

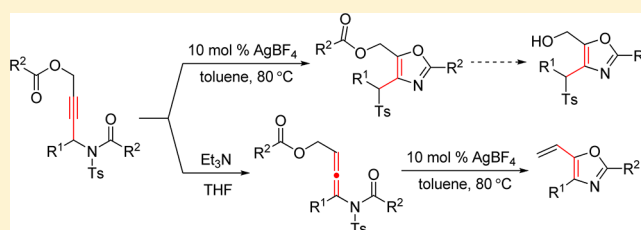
Synthesis of Functionalized Oxazoles via Silver-Catalyzed Cyclization of Propargylamides and Allenylamides

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S Supporting Information

ABSTRACT: Silver(I)-catalyzed [3,3] rearrangement of *N*-sulfonyl propargylamides affords functionalized oxazoles with highly regioselective migration of the sulfonyl group by the introduction of acyloxy groups. The allenylamides, generated from the corresponding propargylamides, can also undergo the silver-catalyzed cyclization to give various 5-vinyloxazoles.



INTRODUCTION

Oxazoles are regarded as privileged heterocyclic motifs in numerous bioactive natural products, synthetic intermediates, and pharmaceuticals.¹ Consequently, many new methods, including the intramolecular cyclization of preformed precursors,² the oxidative coupling of amines and ketone derivatives,³ and one-step bimolecular annulation,⁴ have been widely developed to form oxazoles. Of note, the cyclization of propargylamides to the corresponding oxazole derivatives has been a focus of interest. These transformations have been achieved with transition metal,^{2e-1} acid,^{2m,n} and base^{2o-r} catalysts. According to these previous works, it is well-known that the transition-metal-catalyzed cyclization of propargylamides generally proceeds through *5-exo-dig* mode to give oxazole derivatives. Despite the impressive achievements made in this area, it is still highly desirable to explore more efficient and practical alternatives for the synthesis of functionalized oxazoles. Recently, the synthesis of heterocycles accompanied with sulfonyl migration has gained much attention, and much progress has been achieved.⁵ We have previously reported the base-catalyzed cyclization of 3-aza-1,5-enynes and *N*-sulfonyl propargylamides into pyrroles and oxazoles via sulfonyl migration, respectively (Scheme 1, eqs 1 and 2, left).⁶ However, during further investigations of *N*-sulfonyl propargylamides (**a**), attempts to obtain 4-sulfonylmethyloxazoles (**c**) under the previous optimized condition (140 °C in DMF) did not succeed (Scheme 1, eq 2, right). The major reason is attributed to the failure in the [3,3] rearrangement of **a** under thermal conditions. To overcome this problem, we reasoned that activation of the alkyne moiety by some transition-metal catalysts might promote the rearrangement of **a**. On the other hand, directing groups such as amide, acyloxy, and carboxylic groups, for their potential ability to coordinate with transition-metal catalysts, have been widely used in modern organic synthesis.⁷ On the basis of these precedents, we envisioned that the introduction of directing groups to propargylamides may facilitate the metal-alkyne coordination. Herein, we successfully realized this goal by introducing the acyloxy group to *N*-

sulfonyl propargylamides, which could undergo the silver-catalyzed cyclization smoothly via sulfonyl migration (Scheme 1, eq 3).

RESULTS AND DISCUSSION

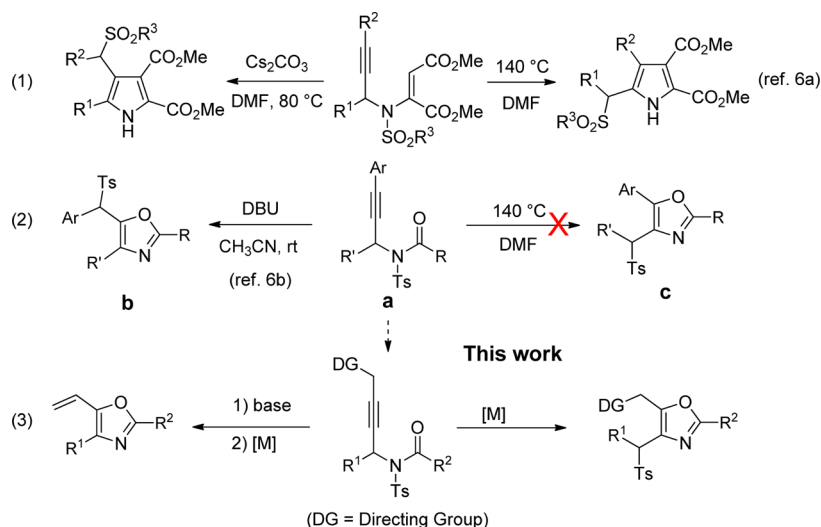
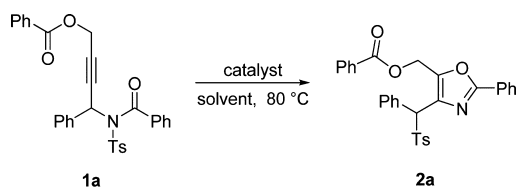
We initiated our studies with the screening of the conditions for the cyclization of *N*-sulfonyl propargylamides **1a**. Substrate **1a** was first performed under thermal and basic conditions (Table 1, entries 1–3) to investigate whether our previous reported conditions⁶ were also suitable for this reaction. Unfortunately, we did not obtain the desired product regardless which condition was used. However, treatment of **1a** with the catalyst [Rh(COD)₂]BF₄ in DCE at 80 °C fortunately obtained the desired sulfonyl-functionalized oxazole **2a** just as we anticipated, albeit with low yield (Table 1, entry 4). The formation of **2a** was confirmed by X-ray crystallography.⁸ Then we focused on various transition-metal catalysts, which were frequently used to activate triple bonds (Table 1, entries 4–8). The results indicated that AgBF₄ produced the desired oxazole in good yield, whereas other catalysts such as PtCl₂ and PPh₃AuCl/AgBF₄ only have a slight improvement. Subsequently, the effect of different silver catalysts was surveyed. Compared with other silver salts, AgBF₄ gave the best result and was chosen as the optimal catalyst (entry 8). It is noteworthy that the yield of oxazole **2a** could be increased to 90% when the reaction was carried out in toluene (entry 12).

With the optimized conditions in hand, we further explored the substrate scope of the reaction, and the results are shown in Table 2. For the R² groups, the phenyl ring with both electron-withdrawing and electron-donating substituents was well-tolerated, providing the desired products in moderate to good yields (Table 2, entries 1–9). Unfortunately, when the aryl groups were changed to alkyl substitutions (**1j**, **1k**), no desired products were observed (entries 10 and 11). Mean-

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Scheme 1. Overview for Methods

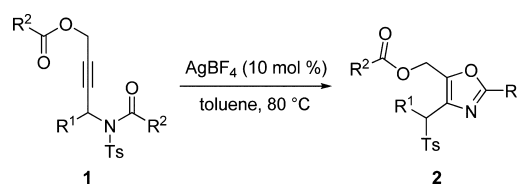
Table 1. Optimization of the Reaction Conditions for the Construction of Oxazole^a

entry	catalyst	solvent	yield (%) ^b
1 ^c		DMF	
2 ^d	DBU	CH ₃ CN	
3 ^e	DABCO	DCM	
4	[Rh(COD) ₂]BF ₄	DCE	36
5	PtCl ₂	DCE	40
6	PPh ₃ AuCl/AgBF ₄	DCE	57
7	[Rh(PPh ₃) ₂ CO]Cl/AgBF ₄	DCE	51
8	AgBF ₄	DCE	86
9	AgSbF ₆	DCE	80
10	AgOTf	DCE	82
11	AgNO ₃	DCE	70
12	AgBF ₄	toluene	90

^aReaction conditions: **1a** (0.1 mmol), catalyst (10 mol %), solvent (1 mL), 80 °C for 10 h. ^bDetermined by HPLC. Benzamide was used as internal standard. ^cDMF (1 mL), 140 °C for 10 h. ^dDBU (10 mol %), CH₃CN (1 mL), rt for 7 h. ^eDABCO (10 mol %), DCM (1 mL), rt for 7 h.

while, other functional groups such as –OMe, –F, and –Br in aromatic R¹ groups were also compatible with this cyclization and afforded the corresponding oxazoles in satisfactory yields (Table 2, entries 12–15). Notably, reaction with naphthyl-derived substrates **1p** and **1q** proceeded well, whereas furanyl-derived substrate **1r** gave no desired oxazole. However, when we tried to prepare other heterocyclic motifs such as the 2-pyridyl group in R¹, we failed to obtain the desired substrate.

Likewise, the scope of the sulfonyl group in the substrate was examined under the same condition. As shown in Table 3, *N*-phenylsulfonyl substrates **1s** and **1t** were also suitable for this cyclization and afforded the corresponding oxazoles in 90 and 81% yield, respectively. Besides, **1u** underwent the cyclization

Table 2. Ag-Catalyzed Cyclization of *N*-Tosyl Propargylamides^a

entry	1	R ¹	R ²	2	yield (%)
1	1a	C ₆ H ₅	C ₆ H ₅	2a	82
2	1b	C ₆ H ₅	<i>o</i> -Me-C ₆ H ₄	2b	75
3	1c	C ₆ H ₅	<i>m</i> -OMe-C ₆ H ₄	2c	79
4	1d	C ₆ H ₅	<i>m</i> -Br-C ₆ H ₄	2d	72
5	1e	C ₆ H ₅	<i>m</i> -F-C ₆ H ₄	2e	80
6	1f	C ₆ H ₅	<i>p</i> -Me-C ₆ H ₄	2f	56
7	1g	C ₆ H ₅	<i>p</i> -Cl-C ₆ H ₄	2g	67
8	1h	C ₆ H ₅	<i>p</i> -F-C ₆ H ₄	2h	81
9	1i	C ₆ H ₅	<i>p</i> -CF ₃ -C ₆ H ₄	2i	79
10	1j	C ₆ H ₅	OEt	2j	0
11	1k	C ₆ H ₅	cyclopentyl	2k	0
12	1l	<i>o</i> -F-C ₆ H ₄	C ₆ H ₅	2l	72
13	1m	<i>m</i> -F-C ₆ H ₄	C ₆ H ₅	2m	90
14	1n	<i>m</i> -OMe-C ₆ H ₄	C ₆ H ₅	2n	81
15	1o	<i>p</i> -Br-C ₆ H ₄	C ₆ H ₅	2o	73
16	1p	1-naphthyl	C ₆ H ₅	2p	83
17	1q	2-naphthyl	C ₆ H ₅	2q	53
18	1r	2-furanyl	C ₆ H ₅	2r	0

^aReaction conditions: **1** (0.2 mmol), AgBF₄ (10 mol %), toluene (1.5 mL), 80 °C for 10 h.

smoothly to give the desired oxazole **2u** in a moderate yield via methylsulfonyl migration.

Moreover, oxazoles **2** can be easily transformed into the corresponding alcohol derivatives by the hydrolysis of esters. For example, as shown in Scheme 2, oxazole **2aa** was readily obtained in 90% yield simply by saponification of **2a**, which could undergo further transformations to construct more valuable molecules.⁹

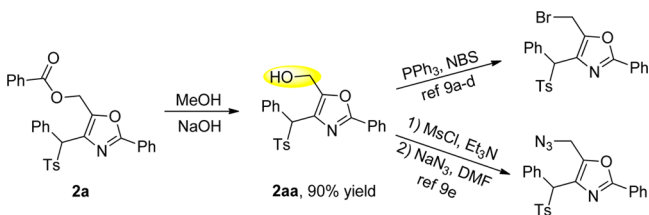
To find out whether the migration of the sulfonyl group occurred in an intramolecular or intermolecular mode, a crossover experiment was performed (Scheme 3). The reaction

Table 3. Scope of the Sulfonyl Group for the Synthesis of Oxazoles^a

entry	1	2	yield (%)
1	 1s	 2s	90
2	 1t	 2t	81
3	 1u	 2u	64

^aReaction conditions: **1** (0.2 mmol), AgBF₄ (10 mol %), toluene (1.5 mL), 80 °C for 10 h.

Scheme 2. Saponification of Oxazolyl Methyl Benzoate **2a**

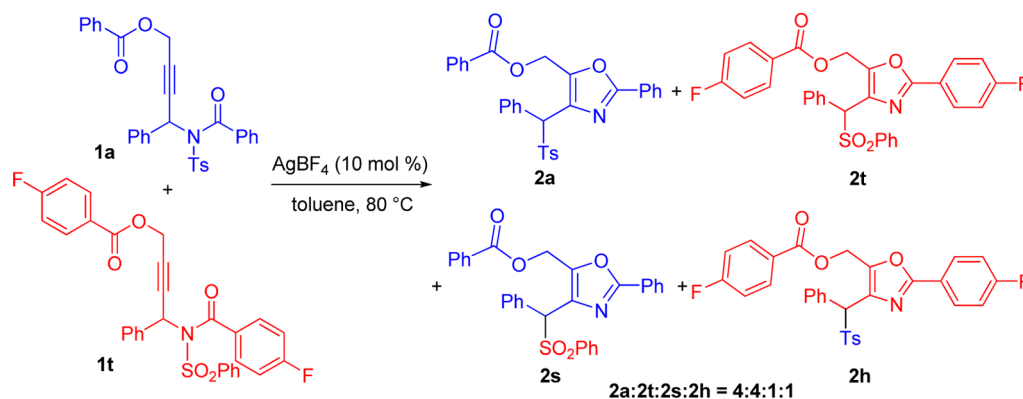


of a mixture 1:1 of **1a** and **1t** in the presence of a catalytic amount of AgBF₄ gave four oxazole products in nearly 4:4:1:1 ratio, which was confirmed by NMR spectroscopy.¹⁰ This result indicated that the migration of the sulfonyl group may proceed in both intra- and intermolecular manner. Moreover, we also tried to synthesize enantiomerically pure propargylamides to

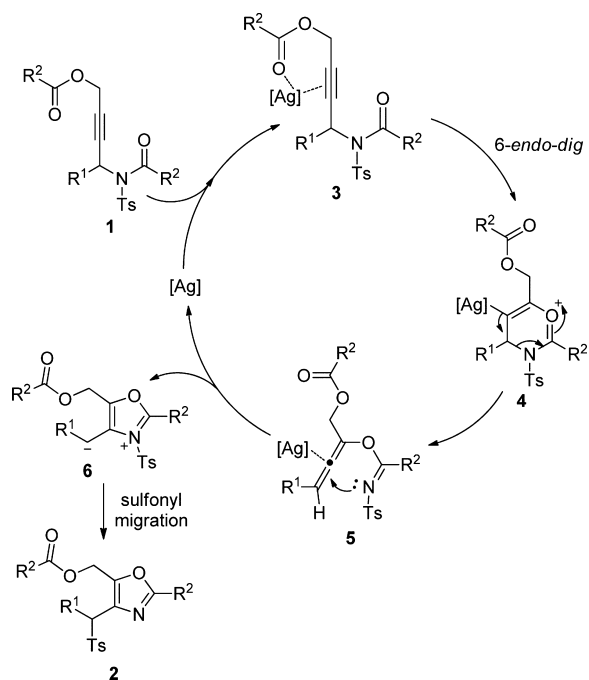
determine if some chiral transfer occurred under the standard condition. Although much effort has been made, unfortunately, we failed to afford the desired enantiomerically pure substrate.

On the basis of these observations, a plausible mechanism was proposed as depicted in Scheme 4. As a first step, we supposed that a π -complex **3** was formed between the alkyne moiety and Ag(I) cation. Meanwhile, the acyloxy group also coordinated with Ag(I) to facilitate subsequent transformations. Then intramolecular nucleophilic attack of the carbonyl oxygen on the amide via 6-*endo-dig* mode resulted in the formation of intermediate **4**, which collapsed into the allene intermediate **5**.¹¹ It is worth noting that 6-*endo-dig* cyclization of propargylamides has been well studied by some other groups.¹² Then, nucleophilic attack of the nitrogen at the allenyl carbon followed to give a zwitterionic intermediate **6** and then

Scheme 3. Crossover Experiment To Probe the Possible Pathway



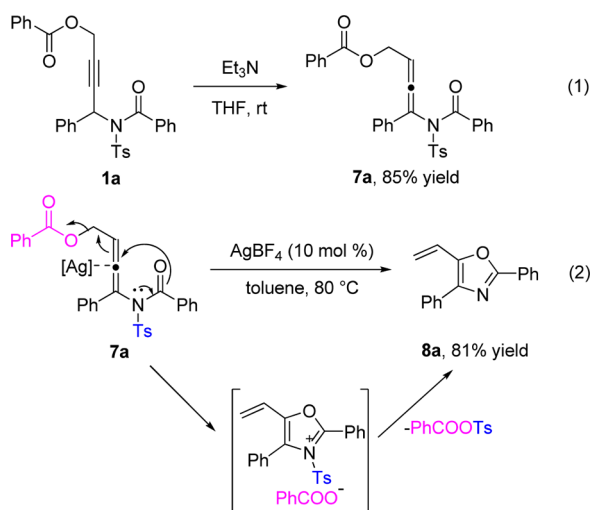
Scheme 4. Proposed Mechanism for the Synthesis of Oxazoles via Sulfonyl Migration



arranged to oxazole **2** via sulfonyl shift in both intra- and intermolecular manner.

Meanwhile, in the course of the synthesis of *N*-sulfonyl propargylamides, we found that the alkyne moiety of the substrate could be easily transformed into allene under basic conditions. For example, allenylamide **7a** was obtained in 85% yield from propargylamide **1a** just using Et₃N as the base. Inspired by this result, we suspected that allenylamide **7a** could also undergo the similar reaction in the presence of silver catalyst. However, to our surprise, no 4-sulfonylmethyl oxazole product was detected. Instead, 5-vinyl oxazole **8a** was obtained in 81% yield. In this transformation, the allene moiety was proposed to be activated by the Ag(I) cation, followed by the intramolecular nucleophilic attack of the oxygen atom at the amide moiety (Scheme 5). The elimination of both sulfonyl and acyloxy groups generated the final vinyl oxazole product.

Scheme 5. Silver(I)-Catalyzed Cyclization of Allenylamide



For this unique characteristic, the reaction provided an alternative for the synthesis of vinyl oxazoles.¹³ Since 5-vinyl oxazole **8a** had already been obtained in a good yield, it is not necessary to further screen the reaction conditions, and we investigated the scope of the substrates directly.

The allene substrates with both electron-withdrawing and electron-donating substituents in aromatic R² group were well-tolerated, providing the corresponding vinyl oxazoles in good yields (Table 4, entries 1–5). In addition, furanyl-derived substrate **7f** underwent this transformation, as well, albeit with low yield. To our delight, alkyl substitutions such as cyclopentyl and methyl in R² were also tolerated and gave the corresponding oxazoles **8g** and **8h** in 65 and 66% yield, respectively (Table 4, entries 6 and 7). Subsequently, the scope of the R¹ group was investigated. The results suggested that both aryl and heterocyclic R¹ substitutions were compatible with this reaction (Table 4, entries 9–12). Notably, naphthyl-derived substrate **7m** could also participate in the cyclization to afford the desired product **8m** in 65% yield.

CONCLUSION

In summary, we have developed a silver(I)-catalyzed cyclization of *N*-sulfonyl propargylamides for the synthesis of 4-(sulfonylmethyl)oxazoles via [3,3] rearrangement and highly regioselective migration of the sulfonyl group. The introduction of the acyloxy group was found to be essential for [3,3] rearrangement. This strategy may provide a potential route for other unrealized rearrangements. Moreover, the allenylamides, generated from the corresponding propargylamides, can also undergo the silver-catalyzed cyclization to give various 5-vinyl oxazoles. This method may find applications in the synthesis of more valuable molecules.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all reactions and manipulations were carried out under an atmosphere of argon using standard Schlenk techniques or in an argon-filled glovebox. Solvents were treated prior to use according to the standard methods. All chemicals were obtained from commercial sources and were used without further purification. Column chromatography was carried out on silica gel (300–400 mesh) using a forced flow of eluent at 0.3–0.5 bar pressure. NMR spectra were recorded at room temperature in CDCl₃ on 400 or 500 MHz spectrometers. The chemical shifts for ¹H NMR were recorded in parts per million downfield from tetramethylsilane (TMS) with CDCl₃ (7.26 ppm) as the internal standard. The chemical shifts for ¹³C NMR were recorded in parts per million downfield using the central peak of CDCl₃ (77.16 ppm) as the internal standard. Coupling constants (*J*) are reported in hertz and refer to apparent peak multiplications.

General Procedure for the Synthesis of *N*-Sulfonyl Propargylamides.

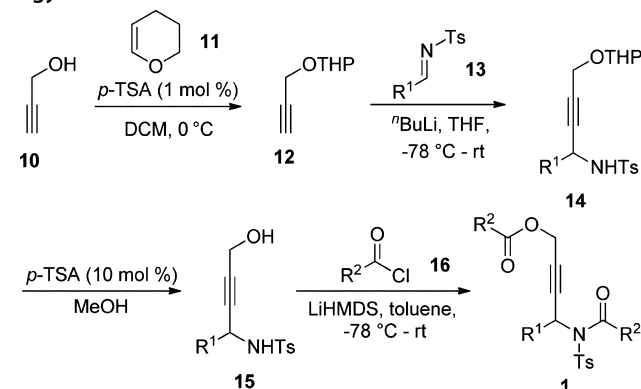
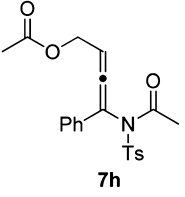
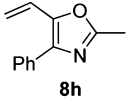
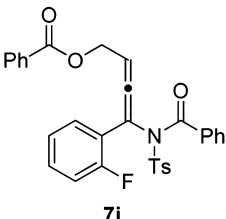
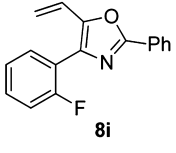
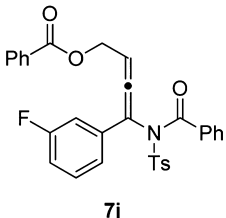
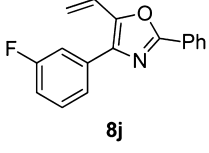
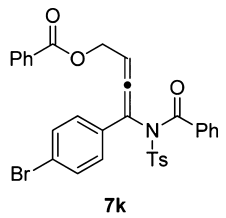
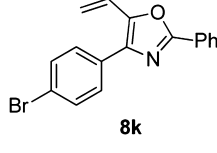
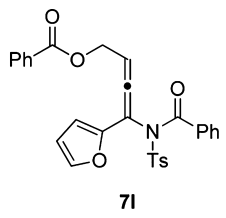
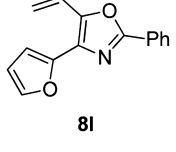
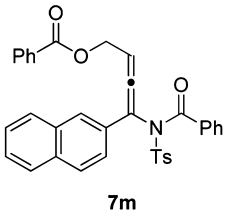
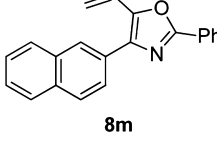


Table 4. Substrate Scope for the Synthesis of Vinyloxazoles^a

Reaction scheme showing the synthesis of vinyloxazoles (8) from vinyloxazones (7) using AgBF_4 (10 mol %) in toluene at 80°C .

entry	7	8	yield (%)
1	<p>7a</p>	<p>8a</p>	81
2	<p>7b</p>	<p>8b</p>	79
3	<p>7c</p>	<p>8c</p>	81
4	<p>7d</p>	<p>8d</p>	81
5	<p>7e</p>	<p>8e</p>	78
6	<p>7f</p>	<p>8f</p>	58
7	<p>7g</p>	<p>8g</p>	65

Table 4. continued

entry	7	8	yield (%)
8			66
9			76
10			85
11			80
12			40
13			65

^aReaction conditions: 7 (0.15 mmol), AgBF₄ (10 mol %), toluene (1.5 mL), 80 °C for 16–20 h.

To a solution of prop-2-yn-1-ol (**10**, 23.4 mL, 400 mmol) in CH₂Cl₂ (200 mL) at 0 °C was added *p*-TsOH (0.760 g, 4 mmol) followed by slow addition of 3,4-dihydro-2*H*-pyran (**11**, 42.00 mL, 460 mmol). After stirring at 0 °C for 5 min, the reaction was warmed to room temperature and stirred for 3 h. The reaction was quenched with saturated NaHCO₃, and the layers were separated. The aqueous layer

was extracted with Et₂O, and the combined organic layers were dried over MgSO₄, concentrated in vacuo, and purified by distillation to give **12** as a colorless oil (50 mL, 90% yield).

To a solution of 2-(prop-2-yn-1-yloxy)tetrahydro-2*H*-pyran **12** (1.40 g, 10.0 mmol) in THF (20 mL) at –78 °C under argon was added *n*-BuLi (4.00 mL, 2.5 M in hexanes, 10.0 mmol), and the

resulting solution was stirred for 40 min at $-78\text{ }^{\circ}\text{C}$. Tosyl imine (**13**, 10.0 mmol) in THF (20 mL) was then added, and the reaction was warmed to room temperature and stirred for 3 h. The reaction was quenched with water, and the layers were separated. The aqueous layer was extracted with Et_2O , and the combined organic layers were washed twice with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by direct crystallization from EtOH/pentane to yield **14** as a white or yellow solid.

To a solution of **14** (8.00 mmol) in MeOH (80 mL) was added *p*-TsOH (0.152 g, 0.8 mmol), and the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with saturated NaHCO_3 , and the resulting suspension was extracted with Et_2O . The combined organic phases were dried over MgSO_4 , and the solvent was removed via rotary evaporation. The crude residue was purified by direct crystallization from EtOH/pentane to afford **15** as a white or yellow solid.

A solution of **15** (2.50 mmol) in 30 mL of toluene was treated at $-78\text{ }^{\circ}\text{C}$ with 5.00 mL (5.00 mmol) of a 1.0 M solution of LiHMDS in THF and stirred for 40 min at $-78\text{ }^{\circ}\text{C}$. The resulting mixture was then treated with acyl chloride **16** (6.00 mmol) and stirred at room temperature for 1 h. The reaction was quenched with water, and the layers were separated. The aqueous layer was extracted with Et_2O , and the combined organic layers were washed twice with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography over silica gel (petroleum ether/EtOAc: 10/1) to give **1** as a white or yellow solid.

4-Phenyl-4-(*N*-tosylbenzamido)but-2-yn-1-yl benzoate (1a): White solid, 1.0462 g, 80% yield, mp $101\text{--}102\text{ }^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.09–8.01 (m, 2H), 7.63 (d, $J = 8.3$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.47–7.37 (m, 4H), 7.36–7.28 (m, 3H), 7.35–7.20 (m, 3H), 7.17–7.13 (m, 4H), 6.35 (s, 1H), 4.99 (d, $J = 1.4$ Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.9, 165.9, 144.9, 136.1, 135.6, 135.0, 133.5, 131.7, 129.9, 129.6, 129.4, 128.9, 128.6, 128.5, 128.4, 128.3, 128.0, 127.8, 82.5, 81.7, 53.8, 52.9, 21.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{25}\text{NO}_5\text{NaS}$ [$\text{M} + \text{Na}$] $^+$ 546.1351, found 546.1349.

4-(2-Methyl-*N*-tosylbenzamido)-4-phenylbut-2-yn-1-yl 2-methylbenzoate (1b): Yellow solid, 0.7171 g, 52% yield, mp $44\text{--}45\text{ }^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.97 (dd, $J = 8.4, 1.3$ Hz, 1H), 7.60–7.55 (m, 4H), 7.44 (td, $J = 7.6, 1.4$ Hz, 1H), 7.35–7.27 (m, 5H), 7.20 (td, $J = 7.5, 1.4$ Hz, 1H), 7.14 (d, $J = 8.1$ Hz, 2H), 7.04 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.01–6.95 (m, 2H), 6.58 (s, 1H), 5.06 (t, $J = 1.9$ Hz, 2H), 2.63 (s, 3H), 2.34 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.1, 166.6, 144.8, 140.6, 136.4, 136.2, 136.0, 134.3, 132.4, 131.8, 130.8, 130.22, 130.18, 129.2, 128.9, 128.7, 128.4, 128.1, 127.5, 127.3, 125.8, 124.8, 82.4, 81.4, 53.1, 52.5, 21.8, 21.6, 18.9; HRMS (ESI-TOF) m/z calcd for $\text{C}_{33}\text{H}_{29}\text{NO}_5\text{NaS}$ [$\text{M} + \text{Na}$] $^+$ 574.1664, found 574.1653.

4-(3-Methoxy-*N*-tosylbenzamido)-4-phenylbut-2-yn-1-yl 3-methoxybenzoate (1c): Yellow solid, 0.4815 g, 33% yield, mp $43\text{--}44\text{ }^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.72–7.64 (m, 3H), 7.61 (dd, $J = 2.6, 1.5$ Hz, 1H), 7.51–7.43 (m, 2H), 7.38 (t, $J = 8.0$ Hz, 1H), 7.32–7.26 (m, 3H), 7.20–7.12 (m, 4H), 7.05–7.02 (m, 1H), 6.94–6.89 (m, 1H), 6.82 (dd, $J = 2.4, 1.6$ Hz, 1H), 6.40 (s, 1H), 5.06 (d, $J = 1.9$ Hz, 2H), 3.85 (s, 3H), 3.65 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.7, 165.8, 159.8, 159.2, 144.9, 136.2, 136.0, 135.6, 130.9, 129.7, 129.4, 129.2, 129.0, 128.6, 128.4, 127.9, 122.4, 120.8, 120.0, 118.4, 114.5, 112.7, 82.7, 81.7, 55.6, 55.3, 54.1, 53.0, 21.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{33}\text{H}_{29}\text{NO}_7\text{NaS}$ [$\text{M} + \text{Na}$] $^+$ 606.1562, found 606.1542.

4-(3-Bromo-*N*-tosylbenzamido)-4-phenylbut-2-yn-1-yl 3-bromobenzoate (1d): Yellow solid, 0.8688 g, 51% yield, mp $53\text{--}54\text{ }^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.24 (t, $J = 1.7$ Hz, 1H), 8.08–7.99 (m, 1H), 7.74 (ddd, $J = 8.0, 2.0, 1.0$ Hz, 1H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.51–7.43 (m, 3H), 7.37 (t, $J = 7.9$ Hz, 1H), 7.33–7.27 (m, 4H), 7.26–7.22 (m, 3H), 7.09 (t, $J = 7.9$ Hz, 1H), 6.47 (s, 1H), 5.05 (d, $J = 1.8$ Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.3, 164.6, 145.4, 136.9, 136.5, 135.9, 135.4, 134.4, 133.0, 131.6, 131.1, 130.3, 129.7, 129.5, 128.8, 128.7, 128.58, 128.56, 127.8, 126.9, 122.8,

122.0, 82.7, 81.6, 53.5, 53.2, 21.8; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{23}\text{NO}_5\text{NaSBr}_2$ [$\text{M} + \text{Na}$] $^+$ 701.9561, found 701.9540.

4-(3-Fluoro-*N*-tosylbenzamido)-4-phenylbut-2-yn-1-yl 3-fluorobenzoate (1e): Yellow solid, 0.6015 g, 43% yield, mp $69\text{--}70\text{ }^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.93–7.86 (m, 1H), 7.77 (ddd, $J = 9.2, 2.4, 1.5$ Hz, 1H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.52–7.41 (m, 3H), 7.33–7.22 (m, 6H), 7.20–7.12 (m, 2H), 7.06 (tdd, $J = 8.3, 2.5, 1.1$ Hz, 1H), 7.01–6.94 (m, 1H), 6.42 (s, 1H), 5.03 (d, $J = 1.8$ Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.5 (d, $J = 2.3$ Hz), 164.8 (d, $J = 2.9$ Hz), 162.7 (d, $J = 247.5$ Hz), 162.0 (d, $J = 248.3$ Hz), 145.3, 137.0 (d, $J = 7.1$ Hz), 135.9, 135.39, 131.8 (d, $J = 7.4$ Hz), 130.4 (d, $J = 7.8$ Hz), 129.7 (d, $J = 7.8$ Hz), 129.6, 128.9, 128.6, 128.5, 127.8, 125.7 (d, $J = 2.9$ Hz), 124.2 (d, $J = 3.0$ Hz), 120.6 (d, $J = 21.3$ Hz), 118.7 (d, $J = 21.1$ Hz), 116.8 (d, $J = 23.1$ Hz), 115.4 (d, $J = 23.6$ Hz), 82.6, 81.6, 53.6, 53.2, 21.7; ^{19}F NMR (377 MHz, CDCl_3) δ $-112.5, -112.6$; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{23}\text{NO}_5\text{NaSF}_2$ [$\text{M} + \text{Na}$] $^+$ 582.1163, found 582.1145.

4-(4-Methyl-*N*-tosylbenzamido)-4-phenylbut-2-yn-1-yl 4-methylbenzoate (1f): Yellow solid, 0.4689 g, 34% yield, mp $51\text{--}52\text{ }^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.99 (d, $J = 8.2$ Hz, 2H), 7.68 (d, $J = 8.3$ Hz, 2H), 7.47 (dd, $J = 7.0, 1.2$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.30–7.24 (m, 5H), 7.18 (d, $J = 8.1$ Hz, 2H), 7.02 (d, $J = 7.9$ Hz, 2H), 6.33 (s, 1H), 5.00 (d, $J = 1.8$ Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 171.1, 166.0, 144.8, 144.3, 142.6, 136.2, 135.6, 132.2, 130.0, 129.39, 129.37, 129.0, 128.8, 128.5, 128.3, 128.0, 127.0, 82.5, 81.8, 54.1, 52.8, 21.8, 21.7, 21.6; HRMS (ESI-TOF) m/z calcd for $\text{C}_{33}\text{H}_{29}\text{NO}_5\text{NaS}$ [$\text{M} + \text{Na}$] $^+$ 574.1664, found 574.1659.

4-(4-Chloro-*N*-tosylbenzamido)-4-phenylbut-2-yn-1-yl 4-chlorobenzoate (1g): Yellow solid, 0.5925 g, 40% yield, mp $142\text{--}143\text{ }^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.05–8.00 (m, 2H), 7.71–7.63 (m, 2H), 7.48–7.41 (m, 4H), 7.31–7.25 (m, 5H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.19–7.14 (m, 2H), 6.37 (s, 1H), 4.99 (dd, $J = 1.8, 0.7$ Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.0, 165.0, 145.2, 140.1, 138.2, 135.9, 135.3, 133.5, 131.3, 130.0, 129.5, 129.0, 128.8, 128.6, 128.5, 128.2, 128.0, 127.8, 82.5, 81.6, 53.6, 53.0, 21.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{23}\text{NO}_5\text{NaSCL}_2$ [$\text{M} + \text{Na}$] $^+$ 614.0572, found 614.0570.

4-(4-Fluoro-*N*-tosylbenzamido)-4-phenylbut-2-yn-1-yl 4-fluorobenzoate (1h): Yellow solid, 0.8393 g, 60% yield, mp $46\text{--}47\text{ }^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.15–8.07 (m, 2H), 7.68 (d, $J = 8.3$ Hz, 2H), 7.48–7.36 (m, 4H), 7.31–7.21 (m, 5H), 7.16 (t, $J = 8.7$ Hz, 2H), 6.89 (t, $J = 8.6$ Hz, 2H), 6.37 (s, 1H), 5.00 (d, $J = 1.1$ Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.1, 166.2 (d, $J = 254.8$ Hz), 165.0, 164.9 (d, $J = 253.4$ Hz), 145.1, 136.0, 135.4, 132.6 (d, $J = 9.4$ Hz), 131.3 (d, $J = 9.2$ Hz), 129.6, 128.9, 128.6, 128.5, 127.9, 125.9 (d, $J = 2.8$ Hz), 115.9 (d, $J = 22.1$ Hz), 115.2 (d, $J = 22.1$ Hz), 82.6, 81.7, 53.7, 53.0, 21.8; ^{19}F NMR (471 MHz, CDCl_3) δ -104.6 (dd, $J = 13.3, 7.4$ Hz), -105.8 (m); HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{23}\text{NO}_5\text{NaSF}_2$ [$\text{M} + \text{Na}$] $^+$ 582.1163, found 582.1171.

4-Phenyl-4-(*N*-tosyl-4-(trifluoromethyl)benzamido)but-2-yn-1-yl 4-(trifluoromethyl)benzoate (1i): White solid, 0.4617 g, 28% yield, mp $115\text{--}116\text{ }^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.21 (d, $J = 8.1$ Hz, 2H), 7.75 (d, $J = 8.2$ Hz, 2H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.48–7.40 (m, 4H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.29–7.25 (m, 3H), 7.21 (d, $J = 8.1$ Hz, 2H), 6.45 (s, 1H), 5.05 (d, $J = 1.8$ Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.7, 164.8, 145.4, 138.4, 135.8, 135.2, 135.0, 133.2, 132.9, 132.8, 130.3, 129.9, 129.8, 129.7, 129.5, 128.8, 128.7, 128.6, 128.2, 127.8, 127.0, 126.3, 125.8 (dd, $J = 7.1, 3.5$ Hz), 124.9 (dd, $J = 6.9, 3.6$ Hz), 123.7 (d, $J = 272.8$ Hz), 123.6 (d, $J = 272.5$ Hz), 82.6, 81.5, 53.4, 53.3, 21.7; ^{19}F NMR (377 MHz, CDCl_3) δ $-63.7, -63.8$; HRMS (ESI-TOF) m/z calcd for $\text{C}_{33}\text{H}_{23}\text{NO}_5\text{NaSF}_6$ [$\text{M} + \text{Na}$] $^+$ 682.1099, found 682.1087.

Ethyl 4-(*(ethoxycarbonyloxy)-1-phenylbut-2-yn-1-yl*)(tosyl)carbamate (1j): Yellow solid, 0.4365 g, 38% yield, mp $64\text{--}65\text{ }^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.89 (d, $J = 8.4$ Hz, 2H), 7.70–7.52 (m, 2H), 7.39–7.30 (m, 5H), 6.72 (s, 1H), 4.86 (d, $J = 1.8$ Hz, 2H), 4.25 (q, $J = 7.1$ Hz, 2H), 4.00 (qd, $J = 7.1, 3.3$ Hz, 2H), 2.45 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.00 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.7, 151.3, 144.8, 136.6, 136.5, 129.5, 128.7, 128.4,

128.1, 127.3, 83.1, 80.2, 64.7, 63.6, 55.5, 52.2, 21.8, 14.4, 13.8; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{25}NO_7NaS$ [$M + Na$] $^+$ 482.1249, found 482.1250.

4-Phenyl-4-(*N*-tosylcyclopentanecarboxamido)but-2-yn-1-yl-cyclopentanecarboxylate (1k): White solid, 0.2284 g, 18% yield, mp 56–57 °C; 1H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, $J = 8.3$ Hz, 2H), 7.57 (d, $J = 8.0$ Hz, 2H), 7.40–7.29 (m, 5H), 6.82 (s, 1H), 4.81 (d, $J = 1.7$ Hz, 2H), 2.96 (p, $J = 7.9$ Hz, 1H), 2.78 (p, $J = 8.0$ Hz, 1H), 2.45 (s, 3H), 2.00–1.18 (m, 15H), 0.98–0.77 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.0, 175.9, 144.7, 137.0, 136.9, 129.7, 128.8, 128.2, 128.1, 126.7, 82.4, 81.8, 52.0, 51.6, 45.4, 43.6, 31.5, 31.0, 30.1, 26.34, 26.29, 25.9, 21.8; HRMS (ESI-TOF) m/z calcd for $C_{29}H_{33}NO_5NaS$ [$M + Na$] $^+$ 530.1977, found 530.1968.

4-(2-Fluorophenyl)-4-(*N*-tosylbenzamido)but-2-yn-1-yl benzoate (1l): Yellow solid, 0.3520 g, 26% yield, mp 106–107 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, $J = 7.8$ Hz, 2H), 7.93 (t, $J = 7.5$ Hz, 1H), 7.61 (t, $J = 8.7$ Hz, 3H), 7.53–7.41 (m, 5H), 7.37–7.27 (m, 3H), 7.19 (t, $J = 7.6$ Hz, 1H), 7.08 (d, $J = 8.2$ Hz, 2H), 6.96–6.79 (m, 1H), 6.35 (s, 1H), 5.15 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 165.9, 160.8 (d, $J = 249.6$ Hz), 144.6, 136.2, 134.5, 133.5, 132.2 (d, $J = 2.4$ Hz), 132.0, 130.9, 130.8, 129.9, 129.6, 129.1, 128.9, 128.6, 128.5, 128.3, 124.2 (d, $J = 3.4$ Hz), 122.1 (d, $J = 12.0$ Hz), 115.2 (d, $J = 20.6$ Hz), 82.0, 81.7, 53.0, 50.4, 21.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.5 (dd, $J = 13.6$, 9.6 Hz); HRMS (ESI-TOF) m/z calcd for $C_{31}H_{24}NO_5FNaS$ [$M + Na$] $^+$ 564.1257, found 564.1248.

4-(3-Fluorophenyl)-4-(*N*-tosylbenzamido)but-2-yn-1-yl benzoate (1m): Red solid, 0.6228 g, 46% yield, mp 88–89 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, $J = 7.5$ Hz, 2H), 7.69 (d, $J = 8.2$ Hz, 2H), 7.62 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.41–7.35 (m, 3H), 7.31–7.18 (m, 7H), 6.97 (t, $J = 7.7$ Hz, 1H), 6.39 (s, 1H), 5.04 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 165.9, 162.8 (d, $J = 246.8$ Hz), 145.2, 138.3 (d, $J = 7.3$ Hz), 136.0, 134.9, 133.6, 131.8, 130.1, 130.1, 130.0, 129.6, 129.6, 128.9, 128.7, 128.4, 128.0, 123.4, 115.4 (d, $J = 21.6$ Hz), 115.2 (d, $J = 23.7$ Hz), 82.0, 81.6, 53.2, 52.8, 21.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.0; HRMS (ESI-TOF) m/z calcd for $C_{31}H_{24}NO_5FNaS$ [$M + Na$] $^+$ 564.1257, found 564.1252.

4-(3-Methoxyphenyl)-4-(*N*-tosylbenzamido)but-2-yn-1-yl benzoate (1n): Yellow solid, 0.4982 g, 36% yield, mp 47–48 °C; 1H NMR (500 MHz, $CDCl_3$) δ 8.14–8.07 (m, 2H), 7.77–7.71 (m, 2H), 7.66–7.55 (m, 1H), 7.50–7.47 (m, 2H), 7.39–7.32 (m, 3H), 7.22–7.16 (m, 5H), 7.04–6.99 (m, 1H), 6.96 (s, 1H), 6.78 (dd, $J = 8.2$, 2.5 Hz, 1H), 6.37 (s, 1H), 5.03 (dd, $J = 1.8$, 0.9 Hz, 2H), 3.69 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 165.9, 159.8, 145.0, 137.1, 136.1, 135.1, 133.6, 131.7, 130.0, 129.7, 129.6, 129.5, 129.0, 128.7, 128.5, 128.0, 120.0, 114.3, 113.3, 82.6, 81.8, 55.3, 53.8, 52.9, 21.7; HRMS (ESI-TOF) m/z calcd for $C_{32}H_{27}NO_6NaS$ [$M + Na$] $^+$ 576.1457, found 576.1456.

4-(4-Bromophenyl)-4-(*N*-tosylbenzamido)but-2-yn-1-yl benzoate (1o): Red solid, 0.4669 g, 31% yield, mp 56–57 °C; 1H NMR (500 MHz, $CDCl_3$) δ 8.12–8.07 (m, 2H), 7.69–7.65 (m, 2H), 7.63–7.58 (m, 1H), 7.51–7.46 (m, 2H), 7.43–7.34 (m, 7H), 7.25–7.18 (m, 4H), 6.33 (s, 1H), 5.02 (dd, $J = 1.8$, 0.5 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 165.9, 145.2, 136.0, 134.9, 133.6, 131.9, 131.7, 130.0, 129.65, 129.56, 128.8, 128.7, 128.5, 128.1, 122.6, 82.00, 81.99, 53.3, 52.8, 21.8; HRMS (ESI-TOF) m/z calcd for $C_{31}H_{24}BrNO_5NaS$ [$M + Na$] $^+$ 624.0456, found 624.0441.

4-(Naphthalen-1-yl)-4-(*N*-tosylbenzamido)but-2-yn-1-yl benzoate (1p): White solid, 0.2983 g, 36% yield, mp 108–109 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, $J = 8.6$ Hz, 1H), 8.12 (d, $J = 7.7$ Hz, 2H), 8.05 (d, $J = 7.2$ Hz, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.77 (d, $J = 8.1$ Hz, 1H), 7.65–7.44 (m, 7H), 7.40–7.35 (m, 4H), 7.17 (t, $J = 7.7$ Hz, 2H), 7.09 (d, $J = 8.1$ Hz, 2H), 6.98 (s, 1H), 5.00 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 166.0, 144.8, 136.0, 135.5, 133.9, 133.5, 132.3, 130.6, 130.5, 130.0, 129.7, 129.4, 129.33, 129.30, 129.2, 128.7, 128.7, 127.9, 127.2, 125.9, 125.1, 122.7, 83.3, 81.8, 53.0, 52.1, 21.7; HRMS (ESI-TOF) m/z calcd for $C_{35}H_{27}NO_5NaS$ [$M + Na$] $^+$ 596.1508, found 596.1519.

4-(Naphthalen-2-yl)-4-(*N*-tosylbenzamido)but-2-yn-1-yl benzoate (1q): Yellow solid, 0.2386 g, 32% yield, mp 101–102 °C; 1H

NMR (400 MHz, $CDCl_3$) δ 8.13 (d, $J = 7.8$ Hz, 2H), 7.94 (s, 1H), 7.81–7.66 (m, 5H), 7.60 (t, $J = 7.3$ Hz, 1H), 7.55–7.42 (m, 5H), 7.39 (d, $J = 7.7$ Hz, 2H), 7.31 (t, $J = 7.4$ Hz, 1H), 7.14 (t, $J = 8.5$ Hz, 4H), 6.54 (s, 1H), 5.09 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 165.9, 144.9, 135.9, 134.9, 133.5, 133.0, 132.9, 132.7, 131.8, 129.9, 129.6, 129.4, 128.9, 128.6, 128.4, 127.9, 127.7, 127.6, 126.6, 126.4, 124.9, 82.5, 81.9, 54.0, 52.9, 21.7; HRMS (ESI-TOF) m/z calcd for $C_{35}H_{27}NO_5NaS$ [$M + Na$] $^+$ 596.1508, found 596.1504.

4-(Furan-2-yl)-4-(*N*-tosylbenzamido)but-2-yn-1-yl benzoate (1r): Brown solid, 0.1926 g, 15% yield, mp 58–59 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.10–8.04 (m, 2H), 7.66 (d, $J = 8.3$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.47–7.43 (m, 4H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.26–7.15 (m, 5H), 6.43 (d, $J = 3.2$ Hz, 1H), 6.29 (s, 1H), 6.28 (dd, $J = 3.2$, 1.8 Hz, 1H), 5.02 (d, $J = 1.2$ Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 165.9, 148.2, 144.8, 142.8, 136.2, 134.5, 133.5, 131.9, 129.9, 129.6, 129.3, 128.9, 128.8, 128.6, 128.21, 128.17, 127.9, 111.0, 110.9, 81.2, 80.3, 52.7, 48.6, 21.7; HRMS (ESI-TOF) m/z calcd for $C_{29}H_{23}NO_6NaS$ [$M + Na$] $^+$ 536.1144, found 536.1147.

4-Phenyl-4-(*N*-(phenylsulfonyl)benzamido)but-2-yn-1-yl benzoate (1s): Yellow solid, 0.3822 g, 30% yield, mp 107–108 °C; 1H NMR (500 MHz, $CDCl_3$) δ 8.13–8.08 (m, 2H), 7.84–7.77 (m, 2H), 7.65–7.57 (m, 1H), 7.55–7.46 (m, 5H), 7.43–7.35 (m, 5H), 7.30–7.25 (m, 3H), 7.23–7.19 (m, 2H), 6.39 (s, 1H), 5.03 (dd, $J = 1.7$, 1.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 165.9, 139.1, 135.5, 135.0, 133.8, 133.6, 131.9, 130.0, 129.7, 128.90, 128.86, 128.7, 128.6, 128.5, 128.4, 128.1, 127.9, 82.4, 81.8, 54.0, 52.9; HRMS (ESI-TOF) m/z calcd for $C_{30}H_{23}NO_5NaS$ [$M + Na$] $^+$ 532.1195, found 532.1203.

4-(4-Fluoro-*N*-(phenylsulfonyl)benzamido)-4-phenylbut-2-yn-1-yl-4-fluorobenzoate (1t): White solid, 0.7465 g, 54% yield, mp 99–100 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.17–8.05 (m, 2H), 7.87–7.76 (m, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.46–7.42 (m, 6H), 7.28–7.26 (m, 3H), 7.21–7.10 (m, 2H), 6.89 (t, $J = 8.6$ Hz, 2H), 6.37 (s, 1H), 4.98 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 167.4, 164.9 (d, $J = 253.8$ Hz), 164.9, 138.8, 135.2, 133.9, 132.6, 132.5, 131.3, 131.25, 131.18, 131.1, 128.9, 128.8, 128.6, 128.5, 127.9, 125.8 (d, $J = 3.0$ Hz), 115.9 (d, $J = 22.1$ Hz), 115.2 (d, $J = 22.1$ Hz), 82.3, 81.8, 53.8, 52.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -104.5 (m), -106.1 (m); HRMS (ESI-TOF) m/z calcd for $C_{30}H_{21}NO_5F_2NaS$ [$M + Na$] $^+$ 568.1006, found 568.1002.

4-(*N*-(Methylsulfonyl)benzamido)-4-phenylbut-2-yn-1-yl benzoate (1u): Yellow solid, 0.1074 g, 12% yield, mp 100–101 °C; 1H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, $J = 8.3$, 1.2 Hz, 2H), 7.64–7.54 (m, 3H), 7.50–7.42 (m, 5H), 7.33–7.27 (m, 5H), 6.22 (s, 1H), 5.10–5.06 (m, 2H), 3.16 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 165.9, 135.3, 134.1, 133.6, 132.5, 129.9, 129.6, 128.7, 128.5, 128.0, 82.5, 82.2, 54.7, 52.8, 43.1; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{21}NO_5NaS$ [$M + Na$] $^+$ 470.1038, found 470.1034.

Representative Procedures for the Synthesis of 4-(Sulfonylmethyl)oxazoles. In a 10 mL flame-dried Schlenk tube, $AgBF_4$ (10 mol %) and *N*-sulfonyl propargylamide **1** (0.2 or 0.1 mmol) were introduced under argon and dissolved in 2 mL of dry and degassed toluene. The resulting yellow solution was stirred at 80 °C for 10 h and concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether/EtOAc: 10/1) afforded the expected product.

(2-Phenyl-4-(phenyl(tosyl)methyl)oxazol-5-yl)methyl benzoate (2a): White solid, 85.8 mg, 82% yield, mp 164–165 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.10–8.02 (m, 2H), 8.00 (d, $J = 7.5$ Hz, 2H), 7.79 (d, $J = 7.1$ Hz, 2H), 7.54–7.35 (m, 8H), 7.30–7.28 (m, 3H), 7.14 (d, $J = 8.0$ Hz, 2H), 5.83 (s, 1H), 5.60 (d, $J = 13.9$ Hz, 1H), 5.27 (d, $J = 13.9$ Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 161.6, 146.3, 144.7, 134.3, 133.7, 133.4, 131.4, 131.1, 130.9, 129.9, 129.8, 129.4, 129.2, 128.9, 128.8, 128.5, 128.2, 127.0, 126.8, 68.0, 54.9, 21.7; HRMS (ESI-TOF) m/z calcd for $C_{31}H_{25}NO_5NaS$ [$M + Na$] $^+$ 546.1351, found 546.1349.

(4-(Phenyl(tosyl)methyl)-2-(*o*-tolyl)oxazol-5-yl)methyl 2-methylbenzoate (2b): White solid, 41.4 mg, 75% yield, mp 143–144 °C; 1H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 8.3$ Hz, 1H), 7.80–7.73 (m, 2H), 7.50–7.46 (m, 2H), 7.39–7.26 (m, 7H), 7.20 (d, $J = 7.7$ Hz, 2H), 7.15 (d, $J = 7.9$ Hz, 2H), 5.84 (s, 1H),

5.61 (d, $J = 13.8$ Hz, 1H), 5.24 (d, $J = 13.8$ Hz, 1H), 2.69 (s, 3H), 2.54 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.0, 161.8, 146.0, 144.7, 140.8, 138.2, 134.5, 133.3, 132.5, 131.9, 131.8, 131.5, 131.3, 131.0, 130.5, 129.9, 129.2, 129.0, 128.9, 128.8, 128.2, 126.1, 125.9, 68.3, 54.7, 22.3, 21.9, 21.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{33}\text{H}_{29}\text{NO}_5\text{NaS} [\text{M} + \text{Na}]^+$ 574.1664, found 574.1665.

(2-(3-Methoxyphenyl)-4-(phenyl(tosyl)methyl)oxazol-5-yl)methyl 3-methoxybenzoate (**2c**): White solid, 46.1 mg, 79% yield, mp 50–51 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.78–7.72 (m, 2H), 7.67–7.62 (m, 1H), 7.61–7.58 (m, 1H), 7.57 (dd, $J = 2.5, 1.5$ Hz, 1H), 7.52 (dd, $J = 2.6, 1.5$ Hz, 1H), 7.50–7.45 (m, 2H), 7.36 (t, $J = 8.0$ Hz, 1H), 7.33–7.26 (m, 4H), 7.15 (d, $J = 7.9$ Hz, 2H), 7.08 (ddd, $J = 8.2, 2.7, 1.0$ Hz, 1H), 7.00 (ddd, $J = 8.3, 2.6, 0.9$ Hz, 1H), 5.78 (s, 1H), 5.59 (d, $J = 13.9$ Hz, 1H), 5.27 (d, $J = 13.9$ Hz, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.2, 161.5, 160.6, 159.8, 146.4, 144.8, 134.4, 133.8, 131.5, 131.2, 130.8, 130.0, 129.9, 129.6, 129.2, 129.0, 128.3, 122.4, 120.0, 119.4, 117.1, 114.4, 112.0, 68.2, 55.6, 55.2, 21.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{33}\text{H}_{29}\text{NO}_7\text{NaS} [\text{M} + \text{Na}]^+$ 606.1562, found 606.1560.

(2-(3-Bromophenyl)-4-(phenyl(tosyl)methyl)oxazol-5-yl)methyl 3-bromobenzoate (**2d**): Yellow solid, 49.2 mg, 72% yield, mp 77–78 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.18 (t, $J = 1.7$ Hz, 1H), 8.13 (t, $J = 1.7$ Hz, 1H), 8.00–7.96 (m, 1H), 7.95–7.90 (m, 1H), 7.76–7.70 (m, 2H), 7.66 (ddd, $J = 8.0, 2.0, 1.1$ Hz, 1H), 7.58 (ddd, $J = 8.0, 2.0, 1.0$ Hz, 1H), 7.49–7.44 (m, 2H), 7.34–7.26 (m, 5H), 7.17 (d, $J = 7.9$ Hz, 2H), 5.77 (s, 1H), 5.62 (d, $J = 13.9$ Hz, 1H), 5.29 (d, $J = 13.9$ Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 165.0, 160.3, 146.6, 144.9, 136.5, 134.3, 134.2, 134.0, 132.9, 131.4, 131.0, 130.4, 130.2, 129.9, 129.8, 129.3, 129.1, 128.8, 128.6, 128.4, 125.4, 123.0, 122.7, 68.1, 55.3, 21.8; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{23}\text{NO}_5\text{NaSBr}_2 [\text{M} + \text{Na}]^+$ 701.9561, found 701.9552.

(2-(3-Fluorophenyl)-4-(phenyl(tosyl)methyl)oxazol-5-yl)methyl 3-fluorobenzoate (**2e**): Yellow solid, 48.9 mg, 80% yield, mp 66–67 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.87–7.83 (m, 1H), 7.83–7.78 (m, 1H), 7.74 (ddd, $J = 8.1, 3.4, 1.6$ Hz, 3H), 7.68 (ddd, $J = 9.2, 2.6, 1.5$ Hz, 1H), 7.50–7.35 (m, 4H), 7.33–7.21 (m, 4H), 7.19–7.12 (m, 3H), 5.79 (s, 1H), 5.64 (d, $J = 13.9$ Hz, 1H), 5.30 (d, $J = 13.9$ Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 165.2 (d, $J = 2.9$ Hz), 163.0 (d, $J = 246.7$ Hz), 162.6 (d, $J = 247.6$ Hz), 160.6 (d, $J = 3.4$ Hz), 146.6, 144.9, 134.3, 134.2, 131.6 (d, $J = 7.6$ Hz), 131.4, 131.0, 130.6 (d, $J = 8.1$ Hz), 130.2 (d, $J = 7.8$ Hz), 129.9, 129.3, 129.1, 128.9 (d, $J = 8.5$ Hz), 128.4, 125.7 (d, $J = 2.9$ Hz), 122.6, 120.6 (d, $J = 21.3$ Hz), 118.0 (d, $J = 21.3$ Hz), 116.8 (d, $J = 23.2$ Hz), 113.9 (d, $J = 24.1$ Hz), 68.1, 55.3, 21.7; ^{19}F NMR (377 MHz, CDCl_3) δ -112.58, -112.59; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{23}\text{NO}_5\text{NaSF}_2 [\text{M} + \text{Na}]^+$ 582.1163, found 582.1154.

(4-(Phenyl(tosyl)methyl)-2-(p-tolyl)oxazol-5-yl)methyl 4-methylbenzoate (**2f**): White solid, 30.7 mg, 56% yield, mp 157–158 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.95–7.91 (m, 2H), 7.90–7.85 (m, 2H), 7.76 (dd, $J = 7.7, 1.8$ Hz, 2H), 7.51–7.45 (m, 2H), 7.31–7.23 (m, 5H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 5.78 (s, 1H), 5.55 (d, $J = 13.9$ Hz, 1H), 5.23 (d, $J = 13.9$ Hz, 1H), 2.40 (s, 3H), 2.37 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.4, 161.9, 146.2, 144.7, 144.2, 141.3, 134.6, 133.6, 131.5, 131.2, 130.0, 129.9, 129.5, 129.3, 129.2, 129.0, 128.3, 126.9, 124.5, 68.19, 54.9, 21.81, 21.75, 21.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{33}\text{H}_{29}\text{NO}_5\text{NaS} [\text{M} + \text{Na}]^+$ 574.1664, found 574.1672.

(2-(4-Chlorophenyl)-4-(phenyl(tosyl)methyl)oxazol-5-yl)methyl 4-chlorobenzoate (**2g**): White solid, 40.5 mg, 67% yield, mp 111–112 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.02–7.97 (m, 2H), 7.96–7.90 (m, 2H), 7.74–7.70 (m, 2H), 7.49–7.41 (m, 4H), 7.40–7.35 (m, 2H), 7.32–7.26 (m, 3H), 7.16 (d, $J = 8.0$ Hz, 2H), 5.77 (s, 1H), 5.62 (d, $J = 13.9$ Hz, 1H), 5.28 (d, $J = 13.9$ Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 165.5, 160.9, 146.5, 144.9, 140.1, 137.2, 134.4, 134.0, 131.4, 131.4, 131.1, 129.9, 129.3, 129.2, 129.1, 129.0, 128.4, 128.2, 128.0, 125.5, 68.2, 55.2, 21.8; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{23}\text{NO}_5\text{NaS} [\text{M} + \text{Na}]^+$ 614.0572, found 614.0574.

(2-(4-Fluorophenyl)-4-(phenyl(tosyl)methyl)oxazol-5-yl)methyl 4-fluorobenzoate (**2h**): White solid, 88.9 mg, 81% yield, mp 61–62 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.09–7.98 (m, 4H), 7.74 (dd, $J = 8.0,$

1.5 Hz, 2H), 7.50–7.42 (m, 2H), 7.32–7.26 (m, 3H), 7.18–7.11 (m, 5H), 7.10–7.04 (m, 2H), 5.78 (s, 1H), 5.61 (d, $J = 13.9$ Hz, 1H), 5.27 (d, $J = 13.9$ Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.1 (d, $J = 254.7$ Hz), 165.3, 164.5 (d, $J = 251.9$ Hz), 160.9, 146.4, 144.8, 134.4, 133.9, 132.6, 132.5, 131.4, 131.1, 129.8, 129.23, 129.16, 129.13, 129.06, 129.0, 128.4, 128.3, 125.8 (d, $J = 2.9$ Hz), 125.4, 123.4 (d, $J = 3.1$ Hz), 116.1 (d, $J = 22.2$ Hz), 115.8 (d, $J = 22.1$ Hz), 68.1, 55.1, 21.8; ^{19}F NMR (377 MHz, CDCl_3) δ -105.2, -109.0; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{23}\text{NO}_5\text{NaSF}_2 [\text{M} + \text{Na}]^+$ 582.1163, found 582.1162.

(4-(Phenyl(tosyl)methyl)-2-(4-(trifluoromethyl)phenyl)oxazol-5-yl)-methyl-4-(trifluoromethyl)benzoate (**2i**): White solid, 52.6 mg, 79% yield, mp 128–129 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.17 (d, $J = 8.1$ Hz, 2H), 8.13 (d, $J = 8.2$ Hz, 2H), 7.75–7.70 (m, 4H), 7.68 (d, $J = 8.3$ Hz, 2H), 7.47 (d, $J = 8.2$ Hz, 2H), 7.34–7.27 (m, 3H), 7.17 (d, $J = 8.0$ Hz, 2H), 5.79 (s, 1H), 5.71 (d, $J = 13.9$ Hz, 1H), 5.38 (d, $J = 13.9$ Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 165.2, 160.4, 146.9, 145.0, 135.5, 135.2, 135.0, 134.7, 134.4, 134.3, 133.0, 132.8, 132.7, 132.6, 131.4, 131.0, 130.4, 130.1, 129.9, 129.3, 129.2, 128.4, 127.2, 126.0, 125.93, 125.90, 125.7, 125.63, 125.60, 123.9 (d, $J = 272.5$ Hz), 123.6 (d, $J = 272.7$ Hz), 68.2, 55.4, 21.8; ^{19}F NMR (377 MHz, CDCl_3) δ -63.5, -63.8; HRMS (ESI-TOF) m/z calcd for $\text{C}_{33}\text{H}_{23}\text{NO}_5\text{NaSF}_6 [\text{M} + \text{Na}]^+$ 682.1099, found 682.1083.

(4-(2-Fluorophenyl)(tosyl)methyl)-2-phenyloxazol-5-yl)methyl benzoate (**2j**): White solid, 77.0 mg, 72% yield, mp 66–67 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.59–8.48 (m, 1H), 8.12–7.99 (m, 4H), 7.56–7.52 (m, 3H), 7.48–7.38 (m, 5H), 7.30 (d, $J = 7.4$ Hz, 1H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.16 (d, $J = 8.1$ Hz, 2H), 6.92 (t, $J = 9.1$ Hz, 1H), 6.20 (s, 1H), 5.54 (d, $J = 13.9$ Hz, 1H), 5.36 (d, $J = 13.9$ Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.1, 161.7, 161.0 (d, $J = 249.4$ Hz), 146.8, 145.0, 134.5, 133.4, 133.3, 132.6, 131.0, 130.8 (d, $J = 8.5$ Hz), 130.0, 129.6, 129.6, 129.4, 128.8, 128.5, 127.0, 126.9, 124.1 (d, $J = 3.4$ Hz), 118.7 (d, $J = 13.0$ Hz), 115.0 (d, $J = 22.7$ Hz), 58.8 (d, $J = 4.1$ Hz), 55.2, 21.7; ^{19}F NMR (471 MHz, CDCl_3) δ -116.8 (dd, $J = 15.4, 6.9$ Hz); HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{24}\text{NO}_5\text{FNaS} [\text{M} + \text{Na}]^+$ 564.1257, found 564.1250.

(4-(3-Fluorophenyl)(tosyl)methyl)-2-phenyloxazol-5-yl)methyl benzoate (**2m**): Red solid, 98.9 mg, 90% yield, mp 123–124 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.07–8.03 (m, 2H), 8.02–7.98 (m, 2H), 7.68–7.63 (m, 1H), 7.55–7.38 (m, 9H), 7.26–7.22 (m, 1H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.05–6.98 (m, 1H), 5.85 (s, 1H), 5.60 (d, $J = 13.9$ Hz, 1H), 5.24 (d, $J = 13.9$ Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.3, 162.4 (d, $J = 245.9$ Hz), 161.8, 146.6, 145.0, 134.2, 133.5, 133.4 (d, $J = 8.2$ Hz), 133.3, 131.0, 129.9, 129.8, 129.64, 129.58, 129.5, 129.3, 128.8, 128.6, 127.3 (d, $J = 2.7$ Hz), 126.93, 126.91, 118.5 (d, $J = 23.2$ Hz), 116.0 (d, $J = 21.0$ Hz), 67.6, 54.9, 21.7; ^{19}F NMR (471 MHz, CDCl_3) δ -112.5 (dd, $J = 15.4, 9.0$ Hz); HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{24}\text{NO}_5\text{FNaS} [\text{M} + \text{Na}]^+$ 564.1257, found 564.1274.

(4-(3-Methoxyphenyl)(tosyl)methyl)-2-phenyloxazol-5-yl)methyl benzoate (**2n**): Yellow solid, 89.8 mg, 81% yield, mp 61–62 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.06–8.02 (m, 2H), 8.00 (dt, $J = 8.5, 1.5$ Hz, 2H), 7.55–7.50 (m, 3H), 7.46–7.43 (m, 4H), 7.40 (dd, $J = 8.0, 7.5$ Hz, 2H), 7.27 (dd, $J = 6.6, 1.1$ Hz, 1H), 7.20–7.14 (m, 3H), 6.86 (ddd, $J = 8.2, 2.6, 0.9$ Hz, 1H), 5.78 (s, 1H), 5.58 (d, $J = 13.9$ Hz, 1H), 5.28 (d, $J = 13.9$ Hz, 1H), 3.76 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.2, 161.6, 159.4, 146.4, 144.8, 134.5, 133.8, 133.5, 132.4, 130.9, 129.9, 129.5, 129.2, 128.8, 128.5, 127.1, 126.8, 123.9, 116.4, 115.4, 68.1, 55.3, 55.0, 21.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{32}\text{H}_{27}\text{NO}_5\text{NaS} [\text{M} + \text{Na}]^+$ 576.1457, found 576.1446.

(4-(4-Bromophenyl)(tosyl)methyl)-2-phenyloxazol-5-yl)methyl benzoate (**2o**): Yellow solid, 43.7 mg, 73% yield, mp 155–156 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.06–8.02 (m, 2H), 8.01–7.96 (m, 2H), 7.70–7.62 (m, 2H), 7.56–7.52 (m, 1H), 7.52–7.49 (m, 2H), 7.47–7.38 (m, 7H), 7.19 (d, $J = 8.0$ Hz, 2H), 5.82 (s, 1H), 5.60 (d, $J = 13.9$ Hz, 1H), 5.22 (d, $J = 13.9$ Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.3, 161.8, 146.6, 145.0, 134.2, 133.6, 133.3, 133.2, 131.5, 131.0, 130.2, 129.9, 129.8, 129.5, 129.4, 128.9, 128.6, 127.0, 126.9, 123.6, 67.4, 54.9, 21.8; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{24}\text{BrNO}_5\text{NaS} [\text{M} + \text{Na}]^+$ 624.0456, found 624.0444.

(4-(Naphthalen-1-yl(tosyl)methyl)-2-phenyloxazol-5-yl)methyl benzoate (**2p**): Yellow solid, 71.2 mg, 83% yield, mp 63–64 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.59 (dd, *J* = 7.4, 1.1 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.04–8.01 (m, 2H), 7.93–7.88 (m, 2H), 7.79–7.71 (m, 2H), 7.46 (t, *J* = 7.8 Hz, 4H), 7.42–7.31 (m, 7H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.76 (s, 1H), 5.53 (d, *J* = 13.9 Hz, 1H), 5.37 (d, *J* = 13.9 Hz, 1H), 2.19 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 166.4, 161.6, 146.6, 144.6, 134.7, 134.2, 133.8, 133.4, 132.2, 131.0, 130.7, 130.0, 129.8, 129.7, 129.5, 129.1, 129.0, 128.8, 128.5, 127.1, 127.0, 126.9, 126.8, 125.5, 125.2, 122.9, 61.8, 55.1, 21.6; HRMS (ESI-TOF) *m/z* calcd for C₃₅H₂₇NO₅NaS [M + Na]⁺ 596.1508, found 596.1516.

(4-(Naphthalen-2-yl(tosyl)methyl)-2-phenyloxazol-5-yl)methyl benzoate (**2q**): Yellow solid, 20.2 mg, 53% yield, mp 81–82 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.19 (d, *J* = 1.3 Hz, 1H), 8.11–8.05 (m, 2H), 8.02–7.97 (m, 2H), 7.93 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.82–7.75 (m, 3H), 7.55–7.49 (m, 3H), 7.48–7.43 (m, 5H), 7.41–7.36 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.97 (s, 1H), 5.62 (d, *J* = 13.9 Hz, 1H), 5.31 (d, *J* = 13.9 Hz, 1H), 2.33 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 166.3, 161.7, 146.4, 144.8, 134.5, 134.0, 133.5, 133.4, 133.1, 131.4, 131.0, 130.0, 129.9, 129.6, 129.3, 128.9, 128.7, 128.6, 128.4, 127.9, 127.7, 127.1, 127.0, 126.7, 126.2, 68.3, 55.1, 21.7; HRMS (ESI-TOF) *m/z* calcd for C₃₅H₂₇NO₅NaS [M + Na]⁺ 596.1508, found 596.1525.

(2-Phenyl-4-(phenyl(phenylsulfonyl)methyl)oxazol-5-yl)methyl benzoate (**2s**): White solid, 47.7 mg, 90% yield, mp 167–168 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.08–8.03 (m, 2H), 8.00 (dt, *J* = 8.5, 1.5 Hz, 2H), 7.78–7.74 (m, 2H), 7.64–7.59 (m, 2H), 7.56–7.50 (m, 2H), 7.47–7.43 (m, 3H), 7.42–7.34 (m, 4H), 7.31–7.25 (m, 3H), 5.84 (s, 1H), 5.61 (d, *J* = 13.9 Hz, 1H), 5.27 (d, *J* = 13.9 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 166.3, 161.7, 146.5, 137.4, 133.8, 133.6, 133.5, 131.5, 131.03, 130.97, 130.0, 129.9, 129.5, 129.0, 128.8, 128.5, 128.3, 127.1, 126.9, 68.2, 55.0; HRMS (ESI-TOF) *m/z* calcd for C₃₀H₂₃NO₅NaS [M + Na]⁺ 532.1195, found 532.1191.

(2-(4-Fluorophenyl)-4-(phenyl(phenylsulfonyl)methyl)oxazol-5-yl)methyl-4-fluorobenzoate (**2t**): White solid, 88.5 mg, 81% yield, mp 69–70 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.08–7.99 (m, 4H), 7.74–7.69 (m, 2H), 7.63–7.59 (m, 2H), 7.58–7.52 (m, 1H), 7.40–7.35 (m, 2H), 7.32–7.24 (m, 3H), 7.18–7.11 (m, 2H), 7.10–7.04 (m, 2H), 5.81 (s, 1H), 5.62 (d, *J* = 13.9 Hz, 1H), 5.27 (d, *J* = 13.9 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 166.2 (d, *J* = 255.0 Hz), 165.4, 164.6 (d, *J* = 251.9 Hz), 161.0, 146.5, 137.3, 133.8, 133.7, 132.6, 132.5, 131.4, 131.0, 129.9, 129.15, 129.13, 129.08, 128.6, 128.4, 125.8 (d, *J* = 2.8 Hz), 123.4 (d, *J* = 3.1 Hz), 116.1 (d, *J* = 22.2 Hz), 115.8 (d, *J* = 22.0 Hz), 68.2, 55.1; ¹⁹F NMR (471 MHz, CDCl₃) δ –104.2 to –105.2 (m), –108.2 to –108.9 (m); HRMS (ESI-TOF) *m/z* calcd for C₃₀H₂₁NO₅F₂NaS [M + Na]⁺ 568.1006, found 568.1023.

(4-((Methylsulfonyl)(phenyl)methyl)-2-phenyloxazol-5-yl)methyl benzoate (**2u**): Yellow solid, 13.3 mg, 64% yield, mp 63–64 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.12–8.08 (m, 2H), 8.00–7.96 (m, 2H), 7.96–7.91 (m, 2H), 7.56–7.51 (m, 1H), 7.50–7.46 (m, 3H), 7.43–7.37 (m, 5H), 5.70 (s, 1H), 5.64 (d, *J* = 13.9 Hz, 1H), 5.37 (d, *J* = 13.9 Hz, 1H), 2.99 (d, *J* = 0.5 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 166.2, 162.0, 146.4, 134.0, 133.5, 131.8, 131.2, 130.7, 130.0, 129.5, 129.3, 129.0, 128.9, 128.6, 126.9, 67.0, 55.2, 38.2; HRMS (ESI-TOF) *m/z* calcd for C₂₅H₂₁NO₅NaS [M + Na]⁺ 470.1038, found 470.1034.

(2-Phenyl-4-(phenyl(tosyl)methyl)oxazol-5-yl)methanol (**2aa**). To a solution of **2a** (0.20 mmol) in MeOH (15 mL) was added 5% NaOH (aq, 1.50 mL), and the reaction mixture was stirred at room temperature for 1.5 h. The reaction was washed with water, and the resulting suspension was extracted with Et₂O. The combined organic phases were dried over MgSO₄, and the solvent was removed via rotary evaporation. The crude residue was purified by direct crystallization from EtOH/pentane to afford **2aa** as a white solid (75.5 mg, 90% yield, mp 129–130 °C): ¹H NMR (400 MHz, CDCl₃) δ 8.02–7.95 (m, 2H), 7.72–7.63 (m, 2H), 7.48–7.40 (m, 3H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.33–7.26 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.49 (s, 1H), 4.82 (q, *J* = 14.3 Hz, 2H), 3.08 (s, 1H), 2.38 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 160.8, 150.9, 145.1, 133.5, 131.5, 130.9, 130.7, 130.6, 129.9, 129.2, 129.1, 128.8, 128.3, 127.2, 126.7, 69.0, 55.0, 21.8; HRMS (ESI-TOF) *m/z* calcd for C₂₄H₂₁NO₄NaS [M + Na]⁺ 442.1089, found 442.1090.

General Procedures for the Synthesis of *N*-Sulfonyl Allenylamides. **GP 1:** To a solution of **1** (0.40 mmol) in THF (5 mL) was added Et₃N (0.20 mL, 1.20 mmol), and the reaction mixture was stirred at room temperature for 3 h. The reaction was then quenched with water, and the resulting suspension was extracted with Et₂O. The combined organic phases were dried over MgSO₄, and the solvent was removed via rotary evaporation. The crude residue was purified by flash chromatography over silica gel (petroleum ether/EtOAc: 10/1) to give **7** as a white or yellow solid.

GP 2: A solution of **15** (2.00 mmol) in 30 mL of THF was treated at –78 °C with 4.00 mL (4.00 mmol) of a 1.0 M solution of LiHMDS in THF and stirred for 40 min at –78 °C. The resulting mixture was then treated with chloride **16** (6.00 mmol) and stirred at room temperature for 3 h. Subsequently, to the dark resulting solution was added Et₃N (1.00 mL, 6.00 mmol) and stirred at room temperature for 1–2 h. The reaction was quenched with water, and the layers were separated. The aqueous layer was extracted with Et₂O, and the combined organic layers were washed twice with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography over silica gel (petroleum ether/EtOAc: 10/1) to give **7** as a white or yellow solid.

4-Phenyl-4-(*N*-tosylbenzamido)buta-2,3-dien-1-yl benzoate (7a**).** By following **GP 1** (0.2 mmol), the compound was obtained as a yellow solid: 99.1 mg, 90% yield, mp 71–72 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.05–8.02 (m, 2H), 8.00–7.96 (m, 2H), 7.59–7.55 (m, 1H), 7.53–7.49 (m, 2H), 7.47–7.41 (m, 4H), 7.39–7.28 (m, 6H), 7.21–7.14 (m, 2H), 5.83 (t, *J* = 6.7 Hz, 1H), 4.45 (qd, *J* = 12.6, 6.8 Hz, 2H), 2.40 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 207.7, 170.3, 166.1, 145.3, 135.4, 134.2, 133.8, 133.5, 131.94, 129.88, 129.8, 129.7, 129.4, 128.9, 128.6, 128.2, 127.8, 126.0, 114.0, 96.2, 60.6, 21.8; HRMS (ESI-TOF) *m/z* calcd for C₃₁H₂₆NO₅S [M + H]⁺ 524.1532, found 524.1535.

4-(3-Bromo-*N*-tosylbenzamido)-4-phenylbuta-2,3-dien-1-yl 3-bromobenzoate (7b**).** By following **GP 1** (0.3 mmol), the compound was obtained as a yellow solid: 125.4 mg, 70% yield, mp 75–76 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.11 (t, *J* = 1.7 Hz, 1H), 8.04–7.98 (m, 2H), 7.96–7.88 (m, 1H), 7.69 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1H), 7.59 (t, *J* = 1.7 Hz, 1H), 7.47–7.41 (m, 3H), 7.38–7.33 (m, 3H), 7.33–7.28 (m, 4H), 7.02 (t, *J* = 7.9 Hz, 1H), 5.92 (t, *J* = 6.6 Hz, 1H), 4.61 (qd, *J* = 12.6, 6.7 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 207.7, 168.6, 164.8, 145.6, 136.4, 136.0, 135.1, 134.7, 133.3, 132.8, 131.5, 131.0, 130.2, 129.8, 129.7, 129.4, 129.0, 128.8, 128.4, 126.0, 125.9, 122.6, 122.2, 113.6, 96.1, 60.9, 21.8; HRMS (ESI-TOF) *m/z* calcd for C₃₁H₂₃NO₅NaSBr₂ [M + Na]⁺ 701.9561, found 701.9580.

4-(3-Methoxy-*N*-tosylbenzamido)-4-phenylbuta-2,3-dien-1-yl 3-methoxybenzoate (7c**).** By following **GP 2** (2.0 mmol), the compound was obtained as a yellow solid: 212.3 mg, 20% yield, mp 54–55 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.10–7.99 (m, 2H), 7.61–7.55 (m, 3H), 7.47 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.42–7.37 (m, 2H), 7.35–7.29 (m, 4H), 7.12–7.04 (m, 3H), 6.97–6.92 (m, 1H), 6.86 (ddd, *J* = 7.9, 2.6, 1.4 Hz, 1H), 5.81 (t, *J* = 6.5 Hz, 1H), 4.45 (qd, *J* = 12.6, 6.6 Hz, 2H), 3.76 (s, 3H), 3.39 (s, 3H), 2.40 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 207.5, 170.1, 166.0, 159.8, 159.1, 145.4, 135.3, 135.2, 133.9, 130.9, 129.9, 129.6, 129.4, 129.3, 128.9, 128.6, 126.1, 122.26, 120.28, 120.2, 119.0, 114.12, 114.09, 111.9, 96.3, 60.6, 55.5, 55.1, 21.8; HRMS (ESI-TOF) *m/z* calcd for C₃₃H₂₉NO₇NaS [M + Na]⁺ 606.1562, found 606.1567.

4-(4-Methyl-*N*-tosylbenzamido)-4-phenylbuta-2,3-dien-1-yl 4-methylbenzoate (7d**).** By following **GP 1** (0.3 mmol), the compound was obtained as a yellow solid: 101.0 mg, 62% yield, mp 111–112 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.07–8.00 (m, 2H), 7.90–7.81 (m, 2H), 7.60–7.50 (m, 2H), 7.41–7.34 (m, 4H), 7.32–7.26 (m, 3H), 7.23–7.19 (m, 2H), 6.95 (dd, *J* = 8.5, 0.5 Hz, 2H), 5.81 (t, *J* = 6.7 Hz, 1H), 4.42 (qd, *J* = 12.6, 6.7 Hz, 2H), 2.39 (s, 3H), 2.38 (s, 3H), 2.22 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 207.7, 170.3, 166.1, 145.1, 144.2, 142.7, 135.4, 133.8, 131.1, 129.8, 129.3, 129.2, 128.81, 128.78, 128.5, 128.0, 126.9, 126.0, 114.1, 96.2, 60.4, 21.7, 21.5; HRMS (ESI-TOF) *m/z* calcd for C₃₃H₂₉NO₅NaS [M + Na]⁺ 574.1664, found 574.1649.

4-(4-Fluoro-*N*-tosylbenzamido)-4-phenylbuta-2,3-dien-1-yl 4-fluorobenzoate (**7e**). By following GP 1 (0.4 mmol), the compound was obtained as a white solid: 114.0 mg, 50% yield, mp 106–107 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.05–7.97 (m, 4H), 7.53–7.49 (m, 2H), 7.47 (d, $J = 7.6$ Hz, 2H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.32–7.28 (m, 3H), 7.09 (t, $J = 8.5$ Hz, 2H), 6.85 (t, $J = 8.5$ Hz, 2H), 5.86 (t, $J = 6.5$ Hz, 1H), 4.70–4.46 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 207.5, 169.1, 166.1 (d, $J = 254.8$ Hz), 165.1, 164.8 (d, $J = 253.8$ Hz), 145.4, 135.3, 133.5, 132.4 (d, $J = 9.4$ Hz), 130.5 (d, $J = 9.0$ Hz), 130.2 (d, $J = 3.0$ Hz), 129.8, 129.3, 128.9, 128.7, 125.9, 125.8, 115.8 (d, $J = 22.1$ Hz), 115.4 (d, $J = 22.0$ Hz), 113.9, 96.2, 60.6, 21.8; ^{19}F NMR (377 MHz, CDCl_3) δ –104.7, –106.0; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{23}\text{NO}_5\text{F}_2\text{NaS}$ [$\text{M} + \text{Na}$] $^+$ 582.1163, found 582.1150.

4-Phenyl-4-(*N*-tosylfuran-2-carboxamido)buta-2,3-dien-1-yl furan-2-carboxylate (**7f**). By following GP 2 (2.0 mmol), the compound was obtained as a white solid: 376.0 mg, 38% yield, mp 139–140 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.07–8.00 (m, 2H), 7.59 (dd, $J = 1.7, 0.8$ Hz, 1H), 7.57–7.54 (m, 2H), 7.41–7.36 (m, 3H), 7.34–7.30 (m, 3H), 7.21 (dd, $J = 3.5, 0.8$ Hz, 1H), 7.02 (dd, $J = 3.6, 0.7$ Hz, 1H), 6.51 (dd, $J = 3.5, 1.7$ Hz, 1H), 6.32 (dd, $J = 3.6, 1.7$ Hz, 1H), 5.99 (t, $J = 6.4$ Hz, 1H), 4.88–4.56 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 207.0, 158.2, 146.9, 146.6, 145.39, 145.37, 144.1, 135.6, 133.8, 129.9, 129.4, 129.0, 128.7, 126.0, 119.7, 119.0, 113.3, 112.2, 112.1, 96.2, 60.6, 21.8; HRMS (ESI-TOF) m/z calcd for $\text{C}_{27}\text{H}_{21}\text{NO}_6\text{NaS}$ [$\text{M} + \text{Na}$] $^+$ 526.0936, found 526.0931.

4-Phenyl-4-(*N*-tosylcyclopentanecarboxamido)buta-2,3-dien-1-ylcyclopentanecarboxylate (**7g**). By following GP 2 (2.0 mmol), the compound was obtained as colorless oil: 144.0 mg, 18% yield; ^1H NMR (500 MHz, CDCl_3) δ 7.94 (d, $J = 8.2$ Hz, 2H), 7.43 (d, $J = 7.5$ Hz, 2H), 7.41–7.37 (m, 2H), 7.31 (t, $J = 7.5$ Hz, 3H), 6.13 (s, 1H), 4.85–4.78 (m, 2H), 2.85–2.78 (m, 2H), 2.44 (s, 3H), 1.94–1.49 (m, 16H); ^{13}C NMR (126 MHz, CDCl_3) δ 206.2, 176.8, 176.4, 144.8, 136.3, 133.4, 129.2, 128.9, 128.6, 125.5, 111.8, 96.8, 60.2, 43.6, 30.1, 30.0, 26.3, 25.8, 21.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{29}\text{H}_{33}\text{NO}_5\text{NaS}$ [$\text{M} + \text{Na}$] $^+$ 530.1977, found 530.1979.

4-Phenyl-4-(*N*-tosylacetamido)buta-2,3-dien-71-yl acetate (**7h**). By following GP 2 (2.0 mmol), the compound was obtained as a yellow solid: 543.7 mg, 68% yield, mp 130–131 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.95 (d, $J = 8.2$ Hz, 2H), 7.46–7.42 (m, 2H), 7.41–7.37 (m, 2H), 7.35–7.30 (m, 3H), 6.11 (s, 1H), 4.86–4.75 (m, 2H), 2.44 (s, 3H), 2.09 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 205.4, 169.9, 145.1, 136.0, 132.9, 129.3, 129.2, 129.0, 128.7, 125.4, 112.8, 96.8, 60.0, 23.9, 21.7, 20.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_5\text{NaS}$ [$\text{M} + \text{Na}$] $^+$ 422.1038, found 422.1046.

4-(2-Fluorophenyl)-4-(*N*-tosylbenzamido)buta-2,3-dien-1-yl benzoate (**7i**). By following GP 1 (0.4 mmol), the compound was obtained as a yellow solid: 104.3 mg, 49% yield, mp 124–125 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.05–8.01 (m, 2H), 7.99 (dt, $J = 8.4, 1.5$ Hz, 2H), 7.69 (td, $J = 7.9, 1.7$ Hz, 1H), 7.59–7.54 (m, 1H), 7.49–7.46 (m, 2H), 7.45–7.40 (m, 2H), 7.39–7.33 (m, 1H), 7.30–7.26 (m, 3H), 7.25–7.19 (m, 3H), 7.00 (ddd, $J = 11.3, 8.1, 1.2$ Hz, 1H), 5.70 (t, $J = 6.9$ Hz, 1H), 4.48 (qd, $J = 12.5, 6.9$ Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 210.0 (d, $J = 2.7$ Hz), 170.0, 166.1, 159.6 (d, $J = 252.8$ Hz), 145.4, 135.2, 134.2, 133.4, 131.9, 130.2 (d, $J = 8.6$ Hz), 129.8, 129.7, 129.3, 128.6, 128.5, 128.2, 127.8, 124.6 (d, $J = 3.6$ Hz), 122.2 (d, $J = 8.7$ Hz), 116.4 (d, $J = 21.7$ Hz), 107.5, 94.0, 60.6, 21.7; ^{19}F NMR (377 MHz, CDCl_3) δ –112.0; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{24}\text{NO}_5\text{FNaS}$ [$\text{M} + \text{Na}$] $^+$ 564.1257, found 564.1248.

4-(3-Fluorophenyl)-4-(*N*-tosylbenzamido)buta-2,3-dien-1-yl benzoate (**7j**). By following GP 1 (0.4 mmol), the compound was obtained as a white solid: 161.7 mg, 79% yield, mp 113–114 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.03 (d, $J = 8.3$ Hz, 2H), 7.99 (dd, $J = 8.2, 1.0$ Hz, 2H), 7.69 (td, $J = 7.9, 1.5$ Hz, 1H), 7.59–7.54 (m, 1H), 7.49–7.45 (m, 2H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.39–7.34 (m, 1H), 7.31–7.26 (m, 3H), 7.25–7.18 (m, 3H), 7.04–6.97 (m, 1H), 5.70 (t, $J = 6.9$ Hz, 1H), 4.48 (qd, $J = 12.5, 6.9$ Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 210.1, 170.0, 166.1, 159.6 (d, $J = 252.7$ Hz), 145.4, 135.2, 134.2, 133.4, 131.9, 130.2 (d, $J = 8.5$ Hz), 129.8, 129.7, 129.3, 128.7, 128.6, 128.4, 128.2, 127.8, 124.6 (d, $J = 3.7$ Hz), 122.2 (d, $J =$

8.6 Hz), 116.4 (d, $J = 21.8$ Hz), 107.5, 94.0, 60.6, 21.7; ^{19}F NMR (377 MHz, CDCl_3) δ –112.0; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{24}\text{NO}_5\text{FNaS}$ [$\text{M} + \text{Na}$] $^+$ 564.1257, found 564.1251.

4-(4-Bromophenyl)-4-(*N*-tosylbenzamido)buta-2,3-dien-1-yl benzoate (**7k**). By following GP 1 (0.3 mmol), the compound was obtained as a yellow solid: 97.3 mg, 54% yield, mp 61–62 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.02 (d, $J = 8.4$ Hz, 2H), 7.99–7.94 (m, 2H), 7.60–7.54 (m, 1H), 7.52–7.47 (m, 2H), 7.45–7.38 (m, 6H), 7.37–7.32 (m, 1H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.22–7.16 (m, 2H), 5.80 (t, $J = 6.6$ Hz, 1H), 4.56–4.32 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 207.4, 170.1, 166.0, 145.5, 135.2, 133.9, 133.5, 133.0, 132.1, 132.0, 129.81, 129.78, 129.5, 129.4, 128.6, 128.2, 127.7, 127.6, 122.7, 113.3, 96.7, 60.3, 21.8; HRMS (ESI-TOF) m/z calcd for $\text{C}_{31}\text{H}_{24}\text{NO}_5\text{BrNaS}$ [$\text{M} + \text{Na}$] $^+$ 624.0456, found 624.0465.

4-(Furan-2-yl)-4-(*N*-tosylbenzamido)buta-2,3-dien-1-yl benzoate (**7l**). By following GP 2 (4.0 mmol), the compound was obtained as a yellow solid: 440.1 mg, 22% yield, mp 53–54 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.03–7.98 (m, 4H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.54–7.51 (m, 2H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.38 (t, $J = 7.5$ Hz, 1H), 7.35 (s, 1H), 7.29 (d, $J = 8.2$ Hz, 2H), 7.24 (t, $J = 7.9$ Hz, 2H), 6.48 (d, $J = 3.4$ Hz, 1H), 6.43 (dd, $J = 3.3, 1.8$ Hz, 1H), 5.94 (t, $J = 6.7$ Hz, 1H), 4.53 (qd, $J = 12.7, 6.7$ Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 206.6, 169.9, 166.0, 147.1, 145.1, 143.2, 135.3, 133.9, 133.3, 131.9, 129.7, 129.6, 129.2, 128.4, 128.1, 127.8, 112.0, 110.0, 106.0, 97.1, 60.5, 21.6; HRMS (ESI-TOF) m/z calcd for $\text{C}_{29}\text{H}_{23}\text{NO}_6\text{NaS}$ [$\text{M} + \text{Na}$] $^+$ 536.1144, found 536.1148.

4-(Naphthalen-2-yl)-4-(*N*-tosylbenzamido)buta-2,3-dien-1-yl benzoate (**7m**). By following GP 1 (0.2 mmol), the compound was obtained as a yellow solid: 49.0 mg, 38% yield, mp 59–60 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.08 (d, $J = 8.0$ Hz, 2H), 8.00 (d, $J = 6.6$ Hz, 3H), 7.83–7.78 (m, 3H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.53–7.48 (m, 5H), 7.42 (t, $J = 7.8$ Hz, 2H), 7.30 (dd, $J = 7.7, 3.6$ Hz, 3H), 7.13 (t, $J = 7.9$ Hz, 2H), 5.90 (t, $J = 6.7$ Hz, 1H), 4.48–4.52 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 208.4, 170.3, 166.2, 145.4, 135.4, 134.1, 133.45, 133.4, 133.3, 131.9, 131.2, 129.9, 129.8, 129.7, 129.4, 128.7, 128.65, 128.6, 128.2, 127.8, 126.8, 126.7, 125.4, 123.6, 114.2, 96.4, 60.6, 21.8; HRMS (ESI-TOF) m/z calcd for $\text{C}_{35}\text{H}_{27}\text{NO}_5\text{NaS}$ [$\text{M} + \text{Na}$] $^+$ 596.1508, found 596.1502.

General Procedure for the Synthesis of 5-Vinyloxazoles. In a 10 mL flame-dried Schlenk tube, AgBF_4 (10 mol %) and *N*-sulfonyl allenylamide **7** (0.15 mmol) were introduced under argon and dissolved in 2 mL of dry and degassed toluene. The resulting yellow solution was stirred at 80 °C for 16–20 h and concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether/ether: 100/1) afforded the expected product.

2,4-Diphenyl-5-vinyloxazole (**8a**). By following the general procedure (0.20 mmol), the compound was obtained as a yellow solid: 39.4 mg, 81% yield, mp 59–60 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.17–8.11 (m, 2H), 7.77–7.71 (m, 2H), 7.50–7.43 (m, 5H), 7.39–7.34 (m, 1H), 6.87 (dd, $J = 17.3, 11.3$ Hz, 1H), 5.93 (dd, $J = 17.3, 1.2$ Hz, 1H), 5.40 (dd, $J = 11.3, 1.2$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.3, 145.1, 138.3, 132.1, 130.7, 128.9, 128.8, 128.3, 127.9, 127.5, 126.8, 122.5, 115.5; HRMS (ESI-TOF) m/z calcd for $\text{C}_{17}\text{H}_{13}\text{NONa}$ [$\text{M} + \text{Na}$] $^+$ 270.0895, found 270.0894.

2-(3-Bromophenyl)-4-phenyl-5-vinyloxazole (**8b**). By following the general procedure (0.15 mmol), the compound was obtained as colorless oil: 38.6 mg, 79% yield; ^1H NMR (500 MHz, CDCl_3) δ 8.28 (t, $J = 1.7$ Hz, 1H), 8.10–8.02 (m, 1H), 7.74–7.71 (m, 2H), 7.58 (ddd, $J = 8.0, 1.9, 1.0$ Hz, 1H), 7.49–7.42 (m, 2H), 7.41–7.30 (m, 2H), 6.86 (dd, $J = 17.3, 11.3$ Hz, 1H), 5.95 (dd, $J = 17.3, 1.1$ Hz, 1H), 5.43 (dd, $J = 11.3, 1.1$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.7, 145.5, 138.4, 133.5, 131.8, 130.5, 129.6, 129.3, 128.9, 128.4, 127.8, 125.2, 123.0, 122.3, 116.1; HRMS (ESI-TOF) m/z calcd for $\text{C}_{17}\text{H}_{12}\text{NONaBr}$ [$\text{M} + \text{Na}$] $^+$ 348.0000, found 347.9994.

2-(3-Methoxyphenyl)-4-phenyl-5-vinyloxazole (**8c**). By following the general procedure (0.20 mmol), the compound was obtained as colorless oil: 44.6 mg, 81% yield; ^1H NMR (500 MHz, CDCl_3) δ 7.76–7.71 (m, 3H), 7.67 (dd, $J = 2.5, 1.5$ Hz, 1H), 7.47–7.43 (m, 2H), 7.40–7.34 (m, 2H), 7.01 (ddd, $J = 8.3, 2.6, 0.9$ Hz, 1H), 6.86 (dd, $J = 17.3, 11.3$ Hz, 1H), 5.93 (dd, $J = 17.3, 1.2$ Hz, 1H), 5.40 (dd, $J =$

= 11.3, 1.2 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.2, 160.0, 145.1, 138.3, 132.0, 130.0, 128.8, 128.7, 128.3, 127.9, 122.4, 119.3, 117.1, 115.6, 111.5, 55.6; HRMS (ESI-TOF) m/z calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 300. 1000, found 300.1006.

4-Phenyl-2-(*p*-tolyl)-5-vinylloxazole (8d). By following the general procedure (0.15 mmol), the compound was obtained as colorless oil: 31.7 mg, 81% yield; ^1H NMR (500 MHz, CDCl_3) δ 8.08–7.99 (m, 2H), 7.77–7.71 (m, 2H), 7.47–7.42 (m, 2H), 7.38–7.33 (m, 1H), 7.27 (d, $J = 7.9$ Hz, 2H), 6.86 (dd, $J = 17.3, 11.3$ Hz, 1H), 5.91 (dd, $J = 17.3, 1.2$ Hz, 1H), 5.38 (dd, $J = 11.3, 1.2$ Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.5, 144.8, 141.0, 138.2, 132.2, 129.6, 128.8, 128.2, 127.8, 126.7, 124.8, 122.5, 115.2, 21.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{18}\text{H}_{15}\text{NONa}$ [$\text{M} + \text{Na}$] $^+$ 284. 1051, found 284.1043.

2-(4-Fluorophenyl)-4-phenyl-5-vinylloxazole (8e). By following the general procedure (0.15 mmol), the compound was obtained as colorless oil: 31.0 mg, 78% yield; ^1H NMR (500 MHz, CDCl_3) δ 8.18–8.08 (m, 2H), 7.77–7.69 (m, 2H), 7.51–7.42 (m, 2H), 7.40–7.33 (m, 1H), 7.20–7.13 (m, 2H), 6.86 (dd, $J = 17.3, 11.3$ Hz, 1H), 5.91 (dd, $J = 17.3, 1.2$ Hz, 1H), 5.40 (dd, $J = 11.3, 1.2$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 164.4 (d, $J = 251.4$ Hz), 159.5, 145.1, 138.3, 132.0, 128.92, 128.86, 128.3, 127.8, 123.8 (d, $J = 3.2$ Hz), 122.4, 116.1 (d, $J = 22.2$ Hz), 115.5; ^{19}F NMR (377 MHz, CDCl_3) δ -109.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{17}\text{H}_{12}\text{NOFNa}$ [$\text{M} + \text{Na}$] $^+$ 288. 0801, found 288.0802.

2-(Furan-2-yl)-4-phenyl-5-vinylloxazole (8f). By following the general procedure (0.12 mmol), the compound was obtained as colorless oil: 16.2 mg, 58% yield; ^1H NMR (500 MHz, CDCl_3) δ 7.78–7.69 (m, 2H), 7.59 (dd, $J = 1.8, 0.8$ Hz, 1H), 7.49–7.41 (m, 2H), 7.40–7.30 (m, 1H), 7.11 (dd, $J = 3.5, 0.8$ Hz, 1H), 6.86 (dd, $J = 17.3, 11.3$ Hz, 1H), 6.57 (dd, $J = 3.5, 1.8$ Hz, 1H), 5.91 (dd, $J = 17.3, 1.2$ Hz, 1H), 5.41 (dd, $J = 11.3, 1.2$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.1, 144.8, 144.6, 143.0, 138.0, 131.6, 128.8, 128.4, 127.9, 122.2, 115.9, 112.2, 112.1; HRMS (ESI-TOF) m/z calcd for $\text{C}_{15}\text{H}_{11}\text{NO}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 260. 0687, found 260.0678.

2-Cyclopentyl-4-phenyl-5-vinylloxazole (8g). By following the general procedure (0.23 mmol), the compound was obtained as colorless oil: 36.2 mg, 65% yield; ^1H NMR (500 MHz, CDCl_3) δ 7.69–7.58 (m, 2H), 7.46–7.37 (m, 2H), 7.35–7.28 (m, 1H), 6.79 (dd, $J = 17.3, 11.3$ Hz, 1H), 5.75 (dd, $J = 17.3, 1.3$ Hz, 1H), 5.29 (dd, $J = 11.3, 1.3$ Hz, 1H), 3.26 (p, $J = 8.1$ Hz, 1H), 2.19–2.04 (m, 2H), 2.05–1.91 (m, 2H), 1.90–1.77 (m, 2H), 1.75–1.63 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.2, 144.5, 136.6, 132.3, 128.7, 127.9, 127.7, 122.6, 114.5, 38.8, 31.7, 25.8; HRMS (ESI-TOF) m/z calcd for $\text{C}_{16}\text{H}_{17}\text{NONa}$ [$\text{M} + \text{Na}$] $^+$ 262. 1208, found 262.1201.

2-Methyl-4-phenyl-5-vinylloxazole (8h). By following the general procedure (0.50 mmol), the compound was obtained as colorless oil: 62.7 mg, 66% yield; ^1H NMR (500 MHz, CDCl_3) δ 7.70–7.58 (m, 2H), 7.46–7.37 (m, 2H), 7.36–7.29 (m, 1H), 6.79 (dd, $J = 17.3, 11.3$ Hz, 1H), 5.76 (dd, $J = 17.3, 1.3$ Hz, 1H), 5.31 (dd, $J = 11.3, 1.3$ Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.5, 144.9, 136.8, 132.1, 128.8, 128.0, 127.6, 122.4, 114.8, 14.1; HRMS (ESI-TOF) m/z calcd for $\text{C}_{12}\text{H}_{11}\text{NONa}$ [$\text{M} + \text{Na}$] $^+$ 208. 0738, found 208.0736.

4-(2-Fluorophenyl)-2-phenyl-5-vinylloxazole (8i). By following the general procedure (0.15 mmol), the compound was obtained as a white solid: 30.2 mg, 76% yield, mp 76–77 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.18–8.07 (m, 2H), 7.71 (td, $J = 7.5, 1.8$ Hz, 1H), 7.52–7.43 (m, 3H), 7.36 (dddd, $J = 8.2, 7.1, 5.1, 1.8$ Hz, 1H), 7.28–7.20 (m, 1H), 7.16 (ddd, $J = 10.2, 8.3, 1.0$ Hz, 1H), 6.69 (ddd, $J = 17.4, 11.3, 2.7$ Hz, 1H), 5.89 (dt, $J = 17.4, 1.0$ Hz, 1H), 5.37 (dd, $J = 11.3, 1.2$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.7 (d, $J = 248.0$ Hz), 146.5, 132.9, 131.4 (d, $J = 3.0$ Hz), 130.7, 130.3 (d, $J = 8.2$ Hz), 128.9, 127.4, 126.8, 124.6 (d, $J = 3.5$ Hz), 122.5 (d, $J = 7.7$ Hz), 119.9 (d, $J = 14.4$ Hz), 116.2 (d, $J = 22.1$ Hz), 115.4; ^{19}F NMR (377 MHz, CDCl_3) δ -114.1; HRMS (ESI-TOF) m/z calcd for $\text{C}_{17}\text{H}_{12}\text{NOFNa}$ [$\text{M} + \text{Na}$] $^+$ 288. 0801, found 288.0806.

4-(3-Fluorophenyl)-2-phenyl-5-vinylloxazole (8j). By following the general procedure (0.16 mmol), the compound was obtained as a white solid: 35.7 mg, 85% yield, mp 74–75 °C; ^1H NMR (500 MHz,

CDCl_3) δ 8.17–8.08 (m, 2H), 7.71 (td, $J = 7.6, 1.8$ Hz, 1H), 7.51–7.43 (m, 3H), 7.36 (dddd, $J = 8.2, 7.2, 5.1, 1.8$ Hz, 1H), 7.24 (td, $J = 7.5, 1.1$ Hz, 1H), 7.16 (ddd, $J = 10.1, 8.3, 1.0$ Hz, 1H), 6.70 (ddd, $J = 17.4, 11.3, 2.7$ Hz, 1H), 5.89 (dt, $J = 17.5, 1.0$ Hz, 1H), 5.37 (dd, $J = 11.3, 1.2$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.7 (d, $J = 248.3$ Hz), 146.5, 132.9, 131.4 (d, $J = 3.0$ Hz), 130.7, 130.3 (d, $J = 8.2$ Hz), 128.9, 127.4, 126.8, 124.6 (d, $J = 3.5$ Hz), 122.5 (d, $J = 7.7$ Hz), 119.9 (d, $J = 14.5$ Hz), 116.2 (d, $J = 22.1$ Hz), 115.4; ^{19}F NMR (377 MHz, CDCl_3) δ -114.0; HRMS (ESI-TOF) m/z calcd for $\text{C}_{17}\text{H}_{12}\text{NOFNa}$ [$\text{M} + \text{Na}$] $^+$ 288. 0801, found 288.0809.

4-(4-Bromophenyl)-2-phenyl-5-vinylloxazole (8k). By following the general procedure (0.15 mmol), the compound was obtained as colorless oil: 48.0 mg, 80% yield; ^1H NMR (500 MHz, CDCl_3) δ 8.12 (ddd, $J = 7.1, 4.1, 2.3$ Hz, 2H), 7.70–7.54 (m, 4H), 7.52–7.41 (m, 3H), 6.81 (dd, $J = 17.3, 11.3$ Hz, 1H), 5.95 (dd, $J = 17.3, 1.1$ Hz, 1H), 5.43 (dd, $J = 11.3, 1.1$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.4, 145.2, 137.2, 132.0, 131.0, 130.8, 129.3, 128.9, 127.3, 126.8, 122.4, 122.1, 116.2; HRMS (ESI-TOF) m/z calcd for $\text{C}_{17}\text{H}_{12}\text{NOBrNa}$ [$\text{M} + \text{Na}$] $^+$ 348. 0000, found 348.0008.

4-(Furan-2-yl)-2-phenyl-5-vinylloxazole (8l). By following the general procedure (0.20 mmol), the compound was obtained as colorless oil: 18.8 mg, 40% yield; ^1H NMR (500 MHz, CDCl_3) δ 8.16–8.07 (m, 2H), 7.51 (dd, $J = 1.8, 0.8$ Hz, 1H), 7.50–7.42 (m, 3H), 7.13 (dd, $J = 17.5, 11.4$ Hz, 1H), 6.83 (dd, $J = 3.4, 0.7$ Hz, 1H), 6.52 (dd, $J = 3.4, 1.8$ Hz, 1H), 5.90 (dd, $J = 17.5, 1.2$ Hz, 1H), 5.41 (dd, $J = 11.4, 1.2$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.7, 147.9, 144.5, 142.9, 130.8, 130.1, 128.9, 127.2, 126.9, 122.6, 115.1, 111.6, 108.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{15}\text{H}_{11}\text{NO}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 260. 0687, found 260.0688.

4-(Naphthalen-2-yl)-2-phenyl-5-vinylloxazole (8m). By following the general procedure (0.20 mmol), the compound was obtained as a white solid: 38.2 mg, 65% yield, mp 68–69 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.40–8.06 (m, 3H), 7.99–7.81 (m, 4H), 7.63–7.38 (m, 5H), 6.98 (dd, $J = 17.3, 11.3$ Hz, 1H), 5.98 (dd, $J = 17.3, 1.2$ Hz, 1H), 5.45 (dd, $J = 11.3, 1.2$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.4, 145.4, 138.3, 133.6, 133.2, 130.7, 129.5, 128.9, 128.5, 128.4, 127.9, 127.5, 127.0, 126.8, 126.6, 126.5, 125.6, 122.6, 115.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{21}\text{H}_{15}\text{NONa}$ [$\text{M} + \text{Na}$] $^+$ 320. 1051, found 320.1054.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra of all compounds and crystallographic data (CIF) of **2a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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