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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b02935 • Publication Date (Web): 30 Nov 2018

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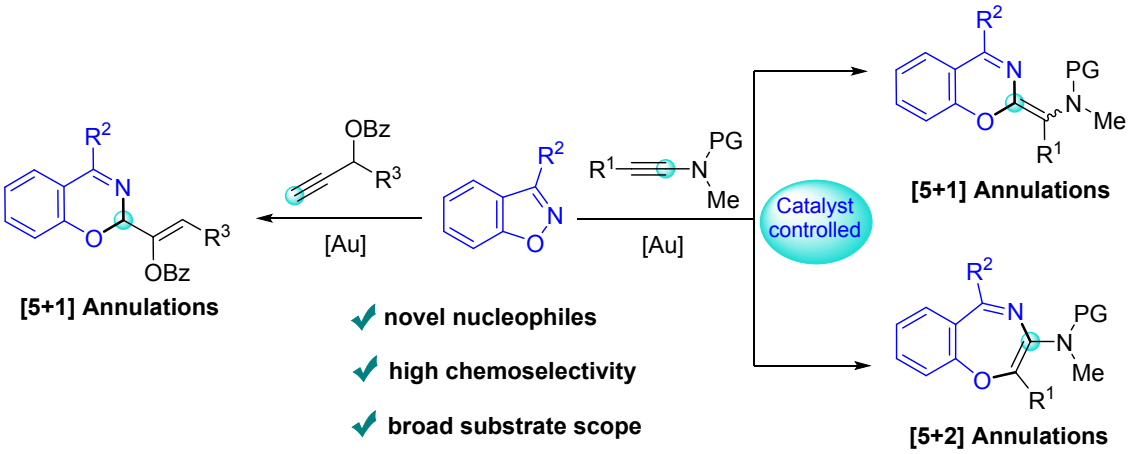


Abstract: Benzo[*d*]isoxazoles are found to act as novel nucleophiles to undergo gold-catalyzed [5+1] or [5+2] cycloaddition reactions with ynamides. The reaction provides a concise and chemoselective access to polysubstituted 2*H*-benzo[*e*][1,3]oxazines or benzo[*f*][1,4]oxazepines. In addition,

benzo[*d*]isoxazoles can also react with gold-carbene intermediates derived from propargyl esters to afford [5+1] annulation products.

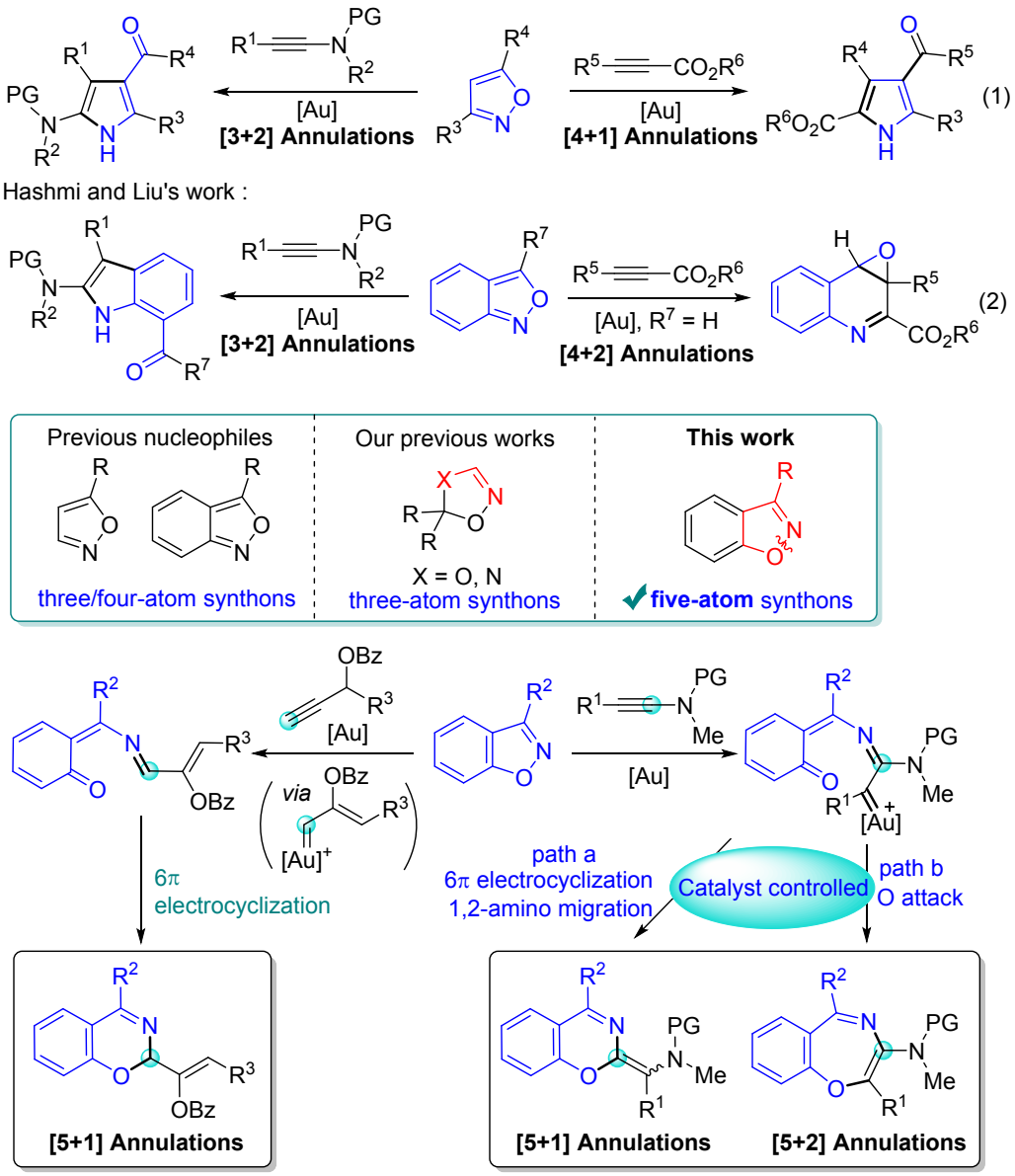
INTRODUCTION

In recent years, gold-catalyzed reactions involving α-imino gold carbenes [1-5] have attracted extensive attention because of their high efficiency in constructing nitrogen-containing heterocyclic compounds. Up to now, many substrates (so called nucleophilic nitrenoids) which could initiate the generation of α-imino gold carbenes have been developed, including isoxazoles,[1] anthranils,[2] 2*H*-azirines,[3] *N*-iminopyridium ylides[4] and triazapentalene,[5] *et al*. Among them, isoxazoles and anthranils were two significant kinds of nucleophilic reagents since they could react with ynamides or propiolates to trigger efficient cycloaddition reactions. For example, Ye[1a] and Liu[1b] *et al* reported various catalytic annulations between isoxazoles and ynamides/propiolates to afford 4-carbonly-2-aminopyrroles or 2,4-dicarbonylpyrroles via [3+2] or [4+1] annulations, respectively (Scheme 1, eq 1). Hashmi[2a] and Liu[2b] *et al* found that anthranils could also cycloisomerize with ynamides/propiolates via [3+2] or [4+2] cycloaddition reactions (Scheme 1, eq 2). Of particular note is that isoxazoles and anthranils usually serve as three-atom or four-atom synthons in these reactions, affording the corresponding five- or six-membered nitrogen heterocycles. However, substrates which could act as more than four-atom building blocks in the cycloaddition reactions have rarely been reported.[6]

Benzo[*d*]isoxazoles are easily available heterocyclic substrates, which have been applied in a number of metal-catalyzed transformation reactions,[7] such as the

Rh-catalyzed [4+2] annulations with alkynes[7a] and Lewis acid-catalyzed [4+2] annulations with propargylic alcohols.[7b] However, to the best of our knowledge, benzo[*d*]isoxazoles have not been studied in gold-catalyzed reactions. We recently found that 1,4,2-dioxazoles[8a] and 4,5-dihydro-1,2,4-oxadiazoles[8b] could be used as three-atom synthons to oxazoles and imidazoles. As our continuous interests in oxazole chemistry, herein, we report our success on gold-catalyzed cyclization of benzo[*d*]isoxazoles and ynamides, which provided an efficient and controllable synthesis of 2*H*-benzo[*e*][1,3]oxazines or benzo[*f*][1,4]oxazepines through [5+1] or [5+2] cycloaddition reactions. Remarkably, a novel 1,2-amino migration[9] of the ynamide substrate was observed during the [5+1] process. During the preparation of this paper, a gold-catalyzed cycloaddition reaction of ynamides and 1,2-benzisoxazoles without substituents on the isoxazole ring was reported by Liu's group.[10] Compared with their work, our method accomodates with diversely benzo[*d*]isoxazoles bearing substituents on the isoxazole ring, and proceeds with generally higher chemoselectivity in the course of [5+1] annulation. Furthermore, we found that these substrates could also trap gold-carbene intermediates derived from propargyl esters,[11] leading to [5+1] cycloaddition products.

Scheme 1. Gold-catalyzed cycloaddition reactions with isoxazoles, anthranils and benzo[*d*]isoxazoles



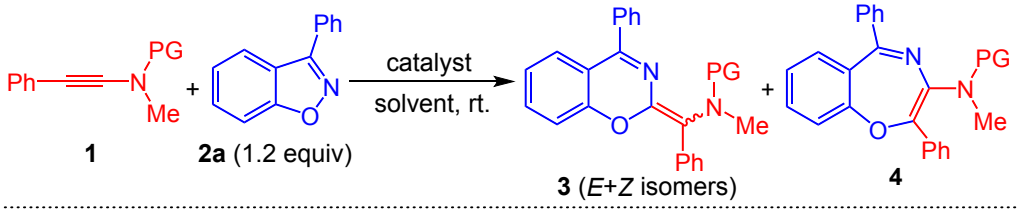
RESULTS AND DISCUSSION

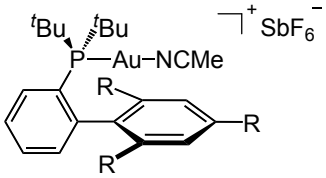
To test the feasibility of our hypothesis, we initially investigated the cyclization reaction of 3-phenylbenzo[*d*]isoxazole **2a** with ynamide **1a** bearing a *p*-methoxyphenylsulfonyl protecting group. To our delight, the use of common gold catalysts such as PPh_3AuNTf_2 and PPh_3AuSbF_6 formed *in situ* afforded 2*H*-benzo[*e*][1,3]oxazine **3a** in 75-79% yields as

a mixture of *E*/*Z* isomers (*E*/*Z* = 3.9:1-4:1), along with seven-membered heterocycle benzo[*f*][1,4]oxazepine **4a** in 13-14% yields (Table 1, entries 1-2). Apparently, benzo[*d*]isoxazole **2a** was served as distinctive five-atom synthons in this reaction to deliver the products **3** or **4** via [5+1] or [5+2] annulations, respectively. Interestingly, a 1,2-amino group migration[9,10] was also observed in the formation of product **3**. Considering the steric and electronic effects of ligands could influence the reaction greatly, we then chose JohnphosAu(MeCN)SbF_6 (catalyst **A**) as the catalyst. It was found that **3a** could be formed in 93% yield (*E*/*Z* = 7.5:1) within 6 h (Table 1, entry 3). Under this condition, **4a** was formed in only 3% yield. When gold catalyst **B** with a bulky ^{t}BuXphos as the ligand was used, the reaction was suppressed greatly, affording *E*-**3a** in 15% yield after 24 h (Table 1, entry 4). When *N*-heterocyclic carbene gold(I) complex **C** was employed as the catalyst, the yield of **3a** was increased to 91%, along with **4a** in 3% yield (Table 1, entry 5). The reaction also proceeded smoothly in various solvents like THF, DCM, MeCN and toluene, with the yields of **3a** in the range of 55-87% and **4a** in < 6% yields (Table 1, entries 6-9). The catalytic activity of gold(III) complex such as pyridine-ligated $AuCl_3$ was also tested and only 14% yield of **4a** was obtained (Table 1, entry 10). When $PicAuCl_2$ (catalyst **E**) was used as the catalyst at 50 ^{o}C, the yield of **4a** could be increased to 58% without the formation of **3a** (Table 1, entry 11). Switching the catalyst to simple gold(III) salt of $AuBr_3$ gave **3a** in a higher yield of 66% (Table 1, entry 12). We fould that substrate **1a** could slowly decompose in the presence of $AuBr_3$. To improve the yield of **4a**, 2.0 equiv of **2a** was added under the dilute reaction conditions (0.033 M). However, the yield of **4a** was improved slightly (Table 1,

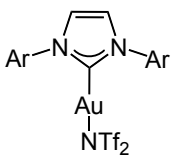
entry 13). After turning the ratio of **1a**: **2a** to 1.2: 1, the yield of **4a** could be increased to 79% (Table 1, entry 14). Employing $AgSbF_6$ alone or Brønsted acid of $HNTf_2$ as the catalyst did not afford desired products, with recovered **1a** in 99% and 45% yields, respectively (Table 1, entries 15-16). The reaction could not proceed without any catalyst, even at 50 ^oC for 24 h (Table 1, entry 17). Then the effects of the protecting groups on nitrogen were examined. In the presence of catalyst **A**, mesyl-protected substrate **1b** and tosyl-protected substrate **1c** gave the corresponding product **3b** and **3c** in 82% and 92% yields, respectively (Table 1, entries 18-19). In addition, when substrate **1c** was tested under the catalysis of $AuBr_3$, **4c** could be isolated in 80% yield (Table 1, entry 20). After careful separation of isomers through recrystallization or column chromatography, the structure of benzo[*e*][1,3]oxazines **3** was confirmed by X-ray crystallographic analyses of the analogous products of *E*-**3b**, *Z*-**3i**, *E*-**3m**, *Z*-**3m**, *E*-**3r**, and product **4** was also confirmed by X-ray crystallographic analysis of **4a**.[12]

Table 1. Optimization of the Reaction Conditions

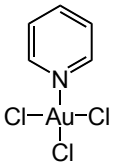




A: R = H
B: R = ^{i}Pr



C: Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$



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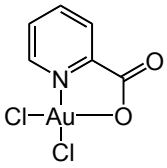


E

entry	PG	catalyst (mol %)	solvent	time(h)	yields (%)[a] **3** (*E*:*Z*)	**4**	**1a**
1	SO_2PMP (**1a**)	PPh_3AuNTf_2 (5)	DCE	3	75 (4:1)	13	-
2	**1a**	$PPh_3AuCl/AgSbF_6$ (5)	DCE	8	79 (3.9:1)	14	-
3	**1a**	**A** (5)	DCE	6	93 (7.5:1)	3	-
4	**1a**	**B** (5)	DCE	24	15 (1:0)	-	60
5	**1a**	**C** (5)	DCE	3.5	91 (5.1:1)	3	-
6	**1a**	**A** (5)	THF	5	55 (8.2:1)	-	-
7	**1a**	**A** (5)	DCM	9	87 (8.7:1)	4	-
8	**1a**	**A** (5)	MeCN	24	77 (6:1)	6	-
9	**1a**	**A** (5)	toluene	11	70 (6:1)	-	-
10	**1a**	**D** (5)	DCE	24	-	14	72
11[b]	**1a**	**E** (5)	DCE	3	-	58	-
12	**1a**	$AuBr_3$ (5)	DCE	1	-	66	-
13[c]	**1a**	$AuBr_3$ (5)	DCE	1	-	70	-
14[d]	**1a**	$AuBr_3$ (5)	DCE	1	-	79	-
15	**1a**	$AgSbF_6$ (10)	DCE	24	-	-	99
16	**1a**	$HNTf_2$ (10)	DCE	24	-	-	45
17[b]	**1a**	none	DCE	24	-	-	99
18	Ms (**1b**)	**A** (5)	DCE	6	82 (6.5:1)	-	-
19	**Ts (1c)**	**A (5)**	**DCE**	**6**	**92 (7.7:1)[e]**	**-**	**-**
20[d]	**Ts (1c)**	**$AuBr_3$ (5)**	**DCE**	**1**	**-**	**80[e]**	**-**

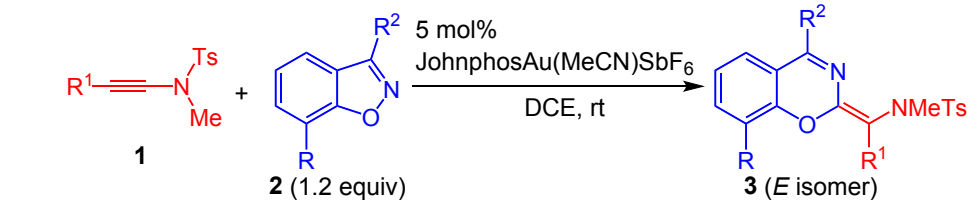
[a]All the reactions were carried out on 0.3 mmol scale (0.1 M). PMP = *p*-methoxyphenyl. ^{1}H NMR yields using 1,3,5-trimethoxybenzene as an internal standard. [b]50 °C. [c]0.033 M in DCE. 2.0 equiv of **2a** was used. [d]0.033 M in DCE.1.2 equiv of **1a** and 1.0 equiv of **2a** were used. [e]Isolated yields.

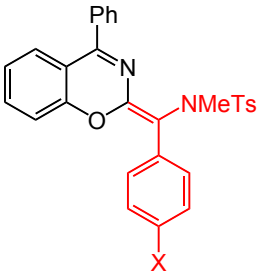
With optimized reaction conditions established (Table 1, entry 19), we first paid our attention to investigate the substrate scope of [5+1] cycloaddition reactions (Scheme 2).

The scope of ynamides with the aryl substituents on R^1 group was first studied. Electron-donating groups such as *p*-methyl and *p*-methoxy on the aryl ring gave **3d** and **3e** in lower yields of 63-67%, along with the formation of **4** in 20-25% yields. The results indicated that the chemoselectivity was decreased between [5+1] and [5+2] cycloaddition mode in these cases. Electron-withdrawing groups such as *p*-F, *p*-Cl and *p*-CO_2Et on the aryl ring tolerated well in the reaction, giving **3f-3h** in 49-93% yields. Heteroaryl-substituted ynamides such as 2-thienyl-containing substrate reacted efficiently to furnish **3i** in 78% yield. According to the above results, it was noted that the stereoselectivity was decreased (**3d**) or opposite (**3e** and **3i**) when ynamides bearing electron-rich aryl groups were employed as the substrates. Besides, ynamide with an 1,3,5(10)-estratrien-3-ol-17-one derivative was also compatible, giving **3j** in a yield of 65%. The reaction can be extended to alkyl-substituted ynamides such as cyclopropyl-substituted **1k**, with the formation of **3k** in an excellent yield of 95%. Subsequently, we investigated the scope of benzo[*d*]isoxazoles using **1c** as the reaction partner. It was found that both electron-donating groups (*p*-OMe) and electron-withdrawing groups (*p*-Cl) on aryl ring were suitable for this reaction, leading to **3l** and **3m** in high yields. Sterically encumbered *o*-OMe substituted aryl benzo[*d*]isoxazole reacted efficiently to afford **3n** in 94% yield. Alkyl-substituted benzo[*d*]isoxazoles with methyl or 2-phenethyl groups turned out to be perfect substrates, giving **3o** and **3p** in yields of 91% and 85%, respectively. In addition, when the R^2 substituent is a methoxy group, **3q** could be formed in 88% yield. The parent phenyl ring substituted with a methyl group was also suitable for this transformation, furnishing the single isomer *E*-**3r** in 87% yield. This

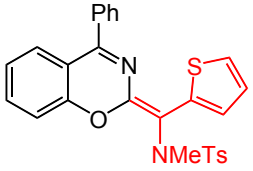
result indicated that the steric effect of the methyl group may also have great influence on the double bond configuration of the products. When R^2 is a hydrogen, a mixture of inseparatable compounds of **3s** (60%) and **4q** (23%) were obtained, indicating that the chemoselectivity was not good in this case.[13]

Scheme 2. Scope of Gold-Catalyzed [5+1] Annulations with Ynamides

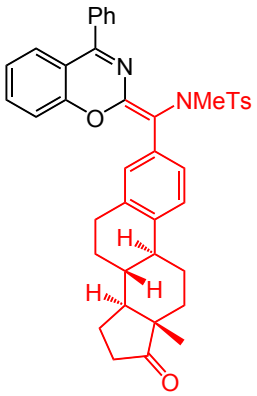




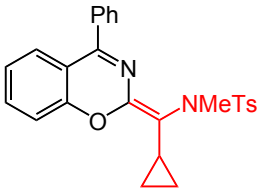
3c, X = H, 6 h, 92%, *E*/*Z* = 7.7:1
3d, X = Me, 7 h, 67%, *E*/*Z* = 3.7:1[b]
3e, X = OMe, 7 h, 63%, *E*/*Z* = 0.74:1[c]
3f, X = F, 5.5 h, 89%, *E*/*Z* = 9.1:1
3g, X = Cl, 9 h, 93%, *E*/*Z* = 10:1
3h, X = CO_2Et, 30 h, 49%, *E*/*Z* = 6.7:1[d]



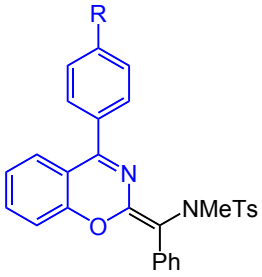
3i, 1 h, 78%, *E*/*Z* = 0.1:1



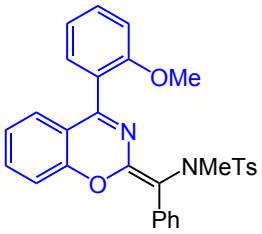
3j, 6 h, 65%, *E*/*Z* = 2.1:1



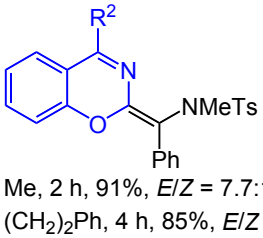
3k, 1 h, 95%, *E*/*Z* = 1.54:1



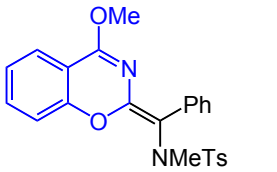
3l, R = OMe, 5 h, 86%, *E*/*Z* = 11.1:1
3m, R = Cl, 5 h, 91%, *E*/*Z* = 7.7:1



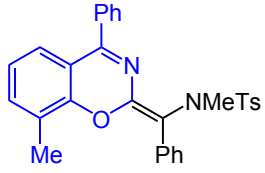
3n, 8 h, 94%, *E*/*Z* = 12.5:1



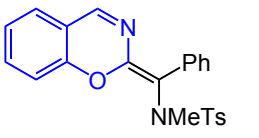
3o, R^2 = Me, 2 h, 91%, *E*/*Z* = 7.7:1[e]
3p, R^2 = $(CH_2)_2Ph$, 4 h, 85%, *E*/*Z* = 9.1:1[e]



3q, 3.5 h, 88%, *E*/*Z* = 0.38:1



3r, 9 h, 87%, *E*/*Z* = 1:0

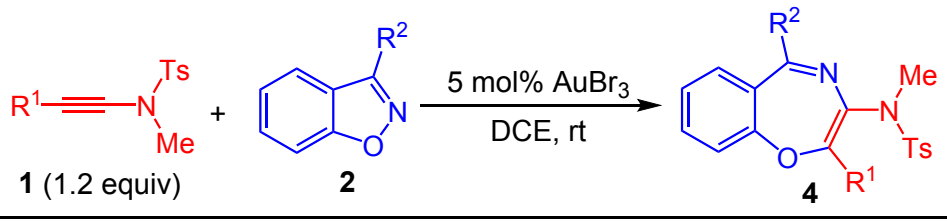


3s, 4 h, 60%, *E*/*Z* = 0.79:1[f]

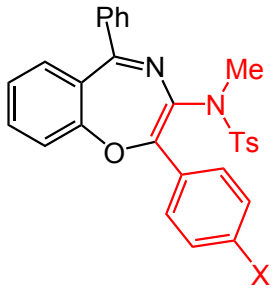
[a]Only the structure of the major isomer was shown in most cases. [b]**4d** was also isolated in 20% yield. [c]**4e** was also isolated in 25% yield. [d]7.5 mol% $IPrAuNTf_2$ was used as the catalyst. [e]2.0 equiv **2** was used. [f]As a mixture of **3s** and **4q** (23%).

Next, the scope of [5+2] cycloaddition reaction was tested by using 5 mol% $AuBr_3$ as the catalyst in DCE at room temperature (Scheme 3). We first examined the electronic effect of R^1 substituents on ynamides. Substrates bearing both electron-donating groups (*p*-Me and *p*-OMe) and electron-withdrawing groups (*p*-F, *p*-Cl and *p*-CO_2Et) on the aryl ring were compatible in the reactions, furnishing **4d**-**4h** in 63-82% yields. In the case of 2-thienyl-substituted ynamides, **4i** could be formed in 57% yield, along with the formation of *Z*-**3i** in 14% yield. Ynamide with an 1,3,5(10)-estratrien-3-ol-17-one derivative or formononetin moiety also reacted efficiently (**4j** and **4k**). Then the effect of R^2 substituents on benzo[*d*]isoxazoles were examined. Substrates bearing *p*-OMe, *p*-Cl and *o*-OMe groups on the aryl ring resulted in **4l**-**4n** in 68-77% yields. Benzo[*d*]isoxazoles with alkyl substituents such as methyl and 2-phenethyl on R^2 group could also react with **1c** smoothly (**4o** and **4p**). When the R^2 substituent is a hydrogen group, the chemoselectivity was decreased, affording a mixture of **3s** (35%) and **4q** (47%).[14]

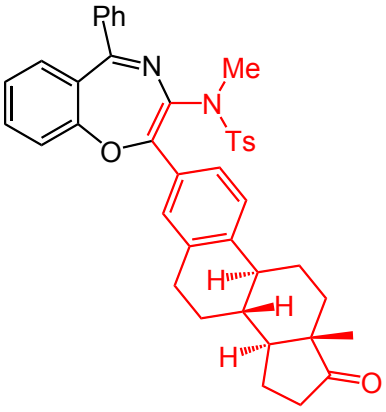
Scheme 3. Scope of Gold-Catalyzed [5+2] Annulations with Ynamides



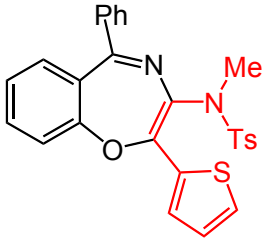
1 (1.2 equiv) **2** **4**



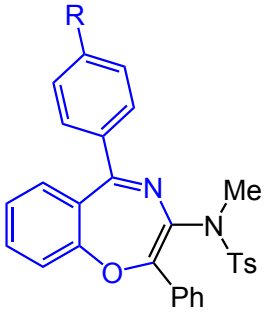
4c, X = H, 1 h, 80%
4d, X = Me, 1 h, 80%
4e, X = OMe, 1 h, 63%
4f, X = F, 1 h, 82%
4g, X = Cl, 1 h, 81%
4h, X = CO_2Et, 1 h, 73%



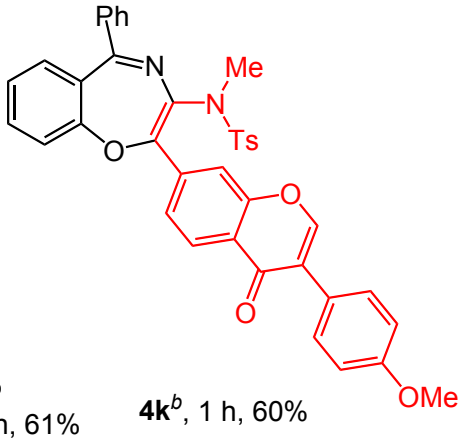
4j, 1.5 h, 65%



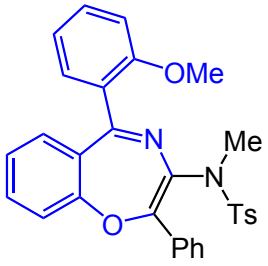
4i, 1.5 h, 57%[a]



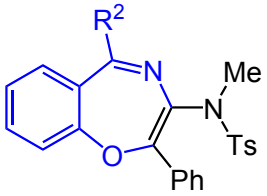
4l, R = OMe, 1 h, 74%
4m, R = Cl, 1 h, 77%



4k[b], 1 h, 60%



4n, 1 h, 68%



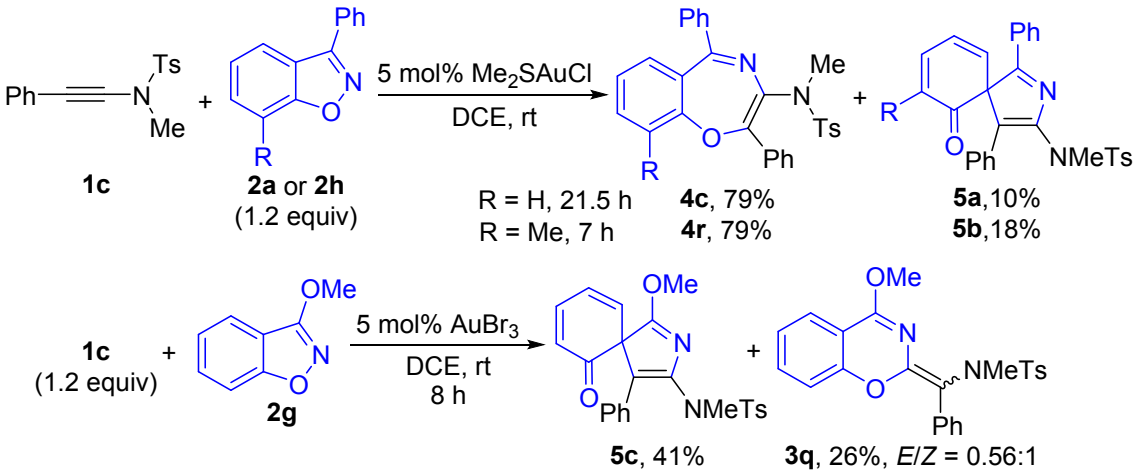
4o[b], R^2 = Me, 2 h, 61%
4p[b], R^2 = $(CH_2)_2Ph$, 2 h, 61%
4q, R^2 = H, 1 h, 47%[c]

[a]*Z*-**3i** was also isolated in 14% yield. [b]1.0 equiv of **1** and 2.0 equiv of **2** were used. [c]As a mixture of **3s** (35%, *E*/*Z* = 0.33:1) and **4q**.

Interestingly, when Me_2SAuCl was used as the catalyst in the reaction of ynamide **1c** with benzo[*d*]isoxazole **2a** or **2h**, benzo[*f*][1,4]oxazepine **4c** or **4r** could be obtained in the same yield of 79%, along with the formation of the unexpected spiro products **5** in 10-18% yields (Scheme 4). The results indicated that the use of less hindered gold catalyst favoured the formation of seven-membered products **4**. The yield of **5** could be increased to 41% by

using methoxy-substituted **2g** as the reaction partner under the catalysis of $AuBr_3$, which indicated that the electronic effect of the substrates played an important role in the formation of the spiro product. The structure of spiro product was confirmed by X-ray crystallographic analysis of **5b**.

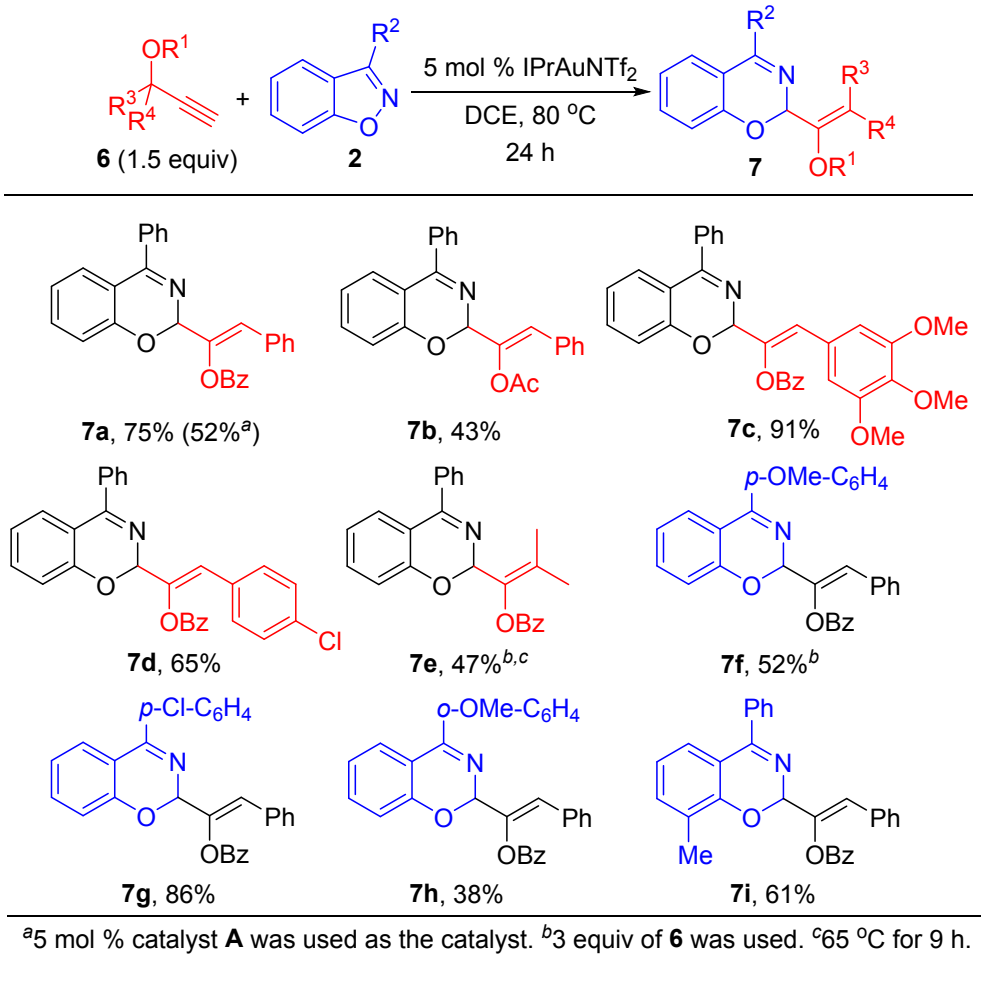
Scheme 4. Formation of Spiro Products



In order to extend the application scope of this reaction, propargyl esters were used as the reaction partner instead of ynamides (Scheme 5). It was found that benzo[*e*][1,3]oxazine analogues **7** were formed through an entirely different pathway. We found that benzoyl-protected substrate **6a** could react with benzo[*d*]isoxazole **2a** to form **7a** in 52% yield by using 5 mol% JohnphosAu(MeCN)SbF_6 (catalyst **A**) in DCE at 80 °C for 24 h. After a brief screening on reaction conditions, it was found that the use of IPrAuNTf_2 could increase the yield of **7a** to 75%. Changing the protecting group to acetyl group decreased the yield of **7b** to 43%. Propargyl esters bearing substituted aryl groups were compatible (**7c** and **7d**), while dimethyl-substituted **6e** resulted in **7e** in a lower yield of

47%. For aryl-substituted benzo[*d*]isoxazoles, the corresponding products **7f-7i** were formed in 38-86% yields. The structure of **7c** was confirmed by X-ray crystallographic analysis.

Scheme 5. Scope of Gold-Catalyzed [5+1] Annulations with Propargyl Esters

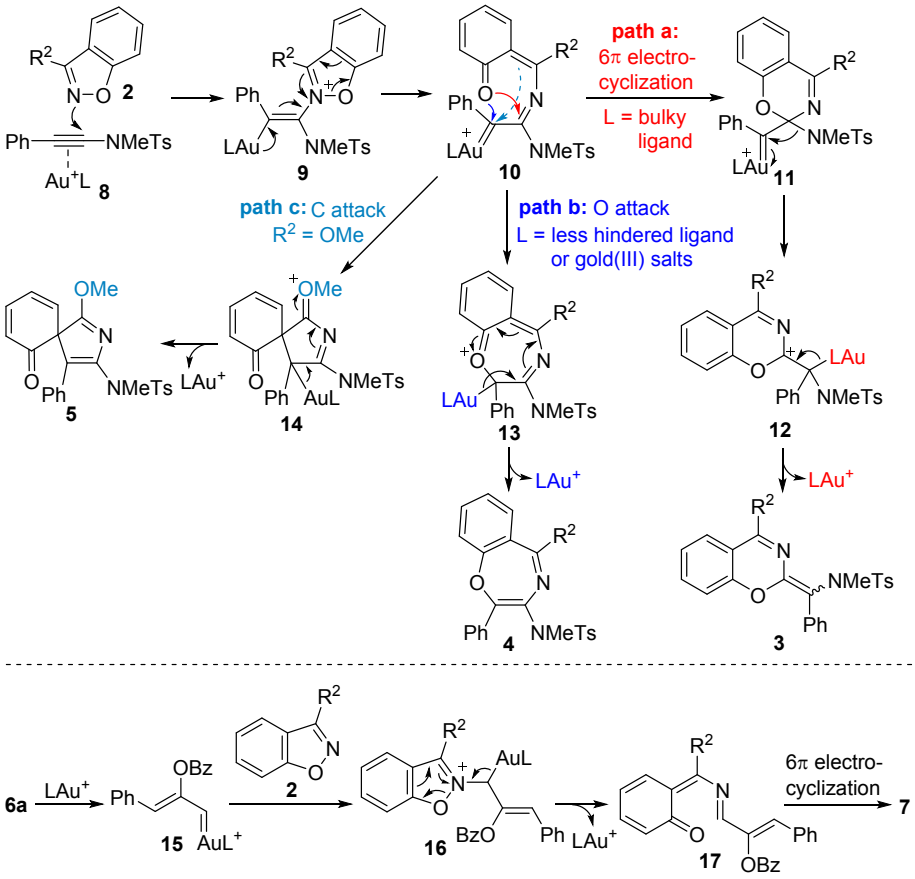


[a]5 mol % catalyst **A** was used as the catalyst. [b]3 equiv of **6** was used. [c]65 °C for 9 h.

On the basis of the above results and our previous work, a possible reaction mechanism is given in Scheme 6. Attack of the imino nitrogen to ynamide activated by gold affords vinyl gold intermediate **9,** which fragmentizes into the α-imino gold- carbene **10**. Then there are three possible pathways: In path a, with a bulky ligand, **11** is formed through 6π

electrocyclization. 1,2-amino group migration followed by elimination of the catalyst affords the products **3**. In path b, O-attack to gold-carbene occurs to furnish intermediate **13**. This is followed by elimination of the gold catalyst to give the product **4**. It is suggested that the O-attack process could be facilitated through the decrease of the steric interaction between the gold-carbene and the carbonyl group caused by the less hindered ligand on gold or increasing the electrophilic reactivity of gold-carbene by the use of gold(III) salts with stronger Lewis acidity. In path c, C-attack to the carbene center occurs due to the nucleophilicity of the exocyclic double bond, especially when OMe-substituted benzo[*d*]isoxazole **2g** is used. Elimination of the gold catalyst gives the spiro product **5** (Scheme 6). When propargyl esters are used as the substrates, gold-carbene intermediate **15** is generated through 1,2-acyloxy migration.[11] This is followed by the nucleophilic attack of nitrogen on benzo[*d*]isoxazole to deliver intermediate **16**. Elimination of the gold catalyst followed by 6π electrocyclization affords the products **7** (Scheme 6).

Scheme 6. Possible Reaction Mechanism



CONCLUSION

In summary, we have disclosed that benzo[*d*]isoxazoles can be used as novel substrates to undergo gold-catalyzed [5+1] or [5+2] cycloaddition reactions with ynamides. The reaction provides a concise and chemoselective access to polysubstituted 2*H*-benzo[*e*][1,3]oxazines or benzo[*f*][1,4]oxazepines. Interestingly, a novel 1,2-amino group migration is observed during the [5+1] process. In addition, benzo[*d*]isoxazoles can also react with gold-carbene intermediates derived from propargyl esters to afford [5+1] annulation products. Further extensions of the reactions with benzo[*d*]isoxazoles are currently underway in our laboratory.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under Argon unless noted. DCM, DCE were distilled from CaH_2. Toluene was distilled from sodium and benzophenone. THF was distilled from sodium and benzophenone or purified using Innovative Technology Solvent Purifier (for the synthesis of substrates). MeCN was purified using Innovative Technology Solvent Purifier. Unless noted, all commercial reagents were used without further purification. (Acetonitrile)[(2-biphenyl)di-*tert*-butylphosphine]gold(I) hexafluoroantimonate (catalyst **A**), Gold complex **D** and $AgSbF_6$ were purchased from Stream Chemicals. Gold complexe **B** was prepared by stirring the [Au(L)Cl] complex and $AgSbF_6$ in MeCN at room temperature overnight.[15] Gold complex **C**,[16] PPh_3AuCl[17] and PPh_3AuNTf_2[18] were prepared according to the published methods. $PicAuCl_2$ (catalyst **E**) and $HNTf_2$ were purchased from Aldrich Chemical Company. $AuBr_3$ was purchased from Alfa Aesar. Beznzo[*d*]isoxazole **2i** was purchased from Tokyo Chemical Industry and further purified by column chromatography on silica gel before use.

^1H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ (containing 0.03% TMS) or $CDCl_3$ (containing 0.03% TMS), on Varian XL-400 MHz spectrometer, Agilent 400 MHz NMR spectrometer or Bruker 400 MHz NMR spectrometer. ^1H NMR spectra was recorded at 400 MHz, ^{13}C NMR spectra was recorded at 100 MHz. ^1H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference in $CDCl_3$; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. High-resolution mass spectra were obtained by using Agilent Technologies 5973N. Elemental analyses were performed on an Italian Carlo-Erba 1106 analyzer. IR spectra

were obtained by using a Nicolet iS10 spectrometer. Melting points were measured using a SGW-4 microscopic melting point apparatus and were uncorrected. Single crystal X-ray diffraction data were collected at 296(2) K for *E*-**3b**, *E*-**3m**, **4a**, **7c** and 173(2) for Z-**3i**, *Z*-**3m**, *E*-**3r**, **5b** on a Bruker APEX-II diffractometer or Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å).

Ynamides **1** were synthesized according to published methods.[16]

For the characterization of new ynamide substrates, see following:

Ethyl 4-(((*N*,4-dimethylphenyl)sulfonamido)ethynyl)benzoate (1h). 3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a white solid in 86% (925.3 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.40-7.27 (m, 4H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.18 (s, 3H), 2.46 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.0, 145.0, 133.1, 130.6, 129.9, 129.4, 129.1, 127.7, 127.5, 87.0, 69.0, 61.0, 39.1, 21.6, 14.2. IR (neat): 2979, 2945, 2901, 2228, 1712, 1604, 1359, 1164 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{19}H_{20}NO_4S$ $[M+H]^+$: 358.1108, found 358.1102.

Synthesis of 1j.

To a solution of 1,3,5(10)-estratrien-3-ol-17-one (5.407 g, 20 mmol) in DCM (80 mL) was added pyridine (3.2 mL, 40 mmol). Then Tf_2O (4.0 mL, 24 mmol, diluted with 40 mL DCM) was added dropwise to the mixture at 0 °C. The resulting solution was warmed up

to room temperature and stirred for 3 h. Then the mixture was quenched with saturated ammonium chloride solution, extracted with dichloromethane, and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) to afford (8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl trifluoromethanesulfonate (**s1-1j**) in 94% yield (7.535 g) as a white solid.

To a solution of the above **s1-1j** (7.445 g, 18.5 mmol) in triethylamine (16 mL) and DMF (40 mL) were added ethynyltrimethylsilane (2.18 g, 22.2 mmol) and $Pd(PPh_3)_2Cl_2$ (779.1 mg, 1.11 mmol) at room temperature. Then the mixture was stirred at 50 ^oC for 5 h. After the starting material was consumed, the reaction mixture was quenched with 3 N HCl solution, extracted with dichloromethane, washed with water and brine followed by drying over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 8:1 to 5:1) to afford compound (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((trimethylsilyl)ethynyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**s2-1j**) (4.9 g, 76%) as a yellow solid.

To a solution of the above **s2-1j** (4.9 g, 14 mmol) in THF (45 mL) was added TBAF (15.4 mL, 1M in THF, 15.4 mmol) at 0 ^oC. The resulting solution was warmed up to room temperature and stirred for 1 h. Then the mixture was quenched with water, extracted with dichloromethane, and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by chromatography on silica gel (eluent:

petroleum ether: ethyl acetate: dichloromethane = 10:1:1) to afford (8*R*,9*S*,13*S*,14*S*)-3-ethynyl-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**s3-1j**) in 46% yield (1.792 g) as a white solid.

To a solution of **s3-1j** (1.058 g, 3.8 mmol) in acetone (20 mL) were added *N*-bromosuccinimide (811.6 mg, 4.56 mmol) and $AgNO_3$ (32.3 mg, 0.19 mmol) at room temperature. The mixture was stirred at the same temperature for 12 h. The reaction mixture was diluted with hexane and filtered through a pad of celite using dichloromethane as an eluent. The filtrate was collected and evaporated under the reduced pressure, the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate/dichloromethane = 5:1:1) to afford compound (8*R*,9*S*,13*S*,14*S*)-3-(bromoethynyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**s4-1j**) (1.053 g, 78%) as a white solid.

To a dry flask were added *N,4*-dimethylbenzenesulfonamide (222.3 mg, 1.2 mmol), anhydrous toluene (10 mL), $CuSO_4 \cdot 5H_2O$ (25.0 mg, 0.1 mmol), 1,10-phenanthroline (36.0 mg, 0.2 mmol) and K_2CO_3 (276.4 mg, 2 mmol). Then **s4-1j** (357.3 mg, 1 mmol) was added, and the resulting mixture was stirred at 80 °C for 48 h under an atmosphere of argon. When the reaction was complete, the crude mixture was cooled down to room temperature, filtered through celite and washed with ethyl acetate. After solvent evaporation, the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:1:1) to afford compound **1j** (323.4 mg, 70%) as a white solid.

_N_,4-Dimethyl-_N_-(((8_R_,9_S_,13_S_,14_S_)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6_H_-cyclopenta[_a_]phenanthren-3-yl)ethynyl)benzenesulfonamide (1j). M.p. 177-179 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.22-7.20 (m, 1H), 7.15-7.12 (m, 2H), 3.13 (s, 3H), 2.89-2.86 (m, 2H), 2.54-2.38 (m, 5H), 2.30-2.26 (m, 1H), 2.19-1.95 (m, 4H), 1.66-1.38 (m, 6H), 0.91 (s, 3H).; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 220.7, 144.7, 139.8, 136.5, 133.1, 131.9, 129.7, 128.7, 127.8, 125.2, 119.8, 83.2, 68.8, 50.3, 47.8, 44.3, 39.3, 37.9, 35.7, 31.4, 29.0, 26.2, 25.5, 21.6, 21.5, 13.7. IR (neat): 2961, 2932, 2875, 2236, 1731, 1597, 1456, 1365, 1168, 721 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{28}H_{32}NO_3S$ $[M+H]^+$: 462.2097, found 462.2096.

Synthesis of 1l.

To a solution of 7-hydroxy-3-(4-methoxyphenyl)-4*H*-chromen-4-one (4.292 g, 16 mmol) in DCM (60 mL) was added pyridine (2.6 mL, 32 mmol). Then Tf_2O (3.2 mL, 19.2 mmol, diluted with 30 mL DCM) was added dropwise to the mixture at 0 °C. The resulting solution was warmed up to room temperature and stirred for 1 h. Then the mixture was quenched with saturated ammonium chloride solution, extracted with dichloromethane, washed with saturated $CuSO_4$ solution, brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: dichloromethane = 1:1) to afford 3-(4-methoxyphenyl)-4-oxo-4*H*-chromen-7-yl trifluoromethanesulfonate (**s2-1l**) which was directly used in the following reaction.

To a solution of the above **s2-1l** in triethylamine (16 mL) and DMF (40 mL) were

added ethynyltrimethylsilane (1.886 g, 19.2 mmol) and $Pd(PPh_3)_2Cl_2$ (673.8 mg, 0.96 mmol) at room temperature under Agron. Then the mixture was stirred at 50 °C for 3.5 h. After the starting material was consumed, the reaction mixture was quenched with 3 N HCl solution, extracted with dichloromethane, washed with water and brine followed by drying over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:1:1) to afford compound 3-(4-methoxyphenyl)-7-((trimethylsilyl)ethynyl)-4*H*-chromen-4-one (**s3-1l**) which was directly used in the following reaction.

To a solution of the above **s3-1l** in MeOH (100 mL) was added K_2CO_3 (663.4 mg, 4.8 mmol) at room temperature and stirred for 2 h. Then the mixture was quenched with water and MeOH was evaporated under the reduced pressure. The residue was extracted with dichloromethane, washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by chromatography on silica gel (eluent: petroleum ether: dichloromethane = 2:1) to afford 7-ethynyl-3-(4-methoxyphenyl)-4*H*-chromen-4-one (**s4-1l**) in 38% (3 steps) yield (1.68 g) as a white solid.

To a solution of **s4-1l** (663.1 mg, 2.4 mmol) in acetone (15 mL) were added *N*-bromosuccinimide (469.9 mg, 2.64 mmol) and $AgNO_3$ (40.8 mg, 0.24 mmol) at room temperature. The mixture was stirred at the same temperature for 8 h. The solution was evaporated under the reduced pressure and the residue was quenched with saturated NH_4Cl solution, extracted with dichloromethane, washed with brine and dried over anhydrous

Na_2SO_4. The solution was evaporated under the reduced pressure and the residue was filtered through a pad of silica gel. The crude product 7-(bromoethynyl)-3-(4-methoxyphenyl)-4*H*-chromen-4-one (**s5-1l*)*** was used directly without further purification.

To a dry flask were added *N,4*-dimethylbenzenesulfonamide (533.5 mg, 2.88 mmol), anhydrous toluene (20 mL), $CuSO_4 \cdot 5H_2O$ (59.9 mg, 0.24 mmol), 1,10-phenanthroline (86.5 mg, 0.48 mmol) and K_2CO_3 (663.4 mg, 4.8 mmol). Then **s5-1l** was added, and the resulting mixture was stirred at 80 °C for 14 h under an atmosphere of argon. When the reaction was complete, the crude mixture was cooled down to room temperature, filtered through celite and washed with ethyl acetate. The mixture was washed with 10% NaOH solution, brine and dried over anhydrous Na_2SO_4. After solvent evaporation, the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:1:1 to dichloromethane) to afford compound **1l** (522.7 mg, 47% for 2 steps) as a light yellow solid.

***N*-((3-(4-Methoxyphenyl)-4-oxo-4*H*-chromen-7-yl)ethynyl)-*N*,4-dimethylbenzenesulfonamide (1l).** M.p. 158-160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.95 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.40-7.38 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 3.82 (s, 3H), 3.19 (s, 3H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.6, 159.5, 155.7, 152.4, 145.1, 132.9, 129.9, 128.3, 127.6, 127.2, 126.1, 124.9, 123.7, 123.1, 119.4, 113.8, 88.0, 68.6, 55.1, 39.0, 21.5. IR (neat): 3066, 2937, 2841, 2239, 1637, 1619, 1358, 1165 cm^{-1}. HRMS (ESI-TOF) calcd for

$C_{26}H_{22}NO_5S$ $[M+H]^+$: 460.1213, found 460.1210.

General procedure for the synthesis of benzo[*d*]isoxazoles 2.

Method A : For 2a-2d[19]

Typical procedure for the synthesis of 3-phenylbenzo[*d*]isoxazole 2a.

To a solution of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (2.984 g, 10 mmol) in MeCN (60 mL) was added CsF (4.56 g, 30 mmol). Then *N*-hydroxybenzimidoyl chloride (777.9 mg, 5 mmol) in MeCN (60 mL) was added slowly to the reaction mixture at room temperature within 4 h and stirred for another 2 h. After the reaction was completed, the solvent was evaporated under the reduced pressure and the residue was quenched with brine, extracted with dichloromethane, washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 40:1) to obtain a light yellow solid. The product was washed with a small amount of pentane to afford **2a** (630.7 mg, 65%) as a white solid. This compound can also be synthesized by method B.

Method B : For 2e, 2f, 2h[20]

Typical procedure for the synthesis of 3-methylbenzo[*d*]isoxazole 2e.

To a solution of NH_3 in MeOH (7 mL, 7 M) was added 1-(2-hydroxyphenyl)ethan-1-one (1.362 g, 10 mmol) and stirred at room temperature for 2 h. Then MeOH was evaporated under the reduced pressure to afford a yellow solid.

Subsequently, to a solution of the above product in THF (30 mL) was added *N*-chlorosuccinimide (2.003 g, 15 mmol) and K_2CO_3 (2.764 g, 20 mmol) and stirred at room temperature for 15 h. The mixture was quenched with H_2O, extracted with ethyl acetate, washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 100:1) to afford **2e** (487.2 mg, 37%) as light yellow oil.

3-Phenylbenzo[*d*]isoxazole (2a). Method A was used. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.64-7.52 (m, 5H), 7.38-7.34 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.8, 157.2, 130.2, 129.7, 129.1, 128.9, 128.0, 123.8, 122.1, 120.4, 110.1. The spectroscopic data is in agreement with that previously reported.[21]

3-(4-Methoxyphenyl)benzo[*d*]isoxazole (2b). Method A was used. 4 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 40:1) followed by washing with pentane afforded the title product in 73% yield (660.5 mg) as a white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.89 (m, 3H), 7.63-7.54 (m, 2H), 7.37-7.33 (m, 1H), 7.08-7.05 (m, 2H), 3.87 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.6, 161.1, 156.7, 129.6, 129.3, 123.6, 122.2, 121.2, 120.5, 114.5, 110.0, 55.3. The spectroscopic data is in agreement with that previously reported.[21]

3-(4-Chlorophenyl)benzo[*d*]isoxazole (2c). Method A was used. 4 mmol scale. Column

chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) followed by washing with pentane afforded the title product in 53% yield (484.5 mg) as a light yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.86 (m, 3H), 7.65-7.57 (m, 2H), 7.53-7.51 (m, 2H), 7.39-7.35 (m, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.8, 156.2, 136.3, 129.9, 129.4, 129.2, 127.3, 124.0, 121.8, 120.1, 110.2. The spectroscopic data is in agreement with that previously reported.[22]

3-(2-Methoxyphenyl)benzo[*d*]isoxazole (2d). Method A was used. 4 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 85% yield (761.7 mg) as light yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.62 (m, 2H), 7.57-7.55 (m, 1H), 7.50-7.43 (m, 2H), 7.25 (t, J = 7.6 Hz, 1H), 7.08-7.01 (m, 2H), 3.78 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.0, 157.2, 156.3, 131.5, 131.0, 129.3, 123.3, 123.0, 121.6, 120.7, 117.3, 111.2, 109.5, 55.2. The spectroscopic data is in agreement with that previously reported.[21]

3-Methylbenzo[*d*]isoxazole (2e). Method B was used. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 1H), 7.54-7.51 (m, 2H), 7.32-7.27 (m, 1H), 2.58 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.7, 154.9, 129.6, 123.1, 122.1, 121.1, 109.7, 10.0. The spectroscopic data is in agreement with that previously reported.[23]

3-Phenethylbenzo[*d*]isoxazole (2f). Method B was used. 5 mmol scale. Column chromatography on basic aluminum oxide (eluent: petroleum ether: ethyl acetate = 20:1 to

5:1) afforded the title product in 55% yield (613.3 mg) as colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.47 (m, 3H), 7.30-7.19 (m, 6H), 3.29-3.25 (m, 2H), 3.18-3.14 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.8, 157.8, 140.5, 129.6, 128.5, 128.3, 126.3, 123.0, 121.5, 121.1, 109.8, 33.7, 27.3. The spectroscopic data is in agreement with that previously reported.[20]

7-Methyl-3-phenylbenzo[*d*]isoxazole (2h). Method B was used. 5 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 100:1) afforded the title product in 43% yield (450.7 mg) as a yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), 7.73 (d, J = 8.0 Hz, 1H), 7.58-7.52 (m, 3H), 7.35 (d, J = 7.2 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 2.62 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.1, 157.5, 130.1, 130.1, 129.2, 129.0, 128.0, 124.1, 120.9, 119.9, 119.4, 15.2. IR (neat): 3053, 2977, 2917, 1603, 1382, 902, 742, 695 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{14}H_{12}NO$ $[M+H]^+$: 210.0913, found 210.0912.

The procedure for the synthesis of 3-methoxybenzo[*d*]isoxazole 2g.[24]

To a solution of benzo[*d*]isoxazol-3-ol (405.4 mg, 3 mmol) in DMSO (5 mL) was added K_2CO_3 (1.244 g, 9 mmol), MeI (0.37 mL, 6 mmol) and stirred at room temperature for 3 h. The mixture was quenched with H_2O, extracted with ethyl ether, washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 7.5:1 to 5:1 to 3:1) to afford **2g** (214.1 mg, 48%) as colorless oil. ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 1H), 7.51-7.47 (m, 1H), 7.41-7.39 (m, 1H), 7.23 (t, J = 7.6 Hz, 1H), 4.15 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.9, 163.8, 130.2, 122.8, 120.6, 113.9, 110.0, 57.1. IR (neat): 2987, 2943, 1613, 1541, 1453, 1390, 1235, 746 cm^{-1}. HRMS (EI-TOF) calcd for $C_8H_7NO_2$ $[M]^+$: 149.0477, found 149.0479.

Propargyl esters **6** were synthesized by the protection of corresponding propargyl alcohols.[25,26]

For the characterization of new propargyl esters, see following:

1-(3,4,5-Trimethoxyphenyl)prop-2-yn-1-yl benzoate (6c). 10 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) to afford the title compound (2.985 g, 91%) as light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 7.6 Hz, 1H), 7.29 (t, J = 8.0 Hz, 2H), 6.76 (s, 2H), 6.54 (d, J = 2.0 Hz, 1H), 3.75 (s, 6H), 3.73 (s, 3H), 2.66 (d, J = 2.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.0, 153.1, 138.3, 133.1, 131.7, 129.5, 129.2, 128.2, 104.7, 79.9, 75.7, 65.7, 60.5, 55.8. IR (neat): 3291, 3000, 2940, 2835, 2252, 1719, 1593, 1151 cm^{-1}. HRMS (EI-TOF) calcd for $C_{19}H_{18}O_5$ $[M]^+$: 326.1154, found 326.1155.

1-(4-Chlorophenyl)prop-2-yn-1-yl benzoate (6d). 5 mmol scale. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product (1.14 g, 84%) as yellow oil). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.6 Hz, 2H), 7.48-7.46 (m, 3H), 7.36-7.28 (m, 4H), 6.58 (d, J = 1.6 Hz, 1H), 2.62 (d, J = 2.4

Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 165.2, 135.0, 133.4, 129.8, 129.3, 129.1, 128.9, 128.4, 79.8, 76.0, 65.0. IR (neat): 3260, 3079, 2932, 2121, 1721, 1491, 1247, 1067 cm^{-1}. HRMS (EI-TOF) calcd for $C_{16}H_{11}O_2Cl$ $[M]^+$: 270.0448, found 270.0453.

General procedure for the synthesis of 2*H*-benzo[*e*][1,3]oxazine 3.

Typical procedure for the synthesis of 3a.

To a Schlenk tube were added ynamide **1a** (90.4 mg, 0.3 mmol), DCE (3 mL), benzo[*d*]isoxazole **2a** (70.3 mg, 0.36 mmol) and JohnphosAu(MeCN)SbF_6 (catalyst **A)** (11.6 mg, 0.015 mmol) under Argon. After the reaction mixture was stirred at room temperature for 6 h as monitored by thin-layer chromatography, the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:2:1 to 10:1:1 to 10:1:2) to afford **3a** in 92% yield (137.1 mg, *E*/*Z* = 7.1:1) as a red solid.

4-Methoxy-*N*-methyl-*N*-(phenyl(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)methyl)benzenesulfonamide (3a). *E*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.47-7.30 (m, 9H), 7.26-7.21 (m, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 3.60 (s, 3H), 3.28 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.0, 159.8, 154.8, 150.0, 136.6, 135.2, 134.2, 131.6, 130.0, 129.7, 128.6, 127.9, 127.9, 127.4, 127.1, 126.8, 123.0, 116.4, 116.2, 115.8, 113.0, 55.0, 38.1. Partial NMR for *Z*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.67-7.65 (m, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.29 (d, *J* = 8.4 Hz, 1H), 3.73 (s, 3H). $^{13}C\{^{1}H\}$

NMR (100 MHz, $CDCl_3$) δ 162.4, 161.2, 155.0, 149.2, 136.4, 135.5, 133.8, 131.9, 130.3, 129.4, 128.9, 128.5, 128.3, 127.5, 126.6, 122.8, 116.5, 115.8, 115.5, 113.6, 55.4, 37.1. IR (neat): 3053, 2924, 2851, 1595, 1577, 1336, 1145, 1020 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{29}H_{25}N_2O_4S$ $[M+H]^+$: 497.1530, found 497.1523.

***N*-Methyl-*N*-(phenyl(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)methyl)methanesulfonamide (3b).** Following the typical procedure, 0.3 mmol scale, **1b** (62.8 mg, 0.3 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room temperature for 6 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:1:1 to 10:1:1 to 5:1:1) afforded the *Z*-**3b** in 11% (13.5 mg) yield as a red solid and *E*-**3b** which was further purified by Recycling Preparative HPLC in 57% (69.1 mg) yield as a red solid. *E*-isomer: m.p. 211-213 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.69-7.67 (m, 2H), 7.54-7.51 (m, 3H), 7.46-7.39 (m, 4H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.05-7.02 (m, 2H), 3.26 (s, 3H), 2.95 (s, 3H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.2, 154.9, 150.2, 135.8, 135.5, 134.6, 130.5, 128.5, 128.1, 127.5, 127.1, 123.3, 116.6, 116.2, 115.9, 38.9, 37.6. IR (neat): 3058, 3032, 2934, 1576, 1532, 1324, 1138 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{23}H_{21}N_2O_3S$ $[M+H]^+$: 405.1267, found 405.1255. *Z*-isomer: m.p. 198-200 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.72-7.69 (m, 2H), 7.51-7.45 (m, 5H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.09-7.02 (m, 2H), 3.31 (s, 3H), 3.07 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.5, 155.5, 149.5, 135.7, 135.7, 134.5, 130.5, 129.0, 128.6, 128.5, 127.8, 127.8, 127.0, 123.3, 117.1, 115.7, 115.5, 39.2, 37.0. IR (neat): 3055, 2932, 1579, 1538, 1322, 1139, 963

cm^{-1}. HRMS (ESI-TOF) calcd for $C_{23}H_{21}N_2O_3S$ $[M+H]^+$: 405.1267, found 405.1257.

***N*,4-Dimethyl-*N*-(phenyl(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)methyl)benzenesulfonamide (3c).** Following the typical procedure, 0.3 mmol scale, **1c** (85.6 mg, 0.3 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room temperature for 6 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:2:1) afforded the title product as a red solid in 92% (132.8 mg, *E*/*Z* = 7.7:1) yield. *E*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.48-7.18 (m, 10H), 7.01-6.97 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.30 (s, 3H), 2.15 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.8, 154.9, 150.0, 142.3, 137.0, 136.6, 135.3, 134.2, 130.1, 128.7, 128.6, 127.98, 127.97, 127.8, 127.5, 127.2, 126.9, 123.1, 116.5, 116.3, 115.9, 38.2, 21.4. Partial NMR for *Z*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 6.20 (d, *J* = 8.4 Hz, 1H), 3.29 (s, 3H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.2, 155.0, 142.7, 137.3, 136.4, 135.6, 133.7, 130.4, 129.1, 129.0, 128.6, 128.4, 127.6, 127.5, 126.7, 122.8, 115.8, 115.6, 37.2. IR (neat): 3045, 2919, 2846, 1597, 1529, 1338, 1146, 748 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{29}H_{25}N_2O_3S$ $[M+H]^+$: 481.1580, found 481.1575.

***N*,4-Dimethyl-*N*-((4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(*p*-tolyl)methyl)benzenesulfonamide (3d).** Following the typical procedure, 0.3 mmol scale, **1d** (89.8 mg, 0.3 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room temperature for 7 h. Column chromatography on silica gel (eluent:

petroleum ether: ethyl acetate: dichloromethane = 30:2 :1 to 20:2:1) afforded the title product **3d** as a red solid in 67% (99.1 mg, *E*/*Z* = 3.7:1) yield and **4d** in 20% yield (29.8 mg) as a yellow solid. For **3d**, *E*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.47-7.13 (m, 9H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 3.29 (s, 3H), 2.37 (s, 3H), 2.15 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.2, 155.0, 149.6, 142.2, 136.9, 136.7, 135.6, 135.3, 134.1, 133.8, 130.0, 128.8, 128.7, 128.6, 127.9, 127.8, 127.4, 127.1, 123.0, 116.6, 116.4, 115.8, 38.2, 21.4, 21.2. Partial NMR for *Z*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 6.16 (d, *J* = 8.4 Hz, 1H), 3.27 (s, 3H), 2.34 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.7, 155.1, 148.7, 142.6, 137.3, 136.5, 133.6, 133.5, 130.3, 129.1, 128.9, 128.5, 128.4, 127.4, 122.7, 116.0, 115.5, 37.2, 21.4, 21.1. IR (neat): 3053, 2919, 1600, 1530, 1337, 1150, 661 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{30}H_{27}N_2O_3S$ $[M+H]^+$: 495.1737, found 495.1730.

***N*-((4-Methoxyphenyl)(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)methyl)-*N*,4-dimethylbenzenesulfonamide (3e).** Following the typical procedure, 0.3 mmol scale, **1e** (94.6 mg, 0.3 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room temperature for 7 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:2:1) afforded the title product **3e** as a red solid in 63% (95.8 mg, *E*/*Z* = 0.74:1) yield and **4e** in 25% yield (38.2 mg) as a yellow solid. For **3e**, two isomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz), 7.79-7.76 (m), 7.67 (d, *J* = 8.0 Hz), 7.47-7.44 (m), 7.37-7.19 (m), 6.99-6.87 (m), 6.14 (d, *J*

= 8.0 Hz), 3.83 (s), 3.80 (s), 3.29 (s), 3.27(s), 2.34 (s), 2.14 (s). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.5, 158.7, 158.5, 158.4, 155.1, 154.9, 149.0, 148.1, 142.6, 142.2, 137.2, 136.9, 135.6, 135.3, 134.0, 133.5, 130.2, 130.0, 129.8, 129.2, 129.1, 129.0, 128.9, 128.63, 128.57, 128.4, 127.9, 127.7, 127.4, 127.0, 122.9, 122.7, 116.6, 116.2, 115.8, 115.4, 113.4, 113.1, 55.13, 55.11, 38.2, 37.2, 21.4, 21.3. IR (neat): 3060, 2930, 2835, 1601, 1507, 1338, 1177, 1147 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{30}H_{27}N_2O_4S$ $[M+H]^+$: 511.1686, found 511.1682.

***N*-((4-Fluorophenyl)(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)methyl)-*N*,4-dimethylbenzenesulfonamide (3f).** Following the typical procedure, 0.3 mmol scale, **1f** (91.0 mg, 0.3 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room temperature for 5.5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:2:1 to 20:2:1) afforded the title product as a red solid in 89% (133.3 mg, *E*/*Z* = 9.1:1) yield. *E*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.87 (m, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.50-7.47 (m, 1H), 7.44-7.36 (m, 4H), 7.30-7.28 (m, 2H), 7.09 (t, *J* = 8.8 Hz, 2H), 7.03-7.00 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 3.30 (s, 3H), 2.16 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 161.6(d, $^{1}J_{C\text{-}F}$ =246.3 Hz), 159.8, 154.9, 149.8(d, $^{5}J_{C\text{-}F}$ =1.5 Hz), 142.5, 136.8, 135.3, 134.3, 132.9 (d, $^{4}J_{C\text{-}F}$ =3.2 Hz), 130.2, 129.3 (d, $^{3}J_{C\text{-}F}$ =7.9 Hz), 128.8, 128.7, 128.0, 127.8, 127.3, 123.2, 116.6, 115.9, 115.5, 114.9 (d, $^{2}J_{C\text{-}F}$ =21.4 Hz), 38.3, 21.5. Partial NMR for *Z*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.75 (m, 4H), 7.23 (t, *J* = 8.4 Hz, 4H), 6.19 (d, *J* = 8.4 Hz, 1H), 2.36 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 133.8, 130.5, 129.2, 129.0, 128.5, 127.5,

123.0, 114.6, 114.4. IR (neat): 3063, 2930, 1603, 1505, 1317, 1165, 1146, 749 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{29}H_{24}FN_2O_3S$ $[M+H]^+$: 499.1486, found 499.1482.

***N*-((4-Chlorophenyl)(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)methyl)-*N*,4-dimethylbenzenesulfonamide (3g).** Following the typical procedure, 0.3 mmol scale, **1g** (95.9 mg, 0.3 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room temperature for 9 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:2:1) afforded the title product as a red solid in 93% (143.1 mg, *E*/*Z* = 10:1) yield. *E*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.51-7.35 (m, 7H), 7.31-7.21 (m, 2H), 7.05-7.01 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 3.29 (s, 3H), 2.17 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.2, 154.9, 150.2, 142.5, 136.8, 135.4, 135.2, 134.4, 132.3, 130.3, 128.8, 128.7, 128.2, 128.1, 127.8, 127.4, 123.3, 116.5, 115.9, 115.4, 38.3, 21.5. Partial NMR for *Z*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.76 (m, 4H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.21 (d, *J* = 8.4 Hz, 1H), 3.28 (s, 3H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 129.8, 129.2, 129.0, 128.5, 127.8, 127.5. IR (neat): 3058, 2922, 2848, 1595, 1520, 1313, 1147 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{29}H_{24}ClN_2O_3S$ $[M+H]^+$: 515.1191, found 515.1187.

Ethyl 4-(((*N*,4-dimethylphenyl)sulfonamido)(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)methyl)benzoate (3h). Following the typical procedure, 0.3 mmol scale, **1h** (107.2 mg, 0.3 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **C** (19.5 mg, 0.0225 mmol) were

stirred at room temperature for 30 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:2:1 to 16:2:1) afforded the title product which was further purified by Recycling Preparative HPLC in 49% (80.8 mg, *E*/*Z* = 6.7:1) yield as a red solid. *E*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.51-7.37 (m, 5H), 7.32-7.29 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 3.32 (s, 3H), 2.16 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.4, 160.9, 154.7, 151.2, 142.5, 141.5, 136.8, 135.1, 134.5, 130.4, 129.2, 128.8, 128.7, 128.0, 127.7, 127.5, 127.1, 123.4, 116.4, 115.9, 115.4, 60.7, 38.2, 21.4, 14.3. Partial NMR for *Z*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.24 (d, *J* = 8.4 Hz, 1H), 3.30 (s, 3H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.5, 162.3, 154.8, 150.5, 142.9, 141.4, 137.1, 135.3, 134.1, 130.7, 129.2, 129.0, 128.9, 128.5, 128.1, 123.2, 116.3, 115.7, 114.8, 60.6, 37.1, 21.4. IR (neat): 3058, 2990, 2924, 1703, 1524, 1333, 1273, 1108 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{32}H_{29}N_2O_5S$ $[M+H]^+$: 553.1792, found 553.1787.

_N_,4-Dimethyl-_N_-((4-phenyl-2_H_-benzo[_e_][1,3]oxazin-2-ylidene)(thiophen-2-yl)methyl)benzenesulfonamide (3i). Following the typical procedure, 0.3 mmol scale, **1i** (87.4 mg, 0.3 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room temperature for 1 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:2:1 to 10:2:1) afforded the title product as a dark purple solid in 78% (114.2 mg, *E*/*Z* = 0.1:1) yield. Single *Z* isomer could

be obtained by recrystallization from the mixture in petroleum ether/dichloromethane. *Z*-isomer: m.p. 195-197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 4H), 7.54-7.50 (m, 3H), 7.48-7.19 (m, 6H), 7.00-6.97 (m, 2H), 6.21 (d, *J* = 8.0 Hz, 1H), 3.24 (s, 3H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.1, 155.0, 147.7, 143.0, 139.2, 137.8, 135.4, 134.1, 130.8, 129.7, 129.4, 128.6, 127.8, 127.6, 127.4, 126.3, 125.6, 123.3, 116.5, 115.8, 113.0, 36.5, 21.6. Partial NMR for *E*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 4.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 2H), 3.28 (s, 3H), 2.14 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.0, 142.4, 140.3, 137.0, 134.3, 130.2, 128.9, 128.8, 128.2, 128.1, 127.3, 127.0, 125.8, 123.4, 116.6, 116.1, 37.6. IR (neat): 3050, 2930, 1597, 1530, 1342, 1160, 690 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{27}H_{23}N_2O_3S_2$ $[M+H]^+$: 487.1145, found 487.1141.

***N*,4-Dimethyl-*N*-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)methyl)benzenesulfonamide (3j)**. Following the typical procedure, 0.3 mmol scale, **1j** (138.5 mg, 0.3 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room temperature for 6 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:2) afforded the title product as a red solid in 65% (127.3 mg, *E*/*Z* = 2.1:1) yield. Two isomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz), 7.74-7.56 (m), 7.48-7.24 (m), 7.20 (d, *J* = 8.0 Hz), 7.02-6.96 (m), 6.91 (d, *J* =8.0 Hz). 6.19 (d, *J* = 8.4 Hz), 3.30 (s), 3.29 (s), 2.97-2.91 (m), 2.54-2.45 (m), 2.36 (s), 2.34-2.30 (m), 2.17 (s), 2.14-1.97 (m), 1.66-1.44 (m), 0.92 (s), 0.90 (s);

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 220.98, 220.92, 160.7, 159.3, 155.1, 154.9, 149.7, 148.8, 142.6, 142.2, 138.6, 138.4, 137.3, 136.9, 135.8 135.6, 135.3, 135.2, 134.1, 133.7, 133.6, 130.3, 130.0, 129.1, 129.0, 128.9, 128.7, 128.6, 128.3, 127.94, 127.91, 127.7, 127.4, 127.1, 127.0, 126.1, 125.0, 124.9, 124.6, 123.0, 122.8, 116.6, 116.5, 116.3, 115.8, 115.5, 50.3, 47.9, 44.4, 44.3, 38.3, 38.0, 37.3, 35.7, 31.5, 29.6, 29.4, 26.5, 25.5, 21.5, 21.4, 13.7. IR (neat): 3058, 2924, 2862, 1735, 1527, 1338, 1151 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{41}H_{41}N_2O_4S$ $[M+H]^+$: 657.2782, found 657.2780.

***N*-(Cyclopropyl(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)methyl)-*N*,4-dimethylbenzenesulfonamide (3k).** Following the typical procedure, 0.3 mmol scale, **1k** (74.8 mg, 0.3 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room temperature for 1 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 15:1) afforded the title product as an orange solid in 95% (127.1 mg, *E*/*Z* = 1.54:1) yield. Two isomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz), 7.67-7.63 (m), 7.49-7.42 (m), 7.38-7.14 (m), 6.95-6.83 (m), 5.82 (d, *J* = 7.6 Hz), 3.09 (s), 3.06 (s), 2.38 (s), 2.36-2.30 (m), 2.10 (s), 2.06-1.99 (m), 1.26 (br), 0.89-0.69 (m); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.7, 157.0, 155.3, 154.7, 150.8, 149.0, 142.6, 142.2, 137.2, 136.7, 135.7, 135.3, 133.7, 133.1, 130.1, 129.7, 129.1, 128.6, 128.4, 128.2, 127.9, 127.8, 127.7, 127.0, 126.9, 122.4, 118.2, 117.1, 116.3, 116.2, 115.6, 115.1, 38.6, 37.2, 21.3, 21.3, 11.7, 11.6, 5.5, 4.9. IR (neat): 3071, 3000, 2927, 1603, 1535, 1446, 1336, 1157, 747 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{26}H_{25}N_2O_3S$ $[M+H]^+$: 445.1580, found 445.1570.

***N*-((4-(4-Methoxyphenyl)-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(phenyl)methyl)-*N*,4-dimethylbenzenesulfonamide (3l).** Following the typical procedure, 0.3 mmol scale, **1c** (85.6 mg, 0.3 mmol), 3 mL DCE, **2b** (81.1 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room temperature for 5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:2:1) afforded the title product as a red solid in 86% (131.0 mg, *E*/*Z* = 11.1:1) yield. *E*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.40-7.31 (m, 4H), 7.28-7.17 (m, 3H), 7.02-6.94 (m, 4H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.29 (s, 3H), 2.17 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.2, 159.1, 154.9, 150.1, 142.2, 137.0, 136.8, 134.0, 130.5, 128.6, 127.9, 127.8, 127.3, 127.2, 126.6, 123.0, 116.6, 115.8, 115.5, 113.3, 55.3, 38.0, 21.3. Partial NMR for *Z*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 6.17 (d, *J* = 8.4 Hz, 1H), 3.82 (s, 3H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.4, 160.5, 155.0, 149.2, 142.6, 137.2, 136.6, 133.5, 130.7, 129.1, 128.5, 127.5, 127.4, 126.5, 122.7, 116.5, 115.5, 114.9, 113.8, 37.2, 21.3. IR (neat): 3066, 2966, 2932, 2835, 1606, 1527, 1327, 1147 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{30}H_{27}N_2O_4S$ $[M+H]^+$: 511.1686, found 511.1681.

***N*-((4-(4-Chlorophenyl)-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(phenyl)methyl)-*N*,4-dimethylbenzenesulfonamide (3m).** Following the typical procedure, 0.3 mmol scale, **1c** (85.6 mg, 0.3 mmol), 3 mL DCE, **2c** (82.7 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room temperature for 5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:2:1 to 20:2:1) afforded the title

product as a red solid in 91% (140.9 mg, *E*/*Z* = 7.7:1) yield. Single *E*-isomer could be obtained by recrystallization from the mixture in petroleum ether/dichloromethane. Singel *Z*-isomer could be obtained by Column chromatography on silica gel from the above filtrate. *E*-isomer: m.p. 223-225 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.47-7.20 (m, 9H), 7.05-6.96 (m, 4H), 3.27 (s, 3H), 2.23 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.7, 155.1, 150.1, 142.4, 137.2, 136.4, 136.4, 134.5, 133.8, 130.2, 128.7, 128.4, 128.1, 127.9, 127.6, 127.1, 126.9, 123.2, 116.9, 116.4, 116.1, 38.1, 21.4. *Z*-isomer: m.p. 186-188 °C. Partial NMR for *Z*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (t, *J* = 8.4 Hz, 4H), 6.26 (d, *J* = 8.4 Hz, 1H), 3.28 (s, 3H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.0, 155.2, 137.4, 134.0, 130.4, 129.2, 128.8, 128.7, 127.7, 127.0, 123.0, 115.8, 37.2, 21.5. IR (neat): 3089, 3060, 2927, 1595, 1522, 1335, 1150 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{29}H_{24}ClN_2O_3S$ $[M+H]^+$: 515.1191, found 515.1188.

***N*-((4-(2-Methoxyphenyl)-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(phenyl)methyl)-*N*,4-dimethylbenzenesulfonamide (3n).** Following the typical procedure, 0.3 mmol scale, **1c** (85.6 mg, 0.3 mmol), 3 mL DCE, **2d** (81.1 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room temperature for 8 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:2:1) afforded the title product as a red solid in 94% (144.4 mg, *E*/*Z* = 12.5:1) yield. *E*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.45-7.38 (m, 3H), 7.35-7.31 (m, 1H), 7.29-7.13 (m, 1H), 6.96-6.85 (m, 8H), 3.71 (s, 3H), 3.24 (s, 3H), 2.17 (s, 3H). ^{13}C{^{1}H}

NMR (100 MHz, $CDCl_3$) δ 159.6, 157.0, 153.9, 150.5, 141.9, 137.0, 136.5, 133.9, 131.0, 130.3, 128.4, 128.0, 127.9, 127.5, 127.5, 126.8, 124.9, 122.8, 120.5, 117.3, 116.0, 115.4, 110.8, 55.2, 38.3, 21.5. Partial NMR for *Z*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 6.14 (d, *J* = 8.4 Hz, 1H), 3.76 (s, 3H), 3.29 (s, 3H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 129.1, 128.5. IR (neat): 3058, 2932, 1600, 1530, 1329, 1148, 1023, 755 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{30}H_{27}N_2O_4S$ $[M+H]^+$: 511.1686, found 511.1677.

***N*,4-Dimethyl-*N*-((4-methyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(phenyl)methyl)benzen esulfonamide (3o).** Following the typical procedure, 0.3 mmol scale, **1c** (85.6 mg, 0.3 mmol), 3 mL DCE, **2e** (79.9 mg, 0.6 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room temperature for 2 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 40:2:1 to 30:2:1 to 20:2:1) afforded the title product as an orange solid in 91% (114.2 mg, *E*/*Z* = 7.7:1) yield. *E*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.40-7.16 (m, 7H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 3.23 (s, 3H), 2.39 (s, 3H), 1.90 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.9, 153.4, 149.9, 142.3, 137.3, 136.3, 134.3, 128.7, 128.0, 127.9, 127.4, 126.7, 124.9, 123.2, 117.2, 115.4, 114.5, 37.9, 21.3, 21.0. Partial NMR for *Z*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 6.09 (d, *J* = 8.4 Hz, 1H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.4, 153.6, 149.2, 142.6, 137.5, 133.9, 129.0, 128.3, 127.6, 127.4, 126.5, 126.0, 123.0, 117.3, 115.0, 114.1, 37.0, 21.7. IR (neat): 3071, 2922, 1618, 1557, 1329, 1146, 1083 cm^{-1}. HRMS (ESI-TOF) calcd

for $C_{24}H_{23}N_2O_3S$ $[M+H]^+$: 419.1424, found 419.1417.

***N*,4-Dimethyl-*N*-((4-phenethyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(phenyl)methyl)benzenesulfonamide (3p).** Following the typical procedure, 0.3 mmol scale, **1c** (85.6 mg, 0.3 mmol), 3 mL DCE, **2f** (134.0 mg, 0. 6 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room temperature for 4 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 40:2:1 to 30:2:1) afforded the title product as an orange solid in 85% (129.4 mg, *E*/*Z* = 9.1:1) yield. *E*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) 7.84 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 3H), 7.31-7.19 (m, 7H), 7.10 (d, *J* = 7.2 Hz, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 3.21 (s, 3H), 3.07-2.52 (m, 4H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.9, 153.6, 149.7, 142.4, 140.8, 137.3, 136.6, 134.2, 128.8, 128.3, 128.0, 127.9, 127.8, 127.3, 126.6, 125.9, 124.3, 123.2, 116.8, 115.5, 114.8, 37.8, 34.8, 31.4, 21.2. Partial NMR for *Z*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (d, *J* = 7.6 Hz, 1H), 3.25 (s, 3H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.7, 149.1, 142.6, 140.9, 136.3, 133.7, 129.0, 128.3, 128.2, 127.4, 127.3, 126.3, 126.0, 124.2, 123.0, 116.6 115.1, 114.3, 36.9, 35.3, 31.3. IR (neat): 3063, 3026, 2940, 1556, 1332, 1148, 1036, 750 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{31}H_{29}N_2O_3S$ $[M+H]^+$: 509.1893, found 509.1889.

***N*-((4-Methoxy-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(phenyl)methyl)-*N*,4-dimethylbenzenesulfonamide (3q).** Following the typical procedure, 0.3 mmol scale, **1c** (85.6 mg, 0.3 mmol), 3 mL DCE, **2g** (53.7 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were

stirred at room temperature for 3.5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:2:1) afforded the title product as an orange solid in 88% (114.5 mg, *E*/*Z* = 0.38:1) yield. Two isomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz), 7.76 (d, *J* = 8.0 Hz), 7.71 (d, *J* = 8.4 Hz), 7.47 (d, *J* = 7.6 Hz), 7.40 (t, *J* = 8.0 Hz), 7.36-7.13 (m), 7.01 (t, *J* = 8.0 Hz), 6.96 (t, *J* = 6.8 Hz), 6.11 (d, *J* = 8.0 Hz), 3.98 (s), 3.49 (s), 3.25 (s), 3.24 (s), 2.37 (s), 2.31 (s). *Z*-isomer: ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.2, 155.1, 149.2, 142.4, 137.6, 136.6, 134.1, 129.0, 127.5, 127.40, 127.38, 125.6, 123.8, 122.7, 114.8, 111.6, 109.9, 54.2, 37.0, 21.2. *E*-isomer: ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.5, 155.2, 150.2, 142.5, 137.7, 136.9, 134.6, 128.9, 127.8, 127.7, 126.9, 125.9, 123.9, 122.9, 115.1, 112.0, 110.7, 53.5. IR (neat): 3047, 2945, 1620, 1590, 1566, 1360, 1338, 1152 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{24}H_{23}N_2O_4S$ $[M+H]^+$: 435.1373, found 435.1367.

(*E*)-*N*,4-Dimethyl-*N*-((8-methyl-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(phenyl)methyl)benzenesulfonamide (3r). Following the typical procedure, 0.3 mmol scale, **1c** (85.6 mg, 0.3 mmol), 3 mL DCE, **2h** (75.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room temperature for 9 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:2:1) afforded the title product as a red solid in 87% (128.8 mg) yield. Only *E*-isomer was obtained. M.p. 186-188 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.47-7.22 (m, 9H), 7.17 (d, *J* = 7.6 Hz, 1H), 6.89-6.86 (m, 3H), 3.31 (s, 3H), 2.28 (s, 3H), 2.13 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.2, 153.2, 150.2, 142.2, 136.9, 136.7, 135.49,

135.47, 130.0, 128.7, 128.6, 127.9, 127.8, 127.7, 127.5, 126.7, 125.0, 124.8, 122.4, 116.0, 115.9, 38.3, 21.4, 15.6. IR (neat): 3042, 2974, 2914, 1579, 1530, 1323, 1144, 743 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{30}H_{27}N_2O_3S$ $[M+H]^+$: 495.1737, found 495.1731.

***N*-((2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(phenyl)methyl)-*N*,4dimethylbenzene-sulfonamide (3s)** and ***N*,4-dimethyl-*N*-(2-phenylbenzo[*f*][1,4]oxazepin-3-yl)benzenesulfonamide (4q).** Following the typical procedure, 0.3 mmol scale, **1c** (85.6 mg, 0.3 mmol), 3 mL DCE, benzo[d]isoxazole **2i** (42.9 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room temperature for 4 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 3:1) afforded the product as an orange solid in 83% (100.3 mg) yield, which contains **3s** in 60% (*E*/*Z* = 0.79:1) yield and **4q** in 23% yield. Note: We found that **3s** and **4q** can be decomposed slowly on silica gel, so column chromatography should be finished within 15 minutes. ^{1}H NMR for the mixture of **3s** and **4q** (400 MHz, $CDCl_3$): δ 8.23 (s), 7.87-7.83 (m), 7.71-7.69 (m), 7.64-7.61 (m), 7.53-7.49 (m), 7.37-7.20 (m), 7.17-7.01 (m), 7.03-7,01 (m), 6.93-6.84 (m), 7.78 (d, *J* = 8.0 Hz,), 6.05 (d, *J* = 8.0 Hz), 3.14 (s), 3.09 (s), 2.90 (s), 2.30 (s), 2.23 (s). ^{13}C{^{1}H} NMR for *E*-**3s** (100 MHz, $CDCl_3$): δ 153.8, 153.3, 150.9, 142.6, 136.8, 135.5, 134.6, 128.8, 127.9, 127.9, 127.6, 127.1, 126.7, 123.6, 117.1, 116.1, 114.8, 37.7, 21.4. ^{13}C{^{1}H} NMR for *Z*-**3s** (100 MHz, $CDCl_3$): δ 154.6, 153.9, 149.7, 142.7, 137.3, 136.0, 134.2, 129.0, 128.2, 127.6, 127.4, 127.0, 126.8, 123.4, 117.0, 116.2, 115.1, 36.9, 21.3. ^{13}C{^{1}H} NMR for **4q** (100 MHz, $CDCl_3$): δ 160.2, 158.9, 147.4, 143.3, 135.3, 134.1, 133.9, 133.2, 129.1, 129.0, 128.7, 128.6, 128.2, 128.2, 128.1, 125.4, 120.6, 35.8, 21.4. HRMS (ESI-TOF) calcd for

$C_{23}H_{21}N_2O_3S$ $[M+H]^+$: 405.1267, found 405.1274.

General procedure for the synthesis of benzo[*f*][1,4]oxazepine 4.

Typical procedure for the synthesis of 4a.

To a Schlenk tube were added ynamide **1a** (108.5 mg, 0.36 mmol), DCE (9 mL), benzo[*d*]isoxazole **2a** (58.6 mg, 0.3 mmol) and $AuBr_3$ (6.6 mg, 0.015 mmol) under Argon. After the reaction mixture was stirred at room temperature for 1 h as monitored by thin-layer chromatography, the mixture was filtered through a pad of silica gel, evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:2:1 to 20:2:1) to afford **4a** in 79% yield (118.3 mg) as a yellow solid.

***N*-(2,5-Diphenylbenzo[*f*][1,4]oxazepin-3-yl)-4-methoxy-*N*-methylbenzenesulfonamide (4a).** M.p. 171-173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.51-7.34 (m, 5H), 7.28-7.20 (m, 6H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 2H), 3.72 (s, 3H), 3.17 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.7, 162.8, 159.9, 146.9, 138.0, 133.7, 133.6, 133.0, 130.6, 130.2, 130.0, 129.6, 129.4, 128.9, 128.1, 127.9, 127.7, 124.8, 121.0, 113.8, 55.4, 36.3. IR (neat): 3016, 2934, 1594, 1345, 1155, 1024, 675 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{29}H_{25}N_2O_4S$ $[M+H]^+$: 497.1530, found 497.1520.

***N*-(2,5-Diphenylbenzo[*f*][1,4]oxazepin-3-yl)-*N*,4-dimethylbenzenesulfonamide (4c).**

Following the typical procedure, 0.3 mmol scale, **1c** (102.7 mg, 0.36 mmol), 9 mL DCE, **2a** (58.6 mg, 0.3 mmol), $AuBr_3$ (6.6 mg, 0.015 mmol) were stirred at room temperature for 1 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:2:1) afforded **4c** as a yellow solid in 80% (115.8 mg) yield. M.p. 170-172 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.53-7.47 (m, 3H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.39-7.34 (m, 2H), 7.26-7.21 (m, 4H), 7.17-7.11 (m, 5H), 3.19 (s, 3H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.7, 159.9, 147.0, 143.2, 138.0, 135.4, 133.6, 133.6, 133.0, 130.5, 129.5, 129.4, 129.2, 128.9, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 124.8, 121.0, 36.4, 21.4. IR (neat): 3066, 2920, 1594, 1553, 1339, 1154, 759, 672 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{29}H_{25}N_2O_3S$ $[M+H]^+$: 481.1580, found 481.1574.

***N*,4-Dimethyl-*N*-(5-phenyl-2-(*p*-tolyl)benzo[*f*][1,4]oxazepin-3-yl)benzenesulfonamide (4d).** Following the typical procedure, 0.3 mmol scale, **1d** (107.8 mg, 0.36 mmol), 9 mL DCE, **2a** (58.6 mg, 0.3 mmol), $AuBr_3$ (6.6 mg, 0.015 mmol) were stirred at room temperature for 1 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:2:1 to 10:2:1) afforded **4d** as a yellow solid in 80% (118.3 mg) yield. M.p. 197-198 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.55-7.47 (m, 3H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.26-7.21 (m, 6H), 7.18-7.10 (m, 5H), 3.18 (s, 3H), 2.39 (s, 3H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.4, 160.0, 147.4, 143.3, 139.2, 138.2, 135.7, 133.7, 133.2, 130.6, 130.3, 129.6, 129.5, 129.4, 129.1, 128.3, 128.2, 128.0, 127.9, 127.8, 124.9, 121.2, 36.6, 21.53, 21.48. IR (neat): 3069, 3024, 2937, 2914, 1591, 1344, 671 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{30}H_{27}N_2O_3S$ $[M+H]^+$: 495.1737,

found 495.1728.

***N*-(2-(4-Methoxyphenyl)-5-phenylbenzo[*f*][1,4]oxazepin-3-yl)-*N*,4-dimethylbenzenesulfonamide (4e)**. Following the typical procedure, 0.3 mmol scale, **1e** (113.5 mg, 0.36 mmol), 9 mL DCE, **2a** (58.6 mg, 0.3 mmol), $AuBr_3$ (6.6 mg, 0.015 mmol) were stirred at room temperature for 1 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:2:1) afforded **4e** as a yellow solid in 63% (96.8 mg) yield. M.p. 202-204 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.43-7.38 (m, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.17-7.13 (m, 4H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.04-7.01 (m, 3H), 6.88 (d, *J* = 9.2 Hz, 2H), 3.75 (s, 3H), 3.10 (s, 3H), 2.26 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.8, 160.0, 159.7, 147.0, 143.2, 138.1, 135.6, 133.5, 132.4, 130.3, 129.6, 129.43, 129.38, 129.3, 128.2, 128.1, 127.7, 125.5, 124.7, 121.0, 113.6, 55.2, 36.4, 21.4. IR (neat): 3069, 3010, 2971, 2934, 1603, 1508, 1343, 1031, 670 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{30}H_{27}N_2O_4S$ $[M+H]^+$: 511.1686, found 511.1678.

***N*-(2-(4-Fluorophenyl)-5-phenylbenzo[*f*][1,4]oxazepin-3-yl)-*N*,4-dimethylbenzenesulfonamide (4f).** Following the typical procedure, 0.3 mmol scale, **1f** (109.2 mg, 0.36 mmol), 9 mL DCE, **2a** (58.6 mg, 0.3 mmol), $AuBr_3$ (6.6 mg, 0.015 mmol) were stirred at room temperature for 1 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 40:2:1) afforded **4f** as a yellow solid in 82% (123.3 mg) yield. M.p. 172-174 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.12 (m, 2H), 7.54-7.48 (m, 3H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.26-7.08 (m, 11H), 3.18 (s, 3H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (100

MHz, $CDCl_3$) δ 165.7, 162.8 (d, $^1J_{C\text{-}F}$ = 248.1 Hz), 159.8, 146.1, 143.4, 137.9, 135.2, 133.7, 133.4, 130.6, 130.0 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 129.6, 129.4, 129.3, 129.2, 128.1, 127.9, 127.7, 124.9, 120.9, 115.1 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 36.4, 21.3. IR (neat): 3078, 2917, 1595, 1499, 1345, 1145, 671 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{29}H_{24}FN_2O_3S$ $[M+H]^+$: 499.1486, found 499.1475.

***N*-(2-(4-Chlorophenyl)-5-phenylbenzo[*f*][1,4]oxazepin-3-yl)-*N*,4-dimethylbenzenesulfonamide (4g).** Following the typical procedure, 0.3 mmol scale, **1g** (115.1 mg, 0.36 mmol), 9 mL DCE, **2a** (58.6 mg, 0.3 mmol), $AuBr_3$ (6.6 mg, 0.015 mmol) were stirred at room temperature for 1 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 40:2:1 to 30:2:1) afforded **4g** as a yellow solid in 81% (124.5 mg) yield. M.p. 202-204 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 2H), 7.53-7.49 (m, 3H), 7.41-7.38 (m, 3H), 7.27-7.17 (m, 6H), 7.13-7.08 (m, 3H), 3.17 (s, 3H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.0, 159.9, 145.9, 143.4, 137.9, 135.2, 134.7, 134.0, 133.7, 131.6, 130.7, 129.7, 129.4, 129.3, 129.3, 128.4, 128.1, 127.9, 127.7, 124.9, 120.9, 36.4, 21.4. IR (neat): 3066, 2940, 1592, 1489, 1346, 1158, 818 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{29}H_{24}ClN_2O_3S$ $[M+H]^+$: 515.1191, found 515.1185.

Ethyl 4-(3-((*N*,4-dimethylphenyl)sulfonamido)-5-phenylbenzo[*f*][1,4]oxazepin-2-yl)benzoate (4h). Following the typical procedure, 0.3 mmol scale, **1h** (128.7 mg, 0.36 mmol), 9 mL DCE, **2a** (58.6 mg, 0.3 mmol), $AuBr_3$ (6.6 mg, 0.015 mmol) were stirred at room

temperature for 1 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:2:1) afforded **4h** as a yellow solid in 73% (120.5 mg) yield. M.p. 174-176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.18 (m, 2H), 8.13-8.11 (m, 2H), 7.56-7.52 (m, 3H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.28-7.21 (m, 4H), 7.19-7.13 (m, 5H), 4.40 (q, *J* = 6.8 Hz, 2H), 3.19 (s, 3H), 2.36 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.5, 166.1, 160.0, 146.0, 143.4, 137.9, 137.3, 135.2, 135.0, 133.8, 130.8, 130.2, 129.8, 129.5, 129.4, 129.3, 128.1, 127.9, 127.8, 127.7, 125.0, 121.0, 60.9, 36.4, 21.4, 14.2. IR (neat): 3083, 2985, 1718, 1595, 1343, 1094, 767 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{32}H_{29}N_2O_5S$ [M+H]$^+$: 553.1792, found 553.1784.

***N*,4-dimethyl-*N*-(5-phenyl-2-(thiophen-2-yl)benzo[*f*][1,4]oxazepin-3-yl)benzenesulfonamide (4i).** Following the typical procedure, 0.3 mmol scale, **1i** (104.9 mg, 0.36 mmol), 9 mL DCE, **2a** (58.6 mg, 0.3 mmol), $AuBr_3$ (6.6 mg, 0.015 mmol) were stirred at room temperature for 1.5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:2:1 to 10:2:1) afforded **4i** as a orange solid in 57% (83.9 mg) yield and *Z*-**3i** in 14% yield (21.0 mg) as a dark purple solid. For **4i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 3.6 Hz, 1H), 7.57-7.50 (m, 3H), 7.41-7.36 (m, 2H), 7.27-7.17 (m, 7H), 7.11 (t, *J* = 4.4 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 3.27 (s, 3H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.7, 159.3, 143.4, 138.0, 135.4, 135.0, 133.8, 130.4, 129.7, 129.4, 129.3, 128.9, 128.4, 128.2, 128.2, 127.7, 127.0, 125.0, 121.2, 35.9, 21.4. IR (neat): 3068, 2932, 1595, 1445, 1349, 1165, 669 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{27}H_{23}N_2O_3S_2$ [M+H]$^+$: 487.1145, found 487.1149.

***N*,4-Dimethyl-*N*-(2-((8*R*,9*S*,13S,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)-5-phenylbenzo[*f*][1,4]oxazepin-3-yl)benzenesulfonamide (4j).** Following the typical procedure, 0.3 mmol scale, **1j** (166.2 mg, 0.36 mmol), 9 mL DCE, **2a** (58.6 mg, 0.3 mmol), $AuBr_3$ (6.6 mg, 0.015 mmol) were stirred at room temperature for 1.5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:2) afforded **4j** as a yellow solid in 65% (128.7 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.87 (s, 1H), 7.55-7.48 (m, 3H), 7.40-7.35 (m, 2H), 7.27-7.13 (m, 9H), 3.18 (s, 3H), 3.01-2.99 (m, 2H), 2.52-2.42 (m, 2H), 2.36-2.33 (m, 4H), 2.15-1.96 (m, 4H), 1.66-1.46 (m, 6H), 0.92 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 220.7, 165.2, 159.8, 147.1, 143.1, 140.7, 138.0, 136.1, 135.5, 133.5, 133.2, 130.4, 129.4, 129.3, 129.2, 128.4, 128.05, 127.99, 127.6, 125.3, 125.1, 124.7, 121.0, 50.3, 47.8, 44.4, 37.8, 36.4, 35.7, 31.4, 29.5, 26.3, 25.4, 21.43, 21.35, 13.7. IR (neat): 3061, 2928, 2858, 1735, 1598, 1347, 1163, 727 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{41}H_{41}N_2O_4S$ $[M+H]^+$: 657.2782, found 657.2773.

***N*-(2-(3-(4-Methoxyphenyl)-4-oxo-4*H*-chromen-7-yl)-5-phenylbenzo[*f*][1,4]oxazepin-3-yl)-*N*,4-dimethylbenzenesulfonamid*e* (4k).** Following the typical procedure, 0.3 mmol scale, **1l** (137.9 mg, 0.3 mmol), 9 mL DCE, **2a** (117.1 mg, 0.6 mmol), $AuBr_3$ (6.6 mg, 0.015 mmol) were stirred at room temperature for 1 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:1:10 to 15:1:10 to 10:1:10) afforded **4k** as a yellow solid in 60% (117.5 mg) yield. M.p. 220-222 ^{o}C. ^{1}H

NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.8 Hz, 1H), 8.26 (d, *J* = 1.6 Hz, 1H), 8.18-8.16 (m, 1H), 8.01 (s, 1H), 7.58-7.52 (m, 5H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.29-7.23 (m, 4H), 7.19-7.14 (m, 5H), 6.98-6.95 (m, 2H), 3.81 (s, 3H), 3.23 (s, 3H), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.8, 167.0, 160.0, 159.4, 155.8, 152.7, 144.8, 143.6, 138.2, 137.7, 135.7, 134.8, 134.0, 130.9, 130.0, 129.9, 129.5, 129.3, 128.1, 127.8, 126.0, 125.1, 125.0, 124.3, 124.0, 124.0, 120.9, 117.3, 113.8, 55.2, 36.3, 21.4. IR (neat): 3063, 2993, 2937, 2838, 1641, 1621, 1422, 1347 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{39}H_{31}N_2O_6S$ $[M+H]^+$: 655.1897, found 655.1896.

***N*-(5-(4-Methoxyphenyl)-2-phenylbenzo[*f*][1,4]oxazepin-3-yl)-*N*,4-dimethylbenzenesulfonamide (4l).** Following the typical procedure, 0.3 mmol scale, **1c** (102.7 mg, 0.36 mmol), 9 mL DCE, **2b** (67.6 mg, 0.3 mmol), $AuBr_3$ (6.6 mg, 0.015 mmol) were stirred at room temperature for 1 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:2:1) afforded **4l** as a yellow solid in 74% (113.9 mg) yield. M.p. 152-154 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.2 Hz, 2H), 7.54-7.41 (m, 5H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.26-7.21 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12-7.10 (m, 3H), 6.76 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 3.18 (s, 3H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.0, 161.6, 159.9, 146.5, 143.1, 135.5, 133.9, 133.5, 133.1 131.1, 130.6, 129.6, 129.2, 128.7, 128.1, 127.9, 127.8, 124.7, 121.0, 113.0, 55.3, 36.5, 21.4. IR (neat): 3055, 2935, 2841, 1593, 1550, 1342, 1258, 1028 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{30}H_{27}N_2O_4S$ $[M+H]^+$: 511.1686, found 511.1677.

***N*-(5-(4-Chlorophenyl)-2-phenylbenzo[*f*][1,4]oxazepin-3-yl)-*N*,4-dimethylbenzenesulfonamide (4m).** Following the typical procedure, 0.3 mmol scale, **1c** (102.7 mg, 0.36 mmol), 9 mL DCE, **2c** (68.9 mg, 0.3 mmol), $AuBr_3$ (6.6 mg, 0.015 mmol) were stirred at room temperature for 1 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 40:2:1) afforded **4m** as a yellow solid in 77% (118.6 mg) yield. M.p. 170-171 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.2 Hz, 2H), 7.53-7.50 (m, 3H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.39-7.36 (m, 1H), 7.27-7.17 (m, 6H), 7.13-7.07 (m, 3H), 3.18 (s, 3H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.4, 159.9, 147.2, 143.3, 136.7, 136.5, 135.5, 133.9, 133.6, 132.8, 130.7, 129.3, 129.2, 129.1, 128.2, 128.1, 128.0, 127.6, 124.9, 121.2, 36.5, 21.4. IR (neat): 3058, 2964, 2919, 1595, 1537, 1345, 1159, 1088, cm^{-1}. HRMS (ESI-TOF) calcd for $C_{29}H_{24}ClN_2O_3S$ $[M+H]^+$: 515.1191, found 515.1183.

***N*-(5-(2-Methoxyphenyl)-2-phenylbenzo[*f*][1,4]oxazepin-3-yl)-*N*,4-dimethylbenzenesulfonamide (4n).** Following the typical procedure, 0.3 mmol scale, **1c** (102.7 mg, 0.36 mmol), 9 mL DCE, **2d** (67.6 mg, 0.3 mmol), $AuBr_3$ (6.6 mg, 0.015 mmol) were stirred at room temperature for 1 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:2:1) afforded **4n** as a yellow solid in 68% (103.5 mg) yield. M.p. 182-184 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.07 (m, 2H), 7.49-7.41 (m, 5H), 7.37-7.33 (m, 2H), 7.16-7.11 (m, 4H), 6.95-6.93 (m, 1H), 6.84-6.79 (m, 2H), 6.49-6.47 (m, 1H), 3.47 (s, 3H), 3.20 (s, 3H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.4, 158.6, 157.9, 147.8, 143.2, 135.5, 133.4, 132.9, 132.7, 131.5, 130.8, 130.7, 129.3, 128.8, 128.2, 128.12, 128.10, 128.03, 127.96, 124.7, 120.6, 120.1, 111.4,

55.4, 36.2, 21.4. IR (neat): 3003, 2943, 2833, 1594, 1487, 1350, 1237, 1027, 761 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{30}H_{27}N_2O_4S$ $[M+H]^+$: 511.1686, found 511.1677.

***N*,4-Dimethyl-*N*-(5-methyl-2-phenylbenzo[*f*][1,4]oxazepin-3-yl)benzenesulfonamide (4o).** Following the typical procedure, 0.3 mmol scale, **1c** (85.6 mg, 0.3 mmol), 9 mL DCE, **2e** (79.9 mg, 0.6 mmol), $AuBr_3$ (6.6 mg, 0.015 mmol) were stirred at room temperature for 2 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:2:1 to 20:2:1) afforded **4o** as a light yellow solid in 61% (76.3 mg) yield. M.p. 173-175 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.2 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.42-7.38 (m, 4H), 7.35-7.32 (m, 1H), 7.24-7.21 (m, 3H), 7.01-6.99 (m, 1H), 3.02 (s, 3H), 2.40 (s, 3H), 2.30 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.9, 159.3, 145.9, 143.1, 135.6, 134.0, 133.3, 132.9, 129.6, 128.9, 128.8, 128.3, 128.1, 127.8, 127.3, 125.2, 120.8, 36.1, 25.9, 21.4. IR (neat): 3081, 2972, 2922, 1597, 1486, 1345, 1154, 765 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{24}H_{23}N_2O_3S$ $[M+H]^+$: 419.1424, found 419.1419.

***N*,4-Dimethyl-*N*-(5-phenethyl-2-phenylbenzo[*f*][1,4]oxazepin-3-yl)benzenesulfonamide (4p).** Following the typical procedure, 0.3 mmol scale, **1c** (85.6 mg, 0.3 mmol), 9 mL DCE, **2f** (134.0 mg, 0.6 mmol), $AuBr_3$ (6.6 mg, 0.015 mmol) were stirred at room temperature for 2 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 40:2:1) afforded **4p** as a yellow solid in 61% (93.4 mg) yield. M.p. 123-125 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.4

Hz, 2H), 7.42-7.32 (m, 5H), 7.28-7.15 (m, 6H), 7.08 (d, J = 7.2 Hz, 2H), 7.01 (d, J = 8.0 Hz, 1H), 3.08 (s, 3H), 2.88 (t, J = 8.0 Hz, 2H), 2.58-2.55 (m, 2H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.6, 159.6, 146.3, 143.1, 141.4, 135.7, 133.7, 133.2, 132.9, 129.2, 128.9, 128.8, 128.3, 128.2, 128.12, 128.08, 127.8, 126.7, 125.9, 125.3, 120.9, 40.0, 36.2, 31.8, 21.4. IR (neat): 3060, 3029, 2964, 2924, 2851, 1597, 1443, 1347, 1152 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{31}H_{29}N_2O_3S$ $[M+H]^+$: 509.1893, found 509.1885.

When the reaction of ynamide **1c** with benzo[*d*]isoxazole **2i** was performed using $AuBr_3$ as the catalyst, a mixture of **4q** (47% yield) and **3s** (35% yield, *E*/*Z* = 0.33:1) was obtained.

Synthesis of spiro products.

The procedure for the reaction of 1c with 2a.

To a Schlenk tube were added ynamide **1c** (85.6 mg, 0.3 mmol), DCE (3 mL), benzo[*d*]isoxazole **2a** (70.3 mg, 0.36 mmol) and Me_2SAuCl (4.4 mg, 0.015 mmol) under Argon. After the reaction mixture was stirred at room temperature for 21.5 h as monitored by thin-layer chromatography, the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 40:2:1) to afford **4c** in 79% yield (113.7 mg) as a yellow solid and **5a** in 10% yield (13.9 mg) as a yellow solid.

***N*,4-Dimethyl-*N*-(10-oxo-1,4-diphenyl-2-azaspiro[4.5]deca-1,3,6,8-tetraen-3-yl)benzenesulfonamide (5a).** M.p. 194-196 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.0 Hz,

2H), 7.59-7.57 (m, 2H), 7.46-7.44 (m, 2H), 7.41-7.26 (m, 9H), 6.57 (dd, J = 9.6 Hz, 6.4 Hz, 1H), 6.49 (d, J = 10 Hz, 1H), 6.23 (d, J = 10 Hz, 1H), 3.11 (s, 3H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 192.2, 172.5, 151.6, 143.6, 143.0, 138.9, 135.3, 134.7, 131.7, 131.2, 130.7, 129.2, 128.8, 128.8, 128.7, 128.43, 128.39, 127.8, 127.5, 123.6, 75.9, 36.8, 21.6. IR (neat): 3071, 2972, 2932, 1655, 1590, 1345, 1168, 674 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{29}H_{25}N_2O_3S$ $[M+H]^+$: 481.1580, found 481.1570.

The procedure for the reaction of 1c with 2h.

To a Schlenk tube were added ynamide **1c** (85.6 mg, 0.3 mmol), DCE (3 mL), benzo[*d*]isoxazole **2h** (75.3 mg, 0.36 mmol) and Me_2SAuCl (4.4 mg, 0.015 mmol) under Argon. After the reaction mixture was stirred at room temperature for 7 h as monitored by thin-layer chromatography, the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:2:1 to 20:2:1) to afford **4r** in 79% yield (117.5 mg) as a yellow solid and **5b** in 18% yield (26.4 mg) as a yellow solid.

***N*,4-Dimethyl-*N*-(9-methyl-2,5-diphenylbenzo[*f*][1,4]oxazepin-3-yl)benzenesulfonamide (4r).** M.p. 202-204 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.2 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.45-7.32 (m, 5H), 7.26-7.22 (m, 4H), 7.12-7.09 (m, 3H), 7.05-7.03 (m, 1H), 3.07 (s, 3H), 2.40 (s, 3H), 2.06 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.3, 158.9, 147.7, 143.2, 138.3, 135.8, 134.5, 134.5, 133.3, 130.8, 130.4, 129.5, 129.4, 128.9, 128.3, 128.2, 127.9, 127.6, 127.1, 124.3, 36.9, 21.5, 16.4. IR (neat): 3066, 2922, 1600,

1561, 1440, 1342, 1159, 671 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{30}H_{27}N_2O_3S$ $[M+H]^+$: 495.1737, found 495.1726.

***N*,4-Dimethyl-*N*-(9-methyl-10-oxo-1,4-diphenyl-2-azaspiro[4.5]deca-1,3,6,8-tetraen-3-yl)benzenesulfonamide (5b).** M.p. 160-162 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.43-7.36 (m, 3H), 7.34-7.25 (m, 7H), 7.13 (d, *J* = 6.4 Hz, 1H), 6.48 (dd, *J* = 9.2 Hz, 6.0 Hz, 1H), 6.10 (d, *J* = 9.2 Hz, 1H), 3.11 (s, 3H), 2.45 (s, 3H), 2.03 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 192.5, 172.7, 151.2, 143.6, 139.3, 136.8, 136.2, 135.3, 135.1, 131.8, 131.1, 130.7, 129.2, 128.8, 128.6, 128.4, 128.3, 127.7, 127.4, 123.9, 75.5, 36.8, 21.6, 16.1. IR (neat): 3060, 2919, 1652, 1592, 1352, 1153, 1084, 672 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{30}H_{27}N_2O_3S$ $[M+H]^+$: 495.1737, found 495.1725.

The procedure for the reaction of 1c with 2g.

To a Schlenk tube were added ynamide **1c** (102.7 mg, 0.36 mmol), DCE (9 mL), benzo[*d*]isoxazole **2g** (44.7 mg, 0.3 mmol) and $AuBr_3$ (6.6 mg, 0.015 mmol) under Argon. After the reaction mixture was stirred at room temperature for 8 h as monitored by thin-layer chromatography, the mixture was filtered through a pad of silica gel, evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:2:1 to 10:2:1) to afford **5c** in 41% yield (53.4 mg) as a light yellow oil and **3q** in 26% yield (33.5 mg, E/Z = 0.56:1) as a yellow solid.

***N*-(1-Methoxy-10-oxo-4-phenyl-2-azaspiro[4.5]deca-1,3,6,8-tetraen-3-yl)-*N*,4-dimethyl benzenesulfonamide (5c).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.29-7.23 (m, 5H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.53 (dd, *J* = 9.2 Hz, 6.0 Hz, 1H), 6.31 (d, *J* = 10.0 Hz, 1H), 6.19 (d, *J* = 9.2 Hz, 1H), 3.75 (s, 3H), 3.08 (s, 3H), 2.42 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.2, 173.5, 147.9, 143.6, 143.0, 136.8, 135.1, 130.9, 129.0, 128.8, 128.5, 127.44, 127.39, 127.2, 126.6, 124.3, 70.7, 57.0, 36.4, 21.5. IR (neat): 3050, 2945, 1665, 1597, 1348, 1299, 1154, 971, 661 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{24}H_{23}N_2O_4S$ $[M+H]^+$: 435.1373, found 435.1364.

General procedure for the synthesis of 2*H*-benzo[*e*][1,3]oxazine 7.

Typical procedure for the synthesis of 7a.

To a Schlenk tube were added 1-phenylprop-2-yn-1-yl benzoate (106.3 mg, 0.45 mmol), DCE (3 mL), benzo[*d*]isoxazole **2a** (58.6 mg, 0.3 mmol) and $IPrAuNTf_2$ (catalyst **C**) (13.0 mg, 0.015 mmol) under Argon. After the reaction mixture was stirred at 80 °C for 24 h as monitored by thin-layer chromatography, the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) to afford **7a** in 75% yield (97.1 mg) as a white solid.

(*Z*)-2-Phenyl-1-(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-yl)vinyl benzoate (7a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.64-7.62 (m, 2H), 7.57 (t, *J* = 7.6 Hz, 1H),

7.49-7.41 (m, 7H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.23-7.15 (m, 4H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.91-6.85 (m, 2H), 6.47 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 165.1, 163.8, 155.6, 144.4, 136.4, 133.6, 133.5, 133.1, 130.1, 130.0, 129.0, 128.9, 128.8, 128.4, 128.3, 128.2, 127.89, 127.87, 121.3, 120.1, 118.2, 116.8, 85.9. IR (neat): 3058, 3027, 1732, 1605, 1448, 1240, 1062, 693 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{29}H_{22}NO_3$ $[M+H]^+$: 432.1594, found 432.1585.

(*Z*)-2-Phenyl-1-(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-yl)vinyl acetate (7b). Following the typical procedure, 0.3 mmol scale, 1-phenylprop-2-yn-1-yl acetate (78.4 mg, 0.45 mmol), 3 mL DCE, **2a** (58.6 mg, 0.3 mmol), catalyst **C** (13.0 mg, 0.015 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) afforded **7b** as light yellow oil in 43% (47.7 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.65 (m, 2H), 7.52-7.39 (m, 6H), 7.32-7.21 (m, 4H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.73 (s, 1H), 6.25 (s, 1H), 2.18 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 168.2, 165.2, 155.7, 144.2, 136.5, 133.7, 133.3, 130.1, 129.0, 128.8, 128.4, 128.3, 127.9, 127.9, 121.5, 119.9, 118.3, 116.8, 86.1, 20.9. IR (neat): 3061, 3027, 1759, 1605, 1192, 694 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{24}H_{20}NO_3$ $[M+H]^+$: 370.1438, found 370.1429.

(*Z*)-1-(4-Phenyl-2*H*-benzo[*e*][1,3]oxazin-2-yl)-2-(3,4,5-trimethoxyphenyl)vinyl benzoate (7c). Following the typical procedure, 0.3 mmol scale, **6c** (146.9 mg, 0.45 mmol), 3 mL DCE, **2a** (58.6 mg, 0.3 mmol), catalyst **C** (13.0 mg, 0.015 mmol) were

stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded **7c** as a white solid in 91% (141.7 mg) yield. M.p. 86-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.50-7.44 (m, 5H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.79 (s, 1H), 6.74 (s, 2H), 6.38 (s, 1H), 3.78 (s, 3H), 3.57 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.1, 163.7, 155.7, 152.7, 143.9, 137.7, 136.3, 133.64, 133.58, 130.00, 129.96, 128.9, 128.5, 128.4, 128.1, 127.8, 121.3, 119.8, 118.1, 116.7, 105.9, 86.1, 60.6, 55.5. IR (neat): 3061, 2999, 2937, 2833, 1735, 1605, 1580, 1234, 1124, 699 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{32}H_{28}NO_6$ $[M+H]^+$: 522.1911, found 522.1901.

(*Z*)-2-(4-Chlorophenyl)-1-(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-yl)vinyl benzoate (7d). Following the typical procedure, 0.3 mmol scale, **6d** (121.8 mg, 0.45 mmol), 3 mL DCE, **2a** (58.6 mg, 0.3 mmol), catalyst **C** (13.0 mg, 0.015 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded **7d** as light yellow oil in 65% (90.6 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.64-7.59 (m, 3H), 7.48-7.35 (m, 8H), 7.23-7.18 (m, 3H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.83 (s, 1H), 6.41 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.3, 163.8, 155.6, 145.1, 136.4, 133.7, 133.6, 131.7, 130.2, 130.1, 130.1, 129.0, 128.9, 128.60, 128.57, 128.3, 128.0, 121.5, 119.0, 118.3, 116.8, 85.9. IR (neat): 3061, 3033, 1733, 1605, 1491, 1240, 1062, 697 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{29}H_{21}ClNO_3$ $[M+H]^+$: 466.1204, found 466.1197.

2-Methyl-1-(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-yl)prop-1-en-1-yl benzoate (7e). Following the typical procedure, 0.3 mmol scale, 2-methylbut-3-yn-2-yl benzoate (169.4 mg, 0.9 mmol), 3 mL DCE, **2a** (58.6 mg, 0.3 mmol), catalyst **C** (13.0 mg, 0.015 mmol) were stirred at 65 °C for 9 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) afforded **7e** as light yellow oil in 47% (53.8 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.51-7.49 (m, 2H), 7.45-7.36 (m, 4H), 7.29-7.23 (m, 3H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.76 (s, 1H), 6.72 (t, *J* = 8.0 Hz, 1H), 2.06 (s, 3H), 1.69 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.5, 164.1, 155.9, 138.5, 136.5, 133.4, 132.9, 129.9, 129.6, 129.1, 128.7, 128.1, 128.0, 127.7, 126.1, 120.6, 117.2, 116.4, 84.2, 18.78, 18.76. IR (neat): 3063, 2996, 2917, 1736, 1604, 1451, 1239, 698 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{25}H_{22}NO_3$ $[M+H]^+$: 384.1594, found 384.1585.

(*Z*)-1-(4-(4-Methoxyphenyl)-2*H*-benzo[*e*][1,3]oxazin-2-yl)-2-phenylvinyl benzoate (7f). Following the typical procedure, 0.3 mmol scale, 1-phenylprop-2-yn-1-yl benzoate (212.6 mg, 0.9 mmol), 3 mL DCE, **2b** (67.6 mg, 0.3 mmol), catalyst **C** (13.0 mg, 0.015 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 15:1) afforded **7f** as light yellow oil in 52% (72.2 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.6 Hz, 2H), 7.63-7.58 (m, 3H), 7.48-7.43 (m, 4H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.28-7.15 (m, 4H), 6.98-6.90 (m, 4H), 6.84 (s, 1H), 6.41 (s, 1H), 3.84 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.5, 163.9, 161.2, 155.8, 144.6, 133.5,

133.4, 133.2, 130.7, 130.2, 129.1, 129.0, 128.9, 128.5, 128.4, 128.0, 127.9, 121.3, 120.1, 118.5, 116.9, 113.6, 85.8, 55.3. IR (neat): 3061, 2931, 2836, 1732, 1603, 1513, 1241, 1062, 706 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{30}H_{24}NO_4$ $[M+H]^+$: 462.1700, found 462.1692.

(*Z*)-1-(4-(4-Chlorophenyl)-2*H*-benzo[*e*][1,3]oxazin-2-yl)-2-phenylvinyl benzoate (7g). Following the typical procedure, 0.3 mmol scale, 1-phenylprop-2-yn-1-yl benzoate (106.3 mg, 0.45 mmol), 3 mL DCE, **2c** (68.9 mg, 0.3 mmol), catalyst **C** (13.0 mg, 0.015 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30:1) afforded **7g** as light yellow oil in 86% (120.2 mg) yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.59-7.56 (m, 3H), 7.48-7.34 (m, 7H), 7.23-7.14 (m, 4H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.83 (s, 1H), 6.43 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.0, 163.8, 155.7, 144.2, 136.2, 134.8, 133.8, 133.5, 133.0, 130.4, 130.1, 129.0, 128.8, 128.5, 128.3, 127.9, 127.5, 121.5, 120.1, 117.9, 116.9, 86.0. IR (neat): 3061, 3027, 1732, 1604, 1450, 1240, 1062, 705 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{29}H_{21}ClNO_3$ $[M+H]^+$: 466.1204, found 466.1197.

(*Z*)-1-(4-(2-Methoxyphenyl)-2*H*-benzo[*e*][1,3]oxazin-2-yl)-2-phenylvinyl benzoate (7h). Following the typical procedure, 0.3 mmol scale, 1-phenylprop-2-yn-1-yl benzoate (106.3 mg, 0.45 mmol), 3 mL DCE, **2d** (67.6 mg, 0.3 mmol), catalyst **C** (13.0 mg, 0.015 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1 to 7:1) afforded **7h** as light yellow oil in 38% (52.5 mg) yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H),

7.48-7.40 (m, 5H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.30-7.27 (m, 1H), 7.23-7.17 (m, 3H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.90-6.85 (m, 3H), 6.80 (t, *J* = 7.6 Hz, 1H), 6.61 (s, 1H), 3.73 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 164.6, 163.8, 157.1, 154.1, 144.2, 133.51, 133.47, 133.3, 130.7, 130.2, 129.9, 129.2, 128.8, 128.5, 128.4, 127.8, 127.8, 126.2, 121.2, 120.8, 120.4, 118.7, 116.5, 111.1, 86.2, 55.4. IR (neat): 3061, 2931, 2833, 1732, 1602, 1240, 1062, 706 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{30}H_{24}NO_4$ $[M+H]^+$: 462.1700, found 462.1691.

(*Z*)-1-(8-Methyl-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-yl)-2-phenylvinyl benzoate (7i). Following the typical procedure, 0.3 mmol scale, 1-phenylprop-2-yn-1-yl benzoate (106.3 mg, 0.45 mmol), 3 mL DCE, **2h** (62.8 mg, 0.3 mmol), catalyst **C** (13.0 mg, 0.015 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded **7i** as light yellow oil in 61% (81.3 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.66-7.58 (m, 3H), 7.50-7.42 (m, 7H), 7.25-7.15 (m, 4H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.90 (s, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 6.47 (s, 1H), 2.15 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 165.6, 163.9, 153.7, 144.6, 136.8, 134.9 133.6, 133.3, 130.2, 130.0, 129.1, 129.1 128.9, 128.5, 128.4, 128.2, 127.9, 126.1, 125.6, 120.7, 119.9, 118.0, 85.5, 15.0. IR (neat): 3058, 3027, 2917, 1732, 1599, 1240, 1062, 693 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{30}H_{24}NO_3$ $[M+H]^+$: 446.1751, found 446.1742.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org.

X-ray crystal structures and NMR spectra of all new compounds (PDF)

X-ray crystallography of compound *E*-**3b** (CIF)

X-ray crystallography of compound *Z*-**3i** (CIF)

X-ray crystallography of compound *E*-**3m** (CIF)

X-ray crystallography of compound *Z*-**3m** (CIF)

X-ray crystallography of compound *E*-**3r** (CIF)

X-ray crystallography of compound **4a** (CIF)

X-ray crystallography of compound **5b** (CIF)

X-ray crystallography of compound **7c** (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We thank the National Key Research and Development Program (2016YFA0202900), the National Natural Science Foundation of China (21572256), the Science and Technology Commission of Shanghai Municipality (18XD1405000), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB20000000), and the Shanghai Institute of Organic Chemistry (sioczz201807) for financial support.

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(13) It should be noted that these products were unstable upon column chromatography on silica gel. Fast column separation is required to obtain the pure sample that contains only **3s** and **4q**.

(14) As suggested by a reviewer, the reaction of **1c** with benzoisoxazoles bearing R^2 = H (**2i)** using IPrAuCl/$AgNTf_2$ or $AuCl_3$ as the catalyst were also examined. In the former case, a mixture of **3s** (12%, *E*/*Z* = 1:1) and **4q** (65%) were obtained. In the latter case, a mixture of **3s** (21%, *E*/*Z* = 0.43:1) and **4q** (26%) were obtained. The results suggested that the chemoselectivity could be altered through the change of the substrates bearing R^2 = H.

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