An Efficient Stereoselective Synthesis of Fluorinated Trisubstituted Alkenes

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Several highly selective synthetic methods have been developed which allow the preparation of various types of materials with excellent regio-, stereo-, and chemoselectivity. In general, the usual synthetic procedure for the target materials is the stepwise formation of the individual bonds. While sequential syntheses (domino reactions) that could form several bonds in one sequence without isolating the intermediates, changing the reaction conditions, or adding reagents have been recognized as being useful in organic synthesis,[1] their synthetic value for alkenes[2,3] and fluorinated alkenes still appears to be grossly underestimated. In nonfluorinated chemistry, the Wittig−Horner reactions and/or tandem vicinal difunctionalization reactions of alkynes are well-known as stereoselective synthetic methods for tri- and tetrasubstituted alkenes.[4] Further, fluorinated alkenes are prepared from the Horner−Wadsworth−Emmons reaction,[5] addition−elimination of polyfluoroethenes,[6] chlorofluorocarbene,[7] ethyl phenylsulfinylfluoroacetate,[8] diethyl 2-oxo-3-fluorobutan-1,4-dioate,[9] and organometallics.[10] Obviously, practical synthetic methods for stereoselective fluorinated alkenes remain an important synthetic challenge.

In this article, we describe the domino reaction to open a new avenue for the stereoselective construction of fluorinated trisubstituted alkenes. The present domino reaction summarized in Table 1 is the same as the "abnormal" Michael reaction.[11] In 1931, Holden and Lapworth have been reported the synthesis of ethyl α-methylcinnamate from the reaction of benzylideneacetophenone and diethyl methylmalonate in the system of powdered sodium−benzene under reflux.[12] However, no other examples have been reported to our knowledge. To use the above system as a selective synthetic method for trisubstituted alkenes, we have modified the starting substrates and reaction conditions.

In the present reaction, when the reaction was attempted at room temperature, the Michael addition reaction proceeded except for entries 7, 9, and 10; however, under refluxing the reaction pathway changed from a Michael addition to a domino reaction to produce the stereocontrolled alkenes. Table 1 summarized the reaction of various types of donors with α,β-unsaturated carbonyl compounds.

The stereochemistry of products **2** was confirmed by ^{1}H NMR coupling constants (J_{H-F}) and chemical shifts of the olefinic protons. It is well-known that the coupling constant (J_{H-F}) of the *Z*-isomer is 25−45 Hz and that J_{H-F} of the *E*-isomer is 10−20 Hz.[13] Further, the signal of the olefinic proton for the case of the carbonyl group in the *cis* position is present in the area δ 6−7 ppm and that for the *trans* position is present at δ 5.5−6 ppm.[14] On the basis of the coupling constant (J_{H-F} = ∼35 Hz) and chemical shift of produced materials, the stereochemistry of the obtained materials is that of the *Z*-isomer. In the case of ethyl 3-fluoroalkyl-2-propenoates, the stereochemistry is that of the *E*-isomer on the basis of the signal area (δ 6−7 ppm) of the olefinic proton.

Furthermore, this stereoselective synthesis of alkenes was observed when α,β-unsaturated ketones and esters were employed as acceptors (entries 16−21). For example, in the case of R^1 being Me (entries 16−18), the influence of the substitution pattern of the Y group (from methyl and phenyl to methoxy) directly appeared on the reaction pathway. In sharp contrast to the present case, it is interesting to note that the methyl substitutent (entry 16) proceeds as the normal Michael addition reaction in 59% yield. However, employment of the phenyl substituent (R = Ph, entry 19) and/or phenyl or methoxy instead of methyl group (R^1) turned out to completely accelerate the desired reaction pathway to furnish the alkene (entries 17−21). In the cases of 2-alkylmalonates (entries 24 and 25), the starting material (2-alkylmalonate; 50% recovered in entry 24 and 53% recovered in entry 25) was recovered after quenching the reaction. From the above result, it seems that the Michael addition reaction as a first step in this system is not easy in entries 24 and 25. However, as the carbon−carbon double bond modified by the fluoroalkyl group is revealed to have a significantly lower LUMO energy level than the corresponding nonfluorinated

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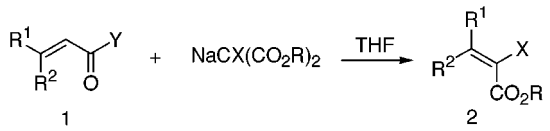
Table 1. Stereoselective Synthesis of Trisubstituted Alkenes



entry	product no.	R^1	R^2	R	X	Y	yield (%)	*E*:*Z* ratio
1	2a	Me	H	Me	F	*t*-Bu	30	0:100
2	2b	Et	H	Me	F	*t*-Bu	71	2:98
3	2c	*n*-Pr	H	Me	F	*t*-Bu	68	0:100
4	2d	*i*-Pr	H	Me	F	*t*-Bu	63	3:97
5	2e	*n*-Bu	H	Me	F	*t*-Bu	38	0:100
6	2f	*t*-Bu	H	Me	F	*t*-Bu	29	0:100
7	2g	*n*-Pent	H	Me	F	*t*-Bu	26[a]	0:100
8		*n*-Pent	H	Me	F	*t*-Bu	9	0:100
9	2h	Ph	H	Me	F	*t*-Bu	60[a]	0:100
10		Ph	H	Me	F	*t*-Bu	46[a]	0:100
11		Ph	H	Me	F	*t*-Bu	30	0:100
12	2i	$CH_3CH(OTBS)$	H	Me	F	*t*-Bu	58	9:91
13	2j	$CH_3CH(OMOM)$	H	Me	F	*t*-Bu	62	5:95
14	2k	$CH_3CH(Ph)$	H	Me	F	*t*-Bu	94	3:97
15	2l	$CH_3CH(OTBS)CH_2$	H	Me	F	*t*-Bu	93	0:100
16	2a	Me	H	Me	F	Me	(59)[d]	
17		Me	H	Me	F	Ph	50	0:100
18		Me	H	Me	F	OMe	57	0:100
19	2h	Ph	H	Me	F	Me	73	0:100
20		Ph	H	Me	F	Ph	73	0:100
21		Ph	H	Me	F	OMe	82	0:100
22	2m	Ph	Me	Me	F	*t*-Bu	NR[e]	
23	2n	Ph	Me	Et	Me	*t*-Bu	NR[e]	
24	2o	Ph	H	Et	Me	Ph	30[f]	0:100
25	2h	Ph	H	Et	Et	Ph	13[g]	0:100
26	2p	CF_3	H	Et	Me	OEt	64[b]	100:0
27	2q	CF_3	H	Et	Et	OEt	55[b]	100:0
28	2r	CHF_2	H	Et	Me	OEt	53[c]	100:0
29	2s	CHF_2	H	Et	Et	OEt	51[c]	100:0

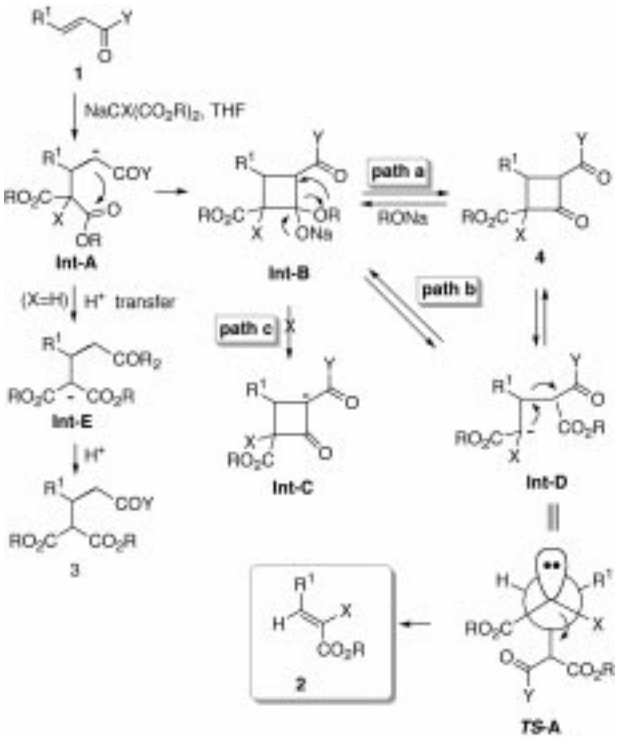
[a] Reactions were carried out under reflux except for entries 7, 9, and 10. Entries 7 and 9 were carried out at 0 °C, and entry 10 was reacted at rt. [b] Entries 26 and 27 were carried out at −40 °C. [c] Entries 28 and 29 were reacted at 0 °C at rt. [d] Yield of the normal Michael addition reaction. [e] Recovered the starting material. [f] Recovered starting material: 50%. [g] Recovered starting material: 53%.

materials, which demonstrates the higher electrophile reactivity,[15] employment of 3-fluoromethyl-2-propenoates accelerated the Michael addition reaction pathway to furnish the desired alkenes (entries 26−29).

When we examined the above reaction using $NCCH_2CO_2Et$ or $CH_2(CO_2Et)_2$ as a donor, the target alkene was not obtained, and (*Z*)-olefin $MeCH(OTBS)CH{=}CHCO_2Me$ as an acceptor was recovered. Further, entries 22 and 23 suggest that this synthetic process did not work for the preparation of tetrasubstituted alkene.

In the next stage, we tried to reveal the reaction pathway (Scheme 1). In this system, it is important to note that two kinds of products, such as fluorinated α,*β*-unsaturated esters **2** and *β*-keto esters, are obtained. Further, diethyl malonate as the donor only produced a Michael addition product, and this observation might be explained by the formation of a stable intermediate by the proton transfer of malonate (proton transfer from **Int-A** to **Int-E**) to produced a Michael addtion product **3**, which led us to conclude that 2-substituted malonates were required as a donor in the present domino reaction. Moreover, to make clear the conversion to **Int-C** by the elimination of RONa from **Int-B**, ethyl α-methyl cinnamate as an acceptor to deter the path c only produced methyl (*Z*)-3-phenyl-2-fluoropropenoate (**2h**). From the above results, the mechanism of the present reaction was explained as follows. The path a was one possible route for conversion to compound **4** by the elimination of MeONa from **Int-B** and then alkoxide anion attack on

Scheme 1. Reaction Mechanism of the Present Domino Reaction



the ketone carbonyl group of cyclobutanone **4**, accelerating the C−C bond dissociation of cyclobutanone to furnish **Int-D** (***TS*-A**). The other route was path b which involved conversion directly from **Int-B** to **Int-D**.

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The stereoselective synthesis of alkenes described above was thus attributed to the bulkiness of substituent groups and the anti elimination reaction process via ***TS-A***.

As depicted in the several types of combinations shown in Table 1, we have found that this process was a convienient synthetic procedure for production of fluorinated trisubstituted alkenes.

Experimental Section

General Methods. All commercially available reagents were used without further purification. Chemical shifts of ^{1}H (500 MHz and/or 300 MHz) and ^{13}C NMR (50 MHz) spectra were recorded in ppm (δ) downfield from the internal standard of Me_4-Si, δ 0.00, in $CDCl_3$. The ^{19}F (470 or 280 MHz) NMR spectra were recorded in ppm downfield from internal standard of C_6F_6 in $CDCl_3$ using a VXR 500 or a VXR 300 instrument.

Methyl (*Z*)-3-Substituted 2-fluoro-2-propenoate (2). To a solution of NaH (0.08 g, 2 mmol) and THF (2 mL), dimethyl 2-fluoromalonate (0.30 g, 2 mmol) in dried THF (2 mL) was added at 0 °C under a nitrogen atmosphere, and then the mixture was stirred for 30 min at that temperature. To the above solution, α,β-unsaturated *tert*-butyl ketone (2 mmol) was added, and the whole batch was refluxed for 4 h under a nitrogen atmosphere. After the reaction was quenched with ice water, oily materials were extracted with diethyl ether (3 × 15 mL), and the ethereal extract was washed with brine (3 × 10 mL) and dried over $MgSO_4$. On removal of the solvent, the yield was determined by the ^{19}F NMR integral intensities using hexafluorobenzene as an internal stadard. The resultant crude product was purified by chromatography on silica gel.

Methyl (*Z*)-2-Fluoro-2-butenoate (2a).[9] ^{1}H NMR: δ 1.80 (3 H, dd, J = 7.50, 3.00 Hz), 3.82 (3 H, s), 6.18 (1 H, dq, J = 33.0, 7.25 Hz). ^{19}F NMR: δ 30.0 (dq, J = 32.0, 3.06 Hz). ^{13}C NMR: δ 9.47 (d, J = 4.20 Hz), 52.1 (s), 148.5 (d, J = 255 Hz), 161.0 (d, J = 35.5 Hz).

Methyl (*Z*)-2-Fluoro-2-pentenoate (2b).[9] ^{1}H NMR: δ 1.07 (3 H, t, J = 7.57 Hz), 2.27 (2 H, dquint, J = 7.57, 2.20 Hz), 3.82 (3 H, s), 6.13 (1 H, dt, J = 33.5, 7.82 Hz). ^{19}F NMR: δ 30.1 (d, J = 33.6 Hz). ^{13}C NMR: δ 17.7 (d, J = 3.30 Hz), 26.0 (d, J = 2.60 Hz), 52.2 (s), 122.4 (d, J = 11.7 Hz), 147.3 (d, J = 254 Hz), 161.3 (d, J = 35.4 Hz).

Methyl (*Z*)-2-Fluoro-2-hexenoate (2c).[10a] ^{1}H NMR: δ 0.95 (3 H, t, J = 7.50 Hz), 1.48 (2 H, sex., J = 7.00 Hz), 2.23 (2 H, dq, J = 7.50, 2.00 Hz), 3.82 (3 H, s), 6.13 (1 H, dt, J = 33.5, 8.00 Hz,). ^{19}F NMR: δ 30.5 (d, J = 33.6 Hz). ^{13}C NMR: δ 13.4 (s), 26.0 (d, J = 2.60 Hz), 52.1 (s), 120.6 (d, J = 11.6 Hz), 147.7 (d, J = 254 Hz), 161.1 (d, J = 35.4 Hz).

Methyl (*Z*)-2-Fluoro-4-methyl-2-pentenoate (2d).[10a] ^{1}H NMR: δ 1.06 (3 H, s), 1.07 (3 H, s), 2.86 (1 H, dsept, J = 6.83, 0.97 Hz), 3.81 (3 H, s), 5.99 (1 H, dd, J = 33.7, 9.77 Hz). ^{19}F NMR: δ 29.9 (d, J = 33.6 Hz). ^{13}C NMR: δ 21.7 (s), 24.3 (d, J = 2.10 Hz), 52.0 (s), 127.1 (d, J = 11.1 Hz), 140.1 (d, J = 254 Hz), 161.2 (d, J = 35.8 Hz).

Methyl (*Z*)-2-Fluoro-2-heptenoate (2e).[9] ^{1}H NMR: δ 0.92 (3 H, t, J = 7.50 Hz), 1.36 (2 H, m), 1.43 (2 H, m), 2.25 (2 H, qd, J = 7.50, 2.00 Hz), 3.82 (3 H, s), 6.13 (1 H, dt, J = 33.5, 7.50 Hz). ^{19}F NMR: δ 30.4 (d, J = 33.4 Hz). ^{13}C NMR: δ 13.7 (s), 22.2 (s), 23.9 (d, J = 2.70 Hz), 30.4 (s), 52.3 (s), 121.1 (d, J = 11.9 Hz), 147.7 (d, J = 255 Hz), 161.3 (d, J = 35.7 Hz).

Methyl (*Z*)-2-Fluoro-4,4-dimethyl-2-pentenoate (2f).[10a] ^{1}H NMR: δ 1.19 (9 H, d, J = 0.94 Hz), 3.80 (s), 6.07 (d, J = 38.5 Hz). ^{19}F NMR: δ 32.8 (d, J = 38.1 Hz). ^{13}C NMR: δ 29.5 (d, J = 3.4 Hz), 32.1 (d, J = 1.9 Hz), 52.2 (s), 129.2 (d, J = 6.7 Hz), 146.3 (d, J = 256 Hz), 161.8 (d, J = 35.8 Hz).

Methyl (*Z*)-2-Fluoro-2-octenoate (2g).[8] ^{1}H NMR: δ 0.89 (3 H, t, J = 7.00 Hz), 1.31 (4 H, m), 1.44 (2 H, quint, J = 7.00 Hz), 2.24 (2 H, qd, J = 7.50, 2.50 Hz), 3.81 (3 H, s), 6.12 (1 H, dt, J = 33.5, 8.00 Hz). ^{19}F NMR: *Z*-isomer, δ 28.6 (d, J = 30.1 Hz); *E*-isomer, δ 36.2 (d, J = 19.7 Hz). ^{13}C NMR: δ 13.8 (s), 22.2 (s), 24.1 (d, J = 2.70 Hz), 27.9 (s), 31.2 (s), 52.1 (s), 121.0 (d, J = 11.7 Hz), 147.6 (d, J = 255 Hz), 161.2 (d, J = 35.5 Hz).

Methyl (*Z*)-2-Fluorocinnamate (2h).[10a] ^{1}H NMR: δ 3.83 (3 H, s), 6.86 (1 H, d, J = 35.2 Hz), 7.32−7.58 (5 H, m). ^{19}F NMR: δ 36.1 (d, J = 35.1 Hz). ^{13}C NMR: δ 52.4 (s), 117.6 (d, J = 4.60 Hz), 127.9 (s), 128.7 (s), 129.6 (d, J = 2.80 Hz), 130.2 (d, J = 8.10 Hz), 130.9 (d, J = 4.30 Hz), 146.6 (d, J = 267 Hz), 161.7 (d, J = 34.5 Hz). Anal. Calcd for $C_{10}H_9FO_2$: C, 66.66; H, 5.03. Found: C, 66.78; H, 5.25.

Methyl 2-Fluoro-4-[(*tert*-butyldimethylsilyl)oxy]-2-pentenoate (2i). ^{1}H NMR: δ 0.05 (s), 0.07 (s), 0.88 (s), 1.29 (3 H, d, J = 6.00 Hz), 3.84 (s), 4.81 (1 H, qd, J = 8.00, 1.50 Hz), 6.13 (dd, J = 33.5, 8.50 Hz). ^{19}F NMR: *Z*-isomer, δ 32.8 (d, J = 33.4 Hz); *E*-isomer, 36.5 (d, J = 19.7 Hz). ^{13}C NMR: δ −5.09 (s), −4.94 (s), 18.0 (s), 25.7 (s), 26.0 (s × 3), 52.4 (s), 62.4 (d, J = 3.10 Hz), 124.9 (d, J = 9.50 Hz), 145.3 (d, J = 257 Hz), 161.1 (d, J = 36.0 Hz). Anal. Calcd for $C_{13}H_{23}FO_3Si$: C, 54.93; H, 8.83. Found: C, 54.67; H, 8.98.

Methyl 2-Fluoro-4-[(1-methoxymethyl)oxy]-2-pentenoate (2j). ^{1}H NMR: *Z*-isomer, δ 1.33 (3 H, d, J = 6.59 Hz), 3.37 (3 H, s), 3.83 (3 H, s), 4.59 (1 H, d, J = 6.84 Hz), 4.62 (1 H, dd, J = 6.83, 0.49 Hz), 4.73 (1 H, quint d, J = 6.59, 0.98 Hz), 6.10 (1 H, dd, J = 33.2, 8.54 Hz). ^{19}F NMR: *Z*-isomer, δ 34.6 (d, J = 32.0 Hz); *E*-isomer, 40.4 (d, J = 19.8 Hz). ^{13}C NMR: *Z*-isomer, δ 20.5 (d, J = 1.90 Hz), 55.2 (s), 65.5 (s), 94.5 (s), 121.8 (d, J = 9.80 Hz), 147.2 (d, J = 260 Hz), 160.7 (d, J = 35.7 Hz). Anal. Calcd for $C_8H_{13}FO_4$: C, 50.00; H, 6.82. Found: C, 50.09; H, 6.78.

Methyl 2-Fluoro-4-phenyl-2-pentenoate (2k).[10e] ^{1}H NMR: *Z*-isomer, δ 1.44 (3 H, d, J = 6.84 Hz), 3.81 (3 H, s), 4.04 (1 H, dq, J = 10.8, 7.08 Hz), 6.27 (1 H, dd, J = 32.5, 10.3 Hz), 7.29 (5 H, m). ^{19}F NMR: *Z*-isomer, δ 31.0 (d, J = 33.6 Hz); *E*-isomer, δ 38.1 (d, J = 21.4 Hz). ^{13}C NMR: *Z*-isomer, δ 20.8 (s), 34.9 (s), 52.3 (s), 124.9 (d, J = 10.9 Hz), 126.7 (s), 126.8 (s), 128.7 (s), 143.3 (s), 146.3 (d, J = 256 Hz), 161.2 (d, J = 35.7 Hz). Anal. Calcd for $C_{11}H_{13}FO_2$: C, 67.33; H, 6.68. Found: C, 67.71; H, 6.38.

Methyl (*Z*)-2-Fluoro-5-[(*tert*-butyldimethylsilyl)oxy]-2-heptenoate (2l). ^{1}H NMR: δ 0.04 (3 H, s), 0.05 (3H, s), 0.88 (9 H, s), 1.16 (3 H, d, J = 6.10 Hz), 2.36 (2 H, dt, J = 7.81, 1.96 Hz), 3.82 (s), 3.93 (1 H, sex., J = 5.86 Hz), 4.18 (2 H, q), 6.21 (1 H, dt, J = 32.1, 7.81 Hz). ^{19}F NMR: δ 30.2 (d, J = 32.1 Hz). ^{13}C NMR: δ −5.06 (s), −4.71 (s), 17.9 (s), 23.5 (s), 25.6 (s × 3), 34.2 (s), 53.4 (s), 67.2 (s), 117.6 (d, J = 11.5 Hz), 148.3 (d, J = 252 Hz), 161.0 (d, J = 35.7 Hz). Anal. Calcd for $C_{14}H_{25}FO_3Si$: C, 56.49; H, 9.12. Found: C, 56.31; H 8.83.

Ethyl (*E*)-3-(Trifluoromethyl)-2-methyl-2-propenoate (2p). To a solution of NaH (0.08 g, 2 mmol) and THF (2 mL), diethyl 2-methylmalonate (2 mmol) in dried THF (2 mL) was added at 0 °C under a nitrogen atmosphere, and then the mixture was stirred for 30 min at that temperature. To the above solution, ethyl 3-(trifluoromethyl)-2-propenoate (4 mmol) was added, and the whole batch was stirred at −78 to −40 °C for 4 h under a nitrogen atmosphere. After quenching with ice water, oily materials were extracted with diethyl ether (3 × 15 mL) and the ethereal extract was washed with brine (3 × 10 mL) and dried over $MgSO_4$. On removal of the solvent, the yield was determined by the ^{19}F NMR integral intensities using hexafluorobenzene as an internal stadard. The resultant crude product was purified by chromatograph on silica gel. ^{1}H NMR: δ 1.33 (3 H, t, J = 7.14 Hz), 2.10 (3 H, dq, J = 2.50, 1.65 Hz), 4.27 (2 H, q, J = 7.14 Hz), 6.68 (1 H, qq, J = 8.24, 1.65 Hz). ^{19}F NMR: δ 102.4 (dq, J = 8.60, 2.60 Hz). ^{13}C NMR: δ 13.4 (s), 13.9 (s), 61.8 (s), 122.9 (q, J = 267 Hz), 125.8 (q, J = 34.8 Hz), 139.7 (q, J = 5.40 Hz), 165.9 (s). Anal. Calcd for $C_7H_9F_3O_2$: C, 46.16; H, 9.82. Found: C, 45.94; H, 4.82.

Ethyl (*E*)-3-(Trifluoromethyl)-2-ethyl-2-propenoate (2q). ^{1}H NMR: δ 1.10 (3 H, t, J = 7.42 Hz), 1.34 (3 H, t, J = 7.14 Hz), 2.53 (2 H, qq, J = 7.42, 1.37 Hz), 4.27 (2 H, q, J = 7.14 Hz), 6.61 (1 H, q, J = 8.51 Hz). ^{19}F NMR: δ 102.9 (dt, J = 8.62, 1.73 Hz). ^{13}C NMR: δ 13.4 (s), 13.9 (s), 21.3 (s), 61.7 (s), 122.9 (q, J = 272 Hz), 125.2 (q, J = 35.1 Hz), 145.6 (t, J = 4.60 Hz), 165.6 (s). Anal. Calcd for $C_8H_{11}F_3O_2$: C, 48.98; H, 5.65. Found: C, 48.59; H, 5.73.

Ethyl (*E*)-3-(Difluoromethyl)-2-methyl-2-propenoate (2r). ^{1}H NMR: δ 1.15 (3 H, t, J = 7.14 Hz), 1.82 (3 H, dt, J = 1.65, 1.37 Hz), 4.07 (2 H, q, J = 7.14 Hz), 6.25 (1 H, dt, J = 54.9, 6.32 Hz), 6.49 (1 H, qdt, J = 8.24, 4.95, 1.37 Hz). ^{19}F NMR: δ 48.5 (ddq, J = 55.2, 9.47, 2.59 Hz). ^{13}C NMR: δ 12.9 (s), 13.9 (s), 61.4 (s), 111.9 (t, J = 233 Hz), 130.3 (t, J = 26.4 Hz), 136.5 (t, J = 11.2 Hz), 166.3 (s). Anal. Calcd for $C_7H_{10}F_2O_2$: C, 51.22; H, 6.14. Found: C, 51.54; H, 6.49.

Ethyl (*E*)-3-(Difluoromethyl)-2-ethyl-2-propenoate (2s). ^{1}H NMR: δ 1.10 (3 H, t, J = 7.69 Hz), 1.33 (3 H, t, J = 7.15 Hz), 2.43 (2 H, qt, J = 7.42, 1.65 Hz), 4.26 (2 H, q, J = 7.14 Hz), 6.43 (1 H, td, J = 55.2, 6.32 Hz), 6.61 (1 H, td, J = 9.34, 6.32 Hz). ^{19}F NMR: δ 49.4 (ddt, J = 54.3, 10.3, 1.72 Hz). ^{13}C NMR: δ 12.9 (s), 14.0 (s), 20.8 (s), 61.3 (s), 111.7 (t, J = 233 Hz), 129.8 (t, J = 26.6 Hz), 142.6 (t, J = 11.7 Hz), 166.0 (s). Anal. Calcd for $C_8H_{12}F_2O_2$: C, 53.93; H, 6.79. Found: C, 53.95; H, 6.48.

Supporting Information Available: NMR spectra (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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