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Synthesis of Cyclic Ethers with Fluorinated Side Chains

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Di-*tert*-butyl peroxide initiated free radical addition of THF to various fluorinated alkenes ($CF_2{=}CH_2$, $CF_2{=}CFH$, $CH_2{=}CHCF_3$, $CF_2{=}CFCF_3$, $CF_2{=}CFC_5F_{11}$, $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$) gives either bidirectional addition products [$\overline{CH_2CH_2CH_2OCH}(CF_2CH_3)$ (**1**), $\overline{CH_2CH_2CH_2OCH}(CH_2CHF_2)$ (**2**), $\overline{CH_2CH_2CH_2OCH}(CF_2CH_2F)$ (**3**), and $\overline{CH_2CH_2CH_2OCH}(CFHCHF_2)$ (**4**)] or unidirectional products [$\overline{CH_2CH_2CH_2OCH}(CH_2CH_2CF_3)$ (**5**), $\overline{CH_2CH_2CH_2OCH}(CF_2CHFCF_3)$ (**6**), $\overline{CH_2CH_2CH_2OCH}(CF_2CHFC_5F_{11})$ (**7**), and $\overline{CH_2CH_2CH_2OCH}(CF_2CHFOCF_2CF(CF_3)OCF_2CF_2SO_2F)$ (**8**)] depending on the structure of the alkene. Reaction of dioxane with $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ gives a single product, $\overline{CH_2OCH_2CH_2OCH}(CF_2CHFOCF_2CF(CF_3)OCF_2CF_2SO_2F)$ (**9**). In the case of hexafluoropropene or perfluoroallylbenzene, reaction with an excess of tetrahydrofuran gives only the monosubstituted products $\overline{CH_2CH_2CH_2OCH}(CF_2CHFCF_3)$ (**6**) and $\overline{CH_2CH_2CH_2OCH}(CF_2CFHCF_2C_6F_5)$ (**11**) respectively. When tetrahydrofuran is reacted with a 3:1 molar excess of the same two perfluoroalkenes, the disubstituted products $\overline{CH_2CH_2CH(CF_2CHFCF_3)OCH}(CF_2CHFCF_3)$ (**10**) and $\overline{CH_2CH_2CH(CF_2CFHCF_2C_6F_5)OCH}(CF_2CFHCF_2C_6F_5)$ (**12**) are formed respectively. When 18-crown-6 is reacted in the same way with fluoroalkenes in a 1:1 molar ratio, the monosubstituted products 18-crown-6-$CH_2CH_2CF_3$ (**13**), 18-crown-6-CF_2CHFCF_3 (**14**), 18-crown-6-$CF_2CFHCF_2C_6F_5$ (**15**), and 18-crown-6-$CF_2CHFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ (**16**) are obtained. Polyfluorinated 18-crown-6 products containing three and two polyfluroalkyl/aryl groups are prepared when 18-crown-6 is reacted with a 3:1 molar excess of perfluoropropene and perfluoroallylbenzene to give 18-crown-6-$(CF_2CHFCF_3)_3$ (**17**) and 18-crown-6-$(CF_2CFHCF_2C_6F_5)_2$ (**18**), respectively. (Pentafluorophenoxy)trimethylsilane reacts with **11** in the presence of a catalytic amount of cesium fluoride to give compound **19**, $\overline{CH_2CH_2CH_2OCH}(CF_2CFHCF_2C_6F_4OC_6F_5)$. Two molecules of **11** are bridged by reaction with $Me_3SiOCH_2CF_2CF_2CF_2CH_2OSiMe_3$ to give $\overline{CH_2CH_2CH_2OCH}CF_2CFHCF_2C_6F_4OCH_2CF_2CF_2CF_2CH_2OC_6F_4CF_2CHFCF_2\overline{CHOCH_2CH_2CH_2}$ (**20**), while **12** forms the macroheterocycle $\underline{\overline{OCHCH_2CH_2CH}CF_2CFHCF_2C_6F_4OCH_2CF_2CF_2CF_2CH_2OC_6F_4CF_2CFHCF_2}$ (**21**) under similar reaction conditions. The lanthanum triflate complexes of 18-crown-6 (**22**) and 18-crown-6(CF_2CFHCF_3) (**23**) were prepared and the structures were obtained via single-crystal X-ray analysis. Although crystals suitable for single-crystal X-ray analysis could not be formed, lanthanum triflate complexes were formed with polyfluorinated ethers **15** and **16** to give the fluorinated complexes $La(OSO_2CF_3)_3$(18-crown-6-$CF_2CFHCF_2C_6F_5$)(H_2O) (**24**) and $[La(OCH_2CH_2)_5OCH_2CHCF_2CFHOCF_2C(CF_3)FOCF_2CF_2SO_2F]^{3+}[CF_3SO_3^-]_3$ (**25**) respectively. The acid salt $La[N(SO_2CF_3)_2]_3$ (**26**) was also prepared and characterized, and reacted with dibenzo-18-crown-6 to give the complex dibenzo-18-crown-6-$La[N(SO_2CF_3)_2]_3$ (**27**).

Introduction

Since the complexing ability and selectivity as well as the physical/chemical properties of crown ethers can be modified remarkably by introducing side arms, much attention has been paid to such functionalization.[1] The fact that a number of fluorinated compounds exhibit high solubility in supercritical carbon dioxide[2] prompted us to find a way to introduce fluorinated chains into those cyclic ethers.

Recently, there is increasing interest in using free radical addition of ethers to fluoroalkenes to make fluorinated ethers. A series of papers[3−5] has appeared that is focused mainly on the introduction of hexafluoropropene into cyclic ethers and fluorination of the resultant adducts with F_2/N_2 to make substituted perfluorocyclic ethers. Chambers and his co-workers obtained a variety of products using γ-irradiation to initiate the addition of 18-crown-6 to hexafluoropropene.[6] Free radical reaction between a cyclic ether and a fluoroalkene was originally reported more than 20 years ago;[7] however, the reaction has not been studied in detail. Although there are several reports on the γ-irradiated free radical addition of simple cyclic ethers to perfluoroalkenes, the interesting spectral properties of these adducts have not been explained.[3−5,7] In this work, we use tetrahydrofuran as a template to study the free radical reaction of cyclic ethers with various fluoroalkenes, and the complex

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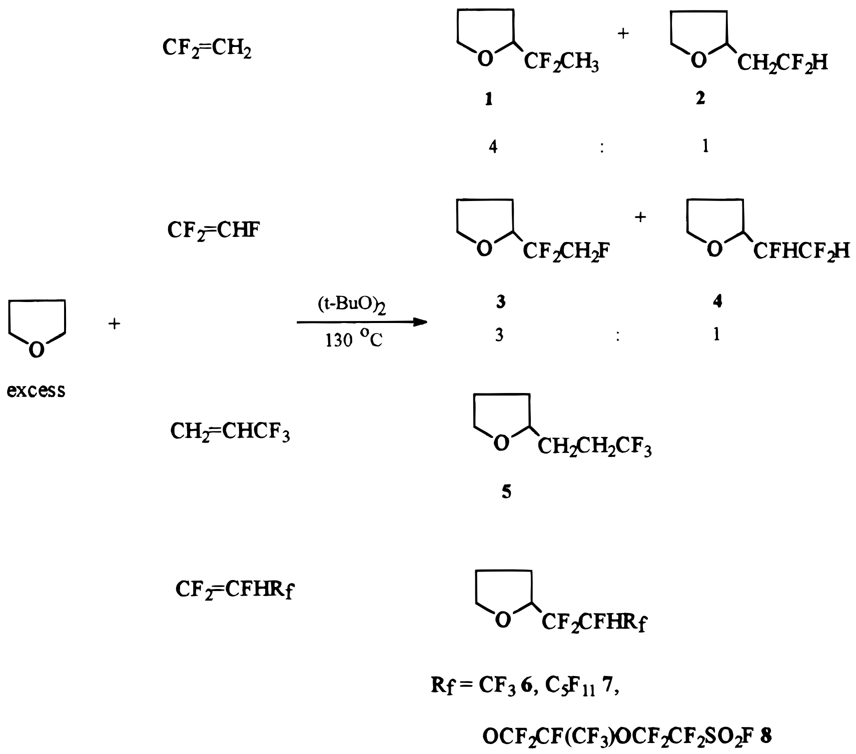

Figure 1.

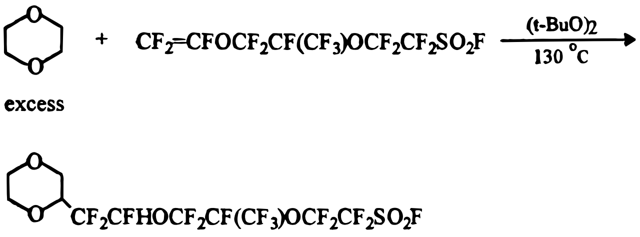

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Figure 2.

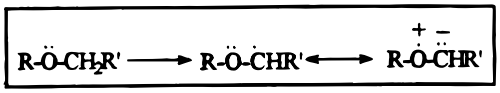

Figure 3.

^{19}F NMR patterns of the products. While using this method to prepare a series of crown ethers with fluorinated side arms, the similarity and difference between 18-crown-6 and THF in their free radical additions to perfluoroalkenes are then addressed. Several 18-crown-6 derivatives containing different fluorinated side chains are prepared. The synthesis of $CF_3CH_2CH_2$-18-crown-6 isolates the electron-withdrawing trifluoromethane group[8] from the ring oxygens via methylene spacers and consequently prevents reduction in the basicity of the adjacent ring oxygen atoms. Thus the complexing ability of the crown ether is not sacrificed, and in this study we have been able to prepare the first example of a stable lanthanide metal complex with an 18-crown-6 ligand containing a fluoroalkyl substituent.

Results and Discussion

Di-*tert*-butyl peroxide initiated free radical addition of THF to various fluorinated alkenes gives, depending on the structure of the alkenes, unidirectional addition or bidirectional addition products as demonstrated in Figure 1. We find that the vinyl ether $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ is very reactive under the same conditions. This is also the case in its reaction with dioxane (Figure 2). Examination of the product distribution shows that the free radical adds preferentially to the carbon bearing more fluorine (rather than perfluoroalkyl groups). This can be rationalized by the fact that an intermediate radical adjacent to an oxygen atom is relatively electron rich by virtue of the resonance structures shown in Figure 3.[6] When such an electron rich radical adds across a double bond, it tends to attack the carbon atom which is more electrophilic (more electron deficient), forming only a single reaction product. This reaction can also give di- as well as monosubstituted tetrahydrofuran depending on the molar ratios of the reactants. Thus, in the case of hexafluoropropene, when an excess of tetrahydrofuran is used, the reaction gives solely the monosubstituted product. When tetrahydrofuran and perfluoropropene are reacted in a 1:3 molar ratio (excess perfluoropropene), the only product formed is the disubstituted one. A 1:2 molar ratio of tetrahydrofuran to perfluoropropene results in the formation of a mixture of 80% monosubstituted and 20% disubstituted product (Figure 4). Perfluoroallylbenzene reacts in the same way with tetrahydrofuran to give either the monosubstituted product **11** or the disubstituted product **12**, or mixtures of both **11** and **12** depending on the molar ratios of the reactants used. This is indicative of the higher reactivity of unsubstituted tetrahydrofuran, an observation that is consistent with results reported previously.[3-5,7] At least two asymmetric centers are introduced in this reaction. Consequently, two pairs of enantiomers in the case of monosubstitution are formed, and in the case of disubstitution, the number of diastereoisomers is even larger. In fact, there are two AB patterns in the ^{19}F NMR of compound **6** and four AB patterns in the ^{19}F NMR of compound **11**, exhibiting two pairs of enationers each with one pair of prochiral fluorines in compound **8** and two pairs of prochiral fluorines in compound **11** (see the spectrum for compound **11** in Figure 5). Monosubstituted 18-crown-6 can be obtained by reacting 18-crown-6 with perfluoroalkenes in a 1:1 molar ratio (Figure 6a). When 18-crown-6 and perfluoroalkenes are reacted in a 1:2 or

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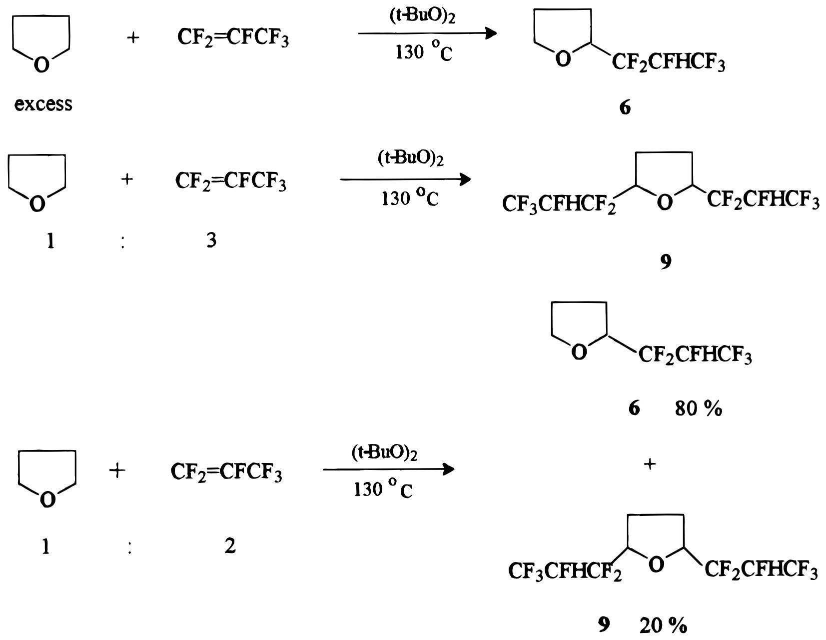

Figure 4.

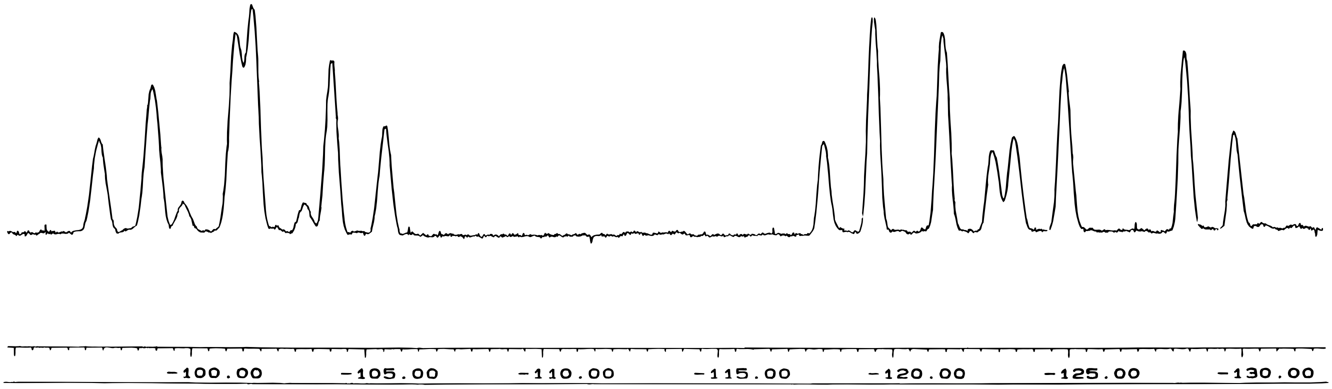

Figure 5. ^{19}F NMR spectrum showing the AB patterns for the prochiral fluorine atoms of **11**.

1:3 molar ratio, the 18-crown-6 derivative containing two or three fluorinated side arms is obtained in good yield (Figure 6b). Further increases in the ratio of perfluoroalkene to crown ether result in the formation of mixtures of products that are difficult to separate. Although more overlapping occurs in the ^{19}F NMR of these compounds, the AB patterns are still discernible, suggesting the presence of chiral centers in the products. It is worth mentioning that the resultant adducts of cyclic ethers with perfluoroallylbenzene can be further modified at the perfluorobenzene site on the side arms to further modify the solubility properties of the molecules. For example, one more pentafluorophenoxy group can be introduced by using the siloxane derivative of pentafluorophenol in the presence of a catalytic amount of cesium fluoride.[9,10] Two such molecules can be joined together by using siloxane derivatives of polyfluorinated diols (Figure 7).[11] By carefully choosing the reaction conditions in the case of the disubstituted compound, the macrocyclic product **21** shown in Figure 8 can be obtained.

Single-crystal X-ray crystallographic parameters for **22** and **23** are given in Table 1. The molecular structure of [La(OSO$_2$CF$_3$)$_2$(OH$_2$)$_2$L]$^+$[O$_3$SCF$_3$]$^-$ [L = 18-crown-6] (**22**) is shown in Figure 9. The lanthanum(III) metal ion is 10-coordinate, six from the oxygen atoms of L, and the remaining four from the oxygen atoms of two triflate and two water molecules (Figure 10). A maximum coordination number of 12 is reported for [La(NO$_3$)$_3$L] where the more basic nitrate groups are bound to lanthanum in a bidentate fashion.[12] Decacoordinated La(III) has been structurally characterized in the amine complex [La(O$_3$SCF$_3$)$_2$L*·CH$_3$CN]$^+$ where L* = 1,9-bis(2-aminoethyl)-1,4,6,9,12,14-hexaazacyclohexadecane.[13] The final atomic coordinates and selected bond lengths and bond angles for **22** are listed in Tables 2 and 3, respectively, and in Tables 4 and 5 for **23**. As in the case of other lanthanide 18-crown-6 complexes,[14] the crown ether ring is distorted from the normally observed D_{3d} conformation of the 18-crown-6 metal complexes.[15-17] The crown ether ring folds around the lanthanum ion, away from the more sterically crowded "top" plane containing two water

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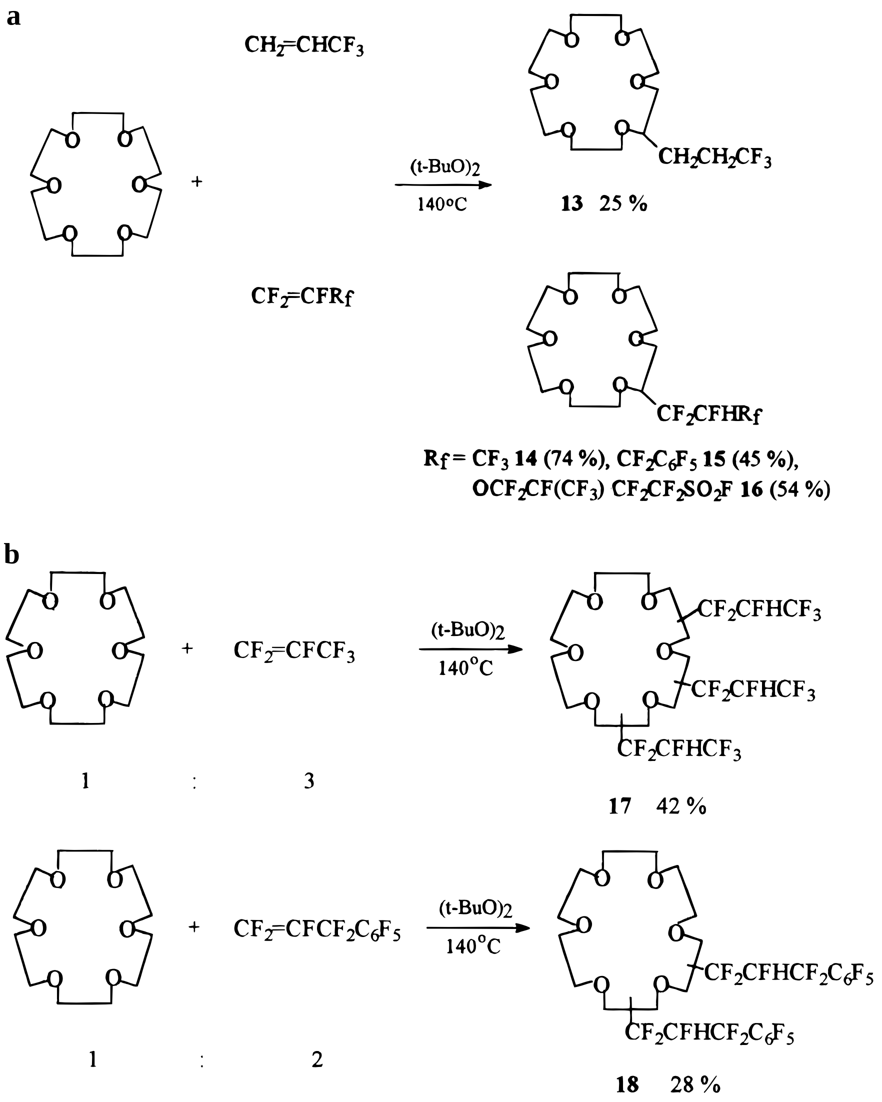

Figure 6.

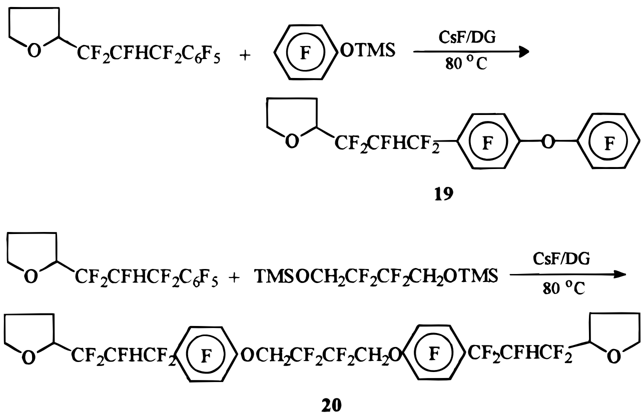

Figure 7.

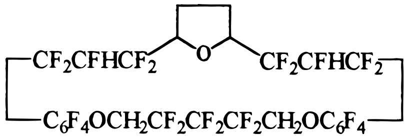

Figure 8.

molecules and a triflate group. The La−O(triflate) distances are similar [2.503(5) and 2.508(5) Å] and are shorter than the lanthanum-oxygen bonds in $[La(O_3SCF_3)_2L^*\cdot CH_3CN]^+$ where La−O(triflate) = 2.585(3) and 2.632(3) Å. The La−O(crown) distances vary over the range 2.642(6)−2.730(6) Å. These distances are slightly less than lanthanum−oxygen (crown) bonds reported for $La(NO_3)_3L$ [2.662(6)−2.780(6) Å] (where L = 18-crown-6). The longest La-O (crown) distances, La(1)−O(4) (2.707 Å) and La(1)−O(6) (2.730 Å), can be explained on the basis of close interligand approach between the crown ether and the triflate oxygen atoms (listed in Table 6) i.e., O(4)−O(2A) and O(6)−O(1A) = 2.943 and 2.860 Å, respectively. Elongation of these bonds relieves the O−O repulsion between oxygen atoms of 18-crown-6 and the triflate groups. Conversely, La(1)−O(1) has the shortest La−O(crown) bond length (2.642 Å) because O(1) does not have a close interligand approach (<3 Å). Least-squares analysis of the O(1)···O(6) plane is listed in Table 7. The lanthanum atom is located 0.5978 Å below the mean O(1)···O(6) plane. The oxygen atoms O(1) and O(2) are nearly in the mean plane but O(3) and O(6), and O(5) and O(4) are displaced below and above the plane by ~0.24 and ~0.45 Å respectively, with O(1)−La(1)−O(4) = 144.6(2)°, O(2)−La(1)−O(5) = 162.8(2)°, and O(3)−La(1)−O(6) = 154.7(2).° The torsion angles, given in Table 6, suggest that the macrocycle adopts a distorted conformation following the sequence $g^-g^+g^+g^-g^-g^+$, where g^-

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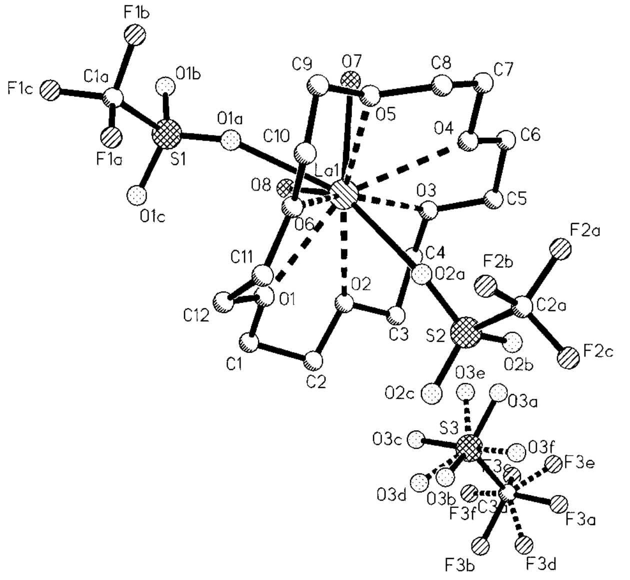

Figure 9. Molecular structure of **22** including the disordered triflate anion.

Table 1. X-ray Crystallographic Parameters for **22** and **23**

	22	**23**
	Crystal Data	
empirical formula	$C_{15}H_{28}F_9LaO_{17}S_3$	$C_{18}H_{26}F_{15}LaO_{16}S_3$
fw	886.46	1018.48
color, habit	colorless, chunk	colorless, rod
cryst size (mm)	0.25 × 0.17 × 0.10	0.33 × 0.27 × 0.18
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
unit cell dimens		
a (Å)	8.965(2)	10.134(2)
b (Å)	23.033(5)	32.641(7)
c (Å)	15.345(3)	10.577(2)
β (deg)	102.57(3)	98.14(3)
vol (Å^3)	3092(11)	3463.5(12)
Z	4	4
ρ_{calc} (Mg/m^3)	1.904	1.953
F(000)	1760	2008
abs coeff (mm^{-1})	1.708	1.560
	Data Collection	
2θ range (deg	3.0−45.0	3.5−45.0
index ranges	$-1 \le h \le 9$	$-1 \le h \le 10$
	$-1 \le k \le 24$	$-1 \le k \le 35$
	$-16 \le l \le 16$	$-11 \le l \le 11$
no. of data collcd	5264	5646
no. of unique data	4047 (R_{int} = 0.0591)	4515 (R_{int} = 0.0407)
no. of data with I > 2σ(I)	2924	3322
$T_{max}/T_{min.}$	0.937/0.789	0.889/0.731
extinction coeff.	0.0018(3)	
	Solution and Refinement on F^2	
params refined	470 (459 restraints)	478 (0 restraints)
final R indices (2σ data)		
R	0.0431	0.0508
R_w	0.0930	0.1066
final R indices (all data)		
R	0.0739	0.0808
R_w	0.1098	0.1221
goodness-of-fit, S (F^2)	0.978	1.077
largest diff peak (e Å^{-3})	0.476	0.717
largest diff hole (e Å^{-3})	−0.483	−0.464

~ −60°. The triflate anion suffers from rotational disorder and therefore the bond distances and angles have large esds. The hydrogen atoms belonging to the water molecules are located from the difference electron density map and, therefore, discussion of the hydrogen bond network formation is meaningful. The O···H(water) bond distances vary over the range 1.956−2.573 Å and are also supported by the short intermolecular contacts between O(water) and O(triflate) and O(crown). Figure 11 shows a crystal packing diagram for **22** incorporating the rotationally disordered triflate anion. Each crown ether complex has one neighbor with similar crown ring conformation while the other moiety shows the “flip” ring conformation. Thus, one of the hydrogen atoms on O(7), H(7AA), forms a hydrogen bond with the oxygen atom belonging to the triflate group situated in the “bottom” plane of the neighboring molecule, O(2C), having similar ring conformation. This “top−bottom” H···O-(triflate) distance is 2.326 Å^{I} (I_{symm}: $-1 + x, y, z$). Similarly, there is a “top−top” interaction between H(8AA) of O(8) and O(1C) with a distance of 2.055 Å^{II} (II_{symm}: $-x, 1 - y, - z$) of the triflate group in the neighboring molecule with “flip” ring conformation. The remaining hydrogen atoms, H(7BB) and H(8BB), located on O(7) and O(8), respectively, form two contacts each with O(3B/F) at 2.123 and 1.956 Å^{I}, and O(3B/D) at 2.130 and 2.283 Å^{I}. In addition to these bonds, there is weak H(crown)···O(triflate) interaction, H(2B)···O(1B) at 2.538 Å^{II} and H(crown)···F(triflate$^-$) interaction, H(2B)···F(3D) at 2.472 Å^{I}. In the absence of the triflate anion, the packing diagram shows interlinked pairs of hydrogen-bonded dimers (Figure 12).

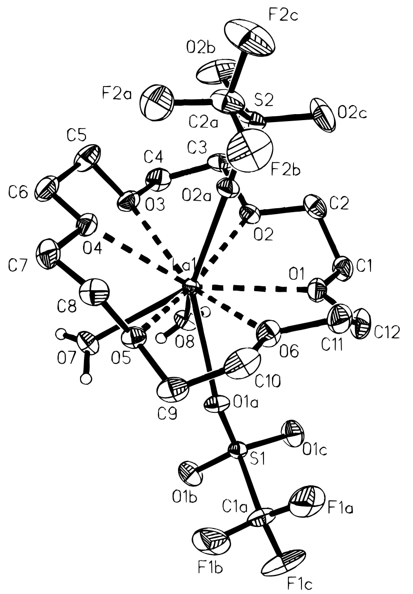

Figure 10. Molecular structure of the cation in **22** (thermal ellipsoids at 30% probability level).

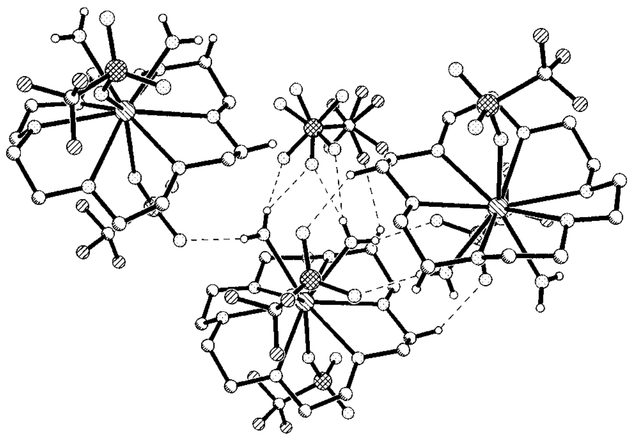

Figure 11. Crystal packing diagram of **22** showing intermolecular interactions.

The structure of complex **23** is the first single-crystal X-ray anaylsis of a metal complex of a crown ether bearing a fluoroalkyl side chain (Figure 13). This complex is a neutral

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for **22**

	x	*y*	*z*	*U*(eq)[a]
La(1)	1366(1)	4201(1)	2319(1)	31(1)
S(1)	−1862(2)	3960(1)	328(1)	37(1)
O(1A)	−877(6)	3839(3)	1175(4)	50(2)
O(1B)	−3097(7)	4334(3)	369(5)	66(2)
O(1C)	−1077(7)	4072(3)	−359(4)	69(2)
C(1A)	−2733(11)	3253(4)	33(7)	63(3)
F(1A)	−1715(9)	2854(3)	18(6)	120(3)
F(1B)	−3538(8)	3090(3)	613(5)	116(3)
F(1C)	−3662(10)	3272(4)	−751(5)	140(3)
S(2)	5593(2)	3828(1)	3386(2)	51(1)
O(2A)	3972(6)	3848(3)	3063(4)	53(2)
O(2B)	6223(10)	4336(4)	3852(6)	114(3)
O(2C)	6400(8)	3620(4)	2762(5)	106(3)
C(2A)	5825(11)	3285(5)	4230(7)	72(3)
F(2A)	5151(9)	3445(4)	4888(4)	111(3)
F(2B)	5162(10)	2795(3)	3941(6)	131(3)
F(2C)	7258(8)	3179(4)	4588(6)	145(4)
S(3)	7731(3)	6135(1)	2552(2)	71(1)
O(3A)	6898(28)	6201(14)	3203(12)	119(12)
O(3B)	8072(24)	5639(6)	2186(17)	109(8)
O(3C)	6842(24)	6525(8)	1739(13)	141(9)
O(3D)	7865(26)	5907(8)	1739(8)	92(7)
O(3E)	6431(22)	6372(11)	2703(17)	108(10)
O(3F)	8425(21)	5703(5)	3264(8)	82(5)
C(3A)	9211(14)	6672(6)	2805(9)	99(4)
F(3A)	10079(25)	6443(15)	3521(13)	187(15)
F(3B)	10042(19)	6625(9)	2171(11)	108(7)
F(3C)	8892(25)	7198(8)	2862(26)	148(13)
F(3D)	10561(19)	6512(13)	2827(30)	298(29)
F(3E)	9159(32)	6947(10)	3564(14)	131(9)
F(3F)	8736(38)	7054(11)	2171(16)	233(19)
O(1)	2571(7)	3861(3)	979(4)	57(2)
O(2)	3319(6)	4887(3)	1722(4)	49(2)
O(3)	2341(7)	5180(3)	3188(4)	59(2)
O(4)	1793(7)	4245(3)	4120(4)	57(2)
O(5)	186(6)	3380(3)	3203(4)	49(2)
O(6)	1542(7)	3053(3)	1909(4)	60(2)
O(7)	−1008(7)	4567(3)	2801(5)	54(2)
O(8)	133(7)	5053(3)	1372(5)	50(2)
C(1)	3152(8)	4290(3)	459(5)	63(3)
C(2)	4185(8)	4669(3)	1117(5)	61(3)
C(3)	4090(11)	5347(4)	2250(7)	63(3)
C(4)	2987(12)	5615(4)	2710(7)	65(3)
C(5)	2927(14)	5172(5)	4107(7)	81(4)
C(6)	2005(14)	4797(6)	4551(7)	88(4)
C(7)	1012(14)	3860(6)	4566(7)	80(4)
C(8)	871(12)	3293(5)	4115(7)	65(3)
C(9)	−301(13)	2846(4)	2721(7)	68(3)
C(10)	936(14)	2595(4)	2366(7)	79(4)
C(11)	2530(13)	2877(5)	1344(8)	78(3)
C(12)	2437(14)	3292(5)	630(9)	84(4)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

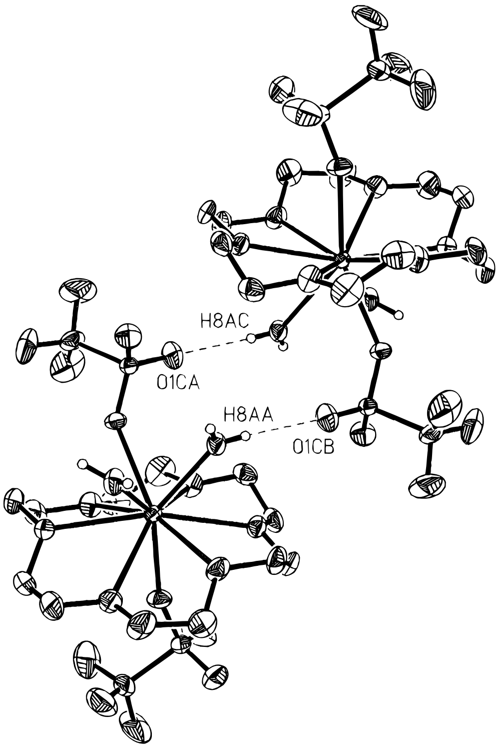

Figure 12. Dimer formation via H-bonding in the crystal packing of **22** (triflate ion omitted).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **22**

Bond Lengths			
La(1)−O(1)	2.642(6)	O(2)−C(3)	1.420(11)
La(1)−O(2)	2.664(6)	O(2)−C(2)	1.424(8)
La(1)−O(3)	2.667(6)	O(3)−C(5)	1.395(11)
La(1)−O(4)	2.707(6)	O(3)−C(4)	1.435(11)
La(1)−O(5)	2.676(6)	O(4)−C(7)	1.399(11)
La(1)−O(6)	2.730(6)	O(4)−C(6)	1.427(12)
La(1)−O(7)	2.543(6)	O(5)−C(8)	1.415(11)
La(1)−O(8)	2.546(6)	O(5)−C(9)	1.453(11)
La(1)−O(1A)	2.508(5)	O(6)−C(11)	1.428(12)
La(1)−O(2A)	2.503(5)	O(6)−C(10)	1.437(11)
O(1)−C(12)	1.410(12)	C(1)−C(2)	1.49(2)
O(1)−C(1)	1.438(9)	C(3)−C(4)	1.470(14)

Bond Angles			
O(1)−La(1)−O(2)	59.8(2)	O(3)−La(1)−O(6)	154.7(2)
O(1)−La(1)−O(3)	119.6(2)	O(4)−La(1)−O(5)	59.5(2)
O(1)−La(1)−O(4)	144.6(2)	O(4)−La(1)−O(6)	105.6(2)
O(1)−La(1)−O(5)	117.3(2)	O(5)−La(1)−O(6)	58.7(2)
O(1)−La(1)−O(6)	58.6(2)	O(2A)−La(1)−O(1A)	137.5(2)
O(2)−La(1)−O(3)	60.2(2)	S(1)−O(1A)−La(1)	144.4(4)
O(2)−La(1)−O(4)	111.8(2)	S(2)−O(2A)−La(1)	161.0(4)
O(2)−La(1)−O(5)	162.8(2)	C−C−O(av)	108.8(9)
O(2)−La(1)−O(6)	114.8(2)	C−O−C(av)	114.2(8)
O(3)−La(1)−O(4)	60.0(2)	C−O−La(1)	119.8(6)
O(3)−La(1)−O(5)	117.8(2)		

species and the central metal ion is 10-coordinate with the ether ring, and three covalent monodentate triflate groups in addition to a water molecule. As in the case of **22**, there is only one triflate group in the direction of the crown ether fold. The "top" plane contains two triflate groups and a water molecule. In order to alleviate intermolecular repulsion, the fluoroalkyl chain is bent away from the "top" plane and is roughly perpendicular (106.7°) to the mean 18-crown-6 plane. The La−O(triflate) bond distances vary between 2.497(6)−2.537(6) Å. Although the mean La−crown distance in **23** (2.673 Å) is almost the same as that found in **22** (2.681 Å), the individual distances in the former complex vary over a much larger range (0.288 Å *vs* 0.088 Å for **22**). The most significant feature of the structure is the long La(1)−O(1) bond of 2.885(6) Å which can be explained primarily because of the reduced basicity of O(1) due to the presence of an electron withdrawing fluoroalkyl group on the α-carbon and, less importantly, due to contact with O(1A) at 2.949 Å. Further, as a consequence of the elongated La(1)−O(1) bond, the trans bond, La(1)−O(4) is appreciably shortened to 2.597(6) Å. Comparison of the remaining La−O(crown) bonds suggest that the lanthanum ion is situated closer to O(4), O(5), and O(6) *vis-á-vis* O(1), O(2), and O(3) (Figure 14). There are some interesting modifications of the torsion angles in the fluoroalkyl crown ether. The O(6)−C(11)−C(12)−O(1) and O(1)−C(1)−C(2)−O(2) angles are directly affected by the presence of the fluoroalkyl chain and are reduced to 22.1 and 38.1°, respectively. Also, the 18-crown-6 ring shows a deviation from the mean plane of 0.1856 Å, which is less than that found in **22** (0.2473 Å). All but one of the C−O−C−C torsion angles [C(11)−O(6)−C(10)−C(9), 118.3(12)°] indicate that the conformations tend to an anti geometry whereas

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **23**

	x	*y*	*z*	*U*(eq)[a]
La(1)	6572(1)	1521(1)	274(1)	33(1)
O(1)	7615(7)	702(2)	166(6)	53(2)
O(2)	8797(6)	1248(2)	1655(6)	54(2)
O(3)	7264(6)	1770(2)	2651(5)	46(2)
O(4)	5063(7)	2029(2)	1306(6)	53(2)
O(5)	4015(6)	1594(2)	−664(6)	50(2)
O(6)	5523(8)	998(2)	−1436(7)	68(2)
O(7)	6006(6)	1987(2)	−1681(6)	54(2)
C(1)	8946(12)	601(3)	652(11)	66(3)
C(2)	9699(11)	987(4)	1080(10)	66(3)
C(3)	9421(11)	1497(3)	2667(10)	61(3)
C(4)	8414(11)	1606(3)	3466(9)	61(3)
C(5)	6357(11)	1980(3)	3313(10)	61(3)
C(6)	5478(12)	2242(4)	2451(10)	70(3)
C(7)	3876(11)	2181(4)	575(11)	68(3)
C(8)	3128(11)	1824(4)	−27(11)	70(3)
C(9)	3348(11)	1302(4)	−1570(12)	74(3)
C(10)	4384(11)	1143(3)	−2322(10)	67(3)
C(11)	5824(14)	599(4)	−1503(15)	102(5)
C(12)	7028(14)	454(4)	−863(12)	88(4)
S(1)	8957(2)	1617(1)	−2212(2)	47(1)
O(1A)	8193(6)	1435(2)	−1291(6)	49(2)
O(1B)	10241(7)	1757(3)	−1698(8)	88(3)
O(1C)	8195(7)	1886(2)	−3095(7)	71(2)
C(1A)	9329(14)	1174(4)	−3132(11)	68(3)
F(1A)	8246(9)	1007(3)	−3738(7)	107(3)
F(1B)	9936(9)	892(2)	−2360(7)	110(3)
F(1C)	10110(8)	1264(2)	−3983(6)	92(2)
S(2)	8685(3)	2540(1)	840(2)	50(1)
O(2A)	8023(7)	2158(2)	431(6)	50(2)
O(2B)	8629(7)	2643(2)	2153(6)	67(2)
O(2C)	9950(8)	2599(3)	424(7)	78(2)
C(2A)	7600(14)	2920(3)	−33(11)	69(3)
F(2A)	8007(10)	3290(2)	259(8)	118(3)
F(2B)	7567(8)	2877(2)	−1285(6)	90(2)
F(2C)	6349(8)	2886(2)	186(8)	98(2)
S(3)	4451(3)	744(1)	1844(3)	68(1)
O(3A)	5403(7)	1059(2)	1633(7)	62(2)
O(3B)	4984(11)	342(2)	1822(10)	115(4)
O(3C)	3178(11)	790(4)	1175(13)	156(5)
C(3A)	4272(34)	804(7)	3462(24)	161(11)
F(3A)	5323(21)	841(7)	4182(11)	256(12)
F(3B)	3635(24)	1176(5)	3502(24)	326(15)
F(3C)	3472(17)	543(4)	3862(13)	249(8)
C(13)	9034(15)	272(5)	1671(15)	99(5)
C(14)	8360(16)	342(5)	2777(14)	99(5)
C(15)	8146(18)	−34(6)	3592(16)	103(5)
F(13A)	10325(8)	175(3)	2063(8)	117(3)
F(13B)	8416(11)	−103(2)	1109(8)	131(4)
F(14A)	9156(9)	625(2)	3505(7)	104(3)
F(15A)	9242(10)	−241(2)	3943(7)	111(3)
F(15B)	7217(14)	−275(4)	3125(13)	211(7)
F(15C)	7812(11)	112(3)	4667(11)	139(4)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **23**

Bond Lengths

La(1)−O(1)	2.885(6)	O(2)−C(2)	1.446(12)
La(1)−O(2)	2.661(6)	O(3)−C(5)	1.409(12)
La(1)−O(3)	2.641(6)	O(3)−C(4)	1.450(11)
La(1)−O(4)	2.597(6)	O(4)−C(6)	1.408(12)
La(1)−O(5)	2.651(6)	O(4)−C(7)	1.424(12)
La(1)−O(6)	2.602(7)	O(5)−C(8)	1.412(12)
La(1)−O(7)	2.566(6)	O(5)−C(9)	1.451(12)
La(1)−O(1A)	2.509(6)	O(6)−C(11)	1.343(12)
La(1)−O(2A)	2.537(6)	O(6)−C(10)	1.459(12)
La(1)−O(3A)	2.497(6)	C(1)−C(2)	1.51(2)
O(1)−C(1)	1.412(13)	C(1)−C(13)	1.52(2)
O(1)−C(12)	1.417(12)	C(3)−C(4)	1.46(2)
O(2)−C(3)	1.419(11)	S(1)−O(1A)	1.454(6)

Bond Angles

O(1)−La(1)−O(2)	54.8(2)	O(1A)−La(1)−O(2A)	73.0(2)
O(1)−La(1)−O(3)	105.9(2)	O(1A)−La(1)−O(3A)	136.1(2)
O(1)−La(1)−O(4)	148.1(2)	O(2A)−La(1)−O(3A)	140.8(2)
O(1)−La(1)−O(5)	114.4(2)	O(1A)−La(1)−O(7)	68.1(2)
O(1)−La(1)−O(6)	58.6(2)	O(2A)−La(1)−O(7)	68.2(2)
O(2)−La(1)−O(3)	59.3(2)	O(3A)−La(1)−O(7)	138.8(2)
O(2)−La(1)−O(4)	119.1(2)	C(1)−O(1)−C(12)	115.0(9)
O(2)−La(1)−O(5)	160.5(2)	C(1)−O(1)−La(1)	122.5(6)
O(2)−La(1)−O(6)	113.1(2)	C(12)−O(1)−La(1)	116.3(6)
O(3)−La(1)−O(4)	59.8(2)	O(1)−C(1)−C(2)	109.4(8)
O(3)−La(1)−O(5)	116.3(2)	O(1)−C(1)−C(13)	112.4(10)
O(3)−La(1)−O(6)	153.0(2)	C−O−La(*av*)	120.9(6)
O(4)−La(1)−O(5)	59.8(2)	C−O−C(*av*)	114.7(8)
O(4)−La(1)−O(6)	120.3(2)	C−C−O(*av*)	109.8(9)
O(6)−La(1)−O(5)	61.2(2)		

Table 6. Coordination Sphere O···O Close Contacts (Å) <3 Å and Hydrogen Bonding Geometry for **22** and **23**

	22	**23**
O(1)···O(2)	2.645	2.561
O(1)···O(1A)		2.949
O(2)···O(3)	2.673	2.625
O(2)···O(8)	2.815	
O(3)···O(4)	2.689	2.610
O(3)···O(2A)		2.866
O(4)···O(5)	2.672	2.618
O(4)···O(2A)	2.943	
O(4)···O(7)	2.955	
O(5)···O(6)	2.652	2.673
O(5)···O(7)	2.951	2.737
O(6)···O(1)	2.631	2.698
O(6)···O(1A)	2.860	
O(7)···O(1A)		2.842
O(7)···O(8)	2.844	
O(8)···O(1A)	2.935	

Hydrogen Bonding Geometry (Å) in **22**

H(7AA)···O(2C)	2.326^{I}	H(8AA)···O(1C)	2.055^{II}
H(7BB)···O(3B)	2.123^{I}	H(7BB)···O(3F)	1.956^{I}
H(8BB)···O(3B)	2.130^{I}	H(8BB)···O(3D)	2.283^{I}
H(2B)···O(1B)	2.538^{II}	H(7B)···O(3A)	2.573^{III}
H(4B)···F(3D)	2.472^{I}	O(7)···O(3B)	2.707^{I}
O(7)···O(3F)	2.787^{I}	O(8)···O(1C)	2.788^{II}
O(8)···O(3B)	2.793^{I}	O(8)···O(3D)	2.971^{I}

Hydrogen Bonding Geometry (Å) in 23

H(8B)···O(1B)	2.351^{I}	O(2B)···O(7)	2.817^{II}

[a] Symmetry operations: I = $-1 + x, y, z$; II = $-x, 1 - y, -z$; III = $1 - x, 1 - y, 1 - z$.

in the case of **23**, there are two such angles, [C(8)−O(5)−C(9)−C(10), −87.9(10)°, and C(5)−O(3)−C(4)−C(3), 103.1(10)°], that tend to have a *gauche* conformation. Least squares analysis (Table 7) of the O(1)···O(6) plane reveals that the lanthanum atom is displaced below the crown ring by a distance of 0.5979 Å. In the 18-crown-6 ring bearing a fluorinated side chain, O(1) and O(3), and O(2) and O(6) oxygen atoms are situated ∼0.34 and 0.18 Å above and below the ring, respectively, while O(4) and O(5) lie approximately in the mean plane (∼0.03 Å). The O−C−C−O torsion angles indicate that the macrocycle adopts a different sequence, $g^+g^-g^+g^-g^+g^+$, compared to that of **22**. The packing diagram of **23** is shown in Figure 15. Although the hydrogen atoms on the water molecule were not located, evidence for the formation of hydrogen bonds is indicated by the close O(2B)···O(7) contact of 2.817 Å$^{I'}$ (I$'_{symm}$: $^1/_2 + x$, $^1/_2 - y$, $^1/_2 + z$). Also present in the crystal packing are hydrogen bonds H(8B)(crown)···O(1B) at 2.351 Å^{I} (I$_{symm}$: $-1 + x, y, z$) and F(3B)···F(2A) at 2.691 Å$^{I''}$ (I$''_{symm}$: $-\,^1/_2 + x$, $^1/_2 - y$, $^1/_2 + z$).

We have also synthesized complexes of lanthanum triflate with the fluorinated macrocyclic ligands **15** and **16** to give the complexes $La(OSO_2CF_3)_3$(18-crown-6-$CF_2CFHCF_2C_6F_5$)(H_2O) (**24**) and $La(OSO_2CF_3)_3$(18-crown-6-$CF_2CFHOCF_2C(CF_3)FOCF_2$-

Table 7. Torsion Angles (deg) and Least-Squares Plane Analysis for **22** and **23**

torsion angle	**22**	**23**
O(1)C(1)C(2)O(2)	−55.7(4)	38.1(11)
O(2)C(3)C(4)O(3)	53.9(10)	−51.2(11)
O(3)C(5)C(6)O(4)	50.2(14)	42.7(12)
O(4)C(7)C(8)O(5)	−54.2(12)	−51.9(12)
O(5)C(9)C(10)O(6)	−49.4(11)	52.5(12)
O(6)C(11)C(12)O(1)	47.8(13)	22.1(22)
C(1)O(1)C(12)C(11)	154.0(8)	−168.1(12)
C(12)O(1)C(1)C(2)	−140.7(7)	145.6(10)
C(2)O(2)C(3)C(4)	168.7(7)	−157.0(9)
C(3)O(2)C(2)C(1)	−167.3(5)	147.6(9)
C(4)O(3)C(5)C(6)	169.1(10)	162.0(9)
C(5)O(3)C(4)C(3)	103.1(10)	−165.1(9)
C(6)O(4)C(7)C(8)	−178.0(9)	−144.4(9)
C(7)O(4)C(6)C(5)	175.6(10)	159.0(9)
C(8)O(5)C(9)C(10)	−87.9(10)	169.8(9)
C(9)O(5)C(8)C(7)	−168.2(8)	−164.4(9)
C(10)O(6)C(11)C(12)	151.6(9)	168.2(13)
C(11)O(6)C(10)C(9)	−166.5(8)	118.3(12)

Least-Squares Plane Analysis

	22	**23**
A	7.310	−5.574
B	−7.644	−19.466
C	4.381	6.945
D	−0.5991	−5.8364
mean dev from the plane (Å)	0.2473	0.1856
La(1)	−0.5978	−0.5979
O(1)	−0.0438	0.3412
O(2)	0.0441	−0.3463
O(3)	−0.2524	0.1822
O(4)	0.4694	−0.0278
O(5)	−0.4458	0.0334
O(6)	0.2286	−0.1827

[a] In the form $Ax + By + Cz = D$, where x, y, and z are the crystal coordinates with deviations (Å) of the relevant atoms for **22** and **23**.

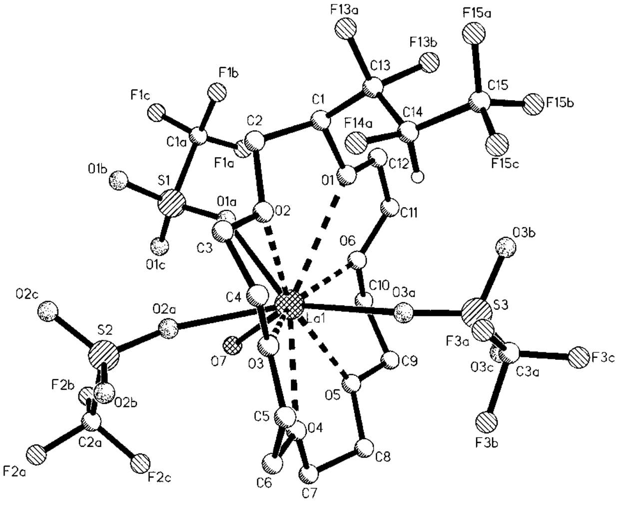

Figure 13. Molecular structure of **23**.

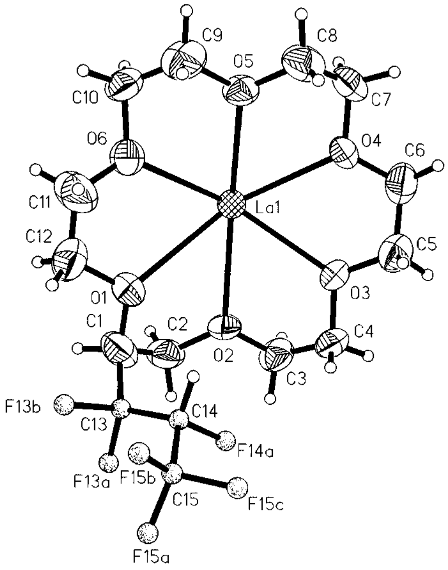

Figure 14. Lanthanum-18-C-6-crown with fluorinated side chain representing the core of **23**.

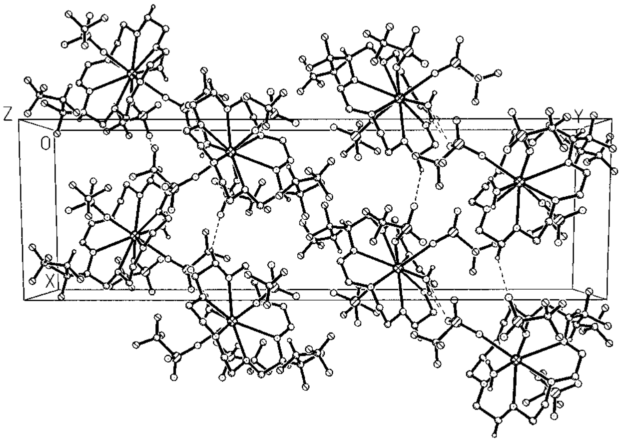

Figure 15. Crystal packing diagram for **23** along the *c*-axis.

CF_2SO_2F) (**25**), respectively. To date, however, we have not been able to prepare crystals of **24** and **25** suitable for single-crystal X-ray analysis. We have characterized these compounds with infrared, NMR (^{19}F and ^{1}H), and mass spectral analysis. Similarly, we have prepared $La[N(SO_2CF_3)_2]_3$ (**26**) from the reaction between La_2O_3 and $HN(SO_2CF_3)_2$ and have found that it readily forms a stable complex with dibenzo-18-crown-6, $La[N(SO_2CF_3)_2]_3$dibenzo-18-crown-6 (**27**). Attempts to obtain crystals of this complex for single-crystal X-ray analysis have also not been successful, although we are continuing our efforts in that direction. The preparation of additional polyfluorinated ligands and studies of their complexing ability with a variety of metals are subjects of a great deal of interest in this laboratory, and in many others. The solubility properties exhibited by these polyfluorinated metal complexes, and the nature of metal−ligand bonding exhibited by them are topics of particular importance to our research interests in this area, and are subjects that we continue to pursue vigorously.

Experimental Section

Materials. Before use, CsF is oven-dried. The compounds $C_6F_5O(TMS)$ (TMS = $(CH_3)_3Si-$), $(TMS)OCH_2CF_2CF_2CH_2O(TMS)$, $(TMS)OCH_2CF_2CF_2CF_2CH_2O(TMS)$,[10,11,18] and $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$[19] are prepared according to literature methods. Both tetrahydrofuran (THF) and dioxane (Fisher Chemicals) are distilled from Na/benzophenone before use. Diglyme is distilled from Na and stored over 4 Å molecular sieve. Acetonitrile is distilled from P_4O_{10} before use. The starting materials 18-crown-6, 15-crown-5, di-*tert*-butyl peroxide, La_2O_3 (Aldrich), $CF_2{=}CH_2$, $CF_2{=}CFH$ $CH_2{=}CHCF_3$, $CF_2{=}CFCF_3$, $CH_2{=}CHC_8F_{17}$ (PCR), $C_6F_5CF_2CF{=}CF_2$ (BNFL), and trifluoromethanesulfonic acid (3M) are purchased and used as received.

X-ray Crystal Structure Analysis. The X-ray diffraction data for compounds **22** and **23** are collected on a Syntex P2$_1$ diffractometer upgraded to Siemens P4 at 293(2) K using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The cell constants are determined

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(18) Bruynes, C. A.; Jurriens, T. K. *J. Org. Chem.* **1982**, *47*, 3966.

(19) (a) Putnam, R. E.; Nicoll, W. D., E. I. DuPont Fr. 1,406,778. (b) *Chem. Abstr.* **1965**, *63*, 16216h; E. I DuPont Brit. 1,034,197 1966; *Chem. Abstr.* **1967**, *66*, 11326z.

initially from the Hemispherical Search (XSCANS[20]) from six and nine reflections with $9 < 2\theta < 20°$ for **22** and **23**, respectively. Finally, the precise unit cell dimensions are determined by the least square refinement of an additional 27 (compound **22**) and 23 (compound **23**) computer-centered reflections from the Thin Shell Search routine with $25 < 2\theta < 30°$. The diffraction data are collected for 2θ values between 3° (3.5° for **23**) and 45° using omega scans, with online profile fitting and variable scan speeds using the XSCANS program.[20] Monitoring of three standard reflections 215, 234, and 113 for **22**; and 071, 0,13,1 and 1,12,2 for **23**, after an interval of 97 reflections did not show any crystal decomposition during the data collection. The data are corrected for Lorentz/ polarization effects and for absorption using emperical ψ-scans. The structures were solved by the direct method using the SHELX86[21] program incorporated in SHELXTL-PC V 4.1.[22] and refined by the least square method on F^2 using SHELXL-93.[23] In the case of **22**, the triflate anion suffered rotational disorder and was modeled by restraining the bond distances to those of relatively more ordered covalent triflate groups on lanthanum. On the basis of difference electron density maps, three additional oxygen/fluorine atom positions were added at 60° to O3A, O3B, and O3C, and F3A, F3B, and F3C to the original model. Following several iterative refinement cycles, the site occupancies for these oxygen and fluorine atoms are fixed at 50%. All non-hydrogen atoms are refined anisotropically. The hydrogen atoms of the two water molecules in **22** were located from the difference electron density maps while the remaining hydrogen atoms are fixed by the riding model. A summary of data collection and refinement parameters is given in Table 1.

General Procedures. Volatile liquids are handled in a Pyrex vacuum system equipped with a Heise Bourdon tube gauge and a Televac thermocouple gauge. Conventional *PVT* techniques are used to quantitate volatile starting materials and products. All reactions are either conducted in a steel bomb or in a flask under nitrogen atmosphere. Products are either separated by low temperature trap-to-trap distillation on a dynamic vacuum line or by vacuum distillation and are further purified by preparative GC using a 6 ft by $^1/_4$ in. 25% SE-30 (silica) copper column, and column chromatography with 70−230 mesh silica in a 30 cm by 1.2 cm glass column. Infrared spectra are recorded on a Perkin-Elmer Model 1710 FTIR spectrometer equipped with an IBM PS/2 data station. Both ^{19}F and ^1H NMR are obtained with a Bruker AC 200 Fourier transform NMR spectrometer using $CDCl_3$ as solvent unless otherwise indicated. Mass spectra are obtained with a VG 7070HS mass spectrometer. Elemental analyses are performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Reactions of THF with Fluorinated Olefins in the Presence of Di-*tert*-butyl Peroxide. To a 120 mL stainless steel bomb containing approximately 6 mmol of di-*tert*-butyl peroxide at −196 °C are added 15 mmol of fluorinated olefin and a molar excess of THF. After the reaction mixture is allowed to warm to room temperature, the bomb is placed in a 140 °C oven and maintained at that temperature overnight. The products are separated by trap-to-trap distillation, and any residual THF is washed away with water. Further purification is accomplished by preparative GC.

Properties of $CH_2CH_2CH_2CH(CF_2CH_3)O$ (1) and $CH_2CH_2CH_2CH(CH_2CF_2H)O$ (2). Reaction of THF with $CF_2{=}CH_2$ by method A gives a 4:1 mixture of **1** and **2**. Separation of the mixture by GC results in a pure fraction of **1** and a fraction containing **1** and **2**. Spectral data for **1** are as follows. IR (film): 2985 s, 2877 s, 1401 s, 1250 s, 1144 s, 1083 s, 924 s, 821 m cm^{-1}. ^1H NMR: δ 1.57 (t, $^3J_{H-F} = 18.9$ Hz, CF_2CH_3), 1.77−2.00 (m, CH_2CH_2), 3.78−3.98 (m, CH_2OCH) ppm. ^{19}F NMR: δ −100.1, −107.0 (CF_2, AB pattern, $^2J_{A-B} = 248.5$ Hz; A, quartet-doublet, $^3J_{H-F} = 19.8$, 7.1 Hz; B, quintet, $^3J_{H-F} = 18.4$ Hz) ppm. MS (CI$^+$) [*m/e* (species) intensity]: 137 ($M^+ + 1$) 8.9; 135 ($M^+ - 1$) 8.9; 121 ($M^+ - CH_3$) 1.2; 119 ($M^+ - OH$) 15.8; 117 ($M^+ - F$) 80.2; 99 ($M^+ - HF - OH$) 10.0; 71 ($M^+ - CF_2CH_3$) 100; 57 ($M^+ - CF_2CH_3 - CH_2$) 14.5. Anal. Calcd for $C_6H_{10}F_2O$ (**1**): C, 52.94; H, 7.35; F, 27.9. Found: C, 53.33; H, 7.70; F, 27.6. Spectral data obtained for **2** are as follows. ^1H NMR: δ 1.81−2.03 (m, CH_2CH_2), 3.67−3.99 (m, CH_2OCH), 5.91 (t−t, $^2J_{H-F} = 56.9$ Hz, $^3J_{H-H} = 4.84$ Hz, CFH) ppm. ^{19}F NMR: δ −115.47, −117.76 (CF_2, AB pattern, $^2J_{A-B} = 286.2$ Hz; A, d−t, $^2J_{H-F} = 57.5$ Hz, $^3J_{H-F} = 13.2$ Hz; B, d−t, $^2J_{H-F} = 56.5$ Hz, $^3J_{H-F} = 18.8$ Hz) ppm.

Properties of $CH_2CH_2CH_2CH(CF_2CH_2F)O$ (3) and $CH_2CH_2CH_2CH(CHFCF_2H)O$ (4). Reaction of THF with $CF_2{=}CHF$ gives a 3:1 ratio of **3** and **4** as a mixture of diastereoisomeric pairs. Spectral data obtained for the mixture are as follows. IR (film): 2970 s, 2886 s, 1456 s, 1407 m, 1385 m, 1277 s, 1245 s, 1206 s, 1181 s, 1125 s, 1083 s, 1025 s, 936 s, 913 s cm^{-1}. NMR data for **3** are as follows. ^1H NMR: δ 1.87−2.13 (m, CH_2CH_2), 3.80−3.86 (m, CH_2O), 4.13−4.21 (m, OCH), 4.40−4.71 (m, CH_2F) ppm. ^{19}F NMR: −117.1, −128.4 (AB pattern, $^2J_{A-B} = 266.1$ Hz, CF_2; A, d−t−d, $^3J_{H-F} = 19.2$ Hz, 4.4 Hz, $^3J_{F-F} = 14.4$ Hz; B, octet, $J = 7.3$ Hz), −239.4 (t−t, $^2J_{H-F} = 46.3$ Hz, $^3J_{F-F} = 14.4$ Hz, CH_2F) ppm. NMR data for **4** are as follows. ^1H NMR: δ 1.87−2.13 (m, CH_2CH_2), 3.80−3.86 (m, CH_2OCH), 5.69−6.12 (m, CFH and CF_2H) ppm. ^{19}F NMR: δ −130.13, −131.87 (AB pattern, $^2J_{A-B} = 305.3$ Hz; A, d−d−d, $^2J_{H-F} = 57.9$ Hz, $^3J_{F-F} = 11.3$ Hz, $^3J_{H-F} = 12.7$ Hz; B, d−d−d, $^2J_{H-F} = 53.7$ Hz, $^3J_{F-F} = 5.7$ Hz, $^3J_{H-F} = 11.3$ Hz, CF_2H), −132.0 to −134.62 (AB pattern, $^2J_{A-B} = 294.4$ Hz; A, d−d−d, $^2J_{H-F} = 53.7$ Hz, $^3J_{F-F} = 8.5$ Hz, $^3J_{H-F} = 13.4$ Hz; B, d−d−d, $^2J_{H-F} = 54.4$ Hz, $^3J_{F-F} = 11.3$ Hz, $^3J_{H-F} = 14.1$ Hz, CF_2H) ppm. MS (CI$^+$) [*m/e* (species) intensity] of the mixture: 155 ($M^+ + 1$) 54.7; 153 ($M^+ - 1$) 10.5; 137 ($M^+ - OH$) 16.6; 135 ($M^+ - F$) 66.8; 117 ($M^+ - HF - OH$) 8.1; 115 ($M^+ - HF - F$) 10.1; 93 ($M^+ - CH_2F - CH_2CH_2$) 48.8; 87 ($M^+ - CH_2F - HF - CH_2$) 49.7; 71 ($M^+ - C_2H_2F_3$) 76.6; 59 ($C_3H_7O^+$) 100. Anal. Calcd for $C_6H_9F_3O$: C, 46.75; H, 5.84; F, 37.01. Found: C, 46.59; H, 5.86; F, 36.9.

Properties of $CH_2CH_2CH_2CH(CH_2CH_2CF_3)O$ (5). Reaction of THF with $CH_2{=}CHCF_3$ gives a single compound (**5**) in 48% yield. Spectral data obtained for **5** are as follows. IR (film): 2980 m, 1455 s, 1374 s, 1255 s, 1145 s, 1050 s, 991 s, cm^{-1}. ^1H NMR: δ 1.61−2.02 (8H, m, CH_2), 3.62−3.86 (m, CH_2OCH) ppm. ^{19}F NMR: δ −66.8 (t, $^3J_{H-F} = 9.4$, CF_3) ppm. MS (CI$^+$) [*m/e* (species) intensity]: 169 ($M^+ + 1$) 17.7; 167 ($M^+ - 1$) 10.2; 152 ($M^+ - O$) 5.6; 151 ($M^+ - OH$) 78.1; 149 ($M^+ - F$) 23.7; 107 ($CF_2CH_2CH_2CHO^+$) 100; 71 ($C_4H_7O^+$) 46.9; 57 ($C_3H_5O^+$) 74.5. Anal. Calcd for $C_7H_{11}F_3O$: C, 50.00; H, 6.55; F, 33.93. Found: C, 50.26; H, 6.78; F, 34.1.

Properties of $CH_2CH_2CH_2CH(CF_2CFHCF_3)O$ (6). Reaction of an excess amount of THF with $CF_2{=}CFCF_3$ gives **6** as a single product in 76% yield (bp = 75 °C at 40 mmHg).[3−5,7] Spectral data not previously reported for **6** are as follows. IR (film): 2993 m, 2886 m, 1396 s, 1345 s, 1289 s, 1248 s, 1186 s, 1085 s, 1031 s, 936 m, 896 m, 831 m, 676 m cm^{-1}. ^1H NMR: δ 4.84−5.26 (m, CFH), 4.10−4.37 (m, OCH), 3.82−3.90 (m, OCH_2), 1.82−2.16 (m, CH_2CH_2) ppm. ^{19}F NMR: δ −74.3 (m, CF_3), −120.4 to −124.5 (AB pattern, $^2J_{AB} = 263.8$ Hz), −125.1 to −130.6 (AB pattern, $^2J_{AB} = 269.3$ Hz), −192.2 to −197.5 (m, CFH, diastereoisomers) ppm. MS (CI$^+$) [*m/e* (species) intensity]: 223 ($M^+ + 1$) 100; 221 ($M^+ - 1$) 8.6; 203 ($M^+ - F$) 44.0; 183 ($M^+ - F - HF$) 32.3; 161 ($M^+ - F - C_3H_6$) 27.3; 71 ($CH_2CH_2CH_2CHO^+$) 82.5.

Properties of $CH_2CH_2CH_2CH(CF_2CFH(CF_2)_4CF_3)O$ (7). Reaction of THF with $CF_2{=}CFC_5F_{11}$ gives a single compound in 55% yield. Spectral data obtained for **7** are as follows. IR (film): 2991 m, 2888 m, 1454 s, 1392 m, 1348 s, 1240 s, 1142 s, 1088 s, 999 s, 940 s, 876 m cm^{-1}. ^1H NMR: δ 1.96 (m, CH_2), 2.14 (m, CH_2), 3.86 (t, OCH_2), 4.18−4.38 (m, OCH), 5.05−5.47 (m, CFH) ppm. ^{19}F NMR: δ −81.3 (t, CF_3), −116.7 to −130.1 (m, CF_2), −192.4, −198.4 (m, CFH, two AB patterns) ppm. MS (CI$^+$) [*m/e* (species) intensity]: 423 ($M^+ + 1$) 21.0; 403 ($M^+ - F$) 17.2; 383 ($M^+ - F - HF$) 6.5; 121 ($C_5H_7F_2O^+$) 78.1; 91 ($C_4H_5F_2^+$) 7.3; 71 ($C_4H_7O^+$) 100.

Properties of $CH_2CH_2CH_2CH(CF_2{}^aCF^bHOCF_2{}^cCF^d(CF_3{}^e)OCF_2{}^fCF_2{}^gSO_2F^h)O$ (8). This compound boils at 63−65 °C at 1 mmHg and is obtained in 75% yield. Spectral data obtained for **8** are as

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(20) XSCANS 2.0, Siemens Analytical Instruments Division, Madison, WI, 1992.

(21) Sheldrick, G. M. SHELXS86, Program for the Solution of Crystal Structure, University of Göttingen, Germany, 1986.

(22) SHELXTL 4.2 (PC Version), Program library for Structure solution and Molecular graphics, Siemens Analytical Instruments Division, Madison, WI, 1992.

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

follows. IR (film): 2995 m, 2888 m, 1465 s, 1312 s, 1245 s, 1207 s, 1163 s, 1143 s, 1114 s, 1088 m, 1025 s, 988 m cm^{-1}. ^{1}H NMR: δ 1.86−2.25 (m, CH_2CH_2), 3.81 (t, $^{3}J_{H-H} = 6.1$ Hz, OCH_2), 4.00−4.31 (t−m, OCH), 6.15 (d−m, $^{2}J_{H-F} = 62.8$ Hz, CFH, overlap of diastereoisomers) ppm. ^{19}F NMR: δ 45.0 (s, H), −79.7 (m, C), −80.5 (m, E), −84.2 (m, F), −112.4 (m, G), −129.1, −131.5 (2F/2, AB pattern, $^{2}J_{A-B} = 266.1$ Hz, A, d−t−d, B, d−d−d), −145.0 (m, D), −152.2 (m, B) ppm. MS (CI$^+$) [*m/e* (species) intensity]: 519 ($M^+ + 1$) 1.4; 509 ($M^+ - F$) 1.9; 153 ($C_4H_7OCF_2CFH^+$) 5.4; 105 ($C_4H_7CF_2^+$) 16.1; 91 ($C_3H_5CF_2^+$) 10.9; 71 ($C_4H_7O^+$) 100; 69 (CF_3^+) 26.5.

Properties of $CH_2CH_2OCH_2CH(CF_2{}^{a}CF^{b}HOCF_2{}^{c}CF^{d}(CF_3{}^{e})$-$OCF_2{}^{f}CF_2{}^{g}SO_2F^{h})O$ (9). This compound boils at 80 °C at 1 mmHg and is obtained in 84% yield. Spectral data obtained for **9** are as follows. IR (film): 2982 s, 2927 s, 2871 s, 1463 vs, 1383 s, 1358 s, 1311 vs, 1187 vs, 1023 vs, 986 s, 914 s, 896 s cm^{-1}. ^{1}H NMR: δ 3.52−3.67 (6H, m, OCH_2), 3.84 (t, $^{3}J_{H-H} = 12.0$ Hz, OCH), 5.93−5.99, 6.19−6.28 (1H, d−t, $^{2}J_{H-F} = 54.5$ Hz, CFH, overlap of diastereoisomers) ppm. ^{19}F NMR: δ 44.5 (s, H), −79.2 (m, C), −82.4 (m, E), −85.8 (m, F), −112.9 (m, G), 128.1 to −140.1 (overlapping AB patterns, A), −145.4 (m, D), −144.5, −154.2 (m, B, diastereoisomers) ppm. MS (CI$^+$) [*m/e* (species) intensity]: 535 ($M^+ + 1$) 1.0; 533 ($M^+ - 1$) 1.0; 515 ($M^+ - F$) 7.3; 169 ($C_4H_7O_2CF_2CFH^+$) 15.3; 125 ($C_2H_3OCF_2CFH^+$) 16.2; 87 ($C_4H_7O_2^+$) 100; 69 (CF_3^+) 6.8. Anal. Calcd for $C_{11}H_8F_{14}O_6S$: C, 24.72; H, 1.50; F, 49.81. Found: C, 24.74; H, 1.72; F, 50.6.

Properties of $(CF_3CFHCF_2)CHCH_2CH_2CH(CF_2CFHCF_3)O$ (10). Reaction of THF with $CF_2{=}CFCF_3$ in a 1:3 molar ratio respectively gives, after column chromatography, compound **10** in 81% yield. Spectral data obtained for **10** are as follows. IR (film): 2983 m, 1386 s, 1348 m, 1289 s, 1246 s, 1186 s, 1104 s, 1055 s, 1018 s, 961 m, 890 s cm^{-1}. ^{1}H NMR: δ 2.27 (m, CH_2CH_2); 4.38−4.58 (2H, t, m, OCH); 4.80−5.15 (2H, d, m, CFH) ppm. ^{19}F NMR: δ −74.0 and −74.9 (3F, m, CF_3); −118.7 and −131.3 (4F, overlap of AB patterns, OCH*CF₂*); −191.9 and −197.0 (2F, m, CHF, mixture of diastereoisomers) ppm. MS (CI$^+$) [*m/e* (species) intensity]: 373 ($M^+ + 1$) 90.5; 371 ($M^+ - 1$) 6.4; 353 ($M^+ - F$) 100; 333 ($M^+ - F - HF$) 24.9; 313 ($M^+ - F - 2HF$) 15.9; 221($M^+ - CF_2CFHCF_3$) 41.5; 205 ($M^+ - CF_2CFHCF_3 - O$) 11.2; 159 ($C_5F_5H_4^+$) 23.1; 69 (CF_3^+) 12.4.

Properties of $OCH_2CH_2CH_2CH(CF_2CFHCF_2C_6F_5)$ (11). Reaction of an excess of THF with $CF_2{=}CFCF_2C_6F_5$ gives a single compound **11** in 55% yield, bp 112 °C at 0.5 mmHg. Spectral data obtained for **11** are as follows. IR (film): 2969 s, 2877 s, 1658 s, 1531 s, 1510 s, 1426 s, 1390 s, 1355 s, 1328 s, 1212 s, 1089 s, 1024 s, 998 s cm^{-1}. ^{1}H NMR: δ 2.04−2.41 (m, CH_2CH_2), 3.99 (t, CH_2O), 4.35−4.47 (m, OCH), 5.18−5.60 (d, m, CFH) ppm. ^{19}F NMR: δ −98.20, −104.69 (AB pattern, $^{2}J_{A-B} = 266.1$ Hz, CF_2; A, d−t−d, $^{3}J_{H-F} = 19.2$, 4.4 Hz, $^{3}J_{F-F} = 14.4$ Hz; B, octet, $J = 7.3$ Hz), −239.4 (t−t, $^{2}J_{H-F} = 46.3$ Hz, $^{3}J_{F-F} = 14.4$ Hz, CH_2F) ppm. ^{19}F NMR: δ −98.20 to −104.69 (2F/2, AB pattern, $^{2}J_{A-B} = 291.9$ Hz, C_6F_5*CF₂*); −100.86 to −102.14 (2F/2, AB pattern, $^{2}J_{A-B} = 285.3$ Hz, C_6F_5*CF₂*, diastereoisomers); −118.89 to −121.97 (2F/2, AB pattern, $^{2}J_{A-B} = 264.58$ Hz; OCH*CF₂*); −124.29 to −128.97(2F/2, AB pattern, $^{2}J_{A-B} = 271.17$ Hz, OCH*CF₂*, diastereoisomers); −139.34 (2F, m, *o*-F); −148.93 (1F, m, *p*-F); −160.76 (2F, m, *m*-F); −196.45, −200.06 (1F, m, CHF, mixture of diastereoisomers). MS (CI$^+$) [*m/e* (species) intensity]: 369 ($M^+ - 1$) 3.4; 351 ($M^+ - F$) 78.1; 331 ($M^+ - F - HF$) 28.1; 311 ($M^+ - F - 2HF$) 18.5. Anal. Calcd for $C_{13}H_8F_{10}O$: C, 42.16; H, 2.16; F, 51.35. Found: C, 42.30; H, 2.28; F, 51.1.

Properties of $(C_6F_5CF_2CFHCF_2)CHCH_2CH_2CH(CF_2CFHCF_2$-$C_6F_5)O$ (12). Reaction of THF with $CF_2{=}CFCF_2C_6F_5$ in a 1:2 molar ratio respectively gives compound **11** in 33% yield and compund **12** in 37% yield. Spectral data obtained for **12** are as follows. IR (film): 2979 s, 1657 s, 1532 s, 1505 s, 1426 s, 1357 s, 1329 s, 1215 s, 1097 s, 1024 s, 998 s, 883 m cm^{-1}. ^{1}H NMR: δ 2.15−2.30 (m, CH_2CH_2); 4.46−4.58 (2H, m, OCH); 4.93−5.38 (2H, m, CFH) ppm. ^{19}F NMR: δ −98.14 to −107.82 (4F, overlap of AB patterns, C_6F_5*CF₂*); −118.84 to −130.24 (4F, overlap of AB patterns, OCH*CF₂*); −139.85 (4F, m, *o*-F); −148.39 (2F, m, *p*-F); −160.57 (4F, m, *m*-F); −196.46 to −201.45 (2F, m, CHF, mixture of diastereoisomers). MS (CI$^+$) [*m/e* (species) intensity]: 668 (M^+) 0.8; 667 ($M^+ - 1$) 3.2; 649 ($M^+ - F$) 77.5; 629 ($M^+ - F - HF$) 32.2; 369 ($M^+ - C_6F_5CF_2CFHCF_2$) 69.9; 350 ($M^+ - C_6F_5CF_2CFHCF_2 - F$) 12.5; 331 ($M^+ - C_6F_5CF_2CFHCF_2 - 2F$) 100; 311 ($M^+ - C_6F_5CF_2CFHCF_2 - 2F - HF$) 17.8; 217 ($C_7F_7^+$) 62.1; 71 ($C_4H_6O^+$) 28.9.

Properties of 18-Crown-6-$CH_2CH_2CF_3$ (13). This compound boils at 128−132 °C at 0.2 mmHg and is obtained in 31% yield. Spectral data for **13** are as follows. IR (film): 2869 s, 1508 s, 1455 s, 1352 s, 1248 s, 1113 s, 991 s, 965 s, 839 s cm^{-1}. ^{1}H NMR: δ 1.61 (d, t, OCH*CH₂*), 2.07 (t, *CH₂*CF_3), 3.26−3.56 (23H, m, ring H) ppm. ^{19}F NMR: δ −66.6 (t, CF_3) ppm. MS (CI$^+$) [*m/e* (species) intensity]: 361 ($M^+ + 1$) 11.6; 360 (M^+) 2.2; 359 ($M^+ - 1$) 11.9; 341 ($M^+ - F$) 17.3; 315 ($M^+ - C_2H_4O - 1$) 5.1; 263 ($M^+ - CH_2CH_2CF_3$) 2.6; 219 ($M^+ - CH_2CH_2CF_3 - CH_2CH_2O$) 9.6; 204 ($C_{10}H_{20}O_4^+$) 4.3; 125 ($CF_3$-$CH_2CH_2CHCH_2^+ + 1$) 10.7; 121 ($CF_2CH_2CH_2CHCH_2O^+$) 25.9; 105 ($CF_2CH_2CH_2CHCH_2^+$) 8.6; 97 ($CF_3CH_2CH_2^+$) 13.7; 77 ($CF_2CHCH_2^+$) 16.1; 69 ($CF_3^+$) 25.1; 57 ($C_3H_5O^+$) 100.

Preparation and Properties of 18-Crown-6-(CF_2CFHCF_3) (14). This compound has been prepared previously by a different procedure.[6] In this study, **14** (bp = 140−145 °C at 0.1 mmHg) is obtained in 40% yield when excess 18-crown-6 is reacted with 10 mmol of $CF_3CF{=}CF_2$ at 130 °C for 24 h in a 150 mL stainless steel vessel in the presence of 2 mmol of *tert*-butyl peroxide. Spectral data not previously reported for **14** are as follows. IR (film, KBr): 2883 s, 1456 s, 1392 s, 1289 s, 1067 s, 1056 s, 1041 s, 974 s, 840 s, 684 s cm^{-1}. ^{1}H NMR: δ 3.61−3.97 (23H, mult, ring protons), 4.98−5.36 (1H, mult, CFH) ppm. ^{19}F NMR: δ −74.0, −74.3 (mult, CF_3), −119.5, −122.2 (AB pattern, J_{AB} = 274.9 Hz), −122.8, −125.5 (AB pattern, J_{AB} = 274.9 Hz), −196.3, −198.0 (mult, CFH) ppm. MS (CI$^+$) [*m/e* (species) intensity]: 327 ($M^+ + 1 - C_4H_8O_2$) 9.8; 283 ($M^+ + 1 - C_6H_{12}O_3$) 24.2; 263 ($M^+ - C_3F_6H$) 11.3; 239 ($C_3F_6C_4H_8O_2^+ + 1$) 78.1; 223 ($C_7H_8F_6O^+ + 1$) 52.0; 219 ($C_{10}H_{19}O_5^+$) 27.3; 209 ($C_6H_6F_6O^+ + 1$) 28.7; 89 ($C_4H_8O_2^+ + 1$) 100; 73 ($C_4H_8O^+ + 1$) 85.2.

Properties of 18-Crown-6-$CF_2CFHCF_2C_6F_5$ (15). This compound that boils at 144−147 °C at 0.02 mmHg is obtained in 43% yield. Spectral data are as follows. IR (film): 2922 s, 1714 s, 1658 s, 1504 s, 1426 s, 1328 s, 1138 s, 842 s cm^{-1}. ^{1}H NMR: δ 3.61−4.04 (23H, m, ring-H), 5.08−5.51 (1H, m, CFH) ppm. ^{19}F NMR: δ −98.6 to −104.3 (2F, overlap of AB patterns, C_6F_5*CF₂*), −118.5, −121.0 (2F/2, AB pattern, $^{2}J_{A-B} = 270.2$ Hz, $OCHCF_2$), −122.1, −124.1 (2F/2, AB pattern, $^{2}J_{A-B} = 272.1$ Hz, $OCHCF_2$, diastereoisomers), −139.4 (2F, m, *o*-F), −148.7 (1F, m, *p*-F), −160.5 (2F, m, *m*-F), −199.8, −201.1 (1F, m, CFH, diastereoisomers) ppm. MS (CI$^+$) [*m/e* (species) intensity]: 563 ($M^+ + 1$) 20.3; 561 ($M^+ - 1$) 1.2; 543 ($M^+ - F$) 1.1; 475 ($M^+ + 1 - C_4H_8O_2$) 27.3; 431 ($M^+ + 1 - C_6H_{12}O_3$) 24.4; 415 ($M^+ + 1 - C_6H_{12}O_4$) 5.6; 411 ($M^+ - C_6H_{12}O_3 - F$) 12.4; 387 ($M^+ + 1 - C_8H_{16}O_4$) 21.5; 367 ($M^+ - C_8H_{16}O_4 - F$) 36.5; 347 ($M^+ - C_8H_{16}O_4 - F - HF$) 13.4; 327 ($C_{10}F_{10}HO^+$) 7.9; 177 ($C_8H_{16}O_4^+ + 1$) 11.2; 133 ($C_6H_{12}O_3^+ + 1$) 27.5; 117 ($C_6H_{12}O_2^+ + 1$) 26.5; 89 ($C_4H_8O_2^+ + 1$) 100; 72 ($C_4H_8O^+$) 79.5.

Reaction of 18-Crown-6 with Perfluoro-5-methyl-3,6-dioxa-7-octenesulfonyl Fluoride in the Presence of Di-*tert*-butyl Peroxide. To a 100 mL three-necked round-bottomed flask equipped with a magnetic stirrer and a nitrogen inlet are added 2.7 mmol of 18-crown-6, 2.1 mmol of perfluoro-5-methyl-3,6-dioxa-7-octenesulfonyl fluoride, and 0.5 mmol of di-*tert*-butyl peroxide. After being heated at 140−150 °C under nitrogen for 8 h, the reaction mixture is poured into 50 mL of water, and extracted with 3 × 25 mL of ether. The etheral extract is dried over $MgSO_4$. Evaporation of the solvent under vacuum gives a viscous liquid product, **16**, that is purified by vacuum fractionation.

Properties of 18-Crown-6-$CF_2CFHOCF_2CF(CF_3)OCF_2CF_2SO_2F$ (16). This compound boils at 150−155 °C at 0.1 mmHg and is obtained in 54% yield. Spectral data are as follows. IR (film): 2887 m, 1465 s, 1355 m, 1310 s, 1245 s, 1206 s, 1142 s, 1114 s, 1068 m, 989 m cm^{-1}. ^{1}H NMR: δ 3.58−3.94 (23H, m, ring-H), 6.18 (1H, d−t, $^{2}J_{H-F} = 53.5$ Hz, $^{3}J_{H-F} = 6.2$ Hz, CFH) ppm. ^{19}F NMR: δ 45.2 (1F, s, SO_2F), −79.6 (2F, m, CF_2), −80.2 (3F, m, CF_3), −84.2 (2F, m, CF_2), −112.0 (2F, m, CF_2), −125.1, −128.8 (2F/2, AB pattern, $^{2}J_{A-B} = 270.5$ Hz, CF_2), −128.1 (2F/2, m, CF_2), −145.0 (1F, m, CF), −145.3, −148.5 (1F, m, d−d−t, $^{2}J_{H-F} = 58.7$ Hz, $^{3}J_{H-F} = 5.9$ Hz, CF, diastereoisomers) ppm. MS (CI$^+$) [*m/e* (species) intensity]: 711 $(M^+ + 1)$ 1.2; 710 (M^+) 6.3; 622 $(M^+ - C_4H_8O_2)$ 7.8; 578 $(M^+ - C_6H_{12}O_3)$ 8.1; 534 $(M^+ - C_8H_{16}O_4)$ 14.1; 518 $(M^+ - C_8H_{16}O_5)$ 9.7; 175 $(C_8H_{14}O_4^+ + 1)$ 7.9; 169 $(C_6H_8F_3O_2^+)$ 14.2; 149 $(C_6H_{12}O_4^+ + 1)$ 4.9; 133 $(CF_2SO_2F^+)$ 26.1; 89 $(C_4H_8O_2^+ + 1)$ 93.5; 88 $(C_4H_8O_2^+)$ 29.7; 87 $(C_4H_7O_2^+)$ 100; 73 $(C_4H_8O^+ + 1)$ 60.6.

Properties of 18-Crown-6-$(CF_2CFHCF_3)_3$ (17). Reaction of 18-crown-6 with $CF_2{=}CFCF_3$ in a 1:3 molar ratio respectively gives a **17** in 42% yield. Spectral data obtained for **17** are as follows. IR (film): 2890 s, 1456 m, 1387 s, 1284 s, 1109 s, 948 m, 841 s cm^{-1}. ^{1}H NMR: δ 3.61−3.99 (21H, m, ring-H), 4.98−5.24 (3H, m, CFH) ppm. ^{19}F NMR: δ −74.4 (3F, m, CF_3), −118.2 to -126.6 (2F, overlap of AB patterns, CF_2), −195.1 to −198.1, −199.6 (1F, m, CFH, diastereoisomers) ppm. MS (CI$^+$) [*m/e* (species) intensity]: 715 $(M^+ + 1)$ 1.2; 714 (M^+) 6.3; 695 $(M^+ - F)$ 2.8; 627 $(M^+ + 1 - C_4H_8O_2)$ 10.8; 566 $(M^+ - C_6H_{12}O_4)$ 2.8; 565 $(M^+ - C_6H_{13}O_4)$ 15.8; 563 $(M^+ - CF_3CFHCF_2)$ 4.3; 413 $(M^+ + 1 - 2CF_2CFHCF_3)$ 13.8; 389 $(C_{10}H_8F_{12}O_2^+ + 1)$ 26.5; 373 $(C_{10}H_8F_{12}O^+ + 1)$ 6.4; 369 $(C_{13}H_{19}F_6O_5^+)$ 13.3; 327 $(C_{11}H_{16}F_6O_4^+ + 1)$ 9.5; 283 $(C_9H_{12}F_6O_3^+ + 1)$ 22.9; 267 $(C_9H_{12}F_6O_2^+ + 1)$ 17.5; 239 $(C_7H_8F_6O_2^+ + 1)$ 100; 223 $(C_7H_8F_6O^+ + 1)$ 79.8; 219 $(C_{10}H_{19}O_5^+)$ 44.8; 209 $(C_6H_6F_6O^+ + 1)$ 32.4; 195 $(C_5H_4F_6O^+ + 1)$ 52.8; 175 $(C_5H_4F_5O^+)$ 32.4; 159 $(C_5H_4F_5^+)$ 19.8; 89 $(C_4H_8O_2^+ + 1)$ 38.1; 73 $(C_4H_8O^+ + 1)$ 52.5.

Properties of 18-Crown-6-$(CF_2CFHCF_2C_6F_5)_2$ (18). Reaction of 18-crown-6 with perfluoroallylbenzene gives a disubstituted compound (**18**) in 28% yield. Spectral data are as follows. IR (film): 2888 s, 1657 s, 1532 s, 1515 s, 1505 s, 1426 s, 1352 s, 1328 s, 1151 s, 991 s, 840 cm^{-1}. ^{1}H NMR: δ 3.61−4.02 (22H, m, ring-H), 5.10−5.52 (2H, m, CFH) ppm. ^{19}F NMR: δ −100.9 to −103.9 (4F, overlap of AB patterns, $C_6F_5\mathit{CF}_2$), −119.1 to −123.5 (4F, overlap of AB patterns, $OCH\mathit{CF}_2$,), −139.6 (4F, m, *o*-F), −148.7 (2F, m, *p*-F), −160.1 (4F, m, *m*-F), −200.0 to −201.2 (2F, m, CFH, diastereoisomers) ppm. MS (CI$^+$) [*m/e* (species) intensity]: 861 $(M^+ + 1)$ 4.2; 860 (M^+) 12.9; 772 $(M^+ - C_4H_8O_2)$ 9.6; 657 $(M^+ - C_8H_{17}O_5)$ 3.9; 555 $(M^+ - C_6F_5CF_2 - C_4H_8O_2)$ 16.3; 554 $(M^+ - C_6F_5CF_2 - C_4H_9O_2)$ 70.0; 513 $(M^+ - C_6F_5CF_2CFHCF_2C_2H_4 - HF)$ 10.6; 490 $(M^+ - C_6F_5CF_2CFHCF_2CHCH_2OCH_2CH_2)$ 13.4; 474 $(M^+ - C_6F_5CF_2CFHCF_2CHCH_2OCH_2CH_2O)$ 72.3; 455 $(M^+ - C_6F_5CF_2CFHCF_2CHCH_2OCH_2CH_2O - F)$ 20.9; 431 $(M^+ + 1 - C_6F_5CF_2CFHCF_2CHCH_2OCH_2CH_2OCH_2CH_2O)$ 70.6; 411 $(M^+ - C_6F_5CF_2CFHCF_2CHCH_2OCH_2CH_2OCH_2CH_2O - F)$ 37.4; 387 $(M^+ + 1 - C_6F_5CF_2CFHCF_2CHCH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2O)$ 63.1; 367 $(M^+ - C_6F_5CF_2CFHCF_2CHCH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2O - F)$ 100; 347 $(M^+ - C_6F_5CF_2CFHCF_2CHCH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2O - F - HF)$ 38.4; 327 $(M^+ - C_6F_5CF_2CFHCF_2CHCH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2O - F - 2HF)$ 25.7; 323 $(C_6F_5CF_2CHCF_2CHCH_2O^+)$ 53.9; 303 $(C_6F_5CFCHCF_2CCH_2O^+)$ 34.0; 217 $(C_6F_5CF_2^+)$ 46.2; 177 $(C_8H_{16}O_4^+ + 1)$ 29.2; 133 $(C_6H_{12}O_3^+ + 1)$ 80.0; 117 $(C_6H_{12}O_2^+ + 1)$ 74.6.

Properties of $OCH_2CH_2CH_2CHCF_2{}^aCF^bHCF_2{}^cC_6F_4{}^d$, ${}^eOC_6F_5{}^{f,g,h}$ (19). This compound is obtained in 45% yield from the reaction between (pentafluorophenyl)trimethylsilane and **11**. Spectral data obtained are as follows. IR (film): 2990 m, 2888 m, 1651 s, 1505 s, 1425 s, 1395 m, 1354 s, 1322 s, 1180 s, 1129 s, 1087 s, 997 s, 936 m, 894 m cm^{-1}. ^{1}H NMR: δ 1.87−2.22 (m, CH_2CH_2), 3.81−3.98 (m, OCH_2), 4.17−4.41 (m, OCH), 4.99−5.41 (m, CFH) ppm. ^{19}F NMR: δ −119.33 to −122.30 (2F/2, AB pattern, $^2J_{A-B} = 271.2$ Hz, ^{a}F), −124.67 to −129.37 (2F/2, AB pattern, $^2J_{A-B} = 267.4$ Hz, ^{a}F, diastereoisomers), −197.53 to −201.10 (1F, two doublet-multiplets, ^{b}F, diastereoisomers), −98.97 to −105.17 (2F/2, AB pattern, $^2J_{A-B} = 286.2$ Hz, ^{c}F), −101.79 to −102.51 (2F/2, AB pattern, $^2J_{A-B} = 286.2$ Hz, ^{c}F, diastereoisomers), −139.77 (2F, m, ^{d}F), −156.36 (2F, m, ^{e}F), −156.46 (2F, m, ^{f}F), −159.28 (1F, m, ^{g}F), −162.09 (2F, m, ^{h}F) ppm. MS (CI$^+$) [*m/e* (species) intensity]: 533 $(M^+ - 1)$ 2.0; 517 $(M^+ - O - 1)$ 2.0; 515 $(M^+ - F)$ 91.3; 495 $(M^+ - F - HF)$ 15.3; 329 $(M^+ - C_6F_5 - 2F)$ 12.0; 121 $(C_4H_7OCF_2^+)$ 5.5; 71 $(C_4H_7O^+)$ 100.

Reaction of $(TMS)OCH_2(CF_2)_2CH_2O(TMS)$ with $OCH_2CH_2CH_2CHCF_2CFHCF_2C_6F_5$ in the Presence of CsF. To an oven-dried 50-mL Pyrex round-bottomed flask equipped with a magnetic stirrer are added 0.4 g (2.7 mmol) of CsF, 2.13 g (5.8 mmol) of $OCH_2CH_2CH_2CHCF_2CFHCF_2C_6F_5$, 1.0 g (3.3 mmol) of $(TMS)OCH_2(CF_2)_2CH_2O(TMS)$, and 3 mL of diglyme under a dry nitrogen atmosphere. The mixture is heated to 80 °C and stirred at that temperature for 12 h. After cooling to room temperature, the product is extracted with 3 × 20 mL portions of ether. The ether extract is washed with water several times and dried over $MgSO_4$. Evaporation of the solvent under vacuum gives a viscous liquid, crude product, **20**, that is further purified by column chromatography.

Properties of $(OCH_2CH_2CH_2CHCF_2{}^aCF^bHCF_2{}^cC_6F_4{}^{d,e}OCH_2CF_2{}^f)_2$ (20). This compound is obtained in 53% yield. Spectral data are as follows. IR (film): 2964 s, 2887 s, 1651 s, 1505 s, 1456 s, 1424 s, 1395 s, 1354 s, 1320 s, 1143 s, 894 m cm^{-1}. ^{1}H NMR: δ 2.12 (8H, m, CH_2CH_2), 3.78−3.87 (4H, m, OCH_2), 4.17−4.49 (2H, m, OCH), 4.74 (4H, t, CF_2CH_2), 4.95−5.40 (2H, m, CFH) ppm. ^{19}F NMR: δ −119.13 to −121.87 (4F/2, AB pattern, $^2J_{A-B} = 269.3$ Hz, F^a), −124.33 to −128.97 (4F/2, AB pattern, $^2J_{A-B} = 269.3$ Hz, F^a, diastereoisomers), −197.25 to −200.84 (2F, two d-m, $^2J_{H-F} = 37.7$ Hz, F^b, diastereoisomers), −98.43 to −105.04 (4F/2, AB pattern, $^2J_{A-B} = 282.47$ Hz, F^c), −100.97 to −102.54 (4F/2, AB pattern, $^2J_{A-B} = 290.0$ Hz, F^c, diastereoisomers), −140.39 (4F, m, Ar−F), −155.87 (4F, m, Ar−F), −122.77 (4F, t−t, F^f). MS CI$^+$ [*m/e* (species) intensity]: 862 (M^+) 0.6; 861 $(M^+ - 1)$ 1.9; 843 $(M^+ - F)$ 35.6; 823 $(M^+ - F - HF)$ 43.7; 803 $(M^+ - C_3H_6O - 1)$ 100; 783$(M^+ - C_3H_8FO)$ 64.8; 763 $(M^+ - C_5H_7O_2)$ 16.0; 743 $(M^+ - C_5H_8FO_2)$ 4.3; 456 $(C_6F_4OCH_2CF_2CF_2CH_2OC_6F_4^+)$ 50.4; 437 $(C_6F_4OCH_2CF_2CF_2CH_2OC_6F_3^+)$ 16.2; 367 $(OCH_2CH_2CH_2CHCF_2CFHCF_2C_6F_4O^+)$ 3.9; 349 $(OCH_2CH_2CH_2CHCF_2CFHCF_2C_6F_3O^+ + 1)$ 46.1; 329 $(THFCF_2CFHCF_2C_6F_2O^+)$ 27.3; 279 $(C_6F_4CF_2CFCF_2^+)$ 10.3; 121 $(OCH_2CH_2CH_2CHCF_2^+)$ 14.6; 113 $(C_3F_4H^+)$ 32.0.

Properties of 21. This compound is obtained in 30% yield. Spectral data obtained are as follows. IR (film): 2937 s, 1651 s, 1505 s, 1426 s, 1394 s, 1162 s, 998 s cm^{-1}. ^{1}H NMR: δ 2.11−2.21 (m, CH_2CH_2), 4.43−4.53 (2H, m, OCH), 4.72 (4H, t, $^3J_{H-F} = 12.0$ Hz, OCH_2), 4.99−5.24 (2H, m, CFH) ppm. ^{19}F NMR (mixture of diastereoisomers): δ −97.0 to −107.3 (4F, overlap of AB patterns, ^{c}F, $C_6F_5\mathit{CF}_2$), −120.0 to −129.7 (4F, overlap of AB patterns, ^{a}F, $OCH\mathit{CF}_2$), −140.5 (4F, m, ^{e}F, Ar−F), −155.5 (4F, m, ^{d}F, Ar−F), −196.1 to −200.6 (2F, m, CHF, mixture of diastereoisomers) ppm. MS (CI$^+$) [*m/e* (species) intensity]: 841 $(M^+ + 1)$ 1.8; 840 (M^+) 3.7; 821 $(M^+ - F)$ 23.4; 801 $(M^+ - F - HF)$ 23.6; 719 $(M^+ - OCH_2CH_2CH_2CHCF_2)$ 27.3; 699 $(M^+ - OCH_2CH_2CH_2CHCF_2 - HF)$ 12.5; 649 $(M^+ - OCH(CF_2)CH_2CH_2CH(CF_2) - HF - H)$ 100; 630 $(M^+ - C_6H_8F_6O)$ 9.2; 629 $(M^+ - C_6H_9F_6O)$ 38.9; 351 $(OCH_2CH_2CH_2CHCF_2CFHCF_2C_6F_4^+)$ 29.0; 347; 331 $(OCH_2CH_2CH_2CHCF_2CFHCF_2C_6F_4^+ - HF)$ 38.3; 195 $(CF_2CFHCF_2C_2H_4FO^+)$ 18.6; 103 $(C_5H_5F_2^+)$ 54.6.

Preparation and Properties of $La(OSO_2CF_3)_3$(18-crown-6) (22). Compound **22** has been prepared previously.[24] We have obtained this compound as a colorless, crystalline solid in 89.8% yield from the reaction between 18-crown-6 and $La(OSO_2CF_3)_3$ in acetone as solvent. Spectral data not previously reported are as follows. IR (KBr pellet): 3436 br, s, 2964 m, 2936 sh, m, 2901 sh, m, 2346 br, w, 1636 m, 1477 m, 1460 sh, w, 1355 sh, m, 1299 vs, 1235 vs, 1166 sh, vs, 1083 vs, 1032 vs, 970 sh, s, 883 w, 835 m, 815 w, sh, 762 w, 638 s, 578 m, 516 m cm^{-1}. MS (FAB$^+$) [*m/e* (species) intensity]: 701 $(M^+ - CF_3SO_3)$ 100; 551 $(M^+ - 2(CF_3SO_3) - 1)$ 5.3; 481 $(M^+ - 2(CF_3SO_3) - CF_3 - 2H)$ 2.4; 397 $(M^+ - 3(CF_3SO_3) - 6H)$ 3.0.

Preparation and Properties of $La(OSO_2CF_3)_3$(18-crown-6-CF_2CFHCF_3)(H_2O) (23). An acetone solution (20 mL) of $La(OSO_2CF_3)_3$ (0.21 g, 0.35 mmol) and 18-crown-6-CF_2CFHCF_3 (0.19 g, 0.46 mmol) is stirred for 2 days at room temperature. Evaporation of the solvent gives a viscous liquid. After being dried under vacuum and after extraction with a large excess of anhydrous diethyl ether, **23** is isolated as a white powder. Traces of diethyl ether are removed under vacuum over a period of 24 h to give the final product (0.33 g, 0.33

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(24) Almasio, M. C.; Arnaud-Neu, R.; Schwing-Weill, M. J. *Helv. Chim. Acta* **1983**, *66*, 1296.

mmol; yield, 94%). Crystals suitable for X-ray structural analysis are obtained by diffusing hexane slowly into a solution of the complex **23** in tetrahydrofuran. Spectral data obtained for **23** are as follows. ^{1}H NMR ($CDCl_3$): δ 5.5 (1H, br mult, CFH), 3.5−5.2 (23H, m, ring), 2.65 (2H, br, H_2O) ppm. ^{1}H NMR (CD_3CN): δ 5.6 (1H, br mult, CFH), 3.5−4.7 (25H, m, ring and H_2O) ppm. ^{19}F NMR ($CDCl_3$): δ −73.7 (3F, br, CF_3 groups of the two diastereoisomers), −78.2 (9F, s, CF_3SO_3), −105 to −129.7 (2F, complex, CF_2 groups of the two diastereoisomers), −212.5 (1F, br, CFH group of the two diastereoisomers) ppm. ^{19}F NMR (CD_3CN): δ −73.2, −73.4 (3F, m, CF_3 groups of the two diastereoisomers), −77.9 (9F, s, CF_3SO_3), −115.4, −117.4 (2F/2, AB quartets, $^2J_{A-B}$ = 286.2 Hz, CF_2 group of one of the two diastereoisomers), −119.4, −120.4 (2F/2, AB quartets, $^2J_{A-B}$ = 284.3 Hz, CF_2 group of the other two diastereoisomers), −209.8, −212.0 (1F, m, CFH group of the two diastereoisomers) ppm. IR (KBr): 3650 s, br, 2962 m, 1637 m, 1560 w, 1476 m, 1246 s, br, 1085 s, 1028 s, 976 m, 908 w, 885 w, 859 w, 843 m, 765 w, 703 w, 638 s, 575 m, 517 m cm^{-1}. IR (THF, CN bond stretch): 2251 (free CN), 2291 (CN coordinated to La^2) cm^{-1}; MS (FAB$^+$) [*m/e* (species) intensity]: 849 ($M^+ - H_2O - CF_2CFHCF_3$) 2.8; 587 ($La(OSO_2CF_3)_3^+ + 1$) 2.8; 453 ($LaO(OSO_2CF_3)_2^+$) 24.7; 437 ($La(OSO_2CF_3)_2^+$) 100; 415 (18-crown-6-$CF_2CFHCF_3^+ + 1$) 39.4; 151 ($CF_2CFHCF_3^+$) 12.9; 149 (CF_3SO_3+) 29.6.

Preparation and Properties of $La(OSO_2CF_3)_3$(18-crown-6-$CF_2CFHCF_2C_6F_5$)(H_2O) (24). An acetone solution (16 mL) of $La(OSO_2CF_3)_3$ (0.18 g, 0.30 mmol) and [(18-crown-6)- $CF_2CF(H)$-$CF_2C_6F_5$] (0.21 g, 0.37 mmol) is stirred for 2 days at room temperature. After the same workup as described for the preparation of **23**, a white powder **24** is obtained (0.24 g, 0.21 mmol; yield 70%). Crystals suitable for X-ray structural analysis could not be obtained. Spectral data obtained for **24** are as follows. ^{1}H NMR (CD_3CN): δ 5.5 (1H, br mult, CFH), 3.4−4.7 (25H, complex, ring-H and H_2O) ppm. ^{1}H NMR ($CDCl_3$): δ 3.5−6.0 (1H, br mult, CFH) ppm. ^{19}F NMR (CD_3CN): δ −77.9 (9F, s, CF_3SO_3), −98.0 to −106 (2F, m, $C_6F_5\mathit{CF_2}$, overlap of AB quartets of diastereoisomers), −113.4, −116.7 (2F/2, AB quartet, $^2J_{A-B}$ = 282.5 Hz, $CH\mathit{CF_2}$ of the two diastereoisomers), −117.9, −119.0 (2F/2, AB quartet, $^2J_{A-B}$ = 252.3 Hz, CF_2 group of the other diastereoisomer), −139.6 (2F, m, o-F), −149.2, −149.7 (1F, two triplets, *J* = 19 Hz, *p*-F), −161.3, −161.6 (2F, two triplets, *J* = 19 Hz, *m*-F), +205.7, −208.9 (1F, m, CFH, mixture of diastereoisomers) ppm. IR (KBr): 3449 s, br, 2969 m, 1656 m, 1532 s, 1511 s, 1478 w, 1427 w, 1317 s, br, 1225 s, br, 1084 s, 1028 s, 997 s, 907 w, 884 w, 861 w, 841 w, 765 w, 733 w, 639 s, 573 m, 516 m, 415 w cm^{-1}. MS (FAB$^+$) [*m/e* (species) intensity]: 1166 (M^+) 0.8; 1130 ($M^+ + 1 - H_2O - F$) 1.2; 849 ($M^+ - H_2O - CF_2CFHCF_2C_6F_5$) 2.0; 587 ($La(OSO_2CF_3)_3^+ + 1$) 1.8; 551 ($M^+ - H_2O - CF_2CFHCF_2C_6F_5 - 2CF_3SO_3$) 1.6; 453 ($LaO(OSO_2CF_3)_2^+$) 1.6; 437 ($La(OSO_2CF_3)_2^+$) 5.1; 155 ($LaO^+$) 100; 149 ($CF_3SO_3^+$), 29.6.

Properties of $[La(OCH_2CH_2)_5OCH_2CHCF_2CFHOCF_2C(CF_3)FOCF_2CF_2SO_2F]^{3+}[CF_3SO_3^-]_3$ (25). When 0.30 mmol of $La(OSO_2F)_3$ and 0.40 mmol of **16** are combined in acetone as solvent and stirring at room temperature is maintained for 2 d, compound **25** is obtained in 36% yield as a rust colored solid after workup as described for the preparation of product **23**. Spectral data obtained are as follows. IR (thin film, KBr): 3600−2800 m, b, 1703 w, 1621 m, 1466 w, 1340 s, sh, 1290 s, sh, 1243 vs, 1200 s, sh, 1049 s, 773 w, 645 s, 581 w, 571 w, 516 m, 429 w. ^{1}H NMR: δ 3.6 (ring-H, 23H), 6.3 (CFH, 1H) ppm. ^{19}F NMR: δ 49.7 (SO_2F, 1F), −74.8 to −79.3 (CF_2, m, and CF_3, 16F), −107.4 (CF_2, mult), −140 (CFH, mult) ppm. MS (FAB$^+$) [*m/e* (species) intensity]: 1164 ($M^+ + 1 - CF_3SO_2$) 0.5; 1015 ($M^+ + 1 - CF_3SO_3 - CF_3SO_2$) 0.7; 906 ($(La(O_5C_{17}H_{20}F_{13}SO_2F(CF_3SO_2))^+$) 14.0; 470 ($La(O_6C_{10}H_{20})CHCF_2CFH^+$) 100.

Preparation of $La[N(SO_2CF_3)_2]_3$ (26). Under an atmosphere of nitrogen, 8.4 mmol of bis(trifluoromethyl)sulfonamide is added to a 50 mL Pyrex round-bottomed flask. Then 1.5 mmol of La_2O_3 is placed into the flask concomitantly with 20 mL of deionized water. The flask is then connected to a condenser and the reaction mixture is refluxed for 1 day. The mixture is cooled and filtered, and the solvent is reduced to a volume of 2 mL by heating. The remaining water is removed under vacuum with heating over a period of 2 days. Yields of the white solid **26** range from 60 to 84%. Spectral data obtained are as follows. IR (Nujol mull, KBr): 1368 vs, 1232 s, 1209 s, 1139 s, 898 m, 710 m cm^{-1}. ^{19}F NMR: δ −79.6 (CF_3, s). MS (FAB$^+$) [*m/e* (species) intensity]: 979 (M^+) 0.4.

Preparation of Dibenzo-18-crown-6-$La[N(SO_2CF_3)_2]_3$ (27). To 1.11 mmol of **26** in a 50 mL Pyrex round-bottomed flask containing 20 mL of methylene chloride is added 1.11 mmol of dibenzo-18-crown-6 dissolved in approximately 2 mL of acetonitrile and 2 mL of acetone. The reaction mixture is stirred at 25 °C for 3 days. The solution is filtered, and the solvent is removed under vacuum. Spectral data obtained for **27** are as follows. IR (KBr pellet): 3406 m, 2940 s, 1625 s, 1598 vs, 1508 vs, 1477 s, 1353 s, 1330 vs, 1248 vs, 1209 s, 1165 vs, 1135 s, 1135 s, 1109 s, 1087s, 910 m, 755 m. ^{19}F NMR: δ −79.0 (CF_3, s). ^{1}H NMR: δ 4.6 (CH_2, mult), 7.1 (Ar−H, mult). MS (FAB$^+$) [*m/e* (species) intensity]: 1339 (M^+) 1.2; 1142 ($M^+ - CF_3SO_2 - CH_2CH_2O - H - F$) 35.1; 909 ($M^+ - (CF_3SO_2)_2N - C_6H_4OCH_2(OCH_2CH_2)$) 100.

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Supporting Information Available: For compounds **22** and **23**, 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 (17 pages). Ordering information is given on any current masthead page.

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