Synthetic Applications of the Carbanion with a Fluoroalkyl Group Generated by Palladium(0) Catalyst under Neutral Conditions

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The generation and synthetic application of stable carbanions situated in the β position from fluorine atom(s) are described. Palladium(0)-catalyzed allylation reactions under neutral conditions proceeded smoothly in the system where a methylene group is activated by fluoroalkyl and carbonyl groups. In the above systems, the 2,2,2-trifluoroethyl moiety has been introduced onto the allylic position without the release of fluoride. Further, palladium(0)-catalyzed heterocyclization was achieved from the reaction of vinyl epoxide with 2-(trifluoromethyl)acrylate and/or 2,3,3,3-tetrafluoropropionate.

The chemistry of β-fluorocarbanions, which do not undergo elimination to form fluoroolefins, has not been studied in detail.[1] The synthesis and chemical reactivity of such carbanions are of considerable interest. The generation and synthetic applications of these carbanions have been based on several methods: (1) use of nitrotrifluoroethane and *n*-BuLi,[2] (2) employment of dimethyl 2-trifluoromethyl malonate and/or dialkyl 2-bromo-2-difluoromethyl malonate,[3] (3) application of α-CF_3-silylenol ether and Reformatsky-type reactions of bromotrifluoropropionate,[4] (4) use of 2,3,3,3-tetrafluoropropionate and 2,3,3,3- tetrafluoropropionamide,[5] and (5) indium-mediated allylation using 1,1,1-trifluoro-4-bromo-2-butene.[6] In these reports, the only electrophiles utilized were acetals, acid chlorides, and aldehydes, and to our knowledge no other electrophiles have been successfully utilized. Moreover, in the cases of (1) and (4), employment of alkyl halides instead of aldehydes accelerated the release of fluoride ion to furnish the olefin. Obviously, practical generation for β-fluorocarbanions remains an important synthetic challenge. Although palladium-catalyzed allylation reactions under neutral condition have been recognized to be useful for organic synthesis,[7] their synthetic value in fluorine chemistry still appears to be grossly underestimated.[8]

In this paper, we describe the generation and synthetic applications of β-fluorocarbanions derived from a methylene group activated with fluoroalkyl and carbonyl groups.

Results and Discussion

Allylation Reaction. $Pd(PPh_3)_4$ was used under neutral conditions in the reaction of ethyl 3,3,3-trifluoropropionate with cinnamyl carbonate in tetrahydrofuran to obtain ethyl 2-trifluoromethyl-5-phenyl-4-pentenoate in 29% yield with S_N2 regioselectivity. Moreover, this Pd(0)-catalyzed allylation reaction did not proceed under basic conditions. In this reaction type, an important factor is to find a match between the Pd(0) catalyst and additives to increase the chemical yield. Therefore, we examined several palladium(0) catalysts and the effect of additives. The $Pd(dba)_2{\cdot}CHCl_3$−2dppe system increased the chemical yield to 50%, and bisallylation product decreased to 13% yield. However, there are numerous disadvantages associated with the above approach, e.g., the yield is not high and bisallylated product is a major byproduct. To obviate these disadvantages, molecular sieves (5A) and binap were substituted for dppe (entry 4, Table 1, Scheme 1); the chemical yield increased to 61% while bisallylation product decreased to 8% yield.

Molecular sieves (5A) are acceptable to trap ethanol generated from the carbonate group via the η^3-allyl system. The cis and/or trans stereochemistry was confirmed using ^1H NMR coupling constants. The reaction is effective with both primary and secondary allylic carbonates. In the case of secondary carbonate PhCH-$(OCO_2Et)CH{=}CH_2$ (entry 5), the allylation reaction proceeded to afford the S_N2' allylation product in 66% yield. Regioisomeric carbonates produce only **3** (see entries 4 and 6−8).

Furthermore, in entries 9−20 (Table 2, Scheme 2), 2-fluoro-, 2-methyl, and/or 2-benzyloxy-3,3,3-trifluoro-

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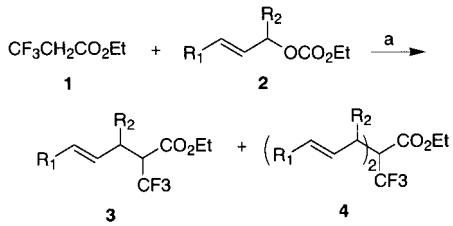
Scheme 1[a]



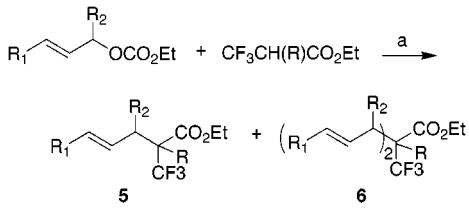
[a] a = $Pd_2(dba)_3CHCl_3$-2 binap (5 mol %), MS-5A, THF, 50 °C.

Table 1. Palladium(0)-Catalyzed Allylation Reaction

	allylcarbonates			yield (%)	
entry	R_1	R_2	reaction time (h)	**3** (*E*:*Z* ratio)	**4**
1	H	H	6	70 (**3a**)[a]	6 (**4a**)
2	Me	H	10	51 (**3b**) (96:4)	(9)[b]
3	Me	Me	20	17 (**3c**) [63:37][c]	0
4	Ph	H	6	61 (**3d**) (100:0)	8 (**4d**)
5	H	Ph	6	66 (**3d**) (100:0)	13 (**4d**)
6	Pr[e]	H	8	67 (**3e**) (100:0)	0
7	Pr[f]	H	8	66 (**3e**) (100:0)	0
8	$PhCH_2CH_2$	H	8	61 (**3f**) (100:0)	26[d]

[a] Compound number. [b] S_N2' allylation product. [c] Diastereomeric ratio in the parenthesis. [d] $PhCH_2CH{=}CH_2$ was obtained in 26% yield. [e] (*E*) isomer. [f] (*Z*) isomer.

Scheme 2[a]



[a] a = $Pd(dppe)_2$ (5 mol %), MS-5A, THF, 50 °C.

Table 2. Palladium(0)-Catalyzed Allylation Reaction

	carbonates			reaction	yield	
entry	R_1	R_2	R	time (h)	**5** (*E*:*Z* ratio)	**6**
9	H	H	F	3	94 (**5a**)[a]	0
10	Me	H	F	4	74 (**5b**) (85:15)	(26)[b]
11	Me	Me	F	7	73 (**5c**) [51:49][c]	0
12	Ph	H	F	3	98 (**5d**) (100:0)	0
13	H	H	Me	7	79 (**5e**)	0
14	Me	H	Me	12	29 (**5f**) (100:0)	(16)[b]
15	Me	Me	Me	24	21 (**5g**) (57:43)[c]	0
16	Ph	H	Me	8	75 (**5h**) (100:0)	0
17	H	H	OBn	3	97 (**5i**)	
18	Me	H	OBn	4	80 (**5j**) (85:15)	
19	Me	Me	OBn	8	54 (**5k**) [57:43][c]	
20	Ph	H	OBn	3	98 (**5l**) (100:0)	

[a] Compound number. [b] Yield of S_N2' allylation product. [c] Diastereomeric ratio in the parenthesis.

propionates in the presence of $Pd(dppe)_2$−MS-5A without binap reacted smoothly to produce the corresponding allylic product in this system.

The mechanism of the above palladium(0)-catalyzed allylation reaction is explained as follows. In the case of neutral conditions, alkoxide anion in the possible intermediate **Int-A** reacts with the activated methylene group in substrate ($RCH(R_F)CO_2Et$), resulting in the formation of intermediate **Int-B** (Figure 1). In this reaction step, it appears that free β-carbanion with a fluoromethyl group, such as $^-CR(R_F)CO_2Et$, is not generated and that the EtO ligand on the palladium atom is replaced by $CR(R_F)CO_2$-

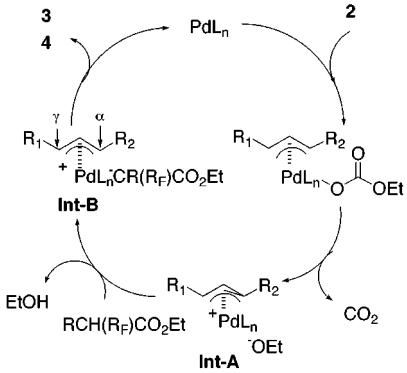
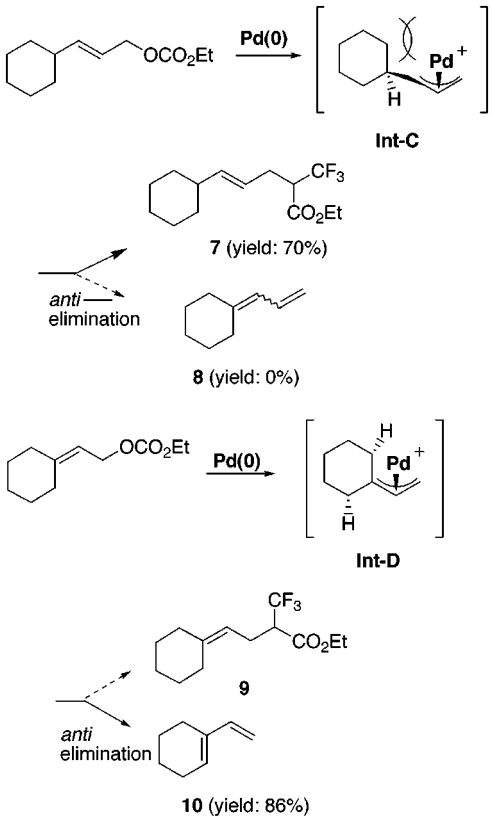


Figure 1. Pd(0)-catalyzed reaction system.

Scheme 3. Synthetic Route to Diene



Et. Finally, reductive elimination from **Int-B** produces the S_N2 allylation product as the main product.

In the case of the cyclohexane system shown in Scheme 3, the formation of diene **10** can be rationalized via stereospecific *anti* elimination of the elements LnPd(X)-H from an intermediate such as **Int-D**. However, the *anti* elimination of the Pd complex from **Int-C** is not reasonable, probably because of the steric repulsion between Pd−metal and the cyclohexane ring to produce the diene **8**. On the basis of these considerations, the allylation product **7** was obtained as the main one from **Int-C**, and the diene **10** was produced from **Int-D**.

Elimination Reaction. In the case of the Pd(0)-catalyzed reaction of 2-substituted 3,3-difluoropropionates **11**(Table 3, Scheme 4), release of fluoride ion instead of the allylation reaction was observed to produce (*E*)-3-fluoro-2-substituted-2-alkenoic acid esters as single stereoisomers.[9] The difference in stability between the carbanion attached with CF_3 and that with the CHF_2 group may be due to the fact that the C−F bond length

Scheme 4. Stereoselective Synthesis of Trisubstituted Alkenes

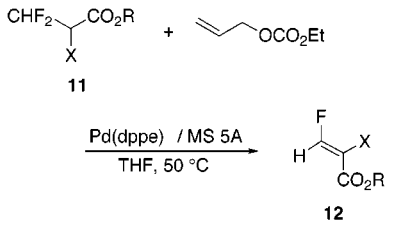


Table 3. Synthesis of Fluorinated Alkenes

entry	compd no.	X	R	reaction time (h)	yield (%)
22	**12a**	Me	CH_2CH_2Ph	10	71
23	**12b**	OBn	Et	6	83
24	**12b**	OBn	Et	10	64

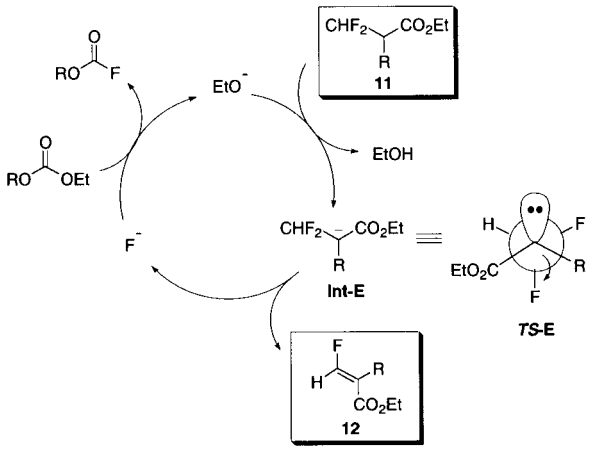
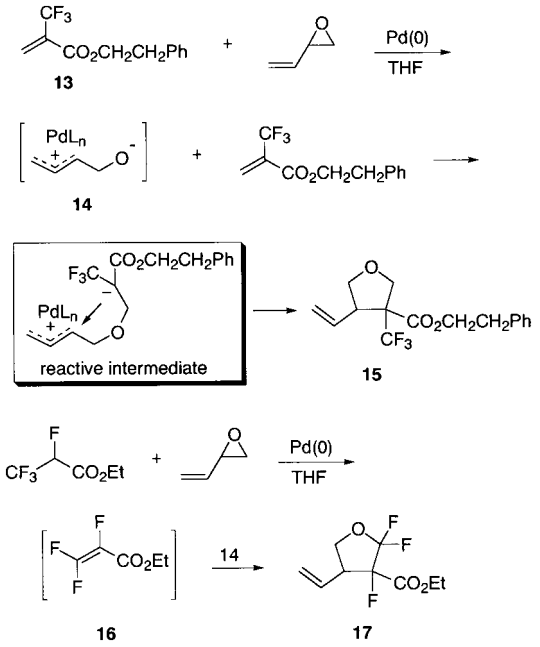


Figure 2. Reaction mechanism of the present elimination reaction.

in the CHF_2 group is longer than that of CF_3 group.[10] The stereochemistry of the product was confirmed by the chemical shift of the olefinic proton ($CHF{=}C(R)CO_2R'$), because the signal from the olefinic proton in the (*Z*) isomer occurs in the region $\delta = 5.50-6.00$ ppm, and that of the (*E*) isomer is at $\delta = 6.80-7.50$.[11] On the basis of the chemical shift ($\delta = 7.20-7.50$) and coupling constant ($J_{H-F} \approx 70-80$ Hz), the product was identified as the (*E*) isomer. When the reaction was attempted in the presence of other bases (lithium or Grignard reagents), the target olefins did not form. Moreover, this Pd(0)-catalyzed olefin synthesis also failed to proceed under basic conditions. To clarify the reaction mechanism of this palladium(0)-catalyzed olefin synthesis, we have examined the reaction system using substrate **11** (1 equiv), a catalytic amount of allyl carbonate (0.1 equiv), and $Pd(dppe)_2$ (0.05 equiv) in the presence of diethyl carbonate (1.2 equiv). A proposed mechanism for the eliminated reaction is shown in Figure 2. Under neutral conditions, ethoxide anion, generated from the reaction of allyl carbonate and

Scheme 5. Cyclization Reaction with Pd(0) Catalyst



$Pd(dppe)_2$, reacts with the activated methylene group in the substrate ($CHF_2CH(R)CO_2Et'$), resulting in the formation of intermediate **Int-E**. The release of fluoride from **Int-E** leads to the formation of (*E*)-3-fluoro-2-substituted-2-alkenoic acid esters. Finally, the active ethoxide ion was regenerated when diethyl carbonate is attacked by fluoride ion. Obviously, in this process, molecular sieves (5A) are acceptable to trap the ethanol generated from the carbonate group.

The stereoselective synthesis of alkenes described above was thus attributed to the bulkiness of substituent groups and the *anti* elimination reaction process via ***TS*-E**. As depicted in the several types of combinations shown in Table 3, we have found that this process provides a convienient synthetic route to fluorinated trisubstituted alkenes.

Cyclization Reaction. It is well established that fluoride ion is eliminated from the carbanion generated by nucleophilic attack on the substituted 2-(trifluoromethyl)-acrylate **13** to form the difluoroolefin. Therefore, we examined the intramolecular cyclization reaction of the generated carbanion as an activated reaction intermediate (Scheme 5). After forming the π-allylpalladium complex of vinyl epoxide **14**, Pd-complex-O nucleophile attacked the carbon−carbon double bond of **13** to generate the corresponding β-fluoro carbanion. Pd-catalyzed intramolecular allylation of the carbanion gave the five-membered heterocyclic compound **15**. Further, in the case of the π-allylpalladium complex of vinyl epoxide **14**, ethyl 2,3,3,3-tetrafluoropropionate formed the cyclic compound **17** via nucleophilic attack and intramolecular cyclization of trifluoroolefin **16**, generated by the release of fluoride from the β-fluorocarbanion.

In conclusion, we have described methods for the generation of stable carbanions in the β-position to a trifluoromethyl group by palladium(0)-catalyzed allylation reactions. 3,3,3-Trifluoropropionate esters were used as the nucleophile with allyl carbonates as the electrophile, or 2-(trifluoromethyl)acrylate served as the elec-

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trophile with vinyl epoxide as the nucleophile. Good yields of the desired products were isolated.

Experimental Section

General. All commercially available reagents were used without further purification. Chemical shifts of ^{1}H (500 MHz) and ^{13}C NMR (50 MHz) spectra were recorded in ppm (δ) downfield from an internal standard (Me_4Si, δ 0.00). The ^{19}F (470 MHz) NMR spectra were recorded in ppm downfield from internal standard C_6F_6 in $CDCl_3$ using a VXR 500 instrument. Gas−liquid chromatography (GLC) was performed using Silicone GE XE−60 or ULBON HR-20M on Chromosorb W, 30 m × 3 mm. Optical purities of materials were determined by GLC.

Palladium(0)-Catalyzed Allylation Reaction under Neutral Conditions. A mixture of ethyl 3,3,3-trifluoropropionate (156 mg, 1.00 mmol) and (*E*)-cinnnamyl ethyl carbonate (247 mg, 1.20 mmol) was added to a solution of $Pd_2(dba)_3$•$CHCl_3$ (26 mg, 0.025 mmol), binap (62 mg, 0.10 mmol), and MS-5A (500 mg) in THF (5 mL) under an argon atmosphere. After the reaction mixture was stirred for 6 h at 50 °C, the mixture was diluted with diethyl ether and then passed though a pad of Celite. On removal of the solvent, the residue was purified by column chromatography on silica gel, eluting with a mixture solution of hexanes−ether (50:1) to give ethyl 5-phenyl-2-trifluoromethyl-4-pentenoate (0.161 g) in 61% yield.

Ethyl 2-Trifluoromethyl-4-pentenoate (3a). ^{1}H NMR ($CDCl_3$): δ 1.28 (3 H, t, J = 7.08 Hz), 2.61−2.52 (1 H, m), 2.61−2.69 (1 H, m), 3.19 (1 H, ddq, J = 4.64, 10.0, 8.30 Hz), 4.23 (2 H, q, 7.08 Hz), 5.12 (1 H, ddd, J = 1.22, 2.44, 10.3 Hz), 5.17 (1 H, ddd, J = 1.47, 2.93, 17.1 Hz), 5.67−5.78 (1 H, m). ^{13}C NMR ($CDCl_3$): δ 14.55, 30.91 (q, J = 2.5 Hz), 50.73 (q, J = 27.1 Hz), 62.32, 119.06, 125.05 (q, J = 280 Hz), 133.00, 167.45 (q, J = 3.2 Hz). ^{19}F NMR ($CDCl_3$): δ −69.40 (d, J = 9.16 Hz). IR (neat): ν 1270, 1647, 1748 (C═O) cm^{-1}.

Ethyl 2-Allyl-2-trifluoromethyl-4-pentenoate (4a). ^{1}H NMR ($CDCl_3$): δ 1.29 (3 H, t, J = 7.08 Hz), 2.60 (4 H, dd, J = 7.57, 13.9 Hz), 4.23 (2 H, q, J = 7.08 Hz), 5.13 (2 H, ddd, J = 1.01, 1.71, 7.33 Hz), 5.16 (2 H, dd, J = 1.45, 14.7 Hz), 5.72−5.80 (2 H, m). ^{13}C NMR ($CDCl_3$): δ 14.48, 36.68 (2 C, q, J = 1.8 Hz), 56.25 (q, J = 23.4 Hz), 62.29, 120.02 (2 C), 126.47 (q, J = 285 Hz), 132.22 (2 C), 168.97 (q, J = 1.7 Hz). ^{19}F NMR ($CDCl_3$): δ −69.47 (s). IR (neat): ν 1217, 1643, 1743 (C═O) cm^{-1}.

Ethyl 2-Trifluoromethyl-4-hexenoate (3b). ^{1}H NMR ($CDCl_3$): δ 1.28 (3 H, t, J = 7.08 Hz), 1.65 (3 H, ddd, J = 1.22, 2.68, 6.35 Hz), 2.44−2.50 (1 H, m), 2.53−2.61 (1 H, m), 3.12 (1 H, ddq, J = 4.64, 13.19, 8.30 Hz), 4.224 (1 H, q, J = 7.08 Hz), 4.225 (1 H, q, J = 7.08 Hz), 5.34 (1 H, dt, J = 15.4, 6.11 Hz), 5.58, (1 H, dtq, J = 15.1, 1.46, 6.35 Hz). ^{13}C NMR ($CDCl_3$): δ 14.60, 18.35, 29.93 (q, J = 2.5 Hz), 51.27 (q, J = 27.2 Hz), 62.17, 125.09 (q, J = 280 Hz), 125.42, 129.98, 167.65 (q, J = 3.2 Hz). ^{19}F NMR ($CDCl_3$): δ −69.38 (d, J = 9.14 Hz). IR (neat): ν 1263, 1749 cm^{-1}. Anal. Calcd for $C_9H_{13}F_3O_2$: C, 51.43; H, 6.23. Found: C, 51.82; H, 6.26.

Ethyl 3-Methyl-2-trifluoromethyl-4-hexenoate (3c). Diastereomeric ratio, 63:17. IR (neat): ν 1261, 1672, 1742 (C═O) cm^{-1}. **Major isomer.** ^{1}H NMR ($CDCl_3$): δ 1.06 (3 H, d, J = 6.83 Hz), 1.25 (3 H, t, J = 7.08 Hz), 1.63 (3 H, dd, J = 1.46, 6.35 Hz), 2.98 (1 H, sep, J = 8.79 Hz), 4.17 (1 H, q, J = 7.08 Hz), 4.19 (1 H, q, J = 7.08 Hz), 5.25−5.36 (1 H, m), 5.52, (1 H, ddd, J = 0.73, 6.59, 15.1 Hz). ^{13}C NMR ($CDCl_3$): δ 14.82, 18.31, 19.46, 36.54 (q, J = 1.8 Hz), 56.79 (q, J = 26.2 Hz), 61.91, 125.16 (q, J = 281 Hz), 127.57, 132.09, 168.12 (q, J = 3.8 Hz). ^{19}F NMR ($CDCl_3$): δ −65.49 (d, J = 7.63 Hz). **Minor isomer.** ^{1}H NMR ($CDCl_3$): δ 1.15 (3 H, dd, J = 1.22, 6.84 Hz), 1.30 (3 H, t, J = 7.08 Hz), 1.67 (3 H, dd, J = 1.46, 6.35 Hz), 2.80 (1 H, sep, J = 6.59 Hz), 4.231 (1 H, q, J = 7.08 Hz), 4.237 (1 H, q, J = 7.08 Hz), 5.25−5.36 (1 H, m), 5.53, (1 H, ddd, J = 0.73, 6.59, 14.4 Hz). ^{13}C NMR ($CDCl_3$): δ 14.65, 18.31, 19.10, 36.22 (q, J = 1.8 Hz), 56.65 (q, J = 26.2 Hz), 62.08, 125.03 (q, J = 281 Hz), 127.00, 132.45, 167.73 (q, J = 3.5 Hz). ^{19}F NMR ($CDCl_3$): δ −65.68 (d, J = 9.15 Hz).

Ethyl 5-Phenyl-2-trifluoromethyl-4-pentenoate (3d). ^{1}H NMR ($CDCl_3$): δ 1.25 (3 H, t, J = 7.08 Hz), 2.71 (1 H, dddd, J = 1.46, 4.88, 6.84, 14.2 Hz), 2.81 (1 H, dddd, J = 1.22, 7.56, 8.06, 10.0 Hz), 3.26 (1 H, ddq, J = 4.86, 10.0, 14.4 Hz), 4.222 (1 H, q, 7.08 Hz), 4.224 (1 H, q, 7.08 Hz), 6.09 (1 H, dt, J = 15.6, 7.33 Hz), 6.51 (1 H, d, J = 15.9), 7.34−7.22 (5 H, m).^{13}C NMR ($CDCl_3$): δ 14.60, 30.28 (q, J = 2.5 Hz), 51.05 (q, J = 27.10), 62.39,124.24, 126.80 (2C), 128.13, 125.03 (q, J = 280 Hz), 129.14 (2C), 134.25, 137.23, 167.43 (q, J = 3.1 Hz). ^{19}F NMR ($CDCl_3$): δ −69.25 (d, J = 9.17 Hz). IR: ν 2380, 1746 (C═O) cm^{-1}. Anal. Calcd for $C_{14}H_{15}F_3O_2$: C, 61.67; H, 5.55. Found: C, 61.63; H, 5.57.

Ethyl 2-Cinnamyl-5-phenyl-2-trifluoromethyl-4-pentenoate (4d). ^{1}H NMR ($CDCl_3$): δ 1.30 (3 H, t, J = 7.08 Hz), 2.80 (4 H, d, J = 7.57 Hz), 4.27 (2 H, q, 7.08 Hz), 6.16 (2 H, dt, J = 15.4, 7.81 Hz), 6.50 (2 H, d, J = 15.6 Hz), 7.23−7.35 (10 H, m). ^{13}C NMR ($CDCl_3$): δ 14.66, 36.12 (2 C, q, J = 2 Hz), 56.89, (q, J = 23 Hz), 62.40, 124.55 (q, J = 284.8 Hz), 123.64 (2 C), 126.81 (4 C), 128.12 (2 C), 129.12 (4C), 135.13 (2 C), 137.48 (2 C), 169.05 (q, J = 1.8 Hz). ^{19}F NMR ($CDCl_3$): δ −69.38 (s).

Ethyl 2-Trifluoromethyl-4-octenoate (3e). ^{1}H NMR ($CDCl_3$): δ 0.87 (3 H, t, J = 7.57), 1.28 (3 H, t, J = 7.08 Hz), 1.35 (2 H, q, J = 7.41 Hz), 1.96 (2 H, q, J = 6.84 Hz), 2.49 (1 H, ddd, J = 5.13, 6.35, 14.4 Hz), 2.58 (1 H, ddd, J = 8.79, 10.0, 14.4 Hz), 3.13 (1 H, ddq, J = 5.13, 10.0, 8.30 Hz), 4.21 (1 H, q, J = 7.08 Hz), 4.22 (1 H, q, J = 7.08 Hz), 5.31 (1 H, dt, J = 15.1, 7.08 Hz), 5.56, (1 H, dt, J = 15.1, 6.84 Hz). ^{13}C NMR ($CDCl_3$): δ 14.03, 14.58, 22.86, 29.95 (q, J = 2.5 Hz), 35.03, 51.30 (q, J = 27.2 Hz), 62.18, 124.36, 125.10 (q, J = 280 Hz), 135.37, 167.65 (q, J = 3.2 Hz). ^{19}F NMR ($CDCl_3$): δ −69.39 (d, J = 9.16 Hz). IR (neat): ν 1270, 1749 cm^{-1}.

Ethyl 2-Trifluoromethyl-7-phenyl-4-heptenoate (3f). ^{1}H NMR: δ 1.27 (3 H, t, J = 7.33 Hz), 2.31 (2 H, q, J = 7.57 Hz), 2.48 (1 H, dt, J = 14.16, 4.88 Hz), 2.59 (1 H, dddd, J = 0.97, 7.57, 10.01, 14.40 Hz), 2.65 (2 H, dd, J = 7.56, 8.06 Hz), 3.11 (1 H, ddq, J = 4.64, 10.01, 8.30 Hz), 4.20 (1 H, q, 7.33 Hz), 4.21 (1 H, q, 7.33 Hz), 5.36 (1 H, dt, J = 15.38, 6.84 Hz), 5.61, (1 H, dtt, J = 15.39, 1.22, 6.49 Hz), 7.15−7.20 (2 H, m), 7.26−7.30 (3 H, m). ^{13}C NMR: δ 14.56, 29.84 (q, J = 2.5 Hz), 34.72, 36.18, 51.16 (q, J = 26.8 Hz), 62.17, 124.99, 125.07 (q, J = 280.2 Hz), 126.40, 128.85 (2 C), 128.91 (2 C), 134.41, 142.13, 167.50 (q, J = 3.2 Hz). ^{19}F NMR: δ −69.35 (d, J = 7.63 Hz). IR (neat): ν 1270, 1603, 1747 (C═O) cm^{-1}. Anal. Calcd for $C_{16}H_{19}F_3O_2$: C, 63.99; H, 6.38. Found: C, 63.66; H, 6.15.

Ethyl 2-Fluoro-2-trifluoromethyl-4-pentenoate (5a). ^{1}H NMR ($CDCl_3$): δ 1.33 (3 H, t, J = 7.08 Hz), 2.79−3.00 (2 H, m), 4.34 (2 H, q, J = 7.08 Hz), 5.24−5.26 (1 H, m), 5.27−5.30 (1 H, m) 5.73 (1 H, dddd, J = 6.84, 7.57, 9.77, 14.2 Hz). ^{13}C NMR ($CDCl_3$): δ 14.34, 36.46 (d, J = 21.6 Hz), 63.49, 92.63 (dq, J = 202, 31.2 Hz), 121.93 (dq, J = 28.4, 285 Hz), 122.22, 127.84 (d, J = 3.0 Hz), 164.36 (d, J = 24.9 Hz). ^{19}F NMR ($CDCl_3$): δ −79.15 (3 F, d, J = 7.63 Hz), −178.18 (1 F, dquint, J = 39.7, 7.63 Hz). IR (neat): ν 1318, 1647, 1770 (C═O) cm^{-1}.

Ethyl 2-Fluoro-2-trifluoromethyl-4-hexenoate (5b). ^{1}H NMR ($CDCl_3$): δ 1.32 (3 H, t, J = 7.08 Hz), 1.68 (3 H, dd, J = 1.22, 6.59 Hz), 2.70−3.07 (2 H, m), 4.33 (2 H, q, J = 7.08 Hz), 5.13−5.24 (1 H, m), 5.30−5.36 (1 H, m) 5.67 (1 H, dq, J = 15.1, 6.35 Hz). ^{13}C NMR ($CDCl_3$): δ 14.53, 18.52, 35.13 (d, J = 21.1 Hz), 63.48, 93.97 (dq, J = 201, 31.0 Hz), 121.93 (dq, J = 28.4, 285.4 Hz), 120.23(d, J = 1.8 Hz), 133.37, 164.62 (d, J = 25.9 Hz). ^{19}F NMR ($CDCl_3$): δ −79.11 (3 F, d, J = 7.62 Hz), −178.30 (1 F, ddq, J = 21.4, 33.6, 7.63 Hz). IR (neat): ν 1266, 1771 (C═O) cm^{-1}. Anal. Calcd for $C_9H_{12}F_4O_2$: C, 47.37; H, 5.30. Found: C, 47.19; H, 5.27.

Ethyl 2-Fluoro-3-methyl-2-trifluoromethyl-4-hexenoate (5c). Diastereomeric ratio, 51:49. IR (neat): ν 1272, 1772 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 14.47, 14.73, 15.73, 19.33, 40.36 (d, J = 20.1 Hz), 40.74 (d, J = 20.1 Hz), 95.84 (dq, J = 205, 30.6 Hz), 96.00 (dq, J = 200, 34.4 Hz), 121.85 (dq, J = 29.3, 286 Hz), 122.26 (dq, J = 286, 28.9 Hz), 127.56, 127.61, 128.14, 128.19, 129.46, 129.99, 165.08 (dq, J = 0.2, 25.6 Hz), 165.29 (dq, J = 2.2, 25.0 Hz). Anal. Calcd for $C_{10}H_{14}F_4O_2$: C, 49.59; H, 5.83. Found: C, 49.50; H, 5.87. **Major isomer.** ^{1}H NMR ($CDCl_3$): δ 1.08 (3 H, d, J = 7.08 Hz), 1.35 (3 H, t, J = 7.08 Hz), 1.65 (3

H, dd, J = 1.69, 6.59 Hz), 2.90−3.05 (1 H, m), 4.34 (1 H, q, J = 7.08 Hz), 4.36 (1 H, q, J = 7.08 Hz), 5.35 (1 H, ddd, J = 1.71, 9.28, 15.4 Hz), 5.63 (1 H, dd, J = 6.59, 15.4 Hz). ^{19}F NMR ($CDCl_3$): δ −74.82 (3 F, d, J = 6.10 Hz), −187.04 (1 F, dq, J = 27.5, 6.10 Hz). **Minor isomer.** ^{1}H NMR ($CDCl_3$): δ 1.18 (3 H, d, J = 6.84 Hz), 1.31 (3 H, t, J = 7.08 Hz), 1.69 (3 H, dd, J = 1.71, 6.59 Hz), 2.90−3.05 (1 H, m), 4.29 (1 H, q, J = 7.08 Hz), 4.30 (1 H, q, J = 7.08 Hz), 5.40 (1 H, dd, J = 9.03, 15.4 Hz), 5.58 (1 H, dd, J = 6.59, 15.1 Hz). ^{19}F NMR ($CDCl_3$): δ −74.56 (3 F, d, J = 6.10 Hz), −187.68 (1 F, dq, J = 27.5, 6.10 Hz).

Ethyl 2-Fluoro-5-phenyl-2-trifluoromethyl-4-pentenoate (5d). ^{1}H NMR ($CDCl_3$): δ 1.29 (3 H, t, J = 7.08 Hz), 2.99 (1 H, ddd, J = 1.46, 6.35, 14.9 Hz), 3.01 (1 H, dd, J = 8.30, 27.2 Hz), 4.32 (2 H, q, J = 7.08 Hz), 6.08 (1 H, ddd, J = 6.59, 8.06, 15.9 Hz), 6.57 (1 H, d, J = 15.9 Hz), 7.22−7.35 (5 H, m). ^{13}C NMR ($CDCl_3$): δ 14.50, 35.49 (d, J = 19.8 Hz), 63.64, 93.89 (dq, J = 31.1, 202 Hz), 122.10 (dq, J = 28.4, 285 Hz), 118.85 (d, J = 2.3 Hz), 126.95 (2 C), 128.58, 129.16 (2C), 136.83, 137.04, 164.51 (d, J = 24.8 Hz). ^{19}F NMR ($CDCl_3$): δ −78.98 (3 F, q, J = 7.63 Hz), −177.79 (1 F, ddq, J = 15.3, 32.1, 7.63 Hz). IR (neat): ν 1313, 1767 (C=O) cm^{-1}. Anal. Calcd for $C_{14}H_{14}F_4O_2$: C, 57.93; H, 4.86. Found: C, 57.62; H, 4.92.

Ethyl 2-Fluoro-2-trifluoromethyl-4-pentenoate (5e). ^{1}H NMR ($CDCl_3$): δ 1.33 (3 H, t, J = 7.08 Hz), 2.79−3.00 (2 H, m), 4.34 (2 H, q, J = 7.08 Hz), 5.24−5.26 (1 H, m), 5.27−5.30 (1 H, m) 5.73 (1 H, dddd, J = 6.84, 7.57, 9.77, 14.2 Hz). ^{13}C NMR ($CDCl_3$): δ 14.34, 36.46 (d, J = 21.6 Hz), 63.49, 92.63 (dq, J = 202, 31.2 Hz), 121.93 (dq, J = 28.4, 285 Hz), 122.22, 127.84 (d, J = 3.0 Hz), 164.36 (d, J = 24.9 Hz). ^{19}F NMR ($CDCl_3$): δ −79.15 (3 F, d, J = 7.63 Hz), −178.18 (1 F, dquint, J = 39.7, 7.63 Hz). IR (neat): ν 1318, 1647, 1770 (C=O) cm^{-1}.

Ethyl 2-Methyl-2-trifluoromethyl-4-hexenoate (5f). ^{1}H NMR ($CDCl_3$): δ 1.21 (3 H, t, J = 7.08 Hz), 1.27 (3H, s), 1.59 (3 H, dd, J = 1.22, 6.59 Hz), 2.23 (1 H, dd, J = 8.78, 13.9 Hz), 2.61 (1 H, dd, J = 6.84, 13.7 Hz), 4.15 (2 H, q, J = 7.08 Hz), 5.21 (1 H, dt, J = 14.9, 7.08 Hz), 5.49, (1 H, dtq, J = 15.1, 1.22, 6.59 Hz). ^{13}C NMR ($CDCl_3$): δ 14.43, 16.82, 18.34, 36.79 (q, J = 2.2 Hz), 52.85 (q, J = 24.5 Hz), 62.19, 124.08, 126.08 (q, J = 290 Hz), 131.08, 169.83. ^{19}F NMR ($CDCl_3$): δ −74.13 (s). IR (neat): ν 1261, 1672, 1742 (C=O) cm^{-1}.

Ethyl 2,3-Dimethyl-2-trifluoromethyl-4-hexenoate (5g). Diastereomeric ratio, 57:43. IR (neat): ν 1265, 1744 (C=O) cm^{-1}. **Major isomer.** ^{1}H NMR ($CDCl_3$): δ 0.87 (3 H, d, J = 7.08 Hz), 1.22 (3 H, t, J = 7.08 Hz), 1.60 (3 H, dd, J = 1.71, 6.60 Hz), 2.82−2.93 (1 H, m), 4.162 (1 H, q, J = 7.08 Hz), 4.154 (1 H, d, J = 7.08 Hz), 5.28 (1 H, dd, J = 8.55, 15.1 Hz), 5.47 (1 H, dq, J = 15.1, 6.35 Hz). ^{13}C NMR ($CDCl_3$): δ 12.90, 14.55, 16.79, 18.52, 39.99, 56.85 (q, J = 23.4 Hz), 62.25, 126.87 (q, J = 285 Hz), 127.97, 130.65, 170.43 (q, J = 2.2 Hz). ^{19}F NMR ($CDCl_3$): δ −70.12 (s). **Minor isomer.** ^{1}H NMR ($CDCl_3$): δ 1.00 (3 H, dd, J = 0.97, 7.08 Hz), 1.20 (3 H, t, J = 7.08 Hz), 1.56 (3 H, dd, J = 1.71, 6.34 Hz), 2.82−2.93 (1 H, m), 4.104 (1 H, q, J = 7.08 Hz), 4.119 (1 H, d, J = 7.08 Hz), 5.16 (1 H, dd, J = 8.76, 15.1 Hz), 5.42 (1 H, dq, J = 15.1, 6.59 Hz). ^{13}C NMR ($CDCl_3$): δ 12.36, 14.55, 16.11, 18.48, 40.17, 56.75 (q, J = 23.7 Hz), 62.13, 126.92 (q, J = 285 Hz), 128.31, 130.79, 170.35 (q, J = 2.2 Hz). ^{19}F NMR ($CDCl_3$): δ −69.73 (s).

Ethyl 2-Methyl-5-phenyl-2-trifluoromethyl-4-pentenoate (5h). ^{1}H NMR ($CDCl_3$): δ 1.28 (3 H, t, J = 7.08 Hz), 1.42 (3 H, s) 2.55 (1 H, ddd, J = 1.22, 8.06, 13.9 Hz), 2.91 (1 H, ddd, J = 1.22, 7.08, 13.9 Hz), 4.241 (1 H, q, J = 7.08 Hz), 4.240 (1 H, q, J = 7.08 Hz), 6.05 (1 H, dt, J = 15.6, 7.33 Hz), 6.48 (1 H, d, J = 15.6 Hz), 7.34−7.22 (5 H, m). ^{13}C NMR ($CDCl_3$): δ 14.53, 17.21 (q, J = 2.4 Hz), 37.32 (q, J = 2.2 Hz), 53.06 (q, J = 24.6 Hz), 62.39, 124.24, 126.75 (q, J = 284 Hz), 126.79 (2 C), 128.15, 129.09 (2 C), 135.36, 137.36, 169.70. ^{19}F NMR ($CDCl_3$): δ −73.99 (s). IR (neat): ν 1271, 1740 cm^{-1}. Anal. Calcd for$C_{15}H_{17}F_3O_2$: C, 62.93; H, 5.98. Found: C, 63.36; H, 5.98.

Ethyl 2-Benzyloxy-2-trifluoromethyl-4-pentenoate (5i). ^{1}H NMR ($CDCl_3$): δ 1.32 (3 H, t, J = 7.08 Hz), 2.78 (2 H, d, J = 7.08 Hz), 4.31 (2 H, q, J = 7.08 Hz), 4.66 (1 H, d, J = 10.7 Hz), 4.81 (1 H, d, J = 10.7 Hz), 5.14−5.20 (1 H, m), 5.86 (1 H, ddt, J = 10.1, 17.9, 7.33 Hz), 7.30−7.42 (5 H, m). ^{13}C NMR ($CDCl_3$): δ 14.54, 38.75 (q, J = 1.9 Hz), 69.55 (q, J = 1.7 Hz), 83.42 (q, J = 26.7 Hz), 120.17, 124.45 (q, J = 289 Hz), 128.19 (2 C), 128.35, 128.83 (2 C), 130.75, 138.02, 167.17. ^{19}F NMR ($CDCl_3$): δ −72.04 (s). IR (neat): ν 1262, 1643, 1751 (C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{17}F_3O_3$: C, 59.60; H, 5.67. Found: C, 59.38; H, 5.60.

Ethyl 2-Benzyloxy-2-trifluoromethyl-4-hexenoate (5j). ^{1}H NMR ($CDCl_3$): δ 1.31 (3 H, t, J = 7.08 Hz), 1.66 (3 H, dd, J = 1.22, 6.10 Hz), 2.72 (2 H, d, J = 6.59 Hz), 4.30 (2 H, q, J = 7.08 Hz), 4.66 (1 H, d, J = 10.7 Hz), 4.81 (1 H, d, J = 10.7 Hz), 5.43−5.50 (1 H, m), 5.57 (1 H, ddt, J = 6.34, 15.1, 1.22 Hz), 7.30−7.45 (5 H, m). ^{13}C NMR ($CDCl_3$): δ 14.66, 18.53, 37.69 (q, J = 1.8 Hz), 62.62 (q, J = 1.6 Hz), 83.70 (q, J = 26.3 Hz), 123.08, 124.69 (q, J = 273 Hz), 128.17 (2 C), 128.34, 128.87 (2 C), 131.10, 138.19, 167.40. ^{19}F NMR ($CDCl_3$): δ −72.06 (s). IR (neat): ν 1251, 1752 cm^{-1}. Anal. Calcd for $C_{16}H_{19}F_3O_3$: C, 60.75; H, 6.05. Found: C, 60.83; H, 5.90.

Ethyl 2-Benzyloxy-3-methyl-2-trifluoromethyl-4-hexenoate (5k). Diastereomeric ratio, 52:48. IR (neat): ν 1247, 1753 cm^{-1}. Anal. Calcd for $C_{17}H_{21}F_3O_3$: C, 61.81; H, 6.41. Found: C, 61.60; H, 6.41. **Major isomer.** ^{1}H NMR ($CDCl_3$): δ 1.06 (3 H, d, J = 7.08 Hz), 1.33 (3 H, t, J = 7.08 Hz), 1.65 (3 H, d, J = 5.13 Hz), 2.90 (1 H, quint, J = 7.57 Hz), 4.314 (1 H, q, 7.08 Hz), 4.312 (1 H, d, J = 7.08 Hz), 4.61 (1 H, d, J = 10.7 Hz), 5.45−5.57 (2 H, m), 7.30−7.45 (5 H, m). ^{13}C NMR ($CDCl_3$): δ 14.62, 16.71, 43.56 (q, J = 1.8 Hz), 62.50, 69.47, 86.25 (q, J = 24.9 Hz), 124.61 (q, J = 291 Hz), 127.99, 130.17, 138.66, 168.02. ^{19}F NMR ($CDCl_3$): δ −66.90 (s). **Minor isomer.** ^{1}H NMR ($CDCl_3$): δ 1.14 (3 H, dd, J = 0.98, 6.84 Hz), 1.29 (3 H, t, J = 7.08 Hz), 1.63 (3 H, d, J = 4.64 Hz), 2.90 (1 H, quint, J = 7.57 Hz), 4.246 (1 H, q, J = 7.08 Hz), 4.244 (1 H, d, J = 7.08 Hz), 4.61 (1 H, d, J = 10.7 Hz), 4.99 (1 H, d, J = 10.74 Hz), 5.45−5.57 (2 H, m), 7.30−7.45 (5 H, m). ^{13}C NMR ($CDCl_3$): δ 14.62, 15.64, 43.49 (q, J = 1.8 Hz), 62.30, 69.38, 86.07 (q, J = 25.1 Hz), 124.65 (q, J = 292 Hz), 128.11, 130.85, 138.88, 167.88. ^{19}F NMR ($CDCl_3$): δ −66.65 (s).

Ethyl 2-Benzyloxy-5-phenyl-2-trifluoromethyl-4-pentenoate (5l). ^{1}H NMR ($CDCl_3$): δ 1.29 (3 H, t, J = 7.08 Hz), 2.94 (2 H, d, J = 6.82 Hz), 4.29 (2 H, q, J = 7.08 Hz), 4.70 (1 H, d, J = 10.8 Hz), 4.85 (1 H, d, J = 10.8 Hz), 6.21 (1 H, dt, J = 7.09, 15.9 Hz), 6.48 (1 H, d, J = 15.9 Hz), 7.24−7.42 (10 H, m). ^{13}C NMR ($CDCl_3$): δ 14.53, 37.09 (q, J = 2.0 Hz), 61.75 (q, J = 1.5 Hz), 68.72 (q, J = 1.5 Hz), 82.67 (q, J = 26.5 Hz), 123.49 (q, J = 290 Hz), 125.83 (2 C), 127.12, 127.23 (2 C), 127.40, 127.88 (2 C), 128.06 (2 C), 134.10, 136.42, 137.01, 166.21. ^{19}F NMR ($CDCl_3$): δ −71.97 (s). IR (neat): ν 1249, 1600, 1749 cm^{-1}. Anal. Calcd for $C_{21}H_{21}F_3O_3$: C, 66.66; H, 5.59. Found: C, 66.53; H, 5.87.

Ethyl 5-Cyclohexyl-2-trifluoromethyl-4-pentenoate (7). A mixture of ethyl 3,3,3-trifluoropropionate (343 mg, 2.2 mmol) and γ-cyclohexyl allyl carbonate (424 mg, 2.0 mmol) was added to a solution of $Pd_2(dba)_3$·$CHCl_3$ (51 mg, 0.05 mmol) and diphenyldiphosphinoethane (dppe) (79 mg, 0.10 mmol) in THF (10 mL) under an argon atmosphere. After the reaction mixture was stirred for 10 h at 60 °C, the mixture was diluted with diethyl ether and then passed though a pad of Celite. On removal of the solvent, the residue was purified by column chromatography on silica gel, eluting with a mixture solution of hexanes−ether (25:1) to give ethyl 5-cyclohexyl-2-trifluoromethyl-4-pentenoate **7** (389 mg) in 70% yield. ^{1}H NMR ($CDCl_3$): δ 0.98−1.05 (1 H, m), 1.11−1.16 (1 H, m), 1.21 (3 H, t, J = 7.08 Hz), 1.26−1.29 (4 H, m), 1.62−1.71 (4 H, m), 1.85−1.90 (1 H, m), 2.45−2.49 (1 H, m), 2.52−2.58 (1 H, m), 3.12 (1 H, dqd, J = 10.0, 8.30, 4.88 Hz), 4.21 (2 H, qd, J = 7.32, 2.19 Hz), 5.26 (1 H, dt, J = 15.4, 7.08 Hz), 5.51 (1 H, dd, J = 15.1, 6.59 Hz).^{13}C NMR ($CDCl_3$): δ 14.6 (s), 26.5 (s), 26.6 (s), 30.0 (q, J = 2.40 Hz), 33.3 (s), 41.1 (s), 51.3 (q, J = 26.8 Hz), 62.1 (s), 121.6 (s), 125.0 (q, J = 280 Hz), 141.4 (s), 167.6 (s). ^{19}F NMR ($CDCl_3$): δ −69.35 (d, J = 9.15 Hz). IR: 1748 (C=O) cm^{-1}. Anal. Calcd for $C_{14}H_{21}F_3O_2$: C, 60.42; H, 7.61. Found: C, 60.69; H, 7.88.

1-Vinyl-1-cyclohexene (10). In the above reaction, [(ethoxycarbonyl)oxymethyl]-methylene-cyclohexane (343 mg, 2.2 mmol) was used and worked up similarly. After stirring for 3 h at 60 °C, the mixture was diluted with diethyl ether and then passed though a pad of Celite. On removal of the solvent,

the residue was purified by column chromatography on silica gel, eluting with a mixture solution of hexanes−ether (25:1) to give 1-vinyl-1-cyclohexene **10** in 86% yield. ^{1}H NMR ($CDCl_3$): δ 1.58−1.63 (2 H, m), 2.11−2.15 (4 H, m), 4.89 (1 H, d, J = 10.5 Hz), 5.06 (1 H, dm, J = 17.4 Hz), 5.76 (1 H, m), 6.35 (1 H, dd, J = 10.7, 17.6 Hz).

2-Phenylethyl 3-Fluoro-2-methylacrylate (12a). ^{1}H NMR ($CDCl_3$): δ 1.80 (3 H, dd, J = 1.46, 3.66 Hz), 2.97 (2 H, t, J = 6.83 Hz), 4.37 (2 H, t, J = 6.84 Hz), 7.20−7.46 (5 H, m), 7.49 (1 H, dq, J = 8.18, 1.47 Hz). ^{13}C NMR ($CDCl_3$): δ 9.03 (d, J = 4.0 Hz), 35.57, 65.64, 114.55 (d, J = 10.9 Hz), 127.09, 129.09 (2 C), 129.35 (2 C), 138.23, 158.49 (d, J = 276 Hz), 167.32 (d, J = 18.5 Hz). ^{19}F NMR ($CDCl_3$): δ −117.19 (dq, J = 80.9, 3.05 Hz). IR (neat): ν 1277, 1663, 1721 (C═O) cm^{-1}. Anal. Calcd for $C_{12}H_{13}FO_2$: C, 69.22; H, 6.29. Found: C, 68.91; H, 6.27.

Ethyl 2-Benzyloxy-3-fluoroacrylate (12b). ^{1}H NMR ($CDCl_3$): δ 1.30 (3 H, t, J = 7.08 Hz), 4.25 (2 H, q, J = 7.08 Hz), 5.03 (2H, s), 7.36 (1 H, d, J = 75.0 Hz), 7.28−7.44 (5 H, m). ^{13}C NMR ($CDCl_3$): δ 14.71, 61.75, 75.13 (d, J = 4.3 Hz), 128.88 (2 C), 128.97 (2 C), 134.41, 136.96, 149.25 (d, J = 275 Hz), 164.08 (d, J = 4.2 Hz). ^{19}F NMR ($CDCl_3$): δ −103.95 (d, J = 74.8 Hz). IR (neat): ν 1275, 1663, 1742 (C═O) cm^{-1}. Anal. Calcd for $C_{12}H_{13}FO_3$: C, 64.28; H, 5.84. Found: C, 64.28; H, 5.69.

4-Ethenyl-3-(2-phenylethoxycarbonyl)-3-trifluoromethyloxolane (15). Diastereomeric ratio, 65:35. IR (neat): ν 1254, 1643, 1741 (C═O) cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 35.29, 49.89, 50.73, 62.53 (q, J = 24.4 Hz), 63.13 (q, J = 25.2 Hz), 67.17, 67.40, 72.57 (q, J = 2.4 Hz), 72.92 (q, J = 1.8 Hz), 73.03, 120.05, 120.95, 125.61 (q, J = 283 Hz), 126.34 (q, J = 289 Hz), 127.31, 129.08, 129.44, 131.61, 131.74, 137.60, 137.79, 167.68 (q, J = 1.6 Hz), 168.60 (q, J = 2.5 Hz). **Major isomer.** ^{1}H NMR ($CDCl_3$): δ 2.98 (1 H, t, J = 6.83 Hz), 3.20 (1 H, q, 8.06 Hz), 3.66 (1 H, t, J = 9.03 Hz), 4.08 (1 H, t, J = 8.07 Hz), 4.31−4.26 (1 H, m), 4.21 (1 H, d, J = 10.0 Hz), 4.38 (2 H, t, J = 7.08 Hz), 5.07 (1 H, d, J = 10.3 Hz), 5.12 (1 H, dt, J = 17.0, 0.98 Hz), 5.44 (1 H, ddd, J = 8.32, 10.3, 17.1 Hz), 7.33−7.21 (5 H, m). ^{19}F NMR ($CDCl_3$): δ −71.80 (s). **Minor isomer.** ^{1}H NMR ($CDCl_3$): δ 2.99 (1 H, t, J = 6.84 Hz), 3.39−3.44 (1 H, m), 3.66−3.70 (1 H, m), 4.04 (1 H, t, J = 7.82 Hz), 4.31−4.26 (1 H, m), 4.14 (1 H, d, J = 10.3 Hz), 4.438 (1 H, t, J = 7.08 Hz), 4.441 (1 H, t, J = 7.08 Hz), 5.16 (1 H, dt, J = 17.1, 1.22 Hz), 5.19 (1 H, d, J = 12.0 Hz), 5.78−5.86 (1 H, m), 7.33−7.21 (5 H, m). ^{19}F NMR ($CDCl_3$): δ −65.93 (s).

4-Ethenyl-3-ethoxycarbonyl-2,2,3-trifluoroxolane (17). Diastereomeric ratio, 65:35. **Major isomer.** ^{1}H NMR ($CDCl_3$): δ 1.36 (3 H, t, J = 7.08 Hz), 3.50−3.59 (1H, m), 4.30−4.39 (2 H, m), 4.36 (1 H, q, J = 7.08 Hz), 4.37 (1 H, q, J = 7.08 Hz), 0.5.33 (1 H, d, J = 7.08 Hz), 5.39 (1 H, d, J = 13.9 Hz), 5.69 (1 H, ddd, J = 7.82, 10.3, 17.1 Hz). ^{13}C NMR ($CDCl_3$): δ 14.51, 47.83 (d, J = 18.4 Hz), 63.68, 71.71, 96.36 (ddd, J = 23.5, 39.5, 208 Hz), 123.22, 127.49 (ddd, J = 25.2, 261, 266 Hz), 127.51 (d, J = 6.9 Hz), 164.02 (d, J = 25.5 Hz). ^{19}F NMR ($CDCl_3$): δ −70.84 (1 F, ddd, J = 7.63, 12.2, 140 Hz), −87.17 (1 F, ddd, J = 3.05, 7.63, 140 Hz), −174.32 (1 F, ddd, J = 7.63, 12.2, 21.4 Hz). IR (neat): ν 1267, 1647, 1768 (C═O) cm^{-1}. **Minor isomer.** ^{1}H NMR ($CDCl_3$): δ 1.35 (3 H, t, J = 7.08 Hz), 3.76−3.88 (1H, m), 4.18 (1 H, ddd, J = 6.38, 8.54, 10.5 Hz), 4.31−4.40 (1 H, m), 4.36 (1 H, q, J = 7.08 Hz), 4.38 (1 H, q, J = 7.08 Hz), 0.5.36 (1 H, dd, J = 0.49, 10.3 Hz), 5.37 (1 H, d, J = 17.3 Hz), 5.74 (1 H, ddd, J = 8.34, 10.3, 17.3 Hz). ^{13}C NMR ($CDCl_3$): δ 14.56, 49.53 (dt, J = 1.6, 21.9 Hz), 63.41, 70.68, 97.36 (ddd, J = 26.6, 31.6, 220 Hz), 123.32, 126.69 (ddd, J = 22.5, 258, 269 Hz), 128.72, 164.33 (dd, J = 2.1, 26.3 Hz). ^{19}F NMR ($CDCl_3$): δ −70.77 (1 F, ddd, J = 3.05, 7.63, 145 Hz), −90.29 (1 F, ddd, J = 4.58, 13.7, 145 Hz), −184.82 (1 F, dd, J = 13.7, 29.0 Hz). IR (neat): ν 1275, 1646, 1757 (C═O) cm^{-1}.

Supporting Information Available: Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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