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Fluorinated phosphorus compounds
Part 10. Bis(fluoroalkyl) *S*-alkyl phosphorothiolates and tris(fluoroalkyl) phosphorothionates

Christopher M. Timperley *, Sue Kirkpatrick,
Mark Sandford, Matthew J. Waters

Defence Science and Technology Laboratory, Chemical and Biological Sciences,
Porton Down, Salisbury, Wiltshire SP4 0JQ, UK

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Abstract

Treatment of bis(fluoroalkyl) phosphites $(R_FCH_2O)_2P(O)H$, where R_F was CF_3 or C_2F_5 with sulfur in pyridine at 80 °C gave salts of structure $[(R_FCH_2O)_2P(O)SH]NC_5H_5$ in 90 and 88% yield, respectively. The salts reacted with alkyl iodides in acetonitrile at 50 °C to furnish bis(fluoroalkyl) *S*-alkyl phosphorothiolates $(R_FCH_2O)_2P(O)SR$, where R was Me, Et, *n*- and *i*-Pr (when $R_F = CF_3$) and Me (when $R_F = C_2F_5$). Yields ranged from 21 to 57%. Bis(trifluoroethyl) *S*-methyl phosphorothiolate $(CF_3CH_2O)_2P(O)SMe$ underwent fluorination by silver(I) fluoride in acetonitrile at room temperature to yield the phosphorofluoridate $(CF_3CH_2O)_2P(O)F$ in 75% yield. Tris(fluoroalkyl) phosphorothionates $(R_FCH_2O)_3P = S$, where R_F was CF_3, C_2F_5 and C_3F_7, were prepared in 30–34% yield by heating the tris(fluoroalkyl) phosphites $(R_FCH_2O)_3P$ and sulfur to 200 °C in a sealed tube for 8 h.

Keywords: Bis(fluoroalkyl) *S*-alkyl phosphorothiolate; Bis(fluoroalkyl) phosphite; Bis(trifluoroethyl) phosphorofluoridate; Tris(fluoroalkyl) phosphite; Tris(fluoroalkyl) phosphorothionate

1. Introduction

Two retrosynthetic pathways to bis(fluoroalkyl) *S*-alkyl phosphorothiolates **A** can be devised. The first involves the reaction between bis(fluoroalkyl) phosphorohalidates and thiols, the second the reaction between bis(fluoroalkyl) phosphorothioates and alkyl halides (Scheme 1). In Part 8, we used the former route to prepare a selection of phosphorothiolates **A**, where R_F included CF_3 and C_2F_5, and R was Et or *n*-Pr [1]. A disadvantage of this route was the low reactivity of the thiols towards the phosphorochloridates and low yields of product (13–21%). The simplest homologues, where R equalled Me could not be prepared from methanethiol and triethylamine.

In this paper, we report a more versatile route to bis(fluoroalkyl) *S*-alkyl phosphorothiolates based on the second retrosynthetic pathway. We also describe the synthesis of bis(trifluoroethyl) phosphorofluoridate $(CF_3CH_2O)_2P(O)F$ from one of the thiolates, and the isolation of some new tris(fluoroalkyl) phosphorothionates $(R_FCH_2O)_3P{=}S$, where R_F equals CF_3, C_2F_5 and C_3F_7.[1]

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* Corresponding author. Tel.: +44 1980 613 566; fax: +44 1980 613 834.
E-mail address: cmtimperley@dstl.gov.uk (C.M. Timperley).

[1] The nomenclature of phosphorus compounds can be confusing and the names used in the text were chosen for clarity. For details on the naming of phosphorus–sulfur compounds, see ref. [1]. The terms thiolo and thiono describe sulfur singly (P–S) or doubly (P═S) bonded to the phosphorus atom.

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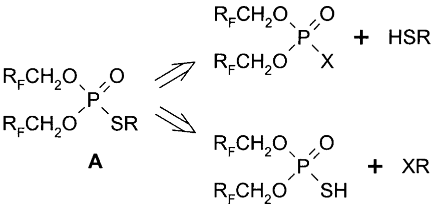
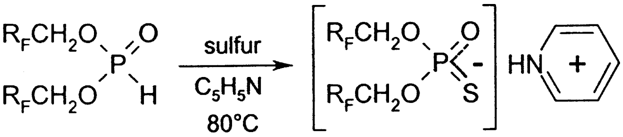


Scheme 1. Retrosynthetic pathways to bis(fluoroalkyl) *S*-alkyl phosphorothiolates **A** where R_F = fluoroalkyl, R = alkyl and X = halide (usually Cl or Br in the case of the phosphorohalidate and I in the case of the alkyl halide).

2. Results and discussion

2.1. Bis(fluoroalkyl) S-alkyl phosphorothiolates

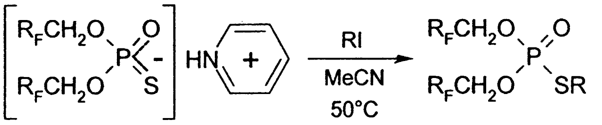
We found that bis(trifluoroethyl) phosphite and bis(pentafluoropropyl) phosphite reacted with sulfur in pyridine to yield the pyridinium salts **1** and **2**.



$R_F = CF_3$ **1** 90%
C_2F_5 **2** 88%

Salt **1** was obtained as a white solid with mp 53–56 °C from isopropanol, whereas salt **2** was a pale yellow liquid that resisted crystallization. Structures of the salts were confirmed by multinuclear NMR spectroscopy, the value of the chemical shift δ_P at 59 ppm being diagnostic for thiono compounds [2].

Alkylation of salts of phosphorothioic acid is known to yield products of thiolic structure [3]. We found that salts **1** and **2** reacted with alkyl iodides in warm acetonitrile to give the desired phosphorothiolates **3**–**7** as colourless or pale yellow liquids. Although the pyridinium salts are potentially capable of reacting via the oxo or thiolo anion, reaction took place via the latter because of its greater reactivity towards the alkyl iodide.



R_F		R_F	R		Yield (%)
CF_3	**1**	CF_3	Me	**3**	57
C_2F_5	**2**		Et	**4**	29
			n-Pr	**5**	21
			i-Pr	**6**	22
		C_2F_5	Me	**7**	21

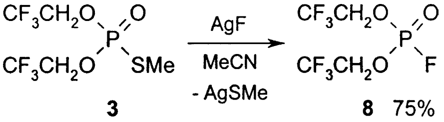
The isolated yields are based on products >98% pure from small-scale experiments and after fractionation using micro-distillation apparatus. Material obtained below this purity was not included in the calculation of yields. Larger scale experiments, using larger fractionation equipment, would be expected to lead to increased yields.

All the products obtained had chemical shifts δ_P in the region of 30 ppm, which is typical for dialkyl *S*-alkyl phosphorothiolates [2]. In the proton NMR spectrum, a characteristic difference in the values of the spin–spin coupling constants was observed: J_{HCSP} (15–17 Hz) was greater than J_{HCOP} (8 Hz).

In summary, the new route has permitted the synthesis of the *S*-methyl and *S*-isopropyl analogues for the first time and should be viewed as complementary to the earlier explored route. Starting from the fluoroalcohol, it is now possible to construct bis(fluoroalkyl) phosphorothiolates in three steps from simple and commonly available precursors (Scheme 2).

2.2. Bis(trifluoroethyl) phosphorofluoridate

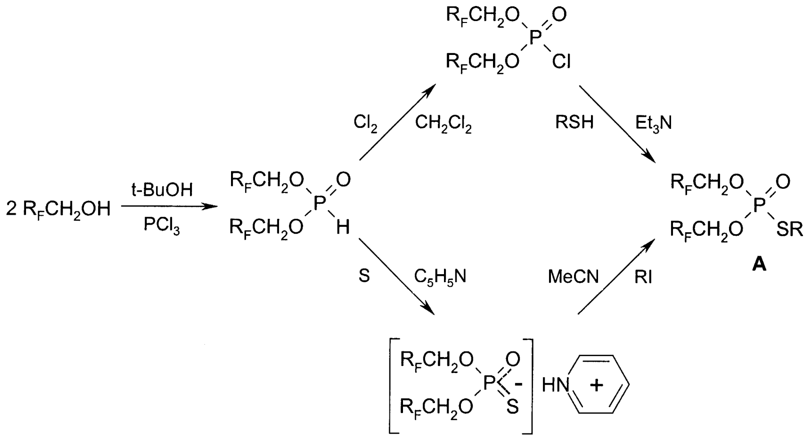
The phosphorus–sulfur bond can be cleaved by fluorinating agents such as 1-fluoro-2,4-dinitrobenzene [4], 2,4,6-trinitrofluorobenzene [5] or triethylamine tris(hydrofluoride) in the presence of iodine [6]. However, one of the most effective and convenient fluorinating agents for this purpose is silver(I) fluoride [7,8]. We found that treatment of bis(trifluoroethyl) *S*-methyl phosphorothiolate **3** with silver(I) fluoride in acetonitrile at room temperature resulted in efficient conversion to the bis(trifluoroethyl) phosphorofluoridate **8**.



This example was chosen to illustrate the synthetic potential of the new bis(fluoroalkyl) *S*-alkyl phosphorothiolates: the fluoridate had been prepared previously in 84% yield by fluorinating the corresponding phosphorochloridate with potassium fluoride in warm dichloromethane in the presence of trifluoroacetic acid catalyst [9].

2.3. Tris(fluoroalkyl) phosphorothionates

Compounds of structure $(R_FO)_3P{=}S$ appear to be very rare. Reference to only four could be found: $(CF_3CH_2O)_3P{=}S$, prepared in 53% yield by treatment of thiophosphoryl chloride with sodium trifluoroethoxide [10], $[(CF_3)_2CHO]_3P{=}S$, prepared in 73% by treatment of thiophosphoryl chloride with lithium hexafluoroisopropoxide [11] and $[H(CF_2)_nCH_2O]_3P{=}S$, where *n* equalled 2 and 4, prepared in 95 and 83% yield, respectively, by adding sulfur to the tris(fluoroalkyl) phosphites [12]. Tertiary



Scheme 2. Two routes to bis(fluoroalkyl) *S*-alkyl phosphorothiolates **A** having the same number of stages.

phosphites usually add sulfur readily on warming in inert solvents but those with β-fluorine atoms react less easily as the nucleophilicity of the phosphorus atom is reduced. Thus, inappreciable conversion of the two fluorinated phosphites occurred after prolonged boiling with excess sulfur in dioxane in the presence of triethylamine catalyst [12]. However, the reaction proceeded, under anhydrous conditions in the absence of solvent, on heating to 190–210 °C in a sealed glass tube for over 8 h.

We found that the related tris(fluoroalkyl) phosphites **9–11** added sulfur under comparable conditions, although conversion to product could only partially be effected. The tris(fluoroalkyl) phosphorothionates **12–14** were isolated as yellow liquids in greater than 98% purity after column chromatography.

$$(R_FCH_2O)_3P \xrightarrow[\text{8 h}]{\text{S, 200°C}} (R_FCH_2O)_3P{=}S$$

sealed tube

R_F			*Yield*
CF_3	**9**	**12**	30%
C_2F_5	**10**	**13**	34%
C_3F_7	**11**	**14**	31%

The phosphorothionates had chemical shifts δ_P in the region of 68 ppm which is characteristic for compounds of this structure [2]. In the infrared spectra, two strong bands at 908 and 738–734 cm^{-1} were present, indicative of the P=S bond [13].

3. Conclusion

Some novel bis(fluoroalkyl) *S*-alkyl phosphorothiolates and tris(fluoroalkyl) phosphorothionates have been prepared. Although the yields were not high, sufficient amounts have now been obtained to permit their chemistry to be explored for the first time.

4. Experimental

The bis(fluoroalkyl) phosphites were prepared in high purity using a reported method [9]. Fluoroalcohols from Apollo Scientific Ltd. (Stockport, UK) and other reagents from Aldrich (Gillingham, UK) were used as received. Anhydrous solvents were used in all experiments. Thin layer chromatography (TLC) plates, MK6F silica gel 60 Å (2.5 cm × 7.5 cm) were obtained from Whatman (Maidstone, UK). Spots were visualised by iodine vapour. Silica gel for column chromatography was obtained from BDH Laboratory Supplies (Poole, UK). NMR spectra were obtained on a JEOL Lambda 500 instrument (operating at 500 MHz for ^{1}H, 125 MHz for ^{13}C, 470 MHz for ^{19}F and 202 MHz for ^{31}P spectra) or a JEOL Lambda 300 instrument (operating at 300 MHz for ^{1}H, 75 MHz for ^{13}C, 282 MHz for ^{19}F and 121.5 MHz for ^{31}P spectra) as solutions in $CDCl_3$, with internal reference $SiMe_4$ for ^{1}H and ^{13}C, external $CFCl_3$ for ^{19}F and external $(MeO)_3P$ (δ 140 ppm) for ^{31}P spectra. Data were recorded as follows: chemical shifts in ppm from reference on the δ scale, integration, multiplicity, coupling constant and assignment. IR spectra were recorded as liquid films on a Nicolet SP210 instrument using Omnic software. Reaction mixtures were monitored by gas chromatography–mass spectrometry (GC–MS) using a Finnigan MAT GCQ instrument with chemical ionisation (CI) using methane as reagent gas. Molecular weights of pure products were confirmed with methane +ve CI data (70 eV).

4.1. Pyridinium bis(2,2,2-trifluoroethyl) phosphorothioate (1)

Pyridine (4.9 ml, 60.98 mmol) was added dropwise to a stirred mixture of finely divided sulfur (1.3 g, 40.65 mmol) and bis(2,2,2-trifluoroethyl) phosphite (10 g, 40.65 mmol) at room temperature. The temperature was increased to 80 °C and the sulfur aggregated into solid lumps. The mixture was maintained at this temperature for 8 h. Solids were filtered off and the filtrate was concentrated by rotary evaporation to remove residual pyridine. The resultant yellow oil was dissolved in isopropanol and concentrated again to reveal the title compound as white crystals (13.1 g, 90%); mp 53–56 °C. ^{1}H NMR: $\delta = 8.87$ (2H, dd, $J = 2$ and 5 Hz, pyridine 2- and 6-H), 8.40 (1H, dt, $J = 2$ and 8 Hz, pyridine 4-H), 7.91 (2H, dt, $J = 1$ and 8 Hz, pyridine 3- and 5-H), 4.36 (4H, m, OCH_2). ^{13}C NMR: $\delta = 144.5$ (s, pyridine 4-C), 142.5 (s, pyridine 2- and 6-C), 126.7 (s, pyridine 3- and 5-C), 63.3 (dq, $J = 4$ and 37 Hz, OCH_2). ^{19}F NMR: $\delta = -73.8$ (t, $J = 9$ Hz, CF_3). ^{31}P NMR: $\delta = 59.6$. The product was analytically pure by TLC analysis.

4.2. *Pyridinium bis(2,2,3,3,3-pentafluoropropyl) phosphorothioate (**2**)*

The above procedure was followed, starting with bis(2,2,3,3,3-pentafluoropropyl) phosphite (14.06 g, 40.65 mmol). The title compound was obtained as a pale yellow liquid that failed to crystallize (16.3 g, 88%). ^{1}H NMR: $\delta = 8.81$ (2H, dd, $J = 2$ and 5 Hz, pyridine 2- and 6-H), 8.15 (1H, dt, $J = 2$ and 8 Hz, pyridine 4-H), 7.68 (2H, dt, $J = 1$ and 8 Hz, pyridine 3- and 5-H), 4.41 (4H, m, OCH_2). ^{13}C NMR: $\delta = 143.9$ (s, pyridine 4-C), 141.5 (s, pyridine 2- and 6-C), 126.4 (s, pyridine 3- and 5-C), 63.1 (dq, $J = 4$ and 37 Hz, OCH_2). ^{19}F NMR: $\delta = -123.28$ (4F, m, CF_2), -82.6 (6F, m, CF_3). ^{31}P NMR: $\delta = 59.6$. The product was analytically pure by TLC analysis.

4.3. *Bis(fluoroalkyl) S-alkyl phosphorothiolates (**3**–**7**)*

The appropriate alkyl iodide (35 mmol) was added in one portion to a stirred solution of pyridinium salt **1** (5 g, 14 mmol) or **2** (6.4 g, 14 mmol) in acetonitrile (15 ml). The mixture was stirred at 50 °C for 1 h, during which pyridine hydroiodide precipitated. The mixture was allowed to cool to room temperature. Removal of the solids by filtration through a Pasteur pipette containing a small plug of cotton wool and rotary evaporation of the filtrate gave crude product (generally 92% pure by multinuclear NMR analyses) which was fractionated under reduced pressure to yield the title compounds as colourless or pale yellow liquids. Physical constants and analytical data appear in Table 1.

4.4. *Bis(trifluoroethyl) phosphorofluoridate (**8**)*

Silver(I) fluoride (1.68 g, 13.22 mmol), a brown powder, was added in one portion via a funnel to a stirred solution of bis(2,2,2-trifluoroethyl) *S*-methyl phosphorothiolate (1.93 g, 6.61 mmol) at room temperature. The solution assumed a yellow colour. The suspension was stirred for 12 h. The solids were removed by filtration through a short column of silica gel. The filtrate was concentrated to give a liquid. Distillation under reduced pressure gave the title compound as a colourless liquid (1.3 g, 75%); bp 46–47 °C/10 mmHg (oil bath temperature ~100 °C). Spectroscopic

Table 1
Physical constants and analytical data for bis(fluoroalkyl) *S*-alkyl phosphorothiolates $(R_FCH_2O)_2P(O)SR$ **3**–**7** (NMR data recorded in $CDCl_3$)

Compound	R_F	R	bp (°C/mmHg)	^{1}H NMR δ, J (Hz)	^{13}C{^{1}H} NMR δ, J (Hz)	^{19}F NMR δ, J (Hz)	^{31}P{^{1}H} NMR δ	IR ν (cm^1)	Elemental analysis (%)
3 (M_w 292)	CF_3	Me	43–52/0.02	4.44 (4H, dq, each 8, OCH_2), 2.37 (3H, d, $J = 17$, SCH_3)	122.9 (dq, $J = 11$ and 278, CF_3), 63.3 (dq, $J = 5$ and 38, OCH_2), 12.1 (d, $J = 5$, SCH_3)	−74.6 (t, $J = 6$, CF_3)	31.0	1419, 1290, 1257, 1173, 1095, 1063, 962, 870, 852	Calculated for $C_5H_7F_6O_3PS$: C 20.6; H 2.4; F 39. Found: C 20.4; H 2.5; F 39.1
4 (M_w 306)	CF_3	Et	62/0.05	4.45 (4H, m, OCH_2), 2.95 (2H, dq, $J = 15$ and 7, SCH_2), 1.42 (3H, t, $J = 7$, CH_3)	122.3 (dq, $J = 11$ and 277, CF_3), 62.3 (dq, $J = 6$ and 38, OCH_2), 25.5 (d, $J = 4$, SCH_2), 15.9 (d, $J = 7$, CH_3)	−74.6 (t, $J = 6$, CF_3)	30.7	1456, 1419, 1296, 1174, 1063, 964, 874, 659	Calculated for $C_6H_9F_6O_3PS$: C 23.5, H 2.9, F 37.3. Found: C 24.1, H 3.1, F 37.5
5 (M_w 320)	CF_3	*n*-Pr	50/0.02	4.41 (4H, m, OCH_2), 2.91 (2H, dt, $J = 15$ and 7, SCH_2), 1.74 (2H, sextet, $J = 7$, CH_2), 1.05 (3H, t, $J = 7$, CH_3)	123.4 (dq, $J = 11$ and 277, CF_3), 63.9 (dq, $J = 6$ and 38, OCH_2), 33.3 (d, $J = 4$, SCH_2), 23.8 (d, $J = 6$, CH_2), 13.7 s, CH_3)	−74.0 (t, $J = 9$, CF_3)	31.1	1458, 1419, 1294, 1259, 1173, 1095, 1061, 962, 874, 659	Calculated for $C_7H_{11}F_6O_3PS$: C 26.3, H 3.4, F 35.6. Found: C 26.4, H 3.7, F 35.2
6 (M_w320)	CF_3	*i*-Pr	45/0.05	4.42 (4H, complex m, OCH_2), 3.59 (1H, complex m, CH), 1.45 (6H, dd, $J = 1$ and 7, CH_3)	122.46 (dq, $J = 1$ and 278, CF_3), 63.2 (dq, $J = 6$ and 39, OCH_2), 39.6 (d, $J = 4$, CH), 25.1 (d, $J = 7$, CH_3)	−74.6 (t, $J = 9$, CF_3)	29.8	1454, 1419, 1296, 1263, 1176, 1095, 1061, 964, 874, 737	Calculated for $C_7H_{11}F_6O_3PS$: C 26.3, H 3.4, F 35.6. Found: C 26.5, H 3.3, F 35.5
7 (M_w 392)	C_2F_5	Me	37/0.04	4.58 (4H, m, OCH_2), 2.38 (3H, d, $J = 17$, SCH_3)	116.5 (m, CF_3), 112 (m, CF_2), 62.6 (dt, $J = 4$ and 29, OCH_2), 12.0 (d, $J = 5$, SCH_3)	−123.9 (4F, m, CF_2), −83.1 (6F, m, CF_3)	31.0	1458, 1377, 1354, 1271, 1205, 1122, 1111, 1057, 1026, 935, 872, 841	Calculated for $C_7H_7F_{10}O_3PS$: C 21.4; H 1.8; F 48.4. Found: C 21.2; H 1.9; F 48.1

details were the same as those for a specimen of the same compound prepared by a different route [9].

4.5. *Tris(fluoroalkyl) phosphites (**9–11**)*

These were isolated in 60–70% yield by heating the respective fluoroalcohol with phosphorus trichloride in a 3:1 molar ratio, according to the method of Krogh et al. [14]. Boiling points for phosphites **9**, **10** and **11** were 43 °C/10 mmHg, 38 °C/2 mmHg and 96 °C/16 mmHg, respectively. After careful fractionation, they were obtained as colourless liquids of purity no greater than 90–95%. The impurities comprised the bis(fluoroalkyl) phosphites $(R_FCH_2O)P(O)H$, which presumably arose from HCl-promoted dealkylation of the tris(fluoroalkyl) phosphite in the reaction mixture. These impurities co-distilled with the desired phosphites; further fractionation generally resulted in material of lower purity. For example, repeat fractionation of tris(trifluoroethyl) phosphite (δ_P 138.2 ppm) always gave a product contaminated with about 5% $(CF_3CH_2O)_2P(O)H$ (δ_P 6.9, compared to 7.0 ppm for a pure specimen, ref. [9]). The phosphite mixtures were used for the sulfur addition experiments.

4.6. *Tris(fluoroalkyl) phosphorothionates (**12–14**)*

The appropriate tris(fluoroalkyl) phosphite (20 mmol) was placed in a borosilicate glass tube (Pierce vacuum hydrolysis tube, Rockford, IL, USA) and finely divided sulfur (2.56 g, 80 mmol) added. The tube was sealed by tightening the Teflon® screw valve at the top and heated in an aluminium block (Reacti-Therm™ heating module, Rockford, IL, USA) at 200 °C for 8 h. The mixture was allowed to cool to room temperature and an aliquot withdrawn. Analysis by GC–MS showed no greater than 50% conversion to product. Excess sulfur was removed from the reaction mixture by filtration and the filtrate concentrated by rotary evaporation. Chromatography of the residue over silica gel, eluting with 20:1 hexane–acetone, gave the title compounds as yellow liquids.

Compound **12**. ^1H NMR $\delta = 4.42$ (6H, dq, $J = 8$ and 12 Hz, OCH_2). ^{13}C NMR $\delta = 124.5$ (dq, $J = 11$ and 277 Hz, CF_3), 64.5 (dq, $J = 3$ and 38 Hz, OCH_2). ^{19}F NMR $\delta = -74$ (9F, t, $J = 9$ Hz, CF_3). ^{31}P NMR $\delta = -68.5$. Calculated for $C_6H_6F_9O_3PS$: C, 20.0; H, 1.7; S, 8.9. Found: C, 20.1; H, 1.7; S, 8.8%.

Compound **13**. ^1H NMR $\delta = 4.48$ (6H, q, $J = 12$ Hz, OCH_2). ^{13}C NMR $\delta = 118.2$ (tq, $J = 34$ and 286 Hz, CF_3), 111.7 (dtq, $J = 10$, 257 and 34 Hz, CF_2), 63.6 (dt, $J = 4$ and 29 Hz, OCH_2). ^{19}F NMR $\delta = -124.1$ (6F, t, $J = 12$ Hz, CF_2), -83.3 (9F, m, CF_3). ^{31}P NMR $\delta = -68.0$. Calculated for $C_9H_6F_{15}O_3PS$: C, 21.2; H, 1.2; S, 6.3. Found: C, 21.1; H, 1.1; S, 6.3%.

Compound **14**. ^1H NMR $\delta = 4.51$ (6H, dt, $J = 10$ and 13 Hz, OCH_2). ^{13}C NMR $\delta = 114.1$ (tq, $J = 34$ and 287 Hz, CF_3), 108.5 (m, OCH_2CF_2), 108.5 (t, $J = 265$ Hz, CF_2CF_3), 63.8 (t, $J = 28$ Hz, OCH_2). ^{19}F NMR $\delta = -127.4$ (6F, m, CH_2CF_2), -121.1 (6F, m, CF_2CF_3), -80.8 (9F, m, CF_3). ^{31}P NMR $\delta = -68.1$. Calculated for $C_{12}H_6F_{21}O_3PS$: C, 21.8; H, 0.9; S, 4.9. Found: C, 21.8; H, 0.8; S, 5.0%.

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