Preparation of Fluorinated 1,2- and α,ω-Diols

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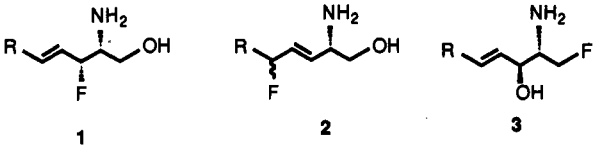
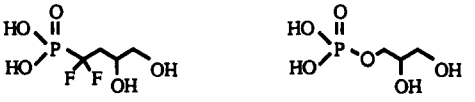
The addition of perfluoroalkyl iodides to 7-octene-1,2-diol or 5-hexene-1,2-diol in the presence of $Pd(Ph_3P)_4$ or benzoyl peroxide gives the corresponding adducts in 71–88% yields. The adducts have been successfully reduced by hydrogenation using palladium on activated carbon as a catalyst to afford the fluorinated 1,2-diols $R_f(CH_2)_nCH(OH)CH_2OH$ (n = 4, 6) in good yields. The fluorinated α,ω-diol $HO(CH_2)_3CH(CH_2C_6F_{13})(CH_2)_3OH$ has been prepared by $Pd(Ph_3P)_4$-catalyzed addition of $C_6F_{13}I$ to the diester $(EtO_2CCH_2CH_2)_2C{=}CH_2$ followed by $LiAlH_4$ reduction.

Introduction

Fluorinated alcohols are important compounds in organic synthesis and material science. For example, 1,1,1-trifluoroethanol has been utilized as a nonnucleophilic solvent and as a protecting group for carboxylic acids.[1] $R_fCH_2CH{=}CH(CH_2)_{15}OH$ has been utilized to prepare coating materials for magnetic tape, imparting low surface roughness and reduced heat clogging.[2] On the other hand, fluorinated alcohols and their derivatives are important building blocks in organic synthesis[3] and often exhibit enhanced biological activity.[4] For instance, fluorine-containing isosteres 1, 2, and 3 have been found to be inhibitors of protein kinase C.[4c] Although a variety of syntheses of fluorinated alcohols has been documented,[5] there are few reports describing the preparation of fluorinated diols. For example, Reiss has isolated the diol, $R_fC(CH_3)(OH)CH_2C(CH_3)_2OH$ as a byproduct from the reaction of perfluoroalkyl iodides with amalgamated calcium and acetone.[6] The reaction of 1,6-bis(bromomagnesium)perfluorohexane with ketones afforded the corresponding fluorinated diols in low yield.[7] The diol $C_6F_{13}(CH_2)_3CH(CH_2OH)_2$ has been prepared via the addition of the perfluorohexyl iodide to diethyl (2-propenyl)propanedioate followed by reduction.[8] Treatment of fluorinated ketones with bis(bromomagnesium)-ethyne gave the corresponding fluorinated diols.[9] More recently, we and others have reported the synthesis of 1,1-difluoro-3,4-dihydroxylbutylphosphonic acid (4) which is regarded as an isosteric and isoelectronic analog of glycerol 3-phosphate (5).[10] In this paper, we describe the synthesis of the fluorinated 1,2-diols $R_f(CH_2)_nCH(OH)CH_2OH$ (n = 4, 6) (**7a–f**) and the fluorinated α,ω-diol $(HOCH_2CH_2CH_2)_2CHCH_2C_6F_{13}$ (**15**).



R= n-$C_{13}H_{27}$



Results and Discussion

The addition of perfluoroalkyl iodides to 5-hexene-1,2-diol or 7-octene-1,2-diol was catalyzed by tetrakis(triphenylphosphine)palladium[11] at room temperature or by benzoyl peroxide[12] at 110 °C to give the corresponding adducts **6a–g** in 71–88% yields. In the presence of $Pd(Ph_3P)_4$, for example, the addition of perfluoropropyl iodide to 7-octene-1,2-diol afforded **6g** in 88% yield. These results are summarized in Table I.

$$R_fI + CH_2{=}CHR \xrightarrow{Pd(Ph_3P)_4/RT \text{ or } (PhCO_2)_2/110^\circ C} R_fCH_2CHIR \quad \mathbf{6}$$

R: $(CH_2)_2CH(OH)CH_2OH$, $(CH_2)_4CH(OH)CH_2OH$.

Reduction of **6d** by zinc and nickel chloride hexahydrate

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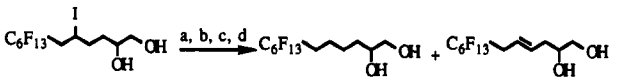
Table I. Addition of R_fI to Alkene-1,2-diols

$$R_fI + CH_2{=}CHR \xrightarrow{Pd(Ph_3P)_4/rt\ or\ (PhCO_2)_2/110\ °C} \underset{6}{R_fCH_2CHIR}$$

6	R_f	R	catalyst	yield[a] (%)
6a	C_4F_9	$(CH_2)_4CH(OH)CH_2OH$	$Pd(PPh_3)_4$	76
6b	C_4F_9	$(CH_2)_2CH(OH)CH_2OH$	$Pd(PPh_3)_4$	75
6c	C_6F_{13}	$(CH_2)_4CH(OH)CH_2OH$	$Pd(PPh_3)_4$	75
6d	C_6F_{13}	$(CH_2)_2CH(OH)CH_2OH$	$Pd(PPh_3)_4$	79
6e	C_8F_{17}	$(CH_2)_4CH(OH)CH_2OH$	$Pd(PPh_3)_4$	77
6f	C_8F_{17}	$(CH_2)_2CH(OH)CH_2OH$	$(PhCO_2)_2$	71
6f	C_8F_{17}	$(CH_2)_2CH(OH)CH_2OH$	$Pd(PPh_3)_4$	75
6g	C_3F_7	$(CH_2)_4CH(OH)CH_2OH$	$Pd(PPh_3)_4$	88

[a] Isolated yields.

Scheme I[a]



6 d 7 d 8 d

a)	85%	15%
b)	75%	25%
c)	70%	30%
d)	90%	10%

[a] Key: (a) $Zn/NiCl_2{\cdot}6H_2O$/THF/rt; (b) Zn/HOAc/MG/80 °C; (c) H_2 (1atm)/Pd–C/MeOH/Et_3N/rt; (d) H_2 (1atm)/Pd–C/MeOH/NaOAc/rt.

in wet THF[13] gave a mixture of 1,2-diol **7d** and alkene **8d**. A mixture of **7d** and **8d** was also obtained by the reaction of **6d** with zinc in HOAc and monoglyme (MG) at 80 °C.[14] Pd–C-catalyzed hydrogenation of **6d** in the presence of triethylamine[15] or sodium acetate[16] afforded 70:30 and 90:10 mixtures of **7d** and **8d**, respectively. The structure of **8d** was confirmed by NMR spectroscopic analysis. In the ^1H NMR spectrum, an AB quartet of triplets ($CH_2CH{=}CHCH_2$, $^3J_{H,H}$ = 16 and 7 Hz) appeared at 5.5 ppm and a triplet of doublets was observed at 2.8 ppm ($CF_2CH_2CH{=}$, $^3J_{H,F}$ = 21 and $^3J_{H,H}$ = 7 Hz). In the ^{13}C NMR spectrum, no splitting of the olefinic carbons by fluorine was observed, which indicates that the elimination product **8d** was formed, rather than its isomer C_6F_{13}-$CH{=}CH(CH_2)_2CH(OH)CH_2OH$.

However, reduction of **6a–g** to the corresponding **7a–g** was achieved in good yield by catalytic hydrogenation (Pd–C, MeOH) in the presence of sodium bicarbonate. If the reduction of **6a–g** was monitored by ^{19}F NMR analysis, **8** was detected during the reaction (the $-CF_2CH_2-$ peak in **7** is 1 ppm downfield of the corresponding signal in **8**). However, under these conditions all of **8** was hydrogenated to afford the diol **7**. For comparison, methods c and d (described in Scheme I) still have mixtures of **7d** and **8d** after the reactions were carried out for 7 days. These results are summarized in Table II. Adducts **6a–g** are oils or waxy solids and darken during storage. The diols **7a–f** are stable white solids or yellowish oils.

The reported one-pot preparation of α,α-difluoro esters via the addition of difluoroiodoacetate to alkenes in the

Table II. Preparation of Fluorinated 1,2-Diols 7a–f

$$\underset{6}{R_fCH_2CHI(CH_2)_nCH(OH)CH_2OH} \xrightarrow[NaHCO_3/MeOH]{H_2[a]/Pd\text{-}C\ (5\%)} \underset{7}{R_f(CH_2)_{n+2}CH(OH)CH_2OH}$$

7	R_f	n	yield[b] (%)
7a	C_4F_9	4	78
7b	C_4F_9	2	70
7c	C_6F_{13}	4	72
7d	C_6F_{13}	2	69
7e	C_8F_{17}	4	62
7f	C_8F_{17}	2	80

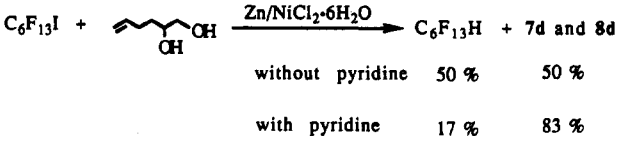
[a] H_2 was passed through the reaction mixture for 6 days. [b] Isolated yields.

Scheme II

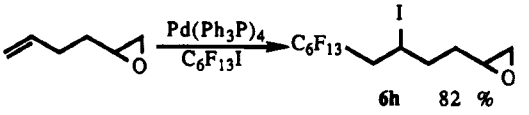
$$\underset{6a\text{–}f}{R_fCH_2CHI(CH_2)_nCH(OH)CH_2OH} \xrightarrow[Pd\text{–}C\ (5\%)/H_2{}^*\ 6\ days]{NaHCO_3/MeOH} \underset{7a\text{–}f}{R_f(CH_2)_{n+2}CH(OH)CH_2OH}$$

*H_2 was passed through the reaction mixture.

presence of zinc and nickel chloride hexahydrate[17] prompted us to investigate the one-pot preparation of **7d** via this methodology. However, the main product from the addition of $C_6F_{13}I$ to 5-hexene-1,2-diol with this catalyst system was $C_6F_{13}H$. Pyridine increased the amount of **7d** and **8d** but did not totally avoid reduction of the perfluoroalkyl iodide.



Compound **6h**, as an alternative precursor to **6d**, could be prepared via the same methodology.



6h 82 %

Fluorinated α,ω-diols are useful compounds. For example, $C_6F_{13}(CH_2)_3CH(CH_2OH)_2$ is a precursor for the preparation of fluorinated resins and water repellents.[8] We describe here the synthesis of the new longer chain fluorinated α,ω-diol $C_6F_{13}CH_2CH(CH_2CH_2CH_2OH)_2$ (**15**).

A possible route to **15** employs diol **11** in an addition/reduction with $C_6F_{13}I$. Diol **11** is an attractive precursor since it could potentially be prepared by olefination of the commercially available diethyl 4-oxopimelate (**9**) followed by $LiAlH_4$ reduction. Attempted reaction of **9** with methylenetriphenylphosphorane gave less than 5% of diethyl 4-methylidenepimelate (**10**). However, **10** could be prepared by the reaction of **9** with $CH_2Br_2/Zn/TiCl_4$ in dry THF and CH_2Cl_2 in 50% yield.[18] Treatment of **10**

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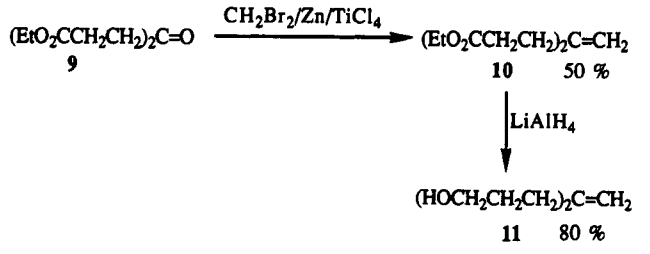
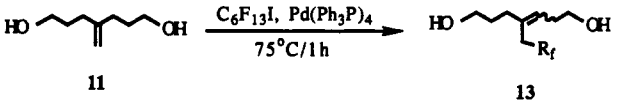
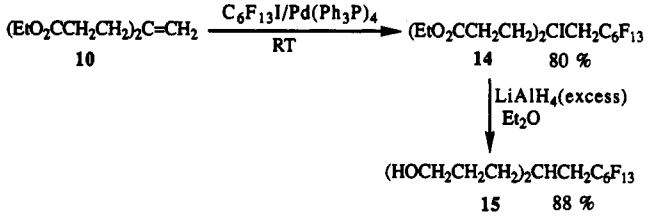
with $LiAlH_4$[19] afforded 4-methylideneheptane-1,7-diol (11) in 80% yield.



The $Pd(Ph_3P)_4$-catalyzed addition of $C_6F_{13}I$ to 11 gave only 15% conversion of $C_6F_{13}I$ at room temperature. At 75 °C, the addition gave a 50% conversion based on ^{19}F NMR analysis. No $(HOCH_2CH_2CH_2)_2ClCH_2C_6F_{13}$ (12) was detected, and only 35% $HO(CH_2)_3C(CH_2C_6F_{13})$=$CHCH_2CH_2OH$ (13) was isolated by silica gel chromatography. The intermediate 12 may not be stable under the reaction conditions, and elimination of HI would form 13. The structure of 13 was confirmed by NMR analysis. In the ^1H NMR spectrum, two sets of triplets (vinyl protons of cis and trans 13, $^3J_{HH}$ = 7 Hz) appeared at 5.66 and 5.45 ppm, and two triplets were observed at 2.87 and 2.76 ppm (CF_2CH_2 of cis and trans 13, $^3J_{HF}$ = 20 Hz). In the ^{13}C NMR spectrum, no splitting of the olefinic carbons by fluorine was observed, which indicates that 13 was formed, rather than $(HOCH_2CH_2CH_2)_2C$=CHC_6F_{13}. Similar regiochemistry was noted in the formation of 8d (Scheme I) and with related fluorocontaining phosphonates.[20]



Diol 15 could be prepared by an alternative route: room-temperature $Pd(Ph_3P)_4$-catalyzed addition of $C_6F_{13}I$ to 10 gave 14 as a pale yellow viscous oil in 80% isolated yield. $LiAlH_4$ reduction of 14 afforded 15 as a pale yellow viscous oil in 88% isolated yield.



Experimental Section

^{19}F NMR, ^1H NMR, and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer. All chemical shifts are reported in parts per million downfield (positive) of the standard. ^1H NMR and ^{13}C NMR chemical shifts are reported relative to internal TMS. ^{19}F NMR chemical shifts are reported relative to internal $CFCl_3$. ^{13}C NMR spectra were broadband decoupled from hydrogen nuclei. $CDCl_3$ served as the solvent for all NMR spectra except where indicated. IR spectra were recorded on a Mattson Cygnus 100 FT-IR spectrometer. DIP-MS were recorded on a VG TRIO-1 spectrometer operating at 70 eV. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, NY. All of the products (6, 7, 10, 11, 14, and 15) gave greater than 97% purities based on ^{13}C, ^1H, and ^{19}F NMR spectroscopic analysis.

Representative General Procedure for the Preparation of Adducts 6: Preparation of 9,9,10,10,11,11,12,12,12-Nonafluoro-7-iodododecane-1,2-diol (6a). A 500-mL flask was charged with 28.8 g (200 mmol) of 7-octene-1,2-diol and 69.2 g (200 mmol) of C_4F_9I. $Pd(Ph_3P)_4$ (1.7 g, 1.5 mmol) was added at room temperature with stirring. After a few seconds an exothermic reaction occurred. The reaction mixture was stirred at room temperature for 2 h. Chromatography (silica gel column 60 × 600 mm) with CH_2Cl_2/EtOAc (2:1) eluent gave 74.5 g (76% yield) of 6a as an oil: ^{19}F NMR δ −81.5 (s, 3 F, CF_3), −113.8 (AB quartet, J = 266 Hz, 2 F, CF_2CH_2), −125.0 (s, 2 F), −126.4 (s, 2 F); ^1H NMR δ 4.33 (m, 1 H, CHI), 3.41–3.71 (m, 3 H), 2.84 (m, 2 H), 2.17 (br s, 2 H), 1.82 (m, 2 H), 1.37–1.58 (m, 6 H); ^{13}C NMR δ 20.7, 24.7, 29.8, 32.9, 40.3, 41.7 (t, J = 21 Hz, CF_2CH_2), 66.9 (2s), 72.3 (2s), 105.0–123.6 (m); FT-IR (CCl_4) 3410 (br), 2937 (m), 1229 (s) cm^{-1}; DIP-MS (m/e) 459 ($M^+ - CH_2OH$, 0.95), 454 ($M^+ - 2H_2O$, 0.93), 363 ($M^+ - I$, 0.42), 345 ($M^+ - I - H_2O$, 9.53), 327 ($M^+ - I - 2H_2O$, 75.78).

Preparation of 7,7,8,8,9,9,10,10,10-Nonafluoro-5-iododecane-1,2-diol (6b). 6b (68 g, 75%, oil) was similarly prepared from 25 g (194 mmol) of 5-hexene-1,2-diol, 67.1 g (194 mmol) of C_4F_9I, and 2.2 g of $Pd(Ph_3P)_4$: ^{19}F NMR δ −81.5 (s, 3 F, CF_3), −113.9 (AB quartet, J = 273 Hz, 2 F, CF_2CH_2), −125.0 (s, 2 F), −126.4 (s, 2 F); ^1H NMR δ 4.37 (m, 1 H, CHI), 3.80 (2 H, br s, OH), 3.42–3.76 (m, 3 H, $CHOHCH_2OH$), 2.88 (m, 2 H, CF_2CH_2), 1.48–2.11 (m, 4 H); ^{13}C NMR δ 20.3 and 20.5 (2s), 33.0 and 33.3 (2s), 36.4 and 36.9 (2s) 41.7 (t, J = 21 Hz, CF_2CH_2), 66.8 (2s) and 71.5 (2s), 109.0–121.7 (m); FT-IR (CCl_4) 3421 (br), 2934 (m), 1237 (s) cm^{-1}; DIP-MS (m/e) 431 ($M^+ - CH_2OH$, 0.13), 335 ($M^+ - I$, 7.80), 317 ($M^+ - I - H_2O$, 56.64), 299 ($M^+ - I - 2H_2O$, 16.37).

Preparation of 9,9,10,10,11,11,12,12,13,13,14,14,14-Tridecafluoro-7-iodotetradecane-1,2-diol (6c). 6c (22.2 g, 75%, oil) was similarly prepared from 25 g (194 mmol) of 7-octene-1,2-diol, 22.3 g (50 mmol) of $C_6F_{13}I$, and 1.2 g (1 mmol) of $Pd(Ph_3P)_4$: ^{19}F NMR δ −81.3 (t, J = 9 Hz, 3 F, CF_3), −113.6 (AB quartet, J = 269 Hz, 2 F, CF_2CH_2), −122.2 (s, 2 F), −123.3 (s, 2 F), −124.1 (s, 2 F), −126.6 (s, 2 F); ^1H NMR δ 4.34 (m, 1 H, CHI), 3.42–3.73 (m, 3 H, $CHOHCH_2OH$), 2.85 (m, 2 H, CF_2CH_2), 2.11 (m) 1.45–1.84 (m, 8 H); ^{13}C NMR δ 20.6, 24.8 (2s), 29.9, 33.0, 40.3, 41.9 (t, J = 21 Hz, CF_2CH_2), 66.9, 72.3, 105.6–121.9 (m); FT-IR (CCl_4) 3403 (br), 2938 (m), 1244 (s) cm^{-1}; DIP-MS (m/e) 559 ($M^+ - CH_2OH$, 1.17), 554 ($M^+ - 2H_2O$, 1.00), 463 ($M^+ - I$, 0.46), 427 ($M^+ - I - 2H_2O$, 100).

Preparation of 7,7,8,8,9,9,10,10,11,11,12,12,12-Tridecafluoro-5-iododododecane-1,2-diol (6d). 6d (2.5 g, 79%, oil) was similarly prepared from 0.73 g (5.7 mmol) of 5-hexene-1,2-diol, 2.55 g (5.7 mmol) of $C_6F_{13}I$, and 0.12 g (0.1 mmol) of $Pd(Ph_3P)_4$: ^{19}F NMR δ −81.6 (3 F, CF_3), −113.5 (AB quartet, J = 269 Hz, 2 F, CF_2CH_2), −122.2 (s, 2 F), −123.3 (s, 2 F), −124.1 (s, 2 F), −126.8 (s, 2 F); ^1H NMR δ 4.36 (m, 1 H, CHI), 3.26–3.74 (m, 5 H, $CHOHCH_2OH$), 2.86 (m, 2 H, CF_2CH_2), 1.51–2.11 (m, 4 H, CH_2CH_2CHOH); ^{13}C NMR δ 20.4 and 20.7 (2s, $CHICH_2$), 33.2 and 33.3 (2s, $CHICH_2CH_2$), 36.5 and 36.9 (2s, CHI), 41.7 and 41.8 (2t, J = 20 Hz, CF_2CH_2), 66.7 and 66.8 (2s), 71.2 and 71.8 (2s), 107.1–132.3 (m); DIP-MS (m/e) 531 ($M^+ - CH_2OH$, 4.52), 435 ($M^+ - I$, 5.68), 417 ($M^+ - I - H_2O$, 30.62), 399 ($M^+ - I - 2H_2O$, 8.61); FT-IR (CCl_4) 3392 (br), 2934 (m), 1219 (s) cm^{-1}.

Preparation of 9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Heptadecafluoro-7-iodohexadecane-1,2-diol (6e). 6e (10.6 g, 77%, waxy solid mp 55–65 °C) was similarly prepared from 2.9 g (20 mmol) of 7-octene-1,2-diol, 11 g (20 mmol) of $C_8F_{17}I$, and 0.3 g (0.25 mmol) of $Pd(Ph_3P)_4$: ^{19}F NMR δ −81.5 (s, 3 F, CF_3), −113.6 (AB quartet, J = 269 Hz, 2 F, CF_2CH_2), −122.1 (s, 2 F), −122.5 (s, 4 F), −123.3 (s, 2 F), −124.1 (s, 2 F), −126.7 (s, 2 F); ^1H NMR δ 4.33 (m, 1 H, CHI), 3.41–3.70 (m, 3 H, $CHOHCH_2OH$), 2.43–3.03 (m, 4 H, CF_2CH_2 + OH), 1.45–1.84 (m, 8 H); ^{13}C NMR δ 20.6, 24.6, 29.8, 33.0, 40.3, 41.9 (t, J = 21 Hz, CF_2CH_2), 66.9, 72.2, 104.7–119.2 (m); FT-IR (CCl_4) 3417 (br), 2938 (m), 1241 (s) cm^{-1}; DIP-MS (m/e) 659 ($M^+ - CH_2OH$, 0.67), 654 ($M^+ - 2H_2O$, 1.10), 545 ($M^+ - I - H_2O$, 6.93), 527 ($M^+ - I - 2H_2O$, 43.92), 513 (20.95).

Preparation of 7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Heptadecafluoro-5-iodotetradecane-1,2-diol (6f). 6f (124.6 g, 75%, waxy solid mp 50–62 °C) was similarly prepared from

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(20) Yang, Z.-Y.; Burton, D. J. *J. Org. Chem.* **1992**, *57*, 4676.

32.4 g (250 mol) of 5-hexene-1,2-diol, 136.5 g (250 mmol) of $C_8F_{17}I$, and 4.6 g (4 mmol) of $Pd(Ph_3P)_4$: ^{19}F NMR δ -81.7 (t, J = 9 Hz, 3 F, CF_3), -113.6 (AB quartet, J = 269 Hz, 2 F, CF_2CH_2), -122.1 (s, 2 F), -122.5 (s, 4 F), -123.4 (s, 2 F), -124.2 (s, 2 F), -126.9 (s, 2 F); ^1H NMR δ 4.29 (m, 1 H, CHI), 3.49-3.82 (m, 3 H, $CHOHCH_2OH$), 2.70-3.05 (m, 2 H, CF_2CH_2), 1.49-2.27 (m, 6 H); ^{13}C NMR δ 20.5 and 20.7 (2s), 33.5 and 33.56 (2s), 36.6 and 37.1 (2s), 41.9 and 42.0 (2t, J = 21 Hz, CF_2CH_2), 66.8 and 66.9 (2s), 71.3 and 72.0 (2s), 104.8-123.1 (m); FT-IR (CCl_4) 3420 (br), 2934 (m), 1241 (s) cm^{-1}; DIP-MS (m/e) 631 ($M^+ - CH_2OH$, 2.68), 535 ($M^+ - I$, 2.07), 517 ($M^+ - I - H_2O$, 59.74), 499 ($M^+ - I - 2H_2O$, 20.94).

Preparation of 6f Catalyzed by $(PhCO_2)_2$. A mixture of 20.1 g (45 mmol) of $C_8F_{17}I$, 6.5 g (45 mmol) of 5-hexene-1,2-diol, and 0.85 g (3.5 mmol) of $(PhCO_2)_2$ was stirred at 110 °C for 1 h. Chromatography on silica gel with CH_2Cl_2 and EtOAc (1:1) eluent gave 19.0 g (71% yield) of **6f**.

Preparation of 9,9,10,10,11,11,11-Heptafluoro-7-iodoundecane-1,2-diol (6g). **6g** (7.8 g, 88%, oil) was similarly prepared from 2.9 g (20.3 mmol) of 7-octene-1,2-diol, 6.5 g (22 mmol) of C_3F_7I, and 0.17 g (0.15 mmol) of $Pd(Ph_3P)_4$: ^{19}F NMR δ -80.9 (t, J = 10 Hz, 3 F, CF_3), -114.6 (AB quartet, J = 269 Hz, 2 F, CF_2CH_2), -128.4 (s, 2 F, CF_2CF_3); ^1H NMR δ 4.33 (m, 1 H, CHI), 3.41-3.76 (m, 3 H, $CHOHCH_2OH$), 2.84 (m, 2 H, CF_2CH_2), 2.37 (2 H, OH), 1.82 (m, 2 H, $CH_2CHOHCH_2OH$), 1.39-1.59 (m, 6 H); ^{13}C NMR δ 20.4, 24.6, 29.6, 32.66 and 32.70 (2s), 40.2, 41.3 (t, J = 21 Hz, CF_2CH_2), 66.5 (2s) and 72.1 (2s), 108.4 (th, J = 264, 38 Hz, CF_2CF_3), 117.2 (tt, J = 256, 31 Hz, CF_2CH_2), -117.6 (qt, J = 287, 36 Hz, CF_3); FT-IR (CCl_4) 3411 (br), 2939 (m), 1230 (s) cm^{-1}; DIP-MS (m/e) 423 ($M^+ - OH$, 0.84), 313 ($M^+ - I$, 4.25), 295 ($M^+ - I - H_2O$, 0.47), 277 ($M^+ - I - 2H_2O$, 1.70).

Addition of $C_6F_{13}I$ to 1,2-Epoxy-5-hexene. A mixture of 1.0 g (10 mmol) of 1,2-epoxy-5-hexene, 4.2 g (9.4 mmol) of $C_6F_{13}I$, and 0.2 g (0.2 mmol) of $Pd(Ph_3P)_4$ was stirred at room temperature for 15 min. The reaction mixture was purified by chromatography with methylene chloride eluent to give 4.2 g (82% yield) of 7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iodo-1,2-epoxydodecane (**6h**) as an oil: ^1H NMR δ 4.38 (m, 1 H, CHI), 2.96 (m, 1 H, CH_2CHO), 2.86 (m, 2 H, CF_2CH_2), 2.78 and 2.79 (2dd, J = 5, 4 Hz, 1 H), 2.55 and 2.52 (2dd, 1 H, J = 5, 2.7 Hz), 1.58-2.08 (m, 4 H, $CHICH_2CH_2$); ^{19}F NMR δ -81.3 (t, J = 9 Hz, 3 F, CF_3), -113.5 (AB quartet, J = 273 Hz, 2 F, CF_2CH_2), -122.2 (s, 2 F), -123.3 (s, 2 F), -124.1 (s, 2 F), -126.6 (s, 2 F); ^{13}C NMR δ 19.4 and 19.7 (2s, $CHICH_2CH_2$), 32.5 and 32.9 (2s, $CHICH_2CH_2$), 36.6 and 37.2 (2s, CHI), 41.8 and 41.9 (2t, J = 20 Hz, CF_2CH_2), 47.0 and 46.9 (2s), 50.9 and 51.3 (2s) (for epoxide ring), 108-132 (m); FT-IR (CCl_4) 2926 (s), 1241 (s) cm^{-1}; DIP-MS (m/e) 530 (M^+, 1.67), 487 (3.74).

Representative General Procedure for the Preparation of Fluorinated 1,2-Diols 7: Preparation of 9,9,10,10,-11,11,12,12,12-Nonafluorododecane-1,2-diol (7a). A mixture of 40 g (82 mmol) of **6a**, 7.6 g (90 mmol) of $NaHCO_3$, 3 g of Pd-C (5%), and 250 mL of MeOH was stirred at room temperature for 6 days with hydrogen passed through the reaction mixture. After removal of the Pd-C by filtration, the filtrate was concentrated and dried under vacuum (25 °C/1 mmHg) to give a residue which was further purified by chromatography (silica gel column 60 × 500 mm) with CH_2Cl_2 and EtOAc (1:1) eluent to afford 23.2 g (78% yield) of **7a** as an oil: ^{19}F NMR δ -81.7 (s, 3 F, CF_3), -115.2 (s, 2 F, CF_2CH_2), -125.0 (s, 2 F), -126.6 (s, 2 F); ^1H NMR δ 3.38-3.69 (m, 5 H, $CHOHCH_2OH$), 2.05 (m, 2 H, CF_2CH_2), 1.37-1.61 (m, 8 H); ^{13}C NMR δ 20.4, 25.8, 29.4, 29.7, 31.1 (t, J = 22 Hz, CF_2CH_2), 33.3, 67.1, 72.7, 105.4-123.6 (m); FT-IR (CCl_4) 3394 (br), 2936 (m), 1243 (s) cm^{-1}; DIP-MS (m/e) 333 ($M^+ - CH_2OH$, 20.06), 328 ($M^+ - 2H_2O$, 0.31), 315 ($M^+ - CH_2OH - H_2O$, 42.94).

Preparation of 7,7,8,8,9,9,10,10,10-Nonafluorodecane-1,2-diol (7b). **7b** (23.0 g, 70%, oil) was similarly prepared from 45 g (97 mmol) of **6b**, 9.0 g (107 mmol) of $NaHCO_3$, 5 g of Pd-C (5%), and 250 mL of MeOH: ^{19}F NMR δ -81.6 (s, 3 F, CF_3), -115.2 (s, 2 F, CF_2CH_2), -125.1 (2 F), -126.6 (2 F); ^1H NMR δ 3.42-3.72 (m, $CHOHCH_2OH$, 3 H), 1.99-2.90 (m, CF_2CH_2 + OH, 4 H), 1.48-1.63 (m); ^{13}C NMR δ 20.3, 25.2, 30.8 (t, J = 22 Hz, CF_2CH_2), 32.7, 66.8, 72.0, 106.1-128.6 (m); FT-IR (CCl_4) 3416 (br, OH), 2954 (w), 1235 (s) cm^{-1}; DIP-MS (m/e) 305 ($M^+ - CH_2OH$, 6.12), 287 ($M^+ - CH_2OH - H_2O$, 9.42).

Preparaton of 9,9,10,10,11,11,12,12,13,13,14,14,14-Tridecafluorotetradecane-1,2-diol (7c). **7c** (17.1 g, 72%, mp 49-52 °C) was similarly prepared from 30 g (51 mmol) of **6c**, 5.2 g (62 mmol) of $NaHCO_3$, 2 g of Pd-C (5%), and 250 mL of MeOH: ^{19}F NMR δ -81.4 (t, J = 9 Hz, 3 F, CF_3), -115.0 (t, J = 15 Hz, 2 F, CF_2CH_2), -122.5 (s, 2 F), -123.4 (s, 2 F), -124.1 (s, 2 F), -126.7 (s, 2 F); ^1H NMR δ 3.85 (br s, 2 H, OH), 3.64-3.41 (m, 3 H, $CHOHCH_2OH$), 2.04 (m, 2 H, CF_2CH_2), 1.39-1.61 (m, 8 H); ^{13}C NMR (DMSO-d_6) δ 20.2, 25.5, 29.2, 29.4, 30.9 (t, J = 22 Hz, CF_2CH_2), 33.1, 66.9, 72.4, 105.3-122.3 (m); FT-IR (CCl_4) 3410 (br), 2933 (m), 1243 (s) cm^{-1}; DIP-MS (m/e) 433 ($M^+ - CH_2OH$, 1.06), 428 ($M^+ - 2H_2O$, 3.22), 415 ($M^+ - CH_2OH - H_2O$, 2.34). Anal. Calcd for $C_{14}H_{17}F_{13}O_2$: C, 36.20; H, 3.69; F, 53.22. Found: C, 36.39; H, 3.35; F, 52.98.

Preparation of 7,7,8,8,9,9,10,10,11,11,12,12,12-Tridecafluorododecane-1,2-diol (7d). **7d** (26.1 g, 69%, mp 43-46 °C) was similarly prepared from 50 g (89 mmol) of **6d**, 8.2 g (98 mmol) of $NaHCO_3$, 5 g of Pd-C (5%), and 250 mL of MeOH: ^{19}F NMR δ -81.5 (t, J = 9 Hz, 3 F, CF_3), -115.1 (t, J = 15 Hz, 2 F, CF_2CH_2), -122.6 (s, 2 F), -123.5 (s, 2 F), -124.2 (s, 2 F), -126.8 (s, 2 F); ^1H NMR δ 3.39-3.70 (m, 5 H, $CHOHCH_2OH$), 2.07 (m, 2 H, CF_2CH_2), 1.45-1.65 (m, 6 H); ^{13}C NMR δ 20.3, 25.3, 30.9 (t, J = 22 Hz, CF_2CH_2), 32.8, 66.9, 72.1, 107.2, -122.6 (m); FT-IR (CCl_4) 3403 (br), 2950 (m), 1241 (s) cm^{-1}; DIP-MS (m/e) 405 ($M^+ - CH_2OH$, 4.73), 387 ($M^+ - CH_2OH-H_2O$, 6.76).

Preparation of 9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Heptadecafluorohexadecane-1,2-diol (7e). **7e** (25.0 g, 62%, mp 87-90 °C) was similarly prepared from 49 g (71 mmol) of **6e**, 6.6 g (78 mmol) of $NaHCO_3$, 3 g of Pd-C (5%), and 250 mL of MeOH: ^{19}F NMR δ -81.3 (t, J = 9 Hz, 3 F, CF_3), -114.9 (s, 2 F, CF_2CH_2), -122.4 (s, 6 F), -123.2 (s, 2 F), -124.0 (s, 2 F), -126.6 (s, 2 F); ^1H NMR δ 3.42-3.75 (m, 3 H, $CHOHCH_2OH$), 1.30-2.10 (m); ^{13}C NMR (DMSO-d_6) δ 19.5, 25.0, 28.4, 29.0, 29.8 (t, J = 22 Hz, CF_2CH_2), 33.1, 65.9, 71.0, 106.5-118.7 (m); FT-IR (CCl_4) 3410 (br), 2933 (m), 1243 (s) cm^{-1}; DIP-MS (m/e) 565 ($M^+ + 1$, 0.06), 533 ($M^+ - CH_2OH$, 0.05). Anal. Calcd for $C_{16}H_{17}F_{17}O_2$: C, 34.04; H, 3.04; F, 57.25. Found: C, 34.64; H, 3.05; F, 57.02.

Preparation of 7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Heptadecafluorotetradecane-1,2-diol (7f). **7f** (18 g, 80%, mp 77-83 °C) was similarly prepared from 27.8 g (42 mmol) of **6f**, 3.9 g (46 mmol) of $NaHCO_3$, 2.5 g of Pd-C (5%), and 250 mL of MeOH: ^{19}F NMR δ -81.3 (t, J = 9 Hz, 3 F, CF_3), -114.9 (s, 2 F, CF_2CH_2), -122.4 (s, 6 F), -123.2 (s, 2 F), -124.0 (s, 2 F), -126.6 (s, 2 F); ^1H NMR δ 3.42-3.72 (m, 3 H, $CHOHCH_2OH$), 1.48-2.14 (m, 10 H); ^{13}C NMR (DMSO-d_6) δ 20.4, 25.3, 30.6 (t, J = 21 Hz, CF_2CH_2), 33.5, 66.7, 71.6, 106.7-122.5 (m); FT-IR (CCl_4) 3461 (br), 2935 (m), 1243 (s) cm^{-1}; DIP-MS (m/e) 535 ($M^+ - 1$, 0.16), 505 ($M^+ - CH_2OH$, 19.60), 487 ($M^+ - CH_2OH - H_2O$, 31.6).

Preparation of Diethyl 4-Methylidenepimelate (10). A 1-L flask fitted with a mechanical stirrer was charged with 28 g (43 mmol) of Zn, 150 mL of freshly distilled THF (from Na/Ph_2CO) and 17.9 g (103 mmol) of CH_2Br_2. The mixture was stirred and cooled to -40 °C, and then $TiCl_4$ (11.5 mL) was added dropwise. After the resultant mixture was stirred at 5 °C for 3 days, CH_2Cl_2 (50 mL) and 20 g (87 mmol) of diethyl 4-oxopimelate in 50 mL of CH_2Cl_2 were slowly added into the reaction mixture at 5 °C, respectively. The reaction mixture was stirred at room temperature overnight and then diluted with 300 mL of ether and poured into a mixture of 100 g of sodium bicarbonate and 50 g of water with stirring. The mixture was stirred for 3 h and filtered, and the solids were washed with ether (3 × 400 mL). The combined filtrate and ether solution were dried over Na_2SO_4 and concentrated to give a residue which was further purified by chromatography on silica gel with hexane and ethyl acetate (9:1-6:1) eluent to afford 9.0 g (50% yield) of **10** as an oil: ^1H NMR δ 1.25 (t, J = 7 Hz, 6 H, CH_3), 2.33-2.49 (m, 8 H, CH_2CH_2), 4.12 (q, J = 7 Hz, 4 H, OCH_2), 4.77 (s, 2 H, $=CH_2$); ^{13}C NMR 14.3, 31.2, 32.7, 60.3, 109.0, 146.7, 172.9.

Preparation of 4-Methylideneheptane-1,7-diol (11). A 100-mL flask fitted with a mechanical stirrer was charged with 1.1 g (29 mmol) of $LiAlH_4$ and 30 mL of dry ether. **10** (4.5 g, 20 mmol) in 15 mL of ether was slowly added to the mixture. After addition, the reaction mixture was stirred for 30 min at room temperature. Ethyl acetate (3 g) was added to decompose the excess $LiAlH_4$. The mixture was filtered. Solids were added into 120 mL of 20% H_2SO_4 (aq) portion by portion and then

extracted by ether (3 × 200 mL). The combined ether solution was dried over $NaHCO_3$ and anhydrous Na_2SO_4. Concentration of the ether solution gave 2.3 g (80% yield) of 11 as an oil: ^1H NMR δ 1.70 (m, 6 H, middle CH_2 + OH), 2.13 (t, J = 7 Hz, 4 H, CH_2C=), 3.66 (t, J = 6 Hz, 4 H, CH_2OH), 4.78 (s, 2 H, =CH_2); ^{13}C NMR δ 30.7, 32.3, 62.4, 148.9, 109.4.

Preparation of Diethyl 4-(2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptyl)-4-iodoheptanedioate (14). A mixture of 8.5 g (37 mmol) of 10, 18 g (40 mmol) of $C_6F_{13}I$, and 1.7 g (1.5 mmol) of $Pd(Ph_3P)_4$ was stirred at room temperature overnight. Chromatography on silica gel with hexane and ethyl acetate (10:1) eluent gave 20 g (80% yield) of 14 as an oil: ^1H NMR δ 1.28 (t, J = 7 Hz, 6 H, CH_3), 4.17 (q, J = 7 Hz, 4 H, CH_2CH_3), 2.96 (t, J = 20 Hz, 2 H, CF_2CH_2), 2.25 (AB quartet dd, J = 15, 11, 5 Hz, 4 H, CH_2CH_2C=O), 2.65 (AB quartet dd, J = 16, 11, 5 Hz, 4 H, CH_2C=O); ^{19}F NMR δ −81.3 (t, J = 9 Hz, 3 F, CF_3), −114.8 (s, 2 F, CF_2CH_2), −122.4 (s, 2 F), −123.4 (s, 2 F), −124.1 (s, 2 F), 126.6 (s, 2 F); ^{13}C NMR δ 14.5, 61.0, 52.4, 42.6 (t, J = 20 Hz, CF_2CH_2), 40.6, 33.9, 172.1, 111.1–119.2 (m); FT-IR (CCl_4) 1186 (s), 1208 (s), 1241 (vs), 1740 (s), 2984 (w) cm^{-1}; DIP-MS (m/e) 629 (M^+ − EtO, 10.77), 547 (M^+ − I, 27.48), 501 (M^+ − HI − OEt, 41.89), 473 (M^+ − HI − CO_2Et, 62.38), 455 (M^+ − HI − 2OEt, 100), 427 (M^+ − HI − OEt − CO_2Et, 80.69), 399 (M^+ − HI − 2CO_2Et, 76.24).

Preparation of 4-(2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptyl)heptane-1,7-diol (15). A 500-mL flask fitted with a mechanical stirrer was charged with 2 g (53 mmol) of $LiAlH_4$ and 150 mL of dry ether. 14 (19.5 g, 29 mmol) in 50 mL of ether was slowly added to the mixture. After addition was complete, the reaction mixture was stirred at room temperature overnight. Water (4 mL) was slowly (1 h) added to decompose the excess $LiAlH_4$ at −78 °C. The mixture was filtered. The resultant solids were added to 20% aqueous H_2SO_4 (100 mL) and then extracted with ether (2 × 100 mL). The combined filtrate and ether solution was washed with $NaHCO_3$(aq) and H_2O, dried over anhydrous Na_2SO_4, and concentrated to give 11.8 g (88% yield) of 15 as an oil: ^1H NMR δ 1.45–1.60 (m, 8 H), 1.96–2.08 (m, 5 H, CF_2CH_2CH and OH), 3.64 (t, J = 6 Hz, 4 H, CH_2OH); ^{13}C NMR δ 29.2 (s, $CHCH_2$), 30.2 (s, CH_2CH_2OH), 30.76 (s, CH), 34.2 (t, J = 21 Hz, CF_2CH_2), 62.8 (s, CH_2OH), 109.0–123.0 (m); ^{19}F NMR δ −81.3 (s, 3 F, CF_3), −113.5 (s, 2 F, CF_2CH_2), −122.3 (s, 2 F), −123.4 (s, 2 F), −124.1 (s, 2 F), −126.7 (s, 2 F); FT-IR (CCl_4) 3500 (br), 2924 (w), 1221 (s), 1188 (m), 1128 (m) cm^{-1}; DIP-MS (m/e) 464 (M^+, 0.16), 446 (M^+ − H_2O, 0.29), 428 (M^+ − 2H_2O, 3.55), 401 (M^+ − H_2O − CH_2CH_2OH, 6.65), 400 (M^+ − H_2O − CH_2CH_2OH − 1, 58.16), 374 (M^+ − 2CH_2CH_2OH, 16.67), 131 (M^+ − $CH_2C_6F_{13}$, 37.41), 113 (M^+ − $CH_2C_6F_{13}$ − H_2O, 31.91).

$Pd(Ph_3P)_4$-Catalyzed Addition of $C_6F_{13}I$ to 11 at Room Temperature. A mixture of 1.5 g (13 mmol) of 11, 6 g (13.5 mmol) of $C_6F_{13}I$, and 0.55 g (0.5 mmol) of $Pd(Ph_3P)_4$ was stirred at room temperature for 3 h. ^{19}F NMR analysis indicated a 15% conversion of $C_6F_{13}I$.

$Pd(Ph_3P)_4$-Catalyzed Addition of $C_6F_{13}I$ to 11 at 75 °C. A mixture of 1.5 g (13 mmol) of 11, 7 g (15.7 mmol) of $C_6F_{13}I$, and 0.55 g (0.5 mmol) of $Pd(Ph_3P)_4$ was stirred at 75 °C for 1 h. ^{19}F NMR analysis indicated about 50% conversion of $C_6F_{13}I$. Chromatography on silica gel column with CH_2Cl_2/EtOAc (2:1) eluent gave $HO(CH_2)_3C(CH_2C_6F_{13})$=$CHCH_2CH_2OH$ (13) (35%) as a cis and trans mixture. No adduct 12 was detected. 13: ^1H NMR δ 5.66 (t, J = 7 Hz, 0.7 H), 5.45 (t, J = 7 Hz, 0.3 H), 3.63 (m, CH_2OH, 4 H), 3.57 (br, OH, 2 H), 2.87 (t, J = 20 Hz, 1.4 H), 2.76 (t, J = 20 Hz, 0.6 Hz, 0.6 H), 2.28 (m, 4 H), 1.70 (m, 2 H).

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Supplementary Material Available: ^{13}C NMR spectra (17 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.