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Synthesis of new aromatic perfluorovinyl ether monomers containing phosphonic acid functionality

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Abstract

The synthesis of a new perfluorovinyl ether monomer containing phosphonic acid functionality is reported. It started from 4-[(α,β,β -trifluorovinyl)oxy]bromo benzene prepared in two steps from the nucleophilic substitution of 4-bromophenate to 1,2-dibromotetrafluoroethane. The [(α,β,β -trifluorovinyl)oxy]benzene dialkyl phosphonate was prepared according to various methods of phosphonation like a Michaelis–Arbuzov or a Michaelis–Becker or a palladium catalysed arylation in the presence of various reactants. The influence of the nature of the method and of the reactants onto the yields is discussed. It was shown that reaction involving a palladium triphenyl phosphine catalyst led to the best yield. All different aromatic intermediates and fluoromonomers were characterised by ¹H, ³¹P and ¹⁹F NMR, mass spectrometry (EI), and by FTIR.

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1. Introduction

In the past few decades, the synthesis and (co)polymerisation of functionalised [$(\alpha, \beta, \beta$ -trifluorovinyl)oxy]benzene have drawn a growing interest [1] especially for polymers incorporating such a monomer because of the combination of processability and performance (chemical and thermal stability) provided by trifluorovinyl ethers.

The most important properties of aromatic trifluorovinyl ethers arise from the fact that they could undergo thermal cyclopolymerisation $[2\pi + 2\pi]$ giving a thermoplastic and thermoset polymers containing perfluorocyclobutane rings (PFCB) (Scheme 1) [2]. This thermodynamically favoured $[2\pi + 2\pi]$ thermocyclodimerisation arises from an increase of the double bond strain [3], a lower C=C π -bond energy [4], and the strength of the resulting fluorinated C–C single bond. Such thermocyclodimerisation is usually observed at temperatures ranging from 140 to 210 °C [5].

Although prepared for the first time by Beckerbauer [2a], aromatic trifluorovinyl have received much attention by various research groups from 1990s [2,6]. Babb et al. [2b,2c,7] developed methods for the preparation and the characterisation of trifluorovinyl ethers synthesised from the readily bis- and tris-phenols, such as tris(hydroxyphenyl)ethane (Scheme 1). A high T_g thermoset polymers endowed with a good thermal stability (they are stable up to 434 °C), thermal/oxidative stability and mechanical properties, was prepared with such monomer [2d,8].

In 1996, Smith and Babb [2f] synthesised perfluorocyclobutane aromatic polyethers incorporating siloxane groups such as bis[1,3-[4-[(trifluorovinyl)oxy]phenyl]]-1,1,3,3-tetramethyldisiloxane (employed commercially as high-temperature lubricants, elastomers, and adhesives with excellent chemical, thermal, and oxidative resistance).

In 2000, a series of different perfluorocyclobutane (PFCB) polyarylethers was synthesised by the same group [8]. Authors reported the synthesis of poly(aryl vinyl ether) based on a two steps synthetic route (Scheme 1) [9]: the first one concerned a fluoroalkylation with $BrCF_2CF_2Br$ while the second one dealt with a zinc mediated elimination.

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Scheme 1. Formation of aromatic perfluorocyclobutane polymers (PFCB) [2,7,9].

Materials prepared from aromatic trifluorovinyl ethers can find relevant applications in ion exchange resins [6e], fuel cell membranes [6e,10a,10b], microphonics [11], optics [12], liquid crystals [13], interlayer dielectrics [14], and coating applications [8,15].

In the course of the last decades, fluoropolymers incorporating aromatic or aliphatic monomers and bearing sulphonic [6e,16] and phosphonic [17] acid functionalities have led to a growing interest due to their potential applications in proton exchange membranes for fuel cells (PEMFC) and ionomer membranes [6e,16].

The current intensified interests in the preparation of PEMFC based on electrolyte polymers has prompted us to develop the syntheses of aromatic monomers such as trifluorovinyl ethers functionalised by acid groups. In particular, we report the preparation of 4-[$(\alpha,\beta,\beta$ -trifluoroviny-I)oxy]benzene phosphonic acid which, to the best of our knowledge, has never been described in the literature. This present paper focuses on the synthesis of fluorinated mono-

mer using different methodologies and the characterisation of all intermediates (by ¹⁹F, ¹H, ³¹P NMR and FTIR spectroscopies, and Mass spectrometry (EI)).

2. Results and discussion

4-[(α,β,β -trifluorovinyl)oxy]bromo benzene, Monomer 1, was prepared by published method [2f]. The synthesis of Monomer 1 is based on a nucleophilic substitution of 4-bromophenate to 1,2-dibromotetrafluoroethane followed by a dehalogenation reaction.

2.1. Synthesis and characterisation of 4-[(α,β,β -trifluorovinyl)oxy]benzene phosphonic acid (Monomer **3**)

The various chemical pathways to prepare 4-[(α,β,β -trifluorovinyl)oxy]benzene (diethyl or dimethyl)phosphonate (Monomer **2**, Scheme 2) consecutively dealkylated into



Scheme 2. Synthesis of $4-[(\alpha,\beta,\beta-trifluoroviny])$ oxy]benzene (diethyl or dimethyl)phosphonate (Monomer 2).

4-[$(\alpha,\beta,\beta$ -trifluorovinyl)oxy]benzene phosphonic acid (Monomer **3**, Scheme 4) made this study attractive. The synthesis of 4-[$(\alpha,\beta,\beta$ -trifluorovinyl)oxy]benzene (dialkyl) phosphonate was carried out according to methods of Michaelis–Arbuzov reaction (synthetic route I, Scheme 2) or Michaelis–Becker (synthetic route II, Scheme 2) or a palladium catalysed arylation of diethyl phosphite (synthetic route III, Scheme 2) or by a reaction between a chlorophosphate and aryl lithium of Monomer **1** (synthetic route IV, Scheme 2). These methods are detailed below.

2.1.1. Synthesis of Monomer 2 via a Michaelis–Arbuzov reaction

Michaelis-Arbuzov reactions (synthetic route L Scheme 2) [18] were carried out by dropwise addition of Monomer 1 [2f] to trimethyl (R: Me, Scheme 2) or triethyl (R: Et, Scheme 2) phosphite at 110 °C. These experiments led to several statements. (i) A first series of experiments (#1 and #2, Table 1) has shown that the Michaelis-Arbuzov reaction required to be performed in the presence of Lewis acid such as NiCl₂ (12 mol%) under nitrogen conditions which catalysed the nucleophilic substitution of bromine by the trialkyl phosphite. (ii) In a second series of experiment (#2 and #3, Table 1), was noted that the use of triethylphosphite instead of trimethylphosphite slightly increases the yields of the synthesis. Using an excess of triethylphosphite (2 equivalent) about Monomer 1 (1 equivalent) led to better yields of phosphonated monomer. (iii) Last experiments (#4 and #5, Table 1) showed that the uses of sonication conditions instead of heating conditions at 110 °C did not improve the overall yield of the synthesis of Monomer 2. (iv) Finally, Experiment 6 evidenced that the Mickaelis-Arbuzov carried out sonic conditions at room temperature (instead of 110 $^{\circ}$ C) did not improve the yields of phosphonation. This first study, using a Michaelis-Arbuzov reaction, allowed us to synthesise Monomer 2 in 10% yield.

The structure of 4-[$(\alpha,\beta,\beta$ -trifluorovinyl)oxy]benzene diethyl phosphonate was confirmed by ³¹P, ¹H, and ¹⁹F NMR spectroscopy. The ¹H NMR spectrum of Monomer **2** (R: Et, Spectrum A in Fig. 1) shows a triplet (³*J*_{HH} = 7.1 Hz) and a multiplet (²*J*_{HP} = 3.5 Hz) centred at 1.09 and 3.91 ppm, characteristics of the six protons of the methyl groups and four methylene protons of the phosphonate group, respectively. As expected, the aromatic

protons were observed between 7.2 and 7.8 ppm. In the 31 P NMR (Spectrum B in Fig. 1), a singlet was noted at 17.9 ppm assigned to the phosphorus atom in the aromatic phosphonate group [17c]. ¹⁹F NMR (Spectrum C in Fig. 1) spectrum exhibits three doublet of doublets centred at -119.1, -126.2 and -135.4 ppm characteristic of F_a, F_b and F_c atoms, respectively (Table 2).

2.1.2. Synthesis of Monomer 2 via a Michaelis–Becker reaction

In addition, a further interest was focused on a Michaelis– Becker reaction (synthetic route II, Scheme 2) [18d,19] to obtain the Monomer **2** with better yields. The Michaelis– Becker reaction was carried out at low temperature (0 $^{\circ}$ C) in two steps. The first one dealt with the preparation of the phosphonic salt from diethylphosphite and sodium hydride. The second step involves in the addition of the phosphonic salt onto the Monomer **1**. After purification by distillation, Monomer **2** was obtained in 12%, which was slightly better than those obtained via the Michaelis–Arbuzov reaction.

2.1.3. Synthesis of Monomer 2 via a palladium catalysed reaction

To improve the yields of the phosphonylation of Monomer 1, a palladium catalysed arylation (synthetic route III, Scheme 2) was investigated [20] using diethyl hydrogen phosphonate and tetrakis[triphenylphosphine]palladium in the presence of triethylamine. This arylation, realised in toluene and under nitrogen conditions, afforded us better yields (32%) than those obtained in the previous reactions.

2.1.4. Synthesis of Monomer 2 via an organometallic reaction

Furthermore, a last synthetic route was performed via an organometallic reaction (synthetic route IV, Scheme 2). As a matter of fact, 4-[(trifluorovinyl)oxy)]bromobenzene (Monomer 1, Scheme 2) can be converted to a reactive Grignard (M: Mg, Scheme 3) [21] or lithium (M: Li, Scheme 3) compound [22]. Followed by a condensation reaction with different reactants, a wide range of organic– inorganic fluorinated compounds can be prepared [2f,22a,23] such as 3-(4-trifluorovinyloxy phenyl)thiophene [21], novel triaryl phosphine oxide trifluorovinyl ether monomers [24], 1,3,5-tris[(4-trifluorovinyloxy)phenyl]ben-

Table I

Attempted for phosphonylation of Monomer 1 via a Michaelis-Arbuzov reaction

Exp. #	Monomer 1 (mol in feed)	P(OR) ₃		NiCl ₂	Temperature	Sonic conditions	Yields (%)
		R	(mol in feed)	(mol in feed)	(°C)/time (h)		
1	0.08	Et	0.16	0	110/72	No	0
2	0.08	Et	0.16	0.03	110/72	No	10
3	0.09	Me	0.17	0.03	110/72	No	6
4	0.07	Et	0.15	0.03	110/72	No	10
5	0.07	Et	0.15	0.03	110/72	Yes	10
6	0.07	Et	0.15	0.03	RT/72	Yes	10



Fig. 1. (a) ¹H, (b) ³¹P and (c) ¹⁹F NMR spectra recorded in deuterated acetone of Monomer 2.

zene [9b], 1,2-bis[4-(dimethylhydroxysilyl)phenoxy]-1,2,3, 3,4,4-hexafluorocyclobutane and 1,2-bis[3-(dimethylhydroxysilyl)phenoxy]1,2,3,3,4,4-hexafluorocyclobutane [23], aromatic trifluorovinyl ether containing the sulphonamide and the sulphonic acid functionality [22c]. Furthermore, aromatic perfluorovinyl ether monomers containing chromophores [12d], heterocycles [25] and macrocyclic ligands [26] have been also synthesised. According to Neilson et al. [27], Grignard reagent from 4-[(α,β,β -trifluorovinyl)oxy]bromobenzene monomer was not reactive enough (compared to the lithium agent) toward many electrophiles.

In our study, the synthetic route is similar to that of the former example, using a lithium reagent from the 4-[(tri-fluorovinyl)oxy]bromobenzene (Monomer 1) which was reacted at -80 °C with dimethyl-chlorophosphate. Monomer 2 (R: Me, Scheme 2) was obtained in 25% overall yield.

2.1.5. Dealkylation of Monomer 2

As previously mentioned, Monomer **2** possesses phosphonic ethyl groups which could be dealkylated with either concentrated acidic solution (HCl or HBr) [20,28], or alkaline solution [20,29], or using silylating reagents [28b,30], or inorganic halides [18d,31] (this deprotection method led

Table 2

$F_{b} \longrightarrow F_{b} \longrightarrow F_{b$										
X	$F_a \delta$ (ppm)	$F_b \delta$ (ppm)	$F_c \delta$ (ppm)	$H_a \delta (ppm)$	${\rm H_b}\;\delta\;({\rm ppm})$	$^{31}\mathrm{P}~\delta$ (ppm)	v (X) (cm ⁻¹)			
Br	-119.8	-126.7	-134.9	7.1	7.5	_				
P(O)(OMe) ₂	-119.5	-126.4	-135.2	7.1	7.6	20.1	1260 (P=O stretch) 1190 (P-O-C stretch)			
$P(O)(OEt)_2$	-119.1	-126.2	-135.4	7.2	7.8	17.9	1253 (P=O stretch) 1026 (P-O-C stretch)			
$P(O)(OH)_2$	-118.5	-125.4	-134.4	7.2	7.8	18.1	2955 (P(O)(OH) ₂ stretch) 2285 (P(O)(OH) ₂ stretch)			
SO ₂ Cl	-117.8	-124.7	-136.1	7.2	8.1	_	1381 (O=S=O stretch)			
SO_2F	-117.1	-124.1	-136.2	7.4	8.2	_	1421 (O=S=O stretch)			
SO ₃ H	-115.1	-122.2	-137.1	7.5	8.1	_	3373 (S(O)(OH) ₂ stretch) 1029 (S(O)(OH) ₂ stretch)			

Chemical shifts and IR frequencies of $[(\alpha,\beta,\beta-trifluorovinyl)oxy]$ bromobenzene functionalised by dialkylphosphonate or phosphonic or halogensulfonyl or sulphonic acid groups

F. Ha

H.

F.



M: Li or MgBr

Scheme 3. Grignard [21] and lithium agent [22] of 4-[(trifluorovinyl) oxy)]bromobenzene.

only to monoacid structures). In our work, Monomer 2 was dealkylated using silylating reagents such as BrSiMe₃ in dichloromethane at room temperature (Scheme 4). The hydrolysis reaction was monitored by ¹H NMR (by checking the absence of signals centred at 1.1 and 3.8 ppm, characteristic of methyl and methylene groups of the diethylphosphonate, respectively). Monomer **3** was obtained in 85% yield.

From these results, the different synthetic ways afforded fair to good overall yields. As a matter of fact, Michaelis– Arbuzov and Michaelis–Becker reactions are based on a substitution of bromine by a nucleophile such as P(OEt)₃ or NaP(O)(OEt)₂. Furthermore, this reaction was carried out with difficulties without any catalyst or a strong electronwithdrawing group linked onto the aromatic ring. Also, it was necessary to use palladium catalyst (synthetic route III, Scheme 2) to afford the best overall yields.

2.2. Characterisation of the aromatic perfluorovinyl ethers

As mentioned above, phosphonic compounds (Monomers 2 and 3) were characterised by ³¹P, ¹H, and ¹⁹F NMR. The ³¹P NMR showed a singlet corresponding to the phosphorus atom in the aromatic phosphonate group. ¹⁹F NMR spectrum exhibits three doublet of doublets characteristic of Fa, Fb and F_c. ¹H NMR exhibits signals characteristics of the dialkyl phosphonate and of the aromatic protons. FTIR was utilised as a means of determining the presence of the phosphonate or phosphonic acid functions in the aromatic perfluorovinyl ether (Table 2). Furthermore, it was worth examining the influence of the functional groups (P(O)(OR)₂, R: H, Me or Et, SO₂R', R': Cl, OH)) on the chemical shifts in the 19 F, 1 H and ³¹P NMR spectra. However, the results listed in Table 2, showed that the presence of $P(O)(OR)_2$ (R: Et, H) or SO_2X (X: Cl, F, OH) functions, which are electron-withdrawing groups, induced a low field shift (from -119.8 to -115.1 ppm when X stands for Br or SO₃H, respectively). Hence, the results listed in Table 2 clearly showed that sulphonic (X: SO_3H , Table 2) or phosphonic (X: $P(O)(OH)_2$, Table 2) acid functions have stronger electron-withdrawing behaviours than those of their halogenosulfonyl (X: SO₂Cl, SO₂F) or phosphonate (X: P(O)(OR)₂, R: Et) or brominated (X: Br) homologues, respectively.



Scheme 4. Dealkylation of Monomer 2.

3. Conclusion

This study describes the synthesis of $[(\alpha,\beta,\beta-\text{trifluorovi-nyl})\text{oxy}]$ benzene phosphonic acid (Monomers **3**). The preparation of ester form of Monomer **3** was carried out according to various methods of phosphonation such as Michaelis–Arbuzov, Michaelis–Becker, organometallic techniques or palladium catalysed arylation described in the literature. These different synthetic routes afforded moderate to fair yields. The best overall yields were obtained when the reaction was catalysed by a complex of palladium [Pd(PPh_3)_4]. These new aromatic perfluorovinyl ether derivatives are potential monomers for proton exchange membranes for fuel cells (PEMFC), and their (co)polymerisations are under investigation.

4. Experimental

4.1. Materials

Trimethyl- or triethyl-phosphite, HP(O)(OMe)₂, HP(O)-(OEt)₂, ClP(O)(OMe)₂, NaH, BrSiMe₃ were purchased from Aldrich and distilled prior to use. Anhydrous THF and diethyl ether were distilled over calcium hydride. All reagents and all solvents were used as received.

4.2. Analyses

4.2.1. Characterisation by NMR spectroscopy

The produced fluorinated monomers were characterised by ¹H, ³¹P and ¹⁹F nuclear magnetic resonance (NMR) spectroscopies. The spectra were recorded on a Bruker AC 200 or Bruker A-250 MHz at room temperature in deuterated acetone or DMF, using tetramethylsilane (TMS) or CFCl₃ as internal references for ¹H and ³¹P, or ¹⁹F NMR spectroscopies, respectively. The experimental conditions for recording ¹H (¹⁹F) NMR spectra were as follows: flip angle 90° (30°); acquisition time 4.5 s (0.7 s); pulse delay 2 s (5 s); 64 (128) scans and pulse width of 5 µs for ¹⁹F NMR. The chemical shifts, δ , were given in ppm relative to tetramethylsilane (TMS) used as s: singlet, d: doublet, t: triplet, q: quartet and m: multiplet.

4.2.2. Characterisation by FTIR spectroscopy

Infrared spectra were recorded on a Nicolet 510P Fourier Transformed spectrometer from KBr pellets and the intensities of the absorption bands were noted as s: strong, m: medium and w: weak, given in cm^{-1} .

4.2.3. Characterisation by mass spectrometry

Mass spectra (GC–MS) were recorded on an Agilent Technologies 6890 N instrument with an Agilent 5973 N mass detector (EI) and a HP5-MS $30 \text{ m} \times 0.25 \text{ mm}$ capillary apolar column (stationary phase: 5% diphenyldimethylpolysiloxane film, 0.25 µm).

4.3. Synthesis

4-[$(\alpha,\beta,\beta$ -Trifluorovinyl)oxy]bromobenzene (Monomer 1) was prepared by known method [2f].

4.3.1. Synthesis of Monomer 2 according to Michaelis– Arbuzov reaction

Into a two-necked round bottom flask equipped with a reflux condenser and a magnetic stirrer were introduced, under nitrogen atmosphere, 28.203 g of triethylphosphite (0.170 mol) and 4.011 g of nickel dichloride (0.031 mol). The mixture was heated at 110 °C. To this solution, 22.701 g of Monomer 1 (0.090 mol) were slowly added. After complete addition, the mixture was stirred at 110 °C for 72 h (bromoethane was eliminated in the course of the reaction). Afterwards, the mixture was allowed to cool at room temperature. The unreacted triethylphosphite was evaporated under vacuum. Monomer 2 was purified (yield 10%; colourless liquid) from the crude oil by distillation (bp, 110-115 °C/5 mm Hg). ¹H NMR (250 MHz, Fig. 1a, CDCl₃) δ: 1.1 (t, P(O)(OCH₂CH₃)₂, ${}^{3}J_{HH} = 7.0$ Hz, 6H), 3.8 (m, $P(O)(OCH_2CH_3)_2$, ${}^{3}J_{HH} = 6.9$ Hz, 4H), 7.2–7.3 (m, ArH, 2H), 7.7-7.8 (m, ArH, 2H); ³¹P{¹H} NMR (250 MHz, Fig. 1b, CDCl₃); δ: 17.9 (s); ¹⁹F NMR (250 MHz, Fig. 1c, CDCl₃); δ : -119.1 (dd, *cis*-CF=CF₂, F_a, ²J_{FaFb} = 92 Hz, ${}^{3}J_{F_{a}F_{c}} = 63$ Hz, 1F, -126.2 (dd, *trans*-CF=CF₂, F_b, ${}^{2}J_{\rm F_bF_a} = 92$ Hz, ${}^{3}J_{\rm F_bF_c} = 109$ Hz, 1F), -135.4 (dd, CF=CF₂, F_c, ${}^{3}J_{\rm F_cF_a} = 63$ Hz, ${}^{3}J_{\rm F_cF_a} = 109$ Hz, 1F). FTIR: 1253 (s, P=O stretch), 1026 (s, P-O-C stretch). Pos EI MS: $m/z = 310 \ (81\%, \ [M^{\bullet}]^{+}), \ 282 \ (90\%, \ [M^{\bullet}]^{+}), \ 237 \ (100\%, \ [M^{\bullet}]^{+}), \ (100\%, \ [M^{\bullet}]^{+}), \ (100\%, \ [M^{\bullet}]^{+}), \ (10\%, \$ $[M^{\bullet}]^{+}$ - $[O(C_{2}H_{5})_{2}]$; 201 (55%); 167 (14%); 139 (90%); 103 (92%); 76 (45%); 50 (12%, CF₂).

4.3.2. Synthesis of Monomer 2 according to Michaelis– Becker reaction

The 1.203 g (0.050 mol) of sodium hydride in 40 ml of anhydrous tetrahydrofuran were introduced into a twonecked round bottom flask equipped with a reflux condenser and a magnetic stirrer, under an nitrogen atmosphere. The solution was cooled to 0 °C under magnetic stirring. The 7.402 g (0.061 mol) of diethyl phosphite were slowly added to this solution. Hydrogen emission was observed. A solution of 12.604 g of 1 (0.051 mol) of Monomer 1 in anhydrous THF and 0.701 g of NaI (0.005 mol) was dropwise added to the mixture at 0 °C. After addition, the mixture was allowed to warm to room temperature and was stirred for 16 h. The salt formed was removed by precipitation from ethyl acetate and then by filtration. The filtrate was concentrated and Monomer 2 was distilled (12% yield, colourless liquid) (bp, 110–115 °C/5 mm Hg).

4.3.3. Synthesis of Monomer 2 according to palladium catalysed reaction

The 10.801 g (0.040 mol) of Monomer 1 and 6.602 g (0.050 mol) of diethyl phosphite (0.050 mol) in 70 ml of dry toluene were placed into a two-necked round bottom

flask equipped with a reflux condenser and a magnetic stirrer, under nitrogen. The 5.007 g (0.004 mol) of tetrakis[-triphenylphosphine]palladium and 15 ml of triethyl amine were added. Then, the reaction mixture was heated at 110 °C for 72 h. Afterwards, the mixture was cooled to room temperature. Ethyl acetate was added and the solid was filtered off. Monomer **2** was distilled (yield 32%, colourless liquid, purity 96%) from the crude oil by distillation under

4.3.4. Synthesis of Monomer **2** according to organometallic reaction

vacuum (bp, 110–115 °C/5 mm Hg).

In a two-necked round bottom flask containing a septum and a nitrogen purge, 20.205 g (0.080 mol) of Monomer 1 and 50 ml of diethyl ether were introduced under nitrogen atmosphere, then cooled at -80 °C. The 50 ml of 1.7 M tbutyl lithium (in hexane) (0.087 mol) was added dropwise to this mixture over 45 min and additionally stirred for 2 h while maintaining the temperature at -80 °C. This lithium reagent was added dropwise, using a canular, into a separate two-necked round bottom flask containing 25 ml of ether and 26.801 g (25 ml) (0.180 mol) of ClP(O)(OMe)₂ also maintaining at -80 °C. The reaction mixture was stirred for 30 min at -80 °C. Then, 100 ml of deionised water was added to the reaction forming an organic and an aqueous layer. The two layers were separated. Monomer 2 was purified by vacuum distillation (bp, 105-112 °C/5 mm Hg) and was obtained in 25% yield (colourless liquid). ¹H NMR (250 MHz, CDCl₃) δ : 3.5 (d, P(O)(OCH₃)₂, $J_{\rm HP} = 10.9$ Hz, 3H), 7.0–7.2 (m, ArH, 2H), 7.4–7.6 (m, ArH, 2H); ³¹P{¹H} NMR (250 MHz, CDCl₃); δ: 17.9 (s); ¹⁹F NMR (250 MHz, CDCl₃); δ: -119.5 (dd, *cis*-CF=CF₂, F_{a} , ${}^{2}J_{F_{a}F_{b}} = 98$ Hz, ${}^{3}J_{F_{a}F_{c}} = 59$ Hz, 1F), -126.2 (dd, trans-CF=CF₂, F_b, ${}^{2}J_{F_{b}F_{a}} = 98$ Hz, ${}^{3}J_{F_{b}F_{c}} = 105$ Hz, 1F), -135.4 (dd, CF=CF₂, F_c, ${}^{3}J_{F_{c}F_{a}} = 59$ Hz, ${}^{3}J_{F_{c}F_{b}} = 105$ Hz, 1F). FTIR: 1260 (s, P=O stretch), 1190 (s, P-O-C stretch).

4.3.5. Dealkylation of Monomer 2

A two-necked round bottom flask equipped with a reflux condenser and a magnetic stirrer was charged, under a nitrogen atmosphere, with 2.904 g (0.009 mol) of Monomer 2 and solubilised in 20 ml of dichloromethane. 6.101 g (5 ml) of BrSiMe₃ were added dropwise for 30 min. The reaction mixture was stirred at room temperature for 6 h. After the reaction, the solvent was evaporated and 50 ml of methanol were added. The mixture was stirred for 2 h. Monomer 3 was obtained after drying under vacuum line (a yellow liquid was obtained in 80% yield). ¹H NMR (250 MHz, CDCl₃) δ: 5.5 (s, P(O)(OH)₂, 2H), 7.1–7.3 (m, ArH, 2H), 7.7–7.9 (m, ArH, 2H); ³¹P{¹H} NMR (250 MHz, CDCl₃); δ: 18.1 (s); ¹⁹F NMR (250 MHz, CDCl₃); δ: -118.5 (dd, *cis*-CF=CF₂, F_a , ${}^2J_{F_aF_b}$ = 96 Hz, ${}^2J_{F_aF_c}$ = 63 Hz, 1F), -125.4 (dd, *trans*-CF=CF₂, F_b, ${}^{2}J_{F_{b}F_{a}} = 96$ Hz, ${}^{2}J_{F_{b}F_{c}} =$ 114 Hz, 1F), -134.4 (dd, CF=CF₂, F_c, ${}^{2}J_{F_{c}F_{a}} = 63$ Hz, ${}^{2}J_{F_{c}F_{b}} = 114 \text{ Hz}, 1\text{F}$). FTIR: 2955–2285 (s, P(O)(OH)₂) stretch).

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