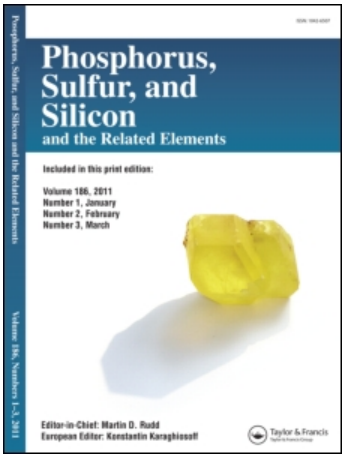

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Synthesis and Characterization of New Ortho-Acetyl or Ortho-bis- p -aminophenoxy Phosphonate Monomers

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SYNTHESIS AND CHARACTERIZATION OF NEW ORTHO-ACETYL OR ORTHO-BIS-*P*-AMINOPHENOXY PHOSPHONATE MONOMERS

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*Some new aryl phosphonic acid ethyl ester analogs of acetyl salicylic acids, and bis-*p*-aminophenoxy-benzo-phosphonic acid ethyl esters have been prepared in good yield. Characterization by spectroscopic techniques indicates that in the phosphorus NMR spectra a significant change in chemical shift values between the starting phenolic phosphonate and both the corresponding derivative is observed; thus this up-field shift is very diagnostic for this type of compounds.*

Keywords: Electrophilic condensations; monomers for polycondensates; NMR and FAB characterizations; nucleophilic substitutions

INTRODUCTION

The 1,3 phosphorotropic rearrangement of dialkyl aryl phosphates to dialkyl aryl phosphonates already has been described in the literature,[1–13] and we recently used the procedure extensively for preparing suitable monomers in order to enhance the flame-retarding properties of epoxy resins[14] and for the synthesis of a variety of medium size cyclophanes containing phosphonic units.[15]

In connection with our continous interest in searching phosphonates for agrochemistry and as starting blocks for engineering polymers, we decided to functionalize the phenolic hydroxy groups of molecules **1–5** both by electrophilic and nucleophilic reactions in order to dispose of new derivatives useful for the purposes mentioned above.

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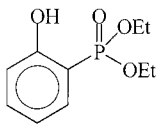

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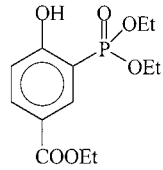

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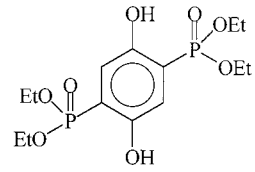

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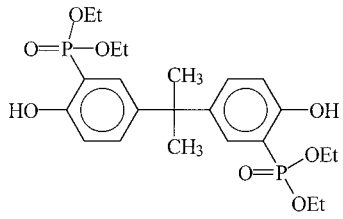

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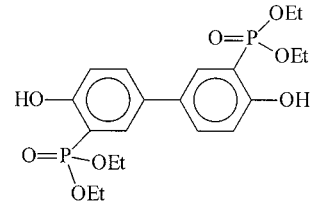

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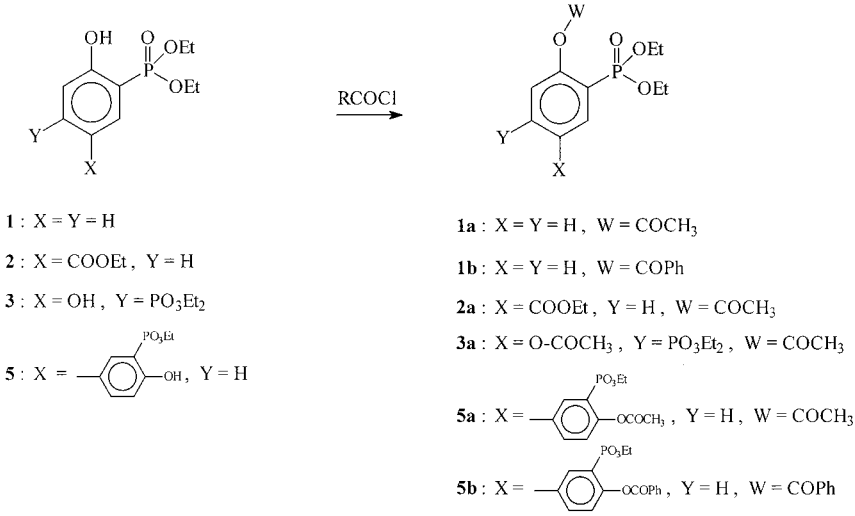
Therefore, this article is devoted to the synthesis and characterization of aryl phosphonates bearing ancillary groups which render them relevant to polymer chemistry and as potential new derivatives for agriculture and pharmacology.

RESULTS AND DISCUSSIONS

Functionalization of the starting molecules **1–3**, and **5** via an electrophilic reaction has been performed by aliphatic and aromatic acyl chlorides in order to esterify the free hydroxyl group and thus trasform these molecules to analogs of acetyl salicylic acids useful as agrochemicals. The reaction proceeds with good yields according to the procedure outlined in Scheme 1.

In the Experimental section of this article, we report on the full characterization, together with the NMR signals, of the synthesized compounds. In the proton NMR spectra all signals are in the expected range of chemical shifts and the substitution pattern in the aromatic ring does not greatly affect their values. On the contrary, the phosphorus NMR spectra are very diagnostic for these compounds. In fact, as an example, a significant change in chemical shift values between the starting phenolic phosphonate (i.e., **2**, $\delta = 21.29$ ppm) and the corresponding acetoxy (**2a**, $\delta = 13.77$ ppm) derivative is observed. This up-field shift is due to the presence of a strong intramolecular hydrogen bond present in compounds **1–5** involving the phenolic OH and the adjacent P=O group, which breaks down after the formation of ester. Analogously, the



SCHEME 1

same trend is observed in all compounds where the free phenolic OH is trasformed into an ester group.

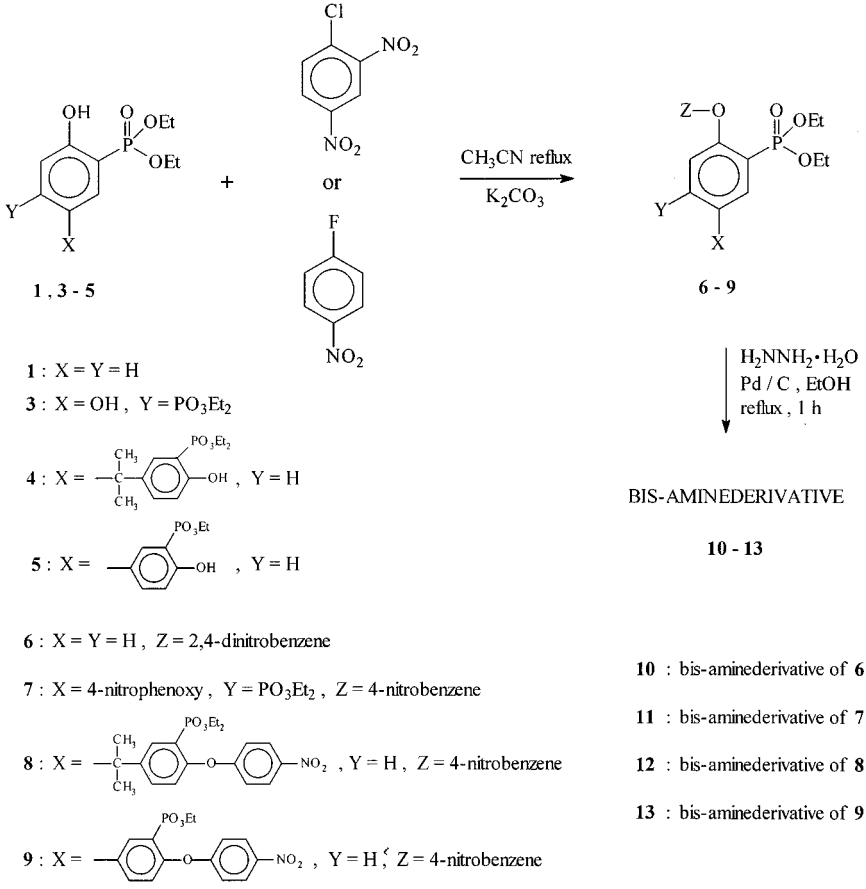
In order to prepare amino compounds containing the phosphonic unit in the molecule, we switched to nucleophilic reactions using substrates **1**, and **3–5** having in mind the idea of using such substrates as preorganized building blocks for the preparation of peculiar macrocyclic receptors and for the synthesis of new polymers incorporating the phosphonic moieties in the chain.

For this purpose we followed a general and convenient procedure, recently reported by us,[16] which enables to obtain in good yields nitrophenoxy derivatives which then can be easily reduced to the corresponding amines.

Condensation of hydroxy-phosphonates **1** and **3–5** with fluoronitrobenzene or 2,4-dinitrochlorobenzene in anhydrous acetonitrile as solvent in the presence of potassium carbonate at refluxing temperature yielded the desidered nitro derivatives as depicted in Scheme 2.

All the nitro compounds prepared were then readily reduced by hydrazine in the presence of a palladium catalyst, according to a published procedure.[17]

The full characterization of these new compounds is given in the Experimental section. The appearance of an AB spin system in the proton NMR spectra, centered down-field typical for aromatic *p*-nitro substitution, which shifted to up-field for the cognate amino derivative, confirm that our synthesis leads to ortho-bis-aminophenoxy phosphonate



SCHEME 2

derivatives. Once again, the difference in ^{31}P chemical shifts between starting ortho-phenolic phosphonates and the corresponding nitro derivatives is very diagnostic (see Experimental section).

In conclusion, a general and convenient synthesis of functionalized aryl phosphonates has been developed using both electrophilic and nucleophilic reactions. The new compounds could be of interest in agrochemistry, in pharmacology, and as building blocks for polycondensates.

EXPERIMENTAL

All reactions were performed under an inert nitrogen atmosphere, and the solvents were refluxed and freshly distilled before use. ^{1}H-,

^{13}C-, ^{31}P-NMR spectra were recorded on a Varian-Inova 500 MHz instrument operating at 500 MHz, 125 MHz, and 200 MHz, respectively, using $SiMe_4$ as internal reference and 85% H_3PO_4 as external reference. 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.

Acetonitrile was dried by distillation from calcium hydride under nitrogen. Compound **1**, and phenols **3** and **4** were prepared according to published procedure.[12,18] Unless otherwise stated, commercial chemicals were used as supplied.

General Synthetic Procedure of Functionalized Ortho-Acetyl Derivatives

In a three-necked round flask equipped with condenser, magnetic stirring bar, nitrogen inlet and a dropping funnel, was dissolved a phenol (**1–3**, **5**, 5 meq) in 50 mL of anhydrous THF and 10 meq of triethylamine. Then 10 meq of acetyl or benzyl chloride were added by syringe. The reaction mixture was stirred for 3 h and the solvent evaporated to give an oil, to which was added $CHCl_3$ and washed with 1 N solution of NaOH and then several times with water. The organic solution dried and evaporated to give an oil, which was purified by column chromatography (SiO_2; cyclohexane:ethylacetate 5:5) to give the corresponding derivatives.

General Synthetic Procedure of Functionalized Bis-*p*-Nitrophenoxy Derivatives

In a three-necked round flask equipped with condenser, magnetic stirring bar, nitrogen inlet and a dropping funnel, were placed anhydrous K_2CO_3 (6.9 g, 50 mmol), a functionalized phenol (**1**, **3–5**, 10 meq) and freshly distilled anhydrous CH_3CN (100 mL). The reaction mixture was heated to refluxing temperature; to this stirred suspension a solution of 1-fluoro-4-nitrobenzene (11 meq) in freshly distilled CH_3CN (25 mL) was added over a period of 0.5 h from a dropping funnel. After the addition was completed, the reaction mixture was refluxed and stirred overnight, filtered, and the solvent was evaporated to give a powder, which was collected with hexane by filtration and washed several times with water. The product was purified by crystallization from hexane/ethylacetate to give **6–9** as pale yellow crystals.

General Synthetic Procedure of Functionalized Bis-*p*-Aminophenoxy Derivatives

To a solution (EtOH 30 mL) of bis-*p*-nitrophenoxy derivative (5 meq) synthesized as described above was added 10% Pd/C and heated to refluxing temperature, then hydrazine monohydrate (1 mL, 20 meq) was added over a period of 0.5 h. Refluxing was continued for a period of 1 h, after which the catalyst was filtered off and the solvent evaporated at reduced pressure. The oily residue was crystallized from a mixture of hexane/ethylacetate, to give the corresponding amine as white crystals.

Compound (**2**). ^{1}H-NMR ($CDCl_3$, ppm) δ: 10.76 (s, 1H, OH), 8.09 (m, 2H, ArH), 6.96 (m, 1H, ArH), 4.33 (q, 2H, $^3J_{HH} = 7.2$ Hz, $COO\underline{CH_2}CH_3$), 4.13 (m, 4H, $PO\underline{CH_2}CH_3$), 1.36 (t, $^3J_{HH} = 7.0$ Hz, 3H, $COOCH_2\underline{CH_3}$), 1.31 (t, 6H, $POCH_2\underline{CH_3}$, $^3J_{HH} = 7.0$ Hz). ^{13}C-NMR ($CDCl_3$, ppm) δ: 165.63, 165.46, 136.17 (d, $J_{CP} = 2.0$ Hz), 134.18 (d, $J_{CP} = 6.95$ Hz), 122.06 (d, $J_{CP} = 13.6$ Hz), 117.62 (d, $J_{CP} = 11.55$ Hz), 108.99 (d, $^1J_{CP} = 180.7$ Hz), 63.02 (d, $J_{CP} = 6.9$ Hz), 60.92, 16.11 (d, $J_{CP} = 6.6$ Hz), 14.28. ^{31}P-{H}-NMR ($CDCl_3$): 21.29 ppm; FAB-MS: *m/z*: 345 (30%, M + H^+), 303 (100%). White crystals, m.p. 48–49°C, yield 78%.

Compound (**5**). ^{1}H-NMR 10.26 (s, 2H, ArOH), 7.61 (dd, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 2.2$ Hz, 2H, ArH), 7.48 (dd, $^3J_{HP} = 14.8$ Hz, $^4J_{HH} = 2.2$ Hz, 2H, ArH), 7.04 (dd, $^3J_{HH} = 8.6$ Hz, $J_{HP} = 6.8$ Hz, 2H, ArH), 4.15 (m, 8H), 1.36 (t, $^3J_{HH} = 7.0$ Hz). ^{13}C-NMR ($CDCl_3$, ppm) δ: 161.32 (d, $J_{CP} = 7.1$ Hz), 133.49 (d, $J_{CP} = 13.4$ Hz), 131.56 (d, $J_{CP} = 13.4$ Hz), 129.06 (d, $J_{CP} = 6.6$ Hz), 118.23 (d, $J_{CP} = 12.7$ Hz), 114.11 (d, $^1J_{CP} = 179.1$ Hz), 63.84 (d, $J_{CP} = 4.8$ Hz), 16.18 (d, $J_{CP} = 6.6$ Hz). ^{31}P-{H}-NMR ($CDCl_3$): 22.36 ppm; FAB-MS: *m/z*: 459.4 (100%, M + H^+), 481 (20%). White crystals, m.p. 165–167°C; yield 75%.

Compound (**1a**). ^{1}H-NMR ($CDCl_3$, ppm) δ: 7.41 (t, $^3J_{HH} = 7.5$ Hz, 1H, ArH), 7.34 (dd, $^3J_{HH} = 7.5$ Hz, $^3J_{HP} = 14.5$ Hz, 1H, ArH), 6.93 (t, $^3J_{HH} = 7.5$ Hz, 1H, ArH), 6.89 (m, 1H, ArH), 4.06 (m, 4H, $PO\underline{CH_2}CH_3$), 2.05 (s, 3H, $COOCH_3$), 1.29 (t, 6H, $POCH_2\underline{CH_3}$, $^3J_{HH} = 7.0$ Hz.). FAB-MS: *m/z*: 273 (100%, M + H^+). Oil, yield 58%.

Compound (**1b**). ^{1}H-NMR ($CDCl_3$, ppm) δ: 8.24 (d, $^3J_{HH} = 8.0$ Hz, 2H, ArH), 8.01 (dd, $^3J_{HH} = 8.0$ Hz, $^3J_{HP} = 9.5$ Hz, 1H, ArH), 7.64 (t, $^3J_{HH} = 7.5$ Hz, 2H, ArH), 7.51 (t, $^3J_{HH} = 7.5$ Hz, 2H, ArH), 7.37 (m, 1H, ArH), 7.31 (m, 1H, ArH), 4.03 (m, 4H, $PO\underline{CH_2}CH_3$), 1.19 (t, 6H, $POCH_2\underline{CH_3}$, $^3J_{HH} = 7.0$ Hz). FAB-MS: *m/z*: 335 (100%, M + H^+). Oil, yield 55%.

Compound (**2a**). ^{1}H-NMR ($CDCl_3$, ppm) δ: 8.57 (dd, $^4J_{HH} = 2.2$ Hz, $^3J_{HP} = 14.2$ Hz, 1H, ArH), 8.25 (dd, $^3J_{HH} = 8.4$ Hz, $^4J_{HH} = 2.2$ Hz, 1H, ArH), 7.22 (dd, $^3J_{HH} = 8.4$ Hz, $J_{HP} = 5.6$ Hz, 1H, ArH), 4.38 (q, 2H, $^3J_{HH} = 7.0$ Hz, $COO\underline{CH_2}CH_3$), 4.11 (m, 4H, $PO\underline{CH_2}CH_3$), 2.35 (s, 3H, $COOCH_3$), 1.38 (t, $^3J_{HH} = 7.0$ Hz, 3H, $COOCH_2\underline{CH_3}$), 1.31 (t, 6H, $POCH_2\underline{CH_3}$, $^3J_{HH} = 7.0$ Hz). ^{13}C-NMR ($CDCl_3$, ppm) δ: 168.84,

164.94, 155.69, 136.16 (d, $J_{CP} = 7.9$ Hz), 135.10 (d, $J_{CP} = 2.3$ Hz), 128.34 (d, $J_{CP} = 13.8$ Hz), 124.10 (d, $J_{CP} = 9.3$ Hz), 121.99 (d, $^1J_{CP} = 186$ Hz), 62.55 (d, $J_{CP} = 5.3$ Hz), 61.39, 20.99, 16.21 (d, $J_{CP} = 6.6$ Hz), 14.24. ^{31}P-{H}-NMR ($CDCl_3$): 13.77 ppm; FAB-MS: *m/z*: 345 (30%, M + H^+), 303 (100%).

Compound (**3a**). ^{1}H-NMR ($CDCl_3$, ppm) δ: 7.63 (m, 2H, ArH), 4.10 (m, 8H, $PO\underline{CH_2}CH_3$), 2.32 (s, 6H, $COOCH_3$), 1.31 (t, $^3J_{HH} = 7.0$ Hz, 12H, $POCH_2\underline{CH_3}$). ^{31}P-{H}-NMR ($CDCl_3$): 11.98 ppm; FAB-MS: *m/z*: 467.3 (100%, M + H^+). White crystals, m.p. 150–153°C, yield 50%.

Compound (**5a**). ^{1}H-NMR ($CDCl_3$, ppm) δ: 7.91 (m, 2H, ArH), 7.54 (d, $^3J_{HP} = 14.2$ Hz, 2H, ArH), 7.18 (d, $^3J_{HH} = 7.2$ Hz, 2H, ArH), 4.10 (m, 8H, $PO\underline{CH_2}CH_3$), 2.22 (s, 6H, $COOCH_3$), 1.27 (t, 12H, $^3J_{HH} = 7.0$ Hz, $POCH_2\underline{CH_3}$). ^{31}P-{H}-NMR ($CDCl_3$): 16.91 ppm, FAB-MS: *m/z*: 543.5 (100%, M + H^+).

Compound (**5b**). ^{1}H-NMR ($CDCl_3$, ppm) δ: 7.81 (m, 4H, ArH), 7.51 (d, $^3J_{HP} = 13.9$ Hz, 2H, ArH), 7.21 (d, $^3J_{HH} = 8.2$ Hz, 4H, ArH), 7.15 (m, 3H, ArH), 7.03 (m, 3H, ArH), 4.05 (m, 8H, $PO\underline{CH_2}CH_3$), 1.24 (t, $^3J_{HH} = 7.0$ Hz, 12H, $POCH_2\underline{CH_3}$). ^{31}P-{H}-NMR ($CDCl_3$): 17.21 ppm; FAB-MS: *m/z*: 667.4 (100%, M + H^+).

Compound (**6**). ^{1}H-NMR ($CDCl_3$, ppm) δ: 8.86 (d, $^4J_{HH} = 2.5$ Hz, 1H, ArH), 8.30 (dd, $^3J_{HH} = 9.0$ Hz, $^4J_{HH} = 2.5$ Hz, 1H, ArH), 8.03 (dd, $^3J_{HH} = 7.5$ Hz, $^3J_{HP} = 14.5$ Hz, 1H, ArH), 7.68 (t, $^3J_{HH} = 7.5$ Hz, 1H, ArH), 7.45 (tt, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 2.5$ Hz, 1H, ArH), 7.16 (t, $^3J_{HH} = 7.5$ Hz, 1H, ArH), 6.92 (d, $^3J_{HH} = 9$ Hz, 1H, ArH), 4.08 (m, 4H, $PO\underline{CH_2}CH_3$), 1.21 (t, 6H, $POCH_2\underline{CH_3}$, $^3J_{HH} = 7.0$ Hz). FAB-MS: *m/z*: 397.2 (100%, M + H^+), 793.2 (2M + H^+ 45%). Yellow crystals, m.p. 45–47°C, yield 75%.

Compound (**7**). ^{1}H-NMR ($CDCl_3$, ppm) δ: 8.26 (d, $^3J_{HH} = 9.0$ Hz, 4H, ArH), 7.65 (m, 2H, ArH), 7.06 (d, $^3J_{HH} = 9.0$ Hz, 4H, ArH), 4.11 (m, 8H, $PO\underline{CH_2}CH_3$), 1.19 (t, 12H, $POCH_2\underline{CH_3}$, $^3J_{HH} = 7.0$ Hz). ^{31}P-{H}-NMR ($CDCl_3$): 11.36 ppm; FAB-MS: *m/z*: 625.5 (100%, M + H^+). Yellow crystals, m.p. 156–158°C, yield 72%.

Compound (**8**). ^{1}H-NMR ($CDCl_3$, ppm) δ: 8.21 (d, $^3J_{HH} = 9.2$ Hz, 4H, ArH), 7.89 (dd, $^3J_{HP} = 15.4$ Hz, $^4J_{HH} = 2.5$ Hz, 2H, ArH), 7.39 (dd, $^3J_{HH} = 8.8$ Hz, $^4J_{HH} = 2.5$ Hz, 2H, ArH), 7.02 (d, $^3J_{HH} = 79.2$ Hz, 4H, ArH), 6.96 (d, $^3J_{HH} = 8.8$ Hz, 2H, ArH), 4.04 (m, 8H, $PO\underline{CH_2}CH_3$), 1.77 (s, 6H, CH_3), 1.18 (t, 6H, $POCH_2\underline{CH_3}$, $^3J_{HH} = 7.0$ Hz). ^{13}C-NMR ($CDCl_3$, ppm) δ: 162.87, 154.36, 146.96 (d, $J_{CP} = 13.2$ Hz), 142.95, 133.18 (d, $J_{CP} = 7.9$ Hz), 133.04, 125.83, 121.61 (d, $^1J_{CP} = 188.1$ Hz), 121.13 (d, $J_{CP} = 9.9$ Hz), 117.32, 62.38 (d, $J_{CP} = 6.0$ Hz), 42.85, 30.79, 16.24 (d, $J_{CP} = 6.4$ Hz). ^{31}P-{H}-NMR ($CDCl_3$): 14.99 ppm. FAB-MS: *m/z*: 743.7 (100%, M + H^+). Yellow crystals, m.p. 80–82°C, yield 55%.

Compound (**9**). ^{1}H-NMR 8.24 (m, 6H, ArH), 7.83 (dd, $^3J_{HH} = 8.2$ Hz, $^4J_{HH} = 2.2$ Hz, 2H, ArH), 7.18 (dd, $^3J_{HH} = 8.2$ Hz, $J_{HP} = 6.8$ Hz, 2H,

ArH), 7.08 (d, $^3J_{HH}$ = 8.6 Hz, 4H, ArH), 4.15 (m, 8H), 1.23 (t, $^3J_{HH}$ = 7.0 Hz); ^{31}PNMR: δ 14.28 ppm. White crystals, m.p. 158–160°C, yield 72%.

Compound (**10**). ^{1}H-NMR ($CDCl_3$, ppm) δ: 7.75 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 14.5 Hz, 1H, ArH), 7.38 (t, $^3J_{HH}$ = 7.5 Hz, 1H, ArH), 7.04 (m, 1H, ArH), 6.86 (t, $^3J_{HH}$ = 7.5 Hz, 1H, ArH), 6.82 (d, $^3J_{HH}$ = 8.5 Hz, 1H, ArH), 6.11 (d, $^4J_{HH}$ = 2.5 Hz, 1H, ArH), 6.05 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.5 Hz, 1H, ArH), 4.21 (m, 4H, $PO\underline{CH_2}CH_3$), 3.6 (brs, 4H, $ArNH_2$), 1.36 (t, 6H, $POCH_2\underline{CH_3}$, $^3J_{HH}$ = 7.0 Hz). ^{13}C-NMR ($CDCl_3$, ppm) δ: 160.64, 144.76, 140.49, 134.05 (d, J_{CP} = 2.0 Hz), 133.98 (d, J_{CP} = 6.87 Hz), 133.90, 123.32, 121.48 (d, J_{CP} = 14.15 Hz), 117.12 (d, $^1J_{CP}$ = 189.4 Hz), 114.15 (d, J_{CP} = 8.63 Hz), 104.62, 103.04, 62.37 (d, J_{CP} = 6 Hz), 16.40 (d, J_{CP} = 6.4 Hz). ^{31}P-{H}-NMR ($CDCl_3$): 17.46 ppm. FAB-MS: *m/z*: 337.3 (100%, M + H^+). Purple crystals, m.p. 126–128°C, yield 60%.

Compound (**11**). ^{1}H-NMR ($CDCl_3$, ppm) δ: 7.31 (m, 2H, ArH), 6.84 (d, $^3J_{HH}$ = 8.5 Hz, 4H, ArH), 6.65 (d, $^3J_{HH}$ = 8.5 Hz, 4H, ArH), 4.10 (m, 8H, $PO\underline{CH_2}CH_3$), 3.5 (brs, 4H, $ArNH_2$), 1.23 (t, 12H, $POCH_2\underline{CH_3}$, $^3J_{HH}$ = 7.0 Hz). ^{13}C-NMR ($CDCl_3$, ppm) δ: 154.51, 148.39, 143.12, 124.28 (d, $^1J_{CP}$ = 185.1 Hz), 122.91 (d, J_{CP} = 9.25 Hz), 120.74, 116.26, 62.64 (d, J_{CP} = 6.1 Hz), 16.23 (d, J_{CP} = 6.8 Hz). ^{31}P-{H}-NMR ($CDCl_3$): 13.99 ppm; FAB-MS: *m/z*: 565.5 (100%, M + H^+). White crystals, m.p. 190–192°C, yield 68%.

Compound (**12**). ^{1}H-NMR ($CDCl_3$, ppm) δ: 7.82 (dd, $^3J_{HP}$ = 15.1 Hz, $^4J_{HH}$ = 2.5 Hz, 2H, ArH), 7.33 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.5 Hz, 2H, ArH), 7.01 (d, $^3J_{HH}$ = 9.0 Hz, 4H, ArH), 6.91 (d, $^3J_{HH}$ = 8.5 Hz, 2H, ArH), 6.68 (d, $^3J_{HH}$ = 9.0 Hz, 4H, ArH), 4.08 (m, 8H, $PO\underline{CH_2}CH_3$), 3.57 (brs, 4H, $ArNH_2$), 1.70 (s, 6H, CH_3), 1.16 (t, 6H, $POCH_2\underline{CH_3}$, $^3J_{HH}$ = 7.0 Hz). FAB-MS: *m/z*: 683.7 (100%, M + H^+).

Compound (**13**). ^{1}H-NMR 8.05 (dd, $^3J_{HP}$ = 15.2 Hz, $^4J_{HH}$ = 2.2 Hz, 2H, ArH), 7.58 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.2 Hz, 2H, ArH), 6.90 (d, $^3J_{HH}$ = 8.6 Hz, 4H, ArH), 6.83 (dd, $^3J_{HH}$ = 8.4 Hz, J_{HP} = 6.8 Hz, 2H, ArH), 6.70 (d, $^3J_{HH}$ = 8.6 Hz, 4H, ArH), 4.20 (m, 8H), 1.34 (t, $^3J_{HH}$ = 7.0 Hz); ^{31}P 16.35 ppm. FAB-MS: *m/z*: 641.3 (100%, M + H^+). White crystals, m.p. 226–227°C, yield 75%.

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