Synthesis D. Li et al. Feature

Oxidation of 4-Aryl-1,1,1-trifluorobut-2-en-2-yl Trifluoromethanesulfonates by 4-Picoline-*N*-Oxide: A Novel Approach to β-Trifluoromethyl-α,β-enones

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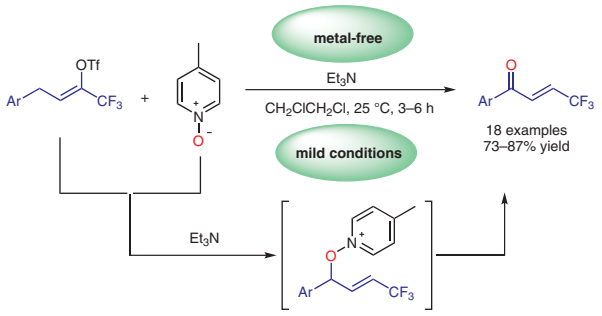

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Abstract An efficient approach to β-trifluoromethyl-α,β-enones via oxidation of 4-aryl-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonates is described. The reaction proceeds smoothly under mild and metal-free conditions and tolerates a wide range of functional groups. Various β-trifluoromethyl-α,β-enones were obtained in moderate to good yields.

Key words fluorine, enones, oxidation, β-trifluoromethyl-α,β-enones, 4-aryl-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonates, pyridine *N*-oxides

Compounds containing a trifluoromethyl group have received great attention because of their application in materials, pharmaceuticals and agrochemicals.[1] β-Trifluoromethyl-α,β-enones, as an important series of trifluoromethyl building blocks, can be used in a variety of reactions, such as Michael additions,[2] Diels–Alder cycloadditions,[3] Friedel–Crafts reactions[4] and some other novel reactions.[5] So, it is not surprising that the synthesis of β-trifluoromethyl-α,β-enones has been attracting more and more attention. Trifluoromethylated propargylic alcohols have been widely used in the synthesis of β-trifluoromethyl-α,β-enones (Scheme 1, a).[6] However, the high price of trifluoromethylated propargylic alcohols hinders their application. Some other synthetic methods, such as the gold-catalyzed rearrangement of trifluoromethyl-substituted propargylic carboxylates (Scheme 1, b)[3a] and ZnI_2-catalyzed deamination–elimination of 1,1-bis(dimethylamino)-2,2,2-trifluoroethane with silyl enol ethers (Scheme 1, c),[7] have been reported but metal catalysts are essential. Because of the strict restrictions on the residual amount of heavy metals in the pharmaceutical industry, metal-free procedures are more favorable. Therefore, convenient synthetic approaches to β-trifluoromethyl-α,β-enones are still highly desired.

In recent years, our group has focused on the synthesis of different molecules containing a trifluoromethyl group. Based on the useful trifluorinated building blocks, α-(trifluoromethyl)alkenyl trifluoromethanesulfonates, a variety of methods for the synthesis of trifluoromethyl derivatives such as alkynes, diarylethylenes, benzofurans, 2*H*-chromenes, enynes, allyl azides and β-trifluoromethyl ketones have been developed.[8] Especially, the double-bond migration/hydrolysis/isomerization of 4-aryl-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonates has been documented (Scheme 1, d).[8e] Thus, we proposed that this method in combination with an oxidant may result in β-trifluoromethyl-α,β-enone formation. Herein, we report our progress on the synthesis of β-trifluoromethyl-α,β-enones via oxidation of 4-aryl-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonates under metal-free conditions (Scheme 1, e).

Initially, (*Z*)-1,1,1-trifluoro-4-phenylbut-2-en-2-yl trifluoromethanesulfonate (**1a**) was selected as the representative substrate for optimization of the oxidant (Table 1). Due to its oxidizing capacity, pyridine *N*-oxide[9] was first examined in the presence of Et_3N in CH_2Cl_2 at 25 °C. The desired product **2a** was formed in 84% yield with (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (**2a'**) as byproduct (**2a**/**2a'** = 95:5, Table 1, entry 1). ^1H NMR analysis of **2a** showed that the coupling constant of the two hydrogens on the C=C double bond is 15.5 Hz, which indicates that it is the *E*-isomer. Then, different oxidants, such as methyl- (Table 1, entries 3, 5 and 7), chloro- (Table 1, entries 2 and 6) and nitro-substituted (Table 1, entry 4) pyridine *N*-oxides, were employed. 4-Picoline *N*-oxide proved to be the best oxidant for this reaction (Table 1, entry 5, 81% yield,

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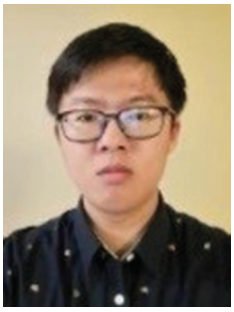
2a/**2a′** = 100:0). When the amount of 4-picoline *N*-oxide was decreased to 1.0 equivalent, the yield of **2a** decreased to 57% (Table 1, entry 8).

Then, the effect of base was investigated (Table 2). Many bases, including Et_3N, pyrrolidine, DBU and DMAP, can promote this reaction smoothly. However, some of them gave low selectivity (Table 2, entries 3–5, 10 and 11). In particular, 4,4,4-trifluoro-1-phenylbutan-1-one was formed as a byproduct when DBU was used;[8e] (*E*)-1-(1,1,1-trifluoro-4-phenylbut-3-en-2-yl)pyrrolidine and (*E*)-1-(4,4,4-trifluoro-1-phenylbut-2-en-1-yl)pyrrolidine were formed when pyrrolidine was used. Finally, Et_3N still proved to be the best base for this reaction (Table 2, entry 1). Reducing the amount of Et_3N to 20 mol% resulted in much lower yield of **2a** (Table 2, entry 12), and the reaction cannot occur without a base (Table 2, entry 13).

Biographical Sketches

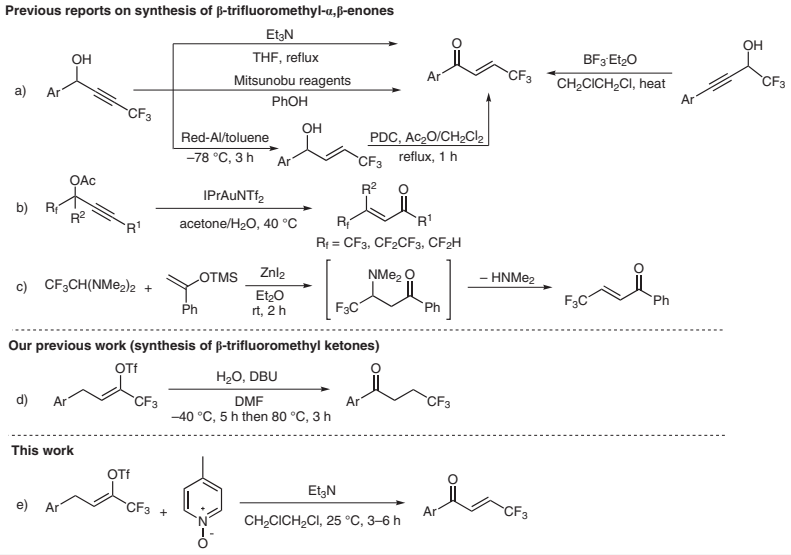
Dong Li received his B.S. degree in Chemical Engineering and Technology from Liaocheng University (China). After that, he entered Yunnan University to undertake his M.S. degree in Pharmaceutical Engineering under the supervision of Prof. Jun Lin, from 2013 to 2016. Currently, he is working towards his doctor's degree at Dalian University of Technology under the supervision of Prof. Yuhan Zhou.



Shujun Lv participated in an undergraduate research program from January to June 2019 under the supervision of Prof. Yuhan Zhou. He has now obtained his B.S. degree in Pharmaceutical Engineering from Dalian University of Technology.

Jingping Qu was born in Dalian (China) in 1960. In 1983, he received his bachelor's degree from Dalian University of Technology (China) in Basic Organic Chemical Engineering. He received his Ph.D., under the direction of Prof. Masanoubu Hidai, from The University of Tokyo (Japan) in 1996. After working at Mitsubishi Chemical Corporation (Japan) for seven years, he returned to Dalian University of Technology as a professor in 2004. Currently, he is the president of East China University of Science and Technology (China). His research interests are organometallics chemistry and organic synthesis.

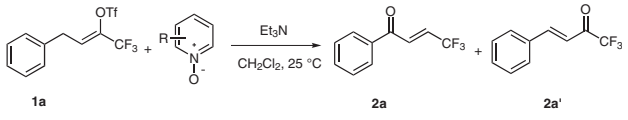
Yuhan Zhou was born in Fuling (China) in 1974. In 2003, he received his Ph.D. in Applied Chemistry from Dalian University of Technology (China) under the direction of Prof. Lvbai Cheng and Prof. Weirong Miao. Then, he became a teacher at that university. From February 2009 to January 2010, he worked with Prof. Laurent Micouin at Paris Descartes University (France) as a postdoctoral fellow. Currently, he is a professor in the School of Chemical Engineering, Dalian University of Technology. His research interest is organic synthesis, especially the synthesis of fluorine-containing and heterocyclic compounds.



Scheme 1 Preparation of β-trifluoromethyl-α,β-enones

Moreover, a series of solvents was screened (Table 3, entries 1–7). Upon switching the solvent to DMF or DMSO, as well as solvent free, the reaction became complicated with some compounds that could not be characterized (Table 3, entries 1, 2 and 5). THF, toluene, chloroform and 1,2-dichloroethane were next examined (Table 3, entries 3, 4, 6 and 7): 1,2-dichloroethane provided excellent reactivity with 84% yield of **2a** and 100:0 selectivity between **2a**/**2a′** (Table 3, entry 7). The yield of **2a** decreased to 80% when the reaction temperature was reduced to 15 °C (Table 3, entry 8).

Table 1 Optimization of the Reaction Conditions: Oxidant[a]

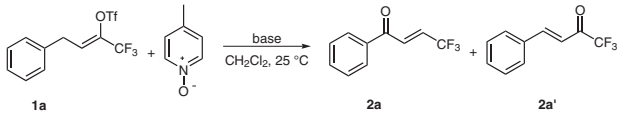


Entry	R	Conv. (%)[b]	**2a**/**2a′**[c]	Yield (%) **2a**[b]
1	H	98	95:5	84
2	2-Cl	88	95:5	65
3	2-Me	99	98:2	82
4	4-NO_2	80	97:3	55
5	4-Me	98	100:0	81
6	2,6-Cl_2	73	80:20	43
7	2,6-Me_2	95	100:0	71
8[d]	4-Me	70	100:0	57

[a] Reaction conditions: **1a** (167 mg, 0.5 mmol), oxidant (1.0 mmol), Et_3N (51 mg, 0.5 mmol), CH_2Cl_2 (3 mL), argon atmosphere, stirring, 25 °C, 3 h.
[b] Determined by ^1H NMR with dimethyl terephthalate as an internal standard.
[c] Determined by ^1H NMR.
[d] 4-Picoline *N*-oxide (0.5 mmol) was used.

With optimal conditions identified (Table 3, entry 7), the scope of this reaction was next explored (Scheme 2). Substrates **1** containing a phenyl group or an aryl group

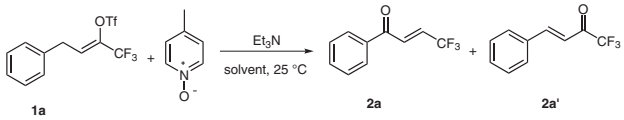
Table 2 Optimization of the Reaction Conditions: Base[a]



Entry	Base	Conv. (%)[b]	**2a**/**2a′**[c]	Yield (%) **2a**[b]
1	Et_3N	98	100:0	81
2	pyridine	0	–	–
3	pyrrolidine	62	100:0	30
4	DBU	95	100:0	29
5	DMAP	95	99:1	47
6	KF	0	–	–
7	$(n\text{-Bu})_3N$	95	100:0	77
8	$Me_2NCH_2CH_2NMe_2$	98	99:1	78
9	$PhNMe_2$	0	–	–
10	$(i\text{-Pr})_2NEt$	63	100:0	26
11	$BnNMe_2$	40	93:7	19
12[d]	Et_3N	17	100:0	10
13	–	0	–	–

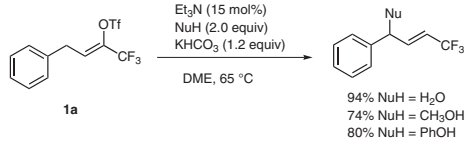
[a] Reaction conditions: **1a** (167 mg, 0.5 mmol), 4-picoline *N*-oxide (109 mg, 1.0 mmol), base (0.5 mmol), CH_2Cl_2 (3 mL), argon atmosphere, stirring, 25 °C, 3 h.
[b] Determined by ^1H NMR with dimethyl terephthalate as an internal standard.
[c] Determined by ^1H NMR.
[d] Et_3N (0.1 mmol, 0.2 equiv) was used.

Table 3 Optimization of the Reaction Conditions: Solvent[a]



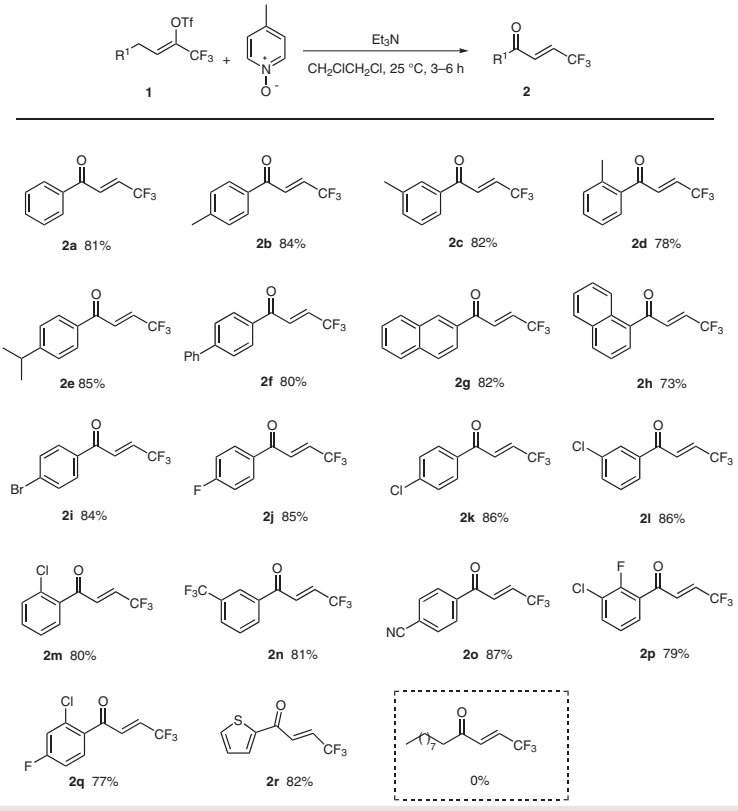
Entry	Solvent	Conv. (%)[b]	**2a**/**2a'**[c]	Yield (%) **2a**[b]
1	DMF	99	76:24	32
2	DMSO	100	67:33	48
3	THF	100	100:0	76
4	toluene	72	95:5	50
5	–	95	85:15	47
6	$CHCl_3$	98	100:0	78
7	CH_2ClCH_2Cl	100	100:0	84
8[d]	CH_2ClCH_2Cl	98	100:0	80

[a] Reaction conditions: **1a** (167 mg, 0.5 mmol), 4-picoline *N*-oxide (109 mg, 1.0 mmol), Et_3N (51 mg, 0.5 mmol), solvent (3 mL), argon atmosphere, stirring, 25 °C, 3 h.
[b] Determined by ^1H NMR with dimethyl terephthalate as an internal standard.
[c] Determined by ^1H NMR.
[d] Performed at 15 °C.

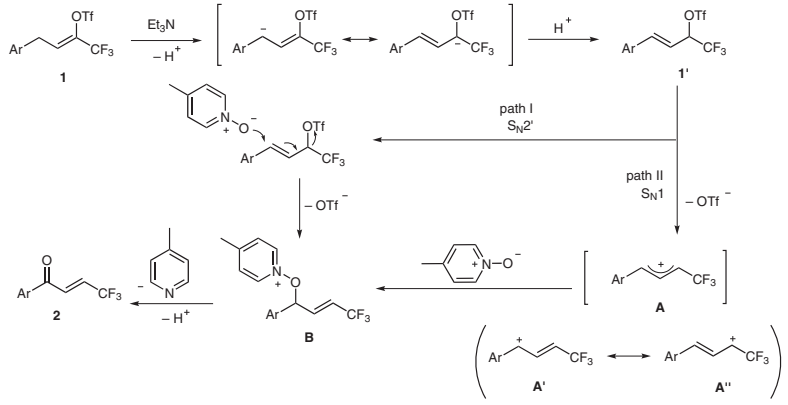


Scheme 3 Our previous report on the substitution of **1a**[8c]

substituted by an electron-withdrawing group or an electron-donating group can be efficiently transformed into the corresponding products in moderate to good yields. Substrates with electron-donating substituents, including methyl and isopropyl, furnished the desired products in 78–85% yield (**2b**–**2e**). Substrates with electron-withdrawing substituents, including chloro, fluoro, trifluoromethyl, bromo, phenyl and cyano, furnished the desired products in 80–87% yield (**2f**, **2i**–**2o**). Thus, there is no obvious substituent effect. The 2′-methyl substrate gave slightly lower yield than the 3′-methyl and 4′-methyl ones (**2b**–**2d**) and the 2′-chloro substrate also gave slightly lower yield than the 3′-chloro and 4′-chloro ones (**2k**–**2m**), exhibiting a slight steric effect. In addition, naphthyl derivatives gave moderate yields (**2g** and **2h**), as did multisubstituted substrates (**2p** and **2q**). A thienyl-substituted substrate, as a heteroaryl example, also gave a good yield (**2r**). (*Z*)-1,1,1-Trifluoro-



Scheme 2 Preparation of β-trifluoromethyl-α,β-enones. *Reagents and conditions*: **1** (1.0 mmol), 4-picoline *N*-oxide (218 mg, 2.0 mmol), Et_3N (101 mg, 1.0 mmol), 1,2-dichloroethane (4 mL), argon atmosphere, stirring, 25 °C, 3–6 h. Yield of the isolated product.



Scheme 4 Possible mechanism for the formation of product **2**

tridec-2-en-2-yl trifluoromethanesulfonate was also examined, as the representative example of an alkyl-substituted substrate at the 4-position, but the reaction did not occur. This is attributed to the relatively lower acidity of 4-H in that molecule.

Based on the oxidizing capacity of pyridine *N*-oxides,[9] reports on base-promoted isomerization[10] and our previous reports on the substitution of 4-aryl-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonates (Scheme 3),[8c] a plausible mechanism for the synthesis of β-trifluoromethyl-α,β-enones via oxidation of 4-aryl-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonates is shown in Scheme 4. First, double-bond isomerization in the presence of Et_3N generates intermediate **1′**. Then, intermediate **1′** could be transformed into **B** by two possible pathways. The first way is S_N2' substitution, with the OTf group substituted by 4-picoline *N*-oxide directly (path I). In another way, (trifluoromethyl)allyl cation **A**, which has two resonance forms (**A′** and **A″**), is formed after the OTf group has left. Then, the allyl cation is captured by 4-picoline *N*-oxide, through resonance form **A′**, to form intermediate **B** (path II), because of the electron-withdrawing character of the trifluoromethyl group.[11] Finally, 4-methylpyridine and proton leave from intermediate **B**, resulting in the formation of desired product **2**.

In conclusion, an efficient method for the synthesis of β-trifluoromethyl-α,β-enones has been developed. Oxidized by 4-picoline *N*-oxide, 4-aryl-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonates are transformed into β-trifluoromethyl-α,β-enones efficiently, in moderate to good yields. Both electron-donating groups and electron-withdrawing groups, such as chloro, fluoro, trifluoromethyl, methyl, phenyl and isopropyl, are well tolerated.

Unless otherwise noted, all reactions were performed under an argon atmosphere in glassware with magnetic stirring. NaH (60% in mineral oil) was washed with anhydrous *n*-hexane to remove mineral oil prior to use. Other reagents and solvents were purchased from commercial sources and used without further purification. Column chromatography was performed on silica gel (200–300 mesh) using petroleum ether/EtOAc as eluent. All ^1H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F NMR (377 MHz or 470 MHz) were recorded on Bruker AVANCE II-400 or Bruker AVANCE III-500 spectrometers with chemical shifts reported as ppm (in $CDCl_3$ with TMS as internal standard). Melting points were recorded on a Novel X-4 spectrometer. IR spectra were recorded on a Thermo Fisher (6700) spectrophotometer. HRMS (ESI) were recorded on a Thermo LTQ Orbitrap XL spectrometer. HRMS (EI) were recorded on a Micromass GCT spectrometer.

4-Aryl-1,1,1-trifluorobut-2-en-2-yl Trifluoromethanesulfonates 1; General Procedure

4-Aryl-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonates **1** were prepared according to our previous work.[8a] To a suspension of NaH (600 mg, 25.0 mmol) in MTBE (30 mL) was added ethyl trifluoroacetate (3.0 mL, 25.0 mmol) at room temperature under an argon atmosphere. After about 1 min of stirring, enolizable ketone (12.5 mmol) was added, and the mixture was refluxed for 6–12 h. After the reaction was complete (monitored by TLC or GC analyses), the reaction solution was cooled to 0 °C. Tf_2O (3.56 mL, 25.0 mmol) was added slowly into the reaction mixture. After the reaction was complete (monitored by TLC or GC analyses), the reaction was quenched with ice–water. The aqueous layer was separated and extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel to afford product **1**. **1c**, **1d** and **1g** are new compounds. **1a**,[8a] **1b**,[8a] **1e**,[8c] **1f**,[8c] **1h**,[8b] **1i**,[8c] **1j**,[8b] **1k**,[8b] **1l**,[8a] **1m**,[8b] **1n**,[8c] **1o**,[8b] **1p**,[8c] **1q**[8c] and **1r**[8e] have been reported in our previous work.

(*Z*)-1,1,1-Trifluoro-4-(*m*-tolyl)but-2-en-2-yl Trifluoromethanesulfonate (1c)

Yield: 3.52 g (81%); light yellow liquid.

IR (KBr): 1695, 1609, 1427, 1329, 1203, 1135, 997, 755, 607 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 7.9 Hz, 1 H), 7.12 (d, *J* = 7.6 Hz, 1 H), 7.03–7.01 (m, 2 H), 6.51 (t, *J* = 7.5 Hz, 1 H), 3.66 (d, *J* = 7.5 Hz, 2 H), 2.37 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.9, 135.6, 133.8 (q, *J* = 39.4 Hz), 130.1 (q, *J* = 3.0 Hz), 129.3, 129.0, 128.2, 125.5, 118.7 (q, *J* = 280.8 Hz), 118.4 (q, *J* = 314.1 Hz), 32.1, 21.3.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –69.72 to –69.89 (m, 3 F), –72.79 to –72.82 (m, 3 F).

HRMS (EI): *m*/*z* calcd for $C_{12}H_{10}F_6O_3S$ [M$^{+\cdot}$]: 348.0255; found: 348.0245.

(*Z*)-1,1,1-Trifluoro-4-(*o*-tolyl)but-2-en-2-yl Trifluoromethanesulfonate (1d)

Yield: 3.61 g (83%); light yellow liquid.

IR (KBr): 1691, 1428, 1330, 1202, 1135, 998, 902, 748, 608 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.19 (m, 3 H), 7.16 (d, *J* = 4.7 Hz, 1 H), 6.45 (t, *J* = 7.4 Hz, 1 H), 3.69 (d, *J* = 7.4 Hz, 2 H), 2.33 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 136.3, 134.1, 134.0 (q, *J* = 39.4 Hz), 130.8, 129.6 (q, *J* = 3.0 Hz), 129.0, 127.7, 126.7, 118.7 (q, *J* = 283.8 Hz), 118.4 (q, *J* = 312.1 Hz), 30.0, 19.3.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –69.90 (s, 3 F), –72.82 to –72.95 (m, 3 F).

HRMS (EI): *m*/*z* calcd for $C_{12}H_{10}F_6O_3S$ [M$^{+\cdot}$]: 348.0255; found: 348.0244.

(*Z*)-1,1,1-Trifluoro-4-(naphthalen-2-yl)but-2-en-2-yl Trifluoromethanesulfonate (1g)

Yield: 4.08 g (85%); light yellow solid; mp 50–51 °C.

IR (KBr): 1691, 1425, 1328, 1223, 1152, 1081, 1001, 962, 825, 746, 608 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.80 (m, 3 H), 7.67 (s, 1 H), 7.56–7.47 (m, 2 H), 7.34–7.31 (m, 1 H), 6.64–6.56 (m, 1 H), 3.86 (d, *J* = 7.5 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 134.1 (q, *J* = 39.4 Hz), 133.6, 133.0, 132.6, 129.9 (q, *J* = 3.0 Hz), 129.0, 127.8, 127.7, 127.2, 126.6, 126.4, 126.2, 118.7 (q, *J* = 283.8 Hz), 118.5 (q, *J* = 312.1 Hz), 32.3.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –69.80 to –69.84 (m, 3 F), –72.72 to –72.76 (m, 3 F).

HRMS (EI): *m*/*z* calcd for $C_{15}H_{10}F_6O_3S$ [M$^{+\cdot}$]: 384.0255; found: 384.0244.

β-Trifluoromethyl-α,β-enones 2; General Procedure

To a solution of (*Z*)-(trifluoromethyl)alkenyl triflate **1** (1.0 mmol) in 1,2-dichloroethane (4 mL) was added 4-picoline *N*-oxide (218 mg, 2.0 mmol) and Et_3N (101 mg, 1.0 mmol) at room temperature under an argon atmosphere. Then, the mixture was stirred at 25 °C for 3–6 h. After the reaction was complete (monitored by TLC), solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford product **2**. Compounds **2e**, **2l**, **2m**, **2p** and **2q** are new.

(*E*)-4,4,4-Trifluoro-1-phenylbut-2-en-1-one (2a)[3a]

Yield: 162 mg (81%); light yellow liquid.

IR (KBr): 1688, 1650, 1449, 1307, 1136, 967, 695, 625 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 4.4 Hz, 2 H), 7.64 (t, *J* = 7.4 Hz, 1 H), 7.57–7.49 (m, 3 H), 6.82 (dq, *J* = 15.5, 6.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 188.0, 136.2, 134.1, 131.1 (q, *J* = 6.1 Hz), 130.3 (q, *J* = 35.4 Hz), 129.0, 128.8, 122.6 (q, *J* = 271.7 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –65.13 (s, 3 F).

HRMS (ESI): *m*/*z* calcd for $C_{10}H_8F_3O$ [M + H]$^+$: 201.0527; found: 201.0522.

(*E*)-4,4,4-Trifluoro-1-(*p*-tolyl)but-2-en-1-one (2b)[6d]

Yield: 180 mg (84%); light yellow liquid.

IR (KBr): 1685, 1642, 1309, 1135, 974, 815, 726, 654 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.2 Hz, 2 H), 7.55–7.51 (m, 1 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 6.80 (dq, *J* = 15.4, 6.7 Hz, 1 H), 2.44 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 187.5, 145.3, 131.1 (q, *J* = 6.1 Hz), 130.7, 129.9 (q, *J* = 35.5 Hz), 129.7, 129.0, 122.6 (q, *J* = 270.7 Hz), 21.8.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –65.07 (s, 3 F).

HRMS (ESI): *m*/*z* calcd for $C_{11}H_{10}F_3O$ [M + H]$^+$: 215.0684; found: 215.0679.

(*E*)-4,4,4-Trifluoro-1-(*m*-tolyl)but-2-en-1-one (2c)[5a]

Yield: 175 mg (82%); light yellow liquid.

IR (KBr): 1688, 1646, 1307, 1134, 971, 790, 713, 627 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.75 (m, 2 H), 7.55–7.50 (m, 1 H), 7.46–7.39 (m, 2 H), 6.81 (dq, *J* = 15.5, 6.7 Hz, 1 H), 2.44 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 188.1, 139.0, 136.2, 134.9, 131.2 (q, *J* = 5.1 Hz), 130.1 (q, *J* = 34.3 Hz), 129.2, 128.8, 126.1, 122.6 (q, *J* = 270.7 Hz), 21.3.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –65.09 (s, 3 F).

HRMS (EI): *m*/*z* calcd for $C_{11}H_9F_3O$ [M$^{+\cdot}$]: 214.0605; found: 214.0602.

(*E*)-4,4,4-Trifluoro-1-(*o*-tolyl)but-2-en-1-one (2d)[4c]

Yield: 167 mg (78%); light yellow liquid.

IR (KBr): 1689, 1646, 1304, 1134, 970, 769, 729, 628 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (dd, *J* = 6.8, 2.2 Hz, 1 H), 7.48–7.42 (m, 1 H), 7.33–7.29 (m, 2 H), 7.28–7.21 (m, 1 H), 6.63 (dq, *J* = 15.8, 6.6 Hz, 1 H), 2.50 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.0, 138.9, 136.3, 134.5 (q, *J* = 5.1 Hz), 132.2, 132.1, 130.2 (q, *J* = 35.3 Hz), 129.2, 125.8, 122.5 (q, *J* = 271.7 Hz), 20.8.

^{19}F NMR (377 MHz, $CDCl_3$): δ = –65.06 to –65.11 (m, 3 F).

HRMS (EI): *m*/*z* calcd for $C_{11}H_9F_3O$ [M$^{+\cdot}$]: 214.0605; found: 214.0596.

(*E*)-4,4,4-Trifluoro-1-(4-isopropylphenyl)but-2-en-1-one (2e)

Yield: 206 mg (85%); light yellow liquid.

IR (KBr): 1686, 1649, 1606, 1307, 1135, 967, 828, 650 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.3 Hz, 2 H), 7.57–7.50 (m, 1 H), 7.38 (d, *J* = 8.3 Hz, 2 H), 6.81 (dq, *J* = 15.5, 6.7 Hz, 1 H), 3.07–2.93 (m, 1 H), 1.29 (d, *J* = 6.9 Hz, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 187.5, 156.0, 134.1, 131.2 (q, *J* = 5.1 Hz), 129.9 (q, *J* = 35.4 Hz), 129.1, 127.1, 122.6 (q, *J* = 271.7 Hz), 34.4, 23.6.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –65.06 (s, 3 F).

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{14}F_3O$ [M + H]$^+$: 243.0977; found: 243.0998.

(*E*)-1-([1,1′-Biphenyl]-4-yl)-4,4,4-trifluorobut-2-en-1-one (2f)[3a]

Yield: 221 mg (80%); white solid; mp 63–64 °C.

IR (KBr): 1683, 1640, 1603, 1314, 1142, 970, 836, 770, 733, 691, 623 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.4 Hz, 2 H), 7.77 (d, *J* = 8.4 Hz, 2 H), 7.70–7.65 (m, 2 H), 7.61–7.57 (m, 1 H), 7.54–7.50 (m, 2 H), 7.49–7.42 (m, 1 H), 6.88 (dq, *J* = 15.5, 6.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 187.4, 146.9, 139.5, 134.9, 131.0 (q, *J* = 6.1 Hz), 130.2 (q, *J* = 35.4 Hz), 129.5, 129.1, 128.6, 127.6, 127.3, 122.6 (q, *J* = 271.7 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –65.02 (s, 3 F).

HRMS (EI): *m*/*z* calcd for $C_{16}H_{11}F_3O$ [M$^{+\bullet}$]: 276.0762; found: 276.0768.

(*E*)-4,4,4-Trifluoro-1-(naphthalen-2-yl)but-2-en-1-one (2g)[4c]

Yield: 205 mg (82%); white solid; mp 69–70 °C.

IR (KBr): 1685, 1645, 1621, 1306, 1126, 970, 822, 753, 654 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (s, 1 H), 8.02–7.88 (m, 4 H), 7.71–7.57 (m, 3 H), 6.89 (dq, *J* = 15.5, 6.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 187.7, 136.0, 133.6, 132.4, 131.05 (q, *J* = 5.1 Hz), 131.03, 130.2 (q, *J* = 35.4 Hz), 129.7, 129.2, 129.1, 127.9, 127.2, 123.9, 122.7 (q, *J* = 270.7 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): δ = –64.93 (d, *J* = 5.9 Hz, 3 F).

HRMS (EI): *m*/*z* calcd for $C_{14}H_9F_3O$ [M$^{+\bullet}$]: 250.0605; found: 250.0594.

(*E*)-4,4,4-Trifluoro-1-(naphthalen-1-yl)but-2-en-1-one (2h)[6d]

Yield: 183 mg (73%); white solid; mp 72–73 °C.

IR (KBr): 1684, 1639, 1504, 1303, 1135, 970, 803, 776, 617 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (d, *J* = 8.5 Hz, 1 H), 8.08 (d, *J* = 8.2 Hz, 1 H), 7.93 (d, *J* = 8.0 Hz, 1 H), 7.87 (d, *J* = 7.2 Hz, 1 H), 7.67–7.54 (m, 3 H), 7.42 (d, *J* = 15.6 Hz, 1 H), 6.77 (dq, *J* = 15.6, 6.5 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.5, 134.7 (q, *J* = 5.1 Hz), 134.1, 134.0, 133.9, 130.42 (q, *J* = 35.4 Hz), 130.41, 129.3, 128.7, 128.5, 127.0, 125.5, 124.3, 122.6 (q, *J* = 271.7 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –64.97 (s, 3 F).

HRMS (EI): *m*/*z* calcd for $C_{14}H_9F_3O$ [M$^{+\bullet}$]: 250.0605; found: 250.0603.

(*E*)-1-(4-Bromophenyl)-4,4,4-trifluorobut-2-en-1-one (2i)[6a]

Yield: 234 mg (84%); light yellow liquid.

IR (KBr): 1684, 1650, 1586, 1307, 1130, 1007, 961, 636 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.82 (m, 2 H), 7.70–7.65 (m, 2 H), 7.51–7.46 (m, 1 H), 6.83 (dq, *J* = 15.5, 6.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 186.9, 134.9, 132.4, 130.7 (q, *J* = 35.4 Hz), 130.4 (q, *J* = 5.1 Hz), 130.2, 129.6, 122.4 (q, *J* = 270.7 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –65.15 (d, *J* = 4.7 Hz, 3 F).

HRMS (EI): *m*/*z* calcd for $C_{10}H_6BrF_3O$ [M$^{+\bullet}$]: 277.9554; found: 277.9547.

(*E*)-4,4,4-Trifluoro-1-(4-fluorophenyl)but-2-en-1-one (2j)[12]

Yield: 185 mg (85%); light yellow liquid.

IR (KBr): 1687, 1596, 1307, 1135, 964, 838, 593 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06–7.98 (m, 2 H), 7.51 (dq, *J* = 15.5, 1.9 Hz, 1 H), 7.24–7.15 (m, 2 H), 6.82 (dq, *J* = 15.4, 6.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 186.3, 166.4 (d, *J* = 257.6 Hz), 132.6 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 9.1 Hz), 130.6 (q, *J* = 5.1 Hz), 130.5 (q, *J* = 35.4 Hz), 122.5 (q, *J* = 271.7 Hz), 116.2 (d, *J* = 22.2 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –65.18 (s, 3 F), –102.76 (s, 1 F).

HRMS (EI): *m*/*z* calcd for $C_{10}H_6F_4O$ [M$^{+\bullet}$]: 218.0355; found: 218.0354.

(*E*)-1-(4-Chlorophenyl)-4,4,4-trifluorobut-2-en-1-one (2k)[6d]

Yield: 201 mg (86%); light yellow liquid.

IR (KBr): 1686, 1650, 1588, 1307, 1140, 970, 827, 641 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.9 Hz, 2 H), 7.51–7.48 (m, 3 H), 6.82 (dq, *J* = 15.5, 6.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 186.7, 140.8, 134.5, 130.8 (q, *J* = 35.3 Hz), 130.5 (q, *J* = 5.1 Hz), 130.2, 129.3, 122.4 (q, *J* = 271.7 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): δ = –65.20 (d, *J* = 5.9 Hz, 3 F).

HRMS (EI): *m*/*z* calcd for $C_{10}H_6ClF_3O$ [M$^{+\bullet}$]: 234.0059; found: 234.0052.

(*E*)-1-(3-Chlorophenyl)-4,4,4-trifluorobut-2-en-1-one (2l)

Yield: 201 mg (86%); light yellow liquid.

IR (KBr): 1689, 1646, 1306, 1137, 966, 790, 626 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (t, *J* = 1.8 Hz, 1 H), 7.87–7.82 (m, 1 H), 7.63–7.60 (m, 1 H), 7.52–7.45 (m, 2 H), 6.84 (dq, *J* = 15.5, 6.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 186.7, 137.6, 135.4, 134.1, 131.0 (q, *J* = 35.4 Hz), 130.4 (q, *J* = 5.1 Hz), 130.3, 128.8, 126.8, 122.4 (q, *J* = 270.1 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –65.19 (s, 3 F).

HRMS (EI): *m*/*z* calcd for $C_{10}H_6ClF_3O$ [M$^{+\bullet}$]: 234.0059; found: 234.0067.

(*E*)-1-(2-Chlorophenyl)-4,4,4-trifluorobut-2-en-1-one (2m)

Yield: 187 mg (80%); light yellow liquid.

IR (KBr): 1686, 1646, 1304, 1137, 970, 764, 623 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.51 (m, 1 H), 7.51–7.45 (m, 2 H), 7.42–7.36 (m, 1 H), 7.26–7.19 (m, 1 H), 6.64 (dq, *J* = 15.8, 6.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 190.6, 137.1, 134.2 (q, *J* = 5.1 Hz), 133.0, 131.9, 130.7, 130.1, 130.09 (q, *J* = 35.4 Hz), 127.2, 122.4 (q, *J* = 270.1 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –65.21 (s, 3 F).

HRMS (EI): *m*/*z* calcd for $C_{10}H_6ClF_3O$ [M$^{+\bullet}$]: 234.0059; found: 234.0058.

(*E*)-4,4,4-Trifluoro-1-(3-(trifluoromethyl)phenyl)but-2-en-1-one (2n)[5a]

Yield: 217 mg (81%); light yellow liquid.

IR (KBr): 1692, 1646, 1305, 1132, 967, 693, 628 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (s, 1 H), 8.16 (d, *J* = 7.8 Hz, 1 H), 7.91 (d, *J* = 7.8 Hz, 1 H), 7.69 (t, *J* = 7.8 Hz, 1 H), 7.53 (d, *J* = 15.5 Hz, 1 H), 6.88 (dq, *J* = 15.5, 6.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 186.7, 136.7, 131.8, 131.4 (q, *J* = 35.4 Hz), 131.2 (q, *J* = 76.8 Hz), 130.5 (q, *J* = 4.0 Hz), 130.1 (q, *J* = 6.1 Hz), 129.7, 125.5 (q, *J* = 4.0 Hz), 123.5 (q, *J* = 273.7 Hz), 122.3 (q, *J* = 271.7 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): δ = –62.94 (s, 3 F), –65.24 (dd, *J* = 6.5, 1.9 Hz, 3 F).

HRMS (EI): *m*/*z* calcd for $C_{11}H_6F_6O$ [M$^{+\bullet}$]: 268.0323; found: 268.0322.

4-((*E*)-4,4,4-Trifluorobut-2-enoyl)benzonitrile (2o)[6d]

Yield: 196 mg (87%); light yellow liquid.

IR (KBr): 2234, 1687, 1649, 1309, 1132, 968, 833, 648 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.0 Hz, 2 H), 7.84 (d, *J* = 8.5 Hz, 2 H), 7.52–7.48 (m, 1 H), 6.87 (dq, *J* = 15.5, 6.5 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 186.9, 139.0, 132.8, 131.6 (q, *J* = 35.4 Hz), 130.2 (q, *J* = 5.1 Hz), 129.2, 122.3 (q, *J* = 270.7 Hz), 117.6, 117.3.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –65.28 (s, 3 F).

HRMS (EI): *m*/*z* calcd for $C_{11}H_6F_3NO$ [M$^{+\bullet}$]: 225.0401; found: 225.0404.

(*E*)-1-(3-Chloro-2-fluorophenyl)-4,4,4-trifluorobut-2-en-1-one (2p)

Yield: 199 mg (79%); light yellow liquid.

IR (KBr): 1689, 1601, 1455, 1306, 1137, 970, 640 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.70 (m, 1 H), 7.69–7.63 (m, 1 H), 7.43–7.35 (m, 1 H), 7.26–7.20 (m, 1 H), 6.83–6.74 (m, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.6, 157.3 (d, *J* = 257.6 Hz), 135.8, 133.6 (q, *J* = 5.1 Hz), 130.5 (q, *J* = 35.4 Hz), 129.3, 126.4 (d, *J* = 13.1 Hz), 125.2 (d, *J* = 4.0 Hz), 122.7 (d, *J* = 19.2 Hz), 122.3 (q, *J* = 271.7 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): δ = –65.27 (dd, J = 6.6, 1.9 Hz, 3 F), –112.42 to –112.47 (m, 1 F).

HRMS (EI): *m*/*z* calcd for $C_{10}H_5ClF_4O$ [M$^{+\bullet}$]: 251.9965; found: 251.9969.

(*E*)-1-(2-Chloro-4-fluorophenyl)-4,4,4-trifluorobut-2-en-1-one (2q)

Yield: 194 mg (77%); light yellow liquid.

IR (KBr): 1698, 1603, 1450, 1310, 1139, 970, 905, 788, 640 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.40 (m, 1 H), 7.28 (d, *J* = 8.8 Hz, 1 H), 7.11 (t, *J* = 8.6 Hz, 1 H), 6.99 (d, *J* = 15.9 Hz, 1 H), 6.58–6.50 (m, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 187.8, 159.8 (d, *J* = 254.5 Hz), 134.8 (q, *J* = 6.1 Hz), 132.6, 132.5, 132.2 (d, *J* = 5.1 Hz), 131.6 (q, *J* = 35.4 Hz), 126.1 (q, *J* = 6.1 Hz), 122.2 (q, *J* = 271.7 Hz), 114.8 (d, *J* = 21.2 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): δ = –65.37 (d, *J* = 6.1 Hz, 3 F), –112.22 (dd, *J* = 15.1, 7.5 Hz, 1 F).

HRMS (EI): *m*/*z* calcd for $C_{10}H_5ClF_4O$ [M$^{+\bullet}$]: 251.9965; found: 251.9964.

(*E*)-4,4,4-Trifluoro-1-(thien-2-yl)but-2-en-1-one (2r)[4c]

Yield: 169 mg (82%); light yellow liquid.

IR (KBr): 1680, 1627, 1305, 1140, 962, 727, 630 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.81 (m, 1 H), 7.79 (dd, *J* = 4.9, 0.7 Hz, 1 H), 7.40 (dq, *J* = 15.4, 1.9 Hz, 1 H), 7.24–7.18 (m, 1 H), 6.86 (dq, *J* = 15.4, 6.7 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 179.7, 143.7, 136.1, 133.6, 130.8 (q, *J* = 5.1 Hz), 129.8 (q, *J* = 35.4 Hz), 128.7, 122.5 (q, *J* = 271.7 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –65.06 (d, *J* = 9.4 Hz, 3 F).

HRMS (EI): *m*/*z* calcd for $C_8H_5F_3OS$ [M$^{+\bullet}$]: 206.0013; found: 206.0010.

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Supporting Information

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