Magnesium triflate [Mg(OTf)$_2$] a highly stable, non-hygroscopic and a recyclable catalyst for the high yielding preparation of diethyl α-trimethylsilyloxyphosphonates from diethyl α-hydroxyphosphonates by HMDS under solventless conditions

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Abstract

A broad, adaptable, high yielding and convenient procedure for the easy conversion of various α-hydroxyphosphonates to α-trimethylsilyloxyphosphonates under mild conditions with HMDS in the presence of a catalytic amount of magnesium triflate as a highly stable and a non-hygroscopic recyclable catalyst in neat conditions is described. In order to show the general applicability of this method, we have also applied this procedure successfully for the silylation of ordinary alcohols and phenols.
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1. Introduction

α-Trimethylsilyloxyphosphonates are interesting compounds from different views. They are attractive in biology, industry and organic chemistry [1–3]. The interest on the preparation of α-trimethylsilyloxyphosphonates arises on one hand from the existence of an α-acidic hydrogen in these compounds which can be metalated by lithium diisopropylamide to produce relatively stable α-carbanionic species [4]. On the other hand, the C–P and Si–O bonds of α-trimethylsilyloxyphosphonates are easily hydrolyzed in alkaline and acidic conditions [5]. Therefore, α-lithiated α-trimethylsilyloxyphosphonates have become important synthons of masked acyl anions and have been widely used for

carbon–carbon bond forming reactions. They react with various ketones to produce the corresponding α-trimethylsilyloxy ketones [6]. Unsymmetrical ketones, β,γ-unsaturated ketones and carboxylic acids can be produced by the reaction of α-lithiated α-trimethylsilyloxyphosphonates with alkylating agents followed by hydrolysis of C–P and Si–O bonds [5,7,8]. α-Lithiated α-trimethylsilyloxyphosphonates can also undergo easy acylation with varieties of acylating agents producing the corresponding α-acylated products. These compounds in turn, are easily converted to α-hydroxy ketones by the cleavage of Si–O bond and elimination of dialkyl phosphite in alkaline media [4].

The common methods for the preparation of α-trimethylsilyloxyphosphonates include reaction of aldehydes with diethyl trimethylsilyloxyphosphite [5,7,8] or with the mixture of triethylphosphite and trimethylsilyl chloride [2,3]. The reported procedures need harsh reaction conditions accompanied with rather long reaction times. The other method used for this purpose is

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the reaction of trialkyl phosphate with silyl phenyl ketone, which requires a long reaction time (12 h) and also proceeded at a high temperature (80 °C) [9]. Trimethylsilyl chloride has also been used for the preparation of diethyl α-trimethylsilyloxybenzylphosphonate from sodium salt of diethylphosphite and benzaldehyde in moderate yield (67%) [7]. Procedures for the direct silylation of α-hydroxyphosphonates [10–12] to their α-trimethylsilyloxyphosphonates are rare in the literature and to the best of our knowledge there is only one report available for this purpose. In that report, hexamethylsilathiane has been used as a silylating agent at 50–70 °C to produce the desired products in moderate yields (55–78%) [13].

In conjunction with our interest in the development of synthetic methods for the preparation of phosphonate derivatives from α-hydroxyphosphonates we have focused our attention to the preparation of α-trimethylsilyloxy phosphonates by direct silylation of α-hydroxyphosphonates [14–23].

2. Results and discussion

In connection with our ongoing work on the catalytic properties of metal triflates [24–28], herein we report $Mg(OTf)_2$ [29] as a highly stable, non-hygroscopic and a recyclable catalyst for the high yielding preparation of diethyl α-trimethylsilyloxyphosphonates (**2a–o**) by the direct reaction of diethyl α-hydroxyphosphonates (**1a–o**) with 1,1,1,3,3,3-hexamethylsilazane (HMDS) at room temperature in the absence of solvent (Scheme 1 and Table 1).

As shown in Table 1, various types of α-hydroxy-(phenylmethyl) phosphonates (**1a–k**) were cleanly converted into their corresponding α-trimethylsilyloxyphosphonates (**2a–k**) in excellent yields (90–96%). α-Hydroxy-2-naphthyl-, 3-pyridyl-, alkyl- and aryl-β,γ-unsaturated phosphonates (**1l–o**) were also silylated efficiently giving the corresponding α-trimethylsilyloxyphosphonates (**2l–o**) in 90–95% yields.

We have observed that cleavage of C–P and Si–O bonds of α-trimethylsilyloxyphosphonates was not occurred in the presence of this catalyst in the absence of solvent. Therefore, the products of high purity were obtained after work-up and further purification was not required.

The spectral data of the known products (**2a**, **b**, **g**, **k**, **n** and **o**) are compared with those reported in the literature. The spectral data of the other known products (**2c**, **e**, **f**, **i** and **j**) which their spectral data have not been reported in the literature and also the spectral data (^{1}H NMR, ^{13}C NMR, IR and MS) of unknown products (**2d**, **h**, **l**, **m**) are presented in Section 3.

We have compared the catalytic activity of $Mg(OTf)_2$ [29] with other metal triflates including LiOTf [32],
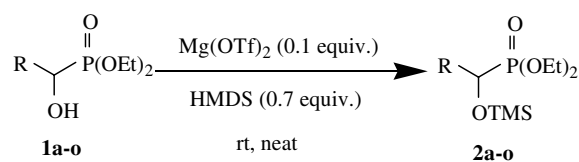
Scheme 1.

Table 1
Silylation of diethyl α-hydroxyphosphonates (**1a–o**) to diethyl α-trimethylsilyloxyphosphonates (**2a–o**) with HMDS in the presence of $Mg(OTf)_2$ in neat conditions at room temperature

Product 2 Ref.	R–	$Mg(OTf)_2$	
		Time (min)	Yield[a] (%)
a [3,9]	C_6H_5–	–[b]	96
b [30]	4-$CH_3C_6H_4$–	–[b]	90
c	4-$CH_3OC_6H_4$–	40	91
d	2,4,6-$(CH_3)_3C_6H_2$–	45	92
e	2-ClC_6H_4–	–[b]	93
f	3-ClC_6H_4–	–[b]	90
g [31]	4-ClC_6H_4–	–[b]	92
h	2,6-$Cl_2C_6H_3$–	–[b]	94
i	2-$O_2NC_6H_4$–	70	90
j	3-$O_2NC_6H_4$–	120	92
k [31]	4-$O_2NC_6H_4$–	95	91
l	2-Naphthyl	35	90
m	3-Pyridyl	–[b]	94
n [7]	PhCH=CH–	45	95
o [7]	MeCH=CH–	80	90

[a] Yields refer to isolated products. The equivalent ratios of substrate/HMDS/catalyst are 1/0.7/0.1.
[b] Immediate reaction occurred.

$Ce(OTf)_4$ [33], $Hg(OTf)_2$ [34], $Cu(OTf)_2$ [35] and some other Lewis acids such as $ZnCl_2$ [36], $Zn(bipy)_3Cl_2$ [37], $FeCl_3$, $Fe(bipy)Cl_3$ [37], $CuCl_2$, $MgCl_2$, $AlCl_3$ and $ZrOCl_2 \cdot 8H_2O$ for the silylation of diethyl α-hydroxy-(phenylmethyl)-phosphonate (**1a**), as a model compound, with HMDS in the absence of solvent at room temperature (Table 2). We found that $Mg(OTf)_2$ was the most effective catalyst for this purpose and the immediate conversion of **1a** to the corresponding silylated product **2a** (100%, monitored by TLC) was observed.

In all reactions, we have studied, fast evolution of ammonia gas was observed. We were also able to isolate $Mg(OTf)_2$ from the reaction mixture and reused it for the similar reaction without observable loss of its catalytic activity. With these observations we have proposed a mechanism in which the generation of NH_3 and the catalytic role of $Mg(OTf)_2$ in a catalytic cycle are clarified (Scheme 2).

In this mechanism, we have suggested that a Lewis acid–base interaction between metal triflate and nitrogen in HMDS polarizes N–Si bond of HMDS to produce a reactive silylating agent (**3**). Mg^{+2} that is a harder Lewis acid in comparison with Li^+, Cu^{+2}, Ce^{+4}
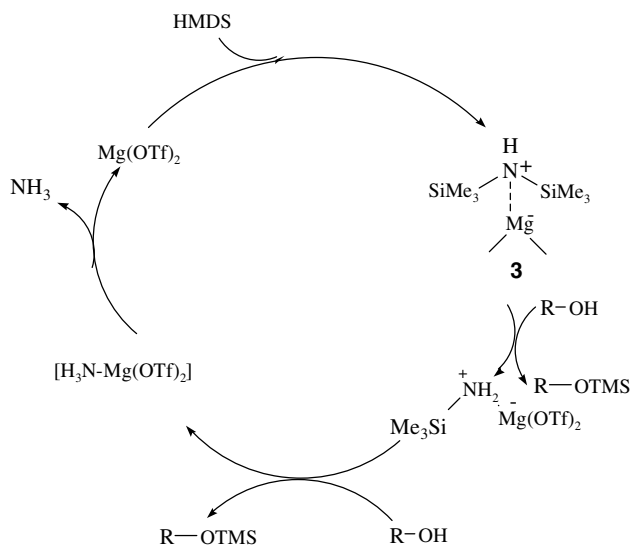
Table 2
Silylation of diethyl α-hydroxy-(phenylmethyl)-phosphonate (1a) with HMDS in the presence of various Lewis acids in neat conditions at room temperature

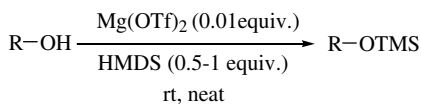| Entry	Lewis acid[a]	Time (h)	% Conversion based on ^{1}H NMR 2a
2	Mg(OTf)$_2$	–[b]	100
3	Cu(OTf)$_2$	4.5	60
4	Ce(OTf)$_4$	3	80
5	Hg(OTf)$_2$	10	60
6	LiOTf	1.5	100
7	ZnCl$_2$	1	100
8	Zn(bipy)$_3$Cl$_2$	24	20
9	FeCl$_3$	1.5	80
10	Fe(bipy)Cl$_3$	1.5	30
11	ZrOCl$_2 \cdot$ 8H$_2$O	1.5	30
12	AlCl$_3$	4.5	80
14	CuCl$_2$	10	20
15	MgCl$_2$	6.5	50

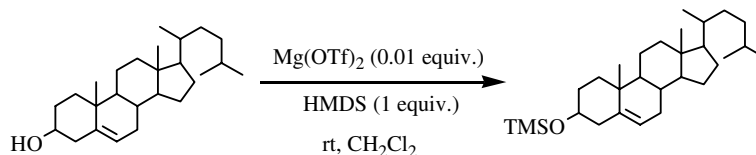[a] The equivalent ratios of substrate/HMDS/catalyst are 1/0.7/0.1.
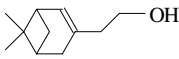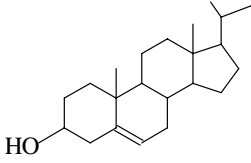[b] Immediate reaction occurred.

Scheme 2.

Scheme 3.

Table 3
Silylation of alcohols and phenols to the corresponding trimethylsilylethers with HMDS in the presence of Mg(OTf)$_2$ in neat conditions at room temperature

Entry	Substrate	Mg(OTf)$_2$	
		Time (min)	Yield[a] (%)
1	C$_6$H$_5$CH$_2$OH	38	95[b]
2	4-CH$_3$C$_6$H$_4$CH$_2$OH	15	93[b]
3	4- CH$_3$OC$_6$H$_4$CH$_2$OH	34	93[b]
4	4-ClC$_6$H$_4$CH$_2$OH	35	91[b]
5	4-O$_2$NC$_6$H$_4$CH$_2$OH	50	93[b]
6	PhCH(C$_2$H$_5$)OH	140	90[c]
7	Anthracene-9-methanol	60	70[d]
8	(Ph)$_2$CHOH	120	70[c]
9	PhCH$_2$CH$_2$OH	20	97[c]
10	Ph(CH$_2$)$_2$CH$_2$OH	50	98[c]
11	1-Octanol	50	95[c]
12		3 h	98[c]
13	2-Octanol	120	97[c]
14		24 h	–[d,g]
15	(CH$_3$)$_2$CdbondHCH$_2$OH	125	92[b]
16	CH$_3$(CH$_2$)$_5$CH(CH=CH$_2$)OH	6.75 h	84[b]
17	1-Aadamantanol	120	92[c]
18	5-CH$_3$-5-decanol	90	92[c]
19	4-CH$_3$C$_6$H$_4$OH	35	90[c]
20	C$_6$H$_5$OH	60	70[c]
21	4-O$_2$NC$_6$H$_4$OH	24 h	–[d,f]
22	4-AcetylC$_6$H$_4$OH	24 h	–[d,f]

[a] Isolated yields: the structures which were predicted for the products were confirmed by their spectral data (^{1}H NMR, ^{13}C NMR, IR and MS). The equivalent ratios of substrate/HMDS/catalyst are [b]1/0.5/0.01, [c]1/0.7/0.01 or [d]1/1/0.01. [e]Immediate reaction occurred. [f]No reaction was observed in neat conditions and in CH$_2$Cl$_2$ as solvent. [g]No reaction was observed in neat conditions.

and Hg^{+2} interacts more strongly with the nitrogen atom as a hard Lewis base in HMDS. Therefore, N–Si bond polarization effected by Mg(OTf)$_2$ is more pronounced than those generated by LiOTf, Cu(OTf)$_2$, Ce(OTf)$_4$ and Hg(OTf)$_2$. This qualitative explanation justifies the more catalytic activity of Mg(OTf)$_2$ than the other triflates we have studied.

Scheme 4.

Silylation of alcohols are among the most frequently used processes in organic synthesis and provides cheap and efficient means for the protection of hydroxyl groups during oxidation, peptide coupling and halogenation reactions [38–40].

In order to show the general applicability of this catalyst, we have also tried silylation of hydroxyl functional groups in alcohols and phenols with HMDS (Scheme 3). We have observed that the reactions proceeded smoothly in similar reaction conditions from good to excellent yields (70–98%). The results are summarized in Table 3.

As it is shown in Table 3, *p*-substituted benzylic alcohols containing electron-donating and electron-withdrawing groups, primary and secondary aliphatic alcohols were protected efficiently in short reaction times (entries 1–13). Longer reaction times are required for complete conversion of allylic and tertiary aliphatic alcohols to the corresponding silylated products (entries 15–18). *p*-Cresole was silylated faster and with higher yield than phenol (entries 19, 20). While even after 24 h stirring, conversion of phenols substituted at *para* positions with nitro and acetyl groups was not observed under similar reaction conditions (entries 21, 22). We have also tried silylation of cholesterol under solvent-free conditions in the presence of this catalyst with HMDS. Our observation shows that this compound does not undergo silylation reaction under such conditions and the starting material was isolated intact after 24 h. However, we tried this reaction at room temperature in solution using CH_2Cl_2. The reaction proceeded well and the desired compound was isolated in 95% yield after 65 min (Scheme 4).

Conclusively, we have found that $Mg(OTf)_2$ can be used as a reusable and efficient catalyst for the preparation of varieties of diethyl α-trimethylsilyloxyphosphonates by direct silylation of the corresponding diethyl α-hydroxyphosphonates with HMDS in the absence of solvent without cleavage of C–P and Si–O bonds. We have also applied this protocol for the efficient silylation of ordinary alcohols and phenols with success.

3. Experimental

Chemicals were purchased from Merck and Fluka Chemical Companies. IR spectra were run on a Shimadzu model 8300 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-250. Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX. The purity of the products and the progress of the reactions were accomplished by TLC on silica-gel polygram SILG/UV$_{254}$ plates.

3.1. Typical procedure for the preparation of *2a* from *1a* catalyzed by $Mg(OTf)_2$ in neat conditions

$Mg(OTf)_2$ (0.032 g, 0.1 mmol) was added to the stirring mixture of *1a* (0.244 g, 1 mmol,) and HMDS (0.113 g, 0.7 mmol) at room temperature. Immediate reaction was occurred with complete conversion of the starting material (TLC). CH_2Cl_2 (10 mL) was added to the resulting reaction mixture and then the organic layer was washed with H_2O (3 × 10 mL), separated and dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent afforded the pure product (*2a*) as a known compound in 96% yield.

3.2. Typical procedure for trimethylsilylation of benzyl alcohol with HMDS using $Mg(OTf)_2$ in neat conditions

$Mg(OTf)_2$ (0.003 g, 0.01 mmol) was added to the stirring mixture of benzyl alcohol (0.108 g, 1 mmol) and HMDS (0.113 g, 0.7 mmol) at room temperature. The progress of the reaction was monitored by TLC. After complete conversion of the starting material (38 min), CH_2Cl_2 (10 mL) was added to the resulting reaction mixture and then the organic layer was washed with H_2O (3 × 10 mL), separated and dried over anhydrous Na_2SO_4. After evaporation of the solvent, pure benzyl trimethylsilyl ether in 95% yields was obtained.

3.3. Spectral data and the elemental analysis of unknown diethyl α-trimethylsilyloxyphosphonates

3.3.1. Diethyl α-trimethylsilyloxy-2,4,6-trimethylbenzyl phosphonate (*2d*)

^{1}H NMR (CDCl$_3$): δ −0.04 [s, 9H, –Si(CH_3)$_3$], 1.02 (t, 3H, $^2J_{HH}$ = 7 Hz, 2-OCH$_2$CH_3), 1.22 (t, 3H, $^2J_{HH}$ = 7 Hz, 2-OCH$_2$CH_3), 2.12 (s, 3H, –CH$_3$), 2.25 (s, 3H, –CH$_3$), 2.51 (s, 3H, CH$_3$), 3.58–3.68 (m, 1H, 2-OCH_2CH$_3$), 3.81–3.90 (m, 1H, 2-OCH_2CH$_3$), 3.98–4.10 (m, 2H, 2-OCH_2CH$_3$), 5.28 (d, 1H, $^1J_{PH}$ = 18.3 Hz, CH), 6.66 (s, 1H, C$_6$H$_2$), 6.72 (s, 1H, –C$_6$H$_2$) ppm; ^{13}C NMR (CDCl$_3$): 0.00 [–Si(CH$_3$)$_3$], 16.56 (d, $^3J_{CP}$ = 5.9 Hz, 2-OCH$_2$CH$_3$), 16.87 (d, $^3J_{CP}$ = 5.9 Hz, 2-OCH$_2$CH$_3$), 21.16, 21.67, 21.69 (–CH$_3$), 62.70 (d, $^2J_{CP}$ = 7.1 Hz, 2-OCH$_2$CH$_3$), 62.92 (d, $^2J_{CP}$ = 7.1 Hz, 2-OCH$_2$CH$_3$), 69.60 (d, $^1J_{CP}$ = 177.2 Hz, –CH) 129.05 (d, J_{CP} = 2 Hz, –C$_6$H$_2$), 130.25 (–C$_6$H$_2$), 131.57 (d, J_{CP} = 3.3 Hz, –C$_6$H$_2$), 136.08 (d, J_{CP} = 8.1 Hz, –C$_6$H$_2$), 137.41 (d, J_{CP} = 3.4 Hz, –C$_6$H$_2$), 139.88 (d, J_{CP} = 4.2 Hz, –C$_6$H$_2$) ppm; IR (neat): OH peak was absent; MS (70 eV), *m/e* (relative intensity %): 431 [M + Si(CH$_3$)$_3$, 19.3], 358 (M$^+$, 3.2), 221 [M – P(O)(OEt)$_2$, 100], 147 [221-Si(CH$_3$)$_3$, 12], 73 [Si(CH$_3$)$_3$, 44.3]; C$_{17}$H$_{31}$O$_4$PSi requires C, 56.98; H, 8.66, found: C, 56.90; H, 8.70%.

3.3.2. Diethyl α-trimethylsilyloxy-26-dichlorobenzylphosphonate (2h)

^{1}H NMR (CDCl$_3$): δ 0.00 [s, 9H, –Si(CH$_3$)$_3$], 1.07–1.24 (m, 6H, 2-OCH$_2$CH$_3$), 3.89–4.15 (m, 4H, 2-OCH$_2$CH$_3$), 5.81 (d, 1H, $^1J_{PH}$ = 19.3 Hz, –CH), 7.03–7.10 (m, 1H, –C$_6$H$_3$), 7.20–7.25 (m, 1H, –C$_6$H$_3$), ppm; ^{13}C NMR (CDCl$_3$): 0.00 [–Si(CH$_3$)$_3$], 16.86 (d, $^3J_{CP}$ = 6.8 Hz, 2-OCH$_2$CH$_3$), 16.96 (d, $^3J_{CP}$ = 6.8 Hz, 2-OCH$_2$CH$_3$), 63.35 (d, $^2J_{CP}$ = 7.1 Hz, 2-OCH$_2$CH$_3$), 63.60 (d, $^2J_{CP}$ = 7.1 Hz, 2-OCH$_2$CH$_3$), 70.02 (d, $^1J_{CP}$ = 179.8 Hz, –CH), 128.60 (d, J_{CP} = 2.0 Hz, –C$_6$H$_3$), 129.99 (d, J_{CP} = 2.9 Hz, –C$_6$H$_3$), 131.31 (d, J_{CP} = 2.8 Hz, –C$_6$H$_3$), 135.73 (d, J_{CP} = 8.2 Hz, –C$_6$H$_3$), 136.87 (d, J_{CP} = 4.9 Hz, –C$_6$H$_3$) ppm; IR (neat): OH peak was absent; MS (70 eV), *m/e* (relative intensity %): 457 [M + Si(CH$_3$)$_3$, 100], 389 (M + 4, 2.3), 387 (M + 2, 10.8), 385 (M$^+$, 14), 247 [M − P(O)(OEt)$_2$, 52.2], 173 [247-Si(CH$_3$)$_3$, 2.4], 73 [Si(CH$_3$)$_3$, 93.5]; C$_{14}$H$_{23}$Cl$_2$O$_4$PSi requires C, 43.64; H, 5.97, found: C, 43.60; H, 5.91%.

3.3.3. Diethyl α-trimethylsilyloxy-2-naphthylphosphonate (2l)

^{1}H NMR (CDCl$_3$): δ 0.00 [s, 9H, –Si(CH$_3$)$_3$], 1.10 (t, 6H, $^2J_{HH}$ = 7.1 Hz, 2-OCH$_2$CH$_3$), 3.79–3.99 (m, 4H, 2-OCH$_2$CH$_3$), 5.03 (d, 1H, $^1J_{PH}$ = 14.5 Hz, –CH), 7.33–7.37 (m, 2H, –C$_{10}$H$_7$), 7.49–7.52 (m, 1H, –C$_{10}$H$_7$), 7.69–7.84 (m, 4H, –C$_{10}$H$_7$) ppm; ^{13}C NMR (CDCl$_3$): 0.00 [–Si(CH$_3$)$_3$], 16.39 (d, $^3J_{CP}$ = 5.6 Hz, 2-OCH$_2$CH$_3$), 16.48 (d, $^3J_{CP}$ = 5.6 Hz, 2-OCH$_2$CH$_3$), 62.77 (d, $^2J_{CP}$ = 7.3 Hz, 2-OCH$_2$CH$_3$), 63.22 (d, $^2J_{CP}$ = 7.3 Hz, 2-OCH$_2$CH$_3$), 72.13 (d, $^1J_{CP}$ = 174.4 Hz, –CH), 125.23–126.44, 127.61–128.06, 133.07–133.21, 134.94–135.48 (–C$_{10}$H$_7$) ppm; IR (neat): OH peak was absent; MS (70 eV), *m/e* (relative intensity %): 439 [M + Si(CH$_3$)$_3$, 16.2], 366 (M$^+$, 4.8), 229 [M − P(O)(OEt)$_2$, 100], 155 [229-Si(CH$_3$)$_3$, 18.8], 73 [Si(CH$_3$)$_3$, 87.5]; C$_{18}$H$_{27}$O$_4$PSi requires C, 59.02; H, 7.38, found: C, 59.04; H, 7.35%.

3.3.4. Diethyl α-trimethylsilyloxy-3-pyridylphosphonate (2m)

^{1}H NMR (CDCl$_3$): δ 0.00 [s, 9H, –Si(CH$_3$)$_3$], 1.13 (t, 6H, $^2J_{HH}$ = 7.0 Hz, 2-OCH$_2$CH$_3$), 3.91–3.99 (m, 4H, 2-OCH$_2$CH$_3$), 4.89 (d, 1H, $^1J_{PH}$ = 14.5 Hz, –CH), 7.15–7.21 (m, 1H, –C$_5$H$_4$N), 7.74 (d, 1H, J_{PH} = 7.3 Hz, –C$_5$H$_4$N), 8.43 (d, 1H, J_{PH} = 4.1 Hz, –C$_5$H$_4$N), 8.54 (s, 1H, –C$_5$H$_4$N) ppm; ^{13}C NMR (CDCl$_3$): 0.00 [–Si(CH$_3$)$_3$], 16.51 (d, $^3J_{CP}$ = 5.1 Hz, 2-OCH$_2$CH$_3$), 16.58 (d, $^3J_{CP}$ = 5.1 Hz, 2-OCH$_2$CH$_3$), 63.06 (d, $^2J_{CP}$ = 7.3 Hz, 2-OCH$_2$CH$_3$), 63.43 (d, $^2J_{CP}$ = 7.3 Hz, 2-OCH$_2$CH$_3$), 69.88 (d, $^1J_{CP}$ = 175.8 Hz, –CH), 123.31 (d, J_{CP} = 2.6 Hz, –C$_5$H$_4$N), 133.53 (–C$_5$H$_4$N), 135.14 (d, J_{CP} = 4.9 Hz, –C$_5$H$_4$N), 148.69 (d, J_{CP} = 6.7 Hz, –C$_5$H$_4$N), 149.43 (d, J_{CP} = 3.3 Hz, –C$_5$H$_4$N) ppm; IR (neat): OH peak was absent; MS (70 eV), *m/e* (relative intensity %): 390 [M + Si(CH$_3$)$_3$, 62.1], 317 (M$^+$, 1.2), 180 [M − P(O)(OEt)$_2$, 86.2], 108 [180-Si(CH$_3$)$_3$, 48.8], 73 [Si(CH$_3$)$_3$, 100]; C$_{13}$H$_{24}$NO$_4$PSi requires C, 49.21; H, 7.57, found: C, 49.18 H, 7.51%.

3.4. Spectral data of known α-trimethylsilyloxyphosphonates which are not reported in the literature

3.4.1. Diethyl α-trimethylsilyloxy-4-methoxybenzylphosphonate (2c)

^{1}H NMR (CDCl$_3$): δ 0.00 [s, 9H, –Si(CH$_3$)$_3$], 1.11–1.19 (m, 6H, 2-OCH$_2$CH$_3$), 3.71 (s, 3H, 4-OCH$_3$), 3.81–3.99 (m, 4H, 2-OCH$_2$CH$_3$), 4.83 (d, 1H, $^1J_{PH}$ = 13.4 Hz, –CH), 7.79 (d, $^2J_{HH}$ = 8.4 Hz, 2H, –C$_6$H$_4$), 7.30 (d, $^2J_{HH}$ = 6.9 Hz, 2H, –C$_6$H$_4$) ppm; ^{13}C NMR (CDCl$_3$): 0.00 [–Si(CH$_3$)$_3$], 16.38–16.59 (2-OCH$_2$CH$_3$), 55.20 (4-OCH$_3$), 62.65–63.21 (2-CH$_2$CH$_3$), 71.50 (d, $^1J_{CP}$ = 173.7 Hz, –CH), 113.58–113.62, 128.49–129.30, 159.47–159.51 (–C$_6$H$_4$) ppm; IR (neat): OH peak was absent.

3.4.2. Diethyl α-trimethylsilyloxy-2-chlorobenzylphosphonate (2e)

^{1}H NMR (CDCl$_3$): δ 0.00 [s, 9H, –Si(CH$_3$)$_3$], 1.08–1.24 (m, 6H, 2-OCH$_2$CH$_3$), 3.79–4.10 (m, 4H, 2-OCH$_2$CH$_3$), 5.50 (d, 1H, $^1J_{PH}$ = 12.3 Hz, –CH), 7.11–7.27 (m, 3H, –C$_6$H$_4$), 7.65–7.73 (m, 1H, –C$_6$H$_4$) ppm; ^{13}C NMR (CDCl$_3$): 0.47 [–Si(CH$_3$)$_3$], 16.47–16.73 (2-OCH$_2$CH$_3$), 63.20–63.69 (2-CH$_2$CH$_3$), 67.89 (d, $^1J_{CP}$ = 175.8 Hz, –CH), 127.08–135.80 (–C$_6$H$_4$) ppm; IR (neat): OH peak was absent.

3.4.3. Diethyl α-trimethylsilyloxy-3-chlorobenzylphosphonate (2f)

^{1}H NMR (CDCl$_3$): δ 0.00 [s, 9H, –Si(CH$_3$)$_3$], 1.09–1.17 (m, 6H, 2-OCH$_2$CH$_3$), 3.90–4.01 (m, 4H, 2-OCH$_2$CH$_3$), 4.83 (d, 1H, $^1J_{PH}$ = 14.5 Hz, –CH), 7.14–7.41 (m, 4H, –C$_6$H$_4$) ppm; ^{13}C NMR (CDCl$_3$): 0.47 [–Si(CH$_3$)$_3$], 16.44–16.59 (2-OCH$_2$CH$_3$), 62.94–63.50 (2-CH$_2$CH$_3$), 71.43 (d, $^1J_{CP}$ = 171.6 Hz, –CH), 125.47–139.73 (–C$_6$H$_4$) ppm; IR (neat): OH peak was absent.

3.4.4. Diethyl α-trimethylsilyloxy-2-nitrobenzylphosphonate (2i)

^{1}H NMR (CDCl$_3$): δ 0.00 [s, 9H, –Si(CH$_3$)$_3$], 1.01–1.11 (m, 6H, 2-OCH$_2$CH$_3$), 3.83–3.97 (m, 4H, 2-OCH$_2$CH$_3$), 6.02 (d, 1H, $^1J_{PH}$ = 15.9 Hz, –CH), 7.28 (t, 1H, $^2J_{HH}$ = 7.3 Hz, –C$_6$H$_4$), 7.48 (t, 1H, $^2J_{HH}$ = 7.3 Hz, –C$_6$H$_4$), 7.72–7.80 (m, 2H, –C$_6$H$_4$) ppm; ^{13}C NMR (CDCl$_3$): 0.46 [–Si(CH$_3$)$_3$], 16.41–16.60 (2-OCH$_2$CH$_3$), 63.26–63.62 (2-CH$_2$CH$_3$), 66.40 (d,

$^1J_{CP}$ = 172.0 Hz, –CH), 124.70–134.02, 147.94–148.04 (–C_6H_4) ppm; IR (neat): OH peak was absent.

3.4.5. *Diethyl α-trimethylsilyloxy-3-nitrobenzylphosphonate (2j)*

^{1}H NMR (CDCl$_3$): δ 0.00 [s, 9H, –Si(CH$_3$)$_3$], 1.08–1.17 (m, 6H, 2-OCH$_2$CH_3), 3.91–3.99 (m, 4H, 2-OCH_2CH$_3$), 4.96 (d, 1H, $^1J_{PH}$ = 14.8 Hz, –CH), 7.41 (t, 1H, $^2J_{HH}$ = 7.8 Hz, –C$_6$H$_4$), 7.70 (d, 1H, $^2J_{HH}$ = 7.4 Hz, –C$_6$H$_4$), 8.01 (d, 1H, $^2J_{HH}$ = 7.9 Hz, –C$_6$H$_4$), 8.19 (s, 1H, –C$_6$H$_4$) ppm; ^{13}C NMR (CDCl$_3$): 0.47 [–Si(CH$_3$)$_3$], 16.50–16.63 (2-OCH$_2$CH$_3$), 63.20–63.75 (2-CH$_2$CH$_3$), 71.16 (d, $^1J_{CP}$ = 171.5 Hz, –CH), 122.11–123.07, 129.12–129.33, 133.32–133.40, 140.23, 148.28–148.33 (–C$_6$H$_4$) ppm; IR (neat): OH peak was absent.

Acknowledgements

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