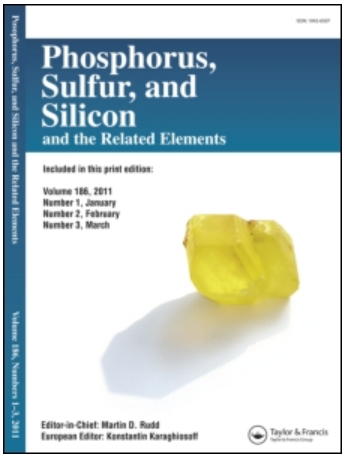

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PREPARATIONS AND PROPERTIES OF SOME PHOSPHORUS-CONTAINING DIALDEHYDES AND DIALCOHOLS

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PREPARATIONS AND PROPERTIES OF SOME PHOSPHORUS- CONTAINING DIALDEHYDES AND DIALCOHOLS

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Di(4-formyl-2-methoxyphenyl)phosphates (DFMPP) were synthesized by the condensation of vanillin with phosphoryldichlorides. The di(4-hydroxymethyl-2-methoxyphenyl)phosphates (DHMPP) were prepared by the reduction of DFMPP with potassium borohydride. The ^{31}P-^{1}H coupling in DFMPP (compounds 1a-h) was investigated and the splitting of the ^{31}P signal by the ^{1}H nuclei was observed only with the alkyl DFMPP (1a-e). In the non-decoupled ^{31}P spectra a quartet at −11.3 ppm was seen for 1a (**P**-OC**H**$_3$) with J_{PH}= 11.4 Hz, and a triplet for 1b, 1c, 1d and 1e respectively (1b, **P**-OC**H**$_2$CH$_3$, δ= − 12.3 ppm, J_{PH}=8.4 Hz; 1c, **P**-OC**H**$_2$CH$_2$CH$_3$, δ= − 12.6 ppm, J_{PH}=7.1 Hz; 1d, **P**-OC**H**$_2$CH$_2$CH$_2$CH$_3$, δ= − 12.9 ppm, J_{PH}=8.4 Hz and 1e, **P**-OC**H**$_2$CH$_2$Cl, δ= − 13.0 ppm, J_{PH}=8.1Hz).

Keywords: Phosphorus-containing dialdehyde and dialcohol; condensation; reduction; coupling

INTRODUCTION

As biodegradable materials polyphosphoesters have promising applications in drug controlled release and tissue engineering[1]. In our previous papers, several series of polyphosphoesters were prepared by the polycondensation of phosphoryldichlorides with dihydroxy monomers[2,3]. Recently, the polycondensation reaction of phosphorus-containing dialdehydes with diamines and the polyaddition reaction of phosphorus-containing dialcohols with diisocyanates were also tried in polyphosphoesters

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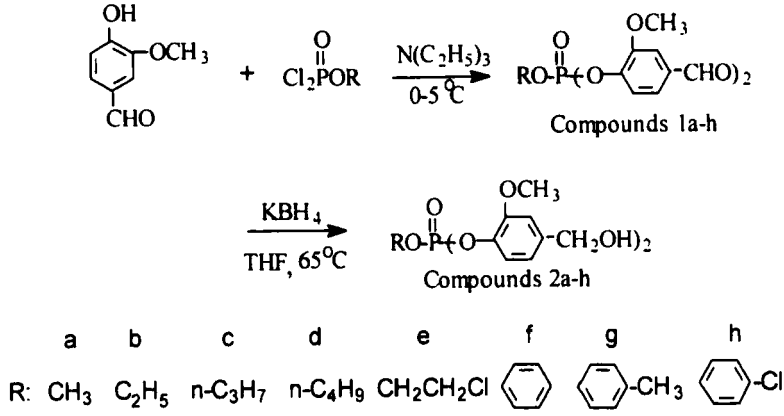
preparation in our lab. In this paper the preparations and properties of some novel phosphorus-containing dialdehydes and dialcohols will be presented. The synthetic route is shown in Scheme I.

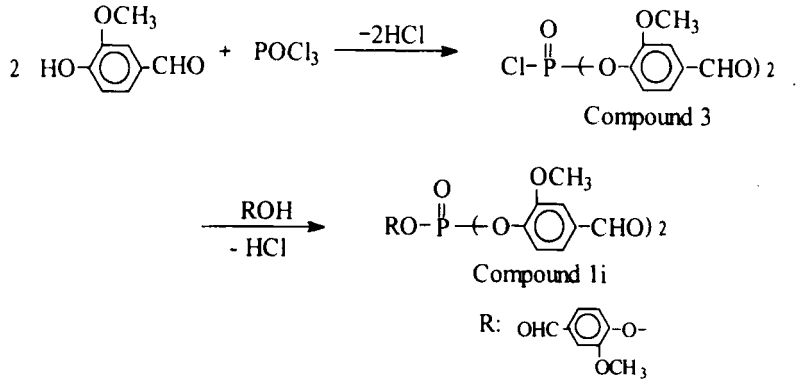


SCHEME I

RESULTS AND DISCUSSION

Eight di(4-formyl-2-methoxyphenyl)phosphates (DFMPP, compounds la-h) were synthesized conveniently by the reaction of vanillin with some phosphoryldichlorides in a molar ratio of 2 to 1 in the presence of triethylamine (Scheme I). In our first approach, an alternate route was used to prepare DFMPP with phosphorylchloride and vanillin as starting materials (Scheme II). It was thought that by Scheme II various DFMPP would result from the intermediate compound 3. However, the attempt to purify compound 3 was unsuccessful, and even a one-pot reaction (Scheme II) gave small amounts of 1a-h. When the molar ratio of $POCl_3$ and vanillin was 1 to 3, compound 1i was obtained in a yield of 85%.

The yields of the reactions of vanillin with several phosphoryldichlorides ranged from 49 to 92 percent (Table I). The differences in the yields were induced mainly by the variation and size of the R group. The yields of the three aryl phosphoryldichlorides (49–65%) were lower than the alkyl ones (74 – 92%). The longer the carbon chain, the lower the yield



SCHEME II

(group R, Yield(%): CH_3, 92; C_2H_5, 88; n-C_3H_7, 87; n-C_4H_9, 74). Some experimental data for DFMPP are listed in Table I.

TABLE I Experimental Data of Compounds 1a-h

Comp.	*Group R*	*m.p. (°C)*	*Yield (%)*	*^{31}P NMR*[a]	*^{1}H NMR*[b] *-CHO*	*IR (KBr, ν cm^{-1})*
1a	CH_3	72–73	92	−11.3(q)	9.84	1702,1190,1115
1b	C_2H_5	86–88	88	−12.3(t)	9.84	1688,1194,1116
1c	n-C_3H_7	88	87	−12.6(t)	9.84	1689,1196,1117
1d	n-C_4H_9	semi-solid	74	−12.9(t)	9.84	1701,1192,1112
1e	2-C_2H_4Cl	67	82	−13.0(t)	9.84	1694,1198,1115
1f	C_6H_5	61–62	65	−18.2(s)	9.84	1702,1192,1119
1g	p-$C_6H_4CH_3$	79–80	61	−18.0(s)	9.84	1686,1189,1130
1h	p-C_6H_4Cl	95–96	49	−18.0(s)	9.84	1691,1195,1129

a.$CDCl_3$,85%H_3PO_4, δ ppm; non-decoupled.
b.$CDCl_3$, TMS, δ ppm.

It is well known that a formyl group can be smoothly reduced to a hydroxymethyl group by borohydrides. Therefor, the reduction reaction of DFMPP by potassium borohydride was used to prepare di(4-hydroxymethyl-2-methoxyphenyl)phosphates (DHMPP, compounds 2a-h). The

chemical changes from the formyl groups in DFMPP to the hydroxymethyl groups in DHMPP were identified by ^1H NMR and IR methods. As expected, two proton signals of the hydroxymethyl group (**H**O**CH**$_2$-) appeared in the ^1H NMR spectra at 2.5–3.90 ppm (O**H**) and at 4.42–4.50 ppm (C**H**$_2$) (Table II). The signal at 9.84 ppm was no longer observed (Table I). The vibration spectra of DHMPP showed signals at 3329–3409 cm^{-1} (OH), but showed no signals around 1690 cm^{-1}(CHO). The experimental data of compounds 2a-h are shown in Table II.

TABLE II Experimental Data of Compounds 2a-h

Comp.	*Group R*	*Physical State*	*Yield (%)*	*^{31}P NMR*[a]	*^1H NMR*[b] **H**O**CH**$_2$-	*IR (KBr, υ cm^{-1})*
2a	CH_3	semi-solid	82	−11.5	2.50(s), 4.50(s)	3392,1190,1120
2b	C_2H_5	semi-solid	73	−10.8	3.41(s), 4.49(s)	3377,1190,1120
2c	n-C_3H_7	semi-solid	74	−10.7	3.43(b), 4.50(s)	3329,1196,1120
2d	n-C_4H_9	oil	67	−10.8	3.90(s), 4.48(s)	3409,1197,1121
2e	2-C_2H_4Cl	oil	70	−11.1	3.77(s), 4.48(s)	3407,1196,1120
2f	C_6H_5	oil	68	−16.3	3.63(b), 4.44(s)	3411,1192,1120
2g	p-$C_6H_4CH_3$	oil	63	−16.5	2.99(s), 4.46(s)	3390,1191,1120
2h	p-C_6H_4Cl	oil	57	−16.2	3.17(s), 4.42(s)	3384,1197,1121

a.$CDCl_3$, 85%H_3PO_4, δ ppm.
b.$CDCl_3$, TMS, δ ppm.

Generally, water, methanol and tetrahydrofuran (THF) are good solvents for the reduction of formyl groups with potassium borohydride. In practice it was found that the reduction of DFMPP in water or in methanol gave no DHMPP. Only with THF as solvent did the reduction go smoothly. The reaction velocity was enhanced with increasing temperature. As an example, the experimental results of the reduction of bis(4-formyl-2-methoxyphenyl) ethyl phosphate (compound 1b) are given out in Table III. The molar ratio of Ib and potassium borohydride was 2:3 in all cases. With the yield of 2b around 80% the reduction time of 1b in THF was 36 hours at 25 °C, but it decreased to 24 hours at 40 °C and to 12 hours at 65 °C.

The range of ^{31}P chemical shifts of DFMPP was from −11.3 to −18.2 ppm, but that of DHMPP was from −10.7 to −16.5 ppm. Except that the

chemical shift of methyl DFMPP (1a,-11.3 ppm) was lower than that of methyl DHMPP (2a, −11.5 ppm), each ^{31}P chemical shift of all other DFMPP (1b–h) was higher than that of the reduced corresponding (2b–h) respectively with a difference between 1.5–2.1 ppm (Table I and Table II). Obviously, the screening effect to phosphorus by the formyl group at substituted benzene ring was stronger than that by the hydroxymethyl group.

TABLE III Experimental Results of the Reduction of 1b by Potassium Borohydride

No.	*Solvent*	*Temperature (°C)*	*Time (h.)*	*Yield of 2b(%)*
1	H_2O	25	36	No
2	CH_3OH	25	36	No
3	THF	25	36	80
4	THF	40	24	75
5	THF	65	12	88

The coupling between the ^{31}P and ^{1}H nuclei in DFMPP was investigated and only the spin-spin splitting between ^{31}P nucleus and ^{1}H nuclei in group R was observed when R was alkyl. In the non-decoupled ^{31}P spectra a quartet at -11.3 ppm was for 1a (P-O-CH_3) with J_{PH}=11.4 Hz, and a triplet for 1b, 1c, 1d and 1e respectively (With R being -CH_2CH_3(1b, δ=-12.3 ppm, J_{PH}=8.4 Hz), -$CH_2CH_2CH_3$(1c, δ= − 12.6 ppm, J_{PH}=7.1 Hz), -$CH_2CH_2CH_2CH_3$(1d, δ= − 12.9 ppm, J_{PH}=8.4 Hz), and -CH_2CH_2Cl(1e, δ= − 13.0 ppm, J_{PH}=8.1Hz)).

The splitting of ^{1}H peaks of methyl and methylene groups in group R in DFMPP by the ^{31}P nucleus was also studied. In 1a there was only an atom (oxygen atom) between the methyl group and phosphorus atom (CH_3-O-P), and the proton signal of methyl group was split into a doublet at 4.02 ppm by the ^{31}P nucleus. The coupling constant, J_{HP}, was 11.1 Hz. In 1b (R= CH_3CH_2) the methyl group was split into a triplet by methylene group, and which was further split into a doublet by the ^{31}P nucleus with J_{HP} being 1.36 Hz which was much smaller than that in 1a. However, no coupling by ^{31}P nucleus to ^{1}H nuclei of methyl group was observed when R was n-propyl group (1c) and the signal of ^{1}H nuclei of methyl group was just split into a triplet by its adjacent methylene group (Fig. 1).

The splitting of methylene groups in 1b, 1c and 1e by ^{31}P nucleus is shown in Fig. 2.

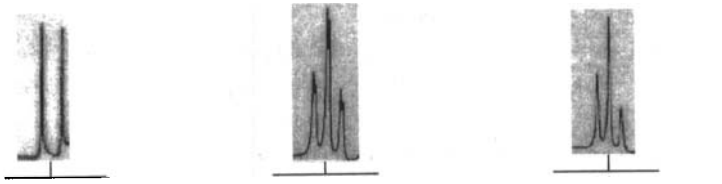


FIGURE 1 Splitting of ^{1}H peaks of methyl group in 1a–c by ^{31}P nucleus

In 1b the ^{1}H peaks of methylene group were two quartets; the methylene group was coupled not only by the methyl group but also by the phosphorus atom. The coupling constant J_{HP} was 8.3 Hz. The ^{1}H signal of methylene group linked with oxygen atom which was adjacent to phosphorus in 1c and 1e (R=$ClCH_2CH_2$) was two triplets respectively. Obviously, the splitting of triplet was induced by the ^{31}P nucleus.

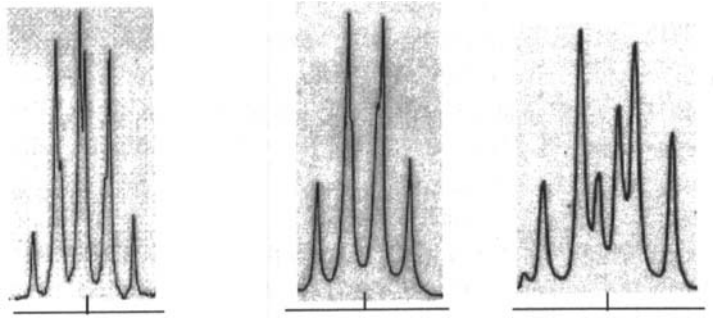


FIGURE 2 Splitting of ^{1}H peaks of methylene group in 1b, 1c and 1e by ^{31}P nucleus

EXPERIMENTAL

^{1}H NMR ($CDCl_3$, TMS) and ^{31}P NMR ($CDCl_3$, 85%H_3PO_4) spectra were recorded on JEOL FX 90Q or Bruker ARX-500 spectrometer, FT-IR spec-

tra were recorded on a Nicolet-170SX spectrophotometer. The elemental analyses were performed by Carlo Erba 1106 instrument. All reactions were performed under a nitrogen atmosphere. Vanillin was purchased from Shuangxi Flavor Factory, Shanghai, China. The phosphoryldichlorides were synthesized by literature methods.

General procedure for the synthesis of di(4-formyl-2-methoxyphenyl)phosphates (DFMPP, compounds 1a-h)

A typical procedure for the synthesis of compounds 1a-h is described below with the preparation of bis(4-formyl-2-methoxyphenyl) ethyl phosphate (1b) as an example.

Vanillin (3.04 g, 20 mmol) was dissolved in 60 ml of anhydrous ether, and triethylamine (2.8 ml, 20 mmol) was added. Then a solution of ethyl phosphoryldichloride (1.63g, 10 mmol) in ether (10 ml) was dropped in slowly at 3–5 °C under stirring. After no vanillin was detected by TLC (2 volumes of petroleum ether/1 volume of ethyl acetate) the solid mixture of product and amine salt was filtered off and washed several times with distillated water and ether. Bis(4-formyl-2-methoxyphenyl) ethyl phosphate (1b) was crystallized from the mixed chloroform and petroleum ether (1:1) and the yield was 88%.

The experimental data of 1b: m.p. 86–88 °C. Anal. Calcd. for $C_{18}H_{19}O_8P$: C, 54.82; H, 4.82. Found: C, 54.82; H, 5.00. ^{31}P NMR (Non-decoupled): δ −12.3 ppm, (t, J_{PH}=8.4 Hz). ^1H NMR: δ 1.41 (3H, 2t, J_{HH}=6.8 Hz, J_{HP}=1.36 Hz, $C\underline{H}_3CH_2$); δ 3.87 (6H, s, $2C\underline{H}_3OAr$); δ 4.45 (2H, 2q, J_{HH}=6.8 Hz, J_{HP}=8.3 Hz, $C\underline{H}_2OP$); δ 7.29 (6H, m, $2C_6\underline{H}_3$); δ 9.84 (2H, s, $2C\underline{H}O$) [ppm]. IR: ν 1688, 1592, 1504, 1272, 1194, 1116, 1027, 957 cm^{-1}.

Bis(4-formyl-2-methoxyphenyl) methyl phosphate (1a): m.p. 72–73 °C. Anal. Calcd. for $C_{17}H_{17}O_8P$: C, 53.68; H, 4.47. Found: C, 53.61; H, 4.88. ^{31}P NMR Non-decoupled): δ −11.3 ppm, (q, J_{PH}=11.4 Hz). ^1H NMR: δ 3.90 (6H, s, $2C\underline{H}_3OAr$); δ 4.02 (3H, d, J_{HP}=11.1 Hz, $C\underline{H}_3OP$); δ 7.32 (6H, d, $2C_6\underline{H}_3$); δ 9.84 (2H, s, $2C\underline{H}O$) [ppm]. IR: ν 1702, 1598, 1507, 1275, 1190, 1115, 1029, 947 cm^{-1}.

Bis(4-formyl-2-methoxyphenyl) n-propyl phosphate (1c): m.p. 88 °C. Anal. Calcd. for $C_{19}H_{21}O_8P$: C, 55.88; H, 5.15. Found: C, 55.38; H, 5.38. ^{31}P NMR Non-decoupled): δ −12.6 ppm, (t, J_{PH}=7.1 Hz). ^1H NMR: δ 0.93 (3H, t, J_{HH}=5.2 Hz, $C\underline{H}_3CH_2$); δ 1.74 (2H, m, J_{HH}=5.2 Hz, $CH_3C\underline{H}_2$); δ

3.87 (6H, s, $2C\underline{H}_3OAr$); δ 4.27 (2H, 2q, J_{HH}=5.2 Hz, J_{HP}=8.5 Hz, $C\underline{H}_2OP$); δ 7.29 (6H, 2s, $2C_6\underline{H}_3$); δ 9.84 (2H, s, $2C\underline{H}O$) [ppm]. IR: ν 1689, 1593, 1509, 1274, 1196, 1117, 1021, 940 cm^{-1}.

Bis(4-formyl-2-methoxyphenyl) n-butyl phosphate (1d): Semi-solid. Anal. Calcd. for $C_{20}H_{23}O_8P$: C, 56.87; H,5.45. Found: C, 57.14; H, 5.15. ^{31}P NMR (Non-decoupled): δ −12.9 ppm, (t, J_{PH}=8.4 Hz). ^1H NMR: δ 0.9 (3H, t, $C\underline{H}_3CH_2$); δ 1.59 (4H, m, $CH_3C\underline{H}_2C\underline{H}_2$); δ 3.87 (6H, s, $2C\underline{H}_3OAr$); δ 4.29 (2H, m, $C\underline{H}_2OP$); δ 7.29 (6H, s, $2C_6\underline{H}_3$); δ 9.84 (2H, s, $2C\underline{H}O$) [ppm]. IR: ν 1701, 1593, 1507, 1280, 1192, 1112, 1031, 971 cm^{-1}.

Bis(4-formyl-2-methoxyphenyl) 2-chloroethyl phosphate (1e): m.p. 67°C. Anal. Calcd. for $C_{18}H_{18}ClO_8P$: C, 50.41; H, 4.20. Found: C, 50.86; H, 4.35. ^{31}P NMR (Non-decoupled): δ −13.0 ppm, (t, J_{PH}=8.1 Hz). ^1H NMR: δ 3.75 (2H, t, J_{HH}=5.7 Hz, $ClC\underline{H}_2$); δ 3.87 (6H, s, $2C\underline{H}_3OAr$); δ 4.50 (2H, 2t, J_{HH}=5.7 Hz, J_{HP}=8.7 Hz, $C\underline{H}_2OP$); δ 7.29 (6H, 2s, $2C_6\underline{H}_3$); δ 9.84 (2H, s, $2C\underline{H}O$) [ppm]. IR: ν 1694, 1595, 1507, 1287, 1198, 1115, 1029, 953 cm^{-1}.

Bis(4-formyl-2-methoxyphenyl) phenyl phosphate (1f): m.p. 61–62°C. Anal. Calcd. for $C_{22}H_{19}O_8P$: C, 59.73; H, 4.30. Found: C, 59.73; H, 4.63. ^{31}P NMR (Non-decoupled): δ −18.2 ppm, (s,). ^1H NMR: δ 3.87 (6H, s, $2C\underline{H}_3OAr$); δ 7.27 (5H, s, $C_6\underline{H}_5$); δ 7.41 (6H, s, $2C_6\underline{H}_3$); δ 9.84 (2H, s, $2C\underline{H}O$) [ppm]. IR: ν 1702, 1596, 1505, 1276, 1192, 1119, 1029, 964 cm^{-1}.

Bis(4-formyl-2-methoxyphenyl) 4-methylphenyl phosphate (1g): m.p. 79–80°C. Anal. Calcd. for $C_{23}H_{21}O_8P$: C, 60.53; H, 4.61. Found: C, 60.12; H, 4.53. ^{31}P NMR (Non-decoupled): δ −18.0 ppm, (s). ^1H NMR: δ 2.34 (3H, s, $C\underline{H}_3C_6H_4$); δ 3.87 (6H, s, $2C\underline{H}_3OAr$); δ 7.21 (4H, 2s, $CH_3C_6\underline{H}_4$); δ 7.29 (6H, m, $2C_6\underline{H}_3$); δ 9.84 (2H, s, $2C\underline{H}O$) [ppm]. IR: ν 1686, 1597, 1504, 1277, 1189, 1130, 1038, 976 cm^{-1}.

Bis(4-formyl-2-methoxyphenyl) 4-chlorophenyl phosphate 1h): m.p. 95–96°C. Anal. Calcd. for $C_{22}H_{18}ClO_8P$: C, 55.40; H, 3.78. Found: C, 54.99; H, 3.99. ^{31}P NMR (Non-decoupled): δ −18.0 ppm, (s). ^1H NMR: δ 3.87 (6H, s, $2C\underline{H}_3OAr$); δ 7.23 (4H, 2s, $ClC_6C\underline{H}_4$); δ 7.41 (6H, s, $2C_6\underline{H}_3$); δ 9.84 (2H, s, $2C\underline{H}O$) [ppm]. IR: ν 1691, 1596, 1506, 1272, 1195, 1129, 1031, 977 cm^{-1}.

Preparation of tri(4-formyl-2-methoxyphenyl)phosphate (1i)

Phosphorylchloride (0.25 g, 1.6 mmol) and triethylamine (0.49 g, 4.8 mmol) were added dropwise to a stirred solution of Vanillin (0.73 g, 4.8

mmol) in 20 ml of ether at 5–10 °C. The mixture then was stirred for 3 min. at same temperature. The precipitate was filtered out and washed with water and alcohol. Pure tri(4-formyl-2-methoxyphenyl)phosphate, m.p. 150–151 °C (Literature[4]: 151–152°C), was obtained in the yield of 85% by crystallization from the mixed chloroform and petroleum ether. ^{1}H NMR ($CDCl_3$, TMS): δ 3.9 (9H, s, $3C\underline{H}_3OAr$); δ 7.7 (9H, m, $3C_6C\underline{H}_3$); δ 10.2 (3H, s, $3C\underline{H}O$) [ppm]. IR: ν 3030, 2899, 1705, 1595, 1507, 1471, 1394, 1308, 1126, 863 cm^{-1}.

General procedure for the synthesis of di(4-hydroxymethyl-2-methoxyphenyl)phosphates (DHMPP, compounds 2a-h)

To a stirred solution of di(4-formyl-2-methoxyphenyl)phosphate (8 mmol) in 20 ml of anhydrous tetrahydrofuran was added potassium borohydride (16 mmol) at 65°C. After the mixture was stirred continuously for 24 h the solid materials was filtered off and the filtrate was concentrated. The residue was purified by silica gel column chromatography eluted with ethyl acetate.

Bis(4-hydroxymethyl-2-methoxyphenyl) methyl phosphate (2a): Semi-solid. Anal. Calcd. for $C_{17}H_{21}O_8P$: C, 53.13; H, 5.47. Found: C, 53.21; H, 6.06. ^{31}P NMR: δ –11.5 ppm. ^{1}H NMR: δ 2.53 (2H, s, $2O\underline{H}$); δ 3.76 (6H, s, $2C\underline{H}_3OAr$); δ 4.33 (3H, m, $C\underline{H}_3OP$); δ 4.50 (4H, s, $2C\underline{H}_2OH$) δ 6.76–7.33 (6H, m, $2C_6\underline{H}_3$) [ppm]. IR: ν 3392, 1601, 1501, 1282, 1190, 1120, 1030, 975 cm^{-1}.

Bis(4-hydroxymethyl-2-methoxyphenyl) ethyl phosphate (2b): Semi-solid. Anal. Calcd. for $C_{18}H_{23}O_8P$: C, 54.27; H, 5.78. Found: C, 54.45; H, 5.34. ^{31}P NMR: δ –10.8 ppm. ^{1}H NMR: δ 1.40 (3H, t, $C\underline{H}_3CH_2$); δ 3.41 (2H, s, $2O\underline{H}$); δ 3.76 (6H, s, $2C\underline{H}_3OAr$); δ 4.38 (2H, m, $C\underline{H}_2OP$); δ 4.50 (4H, s, $2OC\underline{H}_2Ar$); δ 6.76–7.17 (6H, m, $2C_6\underline{H}_3$) [ppm]. IR: ν 3377, 1601, 1510, 1282, 1197, 1121, 1029, 964 cm^{-1}.

Bis(4-hydroxymethyl-2-methoxyphenyl) n-propyl phosphate (2c): Semi-solid. Anal. Calcd. for $C_{19}H_{25}O_8P$: C, 55.34; H,6.07. Found: C, 55.96; H, 6.09. ^{31}P NMR: δ -10.7 ppm. ^{1}H NMR: δ 0.98 (3H, t, $C\underline{H}_3CH_2$); δ 1.77 (2H, m, $CH_3C\underline{H}_2CH_2$); δ 3.43 (2H, b, $2O\underline{H}$); δ 3.76 (6H, s, $2C\underline{H}_3OAr$); δ 4.28 (2H, m, $C\underline{H}_2OP$); δ 4.50 (4H, s, $2OC\underline{H}_2Ar$); δ 6.75–7.17 (6H, m, $2C_6\underline{H}_3$) [ppm]. IR: ν 3329, 1603, 1512, 1276, 1196, 1120, 1041, 972 cm^{-1}.

Bis(4-hydroxymethyl-2-methoxyphenyl) n-butyl phosphate (2d): Oil. Anal. Calcd. for $C_{20}H_{27}O_8P$: C, 56.34; H,6.34. Found: C, 56.00; H, 6.08. ^{31}P NMR: δ –10.8 ppm. ^1H NMR: δ 0.94 (3H, t, CH_3CH_2); δ 1.44 (2H, m, $CH_3CH_2CH_2$); δ 1.72 (2H, m, $CH_2CH_2CH_2$); δ 3.76 (6H, s, $2CH_3OAr$); δ 3.89 (2H, s, 2OH); δ 4.32 (2H, m, CH_2OP); δ 4.47 (4H, s, $2OCH_2Ar$); δ 6.75–7.17 (6H, m, $2C_6H_3$) [ppm]. IR: ν 3409, 1601, 1511, 1282, 1197, 1121, 1033, 964 cm^{-1}.

Bis(4-hydroxymethyl-2-methoxyphenyl) 2-chloroethyl phosphate (2e): Oil. Anal. Calcd. for $C_{18}H_{22}ClO_8P$: C, 49.94; H, 5.09. Found: C, 50.40; H, 5.14. ^{31}P NMR: δ –11.1 ppm. ^1H NMR: δ 3.73 (2H, m, $ClCH_2$); δ 3.75 (6H, s, $2CH_3OAr$); δ 3.77 (2H, s, 2OH); δ 4.47(4H, s, $2OCH_2Ar$); δ 4.50 (2H, m, CH_2OP); δ 6.76–7.15 (6H, m, $2C_6H_3$) [ppm]. IR: ν 3407, 1602, 1510, 1284, 1196, 1120, 1033, 970 cm^{-1}.

Bis(4-hydroxymethyl-2-methoxyphenyl) phenyl phosphate (2f): Oil. Anal. Calcd. for $C_{22}H_{23}O_8P$: C, 59.19; H, 5.16. Found: C, 58.70; H, 5.41. ^{31}P NMR: δ –16.3 ppm. ^1H NMR: δ 3.63 (2H, b, 2OH); δ 3.66 (6H, s, $2CH_3OAr$); δ 4.46 (4H, s, $2OCH_2Ar$); δ 6.73–7.18 (6H, m, $2C_6H_3$); δ 7.32 (5H, m, C_6H_5) [ppm]. IR: ν 3411, 1602, 1506, 1282, 1192, 1120, 1034, 967 cm^{-1}.

Bis(4-hydroxymethyl-2-methoxyphenyl) 4-methylphenyl phosphate (2g): Oil. Anal. Calcd. for $C_{23}H_{25}O_8P$: C, 60.00; H, 5.43. Found: C, 59.51; H, 4.98. ^{31}P NMR: δ -16.5 ppm. ^1H NMR: δ 2.27 (3H, s, $CH_3C_6H_4$); δ 2.99 (2H, s, 2OH); δ 3.63 (6H, s, $2CH_3OAr$); δ 4.66 (4H, s, $2OCH_2Ar$); δ 6.70–7.08 (6H, m, $2C_6H_3$); δ 7.11–7.22 (4H, m, $CH_3C_6H_4$) [ppm]. IR: ν 3390, 1602, 1510, 1283, 1191, 1120, 1030, 967 cm^{-1}.

Bis(4-hydroxymethyl-2-methoxyphenyl) 4-chlorophenyl phosphate (2h): Oil. Anal. Calcd. for $C_{22}H_{22}ClO_8P$: C, 54.94; H, 4.58. Found: C, 54.47; H, 4.87. ^{31}P NMR: δ –16.2 ppm. ^1H NMR: δ 3.17 (2H, s, 2OH); δ 3.60 (6H, s, $2CH_3OAr$); δ 4.42 (4H, s, $2OCH_2Ar$); δ 6.68–7.08 (6H, m, $2C_6H_3$); δ 7.19–7.25 (4H, m, ClC_6H_4) [ppm]. IR: ν 3384, 1603, 1511, 1284, 1197, 1121, 1034, 967 cm^{-1}.

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