JOC The Journal of Organic Chemistry

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Catalyst-Free [4+2] Cycloaddition of Ynamides with 2-Halomethyl Phenols To Construct 2-Amino-4*H*-Chromenes and α-Halo Enamides Simultaneously

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Cite This: https://dx.doi.org/10.1021/acs.joc.0c01258 Read Online

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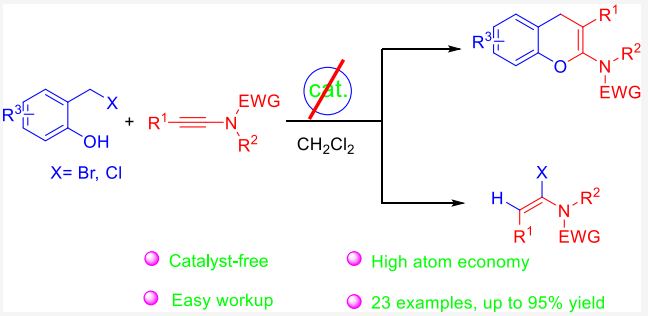
ABSTRACT: We report the development of a facile protocol for the [4+2] cycloaddition of ynamides and 2-halomethyl phenols to afford the corresponding 2-amino-4*H*-chromenes and α-halo enamides under catalyst-free conditions. The reaction proceeds under mild conditions and exhibits good tolerance toward various functional groups and generates high yields. The plausible mechanism involves the formation of an active intermediate keteniminium as well as *o*-methylene quinone.



INTRODUCTION

The 2-amino-4*H*-chromene skeleton belongs to the privileged structural motifs in numerous natural products as well as medicinal agents which exhibit diverse biological activities, including antitumor, antibacterial, antioxidative, and antihypertensive (Figure 1).[1] For instance, 2-amino-4-aryl-4*H*-chromene (HFI-437) is a high-affinity inhibitor of insulin-regulated aminopeptidase, which has potential in the treatment of neurodegenerative disease.[1a] Compound MX 58151 was used as a tubulin inhibitor that binds at or close to the colchicine site of β-tubulin.[1b] In addition, EPC2407 (crinobulin) is a potential vascular-targeting anticancer agent and apoptosis inducer in the treatment of patients with advanced solid tumors.[1c] HA 14-1 and sHA 14-1 could mitigate drug resistance and synergize with a variety of cancer therapies in leukemia cells.[1d−f]

Owing to the highly pronounced biological activities of 2-amino-4*H*-chromenes, a multitude of effective protocols have been developed to access 2-amino-4*H*-chromenes.[2] Classic methods for the syntheses of 2-amino-4*H*-chromene motifs usually include two-component cascade reactions of salicylaldehyde with active methylene compounds and three-component reactions of aldehydes and phenols with malononitriles using various catalysts such as ethylenediamine diacetate, β-cyclodextrin, $InCl_3$, $Zr(KPO_4)_2$, aminosilane-modified Fe_3O_4 nanoparticles, and silica-bonded 2-hydroxyethylammonium acetate via Knoevenagel condensation and Michael addition. However, these methods show varying degree success as well as limitations such as the requirement of expensive catalysts, complex catalytic systems, complicated operations, and low yields.

Ynamides have attracted growing attention as useful building blocks.[3] Notably, cycloaddition of ynamides with various precursors provides an efficient and straightforward strategy to construct heterocycles, such as pyridines,[4] pyrroles,[5] indoles,[6] and carbolines.[7] Recently, some elegant methods have been reported for the synthesis of 2-amino-4*H*-chromenes via cycloaddition of ynamides. For example, in 2016, Cao and his co-workers[8] developed $ZnBr_2$-promoted formal [4+2] annulation of ynamides with *o*-methoxybenzyl silyl ethers to construct this framework (Scheme 1a). However, this method suffered from certain salient drawbacks, for example, low yields (41−65%), narrow substrate scopes, and 1.2 equiv Lewis acid $ZnBr_2$. Besides, Wang et al.[9] reported an efficient method via $AlCl_3$-catalyzed [4+2] cycloaddition of ynamides with *o*-quinone methides at −40 °C (Scheme 1b). However, substrates of this reaction were limited to terminally unsubstituted ynamides and *o*-quinone methides bearing electron-donating groups. Maintaining the reaction temperature at −40 °C and using a strong and moisture-sensitive Lewis acid were necessary. Therefore, it is still deemed worthwhile to explore green and efficient ways to synthesize 2-amino-4*H*-chromenes. To the best of our knowledge, catalyst-free reactions of ynamides are very rare. Herein, we developed an efficient and concise catalyst-free approach to furnish this

Received: May 26, 2020

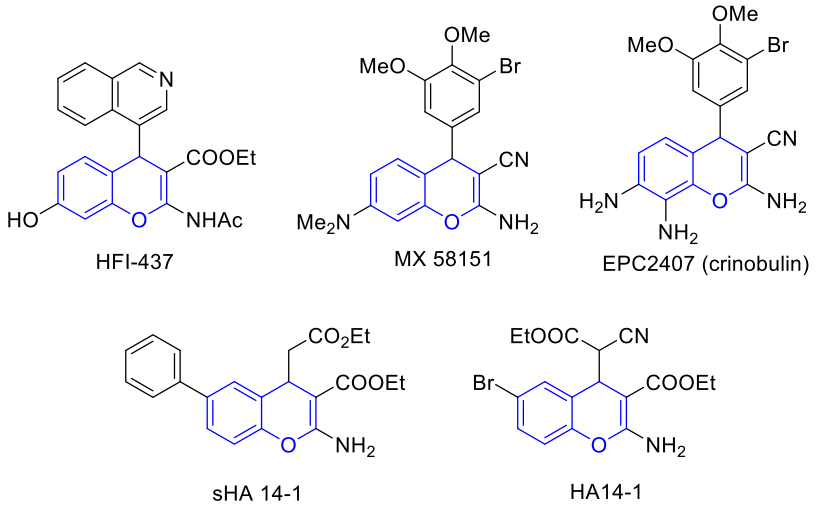
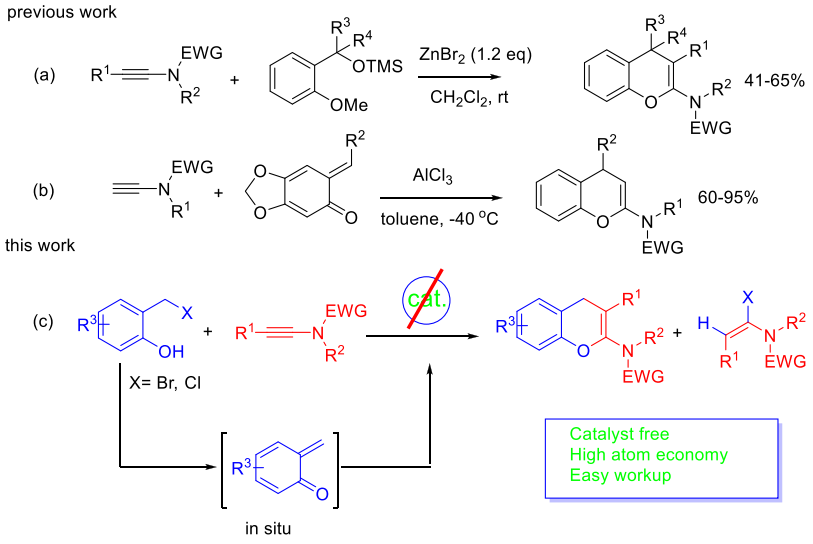


Figure 1. Biologically active molecules containing 4*H*-chromenes.

Scheme 1. Synthesis of 2-Amino-4*H*-Chromenes via Ynamides



class of molecules via formal [4+2] cycloaddition of ynamides with readily available 2-halomethylphenols (Scheme 1c). Furthermore, in this reaction, we have obtained α-halo enamides in good yields which are versatile intermediates[10] and readily converted into various functional groups by halogen−metal exchange reactions. Although considerable efforts have been made for the syntheses of α-halo enamides,[11] most of them suffered from serious disadvantages such as complex reaction conditions and tedious manipulation. On the other hand, we recently reported a highly regio- and stereoselective synthesis of α-halo enamides using aqueous hydrogen halides in two-phase systems.[12] Therefore, developing a green and simple method to synthesize α-halo enamides is highly desirable.

RESULTS AND DISCUSSION

Initially, 2-(bromomethyl)-4-nitrophenol **1a** and ynamide **2a** were selected as model substrates to investigate the feasibility of [4+2] cycloaddition. To our delight, the desired 2-amino-4*H*-chromene **3a** was obtained in 45% yield in the presence of NaOH in CH_2Cl_2 at room temperature (rt) (Table1, entry 1). Unexpectedly, (*E*)-α-bromoenamide **4a** was isolated in 18% yield from this reaction simultaneously. Then, different inorganic bases were investigated, and Cs_2CO_3 gave the best results (entries 2−7). Surprisingly, in the absence of a base in this reaction, the desired product **3a** was achieved in 53% yield, and **4a** was obtained in 23% yield (entry 8). Presumably, because bases transformed 2-(bromomethyl)-4-nitrophenol **2a** into *o*-quinone methides, which easily formed dimers or trimers, the use of bases lowered the yields of this reaction. Next, evaluation of solvents disclosed that dichloromethane (DCM) was the best choice (entries 8−15). Considering the consumption of a stoichiometric amount of ynamide **2a**, we decided to increase the amount of ynamides. To our delight, when the amount of ynamides **2a** was increased to 1.5 equiv, the yields of cycloaddition product **3a** and (*E*)-α-bromoenamide **4a** were increased to 76 and 59%, respectively (entry 16). With the continuous increase of the amount of ynamide to 2.0 equiv, the yields of products **3a** and **4a** were increased to 91 and 81%, respectively (entry 17). Increasing the reaction temperature has a beneficial effect on the reaction efficiency, shortening the reaction time to 12 h (entry 18). In addition, this transformation was catalyzed in the presence of 0.2 equiv of Lewis acids, such as $Sc(OTf)_3$, $Fe(OTf)_3$, $Cu(OTf)_2$, and

https://dx.doi.org/10.1021/acs.joc.0c01258
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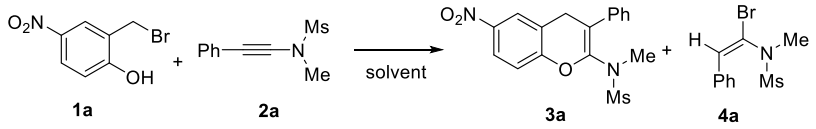
Table 1. Condition Optimization of Ynamides 2a and 2-(Bromomethyl)-4-nitrophenol 1a[a,b]



1a 2a 3a 4a

entry	base	solvent	temperature	3a yield (%)	4a yield (%)
1	NaOH	DCM	rt	45	18
2	Cs_2CO_3	DCM	rt	46	23
3	K_2CO_3	DCM	rt	41	21
4	Na_2CO_3	DCM	rt	37	17
5	$NaHCO_3$	DCM	rt	40	18
6	*t*-BuOK	DCM	rt	27	5
7	MeONa	DCM	rt	25	9
8		DCM	rt	53	23
9		DCE	rt	46	37
10		DMF	rt	NR	NR
11		DMSO	rt	NR	NR
12		MeOH	rt	NR	NR
13		CH_3CN	rt	42	25
14		THF	rt	31	19
15		toluene	rt	37	21
16[c]		DCM	rt	76	59
17[d]		DCM	rt	91	81
18[e]		**DCM**	**reflux**	**93**	**87**

[a]Unless otherwise specified, reactions were conducted with **1a** (0.15 mmol), **2a** (0.15 mmol), and the base (0.165 mmol) in 2.0 mL of the solvent at rt for 48 h. [b]Isolated yield. [c]Reactions were conducted with **1a** (0.15 mmol) and **2a** (0.225 mmol) in 2.0 mL of the solvent at rt for 48 h. [d]Reactions were conducted with **1a** (0.15 mmol) and **2a** (0.3 mmol) in 2.0 mL of the solvent at rt for 48 h. [e]Reactions were conducted with **1a** (0.15 mmol) and **2a** (0.3 mmol) in 2.0 mL of the solvent under reflux in an oil bath for 12 h.

$Mg(OTf)_2$, giving lower yields of **3a** and **4a**, respectively (see Table S1 in the Supporting Information for more details). Therefore, the optimal reaction conditions were identified as follows: **1a** (0.15 mmol) and **2a** (0.3 mmol) in refluxing DCM for 12 h without any other catalysts, reagents, or additives.

With the optimal reaction conditions in hand, we began to explore the scopes of the reaction first by varying the ynamides (Scheme 2). When phenyl-terminated ynamides were employed as reactants, both electron-donating and electron-withdrawing groups were well tolerated, affording the desired products 2-amino-4*H* chromenes **3a**−**3e** in good to excellent yields and (*E*)-*α*-bromoenamide **4a**−**4e** in moderate to good yields. Terminally unsubstituted ynamides **2g** were also compatible for this reaction to give [4+2] cycloaddition products **3g** in 72% yield. In this case, hydrolysis products **4g** were obtained instead of *α*-bromoenamide. Our assumption is that the terminal ynamide was more unstable than internal ynamides and readily underwent hydrolysis reaction. Similarly, the *tert*-butyl-substituted ynamide was subjected to the optimal conditions, furnishing the desired cycloaddition product **3h** in 86% yield, and hydrolysis product **4h** was obtained in 31% yield. However, when N-Ns-protected ynamide **2i** was employed, the reaction proceeded smoothly, affording the corresponding products **3i** and **4i** in good yields. Other alkyl (cyclopropyl), thienyl-terminated, and *N*-alkyl-substituted ynamides (**2j**−**2l**) afforded **3j**−**3l** and **4j**−**4l** with excellent yields. Ynamide **2m** incorporating the Boc group on the N atom also tolerated during the smooth formation of the corresponding products **3m** and **4m** in 95 and 93% yields, respectively. In addition to *N*-sulfonyl ynamides, oxazolidinone ynamide **2n** was also an ideal substrate, which provided the desired products **3n** and **4n** in moderate yields.

Next, various 2-bromomethyl phenol derivatives were also investigated (Scheme 3). The nitro group on the phenyl had no significant impact on the reaction, delivering the corresponding products in excellent yields (**5a**−**5d**, **4a**). Besides, a list of aldehyde-containing 2-bromomethyl phenols was examined and the corresponding products **5e**−**5g** were furnished in moderate yields under standard conditions. Besides 2-bromomethyl phenol derivatives, 2-chlorophenols bearing the acetyl or aldehyde group were employed as substrates to successfully deliver cycloaddition product **5h** and **5i** in 73 and 79% yields, respectively, and (*E*)-*α*-chloro enamides were obtained in moderate yields.

To demonstrate the applicability of this method in organic synthesis, we carried out the reaction on a gram scale under standard conditions, furnishing the desired products **3a** and **4a** in 89 and 84% yields, respectively, while the reaction time was extended to 24 h (Scheme 4).

To explore the mechanism of this reaction, control experiments were carried out (Scheme 5). **1a** was treated with CH_3OD, and 30% deuterium incorporation was observed at the hydroxyl group of **1a′**. Then, the reaction between **1a′** and ynamide **2a** was performed under standard conditions, and 28% deuterium incorporation was found in **4a′**. These results indicated that hydrogen in the alkenyl group of **4a′** directly comes from the hydroxyl group of **1a′** (eq 1, Scheme 5). Chromene **3a** was not detected using (*E*)-*α*-bromoenamide **4a** and **1a** as substrates (eq 2, Scheme 5). Therefore, it was impossible that **4a** participated in the [4+2] cycloaddition giving the desired product **3a** (eq 2, Scheme 5). In addition, treatment of **1a** with 2.0 equiv of NaH for 0.5 h, followed by reaction with **2a** to give **3a** in 43% yield along with less than 10% of **4a**, proved that this transformation was probably

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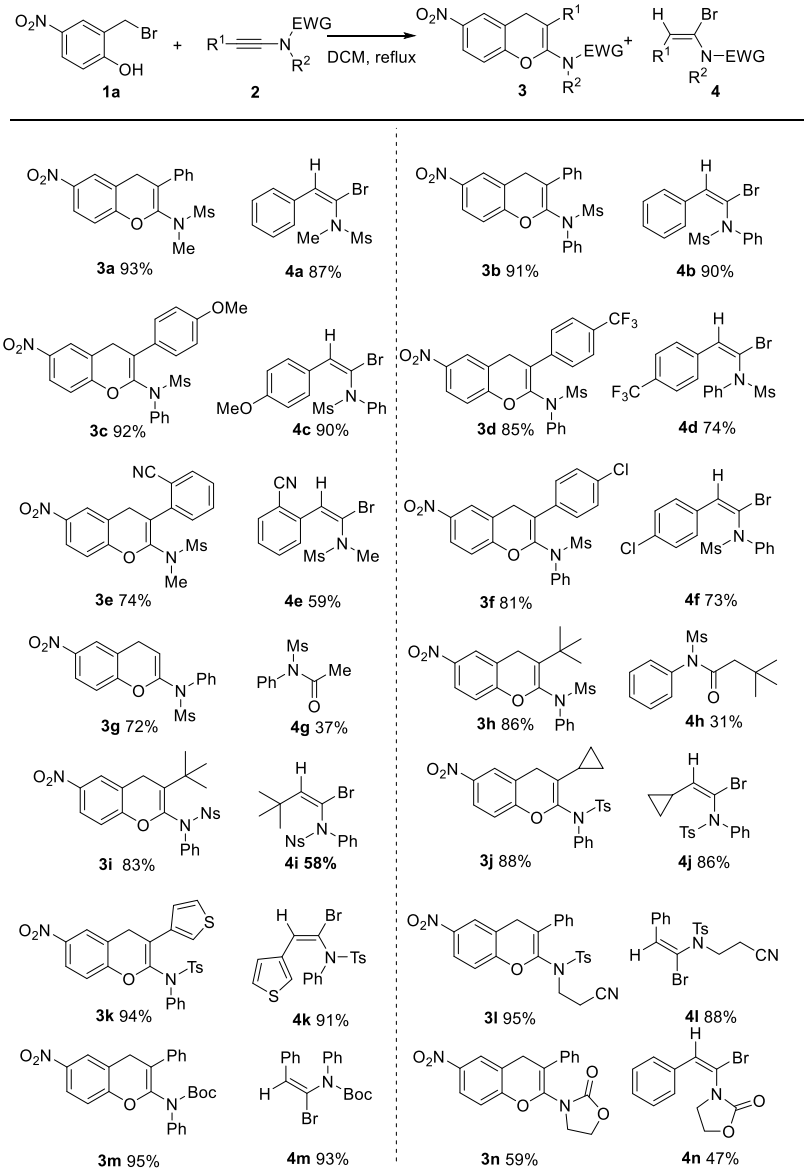
Scheme 2. Substrate Scope of Ynamides[a,b]



[a]Unless otherwise specified, reactions were conducted with **1a** (0.15 mmol) and **2** (0.3 mmol) in 2.0 mL of the solvent under reflux in an oil bath for 12 h. [b]Isolated yield.

achieved through the *o*-methylene quinone intermediate (eq 3, Scheme 5).

A plausible reaction mechanism was proposed based on our experimental results (Scheme 6). Initially, one equivalent of ynamide **2a** acted as a base, which reacted with **1a**, leading to keteniminium **A** and *o*-methylene quinone **B**,[13] respectively. Subsequently, keteniminium **A** was nucleophilic-attacked by Br^- from the side of least steric hindrance to yield the corresponding (*E*)-*α*-bromoenamide **4a**. In the meanwhile, an intermolecular [4+2] cycloaddition between *o*-methylene quinone **B** and another equivalent of ynamide **2a** was achieved to afford 2-amino-4*H*-chromenes **3a**.

CONCLUSIONS

In conclusion, a novel and highly efficient catalyst-free symbiotic reaction of 2-halomethylphenols and ynamides has been developed. This method provides a general and straightforward way to construct 2-amino-4*H*-chromenes and *α*-halo enamide derivatives simultaneously in one step. Besides, this strategy features simplicity, mild conditions, high yields, and good functional group compatibility.

EXPERIMENTAL SECTION

General Information. Unless otherwise mentioned, all reactions were performed in flame-dried glassware under air. Solvents were distilled prior to use. Reagents were purchased from commercially available sources and used without purification unless otherwise noted. Chromatographic separations were performed using Kangbino 48−75 Å SiO_2. ^1H, ^{19}F, and ^{13}C NMR spectra were recorded on Agilent ProPulse spectrometers using $CDCl_3$ with tetramethylsilane or a residual solvent as a standard unless otherwise noted. The melting points were determined using a melting point apparatus and were uncorrected/calibrated. Thin-layer chromatography (TLC) analysis was performed using Kangbino glass-backed plates (60 Å, 250 *μ*m) and visualized using UV and iodine stains. Low-resolution mass spectra were obtained using an Agilent 1100 series LS/MSD. All spectral data obtained for new compounds are reported here.

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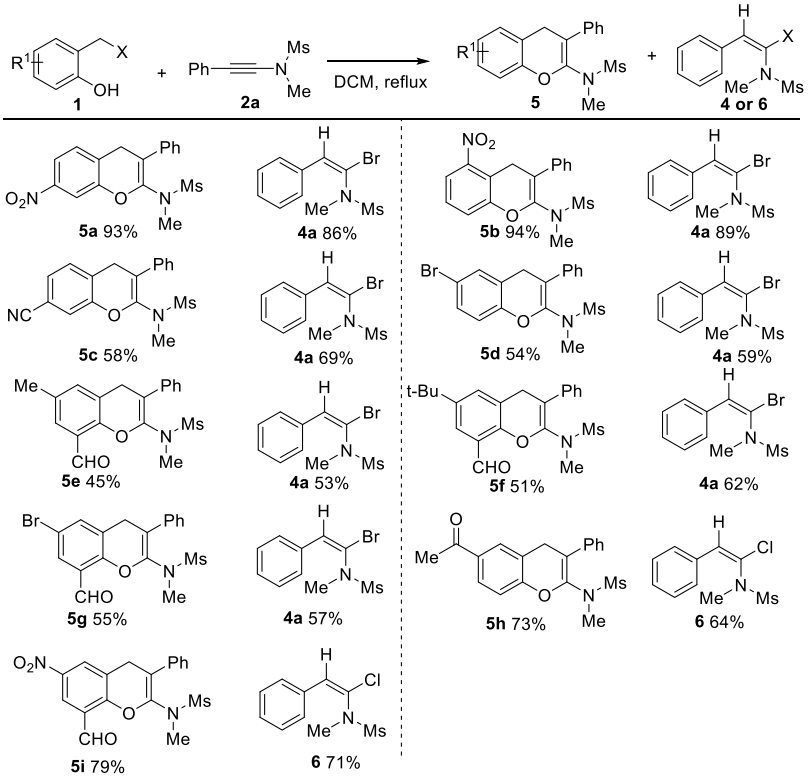
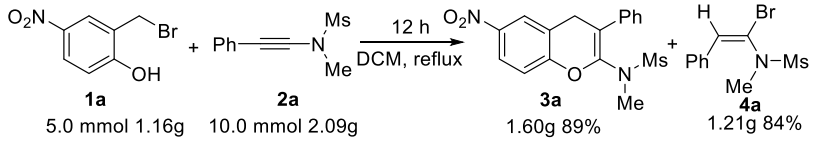
Scheme 3. Substrate Scope of 2-Halomethyl Phenols[a,b]

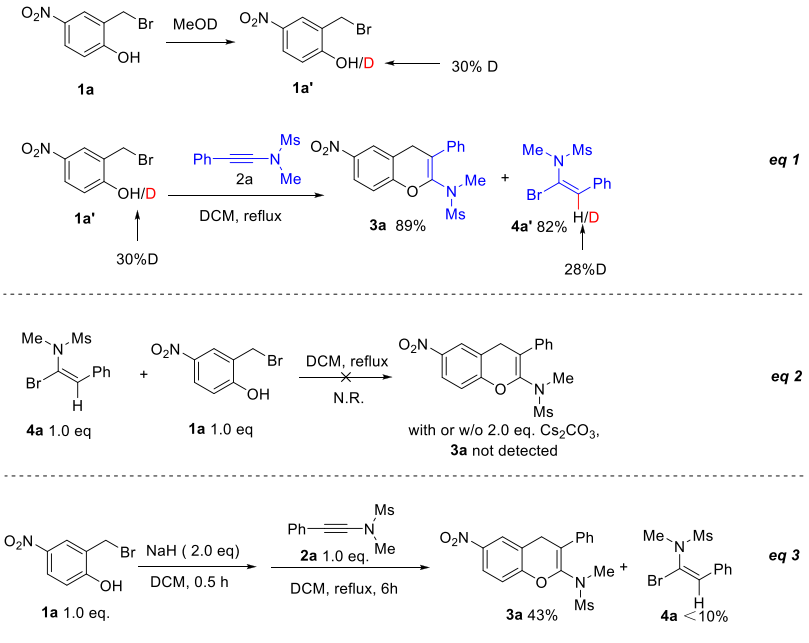


[a]Unless otherwise specified, reactions were conducted with **1** (0.15 mmol) and **2a** (0.3 mmol) in 2.0 mL of the solvent under reflux in an oil bath for 12 h. [b]Isolated yield.

Scheme 4. Gram-Scale Reaction



Scheme 5. Control Experiments



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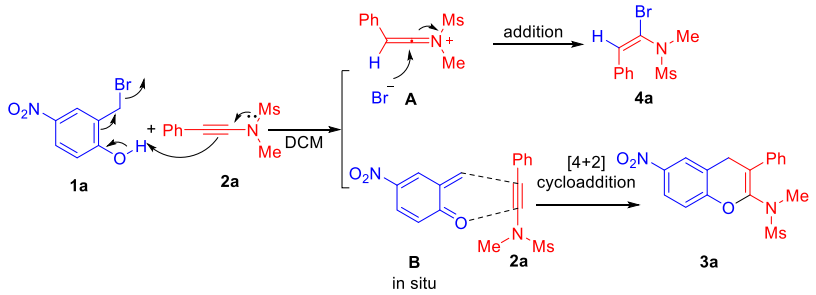
Scheme 6. Proposed Reaction Mechanism



General Procedure. *General Procedure **1** for the Synthesis of Ynamides (**2a**).*[14] $CuCl_2$ (20 mol %), sulfonamide (2.0 equiv), and Na_2CO_3 (2.0 equiv) were added to a three-necked round-bottomed flask. The flask was purged with oxygen for 15 min, and a solution of pyridine (2.0 equiv) in dry toluene (0.2 M) was added. A balloon filled with oxygen was connected to the flask, and the stirred mixture was heated in an oil bath at 70 °C. After 15 min, a solution of alkyne (1.0 equiv) in anhydrous toluene (0.2 M) was added using a syringe pump over 4 h. The mixture was allowed to stir at 70 °C for another 4 h and allowed to cool to rt. The reaction mixture was filtered through a plug of silica gel, washed with ethyl acetate, and concentrated. The crude residue was purified by flash chromatography over silica gel.

*General Procedure **2** for the Synthesis of Ynamides (**2b**).*[15] To a solution of phenylacetylene (1.0 equiv) in acetone (100 mL) were added *N*-bromosuccinimide (1.1 equiv) and $AgNO_3$ (10 mol %). The resulting solution was stirred under nitrogen at rt for 6 h. After removing excess acetone, the reaction mixture was quenched with water, extracted with EtOAc three times, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was eluted through a short silica column (petroleum ether) to obtain the bromoalkyne.

To a dried flask were added *N*-phenylmethanesulfonamide (1.0 equiv), $CuSO_4{\cdot}5H_2O$ (0.5 equiv), 1,10-phenanthroline (30 mol % equiv), K_2CO_3 (2.0 equiv), and bromoalkyne (1.2 equiv), and this mixture was subsequently treated with anhydrous toluene (100 mL) and the bromoalkyne. The flask was charged with nitrogen, and the solution was heated at 80 °C overnight. After completion, the crude reaction mixture was cooled to rt, filtered through Celite, and concentrated in vacuo. Purification of the crude residue using silica gel flash column chromatography yielded pure ynamide **1l** as a white solid.

*General Procedure **3** for the Synthesis of Ynamide **2g**.*[7c] To a solution of *N*-(2-cyanophenyl)methanesulfonamide (30 mmol) in dimethylformamide (DMF) (70 mL) was added Cs_2CO_3 (1.0 equiv). The solution was stirred at rt for 30 min, and then, phenyl-((trimethylsilyl)ethynyl)iodonium triflate (1.3 equiv) in DCM (30 mL) was added to the mixture and stirred until the reaction proceeded to completion as monitored by TLC. The reaction mixture was quenched by water and stirred for 30 min. The resulting mixture was extracted with CH_2Cl_2, washed with water and brine, and dried over anhydrous $MgSO_4$. The mixture was filtered, and the solvent was evaporated under reduced pressure; then, the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1 to petroleum ether/DCM = 1/1) to afford the desired product as a white solid.

*General Procedure **4** for the Synthesis of Ynamide **2e**.*[14,16] Under an atmosphere of argon, a solution of triphenylphosphine (4.0 equiv) and tetrabromomethane (2.0 equiv) in absolute CH_2Cl_2 (0.15 M) was stirred at 0 °C for 30 min. The aldehyde was added over a period of 5 min, and the mixture was stirred at 0 °C for 1 h. After addition of water, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (three times). The combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was dry-loaded on silica and subjected to flash chromatography.

To the vigorously stirred solution of 1,1-dibromoethene (5 mmol) in CH_2Cl_2 (25 mL) at 0 °C, $BnEt_3Cl$ (4.4 mmol) was added. Subsequently, a solution of KOH (230 mmol) in H_2O (10 mL) was added to the reaction mixture. After stirring for 5 h at 0 °C, H_2O (20 mL) was added to the reaction mixture. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was washed with brine and dried over $MgSO_4$. All volatiles were removed under reduced pressure. The product was purified by SiO_2 column chromatography.

To a dried flask were added *N*-methylmethanesulfonamide (4.85 mmol), $CuSO_4{\cdot}5H_2O$ (0.40 mmol), 1,10-phenanthroline (0.81 mmol), K_2CO_3 (10.01 mmol), and bromoalkyne (4.04 mmol), and this mixture was subsequently treated with anhydrous toluene (100 mL) and the bromoalkyne. The flask was charged with nitrogen, and the solution was heated at 80 °C in an oil bath overnight. After completion, the crude reaction mixture was cooled to rt, filtered through Celite, and concentrated in vacuo. Purification of the crude residue using silica gel flash column chromatography yielded the pure product as a white solid.

*General Procedure **5** for the Synthesis of 2-Amino-4H-Chromenes (**3a**) and α-Halo Enamides (**4a**).* 2-(Bromomethyl)-4-nitrophenol **1a** (0.15 mmol), ynamide **2a** (0.3 mmol), and dry CH_2Cl_2 (2.0 mL) were added to a 10 mL sealed tube. The mixture was stirred in reflux for 12 h. The reaction was monitored by TLC until the starting material disappeared. Then, the solvent was removed in vacuo, and the residue was purified by flash chromatography to give the desired product.

Characterization of Products. *N-Methyl-N-(phenylethynyl)-methanesulfonamide (**2a**).*[12] Following general procedure **1**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **2a**; white solid, mp 58−60 °C, yield: 82% (380.65 mg); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44−7.39 (m, 2H), 7.33−7.28 (m, 3H), 3.30 (s, 3H), 3.13 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 131.5, 128.3, 128.1, 122.3, 83.0, 69.5, 39.3, 36.8; mass spectrum [electrospray ionization (ESI)]: *m*/*z* (% relative intensity) 232.0 (100) $[M + Na]^+$.

*N-Phenyl-N-(phenylethynyl)methanesulfonamide (**2b**).*[12] Following general procedure **1**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **2b**; white solid, mp 67−68 °C, yield: 52% (458.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62−7.58 (m, 2H), 7.49−7.44 (m, 4H), 7.41−7.36 (m, 1H), 7.34−7.30 (m, 3H), 3.17 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 138.7, 131.6, 129.5, 128.34, 128.32, 128.2, 125.6, 122.3, 82.0, 71.0, 36.9; mass spectrum (ESI): *m*/*z* (% relative intensity) 294.0 (100) $[M + Na]^+$.

*N-((4-Methoxyphenyl)ethynyl)-N-phenylmethanesulfonamide (**2c**).*[12] Following general procedure **1**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **2c**; white solid, mp 96−97 °C, yield: 66% (427.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.9 Hz, 2H), 7.48−7.33 (m, 5H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 3.16 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 159.8, 138.9, 133.6, 129.4, 128.2, 125.5, 114.2, 114.0, 80.6, 70.7, 55.3, 42.7, 36.7; mass spectrum (ESI): *m*/*z* (% relative intensity) 324.1 (100) $[M + Na]^+$.

https://dx.doi.org/10.1021/acs.joc.0c01258
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*N-Phenyl-N-((4-(trifluoromethyl)phenyl)ethynyl)-methanesulfonamide (**2d**).* Following general procedure **1**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4/1 to petroleum ether/ethyl acetate = 3/1) to afford the desired product **2d**; white solid; mp 114−115 °C; mp 98−99 °C; yield: 69% (469.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61−7.56 (m, 4H), 7.54 (d, J = 8.5 Hz, 2H), 7.48 (t, J = 7.8 Hz, 2H), 7.42 (t, J = 7.4 Hz, 1H), 3.18 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 138.3, 131.3, 129.67, 129.66 (q, J = 32.8 Hz), 128.7, 126.3 (q, J = 1.3 Hz), 125.7, 125.3 (q, J = 3.8 Hz), 123.9 (q, J = 272.1 Hz), 84.5, 74.1, 37.2; ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.79. High-resolution mass spectroscopy (HRMS) (ESI) m/z: [M + H]$^+$ calcd for $C_{16}H_{13}F_3NO_2S$, 340.0614; found, 340.0609.

*N-((2-Cyanophenyl)ethynyl)-N-methylmethanesulfonamide (**2e**).*[12] Following general procedure **4**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **2e**; white solid, mp 54−55 °C, yield: 52% (491.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65−7.61 (m, 1H), 7.56−7.49 (m, 2H), 7.40−7.35 (m, 1H), 3.37 (s, 3H), 3.23 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 132.5, 132.4, 131.4, 127.9, 126.8, 117.8, 114.6, 89.5, 66.9, 39.2, 37.4; mass spectrum (ESI): m/z (% relative intensity) 257.0 (100) [M + Na]$^+$

*N-((4-Chlorophenyl)ethynyl)-N-phenylmethanesulfonamide (**2f**).*[12] Following general procedure **2**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **2f**; white solid, mp 112−114 °C, yield: 32% (314.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, J = 7.8 Hz, 2H), 7.49−7.43 (m, 2H), 7.42−7.35 (m, 3H), 7.34−7.28 (m, 2H), 3.17 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 138.5, 134.2, 132.7, 129.6, 128.7, 128.5, 125.6, 120.8, 82.9, 69.9, 37.0. Mass spectrum (ESI): m/z (% relative intensity) 328.0 (100) [M + Na]$^+$.

*N-Ethynyl-N-phenylmethanesulfonamide (**2g**).* Following general procedure **3**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **2g**; white solid; yield: 89% (288.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 7.7 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 3.13 (s, 3H), 2.97 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 138.0, 129.5, 128.6, 125.6, 75.8, 59.7, 36.7; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_9H_{10}NO_2S$, 196.0432; found, 196.0423.

*N-(3,3-Dimethylbut-1-yn-1-yl)-N-phenylmethanesulfonamide (**2h**).* Following general procedure **1**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **2h**; white solid; yield: 39% (196.56 mg); mp 86−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52−7.48 (m, 2H), 7.43−7.37 (m, 2H), 7.35−7.29 (m, 1H), 3.05 (s, 3H),1.28 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 139.3, 129.4, 128.0, 125.3, 79.2, 72.4, 35.8, 31.1, 27.7; HRMS (APCI−orbitrap) m/z: [M + H]$^+$ calcd for $C_{13}H_{18}NO_2S$, 252.1053; found, 252.1054.

*N-(3,3-Dimethylbut-1-yn-1-yl)-4-nitro-N-phenylbenzenesulfonamide (**2i**).* Following general procedure **1**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **2i**; pale yellow solid; yield: 45% (323.1 mg); mp 144−146 °C; R_f = 0.55 (petroleum ether/ethyl acetate = 95:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 8.8 Hz, 2H), 7.38−31 (m, 3H), 7.24−7.19 (m, 2H), 1.24 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.8, 140.9, 138.8, 129.6, 129.3, 128.6, 125.9, 123.9, 79.4, 72.2, 31.0, 27.6; HRMS (APCI−orbitrap) m/z: [M + H]$^+$ calcd for $C_{18}H_{19}N_2O_4S$, 359.1060; found, 359.1060.

*N-(Cyclopropylethynyl)-4-methyl-N-phenylbenzenesulfonamide (**2j**).*[12] Following general procedure **1**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **2j**; white solid, mp 103−105 °C, yield: 41% (410.8 mg);^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58−7.55 (m, 2H), 7.33−7.30 (m, 1H), 7.30−7.26 (m, 4H), 7.25−7.22 (m, 2H), 2.44 (s, 3H), 1.37−1.31 (m, 1H), 0.83−0.78 (m, 2H), 0.69−0.65 (m, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 145.3, 140.1, 133.8, 130.0, 129.6, 128.9, 128.6, 126.8, 75.3, 70.0, 22.4, 9.5; mass spectrum (ESI): m/z (% relative intensity) 334.1 (100) [M + Na]$^+$.

*4-Methyl-N-phenyl-N-(thiophen-3-ylethynyl)-benzenesulfonamide (**2k**).*[12] Following general procedure **1**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4/1 to petroleum ether/ethyl acetate = 3/1) to afford the desired product **2k**; white solid, mp 150−151 °C, yield: 32% (240.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64−7.60 (m, 2H), 7.41−7.38 (m, 1H), 7.36−7.23 (m, 8H), 7.07 (d, J = 4.9 Hz, 1H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 144.9, 138.9, 133.0, 130.1, 129.5, 129.1, 128.9, 128.3, 128.2, 126.3, 125.2, 121.4, 82.3, 65.6, 21.7; mass spectrum (ESI): m/z (% relative intensity) 376.1 (100) (M + Na)$^+$.

*N-(2-Cyanoethyl)-4-methyl-N-(phenylethynyl)-benzenesulfonamide (**2l**).*[7d] Following general procedure **1**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **2l**; white solid; mp 94−96 °C; yield: 88% (570.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, J = 8.3 Hz, 2H), 7.42−7.37 (m, 4H), 7.34−7.30 (m, 3H), 3.75 (t, J = 7.2 Hz, 2H), 2.79 (t, J = 7.2 Hz, 2H), 2.48 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.5, 133.9, 131.6, 130.1, 128.39, 128.38, 127.8, 122.0, 116.4, 80.6, 71.9, 47.3, 21.7, 17.5.

*tert-Butyl Phenyl(phenylethynyl)carbamate (**2m**).* Following general procedure **11**; white solid; 42% (247.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56−7.51 (m, 2H), 7.42−7.37 (m, 4H), 7.31−7.23 (m, 2H), 1.57 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.1, 139.8, 131.0, 128.9, 128.4, 127.5, 126.8, 124.8, 123.5, 83.8, 83.6, 70.2, 28.1; HRMS(ESI) m/z: [M + H]$^+$ calcd for $C_{19}H_{20}NO_2$, 294.1494; found, 294.1491.

*3-(Phenylethynyl)oxazolidin-2-one (**2n**).*[12] Following general procedure **1**; white solid; mp 84−85 °C; yield: 62% (260.4 mg); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47−7.41 (m, 2H), 7.32−7.28 (m, 3H), 4.48 (t, J = 8.0 Hz, 2H), 3.98 (t, J = 8.0 Hz, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 155.9, 131.6, 128.3, 128.2, 122.2, 79.0, 71.2, 63.1, 47.1; mass spectrum (ESI): m/z (% relative intensity) 210.1 (100) [M + Na]$^+$.

*N-Methyl-N-(6-nitro-3-phenyl-4H-chromen-2-yl)-methanesulfonamide (**3a**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **3a**; white solid; mp 207−209 °C; yield: 93% (50.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (dd, J = 8.9, 2.7 Hz, 1H), 8.02 (d, J = 2.6 Hz, 1H), 7.44−7.36 (m, 4H), 7.34−7.29 (m, 1H), 7.02 (d, J = 8.9 Hz, 1H), 3.89 (s, 2H), 3.02 (s, 3H), 2.81 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.9, 128.8, 128.2, 124.8, 124.0, 120.9, 116.8, 111.3, 39.7, 36.4, 31.0; HRMS (APCI−orbitrap) m/z: [M + H]$^+$ calcd for $C_{17}H_{17}N_2O_5S$, 361.0853; found, 361.0850.

*N-(6-Nitro-3-phenyl-4H-chromen-2-yl)-N-phenylmethanesulfonamide (**3b**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **3b**; pale yellow solid; mp 80−82 °C; yield: 91% (57.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (dd, J = 9.0, 2.7 Hz, 1H), 8.04−8.05 (m, 1H), 7.37−7.30 (m, 5H), 7.26−7.20 (m, 3H), 7.15−7.09 (m, 3H), 3.86 (s, 2H), 3.06 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.1, 144.1, 141.1, 139.1, 136.0, 129.4, 128.6, 128.3, 128.2, 127.9, 126.8, 124.9, 124.0, 121.1, 116.9, 113.0, 40.4, 31.4; HRMS (APCI−orbitrap) m/z: [M + H]$^+$ calcd for $C_{22}H_{19}N_2O_5S$, 423.1009; found, 423.1006.

*N-(3-(4-Methoxyphenyl)-6-nitro-4H-chromen-2-yl)-N-phenylmethanesulfonamide (**3c**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **3c**; yellow solid, mp 130−132 °C, yield: 92% (62.4 mg);^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (dd, J

https://dx.doi.org/10.1021/acs.joc.0c01258
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= 8.9, 2.7 Hz, 1H), 8.03 (d, J = 2.6 Hz, 1H), 7.33−7.27 (m, 2H), 7.26−7.23 (m, 3H), 7.17−7.14 (m, 2H), 7.11 (d, J = 9.0 Hz, 1H), 6.92−6.85 (m, 2H), 3.83 (s, 2H), 3.82 (s, 3H), 3.08 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.4, 156.1, 144.0, 140.7, 139.1, 129.4, 129.1, 128.3, 128.1, 126.8, 125.0, 124.0, 121.1, 116.8, 113.9, 112.6, 55.4, 40.41, 31.41; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{23}H_{21}N_2O_6S$, 453.1115; found, 453.1113.

*N-(6-Nitro-3-(4-(trifluoromethyl)phenyl)-4H-chromen-2-yl)-N-phenylmethanesulfonamide (**3d**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **3d**; white solid; mp 193−195 °C; yield: 85% (62.6. mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.8 Hz, 1H), 8.05 (s, 1H), 7.61 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 7.8 Hz, 2H), 7.27−7.21 (m, 3H), 7.18−7.07 (m, 7.0 Hz, 3H), 3.87 (s, 2H), 3.11 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.7, 144.3, 142.0, 139.7, 138.9, 130.2 (q, J = 32.4 Hz), 129.6, 128.53, 128.46, 126.5, 125.6 (q, J = 4.1 Hz), 125.0, 124.2, 124.1 (q, J = 271.3 Hz), 120.7, 117.0, 111.7, 40.4, 31.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.47 (s, 3F); HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{23}H_{18}F_3N_2O_5S$, 491.0883; found, 491.0878.

*N-(3-(2-Cyanophenyl)-6-nitro-4H-chromen-2-yl)-N-methylmethanesulfonamide (**3e**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **3e**; white solid; mp 99−101 °C; yield: 74% (42.7 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.11 (dd, J = 9.0, 2.7 Hz, 1H), 8.03 (d, J = 2.5 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.66 (td, J = 7.7, 1.2 Hz, 1H), 7.57 (d, J = 7.3 Hz, 1H), 7.45 (td, J = 7.7, 1.1 Hz, 1H), 7.05 (d, J = 9.0 Hz, 1H), 3.92 (s, 2H), 3.10 (s, 3H), 2.88 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.7, 144.2, 142.3, 140.7, 133.5, 133.1, 130.7, 128.7, 124.9, 124.2, 120.3, 118.2, 117.1, 111.6, 109.8, 38.9, 36.0, 31.0; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{18}H_{16}N_3O_5S$, 386.0605; found, 386.0604.

*N-(3-(4-Chlorophenyl)-6-nitro-4H-chromen-2-yl)-N-phenylmethanesulfonamide (**3f**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **3f**; pale yellow solid; mp 212−214 °C; yield: 81% (55.4 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.12 (dd, J = 9.0, 2.7 Hz, 1H), 8.03 (d, J = 2.6 Hz, 1H), 7.35−7.25 (m, 7H), 7.15−7.11 (m, 3H), 3.83 (s, 2H), 3.10 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.8, 144.1, 141.4, 138.9, 134.3, 134.0, 129.6, 129.4, 128.8, 128.5, 126.6, 125.0, 124.1, 120.8, 116.9, 111.9, 40.4, 31.2; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{22}H_{18}ClN_2O_5S$, 457.0620; found, 457.0617.

*N-(6-Nitro-4H-chromen-2-yl)-N-phenylmethanesulfonamide (**3g**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1 to petroleum ether/ethyl acetate = 2/1) to afford the desired product **3g**; pale yellow solid; mp 114−116 °C; yield: 72% (37.4 mg); ^1H NMR (500 MHz, $CDCl_3$): δ 8.08 (dd, J = 8.9, 2.5 Hz, 1H), 8.01 (d, J = 1.9 Hz, 1H), 7.54 (d, J = 8.1 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 7.04 (d, J = 9.0 Hz, 1H), 5.33 (t, J = 3.8 Hz, 1H), 3.65 (d, J = 3.8 Hz, 2H), 3.17 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 156.3, 144.1, 144.0, 139.2, 129.7, 128.5, 126.9, 125.1, 123.8, 120.1, 117.2, 101.0, 40.3, 25.4; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{16}H_{15}N_2O_5S$, 347.0696; found, 347.0694.

*N-(3-(tert-Butyl)-6-nitro-4H-chromen-2-yl)-N-phenylmethanesulfonamide (**3h**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **3h**; white solid; mp 144−146 °C; yield: 86% (52.0 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.11−8.05 (m, 2H), 7.58 (d, J = 7.7 Hz, 2H), 7.37 (t, J = 7.9 Hz, 2H), 7.28−7.22 (s, 1H), 6.99 (d, J = 9.3 Hz, 1H), 3.64 (q, J = 24.8 Hz, 2H), 3.06 (s, 3H), 1.18 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.6, 143.9, 140.5, 138.4, 129.7, 126.6, 124.7, 123.9, 122.8, 122.0, 121.0, 115.8, 40.0, 34.9, 29.4, 27.9; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{20}H_{23}N_2O_5S$, 403.1322; found, 403.1321.

*N-(3-(tert-Butyl)-6-nitro-4H-chromen-2-yl)-4-nitro-N-phenylbenzenesulfonamide (**3i**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **3i**; white solid; mp 202−204 °C; yield: 83% (63.4 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.4 Hz, 2H), 8.10−8.03 (m, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.47−7.42 (m, 2H), 7.35−7.27 (m, 3H), 6.60 (d, J = 9.0 Hz, 1H), 3.80−3.50 (m, 2H), 1.26 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.9, 150.4, 144.6, 143.9, 139.8, 138.3, 129.8, 129.6, 127.8, 124.81, 124.79, 124.0, 123.6, 121.6, 121.5, 115.1, 35.1, 29.6, 28.1; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{25}H_{24}N_3O_7S$, 510.1330; found, 510.1327.

*N-(3-Cyclopropyl-6-nitro-4H-chromen-2-yl)-4-methyl-N-phenylbenzenesulfonamide (**3j**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **3j**; pale yellow solid; mp 204−206 °C; yield: 88% (61.0 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.9 Hz, 1H), 7.97 (s, 1H), 7.59 (d, J = 8.1 Hz, 2H), 7.38−7.21 (m, 8H), 6.78 (d, J = 8.9 Hz, 1H), 3.21 (s, 2H), 2.44 (s, 3H), 2.11−2.00 (m, 1H), 0.80−0.5 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.4, 144.1, 143.5, 139.5, 139.3, 136.5, 129.3, 128.5, 128.1, 127.4, 125.1, 123.8, 120.2, 116.4, 113.3, 25.4, 21.8, 11.5, 3.3; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{25}H_{22}N_2O_5S$, 463.1322; found, 463.1321.

*4-Methyl-N-(6-nitro-3-(thiophen-3-yl)-4H-chromen-2-yl)-N-phenylbenzenesulfonamide (**3k**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **3k**; yellow solid, mp 200−202 °C, yield: 94% (71.1 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.11−8.05 (m, 2H), 7.57−7.52 (m, 3H), 7.48 (dd, J = 3.0, 1.4 Hz, 1H), 7.37 (dd, J = 5.1, 3.0 Hz, 1H), 7.27 (s, 1H), 7.23−7.17 (m, 3H), 7.13−7.10 (m, 2H), 6.86 (d, J = 8.8 Hz, 1H), 3.91 (s, 2H), 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.7, 144.4, 143.9, 140.6, 139.0, 136.2, 135.6, 129.3, 129.2, 128.63, 128.2, 127.4, 127.0, 125.6, 125.0, 123.9, 123.7, 120.8, 116.4, 108.5, 30.6, 21.8; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{26}H_{21}N_2O_5S_2$, 505.0886; found, 505.0883.

*N-(2-Cyanoethyl)-4-methyl-N-(6-nitro-3-phenyl-4H-chromen-2-yl)benzenesulfonamide (**3l**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **3l**; white solid; mp 163−165 °C; yield: 95% (67.7 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.08−8.00 (m, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 7.0 Hz, 2H), 7.45−7.32 (m, 5H), 6.84−6.76 (m, 1H), 3.95 (s, 2H), 3.40 (t, J = 7.2 Hz, 2H), 2.48 (s, 3H), 2.3−2.20 (t, J = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.7, 145.0, 144.0, 139.1, 135.9, 135.6, 129.9, 129.0, 128.6, 128.4, 127.8, 124.9, 124.0, 120.7, 117.0, 116.5, 114.4, 45.1, 31.4, 21.8, 17.5; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{25}H_{22}N_3O_5S$, 476.1275; found, 476.1273.

*t. ert-Butyl (6-Nitro-3-phenyl-4H-chromen-2-yl)(phenyl)carbamate (**3m**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **3m**; yellow liquid; yield: 95% (63.1 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.01−8.03 (m, 2H), 7.31−7.17 (m, 7H), 7.14−7.03 (m, 4H), 3.88 (s, 2H), 1.37 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.8, 152.9, 143.8, 142.1, 140.2, 136.8, 128.7, 128.6, 127.9, 127.0, 126.0, 124.7, 124.7, 123.9, 121.4, 117.0, 82.1, 30.7, 28.1; HRMS (ESI) (m/z): $[M-C_5H_8O_2 + H]^+$ calcd for $C_{21}H_{17}N_2O_3$, 345.1234; found, 345.1231.

*3-(6-Nitro-3-phenyl-4H-chromen-2-yl)oxazolidin-2-one (**3n**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **3n**; pale yellow solid, mp 100−102 °C, 59% (29.9 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.09−8.01 (m, 2H), 7.40−7.32 (m, 5H), 7.04 (d, J = 8.9 Hz, 1H), 4.30 (dd, J = 8.7, 7.3 Hz, 2H), 3.91 (s, 2H),

https://dx.doi.org/10.1021/acs.joc.0c01258
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3.66 (dd, J = 8.7, 7.3 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.2, 156.0, 143.8, 137.5, 136.1, 129.0, 128.3, 127.1, 124.0, 120.7, 117.1, 111.0, 62.8, 44.9, 30.7; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{18}H_{15}N_2O_5$, 339.0976; found, 339.0976.

*(E)-N-(1-Bromo-2-phenylvinyl)-N-methylmethanesulfonamide (**4a**).*[11h] Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **4a**; white solid; mp 89−91 °C; yield: 87% (38.0 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.58−7.54 (m, 2H), 7.38−7.30 (m, 3H), 6.88 (s, 1H), 3.07 (s, 3H), 2.98 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 137.4, 133.6, 129.3, 128.9, 128.8, 120.6, 37.5, 36.6.

*(Z)-N-(1-Bromo-2-phenylvinyl)-N-phenylmethanesulfonamide (**4b**).*[12] Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **4b**; white solid, mp 135−136 °C, 90% (47.4 mg); R_f = 0.5 (20% EtOAc/petroleum ether);^1H NMR (500 MHz, $CDCl_3$): δ 7.60−55 (m, 4H), 7.38−7.31 (m, 5H), 7.31−7.26 (m, 1H), 7.08 (s, 1H), 3.16 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 138.9, 138.6, 133.4, 129.5, 129.2, 128.7, 128.6, 127.4, 123.7, 118.0, 39.1.

*(E)-N-(1-Bromo-2-(4-methoxyphenyl)vinyl)-N-phenylmethanesulfonamide (**4c**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **4c**; colorless liquid; yield: 90% (51.4 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.61−7.57 (m, 2H), 7.56−7.51 (m, 2H), 7.38−7.32 (m, 2H), 7.29−7.26 (m, 1H), 6.98 (s, 1H), 6.87−6.83 (m, 2H), 3.78 (s, 3H), 3.16 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.3, 139.0, 138.3, 130.4, 129.7, 127.3, 126.0, 123.4, 115.5, 114.2, 55.4, 39.2; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{16}H_{17}BrNO_3S$, 382.0107; found, 382.0105.

*(E)-N-(1-Bromo-2-(4-(trifluoromethyl)phenyl)vinyl)-N-phenylmethanesulfonamide (**4d**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **4d**; white solid; mp 142−144 °C; yield: 74% (46.5 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2H), 7.35 (t, J = 8.0 Hz, 2H), 7.29 (d, J = 8.2 Hz, 1H), 7.09 (s, 1H), 3.15 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 138.8, 137.1, 136.8, 130.8 (q, J = 32.6 Hz), 129.8, 128.9, 127.8, 125.8 (q, J = 3.8 Hz), 123.9 (q, J = 271.0 Hz), 123.8, 120.4, 39.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.71 (s, 3F); HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}BrF_3NO_2S$, 419.9875; found, 419.9871.

*(E)-N-(1-Bromo-2-(2-cyanophenyl)vinyl)-N-methylmethanesulfonamide (**4e**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **4e**; colorless liquid; yield: 59% (27.8 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.00−7.93 (m, 2H), 7.67−7.54 (m, 2H), 7.44−7.35 (m, 1H), 7.22 (s, 1H), 3.06 (s, 3H), 2.98 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 136.9, 133.3, 133.1, 132.8, 129.1, 128.6, 125.0, 117.6, 112.1, 37.3, 37.0; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{11}H_{12}BrN_2O_2S$, 314.9797; found, 314.9796.

*(E)-N-(1-Bromo-2-(4-chlorophenyl)vinyl)-N-phenylmethanesulfonamide (**4f**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **4f**; white solid; mp 119−121 °C; yield: 73% (44.6 mg); R_f = 0.5 (20% EtOAc/petroleum ether); ^1H NMR (500 MHz, $CDCl_3$): δ 7.57−7.48 (m, 4H), 7.40−7.34 (m, 2H), 7.33−7.28 (m, 3H), 7.02 (s, 1H), 3.16 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 138.8, 137.3, 135.0, 131.8, 129.8, 129.7, 129.0, 127.6, 123.6, 118.5, 39.0. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{13}BrClNO_2SNa$, 407.9431; found, 407.9434.

*N-(Methylsulfonyl)-N-phenylacetamide (**4g**).*[17] Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **4g**; pale yellow liquid; yield: 37% (11.8 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.50−7.46 (m, 3H), 7.31−7.27 (m, 2H), 3.45 (s, 3H), 1.95 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 171.7, 136.1, 130.3, 130.2, 129.8, 42.2, 25.2.

*3,3-Dimethyl-N-(methylsulfonyl)-N-phenylbutanamide (**4h**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4/1 to petroleum ether/ethyl acetate = 3/1) to afford the desired product **4h**; colorless oil; yield: 31% (12.5 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.51−7.44 (m, 3H), 7.29−7.22 (s, 2H), 3.44 (s, 3H), 2.00 (s, 2H), 0.98 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 173.4, 136.0, 130.09, 130.06, 130.0, 48.1, 42.0, 31.8, 29.6; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{13}H_{20}NO_3S$, 270.1158; found, 270.1157.

*(E)-N-(1-Bromo-3,3-dimethylbut-1-en-1-yl)-4-nitro-N-phenylbenzenesulfonamide (**4i**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **4i**; white solid; mp 139−141 °C; yield: 58% (38.1 mg);^1H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 8.9 Hz, 2H), 7.88 (d, J = 8.9 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 7.40−7.27 (m, 3H), 6.16 (s, 1H), 1.16 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.9, 150.5, 143.0, 140.0, 130.6, 129.5, 127.9, 124.4, 123.7, 114.5, 36.5, 29.6; HRMS (ESI) m/z: $[M + H_2O\text{-}H]^-$ calcd for $C_{18}H_{20}N_2O_5BrS$, 455.0282; found, 455.0272.

*(E)-N-(1-Bromo-2-cyclopropylvinyl)-4-methyl-N-phenylbenzenesulfonamide (**4j**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **4j**; white solid; mp 110−112 °C; yield: 86% (52.1 mg); R_f = 0.6 (30% EtOAc/petroleum ether); ^1H NMR (500 MHz, $CDCl_3$): δ 7.77−7.74 (m, 2H), 7.39−7.32 (m, 5H), 7.30−7.26 (m, 2H), 5.48 (d, J = 10.1 Hz, 1H), 2.44 (s, 3H), 2.05−1.96 (m, 1H), 0.96−0.82 (m, 2H), 0.62−0.46 (m, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 145.1, 144.3, 139.2, 135.9, 129.3, 129.2, 128.8, 128.2, 127.4, 114.3, 21.6, 12.9, 7.2; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{16}BrNO_3SNa$, 403.9926; found, 403.9927.

*(E)-N-(1-Bromo-2-(thiophen-3-yl)vinyl)-4-methyl-N-phenylbenzenesulfonamide (**4k**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **4k**; white solid, mp 154−156 °C, yield: 91% (62.1 mg); R_f = 0.7 (20% EtOAc/petroleum ether); ^1H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 8.2 Hz, 2H), 7.71−7.68 (m, 1H), 7.61 (d, J = 4.4 Hz, 1H), 7.44−7.38 (m, 2H), 7.35−7.32 (m, 1H), 7.31−7.24 (m, 5H), 7.06 (s, 1H), 2.44 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 144.7, 139.1, 135.0, 134.9, 133.0, 129.30, 129.27, 129.2, 128.0, 127.5, 127.0, 126.0, 125.8, 117.6, 21.7; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{16}BrNO_2S_2Na$, 455.9698; found, 455.9695.

*(E)-N-(1-Bromo-2-phenylvinyl)-N-(2-cyanoethyl)-4-methylbenzenesulfonamide (**4l**).* Following the general procedure, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **4l**; white solid; mp 115−117 °C; yield: 88% (53.3 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.2 Hz, 2H), 7.71−7.63 (m, 2H), 7.42−7.30 (m, 5H), 7.05 (s, 1H), 3.98−3.85 (m, 1H), 3.3−3.15 (m, 1H), 2.65−2.45 (m, 2H), 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 145.6, 140.7, 133.5, 133.1, 130.0, 129.8, 129.2, 117.7, 116.7, 45.5, 21.8, 16.8; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{18}H_{18}BrN_2O_2S$, 405.0267; found, 405.0264.

*(E)-tert-Butyl (1-Bromo-2-phenylvinyl)(phenyl)carbamate (**4m**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **4m**; yellow liquid; yield: 93% (52.0 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.43−7.21 (m, 10H), 6.88 (s, 1H), 1.35 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.7, 139.1, 134.6, 133.3,

https://dx.doi.org/10.1021/acs.joc.0c01258
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129.0, 128.7, 127.7, 126.5, 124.6, 121.0, 82.8, 28.0; HRMS (ESI) m/z: $[M-C_5H_8O_2 + H]^+$ calcd for $C_{14}H_{13}BrN$, 274.0226; found, 274.0226.

*(E)-3-(1-Bromo-2-phenylvinyl)oxazolidin-2-one (**4n**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **4n**; white solid, mp 103−105 °C, 47% (20.4 mg); R_f = 0.3 (20% EtOAc/petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37−7.30 (m, 5H), 6.96 (s, 1H), 4.45 (t, J = 8.0 Hz, 3H), 3.74 (t, J = 8.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 155.3, 135.5, 133.7, 128.84, 128.83, 127.9, 116.4, 62.7, 45.2; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{11}H_{10}BrNO_2Na$, 289.9787; found, 289.9793.

*N-Methyl-N-(7-nitro-3-phenyl-4H-chromen-2-yl)-methanesulfonamide (**5a**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **5a**; yellow solid; mp 148−150 °C; yield: 93% (50.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, J = 8.4, 2.2 Hz, 1H), 7.80 (d, J = 2.2 Hz, 1H), 7.45−7.36 (m, 4H), 7.34−7.29 (m, 1H), 7.27−7.23 (s, 1H), 3.90 (s, 2H), 3.01 (s, 3H), 2.90 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.6, 147.6, 141.5, 136.3, 129.4, 128.8, 128.1, 127.6, 127.5, 119.0, 111.6, 110.5, 39.8, 36.4, 31.2; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}N_2O_5S$, 361.0853; found, 361.0851.

*N-Methyl-N-(5-nitro-3-phenyl-4H-chromen-2-yl)-methanesulfonamide (**5b**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **5b**; yellow solid; mp 144−146 °C; yield: 94% (50.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, J = 8.2, 1.3 Hz, 1H), 7.45−7.35 (m, 4H), 7.34−7.28 (m, 2H), 7.22−7.19 (m, 1H), 4.13 (s, 2H), 3.01 (s, 3H), 2.80 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.6, 148.4, 140.8, 136.4, 128.8, 128.1, 128.0, 127.7, 121.5, 120.4, 116.6, 110.6, 39.8, 36.4, 29.5; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}N_2O_5S$, 361.0853; found, 361.0851.

*N-(7-Cyano-3-phenyl-4H-chromen-2-yl)-N-methylmethanesulfonamide (**5c**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **2w**; white solid; mp 148−150 °C; yield: 58% (29.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.29 (m, 6H), 7.23−7.17 (m, 2H), 3.86 (s, 2H), 3.00 (s, 3H), 2.86 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.5, 141.4, 136.5, 129.7, 128.8, 128.1, 127.7, 127.5, 125.8, 119.7, 118.2, 111.6, 110.7, 39.7, 36.4, 31.2; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{18}H_{17}N_2O_3S$, 341.0954; found, 341.0956.

*N-(6-Bromo-3-phenyl-4H-chromen-2-yl)-N-methylmethanesulfonamide (**5d**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **5d**; colorless liquid; yield: 54% (31.8 mg); ^{1}H NMR [400 MHz, dimethyl sulfoxide- d_6 (DMSO-d_6)]: δ 7.46−7.33 (m, 6H), 7.30−7.23 (m, 1H), 7.02 (d, J = 8.5 Hz, 1H), 3.78 (s, 2H), 2.98 (s, 3H), 2.88 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 150.6, 141.8, 137.4, 131.7, 131.0, 128.8, 127.9, 127.9, 123.1, 118.6, 115.9, 39.7, 36.6, 30.2; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}BrNO_3S$, 394.0107; found, 394.0105.

*N-(8-Formyl-6-methyl-3-phenyl-4H-chromen-2-yl)-N-methylmethanesulfonamide (**5e**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **5e**; yellow solid; mp 64−66 °C; yield: 45% (24.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.31 (s, 1H), 7.48−7.37 (m, 5H), 7.33−7.28 (m, 1H), 7.15 (s, 1H), 3.81 (s, 2H), 3.02 (s, 3H), 2.95 (s, 3H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.8, 150.7, 141.4, 136.8, 135.6, 133.6, 129.1, 128.7, 127.9, 127.6, 123.5, 121.0, 111.6, 39.4, 36.5, 30.8, 20.6; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{19}H_{20}NO_4S$, 358.1108; found, 358.1107.

*N-(6-(tert-Butyl)-8-formyl-3-phenyl-4H-chromen-2-yl)-N-methylmethanesulfonamide (**5f**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **5f**; yellow liquid; yield: 51% (30.5 mg); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.28 (s, 1H), 7.65−7.55 (m, 2H), 7.45−7.25 (m, 5H), 3.84 (s, 2H), 3.09 (s, 3H), 2.96 (s, 3H), 1.26 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 189.7, 150.7, 146.9, 141.6, 137.4, 132.9, 128.8, 128.0, 124.6, 123.1, 121.6, 111.7, 39.3, 36.6, 34.7, 31.5, 30.4; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{22}H_{26}NO_4S$, 400.1577; found, 400.1576.

*N-(6-Bromo-8-formyl-3-phenyl-4H-chromen-2-yl)-N-methylmethanesulfonamide (**5g**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **5g**; yellow liquid; yield 73% (46.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.27 (s, 1H), 7.79 (d, J = 2.4 Hz, 1H), 7.46−7.44 (m, 1H), 7.42−7.39 (m, 4H), 7.34−7.30 (m, 1H), 3.83 (s, 2H), 3.03 (s, 3H), 2.87 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.1, 151.8, 141.3, 137.2, 136.3, 131.2, 128.8, 128.2, 127.5, 125.0, 123.7, 116.6, 111.7, 39.5, 36.4, 30.6; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{18}H_{17}BrNO_4S$, 422.0056; found, 422.0057.

*N-(6-Acetyl-3-phenyl-4H-chromen-2-yl)-N-methylmethanesulfonamide (**5h**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **5h**; yellow liquid; yield 73% (39.1 mg); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.83−7.89 (m, 2H), 7.47−7.43 (m, 2H), 7.40−7.35 (m, 2H), 7.31−7.26 (m, 1H), 7.15 (d, J = 9.1 Hz, 1H), 3.85 (s, 2H), 2.99 (s, 3H), 2.91 (s, 3H), 2.51 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 197.0, 154.9, 141.6, 137.3, 133.4, 130.1, 129.0, 128.9, 128.0, 127.9, 120.5, 116.5, 111.1, 39.7, 36.6, 30.3, 27.1; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{19}H_{20}NO_4S$, 358.1108; found, 358.1106.

*N-(8-Formyl-6-nitro-3-phenyl-4H-chromen-2-yl)-N-methylmethanesulfonamide (**5i**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1 to petroleum ether/ethyl acetate = 1/1) to afford the desired product **5i**; pale yellow solid; mp 120−122 °C; yield: 79% (46.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.34 (s, 1H), 8.57 (d, J = 2.8 Hz, 1H), 8.23 (dt, J = 2.7, 1.0 Hz, 1H), 7.45−7.41 (m, 4H), 7.39−7.34 (m, 1H), 3.97 (s, 2H), 3.05 (s, 3H), 2.86 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 186.5, 156.7, 143.6, 141.2, 135.6, 129.2, 129.0, 128.6, 127.4, 124.6, 123.87, 123.1, 112.1, 39.6, 36.4, 30.8; HRMS (APCI−orbitrap) m/z: $[M + H]^+$ calcd for $C_{18}H_{17}N_2O_6S$, 389.0802; found, 389.0800.

*(E)-N-(1-Chloro-2-phenylvinyl)-N-methylmethanesulfonamide (**6**).* Following general procedure **5**, the product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **6**; white oil; yield: 71% (28.4 mg); R_f = 0.8 (30% EtOAc/petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59−7.56 (m, 2H), 7.39−7.29 (m, 3H), 6.70 (s, 1H), 3.15 (s, 3H), 3.02 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 132.8, 132.5, 129.13, 129.09, 128.8, 128.7, 38.1, 35.8; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{10}H_{12}ClNO_2SNa$, 268.0169; found, 268.0170.

*2-(Bromomethyl)-4-nitrophenol (**1a′**).* The product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **1a′**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 2.7 Hz, 1H), 8.14 (d, J = 2.7 Hz, 1H), 8.12 (d, J = 2.7 Hz, 1H), 6.92 (d, J = 8.9 Hz, 0.7H), 4.54 (s, 2H).

*(E)-N-(1-Bromo-2-phenylvinyl)-N-methylmethanesulfonamide (**4a′**).* The product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to petroleum ether/ethyl acetate = 4/1) to afford the desired product **4a′**; yield: 85% (37.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58−7.53 (m, 2H), 7.38−7.31 (m, 3H), 6.89 (s, 0.72H), 3.08 (s, 3H), 2.99 (s, 3H).

https://dx.doi.org/10.1021/acs.joc.0c01258
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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c01258.

NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (21772181) and the NSFC-Shandong Joint Fund for Marine Science Research Centers (U1606403) for financial support. The Fundamental Research Funds for the Central Universities (201612013) and the Qingdao Scientific and Technological Innovation Center for Marine Biomedicine Development grant (2017-CXZX01-1-1) for financial support are also gratefully acknowledged.

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https://dx.doi.org/10.1021/acs.joc.0c01258
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