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Convenient One-Pot Synthesis of α-Amino Phosphonates in Water Using *p*-Toluenesulfonic Acid as Catalyst for the Kabachnik–Fields Reaction

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ABSTRACT: *The three-component Kabachnik–Fields reaction of substituted salicylaldehydes, aromatic amine, and triphenyl phosphite in water was effectively catalyzed by p-toluenesulfonic acid to give various α-amino phosphonates in good yields. The catalyst is easily available and inexpensive, and the process is green and mild.* © 2013 Wiley Periodicals, Inc. Heteroatom Chem 24:110–115, 2013; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21071

INTRODUCTION

The chemistry of organophosphorus compounds has received much attention due to the unique structural features and the significant biological activities of these compounds and, therefore utility in a wide range of applications in the areas of industrial, agricultural, and medicinal chemistry as well as their utility as synthetic intermediates [1]. As a kind of structural analogy to natural amino acid, α-amino phosphonates constitute an important class of compounds with diverse biological activities such as antibacterial, anti-HIV, peptidomimetics, enzyme inhibitors, pharmacogenic agents, haptens of catalytic antibodies, herbicidals, inhibitors of serine hydrolases, and antitumor agents [2].

A large number of methodologies for the synthesis of various α-amino phosphonate compounds have been extensively developed under various conditions. However, the one-pot synthesis of α-aminophosphonates via the Kabachnik–Fields reaction remains favorable because of its versatile route and highly efficient reactions. Recently, the three-component synthesis starting with aldehydes, amines, and diethyl phosphite or triethyl phosphite was reported using Lewis and Brønsted acid catalysts such as $LiClO_4$ [3], $InCl_3$ [4], lanthanide triflates/magnesium sulfate [5], $TaCl_5$–SiO_2 [6], Amberlyst-15 [7], Al_2O_3-MW [8], sulfamic acid [9], scandium tris(dodecyl sulfate) [10], BF_3-Et_2O [11], $M(OTf)_n$ [12], $M(ClO_4)_n$ [13], lanthanide triflates/ionic liquids [14], SmI_2 [15], $AlCl_3$ [16], $ZrOCl_2 \cdot 8H_2O$ [17], and TiO_2 [18]. The majority of these processes suffer from some drawbacks such as long reaction times, low yields of the products, the requirement of a stoichiometric amount of catalysts, costly metal ion, and the use of highly toxic catalysts. Therefore, it is still necessary to develop a more efficient method, particularly considering today's environmental concerns combined with economic aspects.

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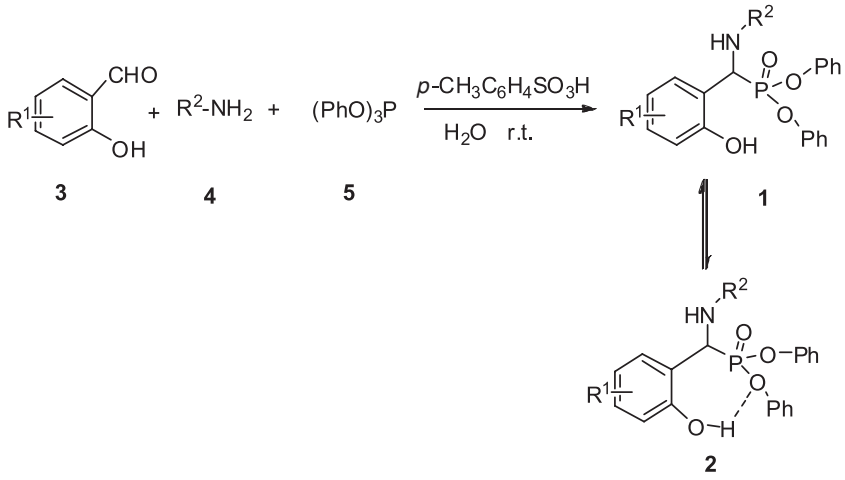


a: R^1= H, R^2= C_6H_5 ; **b:** R^1= H, R^2= 2-$CH_3C_6H_4$

c: R^1= H, R^2= 4-BrC_6H_4 ; **d:** R^1= H, R^2= 3-$NO_2C_6H_4$

e: R^1= H, R^2= 4-ClC_6H_4 ; **f:** R^1= H, R^2= 2,5-$Cl_2C_6H_4$

g: R^1= H, R^2= 4-$CH_3C_6H_4$; **h:** R^1= H, R^2= 2-$CH_3OC_6H_4$

i: R^1=5-Cl, R^2= 2-$CH_3C_6H_4$; **j:** R^1=5-Cl, R^2= 2-$CH_3OC_6H_4$

k: R^1= 5-Br, R^2= 2-$CH_3C_6H_4$; **l:** R^1= 5-NO_2, R^2= 4-$CH_3C_6H_4$

SCHEME 1 Synthesis of α-amino phosphonates using *p*-toluenesulfonic acid as a catalyst in water.

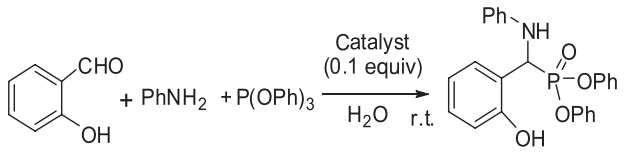
More recently, the use of an aqueous medium as a reaction solvent has attracted much attention. Scandium tris(dedecyl sulfate) [19], magnesium dodecyl sulfate [20], and thiamine hydrochloride (VB_1) [21] are reported to be effective catalysts for the formation of α-amino phosphonates using a three-component system consisting of aldehydes, amines, and triethyl phosphite in an aqueous medium. However, these catalysts are expensive and not easily available. And so we report on an ecofriendly, facile, and efficient methodology for the synthesis of α-amino phosphonates using *p*-toluenesulfonic acid as the catalyst by a three-component Kabachnik–Fields reaction system comprising substituted salicylaldehydes, amines, and triphenyl phosphite in an aqueous medium (Scheme 1). As shown in Scheme 1, substituted salicylaldehydes **3** was allowed to react with aromatic amines **4** and triphenyl phosphite using a small amount of *p*-toluenesulfonic acid as the catalyst in an aqueous medium to give the title compounds **1** in good yields. However, this method appears to have limited aromatic amine and some salicylaldehydes, since the attempts to extend the reaction to aliphatic amines failed. All the products were isolated from the reaction mixture by filtration, washed with cool water, and recrystallized from aqueous ethanol, and their structures were characterized by ^{1}H NMR, ^{31}P NMR, IR, and elemental analysis.

RESULTS AND DISCUSSION

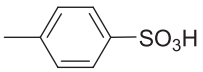
To study the reaction in water, the reaction of salicylaldehydes **3a**, aniline **4a**, and triphenyl phosphite **5** was tested as a model reaction at room temperature in the presence of various catalysts in water (Table 1). It was found that *p*-toluenesulfonic acid (entry 1) was the catalyst of choice for the reaction and the desired product (**1a**) was obtained in excellent yields (80%).

After optimizing the conditions, the generality of this method was examined by the reaction of several substituted salicylaldehydes (**3**), substituted amine (**4**)**,** with triphenyl phosphate and *p*-toluenesulfonic acid. The results are presented in Table 2. All α-amino phosphonates derivatives thus obtained show diagnostic doublets of methylene carbons bearing phosphonate groups due to their coupling with a phosphorus atom in their ^{13}C NMR spectra. ^{31}P NMR chemical shifts of these compounds (**1a, 1c, 1d**, **1e**, **1g**) showed four signals each in the region 16.96–18.35 ppm, and other compounds (**1b**, **1f**, **1h**, **1i**, **1j**, **1k**, **1l**) showed two signals each in

TABLE 1 Optimization of the Catalyst Effect on the Model Reaction[a]



3a 4a 5 1a

Entry	*Catalyst*	*Time (h)*	*Yield (%)*[b]
1		2	80
2	$(CH_3COO)_2Mn$	2	65
3	$NiCl{\cdot}6H_2O$	2	63
4	$CoCl{\cdot}6H_2O$	2	73
5	$InCl_2$	2	56
6	$ZnCl_2$	2	53
7	$FeCl_3{\cdot}6H_2O$	2	52
8	$CeCl_3$	2	75

[a]Reaction conditions: All reactions were carried out in 10 mL H_2O at room temperature with 1 mmol of reactants and 10% mol catalyst.
[b]Isolated yield.

region 16.00–18.35 ppm (Table 2). The magnetic nonequivalence of the phosphorus atom in phosphonate ester groups may be due to a restricted rotation at the phosphorus center by intramolecular hydrogen bonds between the phenolic hydoxyl group and phosphonate ester group (**2**), and so the two stereogenic centers were created. Consequently, the four diastereoisomers should be found. The results are in agreement with those of analogs described in the literature [22]. In the ^{1}H NMR spectra of all compounds, the proton at the α-carbon position resonated as two doublets due to its coupling with the phosphorus atom and the neighboring N—H proton. The N—H proton signal appeared as doublets at δ 5.12–5.68 ppm, owing to its coupling with the neighboring C—H proton.

CONCLUSIONS

In conclusion, the three-component Kabachnik–Fields reaction of substituted salicylaldehydes, aromatic amine, and triphenyl phosphite in water was effectively catalyzed by *p*-toluenesulfonic acid to give various α-amino phosphonates in good yields. The method displays the advantages of green synthesis without organic solvents involved, mild conditions, ready operations, and an easily available catalyst. The results showed that substituted salicylaldehydes containing electron-withdrawing groups could not provide better yields than ones not containing substituted groups. The influence of substituted groups of aromatic amines on the yields does not seem obvious. Unfortunately, the attempts to extend the reaction to aliphatic amines failed.

EXPERIMENTAL

All melting points were determined on a Yanaco apparatus (Japan) and are uncorrected. NMR spectra were measured on a Brucker 400 NMR instrument (Switzerland) in DMSO-d_6, and chemical shifts were expressed as units. TMS was used as an internal standard for ^{1}H NMR, and ^{13}C NMR and 85% H_3PO_4 were used as an external standard for ^{31}P NMR spectroscopy. IR spectra were determined as KBr pellets on an Avatar 360 FT-IR spectrophotometer.

TABLE 2 Synthesis of α-Amino Phosphonate from Various Substituted Salicylaldehydes, Amines and Triphenyl Phosphite

Entry	*R^1*	*R^2*	*Product*	*Time (h)*	*Yield (%)*[a]	*mp (°C)*	*^{31}P NMR DMSO-d_6/H_3PO_4*
1	H	C_6H_5	**1a**	3	93.8	126–128	17.45/17.60 17.86 /18.02
2	H	2-$CH_3C_6H_4$	**1b**	3	82.2	142–143	17.11/17.27
3	H	4-Br C_6H_4	**1c**	4	88.8	147–148	16.96/17.12 17.48/17.63
4	H	3-$NO_2C_6H_4$	**1d**	5	89.2	131–132	17.00/17.15 16.42/16.58
5	H	4-ClC_6H_4	**1e**	5	91.1	143–145	17.01/17.17 17.44/17.59
6	H	2,5-$Cl_2C_6H_3$	**1f**	5	82.3	146–148	15.89/16.03
7	H	4-$CH_3C_6H_4$	**1g**	4	82.0	136–138	18.35/18.20 17.76/17.61
8	H	2-$OCH_3C_6H_4$	**1h**	4	91.2	148–149	17.50/17.35
9	5-Cl	2-$CH_3C_6H_4$	**1i**	5	86.4	158–159	16.28/16.12
10	5-Cl	2-$OCH_3C_6H_4$	**1j**	5	83.1	159–160	16.57/16.42
11	5-Br	2-$CH_3C_6H_4$	**1k**	5	83.7	151–152	16.23/16.16
12	5-NO_2	4-$CH_3C_6H_4$	**1l**	5	83.4	143–144	16.15/16.00

[a]Isolated yields.

Elemental analysis was carried out with a Yanaco Chncorder MT-3 analyzer (Japan).

General Procedure for the Synthesis of the α-Aminophosphonates **1**

In a typical experiment, to a round-bottomed flask charged with substituted salicylaldehydes (1 mmol), triphenyl phosphite (1.2 mmol), and aromatic amine (1 mmol) in 5 mL of water, *p*-toluenesulfonic acid (5 mol%) was added under stirring. The mixture was stirred at room temperature for the appropriate time (Table 2). After complete conversion, as indicated by TLC, the mixture was quenched with H_2O (20 mL ice-cold water) and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous sodium sulfate. The solvent was distilled on a Rota-evaporator under reduced pressure to afford the crude products. The crude product was purified by recrystallization from aqueous ethanol, filtration, washed with cool water, and dried under in vacuo.

*Diphenyl(2-hydroxyphenyl)(phenylamino)methyl Phosphonate (***1a***)*. White solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.67 (dd, J_{PH} = 25.3 Hz, J = 8 Hz, 1H, CHP), 5.25 (d, $^3J_{PH}$ = 8 Hz, 1H, NH), 6.57–7.51 (m, 19H, ArH), 10.05 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 46.2 (d, J_{PC} = 161 Hz), 113.2, 114.9, 117.3, 119.2, 120.1, 120.2, 120.6, 120.7, 121.7, 125.1, 125.2, 128.9, 129.7, 129.8, 147.1, 150.1, 150.2, 155.3; IR (KBr) ν: 3421 (NH), 3234 (Ph—OH), 1246 (P=O), 1178 (P—O—C); Found: C, 60.59; H, 5.33, N, 3.15. Calcd. for $C_{25}H_{22}NO_4P$ (431.13); C, 69.60; H, 5.14, N, 3.25.

*Diphenyl(2-hydroxyphenyl)(2-methylphenylamino)methyl Phosphonate (***1b***)*. Light yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.18 (s, 3H, CH_3); 5.69 (dd, J_{PH} = 25.4 Hz, J = 8 Hz, 1H, CHP), 5.23 (br, 1H, NH), 6.62–7.64 (m, 18H, ArH), 10.17 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 17.3, 48.1 (d, J_{PC} = 160.7 Hz), 111.1, 115.2, 118.1, 120.1, 120.2, 120.5, 120.6, 121.3, 123.6, 125.1, 125.3, 126.8, 129.4, 129.7, 129.8, 130.1, 144.3, 150.2, 150.3, 155.4; IR (KBr) ν: 3442 (NH), 3063 (Ph—OH), 1206 (P=O), 1069(P—O—C); Found: C, 70.19; H, 5.33, N, 3.18. Calcd. for $C_{26}H_{24}NO_4P$ (445.14); C, 70.10; H, 5.43, N, 3.14.

*Diphenyl(4-bromophenyl amino)(2-hydroxyphenyl)methyl Phosphonate (***1c***)*. White solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.63 (dd, J_{PH} = 24.7 Hz, J = 8 Hz, 1H, CHP), 5.22(d, J = 10 Hz, 1H, NH), 6.67–7.61 (m, 18H, ArH), 10.12 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 46.2 (d, J_{PC} = 161.7 Hz), 108.2, 115.0, 115.2, 119.3, 120.1,120.2, 120.6, 120.7, 121.3, 125.1, 125.3, 129.7, 129.8, 131.4, 146.4, 150.0, 150.1, 155.3; IR (KBr) ν: 3418 (NH), 3020 (Ph—OH), 1244 (P=O), 1072 (P—O—C); Found: C, 58.79; H, 4.13, N, 2.78. Calcd. for $C_{25}H_{21}BrNO_4P$ (509.04); C, 58.84; H, 4.15, N, 2.74.

*Diphenyl(3-nitrophenyl amino)(2-hydroxyphenyl) methyl Phosphonate (***4d***)*. Brown solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.80 (m, 1H, NH), 5.30 (d, J_{PH} = 24.1 Hz, 1H, CHP), 6.76–7.69 (m, 18H, ArH), 10.25 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 46.3 (d, J_{PC} = 156.6 Hz), 106.2, 107.1, 109.9, 110.8,111.6, 114.9, 119.1, 120.1, 120.5, 122.8, 124.1, 125.3, 128.4, 129.4, 129.9, 148.7, 149.8, 150.1, 151.0, 155.3; IR (KBr) ν: 3412 (NH), 2927 (Ph—OH), 1264 (P=O), 1049 (P—O—C); Found: C, 63.19; H, 4.33, N, 5.78. Calcd. for $C_{25}H_{21}N_2O_6P$ (476.11); C, 63.03; H, 4.44, N, 5.88.

*Diphenyl(4-chlorophenyl amino) (2-hydroxyphenyl)methyl Phosphonate (***4e***)*. White solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.65 (dd, J_{PH} = 25.1 Hz, J = 9.2 Hz, 1H, CHP), 6.79–7.60 (m, 19H, ArH, HN), 10.10 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 46.3 (d, J_{PC} = 161.8 Hz), 114.6, 115.0, 119.2, 119.3, 120.1, 120.2, 120.6, 120.7, 121.3, 125.1, 125.3, 128.6, 129.7, 129.8, 145.9, 149.9, 150.0, 155.2; IR (KBr) ν: 3416 (NH), 3219 (Ph—OH), 1284 (P=O), 1071 (P—O—C); Found: C, 64.29; H, 4.43, N, 3.18. Calcd. for $C_{25}H_{21}ClNO_4P$ (465.09); C, 64.45; H, 4.54, N, 3.01.

*Diphenyl(2,5-dichlorophenyl amino)(2-hydroxyphenyl)methyl Phosphonate (***4f***)*. White solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.83 (dd, J_{PH} = 23.8 Hz, J = 12 Hz, 1H, CHP), 6.13 (m, 1H, NH), 6.73–7.56 (m, 17H, ArH), 10.38 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 49.2 (d, J_{PC} = 158.5 Hz), 112.4, 115.6, 117.7, 118.2, 119.4, 119.8, 120.1, 120.14, 120.4, 125.3, 125.4, 129.8, 129.9, 130.4, 132.7, 143.0,149.8, 149.9, 155.7; IR (KBr) ν: 3425 (NH), 3255 (Ph—OH), 1247(P=O), 1097 (P—O—C); Found: C, 60.09; H, 4.13, N, 2.88. Calcd. for $C_{25}H_{20}Cl_2NO_4P$ (499.05); C, 60.02; H, 4.03, N, 2.80.

*Diphenyl(p-tolyl amino)(2-hydroxyphenyl)methyl Phosphonate (***4g***)*. White solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.09 (s, 3H, CH_3), 5.23 (d, J_{PH} = 24.7 Hz, 1H, CHP), 5.63 (d, J = 9 Hz, 1H, NH), 6.61–7.60 (m, 18H, ArH), 10.01 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 20.0, 46.8 (d, J_{PC} = 156.1 Hz), 113.3, 114.9, 118.9, 120.2, 120.5, 120.7, 121.8, 123.7, 124.0,

125.2, 125.8, 128.1, 129.3, 129.6, 144.8,150.1, 151.1, 155.2; IR (KBr) ν: 3416 (NH), 3228 (Ph—OH), 1242 (P=O), 1077 (P—O—C); Found: C, 70.09; H, 5.43, N, 3.18. Calcd. for $C_{26}H_{24}NO_4P$ (445.14); C, 70.10; H, 5.43, N, 3.14.

*Diphenyl(2-methoxyphenyl amino)(2-hydroxyphenyl)methyl Phosphonate (***4h***).* Hazel solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.75 (s, 3H, OCH_3), 5.38 (br, 1H, NH), 5.66 (d, J_{PH} = 20 Hz, 1H, CHP), 6.67–7.40 (m, 18H, ArH), 10.14 (br, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 47.2 (d, J_{PC} = 157.5 Hz), 55.6, 110.2, 110.7, 115.3, 117.9, 119.3, 120.1, 120.5, 120.9, 121.2, 125.2, 125.4, 128.4, 128.5, 129.2, 129.7, 129.9, 135.4, 147.0, 149.9, 150.0, 155.5; IR (KBr) ν: 3435 (NH), 2966 (Ph—OH), 1226 (P=O), 1105 (P—O—C); Found: C, 67.69; H, 5.33, N, 3.15. Calcd. for $C_{26}H_{24}NO_5P$ (461.14); C, 67.67; H, 5.24, N, 3.04.

*Diphenyl(o-tolyl amino)(5-chloro-2-hydroxyphenyl)methyl Phosphonate (***4i***).* White solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.21 (s, 3H, Ar-CH_3), 5.46 (br, 1H, NH), 5.63 (d, J_{PH} = 24.3 Hz, J = 10 Hz, 1H, CHP), 6.67–7.40 (m, 17H, ArH), 10.52 (s, 1H, Ph—OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 17.4, 48.1 (d, J_{PC} = 160.7 Hz), 111.1, 115.2, 116.7, 118.4, 120.0, 120.4, 122.9, 123.8, 124.1, 125.2, 125.3, 126.7, 128.9, 129.4, 129.8, 130.2, 144.1, 149.9, 150.0, 154.3; IR (KBr) ν: 3440 (NH), 3244 (Ph—OH), 1270 (P=O), 1067 (P—O—C); Found: C, 65.07; H, 4.73, N, 2.85. Calcd. for $C_{26}H_{23}ClNO_4P$ (479.11); C, 65.07; H, 4.83;, N, 2.92.

*Diphenyl(2-methoxyphenyl amino)(5-chloro-2-hydroxyphenyl)methyl Phosphonate (***4j***).* Light green solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.85 (s, 3H, OCH3), 5.59 (br, 1H, NH), 5.66 (d, J_{PH} = 24.7 Hz, 1H, CHP), 6.66–7.47 (m, 17H, ArH), 10.51 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 47.6 (d, J_{PC} = 160.7 Hz), 55.6, 110.4, 110.9, 117.0, 118.2, 120.0, 120.4, 120.9, 122.8, 123.5, 125.3, 125.4, 128.2, 129.0, 129.8, 135.1, 147.2, 149.8, 149.9, 150.0, 154.6; IR (KBr) ν: 3411 (NH), 2938 (Ph—OH), 1226 (P=O), 1070 (P—O—C); Found: C, 62.87; H, 4.53, N, 2.85. Calcd. for $C_{26}H_{23}ClNO_5P$ (495.10); C, 62.97; H, 4.46, 2.82.

*Diphenyl(o-tolyl amino)(5-bromo-2-hydroxyphenyl)methyl Phosphonate (***4k***).* Lihgt green solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.21 (s, 3H, Ar-CH_3), 5.47 (br, 1H, NH), 5.64 (dd, J_{PH} = 24.3 Hz, J = 9 Hz, 1H, CHP), 6.63–7.93 (m, 17H, ArH), 10.58 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 17.4, 48.1 (d, J_{PC} = 160.3 Hz), 110.5, 111.2, 115.2, 117.3, 118.4, 120.1, 120.4, 124.2, 124.3, 125.2, 126.7, 129.3, 129.8, 130.2, 131.5, 131.8, 144.2, 150.2, 150.3, 154.7; IR (KBr) ν: 3444 (NH), 3244 (Ph—OH), 1206 (P=O), 1058 (P—O-—C); Found: C, 59.57; H, 4.53, N, 2.80. Calcd. for $C_{26}H_{23}BrNO_4P$ (523.05); C, 59.56; H, 4.42, N, 2.67.

*Diphenyl(p-tolyl amino)(2-hydroxy-5-nitrophenyl)methyl Phosphonate (***4l***).* Yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.12 (s, 3H, Ar-CH_3), 5.65 (d, J_{PH} = 25.5 Hz, J = 8 Hz, 1H, CHP), 6.69–7.40 (m, 15H, ArH), 8.08 (d, J = 8 Hz, 1H, ArH), 8.60 (s, 1H, ArH), 11.83 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 20.0, 46.5 (d, J_{PC} = 157.5 Hz), 113.4, 115.4, 120.0, 120.1, 120.5, 120.6, 123.7, 125.3, 125.4, 126.3, 129.4, 129.8, 129.9, 139.9, 144.2, 149.8, 149.9, 161.6; IR (KBr) ν: 3748 (NH), 3090 (Ph—OH), 1187 (P=O), 1099 (P—O—C); Found: C, 63.58; H, 4.63, N, 5.80. Calcd. for $C_{26}H_{23}N_2O_6P$ (490.13); C, 63.67; H, 4.73, N, 5.71.

SUPPORTING INFORMATION

Supporting Information is available from the corresponding author on request.

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