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Perfluoroalkyl- and perfluoroalkylether-substituted aromatic phosphates and phosphonates

K.J.L. Paciorek *, W.-H. Lin, S.R. Masuda

Lubricating Specialties, Technolube Products Division, 1425 Seacrest Drive, Corona Del Mar, CA 92625, USA

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Abstract

A series of phosphates and phosphonates, $(p\text{-}R_fC_6H_4O)_{3-x}P(O)(OC_6H_5)_x$ and $(p\text{-}R_fC_6H_4O)_{3-x}P(O)(C_6H_5)_x$, respectively ($R_f = C_2F_5$, $n\text{-}C_8F_{17}$ and $C_3F_7(OCF(CF_3)CF_2)_n$ wherein $n = 2$, 3, 4 and 6) were prepared by reaction of the appropriate phenols with corresponding phosphorus halides. The majority of phenols were obtained from $p\text{-}R_fC_6H_4Br$ via $p\text{-}R_fC_6H_4B(OCH_3)_2$ intermediates followed by hydrolysis. The presence of $R_fC_6H_4O$ groups promoted hydrolytic instability; phosphates were more susceptible to hydrolysis than the corresponding phosphonates. An increase in the number of $R_fC_6H_4O$ groups resulted in lower hydrolytic stability. It required the presence of two $p\text{-}C_3F_7(OCF(CF_3)CF_2)_nC_6H_4O$ substituents for the compounds to be soluble in perfluoropolyalkylether fluids at low temperature; solubility increased with the increase in n. © 1998 Elsevier Science S.A.

Keywords: Perfluoroalkyl; Phosphates; Phosphonates; Perfluoroalkylether

1. Introduction

Perfluoropolyalkylethers, due to their wide liquid ranges, high viscosity index and high thermal oxidative stability, offer lubricants for applications where extremes of temperatures and environments are encountered [1–4]. However, at elevated temperatures in the presence of metals in oxidizing atmospheres, these materials undergo decomposition accompanied by metal corrosion [4,5]. The degradation process can be arrested by additives such as phosphines and phospha-*s*-triazines. Neither of these materials provide lubricity enhancement, nor are they amenable to be modified to offer rust protection. The latter is a very serious problem associated with halogenated fluids such as poly(chlorotrifluoroethylene) and perfluoropolyalkylether fluids [6,7].

Aromatic phosphates are widely utilized as lubrication additives in hydrocarbon based fluids; thus there was a good probability that these materials, if rendered soluble, would also function as lubricity additives in fluorinated fluids. Ideally, in addition, these materials could act as degradation inhibitors, and when appropriately substituted, as rust-preventing agents. Similar reasoning applied to phosphonates, the latter in view of the *p*-aromatic linkage, present also in phosphines, offered a better likelihood of inhibiting perfluoropolyalkylethers' thermal oxidative degradation. Based on these premises, perfluoroalkyl- and perfluoroalkylether-substituted aromatic phosphates and phosphonates were synthesized and evaluated. The investigations discussed here pertain only to synthesis and characterizations. Evaluations have been described elsewhere [7–11]. It is of interest that several of these materials combined all the desired properties and were more effective, as thermal oxidative degradation inhibitors, than the currently known additives.

2. Results and discussion

Based on past investigations of additives for perfluorinated fluids [11], it was apparent that it is mandatory to incorporate perfluoroalkyl or perfluoroalkylether chains to render phosphates and phosphonates soluble in perfluoropolyalkylether fluids. Direct attachment of the fluorinated moieties to phosphorus was not considered, since such materials exhibit low thermal stability due to the preferential P–F bond formation. To simplify the synthesis process, the two general classes of candidates selected were: $(R_fC_6H_4O)_{3-x}P(O)(OC_6H_5)_x$ ($x = 0$, 1 or 2) and $(R_fC_6H_4O)_{3-x}P(O)(C_6H_5)_x$ ($x = 1$ or 2). This limited the chlorophosphorus starting materials to $POCl_3$, $C_6H_5OPOCl_2$, $(C_6H_5O)_2POCl$, $C_6H_5POCl_2$ and $(C_6H_5)_2POCl$. Thus, the only reagents required for the preparation of the phosphates and phosphonates were perfluoroalkyl- and perfluoroalkylether-substituted phenols, i.e.,

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* Corresponding author.

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$$Cl_{3-x}P(O)\left(OC_6H_5\right)_x + 3-xR_fC_6H_4OH$$
$$\rightarrow \left(R_fC_6H_4O\right)_{3-x}P(O)\left(OC_6H_5\right)_x + 3-xHCl$$
$$Cl_{3-x}P(O)\left(C_6H_5\right)x + 3-xR_fC_6H_4OH$$
$$\rightarrow \left(R_fC_6H_4O\right)_{3-x}P(O)\left(C_6H_5\right)_x + 3-xHCl$$

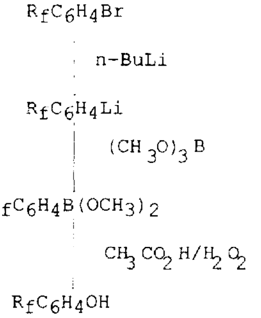
To assure the required low temperature solubilities, of the phosphates and phosphonates, utilization of perfluoroalkylether-substituted phenols represented by the series $C_3F_7[OCF(CF_3)CF_2]_nC_6H_4OH$ offered the best promise. Unfortunately, the copper-assisted coupling process proceeds with difficulty, if at all, when the ether function is separated by less than three carbons from the iodo or other halo group [12]. Thus, the preparation of these phenols by direct coupling of $C_3F_7[OCF(CF_3)CF_2]_nCF(CF_3)I$ and IC_6H_4OH was not possible. An alternate route was to utilize the readily accessible methyl esters $C_3F_7[OCF(CF_3)CF_2]_{n-1}OCF(CF_3)CO_2CH_3$, to form the bromides p-$C_3F_7[OCF(CF_3)CF_2]_nC_6H_4Br$, by reaction with 1,4-dibromobenzene followed by SF_4 fluorination [13]. A number of routes were investigated to transform the bromides into phenols utilizing p-$C_2F_5C_6H_4Br$ as a model compound. The latter was obtained also via the two-step process:

$$CF_3CO_2CH_3 + BrC_6H_4Br \xrightarrow{LiC_4H_9} CF_3COC_6H_4Br \xrightarrow{SF_4} C_2F_5C_6H_4Br$$

The reason for this approach, instead of the Cu coupling, was to optimize the SF_4 fluorination process. We have found that the reported high temperatures, > 180°C [13] lead to formation of mono- and disulfides shown below:

By conducting fluorinations at 105–110°C yields >95% were attained. This applied subsequently also to $C_3F_7[OCF(CF_3)CF_2]_nC_6H_4Br$ compounds.

The path ultimately chosen to obtain the corresponding phenol is depicted below:



The process was originally developed for non-fluorinated materials [14]. After optimization yields >75% were reproducibly realized without the need to isolate any of the intermediates.

The phosphates and phosphonates synthesized using the series of phenols are listed in Table 1. None of the $C_2F_5C_6H_4O$-substituted products were soluble at room temperature in the perfluoropolyalkylether fluids, which was to be expected. These materials however, functioned as degradation inhibitors at elevated temperatures [7]. Compounds having only one $C_2F_5C_6H_4O$ grouping were relatively resistant to hydrolysis. Increasing the number of the $C_2F_5C_6H_4O$ groups resulted in a progressively lower hydrolytic stability i.e., $C_2F_5C_6H_4OP(O)R_2 > (C_2F_5C_6H_4O)_2P(O)R > (C_2F_5C_6H_4O)_3P(O)$, wherein $R = C_6H_5$ or OC_6H_5. Thus, in the case of $(C_2F_5C_6H_4O)_3P(O)$ only 6% of the starting material was recovered following a 24-h exposure to water at 100°C. These results indicate that a strongly electronegative group on the aromatic ring must be responsible for this behavior. Limited modeling studies showed the initial attack to occur at $R_fC_6H_4O$–P bond. In view of these findings, the phosphates $(R_fC_6H_4O)_3P(O)$ were not further investigated.

It is apparent from Table 1 data that $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)OC_6H_5$ is the least hydrolytically stable compound having to phenoxy groups *para*-substituted by either perfluoroalkyl or perfluoroalkylether chains. Increasing the chain length by one $OCF(CF_3)CF_2$ unit increased the hydrolytic stability, as measured by the starting material recovery, by a factor of three. As expected, the phosphonates were more hydrolytically stable than the corresponding phosphates. On the other hand, phosphates were more effective as thermal oxidative degradation inhibitors and their diesters $R_fC_6H_4OP(O)(OC_6H_5)OH$, as rust-preventing agents [7–11].

In the compounds substituted by the phenoxy group, $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O$ (V–VIII), only the disubstituted phosphate and phosphonate exhibited low temperature, −40°C, solubility in perfluoropolyalkylether fluids. The longer chain, $C_3F_7[OCF(CF_3)CF_2]_4$, lowered the cloud point of the mono-substituted phosphate and phosphonate by ~35°C. Increasing the chain length by two additional units rendered the phosphate $[C_3F_7[OCF(CF_3)CF_2]_6C_6H_4O]_2P(O)OC_6H_5$ soluble at room temperature in Krytox 143AC. Based on overall properties, namely, effectiveness in degradation inhibition, rust prevention, solubility and volatility (as measured by TGA weight loss onset) the mixture of $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$ and $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OP(O)(OC_6H_5)OH$ presented the optimum candidate system [7,8].

In view of the multistep reaction sequence necessary to form $C_3F_7[OCF(CF_3)CF_2]_nC_6H_4OH$, the series of phosphates and phosphonates based on p-$C_8F_{17}C_6H_4OH$ were investigated. The phenol was described previously [15]. In our studies, we have found that using dimethylformamide instead of dimethylsulfoxide, in the copper assisted coupling of 4-iodophenol and n-perfluorooctyl iodide, eliminated the formation of n-$C_7F_{15}COC_6H_4OH$ and gave a high yield (97%) of the *para* n-$C_8F_{17}C_6H_4OH$. None of the derived

Table 1
The summary of data for phosphates and phosphonates

Compound [a,b]		Yield (%)	MP (°C)	BP (°C 10 $^{-3}$ mm)	MW		Hydrolytic (% rec.) [d]	TGA [e] (°C)		Solubility (°C) [f]		
					Calculated	Experimental[c]		Onset	T	Krytox 143AC	Fomb. Z25	Demnu S-100
$R_fP(O)(OPh)_2$	I	75	–	144–146	444	480	96	130	223	57	146	n.d. [g]
$R_fP(O)Ph_2$	II	86	69–71	–	412	440	79	150	232	85	172	n.d.
$(R_f)_2P(O)OPh$	III	88	–	144–146	562	635	38	130	227	65	95	n.d.
$(R_f)_3P(O)$	IV	87	89–90	–	680	750	6	135	223	82	77	n.d.
$R_f'P(O)(OPh)_2$	V	94	–	145–148	826	860	58	150	245	95	101	105
$R_f'P(O)Ph_2$	VI	75	67–70		784	830	97	150	245	106	112	n.d.
$(R_f')_2P(O)OPh$	VII	79	–	169–170	1326	1320	19	170	267	< −40	−8	< −40
$(R_f')_2P(O)Ph$	VIII	79	–	175–180	1310	1300	79	155	253	< −40	−15	< −40
$R_f''P(O)Ph_2$	IX	45	WAX	–	1126	1100	99	165	296	78	85	
$(R_f'')_2P(O)Ph$	X	41	–	n.d.	1974	1850	100	203	308	< −40	< −40	< −40
$R_f''P(O)(OPh)_2$	XI	74	–	n.d.	1158	1100	99	190	293	60	64	65
$(R_f'')_2P(O)OPh$	XII	38	–	n.d.	1990	1980	70	195	304	< −40	< −40	< −40
$(R''')_2P(O)OPh$	XIII	82	–	n.d.	1858	1540	62	180	285	< −40	< −40	< −40
$(R''')_2P(O)Ph$	XIV	53	–	n.d.	1642	1570	93	215	298	< −40	< −40	< −40
$R_f^{iv}P(O)(OPh)_2$	XV	87	–	n.d.	1490	1550	97	200	302	25	46	n.d.
$R_f^{v}P(O)(Ph)_2$	XVI	63	110–111	–	712	740	98	190	280	115	162	n.d.
$(R^{v})_2P(O)Ph$	XVII	32	84–85	–	1146	1150	81	180	294	78	78	81
$R_f^{v}P(O)(OPh)_2$	XVIII	57	61–62	–	744	750	50	160	283	102	134	n.d.
$(R_f^{v})_2P(O)Ph$	XIX	89	68–69	–	1162	1170	n.d.	165	290	74	76	n.d.

[a] $R_f = C_2F_5C_6H_4O$, $R_f' = C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O$, $R_f'' = C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O$, $R_f''' = C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O$, $R_f^{iv} = C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O$, $R_f^{iv} = C_3F_7[OCF(CF_3)CF_2]_6C_6H_4O$. $R_f^{v} = C_8F_7C_6H_4O$.
[b] All compounds were ≥99% pure by GC analysis.
[c] Molecular weights of compounds I–VI were determined in C_6H_6; others in C_6F_6.
[d] Hydrolytic stability evaluations were carried out in water at 100°C for 24 h: the values given are percent of starting material.
[e] Thermogravimetric analyses were performed at 10°C/min in N_2.
[f] The cloud point was determined on an one percent by weight solution of an additive in a given fluid.
[g] n.d. = not determined.

Table 2
The pyrolysis data for phosphates XIII and XV [a]

Phosphate [b]		Quantity		Temperature (°C)	Residue [c] (mg)	% S.M. [d]	Volatiles [e] (mg)
		mg	mmol				
$R_f^{iv}C_6H_4OP(O)(OC_6H_5)_2$	XV	197.1	0.132	300	197.0	93	None
$R_f^{iv}C_6H_4OP(O)(OC_6H_5)_2$	XV	203.8	0.137	343	191.6	45	0.5
$R_f^{iv}C_6H_4OP(O)(OC_6H_5)_2$	XV	209.2	0.140	316	207.9	91	None
$(R_f'''C_6H_4O)_2P(O)OC_6H_5$	XIII	199.2	0.120	300	197.9	90	None
$(R_f'''C_6H_4O)_2P(O)OC_6H_5$	XIII	204.0	0.123	316	198.2	88	0.7
$(R_f'''C_6H_4O)_2P(O)OC_6H_5$	XIII	212.0	0.128	343	204.7	30	0.6

[a] All of the pyrolyses were performed in evacuated ampules over 24 h.
[b] $R_f^{iv} = C_3F_7[OCF(CF_3)CF_2]_6$, $R_f''' = C_3F_7[OCF(CF_3)CF_2]_3$.
[c] This material was involatile at room temperature.
[d] The percent of starting material recovered is given with respect to the quantity of starting material used.
[e] Room temperature volatiles condensable at −196°C.

phosphates and phosphonates, compounds XVI–XIX, were soluble in perfluoropolyalkylether fluids at room temperature. The lowest cloud point (~75°C) was exhibited, as expected, by $(n\text{-}C_8F_{17}C_6H_4O)_2P(O)OC_6H_5$. On the other hand, these materials exhibited low volatility and were fully effective in arresting the thermal oxidative degradation of perfluoropolyalkylether fluids in the presence of metals [7]. Thus, in particular compound XIX alone or in combination with its diester, offer additives for use in perfluoropolyalkylether derived greases. Mixtures of $(n\text{-}C_8F_{17}C_6H_4O)_2P(O)OC_6H_5$ and $n\text{-}C_8F_{17}C_6H_4OP(O)(OC_6H_5)OH$ were found to be soluble in poly(chlorotrifluoroethylene) fluids and to function as rust-preventing agents [8].

Phosphates: $C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$ (XV) and $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$ (XIII) were essentially stable at 316°C as shown by the data given in Table 2. Based on the volatiles formed and starting materials recovery it would appear that XV is somewhat more stable than XIII. It is of interest that both these materials were fully effective in arresting thermal oxidative degradation of perfluoropolyalkylether fluids at 330°C over a 24-h period [7,9–11].

3. Experimental details

3.1. General

Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93BO) under nitrogen bypass or using vacuum line techniques.

All melting points are uncorrected and were determined in evacuated sealed capillaries. Infrared spectra were recorded neat (on liquids) and as double mulls (Kel-F oil No. 10 and Nujol) on solids using a Perkin-Elmer infrared spectrophotometer Model 1330. The mass spectrometric (MS) analyses were obtained employing a Du Pont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 2700 gas chromatograph, equipped with a flame ionization detector and a Du Pont 21-094 data acquisition and processing system. The majority of product mixture identifications were performed using combined gas chromatography/mass spectrometry (GC/MS). Gas chromatography (GC) was conducted employing a 10 ft × 1/8 in. stainless steel column packed with 4% OV-101 on 80/100 mesh Chromosorb G or a 3 ft × 1/8 in. stainless steel column packed with 3% Dexsil 300 on 100/120 mesh Chromosorb WAW, using a programming rate of 8°C/min from 50–300°C. Molecular weights were determined in hexafluorobenzene using a Mechrolab Model 302 vapor pressure osmometer. Thermal gravimetric analyses (TGA) were carried out in nitrogen at 10°C/min.

3.2. Fluids

Poly(hexafluoropropene oxide) fluid, $F(CF(CF_3)CF_2O)_nC_2F_5$, Krytox 143AC product of Du Pont was obtained from US Air Force; Demnum S-100—$[CF_2CF_2CF_2O]_n$—was received from Daikin and Fomblin Z25—$(CF_2O)_x(CF_2CF_2O)_y$—was received from Ausimont USA.

3.3. Typical preparation of p-$R_fC_6H_4OH$, preparation of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$

Under nitrogen bypass, to diethyl ether (200 ml) and *n*-butyllithium (36 ml, 2.5 M in hexanes, 90.0 mmol) at −15°C was added $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4Br$ (57.5 g, 69.9 mmol) admixed with diethyl ether (15 ml), over a period of 1.25 h. After stirring for an additional 1 h at −15°C, the cold solution was added over a 1-h period to a solution of trimethyl borate (32.8 g, 316 mmol; distilled over sodium) in diethyl ether (200 ml) at −15°C. After 2 h stirring, acetic acid (20 g, 0.3 mol) was introduced, and the solution was stirred for an additional 0.75 h. Hydrogen peroxide (30%, 47 ml in H_2O 47 ml) was then added at −15°C and, after warming to room temperature, the reaction mixture was stirred overnight. Following addition of water (250 ml), the organic layer was washed with ferrous sulfate solution (30 g $FeSO_4 \cdot 7H_2O$, 12 ml concentrated hydrochloric acid, 30 ml H_2O), water, and dried over anhydrous $MgSO_4$.

After solvent removal, the crude product (51.7 g, 97.4% yield) was purified by silica gel column chromatography (150 g, 3.0 cm × 44 cm, packed in 5% ether/hexanes). Elution using ether/hexanes 5% (535 ml), 10% (150 ml), 20% (50 ml) and 50% (400 ml) resulted in 4.4 g mainly of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_5$ and 44.9 g (84.6% yield: GC purity 95%) of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$. The latter portion was distilled to give 40.6 g (76.4% yield: GC purity >99%) of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$, b.p. 75–77°C/0.001 mm Hg.

3.4. p-$R_fC_6H_4OH$ characterization data

$C_2F_5C_6H_4OH$. Yield, 72%; m.p. 97–98°C. IR (Kel-F/Nujol mull, cm^{1}): 3350 (vbr, s); 1615 (m); 1602 (m); 1519 (m); 1455 (m); 1410 (m); 1370 (m); 1345 (s); 1290 (s); 1255 (br, s); 1200 (br, vs); 1180 (s); 1140 (m); 1103 (s); 1095 (s); 1020 (w); 970 (s); 940 (m); 830 (s); 750 (m); 730 (w); 700 (vw); 650 (m); 600 (m). $C_2F_5C_6H_4OSi(CH_3)_3$ MS (70 eV) *m/e* (relative intensity, ion): 284 (68.6%, M); 269 (base, M–CH_3); 265 (12.4%, M–F); 215 (18.8%, M–CF_3); 145 (14.3%, $CF_3C_6H_4$); 77 (27.7%, C_6H_5); 73 (30.7%, $Si(CH_3)_3$).

$C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$. Yield, 75%; b.p. 63–65°C/0.001 mm Hg. IR (capillary film, cm^{-1}): 3620 (w); 3320 (vbr, m); 1620 (m); 1605 (m); 1519 (m); 1445 (m); 1335 (s); 1296 (s); 1235 (br, s); 1200 (s); 1180 (s); 1150 (br, s); 1135 (m); 1070 (w); 1030 (m); 1015 (w); 991 (m); 982 (m); 950 (w); 925 (m); 885 (m); 835 (m); 811 (m); 751 (m); 745 (m); 710 (w). MS (70 eV) *m/e* (relative intensity, ion): 594 (7.7%, M); 574 (3.3%, M–HF); 243 (15.2%, $C_3F_6C_6H_4OH$; 193 (13.0%, $C_2F_4C_6H_4OH$); 169 (17.6%, C_3F_7); 143 (base, $CF_2C_6H_4OH$).

$C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$. Yield, 76%; b.p. 75–77°C/0.001 mm Hg. IR (capillary film, cm^{-1}): 3619 (w); 3350 (vbr, m); 1616 (m); 1604 (m); 1519 (m), 1442 (w); 1332 (s); 1305 (s); 1290 (s); 1235 (br, vs); 1200 (s); 1176 (s); 1145 (br, s); 1105 (s); 1064 (w); 1030 (w); 991 (s); 980 (s); 947 (vw); 922 (m); 886 (m); 837 (m); 810 (m); 745 (m); 710 (w). MS (70 eV) *m/e* (relative intensity, ion): 760 (25.4%, M); 741 (13.1%, M–F); 409 (12.9%, M–$C_3F_7OCF(CF_3)CF_2O$); 243 (30.2%, $CF(CF_3)CF_2C_6H_4OH$); 193 (22.6%, $C_2F_4C_6H_4OH$); 143 (base, $CF_2C_6H_4OH$).

$C_3F_7[OCF(CF_3CF_2]_4C_6H_4OH$. Yield, 48%; b.p. 86–88°C/0.001 mm Hg. IR (capillary film, cm^{-1}): 3620 (w); 3350 (vbr, m); 1618 (m); 1604 (m); 1519 (m); 1444 (w); 1330 (s); 1305 (s); 1287 (s); 1235 (br, vs); 1200 (s); 1176 (s); 1140 (br, s); 1065 (w); 1032 (w); 993 (s); 981 (s); 949 (vw); 922 (m); 888 (m); 838 (m); 810 (m); 744 (m);

710 (w). MS (70 eV) *m/e* (relative intensity, ion): 926 (17.7%, M); 907 (13.2%, M–F); 906 (7.0%, M–HF); 335 (13%, $C_3F_7OCF(CF_3)CF_2$); 243 (27.7%, $C_3F_6C_6H_4OH$); 193 (18.8%, $C_2F_4C_6H_4OH$); 169 (62.2%, C_3F_7); 143 (base, $CF_2C_6H_4OH$).

$C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OH$. Yield, 62%; b.p. 118–120°C/0.001 mm Hg. IR (capillary film. cm^{-1}): 3615 (w); 3350 (Vbr, m); 1617 (m); 1604 (m); 1520 (m); 1446 (w); 1334 (s), 1309 (s); 1292 (s); 1235 (br, vs); 1200 (s), 1180 (s); 1145 (br, s); 1069 (w); 1034 (w); 985 (s); 950 (vw); 925 (m); 889 (m); 839 (m); 810 (m); 746 (m); 711 (w). MS (70 eV) *m/e* (relative intensity, ion): 953 (9.4%, M–$C_3F_7OCF(CF_3)$–HF); 807 (3.1%, $CF_2(OCF(CF_3)CF_2)_4C_6H_4OH$); 641 (4.9%, $CF_2(OCF(CF_3)CF_2)_3C_6H_4OH$); 409 (6.6%, $CF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OH$); 335 (26.4%, $C_3F_7OCF(CF_3)CF_2$); 243 (22.9%, $C_3F_6C_6H_4OH$); 143 (87.8%, $CF_2C_6H_4OH$); 69 (base, CF_3).

n-$C_8F_{17}C_6H_4OH$. Yield, 95%; m.p. 74–75°C. IR (Kel-F/Nujol mull, cm^{-1}): 3350 (vbr, s); 1613 (m); 1601 (m); 1517 (m); 1450 (m); 1369 (m); 1330 (w); 1299 (m); 1200 (br, s); 1148 (s); 1134 (m); 1117 (m); 1102 (m); 1090 (m); 1049 (vw); 1028 (vw); 1013 (vw); 954 (w); 935 (w); 868 (vw); 838 (m); 800 (w); 730 (w); 700 (vw). MS (70 eV) *m/e* (relative intensity, ion): 512 (20.2%, M); 493 (17.2%, M–F); 492 (29.6%, M–HF); 173 (81.5%, $C_2F_3C_6H_4O$); 143 (base, $CF_2C_6H_4OH$).

3.5. Typical preparation of phosphates and phosphonates, preparation of $[p\text{-}C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$ (XVI)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$ (40.09 g, 52.73 mmol) and $C_6H_5OP(O)Cl_2$ (5.70 g, 27.02 mmol) in Freon-113 (140 ml) and benzene (25 ml) was added triethylamine (10.7 g, 0.105 mol) in benzene (35 ml) over a period of 1.5 h. Stirring at room temperature was continued for an additional 0.5 h, then the reaction mixture was heated at 65°C under nitrogen bypass for 44 h. After cooling, the precipitated triethylamine hydrochloride (7.4 g) was filtered off and rinsed with Freon-113. The product (44.0 g), obtained after solvent removal in vacuo, was purified by a silica gel chromatography (200 g, 53 cm × 3 cm, packed in 10% diethyl ether/hexanes). Elution was carried out with 10% (360 ml), 20% (200 ml), 25% (100 ml), and 30% (600 ml) of diethyl ether/hexanes. No phosphate was present in the first 660 ml, the next 600 ml gave clear, colorless liquid (37.7 g), which was further purified by subliming out the remaining impurities at 85–90°C. This resulted in 35.8 g (82% yield) of $\{C_3F_7[OCF(CF_3)$-$CF_2]_3C_6H_4O\}_2P(O)OC_6H_5$ (GC purity >99%).

3.6. $(p\text{-}R_fC_6H_4O)_{3-x}P(O)(OC_6H_5)_x$ and $(p\text{-}R_fC_6H_4O)_{3-x}P(O)(C_6H_5)_x$ IR and MS data

$C_2F_5C_6H_4OP(O)(OC_6H_5)_2$ (I). IR (capillary film, cm^{-1}): 3075 (br, w); 1610 (m); 1591 (m); 1513 (m); 1490 (s); 1460 (vw); 1420 (vw); 1344 (w); 1317 (m); 1290 (s); 1200 (br, vs); 1097 (s); 1071 (w); 1027 (m); 1011 (m); 960 (br, vs); 904 (w); 844 (m); 788 (m); 765 (m); 754 (m); 719 (vw); 689 (m); 645 (w). MS (relative intensity, ion) *m/e* (70 eV): 444 (74.8%, M); 443 (56.2%, M–H); 375 (8.8%, M–CF_3); 351 (6.2%, M–OC_6H_5); 233 (9.4%; M–$OC_6H_4C_2F_5$); 219 (23.2%, $C_2F_3C_6H_3OPO$); 205 (15%, $CF_2C_6H_4OPO_2$); 77 (base, C_6H_5).

$C_2F_5C_6H_4OP(O)(C_6H_5)_2$ (II). IR (Kel-F/Nujol mull, cm^{-1}): 3052 (m); 1611 (m); 1595 (w); 1514 (m); 1489 (vw); 1442 (m); 1420 (vw); 1394 (vw); 1345 (m); 1345 (m); 1317 (vw); 1291 (m); 1233 (s); 1219 (s); 1196 (s); 1180 (m); 1151 (m); 1137 (m); 1105 (s); 1074 (w); 1027 (w); 1000 (vw); 976 (m); 955 (w); 914 (s); 857 (m); 849 (m); 779 (m); 757 (m); 741 (m); 730 (m); 695 (m); 644 (m). MS (relative intensity, ion) *m/e* (70 eV): 412 (63.4%, M); 411 (67.1%, M–H); 393 (5.3%, M–F); 201 (base, M–$OC_6H_4C_2F_5$); 173 ($C_2F_3C_6H_4O$); 171 (13.7%, $C_2F_3C_6H_2O$).

$(C_2F_5C_6H_4)_2POC_6H_5$ (III). IR (capillary film, cm^{-1}): 3075 (br, w); 1610 (s); 1593 (m); 1510 (s); 1490 (s); 1458 (vw); 1420 (w); 1340 (m); 1320 (s); 1289 (s); 1205 (br, vs); 1171 (s); 1149 (s); 1097 (s); 1022 (m); 1009 (m); 960 (br, vs); 840 (s); 789 (m); 764 (m); 746 (m); 720 (w); 687 (m); 644 (m). MS (relative intensity, ion) *m/e* (70 eV): 562 (98.3%, M); 543 (10.9%, M–F); 493 (31.5%, M–CF_3); 351 (14.0%; M–$C_2F_5C_6H_4O$); 212 (25.0%, $C_2F_5C_6H_4OH$); 143 (26.8%, $CF_2C_6H_4OH$); 77 (base, C_6H_5).

$(C_2F_5C_6H_4O)_3PO$ (IV). IR (Kel-F/Nujol mull. cm^{-1}): 3120 (vw); 3080 (vw); 1610 (m); 1509 (s); 1420 (w); 1348 (m); 1315 (s); 1304 (s); 1289 (s); 1248 (w); 1207 (br, vs); 1172 (s); 1148 (m); 1097 (s); 1020 (w); 987 (m); 969 (s); 960 (s); 948 (s); 925 (m); 840 (s), 828 (w); 790 (w); 768 (vw); 749 (m); 728 (vw); 717 (vw); 650 (m). MS (relative intensity, ion) *m/e* (70 eV): 611 (77.9%, M–CF_3); 469 (16.4%, M–$OC_6H_4C_2F_5$); 450 (18.5%, M–$OC_6H_4C_2F_5$–F); 399 (20.0%, M-$OC_6H_4C_2F_5$-CF_3-H); 271 (74.2, $C_2F_4C_6H_4OPO_3$); 205 (39.1%, $CF_2C_6H_4OPO_2$); 189 (51.5%, $CF_2C_6H_4OPO$); 145 (base, $CF_3C_6H_4$).

$C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(OC_6H_5)_2$ (V). IR (capillary film, cm^{-1}): 3075 (br, w); 1610 (m); 1592 (m); 1512 (m); 1491 (m); 1459 (vw); 1420 (vw); 1331 (m); 1300 (s); 1287 (s); 1238 (br, s); 1200 (s); 1162 (s); 1130 (m); 1115 (m); 1069 (w); 1027 (m); 1010 (m); 992 (m); 968 (br, s); 925 (m); 890 (m); 840 (m); 810 (vw); 780 (m); 751 (m); 705 (vw); 689 (m). MS (relative intensity, ion) *m/e* (70 eV): 826 (65.4%, M); 825 (32.8%, M–H); 807 (11.6%, M–F); 475 (10.0%, M–$C_3F_7OCF(CF_3)CF_2O$); 375 (base, M–$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$); 233 (17.8%, $OP(OC_6H_5)_2$).

$C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(C_6H_5)_2$ (VI). IR (Kel-F/Nujol mull cm^{-1}): 3060 (w); 1610 (m); 1595 (w); 1514 (m); 1488 (vw); 1441 (m); 1420 (vw); 1335 (m); 1309 (m); 1288 (s); 1236 (vs); 1221 (vs); 1210 (s); 1180 (s); 1160 (br, s); 1135 (s); 1117 (s); 1102 (m); 1067 (w);

1036 (vw); 1020 (vw); 995 (m); 983 (m); 959 (vw); 917 (s); 893 (w); 858 (m); 840 (w); 807 (vw); 750 (m); 731 (m); 710 (w); 695. MS (relative intensity, ion) *m/e* (70 eV): 794 (22.6%, M); 793 (21.1%, M–H); 343 (11.0%, $CF_2C_6H_4OPO(C_6H_5)_2$); 201 (base, $OP(C_6H_5)_2$); 169 (17.1, C_3F_7); 143 (13.5%, $CF_2C_6H_4OH$).

$[C_3F_7(OCF(CF_3)CF_2)_2C_6H_4O]_2P(O)OC_6H_5$ (VII). IR (capillary film, cm^{-1}): 3080 (br, vw); 1610 (m); 1594 (m); 1510 (m); 1491 (m); 1420 (w); 1332 (s); 1304 (s); 1285 (s); 1235 (br, vs); 1200 (s); 1160 (br, s); 1130 (s); 1110 (s); 1068 (w); 1034 (w); 1009 (w); 992 (s); 975 (br, s); 924 (m); 890 (m); 840 (m); 810 (vw); 783 (w); 760 (w); 750 (m); 742 (m); 705 (w); 687 (w): 672 (vw). MS (relative intensity, ion) *m/e* (70 eV): 1326 (30.7, M); 1207 (16.5%, M–C_2F_5); 1041 (15.8%, M–$C_3F_7OCFCF_3$); 975 (17.0%, M–$C_3F_7OCF(CF_3)CF_2O$); 875 (74.9%. M–$C_3F_7OCF(CF_3)CF_2OCFCF_3$); 212 (46.3%, $CF_3CF_2C_6H_4OH$); 205 (15.5%, $CF_2C_6H_4OPO_2$): 189 (12.2%. $CF_2C_6H_4OPO$); 69 (base, CF_3).

$[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ (VIII). IR (capillary film, cm^{-1}): 3070 (vw); 1610 (m); 1598 (w); 1510 (m); 1444 (w); 1420 (w); 1334 (s); 1286 (s); 1235 (br, vs); 1205 (s); 1171 (s); 1150 (s); 1130 (s); 1116 (s); 1105 (s); 1068 (w); 1034 (w); 1017 (w); 994 (s); 981 (s); 922 (br, s): 890 (m): 840 (m): 810 (w): 775 (w): 762 (vw); 745 (m); 729 (vw); 705 (w); 692 (w). MS (relative intensity, ion) *m/e* (70 eV): 1310 (35.6%, M): 1191 (17.6%, M–C_2F_5); 1025 (M–$C_3F_7OCFCF_3$): 959 (18.0%, M–$C_3F_7OCF(CF_3)CF_2O$); 859 (82.4%. M–$C_3F_7OCF(CF_3)CF_2OCFCF_3$); 335 (13.6%, $C_3F_7OCF(CF_3)CF_2$); 285 (27.0%, $C_3F_7OCFCF_3$): 204 (56.5%, $CF_2C_6H_3OPO_2$); 69 (base, CF_3).

$C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(C_6H_5)_2$ (IX). IR (Capillary film, cm^{-1}): 3058 (w); 1610 (m); 1592 (w); 1510 (m); 1484 (vw): 1440 (m); 1418 (vw): 1330 (s): 1304 (s); 1286 (s); 1235 (br, vs); 1200 (s) 1173 (s); 1141 (s); 1130 (s); 1110 (s); 1065 (w); 1031 (w); 1014 (w): 991 (s); 980 (s); 950 (vw); 910 (br, s); 889 (m); 840 (m): 807 (w); 740 (m); 729 (m); 692 (m). MS (relative intensity, ion) *m/e* (70 eV): 1126 (66.5%, M): 1125 (52.4%, M–H); 1107 (17.5%, M–F); 1057 (7.9%. M–CF_3); 343 (14.0%, M–$C_3F_7[OCF(CF_3)CF_2]_3OCFCF_3$); 201 (base, $PO(C_6H_5)_2$); 169 (24.9, C_3F_7); 69 (42.2%. CF_3).

$[C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O]_2P(O)C_6H_5$ (X). IR (capillary film, cm^{-1}: 3060 (br, vw); 1609 (m); 1595 (w); 1510 (m); 1441 (vw); 1419 (vw); 1330 (s); 1305 (s); 1285 (s); 1235 (br, vs); 1200 (s); 1170 (s): 1142 (br, s); 1065 (w); 1032 (w); 1015 (w); 991 (s); 981 (s); 920 (br, m); 889 (w); 840 (m); 806 (w); 743 (m); 690 (w). MS (relative intensity, ion) *m/e* (70 eV): 1191 (57.7%. M–$C_3F_7[OCF(CF_3)CF_2]_3OCFCF_3$); 1049 (2.6%, M–$C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O$); 926 (4.6%, $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$); 285 (24.5%, $C_3F_7OCFCF_3$): 204 (18.8%. $CF_2C_6H_3OPO_2$); 169 (53.8%, C_3F_7); 69 (base, CF_3).

$C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(OC_6H_5)_2$ (XI). IR (capillary film, cm – 1): 3071 (br, w): 1610 (m); 1591 (m): 1512 (m): 1490 (s); 1458 (vw); 1420 (vw); 1300 (br, s); 1240 (br, vs); 1200 (br, vs); 1150 (br, s); 1069 (w); 1028 (m); 1010 (m); 975 (br, s); 925 (m); 890 (m); 841 (m); 809 (w), 783 (m), 752 (m); 712 (vw); 689 (m). MS (relative intensity, ion) *m/e* (70 eV): 1158 (71.7%, M); 1139 (12.8%, M–F); 1039 (18.3%, M–C_2F_5); 873 (15.8%, M–$C_3F_7OCFCF_3$); 375 (base, $CF_2C_6H_4OP(O)(OC_6H_5)_2$); 233 (16.1%, $P(O)(OC_6H_5)_2$); 188 (43.0%, $CF_2C_6H_3OPO$).

$[C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O]_2P(O)OC_6H_5$ (XII). IR (capillary film, cm^{-1}): 3070 (br, vw); 1606 (m); 1591 (m); 1508 (m); 1489 (m); 1418 (w); 1300 (s); 1284 (s); 1235 (br, vs); 1200 (s); 1170 (s); 1144 (br, s); 1065 (w); 1031 (w); 980 (br, s); 921 (m); 888 (m); 839 (m); 806 (w): 781 (w): 742 (m); 710 (vw); 686 (w). MS (relative intensity, ion) *m/e* (70 eV); 1207 (99.5%, M–$C_3F_7[OCF(CF_3)CF_2]_3OCFCF_3$); 1065 (3.0%, M-$C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O$); 335 (11.1%, $C_3F_7OCF(CF_3)CF_2$); 301 (17.0%. $CF_3C_6H_4OP(O)OC_6H_5$); 212 (24.5%. $C_2F_5C_6H_4OH$); 145 (32.2%, $CF_3C_6H_4$): 143 (30.4%. $CF_2C_6H_4OH$); 69 (base, CF_3).

$[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$ (XIII). IR (capillary film, cm^{-1}): 3080 (br, w); 1606 (m); 1590 (m); 1508 (m); 1489 (m); 1456 (vw) 1417 (w): 1330 (s); 1305 (s); 1284 (s); 1235 (br, vs): 1200 (br, vs); 1170 (br, vs); 1144 (br, vs); 1104 (s), 1067 (w), 1031 (w). 978 (br, s), 923 (m), 890 (m), 840 (m), 809 (w). 784 (w), 745 (m), 710 (w), 689 (w), 644 (w). MS (relative intensity, ion) *m/e* (70 eV): 1041 (62.8%, M–$C_3F_7[OCF(CF_3)CF_2]_2OCFCF_3$); 918 (51.1%, $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OPF(O)OC_6H_5$); 899 (18.7%. $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OP(O)OC_6H_5$); 740 (77.1%, $[C_3F_6[OCF(CF_3)CF_2]_3C_6H_4O$); 621 (22.3%. $CF_2OCFCF_2CF_2[OCF(CF_3)CF_2]_2C_6H_4O$); 301 (74.4%. $CF_3C_6H_4OP(O)OC_6H_5$); 223 (82.3%, $CF_3CF{=}CFC_6H_4O$); 69 (base, CF_3).

$[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)C_6H_5$ (XIV). Ir (capillary film, cm^{-1}): 3070 (br, w); 1606 (m); 1593 (m); 1508 (s); 1440 (w); 1415 (w); 1330 (s); 1305 (s); 1280 (s); 1235 (br, vs); 1200 (s); 1168 (s); 1141 (s); 1127 (s); 1100 (s): 1064 (w); 1030 (m): 1014 (w); 990 (s): 980 (s); 920 (br, s); 889 (m); 840 (m); 807 (w); 744 (m); 726 (vw); 710 (w); 691 (w): 642 (w). MS (relative intensity, ion) *m/e* (70 eV): 1025 (61.6%, M–$C_3F_7[OCF(CF_3)CF_2]_2OCFCF_3$);902 (19.8%, $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OPF(O)C_6H_5$); 883 (10.0%, $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OP(O)C_6H_5$); 740 (13.4%, $C_3F_6[OCF(CF_3)CF_2]_3C_6H_4O$); 355 (27.9%, $C_2F_4C_6H_4PF(O)C_6H_5$): 285 (89.2%, $CF_3C_6H_4OP(O)C_6H_5$); 143 (71.6%. $CF_2C_6H_4OH$); 69 (base, CF_3).

$C_3F_7[OCF(CF_3)CF_2]_6C_6H_4OP(O)(OC_6H_5)_2$ (XV). IR (capillary film, cm^{-1}): 3070 (br, w); 1608 (m); 1590 (m): 1510 (m); 1490 (m); 1455 (vw); 1417 (vw); 1305 (br, s); 1240 (br, vs); 1200 (br, s); 1140 (br, s); 1069 (w); 1028 (m); 981 (br, s); 925 (m); 891 (w); 842 (w); 809 (w): 750 (m); 715 (vw); 690 (m). MS (relative intensity, ion) *m/e* (70 eV): 1039 (10.8%, $CF_2[OCF(CF_3)CF_2]_4C_6H_4$-

$OP(O)\ (OC_6H_5)_2$); 1038 (28.4%, $CF_2[OCF(CF_3)CF_2]_4$-$C_6H_3OP(O)\ (OC_6H_5)_2$); 873 (22.8%, $CF_2[OCF(CF_3)$-$CF_2]_3C_6H_4OP(O)\ (OC_6H_5)_2$); 707 (18.0%, $CF_2[OCF$-$((CF_3)CF_2]_3C_6H_4OP(O)\ (OC_6H_5)_2$); 541 (10.1%, $CF_2OCF(CF_3)CF_2C_6H_4OP(O)\ (OC_6H_5)_2$); 475 (14.5%, $CF(CF_3)CF_2C_6H_4OP(O)\ (OC_6H_5)_2$); 375 (91.0%, $CF_2C_6H_4OP(O)\ (OC_6H_5)_2$); 233 (15.8%, $PO(OC_6H_5)_2$); 69 (base, CF_3).

n-$C_8F_{17}C_6H_4OP(O)\ (C_6H_5)_2$ (XVI). IR (Kel-F/Nujol mull, cm^{-1}): 3052 (w); 1610 (m); 1590 (w); 1511 (m); 1440 (m); 1420 (vw); 1370 (w); 1325 (w); 1312 (vw); 1298 (m); 1230 (s); 1198 (s); 1177 (m); 1150 (s); 1113 (m); 1102 (m); 1090 (w); 1048 (w); 1027 (w); 1017 (vw); 997 (vw); 968 (w); 956 (w); 939 (w); 917 (s); 848 (m); 831 (vw); 815 (w); 800 (vw); 751 (m); 730 (m); 700 (m); 655 (w); 629 (w). MS (relative intensity, ion) *m/e* (70 eV): 712 (32.8%, M); 693 (5.9%, M–F); 219 (14.4%, C_4F_9); 201 (base, $P(O)\ (C_6H_5)_2$); 145 (10.2%, $CF_3C_6F_4$); 143 (13.7%, $CF_2C_6H_4OH$).

(*n*-$C_8F_{17}C_6H_4O)_2P(O)C_6H_5$ (XVII). IR (Kel-F/Nujol mull, cm^{-1}): 3060 (w); 1608 (m); 1594 (m); 1510 (m); 1486 (w); 1441 (w); 1416 (w); 1370 (w); 1329 (vw); 1297 (m); 1260 (s); 1223 (s); 1200 (s); 1171 (m); 1150 (s); 1133 (m); 1115 (w); 1102 (w); 1090 (w); 1049 (w); 1028 (w); 1017 (vw); 958 (w); 937 (m); 919 (m); 861 (w); 850 (vw); 834 (vw); 815 (vw); 764 (vw); 750 (w); 728 (vw); 712 (vw); 691 (w); 650 (m). MS (relative intensity, ion) *m/e* (70 eV): 1146 (92.2%, M); 1145 (65.2%, M–H); 1127 (26.3%, M–F); 777 (79.3%, M–C_7F_{15}); 635 (62.3%, $C_8F_{17}C_6H_4OP(O)C_6H_5$); 285 (29.0%, $CF_3C_6H_4OP(O)C_6H_5$); 204 (base, $CF_2C_6H_3OPO_2$); 145 (40.4%, $CF_3C_6H_4$).

n-$C_8F_{17}C_6H_4OP(O)\ (OC_6H_5)_2$ (XVIII). IR (Kel-F/Nujol mull, cm^{-1}): 3060 (w); 1611 (w); 1589 (m); 1511 (m); 1485 (s); 1458 (vw); 1420 (vw); 1370 (w); 1317 (w); 1288 (s); 1240 (br, s); 1195 (br, s); 1179 (s); 1144 (s); 1115 (m); 1106 (m); 1092 (m); 1071 (w); 1050 (w); 1021 (w); 1010 (s); 968 (br, s); 940 (m); 918 (vw); 906 (w); 841 (m); 818 (m); 780 (m); 770 (m); 756 (w); 720 (m); 690 (m); 675 (w); 657 (m). MS (relative intensity, ion) *m/e* (70 eV): 744 (base, M); 725 (81.4%, M–C_7F_{15}); 219 (21.1%, C_4F_9); 205 (19.9%, $CF_2C_6H_4OPO_2$); 143 (23.9%, $CF_2C_6H_4OH$).

(*n*-$C_8F_{17}C_6H_4O)_2P(O)OC_6H_5$ (XIX). IR (Kel-F/Nujol mull, cm^{-1}): 3080 (w); 1605 (m); 1585 (m); 1507 (m); 1484 (m); 1407 (w); 1367 (m); 1315 (m); 1305 (m); 1281 (w); 1200 (br, s); 1170 (s); 1145 (s); 1115 (m); 1100 (m); 1090 (w); 1050 (w); 1025 (m); 1014 (m); 938 (m); 965 (m); 950 (w); 938 (m); 850 (m); 782 (m); 758 (m); 713 (w); 705 (m). MS (relative intensity, ion) *m/e* (70 eV): 993 (3.3%, M–C_3F_7); 793 (base, M–C_7F_{15}); 670 (10.0%, $C_8F_{17}C_6H_4OP(O)\ FOC_6H_5$); 301 (27.0%, $CF_3C_6H_4OP(O)OC_6H_5$); 219 (21.6%, C_4F_9); 212 (74%, $C_2F_5C_6H_4OH$); 205 (26.3%, $CF_2C_6H_4OPO_2$); 189 (29.0%, $CF_2C_6H_4OPO$).

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