# Preparation of Perfluoroalkyl Ketones by the Reaction of Perfluoroalkyllithiums with Esters

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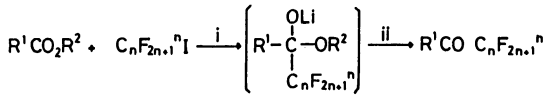
(Received April 27, 1989)

A variety of esters react with perfluoroalkyllithiums in situ generated from perfluoroalkyl iodides and methyllithium to give perfluoroalkyl ketones in good yields. Perfluoroalkyllithiums add to α, β-unsaturated esters only in the 1,2-addition mode even in the presence of copper salt. Exception was observed in the reaction with maleates where perfluoroalkylated succinic esters and normal 1,2-addition products are obtained in comparable amounts.

In recent years increasing attention has been paid to perfluoroalkyl-containing substances because of their unique properties which are not observed for fluorine-free partners. Straight chain perfluoroalkylalkanes are reported to form two different kinds of micelles depending on solvents[1] and to crystallize as a smetic liquid crystal.[2] Methodology for the introduction of the perfluoroalkyl group into a molecule[3] is, however, as yet far from maturity which makes a target compound often difficult to access. One of the important problems involved therein is thermal instability of perfluoroalkyl Grignard and lithium reagents which easily suffer β-elimination.[4] Thus, most efforts have been placed on the activation of thermally more stable reagents such as perfluoroalkylzinc[5] and -copper.[6] Unfortunately, these reagents, can not be successfully used for the perfluoroalkylation of unactivated esters due to their low nucleophilicity. Gassman and his co-worker have reported that pentafluoroethyllithium was conveniently generated from a metal halogen exchange reaction of pentafluoroethyl iodide with methyllithium at −78 °C and it reacted smoothly with aldehydes and ketones to give alcohols.[7] Gassman and our group have recently shown that this methodology can be extended to the preparation of perfluoroalkyl ketones from non-activated



Scheme 1. Reagents and conditions: i, MeLi-LiBr, ether, −78 °C, 1 h. ii, $H^+$.

Table 1. Perfluoroalkylation of Esters

| Entry | Ester **1** | Perfluoroalkyl iodide **2** | Product | Yield/%[a] |
|---|---|---|---|---|
| 1 | $PhCO_2CH_3$ (**1a**) | $C_8F_{17}{}^nI$ (**2a**) | $PhCOC_8F_{17}{}^n$ (**3**) | 86 |
| 2 | (*E*)-$PhCH{=}CHCO_2CH_3$ (**1b**) | **2a** | (*E*)-$PhCH{=}CHCOC_8F_{17}{}^n$ (**4a**) | 93 |
| 3 | **1b** | $C_6F_{13}{}^nI$ (**2b**) | (*E*)-$PhCH{=}CHCOC_6F_{13}{}^n$ (**4b**) | 83 |
| 4 | **1b** | $C_4F_9{}^nI$ (**2c**) | (*E*)-$PhCH{=}CHCOC_4F_9{}^n$ (**4c**) | 85 |
| 5 | **1b** | $C_3F_7{}^iI$ (**2d**) | — | — |
| 6 | **1b** | **2a** | $PhCH(CH_3)CH_2COC_8F_{17}{}^n$ (**5a**)[b] | 75 |
| 7 | **1b** | **2b** | $PhCH(CH_3)CH_2COC_6F_{13}{}^n$ (**5b**)[b] | 52 |
| 8 | **1b** | **2c** | $PhCH(CH_3)CH_2COC_4F_9{}^n$ (**5c**)[b] | 37 |
| 9 | (*E*)-$PhCH{=}CHCO_2C_2H_5$ (**1c**) | **2a** | **4a** | 83 |
| 10 | $PhC{\equiv}CCO_2CH_3$ (**1d**) | **2a** | $PhC{\equiv}CCOC_8F_{17}{}^n$ (**6**) | 95 |
| 11 | $PhCH_2CH_2CO_2CH_3$ (**1e**) | **2a** | $PhCH_2CH_2COC_8F_{17}{}^n$ (**7**) | 86 |
| 12 | $(CH_3)_2CHCO_2CH_3$ (**1f**) | **2a** | $(CH_3)_2CHCOC_8F_{17}{}^n$ (**8**) | 72 |
| 13 | $(CH_3)_3CCO_2CH_3$ (**1g**) | **2a** | $(CH_3)_3CCOC_8F_{17}{}^n$ (**9**) | 60 |
| 14 | $BrCH_2CO_2CH_3$ (**1h**) | **2a** | $BrCH_2COC_8F_{17}{}^n$ (**10**) | 86 |
| 15 | (*E*)-$CH_3CH{=}CHCO_2CH_3$ (**1i**) | **2a** | (*E*)-$CH_3CH{=}CHCOC_8F_{17}{}^n$ (**11**) | 58 |
| 16 | (*E*)-$CH_3CH{=}C(CH_3)CO_2CH_3$ (**1j**) | **2a** | (*E*)-$CH_3CH{=}C(CH_3)COC_8F_{17}{}^n$ (**12**) | 74 |
| 17 | $CH_2CH_2CH_2C{=}O$ (**1k**)  | **2a** | $CH_2CH_2CH_2C(OH)C_8F_{17}{}^n$ (**13**)  | 99 |
| 18 | $CH_2{=}CHCO_2CH_3$ (**1l**) | **2a** | $PhSCH_2CH_2COC_8F_{17}{}^n$ (**14**)[c] | 58 |
| 19 | $CH_2{=}C(CH_3)CO_2CH_3$ (**1m**) | **2a** | $PhSCH_2CH(CH_3)COC_8F_{17}{}^n$ (**15**)[c] | 80 |

a) Isolated yield. b) The reaction was carried out by using 2 equiv of methyllithium-lithium bromide in the presence of MeCu (1 equiv). c) Thiophenol was added to the reaction mixture and the mixture was stirred for 1 h at the room temperature before quenching with aqueous $NH_4Cl$.

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esters (Scheme 1).[8-10] During the course of examining the scope of preparative utility of perfluoroalkyllithiums, we have also found the reaction with maleic esters affords perfluoroalkylsuccinates, which may be considered as a potential building block for synthesis of perfluoroalkyl-bearing cyclic compounds. In this paper, we report the full results of our study on the reaction of perfluoroalkyllithiums with various esters.

## Results and Discussion

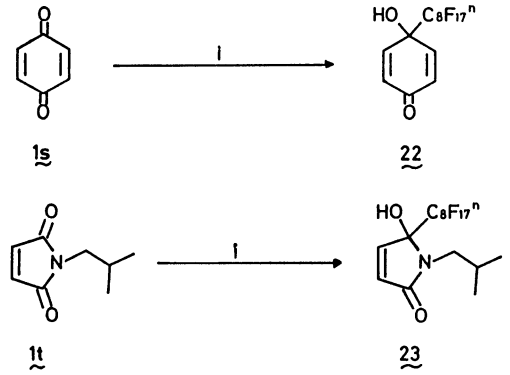
In situ generation of perfluoroalkyllithiums (1.1 equiv) by the reaction of perfluoroalkyl iodides with methyllithium in the presence of esters at −78 °C led to the formation of perfluoroalkyl ketones in good yields (Table 1). Addition of perfluoroalkyllithiums occurred only at the ester carbonyl group in the reactions with α,β-unsaturated esters and an α-bromo ester. It is noteworthy that methyl acrylate (**1l**) and methacrylate (**1m**) were also subject to 1,2-addition of the perfluoroalkyllithium reagent to give vinyl ketones (or hemiacetals) which could be easily isolated as the thiophenol-trapped compounds **14** and **15**, respectively. In the presence of methylcopper (1 equiv) and excess amounts of methyllithium (2 equiv), methyl cinnamate (**1b**) first underwent 1,2-addition of perfluoroalkyllithiums to form unsaturated ketones **4a—4c**, which then suffer 1,4-addition of methyllithium to afford saturated ketones **5a—5c**. In neither case bis-perfluoroalkylated compounds could be isolated in detectable amounts, which forms a marked contrast to the results obtained by Gassman and his co-worker.[10] This discrepancy may be rationalized by taking into account of the difference in amount and concentration of the lithium reagent employed. In order to obtain a perfluoroalkyl ketone, the use of a slightly excess of perfluoroalkyllithium is essential. When a large excess of perfluoroalkyllithium is used, the heat evolved during the generation of the lithium reagent will destroy the hemiacetal intermediate derived from the reagent and the ester. From this point of view, lower concentration of the reagent appears to be desirable, but it is not crucial as far as the reagents are satisfactorily soluble at low temperatures employed. We carried out the reaction by using 1.1 equiv of perfluorooctyl iodide (**2a**) to esters at 0.1 mol $dm^{-3}$ concentration so as to keep them good soluble in ether at −78 °C. Under these conditions, the amount of methyllithium should be only in a slightly excess to the ester in order to prevent further reactions with perfluoroalkyllithium or methyllithium.

To get further insight into the reactivity of the reagents and regioselectivity of perfluoroalkylation, we conducted the reaction of perfluorooctyllithium with α,β-unsaturated diesters and the results are summarized in Table 2. Under the conditions employed (1.1 molar ratio of perfluorooctyllithium to esters), neither two perfluoroalkyl groups nor a pair of perfluoroalkyl and methyl groups could be introduced into molecules. The reaction with diethyl acetylenedicarboxylate (**1n**) gave the α-amino α,β-unsaturated ester **16**, which was presumably derived from 1,2-addition of perfluorooctyllithium followed by conjugate addition of ammonia generated upon quenching from aqueous ammonium chloride. When the reaction with **1n** was quenched with dilute hydrochloric acid, an intractable mixture was obtained. Perfluoroalkylation of diethyl azodicarboxylate (**1o**) occurred at the nitrogen atom to give *N*-perfluorooctyl-*N*,*N*′-hydrazinedicarboxylate **17** in 65% yield. From the reaction mixture diethyl *N*-methylhydrazine-*N*,*N*′-dicarboxylate (**18**) was also isolated in 18% yield. It is interesting to note that the reaction with the fumarate **1p** gave the trans γ-keto ester **19a** as a single product in 61% yield, while a similar reaction with the maleate **1q** produced the perfluorooctylsuccinate **20a** and an isomeric mixture of **19a** (*E*/*Z*=ca. 10/1) in comparable yields. Such Michael-type addition of a perfluoroalkylmetallic reagent is very rare.[11] In order to find

Table 2. Perfluorooctylation of α,β-Unsaturated Diesters

| Entry | Ester | Products (Yield/%)[a] |
|---|---|---|
| 20 | $MeO_2CC{\equiv}CCO_2Me$ **1n** | $MeO_2CC(NH_2)=CHCORf$ **16** (71) |
| 21 | $EtO_2CN=NCO_2Et$ **1o** | $EtO_2CNNHCO_2Et$ (Rf) **17** (65) + $EtO_2CNNHCO_2Et$ (Me) **18** (18) |
| 22 | (*E*)-$Bu^nO_2CCH=CHCO_2Bu^n$ **1p** | (*E*)-$Bu^nO_2CCH=CHCORf$ (*E*)-**19a** (61) |
| 23 | (*Z*)-$Bu^nO_2CCH=CHCO_2Bu^n$ **1q** | **19a**[b] (46) + $Bu^nO_2CC(Rf)HCH_2CO_2Bu^n$ **20a** (21) |
| 24 | (*E*)-$MeO_2CCH=CHCO_2Me$ **1r** | (*E*)-$MeO_2CCH=CHCORf$ (*E*)-**21** (63) |

a) Rf denotes $C_8F_{17}{}^n$. The yields refer to isolated ones. b) *E*/*Z*=ca. 10/1 (determined by NMR).



Scheme 2. Reagents and conditions: i, $C_8F_{17}{}^nI$, MeLi-LiBr, ether, −78 °C, 1 h.

additional examples, substrates with a cis-enedione structure similar to maleate were subjected to this perfluoroalkylation. The reactions of 1,4-benzoquinone (**1s**) and *N*-isobutylmaleimide (**1t**), however, resulted only in the expected formation of the quinol **22** and the lactam **23**, respectively (Scheme 2).

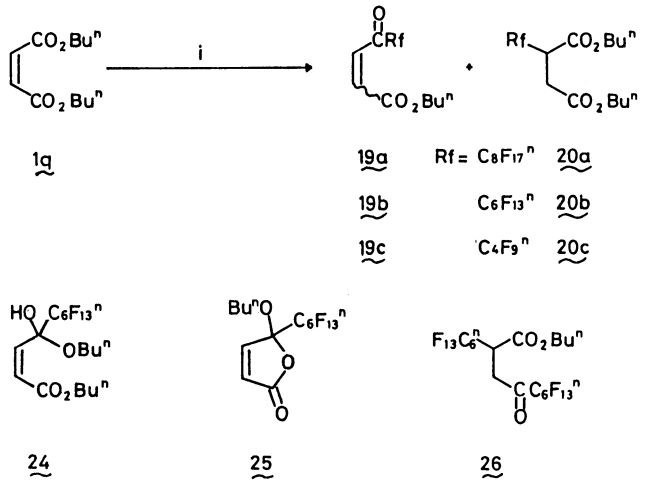
Since the formation of perfluoroalkylsuccinates appeared us to be quite interesting both from mechanistic and synthetic points of view, we examined the product selectivity for the reaction of dibutyl maleate under various conditions (Scheme 3 and Table 3). The important point is whether the perfluoroalkylsuccinate **20** will be formed by reactions with reagents other than perfluoroalkyllithium. Participation of perfluoroalkyl radical species could be ruled out because neither the formation of a radical addition product nor a marked change in the relative ratio of **19** and **20** was observed in the presence or absence of norbornene and styrene (Entries 30 and 31).[12] As the hypervalent iodine species such as $Rf_2I^-$ were suggested to increase the stability of perfluoroalkyl anions,[13] we next examined whether such species play a role in determining the product distribution. The generation of perfluorobutyllithium from the metal-exchange reaction of the perfluorobutyl stannane **27** with methyllithium, in the presence of the maleate **1q**, led to the formation of both succinate **20c** and γ-keto ester **19c** in a ratio similar to that obtained from the reaction of the corresponding perfluoroalkyl iodide (Entry 32). In the reaction of **1q** using an excess of perfluorooctyl iodide (Entry 25), the ratio was also similar. Thus we may hold at present that the hypervalent perfluoroalkyl iodine species, even if they might exist, exsert little influence upon the partition between conjugate and 1,2-mode additions to maleates.

Perfluoroalkylation of the maleate **1q** in the presence of $BF_3$ is worthy to note (Entry 29). Proton and $^{13}C$ NMR analyses of the reaction mixture revealed the presence of three major products: **19b** (*Z*/*E*=>20/1), the succinate **20b**, and the hemiacetal[14] **24** (**19b** : **20b** : **24**=7 : 10 : 23). The hemiacetal structure of

Table 3. Perfluoroalkylation of Dibutyl Maleate (**1q**)

| Entry | RfX | Additive (equiv) | Yield/%[a] | |
|---|---|---|---|---|
| | | | **19** | **20** |
| 25 | **2a**[b] | — | 36 | 28 |
| 26 | **2b** | — | 63 (1.8 : 1)[c] | |
| 27[d] | **2b** | — | 39 (1.7 : 1)[c] | |
| 28 | **2c** | — | 52 (1.7 : 1)[c] | |
| 29 | **2b** | $BF_3 \cdot OEt_2$ (1) | 91 (3.0 : 1)[c] | |
| 30 | **2b** | Norbornene (1) | 55 (1.8 : 1)[c] | |
| 31 | **2a** | Styrene (1) | 76 (2.0 : 1)[c] | |
| 32 | $C_4F_9{}^nSnBu^n{}_3$ **27** | — | 64 (2.1 : 1)[c] | |

a) Isolated yield. b) Five equiv. to **1q**. c) Separation of **19** and **20** was not attempted. Numerals in parentheses refer to the ratios of 1,2- and 1,4-addition products in the crude reaction mixture estimated by NMR. d) Reaction temperature was −100 °C.



Scheme 3. Reagents and conditions: i, RfX, MeLi-LiBr, ether, −78 °C, 1 h.

**24** was supported by the following observations: The NMR signals of **24** gradually disappeared as time passed. The signals of **19b** and 1-butanol became relatively stronger as compared with those of the succinate **20b** and new signals due to the lactone **25** appeared. After 3 days the reaction mixture was subjected to chromatographic separation to yield a mixture of **19b** (*Z*/*E*=6/5), **20b**, **25** (91%, **19b** : **20b** : **25**= 56 : 24 : 5), and a trace amount of the bisperfluorohexylated compound **26** (0.3%). Regiochemical assignment of **26** was based on the $^{13}C$ NMR absorptions of the ester carbonyl which appeared as double of doublets attributable to $^3J_{CF}$ coupling (6 and 3 Hz). The lactone **25** was isolated by GPC and its structure was confirmed by spectroscopic data. Thus in this reaction too, the 1,2-addition to one of the ester carbonyls was preferred to the conjugate addition. Coordination of $BF_3$ to the ester group would favor the 1,2-mode of addition of perfluoroalkyllithium[15] under these amphiphilic conditions.[16] The high yield and (*Z*)-stereoselectivity of **19b** may also reflect the stabilizing effect of $BF_3$ for the anion of the hemiacetal **24**.

## Experimental

Melting points were measured with a Yanagimoto micro-melting point apparatus and are uncorrected. All distillation temperatures refer to the Kugelrohr bath temperature. Unless otherwise noted, all NMR spectra were observed with JEOL PMX-60 and GSX-270 spectrometers by using $CDCl_3$ as solvent, tetramethylsilane as an internal standard for $^1H$ and $^{13}C$, and $CFCl_3$ for $^{19}F$. Mass spectra were measured with a Hitachi M80LCAPI spectrometer under the following ionizing conditions: EI (20 eV) and CI (70 eV, methane as CI gas). IR spectra were recorded on a Hitachi 270-30 spectrophotometer. Column chromatography was carried out using Wakogel C-200. Preparative GPC was performed using JAI LC-08 with JAI-1H (20 mmID×60 cm) and JAI-2H (20 mmID×60 cm) columns. Diethyl ether was distilled from sodium benzophenone ketyl and stored over sodium wire. Dichloromethane was distilled from calcium hydride and stored over 4A Molecular Sieves. Esters and perfluoroalkyl iodides were purified by simple distillation. Methyllithium was titrated prior to use. Other commercially available materials were used without further purification. Perfluorobutyltributylstannane (**27**) was prepared according to a procedure similar to that used for pentafluoroethyltriallylstannane.[17]

**Preparation of Perfluorobutyltributylstannane (27).** To an ethereal solution (100 ml) of **2c** (5.19 g, 15 mmol) was added dropwise an ethereal solution of methyllithium-lithium bromide (10 mmol) at −90—−80 °C over 10 min. With an interval of 10 min tributylstannyl chloride (3.26 g, 10 mmol) in ether (10 ml) was added to the white suspension at −80 °C and the reaction mixture was allowed gradually to warm to room temperature with stirring. After 1 h the solvent was removed and the residual syrup was distilled under reduced pressure to give 2.05 g of **27** as a colorless oil (110—115 °C/0.15 mmHg††). The purity of **27** estimated by NMR was ca. 70%. Major contaminants were tributylmethylstannane (ca. 10%), tributylstannyl bromide (ca. 15%), and tributylstannyl chloride (ca. 5%). The product was used without further purification. **27**: $^1H$ NMR $\delta$=0.92 (9H, t, $J$=7.3 Hz) and 1.15—1.70 (12H, m); $^{19}F$ NMR $\delta$=−81.72 (3F, tt, $J$=9 and 4 Hz), −118.12 (2F, m, $J_{Sn\text{-}F}$=ca. 187 Hz), −119.22 (2F, m), and −126.53 (2F, br t, $J$=12 Hz); IR (neat) 2964s, 2924s, 1466m, 1348m, and 1300—1100vs cm$^{-1}$; MS (EI) $m/z$ (rel intensity) 453 [$M^+$−Bu ($^{120}$Sn), 15%], 452 [$M^+$−Bu ($^{119}$Sn), 6], 451 [$M^+$−Bu ($^{118}$Sn), 12], 450 [$M^+$−Bu ($^{117}$Sn), 6], 449 [$M^+$−Bu ($^{116}$Sn), 6], 397 (4), 291 (100), 253 (71), and 235 (75).

**General Procedure for Perfluoroalkylation of Esters.** To an ethereal solution of **1** (1 mmol) and **2** (1.2 mmol) was added an ethereal solution of methyllithium-lithium bromide (1.1 mmol) at −78 °C during the course of 5 min and the mixture was stirred for 1 h at this temperature. The reaction was quenched by the addition of aqueous $NH_4Cl$ and the product was extracted with ether. The organic phase was washed with brine, dried over $Na_2SO_4$, and evaporated. The residue was purified by column chromatography (hexane-$CH_2Cl_2$) and/or distillation.

**Compound 3.** Distillation temp 140 °C/22 mmHg; $^1H$ NMR ($CCl_4$) $\delta$=7.44—7.62 (3H, m) and 8.01 (2H, m); $^{19}F$ NMR $\delta$=−80.42 (3F, tt, $J$=10 and 2 Hz), −113.13 (2F, t, $J$=13 Hz), −121.32 (4F, m), −122.29 (4F, m), −123.19 (2F, m), and −126.62 (2F, m); IR (neat) 1714vs, 1600s, 1454s, 1328s, and 1300—1100vs cm$^{-1}$; MS (CI) $m/z$ (rel intensity) 525 ($M^+$+1, 99) and 105 (100) (Found: C, 34.21; H, 1.09%. Calcd for $C_{15}H_5OF_{17}$: C, 34.37; H, 0.96%).

**Compound 4a.** Mp 61—62 °C; $^1H$ NMR ($CCl_4$) $\delta$=7.11 (1H, d, $J$=16 Hz), 7.41—7.75 (5 H, m), and 8.03 (1H, d, $J$=16 Hz); $^{19}F$ NMR $\delta$=−81.25 (3F, tt, $J$=10 and 2 Hz), −121.38 (2F, t, $J$=13 Hz), −121.78 (2F, m), −122.34 (4F, m), −122.61 (2F, m), −123.18 (2F, m), and −126.58 (2F, m); IR (KBr) 1708vs, 1610vs, 1348s, 1330s, and 1300—1100vs cm$^{-1}$; MS (EI) $m/z$ (rel intensity) 550 ($M^+$, 15%), 131 (100), and 77 (25) (Found: C, 37.02; H, 1.36%. Calcd for $C_{17}H_7OF_{17}$: C, 37.11; H, 1.28%).

**Compound 4b.** Mp 47—48 °C; $^1H$ NMR ($CCl_4$) $\delta$=7.03 (1H, d, $J$=16 Hz), 7.74 (5H, m), and 7.92 (1H, d, $J$=16 Hz); $^{19}F$ NMR $\delta$=−81.25 (3F, tt, $J$=10 and 2 Hz), −121.39 (2F, t, $J$=13 Hz), −122.68 (2F, m), −123.27 (2F, m), −126.60 (2F, m), and −121.97 (2F, m); IR (KBr) 1708vs, 1610vs, 1348s, and 1300—1100vs cm$^{-1}$; MS (EI) $m/z$ (rel intensity) 450 ($M^+$, 18), 131 (100), 103 (59), and 77 (33) (Found: C, 39.94; H, 1.65%. Calcd for $C_{15}H_7OF_{13}$: C, 40.02; H, 1.57%).

**Compound 4c.** Mp 29 °C; $^1H$ NMR ($CCl_4$) $\delta$=7.03 (1H, d, $J$=16 Hz), 7.44 (5H, m), and 7.90 (1H, d, $J$=6 Hz); $^{19}F$ NMR $\delta$=−81.43 (3F, tt, $J$=10 and 2 Hz), −121.54 (2F, t, $J$=12 Hz), −123.61 (2F, m), and −126.16 (2F, m); IR (neat) 1710vs, 1610vs, 1340vs, and 1300—1100vs cm$^{-1}$; MS (EI) $m/z$ (rel intensity) 350 ($M^+$, 24%), 131 (100), 103 (58), and 77 (30).

**Compound 5a.** Mp 37—38 °C; $^1H$ NMR $\delta$=1.26 (3H, d, $J$=7 Hz), 2.96 (2H, d, $J$=7 Hz), 3.43 (1H, m), and 7.22 (5H, m); $^{19}F$ NMR $\delta$=−81.24 (3F, tt, $J$=10 and 2 Hz), −120.96 (2F, m), −121.85 (2F, m), −122.43 (6F, m), −123.21 (2F, m), and −126.61 (2F, m); IR (neat) 2972m, 1760vs, 1456m, 1370s, and 1300—1100vs cm$^{-1}$; MS (EI) $m/z$ (rel intensity) 566 ($M^+$, 37%), 147 (58), 131 (43), 119 (52), and 105 (100) (Found: C, 38.16; H, 2.10%. Calcd for $C_{18}H_{11}OF_{17}$: C, 38.18; H, 1.96%).

**Compound 5b.** Distillation temp 83—85 °C/0.7 mmHg; $^1H$ NMR $\delta$=1.26 (3H, d, $J$=7 Hz), 2.96 (2H, d, $J$=7 Hz), 3.38 (1H, m), and 7.22 (5H, m); $^{19}F$ NMR $\delta$=−81.33 (3F, tt, $J$=10 and 2 Hz), −120.91 (2F, m), −121.99 (2F, m), −122.65 (2F, m), −123.32 (2F, m), and −126.64 (2F, m); IR (neat) 2972m, 1760vs, 1498m, 1366m, 1316m, and 1300—1100vs cm$^{-1}$; MS (EI) $m/z$ (rel intensity) 466 ($M^+$, 22%), 147 (49), and 105 (100) (Found: C, 41.12; H, 2.40%. Calcd for $C_{16}H_{11}OF_{13}$: C, 41.22; H, 2.40%).

**Compound 5c.** Distillation temp 68—71 °C/0.6 mmHg; $^1H$ NMR $\delta$=1.25 (3H, d, $J$=7 Hz), 2.90 (2H, d, $J$=7 Hz), 3.28 (1H, m), and 7.14 (5H, m); $^{19}F$ NMR $\delta$=−81.44 (3F, tt, $J$=10 and 2 Hz), −121.16 (2F, m), −123.65 (2F, m), and −126.25 (2F, m); IR (neat) 2972m, 1758vs, 1356vs, and 1300—1100vs cm$^{-1}$; MS (EI) $m/z$ (rel intensity) 366 ($M^+$, 12%), 147 (10), and 105 (100) (Found: C, 45.80; H, 3.03%. Calcd for $C_{14}H_{11}OF_9$: C, 45.92; H, 3.03%).

**Compound 6.** Mp 25 °C; $^1H$ NMR ($CCl_4$) $\delta$=7.40—7.85 (br m); $^{19}F$ NMR $\delta$=−81.40 (3F, tt, $J$=10 and 2 Hz), −118.81 (2F, t, $J$=13 Hz), −121.70 (2F, m), −122.13 (2F, m), −122.33 (2F, m), −123.20 (2F, m), and −126.65 (2F, m); $^{13}C$ NMR $\delta$=84.23, 101.41, 118.16, 100—125 (8 C), 128.96, 132.62, 134.00, and 168.96 (t, $J$=31 Hz); IR (neat) 2196vs, 1702vs, 1330s, and 1300—1100vs cm$^{-1}$; MS (EI) $m/z$ (rel intensity) 548 ($M^+$, 7%), 129 (90), and 101 (100) (Found: C, 37.25; H, 0.92%. Calcd for $C_{17}H_5OF_{17}$: C, 37.25; H, 0.92%).

**Compound 7.** Mp 38—39 °C; $^1H$ NMR ($CCl_4$) $\delta$=2.97

†† 1 mmHg≈133.322 Pa.

(4H, m) and 7.17 (5H, m); $^{19}$F NMR $\delta$=−81.27 (3F, tt, $J$=10 and 2 Hz), −120.77 (2F, t, $J$=13 Hz), −121.82 (2F, m), −122.36 (4F, m), −122.66 (2F, m), −123.18 (2F, m), and −126.60 (2F, m); IR (neat) 2924m, 2856m, 1758vs, and 1300—1100vs cm$^{-1}$; MS (EI) $m/z$ (rel intensity) 552 ($M^+$, 3%), 132 (45), and 105 (100) (Found: C, 37.20; H, 1.52%. Calcd for $C_{17}H_9OF_{17}$: C, 36.97; H, 1.64%).

**Compound 8.** Distillation temp 125 °C; $^1$H NMR ($CCl_4$) $\delta$=1.23 (6H, d, $J$=7 Hz) and 3.16 (1H, m); $^{19}$F NMR $\delta$=−81.41 (3F, tt, $J$=10 and 2Hz), −119.93 (2F, t, $J$=12 Hz), −121.77 (2F, m), −122.44 (6F, m), −123.24 (2F, m), and −126.69 (2F, m); IR (neat) 2988s, 2948m, 1756vs, 1326s, and 1300—1100vs cm$^{-1}$; MS (CI) $m/z$ (rel intensity) 491 ($M^+$+1, 100%) and 71 (16) (Found: C, 29.01; H, 1.43%. Calcd for $C_{12}H_7OF_{17}$: C, 29.41; H, 1.44%).

**Compound 9.** Distillation temp 125 °C; $^1$H NMR ($CCl_4$) $\delta$=1.34 (s); $^{19}$F NMR $\delta$=−81.42 (3F, tt, $J$=10 and 2 Hz), −113.25 (2F, t, $J$=13 Hz), −121.40 (4F, m), −122.41 (4F, m), −123.28 (2F, m), and −126.72 (2F, m); IR (neat) 2984s, 1738vs, 1372s, and 1300—1100vs cm$^{-1}$; MS (CI) $m/z$ (rel intensity) 505 ($M^+$+1, 100%) and 101 (87) (Found: C, 30.68; H, 1.75%. Calcd for $C_{13}H_9OF_{17}$: C, 30.97; H, 1.80%).

**Compound 10.** Mp 39 °C; $^1$H NMR $\delta$=4.31 (s); $^{19}$F NMR $\delta$=−81.25 (3F, tt, $J$=10 and 2 Hz), −118.53 (2F, t, $J$=12 Hz), −121.70 (2F, m), −122.34 (6F, m), −123.19 (2F, m), and −126.62 (2F, m); IR (KBr) 1770vs, 1336vs, and 1300—1100vs cm$^{-1}$; MS (CI) $m/z$ (rel intensity) 543 ($M^+$+1 $^{81}$Br, 100%), 541 ($M^+$+1 $^{79}$Br, 98), 123 (75), 121 (77), 95 (23), and 93 (28) (Found: C, 22.17; H, 0.37%. Calcd for $C_{10}H_2BrOF_{17}$: C, 22.20; H, 0.37%).

**Compound. 11.** Distillation temp 60—63 °C/0.8 mmHg; $^1$H NMR $\delta$=2.04 (3H, dd, $J$=7.0 and 1.7 Hz), 6.56 (1H, dm, $J$=15.4 Hz), and 7.37 (1H, dq, $J$=15.4 and 7.0 Hz); $^{19}$F NMR $\delta$=−81.32 (3F, tt, $J$=10 and 2 Hz), −121.71 (4F, m), −122.40 (4F, m), −122.78 (2F, m), −123.22 (2F, m), and −126.63 (2F, m); IR (neat) 1724s, 1634s, 1324s, and 1300—1100vs cm$^{-1}$; MS (EI) $m/z$ (rel intensity) 488 ($M^+$, 3%), 468 (100), 441 (78), 219 (39), 169 (43) and 119 (57) (Found: C, 29.20; H, 1.08%. Calcd for $C_{12}H_5OF_{17}$: C, 29.53; H, 1.03%).

**Compound 12.** Distillation temp 80—81 °C/0.6 mmHg; $^1$H NMR $\delta$=1.89 (3H, s), 1.98 (3H, d, $J$=7.0 Hz), and 7.09 (1H, q, $J$=7.0 Hz); $^{19}$F NMR $\delta$=−81.37 (3F, tt, $J$=10 and 2 Hz), −111.05 (2F, m), −121.37 (4F, m), −122.35 (4F, m), −123.23 (4F, m), and −126.65 (2F, m); IR (neat) 2963m, 1694vs, 1638vs, 1328s, and 1300—1100vs cm$^{-1}$; MS (EI) $m/z$ (rel intensity) 502 ($M^+$, 6%), 483 (100), 455 (33), 169 (16), and 119 (18) (Found: C, 31.05; H, 1.70%; Calcd for $C_{13}H_7OF_{17}$: C, 31.09; H, 1.40%).

**Compound 13.** Mp 80 °C; $^1$H NMR $\delta$=2.17 (2H, m), 2.25 (2H, m), 2.82 (1H, br s), 4.01 (1H, td, $J$=7.7 and 6.7 Hz), and 4.21 (1H, td, $J$=7.7 and 4.6 Hz); $^{19}$F NMR $\delta$=−81.26 (3F, tt, $J$=10 and 2 Hz), −120.67 (2F, m), −121.28 (1F, dm, $J$=284 Hz), −122.37 (6F, m), −123.23 (2F, m), −123.71 (1F, dm, $J$=284 Hz), and −126.64 (2F, m); IR (KBr) 3372s, 2996m, 1336s, and 1300—1100vs cm$^{-1}$; MS (CI) $m/z$ (rel intensity) 505 ($M^+$−1, 1%) 489 (100), and 467 (9); MS (EI) $m/z$ (rel intensity) 505 ($M^+$−1, 8%), 489 (14), 476 (26), 131 (76), 107 (45), and 87 (100) (Found: C, 28.19; H, 1.29%. Calcd for $C_{12}H_7O_2F_{17}$: C, 28.48; H, 1.39%).

**Compound 14.** Mp 66—67 °C; $^1$H NMR $\delta$=3.05 (2H, m), 3.19 (2H, m), and 7.31 (5H, m); $^{19}$F NMR $\delta$=−81.23 (3F, tt, $J$=10 and 2 Hz), −120.82 (2F, t, $J$=13 Hz), −121.76 (2F, m), −122.32 (4F, m), −122.63 (2F, m), −123.17 (2F, m), and −126.58 (2F, m); IR (KBr) 2920m, 1760vs, 1336s, and 1300—1100vs cm$^{-1}$; MS (EI) $m/z$ (rel intensity) 584 ($M^+$, 84%), 137 (29), 123 (100), 110 (50), and 109 (30) (Found: C, 35.08; H, 1.44%. Calcd for $C_{17}H_9OSF_{17}$: C, 34.95; H, 1.55%).

**Compound 15.** Mp<20 °C; $^1$H NMR ($CCl_4$) $\delta$=1.23 (3H, m), 3.05 (3H, m), and 7.32 (5H, m); $^{19}$F NMR $\delta$=−81.37 (3F, tt, $J$=10 and 2 Hz), −118.65 (1F, dt, $J$=292 and 13 Hz), −120.98 (1F, dt, $J$=292 and 13 Hz), −121.65 (2F, m), −122.31 (6F, m), −123.19 (2H, m), and −126.63 (2F, m); IR (neat) 3080m, 2988m, 1754vs, 1328s, and 1300—1100vs cm$^{-1}$; MS (EI) $m/z$ (rel intensity) 598 ($M^+$, 33%), 151 (11), 123 (100), and 110 (17) (Found: C, 36.21; H, 1.87%. Calcd for $C_{18}H_{11}OSF_{17}$: C, 36.13; H, 1.85%).

**Compound 16.** Mp 86—87 °C; $^1$H NMR (acetone-$d_6$) $\delta$=3.95 (3H, s), 6.14 (1H, m), 8.22 (1H, br s), and 9.63 (1H, br s); $^{19}$F NMR (acetone-$d_6$) $\delta$=−80.69 (3F, tt, $J$=10 and 2 Hz), −119.79 (2F, t, $J$=12 Hz), −121.10 (2F, m), −121.53 (4F, m), −122.09 (2F, m), −122.09 (2F, m), −122.36 (2F, m), and −125.83 (2F, m); $^{13}$C NMR $\delta$=54.55, 90.04 (t, $J$=1 Hz), 100—125 (8 C), 154.01, 163.36, and 181.26 (t $J$=24 Hz); IR (KBr) 3484s, 3340s, 1740vs, 1664s, 1612vs, 1436vs, 1336vs, and 1300—1100vs cm$^{-1}$; MS (EI) $m/z$ (rel intensity) 547 ($M^+$, 8%), 528 (3), 488 (6), and 128 (100) (Found: C. 28.77; H, 0.99; N, 2.60%. Calcd for $C_{13}H_6NO_3F_{17}$: C, 28.54; H, 1.11; N, 2.56%).

**Compound 17.** Distillation temp 101—103 °C/0.1 mmHg; $^1$H NMR $\delta$=1.29 (3H, t, $J$=7.0 Hz), 1.30 (3H, t, $J$=7.0 Hz), 4.26 (2H, m), 4.31 (2H, m), and 7.23 (1H, br s); $^{19}$F NMR (50 °C) $\delta$=−81.42 (3F, t, $J$=10 Hz), −92.21 (1F, dm, $J$=222 Hz), −93.64 (1F, dm, $J$=222 Hz), −121.38 (2F, m), −122.20 (6F, m). −123.03 (2F, m), and −126.47 (2F, m); $^{19}$F NMR (23 °C) $\delta$=−81.39 (3F, t, $J$=10 Hz), −92.25 (1F, dm, $J$=222 Hz, major conformation isomer, ca. 70%), −92.57 (1F, dm, $J$=222 Hz, minor conformation isomer, ca. 30%), −93.84 (1F, dm, $J$=222 Hz), −121.73 (2F, m), −122.43 (6F, m), −123.23 (2F, m), and −126.68 (2F, m); $^{13}$C NMR $\delta$=13.72, 14.00, 62.88, 64.43, 100—125 (8 C), 152.09, and 155.82; IR (neat) 3308s, 2992s, 2890m, 1746vs, 1514s, 1380s, and 1300—1100vs cm$^{-1}$; MS (CI) $m/z$ (rel intensity) 595 ($M^+$+1, 12%), 551 (11), 531 (14), 503 (100), 475 (20), and 450 (15) (Found: C, 28.49; H, 1.75; N, 4.85%. Calcd for $C_{14}H_{11}N_2O_4F_{17}$: C, 28.30; H, 1.87; N, 4.71%).

**Compound 19a.** (*E*)-Isomer: mp 46 °C; $^1$H NMR $\delta$=0.96 (3H, t, $J$=7.3 Hz), 1.42 (2H, m), 1.70 (2H, m), 4.26 (2H, t, $J$=6.7 Hz), 7.05 (1H, d, $J$=15.6 Hz), and 7.43 (1H, d, $J$=17.6 Hz); $^{19}$F NMR $\delta$=−81.26 (3F, tt, $J$=10 and 2 Hz), −121.40 (2F, tm, $J$=12 Hz), −121.74 (2F, m), −122.41 (6F, m), −123.22 (2F, m), and −126.61 (2F, m); IR (KBr) 2968s, 2888s, 1722vs, 1316vs, and 1300—1100 vs cm$^{-1}$; MS (CI) $m/z$ (rel intensity) 575 ($M^+$+1, 80%), 547 (14), 520 (13), 519 (100), 501 (19), and 155 (70).

**Compound 19b.** (*E*)-Isomer: $^1$H NMR $\delta$=0.97 (3H, t, $J$=7.3 Hz), 1.42 (2H, m), 1.70 (2H, m), 4.27 (2H, t, $J$=6.7 Hz), 7.07 (1H, d, $J$=15.9 Hz), and 7.44 (1H, d, $J$=15.9 Hz); $^{19}$F NMR $\delta$=−81.35 (3 F, tt, $J$=10 and 3 Hz), −121.33 (2F, t, $J$=12 Hz), −122.52 (2F, m), −123.24 (2F, m), and −126.61 (2F, m); $^{13}$C NMR $\delta$=13.48, 19.03, 30.46, 65.95, 100—125 (6C), 130.66, 137.43, 163.99, and 182.29 (t, $J$=27 Hz); IR (neat) 2968s, 1728vs, 1626m, 1470m, 1386s, 1360s, 1308s, and 1300—1100vs cm$^{-1}$; MS (CI) $m/z$ (rel intensity) 475 ($M^+$+1, 28%) 447 (8), 433 (8), 419 (100), 403 (15), 401 (27), and 155 (94) (Found: C, 35.43; H, 2.42%. Calcd for $C_{14}H_{11}O_3F_{13}$: C, 35.46; H, 2.34%).

(*Z*)-Isomer: $^1$H NMR $\delta$=0.94 (3H, t, $J$=7.3 Hz), 1.38 (2H,

m), 1.65 (2H, m), 4.23 (2H, t, $J$=6.7 Hz), 6.47 (1H, d, $J$=11.6 Hz), and 6.60 (1H, d, $J$=11.6 Hz); $^{19}$F NMR $\delta$=−81.31 (3F, tt, $J$=10 and 2 Hz), −120.78 (2F, t, $J$=12 Hz), −122.05 (2F, m), −122.70 (2F, m), −123.28 (2F, m), and −126.62 (2F, m); $^{13}$C NMR $\delta$=13.28, 18.92, 30.22, 65.90, 100—125 (6 C), 130.37, 134.04, 164.69, and 184.58 (t, $J$=28 Hz); IR (neat) 2968s, 1730s, 1626m, 1470m, 1404s, 1366s, 1316s, and 1300—1100vs cm$^{-1}$.

**Compound 19c.** Distillation temp 70—80 °C/0.07 mmHg; $^1$H NMR $\delta$=0.96 (3H, t), 1.42 (2H, m), 1.70 (2H, m), 4.26 (2H, t, $J$=6.7 Hz), 7.05 (1H, d, $J$=15.6 Hz), and 7.43 (1H, d, $J$=15.6 Hz); $^{19}$F NMR $\delta$=−81.38 (3F, tt, $J$=10 and 2 Hz), −121.57 (2F, m), −123.53 (2F, m), and −126.13 (2F, m); IR (neat) 2968s, 2880s, 1726vs, 1314vs, and 1300—1100vs cm$^{-1}$; MS (CI) $m/z$ (rel intensity) 375 ($M^+$+1, 29%), 319 (100), 303 (82), 301 (29), 263 (38), 209 (26), 157 (26), and 155 (48) (Found: C, 38.12; H, 2.92%; Calcd for $C_{12}H_{11}O_3F_9$: C, 38.52; H, 2.96%).

**Compound 20a.** Distillation temp 95 °C/0.08 mmHg; $^1$H NMR $\delta$=0.93 (6 H, t, $J$=7.3 Hz), 1.38 (4H, m), 1.58 (4H, m), 2.78 (1H, dd, $J$=17.1 and 3.7 Hz), 3.10 (1H, dd, $J$=17.1 and 11.5 Hz), 3.70 (1H, m), 4.11 (2H, t, $J$=6.7 Hz), and 4.19 (2H, t, $J$=6.7 Hz); $^{19}$F NMR $\delta$=−81.30 (3F, tt, $J$=10 and 2 Hz), −112.9 (1F, dm, $J$=278 Hz), −114.1 (1F, dm, $J$=278 Hz), −121.28 (2F, m), −122.01 (2F, m), −122.33 (4F, m), −123.18 (2F, m), and −126.60 (2F, m); $^{13}$C NMR $\delta$=13.47, 13.58, 18.88, 19.01, 30.24, 30.34, 30.50, 44.60 (t, $J$=22 Hz), 65.36, 66.20, 100—125 (8 C), 166.55 (dd, $J$=6 and 3 Hz), and 170.04; IR (neat) 2969vs, 2880s, 1746vs, 1312s, and 1300—1100vs cm$^{-1}$; MS (CI) $m/z$ (rel intensity) 649 ($M^+$+1, 51%), 593 (16), 547 (7), 519 (100), 499 (16), and 473 (10) (Found: C, 36.74; H, 3.21%. Calcd for $C_{20}H_{21}O_4F_{17}$: C, 37.05; H, 3.26%).

**Compound 20b.** Distillation temp 104 °C/0.3 mmHg; $^1$H NMR $\delta$=0.91 (6H, t, $J$=7.3 Hz), 1.40 (4H, m), 1.63 (4H, m), 2.80 (1H, dd, $J$=17.1 and 3.3 Hz), 3.11 (1H, dd, $J$=17.1 and 11.3 Hz), 3.71 (1H, m), 4.13 (2H, t, $J$=6.7 Hz), 4.20 (2H, t, $J$=6.7 Hz); $^{19}$F NMR $\delta$=−81.30 (3F, tt, $J$=10 and 3 Hz), −112.9 (1F, dm, $J$=279 Hz), −114.1 (1F, dm, $J$=279 Hz), −121.40 (2F, m), −122.25 (2F, m), −123.30 (2F, m), −126.65 (2F, m); $^{13}$C NMR $\delta$=13.22, 13.33, 18.86, 18.96, 30.20 (br), 30.26, 30.52, 44.68 (t, $J$=22 Hz), 65.35, 66.18, 100—125 (6 C), 166.62 (dd, $J$=6 and 3 Hz), 170.13; IR (neat) 2964s, 2880m, 1746vs, 1470m, 1420m, 1400m, 1348s, 1318s, and 1300—1100vs cm$^{-1}$. MS (CI) $m/z$ (rel intensity) 549 ($M^+$+1, 7%), 493 (7), 447 (7), 419 (100), 399 (20), and 373 (6).

**Compound 20c.** Distillation temp 84—90 °C/0.1 mmHg; $^1$H NMR $\delta$=0.93 (6 H, t, $J$=7.0 Hz), 1.38 (4H, m), 1.62 (4H, m), 2.79 (1H, dd, $J$=17.4 and 3.4 Hz), 3.11 (1H, dd, $J$=17.4 and 11.3 Hz), 3.72 (1H, m), 4.11 (1H, t, $J$=6.7 Hz), and 4.19 (1H, t, $J$=6.7 Hz); $^{19}$F NMR $\delta$=−81.46 (3F, tt, $J$=10 and 2 Hz), −113.01 (1F, dm, $J$=277 Hz), −114.27 (1F, dm, $J$=277 Hz), −122.36 (2F, m), and −126.41 (2F, m); $^{13}$C NMR $\delta$=13.49, 13.58, 18.88, 19.00, 30.22, 30.23 (br m), 30.49, 44.48 (t, $J$=22 Hz), 65.34, 66.19, 108.60 (tqt, $J$=270, 39, and 33 Hz), 110.69 (ttt, $J$=266, 36, and 32 Hz), 115.97 (tt, $J$=261 and 33 Hz), 117.29 (qt, $J$=188 and 33 Hz), 166.54 (dd, $J$=6 and 3 Hz), and 170.02; IR (neat) 2964s, 2876s, 1748vs, 1344s, 1312s, and 1300—1100vs cm$^{-1}$; MS (CI) $m/z$ (rel intensity) 449 ($M^+$+1, 5%), 393 (8), 347 (8), 337 (9), 320 (10), 319 (100), and 299 (19) (Found: C, 42.68; H, 4.57%. Calcd for $C_{16}H_{21}O_4F_9$: C, 42.87; H, 4.72%).

**Compound 21.** (*E*)-Isomer: $^1$H NMR $\delta$=3.87 (3H, s), 7.05 (1H, d, $J$=15.6 Hz), and 7.45 (1H, d, $J$=15.6 Hz); $^{19}$F NMR $\delta$=81.32 (3F, tt, $J$=10 and 2 Hz), −121.48 (2F, t, $J$=12 Hz), −121.75 (2F, m), −122.40 (6F, m), −123.21 (2F, m), and −126.63 (2F, m); IR (neat) 2960m, 1730vs, 1316vs, and 1300—1100vs cm$^{-1}$; MS (CI) $m/z$ (rel intensity) 533 ($M^+$+1, 100%), 503 (7), 501 (8), 130 (9), 117 (9), and 113 (84).

(*Z*)-Isomer: $^1$H NMR $\delta$=3.82 (3H, s), 6.47 (1H, d, $J$=11.9 Hz), and 6.61 (1H, d $J$=11.9 Hz); $^{19}$F NMR $\delta$=−81.28 (3F, tt, $J$=10 and 2 Hz), −120.77 (2F, t, $J$=12 Hz), −121.48 (2F, m), −122.37 (4F, m), −122.68 (2F, m), −123.21 (2F, m), and −126.62 (2F, m); IR (KBr) 3090m, 1744vs, 1716vs, 1332vs, and 1300—1100vs cm$^{-1}$.

**Reaction with 1,4-Benzoquinone.** To a solution of **1s** (1.08 g, 10 mmol) and **2a** (5.46 g, 10 mmol) in ether (150 ml) was added an ethereal solution of methyllithium-lithium bromide (10 mmol) at −78 °C over 10 min. During the course of addition, the yellow solution gradually turned to a bluish purple suspension. After stirring for 1 h, the reaction was quenched with aqueous $NH_4Cl$. The organic phase was separated and the aqueous phase was extracted with ether. The combined extracts were washed with brine and dried over $Na_2SO_4$. The solvent was evaporated and the residue was chromatographed on silica gel ($CHCl_3$ as eluant). The fractions containing **22** was collected and concentrated to ca. 20 ml. Forced cooling of this concentrate followed by filtration gave 2.66 g (50%) of **22** as colorless crystals; mp 107—108 °C. $^1$H NMR $\delta$=1.59 (1H, br s), 6.43 (2H, d, $J$=10.1 Hz), and 6.91 (2H, d, $J$=10.1 Hz); $^{13}$C NMR (acetone-$d_6$) $\delta$=72.52 (tt, $J$=24 and 1 Hz), 100—125 (8 C), 132.28, 143.21 (m), and 184.99. $^{19}$F NMR $\delta$=−81.25 (3F, tt, $J$=10 and 2 Hz), −119.45 (4F, m), −122.0—−122.5 (6F, m), −123.17 (2F, m), and −126.58 (2F, m); IR (KBr) 3224m, 1674vs, 1628s, 1408s, 1392s, 1372s, 1330s, and 1300—1100vs cm$^{-1}$; MS (EI) $m/z$ (rel intensity) 528 ($M^+$, 1%), 512 (1), 488 (3), 173 (8), 169 (2), 143 (9), and 109 (100) (Found: C, 31.87; 0.87%. Calcd for $C_{14}H_5O_2F_{17}$: C, 31.84; H, 0.95%).

**Reaction with *N*-Isobutylmaleimide.** To an ethereal solution (20 ml) of **1t** (153 mg, 1 mmol) and **2a** (546 mg, 1 mmol) was added an ethereal solution of methyllithium-lithium bromide (1 mmol) at −78 °C. After stirring for 30 min, the reaction was quenched with aqueous $NH_4Cl$. The reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine and dried over $Na_2SO_4$. The solvent was evaporated and the residue was chromatographed on silica gel ($CHCl_3$ as eluant) to give 241 mg (42%) of **23** as colorless crystals; mp 122—123 °C; $^1$H NMR $\delta$=0.88 (6H, d, $J$=7.3 Hz), 2.21 (1H, m), 3.10 (1H, dd, $J$=14.3 and 8.2 Hz), 3.32 (1H, br s), 3.44 (1H, dd, $J$=14.3 and 7.0 Hz), 6.29 (1H, d, $J$=6.1 Hz), and 6.97 (1H, dt, $J$=6.1 and 2.7 Hz); $^{19}$F NMR $\delta$=−81.24 (3F, tt, $J$=10 and 2 Hz), −118.85 (1F, dm, $J$=280 Hz), −119.60 (1F, dm, $J$=285 Hz), −119.83 (1F, dm $J$=280 Hz), −121.29 (1 F, dm, $J$=285 Hz), −122.20 (6F, m), −123.18 (2F, m), and −126.58 (2F, m); IR (KBr) 3128s, 2964s, 1672vs, 1372s, and 1300—1100vs cm$^{-1}$; MS (EI) $m/z$ (rel intensity) 573 ($M^+$, 7%), 530 (100), 518 (74), 501 (26), and 154 (53) (Found: C, 33.85; H, 2.16; N, 2.56%. Calcd for $C_{16}H_{12}NO_2F_{17}$: C, 33.52; H, 2.11; N, 2.44%).

**Entry 29.** To a solution of **1q** (1.14 g, 5 mmol), **2b** (2.68 g, 6 mmol), and $BF_3 \cdot OEt_2$ (0.65 ml, 5 mmol) was added an ethereal solution of methyllithium-lithium bromide (5.5 mmol) at −78 °C over 20 min. After stirring for 1 h, the reaction mixture was quenched by the addition of aqueous $NH_4Cl$. The ethereal layer was separated and the aqueous phase was extracted with ether. The combined organic

phase was washed with brine and dried over $Na_2SO_4$. Evaporation of the solvent gave 3.57 g of a reddish brown oil, of which NMR analysis showed the presence of **19b** ($Z/E \geqq 20/1$), **20b**, **24**, and a small amount of 1-butanol (**19b** : **20b** : **24**=7 : 10 : 23). Column chromatography of the crude oil on silica gel (hexane-$CH_2Cl_2$ as eluant) gave 0.013 g of **26** and 2.25 g of a mixture of **19b** (Z/E=6/5), **20b**, and **25** (**19b** : **20b** : **25**=56 : 24 : 5). Separation of these compounds was carried out by preparative GPC.

**Compound 24.** $^1$H NMR (typical signals) $\delta$=6.20 (1H, d, $J$=13.2 Hz), 6.30 (1H, br d, $J$=13.2 Hz), and 8.88 (1H, br s); $^{13}$C NMR (typical signals) $\delta$=97.62 (t, $J$=26 Hz), 125.59, 144.20, and 168.23.

**Compound 25.** $^1$H NMR $\delta$=0.91 (3H, t, $J$=7.3 Hz), 1.38 (2H, m), 1.60 (2H, m), 3.43 (1H, dt, $J$=8.9 and 6.3 Hz), 3.57 (1H, dt, $J$=8.9 and 6.3 Hz), 6.52 (1H, d, $J$=5.8 Hz), and 7.27 (1H, d, $J$=5.8 Hz); $^{19}$F NMR $\delta$=−81.35 (3F, tt, $J$=10 and 2 Hz), −118.75 (1F, dm, $J$=282 Hz), −120.77 (2F, m), −121.51 (1F, dm, $J$=282 Hz), −122.35 (2F, m), −123.18 (2F, m), and −126.62 (2F, m); $^{13}$C NMR $\delta$=13.41, 18.76, 31.07, 64.87, 106.86 (dd, $J$=30 and 28 Hz), 100—125 (6 C), 128.65, 147.36 (d, $J$=2 Hz), and 167.47; IR (neat) 2968m, 1816vs, 1620m, 1474m, 1366s, 1332s, and 1300—1100vs cm$^{-1}$; MS (CI) $m/z$ (rel intensity) 475 ($M^+$+1, 5%), 447 (11), 419 (100), 401 (64), and 383 (6).

**Compound 26.** $^1$H NMR $\delta$=0.94 (3H, t, $J$=7.3 Hz), 1.40 (2 H, m), 1.63 (2H, m), 3.20 (1H, dd, $J$=19.4 and 2.6 Hz), 3.60 (1H, dd, $J$=19.4 and 10.9 Hz), 3.79 (1H, m), and 4.20 (2H, m); $^{19}$F NMR $\delta$=−81.29 (6F, t, $J$=10 Hz), −112.0 (1F, dm, $J$=284 Hz), −113.3 (1F, dm, $J$=284 Hz), −120.49 (2F, t, $J$=12 Hz), −121.23 (2F, m), −121.98 (2F, m), −122.25 (2F, m), −122.60 (2F, m), −123.27 (4F, m), and −126.60 (4F, m); $^{13}$C NMR $\delta$=13.41, 18.81, 30.15, 34.67 (br), 43.11 (t, $J$=22 Hz), 66.77, 100—125 (12 C), 165.45 (dd, $J$=6 and 3 Hz), and 190.69 (t, $J$=27 Hz); IR (neat) 2968s, 1754vs, 1404m, 1348s, 1320s, and 1300—1100vs cm$^{-1}$; MS (CI) $m/z$ (rel intensity) 796 ($M^+$+2, 2%), 795 ($M^+$+1, 3), 767 (9), 739 (30), 735 (69), 721 (100), 699 (40), 681 (23), 535 (18), and 479 (6).

**Reaction of Perfluorobutyltributylstannane (27) with Dibutyl Maleate (1q).** To an ethereal solution (10 ml) of **1q** (228 mg, 1 mmol) and **27** (815 mg, purity ca. 70%) was added an ethereal solution of methyllithium-lithium bromide (1.5 mmol) at −78 °C. After stirring for 1 h, the reaction mixture was quenched by the addition of aqueous $NH_4Cl$ and extracted with ether. The extract was washed with brine and dried over $Na_2SO_4$. Evaporation of the solvent gave a pale yellow oil, of which NMR analysis revealed the presence of **19c** ($E/Z$=10/1), **20c** (**19c** : **20c**=2.1 : 1), and tributylmethylstannane. Chromatography of the crude oil on silica gel gave tributylmethylstannane (510 mg) and a mixture of **19c** and **20c** (**19c** : **20c**=33 : 10).

We thank Dr. Kazuhiro Shimokawa (Daikin Kogyo Co., Ltd.) for a gift of perfluoroalkyl iodides.

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