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Perfluoroalkylation of Olefins by Electrooxidation of Perfluoroalkanoic Acids: Relations between Product-Selectivity and Current Density and Structures of Olefins

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Electrooxidation of perfluoroalkanoic acids $RfCO_2H$ ($Rf=CF_3$, C_3F_7, C_7F_{15} together with CHF_2, CH_2F) in the presence of electron-deficient olefins (methyl acrylate, methyl methacrylate, acrylamide, and acrylonitrile) provided perfluoroalkylated products. The electrolysis was conducted in $MeCN-H_2O$ (7 : 1) using platinum electrodes in an undivided cell. Dimerization of methyl acrylate accompanying perfluoroalkylation, occurs in 40—50% yield under 20 mA cm^{-2} current density. 1,2-Addition of trifluoromethyl or difluoromethyl radicals to carbon-carbon double bond predominates in acrylamide under the high current density (100—200 mA cm^{-2}). On the other hand, 1,2-addition of trifluoromethyl and acetamido groups and 1,2-addition of trifluoromethyl and hydroxyl groups occur in the low current density (<5 mA cm^{-2}) electrolysis of methyl methacrylate.

Organofluorine compounds have attracted increasing attention for medicinal and agricultural usage and for material science.[1,2] Among them, the trifuoromethylated compounds are promising so that a variety of trifluoromethylated compounds have been prepared. Trifluoromethylmetal complexes have been extensively employed for trifluoromethylation of carbonyl compounds[3-5] and aryl halides.[4] Perfluoroalkanoyl peroxide,[5] *N*-(trifluoromethyl)-*N*-nitrosotrifluoromethanesulfonamide,[6] and xenon difluoride-trifluoroacetic acid[7] can trifluoromethylate aromatic compounds. Recently, electrochemical trifluoromethylation has received much attention. Electroreductive generation of CF_3 anion[8] or CF_3 radical[9] from CF_3Br has been actively investigated by Saveant et al. Trifluoroacetic acid (TFA) is another source of a trifluoromethyl group because it is one of the most available and economically feasible starting materials and its electrooxidation generates CF_3 radicals.

Since 1970, Renaud,[10] Brookes,[11] and Muller[12] paid much attention to the electrooxidation of TFA in the presence of various olefins for the preparation of the trifluoromethylated aliphatic compounds, and showed that the electrochemically generated CF_3 radicals can be trapped efficiently with electron-deficient olefins. A variety of trifluoromethylated compounds can be prepared, although the selectivity of the desired products is not necessarily satisfactory. Recently, we also proposed a temperature-dependent quantitative generation of CF_3 radicals[13,14] and demonstrated 1,2-addition of trifluoromethyl and acetamido groups of methyl methacrylate (MMA),[15] bis(trifluoromethylation)[16] of acrylamide (AA), and hydrogenation with trifluoromethylation of fumaronitrile.[14]

One of the problems is how to control electrochemical reaction conditions so as to selectively prepare target trifluoromethylated compounds. The problems which must be solved are how to control the chemical and electrochemical fate of the intermediate radicals **2** and **3** (Scheme 1). We describe here marked effects of current density and structures of olefins on the product-selectivity for some electrochemical perfluoroalkylations. The perfluoroalkanoic acids examined in the present study are shown in Scheme 1.

Results and Discussion

Electrooxidation of trifluoroacetic acid (**1a**) proceeded effectively in an $MeCN-H_2O-(Pt)$ system in an undivided cell. Similarly, both difluoroacetic acid (**1b**) and perfluorobutanoic acid (**1d**) electrochemically decarboxylated smoothly. Figure 1 shows a relation between terminal voltage of the anode and electricity. The carboxylic acid **1d** revealed a very sharp increase of the voltage after 1.1 F mol^{-1} in a similar manner to **1a**,[13] clearly demonstrating an excellent current efficiency for

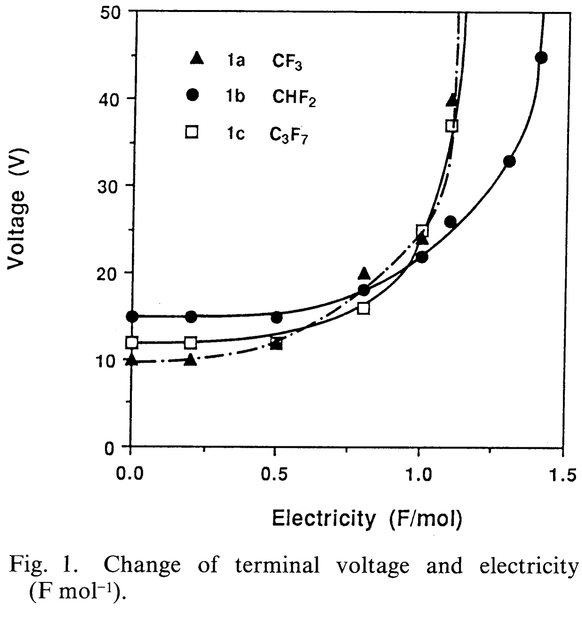
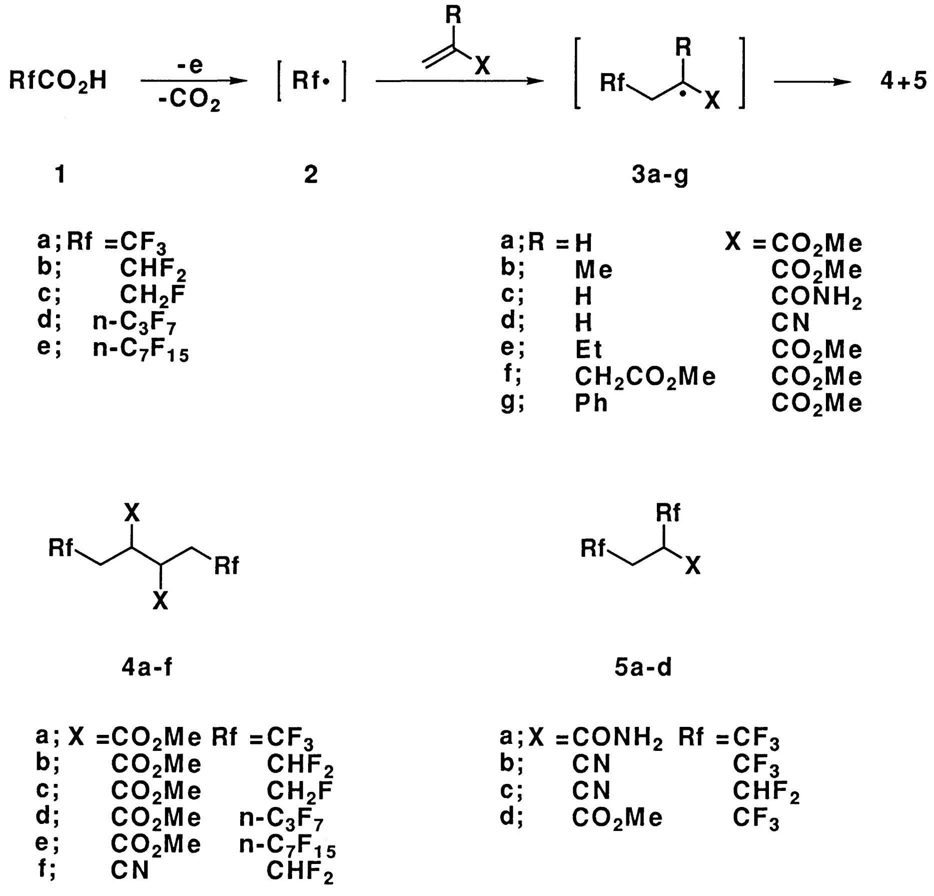


Fig. 1. Change of terminal voltage and electricity (F mol^{-1}).



Scheme 1.

Table 1. Perfluoroalkylation of MA

R_f	Electricity (F mol^{-1} based on acid)	Yield of **4** (%)[a] C. D. (mA cm^{-2}) 20	100
CF_3	1.0	50	47
CHF_2	1.5	45	25
CH_2F[b]	2.0	Trace	Trace
C_3F_7	1.0	70	32
C_7F_{15}	2.2	19	Trace

a) Based on acid. b) Electrolyzed in MeOH.

the electro-oxidation. The oxidation of **1b** required 1.5 F mol^{-1} of electricity to complete the conversion but the terminal voltage change was essentially the same as those of **1a** and **1d**.

Trifluoromethyl radicals attack the carbon–carbon double bond of methyl acrylate (MA) to form the intermediate **3a** (Rf=CF_3) (Scheme 1). The radicals **3a** dimerize providing **4a** as a mixture of *dl*- and *meso*-isomers (50 : 50).[13] Likewise, electrooxidation of **1b**, **1d**, and **1e** afforded **4b**, **4d**, and **4e** as a mixture of *dl*- and *meso*-isomers (50 : 50 by vapar-phase chromatography and ^{19}F NMR) in 45, 70, and 19% yields, respectively. Perfluoropropyl radicals gave **4d** in an excellent yield. Perfluoroheptyl radicals attack the carbon–carbon double bond of MA less efficiently[17] but instead dimerize predominantly to give perfluorotetradecane which deposits as crystals on the anode. In contrast to efficient generation of CF_3, CF_2H, and Rf radicals from the corresponding carboxylic acids, fluoroacetic acid[18] was hardly electrooxidized in an MeCN–H_2O–NaOH–(Pt) system. The ^{19}F NMR analysis of fluoroacetic acid in the remaining reaction mixture after 2 F mol^{-1} revealed no practical consumption of fluoroacetic acid. Electrolysis in distilled methanol at 0 °C under ultrasound irradiation promoted the decarboxylation slightly, affording **4c** in 5% yield (GC yield). Only about 30% of fluoroacetic acid reacted after 2 F mol^{-1} under these conditions.

The dimerization of **3** was optimized at around 20 mA cm^{-2} of current density (Fig. 2).[19] Increase in current density leads to a lower yield of **4**. A higher current density would concentrate radicals **2** on the anode surface and thus would promote dimerization of **2** and also 1,2-addition of **2** to carbon–carbon double bond of olefins.

Changing the substituents on the carbon–carbon double bond affected the yield and selectivity of products. In contrast to dimerization of **3a** to **4a** (R=H) using MA, the reaction of acrylamide with CF_3 radicals led to bis(trifluoromethylation) on the carbon–carbon double bond,[20] providing **5a** (R=H) as the major product. The reaction is highly dependent on current

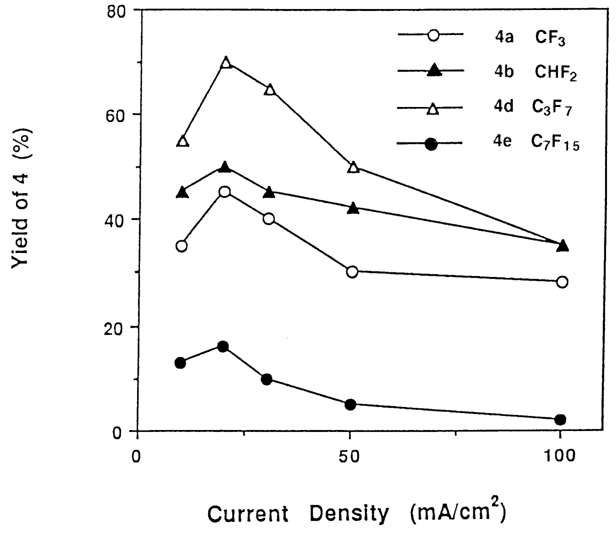


Fig. 2. Effect of current density for the dimerization of 3.

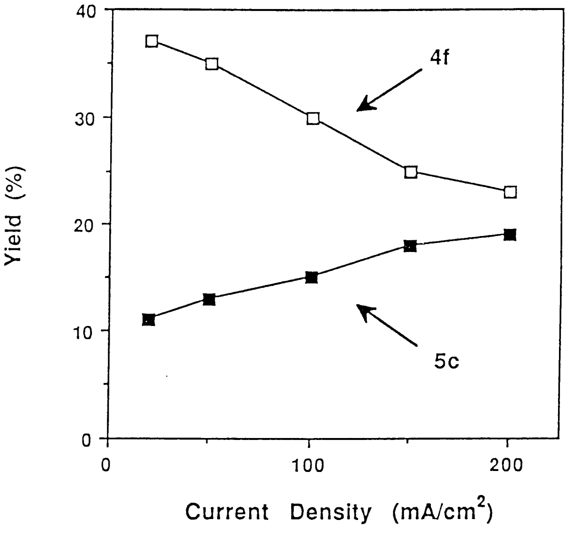


Fig. 4. Difluoromethylation of acrylonitrile. Effect of current density on the yield of **4f** and **5c**.

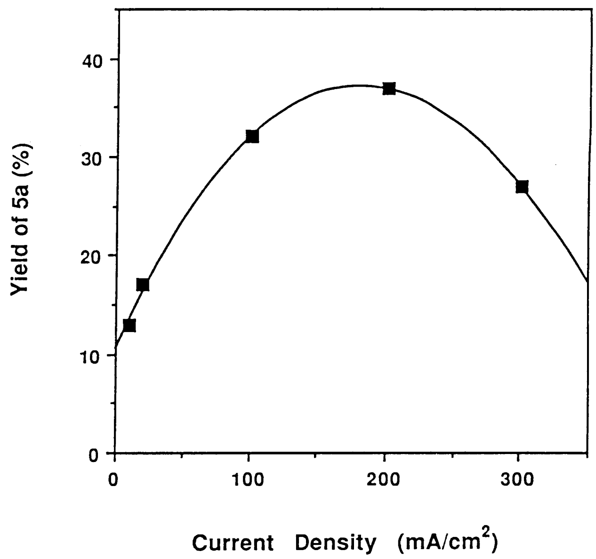


Fig. 3. Bis(trifluoromethylation) of acrylamide dependent on the current density. A mixture of **1a** (4 mmol), acrylamide (1 mmol), and NaOH (0.4 mmol) dissolved in MeCN (7 ml) and H_2O (1 ml) was electrolyzed (Pt–Pt, 2×1.5 cm^2). A constant current was supplied for 1 F mol^{-1} based on **1a**.

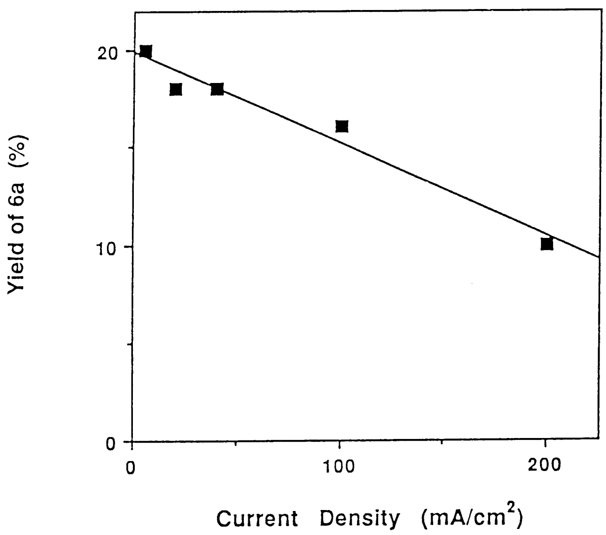
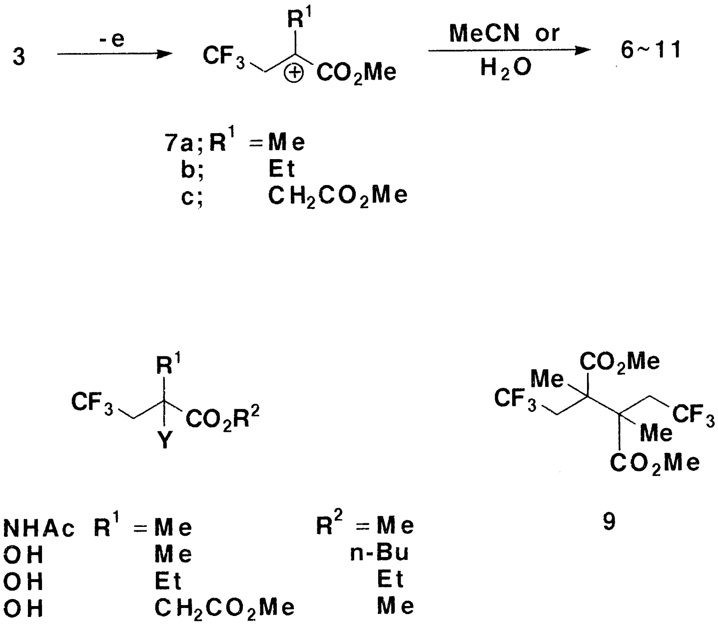


Fig. 5. 1,2-Addition of trifluoromethyl and acetamido groups to MMA dependent on the current density. A mixture of **1a** (6 mmol), MMA (2 mmol), and NaOH (0.6 mmol) dissolved in MeCN (20 ml) and H_2O (3 ml) was electrolyzed (Pt–Pt, 2×1.5 cm^2). A constant current was supplied for 1 F mol^{-1} based on **1a**.

density[21] so that the higher current density promotes the desired bis (trifluoromethylation) (Fig. 3).[22] The dramatic change in products may be due to the longer lifetime of intermediate **3c** as compared with **3a**, as well as the high concentration of CF_3 radicals on the anode. Because of an affinity of the nitrogen atom of acrylamide on the platinum surface,[23] the intermediate **3c** may be adsorbed on the anode more tightly than **3a** and thus stay for a longer time on the anode surface. Therefore, at high current density more CF_3 redicals are generated on the anode surface so that the intermediate **3c** has a greater chance to couple with CF_3 radicals, leading to the predominant formation of **5a**. The behavior of the cyano group (acrylonitrile) appears to be intermediate between methoxycarbonyl and carbamoyl groups. Electrolysis of difluoroacetic acid (**1b**) in the presence of acrylonitrile provided both **4f** and **5c**, with yields dependent on current density as shown in Fig. 4. Higher current density favored formation of **5c**.

In contrast to the preferential bis(trifluoromethylation) at higher current density, 1,2-addition of trifluoromethyl and acetamido groups occured at lower current density[15] (Fig. 5). The amide **6** (Scheme 2)



Scheme 2.

would arise from nucleophilic attack of acetonitrile on the carbocation **7a**, presumably generated by further one-electron oxidation of the trifluoromethylated radicals **3b**.[24] The electron-donating nature of the α-methyl group may enhance the oxidation of the radicals **3b** relative to **3a**. By maintaining the concentration of **3b** as low as possible on the anode surface by applying a low current density, neither dimerization of **3b** nor bis(trifluoromethylation) would be favored, but one-electron oxidation of **3b** to **7a** would be preferable. In fact, the dimer of the radicals **3b** was obtained in only 3% yield under these conditions. Renaud reported a 9.8% isolated yield of the dimer **9** in methanol or acetic acid[25] (Scheme 2).

1,2-Addition of trifluoromethyl and hydroxyl groups via the carbocation intermediate was observed under the low current density electrolysis. On electrolyzing TFA in the presence of butyl methacrylate[26] in aqueous acetone under a low current density (1 mA cm^{-2}), 1,2-addition of trifluoromethyl and hydroxyl groups was observed (**8**, 34% yield). Likewise, ethyl 2-ethyl-2-propenoate and dimethyl 2-methylenesuccinate provided the corresponding alcohols **10** (35%) and **11** (30%), respectively. This fact suggests a generality of a sequence of one-electron oxidation of **3b**, **3e**, and **3f** to the corresponding carbocation **7a**, **7b**, and **7c** at low current density electrolysis and followed by trapping with nucleophile (H_2O). The present electrochemical method is noteworthy because these compounds produced by 1,2-addition of trifluoromethyl and acetamido groups or trifluoromethyl and hydroxyl groups are otherwise difficult to prepare.

Experimental

The boiling points are indicated by a temperature of a glass tube oven. Infrared spectra were taken on a Hitachi 270-30 spectrometer. The ^{1}H and ^{19}F NMR spectra were measured on a Varian VXR-500 using TMS for ^{1}H and C_6F_6 for ^{19}F NMR as internal standards. Mass spectra (MS) were obtained with a Hitachi M-80 spectrometer.

General Procedure of Electrolysis: A mixture of **1** (1 mmol), olefin (2 mmol), and NaOH (0.1 mmol) dissolved in MeCN (3.5 ml) and H_2O (0.5 ml) was electrolyzed at 0 °C in an undivided beaker type cell (10 cm tall and 1.5 cm in diameter) fitted with platinum foil electrodes (2×1.5 cm^2). A constant current (20 mA cm^{-2}) was supplied until the charge reached 1.1—2.0 faraday per mol based on **1**. The solvent was evaporated under reduced pressure. The residue was extracted with AcOEt, washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude residue was chromatographed on silica gel (hexane–AcOEt). The yields of the isolated products are based on **1**.

Dimethyl 2,3-Bis(2,2-difluoroethyl)succinate (4b): A colorless liquid (62 mg, 45%, GC analysis (Silicone OV-101, N_2, 100—120 °C) revealed a mixture of *dl* and *meso* (50 : 50)) ; bp 150 °C (3 mmHg); IR (neat) 3012, 2964, 1740 (C=O), 1442, 1410, 1376, 1320 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=5.93 (tm, J_{HF}=56.5 Hz, CHF_2), 3.76 (s, CH_3O), 3.74 (s, CH_3O), 3.09—3.02 (m, 1H, CH), 2.54—2.30 (m, 1H, CH_2), 2.04—1.87 (m, 1H, CH_2); ^{19}F NMR ($CDCl_3$) δ=46.8 (m, 1F), 43.8 (m, 1F); MS *m*/*z* (relative intensity) 243 (M^+—OCH_3, 26), 195, 138, 109, 87, 59 (CO_2CH_3, 100). Anal. Calcd for $C_{10}H_{14}O_4F_4$: C, 43.80; H, 5.15%. Found: C, 43.89; H, 5.09%.

Dimethyl 2,3-Bis(2-fluoroethyl)succinate (4c): A colorless liquid (5.0% GC yield, mixture of *dl* and *meso* by vapor-phase chromatography); bp 200 °C (15 mmHg); one isomer: ^{1}H NMR ($CDCl_3$) δ=4.51 (dm, J_{HF}=46.9 Hz, 2H, CH_2F), 3.72 (s, CH_3O), 3.04—2.96 (m, 1H, CH), 2.29—1.83 (m, 2H, CH_2); ^{19}F NMR ($CDCl_3$) δ=—58.6 (m, CH_2F). HRMS Calcd for $C_9H_{13}O_3F_2$:

(M^+-OCH_3), 207.0833. Found: *m*/*z* 207.0837. Another isomer: ^{1}H NMR ($CDCl_3$) δ=4.45 (dm, J_{HF}=44.0 Hz, 2H, CH_2F), 3.67 (s, CH_3O), 2.96—2.89 (m, 1H, CH), 2.22—1.69 (m, 2H, CH_2); ^{19}F NMR ($CDCl_3$) δ=−58.4. HRMS Calcd for $C_9H_{13}O_3F_2$: (M^+-OCH_3), 207.0833. Found: *m*/*z* 207.0810. Isomers (*dl* and *meso*) are not specified.

Dimethyl 2,3-Bis(2,2,3,3,4,4,4-heptafluorobutyl)succinate (4d): Colorless crystals and liquid (178 mg, 70%, mixture of *dl* and *meso*); crystals, mp 143 °C; IR (nujol) 1746 (C=O), 1460, 1378, 1316, 1224, 1174 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.78 (s, CH_3O), 3.25—3.21 (m, 1H, CH), 2.92—2.80 (m, 1H, CH_2), 2.40—2.29 (m, 1H, CH_2); ^{19}F NMR ($CDCl_3$) δ=81.3, 46.4, 34.1; MS *m*/*z* (rel intensity) 510 (M^+, 3), 479 (M^+-CH_3O), 451 ($M^+-CO_2CH_3$), 256, 59 (CO_2CH_3, 100). Anal. Calcd for $C_{14}H_{12}O_4F_{14}$: C, 32.96; H, 2.37%. Found: C, 32.85; H, 2.40%. Liquid: bp 135 °C (5 mmHg, 1 mmHg=133.322 Pa); IR (neat) 3008, 2975, 1745 (C=O), 1460, 1390, 1235, 1175 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.76 (s, CH_3O), 3.25—3.17 (m, 1H, CH), 2.87—2.74 (m, 1H, CH_2), 2.17—2.06 (m, 1H, CH_2); ^{19}F NMR ($CDCl_3$) δ=81.3, 47.1, 34.1. Anal. Calcd for $C_{14}H_{12}O_4F_{14}$: C, 32.96; H, 2.37%. Found: C, 32.82; H, 2.33%.

Dimethyl 2,3-Bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)succinate (4e): Colorless crystals (71 mg, 16%, mixture of *dl* and *meso*); one isomer; mp 137 °C; IR (nujol) 1746 (C=O), 1464, 1378, 1250, 1168 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.84 (s, CH_3O), 3.26—3.23 (m, 1H, CH), 2.94—2.86 (m, 1H, CH_2), 2.42—2.29 (m, 1H, CH_2); ^{19}F NMR ($CDCl_3$) δ=81.0, 48.5, 40.2, 39.8, 39.1, 38.5, 35.7; MS *m*/*z* (rel intensity) 714 (50), 699, 59 (100, CO_2CH_3). Anal. Calcd for $C_{22}H_{12}O_4F_{30}$: C, 51.76; H, 2.35%. Found: C, 51.77; H, 2.22%. Another isomer; mp 143 °C; IR (nujol) 1745 (C=O), 1470, 1377, 1253, 1170 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.75 (s. CH_3O), 3.23—3.19 (m, 1H, CH), 2.96—2.75 (m, 1H, CH_2), 2.19—2.07 (m, 1H, CH_2); ^{19}F NMR ($CDCl_3$) δ=81.1, 48.1, 40.1, 39.7, 39.0, 38.4, 35.64; MS *m*/*z* (rel intensity) 383 ($C_7F_{15}CH_2$, 22), 356, 84, 59 (CO_2CH_3, 100). Anal. Calcd for $C_{22}H_{12}O_4F_{30}$: C, 51.76; H, 2.35%. Found: C, 51.83; H, 2.40%.

2,3-Bis(2,2-difluoroethyl)succinonitrile (4f): Colorless crystals and liquid (38 mg, 37%, mixture of *dl* and *meso*); crystals; mp 148 °C; IR (nujol) 2256 (CN), 1440, 1416, 1386, 1216, 1122 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.13 (tt, J_{HF}=55.0 Hz, J_{HH}=3.5 Hz, CHF_2), 3.27—3.22 (m, 1H, CH), 2.50—2.37 (m, 2H, CH_2); ^{19}F NMR ($CDCl_3$) δ=45.0, 44.4; MS *m*/*z* (rel intensity) 157 (M^+-CHF_2, 25), 104 (CHF_2CH_2CHCN), 54 (100). Anal. Calcd for $C_8H_8N_2F_4$: C, 46.15; H, 3.85; N, 13.46%. Found: C, 46.22; H, 3.74; N, 13.70%. Liquid: Bp 220 °C (5 mmHg); IR (neat) 3003, 2974, 2257 (CN), 1445, 1420, 1220, 1137 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.10 (tdd, J_{HF}=55.3 Hz, J_{HH}=4.5 Hz, J_{HH}=2.3 Hz, CHF_2), 3.26—3.18 (m, 1H, CH), 2.60—2.48 (m, 1H, CH_2), 2.42—2.30 (m, 1H, CH_2); ^{19}F NMR ($CDCl_3$) δ=43.3, 45.2. Anal. Calcd for $C_8H_8N_2F_4$: C, 46.15; H, 3.85; N, 13.46%. Found: C, 45.98; H, 3.67;N, 13.20%.

4,4-Difluoro-2-(difluoromethyl)butyronitrile (5c): A colorless liquid (10 mg, 12%); bp 85 °C (5 mmHg); IR (neat) 2598, 2903, 2234 (CN), 1416, 1357, 1209 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.11 (tt, J_{HF}=55.5 Hz, J_{HH}=4.0 Hz, $C\underline{H}F_2CH_2$), 6.08 (td, J_{HF}=55.0 Hz, J_{HH}=3.0 Hz, $C\underline{H}F_2CH$), 3.44—3.35 (m, 1H, CH), 2.45—2.36 (m, 2H, CH_2); ^{19}F NMR ($CDCl_3$) δ=44.5, 41.9, 41.3; MS *m*/*z* (rel intensity) 104 (M^+-CHF_2, 87), 65 (CHF_2CH_2), 54 (100), 51 (CHF_2). Anal. Calcd for $C_5H_5NF_4$: C, 38.71; H, 3.23; N, 9.03%. Found: C, 38.75; H, 3.24; N, 9.24%.

***n*-Butyl 2-Hydroxy-2-methyl-4,4,4-trifluorobutyrate (8):** A mixture of **1a** (0.23 ml, 3.0 mmol), butyl methacrylate (0.16 ml, 1.0 mmol), and NaOH (12 mg, 0.3 mmol) dissolved in acetone (16 ml) and H_2O (8 ml) was electrolyzed at 0 °C in an undivided cell fitted with platinum foil electrodes (6×4 cm^2 for an anode and 1.5×2 cm^2 for a cathode). A constant current (1 mA cm^{-2}) was supplied until the charge reached 1.2 faraday per mol based on **1a**. The G.C. analysis using diethyl fumarate as an internal standard showed the formation of **8** (34%).

8: Bp 70 °C (4 mmHg); IR (neat) 3540 (OH), 2972, 1740 (C=O), 1372, 1340, 1272, 1190, 1154, 1074 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.23 (t, *J*=6.6 Hz, 2H, OCH_2), 3.2—3.7 (br, 1H, OH), 2.70 (dq, J_1=15.2 Hz, J_2=10.4 Hz, 1H, CH_2CF_3), 2.55 (dq, J_1=15.2 Hz, J_2=10.4 Hz, 1H, CH_2CF_3), 1.3—1.75 (m, 4H), 1.49 (s, 3H, CH_3), 0.95 (t, *J*=7.3 Hz, 3H, CH_3); ^{19}F NMR ($CDCl_3$) δ=100.1; MS *m*/*z* (rel intensity) 229 (M+1, 2), 213 (M^+-CH_3), 127 (M^+-CO_2Bu, 100), 57, 47. Anal. Calcd for $C_9H_{15}O_3F_3$: C, 47.37; H, 6.62%. Found: C, 47.18; H, 6.80%.

Ethyl 2-Ethyl-4,4,4-trifluoro-2-hydroxybutyrate (10): Bp 50—60 °C (28 mmHg); IR (neat) 3544 (OH), 1738 (C=O), 1370, 1260, 1180, 1148 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.30 (q, *J*=7.1 Hz, CH_3), 2.67 (dq, J_1=15.2 Hz, J_2=10.4 Hz, 1H, CH_2CF_3), 2.53 (dq, J_1=15.2 Hz, J_2=10.4 Hz, 1H, CH_2CF_3), 1.82—1.62 (m, 2H, CH_2), 1.31 (t, *J*=7.1 Hz, 3H, CH_3), 0.88 (t, *J*=7.4 Hz, 3H, CH_3); ^{19}F NMR ($CDCl_3$) δ=100.4 (t, *J*=10.4 Hz); This compound was so unstable that high-resolution mass spectroscopy was examined instead of an elemental analysis. HR-MS (70 eV): Calcd for $C_6H_8F_3O_3$: ($M^+-C_2H_5$), 185.0425. Found: *m*/*z* 185.0454. Calcd for $C_5H_8F_3O$: ($M^+-CO_2C_2H_5$), 141.0574. Found: *m*/*z* 141.0579.

Dimethyl 2-Hydroxy-2-(2,2,2-trifluoroethyl)succinate (11): Mp 67—68 °C; IR (Nujol) 3512 (OH), 1740 (C=O), 1444, 1374, 1134, 890 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.96 (s, 1H, OH), 3.86 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 2.96 (d, *J*=16.0 Hz, 1H, CH_2), 2.78 (d, *J*=16.0 Hz, 1H, CH_2), 2.64 (q, J_{HF}=10.3 Hz, 2H, CH_2CF_3); ^{19}F NMR ($CDCl_3$) 100.3 (t, J_{HF}=10.3 Hz). Anal. Calcd for $C_8H_{11}O_5F_3$: C, 39.35; H, 4.54%. Found: C, 39.26; H, 4.71%.

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