366 *Inorg. Chem.* **1997,** *36,* 366−381

Studies on the Reactivity of Tetrafluoro- and Pentafluorophenyl Trimethylsilyl Ether with Pentafluorobenzenes. Chemistry and X-ray Structural Investigations of Polyfluorodiphenyl Ethers[†]

Burkhard Krumm, Ashwani Vij, Robert L. Kirchmeier, and Jean'ne M. Shreeve*

Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343

Received July 23, 1996[⊗]

The introduction of tetrafluoro- and pentafluorophenoxy moieties into a variety of pentafluorobenzenes C_6F_5R (R = CF_3, CN, NO_2) is accomplished by employing the trimethylsilyl ethers (siloxanes) 4-$HC_6F_4OSiMe_3$ (**1**) and $C_6F_5OSiMe_3$ (**2**) as transfer agents. Depending on the nature of the electrophile, the stoichiometry of the reaction, and the reaction conditions, polysubstituted polyfluorodiphenyl ethers are obtained. Excess C_6F_5R results in the formation of the 1,4-monosubstituted benzenes (diphenyl ethers) 4-(4′-$XC_6F_4O)C_6F_4R$ (R = CF_3, X = H (**3**), F (**4**); R = CN, X = H (**5**), F (**6**); R = NO_2, X = H (**9**), F (**10**)). When R = NO_2, the 1,2-substituted isomers are also detected. Additional byproducts that are isolable are the disubstituted benzenes 2,4-(4′-$XC_6F_4O)_2C_6F_3R$ (R = CN, X = H (**7**), F (**8**); R = NO_2, X = H (**11**), F (**12**)). Excess **1** or **2**, when reacted with C_6F_5R, results in the formation of the trisubstituted benzenes 2,4,6-(4′-$XC_6F_4O)_3C_6F_2R$ (R = CN, X = H (**13**), F (**14**); R = NO_2, = H (**15**), F (**16**)). The hydrolysis of nitrile-containing diphenyl ethers (**5**, **6**, **13**, and **14**) under acidic conditions results in the substituted benzoic acids 4-(4′-$XC_6F_4O)C_6F_4COOH$ (X = H (**17**), F (**18**)) and 2,4,6-(4′-$XC_6F_4O)_3C_6F_2$-COOH (X = H (**19**), F (**21**)). These acids are decarboxylated to form the respective hydropolyfluoro aromatics (4-$HC_6F_4)_2O$ (**23**), 4-($C_6F_5O)C_6F_4H$ (**24**), and 2,4,6-(4′-$XC_6F_4O)_3C_6F_2H$ (X = H (**20**), F (**22**)). In addition to acid **17**, alkaline hydrolysis of **5** gives the α-hydroxy-substituted acid 4-(4′-$HC_6F_4O)C_6F_3$(2-OH)COOH (**25**). Alkaline hydrolysis under milder conditions enables the isolation of the amide 4-(4′-$HC_6F_4O)C_6F_4CONH_2$ (**26**). The compounds **3**, **4**, **14**−**18**, **23**, and **26** have been characterized by single-crystal X-ray diffraction analysis. The presence of a hydrogen atom in **3**, as well as protection of the reactive 4′-position with a trifluoromethyl group, gives 4-(4′-$CF_3C_6F_4O)C_6F_4Li$ (**3a**) on reaction with *n*-butyllithium. *In situ* reactions between **3a** and ketones or acid chlorides result in novel mono- or bis(perfluorodiphenyl ether)-substituted tertiary alcohols 4-(4′-$CF_3C_6F_4O$)-$C_6F_4C(R)(R')OH$ (R/R′ = CF_3 (**27**), C_6F_5 (**28**), C_6H_5 (**29**), C_3F_7/C_8F_{17} (**30**), C_6F_5/CH_3 (**31**)), [4-(4′-$CF_3C_6F_4O$)-$C_6F_4]_2C(R)OH$ (R = CF_3 (**32**), C_3F_7 (**33**), C_7F_{15} (**34**), *i*-C_3H_7 (**35**)). When R = *i*-C_3H_7, the major product is the ester [4-(4′-$CF_3C_6F_4O)C_6F_4]_2C$(*i*-C_3H_7)OC(O)(*i*-C_3H_7) (**36**). The ketone $C_3F_7(C_8F_{17})CO$ (**37**) is synthesized and characterized. Reaction of **3a** with hexafluoroglutaryl chloride gives [4-(4′-$CF_3C_6F_4O)C_6F_4]_2C(OH)$-$(CF_2)_3C(O)C_6F_4O$(4″-$C_6F_4CF_3$) (**38**), whereas with dimethyl carbonate or carbonyl fluoride, [4-(4′-$CF_3C_6F_4O)C_6F_4]_2$-CO (**39**) as well as small amounts of [4-(4′-$CF_3C_6F_4O)C_6F_4]_3COH$ (**40**) and [4-(4′-$CF_3C_6F_4O)C_6F_4]_3COC(O)C_4H_9$ (**41**) are formed. Residual *n*-butyllithium cleaves the intermediate 4-(4′-$CF_3C_6F_4O)C_6F_4COOCH_3$ to form 4-$CF_3C_6F_4C_4H_9$ (**42**) and 4-$HOC_6F_4COOCH_3$ (**43**).

Introduction

The utilization of silyl ethers (siloxanes) as transfer agents provides a powerful preparative pathway for the synthesis of new or heretofore difficultly accessible per- and polyfluorinated compounds.[1−7] These transfer reactions that ordinarily occur under relatively mild conditions, compared to those required when the analogous metalated compounds (alkoxy or aryloxy) are employed, are catalyzed by the presence of fluoride ion.

The nucleophilicity of the ether group is markedly enhanced by the formation of the strong silicon−fluorine bond (∼142 kcal/mol)[8] found in the volatile trimethylsilyl fluoride byproduct. The silyl ethers are readily synthesized, are stable, are straightforward to handle, and provide the synthetic chemist with remarkable control over the product(s) obtained. Additionally, purification of the products is easily carried out. Such advantages are not always observed when metalated nucleophiles are employed.[2]

We and others used this methodology to explore the reactivity of mono- and disiloxy per- and polyfluorinated derivatives with a large number of halogenated compounds in order to prepare a variety of new perfluoro and polyfluoro ethers.[1−7] Also studied was the behavior of perfluorinated aromatic siloxanes, *e.g.*, $C_6F_5OSiMe_3$,[3,6,7,9,10] 1,4-$(Me_3SiO)_2C_6F_4$, 1,4-$[Me_3SiOC(CF_3)_2]_2C_6F_4$,[3] toward a range of electrophiles. The reaction of a nonfluorinated aromatic siloxane in excess, *i.e.*, $C_6H_5OSiMe_3$, with electrophiles C_6F_6 or C_6F_5CN leads to

---

[†] Dedicated to Professor Dr. Hans Bürger on the occasion of his 60th birthday.

[⊗] Abstract published in *Advance ACS Abstracts*, January 1, 1997.

(1) Zhang, Y. F.; Kirchmeier, R. L.; Shreeve, J. M. *J. Fluorine Chem.* **1994**, *68*, 267.

(2) Patel, N. R.; Chen, J.; Zhang, Y. F.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1994**, *33*, 5463 and references therein.

(3) Patel, N. R.; Chen, J.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1995**, *34*, 13 and references therein.

(4) Nishida, M.; Vij, A.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1995**, *34*, 6085.

(5) Krumm, B.; Vij, A.; Kirchmeier, R. L.; Shreeve, J. M. 211th ACS National Meeting, New Orleans, LA, 1996; Abstract 26.

(6) Chen, J.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1996**, *35*, 1718.

(7) Chen, J.; Zhang, Y. F.; Zheng, X.; Vij, A.; Wingate, D.; Meng, D.; White, K.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1996**, *35*, 1590.

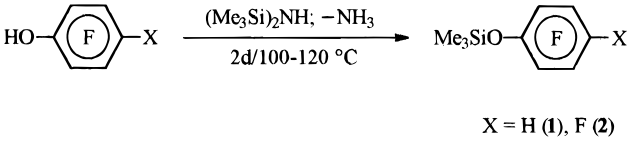
(8) Weber, W. P. *Silicon Reagents in Organic Synthesis*; Springer Verlag: New York, 1983.

(9) Oliver, A. J.; Graham, W. A. G. *J. Organomet. Chem.* **1969**, *19*, 17.

(10) Hogben, M. G.; Graham, W. A. G. *J. Am. Chem. Soc.* **1969**, *91*, 283.

S0020-1669(96)00879-8 CCC: $14.00

Scheme 1



complete substitution of all fluorine atoms to form $(C_6H_5O)_6C_6$[1] and $(C_6H_5O)_5C_6CN$.[2] Similarly, in the reaction of excess $4\text{-}FC_6H_4OSiMe_3$ with C_6F_6, the compounds $(4\text{-}FC_6H_4O)_{6-n}C_6F_n$ ($n = 0, 1, 2$) were obtained as a mixture.[1]

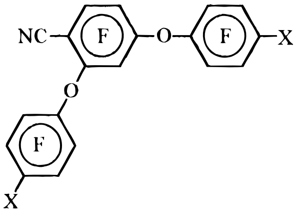
In this work, we have taken advantage of the controllable reactivity of the polyfluorinated aromatic silyl ethers, $4\text{-}HC_6F_4\text{-}OSiMe_3$ and $C_6F_5OSiMe_3$, to prepare stable polysubstituted polyfluorodiphenyl ethers, highly substituted benzoic acids, tertiary perfluoro(diaryl)(alkyl) alcohols, and precursors to new, high molecular weight poly- and perfluorophenyl derivatives. In some cases involving the pentafluorophenoxy moiety, the products are known materials[11−15] that now can be prepared in better yields and/or under milder conditions. We have characterized them thoroughly. To our knowledge, no fluorinated aromatic compounds containing the 4-hydrotetrafluorophenoxy group are reported. Here, the carbon−hydrogen bond provides a potentially reactive site for extended reactions of these compounds. In addition, for some compounds, structural studies of the solid state using single-crystal X-ray crystallography was accomplished.

The high molecular weight polyfluoro- and perfluoroaryl derivatives exhibit relatively high thermal stability and low volatility. They have been synthesized for study as stabilizing agents in high temperature applications of commercially useful fluorinated lubricants.[16−20] These stability studies are currently underway.

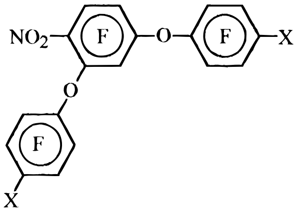
Results and Discussion

Tetrafluoro- and pentafluorophenylsiloxane are prepared by refluxing the respective phenols in a 2-fold excess of hexamethyldisilazane at 100−120 °C, Scheme 1. The reactivity of **1** and **2** toward electrophiles is approximately identical since the replacement of the *para*-hydrogen by fluorine does not cause a significant change in the nucleophilicity of the oxygen. Both siloxanes are reacted with an excess of various pentafluorobenzenes bearing strong electron-withdrawing groups. No reaction of these two particular siloxanes occurs with hexafluorobenzene or pentafluorobenzenes containing electron-releasing groups, Scheme 2.

Byproducts found in the reactions with the more reactive pentafluorobenzonitrile and pentafluoronitrobenzene are the disubstituted benzenes **7**, **8**, and **11**, **12**.



X = H (**7**), F (**8**)



H (**11**), F (**12**)

In addition, with pentafluoronitrobenzene, significant amounts (20−30%) of the *ortho*-isomers of **9** and **10** are formed.

The use of excess siloxane with octafluorotoluene does not lead to substitution in the *ortho*-position. However, with pentafluorobenzonitrile and pentafluoronitrobenzene, further substitution occurs readily, Scheme 3.

Further substitution of the *meta*-fluorine atoms could not be accomplished with **1** or **2**, even when a large excess of siloxane and temperatures up to 150 °C were employed. As a result of these studies, we can report an increasing reactivity of **1** and **2** toward substituted pentafluorobenzenes as a function of the *para*-activating influence of the substituent in the order: $C_6F_6 < C_6F_5CF_3 < C_6F_5CN < C_6F_5NO_2$.

It is well-known that fluorinated aromatic nitriles undergo hydrolysis in strongly acidic as well as alkaline media to give carboxylic acids.[21,22] We found that under optimized conditions, acidic hydrolysis of **5** and **6,** as well as of **13** and **14**, leads to the respective acids in high yields, although the latter two require slightly higher temperatures and longer reaction times, Scheme 4.

Hydrolysis does not occur under milder conditions, such as lower temperatures and/or in less concentrated sulfuric acid. Compound **17** forms crystals that contain variable amounts of water, as is indicated in the IR spectrum and elemental analysis data. Also, an X-ray structure of **17** shows water in the crystal lattice, but the data set exhibits large thermal motion that precludes adequate refinement. The structure of a different crystal reveals the anhydrous acid **17**.

During the acidic hydrolysis of **13** and **14** the formation of the decarboxylated species **20** and **22** is observed, as shown in Scheme 4. The relative ratio of acid to hydroaromatic is found to be ∼4:1 based on the ^{19}F NMR results. When heated to 230−250 °C, neat acids **17**, **18**, **19**, and **21** are completely decarboxylated and, therefore, require slightly higher temperatures than those observed in acidic solution, Scheme 5.

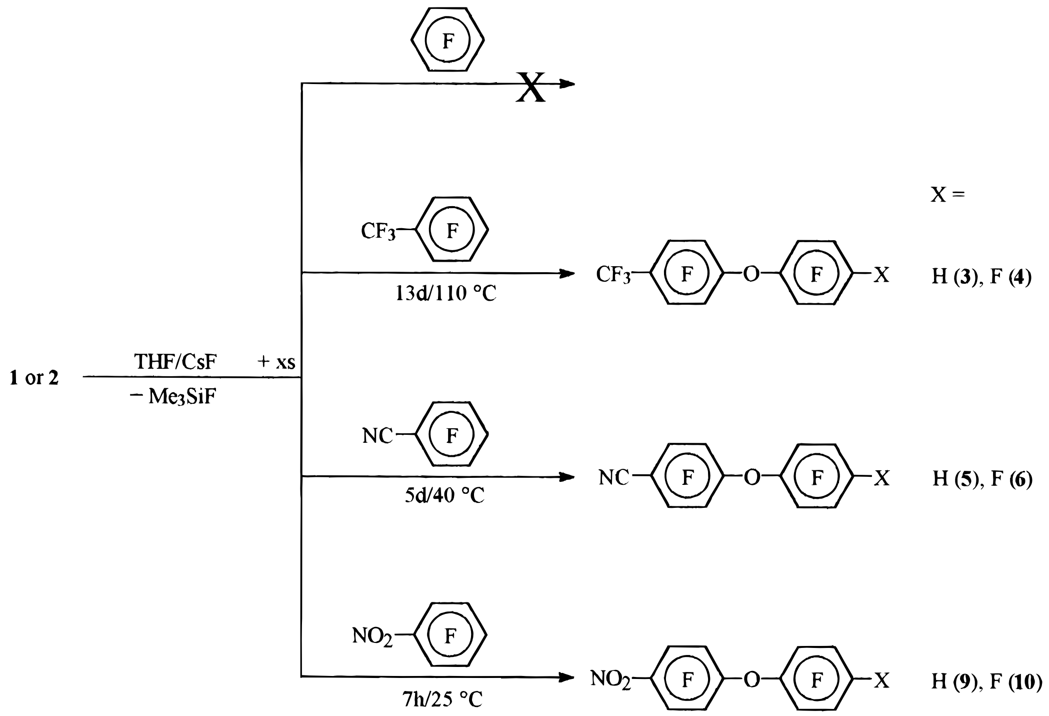
The alkaline hydrolysis of **5** occurs at lower temperatures than under acidic conditions but is more complex, Scheme 6. Depending on the temperature, it is possible to isolate the acid **17** or the intermediate amide **26**, which is not observed under acidic conditions. The formation of **17** is accompanied by the formation of **25**, which results from the nucleophilic attack of hydroxide at the 2-position. The alkaline hydrolysis of **6** is even more complex because of the presence of the *para*-fluorine atom, which is also very sensitive to nucleophilic attack. Compounds that are similar to **17**, **25**, and **26**, as well as others with X = F, were observed by using ^{19}F NMR spectroscopy but could not be separated and isolated.

The presence of an active hydrogen in **3** provides a potential site for further chemistry. It can be lithiated in the same way as $4\text{-}(C_6F_5O)C_6F_4H$.[23,24] But here, the reactive 4′-position is protected by a CF_3 group, Scheme 7. Consequently, butylation, observed as a side reaction during the

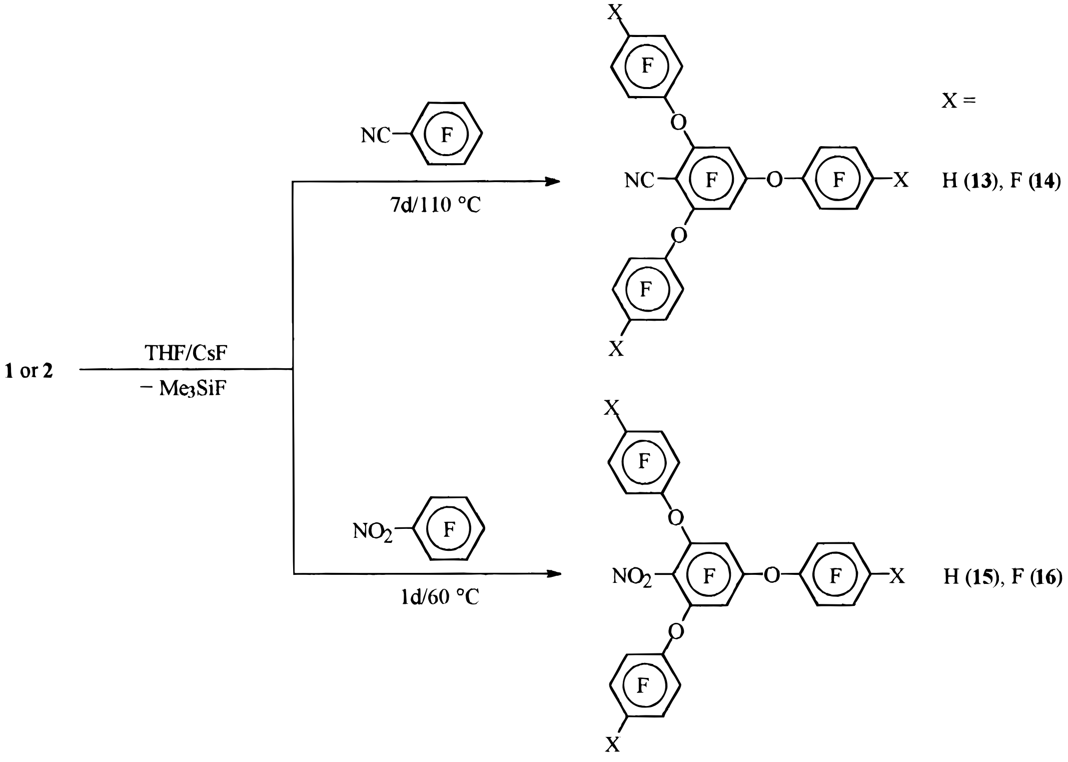
---

(11) De Pasquale, R. J.; Tamborski, C. *J. Org. Chem.* **1967**, *32*, 3163.
(12) De Pasquale, R. J.; Tamborski, C. U.S Pat. 3,637,866, 1972.
(13) De Pasquale, R. J.; Tamborski, C. *J. Org. Chem.* **1968**, *33*, 1658.
(14) Kobrina, L. S.; Furin, G. G.; Yakobson, G. G. *Zh. Obshch. Khim.* **1968**, *38*, 514.
(15) Kobrina, L. S.; Furin, G. G.; Yakobson, G. G. U.S.S.R. Pat. 213,792, 1968.
(16) Paciorek, K. J. L.; Kratzer, R. H. *J. Fluorine Chem.* **1994**, *67*, 169 and references therein.
(17) Kasai, P. H. *Macromolecules* **1992**, *25*, 6791.
(18) Johns, K.; Corti, C.; Montagna, L.; Srinivasan, P. *J. Phys. D: Appl. Phys.* **1992**, *25*, A141.
(19) Gschwender, L. J.; Snyder, C. E., Jr.; Fultz, G. W. *Lubr. Eng.* **1993**, *49*, 702.
(20) Snyder, C. E., Jr.; Dolle, R. E., Jr. *ASLE Trans.* **1976**, *19*, 171.
(21) Birchall, J. M.; Haszeldine, R. N.; Jones, M. E. *J. Chem. Soc. C*, **1971**, 1343.
(22) Aroskar, E. V.; Brown, P. J. N.; Plevey, R. G.; Stephens, R. *J. Chem. Soc. C* **1968**, 1569.
(23) De Pasquale, R. J.; Tamborski, C. *J. Organomet. Chem.* **1968**, *13*, 273.
(24) De Pasquale, R. J. *J. Organomet. Chem.* **1968**, *15*, 233.

Scheme 2



Scheme 3



preparation of 4-(C_6F_5O)C_6F_4Li,[23] is prevented. Although no attempt was made to isolate **3a**, in solution it is stable to ∼−40 °C with rapid darkening of the colorless solution at higher temperatures. Formation of the lithiated species is confirmed by isolating the products that are obtained when reactions with several ketones, acid chlorides, carbonyl fluoride, and dimethyl carbonate are carried out.

The novel perfluoroaromatic tertiary alcohols as well as the bis(perfluoroaromatic) tertiary alcohols derived from these reactions of **3a** are obtained as viscous oils or solids that are isolated and purified by column chromatography. The intermediate ketones in the reactions with acid chlorides are never detected, even when excess acid chloride is used, Scheme 8.

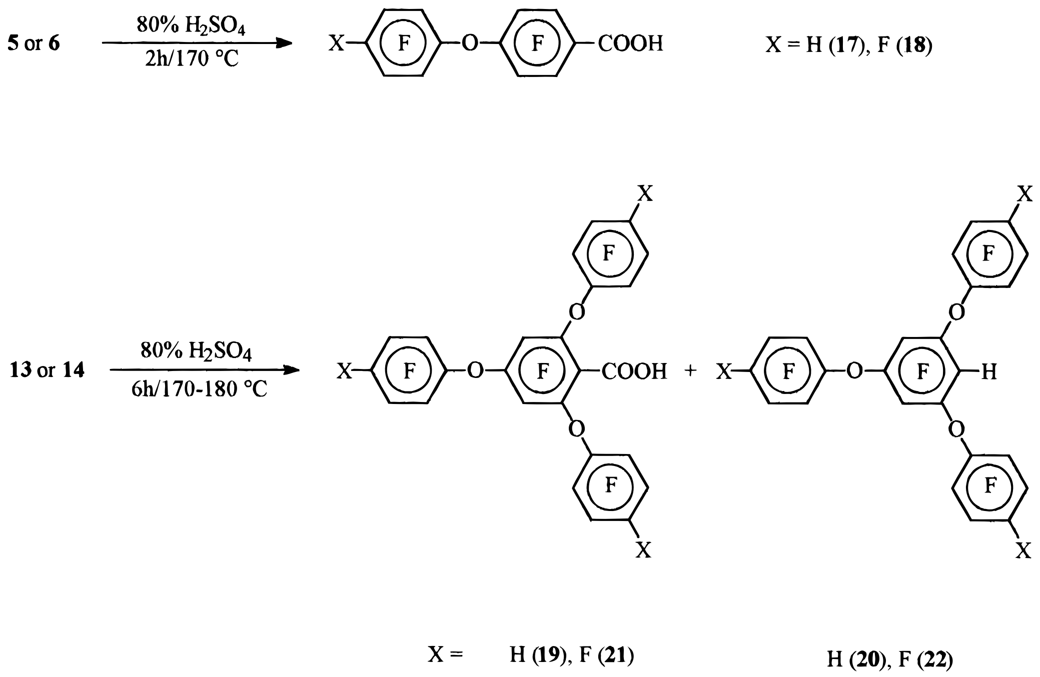
The formation of the ester **36** results from reaction of the alkoxide $(R_F)_2(i\text{-}C_3H_7)COLi$ with excess $(i\text{-}C_3H_7)C(O)Cl$ present ($R_F = CF_3{-}Ar_f{-}O{-}Ar_f{-}$). In this case, the alcohol **35** is only found in traces. This behavior is not observed with the fluorinated acid chlorides.

The new ketone $C_3F_7(C_8F_{17})CO$ (**37**) was prepared following a literature method for the synthesis of perfluoroalkyl ketones, Scheme 9.[25]

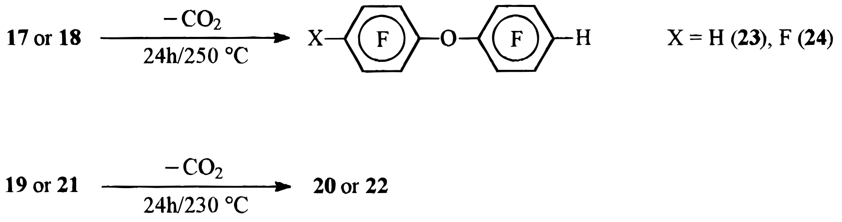
---

(25) Chen, L. S.; Chen, G. J. *J. Fluorine Chem.* **1989**, *42*, 371.

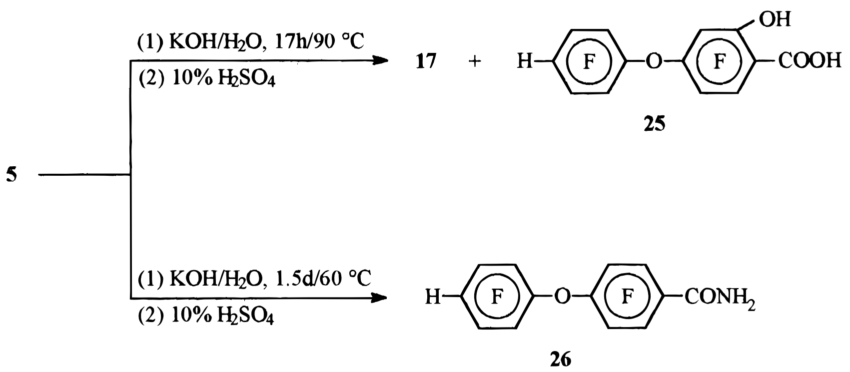
Scheme 4



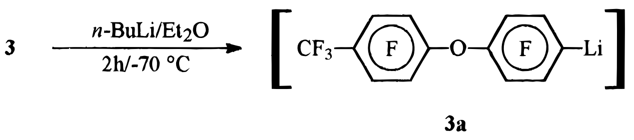
Scheme 5



Scheme 6



Scheme 7



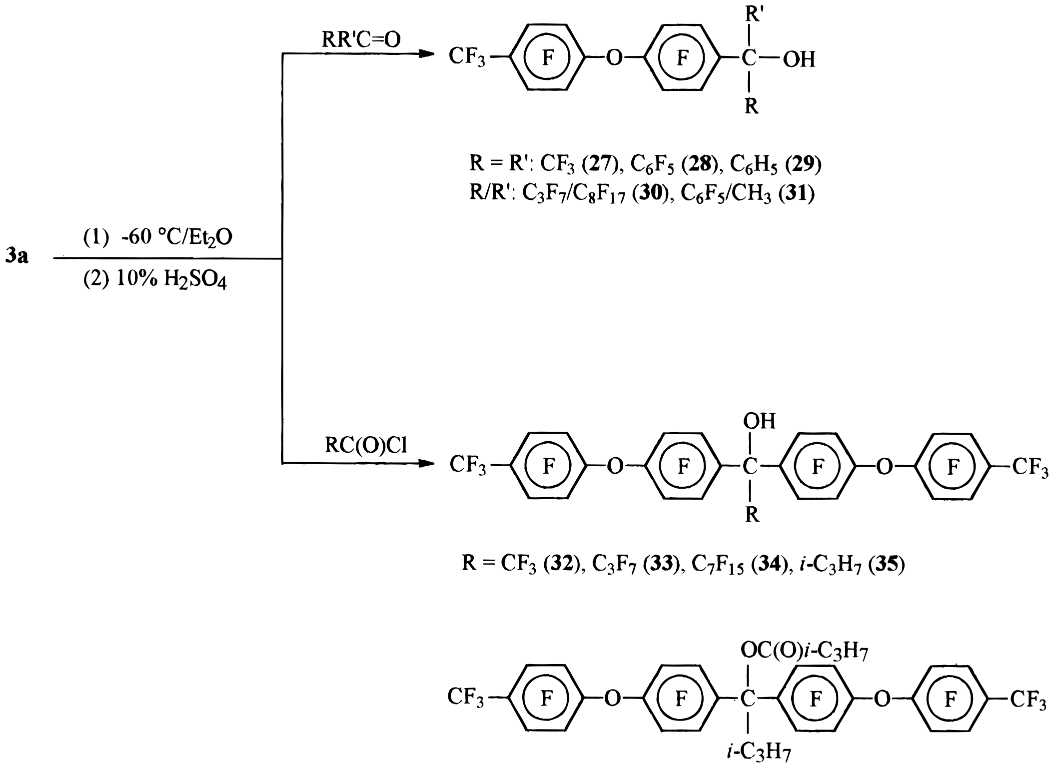
The resonances of the aromatic fluorine atoms in the ^{19}F NMR spectrum of **27** show interesting splitting in both the 2- and 3-positions relative to those of the $-C(CF_3)_2OH$ group. Normally, these fluorine atoms, as well as those in the 2′- and 3′-positions in compounds of the type $CF_3C_6F_4OC_6F_4C(R)_2OH$, show a single resonance. But in the case of **27** at 25 °C, the resonance for 2-F is split into two very broad humps and for 3-F into a single broadened signal. Variable temperature studies in the region for the aromatic fluorine atoms between −130 and −160 ppm (Figure 1) show that both types of fluorines coalesce at different temperatures. Below the coalescence temperature, both sets of fluorine atoms in the 2- and 3-position split into two signals. The fluorine atoms in the 2′- and 3′-position remain unaffected.

The free energies of activation (ΔG) for this coalescence phenomena are calculated by using the Eyring equation.[26] The temperatures of coalescence (T_c) and the shift differences between both signals ($\Delta\nu$) are obtained from the ^{19}F NMR spectra. The measured values of T_c and the calculated free energies are given in Table 1. This inequivalence of the fluorine atoms in the 2- and 3-positions in our compounds of the type $CF_3C_6F_4OC_6F_4C(R)_2OH$ is only observed when the tertiary carbon bears relatively bulky perfluorinated alkyl groups. The same effect seems to be present in **30** (R/R′ = C_3F_7/C_8F_{17}), but

---

(26) Oki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH Publishers, Inc.: New York, 1985.

Scheme 8



R = R': CF_3 (**27**), C_6F_5 (**28**), C_6H_5 (**29**)
R/R': C_3F_7/C_8F_{17} (**30**), C_6F_5/CH_3 (**31**)

R = CF_3 (**32**), C_3F_7 (**33**), C_7F_{15} (**34**), *i*-C_3H_7 (**35**)

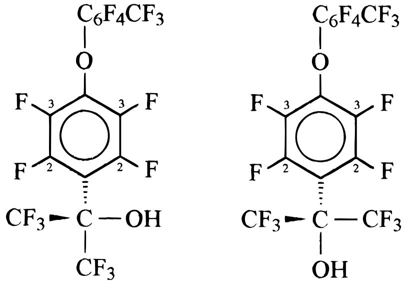
36

Scheme 9

$$C_3F_7CO_2Et + C_8F_{17}I \xrightarrow[(2)\ \text{conc. HCl}]{(1)\ \text{MeLi/Et}_2\text{O/-78 °C}} C_3F_7(C_8F_{17})CO$$

37

here, the resonances of the aromatic fluorine atoms partially overlap, which does not allow definitive assignments to be made. The inequivalence of the 2- and 3-fluorine atoms indicates a restricted rotation around the $C_1-C(CF_3)_2OH$ bond, resulting in two different conformations (**A**/**B**) around the tertiary carbon.



A B

Conformation **A** leads to inequivalent fluorine atoms in both the 2- and 3-positions, indicating restricted rotation, whereas conformation B gives rise to equivalent fluorine atoms in the 2- and 3-positions, indicating free rotation after reaching the coalescence temperature, T_c.

The reaction with hexafluoroglutaryl chloride does not result in the formation of the respective dialcohol. Instead, we observe the formation of a mixed ketone–alcohol, *i.e.*, the introduction of a fourth perfluorodiphenyl ether moiety does not occur probably due to the low solubility of the latter at low temperatures in ether, Scheme 10.

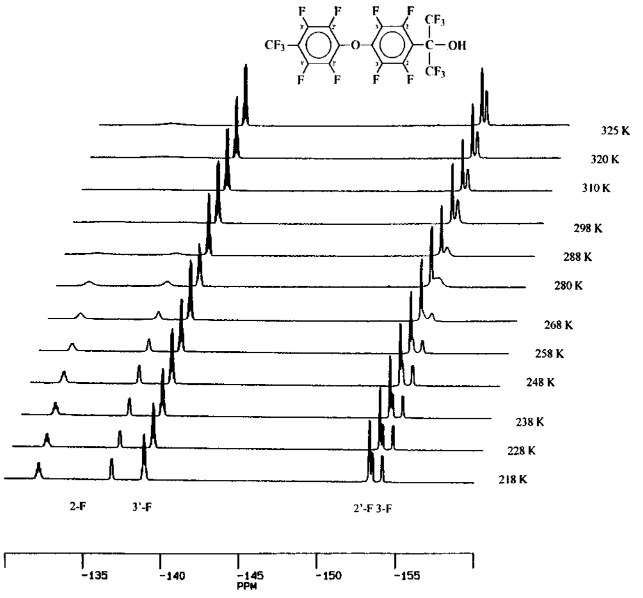


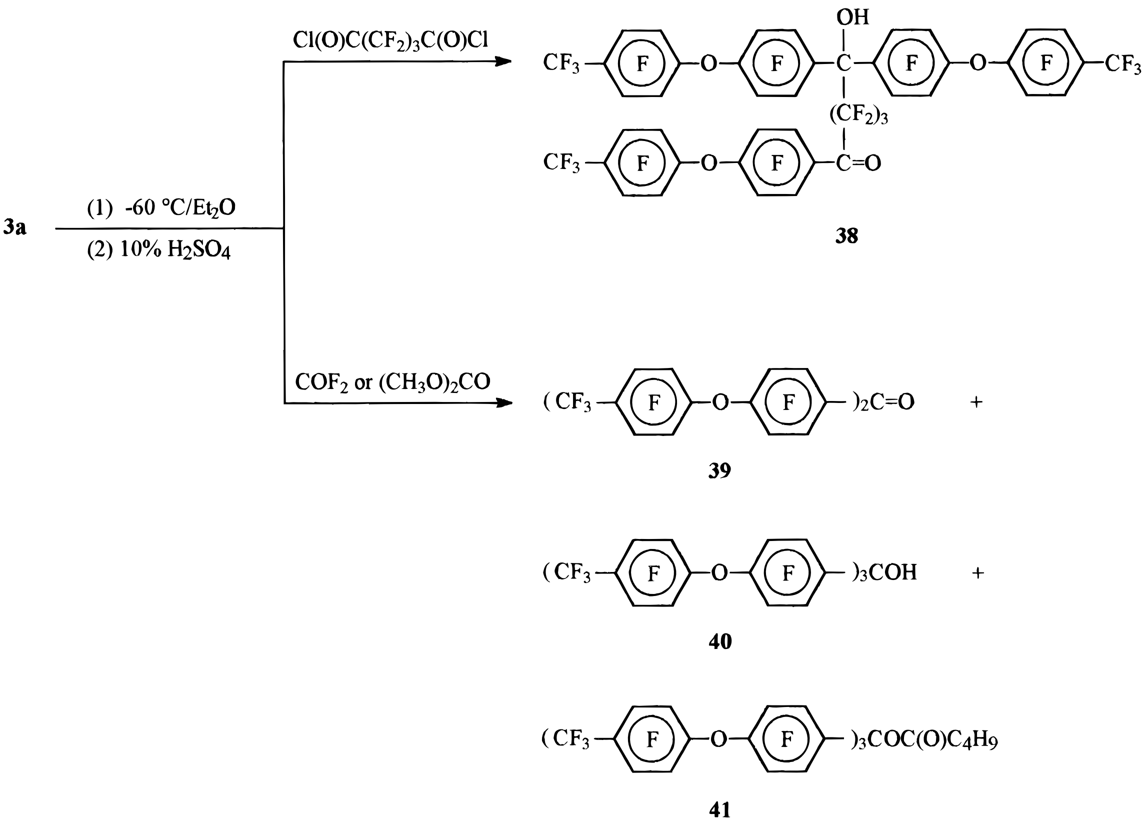
Figure 1. Variable temperature ^{19}F NMR spectrum of $CF_3C_6F_4$-$OC_6F_4C(CF_3)_2OH$ (**27**) (aromatic fluorines region).

Table 1. Results of Variable Temperature ^{19}F NMR Studies of **27** and Calculation Of Free Energies (ΔG)

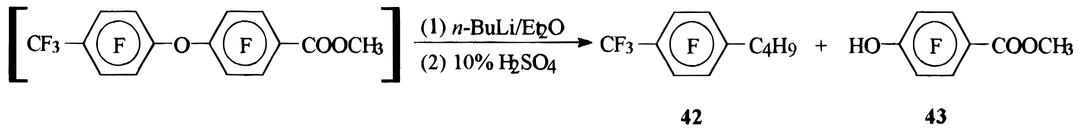
27	T_c (K)	$\Delta\nu$ (Hz)	ΔG (kcal/mol)	solvent
2-F	310	1334	13.2	$CDCl_3$
3-F	280	179	13.0	$CDCl_3$

The tertiary alcohol **40** is the product of choice in the reaction with carbonyl fluoride or dimethyl carbonate, but it is only formed as a minor product. The major product in either reaction is the precursor ketone **39** that is insoluble in ether. This prevents or radically slows reaction with a third mole of **3a**, which accounts for the low yields of **40** even when the reactions involve an excess of **3a**. However, this is an excellent route to

Scheme 10



Scheme 11



the interesting ketone **39**. Unfortunately, a suitable solvent for the preparation of **40** has not been found.

Dimethyl carbonate is a convenient substitute for carbonyl fluoride. A similar preparation by using diethyl carbonate is reported for $(C_6F_5)_3COH$.[27,28] Here, the intermediate ketone $(C_6F_5)_2CO$ is soluble in ether, and further reaction with C_6F_5Li takes place readily. With carbonyl fluoride, in addition to **39** and **40**, the ester **41** is formed. This may be due to the reaction of the alkoxide $(R_F)_3COLi$ with *n*-BuC(O)F. This acid fluoride is formed from the reaction of unreacted *n*-BuLi with carbonyl fluoride.

When *n*-BuLi and dimethyl carbonate are added to concentrated solutions of **3** in ether, cleavage of the intermediate ester 4-(4′-$CF_3C_6F_4O$)$C_6F_4COOCH_3$ results in formation of 4-$CF_3C_6F_4C_4H_9$ (**42**) and 4-$HOC_6F_4COOCH_3$ (**43**). These compounds, reported in the literature[29−31] and identified by their spectroscopic data, confirm the presence of the precursor ester, which, although never isolated, appears to be highly sensitive to attack by unreacted butyllithium at the 1′-carbon. The decreased solubility of **3** in ether at −70 °C results in its incomplete lithiation. The residual unreacted *n*-BuLi cleaves the ether bond in the intermediate ester as shown in Scheme 11. This reaction demonstrates the sensitivity of the etheral carbon atoms toward potentially undesirable side reactions.

X-ray structures of the polyfluorodiphenyl ethers. A survey of the Cambridge Crystallographic Structure Database reveals that the number of crystal structures determined for fluorinated ethers is very small. Those reported are ethers that contain trifluoromethyl groups[1,32,33] and more recently a highly fluorinated ether, $CF_3(C_6F_5)_2COCH_2C_6F_5$, derived from a perfluoro tertiary alcohol.[4] The property of some of the perfluoroaromatic ethers and their derivatives in our study to sublime/crystallize provides a unique opportunity to investigate their solid state structures using single-crystal X-ray diffraction techniques.

Since compounds **3** and **4** are extremely volatile at room temperature, crystal mounting and data collection are carried out under a stream of cold nitrogen gas. In the case of **3**,[34] data collection at −60 and −100 °C shows that the CF_3 group is highly disordered due to free rotation about the C4−C7 bond (Figure 2). However, at −110 °C this rotation can be frozen out to give an ordered structure. In contrast, **4**[35] shows no disorder at −100 °C (Figure 3). The symmetric ether **23**[36]

---

[27] Chambers, R. D.; Spring, D. J. *J. Chem. Soc. C* **1968**, 2394.

[28] Filler, R.; Wang, C. S.; McKinney, M. A.; Miller, F. N. *J. Am. Chem. Soc.* **1967**, *89*, 1026.

[29] Davydov, D. V.; Beletskaya, I. P. *Metalloorg. Khim.* **1988**, *1*, 899.

[30] Davydov, D. V.; Beletskaya, I. P. *Metalloorg. Khim.* **1990**, *3*, 196.

[31] Voronkov, M. G.; Lopyrev, V. A.; Popova, L. I.; Taturov, G. P.; Voronova, L. K.; Ignat'ev, N. V.; Byalkovskii, K. L. *Dokl. Akad. Nauk SSSR* **1975**, *225*, 628.

[32] Kennard, C. H. L.; Smith, G.; Hari, T. *Aust. J. Chem.* **1987**, *40*, 1131.

[33] Whitmire, K. H.; Roesky, H. W.; Brooker, S.; Sheldrick, G. M. *J. Organomet. Chem.* **1991**, *402*, C4.

[34] Selected bond lengths (Å) and angles (deg) (**3**): C2−F2 = 1.339(4); C7−C7A = 1.303(5); C1−O1 = 1.374(4); C1−O1−C8 = 116.2.

[35] Selected bond lengths (Å) and angles (deg) (**4**): C3−F3 = 1.344(3); C11−F11 = 1.336(3); C8−O1 = 1.392(3); C1−O1−C8 = 116.2(2).

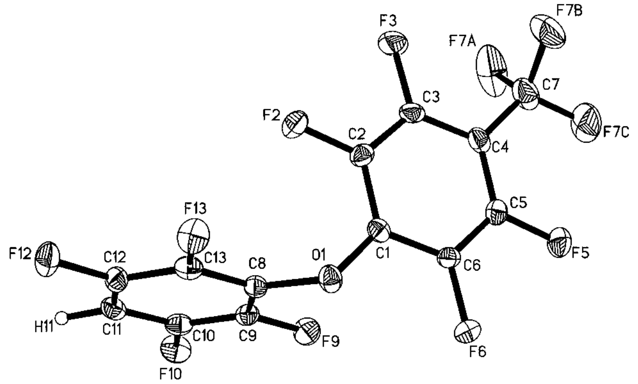


Figure 2. Molecular structure of $CF_3C_6F_4OC_6F_4H$ (**3**), with thermal ellipsoids at 30% probability level.

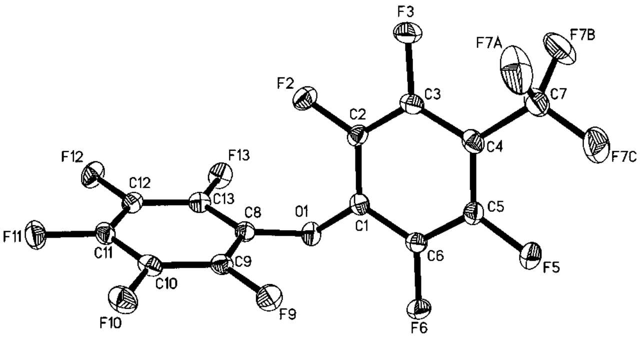


Figure 3. Molecular structure of $CF_3C_6F_4OC_6F_5$ (**4**), with thermal ellipsoids at 30% probability level.

crystallizes in the space group $P2_1/c$ as do **3** and **4**, but the oxygen atom sits on a 2-fold screw axis. The remaining atoms C1A−C6A and H4A are generated by the symmetry operation $-x, y, {}^3/_2 - z$ to complete the molecular geometry (Figure 4a). Although the molecular weight of **23** is lower ($M_w = 314$) than that of **3** ($M_w = 382$) or **4** ($M_w = 400$), the former melts at a higher temperature (67−68 °C) *vis-à-vis* **3** (39−41 °C) or **4** (56−58 °C). This can be explained on the basis of intermolecular H3$\cdots$F3^a interactions in **23** (2.551 Å, $a = -1 - x, -y, 1 - z$) that result in the formation of dimers (Figure 4b).

Compounds **14**,[37] **15**,[38] and **16**,[39] represent unique examples of fluoroaromatic polyethers where the ether substituents are present at the 2-, 4-, and 6-positions on a functionalized 3,5-difluorobenzene. In order to minimize the steric effects in these 2,4,6-fluorophenoxy compounds, substituents are twisted alternatively above and below the plane that contains the functionalized 3,5-difluorobenzene in a roughly perpendicular fashion (80−89°) (Figures 5−7). The C4−O2 distances in these molecules are shorter than those of C2−O1 and C6−O3, probably due to increased crowding on C1 thereby elongating the latter bonds. An analysis of the relative mean planes between the phenoxy rings B (ring linked to O1), C (ring linked to O2), and D (ring linked to O3) was undertaken to see the orientations of these rings. In **14**, these planes are 36.2(1)° (rings BC), 28.8(1)° (rings BD), and 64.3(1)° (rings CD), showing that the rings C and D lie roughly parallel to ring B while ring C shows twice as much tilt toward ring D *vis-à-vis* ring B. In **15**, the NO_2 group lies at 43.3(2)° with respect to the plane containing the 3,5-difluorobenzene ring. This angle increases to 51.8(3)° in **16**, which contains the pentafluorophe-

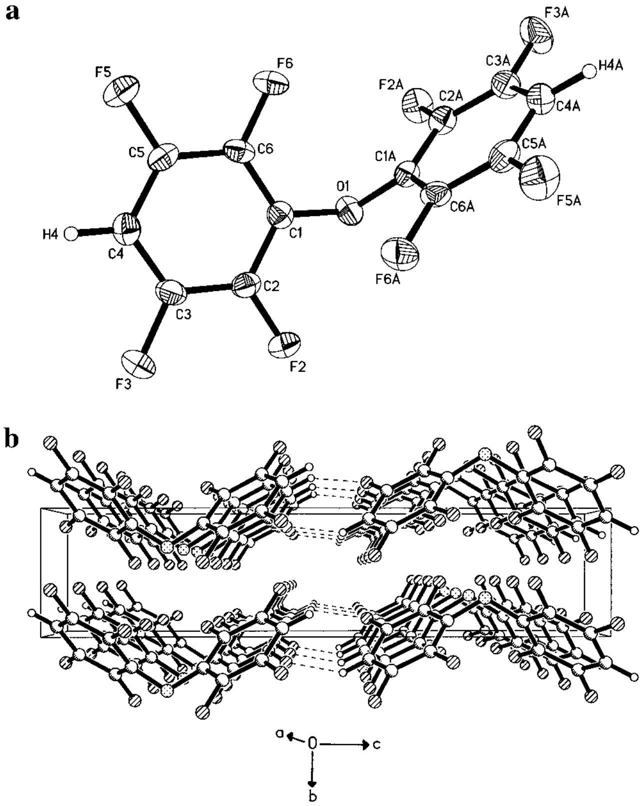


Figure 4. (a) Molecular structure of $(HC_6F_4)_2O$ (**23**), with thermal ellipsoids at 50% probability level. (b) Crystal packing diagram of $(HC_6F_4)_2O$ (**23**), along the *a*-axis showing intermolecular H$\cdots$F interactions.

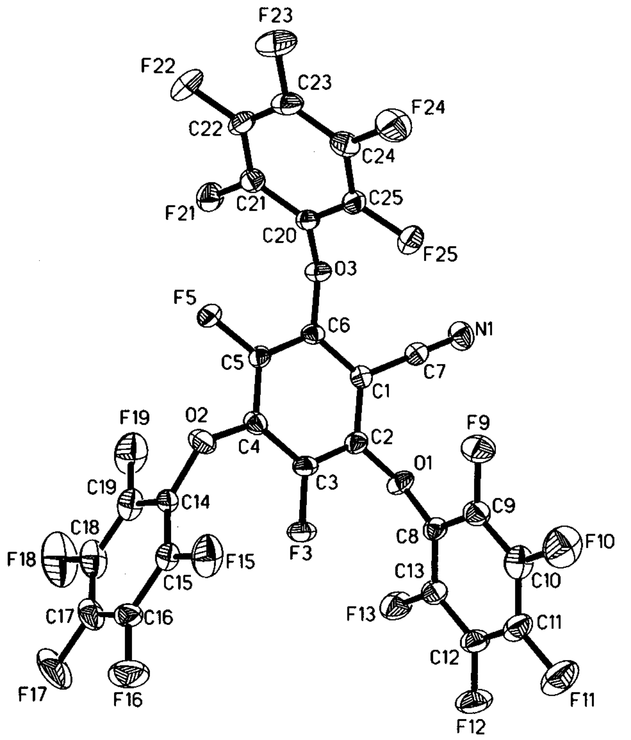


Figure 5. Molecular structure of $(C_6F_5O)_3C_6F_2CN$ (**14**), with thermal ellipsoids at 40% probability level.

---

[36] Selected bond lengths (Å) and angles (deg) (**23**): C1−O1 = 1.384(2); C2−F2 = 1.339(3); C5−F5 = 1.343(3); C1−O1−C′1 = 117.7(2); O1−C1−C2 = 118.4(2).

[37] Selected bond lengths (Å) and angles (deg) (**14**): C7 − N1 = 1.139(3); C9−F9 = 1.347(3); C2−O1 = 1.387(3); N1−C7−C1 = 176.7(3); C2−O1−C8 = 118.8(2); C4−O2−C14 = 118.4(2).

[38] Selected bond lengths (Å) and angles (deg) (**15**): C1−N1 = 1.463(2); N1−O4 = 1.230(2); C8−F8 = 1.339(3); O4−N1−O5 = 124.9(2); C1−N1−O5 = 117.9(2); C2−O1−C7 = 117.11(14).

[39] Selected bond lengths (Å) and angles (deg) (**16**): C1−N1 = 1.462(4); N1−O4 = 1.220(4); C24−F24 = 1.346(4); O4−N1−O5 = 124.9(3); C1−N1−O4 = 118.5(3); C6−O3−C19 = 117.9(2).

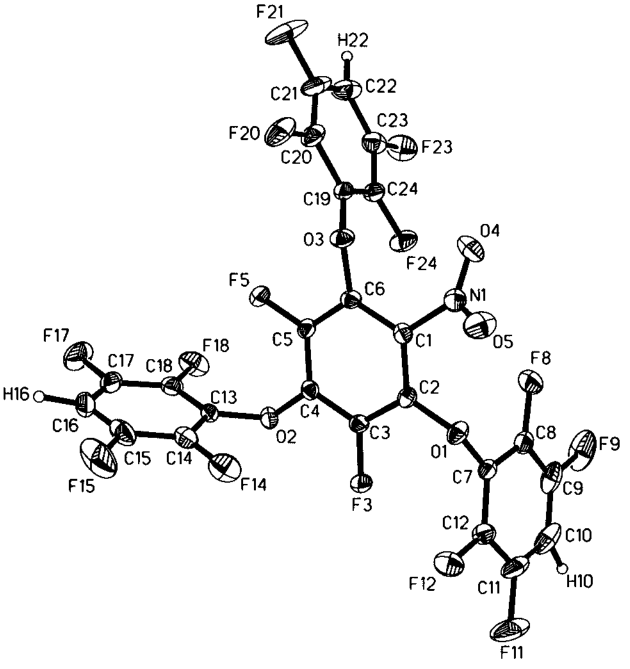


Figure 6. Molecular structure of $(HC_6F_4O)_3C_6F_2NO_2$ (**15**), with thermal ellipsoids at 30% probability level.

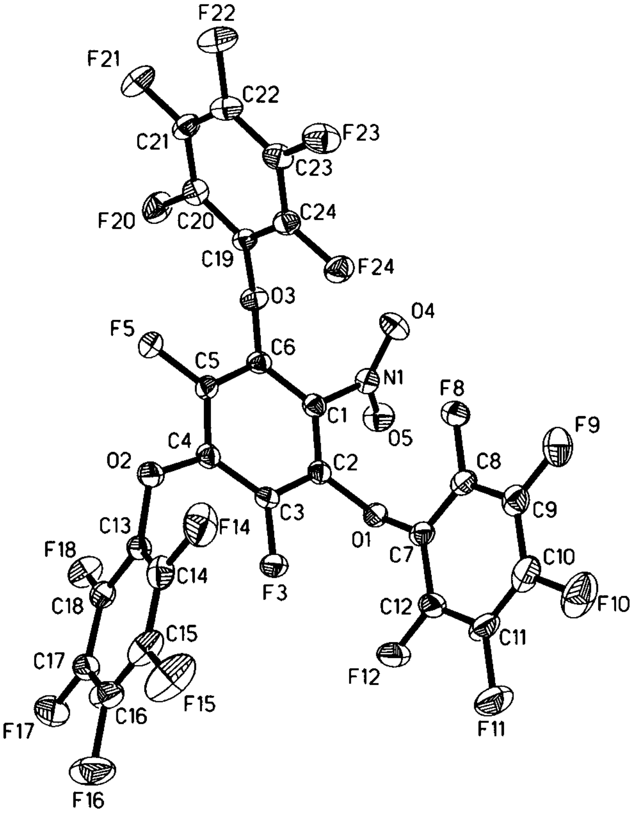


Figure 7. Molecular structure of $(C_6F_5O)_3C_6F_2NO_2$ (**16**), with thermal ellipsoids at 30% probability level.

noxy groups in place of tetrafluorophenoxy in **15**. The relative values for the orientation of the BC, BD, and CD phenoxy rings are 65.8(1)°, 19.5°, and 53.0(1)° for **15** and 19.4(2)°, 34.6°, 49.3(1)° for **16**, respectively.

Compounds **17**[40] and **18**[41] crystallize in the $P\bar{1}$ space group. These are unique examples of fluoroaromatic carboxylic acids that contain an ether linkage. In pentafluorobenzoic acid, interactions between the fluorine atoms in the *ortho*-positions and the oxygen atoms of the carboxyl group are assumed to be very weak.[42] The orientation of the carboxyl group and its dimer in **17** and **18**, therefore, is independent of the inter- or intramolecular forces, analogous to pentafluorobenzoic acid. These interactions are present in nonfluorinated aromatic acids.[42] The disorder in the carboxyl group in **17** is shown in Figure 8. This disorder was modeled with two components with relative mean planes at 44(1)°: a major (O2A−C7−O3A) (part A) and a minor (O2B−C7−O3B) (part B) component with an occupancy of 71 and 29%, respectively. The molecule is nonplanar, and parts A and B of the carboxylate group are twisted with respect to the arene ring C1−C6 19.9(9)° and 24(1)°, respectively. In contrast, there is no disorder in the carboxyl groups of **18**, as evident from the C=O and C−OH bond distances [1.247(5) and 1.283(5) Å] and the location of H3 bonded to O3 in the difference electron density map. The carboxyl group is twisted out of the C1−C6 arene plane by 34.7(5)° (Figure 9). In comparison to **17** and **18**, the twist of the carboxy groups in pentafluorobenzoic acid and 2-fluorobenzoic acid[43,44] have values of 29.8° and 6.7°, respectively.

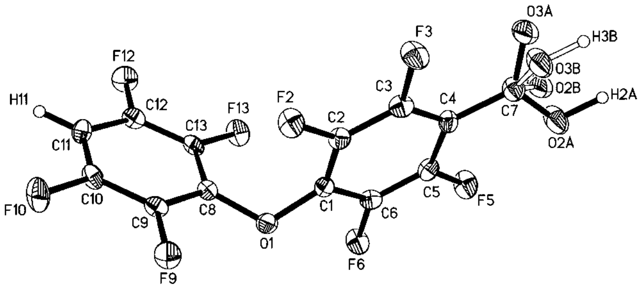


Figure 8. Molecular structure of $HC_6F_4OC_6F_4COOH$ (**17**), with thermal ellipsoids at 30% probability level.

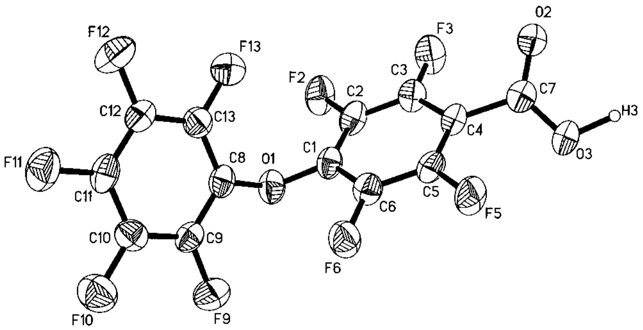


Figure 9. Molecular structure of $C_6F_5OC_6F_4COOH$ (**18**), with thermal ellipsoids at 50% probability level.

The most interesting feature of the crystal structures of **17** and **18** is the intermolecular H···O and H···F bonding. The acid **17** exists as a dimer, resulting from a very short intermolecular (involving part A of the carboxyl group) H2A···O3A^a contact at 1.61(11) Å ($a = 2 - x, 2 - y, 1 - z$) and angle O2A−H2A···O3A^a = 169°. The H3B···O2B^a contact from part B is at 1.68 Å.

Interestingly, the proton (H11) located at the position *para* to O1 forms dimeric contacts with F10 of a neighboring

---

(40) Selected bond lengths (Å) and angles (deg) (**17**): C7−O2A = 1.20(2); C7−O2B = 1.293(7); C7−O3A = 1.22(2); C7−O3B = 1.254(8); C4−C7 = 1.467(6); C3−F3 = 1.348(5); C1−O1 = 1.374(5); C8−O1−C1 = 118.0(3); O3A−C7−O2A = 121.0(12); O3B−C7−O2B = 123.1(5); O2A−C7−C4 = 22.0(9).

(41) Selected bond lengths (Å) and angles (deg) (**18**): C7−O2 = 1.247(5); C7−O3 = 1.283(5); C4−C7 = 1.496(6); C1−O1 = 1.390(5); C5−F5 = 1.346(4); O2−C7−O3 = 124.5(4); C4−C7−O2 = 119.0(4); C8−O1−C1 = 117.0(3).

(42) Benghiat, V.; Leiserowitz, L. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1778.

(43) Krausse, J.; Dunken, H. *Acta Crystallogr.* **1966**, *20*, 67.

(44) Ferguson, G.; Islam, K. M. S. *Acta Crystallogr.* **1966**, *21*, 1000.

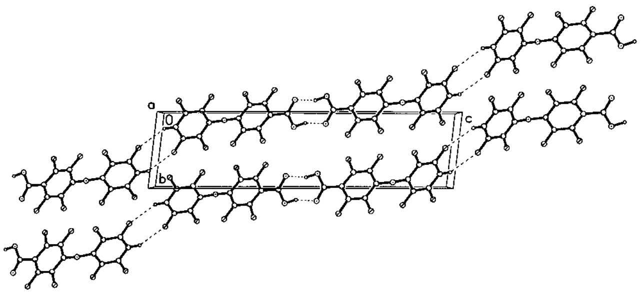


Figure 10. Crystal packing diagram of $HC_6F_4OC_6F_4COOH$ (**17**), along the *a*-axis showing dimer formation with intermolecular H···O and H···F interactions.

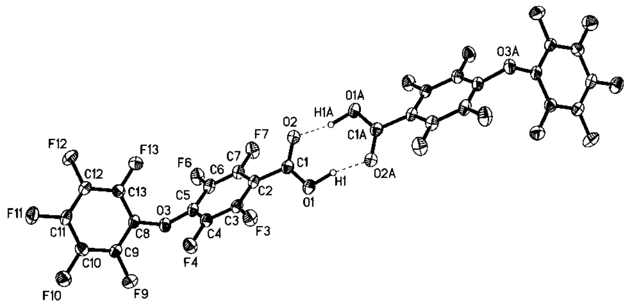


Figure 11. Dimeric structure of $C_6F_5OC_6F_4COOH$ (**18**).

molecule with a $H10\cdots F10^b$ distance of 2.54(4) Å ($b = 1 - x$, $3 - y$, $-z$), thereby resulting in a zig zag chain-type of polymeric structure (Figure 10). In the absence of a proton, such secondary dimer formation is not seen in **18** and only discrete carboxyl-bridged dimeric units can be seen in the crystal packing diagram (Figure 11). The $H3\cdots O2^c$ contact in this case is 1.52(8) Å ($c = 1 - x$, $1 - y$, $2 - z$) with $O3\text{-}H3\cdots O2^c$ angle at 172(6)°. The short distance of the intermolecular hydrogen–oxygen bonds in **17** and **18** is unique, as these values lie around 2.6 Å for fluorinated carboxylic acids (C_6F_5COOH;[42] CF_3COOH[45]). A much shorter value of 1.91(7) Å has been reported recently for (fluorosulfonyl)fluoroacetic acid.[46]

The molecular structure of **26**,[47] a fluorinated ether containing an amide functional group, is shown in Figure 12a. The $CONH_2$ group is twisted out of the C1–C6 arene plane by 55.1(5)°. Although there is no evidence for keto–enol tautomerism, the lone pair of electrons from the nitrogen atom is involved in the formation of a partial double bond between C7 and N1, resulting in shortening of the C7–N1 bond to 1.309(8) Å. Consequently, there is an elongation of the C=O bond (C7–O2) to 1.213 (7) Å. These distances are shorter than those found in $(CF_2)_2O(CF_2)_2$-$NCHFC(O)N(CH_3)_2$, where the $>C{=}O$ and $-C(O){-}N<$ values are 1.233(3) and 1.333(3) Å, respectively.[48] The packing diagram of **26** shows a strong intermolecular $O2\cdots H1A^d$ bond at 2.11 Å ($d = x$, $1 + y$, z), resulting in the stacking of the molecules in a parallel fashion (Figure 12b). In addition to this, H1B forms two intermolecular H···F contacts, $H1B\cdots F3^e$ and $H1B\cdots F5^f$ ($e = 2 - x$, $1 - y$, $-z$; $f = 1 - x$, $-y$, $-z$) at 2.569 and 2.529 Å, respectively.

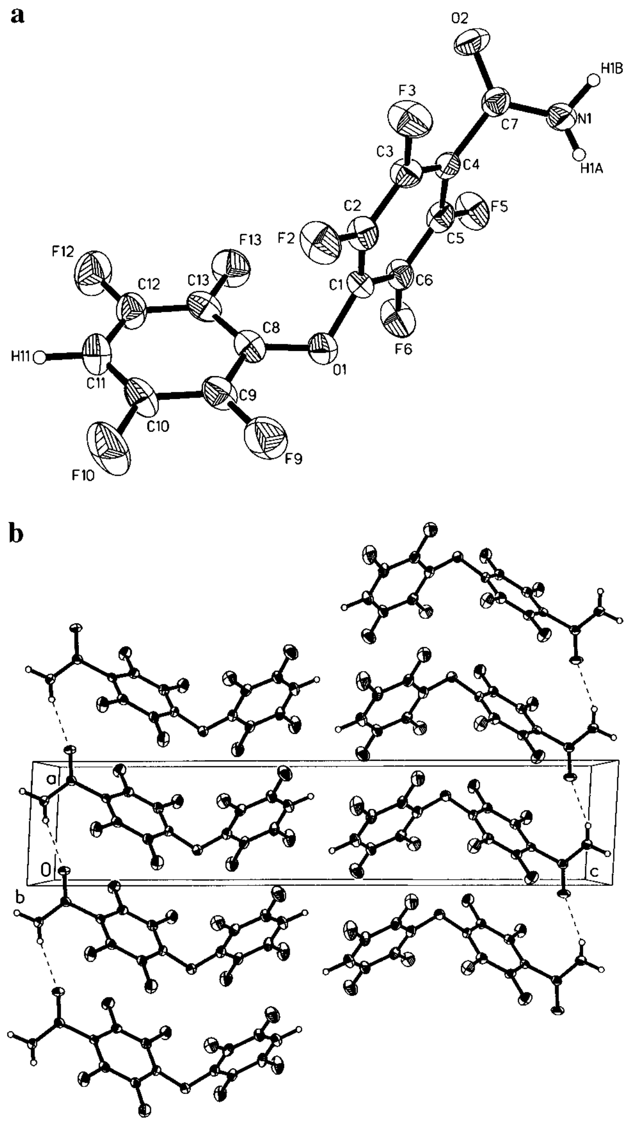


Figure 12. (a) Molecular structure of $HC_6F_4OC_6F_4CONH_2$ (**26**), with thermal ellipsoids at 40% probability level. (b) Crystal packing diagram of $HC_6F_4OC_6F_4CONH_2$ (**26**), along the *b*-axis showing parallel stacking of molecules with intermolecular H···O bonding.

Table 2. Torsion angles C–O–C–C (φ_1 and φ_2) and Mean Plane Least-Square Analysis (MPLA) for Fluorinated Diphenyl ethers $Ar_F{-}O{-}Ar_F$

compound	Tors C–O–C–C		MPLA (deg)
	φ_1 (deg)	φ_2 (deg)	for ($Ar_F{-}O{-}Ar_F$)
3	58.3(4)^a	61.9(4)^b	83.3(1)
4	59.1(3)^a	62.7(3)^b	82.4(1)
17	53.8(5)^a	58.9(5)^c	86.5(1)
18	66.6(5)^d	63.4(5)^c	74.4(1)
23	57.7(2)^e	57.7(2)^f	85.0(1)
26	53.9(8)^a	57.4(8)^c	87.5(2)

^{a} C8–O1–C1–C2. ^{b} C1–O1–C8–C9. ^{c} C1–O1–C8–C13. ^{d} C8–O1–C1–C6. ^{e} C′1–O1–C1–C6. ^{f} C1–O1–C′1–C′6.

Finally, an analysis of the torsion angles C–C–O–C and least-squares mean planes between $Ar_F{-}O{-}Ar_F$ rings is carried out for 1,4-disubstituted benzenes (diphenyl ethers). The results are listed in Table 2. The relative twist of the phenyl rings lies in the range 74.4(1)–87.5(2)°.

Experimental Section

Materials. The solvents THF and diethyl ether are distilled over sodium prior to use. Cesium fluoride is dried and maintained at 300 °C. All other chemicals are used as received (Aldrich, Fluorochem, PCR).

---

(45) Nahringbauer, I.; Lundgren, J. O.; Andersen, E. K. *Acta Crystallogr.* **1979**, *B35*, 508.

(46) Braden, D. A.; Gard, G. L.; Weakley, T. J. R. *Inorg. Chem.* **1996**, *35*, 1912.

(47) Selected bond lengths (Å) and angles (deg) (**26**): C7–O2 = 1.213(7); C7–N1 = 1.309(8); C4–C7 = 1.518(8); C3–F3 = 1.342(6); C1–O1 = 1.387(7); O2–C7–N1 = 124.7(6); C4–C7–N1 = 115.6(6); C4–C7–O2 = 119.7(5); C8–O1–C1 = 118.4(5).

(48) Vij, A.; Kirchmeier, R. L.; Shreeve, J. M. Unpublished results.

General Considerations. A conventional vacuum system, consisting of a Pyrex glass vacuum line fitted with Teflon needle stopcocks and equipped with a Heise Bourdon tube and Televac thermocouple gauges, is used to handle gases and volatile liquids. Standard pressure−volume−temperature techniques are used to quantitate gaseous starting materials. Infrared spectra are recorded on a Perkin-Elmer 1710 FT-IR spectrometer between KBr plates as neat liquids or solids as Nujol mulls. ^{1}H and ^{19}F NMR spectra are obtained on a Bruker AC200 or AC300 FT-NMR instrument using $CDCl_3$ as the solvent except where otherwise indicated. Chemical shifts are reported with respect to $(CH_3)_4Si$ or $CFCl_3$. Mass spectra are obtained with a Varian VG 7070 HS mass spectrometer by using electron impact (EI) or chemical ionization (CI) techniques. Elemental analyses are performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany. All reactions involving siloxanes and lithiations are carried out in an atmosphere of dry nitrogen.

X-ray Crystal Structure Analysis. The X-ray diffraction data for compounds **3**, **4**, **14**−**18**, **23**, and **26** are collected with SMART[49] software by using a Siemens three-circle platform. A monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) from a fine-focus tube is employed for data collection. The χ-axis on this platform is fixed at 54.74°, and the diffractometer is equipped with a CCD detector maintained near −54 °C. Data collection parameters are listed in Table 3. The cell constants are initially determined by the least-squares refinement of 60 frames collected at 10 s intervals by using the SMART software and finally by the least-squares refinement of all of the observed reflections by the SAINT[50] software. A complete hemisphere of data was scanned on ω (0.3°) with a run time of 10 s or 30 s per frame at the detector resolution of 512 × 512 pixels. A total of 1271 frames are collected in three sets, and a final set of 50 frames, identical to the first 50 frames, are also collected to determine crystal decay. The frames are then processed on a SGI-Indy workstation using the SAINT software to give the *h,k,l* file corrected for Lp/decay. The structures are solved by the direct method using the SHELX-86[51] program and refined by least squares method on F^2, SHELXL-93,[52] incorporated in SHELXTL-PC V 5.03.[53] All non-hydrogen atoms are refined anisotropically. The hydrogen atoms are located from the difference electron density maps and are included in the refinement process in an isotropic manner. The crystals show almost no decomposition during data collection.

Preparation of Siloxanes $4\text{-}HC_6F_4OSiMe_3$ (1) and $C_6F_5OSiMe_3$ (2). A mixture that consists of 0.3 mol of phenol ($4\text{-}HC_6F_4OH$ or C_6F_5OH) and 0.7 mol of hexamethyldisilazane in a round-bottomed flask equipped with a reflux condenser is stirred for 4 h at 25 °C (exothermic reaction with ammonia evolution) and then heated to and maintained at 100−120 °C for **2**. The excess hexamethyldisilazane is removed by distillation, and the siloxane was distilled under reduced pressure to give a colorless hydrolyzable liquid **1** in 88% yield (bp 35 °C/1 Torr) and **2** in 89% yield (bp 28 °C/0.6 Torr). The infrared, ^{1}H NMR,[9] and ^{19}F NMR[10] spectral data of **2** agree with the data obtained from the literature.

Spectral data for $4\text{-}HC_6F_4OSiMe_3$ (1): IR (liquid film/KBr) 3092 w (ν_{CH}), 2966 m, 2910 w, 1645 s, 1516 s, 1505 s, 1417 m, 1259 s, 1220 w, 1173 s, 1111 s, 976 m, 944 s, 859 s, 765 m, 728 w, 710 m, 627 w, 578 m cm^{-1}; ^{19}F NMR δ −141.2 (3-F, m, 2F), −158.4 (2-F, m, 2F); ^{1}H NMR δ 6.64 (4-H, tt, 1H, $^3J_{H-F} = 10.3$ Hz, $^4J_{H-F} = 7.0$ Hz), 0.29 ($SiMe_3$, t, 9H, $^6J_{H-F} = 0.8$ Hz); MS (EI) [*m/e* (species, intensity)] 238 (M^+, 27), 223 ($M^+ - CH_3$, 31), 145 ($C_6F_3O^+$, 14), 137 ($C_5F_4H^+$, 2), 127 ($C_6F_2HO^+$, 29), 118 ($C_5F_3H^+$, 6), 99 ($C_5F_2H^+$, 14), 81 ($MeSiF_2{}^+$, 12), 77 (Me_2SiF^+, 100), 73 ($SiMe_3{}^+$, 59). Elemental analyses data are given in the literature.[54]

Preparation of $4\text{-}(4'\text{-}HC_6F_4O)C_6F_4CF_3$ (3) and $4\text{-}(C_6F_5O)C_6F_4CF_3$ (4). Siloxane (0.15 mol, **1** or **2**) and 0.21 mol of octafluorotoluene in 80 mL of THF that contains catalytic amounts of CsF are heated at 110 °C for 13 days (monitored by ^{19}F NMR). After removal of all volatile materials under reduced pressure, the crude product is sublimed at 25 °C/0.01 Torr. Colorless crystals of **3** or **4** suitable for X-ray analysis are obtained in 91% (mp 39−41 °C) or 87% (mp 56−58 °C) yield, respectively.

Spectral data for $4\text{-}(4'\text{-}HC_6F_4O)C_6F_4CF_3$ (3): IR (Nujol/KBr) 3091 w (ν_{CH}), 1661 m, 1640 m, 1528 s, 1505 s, 1487 s, 1343 s, 1267 w, 1225 s, 1191 s, 1178 s, 1158 s, 1115 m, 1022 m, 1000 s, 952 s, 875 m, 840 m, 798 w, 718 s, 694 w, 681 w, 601 w, 577 w cm^{-1}; ^{19}F NMR δ −56.1 (CF_3, t, 3F, $^4J_{F-F} = 21.6$ Hz), −137.8 (3′-F, m, 2F), −139.8 (2-F, m, 2F), −154.8 (3-F, m, 2F), −156.1 (2′-F, m, 2F); ^{1}H NMR δ 7.00 (4′-H, tt, 1H, $^3J_{H-F} = 9.9$ Hz, $^4J_{H-F} = 7.1$ Hz); MS (EI) [*m/e* (species, intensity)] 382 (M^+, 100), 363 ($M^+ - F$, 39), 335 ($M^+ - F - CO$, 11), 332 ($M^+ - CF_2$, 4), 313 ($M^+ - CF_3$, 23), 304 ($M^+ - CF_2 - CO$, 14), 285 ($M^+ - CF_3 - CO$, 17), 217 ($M^+ - C_6F_4HO$, 8), 198 ($C_7F_6{}^+$, 8), 165 ($C_6F_4HO^+$, 10), 155 ($C_5F_5{}^+$, 14), 149 ($C_6F_4H^+$, 31), 137 ($C_5F_4H^+$, 55), 117 ($C_5F_3{}^+$, 32), 99 ($C_5F_2H^+$, 66), 93 ($C_3F_3{}^+$, 19), 69 ($CF_3{}^+$, 35). Anal. Calcd for $C_{13}HF_{11}O$: C, 40.86; H, 0.26; F, 54.69. Found: C, 40.70; H, 0.32; F, 54.5.

Spectral data for $4\text{-}(C_6F_5O)C_6F_4CF_3$ (4): IR (Nujol/KBr) 1661 m, 1651 m, 1520 s, 1343 m, 1225 m, 1191 m, 1159 m, 1079 m, 1000 m, 977 m, 876 m, 803 w, 718 m cm^{-1}; ^{19}F NMR δ −56.2 (CF_3, t, 3F, $^4J_{F-F} = 21.2$ Hz), −139.6 (2-F, m, 2F), −154.9 (3-F, m, 2F), −155.8 (2′-F, m, 2F), −158.0 (4′-F, t, 1F, $^3J_{F-F} = 21.9$ Hz), −161.1 (3′-F, m, 2F); MS (EI) [*m/e* (species, intensity)] 400 (M^+, 100), 381 ($M^+ - F$, 33), 372 ($M^+ - CO$, 2), 353 ($M^+ - F - CO$, 7), 350 ($M^+ - CF_2$, 3), 331 ($M^+ - CF_3$, 12), 322 ($M^+ - CF_2 - CO$, 9), 303 ($M^+ - CF_3 - CO$, 13), 217 ($M^+ - C_6F_5O$, 10), 198 ($C_7F_6{}^+$, 8), 183 ($C_6F_5O^+$, 50), 167 ($C_6F_5{}^+$, 13), 155 ($C_5F_5{}^+$, 55), 117 ($C_5F_3{}^+$, 47), 105 ($C_4F_3{}^+$, 5), 93 ($C_3F_3{}^+$, 17), 69 ($CF_3{}^+$, 10). Elemental analyses data are given in the literature.[11,12]

Preparation of $4\text{-}(4'\text{-}HC_6F_4O)C_6F_4CN$ (5) and $4\text{-}(C_6F_5O)C_6F_4CN$ (6). A mixture of 20 mmol of siloxane (**1** or **2**) and 25 mmol of pentafluorobenzonitrile in 10 mL of THF that contains catalytic amounts of CsF is heated at 40 °C for 5 days (monitored by ^{19}F NMR). After removal of all volatile materials under reduced pressure, the crude product is sublimed at 40 °C/0.01 Torr. Colorless crystals of **5** or **6** are obtained in 65% (mp 45−48 °C) or 71% (mp 54−56 °C) yield, respectively. Sublimation of the residue at 75 °C/0.01 Torr or 50 °C/0.01 Torr gives the disubstituted benzonitrile $2,4\text{-}(4'\text{-}HC_6F_4O)_2C_6F_3CN$ (**7**, mp 108−110 °C) or $2,4\text{-}(C_6F_5O)_2C_6F_3CN$ (**8**, mp 69−70 °C) in trace amounts.

Spectral Data for $4\text{-}(4'\text{-}HC_6F_4O)C_6F_4CN$ (5): IR (Nujol/KBr) 3090 m (ν_{CH}), 2252 m ($\nu_{C\equiv N}$), 1640 m, 1529 s, 1505 s, 1495 s, 1403 m, 1320 m, 1269 m, 1240 m, 1220 m, 1176 s, 1145 s, 1063 m, 1039 m, 1003 s, 954 s, 842 s, 801 w, 716 m, 692 w, 667 w, 633 w cm^{-1}; ^{19}F NMR δ −131.5 (2-F, m, 2F), −137.5 (3′-F, m, 2F), −153.5 (3-F, m, 2F), −156.0 (2′-F, m, 2F); ^{1}H NMR δ 7.02 (4′-H, tt, 1H, $^3J_{H-F} = 9.8$ Hz, $^4J_{H-F} = 7.1$ Hz); MS (EI) [*m/e* (species, intensity)] 339 (M^+, 100), 320 ($M^+ - F$, 16), 292 ($M^+ - F - CO$, 15), 289 ($M^+ - CF_2$, 4), 261 ($M^+ - CF_2 - CO$, 17), 174 ($M^+ - C_6F_4HO$, 2), 165 ($C_6F_4HO^+$, 7), 149 ($C_6F_4H^+$, 36), 137 ($C_5F_4H^+$, 27), 124 ($C_4F_4{}^+$, 12), 99 ($C_5F_2H^+$, 37), 93 ($C_3F_3{}^+$, 10). Anal. Calcd for $C_{13}HF_8NO$: C, 46.04; H, 0.30; F, 44.82. Found: C, 45.97; H, 0.52; F, 44.8.

Spectral Data for $4\text{-}(C_6F_5O)C_6F_4CN$ (6): IR (Nujol/KBr) 2253 w ($\nu_{C\equiv N}$), 1657 m, 1647 m, 1520 s, 1510 s, 1495 s, 1430 m, 1321 m, 1162 m, 1109 m, 1023 m, 995 s, 926 m cm^{-1}; ^{19}F NMR δ −131.2 (2-F, m, 2F), −153.5 (3-F, m, 2F), −155.6 (2′-F, m, 2F), −157.3 (4′-F, t, 1F, $^3J_{F-F} = 22.0$ Hz), −160.7 (3′-F, m, 2F); MS (EI) [*m/e* (species, intensity)] 357 (M^+, 100), 338 ($M^+ - F$, 6), 329 ($M^+ - CO$, 2), 310 ($M^+ - F - CO$, 11), 279 ($M^+ - CF_2 - CO$, 12), 183 ($C_6F_5O^+$, 33), 174 ($M^+ - C_6F_5O$, 3), 167 ($C_6F_5{}^+$, 14), 155 ($C_5F_5{}^+$, 40), 136 ($C_5F_4{}^+$, 3), 124 ($C_4F_4{}^+$, 14), 117 ($C_5F_3{}^+$, 33), 93 ($C_3F_3{}^+$, 16). Elemental analyses data are given in the literature.[12,13]

Spectral Data for $2,4\text{-}(4'\text{-}HC_6F_4O)_2C_6F_3CN$ (7): IR (Nujol/KBr) 3088 m (ν_{CH}), 2251 m ($\nu_{C\equiv N}$), 1635 m, 1525 s, 1504 s, 1480 s, 1421

---

(49) *SMARTV 4.043 Software for the CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.

(50) *SAINTV 4.035 Software for the CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.

(51) Sheldrick, G. M. *SHELXS-86, Program for the Solution of Crystal Structure*; University of Göttingen: Germany, 1986.

(52) Sheldrick, G. M. *SHELXL-93, Program for the Refinement of Crystal Structure*; University of Göttingen: Germany, 1993.

(53) *SHELXTL 5.03 (PC-Version), Program Library for Structure Solution and Molecular Graphics*; Siemens Analytical Instruments Division: Madison, WI, 1995.

(54) Steiner, E.; Beyeler, H.; Riediker, M.; Desobry, V.; Dietliker, K.; Hüsler, R. *Eur. Pat. Appl. EP 401,165*, 1990.

Table 3. X-ray Crystallographic Parameters for **3**, **4**, **14**, **15**, **16**, **17**, **18**, **23**, and **26**

	3	**4**	**14**	**15**
	Crystal data			
empirical formula	$C_{13}HF_{11}O$	$C_{13}F_{12}O$	$C_{25}F_{17}NO_3$	$C_{24}H_3F_{14}NO_5$
formula weight	382.14	400.13	685.26	651.27
color	colorless	colorless	colorless	pale yellow
crystal size (mm)	0.25 × 0.15 × 0.10	0.45 × 0.35 × 0.30	0.50 × 0.35 × 0.25	0.50 x 0.35 × 0.20
crystal system; space group	monoclinic; $P2_1/c$	monoclinic; $P2_1/c$	monoclinic; $P2_1/c$	monoclinic; $P2_1/c$
unit cell dimensions: a (Å)	12.805(3)	12.9044(2)	12.3475(2)	11.7877(2)
b (Å)	11.583(2)	11.6463(1)	19.7537(1)	19.5406(2)
c (Å)	9.107(2)	8.9883(1)	9.7555(1)	10.1380(1)
β (deg)	108.74(2)	108.788(1)	95.414(1)	96.727(1)
volume (Å^3)	1279.2(5)	1278.86(3)	2368.84(5)	2319.10(5)
Z	4	4	4	4
ρ_{calc} (Mg/m^3)	1.984	2.078	1.921	1.865
$F(000)$	744	776	1336	1280
abs coeff (mm^{-1})	0.234	0.250	0.216	0.204
	Data Collection			
temperature (K)	163(2)	173(2)	193(2)	193(2)
θ_{max} (deg)	24.00	23.24	26.97	27.01
index ranges	$-16 \leq h \leq 8$ $-14 \leq k \leq 13$ $-9 \leq l \leq 11$	$-10 \leq h \leq 14$ $-8 \leq k \leq 12$ $-9 \leq l \leq 9$	$-15 \leq h \leq 9$ $-25 \leq k \leq 24$ $-6 \leq l \leq 7$	$-14 \leq h \leq 13$ $-23 \leq k \leq 24$ $-12 \leq l \leq 10$
no. of reflcns collected	5416	4992	9279	11 844
no. of unique data	1980 ($R_{int} = 0.0322$)	1824 ($R_{int} = 0.024$)	3397 ($R_{int} = 0.0262$)	4475($R_{int} = 0.0245$)
no. of data with $I > 2\sigma(I)$	1633	1783	2988	4047
T (max/min) (ψ-scan)	0.976/0.864	0.970/0.882	0.996/0.924	0.993/0.918
extinction coeff	0.012(1)	0.0067(7)		
	Solution and Refinement on F^2			
parameters refined	230	236	416	409
final indices (2σ data), $R1$(w$R2$)	0.0524 (0.1250)	0.0333 (0.0855)	0.0426 (0.0991)	0.0441 (0.1058)
all data, $R1$ (w$R2$)	0.0667 (0.1341)	0.0344 (0.0863)	0.0497 (0.1048)	0.0494 (0.1099)
goodness-of-fit, S (F^2)	1.049	1.135	1.058	1.065
largest difference peak (eÅ^{-3})	0.685	0.344	0.425	0.272
largest difference hole (eÅ^{-3})	-0.348	-0.216	-0.376	-0.322

	16	**17**	**18**	**23**	**26**
			Crystal data		
empirical formula	$C_{24}F_{17}NO_5$	$C_{13}H_2F_8O_3$	$C_{13}HF_9O_3$	$C_{12}H_2F_8O$	$C_{13}H_3F_8NO_2$
formula weight	705.25	358.15	376.14	314.14	357.16
color	pale yellow	colorless	colorless	colorless	colorless
crystal size (mm)	0.20 × 0.15 × 0.15	0.25 × 0.10 × 0.05	0.50 × 0.40 × 0.10	0.50 x 0.35 × 0.15	0.20 × 0.15 × 0.005
crystal system; space group	monoclinic; $P2_1/c$	triclinic; $P1$	triclinic; $P1$	monoclinic; $P2_1/c$	triclinic; $P\bar{1}$
unit cell dimensions: a (Å)	12.3186(6)	4.5371(4)	6.118(1)	6.0689(7)	4.7586(8)
b (Å)	17.7264(8)	5.9139(6)	9.808(1)	4.4409(5)	5.8954(10)
c (Å)	10.7355(5)	23.234(2)	11.110(1)	19.613(2)	22.252(4)
α (deg)		96.751(2)	79.559(8)		88.956(3)
β (deg)	92.37	91.125(2)	75.970(9)	90.884(2)	87.039(2)
γ (deg)		90.232(2)	80.371(9)		89.144(3)
volume (Å^3)	2342.2(2)	618.97(10)	630.8(2)	528.54(11)	623.3(2)
Z	4	2	2	2	2
ρ_{calc} (Mg/m^3)	2.000	1.922	1.980	1.974	1.903
$F(000)$	1376	352	368	308	352
abs coeff (mm^{-1})	0.228	0.213	0.225	0.221	0.208
			Data Collection		
temperature (K)	193(2)	193(2)	193(2)	173(2)	293(2)
θ_{max} (deg)	24.99	23.50	22.50	23.34	22.50
index ranges	$-15 \leq h \leq 15$ $-22 \leq k \leq 15$ $-13 \leq l \leq 12$	$-5 \leq h \leq 5$ $-7 \leq k \leq 5$ $-23 \leq l \leq 28$	$-7 \leq h \leq 7$ $-11 \leq k \leq 5$ $-13 \leq l \leq 12$	$-6 \leq h \leq 3$ $-4 \leq k \leq 4$ $-21 \leq l \leq 21$	$-5 \leq h \leq 5$ $-6 \leq k \leq 3$ $-24 \leq l \leq 24$
no. of reflcns collected	10 629	2612	2387	1967	2209
no. of unique data	4072 ($R_{int} = 0.036$)	1768 ($R_{int} = 0.0385$)	1600 ($R_{int} = 0.0562$)	761 ($R_{int} = 0.0403$)	1525($R_{int} = 0.0546$)
no. of data with $I > 2\sigma(I)$	3085	1523	1385	745	1186
T (max/min) (ψ-scan)	0.983/0.884	0.989/0.555	0.998/0.714	0.998/0.791	N/A
extinction coeff	0.0066(9)	0.013(6)	0.003(7)	0.038(9)	0.016(4)
			Solution and Refinement on F^2		
parameters refined	425	236	231	101	230
final indices (2σ data), $R1$(w$R2$)	0.0571(0.1229)	0.0653 (0.1615)	0.0645 (0.1732)	0.0379 (0.1029)	0.0714 (0.1370)
all data, $R1$ (w$R2$)	0.0812(0.1377)	0.0767 (0.1765)	0.0713 (0.1835)	0.0387 (0.1036)	0.0955 (0.1501)
goodness-of-fit, S (F^2)	1.09	1.155	1.065	1.235	1.211
largest difference peak (e**Å**$^{-3}$)	0.453	0.317	0.391	0.179	0.221
largest difference hole (e**Å**$^{-3}$)	−0.333	−0.378	−0.343	−0.191	−0.311

m, 1404 m, 1312 w, 1264 m, 1245 m, 1178 s, 1145 s, 1062 m, 1051 m, 1040 m, 977 m, 954 s, 844 s, 808 w, 770 w, 716 m, 688 w, 667 w, 650 w, 598 w cm^{-1}; ^{19}F NMR δ −130.9 (6-F, m, 1F), −137.6 (3′-F, m, 4F), −148.6 (3-F, m, 1F), −152.2 (5-F, m, 1F), −155.7 (2′(2)-F, m, 2F), −156.2 (2′(4)-F, m, 2F); ^{1}H NMR δ 6.99 (4′-H, tt, 2H, $^3J_{\mathrm{H-F}} = 9.8$ Hz, $^4J_{\mathrm{H-F}} = 7.0$ Hz); MS (EI) [*m/e* (species, intensity)] 485 (M^+, 100), 466 ($M^+ - F$, 4), 336 ($M^+ - C_6F_4H$, 9), 320 ($M^+ - C_6F_4HO$, 13), 308 ($M^+ - C_6F_4H - CO$, 8), 292 ($M^+ - C_6F_4HO - CO$, 20), 270 ($M^+ - C_6F_4HO - CF_2$, 6), 165 ($C_6F_4HO^+$, 12), 155 ($M^+ - 2C_6F_4HO$, 13), 149 ($C_6F_4H^+$, 70), 137 ($C_5F_4H^+$, 44), 124 ($C_4F_4^+$, 15), 117 ($C_5F_3^+$, 7), 99 ($C_5F_2H^+$, 54), 93 ($C_3F_3^+$, 22). Anal. Calcd for $C_{19}H_2F_{11}NO_2$: C, 47.03; H, 0.42; F, 43.07. Found: C, 47.01; H, 0.48; F, 43.3.

Spectral data for 2,4-$(C_6F_5O)_2C_6F_3CN$ (8): IR (Nujol/KBr) 2243 m ($\nu_{\mathrm{C\equiv N}}$), 1639 m, 1520 s, 1495 s, 1420 m, 1317 m, 1269 w, 1199 m, 1177 m, 1167 m, 1142 m, 1105 m, 1038 s, 1015 s, 995 s, 926 m, 823 w, 795 w, 657 w cm^{-1}; ^{19}F NMR δ −130.3 (6-F, m, 1F), −149.1 (3-F, m, 1F), −152.1 (5-F, d, 1F, $^3J_{\mathrm{F-F}} = 21.0$ Hz), −155.4/−155.8 (2′-F, m, 4F), −157.5/−157.6 (4′-F, t, 2F, $^3J_{\mathrm{F-F}} = 21.9/21.6$ Hz), −160.7 (3′-F, m, 4F); MS (EI) [*m/e* (species, intensity)] 521 (M^+, 100), 502 ($M^+ - F$, 2), 354 ($M^+ - C_6F_5$, 3), 338 ($M^+ - C_6F_5O$, 6), 310 ($M^+ - C_6F_5O - CO$, 17), 288 ($M^+ - C_6F_5O - CF_2$, 4), 183 ($C_6F_5O^+$, 78), 167 ($C_6F_5^+$, 23), 155 ($C_5F_5^+$, 83), 124 ($C_4F_4^+$, 20), 117 ($C_5F_3^+$, 46), 105 ($C_4F_3^+$, 18), 93 ($C_3F_3^+$, 33). Elemental analyses data are given in the literature.[13]

Preparation of 4-(4′-$HC_6F_4O)C_6F_4NO_2$ (9) and 4-$(C_6F_5O)C_6F_4NO_2$ (10). Siloxane (15 mmol, **1** or **2**) and 25 mmol of pentafluoronitrobenzene in 10 mL of THF that contains catalytic amounts of CsF are stirred at 25 °C for 7 h (monitored by ^{19}F NMR). After removal of all volatile materials under reduced pressure, the crude product is sublimed at 25 °C under high vacuum. The more volatile *ortho*-isomer condenses as a liquid at 25 °C. Slow sublimation at 40 °C/0.01 Torr produces the pure *para*-isomer as pale yellow crystals of **9** in 52% (mp 57−59 °C) or of **10** in 47% (mp 52−54 °C) yield. Sublimation of the residue at 50 °C/0.01 Torr gives the disubstituted nitrobenzene 2,4-(4′-$HC_6F_4O)_2C_6F_3NO_2$ (**11**, mp 96−98 °C) or 2,4-$(C_6F_5O)_2C_6F_3NO_2$ (**12**) as a yellow viscous liquid in trace amounts.

Spectral data for 4-(4′-$HC_6F_4O)C_6F_4NO_2$ (9): IR (Nujol/KBr) 3095 m (ν_{CH}), 1636 m, 1558 s ($\nu_{\mathrm{asym.NO_2}}$), 1524 s, 1505 s, 1407 w, 1364 m ($\nu_{\mathrm{sym.NO_2}}$), 1329 w, 1275 m, 1240 w, 1176 m, 1147 m, 1134 m, 1057 m, 1029 m, 1012 s, 952 s, 927 m, 842 m, 821 m, 772 m, 757 w, 729 w, 717 m, 705 w, 690 w, 638 w, 572 cm^{-1}; ^{19}F NMR δ −137.5 (3′-F, m, 2F), −145.5 (2-F, m, 2F), −153.3 (3-F, m, 2F), −156.0 (2′-F, m, 2F); ^{1}H NMR δ 7.02 (4′-H, tt, 1H, $^3J_{\mathrm{H-F}} = 9.7$ Hz, $^4J_{\mathrm{H-F}} = 7.2$ Hz); MS (EI) [*m/e* (species, intensity)] 359 (M^+, 100), 343 ($M^+ - O$, 6), 329 ($M^+ - NO$, 22), 313 ($M^+ - NO_2$, 9), 294 ($M^+ - NO_2 - F$, 16), 285 ($M^+ - NO_2 - CO$, 25), 235 ($M^+ - NO_2 - CO - CF_2$, 19), 165 ($C_6F_4HO^+$, 20), 149 ($C_6F_4H^+$, 96), 148 ($C_6F_4^+$, 42), 137 ($C_5F_4H^+$, 44), 117 ($C_5F_3^+$, 40), 99 ($C_5F_2H^+$, 59). Anal. Calcd for $C_{12}HF_8NO_3$: C, 40.13; H, 0.28. Found: C, 40.01; H, 0.28.

Spectral data for 4-$(C_6F_5O)C_6F_4NO_2$ (10): IR (Nujol/KBr) 1642 m, 1559 s ($\nu_{\mathrm{asym.NO_2}}$), 1520 s br, 1362 s ($\nu_{\mathrm{sym.NO_2}}$), 1318 m, 1293 m, 1273 m, 1162 m, 1095 m, 1069 m, 1031 m, 1019 m, 1000 s, 928 m, 820 w, 767 m, 750 m, 731 w, 653 w, 634 w, 612 w, 581 w cm^{-1}; ^{19}F NMR δ −145.3 (2-F, m, 2F), −153.4 (3-F, m, 2F), −155.6 (2′-F, m, 2F), −157.3 (4′-F, t, 1F, $^3J_{\mathrm{F-F}} = 21.9$ Hz), −160.7 (3′-F, m, 2F); MS (EI) [*m/e* (species, intensity)] 377 (M^+, 100), 361 ($M^+ - O$, 6), 358 ($M^+ - F$, 1), 347 ($M^+ - NO$, 16), 331 ($M^+ - NO_2$, 7), 312 ($M^+ - NO_2 - F$, 8), 303 ($M^+ - NO_2 - CO$, 23), 253 ($M^+ - NO_2 - CO - CF_2$, 18), 241 ($M^+ - C_5F_4$, 8), 234 ($M^+ - NO_2 - CO - CF_2 - F$, 9), 183 ($C_6F_5O^+$, 73), 167 ($C_6F_5^+$, 67), 155 ($C_5F_5^+$, 43), 148 ($C_6F_4^+$, 54), 136 ($C_5F_4^+$, 10), 117 ($C_5F_3^+$, 13), 93 ($C_3F_3^+$, 2). Elemental analyses data are given in the literature.[14]

Spectral data for 2,4-(4′-$HC_6F_4O)_2C_6F_3NO_2$ (11): IR (Nujol/KBr) 3104 m (ν_{CH}), 1633 m, 1553 s ($\nu_{\mathrm{asym.NO_2}}$), 1526 s, 1495 s, 1406 w, 1355 m ($\nu_{\mathrm{sym.NO_2}}$), 1285 w, 1266 m, 1243 w, 1180 m, 1157 m, 1121 m, 1068 m, 1024 m, 984 m, 950 m, 928 m, 846 m, 835 m, 771 m, 754 w, 731 w, 717 m, 687 w, 666 w, 646 w cm^{-1}; ^{19}F NMR δ −137.6 (3′-F, m, 4F), −145.8 (6-F, m, 1F), −148.0 (3-F, m, 1F), −151.1 (5-F, dt, 1F, $^3J_{\mathrm{F-F}} = 22.2$ Hz, $^6J_{\mathrm{F-F}} = 2.8$ Hz), −156.2 (2′(2)-F, m, 2F), −157.0 (2′(4)-F, m, 2F); ^{1}H NMR δ 6.99 (4′-H, tt, 1H, $^3J_{\mathrm{H-F}} = 9.7$ Hz, $^4J_{\mathrm{H-F}} = 7.1$ Hz), 6.95 (4′-H, tt, 1H, $^3J_{\mathrm{H-F}} = 9.9$ Hz, $^4J_{\mathrm{H-F}} = 7.1$ Hz); MS (EI) [*m/e* (species, intensity)] 505 (M^+, 22), 489 ($M^+ - O$, 2), 475 ($M^+ - NO$, 6), 458 ($M^+ - H - NO_2$, 13), 440 ($M^+ - NO_2 - F$, 8), 340 ($M^+ - C_6F_4HO$, 88), 312 ($M^+ - C_6F_4HO - CO$, 37), 294 ($M^+ - C_6F_4HO - NO_2$, 32), 247 ($M^+ - C_6F_4HO - CO - NO_2 - F$, 54), 165 ($C_6F_4HO^+$, 73), 149 ($C_6F_4H^+$, 100), 137 ($C_5F_4H^+$, 94), 117 ($C_5F_3^+$, 64), 99 ($C_5F_2H^+$, 95). Anal. Calcd for $C_{18}H_2F_{11}NO_4$: C, 42.79; H, 0.40. Found: C, 42.77; H, 0.43.

Spectral Data for 2,4-$(C_6F_5O)_2C_6F_3NO_2$ (12): IR (liquid film/KBr) 1631 m, 1559 s ($\nu_{\mathrm{sym.NO_2}}$), 1521 s br, 1414 m, 1360 s ($\nu_{\mathrm{sym.NO_2}}$), 1319 m, 1289 m, 1273 m, 1169 m, 1130 m, 1093 s, 1033 s, 1000 s, 962 m, 928 m, 833 w, 789 w, 768 s, 652 w, 605 w cm^{-1}; ^{19}F NMR δ −145.5 (6-F, m, 1F), −148.6 (3-F, m, 1F), −151.1 (5-F, dt, 1F, $^3J_{\mathrm{F-F}} = 22.0$ Hz, $^6J_{\mathrm{F-F}} = 3.4$ Hz), −155.9/-156.7 (2′-F, m, 4F), −157.7/−158.7 (4′-F, tt, 2F, $^3J_{\mathrm{F-F}} = 21.9/21.9$ Hz, $^4J_{\mathrm{F-F}} = 0.9/1.3$ Hz), −160.9 (3′-F, m, 4F); MS (EI) [*m/e* (species, intensity)] 541 (M^+, 1), 525 ($M^+ - O$, 1), 494 ($M^+ - CO - F$, 5), 476 ($M^+ - NO_2 - F$, 2), 358 ($M^+ - C_6F_5O$, 41), 330 ($M^+ - C_6F_5O - CO$, 13), 312 ($M^+ - C_6F_5O - NO_2$, 6), 272 ($M^+ - C_6F_5 - 2CO - NO_2$, 24), 265 ($M^+ - C_6F_5O - CO - NO_2 - F$, 23), 183 ($C_6F_5O^+$, 100), 167 ($C_6F_5^+$, 24), 155 ($C_5F_5^+$, 48), 117 ($C_5F_3^+$, 54), 93 ($C_3F_3^+$, 27). Anal. Calcd for $C_{18}F_{13}NO_4$: C, 39.95; F, 45.64. Found: C, 38.86; F, 44.2.

Preparation of 2,4,6-(4′-$HC_6F_4O)_3C_6F_2CN$ (13) and 2,4,6-$(C_6F_5O)_3C_6F_2CN$ (14). Siloxane (21 mmol, **1** or **2**) and 6 mmol of pentafluorobenzonitrile in 10 mL of THF that contains catalytic amounts of CsF are heated at 110 °C for 7 days (monitored by ^{19}F NMR). After removal of all volatile materials under high vacuum, the residue is extracted with CH_2Cl_2 and washed with H_2O. Recrystallization from CH_2Cl_2/petroleum ether mixtures gives colorless crystals of **13** in 65% (mp 158−160 °C) or of **14** in 63% (mp 171−174 °C) yield.

Spectral data for 2,4,6-(4′-$HC_6F_4O)_3C_6F_2CN$ (13): IR (Nujol/KBr) 3095 m (ν_{CH}), 2248 m ($\nu_{\mathrm{C\equiv N}}$), 1645 m, 1627 m, 1529 s, 1489 s, 1418 w, 1401 m, 1266 m, 1238 w, 1179 s, 1159 s, 1135 s, 1067 s, 1033 m, 967 m, 951 s, 844 m, 768 w, 716 m, 687 w, 672 w, 612 w cm^{-1}; ^{19}F NMR δ −137.7 (3′-F, m, 6F), −147.2 (3-F, m, 2F), −155.9 (2′(2,6)-F, m, 4F), −156.4 (2′(4)-F, m, 2F); ^{1}H NMR δ 6.99 (4′(2,6)-H, tt, 2H, $^3J_{\mathrm{H-F}} = 9.9$ Hz, $^4J_{\mathrm{H-F}} = 7.0$ Hz), 6.97 (4′(4)-H, tt, 1H, $^3J_{\mathrm{H-F}} = 9.9$ Hz, $^4J_{\mathrm{H-F}} = 7.0$ Hz); MS (EI) [*m/e* (species, intensity)] 631 (M^+, 100), 612 ($M^+ - F$, 3), 482 ($M^+ - C_6F_4H$, 3), 466 ($M^+ - C_6F_4HO$, 3), 454 ($M^+ - C_6F_4H - CO$, 5), 438 ($M^+ - C_6F_4HO - CO$, 5), 301 ($M^+ - 2C_6F_4HO$, 14), 165 ($C_6F_4HO^+$, 7), 149 ($C_6F_4H^+$, 25), 137 ($C_5F_4H^+$, 32), 136 ($C_6F_2CN^+$, 11), 124 ($C_4F_4^+$, 17), 99 ($C_5F_2H^+$, 32). Anal. Calcd for $C_{25}H_3F_{14}NO_3$: C, 47.56; H, 0.48; F, 42.14. Found: C, 47.41; H, 0.50; F, 41.9.

Spectral data for 2,4,6-$(C_6F_5O)_3C_6F_2CN$ (14). IR (Nujol/KBr) 2247 m ($\nu_{\mathrm{C\equiv N}}$), 1627 m, 1520 s, 1488 s, 1408 m, 1317 m, 1278 w, 1167 m, 1126 w, 1099 m, 1033 s, 997 s cm^{-1}; ^{19}F NMR δ −147.5 (3-F, m, 2F), −155.5 (2′(2,6)-F, m, 4F), −156.0 (2′(4)-F, m, 2F), −157.5 (4′(4)-F, t, 1F, $^3J_{\mathrm{F-F}} = 21.9$ Hz), −157.7 (4′(2,6)-F, t, 2F, $^3J_{\mathrm{F-F}} = 22.0$ Hz), −160.6 (3′(4)-F, m, 2F), −160.8 (3′(2,6)-F, m, 4F); MS (EI) [*m/e* (species, intensity)] 685 (M^+, 100), 666 ($M^+ - F$, 1), 657 ($M^+ - CO$, 1), 638 ($M^+ - F - CO$, 1), 518 ($M^+ - C_6F_5$, 1), 502 ($M^+ - C_6F_5O$, 3), 490 ($M^+ - C_6F_5 - CO$, 11), 483 ($M^+ - C_6F_5O - F$, 4), 319 ($M^+ - 2C_6F_5O$, 16), 183 ($C_6F_5O^+$, 83), 167 ($C_6F_5^+$, 20), 155 ($C_5F_5^+$, 63), 136 ($C_6F_2CN^+$, 33), 124 ($C_4F_4^+$, 41), 117 ($C_5F_3^+$, 26), 93 ($C_3F_3^+$, 12). Elemental analyses data are given in the literature.[13]

Preparation of 2,4,6-(4′-$HC_6F_4O)_3C_6F_2NO_2$ (15) and 2,4,6-$(C_6F_5O)_3C_6F_2NO_2$ (16). Siloxane (38 mmol, **1** or **2**) and 9 mmol of pentafluoronitrobenzene in 10 mL of THF that contains catalytic amounts of CsF are heated at 60 °C for 24 h (monitored by ^{19}F NMR). After removal of all volatile materials under high vacuum, the residue is sublimed at 120 °C/0.01 Torr. Recrystallization from CH_2Cl_2/petroleum ether mixtures gives pale yellow crystals of **15** in 72% (mp 118−120 °C) or of **16** in 60% (mp 142−144 °C) yield.

Spectral data for 2,4,6-(4′-$HC_6F_4O)_3C_6F_2NO_2$ (15): IR (Nujol/KBr) 3095 m (ν_{CH}), 1646 m, 1620 m, 1553 m ($\nu_{\mathrm{sym.NO_2}}$), 1527 s, 1494 s, 1465 s, 1405 m, 1369 m ($\nu_{\mathrm{sym.NO_2}}$), 1266 m, 1244 w, 1180 m, 1158 m, 1122 m, 1065 m, 1019 m, 973 m, 947 m, 840 m, 786 m, 763 m, 738 w, 716 m, 685 w, 672 w, 610 w cm^{-1}; ^{19}F NMR δ −137.8 (3′(4)-F, m, 2F), −138.0 (3′(2,6)-F, m, 4F), −146.3 (3-F, m, 2F), −156.6 (2′(4)-F, m, 2F), −157.1 (2′(2,6)-F, m, 4F); ^{1}H NMR δ 6.96 (4′(4)-H, tt, 1H, $^3J_{\mathrm{H-F}} = 9.9$ Hz, $^4J_{\mathrm{H-F}} = 7.1$ Hz), 6.95 (4′(2,6)-H, tt, 2H, $^3J_{\mathrm{H-F}} = 9.7$ Hz, $^4J_{\mathrm{H-F}} = 7.1$ Hz); MS (EI) [*m/e* (species, intensity)] 651 (M^+, 13), 635 ($M^+ - O$, 1), 621 ($M^+ - NO$, 2), 604 ($M^+ - H - NO_2$, 22), 586 ($M^+ - NO_2 - F$, 13), 486 ($M^+ - C_6F_4HO$, 50), 458 ($M^+ - C_6F_4HO - CO$, 7), 393 ($M^+ - C_6F_4HO - CO - NO_2 - F$, 5), 321 ($M^+ - 2C_6F_4HO$, 74), 247 ($M^+ - 2C_6F_4HO - CO - NO_2$, 68), 165 ($C_6F_4HO^+$, 100), 156 ($C_6F_2NO_2^+$, 13), 149 ($C_6F_4H^+$, 82), 137 ($C_5F_4H^+$, 87), 99 ($C_5F_2H^+$, 83). Anal. Calcd for $C_{24}H_3F_{14}NO_5$: C, 44.26; H, 0.47. Found: C, 44.38; H, 0.51.

Spectral data for 2,4,6-$(C_6F_5O)_3C_6F_2NO_2$ (16): IR (Nujol/KBr) 1654 m, 1617 m, 1558 s ($\nu_{sym.NO_2}$), 1519 s br, 1396 m, 1361 s ($\nu_{sym.NO_2}$), 1316 m, 1277 m, 1171 s, 1120 w, 1086 s, 1037 s, 998 s, 948 m, 925 m, 844 w, 802 m, 772 m, 762 m, 725 m, 691 w, 659 w, 641 w, 613 w, 597 cm^{-1}; ^{19}F NMR δ −146.6 (3-F, p, 2F, $^6J_{F-F} = 3.5$ Hz), −156.1 (2′(4)-F, m, 2F), −156.5 (2′(2,6)-F, m, 4F), −157.7 (4′(4)-F, t, 1F, $^3J_{F-F} = 21.8$ Hz), −158.4 (4′(2,6)-F, t, 2F, $^3J_{F-F} = 22.0$ Hz), −160.7 (3′(4)-F, m, 2F), −160.9 (3′(2,6)-F, m, 4F); MS (EI) [*m/e* (species, intensity)] 705 (M^+, 1), 659 ($M^+ - NO_2$, 1), 658 ($M^+ - CO - F$, 5), 640 ($M^+ - NO_2 - F$, 4), 522 ($M^+ - C_6F_5O$, 16), 339 ($M^+ - 2C_6F_5O$, 29), 265 ($M^+ - 2C_6F_5O - CO - NO_2$, 27), 183 ($C_6F_5O^+$, 100), 167 ($C_6F_5^+$, 16), 156 ($C_6F_2NO_2^+$, 12), 155 ($C_5F_5^+$, 27), 117 ($C_5F_3^+$, 20), 93 ($C_3F_3^+$, 10). Anal. Calcd for $C_{24}F_{17}NO_5$: C, 40.87; F, 45.80. Found: C, 40.79; F, 46.0.

Acidic Hydrolysis of 5 and 6 To Form 17 and 18. Compound **5** or **6** (10 mmol) in 20 mL of 80% H_2SO_4 are heated for 2h at 170 °C, in a round-bottomed flask equipped with a reflux condenser. At 25 °C, the mixture is poured on ice and extracted with ether. The combined ether phases are dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the crude product is sublimed at 90-110 °C/0.01 Torr. The yields for 4-(4′-HC_6F_4O)C_6F_4COOH (monohydrate, **17**, (mp 126−128 °C) is 87% and for 4-$(C_6F_5O)C_6F_4COOH$ **18**, mp 166−168 °C) is 90%.

Spectral data for 4-(4′-HC_6F_4O)C_6F_4COOH (17): IR (Nujol/KBr) 3618 s (ν_{OH}), 3479 s (ν_{H_2O}), 3092 m (ν_{CH}), 2620 m br (ν_{OH}), 1714 s ($\nu_{C=O}$), 1637 m, 1520 s, 1493 s, 1410 w, 1335 m, 1253 m, 1178 m, 1137 m, 1057 w, 1031 m, 998 s, 977 w, 947 s, 844 m, 813 w, 788 w, 721 m, 689 w, 636 w cm^{-1}; ^{19}F NMR δ −136.7 (2-F, m, 2F), −138.0 (3′-F, m, 2F), −155.5 (3-F, m, 2F), −156.1 (2′-F, m, 2F); ^{1}H NMR δ 9.2 (COOH, br, 1H), 6.99 (4-H, tt, 1H, $^3J_{H-F} = 9.9$ Hz, $^4J_{H-F} = 7.1$ Hz); MS (EI) [*m/e* (species, intensity)] 358 (M^+, 73), 341 ($M^+ - OH$, 61), 339 ($M^+ - F$, 5), 314 ($M^+ - CO_2$, 100), 295 ($M^+ - CO_2 - F$, 27), 267 ($M^+ - CO_2 - F - CO$, 26), 245 ($M^+ - CO_2 - F - CF_2$, 15), 236 ($M^+ - CO_2 - CF_2 - CO$, 28), 165 ($C_6F_4HO^+$, 19), 149 ($C_6F_4H^+$, 46), 137 ($C_5F_4H^+$, 58), 117 ($C_5F_3^+$, 11), 99 ($C_5F_2H^+$, 59), 93 ($C_3F_3^+$, 10). Anal. Calcd for $C_{13}H_4F_8O_4$ (monohydrate): C, 41.51; H, 1.07. Found: C, 40.24; H, 0.92.

Spectral data for 4-$(C_6F_5O)C_6F_4COOH$ (18): IR (Nujol/KBr) 2800 m vbr (ν_{OH}), 1708 s ($\nu_{C=O}$), 1658 m, 1647 m, 1520 s br, 1428 s, 1322 s, 1258 s, 1165 s, 1091 s, 999 s br, 929 m, 913 m, 792 w, 772 w, 749 w, 723 s, 661 w, 637 m, 580 w cm^{-1}; ^{19}F NMR δ −136.5 (2-F, m, 2F), −155.6 (3-F/2′-F, m, 4F), −158.2 (4′-F, t, 1F, $^3J_{F-F} = 22.0$ Hz), −161.2 (3′-F, m, 2F); ^{1}H NMR δ 9.0 (COOH, br, 1H); MS (EI) [*m/e* (species, intensity)] 376 (M^+, 6), 359 ($M^+ - OH$, 7), 332 ($M^+ - CO_2$, 100), 313 ($M^+ - CO_2 - F$, 13), 285 ($M^+ - CO_2 - CO - F$, 16), 254 ($M^+ - CO_2 - CO$ - CF_2, 21), 183 ($C_6F_5O^+$, 54), 167 ($C_6F_5^+$, 7), 155 ($C_5F_5^+$, 50), 149 ($M^+ - CO_2 - C_6F_5O$, 46), 137 ($M^+ - CO_2 - C_6F_5 - CO$, 34), 117 ($C_5F_3^+$, 32), 93 ($C_3F_3^+$, 21). Elemental analyses data are given in the literature.[11,12]

Acidic Hydrolysis of 13 and 14 To Form 19, 20, 21, and 22. Compound **13** or **14 (**2 mmol**)** in 20 mL of 80% H_2SO_4 are heated for 6 h at 180 °C in a round-bottomed flask equipped with a reflux condenser. At 25 °C, the mixture is poured on ice and extracted with ether. The combined ether phases are dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the crude product mixture, consisting of the acid and the decarboxylated species in a ratio of ∼4: 1, is separated by slow sublimation at 110−120 °C/0.01 Torr. The more volatile decarboxylated species sublimes at 120 °C/0.01 Torr, while the acid sublimes at 150−170 °C/0.01 Torr. The yields of isolated pure compounds are 32% 2,4,6-(4′-$HC_6F_4O)_3C_6F_2COOH$ (**19**, mp 181−183 °C), 34% 2,4,6-(4′-$HC_6F_4O)_3C_6F_2H$ (**20**, mp 135−137 °C), 36% 2,4,6-$(C_6F_5O)_3C_6F_2COOH$ (**21**, mp 189−191 °C), 8% 2,4,6-$(C_6F_5O)_3C_6F_2H$ (**22**, mp 109−111 °C).

Spectral data for 2,4,6-(4′-$HC_6F_4O)_3C_6F_2COOH$ (19): IR (Nujol/KBr) 3096 m (ν_{CH}), 2900 m vbr (ν_{OH}), 1719 s ($\nu_{C=O}$), 1645 m, 1631 m, 1523 s, 1489 s, 1311 m, 1274 m, 1252 m, 1179 m, 1165 m, 1126 m, 1072 s, 1015 m, 972 m, 945 s, 917 m, 848 m, 831 m, 775 w, 719 m, 687 w, 660 w cm^{-1}; ^{19}F NMR δ −138.0 (3′(4)-F, m, 2F), −138.6 (3′(2,6)-F, m, 4F), −147.1 (3-F, m, 2F), −156.6 (2′(4)-F, m, 2F), −157.3 (2′(2,6)-F, m, 4F); ^{1}H NMR δ 6.93 (4′(4)-H, tt, 1H, $^3J_{H-F} = 9.9$ Hz, $^4J_{H-F} = 7.1$ Hz), 6.88 (4′(2,6)-H, tt, 2H, $^3J_{H-F} = 9.9$ Hz, $^4J_{H-F} = 7.0$ Hz), 4.8 (COOH, br, 1H) ; MS (EI) [*m/e* (species, intensity)] 650 (M^+, 6), 606 ($M^+ - CO_2$, 100), 587 ($M^+ - CO_2 - F$, 43), 586 ($M^+ - CO_2 - HF$, 85), 485 ($M^+ - C_6F_4HO$, 45), 457 ($M^+ - CO_2 - C_6F_4H$, 6), 441 ($M^+ - CO_2 - C_6F_4HO$, 10), 437 ($M^+ - C_6F_4HO - CO - HF$, 20), 429 ($M^+ - CO_2 - C_6F_4H - CO$, 14), 413 ($M^+ - CO_2 - C_6F_4HO - CO$, 20), 393 ($M^+ - CO_2 - C_6F_4HO - CO - HF$, 8), 335 ($M^+ - CO_2 - C_6F_4HO - 2CO - CF_2$, 15), 276 ($M^+ - CO_2 - 2C_6F_4HO$, 31), 236 ($M^+ - CO_2 - 2C_6F_4HO - 2HF$, 6). Anal. Calcd for $C_{25}H_4F_{14}O_5$: C, 46.17; H, 0.62. Found: C, 45.99; H, 0.70.

Spectral data for 2,4,6-(4′-$HC_6F_4O)_3C_6F_2H$ (20): IR (Nujol/KBr) 3092 m (ν_{CH}), 1643 m, 1621 m, 1524 s, 1505 s, 1480 s, 1404 m, 1274 m, 1243 m, 1193 m, 1180 m, 1137 m, 1105 m, 1070 m, 1056 m, 1041 m, 995 m, 950 s, 927 m, 868 w, 843 m, 763 w, 719 m, 686 w, 608 w cm^{-1}; ^{19}F NMR δ −138.0 (3′(2,6)-F, m, 4F), −138.6 (3′(4)-F, m, 2F), −150.8 (3-F, m, 2F), −155.0 (2′(2,6)-F, m, 4F), −156.7 (2′(4)-F, m, 2F); ^{1}H NMR δ 6.96 (4′(2,6)-H, tt, 2H, $^3J_{H-F} = 9.8$ Hz, $^4J_{H-F} = 7.0$ Hz), 6.92 (4′(4)-H, tt, 1H, $^3J_{H-F} = 9.9$ Hz, $^4J_{H-F} = 7.0$ Hz), 6.63 (1-H, t, 1H, $^4J_{H-F} = 7.3$ Hz); MS (EI) [*m/e* (species, intensity)] 606 (M^+, 100), 587 ($M^+ - F$, 5), 586 ($M^+ - HF$, 7), 457 ($M^+ - C_6F_4H$, 6), 441 ($M^+ - C_6F_4HO$, 8), 429 ($M^+ - C_6F_4H - CO$, 16), 413 ($M^+ - C_6F_4HO - CO$, 22), 335 ($M^+ - C_6F_4HO - 2CO - CF_2$, 25), 276 ($M^+ - 2C_6F_4HO$, 51), 236 ($M^+ - 2C_6F_4HO - 2HF$, 31), 229 ($M^+ - 2C_6F_4HO - CO - F$, 21), 201 ($M^+ - 2C_6F_4HO - 2CO - F$, 28), 111 ($C_6F_2H^+$, 40), 99 ($C_5F_2H^+$, 26). Anal. Calcd for $C_{24}H_4F_{14}O_3$: C, 47.54; H, 0.67. Found: C, 47.34; H, 0.72.

Spectral data for 2,4,6-$(C_6F_5O)_3C_6F_2COOH$ (21): IR (Nujol/KBr) 3130 m vbr (ν_{OH}), 1704 s ($\nu_{C=O}$), 1668 w, 1627 m, 1520 s, 1410 m, 1317 m, 1283 m, 1223 m, 1166 m, 1117 m, 1086 m, 1036 s, 998 s, 983 s, 946 m, 891 w, 800 w, 722 w, 707 m, 658 w, 612 w cm^{-1}; ^{19}F NMR δ −147.3 (3-F, m, 2F), −156.2 (2′(4)-F, m, 2F), −156.9 (2′(2,6)-F, m, 4F), −158.5 (4′(4)-F, t, 1F, $^3J_{F-F} = 21.1$ Hz), −160.2 (4′(2,6)-F, t, 2F, $^3J_{F-F} = 19.8$ Hz), −161.1 (3′(4)-F, m, 2F), −161.7 (3′(2,6)-F, m, 4F); ^{1}H NMR δ 3.0 (COOH, br, 1H); MS (EI) [*m/e* (species, intensity)] 660 ($M^+ - CO_2$, 51), 641 ($M^+ - CO_2 - F$, 27), 640 ($M^+ - CO_2 - HF$, 100), 521 ($M^+ - C_6F_5O$, 3), 520 ($M^+ - C_6F_5OH$, 6), 477 ($M^+ - CO_2 - C_6F_5O$, 2), 473 ($M^+ - C_6F_5O - CO - HF$, 17), 371 ($M^+ - CO_2 - C_6F_5O - 2CO - CF_2$, 8), 330 ($M^+ - CO_2 - C_6F_5O - CO - 2CF_2 - F$, 10), 294 ($M^+ - CO_2 - 2C_6F_5O$, 15), 274 ($M^+ - CO_2 - 2C_6F_5O - HF$, 19), 183 ($C_6F_5O^+$, 12), 167 ($C_6F_5^+$, 8), 155 ($C_5F_5^+$, 15), 117 ($C_5F_3^+$, 18), 111 ($C_6F_2H^+$, 41), 93 ($C_3F_3^+$, 9). Anal. Calcd for $C_{25}HF_{17}O_5$: C, 42.63; H, 0.14. Found: C, 42.45; H, 0.21.

Spectral data for 2,4,6-$(C_6F_5O)_3C_6F_2H$ (22). IR (Nujol/KBr) 1625 m, 1520 s br, 1318 m, 1264 m, 1204 m, 1193 m, 1158 m, 1106 m, 1064 s, 1030 s, 997 s, 961 s, 928 m, 869 w, 845 w, 789 w, 752 w, 719 m, 656 w, 610 w cm^{-1}; ^{19}F NMR δ −150.7 (3-F, m, 2F), −154.8 (2′-(2,6)-F, m, 4F), −156.3 (2′(4)-F, m, 2F), −158.4 (4′(2,6)-F, t, 2F, $^3J_{F-F} = 22.0$ Hz, $^4J_{F-F} = 1.3$ Hz), −159.5 (4′(4)-F, tt, 1F, $^3J_{F-F} = 21.8$ Hz, $^4J_{F-F} = 1.6$ Hz), −161.1 (3′(2,6)-F, m, 4F), −161.8 (3′(4)-F, m, 2F); ^{1}H NMR δ 6.62 (1-H, t, 1H, $^4J_{H-F} = 7.3$ Hz); MS (EI) [*m/e* (species, intensity)] 660 (M^+, 100), 641 ($M^+ - F$, 5), 640 ($M^+ - HF$, 10), 477 ($M^+ - C_6F_5O$, 2), 465 ($M^+ - C_6F_5 - CO$, 4), 449 ($M^+ - C_6F_5O - CO$, 5), 371 ($M^+ - C_6F_5O - 2CO - CF_2$, 11), 330 ($M^+ - C_6F_5O - CO - 2CF_2 - F$, 13), 294 ($M^+ - 2C_6F_5O$, 21), 266 ($M^+ - 2C_6F_5O - CO$, 6), 254 ($M^+ - C_6F_5O - C_6F_5 - 2CO$, 10), 247 ($M^+ - 2C_6F_5O - CO - F$, 10). Anal. Calcd for $C_{24}HF_{17}O_3$: C, 43.66; H, 0.15. Found: C, 43.72; H, 0.20.

Decarboxylation of 17 and 18 to Form 23 and 24. Compound of **17** or **18** (7 mmol) in an evacuated stainless steel vessel is heated at 250 °C for 24 h. The crude product is extracted with ether. After removal of the ether under vacuum, the compound is sublimed at 40−50 °C/0.01 Torr. The yields are 82% for $(4\text{-}HC_6F_4)_2O$ (**23**, mp 67−68 °C) and 84% for 4-$(C_6F_5O)C_6F_4H$ (**24**, mp 54−56 °C).

Spectral data for $(4\text{-}HC_6F_4)_2O$ (23): IR (Nujol/KBr) 3092 m (ν_{CH}), 1636 m, 1525 s, 1496 s, 1464 s, 1404 w, 1283 m, 1248 m, 1178 s, 1134 m, 1111 m, 1056 w, 1009 m, 941 s, 844 m, 762 w, 721 m, 686 w, 631 w, 616 w cm^{-1}; ^{19}F NMR δ −138.6 (2-F, m, 2F), −156.6 (3-F, m, 2F); ^{1}H NMR δ 6.94 (4-H, tt, 1H, $^{3}J_{H-F} = 9.9$ Hz, $^{4}J_{H-F} = 6.9$ Hz); MS (EI) [*m/e* (species, intensity)] 314 (M$^+$, 100), 295 (M$^+$ − F, 25), 267 (M$^+$ − F − CO, 22), 264 (M$^+$ − CF$_2$, 3), 245 (M$^+$ − F − CF$_2$, 11), 236 (M$^+$ − CF$_2$ − CO, 22), 165 ($C_6F_4HO^+$, 11), 149 ($C_6F_4H^+$, 27), 137 ($C_5F_4H^+$, 42), 117 ($C_5F_3^+$, 3), 99 ($C_5F_2H^+$, 41), 93 ($C_3F_3^+$, 6). Elemental analyses data are given in the literature.[55]

Spectral data for 4-(C_6F_5O)C_6F_4H (24): IR (Nujol/KBr) 3101 w (ν_{CH}), 1640 m, 1520 s, 1490 s, 1403 w, 1317 m, 1274 m, 1243 m, 1178 m, 1158 m, 1132 m, 1067 s, 1004 s, 976 s, 948 s, 838 m, 796 w, 744 w, 719 m, 690 w, 660 w, 634 w, 587 w cm^{-1}; ^{19}F NMR δ −138.3 (2-F, m, 2F), −156.2/−156.7 (3-F/2′-F, m, 4F), −159.5 (4′-F, t, 1F, $^{3}J_{F-F} = 22.0$ Hz), −161.8 (3′-F, m, 2F); ^{1}H NMR δ 6.95 (1-H, tt, 1H, $^{3}J_{H-F} = 9.6$ Hz, $^{4}J_{H-F} = 7.1$ Hz); MS (EI) [*m/e* (species, intensity)] 332 (M$^+$, 100), 313 (M$^+$ − F, 10), 285 (M$^+$ − F − CO, 14), 263 (M$^+$ − F − CF$_2$, 3), 254 (M$^+$ − CF$_2$ − CO, 17), 183 (M$^+$ − C_6F_4H, 39), 165 ($C_6F_4HO^+$, 3), 155 ($C_5F_5^+$, 35), 149 ($C_6F_4H^+$, 19), 137 ($C_5F_4H^+$, 21), 117 ($C_5F_3^+$, 14), 99 ($C_5F_2H^+$, 24), 93 ($C_3F_3^+$, 9). Elemental analyses data are given in the literature.[11,12]

Decarboxylation of 19 and 21 To Form 20 and 22. Compound of **19** or **21** (0.5 mmol) in an evacuated stainless steel vessel is heated at 230 °C for 24 h. The crude product is extracted with ether. After removal of the ether under vacuum, the compound is sublimed at 120 °C/0.01 Torr. The yield for **20** is 75% and for **22** is 56%.

Alkaline Hydrolysis of 5 To Form 17. Compound **5** (5 mmol) and 70 mmol of KOH in 50 mL of water are heated at 90 °C for 17 h. At 25 °C, the mixture is slowly acidified with 10 mL of 60% H_2SO_4 and extracted with ether. The combined ether phases are dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the crude product mixture is separated and purified by column chromatography using ethyl acetate as an eluent on silica gel (70−230 mesh). Sublimation at 80 °C/0.01 Torr gives pure acid **17** in 41% yield; the hydroxy acid 4-(4′-HC_6F_4O)C_6F_3(2-OH)COOH (**25**) sublimes at 90 °C/0.01 Torr in 13% yield (mp 156−158 °C).

Spectral data for 4-(4′-HC_6F_4O)C_6F_3(2-OH)COOH (25): IR (Nujol/KBr) 3096 w (ν_{CH}), 3050 s vbr (ν_{OH}), 1679 s ($\nu_{C=O}$), 1640 s, 1527 s, 1505 s, 1484 s, 1408 m, 1316 m, 1277 w, 1266 w, 1226 s, 1179 m, 1144 m, 1126 s, 1033 m, 1001 s, 949 s, 914 w, 850 m, 839 m, 798 w, 720 m, 672 w, 639 w cm^{-1}; ^{19}F NMR δ −134.4 (6-F, m, 1F), −138.4 (3′-F, m, 2F), −156.2 (2′-F, m, 2F), −157.1 (5-F, m, 1F), −164.3 (3-F, m, 1F); ^{1}H NMR δ 11.0 (COOH, br, 1H), 6.96 (4-H, tt, 1H, $^{3}J_{H-F} = 9.9$ Hz, $^{4}J_{H-F} = 7.0$ Hz), 4.8 (OH, br, 1H); MS (EI) [*m/e* (species, intensity)] 356 (M$^+$, 37), 339 (M$^+$ − OH, 17), 338 (M$^+$ − H_2O, 100), 312 (M$^+$ − CO$_2$, 33), 291 (M$^+$ − CO$_2$ − HF − H, 6), 282 (M$^+$ − CO$_2$ − CO − 2H, 13), 263 (M$^+$ − CO$_2$ − CO − HF − H, 17), 254 (M$^+$ − CO$_2$ − HF − 2F, 29), 245 (M$^+$ − CO$_2$ − OH − CF$_2$, 6), 220 (M$^+$ − C_5F_4, 79), 173 ($C_7F_3O_2^+$, 10), 161 ($C_6F_3O_2^+$, 19), 149 ($C_6F_4H^+$, 14), 145 ($C_6F_3O^+$, 29), 137 ($C_5F_4H^+$, 8), 133 ($C_5F_3O^+$, 17), 117 ($C_5F_3^+$, 31), 99 ($C_5F_2H^+$, 46), 93 ($C_3F_3^+$, 12). Anal. Calcd for $C_{13}H_3F_7O_4$: C, 43.84; H, 0.85. Found: C, 43.23; H, 0.93.

Alkaline Hydrolysis of 5 To Form the Amide 26. Compound **5** (5 mmol) and 70 mmol of KOH in 50 mL of water are heated at 60 °C for 1.5 days. At 25 °C, the mixture is slowly acidified with 10 mL of 60% H_2SO_4 and extracted with ether. The combined ether phases are dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the crude product is sublimed slowly at 80 °C/0.01 Torr to remove the acid **17** and hydroxy acid **25** as byproducts. Sublimation at 110 °C/0.01 Torr gives pure amide 4-(4′-HC_6F_4O)$C_6F_4CONH_2$ (**26**) in 67% yield (mp 170−172 °C).

Spectral data for 4-(4′-HC_6F_4O)$C_6F_4CONH_2$ (26): IR (Nujol/KBr) 3474 m, 3456 m, 3308 m, 3275 m, 3192 m (ν_{NH_2}), 3092 w (ν_{CH}), 1686 s ($\nu_{C=O}$), 1655 w, 1640 m, 1614 m, 1520 s, 1495 s, 1428 m, 1286 m, 1243 w, 1178 m, 1137 m, 1029 m, 991 s, 948 s, 900 w, 844 m, 822 w, 769 w, 721 m, 695 w, 657 w, 650 w cm^{-1}; ^{19}F NMR δ −138.1 (3′-F, m, 2F), −140.1 (2-F, m, 2F), −155.1 (3-F, m, 2F), −156.2 (2′-F, m, 2F); ^{1}H NMR δ 6.97 (4-H, tt, 1H, $^{3}J_{H-F} = 9.7$ Hz, $^{4}J_{H-F} = 7.1$ Hz), 6.0 (NH$_2$, br, 2H); MS (EI) [*m/e* (species, intensity)] 357 (M$^+$, 100), 342 (M$^+$ − NH, 46), 341 (M$^+$ − NH$_2$, 99), 314 (M$^+$ − CO − NH, 9), 295 (M$^+$ − CO − NH − F, 6), 285 (M$^+$ − 2CO − NH$_2$, 9), 267 (M$^+$ − 2CO − NH − F, 7), 245 (M$^+$ − CO − NH − F − CF$_2$, 3), 236 (M$^+$ − 2CO − NH − CF$_2$, 7), 176 ($C_6F_4CO^+$, 17), 165 ($C_6F_4HO^+$, 6), 149 ($C_6F_4H^+$, 14), 137 ($C_5F_4H^+$, 11), 99 ($C_5F_2H^+$, 2). Anal. Calcd for $C_{13}H_3F_8NO_2$: C, 43.71; H, 0.85. Found: C, 43.78; H, 0.82.

Lithiation of 3 To Give 4-(4′-$CF_3C_6F_4O$)C_6F_4Li (3a). To 2 mmol of **3** dissolved in 5−10 mL of ether is added 2.2 mmol of *n*-BuLi (2.5 M in hexane) at −75 to −70 °C in 30 min and is stirred at that temperature for 2 h.

Reaction of 3a with Ketones. To 2 mmol of **3a**, prepared *in situ*, 3−5 mmol of ketone (($CF_3)_2CO$, ($C_6F_5)_2CO$, ($C_6H_5)_2CO$, C_3F_7(C_8F_{17})CO, C_6F_5(CH_3)CO) is introduced at −60 °C over a 30 min period. The mixture is stirred and slowly warmed from −60 to 10 °C over 6 h and then hydrolyzed with 2 mL 10% H_2SO_4, with additional stirring for 1 h at 25 °C. After extraction with ether and washing with water, the combined ether phases are dried over anhydrous Na_2SO_4. All volatile materials are removed under vacuum, and the crude product is purified by column chromatography repeatedly by using dichloromethane/hexane mixtures as an eluent on silica gel (70−230 mesh).

Spectral data for 4-(4′-$CF_3C_6F_4O$)$C_6F_4C(CF_3)_2OH$ (27): Yield 36%, bp 235 °C; IR (liquid film/KBr) 3626 m, 3606 m (ν_{OH}), 1661 m, 1646 s, 1614 m, 1515 s, 1505 s, 1495 s, 1432 m, 1346 s, 1277 s, 1226 s, 1198 s, 1154 s, 1062 m, 1000 s, 957 m, 945 m, 877 s, 818 m, 803 m, 776 w, 746 m, 735 s, 718 s, 655 w, 637 w cm^{-1}; ^{19}F NMR δ −56.3 (4′-CF$_3$, t, 3F, $^{4}J_{F-F} = 21.9$ Hz), −75.8 (CF$_3$, t, 6F, $^{5}J_{F-F} = 14.3$ Hz), −135 (2-F, br, 2F), −139.3 (3′-F, m, 2F), −154.2 (2′-F, m, 2F), −154.6 (3-F, m, 2F); ^{1}H NMR δ 4.34 (OH, br, 1H); MS (EI) [*m/e* (species, intensity)] 548 (M$^+$, 11), 529 (M$^+$ − F, 6), 509 (M$^+$ − HF$_2$, 4), 479 (M$^+$ − CF$_3$, 23), 409 ($CF_3C_6F_4OC_6F_4CO^+$, 100), 303 ($C_5F_4(CF_3)_2COH^+$, 2), 176 ($C_6F_4CO^+$, 19), 148 ($C_6F_4^+$, 14), 117 ($C_5F_3^+$, 8), 93 ($C_3F_3^+$, 3), 69 (CF_3^+, 13). Anal. Calcd for $C_{16}HF_{17}O_2$: C, 35.05; H, 0.18. Found: C, 35.29; H, 0.26.

Spectral data for 4-(4′-$CF_3C_6F_4O$)$C_6F_4C(C_6F_5)_2OH$ (28): Yield 61% (visc. liq.); IR (liquid film/KBr) 3626 m (ν_{OH}), 1651 s, 1505 s br, 1432 m, 1412 m, 1345 s, 1309 m, 1263 w, 1228 s, 1193 m, 1144 s, 1010 s, 981 s, 910 m, 878 s, 861 m, 795 s, 764 m, 737 m, 717 s, 699 m, 642 m, 581 w cm^{-1}; ^{19}F NMR δ −56.3 (4′-CF$_3$, t, 3F, $^{4}J_{F-F} = 21.9$ Hz), −139.4 (3′-F, m, 2F), −139.9 (2-F, m, 2F), −140.3 (2″-F, m, 4F), −151.3 (4″-F, tt, 2F, $^{3}J_{F-F} = 21.3$ Hz, $^{4}J_{F-F} = 4.1$ Hz), −154.4 (2′-F, m, 2F), −155.3 (3-F, m, 2F), −160.5 (3″-F, m, 4F); ^{1}H NMR δ 4.27 (OH, sept, 1H, $^{5}J_{H-F} = 2.8$ Hz); MS (EI, [*m/e* (species, intensity)] 744 (M$^+$, 6), 727 (M$^+$ − OH, 1), 725 (M$^+$ − F, 1), 577 (M$^+$ − C_6F_5, 22), 409 ($CF_3C_6F_4OC_6F_4CO^+$, 14), 363 (($C_6F_5)_2COH^+$, 45), 195 ($C_6F_5CO^+$, 100), 176 ($C_6F_4CO^+$, 5), 167 ($C_6F_5^+$, 19), 148 ($C_6F_4^+$, 9), 117 ($C_5F_3^+$, 23). Anal. Calcd for $C_{26}HF_{21}O_2$: C, 41.96; H, 0.14; F, 53.61. Found: C, 41.73; H, 0.18; F, 53.5.

Spectral data for 4-(4′-$CF_3C_6F_4O$)$C_6F_4C(C_6H_5)_2OH$ (29): Yield 62%; mp 116−118 °C; IR (Nujol/KBr) 3593 m (ν_{OH}), 3100 w, 3062 w, 1661 m, 1646 m, 1505 s br, 1485 s, 1430 m, 1349 s, 1325 m, 1295 m, 1232 s, 1187 m, 1163 s, 1086 w, 1057 m, 1030 m, 985 s, 967 s, 899 m, 879 m, 794 m, 767 m, 744 m, 718 m, 701 s, 665 m, 614 w cm^{-1}; ^{19}F NMR δ −56.1 (4′-CF$_3$, t, 3F, $^{4}J_{F-F} = 21.6$ Hz), −136.2 (2-F, m, 2F), −139.7 (3′-F, m, 2F), −154.5 (2′-F, m, 2F), −156.3 (3-F, m, 2F); ^{1}H NMR δ 7.5−7.1 (C_6H_5, m, 10H), 3.53 (OH, t, 1H, $^{5}J_{H-F} = 4.2$ Hz); MS (EI) [*m/e* (species, intensity)] 564 (M$^+$, 13), 545 (M$^+$ − F, 4), 487 (M$^+$ − C_6H_5, 24), 409 ($CF_3C_6F_4OC_6F_4CO^+$, 53), 382 (M$^+$ − ($C_6H_5)_2CO$, 6), 183 (($C_6H_5)_2COH^+$, 53), 182 (($C_6H_5)_2CO^+$, 4), 176 ($C_6F_4CO^+$, 13), 155 ($C_5F_5^+$, 17), 148 ($C_6F_4^+$, 13), 117 ($C_5F_3^+$, 8), 105 ($C_6H_5CO^+$, 100), 78 ($C_6H_6^+$, 44), 77 ($C_6H_5^+$, 64), 69 (CF_3^+, 19). Anal. Calcd for $C_{26}H_{11}F_{11}O_2$: C, 55.33; H, 1.97; F, 37.03. Found: C, 55.54; H, 2.00; F, 37.0.

Spectral data for 4-(4′-$CF_3C_6F_4O$)$C_6F_4C(C_3F_7)(C_8F_{17})OH$ (30): Yield 52%; mp 55−57 °C; IR (liquid film/KBr) 3646 m, 3607 m (ν_{OH}), 1645 m, 1520 s, 1489 s, 1434 m, 1410 w, 1347 s, 1226 s br, 1153 s br, 1057 m, 999 s, 970 m, 877 m, 836 w, 810 w, 793 w, 764 m, 744 m, 718 m, 658 m, 637 m, 558 m, 529 m cm^{-1}; ^{19}F NMR δ −56.2 (4′-CF$_3$, t, 3F, $^{4}J_{F-F} = 21.9$ Hz), −80.7 (CF$_3$, t, 3F, $^{4}J_{F-F} = 11.3$ Hz), −81.0 (CF$_3$, tt, 3F, $^{4}J_{F-F} = 9.9$ Hz, $^{5}J_{F-F} = 2.3$ Hz), −113.5 (CF$_2$, br, 2F), −114.5 (CF$_2$, br, 2F), −119.8 (CF$_2$, br, 2F), −121.5 (CF$_2$, br, 2F), −122.0 (CF$_2$, br, 2F), −122.9 (CF$_2$, br, 2F), −124.1 (CF$_2$, br, 2F), −126.4 (CF$_2$, br, 2F), −127.5 (CF$_2$, br, 2F), −139.0 (3′-F, m, 2F), −139.5 (2-F, br, 2F), −153.9 (2′-F, m, 2F), −154.5 (3-F, m, 2F); ^{1}H NMR δ 4.37/4.31 (OH, br, 1H); MS (EI) [*m/e* (species, intensity)] 979 (M$^+$ − F, 8), 867 (M$^+$ − C_3F_5, 1), 829 (M$^+$ − C_3F_7, 56), 781 (M$^+$ −

---

(55) Chen, Q.; Chen, M. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1071.

$CF_3C_6F_4$, 4), 731 ($M^+ - CF_3C_6F_4 - CF_2$, 2), 579 ($M^+ - C_8F_{17}$, 100), 559 ($M^+ - C_8F_{17} - HF$, 9), 531 ($M^+ - CF_3C_6F_4 - C_5F_{10}$, 16), 431 ($M^+ - CF_3C_6F_4 - C_7F_{14}$, 24), 409 ($CF_3C_6F_4OC_6F_4CO^+$, 73), 219 ($C_4F_9^+$, 4), 205 ($C_6F_7^+$, 32), 198 ($C_7F_6^+$, 7), 176 ($C_6F_4CO^+$, 20), 169 ($C_3F_7^+$, 43), 148 ($C_6F_4^+$, 11), 131 ($C_3F_5^+$, 18), 119 ($C_2F_5^+$, 38). Anal. Calcd for $C_{25}HF_{35}O_2$: C, 30.08; H, 0.10. Found: C, 29.94; H, 0.12.

Spectral data for 4-(4′-$CF_3C_6F_4O$)$C_6F_4C(C_6F_5)(CH_3)OH$ (31): Yield 68%; mp 70−72 °C; IR (liquid film/KBr) 3626 m, 3490 m br (ν_{OH}), 3001 w, 2944 w, 1651 m, 1646 m, 1609 w, 1515 s, 1505 s, 1495 s, 1463 m, 1433 m, 1410 m, 1391 w, 1345 s, 1308 m, 1262 w, 1228 s, 1192 s, 1162 s, 1098 m, 1083 m, 1035 m, 983 s, 923 m, 877 m, 846 m, 807 w, 782 m, 754 m, 741 m, 717 s, 689 s, 670 w, 639 m cm^{-1}; ^{19}F NMR δ −56.2 (4′-CF_3, t, 3F, $^4J_{F-F} = 21.5$ Hz), −139.6 (3′-F, m, 2F), −141.4 (2-F, m, 2F), −141.9 (2″-F, m, 2F), −153.9 (4″-F, tt, 1F, $^3J_{F-F} = 21.0$ Hz, $^4J_{F-F} = 3.0$ Hz), −154.4 (2′-F, m, 2F), −155.7 (3-F, m, 2F), −161.1 (3″-F, m, 2F); ^{1}H NMR δ 3.61 (OH, p, 1H, $^5J_{H-F} = 2.8$ Hz), 2.17 (CH_3, p, 1H, $^5J_{H-F} = 2.3$ Hz); MS (EI) [*m/e* (species, intensity)] 592 (M^+, 2), 577 ($M^+ - CH_3$, 100), 575 ($M^+ - OH$, 9), 573 ($M^+ - F$, 8), 425 ($M^+ - C_6F_5$, 20), 409 ($CF_3C_6F_4OC_6F_4CO^+$, 21), 211 ($C_6F_5(CH_3)COH^+$, 33), 195 ($C_6F_5CO^+$, 68), 176 ($C_6F_4CO^+$, 7), 167 ($C_6F_5^+$, 14), 148 ($C_6F_4^+$, 9), 117 ($C_5F_3^+$, 13), 93 ($C_3F_3^+$, 6). Anal. Calcd for $C_{21}H_4F_{16}O_2$: C, 42.59; H, 0.68; F, 51.33. Found: C, 42.51; H, 0.68; F, 51.7.

Preparation of $C_3F_7(C_8F_{17})CO$. To a solution containing 11 mmol of $C_8F_{17}I$ and 10 mmol of $C_3F_7CO_2Et$ in 80 mL of ether is added 11 mmol of MeLi (1.5 M in ether) at −78 °C over 30 min. After additional stirring for 30 min at −78 to −40 °C, the mixture is hydrolyzed at 0 °C with 3 mL of concentrated HCl and poured into 100 mL of 1.5 M HCl. After extraction with ether, the combined extracts are dried over anhydrous Na_2SO_4. Vacuum distillation gives pure ketone (**37**) in 73% yield as a colorless liquid (bp 36 °C/0.01 Torr) which can be stored under vacuum and over P_4O_{10} for indefinite periods for preventing hydrate formation.

Spectral data for $C_3F_7(C_8F_{17})CO$ (37): IR (liquid film/KBr) 1789 s ($\nu_{C=O}$), 1352 s, 1331 s, 1235 vs br, 1148 s, 1068 m, 1014 s, 963 w, 879 m, 870 m, 805 w, 779 m, 748 m, 737 m, 713 m, 658 m, 600 w, 562 m, 527 m cm^{-1}; ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ −81.1 (CF_3, t, 3F, $^4J_{F-F} = 9.0$ Hz), −81.5 (CF_3, t, 3F, $^4J_{F-F} = 9.7$ Hz), −117.8 (CF_2, br, 2F), −118.5 (CF_2, br, 2F), −121.7 (CF_2, br, 4F), −122.3 (CF_2, br, 4F), −123.2 (CF_2, br, 2F), −126.3 (CF_2, br, 2F), −126.7 (CF_2, br, 2F); MS (EI) [*m/e* (species, intensity)] 597 ($M^+ - F$, <1), 419 ($C_8F_{17}^+$, 2), 331 ($C_7F_{13}^+$, 1), 231 ($C_5F_9^+$, 2), 219 ($C_4F_9^+$, 7), 197 ($C_3F_7CO^+$, 6), 181 ($C_4F_7^+$, 3), 169 ($C_3F_7^+$, 100), 131 ($C_3F_5^+$, 17), 119 ($C_2F_5^+$, 24), 109 ($C_2F_3CO^+$, 5), 100 ($C_2F_4^+$, 10), 69 (CF_3^+, 87). Anal. Calcd for $C_{12}F_{24}O$: C, 23.39; F, 74.01. Found: C, 23.34; F, 73.9.

Reaction of 3a with Acid Chlorides. To 2 mmol of **3a**, prepared *in situ*, is introduced 3−5 mmol of acid chloride (RC(O)Cl, R = CF_3, C_3F_7, C_7F_{15}, $(CH_3)_2CH$; $Cl(O)C(CF_2)_3C(O)Cl$) at −60 °C over a 30 min period. The mixture is stirred and slowly warmed from −60 to 10 °C over 6 h and then hydrolyzed with 2 mL of 10% H_2SO_4, with additional stirring for 1 h while warming to 25 °C. After extraction with ether and washing with water, the combined ether phases are dried over anhydrous Na_2SO_4. All volatile materials are removed in vacuum, and the crude product is purified by column chromatography repeatedly by using dichloromethane/hexane mixtures as an eluent on silica gel (70−230 mesh). In the reaction with $(CH_3)_2CHC(O)Cl$, the product alcohol is isolated only in traces, the major product is found as an acylation product of the alcoholate. Both compounds are separated by column chromatography.

Spectral data for [4-(4′-$CF_3C_6F_4O$)$C_6F_4]_2C(CF_3)OH$ (32): Yield 58% (visc. liq.); IR (liquid film/KBr) 3614 s (ν_{OH}), 1646 s, 1620 m, 1505 s br, 1434 s, 1343 s, 1299 m, 1145 s br, 1067 m, 1052 m, 995 s br, 910 m, 876 s, 832 m, 807 w, 783 m, 762 m, 747 m, 730 m, 717 s, 697 m, 654 w, 637 w, 593 w, 548 m cm^{-1}; ^{19}F NMR δ −56.5 (4′-CF_3, t, 6F, $^4J_{F-F} = 21.9$ Hz), −78.9 (CF_3, p, 3F, $^5J_{F-F} = 14.9$ Hz), −138.2 (2-F, m, 4F), −139.6 (3′-F, m, 4F), −154.6 (2′-F, m, 4F), −155.0 (3-F, m, 4F); ^{1}H NMR δ 4.30 (OH, p, 1H, $^5J_{H-F} = 3.5$ Hz); MS (EI) [*m/e* (species, intensity)] 787 ($M^+ - OH - 2CO$, 16), 409 ($CF_3C_6F_4OC_6F_4CO^+$, 73), 362 ($CF_2C_6F_4OC_6F_4^+$, 7), 315 ($(362 - CO - F)^+$, 2), 303 ($(362 - CO - CF)^+$, 14), 284 ($(362 - CO - CF_2)^+$, 10), 265 ($(362 - CO - F - CF_2)^+$, 21), 234 ($(362 - CO - 2CF_2)^+$, 7), 217 ($CF_3C_6F_4^+$, 100). Anal. Calcd for $C_{28}HF_{25}O_3$: C, 39.09; H, 0.12; F, 55.21. Found: C, 38.87; H, 0.15; F, 54.9.

Spectral data for [4-(4′-$CF_3C_6F_4O$)$C_6F_4]_2C(C_3F_7)OH$ (33): Yield 31%; mp 116−117 °C; IR (Nujol/KBr) 3646 m, 3629 m, 3598 w (ν_{OH}), 1661 m, 1651 m, 1606 w, 1505 s br, 1487 s, 1433 m, 1341 s, 1303 w, 1224 s br, 1148 s, 1126 s, 1050 w, 1003 s, 960 m, 886 m, 873 s, 816 m, 794 w, 762 m, 747 m, 734 w, 718 s, 692 w, 677 m, 654 w, 633 w, 599 w, 572 w cm^{-1}; ^{19}F NMR δ −56.2 (4′-CF_3, t, 6F, $^4J_{F-F} = 21.9$ Hz), −81.4 (CF_3, tm, 3F, $^4J_{F-F} = 10.2$ Hz), −112.5 (CF_2, br, 2F), −120.5 (CF_2, br, 2F), −137.1 (2-F, br, 4F), −139.3 (3′-F, m, 4F), −154.2 (2′-F, m, 4F), −154.6 (3-F, m, 4F); ^{1}H NMR δ 4.46 (OH, p, 1H, $^5J_{H-F} = 4.6$ Hz); MS (EI) [*m/e* (species, intensity)] 940 ($M^+ - HF$, 1), 787 ($M^+ - OH - 2CO - C_2F_4$, 36), 569 ($M^+ - OH - 3F - C_2F_4 - CF_3C_6F_4$, 2), 553 ($M^+ - OH - 3F - C_2F_4 - CF_3C_6F_4O$, 4), 409 ($CF_3C_6F_4OC_6F_4CO^+$, 100), 362 ($CF_2C_6F_4OC_6F_4^+$, 4), 315 ($(362 - CO - F)^+$, 2), 303 ($(362 - CO - CF)^+$, 4), 284 ($(362 - CO - CF_2)^+$, 3), 265 ($(362 - CO - F - CF_2)^+$, 11), 234 ($(362 - CO - 2CF_2)^+$, 5), 217 ($CF_3C_6F_4^+$, 28). Anal. Calcd for $C_{30}HF_{29}O_3$: C, 37.52; H, 0.11; F, 57.38. Found: C, 37.46; H, 0.11; F, 57.1.

Spectral data for [4-(4′-$CF_3C_6F_4O$)$C_6F_4]_2C(C_7F_{15})OH$ (34): Yield 30%; mp 112−113 °C; IR (Nujol/KBr) 3645 m, 3601 w (ν_{OH}), 1650 w, 1646 m, 1608 w, 1505 s br, 1430 m, 1411 m, 1349 s, 1302 m, 1230 s br, 1147 s, 1061 m, 1032 m, 991 s, 973 m, 941 m, 879 s, 859 w, 818 w, 804 w, 792 w, 783 w, 764 m, 735 w, 718 s, 706 m, 686 w, 669 m, 657 m, 631 w, 605 w, 555 m, 531 m cm^{-1}; ^{19}F NMR δ −56.2 (4′-CF_3, t, 6F, $^4J_{F-F} = 21.9$ Hz), −81.0 (CF_3, t, 3F, $^4J_{F-F} = 10.2$ Hz), −111.8 (CF_2, br, 2F), −116.7 (CF_2, br, 2F), −121.9 (CF_2, br, 4F), −122.9 (CF_2, br, 2F), −126.3 (CF_2, br, 2F), −137.0 (2-F, br, 4F), −139.2 (3′-F, m, 4F), −154.2 (2′-F, m, 4F), −154.6 (3-F, m, 4F); ^{1}H NMR δ 4.46 (OH, p, 1H, $^5J_{H-F} = 4.5$ Hz); MS (EI) [*m/e* (species, intensity)] 1141 ($M^+ - F$, 1), 822 ($M^+ - C_6F_{14}$, 1), 787 ($M^+ - OH - 2CO - C_6F_{12}$, 55), 569 ($M^+ - OH - 3F - C_6F_{12} - CF_3C_6F_4$, 3), 553 ($M^+ - OH - 3F - C_6F_{12} - CF_3C_6F_4O$, 5), 409 ($CF_3C_6F_4OC_6F_4CO^+$, 100), 362 ($CF_2C_6F_4OC_6F_4^+$, 2), 315 ($(362 - CO - F)^+$, 2), 303 ($(362 - CO - CF)^+$, 4), 284 ($(362 - CO - CF_2)^+$, 4), 265 ($(362 - CO - F - CF_2)^+$, 9), 234 ($(362 - CO - 2CF_2)^+$, 2), 217 ($CF_3C_6F_4^+$, 21). Anal. Calcd for $C_{34}HF_{37}O_3$: C, 35.19; H, 0.09; F, 60.59. Found: C, 35.26; H, 0.16; F, 60.4.

Spectral data for [4-(4′-$CF_3C_6F_4O$)$C_6F_4]_2C(CH(CH_3)_2)OH$ (35): traces (visc. liq.); IR (liquid film/KBr) 3658 m (ν_{OH}), 2981 m, 2945 m, 2887 m, 1661 m, 1645 m, 1505 s br, 1431 m, 1396 m, 1346 s, 1296 m, 1227 s, 1195 s, 1142 s br, 1056 m, 998 s, 970 s, 889 m, 876 s, 826 m, 806 w, 780 w, 757 m, 717 m, 671 w, 637 w, 574 w cm^{-1}; ^{19}F NMR δ −56.2 (4′-CF_3, t, 6F, $^4J_{F-F} = 21.6$ Hz), −139.5 (3′-F, m, 4F), −140.6 (2-F, br, 4F), −154.5 (2′-F, m, 4F), −155.6 (3-F, m, 4F); ^{1}H NMR δ 3.82 (OH, pd, 1H, $^5J_{H-F} = 4.6$ Hz, $^4J_{H-H} = 1.6$ Hz), 3.10 (CH, br sept, 1H, $^3J_{H-H} = 6.4$ Hz), 1.04 (CH_3, d, 6H); MS (EI) [*m/e* (species, intensity)] 817 ($M^+ - OH$, 100), 815 ($M^+ - F$, 23), 799 ($M^+ - HF - CH_3$, 42), 791 ($M^+ - CH(CH_3)_2$, 29), 453 ($CF_3C_6F_4OC_6F_4C(OH)CH(CH_3)_2^+$, 11), 409 ($CF_3C_6F_4OC_6F_4CO^+$, 24), 395 ($CF_3C_6F_4OC_6F_4CH_2^+$, 13), 363 ($CF_2C_6F_4OC_6F_4H^+$, 13), 215 ($CF_2C_6F_4OH^+$, 16), 71 ($CH(CH_3)_2CO^+$, 65).

Spectral data for [4-(4′-$CF_3C_6F_4O$)$C_6F_4]_2C(CH(CH_3)_2)OC(O)CH(CH_3)_2$ (36): Yield 39%; (visc. liq.); IR (Nujol/KBr) 1749 s ($\nu_{C=O}$), 1661 m, 1645 m, 1605 w, 1514 s, 1456 s br, 1343 s, 1297 m, 1226 s, 1191 s, 1158 s, 1140 m, 1058 m, 1002 s, 970 s, 913 m, 893 m, 876 s, 856 m, 826 m, 797 m, 764 m, 738 m, 718 s, 672 w, 655 m, 638 m, 574 w cm^{-1}; ^{19}F NMR δ −56.4 (4′-CF_3, t, 6F, $^4J_{F-F} = 21.6$ Hz), −135.1 (2-F, br, 4F), −139.9 (3′-F, m, 4F), −154.9 (2′-F, m, 4F), −156.3 (3-F, m, 4F); ^{1}H NMR δ 3.92 (CHCOC(O), br sept, 1H, $^3J_{H-H} = 6.4$ Hz), 2.59 (CHC(O), sept, 1H, $^3J_{H-H} = 6.9$ Hz), 1.14 ($CH_3CC(O)$, d, 6H), 0.97 ($CH_3CCOC(O)$, br d, 6H); MS (EI) [*m/e* (species, intensity)] 885 ($M^+ - F$, 13), 817 ($M^+ - (CH_3)_2CHCO_2$, 17), 816 ($M^+ - (CH_3)_2CHCO_2 - H$, 35), 791 ($((CF_3C_6F_4OC_6F_4)_2COH^+$, 12), 774 ($((CF_3C_6F_4OC_6F_4)_2C^+$, 12), 601 ($M^+ - CF_3C_6F_4O - C_3H_6$, 4), 409 ($CF_3C_6F_4OC_6F_4CO^+$, 100), 395 ($CF_3C_6F_4OC_6F_4CH_2^+$, 69), 215 ($CF_2C_6F_4OH^+$, 18). Anal. Calcd for $C_{34}H_{14}F_{22}O_4$: C, 45.15; H, 1.56; F, 46.21. Found: C, 45.30; H, 1.74; F, 46.3.

Spectral data for [4-(4′-$CF_3C_6F_4O$)$C_6F_4]_2C(OH)(CF_2)_3C(O)C_6F_4O(4''-C_6F_4CF_3)$ (38): Yield 46%; mp 54−56 °C; IR (Nujol/KBr) 3621 m, 3555 w (ν_{OH}), 1749 m ($\nu_{C=O}$), 1661 m, 1646 m, 1606 w, 1505 s br, 1456 vs, 1377 s, 1344 s, 1300 m, 1228 s, 1192 s, 1153 s br, 1062 w, 996 s br, 937 m, 876 s, 820 w, 792 w, 782 w, 765 m, 717 s, 683 w, 670 w, 638 w, 607 w cm^{-1}; ^{19}F NMR δ −56.3 (4′(4″)-CF_3, t, 9F, $^4J_{F-F}$ = 21.6 Hz), −110.7 (CF_2, br, 2F), −116.2 (CF_2, br, 2F), −118.9 (CF_2, br, 2F), −137.0 (2-F, br, 4F), −137.5 (2-F, br, 2F), −139.1 (3′-F, m, 2F), −139.3 (3′-F, m, 4F), −153.5 (2′-F, m, 2F), −154.2 (3-F, m, 2F), −154.3 (2′-F, m, 4F), −154.7 (3-F, m, 4F); ^{1}H NMR δ 4.47 (OH, p, 1H, $^5J_{H-F}$ = 4.2 Hz); MS (EI) [*m/e* (species, intensity)] 1350 (M^+, 4), 1006 ($M^+ - 3CF_3 - C_5F_4 - H$, 22), 951 ($M^+ - CF_3C_6F_4O - 2CF_3 - CO$, 8), 941 ($M^+ - CF_3C_6F_4OC_6F_4CO$, 100), 936 ($((CF_3C_6F_4OC_6F_4)_2$-$CC_4F_6^+$, 9), 884 ($M^+ - 2CF_3C_6F_4O$, 11), 879 ($((CF_3C_6F_4OC_6F_4)_2CC_4F_3^+$, 11), 875 ($((CF_3C_6F_4OC_6F_4)_2CHC_2F_4^+$, 2). Anal. Calcd for $C_{44}HF_{39}O_5$: C, 39.13; H, 0.07; F, 54.87. Found: C, 39.52; H, 0.17; F, 55.3.

Reaction of 3a with Carbonyl Fluoride and Dimethyl Carbonate. To 2 mmol of **3a**, prepared *in situ*, 1 mmol of COF_2 is condensed at −80 °C over a 30 min period, or 0.5 mmol $(CH_3O)_2CO$ at −60 °C. The mixture is stirred and slowly warmed from −60 to 10 °C over 6 h and then hydrolyzed with 2 mL of 10% H_2SO_4. Stirring is maintained for 1 h while warming to 25 °C. In the reaction with dimethyl carbonate the mixture is stirred and warmed to −30 °C and then hydrolyzed with 2 mL of 10% H_2SO_4, with additional stirring for 1 h to 25 °C. In both cases, a colorless precipitate is formed. This precipitate (ketone **39**) is separated by filtration and washed with ether. Further purification of **39** can be achieved by recrystallization from acetone or benzene or sublimation at 150 °C/0.01 Torr. The alcohol **40** is obtained in both cases only as a minor product. It is found in the ether phase and purified by column chromatography. In the reaction with COF_2, the ester **41** is separated from **40** by column chromatography repeatedly by using dichloromethane/hexane mixtures as an eluent on silica gel (70−230 mesh).

Spectral data for [4-(4′-$CF_3C_6F_4O)C_6F_4]_2CO$ (39): Yield 40%; mp 212−214 °C; IR (Nujol/KBr) 1701 s ($\nu_{C=O}$), 1650 m, 1512 s, 1499 s, 1437 m, 1411 m, 1351 s, 1331 m, 1271 w, 1232 m, 1193 m, 1166 s, 1095 w, 1046 m, 1010 s, 980 s, 880 m, 828 m, 816 w, 782 m, 721 m, 697 w, 662 w cm^{-1}; ^{19}F NMR (C_6D_6) δ −56.0 (4′-CF_3, t, 6F, $^4J_{F-F}$ = 21.9 Hz), −139.5 (3′-F, m, 4F), −141.5 (2-F, m, 4F), −154.3 (2′-F, m, 4F), −154.8 (3-F, m, 4F); MS (EI) [*m/e* (species, intensity)] 790 (M^+, 79), 771 ($M^+ - F$, 34), 409 ($CF_3C_6F_4OC_6F_4CO^+$, 100), 362 ($CF_2C_6F_4OC_6F_4^+$, 7), 217 ($CF_3C_6F_4^+$, 9), 176 ($C_6F_4CO^+$, 48), 148 ($C_6F_4^+$, 30), 136 ($C_5F_4^+$, 9), 117 ($C_5F_3^+$, 6). Anal. Calcd for $C_{27}F_{22}O_3$: C, 41.03; F, 52.89. Found: C, 41.00; F, 53.6.

Spectral data for [4-(4′-$CF_3C_6F_4O)C_6F_4]_3COH$ (40): Yield 5%; mp 98−100 °C; IR (Nujol/KBr) 3626 m, 3618 w (ν_{OH}), 1661 m, 1651 s, 1646 s, 1505 s br, 1418 m, 1344 s, 1293 m, 1225 s, 1193 s, 1156 s, 1075 m, 1006 s br, 906 w, 875 s, 856 w, 806 w, 787 m, 756 w, 737 w, 718 s, 687 w, 643 w cm^{-1}; ^{19}F NMR δ −56.2 (4′-CF_3, t, 9F, $^4J_{F-F}$ = 21.6 Hz), −139.3 (3′-F, m, 6F), −139.8 (2-F, m, 6F), −154.4 (2′-F, m, 6F), −155.0 (3-F, m, 6F); ^{1}H NMR δ 4.33 (OH, sept, 1H, $^5J_{H-F}$ = 2.8 Hz); MS (EI) [*m/e* (species, intensity)] 1172 (M^+, 1), 1155 ($M^+ - OH$, 1), 1153 ($M^+ - F$, 2), 794 ($M^+ - C_{13}F_{10}O_2$, 23), 793 ($M^+ - C_{13}HF_{10}O_2$, 21), 777 ($M^+ - C_{13}HF_{10}O_3$, 8), 514 ($CF_3C_6F_4OC_6F_4$-$COC_4F_3^+$, 100), 497 ($CF_3C_6F_4OC_6F_4C(O)FCF_3^+$, 22), 409 ($CF_3C_6F_4$-$OC_6F_4CO^+$, 26). Anal. Calcd for $C_{40}HF_{33}O_4$: C, 40.98; H, 0.09. Found: C, 41.06; H, 0.13.

Spectral data for [4-(4′-$CF_3C_6F_4O)C_6F_4]_3COC(O)C_4H_9$ (41): Yield 5%; (visc. liq.); IR (liquid film/KBr) 2968 m, 2941 m, 2880 m, 1742 s ($\nu_{C=O}$), 1646 s, 1510 s br, 1434 m, 1388 m, 1344 s, 1323 s, 1226 s, 1192 m, 1152 s, 1060 m, 1047 m, 998 s, 961 m, 943 m, 876 m, 845 w, 817 w, 793 w, 768 m, 750 m, 718 s, 643 w cm^{-1}; ^{19}F NMR δ −56.2 (4′-CF_3, t, 9F, $^4J_{F-F}$ = 21.6 Hz), −138.3 (2-F, m, 6F), −139.5 (3′-F, m, 6F), −154.5 (2′-F, m, 6F), −155.4 (3-F, m, 6F); ^{1}H NMR δ 4.37 ($CH_2C(O)O$, t, 2H, $^3J_{H-H}$ = 6.5 Hz), 1.73 (CH_2, m, 2H), 1.40 (CH_2, m, 2H), 0.94 (CH_3, t, 3H, $^3J_{H-H}$ = 7.3 Hz); MS (CI) [*m/e* (species, intensity)] 1187 ($M^+ - CF_3$, 8), 1185 ($M^+ - CO - C_3H_7$, 37), 1155 ($M^+ - C_4H_9CO_2$, 15), 1152 ($M^+ - C_4H_9CO - F$, 30), 1105 ($M^+ - C_4H_9CO_2 - CF_2$, 7), 791 ($((CF_3C_6F_4OC_6F_4)_2COH^+$, 100), 771 ($(((CF_3C_6F_4$-$OC_6F_4)_2CO - F)^+$, 70).

Reaction of 3a with Dimethyl Carbonate To Give 4-$CF_3C_6F_4C_4H_9$ (42) and 4-$HOC_6F_4COOCH_3$ (43). To **3a**, prepared *in situ* from 11 mmol of **3** in 40 mL of ether and 6 mL of *n*-BuLi (11 mmol), 5.3 mmol of dimethyl carbonate is added for 3.5 h stirring at −60 °C. The mixture is stirred and slowly warmed from −60 to −30 °C over 2 h and then hydrolyzed with 10 mL of 10% H_2SO_4, with additional stirring for 1 h while warming to 25 °C. Compound **39**, formed only as a minor product, is separated by filtration and washed with ether. The combined ether phases are dried over anhydrous Na_2SO_4. The solvent is removed under reduced pressure. 4-$CF_3C_6F_4C_4H_9$ (**42**), a colorless liquid, is removed from the residue under high vacuum. The ester 4-$HOC_6F_4COOCH_3$ (**43**), a colorless solid, precipitates on treating the residue with benzene and is purified by sublimation at 120 °C/0.01 Torr.

Spectral data for 4-$CF_3C_6F_4C_4H_9$ (42): Yield 68%; bp 162−165 °C. IR (liquid film/KBr) 2966 m, 2938 m, 2879 m, 1663 m, 1610 w, 1537 m, 1495 s, 1421 w, 1409 w, 1384 w, 1338 s, 1280 w, 1259 w, 1220 s, 1186 s, 1150 s, 1114 m, 1087 m, 1039 w, 1024 w, 986 s, 922 m, 886 w, 868 m, 849 m, 746 w, 716 s, 687 w, 621 w cm^{-1}; ^{19}F NMR δ −56.5 (4-CF_3, t, 3F, $^4J_{F-F}$ = 21.5 Hz), −142.1 (3-F, m, 2F), −142.9 (2-F, m, 2F); ^{1}H NMR δ 2.75 ($CF_3C_6F_4CH_2$, tt, 2H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-F}$ = 1.5 Hz), 1.58 (CH_2, m, 2H), 1.36 (CH_2, m, 2H), 0.92 (CH_3, t, 3H, $^3J_{H-H}$ = 7.2 Hz); MS (EI) [*m/e* (species, intensity)] 274 (M^+, 100), 255 ($M^+ - F$, 29), 245 ($M^+ - C_2H_5$, 7), 244 ($M^+ - C_2H_6$, 7), 232 ($M^+ + H - C_3H_7$, 73), 231 ($M^+ - C_3H_7$, 61), 214 ($M^+ - F - C_3H_5$, 23), 205 ($M^+ - CF_3$, 13), 181 ($M^+ - CF_2 - C_3H_7$, 48), 163 ($M^+ + H - CF_3 - C_3H_7$, 18), 69 (CF_3^+, 29), 56 ($C_4H_8^+$, 19).

Spectral data for 4-$HOC_6F_4COOCH_3$ (43): Yield 63%; mp 144−146 °C IR (Nujol/KBr) 3229 m br (ν_{OH}), 1701 s ($\nu_{C=O}$), 1646 m, 1611 m, 1529 m, 1495 s, 1444 s, 1407 m, 1333 s, 1245 s, 1193 m, 1136 m, 1123 m, 997 m, 965 s, 897 m, 792 m, 759 m cm^{-1}; ^{19}F NMR δ −139.8 (2-F, m, 2F), −162.5 (3-F, m, 2F); ^{1}H NMR δ 6.44 (OH, br, 1H), 3.93 (CH_3, s, 3H); MS (EI) [*m/e* (species, intensity)] 224 (M^+, 24), 193 ($M^+ - CH_3O$, 100), 165 ($C_6F_4HO^+$, 8), 137 ($C_5F_4H^+$, 20), 117 ($C_5F_3^+$, 9), 93 ($C_3F_3^+$, 4).

Acknowledgment. We are grateful for the support of British Nuclear Fuels plc and for generous gifts of chemicals by Fluorochem, Ltd. We thank Dr. Gary Knerr for obtaining the mass spectral data and Dr. Richard Staples for assistance during the processing of crystallographic data. The single-crystal CCD X-ray facility at the University of Idaho was established with the assistance of the NSF-Idaho EPSCoR program under NSF OSR-9350539 and the M. J. Murdock Charitable Trust, Vancouver, Washington.

Supporting Information Available: For compounds **3**, **4**, **14**−**18**, **23**, and **26**, tables listing full data collection and processing parameters, bond lengths and bond angles, atomic coordinates, equivalent isotropic and anisotropic displacement coefficients, and hydrogen atom coordinates and isotropic displacement coefficients (45 pages). Ordering information is given on any current masthead page.

IC960879C