Novel and Versatile Reactions of Trifluoroamine Oxide: A New Route to Polyfluorinated Ethers

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A series of pyrimidine methyl and polyfluoroalkyl ethers were synthesized from the reactions of trifluoroamine oxide (**1**) with several 5-substituted uracils in the presence of tetrabutylammonium hydroxide and methanol, 2,2,2-trifluoroethanol (**6**), or 1*H*,1*H*-pentafluoropropanol (**7**). With 5-(trifluoromethyl)uracil (**2**), the new ethers formed were 5-fluoro-5-(trifluoromethyl)-6-methoxypyrimidine-2,4-dione (**8**), 5-fluoro-5-(trifluoromethyl)-6-(trifluoroethoxy)pyrimidine-2,4-dione (**9**), and 5-fluoro-5-(trifluoromethyl)-6-(1*H*,1*H*-pentafluoropropoxy)pyrimidine-2,4-dione (**10**). With 5-chlorouracil (**3**), the new ethers 5-chloro-5-fluoro-6-methoxypyrimidine-2,4-dione (**11**), 5-chloro-5-fluoro-6-(trifluoroethoxy)pyrimidine-2,4-dione (**12**), and 5-chloro-5-fluoro-6-(1*H*,1*H*-pentafluoropropoxy)pyrimidine-2,4-dione (**13**) were obtained. With 5-fluorouracil (**4**), the new ethers 5,5-difluoro-6-methoxypyrimidine-2,4-dione (**14**), 5,5-difluoro-6-(trifluoroethoxy)pyrimidine-2,4-dione (**15**) and 5,5 difluoro-6-(1*H*,1*H*-pentafluoropropoxy)pyrimidine-2,4-dione (**16**) were found. By reaction of 5-nitrouracil (**5**), the new ethers 5-nitro-5-fluoro-6 methoxypyrimidine-2,4-dione (**17**), 5-nitro-5-fluoro-6-(trifluoroethoxy)pyrimidine-2,4-dione (**18**), and 5-nitro-5-fluoro-6-(1*H*,1*H*-pentafluoropropoxy)pyrimidine-2,4-dione (**19**) were obtained. Each of the new compounds was characterized by using IR, ^{19}F and ^{1}H NMR, and mass spectroscopy, and elemental analysis. A single-crystal X-ray diffraction study of **8** was helpful in confirming compound structure.

Introduction

A number of attempts have been made to prepare organic or fluoroorganic derivatives of the novel compound trifluoroamine oxide (NF_3O).[1−3] While trifluoroamine oxide is itself kinetically inert, several compounds of the class of *N*,*N*-difluoro-*O*-hydroxylamines were prepared either by reaction of fluoroalkyl hypofluorites with N_2F_4[4−6] or with $KF-HNF_2$[7] or by homolytic cleavage of fluorinated peroxides in the presence of N_2F_4.[8] The syntheses of $-ONF_2$ derivatives via the BF_3- or AsF_5-catalyzed addition of NF_3O to simple fluoroethylenes[9] or to many trifluoroethylene derivatives[10] are typical reactions. The reaction of NF_3O with NO provides a simple route to the in situ generation of FNO.[11] We have demonstrated that trifluoroamine oxide reacts readily with a variety of secondary amines to form the corresponding *N*-fluoro and *N*-nitroso derivatives.[12] The gas-phase structure of fluorodimethylamine, Me_2NF, has been studied by electron diffraction and microwave spectroscopy.[13]

In this paper we report that trifluoroamine oxide in the presence of tetrabutylammonium hydroxide provides an interesting new route to unknown primidine methyl and polyfluoroalkyl ethers in its reactions with substituted uracils and the appropriate alcohols. These compounds have been isolated and characterized. Although the addition of NF_3O to olefinic double bonds, catalyzed by Lewis acids e.g. BF_3 and AsF_5, has been achieved successfully, this is the first example where NF_3O behaves as an electrophilic fluorinating reagent. We report here our investigation of these reactions as a potentially useful synthetic route for the preparation of polyfluorinated ethers under very mild conditions.

Results and Discussion

It was found that reactions of NF_3O in the presence of tetrabutylammonium hydroxide (TBAH) in methanol (1.0 M) solution proceed smoothly in an excess of acetonitrile. However, in our continuing studies of the reactions of NF_3O with secondary amines, uracil, and substituted uracils, the lack of solubility of these substrates in acetonitrile caused a problem in choosing an appropriate solvent since it must be inert toward NF_3O. Tetrabutylammonium hydroxide in methanol was used as a base to solubilize the substrates (uracil and its derivatives) in order to provide homogeneous reaction conditions. The reaction in Scheme 1 was carried out.

Surprisingly, instead of the formation of the anticipated >NF derivative, compound **8** was isolated and characterized by spectroscopic methods. After crystallization from DMSO, a single-crystal X-ray structure was obtained for **8**·DMSO (Figure 1).

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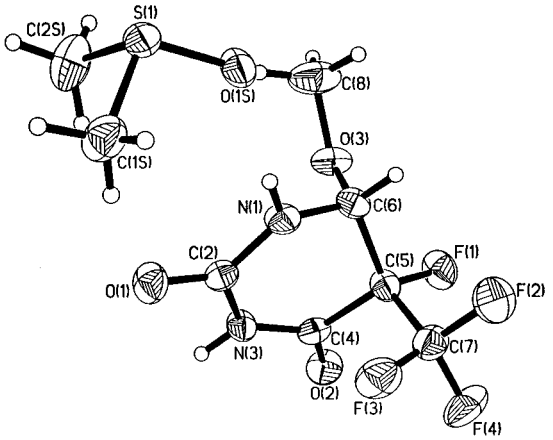
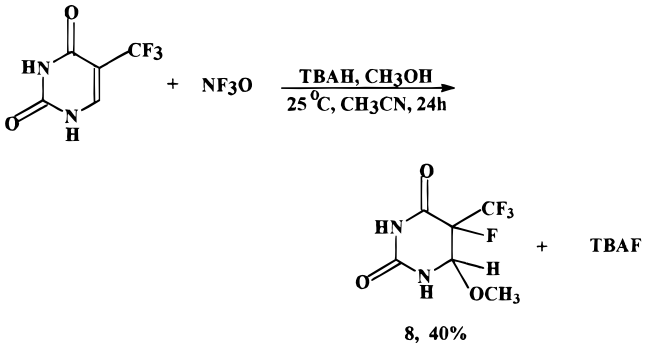
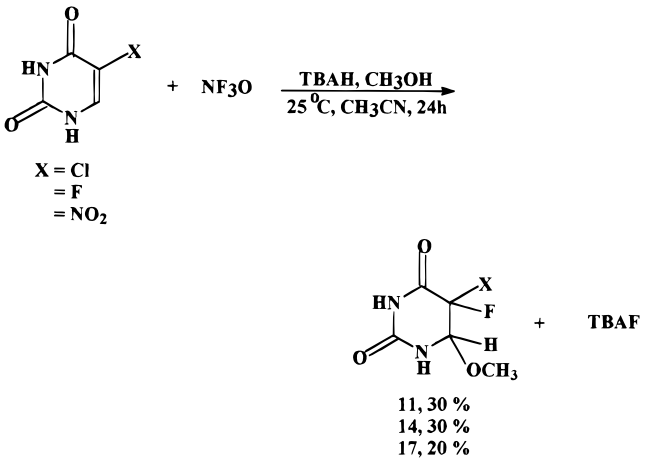


Figure 1. ORTEP drawing of 5-fluoro-5-(trifluoromethyl)-6-methoxypyrimidine-2,4-dione·DMSO (**8**) with thermal ellipsoids drawn at the 30% probability level.

Scheme 1



Scheme 2

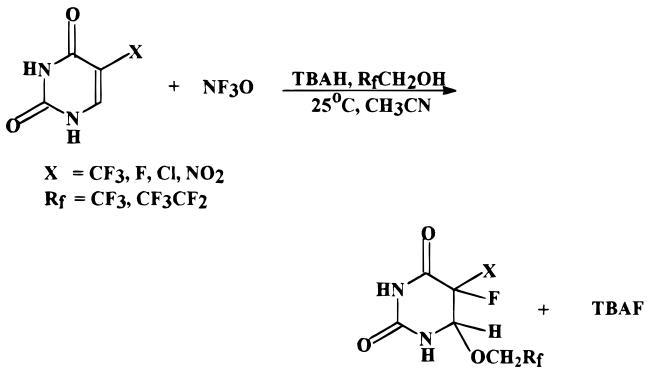


Other uracil derivatives, e.g., 5-chlorouracil, 5-fluorouracil, and 5-nitrouracil, were also reacted with NF_3O under similar conditions, and an analogous set of products were found to result from the saturation of the double bond with the species CH_3O and F (Scheme 2). These reactions of NF_3O did not proceed if TBAH was not present and the starting materials were recovered.

The above compounds were crystallized, but single crystals suitable for X-ray structuring did not form. These compounds are very stable, and no decomposition, e.g., liberation of HF, is observed at room temperature.

To learn if a polyfluoroalkoxy group and fluorine would add under similar conditions, the reaction was repeated in the presence of polyfluorinated alcohols. In these cases methanol was replaced in the reaction with polyfluorinated alcohols as shown in Scheme 3.

Scheme 3



Although the yields are low, the reactions proceeded similarly to those with CH_3OH. It was found that allowing the reaction to proceed for a longer time and/or at higher temperature did not increase the yield of the product. On one occasion, the reaction was also carried out in the absence of CH_3CN with CF_3CH_2OH being used in large amounts as a solvent. The crude product was also identical to that obtained in the reaction with CH_3CN as solvent and was also used to obtain mass spectra. 2,2,3,3,3-Pentafluoro-1-propanol was also used to carry out the reaction of NF_3O with 5-(trifluoromethyl)uracil in the presence of tetrabutylammonium hydroxide by using acetonitrile as the solvent. Initially, when the reaction was attempted at −78 °C, no reaction took place, but when the reaction was carried out by using the reaction conditions described above, the product was obtained.

These compounds have characteristic absorption bands in their infrared spectra. Although molecular ions in the mass spectra are weak (<15%), an intense fragment was usually found at ($M^+ - OR$). In the fluorine NMR spectra, the signal due to the fluorine atom geminal to the $-CF_3$ is far upfield; e.g. in compounds **8**−**10**, it is at $\delta \sim -80$ ppm. In the case of nitro compounds **17**−**19**, the signals due to the fluorine atom geminal to the nitro group are observed around $\delta \sim -130$ ppm.

These new pyrimidine-2,4-dione ethers are reasonably stable with no evidence of glass attack over long periods of time at 25 °C. The ^{19}F NMR data indicate that, in each case, only Markovnikov-type addition products are formed. It is noteworthy that, while the pyrimidine bases did not react with NF_3O in the presence of alcoholic solution (CH_3OH, CF_3CH_2OH, and $CF_3CF_2CH_2OH$), the reactions were complete within 24 h at 25 °C in the presence of TBAH. The kinetics of the reactions have not been studied, but it has been observed that the reactivity of NF_3O depends on the nature of the substituent at the fifth position on the uracil derivative, as well as the length of the alkyl chain of the alcohol used. It was observed that, in all reactions, CH_3OH was found to be the most reactive.

The suitability of trifluoroamine oxide as a useful source of nitrosyl fluoride in the syntheses of fluoroaliphatic nitroso derivatives has been demonstrated, but in our current studies, we did not obtain the nitroso product even in traces in any reaction studied. The formation of tetrabutylammonium fluoride (TBAF) was invariably observed and posed difficulties during the separation and purification of products. The removal of TBAF was achieved by solvent extraction followed by passing through a silica gel (60A) column.

It is tempting to argue that these fluoropyrimidine alkyl or polyfluoroalkyl ethers arise from the addition to the double bond

Scheme 4

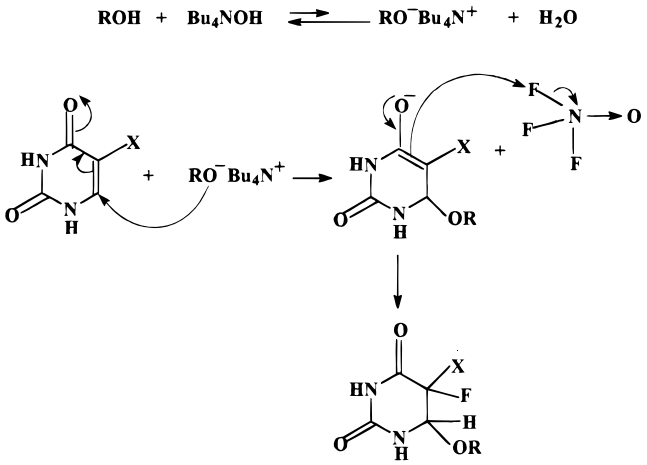


Table l. Crystal Data for **8**·DMSO

empirical formula	$C_8H_{12}F_4N_2O_4S$
fw	308.26
cryst system	triclinic
space group	$P\bar{1}$
color	white
unit cell dimens	$a = 7.0377(9)$ Å; $\alpha = 69.218(2)°$ $b = 8.5877(11)$ Å; $\beta = 75.992(2)°$ $c = 11.5255(14)$ Å; $\gamma = 84.604(2)°$
temp	193(2) K
V, Z	631.86(14) Å^3, 2
R indices (all data)[a]	$R_1 = 0.0687$, $wR_2 = 0.0990$
GOF	1.166

[a] $R = \sum|F_o| - |F_c||/\sum|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

of the uracil by the appropriate ROF or R_fOF that could be formed in situ. However, given the reaction conditions, especially the necessity for the presence of TBAH, it is likely that these materials are formed as shown in Scheme 4.

The most reasonable conclusion is that NF_3O is behaving as an easily controlled, electrophilic fluorinating reagent. This is a mode of behavior for this novel compound that has not been observed earlier.

X-ray Crystal Structure. Compound **8** crystallizes in the $P\bar{1}$ space group. The X-ray crystal structure is depicted in Figure 1. Crystal structure data are given in Table 1. The bond lengths and angles, final atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters are all included in the Supporting Information.

Experimental Section

Materials. Acetonitrile (Fisher) was first dried over CaH_2 for 12 h, then distilled from P_4O_{10}, and stored over activated molecular sieves (3 Å). Trifluoroamine oxide (Allied Chemical Corp.) was passed through two traps cooled to −78 °C to remove NO_2. Tetrabutylammonium hydroxide (TBAH) in 1 M methanol solution (Aldrich) was used as received.

Caution! *The addition of NF_3O to the reaction mixture containing olefins, particularly hydrogen-containing compounds, can proceed explosively. Appropriate safety precautions must be taken when these reactions are carried out.*

General Procedure. A Pyrex vacuum system equipped with a Heise Bourdon tube gauge and a Televac thermocouple gauge was used to handle the volatile reagents. Convenient PVT techniques were used to quantitate volatile starting materials and products. The products are separated by low-temperature trap-to-trap distillation under dynamic vacuum or by vacuum distillation. Both ^{19}F and ^1H NMR spectra were obtained by using a Bruker AC200 Fourier transform NMR spectrometer with $CDCl_3$ as solvent unless otherwise indicated. Mass spectra were obtained with a VG 7070 HS mass spectrometer. Elemental analyses were performed by Beller Mikroanalytisches Laboratrium, Göttingen, Germany. Infrared spectra were recorded with a Perkin-Elmer 1710 infrared spectrometer as liquid films between KBr disks. KBr pellets were prepared for solid samples. The melting points were determined with a Thomas-Hoover apparatus.

X-ray Crystal Structure Analysis. The X-ray diffraction data for compound **8** were collected on a Siemens SMART diffractometer with a CCD detector at −54 °C. Data collection parameters are listed in Table 1. The frame data are acquired with the SMART[14] software using a Siemens three-circle platform using Mo Kα radiation ($\lambda = 0.717\,03$ Å) from a fine focus tube. The *x*-axis on this platform is fixed at 54.74°, and the diffractometer is equipped with a CCD detector maintained near −54 °C. Cell constants are determined from 60 10 s frames. A complete hemisphere of data is scanned on ω (0.3°) with a run time of 10 s per frame at the detector resolution of 512 × 512 pixels. In three sets, a total of 1271 frames identical to the first 50 frames are also collected, and a final set of 50 frames identical to the first 50 frames, are also collected to determine the crystal decay. The frames are then processed on an SGI-Indy workstation using the SAINT[15] software to give the *hkl* file corrected for *Lp*/decay. The structure is solved by using the SHELX-90[16] program and refined by the least-squares method on F^2, SHELXL-93[17] incorporated in SHELXTL-PC V5.03.[18] All non-hydrogen atoms are refined anisotropically. The hydrogen atoms are located from the difference electron density maps and are included in the refinement process in an isotropic manner. The crystal used for the diffraction studies showed no decomposition during data collection.

General Preparative Procedure. Unless otherwise specified, the usual procedure was as follows. A dry 250 mL round-bottomed Pyrex flask equipped with a Teflon stopcock was loaded with 1 mmol of uracil derivative and an equimolar amount of tetrabutylammonium hydroxide (TBAH) in methanol (1 M solution). The flask was cooled to 196 °C and evacuated. Dry CH_3CN (10 mL) was transferred to the flask at −196 °C under vacuum. The flask was allowed to warm to room temperature and the mixture stirred so that the substrate was completely dissolved. The reaction mixture was then cooled to 0−5 °C, and slightly more than the equivalent amount of trifluoroamine oxide was added. It was allowed to warm to and stirred at 25 °C for 24 h. The volatile materials and solvent were removed under vacuum, leaving a nonvolatile yellowish viscous oil. Chromatographic separation on a silica gel (70−230 mesh, 60 Å) column gave pure products. In reactions where a polyfluoro alcohol was the reacting species, a 1.0 M solution of TBAH in methanol was added to the flask and the methanol was removed under vacuum before addition of the fluorine-containing alcohol.

Reaction of NF_3O with 2 in the Presence of CH_3OH. This reaction is carried out in a manner similar to that described above, and compound **8** was isolated as a white solid in 40% yield. The spectral data obtained for compound **8** are as follows: IR (KBr pellet), cm^{-1}: 3273 ms, 3064 s, 2880 ms, 1762 vs, 1724 vs, 1478 m, 1286 ms, 1250 ms, 1223 ms, 1198 s, 1093 bs, 1036 w, 929 w, 824 ms, 772 w, 639 ms. NMR: ^1H, δ 3.43 (s, 3H), 4.93 (s, 1H) 7.43 (brs, 2H); ^{19}F, δ −75.37 (d, 3F), −86.25 (q, 1F). MS (EI^+) [*m*/*z* (species) intensity]: 230 (M^+) 10; 199 ($M^+ - OCH_3$) 18; 179 ($M^+ - OCH_3 - HF$) 100. Anal. Calcd for $C_6H_6N_2O_3F_4$: C, 31.30; H, 2.60; N, 12.17. Found: C, 30.98; H, 2.51; N, 11.96.

Reaction of NF_3O with 2 in the Presence of CF_3CH_2OH (6). This reaction is carried out in a manner similar to that described except that CF_3CH_2OH (**6**) was used in lieu of methanol. Compound **9** was obtained

(14) *SMART V 4.043 Software for the CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.
(15) *SAINT V 4.035 Software for the CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.
(16) Sheldrix, G. M.; *SHELXL-90, Program for the Solution of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1990.
(17) Sheldrix, G.M.; *SHELXL-93, Program for the Refinement of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1993.
(18) *SHELXTL5.03 (PC version) Program Library for Structure Solution and Molecular Graphics*; Siemens Analytical Instruments Division: Madison, WI, 1995.

as white solid in 35% yield. The spectral data obtained for compound **9** are as follows. IR (KBr pellet), cm^{-1}: 3236 brs, 3050 s, 2875 m, 1740 vs, 1460 m, 1290 s, 1245 ms, 1230 ms, 1196 s, 1082 brs, 1039 w, 935 w, 820 ms, 772 w, 645 ms. NMR: ^1H, δ 4.25 (q, 2H), 4.85 (m, 1H), 7.64 (bs, 2H); ^{19}F, δ −73.28 (d, 3F), −77.35 (t, 3F), −86.32 (q, 1F). MS (EI^+) [*m*/*z* (species) intensity]: 298 (M^+) 20, 199 ($M^+ - OCH_2CF_3$) 100; 179 ($M^+ - OCH_2CF_3 - HF$) 40. Anal. Calcd for $C_7H_5N_2O_3F_7$: C, 28.18; H,1.67; N, 9.39. Found: C, 28.84, H, 1.68; N, 9.88.

Reaction of NF_3O with 2 in the Presence of $CF_3CF_2CH_2OH$ (7). This reaction is carried out in a manner similar to that described except that $CF_3CF_2CH_2OH$ (**7**) was used in lieu of methanol. Compound **10** was isolated as a white solid in 28% yield. The spectral data obtained for compound **10** are as follows. IR (KBr pellet), cm^{-1}: 3257 br, 3064 s, 1738 vs, l482 m, 1360 ms, 1179 s, 1105 m, 1026 ms, 969 m, 746 m, 622 m. NMR: ^1H, δ 4.65 (t, 2H), 4.90 (m, 1H), 7.80 (brs, 2H); ^{19}F, δ −75.32 (d, 3F), −83.85 (t, 3F), −126.24 (m, 2F), −186.30 (q, 1F). MS (EI^+) [(*m*/*z* (species) intensity]: 348 (M^+) 23. Anal. Calcd for $C_8H_5N_2O_3F_9$: C, 27.58; H, l.43; N, 8.04. Found: C, 27.84; H, 1.47; N, 8.08.

Reaction of NF_3O with 3 in the Presence of CH_3OH. This reaction is carried out in a manner similar to that described above. Compound **11** was isolated as white solid in 35% yield. The spectral data obtained for compound **11** are as follows. IR (KBr pellet), cm^{-1}: 3210 br, 2956 s, 2865 m, 1763 s, 1729 s, 1477 s, 1433 w, 1392 w, 1287 s, 1251 m, 1223 m, 1198 m, 1180 w, 1093 s, 1036 m, 989 w, 930 m, 853 w, 824 m, 746 m, 669 s, 572 w. NMR: ^1H, δ 7.60 (brs, 2H), 5.35 (m, 1H), 3.65 (s, 3H); ^{19}F, δ −139.27 (s, 1F). MS (EI^+) [*m*/*z* (species) intensity]: 197 ($M^+ + 1$) 8; 196 (M^+) 100; 182 ($M^+ + 1 - CH_3$) 42.

Reaction of NF_3O with 3 in the Presence of CF_3CH_2OH (5). This reaction is carried out in a manner similar to that described except that CF_3CH_2OH (**5**) was used instead of methanol. A 1.0 M solution of TBAH/methanol was used, and the methanol was removed under vacuum. Compound **12** was obtained as a white solid in 25% yield. The spectral data obtained for **12** are as follows. IR (KBr pellet), cm^{-1}: 3215 b, 2967 s, 2855 s, 1727 s, 1547 s, 1443 m, 1284 m, 1251 m, 1163 s, 1100 m, 966 s, 903 m, 815 w, 765 w, 664 m. NMR: ^1H, δ 7.72 (b, 2H), 5.55 (m, 1H), 4.32 (q, 2H); ^{19}F, δ −74.07 (t, 3F), −137.37 (s, 1F). MS (EI^+) [*m*/*z* (species) intensity]: 264 (M^+) 25. Anal. Calcd for $C_6H_5N_2O_3ClF_4$: C, 27.22; H, 1.89. Found: C, 27.76; H, 2.11.

Reaction of NF_3O with 3 in the Presence of $CF_3CF_2CH_2OH$ (6). This reaction is carried out in a manner similar to that described except that $CF_3CF_2CH_2OH$ (**6**) was used instead of methanol. Compound **13** was obtained as a white solid in 30% yield. The spectral data obtained for compound **13** are as follows. IR (KBr pellet), cm^{-1}: 3210 br, 2930 s, 2866 m, 1735 s, 1450 s, 1357 s, 1285 m, 1215 m, 1103 s, 1057 m, 1026 m, 969 m, 830 m, 790 w, 740 w, 621 m, 568 w. NMR: ^1H, δ 7.75 (br, 2H), 5.60 (m, 1H), 4.60 (t, 2H); ^{19}F, δ −83.25 (t, 3F), −123.36 (m, 2F), −139.13 (m, 1F). MS (EI^+) [*m*/*z* (species) intensity]: 314 (M^+) 35. HRMS: calcd, 313.9884; found, 313.9893.

Reaction of NF_3O with 4 in the Presence of CH_3OH. This reaction is carried out in a manner similar to that described above. Compound **14** was isolated as a white solid in 35% yield. The spectral data obtained for compound **14** are as follows. IR (KBr pellet), cm^{-1}: 3170 br, 2962 s, 2857 ms, 1710 s, 1454 m, 1261 s, 1222 ms, 1126 s, 970 s, 901 m, 801 brm. NMR: ^1H, δ 7.15 (br, 1H), 7.30 (b, 1H), 4.77 (m, 1H), 3.45 (m, 3H); ^{19}F, δ −112.73 (d, 1F), −131.57 (d, 1F). MS (EI^+) [*m*/*z* (species) intensity]: 181 ($M^+ + 1$) 100, 150 ($M^+ - OCH_3 + 1$) 15, 130 ($M^+ - CH_3OF$) 23.

Reaction of NF_3O with 4 in the Presence of CF_3CH_2OH (5). This reaction is carried out in a manner similar to that described except that CF_3CH_2OH (**5**) was used instead of methanol. Compound **15** was obtained as a white solid in 30% yield. The spectral data obtained for compound **15** are as follows. IR (KBr pellet), cm^{-1}: 3208 b, 2958 s, 2926 s, 2868 m, 1719 s, 1442 m, 1371 m, 1277 s, 1201 s, 1126 m, 971 m, 901 w, 880 w, 743 m, 596 w, 567 w. NMR: ^1H, δ 7.32 (b, 2H), 4.65 (m, 1H), 3.50 (m, 2H); ^{19}F, δ −73.94 (s, 3F), −112.50 (d, 1F), −131.45 (d, 1F). MS (CI^+) [*m*/*z* (species) intensity]: 249 ($M^+ + 1$) 94; 227 ($M^+ - H_2F$) 5, 182 ($M^+ - 69$) 100.

Reaction of NF_3O with 4 in the Presence of $CF_3CF_2CH_2OH$ (6). This reaction is carried out in a manner similar to that described except that $CF_3CF_2CH_2OH$ (**6**) was used instead of methanol. Compound **16** was isolated as a white solid in 25% yield. The spectral data obtained for compound **16** are as follows. IR (KBr pellet), cm^{-1}: 3212 b, 2996 s, 2849 s, 1732 s, 1555 m, 1446 m, 1279 m, 1205 w, 1128 m, 975 w, 831 w, 766 s, 625 w. NMR: ^1H, δ 7.20 (b, 2H), 4.85 (m, 1H), 3.55 (m, 2H); ^{19}F, δ −83.40 (t, 3F), −112.25 (d, 1F), −123.28 (q, 2F), −131.25 (d, 1F). MS (EI^+) [*m*/*z* (species) intensity]: 299($M^+ + 1$) 45.

Reaction of NF_3O with 5 in the Presence of CH_3OH. This reaction is carried out in a manner similar to that described above, and the yellowish compound **17** was isolated in 30% yield. The spectral data obtained for **17** are as follows. IR (KBr pellet), cm^{-1}: 3274 br, 3079 brs, 2956 ms, 2865 ms, 1763 s, 1729 s, 1477 m ($\nu_{asym}(N0_2)$) 1433 s, 1392 s ($\nu_{sym}(NO_2)$), 1251 s, 1093 vs, 824 w, 638 ms. NMR: ^1H, δ 3.51 (s, 3H), 4.98 (s, 1H), 7.55 (brs, 2H); ^{19}F, δ −138.35 (s, 1F); MS (EI) [*m*/*e* (species) intensity]: 207 (M^+) 20.

Reaction of NF_3O with 5 in the Presence of CF_3CH_2OH(5). This reaction is carried out in a manner similar to that described except that CF_3CH_2OH (**5**) was used instead of methanol. The yellowish compound **18** was isolated in 25% yield. The spectral data obtained for **18** are as follows. IR (KBr pellet), cm^{-1}: 3164 b, 3094 brs, 2934 s, 2863 m, 1678 s, 1501 ms ($\nu_{asym}(NO_2)$), 1440 m, 1337 s ($\nu_{sym}(NO_2)$), 1201 s, 1128 ms, 1058 ms, 970 s, 669 w. NMR: ^1H, δ 3.40 (m, 2H), 4.15 (s, 1H), 7.20 (brs, 2H); ^{19}F, δ −77.23 (s, 3F), −128.96 (s, 1F). MS (EI) [*m*/*e* (species) intensity]: 275 (M^+) 18.

Reaction of NF_3O with 5 in the Presence of $CF_3CF_2CH_2OH$ (6). This reaction was carried out in a manner similar to that described except that $CF_3CF_2CH_2OH$ was used in lieu of methanol. The yellowish compound **19** was obtained in 25% yield. The spectral data obtained for **19** are as follows. IR (KBr pellet), cm^{-1}: 3267 brs, 3093 s, 2930 s, 2866 m, 1735 vs, 1495 ms ($\nu_{asym}(NO_2)$), 1450 ms, 1357 ms ($\nu_{sym}(NO_2)$), 1285 vs, 1215 s, 1103 brs, 1057 m, 1026 m, 830 s, 721 w. NMR: ^1H, δ 3.90 (2H, m), 4.50 (s, 1H), 7.35 (bs, 2H); ^{19}F, δ −84.25 (t, 3F), −126.13 (m, 2F), −139.25 (s, 1F). MS (EI) [*m*/*e* (species) intensity]: 325 (M^+) 20.

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Supporting Information Available: Tables of crystal, structure solution, and refinement data, atomic coordinates and *U* values, bond lengths and angles, and anisotropic thermal parameters for **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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