Ready Carbon−Carbon Bond Formation of 2-(Trifluoromethyl)acrylate via Michael Addition Reactions

Takashi Yamazaki,* Shuichi Hiraoka, and Tomoya Kitazume*

Department of Bioengineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

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We have previously reported the Michael addition reactions of ethyl 3-(trifluoromethyl)acrylate, (*E*)-**1**, with various types of lithium enolates, and this procedure was found to furnish the corresponding adducts **2** with good to excellent chemical yields as well as diastereoselectivities (Scheme 1).[1,2] Intramolecular Li−F interactions[1,3] were computationally proven to play a significantly important role in the above reaction, stabilizing the intermediate **Int-A** and enabling the Michael addition even with ketone enolates under kinetically controlled conditions.

During our continuing study on the stereoselective construction of CF_3-containing materials, our attention was focused on the use of the isomeric α,β-unsaturated ester **3**. Consideration of its electronic structure compared to the corresponding nonfluorinated counterpart or (*E*)-**1** proved that they have basically similar characteristics at the reaction site (β-position of a carbonyl moiety) on the basis of the p_z orbital coefficient of LUMO and electron density[4] (Figure 1). On the other hand, the strongly electron-withdrawing trifluoromethyl group was found to play an important role for lowering the LUMO energy levels compared to that of nonfluorinated methacrylate, the difference being 0.75 eV. These results as well as the possible formation of the similar 6-membered intermediate **Int-B** from **3** when reacted with lithium enolates (Scheme 1) prompted us to employ this material as a Michael acceptor.[5] In spite of our expectations, however, this procedure only yielded polymeric products upon reaction with enolates possessing lithium, sodium, and potassium as the counter cation, probably due to the ready loss of metal fluoride from **Int-B**,[6] followed by the anionic polymerization with **3** and/or **4**. The authors then assumed that the above polymerization would be suppressed by the employment of much weaker *nonmetallic nucleophiles* on the basis of the high activity of the acceptor **3**, and enamines, imines, or active methylene compounds were selected as Michael donors.[7]

As expected, Michael addition reaction of enamines (1.2 equiv) to **3** proceeded very smoothly even at −78 °C within 15 min to afford the corresponding 1,4-adducts **6** in good yields with moderate diastereoselectivity without

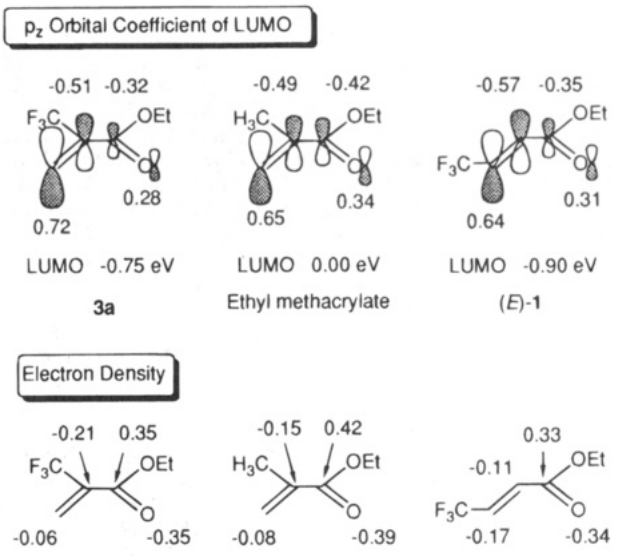
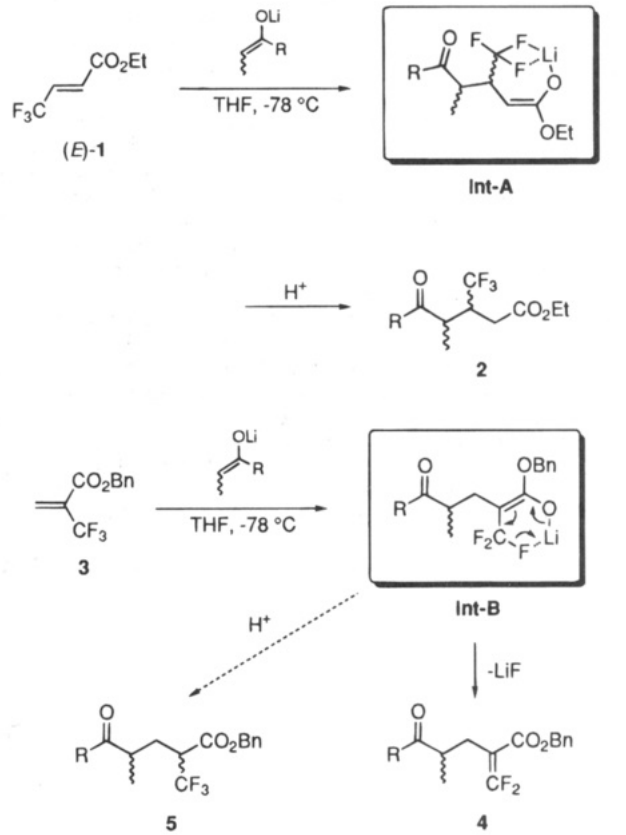


Figure 1.

Scheme 1



(1) Yamazaki, T.; Haga, J.; Kitazume, T.; Nakamura, S. *Chem. Lett.* **1991**, 2171−2174.

(2) Yamazaki, T.; Haga, J.; Kitazume, T. *Chem. Lett.* **1991**, 2175−2178.

(3) The same type of interaction was recently reported by some groups, see: (a) Tonachini, G.; Canepa, C. *Tetrahedron* **1989**, *45*, 5163−5174. (b) Wong, S. S.; Paddon-Row, M. N. *J. Chem. Soc., Chem. Commun.* **1991**, 327−330. (c) Dixon, D. A.; Smart, B. E. In *Selective Fluorination in Organic and Bioorganic Chemistry;* Welch, J. T., Ed.; ACS Symposium Series No. 456; ACS: Washington, D.C., 1991; pp 18−35. (d) van Eikema Hommes, N. J. R.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 755−758. (e) Iwata, S.; Qian, C.-P.; Tanaka, K. *Chem. Lett.* **1992**, 357−360.

(4) The semiempirical molecular orbital calculation was performed by MOPAC v. 6.10 (AM1) implemented in the CAChe Worksystem (SONY/Tektronix Corporation) for the conformers obtained from the rigid search method, followed by their optimization by the eigenvector following the minimization (EF) method with the extra keyword "PRECISE", final gradient norm being less than 0.01 kcal/Å. Molecular mechanics were also carried out with this system.

(5) Yamazaki, T.; Ohnogi, T.; Kitazume, T. *Tetrahedron: Asymmetry* **1990**, *1*, 215−218. For the conjugate addition of heteroatoms, see: (a) Ojima, I.; Jameison, F. A. *BioMed. Chem. Lett.* **1991**, *1*, 581−584. (b) Ojima, I.; Kato, K.; Nakanishi, K. *J. Org. Chem.* **1989**, *54*, 4511−4522. (c) Kitazume, T.; Murata, K.; Kokusho, Y.; Iwasaki, S. *J. Fluorine Chem.* **1988**, *39*, 75−86.

(6) (a) Kitazume, T.; Ohnogi, T.; Miyauchi, H.; Yamazaki, T.; Watanabe, S. *J. Org. Chem.* **1989**, *54*, 5630−5632. (b) Fuchikami, T.; Shibata, Y.; Suzuki, Y. *Tetrahedron Lett.* **1986**, *27*, 3173−3176.

(7) For a review of the Michael addition of enamines, see: Oare, D. A.; Heathcock, C. H. *Top. Stereochem.* **1991**, *20*, 87−170.

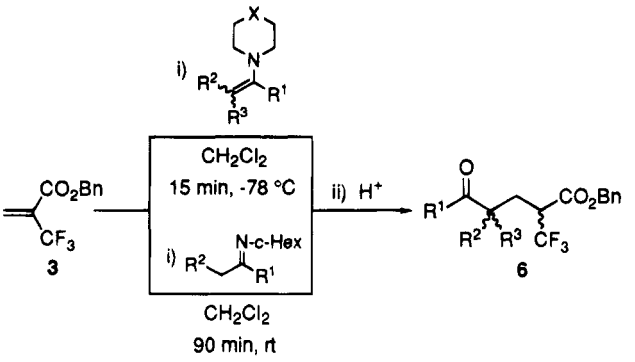
0022-3263/94/1959-5100$04.50/0

Table 1. Michael Addition of 2-(Trifluoromethyl)acrylates with Various Nucleophiles

compd	R^1	R^2	R^3	X	yield[a] (%)	diastereoselectivity[b]
			Enamines			
6a	$-(CH_2)_4-$		H	O	87	75:25
6b	H	Me	Me	O	78	
6c	Et	Me	H	O	66	67:33
6d	H	Me	H	CH_2	75	63:37
6d	H	Me	H	CH_2	75	89:11[c]
			Imines			
6d	H	Me			64	55:45
6a	$-(CH_2)_4-$				69	53:47
			Active Methylene Compounds			
7a	H				98[d]	
7b	AcNH				94	
7c	Me				69	
8	Me[e]				45	

[a] Isolated yields. [b] Determined by capillary GC. [c] 1 equiv of cinchonidine was added. The adduct was found to be almost racemic. [d] 1:1 diastereomer mixture with regard to the two CF_3-attached carbons. [e] NaH was employed as a base.

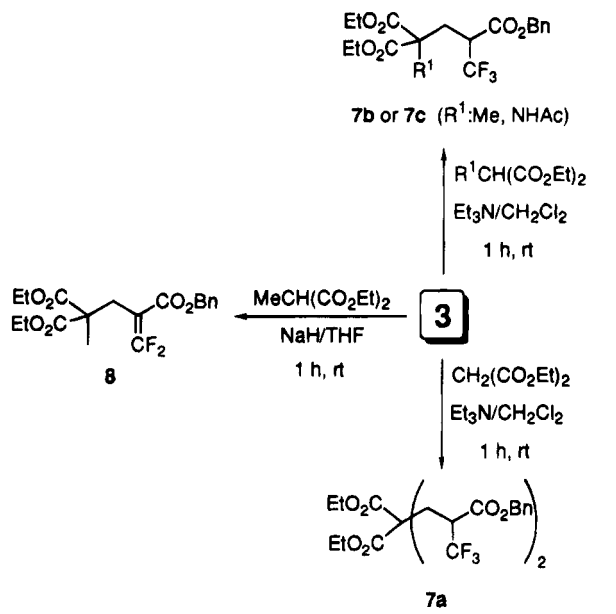
Scheme 2



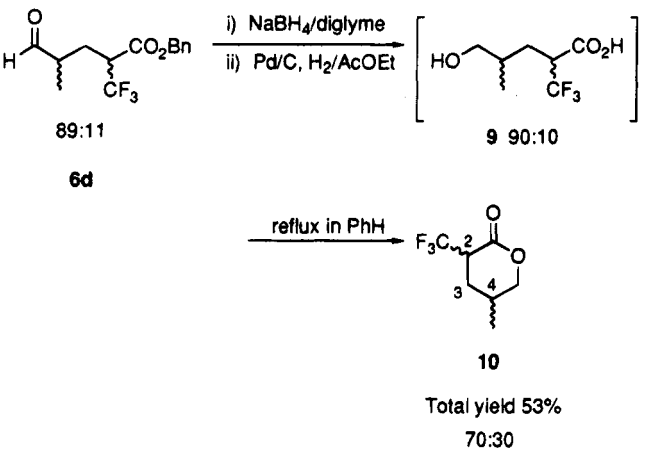
any detectable formation of polymeric products (Table 1, Scheme 2). It was revealed that a wide range of solvents, such as *n*-hexane, ether, THF, methylene chloride, DMF, and so on, could be used in the present procedure. Although many of them furnished comparable results, DMF was the exception, leading to a less clean reaction mixture observed by ^{19}F NMR. For the induction of chirality, when 1 equiv of (−)-cinchonidine was premixed with **3** (for 30 min at room temperature) for constructing the complex, followed by the reaction with enamine under the same reaction conditions, the adduct was isolated with comparable chemical yield and enhanced diastereoselectivity, but with almost no asymmetric induction (Table 1). An important observation during our investigation was that the purity of enamine affects both the reaction rate and diastereoselectivity significantly, and thus, it is highly recommended to employ freshly distilled enamines for this procedure.[8]

On the other hand, imines were also found to add to **3** presumably via their enamine forms,[8,9] but more slowly at −78 °C. This phenomenon could be rationalized as the result of the slow *in situ* tautomerization at that temperature, while they reacted at an acceptable rate at ambient temperature. Michael addition also proceeded with α-substituted malonic esters (1.5 equiv) in the presence of triethylamine (1.5 equiv) in good yields, but the parent diethyl malonate was proven to afford the 1:2 adduct in excellent yield (Scheme 3). The authors also tried the same reaction with the enolate from diethyl methylmalonate using NaH as a base. Although the smooth conjugate addition to **3** was observed, the isolated material **8** (45% yield) was proven to contain the α,β-unsaturated carbonyl structure with two fluorines at the terminal carbons. This experimental result unambiguously supported our hypothesis that the absence of the metal is essential for the isolation of the Michael adducts without any elimination of fluoride ion.

Scheme 3



Scheme 4



For the determination of stereochemistry, 1,4-adduct **6d** in Scheme 2 (R^1, R^3 = H, R^2 = Me) was converted to the corresponding lactone **10**. During this procedure, it was noted that (i) employment of protic solvents for the reduction and hydrogenation processes (such as ethanol for both cases) accelerates the epimerization rate at the 2-position and (ii) the cyclization condition similarly affects the epimerization and addition of standard acid catalysts such as *p*-TsOH or PPTS in benzene only furnished a stereorandom mixture. However, we succeeded in the conversion of **6d** to **9** with the complete retention of the inherent stereochemistry by using aprotic solvents as shown in Scheme 4, while a small amount of epimerization was still observed at the last stage to

(8) Amines in enamines as impurities interfere with the present Michael reaction because, in the separate experiment, the rate of the 1,4-addition of amines is found to be fast enough to compete with the desired reaction course.

(9) For Michael addition of imines, see: Pfau, M.; Revial, G.; Guingant, A.; d'Angelo, J. *J. Am. Chem. Soc.* **1985**, *107*, 273–274.

access **10**. ^{1}H NMR spectrum of this compound showed the coupling constants between H^2—H^3 and H^3—H^4 of 8.67 and 7.45 (or 7.81) Hz for the major isomer and 12.2 and 10.6 Hz for the minor isomer, respectively. On the other hand, MM2 [or MOPAC (PM3)] calculations[4] predicted 5.9 and 4.0 Hz [4.7 and 3.6 Hz] for the *anti* isomer and 8.8 and 8.8 Hz (7.9 and 8.9 Hz) for the *syn* isomer, respectively. While these values did not completely correspond to the observed coupling constants, comparison of these trends assumed the major Michael product possessing the *anti* relationship.

As described above, the authors have observed the ready carbon–carbon bond formation for **3**[10] via the Michael addition reaction and conversion of the obtained Michael adducts to the corresponding lactones, **10**. These data clearly demonstrate the difficulty of preparation or handling of 2-trifluoromethylated carbonyl compounds due to the acidic proton at the 2-position. Studies are in progress in our laboratory for developing a method to construct such materials with retention of the inherent stereochemistry.

Experimental Section[11]

General Procedure for the Michael Addition Reaction. To a solution of benzyl 2-(trifluoromethyl)acrylate (460 mg, 2.0 mmol) in freshly distilled methylene chloride (8 mL) was added an enamine (1.2 equiv) in the same solvent (2 mL) at −78 °C under nitrogen, and the mixture was stirred for 15 min at that temperature. After the reaction was quenched with 1 N HCl (aq), extraction was carried out with methylene chloride twice, and the combined organic layers were washed with water, dried over $MgSO_4$, and concentrated. The desired material was obtained after purification by silica gel chromatography.

When an imine was employed as a donor, the reaction was conducted at room temperature and the mixture was stirred for 1.5 h at that temperature. On the other hand, in the case of an active methylene compound, a donor (1.5 equiv) was added to the above solution containing the acceptor, followed by the addition of triethylamine (1.5 equiv) at room temperature. The mixture was stirred for 2 h at that temperature.

Benzyl 2-(trifluoromethyl)-4-(1-oxocyclohex-2-yl)propanoate (6a): yield 87% (75:25 diastereomer mixture); ^{1}H NMR major diastereomer δ 1.5–2.5 (11 H, m), 3.53 (1 H, ddq, J = 3.6, 8.3, 11.8 Hz), 5.14 (1 H, d, J = 12.2 Hz), 5.25 (1 H, J = 12.2 Hz), 7.30–7.43 (5 H, m); minor diastereomer δ 3.29 (1 H, ddq, J = 5.4, 8.3, 16.6 Hz), 5.14 (1 H, d, J = 12.2 Hz); ^{13}C NMR major diastereomer δ 25.18, 26.64, 28.08, 35.21, 42.13, 47.57, 48.20 (q, J = 27.6 Hz), 67.31, 126.13 (q, J = 280.1 Hz, 128.40, 128.51, 128.69, 135.21, 167.69, 211.67; minor diastereomer δ 25.02, 27.88, 33.77, 42.02, 47.98 (q, J = 27.4 Hz), 67.47; ^{19}F NMR major diastereomer δ 9.61 (d, J = 6.9 Hz); minor diastereomer δ 10.39 (d, J = 8.3 Hz); IR (neat) diastereomer mixture ν 2950, 1710, 1745.

Benzyl 2-(trifluoromethyl)-4-formyl-4-methylpentanoate (6b): yield 78%; ^{1}H NMR δ 1.04 (3 H, s), 1.05 (3 H, s), 1.88 (1 H, dd, J = 2.2, 14.6 Hz), 2.32 (1 H, dd, J = 10.7, 14.6 Hz), 3.16 (1 H, ddq, J = 2.2, 8.5, 10.7 Hz), 5.18 (2 H, s), 7.36 (5 H, s), 9.35 (1 H, s); ^{13}C NMR δ 20.91, 21.76, 32.43 (q, J = 1.9 Hz), 44.89, 46.85 (q, J = 27.6 Hz), 68.00, 124.67 (q, J = 280.0 Hz), 128.55, 128.63, 134.62, 167.6, 203.9; ^{19}F NMR δ 9.51 (d, J = 8.3 Hz); IR (neat) ν 2990, 1730, 1750.

Benzyl 2-(trifluoromethyl)-4-methyl-5-oxoheptanoate (6c): yield 66% (67:33 diastereomer mixture); ^{1}H NMR major diastereomer δ 0.96 (3 H, t, J = 7.3 Hz), 1.08 (3 H, d, J = 7.1 Hz), 1.84 (1 H, ddd, J = 3.9, 11.2, 13.6 Hz), 2.05–2.57 (4 H, m), 3.19 (1 H, ddq, J = 4.1, 8.2, 11.2 Hz), 5.15 (1 H, d, J = 12.1 Hz), 5.23 (1 H, d, J = 12.2 Hz), 7.32–7.39 (5 H, m); minor diastereomer δ 1.00 (3 H, t, J = 7.3 Hz), 1.09 (3 H, d, J = 7.0 Hz), 3.22 (1 H, ddq, J = 5.7, 8.2, 9.8 Hz); ^{13}C NMR major diastereomer δ 7.66, 17.92, 28.64 (q, J = 2.2 Hz), 34.19, 42.55, 48.24 (q, J = 27.9 Hz), 67.51, 124.49 (q, J = 280.0 Hz), 128.13, 128.31, 128.38, 128.47, 128.62, 128.71 (diastereomer mixture), 167.36 (q, J = 3.0 Hz), 213.22; minor diastereomer δ 7.58, 16.44, 34.19, 42.74, 67.62, 124.69 (q, J = 279.9 Hz), 212.93; ^{19}F NMR major diastereomer δ 9.91 (d, J = 8.2 Hz); minor diastereomer δ 10.56 (d, J = 8.2 Hz); IR (neat) diastereomer mixture ν 3000, 1720, 1750; HRMS for $C_{15}H_{19}F_3O_3$ M^+ 304.1286, found 304.1256.

Benzyl 2-(trifluoromethyl)-4-formylpentanoate (6d): yield 75% (63:37 diastereomer mixture); ^{1}H NMR major diastereomer δ 1.13 (3 H, d, J = 7.2 Hz), 1.93 (1 H, ddd, J = 4.6, 10.7, 13.9 Hz), 2.17 (1 H, ddd, J = 4.1, 9.1, 13.8), 2.27–2.49 (1 H, m), 3.36 (1 H, ddq, J = 4.2, 8.2, 10.8 Hz), 5.20 (2 H, s), 7.40 (5 H, s), 9.55 (1 H, s); minor diastereomer δ 5.21 (2 H, s); ^{13}C NMR major diastereomer δ 14.07, 26.60 (q, J = 2.5 Hz), 43.27, 47.97 (q, J = 27.9 Hz), 67.69, 124.47 (q, J = 280.1 Hz), 128.35, 128.67, 128.71, 134.86, 167.17 (q, J = 3.1 Hz), 202.57; minor diastereomer δ 13.11, 43.49, 48.05 (q, J = 28.4 Hz), 67.79, 124.57 (q, J = 285.1 Hz), 202.31; ^{19}F NMR major diastereomer δ 9.84 (d, J = 8.3 Hz); minor diastereomer δ 10.19 (d, J = 8.3 Hz); IR (neat) diastereomer mixture ν 2990, 1730, 1740, 1760; HRMS for $C_{14}H_{15}F_3O_3$ M^+ 288.0973, found 288.0993.

Benzyl 6-(benzyloxycarbonyl)-4,4-bis(ethoxycarbonyl)-2-(trifluoromethyl)-7,7,7-trifluoroheptanoate (7a): yield 98% (diastereomer mixture); ^{1}H NMR δ 1.13–1.28 (6 H, m), 2.25–2.72 (4 H, m), 3.30–3.52 (2 H, m), 3.97–4.26 (4 H, m), 5.08–5.28 (4 H, m), 7.32–7.39 (10 H, m); ^{13}C NMR δ 13.71, 13.76, 13.99, 25.01 (q, J = 2.5 Hz), 29.97 (q, J = 2.2 Hz), 30.38 (q, J = 2.5 Hz), 46.85 (q, J = 27.5 Hz), 46.96 (q, J = 27.5 Hz), 47.94 (q, J = 28.4 Hz), 48.94, 54.92, 55.05, 61.97, 62.29, 62.35, 62.47, 67.88, 68.16, 124.41 (q, J = 279.9 Hz), 124.56 (q, J = 281.3 Hz; two different peaks are overlapped), 128.27, 128.40, 128.62, 128.71, 134.73, 134.84, 166.59 (q, J = 2.7 Hz), 166.96 (q, J = 2.7 Hz), 168.13 (q, J = 2.9 Hz), 169.35, 169.41, 169.56; ^{19}F NMR δ 9.70 (d, J = 8.2 Hz; two different peaks are overlapped), 10.00 (d, J = 8.1 Hz); IR (neat) ν 2900, 1750, 1720; HRMS for $C_{29}H_{30}F_6O_8$ M^+ 620.1845, found 620.1821.

Benzyl 4-(acetylamino)-4,4-dicarbethoxy-2-(trifluoromethyl)pentanoate (7b): yield 94%; ^{1}H NMR δ 1.24 (3 H, t, J = 7.14 Hz), 1.26 (3 H, t, J = 7.14 Hz), 1.87 (3 H, s), 2.86–3.25 (3 H, m), 4.14 (1 H, dq, J = 7.1 Hz, 10.7 Hz), 4.24 (1 H, dq, J = 7.1, 10.7 Hz), 4.26 (2 H, q, J = 7.1 Hz), 5.14 (1 H, d, J = 12.3 Hz), 5.18 (1 H, d, J = 12.3 Hz), 6.67 (1 H, s), 7.38 (5 H, s); ^{13}C NMR δ 13.82, 13.89, 22.59, 29.02 (q, J = 2.3 Hz), 46.46 (q, J = 28.2 Hz), 63.15, 64.57, 67.79, 124.42 (q, J = 281.0 Hz), 128.26, 128.66, 128.72, 134.80, 166.44 (q, J = 2.6 Hz), 167.17, 167.33, 169.62; ^{19}F NMR δ 10.01 (d, J = 7.6 Hz); IR (neat) ν 1680, 1690, 1740, 1760; HRMS for $C_{20}H_{24}F_3NO_7$ M^+ 447.1505, found 447.1517.

Benzyl 4,4-dicarbethoxy-2-(trifluoromethyl)pentanoate (7c): yield 69%; ^{1}H NMR δ 1.23 (3 H, t, J = 7.1 Hz), 1.24 (3 H, t, J = 7.2 Hz), 1.38 (3 H, s), 2.31 (1 H, dd, J = 1.9, 14.9 Hz), 2.62 (1 H, dd, J = 9.6, 14.8 Hz), 3.38 (1 H, ddq, J = 2.0, 8.8, 9.6 Hz), 4.08–4.21 (4 H, m), 5.16 (1 H, dd, J = 12.3 Hz), 5.22 (1 H, d, J = 12.3 Hz), 7.32 (5 H, s); ^{13}C NMR δ 13.90, 20.23, 31.46 (q, J = 2.4 Hz), 46.99 (q, J = 27.2 Hz), 52.34, 61.76, 61.80, 67.91, 124.64 (q, J = 281.0 Hz), 128.37, 128.55, 134.81, 167.35 (q, J = 3.0 Hz), 171.15, 171.04; ^{19}F NMR δ 9.65 (d, J = 9.0 Hz); IR (neat) ν 2900, 1725; HRMS for $C_{19}H_{23}F_3O_6$ M^+ 404.1447, found 404.1472.

Benzyl 4,4-dicarbethoxy-2-(difluoromethylidene)pentanoate (8). To a solution of NaH (36 mg, 1.5 mmol) in freshly distilled THF (5 mL) was added diethyl methylmalonate (333 mg, 1.5 mmol) in the same solvent (2 mL) at 0 °C under nitrogen, and the mixture was stirred for 30 min at that temperature. The resultant sodium salt was subjected to the reaction with benzyl 2-(trifluoromethyl)acrylate (230 mg, 1.0 mmol) at room temperature for 1 h. After being quenched with 1 N HCl (aq) and the usual workup, the crude material was purified by silica gel chromatography to furnish the desired product (173 mg, 0.45 mmol): yield 45%; ^{1}H NMR δ 1.23 (6 H, t, J = 7.14Hz), 1.35 (3 H, d, J = 1.12 Hz), 2.97 (2 H, dd, J = 2.12, 2.48 Hz), 4.01–4.26 (4 H, m), 5.20 (2 H, s), 7.30–7.40 (5 H, m); ^{13}C NMR δ 13.91, 19.37, 30.09, 53.18 (dd, J = 1.9, 2.9 Hz), 61.53, 67.06, 85.11 (dd, J = 22.4, 8.4 Hz), 160.41 (dd, J = 297.4, 310.2 Hz), 164.45 (dd, J = 7.4, 12.9 Hz), 171.38; ^{19}F NMR δ 6.42 (1 F, s), 10.01 (1 F, s);

(10) For the carbon–carbon bond-forming reaction with **3** by the other method, see: (a) Hanzawa, Y.; Suzuki, M.; Sekine, T.; Murayama, T.; Taguchi, T. *J. Chem. Soc., Chem. Commun.* **1991**, 721–722. (b) Hanzawa, Y.; Suzuki, M.; Kobayashi, Y.; Taguchi, T. *J. Org. Chem.* **1991**, *56*, 1718–1725.

(11) Yamazaki, T.; Mizutani, K.; Kitazume, T. *J. Org. Chem.* **1993**, *58*, 4346–4359.

IR (neat) ν 2980, 1730; HRMS for $C_{19}H_{22}F_2O_6$ M^+ 384.1384, found 384.1371.

2-(Trifluoromethyl)-4-methyl-5-pentanolide (10). To a solution of $NaBH_4$ (17 mg, 0.45 mmol, 1.2 equiv) in freshly distilled diglyme (12 mL) was added **6d** (432 mg, 1.5 mmol) in the same solvent (2 mL) at 0 °C under nitrogen, and the mixture was stirred overnight at that temperature. Usual workup gave the crude material, which, after passing through the short path column chromatography, was employed for the next step without further purification.

The obtained product was subjected to hydrogenation by 10% Pd/C (190 mg) in 15 mL of distilled AcOEt under hydrogen. After the mixture was stirred overnight, removal of the catalyst by filtration followed by the short path column chromatography furnished the crude hydroxy carboxylic acid **9**, which, without further purification, was dissolved in 10 mL of benzene. Reflux for 1 h and evaporation of the volatiles gave the crude lactone, which was purified by silica gel chromatography to furnish the desired product (101 mg, 0.55 mmol): total yield 37% (70:30 diastereomer mixture); ^1H NMR (500 MHz) major diastereomer δ 1.08 (3 H, J = 6.71 Hz), 1.92 (1 H, ddd, J = 7.81, 8.67, 13.92 Hz), 2.21 (1 H, dddd, J = 1.22, 7.45, 9.06, 13.84 Hz), 2.24–2.35 (1 H, m), 3.35 (1 H, sex, J = 8.67 Hz), 3.98 (1 H, dd, J = 9.83, 11.54 Hz), 4.33 (1 H, ddd, J = 1.22, 4.64, 11.35 Hz); minor diastereomer δ 1.07 (3 H, d, J = 7.20 Hz), 1.65 (1 H, ddd, J = 11.05, 12.30, 13.43 Hz), 3.29 (1 H, ddq, J = 7.20, 12.33, 8.62 Hz), 3.98 (1 H, dd, J = 9.89, 11.23 Hz), 4.36 (1 H, ddd, J = 2.32, 4.64, 11.23 Hz); ^{13}C NMR major diastereomer δ 16.49, 26.22, 27.04 (q, J = 2.13 Hz), 42.40 (q, J = 27.4 Hz), 73.64, 124.46 (q, J = 278.4 Hz), 165.23 (q, J = 2.2 Hz); minor diastereomer δ 16.75, 27.57, 28.82 (q, J = 2.10 Hz), 44.90 (q, J = 28.0 Hz), 75.01; ^{19}F NMR major diastereomer δ 9.23 (d, J = 8.3 Hz); minor diastereomer δ 9.50 (d, J = 9.0 Hz); IR (neat) diastereomer mixture ν 3000, 1760, 1770; HRMS for $C_7H_9F_3O_2$ M^+ 182.0555, found 182.0560.

Supplementary Material Available: ^1H NMR spectra for compounds **6**, **7**, **8**, and **10** as well as a ^{13}C NMR spectrum for compound **8** (10 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.