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Synthesis of 2-(Trifluoromethyl)oxazoles from β-Monosubstituted Enamines via PhI(OCOCF$_3$)$_2$-Mediated Trifluoroacetoxylation and Cyclization

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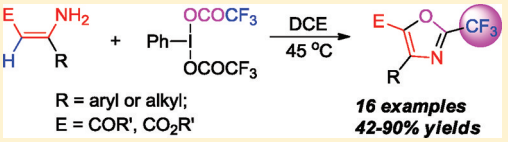
Supporting Information

ABSTRACT: Treatment of β-monosubstituted enamines with phenyliodine bis(trifluoroacetate) (PIFA) was found to give a variety of 4,5-disubstituted 2-(trifluoromethyl)oxazoles. This approach allows the incorporation of the trifluoromethyl moiety in PIFA into the final products, which presumably takes place via the oxidative β-trifluoroacetoxylation of the enamine substrates followed by subsequent intramolecular cyclization.



In the last two decades, hypervalent iodine(**III**) reagents, especially phenyliodine bis(trifluoroacetate) (PIFA) and phenyliodine diacetate (PIDA), have been vastly used in many useful organic transformations.[1] Among them, reactions of hypervalent iodine(III) reagents with enamine compounds have been thoroughly investigated.[2] Various heterocyclic compounds such as pyrroles,[3] indoles,[4] and azirines[5] can be obtained by such reactions, depending on the substitution pattern of the enamine substrates and the type of the iodine(III) reagents used. In all cases, PIFA and PIDA are converted into trifluoroacetate and acetate respectively, with the release of the recyclable iodobenzene, after the oxidative process (Figure 1, type 1).[6] In a few reactions of enamines with

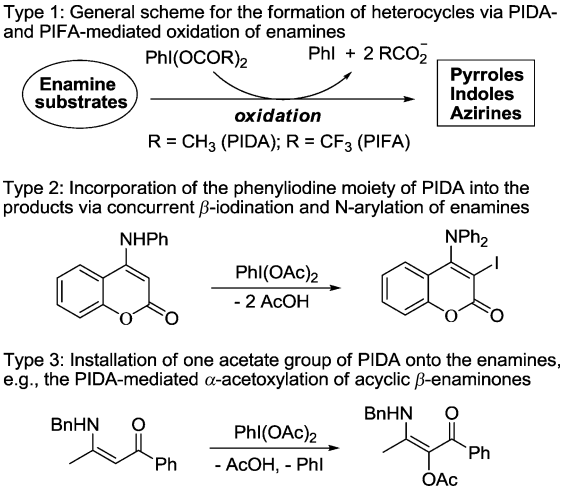


Figure 1. General reaction types of enamine compounds with PIFA and PIDA.

PIDA, the phenyliodine moiety in PIDA can be incorporated into the final products.[7] For example, upon treatment of 4-phenylaminocoumarin with PIDA, both the phenyl and the iodo moieties of PIDA are incorporated into the final product via β-iodination and *N*-arylation respectively (Figure 1, type 2).[7b] It has also been recognized that one acetate group of PIDA can be installed onto the β-position of an enamine compound, possibly through reductive elimination of iodobenzene[6] or nucleophilic substitution by the acetate anion[8] (Figure 1, type 3). However, to our knowledge, reports on the integration of the trifluoroacetate moiety of PIFA into an enamine substrate in the literature are scarce, if any. Herein, we report a novel formation of 2-(trifluoromethyl)oxazole derivatives[9−11] from reactions of β-monosubstituted enamines with PIFA, in which PIFA serves as a fluorinating reagent for the introduction of the trifluoromethyl moiety, a biologically important functional group.[12]

During the course of our study on the reaction of enamines with hypervalent iodine(III) reagents,[4,5a,7c] we found that the β-monosubstituted enamine **1a**, bearing a terminal ethoxycarbonyl group, upon treatment with PIDA, gave no expected azirine compounds.[5a] The replacement of PIDA with the more potent PIFA led us accidentally to discover that an interesting heterocyclic compound **2a**[13] was formed in the process. The structure of this 2-(trifluoromethyl)oxazole **2a** was undoubtedly established by X-ray crystal analysis (see Supporting Information for details).

Enamine **1a** was used as the model substrate for the optimization of reaction conditions, and the results are summarized in Table 1. It was found that the reaction yield was significantly improved and the reaction time shortened when the amount of PIFA was increased from 1.0 equiv to 1.2 equiv and the reaction temperature was increased from room temperature to 45 °C (Table 1, entries 1−2). However, even higher temperature, such as at reflux, reduced the yield of the desired product due to the formation of a complex mixture of byproducts (Table 1, entry 3). Data in Table 1 (entries 4−7)

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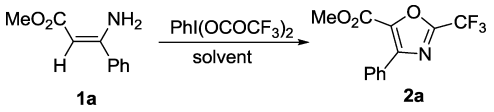
Table 1. Optimization of the Reaction Conditions[a]



1a 2a

entry	PIFA equiv	solvent	[1a] (M)	T (°C)	time (h)	yield[b] (%)
1	1.0	DCE	0.1	rt	3	35
2	1.2	DCE	0.1	45	1	52
3	1.2	DCE	0.1	reflux	0.5	30
4	1.2	DCE	0.05	45	1.5	66
5	1.2	DCE	0.04	45	1.5	73
6	1.2	DCE	0.02	45	2	80[c]
7	1.2	DCE	0.2	45	1	40
8[d]	1.2	DCE	0.02	45	2	73
9[e]	1.2	DCE	0.02	45	2	75[c]
10	1.2	CH_3CN	0.02	45	2	trace
11	1.2	TFE[f]	0.02	45	2	68
12	1.2	toluene	0.02	45	2	64
13	1.2	EtOAc	0.02	45	2	15
14	1.2	DMF	0.02	45	2	0

[a]All reactions were carried out by adding PIFA to a solution of **1a** in dry solvent unless specifically mentioned. [b]Isolated yields. [c]Average of three runs. [d]Enamine **1a** was added portionwise to a solution containing PIFA. [e]4 Å molecular sieves were added. [f]TFE herein refers to 2,2,2-trifluoroethanol.

show that the concentration of substrate **1a** in the solvent can greatly influence the outcome of the reaction. Specifically, when the reaction mixture was diluted to 0.02 M, the yield was dramatically increased to 80%, while at 0.2 M, the yield was only 40%. We also found that addition of the enamine **1a** in a portionwise manner to a solution of PIFA in dry solvent at low concentration, as opposed to one portion, does not greatly affect the reaction yield (Table 1, entry 8). An attempt to further increase the yield by including molecular sieves for the purpose of absorbing the water generated during the reaction course was not successful (Table 1, entry 9). Furthermore, the presence of a Lewis or Brønsted acid such as $CuSO_4$, $BF_3{\cdot}Et_2O$, or TFA somehow reduced the yield in a series of experiments carried out between −20 °C and room temperature (not shown). Finally, our solvent study shows that none of the solvents including TFE, toluene, EtOAc, CH_3CN, or DMF is superior to DCE. Data (Table 1, entries 10−14) show that yields were reduced by around 15% with TFE and toluene as solvent, but tanked to only 15%, trace, and absolutely nothing in the other three solvents.

Under the best conditions (Table 1, entry 6), we explored the scope and limitations[14] of the newly developed method by using various β-monosubstituted enamines[5a,9] bearing a terminal carbonyl functionality. Results show that (i) the presence of either electron-donating or electron-withdrawing substituents in the α-phenyl ring of enamine **1a** does not influence the reaction to any significant extent as the desired oxazoles were all obtained in fairly good yields (Table 2, entries 2−5); (ii) the α-phenyl ring in **1a** is not indispensable for the reaction and can be replaced by an alkyl substituent such as methyl, benzyl, or cyclohexenylmethyl group (Table 2, entries 6−8); (iii) the β-carboxylic ester groups can be replaced by an acyl group (Table 2, entries 9−16). A variety of 4-alkyl-5-aroyl-2-(trifluoromethyl)oxazoles were obtained with the 4-*tert*-butyloxazole **2m** being prepared in the most satisfying yield of 90%. 4-Phenyl-5-pivaloyloxazole **2n** was also obtained from α-phenyl-β-pivaloyl enamine **1n**, the regioisomer of **1m** in a parallel fashion. Oxazoles **2o** and **2p** were obtained (Table 2, entries 15−16), albeit in much lower yields due to the formation of a complex mixture of unidentified byproducts from α-aryl-β-aroyl enamines **1o** and **1p**.

A proposed mechanistic pathway is shown in Scheme 1. Initially, the reaction of β-monosubstituted enamines **1** with PIFA gives the β-iodo iminium salt **A**, which is expected to be a stable intermediate owing to the existence of an internal H-bond.[7c] Next, the generated trifluoroacetate anion, although a relatively weak base, nucleophilically attacks the sp^3 carbon center in **A** to give intermediate **B**,[15] with the leaving group dissociating into an iodobenzene molecule and a trifluoroacetate anion. After the proton transfer from the iminium center to the carbonyl oxygen of the trifluoroacetate moiety, an intramolecular attack on the electron-positive carbonyl group by the N of the amino group occurs in **C** and leads to **D**. Finally, upon protonation of the generated hydroxyl group by the ammonium proton in **D**, the aromatization is realized and gives the heterocyclic oxazoles **2** via the elimination of one H_2O molecule from **E**. The proposed reaction mechanism is consistent with the observation that the presence of a Lewis or Brønsted acid is disadvantageous to the reaction, as Lewis or Brønsted acids will understandably reduce the nucleophilicity of the enamine or compete with PIFA as an additional electrophile during the first nucleophilic substitution step between the enamine and PIFA.

The β-trifluoroacetoxylated enamine intermediate **C** in the mechanistic pathway was not detected in the reaction process. In order to further probe into the reaction mechanism, we studied, under identical reaction conditions, the reaction of the enamine substrates with PIDA,[16] which bears the more nucleophilic acetate groups. To our pleasant surprise, the corresponding β-acetoxylated enamines **3a** and **3b** could both be separated as stable compounds, albeit in lower yields of 44% and 40% respectively. Further treatment of enamines **3a** and **3b** with AcOH under reflux in DCE gave respectively 2-methyloxazoles **4a** and **4b** in excellent yields via intramolecular condensation (Scheme 2). These results imply that the reaction of enamine compound **1** with PIFA also adopts the similar

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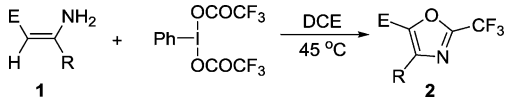
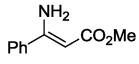
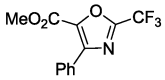
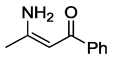
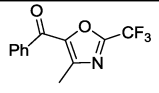
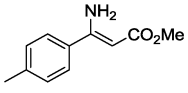
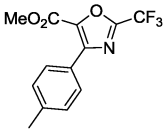
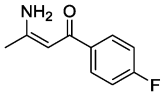
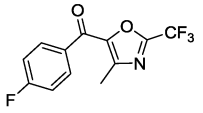
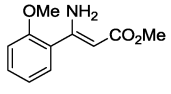
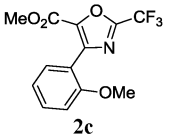
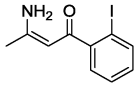
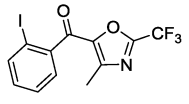
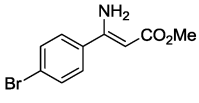
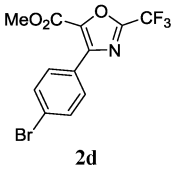
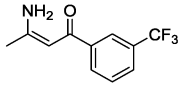
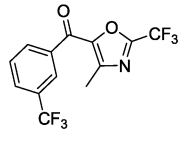
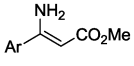
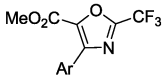
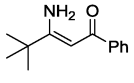
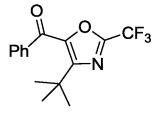
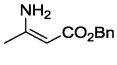
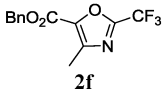
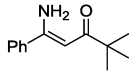
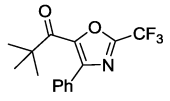
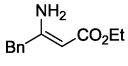
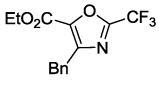
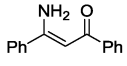
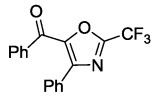
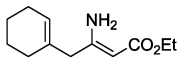
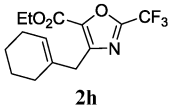
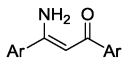
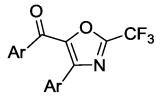
Table 2. Synthesis of 2-(Trifluoromethyl)oxazoles via $PhI(OCOCF_3)_2$-Mediated Trifluoroacetoxylation and Cyclization[a]



entry	enamine **1**	oxazole **2**	time (h)	yield[b] (%)	entry	enamine **1**	oxazole **2**	time (h)	yield[b] (%)
1	 **1a**	 **2a**	2	80	9	 **1i**	 **2i**	3	61
2	 **1b**	 **2b**	2	81	10	 **1j**	 **2j**	3	51
3	 **1c**	 **2c**	2	68	11	 **1k**	 **2k**	3	45
4	 **1d**	 **2d**	2	67	12	 **1l**	 **2l**	2	57
5[c]	 **1e**	 **2e**	2	64	13	 **1m**	 **2m**	1.5	90
6	 **1f**	 **2f**	2	58	14	 **1n**	 **2n**	1.5	72
7	 **1g**	 **2g**	2	48	15	 **1o**	 **2o**	2	42
8	 **1h**	 **2h**	3	60	16[c]	 **1p**	 **2p**	2	46

[a]Optimal conditions: **1** (1.0 equiv), PIFA (1.2 equiv) in DCE stirred at 45 °C. [b]Isolated yield. [c]Ar herein refers to 4-chlorophenyl.

processes of β-trifluoroacetoxylation and condensation, consistent with the proposed mechanism. The only difference is that the corresponding β-trifluoroacetoxylated enamine **C**, due to the presence of the electron-withdrawing trifluoromethyl group, is too reactive and undergoes simultaneous condensation, while the β-acetoxylated enamines **3** are stable enough to be separated, even though relatively harsh conditions were needed for the cyclization step.

CONCLUSION

In conclusion, we have discovered a new approach to the synthesis of a variety of 2-(trifluoromethyl)oxazoles from reactions of β-monosubstituted enamines with PIFA. The key features of this method are the incorporation of the trifluoromethyl moiety in PIFA into the final product and the formation of a heterocyclic oxazole ring. The presence of both the oxazole ring as well as the trifluoromethyl group renders this class of compounds important for their promising applications in pharmaceutical research.

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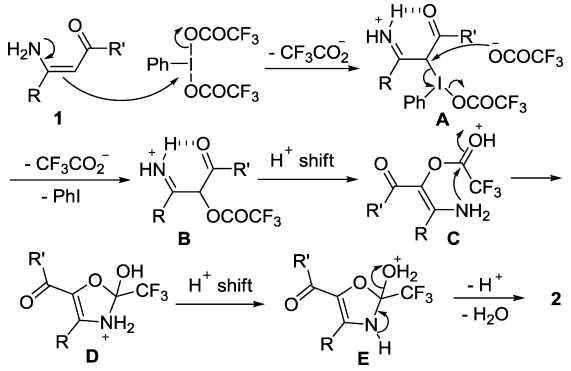
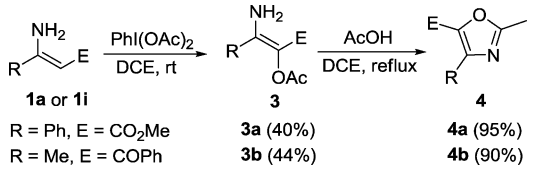
Scheme 1. Proposed Mechanistic Pathway



Scheme 2. Further Probe into the Reaction Mechanism



EXPERIMENTAL SECTION

General Information. All reactions were carried out at 45 °C without precaution of air and stirred magnetically. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a 400 MHz spectrometer at 25 °C. Chemical shift values (ppm) are calibrated according to the internal standard of TMS set as 0.00 ppm. The peak patterns are indicated as follows: br s, broad singlet; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and dd, doublet of doublets. The coupling constants J are reported in hertz (Hz). High resolution mass spectrometry (HRMS) was recorded on a Q-TOF microspectrometer. Melting points were determined with a national micromelting point apparatus without correction. Organic solutions were concentrated by rotary evaporation under vacuum. TLC plates were visualized by exposure to ultraviolet light. Toluene was dried over CaH_2 before use. EtOH was dried over CaO and then distilled before use. 1,2-Dichloroethane was dried over CaH_2 and distilled before use. Other reagents were purchased as reagent grade and used without further purification. All reactions were performed under nitrogen atmosphere in standard glassware, heated at 70 °C for 3 h before use. Flash column chromatography was performed over silica gel (100−200 mesh) and eluents were a mixture of EtOAc and petroleum ether (PE).

The β-ester group substituted enamines **1a−1f**,[4b,5a,17,18,20] **1g−1h**,[21] the β-carbonyl group substituted enamines **1i−1p**,[5a,19,20] and PIFA[22] were prepared according to the literature. PIFA was recrystallized and dried in vacuum before use.

General Procedure for the Synthesis of 2-(Trifluoromethyl)-oxazoles (2a−p). To a solution of enamine **1** (1.0 mmol) in dry DCE (50 mL) was added $PhI(OCOCF_3)_2$ (0.516 g, 1.2 mmol) in one portion at 45 °C. Then the reaction mixture was kept at the same temperature for 1.5−3 h. TLC was used to indicate the reaction process. When the reaction was completed, the solvent was evaporated, and the residue was passed through a silica gel column to give the desired product **2**.

Procedure for the Synthesis of Methyl 2-Acetoxy-3-amino-3-phenylacrylate (3a) and 3-Amino-1-oxo-1-phenylbut-2-en-2-yl Acetate (3b). To a solution of enamine **1** (2.0 mmol) in dry DCE (4 mL) was added $PhI(OAc)_2$ (0.837 g, 2.6 mmol) in one portion at room temperature. Then the reaction mixture was kept at the same temperature for 1 h. TLC was used to indicate the reaction process. When the reaction was completed, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with DCM (10 mL × 3). The organic layers were combined and dried over Na_2SO_4. The solvent was evaporated, and the residue was passed through a silica gel column to give the desired product.

Procedure for the Synthesis of Methyl 2-Methyl-4-phenyl-oxazole-5-carboxylate (4a) and (2,4-Dimethyloxazol-5-yl)-(phenyl)methanone (4b). To a solution of the β-acetoxylated enamines **3a** or **3b** (0.5 mmol) in dry DCE (10 mL) was added AcOH (2.5 mmol, 0.14 mL) at reflux. Then the reaction mixture was kept at the same temperature for 10 h. TLC was used to indicate the reaction process. When the reaction was completed, the solvent was evaporated, and the residue was passed through a silica gel column to give the corresponding desired product **4a** or **4b**.

Ethyl 3-Amino-4-cyclohexenylbut-2-enoate (1h). 1h was purified by silica gel chromatography (EtOAc/PE = 5/95). R_f = 0.5 (EtOAc/PE = 20/80). Yield 2.237 g, 46% as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (br s, 1H, NH_2), 5.60 (s, 1H, CH), 4.76 (br s, 1H, NH_2), 4.55 (s, 1H, CH), 4.11 (q, J = 7.0 Hz, 2H, CH_2) 2.75 (s, 2H, CH_2), 2.04−2.03 (m, 2H, CH_2), 1.90−1.89 (m, 2H, CH_2), 1.62−1.55 (m, 4H, CH_2), 1.26 (t, J = 7.0 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 161.1, 133.7, 126.2, 84.3, 58.5, 45.2, 27.4, 25.3, 22.7, 22.1, 14.6. HRMS (ESI) m/z calcd for $C_{12}H_{20}NO_2^+$ [M + H$^+$] 210.1489, found 210.1493.

3-Amino-1-(2-iodophenyl)but-2-en-1-one (1k). 1k was purified by silica gel chromatography (EtOAc/PE = 10/90). R_f = 0.3 (EtOAc/PE = 20/80). Overall yield (2 steps) 3.070 g, 38% as a yellow solid, mp 130−131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (br s, 1H, NH_2), 7.85 (d, J = 7.5 Hz, 1H, H_{arom}), 7.34−7.27 (m, 2H, H_{arom}), 7.04−7.00 (m, 1H, H_{arom}), 5.81 (br s, 1H, NH_2), 5.24 (s, 1H, CH), 2.00 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.4, 147.2, 144.9, 142.2, 140.1, 132.5, 128.8, 128.3, 91.8, 13.6. HRMS (ESI) m/z calcd for $C_{10}H_{11}INO^+$ [M + H$^+$] 287.9880, found 287.9883.

3-Amino-1-(3-(trifluoromethyl)phenyl)but-2-en-1-one (1l). 1l was purified by silica gel chromatography (EtOAc/PE = 10/90). R_f = 0.4 (EtOAc/PE = 40/60). Overall yield (2 steps) 1.151 g, 39% as a yellow solid, mp 130−131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (br s, 1H, NH_2), 8.13 (s, 1H, H_{arom}), 8.04 (d, J = 8.0 Hz, 1H, H_{arom}), 7.68 (d, J = 8.0 Hz, 1H, H_{arom}), 7.52 (t, J = 8.0 Hz, 1H, H_{arom}), 5.71 (s, 1H, CH), 5.71 (br s, 1H, NH_2), 2.07 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 164.4, 140.9, 130.6 (q, J_{F-C} = 32 Hz), 130.3, 128.8, 127.2 (q, J_{F-C} =3 Hz), 124.1 (q, J_{F-C} = 271 Hz), 124.0 (q, J_{F-C} = 3 Hz), 91.9, 22.7. HRMS (ESI) m/z calcd for $C_{11}H_{11}F_3NO^+$ [M + H$^+$] 230.0787, found 230.0788.

1-Amino-4,4-dimethyl-1-phenylpent-1-en-3-one (1n). 1n was purified by silica gel chromatography (EtOAc/PE = 10/90). R_f = 0.5 (EtOAc/PE = 30/70). Yield 2.678 g, 55% as a white solid, mp 62−63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (br s, 1H, NH_2), 7.55 (d, J = 8.0 Hz, 2H, H_{arom}), 7.43−7.41 (m, 3H, H_{arom}), 5.62 (s, 1H, CH), 5.40 (br s, 1H, NH_2), 1.20 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 161.7, 138.1, 130.4, 128.9, 126.3, 90.7, 42.3, 27.7. HRMS (ESI) m/z calcd for $C_{13}H_{18}NO^+$ [M + H$^+$] 204.1383, found 204.1386.

Methyl 4-Phenyl-2-(trifluoromethyl)oxazole-5-carboxylate (2a). 2a was purified by silica gel chromatography (EtOAc/PE = 1/99). R_f = 0.6 (EtOAc/PE = 5/95). Yield 0.217 g, 80% as a white solid, mp 47−48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11−8.08 (m, 2H, H_{arom}), 7.48−7.46 (m, 3H, H_{arom}), 3.97 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 150.7 (q, J_{F-C} = 45 Hz), 146.9, 137.8, 130.5, 129.4, 128.5, 128.4, 116.0 (q, J_{F-C} = 270 Hz), 52.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ −66.08 to −66.12 (m, 3F). HRMS (EI) m/z calcd for $C_{12}H_9F_3NO_3^+$ [M + H$^+$] 272.0529, found 272.0532.

Methyl 4-*p*-Tolyl-2-(trifluoromethyl)oxazole-5-carboxylate (2b). 2b was purified by silica gel chromatography (EtOAc/PE = 1/99). R_f = 0.5 (EtOAc/PE = 5/95). Yield 0.231 g, 81% as a light-yellow solid, mp 89−90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.0 Hz, 2H, H_{arom}), 7.27 (d, J = 8.0 Hz, 2H, H_{arom}), 3.95 (s, 3H, CH_3), 2.40 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 150.6 (q, J_{F-C} = 45 Hz), 147.0, 140.9, 137.5, 129.3, 129.1, 125.7, 116.1 (q, J_{F-C} = 270 Hz), 52.6, 21.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ −66.12 to −66.15 (m, 3F). HRMS (EI) m/z calcd for $C_{13}H_{11}F_3NO_3^+$ [M + H$^+$] 286.0686, found 286.0689.

Methyl 4-(2-Methoxyphenyl)-2-(trifluoromethyl)oxazole-5-carboxylate (2c). 2c was purified by silica gel chromatography (EtOAc/PE = 1/99). R_f = 0.4 (EtOAc/PE = 5/95). Yield 0.205 g, 68%

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as a light yellow solid, mp 48−49 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 7.5, 1.6 Hz, 1H, H_{arom}), 7.47−7.43 (m, 1H, H_{arom}), 7.06 (t, J = 7.5 Hz, 1H, H_{arom}), 7.00 (d, J = 7.5 Hz, 1H, H_{arom}), 3.87 (s, 3H, CH_3), 3.80 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.8, 157.2, 150.7 (q, J_{F-C} = 47 Hz), 142.7, 149.9, 131.6, 130.9, 120.5, 117.9 (q, J_{F-C} = 270 Hz), 114.8, 111.1, 55.5, 52.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ −65.85 to −65.87 (m, 3F). HRMS (EI) m/z calcd for $C_{13}H_{11}F_3NO_4^+$ [M + H$^+$] 302.0635, found 302.0636.

Methyl 4-(4-Bromophenyl)-2-(trifluoromethyl)oxazole-5-carboxylate (2d). **2d** was purified by silica gel chromatography (EtOAc/PE = 1/99). R_f = 0.6 (EtOAc/PE = 5/95). Yield 0.233 g, 67% as a ligh-yellow solid, mp 74−75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.5 Hz, 2H, H_{arom}), 7.60 (d, J = 8.5 Hz, 2H, H_{arom}), 3.98 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 150.7 (q, J_{F-C} = 45 Hz), 145.8, 137.9, 131.7, 130.9, 127.4, 125.2, 116.0 (q, J_{F-C} = 270 Hz), 52.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ −66.12 (m, 3F). HRMS (EI) m/z calcd for $C_{12}H_8{}^{79}BrF_3NO_3^+$ [M + H$^+$] 349.9634, found 349.9637.

Methyl 4-(4-Chlorophenyl)-2-(trifluoromethyl)oxazole-5-carboxylate (2e). **2e** was purified by silica gel chromatography (EtOAc/PE = 1/99). R_f = 0.5 (EtOAc/PE = 5/95). Yield 0.195 g, 64% as a light-yellow solid, mp 73−74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.5 Hz, 2H, H_{arom}), 7.43 (d, J = 8.5 Hz, 2H, H_{arom}), 3.98 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 150.7 (q, J_{F-C} = 45 Hz), 145.7, 137.9, 136.7, 130.7, 128.7, 126.9, 116.0 (q, J_{F-C} = 270 Hz), 52.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ −66.19 (s, 3F). HRMS (EI) m/z calcd for $C_{12}H_8{}^{35}ClF_3NO_3^+$ [M + H$^+$] 306.0139, found 306.0142.

Benzyl 4-Methyl-2-(trifluoromethyl)oxazole-5-carboxylate (2f). **2f** was purified by silica gel chromatography (EtOAc/PE = 1/99). R_f = 0.5 (EtOAc/PE = 5/95). Yield 0.166 g, 58% as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.42 (m, 2H, H_{arom}), 7.41−7.35 (m, 3H, H_{arom}), 5.39 (s, 2H, CH_2), 2.53 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 150.7 (q, J_{F-C} = 44 Hz), 146.2, 139.3, 134.8, 128.79, 128.76, 128.6, 116.0 (q, J_{F-C} = 270 Hz), 67.5, 13.2. ^{19}F NMR ($CDCl_3$, 377 MHz) δ −66.14 (m, 3F). HRMS (EI) m/z calcd for $C_{13}H_{11}F_3NO_3^+$ [M + H$^+$] 286.0686, found 286.0687.

Ethyl 4-Benzyl-2-(trifluoromethyl)oxazole-5-carboxylate (2g). **2g** was purified by silica gel chromatography (EtOAc/PE = 1/99). R_f = 0.5 (EtOAc/PE = 5/95). Yield 0.144 g, 48% as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.28 (m, 4H, H_{arom}), 7.25−7.21 (m, 1H, H_{arom}), 4.44 (q, J = 7.0 Hz, 2H, CH_2), 4.27 (s, 2H, CH_2), 1.42 (t, J = 7.0 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 150.9 (q, J_{F-C} = 44 Hz), 148.1, 139.2, 136.9, 128.9, 128.7, 127.0, 116.0 (q, J_{F-C} = 271 Hz), 62.1, 32.9, 14.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ −66.00 (s, 3F). HRMS (ESI) m/z calcd for $C_{14}H_{13}F_3NO_3^+$ [M + H$^+$] 300.0842, found 300.0845.

Ethyl 4-(Cyclohexenylmethyl)-2-(trifluoromethyl)oxazole-5-carboxylate (2h). **2h** was purified by silica gel chromatography (EtOAc/PE = 1/99). R_f = 0.6 (EtOAc/PE = 5/95). Yield 0.182 g, 60% as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (s, 1H, CH), 4.43 (q, J = 7.0 Hz, 2H, CH_2), 3.56 (s, 2H, CH_2), 2.01−2.00 (m, 2H, CH_2). 1.97−1.95 (m, 2H, CH_2), 1.65−1.59 (m, 2H, CH_2), 1.57−1.51 (m, 2H, CH_2), 1.42 (t, J = 7.0 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 150.7 (q, J_{F-C} = 44 Hz), 147.7, 139.7, 133.3, 124.5, 116.2 (q, J_{F-C} = 270 Hz), 61.9, 35.1, 28.3, 25.2, 22.7, 22.0, 14.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ −66.00 (m, 3F). HRMS (ESI) m/z calcd for $C_{14}H_{17}F_3NO_3^+$ [M + H$^+$] 304.1155, found 304.1158.

(4-Methyl-2-(trifluoromethyl)oxazol-5-yl)(phenyl)-methanone (2i). **2i** was purified by silica gel chromatography (EtOAc/PE = 1/99). R_f = 0.5 (EtOAc/PE = 5/95). Yield 0.156 g, 61% as a white solid, mp 41−42 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.0 Hz, 2H, H_{arom}), 7.66 (t, J = 7.0 Hz, 1H, H_{arom}), 7.55 (t, J = 7.0 Hz, 2H, H_{arom}), 2.62 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.2, 149.8 (q, J_{F-C} = 47 Hz), 147.1, 145.9, 136.0, 133.7, 129.4, 128.7, 116.3 (q, J_{F-C} = 270 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ −66.01 to −66.02 (m, 3F). HRMS (EI) m/z calcd for $C_{12}H_9F_3NO_2^+$ [M + H$^+$] 256.0580, found 256.0585.

(4-Fluorophenyl)(4-methyl-2-(trifluoromethyl)oxazol-5-yl)-methanone (2j). **2j** was purified by silica gel chromatography (EtOAc/PE = 1/99). R_f = 0.6 (EtOAc/PE = 5/95). Yield 0.139 g, 51% as a light-yellow solid, mp 42−43 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10−8.07 (m, 2H, H_{arom}), 7.25−7.20 (m, 2H, H_{arom}), 2.63 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 166.1 (d, J_{F-C} = 255 Hz), 149.8 (q, J_{F-C} = 44 Hz), 147.4, 145.7, 132.2, 132.1, 116.2 (q, J_{F-C} = 270 Hz), 116.0 (d, J_{F-C} = 220 Hz), 13.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ −66.01 to −66.07 (m, 3F), −103.36- −103.43 (m, 1F). HRMS (EI) m/z calcd for $C_{12}H_8F_4NO_2^+$ [M + H$^+$] 274.0486, found 274.0487.

(2-Iodophenyl)(4-methyl-2-(trifluoromethyl)oxazol-5-yl)-methanone (2k). **2k** was purified by silica gel chromatography (EtOAc/PE = 1/99). R_f = 0.5 (EtOAc/PE = 5/95). Yield 0.171 g, 45% as light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.5 Hz, 1H, H_{arom}), 7.50 (t, J = 7.5 Hz, 1H, H_{arom}), 7.39 (d, J = 7.5 Hz, 1H, H_{arom}), 7.25 (t, J = 7.5 Hz, 1H, H_{arom}), 2.43 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.4, 151.1, 150.6, 146.3 (q, J_{F-C} = 44 Hz), 147.2, 140.1, 132.5, 128.8, 128.4, 116.0 (q, J_{F-C} = 270 Hz), 91.8, 13.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ −66.03 (s, 3F). HRMS (EI) m/z calcd for $C_{12}H_8F_3INO_2^+$ [M + H$^+$] 381.9546, found 381.9547.

(4-Methyl-2-(trifluoromethyl)oxazol-5-yl)(3-(trifluoromethyl)phenyl)methanone (2l). **2l** was purified by silica gel chromatography (EtOAc/PE = 1/99). R_f = 0.6 (EtOAc/PE = 5/95). Yield 0.184 g, 57% as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H, H_{arom}), 8.22 (d, J = 8.0 Hz, 1H, H_{arom}), 7.91 (d, J = 8.0 Hz, 1H, H_{arom}), 7.71 (t, J = 8.0 Hz, 1H, H_{arom}), 2.65 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 150.1 (q, J_{F-C} = 46 Hz), 148.1, 145.4, 136.5, 132.4, 131.5 (q, J_{F-C} = 33 Hz), 130.0 (q, J_{F-C} = 4 Hz), 129.4, 126.3 (q, J_{F-C} = 4 Hz), 123.5 (q, J_{F-C} = 271 Hz), 116.1 (q, J_{F-C} = 271 Hz), 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ −63.09 (s, 3F), −66.14 (s, 3F). HRMS (EI) m/z calcd for $C_{13}H_8F_6NO_2^+$ [M + H$^+$] 324.0454, found 324.0454.

(4-*tert*-Butyl-2-(trifluoromethyl)oxazol-5-yl)(phenyl)-methanone (2m). **2m** was purified by silica gel chromatography (EtOAc/PE = 1/99). R_f = 0.7 (EtOAc/PE = 5/95). Yield 0.267 g, 90% as a white solid, mp 40−41 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.5 Hz, 2H, H_{arom}), 7.65 (t, J = 7.5 Hz, 1H, H_{arom}), 7.53 (t, J = 7.5 Hz, 2H, H_{arom}), 1.43 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8, 156.4, 148.4 (q, J_{F-C} = 44 Hz), 144.5, 136.7, 133.8, 129.6, 128.7, 116.3 (q, J_{F-C} = 269 Hz), 33.2, 28.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ −65.73 (s, 3F). HRMS (ESI) m/z calcd for $C_{15}H_{15}F_3NO_2^+$ [M + H$^+$] 298.1049, found 298.1044.

2,2-Dimethyl-1-(4-phenyl-2-(trifluoromethyl)oxazol-5-yl)-propan-1-one (2n). **2n** was purified by silica gel chromatography (EtOAc/PE = 1/99). R_f = 0.8 (EtOAc/PE = 5/95). Yield 0.214 g, 72% as a white solid, mp 29−30 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−8.03 (m, 2H, H_{arom}), 7.46 (t, J = 4.0 Hz, 3H, H_{arom}), 1.38 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 149.1 (q, J_{F-C} = 47 Hz), 146.8, 144.1, 130.5, 129.5, 129.1, 128.3, 116.2 (q, J_{F-C} = 270 Hz), 44.6, 26.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ −66.06 (m, 3F). HRMS (EI) m/z calcd for $C_{15}H_{15}F_3NO_2^+$ [M + H$^+$] 298.1048, found 298.1047.

Phenyl(4-phenyl-2-(trifluoromethyl)oxazol-5-yl)methanone (2o). **2o** was purified by silica gel chromatography (EtOAc/PE = 1/99). R_f = 0.5 (EtOAc/PE = 5/95). Yield 0.133 g, 42% as a white solid, mp 70−71 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.97 (m, 2H, H_{arom}), 7.90 (d, J = 7.5 Hz, 2H, H_{arom}), 7.62 (t, J = 7.5 Hz, 1H, H_{arom}), 7.48 (t, J = 7.5 Hz, 2H, H_{arom}), 7.43−7.41 (m, 3H, H_{arom}). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.8, 150.3 (q, J_{F-C} = 47 Hz), 146.6, 144.5, 136.2, 133.9, 130.5, 129.7, 129.2, 128.9, 128.7, 128.5, 116.3 (q, J_{F-C} = 270 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ −65.87 (m, 3F). HRMS (ESI) m/z calcd for $C_{17}H_{11}F_3NO_2^+$ [M + H$^+$] 318.0736, found 318.0740.

(4-Chlorophenyl)(4-(4-chlorophenyl)-2-(trifluoromethyl)-oxazol-5-yl)methanone (2p). **2p** was purified by silica gel chromatography (EtOAc/PE = 1/99). R_f = 0.6 (EtOAc/PE = 5/95). Yield 0.178 g, 46% as a white solid, mp 86−87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.5 Hz, 2H, H_{arom}), 7.88 (d, J = 8.5 Hz, 2H, H_{arom}), 7.50 (t, J = 8.5 Hz, 2H, H_{arom}), 7.42 (d, J = 8.5 Hz, 2H, H_{arom}). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2, 150.2 (q, J_{F-C} = 44 Hz), 146.1, 144.3, 140.7, 137.0, 134.4, 131.0, 130.6, 129.2, 128.8, 127.2, 116.1 (q, J_{F-C} = 271 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ −65.93 (s, 3F). HRMS (EI) m/z calcd for $C_{17}H_9{}^{35}Cl_2F_3NO_2^+$ [M + H$^+$] 385.9957, found 385.9961.

Methyl 2-Acetoxy-3-amino-3-phenylacrylate (3a). **3a** was purified by silica gel chromatography (TEA/EtOAc/PE = 1/10/90). R_f = 0.3 (EtOAc/PE = 20/80). Yield 0.226 g, 40% as a white solid, mp 69−71 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.40 (m, 5H, H_{arom}), 3.75 (s, 3H, CH_3), 1.92 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 166.1, 152.9, 135.0, 129.7, 128.5, 127.5, 112.1, 51.2, 20.3. HRMS (ESI) m/z calcd for $C_{12}H_{14}NO_4^+$ [M + H$^+$] 236.0813, found 236.0815.

3-Amino-1-oxo-1-phenylbut-2-en-2-yl acetate (3b). **3b** was purified by silica gel chromatography (TEA/EtOAc/PE = 1/15/85). R_f = 0.2 (EtOAc/PE = 30/70). Yield 0.193 g, 44% as a white solid, mp 110−112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.59 (m, 2H, H_{arom}), 7.39−7.34 (m, 3H, H_{arom}), 1.96 (s, 3H, CH_3), 1.95 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ188.54, 170.56, 155.78, 139.50, 130.07, 127.84, 127.37, 123.21, 20.52, 18.39. HRMS (ESI) m/z calcd for $C_{12}H_{13}NO_3Na^+$ [M +Na$^+$] 242.0788, found 242.0782.

Methyl 2-Methyl-4-phenyloxazole-5-carboxylate (4a). **4a** was purified by silica gel chromatography (PE). R_f = 0.2 (EtOAc/PE = 5/95). Yield 0.103 g, 95% as a white solid, mp 53−54 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05−8.03 (m, 2H, H_{arom}), 7.46−7.42 (m, 3H, H_{arom}), 3.91 (s, 3H, CH_3), 2.57 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.99, 158.88, 147.19, 136.17, 130.17, 129.62, 129.20, 128.14, 52.11, 14.17. HRMS (ESI) m/z calcd for $C_{12}H_{12}NO_3^+$ [M + H$^+$] 218.0812, found 218.0810.

(2,4-Dimethyloxazol-5-yl)(phenyl)methanone (4b). **4b** was purified by silica gel chromatography (PE). R_f = 0.5 (EtOAc/PE = 30/70). Yield 0.090 g, 90% as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.5 Hz, 2H, H_{arom}), 7.59 (t, J = 7.5 Hz, 1H, H_{arom}), 7.49 (t, J = 7.5 Hz, 2 H, H_{arom}), 2.55 (s, 3H, CH_3), 2.49 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.64, 162.74, 147.80, 145.13, 137.24, 132.72, 129.20, 128.39, 14.28, 14.07. HRMS (ESI) m/z calcd for $C_{12}H_{12}NO_2^+$ [M + H$^+$] 202.0863, found 202.0861.

■ ASSOCIATED CONTENT

Supporting Information

Spectral data for all new compounds; X-ray structural data of **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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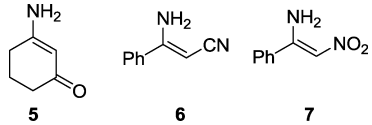

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