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A convenient and mild protocol for preparation of α –trimethylsilyloxyphosphonates using sulfamic acid and their oxidation to α –ketophosphonates in the presence of *N*-bromosuccinimide

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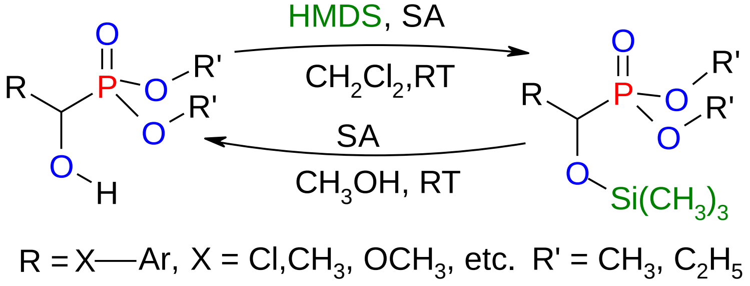
Abstract

A convenient and mild protocol was developed for the trimethylsilylation of α-hydroxyphosphonates using hexamethyldisilazane as the silylating agent in the presence of sulfamic acid (SA) as a heterogeneous solid acid catalyst in dichloromethane as the reaction medium. The utility of SA as the catalyst for deprotection of α-trimethylsilyloxyphosphonates to parent α-hydroxyphosphonates by making a switch to a protic solvent such as methanol was also demonstrated. Furthermore, the oxidation of α–trimethylsilyloxyphosphonates to corresponding α–ketophosphonates was achieved in excellent yields employing *N*-bromosuccinimide in the presence of catalytic quantity of AIBN.



Keywords: Sulfamic acid (SA), α-hydroxyphosphonates, α-trimethylsilyloxyphosphonates, α–ketophosphonates, protection, deprotection

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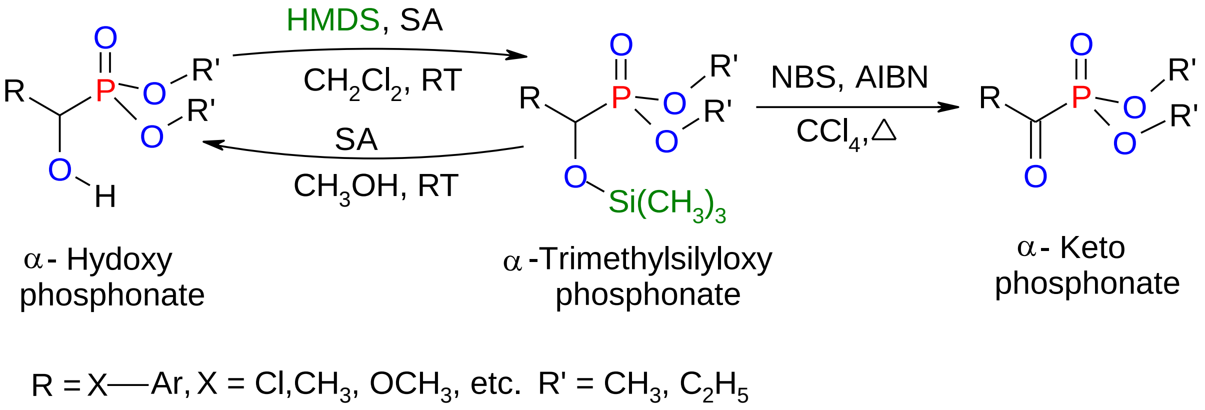
Introduction

The major driving force for development of new methodologies in organic synthesis stems from the need to achieve targeted transformations in a convenient and an efficient manner. In line with these targets, we previously reported use of sulfamic acid (SA) - a thermally robust, commercially available and an inexpensive chemical – as an effective catalyst for the synthesis of α- amino - as well as α-hydroxy - phosphonates.[1] As an extension of these studies, it became apparent to explore the manipulation of hydroxyl group in α-hydroxyphosphonates through its protection *via* silyl group to form α-trimethylsilyloxyphosphonates and subsequent oxidation to the corresponding α-ketophosphonates.[2-6] Both α–trimethylsilyloxyphosphonates and α-ketophosphonates are of great interest on account of their utility as useful precursors. For instance, α–trimethylsilyloxyphosphonates and their α- lithio derivatives have been demonstrated to be useful in the synthesis of α-hydroxyphosphonates,[7,8] β,γ-unsaturated ketones,[9,10] as well as α-trimethylsilyloxyketones.[11] Likewise, α-ketophosphonates are precursors to vinylphosphonates,[12] imines[13] and oximes.[14] Only a limited number of effective and easily accessible reagents have been reported for silylation of α–hydroxyphosphonates[15-18] which include Lewis acids such as I_2[16] or M (OTf)$_X$.[17,18] As a part of research programme in our laboratory on utilization of solid acid catalysts in organic transformations in general ,[19,20] and investigations pertaining to sulfamic acid (SA)[21-33] in particular, we planned to test the utility of SA as a protic acid catalyst for silylation of α- hydroxyphosphonates using hexamethyldisilazane (HMDS) as the silylating agent to obtain α-trimethylsilyloxyphosphonates as well as a catalyst for their deprotection to regenerate parent α–hydroxyphosphonates (Scheme 1).



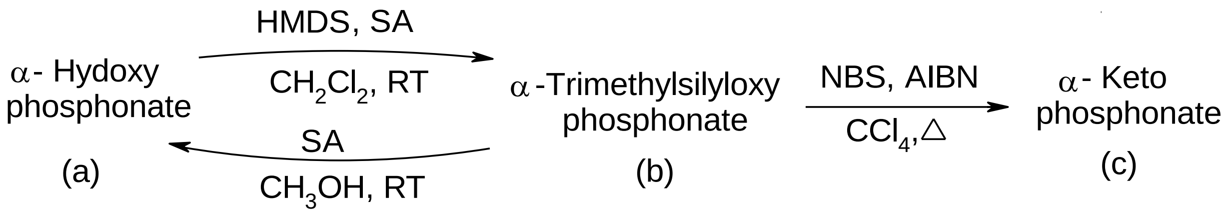
Scheme 1. (De)silylation of α- hydroxyphosphonates and oxidative deprotection of α-trimethylsilyloxyphosphonates to corresponding α-ketophosphonates.

Concerning the preparation of α-ketophosphonates, literature survey revealed that there are two predominent methods *viz*; (i) the Michaelis-Arbuzov reaction between an acid chloride and a trialkylphosphite and (ii) the oxidation of easily accessible α-hydroxyphosphonates.[34] On account of susceptibility of C(O)-P bond in α-ketophosphonates towards hydrolysis,[35,36] only a limited number of reagents such as highvalent metal oxides[37,38] or their mineral salts[39,40] work well for this transformation. In view of these observations, a search for alternate protocols/reagents is desirable. Accordingly, the efficacy of *N*-bromosuccinimide in the presence of AIBN for the oxidatative deprotection of α-trimethylsilyloxyphosphonates to α-ketophosphonates was evaluated (Scheme 1).

Results and Discussion

Diethyl α-hydroxy-(4-methoxyphenylmethyl) phosphonate (**1a**) was selected as a model substrate for the present study. Simply stirring together a mixture of α-hydroxyphosphonate (2 mmol), HMDS (1.6 mmol), dichloromethane (5 ml) and SA (30 mg, 15 mol %) at room temperature resulted in the formation of corresponding α-trimethylsilyloxyphosphonate as the sole product (TLC). This initial success led us to apply the similar reaction conditions for the silylation of a variety of α-hydroxyphosphonates (Table 1). For isolation of the product, the reaction mixture was diluted with dichloromethane and α- trimethylsilyloxyphosphonate was obtained by separation of the catalyst *via* simple filtration followed by the removal of solvent under reduced pressure. The products were purified by column chromatography. In all the cases, complete conversions and excellent isolated yields were obtained.

Table 1. (De)silylation of α- hydroxyphosphonates (a) and oxidative deprotection of α-trimethylsilyloxyphosphonates(b) to corresponding α-ketophosphonates (c)



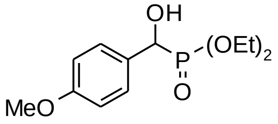
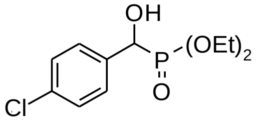
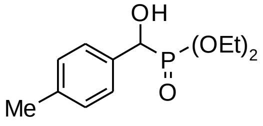
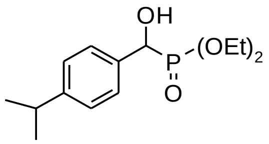
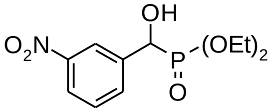
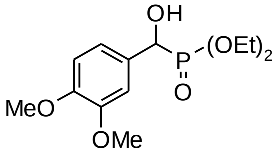
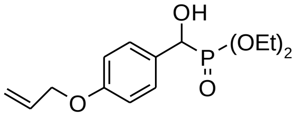
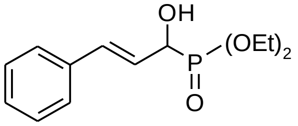
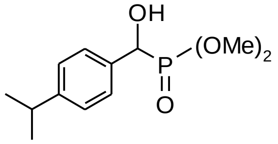
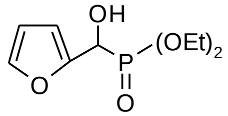
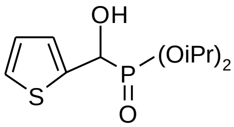
Entry	α-Hydroxyphosphonate **(a)**	α-Trimethylsilyloxy phosphonate **(b)**			α-Hydroxyphosphonate **(a)**			α–Ketophosphonate **(c)**		
		Time (h)	Yield^d (%)	Ref.	Time (h)	Yield^d (%)	Ref.	Time (h)	Yield^d (%)	Ref.
1.		4	94	17	1.5	91	25	1.5	85	39
2.		5	87	17	1	84	25	2.0	88	39
3.		5	86	17	1.5	87	25	3.0	74	39
4.		6	82	e	2	89	25	2.0	82	34

Table 1. Continued

Entry	α-Hydroxyphosphonate **(a)**	α-Trimethylsilyloxy phosphonate **(b)**			α-Hydroxyphosphonate **(a)**			α–Ketophosphonate **(c)**		
		Time (h)	Yield^d (%)	Ref.	Time (h)	Yield^d (%)	Ref.	Time (h)	Yield^d (%)	Ref.
5.		7	91	17	1	92	25	2.0	85	39
6.		8	87	e	2	85	25	3	87	34
7.		5	79	e	1.5	79	25	3	86	34
8.		5	93	17	2	91	25	3	87	39
9.		4	96	e	1	93	25	2.0	81	34
10.		4	92	e	1	94	25	2.5	83	34
11.		3	92	e	1	91	25	2.0	84	34

a: α- Hydroxyphosphonate (2 mmol), HMDS (1.6 mmol), SA (15 mol %), dichloromethane (5 mL), RT ; b: α- Trimethyl-silyloxyphosphonate (2 mmol), SA (15 mol %), methanol (5 mL), RT ; c: α-Trimethylsilyioxyphosphonate (2 mmol), NBS (2 mmol), AIBN (15 mg),carbontetrachloride (5 mL), RT; d: Yields refer to isolated pure products, e : not reported in the literature

It was observed that stirring together α-trimethylsilyloxyphosphonates with sulfamic acid (15 mol %) in a protic solvent such as methanol afforded a convenient route to regenerate the parent α-hydroxyphosphonates in excellent yields (Table 1). This is in accordance with our earlier work wherein we reported the utility of silica sulfuric acid as a catalyst for the protection of alcohols and aldehydes as THP ethers and acylals, respectively and their deprotection to parent compounds.

The attention was then focused towards the oxidation of α-trimethylsilyloxyphosphonates to α-ketophosphonates. Ollis et al.[41] have earlier reported an efficient protocol for the oxidation of trimethylsilylethers to carbonyl compounds using *N*-bromosuccinimide (NBS) in the presence of AIBN. Along the similar lines, we investigated the oxidation of α-trimethylsilyloxyphosphonates using NBS in the presence of AIBN. Refluxing the mixture of α-trimethylsilyloxyphosphonate (2 mmol) and NBS (2 mmol) in carbontetrachloride in the presence of catalytic quantity of AIBN for an appropriate time afforded corresponding α-ketophosphonate as the sole product (Table 1).

Conclusions

In summary, we have demonstrated the utility of a commercially available and inexpensive sulfamic acid as an efficient heterogeneous solid acid catalyst to effect the protection of α-hydroxyphosphonates as α-trimethylsilyloxyphosphonates as well as their deprotection to parent α-hydroxyphosphonates. An efficient oxidative deprotection of α-trimethylsilyloxyphosphonates to α-ketophosphonates was also demonstrated using NBS in the presence of AIBN.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ using Varian 300 MHz / Bruker Avance 200 MHz spectrometer, Bruker Avance (^{1}H NMR: 200 MHz, ^{13}C NMR: 50 MHz), Varian (^{1}H NMR: 300 MHz, ^{13}C NMR: 75 MHz). The chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz, respectively. Merck silica gel (0.043-0.063 mm) was used for column chromatography. α-Hydroxyphosphonates were prepared using reported protocols.[20] Dichloromethane and carbon tetrachloride were distilled prior to use. Other reagents and starting materials were directly used as received from commercial sources.

General experimental procedure

(a) Trimethylsilylation of α-hydroxyphosphonate. The mixture of α-hydroxyphosphonate (2 mmol), HMDS (1.6 mmol), dichloromethane (5 ml) and sulfamic acid (30 mg, 15 mol %) was stirred together till completion of the reaction (TLC). The reaction mixture was diluted with dichloromethane (5 mL) and the catalyst was filtered and washed with dichloromethane (2 x 5 mL). From the combined filtrate, the solvent was removed under reduced pressure and the residue obtained was filtered through a column of silica gel. The elution with a mixture of n-hexane and ethyl acetate (9:1, v/v) afforded pure α-trimethylsilyloxyphosphonate.

(b) Deprotection of α-trimethylsilyloxyphosphonate. The mixture of α-trimethylsilyloxyphosphonate (2 mmol), methanol (5 mL) and sulfamic acid (30 mg, 15 mol %) was stirred together at room temperature till the completion of reaction (TLC). The reaction mixture was poured onto a column of silica gel. The elution with a mixture of n-hexane and ethyl acetate (8:2, v/v) afforded pure α-hydroxyphosphonate.

(c) Oxidation of α-trimethylsilyloxyphosphonate to α-ketophosphonate. To a mixture of α-trimethylsilyloxyphosphonate (2 mmol) and NBS (2 mmol) in carbontetrachloride (5 mL) was added AIBN (10 mg) and the reaction mixture was refluxed until completion of oxidation (TLC). The reaction mixture was directly charged over the column of neutral alumina. The elution with a mixture of n-hexane and ethyl acetate (8:2, v/v) afforded pure α-ketophosphonate.

Diethyl-1-hydroxy-1-(4-methoxyphenyl) methyl phosphonate (1a). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.19-1.31 (m, 6H), 3.81 (s, 3H), 3.96 - 4.14 (m, 4H), 4.95 (d, J_{PH} 10 Hz, 1H), 6.90 (d J 8 Hz, 2H), 7.41 (d, J 8 Hz, 2H) ppm.; ^{13}C NMR (75 MHz, CDCl$_3$): δ 16.46, 55.25, 63.24, 68.78, 71.98, 113.72, 128.54, 159.53 ppm.

Diethyl [(hydroxyl)(4-cholrophenyl) methyl] phosphonate (2a). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.23 (t, J 8 Hz, 3H) 1.26 (t, J 8 Hz, 3H), 4.01- 4.08 (m, 4H), 4.59 (bs, 1H), 5.0 (d, $^{1}J_{PH}$ 12 Hz, 1H), 7.31 (d, J 6 Hz, 2H), 7.41 (d, J6 Hz, 2H) ppm.

Diethyl [(hydroxyl)(4-methylphenyl) methyl] phosphonate (3a). Solid (m.p. = 130-131 ^{0}C) ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.22 (t, J 8 Hz, 3H), 1.27 (t, J 8 Hz, 3H), 2.34 (s, 3H), 3.95- 4.21 (m, 5H), 3.9 - 4.2 (bs, 1H),4.98 (d, J_{PH} 12 Hz, 1H), 7.16 (d, J 8 Hz, 2H), 7.36 (d, J 8 Hz, 2H) ppm.; ^{13}C NMR (75 MHz, CDCl$_3$): δ 16.18, 20.04, 63.11, 68.79, 71.98, 122.02, 128.72, 133.70, 137.52 ppm.

Diethyl-1-hydroxy-1-(4-isopropylphenyl) methyl phosphonate (4a). Solid (m.p. =112-113 ^{0}C) ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.17-1.31 (m, 6H), 2.89 (septet, J 6.9 Hz, 1H), 3.96 - 4.08 (m, 4H), 4.0 - 4.2 (bs, 1H),4.98 (d, $^{1}J_{PH}$10.5 Hz, 1H), 5.41 (bs, 1H), 7.19 (d, J 7.8 Hz, 2H), 7.38 (d, J 7.8 Hz, 2H) ppm.; ^{13}C NMR (75 MHz, CDCl$_3$): δ 16.20, 23.59, 23.82, 33.69, 63.13 (d, $^{2}J_{PC}$7.0 Hz), 63.45 (d, $^{2}J_{PC}$7.0 Hz), 126.20, 127.06, 133.78, 148.62 ppm.

Diethyl-1-hydroxy-1-(3-nitrophenyl methyl phosphonate (5a). ^{1}H NMR (200 M Hz, CDCl$_3$): δ 1.25 (t, J 8 Hz, 3H) 1.28 (t, J 8 Hz, 3H), 4.00 - 4.25 (m, 4H), 5.16 (dd, $^{1}J_{PH}$12Hz, $^{1}J_{H\text{-}OH}$ 6 Hz, 1H), 5.50 (t, J 6 Hz, 1H), 7.49 (t, J 8 Hz, 1H), 7.80 (d, J 8 Hz, 1H), 8.14 (d, J 8 Hz, 1H), 8.40 (bs, 1H) ppm.

Diethyl-1-hydroxy-1-(3,4-dimethoxyphenyl) methyl phosphonate (6a). Solid (m.p. =87-88 ^{0}C) ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.19 (t, , J 8 Hz, 3H), 1.25 (t, J 8 Hz, 3H), 3.84 (s, 2 x 3H), 3.98 - 4.18 (m, 4H), 4.92 (d,$^{1}J_{PH}$10 Hz, 1H), 6.81 (d, J 8 Hz, 1H), 6.99 (d , J 8 Hz, 1H), 7.06 (s, 1H) ppm.; ^{13}C NMR (50 MHz, CDCl$_3$):δ 16.37, 55.72, 63.08, 70.35 (d,$^{1}J_{PC}$161.1 Hz), 110.39, 110.59, 119.53, 129.07, 148.68 ppm.

Diethyl-1-hydroxy-1-(4-allyloxyphenyl) methyl phosphonate (7a). Solid (m.p. = 69-70 ^{0}C) ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.20 (t, J 8 Hz, 3H) 1.26 (t, J 8 Hz, 3H), 2.2(bs, 1H), 3.9- 4.2 (m, 4H), 4.52 (d, J 6 Hz, 2H), 4.93 (d, $^{1}J_{PH}$ 10 Hz, 1H), 5.30 (d, J 9Hz, 1H), 5.37 (dd, J 16 Hz, 2 Hz, 2H), 5.9 - 6.3 (m, 1H), 7.0 (d, J8Hz, 2H), 7.39 (d, J 8Hz, 2H) ppm.; ^{13}C NMR (50 MHz, CDCl$_3$): 16.20, 62.80, 68.64, 70.18 (d, $^{1}J_{PH}$ 154 Hz), 114.32, 117.54, 128.32, 128.78, 130.04, 158.33 ppm.

Diethyl-1-hydroxy-1-(cinnamyl) methyl phosphonate (8a). ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.80 (s, 3H), 3.85 (s, 3H), 4.0 - 4.2 (bs, 1H), 4.68 - 4.78 (m, 1H), 6.26 - 6.40 (m, 1H), 6.75 - 6.87 (m, 1H), 7.28-7.38 (m, 5H) ppm.; ^{13}C NMR (75 MHz, CDCl$_3$): δ 53.47, 53.61, 53.80, 67.29, 70.52, 123.67, 126.47, 128.37, 132.10, 132.37, 136.15 ppm.

Dimethyl-1-hydroxy-1-(4-isopropylphenyl) methyl phosphonate (9a). ^{1}H NMR (200 MHz, CDCl$_3$): 1.14 (d, J 8 Hz, 6H), 2.82 (quin, J 8Hz, 1H), 3.01 (s, 1H), 3.54 (d, J 2Hz, 3H), 3.62 (d, J 2Hz, 3H), 4.91 (d, $^{1}J_{PH}$ 12Hz, 1H), 7.10 (d, J 8Hz, 2H), 7.27(d, J 8Hz, 2H) ppm.

Diethyl-1-hydroxy-1-(2-furyl) methyl phosphonate (10a). ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.25(t, J = 8Hz, 3H) 1.30 (t, J = 8Hz, 3H), 4.0- 4.20 (m,4H), 5.21 (d, $^{1}J_{PH}$ 10Hz, 1H), 7.01 (m, 1H), 7.18 (m, 1H), 7.31 (m, 1H) ppm.; ^{13}C NMR(50 MHz, CDCl$_3$): δ 16.0, 63.44, 65.40 (d, $^{1}J_{PH}$ = 168Hz), 125.17, 125.57, 126.46, 139.78 ppm.

Di-iso-propyl-1-hydroxy-2-(thiophenyl) methyl phosphonate (11a). Solid (m.p. =64-66 ^{0}C) ^{1}H NMR (300 MHz, CDCl$_3$): 1.19 (d, J 6.3 Hz, 3H), 1.31 (d, J 6.3 Hz, 9H,), 3.59 (br s, -OH), 4.67 - 4.74 (m, 2H), 5.16 (d, $^{1}J_{HP}$ 10.8 Hz, 1H), 6.99 (t, J 4.1 Hz, 1H), 7.18 (t, J 3.8 Hz, 1H), 7.28 (1H, dd, J 4.0 Hz and 1.2 Hz) ppm.; ^{13}C NMR (75 MHz, CDCl$_3$): 23.58 (d, $^{3}J_{CP}$ 5.25 Hz), 23.86 (d, $^{3}J_{CP}$ 4.5 Hz), 24.03 (d, $^{3}J_{CP}$ 3.75 Hz), 24.18 (d, $^{3}J_{CP}$ 3.0 Hz), 67.24 (d, $^{1}J_{CP}$ 166.5 Hz, P-C-OH), 72.05 (d, $^{2}J_{CP}$ 3.75 Hz), 72.44 ($^{2}J_{CP}$ 3.75 Hz), 125.49, 126.09, 126.66, 139.22ppm.

Diethyl-α-trimethylsilyloxy-4-methoxybenzylphosphonat (1b). ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.02 (s, 9H), 1.17 (t, *J* 7Hz, 3H), 1.20 (t, *J* 7Hz, 3H), 3.77 (s, 3H), 4.01-4.08 (m, 4H), 4.91 (d, *J* 16Hz, 1H), 6.87 (d, *J* 8 Hz, 1H), 7.37(d, *J* 8 Hz, 1H) ppm.

Diethyl-α-trimethylsilyloxy-4-chlorobenzylphosphonate (2b). ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.03 (s, 9H), 1.17 (t, *J* 7Hz, 3H), 1.21 (t, *J* 7Hz, 3H), 3.96-4.03 (m, 4H), 4.93 (d, *J* 15Hz, 1H), 7.28 (d, *J* 8 Hz, 1H), 7.35 (d, *J* 8 Hz, 1H) ppm.

Diethyl-α-trimethylsilyloxy-4-methylbenzylphosphonate (3b). Colourless oil (b.p.= 81-82 ^{0}C) ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.02 (s, 9H), 1.17(t, *J* 7Hz, 3H), 1.20 (t, *J* 7Hz, 3H), 2.47 (s, 3H), 3.98-4.06 (m, 4H), 4.91 (d, *J* 16Hz, 1H), 6.88 (d, *J* 8 Hz, 1H), 7.32(d, *J* 8 Hz, 1H) ppm. Anal. Calcd. for $C_9H_{13}O_2P$ (184.18): C 58.69, H 7.11; Found, C 58.62, H 7.07.

Diethyl-α-trimethylsilyloxy-4-isopropylbenzylphosphonate (4b). Colourless oil (b.p.= 94-96 ^{0}C)^{1}H NMR (200 MHz, CDCl$_3$): δ 0.02 (s, 9H), 1.2-1.5 (m, 12H), 2.82 (m, 1H), 3.96-4.18 (m, 4H), 4.95 (d, *J* 22 Hz, 1H), 7.16 (d, *J* 8 Hz, 2H), 7.33 (d, *J* 8 Hz, 2H) ppm. Anal. Calcd. for $C_{11}H_{17}O_2P$ (212.23): C 62.25, H 8.07; Found, C 62.31, H 8.03.

Diethyl-α-trimethylsilyloxy-3-nitrobenzyl-phosphonat (5b). ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.02 (s, 9H), 1.15 (t, *J* 7 Hz, 3H), 1.22, (t, *J* 7 Hz, 3H), 3.8.5-4.10 (s, 4H), 4.84 (d, *J* 16 Hz, 1H), 7.40 (m, 1H), 7.72 (d, *J* 7Hz, 1H), 8.25 (d, *J*7 Hz, 1H) ppm.

Diethyl-α-trimethylsilyloxy-3,4-dimethoxy-benzylphosphonate (6b). Colourless oil (b.p. = 102-103 ^{0}C) ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.02(s, 9H), 1.17(t, *J* 7Hz, 3H), 1.20 (t, *J* 7Hz, 3H), 3.52 (s, 3H), 3.56 (s, 3H), 3.75-4.0 (m, 4H), 4.80 (d, *J* 16Hz, 1H), 6.73 (d, *J* 8 Hz, 1H), 6.75 (d, *J* 8 Hz, 1H), 6.97 (bs 1H) ppm. Anal. Calcd. for $C_{10}H_{15}O_4P$ (230.20): C 52.18, H 6.57; Found, C 52.11, H 6.52.

Diethyl-α-trimethylsilyloxy-(4-allyloxybenzoyl)benzylphosphonate (7b). Yellow oil (b.p. = 78-79 ^{0}C) ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.01 (s, 9H), 1.20 (t, *J* 8 Hz, 3H) 1.26 (t, *J* 8 Hz, 3H), 3.9- 4.2 (m, 4H), 4.45 (d, *J* 4Hz, 2H), 4.91 (d, $^1J_{PH}$ 10 Hz, 1H), 5.28 (m, 1H), 5.94 (m, 1H), 6.82 (d, *J* 10 Hz, 2H), 7.31 (d, *J* 10 Hz, 2H) ppm. Anal. Calcd. for $C_{11}H_{15}O_3P$ (226.21): C 58.41, H 6.68; Found, C 58.46, H 6.72.

Dimethyl-α-trimethylsilyloxy-4-isopropyl benzylphosphonate (9b). ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.0 (s, 9H), 1.16 (d, *J* = 8 Hz, 6H), 2.80 (quin, *J* 8Hz, 1H), 3.55(d, *J* 2Hz, 3H), 3.61(d, *J* 2Hz, 3H), 4.91(d, $^1J_{PH}$ 12Hz, 1H), 7.10 (d, *J* 8Hz, 2H), 7.27(d, *J* 8Hz, 2H) ppm.

Diethyl-α-trimethylsilyloxyfurylphosphonate (10b). ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.0 (s, 9H), 1.13 (2t, *J* 6.2 Hz, 6H) 3.92 (m, 4H), 5.10 (d, $^1J_{PH}$ 9Hz, 1H), 6.86 (bs, 1H), 7.0 (bs, 1H), 7.14 (bs, 1H) ppm.

Diethyl (4-methoxybenzoyl) phosphonate (1c). ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.32 (t, *J* 6Hz, 6H), 3.83 (s, 3H), 4.1-4.3(m, 4H), 6.92 (d, *J* 8 Hz, 2H), 8.22 (d, *J* 8Hz, 2H) ppm.

Dimethyl (4-chloro-benzoyl) phosphonate (2c). ^{1}H NMR (200 MHz, CDCl$_3$): δ 3.82 (s, 3H), 3.87 (s, 3H), 7.43 (d, *J* 8Hz, 2H), 8.14 (d, *J* = 8Hz, 2H) ppm.; ^{13}C NMR (75 MHz, CDCl$_3$)**:** δ 16.25 (d, $^3J_{C\text{-}P}$ 6 Hz, OCH_2CH_3), 64.26 (d, $^2J_{C\text{-}P}$ 7. 5 Hz, OCH_2CH_3), 129.24, 131.17, 133.35, 134.21, 141.47, 175.30 (ArCs), 197.63 (d, $^1J_{C\text{-}P}$ 177 Hz, ArCO) ppm.

Diethyl (4-methylbenzoyl) phosphonate (3c). Colorless oil (b.p. = 121-122 ^{0}C) ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.25 (t, *J* 7 Hz, 6H), 2.43 (s, 3H), 3.69- 3.80 (q, *J* 8 Hz, 4H), 7.27 (d, *J* 8 Hz, 2H). 8.01 (d, *J* 8 Hz, 2H) ppm.; ^{13}C NMR (50 MHz, CDCl$_3$)**:** δ 16.68 (d, $^3J_{C\text{-}P}$ 6 Hz, OCH_2CH_3), 22.17, 64.25 (d, $^2J_{C\text{-}P}$ 7.5 Hz, OCH_2CH_3), 127.37, 129.88, 130.312 146.41, 198.45 (d, $^1J_{C\text{-}P}$ 176.6 Hz, ArCO) ppm.

Diethyl (4-isopropylbenzoyl) phosphonate (4c). Colorless oil (B.P. = 156 -157 ^{0}C) ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.22 (d, *J* 8 Hz, 6H), 1.38 (t, *J* 7Hz, 6H), 2.92 (m, 1H), 4.22 (m, 4H), 7.24 (d, *J* 7 Hz, 2H), 8.06 (d, *J* 7Hz, 2H) ppm.

Diethyl (3-nitrobenzoyl) phosphonate (5c).^{1}H NMR (200 MHz, CDCl$_3$): δ 1.31 (t, *J* 6 Hz, 6H), 4.05-4.25 (m, 4H), 7.61 (t, *J* 8Hz, 1H), 8.36 (m, 2H), 8.87 (brs, 1H)ppm. ; ^{13}CNMR (50.4MHz, CDCl$_3$): δ 21.6, 54.34, 55.69, 113.71, 114.32, 127.95, 131.66, 132.60, 133.07, 141.66, 164.0, 165.6, 170, 171.5, 172.3, 194.5, 197.5 ppm.

Diethyl (3,4-di,methoxybenzoyl) phosphonate (6c). Pale yellow oil(b. p. = 108-109 ^{0}C) ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.4 (t, *J* 6 Hz, 6H), 3.96 (s, 3H), 3.98 (s, 3H), 4.36(m, 4H), 6.98(d, *J* 8 Hz, 1H), 7.62 (s, 1H), 8.16 (d, *J* 8Hz, 1H) ppm; ^{13}C NMR (75MHz, CDCl$_3$): δ 16.03, 20.57, 55.69, 63.84, 110.12, 111.94, 124.11, 126.53, 128.20, 129.33, 149.03, 154.80, 147.76, 194.06, 197.94 ppm.

Diethyl (4-allyloxybenzoyl) phosphonate (7c). Colorless oil ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.32- 1.37 (m, 6H), 4.23 (q, *J* 7Hz, 4H), 4.62 (d, *J* 7Hz, 2H), 5.25-5.4 (m, 2H), 6.0 (m, 1H), 6.98 (d, *J* 8Hz, 2H), 8.28 (d, *J* 8Hz, 2H) ppm.; ^{13}C NMR (CDCl$_{3,}$ 75 MHz): 16.11, 64.01, 68.86, 114.73, 118.22, 128.13, 129.44, 132.01, 132.34, 141.35, 163.85, 195.8 (d, $^1J_{CP}$174 Hz) ppm.

Diethyl (cinnamyl benzoyl) phosphonate (8c). ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.16 (t, *J* 7.2 Hz, 3H), 1.27 (t, *J* 7.2 Hz, 3H), 4.0-4.35 (m, 4H), 6.40 (d, *J* 15.6 Hz, 1H), 7.3-7.5 (m, 5H), 7.70 (d, *J* 15.6 Hz, 1H) ppm.; ^{13}C NMR (50.4 MHz, CDCl$_3$): δ 16.36, 29.6, 61.96, 63.5, 64.5, 117.5, 128.6, 129.6, 130.8, 134.2, 147, 171.6 ppm.

Dimethyl (4-isopropylbenzoyl) phosphonate (9c). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.26 (d, *J* 8 Hz, 6H), 2.94 (m, 1H), 3.90 (s, 3H), 3.93 (s, 3H), 7.26 (d, *J* 7 Hz, 1H), 7.35 (d, *J* 8 Hz, 1H), 7.98 (d, *J* 8Hz, 1H), 8.15 (d, *J* 8 Hz, 1H).

Diethyl (furoylbenzoyl) phosphonate (10c).^{1}H NMR (300 MHz, CDCl$_3$): δ 1.38 (t, *J* 7 Hz, 6H), 4.28 (m, 4H), 6.62 (d, *J* 2 Hz, 1H), 7.78 (s, 1H), 7.86 (d, *J* 2 Hz, 1H) ppm.

Diisopropyl (2-thiophenoyl) phosphonate (11c). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.30-1.33 [m, 12H, 2 x OCH(CH$_3$)$_2$], 4.74 - 4.82 [m, 2H, 2 x OCH(CH$_3$)$_2$], 7.17 (t, 1H, ArH), 7.75 - 7.81 (m, 1H, ArH), 8.36 (t, 1H, ArH) ppm.; ^{13}C NMR (75 MHz, CDCl$_3$): 23.75 [d, $^3J_{C-P}$ 4.5 Hz OCH(CH$_3$)$_2$] 23.94 [d, $^3J_{C-P}$4.5 Hz, OCH(CH$_3$)$_2$], 73.33 [d, $^2J_{C-P}$ 7.5 Hz, OCH(CH$_3$)$_2$], 128.85, 136.75, 137.78, 142.70, 143.74, 191.01 (d, $^1J_{C-P}$ 183.75 Hz, ArCO) ppm.

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Supplementary Material

Copies of ^{1}H NMR spectra of compounds**1a**,**3a**,**6a**, **7a**,**1b**,**2b**, **4b**, **7b**, **1c**, **3c**, **4c**, **10c**, **11c** and ^{13}C NMR spectra of compounds **1a**,**3a**,**11c** are given in the supplementary material file associated with this paper.

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