PPh_3-catalysed one-pot three-component syntheses of α-aminophosphonates under solvent-free conditions

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A simple and efficient preparation of α-aminophosphonates under relatively mild conditions by the one-pot reaction of aldehydes with amines and dialkyl phosphites using catalytic amounts of triphenylphosphine is described.

Keywords: α-aminophosphonates, triphenylphosphine, solvent-free, one-pot reaction

The synthesis of α-aminophosphonates has been extensively studied because the α-aminophosphonates are considered to be structural analogues of the corresponding α-amino acids. These compounds have been shown to serve as peptide mimics,[1] enzyme inhibitors,[2] antibiotics,[3] and catalytic antibodies.[4] As a result, many methods have been developed for the synthesis of α-aminophosphonates. One of the most convenient methods is Kabachnik–Fields reaction in which the nucleophilic addition of phosphites to imines catalysed by a base or an acid[5] is a key step. Some traditional Lewis acids catalysts have been used in this reaction.[6,7] However, these reactions cannot be carried out in a one-pot reaction with a carbonyl compound, amine and diethyl phosphite or trialkyl phosphate.[8] Lewis acid catalysts can be decomposed or deactivated in the presence of amine and water. Recently in order to overcome this problem, several new Lewis acids catalysts, TiO_2,[9] $Mg(ClO_4)_2$,[10] $BiNO_3$-$5H_2O$,[11] $InCl_3$,[12] metal triflates[13-16] have been used in this transformation. Moreover microwave, ionic liquid and ultrasonic[17-19] methods were found to be more effective for the synthesis of α-aminophosphonates. However, many of these procedures have some drawbacks including long reaction times, expensive reagents, low yields of the products and a difficult work-up.

Lewis acids catalysts are good for the synthesis of α-aminophosphonates. To the best of our knowledge there are only a few reported procedures[20] using a base as a catalyst in the preparation of α-aminophosphonates, and even then there are some limitations. Triphenylphosphine is a very versatile reagent which has been widely used.[21-24] Due to its relative air-stability and nucleophilicity, it has emerged as an efficient catalyst. Consequently, we conceived a new procedure using triphenylphosphine as a catalyst for the reaction of benzaldehyde, as amine and diethyl phosphite for preparation of α-aminophosphonates under solvent-free conditions in one pot.

Results and discussion

The reaction of benzaldehyde with aniline and diethyl phosphite was examined as a model reaction. First, various bases such as Et_3N, CsF, and NaOEt were used for checking this transformation (Table 1).

From Table 1, one can see that Ph_3P was the most popular base for inducing this transformation in terms of yields and reaction time. The Mitsunobu reaction has been used in the synthesis α-aminophosphonates. However, Ph_3P/diethyl azodicarboxylate (Mitsunobu reagent) as catalyst cannot bring about the synthesis of α-aminophosphonates in one-pot from three component.[25-26] In addition, it often needs one or two equiv Mitsunobu reagent as catalysts. Herein, PPh_3 was chosen as catalyst for the reaction of benzaldehyde with aniline and diethyl phosphite to produce α-aminophosphonates.

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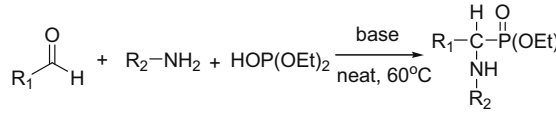

Scheme 1 Preparation of the diethyl 1-anilinobenzylphosphonates.

Table 1 Effect of different base to the reaction of benzaldehyde with aniline and diethyl phosphate

Entry	Catalyst	Time/h	Yield/%[a]
1	PPh_3 (5%)	2	80
2	PPh_3 (10%)	1	87
3	PPh_3 (15%)	1	85
4	NEt_3 (10%)	8	40
5	CsF (10%)	2	70
6	NaOEt (10%)	1.5	80

The reaction of various aldehydes with amines and diethyl phosphite using Ph_3P as catalyst under solvent-free conditions afforded α-aminophosphonates in good to high yields. The results are summarised in Table 2. Different substituents on the aldehyde and amine, such as OCH_3, NO_2, Cl, OH, NMe_2, can be used in this procedure with high efficiency. Most important, aromatic amine carrying electron-withdrawing substituents reacted well to give the corresponding α-aminophosphonates in high yields. These do not work well in previously reported methodologies.

In conclusion, we have demonstrated an efficient and simple alternative for the preparation of α-aminophosphonates *via* Ph_3P catalysed reaction in solvent-free conditions by a three-component one pot reaction. Prominent among the advantages of this new method are operational simplicity, good yields, short reaction times and an easy work-up.

Experimental

Starting materials were obtained from commercial suppliers and were used without further purification. Melting points were determined with an X-5 apparatus in open glass capillaries and were uncorrected. IR spectra were recorded on an EQUINX 55 FT-IR spectrometer using KBr pellets. NMR spectral data were collected on an AVANCF 300 MHz with TMS as an internal standard.

General experimental procedure

The carbonyl compound (1 mmol), amine (1 mmol) and diethyl phosphite (1.2 mmol) were added to PPh_3 (0.1 mmol, 0.0263 g) and the reaction mixture was heated in an oil bath at 60 °C for the fixed period. After completion of the reaction, as indicated by TLC, the reaction mixture was cooled to room temperature. The reaction mixture was quenched with water (10 mL) and extracted with CH_2Cl_2 (2 × 10 mL). The organic phase was separated, dried, and purified by chromatography on silica gel (8 : 2 petroleum ether/EtOAc) to afford the α-aminophosphonate.

The new products were characterised by the melting point, IR, ^1H/^{13}C NMR and elemental analysis. The structure of known product was confirmed by the melting point, IR and ^1H NMR. All

Table 2 One-pot synthesis of α-aminophosphonates catalysed by PPh_3[a]

Entry	R_1	R_2	Product	Reaction time/h	Yields[b]/%
1	Phenyl	2-Naphthyl	**6**[c]	2	97
2	Phenyl	2,6-Dimethylphenyl	**8**[c]	1	82
3	4-Nitrophenyl	Phenyl	**12**[c]	3	83
4	Phenyl	Phenyl	**1**	1	87
5	Phenyl	4-Chlorophenyl	**2**	3	83
6	Phenyl	4-Bromophenyl	**3**	3	95
7	Phenyl	3- Nitrophenyl	**4**	1	94
8	Phenyl	4-Nitrophenyl	**5**	4	87
9	Phenyl	4- Methylphenyl	**7**	1	92
10	4-Methylphenyl	Phenyl	**9**	2	96
11	2-Chlorophenyl	Phenyl	**10**	1	87
12	3- Chlorophenyl	Phenyl	**11**	1	96
13	4-Hydroxyphenyl	Phenyl	**13**	1	91
14	2- Hydroxyphenyl	Phenyl	**14**	1	94
15	4-Hydroxy-3-methoxyphenyl	Phenyl	**15**	1	90
16	3,4,5-Trimethoxyphenyl	Phenyl	**16**	1	92
17	4-Dimethyl-aminophenyl	Phenyl	**17**	1	91

[a]All products were characterised by ^{1}H NMR, IR.
[b]Isolated yield.
[c]Characterisation those compound also by ^{13}C NMR and elemental analyses.

the characterised data of products was consistent with the data for the expected structure or identical with those described in the literature.

Diethyl (naphthalen-2-yl-amino)(phenyl)methylphosphonate (**1**): White solid, m.p. 109–110 °C; IR(cm^{-1}): 3298 (NH), 1243 (P = O), 1097 (P–O–Et); ^{1}H NMR ($CDCl_3$): δ1.15 (3H, *t*, J_{HH} = 6.9 Hz, $-OCH_2CH_3$), 1.28 (3H, *t*, J_{HH} = 6.9 Hz, $-OCH_2CH_3$), 3.63–3.73 (1H, *m*, $-OCH_2CH_3$), 3.91–4.02 (1H, *m*, $-OCH_2CH_3$), 4.09–4.16 (2H, *m*, $-OCH_2CH_3$), 4.90 (1H, *d*, J_{HP} =23.9 Hz, CHP), 6.71(1H, *s*, ArH), 6.97 (1H, *d*, J_{HH} = 8.7 Hz, ArH), 7.26–7.33(5H, *m*, ArH), 7.47–7.62 (5H, *m*, ArH); ^{13}C NMR ($CDCl_3$): δ15.7 (*d, J*pc = 5.8 Hz, $-OCH_2CH_3$), 15.9 (*d, J*pc = 5.6 Hz, $-OCH_2CH_3$), 55.7 (*d, J*pc = 149.7 Hz, -CHP), 62.7 (*d, J*pc = 6.8 Hz, $-OCH_2CH_3$), 62.8 (*d, J*pc = 6.6 Hz, $-OCH_2CH_3$), 106.0, 117.6, 122.0, 125.6, 125.8, 127.1, 127.3, 127.4, 127.5 (*d, J*pc = 3.8 Hz), 128.1 (*d, J*pc = 2.5 Hz), 128.5, 134.3, 135.3, 143.5 (*d, J*pc = 14.3 Hz); Anal. Calcd for $C_{21}H_{24}NO_3P$ (369.39) C, 68.28; H, 6.55; N, 3.79. Found: C, 68.49; H, 6.52; N, 3.81%.

Diethyl (2,6-dimethylphenylamino)(phenyl)methylphosphonate (**2**): White solid, m.p. 76–78 °C; IR(cm^{-1}): 3348 (NH), 1238 (P = O), 1100 (P–O–Et); ^{1}H NMR ($CDCl_3$) δ1.02 (3H, *t*, J_{HH} = 6.9 Hz, $-OCH_2CH_3$), 1.26 (3H, *t*, J_{HH} = 7.0 Hz, $-OCH_2CH_3$), 2.22 (6H, *s*, $ArCH_3$), 3.57–3.64 (1H, *m*, $-OCH_2CH_3$), 3.85–3.93 (1H, *m*, $-OCH_2CH_3$), 4.06–4.13 (2H, *m*, $-OCH_2CH_3$), 4.49 (1H, *d*, J_{HP} = 22.3 Hz, -CHP), 6.74 (1H, *t*, J_{HH} = 7.3 Hz, ArH), 6.90 (2H, *t*, J_{HH} = 7.1 Hz, ArH), 7.25–7.42 (5H, *m*, ArH); ^{13}C NMR ($CDCl_3$): δ15.6 (*d, J*pc = 5.6 Hz, $-OCH_2CH_3$), 15.8 (*d, J*pc = 5.9 Hz, $-OCH_2CH_3$), 18.4 (s, $-Ph(CH_3)_2$), 58.6 (*d, J*pc = 146.6 Hz, –CHP), 62.2 (*d, J*pc = 7.1 Hz, $-OCH_2CH_3$), 62.4 (*d, J*pc = 6.9 Hz, $-OCH_2CH_3$), 121.2, 127.3 (d, *J*pc = 2.3 Hz), 127.7 (d, *J*pc = 6.5 Hz), 128.2, 128.4, 136.5, 143.7 (*d, J*pc = 9.1 Hz); Anal. Calcd for $C_{19}H_{26}NO_3P$ (374.39) C, 65.69; H, 7.54; N, 4.03. Found: C, 65.61; H, 7.49; N, 4.06%.

Diethyl (4-nitrophenyl)(phenylamino)methylphosphonate (**3**): Yellow solid, m.p. 124–126 °C; IR(cm^{-1}): 3287 (NH), 1346(NO_2), 1234 (P = O), 1103 (P–O–Et); ^{1}H NMR ($CDCl_3$) δ1.18 (3H, *t*, J_{HH} = 6.0 Hz, $-OCH_2CH_3$), 1.31 (3H, *t*, J_{HH} = 5.8 Hz, $-OCH_2CH_3$), 3.87–4.14 (4H, *m*, $-OCH_2CH_3$), 4.85 (1H, *d*, J_{HP} = 25.0 Hz, CHP), 6.53 (2H, *d*, J_{HH} = 6.8 Hz, ArH), 6.73 (1H, *t*, J_{HH} = 6.2 Hz, ArH), 7.09–7.27 (2H, *m*, ArH), 7.66 (2H, *d*, J_{HH} = 5.2 Hz, ArH), 8.20 (2H, *t*, J_{HH} = 7.4 Hz, ArH); ^{13}C NMR ($CDCl_3$): δ15.7 (*d, J*pc = 5.6 Hz, $-OCH_2CH_3$), 15.9 (*d, J*pc = 5.6 Hz, $-OCH_2CH_3$), 55.6 (*d, J*pc = 147.4 Hz,–CHP), 62.9 (*d, J*pc = 6.8 Hz, $-OCH_2CH_3$), 63.2 (*d, J*pc = 7.1 Hz, $-OCH_2CH_3$), 113.3, 123.2 (*d, J*pc = 2.6 Hz), 128.1 (*d, J*pc = 5.1 Hz), 128.8, 143.6 (*d, J*pc = 3.2 Hz), 145.2 (*d, J*pc = 13.9 Hz), 147.1; Anal. Calcd for $C_{17}H_{21}N_2O_5P$ (374.39) C, 56.04; H, 5.81; N, 7.69. Found: C, 56.20; H, 5.78; N, 7.72%.

Diethyl phenyl(phenylamino)methylphosphonate (**4**):[18] White solid, m.p. 91–92 °C; IR(cm^{-1}): 3293 (NH), 1235 (P = O), 1094 (P–O–Et); ^{1}H NMR ($CDCl_3$) δ1.10 (3H, *t*, J_{HH} = 6.6 Hz, $-OCH_2CH_3$), 1.28 (3H, *t*, J_{HH} = 6.6 Hz, $-OCH_2CH_3$), 3.65–3.70 (1H, *m*, $-OCH_2CH_3$), 3.91–3.96 (1H, *m*, $-OCH_2CH_3$), 4.07–4.16 (2H, *m*, $-OCH_2CH_3$), 4.76 (1H, *d*, J_{HP} = 24.2 Hz, CHP), 6.58–6.70 (3 H, *m*, ArH), 7.07–7.47 (7H, *m*, ArH).

Diethyl (4-chlorophenylamino)(phenyl)methylphosphonate (**5**):[15] White solid, m.p. 123–124 °C; IR(cm^{-1}): 3292 (NH), 1235 (P = O), 1094 (P–O–Et); ^{1}H NMR ($CDCl_3$) δ1.10 (3H, *t*, J_{HH} = 6.6 Hz, $-OCH_2CH_3$), 1.29 (3H, *t*, J_{HH} = 6.6 Hz, $-OCH_2CH_3$), 3.61–3.68 (1H, *m*, $-OCH_2CH_3$), 3.69–4.14 (3H, *m*, $-OCH_2CH_3$), 4.69 (1H, *d*, J_{HP} = 24.1 Hz, CHP), 6.52 (2H, *t*, J_{HH} = 7.1 Hz, ArH), 7.02–7.06 (2H, *m*, ArH), 7.26–7.44 (5H, *m*, ArH).

Diethyl (4-bromophenylamino)(phenyl)methylphosphonate (**6**):[16] White solid, m.p. 121–123 °C; IR(cm^{-1}): 3291 (NH), 1236 (P = O), 1098 (P–O–Et); ^{1}H NMR ($CDCl_3$) δ1.10 (3H, *t*, J_{HH} = 6.9 Hz, $-OCH_2CH_3$), 1.28 (3H, *t*, J_{HH} = 7.0 Hz, $-OCH_2CH_3$), 3.61–3.71 (1H, *m*, $-OCH_2CH_3$), 3.88–3.98 (1H, *m*, $-OCH_2CH_3$), 4.07–4.14 (2H, *m*, $-OCH_2CH_3$), 4.68 (1H, *d*, J_{HP} = 24.1 Hz, CHP), 6.46 (2H, *d*, J_{HH} = 8.5 Hz, ArH), 7.15–7.44 (7H, *m*, ArH).

Diethyl (3-nitrophenylamino)(phenyl)methylphosphonate (**7**):[13] Yellow solid, m.p. 128–130 °C; IR(cm^{-1}): 3286 (NH), 1351 (NO_2), 1232 (P = O), 1094 (P–O–Et); ^{1}H NMR ($CDCl_3$) δ1.11 (3H, *t*, J_{HH} = 6.9 Hz, $-OCH_2CH_3$), 1.31 (3H, *t*, J_{HH} = 7.0 Hz, $-OCH_2CH_3$), 3.61–3.69 (1H, *m*, $-OCH_2CH_3$), 3.88–4.00 (1H, *m*, $-OCH_2CH_3$), 4.12–4.19 (2H, *m*, $-OCH_2CH_3$), 4.79 (1H, *d*, J_{HP} = 24.0 Hz, CHP), 6.87 (1H, *d*, J_{HH} = 7.8 Hz, ArH), 7.18–7.47 (8H, *m*, ArH).

Diethyl (4-nitrophenylamino)(phenyl)methylphosphonate (**8**):[13] Yellow solid, m.p. 145–147 °C; IR(cm^{-1}): 3268 (NH), 1495 (NO_2), 1229 (P = O), 1110 (P–O–Et); ^{1}H NMR ($CDCl_3$) δ1.10 (3H, *t*, J_{HH} = 6.9 Hz, $-OCH_2CH_3$), 1.30 (3H, *t*, J_{HH} = 7.0 Hz, $-OCH_2CH_3$), 3.57–3.68 (1H, *m*, $-OCH_2CH_3$), 3.88–3.96 (1H, *m*, $-OCH_2CH_3$), 4.10–4.16 (2H, *m*, $-OCH_2CH_3$), 4.80 (1H, *d*, J_{HP} = 23.9 Hz, CHP), 5.73 (1H, *br s*, –NH), 6.58 (2H, *d*, J_{HH} = 8.8 Hz, ArH), 7.26–7.43 (6H, *m*, ArH), 8.01 (1H, *d*, J_{HH} = 8.8 Hz, ArH).

Diethyl (4-methylphenylamino)(phenyl)methylphosphonate (**9**):[13] White solid, m.p. 118–120 °C; IR(cm^{-1}): 3297 (NH), 1237 (P = O), 1101 (P–O–Et); ^{1}H NMR ($CDCl_3$) δ1.10 (3H, *t*, J_{HH} = 7.0 Hz, $-OCH_2CH_3$), 1.26 (3H, *t*, J_{HH} = 7.0 Hz, $-OCH_2CH_3$), 2.1 (3H, *s*, $ArCH_3$), 3.64–3.71 (1H, *m*, $-OCH_2CH_3$), 3.89–3.97 (1H, *m*, $-OCH_2CH_3$), 4.04–4.11 (2H, *m*, $-OCH_2CH_3$), 4.73 (1H, *d*, J_{HP} = 24.2 Hz, CHP), 6.50 (2H, *d*, J_{HH} = 8.2 Hz, ArH), 6.90 (2H, *d*, J_{HH} = 7.9 Hz, ArH), 7.25–7.31 (3H, *m*, ArH), 7.44 (2H, *s*, ArH).

Diethyl (4-methylphenyl)(phenylamino)methylphosphonate (**10**):[14] White solid, m.p. 66–68 °C; IR(cm^{-1}): 3324 (NH), 1234 (P = O), 1099 (P–O–Et); ^{1}H NMR ($CDCl_3$) δ1.13 (3H, *t*, J_{HH} = 6.8 Hz, $-OCH_2CH_3$), 1.28 (3H, *t*, J_{HH} = 6.9 Hz, $-OCH_2CH_3$), 2.30 (3H, *s*, $ArCH_3$), 3.65–3.72 (1H, *m*, $-OCH_2CH_3$), 3.90–3.98 (1H, *m*, $-OCH_2CH_3$), 4.05–4.14 (2H, *m*, $-OCH_2CH_3$), 4.72 (1H, *d*, J_{HP} = 24.0 Hz, CHP), 6.58–6.70 (3H, *m*, ArH), 7.07–7.35 (6H, *m*, ArH).

Diethyl (2-chlorophenyl)(phenylamino)methylphosphonate (**11**):[9] White solid, m.p. 87–89 °C; IR(cm^{-1}): 3299 (NH), 1235 (P = O), 1101 (P–O–Et); ^{1}H NMR ($CDCl_3$) δ1.06 (3H, *t*, J_{HH} = 6.9 Hz, $-OCH_2CH_3$), 1.33 (3H, *t*, J_{HH} = 6.9 Hz, $-OCH_2CH_3$), 3.59–3.67 (1H, *m*, $-OCH_2CH_3$), 3.84–3.94 (1H, *m*, $-OCH_2CH_3$), 4.16–4.26 (2H, *m*, $-OCH_2CH_3$), 5.37 (1H, *d*, J_{HP} = 24.6 Hz, CHP), 6.58 (2H, *d*, J_{HH} = 8.5 Hz, ArH), 6.69 (1H, *t*, J_{HH} = 7.0 Hz, ArH), 7.08–7.27 (4H, *m*, ArH), 7.38 (1H, *d*, J_{HH} = 6.7 Hz, ArH), 7.57 (1H, *d*, J_{HH} = 6.2 Hz, ArH).

Diethyl (3-chlorophenyl)(phenylamino)methylphosphonate (**12**):[9] White solid, m.p. 88–90 °C; IR(cm^{-1}): 3295 (NH), 1233 (P = O), 1093 (P–O–Et); ^{1}H NMR ($CDCl_3$) δ1.15 (3H, *t*, J_{HH} = 6.5 Hz, $-OCH_2CH_3$), 1.29 (3H, *t*, J_{HH} = 6.0 Hz, $-OCH_2CH_3$), 3.73–3.82 (1H, *m*, $-OCH_2CH_3$), 3.94–4.13 (3H, *m*, $-OCH_2CH_3$), 4.72 (1H, *d*, J_{HP} = 24.5 Hz, CHP), 6.55–6.73 (3H, *m*, ArH), 7.09–7.46 (6H, *m*, ArH).

Diethyl (4-hydroxyphenyl)(phenylamino)methylphosphonate (**13**):[9] Oil; IR(cm^{-1}): 3369 (NH), 1227 (P = O), 1097 (P–O–Et); ^1H NMR ($CDCl_3$) δ1.16 (3H, *t*, J_{HH} = 6.8 Hz, $–OCH_2CH_3$), 1.27 (3H, *t*, J_{HH} = 6.9 Hz, $–OCH_2CH_3$), 3.95–4.16 (4H, *m*, $–OCH_2CH_3$), 4.71 (1H, *d*, J_{HP} = 23.7 Hz, CHP), 6.58–6.71 (5H, *m*, ArH), 7.07–7.25 (4H, *m*, ArH).

Diethyl (2-hydroxyphenyl)(phenylamino)methylphosphonate (**14**):[7] Oil, IR(cm^{-1}): 3395 (NH), 1279 (P = O), 1098 (P–O–Et); ^1H NMR ($CDCl_3$) δ1.23 (3H, *t*, J_{HH} = 4.5 Hz, $–OCH_2CH_3$), 1.28 (3H, *t*, J_{HH} = 6.0 Hz, $–OCH_2CH_3$), 3.73–3.83 (1H, *m*, $–OCH_2CH_3$), 3.93–3.99 (1H, *m*, $–OCH_2CH_3$), 4.04–4.16 (2H, *m*, $–OCH_2CH_3$), 4.98 (1H, *d*, J_{HP} = 21 Hz, CHP), 6.68–6.98 (5H, *m*, ArH), 7.13–7.28 (4H, *m*, ArH).

Diethyl (4-hydroxy-3-methoxyphenyl)(phenylamino)methylphosphonate (**15**):[11] Oil, IR(cm^{-1}): 3395 (NH), 1276 (P=O), 1109 (P–O–Et); ^1H NMR ($CDCl_3$) δ1.18 (3H, *t*, J_{HH} = 7.0 Hz, $–OCH_2CH_3$), 1.32 (3H, *t*, J_{HH} = 6.8 Hz, $–OCH_2CH_3$), 3.67–3.75 (1H, *m*, $–OCH_2CH_3$), 3.90–4.15 (3H, *m*, $–OCH_2CH_3$), 3.87–3.90 (3H, *m*, $–OCH_3$), 4.71 (1H, *d*, J_{HP} = 23.7 Hz, CHP), 6.57–7.30 (8H, *m*, ArH).

Diethyl (3,4,5-trimethoxyphenyl)(phenylamino)methylphosphonate (**16**):[10] White solid, m.p. 107–109 °C; IR(cm^{-1}): 3290 (NH), 1236 (P=O), 1124 (P–O–Et); ^1H NMR ($CDCl_3$) δ1.15 (3H, *t*, J_{HH} = 6.6 Hz, $–OCH_2CH_3$), 1.29 (3H, *t*, J_{HH} = 6.6 Hz, $–OCH_2CH_3$), 3.72–4.14 (4H, *m*, $–OCH_2CH_3$), 3.81–3.85 (9H, *m*, $–OCH_3$), 4.66 (1H, *d*, J_{HP} = 24.0 Hz, CHP), 6.57–6.72 (5H, *m*, ArH), 7.10–7.28 (2H, *m*, ArH).

Diethyl (4-(dimethylamino)phenyl)(phenylamino)methylphosphonate (**17**):[11] White solid, m.p. 110–112 °C; IR(cm^{-1}): 3292 (NH), 1235 (P = O), 1100 (P–O–Et); ^1H NMR ($CDCl_3$) δ = s1.14 (3H, *t*, J_{HH} = 6.9 Hz, $–OCH_2CH_3$), 1.28 (3H, *t*, J_{HH} = 6.9 Hz, $–OCH_2CH_3$), 2.91 (6H, *s*, $N(CH_3)_2$), 3.64–3.71 (1H, *m*, $–OCH_2CH_3$), 3.87–3.97 (1H, *m*, $–OCH_2CH_3$), 4.06–4.13 (2H, *m*, $–OCH_2CH_3$), 4.67 (1H, *d*, J_{HP} = 18.1 Hz, CHP), 6.59–6.69 (5H, *m*, ArH), 7.09 (1H, *t*, J_{HH} = 7.3 Hz, ArH), 7.23–7.31 (3H, *m*, ArH).

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