Synthesis of γ-amino-α,β-unsaturated phosphonates via a substitution-elimination sequence of dibromophosphonates

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Dedicated to Prof. G. Hoornaert on the occasion of his 65th birthday and for his outstanding contributions in organic chemistry

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Abstract

A straightforward multigram synthesis of γ-amino-α,β-unsaturated phosphonates is described via a substitution-elimination sequence of dibromopropylphosphonates with primary amines. Depending on the primary amine, a one or two step procedure was utilized.

Keywords: Aminovinylphosphonates, aminophosphonates, bromopropenylphosphonates

Introduction

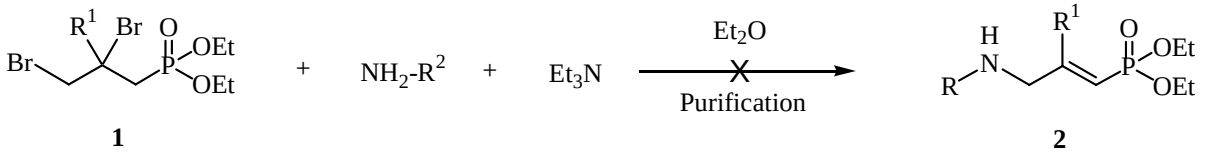
Aminovinylphosphonates and phosphonic acids are important compounds from a biological point of view. It is known that they can act as NMDA antagonists and, therefore they have potential in the treatment of epilepsy, ischemia and migraines.[1,2] They have also attracted an increasing interest because of their clinically useful antimicrobial activity.[3,4] Aminated vinylphosphonates also contain different interesting reactive centers which make them suitable as building block for the synthesis of a range of functionalised phosphonates.

Only a few methods have been described for the synthesis of γ-amino-α,β-unsaturated phosphonates. The corresponding phosphonic acid derivatives have been prepared from allylic α–acetoxyphosphonates in a palladium catalyzed umpolung reaction.[5,6,7] Another route describes the palladium catalyzed amination with *N,O*-protected hydroxylamine derivatives of phosphonylated allylic carbonates.[8,9,10] A similar route was described by Genet[11] et al. by palladium catalyzed alkylations of diethyl aminomethylphosphonate Schiff bases to prepare unsaturated α-aminophosphonates. A slightly different approach describes the palladium catalyzed reaction of 3-acetoxy-1-alkenyl phosphonates with ethyl diphenyl methylene amino

acetate.[12] These pathways, all catalyzed by transition metals, are quite expensive and mostly difficult to scale up. The more straightforward syntheses are very scarce in the literature. A few examples are known, such as the approach to the biologically active *N,O*-protected hydroxylamine phosphonic acids by an allylic bromination of diethyl 1-trans-propenylphosphonate with NBS, followed by substitution with the hydroxylamine derivative. However, the required deprotection of the hydroxylamine derivative could only be performed in 50% yield. A similar strategy was used in the syntheses of homoserine phosphate analogues.[13] Therefore, a method suitable for multigram synthesis is desirable for the further elaboration of the chemistry of these interesting compounds. This manuscript describes a new and short synthesis of an apparently easily preparable class of compounds by a substitution-elimination sequence of dibromophosphonates without the use of any catalyst.

Results and Discussion

In order to prepare γ-aminopropenyl phosphonates, diethyl 2,3-dibromopropylphosphonate **1** was selected as a convenient starting material for a substitution-elimination strategy.
The obvious reaction of one equivalent of primary amines, such as benzylamine or ammonia, with one equivalent of **1** in the presence of one equivalent of triethylamine was evaluated. ^{31}P-NMR showed the appearance of a vinylphosphonate as the major product in the reaction mixture but together with a multitude of unidentified phosphonates (more than 50%), which could not be removed by a purification step (Scheme 1).



1 **2**

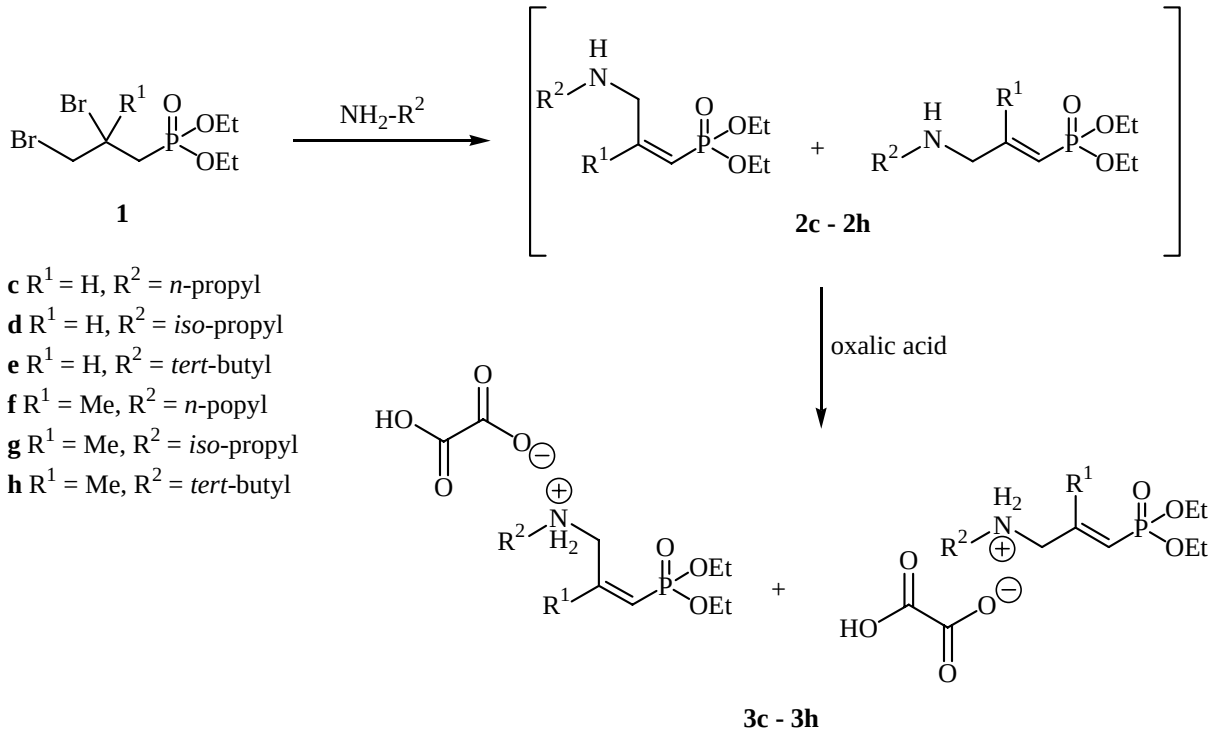
a R^1 = H, R^2 = benzyl
b R^1 = H, R^2 = H

Scheme 1

High vacuum destillation resulted in a total breakdown of the desired aminovinylphosphonates, whereas flash chromatography over silica resulted in complex mixtures and a dramatic loss of material. Also, crystallization of the hydrochloride (prepared by adding an etheral solution of HCl to the aminophosphonate dissolved in ether) failed and no pure fractions could be isolated after preparative gas chromatography.

After extensive experimentation and modification of the preparation and purification procedure, the desired aminophosphonates **2** could be prepared in a suitable way. This optimized

procedure consists of the addition of one equivalent of the dibromophosphonate to three equivalents of primary amine in dichloromethane followed by precipitation of the salt using oxalic acid. The use of oxalic acid is crucial in order to get good results since the more conventionally used hydrochloric acid was not appropriate. Using this procedure, no low yielding protection-deprotection strategies have to be applied. The salts obtained can be stored at room temperature and are stable for months. The free amines could easily be regenerated afterwards using an aqueous solution of NaOH (3N). The E and Z isomers were identified for some derivatives, but were not separated (Scheme2).

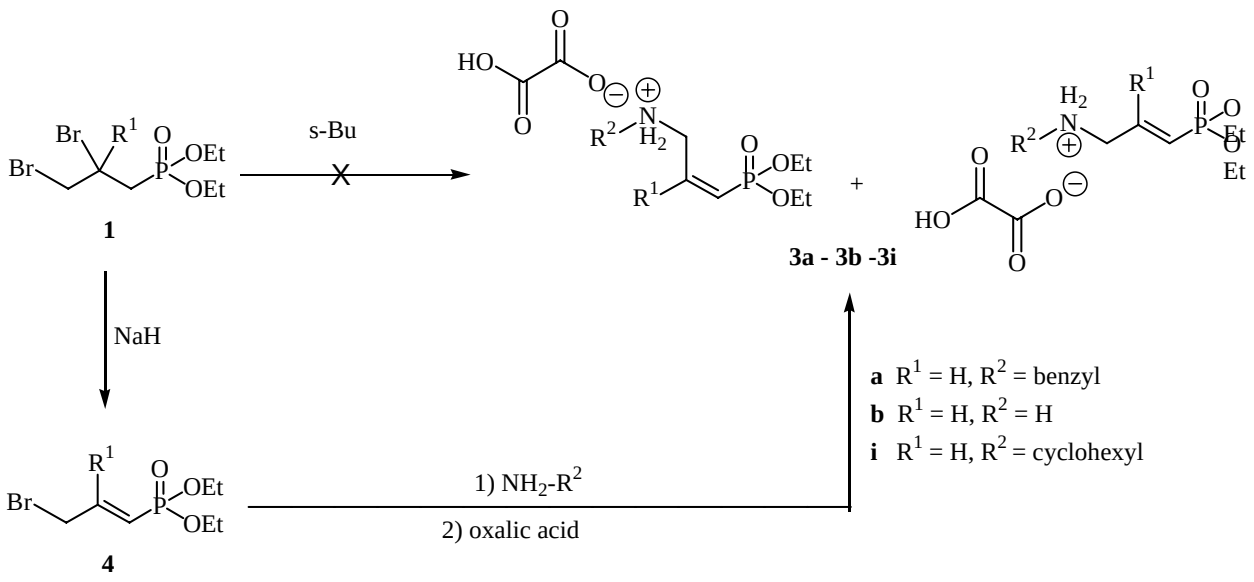


c R^1 = H, R^2 = *n*-propyl
d R^1 = H, R^2 = *iso*-propyl
e R^1 = H, R^2 = *tert*-butyl
f R^1 = Me, R^2 = *n*-popyl
g R^1 = Me, R^2 = *iso*-propyl
h R^1 = Me, R^2 = *tert*-butyl

Scheme 2

Although the procedure works well with a range of amines, it is not general and still failed when benzylamine, cyclohexylamine or ammonia were used as nucleophile. In these cases, the formation of side products could not be suppressed and they could not be separated from the desired vinylphosphonate. Therefore, the elimination-substitution was carried out in two steps using first NaH to induce the elimination, followed by the addition of the primary amine to perform the substitution. Treatment of diethyl (1E)-3-bromoprop-1-enylphosphonate **4** with benzylamine, cyclohexylamine and ammonia resulted, without further purification, in pure γ-amino-α-β-unsaturated phosphonates **2** (Scheme 3). Table 1 gives an overview of the substitution-elimination reactions.

In this way, a multigram synthesis of compound **2b** can easily be carried out.



Scheme 3

Table 1. Substitution-elimination of diethyl 2,3-dibromopropylphosphonate and diethyl 2,3-dibromo-2-methylpropylphosphonate and substitution of diethyl 3-bromopropenyl-phosphonate with primary amines (Spectra were recorded after basic extraction of the salts)

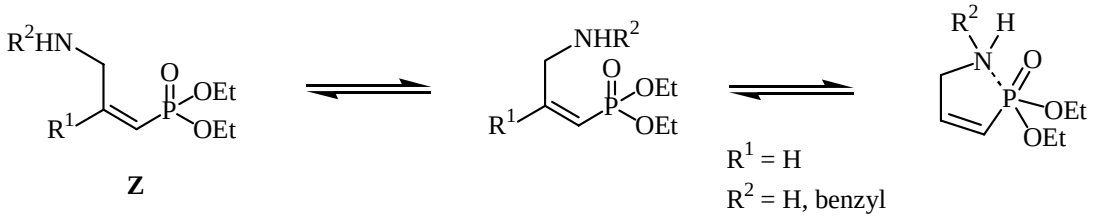
	R_1	R_2	Method	E/Z Ratio	Yield (%)
3c	H	*n*-propyl	A	100/0	94
3d	H	*iso*-propyl	A	100/0	90
3e	H	*tert*-butyl	A	100/0	71
3f	Me	*n*-propyl	A	13/77	89
3g	Me	*iso*-propyl	A	17/83	68
3h	Me	*tert*-butyl	A	31/69	78
3a	H	Benzyl	A	77/13	48
3a	H	Benzyl	B	65/35	93
3b	H	H	A	63/37	19
3b	H	H	B	39/61	97
3i	H	Cyclohexyl	B	100/0	78

Method A: synthesis as indicated in Scheme 2

Method B: synthesis as indicated in Scheme 3

A similar strategy was described with a carbon nucleophile, where the intermediate phosphonate **4** was synthesized by elimination of dibromophosphonate **1** using potassium carbonate.[14] The yield of this reaction, however, was lower than with NaH as a base (Scheme 3).

Considering the E/Z ratio of the aminovinylphosphonates, the disubstituted compounds appear as the E isomer, whereas the trisubstituted compounds appear as a mixture of the E and Z-isomers, with the Z isomer predominating (deduced by comparison of the ^{13}C-value pattern). For compound **2b,** stabilization through a five membered ring due to interaction between the nitrogen atom and the phosphorus atom could rationalize the ratio of the isomers (Scheme 4), as it is known for the intramolecular catalysis of dialkyl ω-aminoalkylphosphonates during hydrolysis.[15] In the case of the benzylamine derivative **2a**, a shift in E/Z ratio was observed after storage of the compound during three months at room temperature, probably due to the same interaction.

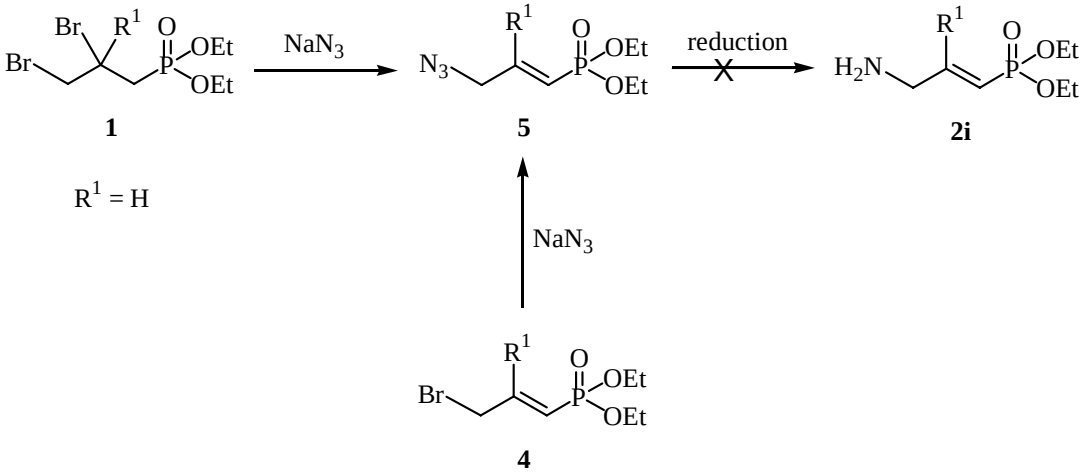


Scheme 4

Although the described procedure is suitable for the synthesis of the unsubstituted amine **3b**, the yield was only 19%. Therefore, another strategy to obtain phosphonate **2b** was evaluated by the reaction of the dibromophosphonate **1** with sodium azide, followed by hydrolysis or reduction. This strategy seemed interesting since only a few pathways leading to **2b** are known in the literature, all requiring multiple steps or giving rise to problems somewhere in the reaction scheme.

Öhler reported a pathway resulting in the azide **5** via the rearrangement of an allylic α-hydroxyphosphonate to an allylic γ-hydroxyphosphonate[16,17] and another one leading to **2b** via a thermal rearrangement of trichloroacetimidic esters of allylic α-hydroxyphosphonates.[18] In general, primary and secondary amines react nicely with 1-acetoxyallylic phosphonates in the presence of palladium, but ammonia failed to do so.[6] However, using sodium azide as a nucleophile resulted smoothly in the synthesis of the corresponding 3-azido-1-alkenylphosphonates. Surprisingly, the azide did not undergo hydrolysis in the presence of Ph_3P according to Murahashi's procedure,[19,20] which describes a palladium catalyzed azidation of allylic acetates followed by hydrolysis resulting in allylic amines. Also Trost[21,22] experienced problems with the hydrolysis of the allylic azide and used a synthon for ammonia, p,p'-dimethoxybenzhydrylamine, as the nucleophile to react with allylic acetates.

Knowing that it would be difficult to hydrolyse the allylic azido function, the easy and big scale synthesis of **5** (Scheme 5) was a motivation to search for an appropriate reduction method. Reductive methods[23] with $SnCl_2$ in MeOH, $NaBH_4$ in MeOH, H_2 / Pd, $NaBH_4$ / 1,3-propanedithiol and Ph_3P all failed. Therefore, the strategy described in Scheme 3 is up to now the most suitable one for the multigram synthesis of **2b** and stays attractive because no protection – deprotection steps are necessary.



Scheme 5

In conclusion, this manuscript describes a straightforward and high yielding synthesis of γ-amino-α,β-unsaturated phosphonates. Considering the literature on some of these and related compounds, it became obvious that this apparently easily obtainable class of compounds needed careful fine tuning of reaction conditions to develop a multigram synthesis. This consideration prompted us to communicate our experience in this field. The utilization of γ-amino-α,β-unsaturated phosphonates for the synthesis of interesting heterocyclic phosphonates will be reported in due course.

Experimental Section

General Procedures. ^{1}H-NMR spectra were recorded at 270 MHz (Jeol JNM EX 270) with $CDCl_3$ as solvent. ^{13}C-NMR spectra were recorded at 68 MHz (Jeol JNM EX 270) with $CDCl_3$ as solvent. ^{31}P-NMR spectra were recorded at 109 MHz (Jeol JNM EX 270) with $CDCl_3$ as solvent and phosphoric acid as internal standard. Mass spectra were obtained on a mass spectrometer (70 eV) using direct inlet. Diethyl ether was distilled from sodium/benzophenone ketyl. Dichloromethane was distilled from CaH_2. Diethyl allylphosphonate can be prepared by Arbuzov reaction of allylbromide and triethylphosphite.[24]

Procedure for the synthesis of diethyl 2,3-dibromopropylphosphonate (1) (R_1=H)

A solution of allylphosphonate (0.1 mol in dichloromethane) was cooled in an ice bath. Bromine (0.12 mol in dichloromethane) was added dropwise and the mixture was left stirring for 2 h at room temperature. This mixture was poored into a saturated solution of Na_2SO_3, extracted with dichloromethane and dried over $MgSO_4$. After evaporation of the solvent, a pale yellow oil was obtained in an equimolar amount and with a purity of 92 %. After high vacuum destillation, the purity was raised to more than 99 % (Yield: 91 %).

Diethyl 2,3-dibromopropylphosphonate (1) (R_1=H). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.35 (6H, m, 2 × $OCH_2C\underline{H}_3$); 2.30 – 2.50 (1H, m, CH-P); 2.70 – 2.85 (1H, m, CH-P); 3.79 (1H, m, CH_2-Br); 3.94 (1H, m, CH_2-Br); 4.15 (4H, m, 2 × $OC\underline{H}_2CH_3$); 4.43 (1H, m, CH-Br). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 16.06 (2 × $OCH_2\underline{C}H_3$); 33.41 ($J_{C\text{-}P}$ = 141.6 Hz, CH_2-P); 37.88 (CH_2-Br); 43.34 (CH-Br, $J_{C\text{-}P}$ = 9.8 Hz); 61.74 ($J_{C\text{-}P}$ = 7.4 Hz, 2 × $O\underline{C}H_2CH_3$). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 24.87. IR (NaCl, cm^{-1}): 1241 (ν P=O). MS (m/z): 341/39/37 (M^++1), 313/11/09, 285/83/81.

Anal. Calcd for $C_7H_{15}Br_2O_3P$: C, 24.88; H, 4.47; Found: C, 24.92; H, 4.49.

Colorless oil; bp = 110°C/0.01 mmHg; Yield after destillation: 91 %; Purity: >99 %.

Procedure for the synthesis of diethyl 2,3-dibromo-2-methylpropylphosphonate (1) (R_1=Me). A solution of methallylphosphonate (0.1 mol in dichloromethane) was cooled in an ice bath. Bromine (0.12 mol in dichloromethane) was added dropwise and the mixture was stirred for 4 h at room temperature. This mixture was poored into a saturated solution of Na_2SO_3, extracted with dichloromethane and dried over $MgSO_4$. After evaporation of the solvent, a pale yellow oil was obtained in 87 % yield and with a purity of 85 %. After high vacuum destillation, the purity was raised to more than 99 % (Yield: 64 %).

Diethyl 2,3-dibromo-2-methylpropylphosphonate (1) (R_1=Me). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.35 (6H, t, J = 7.1 Hz, 2 × $OCH_2C\underline{H}_3$); 2.04 (3H, s, CH_3C-Br); 2.70 (2H, m, CH_2-P); 3.97 (1H, d, J_{AB} = 11 Hz, CH-Br); 4.15 (5H, m, CHBr, 2 × $OC\underline{H}_2CH_3$). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 15.64 ($J_{C\text{-}P}$ = 6 Hz, 2 × $OCH_2\underline{C}H_3$); 31.02 ($J_{C\text{-}P}$ = 7.3 Hz, $\underline{C}H_3C$); 38.54 ($J_{C\text{-}P}$ = 140.3 Hz, CH_2-P); 43.67 ($J_{C\text{-}P}$ = 7.3 Hz, CH_2-Br); 58.90 ($CH_3\underline{C}$); 61.03 ($J_{C\text{-}P}$ = 8.5 Hz, $O\underline{C}H_2CH_3$); 61.14 ($J_{C\text{-}P}$ = 6.1 Hz, $O\underline{C}H_2CH_3$). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 23.81. IR (NaCl, cm $^{-1}$): 1244 (ν P=O). MS (m/z): 351 (M^+-1, 1); 271/73 (48); 215/17 (22); 192 (25); 191 (51); 155 (53); 136 (43); 135 (100); 127 (29); 109 (35); 99 (46); 82 (37); 81 (52).

Anal. Calcd for $C_8H_{17}Br_2O_3P$: C, 27.30; H, 4.87; Found: C, 27.26; H, 4.91.

Colorless oil; bp = 125°C/0.01 mmHg; Yield after destillation: 64 %; Purity: >99 %.

Procedure for the synthesis of diethyl (1E)-3-bromoprop-1-enylphosphonate (4) (R_1=H)

NaH (40 mmol, 60 % in mineral oil) was washed 3 times with petroleumether and dried under vacuum. Dry dichloromethane was then added and the solution was cooled in an ice bath. Diethyl 2,3-dibromopropylphosphonate **1** (R_1=H) (30 mmol in dry dichloromethane) was added dropwise and the mixture was stirred for 24 h at room temperature. The temperature was raised

to reflux for 1 additional hour. Filtration over celite and evaporation of the solvent resulted in a pale yellow oil in 85% yield (purity > 99 %). If purification was strictly needed, flash chromatography was performed over a silica column (pentane : ethylacetate : ethanol / 4 : 5 : 1, R_f = 0.53, Yield = 63 %) or by high vacuum destillation (75°C/0.01 mmHg ,Yield = 56 %).

Diethyl (1E)-3-bromoprop-1-enylphosphonate **(4)** (R_1=H). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.34 (6H, t, J = 7.1 Hz, 2 × $OCH_2C\underline{H}_3$); 4.02 (2H, d, J_{H-P} = 7 Hz, CH_2-Br); 4.11 (4H, d × q, J_{H-P} = J = 7 Hz, 2 × $OC\underline{H}_2CH_3$); 5.94 (1H, d × d, J_{H-P} = 18.2 Hz, J = 16.8 Hz, $C\underline{H}$=CH-P); 6.82 (1H, d × d × t, J_{H-P} = 20.5 Hz, J = 16.5 Hz, J = 6.8 Hz, CH=C<u>H</u>-P) . ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 16.36 (J_{C-P} = 6.1 Hz, 2 × $OCH_2\underline{C}H_3$); 30.57 (J_{C-P} = 26.8 Hz, CH_2-Br); 62.06 (J_{C-P} = 6.2 Hz, 2 × $O\underline{C}H_2CH_3$); 121.28 (J_{C-P} = 186.7 Hz, CH=<u>C</u>H-P); 145.74 (J_{C-P} = 6.1 Hz, <u>C</u>H=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 16.38. IR (NaCl, cm $^{-1}$): 1630 (ν C=C); 1244 (ν P=O). MS (m/z): 257 (M^+, 0.8); 201 (10); 178 (41); 150 (100); 122 (44); 103 (18); 81(10).

Anal. Calcd for $C_7H_{14}BrO_3P$: C, 32.71; H, 5.49; Found: C, 32.85; H, 5.51.

Pale yellow oil; Yield: 85 %; Purity: >99 %.

Procedure A for the synthesis of aminovinylphosphonates (2 and 3)

Solutions of dibromophosphonate **1** (0.03 mol in dry diethyl ether) and primary amine (0.06 mol in dry diethyl ether) were mixed cooling the mixture in an ice bath. These solutions were then mixed, allowed to warm up and brought to reflux temperature. After two hours the mixture was allowed to cool to room temperature. It was poored into 50 ml of 3N NaOH and extracted with 3 × 30 ml dichloromethane. The organic phase was dried over $MgSO_4$. After evaporation of the solvent, the resulting pale yellow oil was dissolved in dry diethyl ether. A 100 ml saturated solution of oxalic acid in ether was prepared (12 g in 100 ml) and filtered just before adding it dropwise to the cooled solution of the yellow oil. The oxalic salt of the γ-amino-α,β-unsaturated phosphonate **3** precipitates and is obtained pure after filtration and drying in vacuo. To record the spectral data, the amines **2** were regenerated with 3N NaOH and extracted with dichloromethane. E/Z isomers were not separated.

Diethyl (1E)-3-(propylamino)prop-1-enylphosphonate (2c). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 0.93 (3H, t, J = 7.3 Hz, CH_3); 1.33 (6H, t, J = 7.1 Hz, 2 × $OCH_2C\underline{H}_3$); 1.52 (2H, sextet, J = 7.3 Hz, $NHCH_2C\underline{H}_2CH_3$); 1.73 (1H, br.s, NH); 2.59 (2H, t, J = 7.1 Hz, $NHC\underline{H}_2CH_2CH_3$); 3.43 (2H, m, $NHC\underline{H}_2CH$=); 4.08 (4H, d × q, J_{H-P} = J = 7.3 Hz, 2 × $OC\underline{H}_2CH_3$); 5.88 (1H, d × d × t, J_{H-P} = 20.8 Hz, J = 17.2 Hz, J = 1.7 Hz, CH=C<u>H</u>-P); 6.83 (1H, d × d × t, J_{H-P} = 22.3 Hz, J = 17.3 Hz, J = 6.8 Hz, C<u>H</u>=CH-P). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 11.72 (CH_3); 16.38 (J_{C-P} = 6.1 Hz, 2 × $OCH_2\underline{C}H_3$); 23.20 ($NHCH_2\underline{C}H_2CH_3$); 51.36 ($NH\underline{C}H_2CH_2CH_3$); 51.66 ($J_{C-P}$ = 22.0 Hz, $NH\underline{C}H_2CH$=); 61.69 (J_{C-P} = 4.9 Hz, 2 × $O\underline{C}H_2CH_3$); 116.78 (J_{C-P} = 187.9 Hz, CH=<u>C</u>H-P); 152.44 (J_{C-P} = 4.9 Hz, <u>C</u>H=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 18.87. IR (NaCl, cm $^{-1}$): 3483 (ν N-H); 1633 (ν C=C); 1244 (ν P=O). MS (m/z): 235 (M^+, 21); 223 (24); 207 (100); 179 (63); 150 (69); 121 (29); 98 (64); 96 (27); 68 (38); 43 (18); 41 (22).

Colorless oil; Yield: 94 %; Purity: 90 %.

Diethyl (1E)-3-(isopropylamino)prop-1-enylphosphonate (2d). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.07 (6H, d, J = 6.3 Hz, $CH(C\underline{H}_3)_2$); 1.33 (6H, t, J = 7.1 Hz, 2 × $OCH_2C\underline{H}_3$); 2.83 (1H, septet, J = 6.2 Hz, $C\underline{H}(CH_3)_2$); 3.42 (2H, m, $NHC\underline{H}_2CH$=); 4.08 (4H, d × q, J_{H-P} = J = 7.3 Hz, 2 × $OC\underline{H}_2CH_3$); 5.87 (1H, d × d × t, J_{H-P} = 20.5 Hz, J = 17.5 Hz, J = 1.7 Hz, CH=C<u>H</u>-P); 6.84 (1H, d × d × t, J_{H-P} = 22.1 Hz, J = 17.2 Hz, J = 4.8 Hz, C<u>H</u>=CH-P). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 16.38 (J_{C-P} = 6.1 Hz, 2 × $OCH_2\underline{C}H_3$); 22.91 ($CH(\underline{C}H_3)_2$); 48.23 ($\underline{C}H(CH_3)_2$); 49.29 (J_{C-P} = 22.0 Hz, $NH\underline{C}H_2CH$=); 61.64 (J_{C-P} = 6.1 Hz, 2 × $O\underline{C}H_2CH_3$); 116.66 (J_{C-P} = 189.2 Hz, CH=<u>C</u>H-P); 151.71 (J_{C-P} = 4.8 Hz, <u>C</u>H=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 18.98. IR (NaCl, cm $^{-1}$): 3295 (ν N-H); 1635 (ν C=C); 1241 (ν P=O). MS (m/z): 235 (M^+, 15); 220 (53); 206 (22); 192 (100); 164 (35); 136 (16); 121 (18); 98 (36); 86 (19); 84 (29); 82 (37); 56 (15).

Anal. Calcd for $C_{10}H_{22}NO_3P$: C, 51.05; H, 9.43; N, 5.95; Found: C, 51.23; H, 9.48, N 5.87. Colorless oil; Yield: 90 %; Purity: >99 %.

Diethyl (1E)-3-(*tert*-butylamino)prop-1-enylphosphonate (2e). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.12 (9H, s, $C(C\underline{H}_3)_3$); 1.33 (6H, t, J = 7.1 Hz, 2 × $OCH_2C\underline{H}_3$); 3.39 (2H, m, $NHC\underline{H}_2CH$=); 4.08 (4H, d × q, J_{H-P} = J = 7.3 Hz, 2 × $OC\underline{H}_2CH_3$); 5.92 (1H, d × d × t, J_{H-P} = 21.1 Hz, J = 17.2 Hz, J = 1.8 Hz, CH=C<u>H</u>-P); 6.87 (1H, d × d × t, J_{H-P} = 22.1 Hz, J = 17.2 Hz, J = 4.8 Hz, C<u>H</u>=CH-P). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 16.38 (J_{C-P} = 6.1 Hz, 2 × $OCH_2\underline{C}H_3$); 29.02 ($C(\underline{C}H_3)_3$); 45.02 (J_{C-P} = 23.2 Hz, $NH\underline{C}H_2CH$=); 50.48 ($\underline{C}(CH_3)_3$); 61.58 (J_{C-P} = 4.9 Hz, 2 × $O\underline{C}H_2CH_3$); 116.25 (J_{C-P} = 189.2 Hz, CH=<u>C</u>H-P); 152.36 (J_{C-P} = 4.9 Hz, <u>C</u>H=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 19.07. IR (NaCl, cm $^{-1}$): 3478 (ν N-H); 1634 (ν C=C); 1246 (ν P=O). MS (m/z): 249 (M^+, 2); 234 (100); 206 (17); 192 (82); 160 (20); 96 (20); 86 (26); 84 (41).

Anal. Calcd for $C_{11}H_{24}NO_3P$: C, 53.00; H, 9.70; N, 5.62; Found: C, 52.86; H, 9.63; N, 5.60. Colorless oil; Yield: 71 %; Purity: >99 %.

Diethyl (1Z)-2-methyl-3-(propylamino)prop-1-enylphosphonate (2f). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 0.92 (3H, t, J = 7.3 Hz, $NHCH_2CH_2C\underline{H}_3$); 1.33 (6H, t, J = 6.9 Hz, 2 × $OCH_2C\underline{H}_3$); 1.51 (2H, sextet, J = 7.3 Hz, $NHCH_2C\underline{H}_2CH_3$); 2.08 (3H, d, J_{H-P} = 2.6 Hz, CH_3C=); 2.55 (2H, t, J = 7.1 Hz, $NHC\underline{H}_2CH_2CH_3$); 3.27 (2H, s, $NHC\underline{H}_2C$=); 4.08 (4H, d × q, J_{H-P} = J = 7.3 Hz, 2 × $OC\underline{H}_2CH_3$); 5.71 (1H, d, J_{H-P} = 18.8 Hz, C=CH-P). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 11.75 ($NHCH_2CH_2\underline{C}H_3$); 16.40 ($J_{C-P}$ = 6.1 Hz, 2 × $OCH_2\underline{C}H_3$); 18.48 (J_{C-P} = 6.1 Hz, $\underline{C}H_3C$=); 23.25 ($NHCH_2\underline{C}H_2CH_3$); 51.23 ($NH\underline{C}H_2CH_2CH_3$); 57.41 ($J_{C-P}$ = 21.9 Hz, $NH\underline{C}H_2C$=); 61.20 (J_{C-P} = 4.9 Hz, 2 × $O\underline{C}H_2CH_3$); 110.50 (J_{C-P} = 189.2 Hz, C=<u>C</u>H-P); 160.79 (J_{C-P} = 7.3 Hz, <u>C</u>=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 19.30.

Diethyl (1E)-2-methyl-3-(propylamino)prop-1-enylphosphonate (2f). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 0.92 (3H, t, J = 7.3 Hz, $NHCH_2CH_2C\underline{H}_3$); 1.33 (6H, t, J = 6.9 Hz, 2 × $OCH_2C\underline{H}_3$); 1.51 (2H, sextet, J = 7.3 Hz, $NHCH_2C\underline{H}_2CH_3$); 2.00 (3H, s, CH_3C=); 2.55 (2H, t, J = 7.1 Hz, $NHC\underline{H}_2CH_2CH_3$); 3.33 (2H, s, $NHC\underline{H}_2C$=); 4.08 (4H, d × q, J_{H-P} = J = 7.3 Hz, 2 × $OC\underline{H}_2CH_3$); 5.50 (1H, d, J_{H-P} = 18.2 Hz, C=CH-P). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 11.41 ($NHCH_2CH_2\underline{C}H_3$); 16.40 ($J_{C-P}$ = 6.1 Hz, 2 × $OCH_2\underline{C}H_3$); 23.14 ($NHCH_2\underline{C}H_2CH_3$); 24.81 ($J_{C-P}$ = 23.2 Hz, $\underline{C}H_3C$=); 51.03 ($NH\underline{C}H_2CH_2CH_3$); 54.72 ($J_{C-P}$ = 2.5 Hz, $NH\underline{C}H_2C$=); 61.90 (J_{C-P} = 6.1 Hz, 2 × $O\underline{C}H_2CH_3$);

114.00 (J_{C-P} = 180.7 Hz, C=CH-P); 161.77 (J_{C-P} = 6.1 Hz, C=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 17.40.
IR (NaCl, cm $^{-1}$): 3468 (ν N-H); 1639 (ν C=C); 1239 (ν P=O). MS (m/z): 249 (M^+, 21); 220 (58); 192 (27); 174 (22); 146 (18); 112 (84); 86 (64); 84 (100); 82 (18); 49 (15); 47 (19).
E/Z-ratio = 77/13; Colorless oil; Yield: 89 %; Purity: 83 %.

Diethyl (1Z)-3-(isopropylamino)-2-methylprop-1-enylphosphonate (2g). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.06 (6H, d, J = 6.3 Hz, NHCH(CH_3)$_2$); 1.33 (6H, t, J = 7.1 Hz, 2 × OCH_2CH_3); 2.08 (2H, d, J_{H-P} = 3 Hz, CH_3C=); 2.78 (1H, septet, J = 6.1 Hz, NHCH); 3.27 (2H, s, $NHCH_2C$=); 4.07 (4H, d × q, J_{H-P} = J = 7.0 Hz, 2 × OCH_2CH_3); 5.72 (1H, d, J_{H-P} = 18.8 Hz, C=CH-P). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 16.37 (J_{C-P} = 7.3 Hz, 2 × OCH_2CH_3); 18.60 (J_{C-P} = 7.3 Hz, CH_3C=); 22.97 (NHCH(CH_3)$_2$); 48.18 ($NHCH(CH_3)_2$); 54.97 (J_{C-P} = 22.0 Hz, $NHCH_2C$=); 61.22 (J_{C-P} = 4.9 Hz, 2 × OCH_2CH_3); 110.46 (J_{C-P} = 190.5 Hz, C=CH-P); 161.20 (J_{C-P} = 7.3 Hz, C=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 19.36.

Diethyl (1E)-3-(isopropylamino)-2-methylprop-1-enylphosphonate (2g). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.06 (6H, d, J = 6.3 Hz, NHCH(CH_3)$_2$); 1.33 (6H, t, J = 7.1 Hz, 2 × OCH_2CH_3); 2.01 (2H, d, J_{H-P} = 1.0 Hz, CH_3C=); 2.78 (1H, heptet, J = 6.1 Hz, NHCH); 3.33 (2H, s, $NHCH_2C$=); 4.07 (4H, d × q, J_{H-P} = J = 7.0 Hz, 2 × OCH_2CH_3); 5.48 (1H, d, J_{H-P} = 17.4 Hz, C=CH-P). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 16.37 (J_{C-P} = 7.3 Hz, 2 × OCH_2CH_3); 22.97 (NHCH(CH_3)$_2$); 25.02 (J_{C-P} = 23.2 Hz, CH_3C=); 48.18 ($NHCH(CH_3)_2$); 49.68 (J_{C-P} = 6.1 Hz, $NHCH_2C$=); 61.22 (J_{C-P} = 4.9 Hz, 2 × OCH_2CH_3); 114.15 (J_{C-P} = 189.2 Hz, C=CH-P); 161.90 (C=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 17.47.
IR (NaCl, cm $^{-1}$): 3407 (ν N-H); 1638 (ν C=C); 1233 (ν P=O). MS (m/z): 249 (8); 235 (65); 207 (100); 179 (18); 164 (17); 162 (26); 161 (18); 147 (25); 135 (19); 134 (17); 112 (93); 96 (66); 91 (80); 82 (18); 72 (55); 70 (21); 65 (18); 58 (24); 41 (16).
Anal. Calcd for $C_{11}H_{24}NO_3P$: C, 53.00; H, 9.70; N, 5.62; Found: C, 53.23; H, 9.72; N, 5.67.
E/Z-ratio = 83/17; Colorless oil; Yield: 68 %; Purity: >99 %.

Diethyl (1Z)-3-(*tert*-butylamino)-2-methylprop-1-enylphosphonate (2h). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.10 (9H, s, NHC(CH_3)$_3$); 1.33 (6H, t, J = 7.3 Hz, 2 × OCH_2CH_3); 2.09 (3H, d, J_{H-P} = 3.0 Hz, CH_3C=); 3.21 (2H, br.s, $NHCH_2C$=); 4.07 (4H, d × q, J_{H-P} = J = 7.3 Hz, 2 × OCH_2CH_3); 5.81 (1H, d, J_{H-P} = 19.5 Hz, C=CH-P). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 16.40 (J_{C-P} = 6.1 Hz, 2 × OCH_2CH_3); 18.78 (J_{C-P} = 7.3 Hz, CH_3C=); 29.13 (NHC(CH_3)$_3$); 50.37 (J_{C-P} = 2.5 Hz, $NHCH_2C$=); 50.66 ((CH_3)$_3$C); 61.08 (J_{C-P} = 6.1 Hz, 2 × OCH_2CH_3); 110.10 (J_{C-P} = 190.5 Hz, C=CH-P); 162.14 (J_{C-P} = 7.4 Hz, C=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 19.83.

Diethyl (1E)-3-(*tert*-butylamino)-2-methylprop-1-enylphosphonate (2h). ^{1}H-NMR ($CDCl_3$, MHz) δ: 1.13 (9H, s, NHC(CH_3)$_3$); 1.33 (6H, t, J = 7.3 Hz, 2 × OCH_2CH_3); 2.02 (3H, br.s, CH_3C=); 3.45 (2H, d, J_{H-P} = 2.0 Hz, $NHCH_2C$=); 4.07 (4H, d × q, J_{H-P} = J = 7.3 Hz, 2 × OCH_2CH_3); 5.45 (1H, d, J_{H-P} = 18.8 Hz, C=CH-P). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 16.40 (J_{C-P} = 6.1 Hz, 2 × OCH_2CH_3); 25.07 (J_{C-P} = 23.2 Hz, CH_3C=); 29.00 (NHC(CH_3)$_3$); 45.50 (J_{C-P} = 7.3

Hz, NHCH$_2$C=); 50.75 ((CH$_3$)$_3$C); 61.23 (J_{C-P} = 6.1 Hz, 2 × OCH$_2$CH$_3$); 113.52 (J_{C-P} = 188.0 Hz, C=CH-P); 162.73 (J_{C-P} = 7.3 Hz, C=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 17.65.
IR (NaCl, cm $^{-1}$): 3455 (ν N-H); 1638 (ν C=C); 1233 (ν P=O). MS (m/z): 263 (5); 249 (83); 207 (100); 136 (17); 111 (34); 100 (80); 87 (16); 71 (26); 59 (18); 45 (17); 42 (31); 41 (29).
E/Z-ratio = 69/31; Colorless oil; Yield: 78 %; Purity: 95 %.

Procedure B for the synthesis of aminovinylphosphonates 2

A solution of (1E)-3-bromoprop-1-enylphosphonate **4** (2.5 mmol in dry diethyl ether) was added to a solution of the primary amine (2.5 mmol in dry diethyl ether)[25] and triethylamine (2.5 mmol in dry diethyl ether). The mixture was stirred for 24 h at room temperature. After an acid-base extraction (3N HCl/3N NaOH) with dichloromethane, pure γ-amino-α,β-unsaturated phosphonate **2** was obtained as an oil.

Diethyl (1E)-3-(benzylamino)prop-1-enylphosphonate (2a). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.33 (6H, t, J = 7.1 Hz, 2 × OCH$_2$CH$_3$); 1.73 (1H, br.s, NH); 3.44 (2H, m, NHCH$_2$CH=); 3.81 (2H, s, NHCH$_2$C$_6$H$_5$); 4.08 (4H, d × q, J_{H-P} = J = 7.3 Hz, 2 × OCH$_2$CH$_3$); 5.94 (1H, d × d × t, J_{H-P} = 19.6 Hz, J = 18.0 Hz, J = 1.8 Hz, CH=CH-P); 6.77 (1H, d × d × t, J_{H-P} = 22.1 Hz, J = 17.2 Hz, J = 5.2 Hz, CH=CH-P); 7.31 (5H, m, NHCH$_2$C$_6$H$_5$). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 16.37 (J_{C-P} = 7.3 Hz, 2 × OCH$_2$CH$_3$); 50.82 (J_{C-P} = 21.9 Hz, NHCH$_2$CH=); 53.24 (NHCH$_2$C$_6$H$_5$); 61.72 (J_{C-P} = 6.1 Hz, 2 × OCH$_2$CH$_3$); 117.08 (J_{C-P} = 189.2 Hz, CH=CH-P); 126.95-128.55 (NHCH$_2$C$_6$H$_5$); 151.08 (J_{C-P} = 4.9 Hz, CH=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 18.90.

Diethyl (1Z)-3-(benzylamino)prop-1-enylphosphonate (2a). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.33 (6H, t, J = 7.1 Hz, 2 × OCH$_2$CH$_3$); 1.73 (1H, br.s, NH); 3.23 (2H, m, NHCH$_2$CH=); 3.60 (2H, s, NHCH$_2$C$_6$H$_5$); 4.07 (4H, d × q, J_{H-P} = J = 7.3 Hz, 2 × OCH$_2$CH$_3$); 5.94 (1H, d × d × t, J_{H-P} = 19.2 Hz, J = 18.1 Hz, J = 1.6 Hz, CH=CH-P); 6.85 (1H, d × d × t, J_{H-P} = 22.1 Hz, J = 17.2 Hz, J = 5.0 Hz, CH=CH-P); 7.31 (5H, m, NHCH$_2$C$_6$H$_5$). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 16.37 (J_{C-P} = 7.3 Hz, 2 × OCH2CH3); 56.00 (J_{C-P} = 23.2 Hz, NHCH$_2$CH=); 58.35 (NHCH$_2$C$_6$H$_5$); 61.72 (J_{C-P} = 6.1 Hz, 2 × OCH$_2$CH$_3$); 119.07 (J_{C-P} = 189.2 Hz, CH=CH-P); 126.95-128.55 (NHCH$_2$C$_6$H$_5$); 149.81 (J_{C-P} = 4.8 Hz, CH=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 18.21.
IR (NaCl, cm $^{-1}$): 3460 (ν N-H); 1634 (ν C=C); 1244 (ν P=O). MS (ES) (m/z): 284 (M^++1)
Anal. Calcd for $C_{14}H_{22}NO_3P$: C, 59.35; H, 7.83; N, 4.94; Found: C, 59.54; H, 7.87; N, 4.82.
E/Z-ratio = 65/35; Colorless oil; Yield: 93 %; Purity: >99 %.

Diethyl (1E)-3-(cyclohexylamino)prop-1-enylphosphonate (2i). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.04 - 1.23 (6H, m, CH$_{2\ cyclohexyl}$); 1.33 (6H, t, J = 7.1 Hz, 2 × OCH$_2$CH$_3$); 1.60 – 1.99 (4H, m, CH$_{2\ cyclohexyl}$); 2.45 (1H, m, CH$_{2\ cyclohexyl}$); 3.45 (2H, m, NHCH$_2$CH=); 4.08 (4H, d × q, J_{H-P} = J = 7.3 Hz, 2 × OCH$_2$CH$_3$); 5.87 (1H, m, CH=CH-P); 6.84 (1H, d × d × t, J_{H-P} = 22.1 Hz, J = 17.2 Hz, J = 4.8 Hz, CH=CH-P). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 16.38 (J_{C-P} = 6.1 Hz, 2 × OCH2CH3); 24.96 (CH$_{2\ cyclohexyl}$); 26.09 (CH$_{2\ cyclohexyl}$); 33.51 (CH$_{2\ cyclohexyl}$); 48.77 (J_{C-P} = 22.0 Hz, NHCH$_2$CH=); 56.19 (CH $_{cyclohexyl}$); 61.66 (J_{C-P} = 6.1 Hz, 2 × OCH$_2$CH$_3$); 116.56 (J_{C-P} = 189.2 Hz, CH=CH-P); 152.02 (J_{C-P} = 4.9 Hz, CH=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 19.02.

Diethyl (1Z)-3-(cyclohexylamino)prop-1-enylphosphonate (2i). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.04 - 1.23 (6H, m, $CH_{2\ cyclohexyl}$); 1.33 (6H, t, J = 7.1 Hz, 2 × $OCH_2C\underline{H}_3$); 1.60 – 1.99 (4H, m, $CH_{2\ cyclohexyl}$); 2.45 (1H, m, $CH_{2\ cyclohexyl}$); 3.26 (2H, m, $NHC\underline{H}_2CH$=); 4.08 (4H, d × q, J_{H-P} = J = 7.3 Hz, 2 × $OC\underline{H}_2CH_3$); 5.87 (1H, m, CH=C<u>H</u>-P); 6.84 (1H, d × d × t, J_{H-P} = 22.1 Hz, J = 17.2 Hz, J = 4.8 Hz, C<u>H</u>=CH-P). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 16.38 (J_{C-P} = 6.1 Hz, 2 × OCH2<u>C</u>H3); 24.96 ($CH_{2\ cyclohexyl}$); 26.09 ($CH_{2\ cyclohexyl}$); 33.51 ($CH_{2\ cyclohexyl}$); 48.77 (J_{C-P} = 22.0 Hz, NH<u>C</u>H_2CH=); 56.19 ($CH_{\ cyclohexyl}$); 61.66 (J_{C-P} = 6.1 Hz, 2 × O<u>C</u>H_2CH_3); 116.56 (J_{C-P} = 189.2 Hz, CH=<u>C</u>H-P); 152.02 (J_{C-P} = 4.9 Hz, <u>C</u>H=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 18.95.
IR (NaCl, cm $^{-1}$): 3460 (ν N-H); 1633 (ν C=C); 1244 (ν P=O). MS (ES) (m/z): 276 (M^++1)
E/Z-ratio = 85/15; Yellow oil; Yield: 78 %; Purity: 90 %.

Diethyl (E)-3-aminoprop-1-enylphosphonate (2b). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.34 (6H, t, J = 6.9 Hz, 2 × $OCH_2C\underline{H}_3$); 2.23 (1H, br.s, NH); 3.43 (2H, m, $NHC\underline{H}_2CH$=); 4.09 (4H, d × q, J_{H-P} = J = 7.3 Hz, 2 × $OC\underline{H}_2CH_3$); 5.91 (1H, m, CH=C<u>H</u>-P); 6.76 (1H, m, C<u>H</u>=CH-P). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 16.36 (J_{C-P} = 6.1 Hz, 2 × $OCH_2\underline{C}H_3$); 50.71 (J_{C-P} = 22.0 Hz, NH<u>C</u>H_2CH=); 61.72 (J_{C-P} = 4.9 Hz, 2 × O<u>C</u>H_2CH_3); 117.28 (J_{C-P} = 189.2 Hz, CH=<u>C</u>H-P); 150.60 (J_{C-P} = 4.9 Hz, <u>C</u>H=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 18.62.

Diethyl (Z)-3-aminoprop-1-enylphosphonate (2b). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.34 (6H, t, J = 6.9 Hz, 2 × $OCH_2C\underline{H}_3$); 2.23 (1H, br.s, NH); 3.23 (2H, m, $NHC\underline{H}_2CH$=); 4.09 (4H, d × q, J_{H-P} = J = 7.3 Hz, 2 × $OC\underline{H}_2CH_3$); 5.91 (1H, m, CH=C<u>H</u>-P); 6.76 (1H, m, C<u>H</u>=CH-P). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 16.36 (J_{C-P} = 6.1 Hz, 2 × OCH2<u>C</u>H3); 56.12 (J_{C-P} = 21.9 Hz, NH<u>C</u>H_2CH=); 61.80 (J_{C-P} = 4.8 Hz, 2 × O<u>C</u>H_2CH_3); 119.27 (J_{C-P} = 186.8 Hz, CH=<u>C</u>H-P); 149.07 (J_{C-P} = 4.9 Hz, <u>C</u>H=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 17.91.
IR (NaCl, cm $^{-1}$): 3463 (ν N-H); 1634 (ν C=C); 1248 (ν P=O). MS (ES) (m/z): 193 (M^+)
Anal. Calcd for $C_7H_{16}NO_3P$: C, 43.52; H, 8.35; N, 7.25; Found: C, 43.66; H, 8.25; N, 7.21. E/Z-ratio = 39/61; Colorless oil; Yield: 87 %; Purity: >99 %.

Procedure for the synthesis of azidovinylphosphonate 5

To a solution of sodium azide (10 mmol in acetonitrile) diethyl (1E)-3-bromoprop-1-enylphosphonate **4** or diethyl 2,3-dibromopropylphosphonate **1** (R_1=H) (2.5 mmol in acetonitrile) was added. The mixture was stirred under reflux for 2 days. After filtration, drying over $MgSO_4$ and evaporation of the solvent the resulting oil was purified by flash chromatography over a silica column (pentane : ethylacetate : ethanol / 5 : 4 : 1, R_f = 0.5, Yield = 82 %).

Diethyl (1*E*)-3-azidoprop-1-enylphosphonate (5). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.34 (6H, t, J = 7.1 Hz, 2 × $OCH_2C\underline{H}_3$); 4.03 (2H, m, $N_3C\underline{H}_2CH$=); 4.10 (4H, d × q, J_{H-P} = J = 7.3 Hz, 2 × $OC\underline{H}_2CH_3$); 5.99 (1H, d × d × t, J_{H-P} = 18.9 Hz, J = 16.8 Hz, J = 1.9 Hz, CH=C<u>H</u>-P); 6.77 (1H, d × d × t, J_{H-P} = 21.6 Hz, J = 17.0 Hz, J = 4.7 Hz, C<u>H</u>=CH-P). ^{13}C-NMR ($CDCl_3$, 68 MHz) δ: 16.36 (J_{C-P} = 6.1 Hz, 2 × $OCH_2\underline{C}H_3$); 52.37 (J_{C-P} = 23.2 Hz, $N_3\underline{C}H_2CH$=); 61.98 (J_{C-P} = 6.1 Hz, 2 × O<u>C</u>H_2CH_3); 119.80 (J_{C-P} = 188.0 Hz, CH=<u>C</u>H-P); 144.79 (J_{C-P} = 6.1 Hz, <u>C</u>H=CH-P). ^{31}P-NMR ($CDCl_3$, 109 MHz) δ: 17.05.

IR (NaCl, cm $^{-1}$): 2105 (ν N_3); 1636 (ν C=C); 1248 (ν P=O). MS (m/z): 218 (M^+-1, 3); 177 (100); 163 (23); 149 (67); 137 (24); 136 (28); 135 (29); 134 (20); 121 (46); 109 (72); 91 (43); 82 (72); 81 (58); 65 (46); 55 (25); 54 (42)
Anal. Calcd for $C_7H_{14}N_3O_3P$: C, 38.36; H, 6.44; N, 19.17; Found: C, 38.48; H, 6.47; N, 19.11. E/Z-ratio = 100/0; Colorless oil; Yield: 82 %; Purity: >99 %.

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