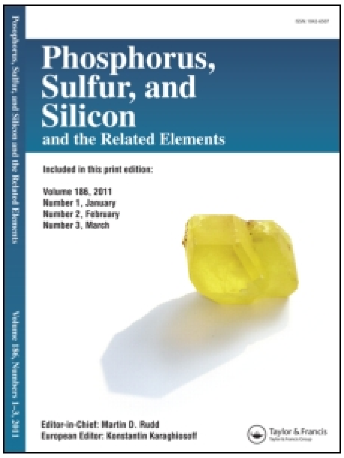

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Synthesis and Characterization of New Organic Phosphonates Monomers as Flame Retardant Additives for Polymers

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Synthesis and Characterization of New Organic Phosphonates Monomers as Flame Retardant Additives for Polymers

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Commercially available polyphenols react with diethylphosphite to give polyphosphonates, which are easily transformed by LDA in good yields to polyorthohydroxy aryl phosphonates. Moreover, some bis-benzyl aminobenzyl phosphonates have been prepared in good yields. These new monomers are of great relevance for the synthesis of thermal resistant polycondensates containing phosphonate moieties.

Keywords Aryl-amine phosphates; environmental friendly additives; NMR and FAB-MS characterizations; poly-hydroxy aryl phosphates

INTRODUCTION

The fire resistance of polymeric materials is an extremely important problem, and generally, a large volume of additives is used for enhancing the fire safety performance. Of course, such additives should have a low impact on the physical properties of the materials and a low production cost. Up to now, the most commonly used additives are halogenated compounds, which are very effective in reducing the heat release rate of commercial polymers, but on the other hand, they present a highly dangerous environmental impact, especially during the process of recycling and incineration. Halogen-based compounds combined with some other additives (i.e., Sb_2O_3) are still widely used as fire retardants,

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in particular for composite organic polymers such as phenolic resins, epoxide or bismaleimide resins.[1] However, when burning they generally release halogen acids and metal halides; the proven efficiency of these additives has to be balanced against this formation of undesired, corrosive, and obscuring fumes.[2] Furthermore, halogenated flame retardants may form extremely toxic dibenzodioxines, and the toxicity of antimony trioxide should be taken into account for this handling and use.[3] The important problem today, therefore, is whether the flame retardants are suited to satisfy a low environmental impact, or if it is wise to consider the development of alternative products.

It is generally recognized that flame retardants, which contain phosphorus or phosphonates, have substantial advantages compared to the more used halogenated phosphate esters and the brominated polyols. Halogen-free materials for electronic devices with new flame retardant principles based on nitrogen and phosphorus structures have been developed by Kettrup et al.[4] and optimized in order to satisfy low environmental impact.

Toxicity tests with the Daphnia Magna Test[5] indicate the lowest toxicity for materials containing only phosphorus as flame retardant and aluminum oxide hydroxide as filling. Furthermore, no neurotoxic compounds were formed during the combustion on flame. In this case, the typical intumescent system composition consists of a source of char (polyhydric compound), a source of phosphonic acid (which promotes the charring process), and a spumific compound, usually amines/amides, which evolve gaseous products on heating, may contribute to blow the char.[6–10] Other typical intumescent systems are built into the basic resin. For example, special epoxy resins act as carbonifics, thus partially contributing to the build up of the char, and novel intumescent epoxy systems have been prepared by the reaction of phosphorus-containing compounds with different epoxy resins.

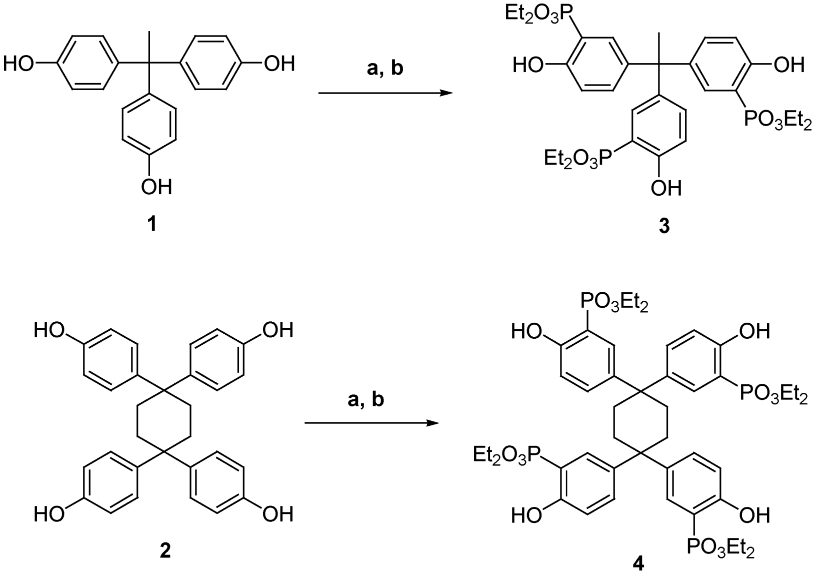
M. R. Buckingam et al.[11–13] have studied more than 20 novel phosphorylated monomers as flame retardants cross-linkable in epoxy resins. Other phosphorus-based dual-function materials, acting both as flame retardant and as curing agents, have been studied. Bis(*m*-aminophenyl)methylphosphine oxide (BAMPO) was found to act as curing agent, mixed in certain percentage to the 4,4′-diaminodiphenylsulphone (DDS), for the epoxy resins TGDDM and DGEBA. Furthermore, these resins cured with BAMPO, show a higher resistance to the fire compared to the same resins cured with only DDS.[14,15]

Imparting flame resistance into epoxy resins can be achieved not only using fire-resistant curing agents but also using phosphorus-containing oxiranes.[16–20] Ying-Ling et al.[16] have synthesized bis-glycidyl phenylphosphate (BGPP), a new phosphorus-containing oxirane. This compound was prepared by a simple synthesis and has high phosphorus content, being very effective in flame retardation.

Considering the great interest in phosphorus containing compounds as antiflammable agents, we decided to synthesize a great variety of phosphonates, which could be used as hardeners in the curing process of thermosetting epoxy resins to limit the flammability of the resulting system. Futhermore, our systems are suitable as monomers for obtaining polycondensates, which contain the phosphonate moiety in polymeric chain.

RESULTS AND DISCUSSION

In a previous paper,[21] we reported the syntheses of new phosphonated derivatives of bis-phenols and used them to reduce flammability of thermosetting DGEBA epoxy resin.[22] As these phosphonated phenols are very interesting as additive for polymeric materials, we decided to synthesize tris and tetrakis phosphonated derivatives of phenol (Scheme 1). For the synthesis of the phosphonates, suitable for polymer chemistry, we used compounds with three and four phenol units, which were



a) $HPO(OEt)_2$, Et_3N, CCl_4, r.t, 24 h; b) LDA, THF, -78 °C, 2 h.

SCHEME 1

transformed into the corresponding diethyl phosphates by treatment with diethyl phosphite in CCl_4 as solvent in the presence of triethylamine as base. After isolation, the crude phosphates were transformed into the corresponding phosphonates **3** and **4** by lithium diisopropylamide (LDA) at –78°C, trough [1,3]-sigmatropic rearrangement that involve the fission of an oxygen-phosphorus bond, and the formation of a new carbon-phosphorus bond. The procedure used is an adaptation of the reaction reported first by Dhawan and Redmore.[23] We have found, that this procedure gives good yields also in the case of polyhydroxy compounds **1** and **2**.

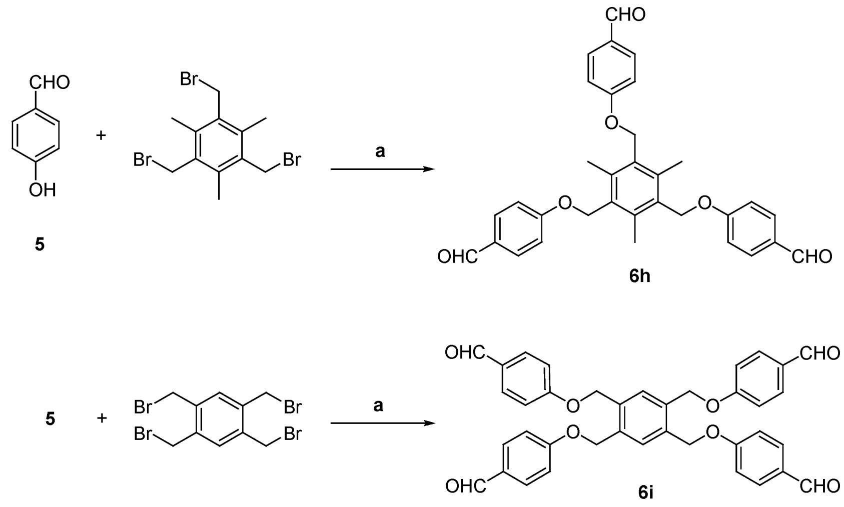
In the Experimental section, we report the full characterization of compounds **3** and **4**, including their NMR data. In the proton, as well as in the phosphorus NMR spectra, all chemical shifts fall into the expected range.

Commonly used epoxy resin formulations are obtained by mixing of oligomers based on diglycid ether of bisphenol A (DGEBA) and aromatic or aliphatic amines as curing agents. Considering that amines are the most used curing agents for epoxy resin systems, we also decided to prepare phosphonate derivatives containing NH groups, in order to help curing process and to bind the fire-retardant additive to the final polymeric material.

Our approach to the synthesis of phosphorus-containing organic compounds consists in using commercially available diethyl (4-aminobenzyl)phosphonate (compound **7**, Scheme 3) and a corresponding aldehyde. Suitable aldehydes are prepared by reacting 4-hydroxybenzaldehyde **5** with a bis-, tris- or tetrakis-halomethyl derivative. An example is represented by compounds **6h** and **6i**, which contain three and four aldehyde groups in the same molecule, respectively (Scheme 2).

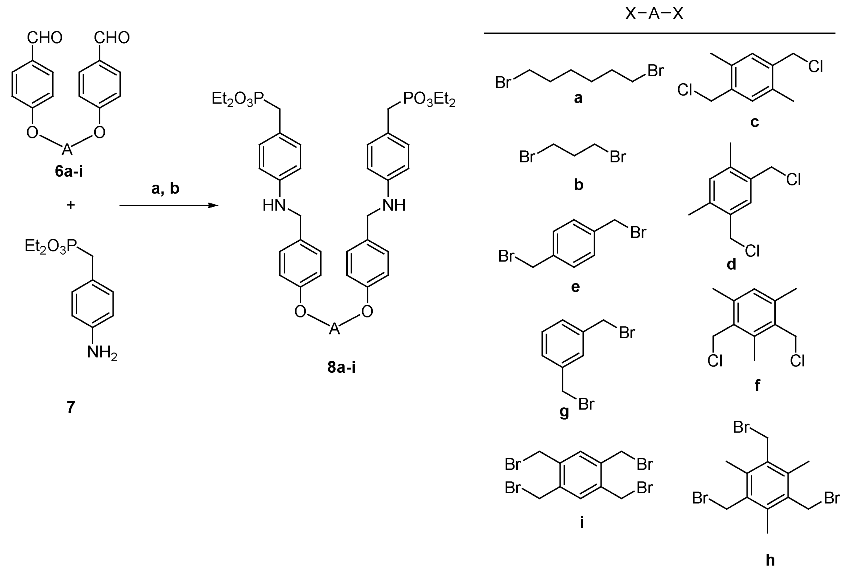
The syntheses of the phosphonates were performed by reacting the amine **7** with the corresponding aldehyde **6a-i** in toluene using a Dean-Stark apparatus; the Schiff bases thus obtained were reduced directly with $NaBH_4$ in EtOH after the toluene was removed in vacuo (Scheme 3). The products were isolated from the reaction mixture by pouring it in water and filtering the solid or extracting the oil thus obtained to give compounds **8a–i** in good yields.

Similarly, bis-aldehydes **9** and **10** were prepared by Duff reaction (Scheme 4) from the related bis-phenols by reacting the phenol with hexamethylenetetramine (HMTA) in acetic acid at 120°C. The reaction mixture was then reacted with H_2SO_4 and H_2O to destroy the intermediate and poured into water. The resulting solid was filtered, washed with water, and crystallized from methanol to give bis-aldehydes **9** and **10** in moderate yields (40–50%).



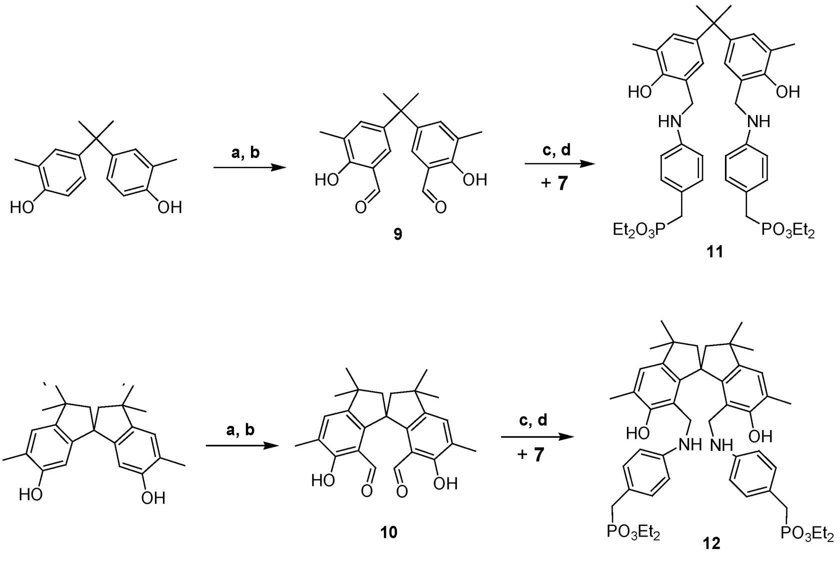
a) CH_3CN, K_2CO_3, reflux, 18 h.

SCHEME 2



a) toluene, reflux, 3 h; b) EtOH, $NaBH_4$, r.t., overnight.

SCHEME 3



a) HMTA, CH_3COOH, H_2O, 120 °C, 7 h; b) H_2SO_4, H_2O, 3 h;
c) toluene, reflux, 3 h; d) EtOH, $NaBH_4$, r.t., overnight.

SCHEME 4

Reaction of these compounds with amine **7** yields the aminophenol derivatives **11** and **12**, respectively (Scheme 4).

Now, we dispose of a large variety of reactive molecules containing one or more phosphonate groups. Bis or polyhydroxy derivatives can be used as fire-retardant blocks in the synthesis of high-performance engineering polymers such as PEK, PES, PEES, PEEK, PC, and so on. The compounds containing reactive NH groups can be useful for the preparation of epoxy resins possessing reduced flammability.

EXPERIMENTAL

All reactions were performed under an inert atmosphere of nitrogen. Acetonitrile was dried by distillation from calcium hydride under nitrogen. All the other solvents were used without any purification. Unless otherwise stated commercial chemicals were used as supplied. Compound **2** was prepared according to a published procedure.[24] ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian-Inova 500 MHz instrument operating at 500 MHz, 125 MHz, and 200 MHz, respectively, using TMS as internal reference (^{1}H, ^{13}C) and 85% H_3PO_4 as external reference(^{31}P). Mass spectra were obtained using a double-focusing Kratos MS 50S instrument equipped with a standard FAB source and DS 90 data system using 3-nitro-benzylalcohol as matrix. Melting points were determined on a Büchi 530 melting point apparatus and are uncorrected.

General Synthetic Procedure for Compounds 6a–i

A suspension of *p*-hydroxybenzaldehyde **5** (10 mmol), an equivalent amount of the corresponding halogen derivative, and potassium carbonate (20 mmol) in CH_3CN (20 mL) was refluxed overnight. The reaction mixture was poured into water, the solid thus obtained was filtered, and washed with water and cold methanol. The white solid was recrystallized or triturated from methanol to give compounds **6a–i** as white needles (yield ∼ 75%). Physical properties of compounds **6a**,[25] **6b**[26] and **6e**,[27] **6g**[27] are the same as those reported in literature.

General Synthetic Procedure for Compounds 8a-i and 11–12

A solution of aldehyde **6a–i** (2 mmol) and an equivalent amount of diethyl (4-aminobenzyl)phosphonate **7** were azeotropically distilled with toluene (20 mL) for 3 h. After cooling, the toluene was removed under vacuum and the residue dissolved in ethanol (10 mL). $NaBH_4$ (8 mmol) was added and the mixture stirred overnight at room temperature. The solvent was evaporated under reduced pressure and the residue was extracted with chloroform/water. The organic phase was washed with water, dried over Na_2SO_4, and concentrated to give amines **8a–i** and**11**, **12** as a white powder or a yellow oil.

Compound 3

^{1}H NMR ($CDCl_3$)δ: 10.12 (s, 3H, ArOH), 7.15 (dd, $^3J_{HH} = 8.5$ Hz, $^4J_{HH} = 2.5$ Hz, 3H, ArH), 6.97 (dd, $^3J_{PH} = 15.5$ Hz, $^4J_{HH} = 2.5$ Hz, 3H, ArH), 6.87 (dd, $^4J_{PH} = 7.5$ Hz, $^3J_{HH} = 8.5$ Hz, 3H, ArH), 4.12–3.93 (m, 12H, $PO\underline{CH_2}CH_3$), 2.07 (s, 3H, CH_3), 1.23 (t, $^3J_{HH} = 7.0$ Hz, 18H, $POCH_2\underline{CH_3}$). ^{13}C NMR ($CDCl_3$) δ: 160.4, 139.5, 135.2, 130.9, 117.4, 108.4 ($^1J_{PC} = 179.1$ Hz), 62.7, 50.4, 30.3, 16.1. ^{31}P NMR ($CDCl_3$) δ: 22.4. FAB MS (%): m/z 715.3 (100%) $[M+H]^+$, m/z 737.2 (15%) $[M+Na]^+$. White crystals; m.p. = 169–171°C; yield 62%.

Compound 4

^{1}H NMR (DMSO-d$_6$, 70 °C) δ: 9.95 (s, 4H, ArOH), 7.27 (m, 8H, ArH), 6.83 (m, 4H, ArH), 4.06-3.99 (m, 16H, PO$\underline{CH_2}$CH$_3$), 2.19 (broad s, 8H, ring-CH$_2$), 1.18 (m, 24H, POCH$_2\underline{CH_3}$). ^{31}P NMR (DMSO-d$_6$, 50 °C) δ: 20.3. FAB MS (%): m/z 997.3 (35%) [M+H]$^+$. White crystals; m.p. = 216–217°C; yield 65%.

Compound 6c

^{1}H NMR (CDCl$_3$) δ: 9.89 (s, 2H, ArCHO), 7.85 (d, $^3J_{HH}$ = 8.5 Hz, 4H, ArH), 7.27 (s, 2H, ArH), 7.05 (d, $^3J_{HH}$ = 8.5 Hz, 4H, ArH), 5.10 (s, 4H, ArCH$_2$O), 2.36 (s, 6H, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 190.7, 163.7, 134.4, 134.0, 132.0, 130.9, 130.2, 115.0, 68.5, 18.4. FAB MS (%): m/z 375.5 (34) [M + H]$^+$. White crystals; m.p. = 180–183°C; yield 80%.

Compound 6d

^{1}H NMR (CDCl$_3$) δ: 9.88 (s, 2H, ArCHO), 7.84 (d, $^3J_{HH}$ = 8.5 Hz, 4H, ArH), 7.41 (s, 1H, ArH), 7.13 (s, 1H, ArH), 7.05 (d, $^3J_{HH}$ = 8.5 Hz, 4H, ArH), 5.09 (s, 4H, ArCH$_2$O), 2.36 (s, 6H, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 190.7, 163.7, 137.3, 133.0, 131.9, 131.6, 130.1, 129.3, 115.0, 68.5, 18.5. FAB MS (%): m/z 375.4 (44) [M + H]$^+$. White crystals; m.p. = 130–133°C; yield 84%.

Compound 6f

^{1}H NMR (CDCl$_3$) δ: 9.88 (s, 2H, ArCHO), 7.86 (d, $^3J_{HH}$ = 8.5 Hz, 4H, ArH), 7.13 (d, $^3J_{HH}$ = 8.5 Hz, 4H, ArH), 7.04 (s, 1H, ArH), 5.15 (s, 4H, ArCH$_2$O), 2.40 (s, 9H, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 190.7, 164.1, 138.9, 132.0, 130.7, 130.5, 130.1, 114.8, 65.1, 19.7, 15.3. FAB MS (%): m/z 389.4 (65) [M + H]$^+$. White crystals; m.p. = 134–135°C; yield 78%.

Compound 6h

^{1}H NMR (CDCl$_3$) δ: 9.91 (s, 3H, ArCHO), 7.87 (d, $^3J_{HH}$ = 8.5 Hz, 6H, ArH), 7.14 (d, $^3J_{HH}$ = 8.5 Hz, 6H, ArH), 5.22 (s, 6H, ArCH$_2$O), 2.46 (s, 9H, CH$_3$). ^{13}C NMR (CDCl$_3$,) δ: 190.7, 163.9, 139.7, 132.0, 131.2, 114.8, 65.2, 16.0. FAB MS (%): m/z 475.6 (34) [M + H]$^+$. White crystals; m.p. = 169–170°C; yield 82%.

Compound 6i

^{1}H NMR (CDCl$_3$) δ: 9.84 (s, 4H, ArCHO), 7.81 (d, $^3J_{HH}$ = 8.5 Hz, 8H, ArH), 7.30 (s, 2H, ArH), 7.19 (d, $^3J_{HH}$ = 8.5 Hz, 8H, ArH), 5.38 (s, 8H, ArCH$_2$O). FAB MS (%): m/z 615.6 (77) [M + H]$^+$. White crystals; m.p. = 194–196°C; yield 41%.

Compound 8a

^{1}H NMR (CDCl$_3$) δ: 7.30 (d, $^{3}J_{\mathrm{HH}} = 9.0$ Hz, 4H, ArH), 7.09 (dd, $^{3}J_{\mathrm{HH}} = 9.0$ Hz, $^{4}J_{\mathrm{PH}} = 2.5$ Hz, 4H, ArH), 6.85 (d, $^{3}J_{\mathrm{HH}} = 9.0$ Hz, 4H, ArH), 6.58 (d, $^{3}J_{\mathrm{HH}} = 9.0$ Hz, 4H, ArH), 4.22 (s 4H, ArCH_2NH), 4.02 (m, 8H, POCH_2CH$_3$), 3.96 (t, $^{3}J_{\mathrm{HH}} = 6.5$ Hz, 4H, ArOCH_2CH$_2$CH$_2$), 3.04 (d, $^{2}J_{\mathrm{PH}} = 21.0$ Hz, 4H, ArCH$_2$P), 1.81 (m, 4H, ArOCH$_2$CH_2CH$_2$), 1.53 (m, 4H, ArOCH$_2$CH$_2$CH_2), 1.21 (t, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, 12H, POCH$_2$CH_3). ^{13}C NMR (CDCl$_3$) δ: 158.4, 146.7, 130.9, 130.5, 128.9, 121.2, 114.6, 113.3, 67.8, 62.0, 48.1, 33.2 (d, $^{1}J_{\mathrm{PC}} = 138.1$ Hz), 29.2, 25.8, 16.4. ^{31}P NMR (CDCl$_3$) δ: 27.5. FAB MS (%): m/z 781.9 (60) [M + H]$^+$. White crystals; m.p. = 106–107°C; yield 87%.

Compound 8b

^{1}H NMR (CDCl$_3$) δ: 7.26 (d, $^{3}J_{\mathrm{HH}} = 8.5$ Hz, 4H, ArH), 7.08 (dd, $^{3}J_{\mathrm{HH}} = 8.5$ Hz, $^{4}J_{\mathrm{PH}} = 2.5$ Hz, 4H, ArH), 6.87 (d, $^{3}J_{\mathrm{HH}} = 8.5$ Hz, 4H, ArH), 6.58 (d, $^{3}J_{\mathrm{HH}} = 8.5$ Hz, 4H, ArH), 4.25 (s, 4H, ArCH_2NH), 4.13 (t, $^{3}J_{\mathrm{HH}} = 6.0$ Hz, 4H, ArOCH_2CH$_2$), 4.02 (m, 8H, POCH_2CH$_3$), 3.03 (d, $^{2}J_{\mathrm{PH}} = 21.0$ Hz, 4H, ArCH$_2$P), 2.25 (quint, $^{3}J_{\mathrm{HH}} = 6.0$ Hz, 2H, ArOCH$_2$CH_2), 1.24 (t, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, 12H, POCH$_2$CH_3). ^{31}P NMR (CDCl$_3$) δ: 27.4. FAB MS (%): m/z 739.3 (56) [M + H]$^+$; yield 81%.

Compound 8c

^{1}H NMR (CDCl$_3$) δ: 7.30 (d, $^{3}J_{\mathrm{HH}} = 8.5$ Hz, 4H, ArH), 7.09 (dd, $^{3}J_{\mathrm{HH}} = 8.5$ Hz, $^{4}J_{\mathrm{PH}} = 2.5$ Hz, 4H, ArH), 6.98 (d, $^{3}J_{\mathrm{HH}} = 8.5$ Hz, 4H, ArH), 6.59 (d, $^{3}J_{\mathrm{HH}} = 8.5$ Hz, 4H, ArH), 5.03 (s, 4H, ArCH$_2$O), 4.25 (s, 4H, ArCH_2NH), 4.00 (m, 8H, POCH_2CH$_3$), 3.03 (d, $^{2}J_{\mathrm{PH}} = 21.0$ Hz, 4H, ArCH$_2$P), 2.33 (s, 6H, ArCH$_3$), 1.24 (t, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, 12H, POCH$_2$CH_3). FAB MS (%): m/z 843.9 (76) [M + H]$^+$. White crystals; m.p. = 163–165°C; yield 91%.

Compound 8d

^{1}H NMR (CDCl$_3$) δ: 7.41 (s, 1H, ArH), 7.27 (d, $^{3}J_{\mathrm{HH}} = 8.5$ Hz, 4H, ArH), 7.09 (dd, $^{3}J_{\mathrm{HH}} = 8.5$ Hz, $^{4}J_{\mathrm{PH}} = 2.5$ Hz, 4H, ArH), 7.08 (s, 1H, ArH), 6.95 (d, $^{3}J_{\mathrm{HH}} = 8.5$ Hz, 4H, ArH), 6.58 (d, $^{3}J_{\mathrm{HH}} = 8.5$ Hz, 4H, ArH), 4.99 (s, 4H, ArCH$_2$O), 4.23 (s, 4H, ArCH_2NH), 4.00 (m, 8H, POCH_2CH$_3$), 3.03 (d, $^{2}J_{\mathrm{PH}} = 21.0$ Hz, 4H, ArCH$_2$P), 2.33 (s, 6H, ArCH$_3$), 1.23 (t, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, 12H, POCH$_2$CH_3). ^{13}C NMR (CDCl$_3$) δ: 158.2, 147.0, 137.0, 132.8, 132.4, 131.5, 130.5, 129.6, 128.5, 119.9, 114.9, 113.1, 68.4, 61.9, 47.9, 33.2 (d, $^{1}J_{\mathrm{PC}} = 138.1$ Hz), 18.5, 16.7. ^{31}P NMR (CDCl$_3$) δ: 27.6. FAB MS (%): m/z 829.9 (69) [M + H]$^+$. White crystals; m.p. = 123–124°C; yield 80%.

Compound 8e

^{1}H NMR (CDCl$_3$) δ: 7.44 (d, $^3J_{HH} = 8.5$ Hz, 4H, ArH), 7.26 (d, $^3J_{HH} = 8.5$ Hz, 4H, ArH), 7.08 (dd, $^4J_{PH} = 2.5$ Hz, 4H, ArH), 6.98 (d, $^3J_{HH} = 8.5$ Hz, 4H, ArH), 6.52 (d, $^3J_{HH} = 8.5$ Hz, 4H, ArH), 5.08 (s, 4H, ArOCH$_2$), 4.23 (s, 4H, ArCH_2NH), 3.98 (m, 8H, POCH_2CH$_3$), 3.03 (d, $^2J_{PH} = 21.0$ Hz, 4H, ArCH$_2$P), 1.23 (t, $^3J_{HH} = 7.0$ Hz, 12H, POCH$_2$CH_3). ^{13}C NMR (CDCl$_3$) δ: 158.0, 147.0, 136.7, 131.7, 130.5, 128.8, 127.6, 119.9, 114.9, 113.0, 69.7, 61.9, 47.8, 33.2 ($^1J_{PC} = 138.1$ Hz), 16.3. ^{31}P NMR (CDCl$_3$) δ: 27.7. FAB MS (%): m/z 1205.3 (56) [M + H]$^+$; yield 70%.

Compound 8f

^{1}H NMR (CDCl$_3$) δ: 7.31 (d, $^3J_{HH} = 8.5$ Hz, 4H, ArH), 7.08 (dd, $^3J_{HH} = 8.5$ Hz, $^4J_{PH} = 2.5$ Hz, 4H, ArH), 7.01 (s, 1H, ArH), 6.97 (d, $^3J_{HH} = 8.5$ Hz, 4H, ArH), 6.57 (d, $^3J_{HH} = 8.5$ Hz, 4H, ArH), 5.05 (s, 4H, ArCH$_2$O), 4.25 (s, 4H, ArCH_2NH), 4.00 (m, 8H, POCH_2CH$_3$), 3.02 (d, $^2J_{PH} = 21.0$ Hz, 4H, ArCH$_2$P), 2.41 (s, 3H, ArCH$_3$), 2.38 (s, 6H, ArCH$_3$), 1.23 (t, $^3J_{HH} = 7.0$ Hz, 12H, POCH$_2$CH_3). ^{13}C NMR (CDCl$_3$) δ: 158.5, 146.9, 138.5, 131.5, 131.2, 130.5, 130.4, 128.8, 114.9, 113.1, 65.9, 61.9, 47.9, 33.2 (d, $^1J_{CP} = 138.1$ Hz), 19.7, 16.4, 15.2. ^{31}P NMR (CDCl$_3$) δ: 27.7. FAB MS (%): m/z 801.9 (63) [M + H]$^+$; yield 97%.

Compound 8g

^{1}H NMR (CDCl$_3$) δ: 7.49 (s, 1H, ArH), 7.38 (m, 3H, ArH), 7.27 (d, $^3J_{HH} = 8.5$ Hz, 4H, ArH), 7.08 (dd, $^4J_{PH} = 2.5$ Hz,$^3J_{HH} = 8.5$ Hz, 4H, ArH), 6.94 (d, $^3J_{HH} = 8.5$ Hz, 4H, ArH), 6.57 (d, $^3J_{HH} = 8.5$ Hz, 4H, ArH), 5.06 (s, 4H, ArCH$_2$O), 4.22 (s, 4H, ArCH_2NH), 4.00 (m, 8H, POCH_2CH$_3$), 3.02 (d, $^2J_{PH} = 21.0$ Hz, 4H, ArCH$_2$P), 1.23 (t, $^3J_{HH} = 7.0$ Hz, 12H, POCH$_2$CH_3). ^{13}C NMR (CDCl$_3$) δ: 157.9, 146.8, 137.7, 131.7, 130.5, 130.4, 128.8, 126.9, 126.3, 119.8, 114.9, 113.1, 69.8, 61.7, 47.9, 33.2 (d, $^1J_{CP} = 138.1$ Hz), 16.4. ^{31}P NMR (CDCl$_3$) δ: 27.6. FAB MS (%): m/z 801.9 (35) [M + H]$^+$. White crystals; m.p. = 127–129°C; yield 87%.

Compound 8h

^{1}H NMR (CDCl$_3$) δ: 7.30 (d, $^3J_{HH} = 8.5$ Hz, 6H, ArH), 7.09 (dd, $^3J_{HH} = 8.5$ Hz, $^4J_{HP} = 2.5$ Hz, 6H, ArH), 6.98 (d, $^3J_{HH} = 8.5$ Hz, 6H, ArH), 6.58 (d, $^3J_{HH} = 8.5$ Hz, 6H, ArH), 5.08 (s, 6H, ArCH_2O), 4.25 (s, 6H, ArCH_2NH), 4.00 (m, 12H, POCH_2CH$_3$), 3.02 (d, $^2J_{HP} = 21.0$ Hz, 6H, ArCH$_2$P), 2.43 (s, 9H, ArCH$_3$), 1.24 (t, $^3J_{HH} = 7.0$ Hz, 18H, POCH$_2$CH_3). ^{13}C NMR (CDCl$_3$) δ: 158.2, 147.1, 139.2, 131.7, 131.6, 130.5, 130.4, 128.8, 114.6, 113.0, 64.9, 61.9, 47.8, 33.2 (d, $^1J_{CP} = 138.1$ Hz), 16.4, 15.8. ^{31}P NMR (CDCl$_3$) δ: 27.6. FAB MS (%): m/z 1204.3 (42) [M + H]$^+$. Yield 82%.

Compound 8i

^{1}H NMR (CDCl$_3$) δ: 7.30 (d, $^3J_{HH}$ = 8.5 Hz, 8H, ArH), 7.15 (s, 2H, ArH), 7.09 (dd, $^4J_{PH}$ = 2.5 Hz,$^3J_{HH}$ = 8.5 Hz, 8H, ArH), 6.98 (d, $^3J_{HH}$ = 8.5 Hz, 8H, ArH), 6.60 (d, $^3J_{HH}$ = 8.5 Hz, 8H, ArH), 5.08 (s, 8H, ArCH$_2$O), 4.26 (s, 8H, ArCH_2NH), 4.00 (m, 16H, POCH_2CH$_3$), 3.03 (d, $^2J_{PH}$ = 21.0 Hz, 8H, ArCH$_2$P), 1.24 (t, $^3J_{HH}$ = 7.0 Hz, 24H, POCH$_2$CH_3). ^{13}C NMR (CDCl$_3$) δ: 158.7, 144.7, 139.5, 134.1, 129.9, 128.1, 127.5, 121.2, 114.2, 113.4, 69.6, 62.0, 47.2, 33.3 ($^1J_{CP}$ = 138.1 Hz), 16.5. ^{31}P NMR (CDCl$_3$) δ: 27.7. FAB MS (%): m/z 1524.6 (56) [M + H]$^+$; yield 88%.

Compound 9

^{1}H NMR (CDCl$_3$) δ: 11.18 (s, 2H, ArOH), 9.84 (s, 2H, ArCHO), 7.28 (s, 4H, ArH), 7.19 (s, 4H, ArH), 2.21 (s, 6H, ArCH$_3$), 1.68 (s, 6 H, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 196.8, 158.3, 141.1, 137.0, 128.3, 126.8, 119.3, 41.5, 30.7, 15.2. FAB MS (%): m/z 313.1 (85%) [M+H]$^+$. Yellowish powder; m.p. = 140–141°C; yield 45%.

Compound 10

^{1}H NMR (CDCl$_3$) δ: 12.01 (s, 2H, CHO), 9.56 (s, 2H, ArOH), 7.20 (s, 2H, ArH), 2.57 (d, $^2J_{HH}$ = 13.5 Hz, 2H, CH$_2$), 2.37 (d, $^2J_{HH}$ = 13.5 Hz, 2H, CH$_2$), 2.26 (s, 3H, CH$_3$), 2.25 (s, 3H, CH$_3$), 1.37 (s, 6H CH$_3$), 1.35 (s, 6H, CH$_3$). FAB MS (%): m/z 393.4 (25%) [M+H]$^+$. Yellowish powder; m.p. = 282–285°C dec.; yield 44%.

Compound 11

^{1}H NMR (CDCl$_3$) δ: 7.14 (dd,$^3J_{HH}$ = 9.0 Hz, $^4J_{PH}$ = 2.5 Hz, 4H, ArH), 6.96 (d,$^4J_{HH}$ = 2.0 Hz, 2H, ArH), 6.82 (d,$^4J_{HH}$ = 2.0 Hz, 2H, ArH), 6.76 (d,$^3J_{HH}$ = 8.5 Hz, 4H, ArH), 4.30 (s, 4H, $\underline{CH_2}$NH), 4.04–3.97 (m, 8H, PO$\underline{CH_2}$CH$_3$), 3.06 (d, $^2J_{PH}$ = 21.5 Hz, 4H, $\underline{CH_2}$P), 2.21 (s, 6H, ArCH$_3$), 1.62 (s, 6H, CH$_3$), 1.25 (t, $^3J_{HH}$ = 7.0 Hz, 12H, POCH$_2\underline{CH_3}$). FAB MS (%): m/z 767.4 (50%) [M+H]$^+$; yield 100%.

Compound 12

^{1}H NMR (DMSO-d$_6$) δ: 8.63 (s, 2H, ArOH), 6.91 (d,$^3J_{HH}$ = 8 Hz, 4H, ArH), 6.90 (s, 2H, ArH), 6.28 (d,$^3J_{HH}$ = 8 Hz, 4H ArH), 5.15 (t, $^3J_{HH}$ = 5.5 Hz, 2H, NH), 3.94–3.91 (m, 8H, PO$\underline{CH_2}$CH$_3$), 3.68–3.32 (m, 4H, CH$_2$NH), 2.98 (d, $^2J_{PH}$ = 21 Hz, 4H, $\underline{CH_2}$P), 2.28 (d, $^2J_{HH}$ = 13 Hz, 2H, CH$_2$), 2.27 (d, $^2J_{HH}$ = 13 Hz, 2H, CH$_2$), 2.15 (s, 6H, CH$_3$), 1.21 (s, 6H, CH_3), 1.14 (t, $^3J_{HH} = 7$ Hz, 12H, $POCH_2\underline{CH_3}$), 1.09 (s, 6H, CH_3) ^{13}C NMR (DMSO-d_6) δ: 154.1, 147.2, 145.9, 142.3, 129.9, 128.3, 124.0, 123.0, 120.1, 119.7, 113.5, 61.2, 57.5, 43.7, 41.8, 40.6, 32.6, 31.4 (d, $^1J_{CP} = 135.6$ Hz) 29.7, 16.7, 16.2. ^{31}P NMR (DMSO-d_6) δ: 28.7. FAB MS (%): m/z 847.3 (50%) $[M+H]^+$. White crystals; m.p. = 199-202 °C; yield 96%.

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