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Copper-Catalyzed Trifluoromethylthiolaton and Radical Cyclization of *N*-Phenylpent-4-Enamides to Construct SCF_3-Substituted γ-Lactams

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Abstract: An efficient method involving copper-catalyzed trifluoromethylthiolation and radical cyclization of *N*-phenylpent-4-enamides using readily available and stable $AgSCF_3$ as the trifluoromethylthiolating reagent is described. The method enables the synthesis of a series of potential medicinally valuable trifluoromethylthio-substituted γ-lactams and relative 2-oxazolidinone derivatives with broad functional group compatibility. Mechanistic investigations indicated that this reaction involved amidyl radical-initiated cascade *5-exo-trig* cyclization followed by trifluoromethylthiolation, resulting in the formation of new C-N and C-S bonds.

Keywords: copper catalysis; cyclization; γ-lactam; radical; trifluoromethylthiolation

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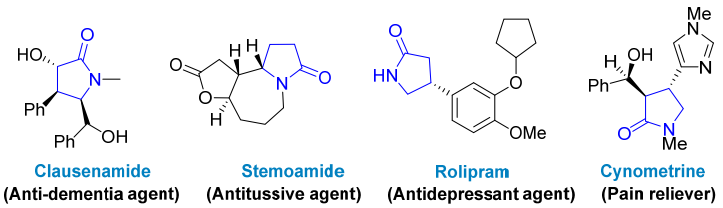
1. Introduction

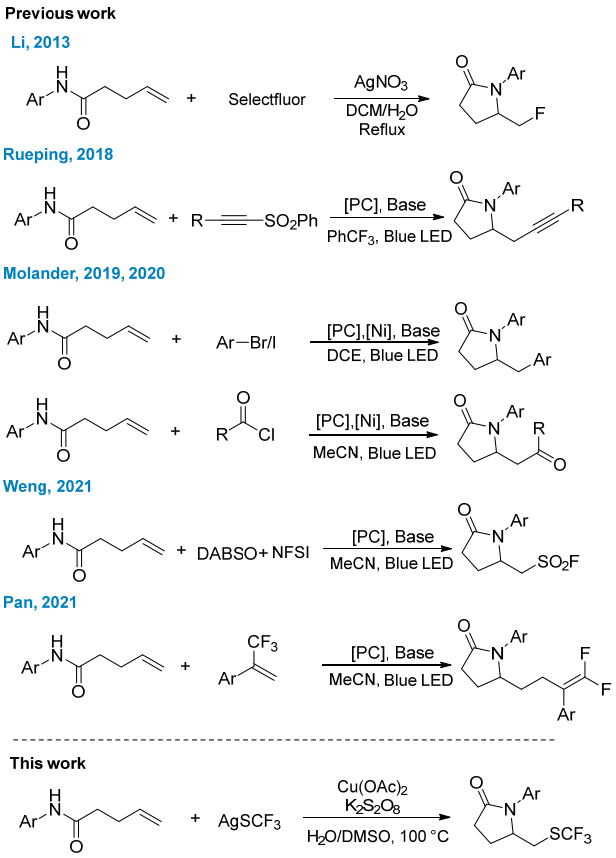
In recent years, the incorporation of fluorinated functional groups into organic molecules has gained significant attention, primarily due to the unique chemical and physical properties these groups impart to the molecules [1–3]. Among these, the trifluoromethylthio group ($-SCF_3$) stands out for its exceptional electronegativity, lipophilicity, and metabolic stability, making it a valuable moiety in the fields of pharmaceuticals, agrochemicals, and materials science [4–6]. As a result, tremendous efforts have been devoted to the direct preparation of trifluoromethylthiolated compounds via electrophilic [7–11], nucleophilic [12–16], and radical [17–21] trifluoromethylthiolation. Recently, the $SCF_3\bullet$ radical-cyclization pathway, initiated by stable and readily available silver trifluoromethylthiolate ($AgSCF_3$) as the SCF_3 radical source, has emerged as an efficient strategy for constructing SCF_3-substituted compounds. In particular, Wang [22], Liang [23], Qing [24], and ourselves [25], along with others [26–28], have utilized this approach to synthesize SCF_3-substituted cyclic compounds through trifluoromethylthiolation/cyclization of alkenes and alkynes. Despite these significant advances, there remains a strong demand for new methods to efficiently synthesize SCF_3-containing compounds, particularly those with medicinally promising scaffolds.

γ-Lactams are a class of five-membered cyclic amides that are present in numerous bioactive natural products and pharmaceutical compounds. For instance, claudsenamide, an *anti*-dementia agent, and stemoamide, an antitussive agent, are notable γ-lactam derivatives that showcase their therapeutic potential in addressing critical health issues. Other representative examples of biologically active γ-lactam derivatives are illustrated in Scheme 1 [29]. Despite their significance in drug development, there is still a need to expand the variety of γ-lactam derivatives to synthesize those with specific biological activities. In the past few years, the cascade radical cyclization/functionalization of *N*-phenyl-4-pentenamides through amidyl radicals for the synthesis of γ-lactam derivatives

has attracted great attention. For example, in 2013, Li reported an efficient silver-catalyzed radical fluorination/cyclization of various *N*-arylpent-4-enamides to afford 5-fluoromethyl-substituted γ-lactams [30]. Afterward, in 2018, Rueping disclosed the synthesis of alkyne and alkene-decorated γ-lactams through the photocatalytic proton-coupled electron transfer (PCET) activation of *N*-phenyl-4-pentenamides [31]. Later, Molander successively developed a photoredox PCET/Ni dual-catalyzed amidoarylation and aminoacylation of *N*-phenyl-4-pentenamides to construct γ-lactam derivatives [32,33]. More recently, Weng [34] and Pan [35] have described a mild photoredox catalytic approach to accessing sulfonyl fluoride and gem-difluoroalkene-substituted γ-lactams via radical cascade cyclization of *N*-phenyl-4-pentenamides, respectively (Scheme 2, top). Inspired by these elegant results and our ongoing interest in trifluoromethylthiolation [25] and γ-lactams [36–39], we became interested in preparing SCF_3-substituted γ-lactams that may be useful in medicinal chemistry. Herein, we disclose a method involving copper-catalyzed trifluoromethylthiolation and radical cyclization of *N*-phenyl-4-pentenamides using stable and easily operable $AgSCF_3$ to access SCF_3-substituted γ-lactams (Scheme 2, bottom).



Scheme 1. Representative examples of bioactive γ-lactam derivatives.

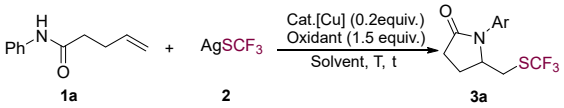


Scheme 2. Strategies to construct trifluoromethylthiolated γ-lactams [30–35].

2. Results and Discussion

In our initial investigation, *N*-phenylpent-4-enamide **1a** and $AgSCF_3$ **2** were selected as the model substrates to screen the reaction conditions, and the results are summarized in Table 1. To our delight, the desired trifluoromethylthiolated product **3a** was obtained in 55% yield when the reaction was conducted with $Cu(OAc)_2$ (0.2 mmol) and $K_2S_2O_8$ (1.5 equiv.) in the H_2O/DMSO (1/1, *v*/*v*) at 80 °C for 12 h (entry 1). Subsequent tests revealed that $Cu(OAc)_2$ was essential in enhancing the reaction efficiency, as other copper salts, whether Cu(I) or Cu(II), led to inferior results (entries 2–8). This is likely due to $Cu(OAc)_2$'s superior ability to generate amidyl radical intermediates, which is crucial for the desired radical cyclization process [40–42]. When water or DMSO was used as the sole solvent, the yield of **3a** dropped to 0% or 43%, respectively (entries 9, 10). These results revealed that water and DMSO mixture solvent may be the best solvent system for the reaction. Further variation in the ratio of mixed solvent systems showed that a H_2O/DMSO (1:3, *v*/*v*) mixture resulted in an improved yield of 67% (entries 11, 12). Next, different oxidants were tested in order to improve yield further, but $K_2S_2O_8$ consistently gave the best results (entries 13–17), which is consistent with the literature indicating that $S_2O_8^{2-}$ is effective for the formation of SCF_3 radicals [22–24]. Finally, the effects of reaction temperature and time were investigated. The results indicated that increasing the reaction temperature to 100 °C further boosted the yield to 73% (entries 18 and 19). Additionally, shortening the reaction time to 6 h did not reduce the yield (entries 20 and 21; for more details regarding the screening of conditions, refer to the Supporting Information). Therefore, the conditions described in entry 20 were selected as the optimal conditions.

Table 1. Optimization of the reaction conditions [a,b].



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

Entry	[Cu]	Oxidant	Solvent	T (°C)	t (h)	Yield (%) [b]
1	$Cu(OAc)_2$	$K_2S_2O_8$	H_2O/DMSO (1:1)	80	12	55
2	$CuSO_4$	$K_2S_2O_8$	H_2O/DMSO (1:1)	80	12	47
3	$CuCl_2$	$K_2S_2O_8$	H_2O/DMSO (1:1)	80	12	46
4	$Cu(acac)_2$	$K_2S_2O_8$	H_2O/DMSO (1:1)	80	12	26
5	$CuBr_2$	$K_2S_2O_8$	H_2O/DMSO (1:1)	80	12	45
6	CuO	$K_2S_2O_8$	H_2O/DMSO (1:1)	80	12	7
7	Cu_2O	$K_2S_2O_8$	H_2O/DMSO (1:1)	80	12	38
8	CuCl	$K_2S_2O_8$	H_2O/DMSO (1:1)	80	12	32
9	$Cu(OAc)_2$	$K_2S_2O_8$	H_2O	80	12	NR
10	$Cu(OAc)_2$	$K_2S_2O_8$	DMSO	80	12	43
11	$Cu(OAc)_2$	$K_2S_2O_8$	H_2O/DMSO (1:2)	80	12	62
12	$Cu(OAc)_2$	$K_2S_2O_8$	H_2O/DMSO (1:3)	80	12	67
13	$Cu(OAc)_2$	$Na_2S_2O_8$	H_2O/DMSO (1:3)	80	12	26
14	$Cu(OAc)_2$	$(NH_4)_2S_2O_8$	H_2O/DMSO (1:3)	80	12	64
15	$Cu(OAc)_2$	TBHP	H_2O/DMSO (1:3)	80	12	NR
16	$Cu(OAc)_2$	*m*-CPBA	H_2O/DMSO (1:3)	80	12	NR
17	$Cu(OAc)_2$	DTBP	H_2O/DMSO (1:3)	80	12	NR
18	$Cu(OAc)_2$	$K_2S_2O_8$	H_2O/DMSO (1:3)	60	12	53
19	$Cu(OAc)_2$	$K_2S_2O_8$	H_2O/DMSO (1:3)	100	12	73
20	$Cu(OAc)_2$	$K_2S_2O_8$	H_2O/DMSO (1:3)	100	6	73
21	$Cu(OAc)_2$	$K_2S_2O_8$	H_2O/DMSO (1:3)	100	18	68

[a] Reaction conditions: **1a** [a] reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv.), Cu catalyst (0.2 equiv.), $K_2S_2O_8$ (1.5 equiv.) in solvent (2.0 mL) at 100 °C for 6 h; [b] isolated yield.

With the optimized conditions established, we then set out to investigate the cascade cyclization reaction between various *N*-arylpent-4-enamides **1** and $AgSCF_3$, as summarized in Figure 1. Various substrates containing either an electron-donating (**3b**, **3c**, **3f**) or

electron-withdrawing (**3d**, **3e**) group at the *para*-position of the aryl group were all tolerated under reaction conditions, leading to the desired products in moderate to good yields. *N*-phenylpent-4-enamides with *ortho*- or *meta*-substitutions also reacted efficiently with **2**, producing trifluoromethylthiolated γ-lactam products in 42–66% yields (**3g**–**3k**). Even when substrates had two substituents on the phenyl ring, including one at the *meta*-position (**3p**, **3q**), the reaction efficiency was not significantly impacted, leading to the formation of products (**3m**–**3r**), which shows that the steric hindrance of *N*-phenylpent-4-enamide did not affect this transformation. Furthermore, substrates with the methyl group at the α-carbonyl position were tried and were compatible with this reaction as well (**3s**, **3t**). Finally, to explore the scope of this transformation, several carbamate substrates were examined under the standard reaction condition and resulted in good yields (**3u**–**3x**).

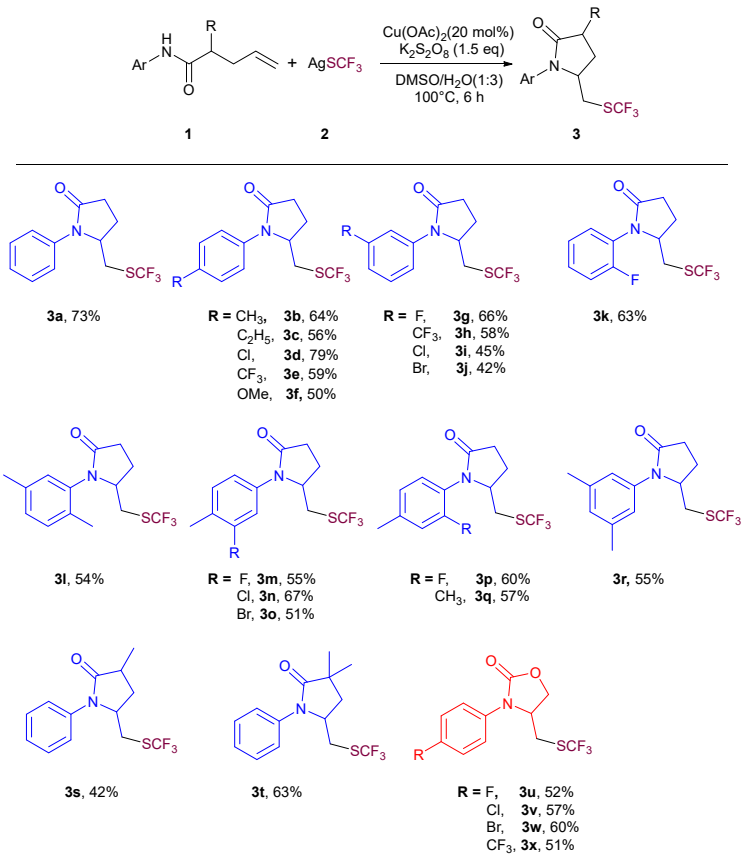
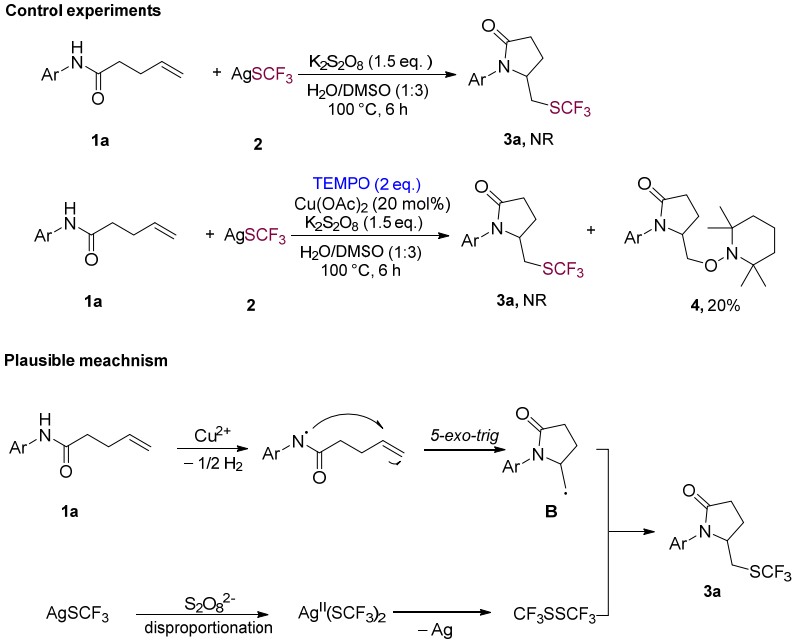


Figure 1. Substrate scope of *N*-arylpent-4-enamides (**1**). Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv.), $Cu(OAc)_2$ (0.2 equiv.), oxidant (1.5 equiv.) in $DMSO/H_2O$ (3:1, 2.0 mL) at 100 °C for 6 h; isolated yield.

To gain deeper insight into the plausible reaction mechanism, we performed several control experiments (Scheme 3, top). First, when **1a** and **2** were subjected to the reaction conditions without $Cu(OAc)_2$, the desired product **3** did not form. This indicates that copper plays a crucial role in the catalytic cycle. Furthermore, the addition of the radical scavenger 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) to the standard reaction of **1a** and **2** resulted in the total inhibition of the reaction, suggesting the possible involvement of a radical process. Notably, the TEMPO-trapped product **4** was observed by ^{1}H NMR spectroscopy in approximately 20% yield [38]. Despite the lack of complete clarity on the process of this transformation, a feasible reaction mechanism was postulated based on prior studies and the experimental data mentioned above (Scheme 3, bottom). Firstly, $Cu(OAc)_2$ facilitated the formation of an amidyl radical via N-H bond activation [40–42]. Subsequently, the amidyl radical underwent addition to the C=C bond, resulting in the formation of intermediate **B** via *5-exo-trig* cyclization. Meanwhile, $AgSCF_3$ was oxidized

by $K_2S_2O_8$ to generate the $AgII(SCF_3)_2$, which further transformed into CF_3SSCF_3 [22–24]. Finally, CF_3SSCF_3 decomposed and released a SCF_3 radical, which was coupled with **B** to give the trifluoromethylthiolation product **3a**.



Scheme 3. Control experiments and plausible mechanism.

3. Experimental Section

General Information: ^1H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra were recorded on a Bruker NMR apparatus (Bremen, Germany) with $CDCl_3$ as the solvent. The chemical shifts are reported in δ (ppm) values. ^1H NMR chemical shifts were determined relative to the internal tetramethylsilane signal at δ 0.0. ^{19}F NMR chemical shifts were determined relative to external $CHCl_3$ at δ 0.0. Data for ^1H, ^{13}C, and ^{19}FNMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, br = broad). Coupling constants (*J*) are reported in Hertz (Hz). Melting points were measured by SGW X-4A microscopic apparatus (Shanghai INESA Physico-Optical Instrument Co., Ltd., Shanghai, China). HRMS was measured by Q Exactive Hybrid Quadrupole-Orbitrap LC/MS spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The starting materials, including the aniline, 4-pentene acid, phosphorus oxychloride, and triethylamine, were obtained from commercial sources such as Aladdin (Calhoun, GA, USA), Macklin (Shanghai, China), Alfa Aesar (Ward Hill, MA, USA), and Ourchem (Guangzhou, China) and used as received unless otherwise noted. Ethyl acetate (Titanchem, Shanghai, China) and petroleum ether (Titanchem, Shanghai, China) were used for column chromatography without further purification.

General procedure for the synthesis of desired products forming SCF_3-substituted γ-lactams (3a–3x).

A mixture of substituted *N*-phenylpent-4-enamides (**1**, 0.2 mmol), $AgSCF_3$ (**2**, 0.3 mmol), $K_2S_2O_8$ (0.3 mmol), and $Cu(OAc)_2$ (0.04 mmol) in H_2O/DMSO (1:3, 2 mL) was stirred at 100 °C for 6 h. After the reaction was completed, it was quenched with saturated $NaHCO_3$, and the crude solution was separated after diluting with ethyl acetate and dried over anhydrous Na_2SO_4. The solvent was removed in vacuum to obtain the crude product, which was further separated and purified by column chromatography to give the desired products (**3a–3x**).

1-phenyl-5-{[(trifluoromethyl)sulfanyl]methyl}pyrrolidin-2-one (3a): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.31 (m, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.22–7.15 (m, 1H), 4.51–4.38 (m, 1H, CH), 3.10 (dd, *J* = 13.8, 3.0 Hz, 1H), 2.80 (dd, *J* = 13.8, 8.3 Hz, 1H), 2.69–2.46 (m, 2H), 2.45–2.35 (m, 1H), 1.99–1.89 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 135.5, 129.6 (q, *J* = 307.0 Hz), 128.4, 125.5, 122.9, 57.4, 32.0 (q, *J* = 2.0 Hz), 29.6, 22.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.65. HRMS: Cal. $C_{12}H_{12}OF_3NS$ $(M + H)^+$: 276.0664, found 276.0665.

1-(4-methylphenyl)-5-{[(trifluoromethyl)sulfanyl]methyl}pyrrolidin-2-one (3b): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 4H), 4.52–4.42 (m, 1H, CH), 3.15 (dd, *J* = 13.7, 2.8 Hz, 1H), 2.87 (dd, *J* = 13.7, 8.3 Hz, 1H), 2.74–2.52 (m, 2H), 2.52–2.39 (m, 1H), 2.35 (s, 3H), 2.05–1.97 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 136.7, 133.9, 132.2 (q, *J* = 304.4 Hz), 130.1, 124.2, 58.7, 33.2 (q, *J* = 1.9 Hz), 30.7, 23.1, 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.56. HRMS: Cal. $C_{13}H_{14}OF_3NS$ $(M + H)^+$: 290.0821, found 290.0822.

1-(4-ethylphenyl)-5-(((trifluoromethyl)thio)methyl)pyrrolidin-2-one (3c): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.7 Hz, 4H), 4.53–4.42 (m, 1H, CH), 3.16 (dd, *J* = 13.7, 3.0 Hz, 1H), 2.92–2.83 (m, 1H), 2.74–2.54 (m, 4H), 2.51–2.39 (m, 1H), 2.07–1.97 (m, 1H), 1.23 (d, *J* = 7.6 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 142.9, 134.0, 131.0 (q, *J* = 394.7 Hz), 128.9, 124.2, 58.7, 33.1 (q, *J* = 1.8 Hz), 30.7, 28.4, 23.0, 15.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.64. HRMS: $C_{14}H_{16}OF_3NS$ $(M + H)^+$: 303.0905, found 303.0906.

1-(4-chlorophenyl)-5-{[(trifluoromethyl)sulfanyl]methyl}pyrrolidin-2-one (3d): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.55–4.45 (m, 1H, CH), 3.21–3.10 (m, 1H), 2.87 (dd, *J* = 13.8, 8.3 Hz, 1H), 2.75–2.64 (m, 1H), 2.63–2.53 (m, 1H), 2.53–2.41 (m, 1H), 2.08–1.96 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 135.2, 131.9, 130.6 (q, *J* = 305.5 Hz), 129.6, 124.9, 58.3, 32.9 (q, *J* = 1.8 Hz), 30.6, 23.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.49. HRMS: $C_{12}H_{11}OClF_3NS$ $(M + H)^+$: 310.0275, found 310.0276.

1-[4-(trifluoromethyl)phenyl]-5-{[(trifluoromethyl)sulfanyl]methyl}pyrrolidin-2-one (3e): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 4.73–4.62 (m, 1H, CH), 3.21 (dd, *J* = 14.0, 2.8 Hz, 1H), 2.94 (dd, *J* = 8.8, 8.4 Hz, 1H), 2.86–2.74 (m, 1H), 2.74–2.63 (m, 1H), 2.64–2.53 (m, 1H), 2.19–2.08 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 139.9, 130.3 (q, *J* = 308.0 Hz), 127.9 (d, *J* = 35.8Hz), 126.5 (q, *J* = 3.8 Hz), 126.2 (d, *J* = 3.6 Hz), 123.8 (d, *J* = 273.9 Hz), 122.8, 118.4, 58.0, 32.7 (q, *J* = 1.8 Hz), 30.7, 22.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.52, −62.48. HRMS:Cal. $C_{13}H_{11}OF_6NS$ $(M + H)^+$: 344.0538, found 344.0533.

1-(4-methoxyphenyl)-5-(((trifluoromethyl)thio)methyl)pyrrolidin-2-one (3f): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.45–4.36 (m, 1H, CH), 3.81 (s, 3H, OCH_3), 3.12 (dd, *J* = 13.7, 3.1 Hz, 1H), 2.94–2.82 (m, 1H), 2.71–2.56 (m, 2H), 2.51–2.38 (m, 1H), 2.06–1.93 (m, 1H). ^{13}C NMR (101 MHz, CDC_{l3}) δ 174.2, 158.2, 130.7 (q, *J* = 306.7 Hz), 129.2, 126.1, 114.7, 59.0, 55.5, 33.2 (q, *J* = 1.9 Hz), 30.5, 23.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.72. HRMS: Cal. $C_{13}H_{14}O_2F_3NS$ $(M + H)^+$: 305.0697, found 305.0698.

1-(3-fluorophenyl)-5-{[(trifluoromethyl)sulfanyl]methyl}pyrrolidin-2-one (3g): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (q, *J* = 8.1 Hz, 1H), 7.24–7.16 (m, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.94–6.84 (m, 1H), 4.55–4.38 (m, 1H, CH), 3.27–3.08 (m, 1H), 2.82 (dd, *J* = 13.9, 8.5 Hz, 1H), 2.71–2.58 (m, 1H), 2.59–2.46 (m, 1H), 2.46–2.34 (m, 1H), 2.03–1.90 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 162.1 (d, *J* = 247.8 Hz), 137.2 (d, *J* = 10.3 Hz), 129.6 (q, *J* = 307.6 Hz), 129.5 (d, *J* = 9.7 Hz), 117.3 (d, *J* = 2.9 Hz), 112.2 (d, *J* = 21.5 Hz), 109.9 (d, *J* = 24.5 Hz), 57.2, 31.7 (q, *J* = 1.8 Hz), 29.6, 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.59, −110.64. HRMS: Cal. $C_{12}H_{11}OF_4NS$ $(M + H)^+$: 294.0570, found 294.0572.

1-[3-(trifluoromethyl)phenyl]-5-{[(trifluoromethyl)sulfanyl]methyl}pyrrolidin-2-one (3h): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 4.69–4.48 (m, 1H, CH), 3.21 (d, *J* = 13.6 Hz, 1H), 2.99–2.81 (m, 1H), 2.79–2.69 (m, 1H), 2.69–2.58 (m, 1H), 2.56–2.43 (m, 1H), 2.16–2.01 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 137.3, 130.6 (d, *J* = 223.1 Hz), 130.5 (q, *J* = 301.5Hz), 130.1, 127.7 (d, *J* = 34.9 Hz), 126.6, 122.9 (q, *J* = 3.7 Hz), 119.8 (d, *J* = 3.9 Hz), 58.2, 32.7 (q, *J* = 1.8 Hz), 30.6, 22.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.61, −62.79. HRMS: Cal. $C_{13}H_{11}OF_6NS$ $(M + H)^+$: 344.0538, found 344.0535.

1-(3-chlorophenyl)-5-(((trifluoromethyl)thio)methyl)pyrrolidin-2-one (3i): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 2.1 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.29–7.19 (m, 2H), 4.60–4.41 (m, 1H, CH), 3.18 (dd, *J* = 13.9, 2.9 Hz, 1H), 2.94–2.81 (m, 1H), 2.75–2.64 (m, 1H), 2.64–2.54 (m, 1H), 2.52–2.44 (m, 1H), 2.11–1.95 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 137.8, 135.1, 130.5 (q, *J* = 306.9 Hz), 130.4, 126.5, 123.7, 121.4, 58.3, 32.8 (q, *J* = 1.8 Hz), 30.6, 22.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.57. HRMS: Cal. $C_{12}H_{11}ClF_3NOS$ $(M + H)^+$: 309.0202, found 309.0203.

1-(3-bromophenyl)-5-(((trifluoromethyl)thio)methyl)pyrrolidin-2-one (3j): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (t, *J* = 2.0 Hz, 1H), 7.40 (dt, *J* = 7.5, 1.7 Hz, 1H), 7.37–7.33 (m, 1H), 7.33–7.28 (m, 1H), 4.59–4.42 (m, 1H, CH), 3.20 (dd, *J* = 13.9, 2.9 Hz, 1H), 2.90 (dd, *J* = 13.9, 8.4 Hz, 1H), 2.78–2.66 (m, 1H), 2.66–2.55 (m, 1H), 2.54–2.42 (m, 1H), 2.12–1.98 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 138.0, 130.6, 130.3 (q, *J* = 307.2 Hz), 129.4, 126.6, 122.9, 121.9, 58.3, 32.8 (q, *J* = 1.8 Hz), 30.6, 22.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.57. HRMS: Cal. $C_{12}H_{11}OBrF_3NS$ $(M + H)^+$: 352.9697, found 302.9698.

1-(2-fluorophenyl)-5-{[(trifluoromethyl)sulfanyl]methyl}pyrrolidin-2-one (3k): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.27 (m, 2H), 7.24–7.13 (m, 2H), 4.49–4.32 (m, 1H, CH), 3.05 (dd, *J* = 13.7, 3.3 Hz, 1H), 2.88 (dd, *J* = 13.6, 7.7 Hz, 1H), 2.72–2.44 (m, 3H), 2.13–1.97 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 157.7 (d, *J* = 252.0 Hz), 130.6 (q, *J* = 306.3 Hz), 129.6 (d, *J* = 8.1 Hz), 129.5 (d, *J* = 1.5 Hz), 124.9 (d, *J* = 3.7 Hz), 123.8 (d, *J* = 12.1 Hz), 116.9 (d, *J* = 19.9 Hz), 58.7 (d, *J* = 3.3 Hz), 33.3 (q, *J* = 1.7 Hz), 30.0, 23.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.90, −119.90–−119.96. HRMS: Cal. $C_{12}H_{11}OF_4NS$ $(M + H)^+$: 294.0570, found 294.0573.

1-(2,5-dimethylphenyl)-5-{[(trifluoromethyl)sulfanyl]methyl}pyrrolidin-2-one (3l): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, *J* = 19.1 Hz, 3H), 4.54–4.37 (m, 1H, CH), 3.15 (dd, *J* = 13.8, 2.7 Hz, 1H), 2.85 (dd, *J* = 13.7, 8.4 Hz, 1H), 2.68–2.52 (m, 2H), 2.50–2.40 (m, 1H), 2.32 (s, 6H, CH_3), 2.06–1.93 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 139.1, 136.3, 130.7 (q, *J* = 306.4 Hz), 128.6, 122.0, 121.2, 121.7, 58.8, 33.0 (q, *J* = 1.8Hz), 30.7, 29.7, 23.1, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.65. HRMS: Cal. $C_{14}H_{16}OF_3NS$ $(M + H)^+$: 304.0977, found 304.0975.

1-(3-fluoro-4-methylphenyl)-5-{[(trifluoromethyl)sulfanyl]methyl}pyrrolidin-2-one (3m): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.10 (m, 2H), 7.01 (dd, *J* = 8.2, 2.1 Hz, 1H), 4.50–4.44 (m, 1H, CH), 3.17 (dd, *J* = 13.8, 2.9 Hz, 1H), 2.88 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.69–2.54 (m, 2H), 2.51–2.39 (m, 1H), 2.26 (s, 3H, CH_3), 2.09- 1.96 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 160.2 (d, *J* = 244.3Hz), 134.5(d, *J* = 9.9 Hz), 130.9(d, *J* = 6.3 Hz), 129.6 (q, *J* = 307.5 Hz), 122.1 (d, *J* = 17.3 Hz), 117.6 (d, *J* = 3.5 Hz), 109.9 (d, *J* = 25.6 Hz), 57.3, 31.8 (q, *J* = 1.8 Hz), 29.5, 21.8, 13.1 (d, *J* = 3.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.60, −114.43–−114.61. HRMS: Cal. $C_{13}H1_3OF_4NS$ $(M + H)^+$: 308.0727, found 308.0729.

1-(3-chloro-4-methylphenyl)-5-{[(trifluoromethyl)sulfanyl]methyl}pyrrolidin-2-one (3n): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 2.3 Hz, 1H), 7.29–7.23 (m, 1H), 7.15 (dd, *J* = 8.2, 2.2 Hz, 1H), 4.54–4.40 (m, 1H, CH), 3.15 (dd, *J* = 13.8, 2.9 Hz, 1H), 2.92–2.81 (m, 1H), 2.71–2.62 (m, 1H), 2.62–2.53 (m, 1H), 2.50–2.41 (m, 1H), 2.36 (s, 3H, CH_3), 2.09–1.97 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9 134.3, 133.9, 133.4, 130.4, 129.6 (q, *J* = 305.6Hz), 123.4, 120.9, 57.3, 31.8 (q, *J* = 1.6 Hz), 29.5, 21.9, 18.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.59. HRMS: Cal. $C_{13}H_{13}OClF_3NS$ $(M + H)^+$: 324.0431, found 324.0432.

1-(3-bromo-4-methylphenyl)-5-{[(trifluoromethyl)sulfanyl]methyl}pyrrolidin-2-one (3o): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 2.1 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.14 (dd, *J* = 8.2, 2.1 Hz, 1H), 4.47–4.29 (m, 1H, CH), 3.09 (dd, *J* = 13.8, 2.9 Hz, 1H), 2.81 (dd, *J* = 13.8, 8.3 Hz, 1H), 2.68–2.47 (m, 2H), 2.44–2.35 (m, 1H), 2.30 (s, 3H, CH_3), 1.99–1.89 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 135.3, 134.3, 130.2, 129.3 (q, *J* = 305.1 Hz), 126.5, 124.1, 121.6, 57.3, 31.8 (d, *J* = 1.8 Hz), 29.5, 21.9, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.58. HRMS: Cal. $C_{13}H_{13}OBrF_3NS$ $(M + H)^+$: 367.9926, found 367.9925.

1-(2-fluoro-4-methylphenyl)-5-{[(trifluoromethyl)sulfanyl]methyl}pyrrolidin-2-one (3p): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.06 (m, 1H), 7.10–6.89 (m, 2H), 4.43–4.27 (m, 1H, CH), 3.05 (dd, *J* = 13.6, 3.5 Hz, 1H), 2.88 (dd, *J* = 13.6, 7.7 Hz, 1H), 2.68–2.56 (m, 2H), 2.53–2.44 (m, 1H), 2.36 (s, 3H, CH_3), 2.08–1.95 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 156.5 (d, *J* = 250.9 Hz), 139.5 (d, *J* = 7.8 Hz), 130.1 (q, *J* = 306.3 Hz), 128.1 (d, *J* = 2.0 Hz), 124.6 (d, *J* = 3.2 Hz), 119.9 (d, *J* = 12.4 Hz), 116.3 (d, *J* = 19.6 Hz), 57.7 (d, *J* = 3.0 Hz), 32.3 (d, *J* = 1.6 Hz), 28.9, 22.8, 20.2 (d, *J* = 1.3 Hz), ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.89, −121.00–−121.05. HRMS: Cal. $C_{13}H_{13}OF_4NS$ $(M + H)^+$: 308.0727, found 308.0725.

1-(2,4-dimethylphenyl)-5-(((trifluoromethyl)thio)methyl)pyrrolidin-2-one (3q): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 2.0 Hz, 1H), 7.04 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 4.40–4.04 (m, 1H, CH), 3.04 (dd, *J* = 13.5, 3.6 Hz, 1H), 2.91–2.76 (m, 1H), 2.68–2.55 (m, 2H), 2.55–2.44 (m, 1H), 2.32 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.09–1.95 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 138.4, 135.9, 132.3, 130.6 (q, *J* = 306.3 Hz), 127.8, 33.3, 30.1, 24.2, 21.01, 18.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.92. HRMS: Cal. $C_{14}H_{16}OF_3NS$ $(M + H)^+$: 303.0905, found 303.0906.

1-(3,5-dimethylphenyl)-5-{[(trifluoromethyl)sulfanyl]methyl}pyrrolidin-2-one (3r): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 2H), 6.90 (s, 1H), 4.50–4.41 (m, 1H, CH), 3.16 (dd, *J* = 13.7, 2.9 Hz, 1H), 2.85 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.75–2.55 (m, 2H), 2.50–2.41 (m, 1H), 2.32 (s, 6H, CH_3), 2.07–1.95 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 139.1, 136.3, 130.7 (q, *J* = 306.1 Hz), 128.5, 121.9, 58.8, 33.1 (q,

J = 1.8 Hz), 30.7, 23.1, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.65. HRMS: Cal. $C_{14}H_{16}OF_3NS$ $(M + H)^+$: 303.0905, found 303.0902.

3-methyl-1-phenyl-5-(((trifluoromethyl)thio)methyl)pyrrolidin-2-one (3s): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.37 (m, 4H), 7.25–7.20 (m, 1H), 4.52–4.41 (m, 1H, CH), 3.16 (dd, *J* = 13.9, 3.0 Hz, 1H), 2.91–2.71 (m, 2H), 2.36–2.26 (m, 1H), 2.10–2.00 (m, 1H), 1.29 (dd, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 136.9, 132.2 (q, *J* = 307.1 Hz), 129.4, 126.1, 123.0, 56.6, 36.0, 32.3 (q, *J* = 1.7 Hz), 31.5, 16.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.63. HRMS: Cal. $C_{13}H_{14}OF_3NS$ $(M + H)^+$: 289.0748, found 289.0749.

3,3-dimethyl-1-phenyl-5-(((trifluoromethyl)thio)methyl)pyrrolidin-2-one (3t): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.38 (m, 2H), 7.33–7.29 (m, 2H), 7.28–7.22 (m, 1H), 4.47–4.33 (m, 1H, CH), 3.22 (dd, *J* = 13.7, 3.1 Hz, 1H), 2.81 (ddd, *J* = 13.7, 8.7, 0.9 Hz, 1H), 2.34 (dd, *J* = 13.0, 7.2 Hz, 1H), 1.81 (dd, *J* = 13.0, 7.7 Hz, 1H), 1.33 (s, 3H, CH_3), 1.24 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 136.7, 130.7 (q, *J* = 307.2 Hz), 129.3, 126.5, 124.2, 54.8, 40.8, 39.4, 33.5 (q, *J* = 1.8 Hz), 25.7, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.69. HRMS: Cal. $C_{14}H_{16}OF_3NS$ $(M + H)^+$: 303.0905, found 303.0906.

3-(4-fluorophenyl)-4-(((trifluoromethyl)thio)methyl)oxazolidin-2-one (3u): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 9.4 Hz, 2H), 4.81–4.72 (m, 1H), 4.69–4.62 (m, 1H, CH), 4.37 (dd, *J* = 9.3, 3.8 Hz, 1H), 3.37–3.28 (m, 1H), 3.01–2.91 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 138.0 (d, *J* = 1.1 Hz), 129.3 (q, *J* = 308.4 Hz), 126.3 (d, *J* = 32.8 Hz), 125.3 (d, *J* = 3.8 Hz), 125.8 (d, *J* = 11.4 Hz), 122.8 (d, *J* = 270.7 Hz), 119.0, 64.7, 54.0, 29.9 (q, *J* = 2.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.16, −62.41. HRMS: Cal. $C_{11}H_9O_2F_3NS$ $(M + H)^+$: 295.0290, found 295.0291.

2-(4-chlorophenyl)-4-(((trifluoromethyl)thio)methyl)oxazolidin-2-one (3v): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 4H), 4.71–4.65 (m, 1H, CH), 4.65–4.60 (m, 1H), 4.32 (dd, 1H), 3.27 (ddd, *J* = 14.5, 2.8, 1.0 Hz, 1H), 3.03–2.87 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 133.3, 130.3, 129.3 (q, *J* = 307.9 Hz), 128.7, 121.5, 64.7, 54.4, 30.0 (q, *J* = 1.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.27. HRMS: Cal. $C1_1H_9O_2ClF_3NS$ $(M + H)^+$: 210.9995, found 310.9996.

3-(4-bromophenyl)-4-(((trifluoromethyl)thio)methyl)oxazolidin-2-one (3w): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.51 (m, 2H), 7.38–7.29 (m, 2H), 4.73–4.65 (m, 1H, CH), 4.65–4.60 (m, 1H), 4.35–4.28 (m, 1H), 3.35–3.21 (m, 1H), 2.95 (dd, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 133.8, 131.7, 129.1 (q, *J* = 306.3 Hz), 121.7, 118.0, 64.7, 54.3, 30.0 (q, *J* = 1.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.25. HRMS: Cal. $C_{11}H_9O_2BrF_3NS$ $(M + H)^+$: 354.9489, found 354.9490.

3-(4-(trifluoromethyl)phenyl)-4-(((trifluoromethyl)thio)methyl)oxazolidin-2-one (3x): The target product was synthesized as a colorless oil and purified by column chromatography (ethyl acetate/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 4.82–4.71 (m, 1H, CH), 4.65 (t, *J* = 8.7 Hz, 1H), 4.36 (dd, *J* = 9.3, 3.8 Hz, 1H), 3.33 (dd, *J* = 14.7, 2.8 Hz, 1H), 2.97 (dd, *J* = 14.6, 9.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 139.0 (d, *J* = 1.3 Hz), 130.3 (d, *J* = 306.1 Hz), 127.3 (d, *J* = 33.2 Hz), 126.8 (d, *J* = 11.4 Hz), 126.8 (q, *J* = 3.8 Hz), 123.7 (d, *J* = 271.8 Hz), 120.1, 65.7, 55.1, 30.9 (d, *J* = 1.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.17, −62.42. HRMS: Cal. $C_{12}H_9O_2F_6NS$ $(M + H)^+$: 345.0258, found 345.0259.

4. Conclusions

In summary, we have developed an efficient method for copper-catalyzed trifluoromethylthiolation and cyclization reaction of *N*-phenylpent-4-enamides using the stable and operationally simple $AgSCF_3$ as the trifluoromethylthiolation reagent. This methodology allows for the synthesis of novel and potentially valuable SCF_3-containing γ-lactam derivatives, which are characterized by a broad substrate scope and excellent functional group compatibility. Mechanistic studies indicate that the reaction likely proceeds via a radical pathway, facilitating the formation of new C-N and C-S bonds. We believe that these γ-lactam derivatives have important application value in the development of new drugs in the future.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal14110797/s1.

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