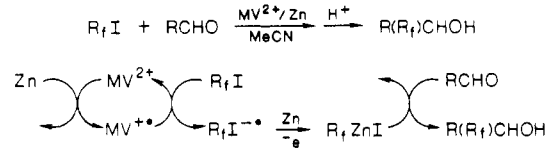
Table I. Preparation of α-Perfluoroalkyl Carbinols

R_fI	RCHO	product[a]	reactn time (h)	yield (%)
CF_3I	PhCHO	$Ph(CF_3)CHOH$[c]	15	52
CF_3I	$CH_3(CH_2)_4CHO$	$CH_3(CH_2)_4(CF_3)CHOH$[d]	15	48
CF_3CF_2I	PhCHO	$Ph(C_2F_5)CHOH$[c]	21	57
CF_3CF_2I	$PhCH_2CH_2CHO$	$PhCH_2CH_2(C_2F_5)CHOH$[b]	17	51
C_4F_9I	PhCHO	$Ph(C_4F_9)CHOH$[c]	14	42
C_4F_9I	$CH_3(CH_2)_4CHO$	$CH_3(CH_2)_4(C_4F_9)CHOH$[d]	25	64
$C_6F_{13}I$	PhCHO	$Ph(C_6F_{13})CHOH$[c]	13	65
$C_6F_{13}I$	$PhCH_2CH_2CHO$	$PhCH_2CH_2(C_6F_{13})CHOH$[b]	39	57
$C_6F_{13}I$	$CH_3(CH_2)_6CHO$	$CH_3(CH_2)_6(C_6F_{13})CHOH$[b]	48	68
$C_8F_{17}I$	PhCHO	$Ph(C_8F_{17})CHOH$[c]	14	52
$C_8F_{17}I$	CH_3CH_2CHO	$CH_3CH_2(C_8F_{17})CHOH$[d]	24	53

[a] Structures were determined by means of IR, NMR, and mass spectral data. [b] New compounds. The microanalysis was in satisfactory agreement with the calculated values (C, H, N; ±0.4%). [c] Kitazume, T.; Ishikawa, N. *J. Am. Chem. Soc.* **1985**, *107*, 5186. [d] Kitazume, T.; Ishikawa, N. *Nippon Kagaku Kaishi* **1984**, 1725.

Scheme I



radiation,[2,3] catalysis by metal complexes,[4] photolysis, electrolysis,[5] thermolysis of free radical initiators, and preferably, an inert atmosphere, and the formation of R_fR_f and/or R_fH have been sometimes observed. Therefore, in the field of fluorine chemistry, it would be useful to have a new moderate technical method to introduce perfluoroalkyl groups in the organic molecules.

This work describes the synthetic utilization of the zinc–methyl viologen system as an effective electron mediator[11–15] which should accelerate the conversion of perfluoroalkyl iodides to α-perfluoroalkyl carbinols in a Barbier-type reaction as shown in Scheme I.

We attempted the Barbier-type reaction in an electron-transfer system containing the reducing agent (Zn) and MV^{2+} as electron-transfer catalyst (ETC). The results shown in Table I support a new approach, which is capable of converting perfluoroalkyl iodides to α-perfluoroalkyl carbinols via Barbier-type reaction. Without methyl viologen, the reaction did not proceed at all. However, in the Zn–MV^{2+} system, the formation of (perfluoroalkyl)zinc reagents in situ were checked by ^{19}F NMR.

Experimental Section

1-(Perfluorohexyl)-1-phenylcarbinol. A suspension of zinc powder (0.35 g, 0.005 g-atom), perfluorohexyl iodide (2.3 g, 5 mmol), and benzaldehyde (1.06 g, 10 mmol) in acetonitrile (20 mL) was stirred at room temperature. Into the mixture, methyl viologen (MV^{2+},$2Cl^{1-}$) (50 mg, 0.16 mmol; 3.2 mol % of perfluorohexyl iodide) was added, and then the whole was stirred at room temperature. After 14 h of stirring, the solution was poured into a 2% HCl solution and an oily material extracted with diethyl ether. After the extereal solution was dried over magnesium sulfate, the solvent was removed. The product was purified by chromatography on silica gel.

1-(Trifluoromethyl)-1-phenylcarbinol. A flask containing commercially available zinc powder (1.30 g, 0.02 g-atom), trifluoromethyl iodide (3.0 g, 20 mmol), and benzaldehyde (3.18 g, 30 mmol) in acetonitrile (50 mL) and then equipped with a dry ice–acetone reflux condenser was stirred at room temperature. Into the mixture, methyl viologen (MV^{2+},$2Cl^{1-}$) (200 mg, 0.64 mmol; 3.2 mol % of trifluoromethyl iodide) was added, and then the whole was stirred for 15 h at room temperature and then worked up as usual. Distillation gave 1-(trifluoromethyl)-1-phenylethanol in a yield of 52%, bp 80–83 °C (3 mmHg): ^{19}F NMR (CCl_4) φ 78.5 (CF_3, d, J_{CF_3-CH} = 6.5 Hz); ^1H NMR ($CDCl_3$) δ 5.00 (CH, q), 4.0 (OH), 7.4 (Ar H).

Registry No. CF_3I, 2314-97-8; PhCHO, 100-52-7; $Ph(CF_3)CHOH$, 340-04-5; $H_3C(CH_2)_4CHO$, 66-25-1; $H_3C(CH_2)_4(CF_3)CHOH$, 80768-53-2; F_3CCF_2I, 354-64-3; $Ph(C_2F_5)CHOH$, 345-40-4; $Ph(CH_2)_2CHO$, 104-53-0; $Ph(CH_2)_2(C_2F_5)CHOH$, 90550-19-9; C_4F_9I, 423-39-2; $Ph(C_4F_9)CHOH$, 78960-83-5; $H_3C(CH_2)_4(C_4H_9)CHOH$, 95452-56-5; $C_6F_{13}I$, 355-43-1; $Ph(C_6F_{13})CHOH$, 57242-02-1; $Ph(CH_2)(C_6F_{13})CHOH$, 111822-76-5; $H_3C(CH_2)_6CHO$, 124-13-0; $H_3C(CH_2)_6(C_6F_{13}CHOH$, 111822-77-6; $C_8F_{17}I$, 507-63-1; $Ph(C_8F_{17})CHOH$, 111822-78-7; H_3CCH_2CHO, 123-38-6; $H_3CCH_2(C_8F_{17})CHOH$, 95452-57-6; Zn, 7440-66-6; methyl viologen, 1910-42-5.

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A Remarkably Simple Route to Perfluoroalkylated Olefins and Perfluoroalkanoic Acids

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Bioactive materials and industrial chemicals that contain a trifluoromethyl group and/or a perfluoroalkyl (R_f) group have been extensively studies.[1,2] In fact, a variety of perfluoroalkylations based on the synthetic applications of perfluoroalkylmetallic reagents[3–9] and/or perfluoroalkyl radicals[9–13] have been reported. However, these methods require ultrasound, photolysis, and thermolysis in excess

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Table I

R_fCF_2I	alkyne	product[a] olefin	reactn time (days)	enzyme	yield (%)[d] olefin
CF_3I	phenylacetylene	(*E*)-PhCH=CHCF$_3$[c]	15	catalase	24
	1-decyne	(*E*)-CH$_3$(CH$_2$)$_7$CH=CHCF$_3$[b]	14	catalase	35
	1-phenylpropyne	PhCH=C(CF$_3$)CH$_3$[b]	15	urease	39
C_2F_5I	phenylacetylene	(*E*)-PhCH=CHC$_2$F$_5$[c]	14	catalase	34 (29)
	1-decyne	(*E*)-CH$_3$(CH$_2$)$_7$CH=CHC$_2$F$_5$[b]	14	urease	41 (35)
C_4F_9I	phenylacetylene	(*E*)-PhCH=CHC$_4$F$_9$[c]	10	catalase	64 (3)
	1-phenylpropyne	PhCH=C(C$_4$F$_9$)CH$_3$[b]	30	catalase	26 (33)
	1-octyne	(*E*)-CH$_3$(CH$_2$)$_5$CH=CHC$_4$F$_9$[b]	14	catalase	46 (25)
			33	urease	31 (40)
	2-octyne	CH$_3$(CH$_2$)$_4$CH=C(C$_4$F$_9$)CH$_3$[b]	36	urease	6 (81)
			30	catalase	10 (67)
$C_6F_{13}I$	phenylacetylene	(*E*)-PhCH=CHC$_6$F$_{13}$[b]	9	catalase	47 (7)
			11	urease	66 (2)
	1-phenylpropyne	PhCH=C(C$_6$F$_{13}$)CH$_3$[b]	21	catalase	28 (66)
	1-octyne	(*E*)-CH$_3$(CH$_2$)$_5$CH=CHC$_6$F$_{13}$[b]	13	catalase	61 (14)
	1-octyne		21	urease	42 (39)
	2-octyne	CH$_3$(CH$_2$)$_4$CH=C(C$_6$F$_{13}$)CH$_3$[b]	30	urease	18 (53)
	2-octyne		28	catalase	0 (66)[e]
$C_8F_{17}I$	phenylacetylene	(*E*)-PhCH=CHC$_8$F$_{17}$[b]	21	catalase	35 (32)
	phenylacetylene		21	urease	53 (28)
	1-phenylpropyne	PhCH=C(C$_8$F$_{17}$)CH$_3$[b]	21	catalase	26 (54)
	1-octyne	(*E*)-CH$_3$(CH$_2$)$_5$CH=CHC$_8$F$_{17}$[b]	20	catalase	36 (43)
	2-octyne		27	catalase	0 (75)[e]
	1-decyne	(*E*)-CH$_3$(CH$_2$)$_7$CH=CHC$_8$F$_{17}$[b]	31	catalase	26 (54)

[a] The structures were confirmed by spectral data. [b] New compound. The microanalysis was in satisfactory agreement with the calculated values (C, H; ±0.4%). [c] Kitazume, T.; Ishikawa, N. *J. Am. Chem. Soc.* **1985**, *107*, 5186. [d] Yield of isolated perfluoroalkanoic acid (R_fCO_2H) in parentheses: Ishikawa, N.; Takahashi, M.; Kitazume, T. *J. Fluorine Chem.* **1983**, *22*, 585. [e] Only perfluoroalkanoic acid produced.

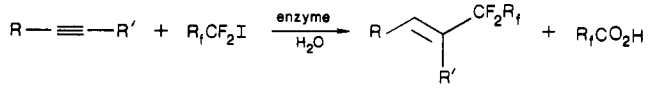
of 160 °C or free radical initiators and, preferably, an inert atmosphere, and the formation of R_fR_f and/or R_fH have been sometimes observed.

Accordingly, we have been studying mild synthetic methods for stereocontrolled fluorinated compounds[14-18] and perfluoroalkanoic acids[19] as one of the most important and general techniques for the synthesis of a variety of functionalized compounds possessing a perfluoroalkyl group.

We report herein an enzyme-assisted procedure for the regio- and stereocontrolled addition of perfluoroalkyl group to alkynes and then the direct conversion of perfluoroalkyl iodides to perfluoroalkanoic acids.

Reactions of alkynes with perfluoroalkyl iodide in the presence of urease with Ni porphin or lipoxygenase with Fe porphin and/or catalase with Fe protoheme gave rise to the corresponding adduct with regio- and stereoselectivity and perfluoroalkanoic acid in good to excellent yields. In the absence of the alkyne, the reaction did not proceed at all. Some results are listed in Table I.

Enzyme-assisted addition of the perfluoroalkyl group to alkynes and/or transformation of perfluoroalkyl iodides



to perfluoroalkanoic acids occurred without the aid of an initiator, such as hydrogen peroxide. In addition, there is no observation of the formation of R_fR_f and/or R_fH in this system.

More significant is the observation of the facile addition of the trifluoromethyl group to alkynes in a reaction vessel equipped with a Teflon stopcock because of the volatile polyfluoromethanes.

The use of inner triple bonds produced mainly the perfluoroalkanoic acids directly from perfluoroalkyl iodides in water at room temperature. When lipoxygenase was used in a 2-octyne–perfluoroalkyl iodide system, the corresponding perfluoroalkanoic acid was only produced experimentally in 83% ($C_3F_7CO_2H$ from C_4F_9I), 84% ($C_5F_{11}CO_2H$ from $C_6F_{13}I$), and 61% ($C_7F_{15}CO_2H$ from $C_8F_{17}I$) yields. The stereochemistry of the disubstituted olefins was assigned by using ^1H NMR coupling constants; the product was only in the *E* geometry. Furthermore, the trisubstituted olefins were also obtained as single isomers; however, the geometry has not been assigned to them.

The results shown in Table I indicate that the combination of perfluoroalkyl iodide and carbon chain length of alkynes are important factors in producing perfluoroalkanoic acids by enzymes with protoheme.

We propose a mechanism that involves a single electron transfer from protoheme in urease, catalase, or lipoxygenase to perfluoroalkyl iodide to explain this simple stereocontrolled perfluoroalkylation and synthesis of perfluoroalkanoic acids. However, details of the catalytic system and mechanism are not yet known.

Our future work will be directed toward the elucidation of the full scope of this unusual bioperfluoroalkylation and/or synthesis of perfluoroalkanoic acid.

Experimental Section

General Procedure. All microbially based reactions were carried out in the Culstir flask or reaction vessel equipped with a Teflon stopcock. All commercially available reagents (perfluoroalkyl iodides and alkynes) were used without further pu-

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rification. Infrared spectra were obtained by using a JASCO A-102 spectrometer and KBr pellets. The ^1H (internal Me_4Si) and ^{19}F (external CF_3CO_2H) NMR spectra were recorded by using Varian EM-390 and Hitachi R-24F spectrometers. Mass spectra were obtained by using a Hitachi M-52 spectrometer at 20 eV. Yields were those of the products actually isolated.

(*E*)-1-(Trifluoromethyl)-1-decene. A suspension of catalase (Nagase Seikagaku Kogyo Co. Ltd., 10 mg; 10^3 unit/mg from *Micrococcus lysodeikticus*) in buffer solution (50 mL, pH 8.0) was prepared from $^1/_{30}$ M aqueous Na_2HPO_4 and KH_2PO_4 solution and was stirred for 15 min at 25–30 °C in a reaction vessel equipped with Teflon stopcock. Into the mixture were added trifluoromethyl iodide (4.0 g, 10 mmol) and 1-decyne (1.3 g, 10 mmol), and then the whole was stirred at 25–30 °C. After 14 days of stirring, the oily materials were extracted with diethyl ether. The ethereal extract was dried over anhydrous magnesium sulfate and then the solvent was removed. Distillation gave (*E*)-1-(trifluoromethyl)-1-decene in 35% yield, bp 85–87 °C (39 mmHg): ^{19}F NMR ($CDCl_3$) δ −12.6 (J_{CF_3-CH} = 2.1 Hz); ^1H NMR ($CDCl_3$) δ 0.90 (CH_3), 1.08–1.80 (12 H, m), 2.50–2.83 (2 H), 6.20 (1 H, d), 6.38 (1 H, d, J_{H-H} = 15.6 Hz); IR (cm^{-1}) 1665 (C=C). Anal. Found: C, 63.25; H, 9.54. Calcd for $C_{11}H_{19}F_3$: C, 63.46; H, 9.20.

1-Phenyl-2-(trifluoromethyl)propene. Trifluoromethyl iodide (4.0 g, 20 mmol), 1-phenylpropyne (1.86 g, 10 mmol), and urease (Nagase Seikagaku Kogyo Co. Ltd., 50 mg; 8.8 unit/mg from jack beans) were used. Distillation gave 1-phenyl-2-(trifluoromethyl)propene in 39% yield, bp 74–76 °C (27 mmHg): ^{19}F NMR ($CDCl_3$) δ −12.4; ^1H NMR ($CDCl_3$) δ 2.31 (CH_3), 7.10–7.25 (6 H, m); IR (cm^{-1}) 1670 (C=C). Anal. Found: C, 64.73; H, 5.06. Calcd for $C_{10}H_9F_3$: C, 64.53; H, 4.87.

(*E*)-1-(Pentafluoroethyl)-1-decene. Pentafluoroethyl iodide (5.0 g, 20 mmol), 1-decyne (1.3 g, 10 mmol), and urease (50 mg) were used. Distillation gave (*E*)-1-(pentafluoroethyl)-1-decene in 41% yield, bp 84–87 °C (25 mmHg), and trifluoroacetic acid in 35% yield. ^{19}F NMR ($CDCl_3$) δ 3.2 (CF_3), 45.5 (CF_2); ^1H NMR ($CDCl_3$) δ 0.91 (CH_3), 1.10–1.75 (12 H, m), 2.45–2.78 (2 H), 6.21 (1 H, d), 6.36 (1 H, d, J_{H-H} = 14.4 Hz); IR (cm^{-1}) 1670 (C=C). Anal. Found: C, 56.09; H, 7.06. Calcd for $C_{12}H_{19}F_5$: C, 55.81; H, 7.42.

1-Phenyl-2-(perfluorobutyl)propene. Perfluorobutyl iodide (6.9 g, 20 mmol), 1-phenylpropyne (1.86 g, 10 mmol), and catalase (10 mg) were used. Distillation gave 1-phenyl-2-(perfluorobutyl)propene in 26% yield and perfluoropropanoic acid in 33% yield. Final purification of 1-phenyl-2-(perfluorobutyl)propene was achieved by the recrystallization from hexane, mp 72–74 °C: ^{19}F NMR ($CDCl_3$) δ 2.8 (CF_3), 24.1, 40.7, 46.5 (3 CF_2); ^1H NMR ($CDCl_3$) δ 2.30 (CH_3), 7.26 (6 H, m); IR (cm^{-1}) 1635 (C=C). Anal. Found: C, 46.09; H, 2.86. Calcd for $C_{13}H_9F_9$: C, 46.44; H, 2.70.

1-(Perfluorobutyl)-1-octene. Perfluorobutyl iodide (6.9 g, 20 mmol), 1-octyne (1.1 g, 10 mmol), and catalase (10 mg) were used. Distillation gave 1-(perfluorobutyl)-1-octene in 46% yield, bp 73–74 °C (2 mmHg), and perfluoropropanoic acid in 25% yield. ^{19}F NMR ($CDCl_3$) δ 2.7 (CF_3), 26.6, 44.6, 46.2 (3 CF_2); ^1H NMR ($CDCl_3$) δ 0.90 (CH_3), 1.10–1.80 (8 H, m), 2.45–2.80 (2 H), 6.22 (1 H, d), 6.37 (1 H, d, J_{H-H} = 14.3 Hz); IR (cm^{-1}) 1635 (C=C). Anal. Found: C, 43.49; H, 4.92. Calcd for $C_{12}H_{15}F_9$: C, 43.65; H, 4.58.

2-(Perfluorobutyl)-2-octene. Perfluorobutyl iodide (6.9 g, 20 mmol), 2-octyne (1.1 g, 10 mmol), and catalase (10 mg) were used. Distillation gave 1-(perfluorobutyl)-2-octene in 10% yield, bp 73–75 °C (3 mmHg), and perfluoropropanoic acid in 67% yield. ^{19}F NMR ($CDCl_3$) δ 2.8 (CF_3), 24.3, 42.8, 46.4 (3 CF_2); ^1H NMR ($CDCl_3$) δ 0.93 (CH_3), 1.15–1.80 (8 H, m), 2.60–2.90 (2 H), 2.62 (3 H, s), 7.29 (1 H, s); IR (cm^{-1}) 1635 (C=C). Anal. Found: C, 43.41; H, 4.42. Calcd for $C_{12}H_{15}F_9$: C, 43.65; H, 4.58.

1-Phenyl-2-(perfluorohexyl)ethylene. Perfluorohexyl iodide (8.9 g, 20 mmol), phenylacetylene (1.0 g, 10 mmol), and urease (50 mg) were used. Recrystallization from hexane gave 1-phenyl-2-(perfluorohexyl)ethylene in 66% yield, mp 38–39.5 °C: ^{19}F NMR ($CDCl_3$) δ 2.6 (CF_3), 25.9, 42.0 (2 CF_2), 43.4 (2 CF_2), 46.5 (CF_2); ^1H NMR ($CDCl_3$) δ 6.48 (1 H, d, J_{H-H} = 13.9 Hz), 6.63 (1 H, d), 7.33 (Ar H); IR (cm^{-1}) 1650 (C=C). Anal. Found: C, 40.18; H, 1.96. Calcd for $C_{14}H_7F_{13}$: C, 39.83; H, 1.67.

1-Phenyl-2-(perfluorohexyl)propene. Perfluorohexyl iodide (8.9 g, 20 mmol), 1-phenylpropyne (1.2 g, 10 mmol), and catalase (10 mg) were used. Distillation gave 1-phenyl-2-(perfluorohexyl)propene in 28% yield and perfluoropentanoic acid in 66% yield. Final purification of 1-phenyl-2-(perfluorohexyl)propene was achieved by recrystallization from pentane, mp 44–46 °C: ^{19}F NMR ($CDCl_3$) δ 2.7 (CF_3), 24.2, 40.2 (2 CF_2), 42–44 (2 CF_2), 47.0 (CF_2); ^1H NMR ($CDCl_3$) δ 2.22 (CH_3), 7.10–7.12 (6 H); IR (cm^{-1}) 1638 (C=C). Anal. Found: C, 41.16; H, 1.85. Calcd for $C_{15}H_9F_{13}$: C, 41.30; H, 2.08.

2-(Perfluorohexyl)-2-octene. Perfluorohexyl iodide (8.9 g, 20 mmol), 2-octyne (1.1 g, 10 mmol), and urease (50 mg) were used. Distillation gave 2-(perfluorohexyl)-2-octene in 18% yield, bp 87–89 °C (3 mmHg), and perfluoropentanoic acid in 53% yield. ^{19}F NMR ($CDCl_3$) δ 2.7 (CF_3), 24.0 (CF_2), 41–44 (3 CF_2), 46.5 (CF); ^1H NMR ($CDCl_3$) δ 0.93 (CH_3), 1.15–1.80 (6 H), 2.60–2.90 (2 H), 2.62 (3 H), 7.20 (Ar H); IR (cm^{-1}) 1620 (C=C). Anal. Found: C, 39.25; H, 3.38. Calcd for $C_{14}H_{15}F_{13}$: C, 39.08; H, 3.51.

1-(Perfluorohexyl)-1-octene. Perfluorohexyl iodide (6.9 g, 20 mmol), 1-octyne (1.1 g, 10 mmol), and catalase (10 mg) were used. Distillation gave 1-(perfluorohexyl)-1-octene in 61% yield, bp 64–66 °C (2 mmHg), and perfluoropentanoic acid in 14% yield. ^{19}F NMR ($CDCl_3$) δ 2.2 (CF_3), 25.9, 41.7 (2 CF_2), 43.0 (2 CF_2), 46.0 (CF_2); ^1H NMR ($CDCl_3$) δ 0.99 (CH_3), 1.10–1.80 (4 H, m), 2.35–2.80 (2 H), 6.22 (1 H, d, J_{H-H} = 14.6 Hz), 6.40 (1 H, d); IR (cm^{-1}) 1635 (C=C). Anal. Found: C, 39.44; H, 3.78. Calcd for $C_{14}H_{15}F_{13}$: C, 39.08, H; 3.51.

1-(Perfluorohexyl)-1-decene. Perfluorohexyl iodide (6.9 g, 20 mmol), 1-decyne (1.3 g, 10 mmol), and urease (50 mg) were used. Distillation gave 1-(perfluorohexyl)-1-decene in 42% yield, bp 107–109 °C (3 mmHg), and perfluoropentanoic acid in 39% yield. ^{19}F NMR ($CDCl_3$) δ 2.7 (CF_3), 26.2, 42.0 (2 CF_2), 43.5 (2 CF_2), 46.0 (CF_2); ^1H NMR ($CDCl_3$) δ 0.92 (CH_3), 1.20–1.80 (12 H, m), 2.50–2.80 (2 H), 6.20 (1 H, d, J_{H-H} = 14.3 Hz), 6.37 (1 H, d); IR (cm^{-1}) 1638 (C=C). Anal. Found: C, 42.15; H, 3.96. Calcd for $C_{16}H_{19}F_{13}$: C, 41.93; H, 4.18.

1-Phenyl-2-(perfluorooctyl)ethylene. Perfluorooctyl iodide (11 g, 20 mmol), phenylacetylene (1.0 g, 10 mmol), and urease (50 mg) were used. Distillation gave 1-phenyl-2-(perfluorooctyl)ethylene in 53% yield and perfluoroheptanoic acid in 28% yield. Final purification of 1-phenyl-2-(perfluorooctyl)ethylene was achieved by the recrystallization from hexane, mp 59–61 °C: ^{19}F NMR ($CDCl_3$) δ 2.7 (CF_3), 22.7 (CF_2), 41.0–44.0 (5 CF_2), 46.7 (CF_2); ^1H NMR ($CDCl_3$) δ 6.58 (1 H, d, J_{H-H} = 13.5 Hz), 6.75 (1 H, d), 7.38 (Ar H); IR (cm^{-1}) 1635 (C=C). Anal. Found: C, 37.09; H, 1.06. Calcd for $C_{16}H_7F_{17}$: C, 36.80; H, 1.35.

1-Phenyl-2-(perfluorooctyl)propene. Perfluorooctyl iodide (11 g, 20 mmol), phenylpropyne (1.2 g, 10 mmol), and catalase (10 mg) were used. Distillation gave 1-phenyl-2-(perfluorooctyl)propene in 26% yield and perfluoroheptanoic acid in 54% yield. Final purification of 1-phenyl-2-(perfluorooctyl)propene was achieved by the recrystallization from hexnae, mp 88–89 °C: ^{19}F NMR ($CDCl_3$) δ 2.8 (CF_3), 24.0, 39.8 (2 CF_2), 42.8 (4 CF_2), 46.5 (CF_2); ^1H NMR ($CDCl_3$) δ 2.30 (CH_3), 7.20 (6 H); Ir (cm^{-1}) 1635 (C=C). Anal. Found: C, 38.16; H, 1.85. Calcd for $C_{17}H_9F_{17}$: C, 38.08; H, 1.69.

1-(Perfluorooctyl)-1-octene. Perfluorooctyl iodide (11 g, 20 mmol), 1-octyne (1.1 g, 10 mmol), and catalase (10 mg) were used. Distillation gave 1-(perfluorooctyl)-1-octene in 36% yield, bp 93–95 °C (2 mmHg), and perfluoroheptanoic acid in 43% yield. ^{19}F NMR ($CDCl_3$) δ 2.6 (CF_3), 27.4 (CF_2), 41.0–44.0 (10 CF_2), 46.6 (CF_2); ^1H NMR ($CDCl_3$) δ 0.90 (CH_3), 1.15–1.80 (8 H, m), 2.45–2.80 (2 H), 6.22 (1 H, d, J_{H-H} = 14.6 Hz), 6.38 (1 H, d); IR (cm^{-1}) 1635 (C=C). Anal. Found: C, 36.47; H, 3.14. calcd for $C_{16}H_{15}F_{17}$: C, 36.24; H, 2.85.

1-(Perfluorooctyl)-1-decene. Perfluorooctyl iodide (11 g, 20 mmol), 1-decyne (1.3 g, 10 mmol), and catalase (10 mg) were used. Distillation gave 1-(perfluorooctyl)-1-decene in 26% yield, bp 118–120 °C (3 mmHg), and perfluoroheptanoic acid in 54% yield. ^{19}F NMR ($CDCl_3$) δ 2.8 (CF_3), 26.3 (CF_2), 41.0–44.5 (5 CF_2), 46.5 (CF_2); ^1H NMR ($CDCl_3$) δ 0.90 (CH_3), 1.10–1.70 (12 H, m), 2.35–2.75 (2 H), 6.22 (1 H, d, J_{H-H} = 14.6 Hz), 6.38 (1 H, d); IR (cm^{-1}) 1635 (C=C). Anal. Found: C, 39.07; H, 3.56. Calcd for $C_{18}H_{19}F_{17}$: C, 38.72; H, 3.43.

Perfluoroheptanoic Acid. Perfluorooctyl iodide (11 g, 20 mmol), 2-octyne (1.1 g, 10 mmol), and lipoxygenase (Sigma Chemical Co. Ltd., 10 mg; 126500 unit/mg from soybean) were used in the Culstir flask. Distillation gave perfluoroheptanoic acid in 61% yield.