

Deamination of 1-Aminoalkylphosphonic Acids: Reaction Intermediates and Selectivity

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1. General Informations

The ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{31}P NMR and DEPT-135 spectra were collected on a Jeol 400yh instrument (400 MHz for ^1H NMR, 162 MHz for ^{31}P NMR and 100 MHz for $^{13}\text{C}\{^1\text{H}\}$ NMR) and were processed with dedicated software (Delta 5.0.5). NMR experiments recorded in D_2O were referenced to the respective residual ^1H signal of the solvent. Multiplicities were reported using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). The reported coupling constants (J) values were those observed from the splitting patterns in the spectrum and may not reflect the true coupling constant values. The composition of post-reaction mixtures (as conversion of substrate to the given product) were calculated based on ^{31}P NMR (recorded in D_2O) of the crude reaction mixture. Structural assignments of **5''g** were made with additional information from gCOSY, gHSQC, and gHMBC experiments.

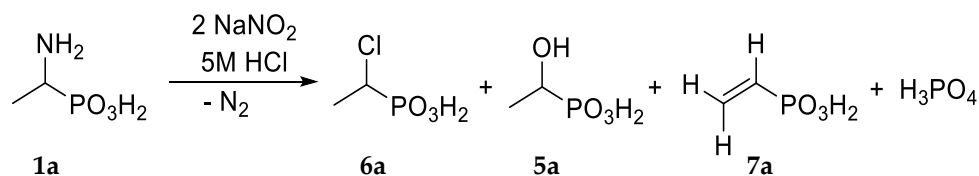
Reagents. Aminomethylphosphonic acid (**1h**) was obtained in the reaction of benzamide, formaldehyde and phosphorous trichloride [1]. 3-Amino-3-phosphonopropanoic acid (**1e**) was synthesized from diethyl acetamidomethylenemalonate [2]. Remaining 1-aminoalkylphosphonic acids **1** were obtained using Sorokas' protocol and the reaction of an appropriate carbonyl compound with acetamide, acetyl chloride and PCl_3 in acetic acid [3].

1-Hydroxyalkylphosphonic acids **5**, which were used as reference materials for confirmation of reaction products structures, were synthesized by dealkylation of diethyl 1-hydroxyalkylphosphonates. The substrates were obtained in the reaction of triethyl phosphite with suitable aldehyde or ketone and hydrogen chloride [4].

2. Deamination of 1-Aminoalkylphosphonic Acids and 2-Aminoalkanoic Acids in 5M HCl

Preliminary deamination experiments were conducted in three-necked flask equipped with reflux condenser, thermometer, dropping funnel and magnetic stirrer, as described in the original protocol [5].

General procedure. Preliminary deamination experiments were conducted in three-necked flask equipped with reflux condenser, thermometer, dropping funnel and magnetic stirrer, as described in the original protocol [5]. The solution of 1-aminoalkylphosphonic acid **1** or 2-aminoalkanoic acid **2** (10 mmol, 1 equiv) in 5M HCl (6.5 equiv, 13mL) was cooled in ice/NaCl cooling bath to temperature $0\text{ }^\circ\text{C}$. Cooled 4M NaNO_2 solution in water (16 mmol, 1.6 equiv, 4.0 mL) was subsequently added dropwise for 2 min. Temperature of the reaction mixture was maintained under $0\text{ }^\circ\text{C}$ for 5h, and then in $25\text{ }^\circ\text{C}$ for 12 h. The samples for ^1H and ^{31}P NMR spectra were prepared by diluting post-reaction mixtures (0.10mL) in D_2O (0.40mL). The samples were re-measured after addition of reference materials. The composition of mixture was calculated based on the integration of signals on the ^{31}P NMR spectra (for phosphorous substrates) or on the ^1H NMR spectra (for 2-aminoalkanoic acids).

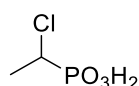
2.1. ABr738. Deamination of **1a** in 5M Hydrochloric Acid

	$\alpha = 0.99$	53%	24%	21%	1%
δ_P [ppm]	16.88 (dq)	20.56 (dq)	25.57 (dq)	17.16 (ddd)	0.39 (s)

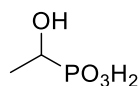
After 12h in 21 °C, post-reaction mixture contained 1-chloroethylphosphonic acid (**6a**) (53%molP), 1-hydroxyethylphosphonic acid (**5a**) (24%molP), vinylphosphonic acid (**7a**) (21%molP), orthophosphoric acid (1%molP) and unreacted substrate **1a** (1%molP) (Figure S1 and Figure S2).

1-Hydroxyethylphosphonic acid (**7a**) was identified on ^1H and ^{31}P NMR spectra by re-measuring the NMR spectra of the reaction mixture with the addition of post-reaction mixture of 1-aminoethylphosphonic acid with NaNO_2 in water (ABr1178), where this compound **5a** was the main product (Figure S3). Vinylphosphonic acid (**7a**) and 1-chlorophosphonic acid (**6a**) were identified by comparing chemical shifts, multiplicity and coupling constants on ^1H and ^{31}P NMR spectra with description in the literature (Table S1) [6, 7].

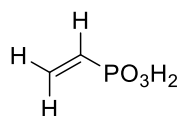
The presence of 1-chloroethylphosphonic acid (**6a**) was additionally confirmed by careful analysis of NMR spectra. In the post-reaction mixture there were two compounds having the structure $-\text{CH}(\text{CH}_3)\text{PO}_3\text{H}_2$ ($\delta_P = 20.56$ ppm and $\delta_P = 25.57$ ppm). 1-Hydroxyethylphosphonic acid (**5a**) ($\delta_P = 25.57$ ppm) was identified earlier. The presence of the unreacted substrate was excluded by re-measuring NMR spectra of post-reaction mixture with addition of 1-aminoethylphosphonic acid (**1a**) (Figure S4), which resulted in appearance of new peak ($\delta_P = 16.88$ ppm). Therefore, the second product was 1-chloroethylphosphonic acid (**6a**) ($\delta_P = 20.56$ ppm).



1-Chloroethylphosphonic acid (6a). ^{31}P NMR (D_2O , ca. 0.8M HCl): δ 20.56 (dq, $^2J_{\text{H-P}} = 9.4$ Hz, $^3J_{\text{H-P}} = 15.9$ Hz); ^1H NMR (D_2O , ca. 0.8M HCl) δ : 3.85 (dq, 1H, $^2J_{\text{H-H}} = 7.3$ Hz, $^2J_{\text{H-P}} = 9.00$ Hz), 1.36 (dd, 3H, $^3J_{\text{H-H}} = 7.3$ Hz, $^3J_{\text{H-P}} = 16.5$ Hz).

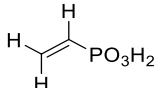
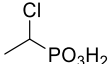


1-Hydroxyethylphosphonic acid (5a). ^{31}P NMR (D_2O , ca. 0.8M HCl): δ 25.57 (dq, $^2J_{\text{H-P}} = 5.6$ Hz, $^3J_{\text{H-P}} = 17.6$ Hz); ^1H NMR (D_2O , ca. 0.8M HCl) δ : 3.77 (dq, 1H, $^2J_{\text{H-P}} = 5.2$ Hz, $^3J_{\text{H-H}} = 7.0$ Hz), 1.16 (dd, 3H, $^3J_{\text{H-H}} = 7.0$ Hz, $^3J_{\text{H-P}} = 17.4$ Hz).



Vinylphosphonic acid (7a). ^{31}P NMR (D_2O , ca. 0.8M HCl) δ : 17.16 (ddd, $^2J_{\text{H-P}} = 24.3$ Hz, $^3J_{\text{H-P (cis)}} = 26.9$ Hz, $^3J_{\text{H-P (trans)}} = 49.3$ Hz); ^1H NMR (D_2O , ca. 0.8M HCl) δ : 5.75–6.03 (m, 3H).

Table S1. Comparison of chemical shifts and coupling constants of 1-aminoethylphosphonic acid (**1a**) deamination products in 5M HCl on ^1H and ^{31}P NMR spectra with literature description.

Structure				
Source	ABr738	Reference [6]	ABr738	Reference [7]
Solvent	D ₂ O, ca. 0.8M HCl	CDCl ₃	D ₂ O, ca. 0.8M HCl	"hydrolyzate"
³¹ P NMR	17.16 (ddd, <i>J</i> = 24.3, 26.9, 49.3 Hz)	17.3 (ddd, <i>J</i> = 20.0, 20.5, 51.3 Hz)	20.56 (dq, <i>J</i> = 9.4, 15.9 Hz)	20.1
¹ H NMR	5.75-6.03 (m, 3H)	6.31 (ddd, 1H, <i>J</i> = 20.5, 16.2, 4.5 Hz)	3.85 (dq, 1H, <i>J</i> = 7.3, 9.00 Hz)	
		6.05 (ddd, 1H, <i>J</i> = 51.3, 11.2, 4.5 Hz),	1.36 (dd, 3H, <i>J</i> = 7.3, 16.5 Hz)	
		6.02 (ddd, 1H, <i>J</i> = 20.0, 16.2, 11.2 Hz)		

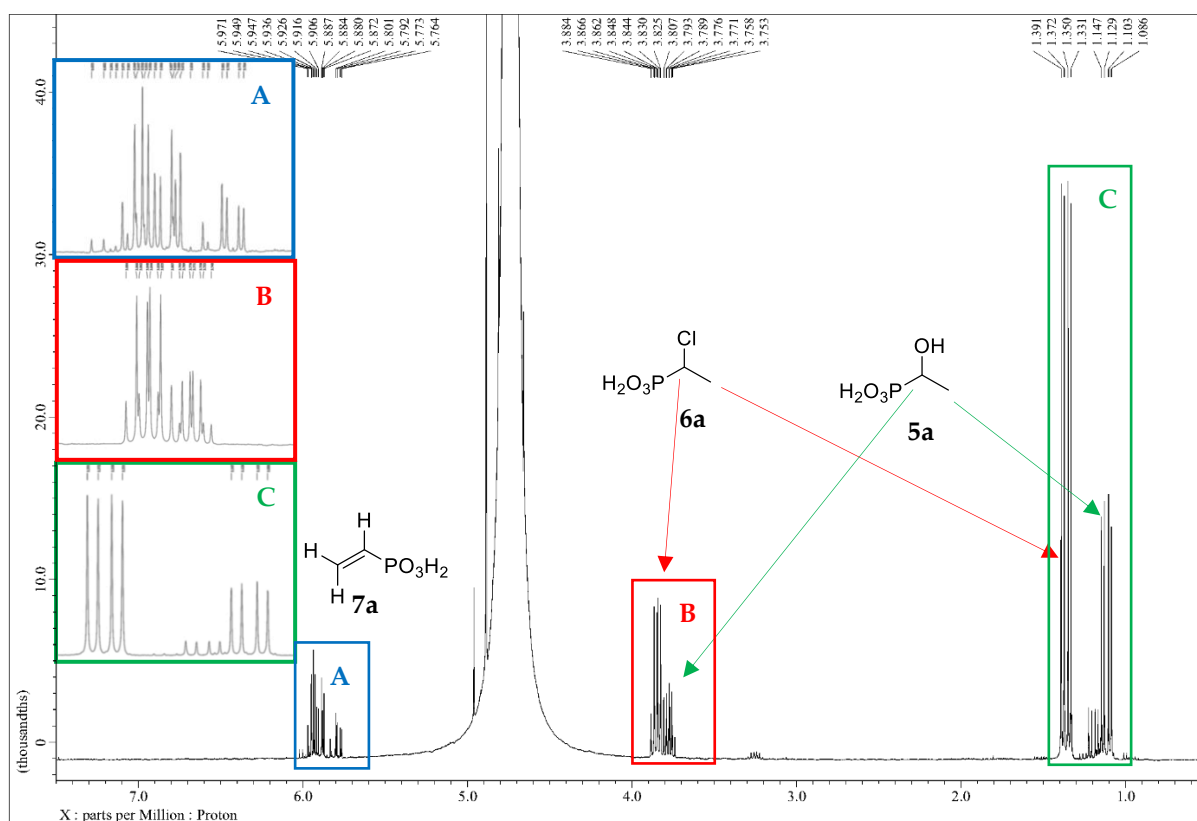


Figure S1. ^1H NMR (D₂O, 400MHz) spectra of post-reaction mixture of 1-aminoethylphosphonic acid (1a) with NaNO₂ in 5M hydrochloric acid.

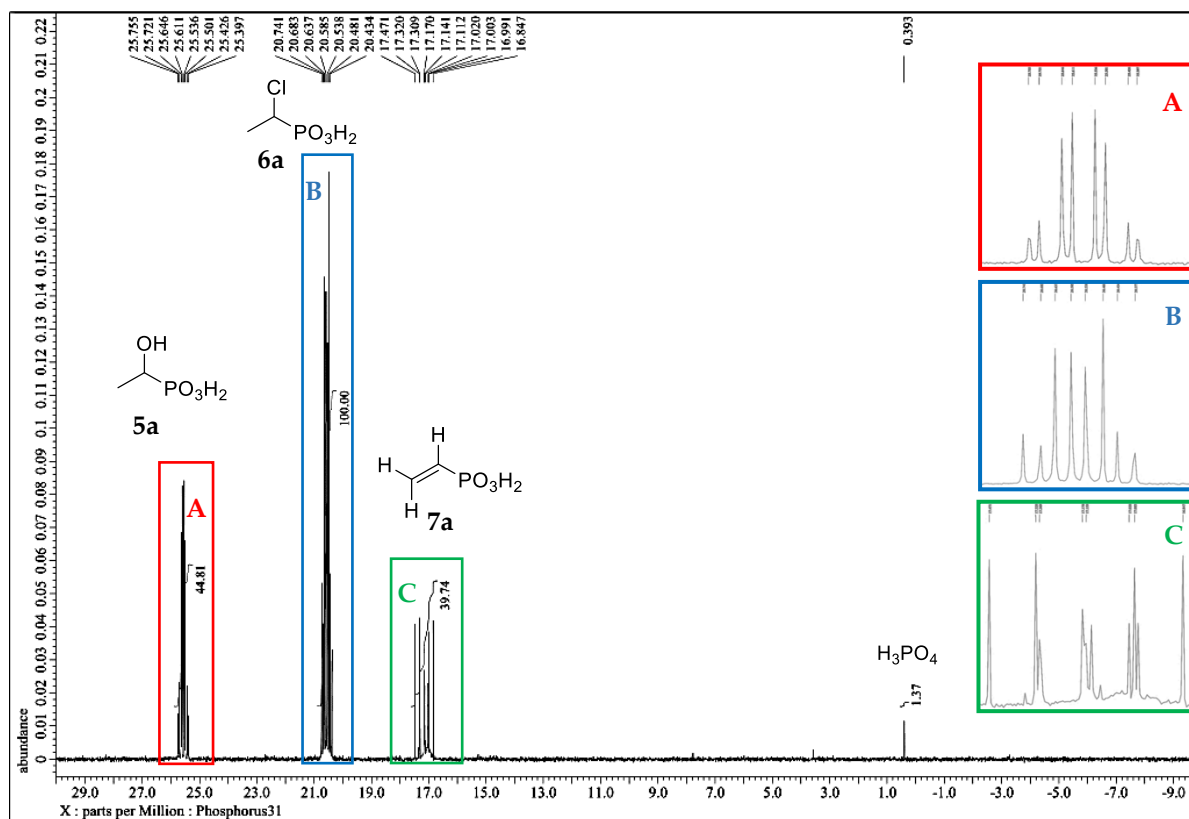


Figure S2. ^{31}P NMR (D₂O, 162MHz) spectra of post-reaction mixture of 1-aminoethylphosphonic acid (1a) with NaNO₂ in 5M hydrochloric acid.

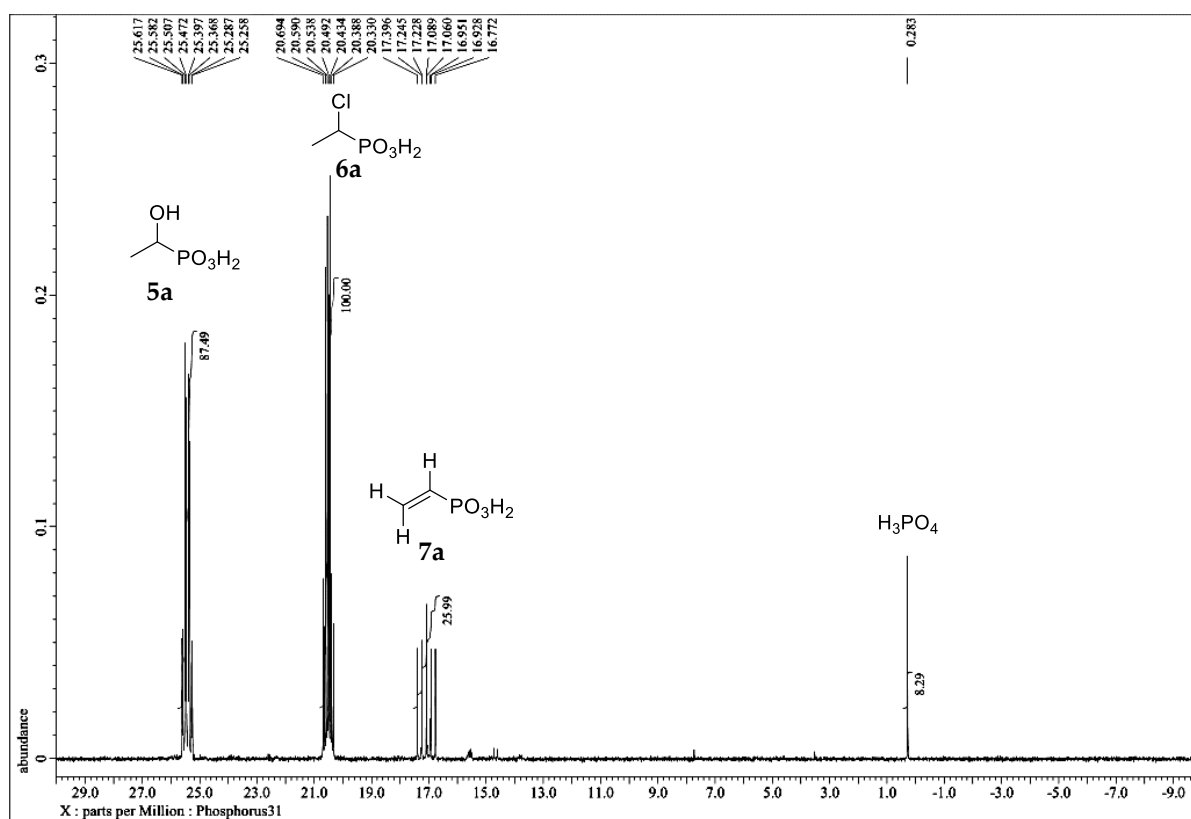


Figure S3. ^{31}P NMR (D₂O, 162MHz) spectra of post-reaction mixture of 1-aminoethylphosphonic acid (1a) with NaNO₂ in 5M hydrochloric acid with addition of 1-hydroxyethylphosphonic acid (5a) as standard.

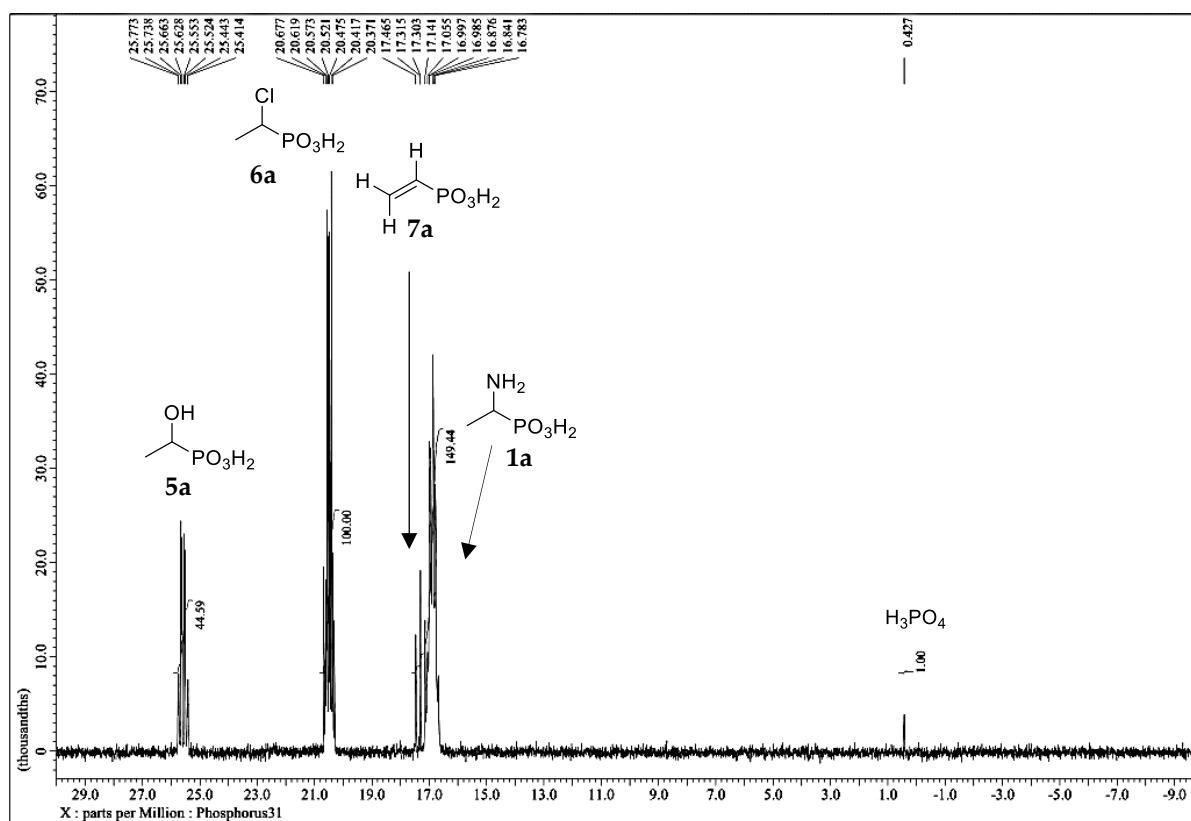
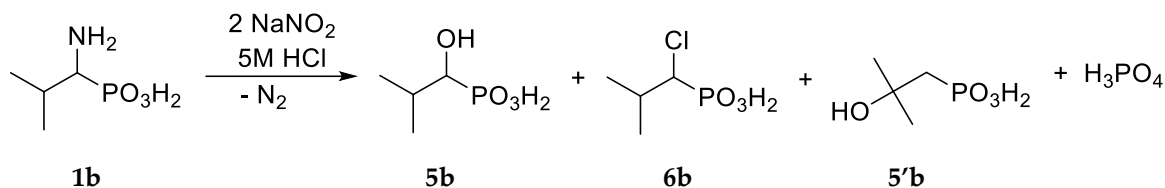


Figure S4. ^{31}P NMR (D₂O, 162MHz) spectra of post-reaction mixture of 1-aminoethylphosphonic acid (1a) with NaNO₂ in 5M hydrochloric acid with addition of substrate (1a) as standard.

2.2. ABr742. Deamination of **1b** in 5M Hydrochloric Acid

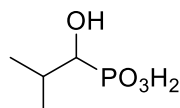
	$\alpha = 0.61$	6%	2%	42%	9%
δ_P [ppm]	16.88 (dq)	25.02 (dq)	19.37 (dq)	27.00 (t)	0.39 (s)

After 12h in 21 °C, post-reaction mixture contained 1-hydroxy-2-methylpropylphosphonic acid (**5b**) (6%molP), 1-chloro-2-methylpropylphosphonic acid (**6b**) (2%molP), 2-hydroxy-2-methylpropylphosphonic acid (**5'b**) (42%molP) and orthophosphoric acid (9%molP) (Figure S5 and Figure S7).

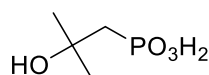
Unreacted 1-amino-2-methylpropylphosphonic acid was identified on ^1H and ^{31}P NMR spectra by re-measuring the NMR spectra of the reaction mixture with the addition of substrate (Figure S6 and Figure S8).

1-Hydroxy-2-methylpropylphosphonic acid (**5b**) was identified by comparing chemical shifts, multiplicity and coupling constants on ^1H and ^{31}P NMR spectra with description in the literature (Table S2).

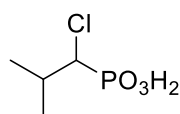
Spectra of 2-hydroxy-2-methylpropylphosphonic acid (**5'b**) and 1-chloro-2-methylpropylphosphonic acid (**6b**) have not been described in the literature. Therefore, these compounds were identified by analysis of the signals multiplicity on the ^1H and ^{31}P NMR spectra. Moreover, ^1H and ^{31}P NMR spectra of 2-hydroxy-2-methylpropylphosphonic acid (**5'b**) were compared with spectra of similar 2-hydroxypropylphosphonic acid (Table S2).



1-Hydroxy-2-methylpropylphosphonic acid (5b). ^{31}P NMR (D_2O , ca. 0.8M HCl): δ 25.02 (dd, $^2J_{\text{H-P}} = 8.4$ Hz, $^3J_{\text{H-P}} = 8.4$ Hz); ^1H NMR (D_2O , ca. 0.8M HCl): δ 3.46 (dd, 1H, $^2J_{\text{H-P}} = 8.3$ Hz, $^3J_{\text{H-H}} = 5.8$ Hz), 1.70-1.93 (m, 1H), 0.81 (d, 3H, $^3J_{\text{H-H}} = 6.7$ Hz), 0.80 (d, 3H, $^3J_{\text{H-H}} = 6.7$ Hz).

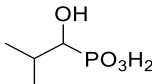
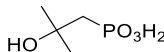
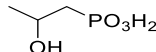


2-Hydroxy-2-methylpropylphosphonic acid (5'b). ^{31}P NMR (D_2O , ca. 0.8M HCl): δ 27.00 (t, $^2J_{\text{H-P}} = 19.2$ Hz); ^1H NMR (D_2O , ca. 0.8M HCl): δ 1.95 (d, 3H, $^2J_{\text{H-P}} = 18.7$ Hz, 2H), 1.16 (s, 6H).



1-Chloro-2-methylpropylphosphonic acid (6b). ^{31}P NMR (D_2O , ca. 0.8M HCl): δ 19.37 (dd, $^2J_{\text{H-P}} = 10.3$ Hz, $^3J_{\text{H-P}} = 7.5$ Hz); ^1H NMR (D_2O , ca. 0.8M HCl): δ 3.83 (dd, 1H, $^2J_{\text{H-P}} = 11.3$ Hz, $^3J_{\text{H-H}} = 3.7$ Hz), 2.10-2.21 (m, 1H), 0.82-0.92 (6H).

Table S2. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of the reaction products of 1-amino-2-methylpropylphosphonic acid (**1b**) with NaNO_2 in 5M HCl with compounds described in the literature.

Structure				
Source	ABr742	Reference [8]	ABr742	Reference [9]
Solvent	(D ₂ O, 0.8M HCl)	D ₂ O	D ₂ O	D ₂ O
³¹ P NMR	25.02 (t, <i>J</i> = 8.4 Hz)	19.6	21.24 (t, <i>J</i> = 17.8 Hz)	19.9
¹ H NMR	3.46 (dd, 1H, <i>J</i> = 8.3, 5.8 Hz)	3.23 (dd, 1H, <i>J</i> = 8.4, 6.0 Hz)		3.80 (1H, dm, <i>J</i> = 6.5 Hz)
	1.70-1.93 (m, 1H)	1.79-1.86 (m, 1H)	1.83 (d, 3H, <i>J</i> = 17.7 Hz)	1.39 (2H, ddd, <i>J</i> = 18.0, 6.6, 15.3 Hz)
	0.81 (d, 3H, <i>J</i> = 6.7 Hz)	0.84 (d, 3H, <i>J</i> = 6.6 Hz)	1.22 (s, 6H)	0.97 (3H, d, <i>J</i> = 6.5 Hz)
	0.80 (d, 3H, <i>J</i> = 6.7 Hz)	0.83 (d, 3H, <i>J</i> = 6.6 Hz)		

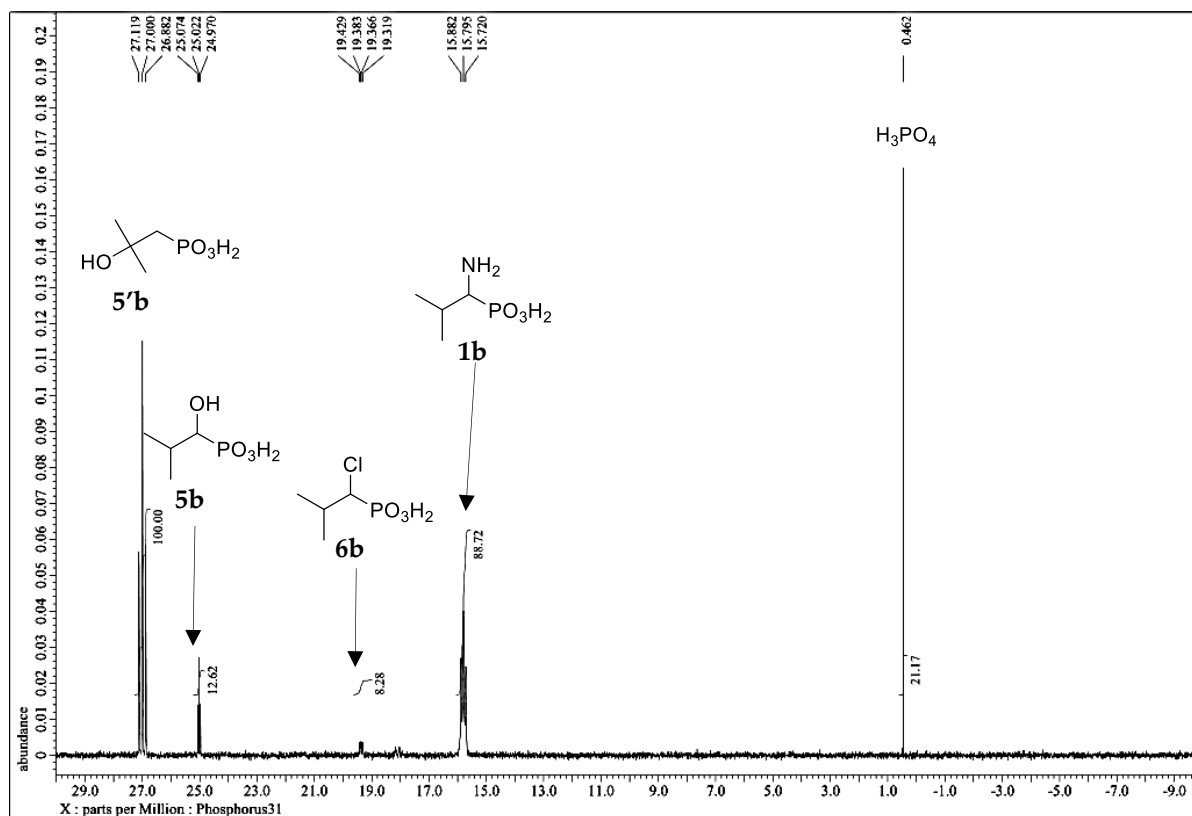


Figure S5. ^{31}P NMR (D₂O, 162MHz) spectra of the crude post-reaction mixture of 1-amino-2-methylpropylphosphonic acid (**1b**) with NaNO₂ in 5M HCl.

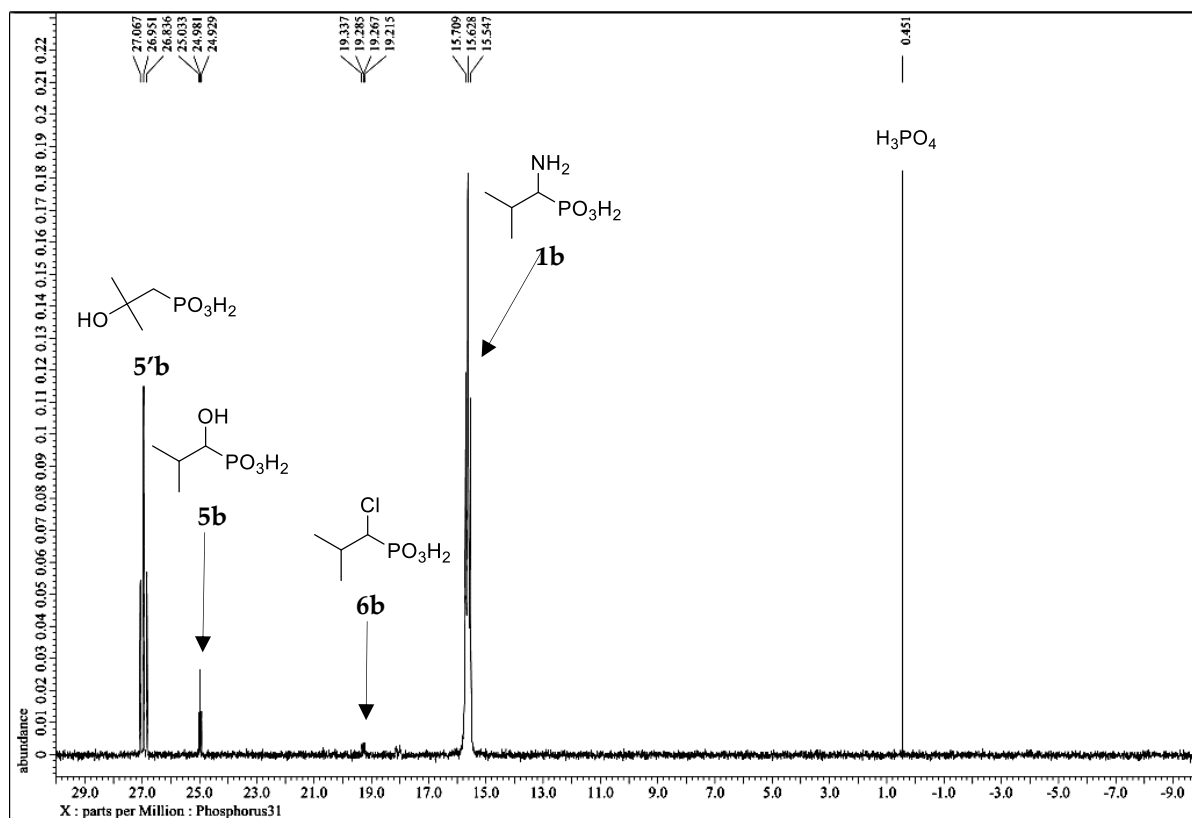


Figure S6. ^{31}P NMR (D₂O, 162MHz) spectra of the crude post-reaction mixture of 1-amino-2-methylpropylphosphonic acid (**1b**) with NaNO₂ in 5M HCl with addition of substrate (**1b**) as standard.

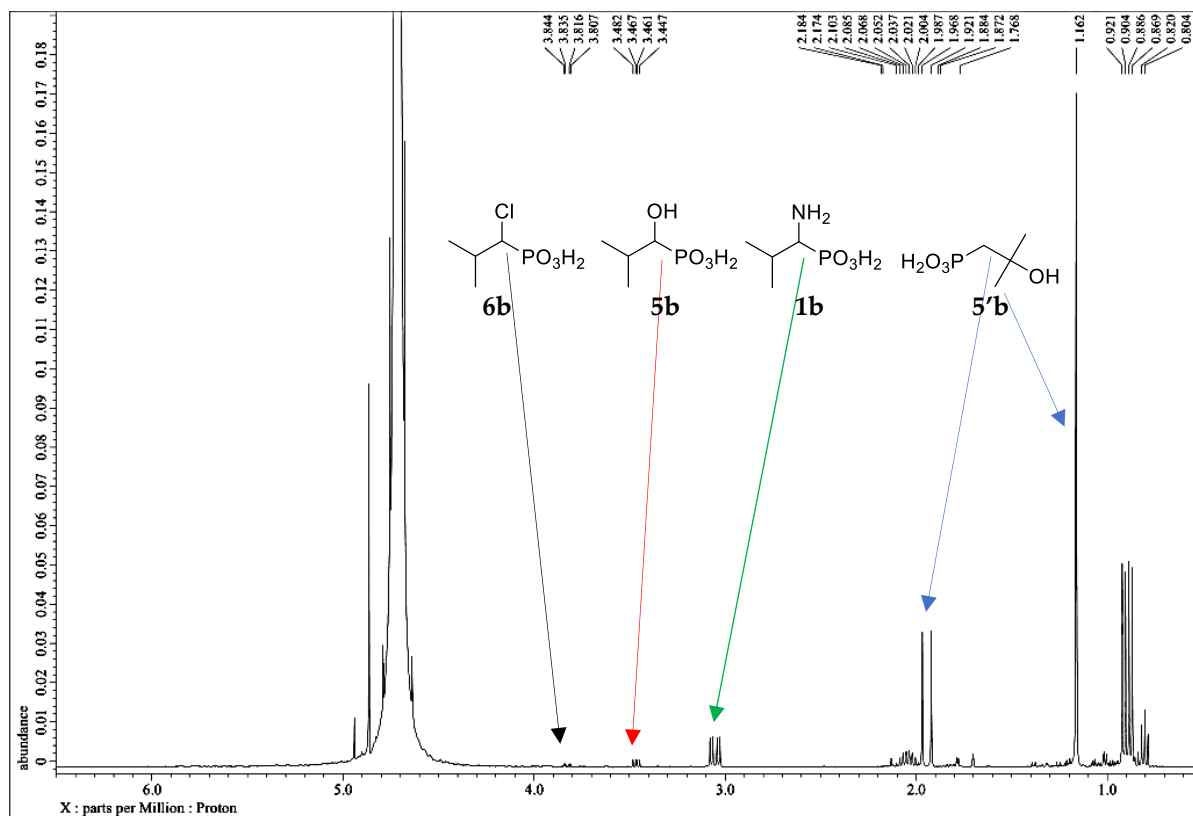


Figure S7. ^1H NMR (D_2O , 400MHz) spectra of the crude post-reaction mixture of 1-amino-2-methylpropylphosphonic acid (**1b**) with NaNO_2 in 5M HCl.

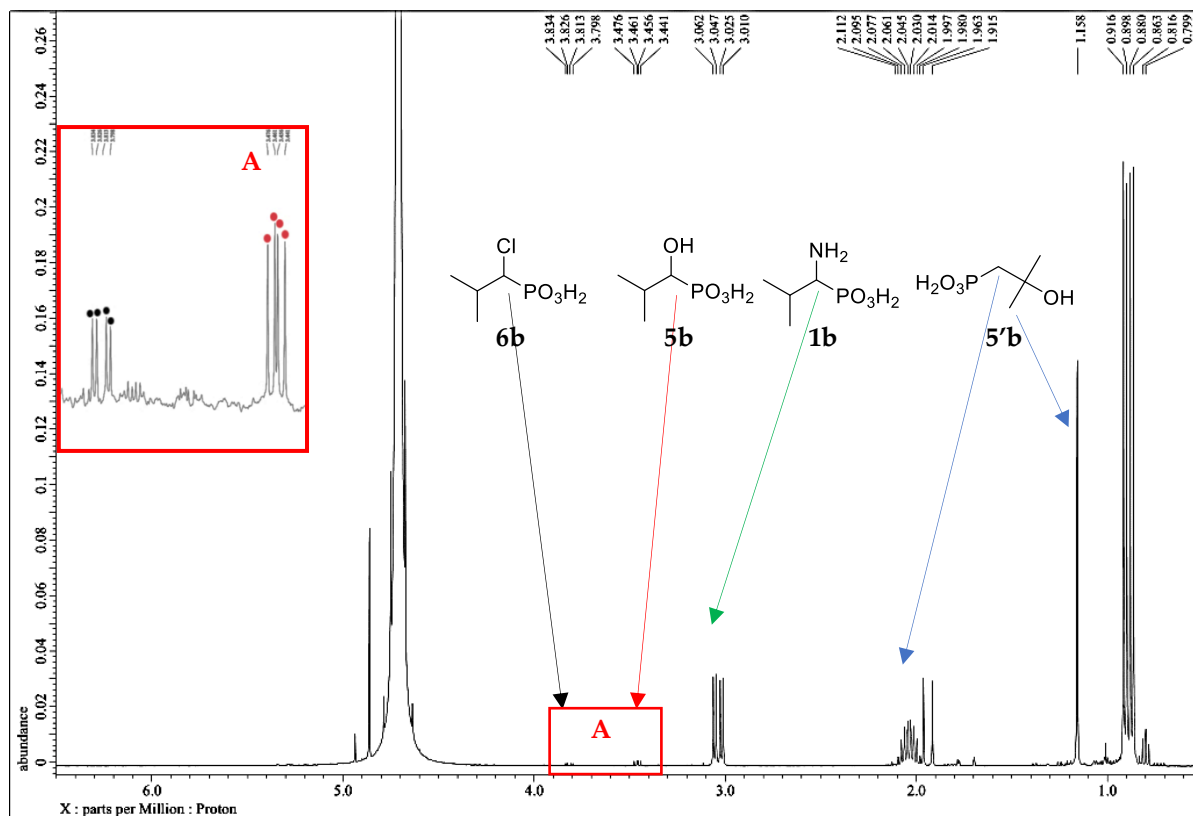
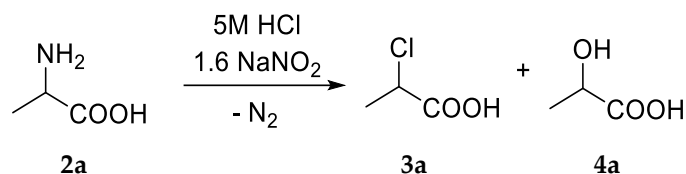


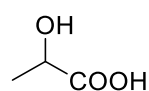
Figure S8. ^1H NMR (D_2O , 400MHz) spectra of the crude post-reaction mixture of 1-amino-2-methylpropylphosphonic acid (**1b**) with NaNO_2 in 5M HCl with addition of substrate (**1b**) as standard.

2.3. ABr746. Deamination of **2a** in 5M Hydrochloric Acid $\alpha = 0.53$

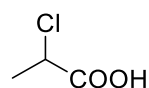
35%

18%

After 24 h in 21 °C, post-reaction mixture contained unreacted substrate **2a** (47%mol), 2-chloropropanoic acid (**3a**) (35%mol) and 2-hydroxypropanoic acid (**4a**) (18%mol) (Figure S9).



2-Hydroxypropanoic acid (4a). ^1H NMR (D_2O , ca. 0.8M HCl) δ : 4.12 (q, 1H, $^3J_{\text{H-H}} = 7.0$ Hz), 1.15 (d, 3H, $^3J_{\text{H-H}} = 7.0$ Hz).



2-Chloropropanoic acid (3a). ^1H NMR (D_2O , ca. 0.8M HCl) δ : 4.35 (q, 1H, $^3J_{\text{H-H}} = 7.0$ Hz), 1.41 (d, 3H, $^3J_{\text{H-H}} = 7.0$ Hz).

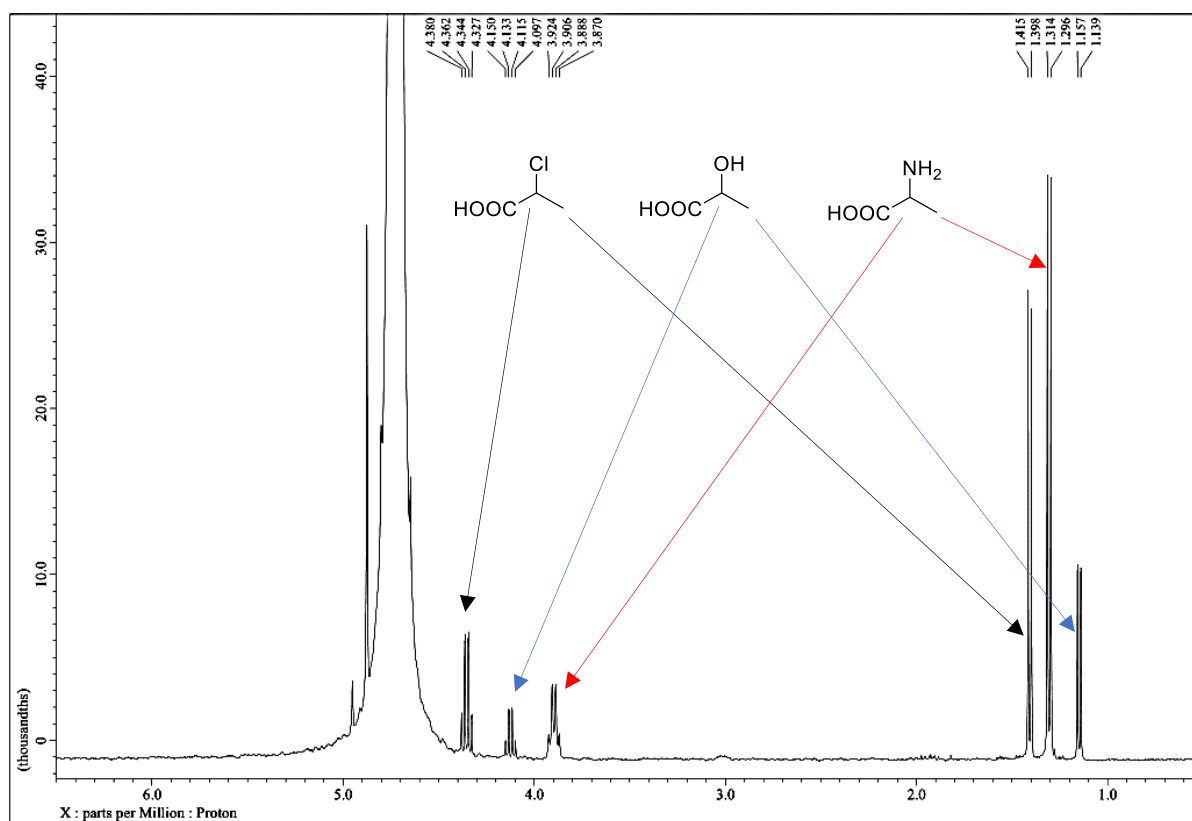
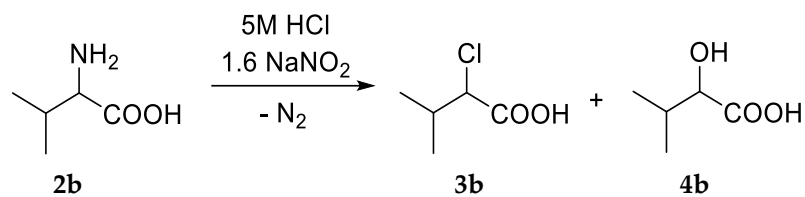
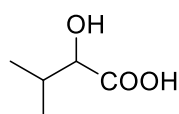


Figure S9. ^1H NMR (D_2O , 400MHz) spectra of crude post-reaction mixture of alanine (**2a**) with NaNO_2 in 5M hydrochloric acid.

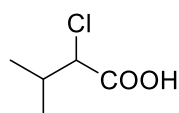
2.4. ABr748. Deamination of **2b** in 5M Hydrochloric Acid

$\alpha = 0.57$	40%	8%
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After 24 h in 21 °C, post-reaction mixture contained unreacted substrate **2b** (43%mol), 2-chloro-3-methylbutanoic acid (**3b**) (40%mol) and 2-hydroxy-3-methylbutanoic acid (**4b**) (8%mol) and unidentified compound (Figure S10).



2-Hydroxy-3-methylbutanoic acid (4b). ¹H NMR (D₂O, ca. 0.8M HCl) δ : 3.86 (d, 1H, ³J_{H-H} = 4.0 Hz), 1.82 (doublet of septets, 1H, ³J_{H-H} = 7.0 Hz, ³J_{H-H} = 4.0 Hz), 0.71 (d, 3H, ³J_{H-H} = 7.0 Hz), 0.62 (d, 3H, ³J_{H-H} = 7.0 Hz).



2-Chloro-3-methylbutanoic acid (3b). ¹H NMR (D₂O, ca. 0.8M HCl) δ : 4.17 (d, 1H, ³J_{H-H} = 5.5 Hz), 2.05 (doublet of septets, 1H, ³J_{H-H} = 6.7 Hz, ³J_{H-H} = 5.8 Hz), 0.76 (d, 3H, ³J_{H-H} = 6.7 Hz), 0.72 (d, 3H, ³J_{H-H} = 6.7 Hz).

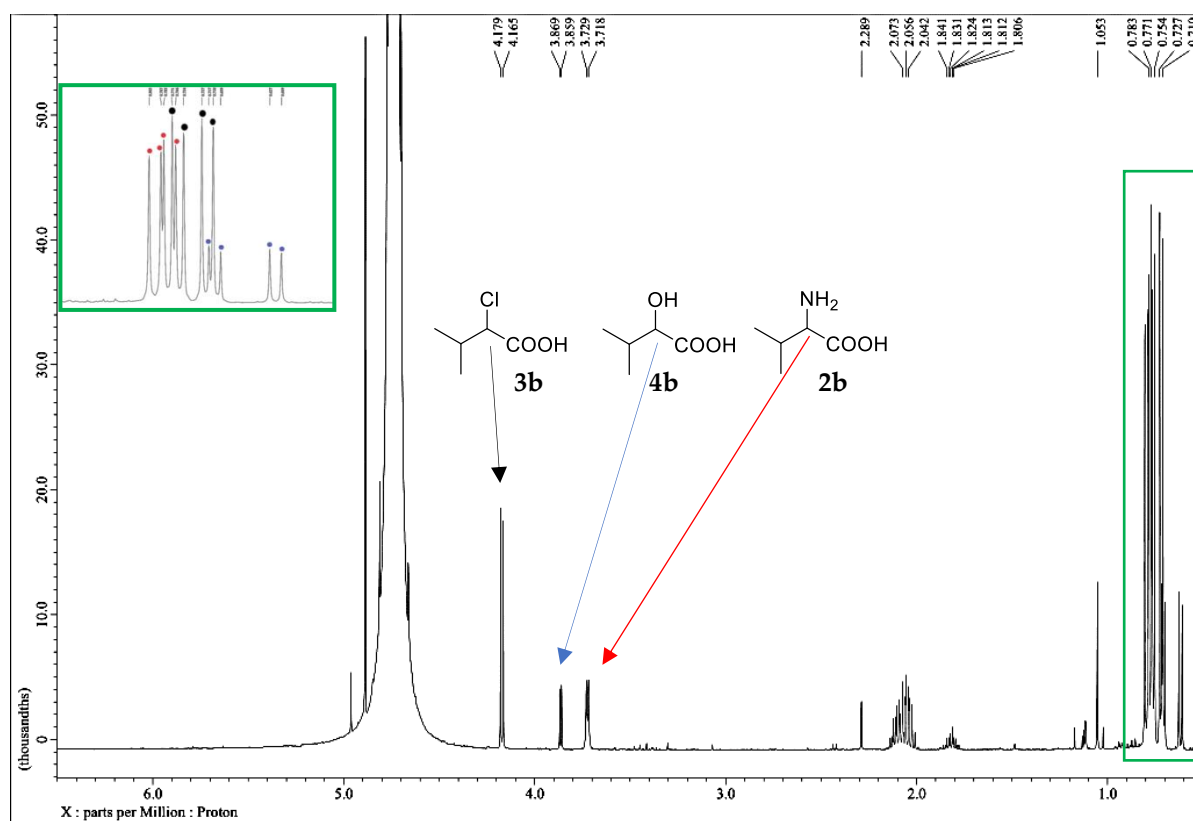


Figure S10. ^1H NMR (D_2O , 400MHz) spectra of crude post-reaction mixture of valine (**2b**) with NaNO_2 in 5M hydrochloric acid.

3. Deamination of 1-Aminoalkylphosphonic Acids in Water

Apparatus. Deamination reactions of 1-aminoalkylphosphonic acids **1** were conducted in round-bottom flask equipped with magnetic stirrer and calibrated gas burette (Figure S11). The flask was placed in a water bath at a temperature of about 20 °C. 1-Aminoalkylphosphonic acid **1** (3.0 mmol, 1 equiv) was added to 0.67 M solution of NaNO₂ (6.0 mmol, 2 equiv, 9.0 mL). Solution or suspension was stirred by the means of magnetic stirrer until the stoichiometric volume of gas was evolved and additionally for 12 h. ¹H and ³¹P NMR spectra were recorded after that time and additionally after few days. The composition of mixture was calculated based on the integration of signals on the ³¹P NMR spectra.

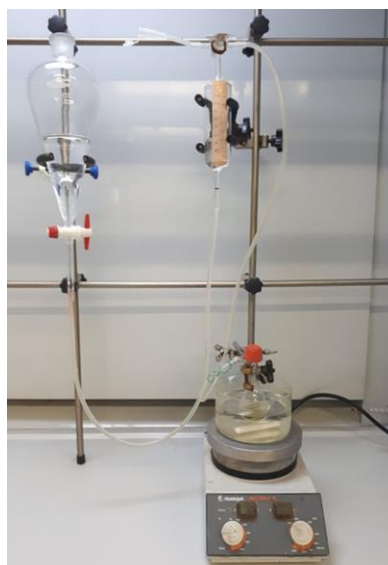
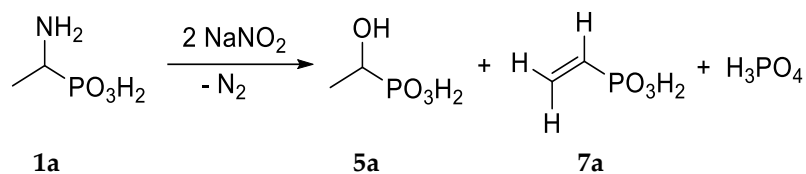


Figure S11. Apparatus used in the deamination reactions of 1-aminoalkylphosphonic acids **1** with sodium nitrite in water.

General Procedure. 1-aminoalkylphosphonic acid **1** (3.0 mmol, 1 equiv) was added to cooled in water bath 0.67M solution of NaNO₂ (6.0 mmol, 2 equiv, 9.0 mL). Solution or suspension was stirred by the means of magnetic stirrer until the stoichiometric volume of gas was evolved and additionally for 12 h. ¹H and ³¹P NMR spectra were recorded after that time and additionally after few days. The composition of mixture was calculated based on the integration of signals on the ³¹P NMR spectra.

3.1. ABr1178. Deamination of **1a** in Water

24 h	$\alpha = 0.98$	85%	1%	9%
312 h	$\alpha = 1.00$	84%	2%	10%
δ_P [ppm]	13.6 (dq)	21.33 (dq)	12.9 (ddd)	1.25 (s)

After 24 h at 21 °C, post-reaction mixture contained 1-hydroxyethylphosphonic acid (**5a**) (85%molP), phosphoric acid (9%molP), vinylphosphonic acid (**7a**) (ca. 1%molP), unreacted substrate (**1a**) (2%molP) and 4 unidentified compounds (ca. 3%molP in total).

After 312 h at 21 °C, post-reaction mixture contained 1-hydroxyethylphosphonic acid (**5a**) (84%molP), orthophosphoric acid (10%molP), vinylphosphonic acid (**7a**) (ca. 2%molP) and 4 unidentified compounds (ca. 4%molP in total) (Figure S12 and Figure S14).

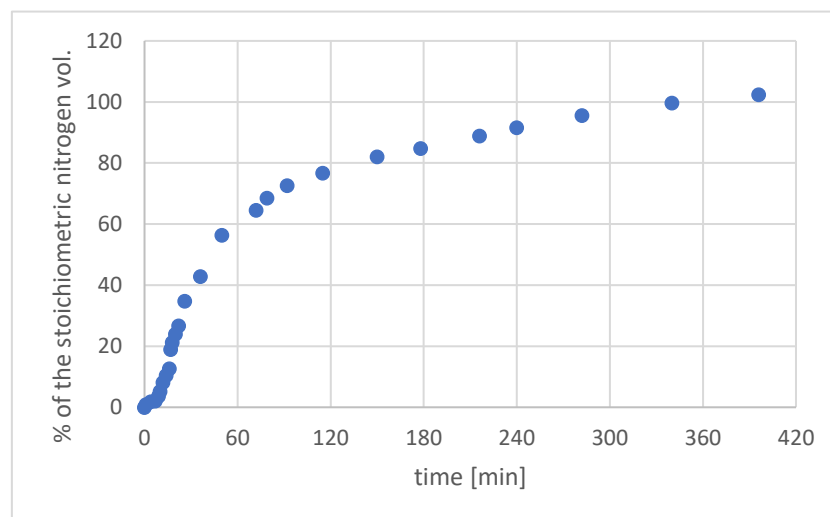
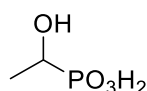


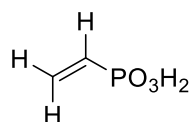
Chart 1. Dependence of the volume of the released gas (in % of the stoichiometric nitrogen volume) on the time in the reaction of 1-aminoethylphosphonic acid (**1a**) with NaNO₂ in water.

Vinylphosphonic acid (**7a**) and 1-hydroxyethylphosphonic acid (**5a**) identified by comparing chemical shifts, multiplicity and coupling constants on ¹H and ³¹P NMR spectra with description in the literature (Table S3)

Additionally, 1-hydroxyethylphosphonic acid (**5a**) was identified on ¹H and ³¹P NMR spectra by re-measuring the NMR spectra from the reaction mixture with the addition of 1-hydroxyethylphosphonic acid (**5a**) standard (Figure S13).

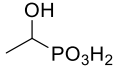
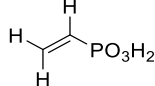


1-Hydroxyethylphosphonic acid (5a). ³¹P NMR (D₂O): δ 21.33 (dq, $^2J_{\text{H-P}} = 5.6$ Hz, $^3J_{\text{H-P}} = 15.4$ Hz); ¹H NMR (D₂O): δ : 3.70 (dq, 1H, $^2J_{\text{H-P}} = 5.9$ Hz, $^3J_{\text{H-H}} = 7.0$ Hz), 1.19 (dd, 3H, $^3J_{\text{H-H}} = 7.0$ Hz, $^3J_{\text{H-P}} = 15.9$ Hz).



Vinylphosphonic acid (7a). ^{31}P NMR (D_2O) δ : 12.9 (ddd, $^2J_{\text{H-P}} = 20.6$ Hz, $^3J_{\text{H-P (cis)}} = 23.4$ Hz, $^3J_{\text{H-P (trans)}} = 46.8$ Hz); ^1H NMR (D_2O) δ : 6.01 (ddd, 1H, $^3J_{\text{H-H}} = 12.7$ Hz, $^3J_{\text{H-H}} = 18.8$ Hz, $^2J_{\text{H-P}} = 20.5$ Hz), 5.75 (ddd, 1H, $^2J_{\text{H-H}} = 2.5$ Hz, $^3J_{\text{H-H}} = 18.9$ Hz, $^3J_{\text{H-P (cis)}} = 23.3$ Hz), 5.66 (ddd, 1H, $^2J_{\text{H-H}} = 2.5$ Hz, $^3J_{\text{H-H}} = 12.7$ Hz, $^3J_{\text{H-P (trans)}} = 46.3$ Hz).

Table S3. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of the reaction products of 1-aminoethylphosphonic acid (**1a**) with NaNO_2 in water with compounds described in the literature.

Structure				
Source	ABr1178	Reference [8]	ABr1178	Reference [6]
Solvent	D2O	D2O	D2O	CDCl3
³¹ P NMR	21.33 (dq, <i>J</i> = 5.6, 15.4 Hz)	19.6	12.9 (ddd, <i>J</i> = 20.6, 23.4, 46.8 Hz)	17.3 (ddd, <i>J</i> = 20.0, 20.5, 51.3 Hz)
¹ H NMR	3.70 (dq, 1H, <i>J</i> = 5.9, 7.0 Hz)	3.53-3.58 (m, 1H)	6.01 (ddd, 1H, <i>J</i> = 12.7, 18.8, 20.5 Hz)	6.31 (ddd, 1H, <i>J</i> = 20.5, 16.2, 4.5 Hz)
	1.19 (dd, 3H, <i>J</i> = 7.0, 15.9 Hz)	1.12 (dd, <i>J</i> = 7.2, 14.4 Hz, 3H)	5.75 (ddd, 1H, <i>J</i> = 2.5, 18.9, 23.3 Hz)	6.05 (ddd, 1H, <i>J</i> = 51.3, 11.2, 4.5 Hz)
			5.66 (ddd, 1H, <i>J</i> = 2.5, 12.7, 46.3 Hz)	6.02 (ddd, 1H, <i>J</i> = 20.0, 16.2, 11.2 Hz)

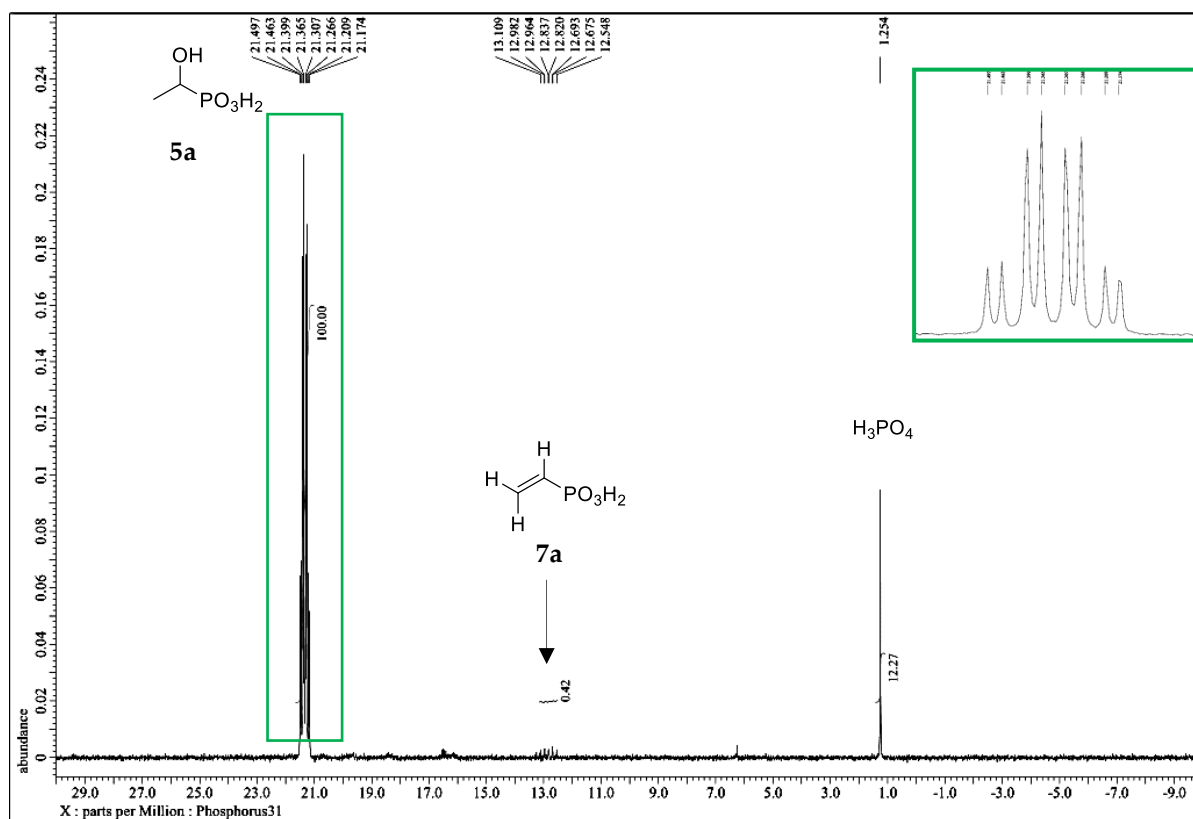


Figure S12. ^{31}P NMR (D_2O , 162MHz) spectra of the crude post-reaction mixture of 1-aminoethylphosphonic acid (**1a**) with NaNO_2 after 312 h.

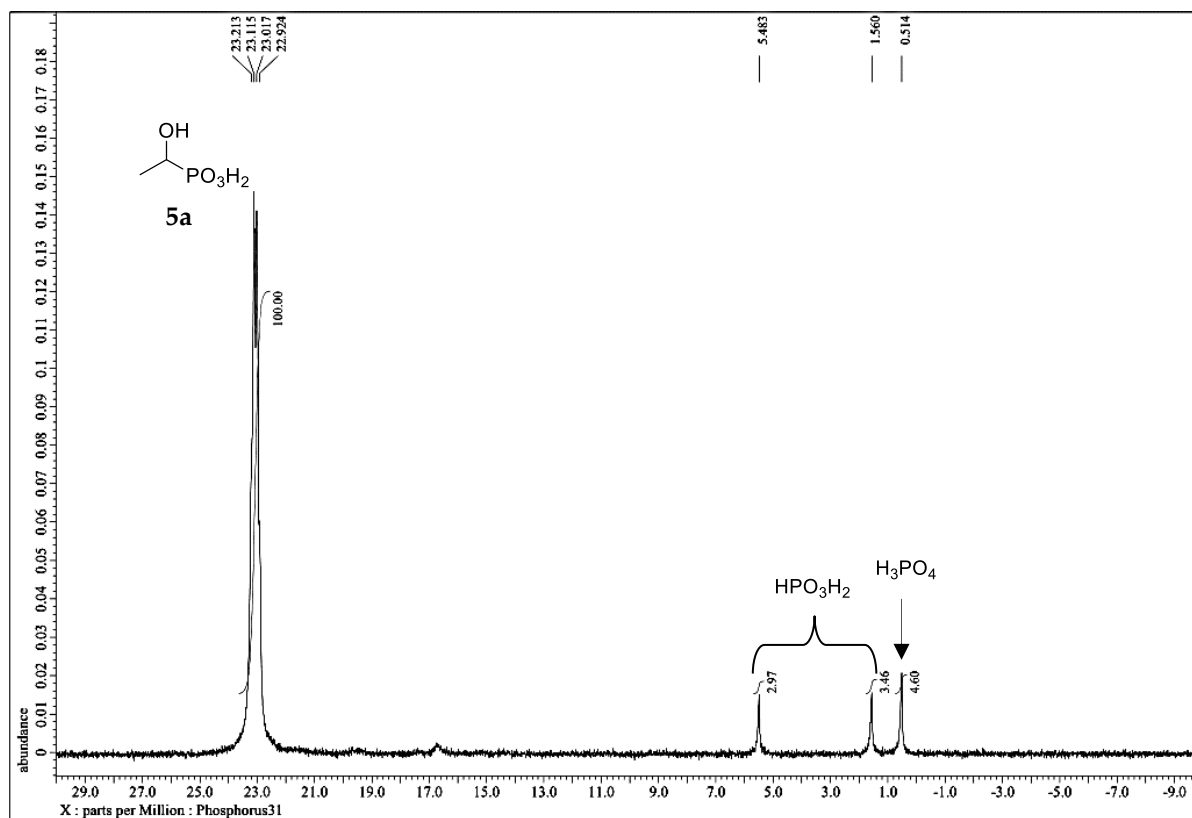


Figure S13. ^{31}P NMR (D₂O, 162 MHz) spectra of the crude post-reaction mixture of 1-aminoethylphosphonic acid (**1a**) with NaNO₂ after 312 h with addition of 1-hydroxyethylphosphonic acid (**5a**) as standard.

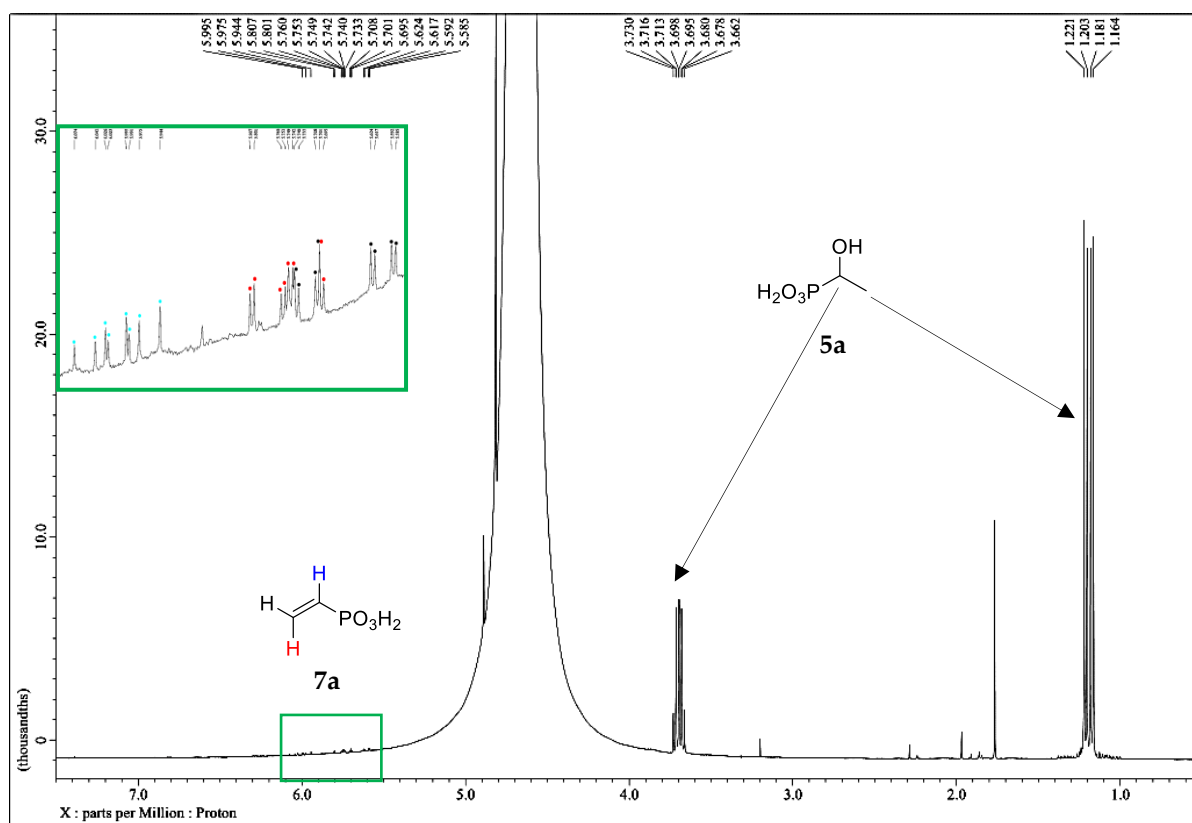
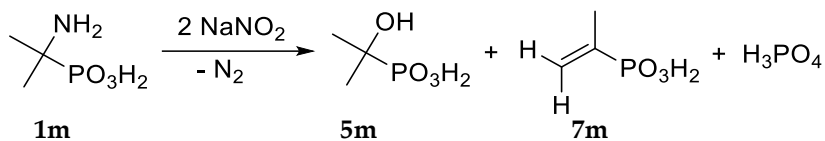


Figure S14. ^1H NMR (D₂O, 400 MHz) spectra of the crude post-reaction mixture of 1-aminoethylphosphonic acid (**1a**) with NaNO₂ after 312 h.

3.2. ABr1204. Deamination of **1m** in Water

24 h	$\alpha = 0.98$	84%	13%	1%
192 h	$\alpha = 1.00$	86%	12%	2%
δ_P [ppm]	16.83 (septet)	23.84 (septet)	15.31 (ddq)	1.15 (s)

After 24 h in 21 °C, post-reaction mixture contained 1-hydroxy-1-methylethylphosphonic acid (**5m**) (84%molP), 1-methylvinylphosphonic acid (**7m**) (13%molP), orthophosphoric acid (1%molP) and unreacted substrate **1m** (2%molP).

After 192 h in 21 °C, post-reaction mixture contained 1-hydroxy-1-methylethylphosphonic acid (**5m**) (86%molP), 1-methylvinylphosphonic acid (**7m**) (12%molP) and orthophosphoric acid (2%molP) (Figure S15 and Figure S17).

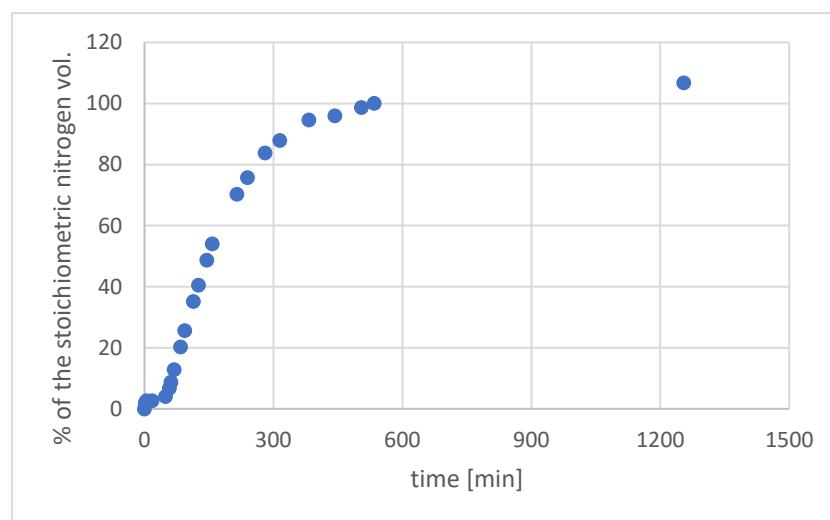
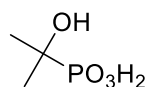


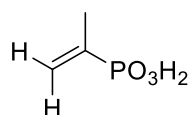
Chart 2. Dependence of the volume of the released gas (in % of the stoichiometric nitrogen volume) on the time in the reaction of 1-amino-1-methylethylphosphonic acid (**1m**) with NaNO₂ in water.

The presence of 1-hydroxy-1-methylethylphosphonic acid (**5m**) was confirmed by re-measuring NMR spectra with addition of reference material—1-hydroxy-1-methylethylphosphonic acid (**5m**) (Figure S16 and Figure S18).

1-Methylvinylphosphonic acid (**7m**) was identified by comparing chemical shifts, multiplicity and coupling constants on ¹H and ³¹P NMR spectra with description in the literature (Table S1).

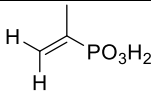


1-Hydroxy-1-methylethylphosphonic acid (5m). ³¹P NMR (D₂O): δ 23.84 (septet, ³J_{H-P} = 14.0 Hz); ¹H NMR (D₂O) δ : 1.23 (d, 6H, ³J_{H-P} = 13.8 Hz).



1-Methylvinylphosphonic acid (7m). ^{31}P NMR (D_2O): δ 15.21 (ddq, $^3J_{\text{H-P (trans)}} = 43.9\text{ Hz}$, $^3J_{\text{H-P (cis)}} = 20.6$, $^3J_{\text{H-P}} = 13.1\text{ Hz}$); ^1H NMR (D_2O) δ : 5.46 (ddq, 1H, $^3J_{\text{H-P (cis)}} = 20.3\text{ Hz}$, $^2J_{\text{H-H}} = 2.1\text{ Hz}$, $^4J_{\text{H-H}} = 1.2\text{ Hz}$), 5.36 (ddq, 1H, $^3J_{\text{H-P (trans)}} = 43.4\text{ Hz}$, $^2J_{\text{H-H}} = 1.8\text{ Hz}$, $^4J_{\text{H-H}} = 1.8\text{ Hz}$), 1.77 (dt, 3H, $^3J_{\text{H-P}} = 13.1\text{ Hz}$, $^4J_{\text{H-H}} = 1.2\text{ Hz}$).

Table S4. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of 1-methylvinylphosphonic acid (7m) description in the literature.

Structure		
Source	ABr1204	Reference [10]
Solvent	D_2O	D_2O
^{31}P NMR	15.21 (ddq, $J = 43.9, 20.6, 13.1\text{ Hz}$)	18.34
^1H NMR	5.46 (ddq, 1H, $J = 20.3, 2.1, 1.2\text{ Hz}$)	5.32–5.47 (q, 2H)
	5.36 (tq, 1H, $J = 43.4, 1.8\text{ Hz}$)	
	1.77 (dt, 3H, $J = 13.1, 1.2\text{ Hz}$)	1.55/1.58 (d, 3H)

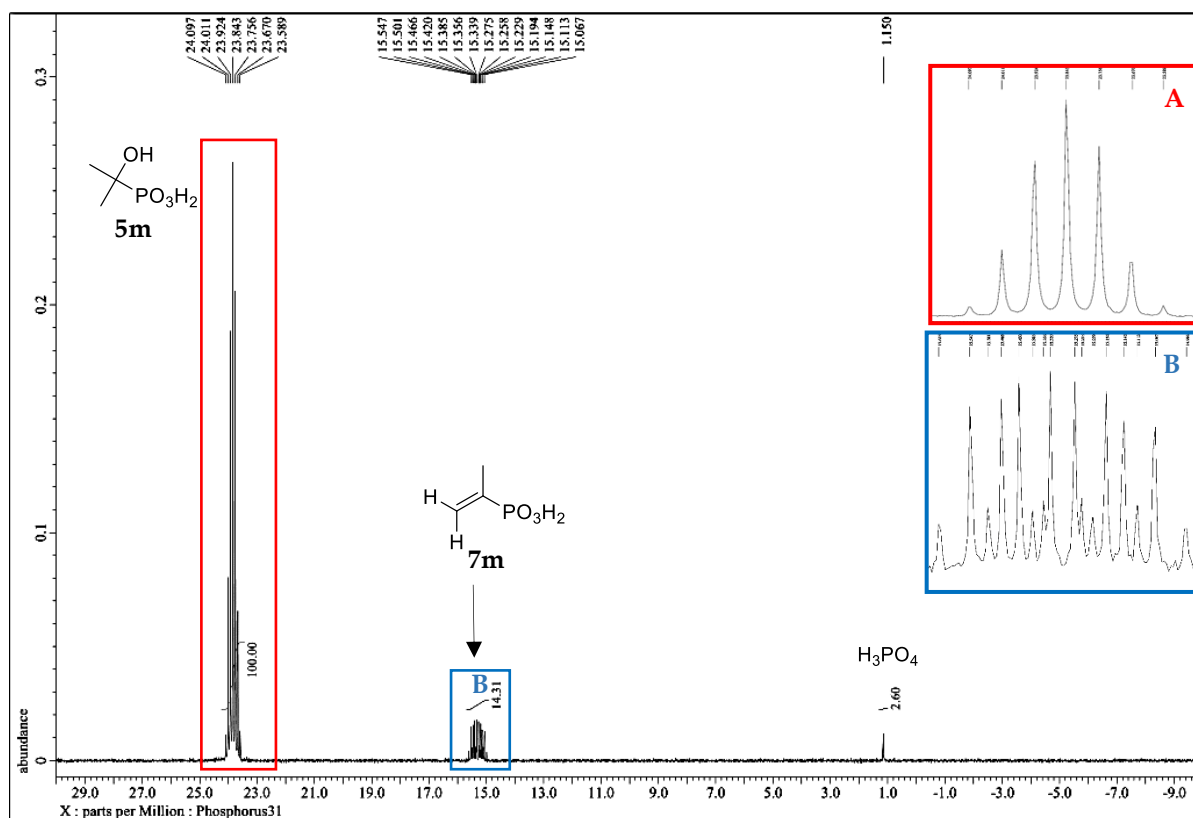


Figure S15. ^{31}P NMR (D₂O, 162 MHz) spectra of the crude post-reaction mixture of 1-amino-1-methylethylphosphonic acid (**1m**) with NaNO₂ after 192 h.

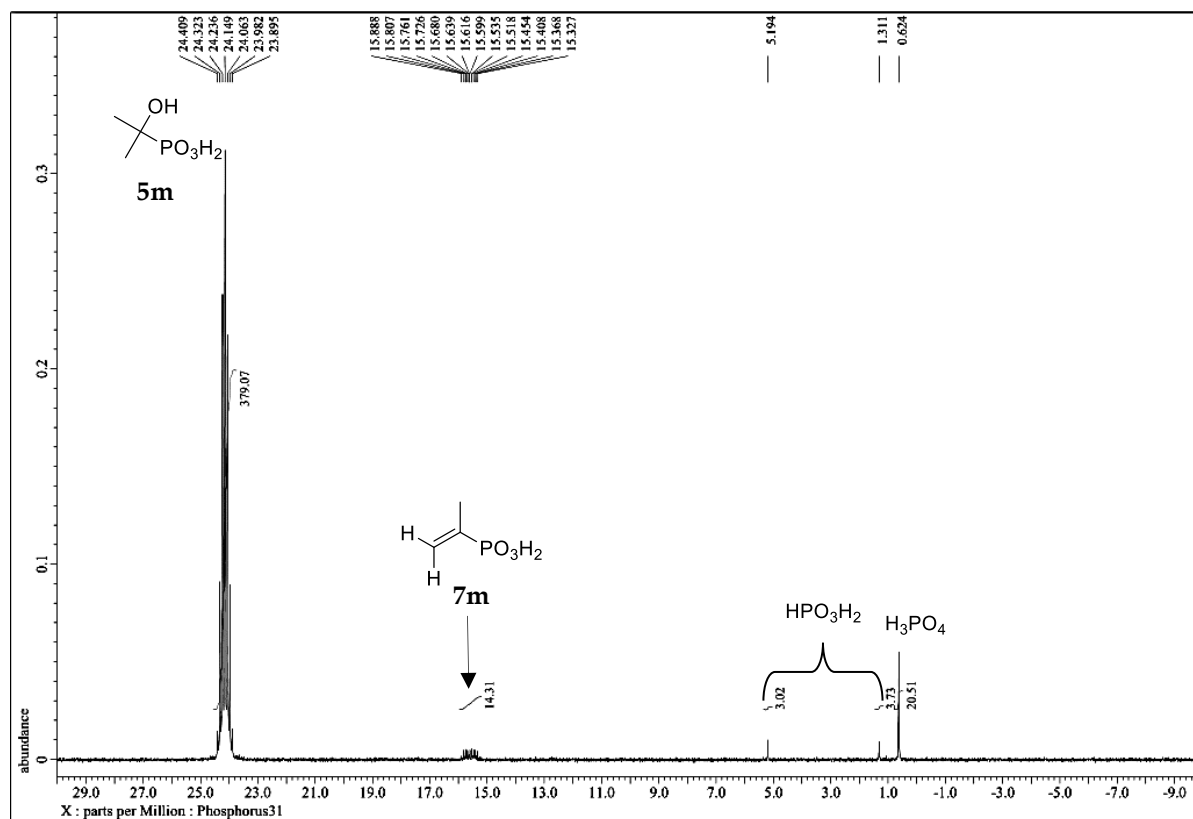


Figure S16. ^{31}P NMR (D₂O, 162 MHz) spectra of the crude post-reaction mixture of 1-amino-1-methylethylphosphonic acid (**1m**) with NaNO₂ after 192 h with addition of 1-hydroxy-1-methylethylphosphonic acid (**5m**) as reference.

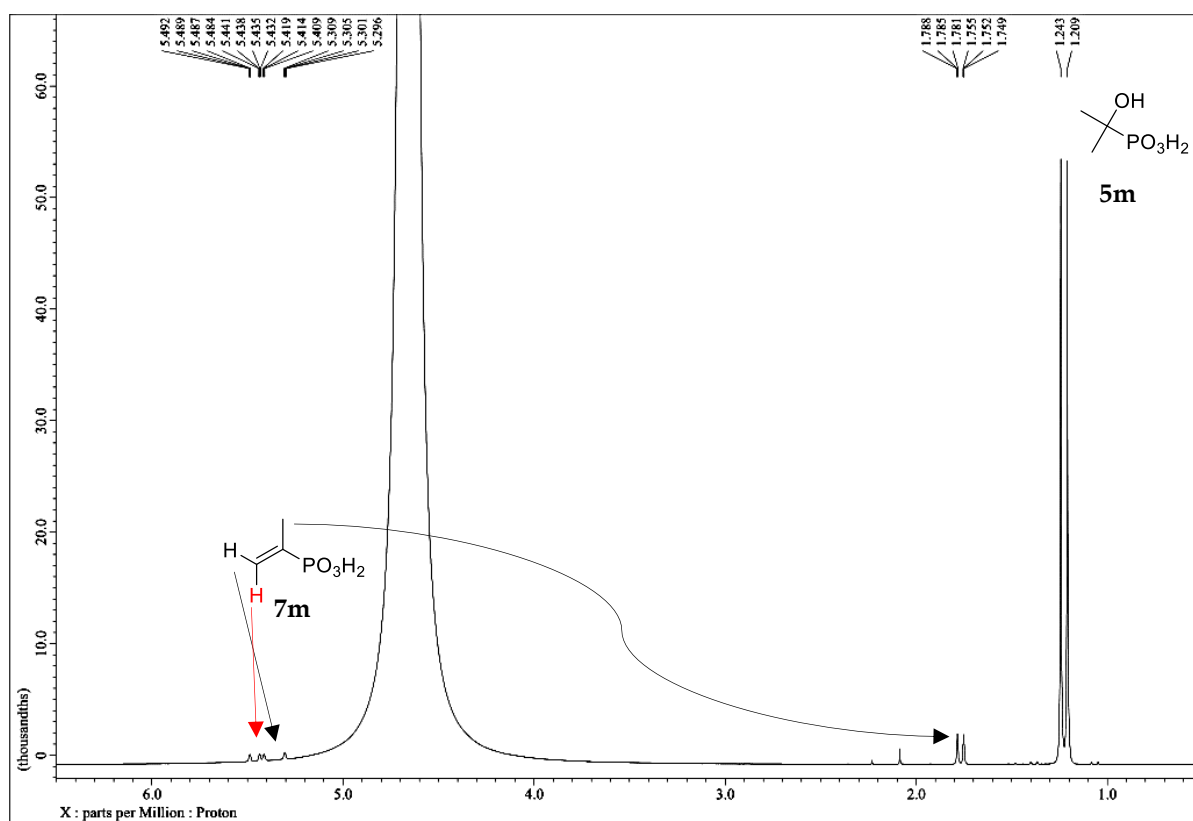


Figure S17. ^1H NMR (D_2O , 400MHz) spectra of the crude post-reaction mixture of 1-amino-1-methylethylphosphonic acid (**1m**) with NaNO_2 after 192 h.

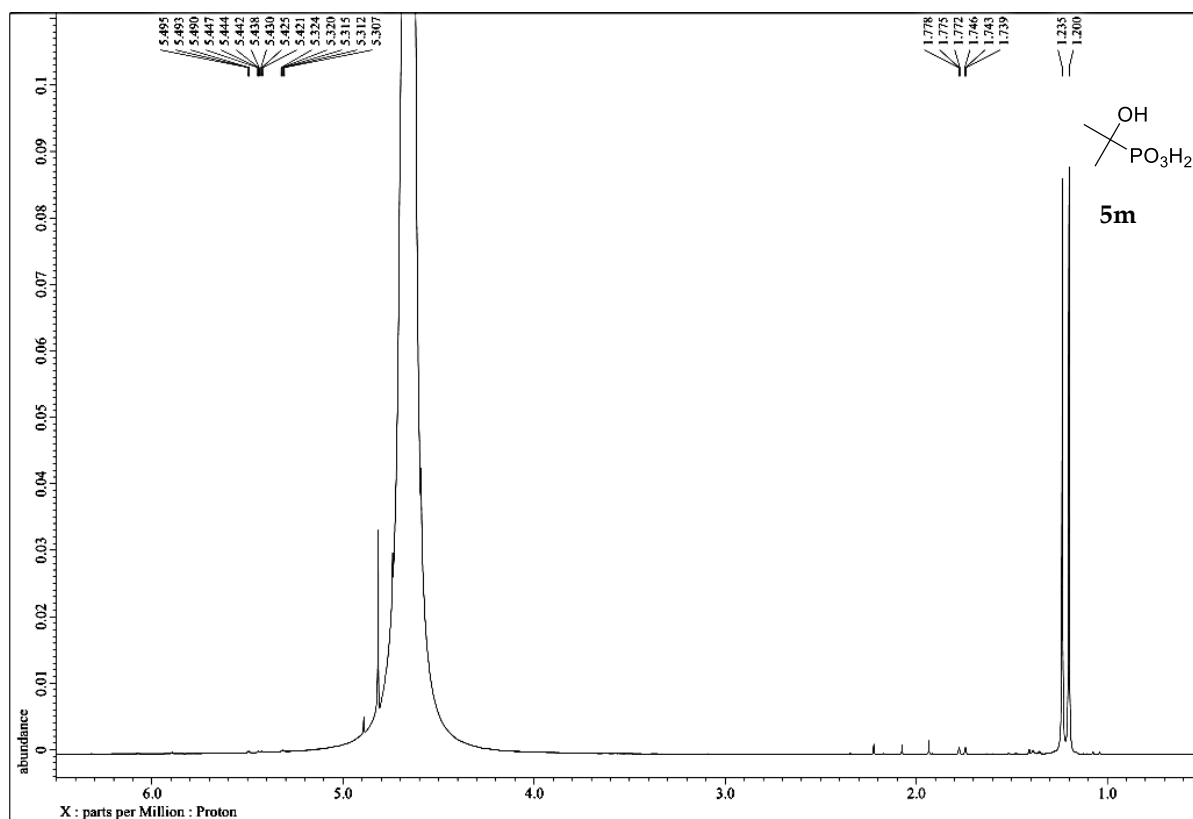
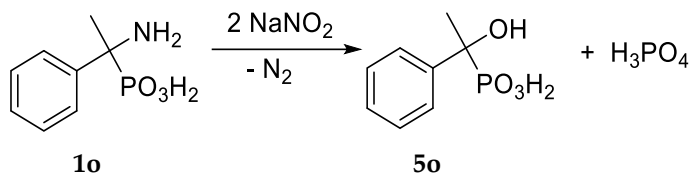


Figure S18. ^1H NMR (D_2O , 400MHz) spectra of the crude post-reaction mixture of 1-amino-1-methylethylphosphonic acid (**1m**) with NaNO_2 after 192 h with addition of 1-hydroxy-1-methylethylphosphonic acid (**5m**) as reference.

3.3. ABr1206. Deamination of **1o** in Water

48h	$\alpha = 1.00$	98%	2%
δ_P [ppm]		20.28 (q)	0.88 (s)

After 48h at 21 °C, post-reaction mixture contained 1-hydroxy-1-phenylethylphosphonic acid (**5o**) (98%molP) and orthophosphoric acid (2%molP) (Figure S19 and Figure S21).

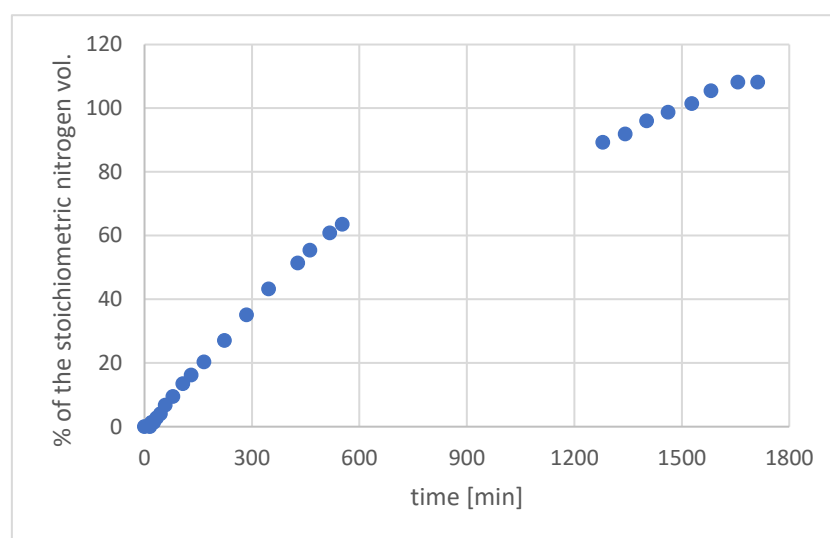
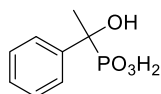


Chart 3. Dependence of the volume of the released gas (in % of the stoichiometric nitrogen volume) on the time in the reaction of 1-amino-1-phenylethylphosphonic acid (**1o**) with NaNO₂ in water.

The presence of 1-hydroxy-1-phenylethylphosphonic acid (**5o**) was confirmed by re-measuring NMR spectra (Figure S20 and Figure S22) with addition of 1-hydroxy-1-phenylethylphosphonic acid (**5o**) as reference material.



1-Hydroxy-1-phenylethylphosphonic acid (5o). ³¹P NMR (D₂O): δ 20.28 (q, $^3J_{\text{H-P}} = 14.0$ Hz); ¹H NMR (D₂O) δ : 7.43–7.48 (m, 2H), 7.26–7.32 (m, 2H), 7.18–7.24 (m, 1H), 1.63 (d, 6H, $^3J_{\text{H-P}} = 13.8$ Hz).

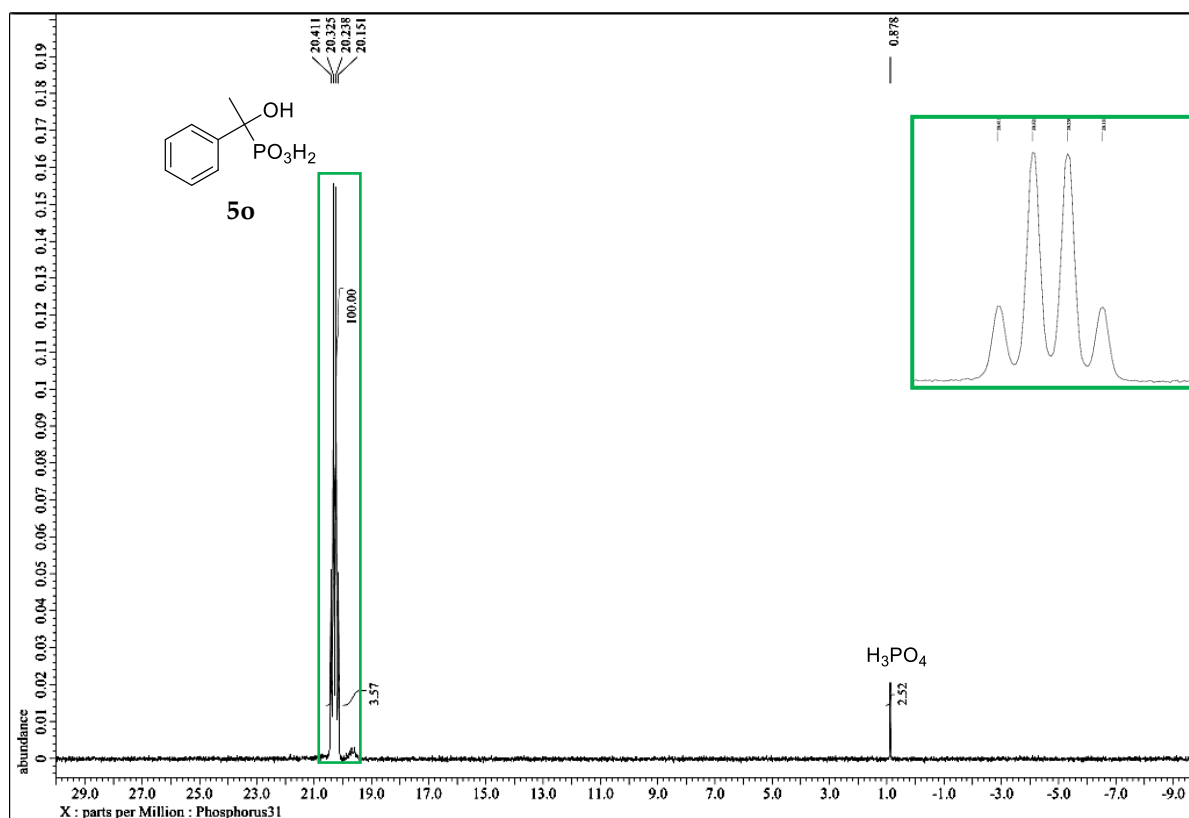


Figure S19. ^{31}P NMR (D₂O, 162MHz) spectra of the crude post-reaction mixture of 1-amino-1-phenylethylphosphonic acid (**1o**) with NaNO₂ after 48h.

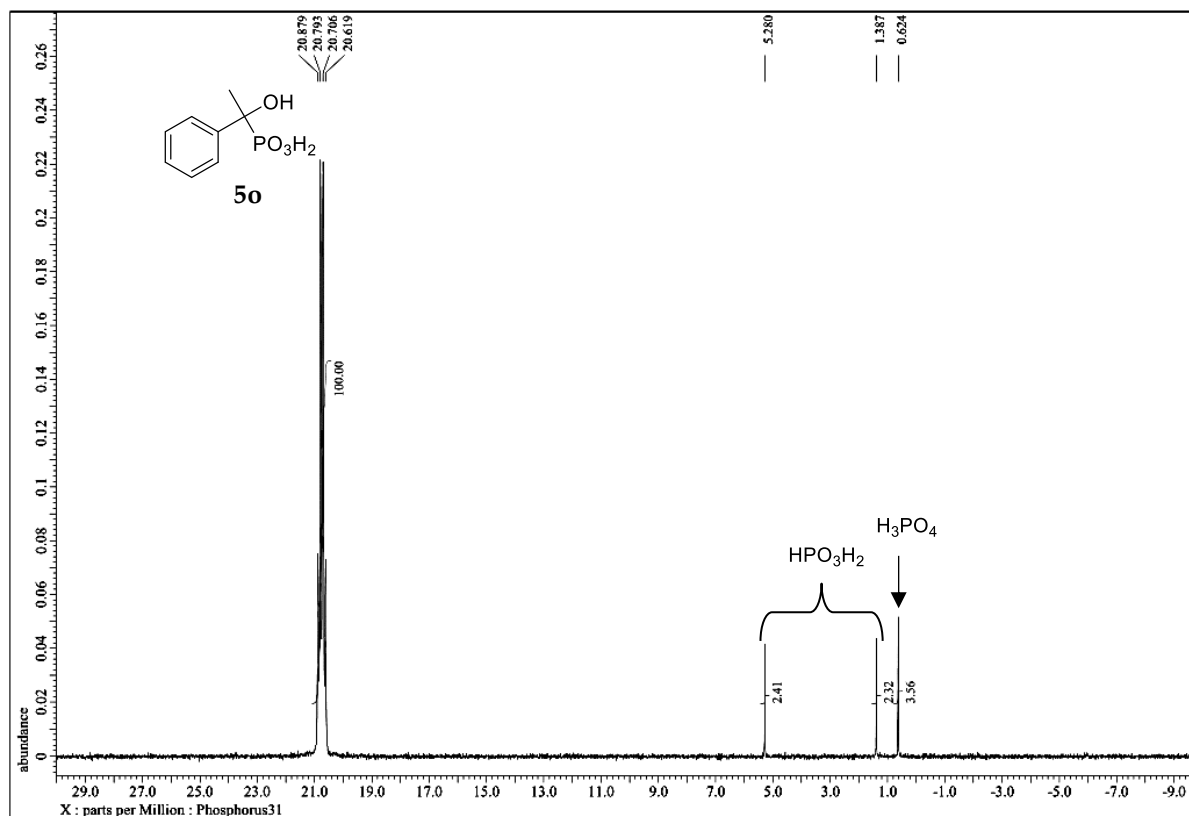


Figure S20. ^{31}P NMR (D₂O, 162MHz) spectra of the crude post-reaction mixture of 1-amino-1-phenylethylphosphonic acid (**1o**) with NaNO₂ after 48h with addition of 1-hydroxy-1-phenylethylphosphonic acid (**5o**) as reference material.

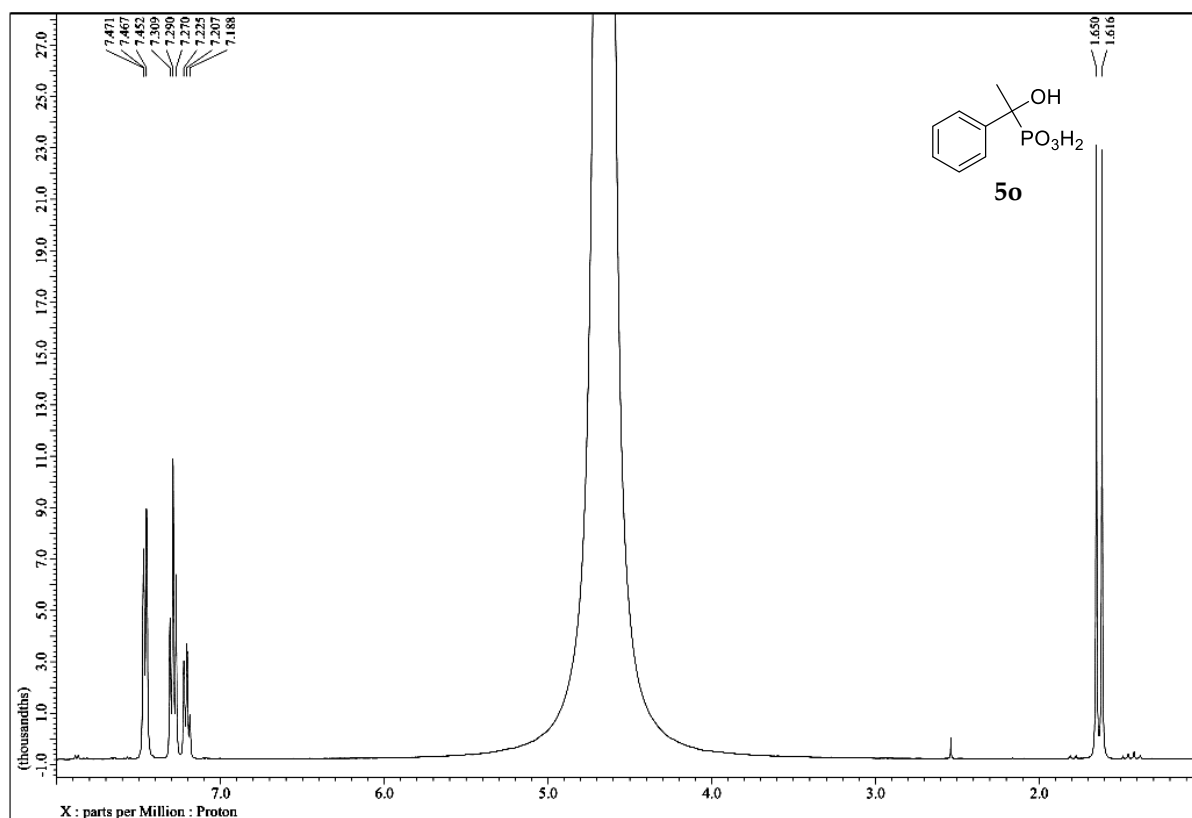


Figure S21. ^1H NMR (D_2O , 400MHz) spectra of the crude post-reaction mixture of 1-amino-1-phenylethylphosphonic acid (**1o**) with NaNO_2 after 48h.

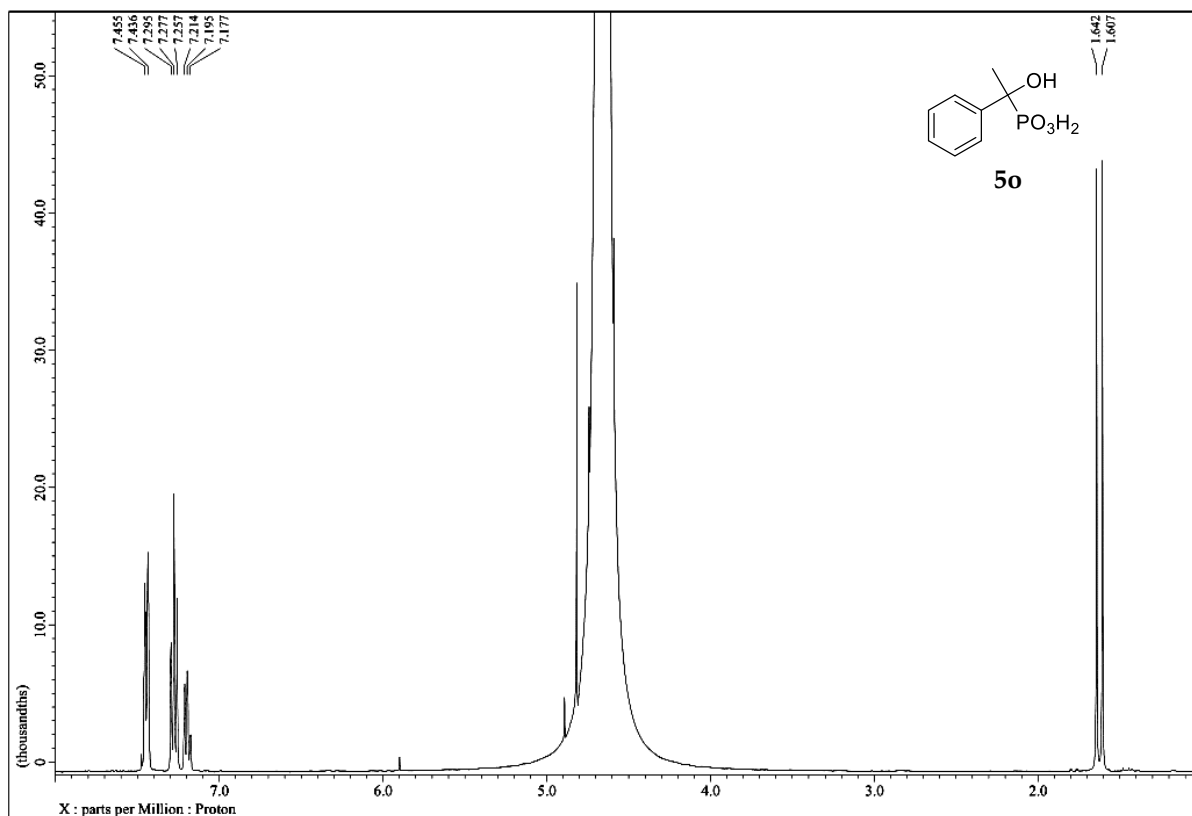
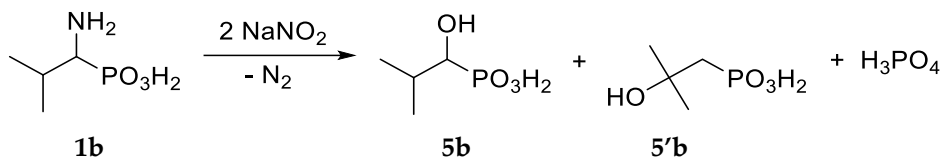


Figure S22. ^1H NMR (D_2O , 400MHz) spectra of the crude post-reaction mixture of 1-amino-1-phenylethylphosphonic acid (**1o**) with NaNO_2 after 48h with addition of 1-hydroxy-1-phenylethylphosphonic acid (**5o**) as reference material.

3.4. ABr1208. Deamination of **1b** in Water

24 h	$\alpha = 1.00$	34%	5%	59%
192 h	$\alpha = 1.00$	33%	5%	58%
δ_P [ppm]		20.57 (dd)	21.24 (t)	0.84 (s)

After 24 h at 21 °C, post-reaction mixture contained orthophosphoric acid (59%molP), 1-hydroxy-2-methylpropylphosphonic acid (**5b**) (34%molP), 2-hydroxy-2-methylpropylphosphonic acid (**5'b**) (5%molP) and unidentified compound (2%molP).

After 192 h, post-reaction mixture contained orthophosphoric acid (58%molP), 1-hydroxy-2-methylpropylphosphonic acid (**5b**) (33%molP), 2-hydroxy-2-methylpropylphosphonic acid (**5'b**) (5%molP) and 3 unidentified compounds (2%molP, 1%molP, >1%molP) (Figure S23 and Figure S25).

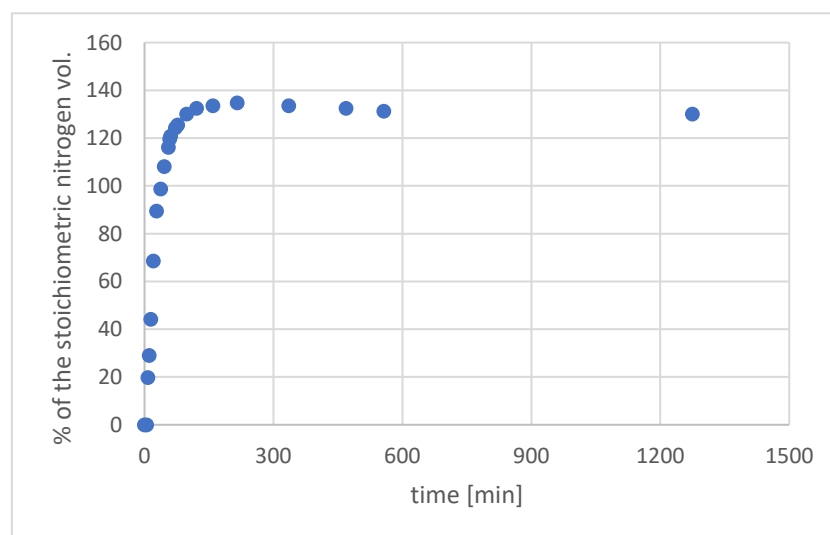
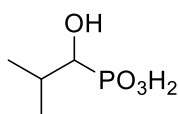


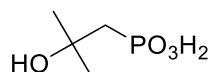
Chart 4. Dependence of the volume of the released gas (in % of the stoichiometric nitrogen volume) on the time in the reaction of 1-amino-2-methylpropylphosphonic acid (**1b**) with NaNO₂ in water.

The presence of 1-hydroxy-2-methylpropylphosphonic acid (**5b**) was confirmed by re-measuring NMR spectra (Figure S24 and Figure S26) with addition of 1-hydroxy-2-methylpropylphosphonic acid (**5b**) as reference material.

2-Hydroxy-2-methylpropylphosphonic acid (**5'b**) has been not described in the chemical literature, therefore it was identified by analysis of the signals multiplicity on the ¹H and ³¹P NMR spectra and by comparing spectra with spectra of similar 2-hydroxypropylphosphonic acid (Table S5).



1-Hydroxy-2-methylpropylphosphonic acid (5b). ³¹P NMR (D₂O): δ 20.57 (dd, $^2J_{\text{H-P}} = 8.4$ Hz, $^3J_{\text{H-P}} = 7.5$ Hz); ¹H NMR (D₂O) δ : 3.56 (dd, 1H, $^2J_{\text{H-P}} = 8.6$ Hz, $^3J_{\text{H-H}} = 5.5$ Hz), 1.87 (doublet of doublets of septets, $^3J_{\text{H-H}} = 5.5$ Hz, $^3J_{\text{H-P}} = 6.8$ Hz, $^3J_{\text{H-H}} = 5.5$ Hz), 0.90 (d, 3H, $^3J_{\text{H-H}} = 7.0$ Hz), 0.87 (d, 3H, $^3J_{\text{H-H}} = 7.0$ Hz)



2-Hydroxy-2-methylpropylphosphonic acid (5'b). ^{31}P NMR (D_2O): δ 21.24 (t, $^2J_{\text{H-P}} = 17.8$ Hz); ^1H NMR (D_2O) δ : 1.83 (d, 3H, $^2J_{\text{H-P}} = 17.7$ Hz), 1.22 (s, 6H).

Table S5. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of 2-hydroxy-2-methylpropylphosphonic acid (**5'b**) with spectra of 2-hydroxypropylphosphonic acid described in the literature.

Structure		
Source	ABr1208	Reference [9]
Solvent	D_2O	D_2O
^{31}P NMR	21.24 (t, $J = 17.8$ Hz)	19.9
^1H NMR		3.80 (1H, dm, $J = 6.5$ Hz)
	1.83 (d, 3H, $J = 17.7$ Hz)	1.39 (2H, ddd, $J = 18.0, 6.6, 15.3$ Hz)
	1.22 (s, 6H)	0.97 (3H, d, $J = 6.5$ Hz)

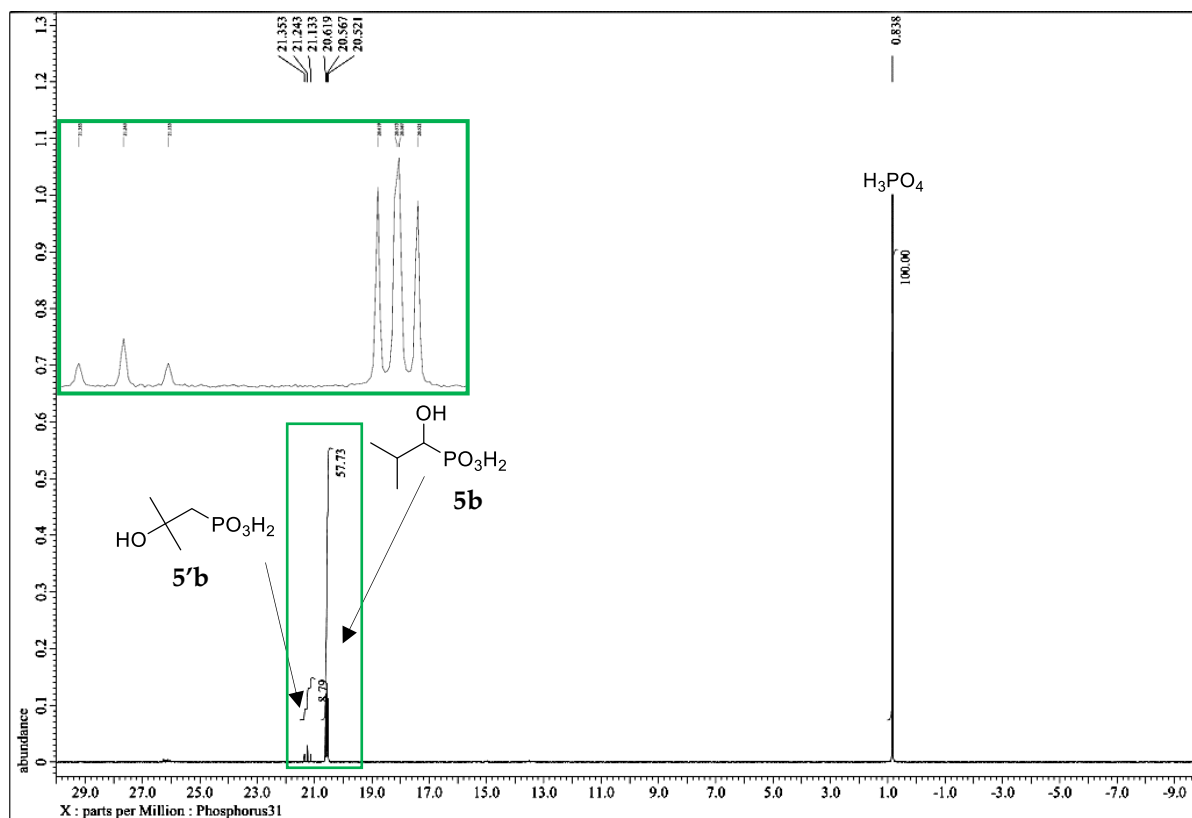


Figure S23. ^{31}P NMR (D₂O, 162 MHz) spectra of the crude post-reaction mixture of 1-amino-2-methylpropylphosphonic acid (**1b**) with NaNO₂ after 192 h.

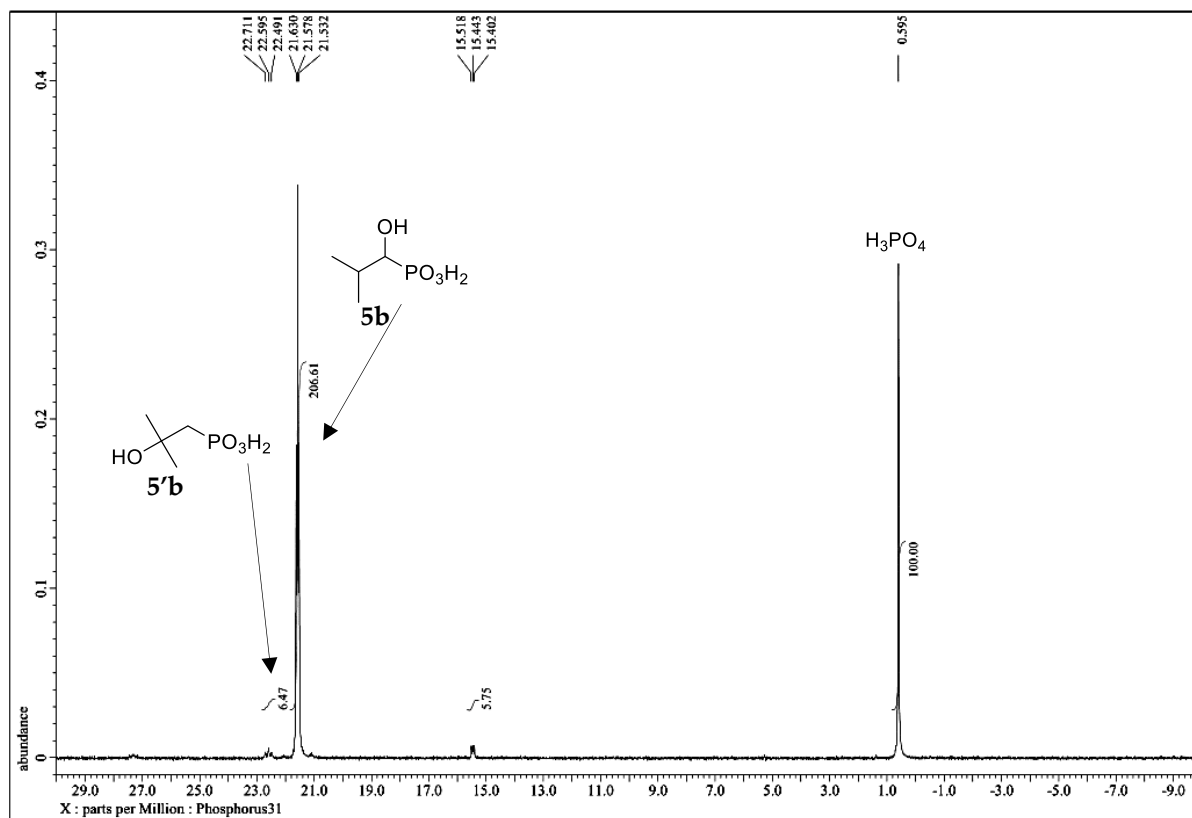


Figure S24. ^{31}P NMR (D₂O, 162 MHz) spectra of the crude post-reaction mixture of 1-amino-2-methylpropylphosphonic acid (**1b**) with NaNO₂ after 192 h with addition of 1-hydroxy-2-methylpropylphosphonic acid (**5b**) as reference material.

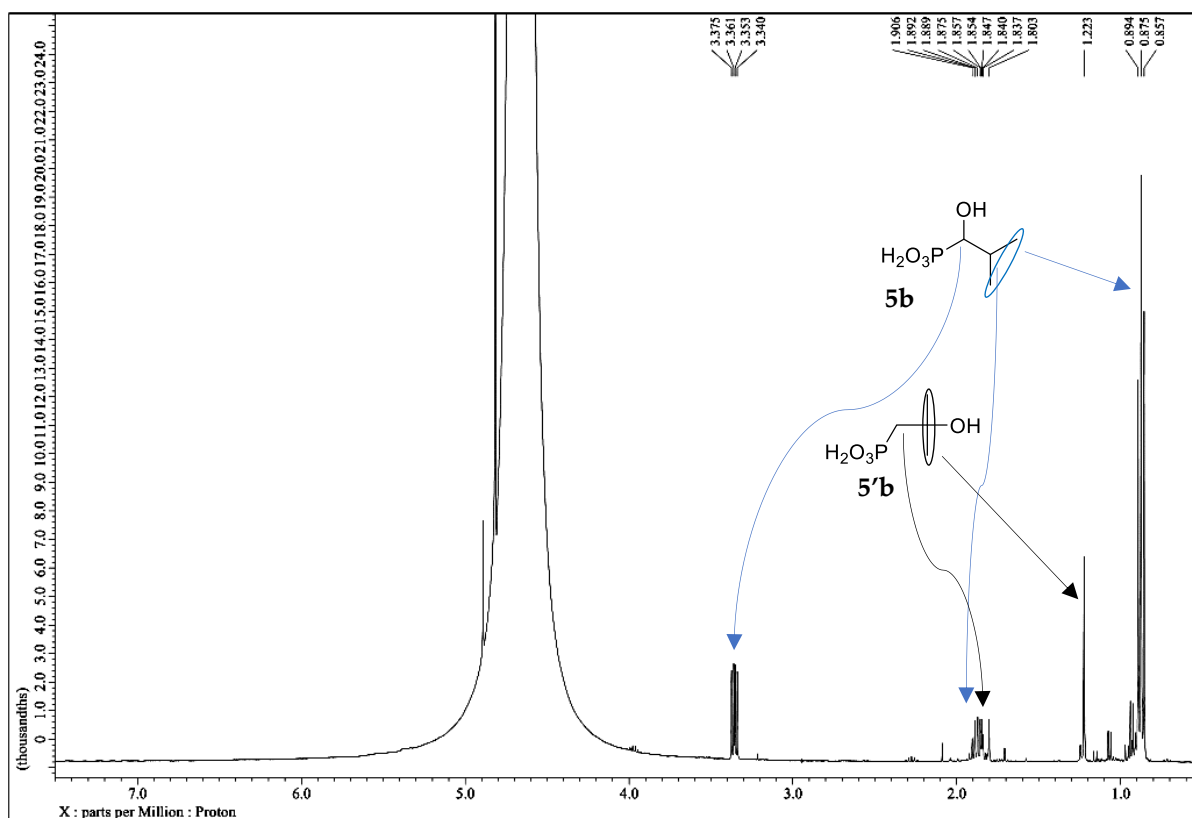


Figure S25. ^1H NMR (D_2O , 400MHz) spectra of the crude post-reaction mixture of 1-amino-2-methylpropylphosphonic acid (**1b**) with NaNO_2 after 192 h.

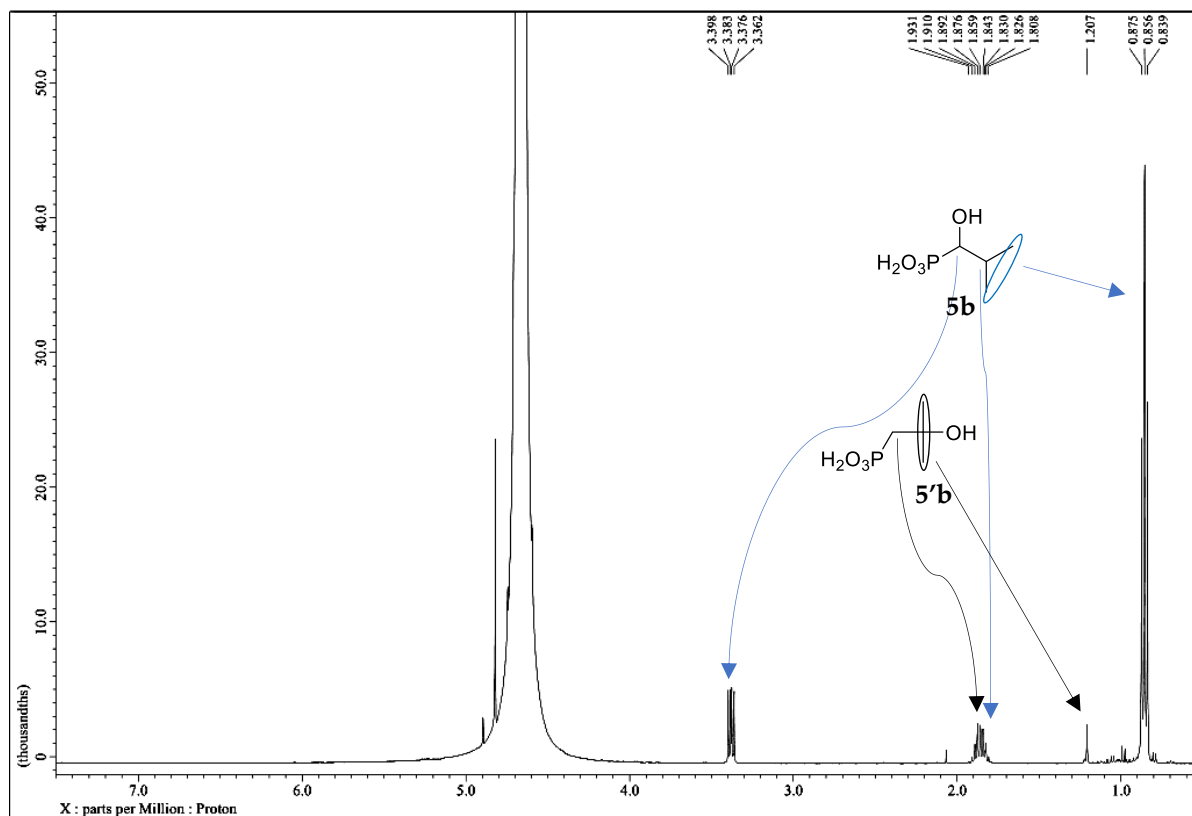
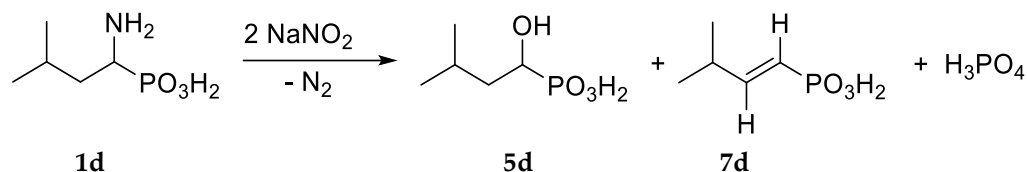


Figure S26. ^1H NMR (D_2O , 400MHz) spectra of the crude post-reaction mixture of 1-amino-2-methylpropylphosphonic acid (**1b**) with NaNO_2 after 192 h with addition of 1-hydroxy-2-methylpropylphosphonic acid (**5b**) as reference material.

3.5. ABr1210. Deamination of **1d** in Water

24 h	$\alpha = 1.00$	61%	6%	24%
168 h	$\alpha = 1.00$	61%	7%	27%
δ_P [ppm]		21.58 (dd)	14.90 (ddd)	1.16 (s)

After 24 h at 21 °C, post-reaction mixture contained 1-hydroxy-3-methylbutylphosphonic acid (**5d**) (61%molP), (*E*)-3-but-1-en-1-ylphosphonic acid (**7d**) (6%molP), orthophosphoric acid (24%molP) and 5 unidentified compounds (9%molP in total).

After 168h post-reaction mixture contained 1-hydroxy-3-methylbutylphosphonic acid (**5d**) (61%molP), (*E*)-3-but-1-en-1-ylphosphonic acid (**7d**) (7%molP), orthophosphoric acid (27%molP) and 4 unidentified compounds (5%molP in total) (Figure S27 and Figure S28).

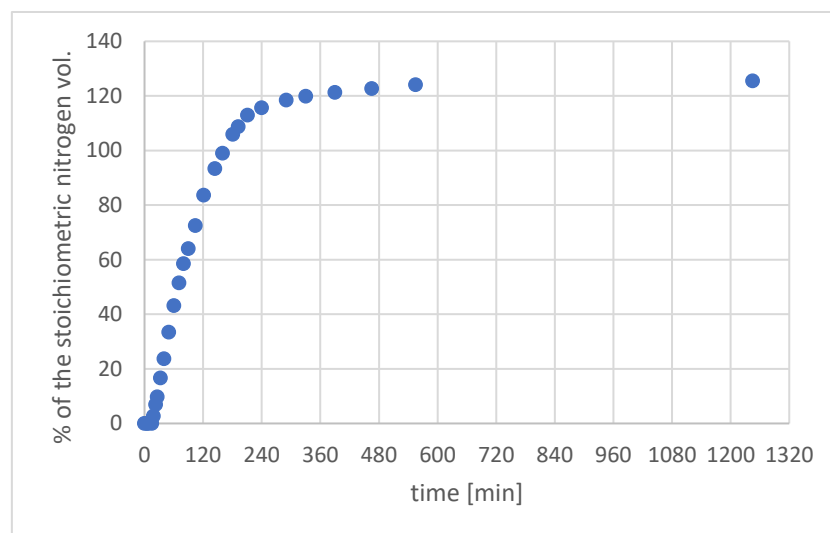
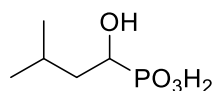
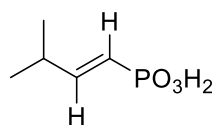


Chart 5. Dependence of the volume of the released gas (in % of the stoichiometric nitrogen volume) on the time in the reaction of 1-amino-3-methylbutylphosphonic acid (**1d**) with NaNO₂ in water.

1-Hydroxy-3-methylbutylphosphonic acid (**5d**) was identified by comparing chemical shifts, multiplicity and coupling constants on ¹H and ³¹P NMR spectra with description in the literature (Table S6). NMR spectra of (*E*)-3-but-1-en-1-ylphosphonic acid (**7d**) were not described in the literature, therefore this compound was identified by comparing signals multiplicity on the ¹H and ³¹P NMR spectra with spectra of structurally similar (*E*)-prop-1-en-1-ylphosphonic acid (Table S6).

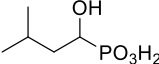
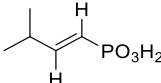
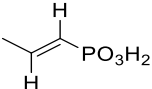


1-Hydroxy-3-methylbutylphosphonic acid (5d). ^{31}P NMR (D_2O): δ 21.61 (dt, $^2J_{\text{H-P}} = 7.5$ Hz, $^3J_{\text{H-P}} = 4.7$ Hz); ^1H NMR (D_2O): δ : 3.64 (ddd, 1H, $^3J_{\text{H-H}} = 11.3$ Hz, $^2J_{\text{H-P}} = 7.8$ Hz, $^3J_{\text{H-H}} = 2.8$ Hz), 1.60–1.72 (m, 1H, J undetermined), 1.47 (dddd, 1H, $^2J_{\text{H-H}} = 14.5$ Hz, $^3J_{\text{H-H}} = 11.3$ Hz, $J_{\text{H-H}} = 8.0$ Hz, $^3J_{\text{H-P}} = 4.0$ Hz), 1.32 (dddd, 1H, $^2J_{\text{H-H}} = 14.6$ Hz, $^3J_{\text{H-H}} = 10.1$ Hz, $^3J_{\text{H-P}} = 4.9$ Hz, $^3J_{\text{H-H}} = 2.8$ Hz), 0.81 (d, 3H, $^3J_{\text{H-H}} = 6.4$ Hz), 0.77 (d, 3H, $^3J_{\text{H-H}} = 6.7$ Hz).



(E)-3-But-1-en-1-ylphosphonic acid (7d). ^{31}P NMR (D_2O): δ 14.90 (ddd, $^3J_{\text{H-P}} = 21.5$ Hz, $^2J_{\text{H-P}} = 18.7$ Hz, $^4J_{\text{H-P}} = 1.9$ Hz); ^1H NMR (D_2O): δ : 6.30 (ddd, 1H, $^3J_{\text{H-P}} = 21.1$ Hz, $^3J_{\text{H-H}} = 17.1$ Hz, $^3J_{\text{H-H}} = 6.1$ Hz), 5.56 (ddd, 1H, $^2J_{\text{H-P}} = 19.6$ Hz, $^3J_{\text{H-H}} = 17.1$ Hz, $^4J_{\text{H-H}} = 1.5$ Hz), 1.74–1.88 (m, 1H, J undetermined), 0.87 (d, 6H, $^3J_{\text{H-H}} = 6.7$ Hz).

Table S6. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of the reaction products of 1-amino-3-methylbutylphosphonic acid (**1d**) with NaNO_2 with spectra of compounds described in the literature.

Structure				
Source	ABr1210	Reference [11]	ABr1210	Reference [12]
Solvent	D ₂ O	D ₂ O	D ₂ O	D ₂ O
³¹ P NMR	21.61 (dt, <i>J</i> = 7.5, <i>J</i> = 4.7 Hz)	25.5	14.90 (ddd, <i>J</i> = 21.5, 18.7, 1.9 Hz)	13.31
¹ H NMR	3.64 (ddd, 1H, <i>J</i> = 11.3, 7.8, 2.8 Hz)	3.82 (m, 1H)	6.30 (ddd, 1H, <i>J</i> = 21.1, 17.1, 6.1 Hz)	6.46 – 6.35 (m, 1H)
	1.60-1.72 (m, 1H, <i>J</i> undetermined)	1.73 (m, 1H)	5.56 (ddd, 1H, <i>J</i> = 19.6, 17.1, 1.5 Hz)	5.78 – 5.69 (m, 1H)
	1.47 (dddd, 1H, <i>J</i> = 14.5, 11.3, 8.0, 4.0 Hz)	1.55 (m, 1H)	1.74-1.88 (m, 1H, <i>J</i> undetermined)	1.79 (dt, 3H, <i>J</i> = 6.5, 2.0 Hz)
	1.32 (dddd, 1H, <i>J</i> = 14.6, 10.1, 4.9, 2.8 Hz)	1.40 (m, 1H)	0.87 (d, 6H, <i>J</i> = 6.7 Hz)	
	0.81 (d, 3H, <i>J</i> = 6.4 Hz)	0.89 (d, 3H, <i>J</i> = 6.6 Hz)		
	0.77 (d, 3H, <i>J</i> = 6.7 Hz)	0.85 (d, 3H, <i>J</i> = 6.6 Hz)		

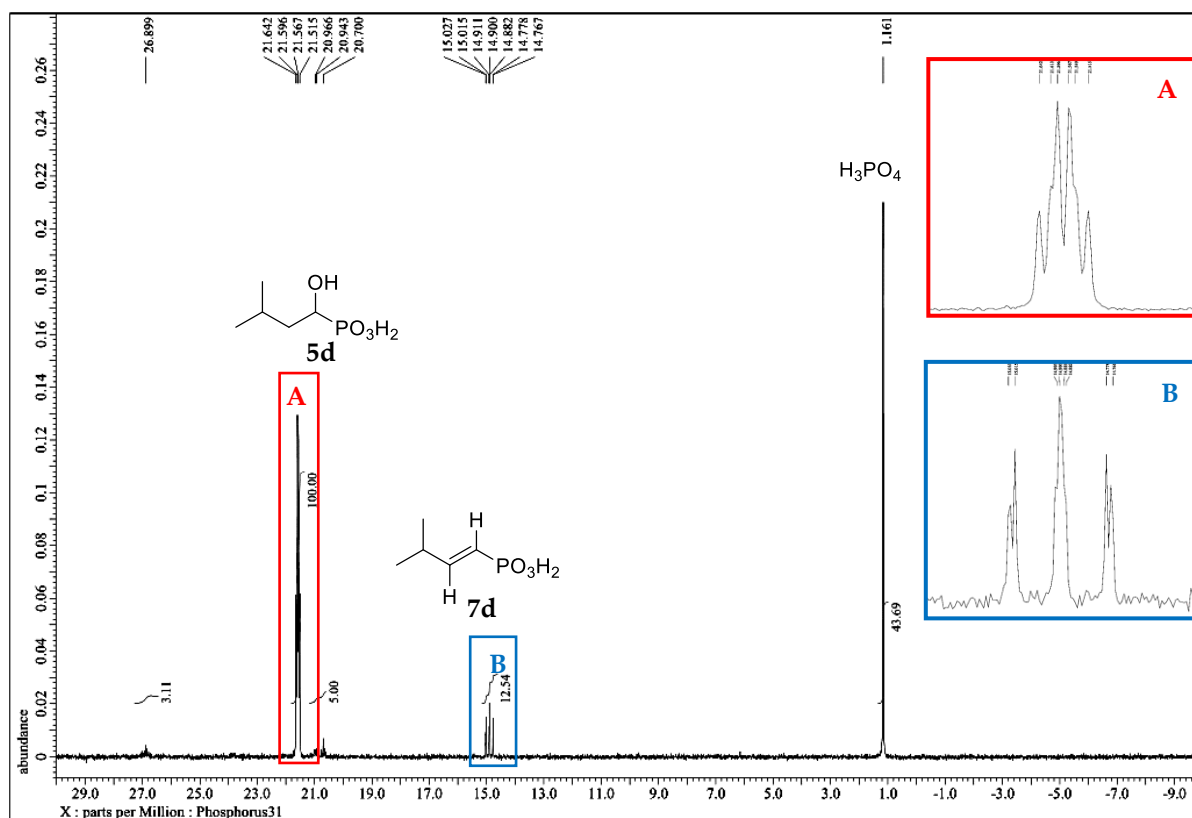


Figure S27. ^{31}P NMR (D_2O , 162MHz) spectra of the crude post-reaction mixture of 1-amino-3-methylbutylphosphonic acid (**1d**) with NaNO_2 after 168h.

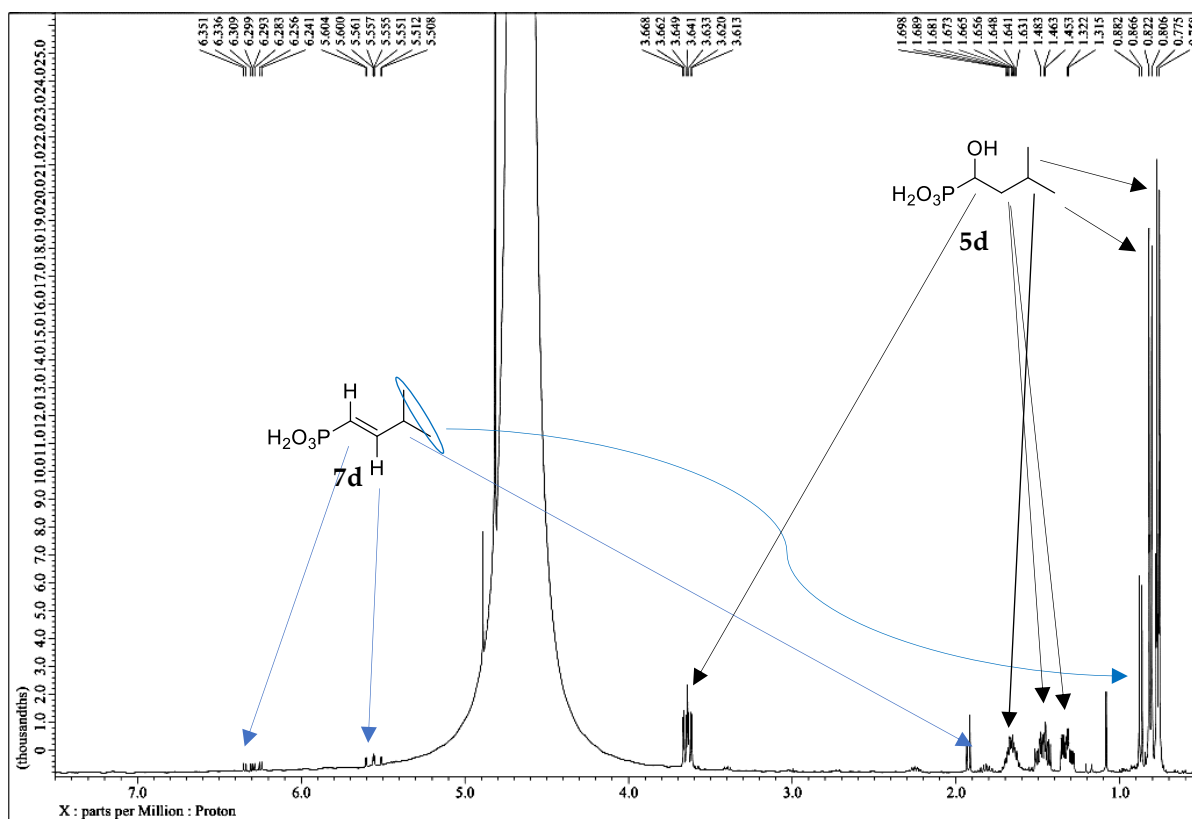
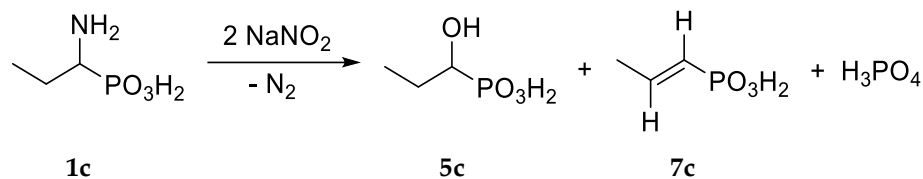


Figure S28. ^1H NMR (D_2O , 400MHz) spectra of the crude post-reaction mixture of 1-amino-3-methylbutylphosphonic acid (**1d**) with NaNO_2 after 168h.

3.6. ABr1212. Deamination of **1c** in Water

24 h	$\alpha = 1.00$	64%	7%	26%
168h	$\alpha = 1.00$	63%	7%	28%
δ_P [ppm]		20.96 (dt)	13.84 (ddq)	1.06 (s)

After 24 h at 21 °C, post-reaction mixture contained 1-hydroxypropylphosphonic acid (**5c**) (64%molP), (*E*)-prop-1-en-1-ylphosphonic acid (**7c**) (7%molP), orthophosphoric acid (26%molP) and 3 unidentified compounds (3%molP in total).

After 168h post-reaction contained 1-hydroxypropylphosphonic acid (**5c**) (63%molP), (*E*)-prop-1-en-1-ylphosphonic acid (**7c**) (7%molP), orthophosphoric acid (28%molP) and 2 unidentified compounds (3%molP in total) (Figure S29 and Figure S30).

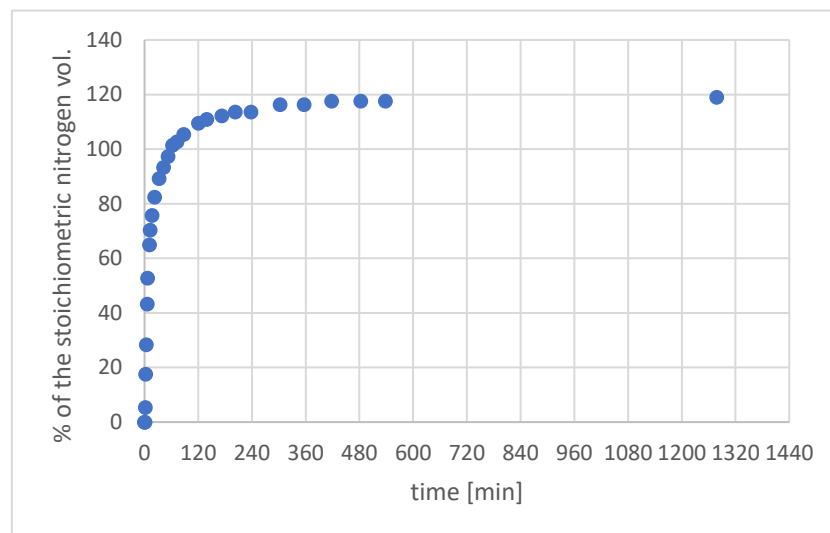
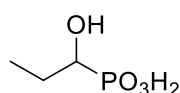
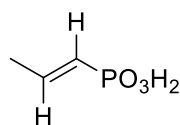


Chart 6. Dependence of the volume of the released gas (in % of the stoichiometric nitrogen volume) on the time in the reaction of 1-aminopropylphosphonic acid (**1c**) with NaNO₂ in water.

1-Hydroxypropylphosphonic acid (**5c**) and (*E*)-3-prop-1-en-1-ylphosphonic acid (**7c**) were identified by comparing chemical shifts, multiplicity and coupling constants on ¹H and ³¹P NMR spectra with description in the literature (Table S7).

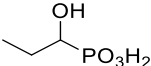
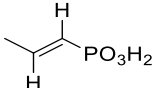


1-Hydroxypropylphosphonic acid (5c). ³¹P NMR (D₂O): δ 21.61 (dt, ²J_{H-P} = 7.5 Hz, ³J_{H-P} = 4.7 Hz); ¹H NMR (D₂O): δ : 3.44 (ddd, 1H, ³J_{H-H} = 10.2 Hz, ²J_{H-P} = 6.7 Hz, ³J_{H-H} = 3.4 Hz), 1.60–1.73 (m, 1H, *J* undetermined), 1.44 (dddq, 1H, *J* = 14.0 Hz, *J* = 10.2 Hz, *J* = 9.0 Hz, *J* = 7.0 Hz), 0.88 (t, 3H, *J*_{H-H} = 7.3 Hz).



(E)-Prop-1-en-1-ylphosphonic acid (7c). ^{31}P NMR (D_2O): δ 13.84 (ddq, $^2J_{\text{H-P}} = 20.6$ Hz, $^3J_{\text{H-P}} = 20.3$ Hz, $^4J_{\text{H-H}} = 1.9$ Hz); ^1H NMR (D_2O): δ : 6.29 (ddq, 1H, $^3J_{\text{H-P}} = 20.3$ Hz, $^3J_{\text{H-H}} = 17.0$ Hz, $^3J_{\text{H-H}} = 6.5$ Hz), 5.63 (ddq, 1H, $^2J_{\text{H-P}} = 20.6$ Hz, $^3J_{\text{H-H}} = 17.0$ Hz, $^3J_{\text{H-H}} = 1.5$ Hz), 1.60–1.73 (m, 3H, J undetermined).

Table S7. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of the reaction products of 1-aminopropylphosphonic acid (**1c**) with NaNO_2 with compounds described in the literature. .

Structure				
Source	ABr1212	Reference [13]	ABr1212	Reference [12]
Solvent	D ₂ O	D ₂ O	D ₂ O	D ₂ O
³¹ P NMR	21.61 (dt, <i>J</i> = 7.5, 4.7 Hz)	23.9	13.84 (ddq, <i>J</i> = 20.6, 20.3, 1.9 Hz)	13.31
	3.44 (ddd, 1H, <i>J</i> = 10.2, 6.7, 3.4 Hz)	2.85 - 3.45 (1H, m)	6.29 (ddq, 1H, <i>J</i> = 20.3, 17.0, 6.5 Hz)	6.46 – 6.35 (m, 1H)
¹ H NMR	1.60-1.73 (m, 1H, <i>J</i> undetermined)	1.45 - 2.25 (2H, m)	5.63 (ddq, 1H, <i>J</i> = 20.6, 17.0, 1.5 Hz)	5.78 – 5.69 (m, 1H)
	1.44 (dddq, 1H, <i>J</i> = 14.0, 10.2, 9.02, 7.0 Hz)		1.60-1.73 (m, 3H)	1.79 (dt, <u>3H</u> , <i>J</i> = 6.5, 2.0 Hz)
	0.88 (t, 3H, <i>J</i> = 7.3 Hz)	1.20 (t, 3H, <i>J</i> = 6.2 Hz)		

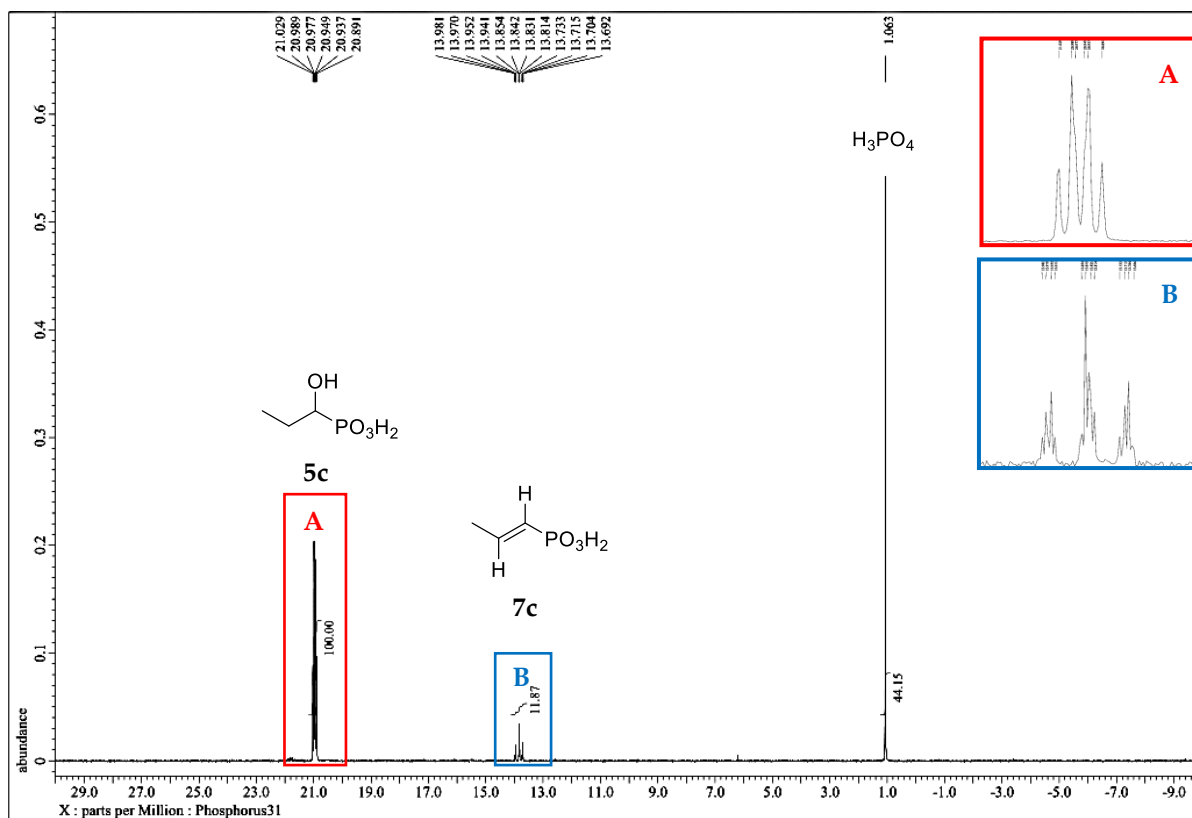


Figure S29. ^{31}P NMR (D₂O, 162MHz) spectra of the crude post-reaction mixture of 1-aminopropylphosphonic acid (1c) with NaNO₂ after 168h.

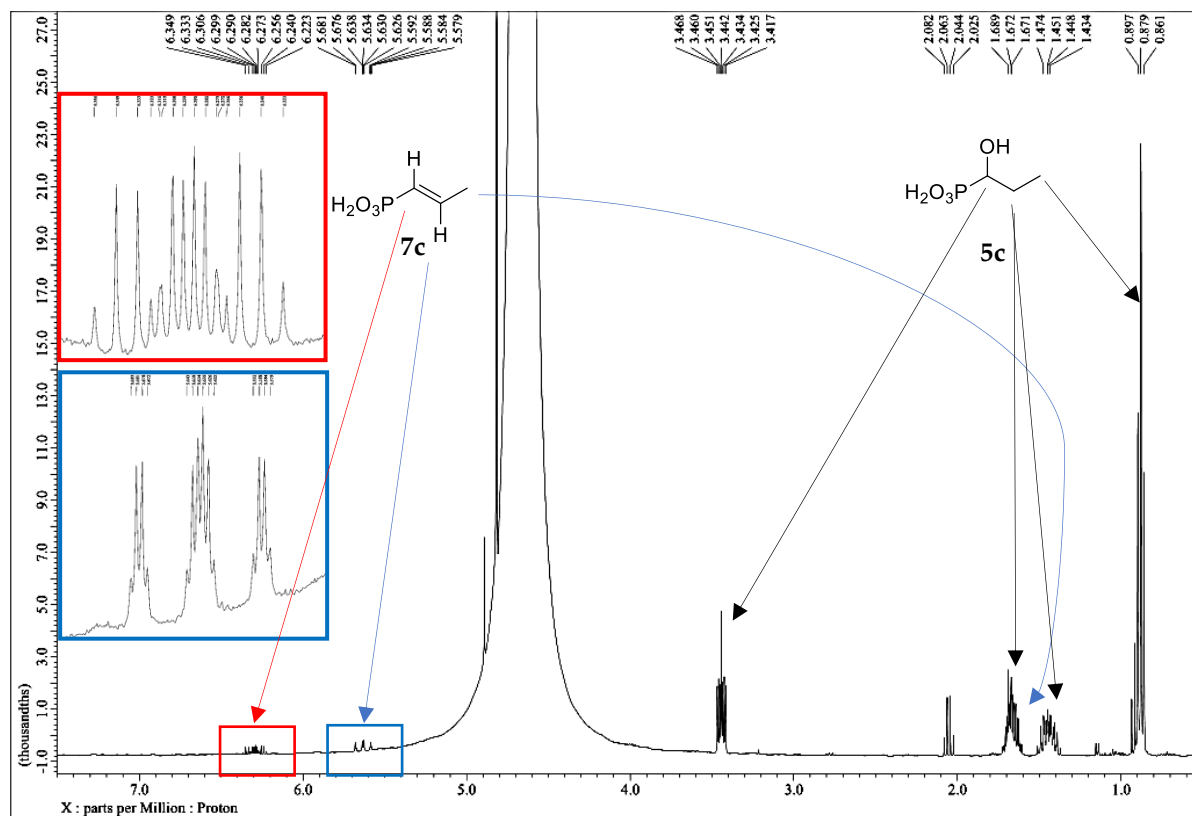
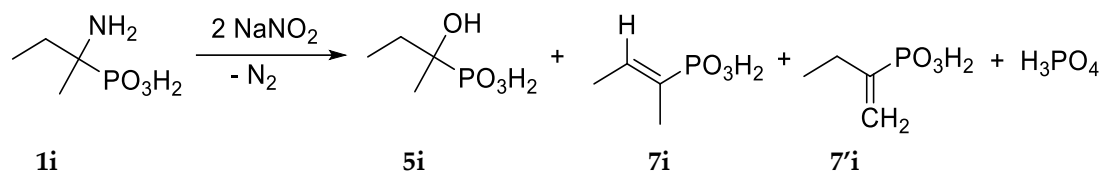


Figure S30. ^1H NMR (D₂O, 400MHz) spectra of the crude post-reaction mixture of 1-aminopropylphosphonic acid (1c) with NaNO₂ after 168h.

3.7. ABr1214. Deamination of **1i** in Water

48h	$\alpha = 0.97$	43%	41%	5%	6%
192 h	$\alpha = 1.00$	43%	42%	8%	7%
δ_P [ppm]	16.82	24.18 (ddq)	17.47 (dqg)	15.63 (ddt)	1.05

After 24 h at 21 °C, post-reaction mixture contained 1-hydroxy-1-methylpropylphosphonic acid (**5i**) (43%molP), (*E*)-1-methylprop-1-en-1-ylphosphonic acid (**7i**) (41%molP), 1-ethylvinylphosphonic acid (**7'i**) (5%molP), orthophosphoric acid (6%molP), unreacted substrate (3%molP) and 2 unidentified compounds (2%molP in total).

After 192 h post-reaction mixture contained 1-hydroxy-1-methylpropylphosphonic acid (**5i**) (43%molP), (*E*)-1-methylprop-1-en-1-ylphosphonic acid (**7i**) (42%molP), 1-ethylvinylphosphonic acid (**7'i**) (8%molP), orthophosphoric acid (7%molP) and trace amounts of 2 unidentified compounds (Figure S31 and Figure S32).

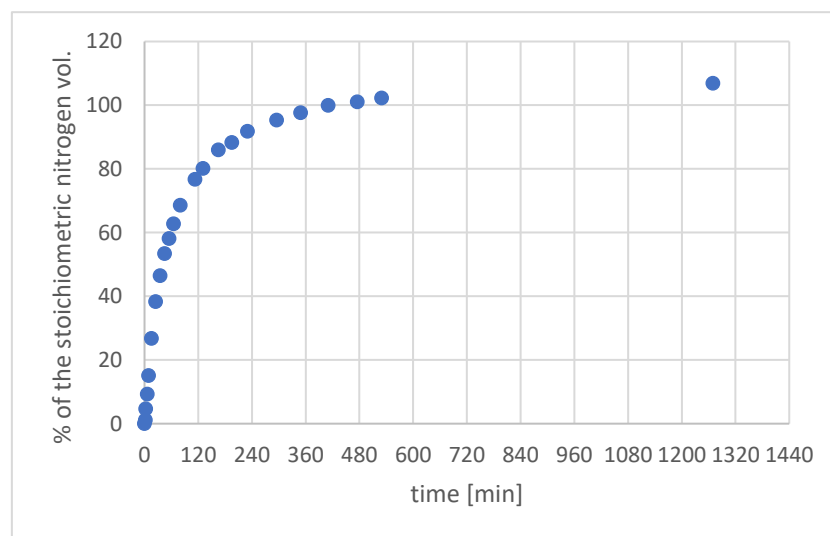
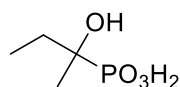


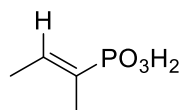
Chart 7. Dependence of the volume of the released gas (in % of the stoichiometric nitrogen volume) on the time in the reaction of 1-amino-1-methylpropylphosphonic acid (**1i**) with NaNO₂ in water.

(*E*)-1-Methylprop-1-en-1-ylphosphonic acid (**7i**) was identified by comparing chemical shifts, multiplicity and coupling constants on ¹H and ³¹P NMR spectra with description in the literature of structurally similar (*E*)-2-(*N*-hydroxylamino)-1-methylpent-1-en-1-ylphosphonic acid (Table S8).

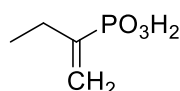
Spectra of 1-hydroxy-1-methylpropylphosphonic acid (**5i**) and 1-ethylvinylphosphonic acid (**7'i**) have been not described in the literature. Therefore these compounds were identified by comparing chemical shifts, multiplicity and coupling constants on ¹H and ³¹P NMR spectra with description in the literature with spectra of structurally similar 1-hydroxy-1-methylethylphosphonic acid (**5m**) and 1-methylvinylphosphonic acid (**7m**) (experiment ABr1204) (Table S9).



1-Hydroxy-1-methylpropylphosphonic acid (5i). ^{31}P NMR (D_2O): δ 24.18 (ddq, $^3J_{\text{H-P}} = 14.5$ Hz, $^3J_{\text{H-P}} = 11.1$ Hz, $^3J_{\text{H-P}} = 7.0$ Hz); ^1H NMR (D_2O): δ : 1.49–1.70 (m, 2H, J undetermined), 1.17 (d, 3H, $^3J_{\text{H-P}} = 14.4$ Hz), 0.81 (t, 3H, $^3J_{\text{H-H}} = 7.3$ Hz).



(E)-1-Methylprop-1-en-1-ylphosphonic acid (7i). ^{31}P NMR (D_2O): δ 17.47 (dq, $^3J_{\text{H-P(cis)}} = 21.7$ Hz, $^3J_{\text{H-P}} = 13.6$ Hz, $^4J_{\text{H-P}} = 3.7$ Hz); ^1H NMR (D_2O): δ : 6.15 (ddq, 1H, $^3J_{\text{H-P}} = 21.7$ Hz, $^3J_{\text{H-H}} = 6.7$ Hz, $^4J_{\text{H-H}} = 1.5$ Hz), 1.63 (ddq, 3H, $^3J_{\text{H-P}} = 13.6$ Hz, $^4J_{\text{H-H}} = 1.2$ Hz, $^5J_{\text{H-H}} = 1.2$ Hz), 1.57 (ddq, 3H, $^3J_{\text{H-H}} = 6.7$ Hz, $^4J_{\text{H-P}} = 3.7$ Hz, $^5J_{\text{H-H}} = 1.2$ Hz).



1-Ethylvinylphosphonic acid (7'i). ^{31}P NMR (D_2O): δ 15.63 (ddt, $^3J_{\text{H-P(trans)}} = 44.4$ Hz, $^3J_{\text{H-P(cis)}} = 21.5$ Hz, $^3J_{\text{H-P}} = 10.3$ Hz); ^1H NMR (D_2O): δ : 5.56 (ddt, 1H, $^3J_{\text{H-P(cis)}} = 21.4$ Hz, $^2J_{\text{H-H}} = 1.5$ Hz, $^4J_{\text{H-H}} = 1.2$ Hz), 5.39 (ddt, 1H, $^3J_{\text{H-P(trans)}} = 44.3$ Hz, $^4J_{\text{H-H}} = 1.8$ Hz, $^2J_{\text{H-H}} = 1.5$ Hz), 2.12 (dddq, 2H, $^3J_{\text{H-P}} = 10.3$ Hz, $^3J_{\text{H-H}} = 7.3$ Hz, $^4J_{\text{H-H}} = 1.8$ Hz, $^4J_{\text{H-P}} = 1.2$ Hz), 0.95 (t, 3H, $^3J_{\text{H-H}} = 7.3$ Hz).

Table S8. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of (E)-1-methylprop-1-en-1-ylphosphonic acid (**7i**) with spectra of structurally similar (E)-2-(N-hydroxylamino)-1-methyl-pent-1-en-1-ylphosphonic acid.

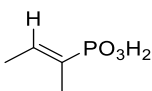
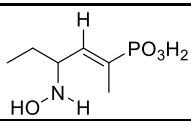
Structure		
Source	ABr1214	Reference [14]
Solvent	D_2O	D_2O
^{31}P NMR	17.47 (dq, $J = 21.7, 13.6, 3.7$ Hz)	n. d.
^1H NMR	6.15 (ddq, 1H, $J = 21.7, 6.7, 1.5$ Hz)	6.12 (dd, 1H, $J = 9.8, 21.2$ Hz)
		4.35 (m, 1H)
		2.05 (m, 2H)
	1.63 (ddq, 3H, $J = 13.6, 1.2, 1.2$ Hz)	2.02 (d, 3H, $J = 13.8$ Hz)
	1.57 (ddq, 3H, $J = 6.7, 3.7, 1.2$ Hz)	1.04 (t, 3H, $J = 7.4$ Hz)

Table S9. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of the reaction products of 1-amino-1-methylpropylphosphonic acid (**1i**) with NaNO_2 with spectra of 1-hydroxy-1-methylethylphosphonic acid (**5m**) and 1-methylvinylphosphonic acid (**7'm**).

Structure				
Source	ABr1214	ABr1204	ABr1214	ABr1204
Solvent	D_2O	D_2O	D_2O	D_2O
^{31}P NMR	24.18 (ddq, $J = 14.5, 11.1, 7.0$ Hz)	23.84 (septet, $J = 14.0$ Hz)	15.63 (ddt, $J = 44.4, 21.5, 10.3$ Hz)	15.21 (ddq, $J = 43.9, 20.6, 13.1$ Hz)
^1H NMR	1.49–1.70 (m, 2H, J undetermined)		5.56 (ddt, 1H, $J = 21.4, 1.5, 1.2$ Hz)	5.46 (ddq, 1H, $J = 20.3, 2.1, 1.2$ Hz)
	1.17 (d, 3H, $J = 14.4$ Hz)	1.23 (d, 6H, $J = 13.8$ Hz)	5.39 (ddt, 1H, $J = 44.3, 1.8, 1.5$ Hz)	5.36 (tq, 1H, $J = 43.4, 1.8$ Hz)
	0.81 (t, 3H, $J = 7.3$ Hz)		2.12 (dddq, 2H, $J = 10.3, 7.3, 1.8, 1.2$ Hz)	1.77 (dt, 3H, $J = 13.1, 1.2$ Hz)
			0.95 (t, 3H, $J = 7.3$ Hz).	

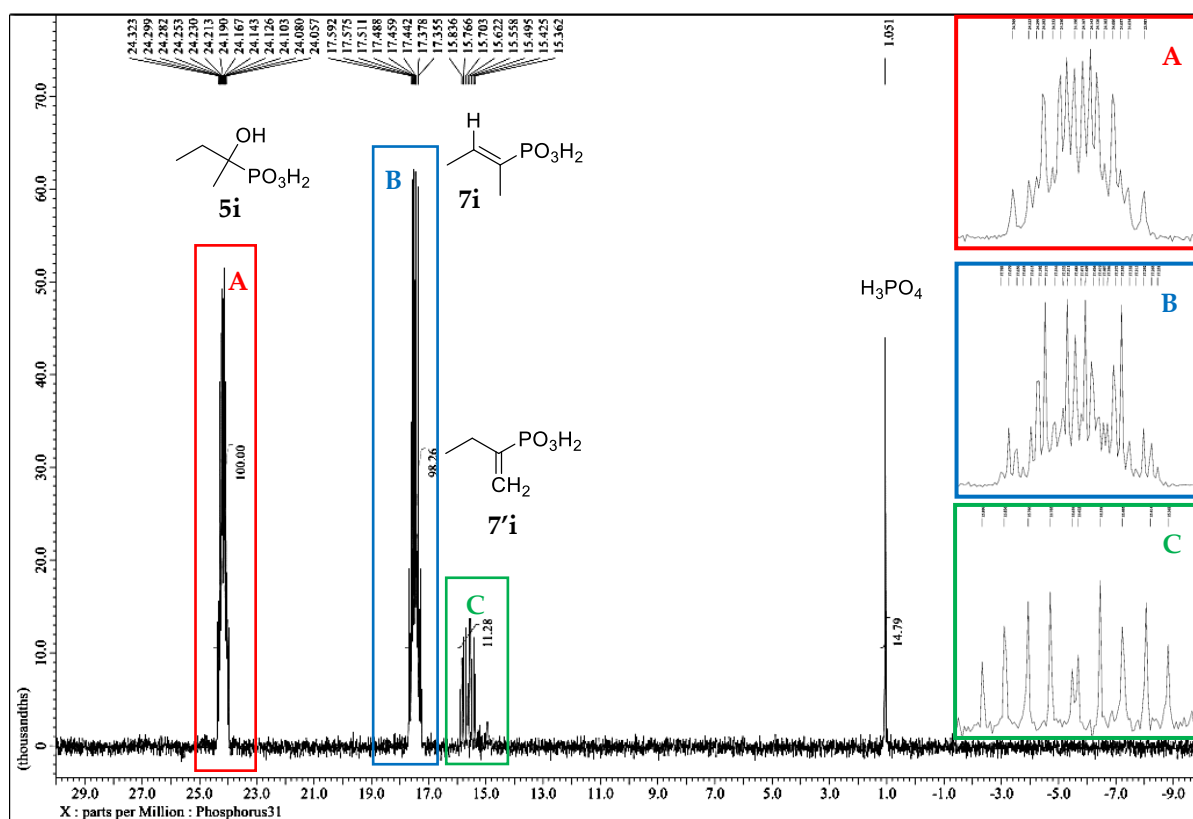


Figure S31. ^{31}P NMR (D $_2$ O, 162 MHz) spectra of the crude post-reaction mixture of 1-amino-1-methylpropylphosphonic acid (**1i**) with NaNO_2 after 192 h.

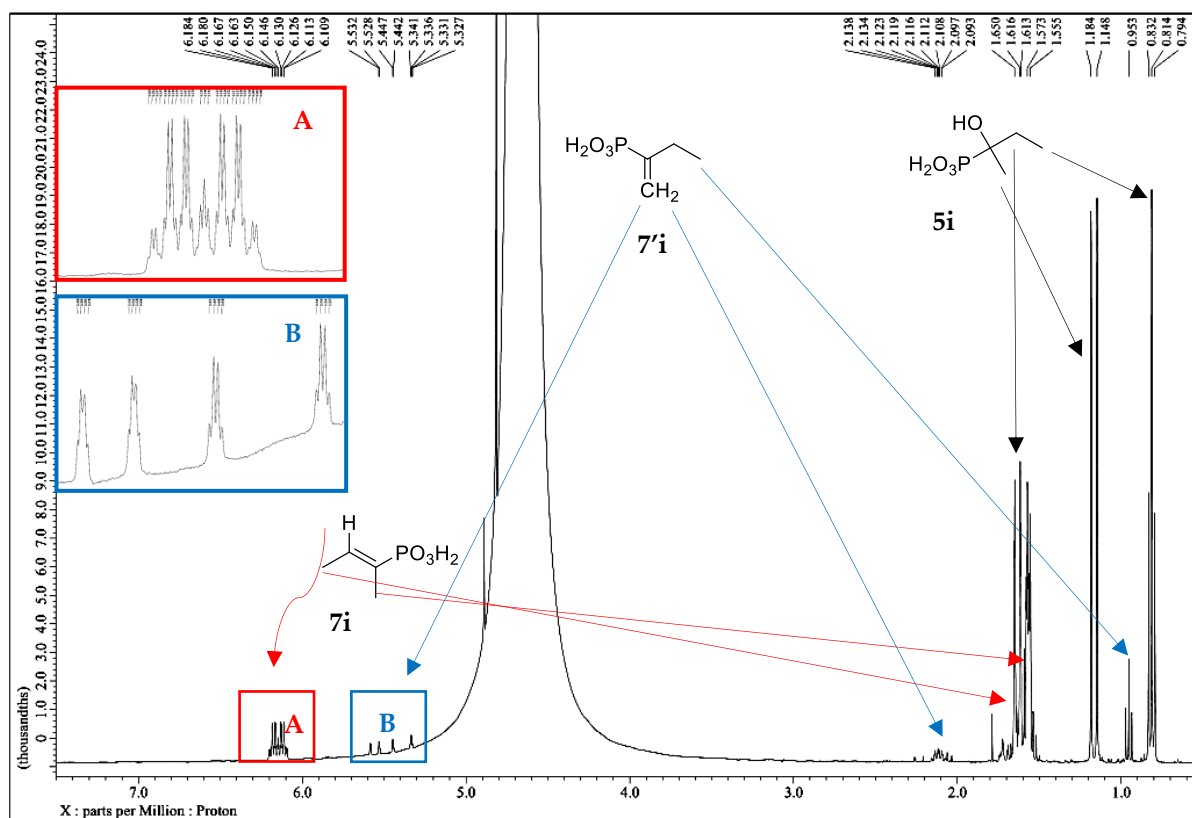
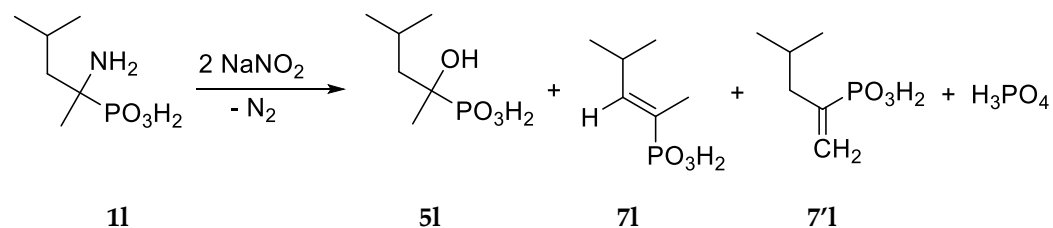


Figure S32. ^1H NMR (D_2O , 400MHz) spectra of the crude post-reaction mixture of 1-amino-1-methylpropylphosphonic acid (**1i**) with NaNO_2 after 192 h.

3.8. ABr1216. Deamination of **11** in Water

	11	51	71	7'1	
24 h	$\alpha = 0.97$	29%	57%	7%	3%
192 h	$\alpha = 1.00$	30%	59%	7%	4%
δ_P [ppm]	16.82	24.18 (tq)	17.87 (ddq)	15.6 (ddt)	1.09

After 24 h at 21 °C, post-reaction mixture contained 1-hydroxy-1,3-dimethylbutylphosphonic acid (**51**) (29%molP), (*E*)-1,3-dimethylbut-1-en-1-ylphosphonic acid (**71**) (57%molP), 4-methylpent-1-en-2-ylphosphonic acid (**7'1**) (7%molP), orthophosphoric acid (3%molP), unreacted substrate (**11**) (3%molP) and unidentified compound (ca. 1%molP).

After 192 h post-reaction mixture contained 1-hydroxy-1,3-dimethylbutylphosphonic acid (**51**) (30%molP), (*E*)-1,3-dimethylbut-1-en-1-ylphosphonic acid (**71**) (59%molP), 4-methylpent-1-en-2-ylphosphonic acid (**7'1**) (7%molP), orthophosphoric acid (4%molP) and trace amounts of unidentified compound (>1%molP) (Figure S33 and Figure S34).

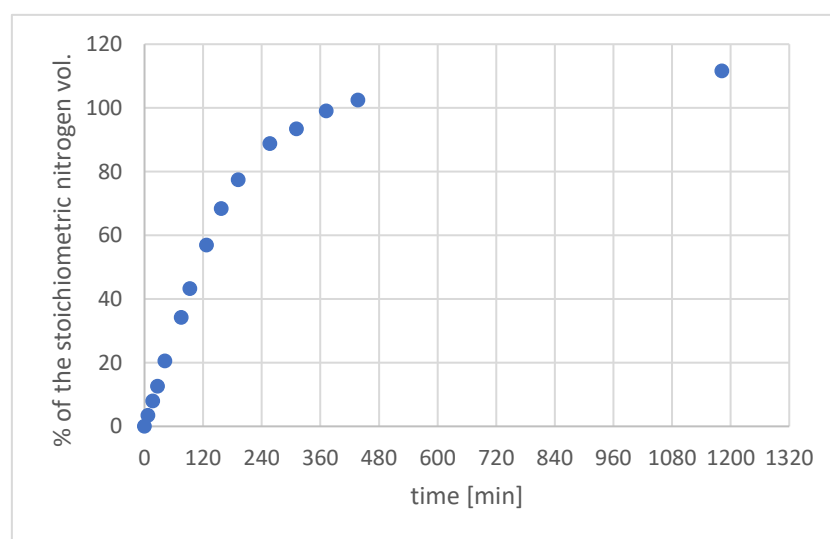
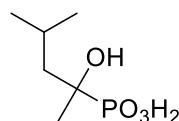


Chart 8. Dependence of the volume of the released gas (in % of the stoichiometric nitrogen volume) on the time in the reaction of 1-amino-1,3-dimethylbutylphosphonic acid (**11**) with NaNO₂ in water.

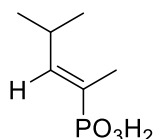
Spectra of (*E*)-1,3-dimethylbut-1-en-1-ylphosphonic acid (**71**) have been not described in the literature. Therefore, this compound was identified by comparing chemical shifts, multiplicity and coupling constants on ¹H and ³¹P NMR spectra with spectra of (*E*)-1-methylprop-1-en-1-ylphosphonic acid (**7i**), which was obtained in the reaction of 1-amino-1-methylpropylphosphonic acid (**1i**) with NaNO₂ (ABr1214) (Table S10).

Spectra of 1-hydroxy-1,3-dimethylbutylphosphonic acid (**51**) and 4-methylpent-1-en-2-ylphosphonic acid (**7'1**) have been not described in the literature. Therefore, these compounds were identified by comparing chemical shifts, multiplicity and coupling constants on ¹H and ³¹P NMR spectra with spectra of 1-hydroxy-1-methylethylphosphonic

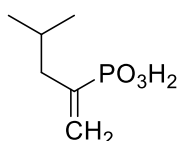
acid (**5m**) and 1-methylvinylphosphonic acid (**7m**), which were obtained in the reaction of 1-amino-1-methylethylphosphonic acid (**1m**) with NaNO₂ (ABr1204) (Table S11).



1-Hydroxy-1,3-dimethylbutylphosphonic acid (5l). ³¹P NMR (D₂O): δ 24.18 (tq, ³J_{H-P} = 15.0 Hz, ³J_{H-P} = 7.5 Hz); ¹H NMR (D₂O) δ: 1.78 (doublet of septets, 1H, ³J_{H-H} = 7.0 Hz, ³J_{H-H} = 6.4 Hz), 1.43–1.55 (m, 2H), 1.23 (d, 3H, ³J_{H-P} = 15.0 Hz), 0.81 (d, 3H, ³J_{H-H} = 6.4 Hz), 0.79 (d, 3H, ³J_{H-H} = 6.1 Hz).



(E)-1,3-Dimethylbut-1-en-1-ylphosphonic acid (7l). ³¹P NMR (D₂O): δ 17.87 (ddq, ³J_{H-P} = 22.4 Hz, ³J_{H-P} = 14.0 Hz, ⁴J_{H-P} = 2.8 Hz); ¹H NMR (D₂O) δ: 5.88 (ddq, 1H, ³J_{H-P} = 22.2 Hz, ³J_{H-H} = 9.3 Hz, ⁴J_{H-H} = 1.8 Hz), 2.51 (doublet of doublets of septets, 1H, ³J_{H-H} = 9.3 Hz, ³J_{H-H} = 6.6 Hz, ³J_{H-H} = 2.8 Hz), 1.65 (dd, 3H, ³J_{H-P} = 13.9 Hz, ⁴J_{H-H} = 1.8 Hz), 0.83 (d, 6H, ³J_{H-H} = 6.7 Hz).



4-Methylpent-1-en-2-ylphosphonic acid (7l). ³¹P NMR (D₂O): δ 15.6 (ddt, ³J_{H-P} (trans) = 44.1 Hz, ³J_{H-P} (cis) = 21.0 Hz, ³J_{H-P} = 14.2 Hz); ¹H NMR (D₂O) δ: 5.61 (ddd, 1H, ³J_{H-P} (cis) = 21.1 Hz, ⁴J_{H-H} = 2.1 Hz, *J* undetermined), 5.37 (ddd, 1H, ³J_{H-P} (trans) = 44.5 Hz, ⁴J_{H-H} = 3.4 Hz, ⁴J_{H-H} = 1.5 Hz), 1.98 (br dddd, 2H, ³J_{H-P} = 14.1 Hz, ³J_{H-H} = 7.0 Hz, *J* nieozn), 1.70–1.85 (m, 1H, *J* undetermined), 0.72 (d, 6H, ³J_{H-H} = 6.7 Hz).

Table S10. Comparison of chemical shifts and coupling constants on ¹H and ³¹P NMR spectra of (*E*)-1,3-7ldimethylbut-1-en-1-ylphosphonic acid (**7l**) with (*E*)-1-methylprop-1-en-1-ylphosphonic acid (**7i**) (ABr1214).

Structure		
Source	ABr1216	ABr1214
Solvent	D ₂ O	D ₂ O
³¹ P NMR	17.87 (ddq, <i>J</i> = 22.4, 14.0, 2.8 Hz)	17.47 (dq, <i>J</i> = 21.7, 13.6, 3.7 Hz)
¹ H NMR	5.88 (ddq, 1H, <i>J</i> = 22.2, 9.3, 1.8 Hz),	6.15 (ddq, 1H, <i>J</i> = 21.7, 6.7, 1.5 Hz)
	2.51 (doublet of doublets of septets, 1H, <i>J</i> = 9.3, 6.6, 2.8 Hz)	
	1.65 (dd, 3H, <i>J</i> = 13.9, 1.8 Hz)	1.63 (ddq, 3H, <i>J</i> = 13.6, 1.2, 1.2 Hz)
	0.83 (d, 6H, <i>J</i> = 6.7 Hz)	1.57 (ddq, 3H, <i>J</i> = 6.7, 3.7, 1.2 Hz)

Table S11. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of post-reaction mixture of 1-hydroxy-1,3-dimethylbutylphosphonic acid (**1l**) with NaNO_2 with 1-hydroxy-1-methylethylphosphonic acid (**5m**) and 1-methylvinylphosphonic acid (**7m**) (ABr1204).

Structure				
Source	ABr1216	ABr1204	ABr1216	ABr1204
Solvent	D_2O	D_2O	D_2O	D_2O
^{31}P NMR	24.18 (tq, $J = 15.0, 7.5$ Hz)	23.84 (septet, $J = 14.0$ Hz)	15.6 (ddt, $J = 44.1, 21.0, 14.2$ Hz);	15.21 (ddq, $J = 43.9, 20.6, 13.1$ Hz)
^1H NMR	1.78 (doublet of septets, 1H, $J = 7.0, 6.4$ Hz),		5.61 (ddd, 1H, $J = 21.1, 2.1$ Hz, J undetermined)	5.46 (ddq, 1H, $J = 20.3, 2.1, 1.2$ Hz)
	1.43-1.55 (m, 2H),		5.37 (ddd, 1H, $J = 44.5, 3.4, 1.5$ Hz)	5.36 (tq, 1H, $J = 43.4, 1.8$ Hz)
	1.23 (d, 3H, $J = 15.0$ Hz)	1.23 (d, 6H, $J = 13.8$ Hz)	1.98 (br dddd, 2H, $J = 14.1, 7.0$ Hz)	1.77 (dt, 3H, $J = 13.1, 1.2$ Hz)
	0.81 (d, 3H, $J = 6.4$ Hz)		1.70-1.85 (m, 1H, J undetermined)	
	0.79 (d, 3H, $J = 6.1$ Hz)		0.72 (d, 6H, $J = 6.7$ Hz)	

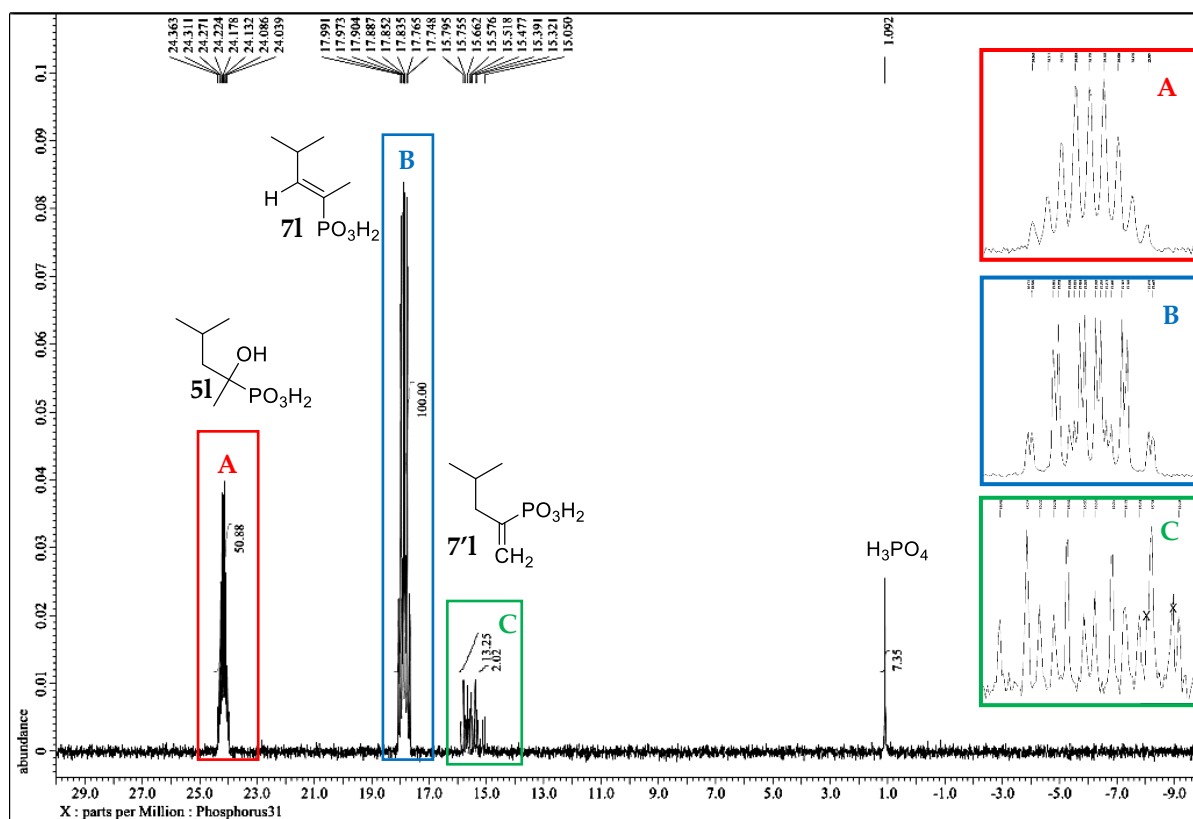


Figure S33. ^{31}P NMR (D_2O , 162MHz) spectra of the crude post-reaction mixture of 1-amino-1,3-dimethylbutylphosphonic acid (**1l**) with NaNO_2 after 192 h.

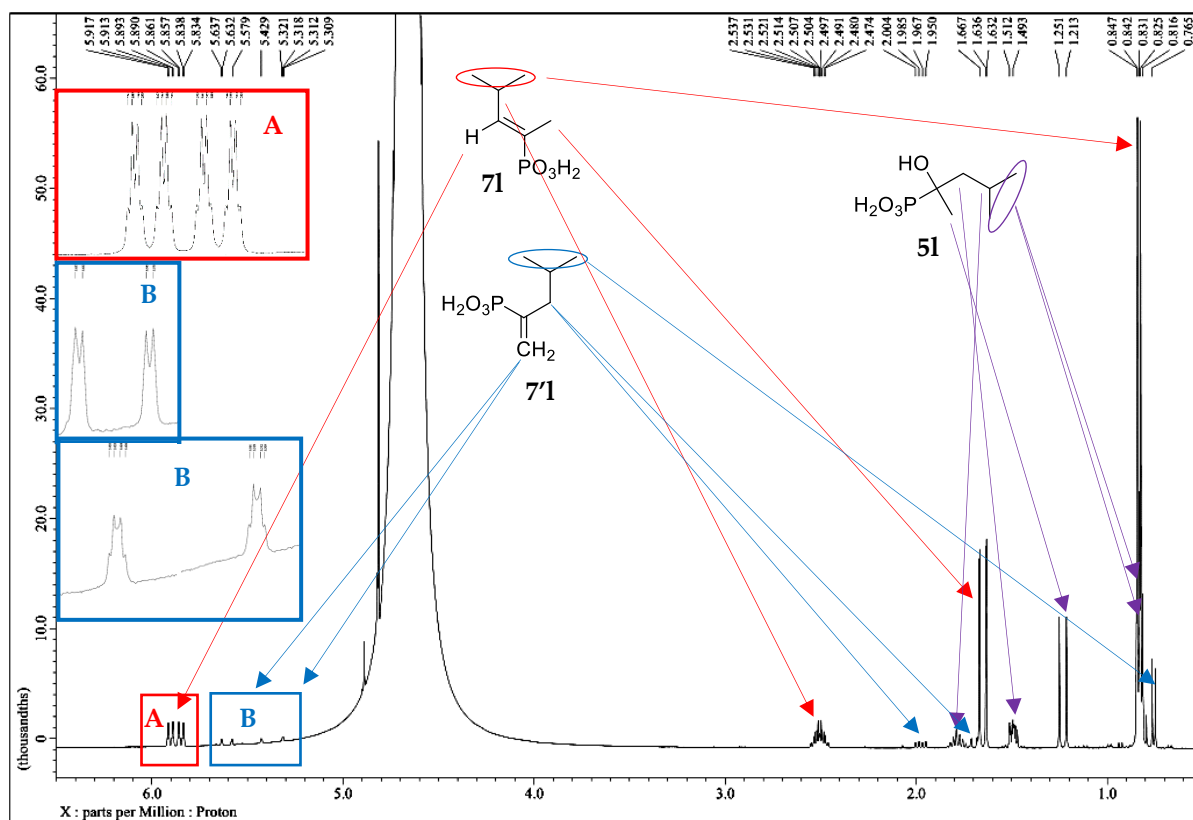
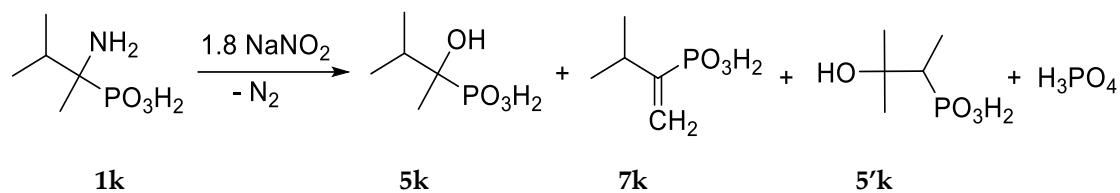


Figure S34. ^1H NMR (D₂O, 400MHz) spectra of the crude post-reaction mixture of 1-amino-1,3-dimethylbutylphosphonic acid (**11**) with NaNO₂ after 192 h.

3.9. ABr1218. Deamination of **1k** in Water

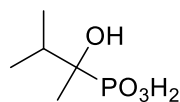
	$\alpha = 0.97$	39%	8%	6%	39%
96h	$\alpha = 1.00$	40%	8%	6%	40%
168h					
δ_P [ppm]	16.82	24.06 (dq)	15.84 (ddd)	26.36 (dq)	1.13

After 96h at 21 °C, post-reaction mixture contained 1-hydroxy-1,2-dimethylpropylphosphonic acid (**5k**) (39%molP), 3-methylbut-1-en-2-ylphosphonic acid (**7k**) (8%molP), 2-hydroxy-2,3-dimethylpropylphosphonic acid (**5'k**) (6%molP), orthophosphoric acid (39%molP) and 2 unidentified compounds (8%molP in total).

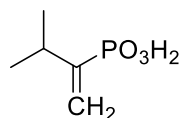
After 168h post-reaction mixture contained 1-hydroxy-1,2-dimethylpropylphosphonic acid (**5k**) (40%molP), 3-methylbut-1-en-2-ylphosphonic acid (**7k**) (8%molP), 2-hydroxy-2,3-dimethylpropylphosphonic acid (**5'k**) (6%molP), orthophosphoric acid (40%molP) and 2 unidentified compounds (6%molP in total) (Figure S35 and Figure S36).

^{31}P and ^1H NMR:

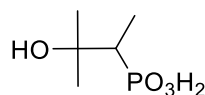
1-Hydroxy-1,2-dimethylpropylphosphonic acid (5k). ^{31}P NMR (D_2O): δ 24.06 (dq, $^3J_{\text{H-P}} = 14.0$ Hz, $^3J_{\text{H-P}} = 8.4$ Hz); ^1H NMR (D_2O): δ : 1.91 (dq, 1H, $^3J_{\text{H-P}} = 8.3$ Hz, $^3J_{\text{H-H}} = 7.0$ Hz, $^3J_{\text{H-H}} = 6.7$ Hz), 1.10 (d, 3H, $^3J_{\text{H-P}} = 14.4$ Hz), 0.86 (d, 3H, $^3J_{\text{H-H}} = 7.0$ Hz), 0.83 (d, 3H, $^3J_{\text{H-H}} = 6.7$ Hz).



3-Methylbut-1-en-2-ylphosphonic acid (7k). ^{31}P NMR (D_2O): δ 15.84 (ddd, $^3J_{\text{H-P(trans)}} = 45.1$ Hz, $^3J_{\text{H-P(cis)}} = 22.0$ Hz, $^3J_{\text{H-P}} = 12.2$ Hz); ^1H NMR (D_2O): δ : 5.59 (ddd, 1H, $^3J_{\text{H-P(trans)}} = 45.2$ Hz, $^3J_{\text{H-H}} = 1.5$ Hz, $^4J_{\text{H-H}} = 1.2$ Hz), 5.45 (ddd, 1H, $^3J_{\text{H-P(cis)}} = 22.0$ Hz, $^3J_{\text{H-H}} = 1.2$ Hz, J undetermined), 2.46 (br septet, 1H, $^3J_{\text{H-H}} = 6.7$ Hz), 0.96 (d, 6H, $^3J_{\text{H-H}} = 6.7$ Hz).



2-Hydroxy-2,3-dimethylpropylphosphonic acid (5'k). ^{31}P NMR (D_2O): δ 26.36 (dq, $^2J_{\text{H-P}} = 17.8$ Hz, $^3J_{\text{H-P}} = 16.8$ Hz); ^1H NMR (D_2O): δ : 1.74 (dq, 1H, $^2J_{\text{H-P}} = 18.3$ Hz, $^3J_{\text{H-H}} = 7.6$ Hz), 1.19 (s, 3H), 1.11 (s, 3H), 1.00 (dd, 3H, $^3J_{\text{H-P}} = 16.7$ Hz, $^3J_{\text{H-H}} = 7.6$ Hz).



1-Hydroxy-1,2-dimethylpropylphosphonic acid (**5k**) and 3-methylbut-1-en-2-ylphosphonic acid (**7k**) were identified by comparing chemical shifts, multiplicity and coupling constants on ^1H and ^{31}P NMR spectra with a description of structurally similar 1-hydroxy-1-methylethylphosphonic acid (**5m**) and 1-methylvinylphosphonic acid (**7m**), which were obtained in the reaction of 1-amino-1-methylethylphosphonic acid (**1m**) with NaNO_2 (ABr1204) (Table S12).

2-hydroxy-2,3-dimethylpropylphosphonic acid (**5'k**) was identified by comparing chemical shifts, multiplicity and coupling constants on ^1H and ^{31}P NMR spectra with z description of structurally similar 2-hydroxypropylphosphonic acid (Table S13).

Table S12. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of the reaction products of 1-amino-1,2-dimethylpropylphosphonic acid (**1k**) z NaNO_2 with spectra of similar 1-hydroxy-1-methylethylphosphonic acid (**5m**) and 1-methylvinylphosphonic acid (**7m**) (ABr1204).

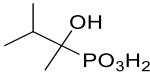
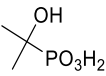
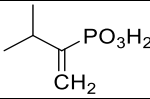
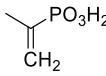
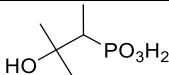
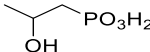
Structure				
Source	ABr1218	ABr1204	ABr1218	ABr1204
Solvent	D ₂ O	D ₂ O	D ₂ O	D ₂ O
^{31}P NMR	24.06 (dq, $J = 14.0, 8.4$ Hz)	23.84 (septet, $J = 14.0$ Hz)	15.84 (ddd, $J = 45.1, 22.0, 12.2$ Hz)	15.21 (ddq, $J = 43.9, 20.6, 13.1$ Hz)
^1H NMR	1.91 (dq, 1H, $J = 8.3, 7.0, 6.7$ Hz)		5.59 (ddd, 1H, $J = 45.2, 1.5, 1.2$ Hz)	5.46 (ddq, 1H, $J = 20.3, 2.1, 1.2$ Hz)
	1.10 (d, 3H, $J = 14.4$ Hz)	1.23 (d, 6H, $J = 13.8$ Hz)	5.45 (ddd, 1H, $J = 22.0, 1.2$ Hz, J undetermined),	5.36 (tq, 1H, $J = 43.4, 1.8$ Hz)
	0.86 (d, 3H, $J = 7.0$ Hz)		2.46 (br septet, 1H, $J = 6.7$ Hz)	1.77 (dt, 3H, $J = 13.1, 1.2$ Hz)
	0.83 (d, 3H, $J = 6.7$ Hz)		0.96 (d, 6H, $J = 6.7$ Hz)	

Table S13. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of the reaction products of 1-hydroxy-1,2-dimethylpropylphosphonic acid (**5'k**) with spectra of similar 2-hydroxypropylphosphonic acid.

Structure		
Source	ABr1218	Reference [9]
Solvent	D ₂ O	D ₂ O
^{31}P NMR	26.36 (dq, $J = 17.8, 16.8$ Hz)	19.9
^1H NMR		3.80 (1H, dm, $J = 6.5$ Hz)
	1.74 (dq, 1H, $J = 18.3, 7.6$ Hz),	1.39 (2H, ddd, $J = 18.0, 6.6, 15.3$ Hz)
	1.19 (s, 3H),	0.97 (3H, d, $J = 6.5$ Hz)
	1.11 (s, 3H),	
	1.00 (dd, 3H, $J = 16.7, J = 7.6$ Hz)	

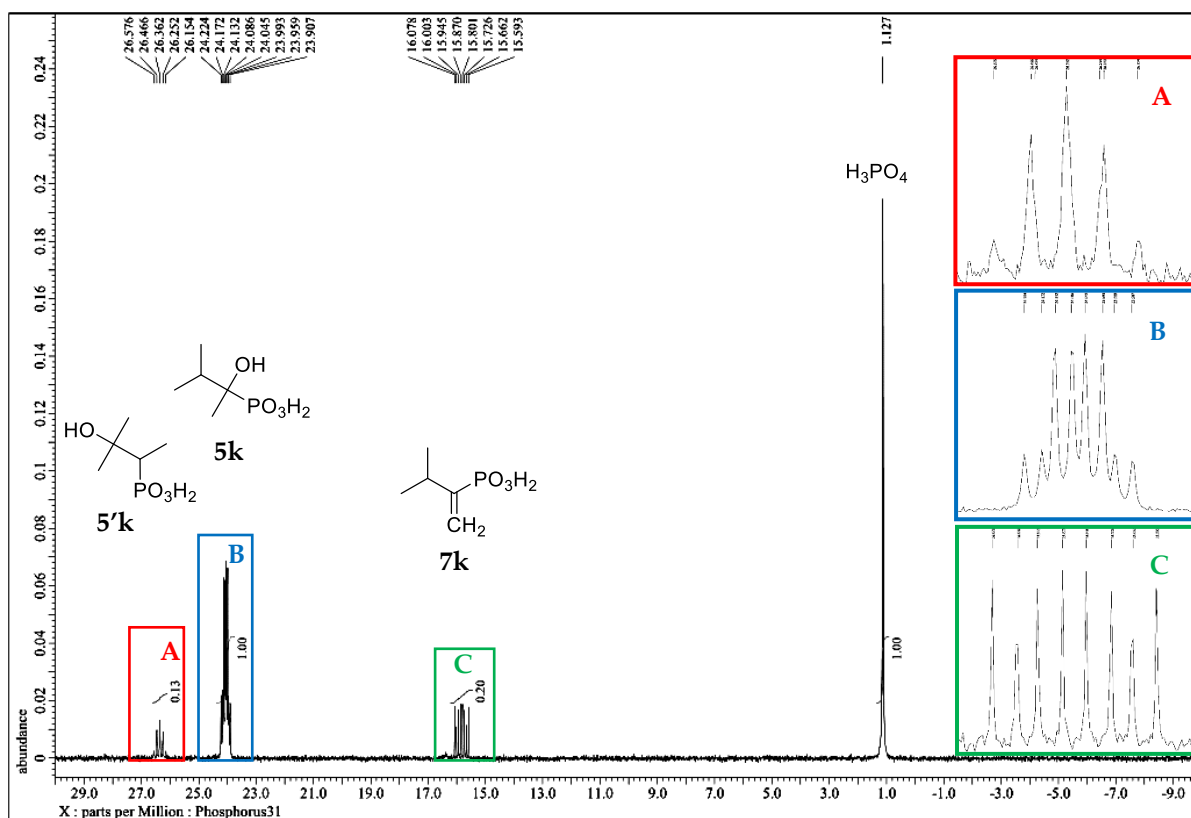


Figure S35. ^{31}P NMR (D $_2$ O, 162 MHz) spectra of the crude post-reaction mixture of 1-amino-1,2-dimethylpropylphosphonic acid (**1k**) z NaNO $_2$ after 168h.

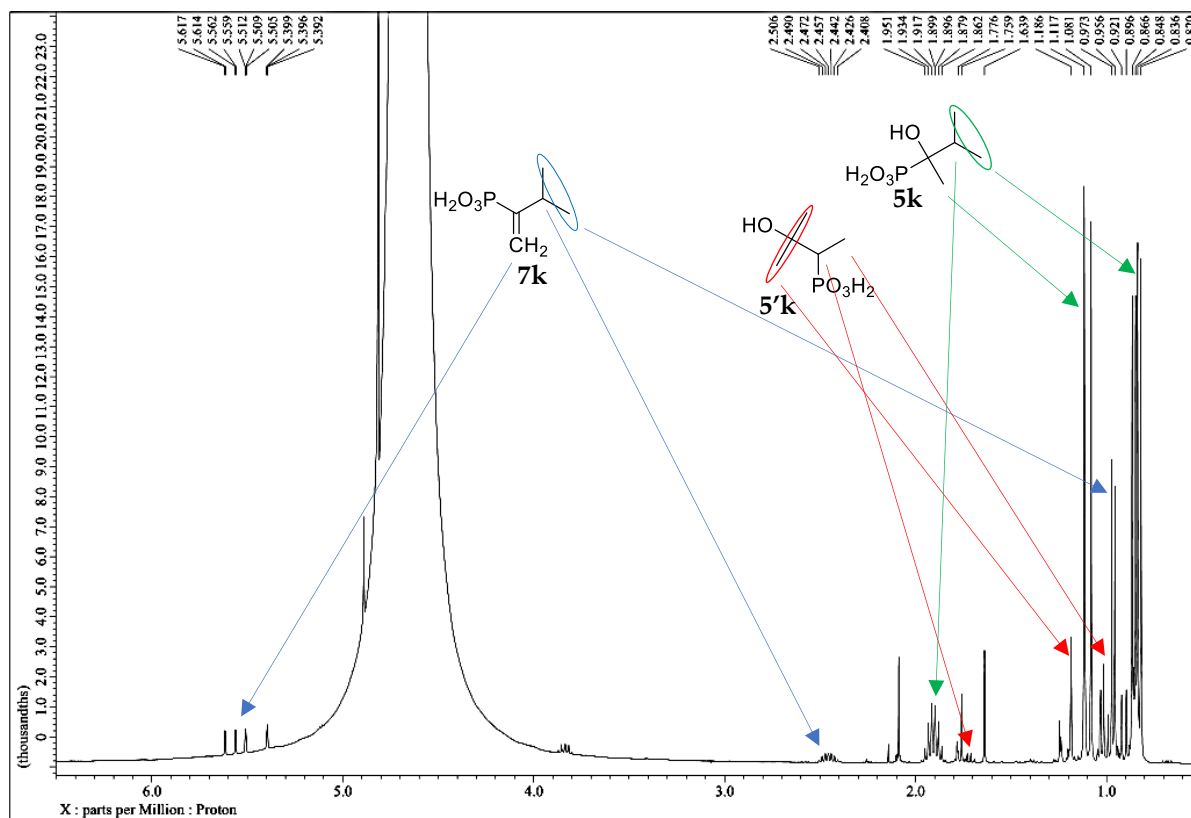
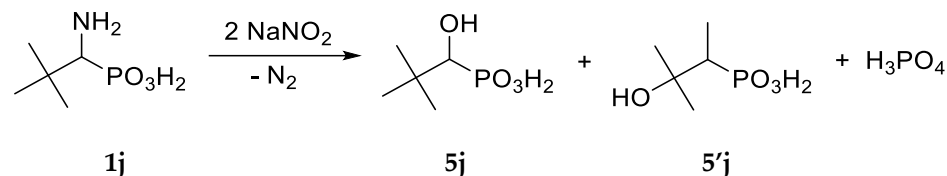


Figure S36. ^1H NMR (D $_2$ O, 400 MHz) spectra of the crude post-reaction mixture of 1-amino-1,2-dimethylpropylphosphonic acid (**1k**) z NaNO $_2$ after 168h.

3.10. ABr1220. Deamination of **1j** in Water

96h	$\alpha = 1.00$	7%	6%	86%
δ_P [ppm]		19.91 (d)	26.44 (dq)	0.86

After 96h at 21 °C, post-reaction mixture contained orthophosphoric acid (86%molP), 1-hydroxy-2,2-dimethylpropylphosphonic acid (**5j**) (7%molP), 2-hydroxy-1,2-dimethylpropyl-phosphonic acid (**5'j**) (6%molP) and unidentified compound (1%molP) (Figure S37 and Figure S38).

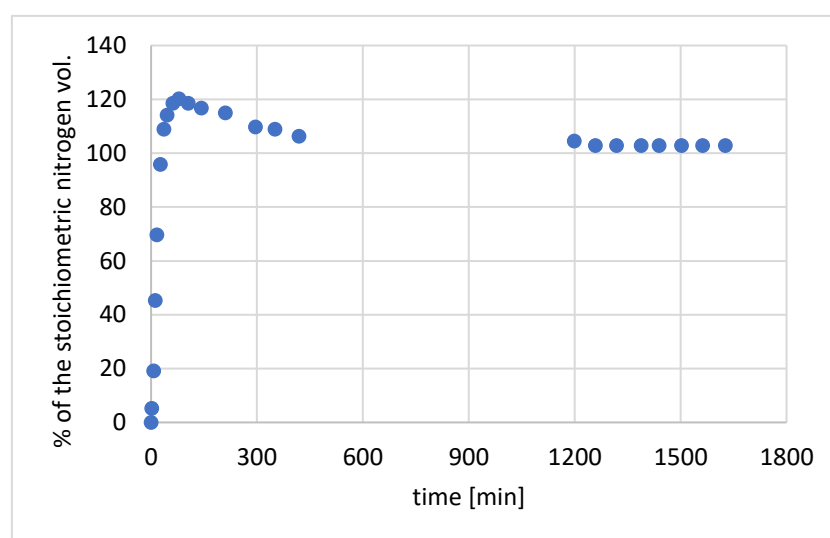
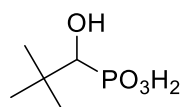
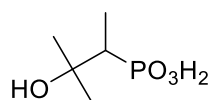


Chart 9. Dependence of the volume of the released gas (in % of the stoichiometric nitrogen volume) on the time in the reaction of 1-amino-2,2-dimethylpropylphosphonic acid (**1j**) with NaNO_2 in water.

1-Hydroxy-2,2-dimethylpropylphosphonic acid (**5j**) was identified by comparing chemical shifts, multiplicity and coupling constants on ^1H and ^{31}P NMR spectra with description in the literature (Table S14). 2-hydroxy-1,2-dimethylpropylphosphonic acid (**5'j**) was identified by comparing chemical shifts, multiplicity and coupling constants on ^1H and ^{31}P NMR spectra with description in the literature with description for structurally similar 1-hydroxy-2,2-dimethylpropylphosphonic acid (**5k**), which was obtained in the reaction of 1-amino-1,2-dimethylpropylphosphonic acid (**1k**) with NaNO_2 (ABr1218) (Table S14).



1-Hydroxy-2,2-dimethylpropylphosphonic acid (5j). ^{31}P NMR (D_2O): δ 19.91 (d, $^2J_{\text{H-P}} = 9.4$ Hz); ^1H NMR (D_2O): δ : 3.29 (d, 1H, $^2J_{\text{H-P}} = 9.8$ Hz), 0.90 (s, 9H).



2-Hydroxy-1,2-dimethylpropylphosphonic acid (5'j). ^{31}P NMR (D_2O): δ 26.44 (dq, $^2J_{\text{H-P}} = 17.8$ Hz, $^3J_{\text{H-P}} = 17.8$ Hz); ^1H NMR (D_2O): δ : 1.75 (dq, 1H, $^2J_{\text{H-P}} = 18.8$ Hz, $^3J_{\text{H-H}} = 7.6$ Hz), 1.18 (s, 3H), 1.11 (s, 3H), 1.00 (dd, 3H, $^3J_{\text{H-P}} = 16.8$ Hz, $^3J_{\text{H-H}} = 7.7$ Hz).

Table S14. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of post-reaction mixture of 1-amino-2,2-dimethylpropylphosphonic acid (**1j**) z NaNO_2 with experimental spectra and description in the literature.

Structure				
Source	ABr1220	Reference [15]	ABr1220	ABr1218
Solvent	D_2O	$\text{DMSO-}d_6$	D_2O	D_2O
^{31}P NMR	19.91 (d, $J = 9.4$ Hz)	n.d.	26.44 (dq, $J = 17.8$ Hz, $J = 17.8$ Hz)	26.36 (dq, $J = 17.8$, 16.8 Hz)
^1H NMR	3.29 (d, 1H, $J = 9.8$ Hz)	3.24 (d, 1H, $J = 8.8$ Hz)	1.75 (dq, 1H, $J = 18.8$, 7.6 Hz)	1.74 (dq, 1H, $J = 18.3$, 7.6 Hz),
	0.90 (s, 9H)	0.98 (s, 9H)	1.18 (s, 3H)	1.19 (s, 3H),
			1.11 (s, 3H)	1.11 (s, 3H),
			1.00 (dd, 3H, $J = 16.8$, 7.7 Hz).	1.00 (dd, 3H, $J = 16.7$, $J = 7.6$ Hz)

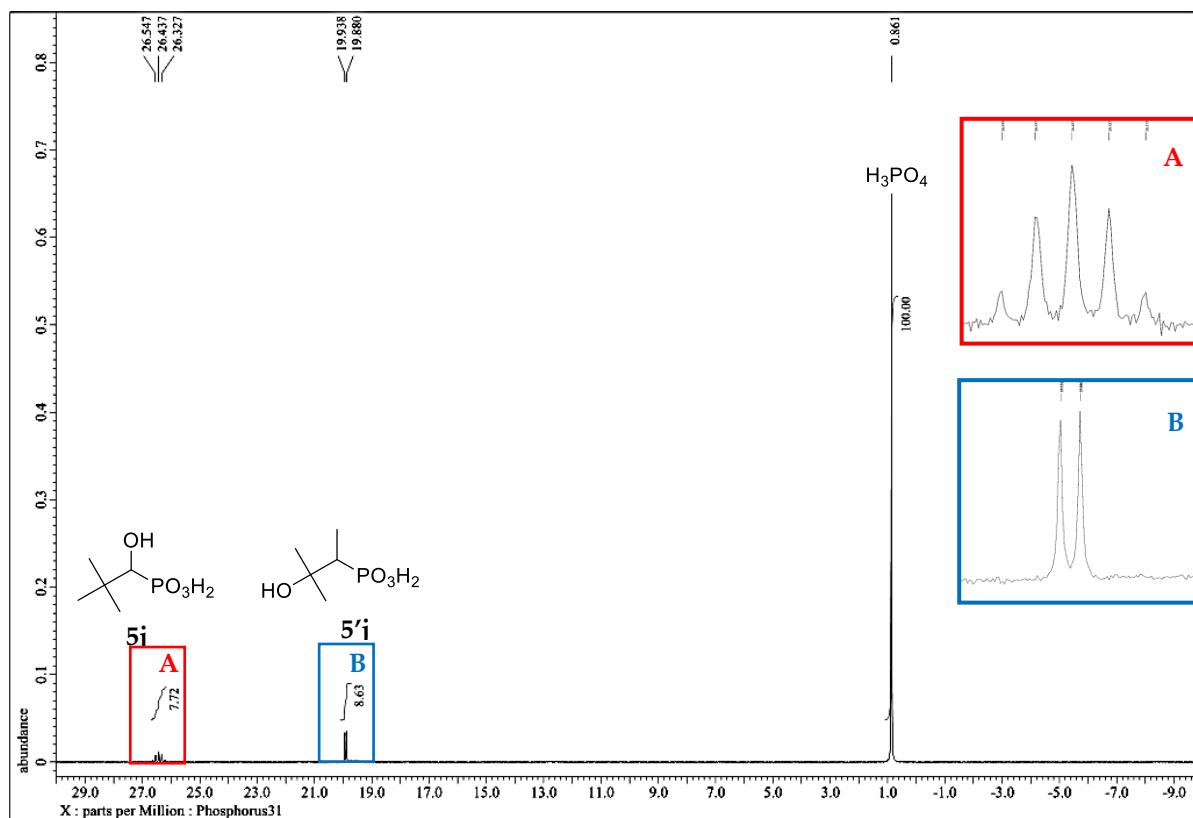


Figure S37. ^{31}P NMR (D₂O, 162 MHz) spectra of the crude post-reaction mixture of 1-amino-2,2-dimethylpropylphosphonic acid (**1j**) with NaNO₂ after 96h.

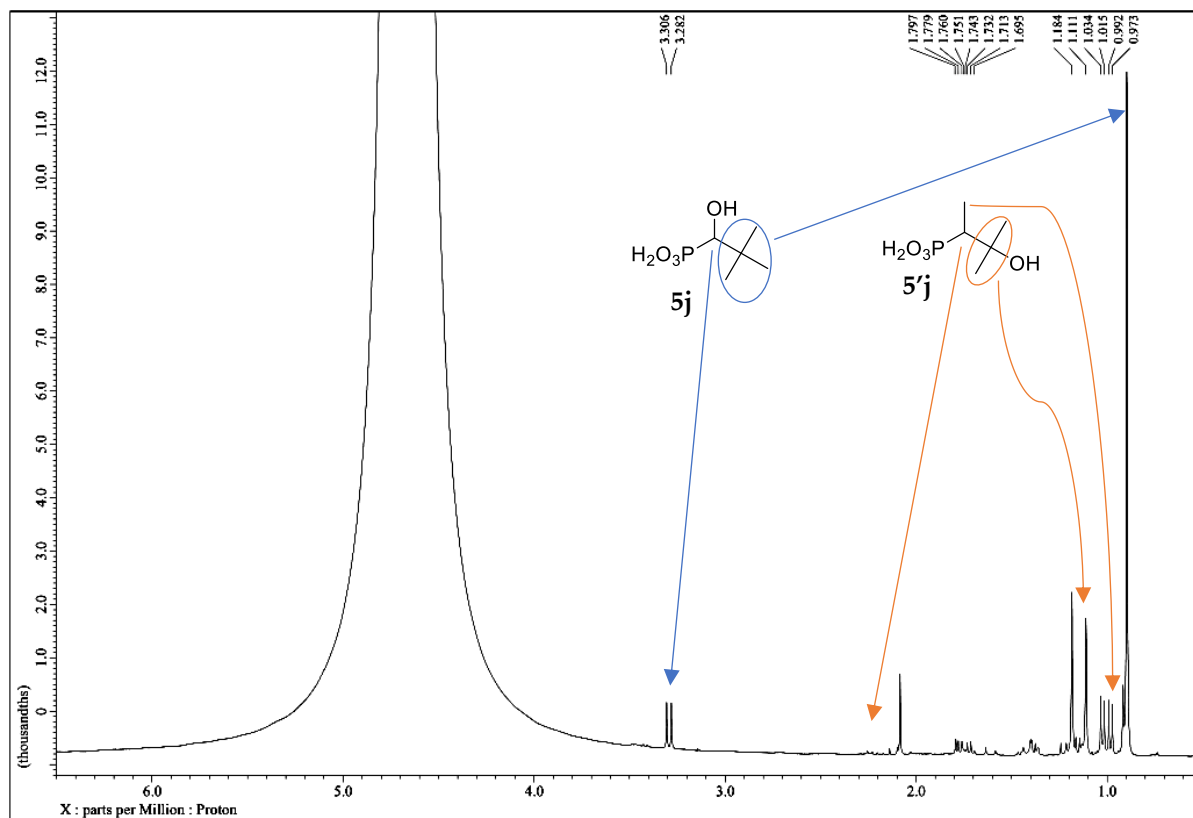
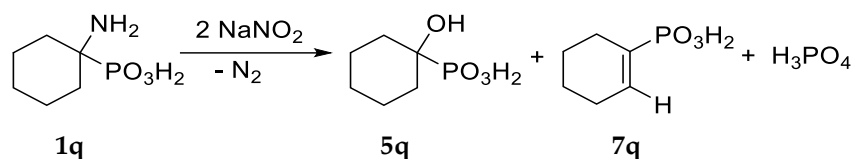


Figure S38. ^1H NMR (D₂O, 400 MHz) spectra of the crude post-reaction mixture of 1-amino-2,2-dimethylpropylphosphonic acid (**1j**) with NaNO₂ after 96h.

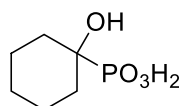
3.11. ABr1222. Deamination of **1q** in Water

98h	$\alpha = 1.00$	16%	75%	7%
δ_{P} [ppm]		23.88 (br s)	16.25 (doublet of quintets)	1.02

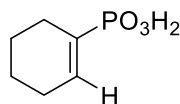
After 98h at 21 °C, post-reaction mixture contained 1-hydroxycyclohexylphosphonic acid (**5q**) (16%molP), cyclohex-1-en-1-ylphosphonic acid (**7q**) (75%molP), orthophosphoric acid (7%molP) and 2 unidentified compounds (2%molP in total) (Figure S39 and Figure S41).

The presence of 1-hydroxycyclohexylphosphonic acid (**5q**) was confirmed by re-measuring the NMR spectra of the reaction mixture with the addition of reference material – 1-hydroxycyclohexylphosphonic acid (**5q**) (Figure S40 and Figure S42).

Cyclohex-1-en-1-ylphosphonic acid (**7q**) was identified by comparing chemical shifts, multiplicity and coupling constants on ^1H and ^{31}P NMR spectra with description in the literature (Table S15).



1-Hydroxycyclohexylphosphonic acid (5q). ^{31}P NMR (D_2O): δ 23.88 (br s); ^1H NMR (D_2O): δ : 1.60-1.70 (m, 2H), 1.36-1.58 (m, 7H), 1.00-1.12 (m, 1H).



Cyclohex-1-en-1-ylphosphonic acid (7q). ^{31}P NMR (D_2O): δ 16.25 (doublet of quintets, $^3J_{\text{H-P}} = 20.6$ Hz, $^3J_{\text{H-P}} = 3.7$ Hz); ^1H NMR (D_2O): δ : 6.28 (dt, 1H, $^3J_{\text{H-P}} = 21.1$ Hz, $^3J_{\text{H-H}} = 3.7$ Hz, $^4J_{\text{H-H}} = 1.8$ Hz), 1.93-2.04 (m, 4H), 1.38-1.52 (m, 4H).

Table S15. Comparison of chemical shifts and coupling constants on experimental ^1H and ^{31}P NMR spectra of cyclohex-1-en-1-ylphosphonic acid (**7q**) with description in the literature.

Structure		
Source	ABr1222	Reference [16]
Solvent	D_2O	D_2O
^{31}P NMR	16.25 (doublet of quintets, $J = 20.6, 3.7$ Hz)	14.0 (d, $J = 19$ Hz)
	6.28 (dt, 1H, $J = 21.1, 3.7, 1.8$ Hz)	6.52 (d, $J = 19$ Hz)
^1H NMR	1.93-2.04 (m, 4H)	
	1.38-1.52 (m, 4H)	

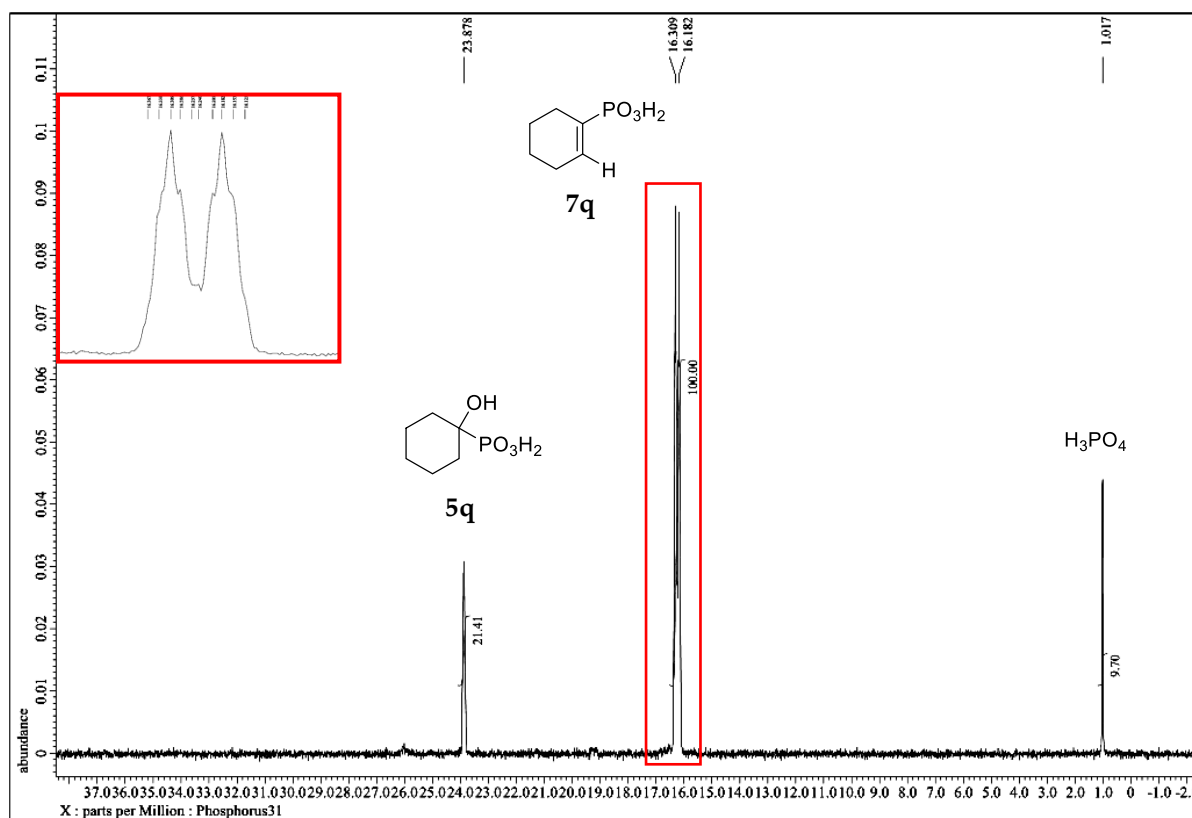


Figure S39. ^{31}P NMR (D₂O, 162MHz) spectra of the crude post-reaction mixture of 1-aminocyclohexylphosphonic acid (**1q**) with NaNO₂ after 98h.

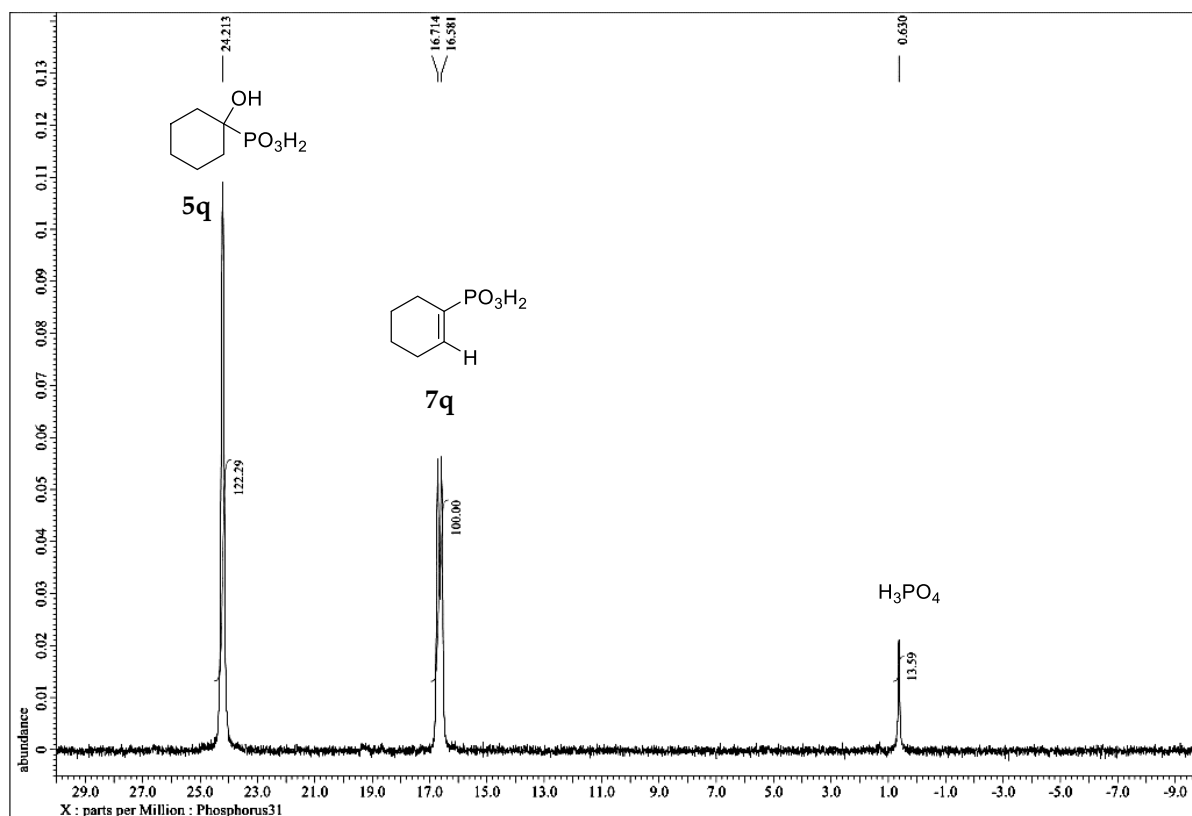


Figure S40. ^{31}P NMR (D₂O, 162MHz) spectra of the crude post-reaction mixture of 1-aminocyclohexylphosphonic acid (**1q**) with NaNO₂ after 98h with addition of reference material - 1-hydroxycyclohexylphosphonic acid (**5q**).

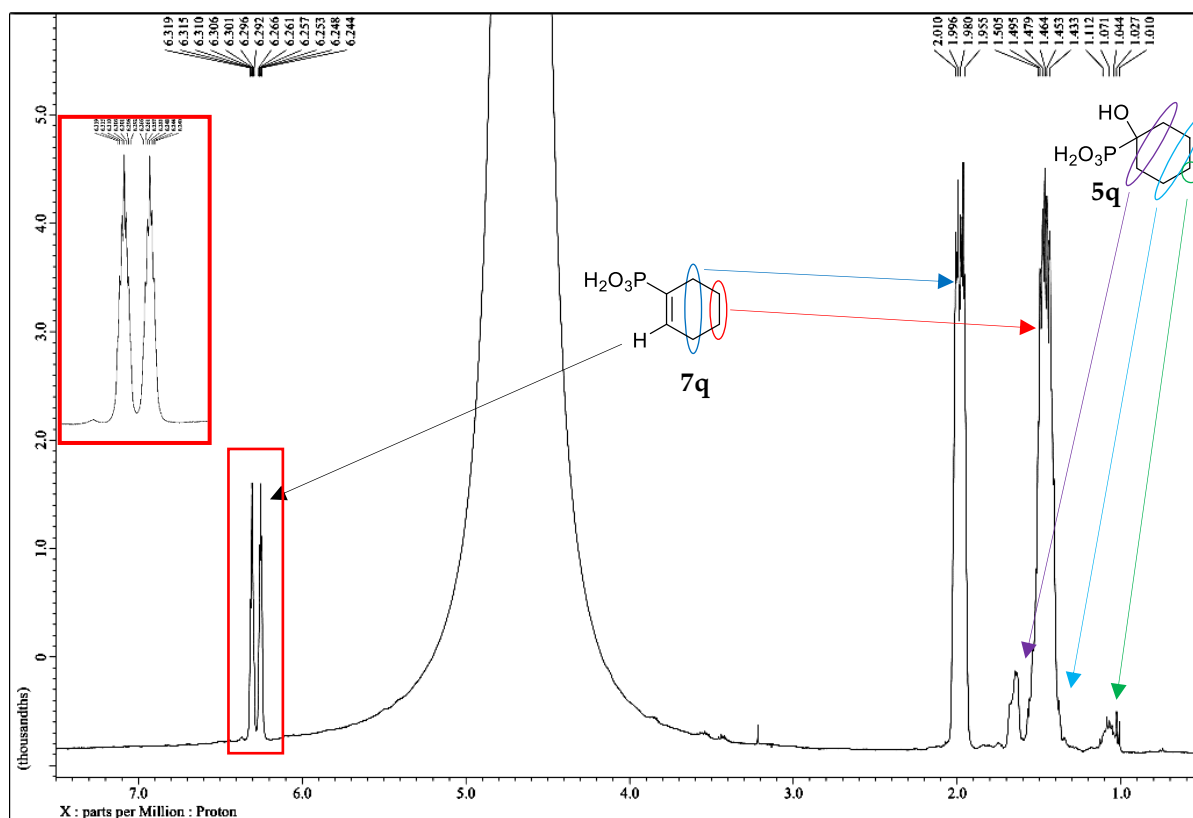


Figure S41. ^1H NMR (D $_2$ O, 400MHz) spectra of the crude post-reaction mixture of 1-aminocyclohexylphosphonic acid (1q) with NaNO $_2$ after 98h.

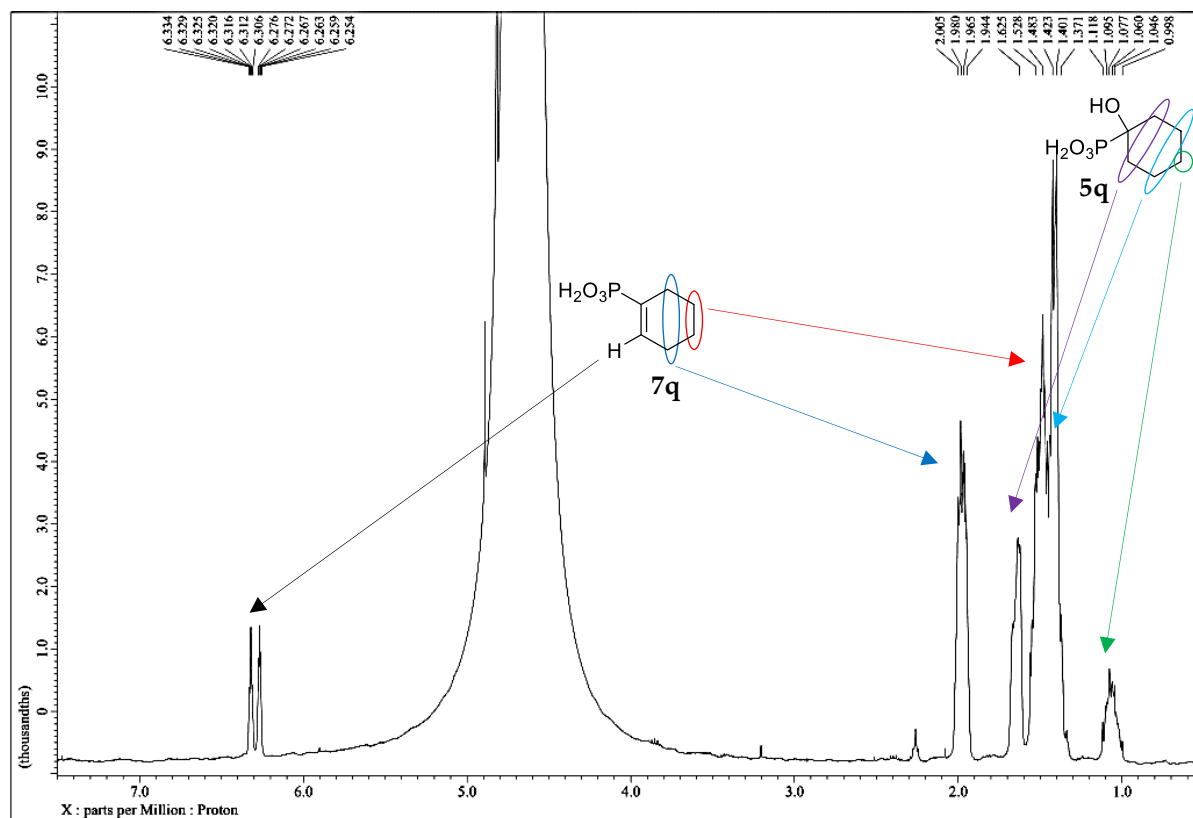
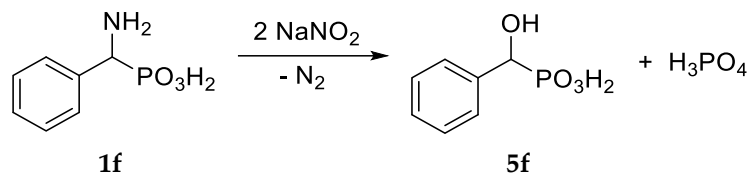


Figure S42. ^1H NMR spectra of the crude post-reaction mixture of 1-aminocyclohexylphosphonic acid (1q) with NaNO $_2$ after 98h with addition of reference material - 1-hydroxycyclohexylphosphonic acid (5q).

3.12. ABr1224. Deamination of **1f** in Water

24 h	$\alpha = 1.00$	97%	3%
δ_P [ppm]		17.27 (d)	0.83
After 24 h at 21 °C, post-reaction mixture contained hydroxy(phenyl)methylphosphonic acid (5f) (97%molP) and orthophosphoric acid (3%molP) (Figure S43 and Figure S45).			

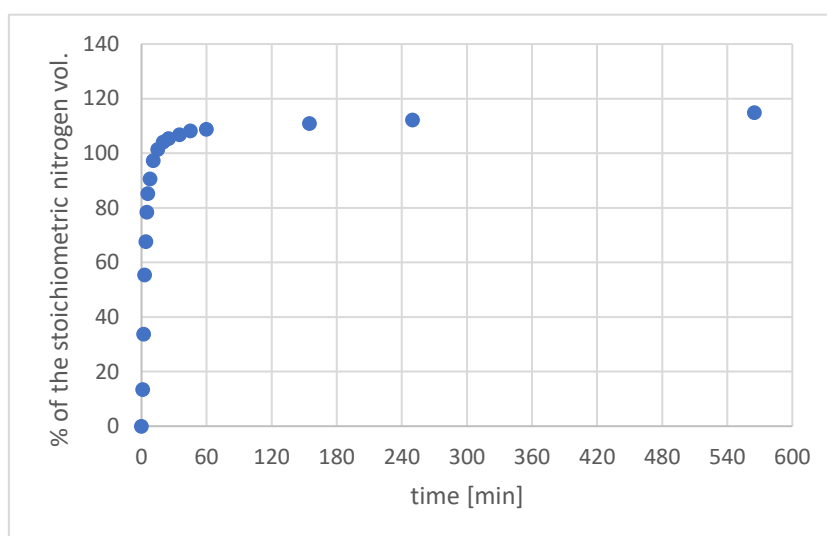
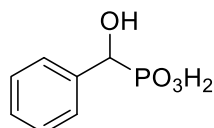


Chart 10. Dependence of the volume of the released gas (in % of the stoichiometric nitrogen volume) on the time in the reaction of amino(phenyl)methylphosphonic acid (**1f**) with NaNO₂ in water.

The presence of phenyl(hydroxy)methylphosphonic acid (**5f**) was confirmed by re-measuring the NMR spectra of the reaction mixture with the addition of reference material – phenyl(hydroxy)methylphosphonic acid (**5f**) (Figure S44 and Figure S46).



Hydroxy(phenyl)methylphosphonic acid (5f**).** ³¹P NMR (D₂O): δ 17.27 (d, $^2J_{\text{H-P}} = 12.2$ Hz); ¹H NMR (D₂O) δ : 7.32–7.38 (m, 2H), 7.26–7.32 (m, 2H), 7.20–7.26 (m, 1H), 4.72 (d, 1H, $^2J_{\text{H-P}} = 12.2$ Hz).

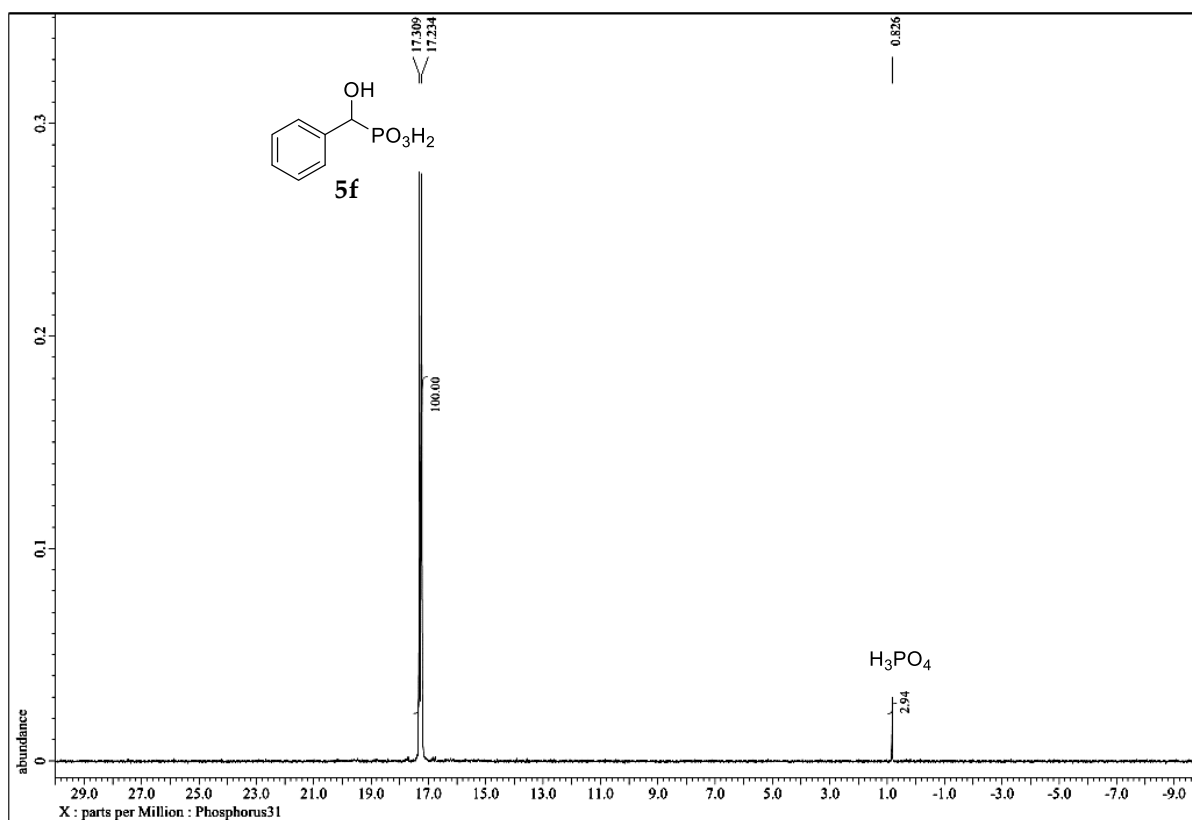


Figure S43. ^{31}P NMR (D_2O , 162MHz) spectra of the crude post-reaction mixture of amino(phenyl)methylphosphonic acid (**1f**) with NaNO_2 after 24 h.

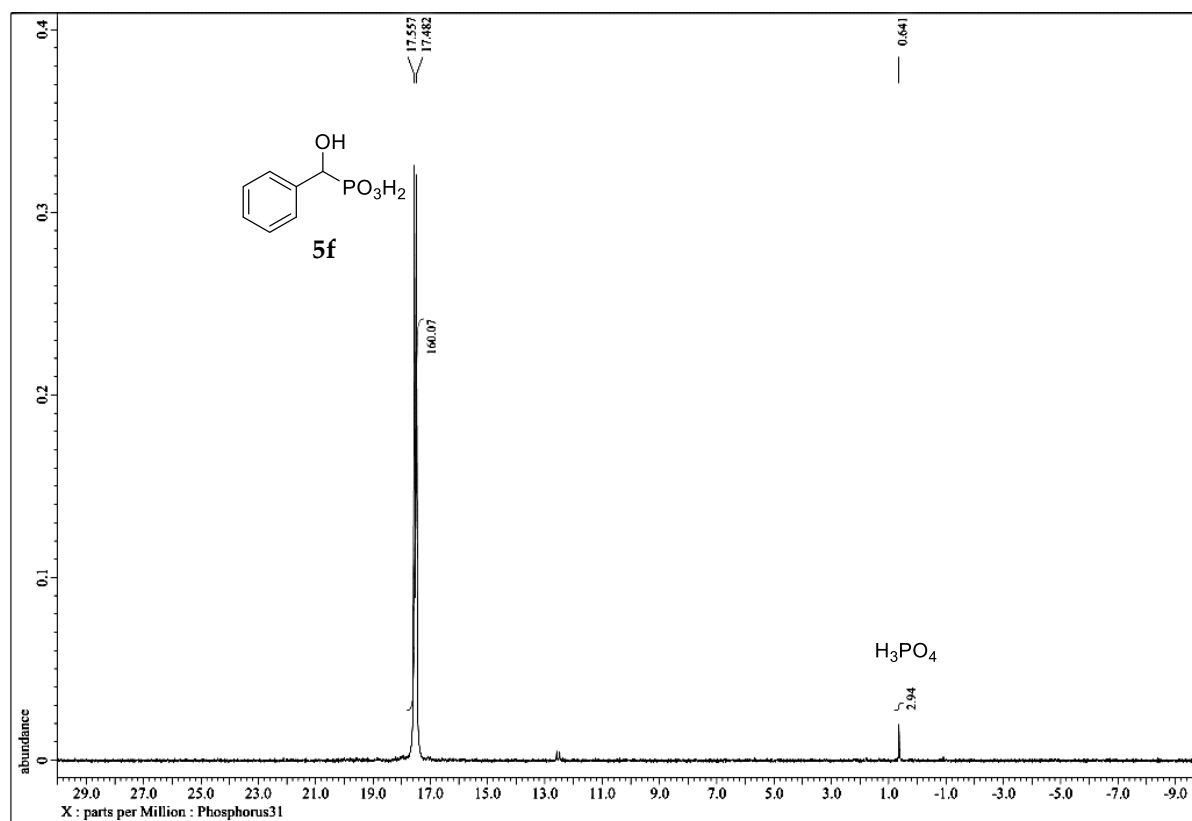


Figure S44. ^{31}P NMR (D_2O , 162MHz) spectra of the crude post-reaction mixture of amino(phenyl)methylphosphonic acid (**1f**) with NaNO_2 after 24 h with addition of reference material - hydroxy(phenyl)methylphosphonic acid (**5f**).

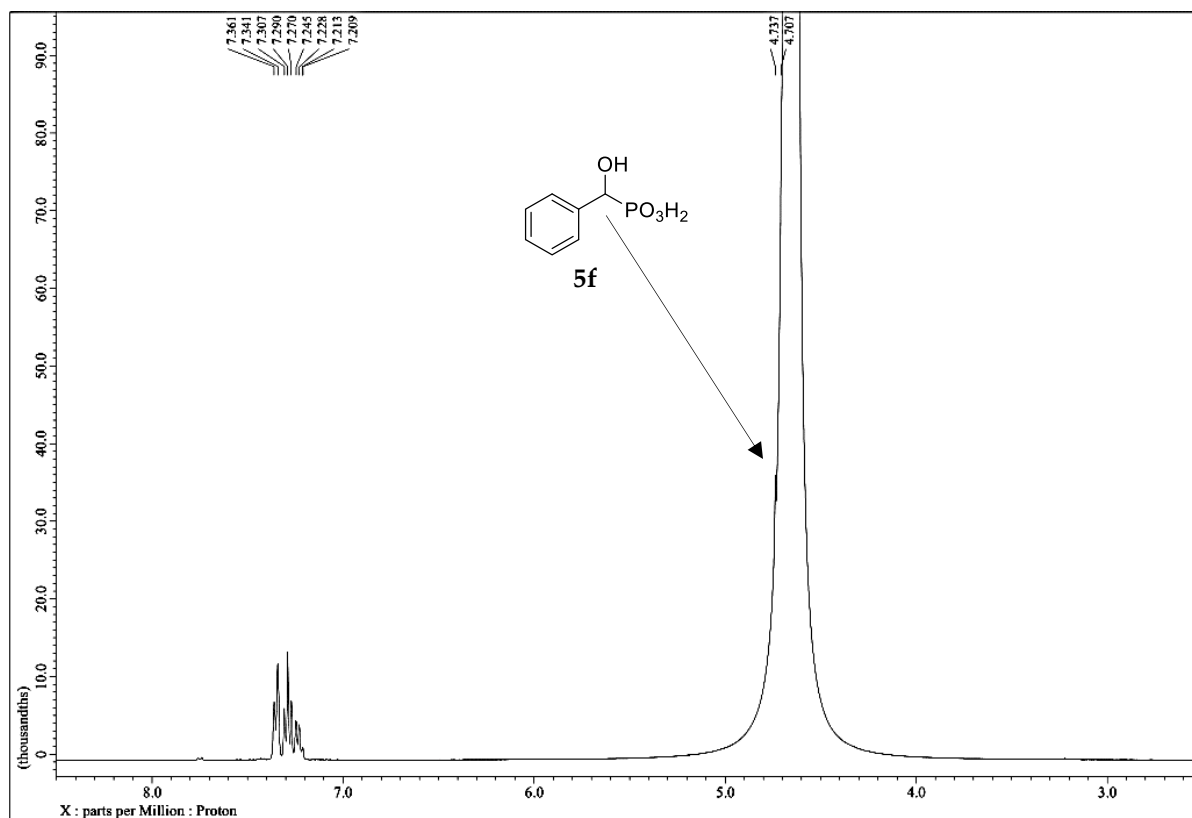


Figure S45. ^1H NMR (D_2O , 400MHz) spectra of the crude post-reaction mixture of amino(phenyl)methylphosphonic acid (**1f**) with NaNO_2 after 24 h.

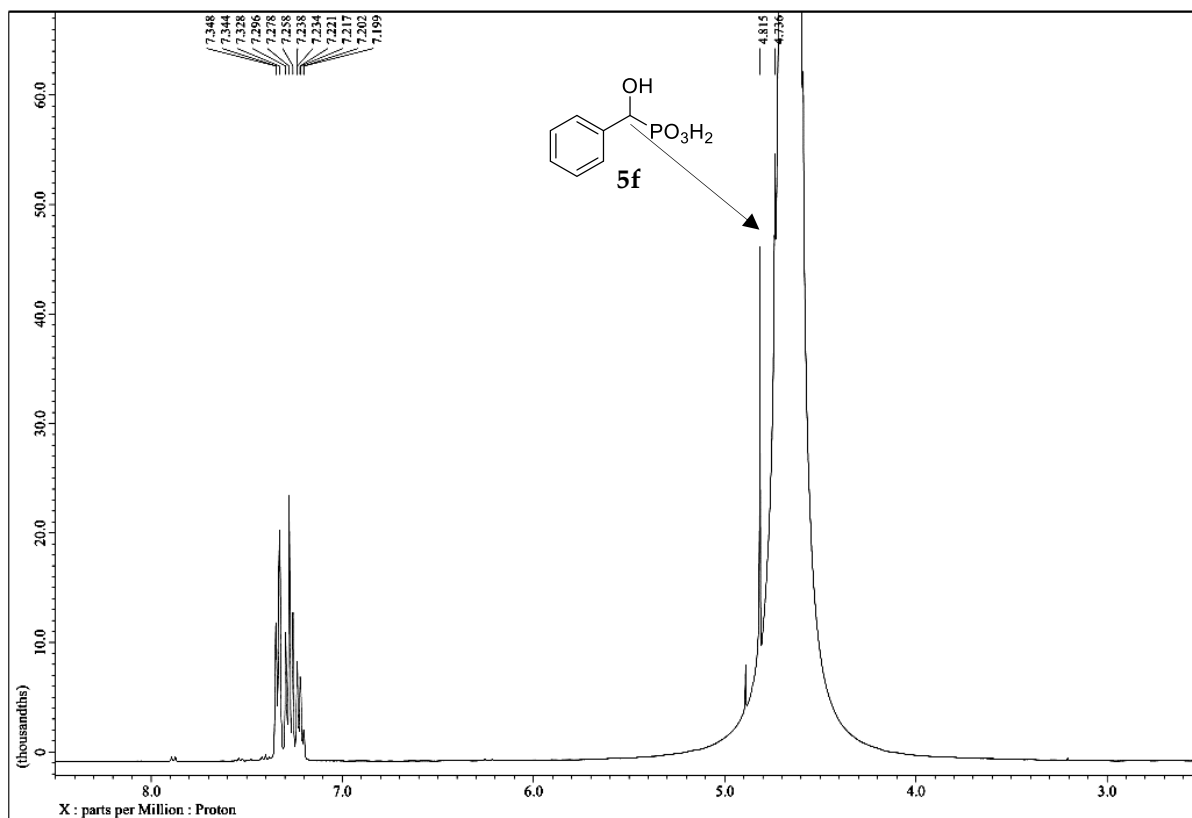
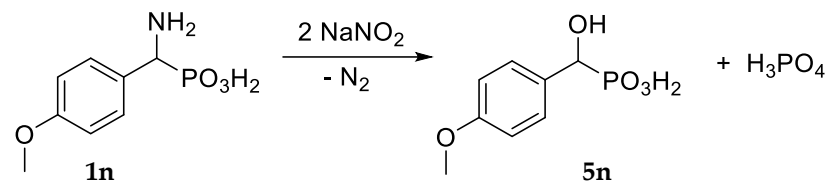


Figure S46. ^1H NMR (D_2O , 400MHz) spectra of the crude post-reaction mixture of amino(phenyl)methylphosphonic acid (**1f**) with NaNO_2 after 24 h with addition of reference material - hydroxy(phenyl)methylphosphonic acid (**5f**).

3.13. ABr1226. Deamination of **1n** in Water

96h	$\alpha = 1.00$	72%	25%
δ_{P} [ppm]		17.23 (d)	1.68

After 144h at 21 °C a suspension was formed. Liquid phase contained hydroxy(4-methoxyphenyl)methylphosphonic acid (**5n**) (72%molP), orthophosphoric acid (25%molP) and 3 unidentified compounds (3%molP in total) (Figure S47 and Figure S48). Precipitate was filtered, washed with water (2 x 1 mL), dried under reduced pressure and orange solid (30mg) was obtained (Figure S51 and Figure S52).

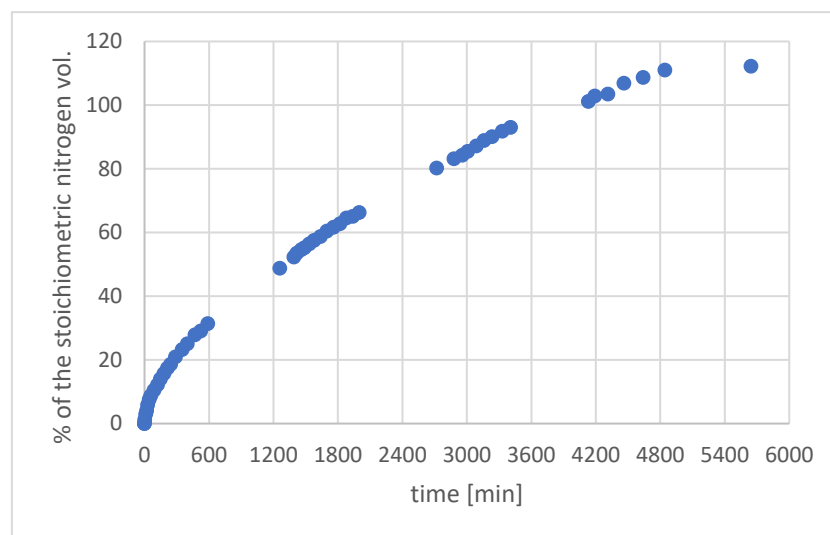
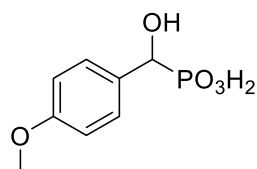


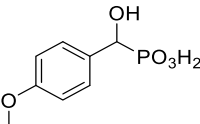
Chart 11. Dependence of the volume of the released gas (in % of the stoichiometric nitrogen volume) on the time in the reaction of amino(4-methoxyphenyl)methylphosphonic acid (**1n**) with NaNO₂ in water.

Hydroxy(4-methoxyphenyl)methylphosphonic acid (**5n**) was identified by comparing chemical shifts, multiplicity and coupling constants on ¹H and ³¹P NMR spectra with description in the literature (Table S16). Spectra of crude hydroxy(4-methoxyphenyl)methylphosphonic acid (**5n**) was additionally re-measured with addition of D₂SO₄, in order to shift HOD signal overlapped on -C(PO₃H₂)H- (Figure S49 and Figure 50).



Hydroxy(4-methoxyphenyl)methylphosphonic acid (5n). ³¹P NMR (D₂O): δ 17.23 (d, $^2J_{\text{H-P}} = 12.2$ Hz); ¹H NMR (D₂O) δ : 7.27 (dd, 2H, $^3J_{\text{H-H}} = 8.9$ Hz, $J = 1.8$ Hz), 6.83–6.86 (m, 2H), 3.69 (s, 3H).

Table S16. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of the reaction products of amino(4-methoxyphenyl)methylphosphonic acid (**1n**) with NaNO_2 in water with description in the literature.

Structure			
	ABr1226	ABr1226	Reference [17]
Solvent	D_2O	$\text{D}_2\text{O} + \text{D}_2\text{SO}_4$	D_2O
^{31}P NMR	17.23 (d, $J = 12.2$ Hz)	20.90 (d, $J = 11.2$ Hz)	20.8
^1H NMR	7.27 (dd, 2H, $J = 8.9, 1.8$ Hz)	6.78 (dd, 2H, $J = 8.8, 2.1$ Hz)	7.12 (d, 2H, $J = 8.0$ Hz)
	6.83–6.86 (m, 2H)	6.38 (d, 2H, $J = 8.6$ Hz)	6.67 (d, 2H, $J = 8.0$ Hz)
	Overlapped with HOD	4.38 (d, 1H, $J = 11.6$ Hz)	4.71 (d, 1H, $J = 12.0$ Hz)
	3.69 (s, 3H)	3.19 (s, 3H)	3.44 (s, 3H)

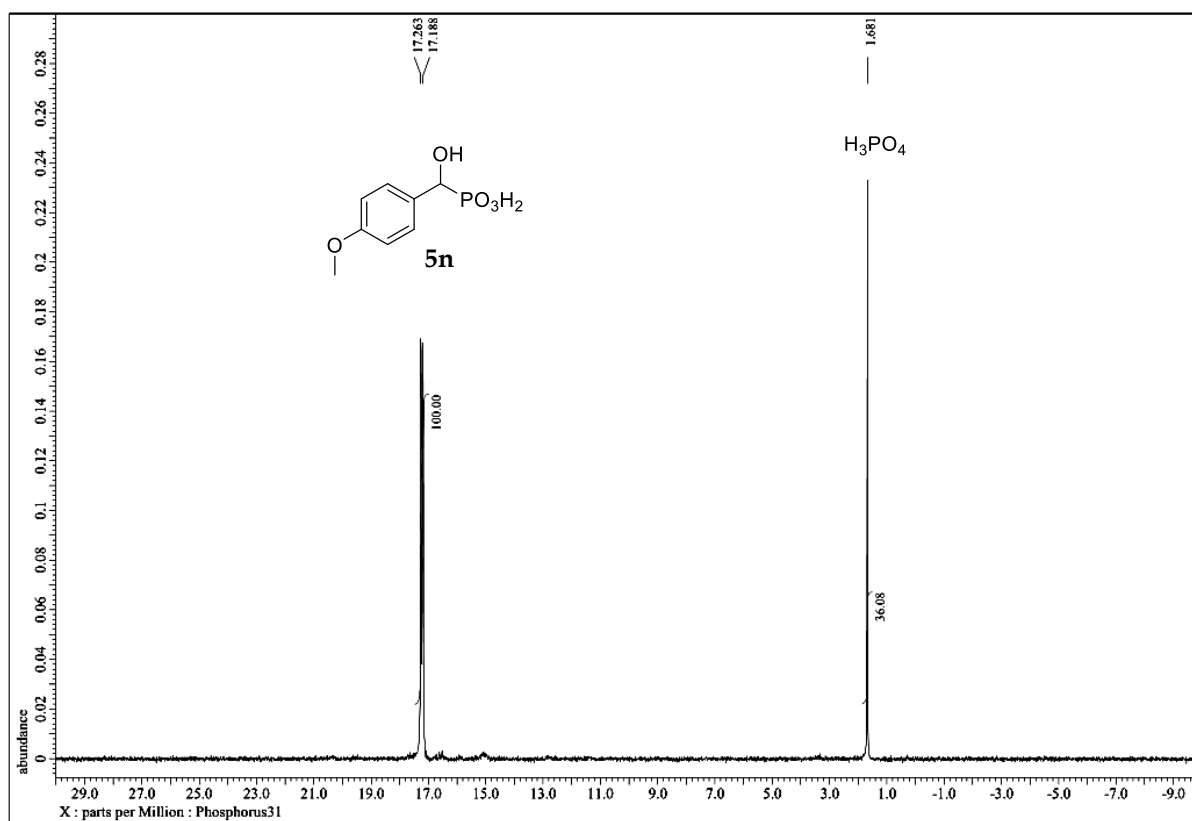


Figure S47. ^{31}P NMR (D_2O , 162MHz) spectra of the crude post-reaction mixture of amino(4-methoxyphenyl)methylphosphonic acid (**1n**) with NaNO_2 after 96h.

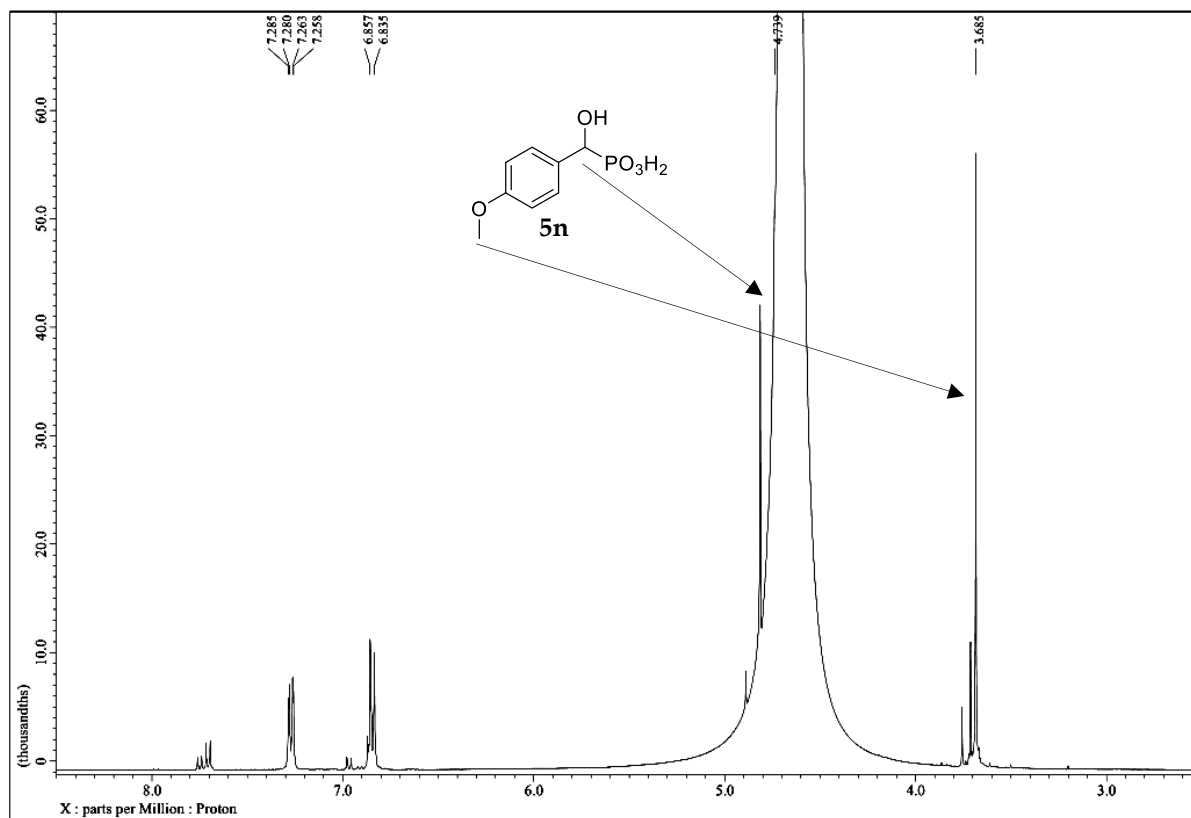


Figure S48. ^1H NMR (D_2O , 162MHz) spectra of the crude post-reaction mixture of amino(4-methoxyphenyl)methylphosphonic acid (**1n**) with NaNO_2 after 96h.

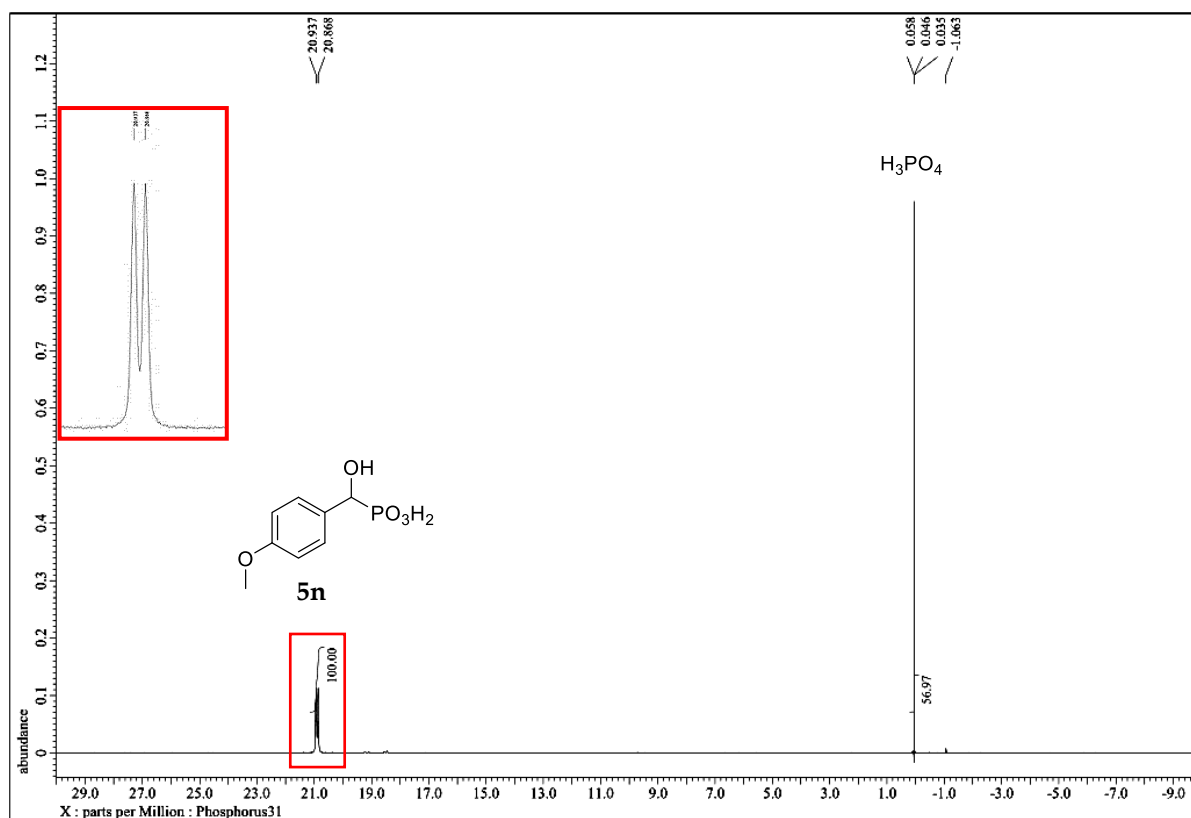


Figure S49. ^{31}P NMR (D_2O , 162MHz) spectra of the crude post-reaction mixture of amino(4-methoxyphenyl)methylphosphonic acid (**1n**) with NaNO_2 after 96h with addition of D_2SO_4 .

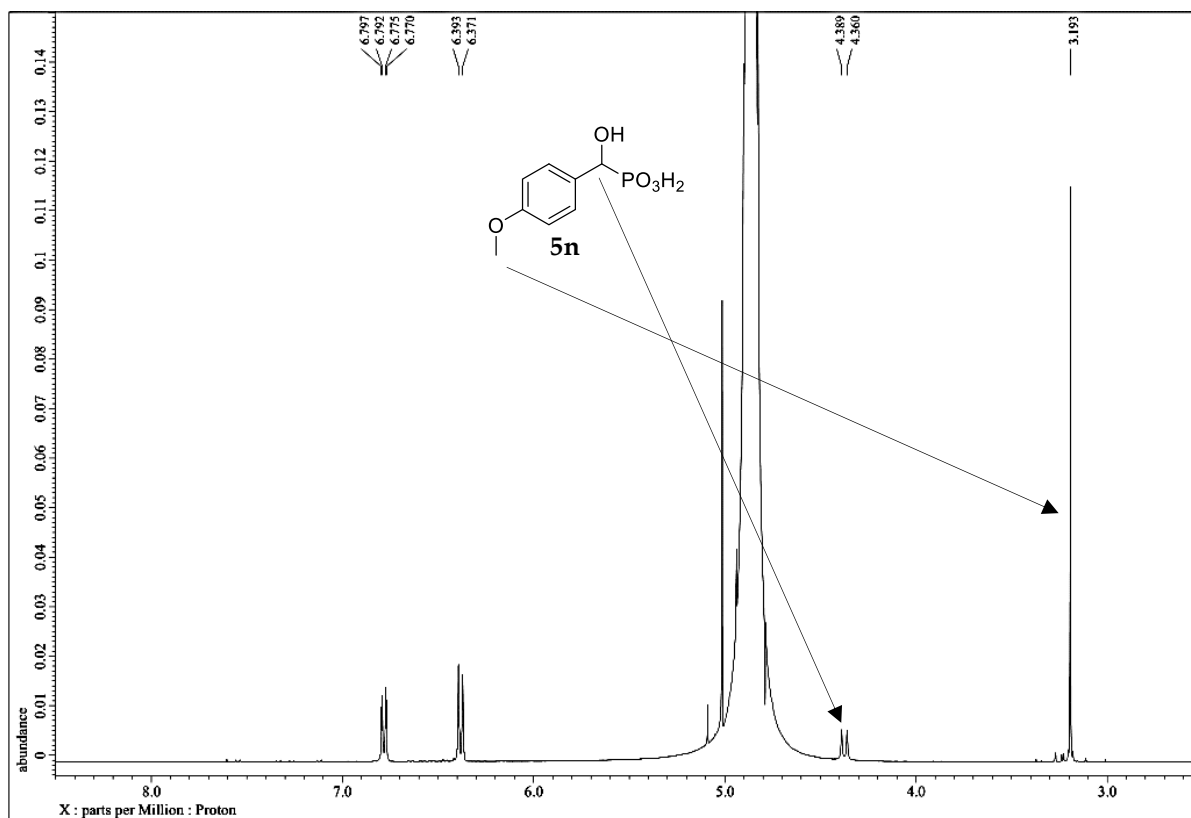


Figure 50. ^1H NMR (D_2O , 400MHz) spectra of the crude post-reaction mixture of amino(4-methoxyphenyl)methylphosphonic acid (**1n**) with NaNO_2 after 96h with addition of D_2SO_4 .

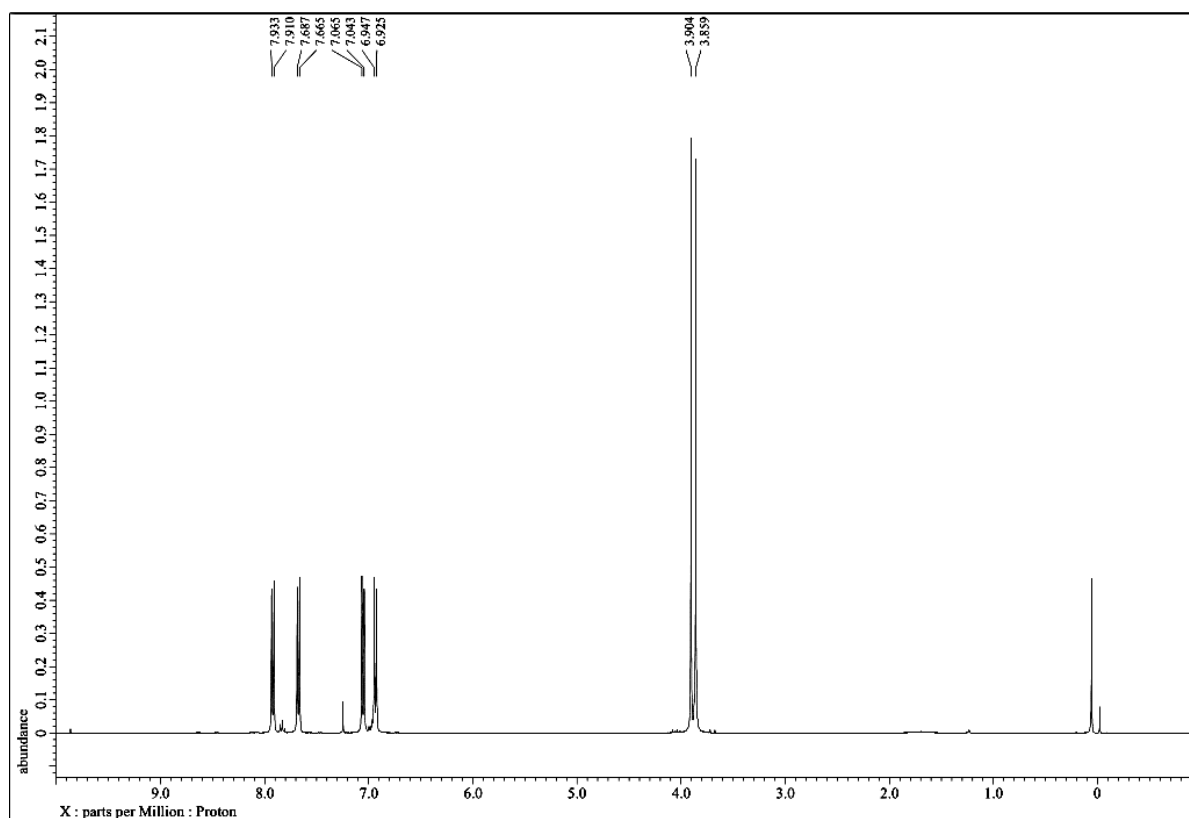


Figure S51. ¹H NMR (D₂O, 400MHz) spectra of the side product of the reaction of amino(4-methoxyphenyl)methylphosphonic acid (**1n**) with NaNO₂.

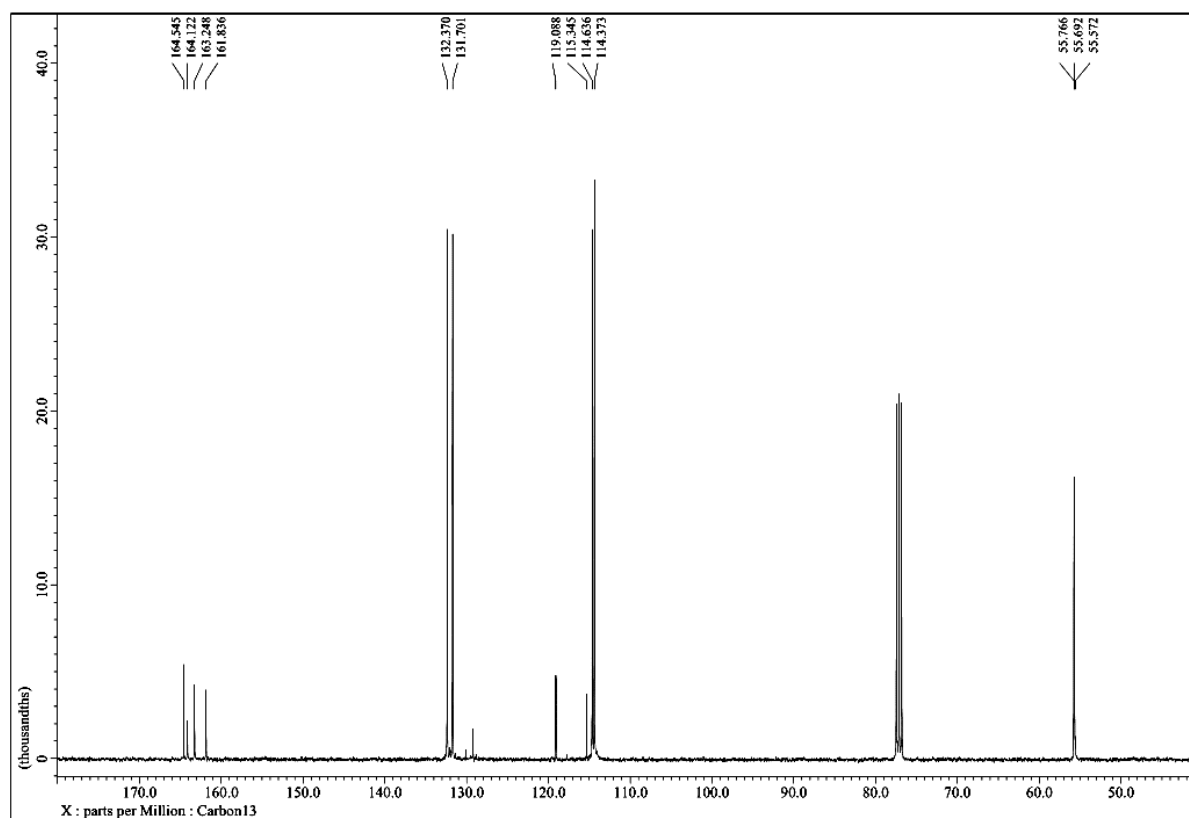
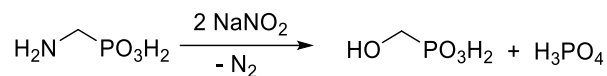


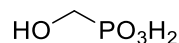
Figure S52. ¹³C{¹H} NMR (D₂O, 100MHz) spectra of the side product of the reaction of amino(4-methoxyphenyl)methylphosphonic acid (**1n**) with NaNO₂.

3.14. ABr1228. Deamination of **1h** in Water

1h		5h	
24 h	$\alpha = 1.00$	74%	9%
δ_{P} [ppm]		18.50 (t)	1.36

After 24 h at 21 °C, post-reaction mixture contained hydroxymethylphosphonic acid (**5h**) (74%molP), orthophosphoric acid (9%molP) and 8 unidentified compounds (17%molP in total) (Figure S60 and Figure S61).

Hydroxymethylphosphonic acid (**5h**) was identified by comparing chemical shifts, multiplicity and coupling constants on ^1H and ^{31}P NMR spectra with description in the literature (Table S18).



Hydroxymethylphosphonic acid (5h). ^{31}P NMR (D_2O): δ 18.50 (t, $^2J_{\text{H-P}} = 7.5$ Hz); ^1H NMR (D_2O) δ : 3.53 (d, 2H, $^2J_{\text{H-P}} = 7.4$ Hz).

Table S18. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of hydroxymethylphosphonic acid (**5h**) with description in the literature.

Structure	$\text{HO}-\text{CH}_2-\text{PO}_3\text{H}_2$	
	ABr1228	Reference [18]
Solvent	D_2O	D_2O (pH = 6.8)
^{31}P NMR	18.50 (t, $J = 7.5$ Hz)	17.5 ($J = 7.9$ Hz)

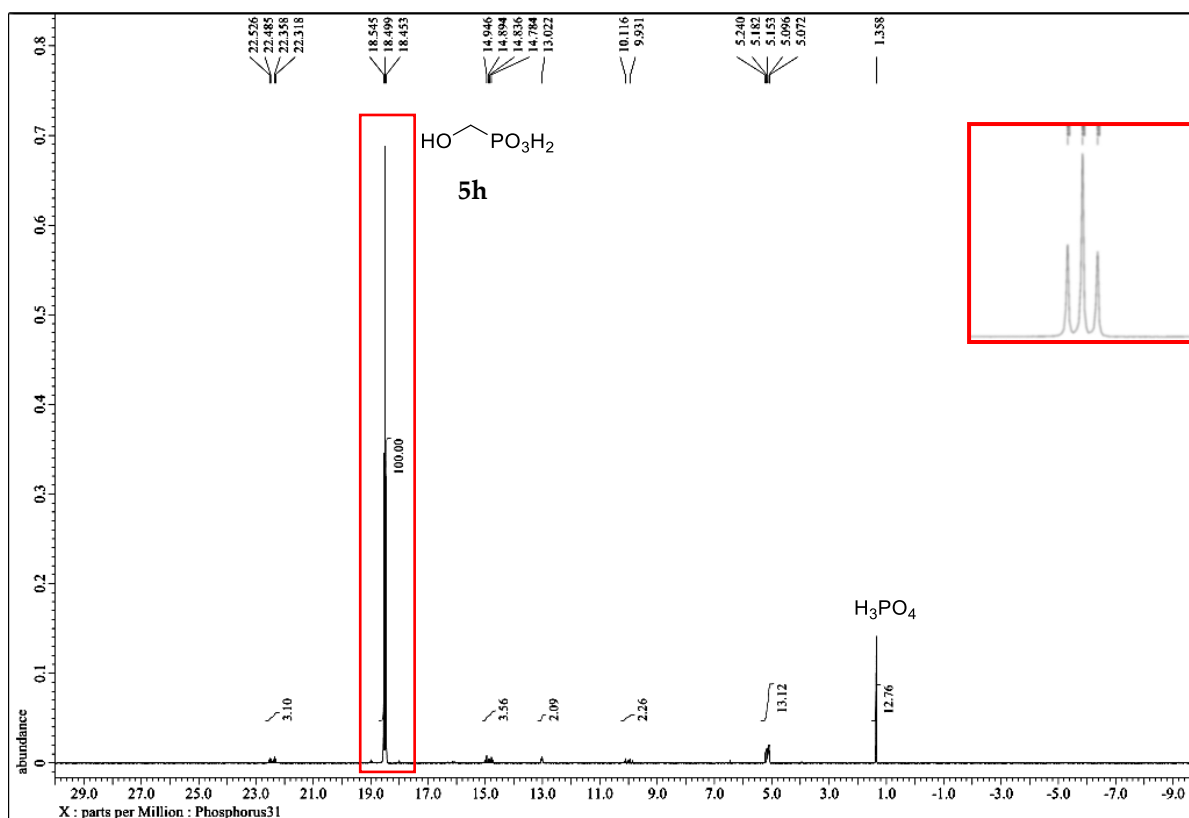


Figure S60. ^{31}P NMR (D_2O , 162MHz) spectra of the crude post-reaction mixture of laminomethylphosphonic acid (**1h**) with NaNO_2 after 24 h.

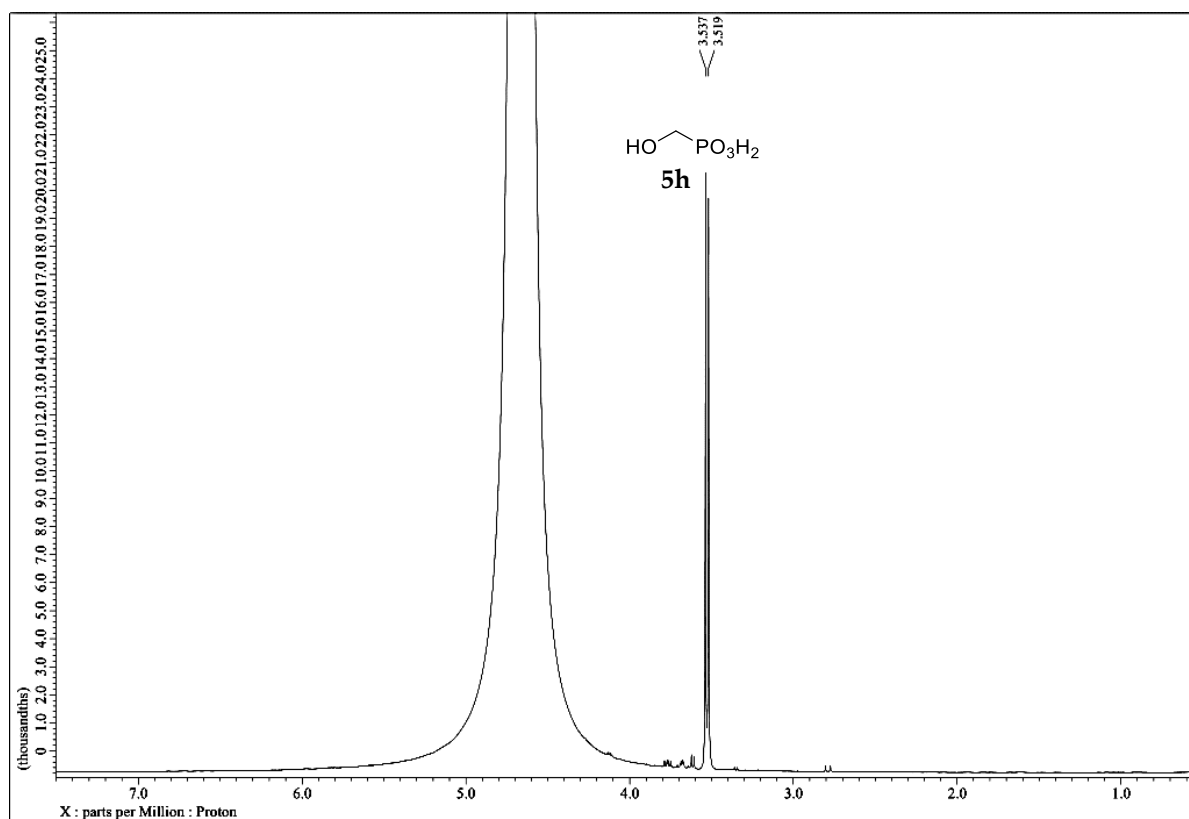
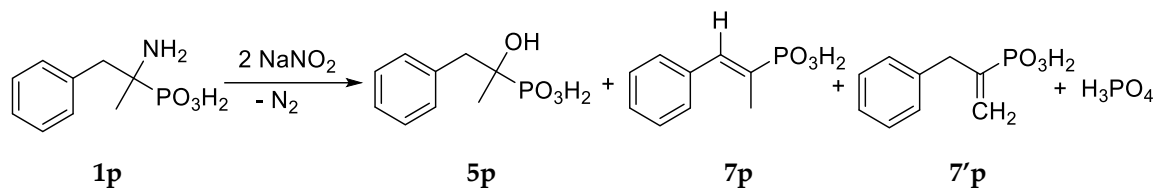


Figure S61. ^1H NMR (D_2O , 400MHz) spectra of the crude post-reaction mixture of laminomethylphosphonic acid (**1h**) with NaNO_2 after 24 h.

3.15. ABr1234. Deamination of **1p** in Water

96h	$\alpha = 1.00$	66%	22%	9%	3%
δ_{P} [ppm]		23.47 (dq)	16.91 (dq)	14.53 (ddt)	1.10

After 96h at 21 °C, post-reaction mixture contained 1-hydroxy-1-methyl-2-phenylethylphosphonic acid (**5p**) (66%molP), (*E*)-3-phenyl-prop-2-en-2-ylphosphonic acid (22%molP) (**7p**), 3-phenyl-prop-1-en-2-ylphosphonic acid (**7'p**) (9%molP) and orthophosphoric acid (3%molP) (Figure S62 and Figure S63).

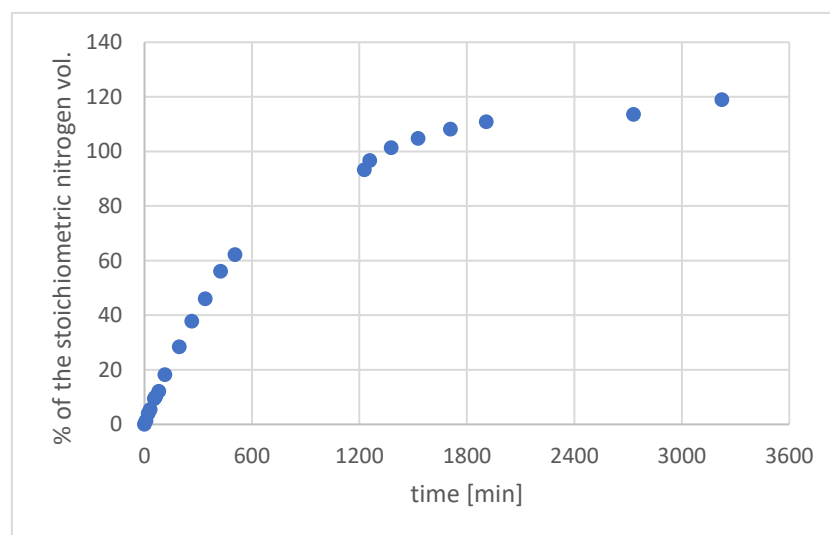
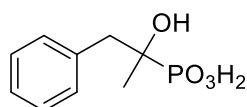
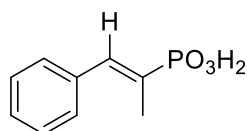


Chart 13. Dependence of the volume of the released gas (in % of the stoichiometric nitrogen volume) on the time in the reaction of 1-amino-1-methyl-2-phenylethylphosphonic acid (**1p**) with NaNO_2 in water.

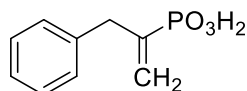
(*E*)-3-Phenyl-prop-2-en-2-ylphosphonic acid (**7p**) was identified by comparing chemical shifts, multiplicity and coupling constants on ^1H and ^{31}P NMR spectra with description of structurally similar (*E*)-1-methylprop-1-en-1-ylphosphonic acid (**7i**), which was obtained in the reaction of 1-amino-1-methylpropylphosphonic acid (**1i**) with NaNO_2 (ABr1214) (Table S19). 1-Hydroxy-1-methyl-2-phenylethylphosphonic acid (**5p**) and 3-phenyl-prop-1-en-2-ylphosphonic acid (**7'p**) were identified by comparing chemical shifts, multiplicity and coupling constants on ^1H and ^{31}P NMR spectra with description of structurally similar compounds: 1-hydroxy-1-methylethylphosphonic acid (**5m**) and 1-methylvinylphosphonic acid (**7m**), which were obtained in the reaction of 1-amino-1-methylethylphosphonic acid (**1m**) with NaNO_2 (ABr1204) (Table S20).



1-Hydroxy-1-methyl-2-phenylethylphosphonic acid (5p). ^{31}P NMR (D_2O): δ 23.47 (ddq, $^3J_{\text{H-P}} = 14.0$ Hz, $^3J_{\text{H-P}} = 7.7$ Hz, $^3J_{\text{H-P}} = 3.7$ Hz); ^1H NMR (D_2O) δ : 7.13–7.34 (m, 5H), 2.97 (dd, 1H, $^2J_{\text{H-H}} = 13.8$ Hz, $^3J_{\text{H-P}} = 7.6$ Hz), 2.79 (dd, 1H, $^2J_{\text{H-H}} = 13.8$ Hz, $^3J_{\text{H-P}} = 4.0$ Hz), 1.03 (d, 3H, $^3J_{\text{H-P}} = 14.4$ Hz).



(E)-3-Phenyl-prop-2-en-2-ylphosphonic acid (7p). ^{31}P NMR (D_2O): δ 16.91 (dq, $^3J_{\text{H-P}} = 22.9$ Hz, $^3J_{\text{H-H}} = 1.5$ Hz); ^1H NMR (D_2O): δ : 7.13–7.34 (m, 5H), 7.03 (dq, 1H, $^3J_{\text{H-P}} = 22.9$ Hz, $^4J_{\text{H-H}} = 1.5$ Hz), 1.90 (dd, 3H, $^3J_{\text{H-P}} = 14.2$ Hz, $^4J_{\text{H-H}} = 1.5$ Hz).



3-Phenyl-prop-1-en-2-ylphosphonic acid (7'p). ^{31}P NMR (D_2O): δ 14.53 (ddt, $^3J_{\text{H-P(trans)}} = 43.9$ Hz, $^3J_{\text{H-P(cis)}} = 20.6$ Hz, $^3J_{\text{H-P}} = 9.4$ Hz); ^1H NMR (D_2O): δ : 7.13–7.34 (m, 5H), 5.64 (ddt, 1H, $^3J_{\text{H-P(cis)}} = 20.5$ Hz, $^4J_{\text{H-H}} = 1.5$ Hz, $^4J_{\text{H-H}} = 1.2$ Hz), 5.07 (ddt, 1H, $^3J_{\text{H-P(trans)}} = 43.3$ Hz, $^4J_{\text{H-H}} = 1.8$ Hz, $^4J_{\text{H-H}} = 1.5$ Hz), 3.43 (ddd, 2H, $^3J_{\text{H-P}} = 9.8$ Hz, J undetermined).

Table S19. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of (*E*)-3-phenyl-prop-2-en-2-ylphosphonic acid (**7p**) and (*E*)-1-methylprop-1-en-1-ylphosphonic acid (**7i**) (ABr1214).

Structure		
Source	ABr1234	ABr1214
Solvent	D_2O	D_2O
^{31}P NMR	16.91 (dq, $J = 22.9, 14.0$ Hz)	17.47 (dq, $J = 21.7, 13.6, 3.7$ Hz)
^1H NMR	7.13–7.34 (m, 5H)	
	7.03 (dq, 1H, $J = 22.9, 1.5$ Hz)	6.15 (ddq, 1H, $J = 21.7, 6.7, 1.5$ Hz)
	1.90 (dd, 3H, $J = 14.2, 1.5$ Hz)	1.63 (ddq, 3H, $J = 13.6, 1.2, 1.2$ Hz)
		1.57 (ddq, 3H, $J = 6.7, 3.7, 1.2$ Hz)

Table S20. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of post-reaction mixture of 1-amino-2-phenyl-1-methylethylphosphonic acid (**1p**) with NaNO_2 and 1-hydroxy-1-methylethylphosphonic acid (**5m**) and 1-methylvinylphosphonic acid (**7m**).

Structure				
Source	ABr1234	ABr1204	ABr1234	ABr1204
Solvent	D_2O	D_2O	D_2O	D_2O
^{31}P NMR	23.47 (ddq, $J = 14.0, 7.7, 3.7$ Hz)	23.84 (septet, $J = 14.0$ Hz)	14.53 (ddt, $J = 43.9, 20.6, 9.4$ Hz)	15.21 (ddq, $J = 43.9, 20.6, 13.1$ Hz)
^1H NMR	7.13–7.34 (m, 5H)		7.13–7.34 (m, 5H)	
	2.97 (dd, 1H, $J = 13.8, 7.6$ Hz)		5.64 (ddt, 1H, $J = 20.5, 1.5, 1.2$ Hz)	5.46 (ddq, 1H, $J = 20.3, 2.1, 1.2$ Hz)
	2.79 (dd, 1H, $J = 13.8, 4.0$ Hz)		5.07 (ddt, 1H, $J = 43.3, 1.8, 1.5$ Hz)	5.36 (tq, 1H, $J = 43.4, 1.8$ Hz)
	1.03 (d, 3H, $J = 14.4$ Hz)	1.23 (d, 6H, $J = 13.8$ Hz)	3.43 (ddd, $J = 9.8$ Hz, J undetermined)	
				1.77 (dt, 3H, $J = 13.1, 1.2$ Hz)

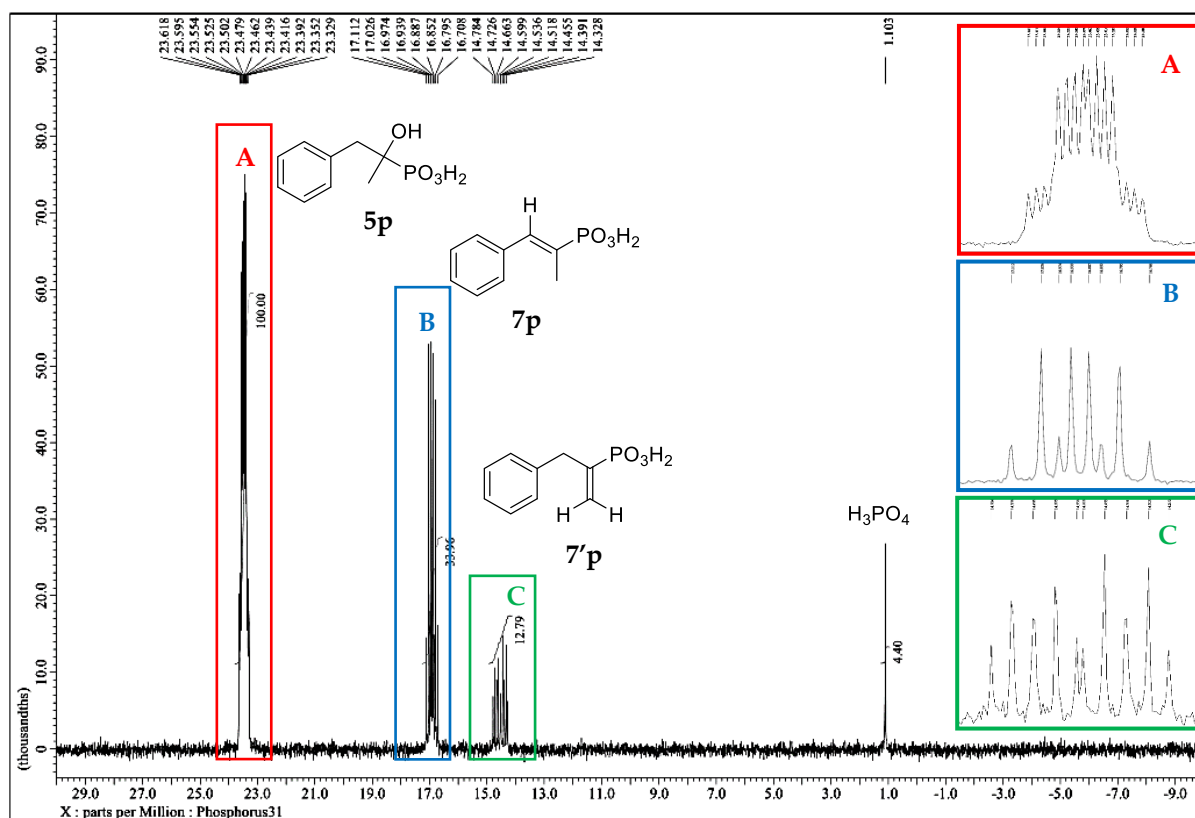


Figure S62. ^{31}P NMR (D₂O, 162 MHz) spectra of the crude post-reaction mixture of 1-amino-1-methyl-2-phenylethylphosphonic acid (**1p**) with NaNO₂ after 96h.

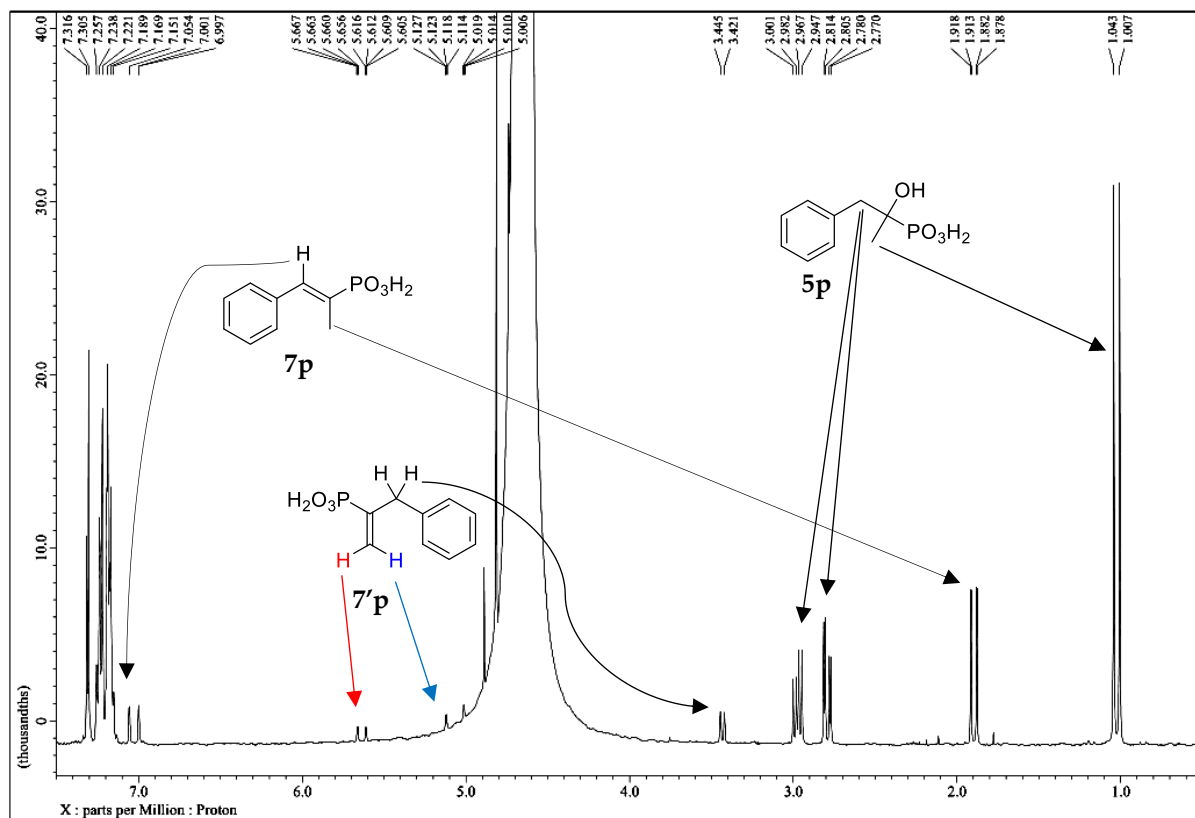
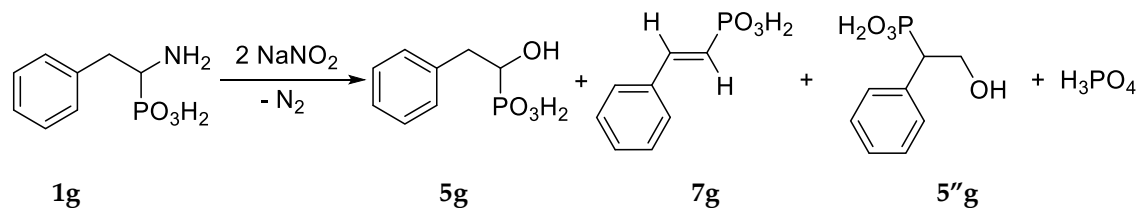


Figure S63. ^1H NMR (D₂O, 400 MHz) spectra of the crude post-reaction mixture of 1-amino-1-methyl-2-phenylethylphosphonic acid (**1p**) with NaNO₂ after 96h.

3.16. ABr1236. Deamination of **1g** in Water

48h	$\alpha = 0.99$	43%	3%	21%	25%
360h	$\alpha = 1.00$	42%	3%	21%	29%
δ_F [ppm]	14.5	19.59 (ddd)	13.37 (t)	18.96 (ddd)	1.58

After 48h at 21 °C, post-reaction mixture contained 1-hydroxy-2-phenylethylphosphonic acid (**5g**) (44%molP), (*E*)-2-phenylvinylphosphonic acid (**7g**) (3%molP), 2-hydroxy-1-phenylethylphosphonic acid (**5''g**) (21%molP), orthophosphoric acid (26%molP), unreacted substrate **1g** (1%molP) and unidentified compounds (5%molP in total).

After 360h at 21 °C, post-reaction mixture contained 1-hydroxy-2-phenylethylphosphonic acid (**5g**) (46%molP), (*E*)-2-phenylvinylphosphonic acid (**7g**) (3%molP), 2-hydroxy-1-phenylethylphosphonic acid (23%molP) (**5''g**), orthophosphoric acid (23%molP) and unidentified compounds (5%molP in total) (Figure S66 and Figure S66).

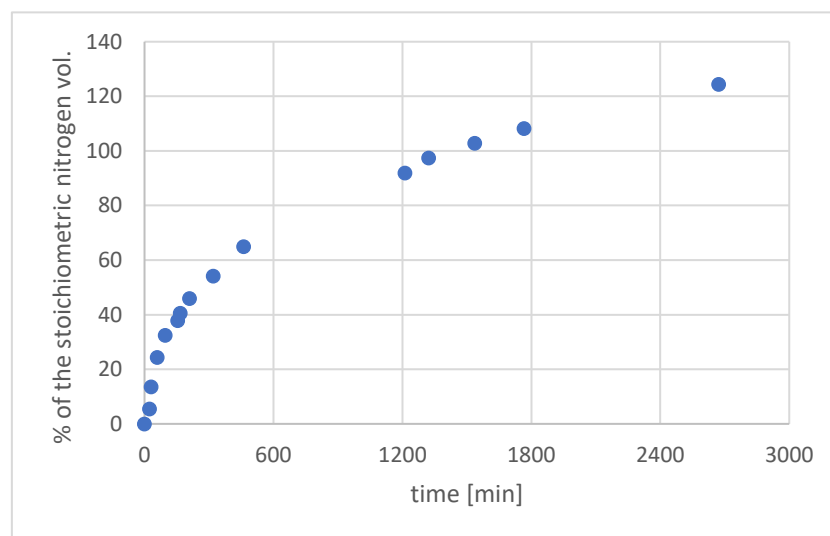


Chart 14. Dependence of the volume of the released gas (in % of the stoichiometric nitrogen volume) on the time in the reaction of 1-amino-2-phenylethylphosphonic acid (**1g**) with NaNO_2 in water.

1-Hydroxy-2-phenylethylphosphonic acid (**5g**) and (*E*)-2-phenylvinylphosphonic acid (**7g**) were identified by comparing chemical shifts, multiplicity and coupling constants on ^1H and ^{31}P NMR spectra with description in the literature (Table S21).

In the reaction 3 hydroxyalkylphosphonic acid could be formed (Figure S64): 1-hydroxy-2-phenylethylphosphonic acid (**7g**) (product of nucleophile addition), 2-hydroxy-2-phenylethylphosphonic acid (**5'g**) (product of rearrangement and nucleophile addition) and 2-hydroxy-1-phenylethylphosphonic acid (**5''g**) (product of phenyl migration and nucleophile addition).

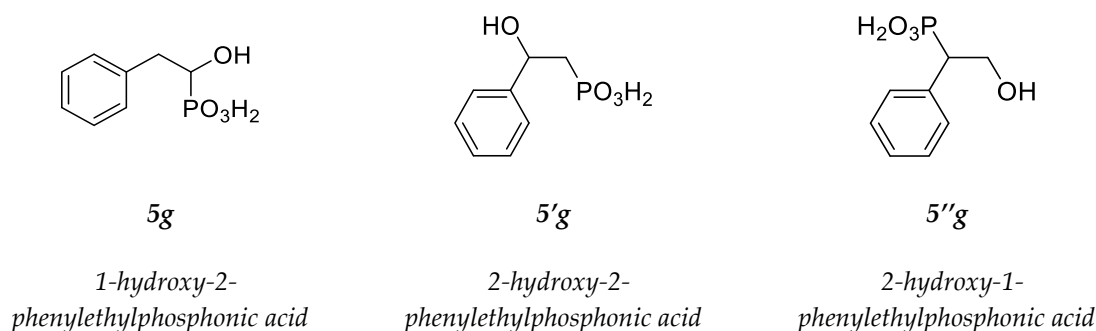
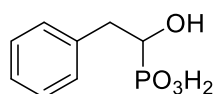
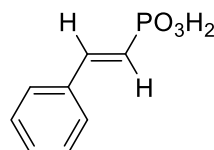


Figure S64. Structures of plausible products of reaction of 1-amino-2-phenylethylphosphonic acid (**1g**) with NaNO_2 in water.

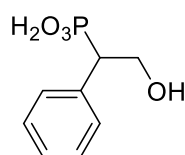
Identification of reaction products was accomplished by analysis of $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (Figure S67) and DEPT-135 spectra (Figure S68): in the post-reaction mixture there were 2 compounds that have structure $-\text{CH}_2\text{CH}(\text{PO}_3\text{H}_2)-$. The comparison of $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of post-reaction mixture with description in the literature confirms that the main reaction product was 1-hydroxy-2-phenylethylphosphonic acid (**5g**) [δ : 70.77 (d, $J = 152.8$ Hz), 38.01]. Therefore, 2-hydroxy-1-phenylethylphosphonic acid (**5''g**) has to be the second reaction product [δ : 62.25, 50.11 (d, $J = 124.1$ Hz)]. Additionally, the NMR spectra description [19] of 2-hydroxy-2-phenylethylphosphonic acid (**5'g**) excludes possibility that this compound was present in the post-reaction mixture.



1-Hydroxy-2-phenylethylphosphonic acid (5g). ^{31}P NMR (D_2O): δ 19.59 (br d, $J_{\text{H-P}} = 2.8$ Hz); ^1H NMR (D_2O , 600MHz) δ : 7.14–7.32 (m, 5H), 3.79 (ddd, 1H, $^2J_{\text{H-P}} = 11.5$ Hz, $^3J_{\text{H-H}} = 7.8$ Hz, $^3J_{\text{H-H}} = 2.5$ Hz), 3.03 (ddd, 1H, $^2J_{\text{H-H}} = 14.3$ Hz, $^3J_{\text{H-P}} = 2.5$ Hz, $^3J_{\text{H-H}} = 2.5$ Hz), 2.64 (ddd, 1H, $^2J_{\text{H-H}} = 14.3$ Hz, $^3J_{\text{H-P}} = 11.9$ Hz, $^3J_{\text{H-H}} = 7.3$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (62mg, D_2O) δ : 70.77 (d, $J_{\text{C-P}} = 152.8$ Hz), 38.01.

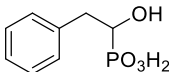
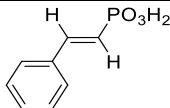


(E)-2-Phenylvinylphosphonic acid (7g). ^{31}P NMR (D_2O): δ 13.38 (m); ^1H NMR (D_2O) δ : 7.14–7.32 (m, 5H), 7.04 (dd, 1H, $J_{\text{H-P}} = 20.8$ Hz, $^3J_{\text{H-H}} = 17.4$ Hz), 6.37 (dd, 1H, $^3J_{\text{H-H}} = 17.4$ Hz, $J_{\text{H-P}} = 16.0$ Hz).



2-Hydroxy-1-phenylethylphosphonic acid (5''g). ^{31}P NMR (D_2O): δ 18.96 (br d $^2J_{\text{H-P}} = 21.5$ Hz); ^1H NMR (D_2O) δ : 7.14–7.32 (m, 5H), 4.07 (dt, $^2J_{\text{H-H}} = 11.3$ Hz, $^3J_{\text{H-P}} = 4.3$ Hz, $^3J_{\text{H-H}} = 4.3$ Hz), 3.96 (dt, 1H, $^2J_{\text{H-H}} = 11.3$ Hz, $^3J_{\text{H-P}} = 5.2$ Hz, $^3J_{\text{H-H}} = 5.2$ Hz), 3.07 (ddd, 1H, $^2J_{\text{H-P}} = 22.0$ Hz, $^3J_{\text{H-H}} = 11.0$ Hz, $^3J_{\text{H-H}} = 4.3$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (62mg, D_2O) δ : 62.25, 50.11 (d, $J_{\text{C-P}} = 124.1$ Hz).

Table S21. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of post-reaction mixture of 1-amino-2-phenylethylphosphonic acid (**1g**) with NaNO_2 with description in the literature.

Structure				
Source	ABr1236	Reference [20]	ABr1236	Reference [21]
Solvent	D2O	D2O	D2O	DMSO-d6
³¹ P NMR	19.59 (ddd, <i>J</i> = 2.8 Hz)	18.22 (m, <i>J</i> = 6.9 Hz)	13.38 (dd, <i>J</i> = 19.6, 15.9 Hz);	14.71
¹ H NMR	7.14-7.32 (m, 5H)	<div>7.27-7.30 (4H, m)</div> <div>7.22-7.27 (m, 1H)</div>	7.14-7.32 (m, 5H)	<div>7.6 (m, 2H)</div> <div>7.4 (m, 3H),</div>
	3.85 (ddd, 1H, <i>J</i> = 11.7, 7.7, 2.4 Hz)	3.77 (ddd, 1H, <i>J</i> = 7.5, 3.1, 9.6 Hz)	7.04 (dd, 1H, <i>J</i> = 20.8, 17.4 Hz)	7.2 (dd, 1H, <i>J</i> = 17.7, 17.4 Hz)
	3.10 (dt, 1H, <i>J</i> = 13.9, 2.7 Hz)	3.07 (ddd, 1H, <i>J</i> = 14.4, 3.1, 3.4 Hz)	6.36 (dd, 1H, <i>J</i> = 17.4, 16.0 Hz)	6.5 (dd, 1H, <i>J</i> = 18.0, 16.2 Hz)
	2.70 (ddd, 1H, <i>J</i> = 14.3, 11.9, 7.3 Hz)	2.66 (ddd, 1H, <i>J</i> = 14.4, 9.6, 7.8 Hz).		

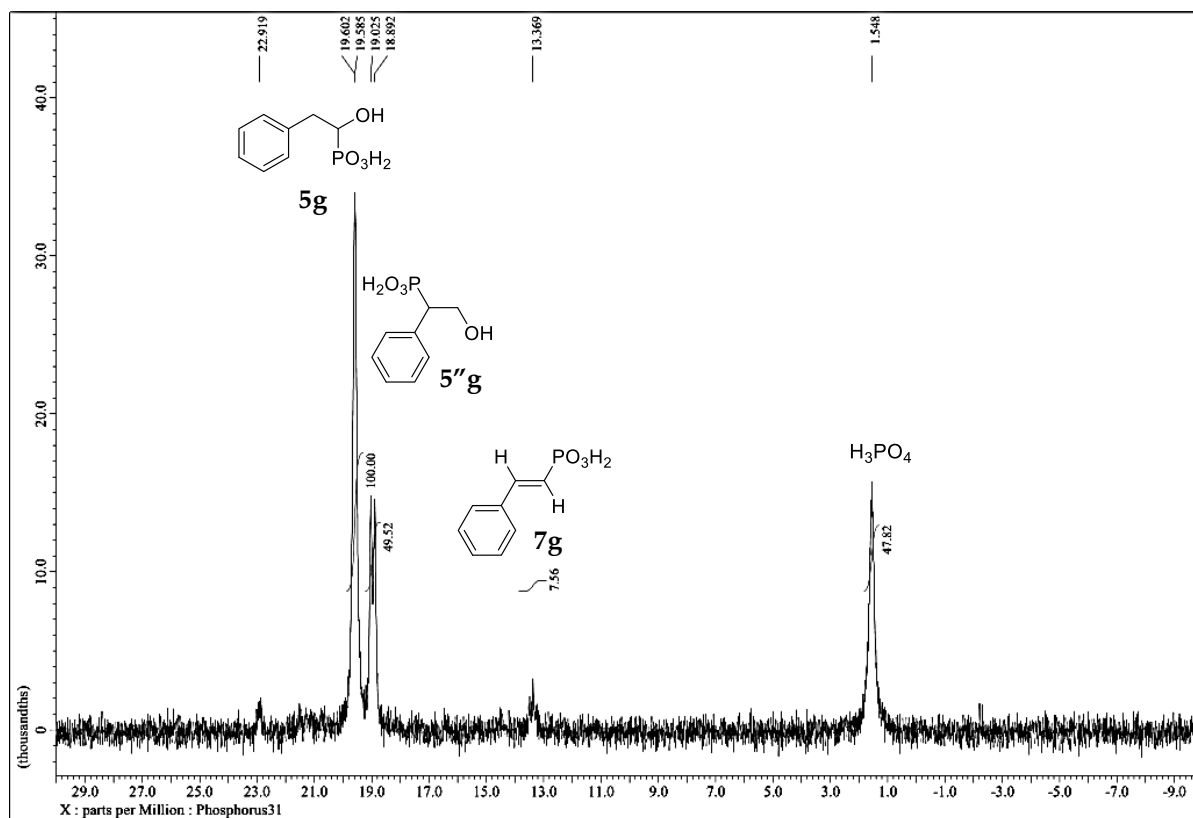


Figure S65. ³¹P NMR (D₂O, 162MHz) spectra of the crude post-reaction mixture of 1-amino-2-phenylethylphosphonic acid (**1g**) with NaNO₂ after 360h.

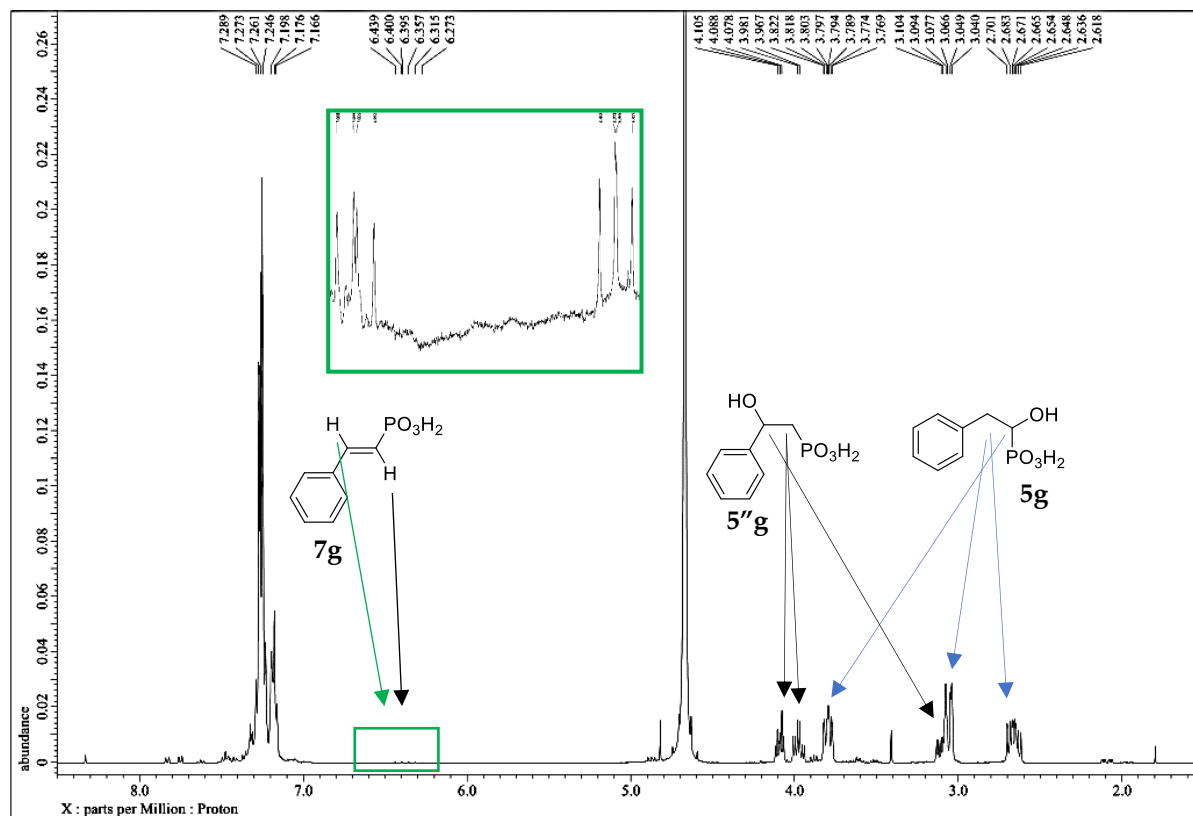


Figure S66. ¹H NMR (D₂O, 400MHz) spectra of the crude post-reaction mixture of 1-amino-2-phenylethylphosphonic acid (**1g**) with NaNO₂ after 360h.

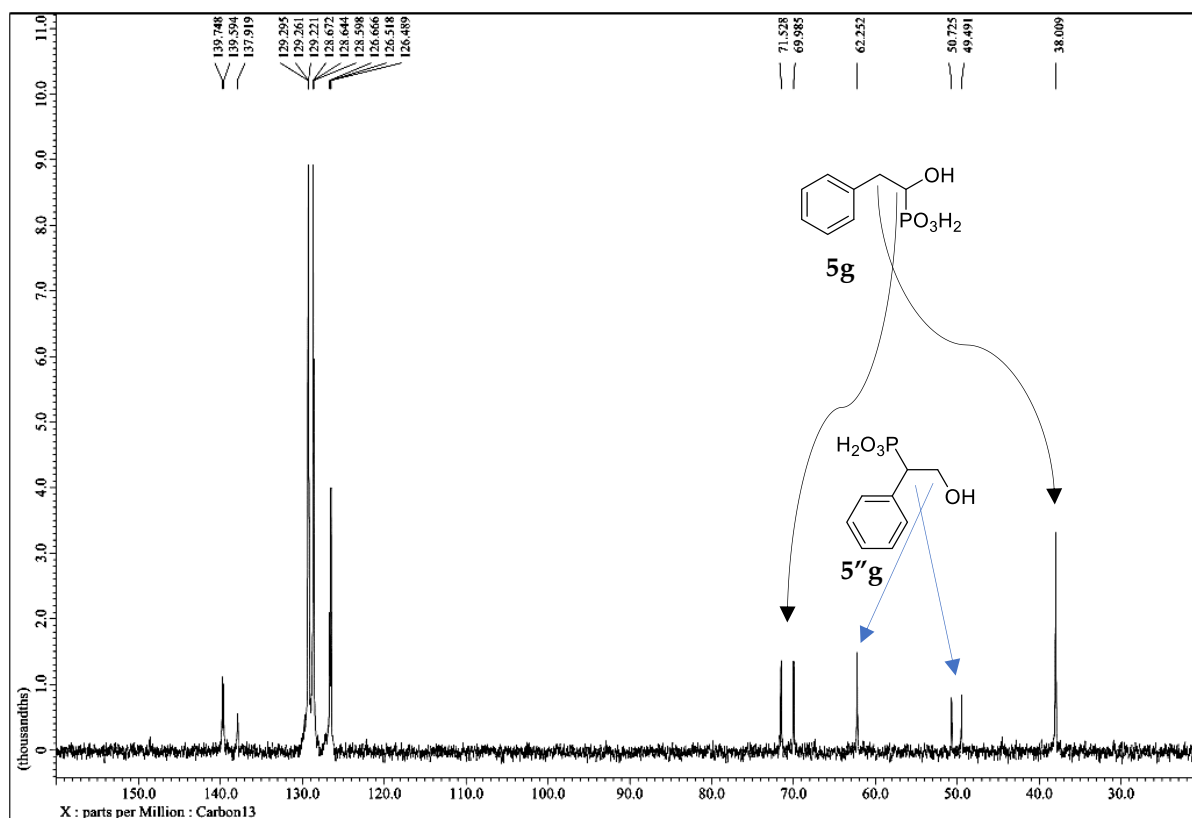


Figure S67. $^{13}\text{C}\{^1\text{H}\}$ NMR (D₂O, 100MHz) spectra of the concentrated post-reaction mixture of 1-amino-2-phenylethylphosphonic acid (**1g**) with NaNO₂ after 360h.

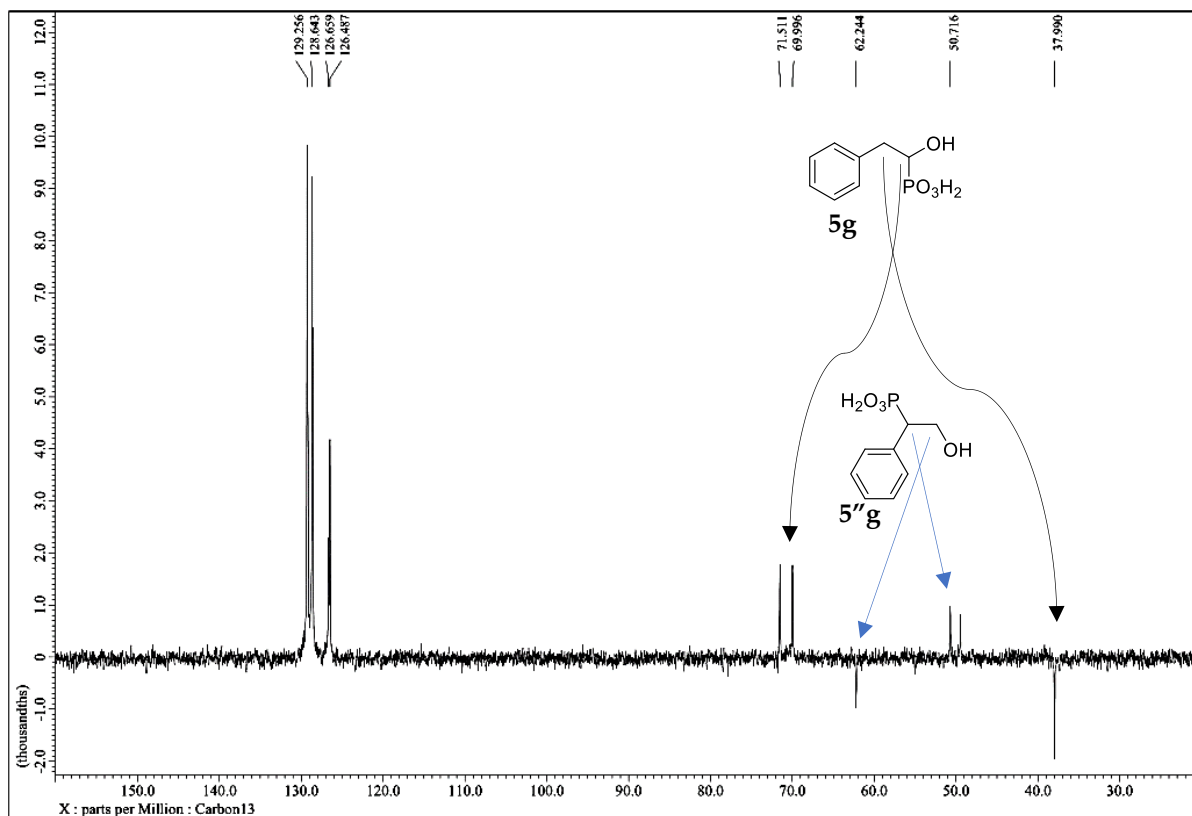
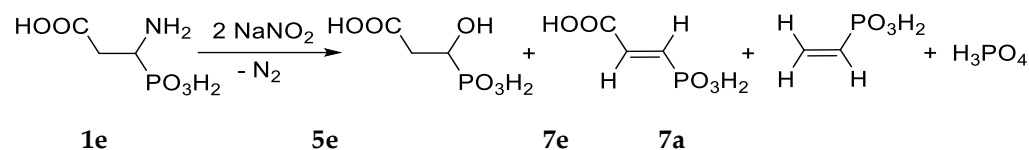


Figure S68. Dept-135 (D₂O) spectra of the concentrated post-reaction mixture of 1-amino-2-phenylethylphosphonic acid (**1g**) with NaNO₂ after 360h..

3.17. ABr1248. Deamination of **1e** in Water

48h	$\alpha = 0.71$	55%	6%	6%	4%
264h	$\alpha = 0.86$	70%	6%	6%	4%
δ_{P} [ppm]	12.23(dt)	19.07(dt)	13.11(dd)	10.65(ddd)	0.64(s)

After 48h at 21 °C, post-reaction mixture contained 3-hydroxy-3-phosphonopropanoic acid (**5e**) (55%molP), (*E*)-3-phosphonoacrylic acid (**7e**) (6%molP), vinylphosphonic acid (**7a**) (6%molP), orthophosphoric acid (4%molP) and unreacted substrate **1e** (29%molP).

After 264h post-reaction mixture contained 3-hydroxy-3-phosphonopropanoic acid (**5e**) (70%molP), (*E*)-3-phosphonoacrylic acid (**7e**) (6%molP), vinylphosphonic acid (**7a**) (6%molP), orthophosphoric acid (4%molP) and unreacted substrate **1e** (14%molP) (Figure S69 and Figure S70).

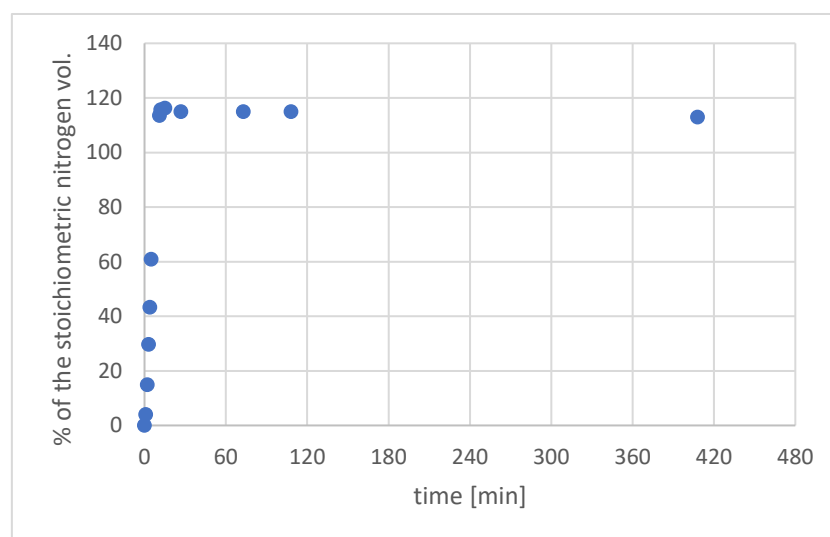
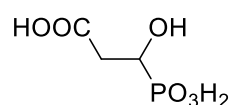
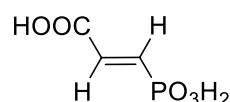


Chart 15. Dependence of the volume of the released gas (in % of the stoichiometric nitrogen volume) on the time in the reaction of 3-amino-3-phosphonopropanoic acid (**1e**) with NaNO₂ in water.

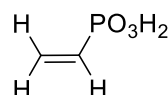
Spectra of 3-hydroxy-3-phosphonopropanoic acid (**5e**) has been not described in the literature therefore this compound was identified by comparing chemical shifts, multiplicity and coupling constants on ¹H and ³¹P NMR spectra with description of structurally similar 1-hydroxy-2-phenylethylphosphonic acid (**5g**), which was obtained in reaction of 1-amino-2-phenylethylphosphonic acid (**1g**) with NaNO₂ (ABr1236) (Table S22). (*E*)-3-phosphonoacrylic acid (**7e**) and vinylphosphonic acid (**7a**) were identified by comparing chemical shifts, multiplicity and coupling constants on ¹H and ³¹P NMR spectra with description in the literature (Table S23).



3-Hydroxy-3-phosphonopropanoic acid (5e). ³¹P NMR (D₂O): δ 19.07 (dt, ²J_{H-P} = 8.0 Hz, ³J_{H-P} = 8.0 Hz, ³J_{H-P} = 5.6 Hz); ¹H NMR (D₂O): δ : 3.99 (ddd, 1H, ³J_{H-H} = 11.0 Hz, ²J_{H-P} = 8.0 Hz, ³J_{H-H} = 2.8 Hz), 2.63 (ddd, 1H, ²J_{H-H} = 15.9 Hz, ³J_{H-P} = 5.5 Hz, ³J_{H-H} = 2.8 Hz), 2.42 (ddd, 2H, ²J_{H-H} = 16.0 Hz, ³J_{H-H} = 11.0 Hz, ³J_{H-P} = 7.6 Hz).



(E)-3-phosphonoacrylic acid (7e). ^{31}P NMR (D_2O): δ 10.65 (dd, $J_{\text{H-P}} = 19.6$ Hz, $J_{\text{H-P}} = 17.8$ Hz); ^1H NMR (D_2O): δ : 6.58 (dd, 1H, $J_{\text{H-P}} = 17.1$ Hz, $^3J_{\text{H-H}} = 17.1$ Hz), 6.30 (dd, 1H, $J_{\text{H-P}} = 19.6$ Hz, $^3J_{\text{H-H}} = 17.4$ Hz).



Vinylphosphonic acid (7a). ^{31}P NMR (D_2O): δ 13.11 (ddd, $^3J_{\text{H-P(trans)}}$ = 47.0 Hz, $^3J_{\text{H-P(cis)}}$ = 23.4 Hz, $^2J_{\text{H-P}} = 20.6$ Hz); ^1H NMR (D_2O): δ : 6.02 (ddd, 1H, $^2J_{\text{H-P}} = 20.9$ Hz, $^3J_{\text{H-H}} = 18.8$ Hz, $^3J_{\text{H-H}} = 12.5$ Hz), 5.82 (ddd, 1H, $^3J_{\text{H-P(cis)}}$ = 23.8 Hz, $^3J_{\text{H-H}} = 18.8$ Hz, $^2J_{\text{H-H}} = 2.5$ Hz), 5.71 (ddd, 1H, $^3J_{\text{H-P(trans)}}$ = 46.9 Hz, $^3J_{\text{H-H}} = 12.7$ Hz, $^2J_{\text{H-H}} = 2.5$ Hz).

Table S22. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of 3-hydroxy-3-phosphonopropanoic (**1e**) with 1-hydroxy-2-phenylethylphosphonic acid (**5g**) (ABr1236).

Structure		
Source	ABr1248	ABr1236
Solvent	D_2O	D_2O
^{31}P NMR	19.07 (dt, $J = 8.0, 5.6\text{Hz}$)	18.22 (m, $J = 6.9$ Hz) 7.27-7.30 (4H, m) 7.22-7.27 (m, 1H)
^1H NMR	3.99 (ddd, 1H, $J = 11.0, 8.0, 2.8$ Hz) 2.63 (ddd, 1H, $J = 15.9, 5.5, 2.8$ Hz) 2.42 (ddd, 2H, $J = 16.0, 11.0, 7.6$ Hz)	3.77 (ddd, 1H, $J = 7.5, 3.1, 9.6$ Hz) 3.07 (ddd, 1H, $J = 14.4, 3.1, 3.4$ Hz) 2.66 (ddd, 1H, $J = 14.4, 9.6, 7.8$ Hz)

Table S23. Comparison of chemical shifts and coupling constants on ^1H and ^{31}P NMR spectra of the reaction products of 3-amino-3-phosphonopropanoic (**1e**) with NaNO_2 with compounds described in the literature.

Structure				
Source	ABr1248	Reference [22]	ABr1248	Reference [6]
Solvent	D ₂ O	D ₂ O (trisodium salt)	D ₂ O	CDCl ₃
³¹ P NMR	10.65 (dd, <i>J</i> = 19.6, 17.8 Hz)	13.88	13.11 (ddd, <i>J</i> = 47.0, 23.4, 20.6 Hz)	17.3 (ddd, <i>J</i> = 20.0, 20.5, 51.3 Hz)
¹ H NMR	6.58 (t, 1H, <i>J</i> = 17.1 Hz)	7.22-7.08 (dd, 1H, <i>J</i> = 12.4, 17.1 Hz)	6.02 (ddd, 1H, <i>J</i> = 20.9, 18.8, 12.5 Hz)	6.31 (ddd, 1H, <i>J</i> = 20.5, 16.2, 4.5 Hz)
	6.30 (dd, 1H, <i>J</i> = 19.6, 17.4 Hz)	5.70-5.82 (dd, 1H, <i>J</i> = 9.0, 7.6 Hz)	5.82 (ddd, 1H, <i>J</i> = 23.8, 18.8, 2.5 Hz)	6.05 (ddd, 1H, <i>J</i> = 51.3, 11.2, 4.5 Hz),
			5.71 (ddd, 1H, <i>J</i> = 46.9, 12.7, 2.5 Hz)	6.02 (ddd, 1H, <i>J</i> = 20.0, 16.2, 11.2 Hz)

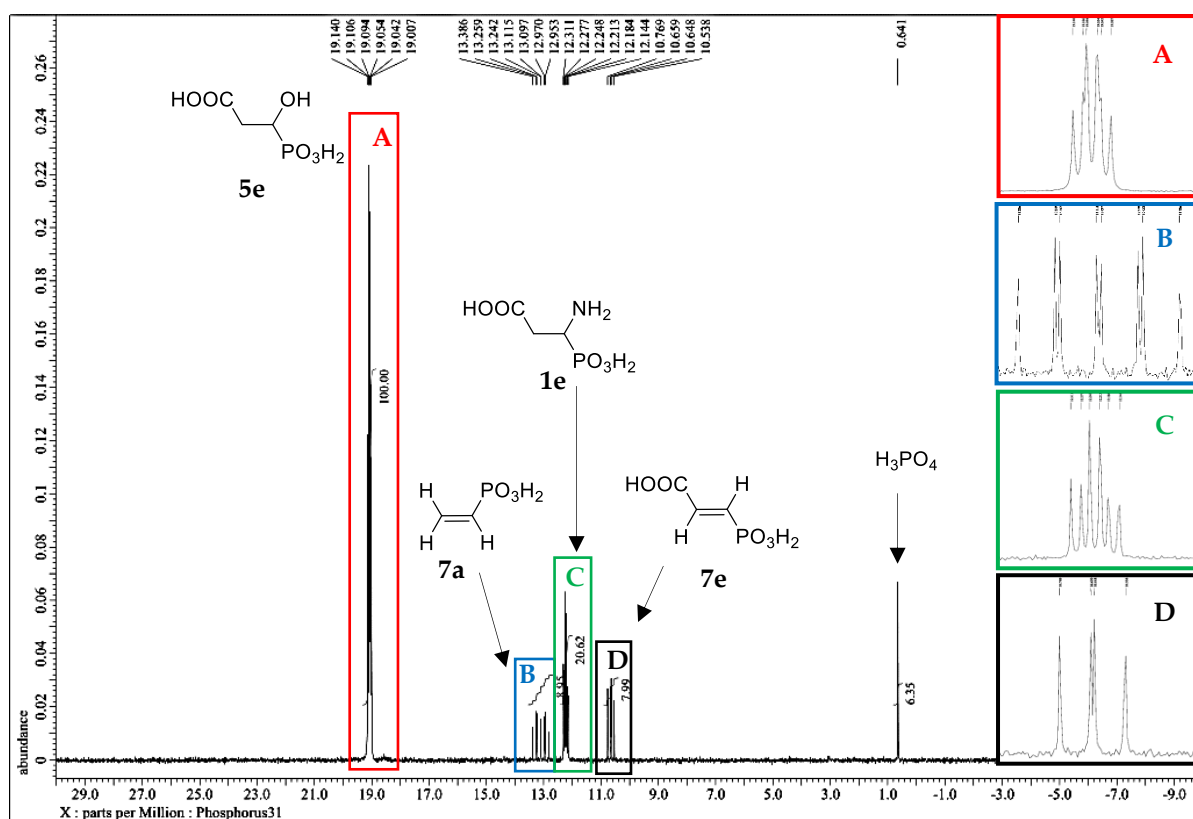


Figure S69. ^{31}P NMR (D₂O, 162MHz) spectra of the crude post-reaction mixture of 3-amino-3-phosphonopropanoic acid (**1e**) with NaNO₂ after 264h.

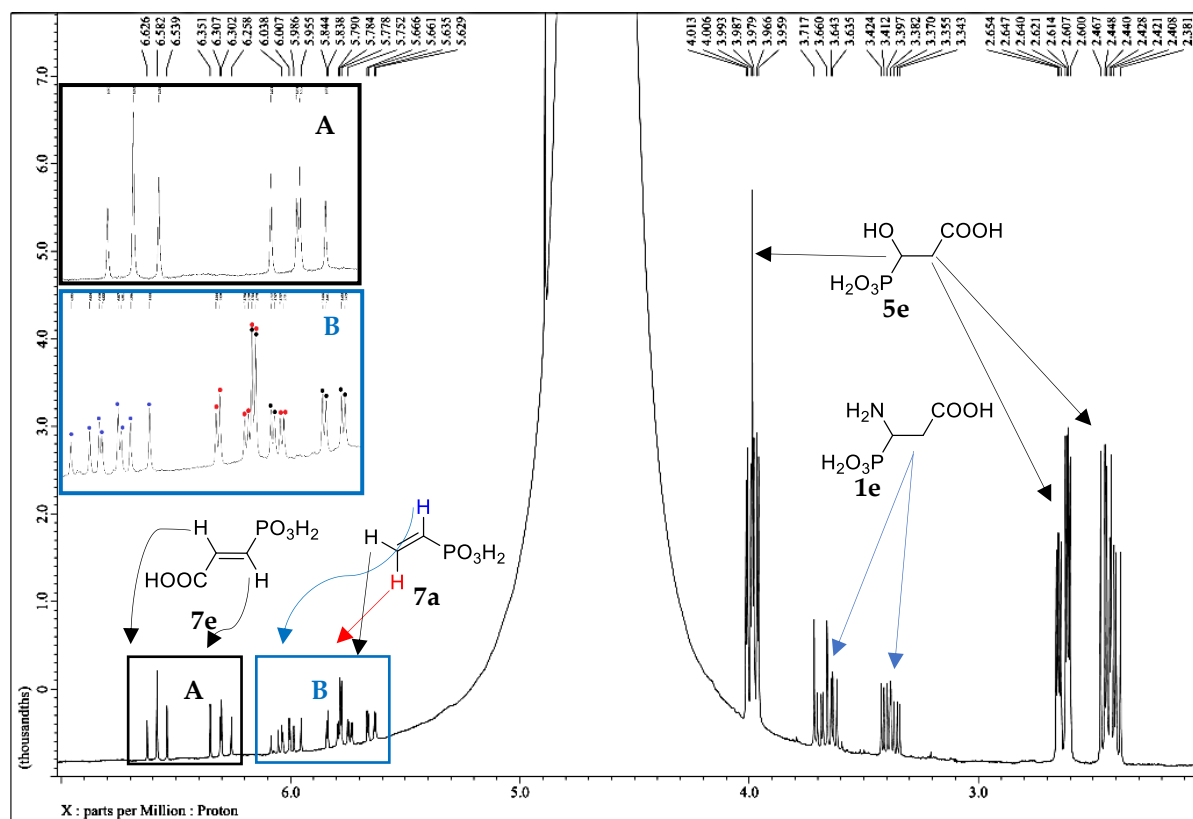
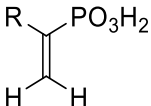
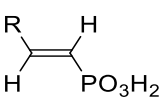
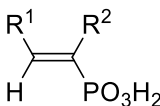
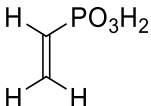
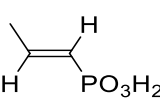
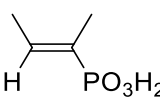
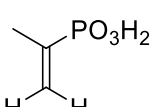
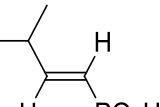
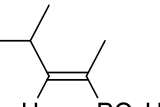
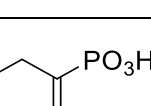
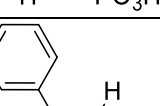
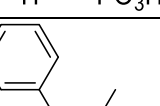
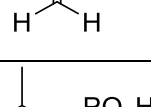
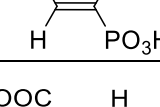
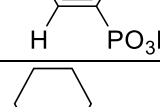
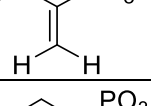
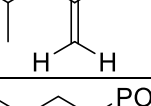


Figure S70. ^1H NMR (D₂O, 400MHz) spectra of the crude post-reaction mixture of 3-amino-3-phosphonopropanoic acid (**1e**) with NaNO₂ after 264h. .

Table S24. Comparison of structures and chemical shifts of 1-hydroxyalkylphosphonic acids **5** and 2-hydroxyalkylphosphonic acids **5'** on ^{31}P NMR spectra of crude post-reaction mixtures of 1-aminoalkylphosphonic acids with NaNO_2 in water.

Structure	^{31}P NMR (D ₂ O)	Structure	^{31}P NMR (D ₂ O)	Structure	^{31}P NMR (D ₂ O)
	17.23 (d)		23.84 (septet)		21.67 (tt)
	17.27 (d)		24.18 (ddq)		21.24 (t)
	18.50 (t)		24.06 (dq)		26.36 (dq)
	21.33 (dq)		24.18 (tq)		26.44 (dq)
	20.96 (dt)		23.47 (dq)		18.96 (ddd)
	20.57 (dd)		23.88 (br s)		
	19.91 (d)		20.28 (q)		
	21.58 (dd)				
	19.59 (ddd)				
	19.07 (dd)				

Table S25. Comparison of structures and chemical shifts of vinylphosphonic acid derivatives **7** and **7'** on ^{31}P NMR spectra of crude post-reaction mixtures of 1-aminoalkylphosphonic acids **1** with NaNO_2 in water.

	^{31}P NMR (D_2O)		^{31}P NMR (D_2O)		^{31}P NMR (D_2O)
	12.9 (ddd)		13.84 (ddq)		17.47 (dq)
	15.31 (ddq)		14.90 (ddd)		17.87 (ddq)
	15.63 (ddt)		13.38 (dd)		16.91 (dq)
	15.84 (ddd)		13.11 (dd)		16.25 (doublet of quintets)
	15.6 (ddt)				
	14.53 (ddt)				

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