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NIS-mediated ring-closure/opening cascade reactions of allylamides: an expedient route to oxazolines

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ABSTRACT

An unprecedented NIS-mediated ring-closure/opening cascade reaction of allylamides is developed. The substrates with various functionalities were well tolerated and the scope can be extended to allylic carboxylates. Notably, the resulting iodinated chain products are versatile building blocks for the synthesis of oxazolines and epoxides. Furthermore, propargylamides can also undergo this reaction smoothly, providing the corresponding diiodoketones in good yields. The protocol offers a value route to explore new reaction patterns of other functionalized alkenes or alkynes.

1. Introduction

Electrophilic cyclization of functionalized alkynes or alkenes represents an important strategy to directly construct complex heterocycles, which are ubiquitous core structures in abundant naturally occurring products.[1,6f] Among them, halonium-triggered cyclizations of allylamides and propargylamides have been well studied to synthesize oxazoles and their derivatives.[2–6] In 1998, Taguchi et al. reported a general I_2-induced cyclization of allylamide **I** into 5-iodomethyloxazoline **II** through the attack of the amide carbonyl oxygen (Scheme 1, a).[2] Later, the *t*-BuOCl/NaI system was also found to be effective for the same reaction (Scheme 1, a).[3] More recently, Han, Pan and co-workers described a facile NBS-mediated oxidative cyclization of allylamide **I** into 5-bromomethyloxazole **III** (Scheme 1, a).[4] Besides, the iodocyclization of propargylamide **IV** led to 5-iodomethyleneoxazoline **V**,[5] which can be further oxidized into oxazole-5-carbaldehyde **VI** (Scheme 1, b).[6e] Inspired by these results and our previous works,[6] we then reasoned that when *N*-substituted allylamide or propargylamide was submitted to the same conditions, iminium intermediate would be first generated via a 5-*exo*-*mode* cyclization pathway, followed by the attack of other nucleophiles such as H_2O to give the corresponding adducts, which possibly could undergo C–N/C–O bond cleavage to yield linear chain compounds (Scheme 1, c).[7] Just as anticipated, by employing H_2O as the nucleophile and NIS as the iodine source, the cyclization/ring-opening cascade reactions of *N*-tosyl allylamides furnished various iodinated chain tosylamides **2**, whereas that of *N*-tosyl propargylamides gave a series of diiodoketones **4** (Scheme 1, d). Here we report these preliminary results of our studies.

2. Results and discussion

Initially, *N*-tosyl allylamide **1a** was chosen as the model substrate to carry out our investigations. When the reaction was performed in DCM in the presence of NIS and H_2O at room temperature, iodinated chain tosylamide **2a** was obtained in 98% yield (Table 1, entry 1). The structure was unambiguously confirmed by X-ray crystallography.[8] Since this reaction had already given excellent results, we explored the scope of the substrates directly and the results are shown in Table 1. Both electron-withdrawing and electron-donating substituents on the phenyl ring of acyl units were well tolerated, giving the corresponding linear chain products **2b**–**2e** in 80–93% yield. Furyl substrate **1f** underwent this transformation as well, albeit with a slightly lower yield. To our delight, when aliphatic moiety such as methyl was employed in R, the desired product **2g** was obtained in 52% yield. NBS could also trigger the reaction and lead to the formation of **2h** in a nearly quantitative yield. Surprisingly, subjecting *N*-phenyl allylamide **1i** to a mixture of DCM, NIS, and H_2O at −20 °C delivered *para*-iodinated aniline derivative **2i** in a satisfactory yield, which possibly was attributed to the strong electron-donating character of the amino group.[9] *N*-(3-Trifluoromethylphenyl) allylamide **1j** and *N*-(4-methylphenyl) allylamide **1k** could also participate in the reaction to give the desired products **2j** and **2k** in 45% and 60%

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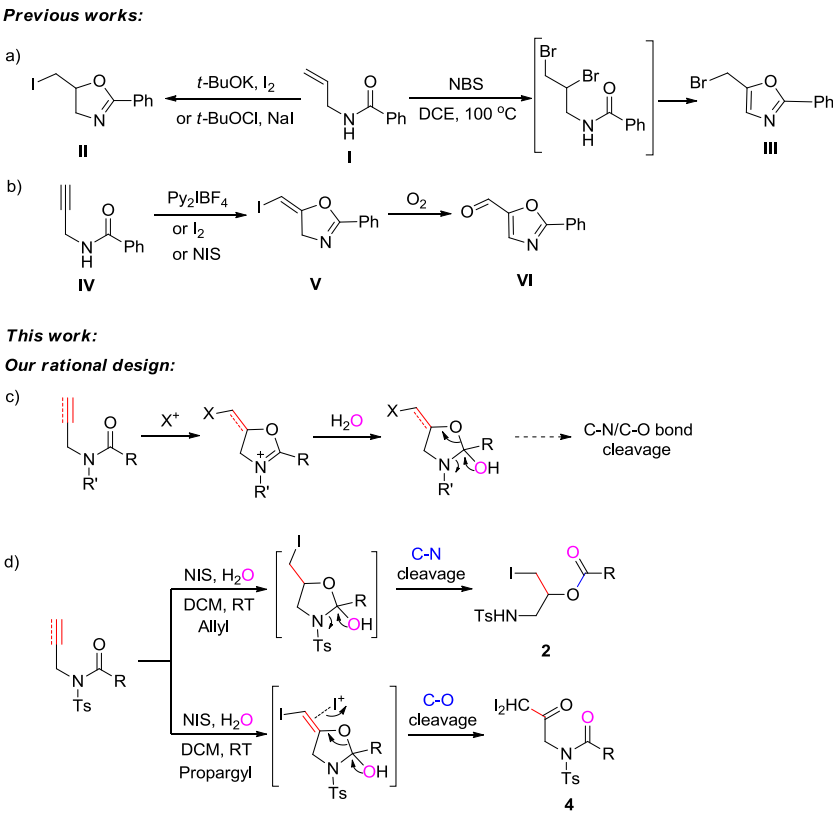
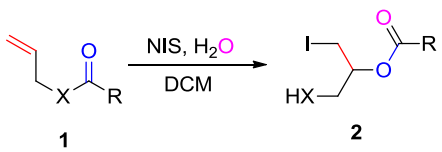


Scheme 1. NIS-mediated ring-closure/opening cascade reactions of allylamides and propargylamides.

Table 1
NIS-mediated ring-closure/opening cascade reactions of allylic substrates[a]



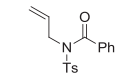
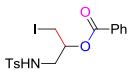
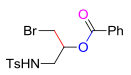
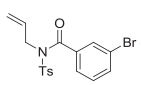
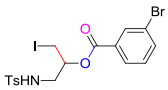
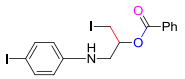
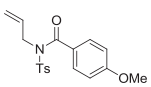
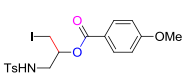
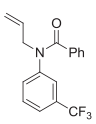
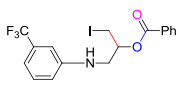
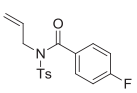
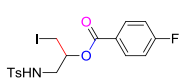
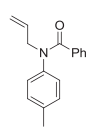
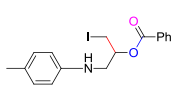
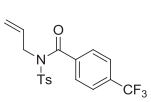
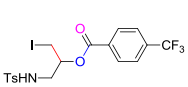
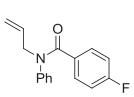
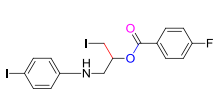
Entry	Substrate **1**	Product **2**	Entry	Substrate **1**	Product **2**
1	 **1a**	 **2a** 98%	8[b]	 **1a**	 **2h** 98%
2	 **1b**	 **2b** 88%	9[c]	 **1i**	 **2i** 80%
3	 **1c**	 **2c** 93%	10[c]	 **1j**	 **2j** 45%
4	 **1d**	 **2d** 88%	11[c]	 **1k**	 **2k** 60%
5	 **1e**	 **2e** 80%	12[c]	 **1l**	 **2l** 81%

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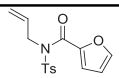
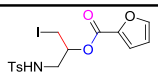
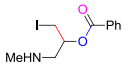
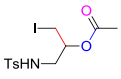
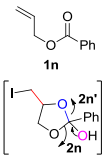
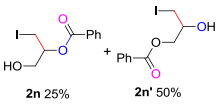
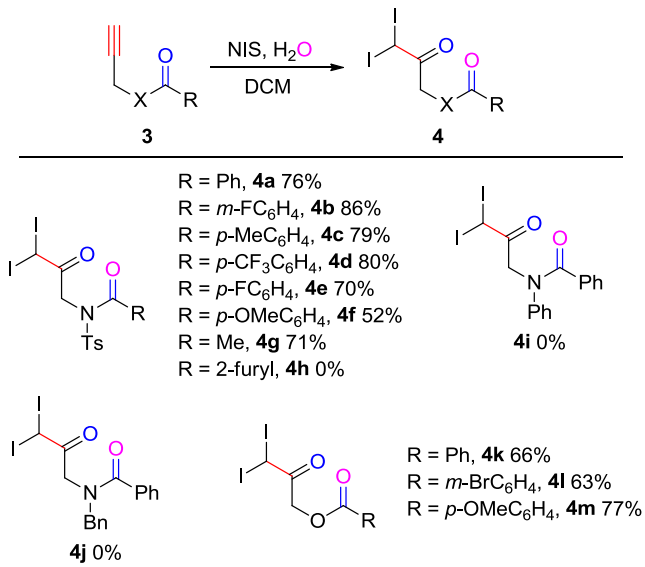
Table 1 (*continued*)

Entry	Substrate **1**	Product **2**	Entry	Substrate **1**	Product **2**
6	 **1f**	 **2f** 65%	13	 **1m**	 **2m** 0%
7	 **1g**	 **2g** 52%	14	 **1n**	 **2n** 25% **2n'** 50%

[a] Reaction conditions: substrate **1** (0.20 mmol), NIS (0.24 mmol), H_2O (0.40 mmol), DCM (3.0 mL), rt, 12 h; isolated yields are reported.
[b] NBS (0.24 mmol) was employed.
[c] NIS (0.48 mmol), −20 °C for 12–18 h.

yields, respectively. In addition, substrate **1l** with 4-F on the phenyl ring of acyl unit worked well to give **2l** in an acceptable yield. However, no desired product was observed when *N*-methyl allylamide **1m** was submitted to the optimized conditions. Notably, the substrate scope of the reaction can be further extended to allylic carboxylates, affording two main products **2n** and **2n′** in 25% and 50% yields, respectively. The results could be explained by taking account into two possible cleavage types of C–O bond.

Having established the transformations of allylamides, we then wondered whether propargylamides could also undergo this similar reaction. To our delight, treatment of *N*-tosyl propargylamide **3a** with 2.4 equiv of NIS and 2.0 equiv of H_2O in DCM at room temperature produced α-diiodoketone **4a** in 76% yield (Scheme 2). This approach provides us an appealing alternative for the synthesis of diiodo-substituted compounds,[10] which are versatile building blocks to elaborate complex quinoxazoline scaffold.[11] Then, the scope of the reaction was investigated. As depicted in Scheme 2, a broad variety of aromatic motifs in R group were well tolerated for this process (**4b**–**4f**, 52–86% yield). The electron-deficient substituents on phenyl ring gave good results (**4d**–**4e**, 70–80% yield), whereas the electron-rich substrate **3f** led to a lower yield. The reaction of methyl-derived substrate **3g** worked well to give diiodoketone **4g** in 71% yield. Unfortunately, **3h** with furyl group in R was not compatible with the transformation. No reactions occurred when *N*-phenyl propargylamide **3i** or *N*-benzyl propargylamide **3j** was employed. Analogously, propargylic carboxylates bearing various aromatic moieties underwent this reaction smoothly to afford the corresponding diiodoketones **4k**–**4m** in acceptable yields.



Scheme 2. NIS-mediated ring-closure/opening cascade reactions of propargylic substrates.[a]

To illustrate the synthetic potential of the iodinated products, additional studies were performed on their further transformations. Pleasingly, treatment of **2** with NaN_3 in DMSO at 80 °C furnished linear azide, without further purification, which can subsequently undergo Staudinger/aza-Wittig tandem reaction to generate various oxazolines **5** in acceptable yields (Scheme 3, Eq. 1).[12] Moreover, **2a** and **2i** can be efficiently converted into the corresponding epoxides **2aa** and **2ia** using Na_2CO_3 as the base (Scheme 3, Eqs. 2 and 3).

3. Conclusion

In summary, an unprecedented and efficient NIS-mediated ring-closure/opening cascade reaction of allylamides was developed. Environmentally benign H_2O serves as the nucleophile in the process. The substrates with various functionalities were well tolerated and the scope can be extended to allylic carboxylates. Notably, the resulting iodinated chain products are versatile building blocks for the synthesis of oxazolines and epoxides. Moreover, propargylamides also underwent this reaction smoothly to give a series of diiodoketones. The protocol offers a new reaction pattern of other functionalized alkenes or alkynes.

4. Experimental section

4.1. General information

Unless otherwise stated, all reactions and manipulations were carried out under argon atmosphere using standard Schlenk techniques or in an argon-filled glove-box. All chemicals were obtained from commercial sources and were used without further purification. Solvents were treated prior to use according to the standard methods. 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 $CDCl_3$ or CD_3COCD_3 on 400 or 500 MHz spectrometer. The chemical shifts for ^1H NMR were recorded in parts per million (ppm) downfield from tetramethylsilane (TMS) with $CDCl_3$ (7.26 ppm) or CD_3COCD_3 (2.05 ppm) as the internal standard. The chemical shifts for ^{13}C NMR were recorded in parts per million (ppm) downfield using the central peak of $CDCl_3$ (77.16 ppm) or CD_3COCD_3 (29.84 ppm) as the internal standard. Coupling constants (*J*) are reported in hertz (Hz) and refer to apparent peak multiplications.

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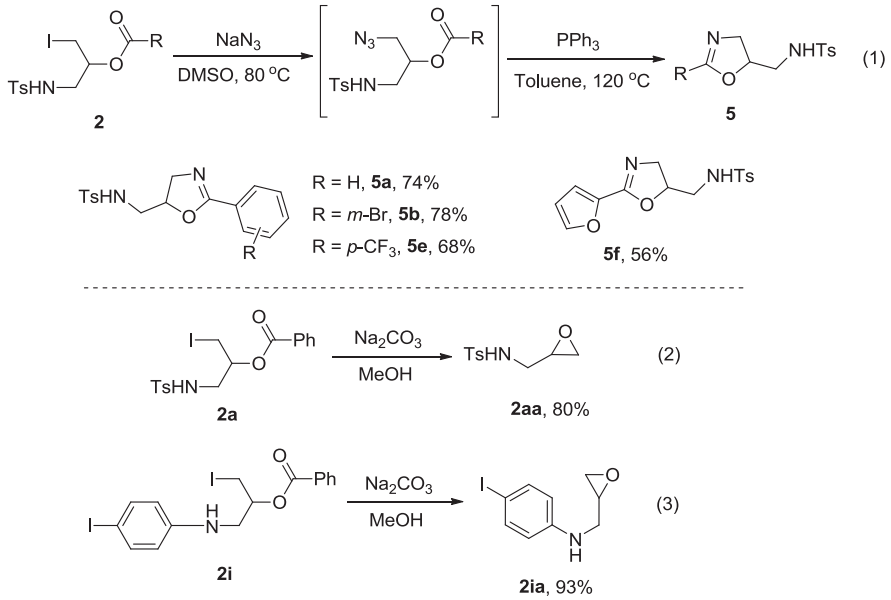
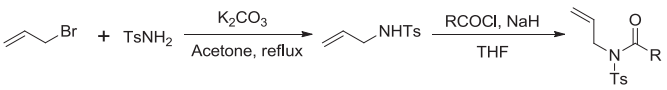


Scheme 3. Transformations of the iodinated products.

4.2. Characterization of starting materials

4.2.1. General procedure for the synthesis of allylamides. Compounds **1i**–**1m**[13] and **1n**[14] were prepared following the reported procedure.



$TsNH_2$ (50.0 mmol) and K_2CO_3 (1.5 equiv) were dissolved in 150 mL acetone and stirred at room temperature for 40 min. Then, allyl bromide (50.0 mmol) was added and stirred at 70 °C for 12 h. The reaction was quenched with water, and the layers were separated. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed twice with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Recrystallization from EtOH and pentane afforded the expected product.

To a solution of NaH (4.8 mmol) in THF (40.0 mL) at 0 °C was added *N*-tosylallylamine (4.0 mmol) and stirred for 40 min. The resulting mixture was then treated with acyl chloride (6.0 mmol) and stirred at room temperature for 3 h. The reaction was quenched with water, and the layers were separated. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed twice with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Recrystallization from EtOH and pentane afforded allylamides.

*4.2.1.1. N-Allyl-N-tosylbenzamide (**1a**).* By following the general procedure (5.60 mmol), the compound was obtained as a white solid (982.5 mg), 58% yield, mp 104–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.78 (m, 2H), 7.50–7.42 (m, 3H), 7.39–7.32 (m, 2H), 7.29 (d, *J*=8.1 Hz, 2H), 5.83 (ddt, *J*=16.8, 10.2, 5.6 Hz, 1H), 5.21–5.10 (m, 2H), 4.41 (dt, *J*=5.7, 1.5 Hz, 2H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.4, 144.8, 136.1, 134.9, 132.9, 131.6, 129.5, 128.8, 128.3, 128.0, 118.8, 50.4, 21.7; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{18}NO_3S$ $[M+H]^+$ 316.1002, found 316.1018.

*4.2.1.2. N-Allyl-3-bromo-N-tosylbenzamide (**1b**).* By following the general procedure (3.00 mmol), the compound was obtained as a white solid (703.1 mg), 59% yield, mp 71–72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J*=8.4 Hz, 2H), 7.58 (ddd, *J*=8.0, 2.0, 1.1 Hz, 1H), 7.47–7.37 (m, 2H), 7.34–7.19 (m, 3H), 5.86 (ddt, *J*=17.1, 10.3, 5.7 Hz, 1H), 5.27–5.14 (m, 2H), 4.42 (dt, *J*=5.7, 1.5 Hz, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.7, 145.2, 136.9, 135.9, 134.4, 132.6, 130.7, 129.8, 129.7, 128.6, 126.6, 122.2, 119.1, 50.1, 21.8; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{17}BrNO_3S$ $[M+H]^+$ 394.0107, found 394.0112.

*4.2.1.3. N-Allyl-4-methoxy-N-tosylbenzamide (**1c**).* By following the general procedure (1.50 mmol), the compound was obtained as a white solid (291.6 mg), 56% yield, mp 73–74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.71 (m, 2H), 7.69–7.48 (m, 2H), 7.40–7.15 (m, 2H), 7.03–6.64 (m, 2H), 5.82 (ddt, *J*=17.6, 10.0, 5.7 Hz, 1H), 5.28–5.01 (m, 2H), 4.35 (dt, *J*=5.8, 1.5 Hz, 2H), 3.84 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.3, 162.9, 144.7, 136.1, 132.9, 131.1, 129.6, 128.7, 127.0, 118.8, 113.6, 55.6, 50.6, 21.7; HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{20}NO_4S$ $[M+H]^+$ 346.1108, found 346.1124.

*4.2.1.4. N-Allyl-4-fluoro-N-tosylbenzamide (**1d**).* By following the general procedure (1.00 mmol), the compound was obtained as a white solid (283.2 mg), 85% yield, mp 88–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.74 (m, 2H), 7.59–7.49 (m, 2H), 7.35–7.27 (m, 2H), 7.10–7.01 (m, 2H), 5.95–5.74 (m, 1H), 5.30–5.08 (m, 2H), 4.37 (dt, *J*=5.7, 1.5 Hz, 2H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.5, 164.8 (d, *J*=253.2 Hz), 145.0, 135.9, 132.6, 131.1 (d, *J*=3.2 Hz), 130.9 (d, *J*=8.9 Hz), 129.6, 128.6, 119.0, 115.5 (d, *J*=22.1 Hz), 50.4, 21.7; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{17}FNO_3S$ $[M+H]^+$ 334.0908, found 334.0923.

*4.2.1.5. N-Allyl-N-tosyl-4-(trifluoromethyl)benzamide (**1e**).* By following the general procedure (1.00 mmol), the compound was obtained as a white solid (273.4 mg), 71% yield, mp 69–70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.69 (m, 2H), 7.62 (d, *J*=8.2 Hz, 2H), 7.54 (d, *J*=8.1 Hz, 2H), 7.30 (d, *J*=8.2 Hz, 2H), 5.85 (ddt, *J*=17.2, 10.4, 5.7 Hz, 1H), 5.35–5.07 (m, 2H), 4.41 (dt, *J*=5.7, 1.5 Hz, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.1, 145.3, 138.6, 135.9, 133.1 (d, *J*=33.1 Hz), 132.5, 129.7, 128.7, 128.3, 125.3 (q, *J*=3.7 Hz), 123.6 (d, *J*=272.5 Hz), 119.2, 50.0, 21.8; HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{17}F_3NO_3S$ $[M+H]^+$ 384.0876, found 384.0882.

*4.2.1.6. N-Allyl-N-tosylfuran-2-carboxamide (**1f**).* By following the general procedure (3.00 mmol), the compound was obtained as a yellow solid (623.8 mg), 69% yield, mp 58–59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28–7.81 (m, 2H), 7.70–7.44 (m, 1H), 7.31 (d, *J*=8.1 Hz, 2H), 7.27–7.09 (m, 1H), 6.49 (dd, *J*=3.6, 1.7 Hz, 1H), 5.91 (ddt, *J*=17.1, 10.5, 5.4 Hz, 1H), 5.36–5.07 (m, 2H), 4.70 (dt, *J*=5.4, 1.6 Hz, 2H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.2, 146.6, 145.9, 144.8, 136.3, 133.3, 129.4, 128.9, 120.3, 118.2, 112.2, 49.5, 21.7; HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{16}NO_4S$ $[M+H]^+$ 306.0795, found 306.0800.

*4.2.1.7. N-Allyl-N-tosylacetamide (**1g**).* By following the general procedure (1.50 mmol), the compound was obtained as colorless oil (233.3 mg), 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.70 (m, 2H), 7.33 (d, *J*=8.2 Hz, 2H), 5.88 (ddt, *J*=17.2, 10.6, 5.5 Hz, 1H), 5.40–5.09 (m, 2H), 4.46 (dt, *J*=5.6, 1.6 Hz, 2H), 2.43 (s, 3H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.9, 144.9, 136.5, 132.7, 129.7, 127.8, 118.0, 48.7, 24.5, 21.5; HRMS (ESI-TOF) *m*/*z* calcd for $C_{12}H_{16}NO_3S$ $[M+H]^+$ 254.0845, found 254.0847.

*4.2.1.8. N-Allyl-N-phenylbenzamide (**1i**).* Known compound,[13a] by following the reported procedure (10.0 mmol), the compound was obtained as colorless oil (2.12 g), 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.27 (m, 2H), 7.26–7.04 (m, 6H), 7.02 (d, *J*=7.6 Hz, 2H), 5.99 (ddt, *J*=16.4, 10.5, 5.9 Hz, 1H), 5.32–5.04 (m, 2H), 4.53 (dd, *J*=6.0, 1.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.2, 143.6, 136.0, 133.2, 129.6, 129.0, 128.8, 127.7, 127.6, 126.6, 117.7, 53.2.

*4.2.1.9. N-Allyl-N-(3-(trifluoromethyl)phenyl)benzamide (**1j**).* By following the reported procedure (5.3 mmol), the compound was obtained as colorless oil (1.22 g), 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.34 (m, 1H), 7.33–7.21 (m, 5H), 7.22–7.12 (m, 3H), 5.96 (ddt, *J*=16.4, 10.3, 5.9 Hz, 1H), 5.28–5.11 (m, 2H), 4.53 (dd, *J*=6.0, 1.5 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.4, 144.2, 135.4, 132.8, 131.3 (q, *J*=32.7 Hz), 130.8, 130.1, 129.6, 128.5, 128.0, 123.8 (q, *J*=3.8 Hz), 123.2 (d, *J*=272.4 Hz), 123.0 (q, *J*=3.8 Hz), 118.1, 53.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{15}F_3NO$ $[M+H]^+$ 306.1100, found 306.1118.

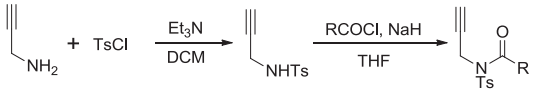
*4.2.1.10. N-Allyl-N-(p-tolyl)benzamide (**1k**).* By following the reported procedure (7.6 mmol), the compound was obtained as colorless oil (1.29 g), 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.28 (m, 2H), 7.25–7.18 (m, 1H), 7.19–7.11 (m, 2H), 7.08–6.96 (m, 2H), 6.95–6.82 (m, 2H), 5.98 (ddt, *J*=17.2, 10.2, 6.0 Hz, 1H), 5.33–5.07 (m, 2H), 4.50 (dt, *J*=6.0, 1.4 Hz, 2H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.3, 141.1, 136.5, 136.3, 133.4, 129.8, 129.6, 128.8, 127.8, 127.5, 117.7, 53.4, 21.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{18}NO$ $[M+H]^+$ 252.1383, found 252.1400.

*4.2.1.11. N-Allyl-4-fluoro-N-phenylbenzamide (**1l**).* By following the reported procedure[13] (5.0 mmol), the compound was obtained as colorless oil (1.11 g), 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.28 (m, 2H), 7.25–7.18 (m, 2H), 7.18–7.10 (m, 1H), 7.07–6.97 (m, 2H), 6.91–6.72 (m, 2H), 5.98 (ddt, *J*=16.5, 10.2, 6.0 Hz, 1H), 5.38–5.07 (m, 2H), 4.52 (dt, *J*=6.0, 1.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.2, 163.3 (d, *J*=250.4 Hz), 143.7, 133.1, 132.1 (d, *J*=3.4 Hz), 131.2 (d, *J*=8.8 Hz), 129.2, 127.6, 126.8, 117.9, 114.9 (d, *J*=21.8 Hz), 53.4; HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{15}FNO$ $[M+H]^+$ 256.1132, found 256.1142.

*4.2.1.12. N-Allyl-N-methylbenzamide (**1m**).* Known compound,[13b] by following the reported procedure[13] (10.0 mmol), the compound was obtained as colorless oil (1.23 g), 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.11 (m, 5H), 6.09–5.51 (m, 1H), 5.35–5.03 (m, 2H), 4.68–3.55 (br, 2H), 3.32–2.70 (br, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.3, 133.0, 132.6, 129.5, 128.3, 126.9, 126.5, 117.6, 117.4, 53.9, 49.9, 36.9, 32.9.

*4.2.1.13. Allyl benzoate (**1n**).* Known compound,[14] by following the reported procedure[14] (10.0 mmol), the compound was obtained as colorless oil (1.17 g), 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17–8.00 (m, 2H), 7.62–7.50 (m, 1H), 7.49–7.35 (m, 2H), 6.04 (ddt, *J*=17.3, 10.4, 5.6 Hz, 1H), 5.41 (dq, *J*=17.2, 1.6 Hz, 1H), 5.28 (dq, *J*=10.4, 1.4 Hz, 1H), 4.82 (dt, *J*=5.6, 1.5 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 133.0, 132.4, 130.3, 129.7, 128.4, 118.2, 65.6.

4.2.2. General procedure for the preparation of propargylic amides. Compounds **3i**,[15] **3j**,[16] and **3k**–**3m**[17] were prepared following the reported procedure.



Propargylamine (30.0 mmol) was added to a mixture of TsCl (1.3 equiv), Et_3N (2.5 equiv), and DCM slowly at 0 °C. The resulting yellow solution was then stirred at room temperature for 4 h and quenched with $NH_3 \cdot H_2O$. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed twice with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Recrystallization in EtOH and pentane afforded the expected product.

To a solution of NaH (4.8 mmol) in THF (40.0 mL) at 0 °C was added *N*-tosyl propargylamine (4.0 mmol) and stirred for 40 min. The resulting mixture was then treated with acyl chloride (6.0 mmol) and stirred at room temperature for 3 h. The reaction was quenched with water, and the layers were separated. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed twice with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Recrystallization from EtOH and pentane afforded terminal propargylamides.

*4.2.2.1. N-(Prop-2-yn-1-yl)-N-tosylbenzamide (**3a**).* By following the general procedure (10.0 mmol), the compound was obtained as a yellow solid (2.63 g), 84% yield, mp 146–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J*=8.3 Hz, 2H), 7.58–7.47 (m, 3H), 7.38 (t, *J*=7.7 Hz, 2H), 7.30 (d, *J*=8.2 Hz, 2H), 4.58 (d, *J*=2.3 Hz, 2H), 2.43 (s, 3H), 2.36 (t, *J*=2.3 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.6, 145.2, 135.6, 134.0, 131.9, 129.5, 129.0, 128.5, 128.0, 78.5, 73.3, 37.7, 21.8; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{16}NO_3S$ $[M+H]^+$ 314.0845, found 314.0852.

*4.2.2.2. 3-Fluoro-N-(prop-2-yn-1-yl)-N-tosylbenzamide (**3b**).* By following the general procedure (4.0 mmol), the compound was obtained as yellow oil (503.6 mg), 38% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J*=8.3 Hz, 2H), 7.44–7.27 (m, 4H), 7.18 (m, 2H), 4.58 (d, *J*=2.3 Hz, 2H), 2.44 (s, 3H), 2.38 (t, *J*=2.3 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.1 (d, *J*=2.6 Hz), 162.2 (d, *J*=248.8 Hz), 145.5, 136.0 (d, *J*=7.1 Hz), 135.3, 130.3 (d, *J*=7.9 Hz), 129.6, 128.9, 123.6 (d, *J*=3.2 Hz), 118.9 (d, *J*=21.1 Hz), 115.1 (d, *J*=23.6 Hz), 78.3, 73.5, 37.5, 21.8; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{15}FNO_3S$ $[M+H]^+$ 332.0751, found 332.0758.

*4.2.2.3. 4-Methyl-N-(prop-2-yn-1-yl)-N-tosylbenzamide (**3c**).* By following the general procedure (2.0 mmol), the compound was obtained as a yellow solid (291.1 mg), 44% yield, mp 88–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J*=8.4 Hz, 2H), 7.48 (d, *J*=8.1 Hz, 2H), 7.30 (d, *J*=8.1 Hz, 2H), 7.20 (d, *J*=7.9 Hz, 2H), 4.56 (d, *J*=2.4 Hz, 2H), 2.43 (s, 3H), 2.39 (s, 3H), 2.34 (t, *J*=2.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.8, 145.1, 142.8, 135.7, 131.2, 129.5, 129.2,

129.0, 128.3, 78.6, 73.3, 37.9, 21.8, 21.7; HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{18}NO_3S$ $[M+H]^+$ 328.1002, found 328.1008.

*4.2.2.4. N-(Prop-2-yn-1-yl)-N-tosyl-4-(trifluoromethyl)benzamide (**3d**).* By following the general procedure (2.0 mmol), the compound was obtained as a white solid (488.1 mg), 64% yield, mp 110–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J*=8.2 Hz, 2H), 7.62 (q, *J*=8.3 Hz, 4H), 7.30 (d, *J*=8.1 Hz, 2H), 4.59 (d, *J*=2.2 Hz, 2H), 2.44 (s, 3H), 2.37 (t, *J*=2.1 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.3, 145.6, 137.6, 135.3, 133.3 (q, *J*=32.9 Hz), 129.7, 128.8, 128.3, 125.4 (q, *J*=3.7 Hz), 123.6 (q, *J*=272.6 Hz), 78.2, 73.5, 37.3, 21.8; HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{15}F_3NO_3S$ $[M+H]^+$ 382.0719, found 382.0724.

*4.2.2.5. 4-Fluoro-N-(prop-2-yn-1-yl)-N-tosylbenzamide (**3e**).* By following the general procedure (4.0 mmol), the compound was obtained as a white solid (657.7 mg), 50% yield, mp 87–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J*=8.4 Hz, 2H), 7.64–7.50 (m, 2H), 7.31 (d, *J*=8.1 Hz, 2H), 7.18–6.97 (m, 2H), 4.56 (d, *J*=2.4 Hz, 2H), 2.44 (s, 3H), 2.35 (t, *J*=2.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.7, 164.9 (d, *J*=253.7 Hz), 145.4, 135.5, 130.9 (d, *J*=9.0 Hz), 129.6, 128.9, 128.6, 115.7 (d, *J*=22.1 Hz), 78.4, 73.4, 37.7, 21.8; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{15}FNO_3S$ $[M+H]^+$ 332.0751, found 332.0750.

*4.2.2.6. 4-Methoxy-N-(prop-2-yn-1-yl)-N-tosylbenzamide (**3f**).* By following the general procedure (2.0 mmol), the compound was obtained as a white solid (336.8 mg), 51% yield, mp 96–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J*=8.3 Hz, 2H), 7.62 (d, *J*=8.7 Hz, 2H), 7.30 (d, *J*=8.1 Hz, 2H), 6.89 (d, *J*=8.7 Hz, 2H), 4.54 (d, *J*=2.2 Hz, 2H), 3.85 (s, 3H), 2.43 (s, 3H), 2.33 (t, *J*=2.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.4, 163.0, 145.0, 135.6, 130.9, 129.5, 128.9, 126.1, 113.8, 78.6, 73.3, 55.6, 38.0, 21.8; HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{18}NO_4S$ $[M+H]^+$ 344.0951, found 344.0949.

*4.2.2.7. N-(Prop-2-yn-1-yl)-N-tosylacetamide (**3g**).* By following the general procedure (3.0 mmol), the compound was obtained as colorless oil (109.4 mg), 19% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J*=8.4 Hz, 2H), 7.35 (d, *J*=8.0 Hz, 2H), 4.67 (d, *J*=2.4 Hz, 2H), 2.45 (s, 3H), 2.35–2.28 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.5, 145.3, 136.0, 129.9, 128.1, 78.4, 72.6, 35.5, 24.5, 21.7; HRMS (ESI-TOF) *m*/*z* calcd for $C_{12}H_{14}NO_3S$ $[M+H]^+$ 252.0689, found 252.0689.

*4.2.2.8. N-(Prop-2-yn-1-yl)-N-tosylfuran-2-carboxamide (**3h**).* By following the general procedure (4.0 mmol), the compound was obtained as yellow oil (157.7 mg), 13% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J*=8.3 Hz, 2H), 7.57 (s, 1H), 7.44–7.29 (m, 3H), 6.53 (dd, *J*=3.5, 1.6 Hz, 1H), 4.93 (d, *J*=2.3 Hz, 2H), 2.43 (s, 3H), 2.32 (t, *J*=2.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.4, 146.4, 146.0, 145.1, 135.9, 129.5, 129.1, 120.6, 112.4, 78.6, 73.3, 36.8, 21.8; HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{14}NO_4S$ $[M+H]^+$ 304.0638, found 304.0636.

*4.2.2.9. N-Benzyl-N-(prop-2-yn-1-yl)benzamide (**3j**).* By following the reported procedure[16] (4.0 mmol), the compound was obtained as a white solid (475.2 mg), 50% yield, mp 48–49 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.16 (m, 10H), 4.73 (br, 2H), 4.02 (br, 2H), 2.76–1.85 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.9, 136.0, 135.1, 129.7, 128.5, 128.2, 127.4, 126.9, 126.6, 78.2, 72.8 (br), 49.3 (br), 35.4 (br); HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{16}NO$ $[M+H]^+$ 250.1226, found 250.1244.

*4.2.2.10. Prop-2-yn-1-yl 3-bromobenzoate (**3l**).* By following the reported procedure[17] (10.0 mmol), the compound was obtained as yellow oil (798.4 mg), 35% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (t, *J*=1.8 Hz, 1H), 8.00 (dt, *J*=7.9, 1.3 Hz, 1H), 7.71 (ddd, *J*=8.0, 2.1, 1.0 Hz, 1H), 7.33 (t, *J*=7.9 Hz, 1H), 4.93 (d, *J*=2.5 Hz, 2H), 2.53 (t, *J*=2.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.6, 136.4, 132.9, 131.5, 130.2, 128.5, 122.7, 77.5, 75.5, 52.9; HRMS (ESI-TOF) *m*/*z* calcd for $C_{10}H_8BrO_2$ $[M+H]^+$ 238.9702, found 238.9712.

*4.2.2.11. Prop-2-yn-1-yl 4-methoxybenzoate (**3m**).* By following the reported procedure[17] (10.0 mmol), the compound was obtained as yellow oil (283.2 mg), 18% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–7.92 (m, 2H), 6.98–6.87 (m, 2H), 4.89 (d, *J*=2.4 Hz, 2H), 3.85 (s, 3H), 2.52 (t, *J*=2.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.5, 163.7, 131.9, 121.8, 113.8, 78.1, 74.9, 55.5, 52.2; HRMS (ESI-TOF) *m*/*z* calcd for $C_{11}H_{11}O_3$ $[M+H]^+$ 191.0703, found 191.0710.

4.3. Representative procedure for the ring-closure/opening cascade reactions of allylamides

In a 10 mL flame-dried Schlenk flask, allylamide **1** (0.20 mmol) and NIS (1.2 equiv) were dissolved in 3 mL of dry dichloromethane and then H_2O (2.0 equiv) was added. The resulting solution was stirred at room temperature for 12 h, and quenched with sodium thiosulfate solution. 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. Purification by flash chromatography on silica gel (petroleum ether/EtOAc: 5:1) afforded the expected product.

*4.3.1. 1-Iodo-3-(4-methylphenylsulfonamido)propan-2-yl benzoate (**2a**).* By following the representative procedure (0.2 mmol), the title compound was obtained as a white solid (91.0 mg), 98% yield, mp 91–92 °C; ^{1}H NMR (400 MHz, acetone) δ 8.12–7.91 (m, 2H), 7.79–7.71 (m, 2H), 7.70–7.59 (m, 1H), 7.57–7.45 (m, 2H), 7.35 (d, *J*=8.1 Hz, 2H), 6.89 (t, *J*=6.5 Hz, 1H), 5.62–4.84 (m, 1H), 3.78–3.45 (m, 2H), 3.51–3.31 (m, 2H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone) δ 165.8, 144.0, 138.8, 134.1, 130.6, 130.49, 130.47, 129.3, 128.0, 72.9, 46.5, 21.4, 5.2; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{19}INO_4S$ $[M+H]^+$ 460.0074, found 460.0082.

*4.3.2. 1-Iodo-3-(4-methylphenylsulfonamido)propan-2-yl 3-bromobenzoate (**2b**).* By following the representative procedure (0.2 mmol), the title compound was obtained as a yellow solid (94.4 mg), 88% yield, mp 94–95 °C; ^{1}H NMR (400 MHz, acetone) δ 8.13 (t, *J*=1.8 Hz, 1H), 8.00 (dt, *J*=7.8, 1.3 Hz, 1H), 7.87–7.79 (m, 1H), 7.78–7.69 (m, 2H), 7.49 (t, *J*=7.9 Hz, 1H), 7.34 (d, *J*=8.0 Hz, 2H), 6.89 (t, *J*=6.5 Hz, 1H), 5.10 (p, *J*=5.4 Hz, 1H), 3.73–3.49 (m, 2H), 3.48–3.26 (m, 2H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, Acetone) δ 164.5, 144.0, 138.8, 137.0, 133.1, 132.8, 131.4, 130.4, 129.4, 127.6, 122.8, 73.5, 46.4, 21.4, 4.7; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{18}IBrNO_4S$ $[M+H]^+$ 537.9179, found 537.9180.

*4.3.3. 1-Iodo-3-(4-methylphenylsulfonamido)propan-2-yl 4-methoxybenzoate (**2c**).* By following the representative procedure (0.2 mmol), the title compound was obtained as colorless oil (110.7 mg), 93% yield; ^{1}H NMR (400 MHz, acetone) δ 8.05–7.88 (m, 2H), 7.82–7.67 (m, 2H), 7.49–7.25 (m, 2H), 7.12–6.95 (m, 2H), 6.87 (t, *J*=6.5 Hz, 1H), 5.02 (p, *J*=5.4 Hz, 1H), 3.89 (s, 3H), 3.74–3.48 (m, 2H), 3.37 (dd, *J*=6.5, 5.5 Hz, 2H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone) δ 165.5, 164.7, 144.0, 138.8, 132.6, 130.5, 127.7, 122.8, 114.5, 72.4, 56.0, 46.5, 21.4, 5.4; HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{21}INO_5S$ $[M+H]^+$ 490.0180, found 490.0180.

*4.3.4. 1-Iodo-3-(4-methylphenylsulfonamido)propan-2-yl 4-fluorobenzoate (**2d**).* By following the representative procedure (0.2 mmol), the title compound was obtained as a yellow solid (83.8 mg), 88% yield, mp 96–97 °C; ^{1}H NMR (400 MHz, acetone) δ 8.33–7.95 (m, 2H), 7.91–7.68 (m, 2H), 7.40–7.32 (m, 2H), 7.32–7.22 (m, 2H), 6.90 (t, *J*=6.5 Hz, 1H), 5.07 (p, *J*=5.4 Hz, 1H), 3.82–3.47 (m, 2H), 3.40 (dd, *J*=6.5, 5.5 Hz, 2H), 2.39 (s, 3H); $^{13}C\{^1H\}$

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NMR (100 MHz, acetone) δ 166.7 (d, *J*=252.3 Hz), 164.9, 144.0, 138.8, 133.3 (d, *J*=9.5 Hz), 130.5, 127.7, 127.1 (d, *J*=3.0 Hz), 116.3 (d, *J*=22.3 Hz), 73.1, 46.4, 21.4, 5.03; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{18}FINO_4S$ $[M+H]^+$ 477.9980, found 477.9978.

*4.3.5. 1-Iodo-3-(4-methylphenylsulfonamido)propan-2-yl 4-(trifluoromethyl)benzoate (**2e**).* By following the representative procedure (0.2 mmol), the title compound was obtained as a yellow solid (84.5 mg), 80% yield, mp 94–95 °C; ^1H NMR (400 MHz, acetone) δ 8.41–8.13 (m, 2H), 7.88 (d, *J*=8.2 Hz, 2H), 7.80–7.60 (m, 2H), 7.35 (d, *J*=8.1 Hz, 2H), 6.92 (t, *J*=6.5 Hz, 1H), 5.13 (p, *J*=5.5 Hz, 1H), 3.81–3.47 (m, 2H), 3.44 (t, *J*=6.0 Hz, 2H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone) δ 164.8, 144.0, 138.9, 134.8 (q, *J*=32.3 Hz), 134.3, 131.2, 130.5, 129.5, 127.7, 126.3 (q, *J*=3.8 Hz), 124.8 (q, *J*=271.9 Hz), 73.7, 46.4, 21.4, 4.7; HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{18}F_3INO_4S$ $[M+H]^+$ 527.9948, found 527.9948.

*4.3.6. 1-Iodo-3-(4-methylphenylsulfonamido)propan-2-yl furan-2-carboxylate (**2f**).* By following the representative procedure (0.2 mmol), the title compound was obtained as yellow oil (58.9 mg), 65% yield; ^1H NMR (400 MHz, acetone) δ 7.91–7.80 (m, 1H), 7.80–7.68 (m, 2H), 7.38 (d, *J*=7.9 Hz, 2H), 7.25 (d, *J*=3.5 Hz, 1H), 6.85 (t, *J*=6.4 Hz, 1H), 6.66 (dd, *J*=3.6, 1.7 Hz, 1H), 5.04 (p, *J*=5.5 Hz, 1H), 3.55 (qd, *J*=10.9, 5.6 Hz, 2H), 3.44–3.22 (m, 2H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone) δ 157.9, 148.2, 145.1, 144.1, 138.9, 130.5, 127.8, 119.6, 112.9, 73.0, 46.4, 21.4, 4.7; HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{17}INO_5S$ $[M+H]^+$ 449.9867, found 449.9871.

*4.3.7. 1-Iodo-3-(4-methylphenylsulfonamido)propan-2-yl acetate (**2g**).* By following the representative procedure (0.2 mmol), the title compound was obtained as yellow oil (41.0 mg), 52% yield; ^1H NMR (400 MHz, acetone) δ 7.87–7.61 (m, 2H), 7.50–7.21 (m, 2H), 6.71 (t, *J*=6.6 Hz, 1H), 4.79 (ddd, *J*=11.1, 6.1, 5.1 Hz, 1H), 3.62–3.32 (m, 2H), 3.31–3.05 (m, 2H), 2.42 (s, 3H), 1.99 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone) δ 170.2, 144.0, 138.8, 130.5, 127.8, 72.2, 46.2, 21.4, 20.8, 4.9; HRMS (ESI-TOF) *m*/*z* calcd for $C_{12}H_{17}INO_4S$ $[M+H]^+$ 397.9917, found 397.9923.

*4.3.8. 1-Bromo-3-(4-methylphenylsulfonamido)propan-2-yl benzoate (**2h**).* By following the representative procedure (0.2 mmol), the title compound was obtained as yellow oil (81.9 mg), 98% yield; ^1H NMR (400 MHz, acetone) δ 8.24–7.93 (m, 2H), 7.88–7.71 (m, 2H), 7.71–7.59 (m, 1H), 7.58–7.41 (m, 2H), 7.35 (d, *J*=8.0 Hz, 2H), 6.93 (t, *J*=6.5 Hz, 1H), 5.32 (p, *J*=5.4 Hz, 1H), 3.94–3.65 (m, 2H), 3.42 (dd, *J*=6.6, 5.5 Hz, 2H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone) δ 165.9, 144.0, 138.8, 134.2, 130.6, 130.5, 129.3, 127.7, 72.8, 45.2, 32.4, 21.4; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{19}BrNO_4S$ $[M+H]^+$ 412.0213, found 412.0217.

4.4. Representative procedure for the ring-closure/opening cascade reactions of *N*-phenyl allylamides

In a 10 mL flame-dried Schlenk flask, *N*-phenyl allylamide **1** (0.20 mmol) and NIS (2.4 equiv) were dissolved in 4 mL of dry dichloromethane and then H_2O (2.0 equiv) was added. The resulting solution was stirred at −20 °C for 12–18 h, and quenched with sodium thiosulfate solution. 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. Purification by flash chromatography on silica gel (petroleum ether/EtOAc: 4:1) afforded the expected product.

*4.4.1. 1-Iodo-3-((4-iodophenyl)amino)propan-2-yl benzoate (**2i**).* By following the representative procedure (0.4 mmol), the title compound was obtained as yellow oil (159.8 mg), 80% yield; ^1H NMR (400 MHz, acetone) δ 8.13–7.94 (m, 2H), 7.74–7.56 (m, 1H), 7.60–7.45 (m, 2H), 7.46–7.33 (m, 2H), 6.77–6.38 (m, 2H), 5.54 (s, 1H), 5.37–4.90 (m, 1H), 4.01–3.44 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone) δ 166.0, 149.0, 138.4, 134.1, 130.7, 130.4, 129.3, 115.9, 77.5, 72.4, 47.0, 6.5; HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{16}I_2NO_2$ $[M+H]^+$ 507.9265, found 507.9273.

*4.4.2. 1-Iodo-3-((3-(trifluoromethyl)phenyl)amino)propan-2-yl benzoate (**2j**).* By following the representative procedure (0.7 mmol), the title compound was obtained as yellow oil (146.4 mg), 45% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09–7.99 (m, 2H), 7.65–7.55 (m, 1H), 7.46 (t, *J*=7.7 Hz, 2H), 7.32–7.19 (m, 1H), 6.96 (d, *J*=7.7 Hz, 1H), 6.91 (s, 1H), 6.88–6.81 (m, 1H), 5.15 (p, *J*=5.5 Hz, 1H), 4.20 (s, 1H), 3.79–3.37 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.0, 147.7, 133.7, 131.9 (d, *J*=31.8 Hz), 130.02, 129.98, 129.5, 128.71, 128.68, 124.4 (d, *J*=272.6 Hz), 116.1 (d, *J*=3.4 Hz), 114.7 (q, *J*=3.9 Hz), 109.5 (q, *J*=4.0 Hz), 71.6, 47.1, 5.0; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{16}F_3INO_2$ $[M+H]^+$ 450.0172, found 450.0192.

*4.4.3. 1-Iodo-3-(p-tolylamino)propan-2-yl benzoate (**2k**).* By following the representative procedure (0.4 mmol), the title compound was obtained as yellow oil (94.5 mg), 60% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.17–7.98 (m, 2H), 7.73–7.52 (m, 1H), 7.52–7.41 (m, 2H), 7.00 (d, *J*=8.6 Hz, 2H), 6.63 (d, *J*=8.4 Hz, 2H), 5.31–4.85 (m, 1H), 4.12–3.66 (m, 1H), 3.71–3.39 (m, 4H), 2.23 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.9, 145.1, 133.5, 130.1, 130.0, 129.7, 128.6, 127.6, 113.4, 71.5, 47.6, 20.5, 5.9; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{19}INO_2$ $[M+H]^+$ 396.0455, found 396.0475.

*4.4.4. 1-Iodo-3-((4-iodophenyl)amino)propan-2-yl 4-fluorobenzoate (**2l**).* By following the representative procedure (0.4 mmol), the title compound was obtained as yellow oil (169.2 mg), 81% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.14–7.82 (m, 2H), 7.57–7.33 (m, 2H), 7.12 (t, *J*=8.6 Hz, 2H), 6.78–6.14 (m, 2H), 5.07 (p, *J*=5.5 Hz, 1H), 3.99 (s, 1H), 3.72–3.35 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.2 (d, *J*=254.8 Hz), 164.9, 147.0, 138.1, 132.6 (d, *J*=9.4 Hz), 125.7 (d, *J*=3.0 Hz), 115.8 (d, *J*=22.1 Hz), 115.3, 79.0, 71.4, 47.1, 5.5; HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{15}FI_2NO_2$ $[M+H]^+$ 525.9171, found 525.9189.

*4.4.5. 1-Hydroxy-3-iodopropan-2-yl benzoate (**2n**).* By following the representative procedure (0.4 mmol), the title compound was obtained as yellow oil (31.2 mg), 25% yield; ^1H NMR (400 MHz, acetone) δ 8.21–7.95 (m, 2H), 7.78–7.59 (m, 1H), 7.61–7.38 (m, 2H), 5.05 (dq, *J*=5.8, 5.1 Hz, 1H), 4.44–4.17 (m, 1H), 4.02–3.75 (m, 2H), 3.74–3.49 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone) δ 166.0, 134.1, 131.0, 130.4, 129.4, 75.0, 63.4, 4.9; HRMS (ESI-TOF) *m*/*z* calcd for $C_{10}H_{11}NaIO_3$ $[M+Na]^+$ 328.9645, found 328.9643.

*4.4.6. 2-Hydroxy-3-iodopropyl benzoate (**2n′**).* By following the representative procedure (0.4 mmol), the title compound was obtained as yellow oil (61.2 mg), 50% yield; ^1H NMR (400 MHz, acetone) δ 8.18–7.94 (m, 2H), 7.71–7.58 (m, 1H), 7.59–7.43 (m, 2H), 4.82 (ddd, *J*=5.3, 3.5, 1.6 Hz, 1H), 4.49–4.30 (m, 2H), 4.02 (h, *J*=5.4 Hz, 1H), 3.68–3.28 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone) δ 166.5, 133.9, 131.0, 130.3, 129.3, 69.5, 68.4, 9.8; HRMS (ESI-TOF) *m*/*z* calcd for $C_{10}H_{12}IO_3$ $[M+H]^+$ 306.9826, found 306.9824.

4.5. Representative procedure for the ring-closure/opening cascade reactions of propargylamides

In a 10 mL flame-dried Schlenk flask, propargylamide **3** (0.20 mmol) and NIS (2.4 equiv) were dissolved in 4 mL of dry dichloromethane and then H_2O (2.0 equiv) was added. The resulting solution was stirred at room temperature for 6–12 h, and quenched with sodium thiosulfate solution. 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

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under reduced pressure. Direct crystallization from ethyl acetate and pentane afforded the expected product.

*4.5.1. N-(3,3-Diiodo-2-oxopropyl)-N-tosylbenzamide (**4a**).* By following the representative procedure (1.0 mmol), the title compound was obtained as a yellow solid (443.2 mg), 76% yield, mp 129–130 °C; ^{1}H NMR (400 MHz, acetone) δ 7.99–7.71 (m, 2H), 7.51 (dq, J=8.2, 4.2 Hz, 1H), 7.45–7.38 (m, 6H), 6.14 (s, 1H), 5.36 (s, 2H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, acetone) δ 194.1, 171.1, 146.1, 136.9, 135.5, 132.2, 130.3, 129.6, 129.3, 128.4, 48.1, 21.6, −31.0; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}I_2NO_4S$ $[M+H]^+$ 583.8884, found 583.8911.

*4.5.2. N-(3,3-Diiodo-2-oxopropyl)-3-fluoro-N-tosylbenzamide (**4b**).* By following the representative procedure (0.2 mmol), the title compound was obtained as a yellow solid (104.9 mg), 86% yield, mp 119–120 °C; ^{1}H NMR (400 MHz, Acetone) δ 7.91–7.72 (m, 2H), 7.59–7.39 (m, 3H), 7.35–7.20 (m, 2H), 7.14 (ddd, J=9.1, 2.6, 1.6 Hz, 1H), 6.16 (s, 1H), 5.38 (s, 2H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, Acetone) δ 194.0, 169.7 (d, J=2.6 Hz), 163.0 (d, J=246.5 Hz), 146.3, 137.6 (d, J=7.3 Hz), 136.7, 131.5 (d, J=8.1 Hz), 130.4, 129.6, 124.4 (d, J=3.2 Hz), 119.1 (d, J=21.2 Hz), 115.4 (d, J=23.9 Hz), 48.0, 21.6, −31.2; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{15}FI_2NO_4S$ $[M+H]^+$ 601.8790, found 601.8801.

*4.5.3. N-(3,3-Diiodo-2-oxopropyl)-4-methyl-N-tosylbenzamide (**4c**).* By following the representative procedure (0.2 mmol), the title compound was obtained as a yellow solid (94.3 mg), 79% yield, mp 111–112 °C; ^{1}H NMR (400 MHz, Acetone) δ 7.93–7.73 (m, 2H), 7.42 (d, J=8.1 Hz, 2H), 7.38–7.28 (m, 2H), 7.23 (d, J=7.9 Hz, 2H), 6.14 (s, 1H), 5.33 (s, 2H), 2.46 (s, 3H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, Acetone) δ 194.1, 171.1, 146.0, 143.0, 137.0, 132.6, 130.3, 129.8, 129.6, 128.7, 48.2, 21.6, 21.5, −30.8; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{18}I_2NO_4S$ $[M+H]^+$ 597.9040, found 597.9070.

*4.5.4. N-(3,3-Diiodo-2-oxopropyl)-N-tosyl-4-(trifluoromethyl)benzamide (**4d**).* By following the representative procedure (0.16 mmol), the title compound was obtained as a yellow solid (83.4 mg), 80% yield, mp 139–140 °C; ^{1}H NMR (400 MHz, Acetone) δ 7.84–7.73 (m, 4H), 7.61 (d, J=8.1 Hz, 2H), 7.43 (d, J=8.1 Hz, 2H), 6.17 (s, 1H), 5.39 (s, 2H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, Acetone) δ 193.9, 169.9, 146.5, 139.5, 136.6, 132.98 (d, J=32.2 Hz), 130.5, 129.5, 129.1, 126.22 (d, J=3.9 Hz), 124.80 (d, J=272.7 Hz), 47.7, 21.6, −31.3; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{15}F_3I_2NO_4S$ $[M+H]^+$ 651.8758, found 651.8753.

*4.5.5. N-(3,3-Diiodo-2-oxopropyl)-4-fluoro-N-tosylbenzamide (**4e**).* By following the representative procedure (0.18 mmol), the title compound was obtained as a yellow solid (74.2 mg), 70% yield, mp 116–117 °C; ^{1}H NMR (400 MHz, Acetone) δ 7.92–7.73 (m, 2H), 7.61–7.48 (m, 2H), 7.48–7.35 (m, 2H), 7.27–7.11 (m, 2H), 6.15 (s, 1H), 5.36 (s, 2H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, Acetone) δ 194.0, 170.3, 165.3 (d, J=250.1 Hz), 146.2, 136.8, 132.0 (d, J=3.4 Hz), 131.4 (d, J=9.2 Hz), 130.4, 129.5, 116.3 (d, J=22.3 Hz), 48.0, 21.6, −31.0; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{15}FI_2NO_4S$ $[M+H]^+$ 601.8790, found 601.8798.

*4.5.6. N-(3,3-Diiodo-2-oxopropyl)-4-methoxy-N-tosylbenzamide (**4f**).* By following the representative procedure (0.16 mmol), the title compound was obtained as a yellow solid (50.9 mg), 52% yield, mp 121–122 °C; ^{1}H NMR (400 MHz, Acetone) δ 7.93–7.71 (m, 2H), 7.59–7.29 (m, 4H), 7.07–6.82 (m, 2H), 6.15 (s, 1H), 5.31 (s, 2H), 3.85 (s, 3H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, Acetone) δ 194.1, 170.9, 163.6, 145.9, 137.0, 131.2, 130.3, 129.5, 127.4, 114.6, 55.9, 48.3, 21.6, −30.6; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{18}I_2NO_5S$ $[M+H]^+$ 613.8990, found 613.9008.

*4.5.7. N-(3,3-Diiodo-2-oxopropyl)-N-tosylacetamide (**4g**).* By following the representative procedure (0.16 mmol), the title compound was obtained as a yellow solid (59.0 mg), 71% yield, mp 88–89 °C; ^{1}H NMR (400 MHz, Acetone) δ 8.18–7.68 (m, 2H), 7.49 (d, J=8.0 Hz, 2H), 6.24 (s, 1H), 5.29 (s, 2H), 2.47 (s, 3H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, Acetone) δ 193.5, 170.1, 146.3, 137.4, 130.8, 128.8, 46.6, 24.3, 21.5, −30.3; HRMS (ESI-TOF) m/z calcd for $C_{12}H_{14}I_2NO_4S$ $[M+H]^+$ 521.8727, found 521.8743.

*4.5.8. 3,3-Diiodo-2-oxopropyl benzoate (**4k**).* By following the representative procedure (0.4 mmol), the title compound was obtained as a yellow solid (113.1 mg), 66% yield, mp 98–99 °C; ^{1}H NMR (400 MHz, Acetone) δ 8.21–7.94 (m, 2H), 7.70 (t, J=7.4 Hz, 1H), 7.56 (t, J=7.6 Hz, 2H), 6.30 (s, 1H), 5.53 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, Acetone) δ 193.9, 166.0, 134.4, 130.5, 130.4, 129.6, 61.0, −30.4; HRMS (ESI-TOF) m/z calcd for $C_{10}H_9I_2O_3$ $[M+H]^+$ 430.8636, found 430.8638.

*4.5.9. 3,3-Diiodo-2-oxopropyl 3-bromobenzoate (**4l**).* By following the representative procedure (0.2 mmol), the title compound was obtained as a yellow solid (64.0 mg), 63% yield, mp 96–97 °C; ^{1}H NMR (400 MHz, Acetone) δ 8.21 (t, J=1.9 Hz, 1H), 8.08 (dt, J=7.9, 1.3 Hz, 1H), 7.88 (ddd, J=8.0, 2.0, 1.0 Hz, 1H), 7.54 (t, J=7.9 Hz, 1H), 6.30 (s, 1H), 5.55 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, Acetone) δ 193.6, 164.8, 137.3, 133.1, 132.4, 131.6, 129.4, 123.0, 61.3, −30.7; HRMS (ESI-TOF) m/z calcd for $C_{10}H_8BrI_2O_3$ $[M+H]^+$ 508.7741, found 508.7751.

*4.5.10. 3,3-Diiodo-2-oxopropyl 4-methoxybenzoate (**4m**).* By following the representative procedure (0.2 mmol), the title compound was obtained as a yellow solid (71.2 mg), 77% yield, mp 99–100 °C; ^{1}H NMR (400 MHz, Acetone) δ 8.05 (d, J=9.0 Hz, 2H), 7.07 (d, J=8.9 Hz, 2H), 6.28 (s, 1H), 5.47 (s, 2H), 3.91 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, Acetone) δ 194.0, 165.7, 164.9, 132.6, 122.4, 114.8, 60.8, 56.0, −30.2; HRMS (ESI-TOF) m/z calcd for $C_{11}H_{11}I_2O_4$ $[M+H]^+$ 460.8741, found 460.8733.

4.6. General procedure for the synthesis of oxazolines via Staudinger/aza-Wittig tandem process

In a 10 mL flame-dried Schlenk flask, iodinated product **2** (0.40 mmol) and NaN_3 (1.5 equiv) were dissolved in 3 mL of dry and degassed DMSO. The resulting solution was stirred at 80 °C for 12 h, and quenched with water. 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. Without further purification, the crude azide product was subjected to a mixture of PPh_3 (2.0 equiv) and toluene (3 mL). The resulting solution was then stirred at 120 °C for 8 h. After completion of the reaction, direct purification by flash chromatography on silica gel (petroleum ether/EtOAc: 2:1) afforded the expected product **5**.

*4.6.1. 4-Methyl-N-((2-phenyl-4,5-dihydrooxazol-5-yl)methyl)benzenesulfonamide (**5a**).* By following the procedure (0.4 mmol), the title compound was obtained as a white solid (97.6 mg), 74% yield, mp 77–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J=7.3 Hz, 2H), 7.74 (d, J=8.2 Hz, 2H), 7.47 (t, J=7.4 Hz, 1H), 7.38 (t, J=7.6 Hz, 2H), 7.31–7.23 (m, 2H), 5.20–5.06 (m, 1H), 4.78 (dtd, J=10.8, 7.2, 3.8 Hz, 1H), 4.07 (dd, J=15.0, 9.7 Hz, 1H), 3.72 (dd, J=15.0, 7.2 Hz, 1H), 3.29

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(ddd, J=13.4, 7.6, 3.8 Hz, 1H), 3.15–3.02 (m, 1H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.5, 143.8, 136.9, 131.7, 130.0, 128.5, 128.3, 127.3, 127.2, 78.1, 57.7, 46.6, 21.6; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{19}N_2O_3S$ $[M+H]^+$ 331.1111, found 331.1134.

*4.6.2. N-((2-(3-Bromophenyl)-4,5-dihydrooxazol-5-yl)methyl)-4-methylbenzenesulfonamide (**5b**).* By following the procedure (2.0 mmol), the title compound was obtained as a white solid (638.2 mg), 78% yield, mp 95–96 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (t, J=1.5 Hz, 1H), 7.73 (t, J=7.5 Hz, 3H), 7.61–7.49 (m, 1H), 7.29–7.17 (m, 3H), 5.74 (t, J=6.5 Hz, 1H), 4.95–4.63 (m, 1H), 4.06 (dd, J=15.1, 9.8 Hz, 1H), 3.76 (dd, J=15.2, 7.3 Hz, 1H), 3.27 (ddd, J=13.7, 7.2, 3.9 Hz, 1H), 3.17–3.05 (m, 1H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.3, 143.7, 136.8, 134.4, 131.2, 129.92, 129.91, 129.2, 127.0, 126.8, 122.3, 78.4, 57.5, 46.3, 21.6; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{18}BrN_2O_3S$ $[M+H]^+$ 409.0216, found 409.0220.

*4.6.3. 4-Methyl-N-((2-(4-(trifluoromethyl)phenyl)-4,5-dihydrooxazol-5-yl)methyl)benzenesulfonamide (**5e**).* By following the procedure (0.6 mmol), the title compound was obtained as a white solid (162.5 mg), 68% yield, mp 80–81 °C; ^1H NMR (400 MHz, acetone) δ 8.07 (d, J=8.2 Hz, 2H), 7.89–7.69 (m, 4H), 7.38 (d, J=8.1 Hz, 2H), 6.92 (t, J=6.3 Hz, 1H), 5.08–4.68 (m, 1H), 4.10 (dd, J=15.4, 9.8 Hz, 1H), 3.89 (dd, J=15.4, 7.1 Hz, 1H), 3.31 (ddd, J=13.9, 6.5, 4.1 Hz, 1H), 3.23–3.12 (m, 1H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, Acetone) δ 162.4, 143.9, 139.2, 132.9 (q, J=32.3 Hz), 132.6, 130.5, 129.6, 127.7, 125.0 (d, J=271.6 Hz), 126.1 (q, J=3.8 Hz), 79.5, 58.3, 47.0, 21.4; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{18}F_3N_2O_3S$ $[M+H]^+$ 399.0985, found 399.0990.

*4.6.4. N-((2-(Furan-2-yl)-4,5-dihydrooxazol-5-yl)methyl)-4-methylbenzenesulfonamide (**5f**).* By following the procedure (0.57 mmol), the title compound was obtained as a white solid (101.6 mg), 56% yield, mp 73–74 °C; ^1H NMR (400 MHz, Acetone) δ 7.98–7.58 (m, 3H), 7.38 (d, J=8.0 Hz, 2H), 6.90 (d, J=3.3 Hz, 2H), 6.68–6.48 (m, 1H), 5.03–4.64 (m, 1H), 4.02 (dd, J=15.0, 9.7 Hz, 1H), 3.81 (dd, J=15.0, 7.1 Hz, 1H), 3.37–3.07 (m, 2H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, Acetone) δ 155.9, 146.2, 144.2, 143.9, 139.0, 130.5, 127.7, 114.9, 112.3, 79.0, 58.2, 46.8, 21.4; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{17}N_2O_4S$ $[M+H]^+$ 321.0904, found 321.0908.

4.7. General procedure for the synthesis of epoxides

In a 10 mL flame-dried Schlenk flask, iodinated product **2a** or **2i** (0.20 mmol) and Na_2CO_3 (2.0 equiv) were dissolved in 3 mL of MeOH. The resulting solution was stirred at room temperature for 12 h, and quenched with water. 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. Purification by flash chromatography on silica gel (petroleum ether/EtOAc: 3:1) afforded the epoxide **2aa** or **2ia**.

*4.7.1. 4-Methyl-N-(oxiran-2-ylmethyl)benzenesulfonamide (**2aa**).* By following the procedure (0.2 mmol), the title compound was obtained as colorless oil (55.4 mg), 80% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95–7.56 (m, 2H), 7.31 (d, J=8.0 Hz, 2H), 5.01 (t, J=6.2 Hz, 1H), 3.45–3.17 (m, 1H), 3.14–2.95 (m, 2H), 2.74 (t, J=4.3 Hz, 1H), 2.62 (dd, J=4.6, 2.3 Hz, 1H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.76, 136.98, 129.91, 127.15, 50.44, 45.28, 44.52, 21.62; HRMS (ESI-TOF) m/z calcd for $C_{10}H_{14}NO_3S$ $[M+H]^+$ 228.0689, found 228.0687.

*4.7.2. 4-Iodo-N-(oxiran-2-ylmethyl)aniline (**2ia**).* By following the procedure (0.24 mmol), the title compound was obtained as colorless oil (61.1 mg), 93% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77–7.25 (m, 2H), 6.78–6.14 (m, 2H), 3.92 (s, 1H), 3.66–3.42 (m, 1H), 3.33–2.97 (m, 2H), 2.80 (dd, J=4.9, 3.8 Hz, 1H), 2.65 (dd, J=4.8, 2.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.6, 138.0, 115.3, 78.6, 50.9, 45.4, 44.9; HRMS (ESI-TOF) m/z calcd for $C_9H_{11}INO$ $[M+H]^+$ 275.9880, found 275.9896.

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Supplementary data

^1H and ^{13}C NMR spectra of all compounds and crystallographic data (CIF) of **2b**. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.07.011.

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