2-ylidene)benzenesulfonamide(4n) was obtained as a white powder (34.1 mg, 26%). M. P. 233 – 238 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.80 (m, 2H), 7.65 (t, J = 7.7 Hz, 2H), 7.60 (dd, J = 7.5, 1.6 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.31 – 7.28 (m, 6H), 7.20 (dd, J = 8.0, 1.5 Hz, 1H), 7.14 – 7.13 (m, 3H), 7.09 – 7.05 (m, 4H), 6.98 (d, J = 8.1 Hz, 2H), 2.30 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.0, 151.3, 149.4, 142.3, 139.0, 135.2, 134.5, 133.7, 133.5, 131.0, 130.6, 130.5, 129.3, 128.9, 128.8, 128.6, 128.6, 128.5, 128.3, 127.6, 127.2, 126.9, 125.1, 121.3, 21.5; IR (KBr, cm^{-1}): 3434, 2919, 1619, 1540, 1444, 1324, 1158, 1087, 1013, 881, 857, 814, 771, 696, 554; HRMS (ESI, *m*/*z*) calcd for $C_{34}H_{26}NO_3S$ ($M+H^+$): 528.1628, found 528.1624.

(*Z*)-*N*-(3,4-diphenyl-2*H*-benzo[h]chromen-2-ylidene)-4-methylbenzenesulfonamide (4o) was obtained as a white powder (100.3 mg, 80%). M. P. 212 – 217 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93 (d, *J* = 8.3 Hz, 1H), 7.89 – 7.83 (m, 3H), 7.78 – 7.75 (m, 1H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.32 – 7.31 (m, 3H), 7.21 (d, *J* = 8.5 Hz, 3H), 7.16 – 7.11 (m, 7H), 2.36 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.9, 152.2, 149.7, 142.5, 140.0, 134.7, 134.5, 133.5, 130.7, 129.4, 129.1, 128.5, 128.3, 128.0, 127.9, 127.6, 127.6, 127.5, 126.4, 125.2, 123.3, 122.9, 122.7, 116.2, 21.49; IR (KBr, cm^{-1}): 3360, 3064, 2925, 1604, 1562, 1541, 1441, 1290, 1166, 1090, 964, 816, 768, 695, 565; HRMS (ESI, *m*/*z*) calcd for $C_{32}H_{23}NO_3SNa$ (M+Na$^+$): 524.1291, found 524.1290.

(*Z*)-4-methyl-*N*-(7-methyl-3,4-diphenyl-2*H*-chromen-2-ylidene)benzenesulfonamide (4p) was obtained as a white powder (66 mg, 57%). M. P. 226 – 233 °C;^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 18.1 Hz, 1H), 7.34 – 7.20 (m, 6H), 7.16 – 7.11 (m, 3H), 7.09 (d, *J* = 8.2 Hz, 1H), 7.08 – 7.01 (m, 4H), 2.48 (s, 3H), 2.38 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.9, 152.2, 151.3, 143.4, 142.6, 134.3, 133.5, 130.8, 129.3, 129.1, 128.4, 128.2, 127.5, 127.0, 126.6, 118.3, 117.0, 77.3, 77.1, 76.8, 21.7, 21.5; IR (KBr, cm^{-1}): 3433, 3055, 2918, 1628, 1537, 1311, 1289, 1154, 1087, 906, 816, 767, 700, 670, 558; HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{24}NO_3S$ (M+H$^+$): 466.1471, found 466.1474.

(*Z*)-*N*-(3,4-di-m-tolyl-2*H*-chromen-2-ylidene)-4-methylbenzenesulfonamide (4q) was obtained as a white powder (55.9 mg, 47%). M. P. 178 – 181 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.55 – 7.53 (m, 2H), 7.26 – 7.22 (m, 4H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.94 – 6.91 (m, 2H), 6.85 – 6.82 (m, 3H), 2.38 (s, 3H), 2.25 (s, 3H), 2.18 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.7, 152.1, 151.2, 142.7, 139.7, 137.9, 136.9, 134.1, 133.3, 131.7, 131.3, 129.8, 129.2, 129.1, 128.4, 128.4, 128.1, 128.0, 127.7, 127.4, 127.0, 126.4, 125.3, 122.8, 120.8, 116.7, 21.5, 21.3, 21.3; IR (KBr, cm^{-1}): 3434, 2918, 1621, 1541, 1296, 1150, 1091, 831, 787, 753, 737, 698, 664, 578, 540; HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{26}NO_3S$ (M+H$^+$): 480.1628, found 480.1630.

(*Z*)-*N*-(3,4-bis(4-methoxyphenyl)-2*H*-chromen-2-ylidene)-4-methylbenzenesulfonamide (4r) was obtained as a white powder (85.6 mg, 67%). M. P. 195 – 203 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.58 – 7.51 (m, 2H), 7.30 – 7.24 (m, 4H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 3.73 (s, 3H), 2.38 (s, 2H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.5, 158.9, 158.8, 152.0, 150.7, 142.7, 139.6, 132.1, 131.6, 130.8, 129.1, 128.0, 127.9, 127.2, 126.4, 125.8, 125.2, 121.0, 116.7, 113.8, 113.1, 55.2, 55.1, 21.5; IR (KBr, cm^{-1}): 3438, 2966, 2839, 1618, 1541, 1302, 1248, 1155, 1088, 1024, 828, 746, 561; HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{26}NO_5S$ (M+H$^+$): 512.1526, found 512.1527.

***(Z)*-*N*-(3,4-bis(4-bromophenyl)-2*H*-chromen-2-ylidene)-4-methylbenzenesulfonamide (4s)** was obtained as a white powder (47.2 mg, 31%). M. P. 228 – 230 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.74 – 7.71 (m, 1H), 7.65 – 7.63 (m, 1H), 7.57 – 7.54 (m, 2H), 7.46 – 7.41 (m, 4H), 7.39 – 7.36 (m, 1H), 7.18 – 7.13 (m, 4H), 7.06 (dd, *J* = 8.0, 1.4 Hz, 1H), 2.37 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, DMSO-d_6) δ 158.4, 151.8, 150.9, 143.7, 139.0, 133.5, 133.5, 133.1, 131.8, 131.7, 131.2, 129.9, 128.1, 128.0, 127.3, 126.6, 122.6, 121.7, 120.7, 116.6, 21.5; IR (KBr, cm^{-1}): 3445, 3077, 2918, 1632, 1541, 1289, 1150, 1091, 1002, 831, 787, 754, 698, 664, 545; HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{19}Br_2NO_3SNa$ (M+Na$^+$): 629.9324, found 629.9345.

(*Z*)-*N*-(3,4-bis(4-chlorophenyl)-2*H*-chromen-2-ylidene)-4-methylbenzenesulfonamide (4t) was obtained as a white powder (58.0 mg, 45%). M. P. 228 – 230 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.43 – 7.37 (m, 6H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.24 – 7.19 (m, 4H), 7.08 (d, *J* = 7.9 Hz, 1H), 2.37 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, DMSO-d_6) δ 158.4, 151.8, 151.0, 143.7, 139.0, 133.8, 133.2, 133.2, 133.1, 132.9, 132.8, 131.5, 129.9, 128.8, 128.2, 128.1, 127.9, 127.4, 126.6, 120.7, 116.6, 21.5; IR (KBr, cm^{-1}): 3435, 3036, 2916, 1619, 1548, 1322, 1152, 1089, 1011, 878, 817, 764, 714, 661, 551; HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{19}Cl_2NO_3SNa$ (M+Na$^+$): 542.0355, found 542.0355.

(*Z*)-*N*-(3,4-di(thiophen-2-yl)-2*H*-chromen-2-ylidene)-4-methylbenzenesulfonamide (4u) was obtained as a white powder (25.0 mg, 22%). M. P. 214 – 218 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.54 (m, 1H), 7.53 – 7.48 (m, 2H), 7.45 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.31 – 7.26 (m, 4H), 7.10 – 7.07 (m, 1H), 7.04 (dd, *J* = 3.5, 1.0 Hz, 1H), 6.94 (dd, *J* = 3.6, 1.0 Hz, 1H), 6.87 – 6.83 (m, 1H), 2.40 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.2, 151.6, 144.5, 143.0, 139.3, 134.4, 133.5, 132.2, 131.0, 130.3, 129.2, 128.8, 128.1, 127.8, 127.2, 126.1, 125.5, 120.6, 116.7, 77.5, 77.3, 77.0, 76.8, 21.6; IR (KBr, cm^{-1}): 3434, 3098, 2918, 1618, 1547, 1451, 1326, 1288, 1161, 1085, 858, 832, 728, 663, 577, 541; HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{18}NO_3S_3$ (M+H$^+$): 464.0443, found 464.0427.

(*Z*)-*N*-(3,4-dipropyl-2*H*-chromen-2-ylidene)-4-methylbenzenesulfonamide (4v) was obtained as a white powder (37.2 mg, 39%). M. P. 149 – 152 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.49 (m, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.29 (m, 3H), 2.81 (t, *J* = 8.0 Hz, 2H), 2.64 (t, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 1.62 – 1.58 (m, 4H), 1.10 (t, *J* = 7.4 Hz, 3H), 1.01 (t, *J* = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (126 MHz , $CDCl_3$) δ 14.4, 14.5, 21.5, 22.0, 23.0, 29.5, 30.7, 116.9, 119.9, 124.6, 125.3, 127.2, 127.4, 129.1, 130.8, 139.7, 142.8, 150.1, 151.4, 158.7; IR (KBr, cm^{-1}): 3445, 3012, 2901, 1619, 1545, 1450, 1317, 1159, 994, 871, 760, 743, 694, 665, 570, 545; HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{26}NO_3S$ (M+H$^+$): 384.1628, found 384.1629.

(*Z*)-*N*-(3-ethyl-4-phenyl-2*H*-chromen-2-ylidene)-4-methylbenzenesulfonamide (4w) was obtained as a white powder (56.1 mg, 56%). M. P. 197 – 203 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.71 – 7.70 (m, 1H), 7.59 – 7.55 (m, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.36 (m, 4H), 7.22 – 7.20 (m, 4H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.36 (s, 3H), 1.13 (t, *J* = 7.6 Hz, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.7, 153.2, 152.1, 143.4, 142.7, 139.5, 139.3, 134.0, 131.7, 129.7, 129.5, 129.1, 128.5, 128.2, 128.1, 127.0, 126.5, 125.6, 125.2, 119.4, 117.2, 23.1, 21.5, 14.1; IR (KBr, cm^{-1}): 3434, 3091, 2908, 1641, 1529, 1266, 1155, 1091, 831, 779, 732, 698, 660, 578, 541; HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{22}NO_3S$ (M+H$^+$): 404.1315, found 404.1315.

(*Z*)-*N*-(3,4-diphenyl-2*H*-chromen-2-ylidene)-4-methoxybenzenesulfonamide (4x) was obtained as a white powder (77.1 mg, 66%). M. P. 200 – 209 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.91 (m, 2H), 7.54 – 7.51 (m, 2H), 7.27 – 7.26 (m, 3H), 7.22 – 7.21 (m, 2H), 7.13 – 7.12 (m, 3H), 7.07 – 7.03 (m, 4H), 6.92 – 6.90 (m, 2H), 3.81 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.6, 158.3, 152.2, 151.1, 134.3, 134.1, 133.4, 131.9, 130.7, 129.3, 129.2, 128.5, 128.5, 128.3, 127.9, 127.7, 127.6, 125.4, 120.7, 116.7, 113.7, 55.6; IR (KBr, cm^{-1}): 3434, 3080, 2919, 1622, 1545, 1491, 1444, 1322, 1148, 1090, 869, 805, 773, 696, 565; HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{22}NO_4S$ (M+H$^+$): 468.1264, found 468.1264.

(*Z*)-*N*-(3,4-diphenyl-2*H*-chromen-2-ylidene)benzenesulfonamide (4y) was obtained as a white powder (68.4 mg, 63%). M. P. 188 – 199 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.96 (m, 2H), 7.57 – 7.42 (m, 5H), 7.28 – 7.23 (m, 5H), 7.25 – 7.20 (m, 3H), 7.14 – 7.04 (m, 4H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.8, 152.1, 151.4, 142.5, 134.0, 133.4, 132.1, 132.0, 130.7, 129.3, 128.6, 128.5, 128.4, 128.3, 127.9, 127.7, 127.6, 127.0, 125.4, 120.7, 116.8; IR (KBr, cm^{-1}): 3436, 3060, 1618, 1552, 1447, 1304, 1204, 1145, 1088, 956, 873, 785, 745, 701, 588, 545; HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{20}NO_3S$ (M+H$^+$): 438.1158, found 438.1158.

(*Z*)-*N*-(3,4-diphenyl-2*H*-chromen-2-ylidene)-4-nitrobenzenesulfonamide (4z) was obtained as a white powder (25.3 mg, 21%). M. P. 205 – 211 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 – 8.24 (m, 2H), 8.06 – 8.04 (m, 2H), 7.64 – 7.63 (m, 2H), 7.32 – 7.29 (m, 5H), 7.17 – 7.16 (m, 3H), 7.09 – 7.07 (m, 4H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.7, 152.4, 152.1, 149.6, 148.3, 133.8, 133.2, 132.4, 130.5, 129.2, 128.8, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 125.8, 123.8, 120.7, 117.0; IR (KBr, cm^{-1}): 3422, 2924, 1716, 1668, 1602, 1449, 1380, 1351, 1242, 1078, 921, 755, 709, 541, 446; HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{19}N_2O_5S$ (M+H$^+$): 483.1009, found 483.1010.

(*Z*)-*N*-(3,4-diphenyl-2*H*-chromen-2-ylidene)methanesulfonamide (4za) was obtained as a white powder (33 mg, 36%). M. P. 228 – 239 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 1H), 7.57 (ddd, *J* = 8.5, 6.6, 2.1 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.22 (ddd, *J* = 7.9, 7.0, 2.7 Hz, 2H), 7.18 – 7.12 (m, 3H), 7.11 – 7.03 (m, 4H), 3.00 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.8, 152.1, 151.2, 134.1, 133.5, 131.9, 130.6, 130.5, 129.4, 129.3, 128.5, 128.2, 128.1, 127.8, 127.6, 127.6, 125.3, 120.6, 117.1, 77.3, 77.1, 76.8, 43.0; IR (KBr, cm^{-1}): 3061, 3027, 2939, 1712, 1624, 1574, 1454, 1301, 1206, 1132, 960, 876, 804, 764, 702, 565, 509; HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{18}NO_3S$ (M+H$^+$): 376.1002, found 376.1003.

The coumarin **5a** was synthesized according to our previous work:[15a] **3,4-diphenyl-2*H*-chromen-2-one (5a)** was obtained as a white powder (120 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.44 (m, 4H), 7.17 – 7.24 (m, 5H), 7.29 – 7.33 (m, 3H), 7.43 – 7.45 (m, 1H), 7.52 – 7.56 (m, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 116.8, 120.5, 124.1, 127.0, 127.6, 127.7, 127.8, 128.2, 128.3, 129.4, 130.5, 131.4, 133.9, 134.5, 151.6, 153.2, 161.3.

The coumarin **5b** was prepared according to the procedure above using *o*-phenyl dimethylcarbamothioate **1a** and 1-phenyl-1-propyne. It was obtained as a white solid (6.6 mg, 28% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.1 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.35 – 7.31 (m, 3H), 2.33 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.0, 152.7, 147.6, 134.5, 131.3, 130.0, 128.5, 128.2, 127.4, 125.1, 124.3, 120.6, 116.9, 16.6.

The thiocoumarin **6** was synthesized according to previous literature:[22] A mixture of coumarin **5b** (0.5 mmol) and Lawesson's reagent (1 mmol) in anhydrous toluene, was refluxed for about 24 h. After cooling, solvent was removed under reduced pressure and the residue was then separated by flash column chromatography with petroleum ether-EtOAc mixtures (9:1) to afford thiocoumarin **6** as a yellow solid (0.108 g, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.3 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.43 – 7.37 (m, 1H), 7.22 (d, *J* = 7.0 Hz, 2H), 2.19 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 197.3, 155.5, 141.3, 138.8, 138.0, 131.7, 129.5, 128.6, 128.0, 125.3, 125.2, 122.0, 116.8, 17.0.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

NMR data and X-ray crystallography data and CIF files.

Accession Codes

CCDC 1949758 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

* Email: zhaoyingwei@hqu.edu.cn

ORCID

Yingwei Zhao: 0000-0001-8688-2363

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