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Clean Procedure for the Synthesis of A-Aminophosphonates Catalyzed by Choline-Based Ionic Liquid

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ABSTRACT: *A sulfated choline-based ionic liquid [Ch-OSO_3H] was prepared and used as a novel catalyst for the synthesis of α-aminophosphonates via a one-pot three-component reaction with aldehydes, amines, and triethyl phosphite/diethyl phosphite at room temperature under solvent-free conditions or in aqueous media. The reaction was completed in short times and products could be simply separated from the reaction mixture in good to excellent yields. The catalyst could be recycled and reused for several times without noticeably reducing catalytic activity.* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 00:1–9, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21251

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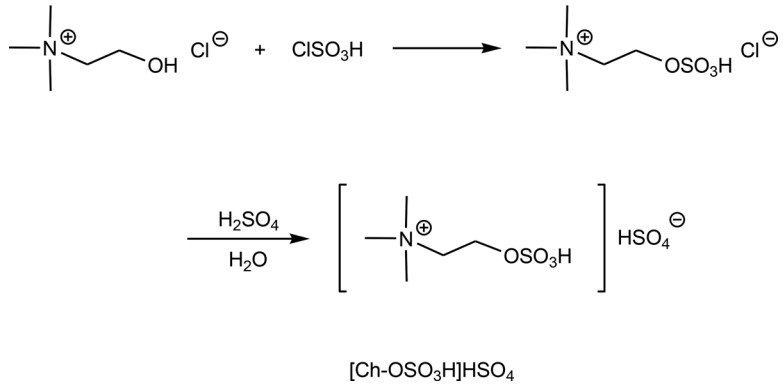
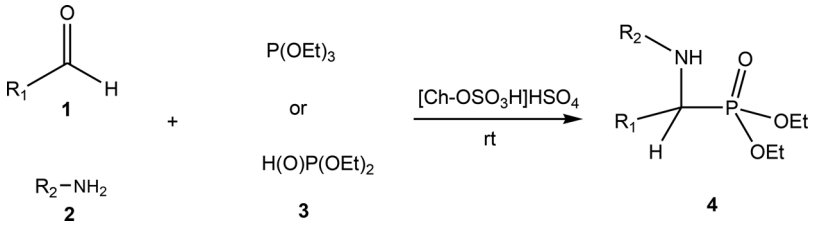
INTRODUCTION

With the increasing public concern over environmental degradation and the future of fossil fuels resources, it has become increasingly necessary to develop the alternative clean and green methods in the organic process in lab and factory. The use of nonhazardous and renewable materials, the energy conservation involving atom economy, and a decrease in the synthetic steps are the fundamental factors of green chemistry [1].

α-Aminophosphonates are pharmacologically important compounds, which have been exhibiting versatile biological activities such as antibacterial agents, pharmacogenic agents, antitumor agents, enzyme inhibitors, inhibitors of UDP-galactopyranose mutase, and antiviral agents [2]. The development of suitable synthetic methodologies for these compounds has been a topic of great interest in these years because of their widespread biological and chemical applications. Among them, the Kabachnik–Fields reaction appears to be still one of the simplest and most efficient method. The reaction proceeds via the imine formed from carbonyl compounds and amines, which then converted to the corresponding aminophosphonates by the reaction with triethyl phosphite or diethyl phosphite [3–9]. Many efforts have been made to develop efficient methods for the synthesis of α-aminophosphonates, including the one-pot multicomponent reaction (MCR)of aldehydes, amines,



SCHEME 1



SCHEME 2

and triethyl phosphite/diethyl phosphite, catalyzed by Lewis/Brønsted acids [4,5], solid acids [6], surfactants [7], metal salts [8], or metal oxides [9]. Many of these works used one kind of P-reagents, triethyl phosphite, or diethyl phosphite, respectively, though a fewer used both of P-reagents [4a]. However, the search for new readily available and green catalysts for this reaction is still actively ongoing.

In this decade ionic liquids (ILs) have been explored to be promising alternative catalysts for green chemistry purpose, some of them such as [bmim]BF_4/[bmim]PF_6 [10], sulfonic acid ILs [11], [bnmim][HSO_4] [12], ethyl ammonium nitrate [13], [bmim][HCl] [14], and [emim]Br [15] have been used to catalyze the synthesis of α-aminophosphonates. However, ILs with imidazole as the cation are relatively expensive, which might hinder the future large-scale applications. Furthermore, some typical ILs with some halogen anions (such as $[PF_6]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$, or $[(CF_3SO_2)_2N]^-$) were confirmed to be less "greenness" [16]. To overcome the problems, choline-based catalysts (choline-based ionic liquids (CILs)) have emerged promptly and exhibited significant activity in organic syntheses; in recent years, Jayaram and co-workers reported the synthesis of α-aminophosphonates with diethyl phosphite in the presence of some kinds of IL, choline chloride·$2ZnCl_2$ [17]. It is generally accepted that CILs are promising in catalytic processes due to their superiority properties such as inexpensive, nontoxic, environmentally benign, and nonflammable [18].

In continuation of our efforts for environmentally benign protocol for various organic transformations [19], the sulfated choline-based IL [Ch-OSO_3H]HSO_4 (Scheme 1) was synthesized to be used as a novel catalyst for the one-pot three-component synthesis of α-aminophosphonates with triethyl phosphite or diethyl phosphite (Scheme 2).

RESULTS AND DISCUSSION

The preparation of the sulfated choline-based IL [Ch-OSO_3H]HSO_4 was made up of two steps reaction in a one-pot apparatus. The new catalyst [Ch-OSO_3H]HSO_4 is a somewhat viscous, colorless liquid at room temperature, entirely miscible with water and soluble or partly soluble in organic solvents. The biodegradable IL [Ch-OSO_3H]HSO_4 that bears a sulfated cholinium cation showed good biodegradation performance and could be biodegraded by the activated sludge process.

The one-pot three-component reaction between benzaldehyde (10 mmol), aniline (10 mmol), and triethyl phosphite (10 mmol) was employed as a model reaction. The reaction completed at room temperature for a length of time was optimized using [Ch-OSO_3H]HSO_4 as a catalyst (Table 1). Although the Kabachnik–Fields reaction was reported to be carried out at 50°C for 1–8 h without a catalyst

TABLE 1 Effect of the Different Catalysts on the Synthesis of α-Aminophosphonates[a]

Entry	*Catalyst (mmol)*	*Time (min)*	*Isolated Yield (%)*
1	Catalyst free	120	–
2	[Ch-OSO_3H]HSO_4 (0.1)	20	55
3	[Ch-OSO_3H]HSO_4 (0.2)	20	62
4	[Ch-OSO_3H]HSO_4 (0.4)	20	70
5	[Ch-OSO_3H]HSO_4 (0.6)	20	90
6	[Ch-OSO_3H]HSO_4 (1.0)	20	95
7	[Ch-OSO_3H]HSO_4 (1.2)	20	95
8	[Ch-OSO_3H]HSO_4 (1.4)	20	95
9	[Ch-OSO_3H]HSO_4 (1.6)	20	94
10	[Ch-OSO_3H]HSO_4 (1.0)	20	92[b]

[a]10 mmol benzaldehyde, 10 mmol aniline, 10 mmol triethyl phosphite, r.t.
[b]0.5 mL H_2O medium.

TABLE 2 [Ch-OSO_3H]HSO_4-Catalyzed Model Reaction in Different Solvents[a]

Entry	*Solvent*	*Time (min)*	*Isolated Yield (%)*
1	H_2O	20	92
2	EtOH	20	86
3	CH_3CN	20	85
4	CH_2Cl_2	20	31
5	C_6H_6	20	45
6	Solvent Free	20	95

[a]10 mmol benzaldehyde, 10 mmol aniline, 10 mmol triethyl phosphite, r.t. 1.0 mmol catalyst.

and solvent [20], we could not detect the product at room temperature (entry 1). It was observed that initially the reaction mixture was clear and after 2–3 min the solid mud mixture formation started. Nearly quantitative conversion of the starting material was obtained using 10 mol% of the catalyst (entries 6 and 10). Additionally, the reaction could be carried out either in aqueous media or under solvent-free conditions with nearly the same yield (entries 6 and 10). A further increase in the catalyst loading did not improve the yield (entries 7–9).

It is noteworthy that no desirable product could be detected when a mixture of benzaldehyde, aniline, and triethyl phosphite was stirred at room temperature in the absence of [Ch-OSO_3H]HSO_4 even after 120 min (entry 1), which indicated that the catalyst was absolutely necessary for this one-pot three-component reaction.

To optimize the reaction conditions, different polar solvents were then selected as a reaction medium. In the previous literature [11], the sulfonic acid functionalized IL could not catalyzed such reaction in the absence of water, but in the presence of water (1 mL) the product formed rapidly. However, the results are different with the literature and summarized in Table 2. The reaction accomplished under solvent-free conditions in good yield. Among the selected reaction media, this MCR was accomplished preferably in polar solvents, including CH_3CN, EtOH, and EtOH/H_2O. For green chemistry and economic reasons, it will facilitate to overcome the volatile organic compounds (VOCs) problems with both solvent-free conditions and aqueous medium reactions.

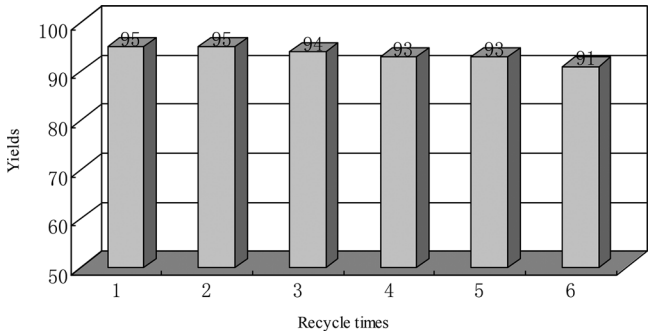


FIGURE 1 The recycling performance of the catalyst.

It is important to note that the [Ch-OSO_3H]HSO_4 was recycled after the reaction. Under solvent-free condition, after the reaction, 1 mL water was added to the reaction mixture flask, stirred, and then filtrated; the catalyst was reused after the extraction with CH_2Cl_2, washed with ether, and dried at 80°C under vacuum in each cycle.

The next reaction was carried out with an equal molar ratio of reactants in the same scale as the first time, and the results are listed in Fig. 1 showing that the catalyst can be reused at least six times without a little decrease in yields.

The generality of this protocol was tested using various aldehydes, amines, and tri/diethyl phosphite as reactants to determine the scope of the [Ch-OSO_3H]HSO_4 under the optimized reaction conditions described above and the results are presented in Table 3.

It can easily be seen that this one-pot three-component MCR was accomplished within 20–50 min and the products were isolated in good yields. First, the aromatic aldehydes carrying either electron-donor or electron-withdrawing substituents could give reasonable to good yields of α-aminophosphonates (entries 2 and 13–16). Second, both the electron-donating and electron-withdrawing substituents (entries 3–7) would facilitate to this MCR in view of the anilines. Additionally, both triethyl phosphite and diethyl phosphite could be employed as one of the reactants in this reaction.

The comparison of the performance of [Ch-OSO_3H]HSO_4 with those relatively good results have been reported in these years (Table 4). It could be

TABLE 3 Synthesis of α-Aminophosphonates Catalyzed by [Ch-OSO_3H]HSO_4[a]

Entry	*R_1*	*R_2*	*3*	*Time (min)*	*Yield[b] (%)*
1	4-$CH_3OC_6H_4$	C_6H_5	$P(OEt)_3$	45	90
2	4-$CH_3OC_6H_4$	C_6H_5	$H(O)P(OEt)_2$	50	92
3	4-$CH_3OC_6H_4$	4-$CH_3C_6H_4$	$P(OEt)_3$	30	91
4	4-$CH_3OC_6H_4$	4-$NO_2C_6H_4$	$H(O)P(OEt)_2$	50	93
5	4-$CH_3OC_6H_4$	4-FC_6H_4	$H(O)P(OEt)_2$	50	83
6	4-$CH_3OC_6H_4$	2,4-$Cl_2C_6H_3$	$H(O)P(OEt)_2$	50	80
7	4-$CH_3OC_6H_4$	4-BrC_6H_4	$H(O)P(OEt)_2$	50	82
8	4-$CH_3C_6H_4$	C_6H_5	$H(O)P(OEt)_2$	50	80
9	C_6H_5	C_6H_5	$P(OEt)_3$	20	95
10	C_6H_5	C_6H_5	$H(O)P(OEt)_2$	30	91
11	C_6H_5	3-$NO_2C_6H_4$	$P(OEt)_3$	50	86
12	C_6H_5	4-$NO_2C_6H_4$	$P(OEt)_3$	30	89
13	2-ClC_6H_4	C_6H_5	$P(OEt)_3$	20	94
14	4-ClC_6H_4	C_6H_5	$P(OEt)_3$	20	95
15	4-HOC_6H_4	C_6H_5	$P(OEt)_3$	20	91
16	4-$NO_2C_6H_4$	C_6H_5	$P(OEt)_3$	20	90

Reaction conditions: [a]10 mmol benzaldehyde, 10 mmol aniline, 10 mmol tri/diethyl phosphite, 1 mmol catalyst, r.t. [b]Isolated yields.

TABLE 4 Comparison of the Results with Different Catalysts

Entry	*Catalyst (mol%)*	*Reaction Conditions*	*Time*	*Yield (%)[Ref.]*
1	$ZrOCl_2 \cdot 8H_2O$ (10%)	Solvent free/r.t	5 min	95 [4a]
2	$NbCl_5$ (5%)	Solvent free/50°C	30 min	95 [4c]
3	TiO_2 (20%)	Solvent free/50°C	3.5 h	98 [9a]
4	[bnmim][HSO_4] (50%)	Solvent free/r.t	10 min	96 [12]
5	Choline chloride·2$ZnCl_2$ (15%)	Solvent free/r.t	60 min	96 [15]
6	[DDPA][HSO_4] (10%)	H_2O/r.t	30 min	95 [19b]
7	[Ch-OSO_3H]HSO_4 (10%)	Solvent free/r.t	20 min	95 [Present work]

seen that the [Ch-OSO_3H]HSO_4 has a good efficiency when compared with many of those reported catalysts in the MCR in addition to its biodegradation.

Without a catalyst and solvent conditions, no intermediate formation of either an imine or a hydroxy phosphonate was observed [20]. So, the mechanism was somewhat similar to the reported work [11]. The reaction might proceed through protonation of the aldehyde, a condensation reaction with the aniline, formation of an activated imine and a subsequent addition of the triethyl phosphite to give a phosphonium intermediate, and then the reaction with the water generated during condensation to give the product (Fig. 2).

CONCLUSIONS

In summary, in this study, an efficient and clean procedure for the synthesis of α-aminophosphonates via a one-pot three-component reaction catalyzed by a sulfated choline-based IL [Ch-OSO_3H] was established. The merit of this methodology is that it is a simple postprocedure, having short reaction time, high yields, and environmentally benign.

EXPERIMENTAL

Melting points were determined by the use of an X_6-Data microscope apparatus. The IR spectra were run on a Bruker Vector 22 spectrometer and expressed in cm^{-1} (KBr). ^1H NMR spectra were recorded on a Bruker DRX300 (300 MHz) and Bruker DRX500 (500 MHz) spectrometer. Elemental analyses were recorded on a PerkinElmer C spectrometer. Mass spectra were obtained with an automated Fininigan TSQ Quantum Ultra AM (Thermal) LC-MS spectrometer. All chemicals (AR grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. Shanghai, China and used without further purification.

Synthesis of Choline-Based IL ([Ch-OSO_3H]HSO_4)

The biodegradable cholium cation IL [Ch-OSO_3H]HSO_4 was synthesized according to previous methods [18] with improvement. The IL was analyzed by ^1H NMR, ^{13}C NMR, MS spectroscopes, and elemental analyses, and the spectral data agreed with their structures (Scheme 1).

To a mixture of choline chloride (0.1 mol, 13.95 g) in hexane, 100 mL of chlorosulfonic acid

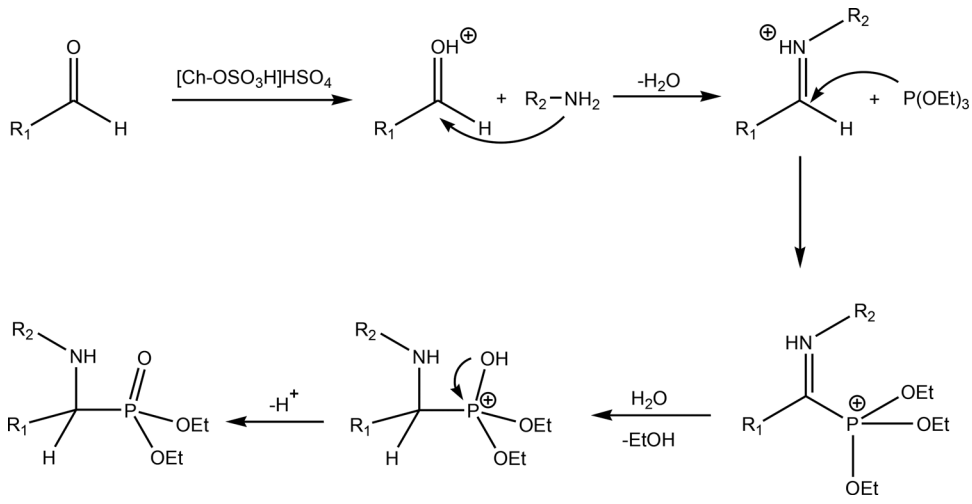


FIGURE 2 The possible mechanism for the synthesis of α-aminophosphonates

(0.10 mol, 6.65 mL) was added in portions within 30 min, and then the mixture was stirred for 1 h at 0–5°C. When HCl gas was no longer evaporated, the mixture was stirred for another 1 h at room temperature. Then, the mixture was filtered, washed with 50 mL of hexane, and dried at room temperature to afford intermediate *N*,*N*,*N*-trimethyl-2-(sulfooxy)ethanaminium chloride. The aqueous solution of intermediate (0.05 mol, 10.98 g) was added dropwise into the aqueous solution of sulfuric acid (98%) (0.05 mol, 5.0 g) at room temperature under nitrogen atmosphere. Then, the combined solution was washed repeatedly with diethyl ether to remove unreacted material, and subsequently distilled to remove the water and dried in a vacuum again, and then the $[Ch\text{-}OSO_3H]HSO_4$ was obtained quantitatively and in high purity as a colorless oil.

^{1}HNMR (300 MHz, D_2O): δ 3.93 (s, 9H, -CH_3), 3.40–3.42 (m, 2H, -CH_2-O), 3.93–3.97 (m, 2H, -CH_2-N). ^{13}CNMR (75 MHz, D_2O): δ 53.8, 53.9, 67.4. MS (*m/z*): 280.30 ($M^+ - 1$). Anal. calcd for $C_5H_{15}NO_8S_2$: C, 21.35; H, 5.37; N, 4.98; found: C, 21.33; H, 5.38; N, 4.97.

General Procedure for the Synthesis of α-Aminophosphonates (Compounds **4***)*

To a round-bottomed flask charged with aldehyde (10 mmol, 1.06 g) and aniline (10 mmol, 0.93 g), $[Ch\text{-}OSO_3H]HSO_4$ (1.0 mmol, 0.28 g) was added under stirring. The mixture was stirred at room temperature for 2–3 min and then triethyl phosphite (10 mmol, 1.66 g)/or diethyl phosphite (10 mmol, 1.38 g) was added and stirred for a length of times. On completion (monitored by thin-layer chromatography), water (1 mL) was added to extract the catalyst from the mixture, and the products were obtained by filtration and dried under vacuum. The products were known compounds and identified by ^{1}H NMR (500 MHz, $CDCl_3$), ^{13}C NMR (125 MHz, $CDCl_3$), ^{31}P (201 MHz, $CDCl_3$), elemental analyses, physical data (m.p.), and compared with published studies [4c,4d,8c,9a,17].

The spectral data for compounds **4** are given in the following.

Diethy(4-methoxyphenyl)-N-(phenyl) aminomethylphosphonate (Table 3, entry 1). Colorless oil [8c], ^{1}H NMR, δ: 1.04 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 1.20 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 3.68 (s, 3H, Ph-OCH_3), 4.09–3.69 (m, 4H, -O-CH_2-C), 4.72 (d, J = 24.9 Hz, 1H, P-CH), 5.20 (brs, 1H, -NH), 6.52 (t, J = 7.1 Hz, 2H, Ar-H), 6.63 (t, J = 7.1 Hz, 1H, Ar-H), 6.77 (d, J = 8.0 Hz, 2H, Ar-H), 6.99 (t, J = 7.8 Hz, 2H, Ar-H), 7.32 (d, J = 7.8 Hz, 2H, Ar-H). ^{13}C NMR: δ 130.1 (Ar-C), 130.0 (Ar-C), 129.5 (Ar-C), 129.4 (Ar-C), 129.3 (Ar-C), 118.6 (Ar-C), 114.4 (Ar-C), 114.3 (Ar-C), 64.0 (d, J = 7.2 Hz, O-CH_2-C), 62.6 (d, J = 7.2 Hz, O-CH_2-C), 55.5 (d, J = 150.0 Hz, P-C), 55.3 (-OCH_3), 16.8 (d, J = 5.7 Hz, O-C-CH_3), 16.6 (d, J = 5.7 Hz, O-C-CH_3). ^{31}P NMR: δ 20.21. Anal. calcd for $C_{18}H_{24}NO_4P$: C, 61.88; H, 6.92; N, 4.01; found: C, 61.85; H, 6.91; N, 4.00.

Diethy(4-methoxyphenyl)-N-(phenyl) aminomethylphosphonate (Table 3, entry 2). Colorless oil [8c], ^{1}H NMR, δ: 1.04 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 1.20 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 3.68 (s, 3H, Ph-OCH_3), 4.09–3.69 (m, 4H, -O-CH_2-C), 4.72 (d, J = 24.9 Hz, 1H, P-CH), 5.20 (brs, 1H, -NH), 6.52 (t, J = 7.1 Hz, 2H, Ar-H), 6.63 (t, J = 7.1 Hz, 1H, Ar-H), 6.77 (d, J = 8.0 Hz, 2H, Ar-H), 6.99 (t,

$J = 7.8$ Hz, 2H, Ar-H), 7.32 (d, $J = 7.8$ Hz, 2H, Ar-H). ^{13}CNMR: δ 129.9 (Ar-C), 129.0 (Ar-C), 129.6 (Ar-C), 129.4 (Ar-C), 129.3 (Ar-C), 118.6 (Ar-C), 114.5 (Ar-C), 114.3 (Ar-C), 63.8 (d, $J = 7.2$ Hz, O-CH_2-C), 62.5 (d, $J = 7.2$ Hz, O-CH_2-C), 55.4 (d, $J = 150.0$ Hz, P-C), 55.3 (-OCH_3), 16.8 (d, $J = 5.7$ Hz, O-C-CH_3), 16.7 (d, $J = 5.7$ Hz, O-C-CH_3).

Diethy(4-methoxyphenyl)-N-(4-methylphenyl) aminomethylphosphonate (Table 3, entry 3). White solid, m.p. 97–99°C [9a], ^{1}H NMR, δ: 1.00 (t, $J = 7.0$ Hz, 3H, -O-C-CH_3), 1.12 (t, $J = 7.0$ Hz, 3H, -O-C-CH_3), 1.98 (s, 3H, Ph-CH_3), 3.49 (s, 3H, Ph-OCH_3), 3.99–3.60 (m, 4H, -O-CH_2-C), 4.61 (d, $J = 24.1$ Hz, 1H, P-CH), 5.32 (brs, 1H, -NH), 6.42 (t, $J = 7.2$ Hz, 2H, Ar-H), 6.70 (t, $J = 7.2$ Hz, 2H, Ar-H), 7.25 (t, $J = 7.8$ Hz, 2H, Ar-H), 7.62 (d, $J = 7.8$ Hz, 2H, Ar-H). ^{13}C NMR: δ 137.0 (Ar-C), 129.7 (Ar-C), 129.5 (Ar-C), 129.4 (Ar-C), 129.3 (Ar-C), 118.6 (Ar-C), 114.5 (Ar-C), 114.3 (Ar-C), 63.9 (d, $J = 7.2$ Hz, O-CH_2-C), 62.4 (d, $J = 7.2$ Hz, O-CH_2-C), 55.2 (d, $J = 150.0$ Hz, P-C), 55.3 (-OCH_3), 24.3 (-CH_3), 16.8 (d, $J = 5.7$ Hz, O-C-CH_3), 16.5 (d, $J = 5.7$ Hz, O-C-CH_3). ^{31}P NMR: δ 20.10. Anal. calcd for $C_{19}H_{26}NO_4P$: C, 62.80; H, 7.21; N, 3.85; found: C, 62.78; H, 7.20; N, 3.83.

Diethy(4-methoxyphenyl)-N-(4-nitrophenyl) aminomethylphosphonate (Table 3, entry 4). Yellow solid, m.p. 112–114°C (112°C) [9a], ^{1}H NMR, δ: 1.01 (t, $J = 7.0$ Hz, 3H, -O-C-CH_3), 1.12 (t, $J = 7.0$ Hz, 3H, -O-C-CH_3), 3.48 (s, 3H, Ph-OCH_3), 3.99–3.80 (m, 4H, -O-CH_2-C), 4.62 (d, $J = 24.3$ Hz, 1H, P-CH), 5.92 (brs, 1H, -NH), 6.41 (t, $J = 7.1$ Hz, 2H, Ar-H), 6.60 (t, $J = 7.1$ Hz, 2H, Ar-H), 7.15 (t, $J = 7.8$ Hz, 2H, Ar-H), 7.92 (d, $J = 7.8$ Hz, 2H, Ar-H). ^{13}C NMR: δ 153.6 (Ar-C), 141.0 (Ar-C), 133.5 (Ar-C), 129.8 (Ar-C), 129.3 (Ar-C), 127.6 (Ar-C), 124.4 (Ar-C), 114.5 (Ar-C), 65.0 (d, $J = 7.2$ Hz, O-CH_2-C), 63.1 (d, $J = 7.2$ Hz, O-CH_2-C), 55.8 (d, $J = 150.0$ Hz, P-C), 55.3 (-OCH_3), 16.8 (d, $J = 5.7$ Hz, O-C-CH_3), 16.6 (d, $J = 5.7$ Hz, O-C-CH_3). ^{31}P NMR: δ 22.25. Anal. calcd for $C_{18}H_{23}N_2O_6P$: C, 54.82; H, 5.88; N, 7.10; found: C, 54.83; H, 5.88; N, 7.11.

Diethy(4-methoxyphenyl)-N-(4-fluorophenyl) aminomethylphosphonate (Table 3, entry 5). White solid, m.p. 53°C [17], ^{1}H NMR, δ: 1.03 (t, $J = 7.0$ Hz, 3H, -O-C-CH_3), 1.20 (t, $J = 7.0$ Hz, 3H, -O-C-CH_3), 3.60 (s, 3H, Ph-OCH_3), 4.01–3.63 (m, 4H, -O-CH_2-C), 4.65 (d, $J = 24.3$ Hz, 1H, P-CH), 5.72 (brs, 1H, -NH), 6.52 (t, $J = 7.1$ Hz, 2H, Ar-H), 6.70 (t, $J = 7.1$ Hz, 2H, Ar-H), 6.81 (d, $J = 8.0$ Hz, 2H, Ar-H), 7.35 (t, $J = 7.8$ Hz, 2H, Ar-H). ^{13}C NMR: δ 162.7 (Ar-C), 140.0 (Ar-C), 133.1 (Ar-C), 129.7 (Ar-C), 129.3 (Ar-C), 127.6 (Ar-C), 125.4 (Ar-C), 115.5 (Ar-C), 65.0 (d, $J = 7.2$ Hz, O-CH_2-C), 63.9 (d, $J = 7.2$ Hz, O-CH_2-C), 55.4 (d, $J = 150.0$ Hz, P-C), 55.2 (-OCH_3), 16.8 (d, $J = 5.7$ Hz, O-C-CH_3), 16.7 (d, $J = 5.7$ Hz, O-C-CH_3). ^{31}P NMR: δ 21.05. Anal. calcd for $C_{18}H_{23}FNO_4P$: C, 58.85; H, 6.31; N, 3.81; found: C, 58.83; H, 6.30; N, 3.80.

Diethy(4-methoxyphenyl)-N-(2,4-dicholorophenyl)aminomethylphosphonate (Table 3, entry 6). White solid, m.p. 140–142°C [4d], ^{1}H NMR, δ: 1.05 (t, $J = 7.0$ Hz, 3H, -O-C-CH_3), 1.21 (t, $J = 7.0$ Hz, 3H, -O-C-CH_3), 3.95 (s, 3H, Ph-OCH_3), 4.03–3.65 (m, 4H, -O-CH_2-C), 4.72 (d, $J = 24.3$ Hz, 1H, P-CH), 5.45 (brs, 1H, -NH), 6.70–7.35 (m, 7H, Ar-H). ^{13}CNMR: δ 157.1 (Ar-C), 141.0 (Ar-C), 136.2 (Ar-C), 129.8 (Ar-C), 129.0 (Ar-C), 128.5 (Ar-C), 128.2 (Ar-C), 127.7 (Ar-C), 125.1 (Ar-C), 115.3 (Ar-C), 64.1 (d, $J = 7.2$ Hz, O-CH_2-C), 62.6 (d, $J = 7.2$ Hz, O-CH_2-C), 58.5 (d, $J = 150.0$ Hz, P-C), 55.3, 16.3 (d, $J = 7.6$ Hz, O-C-CH_3), 16.2 (d, $J = 7.8$ Hz, O-C-CH_3). ^{31}P NMR: δ 21.10. Anal. calcd for $C_{18}H_{22}Cl_2NO_4P$: C, 51.69; H, 5.30; N, 3.35; found: C, 51.66; H, 5.29; N, 3.33.

Diethy(4-methoxyphenyl)-N-(4-bromophenyl) aminomethylphosphonate (Table 3, entry 7). White solid, m.p. 106–107°C [17], ^{1}H NMR, δ: 1.13 (t, $J = 7.0$ Hz, 3H, -O-C-CH_3), 1.30 (t, $J = 7.0$ Hz, 3H, -O-C-CH_3), 3.69–3.72 (m,1H, -O-CH_2-C), 3.93 (s, 3H, Ph-OCH_3), 3.95–3.97 (m, 1H, -O-CH_2-C), 4.15–4.10 (m, 2H, -O-CH_2-C), 4.63 (d, $J = 24.0$ Hz, 1H, P-CH), 6.48 (d, $J = 7.0$ Hz, 2H, Ar-H), 6.88 (t, $J = 7.5$ Hz, 2H, Ar-H), 7.20–7.18 (m, 2H, Ar-H), 7.37–7.35 (m, 2H, Ar-H). ^{13}C NMR: δ 157.7 (Ar-C), 136.9 (Ar-C), 132.9 (Ar-C), 132.6 (Ar-C), 129.7 (Ar-C), 128.7 (Ar-C), 126.3 (Ar-C), 115.6 (Ar-C), 63.3 (d, $J = 7.2$ Hz, O-CH_2-C), 60.9 (d, $J = 7.2$ Hz, O-CH_2-C), 55.3 (-OCH_3), 51.0 (d, $J = 150.0$ Hz, P-C), 17.6 (d, $J = 5.7$ Hz, O-C-CH_3), 17.5 (d, $J = 5.7$ Hz, O-C-CH_3). ^{31}P NMR: δ 20.08. Anal. calcd for $C_{18}H_{23}BrNO_4P$: C, 50.48; H, 5.41; N, 3.27; found: C, 50.46; H, 5.40; N, 3.25.

Diethy(4-methylphenyl)-N-(phenyl) aminomethylphosphonate (Table 3, entry 8). White solid, m.p. 61–62°C [9a], ^{1}H NMR, δ: 1.01 (t, $J = 7.0$ Hz, 3H, -O-C-CH_3), 1.12 (t, $J = 7.0$ Hz, 3H, -O-C-CH_3), 2.17 (s, 3H, Ph-CH_3), 4.06–3.60 (m, 4H, -O-CH_2-C), 4.73 (d, $J = 24.3$ Hz, 1H, P-CH), 5.90 (brs, 1H, -NH), 6.75–6.66 (m, 2H, Ar-H), 7.15–7.09 (m, 2H, Ar-H), 7.55–7.32 (m, 6H, Ar-H). ^{13}C NMR: δ 130.1 (Ar-C), 130.0 (Ar-C), 129.5 (Ar-C), 129.4 (Ar-C), 129.3 (Ar-C), 118.6 (Ar-C), 114.4 (Ar-C), 114.3 (Ar-C), 63.0 (d, $J = 7.2$ Hz, O-CH_2-C), 61.2 (d,

J = 7.2 Hz, O-CH_2-C), 52.2 (d, J = 150.0 Hz, P-C), 24.2 (-CH_3), 16.8 (d, J = 5.7 Hz, O-C-CH_3), 16.6 (d, J = 5.7 Hz, O-C-CH_3). ^{31}P NMR: δ 19.89. Anal. calcd for $C_{18}H_{24}NO_3P$: C, 64.85; H, 7.26; N, 4.20; found: C, 64.83; H, 7.25; N, 4.19.

Diethy(phenyl)-N-(phenyl)aminomethylphosphonate (Table 3, entry 9). White solid, m.p. 89–90°C [lit. 8c], ^{1}H NMR, δ: 1.02 (t, J = 7.0 Hz, 3H), 1.17 (t, J = 7.0 Hz, 3H), 3.36 (s, 1H), 3.72–3.64 (m, 1H), 3.90–3.82 (m, 1H), 4.09–3.99 (m, 2H), 5.02 (d, J = 24.9 Hz, 1H), 6.52 (t, J = 7.1 Hz, 1H), 6.78 (d, J = 8.0 Hz, 2H), 6.99 (t, J = 7.75 Hz, 2H), 7.32–7.20 (m, 3H), 7.52 (d, J = 7.2 Hz, 2H). ^{13}C NMR: δ 146.9 (Ar-C), 146.6 (Ar-C), 136.3 (Ar-C), 129.5 (Ar-C), 128.7 (Ar-C), 128.2 (Ar-C), 118.8 (Ar-C), 114.3 (Ar-C), 64.0 (d, J = 7.2 Hz, O-CH_2-C), 63.2 (d, J = 7.0 Hz, O-CH_2-C), 56.5 (d, J = 150.5 Hz, P-C), 16.8 (d, J = 5.8 Hz, O-C-CH_3), 16.6 (d, J = 5.8 Hz, O-C-CH_3). ^{31}P NMR: δ 20.02. Anal. calcd for $C_{17}H_{22}NO_3P$: C, 63.94; H, 6.94; N, 4.39; found: C, 63.95; H, 6.94; N, 4.40.

Diethy(phenyl)-N-(phenyl)aminomethylphosphonate (Table 3, entry 10). White solid, m.p. 89–90°C [lit. 8c], ^{1}H NMR, δ: 1.13 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 1.30 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 3.71–3.69 (m, 1H, -O-CH_2-C), 3.97–3.93 (m, 1H, -O-CH_2-C), 4.16–4.10 (m, 2H, -O-CH_2-C), 4.79 (d, J = 24.3 Hz, 1H, P-CH), 5.80 (brs, 1H, -NH), 6.73–6.61 (m, 3H, Ar-H), 7.37–7.11 (m, 5H, Ar-H), 7.50–7.49 (d, J = 7.7 Hz, 2H, Ar-H). ^{13}C NMR: δ 146.8 (Ar-C), 146.6 (Ar-C), 136.3(Ar-C), 129.6(Ar-C), 128.7(Ar-C), 128.2(Ar-C), 118.8(Ar-C), 114.3(Ar-C), 63.8 (d, J = 7.0 Hz, O-CH_2-C), 63.0 (d, J = 7.0 Hz, O-CH_2-C), 56.5 (d, J = 150.5 Hz, P-C), 16.8 (d, J = 5.8 Hz, O-C-CH_3), 16.6 (d, J = 5.8 Hz, O-C-CH_3).

Diethy(phenyl)-N-(3-nitrophenyl) aminomethylphosphonate (Table 3, entry 11). Yellow solid, m.p. 124–125°C [4c], ^{1}H NMR, δ: 1.04 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 1.17 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 3.76–3.68 (m, 1H, -O-CH_2-C), 3.93–3.85 (m, 1H, -O-CH_2-C), 4.09–4.02 (m, 2H, -O-CH_2-C), 5.23 (d, J = 24.3 Hz, 1H, P-CH), 7.27–7.20 (m, 3H, Ar-H), 7.33 (t, J = 7.5 Hz, 3H, Ar-H), 7.54 (d, J = 7.1 Hz, 2H, Ar-H), 7.68 (d, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR: δ 149.9 (Ar-C), 149.6 (Ar-C), 136.3 (Ar-C), 129.5 (Ar-C), 128.7 (Ar-C), 128.2 (Ar-C), 122.5 (Ar-C), 118.8 (Ar-C), 114.3 (Ar-C), 111.2 (Ar-C), 64.3 (d, J = 7.2 Hz, O-CH_2-C), 63.5 (d, J = 7.0 Hz, O-CH_2-C), 56.8 (d, J = 150.5 Hz, P-C), 16.8 (d, J = 5.8 Hz, O-C-CH_3), 16.6 (d, J = 5.8 Hz, O-C-CH_3). ^{31}P NMR: δ 21.12. Anal. calcd for $C_{17}H_{21}N_2O_5P$: C, 56.04; H, 5.81; N, 7.69; found: C, 56.02; H, 5.80; N, 7.70.

Diethy(phenyl)-N-(4-nitrophenyl) aminomethylphosphonate (Table 3, entry 12). Yellow solid, m.p. 124–125°C [4c], ^{1}H NMR, δ: 1.05 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 1.15 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 3.76–3.72 (m, 1H, -O-CH_2-C), 3.91–3.87 (m, 1H, -O-CH_2-C), 4.07–4.01 (m, 2H, -O-CH_2-C), 5.12 (d, J = 24.3 Hz, 1H, P-CH), 6.85 (d, J = 7.9 Hz, 2H, Ar-H), 7.32–7.09 (m, 3H, Ar-H), 7.45 (d, J = 8.0 Hz, 2H, Ar-H), 7.68 (d, J = 8.0 Hz, 2H, Ar-H). ^{13}C NMR: δ 151.8 (Ar-C), 148.2 (Ar-C), 146.3 (Ar-C), 139.0 (Ar-C), 128.2 (Ar-C), 126.2 (Ar-C), 121.4 (Ar-C), 111.3 (Ar-C), 64.0 (d, J = 7.2 Hz, O-CH_2-C), 63.3 (d, J = 7.0 Hz, O-CH_2-C), 55.5 (d, J = 150.0 Hz, P-C), 16.7 (d, J = 5.8 Hz, O-C-CH_3), 16.3 (d, J = 5.8 Hz, O-C-CH_3). ^{31}P NMR: δ 21.24. Anal. calcd for $C_{17}H_{21}N_2O_5P$: C, 56.04; H, 5.81; N, 7.69; found: C, 56.01; H, 5.80; N, 7.71.

Diethy(2-cholorophenyl)-N-(phenyl) aminomethylphosphonate (Table 3, entry 13). White solid, m.p. 87–88°C [9a], ^{1}H NMR, δ: 1.02 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 1.14 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 4.16–3.70 (m, 4H, -O-CH_2-C), 5.13 (d, J = 24.3 Hz, 1H, P-CH), 5.99 (brs, 1H, -NH), 6.55 (t, J = 7.5 Hz, 2H, Ar-H), 6.60 (d, J = 7.5 Hz, 1H, Ar-H), 7.15–6.96 (m, 6H, Ar-H). ^{13}C NMR: δ 144.2 (Ar-C), 130.0 (Ar-C), 129.6 (Ar-C), 128.2 (Ar-C), 127.8 (Ar-C), 127.2 (Ar-C), 126.2 (Ar-C), 125.2 (Ar-C), 120.5 (Ar-C), 114.5 (Ar-C), 63.7 (d, J = 7.2 Hz, O-CH_2-C), 63.3 (d, J = 7.0 Hz, O-CH_2-C), 55.4 (d, J = 150.0 Hz, P-C), 16.8 (d, J = 5.8 Hz, O-C-CH_3), 16.6 (d, J = 5.8 Hz, O-C-CH_3). ^{31}P NMR: δ 20.01. Anal. calcd for $C_{17}H_{21}ClNO_3P$: C, 57.72; H, 5.98; N, 3.96; found: C, 57.70; H, 5.98; N, 3.94.

Diethy(4-cholorophenyl)-N-(phenyl) aminomethylphosphonate (Table 3, entry 14). White solid, m.p. 57–58°C [9a], ^{1}H NMR, δ: 1.15 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 1.29 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 3.76–3.68 (m, 1H, -O-CH_2-C), 3.83–3.76 (m, 1H, -O-CH_2-C), 4.19–4.09 (m, 2H, -O-CH_2-C), 4.85 (d, J = 24.5 Hz, 1H, P-CH), 5.99 (brs, 1H, -NH), 6.61 (d, J = 7.5 Hz, 2H, Ar-H), 6.71 (d, J = 7.5 Hz, 1H, Ar-H), 7.35–6.99 (m, 6H, Ar-H). ^{13}C NMR: δ 146.5 (Ar-C), 130.0 (Ar-C), 129.5 (Ar-C), 128.2 (Ar-C), 127.7 (Ar-C), 126.2 (Ar-C), 121.4 (Ar-C), 117.5 (Ar-C), 63.8 (d, J = 7.2 Hz, O-CH_2-C), 63.3 (d, J = 7.0 Hz, O-CH_2-C), 55.5 (d, J = 150.0 Hz, P-C), 16.7 (d, J = 5.8 Hz, O-C-CH_3), 16.3 (d, J = 5.8 Hz, O-C-CH_3). ^{31}P NMR: δ 20.00. Anal. calcd for

$C_{17}H_{21}ClNO_3P$: C, 57.72; H, 5.98; N, 3.96; found: C, 57.74; H, 5.99; N, 3.97.

Diethy(4-hydroxyphenyl)-N-(phenyl) aminomethylphosphonate (Table 3, entry 15). Colorless oil, [9a], ^{1}H NMR, δ: 0.99 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 1.09 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 3.76–3.71 (m, 1H, -O-CH_2-C), 3.83–3.76 (m, 1H, -O-CH_2-C), 4.02–3.95 (m, 2H, -O-CH_2-C), 4.69 (d, J = 24.0 Hz, 1H, P-CH), 4.97 (s, 1H, Ph-OH), 5.49 (brs, 1H, -NH), 6.55–6.49 (m, 3H, Ar-H), 6.65 (d, J = 7.0 Hz, 2H, Ar-H), 6.87 (d, J = 7.5 Hz, 2H, Ar-H), 7.09 (d, J = 7.0 Hz, 2H, Ar-H). ^{13}C NMR: δ 148.8 (Ar-C), 141.2 (Ar-C), 136.3 (Ar-C), 132.0 (Ar-C), 129.7 (Ar-C), 128.6 (Ar-C), 126.3 (Ar-C), 115.6 (Ar-C), 63.6 (d, J = 7.2 Hz, O-CH_2-C), 63.1 (d, J = 7.0 Hz, O-CH_2-C), 52.3 (d, J = 150.0 Hz, P-C), 16.8 (d, J = 5.8 Hz, O-C-CH_3), 16.6 (d, J = 5.8 Hz, O-C-CH_3). ^{31}P NMR: δ 21.29. Anal. calcd for $C_{17}H_{22}NO_4P$: C, 60.89; H, 6.61; N, 4.18; found: C, 60.88; H, 6.60; N, 4.16.

Diethy(4-nitrophenyl)-N-(phenyl) aminomethylphosphonate (Table 3, entry 16). Yellow solid, m.p. 123–125°C [17], ^{1}H NMR, δ: 1.20 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 1.31 (t, J = 7.0 Hz, 3H, -O-C-CH_3), 3.91–3.89 (m, 1H, -O-CH_2-C), 4.04–4.07 (m, 1H, -O-CH_2-C), 4.19–4.13 (m, 2H, -O-CH_2-C), 4.88 (d, J = 25.0 Hz, 1H, P-CH), 6.55 (d, J = 8.0 Hz, 2H, Ar-H), 7.28–6.74 (m, 5H, Ar-H), 8.21 (d, J = 8.5 Hz, 2H, Ar-H). ^{13}C NMR: δ 151.6 (Ar-C), 148.3 (Ar-C), 147.6 (Ar-C), 139.0 (Ar-C), 128.2 (Ar-C), 126.0 (Ar-C), 121.3 (Ar-C), 112.3 (Ar-C), 63.9 (d, J = 7.2 Hz, O-CH_2-C), 63.3 (d, J = 7.0 Hz, O-CH_2-C), 55.2 (d, J = 150.0 Hz, P-C), 16.5 (d, J = 5.8 Hz, O-C-CH_3), 16.2 (d, J = 5.8 Hz, O-C-CH_3). ^{31}P NMR: δ 21.20. Anal. calcd for $C_{17}H_{21}N_2O_5P$: C, 56.04; H, 5.81; N, 7.69; found: C, 56.05; H, 5.80; N, 7.70.

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