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Visible Light-Induced Photoredox Construction of Trifluoromethylated Quaternary Carbon Centers from Trifluoromethylated Tertiary Bromides

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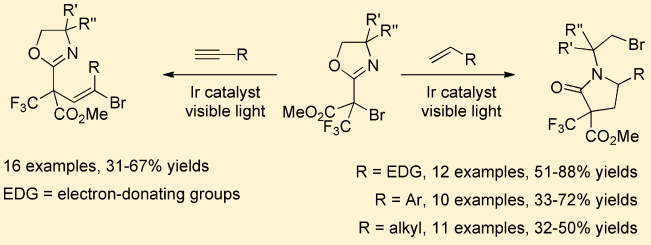
Supporting Information

ABSTRACT: A mild, operationally simple, visible light-induced photoredox method for constructing novel trifluoromethylated quaternary carbon centers from trifluoromethylated tertiary bromides has been developed. Using this method, a wide range of alkenes were successfully bifunctionalized to γ-butyrolactams. As for electron-rich alkenes, reactions catalyzed by $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$ were kinetic processes with high yields and short times. For styrenes, reactions catalyzed by $Ir(ppy)_2(dtbbpy)(PF_6)$ were thermodynamic processes with moderate yields and prolonged reaction times. For aliphatic alkenes, the reactions were neither thermodynamic nor kinetic and *fac*-$Ir(ppy)_3$ was used as catalyst. Thus, reactions were not as efficient as electron-rich alkenes. The atom-transfer radical addition reactions of trifluoromethylated tertiary bromides with alkynes were also achieved. The configuration of products we separated was *E* type only. Some of the products exhibited bactericidal activity.



INTRODUCTION

The incorporation of a trifluoromethyl group into small organic molecules can usually drastically enhance the metabolic stability, lipophilicity, and bioavailability of the origin compounds.[1] Therefore, trifluoromethyl-containing compounds are widely applied in pharmaceuticals, agrochemicals, and materials. Famous examples are the antidepressant Prozac and broad-spectrum insecticide Fipronil. On the other hand, all-carbon quaternary centers usually serve as core functional parts in natural products and drug molecules.[2] For example, the anticancer drug Taxol contains two quaternary carbon centers. Combining trifluoromethyl and quaternary carbon center is trifluoromethylated quaternary carbon center (TFQC, as shown in Figure 1). The structure is expected to have strong rigidity and a unique electrical property through modification of fluorine. Therefore, constructing quaternary carbon centers by introducing fluorine is an important method for developing drugs. For example, flurithromycin is a fluorinated analogue of erythromycin developed to improve stability under acidic conditions.[3]

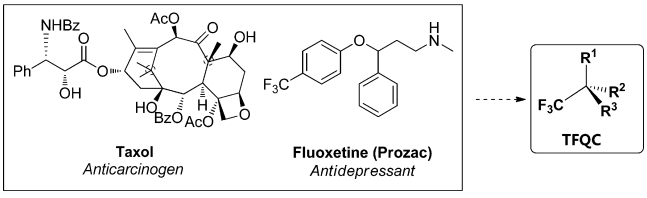


Figure 1. Trifluoromethylated quaternary carbon center (TFQC).

However, bioactive molecules containing TFQC are rare due to the lack of efficient access to it. The most direct access is the trifluoromethylation of tertiary carbon centers. Electrophilic or radical trifluoromethylation of substrates such as 1,3-dicarbonyl compounds[4] and silyl enolates[5] have been developed. However, this method requires the synthesis of tertiary carbon substrates in advance, and the substrate scope is narrow. The second strategy is to use trifluoromethylated olefins as an electrophile. The Michael addition reaction[6] and S_N2' reaction[7] of trifluoromethyl-containing electrophiles were developed along with the cycloaddition reaction.[8] The third strategy is the reaction of trifluoromethylated carbon anions with electrophile. Reactions of trifluoromethyl-substituted necleophiles catalyzed by low-valent iridium complex,[9] palladium[10] or organocatalysts[11] are typical examples. However, the nucleophilicity of the trifluoromethylated carbon anions is reduced because of the electron-withdrawn deactivation of the trifluoromethyl group. Moreover, β-defluorination is often an unavoidable competing reaction, which influences the effective C−C bond formation.

With the aim of providing versatile methodologies for constructing TFQC,[5d,10d,e,11,12] we recently reported a Pd-catalyzed allylation reaction of trifluoromethyl-containing nucleophilic building blocks (Scheme 1).[12] This reaction took place via strong electrophilic π-allyl palladium species. We envisioned that the trifluoromethyl-containing nucleophilic

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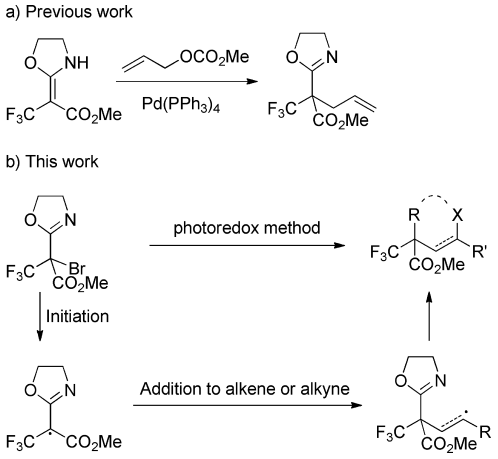
Scheme 1. Reaction Design

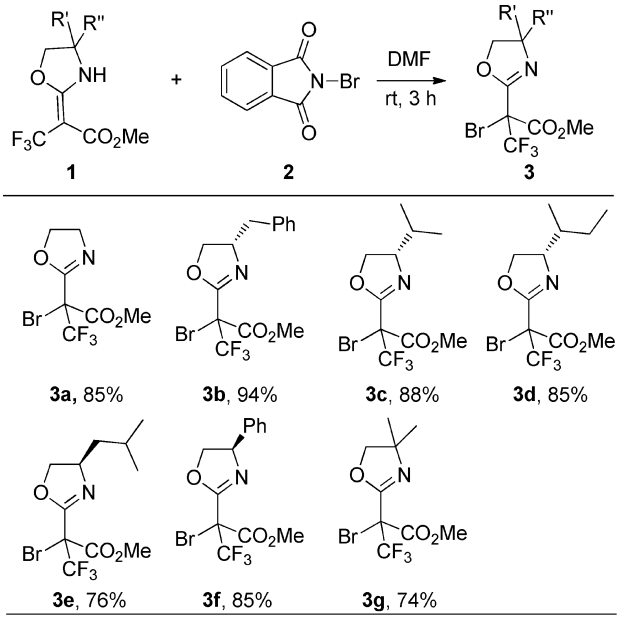


building blocks we used could be brominated, leading to umpolung reactive center. The trifluoromethylated bromides would prefer to react with electron-rich reagents. On the other hand, we reported the reduction of CF_3CH_2I under visible light-induced photoredox catalysis,[13] and we are confident that the trifluoromethylated bromides can be reduced to radicals. Realizing the unique advantage of radical reactions in constructing quaternary carbon centers,[14] we designed to construct TFQC via visible light-induced photoredox methods from this new trifluoromethylated tertiary bromide.

RESULTS AND DISCUSSION

We generated the trifluoromethylated tertiary bromides (**3**) by direct bromination with NBS of the trifluoromethyl-containing nucleophilic building-block (**1**) derived from industrial waste perfluoroisobutylene (Table 1).[12] Reactions took place smoothly in DMF, and reactant **1** was fully converted within 3 h, giving the trifluoromethylated tertiary bromides in good to excellent yields.

Table 1. Substrate Synthesis[a]

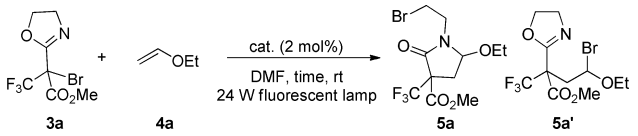


[a]Reaction conditions: substrate **1** (1.0 mmol) and NBS (1.0 mmol) in DMF (5 mL) at room temperature for 3 h. Isolated yield.

The alkyl (**3c**, **3d**, **3e**, **3g**)- and aryl (**3f**)-substituted groups on the oxazolyl ring were all tolerated. The reactions were effective, easy to handle, and could be carried out in air.

Initial experiments were carried out with trifluoromethylated tertiary bromide **3a** and an electron-rich alkene (Table 2). Upon

Table 2. Optimization of Reaction Conditions[a]



entry	cat.	equiv of alkene	time (h)	yield (%)[b]
1	$Ru(bpy)_3(PF_6)_2$	10	10	40
2	$[Ir(ppy)_2Cl]_2$	10	10	23
3	$Ir(ppy)_2(tdbbpy)(PF_6)$	10	10	86
4	$Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$	10	10	95
5	$Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$	3	10	87
6	$Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$	2	10	85
7	$Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$	1.5	10	75
8	$Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$	2	1	81
9		2	10	0[c]
10		2	10	0[c,d]

[a]Conditions: **3a** (0.1 mmol), alkene **4a**, and cat. (2 mol %) in DMF (1 mL) were stirred under the irradiation of a 24 W fluorescent lamp for the time indicated. [b]Determined by ^{19}F NMR using benzotrifluoride as an internal standard. Yields are reported as the sum of two diastereomers. [c]Debromination-hydrogenation product **1a** was detected. [d]Irradiated by blue LED.

treatment of bromide **3a** and ethyl vinyl ether **4a** with 2 mol % of photoredox catalyst $Ru(bpy)_3(PF_6)_2$ in DMF in the presence of light from a 24 W fluorescent lamp for 10 h, two new signals of −70.7 and −70.2 ppm (vs −68.4 ppm of **3a**) appeared in ^{19}F NMR spectroscopy (Table 2, entry 1). Through column chromatography on silica gel, we isolated a mixture containing both proudcts with ^{19}F NMR signals at −70.7 and −70.2 ppm. The products could be diastereomers of **5a** or **5a′**. Because the 4.48 ppm signal in ^1H NMR spectroscopy assigned to OCH_2 in the oxazolyl group disappeared in the isolated products, we judged that our products are a pair of diastereomers of γ-butyrolactam **5a**, which formed by addition, cyclization, and ring-opening processes. Single crystal analysis of one of the diastereomers of **7g** gave further evidence (see the following text). Further screening of photoredox catalysts showed that the reaction could take place under the catalysis of Ru (entry 1) or Ir (entries 2−8) complexes, among which $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$ gave best yield of 95% NMR yield (entry 4). Reducing the loading of alkene resulted in a slight decline in yield (entries 5−7). We decided to use 2 equiv of alkenes as compromise between yield and conversion of reagent. The trifluoromethyl-substituted tertiary bromine can be fully consumed within 1 h (entry 8). Product **5a** could not form without photocatalyst irradiated by either a fluorescent or blue LED lamp (entries 9 and 10). Instead, debromination-hydrogenation product **1a** was detected.

With the optimal reaction conditions in hand, we explored the scope of electron-rich alkenes (Table 3). The diastereomer values were determined by ^{19}F NMR spectroscopies of the reaction mixtures after completion of the reaction. An array of vinyl ethers were converted to the corresponding γ-butyrolactams in good yields (**5a**−**5e**). Bulky substituents such as

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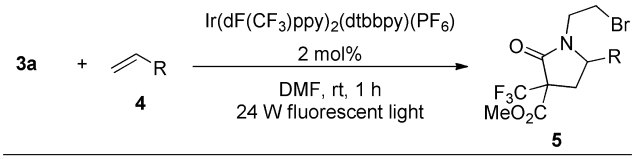
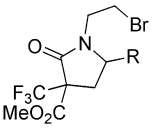
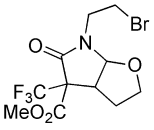
Table 3. Substrate Scope of Electron-Rich Alkenes[a,b]

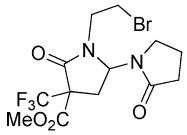




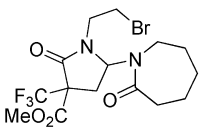
R = OEt, 85% (79%)[c], dr = 1.24:1 **5a**
O^{i}Pr, 83%,dr = 1.5:1 **5b**
O^{t}Bu, 84%, dr = 1.27:1 **5c**
O^{n}Bu, 80%, dr = 1.14:1 **5d**
OCy, 71%, dr = 1.41:1 **5e**
SPh, 52%, dr = 1:1 **5f**



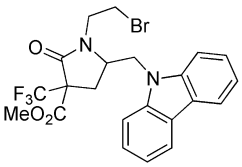
5g, 73%, dr = 1.16:1



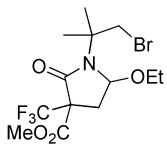
5h, 66%, dr = 1.47:1



5i, 51%, dr = 1.16:1



5j, 88%, dr = 1.21:1



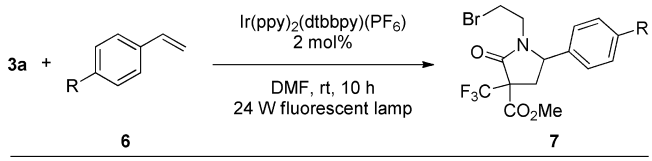
5k 84%, dr =1.24:1

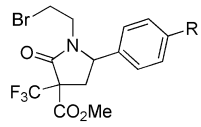
[a]Reaction conditions: **3a** (0.5 mmol), alkene **4** (1.0 mmol), and Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)(PF$_6$) (2 mol %) in DMF (3 mL) were stirred under irradiation of a 24 W fluorescent lamp for 1 h. [b]Isolated yield; dr value was determined by ^{19}F NMR spectroscopy of the reaction mixture. [c]Reaction was conducted on 4.5 mmol scale with catalyst loading of 0.5 mol %.

isopropyl and *t*-butyl in the vinyl ethers can be tolerated (**5b**, **5c**). Cycloether such as 2,3-dihydrofuran was compatible with the reaction conditions, and the TFQC-containing product was obtained in good yield (**5g**); however, 3,4-2*H*-dihydropyran was not reactive. The release of the strain energy of dihydrofuran was profitable for the reaction. Apart from vinyl ethers, vinyl thioethers (**5f**) and vinyl amides (**5h**, **5i**) were also tolerated. Generally, vinyl ethers gave better yields than those of vinyl thioethers and vinyl amides. In addition, the reaction occurred smoothly with trifluoromethylated tertiary bromide (**3g**), which bears substituted groups on the oxazolyl ring. Moreover, the reaction can be scaled up to 4.5 mmol scale without a significant decline in yield even when the loading of catalyst decreased to 0.5 mol % (Table 3, note c).

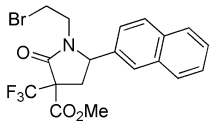
Aryl groups can stabilize radicals by conjugation. Thus, styrenes are common substrates in radical addition reactions. We next studied the reaction of aryl alkenes. No product was detected when the reaction was performed under the standard condition of electron-rich alkenes, which was catalyzed by Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)(PF$_6$). By changing the catalyst to Ir(ppy)$_2$(dtbbpy)(PF$_6$), we found major products with ^{19}F NMR at −69.9 and −70.1 ppm. (see the Supporting Information (SI)). With the new conditions, we examined the scope of styrenes. A wide range of styrenes were transferred to the desired TFQC containing γ-butyrolactam in moderate to good yields (Table 4). Styrenes with either electron-donating groups (Me, MeO, **7a**, **7c**) or electron-withdrawing groups (F, Cl, **7g**, **7h**) were compatible with the reaction conditions. Substitution of alkyl

Table 4. Substrate Scope of Aryl Alkenes[a]

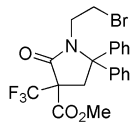




R= Me, 68% dr = 1:1.10 **7a**
H, 66%, dr = 1:1.2 **7b**
OMe, 56%, dr = 1:2.58 **7c**
^{t}Bu, 65%, dr = 1.09:1 **7d**
OAc, 72%, dr = 1:1.07 **7e**
Ph, 59%, dr = 1.02:1 **7f**
F, 42%, dr = 1.18:1 **7g**
Cl, 53%, dr = 1:1.22 **7h**



7i, yield 33%, dr = 1.58:1



7j, yield 46%

[a]Conditions: **3a** (0.5 mmol), alkene **6** (1.0 mmol), and Ir(ppy)$_2$(dtbbpy)(PF$_6$) (0.2 mol %) in DMF (3 mL) were stirred under irradiation of a 24 W fluorescent lamp for 10 h. Isolated yield; dr value was determined by ^{19}F NMR spectroscopy of the reaction mixture. Side products were not identified.

(**7a**, **7d**), alkoxyl (**7c**), ester (**7e**), aryl (**7f**), and halogen (**7g**, **7h**) can be tolerated. However, electron-deficient heteroaryl alkenes such as vinylpyridine were not tolerated. In the ^{1}H NMR spectroscopies of all the products, the signal of OCH$_2$ on the oxazolyl of **3a** disappeared. We reasoned that a ring-opening process had taken place. Product **7g** was confirmed to be a ring-opening product instead of atom-transfer radical addition product by single crystal X-ray analysis (Figure 2).

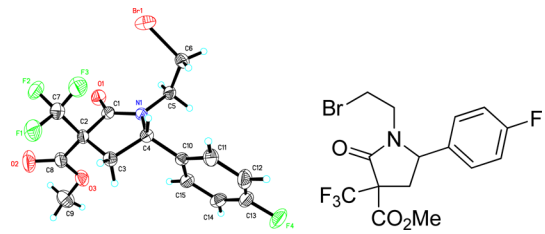


Figure 2. ORTEP diagram of the single crystal of compound **7g** (one of the diastereomers).

Aliphatic alkenes are important intermediates in organic synthesis. Comparatively, aliphatic alkenes are not advantageous either thermodynamically or kinetically in radical reactions. We also examined the reaction with aliphatic alkenes, see the SI for details of screening reaction conditions. Among several photoredox catalysts we tried, *fac*-Ir(ppy)$_3$ gave the best results (see SI). Yields were acceptable due to side reactions. The reaction of alkenes with different functional groups was then examined (Table 5). Various functional groups were tolerated, including ethers (**9b**, **9i**), esters (**9c**−**9h**), cyano (**9d**), and sulfonyl (**9j**).

Alkynes are highly reactive species toward atom-transfer radical addition reactions. We tried different aryl alkynes (Table 6) and found that aryl alkynes with either electron-withdrawing groups such as chlorine (**11c**) and trifluoromethyl (**11f**) or electron-donating groups such as methoxy (**11e**) all gave atom-transfer radical addition products in moderate yields. Sub-

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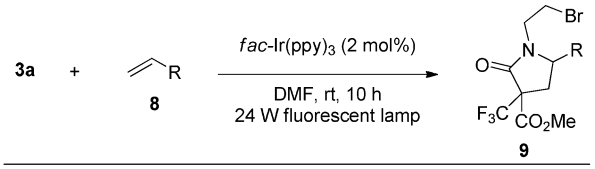
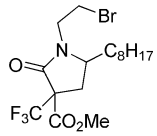
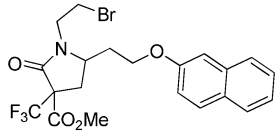
Table 5. Substrate Scope of Aliphatic Alkenes[a]

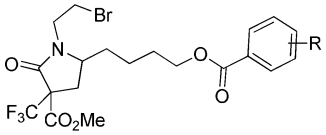




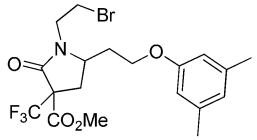
9a, 35% dr = 1:2.25



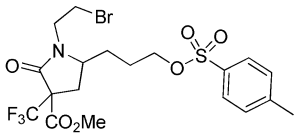
9b, 50% dr = 1:3.35



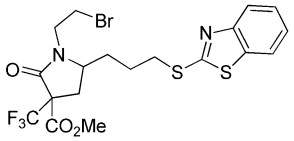
R= H, 43%, dr = 1:1.17 **9c**
4-CN, 47%, dr = 1:1.69 **9d**
4-Me, 42%, dr = 1:1.86 **9e**
2-Me, 32%, dr = 1:1.91 **9f**
4-OMe, 41%, dr = 1:1.76 **9g**
4-I, 41%, dr = 1:1.32:1 **9h**



9i, 31%, dr = 1:1.63



9j, 33% dr = 1:1.22



9k,45%

[a]Standard conditions: **3a** (0.5 mmol), alkene **8** (1.0 mmol), and *fac*-Ir(ppy)$_3$ (0.2 mol %) in DMF (3 mL) were stirred under irradiation of a 24 W fluorescent lamp for 10 h. Isolated yield; dr value was determined by ^{19}F NMR spectroscopy of the reaction mixture. Side products were not identified.

stituents of fluorine (**11b**), chlorine (**11c**), bromine (**11h**), trifluoromethyl (**11f**), methoxyl (**11e**), alkyl (**11g**), and aryl (**11d**) on the aryl ring were compatible. Substitution at the para or meta positions was tolerated (**11b**, **11c**). The configuration of the product we separated is *E* type; the *Z* type products were not found because there were too many side products. Product ***E*-11d** was confirmed by single crystal X-ray analysis to confirm the configuration of the product (Figure 3). Apart from aryl alkynes, enynes such as 1-ethynyl cyclohexene can react smoothly to obtain atom-transfer radical addition product in 67% yield (**11j**). However, low conversions were observed when aliphatic alkynes were used. We also explored the substrate scope of the trifluoromethylated tertiary bromides. Reactions can take place when there are alkyl (**11m**, **11n**, **11o**, **11p**) or aryl (**11l**) substitutes on the oxazolyl ring.

The oxazolyl group in the substrates plays an essential role. No desired product was detected when changing the oxazolyl group to amide groups (Scheme 2).

A plausible mechanism for the reaction of alkenes is proposed in Scheme 3. Oxidative quenching of the visible light-induced excited state *PC^n by the trifluoromethylated tertiary bromides ($E_{1/2}^{red}$ = −0.63 V vs SCE for **3a**[15]) generates an electrophilic radical **Int I** along with the PC$^{(n+1)}$ complex. **Int I** then undergoes a radical addition reaction to generate radical **Int II**. Johnston and Studer reported radical amination reactions by alkyl or aryl radical addition to nitrogen of C═N double bonds, respectively.[16a−f] Similarly, we propose 5-endo cyclization of alkyl radical **Int II** to give **Int III**. **Int III** is readily oxidized by the PC$^{(n+1)}$ complex to form cation **Int IV**.[16g] Then, bromination and ring-opening take place forming the TFQC-containing γ-butyrolactam product.

As for electron-rich alkenes, the reaction was completed in a short time with excellent yields. Photoexcited *Ir(dF(CF$_3$)-ppy)$_2$(dtbbpy)(PF$_6$) ($E_{1/2}$ = −0.89 V vs SCE[17]) could reduce the trifluoromethylated tertiary bromide to radical **Int I**. The SOMO of radical **Int I** is low-lying, and the radical is considered to have electrophilic character. Thus, the SOMO-HOMO orbital interaction increased, and the process was kinetically controlled. Moreover, the lifetime of *Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)(PF$_6$) is very long (2300 ns). Thus, the reactions are efficient.

In the case of styrenes, the reaction is slow, and yields are moderate. The interaction of the SOMO orbital of the trifluoromethylated tertiary radical with the HOMO orbital of styrenes was decreased, and the process was thermodynamically controlled. The oxidative potential of catalyst Ir(dF(CF$_3$)-ppy)$_2$(dtbbpy)(PF$_6$) ($E_{1/2}^{IV/III}$ = +1.69 V vs SCE[17]) is so high that styrenes are oxidized before radical intermediate **Int III** (the $E_{1/2}$ of oxidative potentials of styrene derivatives range from 0.75 to 1.35 V[18]), halting the catalyst cycle. The oxidative potential of catalyst Ir(ppy)$_2$(dtbbpy)(PF$_6$) ($E_{1/2}^{IV/III}$ = +1.21 V vs SCE[17]) is lower, which may not be reduced by styrenes and allows completion of the catalyst cycle. The result of the reaction catalyzed by Ru(bpy)$_3$(PF$_6$)$_2$ as well ($E_{1/2}^{III/II}$ = +1.29 vs SCE[17]) is in accordance with our assumption. On the other hand, the shorter lifetime of the catalyst Ir(ppy)$_2$(dtbbpy)(PF$_6$) (557 ns) is assumed to be the reason for the longer reaction time and moderate yields with styrenes compared with vinyl ethers.

For aliphatic alkenes, it is not advantageous in a thermodynamic or kinetic manner. The reaction took place sluggishly with moderate yields, and more side reactions were observed according to monitoring of the ^{19}F NMR spectroscopy of the crude mixture after the reactions.

For alkyne substrates, the mechanism is almost the same as that with alkenes in the radical initiation step to provide radical **Int I** (Scheme 4). The addition of radical **Int I** to alkyne gives vinyl radical **Int V**. Most likely because of the ring strain, 5-endo cyclization of vinyl radical **Int V** did not occur. Vinyl radical **Int V**, which is a highly active species,[19] is proposed to be oxidized by the intermediate Ir(IV) species ($E_{1/2}^{IV/III}$ = +0.77 V vs SCE) to generate cation **Int VI.** Subsequent bromidation of **Int VI** gives product **11**. Another possible pathway is that active vinyl radicals **Int V** can also directly abstract a bromine atom from substrate **3a** to give product **11** and regenerate radical **Int I**. This radical chain propagation pathway cannot be ruled out. The products we separated were *E* type only. We reasoned that the *Z* type cation intermediate may utilize a different pathway, giving another type of product that we failed to separate because in addition to the major products there were many byproducts.

Alternative light/dark experiments are often used to distinguish the radical chain propagation pathway and radical-polar crossover pathway of the bromination step.[20] In our light/dark alternative experiments for reactions with alkynes, it was observed that the reaction progressed steadily under visible-light irradiation but that the product yield ceased to increase when the light source was removed (Figure 4). However, as mentioned by

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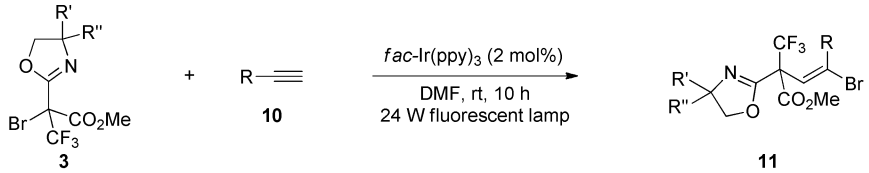
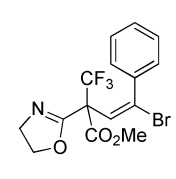
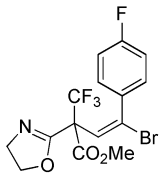
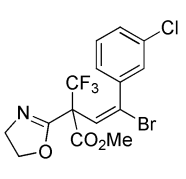
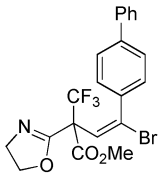
Table 6. Substrate Scope[a]

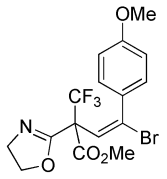


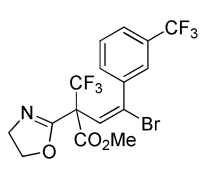

11a, 49%

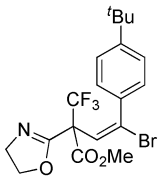

11b, 64%

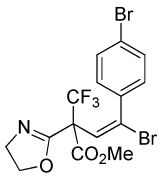

11c, 64%

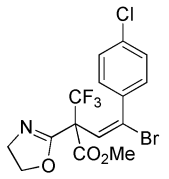

11d, 52%

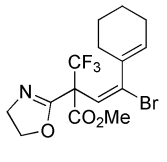

11e, 33%

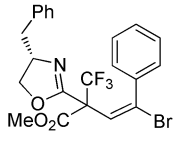

11f, 62%

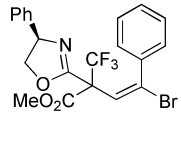

11g, 65%

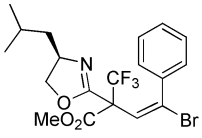

11h, 43%

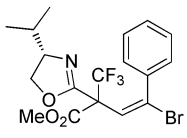

11i, 44%

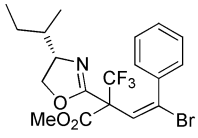

11j, 67%

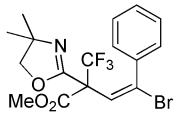

11k, dr = 1:1.01 63%


11l, dr = 1:1.04 43%


11n, dr = 1.18:1 53%


11o, dr = 1:1.41 31%


11p, dr = 1:1.04 56%


11m, 53%

[a]Standard conditions: **3** (0.5 mmol), alkyne **10**(1.0 mmol), and *fac*-Ir(ppy)$_3$ (2 mol %) in DMF (3 mL) were stirred under irradiation of a 24 W fluorescent lamp for 10 h. Isolated yield.

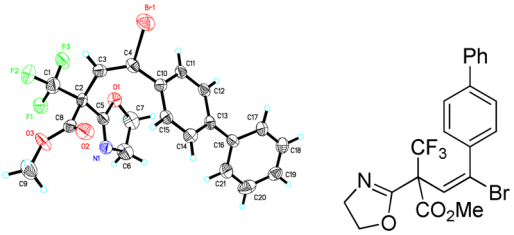
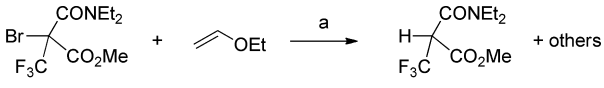


Figure 3. ORTEP diagram of a single crystal of compound **11d**.

Scheme 2. Reaction without Oxazolyl Group



a: Standard conditions in **Table 3**

56% conv, 17% yield

Yoon,[20b] the radical chain propagation pathway can be on a second or subsecond time scale. Although this experiment suggests a radical-polar crossover pathway, the chain propagation pathway cannot be excluded.

The efficiency of this method can be proven by comparison to other methods. For example, although the sulfinatodehalogenation reaction is a mild single-electron transfer radical reaction,[21] over reduction occurs and hydrogenation product **1a** is formed instead of the addition product (Scheme 5). This evidence reflects the milder nature of the visible light photocatalysis system compared with that of traditional reducing methods.[22]

Moreover, it is worth mentioning that some of the products exhibit bactericidal activity against of *Blumeria graminis*, *Puccinia sorghi*, *Ccolletotrichum orbiculare* and *Pseudoperonospora cubensis*.

The product can be transferred into vinyl amide by direct dehydrobromination reaction in the presence of DBU (Scheme 6). There are three alkenyl hydrogens in the ^{1}H NMR spectroscopy of product **12** (chemical shifts of 4.84−5.40 ppm), demonstrating again that structure **5a** is a ring-opening product instead of atom-transfer radical addition product **5a′**. On the other hand, vinyl amide is an electron-rich alkene that can take part in many further reactions. Thus, we expect that the TFQC we constructed can be transferred into more complex molecules.

■ CONCLUSIONS

In conclusion, a visible-light induced photoredox catalysis method of trifluoromethylated tertiary bromides with alkenes and alkynes is reported. Using this method, alkenes are bifunctionalized to TFQC-containing γ-butyrolactams. The process of electron-rich alkenes, vinyl ethers for example, is kinetically controlled with high yields and a short reaction time. The process of styrenes is thermodynamically controlled with moderate yields and a long reaction time. Less active aliphatic alkenes were also applied to give the same type of products as vinyl ethers and styrenes in acceptable yields. The atom-transfer radical addition reaction of trifluoromethylated tertiary bromides with alkynes is also reported with acceptable yields. The configuration of products we separated is *E* type only. In short, two types of novel TFQC-containing structures are constructed

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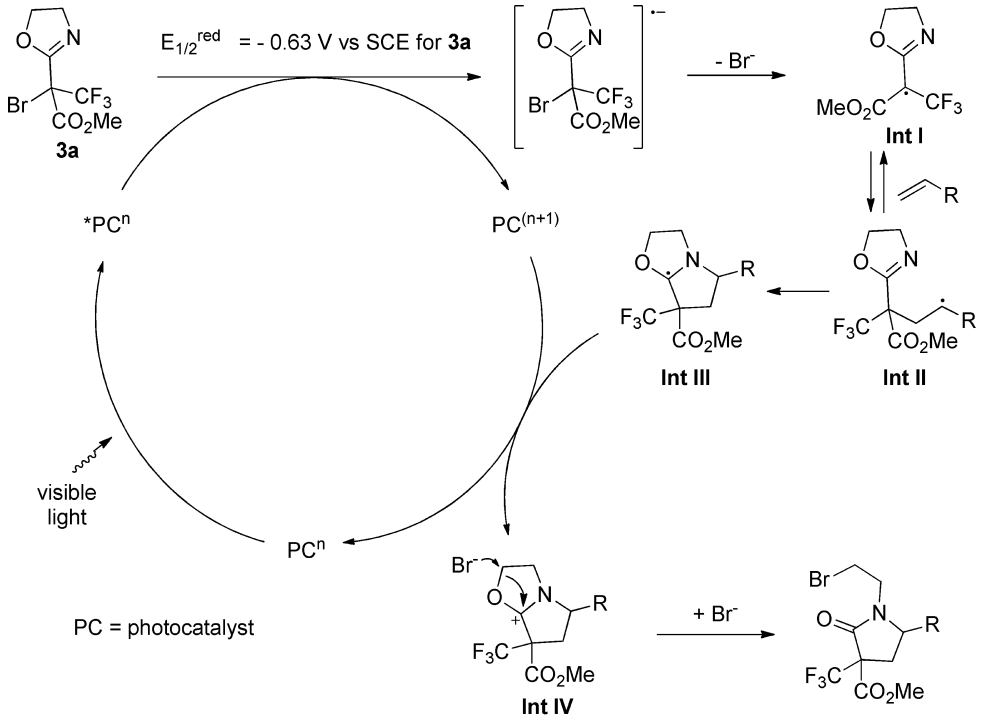
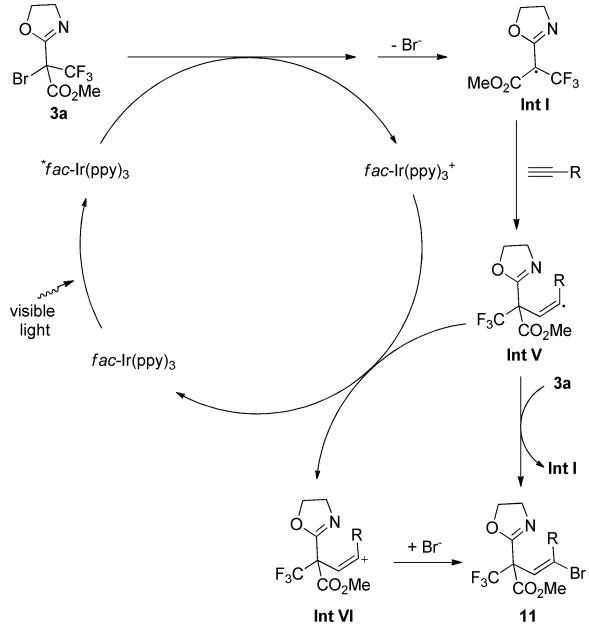
Scheme 3. Proposed Mechanism for the Reaction with Alkenes

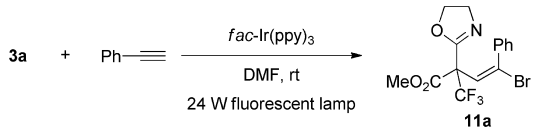


$E_{1/2}$ of PC	M^+/M^* (V)	M^+/M (V)	life time (ns)
$Ir(dF(CF_3)ppy)(dtbbpy)(PF_6)$	-0.89	+1.69	2300
$Ir(ppy)_2(dtbbpy)(PF_6)$	-0.96	+1.21	557
fac-$Ir(ppy)_3$	-1.73	+0.77	1900
$Ru(bpy)_3(PF_6)_2$	-0.81	+1.29	1100

Scheme 4. Proposed Mechanism for the Reaction with Alkynes



by using substrates derived from industrial waste perfluoroisobutylene, avoiding the use of expensive trifluoromethylation reagents. Some of the products behave bactericidal activity, showing a promising method of turning waste into a valuable source.



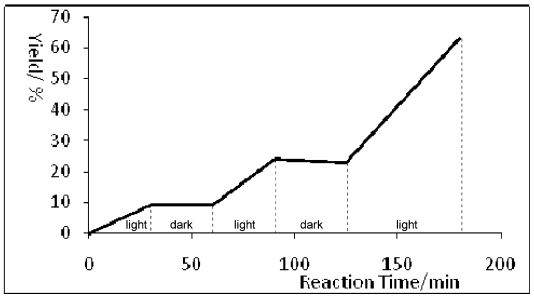
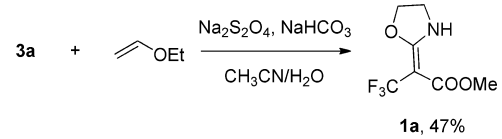


Figure 4. Alternative light/dark experiment. The *x* axis is the reaction time, and the *y* axis is the reaction yield of **11a** based on ^{19}F NMR monitoring using benzotrifluoride as an internal standard.

Scheme 5. Sulfinatodehalogenation Reaction



1a, 47%

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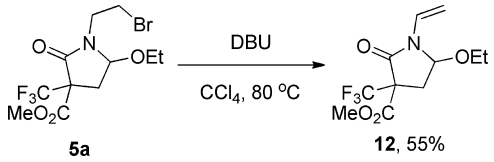
Scheme 6. Dehydrobromination Reaction



5a **12**, 55%

EXPERIMENTAL SECTION

General Experiment Details. All reactions were carried out under N_2. DMF was purified by distillation over CaH_2. Petroleum ether (PE) refers to a hydrocarbon mixture with a boiling range of 60−90 °C. Column chromatography was performed using silica gel (mesh 300−400). Melting points were determined by an SGW X-4 microscopic melting point meter. NMR spectra were obtained on 400 MHz spectrometers and recorded at 25 °C. Chemical shifts for ^{1}H NMR spectra are reported in ppm downfield from TMS. Chemical shifts for ^{13}C NMR spectra are recorded in ppm relative to residual chloroform (δ 77.0 ppm for ^{13}C). ^{13}C NMR was broad-band decoupled from hydrogen nuclei. Chemical shifts for ^{19}F NMR are reported in ppm downfield from fluorotrichloromethane ($CFCl_3$). Coupling constants (J) are reported in hertz. Standard abbreviations are used to denote the signal multiplicities. Infrared spectra (IR) were recorded with an infrared spectrometer; absorbance frequencies are given at maximum intensity in cm^{-1}. The mass analyzer type used for the HRMS is electrospray ionization (ESI). The mass analyzer type uesd for the HRMS is Fourier-transform ion cyclotron resonance mass spectrometry (FTICR-MS).

Generate Procedure of Substrate Synthesis. To a 10 mL Schlenk tube charged with a stir bar were added NBS **2** (1.0 mol), substrate **1a** (1.0 mmol), and DMF (5 mL). The mixture was stirred at room temperature for 3 h. Then, to the mixture were added water (20 mL) and ethyl acetate (20 mL). The organic phase was separated. The aqueous phase was extracted with ethyl acetate three times. The organic phase was combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate mixture as eluent.

*Methyl 2-Bromo-2-(4,5-dihydrooxazol-2-yl)-3,3,3-trifluoropropanoate (**3a**).* Colorless oil; yield 85% (254 mg); IR (neat) ν 2961, 2915, 2888, 1760, 1666, 1590, 1483, 1439, 1359, 1252, 1186, 1086, 1021, 924, 859, 785, 677; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 4.03 (t, J = 9.6 Hz, 2H), 4.48 (t, J = 9.6 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −68.4 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.2 (q, J_{CF} = 32 Hz), 54.9, 55.1, 69.8, 121.4 (q, J_{CF} = 281 Hz), 159.3, 162.0; MS (ESI) m/z (%) 290 $[M + 1]^+$; HRMS (ESI) calcd for $C_7H_8BrF_3NO_3$ $[M + 1]^+$ 289.9634, found 289.9634.

*Methyl 2-((S)-4-Benzyl-4,5-dihydrooxazol-2-yl)-2-bromo-3,3,3-trifluoropropanoate (**3b**).* Yellow oil; yield 94% (356 mg); IR (neat) ν 3063, 3029, 2958, 2925, 2851, 1760, 1666, 1604, 1498, 1474, 1454, 1438, 1356, 1252, 1183, 1026, 961, 784, 702, 646; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.75 (dd, J = 13.6 Hz, 5.4 Hz, 1H), 3.13 (dd, J = 14.0 Hz, 8.8 Hz, 1H), 3.90−3.91 (m, 3H), 4.17−4.21 (m, 1H), 4.35−4.40 (m, 1H), 4.53−4.61 (m, 1H), 7.18−7.24 (m, 3H), 7.29−7.33 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.53 (s, 1.5F), −73.51 (s, 1.5F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.4, 54.2 (q, J_{CF} = 32 Hz), 54.8, 67.9, 73.5, 121.4 (q, J_{CF} = 281 Hz), 126.7, 128.6, 129.4, 136.6, 158.6, 161.9; MS (ESI) m/z (%) 382 $[M + 1]^+$; HRMS (ESI) calcd for $C_{14}H_{14}BrF_3NO_3$ $[M + 1]^+$ 380.0104, found 380.0100.

*Methyl 2-Bromo-3,3,3-trifluoro-2-((S)-4-isopropyl-4,5-dihydrooxazol-2-yl)propanoate (**3c**).* Yellow oil; yield 88% (291 mg); IR (neat) ν 2963, 2877, 1763, 1669, 1469, 1438, 1356, 1251, 1185, 1028, 947, 859, 783; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (d, J = 6.8 Hz, 3H), 0.94 (d, J = 6.8 Hz, 3H), 1.84−1.93 (m, 1H), 3.91 (s, 3H), 4.10−4.16 (m, 1H), 4.21 (t, J = 8.0 Hz, 1H), 4.41 (t, J = 8.8 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −68.5 (s, 1.5F), −68.3 (s, 1.5F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5, 18.2, 32.0, 54.2 (q, J_{CF} = 32 Hz), 54.8, 71.8, 72.4, 121.4 (q, J_{CF} = 281 Hz), 157.9, 162.1; MS (ESI) m/z (%) 334 $[M + 1]^+$; HRMS (ESI) calcd for $C_{10}H_{14}BrF_3NO_3$ $[M + 1]^+$ 332.0104, found 332.0101.

*Methyl 2-Bromo-2-((S)-4-((S)-sec-butyl)-4,5-dihydrooxazol-2-yl)-3,3,3-trifluoropropanoate (**3d**).* Yellow oil; yield 85% (293 mg); IR (neat) ν 2964, 2934, 2879, 1763, 1669, 1480, 1438, 1355, 1259, 1184, 1028, 936, 859, 785; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (d, J = 6.8 Hz, 3H), 0.92 (t, J = 7.6 Hz, 3H), 1.12−1.27 (m, 1H), 1.38−1.48 (m, 1H), 1.72−1.80 (m, 1H), 3.91 (s, 3H), 4.18−4.28 (m, 2H), 4.39 (t, J = 8.4 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −68.4 (s, 1.5F), −68.3 (s, 1.5F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.6, 13.8, 25.9, 38.4, 54.7, 64.5 (q, J_{CF} = 32 Hz), 71.2, 71.3, 121.5 (q, J_{CF} = 281 Hz), 157.9, 162.1; MS (ESI) m/z (%) 346 $[M + 1]^+$; HRMS (ESI) calcd for $C_{11}H_{16}BrF_3NO_3$ $[M + 1]^+$ 346.0260, found 346.0258.

*Methyl 2-Bromo-3,3,3-trifluoro-2-((R)-4-isobutyl-4,5-dihydrooxazol-2-yl)propanoate (**3e**).* Yellow oil; yield 76% (254 mg); IR (neat) ν 2960, 2873, 1764, 1667, 1470, 1452, 1359, 1257, 1184, 1035, 936, 785; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 6.8 Hz, 6H), 1.31−1.40 (m, 1H), 1.61−1.68 (m, 1H), 1.69−1.75 (m, 1H), 3.91 (s, 3H), 4.05 (t, J = 8.0 Hz, 1H), 4.26−4.34 (m, 1H),4.51 (t, J = 8.8 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −68.5 (s, 1.5F), −68.4 (s, 1.5F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5, 22.9, 25.3, 44.5, 54.7, 64.9 (q, J_{CF} = 31 Hz), 65.7, 75.0, 122.5 (q, J_{CF} = 281 Hz), 157.9, 162.1; MS (ESI) m/z (%) 348 $[M + 1]^+$; HRMS (ESI) calcd for $C_{11}H_{16}BrF_3NO_3$ $[M + Na]^+$ 346.0260, found 346.0258.

*Methyl 2-Bromo-3,3,3-trifluoro-2-((R)-4-phenyl-4,5-dihydrooxazol-2-yl)propanoate (**3f**).* Yellow oil; yield 85% (311 mg); IR (neat) ν 3065, 3030, 2960, 2907, 1766, 1666, 1604, 1498, 1438, 1357, 1248, 1184, 1083, 1028, 928, 860, 779, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95(s, 3H), 4.29−4.33 (m, 1H), 4.81−4.85 (m, 1H), 5.34−5.39 (m, 1H), 7.21 (d, J = 7.2 Hz, 2H), 7.29−7.39 (m, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −68.3 (s, 1.5F), −68.2 (s, 1.5F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.2 (q, J_{CF} = 34 Hz), 55.0, 70.2, 77.1, 121.6 (q, J_{CF} = 281 Hz), 126.6, 128.1, 129.0, 140.7, 159.7, 162.1; MS (ESI) m/z (%) 368 $[M + 1]^+$; HRMS (ESI) calcd for $C_{13}H_{12}BrF_3NO_3$ $[M + 1]^+$ 365.9947, found 365.9945.

*Methyl 2-Bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3,3,3-trifluoropropanoate (**3g**).* White solid; mp 97.6−100.8 °C; yield 74% (470 mg on 2 mmol scale); IR (neat) ν 3161, 3096, 1742, 1670, 1585, 1436, 1246, 1081, 1061, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (s, 6H), 3.91 (s, 3H), 4.12 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −68.9 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.4, 54.1 (q, J_{CF} = 32 Hz), 54.8, 68.8, 80.9, 121.4 (q, J_{CF} = 281 Hz), 156.5, 162.2; MS (ESI) m/z (%) 320 $[M + 1]^+$; HRMS (ESI) calcd for $C_9H_{12}BrF_3NO_3$ $[M + 1]^+$ 317.9947, found 317.9945. Anal. Calcd for $C_9H_{11}BrF_3NO_3$: C, 33.98; H, 3.49; N, 4.40. Found: C, 33.95; H, 3.48; N, 4.40.

General Procedure. A 10 mL Schlenk tube was charged with a stir bar and photoredox catalyst (2 mol %). The tube was vacuumed and charged back with N_2 three times. Bromide **3a** (140 mg, 0.5 mmol), alkene (1.0 mmol), and DMF (3 mL) were added under N_2 atmosphere. The mixture was stirred at room temperature under irradiation of a 24 W fluorescent lamp for 1 h or overnight. Then, the mixture was added to 20 mL of water and 20 mL of ethyl acetate. The organic phase was separated. The aqueous phase was extracted with ethyl acetate three times. The organic phase was combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a hexane/ethyl acetate mixture as eluent.

*Methyl 1-(2-Bromoethyl)-5-ethoxy-2-oxo-3-(trifluoromethyl)-pyrrolidine-3-carboxylate (**5a**).* Yellow oil; yield 85% (92 mg on 0.3 mmol scale); IR (neat) ν 2979, 1759, 1722, 1435, 1378, 1280, 1195, 1096, 991, 924, 799; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19−1.27 (m, 3H), 2.29 (dd, J = 14.4, 4.4 Hz, 0.53H), 2.64 (t, J = 4.8 Hz, 1H), 2.86 (dd, J = 14.4, 7.6 Hz, 0.47H), 3.42−3.68 (m, 5H), 3.82 (m, 3H), 3.86−3.94 (m, 1H), 5.08 (dd, J = 4.8, 2.8 Hz, 0.47H), 5.20 (dd, J = 6.4, 3.6 Hz, 0.53H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.7 (s, 1.4F), −70.2 (s, 1.6F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 15.3, 27.8, 28.3, 32.9, 33.4, 43.0, 43.5, 53.7, 53.8, 59.3 (q, J_{CF} = 28 Hz), 63.3, 63.6, 87.0, 123.0 (q, J_{CF} = 279 Hz), 123.3 (q, J_{CF} = 277 Hz), 163.7, 164.6, 165.4, 165.6; MS (ESI) m/z (%) 362 $[M + 1]^+$; HRMS (ESI) calcd for $C_{11}H_{15}BrF_3NNaO_4$ $[M + Na]^+$ 384.0029, found 384.0046.

*Methyl 1-(2-Bromoethyl)-5-isopropoxy-2-oxo-3-(trifluoromethyl)-pyrrolidine-3-carboxylate (**5b**).* Yellow oil; yield 83% (94 mg on 0.3

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mmol scale); IR (neat) ν 2974, 2928, 2856, 1760, 1723, 1435, 1327, 1279, 1143, 1089, 1030, 956, 866, 801, 711; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17−1.29 (m, 6H), 2.27 (dd, J = 14.4, 4.4 Hz, 0.53H), 2.59−2.70 (m, 1H), 2.89 (dd, J = 14.4, 6.0 Hz, 0.47H), 3.44−3.66 (m, 3H), 3.74−3.93 (m, 5H), 5.15 (dd, J = 5.2, 2.4 Hz, 0.47H), 5.26 (dd, J = 6.4, 4.4 Hz, 0.53H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.3 (s, 1.4F), −69.8 (s, 1.6F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 22.4, 23.0, 23.3, 28.2, 28.6, 29.6, 34.5, 35.2, 42.8, 43.3, 53.8, 59.2 (q, J_{CF} = 17 Hz), 70.8, 72.0, 85.7, 86.1, 123.0 (q, J_{CF} = 284 Hz), 123.4 (q, J_{CF} = 274 Hz), 163.5, 164.6, 165.4, 165.7; MS (ESI) m/z (%) 378 $[M + 1]^+$; HRMS (ESI) calcd for $C_{12}H_{17}BrF_3NNaO_4$ $[M + Na]^+$ 398.0185, found 398.0194.

*Methyl 1-(2-Bromoethyl)-5-(tert-butoxy)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**5c**).* White solid; mp 55.6−57.9 °C; yield 84% (163 mg); IR (KBr) ν 2976, 2925, 2853, 1761, 1721, 1436, 1396, 1368, 1322, 1279, 1192, 1086, 1027, 897, 745; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26−1.28 (m, 9H), 2.23 (dd, J = 14.4, 4.4 Hz, 0.57H), 2.55 (d, J = 12.0 Hz, 0.43H), 2.70 (dd, J = 14.0, 6.0 Hz, 0.43H), 2.85 (dd, J = 14.0, 6.4 Hz, 0.57H), 3.42−3.63 (m, 3H), 3.71−3.78 (m, 1H), 3.82 (s, 3H), 5.25−5.35 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.9 (s, 1.3F), −69.5 (s, 1.7F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.4, 28.6, 36.6, 36.9, 42.3, 42.8, 53.7, 59.5 (q, J_{CF} = 28 Hz), 74.8, 75.0, 81.3, 81.4, 123.0 (q, J_{CF} = 280 Hz), 163.4, 164.4, 166.5; MS (ESI) m/z (%) 390 $[M + 1]^+$; HRMS (ESI) calcd for $C_{13}H_{19}BrF_3NNaO_4$ $[M + Na]^+$ 412.0342, found 412.0345.

*Methyl 1-(2-Bromoethyl)-5-butoxy-2-oxo-3-(trifluoromethyl)-pyrrolidine-3-carboxylate (**5d**).* Yellow oil; yield 80% (157 mg); IR (neat) ν 2960, 2931, 2874, 1762, 1723, 1453, 1435, 1365, 1326, 1278, 1197, 1097, 1074. Isomer a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 6.8 Hz, 3H), 1.35−1.44 (m, 2H), 1.56−1.63 (m, 2H), 2.30 (dd, J = 14.0, 4.0 Hz, 1H), 2.86 (dd, J = 14.4, 6.4 Hz, 1H), 3.44−3.68 (m, 5H), 3.84 (s, 3H), 3.87−3.91 (m, 1H), 5.21 (dd, J = 6.0, 3.6 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.8 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.2, 27.8, 31.7, 33.2, 42.0, 53.7, 59.3 (q, J_{CF} = 28 Hz), 67.8, 87.1, 123.6 (q, J_{CF} = 280 Hz), 163.7, 165.5. Isomer b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, J = 6.8 Hz, 3H), 1.32−1.42 (m, 2H), 1.53−1.60 (m, 2H), 2.60−2.69 (m, 2H), 3.47−3.50 (m, 3H), 3.56−3.61 (m, 2H), 3.84 (s, 3H), 3.87−3.94 (m, 1H), 5.08−5.10 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.3 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 18.8, 28.3, 31.6, 32.7, 43.5, 53.8, 59.0 (q, J_{CF} = 27 Hz), 67.5, 87.1, 123.3 (q, J_{CF} = 280 Hz), 164.7, 165.3; MS (ESI) m/z (%) 390, 392 $[M + 1]^+$; HRMS (ESI) calcd for $C_{13}H_{20}BrF_3NO_4$ $[M + 1]^+$ 390.0522, found 390.0523.

*Methyl 1-(2-Bromoethyl)-5-(cyclohexyloxy)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**5e**).* Yellow oil; yield 71% (148 mg); IR (neat) ν 2935, 2858, 1759, 1720, 1452, 1436, 1364, 1436, 1364, 1325, 1279, 1195, 1091, 1026, 980, 925, 713; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20−1.45 (m, 5H), 1.51−1.58 (m, 1H), 1.68−1.95 (m, 4H), 2.27 (dd, J = 14.0, 4.4 Hz, 0.42H), 2.60−2.69 (m, 1H), 2.88 (dd, J = 14.4, 6.4 Hz, 0.58H), 3.41−3.54 (m, 2H), 3.56−3.66 (m, 2H), 3.83 (s, 3H), 3.85−3.91 (m, 1H), 5.18 (dd, J = 4.2, 2.8 Hz, 0.42H), 5.29 (dd, J = 6.0, 4.2 Hz, 0.58H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.3 (s, 1.3F), −69.8 (s, 1.7F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.6, 23.8, 25.2, 27.9, 28.3, 31.9, 32.2, 33.0, 33.3, 34.6, 35.2, 42.8, 43.2, 53.6, 58.8−59.9 (m), 76.3, 77.5, 85.5, 85.9, 122.9 (q, J_{CF} = 279 Hz), 123.3 (q, J_{CF} = 280 Hz), 163.4, 164.5, 165.3, 165.5; MS (ESI) m/z (%) 418 $[M + 1]^+$; HRMS (ESI) calcd for $C_{15}H_{21}BrF_3NO_4Na$ $[M + Na]^+$ 438.0498, found 438.0517.

*Methyl 1-(2-Bromoethyl)-2-oxo-5-(phenylthio)-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**5f**).* Yellow oil; yield 52% (133 mg); IR (neat) ν 3058, 2957, 2860, 1761, 1717, 1583, 1474, 1438, 1413, 1298, 1252, 1193, 1093, 1060, 876, 805, 751, 694, 605; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (dd, J = 14.4, 7.2 Hz, 0.57H), 2.79 (dd, J = 14.8, 4.8 Hz, 0.43H), 2.91−2.98 (m, 1H), 3.41−3.46 (m, 1H), 3.52−3.60 (m, 1H), 3.71 (s, 1.39H), 3.82 (s, 1.71H), 3.91−3.97 (m, 1H), 4.12−4.22 (m, 1H), 5.10−5.17 (m, 1H), 7.34−7.41 (m, 4H), 7.43−7.46 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.3 (s, 1.3F), −70.1 (s, 1.7F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2, 27.5, 32.5, 33.2, 42.9, 43.3, 53.7, 59.3 (m), 64.5, 65.6, 123.4 (q, J_{CF} = 281 Hz), 122.8 (q, J_{CF} = 280 Hz), 129.3, 129.6, 134.7, 134.9, 164.1, 164.3, 165.1; MS (ESI) m/z (%) 428 $[M + 1]^+$; HRMS (ESI) calcd for $C_{15}H_{15}BrF_3NO_3SNa$ $[M + Na]^+$ 447.9800, found 447.9814.

*Methyl 6-(2-Bromoethyl)-5-oxo-4-(trifluoromethyl)hexahydro-2H-furo[2,3-b]pyrrole-4-carboxylate (**5g**).* Yellow oil; yield 73% (132 mg); IR (neat) ν 2960, 2892, 1754, 1716, 1442, 1372, 1301, 1251, 1197, 1087, 1032, 978, 935, 863; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67−1.71 (m, 1H), 2.04−2.27 (m, 2H), 3.27−3.36 (m, 1H), 3.49−3.55 (m, 1H), 3.57−3.66 (m, 1H), 3.68−3.79 (m, 2H), 3.84 (s, 1.70H), 3.85 (s, 1.30H), 3.86−4.02 (m, 1H), 5.64−5.66 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.1 (s, 1.3F), −64.0 (s, 1.7F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.1, 27.6, 41.0, 42.7, 43.4, 44.0, 53.2, 53.9, 62.8 (q, J_{CF} = 21 Hz), 66.5, 66.8, 91.1, 91.6, 123.0 (q, J_{CF} = 281 Hz), 163.8, 165.9; MS (ESI) m/z (%) 360, 362 $[M + 1]^+$; HRMS (ESI) calcd for $C_{11}H_{13}BrF_3NNaO_4$ $[M + Na]^+$ 381.9872, found 381.9889.

*Methyl 1′-(2-Bromoethyl)-2,5′-dioxo-4′-(trifluoromethyl)-[1,2′-bipyrrolidine]-4′-carboxylate (**5h**).* White solid; mp 114.7−116.9 °C; yield 66% (132 mg); IR (KBr) ν 2959, 1762, 1699, 1415, 1261, 1195, 1163, 1080, 1017, 879, 711, 619. Isomer a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.02−2.15 (m, 2H), 2.32 (dd, J = 14.4, 6.4 Hz, 1H), 2.49 (t, J = 8.0 Hz, 2H), 2.79 (dd, J = 14.8, 8.0 Hz, 1H), 3.06−3.19 (m, 2H), 3.36−3.42 (m, 1H), 3.46−3.55 (m, 2H), 3.83 (s, 3H), 3.96−4.03 (m, 1H), 6.07 (t, J = 7.6 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.0 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 26.4, 28.0, 31.2, 40.9, 42.3, 53.8, 59.3 (q, J_{CF} = 28 Hz), 61.9, 123.2 (q, J_{CF} = 287 Hz), 163.9, 165.0, 176.3. Mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98−2.13 (m, 2H), 2.27−2.34 (m, 0.39H), 2.42−2.50 (m, 2H), 2.53−2.59 (m, 0.61H), 2.72−2.81 (m, 1H), 3.04−3.18 (m, 2H), 3.33−3.40 (m, 1H), 3.46−3.47 (m, 2H), 3.78−3.85 (m, 3H), 3.92−4.03 (m, 1H), 5.95−6.07 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.3 (s, 2.0F), −70.0 (s, 1.0F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 26.4, 27.8, 28.1, 31.0, 31.1, 40.8, 41.1, 42.1, 53.7, 53.8, 59.5 (q, J_{CF} = 28 Hz), 61.8, 61.9, 123.2 (q, J_{CF} = 281 Hz), 163.8, 163.9, 164.7, 165.5, 176.1, 176.2; MS (ESI) m/z (%) 401, 403 $[M + 1]^+$; HRMS (ESI) calcd for $C_{13}H_{17}BrF_3N_2O_4$ $[M + 1]^+$ 401.0318, found 401.0317. Anal. Calcd for $C_{13}H_{16}BrF_3N_2O_4$: C, 38.92; H, 4.02; N, 6.98. Found: C, 39.20; H, 4.07; N, 6.99.

*Methyl 1-(2-Bromoethyl)-2-oxo-5-(2-oxoazepan-1-yl)-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**5i**).* White solid; mp 98.5−100.3 °C; yield 51% (220 mg); IR (KBr) ν 2933, 2859, 1762, 1720, 1655, 1436, 1415, 1352, 1307, 1278, 1259, 1193, 1095, 1045, 973; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41−1.68 (m, 3H), 1.75−1.92 (m, 3H), 2.11−2.20 (m, 0.50H), 2.44−2.51 (m, 0.50H), 2.55−2.94 (m, 2H), 2.73−2.84 (m, 1H), 3.01−3.10 (m, 1H), 3.12−3.35 (m, 2H), 3.39−3.55 (m, 2H), 3.81−3.89 (m, 3H), 3.94−4.04 (m, 1H), 6.43−6.57 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.1 (1.5F), −69.9 (s, 1.5F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.2, 26.2, 28.9, 29.2, 29.3, 29.6, 37.5, 41.3, 41.8, 42.2, 53.7, 53.9, 58.8−60.2 (m), 63.7, 64.3, 123.1 (q, J_{CF} = 279 Hz), 123.3 (q, J_{CF} = 281 Hz), 164.1, 164.2, 164.8, 165.9, 177.3; MS (ESI) m/z (%) 429 $[M + 1]^+$; HRMS (ESI) calcd for $C_{15}H_{20}BrF_3N_2O_4Na$ $[M + Na]^+$ 451.0451, found 451.0437. Anal. Calcd for $C_{15}H_{20}BrF_3N_2O_4$: C, 41.97; H, 4.70; N, 6.53. Found: C, 42.28; H, 4.74; N, 6.48.

*Methyl 5-((9H-carbazol-9-yl)methyl)-1-(2-bromoethyl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**5j**).* White solid; mp 57.4−59.2 °C; yield 88% (213 mg); IR (KBr) ν 3053, 2957, 2919, 2849, 1763, 1722, 1625, 1598, 1485, 1451, 1410, 1325, 1267, 1195, 1072, 751, 724; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85−2.96 (m, 1H), 2.99−3.10 (m, 1H), 3.18−3.36 (m, 2H), 3.59−3.68 (m, 1H), 3.96−3.98 (m, 3H), 4.00−4.10 (m, 1H), 6.70−6.80 (m, 1H), 7.25−7.33 (m, 2H), 7.42 (dd, J = 16.0, 8.0 Hz, 1H), 7.48−7.56 (m, 3H), 8.10 (t, J = 8.0 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.6 (s, 1.4F), −68.8 (s, 1.6F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.6, 27.9, 30.8, 31.1, 42.3, 42.5, 54.0, 54.2, 60.3 (m), 67.0, 67.4, 108.4, 110.7, 111.3, 120.7, 120.77, 120.82, 120.9, 121.0, 123.3 (q, J_{CF} = 280 Hz), 123.5, 123.7 (q, J_{CF} = 281 Hz), 124.7, 124.9, 126.50, 126.56, 126.59, 126.7, 136.7, 136.9, 140.0, 163.8, 164.0, 165.0, 165.5; MS (ESI) m/z (%) 485 $[M + 1]^+$; HRMS (ESI) calcd for $C_{21}H_{18}BrF_3N_2O_3Na$ $[M + Na]^+$ 505.0345, found 505.0321.

*Methyl 1-(1-Bromo-2-methylpropan-2-yl)-5-ethoxy-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**5k**).* Colorless oil, yield 84% (164 mg); IR (neat) ν 2980, 2881, 1759, 1716, 1445, 1401, 1304, 1194, 1089, 944, 760, 677; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, J = 6.8 Hz, 1.41H), 1.24 (t, J = 7.2 Hz, 1.59H), 1.53 (s, 3H), 1.59 (s, 3H), 2.33 (d, J = 14.8 Hz, 0.53H), 2.41 (dd, J = 13.6, 4.8 Hz, 0.47H), 2.71 (d, J = 13.6 Hz, 0.47H), 2.83 (dd, J = 14.8, 6.4 Hz, 0.53H), 3.33 (dd, J = 10.0,

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5.6 Hz, 1H), 3.36−3.52 (m, 2H), 3.82−3.83 (m, 3H), 4.48 (d, J = 10.4 Hz, 0.47H), 4.54 (d, J = 10.4 Hz, 0.53H), 4.93 (d, J = 4.4 Hz, 0.53H), 5.05 (d, J = 6.4 Hz, 0.47H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.2 (s, 1.33F), −69.5 (s, 1.67F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1, 31.5, 40.2, 40.9, 53.6, 53.8, 57.4, 58.0, 59.2−60.0 (m), 61.8, 62.1, 86.0, 86.8, 123.0 (q, J_{CF} = 280 Hz), 123.3 (q, J_{CF} = 280 Hz), 164.6, 165.6, 165.8, 165.9; MS (ESI) m/z (%) 390 $[M + 1]^+$; HRMS (ESI) calcd for $C_{13}H_{20}BrF_3NO_4$ $[M + 1]^+$ 390.0522, found 390.0522.

*Methyl 1-(2-Bromoethyl)-2-oxo-5-(p-tolyl)-3-(trifluoromethyl)-pyrrolidine-3-carboxylate (**7a**).* Viscous yellow oil; yield 68% (139 mg); IR (neat) ν 3024, 2958, 2924, 1759, 1713, 1615, 1515, 1434, 1279, 1193, 1097, 1063, 1021, 883, 822, 733, 506; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31−2.36 (m, 3.42H), 2.61 (dd, J = 14.4, 7.2 Hz, 0.58H), 2.86−2.96 (m, 1H), 2.99−3.07 (m, 1H), 3.20−3.27 (m, 1H), 3.40−3.52 (m, 1H), 3.84−3.85 (m, 3H), 3.94−4.00 (m, 1H), 4.83−4.91 (m, 1H), 7.12−7.24 (m, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.1 (s, 1.5F), −70.0 (s, 1.5F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 27.3, 27.4, 35.4, 35.8, 43.0, 43.2, 53.5, 53.6, 59.6, 59.8 (q, J_{CF} = 27 Hz), 60.1, 123.3 (q, J_{CF} = 280 Hz), 123.8 (q, J_{CF} = 282 Hz), 127.0, 127.1, 129.96, 130.02, 134.6, 135.2, 139.0, 139.1, 165.2, 165.3, 165.5, 166.1; MS (ESI) m/z (%) 410 $[M + 1]^+$; HRMS (ESI) calcd for $C_{16}H_{18}BrF_3NO_3$ $[M + 1]^+$ 408.0417, found 408.0414.

*Methyl 1-(2-Bromoethyl)-2-oxo-5-phenyl-3-(trifluoromethyl)-pyrrolidine-3-carboxylate (**7b**).* White solid; mp 49.7−51.6 °C; yield 66% (130 mg); IR (KBr) ν 2958, 1759, 1714, 1496, 1458, 1435, 1300, 1269, 1245, 1193, 1058, 764, 702; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (dd, J = 14.0, 8.8 Hz, 0.50H), 2.66 (dd, J = 15.2, 7.6 Hz, 0.50H), 2.92−3.10 (m, 2H), 3.26−3.32 (m, 1H), 3.46−3.57 (m, 1H), 3.88 (s, 1.50H), 3.91 (s, 1.50H), 4.01−4.08 (m, 1H), 4.91−4.99 (m, 1H), 7.29−7.33 (m, 2H), 7.39−7.47 (m, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.1 (s, 1.5F), −70.0 (s, 1.5F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.4, 27.5, 35.5, 35.9, 43.2, 43.4, 53.7, 53.8, 59.8 (q, J_{CF} = 25 Hz), 60.1. 60.5, 123.4 (q, J_{CF} = 280 Hz), 123.9 (q, J_{CF} = 280 Hz), 127.20, 127.22, 129.2, 129.3, 129.4, 129.5, 137.9, 138.5, 165.3, 165.4, 165.5, 166.1; MS (ESI) m/z (%) 396 $[M + 1]^+$; HRMS (ESI) calcd for $C_{15}H_{16}BrF_3NO_3$ $[M + 1]^+$ 394.0260, found 394.0261.

*Methyl 1-(2-Bromoethyl)-5-(4-methoxyphenyl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**7c**).* Viscous yellow oil; yield 56% (119 mg); IR (neat) ν 2958, 2840, 1758, 1713, 1613, 1587, 1514, 1434, 1301, 1250, 1194, 1177, 1063, 1033, 835; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (dd, J = 14.4, 8.8 Hz, 0.64H), 2.65 (dd, J = 14.8, 8.0 Hz, 0.36H), 2.89−2.97 (m, 1H), 2.99−3.10 (m, 1H), 3.24−3.31 (m, 1H), 3.44−3.55 (m, 1H), 3.83 (s, 3H), 3.89 (s, 1.09H), 3.90 (s, 1.91H), 3.96−4.03 (m, 1H), 4.86−4.94 (m, 1H), 6.95 (d, J = 8.4 Hz, 2H), 7.20−7.28 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.1 (s, 1.9F), −70.0 (s, 1.1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.4, 27.6, 35.6, 35.9, 43.0, 43.2, 53.6, 53.7, 55.3, 59.4, 59.8 (q, J_{CF} = 28 Hz), 60.0, 114.7, 114.8, 123.4 (q, J_{CF} = 279 Hz), 123.9 (q, J_{CF} = 281 Hz), 128.6, 129.4, 130.1, 160.1, 160.2, 165.2, 165.3, 165.6, 166.2; MS (ESI) m/z (%) 426 $[M + 1]^+$; HRMS (ESI) calcd for $C_{16}H_{18}BrF_3NO_4$ $[M + 1]^+$ 424.0366, found 424.0366.

*Methyl 1-(2-Bromoethyl)-5-(4-(tert-butyl)phenyl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**7d**).* Viscous yellow oil; yield 65% (146 mg); IR (neat) ν 2963, 2906, 2870, 1759, 1706, 1512, 1435, 1413, 1268, 1188, 1109, 1061, 1018, 837, 674; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (s, 9H), 2.38 (dd, J = 14.0, 5.2 Hz, 0.29H), 2.65 (dd, J = 14.4, 7.2 Hz, 0.71H), 2.89−2.97 (m, 1H), 3.03−3.10 (m, 1H), 3.26−3.32 (m, 1H), 3.46−3.57 (m, 1H), 3.87 (s, 0.89H), 3.89 (s, 2.11H), 3.99−4.06 (m, 1H), 4.87−4.96 (m, 1H), 7.18−7.24 (m, 2H), 7.42−7.44 (d, J = 8.4 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.1 (s, 2.2F), −70.0 (s, 0.8F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 27.2, 27.3, 35.3, 35.7, 43.1, 43.2, 53.5, 53.6, 59.3, 59.6 (q, J_{CF} = 52 Hz), 59.7, 122.5, 122.6, 123.2 (q, J_{CF} = 279 Hz), 123.7 (q, J_{CF} = 281 Hz), 128.2, 135.2, 135.9, 150.9, 151.0, 165.1, 165.2, 165.9, 169.0; MS (ESI) m/z (%) 452 $[M + 1]^+$; HRMS (ESI) calcd for $C_{19}H_{24}BrF_3NO_3$ $[M + 1]^+$ 450.0886, found 450.0883.

*Methyl 5-(4-Acetoxyphenyl)-1-(2-bromoethyl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**7e**).* Viscous yellow oil; yield 72% (163 mg); IR (neat) ν 2959, 1758, 1713, 1607, 1508, 1434, 1370, 1300, 1281, 1195, 1167, 1062, 1016, 912, 851, 659; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32−2.38 (m, 3.53H), 2.64 (dd, J = 14.4, 6.4 Hz, 0.47 H), 2.93−3.02 (m, 1H), 3.04−3.10 (m, 1H), 3.27−3.34 (m, 1H), 3.47−3.58 (m, 1H), 3.86 (s, 1.41H), 3.89 (s, 1.59H), 4.02−4.09 (m, 1H), 4.95−5.03 (m, 1H), 7.16−7.18 (m, 2H), 7.30−7.37 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.1 (s, 1.6F), −70.0 (s, 1.4F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.4, 27.5, 31.2, 34.7, 36.0, 43.2, 43.4, 53.6, 53.7, 59.8, 60.1 (q, J_{CF} = 20 Hz), 123.4 (q, J_{CF} = 279 Hz), 126.3, 126.4, 126.9, 134.8, 135.4, 152.3, 152.5, 165.3, 165.5, 165.6, 166.2; MS (ESI) m/z (%) 454 $[M + 1]^+$; HRMS (ESI) calcd for $C_{17}H_{18}BrF_3NO_5$ $[M + H]^+$ 452.0315, found 452.0310.

*Methyl 5-([1,1′-Biphenyl]-4-yl)-1-(2-bromoethyl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**7f**).* White solid; mp 100.3−101.5 °C; yield 59% (166 mg); IR (KBr) ν 3030, 2957, 1758, 1713, 1487, 1450, 1435, 1413, 1299, 1270, 1189, 1060, 1008, 842, 765, 698, 503; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (dd, J = 14.0, 8.4 Hz, 0.22H), 2.71 (dd, J = 14.4, 7.2 Hz, 0.78H), 2.99−3.05 (m, 1H), 3.09−3.16 (m, 1H), 3.30−3.35 (m, 1H), 3.50−3.55 (m, 1H), 3.90 (s, 2.43H), 3.92 (s, 0.57H), 4.05−4.12 (m, 1H), 4.97−5.05 (m, 1H), 7.34−7.41 (m, 3H), 7.47 (t, J = 7.6 Hz, 2H), 7.60 (d, J = 7.2 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.0 (s, 0.7F), −69.9 (s, 2.3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.4, 27.5, 35.5, 35.9, 43.3, 43.5, 53.7, 59.9 (q, J_{CF} = 14.1 Hz), 60.3, 123.8 (q, J_{CF} = 281 Hz), 127.0, 127.7, 127.8, 128.1, 128.2, 128.9, 136.8, 137.4, 140.0, 142.2, 142.3, 165.3, 166.1; MS (ESI) m/z (%) 472 $[M + 1]^+$; HRMS (ESI) calcd for $C_{21}H_{19}BrF_3NNaO_3$ $[M + Na]^+$ 492.0393, found 492.0381.

*Methyl 1-(2-Bromoethyl)-5-(4-fluorophenyl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**7g**).* White solid; mp 101.2−104.4 °C; yield 42% (86 mg); IR (KBr) ν 2959, 2924, 2853, 1758, 1714, 1606, 1512, 1436, 1270, 1228, 1188, 1059, 841, 549. Isomer a (for X-ray single crystal analysis): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 (dd, J = 14.8, 7.6 Hz, 1H), 2.94−3.04 (m, 2H), 3.24−3.30 (m, 1H), 3.45−3.51 (m, 1H), 3.87 (s, 3H), 3.99−4.05 (m, 1H), 4.93 (t, J = 7.2 Hz, 1H), 7.11 (t, J = 8.4 Hz, 2H), 7.28−7.31 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.9 to −111.8 (m, 1F), −69.7 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.3, 35.6, 43.4, 53.8, 60.0, 60.1 (q, J_{CF} = 22 Hz), 116.4, 116.6, 123.8 (q, J_{CF} = 281 Hz), 129.0, 129.1, 134.4, 161.8, 164.2, 165.3. Mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (dd, J = 14.0, 8.4 Hz, 0.48H), 2.60 (dd, J = 14.8, 7.2 Hz, 0.52H), 2.90−3.04 (m, 2H), 3.23−3.30 (m, 1H), 3.44−3.57 (m, 1H), 3.85 (s, 1.56H), 3.87 (s, 1.44H), 3.97−4.05 (m, 1H), 4.90−4.98 (m, 1H), 7.08−7.12 (m, 2H), 7.23−7.31 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −120.3−120.0 (m, 0.5F), −111.8−111.7 (m, 0.5 F), −70.1 (s, 1.5F), −70.0 (s, 1.5F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.3, 27.4, 35.5, 35.9, 43.2, 43.3, 53.6, 53.7, 59.4, 59.8, 59.8 (q, J_{CF} = 53 Hz), 116.3, 116.4, 116.5, 116.6, 123.2 (q, J_{CF} = 279 Hz), 123.7 (q, J_{CF} = 281 Hz), 129.0, 129.1, 133.65, 133.68, 134.29, 134.32, 164.1, 164.2, 165.2, 165.3, 165.4, 166.0; MS (ESI) m/z (%) 414 $[M + 1]^+$; HRMS (ESI) calcd for $C_{15}H_{14}BrF_4NO_3Na$ $[M + Na]^+$ 433.9985, found 433.9991.

*Methyl 1-(2-Bromoethyl)-5-(4-chlorophenyl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**7h**).* Viscous yellow oil; yield 53% (113 mg); IR (neat) ν 3030, 2958, 2925, 2852, 1755, 1598, 1493, 1435, 1413, 1274, 1092, 1073, 1021, 883, 833, 785, 759, 508; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (dd, J = 14.0, 8.4 Hz, 0.48H), 2.61 (dd, J = 14.4, 6.8 Hz, 0.52H), 2.93−3.06 (m, 2H), 3.27−3.33 (m, 1H), 3.47−3.59 (m, 1H), 3.88 (s, 1.56H), 3.90 (s, 1.44H), 4.02−4.10 (m, 1H), 4.92−5.01 (m, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.28 (s, 1H), 7.40−7.43 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.1 (s, 1.4F), −70.0 (s, 1.6F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.4, 27.6, 35.4, 35.9, 43.3, 43.4, 53.8, 53.9, 59.6, 60.0 (q, J_{CF} = 25 Hz), 60.0, 123.2 (q, J_{CF} = 276 Hz), 123.7 (q, J_{CF} = 289 Hz), 128.6, 129.7, 129.8, 135.1, 135.3, 136.5, 137.1, 165.3, 163.4, 166.1; MS (ESI) m/z (%) 430 $[M + 1]^+$; HRMS (ESI) calcd for $C_{15}H_{15}BrClF_3NO_3$ $[M + 1]^+$ 427.9870, found 427.9866.

*Methyl 1-(2-Bromoethyl)-5-(naphthalen-2-yl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**7i**).* White solid; mp 82.4−85.1 °C; yield 33% (73 mg); IR (KBr) ν 3050, 2957, 2925, 1760, 1714, 1512, 1434, 1300, 1267, 1195, 1161, 1064, 797, 779; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (dd, J = 14.4, 7.6 Hz, 1H), 2.93−3.05 (m, 1H), 3.16−3.26 (m, 1H), 3.30−3.35 (m, 1H), 3.58−3.64 (m, 1H), 3.96−3.97 (m, 3H), 4.13−4.28 (m, 1H), 5.95 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.44−7.63 (m, 3H), 7.87−7.96 (m, 2H), 8.05 (d, J = 8.4 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.9 (s, 2.1F), −69.3 (s, 0.9F); ^{13}C NMR

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(100 MHz, $CDCl_3$) δ 27.4, 27.9, 33.5, 35.8, 43.2, 43.9, 53.8, 54.9, 60.0 (q, J_{CF} = 28 Hz), 62.9, 121.4, 123.3 (q, J_{CF} = 280 Hz), 122.4, 123.1, 125.2, 125.8, 126.3, 126.4, 127.2, 127.3, 129.2, 129.3, 129.9, 130.2, 130.4, 130.8, 130.9, 134.0, 134.5, 165.3, 165.5, 165.8, 166.0; MS (ESI) m/z (%) 446 $[M + 1]^+$; HRMS (ESI) calcd for $C_{19}H_{17}BrF_3NO_3Na$ $[M + Na]^+$ 466.0236, found 466.0250.

*Methyl 1-(2-Bromoethyl)-2-oxo-5,5-diphenyl-3-(trifluoromethyl)-pyrrolidine-3-carboxylate (**7j**).* White solid; mp 98.9−100.6 °C; yield 46% (108 mg); IR (KBr) ν 3061, 2955, 2864, 1757, 1716, 1494, 1448, 1397, 1318, 1279, 1193, 1168, 1055, 758, 703; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34−2.41 (m, 1H), 2.86−2.93 (m, 1H), 3.26−3.38 (m, 3H), 3.48 (s, 3H), 3.89−3.97 (m, 1H), 7.15−7.17 (m, 2H), 7.21−7.27 (m, 3H), 7.32−7.41 (m, 5H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.7 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9, 43.1, 45.0, 53.4, 59.4 (q, J_{CF} = 27 Hz), 70.2, 123.5 (q, J_{CF} = 280 Hz), 127.6, 128.2, 128.3, 128.5, 128.9, 129.0, 140.8, 140.4, 164.9, 165.1; MS (ESI) m/z (%) 472 $[M + 1]^+$; HRMS (ESI) calcd for $C_{21}H_{19}BrF_3NO_3Na$ $[M + Na]^+$ 492.0393, found 492.0375.

*Methyl 1-(2-Bromoethyl)-5-octyl-2-oxo-3-(trifluoromethyl)-pyrrolidine-3-carboxylate (**9a**).* Colorless oil; yield 35% (76 mg); IR (neat) ν 3409, 2929, 2857, 1759, 1713, 1606, 1594, 1435, 1378, 1275, 1195, 1128, 1062, 1032, 982, 925, 793, 710, 528; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 8.0 Hz, 3H), 1.19−1.41 (m, 12H), 1.62−1.91 (m, 2H), 2.04 (dd, J = 16.0, 8.0 Hz, 1H), 2.36 (dd, J = 14.0, 8.0 Hz, 1H), 2.61−2.68 (m, 1H), 3.37−3.47 (m, 2H), 3.51−3.59 (m, 1H), 3.82−3.83 (m, 3H), 4.00−4.05 (m, 1H); ^{19}F NMR (400 MHz, $CDCl_3$) δ −70.15 (s, 1.49 F), −70.14 (s, 1.51F); ^{13}C NMR (400 MHz, $CDCl_3$) δ 14.1, 22.6, 24.1, 24.4, 27.4, 27.5, 29.1, 29.4, 29.45, 29.5, 31.4, 31.8, 32.2, 33.0, 33.2, 42.9. 43.1, 53.6, 53.7, 55.1, 55.7, 59.5−59.9 (m), 123.3 (q, J_{CF} = 279 Hz), 123.8 (q, J_{CF} = 281 Hz), 165.0, 165.4, 165.8, 166.2; MS (ESI) m/z (%) 430 $[M + 1]^+$; HRMS (ESI) calcd for $C_{17}H_{28}BrF_3NO_3$ $[M + 1]^+$ 430.1199, found 430.1197.

*Methyl 1-(2-Bromoethyl)-5-(2-(naphthalen-2-yloxy)ethyl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**9b**).* Colorless oil; yield 50% (122 mg); IR (neat) ν 3062, 2956, 2877, 1757, 1711, 1629, 1600, 1511, 1466, 1435, 1390, 1258, 1217, 1184, 1120, 1062, 1029, 840, 750, 624; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81−2.04 (m, 1H), 2.30−2.53 (m, 1H), 2.61−2.66 (m, 1H), 2.76−2.87(m, 1H), 3.45−3.51 (m, 3H), 3.78−3.83 (m, 3H), 4.07−4.24 (m, 4H), 7.13−7.15 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 8.0 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.77 (q, J = 8.0 Hz, 3H); ^{19}F NMR (400 MHz, $CDCl_3$) δ −70.2 (s, 1.48F), −70.1 (s, 1.52F); ^{13}C NMR (400 MHz, $CDCl_3$) δ 27.4, 31.2, 23, 32.6, 32.8, 43.1, 43.3, 53.5, 53.6, 53.8, 59.6 (q, J_{CF} = 22 Hz), 63.6, 106.6, 118.4, 123.3 (q, J_{CF} = 226 Hz), 123.7 (q, J_{CF} = 224 Hz), 123.9, 126.5, 126.7, 127.6, 129.1, 129.6, 134.3, 156.1, 165.0, 165.4, 165.6, 166.1; MS (ESI) m/z (%) 490 $[M + 1]^+$; HRMS (ESI) calcd for $C_{21}H_{22}BrF_3NO_4$ $[M + 1]^+$ 488.0679, found 488.0674.

*Methyl 5-(4-(Benzoyloxy)butyl)-1-(2-bromoethyl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**9c**).* Colorless oil; yield 43% (107 mg); IR (neat) ν 2955, 2877, 1758, 1713, 1601, 1452, 1435, 1275, 1190, 1112, 1070, 1027, 714; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39−1.52 (m, 3H), 1.73−1.99 (m, 3H), 2.03 (dd, J = 16.0, 12.0 Hz, 0.54H), 2.36 (dd, J = 12.0, 4.0 Hz, 0.46H), 2.61−2.68 (m, 1H), 3.35−3.44 (m, 2H), 3.46−3.57 (m, 1H), 3.79−3.80 (m, 3H), 3.81−4.06 (m, 2H), 4.33 (t, J = 8.0 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H), 7.54 (t, J = 8.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 2H); ^{19}F NMR (400 MHz, $CDCl_3$) δ −70.14 (s, 1.4F), −70.12 (s, 1.6F); ^{13}C NMR (400 MHz, $CDCl_3$) δ 20.8, 21.0, 27.4, 27.5, 28.5, 31.2, 32.0, 32.6, 32.8, 42.8, 43.1, 53.6, 53.7, 54.9, 55.5, 59.5 (m), 64.2, 123.2 (q, J_{CF} = 279 Hz), 123.7 (q, J_{CF} = 280 Hz), 128.4, 129.4, 130.0, 133.0, 164.9, 165.3, 165.6, 166.1, 166.5; MS (ESI) m/z (%) 494 $[M + 1]^+$; HRMS (ESI) calcd for $C_{20}H_{24}BrF_3NO_5$ $[M + 1]^+$ 494.0784, found 494.0780.

*Methyl 1-(2-Bromoethyl)-5-(4-((4-cyanobenzoyl)oxy)butyl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**9d**).* Colorless oil; yield 47% (120 mg); IR (neat) ν 2958, 2903, 2231, 1758, 1713, 1435, 1276, 1190, 1107, 1020, 862, 768, 692; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.49−1.62 (m, 1H), 1.73−1.86 (m, 2H), 1.93−2.08 (m, 1.34H), 2.39 (dd, J = 16.0, 8.0 Hz, 0.66H), 2.64−2.72 (m, 1H), 3.35−3.57 (m, 3H), 3.79 (s, 3H), 3.89−4.09 (m, 2H), 4.38 (t, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 8.09 (d, J = 8.0 Hz, 2H); ^{19}F NMR (400 MHz, $CDCl_3$) δ −70.06 (s, 1.6F), −70.05 (s, 1.4F); ^{13}C NMR (400 MHz, $CDCl_3$) δ 23.3, 23.6, 27.5, 27.6, 29.2, 29.5, 31.0, 31.8, 42.8, 43.1, 53.6, 53.7, 54.5, 55.1, 59.6 (m), 64.8, 116.5, 117.8, 123.2 (q, J_{CF} = 279 Hz), 123.6 (q, J_{CF} = 281 Hz), 130.0, 132.2, 133.6, 164.7, 164.8, 165.3, 165.5, 165.9; MS (ESI) m/z (%) 507 $[M + 1]^+$; HRMS (ESI) calcd for $C_{20}H_{21}BrF_3N_2O_5$ $[M + 1]^+$ 505.0591, found 505.0578.

*Methyl 1-(2-Bromoethyl)-5-(4-((4-methylbenzoyl)oxy)butyl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**9e**).* Colorless oil; yield 42% (212 mg); IR (neat) ν 3041, 2955, 2882, 1758, 1712, 1612, 1434, 1381, 1275, 1178, 1108, 1036, 842, 755, 691; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37−1.47 (m, 2H), 1.75−1.93 (m, 3H), 2.00−2.04 (m, 1H), 2.35 (s, 3H), 2.59−2.66 (m, 1H), 3.32−3.39 (m, 2H), 3.42−3.55 (m, 1H), 3.76−3.77 (m, 4H), 3.78−4.03 (m, 1H), 4.29 (t, J = 8.0 Hz, 3H), 7.19 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.0 Hz, 2H); ^{19}F NMR (400 MHz, $CDCl_3$) δ −70.2 (1.5F), −70.1 (1.5F); ^{13}C NMR (400 MHz, $CDCl_3$) δ 20.7, 21.0, 21.6, 27.4, 27.5, 28.5, 31.2, 32.0, 32.5, 32.7, 42.8, 43.0, 53.5, 53.6, 54.9, 55.5, 59.5 (m), 64.0, 123.2 (q, J_{CF} = 279 Hz), 123.7 (q, J_{CF} = 281 Hz), 127.3, 129.1, 129.4, 143.7, 164.9, 165.3, 165.6, 166.1, 166.5; MS (ESI) m/z (%) 510 $[M + 1]^+$; HRMS (ESI) calcd for $C_{21}H_{26}BrF_3NO_5$ $[M + 1]^+$ 508.0941, found 508.0939.

*Methyl 1-(2-Bromoethyl)-5-(4-((2-methylbenzoyl)oxy)butyl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**9f**).* Colorless oil; yield 32% (80 mg); IR (neat) ν 2956, 2874, 1763, 1715, 1602, 1572, 1455, 1435, 1293, 1257, 1197, 1146, 1084, 1038, 741; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39−1.51 (m, 3H), 1.74−2.07 (m, 3.45H), 2.36 (dd, J = 16.0, 8.0 Hz, 0.55H), 2.57(s, 3H), 2.61−2.68 (m, 1H), 3.36−3.56 (m, 3H), 3.79−3.80 (m, 3H), 3.81−4.06 (m, 2H), 4.30 (t, J = 8.0 Hz, 2H), 7.22−7.24 (m, 2H), 7.38 (t, J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H); ^{19}F NMR (400 MHz, $CDCl_3$) δ −70.14 (s, 1.3F), −70.13 (s, 1.7F); ^{13}C NMR (400 MHz, $CDCl_3$) δ 20.8, 21.0, 21.7, 27.4, 27.5, 28.5, 31.2, 32.0, 32.5, 32.7, 42.8, 43.0, 53.5, 54.8, 55.5, 59.6 (m), 63.9, 123.2 (q, J_{CF} = 279 Hz), 123.7 (q, J_{CF} = 280 Hz), 125.6, 129.4, 130.1, 131.7, 132.0, 140.0, 164.9, 165.3, 165.6, 166.1, 167.4; MS (ESI) m/z (%) 510 $[M + 1]^+$; HRMS (ESI) calcd for $C_{21}H_{26}BrF_3NO_5$ $[M + 1]^+$ 508.0941, found 508.0933.

*Methyl 1-(2-Bromoethyl)-5-(4-((4-methoxybenzoyl)oxy)butyl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**9g**).* Colorless oil; yield 41% (107 mg); IR (neat) ν 2956, 2865, 2834, 1758, 1712, 1606, 1512, 1435, 1383, 1257, 1178, 1103, 1030, 849, 772, 698, 613; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35−1.50 (m, 3H), 1.72−2.07 (m, 3.54H), 2.34 (dd, J = 12.0, 8.0 Hz, 0.66H), 2.60−2.67 (m, 1H), 3.32−3.52 (m, 3H), 3.77 (s, 3H), 3.81 (s, 3H), 3.94−4.05 (m, 2H), 4.23−4.32 (m, 2H), 6.88 (d, J = 8.0 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H); ^{19}F NMR (400 MHz, $CDCl_3$) δ −70.2 (s, 1.5F), −70.1 (s, 1.5F); ^{13}C NMR (400 MHz, $CDCl_3$) δ 20.7, 21.0, 27.4, 27.5, 28.6, 31.2, 32.0, 32.5, 32.7, 42.8, 43.0, 53.5, 53.6, 54.9, 55.4, 55.5, 59.5 (m), 63.9, 113.6, 122.5, 123.2 (q, J_{CF} = 267 Hz), 123.7 (q, J_{CF} = 277 Hz), 131.4, 163.3, 164.9, 165.3, 165.6, 166.0, 166.2; MS (ESI) m/z (%) 526 $[M + 1]^+$; HRMS (ESI) calcd for $C_{21}H_{26}BrF_3NO_6$ $[M + 1]^+$ 524.0890, found 524.0885.

*Methyl 1-(2-Bromoethyl)-5-(4-((4-iodobenzoyl)oxy)butyl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**9h**).* Colorless oil; yield 41% (127 mg); IR (neat) ν 2954, 2867, 1758, 1713, 1586, 1434, 1393, 1278, 1177, 1103, 1035, 1008, 923, 847, 755, 683; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36−1.47 (m, 3H), 1.75−1.93 (m, 3H), 2.02 (dd, J = 16.0, 8.0 Hz, 0.53H), 2.34 (dd, J = 16.0, 8.0 Hz, 0.47H), 2.60−2.67 (m, 1H), 3.35−3.44 (m, 2H), 3.46−3.55 (m, 1H), 3.79 (s, 3H), 3.82−3.88 (m, 1H), 3.97−4.06 (m, 1H), 4.30 (t, J = 8.0 Hz, 2H), 7.69 (dd, J = 8.4 Hz, 2.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H); ^{19}F NMR (400 MHz, $CDCl_3$) δ −70.10 (s, 1.64F), −70.09 (s, 1.36F); ^{13}C NMR (400 MHz, $CDCl_3$) δ 20.7, 20.9, 27.4, 27.5, 28.5, 31.2, 32.0, 32.5, 32.7, 42.9, 43.1, 53.5, 53.6, 54.9, 55.5, 59.6 (m), 64.4, 100.7, 123.2 (q, J_{CF} = 223 Hz), 123.7 (q, J_{CF} = 225 Hz), 129.5, 130.9, 137.7, 164.9, 165.3, 165.5, 165.9, 166.0; MS (ESI) m/z (%) 622 $[M + 1]^+$; HRMS (ESI) calcd for $C_{20}H_{23}BrIF_3NO_5$ $[M + 1]^+$ 619.9751, found 619.9744.

*Methyl 1-(2-Bromoethyl)-5-(2-(3,5-dimethylphenoxy)ethyl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**9i**).* Colorless oil; yield 31% (71 mg); IR (neat) ν 2956, 2920, 1759, 1713, 1594, 1435, 1322, 1296, 1277, 1193, 1169, 1073, 832, 688; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80−1.94 (m, 1H), 2.30 (s, 6H), 2.39−2.46 (m, 1H), 2.57−2.62 (m, 1H), 2.73−2.83 (m, 1H), 3.45−3.62 (m, 3H), 3.80 (s, 1.19H),

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3.83 (s, 1.81H), 4.04−4.17 (m, 4H), 6.52 (s, 2H), 6.64 (s, 1H); ^{19}F NMR (400 MHz, $CDCl_3$) δ −70.2 (s, 1.23F), −70.1 (s, 1.77F); ^{13}C NMR (400 MHz, $CDCl_3$) δ 27.4, 31.3, 32.4, 32.8, 32.9, 43.1, 43.3, 53.56, 53.64, 53.8, 59.6 (m), 63.4, 112.0, 123.1, 123.3 (q, J_{CF} = 279 Hz), 123.7 (q, J_{CF} = 281 Hz), 139.4, 158.2, 165.0, 165.4, 165.6, 166.2; MS (ESI) m/z (%) 466 $[M + 1]^+$; HRMS (ESI) calcd for $C_{19}H_{24}BrF_3NO_4$ $[M + 1]^+$ 466.0835, found 466.0831.

*Methyl 1-(2-Bromoethyl)-2-oxo-5-(3-(tosyloxy)propyl)-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**9j**).* Colorless oil; yield 33% (87 mg); IR (neat) ν 2959, 2863, 1758, 1711, 1598, 1435, 1358, 1276, 1291, 1283, 1097, 1035, 967, 923, 816, 737, 664, 555; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38−1.48 (m, 1H), 1.52−1.59 (m, 2H), 1.82−1.97 (m, 1.49H), 2.26−2.31 (dd, J = 12.0, 8.0 Hz, 0.51H), 2.43 (s, 3H), 2.56−2.63 (m, 1H), 3.29−3.40 (m, 2H), 3.45−3.54 (m, 1H), 3.80−3.81 (m, 3H), 3.96−4.08 (m, 3H), 7.34 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H); ^{19}F NMR (400 MHz, $CDCl_3$) δ −70.2 (s, 1.47F), −70.1 (1.53F); ^{13}C NMR (400 MHz, $CDCl_3$) δ 21.6, 23.6, 23.9, 27.4, 27.4, 28.9, 29.1, 30.8, 31.6, 42.8, 43.0, 53.6, 53.8, 54.3, 54.9, 59.4 (q, J_{CF} = 14 Hz), 69.4, 123.2 (q, J_{CF} = 279 Hz), 123.6 (q, J_{CF} = 281 Hz), 127.8, 130.0, 145.1, 164.9, 165.3, 165.4, 166.0; MS (ESI) m/z (%) 530 $[M + 1]^+$; HRMS (ESI) calcd for $C_{19}H_{24}BrF_3NO_6S$ $[M + 1]^+$ 530.0454, found 530.0450.

*Methyl 5-(3-(Benzo[d]thiazol-2-ylthio)propyl)-1-(2-bromoethyl)-2-oxo-3-(trifluoromethyl)pyrrolidine-3-carboxylate (**9k**).* Yellow oil; yield 45% (113 mg); IR (neat) ν 3061, 2954, 2869, 1762, 1712, 1459, 1428, 1379, 1334, 1308, 1193, 1075, 996, 756, 728, 704, 672; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52−1.66 (m, 1H), 1.80−1.88 (m, 2H), 1.97−2.11 (m, 1.32H), 2.36 (dd, J = 12.0 Hz, 4.0 Hz, 0.68H), 2.63−2.71 (m, 1H), 3.31−3.56 (m, 5H), 3.77−3.79 (m, 3H), 3.86−4.03 (m, 2H), 7.28 (t, J = 8.0 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H); ^{19}F NMR (400 MHz, $CDCl_3$) δ −70.10 (s, 1.4F), −70.05 (s, 1.6 F); ^{13}C NMR (400 MHz, $CDCl_3$) δ 24.1, 24.3, 27.4, 27.5, 31.1, 31.6, 31.9, 32.6, 42.8, 43.1, 53.5, 53.6, 54.5, 55.0, 59.6 (m), 121.0, 123.2 (q, J_{CF} = 280 Hz), 121.3, 123.6 (q, J_{CF} = 281 Hz), 126.0, 136.1, 152.9, 164.9, 165.3, 165.5, 165.9; MS (ESI) m/z (%) 527 $[M + 1]^+$; HRMS (ESI) calcd for $C_{19}H_{21}BrF_3N_2O_3S_2$ $[M + 1]^+$ 525.0124, found 525.0117. Anal. Calcd for $C_{19}H_{20}BrF_3N_2O_3S_2$: C, 43.43; H, 3.84; N, 5.33. Found: C, 43.48; H, 3.64; N, 4.97.

*(E)-Methyl 4-Bromo-2-(4,5-dihydrooxazol-2-yl)-4-phenyl-2-(trifluoromethyl)but-3-enoate (**11a**).* Yellow oil; yield 59% (96 mg); IR (neat) ν 3067, 2956, 2916, 2882, 1762, 1666, 1437, 1276, 1229, 1182, 1105, 1031, 925; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.48−3.54 (m, 2H), 3.55 (s, 3H), 3.86−3.91 (m, 2H), 6.61 (s, 1H), 7.30−7.39 (m, 5H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.8 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.6, 54.1, 60.3 (q, J_{CF} = 27 Hz), 67.9, 121.9, 122.4 (q, J_{CF} = 264 Hz), 127.7, 128.8, 128.9, 129.1, 137.1, 158.7, 163.5; MS (ESI) m/z (%) 394 $[M + 1]^+$; HRMS (ESI) calcd for $C_{15}H_{14}BrF_3NO_3$ $[M + 1]^+$ 392.0104, found 392.0102.

*(E)-Methyl 4-Bromo-2-(4,5-dihydrooxazol-2-yl)-4-(4-fluorophenyl)-2-(trifluoromethyl)but-3-enoate (**11b**).* Colorless oil; yield 64% (131 mg); IR (neat) ν 3072, 2957, 2908, 2899, 1762, 1667, 1599, 1505, 1439, 1354, 1319, 1257, 1186, 1104, 1032, 936, 842; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.55−3.60 (m, 5H), 3.91−3.99 (m, 2H), 6.61 (s, 1H), 7.02 (t, J = 8.8 Hz, 2H), 7.36−7.40 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −110.7 (m, 1F), −67.8 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.6, 54.2, 60.4 (q, J_{CF} = 27 Hz), 68.1, 114.7, 114.9, 122.4 (q, J_{CF} = 274 Hz), 122.7, 127.6, 131.1, 131.2, 158.8, 161.5, 163.5, 164.0; MS (ESI) m/z (%) 412 $[M + 1]^+$; HRMS (ESI) calcd for $C_{15}H_{13}BrF_4NO_3$ $[M + 1]^+$ 410.0009; found 410.0007.

*(E)-Methyl 4-Bromo-4-(3-chlorophenyl)-2-(4,5-dihydrooxazol-2-yl)-2-(trifluoromethyl)but-3-enoate (**11c**).* Yellow oil; yield 64% (137 mg); IR (neat) ν 3084, 2956, 2912, 2890, 1759, 1667, 1564, 1436, 1354, 1254, 1192, 1109, 1032, 929; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.47−3.54 (m, 2H), 3.59 (s, 3H), 3.89−4.01 (m, 2H), 6.61 (s, 1H), 6.95−7.07 (m, 1H), 7.23−7.30 (m, 2H), 7.34 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.8 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.6, 54.2, 60.3 (q, J_{CF} = 22 Hz), 68.1, 123.0, 123.3 (q, J_{CF} = 227 Hz), 126.7, 127.2, 128.9, 129.15, 129.18, 133.5, 138.7, 158.6, 163.3; MS (ESI) m/z (%) 428 $[M + 1]^+$; HRMS (ESI) calcd for $C_{15}H_{13}BrClF_3NO_3$ $[M + 1]^+$ 425.9714, found 425.9705.

*(E)-Methyl 4-([1,1′-Biphenyl]-4-yl)-4-bromo-2-(4,5-dihydrooxazol-2-yl)-2-(trifluoromethyl)but-3-enoate (**11d**).* Yellow solid; mp 115.2−117.5 °C; yield 52% (121 mg); IR (neat) ν 3084, 3037, 2954, 2877, 1758, 1666, 1486, 1435, 1255, 1187, 1104, 1031, 836; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46−3.56 (m, 2H), 3.60 (s, 3H), 3.87−3.93 (m, 2H), 6.63 (s, 1H), 7.36−7.40 (m, 2H), 7.44−7.47 (m, 4H) 7.56−7.59 (m, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.7 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.7, 54.2, 60.4 (q, J_{CF} = 27 Hz), 68.0, 122.1, 122.4 (q, J_{CF} = 284 Hz), 126.3, 127.0, 127.9, 128.6, 129.0, 129.5, 137.0, 139.9, 141.9, 158.7, 163.6; MS (ESI) m/z (%) 470 $[M + 1]^+$; HRMS (ESI) calcd for $C_{21}H_{18}BrF_3NO_3$ $[M + 1]^+$ 468.0417, found 468.0411.

*(E)-Methyl 4-Bromo-2-(4,5-dihydrooxazol-2-yl)-4-(4-methoxyphenyl)-2-(trifluoromethyl)but-3-enoate (**11e**).* Yellow oil; yield 33% (70 mg); IR (neat) ν 2955, 2933, 2843, 1757, 1701, 1603, 1508, 1435, 1257, 1173, 1113, 1031, 840; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36−3.39 (m, 2H), 3.46 (s, 3H), 3.50−3.62 (m, 2H), 3.80 (s, 3H), 6.50 (s, 1H), 6.84 (d, J = 8.8 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.8 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.1, 41.8, 53.6, 55.3, 64.8 (q, J_{CF} = 25 Hz), 113.5, 122.5 (q, J_{CF} = 284 Hz), 122.6, 129.1, 129.6, 130.1, 160.2, 161.8, 165.2; MS (ESI) m/z (%) 422 $[M + 1]^+$; HRMS (ESI) calcd for $C_{16}H_{16}BrF_3NO_4$ $[M + 1]^+$ 422.0209, found 422.0203.

*(E)-Methyl 4-Bromo-2-(4,5-dihydrooxazol-2-yl)-2-(trifluoromethyl)-4-(3-(trifluoromethyl)phenyl)but-3-enoate (**11f**).* Yellow oil; yield 62% (142 mg); IR (neat) ν 3075, 2959, 2907, 2877, 1760, 1667, 1484, 1437, 1327, 1255, 1167, 1136, 1073, 1033, 701; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 (t, J = 9.2 Hz, 2H), 3.55 (s, 3H), 3.87−4.00 (m, 2H), 6.67 (s, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.67 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.8 (s, 3F), −62.8 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.6, 54.1, 60.4 (q, J_{CF} = 27 Hz), 68.1, 122.3 (q, J_{CF} = 284 Hz), 123.4, 123.6 (q, J_{CF} = 271 Hz), 125.8, 126.5, 128.5, 130.2, 130.5, 132.3, 137.9, 158.6, 163.3; MS (ESI) m/z (%) 462 $[M + 1]^+$; HRMS (ESI) calcd for $C_{16}H_{13}BrF_6NO_3$ $[M + 1]^+$ 459.9978, found 459.9972.

*(E)-Methyl 4-Bromo-4-(4-(tert-butyl)phenyl)-2-(4,5-dihydrooxazol-2-yl)-2-(trifluoromethyl)but-3-enoate (**11g**).* Yellow solid; mp 77.8−79.3 °C; yield 65% (147 mg); IR (neat) ν 2962, 2899, 2869, 1759, 1666, 1436, 1364, 1267, 1202, 1112, 1032, 926, 827; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (s, 9H), 3.42−3.52 (m, 2H), 3.57 (s, 3H), 3.81−3.91 (m, 2H), 6.58 (s, 1H), 7.30−7.35 (m, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.8 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.0, 34.6, 53.5, 54.0, 60.3 (q, J_{CF} = 28 Hz), 67.7, 121.6, 122.4 (q, J_{CF} = 284 Hz), 124.5, 128.7, 129.1, 134.1, 152.2, 158.5, 163.6; MS (ESI) m/z (%) 450 $[M + 1]^+$; HRMS (ESI) calcd for $C_{19}H_{22}BrF_3NO_3$ $[M + 1]^+$ 448.0730, found 448.0724.

*(E)-Methyl 4-Bromo-4-(4-bromophenyl)-2-(4,5-dihydrooxazol-2-yl)-2-(trifluoromethyl)but-3-enoate (**11h**).* Yellow oil; yield 43% (101 mg); IR (neat) ν 3075, 2955, 2916, 2877, 1758, 1666, 1584, 1483, 1436, 1353, 1104, 1086, 1032, 1012, 821; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.42−3.54 (m, 2H), 3.55 (s, 3H), 3.86−3.96 (m, 2H), 6.57 (s, 1H), 7.22 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.8 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.7, 54.2, 60.3 (q, J_{CF} = 27 Hz), 68.1, 122.3 (q, J_{CF} = 274 Hz), 122.7, 123.4, 127.3, 130.6, 130.9, 136.0, 158.6, 163.4; MS (ESI) m/z (%) 472 $[M + 1]^+$; HRMS (ESI) calcd for $C_{15}H_{13}Br_2F_3NO_3$ $[M + 1]^+$ 469.9209, found 469.9205.

*(E)-Methyl 4-Bromo-4-(4-chlorophenyl)-2-(4,5-dihydrooxazol-2-yl)-2-(trifluoromethyl)but-3-enoate (**11i**).* Yellow oil; yield 44% (142 mg); IR (neat) ν 3088, 2956, 2920, 2886, 1759, 1666, 1591, 1487, 1436, 1354, 1256, 1189, 1104, 1032, 927, 826; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.42−3.52 (m, 2H), 3.54 (s, 3H), 3.86−3.97 (m, 2H), 6.58 (s, 1H), 7.24−7.30 (m, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.8 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.6, 54.1, 60.3 (q, J_{CF} = 27 Hz), 68.0, 122.3 (q, J_{CF} = 284 Hz), 122.7, 127.2, 127.9, 130.4, 136.1, 136.5, 158.6, 163.4; MS (ESI) m/z (%) 428 $[M + 1]^+$; HRMS (ESI) calcd for $C_{15}H_{13}BrClF_3NO_3$ $[M + 1]^+$ 425.9714, found 425.9706.

*(E)-Methyl 4-Bromo-4-(cyclohex-1-en-1-yl)-2-(4,5-dihydrooxazol-2-yl)-2-(trifluoromethyl)but-3-enoate (**11j**).* Colorless oil; yield 67% (133 mg); IR (neat) ν 3325, 2936, 2864, 1757, 1665, 1436, 1352, 1253, 1145, 1092, 1031, 928, 891, 827; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52−

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1.58 (m, 2H), 1.62−1.68 (m, 2H), 1.98−2.06 (m, 2H), 2.08−2.25 (m, 2H), 3.80 (s, 3H), 3.95 (t, J = 9.6 Hz, 2H), 4.36 (t, J = 9.6 Hz, 2H), 5.94 (s, 1H), 6.26 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −68.0 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 22.1, 25.1, 26.1, 53.6, 54.4, 59.7 (q, J_{CF} = 27 Hz), 68.6, 119.9, 122.5 (q, J_{CF} = 284 Hz), 130.8, 133.8, 134.5, 160.4, 163.9; MS (ESI) m/z (%) 398 $[M + 1]^+$; HRMS (ESI) calcd for $C_{15}H_{18}BrF_3NO_3$ $[M + 1]^+$ 396.0417, found 396.0412.

*(E)-Methyl 2-((S)-4-Benzyl-4,5-dihydrooxazol-2-yl)-4-bromo-4-phenyl-2-(trifluoromethyl)but-3-enoate (**11k**).* Yellow oil; yield 63% (152 mg); IR (neat) ν 3063, 3028, 2955, 1759, 1666, 1603, 1490, 1472, 1436, 1351, 1272, 1189, 1103, 1031, 948, 864, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (m, 1H), 3.01 (dt, J = 14.4, 5.2 Hz, 1H), 3.40 (s, 1.51H), 3.44 (s, 1.49H), 3.76−3.80 (m, 2H), 4.03−4.11 (m, 1H), 6.56 (s, 0.51H), 6.69 (s, 0.49H), 7.11−7.24 (m, 4H), 7.28−7.42 (m, 6H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.8 (s, 1.5F), −67.7 (s, 1.5F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.4, 40.6, 53.2, 53.3, 60.2 (m), 67.0, 67.1, 71.9, 72.4, 122.1, 122.2, 122.3 (q, J_{CF} = 284 Hz), 122.5 (q, J_{CF} = 284 Hz), 126.5, 127.79, 127.82, 128.4, 128.6, 128.8, 128.9, 129.0, 129.1, 129.13, 129.16, 129.3, 136.9, 137.0, 137.09, 137.11, 158.3, 158.7, 136.27, 163.33; MS (ESI) m/z (%) 484$[M + 1]^+$; HRMS (ESI) calcd for $C_{22}H_{20}BrF_3NO_3$ $[M + 1]^+$ 482.0573, found 482.0566.

*(E)-Methyl 4-Bromo-4-phenyl-2-((R)-4-phenyl-4,5-dihydrooxazol-2-yl)-2-(trifluoromethyl)but-3-enoate (**11l**).* Yellow oil; yield 43% (101 mg); IR (neat) ν 3071, 3032, 2968, 2916, 1755, 1664, 1493, 1436, 1352, 1273, 1236, 1174, 1104, 1030, 775, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.44 (s, 1.51H), 3.46 (s, 1.49H), 3.94 (t, J = 8.4 Hz, 0.51H), 4.04 (t, J = 8.4 Hz, 0.51H), 4.23 (t, J = 8.8 Hz, 0.49H), 4.29 (t, J = 9.6 Hz, 0.49H), 4.83−4.91 (m, 1H), 6.59 (s, 0.51H), 6.81 (s, 0.49H), 7.13−7.19 (m, 2H), 7.28−7.44 (m, 8H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.64 (s, 1.5F), −67.59 (s, 1.5F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.3, 53.4, 60.6 (m), 69.2, 69.4, 75.3, 75.8, 122.0, 122.1, 122.3 (q, J_{CF} = 284 Hz), 122.7 (q, J_{CF} = 284 Hz), 126.4, 126.6, 127.8, 127.9, 128.7, 128.9, 129.1, 129.17, 129.20, 137.0, 141.0, 141.1, 159.3, 160.0, 163.3; MS (ESI) m/z (%) 468 $[M + 1]^+$; HRMS (ESI) calcd for $C_{21}H_{18}BrF_3NO_3$ $[M + 1]^+$ 468.0417, found 468.0412.

*(E)-Methyl 4-Bromo-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-4-phenyl-2-(trifluoromethyl)but-3-enoate (**11m**).* Yellow oil; yield 53% (111 mg); IR (neat) ν 3066, 2970, 2932, 2899, 1758, 1665, 1490, 1463, 1444, 1367, 1351, 1289, 1210, 1172, 1104, 1031, 919, 871, 767, 701; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (s, 6H), 3.27 (s, 3H), 3.78 (q, J = 8.4 Hz, 2H), 6.65 (s, 1H), 7.31−7.39 (m, 5H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −68.0 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.4, 27.5, 53.0, 60.1 (q, J_{CF} = 27 Hz), 67.8, 79.5, 122.5 (q, J_{CF} = 284 Hz), 122.6, 127.9, 128.5, 129.0, 129.2, 137.3, 157.1, 163.3; MS (ESI) m/z (%) 422 $[M + 1]^+$; HRMS (ESI) calcd for $C_{17}H_{18}BrF_3NO_3$ $[M + 1]^+$ 420.0417, found 420.0406.

*(E)-Methyl 4-Bromo-2-((S)-4-((R)-sec-butyl)-4,5-dihydrooxazol-2-yl)-4-phenyl-2-(trifluoromethyl)but-3-enoate (**11n**).* Yellow oil; yield 53% (118 mg); IR (neat) ν 3066, 2962, 2903, 2878, 1761, 1668, 1489, 1436, 1351, 1255, 1185, 1105, 1031, 941, 864, 766, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75 (t, J = 6.4 Hz, 3H), 0.88 (dt, J = 7.2, 3.2 Hz, 3H), 1.06−1.17 (m, 1.51H), 1.25−1.41 (m, 1.49H), 3.36 (s, 1.49H), 3.40 (s, 1.51H), 3.71−3.90 (m, 3H), 6.54 (s, 0.49H), 6.73 (s, 0.51H), 7.28−7.37 (m, 4H), 7.40−7.42 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.8 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.5, 13.5, 13.7, 25.9, 38.0, 38.2, 53.1, 60.1 (m), 69.4, 70.0, 70.1, 70.3, 122.3 (m), 122.6 (q, J_{CF} = 284 Hz), 127.7, 127.8, 128.4, 128.6, 128.9, 128.99, 129.04, 129.06, 137.0, 137.1, 157.5, 158.0, 163.3, 163.4; MS (ESI) m/z (%) 450 $[M + 1]^+$; HRMS (ESI) calcd for $C_{19}H_{22}BrF_3NO_3$ $[M + 1]^+$ 448.0730, found 448.0720.

*(E)-Methyl 4-Bromo-2-((S)-4-isopropyl-4,5-dihydrooxazol-2-yl)-4-phenyl-2-(trifluoromethyl)but-3-enoate (**11o**).* Yellow oil; yield 31% (67 mg); IR (neat) ν 3058, 2960, 2908, 2869, 1761, 1668, 1436, 1350, 1252, 1173, 1104, 1030, 947, 767, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (dd, J = 6.8, 3.6 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H), 1.68−1.79 (m, 1H), 3.34 (s, 1.51H), 3.39 (s, 1.49H), 3.61−3.72 (m, 1H), 3.79−3.90 (m, 2H), 6.55 (s, 0.49H), 6.73 (s, 0.51H), 7.30−7.34 (m, 4H), 7.39−7.41 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.81 (s, 1.5F), −67.78 (s, 1.5F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.3, 17.5, 18.3, 18.4, 31.8, 32.0, 53.1, 60.2 (m), 70.1, 70.6, 71.6, 71.7, 122.3 (q, J_{CF} = 284 Hz), 122.3, 122.5, 122.6 (q, J_{CF} = 284 Hz), 127.7, 127.8, 128.4, 128.6, 128.9, 129.0, 129.1, 137.09, 137.14, 157.7, 158.2, 163.4, 163.5; MS (ESI) m/z (%) 436 $[M + 1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}BrF_3NO_3$ $[M + 1]^+$ 434.0573, found 434.0566.

*(E)-Methyl 4-Bromo-2-((R)-4-isobutyl-4,5-dihydrooxazol-2-yl)-4-phenyl-2-(trifluoromethyl)but-3-enoate (**11p**).* Yellow oil; yield 56% (125 mg); IR (neat) ν 3066, 2957, 2872, 1760, 1663, 1589, 1490, 1469, 1436, 1368, 1256, 1174, 1105, 1031, 939, 864, 766, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86−0.91 (m, 6H), 1.12−1.20 (m, 1H), 1.47−1.52 (m, 1H), 1.60−1.67 (m, 1H), 3.40 (s, 1.49H), 3.43 (s, 1.51H), 3.66 (q, J = 8.0 Hz, 1H), 3.78−3.87 (m, 1H), 3.95−4.00 (m, 1H), 6.56 (s, 0.51H), 6.69 (s, 0.49H), 7.30−7.41 (m, 5H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.9 (s, 1.43F), −67.8 (s, 1.57F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 22.4, 22.8, 22.9, 25.1, 25.2, 44.3, 44.4, 53.2, 60.2 (m), 64.6, 64.8, 73.4, 73.6, 122.3 (q, J_{CF} = 284 Hz), 122.3, 122.4, 122.6 (q, J_{CF} = 284 Hz), 127.7, 127.8, 128.5, 128.6, 128.9, 129.00, 129.04, 129.1, 137.2, 157.5, 157.9, 163.4; MS (ESI) m/z (%) 450 $[M + 1]^+$; HRMS (ESI) calcd for $C_{19}H_{22}BrF_3NO_3$ $[M + 1]^+$ 448.0730, found 448.0717.

*Methyl 5-Ethoxy-2-oxo-3-(trifluoromethyl)-1-vinylpyrrolidine-3-carboxylate (**12**).* A 10 mL Schlenk tube was charged with a stir bar. The tube was vacuumed and charged back with N_2 three times. Compound **5a** (36.2 mg, 0.1 mmol), DBU (15.2 mg, 0.1 mmol), and DMF (1 mL) were added under N_2 atmosphere. The mixture was stirred at 80 °C for 10 h. Then, the mixture was added to water (20 mL) and ethyl acetate (20 mL). The organic phase was separated. The aqueous phase was extracted with ethyl acetate three times. The organic phase was combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a hexane/ethyl acetate mixture as eluent. Colorless oil; yield 55% (15 mg); IR (neat) ν 3190, 2981, 2927, 1762, 1730, 1673, 1430, 1394, 1322, 1292, 1267, 1198, 1102, 1056; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19−1.26 (m, 3H), 2.42−2.58 (m, 1H), 2.78−2.91 (m, 1H), 3.49−3.58 (m, 2H), 3.83−3.85 (m, 3H), 4.70−4.76 (dd, J = 17.6, 8.0 Hz, 1H), 4.84−5.05 (m, 1H), 5.25−5.40 (m, 1H), 6.83−6.94 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.3 (s, 2.0F), −69.4 (s, 1.0F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.0, 31.5, 32.2, 53.9, 54.0, 59.3−59.7 (m), 61.0, 62.4, 84.1, 84.9, 97.4, 100.0, 123.0 (q, J_{CF} = 280 Hz), 123.2 (q, J_{CF} = 280 Hz), 127.6, 127.7, 162.2, 162.9, 165.1, 165.5; MS (ESI) m/z (%) 282 $[M + 1]^+$; HRMS (ESI) calcd for $C_{11}H_{15}F_3NO_4$ $[M + 1]^+$ 282.0948, found 282.0948.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00930.

Crystallographic information for **7g** (CIF)

Crystallographic information for **11d** (CIF)

Screening of reaction conditions for reactions with styrenes, alkyl alkenes and alkynes, X-ray crystal data and spectra data for all new compounds, measurement of the reduction potential of **3a**, and ^{19}F NMR spectroscopy of the reaction mixture to produce **5a**, **7a**, and **9a** (PDF)

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Notes

The authors declare no competing financial interest.

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