Synthesis of 1-Phosphono-2-aza-1,3-dienes and Scope of their Aziridination

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Abstract: Several 1-phosphono-2-aza-1,3-dienes **14** and 1-aryl-1-phosphono-2-aza-1,3-dienes **15**–**17** were prepared by 1,4-dehydrochlorination of the corresponding diethyl [(2-chloro-1-alkylidene)amino]methylphosphonates **10**–**13**. 1-Phosphono-2-aza-1,3-dienes **14** react smoothly with diazomethane to give 2-phosphono-1-vinylaziridines **18**. The synthesis of 2-ethoxycarbonyl-3-phosphono-1-vinylaziridines **19** was performed using ethyl diazoacetate (EDA) in the presence of ytterbium(III) triflate as a catalyst. 2-Phosphono-3-(trimethylsilyl)aziridines **20** were prepared from phosphonoazadienes **14** by treatment with (trimethylsilyl)diazomethane under reflux. 1-Aryl-1-phosphono-2-aza-1,3-dienes are not susceptible to aziridination under these conditions.

Key words: 2-azadienes, 1-phosphono-2-azadienes, phosphonoaziridines, diazo compounds, imines, Lewis acids, lanthanides

Introduction

The importance of acyclic α-aminophosphonates and α-aminophosphonic acids is well established and they are used in agrochemistry, pharmaceutical industry and in protein research, because of their analogy to α-amino acids.[1,2] However, heterocyclic phosphonates or phosphonates containing heterocyclic moieties are less studied although examples of biologically active heterocyclic phosphonates are appearing regularly in the literature. Important examples of such heterocyclic phosphonic acids are phosphomycin (antibiotic),[3,4] triazole substituted phosphonic acid derivatives (herbicides),[5] EB-1053 and CGP-42,446 (antiosteoporosis),[6] phosphonomethylmelamines (flame retardants),[7] phosphonoalkylaminotetrazole derivatives (endothelin converting enzyme inhibitors),[8] etc.

In the context of our continuing interest in agrochemical applications,[9] our attention is focussed on the development of new strategies for the synthesis of heterocyclic aminophosphonates. In particular, the chemistry of aziridines is appealing, because of the possibile ring opening or cross-linking reactions of aziridines. This feature gives these compounds antitumor potential and enzyme inhibitor applications.[10] This paper describes our efforts towards the study of scantly investigated electron-poor azadienes,[11,12] e.g. 1-phosphono-2-aza-1,3-dienes, and their reactivity towards aziridination.

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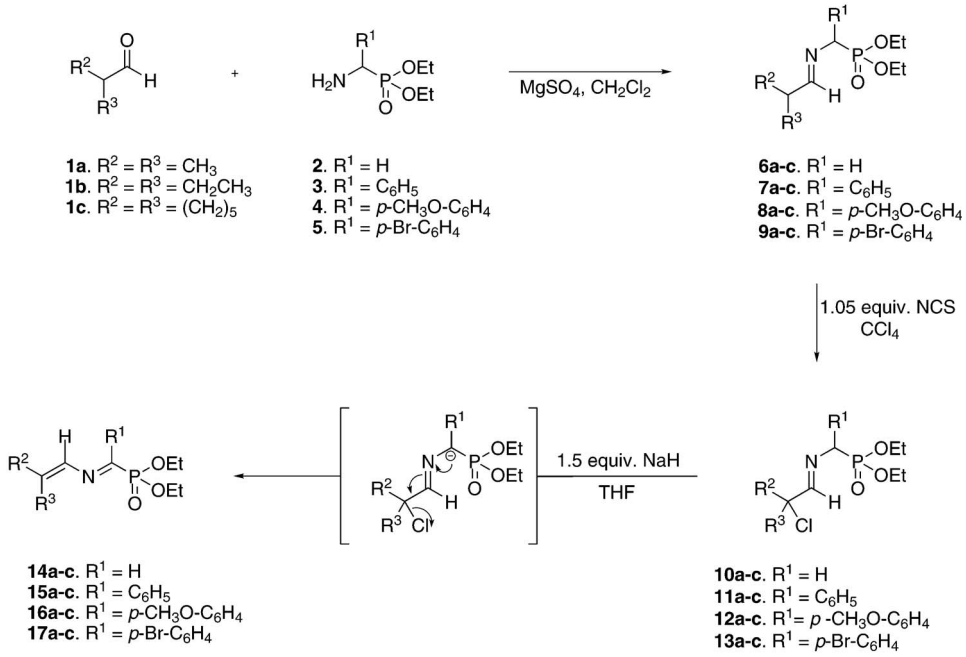
Synthesis of 1-Phosphono-2-aza-1,3-dienes

In order to develop an entry towards 1-phosphono-2-aza-1,3-dienes **14**–**17**, diethyl aminomethylphosphonates were prepared using literature methods based on the Kabachnik–Fields reaction.[13,14]

The first step towards the synthesis of 1-phosphono-2-aza-1,3-dienes **14**–**17** consists in the condensation of an aliphatic aldehyde **1a**–**c** with diethyl aminophosphonate **2**–**5** (Scheme 1). Diethyl aminophosphonates **2**–**5** were reacted with a solution of aldehyde **1a**–**c** in dichloromethane in the presence of magnesium sulfate as a dehydrating agent. The resulting aldimines **6**–**9** were isolated in good yields (92–99%) and could be used without further purification (purity >96%). The aldimines **6**–**9** were then chlorinated at the α-position using 1.05 equivalents of *N*-chlorosuccinimide (NCS) in refluxing carbon tetrachloride. The α-chlorinated aldimines **10**–**13** were obtained in excellent yields (95–99%). No purification was required and the imines were used as such in the following step. The α-chlorinated aldimines **11a**, **12a** and **13a** contained some unidentified products. However, distillation under reduced pressure of the chlorinated aldimines **10**–**13** led to a serious loss of end product due to partial decomposition.

Theoretically, the sequence can also be inverted, starting with the chlorination of aldehyde **1a**–**c** followed by condensation with diethyl aminophosphonates **2**–**5**. However, this alternative reaction pathway resulted in the isolation of impure chlorinated aldimines. Besides, purification of this crude reaction mixture by distillation also resulted in a considerable loss of product (yield: 35%).

The α-chlorinated imines **10**–**13** were then treated with a base in order to induce a 1,4-dehydrochlorination, yielding the 1-phosphono-2-aza-1,3-dienes **14**–**17**. A range of bases was evaluated at different reaction temperatures and reaction times. The use of *t*-BuOK and *n*-butyllithium resulted in complex mixtures, whereas LDA did not convert the starting material completely. Sodium hydride was selected as the most suitable base, although it was difficult to drive the reaction to completion. Use of only 1.1 equivalents of sodium hydride at room temperature led to incomplete conversion. Use of a larger excess of sodium hydride (1.5 equiv) at room temperature for 16 hours, followed by a certain period of reflux (1–3 h) resulted in the complete conversion of the starting material. Small amounts of succinimide, still present in the reaction mixture after workup of the α-chlorination step (supported by



Scheme 1 Synthesis of 1-phosphono-2-aza-1,3-dienes **14**–**17**

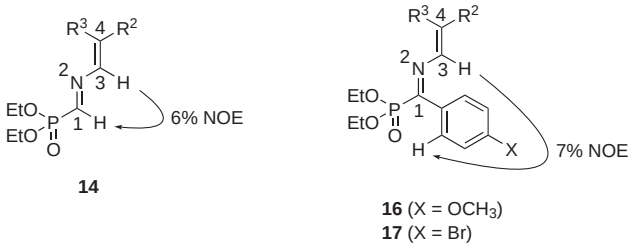
^{1}H NMR spectrum), was responsible for quenching of some sodium hydride. An excess of 0.5 equivalent of sodium hydride was sufficient in all cases to drive the 1,4-dehydrochlorination to completion. The concentration of the starting material in THF is important for the course of the reaction. A concentration exceeding 0.1 M of starting material in THF leads to lower yields or even to the formation of complex reaction mixtures. Since 1-phosphono-2-aza-1,3-dienes **14**–**17** are quite sensitive to prolonged heating, the end of the period of reflux has to be monitored carefully, either by thin layer chromatography, or by ^{31}P NMR spectroscopy (the signal shifts from around 22 to 8–9 ppm). After workup, the azadienes **14**–**17** were isolated in moderate to good overall yield and satisfactory purity (>90%) (Table 1).

Attempts were made to purify the crude reaction mixture by flash chromatography, but this always led to a considerable loss of product because of the high affinity of the azadienes for silica gel. Therefore, the azadienes **14**–**17** were used as such for the evaluation of further conversions.

After 1,4-dehydrochlorination, the formation of only one in-plane isomer is observed. Considering the iminofunction in the azadienes **14**–**17**, only the *E*-isomer is formed as shown in Scheme 1. This conclusion is deduced from NOE experiments performed on azadienes **14**, **16** and **17**. The selective saturation of the signal of the proton at C-3 afforded a positive NOE for the proton on C-1 (in the case of azadiene **14**) as well as for the two *ortho* protons (relative to the substituent bearing the phosphonate moiety) of the aromatic ring (in the case of azadienes **16** and **17**) (Figure 1). This conclusion is also supported by the large heteronuclear coupling between carbon C-3 and phosphorus ($^3J_{C,P}$) in the azadienes **14** ($^3J_{C,P}$ = 40.3 Hz) and **16**–**17** ($^3J_{C,P}$ = 31.6–34.1 Hz). It was shown that the $^3J_{C,P}$ coupling constant is considerably bigger in *trans* derivatives ($^3J_{C,P}$ = ca. 24 Hz) than in the corresponding *cis* derivatives ($^3J_{C,P}$ = 8–10 Hz).[15]

Table 1 Overall Yields for 1-Phosphono-2-aza-1,3-dienes **14**–**17**

Product	R^1	R^2	Yield (%)
14a	H	CH_3	83
15a	C_6H_5	CH_3	78
16a	*p*-$CH_3OC_6H_4$	CH_3	51
17a	*p*-BrC_6H_4	CH_3	73
14b	H	CH_2CH_3	75
15b	C_6H_5	CH_2CH_3	74
16b	*p*-$CH_3OC_6H_4$	CH_2CH_3	65
17b	*p*-BrC_6H_4	CH_2CH_3	70
14c	H	$(CH_2)_5$	80
15c	C_6H_5	$(CH_2)_5$	72
16c	*p*-$CH_3OC_6H_4$	$(CH_2)_5$	62
17c	*p*-BrC_6H_4	$(CH_2)_5$	80



14

16 (X = OCH_3)
17 (X = Br)

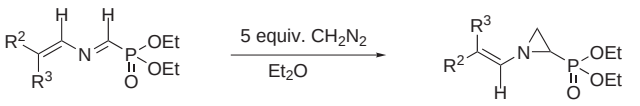
Figure 1 NOE enhancements observed for **14**, **16** and **17**

To our knowledge, 1-phosphono-2-aza-1,3-dienes **14**–**15** are only mentioned twice in literature, e.g. in a preliminary communcation by our group[9] and by a Russian research team, which described a 1,5-hydrogen shift from the methyl group to the imidoyl carbon upon treatment with base.[11]

Reactivity Study of 1-Phosphono-2-aza-1,3-dienes and the Synthesis of 2-Phosphonoaziridines

Because of the lack of information concerning the reactivity of 1-phosphono-2-aza-1,3-dienes, a study was performed in order to evaluate the scope of the reactivity of this new class of compounds. Since the reactivity of azadienes **14**–**17** could be rationalized as an enamine or as an imine, nucleophilic as well as electrophilic reagents were evaluated. Reactions with different nucleophiles (cyanide, methoxide, azide, phosphite, Grignard reagent) did not lead to the expected adducts to the imine function, but resulted in complex reaction mixtures. Similary, the reaction of some electrophilic reagents (bromine, cyanogen bromide) also led to complex reaction mixtures. Therefore, the reactivity pattern of the azadienes cannot be split in an imine or an enamine reactivity.

However, reaction of azadienes **14a**–**c** with an excess of diazomethane (approximately 5 equivalents generated from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide and potassium hydroxide) in diethyl ether led to the fast formation of the corresponding 2-phosphonoaziridines **18a**–**c**. (Equation 1). The regiospecific addition of diazomethane to azadienes **14a**–**c** is directed by the electron-withdrawing phosphonate group resulting in the attack of diazomethane at the electrophilic imino carbon.



14a. $R^2 = R^3 = CH_3$
14b. $R^2 = R^3 = CH_2CH_3$
14c. $R^2 = R^3 = (CH_2)_5$

18a. $R^2 = R^3 = CH_3$ 93% (57%)
18b. $R^2 = R^3 = CH_2CH_3$ 68% (30%)
18c. $R^2 = R^3 = (CH_2)_5$ 72% (29%)

Equation 1 Synthesis of 2-phosphono-1-vinylaziridines **18a**–**c** (the yield in parentheses are those after purification by flash chromatography).

Following the reaction with ^{31}P NMR spectroscopy, no formation of a triazoline intermediate (via a 1,3-dipolar addition), which subsequently loses nitrogen, was observed. After evaporating the solvent and the excess of diazomethane, 2-phosphonoaziridines **18a**–**c** were isolated in good to excellent yield in sufficient purity (>95%) (Equation 1). Analytically pure compounds could be obtained by flash chromatography, although a considerable loss of product was noticed.

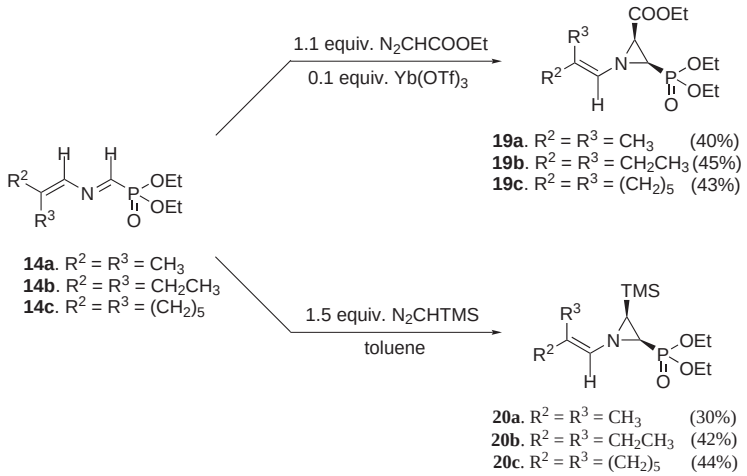
Although azadienes **14a**–**c** reacted most readily with diazomethane yielding the corresponding aziridines **18a**–**c**, the azadienes **15**–**17** did not react at all and the starting material was recovered. An explanation for this complete loss of reactivity could be the extended conjugation between the azadiene and the aromatic ring, causing an increased electronic stability of the azadienes **15**–**17**. This enhanced stability can explain the resistance of azadienes **15**–**17** towards nucleophilic addition of diazomethane at the imino function.

Synthesis of 2-Ethoxycarbonyl-3-phosphonoaziridines and 2-Phosphono-3-(trimethylsilyl)aziridines

To evaluate the generality of the reaction pattern of azadienes **14**–**17** towards diazo compounds, their reactions with ethyl diazoacetate (EDA) and (trimethylsilyl)diazomethane were examined. Although azadienes **14a**–**c** react easily with diazomethane at room temperature, no reaction was observed with EDA. Therefore, the effects of several catalysts [$Cu(OTf)_2$, $Yb(OTf)_3$, $Nd(OTf)_3$] were evaluated.

Using $Cu(OTf)_2$ as a catalyst with the aim to form transient metal carbene species, the conversion was not successful, neither if EDA was added at once or over a period of five hours. Starting material or a trace of aziridine **19** (<10%) was isolated, respectively. Since both reaction conditions afforded diethyl maleate and diethyl fumarate as the main side products, azadienes **14a**–**c** seem not to be susceptible to the aziridination reactions.

Therefore, the Lewis acid-catalyzed activation of the imine function was evaluated, followed by a nucleophilic addition of EDA.[16,17] Since lanthanide triflates were recently reported as effective Lewis acid catalysts for the synthesis of aziridines,[18] $Yb(OTf)_3$ and $Nd(OTf)_3$ were selected as Lewis acid. The aziridination of azadiene **14a** was first evaluated in different solvents (THF, ethanol and dichloromethane) with $Yb(OTf)_3$ as a catalyst. From these experiments, dichloromethane was selected as the most suitable solvent. The crude reaction mixture contained the *cis*- as well as the *trans*-isomer of aziridines **19a**–**c** in a ratio of 85:15 (*cis*/*trans*) (calculated from the ^1H NMR spectrum). By means of flash chromatography, only the *cis*-isomer could be isolated and fully characterized (Scheme 2). Applying these reaction conditions with $Nd(OTf)_3$ instead, the reaction was equally successful in view of the yield, but the reaction took twice as long. Fur-



Scheme 2 Synthesis of 2-ethoxycarbonyl-3-phosphonoaziridines **19a–c** and 2-phosphono-3-(trimethylsilyl)aziridines **20a–c** (The yield in parentheses are those obtained after flash chromatography).

thermore, the ratio of the *cis*- and the *trans*-isomer is approximately the same, e.g. 88:12 (*cis*/*trans*).

In order to obtain 2-phosphono-3-(trimethylsilyl)aziridines **20a–c**, azadienes **14a–c** were treated with (trimethylsilyl)diazomethane under different reaction conditions. At room temperature using different solvents (dichloromethane, THF, toluene), the reaction led to the isolation of starting material when performed in the absence as well as in the presence of $Yb(OTf)_3$. Using $AgSbF_6$ as a catalyst in THF at –78 °C instead, a complex reaction mixture was obtained after workup. Refluxing azadienes **14a–c** in the presence of 1.5 equivalents of (trimethylsilyl)diazomethane in toluene for 48 hours generated 2-phosphono-3-(trimethylsilyl)aziridines **20a–c** in moderate yields (Scheme 2). The crude reaction mixtures contained only the *cis*-isomer and were purified by flash chromatography. Similarly to the lack of reactivity of azadienes **15–17** towards diazomethane, these azadienes with aromatic substituents neither react with EDA nor with (trimethylsilyl)diazomethane under the evaluated reaction conditions.

Conclusion

To conclude, the chemistry of 1-phosphono-2-aza-1,3-dienes **14–17** has been evaluated and a direct synthesis of 2-phosphonoaziridines **18a–c** has been developed. Azadienes **14a–c** can also be transformed into the corresponding 2-ethoxycarbonyl-3-phosphonoaziridines **19a–c** and 2-phosphono-3-(trimethylsilyl)aziridines **20a–c** using ethyl diazoacetate (EDA) and (trimethylsilyl)diazomethane, respectively. 1-Phosphono-2-aza-1,3-dienes **14–17** and the electron-deficient aziridines **18a–c**, **19a–c** and **20a–c** seem interesting building blocks for highly functionalized acyclic and cyclic α-aminophosphonates. The chemistry of both classes of compounds will be further developed for the synthesis of azaphosphonates with potential applications in agrochemistry.

Flash chromatography was performed on silica gel (Acros, 0.035–0.070 mm). ^{1}H NMR spectra were recorded at 270 MHz on a Jeol JNM EX270 FT-NMR instrument. ^{13}C NMR and ^{31}P NMR experiments were acquired at 68 MHz and 109 MHz, respectively. The relative proportions between two diastereoisomers were measured by integration of the ^{1}H peaks. Chemical shifts (δ) are reported in ppm from TMS as an internal reference. Coupling constants (*J*) are given in Hertz. IR-spectra were recorded with a Perkin-Elmer Spectrum One FT-IR spectrometer. Low-resolution mass spectra (MS) were obtained at 70eV on a Varian MAT 112 spectrometer. All solvents were dried extensively over sodium/benzophenone ketyl (Et_2O, THF) or CaH_2 (CH_2Cl_2). Petroleum ether used had bp 40–60 °C. The 1,4-dehydrochlorination experiments as well as the aziridination reactions were performed under N_2.

Diethyl 1-Amino-1-arylmethylphosphonates 3–5; General Procedure

To a solution of the corresponding aldehyde (26 mmol), NH_4OAc (4.0 g, 52 mmol), diethyl phosphite (3.6 g, 26 mmol) and $LiClO_4$ (277 mg, 2.6 mmol) in EtOH (220 mL) in a 500 mL flask, were added anhydrous molecular sieves (4 Å, 2.5 g). The reaction mixture was protected from moisture by a $CaCl_2$ tube on top of the condenser and was heated under reflux for 5 d. The mixture was cooled to r.t. and was filtered over Celite. The solution was extracted with aq 2 M HCl and CH_2Cl_2 after which the aqueous fraction was made alkaline with solid NaOH. Subsequently, the aqueous fraction was extracted with CH_2Cl_2 and the organic fraction was dried ($MgSO_4$). After filtration, the solvent was removed under reduced pressure affording the crude amino phosphonate **3–5** in 30–50% yields as yellowish oils (purity >90%).

Diethyl Amino(phenyl)methylphosphonate (3)

Synthesized according to the general procedure with benzaldehyde; Yield: 3.16 g (50%); yellowish oil. After distillation the yield dropped to 30%; bp 93–95 °C/0.01 mmHg.

IR (neat): 3374, 3295, 1602, 1241, 1053, 1027 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.18 [3 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.28 [3 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.84 (2 H, s, NH_2), 4.05 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.26 (1 H, d, $J_{H,P}$ = 17.2 Hz, CHP), 7.35 (3 H, m, CH), 7.47 (2 H, m, CH).

^{13}C NMR ($CDCl_3$): δ = 16.57 [2 C, t, $J_{C,P}$ = 6.7 Hz, P(O)OCH$_2$*C*H$_3$], 54.22 (d, $J_{C,P}$ = 150.1 Hz, CHP), 62.88 [2 C, t, $J_{C,P}$ = 7.9 Hz, P(O)O*C*H$_2$CH$_3$], 127.83 (CH), 127.92 (2 CH), 128.59 (2 CH), 137.91 (C_{quat}).

^{31}P NMR ($CDCl_3$): δ = 25.24.

MS: *m*/*z* = 243 (2, [M^+]), 242 (3), 185 (2), 133 (29), 107 (44), 106 (100), 104 (34), 84 (18), 81 (21), 79 (56), 77 (54), 65 (19), 51 (17), 47 (12).

Diethyl Amino(4-methoxyphenyl)methylphosphonate (4)
Synthesized according to the general procedure with 4-methoxybenzaldehyde; yield: 3.55 g (50%); yellowish oil.

IR (neat): 3379, 3295, 1610, 1248, 1053, 1027 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.19 [3 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.28 [3 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.83 (2 H, s, NH_2), 3.81 (3 H, s, OCH_3), 4.03 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.21 (1 H, d, $J_{H,P}$ = 16.2 Hz, CHP), 6.89 (2 H, d, *J* = 8.6 Hz, CH), 7.38 (2 H, dd, *J* = 8.9, 2.3 Hz, CH).

^{13}C NMR ($CDCl_3$): δ = 16.44 [2 C, t, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 53.39 (d, $J_{C,P}$ = 151.4 Hz, CHP), 55.25 (OCH_3), 62.62 [d, $J_{C,P}$ = 7.3 Hz, P(O)O*C*H$_2$CH$_3$], 62.78 [d, $J_{C,P}$ = 7.3 Hz, P(O)O*C*H$_2$CH$_3$], 113.87 (2 C, d, $J_{C,P}$ = 2.4 Hz, CH), 128.86 (2 C, d, $J_{C,P}$ = 6.1 Hz, CH), 129.66 (d, $J_{C,P}$ = 3.6 Hz, C_{quat}), 159.26 (d, $J_{C,P}$ = 2.4 Hz, C_{quat}).

^{31}P NMR ($CDCl_3$): δ = 25.50.

MS: *m*/*z* = 273 (8, [M^+]), 229 (3), 175 (4), 164 (13), 137 (36), 136 (100), 135 (16), 134 (26), 121 (11), 109 (23), 91 (19), 83 (11), 65 (10), 43 (4).

Diethyl Amino(4-bromophenyl)methylphosphonate (5)
Synthesized according to the general procedure with 4-bromobenzaldehyde; yield: 2.51 g (30%); yellowish oil.

IR (neat): 3377, 3296, 1590, 1487, 1240, 1026 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.22 [3 H, t, *J* = 7.3 Hz, P(O)OCH$_2$C*H*$_3$], 1.28 [3 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.80 (2 H, s, NH_2), 4.07 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.24 (1 H, d, $J_{H,P}$ = 17.2 Hz, CHP), 7.34 (2 H, dd, *J* = 8.4, 2.1 Hz, CH), 7.49 (2 H, d, *J* = 7.9 Hz, CH).

^{13}C NMR ($CDCl_3$): δ = 16.42 [2 C, t, $J_{C,P}$ = 5.5 Hz, P(O)OCH$_2$*C*H$_3$], 53.56 (d, $J_{C,P}$ = 150.2 Hz, CHP), 62.87 [2 C, t, $J_{C,P}$ = 6.7 Hz, P(O)O*C*H$_2$CH$_3$], 121.77 (d, $J_{C,P}$ = 3.6 Hz, C_{quat}), 129.45 (2 C, d, $J_{C,P}$ = 6.1 Hz, CH), 131.52 (2 C, d, $J_{C,P}$ = 2.4 Hz, CH), 136.84 (d, *J* = 3.7 Hz, C_{quat}).

^{31}P NMR ($CDCl_3$): δ = 24.27.

MS: *m*/*z* = 323/321 (2/1, [M^+]), 265 (2), 263 (2), 186 (84), 185 (23), 184 (100), 183 (24), 111 (21), 83 (14), 77 (14).

Diethyl [(Alkylidene)amino]methylphosphonates 6–9; General Procedure
To a solution of the appropriate diethyl aminomethylphosphonate **2**–**5** (5 mmol) and aldehyde **1** (5 mmol) in CH_2Cl_2 (10 mL) in a 50 mL flask, was added anhyd $MgSO_4$ (0.30 g). The reaction mixture was protected from moisture by a $CaCl_2$ tube on top of the condenser and was heated under reflux for 3 h. The mixture was then cooled to r.t. and the $MgSO_4$ was filtered off. The solvent was removed under reduced pressure to afford the imines **6**–**9** in 93–98% yields as yellowish oils with a purity of >95%.

Diethyl {[(*E*)-2-Methyl-1-propylidene]amino}methylphosphonate (6a)
Synthesized according to the general procedure with diethyl aminomethylphosphonate (**2**) and aldehyde **1a**; yield: 1.08 g (98%); yellowish oil.

IR (neat): 1670, 1250 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.09 (6 H, t, *J* = 6.9 Hz, CH_3), 1.34 [6 H, t, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 2.51 (1 H, m, CH), 3.85 (2 H, d, $J_{H,P}$ = 17.2 Hz, NCH_2P), 4.16 [4 H, m, P(O)OC*H*$_2$CH$_3$], 7.61 (1 H, t, *J* = 4.6 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 16.47 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 19.03 (2 CH_3), 34.34 (CH), 57.00 (d, $J_{C,P}$ = 155.7 Hz, NCH_2P), 62.35 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 175.06 (d, $J_{C,P}$ = 14.3 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 23.06.

MS: *m*/*z* = 178 (4), 152 (57), 125 (100), 108 (36), 97 (50), 84 (45), 80 (20), 65 (13), 55 (23).

Diethyl {[(*E*)-2-Ethyl-1-butylidene]amino}methylphosphonate (6b)
Synthesized according to the general procedure with diethyl aminomethylphosphonate (**2**) and aldehyde **1b**; yield: 1.21 g (97%); yellowish oil.

IR (neat): 1663 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.90 (6 H, t, *J* = 7.4 Hz, CH_3), 1.33 [6 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.49 (4 H, quint, *J* = 7.5 Hz, CH_2), 2.12 (1 H, q, *J* = 6.6 Hz, CH), 3.88 (2 H, d, $J_{H,P}$ = 17.2 Hz, NCH_2P), 4.16 [4 H, m, P(O)OC*H*$_2$CH$_3$], 7.49 (1 H, d, *J* = 5.1 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 11.54 (2 CH_3), 16.47 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 24.87 (2 CH_2), 48.54 (d, $J_{C,P}$ = 2.4 Hz, CH), 57.09 (d, $J_{C,P}$ = 153.8 Hz, NCH_2P), 62.26 [2 C, d, $J_{C,P}$ = 7.3 Hz, P(O)O*C*H$_2$CH$_3$], 174.58 (d, $J_{C,P}$ = 15.9 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 23.17.

MS: *m*/*z* = 152 (67), 125 (100), 108 (35), 97 (42), 83 (29), 65 (23), 55 (27), 41 (31).

Diethyl {[(*E*)-Cyclohexylmethylidene]amino}methylphosphonate (6c)
Synthesized according to the general procedure with diethyl aminomethylphosphonate (**2**) and aldehyde **1c**; yield: 1.28 g (98%); yellowish oil.

IR (neat): 1659 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.27–1.35 (6 H, m, $CH_2CH_2CH_2$), 1.34 [6 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.64–1.84 (4 H, m, 2 CH_2), 2.25 (1 H, m, CH), 3.85 (2 H, d, $J_{H,P}$ = 17.2 Hz, NCH_2P), 4.16 [4 H, m, P(O)OC*H*$_2$CH$_3$], 7.58 (1 H, t, $J_{H,P}$ = 4.8 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 16.38 [2 C, d, J_{CP} = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 25.22 (2 CH_2), 25.89 (CH_2), 29.23 (2 CH_2), 43.40 (CH), 57.09 (d, $J_{C,P}$ = 153.7 Hz, NCH_2P), 62.15 [2 C, d, $J_{C,P}$ = 7.3 Hz, P(O)O*C*H$_2$CH$_3$], 174.82 (d, $J_{C,P}$ = 14.6 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 23.13.

MS: *m*/*z* = 261 (1, [M^+]), 206 (6), 193 (19), 152 (74), 125 (100), 108 (35), 97 (31), 95 (22), 83 (15), 55 (12), 41 (19).

Diethyl {[(*E*)-2-Methyl-1-propylidene]amino}(phenyl)methylphosphonate (7a)
Synthesized according to the general procedure with diethyl amino(phenyl)methylphosphonate (**3**) and aldehyde **1a**; yield: 1.46 g (98%); yellowish oil.

IR (neat): 1663 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.11 (3 H, d, *J* = 7.9 Hz, CH_3), 1.12 (3 H, d, *J* = 7.1 Hz, CH_3), 1.22 [6 H, m, P(O)OCH$_2$C*H*$_3$], 2.57 (1 H, m, CH), 4.01 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.66 (1 H, d, $J_{H,P}$ = 18.1 Hz, NCHP), 7.31 (3 H, m, CH), 7.55 (2 H, m, CH), 7.71 (1 H, t, $J_{H,P}$ = 4.8 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 16.26 [$J_{C,P}$ = 4.9 Hz, P(O)OCH$_2$*C*H$_3$], 16.30 [$J_{C,P}$ = 4.9 Hz, P(O)OCH$_2$*C*H$_3$], 18.99 (2 CH_3), 34.30 (CH), 62.84 [2 C, t, $J_{C,P}$ = 7.9 Hz, P(O)O*C*H$_2$CH$_3$], 73.13 (d, $J_{C,P}$ = 152.6 Hz, NCHP), 127.48 (d, $J_{C,P}$ = 3.7 Hz, CH), 128.21 (2 CH), 128.30 (2 CH), 136.35 (d, $J_{C,P}$ = 7.3 Hz, C_{quat}), 173.41 (d, $J_{C,P}$ = 15.9 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 20.73.

MS: *m*/*z* = 297 (1, [M^+]), 265 (2), 229 (10), 228 (83), 172 (21), 161 (14), 160 (100), 134 (6), 91 (5).

Diethyl {[(*E*)-2-Ethyl-1-butylidene]amino}(phenyl)methylphosphonate (7b)

Synthesized according to the general procedure with diethyl amino(phenyl)methylphosphonate (**3)** and aldehyde **1b**; yield: 1.58 g (97%); yellowish oil.

IR (neat): 1662 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.84 (3 H, t, *J* = 7.1 Hz, CH_3), 0.95 (3 H, t, *J* = 7.1 Hz, CH_3), 1.20 [3 H, t, *J* = 7.4 Hz, P(O)OCH$_2$C*H*$_3$], 1.24 [3 H, t, *J* = 7.4 Hz, P(O)OCH$_2$C*H*$_3$], 1.51 (4 H, m, CH_2), 2.22 (1 H, q, *J* = 7.6 Hz, CH), 4.01 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.68 (1 H, d, $J_{H,P}$ = 17.8 Hz, NCHP), 7.32 (3 H, m, CH), 7.57 (3 H, m, CH, HC=N).

^{13}C NMR ($CDCl_3$): δ = 10.51 (CH_3), 10.62 (CH_3), 15.38 [2 C, d, $J_{C,P}$ = 4.9 Hz, P(O)OCH$_2$*C*H$_3$], 23.88 (2 CH_2), 47.39 (CH), 61.74 [2 C, t, $J_{C,P}$ = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 72.44 (d, $J_{C,P}$ = 152.6 Hz, NCHP), 126.56 (CH), 127.30 (4 CH), 135.60 (d, $J_{C,P}$ = 7.3 Hz, C_{quat}), 171.72 (d, $J_{C,P}$ = 15.8 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 20.71.

MS: *m*/*z* = 325 (1, [M^+]), 296 (3), 268 (10), 229 (18), 228 (100), 200 (18), 189 (22), 188 (92), 172 (42), 160 (26), 134 (39), 118 (16), 106 (33), 91 (27), 81 (6).

Diethyl {[(*E*)-Cyclohexylmethylidene]amino}(phenyl)methylphosphonate (7c)

Synthesized according to the general procedure with diethyl amino(phenyl)methylphosphonate (**3**) and aldehyde **1c**; yield: 1.62 g (96%); yellowish oil.

IR (neat): 1662 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.17–1.47 [12 H, m, 3 CH_2, P(O)OCH$_2$C*H*$_3$], 1.64–1.90 (4 H, m, 2 CH_2), 2.30 (1 H, m, CH), 4.03 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.65 (1 H, d, $J_{H,P}$ = 18.1 Hz, NCHP), 7.33 (3 H, m, CH), 7.53 (1 H, m, CH), 7.68 (1 H, t, $J_{H,P}$ = 4.9 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 16.65 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 25.62 (2 CH_2), 26.29 (CH_2), 29.69 (2 CH_2), 43.90 (CH), 63.22 [2 C, t, $J_{C,P}$ = 7.9 Hz, P(O)O*C*H$_2$CH$_3$], 73.57 (d, $J_{C,P}$ = 152.6 Hz, NCHP), 127.81 (d, $J_{C,P}$ = 3.6 Hz, CH), 128.54 (2 C, d, $J_{C,P}$ = 3.7 Hz, CH), 128.64 (2 CH), 136.74 (d, $J_{C,P}$ = 8.6 Hz, C_{quat}), 173.02 (d, $J_{C,P}$ = 14.6 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 20.77.

MS: *m*/*z* = 337 (0.3, [M^+]), 269 (12), 229 (11), 228 (86), 200 (100), 200 (18), 172 (19), 160 (12), 132 (9), 118 (14), 106 (48), 95 (17), 91 (42), 65 (10), 40 (14).

Diethyl (4-Methoxyphenyl){[(*E*)-2-methyl-1-propylidene]amino}methylphosphonate (8a)

Synthesized according to the general procedure with diethyl amino(4-methoxyphenyl)methylphosphonate (**4**) and aldehyde **1a**; yield: 1.60 g (98%); yellowish oil.

IR (neat): 1662, 1610 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.09 (3 H, d, *J* = 6.6 Hz, CH_3), 1.11 (3 H, d, *J* = 6.9 Hz, CH_3), 1.22 [3 H, t, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 1.24 [3 H, t, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 2.56 (1 H, m, CH), 3.80 (3 H, s, OCH_3), 4.03 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.61 (1 H, d, $J_{H,P}$ = 17.5 Hz, NCHP), 6.89 (2 H, d, *J* = 8.9 Hz, CH), 7.45 (2 H, dd, *J* = 8.9 Hz, $J_{H,P}$ = 2.3 Hz, CH), 7.68 (1 H, t, $J_{H,P}$ = 4.8 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 15.47 [2 C, t, $J_{C,P}$ = 4.9 Hz, P(O)OCH$_2$*C*H$_3$9, 18.11 (2 CH_3), 33.37 (CH), 54.12 (OCH_3), 61.83 [2 C, t, $J_{C,P}$ = 7.9 Hz, P(O)O*C*H$_2$CH$_3$], 71.50 (d, $J_{C,P}$ = 153.8 Hz, NCHP), 112.74 (2 CH), 127.44 (d, $J_{C,P}$ = 7.3 Hz, C_{quat}), 128.54 (2 C, d, $J_{C,P}$ = 6.1 Hz, CH), 158.21 (d, $J_{C,P}$ = 3.7 Hz, *C*OCH_3), 172.10 (d, $J_{C,P}$ = 15.9 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 20.84.

MS: *m*/*z* = 327 (2, [M^+]), 258 (15), 191 (14), 190 (100), 175 (6), 134 (10), 121 (19), 111 (9), 91 (87), 85 (17), 65 (10), 57 (11), 55 (9), 40 (12).

Diethyl {[(*E*)-2-Ethyl-1-butylidene]amino}(4-methoxyphenyl)-methylphosphonate (8b)

Synthesized according to the general procedure with diethyl amino(4-methoxyphenyl)methylphosphonate (**4**) and aldehyde **1b**; yield: 1.74 g (98%); yellowish oil.

IR (neat): 1661, 1610 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.84 (3 H, t, *J* = 7.4 Hz, CH_3), 0.94 (3 H, t, *J* = 7.4 Hz, CH_3), 1.23 [6 H, q, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 1.51 (4 H, m, CH_2), 2.20 (1 H, sextet, *J* = 6.6 Hz, CH), 3.80 (3 H, s, OCH_3), 4.01 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.63 (1 H, d, $J_{H,P}$ = 17.1 Hz, NCHP), 6.88 (2 H, d, *J* = 8.6 Hz, CH), 7.46 (2 H, dd, *J* = 8.6 Hz, $J_{H,P}$ = 2.3 Hz, CH), 7.56 (1 H, dd, *J* = 6.6 Hz, $J_{H,P}$ = 4.6 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 11.52 (CH_3), 11.63 (CH_3), 16.40 [d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 16.44 [d, $J_{C,P}$ = 4.9 Hz, P(O)OCH$_2$*C*H$_3$], 24.89 (2 CH_2), 48.35 (CH), 55.06 (s, OCH_3), 62.69 [2 C, t, $J_{C,P}$ = 7.9 Hz, P(O)O*C*H$_2$CH$_3$], 72.71 (d, $J_{C,P}$ = 155.0 Hz, NCHP), 113.67 (2 CH), 128.49 (d, $J_{C,P}$ = 8.5 Hz, C_{quat}), 129.42 (2 C, d, $J_{C,P}$ = 6.1 Hz, CH), 159.13 (d, $J_{C,P}$ = 2.5 Hz, *C*OCH_3), 172.55 (d, $J_{C,P}$ = 15.8 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 21.07.

MS: *m*/*z* = 355 (0.2, [M^+]), 299 (2), 265 (2), 258 (36) 219 (17), 218 (100) 190 (5), 136 (24), 121 (20), 111 (8), 40 (32).

Diethyl {[(*E*)-Cyclohexylmethylidene]amino}(4-methoxyphenyl)methylphosphonate (8c)

Synthesized according to the general procedure with diethyl amino(4-methoxyphenyl)methylphosphonate (**4)** and aldehyde **1c**; yield: 1.78 g (97%); yellowish oil.

IR (neat): 1661, 1610 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.17–1.38 [12 H, m, 3 CH_2, P(O)OCH$_2$C*H*$_3$], 1.65–1.91 (4 H, m, 2 CH_2), 2.30 (1 H, m, CH), 3.79 (3 H, s, OCH_3), 4.02 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.60 (1 H, d, $J_{H,P}$ = 17.5 Hz, NCHP), 6.88 (2 H, d, *J* = 8.6 Hz, CH), 7.45 (2 H, dd, *J* = 8.6 Hz, $J_{H,P}$ = 2.0 Hz, CH), 7.66 (1 H, t, *J* = 4.8 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 15.42 [2 C, t, $J_{C,P}$ = 4.3 Hz, P(O)OCH$_2$*C*H$_3$], 24.39 (2 CH_2), 25.00 (d, *J* = 8.5 Hz, CH_2), 28.41 (2 CH_2), 42.55 (CH), 54.03 (OCH_3), 61.78 [2 C, t, $J_{C,P}$ = 8.5 Hz, P(O)O*C*H$_2$CH$_3$], 71.55 (d, $J_{C,P}$ = 153.8 Hz, NCHP), 112.63 (2 CH), 127.40 (d, $J_{C,P}$ = 7.3 Hz, C_{quat}), 128.45 (2 C, d, $J_{C,P}$ = 5.9 Hz, CH), 158.13 (d, $J_{C,P}$ = 2.5 Hz, *C*OCH_3), 171.27 (d, $J_{C,P}$ = 14.6 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 20.94.

MS: *m*/*z* = 367 (0.5, [M^+]), 258 (15), 230 (100), 202 (21) 164 (15), 136 (91), 134 (22), 121 (69), 95 (24), 77 (14), 57 (50), 41 (29).

Diethyl (4-Bromophenyl){[(*E*)-2-methyl-1-propylidene]amino}methylphosphonate (9a)

Synthesized according to the general procedure with diethyl amino(4-bromophenyl)methylphosphonate (**5)** and aldehyde **1a**; yield: 1.86 g (99%); yellowish oil.

IR (neat): 1663 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.10 (3 H, d, *J* = 6.9 Hz, CH_3), 1.12 (3 H, d, *J* = 6.9 Hz, CH_3), 1.22 [3 H, t, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 1.25 [3 H, t, *J* = 7.3 Hz, P(O)OCH$_2$C*H*$_3$], 2.57 (1 H, m, CH), 4.03 [4 H, m,

P(O)OCH_2CH$_3$], 4.60 (1 H, d, $J_{H,P}$ = 18.1 Hz, NCHP), 7.44 (4 H, m, CH), 7.71 (1 H, t, J = 4.6 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 16.38 [2 C, d, $J_{C,P}$ = 3.7 Hz, P(O)OCH$_2$CH_3], 18.97 (2 CH$_3$), 34.32 (CH), 62.91 [2 C, t, $J_{C,P}$ = 7.3 Hz, P(O)OCH_2CH$_3$], 72.36 (d, $J_{C,P}$ = 151.4 Hz, NCHP), 121.37 (d, $J_{C,P}$ = 3.7 Hz, CBr), 130.03 (2 C, d, $J_{C,P}$ = 6.1 Hz, CH), 131.23 (2 CH), 135.72 (d, $J_{C,P}$ = 7.3 Hz, C_{quat}), 173.65 (d, $J_{C,P}$ = 14.6 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 19.64.

MS: *m*/*z* = 377/375 (2/3, [M$^+$]), 353 (8), 351 (5), 308 (55), 306 (54), 280 (12), 278 (12), 252 (15), 250 (14), 240 (95), 238 (100), 186 (26), 184 (33), 171 (22), 169 (21), 89 (19), 55 (25), 43 (11).

Diethyl (4-Bromophenyl){[(*E*)-2-ethyl-1-butylidene]amino}methylphosphonate (9b)

Synthesized according to the general procedure with diethyl amino(4-bromophenyl)methylphosphonate (**5**) and aldehyde **1b**; yield: 1.98 g (98%); yellowish oil.

IR (neat): 1661 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.84 (3 H, t, J = 7.4 Hz, CH$_3$), 0.94 (3 H, t, J = 7.4 Hz, CH$_3$), 1.22 [3 H, t, J = 7.1 Hz, P(O)OCH$_2$CH_3], 1.26 [3 H, t, J = 7.1 Hz, P(O)OCH$_2$CH_3], 1.51 (4 H, m, CH$_2$), 2.21 (1 H, sextet, J = 6.5 Hz, CH), 4.02 [4 H, m, P(O)OCH_2CH$_3$], 4.62 (1 H, d, $J_{H,P}$ = 18.1 Hz, NCHP), 7.45 (4 H, m, CH), 7.59 (1 H, dd, J = 6.3 Hz, $J_{H,P}$ = 4.6 Hz, HC=N)

^{13}C NMR ($CDCl_3$): δ = 11.50 (CH$_3$), 11.57 (CH$_3$), 16.39 [2 C, d, $J_{C,P}$ = 4.9 Hz, P(O)OCH$_2$CH_3], 24.81 (2 CH$_2$), 48.37 (CH), 62.91 [2 C, t, $J_{C,P}$ = 7.9 Hz, P(O)OCH_2CH$_3$], 72.69 (d, $J_{C,P}$ = 152.5 Hz, NCHP), 121.46 (d, $J_{C,P}$ = 3.7 Hz, CBr), 129.92 (2 C, d, $J_{C,P}$ = 4.9 Hz, CH), 131.30 (2 CH), 135.70 (d, $J_{C,P}$ = 7.3 Hz, C_{quat}), 173.37 (d, $J_{C,P}$ = 14.7 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 20.06.

MS: *m*/*z* = 405/403 (1/1, [M$^+$]), 353 (6), 309 (97), 307 (100), 268 (80), 266 (82), 252 (30), 250 (31), 171 (38), 169 (38), 89 (17), 65 (10), 57 (11), 55 (18).

Diethyl (4-Bromophenyl){[(*E*)-cyclohexylmethylidene]amino}methylphosphonate (9c)

Synthesized according to the general procedure with diethyl amino(4-bromophenyl)methylphosphonate (**5**) and aldehyde **1c**; yield: 2.04 g (98%); yellowish oil.

IR (neat): 1661 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.22 [3 H, t, J = 7.1 Hz, P(O)OCH$_2$CH_3], 1.25 [3 H, t, J = 7.1 Hz, P(O)OCH$_2$CH_3], 1.30–1.34 (6 H, m, CH$_2$), 1.65–1.85 (4 H, m, CH$_2$), 2.30 (1 H, m, CH), 4.02 [4 H, m, P(O)OCH_2CH$_3$], 4.58 (1 H, d, $J_{H,P}$ = 18.5 Hz, NCHP), 7.44 (4 H, m, CH), 7.68 (1 H, t, $J_{H,P}$ = 4.8 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 16.38 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$CH_3], 25.30 (2 CH$_2$), 25.98 (CH$_2$), 29.31 (2 CH$_2$), 43.52 (CH), 62.95 [2 C, t, $J_{C,P}$ = 7.9 Hz, P(O)OCH_2CH$_3$], 72.48 (d, $J_{C,P}$ = 152.6 Hz, NCHP), 121.39 (d, $J_{C,P}$ = 3.7 Hz, CBr), 129.99 (2 C, d, $J_{C,P}$ = 4.9 Hz, CH), 131.19 (2 C, d, $J_{C,P}$ = 2.5 Hz, CH), 135.70 (d, $J_{C,P}$ = 7.3 Hz, C_{quat}), 172.99 (d, $J_{C,P}$ = 14.6 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 19.80.

MS: *m*/*z* = 417/415 (0.1/0.1, [M$^+$]), 309 (50), 307 (52), 281 (87), 279 (100), 252 (41), 250 (41), 186 (83), 184 (95), 171 (81), 169 (76), 95 (85), 89 (36), 67 (28), 65 (20), 41 (25).

Diethyl [(2-Chloro-1-alkylidene)amino]methylphosphonates 10–13; General Procedure

In a 50 mL flask, the appropriate diethyl [(alkylidene)amino]methylphosphonate **6**–**9** (5 mmol) was dissolved in CCl_4 (15 mL) and *N*-chlorosuccinimide (690 mg, 5.2 mmol, 1.05 equiv) was added. The reaction mixture was protected from moisture by a $CaCl_2$ tube on top of the condenser and was heated under reflux for 1 h. The mixture was cooled for 2 h at –18 °C and the succinimide was filtered. Evaporation of the solvent under vacuum led to the isolation of imine **10**–**13** as yellowish oils in good yields (90–98%) and with a purity of >90% (except for imines **11a**, **12a** and **13a** which were less pure).

Diethyl {[(*E*)-2-Chloro-2-methyl-1-propylidene]amino}methylphosphonate (10a)

Synthesized according to the general procedure with imine **6a**; yield: 1.22 g (95%); yellowish oil. After distillation the yield dropped to 50%; bp 93 °C/0.01 mmHg).

IR (neat): 1662 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.34 [6 H, t, J = 7.3 Hz, P(O)OCH$_2$CH_3], 1.71 (6 H, s, CH$_3$), 3.94 (2 H, dd, $J_{H,P}$ = 17.5 Hz, NCH$_2$P), 4.16 [4 H, dq, J = 6.9, 7.3 Hz, P(O)OCH_2CH$_3$], 7.76 (1 H, d, $J_{H,P}$ = 4.9 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 16.45 [2 C, d, J_{CP} = 6.8 Hz, P(O)OCH$_2$CH_3], 29.09 (CH$_3$), 29.61 (CH$_3$), 56.06 (d, $J_{C,P}$ = 154.4 Hz, NCH$_2$P), 62.62 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH_2CH$_3$], 67.74 (CCl), 169.79 (d, $J_{C,P}$ = 16.6 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 21.64.

MS: *m*/*z* = 219/220 (30), 178 (13), 152 (69), 125 (100), 108 (40), 97 (46), 82 (39), 65 (25).

Diethyl {[(*E*)-2-Chloro-2-ethyl-1-butylidene]amino}methylphosphonate (10b)

Synthesized according to the general procedure with imine **6b**; yield: 1.36 g (96%); yellowish oil.

IR (neat): 1661 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.99 (6 H, t, J = 7.4 Hz, CH$_3$), 1.34 [6 H, t, J = 7.1 Hz, P(O)OCH$_2$CH_3], 1.96 (4 H, m, CH$_2$), 3.95 (2 H, d, $J_{H,P}$ = 17.5 Hz, NCH$_2$P), 4.16 [4 H, m, P(O)OCH_2CH$_3$], 7.68 (1 H, d, $J_{H,P}$ = 5.0 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 8.70 (2 CH$_3$), 16.44 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$CH_3], 31.86 (2 CH$_2$), 56.34 (d, $J_{C,P}$ = 153.8 Hz, NCH$_2$P), 62.51 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH_2CH$_3$], 76.84 (CCl), 169.99 (d, $J_{C,P}$ = 14.7 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 21.98.

MS: *m*/*z* = 281 (5), 247 (15), 232 (15), 152 (81), 150 (23), 125 (100), 110 (45), 108 (47), 97 (52), 84 (48), 51 (44), 49 (65).

Diethyl {[(*E*)-(1-Chlorocyclohexyl)methylidene]amino}methylphosphonate (10c)

Synthesized according to the general procedure with imine **6c**; yield: 1.41 g (95%); yellowish oil.

IR (neat): 1658 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.33 [6 H, t, J = 6.9 Hz, P(O)OCH$_2$CH_3], 1.31–1.74 (6 H, m, CH$_2$), 1.91–1.97 (4 H, m, CH$_2$), 3.95 (2 H, d, $J_{H,P}$ = 17.5 Hz, NCH$_2$P), 4.16 [4 H, m, P(O)OCH_2CH$_3$], 7.69 (1 H, d, $J_{H,P}$ = 3.6 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 15.73 [2 P(O)OCH$_2$CH_3], 21.46 (2 CH$_2$), 24.44 (CH$_2$), 36.05 (2 CH$_2$), 55.46 (d, $J_{C,P}$ = 153.8 Hz, NCH$_2$P), 61.91 [2 C, d, $J_{C,P}$ = 7.3 Hz, P(O)OCH_2CH$_3$], 71.74 (CCl), 169.19 (d, $J_{C,P}$ = 15.8 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 22.01.

MS: *m*/*z* = 260 (15), 242 (8), 207 (9), 193 (16), 152 (68), 150 (23), 125 (100), 122 (59), 108 (51), 95 (51), 86 (33), 51 (34), 49 (52).

Diethyl {[(*E*)-2-Chloro-2-methyl-1-propylidene]amino}(phenyl)methylphosphonate (11a)

Synthesized according to the general procedure with imine **7a** affording 1.61 g of a crude reaction mixture containing **11a** as a yellowish oil.

IR (neat): 1712 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.22 [3 H, t, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 1.23 [3 H, t, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 1.73 (3 H, s, CH_3), 1.77 (3 H, s, CH_3), 4.00 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.78 (1 H, d, $J_{H,P}$ = 18.8 Hz, NCHP), 7.32 (3 H, m, CH), 7.52 (2 H, m, CH), 7.84 (1 H, d, $J_{H,P}$ = 4.9 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 16.23 [d, $J_{C,P}$ = 3.7 Hz, P(O)OCH$_2$*C*H$_3$], 16.32 [d, $J_{C,P}$ = 3.7 Hz, P(O)OCH$_2$*C*H$_3$], 29.15 (CH_3), 29.63 (CH_3), 63.11 [d, $J_{C,P}$ = 7.3 Hz, P(O)O*C*H$_2$CH$_3$], 63.25 [d, $J_{C,P}$ = 7.3 Hz, P(O)O*C*H$_2$CH$_3$], 67.92 (CCl), 72.28 (d, $J_{C,P}$ = 152.6 Hz, NCHP), 127.79 (d, $J_{C,P}$ = 3.7 Hz, CH), 128.31 (4 CH), 135.57 (d, $J_{C,P}$ = 8.5 Hz, C_{quat}), 168.18 (d, $J_{C,P}$ = 15.9 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 19.14.

MS: *m*/*z* = 333/331 (1/1, [M^+]), 296 (24), 294 (25), 229 (42), 195 (48), 159 (38), 136 (39), 109 (100), 107 (83), 79 (96), 53 (31).

Diethyl {[(*E*)-2-Chloro-2-ethyl-1-butylidene]amino}(phenyl)-methylphosphonate (11b)

Synthesized according to the general procedure with imine **7b**; yield: 1.74 g (97%); yellowish oil.

IR (neat): 1714 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.96 (3 H, t, *J* = 7.3 Hz, CH_3), 1.04 (3 H, t, *J* = 7.3 Hz, CH_3), 1.22 [3 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.24 [3 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 2.04 (4 H, m, CH_2), 4.01 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.77 (1 H, d, $J_{H,P}$ = 18.5 Hz, NCHP), 7.33 (3 H, m, CH), 7.51 (2 H, m, CH), 7.78 (1 H, d, $J_{H,P}$ = 4.9 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 8.75 (2 CH_3), 16.35 [2 C, d, $J_{C,P}$ = 4.9 Hz, P(O)OCH$_2$*C*H$_3$], 31.61 (CH_2), 32.20 (CH_2), 63.05 [2 C, t, $J_{C,P}$ = 6.7 Hz, P(O)O*C*H$_2$CH$_3$], 72.28 (d, $J_{C,P}$ = 152.6 Hz, NCHP), 77.05 (CCl), 127.76 (d, $J_{C,P}$ = 2.4 Hz, CH), 128.27 (4 CH), 135.74 (d, $J_{C,P}$ = 7.4 Hz, C_{quat}), 168.38 (d, $J_{C,P}$ = 15.8 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 19.83.

MS: *m*/*z* = 361/359 (2/1, [M^+]), 353 (28), 330 (18), 325 (24), 323 (79), 321 (26), 228 (100), 222 (87), 200 (25), 186 (42), 172 (63), 125 (13), 91 (25).

Diethyl {[(*E*)-(1-Chlorocyclohexyl)methylidene]amino}(phenyl)methylphosphonate (11c)

Synthesized according to the general procedure with imine **7c**; yield: 1.77 g (95%); yellowish oil.

IR (neat): 1714 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.23 [3 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.24 [3 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.58–1.80 (6 H, m, CH_2), 2.00–2.08 (4 H, m, CH_2), 4.01 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.77 (1 H, d, $J_{H,P}$ = 18.5 Hz, NCHP), 7.33 (3 H, m, CH), 7.52 (2 H, m, CH), 7.79 (1 H, d, $J_{H,P}$ = 4.6 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 16.36 [2 C, t, $J_{C,P}$ = 3.1 Hz, P(O)OCH$_2$*C*H$_3$], 22.14 (2 CH_2), 25.14 (CH_2), 36.76 (2 C, d, *J* = 6.1 Hz, CH_2), 62.97 [d, $J_{C,P}$ = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 63.23 [d, $J_{C,P}$ = 7.3 Hz, P(O)O*C*H$_2$CH$_3$], 73.15 ($J_{C,P}$ = 151.4 Hz, NCHP), 72.83 (CCl), 127.77 (d, $J_{C,P}$ = 3.6 Hz, CH), 128.29 (4 CH), 135.71 (d, $J_{C,P}$ = 8.5 Hz, C_{quat}), 168.29 (d, $J_{C,P}$ = 15.8 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 19.75.

MS: *m*/*z* = 373/371 (0.2/0.2, [M^+]), 335 (11), 236 (30), 234 (88), 228 (100), 200 (25), 198 (40), 172 (23), 106 (39), 91 (59), 77 (16), 40 (61).

Diethyl {[(*E*)-2-Chloro-2-methyl-1-propylidene]amino}(4-methoxyphenyl)methylphosphonate (12a)

Synthesized according to the general procedure with imine **8a** affording 1.75 g of crude reaction mixture containing **12a** as a yellowish oil.

IR (neat): 1710 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.24 [6 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.73 (3 H, s, CH_3), 1.76 (3 H, s, CH_3), 3.80 (3 H, s, OCH_3), 4.01 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.72 (1 H, d, $J_{H,P}$ = 18.1 Hz, NCHP), 6.89 (2 H, d, *J* = 8.6 Hz, CH), 7.44 (2 H, dd, *J* = 8.9, 2.3 Hz, CH), 7.81 (1 H, d, $J_{H,P}$ = 4.6 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 16.39 [2 C, $J_{C,P}$ = 4.9 Hz, P(O)OCH$_2$*C*H$_3$], 29.11 (CH_3), 29.15 (CH_3), 55.16 (OCH_3), 62.92 [$J_{C,P}$ = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 63.14 [$J_{C,P}$ = 7.3 Hz, P(O)O*C*H$_2$CH$_3$], 67.96 (CCl), 71.09 ($J_{C,P}$ = 153.8 Hz, NCHP), 113.76 (2 CH), 127.41 (d, $J_{C,P}$ = 8.6 Hz, C_{quat}), 129.44 (2 C, d, $J_{C,P}$ = 6.1 Hz, CH), 159.23 (d, $J_{C,P}$ = 3.7 Hz, *C*OCH$_3$), 167.94 (d, $J_{C,P}$ = 14.6 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 19.91.

MS: *m*/*z* = 361 (1, [M^+]), 258 (20), 257 (13), 228 (12), 226 (32), 224 (100), 188 (36), 155 (20), 135 (20), 134 (14), 121 (18), 91 (11), 77 (7), 40 (22).

Diethyl {[(*E*)-2-Chloro-2-ethyl-1-butylidene]amino}(4-methoxyphenyl)methylphosphonate (12b)

Synthesized according to the general procedure with imine **8b**; yield: 1.93 g (99%); yellowish oil.

IR (neat): 1716 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.96 (3 H, t, *J* = 7.4 Hz, CH_3), 1.04 (3 H, t, *J* = 7.4 Hz, CH_3), 1.24 [6 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 2.03 (4 H, m, CH_2), 3.80 (3 H, s, OCH_3), 4.02 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.73 (1 H, d, $J_{H,P}$ = 17.8 Hz, NCHP), 6.89 (2 H, d, *J* = 8.6 Hz, CH), 7.44 (2 H, dd, *J* = 8.9, 2.3 Hz, CH), 7.76 (1 H, d, $J_{H,P}$ = 4.9 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 8.75 (2 CH_3), 16.36 [d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 16.41 [d, $J_{C,P}$ = 4.8 Hz, P(O)OCH$_2$*C*H$_3$], 31.64 (CH_2), 32.22 (CH_2), 55.15 (OCH_3), 62.94 [2 C, t, $J_{C,P}$ = 7.3 Hz, P(O)O*C*H$_2$CH$_3$], 71.53 ($J_{C,P}$ = 153.8 Hz, NCHP), 76.84 (CCl), 113.78 (2 C, d, $J_{C,P}$ = 2.4 Hz, CH), 127.62 (d, $J_{C,P}$ = 7.3 Hz, C_{quat}), 129.37 (2 C, d, $J_{C,P}$ = 6.1 Hz, CH), 159.20 (d, $J_{C,P}$ = 3.7 Hz, *C*OCH$_3$), 168.13 (d, $J_{C,P}$ = 15.8 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 20.14.

MS: *m*/*z* = 389 (2, [M^+]), 359 (4), 257 (37), 256 (29), 253 (71), 251 (100), 216 (13), 136 (12), 134 (12), 121 (34), 91 (7).

Diethyl {[(*E*)-(1-Chlorocyclohexyl)methylidene]amino}(4-methoxyphenyl)methylphosphonate (12c)

Synthesized according to the general procedure with imine **8c**; yield: 1.95 g (97%); yellowish oil.

IR (neat): 1715 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.24 [6 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.59–1.80 (6 H, m, CH_2), 1.99–2.07 (4 H, m, CH_2), 3.80 (3 H, s, OCH_3), 4.02 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.72 (1 H, d, $J_{H,P}$ = 18.1 Hz, NCHP), 6.89 (2 H, d, $J_{H,P}$ = 8.9 Hz, CH), 7.44 (2 H, dd, *J* = 8.9, 2.3 Hz, CH), 7.76 (1 H, d, $J_{H,P}$ = 4.9 Hz).

^{13}C NMR ($CDCl_3$): δ = 16.36 [d, $J_{C,P}$ = 3.7 Hz, P(O)OCH$_2$*C*H$_3$], 16.45 [d, $J_{C,P}$ = 3.7 Hz, P(O)OCH$_2$*C*H$_3$], 22.17 (2 CH_2), 25.14 (CH_2), 36.73 (CH_2), 36.80 (CH_3), 55.16 (OCH_3), 62.89 [d, $J_{C,P}$ = 7.3 Hz, P(O)O*C*H$_2$CH$_3$], 63.16 (d, $J_{C,P}$ = 7.3 Hz, P(O)O*C*H$_2$CH$_3$), 71.38 (d, $J_{C,P}$ = 152.6 Hz, NCHP), 72.81 (CCl), 113.78 (2 C, d, $J_{C,P}$ = 2.4 Hz, CH), 127.58 (d, $J_{C,P}$ = 7.4 Hz, C_{quat}), 129.42 (2 C, d, $J_{C,P}$ = 6.1 Hz, CH), 159.21 (d, $J_{C,P}$ = 2.5 Hz, *C*OCH$_3$), 168.05 (d, $J_{C,P}$ = 14.6 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 20.08.

MS: *m*/*z* = 403/401 (1/2, [M^+]), 265 (13), 263 (100), 253 (37), 228 (19), 155 (15), 135 (39), 121 (34), 93 (10).

Diethyl (4-Bromophenyl){[(*E*)-2-chloro-2-methyl-1-propylidene]amino}methylphosphonate (13a)

Synthesized according to the general procedure with imine **9a** affording 1.97 g of crude reaction mixture containing **13a** as a yellowish oil.

IR (neat): 1714 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.24 [3 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.25 [3 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.73 (3 H, s, CH_3), 1.76 (3 H, s, CH_3), 4.03 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.72 (1 H, d, $J_{H,P}$ = 18.8 Hz, NCHP), 7.47 (4 H, m, CH), 7.84 (1 H, d, $J_{H,P}$ = 4.6 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 16.32 [2 C, t, $J_{C,P}$ = 4.9 Hz, P(O)OCH$_2$*C*H$_3$], 29.09 (CH_3), 29.63 (CH_3), 63.16 [d, $J_{C,P}$ = 7.3 Hz, P(O)O*C*H$_2$CH$_3$], 63.38 [d, $J_{C,P}$ = 7.3 Hz, P(O)OCH$_2$CH$_3$], 67.76 (CCl), 71.07 (d, $J_{C,P}$ = 151.4 Hz, NCHP), 121.77 (d, $J_{C,P}$ = 3.6 Hz, CBr), 129.94 (2 C, d, $J_{C,P}$ = 6.1 Hz, CH), 131.41 (2 C, d, $J_{C,P}$ = 2.4 Hz, CH), 134.76 (d, $J_{C,P}$ = 8.5 Hz, C_{quat}), 168.62 (d, $J_{C,P}$ = 14.6 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 18.76.

MS: *m*/*z* = 376/374 (1/1, [M^+ – Cl]), 308 (51), 306 (50), 274 (100), 272 (77), 206 (27), 204 (20), 186 (27), 184 (30), 112 (16), 110 (16), 91 (29).

Diethyl (4-Bromophenyl){[(*E*)-2-chloro-2-ethyl-1-butylidene]amino}methylphosphonate (13b)

Synthesized according to the general procedure with imine **9b**; yield: 2.15 g (98%); yellowish oil.

IR (neat): 1716 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.96 (3 H, t, *J* = 7.3 Hz, CH_3), 1.04 (3 H, t, *J* = 7.4 Hz, CH_3), 1.24 [3 H, t, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 1.25 [3 H, t, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 2.03 (4 H, q, *J* = 7.5 Hz, CH_2), 4.02 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.70 (1 H, d, $J_{H,P}$ = 18.5 Hz, NCHP), 7.44 (4 H, m, CH), 7.78 (1 H, d, $J_{H,P}$ = 4.9 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 8.59 (2 CH_3), 16.24 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 31.45 (CH_2), 32.02 (CH_2), 63.04 [2 C, t, $J_{C,P}$ = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 71.46 (d, $J_{C,P}$ = 151.4 Hz, NCHP), 76.73 (CCl), 121.63 (d, $J_{C,P}$ = 4.8 Hz, CBr), 129.74 (2 C, d, $J_{C,P}$ = 4.9 Hz, CH), 131.30 (2 C, d, $J_{C,P}$ = 2.5 Hz, CH), 134.81 (d, $J_{C,P}$ = 7.3 Hz, C_{quat}), 168.67 (d, $J_{C,P}$ = 15.8 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 18.99.

MS: *m*/*z* = 404/402 (5/4, [M^+ – Cl]), 403 (19), 401 (18), 308 (94), 306 (93), 302 (100), 300 (79), 171 (41), 169 (40), 89 (17).

Diethyl (4-Bromophenyl){[(*E*)-(1-chlorocyclohexyl)methylidene]amino}methylphosphonate (13c)

Synthesized according to the general procedure with imine **9c**; yield: 2.14 g (95%); yellowish oil.

IR (neat): 1709 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.24 [3 H, t, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 1.25 [3 H, t, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 1.59–1.80 (6 H, m, CH_2), 1.99–2.06 (4 H, m, CH_2), 4.03 [4 H, m, P(O)OC*H*$_2$CH$_3$], 4.71 (1 H, d, $J_{H,P}$ = 18.8 Hz, NCHP), 7.46 (4 H, m, CH), 7.78 (1 H, d, $J_{H,P}$ = 4.9 Hz, HC=N).

^{13}C NMR ($CDCl_3$): δ = 16.38 [2 C, d, $J_{C,P}$ = 3.7 Hz, P(O)OCH$_2$*C*H$_3$], 22.14 (2 CH_2), 25.08 (CH_2), 36.67 (CH_2), 36.76 (CH_2), 63.04 [d, $J_{C,P}$ = 7.3 Hz, P(O)O*C*H$_2$CH$_3$], 63.30 [d, $J_{C,P}$ = 8.5 Hz, P(O)OCH$_2$CH$_3$], 71.40 (d, $J_{C,P}$ = 152.6 Hz, NCHP), 72.59 (CCl), 121.72 (d, $J_{C,P}$ = 4.9 Hz, CBr), 129.91 (2 C, d, $J_{C,P}$ = 6.1 Hz, CH), 131.39 (2 C, d, $J_{C,P}$ = 2.4 Hz, CH), 134.90 (d, $J_{C,P}$ = 8.5 Hz, C_{quat}), 168.64 (d, $J_{C,P}$ = 14.6 Hz, C=N).

^{31}P NMR ($CDCl_3$): δ = 18.90.

MS: *m*/*z* = 451/449 (3/4, [M^+]), 416 (60), 415 (100), 414 (66), 413 (97), 314 (15), 184 (16), 171 (12), 169 (14), 93 (20).

1-Phosphono-2-aza-1,3-dienes 14–17; General Procedure

NaH (60% in mineral oil, 7.5 mmol) was weighed in a 50 mL flask and was washed twice with pentane (15 mL). After decanting the pentane and addition of THF (10 mL), a solution of the required diethyl [(2-chloro-1-alkylidene)amino]methylphosphonate **10**–**13** (5 mmol) in THF (40 mL) was added dropwise. The flask was placed under N_2 and was stirred overnight at r.t. Then, the flask was fitted with a reflux condenser and the mixture was heated under reflux. The end of the reaction was monitored by TLC. The mixture was cooled to r.t., poured into aq 0.1 M NaOH (25 mL) and extracted with Et_2O (3 × 20 mL). The combined organic layers were ($MgSO_4$) and filtered. Concentration of the reaction mixture under reduced pressure gave phosphonoazadienes **14**–**17** as yellow oils in moderate to good yields (51–83%) and satisfying purity (>90%).

Diethyl (*E*)-{[(*Z*)-2-Methylprop-1-enyl]imino}methylphosphonate (14a)

Synthesized according to the general procedure with imine **10a**; yield: 0.91 g (83%); yellow oil.

IR (neat): 1648, 1561 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.37 [6 H, t, *J* = 7.3 Hz, P(O)OCH$_2$C*H*$_3$], 1.86 (3 H, s, CH_3), 2.05 (3 H, s, CH_3), 4.22 [4 H, m, P(O)OC*H*$_2$CH$_3$], 6.57 (1 H, d, *J* = 1.3 Hz, CH), 7.70 (1 H, d, $J_{H,P}$ = 62.7 Hz, HCP).

^{13}C NMR ($CDCl_3$): δ = 16.40 [2 C, d, J_{CP} = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 18.42 (CH_3), 22.93 (CH_3), 62.93 [2 C, d, J_{CP} = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 138.57 (d, $J_{C,P}$ = 40.3 Hz, CH), 143.86 (C_{quat}), 151.45 (d, $J_{C,P}$ = 228.2 Hz, CHP).

^{31}P NMR ($CDCl_3$): δ = 8.85.

MS: *m*/*z* = 219 (18, [M^+]), 138 (19), 111 (43), 110 (22), 83 (34), 82 (100), 81 (53), 80 (20), 65 (18), 55 (55), 39 (22).

Diethyl (*E*)-{[(*Z*)-2-Ethylbut-1-enyl]imino}methylphosphonate (14b)

Synthesized according to the general procedure with imine **10b**; yield: 0.93 g (75%); yellow oil.

IR (neat): 1635, 1560 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.04 (3 H, t, *J* = 7.6 Hz, CH_3), 1.08 (3 H, t, *J* = 7.6 Hz, CH_3), 1.36 [6 H, t, *J* = 6.8 Hz, P(O)OCH$_2$C*H*$_3$], 2.20 (2 H, q, *J* = 7.6 Hz, CH_2), 2.57 (2 H, q, *J* = 7.6 Hz, CH_2), 4.22 [4 H, m, P(O)OC*H*$_2$CH$_3$], 6.53 (1 H, s, CH), 7.72 (1 H, d, $J_{H,P}$ = 62.7 Hz, CHP).

^{13}C NMR ($CDCl_3$): δ = 12.38 (CH_3), 13.14 (CH_3), 16.40 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 23.38 (CH_2), 27.08 (CH_2), 62.94 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 137.10 (d, $J_{C,P}$ = 40.3 Hz, CH), 151.83 (d, $J_{C,P}$ = 228.3 Hz, CHP), 154.59 (C_{quat}).

^{31}P NMR ($CDCl_3$): δ = 8.86.

MS: *m*/*z* = 247 (16, [M^+]), 138 (14), 111 (42), 110 (100), 109 (43), 94 (33), 82 (28), 65 (17), 55 (36), 41 (22).

Diethyl (*E*)-{[(*Z*)-Cyclohexylidenemethyl]imino}methylphosphonate (14c)

Synthesized according to the general procedure with imine **10c**; yield: 1.04 g (80%); yellow oil.

IR (neat): 1638, 1556 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.36 [6 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.61 (6 H, m, CH_2), 2.21 (2 H, m, CH_2), 2.74 (2 H, m, CH_2), 4.22 [4

H, m, P(O)OCH_2CH$_3$], 6.54 (1 H, d, $J_{H,P}$ = 1.0 Hz, CH), 7.72 (1 H, d, $J_{H,P}$ = 63.0 Hz, CHP).

^{13}C NMR (CDCl$_3$): δ = 16.43 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$CH_3], 26.63 (CH$_2$), 27.62 (CH$_2$), 28.41 (CH$_2$), 28.91 (CH$_2$), 34.68 (CH$_2$), 62.97 [2 C, d, $J_{C,P}$ = 7.3 Hz, P(O)OCH_2CH$_3$], 135.80 (d, $J_{C,P}$ = 40.3 Hz, CH), 151.10 (d, $J_{C,P}$ = 2.4 Hz, C$_{quat}$), 151.97 (d, $J_{C,P}$ = 227.0 Hz, CHP).

^{31}P NMR (CDCl$_3$): δ = 8.27.

MS: *m*/*z* = 259 (14, [M$^+$]), 152 (37), 125 (46), 122 (100), 121 (61), 111 (25), 95 (33), 93 (38), 83 (19), 67 (20), 41 (27).

Diethyl (*E*)-{[(*Z*)-2-Methylprop-1-enyl]imino}(phenyl)methylphosphonate (15a)

Synthesized according to the general procedure with imine **11a**; yield: 1.15 g (78%); yellow oil.

IR (neat): 1635, 1444 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.29 [6 H, t, *J* = 7.3 Hz, P(O)OCH$_2$CH_3], 1.77 (3 H, s, CH$_3$), 2.09 (3 H, s, CH$_3$), 4.22 [4 H, dquint, *J* = 7.3 Hz, $J_{H,P}$ = 2.1 Hz, P(O)OCH_2CH$_3$], 6.68 (1 H, s, NCH), 7.37 (5 H, m, CH).

^{13}C NMR (CDCl$_3$): δ = 16.32 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$CH_3], 18.26 (CH$_3$), 23.29 (d, $J_{C,P}$ = 2.5 Hz, CH$_3$), 63.19 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH_2CH$_3$], 128.33 (2 C, d, $J_{C,P}$ = 3.7 Hz, CH), 128.42 (2 CH), 129.11 (CH), 131.91 (d, $J_{C,P}$ = 31.8 Hz, NCH), 134.21 (d, $J_{C\ P}$ = 31.7 Hz, C$_{quat}$), 143.50 (d, $J_{C,P}$ = 2.5 Hz, C$_{quat}$), 159.52 (d, $J_{C,P}$ = 225.8 Hz, CP).

^{31}P NMR (CDCl$_3$): δ = 8.80.

MS: *m*/*z* = 297 (54, [M$^+$ + 2]), 244 (22), 229 (37), 195 (56), 160 (68), 159 (100), 158 (65), 144 (28), 135 (64), 105 (54), 92 (37), 81 (36), 77 (35).

Diethyl (*E*)-{[(*Z*)-2-Ethylbut-1-enyl]imino}(phenyl)methylphosphonate (15b)

Synthesized according to the general procedure with imine **11b**; yield: 1.20 g (74%); yellow oil.

IR (neat): 1626, 1443 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 0.97 (3 H, t, *J* = 7.6 Hz, CH$_3$), 1.07 (3 H, t, *J* = 7.6 Hz, CH$_3$), 1.29 [6 H, t, *J* = 7.1 Hz, P(O)OCH$_2$CH_3], 2.11 (2 H, q, *J* = 7.5 Hz, CH$_2$), 2.62 (2 H, q, *J* = 7.5 Hz, CH$_2$), 4.22 [4 H, dquint, *J* = 7.2 Hz, $J_{H,P}$ = 2.0 Hz, P(O)OCH_2CH$_3$], 6.66 (1 H, s, NCH), 7.39 (5 H, m, CH).

^{13}C NMR (CDCl$_3$): δ = 11.77 (CH$_3$), 12.47 (CH$_3$), 15.55 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$CH_3], 22.28 (CH$_2$), 26.74 (CH$_2$), 62.41 [2 C, d, $J_{C,P}$ = 7.3 Hz, P(O)OCH_2CH$_3$], 127.52 (2 C, d, $J_{C,P}$ = 3.7 Hz, CH), 127.65 (2 CH), 128.43 (CH), 129.75 (d, $J_{C,P}$ = 32.9 Hz, NCH), 133.44 (d, $J_{C,P}$ = 31.8 Hz, C$_{quat}$), 153.10 (C$_{quat}$), 159.28 (d, $J_{C,P}$ = 227.1 Hz, CP).

^{31}P NMR (CDCl$_3$): δ = 8.37.

MS: *m*/*z* = 323 (36, [M$^+$]), 322 (16), 187 (22), 186 (100), 170 (20), 124 (14), 105 (11), 104 (32), 83 (11), 77 (10), 55 (27), 41 (18).

Diethyl (*E*)-{[(*Z*)-Cyclohexylidenemethyl]imino}(phenyl)methylphosphonate (15c)

Synthesized according to the general procedure with imine **11c**; yield: 1.21 g (72%); yellow oil.

IR (neat): 1628, 1444 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.28 [6 H, t, *J* = 7.1 Hz, P(O)OCH$_2$CH_3], 1.59 (6 H, m, CH$_2$), 2.10 (2 H, m, CH$_2$), 2.73 (2 H, m, CH$_2$), 4.17 [4 H, dquint, *J* = 7.2 Hz, $J_{H,P}$ = 2.6 Hz, P(O)OCH_2CH$_3$], 6.66 (1 H, br s, NCH), 7.37 (5 H, m, CH).

^{13}C NMR (CDCl$_3$): δ = 16.34 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$CH_3], 26.68 (CH$_2$), 27.60 (CH$_2$), 28.43 (CH$_2$), 28.71 (CH$_2$), 34.48 (CH$_2$), 63.21 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH_2CH$_3$], 128.04 (d, $J_{C,P}$ = 13.4 Hz, CH), 128.30 (2 C, d, $J_{C,P}$ = 4.9 Hz, CH), 128.42 (2 CH), 128.90 (d, $J_{C,P}$ = 34.1 Hz, NCH), 134.28 ($J_{C,P}$ = 31.8 Hz, C$_{quat}$), 151.17 (C$_{quat}$), 159.50 ($J_{C,P}$ = 224.8 Hz, CP).

^{31}P NMR (CDCl$_3$): δ = 8.93.

MS: *m*/*z* = 337 (66, [M$^+$ + 2]), 200 (42), 199 (100), 198 (51), 170 (34), 135 (52), 105 (30), 96 (37), 95 (33), 77 (23), 67 (22), 55 (18).

Diethyl (*E*)-(4-Methoxyphenyl){[(*Z*)-2-methylprop-1-enyl]imino}methylphosphonate (16a)

Synthesized according to the general procedure with imine **12a**; yield: 0.83 g (51%); yellow oil.

IR (neat): 1606, 1508 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.30 [6 H, t, *J* = 6.9 Hz, P(O)OCH$_2$CH_3], 1.78 (3 H, s, CH$_3$), 2.08 (3 H, s, CH$_3$), 3.83 (3 H, s, OCH$_3$), 4.20 [4 H, dquint, *J* = 7.2 Hz, $J_{H,P}$ = 1.8 Hz, P(O)OCH_2CH$_3$], 6.75 (1 H, d, $J_{H,P}$ = 1.3 Hz, NCH), 6.93 (2 H, d, *J* = 8.6 Hz, CH), 7.34 (2 H, d, *J* = 8.6 Hz, CH).

^{13}C NMR (CDCl$_3$): δ = 16.25 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$CH_3], 18.15 (CH$_3$), 23.22 (CH$_3$), 55.15 (OCH$_3$), 63.06 [2 C, $J_{C,P}$ = 6.1 Hz, P(O)OCH_2CH$_3$], 113.67 (2 CH), 126.23 (d, $J_{C,P}$ = 33.0 Hz, C$_{quat}$), 129.92 (2 C, d, $J_{C,P}$ = 4.9 Hz, CH), 131.91 (d, $J_{C,P}$ = 31.7 Hz, NCH), 142.64 (C$_{quat}$), 158.96 (d, $J_{C,P}$ = 227.0 Hz, CP), 160.02 (*C*OCH$_3$).

^{31}P NMR (CDCl$_3$): δ = 9.09.

MS: *m*/*z* = 327 (82, [M$^+$ + 2]), 255 (11), 190 (59), 189 (100), 173 (20), 136 (33), 135 (63), 120 (13), 92 (11), 86 (31), 84 (42), 77 (15), 49 (19).

Diethyl (*E*)-{[(*Z*)-2-Ethylbut-1-enyl]imino}(4-methoxyphenyl)methylphosphonate (16b)

Synthesized according to the general procedure with imine **12b**; yield: 1.15 g (65%); yellow oil.

IR (neat): 1605, 1508 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 0.98 (3 H, t, *J* = 7.4 Hz, CH$_3$), 1.07 (3 H, t, *J* = 7.6 Hz, CH$_3$), 1.30 [6 H, t, *J* = 7.1 Hz, P(O)OCH$_2$CH_3], 2.12 (2 H, q, *J* = 7.5 Hz, CH$_2$), 2.60 (2 H, q, *J* = 7.5 Hz, CH$_2$), 4.20 [4 H, dquint, *J* = 7.1 Hz, $J_{H,P}$ = 1.6 Hz, P(O)OCH_2CH$_3$], 6.73 (1 H, s, NCH), 6.93 (2 H, d, *J* = 8.2 Hz, CH), 7.36 (2 H, dd, *J* = 8.9 Hz, $J_{H,P}$ = 1.0 Hz, CH).

^{13}C NMR (CDCl$_3$): δ = 11.97 (CH$_3$), 12.62 (CH$_3$), 15.72 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$CH_3], 22.45 (CH$_2$), 26.87 (CH$_2$), 54.56 (OCH$_3$), 62.51 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH_2CH$_3$], 113.14 (2 CH), 125.62 (d, $J_{C,P}$ = 34.2 Hz, C$_{quat}$), 129.46 (2 C, d, $J_{C,P}$ = 3.6 Hz, CH), 130.00 (d, $J_{C,P}$ = 32.9 Hz, NCH), 152.34 (C$_{quat}$), 158.91 (d, $J_{C,P}$ = 225.9 Hz, CP), 159.64 (*C*OCH$_3$).

^{31}P NMR (CDCl$_3$): δ = 8.79.

MS: *m*/*z* = 354 (2, [M$^+$ + 1]), 353 (12) [M$^+$], 217 (19), 216 (100), 200 (10), 172 (7), 163 (7), 135 (13), 134 (30), 121 (24), 99 (32).

Diethyl (*E*)-{[(*Z*)-Cyclohexylidenemethyl]imino}(4-methoxyphenyl)methylphosphonate (16c)

Synthesized according to the general procedure with imine **12c**; yield: 1.13 g (62%); yellow oil.

IR (neat): 1606, 1509 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.29 [6 H, t, *J* = 7.1 Hz, P(O)OCH$_2$CH_3], 1.59 (6 H, br s, CH$_2$), 2.11 (2 H, m, CH$_2$), 2.70 (2 H, m, CH$_2$), 3.84 (3 H, s, OCH$_3$), 4.17 [4 H, dquint, *J* = 7.2 Hz, $J_{H,P}$ = 2.2 Hz, P(O)OCH_2CH$_3$], 6.73 (1 H, s, NCH), 6.93 (2 H, d, *J* = 8.2 Hz, CH), 7.34 (2 H, d, *J* = 8.2 Hz, CH).

^{13}C NMR ($CDCl_3$): δ = 16.36 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 26.72 (CH$_2$), 27.62 (CH$_2$), 28.46 (CH$_2$), 28.71 (CH$_2$), 34.50 (CH$_2$), 55.22 (OCH$_3$), 63.12 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 113.80 (2 CH), 126.33 (d, $J_{C,P}$ = 32.9 Hz, C_{quat}), 129.11 (d, $J_{C,P}$ = 31.6 Hz, NCH), 130.03 (2 C, d, $J_{C,P}$ = 3.6 Hz, CH), 150.19 ($J_{C,P}$ = 2.5 Hz, *C*OCH$_3$), 159.46 ($J_{C,P}$ = 227 Hz, CP), 160.19 (C_{quat}).

^{31}P NMR ($CDCl_3$): δ = 9.20.

MS: *m*/*z* = 367 (24, [M$^+$ + 2]), 366 (97), 365 (2), 230 (69), 229 (100), 187 (30), 165 (29), 136 (30), 135 (24), 122 (29), 96 (20), 83 (16), 55 (21).

Diethyl (*E*)-(4-Bromophenyl){[(*Z*)-2-methylprop-1-enyl]imino}methylphosphonate (17a)

Synthesized according to the general procedure with imine **13a**; yield: 1.37 g (73%); yellow oil.

IR (neat): 1635, 1586 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.31 [6 H, t, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 1.78 (3 H, s, CH$_3$), 2.09 (3 H, s, CH$_3$), 4.21 [4 H, dquint, *J* = 7.3 Hz, $J_{H,P}$ = 1.9 Hz, P(O)OC*H*$_2$CH$_3$], 6.64 (1 H, d, $J_{H,P}$ = 1.3 Hz, NCH), 7.23 (2 H, dd, *J* = 8.4 Hz, $J_{H,P}$ = 0.8 Hz, CH), 7.54 (2 H, d, *J* = 8.2 Hz, CH).

^{13}C NMR ($CDCl_3$): δ = 16.35 [2 C, d, J_{CP} = 4.9 Hz, P(O)OCH$_2$*C*H$_3$], 18.29 (CH$_3$), 23.32 (CH$_3$), 63.23 [2 C, $J_{C,P}$ = 7.3 Hz, P(O)O*C*H$_2$CH$_3$], 123.50 (CBr), 130.00 (2 C, d, $J_{C,P}$ = 3.7 Hz, CH), 131.68 (2 CH), 131.69 (d, $J_{C,P}$ = 31.7 Hz, NCH), 132.98 (d, $J_{C,P}$ = 33.0 Hz, C_{quat}), 144.36 (d, $J_{C,P}$ = 2.4 Hz, C_{quat}), 158.10 (d, $J_{C,P}$ = 228.3 Hz, CP).

^{31}P NMR ($CDCl_3$): δ = 8.31.

MS: *m*/*z* = 375/373 (10/12, [M$^+$]), 374 (52), 372 (53), 352 (65), 239 (98), 237 (100), 185 (34), 183 (32), 122 (22), 120 (27), 50 (51), 48 (52).

Diethyl (*E*)-(4-Bromophenyl){[(*Z*)-2-ethylbut-1-enyl]imino}methylphosphonate (17b)

Synthesized according to the general procedure with imine **13b**; yield: 1.41 g (70%); yellow oil.

IR (neat): 1708, 1586 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.98 (3 H, t, *J* = 7.4 Hz, CH$_3$), 1.06 (3 H, t, *J* = 7.6 Hz, CH$_3$), 1.31 [6 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 2.12 (2 H, q, *J* = 7.5 Hz, CH$_2$), 2.60 (2 H, q, *J* = 7.6 Hz, CH$_2$), 4.20 [4 H, dquint, *J* = 7.2 Hz, $J_{H,P}$ = 1.7 Hz, P(O)OC*H*$_2$CH$_3$], 6.62 (1 H, s, NCH), 7.25 (2 H, d, *J* = 8.6 Hz, CH), 7.56 (2 H, d, *J* = 8.2 Hz, CH).

^{13}C NMR ($CDCl_3$): δ = 11.95 (CH$_3$), 12.63 (CH$_3$), 15.75 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 22.52 (CH$_2$), 26.97 (CH$_2$), 62.69 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 122.95 (CBr), 129.46 (2 C, d, $J_{C,P}$ = 3.6 Hz, CH), 130.16 (d, $J_{C,P}$ = 40.3 Hz, NCH), 131.07 (2 CH), 132.33 (d, $J_{C,P}$ = 31.8 Hz, C_{quat}), 154.30 (d, $J_{C,P}$ = 2.5 Hz, C_{quat}), 157.83 (d, $J_{C,P}$ = 228.2 Hz, CP).

^{31}P NMR ($CDCl_3$): δ = 7.97.

MS: *m*/z = 403/401 (2/3, [M$^+$]), 402 (12), 400 (12), 265 (96), 263 (100), 184 (32), 182 (26), 157 (10), 154 (11), 55 (32), 41 (17).

Diethyl (*E*)-(4-Bromophenyl){[(*Z*)-cyclohexylidenemethyl]imino}methylphosphonate (17c)

Synthesized according to the general procedure with imine **13c**; yield: 1.66 g (80%); yellow oil.

IR (neat): 1630, 1585 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.30 [6 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.60 (6 H, br s, CH$_2$), 2.11 (2 H, m, CH$_2$), 2.70 (2 H, m, CH$_2$), 4.20 [4 H, dquint, *J* = 7.3 Hz, $J_{H,P}$ = 2.1 Hz, P(O)OC*H*$_2$CH$_3$], 6.62 (1 H, s, NCH), 7.24 (2 H, d, *J* = 8.1 Hz, CH), 7.56 (2 H, d, *J* = 7.9 Hz, CH),

^{13}C NMR ($CDCl_3$): δ = 16.36 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 26.61 (CH$_2$), 27.58 (CH$_2$), 28.39 (CH$_2$), 28.73 (CH$_2$), 34.52 (CH$_2$), 63.27 [2 C, d, $J_{C,P}$ = 7.4 Hz, P(O)O*C*H$_2$CH$_3$], 123.48 (CBr), 128.75 (d, $J_{C,P}$ = 31.7 Hz, NCH), 130.02 (2 C, $J_{C,P}$ = 3.6 Hz, CH), 131.70 (2 CH), 132.99 (d, $J_{C,P}$ = 31.7 Hz, C_{quat}), 152.09 (d, $J_{C,P}$ = 2.5 Hz, C_{quat}), 158.34 ($J_{C,P}$ = 229.5 Hz, CP).

^{31}P NMR ($CDCl_3$): δ = 8.43.

MS: *m*/*z* = 415/413 (15/16, [M$^+$]), 414 (69), 412 (68), 281 (98), 279 (100), 241 (59), 239 (63), 188 (46), 186 (53), 142 (17), 140 (18), 89 (86), 87 (98).

2-(Diethylphosphono)-1-vinylaziridines 18a–c; General Procedure

To a solution of 1-phosphono-2-aza-1,3-dienes **14a–c** (5 mmol) in Et$_2$O (5 mL) were added approximately 5 equivalents of diazomethane (25 mmol) (prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) in Et$_2$O at 0 °C. The mixture was stirred for 5 h at r.t. and the solvent was evaporated under reduced pressure to give 2-(diethylphosphono)-1-vinylaziridines **18a–c** in good yields (68–93%). Supplementary purification could be done by flash chromatography leading to aziridine **18** as a yellowish oil with a purity of >95%.

2-(Diethylphosphono)-1-(2-methylprop-1-enyl)aziridine (18a)

Synthesized according to the general procedure with phosphonoazadiene **14a**; yield: 1.09 g (93%); yellow oil. After flash chromatography, 0.67g (57%) of **18a** was obtained as a yellowish oil; R_f 0.36 [$CHCl_3$–MeCN, 80:20 (1% Et$_3$N)].

IR (neat): 1675 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.34 [6 H, t, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 1.58 (3 H, s, CH$_3$), 1.80 (3 H, s, CH$_3$), 1.71–1.88 (2 H, m, NCH$_2$, NCHP), 2.31–2.37 (1 H, m, NCH$_2$), 4.17 [4 H, m, P(O)OC*H*$_2$CH$_3$], 5.20 (1 H, s, CH).

^{13}C NMR ($CDCl_3$): δ = 16.44 [2 C, d, $J_{C,P}$ = 3.1 Hz, P(O)OCH$_2$*C*H$_3$], 17.02 (CH$_3$), 21.98 (CH$_3$), 33.29 (d, $J_{C,P}$ = 213.7 Hz, NCHP), 33.30 (d, $J_{C,P}$ = 4.9 Hz, NCH$_2$), 62.53 [2 C, d, $J_{C,P}$ = 11.0 Hz, P(O)O*C*H$_2$CH$_3$], 125.78 (C_{quat}), 135.69 (d, $J_{C,P}$ = 6.1 Hz, CH).

^{31}P NMR ($CDCl_3$): δ = 22.52.

MS: *m*/*z* = 233 (11, [M$^+$]), 165 (61), 137 (44), 125 (19), 109 (100), 96 (86), 94 (45), 91 (30), 82 (28), 65 (18), 55 (23), 41 (34).

Anal. Calcd for $C_{10}H_{20}NO_3P$: C, 51.49; H, 8.64; N, 6.01. Found: C, 51.56; H, 8.65; N, 5.97.

2-(Diethylphosphono)-1-(2-ethylbut-1-enyl)aziridine (18b)

Synthesized according to the general procedure with phosphonoazadiene **14b**; yield: 0.89 g (68%). After flash chromatography, 0.39g (30%) of **18b** was obtained as a yellowish oil; R_f 0.33 [$CHCl_3$–MeCN, 80:20 (1% Et$_3$N].

IR (neat): 1657 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.95 (3 H, t, *J* = 7.6 Hz, CH$_3$), 1.01 (3 H, t, *J* = 7.6 Hz, CH$_3$), 1.34 [6 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.75–1.85 (2 H, m, NCH$_2$, NCHP), 1.93 (2 H, q, *J* = 7.4 Hz, CH$_2$), 2.32 (2 H, q, *J* = 7.4 Hz, CH$_2$), 2.27–2.37 (1 H, m, NCH$_2$), 4.17 [4 H, m, P(O)OC*H*$_2$CH$_3$], 5.13 (1 H, s, CH).

^{13}C NMR ($CDCl_3$): δ = 12.54 (CH$_3$), 12.74 (CH$_3$), 16.47 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 21.83 (CH$_2$), 25.93 (CH$_2$), 33.52 (d, $J_{C,P}$ = 213.6 Hz, NCHP), 33.42 (d, $J_{C,P}$ = 4.8 Hz, NCH$_2$), 62.57 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 134.77 (d, $J_{C,P}$ = 7.3 Hz, CH), 137.55 (C_{quat}).

^{31}P NMR ($CDCl_3$): δ = 22.50.

MS: *m*/*z* = 261 (6, [M^+]), 246 (12), 165 (78), 137 (59), 125 (42), 124 (43), 109 (100), 108 (41), 91 (25), 82 (21), 65 (14), 55 (21), 41 (22).

Anal. Calcd for $C_{12}H_{24}NO_3P$: C, 55.16; H, 9.26; N, 5.36. Found: C, 55.23; H, 9.21; N, 5.33.

2-Diethylphosphono-1-(cyclohexylidenemethyl)aziridine (18c)
Synthesized according to the general procedure with phosphonoazadiene **14c**; yield: 0.99 g (72%). After flash chromatography, 0.40 g (29%) of **18c** was obtained as a yellowish oil; R_f 0.52 [$CHCl_3$–MeCN, 80:20 (1% Et_3N)].

IR (neat): 1673 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.34 [6 H, t, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 1.52 (6 H, m, CH_2), 1.74–1.85 (2 H, m, NCH_2, NCHP), 1.94 (2 H, m, CH_2), 2.38 (2 H, m, CH_2), 2.32–2.37 (1 H, m, NCH_2), 4.16 [4 H, m, P(O)OC*H*$_2$CH$_3$], 5.19 (1 H, s, CH).

^{13}C NMR ($CDCl_3$): δ = 16.48 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 26.68 (CH_2), 27.24 (CH_2), 27.60 (CH_2), 28.30 (CH_2), 33.38 (d, $J_{C,P}$ = 213.7 Hz, NCHP), 33.12 (CH_2), 33.50 (d, $J_{C,P}$ = 6.2 Hz, NCH_2), 62.55 [2 C, d, $J_{C,P}$ = 19.0 Hz, P(O)O*C*H$_2$CH$_3$], 133.07 (d, $J_{C,P}$ = 7.3 Hz, CH), 133.51 (C_{quat}).

^{31}P NMR ($CDCl_3$): δ = 22.61.

MS: *m*/*z* = 273 (10, [M^+]), 165 (61), 137 (79), 136 (75), 125 (23), 122 (44), 109 (100), 108 (30), 91 (33), 83 (36), 67 (21), 54 (25), 53 (19), 41 (23).

Anal. Calcd for $C_{13}H_{24}NO_3P$: C, 57.13; H, 8.85; N, 5.12. Found: C, 57.05; H, 8.84; N, 5.16.

3-Diethylphosphono-2-ethoxycarbonyl-1-vinylaziridines 19; General Procedure
To a solution of 1-phosphono-2-aza-1,3-diene **14** (5 mmol) in CH_2Cl_2 (25 mL) was added Yb(OTf)$_3$ (0.5 mmol). The mixture was placed under N_2 and stirred for 5 min at r.t. Ethyl diazoacetate (310 mg, 5.5 mmol) was added dropwise using a syringe. The reaction mixture was stirred for 24 h at r.t. after which the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by means of flash chromatography to afford the pure *cis*-aziridines **19** as yellowish oils.

***cis*-3-Diethylphosphono-2-ethoxycarbonyl-1-(2-methylprop-1-enyl)aziridine (19a)**
Synthesized according to the general procedure with phosphonoazadiene **14a**; yield: 0.61 g (40%); yellowish oil; R_f 0.20 [EtOAc–petroleum ether, 1:1 (1% Et_3N)].

IR (neat): 1753 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.31 [3 H, t, *J* = 7.4 Hz, P(O)OCH$_2$C*H*$_3$], 1.33 [3 H, t, *J* = 6.8 Hz, P(O)OCH$_2$C*H*$_3$], 1.60 (3 H, s, CH_3), 1.82 (3 H, s, CH_3), 2.19 (1 H, dd, $J_{H,P}$ = 18.8 Hz, *J* = 6.9 Hz, NCHP), 2.71 (1 H, dd, $J_{H,P}$ = 5.6 Hz, *J* = 6.9 Hz, NCH), 4.20 [4 H, dq, *J* = 7.3 Hz, $J_{H,P}$ = 1.7 Hz, P(O)OC*H*$_2$CH$_3$], 5.32 (1 H, d, *J* = 1.0 Hz, CH).

^{13}C NMR ($CDCl_3$): δ = 13.95 (CH_3), 16.27 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 16.91 (CH_3), 21.85 (CH_3), 39.63 (d, $J_{C,P}$ = 216.7 Hz, NCHP), 43.87 (d, $J_{C,P}$ = 5.9 Hz, NCH), 61.28 (OCH_2), 62.54 [d, $J_{C,P}$ = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 62.88 [d, $J_{C,P}$ = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 126.63 (C_{quat}), 133.74 (d, $J_{C,P}$ = 6.1 Hz, CH), 166.92 (C=O).

^{31}P NMR ($CDCl_3$): δ = 18.58.

MS: *m*/*z* = 305 (11, [M^+]), 260 (6), 232 (100), 204 (25), 168 (76), 135 (46), 122 (44), 94 (83), 81 (32).

Anal. Calcd for $C_{13}H_{24}NO_5P$: C, 51.14; H, 7.92; N, 4.59. Found: C, 51.17; H, 7.94; N, 4.60.

***cis*-3-Diethylphosphono-2-ethoxycarbonyl-1-(2-ethylbut-1-enyl)aziridine (19b)**
Synthesized according to the general procedure with phosphonoazadiene **14b** ; yield: 0.75 g (45%); yellowish oil; R_f 0.27 [EtOAc–petroleum ether, 1:1 (1% Et_3N)].

IR (neat): 1754 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.94 (3 H, t, *J* = 7.4 Hz, CH_3), 1.01 (3 H, t, *J* = 7.6 Hz, CH_3), 1.30 [6 H, m, P(O)OCH$_2$C*H*$_3$], 1.93 (2 H, q, *J* = 7.3 Hz, CH_2), 2.16 (1 H, dd, $J_{H,P}$ = 18.8 Hz, *J* = 6.9 Hz, NCHP), 2.32 (2 H, q, *J* = 7.6 Hz, CH_2), 2.66 (1 H, dd, $J_{H,P}$ = 5.8 Hz, *J* = 7.0 Hz, NCH), 4.19 [4 H, m, P(O)OC*H*$_2$CH$_3$], 5.21 (1 H, s, CH).

^{13}C NMR ($CDCl_3$): δ = 12.31 (2 CH_3), 13.82 (CH_3), 16.13 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 21.65 (CH_2), 25.64 (CH_2), 39.67 (d, $J_{C,P}$ = 216.1 Hz, NCHP), 43.83 (d, $J_{C,P}$ = 4.9 Hz, NCH), 61.08 (OCH_2), 62.38 [d, $J_{C,P}$ = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 62.74 [d, $J_{C,P}$ = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 132.74 (d, $J_{C,P}$ = 7.4 Hz, CH), 138.29 (C_{quat}), 166.77 (d, $J_{C,P}$ = 2.4 Hz, C=O).

^{31}P NMR ($CDCl_3$): δ = 18.53.

MS: *m*/*z* = 333 (4, [M^+]), 259 (100), 236 (17), 196 (51), 135 (27), 122 (31), 108 (16), 81 (15).

Anal. Calcd for $C_{15}H_{28}NO_5P$: C, 54.04; H, 8.47; N, 4.20. Found: C, 54.12; H, 8.50; N, 4.18.

***cis*-1-Cyclohexylidenemethyl-3-diethylphosphono-2-(ethoxycarbonyl)aziridine (19c)**
Synthesized according to the general procedure with phosphonoazadiene **14c**; yield: 0.74 g (43%); yellowish oil; R_f 0.31 [EtOAc–petroleum ether, 1:1 (1% Et_3N)].

IR (neat): 1753 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.31 [3 H, t, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 1.33 [3 H, t, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 1.53 (6 H, m, CH_2), 1.95 (2 H, m, CH_2), 2.16 (1 H, dd, $J_{H,P}$ = 18.8 Hz, *J* = 6.9 Hz, NCHP), 2.40 (2 H, m, CH_2), 2.69 (1 H, dd, $J_{H,P}$ = 5.8 Hz, *J* = 6.9 Hz, NCH), 4.21 [4 H, m, P(O)OC*H*$_2$CH$_3$], 5.31 (1 H, s, CH).

^{13}C NMR ($CDCl_3$): δ = 13.95 (CH_3), 16.27 [2 C, $J_{C,P}$ = 6.1 Hz, P(O)OCH$_2$*C*H$_3$], 26.40 (CH_2), 26.99 (CH_2), 27.31 (CH_2), 28.07 (CH_2), 32.90 (CH_2), 39.79 (d, $J_{C,P}$ = 216.1 Hz, NCHP), 44.01 (d, $J_{C,P}$ = 4.9 Hz, NCH), 61.31 (OCH_3), 62.60 [d, $J_{C,P}$ = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 62.83 [d, $J_{C,P}$ = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 131.04 (d, $J_{C,P}$ = 6.1 Hz, CH), 134.16 (C_{quat}), 166.93 (C=O).

^{31}P NMR ($CDCl_3$): δ = 18.61.

MS: *m*/*z* = 345 (5, [M^+]), 300 (2), 272 (100), 208 (63), 162 (41), 135 (49), 134 (51), 122 (27), 93 (21), 81 (26).

Anal. Calcd for $C_{16}H_{28}NO_5P$: C, 55.64; H, 8.17; N, 4.06. Found: C, 55.70; H, 8.16; N, 4.10.

2-Diethylphosphono-1-vinyl-3-(trimethylsilyl)aziridines (20); General Procedure
A solution of 1-phosphono-2-aza-1,3-diene **14** (2 mmol) in toluene (10 mL) was placed under N_2. (Trimethylsilyl)diazomethane (3 mmol) was added using a syringe and the reaction mixture was stirred for 48 h under reflux after which the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by means of flash chromatography yielding the pure *cis*-aziridines **20** as yellowish oils.

***cis*-3-Diethylphosphono-1-(2-methylprop-1-enyl)-2-(trimethylsilyl)aziridine (20a)**
Synthesized according to the general procedure with phosphonoazadiene **14a**; yield: 0.22 g (36%); yellowish oil; R_f 0.10 [EtOAc–petroleum ether, 2:8 (1% Et_3N)].

IR (neat): 1674 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.08 [9 H, s, $Si(CH_3)_3$], 1.33 [6 H, t, *J* = 6.9 Hz, P(O)OCH$_2$C*H*$_3$], 1.59 (3 H, s, CH_3), 1.65 (1 H, dd, $J_{H,P}$ = 12.9 Hz, *J* = 5.3 Hz, NCHSi), 1.77 (3 H, s, CH_3), 2.00 (1 H, dd, $J_{H,P}$ = 22.1 Hz, *J* = 5.3 Hz, NCHP), 4.13 [4 H, quint, *J* = 6.9 Hz, P(O)OC*H*$_2$CH$_3$], 5.52 (1 H, s, CH).

^{13}C NMR ($CDCl_3$): δ = –1.89 [3 C, $Si(CH_3)_3$], 16.49 [2 C, t, $J_{C,P}$ = 4.9 Hz, P(O)OCH$_2$*C*H$_3$], 16.96 (CH_3), 22.10 (CH_3), 33.99 (d, $J_{C,P}$ = 3.7 Hz, NCHSi), 36.25 (d, $J_{C,P}$ = 202.0 Hz, NCHP), 62.34 [2 C, d, $J_{C,P}$ = 6.1 Hz, P(O)O*C*H$_2$CH$_3$], 124.85 (C_{quat}), 133.80 (d, $J_{C,P}$ = 7.3 Hz, CH).

^{31}P NMR ($CDCl_3$): δ = 24.45.

MS: *m*/*z* = 305 (55, [M$^+$]), 276 (26), 232 (26), 206 (31), 168 (59), 153 (47), 121 (35), 94 (100), 73 (77).

Anal. Calcd for $C_{13}H_{28}NO_3PSi$: C, 51.12; H, 9.24; N, 4.59. Found: C, 51.21; H, 9.22; N, 4.62.

cis-3-(Diethylphosphono)-1-(2-ethylbut-1-enyl)-2-(trimethylsilyl)aziridine (20b)

Synthesized according to the general procedure with phosphonoazadiene **14b**; yield: 0.28 g (42%); yellowish oil; R_f 0.16 [EtOAc–petroleum ether, 3:7 (1% Et_3N)].

IR (neat): 1660 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.08 [9 H, s, $Si(CH_3)_3$], 0.94 (3 H, t, *J* = 7.6 Hz, CH_3), 0.99 (3 H, t, *J* = 7.6 Hz, CH_3), 1.31 [6 H, m, P(O)OCH$_2$C*H*$_3$], 1.63 (1 H, dd, $J_{H,P}$ = 12.5 Hz, *J* = 5.3 Hz, NCHSi), 1.96 (1 H, dd, $J_{H,P}$ = 22.1 Hz, *J* = 5.3 Hz, NCHP), 2.21 (2 H, q, *J* = 7.0 Hz, CH_2), 2.36 (2 H, q, *J* = 7.0 Hz, CH_2), 4.12 [4 H, q, *J* = 7.3 Hz, P(O)OC*H*$_2$CH$_3$], 5.46 (1 H, s, CH).

^{13}C NMR ($CDCl_3$): δ = –1.74 [3 C, $Si(CH_3)_3$], 12.52 (CH_3), 12.70 (CH_3), 16.49 [d, $J_{C,P}$ = 3.6 Hz, P(O)OCH$_2$*C*H$_3$], 16.58 [d, $J_{C,P}$ = 3.6 Hz, P(O)OCH$_2$*C*H$_3$], 21.69 (CH_2), 26.16 (CH_2), 33.92 (d, $J_{C,P}$ = 3.7 Hz, NCHSi), 36.69 (d, $J_{C,P}$ = 205.7 Hz, NCHP), 62.30 [2 C, t, *J* = 3.6 Hz, P(O)O*C*H$_2$CH$_3$], 132.89 (d, $J_{C,P}$ = 6.1 Hz, CH), 136.33 (C_{quat}).

^{31}P NMR ($CDCl_3$): δ = 24.31.

MS: *m*/*z* = 333 (64, [M$^+$]), 318 (100), 261 (26), 246 (34), 180 (36), 122 (34), 108 (87), 73 (71).

Anal. Calcd for $C_{15}H_{32}NO_3PSi$: C, 54.02; H, 9.67; N, 4.20. Found: C, 54.09; H, 9.63; N, 4.18.

cis-1-(Cyclohexylidenemethyl)-3-diethylphosphono-2-(trimethylsilyl)aziridine (20c)

Synthesized according to the general procedure with phosphonoazadiene **14c**; yield: 0.30 g (44%); yellowish oil; R_f 0.16 [EtOAc–petroleum ether, 3:7 (1% Et_3N)].

IR (neat): 1667 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.08 [9 H, s, $Si(CH_3)_3$], 1.31 [6 H, t, *J* = 7.1 Hz, P(O)OCH$_2$C*H*$_3$], 1.50 (6 H, m, CH_2), 1.61 (1 H, dd, $J_{H,P}$ = 12.5 Hz, *J* = 5.3 Hz, NCHSi), 1.88 (2 H, m, CH_2), 1.95 (1 H, dd, $J_{H,P}$ = 22.1 Hz, *J* = 5.3 Hz, NCHP), 2.25 (2 H, m, CH_2), 4.11 [4 H, m, P(O)OC*H*$_2$CH$_3$], 5.50 (1 H, s, CH).

^{13}C NMR ($CDCl_3$): δ = –1.67 [3 C, $Si(CH_3)_3$], 16.46 [d, $J_{C,P}$ = 2.5 Hz, P(O)OCH$_2$*C*H$_3$], 16.55 [d, $J_{C,P}$ = 2.5 Hz, P(O)OCH$_2$*C*H$_3$], 26.77 (CH_2), 27.10 (CH_2), 27.29 (CH_2), 28.21 (CH_2), 33.35 (CH_2), 33.75 (NCHSi), 36.82 (d, $J_{C,P}$ = 202.9 Hz, NCHP), 62.37 [t, $J_{C,P}$ = 4.8 Hz, P(O)O*C*H$_2$CH$_3$], 130.92 (d, $J_{C,P}$ = 7.3 Hz, CH), 132.31 (C_{quat}).

^{31}P NMR ($CDCl_3$): δ = 24.44.

MS: *m*/*z* = 345 (96, [M$^+$]), 330 (13), 273 (62), 244 (15), 208 (47), 180 (27), 134 (100), 122 (49), 106 (52), 73 (88).

Anal. Calcd for $C_{16}H_{32}NO_3PSi$: C, 55.62; H, 9.34; N, 4.05. Found: C, 55.57; H, 9.30; N, 4.09.

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