Synthesis and Chemistry of $CF_3C_6F_4OC_6F_4$ Group 14/16 Derivatives

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

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

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Reactions of 4′-$CF_3C_6F_4OC_6F_4Li$, generated *in situ*, with elements of group 16 (S, Se, Te) lead to $CF_3C_6F_4OC_6F_4SH$ (**2**), $(CF_3C_6F_4OC_6F_4Se)_2$ (**3**), and $(CF_3C_6F_4OC_6F_3Te)_2$ (**4**)/$(CF_3C_6F_4OC_6F_3)_2Te$ (**4a**). The phenol derivative $CF_3C_6F_4OC_6F_4OH$ (**1**) is obtained by reaction of $CF_3C_6F_4OC_6F_4Li$ with $B(OMe)_3/H_2O_2$. The reaction of $CF_3C_6F_4OC_6F_4Li$ with trimethylsilyl chloride or trimethyltin chloride gives $CF_3C_6F_4OC_6F_4XMe_3$ (X = Si (**5**), Sn (**6**)). Oxidation of **2** in the presence of bromine results in the formation of $(CF_3C_6F_4OC_6F_4S)_2$ (**7**) and $CF_3C_6F_4OC_6F_4SO_2Br$ (**8**). Mixed perfluoroaryloxo/thio ethers $CF_3C_6F_4OC_6F_4SC_6F_4R$ (R = NO_2 (**9**), CN (**10**), CF_3 (**11**)) and $CF_3C_6F_4OC_6F_4SC_5F_4N$ (**12**) are obtained upon reaction of **2** with excess C_6F_5R and pentafluoropyridine in the presence of K_2CO_3. With 4-$C_6F_5OC_6F_4NO_2$, a mixture of (2-$CF_3C_6F_4OC_6F_4S$)(4-C_6F_5O)$C_6F_3NO_2$ (**13**) and **9** is formed. Reaction of excess **2** with C_6F_5R gives the 2,4,6-substituted benzenes $(CF_3C_6F_4OC_6F_4S)_3C_6F_2R$ (R = NO_2 (**14**), CN (**15**)). The trimethylsilyl ether $CF_3C_6F_4OC_6F_4OSiMe_3$ (**16**) is prepared from the reaction of **1** with hexamethyldisilazane. **16** is a convenient reagent for the preparation of the aryl ethers $CF_3C_6F_4OC_6F_4OC_6F_4R$ (R = NO_2 (**17**), CN (**18**)) and $CF_3C_6F_4OC_6F_4OC_5F_4N$ (**19**) upon reaction with C_6F_5R and C_5F_5N. The secondary alcohols $CF_3C_6F_4OC_6F_4CH(C_6H_5)OH$ (**20**) and $CF_3C_6F_4OC_6F_4CH(C_6F_5)OH$ (**21**) are synthesized by the reactions of **5** with benzaldehyde and pentafluorobenzaldehyde in the presence of tetrabutylammonium fluoride as a catalyst. In the synthesis of **21** the byproduct $CF_3C_6F_4OC_6F_4CH(C_6F_5)OC_6F_4CHO$ (**22**) is also formed and isolated.

Introduction

(Perfluoroaryl)lithium reagents are widely employed as useful intermediates for the preparation of a variety of perfluoroarylated compounds. For example, the chemistry of (pentafluorophenyl)-lithium is reviewed in detail.[1,2] However, C_6F_5Li is unstable, difficult to handle, and potentially hazardous.[3,4] Recently, we reported the synthesis of a new perfluorinated aryllithium reagent, 4′-$CF_3C_6F_4OC_6F_4Li$, and its reactions with ketones and acid halides.[5] During our investigations no unexpected sudden decompositions of the reagent that is generated *in situ* occurred. We believe that replacement of the fluorine atom at the para position (relative to lithium) by the relatively bulky $OC_6F_4CF_3$ group has a stabilizing effect and prevents reaction of the (perfluoroaryl)lithium with itself. Now we report the chemistry of $CF_3C_6F_4OC_6F_4Li$ with group 14/16 elements and other substrates.[6]

Results and Discussion

When generated *in situ*, $CF_3C_6F_4OC_6F_4Li$[5] reacts readily with group 16 elements (S, Se, Te) to form $CF_3C_6F_4OC_6F_4SH$ (**2**), $(CF_3C_6F_4OC_6F_4Se)_2$ (**3**), and $(CF_3C_6F_4OC_6F_3Te)_2$ (**4**)/$(CF_3C_6F_4OC_6F_3)_2Te$ (**4a**). The synthesis of $CF_3C_6F_4OC_6F_4OH$ (**1**) is accomplished by reacting $B(OMe)_3/H_2O_2$[7] with $CF_3C_6F_4OC_6F_4Li$. Exposure of $CF_3C_6F_4OC_6F_4Li$ to the atmosphere leads only to hydrolysis and recovery of the precursor $CF_3C_6F_4OC_6F_4H$[5] (Scheme 1).

The reaction with sulfur to give thiol **2** proceeds smoothly just as for C_6F_5Li with sulfur.[8] In the reaction with selenium the selenophenol $CF_3C_6F_4OC_6F_4SeH$ that must be formed initially is not isolable; instead, it oxidizes to form the stable yellow diselenide **3**. The reaction with tellurium is more complex. We have spectral evidence that the initial species formed is the ditelluride $(CF_3C_6F_4OC_6F_4Te)_2$ or the telluride $(CF_3C_6F_4OC_6F_4)_2Te$ (δ_{19F}(*o*-F) = −115.1 ppm, ^{125}Te δ = 299 ppm, t or p, $^3J_{Te-F}$ = 38 Hz ($CDCl_3$)) based on comparison with $(C_6F_5Te)_2$ (δ_{19F}(*o*-F) = −114.0 ppm, ^{125}Te δ = 300.2 ppm, t, $^3J_{Te-F}$ = 70.5 Hz (C_6D_6))[9] and $(C_6F_5)_2Te$ (δ_{19F}(*o*-F) = −115.2 ppm (CH_3CN)[9], ^{125}Te δ = 298.0 ppm, p, $^3J_{Te-F}$ = 50 Hz ($CDCl_3$))[10] . Unfortunately, the multiplicity of the peak in the ^{125}Te NMR spectrum for our intermediate does not clearly distinguish between a triplet (ditelluride) or a pentet (telluride). However, the deep red color indicates the presence of a ditelluride. The ditellurides are in general[11] deep red chromophores, as is the case for $(C_6F_5Te)_2$.[9] It is possible that we have a mixture of both species. The formation of a ditelluride in the course of this reaction can be explained as in the selenium case. In our case, the telluride anion, $CF_3C_6F_4OC_6F_4Te^-$, that forms initially is oxidized to give a ditelluride. In contrast to the stable diselenides, diorganoditellurides are very sensitive to air and can eliminate tellurium, resulting in the formation of diorganotellurides. The two possible intermediates were not isolable and decomposed slowly into a variety of products. Similar difficulties with the isolation of diaryl ditellurides are reported when Grignard reagents are reacted with tellurium.[12]

The two decomposition products isolated in low yield from this reaction are the telluroheterocycles $(CF_3C_6F_4OC_6F_3Te)_2$ (**4**) and $(CF_3C_6F_4OC_6F_3)_2Te$ (**4a**). Identification of **4** and **4a** is

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

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(4) Cohen, S. C.; Tomlinson, A. J.; Wiles, M. R.; Massey, A. G. *Chem. Ind.* **1967**, *21*, 877.
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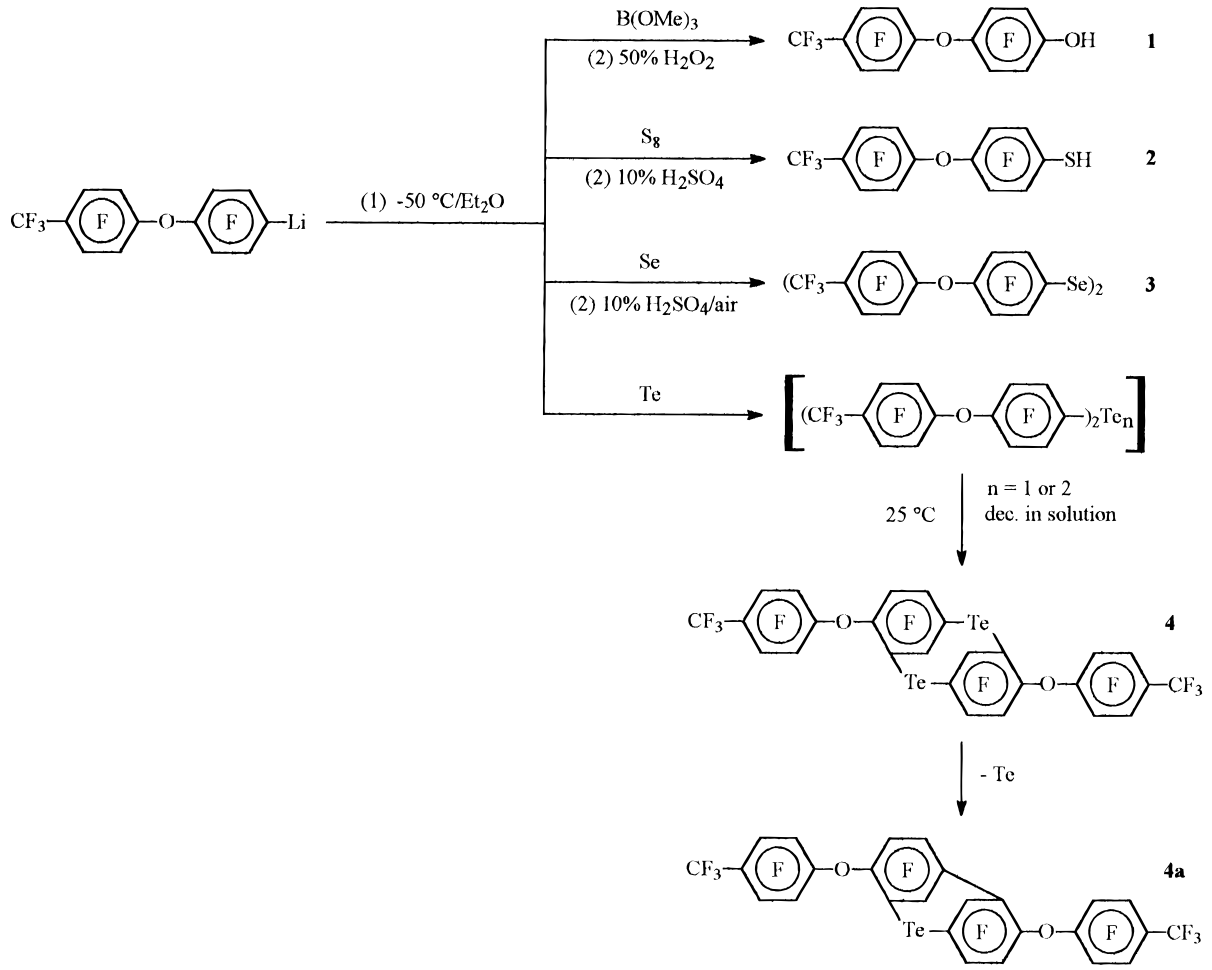
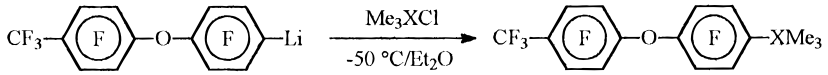
(12) Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97.

S0020-1669(97)00528-4 CCC: $14.00

Scheme 1



Scheme 2



X = Si (**5**), Sn (**6**)

based primarily on spectroscopic data. Perfluoroaryl telluroheterocycles with the proposed structures (Scheme 1) are to the best of our knowledge not known. A possible mechanism for their formation is the intermolecular attack of the strong nucleophile $CF_3C_6F_4OC_6F_4Te^-$ on a second molecule with concomitant elimination of fluoride. We believe that the 3-position is the preferred position for attack compared to the 2-position because of the greater electron-withdrawing effect of the vicinal oxygen. Possible structures with the sum formulas $(CF_3C_6F_4OC_6F_3Te)_2$ (**4**) and $(CF_3C_6F_4OC_6F_3)_2Te$ (**4a**) showing the correct isotope pattern for a compound having two tellurium atoms (**4**) at *m/e* = 984 (^{130}Te) and one tellurium atom (**4a**) at *m/e* = 854 (^{130}Te) other than these eight- and seven-membered rings can be ruled out. The shift ranges of the resonances as well as the correct integrals for **4** and **4a** in the ^{19}F NMR spectra support the structures shown. The other two possible positions for attack to give a metallocycle product, 2′-C and 3′-C (see Experimental Section for atom numbering of **4**) on the OC_6F_4-CF_3-ring, can be eliminated by ^{19}F NMR data. The resonances of the fluorine atoms attached to 2′-C and 3′-C as well as the integrals in the ^{19}F NMR spectrum are identical to the resonances seen for fluorine atoms α and β to CF_3 in compounds **1**−**3**, as well as others containing the $OC_6F_4CF_3$ moiety. Compound **4a** may result from Te elimination by **4**. The ^{125}Te resonances of **4** (δ = 739 ppm) and **4a** (δ = 778 ppm) lie in the range for organotellurides and can be compared to the resonances of telluranthrene $(C_6H_4Te)_2$ (^{125}Te δ = 888 ppm)[13] and diphenyl telluride $(C_6H_5)_2Te$ (^{125}Te δ = 688 ppm).[14] Due to the limited number of reported ^{125}Te NMR shifts, we are not able to compare our shifts for **4** and **4a** to the shifts of other fluoroaromatic telluroheterocycles. For example, the perfluoro analogue of telluranthrene, $(C_6F_4Te)_2$, is known, but no ^{125}Te NMR shift is given.[15] The mass spectral fragment patterns of **4** and **4a**, showing the correct isotope distributions for a Te_2 compound in **4** and a Te_1 compound in **4a**, are consistent with those of similar Te compounds reported in the literature.[16]

The preparation of the trimethylsilyl and trimethyltin derivatives $CF_3C_6F_4OC_6F_4SiMe_3$ (**5**) and $CF_3C_6F_4OC_6F_4SnMe_3$ (**6**) is achieved by reaction of $CF_3C_6F_4OC_6F_4Li$ with trimethylsilyl chloride and trimethyltin chloride (Scheme 2).

In contrast to **5**, the tin derivative **6** is found to be moisture sensitive and hydrolyzes slowly after prolonged periods (2 months). The formation of the products $CF_3C_6F_4OC_6F_4H$ and

(13) Dereu, N. L. M.; Zingaro, R. A. *J. Organomet. Chem.* **1981**, *212*, 141.
(14) McFarlane, H. C. E.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1973**, 2416.
(15) Rainville, D. P.; Zingaro, R. A.; Meyers, E. A. *J. Fluorine Chem.* **1980**, *16*, 245.
(16) Irgolic, K. J.; Haller, W. S. *Int. J. Sulfur Chem., Part A* **1972**, *2*, 267.

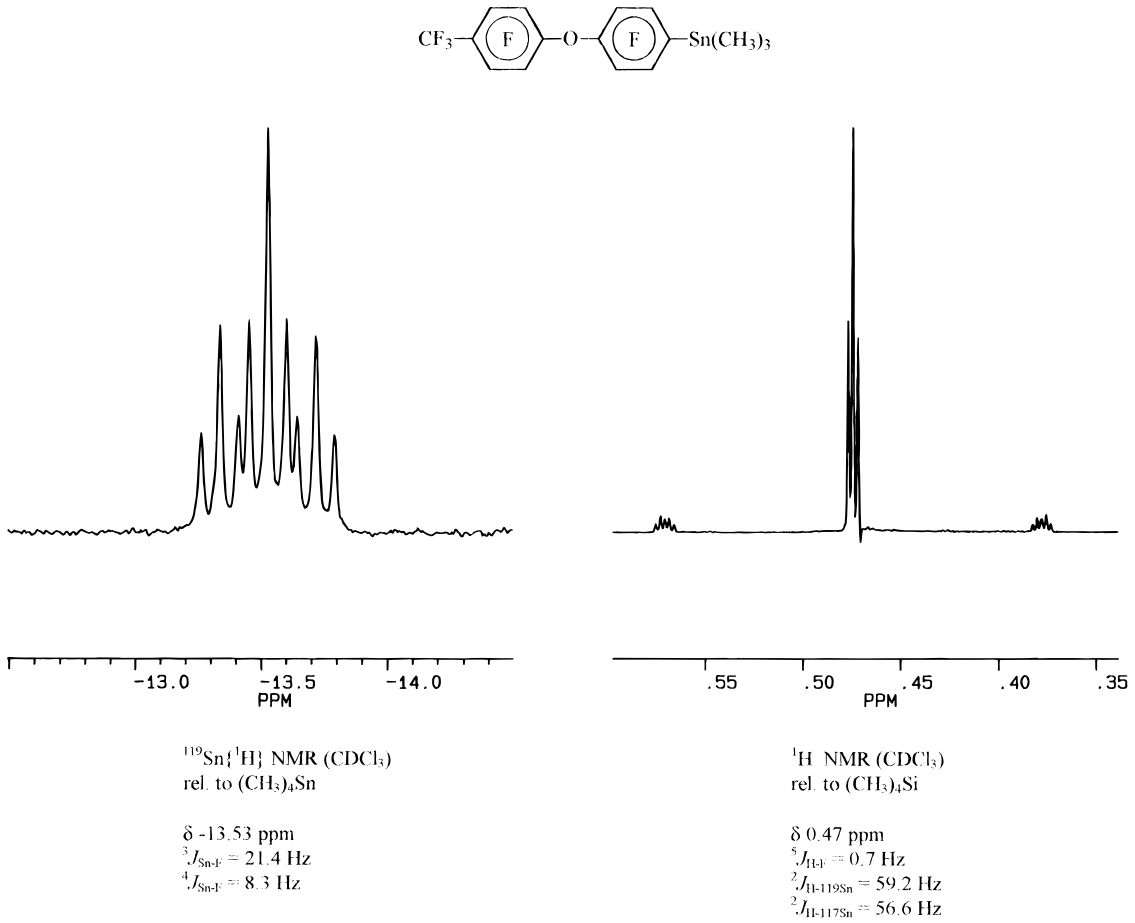
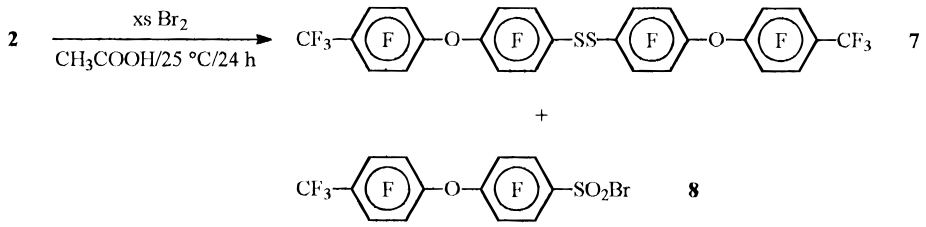


Figure 1. $^{119}Sn\{^1H\}$and ^1H NMR spectra of $CF_3C_6F_4OC_6F_4Sn(CH_3)_3$ (**6**).

Scheme 3



a $Me_3SnOH/(Me_3Sn)_2O$ mixture is confirmed by ^{19}F and ^1H NMR data.

The $^{119}Sn\{^1H\}$ and ^1H NMR spectra of **6** are given in Figure 1. The ^{119}Sn nucleus shows couplings to the *o*- and *m*-fluorine atoms, resulting in a triplet of triplets. The methyl resonances in the ^1H NMR are split by a small coupling to the *o*-fluorine atoms to a triplet. The $^{119}Sn/^{117}Sn$ satellites also show the triplet structure.

Bromine oxidizes **2** to form a mixture of the disulfide $(CF_3C_6F_4OC_6F_4S)_2$ (**7**) and the sulfonyl bromide $CF_3C_6F_4OC_6F_4SO_2Br$ (**8**) (Scheme 3).

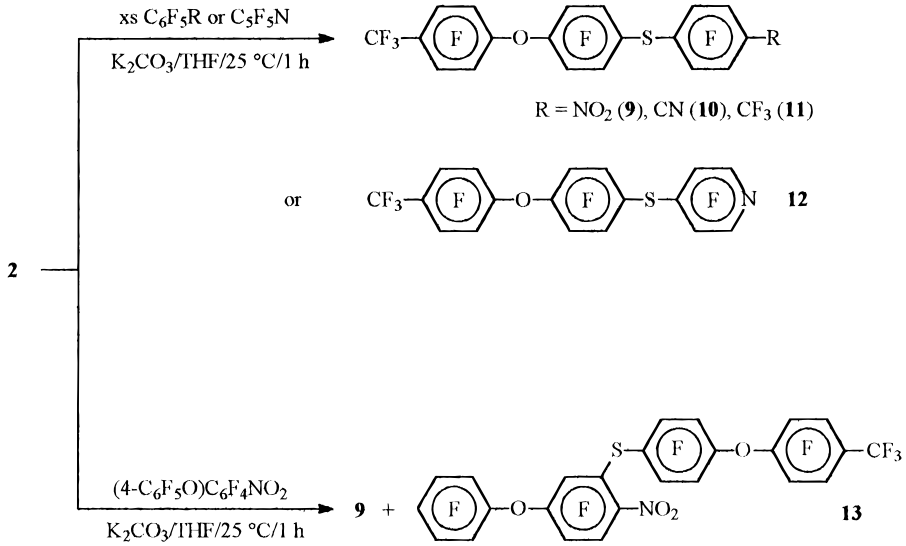
The appearance of another signal in the ^{19}F NMR spectrum in the region of *o*-fluorine atoms bound to sulfur (in addition to **2**, **7**, and **8**) located at −127.1 ppm leads us to believe that the sulfenyl bromide $CF_3C_6F_4OC_6F_4SBr$ is formed as a transient intermediate. Attempts to isolate this compound failed due to its instability, which is common for this class of compounds. The sulfenyl bromide loses bromine to give **7** or is oxidized to **8**. In a separate experiment carried out in acetic acid it was shown that the disulfide **7** also reacts slowly with bromine to give the resonance at −127.1 ppm attributed to the sulfenyl bromide. But due to its instability it re-forms **7** or is oxidized to **8**.

The thiol **2** reacts readily with pentafluorobenzenes C_6F_5R ($R = NO_2$, CN, CF_3, $OC_6F_4NO_2$) and pentafluoropyridine at room temperature in the presence of K_2CO_3 to give the monosubstituted (para) benzenes $CF_3C_6F_4OC_6F_4SC_6F_4R$ ($R = NO_2$ (**9**), CN (**10**), CF_3 (**11**)) and $CF_3C_6F_4OC_6F_4SC_5F_4N$ (**12**) (Scheme 4). When $R = NO_2$, the ortho-substituted product is also formed. In the case where $R = OC_6F_4NO_2$, replacement of the *p*-fluorine atom is not observed. Instead, the carbon atoms ortho as well as para to the nitro group are activated and the resulting products **9** (by loss of pentafluorophenolate) and $(2\text{-}CF_3C_6F_4OC_6F_4S)(4\text{-}C_6F_5O)C_6F_3NO_2$ (**13**) are isolated. The spectroscopic data for the former agree with the data for **9** isolated from the reaction of **2** with pentafluoronitrobenzene.

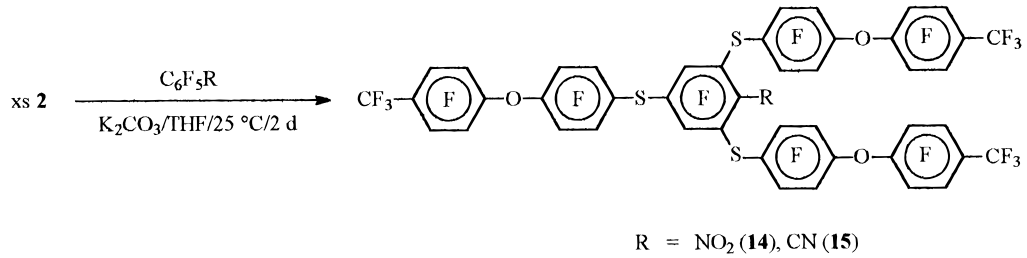
Multiple substitution is achieved by using an excess of **2** with pentafluoronitrobenzene and pentafluorobenzonitrile. As shown in Scheme 5, the 2,4,6-substituted nitrobenzene $(CF_3C_6F_4OC_6F_4S)_3C_6F_2NO_2$ (**14**) and benzonitrile $(CF_3C_6F_4OC_6F_4S)_3C_6F_2CN$ (**15**) are obtained.

Although the reaction to give the trisubstituted products **14** and **15** proceeds at ambient temperature, further substitution of **14** or **15** with **2** does not occur even under more vigorous conditions.

Scheme 4

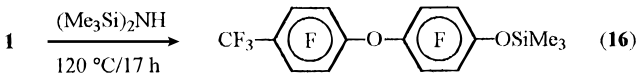


Scheme 5



R = NO_2 (**14**), CN (**15**)

Scheme 6



The phenol **1** reacts with hexamethyldisilazane to form the trimethylsilyl ether $CF_3C_6F_4OC_6F_4OSiMe_3$ (**16**) (Scheme 6).

With pentafluoronitrobenzene, **1** reacts to form $CF_3C_6F_4$-$OC_6F_4OC_6F_4NO_2$ (**17**) under the same conditions employed for the reaction with the sulfur derivative **2**. In this case, however, due to the decreased nucleophilicity of oxygen compared to sulfur, a longer time is required for the reaction to reach completion at 25 °C (Scheme 7).

The reaction time can be reduced by ~50% by using the trimethylsilyl ether **16** in place of **1**. Also at higher temperatures, the less reactive pentafluorobenzonitrile and pentafluoropyridine form monosubstituted derivatives $CF_3C_6F_4OC_6F_4$-OC_6F_4CN (**18**) and $CF_3C_6F_4OC_6F_4OC_5F_4N$ (**19**) (Scheme 8).

The synthesis of the trimethylsilyl derivative **5** prompted us to study the possibility of its use as a transfer agent for $CF_3C_6F_4$-OC_6F_4 groups similar to that described for CF_3SiMe_3[17] and C_6F_5-$SiMe_3$.[18] Compound **5** reacts with pentafluorobenzaldehyde or benzaldehyde in the presence of catalytic amounts of fluoride ion to give the secondary alcohols, $CF_3C_6F_4OC_6F_4CH(C_6H_5)OH$ (**20**) and $CF_3C_6F_4OC_6F_4CH(C_6F_5)OH$ (**21**). A byproduct $CF_3C_6F_4OC_6F_4CH(C_6F_5)OC_6F_4CHO$ (**22**) was detected and isolated from several other unidentified products in the reaction with pentafluorobenzaldehyde (Scheme 9). Its formation can be explained by the reaction of the alkoxide $CF_3C_6F_4$-$OC_6F_4CH(C_6F_5)O^-$ initially formed to displace the fluorine atom in the para position of C_6F_5CHO.

In addition to small amounts of the hydrolysis product $CF_3C_6F_4OC_6F_4H$, undesirable side reactions are observed. It appears that the reactive fluoride catalyst cleaves the aromatic ether bond. Evidence for this cleavage is found in ^{19}F NMR spectra. These signals are not observed when the reaction is carried out with benzaldehyde and $C_6F_5SiMe_3$ under the same conditions. This limits the use of **5** as an effective transfer agent for $CF_3C_6F_4OC_6F_4$ moieties into organic molecules. However, the products shown in Scheme 9 were isolated and purified by column chromatography.

Table 1 shows the influence of the substituent R on the ^{19}F NMR resonance of the *o*-fluorine atoms in some $CF_3C_6F_4OC_6F_4$ derivatives. The shifts range from −163.0 ppm for R = OH to −115.1 ppm for R = $Te_nC_6F_4OC_6F_4CF_3$. In addition to inductive effects, the size of the adjacent atom also plays a role; i.e., with increasing size of the atom adjacent to the *o*-F atom a downfield shift is observed. The shifts for X = H and SH seem to be exceptions.

Experimental Section

Materials. The solvents THF and diethyl ether are distilled over sodium prior to use. Cesium fluoride is dried and maintained at 160 °C. All other chemicals are used as received (Aldrich, Fluorochem, PCR).

General Considerations. A conventional vacuum system, consisting of a Pyrex glass vacuum line fitted with Teflon needle stopcocks and equipped with Heise Bourdon tube and Televac thermocouple gauges, is used to handle volatile liquids. Infrared spectra are recorded on a Perkin-Elmer 1710 FT-IR spectrometer between KBr plates as neat liquids or solids as Nujol mulls. NMR spectra are obtained on a Bruker AC200 or AC300 FT-NMR instrument using $CDCl_3$ as solvent except where otherwise indicated. Chemical shifts are reported with

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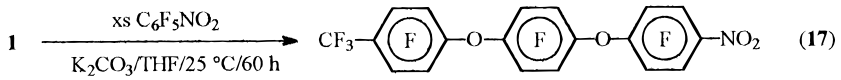
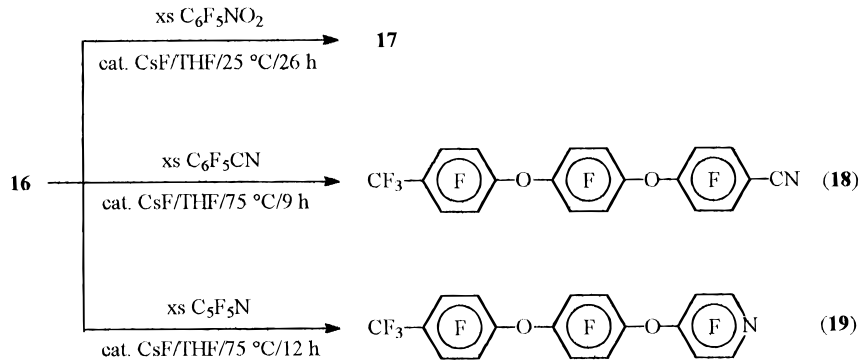
(18) Patel, N. R.; Kirchmeier, R. L. *Inorg. Chem.* **1992**, *31*, 2537 and references therein.

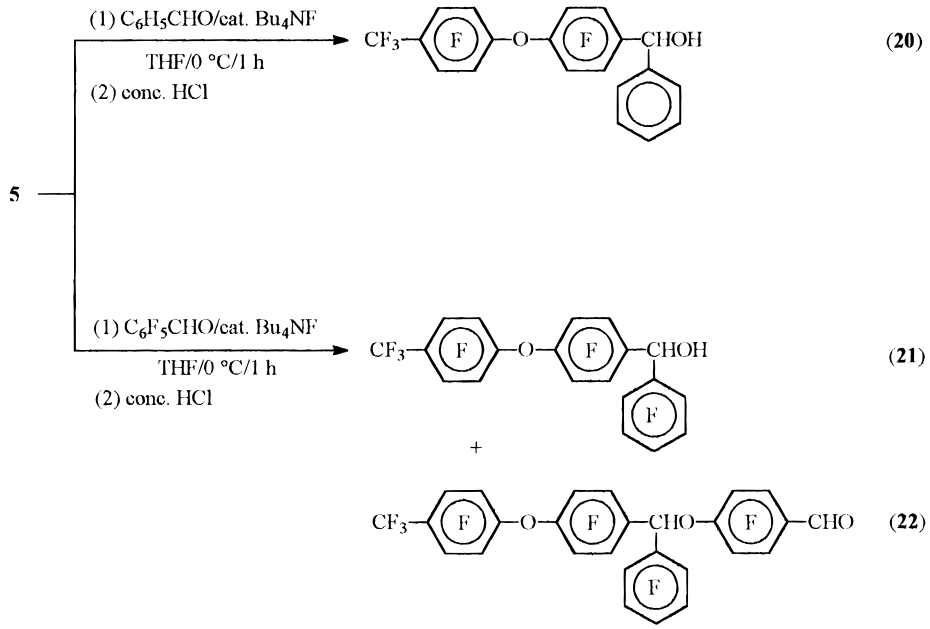
Scheme 7



Scheme 8



Scheme 9



respect to $(CH_3)_4Si$ (^1H, ^{13}C, ^{29}Si), $CFCl_3$ (^{19}F), $(CH_3)_2Se$ (^{77}Se), $(CH_3)_4Sn$ (^{119}Sn), and $(CH_3)_2Te$ (^{125}Te). Mass spectra are obtained with a Varian VG 7070 HS mass spectrometer by using electron impact (EI) techniques. Multi-isotope containing fragments refer to the isotope with the highest abundance. Elemental analyses are performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany. All reactions involving lithiations or silylated compounds are carried out in an atmosphere of dry nitrogen.

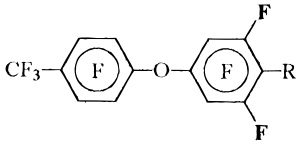
CAUTION! *Experiments involving solutions of $CF_3C_6F_4OC_6F_4Li$ should be handled with care, conducted at low temperatures and under strict exclusion of oxygen and/or moisture!*

Preparation of $CF_3C_6F_4OC_6F_4OH$. To R_FLi (R_F = $CF_3C_6F_4OC_6F_4$),[5] generated by lithiation of 10 mmol of $CF_3C_6F_4OC_6F_4H$ in 80 mL of ether, is added 13 mmol of trimethyl borate at −50 °C. The mixture is warmed with stirring to −10 °C in 2 h; 30 mL of 50% hydrogen peroxide is then added and the mixture warmed to 25 °C and stirred for 1.5 days (under air). After phase separation, the aqueous phase is extracted with dichloromethane. The combined organic phases are dried over anhydrous Na_2SO_4. The solvents are removed under vacuum, and the crude product is sublimed at 50 °C/0.01 Torr. The resulting mixture, consisting of R_FOH (**1**)/R_FH in a relative ratio of ∼2:1, is extracted several times with *n*-hexane, where the hydroaromatic is very soluble, but **1** is not. This purified phenol $CF_3C_6F_4OC_6F_4OH$ (**1**) sublimes at 50 °C/0.01 Torr and crystallizes as a hydrate in 47% yield (mp 74−78 °C) with a typical slightly phenolic odor.

Spectral data for 4-(4′-$CF_3C_6F_4O$)C_6F_4OH (1): IR (Nujol/KBr) 3400 m vbr (ν_{OH}), 1657 m, 1531 s, 1510 s, 1500 s, 1466 m, 1428 w, 1352 s, 1310 w, 1229 m, 1188 m, 1156 s, 1090 m, 1042 w, 1012 s, 1000 s, 980 s, 880 m, 807 w, 782 w, 721 m cm^{-1}; ^{19}F NMR δ −56.2 (4′-CF_3, t, 3F, $^4J_{F-F}$ = 21.5 Hz), −140.0 (3′-F, m, 2F), −155.3 (2′-F, m, 2F), −157.5 (3-F, m, 2F), −163.0 (2-F, m, 2F); ^1H NMR δ 5.9 (OH, br, 1H), 2.1 (H_2O, br) ppm; MS (EI) [*m/e* (species, intensity)] 398 (M^+, 62), 379 (M^+ − F, 14), 351 (M^+ − F − CO, 1), 329 (M^+ − CF_3, 1), 301 (M^+ − CF_3 − CO, 1), 217 ($CF_3C_6F_4^+$, 8), 181 ($OC_6F_4OH^+$, 100), 161 ($OC_6F_3O^+$, 12), 148 ($C_6F_4^+$, 5), 137 ($C_5F_4H^+$, 8), 117 ($C_5F_3^+$, 14), 105 ($C_4F_3^+$, 16), 69 (CF_3^+, 15). Anal. Calcd for $C_{13}H_3F_{11}O_3$ (monohydrate): C, 37.52; H, 0.73. Found: C, 37.42; H, 0.48.

Reaction of $CF_3C_6F_4OC_6F_4Li$ with Sulfur and Selenium. To R_F-Li,[5] generated by lithiation of 10 mmol of $CF_3C_6F_4OC_6F_4H$ in 80 mL of ether, is added 15 mmol of sulfur (selenium powder) at −50 °C. After 1 h of stirring at that temperature, the mixture is warmed to 0 °C in 2 h and treated with 10 mL of 10% H_2SO_4 and 20 mL of water. Stirring is continued for 30 min at 25 °C, and the phases are separated and filtered from unreacted sulfur (selenium). After extraction with ether/water, the combined ether phases are dried over anhydrous Na_2SO_4. The solvent is removed under vacuum and the residue sublimed. The thiol $CF_3C_6F_4OC_6F_4SH$ (**2**) sublimes at 40 °C/0.01 Torr to give colorless crystals with an unpleasant odor in 82% yield (mp 55−57 °C). The yellow, odorless diselenide $(CF_3C_6F_4OC_6F_4Se)_2$ (**3**) sublimes

Table 1. ^{19}F NMR ($CDCl_3$) Resonances *ortho* to R in $CF_3C_6F_4OC_6F_4R$ Derivatives



R	δ (ppm)	R	δ (ppm)
OH	−163.0	$C(CF_3)_2OH$[a]	−135.0
F[a]	−161.1	SO_2Br	−134.4
$OSi(CH_3)_3$	−158.3	$SSC_6F_4OC_6F_4CF_3$	−131.1
$OC_6F_4NO_2$	−154.9	$SC_6F_4CF_3$	−131.0
OC_6F_4CN	−154.9	$SC_6F_4NO_2$	−130.8
OC_5F_4N	−154.8	SC_6F_4CN	−130.8
$CH(C_6F_5)OH$	−142.9	SC_5F_4N	−130.4
$CH(C_6H_5)OH$	−142.7	SBr[b]	−127.1
$C(C_6F_5)_2OH$[a]	−139.9	$Si(CH_3)_3$	−127.1
H[a]	−137.8	$SeSeC_6F_4OC_6F_4CF_3$	−125.0
SH	−136.6	$Sn(CH_3)_3$	−121.3
$C(C_6H_5)_2OH$[a]	−136.2	$Te_nC_6F_4OC_6F_4CF_3$[b]	−115.1

[a] Reference 5. [b] Not isolated, $n = 1$ or 2.

at 130 °C/0.01 Torr in 80% yield (mp 103−105 °C). Thin yellow needles are obtained upon recrystallization from ethanol or *n*-propanol.

Spectral data for 4-(4′-$CF_3C_6F_4O$)C_6F_4SH (2): IR (Nujol/KBr) 2605 w (ν_{SH}), 1659 m, 1634 m, 1497 s, 1463 s, 1344 m, 1284 w, 1227 m, 1190 m, 1157 m, 1118 m, 1032 m, 1017 m, 1001 s, 980 m, 923 m, 882 m, 862 w, 799 w, 718 m, 640 w cm^{-1}; ^{19}F NMR δ −56.2 (4′-CF_3, t, 3F, $^4J_{F-F} = 21.6$ Hz), −136.6 (2-F, m, 2F), −139.8 (3′-F, m, 2F), −154.9 (2′-F, m, 2F), −155.8 (3-F, m, 2F); ^1H NMR δ 3.70 (SH, s, 1H) ppm; MS (EI) [*m/e* (species, intensity)] 414 (M^+, 100), 413 ($M^+ - H$, 16), 395 ($M^+ - F$, 13), 367 ($M^+ - F - CO$, 1), 249 ($M^+ - H - C_6F_4O$, 6), 217 ($CF_3C_6F_4^+$, 10), 197 ($OC_6F_4SH^+$, 61), 181 ($C_6F_4SH^+$, 24), 169 ($C_5F_4SH^+$, 7), 165 ($C_6F_4HO^+$, 12), 155 ($C_5F_5^+$, 5), 149 ($C_5F_3S^+$, 11), 137 ($C_4F_3S^+$, 19), 131 ($C_5F_2SH^+$, 6), 117 ($C_5F_3^+$, 13), 93 ($C_3F_3^+$, 9). Anal. Calcd for $C_{13}HF_{11}OS$: C, 37.69; H, 0.24. Found: C, 37.57; H, 0.25.

Spectral data for [4-(4′-$CF_3C_6F_4O$)C_6F_4Se]$_2$ (3): IR (Nujol/KBr) 1660 m, 1631 m, 1505 s, 1484 s, 1431 m, 1392 m, 1343 m, 1278 w, 1229 m, 1190 m, 1155 s, 1116 m, 1028 m, 999 s, 975 s, 878 m, 824 w, 800 m, 718 m, 674 w, 642 w, 632 w cm^{-1}; ^{19}F NMR δ −56.2 (4′-CF_3, t, 3F, $^4J_{F-F} = 21.6$ Hz), −125.0 (2-F, m, 2F), −139.5 (3′-F, m, 2F), −154.1 (2′-F, m, 2F), −154.7 (3-F, m, 2F); ^{77}Se NMR δ 376 (t, 2Se, $^3J_{Se-F} = 19.9$ Hz) ppm; MS (EI) [*m/e* (^{80}Se) (species, intensity)] 922 (M^+, 20), 903 ($M^+ - F$, 2), 842 ($M^+ - Se$, 17), 823 ($M^+ - Se - F$, 2), 762 ($M^+ - 2Se$, 6), 461 ($M^+/2$, 100), 442 ($M^+/2 - F$, 8), 381 ($M^+/2 - Se$, 62), 362 ($M^+/2 - Se - F$, 14), 297 ($CF_3C_6F_4Se^+$, 10), 244 ($OC_6F_4Se^+$, 32), 228 ($C_6F_4Se^+$, 17), 217 ($CF_3C_6F_4^+$, 15), 164 ($C_6F_4O^+$, 14), 148 ($C_6F_4^+$, 15), 117 ($C_5F_3^+$, 30). Anal. Calcd for $C_{26}F_{22}O_2Se_2$: C, 33.93; F, 45.43. Found: C, 34.13; F, 45.3.

Reaction of $CF_3C_6F_4OC_6F_4Li$ with Tellurium. To R_FLi,[5] generated by lithiation of 5 mmol of $CF_3C_6F_4OC_6F_4H$ in 40 mL of ether, is added 5 mmol of tellurium powder at −50 °C, and the mixture is warmed to 25 °C in 1 h. The mixture is then stirred for an additional 24 h at 25 °C and treated with 5 mL of water. (Shorter reaction times result in inseparable mixtures of $(CF_3C_6F_4OC_6F_4Te)_2$ and **4**). The unreacted tellurium is filtered off, and the remaining solution is extracted with ether/water. After removal of all volatile materials, the residue is heated up to 100 °C/0.01 Torr in the presence of a sublimation finger. All condensable material is discarded. The remaining residue is washed thoroughly with hexane. The residue, soluble in chloroform, is a mixture of two compounds in a ratio of ∼10:1 based on the ^{19}F NMR spectrum. The components are separated and purified by column chromatography using dichloromethane/hexane (1:4) as eluent on silica gel (70−230 mesh). The compounds, based on spectroscopic data and elemental analysis, are identified as $(CF_3C_6F_4OC_6F_3Te)_2$ (**4**) (mp 152 °C dec, yellow-greenish powder, major component, ∼10% yield) and $(CF_3C_6F_4OC_6F_3)_2Te$ (**4a**) (mp 159−161 °C, yellowish powder, minor component, traces, shorter retention time).

Spectral data for [4-(4′-$CF_3C_6F_4O$)C_6F_3Te]$_2$ (4): IR (Nujol/KBr) 1658 m, 1603 m, 1510 s, 1466 s, 1426 s, 1344 s, 1279 w, 1263 w, 1229 m, 1191 m, 1164 m, 1146 m, 1113 m, 1066 m, 996 s, 877 m, 821 m, 801 w, 770 w, 750 w, 738 w, 718 m, 683 w, 644 w, 594 w cm^{-1}; ^{19}F NMR δ −56.1 (4′-CF_3, t, 3F, $^4J_{F-F} = 21.6$ Hz), −102.1 (2-F, dm, 1F), −107.7 (6-F, dd, 1F, $^3J_{F-F} = 23.6$ Hz, $^4J_{F-F} = 13.2$ Hz), −139.8 (3′-F, m, 2F), −145.5 (5-F, dm, 1F), −154.6 (2′-F, m, 2F); ^{125}Te NMR δ 739 (m) ppm; MS (EI) [*m/e* (^{130}Te) (species, intensity)] 984 (M^+, 100), 965 ($M^+ - F$, 8), 854 ($M^+ - Te$, 91), 637 ($M^+ - Te - CF_3C_6F_4$, 14), 621 ($M^+ - Te - CF_3C_6F_4O$, 12), 609 ($M^+ - Te - CF_3C_6F_4 - CO$, 23), 492 ($CF_3C_6F_4OC_6F_3Te^+$, 19), 389 ($C_6F_3Te_2^+$, 15), 377 ($C_5F_3Te_2^+$, 8), 259 ($C_6F_3Te^+$, 67), 233 ($CF_3C_6F_4O^+$, 16). Anal. Calcd for $C_{26}F_{20}O_2Te_2$: C, 31.88; F, 38.80. Found: C, 31.88; F, 40.0.

Spectral data for [4-(4′-$CF_3C_6F_4O$)C_6F_3]$_2$Te (4a): IR (Nujol/KBr) 1659 m, 1622 m, 1505 s, 1462 s, 1341 s, 1278 w, 1224 m, 1193 m, 1155 m, 1113 m, 1074 w, 1058 m, 992 s, 931 w, 880 m, 831 w, 813 w, 718 m, 612 w cm^{-1}; ^{19}F NMR δ −56.1 (4′-CF_3, t, 3F, $^4J_{F-F} = 21.6$ Hz), −115.0 (2-F, m, 1F), −126.0 (6-F, m, 1F), −139.8 (3′-F, m, 2F), −148.3 (5-F, m, 1F), −154.5 (2′-F, m, 2F); ^{125}Te NMR δ 778 (s) ppm; MS (EI) [*m/e* (^{130}Te) (species, intensity)] 854 (M^+, 100), 835 ($M^+ - F$, 11), 724 ($M^+ - Te$, 2), 637 ($M^+ - CF_3C_6F_4$, 6), 621 ($M^+ - CF_3C_6F_4O$, 10), 609 ($M^+ - CF_3C_6F_4 - CO$, 10), 404 ($M^+ - 2CF_3C_6F_4 - O$, 13), 388 ($M^+ - 2CF_3C_6F_4O$, 17), 233 ($CF_3C_6F_4O^+$, 18), 217 ($CF_3C_6F_4^+$, 8). Anal. Calcd for $C_{26}F_{20}O_2Te$: C, 36.66. Found: C, 36.91.

Reaction of $CF_3C_6F_4OC_6F_4Li$ with Trimethylsilyl (or Trimethyltin) Chloride. To R_FLi, [5] generated by lithiation of 10 (or 2) mmol of $CF_3C_6F_4OC_6F_4H$ in 80 (or 10) mL of ether, is added 14 (or 3) mmol of trimethylsilyl (or trimethyltin) chloride at −50 °C, and the mixture is warmed up to 25 °C and stirred for 2 h. The solvent is removed in a slight vacuum and the residue slowly sublimed at 25−40 °C/0.01 Torr. Sublimation at 30 °C/0.01 Torr for final purification gives colorless, volatile crystals of $CF_3C_6F_4OC_6F_4SiMe_3$ (**5**, mp 32−34 °C) in 77% yield [or $CF_3C_6F_4OC_6F_4SnMe_3$ (**6**, mp 34−36 °C) in 64% yield].

Spectral data for 4-(4′-$CF_3C_6F_4O$)$C_6F_4Si(CH_3)_3$ (5): IR (liquid film/KBr) 2964 m/2908 m (ν_{CH}), 1660 m, 1636 m, 1559 w, 1510 s, 1456 s, 1431 m, 1373 m, 1344 s, 1258 m, 1227 s, 1189 m, 1153 s, 1118 s, 1030 s, 1001 s, 971 s, 850 s, 817 m, 795 m, 772 m, 740 w, 730 w, 716 m, 635 m cm^{-1}; ^{19}F NMR δ −56.1 (4′-CF_3, t, 3F, $^4J_{F-F} = 21.6$ Hz), −127.1 (2-F, m, 2F), −140.1 (3′-F, m, 2F), −154.7 (2′-F, m, 2F), −156.3 (3-F, m, 2F); ^1H NMR δ 0.39 ($SiMe_3$, t, 9H, $^5J_{H-F} = 1.5$ Hz); $^{29}Si\{^1H\}$ NMR δ −0.62 (tt, $^3J_{Si-F} = 2.9$ Hz, $^4J_{Si-F} = 1.9$ Hz) ppm; MS (EI) [*m/e* (species, intensity)] 454 (M^+, 23), 439 ($M^+ - CH_3$, 52), 435 ($M^+ - F$, 17), 373 ($M^+ - CH_3SiF_2$, 15), 362 ($M^+ - (CH_3)_3SiF$, 6), 343 ($M^+ - F - (CH_3)_3SiF$, 10), 339 ($M^+ - F - (CH_3)_2SiF_2$, 17), 270 ($M^+ - F - (CH_3)_2SiF_2 - CF_3$, 10), 242 ($C_9F_7H^+$, 34), 206 ($M^+ - CH_3 - CF_3C_6F_4O$, 20), 148 ($C_6F_4^+$, 3), 117 ($C_5F_3^+$, 12), 81 ($CH_3SiF_2^+$, 42), 77 ($(CH_3)_2SiF^+$, 100), 73 ($(CH_3)_3Si^+$, 18), 69 ($CF_3^+$, 10). Anal. Calcd for $C_{16}H_9F_{11}OSi$: C, 42.29; H, 2.00. Found: C, 42.35; H, 2.10.

Spectral data for 4-(4′-$CF_3C_6F_4O$)$C_6F_4Sn(CH_3)_3$ (6): IR (Nujol/KBr) 1658 m, 1633 m, 1510 s, 1485 s, 1368 m, 1343 s, 1278 w, 1258 w, 1227 s, 1190 m, 1156 s, 1113 m, 1060 w, 1024 m, 1000 s, 964 s, 876 m, 783 m, 737 w, 717 m, 639 m, 539 s, 517 cm^{-1}; ^{19}F NMR δ −56.1 (4′-CF_3, t, 3F, $^4J_{F-F} = 21.6$ Hz), −121.3 (2-F, m, 2F), −140.3 (3′-F, m, 2F), −154.9 (2′-F, m, 2F), −155.2 (3-F, m, 2F); ^1H NMR δ 0.47 ($SnMe_3$, t, 9H, $^5J_{H-F} = 0.7$ Hz, $^2J_{H-119Sn} = 59.2$ Hz (dt), $^2J_{H-117Sn} = 56.6$ Hz (dt)); $^{119}Sn\{^1H\}$ NMR δ −13.5 (tt, $^3J_{Sn-F} = 21.4$ Hz, $^4J_{Sn-F} = 8.3$ Hz); $^{13}C\{^1H\}$ NMR δ 148.7 ($^1J_{C-F} = 236$ Hz)/144.9 ($^1J_{C-F} = 264$ Hz)/140.3 ($^1J_{C-F} = 248$ Hz)/139.2 ($^1J_{C-F} = 256$ Hz) (CF, dm), 138.0/134.4 (2 CO, m), 120.7 (CF_3, q, $^1J_{C-F} = 275$ Hz), 113.6 (CSn, tm, $^2J_{C-F} = 47.9$ Hz), 105.7 (CCF_3, m), −7.5 (CH_3, t, $^4J_{C-F} = 2.1$ Hz, $^1J_{C-119Sn} = 381.5$ Hz (dt), $^1J_{C-117Sn} = 364.4$ Hz (dt)) ppm; MS (EI) [*m/e* (^{120}Sn) (species, intensity)] 531 ($M^+ - CH_3$, 100), 527 ($M^+ - F$, 15), 501 ($M^+ - 3CH_3$, 4), 362 ($M^+ - (CH_3)_3SnF$, 8), 343 ($M^+ - F - (CH_3)_3SnF$, 90), 265 ($M^+ - (CH_3)_3SnF - CF_3 - CO$, 13), 217 ($CF_3C_6F_4^+$, 6), 173 ($CH_3SnF_2^+$, 15), 169 ($(CH_3)_2SnF^+$, 62), 148 ($C_6F_4^+$, 7), 139 ($SnF^+$, 44), 135 ($SnCH_3^+$, 13), 117 ($C_5F_3^+$, 26), 69 ($CF_3^+$, 10). Anal. Calcd for $C_{16}H_9F_{11}OSn$: C, 35.26; H, 1.67. Found: C, 35.38; H, 1.75.

Reaction of 2 with Bromine. To 1 mmol of **2** in 5 mL of glacial acetic acid is added 5 mmol of bromine at 25 °C. After 1 h of stirring, **2** has reacted completely according to ^{19}F NMR. A mixture consisting

of R_FSBr (δ −127.1(2-F)), R_FSSR_F (**7**) (δ −131.1(2-F)), and R_FSO_2Br (**8**) (δ −134.5(2-F)) is formed. Adding more bromine results in increased yields of R_FSBr and **8**. Removal of the volatile materials after 2 days at 25 °C leads to debromination of the intermediate R_F-SBr to give **7**. The resulting mixture of **7** and **8** is separated by slow sublimation at 60 °C/0.01 Torr. The yields based on **2** are 24% for $(CF_3C_6F_4OC_6F_4S)_2$ (**7**, mp 105−107 °C, subl 90 °C/0.01 Torr) and 21% for $CF_3C_6F_4OC_6F_4SO_2Br$ (**8**, mp 77−79 °C, subl 50 °C/0.01 Torr).

Spectral data for [4-(4′-$CF_3C_6F_4O$)C_6F_4S]$_2$ (7): IR (Nujol/KBr) 1661 m, 1634 m, 1506 s, 1487 s, 1466 m, 1431 m, 1398 w, 1343 m, 1283 w, 1230 m, 1190 m, 1156 m, 1135 m, 1119 m, 1031 m, 1001 s, 980 m, 881 m, 857 w, 806 w, 718 m, 674 w, 651 w cm^{-1}; ^{19}F NMR δ −56.1 (4′-CF_3, t, 3F, $^4J_{F-F}$ = 21.6 Hz), −131.1 (2-F, m, 2F), −139.4 (3′-F, m, 2F), −154.1 (2′-F, m, 2F), −154.6 (3-F, m, 2F) ppm; MS (EI) [*m/e* (species, intensity)] 826 (M^+, 4), 413 ($M^+/2$, 100), 394 ($M^+/2$ − F, 12), 381 ($M^+/2$ − S, 7), 362 ($M^+/2$ − S − F, 3), 217 ($CF_3C_6F_4^+$, 20), 196 ($OC_6F_4S^+$, 48), 180 ($C_6F_4S^+$, 31), 164 ($C_6F_4O^+$, 11), 149 ($C_5F_3S^+$, 21), 148 ($C_6F_4^+$, 8), 137 ($C_4F_3S^+$, 30), 117 ($C_5F_3^+$, 17). Anal. Calcd for $C_{26}F_{22}O_2S_2$: C, 37.79; F, 50.58. Found: C, 37.90; F, 50.3.

Spectral data for 4-(4′-$CF_3C_6F_4O$)$C_6F_4SO_2Br$ (8): IR (Nujol/KBr) 1661 m, 1635 m, 1511 s, 1465 m, 1433 m, 1394 m ($\nu_{asymSO2}$), 1343 m, 1296 m, 1274 w, 1222 m, 1195 m, 1176 s (ν_{symSO2}), 1126 m, 1071 w, 1035 m, 1007 m, 994 m, 879 m, 851 m, 807 w, 734 w, 716 m, 683 w, 655 m, 640 w, 577 m, 558 m, 547 m cm^{-1}; ^{19}F NMR δ −56.2 (4′-CF_3, t, 3F, $^4J_{F-F}$ = 21.6 Hz), −134.4 (2-F, m, 2F), −138.5 (3′-F, m, 2F), −152.2 (2′-F, m, 2F), −153.7 (3-F, m, 2F) ppm; MS (EI) [*m/e* (^{79}Br) (species, intensity)] 524 (M^+, 1), 505 (M^+ − F, 4), 460 (M^+ − SO_2, 26), 445 (M^+ − Br, 100), 441 (M^+ − SO_2 − F, 3), 429 (M^+ − Br − O, 4), 397 (M^+ − SO - Br, 18), 381 (M^+ − SO_2Br, 27), 362 (M^+ − SO_2Br − F, 22), 353 (M^+ − SO_2Br − CO, 21), 303 (M^+ − SO_2Br − CO − CF_2, 14), 217 ($CF_3C_6F_4^+$, 28), 149 ($C_5F_3S^+$, 33), 148 ($C_6F_4^+$, 61), 137 ($C_4F_3S^+$, 22), 117 ($C_5F_3^+$, 45), 105 ($C_4F_3^+$, 16), 93 ($C_3F_3^+$, 19), 69 (CF_3^+, 29), 64 (SO_2^+, 87), 48 (SO^+, 27). Anal. Calcd for $C_{13}BrF_{11}O_3S$: C, 29.73; F, 39.80. Found: C, 29.09; F, 38.8.

Reaction of 2 with Pentafluorobenzenes C_6F_5R (R = NO_2, CN, CF_3) and Pentafluoropyridine. To a mixture consisting of 0.5 mmol of **2** and 1 mmol of pentafluoronitrobenzene, pentafluorobenzonitrile, octafluorotoluene, or pentafluoropyridine in 5 mL of THF is added 1 mmol of anhydrous K_2CO_3 at 25 °C. After 1 h of stirring (^{19}F NMR monitoring), all volatile materials are removed in vacuum and the residue is sublimed at 70−100 °C/0.01 Torr. The yields are 80% for $CF_3C_6F_4OC_6F_4SC_6F_4NO_2$ (**9**, mp 125−127 °C, subl 80 °C/0.01 Torr), 82% for $CF_3C_6F_4OC_6F_4SC_6F_4CN$ (**10**, mp 108−110 °C, subl 100 °C/0.01 Torr), 63% for $CF_3C_6F_4OC_6F_4SC_6F_4CF_3$ (**11**, mp 93−95 °C, subl 90 °C/0.01 Torr), and 71% for $CF_3C_6F_4OC_6F_4SC_5F_4N$ (**12**, mp 92−94 °C, subl 70 °C/0.01 Torr).

Spectral data for 4-[4′-(4″-$CF_3C_6F_4O$)C_6F_4S]$C_6F_4NO_2$ (9): IR (Nujol/KBr) 1662 m, 1635 m, 1556 m ($\nu_{asymNO2}$), 1509 s, 1485 s, 1404 w, 1348 m (ν_{symNO2}), 1283 w, 1264 m, 1226 m, 1191 m, 1158 m, 1120 m, 1033 m, 1004 m, 979 m, 882 m, 860 m, 803 w, 792 w, 761 m, 718 m, 702 w, 652 w, 635 w cm^{-1}; ^{19}F NMR δ −56.2 (4″-CF_3, t, 3F, $^4J_{F-F}$ = 21.6 Hz), −129.7 (3-F, m, 2F), −130.8 (2′-F, m, 2F), −139.2 (3″-F, m, 2F), −144.9 (2-F, m, 2F), −153.8 (2″-F, m, 2F), −154.3 (3′-F, m, 2F) ppm; MS (EI) [*m/e* (species, intensity)] 607 (M^+, 4), 577 (M^+ − NO, 19), 561 (M^+ − NO_2, 2), 413 (M^+ − $C_6F_4NO_2$, 1), 344 (M^+ − $C_6F_4NO_2$ − CF_3, 3), 217 ($CF_3C_6F_4^+$, 5), 196 ($OC_6F_4S^+$, 19), 149 ($C_5F_3S^+$, 4), 69 (CF_3^+, 27). Anal. Calcd for $C_{19}F_{15}NO_3S$: C, 37.58; F, 46.93. Found: C, 37.60; F, 47.1.

Spectral data for 4-[4′-(4″-$CF_3C_6F_4O$)C_6F_4S]C_6F_4CN (10): IR (Nujol/KBr) 2242 w ($\nu_{C\equiv N}$), 1660 m, 1641 m, 1512 s, 1481 s, 1466 s, 1409 m, 1346 m, 1293 m, 1228 m, 1190 m, 1161 m, 1117 m, 1034 m, 997 m, 975 s, 881 m, 859 m, 843 m, 718 m, 657 w, 637 w cm^{-1}; ^{19}F NMR δ −56.2 (4″-CF_3, t, 3F, $^4J_{F-F}$ = 21.6 Hz), −130.8 (2-F, 3-F, 2′-F, m, 6F), −139.2 (3″-F, m, 2F), −153.8 (2″-F, m, 2F), −154.4 (3′-F, m, 2F) ppm; MS (EI) [*m/e* (species, intensity)] 587 (M^+, 100), 568 (M^+ − F, 8), 518 (M^+ − CF_3, 1), 413 (M^+ − C_6F_4CN, 5), 370 (M^+ − $CF_3C_6F_4$, 28), 354 (M^+ − $CF_3C_6F_4O$, 3), 217 ($CF_3C_6F_4^+$, 6), 196 ($OC_6F_4S^+$, 1), 180 ($C_6F_4S^+$, 3), 148 ($C_6F_4^+$, 4), 124 ($C_5F_2CN^+$, 4), 117 ($C_5F_3^+$, 8), 93 ($C_3F_3^+$, 4), 69 (CF_3^+, 4). Anal. Calcd for $C_{20}F_{15}$-NOS: C, 40.90; F, 48.53. Found: C, 41.04; F, 48.3.

Spectral data for 4-[4′-(4″-$CF_3C_6F_4O$)C_6F_4S]$C_6F_4CF_3$ (11): IR (Nujol/KBr) 1658 m, 1647 m, 1512 m, 1500 s, 1482 s, 1430 m, 1344 m, 1330 m, 1283 w, 1262 w, 1227 m, 1189 m, 1165 s, 1117 m, 1034 w, 998 m, 977 s, 880 m, 860 w, 831 w, 718 m, 704 w, 668 w cm^{-1}; ^{19}F NMR δ −56.2 (4″-CF_3, t, 3F, $^4J_{F-F}$ = 21.6 Hz), −56.6 (1-CF_3, t, 3F, $^4J_{F-F}$ = 21.6 Hz), −131.0 (2′-F, m, 2F), −131.8 (3-F, m, 2F), −138.7 (2-F, m, 2F), −139.3 (3″-F, m, 2F), −154.1 (2″-F, m, 2F), −154.4 (3′-F, m, 2F) ppm; MS (EI) [*m/e* (species, intensity)] 630 (M^+, 100), 611 (M^+ − F, 18), 561 (M^+ − CF_3, 1), 413 (M^+ − $CF_3C_6F_4$, 35), 397 (M^+ − $CF_3C_6F_4O$, 3), 378 (M^+ − $CF_3C_6F_4O$ − F, 4), 217 ($CF_3C_6F_4^+$, 5), 180 ($C_6F_4S^+$, 4), 149 ($C_5F_3S^+$, 32), 117 ($C_5F_3^+$, 6), 69 (CF_3^+, 11). Anal. Calcd for $C_{20}F_{18}OS$: C, 38.11; F, 54.26. Found: C, 38.20; F, 54.5.

Spectral data for 4-[4′-(4″-$CF_3C_6F_4O$)C_6F_4S]C_5F_4N (12): IR (Nujol/KBr) 1660 m, 1635 m, 1510 s, 1489 s, 1465 s, 1446 m, 1408 w, 1344 m, 1289 w, 1238 m, 1226 m, 1191 m, 1160 m, 1126 w, 1036 w, 999 m, 979 m, 959 m, 891 m, 881 m, 801 w, 717 m, 699 w, 651 w, 636 w, 585 m cm^{-1}; ^{19}F NMR δ −56.2 (4″-CF_3, t, 3F, $^4J_{F-F}$ = 21.7 Hz), −88.8 (2-F, m, 2F), −130.4 (2′-F, m, 2F), −137.5 (3-F, m, 2F), −139.2 (3″-F, m, 2F), −153.9 (2″-F, m, 2F), −154.4 (3′-F, m, 2F) ppm; MS (EI) [*m/e* (species, intensity)] 563 (M^+, 100), 544 (M^+ − F, 11), 518 (M^+ − FCN, 1), 494 (M^+ − CF_3, 2), 413 (M^+ − C_5F_4N, 7), 346 (M^+ − $CF_3C_6F_4$, 29), 330 (M^+ − $CF_3C_6F_4O$, 6), 311 (M^+ − $CF_3C_6F_4O$ − F, 5), 217 ($CF_3C_6F_4^+$, 8), 196 ($OC_6F_4S^+$, 2), 180 ($C_6F_4S^+$, 4), 149 ($C_5F_3S^+$, 3), 148 ($C_6F_4^+$, 3), 117 ($C_5F_3^+$, 4), 69 (CF_3^+, 3). Anal. Calcd for $C_{18}F_{15}NOS$: C, 38.38; F, 50.60. Found: C, 38.33; F, 50.4.

Reaction of 2 with 4-Nitroperfluorodiphenyl ether. To a mixture consisting of 0.5 mmol of **2** and 0.6 mmol of $C_6F_5OC_6F_4NO_2$ (**10** in ref 5) in 5 mL THF is added 1 mmol anhydrous K_2CO_3 at 25 °C. After 1 h of stirring (^{19}F NMR monitoring), all volatile materials are removed in vacuum, and the residue, which contains equimolar amounts of **9** and 2-[($CF_3C_6F_4O$)C_6F_4S](4-C_6F_5O)$C_6F_3NO_2$ (**13**), is slowly sublimed at 80 °C/0.01 Torr. The less volatile **13** sublimes at 130 °C/0.01 Torr (26%, mp 103−105 °C).

Spectral data for 2-[4′-(4″-$CF_3C_6F_4O$)C_6F_4S](4-C_6F_5O)$C_6F_3NO_2$ (13): IR (Nujol/KBr) 1659 m, 1635 m, 1616 m, 1553 m ($\nu_{asymNO2}$), 1518 s, 1495 s, 1464 s, 1410 w, 1368 m (ν_{symNO2}), 1344 m, 1320 w, 1273 m, 1231 m, 1199 m, 1161 m, 1126 m, 1110 m, 1066 m, 1032 m, 990 s, 936 m, 882 m, 859 m, 809 w, 760 m, 718 m, 650 m cm^{-1}; ^{19}F NMR δ −56.2 (4″-CF_3, t, 3F, $^4J_{F-F}$ = 22.2 Hz), −121.1 (3-F, m, 1F), −131.8 (2′-F, m, 2F), −139.3 (3″-F, m, 2F), −142.3 (6-F, m, 1F), −143.9 (5-F, m, 1F), −153.9 (2″-F, m, 2F), −154.7 (3′-F, m, 2F), −156.2 (2‴-F, m, 2F), −157.8 (4‴-F, t, 1F, $^3J_{F-F}$ = 21.9 Hz), −160.8 (3‴-F, m, 2F) ppm; MS (EI) [*m/e* (species, intensity)] 771 (M^+, 16), 752 (M^+ − F, 7), 741 (M^+ − NO, 44), 721 (M^+ − CF_2, 31), 706 (M^+ − F − NO_2, 2), 701 (M^+ − CF_3, 1), 687 (M^+ − 2F − NO_2, 2), 606 (M^+ − CF_3 − NO_2 − CF_2, 2), 574 (M^+ − C_6F_5 − NO, 16), 554 (M^+ − $CF_3C_6F_4$, 11), 524 (M^+ − $CF_3C_6F_4$ − NO, 7), 474 (M^+ − $CF_3C_6F_4$ − NO − CF_2, 100), 217 ($CF_3C_6F_4^+$, 5), 196 ($OC_6F_4S^+$, 19), 149 ($C_5F_3S^+$, 4), 69 (CF_3^+, 27). Anal. Calcd for $C_{25}F_{19}NO_4S$: C, 38.93; F, 46.80. Found: C, 39.00; F, 46.8.

Reaction of Excess 2 with Pentafluorobenzenes C_6F_5R (R = NO_2, CN). To a mixture consisting of 0.5 mmol of pentafluoronitrobenzene or pentafluorobenzonitrile and 3 mmol of **2** in 10 mL of THF is added 3 mmol of anhydrous K_2CO_3 at 25 °C. The ^{19}F NMR shows that, after 1 h of stirring, no C_6F_5R or monosubstituted **9** or **10** is present. After 2 days of stirring at 25 °C, the colorless precipitate (R = NO_2), identified as the tris-substituted nitrobenzene $(R_FS)_3C_6F_2NO_2$ **14**, is filtered and washed with THF and water. When R = CN, the solution is filtered from the inorganic salts, and all volatile materials are removed in vacuum. The remaining residue is washed with small portions of ether. The yields are 20% for $(CF_3C_6F_4OC_6F_4S)_3C_6F_2NO_2$ (**14**, mp 211−213 °C) and 35% for $(CF_3C_6F_4OC_6F_4S)_3C_6F_2CN$ (**15**, mp 161−163 °C, pale yellow).

Spectral data for 2,4,6-[4′-(4″-$CF_3C_6F_4O$)C_6F_4S]$_3C_6F_2NO_2$ (14): IR (Nujol/KBr) 1659 m, 1635 m, 1505 s, 1485 s, 1465 m, 1398 m, 1352 m (ν_{symNO2}), 1344 m, 1282 w, 1230 s, 1189 m, 1154 m, 1122 m, 1035 w, 1000 m, 980 m, 881 m, 860 w, 848 w, 800 w, 719 m, 634 w cm^{-1}; ^{19}F NMR (C_6D_6) δ −56.1 (4″-CF_3, t, 9F, $^4J_{F-F}$ = 21.6 Hz), −95.8 (3-F, m, 2F), −134.2 (2′-F, m, 6F), −140.3 (3″-F, m, 6F), −155.4 (2″-F, m, 6F), −155.8 (3′-F, m, 6F) ppm; MS (EI) [*m/e* (species, intensity)] 1366 (M^+ − NO, 100), 1347 (M^+ − NO − F, 11), 1328 (M^+ − NO − 2F, 4), 1327 (M^+ − CF_3, 4), 1114 (M^+ − $CF_3C_6F_4O$ −

NO − F, 5), 881 ($M^+ - 2CF_3C_6F_4O - NO - F$, 53). Anal. Calcd for $C_{45}F_{35}NO_5S_3$: C, 38.72; F, 47.65. Found: C, 38.95; F, 47.4.

Spectral data for 2,4,6-[4′-(4″-$CF_3C_6F_4O$)C_6F_4S]$_3C_6F_2CN$ (15): IR (Nujol/KBr) 2243 vw ($\nu_{C\equiv N}$), 1660 m, 1635 m, 1510 s, 1495 s, 1465 m, 1432 m, 1407 m, 1350 m, 1299 w, 1284 w, 1231 m, 1191 m, 1162 m, 1122 m, 1034 m, 1000 m, 982 m, 882 m, 859 m, 803 w, 718 m, 667 w, 655 w, 635 w cm^{-1}; ^{19}F NMR δ −56.2 (4″(2,6)-CF_3, t, 6F, $^4J_{F-F}$ = 21.6 Hz), −56.3 (4′′(4)-CF_3, t, 3F, $^4J_{F-F}$ = 21.6 Hz), −97.8 dp/−98.5 dt (3/5-F, 1F/1F, $^4J_{F-F}$ = 15.3 Hz, $^6J_{F-F}$ = 4.0 Hz), −131.5 (2′(4)-F, m, 2F), −131.7/−132.4 (2′(2/6)-F, m, 4F), −139.4 (3″-F, m, 6F), −153.9 to −154.9 (2″/3′-F, m, 12F) ppm; MS (EI) [*m/e* (species, intensity)] 1375 (M^+, 100), 1356 ($M^+ - F$, 8), 1158 ($M^+ - CF_3C_6F_4$, 2), 1142 ($M^+ - CF_3C_6F_4O$, 2), 981 ($M^+ - CF_2C_6F_4OC_6F_4 - S$, 37), 962 ($M^+ - CF_3C_6F_4OC_6F_4S$, 28), 943 ($M^+ - CF_3C_6F_4OC_6F_4S - F$, 4). Anal. Calcd for $C_{46}F_{35}NO_3S_3$: C, 40.16; F, 48.34. Found: C, 40.11; F, 48.1.

Preparation of $CF_3C_6F_4OC_6F_4OSiMe_3$. A mixture consisting of 2.5 mmol of **1** and 10 mmol of hexamethyldisilazane is stirred at 100−120 °C for 17 h after having been stirred for 1 h at 25 °C. The excess hexamethyldisilazane is removed in vacuum at 25 °C, and the residue is distilled at 64 °C/0.01 Torr. The liquid solidifies to colorless, hydrolyzable crystals in 93% yield (**16**, mp 29−31 °C).

Spectral data for 4-(4′-$CF_3C_6F_4O$)$C_6F_4OSiMe_3$ (16): IR (liquid film/KBr) 2967 w (ν_{CH}), 1660 m, 1509 s, 1431 m, 1344 m, 1314 m, 1260 m, 1228 m, 1192 m, 1155 m, 1092 m, 1053 w, 1009 m, 992 m, 876 m, 854 m, 761 w, 717 m, 634 w cm^{-1}; ^{19}F NMR δ −56.1 (4′-CF_3, t, 3F, $^4J_{F-F}$ = 21.6 Hz), −140.2 (3′-F, m, 2F), −155.2 (2′-F, m, 2F), −157.8 (3-F, m, 2F), −158.3 (2-F, m, 2F); ^1H NMR δ 0.29 ($SiMe_3$, s, 9H) ppm; MS (EI) [*m/e* (species, intensity)] 470 (M^+, 31), 455 ($M^+ - CH_3$, 1), 451 ($M^+ - F$, 4), 377 ($C_{14}H_3F_{10}O^+$, 3), 359 ($M^+ - F - (CH_3)_3SiF$, 1), 222 ($C_6F_4OSiMe_2^+$, 23), 203 ($C_6F_3OSiMe_2^+$, 1), 133 ($C_5F_3O^+$, 1), 117 ($C_5F_3^+$, 2), 81 ($CH_3SiF_2^+$, 5), 77 ($(CH_3)_2SiF^+$, 32), 73 ($(CH_3)_3Si^+$, 100). Anal. Calcd for $C_{16}H_9F_{11}O_2Si$: C, 40.86; H, 1.93. Found: C, 40.74; H, 1.86.

Reaction of 16 with Pentafluorobenzenes C_6F_5X (X = NO_2, CN) and Pentafluoropyridine. To a mixture consisting of 0.5 mmol of **16** and 1 mmol pentafluoronitrobenzene, pentafluorobenzonitrile, or pentafluoropyridine in 5 mL of THF is added a catalytic amount of CsF at 25 °C. After stirring (26 h/25 °C for $C_6F_5NO_2$; 9 h/75 °C for C_6F_5CN; 12 h/75 °C for C_5F_5N) (^{19}F NMR monitoring), all volatile materials are removed in vacuum and the residue is sublimed at 80 °C/0.01 Torr. When R = NO_2, considerable amounts (∼5−10%) of the *ortho* isomer are formed and can be removed by slow sublimation at 60 °C/0.01 Torr. The yields are 80% for $CF_3C_6F_4OC_6F_4OC_6F_4NO_2$ (**17**, mp 92−94 °C), 71% for $CF_3C_6F_4OC_6F_4OC_6F_4CN$ (**18**, mp 85−87 °C), and 75% for $CF_3C_6F_4OC_6F_4OC_5F_4N$ (**19**, mp 71−73 °C).

Compound **17** can be prepared in 67% yield in a manner similar to that described for the sulfur derivative **9**, using the phenol **1** and anhydrous K_2CO_3. The reaction time is significantly longer (60 h/25 °C), as is the case for the trimethylsilyl ether **16**.

Spectral data for 4-[4′-(4″-$CF_3C_6F_4O$)C_6F_4O]$C_6F_4NO_2$ (17): IR (Nujol/KBr) 1661 m, 1650 m, 1562 m ($\nu_{asymNO2}$), 1505 s, 1463 s, 1409 w, 1360 m (ν_{symNO2}), 1344 m, 1311 w, 1290 m, 1269 w, 1228 m, 1187 m, 1171 m, 1160 m, 1113 m, 1015 s, 990 s, 928 w, 877 m, 826 w, 806 w, 786 w, 768 m, 738 w, 717 m, 664 w, 640 w cm^{-1}; ^{19}F NMR δ −56.2 (4″-CF_3, t, 3F, $^4J_{F-F}$ = 21.6 Hz), −139.3 (3″-F, m, 2F), −145.1 (2-F, m, 2F), −153.2 (3-F, m, 2F), −154.7 (2″-F, m, 2F), −154.9 (2′/3′-F, m, 4F) ppm; MS (EI) [*m/e* (species, intensity)] 591 (M^+, 100), 575 ($M^+ - O$, 2), 572 ($M^+ - F$, 11), 561 ($M^+ - NO$, 38), 545 ($M^+ - NO_2$, 18), 526 ($M^+ - NO_2 - F$, 2), 517 ($M^+ - NO_2 - CO$, 2), 397 ($M^+ - C_6F_4NO_2$, 82), 381 ($M^+ - OC_6F_4NO_2$, 3), 374 ($M^+ - CF_3C_6F_4$, 3), 362 ($M^+ - OC_6F_4NO_2 - F$, 4), 353 ($M^+ - OC_6F_4NO_2 - CO$, 7), 217 ($CF_3C_6F_4^+$, 46), 198 ($CF_2C_6F_4^+$, 10), 180 ($OC_6F_4O^+$, 46), 148 ($C_6F_4^+$, 40), 117 ($C_5F_3^+$, 25), 69 (CF_3^+, 18). Anal. Calcd for $C_{19}F_{15}NO_4$: C, 38.60; F, 48.21. Found: C, 38.67; F, 48.4.

Spectral data for 4-[4′-(4″-$CF_3C_6F_4O$)C_6F_4O]C_6F_4CN (18): IR (Nujol/KBr) 2256 vw ($\nu_{C\equiv N}$), 1651 m, 1505 s, 1466 m, 1428 w, 1411 w, 1398 w, 1353 m, 1322 w, 1306 w, 1265 w, 1232 m, 1187 m, 1153 m, 1126 m, 1066 w, 1008 s, 990 s, 931 w, 879 m, 797 w, 722 m, 655 w, 637 w cm^{-1}; ^{19}F NMR δ −56.1 (4″-CF_3, t, 3F, $^4J_{F-F}$ = 21.6 Hz), −131.0 (2-F, m, 2F), −139.3 (3″-F, m, 2F), −153.4 (3-F, m, 2F), −154.7 (2″-F, m, 2F), −154.9 (2′/3′-F, m, 4F) ppm; MS (EI) [*m/e* (species, intensity)] 571 (M^+, 100), 552 ($M^+ - F$, 10), 397 ($M^+ - C_6F_4CN$, 15), 354 ($M^+ - CF_3C_6F_4$, 15), 217 ($CF_3C_6F_4^+$, 17), 174 ($C_6F_4CN^+$, 13), 148 ($C_6F_4^+$, 9), 124 ($C_5F_2CN^+$, 7), 117 ($C_5F_3^+$, 7), 93 ($C_3F_3^+$, 4), 69 (CF_3^+, 7). Anal. Calcd for $C_{20}F_{15}NO_2$: C, 42.05; F, 49.89. Found: C, 40.64; F, 49.2.

Spectral data for 4-[4′-(4″-$CF_3C_6F_4O$)C_6F_4O]C_5F_4N (19): IR (Nujol/KBr) 1650 m, 1644 m, 1515 s, 1466 s, 1429 m, 1354 m, 1311 m, 1276 m, 1231 m, 1194 m, 1169 m, 1158 m, 1115 m, 1104 m, 1043 m, 992 s, 972 s, 960 m, 880 m, 790 w, 734 w, 722 m, 707 w, 670 w, 644 w, 630 w cm^{-1}; ^{19}F NMR δ −56.2 (4″-CF_3, t, 3F, $^4J_{F-F}$ = 21.7 Hz), −87.1 (2-F, m, 2F), −139.3 (3″-F, m, 2F), −154.8 (2′/3′/2″-F, m, 6F), −157.4 (3-F, m, 2F) ppm; MS (EI) [*m/e* (species, intensity)] 547 (M^+, 100), 528 ($M^+ - F$, 9), 478 ($M^+ - CF_3$, 1), 397 ($M^+ - C_5F_4N$, 16), 330 ($M^+ - CF_3C_6F_4$, 22), 295 ($M^+ - CF_3C_6F_4O - F$, 4), 217 ($CF_3C_6F_4^+$, 33), 150 ($C_5F_4N^+$, 26), 117 ($C_5F_3^+$, 14), 69 (CF_3^+, 14). Anal. Calcd for $C_{18}F_{15}NO_2$: C, 39.51; F, 52.08. Found: C, 39.15; F, 51.6.

Reaction of 5 with Benzaldehyde. To a mixture consisting of 2 mmol of **5** and 6 mmol of benzaldehyde in 3 mL of THF, cooled to 0 °C, is added 1 drop of *n*-$Bu_4N^+F^-$ (1 M in THF), and the mixture is stirred for 1 h. The ^{19}F NMR of the mixture shows complete reaction of **5**. All volatile materials are removed in vacuum, and the residue is treated with 3 mL of concentrated HCl and stirred for 5 h. After extraction with ether/water, the combined ether phases are dried over anhydrous Na_2SO_4 and all volatile materials are removed in vacuum. The crude product is purified by column chromatography twice using dichloromethane/hexane (1:2) as the eluent on silica gel (70−230 mesh). The secondary alcohol $CF_3C_6F_4OC_6F_4CH(C_6H_5)OH$ (**20**) is obtained as a viscous liquid in 36% yield.

Spectral data for 4-(4′-$CF_3C_6F_4O$)$C_6F_4CH(C_6H_5)OH$ (20): IR (liquid film/KBr) 3610 m, 3353 s br (ν_{OH}), 3093 w, 3067 w, 3035 m ($\nu_{CH(Ar)}$), 2925 m (ν_{CH}), 1646 m, 1605 s, 1505 s, 1454 m, 1432 m, 1344 s, 1296 m, 1229 s, 1191 s, 1153 s, 1087 m, 1063 m, 1041 m, 992 s, 942 m, 910 m, 876 m, 844 m, 801 w, 778 m, 738 m, 717 m, 700 m, 668 m, 647 m, 616 m cm^{-1}; ^{19}F NMR δ −56.3 (4′-CF_3, t, 3F, $^4J_{F-F}$ = 21.6 Hz), −139.9 (3′-F, m, 2F), −142.7 (2-F, m, 2F), −154.7 (2′-F, m, 2F), −156.2 (3-F, m, 2F); ^1H NMR δ 7.5−7.3 (C_6H_5, m, 5H), 6.26 (CH, d, 1H, $^3J_{H-H}$ = 7.4 Hz), 2.64 (OH, d) ppm; MS (EI) [*m/e* (species, intensity)] 488 (M^+, 49), 471 ($M^+ - OH$, 4), 469 ($M^+ - F$, 7), 411 ($M^+ - C_6H_5$, 13), 409 ($CF_3C_6F_4OC_6F_4CO^+$, 20), 237 ($M^+ - CF_3C_6F_4O - H_2O$, 7), 217 ($CF_3C_6F_4^+$, 3), 176 ($C_6F_4CO^+$, 6), 148 ($C_6F_4^+$, 7), 117 ($C_5F_3^+$, 3), 107 ($C_6H_5CHOH^+$, 28), 105 ($C_6H_5CO^+$, 20), 79 ($C_6H_7^+$, 100), 78 ($C_6H_6^+$, 26), 77 ($C_6H_5^+$, 27), 69 (CF_3^+, 4). Anal. Calcd for $C_{20}H_7F_{11}O_2$: C, 49.19; H, 1.45. Found: C, 48.23; H, 1.44.

Reaction of 5 with Pentafluorobenzaldehyde. The experiment is carried out analogously to the reaction with benzaldehyde, but a more complex product mixture is obtained, on the basis of ^{19}F NMR (two main components), requiring repeated column chromatography using dichloromethane/hexane mixtures as eluents. The desired secondary alcohol $CF_3C_6F_4OC_6F_4CH(C_6F_5)OH$ (**21**) exhibits a longer retention time than $CF_3C_6F_4OC_6F_4CH(C_6F_5)OC_6F_4CHO$ (**22**) derived from reaction of the alkoxide with the *p*-fluorine atom of pentafluorobenzaldehyde. The yields are ∼10% for **21** (mp 95−97 °C) and ∼10% for **22** (viscous liquid).

Spectral data for 4-(4′-$CF_3C_6F_4O$)$C_6F_4CH(C_6F_5)OH$ (21): IR (Nujol/KBr) 3625 m, 3616 m, 3387 m br (ν_{OH}), 1651 m, 1505 s, 1464 s, 1342 m, 1309 m, 1278 m, 1225 m, 1199 m, 1170 m, 1124 m, 1079 m, 1051 m, 1002 m, 904 m, 874 m, 809 m, 791 w, 779 w, 752 m, 737 m, 716 m, 673 m, 633 m, 596 w, 577 w cm^{-1}; ^{19}F NMR δ −56.2 (4′-CF_3, t, 3F, $^4J_{F-F}$ = 21.5 Hz), −139.5 (3′-F, m, 2F), −142.9 (2-F, m, 2F), −143.4 (2″-F, m, 2F), -152.6 (4″-F, tt, 1F, $^3J_{F-F}$ = 21.0 Hz, $^4J_{F-F}$ = 2.5 Hz), −154.4 (2′-F, m, 2F), −155.4 (3-F, m, 2F), −160.8 (3″-F, m, 2F); ^1H NMR δ 6.50 (CH, d, 1H, $^3J_{H-H}$ = 10.0 Hz), 3.30 (OH, dp, 1H, $^5J_{H-F}$ = 2.0 Hz) ppm; MS (EI) [*m/e* (species, intensity)] 578 (M^+, 26), 561 ($M^+ - OH$, 7), 559 ($M^+ - F$, 10), 411 ($M^+ - C_6F_5$, 67), 409 ($CF_3C_6F_4OC_6F_4CO^+$, 18), 391 ($M^+ - C_6F_5 - HF$, 9), 363 ($M^+ - C_6F_5 - HF - CO$, 5), 217 ($CF_3C_6F_4^+$, 3), 197 ($C_6F_5CHOH^+$, 100), 195 ($C_6F_5CO^+$, 52), 177 ($C_6F_4COH^+$, 13), 167 ($C_6F_5^+$, 14), 148 ($C_6F_4^+$, 18), 137 ($C_5F_4H^+$, 12), 117 ($C_5F_3^+$, 27), 93 ($C_3F_3^+$, 9), 69 (CF_3^+, 16). Anal. Calcd for $C_{20}H_2F_{16}O_2$: C, 41.54; H, 0.35. Found: C, 41.60; H, 0.39.

Spectral data for 4-(4′-$CF_3C_6F_4O$)$C_6F_4CH(C_6F_5)OC_6F_4CHO$

(22): IR (Nujol/KBr) 2727 m ($\nu_{CH(=O)}$), 1717 m ($\nu_{C=O}$), 1647 m, 1511 s, 1465 m, 1344 m, 1309 m, 1226 m, 1158 s, 1070 m, 1004 m, 973 m, 920 m, 875 m, 816 m, 736 w, 719 m, 672 w, 629 w, 577 w cm^{-1}; ^{19}F NMR δ −56.2 (4′-CF_3, t, 3F, $^4J_{F-F}$ = 22.2 Hz), −139.4 (3′-F, m, 2F), −140.1 (2-F, m, 2F), −140.5 (2″-F, m, 2F), -144.4 (2‴-F, m, 2F), −149.8 (4″-F, tt, 1F, $^3J_{F-F}$ = 21.0 Hz, $^4J_{F-F}$ = 3.6 Hz), −154.4 (2′-F, m, 2F), −154.7 (3-F, m, 2F), −155.2 (3‴-F, m, 2F), -159.9 (3″-F, m, 2F); ^1H NMR δ 10.21 (CHO, m, 1H), 7.11 (CH, s, 1H) ppm; MS (EI) [*m/e* (species, intensity)] 734 (M^+ − HF, 1), 561 (M^+ − OC_6F_4CHO, 100), 542 (M^+ − OC_6F_4CHO − F, 1), 332 (M^+ − $CF_3C_6F_4$ − C_6F_5 − 2F, 17), 315 (M^+ − $CF_3C_6F_4O$ − C_6F_5 − HF − F, 21), 305 (M^+ − $CF_3C_6F_4$ − OC_6F_4CHO − HF − F, 6), 289 (M^+ − $CF_3C_6F_4O$ − OC_6F_4-CHO − HF − F, 12), 256 (M^+ − $CF_3C_6F_4OC_6F_4$ − C_5F_3, 10), 217 ($CF_3C_6F_4^+$, 3), 193 ($OC_6F_4CHO^+$, 8), 167 ($C_6F_5^+$, 2), 137 ($C_5F_4H^+$, 9), 117 ($C_5F_3^+$, 11). Anal. Calcd for $C_{27}H_2F_{20}O_3$: C, 42.99; H, 0.27. Found: C, 41.67; H, 0.34.

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