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Note

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Lewis Acid Catalyzed [4 + 2]-Cycloaddition of N-Tosylhydrazones with ortho-Quinone Methides

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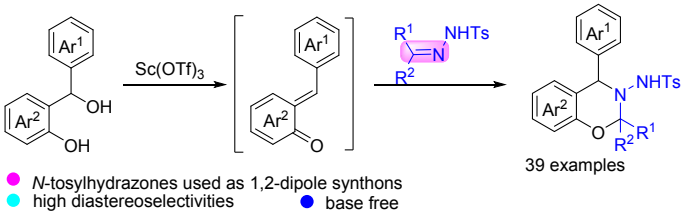
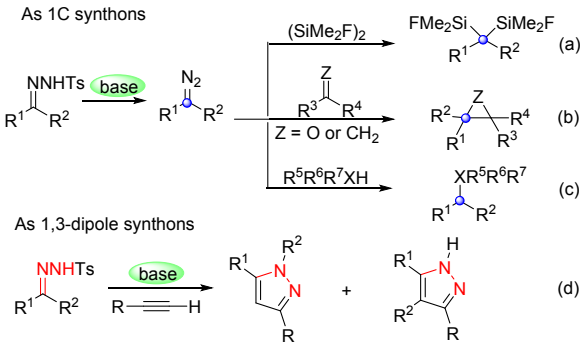
ABSTRACT: A formal [4 + 2] cycloaddition of N-tosylhydrazones with ortho-quinone methides was developed, affording facile synthesis of diverse 1,3-oxazine derivatives under mild conditions. In this transformation, N-tosylhydrazones are used as a 1,2-dipole synthon under base free conditions. Moreover, the substrate scope is broad and the products are formed with high diastereoselectivities in most of the cases.



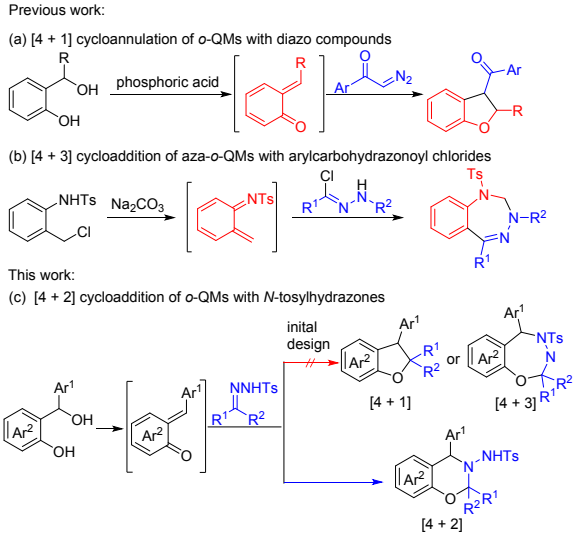
N-tosylhydrazones are versatile and useful intermediates that have various applications in organic synthesis.[1-3] As versatile 1C synthons, they are usually used as carbene precursors in various transformations, including carbene migratory insertions,[4] [1 + n] cycloaddition reactions[5] and carbene induced C−H[6] or X−H bond[7] (X = heteroatoms) insertions and other useful reactions.[8] For example, in 2015, Prof. Wang reported an interesting tandem carbene migratory insertion into Si-Si and Sn-Sn bonds for the facile access of germinal bis(silane) and germinal bis(stannane) derivatives (Scheme 1a).[4e] Prof. Aggarwal used *N*-tosylhydrazones to *in situ* generate diazo compounds and the subsequent asymmetric cycloaddition of carbonyl compounds would deliver epoxides with excellent enantioselectivities (Scheme 1b).[5h] Prof. Zhang also reported a highly enantioselective Co-catalyzed radical cyclopropanation of alkenes with *N*-tosylhydrazones to give di- or tri-substituted cyclopropanes (Scheme 1b).[5c] Recently, Prof. Che and Xu reported a novel Iron porphyrin catalyzed X−H (X = Si, Sn, Ge) bond insertions with wide substrate scope and excellent yields (Scheme 1c).[7a] On the other hand, as 1,3-dipole synthons, *N*-tosylhydrazones readily underwent a wide range of formal [3 + n] cycloadditions.[9] In 2015, Prof. Valdés discovered a 1,3-dipolar cycloaddition/[1,5] sigmatropic rearrangement of *N*-tosylhydrazones with terminal alkynes, affording synthetically valuable 3-substituted or 3,4-disubstituted pyrazoles (Scheme 1d).[9f] After that, Prof. Jiang and Wu also reported that *N*-tosylhydrazones could went through [3 + 2] cycloaddition with *in situ* formed acetylene (Scheme 1d).[9e] Despite all these exciting achievements described above, the applications of *N*-tosylhydrazones as 1,2-dipole synthons are extremely unexplored.[10] The reason may due to that most of the transformations of *N*-tosylhydrazones are performed under basic conditions. Therefore, it is really worthy to try the reactions of *N*-tosylhydrazones under acidic conditions,[9b] which may lead to new reactivities of *N*-tosylhydrazones.

Scheme 1. Reaction patterns of *N*-tosylhydrazones as 1C synthons and 1,3-dipole synthons



Ortho-quinone methides (*o*-QMs) are highly active intermediates that used frequently as Michael acceptors and 1,4-dipoles.[11-13] Recently, Prof. Schneider reported an interesting phosphoric acid catalyzed [4 + 1] cycloannulation of *o*-QMs with diazo compounds, affording highly enantiomerically enriched *cis*-2,3-dihydrobenzofurans (Scheme 2a).[12d] In addition, Prof. Guo also reported an elegant [4 + 3] cycloaddition of aza-*o*-QMs with arylcarbohydrazonoyl chlorides to afford 2,3-dihydro‐1*H*‐benzo[*e*][1,2,4]triazepines (Scheme 2b).[13b] Due to the amphiphilic property of *N*-tosylhydrazones, we envisioned that a [4 + 1] or [4 + 3] cycloaddition of *o*-QMs with *N*-tosylhydrazones would take place to furnish a five- or seven-membered ring system. Surprisingly, catalyzed by a Lewis acid, the [4 + 2] cycloaddition product was obtained. To the best of our knowledge, *N*-tosylhydrazones have never been involved in [4 + 2] cycloaddition reactions as 1,2-dipoles (Scheme 2c). Moreover, the 3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine skeleton exists in many natural products and synthetic pharmaceutical compounds.[14]

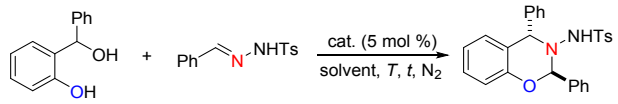
Scheme 2. Previous reported [4 + 1] and [4 + 3] cycloadditions of *o*-QMs and our unprecedented [4 + 2] cycloaddition using *N*-tosylhydrazones as 1,2-dipoles



Our initial study commenced with the reaction between 2-(hydroxy(phenyl)methyl)phenol (**1a**) and tosylhydrazone (**2a**). At the outset, in the presence of different bases, such as K_2CO_3, *t*-BuOK, DBU, and Et_3N, the reactions were found to be complex. Surprisingly, when the reaction was conducted under the catalysis of a strong Lewis acid $B(C_6F_5)_3$, unusual [4+2] cycloaddition product **3aa** was obtained, albeit in only 13% yield (Table 1, entry 1). The *trans*-configuration of **3aa** was unambiguously confirmed by X-Ray diffraction analysis (S1, see SI). Other boron catalysts , like $BF_3{\cdot}Et_2O$ and Ph_2BOH, provided similar yields (Table 1, entry 2−3). Among a set of metal Lewis acids that were screened, $Cu(OTf)_2$ and $Sc(OTf)_3$ gave the highest yield, while $Co(acac)_3$, $Pd(OAc)_2$, $Zn(OTf)_2$, $Yb(OTf)_2$, and $Fe(OTf)_3$ provided

lower yields (Table 1, entries 4−10). Next, a variety of solvents were investigated. It was found that the yield was improved to 50% using DCM as solvent, whereas PhCl and PhMe gave slightly diminished yields (Table 1, entries 11−13). However, the reactions were very sluggish when conducted in MeCN, THF and MeOH, probably due to the coordination of the solvents with the Lewis acid catalyst (Table 1, entries 14−16). To our delight, the addition of 4 Å MS drastically improved the yield, furnishing **3aa** in 80% yield (Table 1, entries 17−19). In addition, increasing the reaction temperature to 40 ℃ did not improve the yield (Table 1, entry 20).

Table 1. Optimization of the reaction conditions[a]



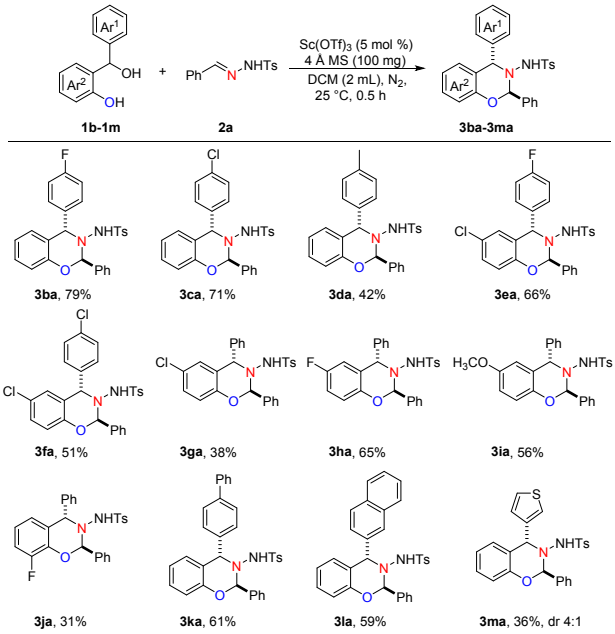
1a **2a** **3aa**

entry	cat.	solvent	T (℃)	t (h)	yield[b] (%)
1	$B(C_6F_5)_3$	DCE	25	1	13
2	$BF_3{\cdot}Et_2O$	DCE	25	1	11
3	Ph_2BOH	DCE	25	1	14
4	$Co(acac)_2$	DCE	70	12	20
5	$Pd(OAc)_2$	DCE	70	12	trace
6	$Zn(OTf)_2$	DCE	25	1	21
7	$Cu(OTf)_2$	DCE	25	1	33
8	$Yb(OTf)_3$	DCE	25	1	8
9	$Fe(OTf)_3$	DCE	25	1	15
10	$Sc(OTf)_3$	DCE	25	1	40
11	$Sc(OTf)_3$	DCM	25	0.5	50
12	$Sc(OTf)_3$	PhCl	25	0.5	46
13	$Sc(OTf)_3$	PhMe	25	0.5	38
14	$Sc(OTf)_3$	MeCN	25	0.5	8
15	$Sc(OTf)_3$	THF	25	0.5	N.D.
16	$Sc(OTf)_3$	MeOH	25	0.5	N.D.
17[c]	**$Sc(OTf)_3$**	**DCM**	**25**	**0.5**	**80**
18[d]	$Sc(OTf)_3$	DCM	25	0.5	76
19[e]	$Sc(OTf)_3$	DCM	25	0.5	70
20[c]	$Sc(OTf)_3$	DCM	40	0.5	68

[a]Unless otherwise stated, the reaction was performed with **1a** (0.20 mmol), **2a** (0.26 mmol) and cat. (5 mol %) in freshly distilled solvent (2 mL) under N_2 atmosphere. DCE: 1,2-Dichloroethane. DCM: Dichloromethane. [b]Isolated yields. [c]4 Å MS (100 mg). [d]4 Å MS (50 mg). [e]4 Å MS (200 mg).

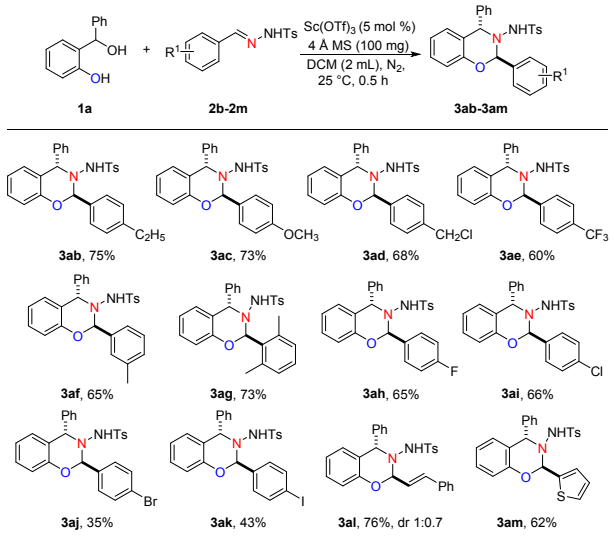
With the optimized reaction conditions in hand, the generality of this special [4+2] cycloaddition with respect to various diols **1** was firstly investigated. As shown in Table 2, better yields were notably obtained when aromatic ring Ar^1 was attached to an electron-withdrawing group (Table 2, **3ba** and **3ca** vs **3da**). The comparison of **3ea**, **3fa** with **3ga** also showed that the yield was improved when aromatic ring Ar^1 possessed an electron-withdrawing group. As for diols with electron-donating group or electron-withdrawing groups on the Ar^2 ring successfully anticipated in the reaction, affording the corresponding products in moderate yields (Table 2, **3ga**−**3ja**). The reaction could also tolerate biphenylyl and naphthyl groups, delivering **3ka** and **3la** in moderate yields. Finally, as for thienyl substituted substrate, the reaction could still afford the desired product **3ma** in 36% yield with a d.r. value of 4:1.

Table 2. Substrate Scope of 2−Hydroxybenzyl Alcohols[a]



[a]Reactions were performed with **1b-1m** (0.20 mmol), **2a** (0.26 mmol) and $Sc(OTf)_3$ (5 mol %) in freshly distilled DCM (2 mL) under N_2 atmosphere.

Table 3. Substrate Scope of Tosylhydrazones stemmed from various substituted aldehydes[a]

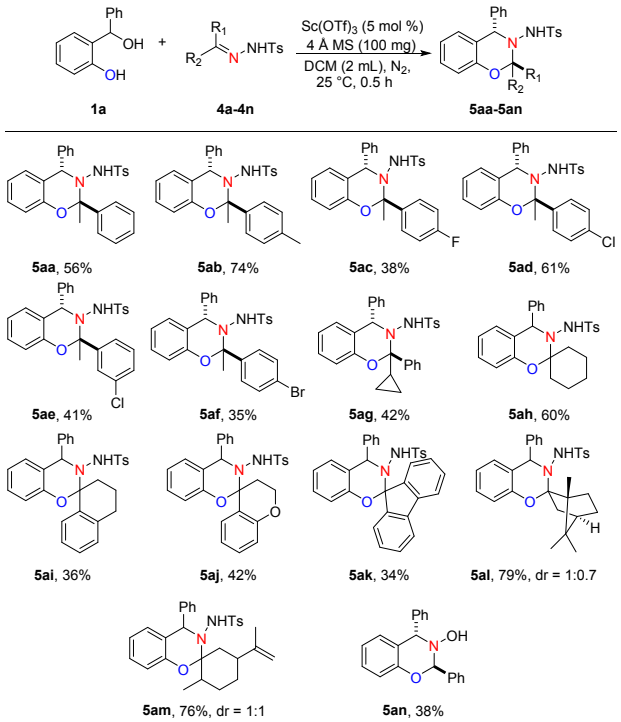


[a]Reactions were performed with **1a** (0.20 mmol), **2b-2m** (0.26 mmol) and $Sc(OTf)_3$ (5 mol %) in freshly distilled DCM (2 mL) under N_2 atmosphere.

After demonstrating the generality of this intriguing [4+2] cycloaddition with respect to diols, we then switched our attention to the scope of tosylhydrazones which were simply prepared from various substituted aldehydes (Table 3). As expected, tosylhydrazones with various electron-donating groups, such as methyl, ethyl, and methoxy groups, served well in this reaction, providing the corresponding products in 65%-75% yields (Table 3, **3ab**, **3ac**, **3ag** and **3af**). Moveover, tosylhydrazones with chloromethyl, trifluoromethyl and halogen groups were well tolerated (**3ad**, **3ae**, and **3ah**−**3ak**). In addition, cinnamyl tosylhydrazone could also take part in the reaction, affording the olefin containing 3,4-

dihydro-2*H*-benzo[*e*][1,3]oxazine **3al** in 76% yield with d.r. value of 1:0.7. This system was also applicable for tosylhydrazone derived from 2-thenaldehyde, affording the thienyl-containing product **3am** in 62% yield.

Table 4. Substrate Scope of Tosylhydrazones Derived Ketones[a]

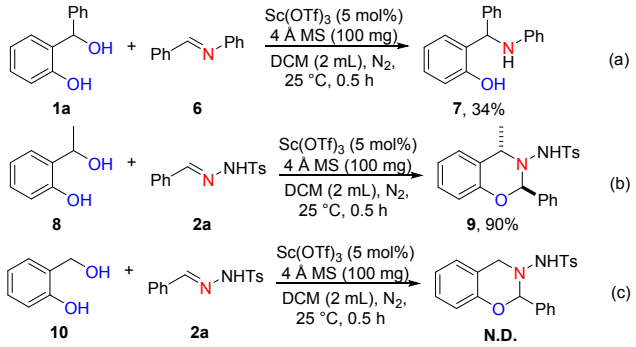


[a]Reactions were performed with **1a** (0.20 mmol), **4a-4n** (0.26 mmol) and $Sc(OTf)_3$ (5 mol %) in freshly distilled DCM (2 mL) under N_2 atmosphere.

To further broaden the reaction scope, tosylhydrazones prepared from ketones were examined. First of all, tosylhydrazones stemed from acetophenones with various substituents such as methyl, fluoro, chloro and bromo groups, were explored, and the reactions afforded the corresponding products in 35−74% yields (Table 4, **5aa**−**5af**). In addition, reaction conditions were also compatible for tosylhydrazones prepared from cyclopropyl phenyl ketone, giving the corresponding product **5ag** in 42% yield. Furthermore, we tested tosylhydrazones prepared from cyclohexanone, offering the desired spiral products **5ah** in 60% yield. 1,2,3,4-Tetrahydronaphthalene, 3,4-dihydro-(1H)-benzopyrane and 9-fluorenone derived tosylhydrazones were also suitable for this reaction, delivering the desired spiral products in relatively lower yields, probably due to the sterical hindrance (Table 4, **5ai**−**5ak**). To our delight, natural products, such as camphor and (+)-dihydrocarvone derived tosylhydrazones were good partners for this cycloaddition, providing the corresponding spiral products in 79% and 76% yield, respectively (Table 4, **5al**−**5am**). It is worth noting that this system was also compatible for benzaldoxime and the desired product **5an** was obtained in 38% yield.

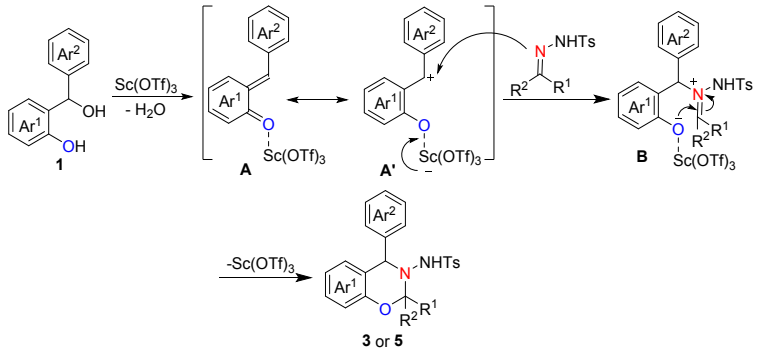
To gain more mechanistic insight into this reaction, several control experiments were carried out (Scheme 3). First, the reactivity of imine with *o*-QMs was tested, and only product **7** from nucleophilic substitution by aniline was detected in 34% yield (Scheme 3a). Under the typical reaction conditions, the reactions of **8** and **10** with hydrazone **2a** gave quite different results. It was found that **8** could react with hydrazone smoothly and provided the desired product **9** in 90% yield (Scheme 3b), while the reaction of **10** with **2a** could not take place (Scheme 3c), indicating that the putative cation intermediate was not stable enough in case of compound **10** used as starting material.

Scheme 3. Control experiments.



On the basis of the experimental results and previous studies in *o*-QMs chemistry,[11-13] a plausible mechanism is proposed and illustrated in Scheme 4. Firstly, in the presence of Lewis acid $Sc(OTf)_3$, diols are converted into *o*-QMs by dehydration. Then, *o*-QMs are activated by $Sc(OTf)_3$ to form highly active intermediates which consist of resonance structures **A** and **A'**. The following nucleophilic attack by imine moiety of *N*-tosylhydrazone gives intermediates **B**, subsequent cyclization furnishes the final products **3** or **5** togother with the regeneration of catalyst.

Scheme 4. Plausible Mechanism



In summary, we have developed a highly diastereoselective [4 + 2] cycloaddition of *o*-QMs with *N*-tosylhydrazones, which provided 3,4-dihydro-2H-benzo[*e*][1,3]oxazines in an easy and practical way from readily accessible starting materials in considerable yields. Different from the basic reaction conditions of *N*-tosylhydrazone transformations reported previously, this reaction mode develops new reactivity of *N*-tosylhydrazones catalyzed by a Lewis acid. Further related studies of extended transformations and applications are currently underway in our laboratory.

EXPERIMENTAL SECTION

General Remarks: ^{1}H NMR and ^{13}C{1H} NMR spectra were recorded on a 400 and 600 MHz spectroscopy in $CDCl_3$, acetone-d_6 or DMSO-d_6; Chemical shifts (δ) are expressed in ppm and *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. The solvents and chemicals were purchased and used as reveived. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

General Procedure for the Synthesis of 1. Method A[15c]**:** Under argon atmosphere, a solution of substituted salicylaldehyde (5.0 mmol) in tetrahydrofuran (10 mL) was added dropwise to a solution of the corresponding Grignard reagent (10.0 mmol, 1.0 M in THF, 10 mL), the mixture was stirred at room

temperature. After complete conversion (monitored by TLC), the reaction mixture was quenched by saturated ammonium chloride (10 mL) and extracted with EtOAc (30 mL × 3). The combined organic layer was dried by anhydrous Na_2SO_4, and concentrated. The residue was chromatographed on silica gel eluting with petroleum ether/EtOAc (5:1) to give the product as a white solid (**1a, 1g-1j**). **Method B**[15a]**:** Under argon atmosphere, to a solution of magnesium (30.0 mmol) and a granule of I_2 in anhydrous THF (15 mL) was added dropwise a solution of Ar^1X (X=Br, Cl) (30.0 mmol) in anhydrous THF (10 mL), controlling the speed to maintain THF boiling. After adding, the system was refluxed for 1 h in oil bath. Then cooled to 0 °C, a solution of substituted salicylaldehyde (10.0 mmol) in THF (5 mL) was added dropwise to the mixture, and the mixture was stirred at room temperature. After complete conversion (monitored by TLC), saturated NH_4Cl was added dropwise to the system at 0 °C, then the resulting solution was extracted with EtOAc (50 mL × 3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on silica gel eluting with petroleum ether/EtOAc (5:1) to give the product as a white solid (**1b-1f**). **Method C**[15d]**:** Under the nitrogen atmosphere, to an oven dried flask charged with a solution of the Ar^1Br (12.5 mmol) in dry THF (12.5 mL) was added *n*-BuLi (12.5 mmol, 1.6 M in hexane, 7.8 mL) dropwise at −78 °C. The resulted mixture was stirred at the same temperature for 1 h and then a solution of substituted salicylaldehyde (5 mmol) in dry THF (2.5 mL) was added dropwise. The reaction mixture was allowed to be warmed to room temperature and stirred overnight. Upon completion (monitored by TLC), the reaction mixture was cooled to 0 °C and treated with saturated aqueous NH_4Cl solution (20 mL). The mixture was extracted with EtOAc (3 × 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel chromatography to afford the pure products (**1k-1m**). **1a**;[15a] **1b**;[15b] **1c**, **1g**, **1i**, **1k-1m**;[15e] **1d**, **8**;[15g] **1f**;[15f] were reported in previous literature; and **1e, 1h, 1j** are reported for the first time, and physical datas and spectroscopics are presented as follows.

General Procedure for the Synthesis of 2 and 4[18]**.** The aldehyde or ketone (5 mmol) was added dropwise to a round-bottom flask charged with hydrazide or hydroxylamine (5 mmol) in methanol (5 mL) at 60 °C in oil bath. After completion of the reaction (monitored by TLC), the resulted mixture was concentrated in vacuo. Then the crude product was filtered, washed with petroleum ether/ethyl acetate (10:1) and dried in vacuo to afford the corresponding pure hydrazones or oximes (**2a-2m**, **4a-4n**). **2a**, **2c**;[16a] **2e, 2h, 2j, 4k**;[16b] **2f, 4a-4f, 4h-4j**;[16c] **4g**;[16d] **2m, 2l**;[16e] **4m**;[16f] **4n**;[16g] **2i**;[16h] **4l**;[16i] were reported in previous literature; and **2b, 2d, 2g, 2k** are reported for the first time, and physical datas and spectroscopics are presented as follows.

General Procedure for the Synthesis of product 3, 5. A 10 mL reaction tube equipped with a magnetic stir bar was charged with dried 4Å molecular sieve (100 mg), diols (0.2 mmol), tosylhydrazones (0.26 mmol), $Sc(OTf)_3$ (5 mmol %) and DCM (2 mL) under N_2. The reaction mixture was stirred at 25 °C for 0.5 h. After completion (checked by TLC), the solution was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (PE:EA = 10:1 or 5:1) to afford **3**, **5**.

General Procedure of 1.0 mmol scale for the Synthesis of product 3aa: A 25 mL reaction tube equipped with a magnetic stir bar was charged with dried 4Å molecular sieve (500 mg), diols (1 mmol), tosylhydrazones (1.3 mmol), $Sc(OTf)_3$ (5 mmol %) and DCM (10 mL) under N_2. The reaction mixture was stirred at 25 °C for 0.5 h. After completion (checked by TLC), the solution was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (PE:EA = 10:1 or 5:1) to afford **3aa** (338 mg, 74%).

*4-Chloro-2-((4-fluorophenyl)(hydroxy)methyl)phenol (**1e**)*, faint yellow solid, mp: 87−88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.36–7.31 (m, 2H), 7.13 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.08–7.03 (m, 2H), 6.82–6.79 (m, 2H), 5.92 (s, 1H), 3.10 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.13 –-113.21 (m); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 248.5 Hz), 153.8, 136.9 (d, *J* = 3.2 Hz), 129.2, 128.6

(d, J = 8.3 Hz), 128.0, 127.7, 124.8, 118.6, 115.8 (d, J = 21.6 Hz), 75.7; IR(KBr): ν 3292, 1602, 1507, 1485, 1222, 904, 728 cm^{-1}; HRMS (ESI-TOF) m/z: [M^-] Calcd for $C_{13}H_9ClFO_2$ 251.0280; Found 251.0275.

4-Fluoro-2-(hydroxy(phenyl)methyl)phenol ***(1h)***, white solid, mp: 66−69 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.37–7.30 (m, 5H), 6.84 (td, J = 8.8, 2.8 Hz, 1H), 6.78–6.75 (m, 1H), 6.54 (dd, J = 8.8, 2.8 Hz, 1H), 5.89 (d, J = 3.2 Hz, 1H), 3.27 (d, J = 3.2 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.07 – -124.13 (m); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.4 (d, J = 238.8 Hz), 151.1 (d, J = 2.1 Hz), 141.2, 128.8, 128.5, 127.8 (d, J = 6.6 Hz), 126.8, 117.9 (d, J = 7.9 Hz), 115.5 (d, J = 23.0 Hz), 114.5 (d, J = 24.2 Hz), 76.2; IR(KBr): ν 3299, 1491, 1438, 1263, 1179, 942, 732 cm^{-1}; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{13}H_{11}FO_2Na$ 241.0637; Found 241.0635.

2-Fluoro-6-(hydroxy(phenyl)methyl)phenol ***(1j)***, colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.38–7.29 (m, 5H), 7.02–6.96 (m, 1H), 6.78–6.72 (m, 2H), 5.99 (s, 1H), 3.60 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.89 – -138.93 (m); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 151.5 (d, J = 241.6 Hz), 142.6 (d, J = 13.9 Hz), 141.8, 130.1 (d, J = 2.1 Hz), 128.5, 128.0, 126.6, 122.9 (d, J = 3.4 Hz), 119.7 (d, J = 7.4 Hz), 115.0 (d, J = 18.4 Hz), 74.8 (d, J = 3.0 Hz); IR(KBr): ν 3279, 1619, 1475, 1259, 1020, 908, 728 cm^{-1}; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{13}H_{11}FO_2Na$ 241.0637; Found 241.0637.

(E)-N'-(4-ethylbenzylidene)-4-methylbenzenesulfonohydrazide ***(2b)***, white solid, mp: 135−137 °C; ^1H NMR (400 MHz, Acetone-d_6) δ 10.05 (s, 1H), 7.96 (s, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 2.63 (q, J = 7.6 Hz, 2H), 2.37 (s, 3H), 1.18 (t, J = 7.6 Hz, 3H); $^{13}C\{1H\}$ NMR (101 MHz, Acetone-d_6) δ 148.1, 147.4, 144.5, 137.5, 132.6, 130.3, 129.0, 128.6, 127.9, 29.3, 21.4, 15.8; IR (KBr): ν 3192, 2965, 1324, 1163, 1042, 942, 704 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{16}H_{18}N_2O_2SH$ 303.1162; Found 303.1164.

(E)-N'-(4-(chloromethyl)benzylidene)-4-methylbenzenesulfonohydrazide ***(2d)***, white solid, mp: 131−132 °C; ^1H NMR (400 MHz, Acetone-d_6) δ 10.20 (s, 1H), 7.99 (s, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 4.71 (s, 2H), 2.37 (s, 3H); $^{13}C\{1H\}$ NMR (101 MHz, Acetone-d_6) δ 147.2, 144.7, 140.6, 137.4, 135.0, 130.4, 129.9, 128.5, 128.0, 46.3, 21.4; IR(KBr): ν 3193, 2959, 1362, 1164, 1053, 943, 704 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{15}H_{15}ClN_2O_2SH$ 323.0616; Found 323.0618.

(E)-N'-(2,6-dimethylbenzylidene)-4-methylbenzenesulfonohydrazide ***(2g)***, white solid, mp: 143–144 °C; ^1H NMR (400 MHz, Acetone-d_6) δ 10.11 (s, 1H), 8.33 (s, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.12–7.09 (m, 1H), 7.00 (d, J = 7.6 Hz, 2H), 2.39 (s, 3H), 2.26 (s, 6H); $^{13}C\{1H\}$ NMR (101 MHz, Acetone-d_6) δ 148.1,144.6, 138.3, 137.5, 131.6, 130.3, 129.7, 129.5, 128.7, 21.4, 21.3; IR(KBr): ν 3192, 2967, 1324, 1162, 1057, 951, 706 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{16}H_{18}N_2O_2SH$ 303.1162; Found 303.1163.

(E)-N'-(4-iodobenzylidene)-4-methylbenzenesulfonohydrazide ***(2k)***, white solid, mp: 194–195 °C; ^1H NMR (600 MHz, DMSO-d_6) δ 11.54 (s, 1H), 7.87 (s, 1H), 7.77–7.75 (m, 4H), 7.41 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 2.36 (s, 3H); $^{13}C\{1H\}$ NMR (151 MHz, DMSO-d_6) δ 146.0, 143.5, 137.6, 136.1, 133.2, 129.7, 128.5, 127.2, 96.8, 21.0; IR(KBr): ν 3193, 2972, 1394, 1167, 1051, 879, 704 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{14}H_{13}IN_2O_2SH$ 400.9815; Found 400.9818.

*N-(2,4-diphenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(****3aa****)*, white solid, mp: 129–130 °C, yield 81% (74.0 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.80 (s, 1H), 7.57–7.55 (m, 2H), 7.50–7.46 (m, 1H), 7.41–7.38 (m, 2H), 7.22–7.21 (m, 4H), 7.19–7.17 (m, 1H), 7.15–7.13 (m, 4H), 6.90 (d, J = 8.0 Hz, 2H), 6.85 (ddd, $J_{1,2}$ = 7.4 Hz, J_3 = 1.2 Hz, 1H), 6.59–6.58 (m, 2H), 2.27 (s, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.0, 155.6, 143.8, 136.7, 133.5, 132.7, 131.6, 130.1, 129.2, 128.9, 128.8, 128.5, 128.3, 128.1, 127.4, 121.3, 119.5, 118.1, 69.0, 21.5; IR(KBr): ν 3062, 1598, 1487, 1185, 1159, 1086, 872, 754 cm^{-1}; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{27}H_{24}N_2O_3SNa$ 479.1400; Found 479.1410.

*N-(4-(4-fluorophenyl)-2-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(****3ba****)*, white solid, mp: 127–128 °C, yield 79% (75.0 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.80 (s, 1H), 7.57 (d, J = 7.3 Hz, 2H), 7.50 (dd, $J_{1,2}$ = 7.2 Hz, 1H), 7.42 (dd, $J_{1,2}$ = 7.4 Hz, 2H), 7.25–7.16 (m, 4H),

7.13 (d, J = 8.2 Hz, 2H), 6.92–6.83 (m, 5H), 6.58 (d, J = 8.0 Hz, 1H), 6.53 (s, 1H), 2.28 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.86 – -114.93 (m); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 166.2, 162.0 (d, J = 247.5 Hz), 155.5, 143.9, 133.4, 132.9, 132.5 (d, J = 3.0 Hz), 131.5, 130.3, 130.1 (d, J = 7.1 Hz), 129.3, 128.9, 128.8, 128.1, 121.2, 119.7, 118.2, 115.4 (d, J = 21.2 Hz), 68.5, 21.5; IR(KBr): ν 3074, 1601, 1505, 1487, 1185, 1160, 905, 724 cm^{-1}; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{27}H_{23}FN_2O_3SNa$ 497.1306; Found 497.1320.

*N-(4-(4-chlorophenyl)-2-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**3ca**)*, white solid, mp: 77–81 °C, yield 71% (69.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.81 (s, 1H), 7.58 (d, J = 7.2 Hz, 2H), 7.50 (dd, $J_{1,2}$ = 7.2 Hz, 1H), 7.42 (dd, $J_{1,2}$ = 7.4 Hz, 2H), 7.17–7.12 (m, 8H), 6.90 (d, J = 8.0 Hz, 2H), 6.85 (dd, $J_{1,2}$ = 7.0 Hz, 1H), 6.59 (d, J = 7.2 Hz, 1H), 6.52 (s, 1H), 2.27 (s, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 166.1, 155.5, 144.0, 135.4, 133.4, 133.3, 132.9, 131.5, 130.3, 129.8, 129.3, 128.9, 128.8, 128.7, 128.1, 121.0, 119.7, 118.2, 68.4, 21.4; IR(KBr): ν 3292, 1600, 1185, 1161, 1085, 905, 726 cm^{-1}; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{27}H_{23}ClN_2O_3SNa$ 513.1010; Found 513.1020.

*4-Methyl-N-(2-phenyl-4-(p-tolyl)-2H-benzo[e][1,3]oxazin-3(4H)-yl)benzenesulfonamide(**3da**)*, white solid, mp: 109–111 °C, yield 42% (39.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.78 (s, 1H), 7.58 (d, J = 7.2 Hz, 2H), 7.50 (dd, $J_{1,2}$ = 7.2 Hz, 2H), 7.42 (dd, $J_{1,2}$ = 7.4 Hz, 2H), 7.19–7.11 (m, 6H), 6.89 (d, J = 8.0 Hz, 2H), 6.84 (dd, $J_{1,2}$ = 7.4 Hz, 1H), 6.74 (d, J = 8.8 Hz, 2H), 6.56 (d, J = 8.0 Hz, 1H), 6.51 (s, 1H), 3.69 (s, 3H), 2.28 (s, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 166.3, 158.7, 155.6, 143.8, 133.5, 133.4, 132.8, 131.7, 130.0, 129.6, 129.2, 129.0, 128.8, 128.6, 128.1, 121.6, 119.5, 118.1, 113.8, 68.8, 55.1, 21.5; IR(KBr): ν 3067, 1608, 1510, 1161, 1087, 910, 729 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{28}H_{26}N_2O_3SH$ 471.1737; Found 471.1731.

*N-(6-chloro-4-(4-fluorophenyl)-2-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**3ea**)*, white solid, mp: 157–158 °C, yield 66% (67.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.81 (s, 1H), 7.60 (d, J = 7.2 Hz, 2H), 7.53 (dd, $J_{1,2}$ = 7.0 Hz, 1H), 7.45 (dd, $J_{1,2}$ = 7.4 Hz, 2H), 7.21–7.15 (m, 4H), 7.11 (s, 1H), 7.08 (d, J = 8.8 Hz, 1H), 6.98 (d, J = 8.0 Hz, 2H), 6.92 (dd, $J_{1,2}$ = 8.4 Hz, 2H), 6.50 (d, J = 8.4 Hz, 1H), 6.40 (s, 1H), 2.30 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.38 – -114.40 (m); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 167.3, 162.1 (d, J = 248.5 Hz), 154.2, 144.3, 133.4, 133.2, 132.6, 131.7 (d, J = 3.0 Hz), 131.3, 130.0 (d, J = 8.1 Hz), 129.9, 129.4, 129.1, 129.0, 128.1, 124.1, 122.8, 119.7, 115.6 (d, J = 22.2 Hz), 67.8, 21.5; IR(KBr): ν 3734, 1600, 1508, 1344, 1183, 1157, 1059, 718 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{27}H_{22}ClFN_2O_3SH$ 509.1096; Found 509.1099.

*N-(6-chloro-4-(4-chlorophenyl)-2-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**3fa**)*, white solid, mp: 152–154 °C, yield 51% (53.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.82 (s, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.53 (dd, $J_{1,2}$ = 7.2 Hz, 1H), 7.44 (dd, $J_{1,2}$ = 7.4 Hz, 2H), 7.21–7.19 (m, 4H), 7.14–7.07 (m, 4H), 6.97 (d, J = 8.0 Hz, 2H), 6.51 (d, J = 8.4 Hz, 1H), 6.39 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 154.2, 144.3, 134.6, 133.6, 133.4, 133.2, 132.6, 131.3, 129.9, 129.6, 129.4, 129.1, 129.0, 128.8, 128.1, 124.1, 122.5, 119.7, 67.7, 21.5; IR(KBr): ν 3733, 1599, 1486, 1385, 1183, 1158, 1086, 710 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{27}H_{22}Cl_2N_2O_3SH$ 525.0801; Found 525.0804.

*N-(6-chloro-2,4-diphenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide (**3ga**)*, white solid, mp: 158−159 °C, yield 38% (37.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.81 (s, 1H), 7.58 (d, J = 7.4 Hz, 2H), 7.51 (dd, $J_{1,2}$ = 7.2 Hz, 1H), 7.42 (dd, $J_{1,2}$ = 7.4 Hz, 2H), 7.25–7.16 (m, 7H), 7.13 (d, J = 1.6 Hz, 1H),7.07 (dd, J = 8.4, 2.0 Hz, 1H), 6.97 (d, J = 8.0 Hz, 2H), 6.51 (d, J = 8.6 Hz, 1H), 6.44 (s, 1H), 2.30 (s, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 167.0, 154.4, 144.1, 136.0, 133.6, 133.0, 132.7, 131.5, 129.7, 129.3, 129.1, 128.9, 128.6, 128.2, 128.1, 127.7, 124.0, 123.0, 119.5, 68.4, 21.5; IR(KBr): ν 3357, 1748, 1480, 1185, 1160, 1086, 906, 728 cm^{-1}; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{27}H_{23}ClN_2O_3SNa$ 513.1010; Found 513.1023.

*N-(6-fluoro-2,4-diphenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide (**3ha**)*, white solid, mp: 148–149 °C, yield 65% (61.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.79 (s, 1H),

7.57 (d, J = 7.6 Hz, 2H), 7.49 (dd, $J_{1,2}$ = 7.0 Hz, 1H), 7.41 (dd, $J_{1,2}$ = 7.2 Hz, 2H), 7.23–7.21 (m, 6H), 7.17–7.15 (m, 1H), 6.97 (d, J = 7.9 Hz, 2H), 6.90 (dd, J = 9.2, 2.4 Hz 1H), 6.85 (td, J = 8.4, 2.4 Hz, 1H), 6.52 (dd, J = 8.4, 3.6 Hz, 1H), 6.47 (s, 1H), 2.29 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.17 – -126.23 (m); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 166.6, 156.1 (d, J = 238.4 Hz), 151.7, 144.1, 136.1, 133.6, 132.9, 131.5, 129.2, 128.9 (d, J = 3.0 Hz), 128.6, 128.2, 128.1, 127.7, 122.4 (d, J = 7.1 Hz), 119.1 (d, J = 23.2 Hz), 118.9 (d, J = 7.8 Hz), 116.4 (d, J = 22.2 Hz), 68.3, 21.5; IR(KBr): ν 3340, 1599, 1493, 1163, 1140, 1060, 905, 724 cm^{-1}; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{27}H_{23}FN_2O_3SNa$ 497.1306; Found 497.1310.

*N-(6-methoxy-2,4-diphenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**3ia**)*, pale yellow solid, mp: 136–137 °C, yield 56% (54.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 8.78 (s, 1H), 7.56 (d, J = 7.6 Hz, 2H), 7.48 (dd, $J_{1,2}$ = 7.2 Hz, 1H), 7.40, (dd, $J_{1,2}$ = 7.4 Hz, 2H), 7.24–7.15 (m, 7H), 6.94 (d, J = 8.0 Hz, 2H), 6.74–6.73 (m, 2H), 6.53–6.50 (m, 2H), 3.78 (s, 3H), 2.29 (s, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 165.9, 152.8, 149.5, 143.9, 136.6, 133.6, 132.7, 131.7, 129.2, 128.9, 128.8, 128.5, 128.3, 128.1, 127.5, 121.8, 118.8, 117.9, 116.0, 68.8, 55.9, 21.5; IR(KBr): ν 3029, 1598, 1495, 1162, 1085, 1040, 906, 724 cm^{-1}; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{28}H_{26}N_2O_4SNa$ 509.1505; Found 509.1511.

*N-(8-fluoro-2,4-diphenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**3ja**)*, white solid, mp: 156–157 °C, yield 31% (29.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 8.77 (s, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.50 (dd, $J_{1,2}$ = 7.2 Hz, 1H), 7.41 (dd, $J_{1,2}$ = 7.4 Hz, 2H), 7.24–7.21 (m, 4H), 7.15 (d, J = 7.9 Hz, 3H), 6.98–6.93 (m, 4H), 6.78–6.73 (m, 1H), 6.57 (s, 1H), 2.30 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.23 – -136.27 (m); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 167.7, 153.1 (d, J = 244.0 Hz), 144.3 (d, J = 7.8 Hz), 144.2 (d, J = 12.4 Hz), 136.2, 133.3, 133.1, 131.2, 129.3, 129.1, 128.7, 128.6, 128.3, 128.1 (d, J = 3.1 Hz), 128.0, 127.7, 123.8, 119.0 (d, J = 7.5 Hz), 116.3 (d, J = 19.2 Hz), 68.4, 21.4; IR(KBr): ν 3029, 1598, 1493, 1185, 1161, 1086, 908, 727 cm^{-1}; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{27}H_{23}FN_2O_3SNa$ 497.1306; Found 497.1314.

*N-(4-([1,1'-biphenyl]-4-yl)-2-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**3ka**)*, white solid, mp: 147–148 °C, yield 61% (65.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.84 (s, 1H), 7.58 (d, J = 7.6 Hz, 2H), 7.49–7.44 (m, 5H), 7.41–7.33 (m, 4H), 7.28 (d, J = 8.0 Hz, 3H), 7.22 (d, J = 7.2 Hz, 1H), 7.19–7.15 (m, 3H), 6.91–6.84 (m, 3H), 6.62–6.60 (m, 2H), 2.27 (s, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 166.0, 155.6, 143.8, 140.4, 140.2, 135.8, 133.5, 133.4, 132.8, 131.6, 130.2, 129.2, 128.9, 128.8, 128.7, 128.6, 128.1, 127.3, 127.2, 126.9, 121.4, 119.6, 118.1, 68.8, 21.5; IR(KBr): ν 3029, 1598, 1486, 1185, 1159, 1086, 906, 728 cm^{-1}; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{33}H_{28}N_2O_3SNa$ 555.1713; Found 555.1714.

*4-Methyl-N-(4-(naphthalen-2-yl)-2-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)benzenesulfonamide(**3la**)*, white solid, mp: 135–137 °C, yield 59% (59.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.83 (s, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 7.5 Hz, 1H), 7.55–7.51 (m, 3H), 7.47 (s, 1H), 7.40 (d, J = 7.2 Hz, 1H), 7.37–7.31 (m, 4H), 7.25–7.19 (m, 2H), 7.16 (d, J = 8.3 Hz, 2H), 6.91–6.85 (m, 3H), 6.72 (s, 1H), 6.64 (d, J = 8.0 Hz, 1H), 2.26 (s, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 166.1, 155.8, 143.8, 134.1, 133.5, 133.1, 132.7, 132.5, 131.5, 130.2, 129.1, 128.9, 128.8, 128.3, 128.2, 128.1, 127.6, 127.3, 126.1, 125.9, 121.2, 119.6, 118.2, 69.2, 21.4; IR(KBr): ν 3346, 1600, 1487, 1161, 1060, 904, 727 cm^{-1}; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{31}H_{26}N_2O_3SNa$ 529.1556; Found 529.1563.

*4-Methyl-N-(2-phenyl-4-(thiophen-3-yl)-2H-benzo[e][1,3]oxazin-3(4H)-yl)benzenesulfonamide(**3ma**)*, white solid, mp: 114–116 °C, yield 36% (33.3 mg), dr = 4:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 0.25H), 9.93 (s, 1H), 8.87 (s, 0.25H), 8.81 (s, 1H), 7.66–7.64 (m, 0.5H), 7.60–7.58 (m, 2H), 7.52–7.47 (m, 1.25H), 7.45–7.40 (m, 2.5H), 7.21–7.19 (m, 1.25H), 7.18–7.16 (m, 1.25H), 7.15–7.11 (m, 3.75H), 7.02 (dd, J = 5.2, 1.2 Hz, 1H), 6.89 (d, J = 8.0 Hz, 2.5H), 6.86–6.85 (m, 1.25H), 6.82 (ddd, $J_{1,2}$ = 7.4 Hz, J_3 = 1.2 Hz, 1.25H), 6.75–6.73 (m, 0.25H), 6.65 (s, 0.25H), 6.62–6.60 (m, 0.25H), 6.57 (dd, J = 8.4, 1.2 Hz, 1H), 6.49 (s, 1H), 2.26 (s, 3.75H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 168.0, 166.2, 155.3, 155.2, 143.9, 143.8, 140.7, 137.9, 133.3, 133.1, 133.0, 132.9, 132.8, 131.6, 131.5, 130.3, 130.1, 129.2, 129.1,

128.9, 128.8, 128.7, 128.2, 128.1, 127.4, 126.7, 126.4, 126.1, 124.4, 122.2, 121.8, 119.4, 119.3, 118.2, 118.1, 66.0, 65.9, 21.4; IR(KBr): ν 2952, 1597, 1486, 1348, 1158, 1085, 734 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{22}N_2O_3S_2H$ 463.1145; Found 463.1149.

*N-(2-(4-ethylphenyl)-4-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**3ab**)*, white solid, mp: 73–75 °C, yield 75% (72.7 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 8.77 (s, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.24–7.18 (m, 7H), 7.16–7.11 (m, 4H), 6.88 (d, J = 8.0 Hz, 2H), 6.83 (dd, $J_{1,2}$ = 7.2 Hz, 1H), 6.57–6.64 (m, 2H), 2.65 (q, J = 7.6 Hz, 2H), 2.27 (s, 3H), 1.21 (t, J = 7.6 Hz, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.9, 155.7, 150.0, 143.7, 136.8, 133.5, 133.4, 130.1, 129.2, 129.1, 128.8, 128.7, 128.4, 128.3, 128.1, 127.4, 121.2, 119.4, 118.1, 69.1, 29.0, 21.4, 15.1; IR(KBr): ν 2965, 1600, 1486, 1181, 1162, 1086, 908, 726 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{28}N_2O_3SNa$ 507.1713; Found 507.1721.

*N-(2-(4-methoxyphenyl)-4-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**3ac**)*, white solid, mp: 122–125 °C, yield 73% (71.0 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 10.42 (s, 1H), 8.70 (s, 1H), 7.55 (d, J = 8.8 Hz, 2H), 7.21–7.16 (m, 5H), 7.15–7.10 (m, 4H), 6.92–6.87 (m, 4H), 6.83 (dd, $J_{1,2}$ = 7.4 Hz, 1H), 6.54–6.51 (m, 2H), 3.83 (s, 3H), 2.28 (s, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.3, 163.5, 155.8, 143.6, 136.8, 133.6, 133.4, 131.1, 130.0, 128.7, 128.5, 128.4, 128.2, 127.4, 124.1, 121.2, 119.4, 118.1, 114.7, 69.2, 55.5, 21.5; IR(KBr): ν 2926, 1595, 1485, 1161, 1086, 1063, 833, 729 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{26}N_2O_4SH$ 487.1686; Found 487.1694.

*N-(2-(4-(chloromethyl)phenyl)-4-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**3ad**)*, white solid, mp: 126–128 °C, yield 68% (68.7 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 8.78 (s, 1H), 7.54 (d, J = 7.6 Hz, 2H), 7.40 (d, J = 7.6 Hz, 2H), 7.21, (m, 5H), 7.15–7.13 (m, 4H), 6.91 (d, J = 8.0 Hz, 2H), 6.85 (dd, $J_{1,2}$ = 7.4 Hz, 1H), 6.60 (m, 2H), 4.54 (s, 2H), 2.28 (s, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.1, 155.6, 143.9, 142.0, 136.7, 133.5, 133.4, 131.7, 130.2, 129.3, 129.1, 128.9, 128.5, 128.3, 128.1, 127.5, 121.4, 119.6, 118.0, 68.9, 45.2, 21.5; IR(KBr): ν 3064, 1602, 1487, 1184, 1162, 1086, 908, 727 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{25}ClN_2O_3SH$ 505.1347; Found 505.1350.

*4-Methyl-N-(4-phenyl-2-(4-(trifluoromethyl)phenyl)-2H-benzo[e][1,3]oxazin-3(4H)-yl)benzenesulfonamide(**3ae**)*, white solid, mp: 69–71 °C, yield 60% (62.9 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.77 (s, 1H), 7.62 (m, 4H), 7.23–7.19 (m, 9H), 6.96, (d, J = 7.6 Hz, 2H), 6.88 (dd, $J_{1,2}$ = 7.2 Hz, 1H), 6.70 (s, 1H), 6.65 (d, J = 8.0 Hz, 1H), 2.29 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.14 (brs); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.5, 155.4, 144.3, 136.6, 135.3, 133.4 (d, J = 31.3 Hz), 133.2, 130.3, 129.1, 128.6 (d, J = 3.2 Hz), 128.2, 128.1, 127.6, 126.2, 126.1 (d, J = 3.7 Hz), 126.0, 123.5 (d, J = 273.4 Hz), 121.8, 119.9, 118.0, 68.5, 21.5; IR (KBr): ν 3065, 1597, 1487, 1322, 1161, 1086, 907, 757, 727 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{23}F_3N_2O_3SNa$ 547.1274; Found 547.1284.

*4-Methyl-N-(4-phenyl-2-(m-tolyl)-2H-benzo[e][1,3]oxazin-3(4H)-yl)benzenesulfonamide(**3af**)*, white solid, mp: 126–127 °C, yield 65% (61.2 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.76 (s, 1H), 7.38–7.37 (m, 1H), 7.35 (s, 1H), 7.29–7.28 (m, 2H), 7.22–7.18 (m, 5H), 7.16–7.13 (m, 4H), 6.89 (d, J = 8.0 Hz, 2H), 6.84 (dd, $J_{1,2}$ = 7.4 Hz, 1H), 6.59–6.56 (m, 2H), 2.35 (s, 3H), 2.27 (s, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.6, 155.7, 143.7, 139.0, 136.8, 133.6, 133.5, 133.4, 131.6, 130.1, 129.9, 129.1, 128.8, 128.5, 128.3, 128.1, 127.4, 125.7, 121.4, 119.5, 118.1, 69.0, 21.5, 21.2; IR(KBr): ν 3063, 1597, 1486, 1185, 1160, 1096, 908, 727 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{26}N_2O_3SNa$ 493.1556; Found 493.1558.

*N-(2-(2,6-dimethylphenyl)-4-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**3ag**)*, white solid, mp: 119–120 °C, yield 73% (70.8 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 9.12 (s, 1H), 7.24 (m, 4H), 7.17–7.09 (m, 6H), 6.98 (d, J = 7.6 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 6.82 (dd, $J_{1,2}$ = 7.2 Hz, 1H), 6.62 (s, 1H), 6.47 (d, J = 8.0 Hz, 1H), 2.26 (s, 3H), 2.03 (s, 6H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.6, 155.6, 143.6, 138.3, 136.7, 133.8, 133.1, 130.6, 130.0, 129.7, 128.9, 128.8, 128.7, 128.6, 128.0, 127.5, 120.9, 119.5, 118.0, 68.6, 21.4, 20.1; IR(KBr): ν 3068,

1596, 1487, 1185, 1160, 1059, 908, 726 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{28}N_2O_3SNa$ 507.1713; Found 507.1715.

*N-(2-(4-fluorophenyl)-4-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**3ah**)*, white solid, mp: 95–98 °C, yield 65% (61.7 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.76 (s, 1H), 7.57 (dd, *J* = 7.8, 2.4 Hz, 2H), 7.21–7.18 (m, 5H), 7.16–7.06 (m, 6H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.85 (dd, $J_{1,2}$ = 7.2 Hz, 1H), 6.58–6.57 (m, 2H), 2.28 (s, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.4 (d, *J* = 256.4 Hz), 164.6, 155.6, 143.9, 136.7, 133.4, 133.1 (d, *J* = 9.2 Hz), 130.2, 128.8, 128.5, 128.3, 128.1, 128.0 (d, *J* = 3.1 Hz), 127.5, 121.3, 119.6, 118.0, 116.6 (d, *J* = 22.2 Hz), 69.0, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.68 – -104.69 (m); IR(KBr): ν 3066, 1600, 1510, 1185, 1156, 1086, 907, 727 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}FN_2O_3SH$ 475.1486; Found 475.1488.

*N-(2-(4-chlorophenyl)-4-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**3ai**)*, white solid, mp: 78–79 °C, yield 66% (64.8 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 8.74 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.23–7.20 (m, 5H), 7.17–7.12 (m, 4H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.86 (dd, $J_{1,2}$ = 7.4 Hz, 1H), 6.60–6.58 (m, 2H), 2.28 (s, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.5, 155.5, 144.0, 138.9, 136.6, 133.5, 133.4, 130.2, 129.9, 129.6, 128.9, 128.5, 128.3, 128.1, 127.5, 121.4, 119.7, 118.0, 68.9, 21.5; IR(KBr): ν 3065, 1595, 1487, 1185, 1086, 907, 729 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}ClN_2O_3SH$ 491.1191; Found 491.1194.

*N-(2-(4-bromophenyl)-4-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**3aj**)*, white solid, mp: 71–76 °C, yield 35% (37.5 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 8.73 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.23–7.19 (m, 5H), 7.17–7.12 (m, 4H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.86 (dd, $J_{1,2}$ = 7.2 Hz, 1H), 6.60–6.58 (m, 2H), 2.29 (s, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.4, 155.5, 144.0, 136.6, 133.5, 133.4, 132.6, 130.6, 130.2, 130.0, 128.9, 128.5, 128.3, 128.1, 127.5, 121.4, 119.7, 118.0, 68.9, 21.5; IR(KBr): ν 3065, 1589, 1486, 1163, 1087, 1022, 909, 732 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{23}BrN_2O_3SNa$ 557.0505; Found 557.0515.

*N-(2-(4-iodophenyl)-4-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**3ak**)*, white solid, mp: 59–60 °C, yield 43% (50.1 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.70 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.23–7.19, (m, 7H), 7.17–7.12 (m, 4H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.86 (dd, $J_{1,2}$ = 7.2 Hz, 1H), 6.60–6.58 (m, 2H), 2.28 (s, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.4, 155.5, 144.0, 138.5, 136.6, 133.5, 133.4, 131.2, 130.2, 129.9, 128.9, 128.5, 128.3, 128.1, 127.5, 121.4, 119.7, 118.0, 99.9, 68.9, 21.5; IR(KBr): ν 3063, 1602, 1484, 1184, 1039, 908, 730, 637, 587 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}IN_2O_3SH$ 583.0547; Found 583.0552.

*(E)-4-methyl-N-(4-phenyl-2-styryl-2H-benzo[e][1,3]oxazin-3(4H)-yl)benzenesulfonamide(**3al**)*, white solid, mp: 81–82 °C, yield 76% (73.4 mg), dr = 1:0.7; ^1H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.58 (d, *J* = 10.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1.4H), 7.45–7.37 (m, 4.4H), 7.36–7.33 (m, 3.4H), 7.33–7.27 (m, 1.7H), 7.24–7.21 (m, 3.4H), 7.20–7.16 (m, 6.8H), 7.15–7.13 (m, 1.7H), 7.07–7.00 (m, 3.4H), 6.95–6.90 (m, 3.4H), 6.83 (ddd, $J_{1,2}$ = 7.4 Hz, J_3 = 1.2 Hz, 1H), 6.72 (dd, *J* = 16.0, 9.8 Hz, 1H), 6.57 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.53–6.47 (m, 1.7H), 6.17 (s, 0.7H), 5.60 (s, 0.7H), 5.20 (dd, *J* = 16, 4.6 Hz, 0.7H), 5.06 (d, *J* = 4.4 Hz, 0.7H), 2.26 (s, 3H), 2.18 (s, 2.1H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.0, 155.8, 153.3, 146.8, 143.9, 143.8, 141.3, 136.9, 135.7, 134.7, 134.5, 133.8, 133.5, 130.4, 130.1, 129.5, 129.3, 129.1, 128.9, 128.8, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.4, 126.7, 123.0, 122.5, 121.7, 121.3, 119.4, 118.3, 117.7, 117.0, 83.6, 69.1, 67.9, 21.4; IR(KBr): ν 2988, 1597, 1485, 1348, 1159, 1087, 730 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{26}N_2O_3SH$ 483.1737; Found 483.1739.

*4-Methyl-N-(4-phenyl-2-(thiophen-2-yl)-2H-benzo[e][1,3]oxazin-3(4H)-yl)benzenesulfonamide(**3am**)*, white solid, mp: 134–135 °C, yield 62% (57.5 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.80 (s, 1H), 7.57–7.55 (m, 2H), 7.50–7.46 (m, 1H), 7.42–7.38 (m, 2H), 7.22–7.21 (m, 3H), 7.19–7.17 (m, 1H), 7.15–7.13 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.85 (ddd, $J_{1,2}$ = 7.4 Hz, J_3 = 1.2 Hz, 1H), 6.59–6.57 (m, 2H), 2.27 (s, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.0, 155.6, 143.8, 136.7, 133.5, 132.7, 131.6, 130.1, 129.2, 128.9, 128.8, 128.5, 128.3, 128.1, 127.4, 121.3, 119.5, 118.1, 69.0, 21.5; IR(KBr): ν 2923, 1589, 1487, 1349, 1160, 1086, 731 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{22}N_2O_3S_2H$ 463.1145; Found 463.1148.

*4-Methyl-N-(2-methyl-2,4-diphenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)benzenesulfonamide(**5aa**)*, white solid, mp: 135–136 °C, yield 56% (52.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.92 (s, 1H), 7.53 (d, J = 7.2 Hz, 2H), 7.48 (dd, $J_{1,2}$ = 7.2 Hz, 1H), 7.40 (dd, $J_{1,2}$ = 7.2 Hz, 2H), 7.30 (d, J = 7.2 Hz, 2H), 7.21–7.11 (m, 6H), 7.06 (dd, $J_{1,2}$ = 7.4 Hz, 1H), 6.90 (d, J = 8.0 Hz, 2H), 6.77 (dd, $J_{1,2}$ = 7.0 Hz, 1H), 6.45–6.42 (m, 2H), 2.54 (s, 3H), 2.30 (s, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 182.2, 155.5, 143.5, 137.0, 135.9, 133.0, 132.8, 131.9, 129.7, 129.0, 128.9, 128.5, 128.4, 128.3, 127.7, 127.2, 121.4, 119.3, 118.2, 70.5, 21.5, 19.5; IR(KBr): ν 3064, 1597, 1486, 1185, 1160, 1087, 907, 726 cm^{-1}; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{28}H_{26}N_2O_3SNa$ 493.1556; Found 493.1558.

*4-Methyl-N-(2-methyl-4-phenyl-2-(p-tolyl)-2H-benzo[e][1,3]oxazin-3(4H)-yl)benzenesulfonamide(**5ab**)*, white solid, mp: 79–82 °C, yield 74% (71.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.03 (s, 1H), 7.45 (d, J = 7.6 Hz, 2H), 7.29 (d, J = 7.2 Hz, 2H), 7.21–7.16 (m, 6H), 7.12 (d, J = 7.2 Hz, 2H), 7.05 (dd, $J_{1,2}$ = 7.2 Hz, 1H), 6.89 (d, J = 7.6 Hz, 2H), 6.76 (dd, $J_{1,2}$ = 7.0 Hz, 1H), 6.44–6.42 (m, 2H), 2.51 (s, 3H), 2.36 (s, 3H), 2.29 (s, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 181.8, 155.5, 143.4, 142.6, 137.0, 133.1, 133.0, 132.8, 129.7, 129.6, 129.0, 128.4, 128.3, 127.7, 127.2, 121.4, 119.2, 118.2, 70.5, 21.5, 21.4, 19.2; IR(KBr): ν 2923, 1597, 1485, 1350, 1162, 1087, 735 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{29}H_{28}N_2O_3SH$ 485.1893; Found 485.1895.

*N-(2-(4-fluorophenyl)-2-methyl-4-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**5ac**)*, white solid, mp: 117–118 °C, yield 38% (37.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.81 (s, 1H), 7.61–7.53 (m, 2H), 7.28 (dd, $J_{1,2}$ = 7.8 Hz, 2H), 7.20–7.15 (m, 4H), 7.13–7.04 (m, 5H), 6.90 (d, J = 8.0 Hz, 2H), 6.77 (dd, $J_{1,2}$ = 7.0 Hz, 1H), 6.45–6.42 (m, 2H), 2.52 (s, 3H), 2.30 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.92 (brs); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 180.9, 165.0 (d, J = 254.7 Hz), 155.4, 143.6, 136.9, 133.0, 132.7, 132.0 (d, J = 3.2 Hz), 129.8, 129.5 (d, J = 9.0 Hz), 129.0, 128.5, 128.4, 128.3, 127.8, 121.3, 119.4, 118.1, 116.1 (d, J = 22.0 Hz), 70.5, 21.5, 19.4; IR(KBr): ν 2988, 1599, 1486, 1351, 1161, 1087, 735 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{28}H_{25}FN_2O_3SH$ 489.1643; Found 489.1644.

*N-(2-(4-chlorophenyl)-2-methyl-4-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**5ad**)*, white solid, mp: 72–76 °C, yield 61% (61.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.71 (s, 1H), 7.48–7.45 (m, 2H), 7.39–7.35 (m, 2H), 7.28 (d, J = 7.2 Hz, 2H), 7.20–7.16 (m, 3H), 7.14–7.11 (m, 3H), 7.08–7.04 (m, 1H), 6.90 (d, J = 8.0 Hz, 2H), 6.77 (ddd, $J_{1,2}$ = 7.2 Hz, J_3 = 1.2 Hz, 1H), 6.45 (s, 1H), 6.43 (dd, J = 8.2, 1.2 Hz, 1H), 2.52 (s, 3H), 2.30 (s, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 181.0, 155.3, 143.6, 138.3, 136.8, 134.2, 132.9, 132.6, 129.8, 129.2, 128.9, 128.5, 128.4, 128.3, 128.2, 127.8, 121.2, 119.3, 118.1, 70.4, 21.5, 19.3; IR(KBr): ν 2988, 1594, 1487, 1352, 1163, 1088, 736 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{28}H_{25}ClN_2O_3SH$ 505.1347; Found 505.1353.

*N-(2-(3-chlorophenyl)-2-methyl-4-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**5ae**)*, white solid, mp: 132–134 °C, yield 41% (41.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.45–7.28 (m, 6H), 7.20 – 7.11 (m, 6H), 7.06 (dd, $J_{1,2}$ = 7.0 Hz, 1H), 6.90 (d, J = 7.2 Hz, 2H), 6.77 (dd, $J_{1,2}$ = 6.8 Hz, 1H), 6.45–6.43 (m, 2H), 2.52 (s, 3H), 2.30 (s, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 181.1, 155.4, 143.7, 137.7, 136.8, 134.9, 133.0, 132.7, 131.8, 130.3, 129.8, 128.9, 128.6, 128.4, 127.9, 127.6, 125.0, 121.2, 119.4, 118.2, 70.5, 21.5, 19.7; IR(KBr): ν 2988, 1598, 1486, 1352, 1161, 1087, 735 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{28}H_{25}ClN_2O_3SH$ 505.1347; Found 505.1351.

*N-(2-(4-bromophenyl)-2-methyl-4-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**5af**)*, white solid, mp: 143–144 °C, yield 35% (38.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.68 (s, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.38, (d, J = 8.0 Hz, 2H), 7.29–7.27 (m, 2H), 7.21–7.11 (m, 6H), 7.06 (dd, $J_{1,2}$ = 7.4 Hz, 1H), 6.90 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 7.2 Hz, 1H), 6.44–6.41 (m, 2H), 2.52 (s, 3H), 2.31 (s, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 181.2, 155.4, 143.7, 136.9, 134.8, 133.0, 132.7, 132.3, 129.8, 129.0, 128.6, 128.5, 128.4, 128.3, 127.8, 126.9, 121.3, 119.4, 118.2, 70.5, 21.5, 19.4; IR(KBr): ν 2925, 1598, 1486, 1350, 1162, 1086, 735 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{28}H_{25}BrN_2O_3SH$ 549.0842; Found 549.0843.

*N-(2-cyclopropyl-2,4-diphenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-4-methylbenzenesulfonamide(**5ag**)*, white solid, mp: 150–152 °C, yield 42% (41.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 7.40 (d, J = 7.2 Hz, 2H), 7.33–7.25 (m, 6H), 7.19 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 7.6, 1.6 Hz, 1H), 7.02–6.98 (m, 1H), 6.84 (d, J = 8.0 Hz, 2H), 6.78–6.76 (m, 2H), 6.73 (ddd, $J_{1,2}$ = 7.4 Hz, J_3 = 1.2 Hz, 1H), 6.43 (s, 1H), 6.30 (dd, J = 8.0, 0.8 Hz, 1H), 3.12–3.06 (m, 1H), 2.23 (s, 3H) 1.23–1.16 (m, 1H), 0.90–0.80 (m, 2H), 0.20–0.14 (m, 1H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 189.3, 155.6, 143.3, 137.0, 133.0, 132.9, 132.7, 129.6, 129.4, 129.3, 128.4, 128.3, 128.2, 128.1, 127.7, 127.1, 121.1, 119.0, 118.3, 70.5, 21.4, 15.7, 9.3, 8.7; IR(KBr): ν 2709, 1588, 1485, 1349, 1162, 1087, 731 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{28}N_2O_3SH$ 497.1893; Found 497.1893.

*4-Methyl-N-(4-phenylspiro[benzo[e][1,3]oxazine-2,1'-cyclohexan]-3(4H)-yl)benzenesulfonamide(**5ah**)*, white solid, mp: 128–130 °C, yield 60% (53.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.21 (s, 1H), 7.26–7.21 (m, 4H), 7.17 (d, J = 7.6 Hz, 3H), 7.40 (q, J = 8.0 Hz, 2H), 6.89 (d, J = 7.6 Hz, 2H), 6.72 (dd, $J_{1,2}$ = 7.4 Hz, 1H), 6.40 (d, J = 8.0 Hz, 1H), 6.30 (s, 1H), 2.84–2.81 (m, 1H), 2.52–2.42 (m, 1H), 2.28 (brs, 5H), 1.76–1.73 (m, 2H), 1.48 (m, 2H), 0.88 (m, 2H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 189.8, 155.4, 143.3, 137.4, 133.0, 132.8, 129.6, 129.1, 128.4, 127.6, 121.3, 119.0, 118.3, 70.0, 35.7, 31.5, 27.1, 26.4, 25.1, 21.4; IR(KBr): ν 2937, 1632, 1483, 1185, 1162, 1087, 907, 728 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{28}N_2O_3SH$ 449.1893; Found 449.1895.

*4-Methyl-N-(4-phenyl-3',4'-dihydro-2'H-spiro[benzo[e][1,3]oxazine-2,1'-naphthalen]-3(4H)-yl)benzenesulfonamide(**5ai**)*, white solid, mp: 149–150 °C, yield 36% (35.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.16 (s, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.39 (dd, $J_{1,2}$ = 7.2 Hz, 1H), 7.31–7.29 (m, 3H), 7.20–7.11 (m, 7H), 7.06 (dd, $J_{1,2}$ = 7.8 Hz, 1H), 6.93 (d, J = 7.6 Hz, 2H), 6.76 (dd, $J_{1,2}$ = 6.8 Hz, 1H), 6.48–6.45 (m, 2H), 3.27–3.23 (m, 1H), 2.92–2.85 (m, 2H), 2.68–2.64 (m, 1H), 2.33 (s, 3H), 1.93–1.90 (m, 1H), 1.26–1.22 (m, 1H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 181.6, 155.5, 143.5, 142.5, 137.2, 133.0, 132.8, 132.5, 130.2, 129.7, 129.3, 129.0, 128.5, 128.4, 128.3, 127.6, 127.0, 126.0, 121.6, 119.2, 118.1, 70.3, 30.2, 29.5, 22.5, 21.5; IR(KBr): ν 2935, 1583, 1485, 1349, 1161, 1087, 735 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{28}N_2O_3SH$ 497.1893; Found 497.1897.

*4-Methyl-N-(4-phenylspiro[benzo[e][1,3]oxazine-2,4'-chroman]-3(4H)-yl)benzenesulfonamide(**5aj**)*, white solid, mp: 151–152 °C, yield 42% (41.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.99 (s, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.40 (dd, $J_{1,2}$ = 7.2 Hz, 1H), 7.29 (d, J = 7.2 Hz, 2H), 7.18–7.06 (m, 7H), 6.99 (dd, $J_{1,2}$ = 7.4 Hz, 1H), 6.93 (d, J = 7.6 Hz, 2H), 6.87 (d, J = 8.4 Hz, 1H), 6.77 (dd, $J_{1,2}$ = 6.8 Hz, 1H), 6.48 (d, J = 8.0 Hz, 1H), 6.43 (s, 1H), 4.35–4.32 (m, 1H), 3.55–3.49 (m, 1H), 3.20–3.18 (m, 2H), 2.32 (s, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 175.0, 158.8, 155.3, 143.7, 137.1, 135.0, 133.0, 132.5, 129.8, 128.9, 128.6, 128.5, 128.4, 127.8, 125.7, 121.6, 121.3, 119.3, 118.2, 118.1, 117.3, 70.4, 65.4, 28.4, 21.5; IR(KBr): ν 2854, 1595, 1481, 1351, 1161, 1087, 733 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{26}N_2O_4SH$ 499.1686; Found 499.1689.

*4-Methyl-N-(4-phenylspiro[benzo[e][1,3]oxazine-2,9'-fluoren]-3(4H)-yl)benzenesulfonamide(**5ak**)*, yellow solid, mp: 122–124 °C, yield 34% (36.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.00 (s, 1H), 8.83 (d, J = 6.8 Hz, 1H), 7.62, (d, J = 6.8 Hz, 1H), 7.44–7.38 (m, 5H), 7.28–7.22 (m, 5H), 7.15 (d, J = 6.8 Hz, 1H), 7.09–7.06 (m, 1H), 6.99 (m, 3H), 6.91 (d, J = 7.2 Hz, 2H), 6.80–6.78 (m, 1H), 6.54 (s, 1H), 6.48 (d, J = 7.6 Hz, 1H), 2.31 (s, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 173.0, 155.3, 144.0, 143.7, 142.3, 136.8, 134.9, 133.9, 133.5, 133.4, 132.6, 131.7, 131.5, 129.8, 128.7, 128.6, 128.5, 128.2, 127.7, 123.7, 121.5, 120.1, 120.0, 119.3, 118.2, 71.3, 21.5; IR(KBr): ν 2788, 1593, 1484, 1353, 1162, 1085, 731 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{26}N_2O_3SH$ 531.1737; Found 531.1738.

*4-Methyl-N-((1'R,2R,4'R)-1',7',7'-trimethyl-4-phenylspiro[benzo[e][1,3]oxazine-2,2'-bicyclo[2.2.1]heptan]-3(4H)-yl)benzenesulfonamide(**5al**)*, white solid, mp: 163–164 °C, yield 79% (79.4 mg), dr = 1:0.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.15 (s, 1H), 11.11 (s, 0.7H), 7.35–7.33 (m, 3.4H), 7.23–7.20 (m, 1.7H), 7.18–7.11 (m, 6.8H), 7.07–7.02 (m, 1.7H), 7.00–6.98 (m, 1.7H), 6.89 (d, J = 8.0 Hz, 3.4H), 6.74–6.71 (m, 0.7H), 6.71–6.67 (m, 1H), 6.40 (d, J = 8.0 Hz, 1.7H), 6.27–6.25 (m, 1.7H), 3.28–3.22 (m, 0.7H), 2.88 (d, J = 19.2 Hz, 1H), 2.29–2.28 (m, 5.1H), 2.24–2.18 (m, 1H), 1.93 (d, J = 19.2 Hz, 0.7H), 1.83–1.76 (m, 3.4H), 1.59–1.54 (m, 1.7H), 1.43–1.34 (m, 1.7H), 1.00 (s, 2.1H), 0.97 (s, 2.1H),

0.94 (s, 3H), 0.84 (s, 2.1H), 0.79 (s, 3H), 0.63–0.51 (m, 1H), 0.30–0.24 (m, 0.7H), – 0.21 (s, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 200.7, 199.5, 155.6, 155.5, 143.3, 143.2, 137.6, 137.3, 132.9, 132.8, 132.5, 132.3, 129.6, 129.5, 129.4, 128.5, 128.4, 128.3, 128.2, 128.1, 127.7, 127.6, 121.4, 121.3, 119.1, 119.0, 118.3, 70.4, 70.0, 55.6, 55.2, 48.9, 47.3, 43.6, 43,4, 39.1, 37.8, 31.8, 31.5, 26.6, 26.4, 21.5, 21.4, 19.6, 18.4, 18.3, 18.2, 11.1, 10.9; IR(KBr): ν 2958, 1598, 1483, 1350, 1160, 1087, 733 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{34}N_2O_3SH$ 503.2363; Found 503.2363.

*4-Methyl-N-(2'-methyl-4-phenyl-5'-(prop-1-en-2-yl)spiro[benzo[e][1,3]oxazine-2,1'-cyclohexan]-3(4H)-yl)benzenesulfonamide(**5am**)*, white solid, mp: 120–122 °C, yield 76% (76.3 mg), dr = 1:1; ^1H NMR (400 MHz, $CDCl_3$) δ 11.00 (s, 1H), 10.73 (s, 1H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.25–7.19 (m, 6H), 7.17–7.12 (m, 6H), 7.07–6.99 (m, 4H), 6.91 (d, *J* = 3.2 Hz, 2H), 6.89 (d, *J* = 2.8 Hz, 2H), 6.77–6.70 (m, 2H), 6.41–6.39 (m, 2H), 6.34 (s, 1H), 6.30 (s, 1H), 4.79–4.70 (m, 4H), 3.69–3.66 (m, 1H), 3.55–3.50 (m, 1H), 2.55–2.42 (m, 2H), 2.30 (s, 3H), 2.29 (s, 3H), 2.03–1.99 (m, 2H), 1.88–1.84 (m, 2H), 1.78 (s, 3H), 1.72–1.70 (m, 4H), 1.56–1.53 (m, 1H), 1.44–1.34 (m, 3H), 1.24–1.17 (m, 1H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.05 (d, *J* = 6.0 Hz, 3H), 1.01–0.95 (m, 1H), 0.77–0.67 (m, 1H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 191.8, 191.5, 155.5, 155.3, 148.0, 147.5, 143.3, 143.2, 137.6, 136.9, 132.8, 132.7, 132.6, 129.6, 129.5, 129.4, 129.0, 128.5, 128.4, 128.3, 128.2, 128.1, 127.6, 127.5, 121.6, 119.1, 119.0, 118.1, 118.0, 109.9, 109.4, 69.9, 45.9, 45.1, 40.8, 40.7, 36.4, 36.3, 35.7, 35.1, 30.5, 30.3, 21.5, 21.4, 20.8, 20.2, 16.4, 16.2; IR(KBr): ν 2932, 1581, 1485, 1350, 1162, 1087, 732 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{34}N_2O_3SH$ 503.2363; Found 503.2367.

*2,4-Diphenyl-2H-benzo[e][1,3]oxazin-3(4H)-ol(**5an**)*, white solid, mp: 61–62 °C, yield 38% (20.6 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.68 (s, 1H), 7.56–7.54 (m, 2H), 7.40–7.33 (m, 8H), 7.25–7.22 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.86 (dd, $J_{1,2}$ = 7.4 Hz, 1H), 6.54 (s, 1H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.4, 150.4, 138.6, 131.1, 130.5, 129.9, 129.8, 128.8, 128.4, 128.0, 127.5, 127.4, 126.3, 120.3, 117.6, 84.6; IR(KBr): ν 3435, 1585, 1455, 1264, 1096, 945, 733 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{17}NO_2H$ 304.1332; Found 304.1333.

*2-(Phenyl(phenylamino)methyl)phenol(**7**)*, a known compound[17], yield 34% (18.7 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 7.36–7.22 (m, 5H), 7.18–7.15 (m, 3H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.89–6.76 (m, 5H), 5.56 (s, 1H), 4.21 (s, 1H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.4, 146.4, 141.2, 129.3, 129.1, 129.0, 128.6, 128.1, 127.6, 125.7, 120.9, 120.2, 117.2, 116.2, 64.1.

*4-Methyl-N-((2R,4S)-4-methyl-2-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)benzenesulfonamide(**9**)*, faint yellow oil, yield 90% (71.0 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.87 (s, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.59–7.49 (m, 3H), 7.15–7.10 (m, 3H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 5.33 (q, *J* = 7.2 Hz, 1H), 2.26 (s, 3H), 1.50 (d, *J* = 7.2 Hz, 3H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.4, 154.8, 143.6, 133.4, 132.9, 131.8, 131.2, 129.4, 129.3, 129.0, 128.7, 128.0, 124.7, 119.3, 117.8, 61.2, 21.4, 18.9; IR(KBr): ν 2930, 1580, 1487, 1348, 1160, 1085, 728 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}N_2O_3SH$ 395.1424; Found 395.1428.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.xxxxxx.

^1H, ^{19}F and ^{13}CNMR spectra of products, X-ray crystallography data and CIF file of product **3aa** (PDF)

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Notes

The authors declare no competing financial interest.

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