EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201501063

Electrophile-Mediated Reactions of Functionalized Propargylic Substrates

Aurelija Urbanaitė,[a] Mantas Jonušis,[a] Rita Bukšnaitienė,[a] Simonas Balkaitis,[a] and Inga Čikotienė*[a]

Keywords: Alkynes / Electrophilic addition / Cyclization / Nitrogen heterocycles / Sulfur heterocycles / Regioselectivity

Metal-free halogen, chalcogen, or oxocarbenium ion mediated yne-carbonyl or yne-thioxo transformations of a range of *N*- and *O*-propargylic compounds have been studied. This investigation has led to the development of a mild, economic, and effective method for the synthesis of functionalized 4*H*-1,3-oxazines, 4*H*-1,3-thiazines, 4,5-dihydrothiazoles, and α-substituted enones. The structure of the propargylic substrate and the nature of electrophile influence both the outcome and regioselectivity of processes.

Introduction

In the past decade an explosive increase of interest in electrophile-mediated cyclizations of alkynes has taken place.[1] These methodologies have become an original field of carbo- and heterocycle synthesis and have enabled the formation of halogen- or chalcogen-substituted compounds. The obtained materials are suitable for further synthetic transformations. Electrophilic cyclizations of alkynes may be defined as processes that involve addition of an electrophilic source to sp-carbon centers and subsequent formation of cyclic compounds through attack of neighboring nucleophilic functionality through either *endo* or *exo* modes. The mode of cyclization normally depends on chain length, substitution pattern on the chain, and on the electrophile employed. Functionalized propargylic substrates are a specific class of alkynes with attractive chemical properties. It is known that these materials can undergo a number of skeletal rearrangements and cyclization reactions and these processes are usually mediated by activation of the triple bond by transition-metal salts.[2] Despite the fact that electrophilic cyclization reactions of alkynes bearing an internal nucleophile have emerged as a very efficient process to obtain a variety of prefunctionalized compounds, this type of activation is still not common for functionalized propargylic substrates.[3] Recently, we have found that electrophilic reagents (iodine or *N*-iodo succinimide, aldehydes or oxocarbenium ions) can be used to induce 1,3-acyloxy shifts in propargylic esters.[4] Moreover, at the beginning of 2015, we presented an electrophilic cyclization of *N*-(3-arylprop-2-ynyl)amides to functionalized 4*H*-1,3-oxazines.[5] These preliminary findings prompted us to study the scope of electrophile-mediated transformations of functionally substituted propargylic substrates. In this work, we present the results of our recent and more detailed investigations.

[a] Department of Organic Chemistry, Faculty of Chemistry, Vilnius University,
Naugarduko 24, 03225 Vilnius, Lithuania
E-mail: inga.cikotiene@chf.vu.lt
http://web.vu.lt/chf/i.cikotiene

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201501063.

Results and Discussion

As starting propargylic substrates we chose six classes of compounds: amides **1**, carbamates **2** and **5**, ureas **3**, thioureas **4**, and esters **6**. We utilized known methods for the preparation of these compounds. The strategy of their synthesis is presented in the Supporting Information. Structures of the starting materials are shown in Figure 1.

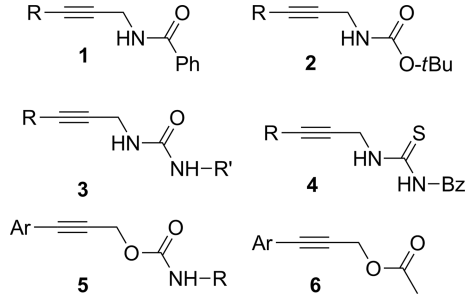
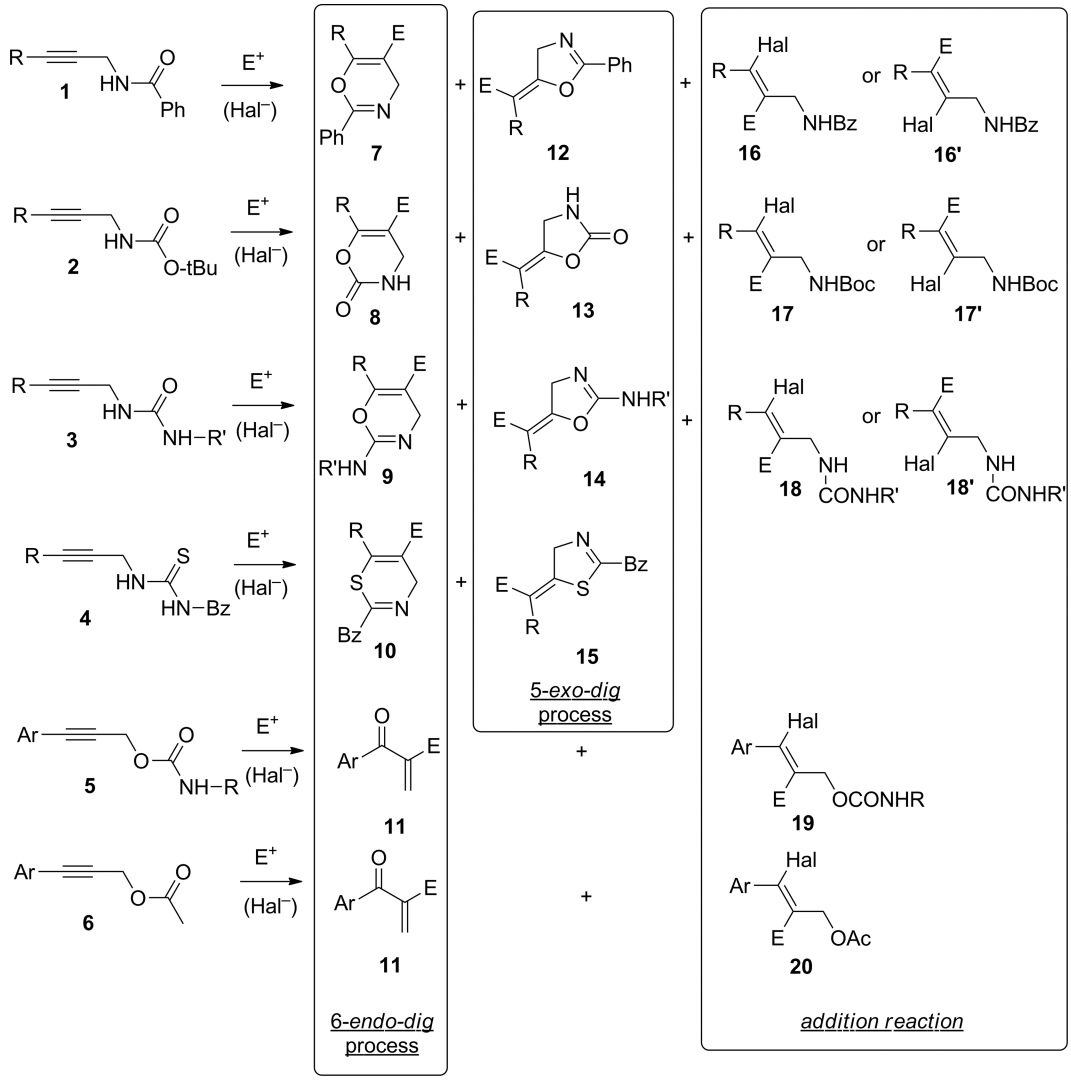


Figure 1. Structures of the starting materials. **1**: R = 4-$MeOC_6H_4$ (**a**); R = 4-$EtOC_6H_4$ (**b**); R = 3,4-$(MeO)_2C_6H_3$ (**c**); R = 3,4,5-$(MeO)_3C_6H_2$ (**d**); R = 4-MeC_6H_4 (**e**); R = Ph (**f**); R = 4-ClC_6H_4 (**g**); R = 4-$O_2NC_6H_4$ (**h**); R = H (**i**). **2**: R = 4-$MeOC_6H_4$ (**a**); R = 3,4-$(MeO)_2C_6H_3$ (**b**); R = 3,4-$(OCH_2O)C_6H_3$ (**c**); R = 4-MeC_6H_4 (**d**); R = Ph (**e**); R = 4-ClC_6H_4 (**f**); R = 4-$O_2NC_6H_4$ (**g**); R = H (**h**). **3**: R = 4-$MeOC_6H_4$; R′ = Ts (**a**); R = 4-$MeOC_6H_4$; R′ = Ph (**b**); R = 4-$MeOC_6H_4$; R′ = Bn (**c**); R = 3,4-$(MeO)_2C_6H_3$; R′ = Ts (**d**); R = 4-MeC_6H_4; R′ = Bn (**e**); R = 4-MeC_6H_4; R′ = Ts (**f**); R = Ph; R′ = Ts (**g**); R = 4-ClC_6H_4; R′ = Ts (**h**); R = H; R′ = Ts (**i**); R = H; R′ = Ph (**j**); R = H; R′ = Bn (**k**). **4**: R = 4-$MeOC_6H_4$ (**a**); R = 4-ClC_6H_4 (**b**); R = Ph (**c**); R = H (**d**). **5**: Ar = 4-$MeOC_6H_4$; R = Ts (**a**); Ar = 4-$MeOC_6H_4$; R = Bn (**b**). **6**: Ar = 4-$MeOC_6H_4$ (**a**); Ar = Ph (**b**).

With synthesized propargylic substrates in hand, we explored the scope of electrophile-mediated reactions. For the



Scheme 1. General outcomes of electrophile-mediated reactions of propargylic substrates.

chosen model substrates and electrophile sources, we performed detailed optimization processes, including an investigation of solvent, temperature, base, and stoichiometry; the results of optimization study are presented in the Supporting Information (Table S1). With appropriate reactions conditions for halogen-, chalcogen-, and oxocarbenium ion mediated reactions established, we synthesized a wide range of functionalized heterocyclic compounds and α-substituted enones. The results are presented in chapters 1–3 together with some concluding remarks on the reactions, which are presented in chapter 4. The general trends of reactivity of the studied propargylic substrates are shown in Scheme 1.

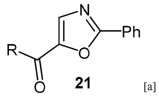
1. Halogen-Mediated Reaction of Propargylic Substrates

Reactions between propargylic substrates and iodine electrophile sources proceeded well and resulted in the formation of iodo-substituted 4*H*-1,3-oxazines **7**–**9**, 4*H*-1,3-thiazines **10**, and α-iodoenones **11** as main reactions products. Whereas amides **1** and carbamates **5** underwent smooth and chromatographically clean transformations with *N*-iodosuccinimide (NIS) in CH_2Cl_2 at ambient temperature, other substrates required some modification of the procedure (see Table S1). Thus, two equivalents of molecular iodine in either CH_2Cl_2 or acetonitrile at 0 °C were the best conditions for iodocyclizations of carbamates **2** and ureas **3**. Ester **6a** participated in competitive electrophilic addition reaction during NIS or molecular iodine[4a] mediated transformation and therefore the yield of isolated iodinated enone **11aa** was low (Table 1, entry 41). *N*-Bromosuccinimide (NBS) was not efficient for such transformations. Whereas carbamates **2** formed six-membered bromoderivatives **8** in low yields (entries 11, 13, 16, 18, and 20), NBS-mediated reactions of amides **1**, ureas **3**, carbamates **5**, and esters **6** were problematic and resulted in low conversions of the starting materials (data not shown). *N*-Chlorosuccinimide was completely ineffective.

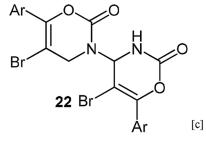
As seen from Table 1, substrates bearing an electron-rich aryl group next to the triple bonds (amides **1a**–**f**, carbamates **2a**–**f** and **5a**,**b**, ureas **3a**,**c**–**g**, and ester **6a**; entries 1–

Table 1. Data on the halogen-mediated reactions of substrates.

Entry	Starting material	Reaction conditions	E^+	Products		
				6-*endo-dig* (yield, %)	5-*exo-dig* (yield, %)	Addition or side reaction (yield, %)
1	**1a**: R = 4-$MeOC_6H_4$		I^+	**7aa** (72)	–	–
2	**1b**: R = 4-$EtOC_6H_4$		I^+	**7ba** (58)	–	–
3	**1c**: R = 3,4-$(MeO)_2C_6H_3$		I^+	**7ca** (52)	–	–
4	**1d**: R = 3,4,5-$(MeO)_3C_6H_2$		I^+	**7da** (60)	–	–
5	**1e**: R = 4-MeC_6H_4	NIS (1.1 equiv.), DCM, r.t.	I^+	**7ea** (58)	–	–
6	**1f**: R = C_6H_5		I^+	**7fa** (52)	–	–
7	**1g**: R = 4-ClC_6H_4		I^+	**7ga** (20)	**12ga** (41), **21ga**[a] (18)	–
8	**1h**: R = 4-$O_2NC_6H_4$		I^+	**7ha** (24)	**21ha**[a] (16)	–
9	**1i**: R = H		I^+	–	**21ia**[a] (16)	**16ia** (Hal = I) (41)[b]
10	**2a**: R = 4-$MeOC_6H_4$	I_2 (2 equiv.), DCM, 0 °C	I^+	**8aa** (68)	–	–
11	**2a**	NBS (1.1 equiv.), DCM, r.t.	Br^+	**8ab** (30)	–	–
12	**2b**: R = 3,4-$(MeO)_2C_6H_3$	I_2 (2 equiv.), DCM, 0 °C	I^+	**8ba** (67)	–	–
13	**2b**	NBS (1.1 equiv.), DCM, r.t.	Br^+	**8bb** (53)	–	–
14	**2c**: R = 3,4-$(OCH_2O)C_6H_3$	I_2 (2 equiv.), DCM, 0 °C	I^+	**8ca** (60)	–	–
15	**2d**: R = 4-MeC_6H_4	I_2 (2 equiv.), DCM, 0 °C	I^+	**8da** (65)	–	–
16	**2d**	NBS (1.1 equiv.), DCM, r.t.	Br^+	**8db** (39)	–	**22db** (7)[c]
17	**2e**: R = C_6H_5	I_2 (2 equiv.), DCM, 0 °C	I^+	**8ea** (52)	–	**17ea** (Hal = I) (9)
18	**2e**	NBS (1.1 equiv.), DCM, r.t.	Br^+	**8eb** (39)	–	**22eb** (7)[c]
19	**2f**: R = 4-ClC_6H_4	I_2 (2 equiv.), DCM, 0 °C	I^+	**8fa** (54)	–	–
20	**2f**	NBS (1.1 equiv.), DCM, r.t.	Br^+	**8fb** (24)	–	**22fb** (14)[c]
21	**2g**: R = 4-$O_2NC_6H_4$	I_2 (2 equiv.), DCM, 0 °C	I^+	traces	**13ga** (17)	–
22	**2g**	NBS (1.1 equiv.), DCM, r.t.	Br^+	traces	**13gb** (11)	–
23	**2h**: R = H	I_2 (2 equiv.), DCM, 0 °C	I^+	–	traces	**17ha** (Hal = I) (26)
24	**3a**: R = 4-$MeOC_6H_4$; R' = Ts		I^+	**9aa** (73)	–	–
25	**3c**: R = 4-$MeOC_6H_4$; R' = Bn		I^+		mixture of products	
26	**3d**: R = 3,4-$(MeO)_2C_6H_3$; R' = Ts		I^+	**9da** (55)	–	–
27	**3e**: R = 4-MeC_6H_4; R' = Bn		I^+		mixture of products	
28	**3f**: R = 4-MeC_6H_4; R' = Ts	I_2 (2 equiv.), MeCN, 0 °C	I^+	**9fa** (93)		
29	**3g**: R = C_6H_5; R' = Ts		I^+	**9ga** (59)	traces	–
30	**3i**: R = H; R' = Ts		I^+	–	**14ia** (71)	**18ia** (Hal = I) (16)
31	**3j**: R = H; R' = Ph		I^+	–	**14ja** (47)	–
32	**3k**: R = H; R' = Bn		I^+	–	**14ka** (49)	–
33	**4a**: R = 4-$MeOC_6H_4$	I_2 (2 equiv.), DCM, 0 °C	I^+	**10aa** (59)	traces	–
34	**4a**	NBS (1.1 equiv.), DCM, r.t.	Br^+	**–**	**15ab** (68)	–
35	**4b**: R = 4-ClC_6H_4	NBS (1.1 equiv.), DCM, r.t.	Br^+		**15bb** (44)	–
36	**4c**: R = C_6H_5	I_2 (2 equiv.), DCM, 0 °C	I^+	**10ca** (18)	**15ca** (25)	–
37	**4c**	NBS (1.1 equiv.), DCM, r.t.	Br^+		**15cb** (67)	–
38	**4d**: R = H	I_2 (2 equiv.), DCM, 0 °C	I^+		**15da** (20)	–
39	**5a**: Ar = 4-$MeOC_6H_4$; R = Ts	NIS (1.1 equiv.), DCM, r.t.	I^+	**11aa** (52)	–	traces
40	**5b**: Ar = 4-$MeOC_6H_4$; R = Bn		I^+	**11aa** (60)	–	–
41	**6a**: Ar = 4-$MeOC_6H_4$	NIS (1.1 equiv.), DCM, r.t.	I^+	**11aa** (36)		**20aa** (27)[b]



21 [a]



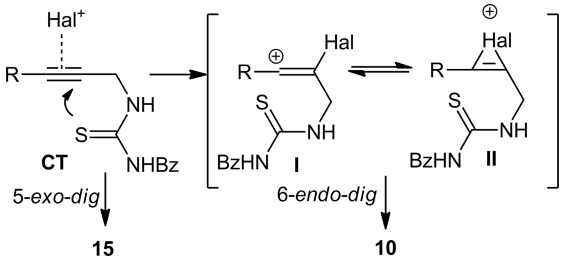
22 [c]

[a] Aryl(2-phenyloxazol-5-yl)methanones **21ga** and **21ha**, and 2-phenyloxazole-5-carbaldehyde **21ia** were isolated. [b] The same compound was obtained by using molecular iodine in CH_2Cl_2 at room temp. [c] 6,6′-Diaryl-5,5′-dibromo-3′,4′-dihydro-2′*H*-3,4′-bi(1,3-oxazine)-2,2′(4*H*)-diones **22** formed as minor products.

6, 10–18, 24, 26, 28, 29, and 39–41) underwent regioselective and dominant 6-*endo-dig* processes under halonium ion mediated reactions. Iodine-mediated reactions of starting materials with electron-poor aryl groups next to the triple bond (**1g**, **1h**, and **2g**) proceeded slowly and ineffectively. Thus, *N*-[3-(4-chloro or 4-nitrophenyl)prop-2-ynyl]benzamides **1g** and **1h** formed a mixture of six-membered and five-membered heterocyclic products **7**, **12**, and **21** in NIS-mediated cyclizations (entries 7 and 8). By using starting *tert*-butyl 3-(4-nitrophenyl)prop-2-ynylcarbamate **2g** (entries 21 and 22) or 1-substituted-3-(prop-2-ynyl)ureas **3j** and **3k** (entries 31 and 32), regioselective formation of 5-*exo-dig* cyclization products in halogen-mediated reactions was observed. In some cases, terminal propargylic substrates in halogen-mediated reactions formed mixtures of isoxazole ring containing compounds and products of electrophilic addition reactions (entries 9, 23 and 30).

In contrast to the chemistry of amides, carbamates and ureas, iodine-mediated cyclizations of electron-rich thioureas **4** were unselective (entries 33 and 36) and we were surprised when these starting materials underwent ring-closure through the 5-*exo-dig* mode exclusively during halogen-mediated cyclizations (entries 34, 35, and 37). The structures of all six- and five-membered cyclic products were established based on NMR spectroscopic analysis. In particular, after assignment of carbon signals by using a combination of COSY, HSQC, and HMBC experiments, the analysis of HMBC spectra of all cyclic products was performed. In the case of compounds **15**, the presenting cross-peaks between *ortho* protons of C(6)-Ar and C_{sp2}-Br or C_{sp2}-I nuclei indicated a five-membered core. In the HMBC spectra of six-membered cyclic compounds **10**, cross-peaks between *ortho* protons of C(6)-Ar and C_{sp2}-Br or C_{sp2}-I nuclei were absent.

It is known that because of the large size and ready polarization, sulfur is a stronger nucleophile than oxygen; therefore, cyclizations of thioureas **4** proceeded more readily than analogous reactions of amides **1**, carbamates **2**, and ureas **3**. We presume that in bromine-mediated cyclizations of thioureas **4**, nucleophilic attack occurs just after the initial formation of the charge-transfer complex between the bromonium ion and the triple bond.[6] The carbon–carbon triple bond in charge transfer (CT) complexes between alkyne and halogen remains linear; therefore, nucleophilic sulfur attack occurs through the 5-*exo-dig* mode. From the results obtained, we hypothesized that during the iodonium-mediated reaction, two possible pathways are possible: 5-*exo-dig* cyclization reaction occurs after formation of a CT complex and competing 6-*endo-dig* cyclization takes place after conversion of the CT complex into open iodovinyl (**I**) or bridged iodirenium[7] (**II**) ions (Scheme 2).



Scheme 2. Possible mechanisms of halogen-mediated 5-*exo-dig* and 6-*endo-dig* cyclizations of thioureas **4**.

2. Phenyl Hypochloroselenoite Mediated Reaction of Propargylic Substrates

After investigation of halogen-mediated reactions, we turned our attention to phenyl hypochloroselenoite as a source of chalcogen-electrophile. It should be noted that the presence of base (*t*BuOK for amides **1** and $K_3PO_4 \cdot H_2O$ for carbamates **2**) is required for successful reactions (see the Supporting information, Table S1). In contrast, ureas **3** and thioureas **4** underwent phenyl hypochloroselenoite-triggered base-independent and selective reactions.

Propargylic amides **1** and Boc-protected propargylic amines **2** during reactions with phenyl hypochloroselenoite underwent smooth 6-*endo-dig* cyclizations. However, both classes of these substrates also underwent side addition reactions and (*E*)-*N*-[3-aryl-3-chloro-2-(phenylselanyl)allyl]-benzamides **16** (Table 2, entries 1–6) or (*E*)-*tert*-butyl 3-aryl-3-chloro-2-(phenylselanyl)allylcarbamates **17** formed (entries 10–14). When starting compounds **1i** and **2h**, with terminal alkyne groups, were used, the regioselectivity of the addition reaction differed and compounds **16′ib** and **17′hc** were isolated (entries 9 and 15).

Ureas **3** and thioureas **4**, having electron-rich aryl groups next to the triple bond, underwent regioselective phenyl hypochloroselenoite triggered base-free 6-*endo-dig* cyclizations, and electrophilic addition did not take place (Table 2, entries 16, 17, 19–21, and 25–27). However, terminal propargylic ureas **3j** and **3k**, and thiourea **4d** in the reaction with phenyl hypochloroselenoite formed 4,5-dihydrothiazoles **14** and **15** through 5-*exo-dig* cyclization (entries 23, 24, and 28). The exception was 4-methyl-*N*-(prop-2-ynylcarbamoyl)-benzenesulfonamide (**3i**), which did not participate in cyclization reaction and, after treatment with the reagent, converted into (*E*)-*N*-[2-chloro-3-(phenylselanyl)allyl-carbamoyl]-4-methylbenzenesulfonamide (**18′ib**; entry 22).

Unfortunately, carbamate **5a** and ester **6a**, having *O*-propargyl functionality, did not undergo the expected rearrangement reaction with phenyl hypochloroselenoite, and high-yielding electrophilic addition reaction took place (Table 2, entries 29 and 30).

3. Oxocarbenium Ion Mediated Reaction of Propargylic Substrates

Another group of electrophiles that we studied were oxocarbenium ions formed from acetals through Lewis acid mediation. The data obtained are presented in Table 3 and Table 4.

Reactions between 1-methoxyisochroman and propargylic substrates proceeded smoothly and regioselectively. However, the activation of the triple bond by an electron-

Table 2. Data for the phenyl hypochloroselenoite mediated reactions of substrates.

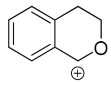
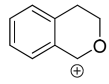
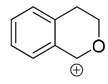
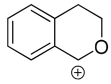
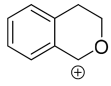
Entry	Starting material	Reaction conditions	Products (E = PhSe-)		
			6-*endo-dig* (yield, %)	5-*exo-dig* (yield, %)	Addition (Hal = Cl) (yield, %)
1	**1a**: R = 4-$MeOC_6H_4$	PhSeCl (1 equiv.), *t*BuOK (1 equiv.), DCM, r.t.	**7ab** (66)	–	**16ab** (13)
2	**1b**: R = 4-$EtOC_6H_4$		**7bb** (65)	–	**16bb** (12)
4	**1c**: R = 3,4-$(MeO)_2C_6H_3$		**7cb** (68)	–	**16cb** (19)
5	**1d**: R = 3,4,5-$(MeO)_3C_6H_2$		**7db** (63)	–	traces
6	**1f**: R = C_6H_5		**7fb** (57)	–	traces
7	**1g**: R = 4-ClC_6H_4		mixture of products		
8	**1h**: R = 4-$O_2NC_6H_4$		no reaction		
9	**1i**: R = H		–	**12ib** (26)	**16'ib** (20)
10	**2a**: R = 4-$MeOC_6H_4$	PhSeCl (1 equiv.), K_3PO_4·H_2O (1 equiv.), MeCN, 0 °C	**8ac** (86)	–	**17ac** (9)
11	**2b**: R = 3,4-$(MeO)_2C_6H_3$		**8bc** (42)	–	**17bc** (18)
12	**2c**: R = 3,4-$(OCH_2O)C_6H_3$		**8cc** (56)	–	**17cc** (26)
13	**2d**: R = 4-MeC_6H_4		**8dc** (42)	–	**17dc** (31)
14	**2g**: R = 4-$O_2NC_6H_4$		**8gc** (10)	–	**17gc** (25)
15	**2h**: R = H		traces	–	**17'hc** (75)
16	**3a**: R = 4-$MeOC_6H_4$; R' = Ts	PhSeCl (1 equiv.), MeCN, 0 °C	**9ab** (82)	–	–
17	**3b**: R = 4-$MeOC_6H_4$; R' = Ph		**9bb** (92)	–	–
18	**3c**: R = 4-$MeOC_6H_4$; R' = Bn		mixture of products		
19	**3d**: R = 3,4-$(MeO)_2C_6H_3$; R' = Ts		**9db** (73)	–	–
20	**3f**: R = 4-MeC_6H_4; R' = Ts		**9fb** (80)	–	–
21	**3g**: R = C_6H_5; R' = Ts		**9gb** (63)	–	–
22	**3i**: R = H; R' = Ts		–	–	**18'ib** (94)
23	**3j**: R = H; R' = Ph		–	**14jb** (27)	
24	**3k**: R = H; R' = Bn		–	**14kb** (40)	–
25	**4a**: R = 4-$MeOC_6H_4$	PhSeCl (1 equiv.), DCM, 0 °C	**10ab** (73)	–	–
26	**4b**: R = 4-ClC_6H_4		**10bb** (51)	–	–
27	**4c**: R = C_6H_5		**10cb** (56)	traces	–
28	**4d**: R = H		–	**15db** (45)	–
29	**5a**: Ar = 4-$MeOC_6H_4$; R = Ts	PhSeCl (1 equiv.), DCM, r.t.	–	–	**19ab** (79)
30	**6a**: Ar = 4-$MeOC_6H_4$		–	–	**20ab** (78)

rich aryl group was required for successful 6-*endo-dig* reaction. Thus, functionalized aryl-substituted propargylic amides **1**, carbamates **2**, ureas **3**, or thioureas **4** in the present reaction formed 5-(isochroman-1-yl)-4*H*-1,3-oxazines or 5-(isochroman-1-yl)-4*H*-1,3-thiazines in good yields (Table 3, entries 1–6, 9–13, 16, 18–21, and 23–25). Compounds bearing either a terminal propargylic fragment or an electron-poor aromatic ring were not active towards 3,4-dihydroisochromenylium ion mediated reactions (entries 7, 8, 14, 15, 22, 26). 1-Benzyl-3-[3-(4-methoxyphenyl)prop-2-ynyl]urea (**3c**) in reaction with 1-methoxyisochroman formed a mixture of inseparable products (entry 17) and we suppose that this is dictated by the two nucleophilic atoms (carbonyl oxygen and the nitrogen of the benzylamino fragment) presenting in the functional group. Analogous unselective reactions of **3c** were observed for halogen- and phenyl hypochloroselenoite triggered reactions (Table 1, entries 25 and 27, and Table 2, entry 18).

Esters **6** and carbamates **5** underwent our previously reported[4a] 6-*endo-dig* rearrangement reactions to 1-aryl-2-(isochroman-1-yl)-1prop-2-en-1-ones **11** (Table 3, entries 27–30). It should be noted that parallel reactions between starting materials and Lewis acids without acetals were also performed. In almost all cases, slow decomposition of the starting materials occurred.

Reactions between propargylic amides **1** and acyclic acetals under the optimized conditions (Table S1) led to the formation of predominantly six-membered products **7**, with minor amounts of enones **23** and **24** (Table 4, entries 1–8). After the activation of acetals by oxophilic Lewis acids

Table 3. Data for the 3,4-dihydroisochromenylium ion mediated reactions of substrates.

Entry	Starting material	Reaction conditions	E^+	6-*endo-dig* process product (yield, %)
1	**1a**: R = 4-$MeOC_6H_4$	1-methoxyisochroman (1 equiv.), TMSOTf (1 equiv.), DCM, r.t.		**7ac** (78)
2	**1b**: R = 4-$EtOC_6H_4$			**7bc** (53)
3	**1c**: R = 3,4-$(MeO)_2C_6H_3$			**7cc** (70)
4	**1d**: R = 3,4,5-$(MeO)_3C_6H_2$			**7dc** (54)
5	**1e**: R = 4-MeC_6H_4			**7ec** (81)
6	**1f**: R = C_6H_5			**7fc** (78)
7	**1h**: R = 4-$O_2NC_6H_4$			**7hc** (14), together with 60% of **1h**
8	**1i**: R = H			no reaction
9	**2a**: R = 4-$MeOC_6H_4$	1-methoxyisochroman (1 equiv.), $BF_3{\cdot}OEt_2$ (1 equiv.), DCM, 0 °C		**8ad** (35)
10	**3b**: R = 3,4-$(MeO)_2C_6H_3$			**8bd** (55)
11	**3d**: R = 4-MeC_6H_4			**8dd** (49)
12	**3e**: R = C_6H_5			**8ed** (40)
13	**3f**: R = 4-ClC_6H_4			**8fd** (29)
14	**2g**: R = 4-$O_2NC_6H_4$			no reaction
15	**2h**: R = H			no reaction
16	**3a**: R = 4-$MeOC_6H_4$; R' = Ts	1-methoxyisochroman (1 equiv.), TMSOTf (1 equiv.), DCM, 0 °C		**9ac** (74)
17	**3c**: R = 4-$MeOC_6H_4$; R' = Bn			mixture of products
18	**3d**: R = 3,4-$(MeO)_2C_6H_3$; R' = Ts			**9dc** (88)
19	**3f**: R = 4-MeC_6H_4; R' = Ts			**9fc** (92)
20	**3g**: R = C_6H_5; R' = Ts			**9gc** (90)
21	**3h**: R = 4-ClC_6H_4; R' = Ts			**9hc** (62)
22	**3k**: R = H; R' = Ts			no reaction
23	**4a**: R = 4-$MeOC_6H_4$	1-methoxyisochroman (1 equiv.), $BF_3{\cdot}OEt_2$ (1 equiv.), MeCN, 0 °C		**10ad** (82)
24	**4b**: R = 4-ClC_6H_4			**10bd** (55)
25	**4c**: R = C_6H_5			**10cd** (64)
26	**4d**: R = H			no reaction
27	**5a**: Ar = 4-$MeOC_6H_4$; R = Ts	1-methoxyisochroman (1 equiv.), TMSOTf (1 equiv.), DCM, r.t.		**11ac** (59)
28	**5b**: Ar = 4-$MeOC_6H_4$; R = Bn			**11ac** (71)
29	**6a**: Ar = 4-$MeOC_6H_4$			**11ac** (90)
30	**6b**: Ar = C_6H_5			**11bc** (83)

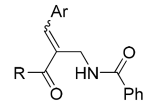
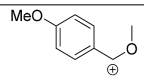
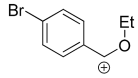
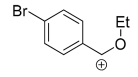
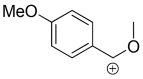
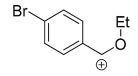
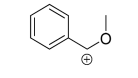
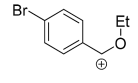
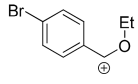
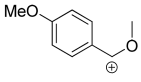
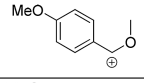
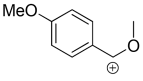
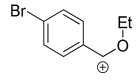
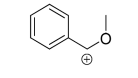
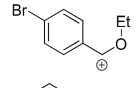
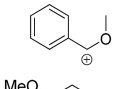
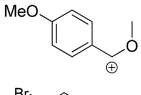
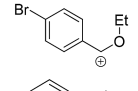
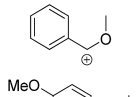
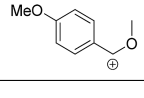
($BF_3{\cdot}OEt_2$ or TMSOTf) the formation of electrophilic oxocarbenium ions occur. After addition of the electrophile to the triple bond of amide **1**, two possible intramolecular reactions of the resulting ion **I** can then take place concurrently. The desired reaction (Route a) is 6-*endo-dig* O-nucleophilic attack resulting in cyclization products. The side reaction is ring closure to four-membered 1,2-dihydrooxetium intermediate **IV** and subsequent cycloreversion to enones[9] (Scheme 3).

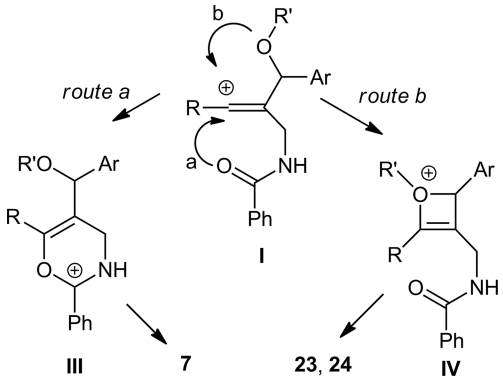
In contrast, *N*-(3-arylprop-2-ynylcarbamothioyl)benzamides **4** reacted with acyclic acetals selectively and formed *N*-{5-[alkoxy(aryl)methyl]-6-aryl-4*H*-1,3-thiazin-2-yl}benzamides **10** in good yield (Table 4, entries 11–18).

4. Factors Affecting the Outcome of Electrophile Mediated Reactions of Propargylic Substrates

Some general remarks on the investigated reactions can be made. First, almost all investigated propargylic substrates undergo cyclization or rearrangement reactions and these processes usually dominate over simple electrophilic addition reactions. Second, the outcomes of the studied reactions depend on three main factors: electron density on the alkyne, the electrophile used, and the structure of the functional nucleophilic group. Thus, the rates of the reactions as well as the regioselectivity of the processes depend strongly on the substituent next to the triple bond. Reac-

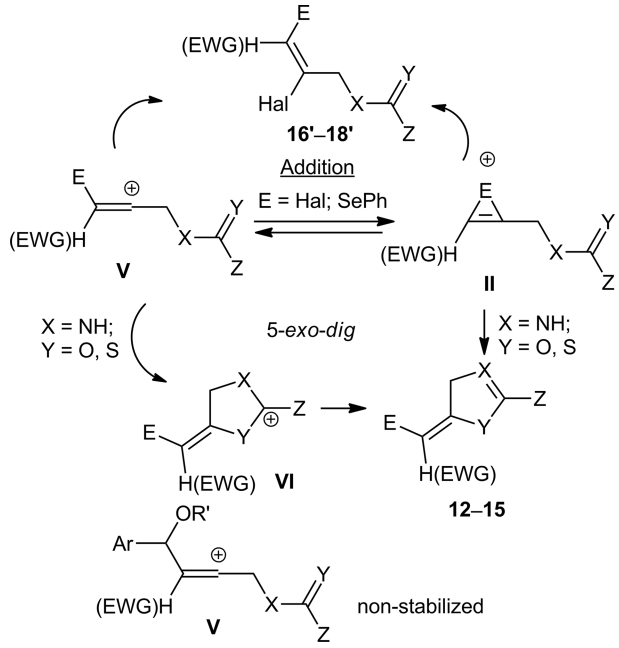
Table 4. Data for arylideneoxonium ion mediated reactions of substrates.

Entry	Starting material	Reaction conditions	E^+	Products	
				6-*endo-dig* (yield, %)	Metathesis  **23**(*E*), **24** (*Z*) (yield, %)
1	**1a**: R = 4-$MeOC_6H_4$	$ArCH(OR')_2$ (1.5 equiv.), $BF_3{\cdot}OEt_2$ (1 equiv.), DCM, −10 °C		**7ad** (51);	**23ad** (10), **24ad** (11)
2	**1a**			**7ae** (54);	**23ae** (15), **24ae** (5)
3	**1c**: R = 3,4-$(MeO)_2C_6H_3$			**7ce** (49)	traces
4	**1e**: R = 4-MeC_6H_4			**7ed** (47)	**23ed** (11)
5	**1e**			**7ee** (48)	**23ee** (22), **24ee** (traces)
6	**1e**			**7ef** (50)	**23ef** (10)
7	**1f**: R = C_6H_5			**7fe** (54)	**23fe** (6)
8	**1g**: R = 4-ClC_6H_4			**7ge** (52)	**23ge** (11)
9	**1h**: R = 4-$O_2NC_6H_4$			no reaction	
10	**1i**: R = H			no reaction	
11	**4a**: R = 4-$MeOC_6H_4$	$ArCH(OR')_2$ (1.5 equiv.), TMSOTf (1 equiv.), DCM, −10 °C		**10ae** (76)	–
12	**4a**			**10af** (59)	–
13	**4a**			**10ag** (58)	–
14	**4b**: R = 4-ClC_6H_4			**10bf** (57)	–
15	**4b**			**10bg** (65)	–
16	**4c**: R = C_6H_5			**10ce** (81)	–
17	**4c**			**10cf** (60)	–
18	**4c**			**10cg** (57)	–
19	**4d**: R = H			no reaction	



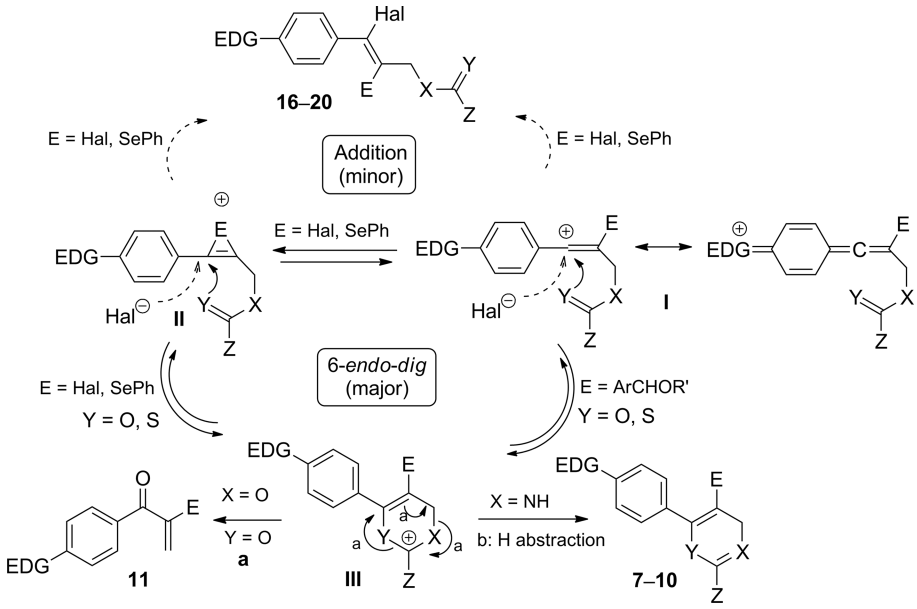
Scheme 3. Intermediates in reactions between propargylic amides with acyclic oxocarbenium electrophiles.

tions of substrates bearing electron-donating aryl groups proceeded smoothly and usually in selective 6-*endo-dig* mode. These observations could be logically explained by participation of the electron-donating aryl group in stabilization of the intermediate vinylic carbocation **I** formed during the first stage of the electrophilic activation (Scheme 4). Starting materials with electron-poor aryl groups (4-ClC_6H_4-, 4-$O_2NC_6H_4$-) next to the triple bond, or terminal propargylic substrates were not so active in electrophile-mediated reactions. These materials required prolonged reactions times for full conversion, and yields of isolated products were not high. Moreover, usually a change of cyclization mode from 6-*endo* into 5-*exo* was observed. The different regioselectivity can be explained by participation of CH_2FG groups in the inductive stabilization of the neighboring cationic center of the formed vinylic carbocation **V** (Scheme 5).



Scheme 5. Stabilization of vinylic carbocation **I** and subsequent 5-*exo-dig* processes of electron-poor propargylic substrates.

Undesired electrophilic additions can take place during halonium- or phenyl hypochloroselenoite mediated reactions, because nucleophilic anions are present in the media. Thus, during activation of the triple bond by Hal^+ or $PhSe^+$ ions, the formation of vinylic carbocations **I** can take place. The open-chain vinylic carbocations **I** can be in equilibrium with haloirenium or selenirenium ions **II**, which is consistent with recent experimental and theoretical studies.[7,8] Neither open-chain nor cyclic antiaromatic ions are very stable and the subsequent nucleophilic attack of the neigh-



Scheme 4. Stabilization of vinylic carbocation **I** and subsequent 6-*endo-dig* processes of electron-rich propargylic substrates.

boring functional group or halogen counterion takes place readily. We suppose that the dominant process is dictated by the nucleophilicity of the internal functional group and by the stability of cyclic intermediates **III**. When the nucleophilicity of the internal functional group is high (as for ureas **3** and thioureas **4**), usually an exclusive cyclization process occurs. In the opposite case, the halogen counterion acts as a nucleophile and formation of side addition products **16**–**20** takes place (Scheme 4). Notably, the stability of the six-membered cationic intermediates **III** depends on the type of heterocyclic cation. Thus, 4*H*-1,3-dioxin-2-ylium ions (X = Y = O) seem to be less stable than 4*H*-1,3-oxazin-3-ium (X = NH; Y = O) or 4*H*-1,3-thiazin-3-ium (X = NH; Y = S) ions. Therefore, electrophilic addition reactions of *O*-propargyl derivatives **5** and **6** can dominate in halonium and phenyl chloroselenoite mediated processes (Table 1, entry 41 and Table 2, entries 29 and 30).

Third, we observed that, in all successful cases, either the carbonyl oxygen or the thiocarbonyl sulfur acted as nucleophiles during the transformations. Fourth, the data obtained from these studies indicate the main difference in electrophile-mediated reactions between compounds bearing *O*- and *N*-propargyl functionality. Whereas compounds bearing *N*-propargyl groups (amides **1**, carbamates **2**, ureas **3**, and thioureas **4**) underwent electrophilic cyclization reactions quite easily, in the case of the corresponding *O*-propargyl derivatives (carbamates **5** and esters **6**), transformations into α-functionalized enones took place (Scheme 4).

It is worth mentioning that propargylic substrates **1h**,**i**, **2g**,**h**, **3k**, and **4d**, bearing a terminal or 4-nitrophenyl substituent, were completely unreactive towards oxocarbenium electrophiles (Table 3, entries 8, 14, 15, 22, and 26; Table 4, entries 9, 10, and 19). However, in contrast, reactions of these materials with iodine or phenylhypochloroselenoite proceeded, albeit ineffectively. This fact indicates that the ability to form cyclic haloirenium or selenirenium ions plays a role in the partial stabilization of vinylic carbocations. Therefore, unactivated propargylic substrates react with halogen- or chalcogen-based electrophiles, but do not undergo oxocarbenium ion mediated transformations because of the lack of stabilization (Scheme 5).

Conclusions

We have shown that substrates with various *N*- and *O*-propargil moieties can undergo electrophile-triggered reactions without the need for transition-metal catalysis. The scope and limitations of these processes were investigated by using a broad range of substrates. Based on our findings, efficient synthetic protocols for functionalized 4*H*-1,3-oxazines, 4*H*-1,3-thiazines, and 4,5-dihydrothiazoles have been developed. These methodologies permit one-step formation of heterocycle and simultaneous installation of halogen, chalcogen, or benzyl ether functionality onto the ring. Moreover, we proved that whereas propargylamine derivatives undergo electrophilic cyclization reactions, materials having a propargyloxy group can rearrange into α-functionalized enones. We expect that the presented processes will find applications in the synthesis of complex structures.

Experimental Section

General Information: IR spectra were recorded from KBr discs. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz in [D]chloroform or [D_6]dimethyl sulfoxide, using residual solvent signal as internal standard. Signal multiplicity is abbreviated as: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet). Unambiguous assignment of signals was made by using a combination of NMR experiments, including COSY, HSQC, and HMBC. High-resolution mass spectra were recorded with a Dual-ESI Q-TOF 6520 mass spectrometer with electrospray ionization. All reactions and the purity of the synthesized compounds were monitored by TLC using silica gel 60 F254 aluminum plates. Visualization was accomplished under UV light and by treating the plates with vanillin stain followed by heating.

General Procedures for Halogen-Mediated Reactions

Method A: To a solution of **1**, **5**, or **6** (1 mmol) in dichloromethane (5 mL), *N*-iodosuccinimide (0.25 g, 1.1 mmol) was added. The mixture was stirred at room temperature.

Method B: To a cooled solution of **2** or **4** (1 mmol) in anhydrous chloroform (5 mL) or **3** (1 mmol) in anhydrous acetonitrile (5 mL), molecular iodine (0.51 g, 2 mmol) was added at 0 °C. The resulting stirred solution was warmed to room temperature.

Method C: To a solution of **2** or **4** (1 mmol) in dichloromethane (5 mL), *N*-bromosuccinimide (0.19 g, 1.1 mmol) was added. The mixture was stirred at room temperature.

Isolation Procedures for All Products: When completion of the reaction was determined by TLC analysis, the reaction was quenched with aqueous sodium thiosulfate. The organic layer was separated, washed with aqueous sodium thiosulfate (2 × 20 mL), and then with water (2 × 20 mL), and dried with anhydrous Na_2SO_4. After the evaporation of solvent under reduced pressure, the residue was purified by flash column chromatography eluting with hexane/ethyl acetate mixtures.

5-Iodo-6-(4-methoxyphenyl)-2-phenyl-4*H*-1,3-oxazine (7aa): Yield 0.28 g (72%); white solid; m.p. 119–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3 H, OCH_3), 4.56 (s, 2 H, CH_2), 6.96 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.40 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.48 (tt, ^3J = 7.6, ^4J = 2.4 Hz, 1 H, ArH), 7.63 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.95–7.97 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.2 (CH_2), 55.4 (OCH_3), 69.8 (CI), 113.6 (ArC), 126.6 (ArC), 127.4 (ArC), 128.4 (ArC), 130.5 (ArC), 131.1 (ArC), 131.7 (ArC), 147.7 (Csp^2), 153.7 (Csp^2), 160.6 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{15}INO_2$ [M + H] 392.0142; found 392.0148.

6-(4-Ethoxyphenyl)-5-iodo-2-phenyl-4*H*-1,3-oxazine (7ba): Yield 0.24 g (58%); white solid; m.p. 108–109 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (t, ^3J = 7.2 Hz, 3 H, OCH_2CH_3), 4.08 (q, ^3J = 7.2 Hz, 2 H, OCH_2CH_3), 4.55 (s, 2 H, CH_2), 6.94 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.39 (t, ^3J = 8.0 Hz, 2 H, ArH), 7.46 (tt, ^3J = 7.6, ^4J = 2.4 Hz, 1 H, ArH), 7.61 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.92–7.94 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9 (CH_3), 55.5 (CH_2), 63.6 (OCH_2CH_3), 69.9 (CI), 114.0 (ArC), 126.6 (ArC), 127.3 (ArC), 128.4 (ArC), 130.5 (ArC), 131.3 (ArC), 131.7 (ArC), 147.8 (Csp^2), 153.0 (Csp^2), 159.9 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{17}INO_2$ [M + H] 406.0298; found 406.0294.

6-(3,4-Dimethoxyphenyl)-5-iodo-2-phenyl-4*H*-1,3-oxazine (7ca): Yield 0.22 g (52%); white solid; m.p. 147–148 °C. ^{1}H NMR

(400 MHz, $CDCl_3$): δ = 3.93 (s, 3 H, OCH_3), 3.93 (s, 3 H, OCH_3), 4.56 (s, 2 H, CH_2), 6.92 (d, ^3J = 8.4 Hz, 1 H, ArH), 7.21 (d, ^4J = 2.0 Hz, 1 H, ArH), 7.27 (dd, ^3J = 8.6, ^4J = 2.0 Hz, 1 H, ArH), 7.40 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.48 (tt, ^3J = 7.6, ^4J = 2.4 Hz, 1 H, ArH), 7.94–7.96 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.1 (CH_2), 56.0 (CH_3), 56.1 (CH_3), 70.0 (CI), 110.6 (ArC), 112.2 (ArC), 122.1 (ArC), 126.7 (ArC), 127.3 (ArC), 128.4 (ArC), 131.3 (ArC), 131.5 (ArC), 147.7 (Csp^2), 148.4 (ArC), 150.1 (ArC), 153.4 (Csp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{16}INNaO_3$ [M + Na] 444.0067; found 444.0060.

5-Iodo-2-phenyl-6-(3,4,5-trimethoxyphenyl)-4*H*-1,3-oxazine (7da): Yield 0.27 g (60%); white solid; m.p. 184–185 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.90 (s, 6 H, 2 × OCH_3), 3.91 (s, 3 H, OCH_3), 4.56 (s, 2 H, CH_2), 6.90 (s, 2 H, ArH), 7.40 (t, ^3J = 8.0 Hz, 2 H, ArH), 7.49 (tt, ^3J = 7.6, ^4J = 2.4 Hz, 1 H, ArH), 7.92–7.94 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4 (CH_2), 56.4 (2 × OCH_3), 61.0 (OCH_3), 70.7 (CI), 106.6 (ArC), 127.2 (ArC), 128.4 (ArC), 129.6 (ArC), 131.4 (ArC), 131.6 (ArC), 139.2 (ArC), 147.8 (Csp^2), 152.8 (Csp^2), 159.9 (2 × ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{19}H_{19}INO_4$ [M + H] 452.0353; found 452.0347.

5-Iodo-2-phenyl-6-*p*-tolyl-*4H*-1,3-oxazine (7ea): Yield 0.22 g (58%); white solid; m.p. 125–126 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3 H, CH_3), 4.57 (s, 2 H, CH_2), 7.26 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.40 (t, ^3J = 8.0 Hz, 2 H, ArH), 7.49 (t, ^3J = 7.6 Hz, 1 H, ArH), 7.57 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.95–7.97 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6 (CH_3), 55.1 (CH_2), 70.3 (CI), 127.5 (ArC), 128.4 (ArC), 129.0 (ArC), 131.0 (ArC), 131.3 (ArC), 131.7 (ArC), 140.0 (ArC), 147.9 (Csp^2), 153.8 (Csp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{15}INO$ [M + H] 376.0193; found 376.0189.

5-Iodo-2,6-diphenyl-4*H*-1,3-oxazine (7fa): Yield 0.18 g (52%); white solid; m.p. 105–106 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.57 (s, 2 H, CH_2), 7.38–7.48 (m, 6 H, ArH), 7.66–7.69 (m, 2 H, ArH), 7.93–7.95 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4 (CH_2), 70.9 (CI), 127.2 (ArC), 128.2 (ArC), 128.3 (ArC), 129.1 (ArC), 129.7 (ArC), 131.3 (ArC), 131.6 (ArC), 134.4 (ArC), 148.0 (Csp^2), 152.8 (Csp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{13}INO$ [M + H] 362.0036; found 362.0036.

6-(4-Chlorophenyl)-5-iodo-2-phenyl-4*H*-1,3-oxazine (7ga): Yield 0.08 g (20%); white solid; m.p. 122–123 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.55 (s, 2 H, CH_2), 7.37–7.43 (m, 4 H, ArH), 7.62 (t, ^3J = 7.2 Hz, 1 H, ArH), 7.89–7.92 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4 (CH_2), 71.4 (CI), 127.2 (ArC), 128.4 (ArC), 128.6 (ArC), 130.5 (ArC), 131.4 (ArC), 131.5 (ArC), 132.9 (ArC), 147.1 (Csp^2), 152.6 (Csp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{11}Cl^{35}INO$ [M + H] 395.9652; found 395.9616.

(*E*)-5-[(4-Chlorophenyl)iodomethylene]-2-phenyl-4,5-dihydrooxazole (12ga): Yield 0.16 g (41%); white solid; m.p. 141–142 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.55 (s, 2 H, CH_2), 7.37–7.43 (m, 4 H, ArH), 7.62 (t, ^3J = 7.2 Hz, 1 H, ArH), 7.89–7.92 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4 (CH_2), 71.4 (CI), 127.2 (ArC), 128.4 (ArC), 128.6 (ArC), 130.5 (ArC), 131.4 (ArC), 131.5 (ArC), 132.9 (ArC), 147.1 (Csp^2), 152.6 (Csp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{11}Cl^{35}INO$ [M + H] 395.9652; found 395.9616.

(4-Chlorophenyl)(2-phenyloxazol-5-yl)methanone (21ga): Yield 49 mg (18%); white solid; m.p. 142–143 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1654 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.56 (m, 5 H, ArH), 7.89 (s, 1 H, CH), 7.96–7.98 (m, 2 H, ArH), 8.19 (dd, ^3J = 8.1, ^4J = 1.6 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.1 (ArC), 127.5 (ArC), 129.0 (ArC), 129.1 (ArC), 130.4 (ArC), 132.0 (ArC), 135.1 (ArC), 137.7 (ArC), 139.8 (ArC), 148.8 (ArC), 164.9 (ArC), 180.0 (C=O) ppm. HRMS (ES): *m*/*z* calcd. for $C_{16}H_{10}ClNNaO_2$ [M + Na] 306.0298; found 306.0299.

5-Iodo-6-(4-nitrophenyl)-2-phenyl-4*H*-1,3-oxazine (7ha): Yield 0.1 g (24%); white solid; m.p. 190–191 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.91 (s, 2 H, CH_2), 7.46 (t, ^3J = 7.2 Hz, 2 H, ArH), 7.56 (t, ^3J = 7.2 Hz, 1 H, ArH), 7.86 (d, ^3J = 9.2 Hz, 2 H, ArH), 7.90–7.92 (m, 2 H, ArH), 8.23 (d, ^3J = 9.2 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 65.7 (CH_2), 67.3 (CI), 123.5 (ArC), 126.2 (ArC), 128.1 (ArC), 128.9 (ArC), 130.4 (ArC), 132.6 (ArC), 144.3 (ArC), 146.7 (Csp^2), 156.0 (Csp^2), 163.9 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{12}IN_2O_3$ [M + H] 406.9887; found 406.9889.

(4-Nitrophenyl)(2-phenyloxazol-5-yl)methanone (21ha): Yield 47 mg (16%); yellowish solid; m.p. 186–187 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.61 (m, 3 H, ArH), 7.94 (s, 1 H, ArH), 8.15–8.20 (m, 4 H, ArH), 8.41 (d, ^3J = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.1 (ArC), 125.9 (ArC), 127.8 (ArC), 129.3 (ArC), 130.1 (ArC), 132.5 (ArC), 138.8 (ArC), 141.8 (ArC), 148.6 (Csp^2), 150.4 (ArC), 165.6 (Csp^2), 179.5 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{11}N_2O_4$ [M + H] 295.0713; found 295.0713.

2-Phenyloxazole-5-carbaldehyde (21ia): Yield 27.7 mg (16%); solid; m.p. 103–104 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1668 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.58 (m, 3 H, ArH), 7.95 (s, 1 H, CH), 8.16–8.19 (m, 2 H, ArH), 9.81 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.0 (ArC), 127.8 (ArC), 129.2 (ArC), 132.4 (ArC), 139.2 (Csp^2), 149.7 (Csp^2), 165.6 (Csp^2), 176.4 (CHO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{10}H_7NNaO_2$ [M + Na] 196.0369; found 196.0368.

(*E*)-*N*-(2,3-Diiodoallyl)benzamide (16ia): Yield 0.16 g (41%); yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.62 (d, ^3J = 3.2 Hz, 2 H, CH_2), 5.79 (t, ^3J = 3.2 Hz, 1 H, CH), 7.44 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.53 (t, ^3J = 7.6 Hz, 1 H, ArH), 7.94–7.97 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.5 (CH_2), 61.1 ($HC_{sp2}I$), 126.4 ($C_{sp2}I$), 128.2 (ArC), 128.7 (ArC), 132.3 (ArC), 157.8 (ArC), 164.2 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_9H_{11}I_2NO$ [M + H] 402.8930; found 402.8936.

5-Iodo-6-(4-methoxyphenyl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (8aa): Yield 0.24 g (68%); yellow solid; m.p. 174–175 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1747 (C=O), 3242 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, OCH_3), 4.23 (d, ^3J = 1.2 Hz, 2 H, CH_2), 6.12 (br. s, 1 H, NH), 6.91 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.57 (d, ^3J = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.8 (CH_2), 55.3 (OCH_3), 62.8 (CI), 113.3 (ArC), 125.7 (ArC), 130.6 (ArC), 148.9 (Csp^2), 150.8 (NHCO), 160.6 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{11}H_{10}INNaO_3$ [M + Na] 353.9598; found 353.9595.

5-Bromo-6-(4-methoxyphenyl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (8ab): Yield 0.09 g (30%); yellow solid; m.p. 166–167 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1737 (C=O), 3271 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, OCH_3), 4.23 (s, 2 H, CH_2), 6.61 (br. s, 1 H, NH), 6.92 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.64 (d, ^3J = 8.0 Hz, 2 H, ArH), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.8 (CH_2), 55.3 (OCH_3), 92.3 (CBr), 113.4 (ArC), 123.8 (ArC), 130.2 (ArC), 146.1 (Csp^2), 150.8 (NHCO), 160.6 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{11}H_{10}{}^{79}BrNNaO_3$ [M + Na] 305.9736; found 305.9732.

6-(3,4-Dimethoxyphenyl)-5-iodo-3,4-dihydro-2*H*-1,3-oxazin-2-one (8ba): Yield 0.24 g (67%); brownish solid; m.p. 186–189 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1724 (C=O), 3246 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.91 (s, 6 H, 2 × OCH_3), 4.23 (d, ^3J = 1.6 Hz, 2 H, CH_2), 6.31 (br. s, 1 H, NH), 6.87 (d, ^3J = 8.4 Hz, 1 H, ArH), 7.12 (d, ^4J = 2.0 Hz, 1 H, ArH), 7.24 (dd, ^3J = 8.4, ^4J = 2.0 Hz, 1 H,

ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.8 (CH_2), 55.9 (OCH_3), 56.0 (OCH_3), 63.0 (CI), 110.2 (ArC), 111.9 (ArC), 122.5 (ArC), 125.8 (ArC), 148.3 (ArC), 148.8 (Csp^2), 150.2 (ArC), 150.8 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{12}H_{12}INNaO_4$ [M + Na] 383.9703; found 383.9708.

5-Bromo-6-(3,4-dimethoxyphenyl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (8bb): Yield 0.17 g (53%); yellowish white solid; m.p. 162–163 °C. IR (KBr): ṽmax = 1766 (C=O), 3251 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.89 (s, 3 H, OCH_3), 3.90 (s, 3 H, OCH_3), 4.22 (d, ^3J = 1.6 Hz, 2 H, CH_2), 6.71 (br. s, 1 H, NH), 6.87 (d, ^3J = 8.4 Hz, 1 H, ArH), 7.18 (d, ^4J = 2.0 Hz, 1 H, ArH), 7.30 (dd, ^3J = 8.4, ^4J = 2.0 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.8 (CH_2), 55.8 (OCH_3), 55.9 (OCH_3), 92.5 (CBr), 110.3 (ArC), 111.4 (ArC), 122.1 (ArC), 123.9 (ArC), 146.0 (ArC), 148.3 (Csp^2), 150.2 (ArC), 150.8 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{12}H_{12}{}^{79}BrNO_4$ 314.0022 [M + H]; found 314.0037.

6-(Benzo[*d*][1,3]dioxol-5-yl)-5-iodo-3,4-dihydro-2*H*-1,3-oxazin-2-one (8ca): Yield 0.21 g (60%); white solid; m.p. 203–204 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1737 (C=O), 3278 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 4.07 (d, ^3J = 1.2 Hz, 2 H, CH_2), 6.09 (s, 2 H, OCH_2O), 6.98 (d, ^3J = 7.6 Hz, 1 H, ArH), 7.03 (d, ^4J = 1.6 Hz, 1 H, ArH), 7.05 (br. s, 1 H, ArH), 7.91 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 50.6 (CH_2), 66.3 (CI), 101.6 (OCH_2O), 108.0 (ArC), 109.1 (ArC), 123.5 (ArC), 127.7 (ArC), 146.9 (ArC), 147.8 (Csp^2), 148.1 (ArC), 149.3 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{11}H_8INNaO_4$ [M + Na] 367.9390; found 367.9391.

5-Iodo-6-*p*-tolyl-3,4-dihydro-2*H*-1,3-oxazin-2-one (8da): Yield 0.2 g (65%); yellow solid; m.p. 183–184 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1747 (C=O), 3242 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.83 (s, 3 H, CH_3), 4.22 (d, ^3J = 1.6 Hz, 2 H, CH_2), 6.69 (br. s, 1 H, NH), 7.21 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.51 (d, ^3J = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4 (CH_3), 51.6 (CH_2), 63.5 (CI), 128.7 (ArC), 128.9 (ArC), 130.5 (ArC), 140.1 (ArC), 149.0 (Csp^2), 151.1 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{11}H_{10}INNaO_2$ [M + Na] 337.9648; found 337.9643.

5-Bromo-6-*p*-tolyl-3,4-dihydro-2*H*-1,3-oxazin-2-one (8db): Yield 0.1 g (39%); white solid; m.p. 160–161 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1754 (C=O), 3248 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 4.23 (d, ^3J = 1.6 Hz, 2 H, CH_2), 6.78 (br. s, 1 H, NH), 7.21 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.58 (d, ^3J = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4 (CH_3), 47.8 (CH_2), 93.0 (CBr), 128.5 (ArC), 128.6 (ArC), 128.7 (ArC), 140.1 (ArC), 146.3 (Csp^2), 150.9 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{11}H_{10}{}^{79}BrNNaO_2$ [M + Na] 289.9787; found 289.9787.

5,5′-Dibromo-6,6′-di-*p*-tolyl-3′,4′-dihydro-2′*H*-3,4′-bi(1,3-oxazine)-2,2′(4*H*)-dione (22db): Yield 18.6 mg (7%); white solid; m.p. 198–199 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1734 (C=O), 3234 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 4.07 (d, ^2J = 14.4 Hz, 1 H, C*H*H), 4.19 (d, ^2J = 14.4 Hz, 1 H, CH*H*), 6.55 (d, ^3J = 3.2 Hz, 1 H, CH), 6.65 (d, ^3J = 2.8 Hz, 1 H, NH), 7.21 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.26 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.59 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.59 (d, ^3J = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4 (CH_3), 21.5 (CH_3), 45.7 (CH_2), 67.8 (CH), 90.5 (CBr), 92.2 (CBr), 127.6 (ArC), 127.8 (ArC), 128.4 (ArC), 128.6 (ArC), 128.8 (ArC), 129.0 (ArC), 140.4 (ArC), 141.3 (ArC), 146.0 (Csp^2), 148.5 (NHCO), 149.8 (NHCO), 151.3 (Csp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{22}H_{18}{}^{79}Br_2N_2NaO_4$ [M + Na] 554.9526; found 554.9523.

5-Iodo-6-phenyl-3,4-dihydro-2*H*-1,3-oxazin-2-one (8ea): Yield 0.16 g (52%); yellow solid; m.p. 165–166 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1723 (C=O), 3386 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.24 (d, ^3J = 1.6 Hz, 2 H, CH_2), 6.70 (br. s, 1 H, NH), 7.39–7.42 (m, 3 H, ArH), 7.60–7.62 (m, 2 H, ArH), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.6 (CH_2), 64.1 (CI), 128.0 (ArC), 129.1 (ArC), 130.0 (ArC), 133.4 (ArC), 148.9 (Csp^2), 151.0 (NHCO), ppm. HRMS (ESI): *m*/*z* calcd. for $C_{10}H_8INNaO_2$ [M + Na] 323.9492; found 323.9497.

(*E*)-*tert*-Butyl 2,3-Diiodo-3-phenylallylcarbamate (17ea): Yield 43.6 mg (9%); white solid; m.p. 103–104 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1685 (C=O), 3384 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (s, 9 H, 3 × CH_3), 4.33 (d, ^3J = 2.0 Hz, 2 H, CH_2), 4.97 (br. s, 1 H, NH), 7.20 (d, ^3J = 7.2 Hz, 2 H, ArH), 7.27–7.31 (m, 1 H, ArH), 7.36 (t, ^3J = 7.2 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.4 (3 × CH_3), 57.1 (CH_2), 80.0 [$C(CH_3)_3$], 96.3 (Csp^2I), 102.8 (Csp^2I), 128.1 (ArC), 128.5 (ArC), 131.7 (ArC), 147.5 (ArC), 155.3 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{14}H_{17}I_2NNaO_2$ [M + Na] 507.9241; found 507.9244.

5-Bromo-6-phenyl-3,4-dihydro-2*H*-1,3-oxazin-2-one (8eb): Yield 0.1 g (39%); white solid; m.p. 154–155 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1721 (C=O), 3380 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.24 (d, ^3J = 1.2 Hz, 2 H, CH_2), 7.05 (br. s, 1 H, NH), 7.40–7.42 (m, 3 H, ArH), 7.66–7.69 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.7 (CH_2), 93.6 (CBr), 128.0 (ArC), 128.6 (ArC), 129.9 (ArC), 131.4 (ArC), 146.1 (Csp^2), 151.0 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{10}H_8{}^{79}BrNNaO_2$ [M + Na] 275.9631; found 275.9635.

5,5′-Dibromo-6,6′-diphenyl-3′,4′-dihydro-2′*H*-3,4′-bi(1,3-oxazine)-2,2′(4*H*)-dione (22eb): Yield 17.6 mg (7%); white solid; m.p. 203–204 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1717 (C=O), 3288 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.24 (s, 2 H, CH_2), 6.30 (s, 1 H, CH), 7.49–7.52 (m, 6 H, ArH), 7.64–7.69 (m, 4 H, ArH), 9.00 (d, ^3J = 2.4 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 47.4 (CH_2), 68.2 (CH), 93.0 (CBr), 94.3 (CBr), 128.8 (ArC), 128.9 (2 × ArC), 129.2 (ArC), 130.6 (ArC), 130.9 (ArC), 131.5 (ArC), 131.8 (ArC), 145.6 (Csp^2), 148.5 (2 × NHCO), 150.3 (Csp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{20}H_{14}{}^{79}Br_2N_2NaO_4$ [M + Na] 526.9213; found 526.9212.

6-(4-Chlorophenyl)-5-iodo-3,4-dihydro-2*H*-1,3-oxazin-2-one (8fa): Yield 0.17 g (54%); yellow solid; m.p. 209–210 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1749 (C=O), 3141 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.10 (d, ^3J = 1.6 Hz, 2 H, CH_2), 7.53 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.58 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.95 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 50.6 (CH_2), 67.4 (CI), 128.3 (ArC), 130.8 (ArC), 132.9 (ArC), 134.2 (ArC), 147.0 (Csp^2), 149.0 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{11}H_{10}{}^{35}ClINNaO_2$ [M + Na] 372.9343; found 372.9340.

5-Bromo-6-(4-chlorophenyl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (8fb): Yield 0.07 g (24%); white solid; m.p. 203–204 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1758 (C=O), 3238 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.14 (d, ^3J = 1.6 Hz, 2 H, CH_2), 7.55 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.63 (d, ^3J = 8.4 Hz, 2 H, ArH), 8.14 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 46.8 (CH_2), 95.2 (CBr), 128.5 (ArC), 130.3 (ArC), 130.7 (ArC), 134.4 (ArC), 144.6 (Csp^2), 148.7 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{10}H_7{}^{79}Br^{35}ClNNaO_2$ [M + Na] 309.9241; found 309.9241.

5,5′-Dibromo-6,6′-bis(4-chlorophenyl)-3′,4′-dihydro-2′*H*-3,4′-bi-(1,3-oxazine)-2,2′(4*H*)-dione (22fb): Yield 40 mg (14%); white solid; m.p. 123–124 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1734 (C=O), 3175 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.22 (d, ^2J = 15.6 Hz, 1 H, C*H*H), 4.27 (d, ^2J = 15.2 Hz, 1 H, CH*H*), 6.28 (s, 1 H, CH), 7.57 (d, ^3J = 3.2 Hz, 2 H, ArH), 7.59 (d, ^3J = 3.6 Hz, 2 H, ArH), 7.68 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.71 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.59

(d, ^3J = 2.4 Hz, 2 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 47.1 (CH$_2$), 67.7 (CH), 93.0 (CBr), 94.6 (CBr), 128.5 (ArC), 128.6 (ArC), 129.8 (ArC), 130.2 (ArC), 130.3 (ArC), 130.7 (ArC), 134.8 (ArC), 135.0 (ArC), 144.1 (Csp^2), 147.8 (NHCO), 147.9 (NHCO), 148.8 (Csp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{20}H_{12}{}^{79}Br_2{}^{35}Cl_2KN_2O_4$ [M + K] 610.8172; found 610.8162.

(*E*)-5-[Iodo(4-nitrophenyl)methylene]oxazolidin-2-one (13ga): Yield 58.8 mg (17%); yellow solid; m.p. 203–204 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1812 (C=O), 3302 (NH) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.34 (s, 2 H, CH$_2$), 7.77 (d, ^3J = 9.2 Hz, 2 H, ArH), 8.23 (d, ^3J = 9.2 Hz, 2 H, ArH), 8.74 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 50.2 (CH$_2$), 68.7 (CI), 123.5 (ArC), 130.5 (ArC), 144.1 (ArC), 146.1 (ArC), 149.7 (Csp^2), 155.6 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{10}H_7IN_2NaO_4$ [M + Na] 368.9343; found 368.9348.

(*E*)-5-[Bromo(4-nitrophenyl)methylene]oxazolidin-2-one (13gb): Yield 32.7 mg (11%); yellow oil. IR (KBr): $\tilde{\nu}_{max}$ = 1735 (C=O), 3302 (NH) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.48 (s, 2 H, CH$_2$), 6.18 (br. s, 1 H, NH), 7.90 (d, ^3J = 8.8 Hz, 2 H, ArH), 8.22 (d, ^3J = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 47.6 (CH$_2$), 93.4 (CBr), 123.5 (ArC), 129.4 (ArC), 140.1 (ArC), 145.6 (ArC), 147.0 (Csp^2), 155.6 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{10}H_7{}^{79}BrN_2NaO_4$ [M + Na] 320.9481; found 320.9482.

(*E*)-*tert*-Butyl 2,3-Diiodoallylcarbamate (17ha): Yield 0.11 g (26%); white solid; m.p. 72–73 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1699 (C=O), 3379 (NH) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.46 (s, 9 H, 3 × CH$_3$), 4.00 (d, ^3J = 5.6 Hz, 2 H, CH$_2$), 4.88 (br. s, 1 H, NH), 7.02 (s, 1 H, Csp^{2}H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 28.4 (3 × CH$_3$), 51.8 (CH$_2$), 80.0 [C(CH$_3$)$_3$], 80.4 (Csp^{2}HI), 102.0 (Csp^{2}I), 155.2 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_8H_{13}I_2NNaO_2$ [M + Na] 431.8928; found 431.8926.

***N*-[5-Iodo-6-(4-methoxyphenyl)-4*H*-1,3-oxazin-2-yl]-4-methylbenzenesulfonamide (9aa):** Yield 0.35 g (73%); white solid; m.p. 190–195 °C (decomp.). IR (KBr): $\tilde{\nu}_{max}$ = 3278 (NH) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.39 (s, 3 H, CH$_3$), 3.88 (s, 3 H, OCH$_3$), 4.33 (s, 2 H, NCH$_2$), 6.93 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.17 (d, ^3J = 8.1 Hz, 2 H, ArH), 7.52 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.71 (d, ^3J = 8.2 Hz, 2 H, ArH), 9.13 (br. s, 1 H, HN) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 21.5 (CH$_3$), 49.8 (NCH$_2$), 55.4 (OCH$_3$), 64.8 (CI), 113.4 (ArC), 124.2 (ArC), 126.9 (ArC), 129.2 (ArC), 130.9 (ArC), 139.2 (ArC), 142.8 (ArC), 147.2 (C-sp^2), 153.8 (HNC-sp^2), 160.9 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{17}IN_2NaO_4S$ [M + Na] 506.9846; found 506.9842.

***N*-[6-(3,4-Dimethoxyphenyl)-5-iodo-4*H*-1,3-oxazin-2-yl]-4-methylbenzenesulfonamide (9da):** Yield 0.28 g (55%); off-white powder; m.p. 211 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3003 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.32 (s, 3 H, CH$_3$), 3.79 (s, 3 H, OCH$_3$), 3.83 (s, 3 H, OCH$_3$), 4.15 (s, 2 H, CH$_2$), 7.04 (d, ^3J = 8.3 Hz, 1 H, ArH), 7.17 (d, ^3J = 8.2 Hz, 1 H, ArH), 7.20–7.34 (m, 3 H, ArH), 7.60 (d, ^3J = 7.6 Hz, 2 H, ArH), 9.19 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 21.3 (CH$_3$), 49.6 (CH$_2$), 56.0 (2 × OCH$_3$), 67.6 (IC-sp^2), 111.4 (ArC), 112.8 (ArC), 122.9 (ArC), 124.6 (ArC), 126.6 (ArC), 129.5 (ArC), 140.1 (ArC), 142.3 (ArC), 146.2 (ArC), 148.4 (IC*C*-sp^2), 150.5 (ArC), 153.1 (HNC-sp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{19}H_{19}IN_2NaO_5S$ [M + Na] 536.9952; found 536.9950.

***N*-[5-Iodo-6-(*p*-tolyl)-4*H*-1,3-oxazin-2-yl]-4-methylbenzenesulfonamide (9fa):** Yield 0.44 g (93%); yellowish solid; m.p. 234 °C (decomp.). IR (KBr): $\tilde{\nu}_{max}$ = 3000 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.33 (s, 3 H, CH$_3$), 2.36 (s, 3 H, CH$_3$), 4.14 (br. s, 2 H, CH$_2$), 7.20–7.28 (m, 4 H, ArH), 7.30–7.38 (m, 2 H, ArH), 7.57 (d, ^3J = 7.9 Hz, 2 H, ArH), 9.15 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 21.3 (CH$_3$), 21.4 (CH$_3$), 49.5 (CH$_2$), 68.6 (CI), 126.6 (ArC), 129.1 (ArC), 129.3 (ArC), 129.5 (ArC), 129.7 (ArC), 140.4 (ArC), 140. 9 (ArC), 142.3 (ArC), 146.3 (C-sp^2), 152.9 (HNC-sp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{18}IN_2O_3S$ [M + H] 469.0077; found 469.0072.

***N*-(5-Iodo-6-phenyl-4*H*-1,3-oxazin-2-yl)-4-methylbenzenesulfonamide (9ga):** Yield 0.27 g (59%); white solid; m.p. 204–208 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3284 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.33 (s, 3 H, CH$_3$), 4.17 (s, 2 H, CH$_2$), 7.21 (d, ^3J = 7.3 Hz, 2 H, ArH), 7.46 (br. s, 5 H, ArH), 7.58 (d, ^3J = 7.5 Hz, 2 H, ArH), 9.17 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 21.4 (CH$_3$), 49.5 (CH$_2$), 69.2 (IC-sp^2), 126.6 (ArC), 128.6 (ArC), 129.4 (ArC), 129.5 (ArC), 130.6 (ArC), 132.6 (ArC), 140.9 (ArC), 142.3 (ArC), 146.2 (IC*C*-sp^2), 152.8 (HNC-sp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{15}IN_2NaO_3S$ [M + Na] 476.9740; found 476.9731.

(*E*)-*N*-[5-(Iodomethylene)-4,5-dihydrooxazol-2-yl]-4-methylbenzenesulfonamide (14ia): Yield 0.27 g (71%); white solid; m.p. 218–223 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3364 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.36 (s, 3 H, CH$_3$), 4.27 (s, 2 H, CH$_2$), 6.22 (s, 1 H, ICH), 7.35 (br. s, 2 H, ArH), 7.73 (br. s, 2 H, ArH), 9.40 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 21.4 (CH$_3$), 46.3 (CH$_2$), 54.1 (IC-sp^2), 126.6 (ArC), 129.8 (ArC), 140.0 (ArC), 142.9 (ArC), 151.1 (ICC-sp^2), 159.2 (HNC-sp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{11}H_{12}IN_2O_3S$ [M + H] 378.9608; found 378.9611.

(*E*)-*N*-(2,3-Diiodoallylcarbamoyl)-4-methylbenzenesulfonamide (18ia): Yield 80.9 mg (16%); white solid; m.p. 184–187 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3234 (NH), 1691 (CO) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.34 (s, 3 H, CH$_3$), 3.80 (d, ^3J = 5.5 Hz, 2 H, CH$_2$), 6.86 (t, ^3J = 5.8 Hz, 1 H, NH), 7.30 (s, 1 H, CH), 7.41 (d, ^3J = 8.1 Hz, 2 H, ArH), 7.80 (d, ^3J = 8.3 Hz, 2 H, ArH), 10.76 (br. s, 1 H, NH) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{11}H_{12}I_2N_2NaO_3S$ [M + Na] 528.8550; found 528.8555.

(*E*)-5-(Iodomethylene)-*N*-phenyl-4,5-dihydrooxazol-2-amine (14ja): Yield 0.15 g (47%); white solid; m.p. 152–155 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3233(NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.38 (d, ^4J = 2.5 Hz, 2 H, CH$_2$), 5.88 (s, 1 H, CH), 6.95 (t, ^3J = 7.3 Hz, 1 H, ArH), 7.26 (t, ^3J = 7.9 Hz, 2 H, ArH), 7.55 (d, ^3J = 7.1 Hz, 2 H, ArH), 9.65 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]-DMSO): δ = 48.3 (IC-sp^2), 59.3 (CH$_2$), 118.2 (ArC), 122.2 (ArC), 129.2 (ArC), 139.9 (ArC), 155.3 (H$_2$C*C*-sp^2), 156.5 (HNC-sp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{10}H_{10}IN_2O$ [M + H] 300.9832; found 300.9830.

(*E*)-*N*-Benzyl-5-(iodomethylene)-4,5-dihydrooxazol-2-amine (14ka): Yield 0.14 g (49%); white solid; m.p 103–105 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3442(NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.17 (d, ^4J = 2.4 Hz, 2 H, CH$_2$), 4.27 (s, 2 H, CH$_2$), 5.77 (s, 1 H, CH), 7.20–7.40 (m, 5 H, ArH), 7.48 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 45.7 (NCH$_2$), 47.7 (IC-sp^2), 58.7 (HNCH$_2$), 127.3 (ArC), 127.6 (ArC), 128.7 (ArC), 139.8 (ArC), 158.4 (H$_2$CC-sp^2), 159.7 (HNC-sp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{11}H_{12}IN_2NaO$ [M + H] 337.9892; found 337.9894.

***N*-[5-Iodo-6-(4-methoxyphenyl)-4*H*-1,3-thiazin-2-yl]benzamide (10aa):** Yield 0.27 g (59%); yellow solid; m.p. 149–150 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1680 (C=O), 3238 (NH) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.83 (s, 3 H, OCH$_3$), 4.52 (s, 2 H, CH$_2$), 6.92 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.35 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.43 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.52 (tt, ^3J = 7.6, ^4J = 1.2 Hz, 1 H, ArH), 8.08 (d, ^3J = 7.2 Hz, 2 H, ArH), 10.61 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 55.3 (OCH$_3$), 57.7 (CH$_2$), 78.1 (CI), 113.9

(ArC), 128.3 (ArC), 128.9 (ArC), 130.5 (ArC), 130.8 (ArC), 132.4 (ArC), 135.0 (ArC), 135.1 (Csp^2), 160.3 (ArC), 164.1 (Csp^2), 174.0 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{16}IN_2O_2S$ [M + H] 450.9972; found 450.9980.

***N*-(5-Iodo-6-phenyl-4*H*-1,3-thiazin-2-yl)benzamide (10ca):** Yield 0.08 g (18%); white solid; m.p. 172–173 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1608 (C=O), 3406 (NH) cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO): δ = 4.57 (s, 2 H, CH_2), 7.33–7.36 (m, 2 H, ArH), 7.42–7.50 (m, 5 H, ArH), 7.58 (t, ^3J = 7.6 Hz, 1 H, ArH), 8.00 (d, ^3J = 7.6 Hz, 2 H, ArH), 10.95 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 57.3 (CH_2), 82.9 (CI), 128.3 (ArC), 128.5 (ArC), 128.8 (ArC), 129.0 (ArC), 129.1 (ArC), 132.3 (ArC), 134.6 (Csp^2), 138.9 (ArC), 140.3 (ArC), 165.4 (Csp^2), 174.1 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{13}IN_2OS$ [M + H] 420.9866; found 420.9873.

(*E*)-*N*-{5-[Iodo(phenyl)methylene]-4,5-dihydrothiazol-2-yl}benzamide (15ca): Yield 0.11 g (25%); yellow solid; m.p. 195–196 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1693 (C=O), 3138 (NH) cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO): δ = 4.50 (s, 2 H, CH_2), 7.33–7.37 (m, 1 H, ArH), 7.42–7.49 (m, 6 H, ArH), 7.56 (t, ^3J = 7.2 Hz, 1 H, ArH), 8.01–8.03 (m, 2 H, ArH), 10.64 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 57.3 (CH_2), 82.5 (CI), 128.2 (ArC), 128.3 (ArC), 128.7 (2 × ArC), 128.8 (ArC), 132.3 (ArC), 134.6 (Csp^2), 139.8 (ArC), 142.6 (ArC), 163.3 (Csp^2), 172.2 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{13}IN_2OS$ [M + H] 420.9866; found 420.9876.

(*E*)-*N*-{5-[Bromo(4-methoxyphenyl)methylene]-4,5-dihydrothiazol-2-yl}benzamide (15ab): Yield 0.27 g (68%); yellow solid; m.p. 195–196 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1687 (C=O), 3127 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, OCH_3), 4.44 (s, 2 H, CH_2), 6.89 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.45–7.49 (m, 4 H, ArH), 7.57 (tt, ^3J = 7.6, ^4J = 1.2 Hz, 1 H, ArH), 7.91–7.93 (m, 2 H, ArH), 10.03 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 61.3 (CH_2), 108.3 (Csp^2), 114.0 (ArC), 128.4 (ArC), 129.0 (ArC), 129.7 (ArC), 131.5 (ArC), 132.8 (ArC), 133.4 (ArC), 134.7 (Csp^2), 159.9 (ArC), 163.8 (Csp^2), 169.9 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{16}{}^{79}BrN_2O_2S$ [M + H] 403.0110; found 403.0106.

(*E*)-*N*-{5-[Bromo(4-chlorophenyl)methylene]-4,5-dihydrothiazol-2-yl}benzamide (15bb): Yield 0.18 g (44%); yellow solid; m.p. 234–235 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1628 (C=O), 3419 (NH) cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO): δ = 4.62 (s, 2 H, CH_2), 7.48 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.55–7.60 (m, 5 H, ArH), 8.02–8.05 (m, 2 H, ArH), 10.81 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 59.7 (CH_2), 105.0 (Csp^2), 128.4 (ArC), 128.6 (ArC), 128.9 (ArC), 130.0 (ArC), 130.6 (ArC), 132.5 (ArC), 133.5 (ArC), 134.3 (Csp^2), 137.7 (ArC), 161.2 (Csp^2), 169.1 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{12}{}^{79}Br^{35}ClN_2OS$ [M + H] 405.9542; found 405.9543.

(*E*)-*N*-{5-[Bromo(phenyl)methylene]-4,5-dihydrothiazol-2-yl}-benzamide (15cb): Yield 0.25 g (67%); yellow solid; m.p. 190–191 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1688 (C=O), 3138 (NH) cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO): δ = 4.61 (s, 2 H, CH_2), 7.40 (tt, ^3J = 7.2, ^4J = 1.2 Hz, 1 H, ArH), 7.45–7.54 (m, 6 H, ArH), 7.57 (t, ^3J = 7.2 Hz, 1 H, ArH), 8.03–8.05 (m, 2 H, ArH), 10.87 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 54.9 (CH_2), 106.7 (CBr), 128.1 (ArC), 128.3 (ArC), 128.7 (ArC), 128.8 (ArC), 129.1 (ArC), 132.4 (ArC), 134.4 (Csp^2), 137.1 (ArC), 138.8 (ArC), 167.9 (Csp^2), 174.2 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{13}{}^{79}BrN_2OS$ [M + H] 371.9932; found 371.9935.

(*E*)-*N*-[5-(Iodomethylene)-4,5-dihydrothiazol-2-yl]benzamide (15da): Yield 0. 07 g (20%); white solid; m.p. 195–196 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1631 (C=O), 3421 (NH) cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO): δ = 4.30 (d, ^4J = 2.8 Hz, 2 H, CH_2), 6.57 (t, ^4J = 2.8 Hz, 1 H, CH), 7.48 (t, ^3J = 7.2 Hz, 2 H, ArH), 7.57 (tt, ^3J = 7.2, ^4J = 1.2 Hz, 1 H, ArH), 8.05–8.08 (m, 2 H, ArH), 10.54 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 56.6 (CH_2), 65.9 (CH), 128.3 (ArC), 128.7 (ArC), 132.3 (ArC), 134.8 (Csp^2), 143.3 (ArC), 167.4 (Csp^2), 172.0 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{11}H_9IN_2OS$ [M + H] 344.9553; found 344.9544.

2-Iodo-1-(4-methoxyphenyl)prop-2-en-1-one (11aa): Yield 0.17 g (60%); yellowish oil. IR (KBr): $\tilde{\nu}_{max}$ = 1653 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.91 (s, 3 H, OCH_3), 6.70 (d, $^2J_{H,H}$ = 2.4 Hz, 1 H, =CH), 6.77 (d, $^2J_{H,H}$ = 2.4 Hz, 1 H, =CH), 6.93 (d, $^3J_{H,H}$ = 9.2 Hz, 2 H, ArH), 7.90 (d, $^3J_{H,H}$ = 9.2 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.57 (OCH_3), 106.76 (=C-I), 113.91 (ArC), 126.15 (=CH_2), 132.57 (ArC), 135.82 (ArC), 163.91 (ArC), 190.63 (C=O) ppm. HRMS (ES): *m*/*z* calcd. for $C_{10}H_9INaO_2$ $[M + Na]^+$ 310.9539; found 310.9537.

(*E*)-2,3-Diiodo-3-(4-methoxyphenyl)allyl Acetate (20aa): Yield 0.12 g (27%); yellowish wax. IR (KBr): $\tilde{\nu}_{max}$ = 1726 (CO) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.17 (s, 3 H, CH_3), 3.82 (s, 3 H, OCH_3), 5.06 (s, 2 H, OCH_2), 6.87 (d, ^3J = 8.8 Hz, 1 H, ArH), 7.19 (d, ^3J = 8.3 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9 (CH_3), 55.3 (OCH_3), 76.5 (OCH_2), 96.7 (Csp_2-I), 99.6 (Csp_2-I), 113.7 (ArC), 129.6 (ArC), 139.7 (ArC), 159.5 (ArC), 170.1 (C=O) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{12}H_{13}I_2O_3$ [M + H] 458.8954; found 458.8966.

General Procedures for the Phenyl Hypochloroselenoite Mediated Reactions

Method A: To a solution of the corresponding *N*-(3-substituted prop-2-ynyl)benzamide **1** (0.5 mmol) in anhydrous dichloromethane (5 mL), phenyl hypochloroselenoite (95.96 mg, 0.5 mmol) together with potassium *tert*-butanoate (0.5 mmol) were added. The reaction mixture was stirred at room temperature.

Method B: To a solution of the corresponding *tert*-butyl prop-2-ynylcarbamate **2** (0.5 mmol) in anhydrous acetonitrile (5 mL), phenyl hypochloroselenoite (95.96 mg, 0.5 mmol) together with potassium phosphate monohydrate (0.5 mmol) were added. The reaction mixture was stirred at room temperature.

Method C: To a cooled solution of urea **3** (0.5 mmol) in anhydrous acetonitrile (5 mL) or to a cooled solution of thiourea **4** (0.5 mmol) in anhydrous dichloromethane, phenyl hypochloroselenoite (95.96 mg, 0.5 mmol) was added at 0 °C. The resulting mixtures were warmed and stirred at room temperature.

Isolation Procedures for All Products: When completion of the reaction was observed by TLC, the solution was evaporated under reduced pressure and the residue was purified by flash column chromatography eluting with hexane/ethyl acetate mixtures.

6-(4-Methoxyphenyl)-2-phenyl-5-(phenylselanyl)-4*H*-1,3-oxazine (7ab): Yield 0.14 g (66%); yellowish oil. ^1H NMR (400 MHz, [D_6]-DMSO): δ = 2.87 (s, 3 H, OCH_3), 3.29 (s, 2 H, CH_2), 6.10 (d, ^3J = 8.8 Hz, 2 H, ArH), 6.34–6.43 (m, 3 H, ArH), 6.51–6.57 (m, 4 H, ArH), 6.62 (t, ^3J = 7.6 Hz, 2 H, ArH), 6.68 (d, ^3J = 8.8 Hz, 2 H, ArH), 6.98–7.00 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, [D_6]-DMSO): δ = 49.2 (CH_2), 55.3 (OCH_3), 98.7 (Csp^2), 113.6 (ArC), 125.3 (ArC), 126.9 (ArC), 127.3 (ArC), 128.4 (ArC), 128.6 (ArC), 129.7 (ArC), 130.1 (ArC), 130.8 (ArC), 131.1 (ArC), 131.4 (ArC), 150.2 (Csp^2), 151.8 (Csp^2), 160.2 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{20}NO_2Se$ [M + H] 422.0655; found 422.0647.

(*E*)-*N*-[3-Chloro-3-(4-methoxyphenyl)-2-(phenylselanyl)allyl]benzamide (16ab): Yield 29.7 mg (13%); yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, OCH_3), 4.56 (d, ^3J = 5.6 Hz,

2 H, CH_2), 6.34 (br. s, NH), 6.89 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.24–7.26 (m, 3 H, ArH), 7.37 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.40–7.43 (m, 4 H, ArH), 7.49 (t, ^3J = 7.2 Hz, 2 H, ArH), 7.64–7.66 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.8 (CH_2), 55.4 (OCH_3), 113.5 (ArC), 125.9 (Csp^2), 127.0 (ArC), 128.1 (ArC), 128.6 (ArC), 129.4 (ArC), 129.6 (ArC), 130.6 (ArC), 131.52 (ArC), 131.59 (ArC), 133.0 (ArC), 134.4 (ArC), 135.2 (Csp^2), 160.2 (ArC), 166.9 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{20}ClNNaO_2Se$ [M + Na] 480.0238; found 480.0230.

6-(4-Ethoxyphenyl)-2-phenyl-5-(phenylselanyl)-4*H*-1,3-oxazine (7bb): Yield 0.14 g (65%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (t, ^3J = 6.8 Hz, 3 H, OCH_2CH_3), 4.08 (q, ^3J = 6.8 Hz, 2 H, OCH_2CH_3), 4.30 (s, 2 H, CH_2), 6.94 (d, ^3J = 9.2 Hz, 2 H, ArH), 7.26–7.28 (m, 3 H, ArH), 7.41 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.45–7.49 (m, 3 H, ArH), 7.62 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.97–7.99 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9 (OCH_2CH_3), 50.0 (CH_2), 63.6 (OCH_2CH_3), 99.5 (Csp^2), 113.9 (ArC), 125.9 (ArC), 127.33 (ArC), 127.36 (ArC), 128.3 (ArC), 128.7 (ArC), 129.4 (ArC), 130.2 (ArC), 131.1 (ArC), 131.90 (ArC), 131.96 (ArC), 150.0 (Csp^2), 152.9 (Csp^2), 159.9 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{22}NO_2Se$ [M + H] 436.0811; found 436.0802.

(*E*)-*N*-[3-Chloro-3-(4-ethoxyphenyl)-2-(phenylselanyl)allyl]benzamide (16bb): Yield 28.3 mg (12%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (t, ^3J = 6.8 Hz, 3 H, OCH_2CH_3), 4.05 (q, ^3J = 6.8 Hz, 2 H, OCH_2CH_3), 4.55 (d, ^3J = 5.6 Hz, 2 H, CH_2), 6.33 (br. s, NH), 6.87 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.14–7.26 (m, 3 H, ArH), 7.36 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.38–7.43 (m, 4 H, ArH), 7.49 (tt, ^3J = 7.2, ^4J = 2.0 Hz, 2 H, ArH), 7.63–7.66 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9 (OCH_2CH_3), 43.8 (CH_2), 63.6 (OCH_2CH_3), 114.0 (ArC), 125.8 (ArC), 127.0 (ArC), 128.1 (ArC), 128.6 (ArC), 129.5 (ArC), 129.6 (Csp^2), 130.6 (ArC), 131.3 (ArC), 131.5 (ArC), 133.1 (ArC), 134.4 (Csp^2), 135.3 (ArC), 159.7 (ArC), 166.9 (NHCO) ppm. HRMS (ES): *m*/*z* calcd.for $C_{24}H_{22}ClNNaO_2Se$ $[M + Na]^+$ 494.0395; found 494.0406.

6-(3,4-Dimethoxyphenyl)-2-phenyl-5-(phenylselanyl)-4*H*-1,3-oxazine (7cb): Yield 0.15 g (68%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.85 (s, 3 H, OCH_3), 3.92 (s, 3 H, OCH_3), 4.31 (s, 2 H, CH_2), 6.92 (d, ^3J = 8.0 Hz, 1 H, ArH), 7.21 (d, ^3J = 2.0 Hz, 1 H, ArH), 7.24–7.29 (m, 4 H, ArH), 7.40 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.45–7.49 (m, 3 H, ArH), 7.97–7.99 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.0 (CH_2), 56.00 (OCH_3), 56.01 (OCH_3), 99.7 (Csp^2), 110.4 (ArC), 111.9 (ArC), 121.7 (ArC), 126.2 (ArC), 127.2 (ArC), 127.3 (ArC), 128.3 (ArC), 128.8 (ArC), 129.5 (ArC), 131.2 (ArC), 131.84 (ArC), 131.88 (ArC), 148.3 (Csp^2), 149.8 (ArC), 150.0 (ArC), 159.9 (Csp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{22}NO_3Se$ [M + H] 452.0761; found 452.0756.

(*E*)-*N*-[3-Chloro-3-(3,4-dimethoxyphenyl)-2-(phenylselanyl)allyl]benzamide (16cb): Yield 46.3 mg (19%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, OCH_3), 3.89 (s, 3 H, OCH_3), 4.56 (d, ^3J = 5.6 Hz, 2 H, CH_2), 6.37 (br. s, NH), 6.83 (d, ^3J = 8.4 Hz, 1 H, ArH), 6.93 (d, ^3J = 2.0 Hz, 1 H, ArH), 7.00 (dd, ^3J = 8.4, ^4J = 2.0 Hz, 1 H, ArH), 7.24–7.26 (m, 3 H, ArH), 7.38–7.43 (m, 4 H, ArH), 7.48 (tt, ^3J = 7.6, ^4J = 2.4 Hz, 1 H, ArH), 7.65–7.67 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.7 (CH_2), 56.00 (OCH_3), 56.03 (OCH_3), 110.4 (ArC), 112.1 (ArC), 122.0 (ArC), 126.1 (Csp^2), 127.0 (ArC), 128.1 (ArC), 128.6 (ArC), 129.5 (ArC), 129.6 (ArC), 131.6 (ArC), 133.0 (ArC), 134.3 (Csp^2), 139.4 (ArC), 148.4 (ArC), 148.8 (ArC), 166.9 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{22}Cl^{35}NNaO_3Se$ [M + Na] 510.0344; found 510.0343.

2-Phenyl-5-(phenylselanyl)-6-(3,4,5-trimethoxyphenyl)-4*H*-1,3-oxazine (7db): Yield 0.15 g (63%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 6 H, 2 × OCH_3), 3.90 (s, 3 H, OCH_3), 4.30 (s, 2 H, CH_2), 6.89 (s, 2 H, ArH), 7.26–7.29 (m, 3 H, ArH), 7.41 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.45–7.50 (m, 3 H, ArH), 7.96–7.99 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.0 (CH_2), 56.2 (2 × OCH_3), 61.0 (OCH_3), 100.6 (Csp^2), 106.1 (ArC), 127.2 (ArC), 127.5 (ArC), 128.4 (ArC), 128.6 (ArC), 128.8 (ArC), 129.5 (ArC), 131.2 (ArC), 131.7 (ArC), 132.0 (ArC), 139.1 (ArC), 149.4 (Csp^2), 152.81 (Csp^2), 152.85 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{23}NNaO_4Se$ [M + Na] 504.0686; found 504.0687.

2,6-Diphenyl-5-(phenylselanyl)-4*H*-1,3-oxazine (7fb): Yield 0.11 g (57%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.32 (s, 2 H, CH_2), 7.27–7.30 (m, 3 H, ArH), 7.39–7.50 (m, 8 H, ArH), 7.66–7.69 (m, 2 H, ArH), 7.97–8.00 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 49.8 (CH_2), 101.0 (Csp^2), 127.3 (ArC), 127.5 (ArC), 128.1 (ArC), 128.3 (ArC), 128.4 (ArC), 129.8 (ArC), 129.5 (ArC), 129.6 (ArC), 131.2 (ArC), 131.8 (ArC), 132.1 (ArC), 133.6 (ArC), 149.8 (Csp^2), 152.8 (Csp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{22}H_{17}NNaOSe$ [M + Na] 414.0373; found 414.0380.

(*E*)-2-Phenyl-5-(phenylselanylmethylene)-4,5-dihydrooxazole (12ib): Yield 40.9 mg (26%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.09 (d, ^3J = 0.8 Hz, 2 H, CH_2), 6.78 (s, 1 H, CH), 7.26–7.31 (m, 3 H, ArH), 7.28–7.45 (m, 3 H, ArH), 7.52–7.54 (m, 2 H, ArH), 7.94–7.96 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6 (CH_2), 125.4 (ArC), 126.3 (ArC), 127.4 (ArC), 128.2 (ArC), 128.8 (ArC), 129.2 (ArC), 129.3 (ArC), 130.3 (sp^2), 134.6 (ArC), 149.5 (Csp^2), 161.4 (Csp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{13}NNaOSe$ [M + Na] 338.0055; found 338.0061.

(*E*)-*N*-[3-Chloro-2-(phenylselanyl)allyl]benzamide (16′ib): Yield 35 mg (20%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.45 (dd, ^3J = 5.6, ^4J = 1.2 Hz, 2 H, CH_2), 6.35 (br. s, 1 H, NH), 6.58 (t, ^3J = 1.2 Hz, 1 H, CH), 7.26–7.29 (m, 3 H, ArH), 7.37 (t, ^3J = 8.0 Hz, 2 H, ArH), 7.45–7.51 (m, 3 H, ArH), 7.59–7.62 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 41.0 (CH_2), 122.7 (Csp^2), 127.0 (ArC), 128.2 (ArC), 128.4 (ArC), 128.5 (ArC), 129.7 (ArC), 130.8 (ArC), 131.6 (ArC), 133.0 (ArC), 134.0 (Csp^2), 167.1 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{14}Cl^{35}NNaOSe$ [M + Na] 373.9819; found 373.9826.

6-(4-Methoxyphenyl)-5-(phenylselanyl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (8ac): Yield 0.16 g (86%); yellow solid; m.p. 125–126 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1742 (C=O), 3420 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, OCH_3), 3.99 (d, ^3J = 1.2 Hz, 2 H, CH_2), 6.49 (br. s, 1 H, NH), 6.90 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.27–7.29 (m, 3 H, ArH), 7.41–7.43 (m, 2 H, ArH), 7.55 (t, ^3J = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.4 (CH_2), 55.3 (OCH_3), 97.3 (Csp^2), 113.2 (ArC), 125.0 (ArC), 127.7 (ArC), 128.3 (ArC), 129.5 (ArC), 130.4 (ArC), 131.9 (ArC), 150.7 (Csp^2), 151.4 (NHCO), 160.6 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{15}NNaO_3Se$ [M + Na] 384.0110; found 384.0111.

(*E*)-*tert*-Butyl 3-Chloro-3-(4-methoxyphenyl)-2-(phenylselanyl)allylcarbamate (17ac): Yield 20.3 mg (9%); white oil. IR (KBr): $\tilde{\nu}_{max}$ = 1714 (C=O), 3368 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45 (s, 9 H, 3 × CH_3), 3.84 (s, 3 H, OCH_3), 4.23 (d, ^3J = 4.8 Hz, 2 H, CH_2), 4.84 (br. s, 1 H NH), 6.89 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.26–7.29 (m, 3 H, ArH), 7.35 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.40–7.43 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.3 (3 × CH_3), 44.1 (CH_2), 55.2 (OCH_3), 79.4 [$C(CH_3)_3$], 113.3 (ArC), 127.0 (Csp^2), 127.8 (ArC), 129.3 (ArC), 129.5 (ArC), 130.4 (ArC), 131.5 (ArC), 133.0 (ArC), 134.2 (Csp^2), 155.2 (NHCO), 160.0 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{21}H_{24}{}^{35}ClNNaO_3Se$ [M + Na] 476.0500; found 476.0504.

6-(3,4-Dimethoxyphenyl)-5-(phenylselanyl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (8bc): Yield 82.1 mg (42%); yellow solid; m.p. 138–139 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1732 (C=O), 3239 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, OCH_3), 3.90 (s, 3 H, OCH_3), 3.99 (d, ^3J = 1.2 Hz, 2 H, CH_2), 6.35 (br. s, 1 H, NH), 6.86 (d, ^3J = 8.4 Hz, 1 H, ArH), 7.13 (d, ^4J = 2.0 Hz, 1 H, ArH), 7.18 (dd, ^3J = 8.4, ^4J = 2.0 Hz, 1 H, ArH), 7.27–7.29 (m, 3 H, ArH), 7.42–7.44 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.5 (CH_2), 55.8 (OCH_3), 55.9 (OCH_3), 97.4 (CSe), 110.1 (ArC), 111.6 (ArC), 122.2 (ArC), 125.1 (ArC), 127.8 (ArC), 128.3 (ArC), 129.5 (ArC), 132.0 (ArC), 148.2 (ArC), 150.2 (ArC), 150.4 (Csp^2), 151.3 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{17}NNaO_4Se$ [M + Na] 414.0216; found 414.0216.

(*E*)-*tert*-Butyl 3-Chloro-3-(3,4-dimethoxyphenyl)-2-(phenylselanyl)-allylcarbamate (17bc): Yield 43.5 mg (18%); yellowish brown solid; m.p. 76–77 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1696 (C=O), 3403 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.42 (s, 9 H, 3 × CH_3), 3.82 (s, 3 H, OCH_3), 3.89 (s, 3 H, OCH_3), 4.21 (d, ^3J = 4.8 Hz, 2 H, CH_2), 4.82 (br. s, 1 H, NH), 6.82 (d, ^3J = 8.4 Hz, 1 H, ArH), 6.87 (d, ^4J = 2.0 Hz, 1 H, ArH), 6.96 (dd, ^3J = 8.4, ^4J = 2.0 Hz, 1 H, ArH), 7.23–7.25 (m, 3 H, ArH), 7.37–7.40 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.4 (3 × CH_3), 44.2 (CH_2), 55.9 (2 × OCH_3), 79.5 [$C(CH_3)_3$], 110.3 (ArC), 112.0 (ArC), 121.9 (ArC), 127.2 (Csp^2), 127.8 (ArC), 129.3 (ArC), 131.5 (ArC), 131.7 (ArC), 133.0 (ArC), 134.0 (Csp^2), 148.3 (ArC), 149.6 (ArC), 155.3 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{22}H_{26}{}^{35}ClNNaO_4Se$ [M + Na] 506.0606; found 506.0601.

6-(Benzo[*d*][1,3]dioxol-5-yl)-5-(phenylselanyl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (8cc): Yield 0.11 g (56%); yellow solid; m.p. 155–156 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1748 (C=O), 3231 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.96 (d, ^3J = 0.8 Hz, 2 H, CH_2), 5.99 (s, 2 H, OCH_2O), 6.62 (br. s, 1 H, NH), 6.81 (d, ^3J = 8.4 Hz, 1 H, ArH), 7.07–7.09 (m, 2 H, ArH), 7.28–7.29 (m, 3 H, ArH), 7.41–7.43 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.3 (CH_2), 98.0 (Csp^2), 101.4 (OCH_2O), 107.7 (ArC), 109.1 (ArC), 123.5 (ArC), 126.3 (ArC), 127.9 (ArC), 128.0 (ArC), 129.5 (ArC), 132.2 (ArC), 147.2 (ArC), 148.7 (ArC), 150.0 (Csp^2), 151.4 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{13}NNaO_4Se$ [M + Na] 397.9903; found 397.9901.

(*E*)-*tert*-Butyl 3-(Benzo[*d*][1,3]dioxol-5-yl)-3-chloro-2-(phenylselanyl)allylcarbamate (17cc): Yield 60.7 mg (26%); yellow oil. IR (KBr): $\tilde{\nu}_{max}$ = 1710 (C=O), 3243 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.42 (s, 9 H, 3 × CH_3), 4.17 (d, ^3J = 5.2 Hz, 2 H, CH_2), 4.79 (br. s, 1 H, NH), 5.98 (s, 2 H, OCH_2O), 6.77 (d, ^3J = 8.4 Hz, 1 H, ArH), 6.85–6.86 (m, 2 H, ArH), 7.24–7.28 (m, 3 H, ArH), 7.39–7.41 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.3 (3 × CH_3), 43.9 (CH_2), 79.4 [$C(CH_3)_3$], 101.4 (OCH_2O), 107.8 (ArC), 109.3 (ArC), 123.3 (ArC), 127.7 (Csp^2), 127.9 (ArC), 129.2 (ArC), 129.3 (ArC), 132.8 (ArC), 133.2 (ArC), 134.3 (Csp^2), 147.3 (ArC), 148.1 (ArC), 151.2 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{21}H_{22}{}^{35}ClNNaO_4Se$ [M + Na] 490.0293; found 490.0293.

5-(Phenylselanyl)-6-*p*-tolyl-3,4-dihydro-2*H*-1,3-oxazin-2-one (8dc): Yield 0.15 g (42%); yellow solid; m.p. 115–116 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1752 (C=O), 3246 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 3.99 (d, ^3J = 1.6 Hz, 2 H, CH_2), 6.44 (br. s, 1 H, NH), 7.20 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.28–7.30 (m, 3 H, ArH), 7.42–7.44 (m, 2 H, ArH), 7.49 (d, ^3J = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4 (CH_3), 46.4 (CH_2), 98.0 (Csp^2), 127.8 (ArC), 128.2 (ArC), 128.6 (ArC), 128.8 (ArC), 129.5 (ArC), 129.7 (ArC), 132.1 (ArC), 140.0 (ArC), 150.8 (Csp^2), 151.3 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{15}NNaO_2Se$ [M + Na] 368.0161; found 368.0158.

(*E*)-*tert*-Butyl 3-Chloro-2-(phenylselanyl)-3-*p*-tolylallylcarbamate (17dc): Yield 67.7 mg (31%); yellowish oil. IR (KBr): $\tilde{\nu}_{max}$ = 1715 (C=O), 3352 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 9 H, 3 × CH_3), 2.37 (s, 3 H, CH_3), 4.21 (d, ^3J = 4.8 Hz, 2 H, CH_2), 4.81 (br. s, 1 H NH), 7.17 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.26–7.28 (m, 5 H, ArH), 7.39–7.41 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3 (CH_3), 28.3 (3 × CH_3), 44.0 (CH_2), 79.4 [$C(CH_3)_3$], 127.3 (Csp^2), 127.8 (ArC), 128.76 (ArC), 128.78 (ArC), 129.3 (ArC), 129.4 (ArC), 133.0 (ArC), 134.3 (Csp^2), 136.3 (ArC), 139.1 (ArC), 155.2 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{21}H_{24}{}^{35}ClNNaO_2Se$ [M + Na] 460.0551; found 460.0549.

6-(4-Nitrophenyl)-5-(phenylselanyl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (8gc): Yield 18.8 mg (10%); yellow solid; m.p. 176–177 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1732 (C=O), 3252 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.05 (d, ^3J = 1.6 Hz, 2 H, CH_2), 6.11 (br. s, 1 H, NH), 7.31–7.33 (m, 3 H, ArH), 7.42–7.45 (m, 2 H, ArH), 7.81 (d, ^3J = 8.8 Hz, 2 H, ArH), 8.26 (d, ^3J = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.7 (CH_2), 102.0 (Csp^2), 123.2 (ArC), 127.1 (ArC), 128.5 (ArC), 129.8 (ArC), 129.9 (ArC), 132.6 (ArC), 138.5 (ArC), 148.0 (ArC), 148.2 (Csp^2), 150.3 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{12}N_2NaO_4Se$ [M + Na] 398.9855; found 398.9854.

(*E*)-*tert*-Butyl 3-Chloro-3-(4-nitrophenyl)-2-(phenylselanyl)allylcarbamate (17gc): Yield 58.5 mg (25%); yellow oil. IR (KBr): $\tilde{\nu}_{max}$ = 1714 (C=O), 3430 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 9 H, 3 × CH_3), 4.25 (d, ^3J = 5.6 Hz, 2 H, CH_2), 4.87 (br. s, 1 H NH), 7.23–7.26 (m, 3 H, ArH), 7.30–7.33 (m, 2 H, ArH), 7.51 (d, ^3J = 8.4 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.3 (3 × CH_3), 44.0 (CH_2), 79.7 [$C(CH_3)_3$], 123.4 (ArC), 123.5 (ArC), 128.1 (ArC), 129.1 (Csp^2), 129.5 (ArC), 130.1 (ArC), 131.2 (Csp^2), 132.9 (ArC), 145.3 (ArC), 147.5 (ArC), 155.3 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{20}H_{21}{}^{35}ClN_2NaO_4Se$ [M + Na] 491.0246; found 491.0253.

(*E*)-*tert*-Butyl 2-Chloro-3-(phenylselanyl)allylcarbamate (17′hc): Yield 0.13 g (75%); yellow oil. IR (KBr): $\tilde{\nu}_{max}$ = 1686 (C=O), 3301 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.41 (s, 9 H, 3 × CH_3), 4.09 (d, ^3J = 5.6 Hz, 2 H, CH_2), 4.80 (br. s, 1 H NH), 6.39 (br. s, 1 H Csp^2H), 7.28–7.30 (m, 3 H, ArH), 7.47–7.50 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.2 (3 × CH_3), 41.2 (CH_2), 79.5 [$C(CH_3)_3$], 120.8 (Csp^2Cl), 128.0 (ArC), 128.2 (ArC), 129.4 (ArC), 132.2 (Csp^2), 133.2 (ArC), 155.3 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{14}H_{18}{}^{35}ClNNaO_2Se$ [M + Na] 370.0081; found 370.0081.

***N*-[6-(4-Methoxyphenyl)-5-(phenylselanyl)-4*H*-1,3-oxazin-2-yl]-4-methylbenzenesulfonamide (9ab):** Yield 0.21 g (82%); white solid; m.p. 218–222 °C. IR (KBr): $\tilde{\nu}_{max}$ = 2997 (NH) cm^{-1}. ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 2.33 (s, 3 H, CH_3), 3.81 (s, 3 H, OCH_3), 3.86 (s, 2 H, CH_2), 7.01 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.25 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.30–7.38 (m, 3 H, ArH), 7.40–7.50 (m, 4 H, ArH), 7.63 (d, ^3J = 8.2 Hz, 2 H, ArH), 9.17 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 21.4 (CH_3), 44.4 (CH_2), 55.8 (OCH_3), 99.8 (SeC-sp^2), 113.9 (ArC), 123.8 (ArC), 126.6 (ArC), 128.1 (ArC), 128.4 (ArC), 129.6 (ArC), 130.3 (ArC), 130.9 (ArC), 132.2 (ArC), 140.9 (ArC), 142.4 (ArC), 148.7 (ArCC-sp^2), 153.1 (HNC-sp^2), 161.0 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{23}N_2O_4SSe$ [M + H] 515.0539; found 515.0536.

6-(4-Methoxyphenyl)-*N*-phenyl-5-(phenylselanyl)-4*H*-1,3-oxazin-2-amine (9bb): Yield 0.2 g (92%); white solid; m.p. 166–170 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3426 (NH) cm^{-1}. ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 3.80 (s, 3 H, OCH_3), 4.02 (s, 2 H, CH_2), 7.03 (s, 2 H, CH_2), 7.03 (d, ^3J = 8.6 Hz, 2 H, ArH), 7.25–7.50 (m, 8 H, ArH), 7.51–7.72 (m, 4 H, ArH), 11.87 (br. s, 1 H, NH) ppm. ^{13}C NMR

(100 MHz, [D$_6$]DMSO): δ = 44.3 (CH_2), 55.8 (OCH_3), 100.7 (SeC-sp^2), 114.1 (ArC), 123.3 (ArC), 124.4 (ArC), 127.3 (ArC), 128.0 (ArC), 129.9 (ArC), 130.3 (ArC), 131.0 (ArC), 132.0 (ArC), 134.5 (ArC), 148.1 (ArC*C*-sp^2), 154.0 (HNC-sp^2), 161.2 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{21}N_2O_2Se$ [M + H] 437.0764; found 437.0760.

***N*-[6-(3,4-Dimethoxyphenyl)-5-(phenylselanyl)-4*H*-1,3-oxazin-2-yl]-4-methylbenzenesulfonamide (9db):** Yield 0.2 g (73%); white solid; m.p. 153–154 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3285 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.32 (s, 3 H, CH_3), 3.75 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 3.86 (br. s, 2 H, CH_2), 7.03 (d, ^3J = 8.4 Hz, 1 H, ArH), 7.13 (dd, ^3J = 8.3, ^4J = 2.2 Hz, 1 H,ArH), 7.25 (d, ^3J = 8.3 Hz, 2 H, ArH), 7.31–7.39 (m, 4 H, ArH), 7.44–7.50 (m, 2 H, ArH), 7.65 (d, ^3J = 8.2 Hz, 2 H, ArH), 9.22 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 21.3 (CH_3), 44.3 (CH_2), 55.9 (OCH_3), 56.0 (OCH_3), 100.0 (SeC-sp^2), 111.3 (ArC), 112.5 (ArC), 122.7 (ArC), 123.9 (ArC), 126.6 (ArC), 128.3 (ArC), 128.4 (ArC), 129.5 (ArC), 130.3 (ArC), 132.3 (ArC), 141.0 (ArC), 142.4 (ArC), 148.5 (ArC), 148.6 (ArCC-sp^2), 150.7 (ArC), 153.6 (HNC-sp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{24}N_2NaO_5SSe$ [M + Na] 567.0464; found 567.0461.

4-Methyl-*N*-[5-(phenylselanyl)-6-(*p*-tolyl)-4*H*-1,3-oxazin-2-yl]benzenesulfonamide (9fb): Yield 0.2 g (80%); white solid; m.p. 224–226 °C. IR (KBr): $\tilde{\nu}_{max}$ = 2918(NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.33 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 3.85 (s, 2 H, CH_2), 7.21–7.29 (m, 4 H, ArH), 7.31–7.36 (m, 3 H, ArH), 7.36–7.40 (m, 2 H, ArH), 7.41–7.47 (m, 2 H, ArH), 7.62 (d, ^3J = 8.2 Hz, 2 H), 9.16 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]-DMSO): δ = 21.4 (2×CH_3), 44.3 (CH_2), 100.8 (SeC-sp^2), 126.6 (ArC), 127.9 (ArC), 128.5 (ArC), 128.8 (ArC), 129.0 (ArC), 129.1 (ArC), 129.5 (ArC), 130.3 (ArC), 132.5 (ArC), 140.5 (ArC), 140.9 (ArC), 142.4 (ArC), 148.6 (ArCC-sp^2), 153.1 (HNC-sp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{22}N_2NaO_3SSe$ [M + Na] 521.0409; found 521.0417.

4-Methyl-*N*-[6-phenyl-5-(phenylselanyl)-4*H*-1,3-oxazin-2-yl]benzenesulfonamide (9gb): Yield 0.15 g (63%); white solid; m.p. 201–204 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3002 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.33 (s, 3 H, CH_3), 3.88 (s, 2 H, CH_2), 7.23 (d, ^3J = 7.7 Hz, 2 H, ArH), 7.34 (br. s, 3 H, ArH), 7.48 (br. s, 7 H, ArH), 7.61 (d, ^3J = 7.8 Hz, 2 H, ArH), 9.17 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 21.4 (CH_3), 44.3 (CH_2), 101.4 (SeC-sp^2), 126.6 (ArC), 127.8 (ArC), 128.5 (ArC), 128.6 (ArC), 129.3 (ArC), 129.5 (ArC), 130.3 (ArC), 130.6 (ArC), 131.7 (ArC), 132.5 (ArC), 140.9 (ArC), 142.4 (ArC), 148.4 (ArC*C*-sp^2), 153.0 (HNC-sp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{20}N_2NaO_3SSe$ [M + Na] 507.0252; found 507.0258.

(*E*)-*N*-{[2-Chloro-3-(phenylselanyl)allyl]carbamoyl}-4-methylbenzenesulfonamide (18′ib): Yield 0.21 g (94%); off-white solid; m.p. 148–149 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1685 (C=O), 3301, 3317 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.38 (s, 3 H, CH_3), 3.94 (d, ^3J = 5.4 Hz, 2 H, CH_2), 6.61 (s, 1 H, CH), 6.70 (t, ^3J = 5.6 Hz, 1 H, NH), 7.27–7.35 (m, 3 H, ArH), 7.36–7.47 (m, 4 H, ArH), 7.77 (d, ^3J = 8.2 Hz, 2 H, ArH), 10.64 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 21.5 (CH_3), 40.6 (CH_2), 121.5 (SeC-sp^2), 127.7 (ArC), 128.4 (ArC), 129.1 (ArC), 129.9 (ArC), 130.1 (ArC), 132.4 (ArC), 133.0 (ClC-sp^2), 137.7 (ArC), 144.1 (ArC), 151.7 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{17}ClN_2NaO_3SSe$ [M + Na] 466.9703, found 466.9704.

(*E*)-*N*-Phenyl-5-[(phenylselanyl)methylene]-4,5-dihydrooxazol-2-amine (14jb): Yield 44.6 mg (27%); white solid; m.p. 160–165 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3436 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 4.59 (d, ^4J = 2.2 Hz, 2 H, CH_2), 6.66 (s, 1 H, CH), 7.25–7.38 (m, 4 H, ArH), 7.43–7.55 (m, 6 H, ArH), 11.53 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 49.0 (CH_2), 90.7 (SeC-sp^2), 123.2 (ArC), 126.9 (ArC), 127.4 (ArC), 129.9 (ArC), 130.4 (2×ArC), 130.5 (ArC), 135.1 (ArC), 154.5 (H_2C*C*-sp^2), 158.5 (HNC-sp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{15}N_2OSe$ [M + H] 331.0345; found 331.0342.

(*E*)-*N*-Benzyl-5-[(phenylselanyl)methylene]-4,5-dihydrooxazol-2-amine (14kb): Yield 68.8 mg (40%); white solid; m.p. 171–176 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3436(NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 4.60 (s, 2 H, CH_2), 4.66 (br. s, 2 H, $HNCH_2$), 6.63 (s, 1 H, CH), 7.25–7.44 (m, 6 H, ArH), 7.45–7.60 (m, 4 H, ArH), 11.16 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 45.7 ($HNCH_2$), 47.8 (CH_2), 91.1 (SeC-sp^2), 127.5 (ArC), 128.3 (2×ArC), 129.0 (ArC), 130.0 (ArC), 130.4 (ArC), 130.6 (ArC), 136.4 (ArC), 153.9 (H_2CC-sp^2), 160.2 (HNC-sp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{17}N_2OSe$ [M + H]$^+$ 345.0501; found 345.0501.

***N*-[6-(4-Methoxyphenyl)-5-(phenylselanyl)-4*H*-1,3-thiazin-2-yl]benzamide (10ab):** Yield 0.18 g (73%); yellow oil. IR (KBr): $\tilde{\nu}_{max}$ = 1681 (C=O), 3196 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, OCH_3), 4.10 (s, 2 H, CH_2), 6.94 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.31–7.32 (m, 3 H, ArH), 7.39–7.41 (m, 3 H, ArH), 7.43–7.47 (m, 3 H, ArH), 7.49 (tt, ^3J = 7.2, ^4J = 1.2 Hz, 1 H, ArH), 7.15–7.17 (m, 2 H, ArH), 10.84 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 49.8 (CH_2), 55.3 (OCH_3), 113.8 (ArC), 116.0 (Csp^2), 128.1 (2×ArC), 128.4 (ArC), 129.0 (ArC), 129.2 (ArC), 129.6 (ArC), 130.9 (ArC), 132.1 (ArC), 133.2 (ArC), 134.2 (Csp^2), 136.0 (ArC), 160.4 (ArC), 168.4 (Csp^2), 176.0 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{21}N_2O_2SSe$ [M + H] 481.0484; found 481.0485.

***N*-[6-(4-Chlorophenyl)-5-(phenylselanyl)-4*H*-1,3-thiazin-2-yl]benzamide (10bb):** Yield 50.8 mg (21%); white solid; m.p. 59–60 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1678 (C=O), 3173 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.13 (s, 2 H, CH_2), 7.33–7.34 (m, 3 H, ArH), 7.40 (br. s, 4 H, ArH), 7.42–7.47 (m, 4 H, ArH), 7.51 (tt, ^3J = 7.6, ^4J = 1.2 Hz, 1 H, ArH), 8.13–8.15 (m, 2 H, ArH), 10.73 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.0 (CH_2), 118.0 (Csp^2), 128.2 (ArC), 128.4 (ArC), 128.5 (ArC), 128.8 (ArC), 129.2 (ArC), 129.8 (ArC), 130.9 (ArC), 132.3 (ArC), 133.0 (ArC), 133.4 (ArC), 134.7 (Csp^2), 135.6 (ArC), 135.8 (ArC), 167.6 (Csp^2), 175.8 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{17}{}^{35}ClN_2OSSe$ [M + H] 484.9986; found 484.9988.

***N*-[6-Phenyl-5-(phenylselanyl)-4*H*-1,3-thiazin-2-yl]benzamide (10cb):** Yield 0.08 g (36%); yellow solid; m.p. 61–62 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1681 (C=O), 3193 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.13 (s, 2 H, CH_2), 7.30–7.34 (m, 3 H, ArH), 7.40–7.52 (m, 10 H, ArH), 8.14–8.16 (m, 2 H, ArH), 10.86 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 49.8 (CH_2), 117.1 (Csp^2), 128.1 (ArC), 128.2 (ArC), 128.5 (ArC), 128.8 (ArC), 129.2 (ArC), 129.5 (2×ArC), 129.7 (ArC), 132.1 (ArC), 133.3 (ArC), 134.2 (Csp^2), 135.9 (ArC), 136.3 (ArC), 168.1 (Csp^2), 175.9 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{18}N_2OSSe$ [M + H] 451.0378; found 451.0388.

(*E*)-*N*-[5-(Phenylselanylmethylene)-4,5-dihydrothiazol-2-yl]benzamide (15db): Yield 74.8 mg (40%); yellow solid; m.p. 160–161 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1634 (C=O), 3410 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.45 (d, ^4J = 2.8 Hz, 2 H, CH_2), 6.82 (t, ^4J = 2.8 Hz, 1 H, CH), 7.26–7.30 (m, 1 H, ArH), 7.32–7.36 (m, 2 H, ArH), 7.45–7.50 (m, 4 H, ArH), 7.57 (tt, ^3J = 7.6, ^4J = 1.2 Hz, 1 H, ArH), 8.07–8.10 (m, 2 H, ArH), 10.43 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 51.9 (CH_2), 105.3 (Csp^{2}H), 127.0 (ArC), 128.3 (ArC), 128.7 (ArC), 129.5 (ArC), 130.4 (ArC), 130.5 (ArC), 132.2 (ArC), 135.0 (Csp^2), 141.2 (ArC), 168.2 (Csp^2),

172.3 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{14}N_2OSSe$ [M + H] 375.0065; found 375.0072.

(*E*)-3-Chloro-3-(4-methoxyphenyl)-2-(phenylselanyl)allyl Tosylcarbamate (19ab): Yield 0.22 g (79%); colorless oil. IR (KBr): $\tilde{\nu}_{max}$ = 1697 (C=O), 3345 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3 H, CH_3), 3.84 (s, 3 H, OCH_3),4.94 (s, 2 H, OCH_2), 6.90 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.18–7.23 (m, 3 H, ArH), 7.33–7.36 (m, 6 H, ArH), 7.96 (d, ^3J = 8.4 Hz, 2 H, ArH), 8.25 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5 (CH_3), 55.2 (OCH_3), 66.7 (OCH_2), 113.4 (ArC), 122.6 (ArC or C-sp^2), 126.3 (ArC or C-sp^2), 128.1 (ArC or C-sp^2), 128.3 (ArC or C-sp^2), 129.2 (ArC or C-sp^2), 129.5 (ArC or C-sp^2), 130.3 (ArC or C-sp^2), 130.7 (ArC or C-sp^2), 133.7 (ArC or C-sp^2), 135.4 (ArC or C-sp^2), 135.9 (ArC or C-sp^2), 144.9 (ArC or C-sp^2), 149.8 (ArC), 160.2 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{22}{}^{35}ClNNaO_5SSe$ [M + Na] 573.9970; found 573.9973.

(*E*)-3-Chloro-3-(4-methoxyphenyl)-2-(phenylselanyl)allyl Acetate (20ab): Yield 0.15 g (78%); colorless oil. IR (KBr): $\tilde{\nu}_{max}$ = 1712 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.02 (s, 3 H, CH_3), 3.85 (s, 3 H, OCH_3), 5.01 (s, 2 H, OCH_2), 6.92 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.28–7.30 (m, 3 H, ArH), 7.43 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.47 (dd, ^3J = 7.4, ^4J = 2.0 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.7 (CH_3), 55.3 (OCH_3), 65.1 (OCH_2), 113.5 (ArC), 123.9 (ArC or C-sp^2), 128.1 (ArC or C-sp^2), 129.2 (ArC or C-sp^2), 130.5 (ArC or C-sp^2), 131.2 (ArC or C-sp^2), 133.7 (ArC or C-sp^2), 135.6 (ArC or C-sp^2), 160.2 (ArC), 170.4 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{17}{}^{35}ClNaO_3Se$ [M + Na] 418.9922; found 418.9917.

General Procedures for Oxocarbenium Ion Mediated Reactions

Method A: To a mixture of **1**, **3**, **5** or **6** (0.5 mmol) and 1-methoxyisochromane (90.2 mg, 0.55 mmol) in anhydrous dichloromethane (5 mL), trimethylsilyl triflate (0.09 mL, 0.5 mmol) was added either at room temperature (for **1**, **5**, and **6**) or at 0 °C (for **3**). The resulting solution was stirred at the same temperature.

Method B: To a cooled solution of **2** or **4** (0.5 mmol) and 1-methoxyisochromane (90.2 mg, 0.55 mmol) in either anhydrous dichloromethane (5 mL, for **2**) or anhydrous acetonitrile (5 mL, for **4**) boron trifluoride etherate (0.06 mL, 0.5 mmol) was added at 0 °C. The resulting solution was stirred at the same temperature.

Method C: To a cooled solution of **1** or **4** (0.5 mmol) and the corresponding dialkoxymethylarene (0.75 mmol) in anhydrous dichloromethane (5 mL), boron trifluoride etherate (0.5 mmol, for **1**) or trimethylsilyl triflate (0.5 mmol, for **4**) was added at –10 °C. The resulting solution was stirred at the same temperature.

Isolation Procedures for All Products: When completion of the reaction was observed by TLC, the reaction was quenched with aqueous sodium hydrogen carbonate solution. The organic layer was separated, washed with water (2 × 20 mL), and dried with anhydrous Na_2SO_4. After the evaporation of solvent under reduced pressure, the residue was purified by flash column chromatography eluting with hexane/ethyl acetate mixtures.

5-(Isochroman-1-yl)-6-(4-methoxyphenyl)-2-phenyl-4*H*-1,3-oxazine (7ac): Yield 0.16 g (78%); yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.63 (d, ^3J = 16.4 Hz, 1 H, CH_2), 3.09–3.17 (m, 1 H, CH_2), 3.76–3.83 (m, 1 H, CH_2), 3.84 (d, ^2J = 18.8 Hz, 1 H, CH_2), 3.85 (s, 3 H, OCH_3), 4.20 (d, ^2J = 18.8 Hz, 1 H, CH_2), 4.21–4.26 (m, 1 H, CH_2), 5.62 (s, 1 H, CH), 7.00 (d, ^3J = 9.2 Hz, 2 H, ArH), 7.10–7.15 (m, 2 H, ArH), 7.17–7.19 (m, 2 H, ArH), 7.40 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.46 (tt, ^3J = 7.2, ^4J = 2.8 Hz, 1 H, ArH), 7.64 (d, ^3J = 8.8 Hz, 2 H, ArH), 8.00–8.03 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.8 (CH_2), 42.7 (CH_2), 55.4 (OCH_3), 64.9 (CH_2), 75.2 (CH), 109.4 (Csp^2), 114.0 (ArC), 125.2 (ArC), 126.6 (ArC), 127.0 (ArC), 127.3 (ArC), 128.3 (ArC), 129.0 (ArC), 130.0 (ArC), 131.0 (ArC), 131.9 (ArC), 134.6 (ArC), 135.1 (ArC), 147.4 (Csp^2), 153.7 (Csp^2), 160.4 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{25}NNaO_4$ [M + Na] 438.1676; found 438.1674.

5-[Methoxy(4-methoxyphenyl)methyl]-6-(4-methoxyphenyl)-2-phenyl-4*H*-1,3-oxazine (7ad): Yield 0.11 g (51%); yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.32 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 3.98 (d, ^2J = 19.2 Hz, 1 H, CH_2), 4.22 (d, ^2J = 19.2 Hz, 1 H, CH_2), 5.10 (s, 1 H, CH), 6.89 (d, ^3J = 8.8 Hz, 2 H, ArH), 6.98 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.29 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.38 (t, ^3J = 7.2 Hz, 2 H, ArH), 7.44 (t, ^3J = 7.2 Hz, 1 H, ArH), 7.48 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.95–7.98 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.0 (CH_2), 55.4 (OCH_3), 55.4 (OCH_3), 56.3 (OCH_3), 79.3 (CH), 108.7 (Csp^2), 113.9 (ArC), 114.0 (ArC), 125.3 (ArC), 127.3 (ArC), 127.6 (ArC), 128.3 (ArC), 130.1 (ArC), 131.0 (ArC), 131.5 (ArC), 132.1 (ArC), 147.6 (Csp^2), 153.5 (NCO), 159.1 (ArC), 160.3 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{26}NO_4$ [M + H] 416.1856; found 416.1862.

(*E*)-*N*-[2-(4-Methoxybenzoyl)-3-(4-methoxyphenyl)allyl]benzamide (23ad): Yield 22 mg (10%); yellowish oil. IR (KBr): $\tilde{\nu}_{max}$ = 3334 (NH), 1639 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 6 H, OCH_3), 3.87 (s, 3 H, OCH_3), 4.72 (d, ^3J = 5.6 Hz, 2 H, CH_2), 6.95 (d, ^3J = 8.8 Hz, 2 H, ArH), 6.97 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.16 (t, ^3J = 5.6 Hz, 1 H, NH), 7.26 (s, 1 H, CH), 7.38 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.46 (t, ^3J = 7.6 Hz, 1 H, ArH), 7.59 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.74–7.77 (m, 2 H, ArH), 7.80 (d, ^3J = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.2 (CH_2), 55.4 (OCH_3), 55.6 (OCH_3), 113.7 (ArC), 114.4 (ArC), 126.9 (ArC), 127.1 (ArC), 128.6 (ArC), 130.6 (ArC), 131.5 (ArC), 131.7 (ArC), 132.1 (ArC), 134.5 (ArC), 134.6 (Csp^2), 143.7 (Csp^2), 160.6 (ArC), 163.1 (ArC), 167.3 (NHCO), 198.7 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{23}NNaO_4$ [M + Na] 424.1519; found 424.1518.

(*Z*)-*N*-[2-(4-Methoxybenzoyl)-3-(4-methoxyphenyl)allyl]benzamide (24ad): Yield 23 mg (11%); yellowish oil. IR (KBr): $\tilde{\nu}_{max}$ = 3326 (NH), 1652 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.69 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 4.41 (d.d, ^3J = 5.6, ^4J = 0.8 Hz, 2 H, CH_2), 6.63 (d, ^3J = 8.8 Hz, 2 H, ArH), 6.75–6.79 (m, 3 H, ArH, NH), 6.94 (s, 1 H, CH), 7.08 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.39 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.47 (t, ^3J = 7.6 Hz, 1 H, ArH), 7.71–7.73 (m, 2 H, ArH), 7.87 (d, ^3J = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.5 (CH_2), 55.2 (OCH_3), 55.5 (OCH_3), 113.8 (ArC), 114.0 (ArC), 127.0 (ArC), 127.6 (ArC), 128.6 (ArC), 128.9 (ArC), 130.5 (ArC), 131.6 (ArC), 132.0 (ArC), 132.2 (ArC), 134.3 (ArC or Csp^2), 134.4 (ArC or Csp^2), 159.5 (ArC), 164.1 (ArC), 167.6 (NHCO), 199.2 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{23}NNaO_4$ [M + Na] 424.1519; found 424.1518.

5-[(4-Bromophenyl)(ethoxy)methyl]-6-(4-methoxyphenyl)-2-phenyl-4*H*-1,3-oxazine (7ae): Yield 0.13 g (54%); yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, ^3J = 7.2 Hz, 3 H, OCH_2CH_3), 3.32–3.40 (m, 1 H, OCH_2CH_3), 3.56–3.64 (m, 1 H, OCH_2CH_3), 3.86 (s, 3 H, OCH_3), 3.92 (d, ^2J = 19.2 Hz, 1 H, CH_2), 4.21 (d, ^2J = 19.2 Hz, 1 H, CH_2), 5.21 (s, 1 H, CH), 6.99 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.27 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.38 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.43–7.48 (m, 5 H, ArH), 7.95–7.97 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.4 (OCH_2CH_3), 42.0 (CH_2), 55.4 (OCH_3), 64.0 (OCH_2CH_3), 77.2 (CH), 108.6 (Csp^2), 114.1 (ArC), 121.4 (ArC), 125.2 (ArC), 127.3 (ArC), 128.1 (ArC), 128.3 (ArC), 130.1 (ArC), 131.0 (ArC), 131.6 (ArC), 132.0 (ArC), 139.0 (ArC),

147.7 (Csp^2), 153.4 (NCO), 160.4 (ArC) ppm. HRMS (ESI): *m/z* calcd. for $C_{26}H_{25}{}^{79}BrNO_3$ [M + H] 478.1018; found 478.1015.

(*E*)-*N*-[3-(4-Bromophenyl)-2-(4-methoxybenzoyl)allyl]benzamide (23ae): Yield 33.7 mg (15%); yellowish oil. IR (KBr): $\tilde{\nu}_{max}$ = 3332 (NH), 1645 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3 H, OCH_3), 4.64 (d, ^3J = 5.6 Hz, 2 H, CH_2), 6.95 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.11 (t, ^3J = 5.6 Hz, 1 H, NH), 7.16 (s, 1 H, CH), 7.37 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.45 (t, ^3J = 7.2 Hz, 1 H, ArH), 7.50 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.57 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.71–7.73 (m, 2 H, ArH), 7.82 (d, ^3J = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.1 (CH_2), 55.5 (OCH_3), 113.8 (ArC), 123.5 (ArC), 126.9 (ArC), 128.5 (ArC), 130.1 (ArC), 131.1 (ArC), 131.5 (ArC), 132.0 (ArC), 132.1 (ArC), 133.3 (ArC), 134.2 (ArC), 137.5 (Csp^2), 141.1 (Csp^2), 163.4 (ArC), 167.3 (NHCO), 198.0 (CO) ppm. HRMS (ESI): *m/z* calcd. for $C_{24}H_{20}Br^{79}NNaO_3$ [M + Na] 472.0519; found 472.0517.

(*Z*)-*N*-[3-(4-Bromophenyl)-2-(4-methoxybenzoyl)allyl]benzamide (24ae): Yield 11.2 mg (5%); yellowish oil. IR (KBr): $\tilde{\nu}_{max}$ = 3325 (NH), 1647 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3 H, OCH_3), 4.43 (dd, ^3J = 5.8, ^4J = 1.4 Hz, 2 H, CH_2), 6.71 (t, ^3J = 5.2 Hz, 1 H, NH), 6.77 (d, ^3J = 8.8 Hz, 2 H, ArH), 6.90 (s, 1 H, CH), 7.01 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.23 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.40 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.48 (t, ^3J = 7.2 Hz, 1 H, ArH), 7.70–7.72 (m, 2 H, ArH), 7.85 (d, ^3J = 9.2 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.3 (CH_2), 55.6 (OCH_3), 114.2 (ArC), 122.3 (ArC), 127.0 (ArC), 128.6 (ArC), 128.7 (ArC), 130.4 (ArC), 130.5 (ArC), 131.5 (ArC), 131.7 (ArC), 132.0 (ArC), 134.0 (ArC or Csp^2), 134.2 (ArC or Csp^2), 137.6 (Csp^2), 164.4 (ArC), 167.7 (NHCO), 198.5 (CO) ppm. HRMS (ESI): *m/z* calcd. for $C_{24}H_{20}Br^{79}NNaO_3$ [M + Na] 472.0519; found 472.0514.

6-(4-Ethoxyphenyl)-5-(isochroman-1-yl)-2-phenyl-4*H*-1,3-oxazine (7bc): Yield 0.11 g (53%); yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.44 (t, ^3J = 7.2 Hz, 3 H, OCH_2CH_3), 2.63 (d, ^3J = 16.4 Hz, 1 H, CH_2), 3.09–3.17 (m, 1 H, CH_2), 3.76–3.82 (m, 1 H, CH_2), 3.82 (d, ^2J = 18.4 Hz, 1 H, CH_2), 4.08 (q, ^3J = 7.2 Hz, 2 H, OCH_2CH_3), 4.18 (d, ^2J = 19.2 Hz, 1 H, CH_2), 4.21–4.25 (m, 1 H, CH_2), 5.61 (s, 1 H, CH), 6.97 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.10–7.15 (m, 2 H, ArH), 7.16–7.19 (m, 2 H, ArH), 7.39 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.46 (tt, ^3J = 7.2, ^4J = 2.8 Hz, 1 H, ArH), 7.61 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.98–8.03 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9 (OCH_2CH_3), 28.8 (CH_2), 42.9 (CH_2), 63.6 (OCH_2CH_3), 64.9 (CH_2), 75.3 (CH), 109.3 (Csp^2), 114.5 (ArC), 125.1 (ArC), 125.3 (ArC), 126.7 (ArC), 127.0 (ArC), 127.3 (ArC), 128.3 (ArC), 129.0 (ArC), 130.0 (ArC), 130.9 (ArC), 132.2 (ArC), 134.7 (ArC), 135.3 (ArC), 148.6 (Csp^2), 153.4 (Csp^2), 169.8 (ArC) ppm. HRMS (ESI): *m/z* calcd. for $C_{27}H_{26}NO_3$ [M + Na] 412.1907; found 412.1914.

6-(3,4-Dimethoxyphenyl)-5-(isochroman-1-yl)-2-phenyl-4*H*-1,3-oxazine (7cc): Yield 0.15 g (70%); yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.62 (d, ^3J = 16.4 Hz, 1 H, CH_2), 3.08–3.17 (m, 1 H, CH_2), 3.76–3.82 (m, 1 H, CH_2), 3.83 (d, ^3J = 19.2 Hz, 1 H, CH_2), 3.92 (s, 6 H,2 × OCH_3), 4.17 (d, ^3J = 19.2 Hz, 1 H, CH_2), 4.21–4.26 (m, 1 H, CH_2), 5.62 (s, 1 H, CH), 6.94 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.08–7.14 (m, 2 H, ArH), 7.15–7.18 (m, 2 H, ArH), 7.23–7.28 (m, 2 H, ArH), 7.39 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.46 (t, ^3J = 7.2 Hz, 1 H, ArH), 7.99–8.01 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.8 (CH_2), 42.8 (CH_2), 56.04 (OCH_3), 56.07 (OCH_3), 64.9 (CH_2), 75.3 (CH), 109.4 (Csp^2), 110.9 (ArH), 111.7 (ArC), 125.2 (ArC), 125.4 (ArC), 126.6 (ArC), 127.0 (ArC), 127.3 (ArC), 128.3 (ArC), 129.0 (ArC), 130.9 (ArC), 132.1 (ArC), 134.6 (ArC), 135.1 (ArC), 148.7 (Csp^2), 148.9 (ArC), 150.0 (ArC), 153.4 (Csp^2) ppm. HRMS (ESI): *m/z* calcd. for $C_{27}H_{26}NO_4$ [M + H] 428.1856; found 428.1859.

5-[(4-Bromophenyl)(ethoxy)methyl]-6-(3,4-dimethoxyphenyl)-2-phenyl-4*H*-1,3-oxazine (7ce): Yield 0.12 g (49%); yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, ^3J = 6.8 Hz, 3 H, OCH_2CH_3), 3.34–3.41 (m, 1 H, OCH_2CH_3), 3.56–3.63 (m, 1 H, OCH_2CH_3), 3.87 (s, 3 H, OCH_3), 3.93 (s, 3 H, OCH_3), 3.94 (d, ^2J = 19.2 Hz, 1 H, CH_2), 4.22 (d, ^2J = 19.2 Hz, 1 H, CH_2), 5.23 (s, 1 H, CH), 6.93 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.03 (d, ^3J = 2.0 Hz, 1 H, ArH), 7.09 (d.d, ^3J = 8.8, ^3J = 2.0 Hz, 1 H, ArH), 7.26 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.39 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.43–7.48 (m, 3 H, ArH), 7.95–7.98 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.4 (OCH_2CH_3), 42.0 (CH_2), 56.0 (OCH_3), 56.1 (OCH_3), 64.1 (OCH_2CH_3), 77.3 (CH), 108.8 (Csp^2), 111.0 (ArC), 111.7 (ArC), 121.5 (ArC), 121.6 (ArC), 125.3 (ArC), 127.3 (ArC), 128.2 (ArC), 128.3 (ArC), 131.1 (ArC), 131.6 (ArC), 138.9 (ArC), 147.6 (Csp^2), 149.1 (ArC), 150.0 (ArC), 153.5 (NCO) ppm. HRMS (ESI): *m/z* calcd. for $C_{27}H_{27}{}^{79}BrNO_4$ [M + H] 508.1123; found 508.1129.

5-(Isochroman-1-yl)-2-phenyl-6-(3,4,5-trimethoxyphenyl)-4*H*-1,3-oxazine (7dc): Yield 0.25 g (54%); yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.63 (d, ^3J = 16.4 Hz, 1 H, CH_2), 3.10–3.18 (m, 1 H, CH_2), 3.78–3.84 (m, 1 H, CH_2), 3.83 (d, ^3J = 19.2 Hz, 1 H, CH_2), 3.90 (s, 6 H, 2 × OCH_3), 3.90 (s, 3 H, OCH_3), 4.16 (d, ^3J = 19.2 Hz, 1 H, CH_2), 4.23–4.28 (m, 1 H, CH_2), 5.64 (s, 1 H, CH), 6.94 (s, 2 H, ArH), 7.06–7.14 (m, 2 H, ArH), 7.15–7.18 (m, 2 H, ArH), 7.40 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.46 (tt, ^3J = 7.2, ^4J = 2.8 Hz, 1 H, ArH), 7.97–8.00 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.8 (CH_2), 42.9 (CH_2), 56.3 (2 × OCH_3), 61.0 (OCH_3), 64.9 (CH_2), 75.3 (CH), 105.9 (ArC), 109.8 (Csp^2), 125.1 (ArC), 126.7 (ArC), 127.0 (ArC), 127.3 (ArC), 128.1 (ArC), 128.3 (ArC), 129.1 (ArC), 131.0 (ArC), 132.0 (ArC), 134.5 (ArC), 134.9 (ArC), 139.0 (ArC), 148.9 (Csp^2), 153.25 (Csp^2), 159.29 (ArC) ppm. HRMS (ESI): *m/z* calcd. for $C_{28}H_{27}NNaO_5$ [M + Na] 480.1781; found 480.1779.

5-(Isochroman-1-yl)-2-phenyl-6-*p*-tolyl-4*H*-1,3-oxazine (7ec): Yield 0.15 g (81%); yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3 H, CH_3), 2.63 (d, ^3J = 16.4 Hz, 1 H, CH_2), 3.09–3.17 (m, 1 H, CH_2), 3.75–3.81 (m, 1 H, CH_2), 3.83 (d, ^3J = 18.8 Hz, 1 H, CH_2), 4.21 (d, ^3J = 18.8 Hz, 1 H, CH_2), 4.21–4.25 (m, 1 H, CH_2), 5.61 (s, 1 H, CH), 7.10–7.15 (m, 2 H, ArH), 7.16–7.19 (m, 2 H, ArH), 7.28 (d, ^3J = 7.6 Hz, 2 H, ArH), 7.40 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.46 (tt, ^3J = 7.2, ^4J = 2.4 Hz, 1 H, ArH), 7.58 (d, ^3J = 8.0 Hz, 2 H, ArH), 8.00–8.02 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5 (CH_3), 28.8 (CH_2), 42.7 (CH_2), 64.9 (CH_2), 75.2 (CH), 109.9 (Csp^2), 125.2 (ArC), 126.7 (ArC), 127.0 (ArC), 127.4 (ArC), 128.3 (ArC), 128.5 (ArC), 129.0 (ArC), 129.3 (ArC), 129.9 (ArC), 131.1 (ArC), 131.8 (ArC), 134.7 (ArC), 135.1 (ArC), 139.5 (ArC), 148.6 (Csp^2), 153.9 (ArC) ppm. HRMS (ESI): *m/z* calcd. for $C_{26}H_{24}NO_2$ [M + Na] 382.1802; found 382.1796.

5-[Methoxy(4-methoxyphenyl)methyl]-2-phenyl-6-*p*-tolyl-4*H*-1,3-oxazine (7ed): Yield 93.7 mg (47%); yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3 H, CH_3), 3.33 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 3.99 (d, ^2J = 19.2 Hz, 1 H, CH_2), 4.24 (d, ^2J = 19.2 Hz, 1 H, CH_2), 5.11 (s, 1 H, CH), 6.89 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.26–7.30 (m, 4 H, ArH), 7.38 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.42–7.46 (m, 3 H, ArH), 7.96–7.98 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5 (CH_3), 41.9 (CH_2), 55.4 (OCH_3), 56.3 (OCH_3), 79.2 (CH), 109.1 (Csp^2), 113.9 (ArC), 127.3 (ArC), 127.5 (ArC), 128.3 (ArC), 128.7 (ArC), 129.3 (ArC), 130.1 (ArC), 130.9 (ArC), 131.4 (ArC), 132.1 (ArC), 139.4 (ArC), 147.8 (Csp^2), 153.5

(NCO), 159.1 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{26}NO_3$ [M + H] 400.1907; found 400.1914.

(*E*)-*N*-[3-(4-Methoxyphenyl)-2-(4-methylbenzoyl)allyl]benzamide (23ed): Yield 21.2 mg (11%); yellowish oil. IR (KBr): $\tilde{\nu}_{max}$ = 3342 (NH),1638 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, CH_3), 3.83 (s, 3 H, OCH_3), 4.74 (d, ^3J = 5.6 Hz, 2 H, CH_2), 6.97 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.13 (t, ^3J = 5.2 Hz, 1 H, NH), 7.27 (d, ^3J = 8.0 Hz, 2 H, ArH),7.31 (s, 1 H, CH), 7.40 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.47 (t, ^3J = 7.2 Hz, 1 H, ArH), 7.60 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.68 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.75–7.78 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7 (CH_3), 38.0 (CH_2), 55.5 (OCH_3), 114.4 (ArC), 126.9 (ArC), 127.1 (ArC), 128.6 (ArC), 129.2 (ArC), 129.8 (ArC), 131.5 (ArC), 131.9 (ArC), 134.6 (ArC or Csp^2), 134.6 (ArC or Csp^2), 135.5 (ArC), 143.0 (ArC), 144.9 (Csp^2), 160.8 (ArC), 167.3 (NHCO), 199.8 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{23}NNaO_3$ [M + Na] 408.1570; found 408.1574.

5-[(4-Bromophenyl)(ethoxy)methyl]-2-phenyl-6-*p*-tolyl-4*H*-1,3-oxazine (7ee): Yield 0.11 g (48%); yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, ^3J = 6.8 Hz, 3 H, OCH_2CH_3), 2.42 (s, 3 H, CH_3), 3.32–3.40 (m, 1 H, OCH_2CH_3), 3.92 (d, ^2J = 19.2 Hz, 1 H, CH_2), 4.21 (d, ^2J = 19.6 Hz, 1 H, CH_2), 5.21 (s, 1 H, CH), 7.26–7.29 (m, 4 H, ArH), 7.36–7.48 (m, 8 H, ArH), 7.95–7.97 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.4 (OCH_2CH_3), 21.5 (CH_3), 41.9 (CH_2), 64.0 (OCH_2CH_3), 77.1 (CH), 109.0 (Csp^2), 121.4 (ArC), 127.3 (ArC), 128.1 (ArC), 128.3 (ArC), 128.6 (ArC), 129.4 (ArC), 130.0 (ArC), 131.0 (ArC), 131.6 (ArC), 132.0 (ArC), 138.9 (ArC), 139.5 (ArC), 147.9 (Csp^2), 153.5 (NCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{25}{}^{79}BrNO_2$ [M + H] 462.1069; found 462.1070.

(*E*)-*N*-[3-(4-Bromophenyl)-2-(4-methylbenzoyl)allyl]benzamide (23ee): Yield 49.8 mg (22%); yellowish oil. IR (KBr): $\tilde{\nu}_{max}$ = 3341 (NH), 1645 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3 H, CH_3), 4.66 (dd, ^3J = 6.0, ^4J = 0.4 Hz, 2 H, CH_2), 7.10 (t, ^3J = 5.2 Hz, 1 H, NH), 7.22 (s, 1 H, CH), 7.27 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.38 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.46 (t, ^3J = 7.2 Hz, 1 H, ArH), 7.51 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.57 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.68 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.72–7.74 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7 (CH_3), 38.0 (CH_2), 123.7 (ArC), 127.0 (ArC), 128.6 (ArC), 129.3 (ArC), 129.9 (ArC), 131.2 (ArC), 131.6 (ArC), 132.1 (ArC), 133.3 (ArC), 134.3 (ArC), 135.1 (ArC), 137.6 (Csp^2), 142.5 (Csp^2), 143.5 (ArC), 167.4 (NHCO), 199.2 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{20}Br^{79}NNaO_2$ [M + Na] 456.0570; found 456.0577.

5-[Methoxy(phenyl)methyl]-2-phenyl-6-*p*-tolyl-4*H*-1,3-oxazine (7ef): Yield 0.09 g (50%); yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3 H, CH_3), 3.36 (s, 3 H, OCH_3), 3.97 (d, ^2J = 19.2 Hz, 1 H, CH_2), 4.25 (d, ^2J = 19.2 Hz, 1 H, CH_2), 5.17 (s, 1 H, CH), 7.27–7.30 (m, 3 H, ArH), 7.34–7.45 (m, 7 H, ArH), 7.47 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.96–7.99 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5 (CH_3), 41.9 (CH_2), 56.3 (OCH_3), 79.5 (CH), 109.0 (Csp^2), 126.3 (ArC), 127.3 (ArC), 127.6 (ArC), 128.3 (ArC), 128.5 (ArC), 128.7 (ArC), 129.4 (ArC), 130.1 (ArC), 130.9 (ArC), 132.1 (ArC), 139.4 (ArC), 139.4 (ArC), 148.0 (Csp^2), 153.4 (NCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{24}NO_2$ [M + H] 370.1807; found 370.1809.

(*E*)-*N*-[2-(4-Methylbenzoyl)-3-phenylallyl]benzamide (23ef): Yield 17.8 mg (10%); yellowish oil. IR (KBr): $\tilde{\nu}_{max}$ = 3254 (NH), 1645 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, CH_3), 4.72 (dd, ^3J = 6.0, ^4J = 0.4 Hz, 2 H, CH_2), 7.11 (t, ^3J = 5.2 Hz, 1 H, NH), 7.28 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.33 (s, 1 H, CH), 7.37–7.40 (m, 3 H, ArH), 7.43–7.48 (m, 2 H, ArH), 7.61 (d, ^3J = 7.2 Hz, 2 H, ArH), 7.71–7.75 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7 (CH_3), 38.0 (CH_2), 127.1 (ArC), 128.6 (ArC), 128.9 (ArC), 129.2 (ArC), 129.4 (ArC), 129.7 (ArC), 129.9 (ArC), 131.5 (ArC), 134.4 (ArC), 134.5 (ArC), 135.2 (ArC), 136.8 (Csp^2), 143.3 (ArC), 144.4 (ArC), 167.3 (NHCO), 199.5 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{21}NNaO_2$ [M + Na] 378.1465; found 378.1467.

5-(Isochroman-1-yl)-2,6-diphenyl-4*H*-1,3-oxazine (7fc): Yield 0.14 g (78%); yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.63 (d, ^2J = 16.4 Hz, 1 H, CH_2), 3.14 (ddd, ^2J = 17.3, ^3J = 11.7 Hz, ^2J = 6.0 Hz, 1 H, CH_2), 3.79 (td, $^{2,3}J$ = 11.6, ^3J = 3.2 Hz, 1 H, CH_2), 3.86 (d, ^2J = 19.2 Hz, 1 H, CH_2), 4.23 (d, ^2J = 19.2 Hz, 1 H, CH_2), 4.22–4.27 (m, 1 H, CH_2), 5.63 (s, 1 H, CH), 7.11–7.15 (m, 2 H, ArH), 7.17–7.20 (m, 2 H, ArH), 7.38–7.24 (m, 2 H, ArH), 7.44–7.51 (m, 4 H, ArH), 7.69–7.22 (m, 2 H, ArH), 8.00–8.02 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.8 (CH_2), 42.8 (CH_2), 64.9 (CH_2), 75.1 (CH), 110.2 (Csp^2), 125.2 (ArC), 126.6 (ArC), 127.0 (ArC), 127.3 (ArC), 128.2 (ArC), 128.6 (2×ArC), 129.0 (ArC), 129.4 (ArC), 130.9 (ArC), 132.0 (ArC), 132.8 (ArC), 134.6 (ArC), 135.1 (ArC), 148.6 (Csp^2), 153.4 (Csp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{22}NO_2$ [M + Na] 368.1645; found 368.1651.

5-[(4-Bromophenyl)(ethoxy)methyl]-2,6-diphenyl-4*H*-1,3-oxazine (7fe): Yield 0.12 g (54%); solid; m.p. 89–90 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.22 (t, ^3J = 7.2 Hz, 3 H, OCH_2CH_3), 3.32–3.39 (m, 1 H, OCH_2CH_3), 3.56–3.64 (m, 1 H, OCH_2CH_3), 3.93 (d, ^2J = 19.2 Hz, 1 H, CH_2), 4.22 (d, ^2J = 19.2 Hz, 1 H, CH_2), 5.20 (s, 1 H, CH), 7.26 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.38 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.43–7.48 (m, 6 H, ArH), 7.52–7.54 (m, 2 H, ArH), 7.94–7.97 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.4 (OCH_2CH_3), 41.9 (CH_2), 64.0 (OCH_2CH_3), 77.1 (CH), 109.4 (Csp^2), 121.5 (ArC), 127.3 (ArC), 128.1 (ArC), 128.3 (ArC), 128.7 (ArC), 128.8 (ArC), 129.5 (ArC), 131.1 (ArC), 131.5 (ArC), 131.9 (ArC), 132.8 (ArC), 138.9 (ArC), 147.8 (Csp^2), 153.4 (NCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{23}{}^{79}BrNO_2$ [M + H] 448.0912; found 448.0911.

(*E*)-*N*-[2-Benzoyl-3-(4-bromophenyl)allyl]benzamide (23fe): Yield 12.6 mg (6%); yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.67 (dd, ^3J = 6.0, ^4J = 0.8 Hz, 2 H, CH_2), 7.05 (t, ^3J = 5.6 Hz, 1 H, NH), 7.25 (s, 1 H, CH), 7.40 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.45–7.49 (m, 3 H, ArH), 7.53 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.56–7.60 (m, 3 H, ArH), 7.73–7.78 (m, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.9 (CH_2), 123.9 (ArC), 127.1 (ArC), 128.6 (ArC), 128.7 (ArC), 129.7 (ArC), 131.3 (ArC), 131.7 (ArC), 132.2 (ArC), 132.6 (ArC), 133.2 (ArC), 134.3 (ArC), 137.5 (ArC or Csp^2), 137.9 (ArC or Csp^2), 143.4 (Csp^2), 167.4 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{19}{}^{79}BrNO_2$ [M + H] 420.0599; found 420.0597.

5-[(4-Bromophenyl)(ethoxy)methyl]-6-(4-chlorophenyl)-2-phenyl-4*H*-1,3-oxazine (7ge): Yield 0.13 g (52%); yellowish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, ^3J = 6.8 Hz, 3 H, OCH_2CH_3), 3.32–3.39 (m, 1 H, OCH_2CH_3), 3.54–3.61 (m, 1 H, OCH_2CH_3), 3.92 (d, ^2J = 19.2 Hz, 1 H, CH_2), 4.22 (d, ^2J = 19.6 Hz, 1 H, CH_2), 5.14 (s, 1 H, CH), 7.24 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.39 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.44–7.49 (m, 7 H, ArH), 7.92–7.95 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.3 (OCH_2CH_3), 42.0 (CH_2), 64.1 (OCH_2CH_3), 77.1 (CH), 110.1 (Csp^2), 121.6 (ArC), 127.3 (ArC), 128.1 (ArC), 128.3 (ArC), 129.1 (ArC), 130.0 (ArC), 131.1 (ArC), 131.1 (ArC), 131.7 (ArC), 131.8 (ArC), 135.5 (ArC), 138.5 (ArC), 146.7 (Csp^2), 153.1 (NCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{22}{}^{79}Br^{35}ClNO_2$ [M + H] 482.0522; found 482.0523.

(*E*)-*N*-[3-(4-Bromophenyl)-2-(4-chlorobenzoyl)allyl]benzamide (23ge): Yield 27.2 mg (11%); yellowish oil. ^1H NMR (400 MHz,

$CDCl_3$): δ = 4.65 (d, ^3J = 5.2 Hz, 2 H, CH_2), 7.00 (t, ^3J = 4.8 Hz, 1 H, NH), 7.19 (s, 1 H, CH), 7.39 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.43–7.49 (m, 3 H, ArH), 7.52 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.59 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.71–7.73 (m, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.9 (CH_2), 124.1 (ArC), 127.0 (ArC), 128.7 (ArC), 128.9 (ArC), 131.1 (ArC), 131.3 (ArC), 131.7 (ArC), 132.2 (ArC), 133.0 (ArC), 134.2 (ArC), 136.1 (ArC), 137.7 (Csp^2), 139.1 (ArC), 143.1 (Csp^2), 167.5 (NHCO), 198.2 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{17}Br^{79}Cl^{35}NNaO_2$ [M + Na] 476.0023; found 476.0022.

5-(Isochroman-1-yl)-6-(4-nitrophenyl)-2-phenyl-4*H*-1,3-oxazine (7hc): Yield 28.8 mg (14%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.66 (d, ^3J = 16.4 Hz, 1 H, CH_2), 3.05–3.18 (m, 1 H, CH_2), 3.79 (td, $^{2,3}J$ = 11.4, ^3J = 3.2 Hz, 1 H, CH_2), 3.85 (d, ^3J = 19.6 Hz, 1 H, CH_2), 4.20 (d, ^3J = 19.2 Hz, 1 H, CH_2), 4.24–4.27 (m, 1 H, CH_2), 5.54 (s, 1 H, CH), 7.01–7.03 (m, 1 H, ArH), 7.14–7.21 (m, 3 H, ArH), 7.41 (t, ^3J = 7.2 Hz, 2 H, ArH), 7.48 (t, ^3J = 7.6 Hz, 1 H, ArH), 7.87 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.94–7.96 (m, 2 H, ArH), 8.33 (d, ^3J = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.7 (CH_2), 42.9 (CH_2), 64.9 (CH_2), 74.8 (CH), 113.2 (Csp^2), 123.9 (ArC), 124.9 (ArC), 126.8 (ArC), 127.3 (ArC), 127.3 (ArC), 128.4 (ArC), 129.3 (ArC), 129.5 (ArC), 131.3 (ArC), 131.6 (ArC), 134.3 (ArC), 134.6 (ArC), 139.0 (ArC), 146.5 (Csp^2), 148.2 (ArC), 152.7 (Csp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{20}N_2NaO_4$ [M + Na] 435.1315; found 435.1314.

5-(Isochroman-1-yl)-6-(4-methoxyphenyl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (8ad): Yield 59 mg (35%); white solid; m.p. 170–171 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1749 (C=O), 3266 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.60 (d, ^2J = 16.4 Hz, 1 H, CH_2), 3.01–3.10 (m, 1 H, CH_2), 3.52 (dd, ^2J = 14.8, ^3J = 1.6 Hz, 1 H, CH_2), 3.74 (td, $^{2,3}J$ = 11.6, ^3J = 2.8 Hz, 1 H, CH_2), 3.82 (s, 3 H, OCH_3), 3.95 (dd, ^2J = 14.8, ^3J = 1.6 Hz, 1 H, CH_2), 4.19 (ddd, ^2J = 10.0, ^3J = 6.0 Hz, ^3J = 1.2 Hz, 1 H, CH_2), 5.53 (s, 1 H, CH), 6.33 (br. s, 1 H, NH), 6.92 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.04–7.06 (m, 1 H, ArH), 7.10–7.12 (m, 1 H, ArH), 7.16–7.19 (m, 2 H, ArH), 7.55 (d, ^3J = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.5 (CH_2), 39.9 (CH_2), 55.2 (OCH_3), 64.8 (CH_2), 74.7 (CH), 108.2 (Csp^2), 113.7 (ArC), 124.2 (ArC), 125.0 (ArC), 126.6 (ArC), 127.1 (ArC), 129.0 (ArC), 130.0 (ArC), 134.4 (ArC), 134.6 (ArC), 149.0 (Csp^2), 151.6 (NHCO), 160.6 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{20}H_{19}NNaO_4$ [M + Na] 360.1206; found 360.1206.

6-(3,4-Dimethoxyphenyl)-5-(isochroman-1-yl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (8bd): Yield 0.1 g (55%); yellow solid; m.p. 168–170 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1750 (C=O), 3334 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.60 (d, ^2J = 15.6 Hz, 1 H, CH_2), 3.01–3.10 (m, 1 H, CH_2), 3.53 (d, ^2J = 14.8 Hz, 1 H, CH_2), 3.75 (td, $^{2,3}J$ = 11.6, ^3J = 3.2 Hz, 1 H, CH_2), 3.88 (s, 3 H, OCH_3), 3.89 (s, 3 H, OCH_3), 3.95 (d, ^2J = 14.4 Hz, 1 H, CH_2), 4.20 (dd, ^2J = 11.2, ^3J = 6.0 Hz, 1 H, CH_2), 5.56 (s, 1 H, CH), 6.13 (br. s, 1 H, NH), 6.87 (d, ^3J = 8.4 Hz, 1 H, ArH), 7.03–7.06 (m, 1 H, ArH), 7.09–7.12 (m, 1 H, ArH), 7.16–7.20 (m, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.5 (CH_2), 40.0 (CH_2), 55.8 (OCH_3), 55.9 (OCH_3), 64.8 (CH_2), 74.8 (CH), 108.3 (Csp^2), 110.5 (ArC), 111.5 (ArC), 121.5 (ArC), 124.3 (ArC), 125.0 (ArC), 126.6 (ArC), 127.1 (ArC), 129.1 (ArC), 134.3 (ArC), 134.5 (ArC), 148.7 (ArC), 149.3 (Csp^2), 150.1 (ArC), 151.5 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{21}H_{21}NNaO_5$ [M + Na] 390.1312; found 390.1308.

5-(Isochroman-1-yl)-6-*p*-tolyl-3,4-dihydro-2*H*-1,3-oxazin-2-one (8dd): Yield 78.6 mg (49%); white solid; m.p. 141–142 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1751 (C=O), 3271 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 2.60 (d, ^2J = 15.6 Hz, 1 H, CH_2), 3.02–3.11 (m, 1 H, CH_2), 3.55 (dd, ^2J = 14.6, ^3J = 1.6 Hz, 1 H, CH_2), 3.75 (td, $^{2,3}J$ = 11.6, ^3J = 3.2 Hz, 1 H, CH_2), 3.99 (dd, ^2J = 14.8, ^3J = 1.2 Hz, 1 H, CH_2), 4.18–4.22 (m, 1 H, CH_2), 5.47 (br. s, 1 H, NH), 5.55 (s, 1 H, CH), 7.05–7.08 (m, 1 H, ArH), 7.10–7.14 (m, 1 H, ArH), 7.19–7.21 (m, 2 H, ArH), 7.22 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.51 (d, ^3J = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4 (CH_3), 28.6 (CH_2), 40.1 (CH_2), 64.9 (CH_2), 74.8 (CH), 108.6 (Csp^2), 125.1 (ArC), 126.7 (2 × ArC), 127.2 (ArC), 128.5 (ArC), 128.9 (ArC), 129.1 (ArC), 134.4 (ArC), 134.7 (ArC), 139.8 (ArC), 149.4 (Csp^2), 151.1 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{20}H_{19}NNaO_3$ [M + Na] 344.1257; found 344.1258.

5-(Isochroman-1-yl)-6-phenyl-3,4-dihydro-2*H*-1,3-oxazin-2-one (8ed): Yield 61.3 mg (40%); white solid; m.p. 189–190 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1751 (C=O), 3255 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.60 (d, ^2J = 16.4 Hz, 1 H, CH_2), 3.02–3.11 (m, 1 H, CH_2), 3.55 (dd, ^2J = 14.8, ^3J = 1.6 Hz, 1 H, CH_2), 3.74 (td, $^{2,3}J$ = 11.4, ^3J = 3.2 Hz, 1 H, CH_2), 3.99 (dd, ^2J = 14.8, ^3J = 1.2 Hz, 1 H, CH_2), 4.20 (ddd, ^2J = 11.4, ^3J = 6.0 Hz, ^3J = 1.2 Hz, 1 H, CH_2), 5.54 (s, 1 H, CH), 6.11 (br. s, 1 H, NH), 7.05–7.07 (m, 1 H, ArH), 7.10–7.13 (m, 1 H, ArH), 7.18–7.21 (m, 2 H, ArH), 7.41–7.43 (m, 3 H, ArH), 7.61–7.63 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.5 (CH_2), 40.0 (CH_2), 64.8 (CH_2), 74.6 (CH), 109.1 (Csp^2), 125.0 (ArC), 126.7 (ArC), 127.2 (ArC), 128.4 (ArC), 128.6 (ArC), 129.1 (ArC), 129.6 (ArC), 131.8 (ArC), 134.4 (ArC), 134.5 (ArC), 149.2 (Csp^2), 151.3 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{19}H_{17}NNaO_3$ [M + Na] 330.1101; found 330.1101.

6-(4-Chlorophenyl)-5-(isochroman-1-yl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (8fd): Yield 49.5 mg (29%); white solid; m.p. 71–172 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1747 (C=O), 3278 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.60 (d, ^2J = 16.4 Hz, 1 H, CH_2), 2.90–2.99 (m, 1 H, CH_2), 3.29 (dd, ^2J = 15.2, ^3J = 1.6 Hz, 1 H, CH_2), 3.68 (td, $^{2,3}J$ = 11.2, ^3J = 3.2 Hz, 1 H, CH_2), 3.75 (dd, ^2J = 15.2, ^3J = 1.2 Hz, 1 H, CH_2), 4.10 (dd, ^2J = 11.4, ^3J = 4.8 Hz, 1 H, CH_2), 5.34 (s, 1 H, CH), 7.06–7.12 (m, 1 H, ArH), 7.15–7.22 (m, 3 H, ArH), 7.57 (br. s, 4 H, ArH), 7.81 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9 (CH_2), 39.1 (CH_2), 64.1 (CH_2), 74.0 (CH), 110.0 (Csp^2), 124.9 (ArC), 126.6 (ArC), 127.1 (ArC), 128.8 (ArC), 129.1 (ArC), 130.2 (ArC), 130.7 (ArC), 134.3 (ArC), 137.6 (ArC), 134.4 (ArC), 147.6 (Csp^2), 149.7 (NHCO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{19}H_{16}{}^{35}ClNNaO_3$ [M + Na] 364.0711; found 364.0704.

***N*-[5-(Isochroman-1-yl)-6-(4-methoxyphenyl)-4*H*-1,3-oxazin-2-yl]-4-methylbenzenesulfonamide (9ac):** Yield 0.18 g (74%); white solid; m.p. 246 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3145 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 2.34 (s, 3 H, CH_3), 2.61 (m, 1 H, $ArCCH_2$), 2.95 (m, 1 H, $ArCCH_2$), 3.33 (m, 1 H, NCH_2), 3.66 (m, 1 H, OCH_2), 3.73 (m, 1 H, NCH_2), 3.82 (s, 3 H, OCH_3), 4.10 (m, 1 H, OCH_2), 5.41 (s, 1 H, CH), 7.03 (d, ^3J = 6.6 Hz, 1 H, ArH), 7.07 (d, ^3J = 8.7 Hz, 2 H, ArH), 7.15–7.23 (m, 3 H, ArH), 7.25 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.44 (d, ^3J = 8.6 Hz, 2 H, ArH), 7.63 (d, ^3J = 8.1 Hz, 2 H, ArH), 9.11 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 21.4 (CH_3), 28.3 ($ArCCH_2$), 38.1 (NCH_2), 55.8 (OCH_3), 64.6 (OCH_2), 74.2 (CH), 110.5 (H_2CC-sp2), 114.5 (ArC), 122.8 (ArC), 125.3 (ArC), 126.6 (ArC), 127.1 (ArC), 127.2 (ArC), 129.5 (ArC), 129.6 (ArC), 130.4 (ArC), 134.3 (ArC), 134.9 (ArC), 141.0 (ArC), 142.3 (ArC), 147.8 (C-sp^2), 153.5 (HNC-sp^2), 160.9 (ArC) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{27}H_{27}N_2O_5S$ $[M + H]^+$ 491.1635; found 491.1639.

***N*-[6-(3,4-Dimethoxyphenyl)-5-(isochroman-1-yl)-4*H*-1,3-oxazin-2-yl]-4-methylbenzenesulfonamide (9dc):** Yield 0.23 g (88%); white needles; m.p. 141 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3300 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 2.32 (s, 3 H, CH_3), 2.61 (d, ^3J = 16.2 Hz, 1 H, $ArCCH_2$), 2.90–3.00 (m, 1 H, $ArCCH_2$), 3.28–3.34 (m, 1 H, NCH_2), 3.68–3.73 (m, 1 H, OCH_2), 3.74–3.76 (m, 1 H,

NCH_2), 3.80 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 4.11 (ddd, ^3J = 11.1, ^3J = 5.8 Hz, ^2J = 1.5 Hz, 1 H, OCH_2), 5.50 (s, 1 H, CH), 7.00–7.12 (m, 3 H, ArH), 7.16–7.26 (m, 5 H, ArH), 7.30 (br. s, 1 H, ArH), 7.64 (d, ^3J = 8.0 Hz, 2 H), 9.13 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 21.3 (CH_3), 28.3 ($ArCCH_2$), 38.1 (NCH_2), 55.9 (OCH_3), 56.0 (OCH_3), 64.6 (OCH_2), 74.2 (CH), 110.6 (H_2CC-sp^2), 111.9 (ArC), 112.3 (ArC), 121.8 (ArC), 122.9 (ArC), 125.3 (ArC), 126.6 (ArC), 127.1 (ArC), 127.7 (ArC), 129.5 (ArC), 129.6 (ArC), 134.4 (ArC), 134.9 (ArC), 141.1 (ArC), 142.2 (ArC), 148.1 (ArCC-sp^2), 149.0 (ArC), 150.7 (ArC), 153.6 (HNC-sp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{28}H_{29}N_2O_6S$ [M + H]$^+$ 521.1741; found 521.1746.

***N*-[5-(Isochroman-1-yl)-6-(*p*-tolyl)-4*H*-1,3-oxazin-2-yl]-4-methylbenzenesulfonamide (9fc):** Yield 0.23 g (92%); white solid; m.p. 259–261 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3300 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.34 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 2.60 (d, ^3J = 16.4, Hz, 1 H, $ArCCH_2$), 2.89–3.00 (m, 1 H, $ArCCH_2$), 3.29–3.33 (m, 1 H, NCH_2), 3.67 (td, ^3J = 11.5, ^2J = 3.0 Hz, 1 H, OCH_2), 3.74 (dd, ^3J = 15.3, ^2J = 1.1 Hz, 1 H, NCH_2), 4.09 (dd, ^3J = 11.1, ^2J = 5.6 Hz, 1 H, OCH_2), 5.40 (s, 1 H, CH), 7.02 (d, ^3J = 6.5 Hz, 1 H, ArH), 7.15–7.28 (m, 5 H, ArH), 7.31 (d, ^3J = 8.1 Hz, 2 H, ArH), 7.36 (d, ^3J = 8.2 Hz, 2 H, ArH), 9.10 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 21.3 (CH_3), 21.4 (CH_3), 28.3 ($ArCCH_2$), 38.1 (NCH_2), 64.6 (OCH_2), 74.1 (CH), 111.1 (H_2CC-sp^2), 125.3 (ArC), 126.6 (ArC), 127.1 (ArC), 127.7 (ArC), 127.8 (ArC), 129.5 (ArC), 129.6 (ArC), 129.7 (ArC), 134.2 (ArC), 134.9 (ArC), 140.4 (ArC), 141.0 (ArC), 142.3 (ArC), 147.8 ($ArCC$-sp^2), 153.4 (HNC-sp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{27}H_{26}N_2NaO_4S$ [M + Na]$^+$ 497.1505; found 497.1500.

***N*-[5-(Isochroman-1-yl)-6-phenyl-4*H*-1,3-oxazin-2-yl]-4-methylbenzenesulfonamide (9gc):** Yield 0.21 g (90%); white solid; m.p. 225–226 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3152 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.34 (s, 3 H, CH_3), 2.61 (d, ^3J = 16.4 Hz, 1 H, $ArCCH_2$), 2.95 (m, 1 H, $ArCCH_2$), 3.35 (d, ^2J = 15.4 Hz, 1 H, NCH_2), 3.68 (td, ^3J = 11.4, ^2J = 8.7 Hz, 1 H, OCH_2), 3.77 (d, ^2J = 15.4 Hz, 1 H, NCH_2), 4.10 (td, ^3J = 10.0, ^2J = 5.4 Hz, 1 H, OCH_2), 5.41 (s, 1 H, CH), 7.04 (d, ^3J = 6.3 Hz, 1 H, ArH), 7.14–7.29 (m, 5 H, ArH), 7.45–7.56 (m, 5 H, ArH), 7.61 (d, ^3J = 8.1 Hz, 2 H, ArH), 9.11 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 21.4 (CH_3), 28.3 ($ArCCH_2$), 38.2 (NCH_2), 64.6 (OCH_2), 74.1 (CH), 111.6 (H_2CC-sp^2), 125.3 (ArC), 126.6 (ArC), 127.1 (ArC), 127.8 (ArC), 128.9 (ArC), 129.1 (ArC), 129.5 (ArC), 129.6 (ArC), 130.6 (ArC), 134.1 (ArC), 134.9 (ArC), 141.0 (ArC), 142.3 (ArC), 147.7 ($ArCC$-sp^2), 153.4 (HNC-sp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{25}N_2O_4S$ [M + H]$^+$ 461.1530; found 461.1536.

***N*-[6-(4-Chlorophenyl)-5-(isochroman-1-yl)-4*H*-1,3-oxazin-2-yl]-4-methylbenzenesulfonamide (9hc):** Yield 0.15 g (62%); white solid; m.p. 275–277 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3124 (NH) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.34 (s, 3 H, CH_3), 2.61 (d, ^3J = 16.2 Hz, 1 H, $ArCCH_2$), 2.88–2.99 (m, 1 H, $ArCCH_2$), 3.69 (d, ^3J = 11.6 Hz, 1 H, OCH_2), 3.75 (d, ^3J = 15.6 Hz, 1 H, NCH_2), 4.05–4.15 (m, 1 H, OCH_2), 5.38 (s, 1 H, CH), 7.03 (d, ^3J = 6.02 Hz, 1 H, ArH), 7.15–7.30 (m, 5 H, ArH), 7.35–7.45 (m, 1 H, ArH), 7.46–7.55 (m, 2 H, ArH), 7.56–7.67 (m, 4 H, ArH), 9.12 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 21.4 (CH_3), 28.3 ($ArCCH_2$), 38.3 (NCH_2), 64.5 (OCH_2), 73.9 (CH), 112.3 (H_2CC-sp^2), 125.4 (ArC), 126.6 (ArC), 127.1 (ArC), 127.8 (ArC), 129.3 (ArC), 129.5 (ArC), 129.6 (ArC), 130.7 (ArC), 133.5 (ArC), 134.0 (ArC), 134.9 (ArC), 135.4 (ArC), 141.0 (ArC), 142.4 (ArC), 146.7 (ArC), ($ArCC$-sp^2), 153.2 (HNC-sp^2) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{24}ClN_2O_4S$ [M + H] 495.1140; found 495.1143.

***N*-[5-(Isochroman-1-yl)-6-(4-methoxyphenyl)-4*H*-1,3-thiazin-2-yl]-benzamide (10ad):** Yield 0.19 g (82%); yellow solid; m.p. 78–79 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1676 (C=O), 3198 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.63 (d, ^2J = 15.2 Hz, 1 H, CH_2), 3.10–3.18 (m, 1 H, CH_2), 3.72 (td, $^{2,3}J$ = 11.6, ^3J = 3.2 Hz, 1 H, CH_2), 3.77 (d, ^2J = 15.2 Hz, 1 H, CH_2), 3.83 (s, 3 H, OCH_3), 3.96 (d, ^2J = 15.2 Hz, 1 H, CH_2), 4.22 (ddd, ^2J = 11.2, ^3J = 5.6, ^3J = 0.8 Hz, 1 H, CH_2), 5.51 (s, 1 H, CH), 6.96–6.98 (m, 3 H, ArH), 7.13–7.21 (m, 3 H, ArH), 7.38–7.42 (m, 2 H, ArH), 7.46–7.50 (m, 1 H, ArH), 7.53 (d, ^3J = 8.8 Hz, 2 H, ArH), 8.17–8.20 (m, 2 H, ArH), 11.0 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.5 (CH_2), 43.7 (CH_2), 55.3 (OCH_3), 64.8 (CH_2), 75.7 (CH), 114.2 (ArC), 125.2 (ArC), 126.7 (ArC), 126.8 (ArC), 127.3 (ArC), 127.4 (Csp^2), 128.0 (ArC), 129.1 (ArC), 129.3 (ArC), 130.8 (ArC), 131.9 (ArC), 134.2 (ArC), 134.9 (ArC), 135.3 (Csp^2), 136.5 (ArC), 160.4 (ArC), 169.5 (Csp^2), 176.7 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{27}H_{25}N_2O_3S$ [M + H] 457.1580; found 457.1585.

***N*-[6-(4-Chlorophenyl)-5-(isochroman-1-yl)-4*H*-1,3-thiazin-2-yl]-benzamide (10bd):** Yield 0.13 g (55%); yellow solid; m.p. 56–57 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1679 (C=O), 3197 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.64 (d, ^2J = 16.0 Hz, 1 H, CH_2), 3.10–3.18 (m, 1 H, CH_2), 3.73 (td, ^2J = 11.6, ^3J = 2.8 Hz, 1 H, CH_2), 3.78 (d, ^2J = 15.2 Hz, 1 H, CH_2), 3.96 (d, ^2J = 15.6 Hz, 1 H, CH_2), 4.22 (dd, ^2J = 11.4, ^3J = 5.2 Hz, 1 H, CH_2), 5.44 (s, 1 H, CH), 6.91 (d, ^3J = 7.2 Hz, 1 H, ArH), 7.13–7.25 (m, 4 H, ArH), 7.39–7.42 (m, 4 H, ArH), 7.52 (d, ^3J = 8.8 Hz, 2 H, ArH), 8.15–8.17 (m, 2 H, ArH), 10.9 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.5 (CH_2), 43.9 (CH_2), 64.9 (CH_2), 75.6 (CH), 125.1 (ArC), 126.4 (ArC), 126.8 (ArC), 127.2 (ArC), 127.4 (Csp^2), 128.1 (ArC), 128.9 (ArC), 129.1 (ArC), 129.2 (ArC), 129.3 (ArC), 130.8 (ArC), 132.0 (ArC), 133.2 (ArC), 134.3 (ArC), 134.5 (ArC), 135.5 (Csp^2), 164.8 (Csp^2), 174.2 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{21}{}^{35}ClN_2O_2S$ [M + H] 461.1085; found 461.1095.

***N*-[5-(Isochroman-1-yl)-6-phenyl-4*H*-1,3-thiazin-2-yl]benzamide (10cd):** Yield 0.14 g (64%); white solid; m.p. 89–90 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1682 (C=O), 3189 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.62 (d, ^2J = 15.2 Hz, 1 H, CH_2), 3.09–3.18 (m, 1 H, CH_2), 3.72 (td, ^2J = 11.6, ^3J = 3.2 Hz, 1 H, CH_2), 3.80 (d, ^2J = 15.2 Hz, 1 H, CH_2), 3.99 (d, ^2J = 15.2 Hz, 1 H, CH_2), 4.22 (ddd, ^2J = 11.2, ^3J = 5.4, ^3J = 1.2 Hz, 1 H, CH_2), 5.49 (s, 1 H, CH), 6.97 (d, ^3J = 7.2 Hz, 1 H, ArH), 7.13–7.21 (m, 3 H, ArH), 7.39–7.49 (m, 6 H, ArH), 7.58–7.60 (m, 2 H, ArH), 8.18–8.20 (m, 2 H, ArH), 10.9 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.5 (CH_2), 43.7 (CH_2), 64.8 (CH_2), 75.6 (CH), 125.2 (ArC), 126.7 (ArC), 127.3 (ArC), 128.0 (ArC), 128.1 (Csp^2), 128.8 (ArC), 129.1 (ArC), 129.2 (ArC), 129.3 (ArC), 129.4 (ArC), 131.9 (ArC), 134.2 (ArC), 134.7 (2 × ArC), 135.2 (Csp^2), 136.4 (ArC), 169.1 (Csp^2), 176.5 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{22}N_2O_2S$ [M + H] 427.1475; found 427.1484.

***N*-{5-[Methoxy(4-methoxyphenyl)methyl]-6-(4-methoxyphenyl)-4*H*-1,3-thiazin-2-yl}benzamide (10ae):** Yield 0.18 g (76%); yellow solid; m.p. 47–48 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1680 (C=O), 3194 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.30 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 3.89 (d, ^2J = 15.2 Hz, 1 H, C*H*H), 4.08 (d, ^2J = 15.2 Hz, 1 H, CH*H*), 5.03 (s, 1 H, CH), 6.89 (d, ^3J = 8.8 Hz, 2 H, ArH), 6.94 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.22 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.38 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.41 (d, ^3J = 7.6 Hz, 2 H, ArH), 7.48 (tt, ^3J = 7.2, ^4J = 1.2 Hz, 1 H, ArH), 8.18–8.20 (m, 2 H, ArH), 11.07 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.4 (CH_2), 55.2 (OCH_3), 55.3 (OCH_3), 56.6 (OCH_3), 79.4 (CH), 114.0 (ArC), 114.3 (ArC), 126.8 (ArC), 127.2 (ArC), 127.9 (Csp^2), 128.0 (ArC), 129.4 (ArC), 130.8 (ArC),

131.1 (ArC), 131.9 (ArC), 134.0 (Csp^2), 136.5 (ArC), 159.2 (ArC), 160.3 (ArC), 170.0 (Csp^2), 176.8 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{27}H_{27}N_2O_4S$ [M + H] 475.1686; found 475.1687.

***N*-{5-[(4-Bromophenyl)(ethoxy)methyl]-6-(4-methoxyphenyl)-4*H*-1,3-thiazin-2-yl}benzamide (10af):** Yield 0.16 g (59%); yellow solid; m.p. 89–90 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1684 (C=O), 3203 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.21 (t, ^3J = 7.2 Hz, 3 H, OCH_2CH_3), 3.29–3.37 (m, 1 H, $OCHHCH_3$), 3.52–3.59 (m, 1 H, $OCHHCH_3$), 3.84–3.87 (m, 4 H, CHH and OCH_3), 4.04 (d, ^2J = 15.2 Hz, 1 H, CHH), 5.13 (s, 1 H, CH), 6.94 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.19 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.35 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.38–7.42 (m, 2 H, ArH), 7.46–7.49 (m, 3 H, ArH), 8.16–8.18 (m, 2 H, ArH), 10.99 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.2 (OCH_2CH_3), 42.5 (CH_2), 55.3 (OCH_3), 64.3 (OCH_2CH_3), 77.2 (CH), 114.3 (ArC), 125.7 (ArC), 126.6 (ArC), 127.6 (Csp^2), 127.7 (ArC), 128.1 (ArC), 129.3 (ArC), 130.7 (ArC), 131.7 (ArC), 132.0 (ArC), 133.6 (Csp^2), 134.2 (ArC), 138.5 (ArC), 160.3 (ArC), 169.4 (Csp^2), 176.6 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{27}H_{25}{}^{79}BrN_2O_3S$ [M + H] 536.0770; found 536.0768.

***N*-{5-[Methoxy(phenyl)methyl]-6-(4-methoxyphenyl)-4*H*-1,3-thiazin-2-yl}benzamide (10ag):** Yield 0.13 g (58%); yellow solid; m.p. 55–56 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1681 (C=O), 3195 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.32 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 3.88 (d, ^2J = 15.2 Hz, 1 H, CHH), 4.08 (d, ^2J = 15.2 Hz, 1 H, CHH), 5.09 (s, 1 H, CH), 6.95 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.30–7.32 (m, 3 H, ArH), 7.35–7.42 (m, 6 H, ArH), 7.48 (tt, ^3J = 7.6, ^4J = 1.6 Hz, 1 H, ArH), 8.17–8.19 (m, 2 H, ArH), 11.03 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.5 (CH_2), 55.3 (OCH_3), 55.6 (OCH_3), 79.6 (CH), 114.3 (ArC), 126.0 (ArC), 126.7 (ArC), 127.6 (ArC), 127.8 (Csp^2), 128.0 (ArC), 128.6 (ArC), 129.3 (ArC), 130.8 (ArC), 131.9 (ArC), 134.3 (Csp^2), 136.4 (ArC), 139.0 (ArC), 160.3 (ArC), 169.7 (Csp^2), 176.7 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{24}N_2O_3S$ [M + H] 445.1580; found 445.1574.

***N*-{6-(4-Chlorophenyl)-5-[methoxy(phenyl)methyl]-4*H*-1,3-thiazin-2-yl}benzamide (10bg):** Yield 0.15 g (65%); yellow solid; m.p. 55–56 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1683 (C=O), 3196 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.32 (s, 3 H, OCH_3), 3.89 (d, ^2J = 15.6 Hz, 1 H, CHH), 4.09 (d, ^2J = 15.6 Hz, 1 H, CHH), 5.01 (s, 1 H, CH), 7.27–7.32 (m, 3 H, ArH), 7.35–7.44 (m, 8 H, ArH), 7.49 (tt, ^3J = 7.2, ^4J = 1.2 Hz, 1 H, ArH), 8.16–8.18 (m, 2 H, ArH), 10.94 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.6 (CH_2), 56.7 (OCH_3), 79.7 (CH), 125.9 (ArC), 128.0 (Csp^2), 128.1 (ArC), 128.7 (ArC), 129.0 (ArC), 129.2 (ArC), 129.3 (ArC), 130.8 (ArC), 132.0 (ArC), 133.2 (ArC and Csp^2), 135.5 (ArC), 136.1 (ArC), 138.7 (ArC), 168.7 (Csp^2), 176.4 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{21}{}^{35}ClN_2O_2S$ [M + H] 449.1085; found 449.1076.

***N*-{5-[(4-Bromophenyl)(ethoxy)methyl]-6-(4-chlorophenyl)-4*H*-1,3-thiazin-2-yl}benzamide (10bf):** Yield 0.15 g (57%); yellow solid; m.p. 73–74 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1682 (C=O), 3188 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.22 (t, ^3J = 7.2 Hz, 3 H, OCH_2CH_3), 3.29–3.37 (m, 1 H, $OCHHCH_3$), 3.50–3.57 (m, 1 H, $OCHHCH_3$), 3.87 (d, ^2J = 15.6 Hz, 1 H, CHH), 4.05 (d, ^2J = 15.6 Hz, 1 H, CHH), 5.05 (s, 1 H, CH), 7.16 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.35–7.39 (m, 2 H, ArH), 7.41–7.43 (m, 3 H, ArH), 7.46–7.49 (m, 3 H, ArH), 7.51–7.56 (m, 1 H, ArH), 8.14–8.17 (m, 2 H, ArH), 10.88 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.2 (OCH_2CH_3), 42.7 (CH_2), 64.5 (OCH_2CH_3), 77.3 (CH), 121.9 (ArC), 125.8 (ArC), 127.7 (ArC), 128.1 (ArC), 128.9 (Csp^2), 129.3 (2 × ArC), 129.7 (ArC), 130.7 (ArC), 131.8 (ArC), 132.1 (ArC), 133.1 (Csp^2), 135.6 (ArC), 138.2 (ArC), 168.3 (Csp^2), 176.3 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{22}{}^{35}Cl^{79}BrN_2O_2S$ [M + H] 540.0274; found 540.0271.

***N*-{5-[Methoxy(4-methoxyphenyl)methyl]-6-phenyl-4*H*-1,3-thiazin-2-yl}benzamide (10ce):** Yield 0.18 g (81%); yellow oil. IR (KBr): $\tilde{\nu}_{max}$ = 1680 (C=O), 3198 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.31 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 3.91 (d, ^2J = 15.6 Hz, 1 H, CHH), 4.09 (d, ^2J = 15.2 Hz, 1 H, CHH), 5.01 (s, 1 H, CH), 6.89 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.21 (d, ^3J = 7.6 Hz, 2 H, ArH), 7.38–7.46 (m, 7 H, ArH), 7.48 (tt, ^3J = 7.6, ^4J = 1.2 Hz, 1 H, ArH), 8.18–8.20 (m, 2 H, ArH), 11.03 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.4 (CH_2), 55.2 (OCH_3), 56.5 (OCH_3), 79.3 (CH), 114.0 (ArC), 127.1 (ArC), 128.0 (ArC), 128.5 (Csp^2), 128.8 (ArC), 129.2 (ArC), 129.3 (ArC), 129.4 (ArC), 130.9 (ArC), 132.0 (ArC), 133.9 (Csp^2), 134.7 (ArC), 136.3 (ArC), 159.1 (ArC), 169.4 (Csp^2), 176.6 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{24}N_2O_3S$ [M + H] 445.1580; found 445.1574.

***N*-{5-[(4-Bromophenyl)(methoxy)methyl]-6-phenyl-4*H*-1,3-thiazin-2-yl}benzamide (10cf):** Yield 0.15 g (60%); yellow oil. IR (KBr): $\tilde{\nu}_{max}$ = 1681 (C=O), 3167 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.21 (t, ^3J = 7.2 Hz, 3 H, OCH_2CH_3), 3.29–3.37 (m, 1 H, $OCHHCH_3$), 3.52–3.60 (m, 1 H, $OCHHCH_3$), 3.86 (d, ^2J = 15.6 Hz, 1 H, CHH), 4.05 (d, ^2J = 15.2 Hz, 1 H, CHH), 5.10 (s, 1 H, CH), 7.19 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.38–7.42 (m, 7 H, ArH), 7.46–7.48 (m, 3 H, ArH), 8.16–8.18 (m, 2 H, ArH), 10.96 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.2 (OCH_2CH_3), 42.5 (CH_2), 64.3 (OCH_2CH_3), 77.1 (CH), 121.7 (ArC), 127.7 (ArC), 128.0 (ArC), 128.1 (Csp^2), 128.9 (ArC), 129.3 (2 × ArC), 131.6 (ArC), 132.0 (ArC), 134.1 (Csp^2), 134.6 (ArC), 136.2 (ArC), 138.4 (ArC), 168.8 (Csp^2), 176.3 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{23}{}^{79}BrN_2O_2S$ [M + H] 506.0664; found 506.0665.

***N*-{5-[Methoxy(phenyl)methyl]-6-phenyl-4*H*-1,3-thiazin-2-yl}benzamide (10cg):** Yield 0.12 g (57%); yellow oil. IR (KBr): $\tilde{\nu}_{max}$ = 1680 (C=O), 3189 (NH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.33 (s, 3 H, OCH_3), 3.89 (d, ^2J = 15.2 Hz, 1 H, CHH), 4.09 (d, ^2J = 15.6 Hz, 1 H, CHH), 5.07 (s, 1 H, CH), 7.28–7.32 (m, 3 H, ArH), 7.35–7.38 (m, 2 H, ArH), 7.40–7.51 (m, 8 H, ArH), 8.18–8.20 (m, 2 H, ArH), 11.01 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.5 (CH_2), 56.6 (OCH_3), 79.5 (CH), 125.9 (ArC), 127.8 (ArC), 128.0 (ArC), 128.2 (Csp^2), 128.9 (ArC), 129.2 (ArC), 129.3 (ArC), 129.4 (ArC), 131.9 (ArC), 134.2 (Csp^2), 134.7 (ArC), 136.3 (ArC), 138.9 (ArC), 169.3 (Csp^2), 176.5 (CO) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{22}N_2O_2S$ [M + H] 415.1475; found 415.1461.

2-(Isochroman-1-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (11ac): Yield 0.13 g (90%); yellowish oil. IR (KBr): $\tilde{\nu}_{max}$ = 1654 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.85–3.00 (m, 2 H, CH_2), 3.90 (s, 3 H, OCH_3), 3.93 (ddd, $^2J_{H,H}$ = 11.3, $^3J_{H,H}$ = 6.3, $^2J_{H,H}$ = 4.9 Hz, 1 H, OCH_2), 4.17 (ddd, $^2J_{H,H}$ = 11.3, $^3J_{H,H}$ = 6.3, $^2J_{H,H}$ = 4.9 Hz, 1 H, OCH_2), 5.71 (s, 1 H, =CH), 5.79 (s, 1 H, =CH), 5.99 (s, 1 H, *CH*O), 6.97 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H, ArH), 7.04 (d, $^3J_{H,H}$ = 7.0 Hz, 1 H, ArH), 7.17–7.22 (m, 3 H, ArH), 7.91 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.58 (CH_2), 55.44 (OCH_3), 62.13 (OCH_2), 74.84 (OCH), 113.53 (ArC), 125.83 (ArC), 126.01 (=CH_2), 126.53 (ArC), 126.70 (ArC), 128.88 (ArC), 130.00 (ArC), 132.11 (ArC), 134.12 (ArC), 135.19 (ArC), 148.81 (=*C*-C=O), 163.36 (ArC), 195.70 (C=O) ppm. HRMS (ES): *m*/*z* calcd. for $C_{19}H_{18}NaO_3$ $[M + Na]^+$ 317.1148; found 317.1149.

2-(Isochroman-1-yl)-1-phenylprop-2-en-1-one (11bc): Yield 0.11 g (83%); yellowish oil. IR (KBr): $\tilde{\nu}_{max}$ = 1660 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.87–2.95 (m, 2 H, CH_2), 3.95 (ddd, $^2J_{H,H}$ = 11.4, $^3J_{H,H}$ = 6.8, $^2J_{H,H}$ = 4.7 Hz, 1 H, OCH_2), 4.18 (ddd, $^2J_{H,H}$

= 11.4, $^3J_{H,H}$ = 6.8, $^2J_{H,H}$ = 4.7 Hz, 1 H, OCH_2), 5.81 (s, 1 H, =CH), 5.88 (s, 1 H, =CH), 6.03 (s, 1 H, *CH*O), 7.03 (d, $^3J_{H,H}$ = 7.0 Hz, 1 H, ArH), 7.16–7.24 (m, 3 H, ArH), 7.46–7.50 (m, 2 H, ArH), 7.57–7.61 (m, 1 H, ArH), 7.86–7.88 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.61 (CH_2), 62.27 (OCH_2), 74.45 (OCH), 125.91 (ArC), 126.43 (ArC), 126.75 (ArC), 127.97 (=CH_2), 128.28 (ArC), 128.92 (ArC), 129.67 (ArC), 132.56 (ArC), 134.17 (ArC), 135.27 (ArC), 137.46 (ArC), 148.82 (=*C*-C=O), 196.96 (C=O) ppm. HRMS (ES): *m*/*z* calcd. for $C_{18}H_{16}NaO_2$ $[M + Na]^+$ 287.1043l; found 287.1045.

Supporting Information (see footnote on the first page of this article): Experimental details for the preparation of the starting materials, the results of optimization studies, and copies of ^1H and ^{13}C NMR spectra.

Acknowledgments

The research was funded by the Research Council of Lithuania (grant number MIP-15016).

[1] For representative publications, see: a) R. C. Larock, in: *Acetylene Chemistry; Chemistry, Biology, and Material Science* (Eds.: F. Diederich, P. J. Stang, R. R. Tykwinski), Wiley-VCH, New York, 2005; chapter 2, p. 51; b) S. Mehta, J. P. Waldo, R. C. Larock, *J. Org. Chem.* **2009**, *74*, 1141; c) J. Barluenga, H. Vazquez-Villa, A. Ballesteros, J. M. Gonzalez, *J. Am. Chem. Soc.* **2003**, *125*, 9028; d) J. Barluenga, M. Trincado, E. Rubio, J. M. Gonzalez, *Angew. Chem.* **2003**, *115*, 2508; e) B. Godoi, R. F. Schumacher, G. Zeni, *Chem. Rev.* **2011**, *111*, 2937; f) B. Gabriele, R. Mancuso, G. Salerno, R. C. Larock, *J. Org. Chem.* **2012**, *77*, 7640; g) B. Gabriele, R. Mancuso, R. C. Larock, *Curr. Org. Chem.* **2014**, *18*, 341; h) K. Dev, R. Maurya, *RSC Adv.* **2015**, *5*, 13102; i) H. Huang, X. Zhu, G. He, Q. Liu, J. Fan, H. Zhu, *Org. Lett.* **2015**, *17*, 2510; j) X. Chen, P. Lu, Y. Wang, *Chem. Eur. J.* **2011**, *17*, 8105; k) B. Godoi, R. F. Schumacher, G. Zeni, *Chem. Rev.* **2011**, *111*, 2937; l) Y. Yamamoto, I. D. Gridnev, N. T. Patild, T. Jinab, *Chem. Commun.* **2009**, 5075.

[2] For representative publications, see: a) W. Yang, A. S. K. Hashmi, *Chem. Soc. Rev.* **2014**, *43*, 2941; b) R. K. Shiroodi, V. Gevorgyan, *Chem. Soc. Rev.* **2013**, *42*, 4991; c) T. Lauterbach, M. Ganschow, M. W. Hussong, M. Rudolph, F. Rominger, A. S. K. Hashmi, *Adv. Synth. Catal.* **2014**, *356*, 680; d) L.-J. Wang, H.-T. Zhu, A.-Q. Wang, Y.-F. Qiu, X.-Y. Liu, Y.-M. Liang, *J. Org. Chem.* **2014**, *79*, 204; e) A. S. K. Hashmi, A. M. Schuster, M. Schmuck, F. Rominger, *Eur. J. Org. Chem.* **2011**, *24*, 4595; f) I. Nakamura, S. Gima, Y. Kudo, M. Terada, *Angew. Chem. Int. Ed.* **2015**, *54*, 7154; g) T. Wang, S. Shi, M. M. Hansmann, E. Rettenmeier, M. Rudolph, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2014**, *53*, 3715; h) Y. Zhu, L. Sun, P. Lu, Y. Wang, *ACS Catal.* **2014**, *4*, 1911; i) G. Verniest, A. Padwa, *Org. Lett.* **2008**, *10*, 4379; j) I. Nakamura, Y. Yamamoto, *Chem. Rev.* **2004**, *104*, 2127; k) A. Bacchi, G. P. Chiusoli, M. Costa, C. Sani, B. Gabriele, G. Salerno, *J. Organomet. Chem.* **1998**, *562*, 35.

[3] For representive publications on electrophile-mediated reactions of propargylic substrates, see: a) B. Godoi, A. Speranca, D. F. Back, R. Brandao, C. W. Nogueira, G. Zeni, *J. Org. Chem.* **2009**, *74*, 3469; b) A. Monleon, G. Blay, L. R. Domingo, M. C. Munoz, J. R. Pedro, *Chem. Eur. J.* **2013**, *19*, 14852; c) A. Monleon, G. Blay, L. R. Domingo, M. C. Munoz, J. R. Pedro, *Eur. J. Org. Chem.* **2015**, *21*, 1020; d) T. Okitsu, K. Sato, A. Wada, *Org. Lett.* **2010**, *12*, 3506; e) S. Karabiyikoglu, Y. Kelgokmen, M. Zora, *Tetrahedron* **2015**, *71*, 4324; f) Y. Hu, X. Xin, B. Wan, *Tetrahedron Lett.* **2015**, *56*, 32; g) Y. Hu, R. Yi, C. Wang, X. Xin, X. Wu, B. Wan, *J. Org. Chem.* **2014**, *79*, 3052; h) F. Yang, T. Jin, M. Bao, Y. Yamamoto, *Tetrahedron* **2011**, *67*, 10147.

[4] a) I. Čikotienė, *Org. Lett.* **2014**, *16*, 2260; b) C. Trujillo, G. Sánchez-Sanz, I. Karpavičienė, U. Jahn, I. Čikotienė, L. Rulíšek, *Chem. Eur. J.* **2014**, *20*, 10360.

[5] R. Bukšnaitienė, I. Čikotienė, *Synlett* **2015**, *26*, 479.

[6] a) R. Bianchini, C. Chiappe, G. Lo Moro, D. Lenoir, P. Lemmen, N. Goldberg, *Chem. Eur. J.* **1999**, *5*, 1570; b) D. Lenoir, C. Chiappe, *Chem. Eur. J.* **2003**, *9*, 1036.

[7] a) R. Volpe, L. Aurelio, M. G. Gillin, E. H. Krenske, B. L. Flynn, *Chem. Eur. J.* **2015**, *21*, 10191; b) V. L. Heasley, D. F. Shellhamer, L. E. Heasley, D. B. Yaeger, G. E. Heasley, *J. Org. Chem.* **1980**, *45*, 4649; c) T. Okazaki, K. K. Laali, *J. Org. Chem.* **2006**, *71*, 9643.

[8] H. Poleschner, K. Seppelt, *Angew. Chem. Int. Ed.* **2008**, *47*, 6461; *Angew. Chem.* **2008**, *120*, 6561.

[9] a) T. Xu, Q. Yang, D. Li, J. Dong, Z. Yu, Y. Li, *Chem. Eur. J.* **2010**, *16*, 9264; b) T. Xu, Q. Yang, W. Ye, Q. Jiang, Z. Xu, J. Chen, Z. Yu, *Chem. Eur. J.* **2011**, *17*, 10547.

Received: August 17, 2015
Published Online: October 12, 2015

