

Selective [5+1] and [5+2] Cycloaddition of Ynamides or Propargyl Esters with Benzo[d]isoxazoles via Gold Catalysis

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4 **Selective [5+1] and [5+2] Cycloaddition of Ynamides or Propargyl Esters with**
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7 **Benzo[*d*]isoxazoles via Gold Catalysis**
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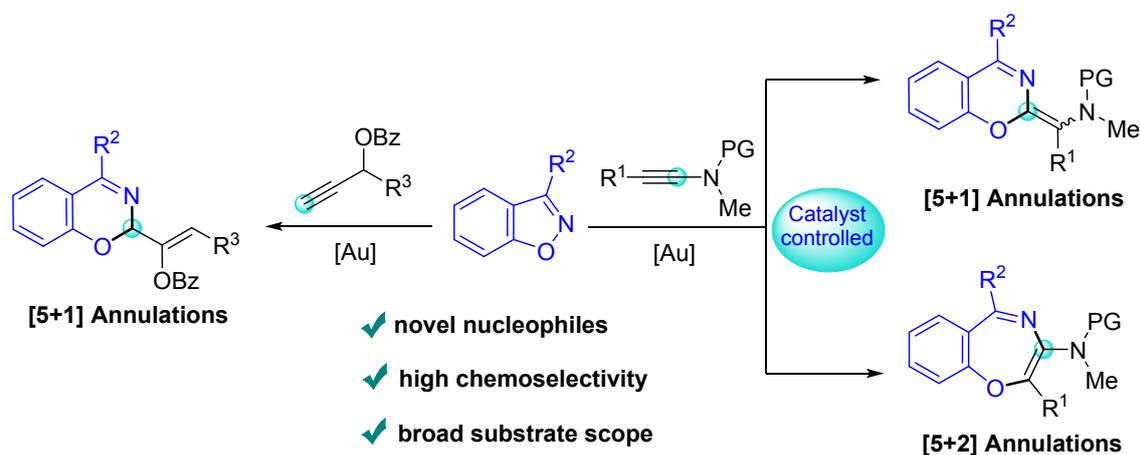
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51 **Abstract:** Benzo[*d*]isoxazoles are found to act as novel nucleophiles to undergo
52 gold-catalyzed [5+1] or [5+2] cycloaddition reactions with ynamides. The reaction
53 provides a concise and chemoselective access to polysubstituted
54 2*H*-benzo[*e*][1,3]oxazines or benzo[*f*][1,4]oxazepines. In addition,
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4 benzo[*d*]isoxazoles can also react with gold-carbene intermediates derived from
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7 propargyl esters to afford [5+1] annulation products.
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10 11 12 INTRODUCTION

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14 In recent years, gold-catalyzed reactions involving α -imino gold carbenes¹⁻⁵ have
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16 attracted extensive attention because of their high efficiency in constructing
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18 nitrogen-containing heterocyclic compounds. Up to now, many substrates (so called
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20 nucleophilic nitrenoids) which could initiate the generation of α -imino gold carbenes have
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22 been developed, including isoxazoles,¹ anthranils,² 2*H*-azirines,³ *N*-iminopyridium ylides⁴
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24 and triazapentalene,⁵ *et al.* Among them, isoxazoles and anthranils were two significant
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26 kinds of nucleophilic reagents since they could react with ynamides or propiolates to
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28 trigger efficient cycloaddition reactions. For example, Ye^{1a} and Liu^{1b} *et al* reported various
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30 catalytic annulations between isoxazoles and ynamides/propiolates to afford
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32 4-carbonyl-2-aminopyrroles or 2,4-dicarbonylpyrroles via [3+2] or [4+1] annulations,
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34 respectively (Scheme 1, eq 1). Hashmi^{2a} and Liu^{2b} *et al* found that anthranils could also
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36 cycloisomerize with ynamides/propiolates via [3+2] or [4+2] cycloaddition reactions
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38 (Scheme 1, eq 2). Of particular note is that isoxazoles and anthranils usually serve as
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40 three-atom or four-atom synthons in these reactions, affording the corresponding five- or
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42 six-membered nitrogen heterocycles. However, substrates which could act as more than
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44 four-atom building blocks in the cycloaddition reactions have rarely been reported.⁶
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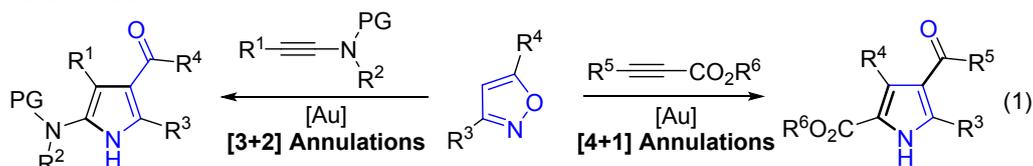
55
56 Benzo[*d*]isoxazoles are easily available heterocyclic substrates, which have been
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58 applied in a number of metal-catalyzed transformation reactions,⁷ such as the
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4 Rh-catalyzed [4+2] annulations with alkynes^{7a} and Lewis acid-catalyzed [4+2]
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6 annulations with propargylic alcohols.^{7b} However, to the best of our knowledge,
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8 benzo[*d*]isoxazoles have not been studied in gold-catalyzed reactions. We recently found
9
10 that 1,4,2-dioxazoles^{8a} and 4,5-dihydro-1,2,4-oxadiazoles^{8b} could be used as three-atom
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12 synthons to oxazoles and imidazoles. As our continuous interests in oxazole chemistry,
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14 herein, we report our success on gold-catalyzed cyclization of benzo[*d*]isoxazoles and
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16 ynamides, which provided an efficient and controllable synthesis of
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18 2*H*-benzo[*e*][1,3]oxazines or benzo[*f*][1,4]oxazepines through [5+1] or [5+2] cycloaddition
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20 reactions. Remarkably, a novel 1,2-amino migration⁹ of the ynamide substrate was
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22 observed during the [5+1] process. During the preparation of this paper, a gold-catalyzed
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24 cycloaddition reaction of ynamides and 1,2-benzisoxazoles without substituents on the
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26 isoxazole ring was reported by Liu's group.¹⁰ Compared with their work, our method
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28 accommodates with diversely benzo[*d*]isoxazoles bearing substituents on the isoxazole ring,
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30 and proceeds with generally higher chemoselectivity in the course of [5+1] annulation.
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32 Furthermore, we found that these substrates could also trap gold-carbene intermediates
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34 derived from propargyl esters,¹¹ leading to [5+1] cycloaddition products.
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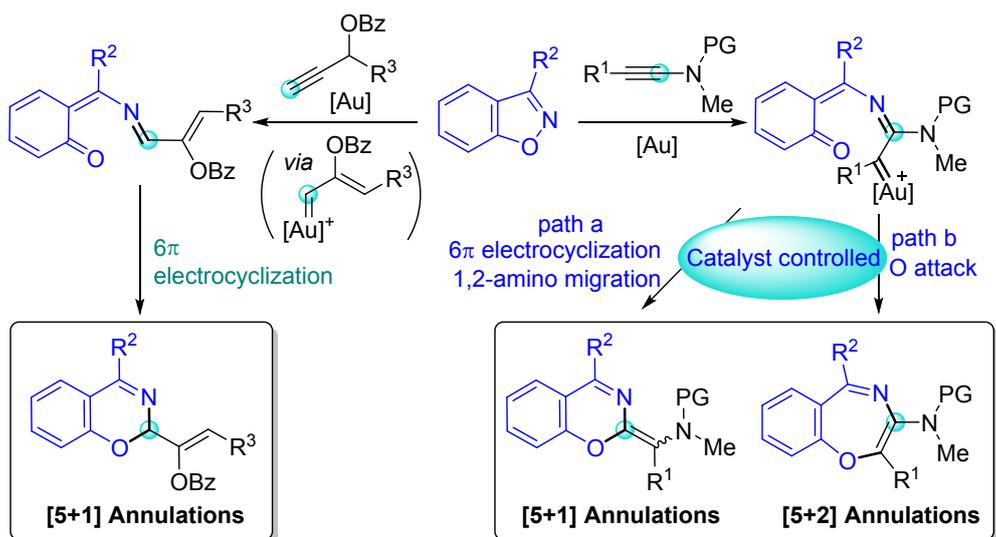
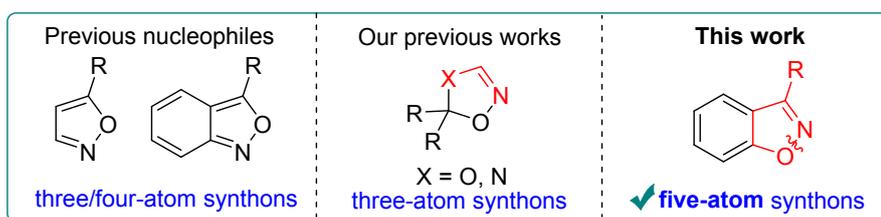
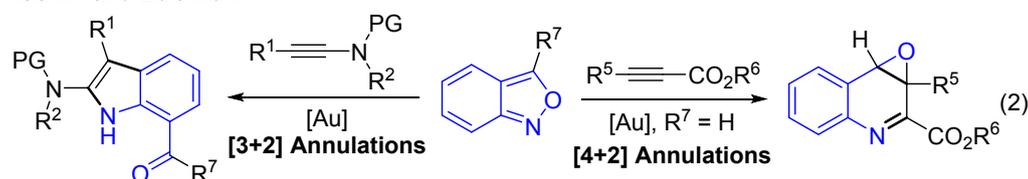
48 **Scheme 1.** Gold-catalyzed cycloaddition reactions with isoxazoles, anthranils and
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50 benzo[*d*]isoxazoles
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Previous work : annulations of isoxazoles and anthranils

Ye and Liu's work :



Hashmi and Liu's work :

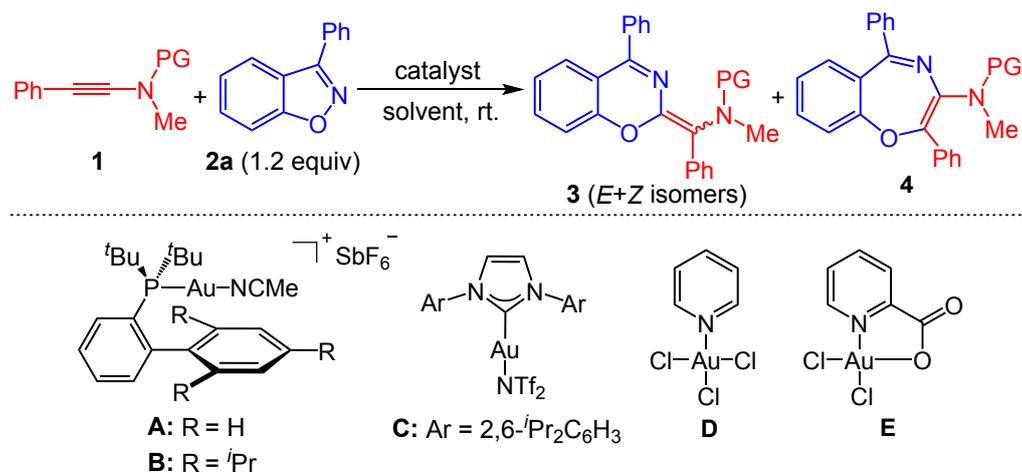


RESULTS AND DISCUSSION

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 $\text{PPh}_3\text{AuNTf}_2$ and $\text{PPh}_3\text{AuSbF}_6$ formed *in situ* afforded 2*H*-benzo[*e*][1,3]oxazine **3a** in 75-79% yields as

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4 a mixture of *E/Z* isomers (*E/Z* = 3.9:1-4:1), along with seven-membered heterocycle
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6 benzo[*f*][1,4]oxazepine **4a** in 13-14% yields (Table 1, entries 1-2). Apparently,
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8 benzo[*d*]isoxazole **2a** was served as distinctive five-atom synthons in this reaction to
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10 deliver the products **3** or **4** via [5+1] or [5+2] annulations, respectively. Interestingly, a
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12 1,2-amino group migration^{9,10} was also observed in the formation of product **3**.
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14 Considering the steric and electronic effects of ligands could influence the reaction greatly,
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16 we then chose JohnphosAu(MeCN)SbF₆ (catalyst **A**) as the catalyst. It was found that **3a**
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18 could be formed in 93% yield (*E/Z* = 7.5:1) within 6 h (Table 1, entry 3). Under this
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20 condition, **4a** was formed in only 3% yield. When gold catalyst **B** with a bulky ^tBuXphos
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22 as the ligand was used, the reaction was suppressed greatly, affording *E*-**3a** in 15% yield
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24 after 24 h (Table 1, entry 4). When *N*-heterocyclic carbene gold(I) complex **C** was
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26 employed as the catalyst, the yield of **3a** was increased to 91%, along with **4a** in 3% yield
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28 (Table 1, entry 5). The reaction also proceeded smoothly in various solvents like THF,
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30 DCM, MeCN and toluene, with the yields of **3a** in the range of 55-87% and **4a** in < 6%
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32 yields (Table 1, entries 6-9). The catalytic activity of gold(III) complex such as
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34 pyridine-ligated AuCl₃ was also tested and only 14% yield of **4a** was obtained (Table 1,
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36 entry 10). When PicAuCl₂ (catalyst **E**) was used as the catalyst at 50 °C, the yield of **4a**
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38 could be increased to 58% without the formation of **3a** (Table 1, entry 11). Switching the
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40 catalyst to simple gold(III) salt of AuBr₃ gave **3a** in a higher yield of 66% (Table 1, entry
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42 12). We found that substrate **1a** could slowly decompose in the presence of AuBr₃.
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44 To improve the yield of **4a**, 2.0 equiv of **2a** was added under the dilute reaction
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46 conditions (0.033 M). However, the yield of **4a** was improved slightly (Table 1,
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4 entry 13). After turning the ratio of **1a**: **2a** to 1.2: 1, the yield of **4a** could be
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6 increased to 79% (Table 1, entry 14). Employing AgSbF₆ alone or Brønsted acid of
7
8 HNTf₂ as the catalyst did not afford desired products, with recovered **1a** in 99% and
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10 45% yields, respectively (Table 1, entries 15-16). The reaction could not proceed
11
12 without any catalyst, even at 50 °C for 24 h (Table 1, entry 17). Then the effects of
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14 the protecting groups on nitrogen were examined. In the presence of catalyst **A**,
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16 mesyl-protected substrate **1b** and tosyl-protected substrate **1c** gave the
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18 corresponding product **3b** and **3c** in 82% and 92% yields, respectively (Table 1,
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20 entries 18-19). In addition, when substrate **1c** was tested under the catalysis of
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22 AuBr₃, **4c** could be isolated in 80% yield (Table 1, entry 20). After careful
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24 separation of isomers through recrystallization or column chromatography, the
25
26 structure of benzo[*e*][1,3]oxazines **3** was confirmed by X-ray crystallographic
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28 analyses of the analogous products of *E*-**3b**, *Z*-**3i**, *E*-**3m**, *Z*-**3m**, *E*-**3r**, and product **4**
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30 was also confirmed by X-ray crystallographic analysis of **4a**.¹²
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Table 1. Optimization of the Reaction Conditions

entry	PG	catalyst (mol %)	solvent	time(h)	yields (%) ^a		
					3 (E:Z)	4	1a
1	SO ₂ PMP (1a)	PPh ₃ AuNTf ₂ (5)	DCE	3	75 (4:1)	13	-
2	1a	PPh ₃ AuCl/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	-

^aAll the reactions were carried out on 0.3 mmol scale (0.1 M). PMP = *p*-methoxyphenyl.

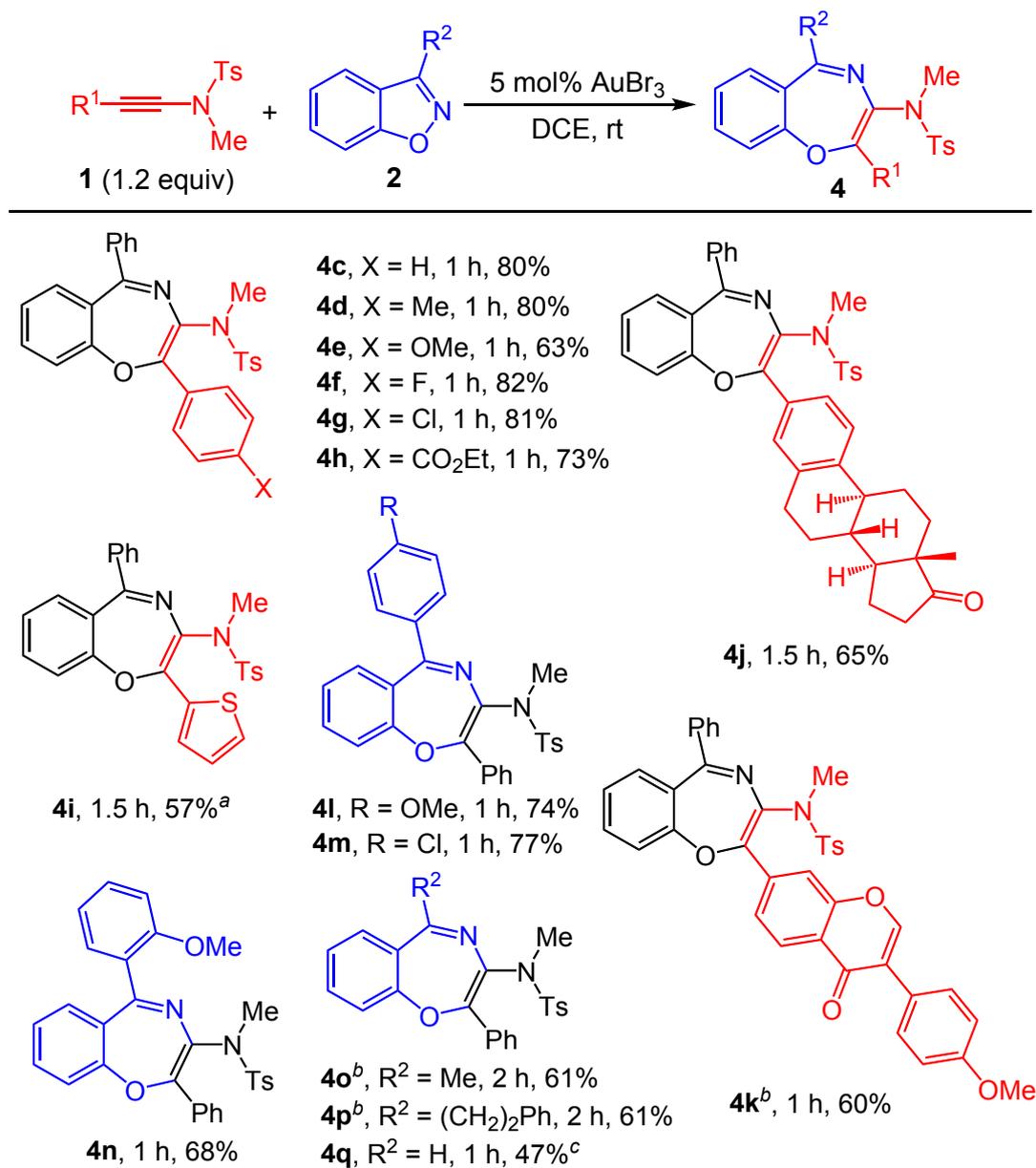
¹H NMR yields using 1,3,5-trimethoxybenzene as an internal standard. ^b50 °C. ^c0.033 M in DCE. 2.0 equiv of 2a was used. ^d0.033 M in DCE. 1.2 equiv of 1a and 1.0 equiv of 2a were used. ^eIsolated yields.

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).

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4 The scope of ynamides with the aryl substituents on R¹ group was first studied.
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7 Electron-donating groups such as *p*-methyl and *p*-methoxy on the aryl ring gave **3d** and **3e**
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9 in lower yields of 63-67%, along with the formation of **4** in 20-25% yields. The results
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11 indicated that the chemoselectivity was decreased between [5+1] and [5+2] cycloaddition
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13 mode in these cases. Electron-withdrawing groups such as *p*-F, *p*-Cl and *p*-CO₂Et on the
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15 aryl ring tolerated well in the reaction, giving **3f-3h** in 49-93% yields.
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18 Heteroaryl-substituted ynamides such as 2-thienyl-containing substrate reacted efficiently
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20 to furnish **3i** in 78% yield. According to the above results, it was noted that the
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22 stereoselectivity was decreased (**3d**) or opposite (**3e** and **3i**) when ynamides bearing
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24 electron-rich aryl groups were employed as the substrates. Besides, ynamide with an
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26 1,3,5(10)-estratrien-3-ol-17-one derivative was also compatible, giving **3j** in a yield of
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28 65%. The reaction can be extended to alkyl-substituted ynamides such as
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30 cyclopropyl-substituted **1k**, with the formation of **3k** in an excellent yield of 95%.
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33 Subsequently, we investigated the scope of benzo[*d*]isoxazoles using **1c** as the reaction
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35 partner. It was found that both electron-donating groups (*p*-OMe) and
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37 electron-withdrawing groups (*p*-Cl) on aryl ring were suitable for this reaction, leading to
38
39 **3l** and **3m** in high yields. Sterically encumbered *o*-OMe substituted aryl benzo[*d*]isoxazole
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41 reacted efficiently to afford **3n** in 94% yield. Alkyl-substituted benzo[*d*]isoxazoles with
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43 methyl or 2-phenethyl groups turned out to be perfect substrates, giving **3o** and **3p** in yields
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45 of 91% and 85%, respectively. In addition, when the R² substituent is a methoxy group, **3q**
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47 could be formed in 88% yield. The parent phenyl ring substituted with a methyl group was
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49 also suitable for this transformation, furnishing the single isomer *E*-**3r** in 87% yield. This
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7 Next, the scope of [5+2] cycloaddition reaction was tested by using 5 mol% AuBr₃ as
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9 the catalyst in DCE at room temperature (Scheme 3). We first examined the electronic
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11 effect of R¹ substituents on ynamides. Substrates bearing both electron-donating groups
12
13 (*p*-Me and *p*-OMe) and electron-withdrawing groups (*p*-F, *p*-Cl and *p*-CO₂Et) on the aryl
14
15 ring were compatible in the reactions, furnishing **4d-4h** in 63-82% yields. In the case of
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17 2-thienyl-substituted ynamides, **4i** could be formed in 57% yield, along with the formation
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19 of *Z*-**3i** in 14% yield. Ynamide with an 1,3,5(10)-estratrien-3-ol-17-one derivative or
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21 formononetin moiety also reacted efficiently (**4j** and **4k**). Then the effect of R² substituents
22
23 on benzo[*d*]isoxazoles were examined. Substrates bearing *p*-OMe, *p*-Cl and *o*-OMe groups
24
25 on the aryl ring resulted in **4l-4n** in 68-77% yields. Benzo[*d*]isoxazoles with alkyl
26
27 substituents such as methyl and 2-phenethyl on R² group could also react with **1c** smoothly
28
29 (**4o** and **4p**). When the R² substituent is a hydrogen group, the chemoselectivity was
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31 decreased, affording a mixture of **3s** (35%) and **4q** (47%).¹⁴
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43 **Scheme 3.** Scope of Gold-Catalyzed [5+2] Annulations with Ynamides
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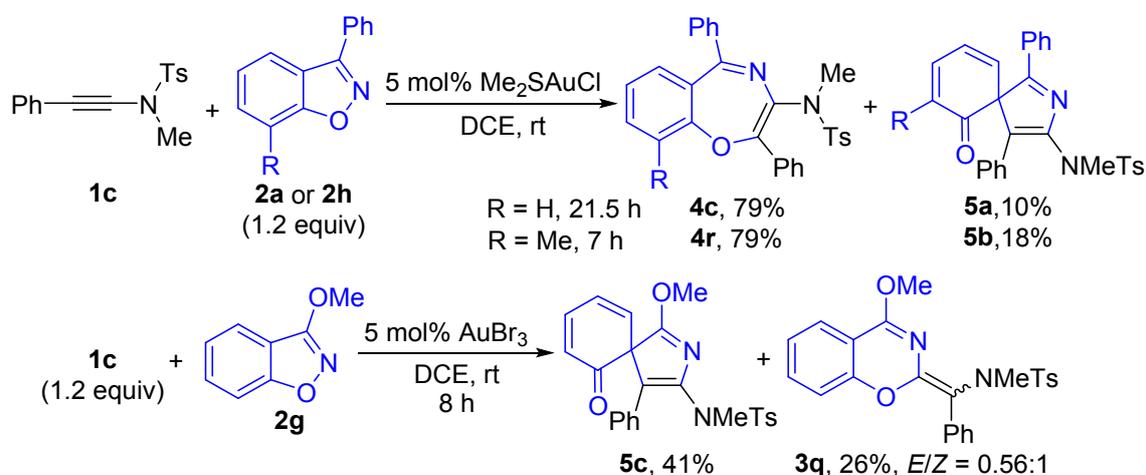


^aZ-**3i** was also isolated in 14% yield. ^b1.0 equiv of **1** and 2.0 equiv of **2** were used. ^cAs a mixture of **3s** (35%, *E/Z* = 0.33:1) and **4q**.

Interestingly, when Me₂SAuCl 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 AuBr₃, 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**.

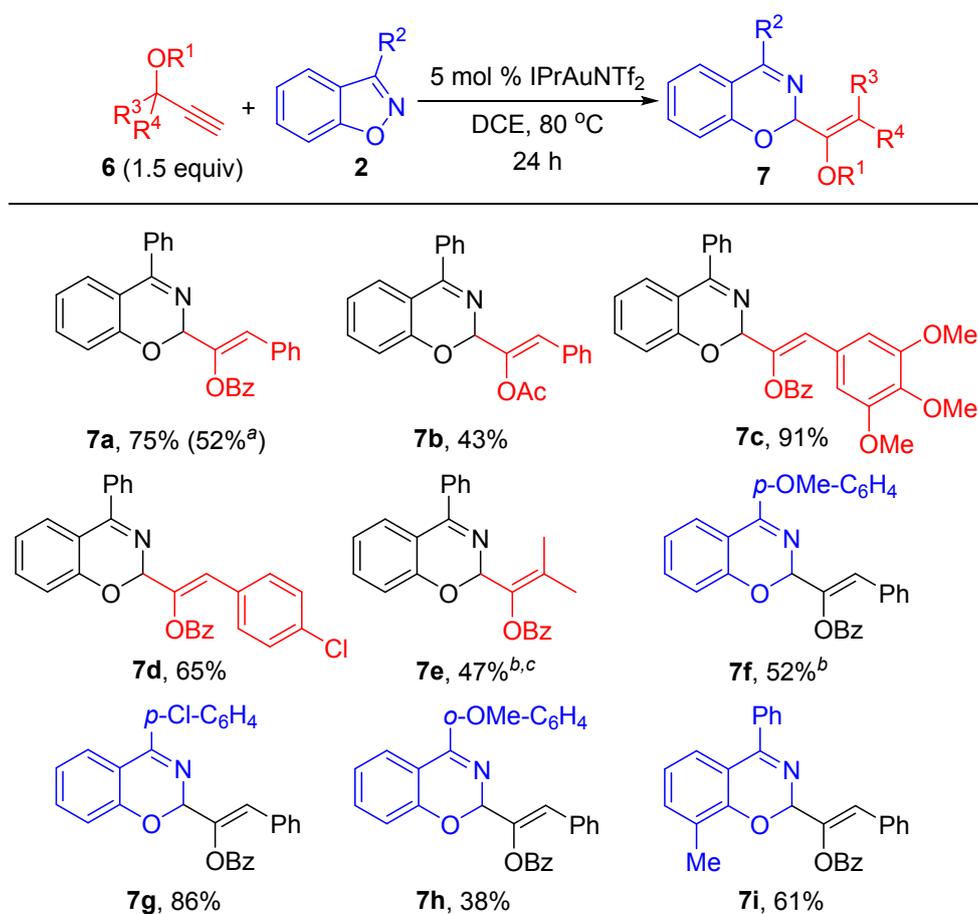
Scheme 4. Formation of Spiro Products



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)SbF₆ (catalyst **A**) in DCE at 80 °C for 24 h. After a brief screening on reaction conditions, it was found that the use of IPrAuNTf₂ 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

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4 47%. For aryl-substituted benzo[*d*]isoxazoles, the corresponding products **7f-7i** were
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7 formed in 38-86% yields. The structure of **7c** was confirmed by X-ray crystallographic
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9 analysis.

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

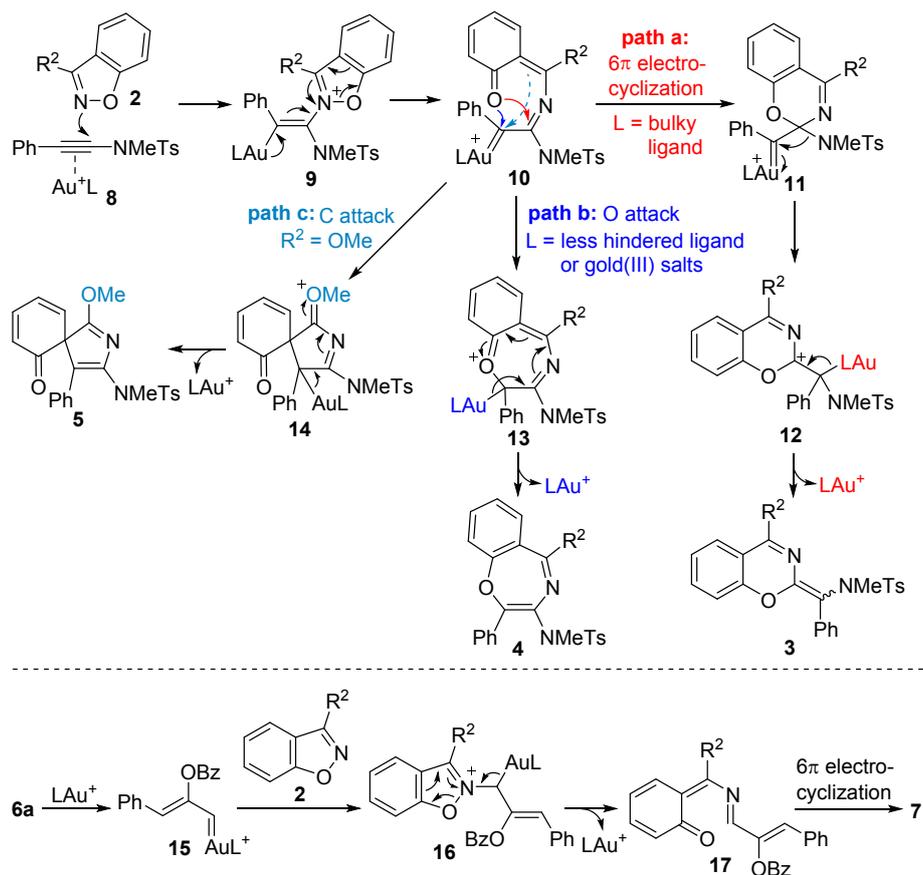


46 ^a5 mol % catalyst **A** was used as the catalyst. ^b3 equiv of **6** was used. ^c65 °C for 9 h.

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51 On the basis of the above results and our previous work, a possible reaction mechanism
52 is given in Scheme 6. Attack of the imino nitrogen to ynamide activated by gold affords
53 vinyl gold intermediate **9**, which fragmentizes into the α -imino gold-carbene **10**. Then
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59 there are three possible pathways: In path a, with a bulky ligand, **11** is formed through 6π
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4 electrocyclization. 1,2-amino group migration followed by elimination of the catalyst
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7 affords the products **3**. In path b, O-attack to gold-carbene occurs to furnish intermediate
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10 **13**. This is followed by elimination of the gold catalyst to give the product **4**. It is
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12 suggested that the O-attack process could be facilitated through the decrease of the steric
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14 interaction between the gold-carbene and the carbonyl group caused by the less hindered
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16 ligand on gold or increasing the electrophilic reactivity of gold-carbene by the use of
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18 gold(III) salts with stronger Lewis acidity. In path c, C-attack to the carbene center occurs
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20 due to the nucleophilicity of the exocyclic double bond, especially when OMe-substituted
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22 benzo[*d*]isoxazole **2g** is used. Elimination of the gold catalyst gives the spiro product **5**
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24 (Scheme 6). When propargyl esters are used as the substrates, gold-carbene intermediate **15**
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26 is generated through 1,2-acyloxy migration.¹¹ This is followed by the nucleophilic attack of
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28 nitrogen on benzo[*d*]isoxazole to deliver intermediate **16**. Elimination of the gold catalyst
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30 followed by 6π electrocyclization affords the products **7** (Scheme 6).
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41 **Scheme 6.** Possible Reaction Mechanism 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60



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 CaH₂. 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 AgSbF₆ were purchased from Stream Chemicals. Gold complex **B** was prepared by stirring the [Au(L)Cl] complex and AgSbF₆ in MeCN at room temperature overnight.¹⁵ Gold complex **C**,¹⁶ PPh₃AuCl¹⁷ and PPh₃AuNTf₂¹⁸ were prepared according to the published methods. PicAuCl₂ (catalyst **E**) and HNTf₂ were purchased from Aldrich Chemical Company. AuBr₃ 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 ¹³C NMR spectra were recorded at room temperature in CDCl₃ (containing 0.03% TMS) or CDCl₃ (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, ¹³C NMR spectra was recorded at 100 MHz. ¹H NMR spectra was recorded with tetramethylsilane ($\delta = 0.00$ ppm) as internal reference in CDCl₃; ¹³C NMR spectra was recorded with CDCl₃ ($\delta = 77.00$ 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

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4 were obtained by using a Nicolet iS10 spectrometer. Melting points were measured using a
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7 SGW-4 microscopic melting point apparatus and were uncorrected. Single crystal X-ray
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10 diffraction data were collected at 296(2) K for *E*-**3b**, *E*-**3m**, **4a**, **7c** and 173(2) for *Z*-**3i**,
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13 *Z*-**3m**, *E*-**3r**, **5b** on a Bruker APEX-II diffractometer or Bruker SMART diffractometer
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15 with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$).
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20 Ynamides **1** were synthesized according to published methods.¹⁶
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22 For the characterization of new ynamide substrates, see following:
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28 **Ethyl 4-(((*N*,4-dimethylphenyl)sulfonamido)ethynyl)benzoate (**1h**).** 3 mmol scale.
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30 Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1)
31
32 afforded the title product as a white solid in 86% (925.3 mg) yield. ¹H NMR (400 MHz,
33
34 CDCl₃) 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* =
35
36 7.2 Hz, 2H), 3.18 (s, 3H), 2.46 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H). ¹³C {¹H} NMR (100 MHz,
37
38 CDCl₃) 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
40 39.1, 21.6, 14.2. IR (neat): 2979, 2945, 2901, 2228, 1712, 1604, 1359, 1164 cm⁻¹. HRMS
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42 (ESI-TOF) calcd for C₁₉H₂₀NO₄S [M+H]⁺: 358.1108, found 358.1102.
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51 **Synthesis of 1j.**

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53 To a solution of 1,3,5(10)-estratrien-3-ol-17-one (5.407 g, 20 mmol) in DCM (80 mL)
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55 was added pyridine (3.2 mL, 40 mmol). Then Tf₂O (4.0 mL, 24 mmol, diluted with 40 mL
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57 DCM) was added dropwise to the mixture at 0 °C. The resulting solution was warmed up
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4 to room temperature and stirred for 3 h. Then the mixture was quenched with saturated
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6 ammonium chloride solution, extracted with dichloromethane, and dried over anhydrous
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8 Na₂SO₄. The solvent was evaporated under the reduced pressure and the residue was
9
10 purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate =
11
12 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-
13
14 6*H*-cyclopenta[*a*]phenanthren-3-yl trifluoromethanesulfonate (**s1-1j**) in 94% yield (7.535
15
16 g) as a white solid.
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18
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20
21

22 To a solution of the above **s1-1j** (7.445 g, 18.5 mmol) in triethylamine (16 mL) and
23
24 DMF (40 mL) were added ethynyltrimethylsilane (2.18 g, 22.2 mmol) and Pd(PPh₃)₂Cl₂
25
26 (779.1 mg, 1.11 mmol) at room temperature. Then the mixture was stirred at 50 °C for 5 h.
27
28 After the starting material was consumed, the reaction mixture was quenched with 3 N HCl
29
30 solution, extracted with dichloromethane, washed with water and brine followed by drying
31
32 over anhydrous Na₂SO₄. The solvent was evaporated under the reduced pressure and the
33
34 residue was purified by column chromatography on silica gel (eluent: petroleum ether:
35
36 ethyl acetate = 8:1 to 5:1) to afford compound
37
38 (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((trimethylsilyl)ethynyl)-6,7,8,9,11,12,13,14,15,16-decahydr
39
40 o-17*H*-cyclopenta[*a*]phenanthren-17-one (**s2-1j**) (4.9 g, 76%) as a yellow solid.
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48 To a solution of the above **s2-1j** (4.9 g, 14 mmol) in THF (45 mL) was added TBAF
49
50 (15.4 mL, 1M in THF, 15.4 mmol) at 0 °C. The resulting solution was warmed up to room
51
52 temperature and stirred for 1 h. Then the mixture was quenched with water, extracted with
53
54 dichloromethane, and dried over anhydrous Na₂SO₄. The solvent was evaporated under the
55
56 reduced pressure and the residue was purified by chromatography on silica gel (eluent:
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4 petroleum ether: ethyl acetate: dichloromethane = 10:1:1) to afford
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7 (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*-cyclopent
8
9
10 a[*a*]phenanthren-17-one (**s3-1j**) in 46% yield (1.792 g) as a white solid.

11
12 To a solution of **s3-1j** (1.058 g, 3.8 mmol) in acetone (20 mL) were added
13
14 *N*-bromosuccinimide (811.6 mg, 4.56 mmol) and AgNO₃ (32.3 mg, 0.19 mmol) at room
15
16 temperature. The mixture was stirred at the same temperature for 12 h. The reaction
17
18 mixture was diluted with hexane and filtered through a pad of celite using dichloromethane
19
20 as an eluent. The filtrate was collected and evaporated under the reduced pressure, the
21
22 residue was purified by column chromatography on silica gel (eluent: petroleum
23
24 ether/ethyl acetate/dichloromethane = 5:1:1) to afford compound
25
26
27 (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*-c
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cyclopenta[*a*]phenanthren-17-one (**s4-1j**) (1.053 g, 78%) as a white solid.

36 To a dry flask were added *N*,4-dimethylbenzenesulfonamide (222.3 mg, 1.2 mmol),
37
38 anhydrous toluene (10 mL), CuSO₄·5H₂O (25.0 mg, 0.1 mmol), 1,10-phenanthroline (36.0
39
40 mg, 0.2 mmol) and K₂CO₃ (276.4 mg, 2 mmol). Then **s4-1j** (357.3 mg, 1 mmol) was
41
42 added, and the resulting mixture was stirred at 80 °C for 48 h under an atmosphere of
43
44 argon. When the reaction was complete, the crude mixture was cooled down to room
45
46 temperature, filtered through celite and washed with ethyl acetate. After solvent
47
48 evaporation, the residue was purified by column chromatography on silica gel (eluent:
49
50 petroleum ether: ethyl acetate: dichloromethane = 10:1:1) to afford compound **1j** (323.4
51
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56 mg, 70%) as a white solid.

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4 ***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-decah**
5 **ydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)ethynyl)benzenesulfonamide (1j).** M.p.
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7
8
9 177-179 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz,
10 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,
11 5H), 2.30-2.26 (m, 1H), 2.19-1.95 (m, 4H), 1.66-1.38 (m, 6H), 0.91 (s, 3H).; ¹³C{¹H}
12 NMR (100 MHz, CDCl₃) δ 220.7, 144.7, 139.8, 136.5, 133.1, 131.9, 129.7, 128.7, 127.8,
13 125.2, 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,
14 21.5, 13.7. IR (neat): 2961, 2932, 2875, 2236, 1731, 1597, 1456, 1365, 1168, 721 cm⁻¹.
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25 HRMS (ESI-TOF) calcd for C₂₈H₃₂NO₃S [M+H]⁺: 462.2097, found 462.2096.
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30 **Synthesis of 1l.**

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32
33 To a solution of 7-hydroxy-3-(4-methoxyphenyl)-4*H*-chromen-4-one (4.292 g, 16
34 mmol) in DCM (60 mL) was added pyridine (2.6 mL, 32 mmol). Then Tf₂O (3.2 mL, 19.2
35 mmol, diluted with 30 mL DCM) was added dropwise to the mixture at 0 °C. The resulting
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To a solution of the above **s2-11** in triethylamine (16 mL) and DMF (40 mL) were

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4 added ethynyltrimethylsilane (1.886 g, 19.2 mmol) and Pd(PPh₃)₂Cl₂ (673.8 mg, 0.96
5
6 mmol) at room temperature under Argon. Then the mixture was stirred at 50 °C for 3.5 h.
7
8
9 After the starting material was consumed, the reaction mixture was quenched with 3 N HCl
10
11 solution, extracted with dichloromethane, washed with water and brine followed by drying
12
13 over anhydrous Na₂SO₄. The solvent was evaporated under the reduced pressure and the
14
15 residue was purified by column chromatography on silica gel (eluent: petroleum ether:
16
17 ethyl acetate: dichloromethane = 10:1:1) to afford compound
18
19 3-(4-methoxyphenyl)-7-((trimethylsilyl)ethynyl)-4*H*-chromen-4-one (**s3-11**) which was
20
21 directly used in the following reaction.
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27
28 To a solution of the above **s3-11** in MeOH (100 mL) was added K₂CO₃ (663.4 mg, 4.8
29
30 mmol) at room temperature and stirred for 2 h. Then the mixture was quenched with water
31
32 and MeOH was evaporated under the reduced pressure. The residue was extracted with
33
34 dichloromethane, washed with brine and dried over anhydrous Na₂SO₄. The solvent was
35
36 evaporated under the reduced pressure and the residue was purified by chromatography on
37
38 silica gel (eluent: petroleum ether: dichloromethane = 2:1) to afford
39
40 7-ethynyl-3-(4-methoxyphenyl)-4*H*-chromen-4-one (**s4-11**) in 38% (3 steps) yield (1.68 g)
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42 as a white solid.
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48
49 To a solution of **s4-11** (663.1 mg, 2.4 mmol) in acetone (15 mL) were added
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51 *N*-bromosuccinimide (469.9 mg, 2.64 mmol) and AgNO₃ (40.8 mg, 0.24 mmol) at room
52
53 temperature. The mixture was stirred at the same temperature for 8 h. The solution was
54
55 evaporated under the reduced pressure and the residue was quenched with saturated NH₄Cl
56
57 solution, extracted with dichloromethane, washed with brine and dried over anhydrous
58
59
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4 Na₂SO₄. The solution was evaporated under the reduced pressure and the residue was
5
6 filtered through a pad of silica gel. The crude product
7
8 7-(bromoethynyl)-3-(4-methoxyphenyl)-4*H*-chromen-4-one (**s5-11**) was used directly
9
10
11 without further purification.
12
13

14
15 To a dry flask were added *N*,4-dimethylbenzenesulfonamide (533.5 mg, 2.88 mmol),
16
17 anhydrous toluene (20 mL), CuSO₄·5H₂O (59.9 mg, 0.24 mmol), 1,10-phenanthroline
18
19 (86.5 mg, 0.48 mmol) and K₂CO₃ (663.4 mg, 4.8 mmol). Then **s5-11** was added, and the
20
21 resulting mixture was stirred at 80 °C for 14 h under an atmosphere of argon. When the
22
23 reaction was complete, the crude mixture was cooled down to room temperature, filtered
24
25 through celite and washed with ethyl acetate. The mixture was washed with 10% NaOH
26
27 solution, brine and dried over anhydrous Na₂SO₄. After solvent evaporation, the residue
28
29 was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl
30
31 acetate: dichloromethane = 10:1:1 to dichloromethane) to afford compound **11** (522.7 mg,
32
33 47% for 2 steps) as a light yellow solid.
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43 ***N*-((3-(4-Methoxyphenyl)-4-oxo-4*H*-chromen-7-yl)ethynyl)-*N*,4-dimethylbenzenesulfo**
44
45 **namide (11)**. M.p. 158-160 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 8.4 Hz, 1H),
46
47 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,
48
49 *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); ¹³C{¹H}
50
51 NMR (100 MHz, CDCl₃) δ 175.6, 159.5, 155.7, 152.4, 145.1, 132.9, 129.9, 128.3, 127.6,
52
53 127.2, 126.1, 124.9, 123.7, 123.1, 119.4, 113.8, 88.0, 68.6, 55.1, 39.0, 21.5. IR (neat):
54
55 3066, 2937, 2841, 2239, 1637, 1619, 1358, 1165 cm⁻¹. HRMS (ESI-TOF) calcd for
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4 $C_{26}H_{22}NO_5S$ [M+H]⁺: 460.1213, found 460.1210.
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9 **General procedure for the synthesis of benzo[d]isoxazoles 2.**

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11
12 **Method A : For 2a-2d**¹⁹

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14
15 **Typical procedure for the synthesis of 3-phenylbenzo[d]isoxazole 2a.**

16
17 To a solution of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (2.984 g, 10 mmol)
18 in MeCN (60 mL) was added CsF (4.56 g, 30 mmol). Then *N*-hydroxybenzimidoyl
19 chloride (777.9 mg, 5 mmol) in MeCN (60 mL) was added slowly to the reaction mixture
20 at room temperature within 4 h and stirred for another 2 h. After the reaction was
21 completed, the solvent was evaporated under the reduced pressure and the residue was
22 quenched with brine, extracted with dichloromethane, washed with brine and dried over
23 anhydrous Na₂SO₄. The solvent was evaporated under the reduced pressure and the residue
24 was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl
25 acetate = 40:1) to obtain a light yellow solid. The product was washed with a small amount
26 of pentane to afford **2a** (630.7 mg, 65%) as a white solid. This compound can also be
27 synthesized by method B.
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48 **Method B : For 2e, 2f, 2h**²⁰

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

52
53 To a solution of NH₃ in MeOH (7 mL, 7 M) was added
54 1-(2-hydroxyphenyl)ethan-1-one (1.362 g, 10 mmol) and stirred at room temperature for 2
55 h. Then MeOH was evaporated under the reduced pressure to afford a yellow solid.
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4 Subsequently, to a solution of the above product in THF (30 mL) was added
5
6 *N*-chlorosuccinimide (2.003 g, 15 mmol) and K₂CO₃ (2.764 g, 20 mmol) and stirred at
7
8 room temperature for 15 h. The mixture was quenched with H₂O, extracted with ethyl
9
10 acetate, washed with brine and dried over anhydrous Na₂SO₄. The solvent was evaporated
11
12 under the reduced pressure and the residue was purified by column chromatography on
13
14 silica gel (eluent: petroleum ether: ethyl acetate = 100:1) to afford **2e** (487.2 mg, 37%) as
15
16 light yellow oil.
17
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24

25 **3-Phenylbenzo[*d*]isoxazole (2a).** Method A was used. ¹H NMR (400 MHz, CDCl₃) δ
26
27 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).
28
29 ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 163.8, 157.2, 130.2, 129.7, 129.1, 128.9, 128.0, 123.8,
30
31 122.1, 120.4, 110.1. The spectroscopic data is in agreement with that previously reported.²¹
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37

38 **3-(4-Methoxyphenyl)benzo[*d*]isoxazole (2b).** Method A was used. 4 mmol scale. Column
39
40 chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 40:1) followed by
41
42 washing with pentane afforded the title product in 73% yield (660.5 mg) as a white solid).
43
44 ¹H NMR (400 MHz, CDCl₃) δ 7.92-7.89 (m, 3H), 7.63-7.54 (m, 2H), 7.37-7.33 (m, 1H),
45
46 7.08-7.05 (m, 2H), 3.87 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 163.6, 161.1, 156.7,
47
48 129.6, 129.3, 123.6, 122.2, 121.2, 120.5, 114.5, 110.0, 55.3. The spectroscopic data is in
49
50 agreement with that previously reported.²¹
51
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59 **3-(4-Chlorophenyl)benzo[*d*]isoxazole (2c).** Method A was used. 4 mmol scale. Column
60

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4 chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) followed by
5
6
7 washing with pentane afforded the title product in 53% yield (484.5 mg) as a light yellow
8
9 solid). ^1H NMR (400 MHz, CDCl_3) δ 7.91-7.86 (m, 3H), 7.65-7.57 (m, 2H), 7.53-7.51 (m,
10
11 2H), 7.39-7.35 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 163.8, 156.2, 136.3, 129.9,
12
13 129.4, 129.2, 127.3, 124.0, 121.8, 120.1, 110.2. The spectroscopic data is in agreement
14
15 with that previously reported.²²
16
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22 **3-(2-Methoxyphenyl)benzo[*d*]isoxazole (2d)**. Method A was used. 4 mmol scale. Column
23
24 chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the
25
26 title product in 85% yield (761.7 mg) as light yellow oil). ^1H NMR (400 MHz, CDCl_3) δ
27
28 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),
29
30 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),
31
32 7.08-7.01 (m, 2H), 3.78 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 163.0, 157.2, 156.3,
33
34 131.5, 131.0, 129.3, 123.3, 123.0, 121.6, 120.7, 117.3, 111.2, 109.5, 55.2. The
35
36 spectroscopic data is in agreement with that previously reported.²¹
37
38
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42

43 **3-Methylbenzo[*d*]isoxazole (2e)**. Method B was used. ^1H NMR (400 MHz, CDCl_3) δ 7.63
44
45 (d, J = 8.0 Hz, 1H), 7.54-7.51 (m, 2H), 7.32-7.27 (m, 1H), 2.58 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR
46
47 (100 MHz, CDCl_3) δ 162.7, 154.9, 129.6, 123.1, 122.1, 121.1, 109.7, 10.0. The
48
49 spectroscopic data is in agreement with that previously reported.²³
50
51
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55

56 **3-Phenethylbenzo[*d*]isoxazole (2f)**. Method B was used. 5 mmol scale. Column
57
58 chromatography on basic aluminum oxide (eluent: petroleum ether: ethyl acetate = 20:1 to
59
60

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4 5:1) afforded the title product in 55% yield (613.3 mg) as colorless oil). ^1H NMR (400
5
6 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,
7
8 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 162.8, 157.8, 140.5, 129.6, 128.5, 128.3, 126.3,
9
10 123.0, 121.5, 121.1, 109.8, 33.7, 27.3. The spectroscopic data is in agreement with that
11
12 previously reported.²⁰
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20 **7-Methyl-3-phenylbenzo[*d*]isoxazole (2h)**. Method B was used. 5 mmol scale. Column
21
22 chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 100:1) afforded the
23
24 title product in 43% yield (450.7 mg) as a yellow solid). ^1H NMR (400 MHz, CDCl_3) δ
25
26 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),
27
28 7.26 (t, J = 7.6 Hz, 1H), 2.62 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 163.1, 157.5,
29
30 130.1, 130.1, 129.2, 129.0, 128.0, 124.1, 120.9, 119.9, 119.4, 15.2. IR (neat): 3053, 2977,
31
32 2917, 1603, 1382, 902, 742, 695 cm^{-1} . HRMS (ESI-TOF) calcd for $\text{C}_{14}\text{H}_{12}\text{NO}$ $[\text{M}+\text{H}]^+$:
33
34 210.0913, found 210.0912.
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43 **The procedure for the synthesis of 3-methoxybenzo[*d*]isoxazole 2g.**²⁴

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45
46 To a solution of benzo[*d*]isoxazol-3-ol (405.4 mg, 3 mmol) in DMSO (5 mL) was
47
48 added K_2CO_3 (1.244 g, 9 mmol), MeI (0.37 mL, 6 mmol) and stirred at room temperature
49
50 for 3 h. The mixture was quenched with H_2O , extracted with ethyl ether, washed with brine
51
52 and dried over anhydrous Na_2SO_4 . The solvent was evaporated under the reduced pressure
53
54 and the residue was purified by column chromatography on silica gel (eluent: petroleum
55
56 ether: ethyl acetate = 7.5:1 to 5:1 to 3:1) to afford **2g** (214.1 mg, 48%) as colorless oil. ^1H
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58
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4 NMR (400 MHz, CDCl₃) δ 7.60 (d, J = 8.0 Hz, 1H), 7.51-7.47 (m, 1H), 7.41-7.39 (m, 1H),
5
6
7 7.23 (t, J = 7.6 Hz, 1H), 4.15 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.9, 163.8,
8
9
10 130.2, 122.8, 120.6, 113.9, 110.0, 57.1. IR (neat): 2987, 2943, 1613, 1541, 1453, 1390,
11
12 1235, 746 cm⁻¹. HRMS (EI-TOF) calcd for C₈H₇NO₂ [M]⁺: 149.0477, found 149.0479.

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17 Propargyl esters **6** were synthesized by the protection of corresponding propargyl
18
19 alcohols.^{25,26}

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22 For the characterization of new propargyl esters, see following:

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27
28 **1-(3,4,5-Trimethoxyphenyl)prop-2-yn-1-yl benzoate (6c)**. 10 mmol scale. Column
29
30 chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) to afford the
31
32 title compound (2.985 g, 91%) as light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, J
33
34 = 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 =
35
36 2.0 Hz, 1H), 3.75 (s, 6H), 3.73 (s, 3H), 2.66 (d, J = 2.4 Hz, 1H). ¹³C{¹H} NMR (100 MHz,
37
38 CDCl₃) 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,
39
40
41 60.5, 55.8. IR (neat): 3291, 3000, 2940, 2835, 2252, 1719, 1593, 1151 cm⁻¹. HRMS
42
43 (EI-TOF) calcd for C₁₉H₁₈O₅ [M]⁺: 326.1154, found 326.1155.

44
45
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51 **1-(4-Chlorophenyl)prop-2-yn-1-yl benzoate (6d)**. 5 mmol scale. Column
52
53 chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the
54
55 title product (1.14 g, 84%) as yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 7.6
56
57 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
58
59 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
60

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4 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 165.2, 135.0, 133.4, 129.8, 129.3, 129.1,
5
6 128.9, 128.4, 79.8, 76.0, 65.0. IR (neat): 3260, 3079, 2932, 2121, 1721, 1491, 1247, 1067
7
8 cm^{-1} . HRMS (EI-TOF) calcd for $\text{C}_{16}\text{H}_{11}\text{O}_2\text{Cl}[\text{M}]^+$: 270.0448, found 270.0453.
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14 **General procedure for the synthesis of 2*H*-benzo[*e*][1,3]oxazine 3.**

15 **Typical procedure for the synthesis of 3a.**

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19
20 To a Schlenk tube were added ynamide **1a** (90.4 mg, 0.3 mmol), DCE (3 mL),
21
22 benzo[*d*]isoxazole **2a** (70.3 mg, 0.36 mmol) and JohnphosAu(MeCN)SbF₆ (catalyst **A**)
23
24 (11.6 mg, 0.015 mmol) under Argon. After the reaction mixture was stirred at room
25
26 temperature for 6 h as monitored by thin-layer chromatography, the solvent was
27
28 evaporated under the reduced pressure and the residue was purified by column
29
30 chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane =
31
32 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.
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41 **4-Methoxy-*N*-methyl-*N*-(phenyl(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)methyl)b**

42
43 **enzenesulfonamide (3a).** *E*-isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, *J* = 7.6 Hz,
44
45 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,
46
47 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 3.60 (s, 3H), 3.28 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)
48
49 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,
50
51 127.4, 127.1, 126.8, 123.0, 116.4, 116.2, 115.8, 113.0, 55.0, 38.1. Partial NMR for
52
53
54
55
56 *Z*-isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H),
57
58 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). $^{13}\text{C}\{^1\text{H}\}$
59
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4 NMR (100 MHz, CDCl₃) δ 162.4, 161.2, 155.0, 149.2, 136.4, 135.5, 133.8, 131.9, 130.3,
5
6
7 129.4, 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
8
9 (neat): 3053, 2924, 2851, 1595, 1577, 1336, 1145, 1020 cm⁻¹. HRMS (ESI-TOF) calcd for
10
11 C₂₉H₂₅N₂O₄S [M+H]⁺: 497.1530, found 497.1523.
12
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17 ***N*-Methyl-*N*-(phenyl(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)methyl)methanesulfo**
18
19 **namide (3b)**. Following the typical procedure, 0.3 mmol scale, **1b** (62.8 mg, 0.3 mmol), 3
20 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room
21
22 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred at room
23
24 temperature for 6 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl
25
26 acetate: dichloromethane = 20:1:1 to 10:1:1 to 5:1:1) afforded the *Z*-**3b** in 11% (13.5 mg)
27
28 yield as a red solid and *E*-**3b** which was further purified by Recycling Preparative HPLC in
29
30 57% (69.1 mg) yield as a red solid. *E*-isomer: m.p. 211-213 °C. ¹H NMR (400 MHz,
31
32 CDCl₃) 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,
33
34 4H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.05-7.02 (m, 2H), 3.26 (s, 3H), 2.95 (s, 3H). ¹³C{¹H} NMR
35
36 (100 MHz, CDCl₃) δ 161.2, 154.9, 150.2, 135.8, 135.5, 134.6, 130.5, 128.5, 128.1, 127.5,
37
38 127.1, 123.3, 116.6, 116.2, 115.9, 38.9, 37.6. IR (neat): 3058, 3032, 2934, 1576, 1532,
39
40 1324, 1138 cm⁻¹. HRMS (ESI-TOF) calcd for C₂₃H₂₁N₂O₃S [M+H]⁺: 405.1267, found
41
42 405.1255. *Z*-isomer: m.p. 198-200 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.0 Hz,
43
44 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,
45
46 1H), 7.09-7.02 (m, 2H), 3.31 (s, 3H), 3.07 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ
47
48 161.5, 155.5, 149.5, 135.7, 135.7, 134.5, 130.5, 129.0, 128.6, 128.5, 127.8, 127.8, 127.0,
49
50 123.3, 117.1, 115.7, 115.5, 39.2, 37.0. IR (neat): 3055, 2932, 1579, 1538, 1322, 1139, 963
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4 cm⁻¹. HRMS (ESI-TOF) calcd for C₂₃H₂₁N₂O₃S [M+H]⁺: 405.1267, found 405.1257.
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10 ***N*,4-Dimethyl-*N*-(phenyl(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)methyl)benzenes**
11
12 **ulfonamide (3c)**. Following the typical procedure, 0.3 mmol scale, **1c** (85.6 mg, 0.3
13 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were
14 stirred at room temperature for 6 h. Column chromatography on silica gel (eluent:
15 petroleum ether: ethyl acetate: dichloromethane = 20:2:1) afforded the title product as a red
16 solid in 92% (132.8 mg, *E/Z* = 7.7:1) yield. *E*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.91
17 (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
18 (d, *J* = 8.0 Hz, 2H), 3.30 (s, 3H), 2.15 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 159.8,
19 154.9, 150.0, 142.3, 137.0, 136.6, 135.3, 134.2, 130.1, 128.7, 128.6, 127.98, 127.97, 127.8,
20 127.5, 127.2, 126.9, 123.1, 116.5, 116.3, 115.9, 38.2, 21.4. Partial NMR for *Z*-isomer: ¹H
21 NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 6.20 (d, *J* =
22 8.4 Hz, 1H), 3.29 (s, 3H), 2.34 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 161.2, 155.0,
23 142.7, 137.3, 136.4, 135.6, 133.7, 130.4, 129.1, 129.0, 128.6, 128.4, 127.6, 127.5, 126.7,
24 122.8, 115.8, 115.6, 37.2. IR (neat): 3045, 2919, 2846, 1597, 1529, 1338, 1146, 748 cm⁻¹.
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HRMS (ESI-TOF) calcd for C₂₉H₂₅N₂O₃S [M+H]⁺: 481.1580, found 481.1575.

51
52 ***N*,4-Dimethyl-*N*-((4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(*p*-tolyl)methyl)benzene**
53
54 **sulfonamide (3d)**. Following the typical procedure, 0.3 mmol scale, **1d** (89.8 mg, 0.3
55 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were
56 stirred at room temperature for 7 h. Column chromatography on silica gel (eluent:
57
58
59
60

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4 petroleum ether: ethyl acetate: dichloromethane = 30:2 :1 to 20:2:1) afforded the title
5
6 product **3d** as a red solid in 67% (99.1 mg, *E/Z* = 3.7:1) yield and **4d** in 20% yield (29.8
7
8 mg) as a yellow solid. For **3d**, *E*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.0 Hz,
9
10 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
11
12 Hz, 2H), 3.29 (s, 3H), 2.37 (s, 3H), 2.15 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ
13
14 159.2, 155.0, 149.6, 142.2, 136.9, 136.7, 135.6, 135.3, 134.1, 133.8, 130.0, 128.8, 128.7,
15
16 128.6, 127.9, 127.8, 127.4, 127.1, 123.0, 116.6, 116.4, 115.8, 38.2, 21.4, 21.2. Partial
17
18 NMR for *Z*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* =
19
20 8.0 Hz, 2H), 6.16 (d, *J* = 8.4 Hz, 1H), 3.27 (s, 3H), 2.34 (s, 6H). ¹³C{¹H} NMR (100 MHz,
21
22 CDCl₃) δ 160.7, 155.1, 148.7, 142.6, 137.3, 136.5, 133.6, 133.5, 130.3, 129.1, 128.9,
23
24 128.5, 128.4, 127.4, 122.7, 116.0, 115.5, 37.2, 21.4, 21.1. IR (neat): 3053, 2919, 1600,
25
26 1530, 1337, 1150, 661 cm⁻¹. HRMS (ESI-TOF) calcd for C₃₀H₂₇N₂O₃S [M+H]⁺: 495.1737,
27
28 found 495.1730.
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41 ***N*-((4-Methoxyphenyl)(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)methyl)-*N*,4-*d***
42 **imethylbenzenesulfonamide (3e)**. Following the typical procedure, 0.3 mmol scale, **1e**
43 (94.6 mg, 0.3 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015
44
45 mmol) were stirred at room temperature for 7 h. Column chromatography on silica gel
46
47 (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:2:1) afforded the title product
48
49 **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
50
51 yellow solid. For **3e**, two isomers: ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.8 Hz),
52
53 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*
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4 = 8.0 Hz), 3.83 (s), 3.80 (s), 3.29 (s), 3.27(s), 2.34 (s), 2.14 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz,
5
6 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,
7
8 136.9, 135.6, 135.3, 134.0, 133.5, 130.2, 130.0, 129.8, 129.2, 129.1, 129.0, 128.9, 128.63,
9
10 128.57, 128.4, 127.9, 127.7, 127.4, 127.0, 122.9, 122.7, 116.6, 116.2, 115.8, 115.4, 113.4,
11
12 113.1, 55.13, 55.11, 38.2, 37.2, 21.4, 21.3. IR (neat): 3060, 2930, 2835, 1601, 1507, 1338,
13
14 1177, 1147 cm^{-1} . HRMS (ESI-TOF) calcd for $\text{C}_{30}\text{H}_{27}\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 511.1686, found
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16 511.1682.
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25 ***N*-((4-Fluorophenyl)(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)methyl)-*N*,4-dimethy**
26 **lbenzenesulfonamide (3f)**. Following the typical procedure, 0.3 mmol scale, **1f** (91.0 mg,
27 0.3 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were
28 stirred at room temperature for 5.5 h. Column chromatography on silica gel (eluent:
29 petroleum ether: ethyl acetate: dichloromethane = 30:2:1 to 20:2:1) afforded the title
30 product as a red solid in 89% (133.3 mg, *E/Z* = 9.1:1) yield. *E*-isomer: ^1H NMR (400 MHz,
31 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,
32 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,
33 2H), 3.30 (s, 3H), 2.16 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 161.6(d, $^1J_{\text{C-F}}$ =246.3
34 Hz), 159.8, 154.9, 149.8(d, $^5J_{\text{C-F}}$ =1.5 Hz), 142.5, 136.8, 135.3, 134.3, 132.9 (d, $^4J_{\text{C-F}}$ =3.2
35 Hz), 130.2, 129.3 (d, $^3J_{\text{C-F}}$ =7.9 Hz), 128.8, 128.7, 128.0, 127.8, 127.3, 123.2, 116.6, 115.9,
36 115.5, 114.9 (d, $^2J_{\text{C-F}}$ =21.4 Hz), 38.3, 21.5. Partial NMR for *Z*-isomer: ^1H NMR (400
37 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
38 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 133.8, 130.5, 129.2, 129.0, 128.5, 127.5,
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4 123.0, 114.6, 114.4. IR (neat): 3063, 2930, 1603, 1505, 1317, 1165, 1146, 749 cm⁻¹.

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6
7 HRMS (ESI-TOF) calcd for C₂₉H₂₄FN₂O₃S [M+H]⁺: 499.1486, found 499.1482.

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12 ***N*-((4-Chlorophenyl)(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)methyl)-*N*,4-dimethy**

13 **lbenzenesulfonamide (3g).** Following the typical procedure, 0.3 mmol scale, **1g** (95.9 mg,

14
15 0.3 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were

16
17 stirred at room temperature for 9 h. Column chromatography on silica gel (eluent:

18
19 petroleum ether: ethyl acetate: dichloromethane = 30:2:1) afforded the title product as a red

20
21 solid in 93% (143.1 mg, *E/Z* = 10:1) yield. *E*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.84

22
23 (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),

24
25 7.05-7.01 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 3.29 (s, 3H), 2.17 (s, 3H). ¹³C{¹H} NMR (100

26
27 MHz, CDCl₃) δ 160.2, 154.9, 150.2, 142.5, 136.8, 135.4, 135.2, 134.4, 132.3, 130.3, 128.8,

28
29 128.7, 128.2, 128.1, 127.8, 127.4, 123.3, 116.5, 115.9, 115.4, 38.3, 21.5. Partial NMR for

30
31 *Z*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.79-7.76 (m, 4H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.21

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33 (d, *J* = 8.4 Hz, 1H), 3.28 (s, 3H), 2.37 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 129.8,

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35 129.2, 129.0, 128.5, 127.8, 127.5. IR (neat): 3058, 2922, 2848, 1595, 1520, 1313, 1147

36
37 cm⁻¹. HRMS (ESI-TOF) calcd for C₂₉H₂₄ClN₂O₃S [M+H]⁺: 515.1191, found 515.1187.

38 39 40 41 42 43 44 45 46 47 48 49 50 51 **Ethyl**

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53 **4-(((*N*,4-dimethylphenyl)sulfonamido)(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)me**

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55 **thyl)benzoate (3h).** Following the typical procedure, 0.3 mmol scale, **1h** (107.2 mg, 0.3

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57 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **C** (19.5 mg, 0.0225 mmol) were

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4 stirred at room temperature for 30 h. Column chromatography on silica gel (eluent:
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6 petroleum ether: ethyl acetate: dichloromethane = 20:2:1 to 16:2:1) afforded the title
7
8 product which was further purified by Recycling Preparative HPLC in 49% (80.8 mg, *E/Z*
9
10 = 6.7:1) yield as a red solid. *E*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.4 Hz,
11
12 = 6.7:1) yield as a red solid. *E*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.4 Hz,
13
14 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,
15
16 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,
17
18 3H), 2.16 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.4,
19
20 160.9, 154.7, 151.2, 142.5, 141.5, 136.8, 135.1, 134.5, 130.4, 129.2, 128.8, 128.7, 128.0,
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22 127.7, 127.5, 127.1, 123.4, 116.4, 115.9, 115.4, 60.7, 38.2, 21.4, 14.3. Partial NMR for
23
24 *Z*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H),
25
26 6.24 (d, *J* = 8.4 Hz, 1H), 3.30 (s, 3H), 2.36 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ
27
28 166.5, 162.3, 154.8, 150.5, 142.9, 141.4, 137.1, 135.3, 134.1, 130.7, 129.2, 129.0, 128.9,
29
30 128.5, 128.1, 123.2, 116.3, 115.7, 114.8, 60.6, 37.1, 21.4. IR (neat): 3058, 2990, 2924,
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32 1703, 1524, 1333, 1273, 1108 cm⁻¹. HRMS (ESI-TOF) calcd for C₃₂H₂₉N₂O₅S [M+H]⁺:
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34 553.1792, found 553.1787.
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46 ***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
47
48 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were
49
50 stirred at room temperature for 1 h. Column chromatography on silica gel (eluent:
51
52 petroleum ether: ethyl acetate: dichloromethane = 20:2:1 to 10:2:1) afforded the title
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54 product as a dark purple solid in 78% (114.2 mg, *E/Z* = 0.1:1) yield. Single *Z* isomer could
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4 be obtained by recrystallization from the mixture in petroleum ether/dichloromethane.

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7 *Z*-isomer: m.p. 195-197 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.0 Hz, 4H),
8
9 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,
10
11 3H), 2.38 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 161.1, 155.0, 147.7, 143.0, 139.2,
12
13 137.8, 135.4, 134.1, 130.8, 129.7, 129.4, 128.6, 127.8, 127.6, 127.4, 126.3, 125.6, 123.3,
14
15 116.5, 115.8, 113.0, 36.5, 21.6. Partial NMR for *E*-isomer: ¹H NMR (400 MHz, CDCl₃) δ
16
17 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
18
19 Hz, 2H), 3.28 (s, 3H), 2.14 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 159.0, 142.4,
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21 140.3, 137.0, 134.3, 130.2, 128.9, 128.8, 128.2, 128.1, 127.3, 127.0, 125.8, 123.4, 116.6,
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23 116.1, 37.6. IR (neat): 3050, 2930, 1597, 1530, 1342, 1160, 690 cm⁻¹. HRMS (ESI-TOF)
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25 calcd for C₂₇H₂₃N₂O₃S₂ [M+H]⁺: 487.1145, found 487.1141.
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36 ***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-decah**
37
38 **ydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)**
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40 **methyl)benzenesulfonamide (3j)**. Following the typical procedure, 0.3 mmol scale, **1j**
41
42 (138.5 mg, 0.3 mmol), 3 mL DCE, **2a** (70.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015
43
44 mmol) were stirred at room temperature for 6 h. Column chromatography on silica gel
45
46 (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:2) afforded the title product
47
48 as a red solid in 65% (127.3 mg, *E/Z* = 2.1:1) yield. Two isomers: ¹H NMR (400 MHz,
49
50 CDCl₃) 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
51
52 (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
53
54 (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);
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¹³C{¹H} NMR (100 MHz, CDCl₃) 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 C₄₁H₄₁N₂O₄S [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: ¹H NMR (400 MHz, CDCl₃) 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); ¹³C{¹H} NMR (100 MHz, CDCl₃) 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 C₂₆H₂₅N₂O₃S [M+H]⁺: 445.1580, found 445.1570.

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4 ***N*-((4-(4-Methoxyphenyl)-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(phenyl)methyl)-*N*,4-dime**
5 **thylbenzenesulfonamide (3i).** Following the typical procedure, 0.3 mmol scale, **1c** (85.6
6 mg, 0.3 mmol), 3 mL DCE, **2b** (81.1 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol)
7 were stirred at room temperature for 5 h. Column chromatography on silica gel (eluent:
8 petroleum ether: ethyl acetate: dichloromethane = 20:2:1) afforded the title product as a red
9 solid in 86% (131.0 mg, *E/Z* = 11.1:1) yield. *E*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.89
10 (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),
11 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);
12 ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 161.2, 159.1, 154.9, 150.1, 142.2, 137.0, 136.8, 134.0,
13 130.5, 128.6, 127.9, 127.8, 127.3, 127.2, 126.6, 123.0, 116.6, 115.8, 115.5, 113.3, 55.3,
14 38.0, 21.3. Partial NMR for *Z*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 7.2 Hz,
15 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). ¹³C{¹H}
16 NMR (100 MHz, CDCl₃) δ 161.4, 160.5, 155.0, 149.2, 142.6, 137.2, 136.6, 133.5, 130.7,
17 129.1, 128.5, 127.5, 127.4, 126.5, 122.7, 116.5, 115.5, 114.9, 113.8, 37.2, 21.3. IR (neat):
18 3066, 2966, 2932, 2835, 1606, 1527, 1327, 1147 cm⁻¹. HRMS (ESI-TOF) calcd for
19 C₃₀H₂₇N₂O₄S [M+H]⁺: 511.1686, found 511.1681.
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48 ***N*-((4-(4-Chlorophenyl)-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(phenyl)methyl)-*N*,4-dimet**
49 **hylbenzenesulfonamide (3m).** Following the typical procedure, 0.3 mmol scale, **1c** (85.6
50 mg, 0.3 mmol), 3 mL DCE, **2c** (82.7 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol)
51 were stirred at room temperature for 5 h. Column chromatography on silica gel (eluent:
52 petroleum ether: ethyl acetate: dichloromethane = 30:2:1 to 20:2:1) afforded the title
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4 product as a red solid in 91% (140.9 mg, *E/Z* = 7.7:1) yield. Single *E*-isomer could be
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6 obtained by recrystallization from the mixture in petroleum ether/dichloromethane. Singel
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10 *Z*-isomer could be obtained by Column chromatography on silica gel from the above
11
12 filtrate. *E*-isomer: m.p. 223-225 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.0 Hz,
13
14 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,
15
16 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 158.7, 155.1, 150.1, 142.4, 137.2, 136.4, 136.4,
17
18 134.5, 133.8, 130.2, 128.7, 128.4, 128.1, 127.9, 127.6, 127.1, 126.9, 123.2, 116.9, 116.4,
19
20 116.1, 38.1, 21.4. *Z*-isomer: m.p. 186-188 °C. Partial NMR for *Z*-isomer: ¹H NMR (400
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22 MHz, CDCl₃) δ 7.77 (t, *J* = 8.4 Hz, 4H), 6.26 (d, *J* = 8.4 Hz, 1H), 3.28 (s, 3H), 2.37 (s,
23
24 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 160.0, 155.2, 137.4, 134.0, 130.4, 129.2, 128.8,
25
26 128.7, 127.7, 127.0, 123.0, 115.8, 37.2, 21.5. IR (neat): 3089, 3060, 2927, 1595, 1522,
27
28 1335, 1150 cm⁻¹. HRMS (ESI-TOF) calcd for C₂₉H₂₄ClN₂O₃S [M+H]⁺: 515.1191, found
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30 515.1188.
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41 ***N*-((4-(2-Methoxyphenyl)-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(phenyl)methyl)-*N*,4-dime**
42
43 **thylbenzenesulfonamide (3n)**. Following the typical procedure, 0.3 mmol scale, **1c** (85.6
44
45 mg, 0.3 mmol), 3 mL DCE, **2d** (81.1 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol)
46
47 were stirred at room temperature for 8 h. Column chromatography on silica gel (eluent:
48
49 petroleum ether: ethyl acetate: dichloromethane = 20:2:1) afforded the title product as a red
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51 solid in 94% (144.4 mg, *E/Z* = 12.5:1) yield. *E*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.94
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53 (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),
54
55 7.29-7.13 (m, 1H), 6.96-6.85 (m, 8H), 3.71 (s, 3H), 3.24 (s, 3H), 2.17 (s, 3H). ¹³C{¹H}
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4 NMR (100 MHz, CDCl₃) δ 159.6, 157.0, 153.9, 150.5, 141.9, 137.0, 136.5, 133.9, 131.0,
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7 130.3, 128.4, 128.0, 127.9, 127.5, 127.5, 126.8, 124.9, 122.8, 120.5, 117.3, 116.0, 115.4,
8
9 110.8, 55.2, 38.3, 21.5. Partial NMR for *Z*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d,
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11 *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,
12
13 3H), 2.35 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 129.1, 128.5. IR (neat): 3058, 2932,
14
15 1600, 1530, 1329, 1148, 1023, 755 cm⁻¹. HRMS (ESI-TOF) calcd for C₃₀H₂₇N₂O₄S
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17 [M+H]⁺: 511.1686, found 511.1677.
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25 ***N*,4-Dimethyl-*N*-((4-methyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(phenyl)methyl)benzen**
26
27 **esulfonamide (3o)**. Following the typical procedure, 0.3 mmol scale, **1c** (85.6 mg, 0.3
28
29 mmol), 3 mL DCE, **2e** (79.9 mg, 0.6 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were stirred
30
31 at room temperature for 2 h. Column chromatography on silica gel (eluent: petroleum
32
33 ether: ethyl acetate: dichloromethane = 40:2:1 to 30:2:1 to 20:2:1) afforded the title
34
35 product as an orange solid in 91% (114.2 mg, *E/Z* = 7.7:1) yield. *E*-isomer: ¹H NMR (400
36
37 MHz, CDCl₃) 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
38
39 (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).
40
41 ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 159.9, 153.4, 149.9, 142.3, 137.3, 136.3, 134.3, 128.7,
42
43 128.0, 127.9, 127.4, 126.7, 124.9, 123.2, 117.2, 115.4, 114.5, 37.9, 21.3, 21.0. Partial
44
45 NMR for *Z*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.0 Hz, 2H), 6.09 (d, *J* =
46
47 8.4 Hz, 1H), 2.32 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 161.4, 153.6, 149.2, 142.6,
48
49 137.5, 133.9, 129.0, 128.3, 127.6, 127.4, 126.5, 126.0, 123.0, 117.3, 115.0, 114.1, 37.0,
50
51 21.7. IR (neat): 3071, 2922, 1618, 1557, 1329, 1146, 1083 cm⁻¹. HRMS (ESI-TOF) calcd
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4 for C₂₄H₂₃N₂O₃S [M+H]⁺: 419.1424, found 419.1417.
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9 ***N*,4-Dimethyl-*N*-((4-phenethyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(phenyl)methyl)benz**
10 **enesulfonamide (3p)**. Following the typical procedure, 0.3 mmol scale, **1c** (85.6 mg, 0.3
11 mmol), 3 mL DCE, **2f** (134.0 mg, 0.6 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were
12 stirred at room temperature for 4 h. Column chromatography on silica gel (eluent:
13 petroleum ether: ethyl acetate: dichloromethane = 40:2:1 to 30:2:1) afforded the title
14 product as an orange solid in 85% (129.4 mg, *E/Z* = 9.1:1) yield. *E*-isomer: ¹H NMR (400
15 MHz, CDCl₃) 7.84 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 3H),
16 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,
17 1H), 3.21 (s, 3H), 3.07-2.52 (m, 4H), 2.30 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ
18 161.9, 153.6, 149.7, 142.4, 140.8, 137.3, 136.6, 134.2, 128.8, 128.3, 128.0, 127.9, 127.8,
19 127.3, 126.6, 125.9, 124.3, 123.2, 116.8, 115.5, 114.8, 37.8, 34.8, 31.4, 21.2. Partial NMR
20 for *Z*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.13 (d, *J* = 7.6 Hz, 1H), 3.25 (s, 3H), 2.33 (s,
21 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 162.7, 149.1, 142.6, 140.9, 136.3, 133.7, 129.0,
22 128.3, 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.
23 IR (neat): 3063, 3026, 2940, 1556, 1332, 1148, 1036, 750 cm⁻¹. HRMS (ESI-TOF) calcd
24 for C₃₁H₂₉N₂O₃S [M+H]⁺: 509.1893, found 509.1889.
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54 ***N*-((4-Methoxy-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(phenyl)methyl)-*N*,4-dimethylbenz**
55 **enesulfonamide (3q)**. Following the typical procedure, 0.3 mmol scale, **1c** (85.6 mg, 0.3
56 mmol), 3 mL DCE, **2g** (53.7 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were
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4 stirred at room temperature for 3.5 h. Column chromatography on silica gel (eluent:
5
6 petroleum ether: ethyl acetate: dichloromethane = 30:2:1) afforded the title product as an
7
8 orange solid in 88% (114.5 mg, *E/Z* = 0.38:1) yield. Two isomers: ¹H NMR (400 MHz,
9
10 CDCl₃) 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
11
12 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*
13
14 = 8.0 Hz), 3.98 (s), 3.49 (s), 3.25 (s), 3.24 (s), 2.37 (s), 2.31 (s). *Z*-isomer: ¹³C{¹H} NMR
15
16 (100 MHz, CDCl₃) δ 158.2, 155.1, 149.2, 142.4, 137.6, 136.6, 134.1, 129.0, 127.5, 127.40,
17
18 127.38, 125.6, 123.8, 122.7, 114.8, 111.6, 109.9, 54.2, 37.0, 21.2. *E*-isomer: ¹³C{¹H} NMR
19
20 (100 MHz, CDCl₃) δ 157.5, 155.2, 150.2, 142.5, 137.7, 136.9, 134.6, 128.9, 127.8, 127.7,
21
22 126.9, 125.9, 123.9, 122.9, 115.1, 112.0, 110.7, 53.5. IR (neat): 3047, 2945, 1620, 1590,
23
24 1566, 1360, 1338, 1152 cm⁻¹. HRMS (ESI-TOF) calcd for C₂₄H₂₃N₂O₄S [M+H]⁺:
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26 435.1373, found 435.1367.
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38 **(*E*)-*N*,4-Dimethyl-*N*-((8-methyl-4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(phenyl)m**
39
40 **ethyl)benzenesulfonamide (3r)**. Following the typical procedure, 0.3 mmol scale, **1c**
41
42 (85.6 mg, 0.3 mmol), 3 mL DCE, **2h** (75.3 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015
43
44 mmol) were stirred at room temperature for 9 h. Column chromatography on silica gel
45
46 (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:2:1) afforded the title product
47
48 as a red solid in 87% (128.8 mg) yield. Only *E*-isomer was obtained. M.p. 186-188 °C. ¹H
49
50 NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.47-7.22
51
52 (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,
53
54 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 160.2, 153.2, 150.2, 142.2, 136.9, 136.7, 135.49,
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4 135.47, 130.0, 128.7, 128.6, 127.9, 127.8, 127.7, 127.5, 126.7, 125.0, 124.8, 122.4, 116.0,
5
6 115.9, 38.3, 21.4, 15.6. IR (neat): 3042, 2974, 2914, 1579, 1530, 1323, 1144, 743 cm⁻¹.
7
8
9 HRMS (ESI-TOF) calcd for C₃₀H₂₇N₂O₃S [M+H]⁺: 495.1737, found 495.1731.
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13

14 ***N*-((2*H*-benzo[*e*][1,3]oxazin-2-ylidene)(phenyl)methyl)-*N*,4-dimethylbenzene-sulfonami**
15 **de (3*s*) and *N*,4-dimethyl-*N*-(2-phenylbenzo[*f*][1,4]oxazepin-3-yl)benzenesulfonamide**
16 **(4*q*).** Following the typical procedure, 0.3 mmol scale, **1c** (85.6 mg, 0.3 mmol), 3 mL
17
18 DCE, benzo[*d*]isoxazole **2i** (42.9 mg, 0.36 mmol), catalyst **A** (11.6 mg, 0.015 mmol) were
19
20 stirred at room temperature for 4 h. Column chromatography on silica gel (eluent:
21
22 petroleum ether: ethyl acetate = 3:1) afforded the product as an orange solid in 83% (100.3
23
24 mg) yield, which contains **3s** in 60% (*E/Z* = 0.79:1) yield and **4q** in 23% yield. Note: We
25
26 found that **3s** and **4q** can be decomposed slowly on silica gel, so column chromatography
27
28 should be finished within 15 minutes. ¹H NMR for the mixture of **3s** and **4q** (400 MHz,
29
30 CDCl₃): 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
31
32 (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
33
34 Hz), 3.14 (s), 3.09 (s), 2.90 (s), 2.30 (s), 2.23 (s). ¹³C{¹H} NMR for *E*-**3s** (100 MHz,
35
36 CDCl₃): δ 153.8, 153.3, 150.9, 142.6, 136.8, 135.5, 134.6, 128.8, 127.9, 127.9, 127.6,
37
38 127.1, 126.7, 123.6, 117.1, 116.1, 114.8, 37.7, 21.4. ¹³C{¹H} NMR for *Z*-**3s** (100 MHz,
39
40 CDCl₃): δ 154.6, 153.9, 149.7, 142.7, 137.3, 136.0, 134.2, 129.0, 128.2, 127.6, 127.4,
41
42 127.0, 126.8, 123.4, 117.0, 116.2, 115.1, 36.9, 21.3. ¹³C{¹H} NMR for **4q** (100 MHz,
43
44 CDCl₃): δ 160.2, 158.9, 147.4, 143.3, 135.3, 134.1, 133.9, 133.2, 129.1, 129.0, 128.7,
45
46 128.6, 128.2, 128.2, 128.1, 125.4, 120.6, 35.8, 21.4. HRMS (ESI-TOF) calcd for
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$C_{23}H_{21}N_2O_3S$ [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 AuBr₃ (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. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C {¹H} NMR (100 MHz, CDCl₃) 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 C₂₉H₂₅N₂O₄S [M+H]⁺: 497.1530, found 497.1520.

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

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4 Following the typical procedure, 0.3 mmol scale, **1c** (102.7 mg, 0.36 mmol), 9 mL DCE,
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6
7 **2a** (58.6 mg, 0.3 mmol), AuBr₃ (6.6 mg, 0.015 mmol) were stirred at room temperature for
8
9
10 1 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate:
11
12 dichloromethane = 30:2:1) afforded **4c** as a yellow solid in 80% (115.8 mg) yield. M.p.
13
14 170-172 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.53-7.47 (m, 3H),
15
16 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,
17
18 3H), 2.33 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 165.7, 159.9, 147.0, 143.2, 138.0,
19
20 135.4, 133.6, 133.6, 133.0, 130.5, 129.5, 129.4, 129.2, 128.9, 128.1, 128.1, 128.0, 127.9,
21
22 127.8, 127.7, 124.8, 121.0, 36.4, 21.4. IR (neat): 3066, 2920, 1594, 1553, 1339, 1154, 759,
23
24 672 cm⁻¹. HRMS (ESI-TOF) calcd for C₂₉H₂₅N₂O₃S [M+H]⁺: 481.1580, found 481.1574.
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33 ***N*,4-Dimethyl-*N*-(5-phenyl-2-(*p*-tolyl)benzo[*f*][1,4]oxazepin-3-yl)benzenesulfonamide**

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35 **(4d)**. Following the typical procedure, 0.3 mmol scale, **1d** (107.8 mg, 0.36 mmol), 9 mL
36
37 DCE, **2a** (58.6 mg, 0.3 mmol), AuBr₃ (6.6 mg, 0.015 mmol) were stirred at room
38
39 temperature for 1 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl
40
41 acetate: dichloromethane = 30:2:1 to 10:2:1) afforded **4d** as a yellow solid in 80% (118.3
42
43 mg) yield. M.p. 197-198 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.4 Hz, 2H),
44
45 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,
46
47 3H), 2.39 (s, 3H), 2.35 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 165.4, 160.0, 147.4,
48
49 143.3, 139.2, 138.2, 135.7, 133.7, 133.2, 130.6, 130.3, 129.6, 129.5, 129.4, 129.1, 128.3,
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51 128.2, 128.0, 127.9, 127.8, 124.9, 121.2, 36.6, 21.53, 21.48. IR (neat): 3069, 3024, 2937,
52
53 2914, 1591, 1344, 671 cm⁻¹. HRMS (ESI-TOF) calcd for C₃₀H₂₇N₂O₃S [M+H]⁺: 495.1737,
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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), AuBr₃ (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 °C. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C{¹H} NMR (100 MHz, CDCl₃) 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 C₃₀H₂₇N₂O₄S [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), AuBr₃ (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 °C. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C{¹H} NMR (100

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4 MHz, CDCl₃) δ 165.7, 162.8 (d, $^1J_{C-F}$ = 248.1 Hz), 159.8, 146.1, 143.4, 137.9, 135.2,
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6
7 133.7, 133.4, 130.6, 130.0 (d, $^3J_{C-F}$ = 8.5 Hz), 129.6, 129.4, 129.3, 129.2, 128.1, 127.9,
8
9 127.7, 124.9, 120.9, 115.1 (d, $^2J_{C-F}$ = 21.5 Hz), 36.4, 21.3. IR (neat): 3078, 2917, 1595,
10
11 1499, 1345, 1145, 671 cm⁻¹. HRMS (ESI-TOF) calcd for C₂₉H₂₄FN₂O₃S [M+H]⁺:
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13 499.1486, found 499.1475.
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20 ***N*-(2-(4-Chlorophenyl)-5-phenylbenzo[*f*][1,4]oxazepin-3-yl)-*N*,4-dimethylbenzenesulfo**
21
22 **namide (4g)**. Following the typical procedure, 0.3 mmol scale, **1g** (115.1 mg, 0.36 mmol),
23
24 9 mL DCE, **2a** (58.6 mg, 0.3 mmol), AuBr₃ (6.6 mg, 0.015 mmol) were stirred at room
25
26 temperature for 1 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl
27
28 acetate: dichloromethane = 40:2:1 to 30:2:1) afforded **4g** as a yellow solid in 81% (124.5
29
30 mg) yield. M.p. 202-204 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.8 Hz, 2H),
31
32 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),
33
34 2.36 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.0, 159.9, 145.9, 143.4, 137.9, 135.2,
35
36 134.7, 134.0, 133.7, 131.6, 130.7, 129.7, 129.4, 129.3, 129.3, 128.4, 128.1, 127.9, 127.7,
37
38 124.9, 120.9, 36.4, 21.4. IR (neat): 3066, 2940, 1592, 1489, 1346, 1158, 818 cm⁻¹. HRMS
39
40 (ESI-TOF) calcd for C₂₉H₂₄ClN₂O₃S [M+H]⁺: 515.1191, found 515.1185.
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51 Ethyl

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53 **4-(3-((*N*,4-dimethylphenyl)sulfonamido)-5-phenylbenzo[*f*][1,4]oxazepin-2-yl)benzoate**
54
55 **(4h)**. Following the typical procedure, 0.3 mmol scale, **1h** (128.7 mg, 0.36 mmol), 9 mL
56
57 DCE, **2a** (58.6 mg, 0.3 mmol), AuBr₃ (6.6 mg, 0.015 mmol) were stirred at room
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59
60

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4 temperature for 1 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl
5 acetate: dichloromethane = 30:2:1) afforded **4h** as a yellow solid in 73% (120.5 mg) yield.
6
7 M.p. 174-176 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.21-8.18 (m, 2H), 8.13-8.11 (m, 2H),
8
9 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,
10
11 *J* = 6.8 Hz, 2H), 3.19 (s, 3H), 2.36 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H). ¹³C{¹H} NMR (100
12
13 MHz, CDCl₃) δ 166.5, 166.1, 160.0, 146.0, 143.4, 137.9, 137.3, 135.2, 135.0, 133.8, 130.8,
14
15 130.2, 129.8, 129.5, 129.4, 129.3, 128.1, 127.9, 127.8, 127.7, 125.0, 121.0, 60.9, 36.4,
16
17 21.4, 14.2. IR (neat): 3083, 2985, 1718, 1595, 1343, 1094, 767 cm⁻¹. HRMS (ESI-TOF)
18
19 calcd for C₃₂H₂₉N₂O₅S [M+H]⁺: 553.1792, found 553.1784.
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30 ***N*,4-dimethyl-*N*-(5-phenyl-2-(thiophen-2-yl)benzo[*f*][1,4]oxazepin-3-yl)benzenesulfona**
31 **mid** (**4i**). Following the typical procedure, 0.3 mmol scale, **1i** (104.9 mg, 0.36 mmol), 9
32 mL DCE, **2a** (58.6 mg, 0.3 mmol), AuBr₃ (6.6 mg, 0.015 mmol) were stirred at room
33 temperature for 1.5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl
34 acetate: dichloromethane = 20:2:1 to 10:2:1) afforded **4i** as a orange solid in 57% (83.9
35 mg) yield and *Z*-**3i** in 14% yield (21.0 mg) as a dark purple solid. For **4i**: ¹H NMR (400
36 MHz, CDCl₃) 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
37 (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).
38
39 ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 164.7, 159.3, 143.4, 138.0, 135.4, 135.0, 133.8, 130.4,
40
41 129.7, 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
42
43 (neat): 3068, 2932, 1595, 1445, 1349, 1165, 669 cm⁻¹. HRMS (ESI-TOF) calcd for
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45 C₂₇H₂₃N₂O₃S₂ [M+H]⁺: 487.1145, found 487.1149.
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7 ***N*,4-Dimethyl-*N*-(2-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-deca**
8 **hydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)-5-phenylbenzo[*f*][1,4]oxazepin-3-yl)benzen**
9 **esulfonamide (4j).** Following the typical procedure, 0.3 mmol scale, **1j** (166.2 mg, 0.36
10 mmol), 9 mL DCE, **2a** (58.6 mg, 0.3 mmol), AuBr₃ (6.6 mg, 0.015 mmol) were stirred at
11 room temperature for 1.5 h. Column chromatography on silica gel (eluent: petroleum ether:
12 ethyl acetate: dichloromethane = 15:1:2) afforded **4j** as a yellow solid in 65% (128.7 mg)
13 yield. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.87 (s, 1H), 7.55-7.48 (m,
14 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,
15 2H), 2.36-2.33 (m, 4H), 2.15-1.96 (m, 4H), 1.66-1.46 (m, 6H), 0.92 (s, 3H). ¹³C{¹H} NMR
16 (100 MHz, CDCl₃) δ 220.7, 165.2, 159.8, 147.1, 143.1, 140.7, 138.0, 136.1, 135.5, 133.5,
17 133.2, 130.4, 129.4, 129.3, 129.2, 128.4, 128.05, 127.99, 127.6, 125.3, 125.1, 124.7, 121.0,
18 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,
19 2928, 2858, 1735, 1598, 1347, 1163, 727 cm⁻¹. HRMS (ESI-TOF) calcd for C₄₁H₄₁N₂O₄S
20 [M+H]⁺: 657.2782, found 657.2773.
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46 ***N*-(2-(3-(4-Methoxyphenyl)-4-oxo-4*H*-chromen-7-yl)-5-phenylbenzo[*f*][1,4]oxazepin-3**
47 **-yl)-*N*,4-dimethylbenzenesulfonamide (4k).** Following the typical procedure, 0.3 mmol
48 scale, **1l** (137.9 mg, 0.3 mmol), 9 mL DCE, **2a** (117.1 mg, 0.6 mmol), AuBr₃ (6.6 mg,
49 0.015 mmol) were stirred at room temperature for 1 h. Column chromatography on silica
50 gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:1:10 to 15:1:10 to
51 10:1:10) afforded **4k** as a yellow solid in 60% (117.5 mg) yield. M.p. 220-222 °C. ¹H
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4 NMR (400 MHz, CDCl₃) δ 8.35 (d, *J* = 8.8 Hz, 1H), 8.26 (d, *J* = 1.6 Hz, 1H), 8.18-8.16
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6 (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
8 7.19-7.14 (m, 5H), 6.98-6.95 (m, 2H), 3.81 (s, 3H), 3.23 (s, 3H), 2.35 (s, 3H). ¹³C{¹H}
9
10 NMR (100 MHz, CDCl₃) δ 175.8, 167.0, 160.0, 159.4, 155.8, 152.7, 144.8, 143.6, 138.2,
11
12 137.7, 135.7, 134.8, 134.0, 130.9, 130.0, 129.9, 129.5, 129.3, 128.1, 127.8, 126.0, 125.1,
13
14 125.0, 124.3, 124.0, 124.0, 120.9, 117.3, 113.8, 55.2, 36.3, 21.4. IR (neat): 3063, 2993,
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16 2937, 2838, 1641, 1621, 1422, 1347 cm⁻¹. HRMS (ESI-TOF) calcd for C₃₉H₃₁N₂O₆S
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18 [M+H]⁺: 655.1897, found 655.1896.
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28 ***N*-(5-(4-Methoxyphenyl)-2-phenylbenzo[*f*][1,4]oxazepin-3-yl)-*N*,4-dimethylbenzenesul**
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30 **fonamide (4l)**. Following the typical procedure, 0.3 mmol scale, **1c** (102.7 mg, 0.36
31
32 mmol), 9 mL DCE, **2b** (67.6 mg, 0.3 mmol), AuBr₃ (6.6 mg, 0.015 mmol) were stirred at
33
34 room temperature for 1 h. Column chromatography on silica gel (eluent: petroleum ether:
35
36 ethyl acetate: dichloromethane = 30:2:1) afforded **4l** as a yellow solid in 74% (113.9 mg)
37
38 yield. M.p. 152-154 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 7.2 Hz, 2H), 7.54-7.41
39
40 (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
41
42 (m, 3H), 6.76 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 3.18 (s, 3H), 2.36 (s, 3H). ¹³C{¹H} NMR
43
44 (100 MHz, CDCl₃) δ 165.0, 161.6, 159.9, 146.5, 143.1, 135.5, 133.9, 133.5, 133.1 131.1,
45
46 130.6, 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
47
48 (neat): 3055, 2935, 2841, 1593, 1550, 1342, 1258, 1028 cm⁻¹. HRMS (ESI-TOF) calcd for
49
50 C₃₀H₂₇N₂O₄S [M+H]⁺: 511.1686, found 511.1677.
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***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), AuBr₃ (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 °C. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C{¹H} NMR (100 MHz, CDCl₃) 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 C₂₉H₂₄ClN₂O₃S [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), AuBr₃ (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 °C. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C{¹H} NMR (100 MHz, CDCl₃) 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 $\text{C}_{30}\text{H}_{27}\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 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 $^\circ\text{C}$. ^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). $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 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 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 8.4$

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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, $J = 8.0$
5
6 Hz, 1H), 3.08 (s, 3H), 2.88 (t, $J = 8.0$ Hz, 2H), 2.58-2.55 (m, 2H), 2.36 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$
7
8 NMR (100 MHz, CDCl_3) δ 168.6, 159.6, 146.3, 143.1, 141.4, 135.7, 133.7, 133.2, 132.9,
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10 129.2, 128.9, 128.8, 128.3, 128.2, 128.12, 128.08, 127.8, 126.7, 125.9, 125.3, 120.9, 40.0,
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12 36.2, 31.8, 21.4. IR (neat): 3060, 3029, 2964, 2924, 2851, 1597, 1443, 1347, 1152 cm^{-1} .
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14
15 HRMS (ESI-TOF) calcd for $\text{C}_{31}\text{H}_{29}\text{N}_2\text{O}_3\text{S} [\text{M}+\text{H}]^+$: 509.1893, found 509.1885.
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23 When the reaction of ynamide **1c** with benzo[*d*]isoxazole **2i** was performed using AuBr_3
24
25 as the catalyst, a mixture of **4q** (47% yield) and **3s** (35% yield, $E/Z = 0.33:1$) was obtained.
26
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28 29 30 Synthesis of spiro products.

31 32 33 The procedure for the reaction of **1c** with **2a**.

34
35 To a Schlenk tube were added ynamide **1c** (85.6 mg, 0.3 mmol), DCE (3 mL),
36
37 benzo[*d*]isoxazole **2a** (70.3 mg, 0.36 mmol) and Me_2SAuCl (4.4 mg, 0.015 mmol) under
38
39 Argon. After the reaction mixture was stirred at room temperature for 21.5 h as monitored
40
41 by thin-layer chromatography, the solvent was evaporated under the reduced pressure and
42
43 the residue was purified by column chromatography on silica gel (eluent: petroleum ether:
44
45 ethyl acetate: dichloromethane = 40:2:1) to afford **4c** in 79% yield (113.7 mg) as a yellow
46
47 solid and **5a** in 10% yield (13.9 mg) as a yellow solid.
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57 ***N*,4-Dimethyl-*N*-(10-oxo-1,4-diphenyl-2-azaspiro[4.5]deca-1,3,6,8-tetraen-3-yl)benzen**
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59 **esulfonamide (5a)**. M.p. 194-196 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.0$ Hz,
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4 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
5 Hz, 1H), 6.49 (d, $J = 10$ Hz, 1H), 6.23 (d, $J = 10$ Hz, 1H), 3.11 (s, 3H), 2.45 (s, 3H).
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9 $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 192.2, 172.5, 151.6, 143.6, 143.0, 138.9, 135.3, 134.7,
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11 131.7, 131.2, 130.7, 129.2, 128.8, 128.8, 128.7, 128.43, 128.39, 127.8, 127.5, 123.6, 75.9,
12
13 36.8, 21.6. IR (neat): 3071, 2972, 2932, 1655, 1590, 1345, 1168, 674 cm^{-1} . HRMS
14
15 (ESI-TOF) calcd for $\text{C}_{29}\text{H}_{25}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 481.1580, found 481.1570.
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23 **The procedure for the reaction of 1c with 2h.**

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25 To a Schlenk tube were added ynamide **1c** (85.6 mg, 0.3 mmol), DCE (3 mL),
26 benzo[*d*]isoxazole **2h** (75.3 mg, 0.36 mmol) and Me_2SAuCl (4.4 mg, 0.015 mmol) under
27 Argon. After the reaction mixture was stirred at room temperature for 7 h as monitored by
28 thin-layer chromatography, the solvent was evaporated under the reduced pressure and the
29 residue was purified by column chromatography on silica gel (eluent: petroleum ether:
30 ethyl acetate: dichloromethane = 30:2:1 to 20:2:1) to afford **4r** in 79% yield (117.5 mg) as
31 a yellow solid and **5b** in 18% yield (26.4 mg) as a yellow solid.
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46 ***N*,4-Dimethyl-*N*-(9-methyl-2,5-diphenylbenzo[*f*][1,4]oxazepin-3-yl)benzenesulfonamid**
47
48 **e (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
49 = 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,
50 1H), 3.07 (s, 3H), 2.40 (s, 3H), 2.06 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.3,
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52 158.9, 147.7, 143.2, 138.3, 135.8, 134.5, 134.5, 133.3, 130.8, 130.4, 129.5, 129.4, 128.9,
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54 128.3, 128.2, 127.9, 127.6, 127.1, 124.3, 36.9, 21.5, 16.4. IR (neat): 3066, 2922, 1600,
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4 1561, 1440, 1342, 1159, 671 cm^{-1} . HRMS (ESI-TOF) calcd for $\text{C}_{30}\text{H}_{27}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$:
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6 495.1737, found 495.1726.
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12 ***N*,4-Dimethyl-*N*-(9-methyl-10-oxo-1,4-diphenyl-2-azaspiro[4.5]deca-1,3,6,8-tetraen-3-**
13 **yl)benzenesulfonamide (5b)**. M.p. 160-162 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J =$
14 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, $J =$
15 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
16 (s, 3H), 2.03 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 192.5, 172.7, 151.2, 143.6,
17 139.3, 136.8, 136.2, 135.3, 135.1, 131.8, 131.1, 130.7, 129.2, 128.8, 128.6, 128.4, 128.3,
18 127.7, 127.4, 123.9, 75.5, 36.8, 21.6, 16.1. IR (neat): 3060, 2919, 1652, 1592, 1352, 1153,
19 1084, 672 cm^{-1} . HRMS (ESI-TOF) calcd for $\text{C}_{30}\text{H}_{27}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 495.1737, found
20 495.1725.
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38 **The procedure for the reaction of 1c with 2g.**

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41 To a Schlenk tube were added ynamide **1c** (102.7 mg, 0.36 mmol), DCE (9 mL),
42 benzo[*d*]isoxazole **2g** (44.7 mg, 0.3 mmol) and AuBr_3 (6.6 mg, 0.015 mmol) under Argon.
43
44 After the reaction mixture was stirred at room temperature for 8 h as monitored by
45 thin-layer chromatography, the mixture was filtered through a pad of silica gel, evaporated
46 under the reduced pressure and the residue was purified by column chromatography on
47 silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:2:1 to 10:2:1) to
48 afford **5c** in 41% yield (53.4 mg) as a light yellow oil and **3q** in 26% yield (33.5 mg, E/Z =
49 0.56:1) as a yellow solid.
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7 ***N*-(1-Methoxy-10-oxo-4-phenyl-2-azaspiro[4.5]deca-1,3,6,8-tetraen-3-yl)-*N*,4-dimethyl**
8 **benzenesulfonamide (5c).** ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.35 (d,
9 *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,
10 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,
11 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 192.2, 173.5, 147.9, 143.6, 143.0, 136.8, 135.1,
12 130.9, 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
13 (neat): 3050, 2945, 1665, 1597, 1348, 1299, 1154, 971, 661 cm⁻¹. HRMS (ESI-TOF) calcd
14 for C₂₄H₂₃N₂O₄S [M+H]⁺: 435.1373, found 435.1364.
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30 **General procedure for the synthesis of 2*H*-benzo[*e*][1,3]oxazine 7.**

31 **Typical procedure for the synthesis of 7a.**

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35 To a Schlenk tube were added 1-phenylprop-2-yn-1-yl benzoate (106.3 mg, 0.45
36 mmol), DCE (3 mL), benzo[*d*]isoxazole **2a** (58.6 mg, 0.3 mmol) and IPrAuNTf₂ (catalyst
37 C) (13.0 mg, 0.015 mmol) under Argon. After the reaction mixture was stirred at 80 °C for
38 24 h as monitored by thin-layer chromatography, the solvent was evaporated under the
39 reduced pressure and the residue was purified by column chromatography on silica gel
40 (eluent: petroleum ether: ethyl acetate = 20:1) to afford **7a** in 75% yield (97.1 mg) as a
41 white solid.
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56 **(*Z*)-2-Phenyl-1-(4-phenyl-2*H*-benzo[*e*][1,3]oxazin-2-yl)vinyl benzoate (7a).** ¹H NMR
57 (400 MHz, CDCl₃) δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.64-7.62 (m, 2H), 7.57 (t, *J* = 7.6 Hz, 1H),
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4 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),
5
6 6.91-6.85 (m, 2H), 6.47 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 165.1, 163.8, 155.6,
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8 144.4, 136.4, 133.6, 133.5, 133.1, 130.1, 130.0, 129.0, 128.9, 128.8, 128.4, 128.3, 128.2,
9
10 127.89, 127.87, 121.3, 120.1, 118.2, 116.8, 85.9. IR (neat): 3058, 3027, 1732, 1605, 1448,
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12 1240, 1062, 693 cm^{-1} . HRMS (ESI-TOF) calcd for $\text{C}_{29}\text{H}_{22}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 432.1594, found
13
14 432.1585.
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22 **(Z)-2-Phenyl-1-(4-phenyl-2H-benzo[e][1,3]oxazin-2-yl)vinyl acetate (7b)**. Following the
23
24 typical procedure, 0.3 mmol scale, 1-phenylprop-2-yn-1-yl acetate (78.4 mg, 0.45 mmol), 3
25
26 mL DCE, **2a** (58.6 mg, 0.3 mmol), catalyst **C** (13.0 mg, 0.015 mmol) were stirred at 80 °C
27
28 for 24 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate =
29
30 10:1) afforded **7b** as light yellow oil in 43% (47.7 mg) yield. ^1H NMR (400 MHz, CDCl_3)
31
32 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
33
34 (t, $J = 7.6$ Hz, 1H), 6.73 (s, 1H), 6.25 (s, 1H), 2.18 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz,
35
36 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,
37
38 128.3, 127.9, 127.9, 121.5, 119.9, 118.3, 116.8, 86.1, 20.9. IR (neat): 3061, 3027, 1759,
39
40 1605, 1192, 694 cm^{-1} . HRMS (ESI-TOF) calcd for $\text{C}_{24}\text{H}_{20}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 370.1438, found
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42 370.1429.
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53 **(Z)-1-(4-Phenyl-2H-benzo[e][1,3]oxazin-2-yl)-2-(3,4,5-trimethoxyphenyl)vinyl**
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55 **benzoate (7c)**. Following the typical procedure, 0.3 mmol scale, **6c** (146.9 mg, 0.45
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57 mmol), 3 mL DCE, **2a** (58.6 mg, 0.3 mmol), catalyst **C** (13.0 mg, 0.015 mmol) were
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4 stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether:
5 ethyl acetate = 5:1) afforded **7c** as a white solid in 91% (141.7 mg) yield. M.p. 86-88 °C.
6
7 ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J*
8 = 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
9 (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
10 (s, 3H), 3.57 (s, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 165.1, 163.7, 155.7, 152.7,
11 143.9, 137.7, 136.3, 133.64, 133.58, 130.00, 129.96, 128.9, 128.5, 128.4, 128.1, 127.8,
12 121.3, 119.8, 118.1, 116.7, 105.9, 86.1, 60.6, 55.5. IR (neat): 3061, 2999, 2937, 2833,
13 1735, 1605, 1580, 1234, 1124, 699 cm⁻¹. HRMS (ESI-TOF) calcd for C₃₂H₂₈NO₆ [M+H]⁺:
14 522.1911, found 522.1901.
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33 **(Z)-2-(4-Chlorophenyl)-1-(4-phenyl-2H-benzo[e][1,3]oxazin-2-yl)vinyl benzoate (7d).**

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35 Following the typical procedure, 0.3 mmol scale, **6d** (121.8 mg, 0.45 mmol), 3 mL DCE,
36 **2a** (58.6 mg, 0.3 mmol), catalyst **C** (13.0 mg, 0.015 mmol) were stirred at 80 °C for 24 h.
37
38 Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1)
39 afforded **7d** as light yellow oil in 65% (90.6 mg) yield. ¹H NMR (400 MHz, CDCl₃) δ 8.10
40 (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* =
41 8.0 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.83 (s, 1H), 6.41 (s, 1H). ¹³C{¹H} NMR (100 MHz,
42 CDCl₃) δ 165.3, 163.8, 155.6, 145.1, 136.4, 133.7, 133.6, 131.7, 130.2, 130.1, 130.1,
43 129.0, 128.9, 128.60, 128.57, 128.3, 128.0, 121.5, 119.0, 118.3, 116.8, 85.9. IR (neat):
44 3061, 3033, 1733, 1605, 1491, 1240, 1062, 697 cm⁻¹. HRMS (ESI-TOF) calcd for
45 C₂₉H₂₁ClNO₃ [M+H]⁺: 466.1204, found 466.1197.
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2-Methyl-1-(4-phenyl-2H-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. ¹H NMR (400 MHz, CDCl₃) 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); ¹³C{¹H} NMR (100 MHz, CDCl₃) 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 C₂₅H₂₂NO₃ [M+H]⁺: 384.1594, found 384.1585.

(Z)-1-(4-(4-Methoxyphenyl)-2H-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. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 164.5, 163.9, 161.2, 155.8, 144.6, 133.5,

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4 133.4, 133.2, 130.7, 130.2, 129.1, 129.0, 128.9, 128.5, 128.4, 128.0, 127.9, 121.3, 120.1,
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6 118.5, 116.9, 113.6, 85.8, 55.3. IR (neat): 3061, 2931, 2836, 1732, 1603, 1513, 1241, 1062,
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8 706 cm⁻¹. HRMS (ESI-TOF) calcd for C₃₀H₂₄NO₄ [M+H]⁺: 462.1700, found 462.1692.
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15 **(Z)-1-(4-(4-Chlorophenyl)-2H-benzo[e][1,3]oxazin-2-yl)-2-phenylvinyl benzoate (7g).**

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17 Following the typical procedure, 0.3 mmol scale, 1-phenylprop-2-yn-1-yl benzoate (106.3
18 mg, 0.45 mmol), 3 mL DCE, **2c** (68.9 mg, 0.3 mmol), catalyst **C** (13.0 mg, 0.015 mmol)
19 were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum
20 ether: ethyl acetate = 30:1) afforded **7g** as light yellow oil in 86% (120.2 mg) yield. ¹H
21 NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.59-7.56 (m, 3H), 7.48-7.34 (m, 7H),
22 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,
23 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 164.0, 163.8, 155.7, 144.2, 136.2, 134.8, 133.8,
24 133.5, 133.0, 130.4, 130.1, 129.0, 128.8, 128.5, 128.3, 127.9, 127.5, 121.5, 120.1, 117.9,
25 116.9, 86.0. IR (neat): 3061, 3027, 1732, 1604, 1450, 1240, 1062, 705 cm⁻¹. HRMS
26 (ESI-TOF) calcd for C₂₉H₂₁ClNO₃ [M+H]⁺: 466.1204, found 466.1197.
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46 **(Z)-1-(4-(2-Methoxyphenyl)-2H-benzo[e][1,3]oxazin-2-yl)-2-phenylvinyl benzoate**

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48 **(7h).** Following the typical procedure, 0.3 mmol scale, 1-phenylprop-2-yn-1-yl benzoate
49 (106.3 mg, 0.45 mmol), 3 mL DCE, **2d** (67.6 mg, 0.3 mmol), catalyst **C** (13.0 mg, 0.015
50 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent:
51 petroleum ether: ethyl acetate = 10:1 to 7:1) afforded **7h** as light yellow oil in 38% (52.5
52 mg) yield. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H),
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4 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,
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6
7 $J = 7.6$ 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
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9 (s, 1H), 3.73 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 164.6, 163.8, 157.1, 154.1,
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11 144.2, 133.51, 133.47, 133.3, 130.7, 130.2, 129.9, 129.2, 128.8, 128.5, 128.4, 127.8, 127.8,
12
13 126.2, 121.2, 120.8, 120.4, 118.7, 116.5, 111.1, 86.2, 55.4. IR (neat): 3061, 2931, 2833,
14
15 1732, 1602, 1240, 1062, 706 cm^{-1} . HRMS (ESI-TOF) calcd for $\text{C}_{30}\text{H}_{24}\text{NO}_4$ $[\text{M}+\text{H}]^+$:
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17 462.1700, found 462.1691.
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25 **(Z)-1-(8-Methyl-4-phenyl-2H-benzo[e][1,3]oxazin-2-yl)-2-phenylvinyl benzoate (7i).**

26
27 Following the typical procedure, 0.3 mmol scale, 1-phenylprop-2-yn-1-yl benzoate (106.3
28 mg, 0.45 mmol), 3 mL DCE, **2h** (62.8 mg, 0.3 mmol), catalyst **C** (13.0 mg, 0.015 mmol)
29
30 were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum
31
32 ether: ethyl acetate = 20:1) afforded **7i** as light yellow oil in 61% (81.3 mg) yield. ^1H NMR
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34 (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),
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36 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,
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38 1H), 2.15 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 165.6, 163.9, 153.7, 144.6, 136.8,
39
40 134.9 133.6, 133.3, 130.2, 130.0, 129.1, 129.1 128.9, 128.5, 128.4, 128.2, 127.9, 126.1,
41
42 125.6, 120.7, 119.9, 118.0, 85.5, 15.0. IR (neat): 3058, 3027, 2917, 1732, 1599, 1240,
43
44 1062, 693 cm^{-1} . HRMS (ESI-TOF) calcd for $\text{C}_{30}\text{H}_{24}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 446.1751, found
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46 446.1742.
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20 X-ray crystallography of compound *Z-3i* (CIF)
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24 X-ray crystallography of compound *E-3m* (CIF)
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27 X-ray crystallography of compound *Z-3m* (CIF)
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30 X-ray crystallography of compound *E-3r* (CIF)
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34 X-ray crystallography of compound **4a** (CIF)
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37 X-ray crystallography of compound **5b** (CIF)
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41 X-ray crystallography of compound **7c** (CIF)
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Notes

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29 crystallographic data for this paper.
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33 (13)It should be noted that these products were unstable upon column chromatography on
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35 silica gel. Fast column separation is required to obtain the pure sample that contains
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37 only **3s** and **4q**.
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45 case, a mixture of **3s** (12%, *E/Z* = 1:1) and **4q** (65%) were obtained. In the latter case,
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47 a mixture of **3s** (21%, *E/Z* = 0.43:1) and **4q** (26%) were obtained. The results
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