Diverse Cycloaddition Chemistry Leading to Overall Michael Addition in the Reactions of 1,1-Bis(dimethylamino)-2,2-difluoroethene with α,β-Unsaturated Aldehydes, Ketones, Esters, and Nitriles

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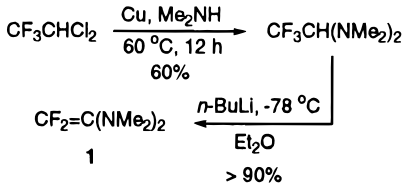
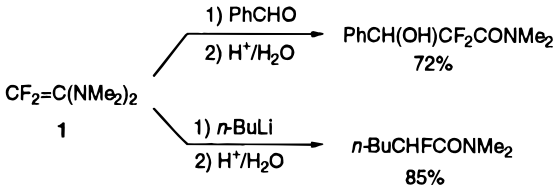
Difluoro ketene aminal **1** undergoes [2 + 4] cycloadditions with α,β-unsaturated aldehydes and ketones and [2 + 2] cycloadditions with α,β-unsaturated esters and nitriles. Both types of adducts can be readily converted, by mild hydrolysis, to the respective Michael addition products.

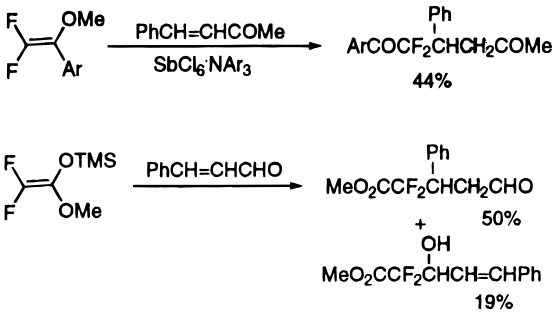
In a recent communication, we reported the synthesis of the highly reactive difluoro ketene aminal building block, 1,1-bis(dimethylamino)-2,2-difluoroethene, **1**,



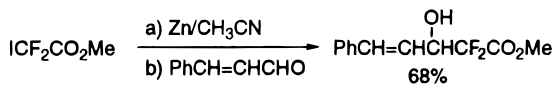
which exhibited both nucleophilic and electrophilic behavior in its reactions.[1]



Reports of *conjugate* additions of difluoro enolate species to potential α,β-unsaturated Michael substrates are uncommon. Reports from Taguchi's group provide the only examples, and these workers also describe some of the limitations of using difluoro enol ethers and ketene acetals for this purpose.[2−4]



In contrast to the limited Michael reactivity exhibited by difluoro enol ethers and ketene acetals, difluoro Reformatsky reagents give exclusively aldol-type products in the few reported examples of their reaction with α,β-unsaturated aldehydes or ketones.[5]



In general, enamines and ketene aminals are much more reactive than enol ethers and ketene acetals in their reactions with α,β-unsaturated aldehydes, ketones, esters, and nitriles, and a diversity of chemistry has been reported for such reagents including Michael additions, [2 + 2] cycloadditions, and hetero-Diels−Alder reactions.[6−15] Indeed, one would expect difluoro ketene aminal **1** to be considerably more reactive toward such α,β-unsaturated, Michael substrates than the other difluoro enolate-type reagents which have been studied. Recognizing that discovery of a reagent which would participate in reliable overall Michael addition of a difluoro enolate-type building block would be a useful synthetic accomplishment, we initiated an investigation of the reactions between **1** and acrolein, methyl vinyl ketone, methyl acrylate, acrylonitrile, methyl methacrylate, and methacrylonitrile.

Results and Discussion

Cycloadditions. Difluoro ketene aminal **1** indeed proved to be very reactive toward all of these substrates, with the reactions being complete after 5 min at room temperature, except for those with methyl methacrylate and methacrylonitrile which required 10 min at 90 °C to reach completion. Consistent with the behavior of its

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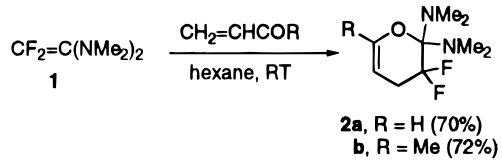
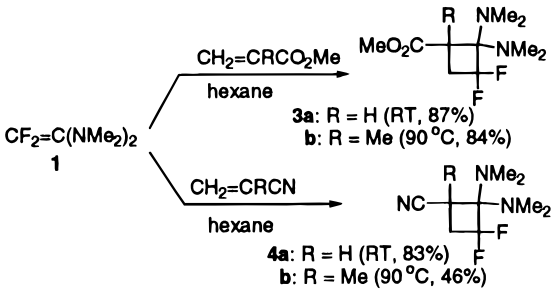
Scheme 1



Scheme 2



non-fluorine-containing enamine and ketene aminal counterparts, the reactions of **1** with acrolein and methyl vinyl ketone led cleanly to hetero-Diels–Alder products **2** (Scheme 1), whereas those with the ester and nitrile substrates led exclusively to [2 + 2] adducts **3** and **4**, respectively (Scheme 2).

Under no circumstances was competition between [2 + 2] and [2 + 4] processes able to be observed in any of these reactions. In an attempt to intercept a potential [2 + 2] "intermediate" in the hetero-Diels–Alder reaction of **1** with acrolein, the reaction was carried out at −78 °C. Indeed, reaction did occur, albeit very slowly, at −78 °C, but the only product which was observable, following the reaction by ^{19}F NMR, was the [2 + 4] adduct **2a**. Conversely, it was not possible to observe rearrangement of [2 + 2] adduct **3a** to a [4 + 2] adduct by heating its reaction mixture (1:1 DMF/hexane) up to a temperature (90 °C) which led to decomposition. The [2 + 2] adducts are readily distinguishable from the [2 + 4] adducts because the fluorine NMR signals for the former compounds are all AB multiplets, whereas those of the latter compounds are all single multiplets. Thus the nature of the products was always clearly discernible by NMR analyses of the crude product mixtures.

In all likelihood, the two cycloaddition processes did *not* involve a common mechanistic pathway. Rather in those cases where a Diels–Alder reaction is observed, the reaction probably involves a concerted pericyclic process, as has been proposed by other workers who have studied the Diels–Alder reactions of acrolein with electron-rich alkenes.[6,7,14] The reactions of **1** with acrolein (and with methyl vinyl ketone) are ideally matched for a reverse electron-demand Diels–Alder ($LUMO_{diene}$-controlled) reaction. There can be no doubt that **1** will have an exceptionally high HOMO, whereas acrolein and methyl vinyl ketone will have low LUMOs (relative to butadiene).[16]

In contrast, methyl acrylate and acrylonitrile, which should have higher LUMO energies than the aldehyde and ketone, are known to preferentially form [2 + 2] adducts in their reactions with nonfluorinated ketene acetals. Therefore, it should have been no surprise that cyclobutane products were obtained with each of the esters and nitriles, presumably via a two-step process involving zwitterionic intermediates.

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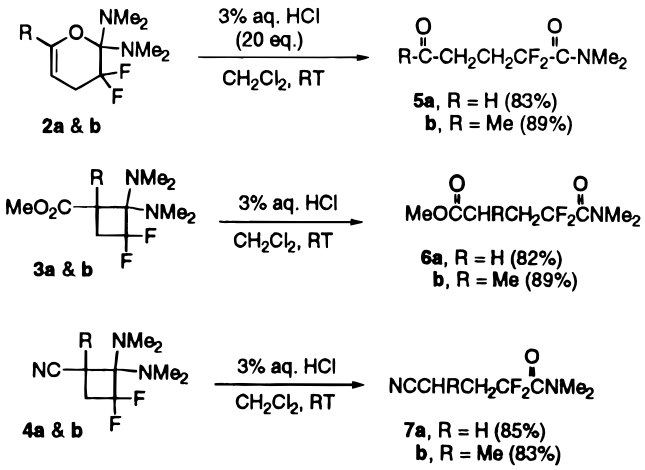
Scheme 3



The dihydropyrans obtained from the hetero-Diels–Alder reactions and the cyclobutane products obtained from the [2 + 2] reactions were readily isolated and characterized, keeping in mind that they are quite sensitive to moisture. These reactive compounds should themselves prove to be useful fluorinated building blocks.

Hydrolyses to Michael Products

All of the adducts could be hydrolyzed, under carefully controlled conditions, to produce the respective Michael addition products **5**–**7**.[8,14] These hydrolyses are carried out in methylene chloride, using a limited amount of 3% HCl, at room temperature (Scheme 3).

These results demonstrate that the readily available difluoro ketene aminal **1** can be used to carry out overall Michael additions to a broad variety of α,β-unsaturated carbonyl and nitrile substrates. It is the first reagent of a difluoro enolate type which has been found to be specific in its participation in Michael additions, and as such this chemistry should find considerable synthetic utility.

Conclusions

Difluoro ketene aminal **1** is a readily prepared, highly nucleophilic *in situ* reagent which undergoes clean [2 + 4] cycloadditions with α,β-unsaturated aldehydes and ketones and clean [2 + 2] cycloadditions with α,β-unsaturated esters and nitriles. Both types of adducts proved to be readily converted, by mild hydrolysis, to the overall Michael addition products. This sequence of two reactions presently comprises the only reported generally useful method for reliably obtaining Michael addition products, to the exclusion of 1,2 adducts, from a difluoro enolate-type reagent.

Experimental Section

General. Melting points and boiling points are uncorrected. NMR spectra were taken in $CDCl_3$ or C_6D_6 using TMS as the internal standard for ^{1}H (300 MHz) and ^{13}C (75.43 MHz). ^{19}F-NMR (282.4 MHz) spectra used $CFCl_3$ as internal standard. Diethyl ether was distilled from sodium/benzophenone under nitrogen immediately prior to use. All reactions with air-sensitive compounds were carried out under a nitrogen atmosphere. Column chromatography was conducted using silica gel (230–400 mesh).

1,1-Bis(dimethylamino)-2,2,2-trifluoroethane. A mixture of 1,1,1-trifluoro-2,2-dichloroethane (50 g, 0.33 mol) and copper powder (43 g, 0.68 mol) in an autoclave was cooled to −78 °C; the air in the autoclave was removed under vacuum.

Then 100 g of dimethylamine was transferred to the autoclave. The reaction mixture was allowed to warm to room temperature and then heated at 60 °C for 12 h, after which the mixture was allowed to cool to room temperature. The liquid was separated, and the solid was washed with 30 mL of methylene chloride. The combined liquid phases were distilled to give 33.8 g (60%) of 1,1-bis(dimethylamino)-2,2,2-trifluoroethane: bp 92−93 °C; ^{1}H NMR δ 2.39 (q, 12H, J = 1.2 Hz), 3.18 (q, 1H, J = 7.3 Hz); ^{19}F NMR δ −67.0 (d, J = 7.3 Hz); ^{13}C NMR δ 41.3, 83.7 (q, J = 26.2 Hz), 126.9 (q, J = 293.6 Hz); IR (neat) 1688 (C−N), 1259 (C−F) cm^{-1}; HRMS calcd for $C_6H_{13}F_3N_2$ 170.1031, found 170.1052. Anal. Calcd for $C_6H_{13}F_3N_2$: C, 42.35; H, 7.65; N, 16.47. Found: C, 42.43; H, 7.89; N, 16.30.

General Procedure for Cycloadditions. To a solution of 1,1-bis(dimethylamino)-2,2,2-trifluoroethane (1.7 g, 10 mmol) in hexane (10 mL) at −78 °C under nitrogen was added *n*-BuLi (2.5 M in hexanes, 4.5 mL), after which the reaction mixture was allowed to warm to room temperature and stirred for 10 h. Then the reaction mixture was distilled at reduced pressure into a dry ice/acetone-cooled receiving flask (100 mL, round bottom) equipped with a rubber septum, magnetic stir bar, and water-cooled condenser. Before and after distillation, the apparatus was maintained under a dry nitrogen atmosphere. Substrate (14 mmol) was added via syringe to this distillate, which contained the 1,1-bis(dimethylamino)-2,2-difluoroethene (**1**), and the mixture was stirred at rt or the given temperature for the required time. The time required for each reaction was determined by following the reactions by ^{19}F NMR. The products were isolated by distillation under reduced pressure. The yields are reported with respect to the 1,1-bis(dimethylamino)-2,2,2-trifluoroethane.

Methyl 2,2-bis(dimethylamino)-3,3-difluorocyclobutanecarboxylate (3a): reaction was complete after 3 min at rt (87%); bp 92−93 °C/1.8 Torr; ^{1}H NMR δ 2.05−2.21 (m, 1H), 2.41 (s, 6H), 2.50 (s, 6H), 2.69−2.88 (m, 1H), 2.96 (ddd, 1H, J = 13.7, 8.5, 3.9 Hz), 3.35 (s, 3H); ^{19}F NMR δ −94.9 (ddd, J = 190.4, 12.1, 7.3 Hz); −101.7 (ddd, J = 190.4, 17.1, 14.7 Hz); ^{13}C NMR δ 33.5 (td, J = 23.2, 3.0 Hz), 40.7, 51.6 (q, J = 5.6Hz), 92.6 (t, J = 21.2 Hz), 121.7 (dd, J = 300.5, 280.5 Hz), 170.9; IR 1737 (C=O), 1672 (C−N), 1172 (C−F) cm^{-1}; HRMS (CI) calcd for $C_{10}H_{19}F_2N_2O_2$ 237.1415, found 237.1458.

2,2-Bis(dimethylamino)-3,3-difluorocyclobutanecarbonitrile (4a): reaction was complete after 3 min at rt (84%); bp 92−93 °C/0.6 Torr; ^{1}H NMR δ 2.10−2.30 (m, 8H), 2.42 (s, 6H), 2.55−2.65 (m, 1H); ^{19}F NMR δ −98.1 (ddd, J = 190.8, 9.8, 7.32 Hz), −101.8 (dt, J = 190.8, 17.1 Hz); ^{13}C NMR δ 26.1, 35.3 (t, J = 24.2 Hz), 41.0, 90.9 (t, J = 20.6 Hz), 118.7, 119.5 (dd, J = 293.6, 286.1 Hz); IR 2246 (CN), 1668 (C−N) cm^{-1}; HRMS (CI) calcd for $C_9H_{16}F_2N_3$ 204.1312, found 204.1311.

Methyl 2,2-bis(dimethylamino)-3,3-difluoro-1-methylcyclobutanecarboxylate (3b): reaction was complete after 10 min at 90 °C (84%): bp 92−93 °C/1.5 Torr; ^{1}H NMR δ 1.39 (s, 3H), 1.92 (ddd, 1H, J = 16.2, 13.7, 2.7 Hz), 2.35 (s, 6H), 2.59 (s, 6H), 2.95−3.18 (m, 1H), 3.31 (s, 3H); ^{19}F NMR δ −93.7 (dd, J = 200.2, 12.2 Hz), −95.0 (ddd, J = 197.8, 19.5, 17.1 Hz); ^{13}C NMR δ 23.0, 40.8, 41.6, 46.9, 51.9, 93.4 (t, J = 17.2 Hz), 121.9 (dd, J = 289.7, 298.9 Hz), 174.5; IR 1739 (C=O), 1674 (C−N), 1183 (C−F) cm^{-1}; HRMS (CI) calcd for $C_{11}H_{20}F_2N_2O_2$ 250.1493, found 250.1504.

2,2-Bis(dimethylamino)-3,3-difluoro-1-methylcyclobutanecarbonitrile (4b): reaction was complete after 10 min at 90 °C (46%); bp 110−112 °C/0.6 Torr; ^{1}H NMR δ 1.18 (s, 3H), 1.68 (ddd, 1H, J = 18.8, 13.2, 7.3 Hz), 2.24 (s, 6H), 2.38−2.44 (m, 7H); ^{19}F NMR δ −93.9 (ddd, J = 202.6, 14.6, 17.1 Hz), −94.8 (ddd, 200.2, 9.8, 7.3 Hz); ^{13}C NMR δ 22.7, 33.8, 40.5, 41.9, 42.8 (t, J = 23.2 Hz), 92.7 (t, J = 18.1 Hz), 122.1, 120.8 (dd, J = 291.6, 294.6 Hz); IR 2236 (CN), 1686 (C−N), 1197 (C−F) cm^{-1}; HRMS (CI) calcd for $C_{10}H_{17}F_2N_3$ 217.1391, found 217.1420.

2,2-Bis(dimethylamino)-3,3-difluoro-6-methyl-2*H*-pyrane (2b): reaction was complete after 5 min at rt (72%); bp 62−64 °C/1.5 Torr; ^{1}H NMR δ 1.59 (m, 3H), 2.35 (th, 2H), 2.49 (t, J = 1.2 Hz, 12H), 4.14 (m, 1H); ^{19}F NMR δ −102.6 (t, J = 14.2 Hz); ^{13}C NMR δ 18.8, 32.7 (t, J = 25.7 Hz), 38.7, 93.4, 123.1 (t, J = 256.3 Hz), 99.3, 149.0; IR 1691 (=C−O), 1192 (C−F) cm^{-1}; HRMS (CI) calcd for $C_{10}H_{19}F_2NO$ 221.1465, found 221.1454. Anal. Calcd for $C_{10}H_{18}F_2N_2O$: C, 54.55; H, 8.18; N, 12.73. Found: C, 54.66; H, 8.49; N, 12.82.

2,2-Bis(dimethylamino)-3,3-difluoro-2*H*-pyran (2a): reaction was complete after 5 min at rt (70%); bp 57−58 °C/1.5 Torr; ^{1}H NMR δ 2.31 (ddt, J = 2.0, 3.7, 15.4 Hz, 2H), 2.47 (t, J = 1.2 Hz, 12H), 4.25−4.32 (m, 1H), 5.99−6.04 (m, 1H); ^{19}F NMR δ −101.2 (t, J = 17.1 Hz); ^{13}C NMR δ 32.5 (t, J = 25.2 Hz), 38.6, 97.8, 99.6 (t, J = 24.2 Hz), 141.7, 123.0 (t, J = 256.8 Hz); IR 1664 (=C−O), 1190 (C−F) cm^{-1}; HRMS (CI) calcd for $C_9H_{17}F_2N_2O$ 207.1309, found 207.1309. Anal. Calcd for $C_9H_{16}F_2N_2O$: C, 52.43; H, 7.77; N, 13.60. Found: C, 52.31; H, 8.10; N, 13.50.

General Procedure for Hydrolysis Reactions. Cycloadduct (1 mmol) was dissolved in 20 mL of methylene chloride, and 0.5 mL of 3% HCl solution was added to the solution. The reaction mixture was stirred for 2−5 h at room temperature, and then 30 mL of ether was added. The organic layer was washed with water and dried. Then the ether was removed, and the residue was distilled at reduced pressure to give the product. If the reaction mixture was allowed to stir for too long, a side reaction occurred leading to a coproduct which was difficult to separate.

***N,N*-Dimethyl 4-carbomethoxy-2,2-difluorobutanoamide (6a):** reaction was complete after 2 h (82%); bp 109−110 °C/3.0 Torr; ^{1}H NMR ($CDCl_3$) δ 2.42−2.62 (m, 4H), 2.98 (s, 3H), 3.16 (t, 3H, J = 1.9 Hz), 3.68 (s, 3H); ^{19}F NMR δ −101.1 (t, J = 17.1 Hz); ^{13}C NMR δ 26.7, 29.9 (t, J = 24.2 Hz), 36.7 (t, J = 7.1 Hz), 36.5 (t, J = 7.1 Hz), 51.6 (q, J = 4.5 Hz), 118.6 (t, J = 254.8 Hz), 162.5 (t, J = 28.7 Hz), 172.3; IR 1722 (C=O), 1667 (C=O), 1190 (C−F) cm^{-1}; HRMS calcd for $C_8H_{14}F_2NO_3$ 210.0942, found 210.0979. Anal. Calcd for $C_8H_{13}F_2NO_3$: C, 45.93; H, 6.22; N, 6.70. Found: C, 46.40; H, 6.45; N, 7.25.

***N,N*-Dimethyl 4-cyano-2,2-difluorobutanoamide (7a):** reaction was complete after 2 h (85%); bp 114−115 °C/2.5 Torr; ^{1}H NMR δ 2.55 (t, J = 2.2 Hz, 3H), 2.46 (t, J = 1.0 Hz, 3H), 1.90−2.20 (m, 4H); ^{19}F NMR δ −101.1 (t, J = 17.2 Hz); ^{13}C NMR δ 10.6 (t, J = 6.6 Hz), 31.1 (t, J = 24.7 Hz), 36.3 (m), 118.3, 118.3 (t, J = 256.8 Hz), 161.8 (t, J = 28.1 Hz); IR 1667 (C=O), 1178 (CN) cm^{-1}; HRMS (CI) calcd for $C_7H_{11}F_2N_2O$ 177.0839, found 177.0851. Anal. Calcd for $C_7H_{10}F_2N_2O$: C, 47.73; H, 5.68; N, 15.91. Found: C, 48.19; H, 5.97; N, 16.27.

***N,N*-Dimethyl 4-carbomethoxy-2,2-difluoro-4-methylbutanoamide (6b):** reaction was complete after 5 h (89%); bp 105−106 °C/ 2.3 Torr; ^{1}H NMR δ 1.06 (d, 3H, J = 7.5 Hz), 2.07−2.27 (m, 1H), 2.70−2.90 (m, 2H), 2.60 (t, 3H, J = 2.3 Hz), 2.47 (3H), 3.36 (s, 3H); ^{19}F NMR δ −98.9 (ddd, J = 280.8, 21.9, 14.7 Hz), −100.3 (ddd, J = 280.8, 19.5, 17.1 Hz); ^{13}C NMR δ 18.6, 34.1, 36.4, 38.5 (t, J = 23.2 Hz), 51.6 (q, J = 7.6 Hz), 175.8, 162.8 (t, J = 28.7 Hz), 19.4 (t, J = 255.3 Hz); IR 1740 (C=O), 1667 (C=O), 1195 (C−F) cm^{-1} ; HRMS (CI) calcd for $C_9H_{15}F_2NO_3$ 224.1098, found 224.1097. Anal. Calcd for $C_9H_{15}F_2NO_3$: C, 48.43; H, 6.73; N, 6.28. Found: C, 48.14; H, 7.27; N, 6.57.

***N,N*-Dimethyl 4-cyano-2,2-difluoro-4-methylbutanoamide (7b):** reaction was complete after 5 h (83%); bp 116−118 °C/2.3 Torr; ^{1}H NMR δ 0.84 (d, J = 7.1 Hz, 3H), 1.96−2.3 (m, 2H), 2.60 (t, 3H, J = 2.2 Hz), 2.49 (t, 3H, J = 1.2 Hz), 2.60−2.75 (m, 1H); ^{19}F NMR δ −97.8 (ddd, J = 288.9, 19.5, 12.2 Hz), −101.1 (ddd, J = 285.6, 19.5, 17.09 Hz); ^{13}C NMR δ 18.6, 19.6 (t, J = 4.0 Hz), 36.3, 38.8 (t, J = 23.7 Hz), 118.4 (t, J = 257.3 Hz), 121.9, 162.1 (t, J = 28.2 Hz); IR 2246 (CN), 1667 (C=O), 1195 (C−F) cm^{-1}; HRMS (EI) calcd for $C_8H_{12}F_2N_2O$ 190.0918, found 190.0915. Anal. Calcd for $C_8H_{12}F_2N_2O$: C, 50.53; H, 6.32; N, 14.74. Found: C, 50.14; H, 6.78; N, 14.70.

***N,N*-Dimethyl 2,2-difluoro-4-oxopentanoamide (5b):** reaction was complete after 2 h (89%); bp 95−97 °C/1.5 Torr; ^{1}H NMR δ 1.57 (s, 3H), 2.30−2.58 (m, 7H), 2.59 (t, J = 3.2 Hz, 3H); ^{19}F NMR δ −99.5 (t, J = 19.5 Hz); ^{13}C NMR δ 29.1, 29.4, 29.7, 36.0 (m), 119.9 (t, J = 253.8 Hz), 162.4 (t, J = 14.1 Hz), 204.1; IR 1722 (C=O), 1667 (C=O), 1190 (C−F) cm^{-1}; HRMS (CI) calcd for $C_8H_{14}F_2NO_2$ 194.0993, found 194.0998. Anal. Calcd for $C_8H_{13}F_2NO_2$: C, 49.74; H, 6.74; N, 7.25. Found: C, 49.41; H, 6.78; N, 7.59.

***N,N*-Dimethyl 2,2-Difluoro-4-oxobutanoamide (5a).** A portion of 1.19 g (15 mmol) of **2a** and 30 mL of methylene chloride were combined in a 100 mL flask. Then 5 mL of 3%

HCl solution was added, and the pH controlled to 5. The mixture was stirred for 1 h, and then 30 mL of ether was added. The ether layer was washed with saturated sodium carbonate (10 mL × 2) and brine and then dried with $MgSO_4$. Removal of solvent gave crude fluorinated aldehyde **5a**: ^{1}H NMR δ 2.16−2.50 (m, 7H), 2.56 (t, 3H, J = 1.9 Hz), 9.20 (m, 1H); ^{19}F NMR δ −99.8 (t, J = 17.1 Hz).

The crude aldehyde was treated directly with 0.1 M 2,4-dinitrophenylhydrazine solution to give yellow crystals of the 2,4-dinitrophenylhydrazone, in 83% yield: mp 138−140 °C; ^{1}H NMR δ 2.28−2.52 (m, 7H), 2.60 (t, J = 1.9 Hz), 5.96 (t, J = 4.2 Hz), 7.20−7.78 (m, 2H), 10.32 (s, 1H); ^{19}F NMR δ −99.8 (t, 2F, J = 17.1 Hz); ^{13}C NMR δ 25.7 (t, J = 5.1 Hz), 31.6 (t, J = 22.9 Hz), 36.2, 115.9, 119.9 (t, J = 255.4 Hz), 130.1, 144.7, 149.3, 162.5 (t, J = 29.1 Hz); HRMS (CI) calcd for $C_{13}H_{16}F_2N_5O_5$ 360.1119, found 260.1113. Anal. Calcd for $C_{13}H_{15}F_2N_5O_5$: C, 43.45; H, 4.18; N, 19.50. Found: C, 43.84; H, 4.06; N, 19.43.

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Acknowledgment. ^{1}H-, ^{13}C-, and ^{19}F-NMR spectra for **3a,b** and **4a,b** (15 pages). This information is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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