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RESEARCH ARTICLE

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Synthesis of alkyl α-aminomethyl-phenylphosphinates and *N*,*N*-bis(alkoxyphenylphosphinylmethyl)amines by the microwave-assisted Kabachnik–Fields reaction

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Abstract

As a novel extension, the Kabachnik–Fields reaction was applied to the synthesis of alkyl α-aminomethyl-phenylphosphinates, and the double phospha-Mannich reaction was utilized in the preparation of bis(alkoxyphenylphosphinylmethyl)amines. A total of 27 new aminophosphinate derivatives were synthesized by the microwave-assisted solvent-free condensation of alkyl phenyl-*H*-phosphinates, paraformaldehyde, and primary or secondary amines. The starting P-species were also prepared under microwave conditions. The formation of the *N*-methylated aminomethyl-phenylphosphinate by-products was also investigated.

1 | INTRODUCTION

α-Aminophosphonates and related derivatives have attracted much attention due to their versatile bioactivity in medicinal[1–9] and agrochemical chemistry.[10–14] They also have importance as complexing agents.[1,15]

Among the methods described, the Kabachnik–Fields (or phospha-Mannich) reaction is the major route toward the synthesis of α-aminophosphonates that involves the one-pot, three-component condensation of an amine, an aldehyde or ketone, and a >P(O)H reagent, such as a dialkyl phosphite or secondary phosphine oxide.[16–19] In most cases, these reactions were performed in the presence of a catalyst using a solvent.[20–28] Obvious disadvantages may be the cost and environmental burden meant by the catalysts. Thus, nowadays greener variations of the phospha-Mannich reaction have come to the front.[29] It was found that under solvent-free conditions there is no need for any catalyst.[30,31] The most efficient protocol for the condensation under discussion is the catalyst- and solvent-free microwave (MW)-assisted accomplishment.[32–35] As a modification, the double Kabachnik–Fields reaction has also been described for the synthesis of bis(aminophosphonates) or bis(aminophosphine oxides).[36–43] The latter species may be used in the synthesis of platinum complexes as bisphosphine ligands after double deoxygenation.[38–41]

α-Aminophosphinates are analogous to α-aminophosphonates, but they were much less studied. Only a few publications were found, where ethyl aminophosphinates were prepared by the addition of ethyl methyl-*H*-phosphinate,[44] ethyl phenyl-*H*-phosphinate,[45,46] ethyl benzyloxymethyl-*H*-phosphinate,[47] or propyl phenyl-*H*-phosphinate[48] to imines in the presence of a catalyst or solvent, as shown in Scheme 1/(1), Scheme 1/(2a and 2b), Scheme 1/(3), and Scheme 1/(4), respectively.

To the best of our knowledge, there are no examples for the synthesis of α-aminophosphinates using the Kabachnik–Fields reaction.

We elaborated a simple method for the preparation of α-aminophosphonates with a mixed ester functionality by the MW-assisted condensation of amines, paraformaldehyde, and ethyl octyl phosphite.[49] As a continuation, in this paper, the synthesis of species containing the -$NHCH_2P(O)PhOR$ moiety is described.

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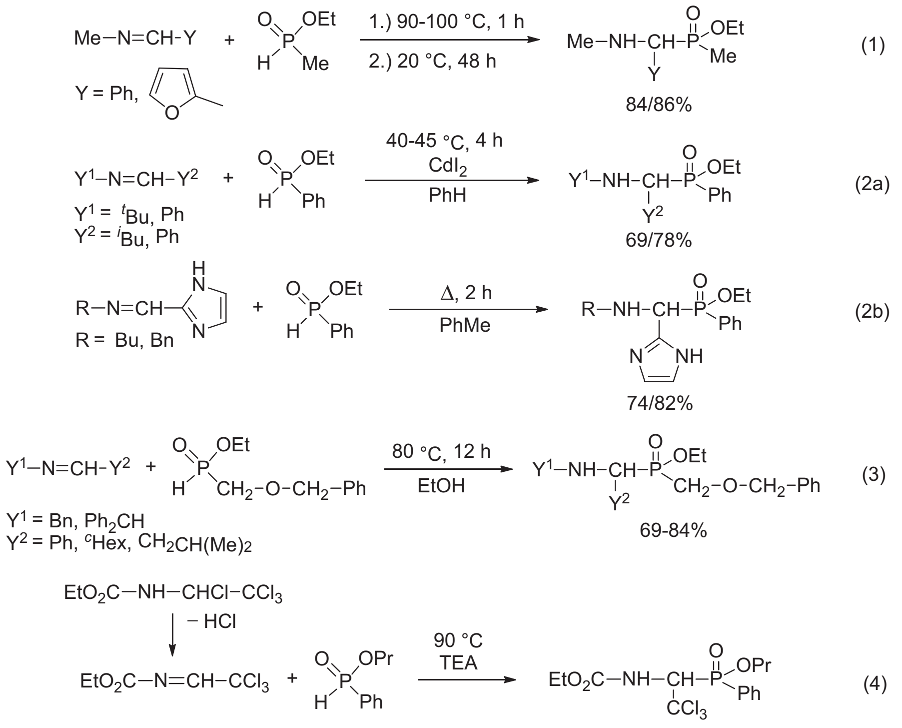


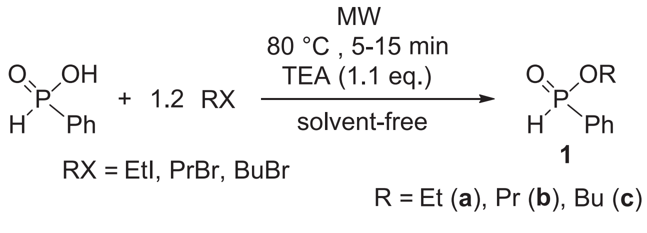
SCHEME 1 Literature methods for the preparation of α-aminophosphinates

2 | RESULTS AND DISCUSSION

2.1 | Synthesis of the starting alkyl phenyl-*H*-phosphinates

First, the alkyl phenyl-*H*-phosphinates (**1a–c**) applied as P-reagents in the Kabachnik–Fields reaction were synthesized by the alkylation of phenyl-*H*-phosphinic acid with ethyl iodide, propyl bromide, or butyl bromide in the presence of triethylamine. The alkylating esterifications were performed at 80°C for 5–15 min under solvent-free and microwave (MW)-assisted conditions (Scheme 2).

The corresponding alkyl phenyl-*H*-phosphinates (**1a–c**) were obtained in yields of 94–97%.

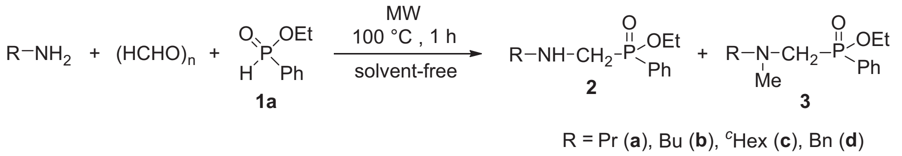


SCHEME 2 Preparation of the P-reagents

2.2 | Microwave-assisted synthesis of alkyl aminomethyl-phenylphosphinates

In the first experiments, ethyl phenyl-*H*-phosphinate (**1a**), paraformaldehyde, and alkylamines, such as propyl-, butyl-, cyclohexyl-, or benzylamine were reacted at 100°C for 1 h under solvent-free and MW-assisted conditions (Scheme 3). To our surprise, using 1 equivalent of the paraformaldehyde, more or less *N*-methylated aminomethyl-phenylphosphinate (**3**) was also formed beside the expected ethyl α-aminomethyl-phenylphosphinate (**2**). It can be seen from Table 1 that the relative quantity of by-product **3** depended also on the amine component (Table 1, entries 1, 4, 6, and 8), and fall in the range of 5–42%. The formation of the methylated aminomethyl-phenylphosphinate (**3**) could be depressed by measuring in less (0.3–0.5 equivalents) of the paraformaldehyde (see Table 1, entries 2, 3, 5, and 7). The target products **2a–d** could be obtained in yields of 42–73% after purification by column chromatography (Table 1, entries 3, 5, 7, and 8).

In the reaction of propyl- or cyclohexylamine with 0.3 equivalents of paraformaldehyde and 1 equivalent of ethyl phenyl-*H*-phosphinate, ethylated by-product **4a** {$[M+H]^+_{found} = 270.1630$, $C_{14}H_{25}NO_2P$ requires 270.1623} or **4c** {$[M+H]^+_{found} = 310.1945$, $C_{17}H_{29}NO_2P$ requires



SCHEME 3 Kabachnik-Fields condensation using ethyl phenyl-*H*-phosphinate

TABLE 1 Condensation of primary amines, paraformaldehyde, and ethyl phenyl-*H*-phosphinate (**1a**)

Entry	*R*	$(HCHO)_n$ (eq.)	Product composition (%)[a] 2	3	Yield (%)[b]
1	Pr (**a**)	1	58	42	
2		0.5	78	22	
3		0.3	86	0[c]	42
4	Bu (**b**)	1	83	17	
5		0.5	100	0	50
6	^{c}Hex (**c**)	1	75	25	
7		0.3	95	0[d]	62
8	Bn (**d**)	1	95	5	73

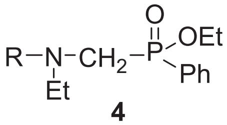
[a] On the basis of GC.

[b] Obtained by column chromatography.

[c] 14% of ethyl (ethyl-propylaminomethyl)-phenylphosphinate (**4a**) was also formed.

[d] 5% of ethyl (ethyl-cyclohexylaminomethyl)-phenylphosphinate (**4c**) was also formed.

310.1936} was also formed in a small amount (Table 1, entries 3 and 7).



4

R = Pr (**a**), ^{c}Hex (**c**)

It is assumed that ethyl phenyl-*H*-phosphinate (**1a**) being in excess in the reactions providing by-product **4** may serve as an ethylating agent. The *N*-methyl by-product may be formed *via* methylation by the excess of formaldehyde (see next section).

Then, the Kabachnik–Fields reaction was investigated with propyl phenyl-*H*-phosphinate (**1b**) under the same conditions shown above (Scheme 4). In the condensation of propyl- or butylamine with propyl phenyl-*H*-phosphinate (**1b**), 0.3 equivalents of the aldehyde had to be used so that the target molecule (**5a** or **5b**) should be the exclusive product (Table 2, entries 3 and 6). Application of larger (up to 1 equivalent) quantity of the paraformaldehyde led to considerable amounts of *N*-methylated substrates **6a** or **6b** (Table 2, entries 1, 2, 4, and 5). At the same time, in the reaction of propyl phenyl-*H*-phosphinate (**1b**), cyclohexylamine, and 1 equivalent of paraformaldehyde, the desired product (**5c**) predominated (Table 2, entry 7). Starting from benzylamine, a quantity of 0.5 equivalents was necessary from the oxo compound to ensure the selective formation of product **5d** (Table 2, entry 9). The corresponding propyl alkylaminomethyl-phenylphosphinates (**5a–d**) were isolated in yields of 48–63% (Table 2, entries 3, 6, 7, and 9).

TABLE 2 Condensation of primary amines, paraformaldehyde, and propyl phenyl-*H*-phosphinate (**1b**)

Entry	*R*	$(HCHO)_n$ (eq.)	Product composition (%)[a] 5	6	Yield (%)[b]
1	Pr (**a**)	1	80	20	
2		0.5	89	11	
3		0.3	100	0	48
4	Bu (**b**)	1	74	26	
5		0.5	94	6	
6		0.3	100	0	54
7	^{c}Hex (**c**)	1	96	4	63
8	Bn (**d**)	1	87	13	63
9		0.5	96	4	

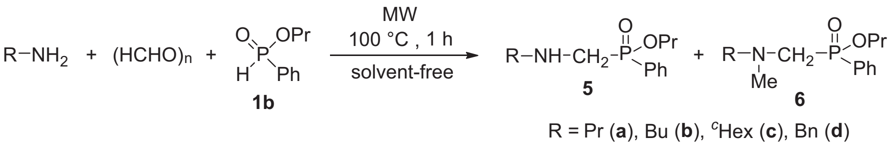
[a] On the basis of GC.

[b] Obtained by column chromatography.

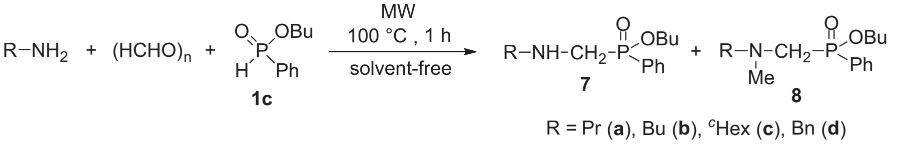
Using butyl phenyl-*H*-phosphinate (**1c**) as the P-component, the condensations took place similarly, as the reactions with ethyl phenyl-*H*-phosphinate (**1a**) (Scheme 5 and Table 3). In all cases, the expected butyl alkylaminomethyl-phenylphosphinates (**7a–d**) were the main products, which were obtained in yields of 52–70% from the reactions applying 0.3 or 0.5 equivalents of paraformaldehyde (Table 3, entries 2, 4, 6, and 8).

The alkyl α-alkylaminomethyl-phenylphosphinates (**2a–d**, **5a–d**, and **7a–d**) are all new compounds that were characterized by ^{31}P, ^{13}C, and ^{1}H NMR, as well as high-resolution mass spectrometry.

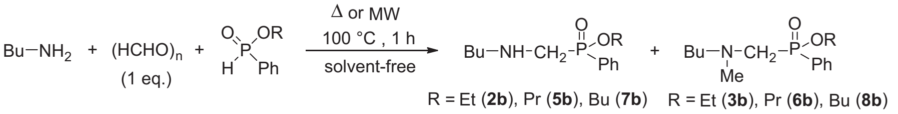
In order to evaluate the potential of the MW irradiation, comparative thermal experiments were also performed in a few cases. The condensation of butylamine with 1 equivalent of paraformaldehyde and ethyl-, propyl-, or butyl phenyl-*H*-phosphinate was repeated under conventional heating applying the same conditions, as in the case of the MW-assisted reactions (Scheme 6). From the results listed in Table 4, it can be seen that on conventional heating, the conversions were 10–15% lower, and the reactions were less selective for the target compounds (**2b**, **5b**, and **7b**), than under MW conditions (Table 4, entry 1 vs. 2, entry 3 vs. 4, and entry 5 vs. 6).



SCHEME 4 Kabachnik-Fields condensation using propyl phenyl-*H*-phosphinate



SCHEME 5 Kabachnik-Fields condensation using butyl phenyl-*H*-phosphinate



SCHEME 6 MW-assisted and comparative thermal phospha-Mannich reactions

TABLE 3 Condensation of primary amines, paraformaldehyde, and butyl phenyl-*H*-phosphinate (**1c**)

Entry	*R*	$(HCHO)_n$ (eq.)	Product composition (%)[a] 7	8	Yield (%)[b]
1	Pr (**a**)	1	75	25	
2		0.3	100	0	54
3	Bu (**b**)	1	72	28	
4		0.5	98	2	52
5	cHex (**c**)	1	60	40	
6		0.3	99	1	63
7	Bn (**d**)	1	92	8	
8		0.5	99	1	70

[a] On the basis of GC.
[b] Obtained by column chromatography.

TABLE 4 Comparative thermal experiments for the condensation of butylamine, paraformaldehyde, and alkyl phenyl-*H*-phosphinates

Entry	*R*	Mode of heating	Conversion (%)[a]	Product composition (%)[a]	
1	Et	Δ	90	65 (**2b**)	35 (**3b**)
2	Et	MW	100	83 (**2b**)	17 (**3b**)
3	Pr	Δ	85	73 (**5b**)	27 (**6b**)
4	Pr	MW	100	74 (**5b**)	26 (**6b**)
5	Bu	Δ	88	59 (**7b**)	41 (**8b**)
6	Bu	MW	100	72 (**7b**)	28 (**8b**)

[a] On the basis of GC.

2.3 | Direct preparation of *N*-methylated aminomethyl-phenylphosphinates

We wished to investigate the formation of the by-products formed by *N*-methylation, for this, the ethyl butylaminomethyl-phenylphosphinate (**2b**) was reacted with paraformaldehyde at 100°C for 1 h under MW irradiation (Scheme 7). The experiments had to be carried out in acetonitrile as the solvent due to the heterogeneity of the neat reaction mixture. Using 1 equivalent of paraformaldehyde, the conversion was complete, and the crude mixture contained 55% of ethyl (formyl-butylaminomethyl)-phenylphosphinate **9** $\{[M+H]^+_{found} = 284.1415, C_{14}H_{23}NO_3P$ requires $284.1410\}$ and 45% of the *N*-methylated aminophosphinate (**3b**) (Table 5, entry 1). Increasing the amount of paraformaldehyde to 3 equivalents, ethyl (methyl-butylaminomethyl)-phenylphosphinate **3b** became the main product (70%) (Table 5, entry 2).

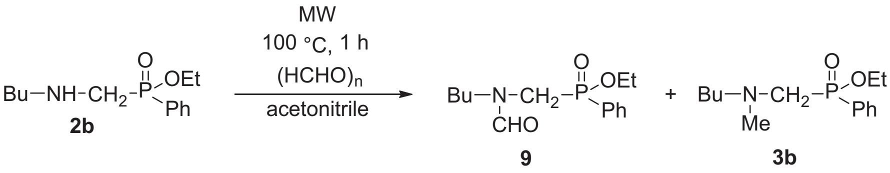
It can be substantiated that the *N*-methyl aminophosphinates (**3**) are formed by the methylation of the amino derivatives (**2**) with paraformaldehyde. This means that first a hydroxymethylation may take place, followed by reduction with a second molecule of formaldehyde. It is also a possibility that the hydroxymethylated intermediate undergoes disproportionation to afford the reduced >N–Me (**3**) and the oxidated >N–CHO (**9**) forms. The direct *N*-formylation of amines by formaldehyde is also known, but requires special iridium or gold catalysts.[50,51]

As a "structure proving synthesis", alkyl (methyl-alkylaminomethyl)-phenylphosphinates **3b–d**, **6b**, and **8b** were prepared by the Kabachnik–Fields reaction using *N*-alkyl-*N*-methylamines (Scheme 8). The condensations were performed under similar conditions (100°C, 1 h) applied in the reaction of primary amines. The alkyl (methyl-alkylaminomethyl)-phenylphosphinates (**3b–d**, **6b**, and **8b**) were isolated in 58–81% yields after column chromatography (Table 6, entries 1–5).

Hence, five new alkyl (alkyl-methylaminomethyl)-phenylphosphinates (**3b–d**, **6b**, and **8b**) were prepared and fully characterized.

2.4 | Microwave-assisted synthesis of *N*,*N*-bis(alkoxyphenylphosphinylmethyl)amines

Finally, the double Kabachnik–Fields reaction was also studied, where the primary amines were reacted with two equivalents of paraformaldehyde and two equivalents of alkyl phenyl-*H*-phosphinate **1** under MW conditions (Scheme 9). The condensations were carried out at 100°C for 1 h in the absence of a catalyst and a solvent, and after purification by column chromatography, the corresponding *N*,*N*-bis(alkoxy-phenylphosphinylmethyl)amines(**10a–d**, **11a–d**, and **12a–d**) were obtained in yields of 59–97% (Table 7).



SCHEME 7 Direct preparation of an *N*-methylated aminomethyl-phenylphosphinate

TABLE 5 Reaction of ethyl butylaminomethyl-phenylphosphinate (**2b**) with paraformaldehyde

		Product composition (%)[a]	
Entry	**$(HCHO)_n$ (eq.)**	**9**	**3b**
1	1	55	45
2	3	30	70

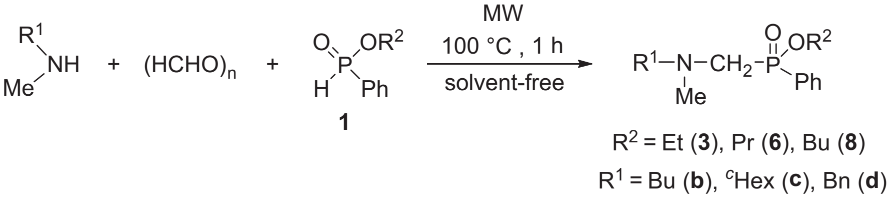
[a] On the basis of GC.

TABLE 6 Condensation of secondary amines, paraformaldehyde, and alkyl phenyl-*H*-phosphinates

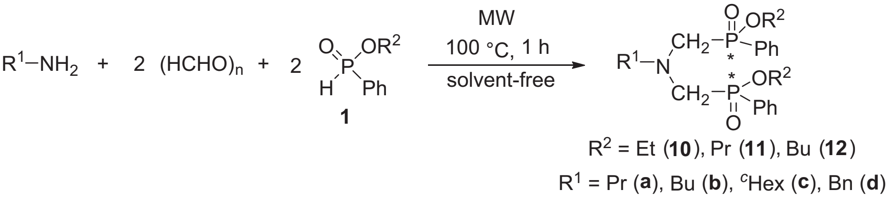
Entry	*R*[2]	*R*[1]	Yield (%)[a]
1	Et (**3**)	Bu (**b**)	72
2		[c]Hex (**c**)	58[b]
3		Bn (**d**)	69[b]
4	Pr (**6**)	Bu (**b**)	70
5	Bu (**8**)	Bu (**b**)	81

[a] Obtained by flash column chromatography.

[b] Obtained by column chromatography.



SCHEME 8 Kabachnik-Fields reaction starting from secondary amines



SCHEME 9 Double Kabachnik-Fields reactions

TABLE 7 Synthesis of *N,N*-bis(alkoxyphenylphosphinylmethyl)-amines

	Yield (%)[a]		
R	**10**	**11**	**12**
Pr (**a**)	84	75	90
Bu (**b**)	80	83	87
[c]Hex (**c**)	60	64	59
Bn (**d**)	97	78	80

[a] Obtained by flash column chromatography.

Structures of the bis(phosphinylmethyl)amines (**10a–d**, **11a–d**, and **12a–d**) were confirmed by ^{31}P, ^{13}C, and ^{1}H NMR, as well as mass spectrometry. Due to the two P-stereogenic centers in the P-functionalities, the *N,N*-bis(alkoxyphenylphosphinylmethyl)amines) (**10a–d**, **11a–d**, and **12a–d**) were formed as a 1:1 mixture of two diastereomers (see Fig. 1).

In summary, alkyl phenyl-*H*-phosphinates could be applied as novel P-reagents in the Kabachnik–Fields reaction. Twelve alkyl alkylaminomethyl-phenylphosphinates, five alkyl alkyl-methylaminomethyl-phenylphosphinates, and twelve *N,N*-bis(alkoxyphenylphosphinylmethyl)amines were synthesized under catalyst-free and solvent-free MW-assisted conditions. MW irradiation had a positive effect on the selectivity of the reactions. Except *N,N*-bis(ethoxyphenylphosphinylmethyl)cyclohexylamine) (**10c**) and *N,N*-bis(etoxyphenyl-phosphinylmethyl)benzylamine (**10d**), that were synthesized by us earlier,[39,40] all of the α-aminophosphinates are new.

3 | EXPERIMENTAL

3.1 | General (instruments)

The ^{31}P, ^{13}C, and ^{1}H NMR spectra were taken in $CDCl_3$ solution on a Bruker AV-300 or DRX-500 spectrometer operating at 121.5, 75.5, and 300 or 202.4, 125.7, and 500 MHz, respectively. Chemical shifts are downfield

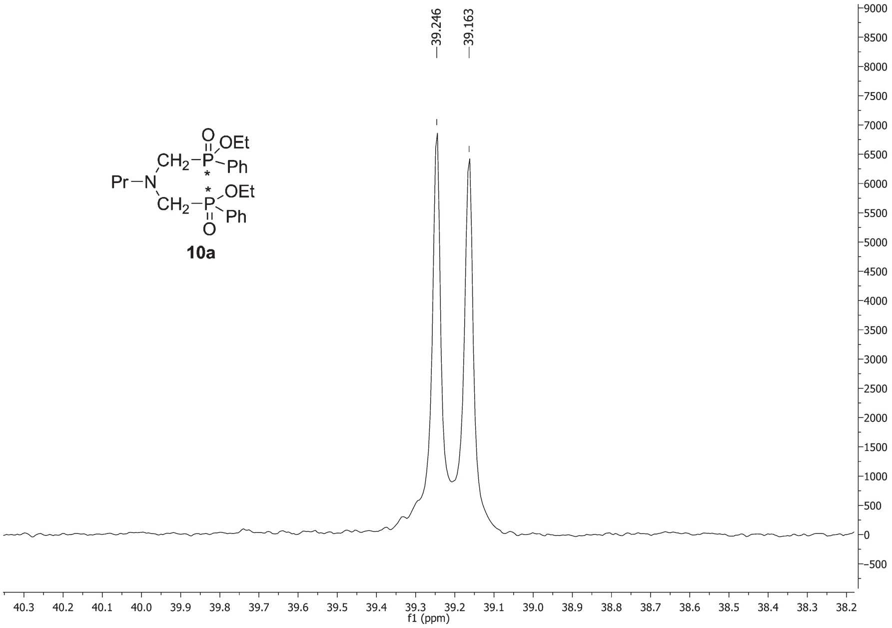


FIGURE 1 ^{31}P NMR spectra of *N,N*-bis(ethoxyphenylphosphinylmethyl)-propylamine (10a)

relative to 85% H_3PO_4 and TMS. The couplings are given in Hz. Mass spectrometric measurements were performed using a Q-TOF Premier mass spectrometer in positive electrospray mode and a Shimadzu LCMS-ITTOF mass spectrometer. The reactions were carried out in a 300 W CEM Discover focused microwave reactor equipped with a pressure controller applying 10–30 W under isothermal conditions.

3.2 | General procedure for the preparation of alkyl phenyl-*H*-phosphinates

A mixture of 0.28 g (2.0 mmol) of phenyl-*H*-phosphinic acid, 2.4 mmol of alkyl halogenide (0.19 mL of ethyl iodide, 0.22 mL of propyl bromide or 0.26 mL of butyl bromide), and 0.31 mL (2.2 mmol) of triethylamine was heated at 80°C for 5 or 15 minutes in a vial in a CEM Discover Microwave reactor equipped with a pressure controller. The crude mixture was passed through a thin (ca. 1–1.5 cm) layer of silica gel using ethyl acetate as the eluent. The alkyl phenyl-*H*-phosphinates (**1a–c**) were obtained as colorless oils. The following products were thus prepared:

3.2.1 | Ethyl phenyl-*H*-phosphinate (1a)

Yield: 94% (0.32 g) of compound **1a** as a colorless oil; ^{31}P NMR ($CDCl_3$) δ: 22.7; $\delta^{[52]}$: 24.7; $[M+H]^+_{found} = 171.0575$, $C_8H_{12}O_2P$-re requires 171.0575.

3.2.2 | Propyl phenyl-*H*-phosphinate (1b)

Yield: 97% (0.36 g) of compound **1b** as a colorless oil; ^{31}P NMR ($CDCl_3$) δ: 25.7; $\delta^{[52]}$: 24.9; $[M+H]^+_{found} = 185.0733$, $C_9H_{14}O_2P$-re requires 185.0731.

3.2.3 | Butyl phenyl-*H*-phosphinate (1c)

Yield: 96% (0.38 g) of compound **1c** as a colorless oil; ^{31}P NMR ($CDCl_3$) δ: 25.1; $\delta^{[52]}$: 24.9; $[M+H]^+_{found} = 199.0888$, $C_{10}H_{16}O_2P$-re requires 199.0888.

3.3 | General procedure for the synthesis of alkyl aminomethyl-phenylphosphinates

A mixture of 1.7 mmol primary amine (0.14 mL of propylamine, 0.17 mL of butylamine, 0.19 mL of cyclohexylamine, or 0.19 mL of benzylamine), 0.05 g (1.7 mmol) or 0.03 g (0.85 mmol) or 0.02 g (0.51 mmol) of paraformaldehyde, and 1.7 mmol of alkyl phenyl-*H*-phosphinate (0.26 mL of ethyl phenyl-*H*-phosphinate, 0.29 mL of propyl phenyl-*H*-phosphinate, or 0.31 mL of butyl phenyl-*H*-phosphinate) was heated at 100°C in a vial in a CEM Discover Microwave reactor equipped with a pressure controller for 1 h. The crude reaction mixture so obtained was passed through a thin (ca. 2–3 cm) layer of silica gel using dichloromethane–methanol (97:3) or purified on silica gel with dichloromethane–methanol (97:3) eluent. After evaporation of the solvent, the products (**2a–d**, **5a–d** and **7a–d**) were obtained as oils. The following products were thus prepared:

3.3.1 | Ethyl propylaminomethyl-phenylphosphinate (2a)

Yield: 42% (0.17 g) of compound **2a** as an oil; ^{31}P NMR ($CDCl_3$) δ: 39.7; ^{13}C NMR ($CDCl_3$) δ: 11.4 ($CH_3(CH_2)_2N$), 16.5 (d, $^3J_{CP} = 6.1$, OCH_2CH_3), 22.7 ($CH_3CH_2CH_2N$), 48.6 (d, $^1J_{CP} = 110.3$, CH_2P), 53.2 (d, $^3J_{CP} = 13.5$, CH_2N), 60.9 (d, $^2J_{CP} = 6.7$, OCH_2), 128.5 (d, $^2J_{CP} = 12.3$, C_2), 130.1 (d, $^1J_{CP} = 122.0$, C_1), 131.8 (d, $^3J_{CP} = 9.7$, C_3), 132.4 (d,

$J_{CP} = 2.7$, C$_4$); ^{1}H NMR (CDCl$_3$) δ: 0.83 (t, $J_{HH} = 7.4$, 3H, CH_3(CH$_2$)$_2$N), 1.29 (t, $J_{HH} = 7.0$, 3H, OCH$_2$CH_3), 1.36–1.50 (m, 2H, CH$_3$CH_2CH$_2$), 1.57 (s, 1H, NH), 2.59 (t, $^3J_{HP} = 7.2$, 2H, CH$_2$N), 3.10 (d, $^1J_{HP} = 9.2$, 2H, CH$_2$P), 3.84–3.99 (m, 1H) and 4.03–4.19 (m, 1H) (OCH$_2$), 7.42–7.59 (m, 3H, C$_3$H, C$_4$H), 7.75–7.90 (m, 2H, C$_2$H); $[\text{M+H}]^+_{\text{found}} = 242.1301$, $C_{12}H_{21}NO_2P$ requires 242.1304.

3.3.2 | Ethyl butylaminomethyl-phenylphosphinate (2b)

Yield: 50% (0.22 g) of compound **2b** as an oil; ^{31}P NMR (CDCl$_3$) δ: 39.8; ^{13}C NMR (CDCl$_3$) δ: 13.9 (*C*H$_3$(CH$_2$)$_3$N), 16.5 (d, $^3J_{CP} = 6.1$, OCH$_2$*C*H$_3$), 20.2 (CH$_3$*C*H$_2$(CH$_2$)$_2$), 31.8 (CH$_3$CH$_2$*C*H$_2$CH$_2$), 48.7 (d, $^1J_{CP} = 110.2$, CH$_2$P), 51.1 (d, $^3J_{CP} = 13.5$, CH$_2$N), 60.9 (d, $^2J_{CP} = 6.5$, OCH$_2$), 128.5 (d, $^2J_{CP} = 12.3$, C$_2$), 130.2 (d, $^1J_{CP} = 122.4$, C$_1$), 131.8 (d, $^3J_{CP} = 9.7$, C$_3$), 132.4 (d, $J_{CP} = 1.9$, C$_4$); ^{1}H NMR (CDCl$_3$) δ: 0.87 (t, $J_{HH} = 7.3$, 3H, CH_3(CH$_2$)$_3$N), 1.24–1.30 (m, 2H, CH$_3$CH_2(CH$_2$)$_2$), 1.31 (t, $J_{HH} = 7.0$, 3H, OCH$_2$CH_3), 1.37–1.45 (m, 2H, CH$_3$CH$_2$CH_2CH$_2$), 1.60 (s, 1H, NH), 2.63 (t, $^3J_{HP} = 7.2$, 2H, CH$_2$N), 3.13 (d, $^1J_{HP} = 10.5$, 2H, CH$_2$P), 3.89–3.98 (m, 1H) and 4.09–4.17 (m, 1H) (OCH$_2$), 7.46–7.53 (m, 2H, C$_3$H), 7.54–7.59 (m, 1H, C$_4$H), 7.81–7.88 (m, 2H, C$_2$H); $[\text{M+H}]^+_{\text{found}} = 256.1469$, $C_{13}H_{23}NO_2P$ requires 256.1461.

3.3.3 | Ethyl cyclohexylaminomethyl-phenylphosphinate (2c)

Yield: 62% (0.30 g) of compound **2c** as an oil; ^{31}P NMR (CDCl$_3$) δ: 40.3; ^{13}C NMR (CDCl$_3$) δ: 16.5 (d, $^3J_{CP} = 6.1$, OCH$_2$*C*H$_3$), 24.7 (C$_3$), 26.0 (C$_4$), 32.9 (C$_2$), 45.8 (d, $^1J_{CP} = 110.7$, CH$_2$P), 57.7 (d, $^3J_{CP} = 13.4$, C$_1$), 60.9 (d, $^2J_{CP} = 6.7$, OCH$_2$), 128.4 (d, $^2J_{CP} = 12.3$, C$_{2'}$), 130.2 (d, $^1J_{CP} = 123.0$, C$_{1'}$), 131.8 (d, $^3J_{CP} = 9.7$, C$_{3'}$), 132.3 (d, $J_{CP} = 2.7$, C$_{4'}$); ^{1}H NMR (CDCl$_3$) δ: 0.91–1.23 (m, 5H, C$_2$H$_{ax}$, C$_3$H$_{ax}$, C$_4$H$_{ax}$), 1.29 (t, $J_{HH} = 7.1$, 3H, OCH$_2$CH_3), 1.51–1.83 (m, 5H, C$_2$H$_{eq}$, C$_3$H$_{eq}$, C$_4$H$_{eq}$), 2.15 (s, 1H, NH), 2.33–2.45 (m, 1H, C$_1$H), 3.12 (d, $^1J_{HP} = 9.8$, 2H, CH$_2$P), 3.84–3.99 (m, 1H) and 4.04–4.18 (m, 1H) (OCH$_2$), 7.40–7.58 (m, 3H, C$_{3'}$H, C$_{4'}$H), 7.75–7.89 (m, 2H, C$_{2'}$H); $[\text{M+H}]^+_{\text{found}} = 282.1612$, $C_{15}H_{25}NO_2P$ requires 282.1617.

3.3.4 | Ethyl benzylaminomethyl-phenylphosphinate (2d)

Yield: 73% (0.36 g) of compound **2d** as an oil; ^{31}P NMR (CDCl$_3$) δ: 39.7; ^{13}C NMR (CDCl$_3$) δ: 16.5 (d, $^3J_{CP} = 6.3$, OCH$_2$*C*H$_3$), 47.6 (d, $^1J_{CP} = 111.4$, CH$_2$P), 54.7 (d, $^3J_{CP} = 14.5$, CH$_2$N), 61.0 (d, $^2J_{CP} = 6.7$, OCH$_2$), 127.1 (C$_4$), 128.1 (C$_3$)*, 128.3 (C$_2$)*, 128.5 (d, $^3J_{CP} = 12.4$, C$_{2'}$), 130.0 (d, $^1J_{CP} = 123.2$, C$_{1'}$), 131.9 (d, $^2J_{CP} = 9.8$ C$_{3'}$), 132.4 (d, $J_{CP} = 2.7$, C$_{4'}$), 139.2 (C$_1$), *may be reversed; ^{1}H NMR (CDCl$_3$) δ: 1.31 (t, $J_{HH} = 7.0$, 3H, OCH$_2$CH_3), 1.78 (s, 1H, NH), 3.09 (d, $^1J_{HP} = 10.3$, 2H, CH$_2$P), 3.83 (s, 2H, CH$_2$N, 4.02–4.20 (m, 2H, OCH$_2$), 7.15–7.33 (m, 5H, ArH), 7.43–7.62 (m, 3H, Ar'H), 7.78–7.90 (m, 2H, Ar'H); $[\text{M+H}]^+_{\text{found}} = 290.1303$, $C_{16}H_{21}NO_2P$ requires 290.1304.

3.3.5 | Propyl propylaminomethyl-phenylphosphinate (5a)

Yield: 48% (0.21 g) of compound **5a** as an oil; ^{31}P NMR (CDCl$_3$) δ: 39.7; ^{13}C NMR (CDCl$_3$) δ: 10.0 (O(CH$_2$)$_2$*C*H$_3$), 11.4 (*C*H$_3$(CH$_2$)$_2$N), 22.7 (CH$_3$*C*H$_2$CH$_2$N), 23.9 (d, $^3J_{CP} = 6.2$, OCH$_2$*C*H$_2$), 48.5 (d, $^1J_{CP} = 110.2$, CH$_2$P), 53.1 (d, $^3J_{CP} = 13.3$, CH$_2$N), 66.3 (d, $^2J_{CP} = 6.9$, OCH$_2$), 128.5 (d, $^2J_{CP} = 12.3$, C$_2$), 130.1 (d, $^1J_{CP} = 122.6$, C$_1$), 131.8 (d, $^3J_{CP} = 9.7$, C$_3$), 132.4 (d, $J_{CP} = 2.7$, C$_4$); ^{1}H NMR (CDCl$_3$) δ: 0.86 (t, $J_{HH} = 7.4$, 3H, CH_3(CH$_2$)$_2$N), 0.94 (t, $J_{HH} = 7.4$, 3H, O(CH$_2$)$_2$CH_3), 1.38–1.52 (m, 2H, CH$_3$CH_2CH$_2$N), 1.67–1.72 (m, 2H, OCH$_2$CH_2CH$_3$), 2.17 (s, 1H, NH), 2.61 (t, $^3J_{HP} = 7.1$, 2H, CH$_2$N), 3.13 (d, $^1J_{HP} = 10.2$, 2H, CH$_2$P), 3.74–3.86 (m, 1H) and 3.96–4.08 (m, 1H) (OCH$_2$), 7.44–7.61 (m, 3H, C$_3$H, C$_4$H), 7.79–7.90 (m, 2H, C$_2$H); $[\text{M+H}]^+_{\text{found}} = 256.1471$, $C_{13}H_{23}NO_2P$ requires 256.1466.

3.3.6 | Propyl butylaminomethyl-phenylphosphinate (5b)

Yield: 54% (0.25 g) of compound **5b** as an oil; ^{31}P NMR (CDCl$_3$) δ: 39.6; ^{13}C NMR (CDCl$_3$) δ: 10.1 (O(CH$_2$)$_2$*C*H$_3$), 13.9 (*C*H$_3$(CH$_2$)$_3$NH), 20.2 (CH$_3$*C*H$_2$(CH$_2$)$_2$NH), 23.9 (d, $^3J_{CP} = 6.2$, OCH$_2$*C*H$_2$CH$_3$), 31.7 (CH$_3$CH$_2$*C*H$_2$CH$_2$NH), 48.6 (d, $^1J_{CP} = 109.8$, CH$_2$P), 51.0 (d, $^3J_{CP} = 13.0$, CH$_2$N), 66.4 (d, $^2J_{CP} = 6.9$, OCH$_2$), 128.5 (d, $^2J_{CP} = 12.3$, C$_2$), 130.1 (d, $^1J_{CP} = 122.8$, C$_1$), 131.8 (d, $^3J_{CP} = 9.7$ C$_3$), 132.4 (d, $J_{CP} = 2.6$, C$_4$); ^{1}H NMR (CDCl$_3$) δ: 0.84 (t, $J_{HH} = 7.3$, 3H, CH_3(CH$_2$)$_3$N), 0.92 (t, $J_{HH} = 7.4$, 3H, O(CH$_2$)$_2$CH_3), 1.22–1.31 (m, 2H, CH$_3$CH_2(CH$_2$)$_2$N), 1.36–1.43 (m, 2H, CH$_3$CH$_2$CH_2CH$_2$N), 1.63–1.71 (m, 2H, OCH$_2$CH_2CH$_3$), 1.95 (s, 1H, NH), 2.62 (t, $^3J_{HP} = 7.2$, 2H, CH$_2$N), 3.12 (d, $^1J_{HP} = 10.5$, 2H, CH$_2$P), 3.74–3.82 (m, 1H, OCH$_2$), 3.97–4.04 (m, 1H, OCH$_2$), 7.44–7.56 (m, 3H, C$_3$H, C$_4$H), 7.79–7.85 (m, 2H, C$_2$H); $[\text{M+H}]^+_{\text{found}} = 270.1620$, $C_{14}H_{25}NO_2P$ requires 270.1617.

3.3.7 | Propyl cyclohexylaminomethyl-phenylphosphinate (5c)

Yield: 63% (0.32 g) of compound **5c** as an oil; ^{31}P NMR (CDCl$_3$) δ: 40.2; ^{13}C NMR (CDCl$_3$) δ: 10.1 (O(CH$_2$)$_2$*C*H$_3$), 23.9 (d, $^3J_{CP} = 6.2$, OCH$_2$*C*H$_2$CH$_3$), 24.7 (C$_3$), 26.0 (C$_4$), 32.9 (C$_2$), 45.7 (d, $^1J_{CP} = 110.4$, CH$_2$P), 57.6 (d, $^3J_{CP} = 13.2$,

$\mathrm{C_1}$), 66.4 (d, $^{2}J_{\mathrm{CP}} = 6.9$, $\mathrm{OCH_2}$), 128.5 (d, $^{2}J_{\mathrm{CP}} = 12.3$, $\mathrm{C_{2'}}$), 130.2 (d, $^{1}J_{\mathrm{CP}} = 123.2$, $\mathrm{C_{1'}}$), 131.8 (d, $^{3}J_{\mathrm{CP}} = 9.7$, $\mathrm{C_{3'}}$), 132.3 (d, $J_{\mathrm{CP}} = 2.7$, $\mathrm{C_{4'}}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 0.89–1.19 [0.94 (t, $J_{\mathrm{HH}} = 7.4$, 3H, $\mathrm{O(CH_2)_2}\mathit{CH_3}$) overlapped by the multiplet of $\mathrm{C_2H_{ax}}$, $\mathrm{C_3H_{ax}}$ and $\mathrm{C_4H_{ax}}$, total int. 8H], 1.52–1.83 (m, 8H, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{CH_3}$, $\mathrm{C_2H_{eq}}$, $\mathrm{C_3H_{eq}}$, $\mathrm{C_4H_{eq}}$, NH), 2.36–2.48 (m, 1H, $\mathrm{C_1H}$), 3.15 (d, $^{1}J_{\mathrm{HP}} = 10.1$, 2H, $\mathrm{CH_2P}$), 3.74–3.87 (m, 1H) and 3.97–4.08 (m, 1H) ($\mathrm{OCH_2}$) 7.44–7.59 (m, 3H, $\mathrm{C_{3'}H}$, $\mathrm{C_{4'}H}$), 7.79–7.89 (m, 2H, $\mathrm{C_{2'}H}$); $[\mathrm{M+H}]^{+}_{\mathrm{found}} = 296.1781$, $\mathrm{C_{16}H_{27}NO_2P}$ requires 296.1774.

3.3.8 | Propyl benzylaminomethyl-phenylphosphinate (5d)

Yield: 63% (0.32 g) of compound **5d** as an oil; ^{31}P NMR ($\mathrm{CDCl_3}$) δ: 39.7; ^{13}C NMR ($\mathrm{CDCl_3}$) δ: 10.1 ($\mathrm{O(CH_2)_2}\mathit{CH_3}$), 23.9 (d, $^{3}J_{\mathrm{CP}} = 6.3$, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{CH_3}$), 47.5 (d, $^{1}J_{\mathrm{CP}} = 111.2$, $\mathrm{CH_2P}$), 54.7 (d, $^{3}J_{\mathrm{CP}} = 14.3$, $\mathrm{CH_2N}$), 66.4 (d, $^{2}J_{\mathrm{CP}} = 6.8$, $\mathrm{OCH_2}$), 127.1 ($\mathrm{C_4}$), 128.1 ($\mathrm{C_3}$)*, 128.3 ($\mathrm{C_2}$)*, 128.5 (d, $^{2}J_{\mathrm{CP}} = 12.4$, $\mathrm{C_{2'}}$), 130.0 (d, $^{1}J_{\mathrm{CP}} = 123.6$, $\mathrm{C_{1'}}$), 131.9 (d, $^{3}J_{\mathrm{CP}} = 9.7$, $\mathrm{C_{3'}}$), 132.4 (d, $J_{\mathrm{CP}} = 2.6$, $\mathrm{C_{4'}}$), 139.2 ($\mathrm{C_1}$), *may be reversed; ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 0.91 (t, $J_{\mathrm{HH}} = 7.4$, 3H, $\mathrm{CH_3}$), 1.63–1.71 (m, 2H, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{CH_3}$), 1.89 (s, 1H, NH), 3.06–3.10 (m, 2H, $\mathrm{CH_2P}$), 3.75–3.81 (m, 1H, $\mathrm{OCH_2}$), 3.82 (s, 2H, $\mathrm{CH_2N}$), 3.97–4.04 (m, 1H, $\mathrm{OCH_2}$), 7.17–7.28 (m, 5H, ArH), 7.44–7.50 (m, 2H, $\mathrm{C_{3'}H}$), 7.53–7.58 (m, 1H, $\mathrm{C_{4'}H}$), 7.78–7.85 (m, 2H, $\mathrm{C_{2'}H}$); $[\mathrm{M+H}]^{+}_{\mathrm{found}} = 304.1464$, $\mathrm{C_{17}H_{23}NO_2P}$ requires 304.1461.

3.3.9 | Butyl propylaminomethyl-phenylphosphinate (7a)

Yield: 54% (0.25 g) of compound **7a** as an oil; ^{31}P NMR ($\mathrm{CDCl_3}$) δ: 39.7; ^{13}C NMR ($\mathrm{CDCl_3}$) δ: 11.4 ($\mathit{CH_3}\mathrm{(CH_2)_2NH}$), 13.5 ($\mathrm{O(CH_2)_3}\mathit{CH_3}$), 18.7 ($\mathrm{O(CH_2)_2}\mathit{CH_2}\mathrm{CH_3}$), 22.7 ($\mathrm{CH_3}\mathit{CH_2}\mathrm{CH_2NH}$), 32.5 (d, $^{3}J_{\mathrm{CP}} = 6.1$, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{CH_2CH_3}$), 48.5 (d, $^{1}J_{\mathrm{CP}} = 110.1$, $\mathrm{CH_2P}$), 53.1 (d, $^{3}J_{\mathrm{CP}} = 13.2$, $\mathrm{CH_2N}$), 64.6 (d, $^{2}J_{\mathrm{CP}} = 6.9$, $\mathrm{OCH_2}$), 128.5 (d, $^{2}J_{\mathrm{CP}} = 12.3$, $\mathrm{C_2}$), 130.1 (d, $^{1}J_{\mathrm{CP}} = 122.6$, $\mathrm{C_1}$), 131.8 (d, $^{3}J_{\mathrm{CP}} = 9.8$, $\mathrm{C_3}$), 132.3 (d, $J_{\mathrm{CP}} = 2.7$, $\mathrm{C_4}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 0.85 (t, $J_{\mathrm{HH}} = 7.4$, 3H, $\mathit{CH_3}\mathrm{(CH_2)_2NH}$), 0.90 (t, $J_{\mathrm{HH}} = 7.4$, 3H, $\mathrm{O(CH_2)_3}\mathit{CH_3}$), 1.29–1.49 (m, 4H, $\mathrm{CH_3}\mathit{CH_2}\mathrm{CH_2NH}$, $\mathrm{O(CH_2)_2}\mathit{CH_2}\mathrm{CH_3}$), 1.54–1.68 (m, 3H, NH, $\mathrm{OCH_2}\mathit{CH_2}$), 2.58 (t, $^{3}J_{\mathrm{HP}} = 7.1$, 2H, $\mathrm{CH_2N}$), 3.10 (d, $^{1}J_{\mathrm{HP}} = 9.6$, 2H, $\mathrm{CH_2P}$), 3.75–3.88 (m, 1H, $\mathrm{OCH_2}$), 3.98–4.10 (m, 1H, $\mathrm{OCH_2}$), 7.39–7.59 (m, 3H, $\mathrm{C_3H}$, $\mathrm{C_4H}$), 7.75–7.87 (m, 2H, $\mathrm{C_2H}$); $[\mathrm{M+H}]^{+}_{\mathrm{found}} = 270.1620$, $\mathrm{C_{14}H_{25}NO_2P}$ requires 270.1617.

3.3.10 | Butyl butylaminomethyl-phenylphosphinate (7b)

Yield: 52% (0.25 g) of compound **7b** as an oil; ^{31}P NMR ($\mathrm{CDCl_3}$) δ: 39.7; ^{13}C NMR ($\mathrm{CDCl_3}$) δ: 13.5 ($\mathit{CH_3}\mathrm{(CH_2)_3NH}$), 13.8 ($\mathrm{O(CH_2)_3}\mathit{CH_3}$), 18.7 ($\mathrm{O(CH_2)_2}\mathit{CH_2}\mathrm{CH_3}$), 20.1 ($\mathrm{CH_3}\mathit{CH_2}\mathrm{(CH_2)_2NH}$), 31.7 ($\mathrm{CH_3CH_2}\mathit{CH_2}\mathrm{CH_2NH}$), 32.5 (d, $^{3}J_{\mathrm{CP}} = 6.1$, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{CH_2CH_3}$), 48.6 (d, $^{1}J_{\mathrm{CP}} = 110.0$, $\mathrm{CH_2P}$), 51.0 (d, $^{3}J_{\mathrm{CP}} = 13.3$, $\mathrm{CH_2N}$), 64.5 (d, $^{2}J_{\mathrm{CP}} = 6.9$, $\mathrm{OCH_2}$), 128.5 (d, $^{2}J_{\mathrm{CP}} = 12.3$, $\mathrm{C_2}$), 130.1 (d, $^{1}J_{\mathrm{CP}} = 122.5$, $\mathrm{C_1}$), 131.8 (d, $^{3}J_{\mathrm{CP}} = 9.7$, $\mathrm{C_3}$), 132.3 (d, $J_{\mathrm{CP}} = 2.7$, $\mathrm{C_4}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 0.85 (t, $J_{\mathrm{HH}} = 7.3$, 3H, $\mathit{CH_3}\mathrm{(CH_2)_3NH}$), 0.88 (d, $J_{\mathrm{HH}} = 10.2$, 3H, $\mathit{CH_3}\mathrm{(CH_2)_3O}$), 1.18–1.42 (m, 6H, $\mathrm{CH_3}\mathit{CH_2}\mathrm{(CH_2)_2NH}$, $\mathrm{CH_3CH_2}\mathit{CH_2}\mathrm{CH_2NH}$, $\mathrm{O(CH_2)_2}\mathit{CH_2}\mathrm{CH_3}$), 1.28 (s, 1H, NH) 1.56–1.67 (m, 2H, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{CH_2CH_3}$), 2.60 (t, $^{3}J_{\mathrm{HP}} = 7.0$, 2H, $\mathrm{CH_2N}$), 3.09 (d, $^{1}J_{\mathrm{HP}} = 9.4$, 2H, $\mathrm{CH_2P}$), 3.73–3.87 and 3.97–4.10 (m, 2H, $\mathrm{OCH_2}$), 7.39–7.58 (m, 3H, $\mathrm{C_3H}$, $\mathrm{C_4H}$), 7.74–7.87 (m, 2H, $\mathrm{C_2H}$); $[\mathrm{M+H}]^{+}_{\mathrm{found}} = 284.1778$, $\mathrm{C_{15}H_{27}NO_2P}$ requires 284.1774.

3.3.11 | Butyl cyclohexylaminomethyl-phenylphosphinate (7c)

Yield: 63% (0.33 g) of compound **7c** as an oil; ^{31}P NMR ($\mathrm{CDCl_3}$) δ: 40.2; ^{13}C NMR ($\mathrm{CDCl_3}$) δ: 13.6 ($\mathrm{O(CH_2)_3}\mathit{CH_3}$), 18.7 ($\mathrm{O(CH_2)_2}\mathit{CH_2}\mathrm{CH_3}$), 24.7 ($\mathrm{C_3}$), 26.0 ($\mathrm{C_4}$), 32.6 (d, $^{3}J_{\mathrm{CP}} = 6.1$, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{CH_2CH_3}$), 32.9 ($\mathrm{C_2}$), 45.7 (d, $^{1}J_{\mathrm{CP}} = 110.3$, $\mathrm{CH_2P}$), 57.6 (d, $^{3}J_{\mathrm{CP}} = 13.1$, $\mathrm{C_1}$), 64.6 (d, $^{2}J_{\mathrm{CP}} = 6.9$, $\mathrm{OCH_2}$), 128.4 (d, $^{2}J_{\mathrm{CP}} = 12.3$, $\mathrm{C_{2'}}$), 130.2 (d, $^{1}J_{\mathrm{CP}} = 123.1$, $\mathrm{C_{1'}}$), 131.8 (d, $^{3}J_{\mathrm{CP}} = 9.6$, $\mathrm{C_{3'}}$), 132.3 (d, $J_{\mathrm{CP}} = 2.7$, $\mathrm{C_{4'}}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 0.88 (t, $J_{\mathrm{HH}} = 7.4$, 3H, $\mathrm{O(CH_2)_3}\mathit{CH_3}$), 0.95–1.26 (m, 5H, $\mathrm{C_2H_{ax}}$, $\mathrm{C_3H_{ax}}$, $\mathrm{C_4H_{ax}}$), 1.29–1.44 (m, 2H, $\mathrm{O(CH_2)_2}\mathit{CH_2}\mathrm{CH_3}$, 1.48–1.85 (m, 8H, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{CH_2CH_3}$, $\mathrm{C_2H_{eq}}$, $\mathrm{C_3H_{eq}}$, $\mathrm{C_4H_{eq}}$, NH), 2.35–2.47 (m, 1H, $\mathrm{C_1H}$), 3.13 (d, $^{1}J_{\mathrm{HP}} = 10.2$, 2H, $\mathrm{CH_2P}$), 3.77–3.89 (m, 1H) and 3.99–4.11 (m, 1H) ($\mathrm{OCH_2}$), 7.41–7.57 (m, 3H, $\mathrm{C_{3'}H}$, $\mathrm{C_{4'}H}$), 7.77–7.87 (m, 2H, $\mathrm{C_{2'}H}$); $[\mathrm{M+H}]^{+}_{\mathrm{found}} = 310.1940$, $\mathrm{C_{17}H_{29}NO_2P}$ requires 310.1930.

3.3.12 | Butyl benzylaminomethyl-phenylphosphinate (7d)

Yield: 70% (0.38 g) of compound **7d** as an oil; ^{31}P NMR ($\mathrm{CDCl_3}$) δ: 39.6; ^{13}C NMR ($\mathrm{CDCl_3}$) δ: 13.6 ($\mathrm{O(CH_2)_3}\mathit{CH_3}$), 18.8 ($\mathrm{O(CH_2)_2}\mathit{CH_2}\mathrm{CH_3}$), 32.6 (d, $^{3}J_{\mathrm{CP}} = 6.2$, $\mathrm{OCH_2}\mathit{CH_2}\mathrm{CH_2CH_3}$), 47.5 (d, $^{1}J_{\mathrm{CP}} = 111.2$, $\mathrm{CH_2P}$), 54.7 (d, $^{3}J_{\mathrm{CP}} = 14.3$, $\mathrm{CH_2N}$), 64.7 (d, $^{2}J_{\mathrm{CP}} = 6.8$, $\mathrm{OCH_2}$), 127.1 ($\mathrm{C_4}$), 128.1 ($\mathrm{C_3}$)*, 128.4 ($\mathrm{C_2}$)*, 128.5 (d, $^{2}J_{\mathrm{CP}} = 12.4$, $\mathrm{C_{2'}}$), 130.1 (d, $^{1}J_{\mathrm{CP}} = 123.5$, $\mathrm{C_{1'}}$), 131.9 (d, $^{3}J_{\mathrm{CP}} = 9.7$, $\mathrm{C_{3'}}$), 132.4 (d, $J_{\mathrm{CP}} = 2.7$, $\mathrm{C_{4'}}$), 139.3 ($\mathrm{C_1}$), *may be reversed; ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 0.82 (t, $J_{\mathrm{HH}} = 7.4$, 3H, $\mathit{CH_3}\mathrm{(CH_2)_3O}$), 1.23–1.38 (m, 2H, $\mathrm{O(CH_2)_2}\mathit{CH_2}\mathrm{CH_3}$), 1.51–1.62 (m, 2H, $\mathrm{CH_3CH_2}\mathit{CH_2}\mathrm{CH_2O}$), 1.74 (s, 1H, NH), 3.02 (d, $^{1}J_{\mathrm{HP}} = 9.8$, 2H, $\mathrm{CH_2P}$), 3.71–3.83 (m, 3H, $\mathrm{CH_2N}$, $\mathrm{OCH_2}$), 3.93–4.05 (m, 1H, $\mathrm{OCH_2}$), 7.11–7.24 (m, 5H, ArH), 7.36–7.54 (m, 3H, $\mathrm{C_{3'}H}$, $\mathrm{C_{4'}H}$), 7.67–7.82 (m, 2H, $\mathrm{C_{2'}H}$); $[\mathrm{M+H}]^{+}_{\mathrm{found}} = 318.1617$, $\mathrm{C_{18}H_{25}NO_2P}$ requires 318.1617.

3.4 | General procedure for the methylation of ethyl butylaminomethyl-phenylphosphinate (2b)

A mixture of 0.025 g (0.098 mmol) of ethyl butylamino-methyl-phenylphosphinate, 0.003 g (0.098 mmol) or 0.009 g (0.294 mmol) of paraformaldehyde, and 0.1 mL of acetonitrile was heated at 100°C in a closed vial in a CEM Discover Microwave reactor equipped with a pressure controller for 1 h. The crude mixture so obtained was analyzed by GC and GC–MS. The results are summarized in Table 5.

3.5 | General procedure for the synthesis of alkyl (methyl-aminomethyl)-phenylphosphinates (3b–d, 6b and 8b)

A mixture of 1.7 mmol secondary amine (0.20 mL of *N*-butyl-*N*-methylamine, 0.22 mL of *N*-cyclohexyl-*N*-methylamine, or 0.22 mL of *N*-benzyl-*N*-methylamine), 0.05 g (1.7 mmol) of paraformaldehyde, and 1.7 mmol of alkyl phenyl-*H*-phosphinate (0.26 mL of ethyl phenyl-*H*-phosphinate, 0.29 mL of propyl phenyl-*H*-phosphinate or 0.31 mL of butyl phenyl-*H*-phosphinate) was heated at 100°C in a vial in a CEM Discover Microwave reactor equipped with a pressure controller for 1 or 1.5 h. The crude product so obtained was passed through a thin (ca. 2–3 cm) layer of silica gel using dichloromethane–methanol (97:3) or purified on silica gel with dichloromethane–methanol (97:3) eluent. After evaporation of the solvent, the products (**3b–d**, **6b**, and **8b**) were obtained as oils. The following products were thus prepared:

3.5.1 | Ethyl (methyl-butylaminomethyl)-phenylphosphinate (3b)

Yield: 72% (0.33 g) of compound **3b** as an oil; ^{31}P NMR (CDCl$_3$) δ: 38.6; ^{13}C NMR (CDCl$_3$) δ: 13.8 ($\mathit{C}H_3(CH_2)_3N$), 16.5 (d, $^3J_{CP} = 6.2$, $OCH_2\mathit{C}H_3$), 20.1 ($CH_3\mathit{C}H_2(CH_2)_2N$), 28.9 ($CH_3CH_2\mathit{C}H_2CH_2N$), 44.0 (d, $^3J_{CP} = 5.2$, CH_3N), 55.9 (d, $^1J_{CP} = 118.8$, CH_2P), 59.0 (d, $^3J_{CP} = 10.6$, CH_2N), 60.9 (d, $^2J_{CP} = 6.8$, OCH_2), 128.5 (d, $^2J_{CP} = 12.3$, C_2), 130.4 (d, $^1J_{CP} = 123.6$, C_1), 132.0 (d, $^3J_{CP} = 9.6$, C_3), 132.4 (d, $J_{CP} = 2.6$, C_4); ^{1}H NMR (CDCl$_3$) δ: 0.81 (t, $J_{HH} = 7.2$, 3H, $C\mathit{H}_3(CH_2)_3N$), 1.10–1.44 [1.31 (t, $J_{HH} = 7.0$, 3H, $OCH_2C\mathit{H}_3$) overlapped by the multiplet of $CH_3C\mathit{H}_2(CH_2)_2N$ and $CH_3CH_2C\mathit{H}_2CH_2N$) total int. 7H], 2.43 (s, 3H, CH_3N), 2.51 (t, $^3J_{HP} = 7.3$, 2H, CH_2N), 3.00 (d, $^1J_{HP} = 9.0$, CH_2P), 3.84–3.98 (m, 1H) and 4.06–4.20 (m, 1H) (OCH_2), 7.40–7.62 (m, 3H, C_3H, C_4H), 7.79–7.94 (m, 2H, C_2H); $[M+H]^+_{found} = 270.1630$, $C_{14}H_{25}NO_2P$ requires 270.1623.

3.5.2 | Ethyl (methyl-cyclohexylaminomethyl)-phenylphosphinate (3c)

Yield: 58% (0.29 g) of compound **3c** as an oil; ^{31}P NMR (CDCl$_3$) δ: 40.2; ^{13}C NMR (CDCl$_3$) δ: 16.4 (d, $^3J_{CP} = 6.4$, $OCH_2\mathit{C}H_3$), 25.7 (d, $J_{CP} = 2.4$, C_3), 26.1 (C_4), 28.4 (C_2), 40.1 (d, $^3J_{CP} = 3.0$, CH_3N), 52.7 (d, $^1J_{CP} = 120.3$, CH_2P), 60.1 (d, $^2J_{CP} = 6.9$, OCH_2), 64.2 (d, $^3J_{CP} = 11.4$, C_1), 128.2 (d, $^2J_{CP} = 12.1$, $C_{2'}$), 130.6 (d, $^1J_{CP} = 121.7$, $C_{1'}$), 132.0 (d, $J_{CP} = 4.0$, $C_{4'}$), 132.1 (d, $^3J_{CP} = 9.3$, $C_{3'}$); ^{1}H NMR (CDCl$_3$) δ: 0.90–1.20 (m, 5H, C_2H_{ax}, C_3H_{ax}, C_4H_{ax}), 1.30 (t, $J_{HH} = 7.0$, 3H, $OCH_2C\mathit{H}_3$), 1.50–1.76 (m, 5H, C_2H_{eq}, C_3H_{eq}, C_4H_{eq}), 2.21–2.33 (m, 1H, C_1H), 2.38 (s, 3H, CH_3N), 2.78–3.10 (m, 2H, CH_2P), 3.83–3.99 (m, 1H) and 4.03–4.20 (m, 1H) (OCH_2), 7.42–7.58 (m, 3H, $C_{3'}H$, $C_{4'}H$), 7.75–7.91 (m, 2H, $C_{2'}H$); $[M+H]^+_{found} = 296.1764$, $C_{16}H_{27}NO_2P$ requires 296.1774.

3.5.3 | Ethyl (methyl-benzylaminomethyl)-phenylphosphinate (3d)

Yield: 69% (0.36 g) of compound **3d** as an oil; ^{31}P NMR (CDCl$_3$) δ: 39.5; ^{13}C NMR (CDCl$_3$) δ: 16.5 (d, $^3J_{CP} = 5.9$, $OCH_2\mathit{C}H_3$), 44.2 (d, $^3J_{CP} = 4.3$, CH_3N), 55.1 (d, $^1J_{CP} = 119.7$, CH_2P), 60.7 (d, $^2J_{CP} = 6.4$, OCH_2), 63.7 (d, $^3J_{CP} = 12.2$, CH_2N), 127.1 (C_4), 128.2 (C_3)*, 128.4 (d, $^2J_{CP} = 12.3$ $C_{2'}$), 129.1 (C_2)*, 130.5 (d, $^1J_{CP} = 110.2$, $C_{1'}$), 132.0 (d, $J_{CP} = 9.6$, $C_{3'}$), 132.2 ($C_{4'}$), 137.8 (C_1), *may be reversed; ^{1}H NMR (CDCl$_3$) δ: 1.29 (t, $J_{HH} = 7.0$, 3H, $OCH_2C\mathit{H}_3$), 2.42 (s, 3H, CH_3N), 2.94 (t, $^1J_{HP} = 9.9$, 2H, CH_2P), 3.60 (dd, 2H, $^3J_{HP} = 36.2$, $J_{HH} = 13.1$, CH_2N), 3.82–3.96 (m, 1H) and 4.03–4.18 (m, 1H) (OCH_2), 7.04–7.22 (m, 5H, ArH), 7.41–7.60 (m, 3H, $C_{3'}H$, $C_{4'}H$), 7.71–7.80 (m, 2H, $C_{2'}H$); $[M+H]^+_{found} = 304.1474$, $C_{17}H_{23}NO_2P$ requires 304.1461.

3.5.4 | Propyl (methyl-butylaminomethyl)-phenylphosphinate (6b)

Yield: 70% (0.34 g) of compound **6b** as an oil; ^{31}P NMR (CDCl$_3$) δ: 39.2; ^{13}C NMR (CDCl$_3$) δ: 10.1 ($O(CH_2)_2\mathit{C}H_3$), 13.9 ($\mathit{C}H_3(CH_2)_3N$), 20.1 ($CH_3\mathit{C}H_2(CH_2)_2N$), 23.9 (d, $^3J_{CP} = 6.4$, $OCH_2\mathit{C}H_2CH_3$), 29.2 ($CH_3CH_2\mathit{C}H_2CH_2N$), 44.2 (d, $^3J_{CP} = 5.3$, CH_3N), 56.3 (d, $^1J_{CP} = 119.2$, CH_2P), 59.2 (d, $^3J_{CP} = 11.2$, CH_2N), 66.1 (d, $^2J_{CP} = 6.9$, OCH_2), 128.4 (d, $^2J_{CP} = 12.2$, C_2), 130.6 (d, $^1J_{CP} = 122.2$, C_1), 132.0 (d, $^3J_{CP} = 9.4$, C_3), 132.2 (d, $J_{CP} = 2.7$, C_4); ^{1}H NMR (CDCl$_3$) δ: 0.80 (t, $J_{HH} = 7.3$, 3H, $C\mathit{H}_3(CH_2)_3N$), 0.94 (t, $J_{HH} = 7.4$, 3H, $O(CH_2)_2C\mathit{H}_3$), 1.11–1.20 (m, 2H, $CH_3C\mathit{H}_2(CH_2)_2N$), 1.24–1.36 (m, 2H, $CH_3CH_2C\mathit{H}_2CH_2N$), 1.64–1.72 (m, 2H, $OCH_2C\mathit{H}_2CH_3$), 2.38 (s, 3H, CH_3N), 2.44 (t, $^3J_{HP} = 7.4$, 2H, $C\mathit{H}_2N$), 2.90–3.00 (m, 2H, CH_2P), 3.73–3.80 (m, 1H) and 3.98–4.06 (m, 1H) (OCH_2), 7.44–7.57 (m, 3H, C_3H, C_4H), 7.79–7.85 (m, 2H, C_2H); $[M+H]^+_{found} = 284.1766$, $C_{15}H_{27}NO_2P$ requires 284.1774.

3.5.5 | Butyl (methyl-butylaminomethyl)-phenylphosphinate (8b)

Yield: 81% (0.41 g) of compound **8b** as an oil, ^{31}P NMR ($CDCl_3$) δ: 39.3; ^{13}C NMR ($CDCl_3$) δ: 13.5 $CH_3(CH_2)_3N$, 13.8 ($O(CH_2)_3CH_3$), 18.8 ($O(CH_2)_2CH_2CH_3$), 20.1 ($CH_3CH_2(CH_2)_2N$), 29.2 ($CH_3CH_2CH_2CH_2N$), 32.6 (d, $^3J_{CP} = 6.3$, $OCH_2CH_2CH_2CH_3$), 44.2 (d, $^3J_{CP} = 5.3$, CH_3N), 56.3 (d, $^1J_{CP} = 119.9$, CH_2P), 59.2 (d, $^3J_{CP} = 11.3$, CH_2N), 64.3 (d, $^2J_{CP} = 6.9$, OCH_2), 128.3 (d, $^2J_{CP} = 12.2$, C_2), 130.6 (d, $^1J_{CP} = 122.1$, C_1), 132.0 (d, $^3J_{CP} = 9.5$, C_3), 132.1 (d, $J_{CP} = 2.7$, C_4); ^{1}H NMR ($CDCl_3$) δ: 0.80 (t, $J_{HH} = 7.2$, 3H, $CH_3(CH_2)_3N$), 0.90 (t, $J_{PH} = 7.3$, 3H, $O(CH_2)_3CH_3$), 1.08–1.44 (m, 6H, CH_2), 1.58–1.70 (m, 2H, $OCH_2CH_2CH_2CH_3$), 2.36 (s, 3H, CH_3N), 2.43 (t, $J_{HP} = 7.2$, 2H, CH_2N), 2.89–2.99 (m, 2H, CH_2P), 3.74–3.86 (m, 1H) and 4.00–4.12 (m, 1H) (OCH_2), 7.43–7.59 (m, 3H, C_3H, C_4H), 7.76–7.87 (m, 2H, C_2H); $[M+H]^+_{found} = 298.1929$, $C_{16}H_{29}NO_2P$ requires 298.1930.

3.6 | General procedure for the synthesis of *N,N*-bis(alkoxyphenylphosphinylmethyl)amines (10a–d, 11a–d, and 12a–d)

A mixture of 1.7 mmol amine (0.14 mL of propylamine, 0.17 mL of butylamine, 0.19 mL of cyclohexylamine or 0.19 mL of benzylamine), 0.10 g (3.4 mmol) of paraformaldehyde, and 3.4 mmol of alkyl phenyl-*H*-phosphinate (0.51 mL of ethyl phenyl-*H*-phosphinate, 0.58 mL of propyl phenyl-*H*-phosphinate, or 0.61 mL of butyl phenyl-*H*-phosphinate) was heated at 100°C in a vial in a CEM Discover Microwave reactor equipped with a pressure controller for 1 h. The crude product so obtained was passed through a thin (ca. 2–3 cm) layer of silica gel using dichloromethane-methanol (97:3). After evaporation of the solvent, the products (**10a–d**, **11a–d**, and **12a–d**) were obtained as oils. The following products were thus prepared:

3.6.1 | *N,N*-bis(Ethoxyphenylphosphinyl-methyl)propylamine (10a)

Yield: 84% (0.60 g) of compound **10a** as an oil, a 49:51 mixture of two isomers; ^{31}P NMR ($CDCl_3$) δ: 39.95 and 40.04; ^{13}C NMR ($CDCl_3$) δ: 10.9 and 11.1 ($CH_3(CH_2)_2N$), 16.5 (d, $^3J_{CP} = 6.5$, OCH_2CH_3), 20.0 and 20.1 ($CH_3CH_2CH_2N$), 54.3 (dd, $^1J_{CP} = 126.8$, $^3J_{CP} = 8.5$) and 54.5 (dd, $^1J_{CP} = 123.4$, $^3J_{CP} = 7.7$) (CH_2P), 58.8 (t, $^3J_{CP} = 7.1$) and 59.0 (t, $^3J_{CP} = 6.9$) (CH_2N), 60.5 (d, $^2J_{CP} = 7.1$) and 60.6 (d, $^2J_{CP} = 7.2$) (OCH_2), 128.2 (d, $J_{CP} = 8.2$) and 128.3 (d, $J_{CP} = 8.2$) (C_2), 130.2 (d, $^1J_{CP} = 122.4$) and 130.5 (d, $^1J_{CP} = 123.3$) (C_1), 131.3 (d, $^4J_{CP} = 1.7$, C_4), 132.0 (d, $J_{CP} = 7.8$) and 132.2 (d, $J_{CP} = 7.5$) (C_3); ^{1}H NMR ($CDCl_3$) δ: 0.46 (t, $^3J_{HH} = 7.3$) and 0.63 (t, $^3J_{HH} = 7.3$) (3H, $CH_3(CH_2)_2N$), 0.70–1.06 (m, 2H, $CH_3CH_2CH_2N$), 1.10–1.35 (m, 6H, OCH_2CH_3), 2.42–2.54 and 2.67–2.91 (m, 2H CH_2N), 2.93–3.53 (m, 4H, CH_2P), 3.71–4.26 (m, 4H, OCH_2), 7.33–7.66 (m, 8H, C_2H, C_3H, C_4H), 7.69–7.92 (m, 2H, C_2H); $[M+H]^+_{found} = 423.1743$, $C_{21}H_{32}NO_4P_2$ requires 423.1728.

3.6.2 | *N,N*-bis(Ethoxyphenylphosphinyl-methyl)butylamine (10b)

Yield: 80% (0.59 g) of compound **10b** as an oil, a 49:51 mixture of two isomers; ^{31}P NMR ($CDCl_3$) δ: 40.12 and 40.19; ^{13}C NMR ($CDCl_3$) δ: 13.8 ($CH_3(CH_2)_3N$), 16.2 (d, $^3J_{CP} = 6.5$, OCH_2CH_3), 19.6 and 19.8 ($CH_3CH_2(CH_2)_2N$), 29.0 ($CH_3CH_2CH_2CH_2N$), 54.3 (dd, $^1J_{CP} = 126.8$, $^3J_{CP} = 8.5$) and 54.5 (dd, $^1J_{CP} = 123.5$, $^3J_{CP} = 7.8$) (CH_2P), 56.8 (t, $^3J_{CP} = 7.1$) and 56.9 (t, $^3J_{CP} = 6.7$) (CH_2N), 60.4 (d, $^2J_{CP} = 7.0$) and 60.6 (d, $^2J_{CP} = 7.2$) (OCH_2), 128.1 (d, $J_{CP} = 8.4$) and 128.3 (d, $J_{CP} = 8.4$) (C_2), 130.1 (d, $^1J_{CP} = 122.4$) and 130.4 (d, $^1J_{CP} = 121.5$) (C_1), 131.2 (d, $^4J_{CP} = 3.9$, C_4), 132.0 (d, $J_{CP} = 7.6$) and 132.1 (d, $J_{CP} = 7.3$) (C_3); ^{1}H NMR ($CDCl_3$) δ: 0.62 (t, $^3J_{HH} = 6.6$) and 0.72 (t, $^3J_{HH} = 7.0$) (3H, $CH_3(CH_2)_3N$), 0.76–1.18 (m, 4H, $CH_3CH_2(CH_2)_2N$, $CH_3CH_2CH_2CH_2N$), 1.20–1.35 (m, 6H, OCH_2CH_3), 2.43–2.54 and 2.70–2.96 (m, 2H CH_2N), 3.01–3.50 (m, 4H, CH_2P), 3.73–4.20 (m, 4H OCH_2), 7.33–7.66 (m, 8H, C_2H, C_3H, C_4H), 7.69–7.92 (m, 2H, C_2H); $[M+H]^+_{found} = 437.1904$, $C_{22}H_{34}NO_4P_2$ requires 434.1885.

3.6.3 | *N,N*-bis(Ethoxyphenylphosphinyl-methyl)cyclohexylamine (10c)

Yield: 60% (0.47 g) of compound **10c** as an oil, a 46:54 mixture of two isomers; ^{31}P NMR ($CDCl_3$) δ 41.7 and 41.8; $\delta^{[39]}$ ($CDCl_3$) 41.9 and 42.0; $[M+H]^+_{found} = 463.2115$, $C_{24}H_{35}NO_4P_2$ requires 463.2041.

3.6.4 | *N,N*-bis(Ethoxyphenylphosphinyl-methyl)benzylamine (10d)

Yield: 97% (0.78 g) of compound **10d** as an oil, a 49:51 mixture of two isomers; ^{31}P NMR ($CDCl_3$) δ: 41.1 and 41.2; $\delta^{[40]}$ ($CDCl_3$) 41.2 and 41.3; $[M+H]^+_{found} = 472.1807$, $C_{25}H_{32}NO_4P_2$ requires 472.1807.

3.6.5 | *N,N*-bis(Propoxyphenylphosphinyl-methyl)propylamine (11a)

Yield: 75% (0.58 g) of compound **11a** as an oil, a 48:52 mixture of two isomers; ^{31}P NMR ($CDCl_3$) δ: 39.24 and 39.31; ^{13}C NMR ($CDCl_3$) δ: 10.0 and 10.1 ($O(CH_2)_2CH_3$), 10.9 and 11.1 ($CH_3(CH_2)_2N$), 20.1 and 20.2 ($CH_3CH_2CH_2N$), 23.7 (d, $^3J_{CP} = 6.9$) and 23.9 (d, $^3J_{CP} = 6.3$) ($OCH_2CH_2CH_3$), 54.3 (dd, $^1J_{CP} = 123.1$, $^3J_{CP} = 7.7$) and 54.4 (dd, $^1J_{CP} = 122.6$,

$^3J_{CP} = 7.3$) (CH_2P), 58.9 (t, $^3J_{CP} = 7.1$) and 59.0 (t, $^3J_{CP} = 6.9$) (CH_2N), 66.0 (d, $^2J_{CP} = 7.9$) and 66.1 (d, $^2J_{CP} = 7.1$) (OCH_2), 128.2 (d, $^2J_{CP} = 15.0$) and 128.6 (d, $^2J_{CP} = 15.6$) (C_2), 129.7 (d, $^1J_{CP} = 125.8$) and 130.0 (d, $^1J_{CP} = 123.2$) (C_1), 131.3 (d, $^3J_{CP} = 10.0$) and 132.1 (d, $^3J_{CP} = 9.8$) (C_3), 131.8 (d, $J_{CP} = 3.1$) and 132.2 (d, $J_{CP} = 2.6$) (C_4); ^{1}H NMR ($CDCl_3$) δ: 0.46 (t, $^3J_{HH} = 7.3$) and 0.63 (t, $^3J_{HH} = 7.3$) (3H, $CH_3(CH_2)_2N$), 0.80–1.05 (m, 6H, $O(CH_2)_2CH_3$), 1.06–1.33 (m, 2H, $CH_3CH_2CH_2N$), 1.53–1.74 (m, 4H, $OCH_2CH_2CH_3$), 2.42–2.54 and 2.69–2.95 (m, 2H CH_2N), 3.04–3.42 (m, 4H, CH_2P), 3.60–3.78 (m, 2H) and 3.82–4.02 (m, 2H) (OCH_2), 7.35–7.65 (m, 8H, C_2H, C_3H, C_4H), 7.69–7.80 (m, 2H, C_2H); $[M+H]^+_{found} = 452.2117$, $C_{23}H_{36}NO_4P_2$ requires 452.2114.

3.6.6 | *N,N*-bis(Propoxyphenylphosphinylmethyl)butylamine (11b)

Yield: 83% (0.66 g) of compound **11b** as an oil, a 47:53 mixture of two isomers; ^{31}P NMR ($CDCl_3$) δ: 39.25 and 39.32; ^{13}C NMR ($CDCl_3$) δ: 10.0 and 10.1 ($O(CH_2)_2CH_3$), 13.6 and 13.9 ($CH_3(CH_2)_3N$), 19.8 and 20.0 ($CH_3CH_2(CH_2)_2N$), 23.7 (d, $^3J_{CP} = 7.1$) and 23.9 (d, $^3J_{CP} = 6.5$) ($OCH_2CH_2CH_3$), 29.1 and 29.2 ($CH_3CH_2CH_2CH_2N$), 54.6 (dd, $^1J_{CP} = 127.8$, $^3J_{CP} = 8.5$) and 54.7 (dd, $^1J_{CP} = 122.5$, $^3J_{CP} = 7.7$) (CH_2P), 58.4 (t, $^3J_{CP} = 7.0$) and 58.5 (t, $^3J_{CP} = 6.9$) (CH_2N), 66.0 (d, $^2J_{CP} = 7.2$) and 66.2 (d, $^2J_{CP} = 7.0$) (OCH_2), 128.1 (d, $^2J_{CP} = 14.5$) and 128.4 (d, $^2J_{CP} = 15.4$) (C_2), 130.0 (d, $^1J_{CP} = 122.7$) and 130.3 (d, $^1J_{CP} = 131.5$) (C_1), 131.4 (d, $^3J_{CP} = 9.8$) and 132.1 (d, $^3J_{CP} = 10.6$) (C_3), 131.6 (d, $J_{CP} = 2.6$) and 132.2 (d, $J_{CP} = 3.1$) (C_4); ^{1}H NMR ($CDCl_3$) δ: 0.62 (t, $^3J_{HH} = 7.7$) and 0.72 (t, $^3J_{HH} = 7.2$) (3H, $CH_3(CH_2)_3N$), 0.77–1.01 (m, 8H, $O(CH_2)_2CH_3$, $CH_3CH_2(CH_2)_2N$), 1.02–1.39 (m, 2H, $CH_3CH_2CH_2CH_2N$), 1.56–1.76 (m, 4H, $OCH_2CH_2CH_3$), 3.07–3.42 (m, 4H, CH_2P), 3.47–4.18 (m, 6H OCH_2, CH_2N), 7.32–7.63 (m, 6H, C_3H, C_4H), 7.71–7.88 (m, 4H, C_2H); $[M+H]^+_{found} = 466.2264$, $C_{24}H_{38}NO_4P_2$ requires 466.2271.

3.6.7 | *N,N*-bis(Propoxyphenylphosphinylmethyl)cyclohexylamine (11c)

Yield: 64% (0.53 g) of compound **11c** as an oil, a 54:46 mixture of two isomers; ^{31}P NMR ($CDCl_3$) δ: 40.0 and 40.1; ^{13}C NMR ($CDCl_3$) δ: 10.1 ($O(CH_2)_2CH_3$), 23.9 (d, $^3J_{CP} = 6.6$, $OCH_2CH_2CH_3$), 24.7 (C_3), 25.5 (C_4), 27.9 (C_2), 50.7 (dd, $^1J_{CP} = 123.6$, $^3J_{CP} = 9.5$) and 50.8 (dd, $^1J_{CP} = 119.7$, $^3J_{CP} = 8.7$) (CH_2P), 60.4 (t, $^3J_{CP} = 6.4$) and 60.8 (t, $^3J_{CP} = 6.8$) (CH_2N), 65.9 (d, $^2J_{CP} = 7.0$) and 66.1 (d, $^2J_{CP} = 7.3$) (OCH_2), 128.1 (d, $^2J_{CP} = 9.1$) and 128.2 (d, $^2J_{CP} = 9.0$) (C_2), 129.9 (d, $^1J_{CP} = 123.0$) and 130.3 (d, $^1J_{CP} = 122.4$) (C_1), 132.3 (d, $^3J_{CP} = 8.0$) and 132.4 (d, $^3J_{CP} = 7.8$) (C_3), 132.1 (d, $J_{CP} = 2.5$) and 132.5 (d, $J_{CP} = 2.7$) (C_4); ^{1}H NMR ($CDCl_3$) δ: 0.80–0.98 (m, 6H, $O(CH_2)_2CH_3$), 1.00–1.28 (m, 5H, $C_2H_{ax.}$, $C_3H_{ax.}$, $C_4H_{ax.}$), 1.42–1.93 (m, 9H, $OCH_2CH_2CH_3$, $C_2H_{eq.}$, $C_3H_{eq.}$, $C_4H_{eq.}$), 2.46–2.66 (m, 1H, C_1H), 2.91–3.39 (m, 4H, CH_2P), 3.60–4.10 (m, 4H, OCH_2), 7.33–7.64 (m, 8H, C_2H, C_3H, C_4H), 7.68–7.90 (m, 2H, C_2H); $[M+H]^+_{found} = 492.2427$, $C_{26}H_{40}NO_4P_2$ requires 492.2427.

3.6.8 | *N,N*-bis(Propoxyphenylphosphinylmethyl)benzylamine (11d)

Yield: 78% (0.66 g) of compound **11d** as an oil, a 54:46 mixture of two isomers; ^{31}P NMR ($CDCl_3$) δ: 39.2 and 39.4; ^{13}C NMR ($CDCl_3$) δ: 10.1 ($O(CH_2)_2CH_3$), 23.9 (d, $^3J_{CP} = 6.5$, $OCH_2CH_2CH_3$), 53.6 (dd, $^1J_{CP} = 112.4$, $^3J_{CP} = 8.2$) and 53.7 (dd, $^1J_{CP} = 115.5$, $^3J_{CP} = 7.6$) (CH_2P), 61.6 (t, $^3J_{CP} = 7.2$, CH_2N), 65.9 (d, $^2J_{CP} = 6.8$) and 66.1 (d, $^2J_{CP} = 7.2$) (OCH_2), 127.9 (C_4), 128.0 (C_2)*, 128.2 (d, $^2J_{CP} = 10.8$) and 128.4 (d, $^2J_{CP} = 12.6$) ($C_{2'}$), 128.9 (C_3)*, 129.8 (d, $^1J_{CP} = 124.0$) and 130.3 (d, $^1J_{CP} = 122.5$) ($C_{1'}$), 131.9 (d, $J_{CP} = 2.6$, $C_{4'}$), 132.1 (d, $^3J_{CP} = 10.2$) and 132.3 (d, $^3J_{CP} = 10.7$) ($C_{3'}$), 137.8 (C_1), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 0.85–0.95 (m, 6H, $O(CH_2)_2CH_3$), 1.55–1.71 (m, 4H, $OCH_2CH_2CH_3$), 3.01–3.15 (m, 1H), 3.30 (d, $^1J_{HP} = 7.9$, 2H) and 3.40–3.55 (m, 1H) (CH_2P), 3.62–3.76 (m, 2H) and 3.84–4.01 (m, 2H) (OCH_2), 3.99 (s, 2H, CH_2N), 6.91–7.17 (m, 5H, ArH), 7.33–7.61 (m, 8H, $C_{2'}H$, $C_{3'}H$, $C_{4'}H$), 7.64–7.74 (m, 2H, $C_{2'}H$); $[M+H]^+_{found} = 500.2105$, $C_{27}H_{36}NO_4P_2$ requires 500.2114.

3.6.9 | *N,N*-bis(Butoxyphenylphosphinylmethyl)propylamine (12a)

Yield: 90% (0.73 g) of compound **12a** as an oil, a 50:50 mixture of two isomers; ^{31}P NMR ($CDCl_3$) δ: 39.22 and 39.29; ^{13}C NMR ($CDCl_3$) δ: 10.9 and 11.1 ($CH_3(CH_2)_2N$), 13.6 ($O(CH_2)_3CH_3$), 18.8 ($O(CH_2)_2CH_2CH_3$), 20.1 and 20.2 ($CH_3CH_2CH_2N$), 32.6 (d, $^3J_{CP} = 6.3$, $OCH_2CH_2CH_2CH_3$), 54.3 (dd, $^1J_{CP} = 118.2$, $^3J_{CP} = 8.5$) and 54.5 (dd, $^1J_{CP} = 115.2$, $^3J_{CP} = 7.6$) (CH_2P), 58.8 (t, $^3J_{CP} = 7.4$) and 59.0 (t, $^3J_{CP} = 6.9$) (CH_2N), 64.2 (d, $^2J_{CP} = 7.2$) and 64.3 (d, $^2J_{CP} = 7.2$) (OCH_2), 128.2 (d, $J_{CP} = 9.0$) and 128.4 (d, $J_{CP} = 9.1$) (C_2)*, 130.2 (d, $^1J_{CP} = 122.4$) and 130.5 (d, $^1J_{CP} = 121.1$) (C_1), 132.0 (d, $J_{CP} = 3.5$, C_4), 132.1 (d, $J_{CP} = 9.6$) and 132.2 (d, $J_{CP} = 9.0$) (C_3)*, *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 0.44 (t, $^3J_{HH} = 7.3$) and 0.63 (t, $^3J_{HH} = 7.3$) (3H, $CH_3(CH_2)_2N$), 0.84–0.92 (m, 6H, $O(CH_2)_3CH_3$), 1.06–1.25 (m, 2H, $CH_3CH_2CH_2N$), 1.27–1.43 (m, 4H, $O(CH_2)_2CH_2CH_3$), 1.52–1.64 (m, 4H, $OCH_2CH_2CH_2CH_3$), 2.68–2.77 and 3.04–3.15 (m, 2H CH_2N), 3.18–3.40 (m, 4H, CH_2P), 3.64–3.80 (m, 2H) and 3.87–4.05 (m, 2H) (OCH_2), 7.35–7.64 (m, 8H, C_2H, C_3H, C_4H), 7.70–7.79 (m, 2H, C_2H); $[M+H]^+_{found} = 479.2365$, $C_{25}H_{40}NO_4P_2$ requires 479.2354.

3.6.10 | *N,N*-bis(Butoxyphenylphosphinylmethyl)butylamine (12b)

Yield: 87% (0.73 g) of compound **12b** as an oil, a 49:51 mixture of two isomers; ^{31}P NMR ($\mathrm{CDCl_3}$) δ: 39.25 and 39.31; ^{13}C NMR ($\mathrm{CDCl_3}$) δ: 13.6 ($\mathrm{O(CH_2)_3}\mathit{C}\mathrm{H_3}$), 13.9 ($\mathit{C}\mathrm{H_3(CH_2)_3N}$), 18.8 ($\mathrm{O(CH_2)_2}\mathit{C}\mathrm{H_2CH_3}$), 19.7 and 19.8 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2(CH_2)_2N}$), 29.18 and 29.22 ($\mathrm{CH_3CH_2}\mathit{C}\mathrm{H_2CH_2N}$), 32.6 (d, $^3J_{\mathrm{CP}} = 6.5$, $\mathrm{OCH_2}\mathit{C}\mathrm{H_2}$), 54.3 (dd, $^1J_{\mathrm{CP}} = 126.5$, $^3J_{CP} = 8.5$) and 54.4 (dd, $^1J_{\mathrm{CP}} = 122.6$, $^3J_{\mathrm{CP}} = 7.4$) ($\mathrm{CH_2P}$), 56.8 (t, $^3J_{\mathrm{CP}} = 7.5$) and 57.0 (t, $^3J_{\mathrm{CP}} = 6.9$) ($\mathrm{CH_2N}$), 64.1 (d, $^2J_{\mathrm{CP}} = 7.2$) and 64.3 (d, $^2J_{\mathrm{CP}} = 7.2$) ($\mathrm{OCH_2}$), 128.2 (d, $J_{\mathrm{CP}} = 9.2$) and 128.3 (d, $J_{\mathrm{CP}} = 9.3$) ($\mathrm{C_3}$)*, 130.2 (d, $^1J_{\mathrm{CP}} = 122.2$) and 130.5 (d, $^1J_{\mathrm{CP}} = 121.2$) ($\mathrm{C_1}$), 131.9 (d, $^4J_{\mathrm{CP}} = 3.5$, $\mathrm{C_4}$), 132.0 (d, $J_{\mathrm{CP}} = 9.3$) and 132.2 (d, $J_{\mathrm{CP}} = 9.9$) ($\mathrm{C_3}$)*, *may be reversed; ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 0.61 (t, $^3J_{\mathrm{HH}} = 6.7$) and 0.71 (t, $^3J_{\mathrm{HH}} = 7.0$) (3H, $\mathrm{C}\mathit{H}_3\mathrm{(CH_2)_3N}$), 0.77–0.96 (m, 8H, $\mathrm{O(CH_2)_3C}\mathit{H}_3$, $\mathrm{CH_3C}\mathit{H}_2\mathrm{(CH_2)_2N}$), 0.98–1.18 (m, 2H, $\mathrm{CH_3CH_2C}\mathit{H}_2\mathrm{CH_2N}$), 1.28–1.42 (m, 4H, $\mathrm{O(CH_2)_2C}\mathit{H}_2\mathrm{CH_3}$), 1.49–1.67 (m, 4H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{CH_2CH_3}$), 2.43–2.53 and 2.71–2.79 (m, 2H $\mathrm{CH_2N}$), 3.02–3.40 (m, 4H, $\mathrm{CH_2P}$), 3.60–3.84 (m, 2H) and 3.86–4.09 (m, 2H) ($\mathrm{OCH_2}$), 7.32–7.63 (m, 6H, $\mathrm{C_3H}$, $\mathrm{C_4H}$), 7.68–7.87 (m, 4H, $\mathrm{C_2H}$); $[\mathrm{M+H}]^+_{\mathrm{found}} = 493.2523$, $\mathrm{C_{26}H_{42}NO_4P_2}$ requires 493.2511.

3.6.11 | *N,N*-bis(Butoxyphenylphosphinylmethyl)cyclohexylamine (12c)

Yield: 59% (0.52 g) of compound **12c** as an oil, a 54:46 mixture of two isomers; ^{31}P NMR ($\mathrm{CDCl_3}$) δ: 40.02 and 40.09; ^{13}C NMR ($\mathrm{CDCl_3}$) δ: 13.6 ($\mathrm{O(CH_2)_3}\mathit{C}\mathrm{H_3}$), 18.8 ($\mathrm{O(CH_2)_2}\mathit{C}\mathrm{H_2CH_3}$), 24.7 ($\mathrm{C_3}$), 25.7 ($\mathrm{C_4}$), 32.6 (d, $^3J_{\mathrm{CP}} = 6.4$, $\mathrm{OCH_2}\mathit{C}\mathrm{H_2}$), 32.8 ($\mathrm{C_2}$), 50.6 (dd, $^1J_{\mathrm{CP}} = 116.7$, $^3J_{CP} = 8.1$) and 50.8 (dd, $^1J_{\mathrm{CP}} = 119.5$, $^3J_{\mathrm{CP}} = 8.7$) ($\mathrm{CH_2P}$), 57.6 (d, $^3J_{\mathrm{CP}} = 13.0$, $\mathrm{C_1}$), 60.8 (t, $^3J_{\mathrm{CP}} = 6.2$ $\mathrm{CH_2N}$), 64.3 (d, $^2J_{\mathrm{CP}} = 7.2$) and 64.7 (d, $^2J_{\mathrm{CP}} = 6.9$) ($\mathrm{OCH_2}$), 128.2 (d, $^2J_{\mathrm{CP}} = 12.5$) and 128.5 (d, $^2J_{\mathrm{CP}} = 12.3$) ($\mathrm{C_{2'}}$), 130.2 (d, $^1J_{\mathrm{CP}} = 123.2$) and 130.3 (d, $^1J_{\mathrm{CP}} = 122.1$) ($\mathrm{C_{1'}}$), 131.8 (d, $^3J_{\mathrm{CP}} = 9.7$) and 132.26 (d, $^3J_{\mathrm{CP}} = 9.9$) ($\mathrm{C_{3'}}$), 132.32 (d, $J_{\mathrm{CP}} = 2.1$, $\mathrm{C_{4'}}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 0.84–0.94 (m, 6H, $\mathrm{O(CH_2)_3C}\mathit{H}_3$), 0.95–1.23 (m, 5H, $\mathrm{C_2H_{ax.}}$, $\mathrm{C_3H_{ax.}}$, $\mathrm{C_4H_{ax.}}$), 1.29–1.43 (m, 4H, $\mathrm{O(CH_2)_2C}\mathit{H}_2\mathrm{CH_3}$), 1.46–1.93 (m, 9H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{CH_2CH_3}$, $\mathrm{C_2H_{eq.}}$, $\mathrm{C_3H_{eq.}}$, $\mathrm{C_4H_{eq.}}$), 2.37–2.50 (m, 1H, $\mathrm{C_1H}$), 2.91–3.38 (m, 4H, $\mathrm{CH_2P}$), 3.64–4.13 (m, 4H, $\mathrm{OCH_2}$), 7.34–7.63 (m, 6H, $\mathrm{C_3H}$, $\mathrm{C_4H}$), 7.68–7.89 (m, 4H, $\mathrm{C_2H}$); $[\mathrm{M+H}]^+_{\mathrm{found}} = 520.2716$, $\mathrm{C_{28}H_{44}NO_4P_2}$ requires 520.2740.

3.6.12 | *N,N*-bis(Butoxyphenylphosphinylmethyl)benzylamine (12d)

Yield: 80% (0.72 g) of compound **12d** as an oil, a 48:52 mixture of two isomers; ^{31}P NMR ($\mathrm{CDCl_3}$) δ: 39.26 and 39.39; ^{13}C NMR ($\mathrm{CDCl_3}$) δ: 13.6 ($\mathrm{O(CH_2)_3}\mathit{C}\mathrm{H_3}$), 18.8 ($\mathrm{O(CH_2)_2}\mathit{C}\mathrm{H_2CH_3}$), 32.6 (d, $^3J_{\mathrm{CP}} = 6.6$, $\mathrm{OCH_2}\mathit{C}\mathrm{H_2}$), 53.6 (dd, $^1J_{\mathrm{CP}} = 112.4$, $^3J_{CP} = 8.1$) and 53.7 (dd, $^1J_{\mathrm{CP}} = 115.7$, $^3J_{\mathrm{CP}} = 7.7$) ($\mathrm{CH_2P}$), 61.6 (t, $^3J_{\mathrm{CP}} = 7.2$, $\mathrm{CH_2N}$), 64.2 (d, $^2J_{\mathrm{CP}} = 6.5$) and 64.3 (d, $^2J_{\mathrm{CP}} = 7.2$) ($\mathrm{OCH_2}$), 127.9 ($\mathrm{C_4}$), 128.0 ($\mathrm{C_2}$)*, 128.2 (d, $^2J_{\mathrm{CP}} = 11.0$) and 128.4 (d, $^2J_{\mathrm{CP}} = 12.6$) ($\mathrm{C_{2'}}$), 129.0 ($\mathrm{C_3}$)*, 129.8 (d, $^1J_{\mathrm{CP}} = 123.9$) and 130.3 (d, $^1J_{\mathrm{CP}} = 122.6$) ($\mathrm{C_{1'}}$), 131.9 (d, $J_{\mathrm{CP}} = 2.1$, $\mathrm{C_{4'}}$), 132.1 (d, $^3J_{\mathrm{CP}} = 10.1$) and 132.3 (d, $^3J_{\mathrm{CP}} = 10.8$) ($\mathrm{C_{3'}}$), 137.8 ($\mathrm{C_1}$), *may be reversed; ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 0.87 (t, $^3J_{\mathrm{HH}} = 7.3$, 6H, $\mathrm{O(CH_2)_3C}\mathit{H}_3$), 1.24–1.41 (m, 4H, $\mathrm{O(CH_2)_2C}\mathit{H}_2\mathrm{CH_3}$), 1.50–1.67 (m, 4H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{CH_2CH_3}$), 2.96–3.14 (m, 1H), 3.27 (d, $^1J_{\mathrm{HP}} = 8.2$, 2H) and 3.36–3.54 (m, 1H) ($\mathrm{CH_2P}$), 3.62–3.78 (m, 2H) and 3.84–3.94 (m, 2H) ($\mathrm{OCH_2}$), 3.97 (s, 2H, $\mathrm{CH_2N}$), 6.88–7.22 (m, 5H, ArH), 7.31–7.59 (m, 6H, $\mathrm{C_3H}$, $\mathrm{C_4H}$), 7.62–7.73 (m, 4H, $\mathrm{C_2H}$); $[\mathrm{M+H}]^+_{\mathrm{found}} = 528.2417$, $\mathrm{C_{29}H_{40}NO_4P_2}$ requires 528.2427.

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REFERENCES

[1] V. P. Kukhar, H. R. Hudson, Aminophosphonic and Aminophosphinic Acids: Chemistry and Biological Activity, Wiley, Chichester **2000**.

[2] P. Kafarski, B. Lejczak, *Phosphorus Sulfur Silicon* **1991**, *63*, 193.

[3] A. Mucha, P. Kafarski, L. Berlicki, *J. Med. Chem.* **2011**, *54*, 5955.

[4] J. G. Allen, F. R. Atherton, M. J. Hall, C. H. Hassall, S. W. Holmes, R. W. Lambert, L. J. Nisbet, P. S. Ringrose, *Nature* **1978**, *272*, 56.

[5] F. R. Atherton, C. H. Hassal, R. W. Lambert, *J. Med. Chem.* **1987**, *30*, 1603.

[6] G. Lavielle, P. Hautefaye, C. Schaeffer, J. A. Boutin, C. A. Cudennec, A. Pierre, *J. Med. Chem.* **1998**, *1991*, 34.

[7] P. Kafarski, B. Lejczak, *Curr. Med. Chem. Anti-Cancer Agents* **2001**, *1*, 301.

[8] J. Grembecka, A. Mucha, T. Cierpicki, P. Kafarski, *J. Med. Chem.* **2003**, *46*, 2641.

[9] M. Sieńczyk, J. Oleksyszyn, *Curr. Med. Chem.* **2009**, *16*, 1673.

[10] G. Forlani, L. Berlicki, M. Duo, G. Dziedziola, S. Giberti, M. Bertazzini, P. Kafarski, *J. Agric. Food Chem.* **2013**, *61*, 6792.

[11] G. Forlani, A. Occhipinti, Ł. Berlicki, G. Dziędzioła, A. Wieczorek, P. Kafarski, *J. Agric. Food Chem.* **2008**, *56*, 3193.

[12] N. Long, X. J. Cai, B. A. Song, S. Yang, Z. Chen, P. S. Bhadury, D. Y. Hu, L. H. Jin, W. Xue, *J. Agric. Food Chem.* **2008**, *56*, 5242.

[13] D. Y. Hu, Q. Q. Wan, S. Yang, B. A. Song, P. S. Bhadury, L. H. Jin, K. Yan, F. Liu, Z. Chen, W. Xue, *J. Agric. Food Chem.* **2008**, *56*, 998.

[14] M. H. Chen, Z. Chen, B. A. Song, P. S. Bhadury, S. Yang, X. J. Cai, D. Y. Hu, W. Xue, S. Zeng, *J. Agric. Food Chem.* **2009**, *57*, 1383.

[15] T. David, S. Prochazkova, J. Havlickova, J. Kotek, V. Kubicek, P. Hermann, I. Lukes, *J. Chem. Soc., Dalton Trans.* **2013**, *42*, 2414.

[16] M. I. Kabachnik, T. Y. Medved, *Dokl. Akad. Nauk SSSR* **1952**, *83*, 689.

[17] E. K. Fields, *J. Am. Chem. Soc.* **1952**, *74*, 1528.

[18] R. A. Cherkasov, V. I. Galkin, *Russ. Chem. Rev.* **1998**, *67*, 857.

[19] G. Keglevich, E. Bálint, *Molecules* **2012**, *17*, 12821.

[20] N. S. Zefirov, E. D. Matveeva, *Arkivoc* **2008**, *1*, 1.

[21] E. D. Matveeva, T. A. Podrugina, E. V. Tishkovskaya, L. G. Tomilova, N. S. E. Zefirov, *Synlett* **2003**, *15*, 2321.

[22] S. Chandrasekhar, S. J. Prakash, V. Jagadeshwar, Ch. Narsihmulu, *Tetrahedron Lett.* **2001**, *42*, 5561.

[23] C. Qian, T. Huang, *J. Org. Chem.* **1998**, *63*, 4125.

[24] R. Ghosh, S. Maiti, A. Chakraborty, D. K. Maiti, *J. Mol. Catal. A* **2004**, *210*, 53.

[25] S. Lee, J. H. Park, J. Kang, J. K. Lee, *Chem. Commun.* **2001**, *17*, 1698.

[26] P. Sun, Z. Hu, Z. Huang, *Synth. Commun.* **2004**, *34*, 4293.

[27] F. Xu, Y. Luo, M. Deng, Q. Shen, *Eur. J. Org. Chem.* **2003**, 4728.

[28] K. Ravinder, A. Vijender Reddy, P. Krishnaiah, *Synth. Commun.* **2004**, *34*, 1677.

[29] P. Kafarski, M. G. Górniak, I. Andrasiak, *Curr. Green Chem.* **2015**, *5*, 218.

[30] B. C. Ranu, A. Hajra, *Green Chem.* **2002**, *4*, 551.

[31] M. Zahouily, A. Elmakssoudi, A. Mezdar, A. Rayadh, S. Sebti, *J. Chem. Res.* **2005**, *5*, 324.

[32] M. M. Kabachnik, E. V. Zobnina, I. P. Beletskaya, *Synlett* **2005**, *9*, 1393.

[33] X.-J. Mu, M.-Y. Lei, J.-P. Zou, W. Zhang, *Tetrahedron Lett.* **2006**, *47*, 1125.

[34] G. Keglevich, A. Szekrényi, *Lett. Org. Chem.* **2008**, *5*, 616.

[35] E. Bálint, J. Takács, L. Drahos, A. Juranovic, M. Kocevar, G. Keglevich, *Heteroatom Chem.* **2013**, *24*, 221.

[36] R. A. Cherkasov, A. R. Garifzyanov, A. S. Talan, R. R. Davletshin, N. V. Kurnosova, *Russ. J. Gen. Chem.* **2009**, *79*, 1480.

[37] A. A. Prishchenko, M. V. Livantsov, O. P. Novikova, L. I. Livantsova, V. S. Petrosyan, *Heteroatom Chem.* **2010**, *21*, 430.

[38] G. Keglevich, A. Szekrényi, Á. Szöllősy, L. Drahos, *Synth. Commun.* **2011**, *41*, 2265.

[39] E. Bálint, E. Fazekas, G. Pintér, Á. Szöllősy, T. Holczbauer, M. Czugler, L. Drahos, T. Körtvélyesi, G. Keglevich, *Curr. Org. Chem.* **2012**, *16*, 547.

[40] E. Bálint, E. Fazekas, P. Pongrácz, L. Kollár, L. Drahos, T. Holczbauer, M. Czugler, G. Keglevich, *J. Organomet. Chem.* **2012**, *717*, 75.

[41] E. Bálint, A. Tripolszky, E. Jablonkai, K. Karaghiosoff, M. Czugler, Z. Mucsi, L. Kollár, P. Pongrácz, G. Keglevich, *J. Organomet. Chem.* **2016**, *801*, 111.

[42] E. Bálint, E. Fazekas, L. Drahos, G. Keglevich, *Heteroatom Chem.* **2013**, *24*, 510.

[43] E. Bálint, E. Fazekas, J. Kóti, G. Keglevich, *Heteroatom Chem.* **2015**, *26*, 106.

[44] A. A. Prishchenko, M. V. Livantsov, O. P. Novikova, L. I. Livantsova, E. R. Milaeva, *Heteroatom Chem.* **2009**, *20*, 70.

[45] M. M. Kabachnik, T. N. Ternovskaya, E. V. Zobnina, I. P. Beletskaya, *Russ. J. Org. Chem.* **2002**, *38*, 480.

[46] B. Boduszek, T. K. Olszewski, W. Goldeman, K. Grzegolec, P. Blazejewska, *Tetrahedron* **2012**, *68*, 1223.

[47] H.-J. Cristau, A. Hervé, D. Virieux, *Tetrahedron* **2004**, *60*, 877.

[48] P. P. Onys'ko, K. A. Zamulko, O. I. Kyselyova, *Phosphorus Sulfur Silicon* **2016**, *191*, 274.

[49] Á. Tajti, E. Bálint, G. Keglevich, *Curr. Org. Synth.* **2016**, *13*, 638.

[50] Z. Ke, Y. Zhang, X. Cui, F. Shi, *Green Chem.* **2016**, *18*, 808.

[51] O. Saidi, M. J. Bamford, A. J. Blacker, J. Lynch, S. P. Marsden, P. Plucinski, R. J. Watson, J. M. J. William, *Tetrahedron Lett.* **2010**, *51*, 5804.

[52] N. Z. Kiss, K. Ludányi, L. Drahos, G. Keglevich, *Synth. Commun.* **2009**, *39*, 2392.