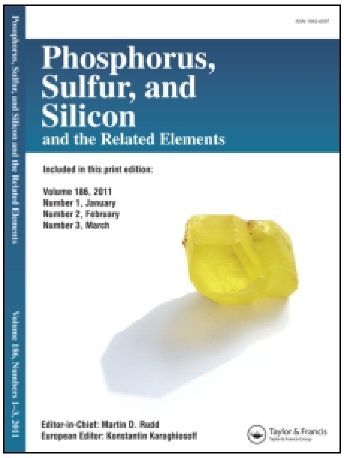

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SIMPLE AND IMPROVED PREPARATION OF α-OXOPHOSPHONATE MONOLITHIUM SALTS

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SIMPLE AND IMPROVED PREPARATION OF α-OXOPHOSPHONATE MONOLITHIUM SALTS

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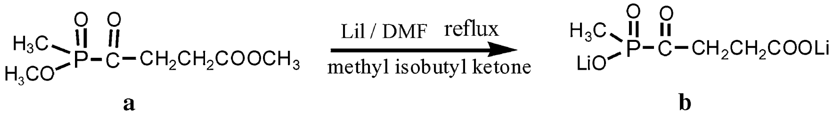
Some α-OxoPhosphonate monolithium salts were synthesized by a facile one-step procedure. In this way, α-(2,4-dichlorophenoxyacetoxy)alkyl phosphonic acid dimethyl esters ***5*** *can be transformed into the corresponding phosophonate monolithium salts* ***6*** *without influence on the carboxylic ester group under mild conditions.*

Keywords: Phosphonate monolithium salt; synthesis

In continuation of our work on the synthesis of substituted phenoxy acetoxy alkyl phosphonic acid derivatives with good biological activities,[1] we are interested in the preparation of phosphonate salts because its corresponding salts would be of greater biological interest, such as for herbicidal activities.[2] A. C. Baillie reported that some phosphinate monolithium salts could be obtained by directly converting a phosphinate ester (**a**) into the corresponding salts (**b**) in a 0.5 M solution of anhydrous lithium iodide in methyl isobutyl ketone[3] (Scheme 1).



SCHEME 1

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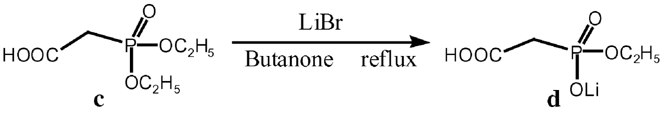
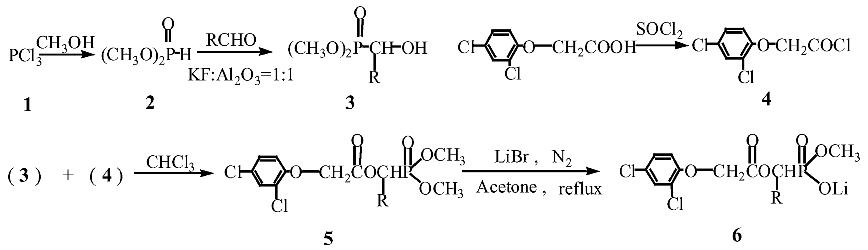
However, this method is not applicable to prepare the title compounds under harsher conditions. This was probably due to the cleavage of the carboxylate ester bond in substituted phenoxy acetoxy alkyl phosphonic acid derivative in methyl isobutyl ketone.

An alternative method,[3] by reaction of a phosphonate ester (**c**) with lithium bromide in butanone giving the corresponding phosphonate monolithium salt (**d**), was reported (Scheme 2). However, attempts to prepare the title compounds in butanone according to these conditions were also unsuccessful.



SCHEME 2

Herein we report the reaction of α-(2,4-dichlorophenoxyacetoxy) alkyl phosphonic acid dimethyl esters with lithium bromide in acetone to produce the corresponding phosphonate monolithium salts. The reaction under mild conditions resulted in high yields of the products **6a–p** (Table I) as shown in Scheme 3.



SCHEME 3 Syntheses of title compounds **6**.

Initially, we prepared the title compounds **6** (Scheme 3) from α-(2,4-dichlorophenoxyacetoxy) alkyl phosphonic acid dimethyl esters according to the method in Scheme 2. The experiment showed that the reaction of compounds **5a–p** with lithium bromide was affected by reaction temperature, base, solvent, and water. We attempted to prepare the title compound **6d** by the reaction of **5d** with lithium bromide, which was dried in the presence of butanone for 36 h, but no title compound **6d** was found. Instead, only 2,4-dichloro phenoxy acetic acid lithium salt and the methyl-1-hydroxy phenyl phosphonate monolithium salt as a by-product were found.

TABLE I Preparation of α-OxoPhosphonate Monolithium Salts

Compd.	R	Formula	Color	m.p. (C)	rt (h)	Yield (%)
6a	H	$C_{10}H_{10}Cl_2LiO_6P$	White	138–139	3	76
6b	CH_3	$C_{11}H_{12}Cl_2LiO_6P$	White	103–105	3	74
6c	n-C_3H_7	$C_{13}H_{16}Cl_2LiO_6P$	White	151–152	4	67
6d	Ph	$C_{16}H_{14}Cl_2LiO_6P$	White	244–245	3	79
6e	o-ClPh	$C_{16}H_{13}Cl_3LiO_6P$	White	76–78	3	69
6f	p-ClPh	$C_{16}H_{13}Cl_3LiO_6P$	White	187–189	3	70
6g	p-FPh	$C_{16}H_{13}Cl_2FLiO_6P$	White	236–237	2.5	91
6h	p-CH_3OPh	$C_{17}H_{16}Cl_2LiO_7P$	White	202–203	4	73
6i	p-CH_3Ph	$C_{17}H_{16}Cl_2LiO_6P$	White	131–133	3	91
6j	2,4-Cl_2Ph	$C_{16}H_{12}Cl_4LiO_6P$	White	259–262	3	81
6k	3,4-OCH_2OPh	$C_{17}H_{14}Cl_2LiO_8P$	White	238–239	2.5	84
6l	m-NO_2Ph	$C_{16}H_{13}Cl_2LiNO_8P$	White	227–228	3	80
6m	p-NO_2Ph	$C_{16}H_{13}Cl_2LiNO_8P$	White	216–218	3	78
6n	o-Fural	$C_{14}H_{12}Cl_2LiO_7P$	White	132–134	2	82
6o	o-Thiophenyl	$C_{14}H_{12}Cl_2LiO_6PS$	White	171–172	1.5	93
6p	o-Pyridyl	$C_{15}H_{13}Cl_2LiNO_6P$	White	227–228	1	95

Therefore, in the molecular structure of 0,0-dimethyl-α-(2,4-dichlorophenoxyacetoxy)alkyl phosphonate, the carboxylate ester bond may be easier to cleave than phosphonate ester bond under such harsh conditions. Based on the above results, we needed milder conditions for selective cleavage of phosphonate ester bond without cleavage carboxylate ester group. Consequently, the formation of the title compounds **6** can be rationalized in terms of direct reaction of

TABLE II Preparation of the Intermediates **5a–p**

Compd.	R	Formula	Color	n_D^{20}	m.p. (°C)	Yield (%)
5a	H	$C_{11}H_{13}Cl_2O_6P$	Yellow	1.5448		75.8
5b	CH_3	$C_{12}H_{15}Cl_2O_6P$	Yellow	1.5178		90.7
5c	n-C_3H_7	$C_{14}H_{19}Cl_2O_6P$	Yellow	1.4859		66.0
5d	Ph	$C_{17}H_{17}Cl_2O_6P$	Yellow	1.5069		58.9
5e	o-ClPh	$C_{17}H_{16}Cl_3O_6P$	White		76–78	58.5
5f	p-ClPh	$C_{17}H_{16}Cl_3O_6P$	Yellow	1.5634		58.9
5g	p-FPh	$C_{17}H_{16}Cl_2FO_6P$	White		90–91	81.5
5h	p-CH_3OPh	$C_{18}H_{19}Cl_2O_7P$	White		96–97	67.8
5i	p-CH_3Ph	$C_{18}H_{19}Cl_2O_6P$	Yellow	1.5429		79.2
5j	2,4-Cl_2Ph	$C_{17}H_{15}Cl_4O_6P$	White		103–104	83.2
5k	3,4-OCH_2OPh	$C_{18}H_{17}Cl_2O_8P$	White		120–121	84.2
5l	m-NO_2Ph	$C_{17}H_{16}Cl_2NO_8P$	White		92–93	73.8
5m	p-NO_2Ph	$C_{17}H_{16}Cl_2NO_8P$	White		126–127	79.5
5n	o-Fural	$C_{15}H_{15}Cl_2O_7P$	White		62–63	81.4
5o	o-Thiophenyl	$C_{15}H_{15}Cl_2O_6PS$	White		92–93	86.2
5p	o-Pyridyl	$C_{16}H_{16}Cl_2NO_6P$	White		86–87	82.5

TABLE III ^{1}H NMR Chemical Shifts (TMS, DMSO) of **6** and Coupling Constants *J*(Hz)

Compd.	^{1}H NMR
6a	3.36 (d, 3H, —OCH$_3$, J = 4.8 Hz), 4.13 (d, 2H, —OCH$_2$P, J = 8.6 Hz), 5.13 (s, 2H, —OCH$_2$CO—), 7.07–7.59 (m, 3H, —C$_6$H$_3$)
6b	1.32 (q, 3H, —CH$_3$, J = 6.75 Hz), 3.41 (d, 3H, —OCH$_3$, J = 9.81 Hz), 4.75 (d, 1H^a, —OCH$_2$CO—, J = 16.53 Hz), 4.89 (d, 1H^b, —OCH$_2$CO—, J = 16.54 Hz), 5.01 (d, 1H, —OCHP, J = 15.63 Hz), 7.06–7.58 (m, 3H, —C$_6$H$_3$)
6c	0.88 (t, 3H, —CH$_2$CH$_2\underline{\mathrm{CH_2}}$, J = 7.4 Hz), 1.25–1.47 (m, 2H, —CH$_2\underline{\mathrm{CH_2}}CH_3$), 1.82–2.05 (m, 2H, —$\underline{\mathrm{CH_2}}CH_2CH_3$), 3.67 (d, 3H, —OCH$_3$, J = 9.90 Hz), 4.96 (d, 1H^a, —OCH$_2$CO—, J = 16.50 Hz), 5.00 (d, 1H^b, —OCH$_2$CO—, J = 16.50 Hz), 5.30 (d, 2H, —OCHP, J = 8.40 Hz), 7.04–7.42 (m, 3H, —C$_6$H$_3$)
6d	3.31 (d, 3H, —OCH$_3$, J = 9.84 Hz), 4.94 (d, 1H^a, —OCH$_2$CO—, J = 16.59 Hz), 5.05 (d, 1H^b, —OCH$_2$CO—, J = 16.56 Hz), 5.80 (d, 1H, —OCHP, J = 12.81 Hz), 7.05–7.59 (m, 8H, —C$_6$H$_5$, —C$_6$H$_3$)
6e	3.31 (d, 3H, —OCH$_3$, J = 9.94 Hz), 4.91 (d, 1H^a, —OCH$_2$CO—, J = 16.56 Hz), 4.98 (d, 1H^b, —OCH$_2$CO—, J = 16.59 Hz), 6.18 (d, 1H, —OCHP, J = 12.06 Hz), 6.98–7.64 (m, 7H, —C$_6$H$_4$, —C$_6$H$_3$)
6f	3.31 (d, 3H, —OCH$_3$, J = 9.9 Hz), 4.90 (d, 1H^a, —OCH$_2$CO—, J = 16.56 Hz), 4.96 (d, 1H^b, —OCH$_2$CO—, J = 16.56 Hz), 6.15 (d, 1H, —OCHP, J = 12.20 Hz), 7.02–7.57 (m, 7H, —C$_6$H$_4$, —C$_6$H$_3$)
6g	3.32 (d, 3H, —OCH$_3$, J = 9.30 Hz), 4.93 (d, 1H^a, —OCH$_2$CO—, J = 16.80 Hz), 5.03 (d, 1H^b, —OCH$_2$CO—, J = 16.80 Hz), 5.80 (d, 1H, —OCHP, J = 12.80 Hz), 7.04–7.58 (m, 7H, —C$_6$H$_4$, —C$_6$H$_3$)
6h	3.29 (d, 3H, —OCH$_3$, J = 9.90 Hz), 3.74 (s, 3H, CH$_3$OPh), 4.88 (d, 1H^a, —OCH$_2$CO—, J = 16.50 Hz), 5.01 (d, 1H^b, —OCH$_2$CO—, J = 16.56 Hz), 5.67–5.73 (d, 1H, —OCHP, J = 13.6 Hz), 6.86–7.58 (m, 7H, —C$_6$H$_4$, —C$_6$H$_3$)
6i	2.26 (s, 3H, —CH$_3$Ph), 3.30 (d, 3H, —OCH$_3$, J = 9.82 Hz), 4.91 (d, 1H^a, —OCH$_2$CO—, J = 16.56 Hz), 5.03(d, 1H^b, —OCH$_2$CO—, J = 16.57 Hz), 5.76 (d, 1H, —OCHP, J = 12.57 Hz), 7.03–7.59 (m, 7H, —C$_6$H$_4$, —C$_6$H$_3$)
6j	3.38 (d, 3H, —OCH$_3$, J = 9.00 Hz), 4.94 (d, 1H^a, —OCH$_2$CO—, J = 16.56 Hz), 4.99 (d, 1H^b, —OCH^{2}CO—, J = 16.62 Hz), 6.12 (d, 1H, —OCHP, J = 12.21 Hz), 6.99–7.65 (m, 6H, —C$_6$H$_3$, —C$_6$H$_3$)
6k	3.34 (d, 3H, —OCH$_3$, J = 9.90 Hz), 4.91 (d, 1H^a, —OCH$_2$CO—, J = 16.50 Hz), 5.03 (d, 1H^b, —OCH$_2$CO—, J = 16.56 Hz), 5.74 (d, 1H, —OCHP, J = 12.42 Hz), 5.97 (s, 2H, —OCH$_2$OPh), 6.77–7.59 (m, 6H, —C$_6$H$_3$, —C$_6$H$_3$)
6l	3.37 (d, 3H, —OCH$_3$, J = 10.02 Hz), 4.99 (d, 1H^a, —OCH$_2$CO—, J = 16.62 Hz), 5.13 (d, 1H^b, —OCH$_2$CO—, J = 16.62 Hz), 5.91 (d, 1H, —OCHP, J = 13.02 Hz), 7.07–8.22 (m, 7H, —C$_6$H$_4$, —C$_6$H$_3$)
6m	3.36 (d, 3H, —OCH$_3$, J = 10.02 Hz), 4.94 (d, 1H^a, —OCH$_2$CO—, J = 16.60 Hz), 5.13 (d, 1H^b, —OCH$_2$CO—, J = 16.50 Hz), 5.90 (d, 1H, —OCHP, J = 12.80 Hz), 7.06–8.10 (m, 7H, —C$_6$H$_4$, —C$_6$H$_3$)
6n	3.35 (d, 3H, —OCH$_3$, J = 9.7 Hz), 4.91 (d, 1H^a, —OCH$_2$CO—, J = 16.80 Hz), 4.96 (d, 1H^b, —OCH$_2$CO—, J = 16.80 Hz), 5.84 (d, 1H, —OCHP, J = 12.6 Hz), 6.37–7.27 (m, 3H, C$_4$H$_3$O—), 7.03–7.65 (m, 3H, —C$_6$H$_3$)
6o	3.37 (d, 3H, —OCH$_3$, J = 8.40 Hz), 4.90 (d, 1H^a, —OCH$_2$CO—, J = 16.80 Hz), 4.97(d, 1H^b, —OCH$_2$CO—, J = 16.40 Hz), 6.06 (d, 1H, —OCHP, J = 12.40 Hz), 6.38–7.05 (m, 3H, —C$_4$H$_3$S), 7.07–7.58 (m, 3H, —C$_6$H$_3$)
6p	3.34 (d, 3H, —OCH$_3$, J = 10.40 Hz), 5.01 (d, 1H^a, —OCH$_2$CO—, J = 16.80 Hz), 5.06 (d, 1H^b, —OCH$_2$CO—, J = 16.80 Hz), 5.85 (d, 1H, —OCHP, J = 13.20 Hz), 7.13–7.65 (m, 3H, —C$_6$H$_3$), 7.15–8.45 (m, 4H, —C$_5$H$_4$N)

the phosphonates **5a–p** with lithium bromide in acetone which was dried by molecular sieves (4 Å) under nitrogen for 1–4 h. Thereby, we could obtain the title compound **6p** by the reaction of compound **5p** and lithium and 1 h at reflux. The preliminary biological tests showed that most of the title compounds **6a–p** have excellent inhibitory activities against *Echinochloa crusgalli, Brassica napus, Digitaria adscendens, Amaranthus retroflexus*, and *Medicago sativa*.

EXPERIMENTAL

Instruments

Melting points (m.p.) were measured on an Electrothermal melting-point apparatus and uncorrected; Elemental analysis were performed by Vario EL III elemental analysis; IR spectra were obtained with a Avatar 360 spectrometer; ^{1}H NMR were measured with a Varian XL-300 spectrometer at 300 MH$_Z$, Tetramethyl Silane (TMS) was used as an internal standard, and chemical shift values are expressed in δ (DMSO) ppm. MS were measured on a Finnigen TRACE spectrometer and API2000LC/MS.

Compounds **3** and **4** were prepared according to the literature.[4,5]

TABLE IV IR Data of Compounds **6**

Compd.	ν ph—H	ν C—H	ν C=O	ν Ph	ν P=O	ν C—O—C	ν P—O—C	ν P—C
6a	3036	2953, 2847	1783	1662, 1583, 1481	1226	1092	1045, 932	775
6b	3028	2952, 2857	1759	1633, 1548, 1484	1205	1082	1055, 928	717
6c	3029	2961, 2875	1759	1638, 1586, 1481	1203	1081	1046, 948	719
6d	3098	2947, 2846	1723	1648, 1590, 1487	1243	1099	1049, 943	726
6e	3078	2956, 2852	1733	1643, 1590, 1480	1242	1078	1052, 948	745
6f	3086	2944, 2852	1750	1638, 1599, 1480	1240	1105	1049, 941	788
6g	3068	2958, 2852	1748	1637, 1511, 1480	1224	1106	1052, 958	787
6h	3038	2948, 2852	1758	1638, 1501, 1480	1226	1086	1052, 938	727
6i	3098	2950, 2857	1746	1646, 1516, 1481	1218	1080	1052, 933	716
6j	3104	2958, 2852	1727	1649, 1587, 1485	1234	1083	1057, 953	760
6k	3059	2947, 2896	1718	1633, 1504, 1482	1235	1082	1040, 949	719
6l	3068	2964, 2857	1740	1635, 1538, 1479	1228	1104	1052, 923	730
6m	3048	2952, 2846	1739	1638, 1548, 1452	1226	1081	1050, 943	731
6n	3064	2957, 2852	1741	1645, 1601, 1465	1216	1078	1053, 918	732
6o	3101	2930, 2848	1761	1654, 1543, 1481	1224	1101	1046, 928	728
6p	3020	2953, 2856	1754	1599, 1575, 1480	1228	1085	1053, 932	721

Preparation of Intermediate 5

A solution of 2,4-dichlorophenoxy acetyl chloride **4** (0.022 mol) in trichloromethane (10 ml) was added to stirred mixture of 1-hydroxyalkyl phosphonate **3** (0.02 mol) and organic base (0.022 mol) in trichloromethane (25 ml) at 20–25°C. The mixture was stirred at

TABLE V Elemental Analysis and MS Data of Compound **6**

	Calcd. (found)			
Compd.	C	H	N/Li	MS/LC-MS
6a	35.85 (35.80)	3.01 (3.49)		334 (M^+), 175, 162, 133, 127, 109, 75, 63, 45 (100%)
6b	37.85 (37.88)	3.47 (3.43)		348 (M^+), 199, 175, 162, 133, 127, 109, 94, 93, 75, 63, 45 (100%)
6c	41.41 (41.01)	4.28 (4.61)		37634 (M^+), 175, 162, 133, 127, 109, 75, 63, 45 (100%)
6d	46.75 (46.38)	3.43 (3.65)	1.71 (1.89)	410 (M^+), 175, 162, 133, 127, 109, 94, 93, 77, 63, 45 (100%)
6e	43.13 (42.87)	2.94 (2.86)		444 (M^+), 175, 162, 133, 127, 111, 109, 94, 93, 75, 63, 45 (100%)
6f	43.13 (42.91)	2.94 (2.89)		444 (M^+), 175, 162, 133, 127, 111, 109, 94, 93, 75, 63, 45 (100%)
6g	44.79 (44.38)	3.05 (2.92)	1.64 (1.72)	428 (M^+), 175, 162, 133, 127, 109, 95, 94, 93, 75, 63, 45 (100%); LC-MS: 421 (M^+–7, 100%, negative); 431 (M^++7, 92.51%, positive), 428 (M^+, 60.43%, positive)
6h	46.29 (46.07)	3.66 (3.58)		440 (M^+), 175, 162, 133, 127, 109, 107, 94, 93, 75, 63, 45 (100%)
6i	48.03 (48.30)	3.79 (3.64)	1.65 (1.57)	424 (M^+), 199, 175, 162, 133, 127, 109, 94, 93, 91, 75, 63, 45 (100%); LC-MS: 417 (M^+–7, 100%, negative); 431 (M^++7, 89.77%, positive), 424 (M^+, 18.98%, positive)
6j	40.04 (39.55)	2.52 (2.80)		478 (M^+), 199, 175, 162, 145, 133, 127, 109, 94, 93, 75, 63, 45, 42 (100%)
6k	44.86 (45.14)	3.10 (3.35)		454 (M^+), 199, 175, 162, 133, 127, 121, 109, 94, 93, 75, 63, 45 (100%)
6l	42.13 (41.71)	2.87 (2.90)	3.07 (2.97)	455 (M^+), 175, 162, 133, 127, 122, 109, 94, 93, 75, 63, 45 (100%)
6m	42.13 (41.83)	2.87 (2.88)	3.07 (2.98)	455 (M^+), 175, 162, 133, 127, 122, 109, 94, 93, 75, 63, 45 (100%)
6n	41.93 (41.68)	3.02 (2.86)		400 (M^+), 199, 175, 162, 133, 127, 109, 94, 93, 75, 67, 63, 45 (100%)
6o	40.31 (40.02)	2.90 (2.72)	1.68 (1.79)	416 (M^+), 175, 162, 133, 127, 109, 94, 93, 83, 63, 45 (100%); LC-MS: 409 (M^+−7, 100%, negative); 423 (M^++7, 92.87%, positive), 416 (M^+, 10.38%, positive)
6p	43.72 (43.63)	3.18 (3.18)	3.40 (3.39)	411 (M^+), 175, 162, 133, 127, 109, 94, 93, 78, 63, 45 (100%)

ambient temperature for 4 h and then at 40°C for 1 h, washed with 0.1 M hydrochloric acid, saturated sodium hydrogen carbonate solution, and brine. The resultant mixture was dried and evaporated. The residue was chromatographed on silica with 20% acetone in petroleum ether as eluent to give the compound **5** as a liquid or solid, which was recrystallized from DCM/petroleum ether. Yield, 58–91%. The intermediates **5a–p** are listed in Table II.

General Preparation of Lithium Monomethyl-α-(2,4-Dichlorophenoxy Acetoxy) Alkyl Phosphonate Salts 6

A solution of 0,0-dimethyl-α-(2,4-dichlorophenoxyacetoxy)alkyl phosphonate (0.02 mol) and lithium bromide (0.02 mol) in acetone (50 ml) dried over molecular sieves (4 Å) was stirred and refluxed under nitrogen for 1–4 h. The solution was evaporated at reduced pressure. The residual solid was recrystallized from dichloromethane/petroleum to afford the pure product as a white crystals **6a–p** (the product was very deliquescent). The salts were isolated directly in 67–95.2% yields. The structures of compounds **6a–p** were confirmed by ^{1}H NMR, IR spectra, LC-MS, and elemental analyses.

In the ^{1}H NMR spectra of **6**, the proton in the P—C moiety and the proton in the P—OCH_3 moiety each displays doublets. The IR spectra of all compounds showed normal stretching absorption bands, indicating the existence of the Ph—H (~3050 cm^{-1}), C—H (~2950 cm^{-1}, ~2860 cm^{-1}), C=O (~1720 cm^{-1}), C=C (~1620, ~1450 cm^{-1}), P=O (~1260 cm^{-1}), C—O—C (~1080 cm^{-1}), P—O—C (~1050 cm^{-1}, ~930 cm^{-1}) and P—C (~750 cm^{-1}). The EI mass spectra of compound 6 gave weak molecular ion peaks. All the fragmentation ions were consistent with the structure and can be clearly assigned. All results are listed in Tables I and III–V.

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APPENDIX

TABLE AI ^{1}H NMR Chemical Shifts (TMS, CDCl$_3$) of Compounds **5a–p**

Compd.	^{1}H NMR
5a	3.80 (dd, 6H, —OCH$_3$, $J = 9.80$ Hz), 4.30 (d, 2H, —OCH$_2$P, $J = 8.28$ Hz), 4.75 (s, 2H, —OCH$_2$CO—), 6.89–7.55 (m, 3H, —C$_6$H$_3$)
5b	1.53 (q, 3H, —CH$_3$, $J = 6.75$ Hz), 3.81 (dd, 6H, —OCH$_3$, $J = 9.86$ Hz), 4.75 (s, 1H, —OCH$_2$CO—), 5.25–5.40 (m, 1H, —OCHP), 6.89–7.56 (m, 3H, —C$_6$H$_3$)
5c	0.92 (t, 3H, —CH$_2$CH$_2\underline{\text{CH}_3}$, $J = 7.20$ Hz), 1.40–1.86 (m, 2H, —CH$_2\underline{\text{CH}_2}CH_3$), 3.85 (dd, 3H, —OCH$_3$, $J = 9.90$ Hz), 4.80 (d, 1H, —OCH$_2$CO—), 5.35 (m, 2H, —OCHP), 6.80–7.46 (m, 3H, —C$_6$H$_3$)
5d	3.70 (dd, 6H, —OCH$_3$, $J = 9.54$ Hz), 4.89 (s, 1H, —OCH$_2$CO—), 6.24 (d, 1H, —OCHP,$J = 11.60$ Hz), 6.72–7.42 (m, 3H, —C$_6$H$_3$)
5e	3.85 (dd, 6H, —OCH$_3$, $J = 9.80$ Hz), 4.81 (s, 1H, —OCH$_2$CO—), 6.40 (d, 1H, —OCHP, $J = 11.80$ Hz), 6.80–7.40 (m, 7H, —C$_6$H$_4$, —C$_6$H$_3$)
5f	3.75 (dd, 6H, —OCH$_3$, $J = 9.80$ Hz), 5.10 (s, 1H, —OCH$_2$CO—), 6.20 (d, 1H, —OCHP, $J = 11.20$ Hz), 7.12–7.67 (m, 7H, —C$_6$H$_4$, —C$_6$H$_3$)
5g	3.85 (dd, 6H, —OCH$_3$, $J = 9.58$ Hz), 4.90 (s, 1H, —OCH$_2$CO—), 6.40 (d, 1H, —OCHP, $J = 11.80$ Hz), 6.94–7.50 (m, 7H, —C$_6$H$_4$, —C$_6$H$_3$)
5h	3.10 (s, 3H, CH$_3$OPh), 3.80 (dd, 6H, —OCH$_3$, $J = 9.80$ Hz), 4.86 (s, 2H, —OCH$_2$CO—), 6.20 (d, 1H, —OCHP, $J = 11.6$ Hz), 6.80–7.68 (m, 7H, —C$_6$H$_4$, —C$_6$H$_3$)
5i	2.30 (s, 3H, —CH$_3$Ph), 3.74 (dd, 6H, —OCH$_3$, $J = 9.80$ Hz), 4.70 (s, 1H, —OCH$_2$CO—), 6.26 (d, 1H, —OCHP, $J = 11.80$ Hz), 6.77–7.42 (m, 7H, —C$_6$H$_4$, —C$_6$H$_3$)
5j	3.76 (dd, 6H, —OCH$_3$, $J = 9.80$ Hz), 4.98 (s, 1H, —OCH$_2$CO—), 6.12 (d, 1H, —OCHP, $J = 11.22$ Hz), 7.20–7.60 (m, 6H, —C$_6$H$_3$, —C$_6$H$_3$)
5k	3.72 (dd, 6H, —OCH$_3$, $J = 9.80$ Hz), 4.97 (s, 1H, —OCH$_2$CO—), 5.67 (d, 1H, —OCHP, $J = 11.80$ Hz), 5.97 (s, 2H, —OCH$_2$OPh), 6.76–7.53 (m, 6H, —C$_6$H$_3$, —C$_6$H$_3$)
5l	3.88 (dd, 6H, —OCH$_3$, $J = 9.80$ Hz), 5.09 (s, 1H, —OCH$_2$CO—), 5.95 (d, 1H, —OCHP, $J = 11.60$ Hz), 7.03–8.16 (m, 7H, —C$_6$H$_4$, —C$_6$H$_3$)
5m	3.86 (dd, 6H, —OCH$_3$, $J = 9.80$ Hz), 5.01 (s, 1H, —OCH$_2$CO—), 5.92 (d, 1H, —OCHP, $J = 11.60$ Hz), 7.00–8.02 (m, 7H, —C$_6$H$_4$, —C$_6$H$_3$)
5n	3.80 (dd, 6H, —OCH$_3$, $J = 9.80$ Hz), 4.76 (d, 1H^a, —OCH$_2$CO—, $J = 16.54$ Hz), 4.78 (d, 1H^b, —OCH$_2$CO—, $J = 16.54$ Hz), 6.38 (d, 1H, —OCHP, $J = 14.83$ Hz), 6.42–6.76 (m, 3H, C$_4$H$_3$O—), 7.12–7.47 (m, 3H, —C$_6$H$_3$)
5o	3.74 (dd, 6H, —OCH$_3$, $J = 10.50$ Hz), 4.74 (d, 1H^a, —OCH$_2$CO—, $J = 16.54$ Hz), 4.77 (d, 1H^b, —OCH$_2$CO—, $J = 16.54$ Hz), 6.48–6.53 (d, 1H, —OCHP, $J = 13.50$ Hz), 6.68–7.01 (m, 3H, C$_4$H$_3$S—), 6.98–7.36 (m, 3H, —C$_6$H$_3$)
5p	3.76 (dd, 6H, —OCH$_3$, $J = 9.95$ Hz), 4.88 (s, 2H, —OCH$_2$CO—), 6.36 (d, 1H, —OCHP, $J = 13.76$ Hz), 6.81–7.39 (m, 3H, —C$_6$H$_3$), 7.27–8.63 (m, 4H, —C$_5$H$_4$N)

TABLE AII IR Data of Compounds **5a–p**

Compd.	ν ph—H	ν C—H	ν C=O	ν Ph	ν P=O	ν C—O—C	ν P—O—C	ν P—C
5a	3020	2990, 2850	1760	1580, 1490	1226	1092	1045, 929	770
5b	3030	2980, 2860	1745	1580, 1480	1260	1170	1060, 937	751
5c	3010	2980, 2850	1740	1590, 1480	1240	1180	1050, 941	739
5d	3020	2956, 2854	1772	1580, 1480	1265	1176	1032, 943	747
5e	3020	2950, 2849	1750	1580, 1490	1250	1180	1030, 937	742
5f	3096	2958, 2855	1773	1587, 1476	1262	1175	1051, 928	768
5g	3018	2952, 2850	1758	1590, 1457	1258	1101	1040, 958	752
5h	3020	2980, 2850	1752	1590, 1490	1245	1170	1040, 939	757
5i	3018	2974, 2857	1750	1585, 1479	1262	1187	1036, 930	732
5j	3035	2962, 2850	1746	1562, 1474	1248	1164	1063, 946	754
5k	3015	2929, 2875	1760	1585, 1470	1260	1180	1052, 940	754
5l	3028	2952, 2845	1774	1580, 1460	1235	1170	1035, 927	758
5m	3043	2958, 2858	1773	1578, 1472	1257	1176	1056, 948	751
5n	3074	2971, 2852	1765	1583, 1483	1285	1188	1036, 934	753
5o	3072	2972, 2852	1763	1582, 1483	1275	1190	1038, 946	732
5p	3056	2963, 2852	1766	1591, 1478	1265	1190	1027, 926	755