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PPh_3/DDQ as a neutral system for the facile preparation of diethyl α-bromo, α-iodo and α-azidophosphonates from diethyl α-hydroxyphosphonates

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Abstract—The mixture of triphenylphosphine (PPh_3) and 2,3-dichloro-5,6-dicyanobenzquinone (DDQ) as a neutral system has been used for the preparation of various types of diethyl α-bromo, α-iodo and α-azidophosphonates from their corresponding diethyl α-hydroxyphosphonates in the presence of *n*-Bu_4NBr, *n*-Bu_4NI and NaN_3 in good to high yields.

1. Introduction

α-Functionalized phosphonates are fascinating organophosphorus compounds in biology, pharmacology and organic chemistry.[1] The main interest in the preparation of these compounds arises from their common applications in the Horner–Wadsworth–Emmons (HWE) olefination reaction to produce α-functionalized olefins and acetylenes.[2] α-Hydroxyphosphonates,[3] which are easily prepared from commercially available materials, are useful precursors for the preparation of various types of α-functionalized phosphonates. Although a wide range of procedures exists in the literature for the conversion of ordinary hydroxyl functional groups into other functional groups, these methods are not readily applicable to α-hydroxyphosphonates.[4] Therefore, introduction of new and suitable methods for the preparation of α-functionalized phosphonates by the replacement of hydroxyl functional groups has received wide spread attention from organic chemists.[3a,5]

Preparation of biologically active diethyl α-halogenated phosphonates, which are also good precursors for the preparation of heavily substituted olefines via HWE olefination reaction, is an interesting reaction in organic chemistry.[1g,2a,d–g] A literature survey indicates that in contrast to the existing methods for the conversion of alcohols to their bromides and iodides, few methods are known for the preparation of diethyl α-bromo and α-iodophosphonates from their corresponding diethyl α-hydroxyphosphonates.[6] However, the reported procedures suffered from at least one of the following drawbacks; such as low yields of the products, use of toxic reagents or requiring rather high temperatures. PPh_3/CBr_4 in refluxing benzene and PPh_3/Br_2/Py in CH_3CN at room temperature are the reported procedures that have been used for the preparation of diethyl α-bromophosphonates in low yields (42–67%).[6a] Toxic $SOBr_2$ is the other reported brominating agent that has been applied for this purpose.[6b] In this report, iodination of diethyl α-hydroxyphosphonates has also been tried in the presence of phosphorus triiodide (PI_3).[6b] However, attempts to obtain α-iodophosphonates in reasonable yields failed and the desired products were obtained in poor yields (~10%).[6b] Allyl bromide/carbonyl diimidazole (CDI) and MeI/CDI have been successfully applied for the preparation of diethyl α-bromo and α-iodophosphonates, respectively from diethyl α-hydroxyphosphonates.[6c] These procedures suffer from requiring a high temperature (150 °C).

α-Azidophosphonates are important precursors for the preparation of heterocyclic compounds via 1,3-cycloaddition reactions[7] and also for the preparation of their primary amines.[5e,8] In this view, α-amino phosphonates, which are phosphorus analogues of the corresponding α-aminoacids, are successfully obtained by catalytic hydrogenation of α-azidophosphonates,[5e] or by the Staudinger reaction of the azido compounds with PPh_3.[8a,b] Methods for the direct preparation of diethyl α-azido-phosphonates from diethyl α-hydroxy phosphonates are limited to Mitsunobu reaction using PPh_3/diethyl azodicarboxylate (DEAD) and HN_3 as a source of the azide anion. This reaction requires long reaction times.[5h] Azidation of diethyl α-chloromethylphosphonates[9] and α-tosylatedbenzylphosphonates[10] by means of sodium azide in dimethylformamide (DMF) or dimethylsulfoxide (DMSO), respectively are the other reported

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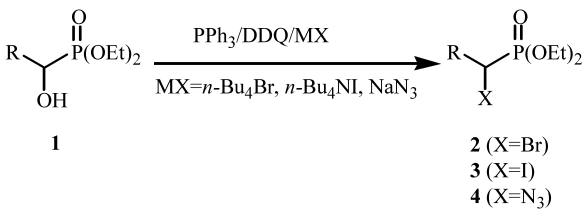
methods for this purpose. Azidation of triethylphosphonoacetate with trifluromethanesulfonyl azide in the presence of Et_3N is the other reported procedure that has been used for the preparation of α-azidophosphonates.[11]

The interaction of quinones as electron-acceptors with derivatives of group VB elements in their trivalent state as electron-donors has been extensively investigated.[12] A number of investigations have dealt more specifically with the structure of the products formed between quinones and tertiary amines, phosphites and phosphines.[13] Although some investigations have been carried out on the reaction of tertiary phosphines with quinones and on their product structures,[12,13] the application of these mixed materials, as reagents in organic synthesis have not been described. Recently we have reported that a mixture of PPh_3 and 2,3-dichloro,5,6-dicanobenzoquinone (DDQ) affords a complex which in the presence of R_4NX (X=CL, Br, I) converts alcohols, selenols and thiols into their corresponding alkyl halides in high yields.[14]

In recent years, we have started extensive studies on the development of new methods for the preparation of diethyl α-functionalized phosphonates from diethyl α-hydroxyphosphonates. Along this line, we have reported mild oxidation and silylation procedures for the preparation of diethyl α-keto and α-trimethylsilyloxyphosphonates in high yields.[15]

We now report that the PPh_3/DDQ system has been successfully applied for the preparation of various types of diethyl α-bromo, α-iodo and α-azidophophonates from their corresponding hydroxyl compounds using MX (*n*-Bu_4NBr, *n*-Bu_4NI and NaN_3) as nucleophilic sources under mild reaction conditions in good to excellent yields (Scheme 1).



Scheme 1.

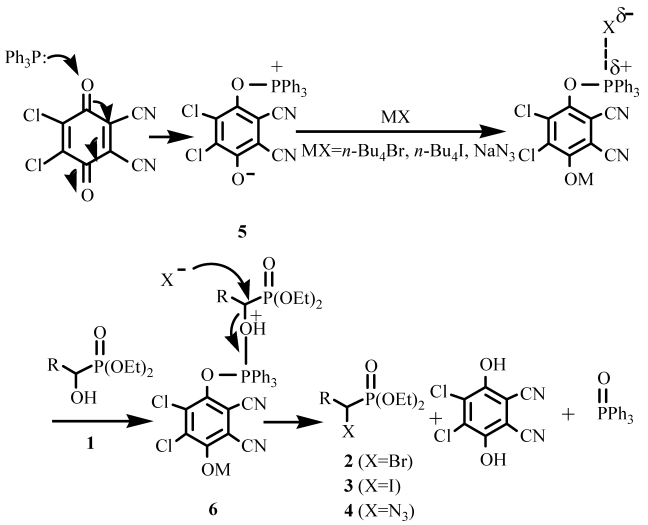
2. Results and discussion

Initially, the halogenation reaction of a variety of diethyl α-hydroxyphosphonates (**1**) with PPh_3/DDQ/*n*-Bu_4NX (X=Br, I) (molar ratio=2:2:2 with respect to **1**) in CH_2Cl_2 at room temperature was studied. The results and the absorption peak of the α-CH group of the products in their ^1H NMR are tabulated in the Tables 1 and 2.

As shown in Tables 1 and 2, various types of diethyl α-bromophosphonates (**2a**–**m**) and diethyl α-iodophosphonates (**3a**, **e**–**g**, **i**–**k**) were obtained in good to excellent yields (60–98%) under similar reaction conditions.

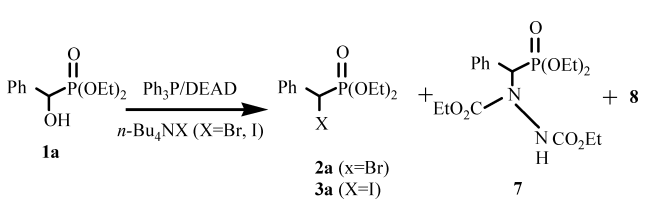
In the second part of our studies, we have applied the PPh_3/DDQ system for the azidation of diethyl α-hydroxyphosphonates. The azidation reaction for the replacement of the hydroxyl functional group of **1a** by PPh_3/DDQ/NaN_3 with the ratio of 2:2:2 equiv. with respect to **1a** in refluxing CH_3CN progressed well in good to high yields (Table 3). The absorption peak of the α-CH group of the products in their ^1H NMR and also the absorption peak of the N_3 group in their IR spectra are tabulated in Table 3.

According to our recent proposed mechanism for the conversion of alcohols, thiols and selenols to their corresponding halides by PPh_3/DDQ/R_4NX (X=Cl, Br, I),[14] we now suggest a similar pathway for the bromination, iodination and azidation of diethyl α-hydroxyphosphonates with *n*-Bu_4NBr, *n*-Bu_4NI and NaN_3 in the presence of PPh_3/DDQ. In the presented method, diethyl α-hydroxyphosphonates react with the adduct formed from the reaction of PPh_3 and DDQ (**5**) to give (**6**). Reaction of **6** with the nucleophile produces the desired products (Scheme 2).



Scheme 2.

In order to show the unique behavior of PPh_3/DDQ system for the preparation of α-functionalized phosphonates, we studied the bromination and iodination of **1a** as a model compound with *n*-Bu_4NBr and *n*-Bu_4NI in the presence of PPh_3/DEAD. The results indicate that under this reaction condition, besides the formation of the desired products **2a** in 41% yield and **3a** in 33% yield, two other by-products **7** and **8** were also isolated. One of the by-products **7** was identified as the alkylated hydrazine derivative and isolated in 5–7% for the bromination and iodination reactions (Scheme 3). The presence of a peak as a doublet for the α-CH at 5.87 ppm with $^2J_{PH}$=13.6 Hz in its ^1H NMR spectra and also two peaks at 3250 and 1730 cm^{-1} for N–H and –C(O)OEt in its IR spectra confirmed the formation of **7**. This type of product is quite familiar in Mitsunobu



Scheme 3.

Table 1. Preparation of diethyl α-bromophosphonates (**2a–n**) from diethyl α-hydroxyphosphonates (**1a–n**) by PPh_3/DDQ/*n*-Bu_4NBr in CH_2Cl_2 at room temperature

Product[Ref]	R–	Time (h)	Yield[a] (%)	^1H NMR ($CDCl_3$) $\delta_{\alpha CH}$ ($^2J_{PH}$)	^{13}C NMR ($CDCl_3$) $\delta_{\alpha CH}$ ($^1J_{PC}$)
2a[6a,16]	C_6H_5–[b]	5	98	4.79 (12.5)	41.85 (159.2)
2b[16]	4-$CH_3C_6H_4$–[b]	5.5	97	4.85 (12.8)	41.80 (159.1)
2c	4-$CH_3OC_6H_4$–	6	97	4.80 (12.7)	41.9 (162.0)
2d	2,4,6-$(CH_3)_3C_6H_2$–	5.5	90	5.65 (14.8)	36.19 (163.2)
2e	2-ClC_6H_4–	7	97	5.53 (13.8)	36.29 (161.6)
2f	3-ClC_6H_4–	9	95	5.36 (13.6)	36.67 (161.5)
2g[16]	4-ClC_6H_4–[b]	8.5	98	5.86 (13.8)	40.91 (159.5)
2h	2,6-$Cl_2C_6H_3$–	6	97	6.1 (13.9)	38.76 (158.0)
2i	2-$O_2NC_6H_4$–	6.5	95	6.01 (14.8)	34.06 (158.2)
2j	3-$O_2NC_6H_4$–	7	94	5.98 (14.6)	38.77 (158.0)
2k[17]	4-$O_2NC_6H_4$–[b]	8.5	96	6.3 (14.8)	40.12 (157.2)
2l	2-Naphthyl	5	94	5.10 (13.9)	41.92 (159.7)
2m	3-Pyridyl	5.5	92	4.91 (13.5)	38.28 (159.5)

[a] Isolated yields.
[b] Registry numbers for **2a**, **b**, **g** and **k**: 23755-78-4, 222850-34-2, 74917-62-7 and 39082-34-3, respectively.

reactions.[18] Therefore, using the PPh_3/DDQ system is a superior method for the high yielding preparation of α-functionalized phosphonates without side product formation.

We have also tried the chlorination of diethyl α-hydroxyphosphonates in the presence of this system with *n*-$Bu_4NCl{\cdot}H_2O$ and *n*-Hex_4NCl. However, chlorination of the phosphonates did not proceed well and the starting materials were isolated intact.

3. Conclusion

In conclusion, in this investigation we have demonstrated the use of PPh_3/DDQ/MX system as a superior and convenient method for the preparation of varieties of diethyl α-bromo-, α-iodo- and α-azidophosphonates from the easily available corresponding diethyl α-hydroxyphosphonates. The ease of handling of the system, mild and neutral reaction conditions, the absence of the formation of the side products and the good to excellent yields of the products are the useful practical points of the presented method.

4. Experimental

Chemicals were either prepared in our laboratories or were purchased from Fluka and Merck Chemical Companies. Products were purified by plate chromatography. The purity determination of the products was accomplished by TLC on silica gel polygram SIL G/UV 254 plates. Mass spectra were run on a Shimadzu GC-Mass-QP 1000 EX at 70 eV. The IR spectra were recorded on a Shimadzu Fourier Transform Infrared Spectrophotometer (FT-IR-8300). The NMR spectra were recorded on a Bruker advance DPX 250 MHz spectrometer. The solvents were purified and dried before use.

4.1. Typical procedure for the preparation of diethyl α-bromobenzylphosphonate (2a) from diethyl α-hydroxybenzylphosphonate (1a)

n-Bu_4NBr (2 mmol, 0.644 g) was added to a stirring mixture of DDQ (2 mmol, 0.454 g) and PPh_3 (2 mmol, 0.524 g) in dry CH_2Cl_2 (10 mL) at room temperature. Then **1a** (1 mmol, 0.244 g) was added to the reaction mixture and the progress of the reaction was monitored by TLC. After 5 h, the reaction mixture was washed with H_2O (3×20 mL). The organic layer was separated and dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent afforded a crude product that was purified by preparative plate chromatography (silica gel) eluted with CCl_4/EtOAc (2:1) to afford diethyl α-bromobenzylphosphonate (**2a**) in 98% yield (0.3 g) as a yellow oily compound.

4.2. Typical procedure for the preparation of diethyl α-iodobenzylphosphonate (3a) from diethyl α-hydroxybenzylphosphonate (1a)

n-Bu_4NI (2 mmol, 0.738 g) was added to a stirring mixture of DDQ (2 mmol, 0.454 g) and PPh_3 (2 mmol, 0.524 g) in dry CH_2Cl_2 (10 mL) at room temperature. Then **1a** (1 mmol, 0.244 g) was added to the reaction mixture and

Table 2. Preparation of diethyl α-iodophosphonates (**3a**, **e–g**, **i–k**) from diethyl α-hydroxyphosphonates (**1a**, **e–g**, **i–k**) by PPh_3/DDQ/*n*-Bu_4NI in CH_2Cl_2 at room temperature

Product[Ref]	R–	Time (h)	Yield[a] (%)	^1H NMR ($CDCl_3$) $\delta_{\alpha CH}$ ($^2J_{PH}$)	^{13}C NMR ($CDCl_3$) $\delta_{\alpha CH}$ ($^1J_{PC}$)
3a[16]	C_6H_5–[b]	3	84	4.98 (13.4)	15.41 (139.9)
3e	2-ClC_6H_4–	5	68	4.63 (13.2)	9.97 (158.2)
3f	3-ClC_6H_4–	4.5	69	4.92 (13.8)	9.96 (158.5)
3g	4-ClC_6H_4–	3.5	65	4.87 (13.6)	14.28 (156.3)
3i	2-$O_2NC_6H_4$–	5	63	6.16 (15.0)	7.00 (155.8)
3j	3-$O_2NC_6H_4$–	4.5	60	6.05 (14.8)	13.0 (155.1)
3k[17]	4-$O_2NC_6H_4$–[b]	5.5	61	5.80 (13.9)	12.98 (154.6)

[a] Isolated yields.
[b] Registry numbers for **3a** and **k**: 222850-36-4 and 39082-35-4, respectively.

Table 3. Preparation of diethyl α-azidohosphonates (**4a**, **e**–**g**, **i**–**k**) from diethyl α-hydroxyphosphonates (**1a**, **e**–**g**, **i**–**k**) by PPh_3/DDQ/NaN_3 in refluxing CH_3CN

Product[Ref]	R–	Time (h)	Yield[a] (%)	IR (neat) ν_{N3}/cm^{-1}	^{1}H NMR ($CDCl_3$) $\delta_{\alpha CH}$ ($^2J_{PH}$)	^{13}C NMR ($CDCl_3$) $\delta_{\alpha CH}$ ($^1J_{PC}$)
4a[1h,8]	C_6H_5–[b]	3	95	2100	4.74 (16.5)	61.96 (158.2)
4e	2-ClC_6H_4–	6	83	2150	5.29 (17.0)	56.35 (161.1)
4f	3-ClC_6H_4–	7.5	89	2123	5.02 (16.4)	47.86 (162.2)
4g	4-ClC_6H_4–	7	80	2110	4.65 (17.0)	61.28 (158.3)
4i	2-$O_2NC_6H_4$–	8.5	76	2125	4.73 (16.4)	56.46 (157.5)
4j	3-$O_2NC_6H_4$–	7.5	83	2140	4.90 (16.4)	61.10 (156.2)
4k[17]	4-$O_2NC_6H_4$–[b]	5.5	75	2134	4.83 (16.7)	61.36 (155.0)

[a] Isolated yields.
[b] Registry numbers for **4a** and **k**: 131523-51-8 and 17986-31-1, respectively.

the progress of the reaction was monitored by TLC. After 3 h, the reaction mixture was washed with H_2O (3×20 mL) and the organic layer was separated and dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent afforded a crude product that was purified by the preparative plate chromatography (silica gel) eluted with CCl_4/EtOAc (2:1) to afford diethyl α-bromobenzylphosphonate (**3a**) in 84% yield (0.297 g) as a yellow brownish oily compound.

4.3. Typical procedure for the preparation of diethyl α-azidobenzylphosphonate (4a) from diethyl α-hydroxybenzylphosphonate (1a)

NaN_3 (2 mmol, 0.13 g) was added to a stirring mixture of DDQ (2 mmol, 0.454 g) and PPh_3 (2 mmol, 0.524 g) in dry CH_3CN (10 mL). Then **1a** (1 mmol, 0.244 g) was added to the reaction mixture and was refluxed for 3 h (progress of the reaction was monitored by TLC). The resulting reaction mixture was washed with H_2O (3×20 mL), the organic layer was separated and dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent afforded a crude product that was purified by preparative plate chromatography (silica gel) eluted with CCl_4/EtOAc (2:1) to afford diethyl α-azidobenzylphosphonate (**4a**) in 95% yield (0.255 g) as a faint yellow oily compound.

4.4. Spectral data and elemental analysis of diethyl α-bromo, α-iodo and α-azidophosphonate are presented bellow

4.4.1. Diethyl α-bromobenzylphosphonate (2a).[6a,16] ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ 1.08 (t, 3H, $^3J_{HH}$=7.1 Hz, 2-OCH$_2$CH_3), 1.26 (t, 3H, $^3J_{HH}$=7.1 Hz, 2-OCH$_2$CH_3), 3.79–3.82 (m, 1H, 2-OCH_2CH$_3$), 3.93–4.00 (m, 1H, 2-OCH_2CH$_3$), 4.03–4.17 (m, 2H, 2-OCH_2CH$_3$), 4.79 (d, 1H, $^2J_{PH}$=12.5 Hz, –C*H*), 7.25–7.28 (m, 3H, –C_6H_5), 7.47–7.49 (m, 2H, –C_6H_5) ppm; ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): 16.57 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$*C*H$_3$), 16.78 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$*C*H$_3$), 41.85 (d, $^1J_{CP}$=159.2 Hz, –*C*H), 64.46 (d, $^2J_{CP}$=4.2 Hz, 2-O*C*H$_2$CH$_3$), 64.57 (d, $^2J_{CP}$=4.2 Hz, 2-O*C*H$_2$CH$_3$), 129.05–129.95, 134.94, 134.99 (–C_6H_5) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=307, M−Br=227, 227−P(O)(OEt)$_2$=90; $C_{11}H_{16}BrO_3P$ requires C, 43.00; H, 5.21%, found: C, 43.02; H, 5.20%.

4.4.2. Diethyl α-bromo-4-methylbenzylphosphonate (2b).[16] ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ 1.16 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$CH_3), 1.34 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$CH_3), 2.34 (s, 3H, 4-CH_3), 3.85–3.92 (m, 1H, 2-OCH_2CH$_3$), 4.01–4.10 (m, 1H, 2-OCH_2CH$_3$), 4.16–4.27 (m, 2H, 2-OCH_2CH$_3$), 4.85 (d, 1H, $^2J_{PH}$=12.8 Hz, –C*H*), 7.15 (d, 2H, $^3J_{HH}$=6.9 Hz, –C_6H_4), 7.45 (d, 2H, $^3J_{HH}$=6.3 Hz, –C_6H_4) ppm; ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): 16.50 (d, $^3J_{CP}$=5.7 Hz, 2-OCH$_2$*C*H$_3$), 16.82 (d, $^3J_{CP}$=5.7 Hz, 2-OCH$_2$*C*H$_3$), 22.18 (4-*C*H$_3$), 41.80 (d, $^1J_{CP}$=159.1 Hz, –*C*H), 63.51 (d, $^2J_{CP}$=4.5 Hz, 2-O*C*H$_2$CH$_3$), 64.70 (d, $^2J_{CP}$=4.5 Hz, 2-O*C*H$_2$CH$_3$), 130.0–132.5, 136.4–138.9 (–C_6H_4) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=321, M−Br=241, 241−P(O)(OEt)$_2$=104; $C_{12}H_{18}BrO_3P$ requires C, 44.86; H, 5.61%, found: C, 44.85; H, 5.60%.

4.4.3. Diethyl α-bromo-4-methoxybenzylphosphonate (2c). ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ 1.09 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$CH_3), 1.27 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$CH_3), 3.74 (s, 3H, 4-OCH_3), 3.79–3.85 (m, 1H, 2-OCH_2CH$_3$), 3.94–4.04 (m, 1H, 2-OCH_2CH$_3$), 4.10–4.21 (m, 2H, 2-OCH_2CH$_3$), 4.80 (d, 1H, $^2J_{PH}$=12.7 Hz, –C*H*), 6.80 (d, 2H, $^3J_{HH}$=8.6 Hz, –C_6H_4), 7.44 (d, 2H, $^3J_{HH}$=7.5 Hz, –C_6H_4) ppm; ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): 16.63 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$*C*H$_3$), 16.80 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$*C*H$_3$), 41.9 (d, $^1J_{CP}$=162.0 Hz, –*C*H), 55.69 (4-OCH_3), 64.33 (d, $^2J_{CP}$=6.7 Hz, 2-O*C*H$_2$CH$_3$), 64.43 (d, $^2J_{CP}$=6.7 Hz, 2-O*C*H$_2$CH$_3$), 114.49, 126.95, 130.64–131.29, 160.45 (–C_6H_4) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=337, M−Br=257, 257−P(O)(OEt)$_2$=120; $C_{12}H_{18}BrO_4P$ requires C, 42.73; H, 5.34%, found: C, 42.71; H, 5.32%.

4.4.4. Diethyl α-bromo-2,4,6-trimethylbenzylphosphonate (2d). ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ 0.98 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$*C*H$_3$), 1.31 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$*C*H$_3$), 2.21 (s, 3H, –CH_3), 2.29 (s, 3H, –CH_3), 2.60 (s, 3H, –CH_3), 3.61–3.64 (m, 1H, 2-OCH_2CH$_3$), 3.87–3.91 (m, 1H, 2-OCH_2CH$_3$), 4.13–4.21 (m, 2H, 2-OCH_2CH$_3$), 5.65 (d, 1H, $^2J_{PH}$=14.8 Hz, –C*H*), 6.75 (s, 1H, –C_6H_2), 6.81 (s, 1H, –C_6H_2) ppm; ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): 15.00–15.39 (m, 2-OCH$_2$*C*H$_3$), 20.07 (–*C*H$_3$), 20.71 (–*C*H$_3$), 28.68 (–*C*H$_3$), 36.19 (d, $^1J_{CP}$=163.2 Hz, –*C*H), 62.88–63.36 (m, 2-O*C*H$_2$CH$_3$), 128.02, 130.56 (–C_6H_2) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=349, M−Br=269, 269−P(O)(OEt)$_2$=132; $C_{14}H_{22}BrO_3P$ requires C, 48.14; H, 6.30%, found: C, 48.12; H, 6.28%.

4.4.5. Diethyl α-bromo-2-chlorobenzylphosphonate (2e). ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ 1.18 (t, 3H, $^3J_{HH}$=7.5 Hz, 2-OCH$_2$CH_3), 1.36 (t, 3H, $^3J_{HH}$=7.5 Hz, 2-OCH$_2$CH_3), 3.88–4.12 (m, 2H, 2-OCH_2CH$_3$), 4.22–4.31

(m, 2H, 2-OCH_2CH$_3$), 5.53 (d, 1H, $^2J_{PH}$=13.8 Hz, –CH), 7.25–7.37 (m, 3H, –C$_6H_4$), 7.99 (d, 1H, $^3J_{HH}$=7.4 Hz, –C$_6H_4$) ppm; ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): 16.19 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$CH_3), 16.43 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$CH_3), 36.29 (d, $^1J_{CP}$=161.6 Hz, –CH), 64.05 (d, $^2J_{CP}$=6.9 Hz, 2-OCH_2CH$_3$), 64.37 (d, $^2J_{CP}$=6.9 Hz, 2-OCH_2CH$_3$), 127.52–133.56 (–C$_6$H$_4$) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=342, M+2=344, M−Br=262, 262−P(O)(OEt)$_2$=125; C$_{11}$H$_{15}$BrClO$_3$P requires C, 38.60; H, 4.39%, found: C, 38.60; H, 4.36%.

4.4.6. Diethyl α-bromo-3-chlorobenzylphosphonate (2f). ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): δ 1.08 (t, 3H, $^3J_{HH}$=7.1 Hz, 2-OCH$_2$CH_3), 1.28 (t, 3H, $^3J_{HH}$=7.1 Hz, 2-OCH$_2$CH_3), 3.78–4.01 (m, 2H, 2-OCH_2CH$_3$), 4.14–4.26 (m, 2H, 2-OCH_2CH$_3$), 5.36 (d, 1H, $^2J_{PH}$=13.6 Hz, –CH), 7.14–7.30 (m, 3H, –C$_6H_4$), 7.89–7.93 (m, 1H, –C$_6H_4$) ppm; ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): 16.54 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$CH_3), 16.78 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$CH_3), 36.67 (d, $^1J_{CP}$=161.5 Hz, –CH), 64.40 (d, $^2J_{CP}$=7.0 Hz, 2-OCH_2CH$_3$), 64.72 (d, $^2J_{CP}$=7.0 Hz, 2-OCH_2CH$_3$), 127.85–133.93 (–C$_6$H$_4$) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=342, M+2=344, M−Br=262, 262−P(O)(OEt)$_2$=125; C$_{11}$H$_{15}$BrClO$_3$P requires C, 38.60; H, 4.39%, found: C, 38.61; H, 4.41%.

4.4.7. Diethyl α-bromo-4-chlorobenzylphosphonate (2g).[16] ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): δ 1.11 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$CH_3), 1.26 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$CH_3), 3.79–3.90 (m, 1H, 2-OCH_2CH$_3$), 3.95–4.04 (m, 1H, 2-OCH_2CH$_3$), 4.10–4.21 (m, 2H, 2-OCH_2CH$_3$), 5.86 (d, 1H, $^2J_{PH}$=13.8 Hz, –CH), 7.24 (d, 2H, $^3J_{HH}$=8.4 Hz, –C$_6H_4$), 7.43 (d, 2H, $^3J_{HH}$=8.4 Hz, –C$_6H_4$) ppm; ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): 16.62 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$CH_3), 16.79 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$CH_3), 40.91 (d, $^1J_{CP}$=159.5 Hz, –CH), 64.43 (d, $^2J_{CP}$=7.0 Hz, 2-OCH_2CH$_3$), 64.67 (d, $^2J_{CP}$=7.0 Hz, 2-OCH_2CH$_3$), 129.24–135.33 (–C$_6$H$_4$) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=342, M+2=344, M−Br=262, 262−P(O)(OEt)$_2$=125; C$_{11}$H$_{15}$BrClO$_3$P requires C, 38.60; H, 4.39%, found: C, 38.59; H, 4.38%.

4.4.8. Diethyl α-bromo-2,6-dichlorobenzylphosphonate (2h). ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): δ 1.12–1.20 (m, 3H, 2-OCH$_2$CH_3), 1.33–1.40 (m, 3H, 2-OCH$_2$CH_3), 3.91–4.06 (m, 2H, 2-OCH_2CH$_3$), 4.19–4.27 (m, 2H, 2-OCH_2CH$_3$), 6.1 (d, 1H, $^2J_{PH}$=13.9 Hz, –CH), 7.16–7.35 (m, 3H, –C$_6H_4$) ppm; ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): 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), 38.76 (d, $^1J_{CP}$=158.0 Hz, –CH), 63.35 (d, $^2J_{CP}$=7.1 Hz, 2-OCH_2CH$_3$), 63.60 (d, $^2J_{CP}$=7.1 Hz, 2-OCH_2CH$_3$), 128.60, 129.99, 131.31, 135.73, 136.87 (–C$_6$H$_3$) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=376, M+2=378, M+4=381, M−Br=296, 296−P(O)(OEt)$_2$=159; C$_{11}$H$_{14}$BrClO$_3$P requires C, 35.11; H, 3.72%, found: C, 35.08; H, 3.69%.

4.4.9. Diethyl α-bromo-2-nitrobenzylphosphonate (2i). ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): δ 1.15 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$CH_3), 1.36 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$CH_3), 3.91–4.16 (m, 2H, 2-OCH_2CH$_3$), 4.22–4.34 (m, 2H, 2-OCH_2CH$_3$), 6.01 (d, 1H, $^2J_{PH}$=14.8 Hz, –CH), 7.46–7.56 (m, 1H, –C$_6H_4$), 7.63–7.70 (m, 1H, –C$_6H_4$), 7.92 (d, 1H, $^3J_{HH}$=7.9 Hz, –C$_6H_4$), 8.18 (d, 1H, $^3J_{HH}$=8.1 Hz, –C$_6H_4$) ppm; ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): 16.10 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$CH_3), 16.38 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$CH_3), 34.06 (d, $^1J_{CP}$=158.2 Hz, –CH), 64.02 (d, $^2J_{CP}$=7.2 Hz, 2-OCH_2CH$_3$), 64.80 (d, $^2J_{CP}$=7.2 Hz, 2-OCH_2CH$_3$), 124.76, 128.47–129.61, 132.07–132.22, 133.28–133.42 (–C$_6$H$_4$) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=352, M−Br=272, 272−P(O)(OEt)$_2$=135; C$_{11}$H$_{15}$BrNO$_5$P requires C, 37.5; H, 4.26%, found: C, 37.8; H, 4.28%.

4.4.10. Diethyl α-bromo-3-nitrobenzylphosphonate (2j). ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): δ 1.14 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$CH_3), 1.28 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$CH_3), 3.92–4.24 (m, 4H, 2-OCH_2CH$_3$), 5.98 (d, 1H, $^2J_{PH}$=14.6 Hz, –CH), 7.49 (t, 1H, $^3J_{HH}$=8.0 Hz, –C$_6H_4$), 7.88 (d, 1H, $^3J_{HH}$=7.7 Hz, –C$_6H_4$), 8.13 (d, 1H, $^3J_{HH}$=7.8 Hz, –C$_6H_4$), 8.32 (s, 1H, –C$_6H_4$) ppm; ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): 15.26 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$CH_3), 15.40 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$CH_3), 38.77 (d, $^1J_{CP}$=158.0 Hz, –CH), 63.25 (d, $^2J_{CP}$=7.1 Hz, 2-OCH_2CH$_3$), 63.65 (d, $^2J_{CP}$=7.1 Hz, 2-OCH_2CH$_3$), 122.76–123.46, 128.74, 134.48–134.57 (–C$_6$H$_4$) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=352, M−Br=272, 272−P(O)(OEt)$_2$=135; C$_{11}$H$_{15}$BrNO$_5$P requires C, 37.5; H, 4.26%, found: C, 37.6; H, 4.27%.

4.4.11. Diethyl α-bromo-4-nitrobenzylphosphonate (2k).[17] ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): δ 1.10–1.14 (m, 3H, 2-OCH$_2$CH_3), 1.27–1.30 (m, 3H, 2-OCH$_2$CH_3), 3.90–4.05 (m, 2H, 2-OCH_2CH$_3$), 4.12–4.21 (m, 2H, 2-OCH_2CH$_3$), 6.3 (d, 1H, $^2J_{PH}$=14.8 Hz, –CH), 7.66–7.69 (m, 2H, –C$_6H_4$), 8.12–8.15 (m, 2H, –C$_6H_4$) ppm; ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): 16.63 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$CH_3), 16.78 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$CH_3), 40.12 (d, $^1J_{CP}$=157.2 Hz, –CH), 64.60 (d, $^2J_{CP}$=7.0 Hz, 2-OCH_2CH$_3$), 65.05 (d, $^2J_{CP}$=7.0 Hz, 2-OCH_2CH$_3$), 124.09, 130.19–130.96, 142.34–142.40 (–C$_6$H$_4$) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=352, M−Br=272, 272−P(O)(OEt)$_2$=135; C$_{11}$H$_{15}$BrNO$_5$P requires C, 37.5; H, 4.26%, found: C, 37.8; H, 4.29%.

4.4.12. Diethyl α-bromo-2-naphthylphosphonate (2l). ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): δ 1.12 (t, 3H, $^3J_{HH}$=7.1 Hz, 2-OCH$_2$CH_3), 1.34 (t, 3H, $^3J_{HH}$=7.1 Hz, 2-OCH$_2$CH_3), 3.81–3.91 (m, 1H, 2-OCH_2CH$_3$), 4.00–4.10 (m, 1H, 2-OCH_2CH$_3$), 4.18–4.30 (m, 2H, 2-OCH_2CH$_3$), 5.10 (d, 1H, $^2J_{PH}$=13.9 Hz, –CH), 7.46–7.50 (m, 2H, –C$_{10}H_7$), 7.71–7.83 (m, 4H, –C$_{10}H_7$), 7.97 (s, 1H, –C$_{10}H_7$) ppm; ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): 16.21 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$CH_3), 16.42 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$CH_3), 41.92 (d, $^1J_{CP}$=159.7 Hz, –CH), 64.11 (d, $^2J_{CP}$=7.4 Hz, 2-OCH_2CH$_3$), 64.22 ($^2J_{CP}$=7.4 Hz, 2-OCH_2CH$_3$), 126.04–128.97, 131.90–133.31 (–C$_{10}$H$_7$) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=357, M−Br=277, 277−P(O)(OEt)$_2$=140; C$_{15}$H$_{18}$BrO$_3$P requires C, 50.42; H, 5.04%, found: C, 50.4; H, 5.0%.

4.4.13. Diethyl α-bromo-3-pyridylphosphonate (2m). ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): δ 1.20 (t, 3H, $^3J_{HH}$=7.1 Hz, 2-OCH$_2$CH_3), 1.35 (t, 3H, $^3J_{HH}$=7.1 Hz, 2-OCH$_2$CH_3), 3.93–4.15 (m, 2H, 2-OCH_2CH$_3$), 4.20–4.31

(m, 2H, 2-OCH_2CH$_3$), 4.91 (d, 1H, $^2J_{PH}$=13.5 Hz, –C*H*), 7.31–7.36 (m, 1H, –C$_5H_4$N), 8.04 (d, 1H, $^3J_{HH}$=8.0 Hz, –C$_5H_4$N), 8.58 (d, 1H, $^3J_{HH}$=4.1 Hz, –C$_5H_4$N), 8.68 (s, 1H, –C$_5H_4$N) ppm; ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): 16.25 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$*C*H$_3$), 16.42 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$*C*H$_3$), 38.28 (d, $^1J_{CP}$=159.5 Hz, –*C*H), 64.46 (d, $^2J_{CP}$=7.1 Hz, 2-O*C*H$_2$CH$_3$), 64.80 (d, $^2J_{CP}$=7.1 Hz, 2-O*C*H$_2$CH$_3$), 123.94, 128.70–128.89, 13.56–132.44, 137.64–137.72, 149.96–150.27 (–*C*$_5$H$_4$N) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=308, M−Br=228, 228−P(O)(OEt)$_2$=91; C$_{10}$H$_{15}$BrNO$_3$P requires C, 38.96; H, 4.87%, found: C, 38.90; H, 4.80%.

4.4.14. Diethyl α-iodobenzylphosphonate (3a).[16] ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): δ 1.13 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$C*H*$_3$), 1.32 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$C*H*$_3$), 3.84–3.90 (m, 1H, 2-OC*H*$_2$CH$_3$), 3.99–3.08 (m, 1H, 2-OC*H*$_2$CH$_3$), 4.18–4.27 (m, 2H, 2-OC*H*$_2$CH$_3$), 4.98 (d, 1H, $^2J_{PH}$=13.4 Hz, –C*H*), 7.28–7.31 (m, 3H, –C$_6H_5$), 7.56–7.59 (m, 2H, –C$_6H_5$) ppm; ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): 15.41 (d, $^1J_{CP}$=139.9 Hz, –*C*H), 16.57 (d, $^3J_{CP}$=5.9 Hz, 2-OCH$_2$*C*H$_3$), 16.7 (d, $^3J_{CP}$=5.9 Hz, 2-OCH$_2$*C*H$_3$), 64.42 (d, $^2J_{CP}$=8.6 Hz, 2-O*C*H$_2$CH$_3$), 64.55 (d, $^2J_{CP}$=8.6 Hz, 2-O*C*H$_2$CH$_3$), 128.95–130.04 (–*C*$_6$H$_5$) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=354, M−Br=226, 226−P(O)(OEt)$_2$=89; C$_{11}$H$_{16}$IO$_3$P requires C, 37.29; H, 4.52%, found: C, 37.2; H, 4.58%.

4.4.15. Diethyl α-iodo-2-chlorobenzylphosphonate (3e). ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): δ 1.08 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$C*H*$_3$), 1.28 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$C*H*$_3$), 3.81–4.02 (m, 2H, 2-OC*H*$_2$CH$_3$), 4.12–4.24 (m, 2H, 2-OC*H*$_2$CH$_3$), 4.63 (d, 1H, $^2J_{PH}$=13.2 Hz, –CH), 7.10–7.25 (m, 3H, –C$_6H_4$), 7.97 (d, 1H, $^3J_{HH}$=7.9 Hz, –C$_6H_4$) ppm; ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): 9.97 (d, $^1J_{CP}$=158.2 Hz, –*C*H), 16.55 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$*C*H$_3$), 16.75 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$*C*H$_3$), 64.45 (d, $^2J_{CP}$=7.0 Hz, 2-O*C*H$_2$CH$_3$), 64.64 (d, $^2J_{CP}$=7.0 Hz, 2-O*C*H$_2$CH$_3$), 127.98, 128.01, 129.69–130.08, 132.84–133.06, 134.80 (–*C*$_6$H$_4$) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=389, M+2=391, M−Br=261, 261−P(O)(OEt)$_2$=125; C$_{11}$H$_{15}$ClIO$_3$P requires C, 33.93; H, 3.86%, found: C, 33.90; H, 3.84%.

4.4.16. Diethyl α-iodo-3-chlorobenzylphosphonate (3f). ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): δ 1.08 (t, 3H, $^3J_{HH}$=6.7 Hz, 2-OCH$_2$C*H*$_3$), 1.29 (t, 3H, $^3J_{HH}$=6.7 Hz, 2-OCH$_2$C*H*$_3$), 3.86–4.00 (m, 2H, 2-OC*H*$_2$CH$_3$), 4.16–4.22 (m, 2H, 2-OC*H*$_2$CH$_3$), 4.92 (d, 1H, $^2J_{PH}$=13.8 Hz, –CH), 7.17–7.23 (m, 3H, –C$_6H_4$), 7.96–7.99 (m, 1H, –C$_6H_4$) ppm; ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): 9.96 (d, $^1J_{CP}$=158.5 Hz, –*C*H), 16.50 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$*C*H$_3$), 16.75 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$*C*H$_3$), 64.51 (d, $^2J_{CP}$=7.1 Hz, 2-O*C*H$_2$CH$_3$), 64.70 (d, $^2J_{CP}$=7.1 Hz, 2-O*C*H$_2$CH$_3$), 128.03, 129.99–130.07, 132.89–132.95, 134.82 (–*C*$_6$H$_4$) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=389, M+2=391, M−Br=261, 261−P(O)(OEt)$_2$=125; C$_{11}$H$_{15}$ClIO$_3$P requires C, 33.93; H, 3.86%, found: C, 33.91; H, 3.84%.

4.4.17. Diethyl α-iodo-4-chlorobenzylphosphonate (3g). ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): δ 1.10 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$C*H*$_3$), 1.27 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$C*H*$_3$), 3.78–4.17 (m, 4H, 2-OC*H*$_2$CH$_3$), 4.87 (d, 1H, $^2J_{PH}$=13.6 Hz, –CH), 7.20 (d, 2H, $^3J_{HH}$=8.2 Hz, –C$_6H_4$), 7.44 (d, 2H, $^3J_{HH}$=8.2 Hz, –C$_6H_4$) ppm; ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): 14.28 (d, $^1J_{CP}$=156.3 Hz, –*C*H), 16.62 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$*C*H$_3$), 16.76 (d, $^3J_{CP}$=5.8 Hz, 2-OCH$_2$*C*H$_3$), 64.59 (d, $^2J_{CP}$=6.8 Hz, 2-O*C*H$_2$CH$_3$), 129.33, 131.19, 131.31, 134.78, 135.48 (–*C*$_6$H$_4$) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=389, M+2=391, M−Br=261, 261−P(O)(OEt)$_2$=125; C$_{11}$H$_{15}$ClIO$_3$P requires C, 33.93; H, 3.86%, found: C, 33.94; H, 3.87%.

4.4.18. Diethyl α-iodo-2-nitrobenzylphosphonate (3i). ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): δ 1.23 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$C*H*$_3$), 1.34 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$C*H*$_3$), 4.00–4.31 (m, 4H, 2-OC*H*$_2$CH$_3$), 6.16 (d, 1H, $^2J_{PH}$=15.0 Hz, –C*H*), 7.48–7.54 (m, 1H, –C$_6H_4$), 7.66–7.72 (m, 1H, –C$_6H_4$), 7.96 (d, 1H, $^2J_{PH}$=8.2 Hz, –C$_6H_4$), 8.09 (d, 1H, $^2J_{PH}$=8.0 Hz, –C$_6H_4$) ppm; ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): 7.00 (d, $^1J_{CP}$=155.8 Hz, –*C*H), 16.50 (d, $^3J_{CP}$=5.9 Hz, 2-OCH$_2$*C*H$_3$), 16.71 (d, $^3J_{CP}$=5.9 Hz, 2-OCH$_2$*C*H$_3$), 63.31 (d, $^2J_{CP}$=8.8 Hz, 2-O*C*H$_2$CH$_3$), 64.50 (d, $^2J_{CP}$=8.8 Hz, 2-O*C*H$_2$CH$_3$), 127.5–129.6 (–*C*$_6$H$_4$) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=399, M−Br=272, 261−P(O)(OEt)$_2$=136; C$_{11}$H$_{15}$INO$_5$P requires C, 33.08; H, 3.76%, found: C, 33.02; H, 3.71%.

4.4.19. Diethyl α-iodo-3-nitrobenzylphosphonate (3j). ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): δ 1.15 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$C*H*$_3$), 1.28 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$C*H*$_3$), 3.90–4.23 (m, 4H, 2-OC*H*$_2$CH$_3$), 6.05 (d, 1H, $^2J_{PH}$=14.8 Hz, –C*H*), 7.44 (t, 1H, $^3J_{HH}$=8.0 Hz, –C$_6H_4$), 7.89 (d, 1H, $^3J_{HH}$=7.7 Hz, –C$_6H_4$), 8.07 (d, 1H, $^3J_{HH}$=7.6 Hz, –C$_6H_4$), 8.31 (s, 1H, –C$_6H_4$) ppm; ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): 13.0 (d, $^1J_{CP}$=155.1 Hz, –*C*H), 16.59–16.80 (2-OCH$_2$*C*H$_3$), 64.68–65.02 (2-O*C*H$_2$CH$_3$), 123.70–124.77, 130.24, 136.10, 136.20, 139.25 (–*C*$_6$H$_4$) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=399, M−Br=272, 261−P(O)(OEt)$_2$=136; C$_{11}$H$_{15}$INO$_5$P requires C, 33.08; H, 3.76%, found: C, 33.06; H, 3.74%.

4.4.20. Diethyl α-iodo-4-nitrobenzylphosphonate (3k).[17] ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): δ 1.04–1.18 (m, 3H, 2-OCH$_2$C*H*$_3$), 1.26–1.31 (m, 3H, 2-OCH$_2$C*H*$_3$), 3.85–4.07 (m, 2H, 2-OC*H*$_2$CH$_3$), 4.12–4.21 (m, 2H, 2-OC*H*$_2$CH$_3$), 5.80 (d, 1H, $^2J_{PH}$=13.9 Hz, –C*H*), 7.65–7.69 (m, 2H, –C$_6H_4$), 8.08–8.18 (m, 2H, –C$_6H_4$) ppm; ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): 12.98 (d, $^1J_{CP}$=154.6 Hz, –*C*H), 16.59–16.82 (2-OCH$_2$*C*H$_3$), 64.70–65.09 (O*C*H$_2$CH$_3$), 124.02, 124.27, 130.19, 130.90, 131.01 (–*C*$_6$H$_4$) ppm; IR (neat): peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=399, M−Br=272, 261−P(O)(OEt)$_2$=136; C$_{11}$H$_{15}$INO$_5$P requires C, 33.08; H, 3.76%, found: C, 33.02; H, 3.71%.

4.4.21. Diethyl α-azidobenzylphosphonate (4a).[1h,8] ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): δ 1.21–1.31 (m, 6H, 2-OCH$_2$C*H*$_3$), 3.94–4.14 (m, 4H, 2-OC*H*$_2$CH$_3$), 4.74 (d, 1H, $^2J_{PH}$=16.5 Hz, –C*H*), 7.38–7.45 (m, 5H, –C$_6H_5$) ppm; ^{13}C

NMR ($CDCl_3$, TMS, 62.9 MHz): 16.80 (d, $^3J_{CP}$=6.0 Hz, 2-OCH$_2$*C*H$_3$), 61.96 (d, $^1J_{CP}$=158.2 Hz, –*C*H), 63.91 (d, $^2J_{CP}$=8.6 Hz, 2-O*C*H$_2$CH$_3$), 128.61–129.28 (–*C*$_6$H$_4$) ppm; IR (neat): ν 2100 (N_3) cm^{-1}, Peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=269, M−N_3=227, 227−P(O)(OEt)$_2$=90; $C_{11}H_{16}N_3O_3P$ requires C, 49.07; H, 5.95%, found: C, 49.10; H, 5.90%.

4.4.22. Diethyl α-azido-2-chlorobenzylphosphonate (4e). ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ 1.15 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$C*H*$_3$), 1.29 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$C*H*$_3$), 3.85–4.20 (m, 4H, 2-OC*H*$_2$CH$_3$), 5.29 (d, 1H, $^2J_{PH}$=17.0 Hz, –C*H*), 7.19–7.37 (m, 3H, –C$_6$*H*$_4$), 7.61–7.64 (m, 1H, –C$_6$*H*$_4$) ppm; ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): 15.13–15.46 (2-OCH$_2$*C*H$_3$), 56.35 (d, $^1J_{CP}$=161.1 Hz, –*C*H), 62.90–63.32 (2-O*C*H$_2$CH$_3$), 126.31, 128.67–129.17 (–*C*$_6$H$_4$) ppm; IR (neat): ν 2150 (N_3) cm^{-1}, Peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=304, M+2=306, M−N_3=261, 261−P(O)(OEt)$_2$=125; $C_{11}H_{15}ClN_3O_3P$ requires C, 43.42; H, 4.93%, found: C, 43.45; H, 4.95%.

4.4.23. Diethyl α-azido-3-chlorobenzylphosphonate (4f). ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ 1.13 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$C*H*$_3$), 1.29 (t, 3H, $^3J_{HH}$=7.0 Hz, 2-OCH$_2$C*H*$_3$), 3.85–4.01 (m, 2H, 2-OC*H*$_2$CH$_3$), 4.11–4.22 (m, 2H, 2-OC*H*$_2$CH$_3$), 5.02 (d, 1H, $^2J_{PH}$=16.4 Hz, –C*H*), 7.20–7.33 (m, 3H, –C$_6$*H*$_4$), 7.80–7.85 (m, 1H, –C$_6$*H*$_4$) ppm; ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): 15.13–15.46 (2-OCH$_2$*C*H$_3$), 47.86 (d, $^1J_{CP}$=162.2 Hz, –*C*H), 62.89–63.32 (2-O*C*H$_2$CH$_3$), 126.30–126.41, 128.31–129.08, 130.30, 130.36 (–*C*$_6$H$_4$) ppm; IR (neat): ν 2123 (N_3) cm^{-1}, Peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=304, M+2=306, M−N_3=261, 261−P(O)(OEt)$_2$=125; $C_{11}H_{15}ClN_3O_3P$ requires C, 43.42; H, 4.93%, found: C, 43.40; H, 4.90%.

4.4.24. Diethyl α-azido-4-chlorobenzylphosphonate (4g). ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ 1.11–1.29 (m, 6H, 2-OCH$_2$C*H*$_3$), 3.90–4.13 (m, 4H, 2-OC*H*$_2$CH$_3$), 4.65 (d, 1H, $^2J_{PH}$=17.0 Hz, –C*H*), 7.27–7.42 (m, 4H, –C$_6$*H*$_4$) ppm; ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): 16.70–16.85 (2-OCH$_2$*C*H$_3$), 61.28 (d, $^1J_{CP}$=158.3 Hz, –*C*H), 63.91–64.16 (2-O*C*H$_2$CH$_3$), 129.30–129.96 (–*C*$_6$H$_4$) ppm; IR (neat): ν 2110 (N_3) cm^{-1}, Peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=304, M+2=306, M−N_3=261, 261−P(O)(OEt)$_2$=125; $C_{11}H_{15}ClN_3O_3P$ requires C, 43.42; H, 4.93%, found: C, 43.41; H, 4.92%.

4.4.25. Diethyl α-azido-2-nitrobenzylphosphonate (4i). ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ 1.07–1.34 (m, 6H, 2-OCH$_2$C*H*$_3$), 3.92–4.20 (m, 4H, 2-OC*H*$_2$CH$_3$), 4.73 (d, 1H, $^2J_{PH}$=16.4 Hz, –C*H*), 7.44 (t, 1H, $^3J_{HH}$=7.5 Hz, –C$_6$*H*$_4$), 7.61 (t, $^3J_{HH}$=7.5 Hz, 1H, –C$_6$*H*$_4$), 7.77 (d, 1H, $^3J_{HH}$=7.7 Hz, –C$_6$*H*$_4$), 7.92 (d, 1H, $^3J_{HH}$=8.2 Hz, –C$_6$*H*$_4$), ppm; ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): 16.56–16.76 (2-OCH$_2$*C*H$_3$), 56.46 (d, $^1J_{CP}$=157.5 Hz, –*C*H), 64.12–64.33 (2-O*C*H$_2$CH$_3$), 125.20–125.53, 129.67–130.39, 133.78, 133.83 (–*C*$_6$H$_4$) ppm; IR (neat): ν 2125 (N_3) cm^{-1}, IR (neat): peak of OH was bsent.; MS (70 eV), *m/e*: M$^+$=314, M−N_3=272, 272−P(O)(OEt)$_2$=135; $C_{11}H_{15}N_4O_5P$ requires C, 42.04; H, 4.78%, found: C, 42.03; H, 4.71%.

4.4.26. Diethyl α-azido-3-nitrobenzylphosphonate (4j). ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ 1.26–1.37 (m, 6H, 2-OCH$_2$C*H*$_3$), 4.06–4.26 (m, 4H, 2-OC*H*$_2$CH$_3$), 4.90 (d, 1H, $^2J_{PH}$=16.4 Hz, –C*H*), 7.55–7.62 (m, 1H, –C$_6$*H*$_4$), 7.80–7.83 (m, 1H, –C$_6$*H*$_4$), 8.21–8.39 (m, 2H, –C$_6$*H*$_4$) ppm; ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): 16.75 (d, $^3J_{CP}$=5.9 Hz, 2-OCH$_2$*C*H$_3$), 61.10 (d, $^1J_{CP}$=156.2 Hz, –*C*H), 63.1 (d, $^2J_{CP}$=8.2 Hz, 2-O*C*H$_2$CH$_3$), 123.33–123.94, 128.83–130.06, 132.44–132.60, 134.31 (–*C*$_6$H$_4$) ppm; IR (neat): ν 2140 (N_3) cm^{-1}, Peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=314, M−N_3=272, 272−P(O)(OEt)$_2$=135; $C_{11}H_{15}N_4O_5P$ requires C, 42.04; H, 4.78%, found: C, 42.02; H, 4.70%.

4.4.27. Diethyl α-azido-4-nitrobenzylphosphonate (4k).[17] ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ 1.18–1.27 (m, 6H, 2-OCH$_2$C*H*$_3$), 3.99–4.14 (m, 4H, 2-OC*H*$_2$CH$_3$), 4.83 (d, 1H, $^2J_{PH}$=16.7 Hz, –C*H*), 7.57 (m, 2H, –C$_6$*H*$_4$), 8.18 (d, 2H, –C$_6$*H*$_4$) ppm; ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): 16.80 (d, $^3J_{CP}$=5.5 Hz, 2-OCH$_2$*C*H$_3$), 61.36 (d, $^1J_{CP}$=155.0 Hz, –*C*H), 64.35 (2-O*C*H$_2$CH$_3$), 124.12–124.30, 129.00–129.33, 131.51 (–*C*$_6$H$_4$) ppm; IR (neat): ν 2134 (N_3) cm^{-1}, Peak of OH was absent.; MS (70 eV), *m/e*: M$^+$=314, M−N_3=272, 272−P(O)(OEt)$_2$=135; $C_{11}H_{15}N_4O_5P$ requires C, 42.04; H, 4.78%, found: C, 42.01; H, 4.72%.

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References and notes

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