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Ultrafast hydrolytic degradation of 2,3-dihydroxypropyl functionalized poly(ethylene phosphates)

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SUPPORTING INFORMATION

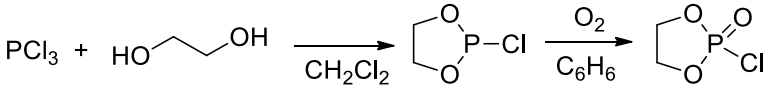
S1. General experimental remarks

All of the synthetic and polymerization experiments were conducted under an argon atmosphere. Diethyl ether, THF and triethylamine were refluxed with Na/benzophenone/dibenzo-18-crown-6 and distilled prior to use. Glycidol (Sigma-Aldrich, 99%), (2,2-dimethyl-1,3-dioxolan-4-yl)methanol (Sigma-Aldrich, 98%) and acetic acid (Acros, ≥99.9%) were used as purchased. BHT-Mg catalyst was prepared as previously reported [I. E. Nifant'ev, A. V. Shlyakhtin, V. V. Bagrov, M. E. Minyaev, A. V. Churakov, S. G. Karchevsky, K. P. Birin and P. V. Ivchenko, *Dalton Trans.*, 2017, **46**, 12132]. Dialysis membrane (Benzylated cellulose, MWCO 2 kDa) was used for purification of 2,3-dihydroxypropyl-functionalized polymers.

$CDCl_3$ and D_2O (Cambridge Isotope Laboratories, Inc., D 99.8 atom %) were used as purchased. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400 MHz) at 20 °C. The chemical shifts are reported in ppm relative to the solvent residual peaks.

GPC measurements of the polymers were performed in DMF (containing 0.1 g dm^{-3} lithium bromide as additive) with a flow rate of 1 ml/min at 50 °C using an Agilent PL-GPC 220 integrated instrument with an autosampler and RI-detector. Calibration was achieved using poly(ethylene glycol) standards.

S2. Preparation of ethylene phosphates 1 and 2



2-Chloro-1,3,2-dioxaphospholane.

The compound was synthesized via a modified literature protocol [G. Becker and F. R. Wurm, *Tetrahedron*, 2017, **73**, 3536]. A flame-dried 500 ml three-neck flask, equipped with a dropping funnel and a reflux condenser with a calcium chloride tube, was charged with phosphorous trichloride (137.33 g, 1 mol) in dry dichloromethane (150 ml). Ethylene glycol (62.07 g, 1 mol) was added dropwise to the stirring solution. Argon was bubbled through the solution to remove hydrogen chloride. After 2 h, the solvent was removed and the residue was distilled under reduced pressure. The yield was 80.7 g (64%). B. p. 83-84 °C (80 Torr), colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.44 (m, 2H, OC*H*$_2$C*H*$_2$O); 4.22 (m, 2H, OC*H*$_2$C*H*$_2$O). ^{31}P{H} NMR (162 MHz, $CDCl_3$, 20 °C): δ 167.61.

2-Chloro-1,3,2-dioxaphospholane 2-oxide.

The compound was synthesized according to a modified literature procedure [G. Becker and F. R. Wurm, *Tetrahedron*, 2017, **73**, 3536]. A flame-dried 500 ml three-neck flask, equipped with a reflux condenser, was charged with 2-chloro-1,3,2-dioxaphospholane (50 g, 0.4 mol) dissolved in benzene (200 ml) and heated to 50 °C. A stream of dry oxygen was passed through the solution for 12 hours. The solvent was removed *in vacuo* and the residue was purified by distillation under reduced pressure. The yield was 40.1 g (71%). B. p. 79-80 °C (0.4 Torr), colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.63-4.46 (m, 4H, OC*H*$_2$C*H*$_2$O). ^{13}C{H} NMR (101 MHz, $CDCl_3$, 20 °C): δ 66.7 (s). ^{31}P{H} NMR (162 MHz, $CDCl_3$, 20 °C): δ 22.81.

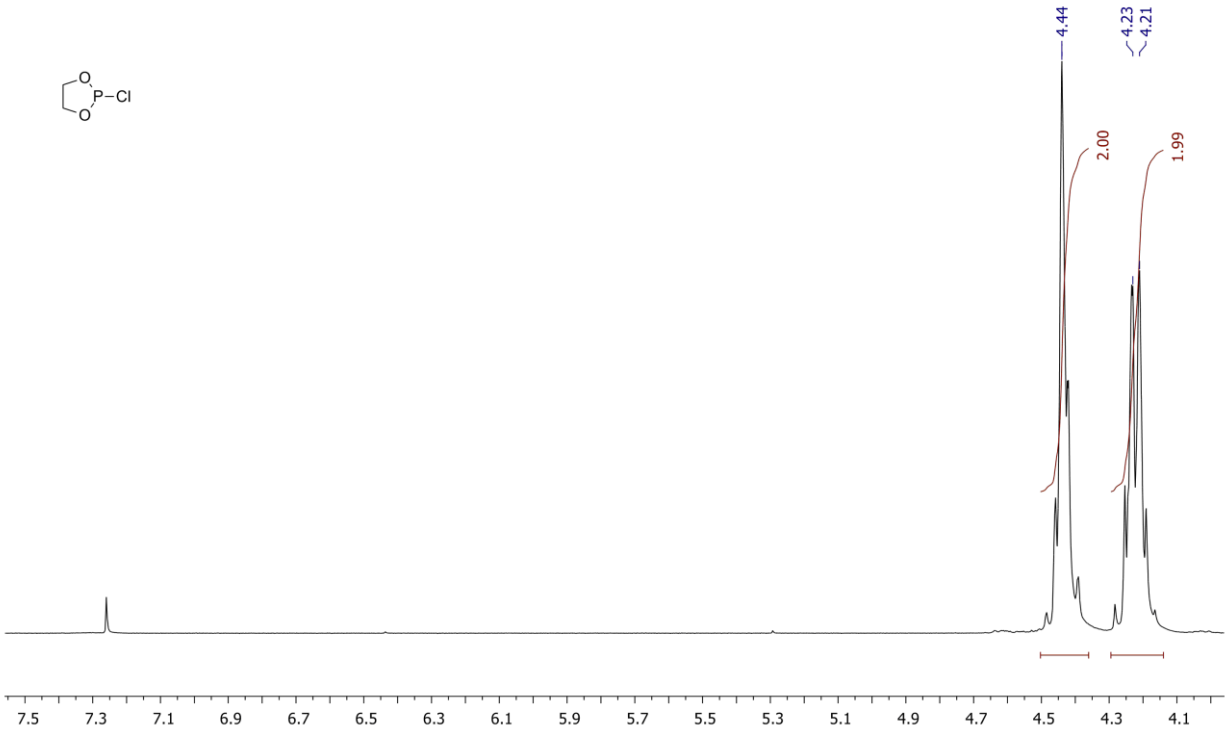


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of 2-chloro-1,3,2-dioxaphospholane

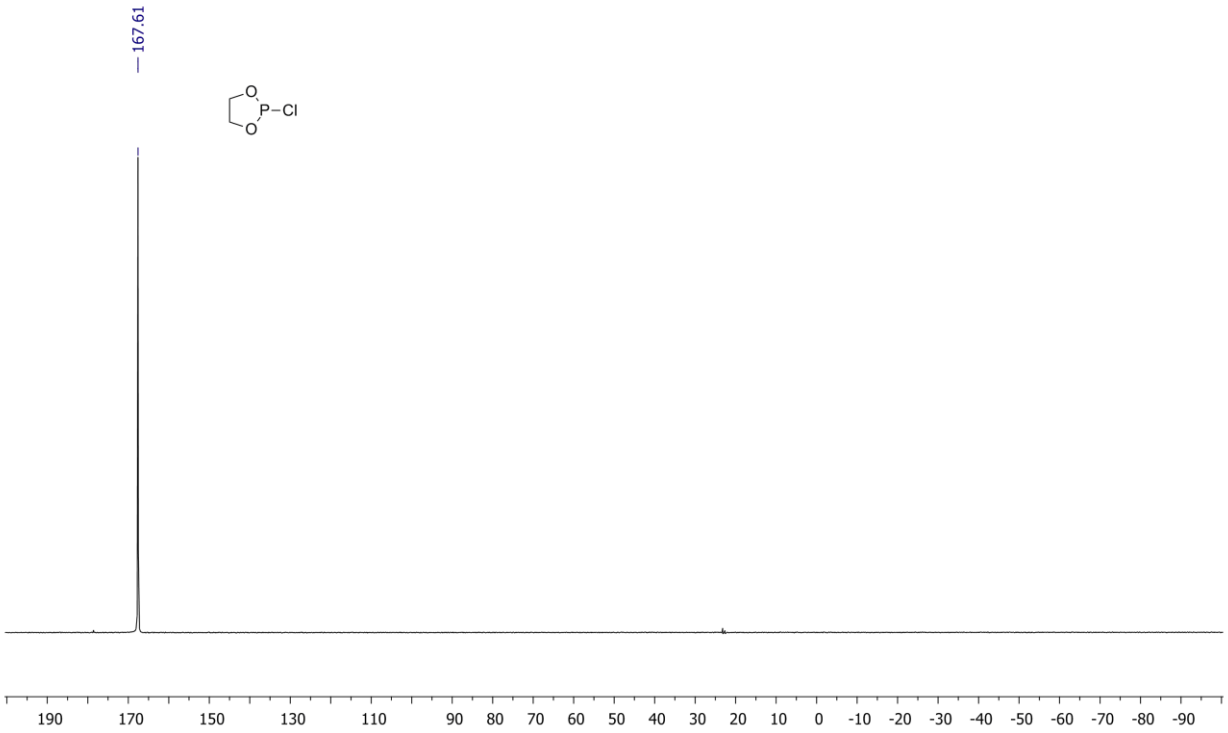


Figure S2. ^{31}P{H} NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of 2-chloro-1,3,2-dioxaphospholane

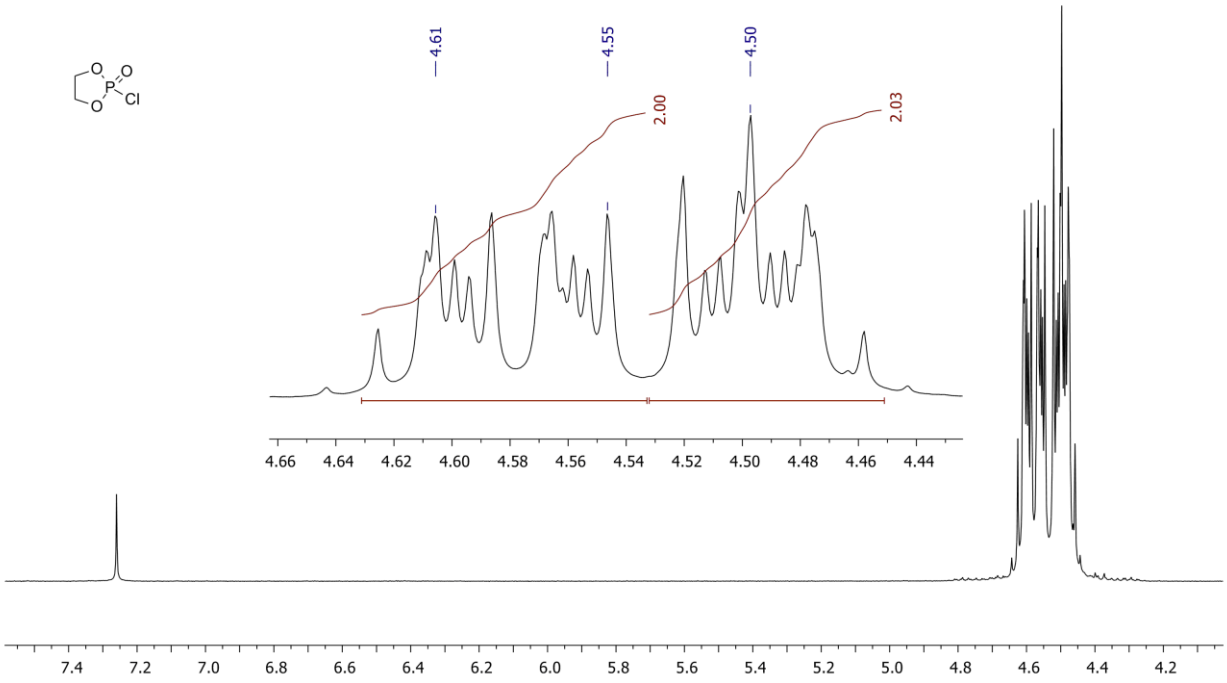


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of 2-chloro-1,3,2-dioxaphospholane 2-oxide

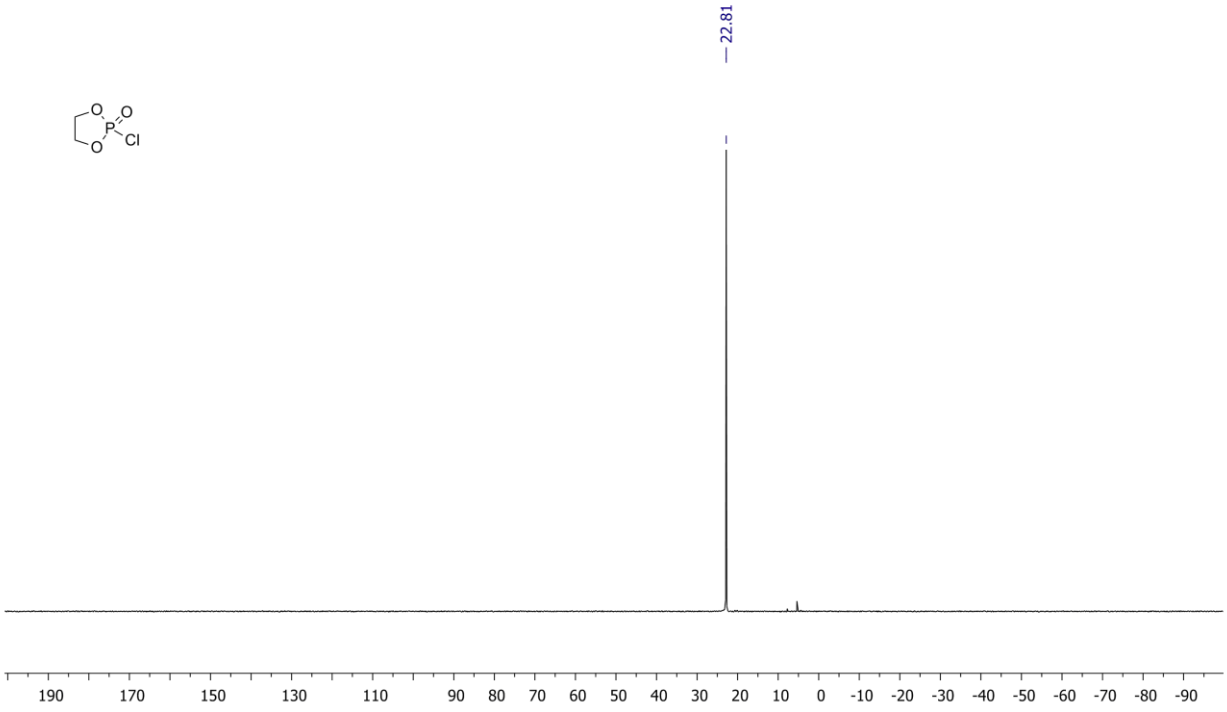
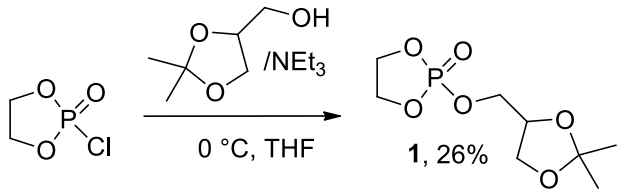


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of 2-chloro-1,3,2-dioxaphospholane 2-oxide



2-[(2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy]-1,3,2-dioxaphospholane 2-oxide (**1**)

A flame-dried 250 ml three-neck flask, equipped with a dropping funnel, was charged with (2,2-dimethyl-1,3-dioxolan-4-yl)methanol (13.22 g, 0.1 mol), dry triethylamine (10.12 g, 0.1 mol) and dry THF (120 ml). A solution of 2-chloro-1,3,2-dioxaphospholane 2-oxide (14.25 g, 0.1 mol) in dry THF (30 ml) was added dropwise under stirring at –10 °C within 30–40 min. Then, the mixture was placed into refrigerator and stored 16 h at 2 °C. Triethylammonium chloride was filtered off, the precipitate of thiethylammonium hydrochloride was washed with THF (2×30 ml). The combined filtrate was evaporated under reduced pressure to obtain pale yellow oil with a touch of crystals. Then, a 1:10 THF/Et_2O (200 ml) was added, the mixture was heated to reflux, the solution was separated by decantation, and crystallized at 2 °C (16 h). The crystalline product was filtered off, and recrystallized from 1:10 THF/Et_2O (200 ml) in the same manner. The product was filtered off and dried *in vacuo*. The yield was 6.23 g (26%).

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.47–4.28 (m, 5H), 4.19 – 4.12 (m, 2H), 4.06 (dd, ^3J = 8.7 and 6.5 Hz, 1H), 3.80 (dd, ^3J = 8.6 and 5.6 Hz, 1H), 1.41 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 20 °C): δ 110.07 (s), 74.15 (d, J = 6.8 Hz), 68.60 (d, J = 5.9 Hz), 66.15 (d, J = 2.5 Hz), 65.91 (s), 26.70 (s), 25.29 (s). ^{31}P NMR (162 MHz, $CDCl_3$, 20 °C): δ 17.86 (s).

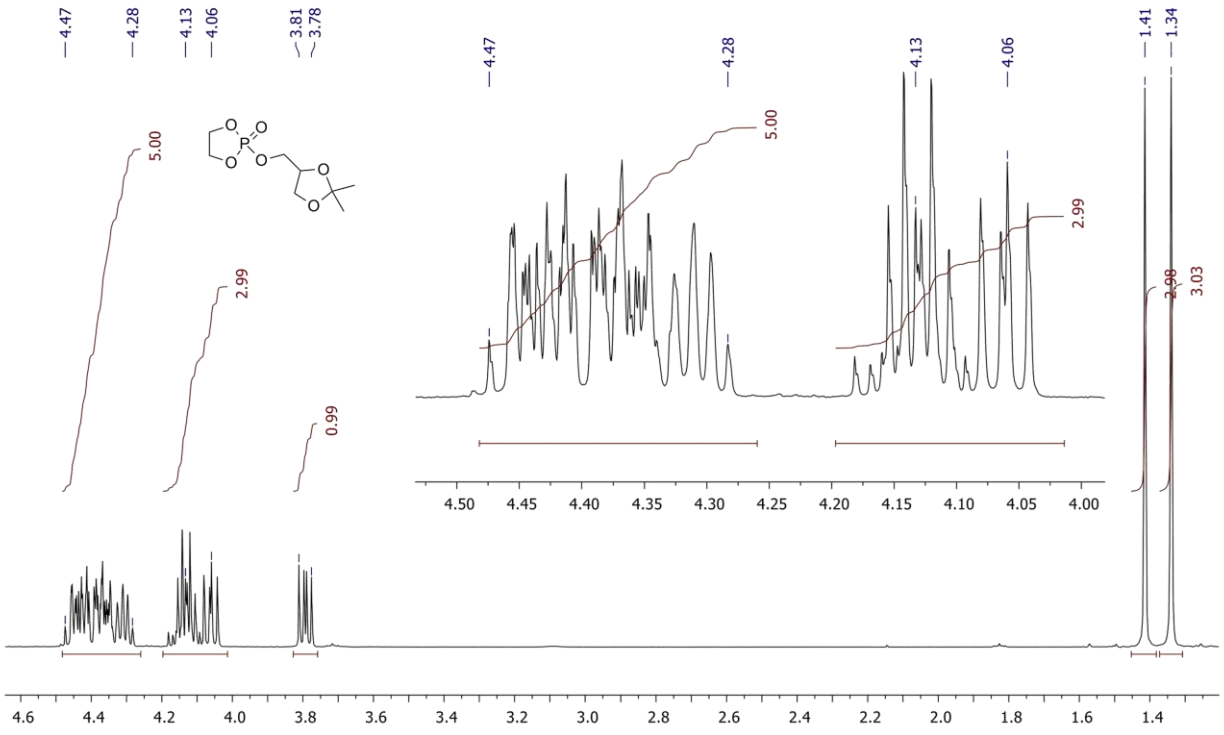


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of 2-[(2,2-dimethyl-1,3-dioxolan-4-yl)methoxy]-1,3,2-dioxaphospholane 2-oxide **1**

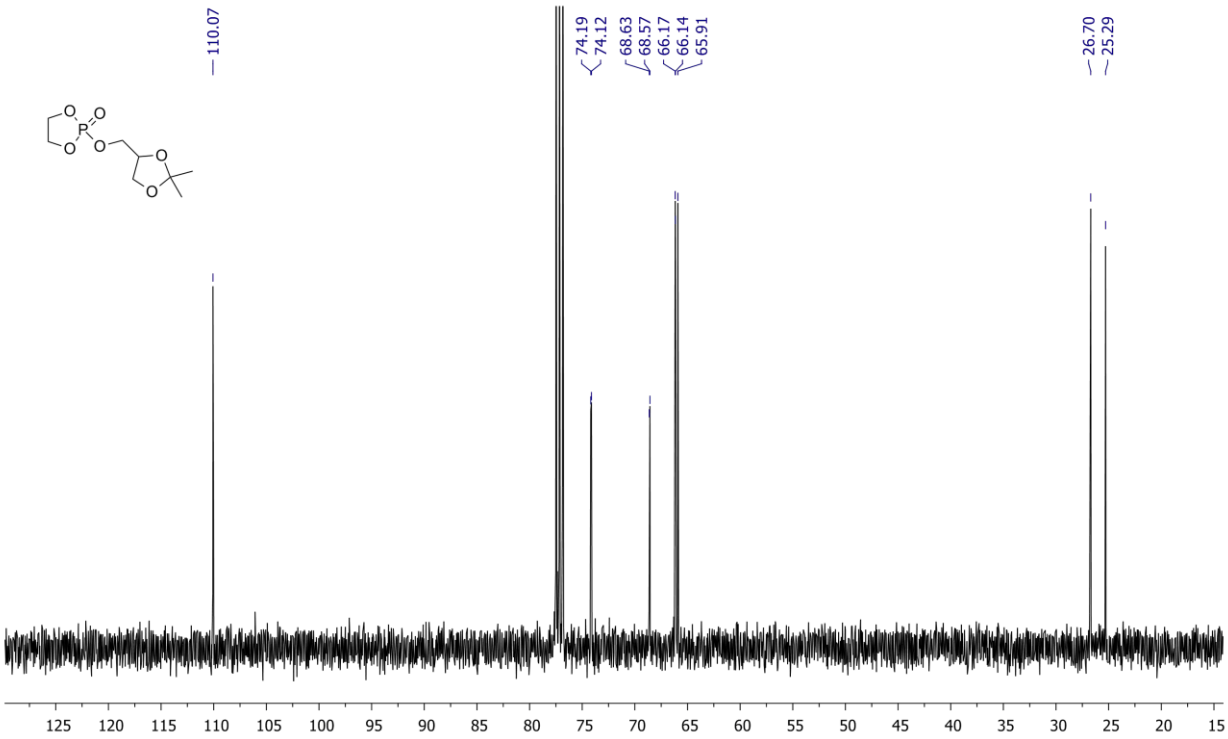


Figure S6. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of 2-((2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)-1,3,2-dioxaphospholane 2-oxide **1**

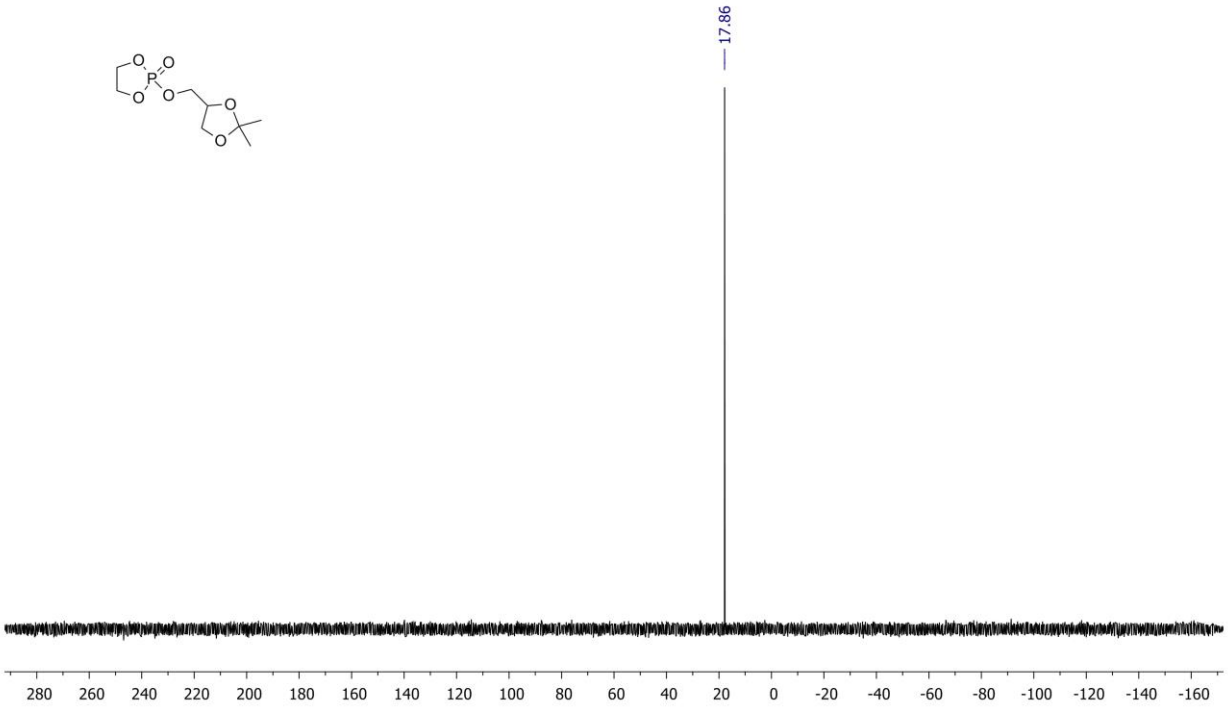
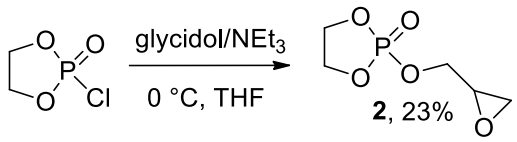


Figure S7. ^{31}P NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of 2-((2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)-1,3,2-dioxaphospholane 2-oxide **1**



2-(Oxiran-2-ylmethoxy)-1,3,2-dioxaphospholane 2-oxide (**2**)

A flame-dried 1000 ml three-neck flask, equipped with a dropping funnel, was charged with dry glycidol (18.5 g, 0.25 mol), dry triethylamine (35 ml, 0.25 mol) and dry THF (500 ml). A solution of 2-chloro-1,3,2-dioxaphospholane 2-oxide (35.5 g, 0.25 mol) in dry THF (70 ml) was added dropwise under stirring at 0 °C. The mixture was allowed to warm to room temperature and stirred overnight. Triethylammonium chloride was filtered off, and the filtrate was concentrated *in vacuo*. The residue was extracted 10 times with 50 ml portions of toluene, combined extract was concentrated *in vacuo*. The residue was divided into two portions, that were distilled separately under reduced pressure. The total yield was 9.5 g (23%). B. p. 150-155 °C (0.5 Torr), colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.44-4.31 (m, 5H, OC*H*$_2$C*H*$_2$O and O-CH*H*CH(O)CH$_2$); 3.99-3.91 (m, 1H, O-CH*H*CH(O)CH$_2$); 3.19 (m, 1H, O-CH$_2$C*H*(O)CH$_2$); 2.80 (m, 1H, O-CH$_2$CH(O)C*H*H); 2.62 (m, 1H, O-CH$_2$CH(O)C*H*H). ^{13}C{H} NMR (101 MHz, $CDCl_3$, 20 °C): δ 68.97 (d, $^{2}J_{CP}$ = 5.9 Hz, 1C, O-*C*H$_2$CH(O)CH$_2$); 66.18 (d, $^{2}J_{CP}$ = 2.9 Hz, 2C, O*C*H$_2$*C*H$_2$O); 49.90 (d, $^{2}J_{CP}$ = 6.7 Hz, 1C, O-CH$_2$*C*H(O)CH$_2$); 44.33 (s, 1C, O-CH$_2$CH(O)*C*H$_2$). ^{31}P{H} NMR (162 MHz, $CDCl_3$, 20 °C): δ 17.84 (s).

For $C_5H_9O_5P$ Calc.: C, 33.35; H, 5.04; O, 44.42. Found: C, 33.41; H, 5.11; O, 44.44.

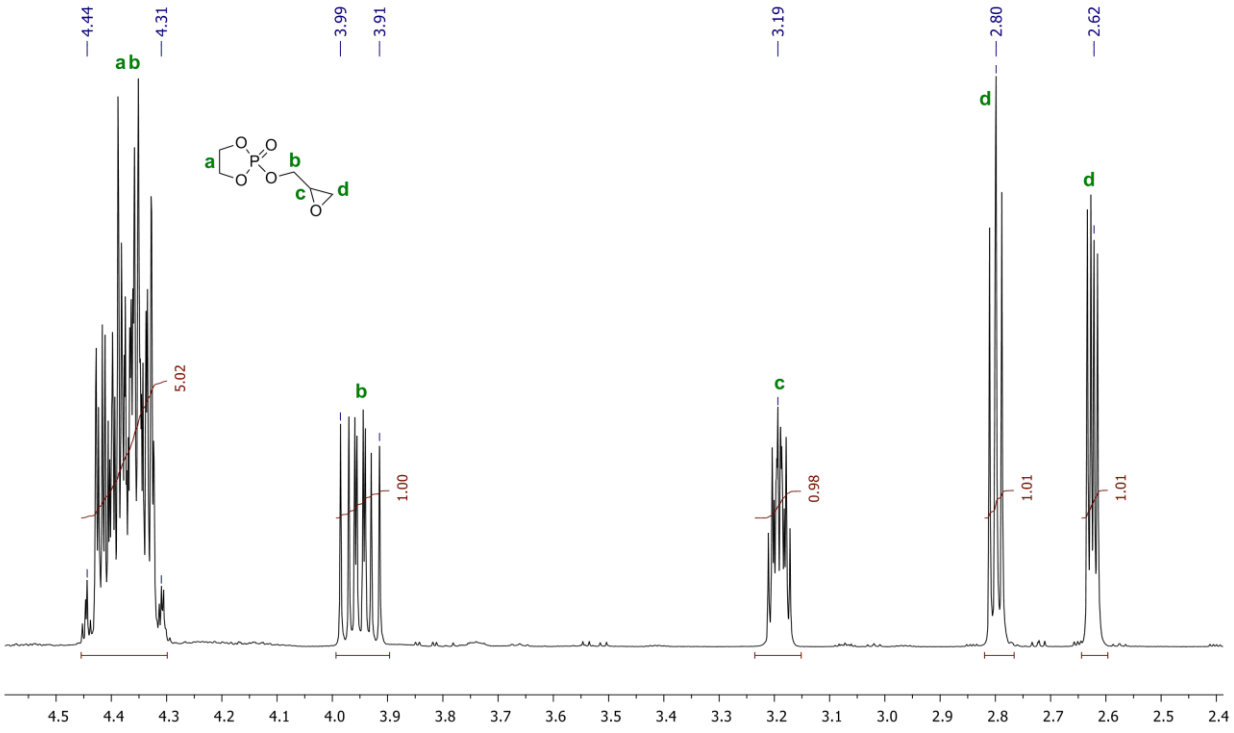


Figure S8. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of 2-(oxiran-2-ylmethoxy)-1,3,2-dioxaphospholane 2-oxide **2**

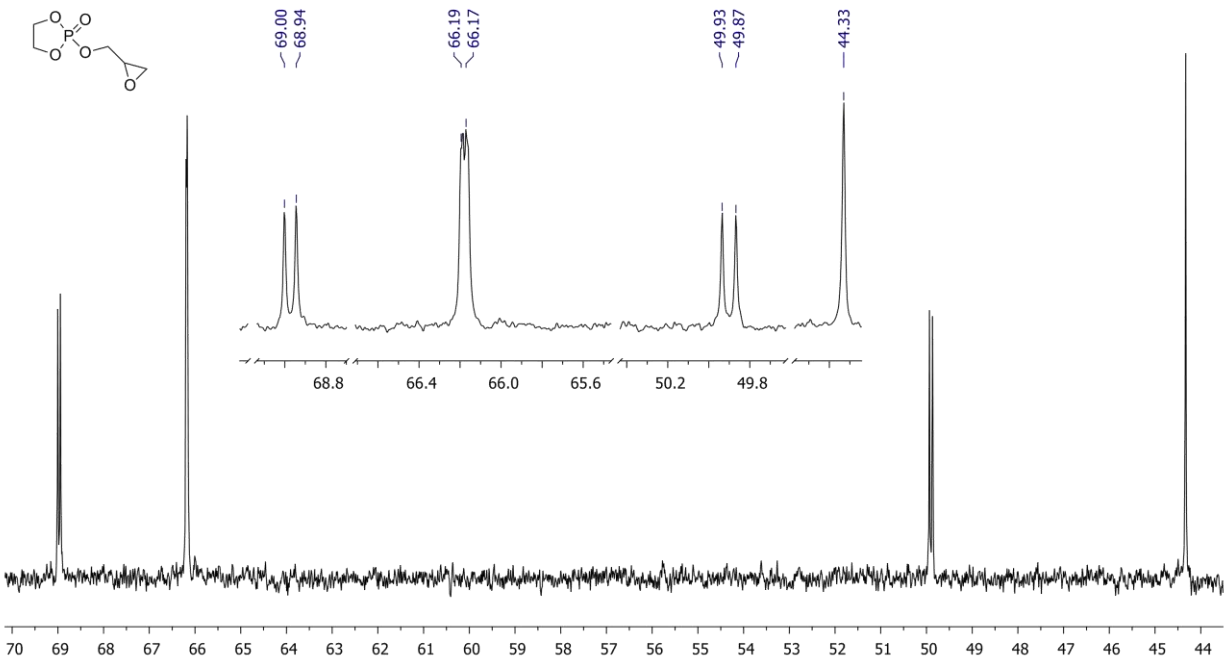


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of 2-(oxiran-2-ylmethoxy)-1,3,2-dioxaphospholane 2-oxide **2**

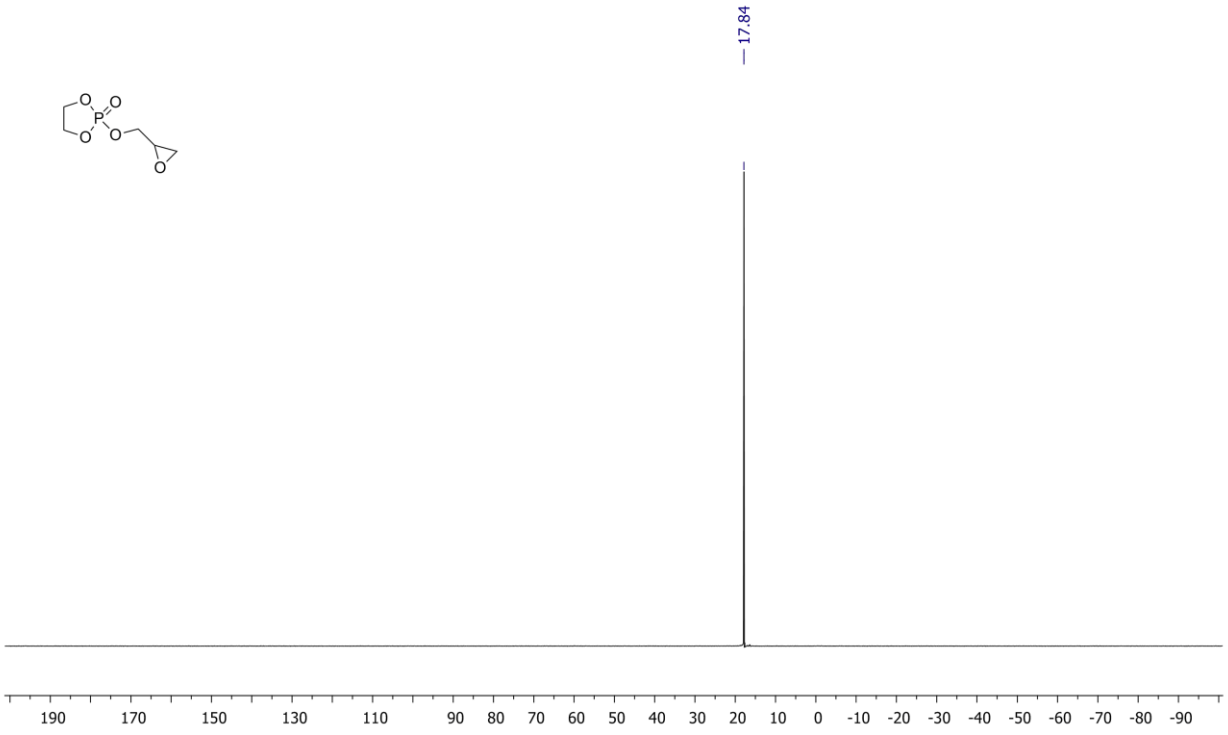


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of 2-(oxiran-2-ylmethoxy)-1,3,2-dioxaphospholane 2-oxide **2**

S3. Polymerization of monomers 1 and 2

Polymerization of DdmOEP at 20 °C (Table 1, run 1).

Monomer **1** (2.130 g, 8.94 mmol) was introduced into a vial equipped with magnetic stirrer and septum, dry CH_2Cl_2 (5.75 ml) was added. Polymerization was initiated by rapid addition of catalyst solution (75 mg of BHT-Mg catalyst, 0.177 mmol) in THF (1 ml). The polymerization was terminated after 1 hour by the addition of an excess of acetic acid in CH_2Cl_2. The polymer was isolated by precipitation using a 5-fold volume excess of dry diethyl ether and subsequent centrifugation (5 min, 4000 rpm). The yield was 2.055 g (97%). For ^{1}H and ^{31}P NMR spectra, see Figures S11 and S12.

^{1}H NMR (400 MHz, $CDCl_3$, 20 ℃): δ 5.10 (d, $^3J_{HP}$ = 8.0 Hz, PhCH_2); 4.32 (m, 1H); 4.27 (br, 4H, –OCH_2CH_2O–); 4.07 (m, 3H); 3.81 (m, 1H); 1.41 (s, 3H); 1.34 (s, 3H). ^{31}P{H} NMR (162 MHz, $CDCl_3$, 20 ℃): δ –1.13.

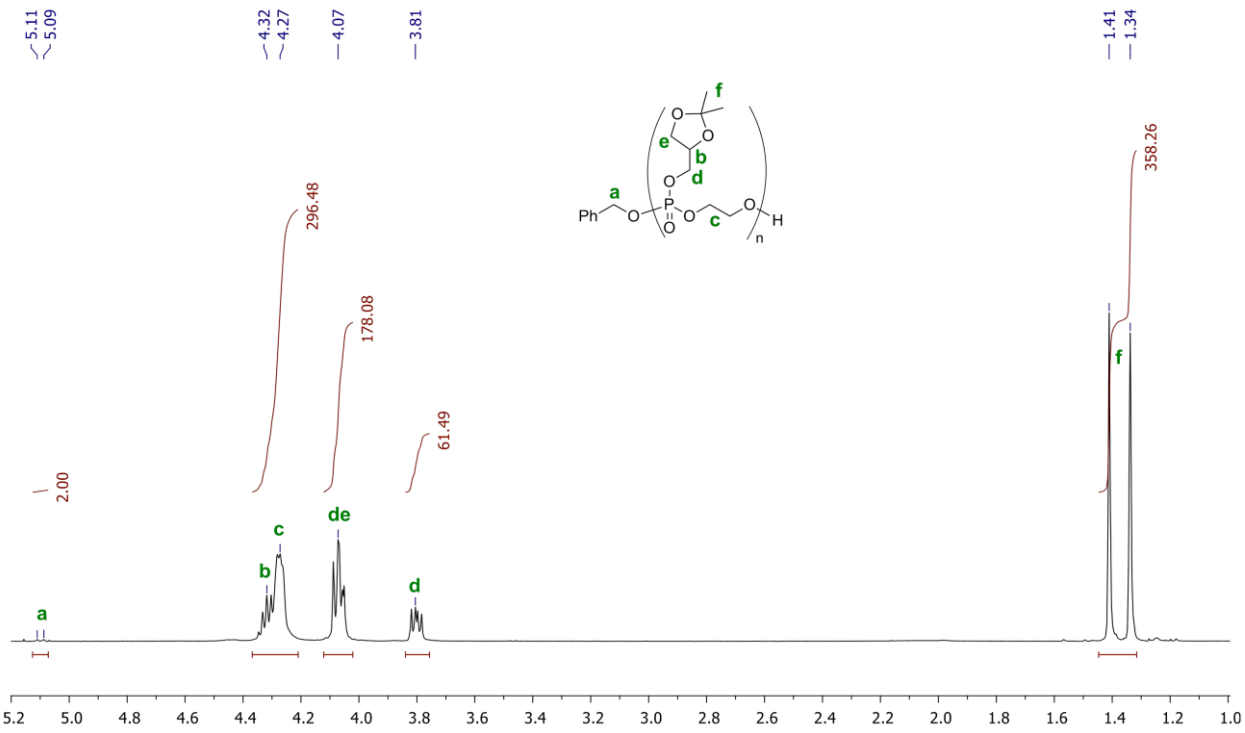


Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of poly(DdmOEP) prepared at 20 °C (Table 1, run 1)

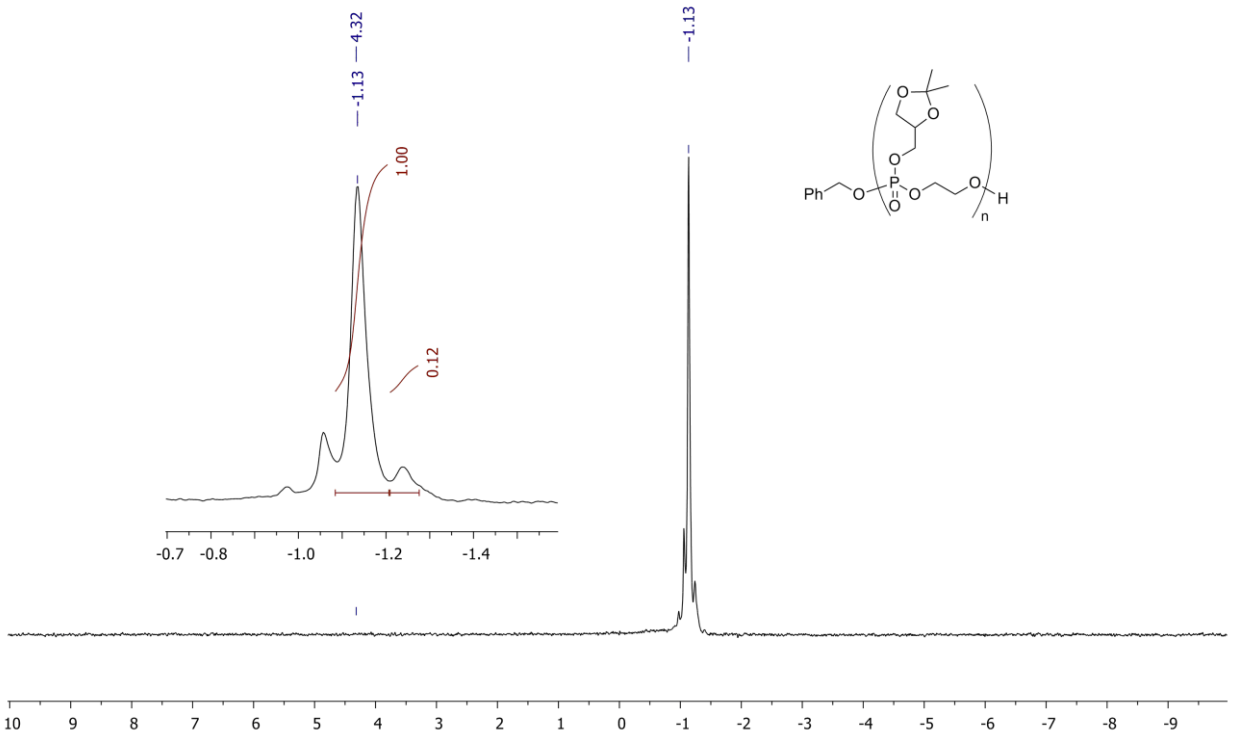


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of poly(DdmOEP) prepared at 20 °C (Table 1, run 1)

Polymerization of DdmOEP at 20 °C in the presence of TMP (Table 1, run 2). Monomer **1** (0.696 g, 2.92 mmol) and trimethyl phosphate (0.414 g, 2.96 mmol) were dissolved in CH_2Cl_2 (1 ml). Polymerization was initiated by 25 mg of BHT-Mg catalyst (0.059 mmol) in CH_2Cl_2 (1 ml). Reaction time 1 h, the mixture was treated as described above. The yield was 0.538 g (77%).

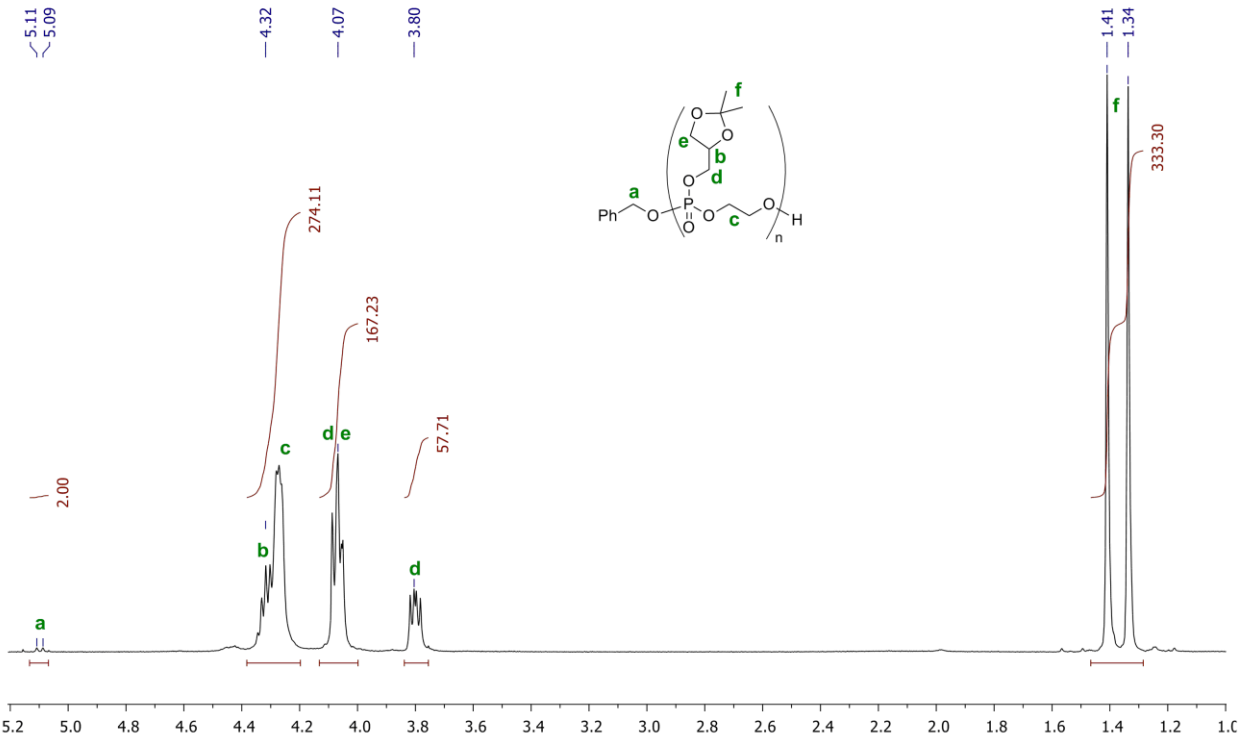


Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of poly(DdmOEP) prepared at 20 °C in the presence of TMP (Table 1, run 2)

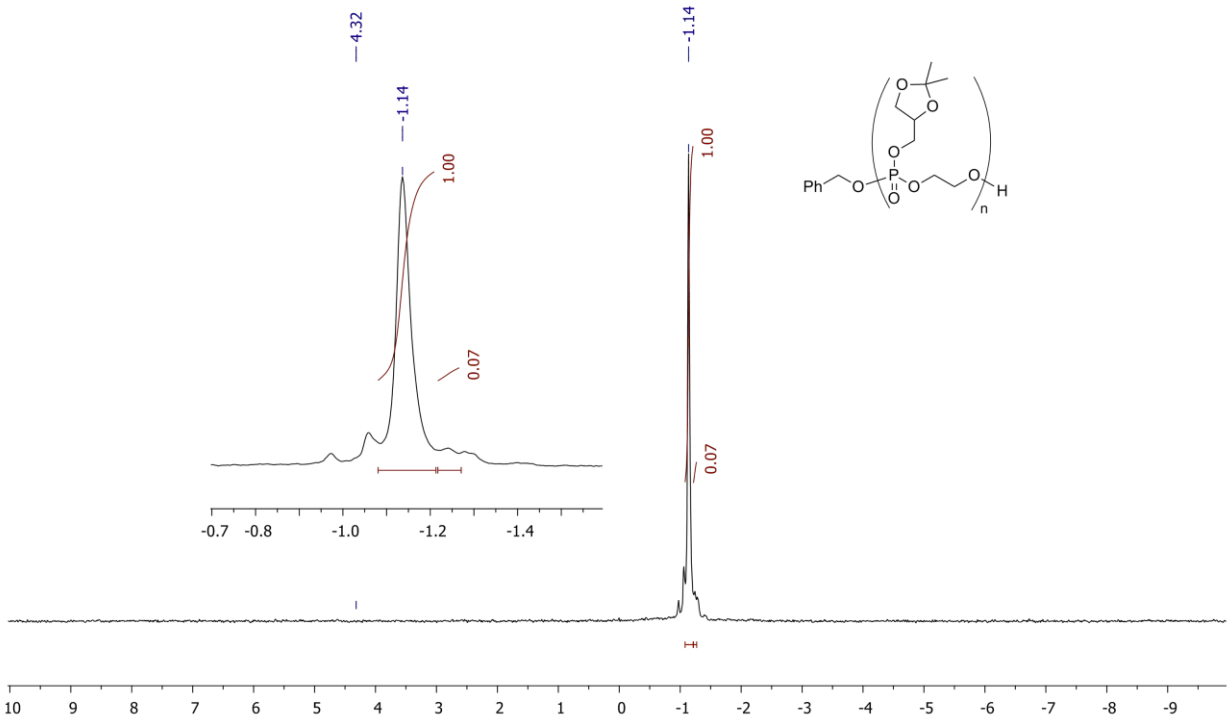


Figure S14. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of poly(DdmOEP) prepared at 20 °C in the presence of TMP (Table 1, run 2)

Polymerization of DdmOEP at 0 °C in the presence of TMP (Table 1, run 3). Monomer **1** (0.705 g, 2.96 mmol) and trimethylphosphate (0.427g, 3.05 mmol) were dissolved in CH_2Cl_2 (1 ml). Polymerization was initiated by 25 mg of BHT-Mg catalyst (0.059 mmol) in CH_2Cl_2 (1 ml) and conducted at 0 °C. Reaction time was 1 h. The yield was 0.577 g (79%).

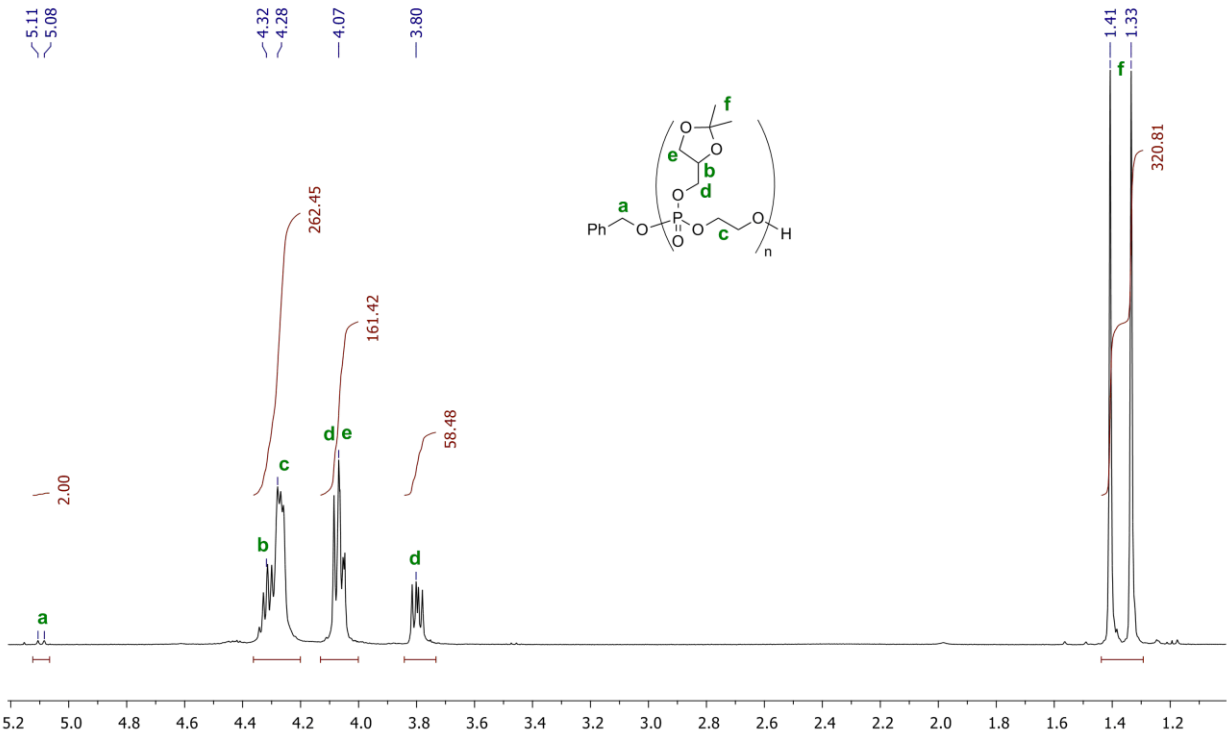


Figure S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of poly(DdmOEP) prepared at 0 °C in the presence of TMP (Table 1, run 3)

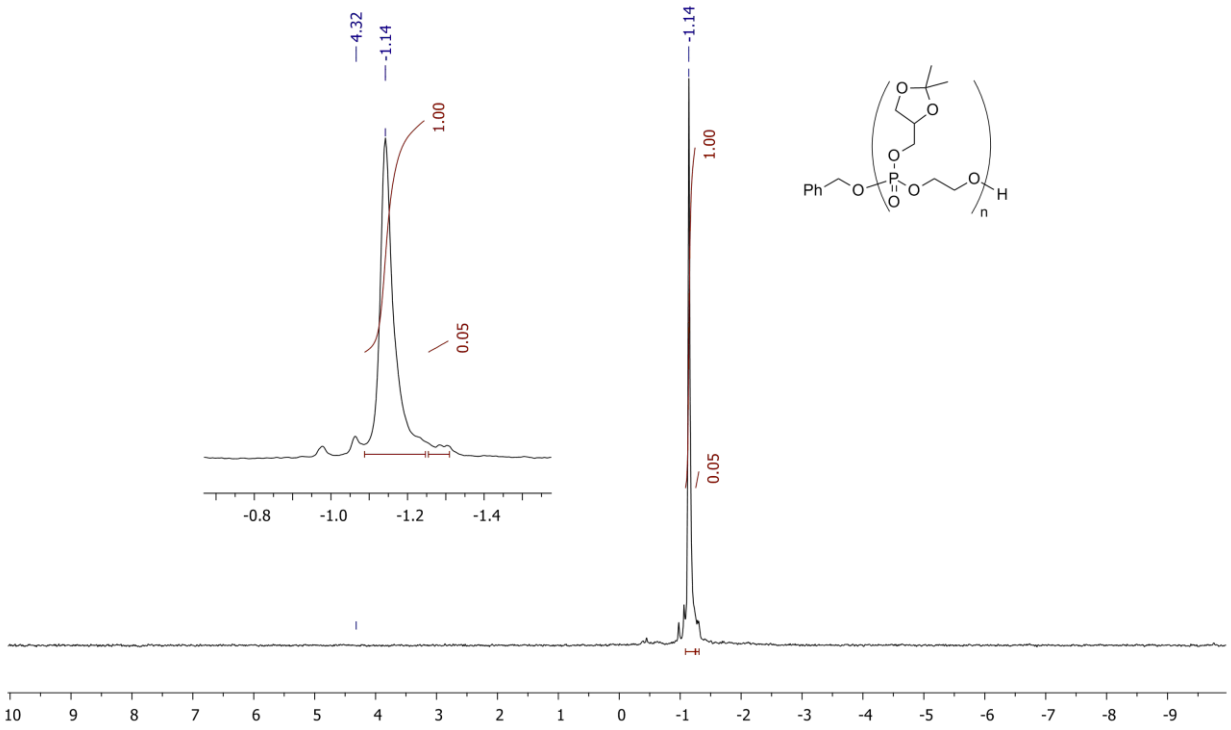


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of poly(DdmOEP) prepared at 0 °C in the presence of TMP (Table 1, run 3)

Polymerization of GlyOEP at 20 °C (Table 1, run 4). Monomer **2** (1.320 g, 7.33 mmol) was introduced into a vial equipped with magnetic stirrer and septum, dry CH_2Cl_2 was added to give a total reaction volume of 3.3 ml. The polymerization was started by rapid addition of catalyst solution ($7.31 \cdot 10^{-5}$ mol Mg) to the stirred solution of GlyOEP by a syringe to providee a total monomer concentration of 1 *M*. The polymerization was terminated after 1 hour by the addition of an excess of acetic acid in CH_2Cl_2. The polymer was purified by precipitation using a 5-fold volume excess of dry diethyl ether and subsequent centrifugation (5 min, 4000 rpm), the supernatant was decanted and re-dissolved in dry CH_2Cl_2, then precipitated and centrifuged again. The yield was 1.08 g (82%). The amount of branches in polymer chain was estimated using ^{31}P NMR spectroscopy by integration of the resonance signals of branched (δ –1.45 ppm) and unbranched (δ –1.3 ppm) phosphorus atoms, see Figure S18.

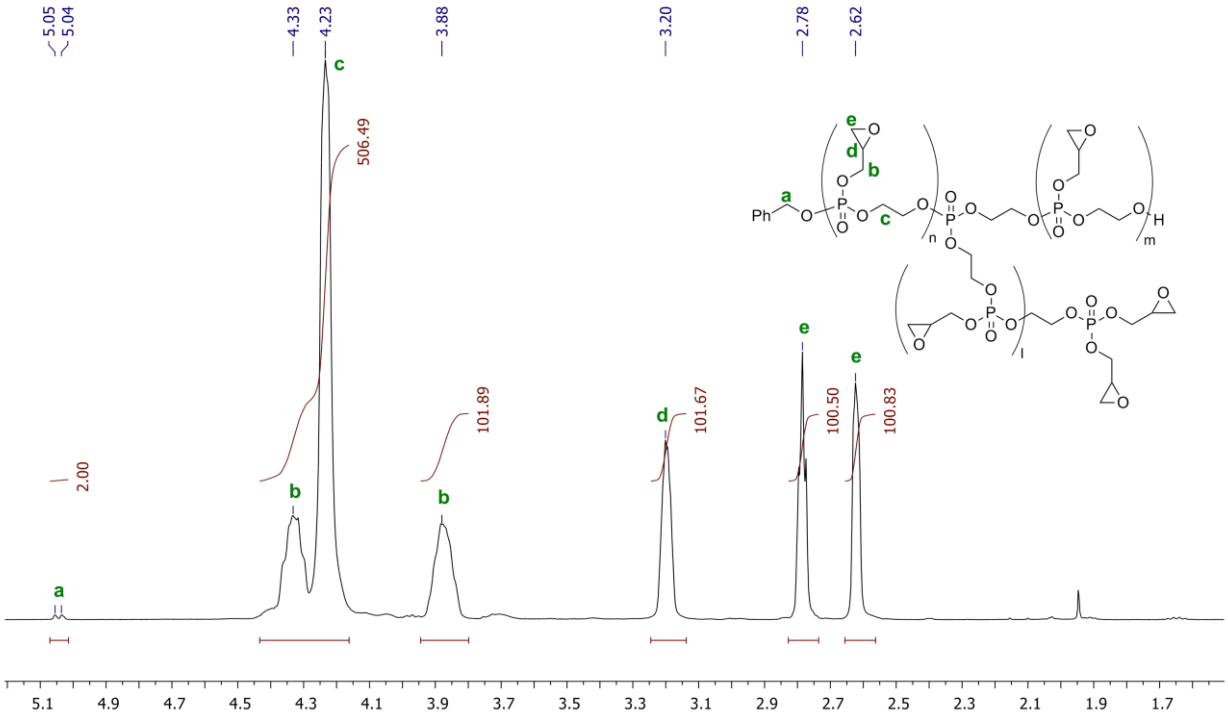


Figure S17. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of poly(GlyOEP) prepared at 20 °C (Table 1, run 4)

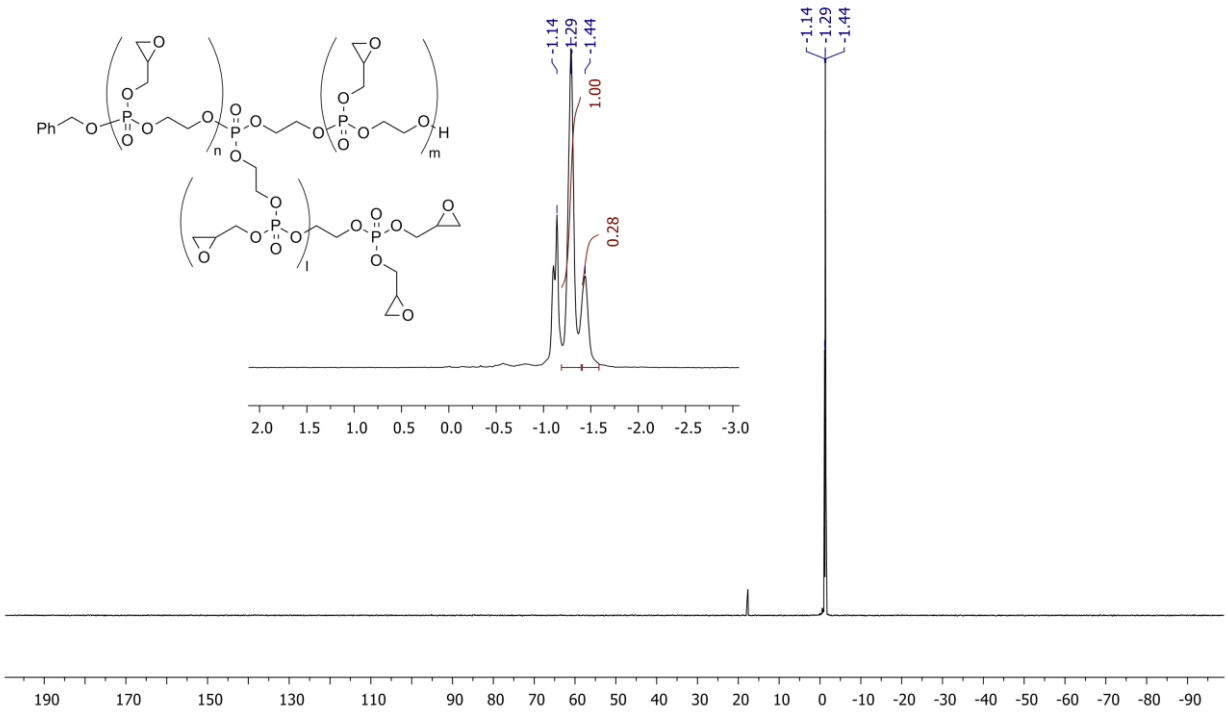


Figure S18. ^{31}P{^{1}H} NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of poly(GlyOEP) prepared at 20 °C (Table 1, run 4)

Polymerization of GlyOEP at -50 °C (Table 1, run 5). The polymerization of **2** (1.320 g, 7.33 mmol) was performed in the same manner at –50 °C. The reaction was terminated after 10 min. The yield was 1.16 g (86%). The product was highly linear homopolymer containing only traces of branches, see Figure S20.

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 5.05 (d, $^{3}J_{HP}$ = 8.1 Hz, PhCH_2); 4.34 (m, 1H); 4.24 (dd, $^{3}J_{HP}$ = 4.3 Hz, 4H, –OCH_2CH_2O–); 3.89 (m, 1H) {–CH_2CHOCH_2}; 3.20 (m, 1H, –

CH_2CHOCH_2); 2.79 (m, 1H); 2.63 (m, 1H) {$–CH_2CHOCH_2$}. $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$, 20 °C): δ –1.29.

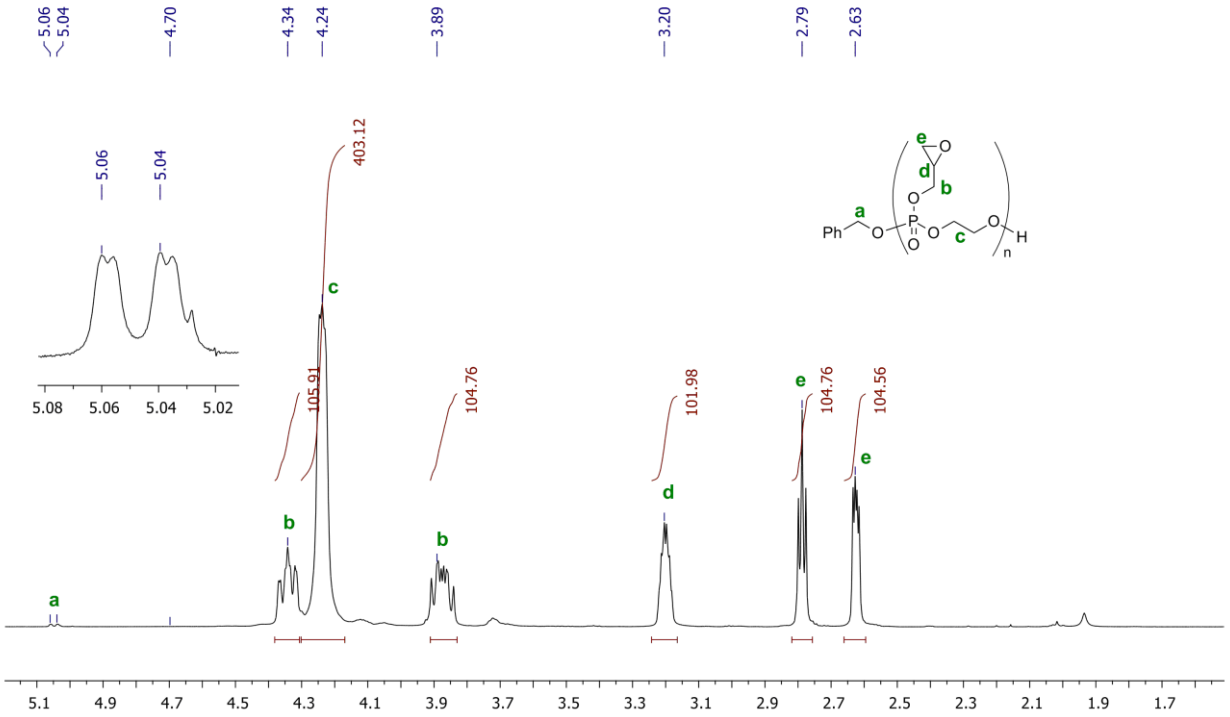


Figure S19. ^1H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of poly(GlyOEP) prepared at –50 °C (Table 1, run 5)

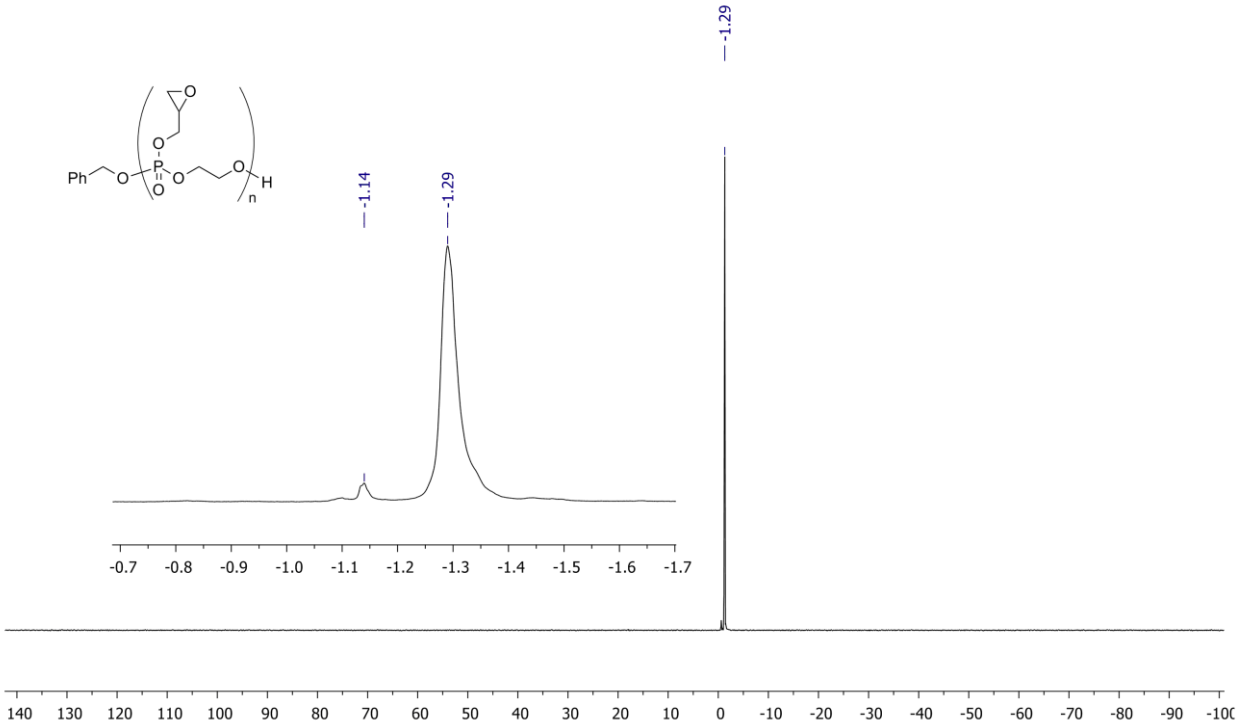


Figure S20. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of poly(GlyOEP) prepared at –50 °C (Table 1, run 5)

S4. Acid hydrolysis of poly(DdmOEP) and poly(GlyOEP)

Synthesis and purification of 2,3-dihydroxypropyl-sunstituted polymers

A sample of poly(DdmOEP) (200 mg) was dispersed in H_2O (7.7 ml) with stirring within 10 min. Conc. HCl (0.14 ml) was added, and the mixture was stirred for 1 h. The resulting solution was transferred into dialysis membrane tube (Benzylated cellulose, MWCO 2 kDa) that was placed into water (1 liter). After 2 h, the water was replaced; after 16 h the dialysate was concentrated under reduced pressure and used for hydrolytic experiments. The typical yield ~180 mg.

Note that dialysis in acid solutions did not affect the MW of 2,3-dihydroxypropyl-substituted polyphosphates (SEC). M_n (NMR) was slightly increased due to partial hydrolysis of BnO–P end groups (Fig. S21).

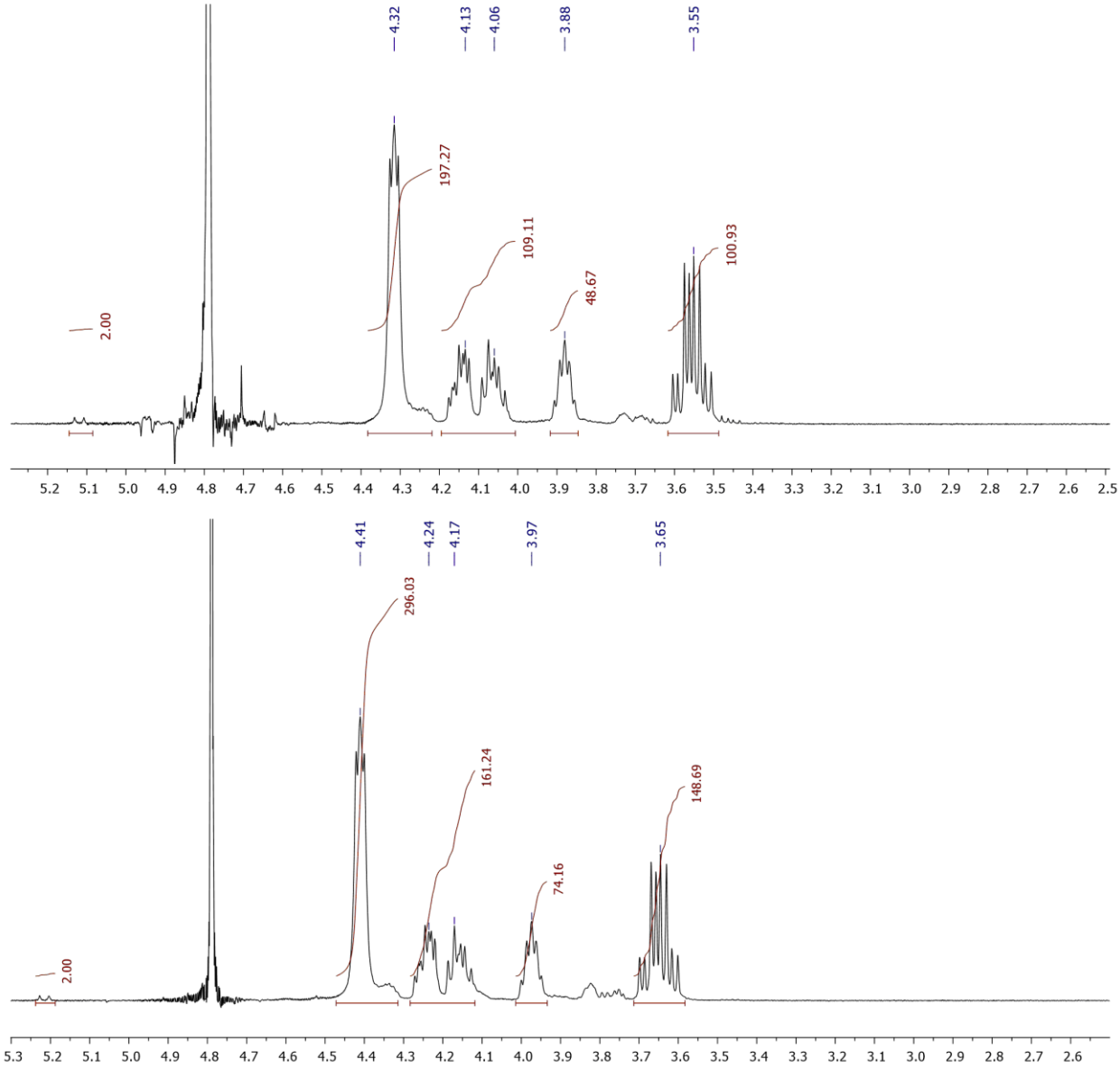


Figure S21. ^{1}H NMR spectra (400 MHz, D_2O, 20 °C) of 2,3-dihydroxypropyl-substituted PEPs before (top) and after (bottom) dialysis

Acid hydrolysis of poly(GlyOEP)

A sample of poly(GlyOEP) (40 mg, 0.22 mmol of monomer units) was dissolved in D_2O (0.30 ml), and H_2SO_4 (4.2 µl, 0.074 mmol) in D_2O (0.30 ml) was added. ^1H NMR spectrum of the reaction mixture after 2.5 h is presented in Figure S22 (bottom). For comparison, ^1H NMR spectrum of the starting poly(GlyOEP) is presented in Figure S22 (top).

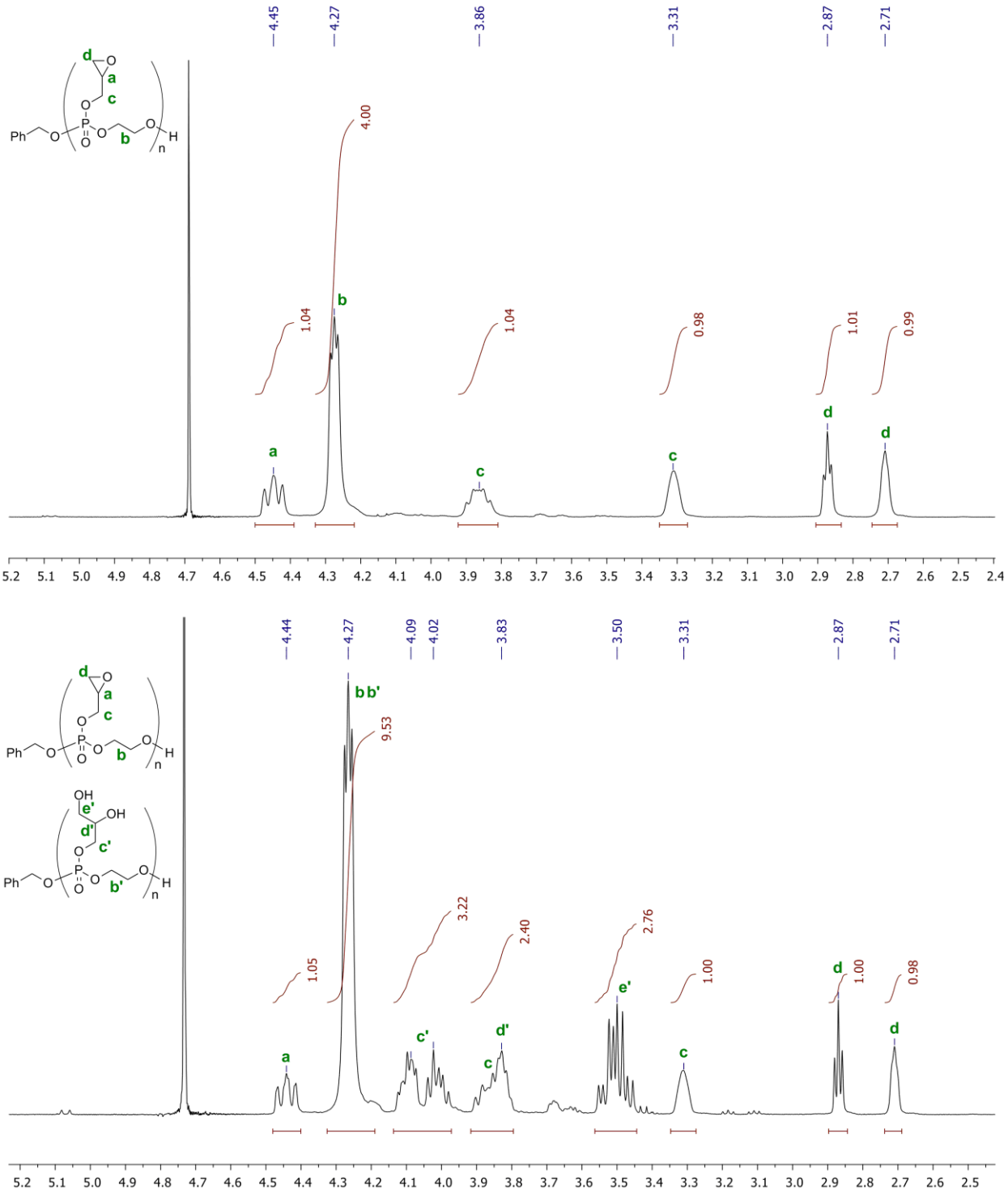


Figure S22. ^1H NMR spectra (400 MHz, D_2O, 20 °C) of poly(GlyOEP) (top) and reaction mixture after acid hydrolysis (2.5 h, bottom)

S5. Basic hydrolysis of 2,3-dihydroxypropyl-functionalized PEP

2,3-Dihydroxypropoxy-functionalized polymer, obtained by acid hydrolysis of poly(DdmOEP), was dissolved in D_2O (0.75 ml), then $NaHCO_3$ (51 mg) or $Na_2CO_3x10H_2O$ (90 mg) were added as a bases. The hydrolysis may be performed in two stages from poly(DdmOEP) (20 mg) by addition of HCl (14 µl) followed by addition of $NaHCO_3$ or Na_2CO_3. When Na_2CO_2 was used, fast destruction of polyphosphate was detected.

NMR spectra of hydrolysis in the presence of Na_2CO_3 are provided in Figure S23.

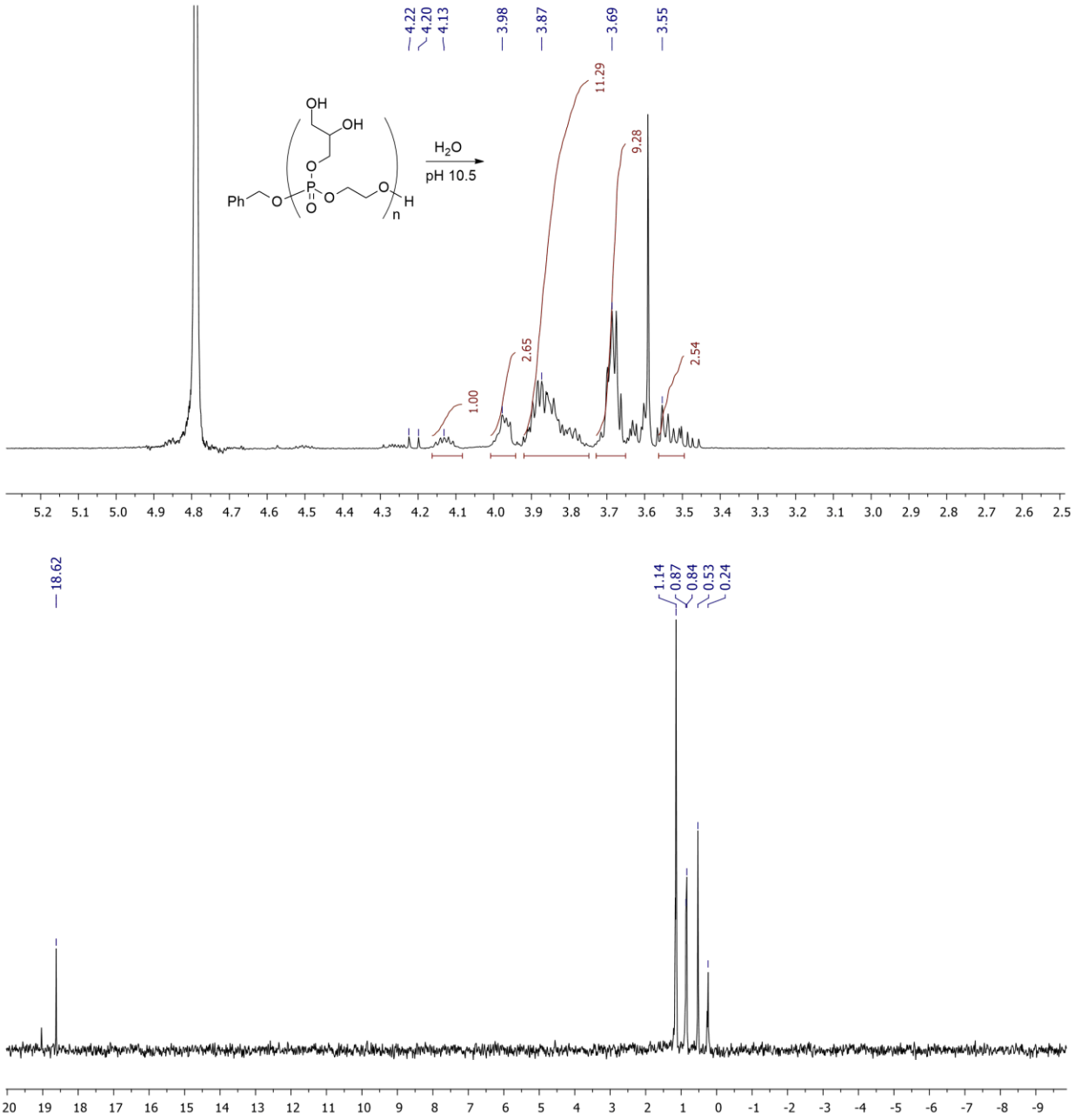


Figure S23. ^{1}H (top) and ^{31}P (bottom) NMR spectra of the reaction mixture after 3 days of the hydrolysis of 2,3-dihydroxypropyl-sunstituted PEP

In the presence of $NaHCO_3$, we observed slow hydrolysis, the signal of five-membered cyclic intermediate was detected in the reaction mixture (Figure S24).

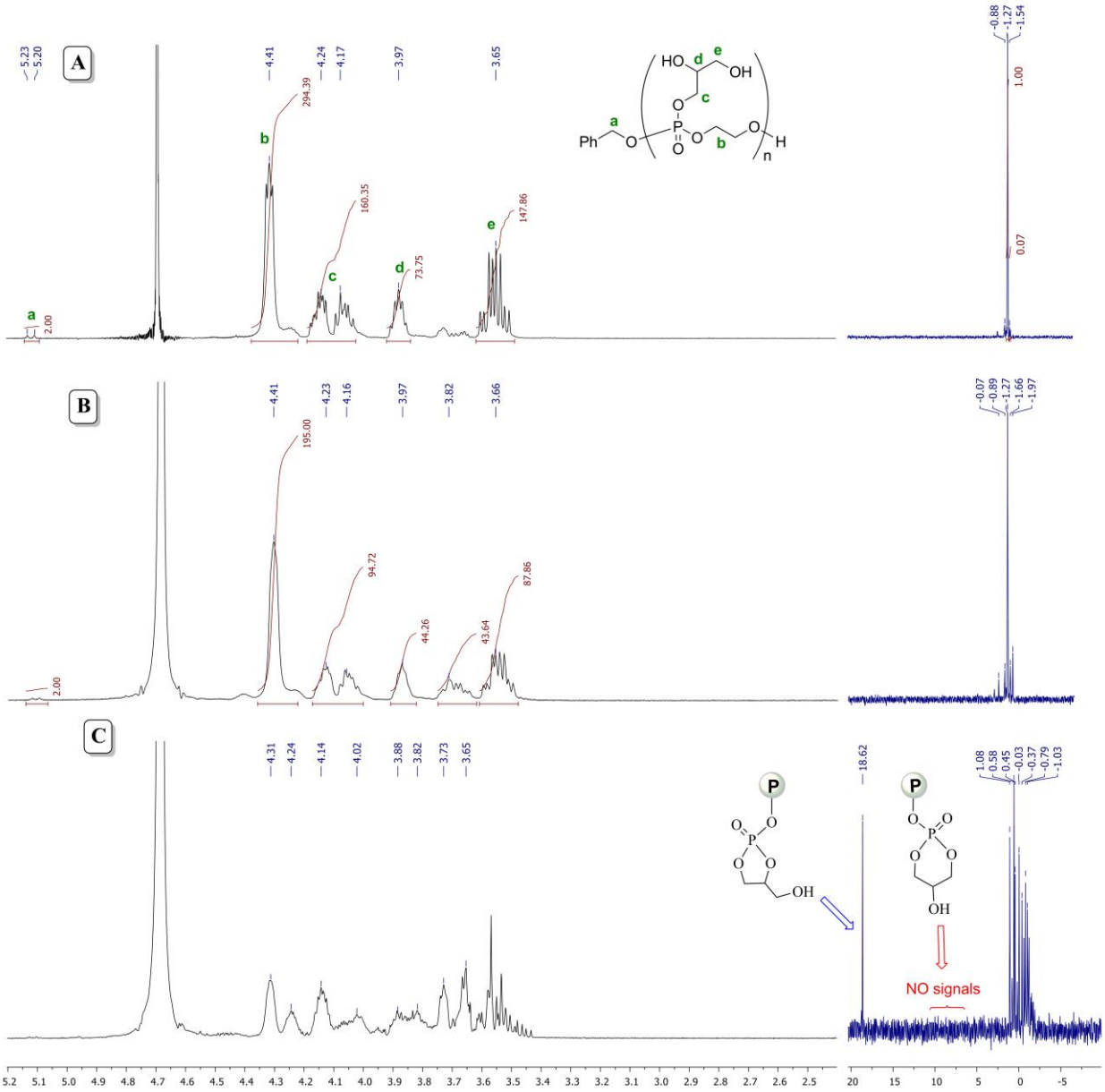
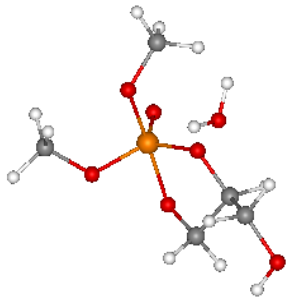


Figure S24 ^{1}H (left) and ^{31}P (right) NMR spectra (D_2O, 20 °C) of 2,3-dihydroxypropoxy-functionalized PEP (A) and products of hydrolysis in $NaHCO_3$ after 7 min and 6 h (B and C, respectively)

S6. DFT calculations

D1

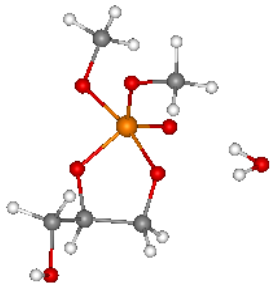


Zero-point vibrational energy	560527.9 (Joules/Mol)
	133.96939 (Kcal/Mol)
Zero-point correction=	0.213494 (Hartree/Particle)
Thermal correction to Energy=	0.230765
Thermal correction to Enthalpy=	0.231709
Thermal correction to Gibbs Free Energy=	0.166410
Sum of electronic and zero-point Energies=	-1066.529501
Sum of electronic and thermal Energies=	-1066.512230
Sum of electronic and thermal Enthalpies=	-1066.511286
Sum of electronic and thermal Free Energies=	-1066.576585

Cartesian

8	-1.83131850	1.11604440	0.11595929	1	1.86418152	1.46294451	-0.68884075
15	-0.81261843	0.00334442	0.26895928	1	-1.64911854	-2.96575546	0.72815925
8	-0.93901843	-1.14485550	1.46595931	1	-2.16571832	3.85824442	-0.64844072
6	-1.90351856	-2.18355560	1.45055926	6	2.94338155	-0.40815559	-0.62524074
1	-1.90671849	-2.60455561	2.46395922	1	-1.63671851	2.87294436	0.37795928
8	-1.52021849	-1.12925553	-0.83754075	8	-1.73161852	3.84744453	0.21435928
6	-1.91741848	-0.64855558	-2.09564066	1	-2.90441847	-1.80725551	1.21675932
1	-2.60401845	0.20264442	-2.00094080	1	-2.42931843	-1.46825552	-2.61964083
1	-1.05471849	-0.33775556	-2.70534062	8	4.19468117	0.11954442	-0.16994071
8	0.19808155	0.89124441	1.41645932	1	3.02568173	-0.47295555	-1.71294069
8	0.58248156	-0.15585557	-0.70034075	1	2.77738166	-1.42415559	-0.23854071
6	1.54878151	0.61104441	1.27545929	1	4.13638115	0.19514441	0.79325926
6	1.76068151	0.46714443	-0.23274073	1	1.83448148	-0.33145556	1.78925931
1	2.14028168	1.43464446	1.69905925				

D2

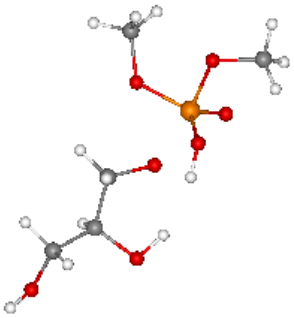


Zero-point vibrational energy	563425.7 (Joules/Mol)
	134.66197 (Kcal/Mol)
Zero-point correction=	0.214598 (Hartree/Particle)
Thermal correction to Energy=	0.231251
Thermal correction to Enthalpy=	0.232195
Thermal correction to Gibbs Free Energy=	0.170508
Sum of electronic and zero-point Energies=	-1066.531316
Sum of electronic and thermal Energies=	-1066.514662
Sum of electronic and thermal Enthalpies=	-1066.513718
Sum of electronic and thermal Free Energies=	-1066.575406

Cartesian

8	-1.57445550	0.37674448	1.33808148	1	1.17274451	1.45034444	1.71668148
15	-0.73175561	-0.40425551	0.34838149	1	-3.18025565	-1.85215557	-0.51561850
8	-1.37415552	-1.97505558	0.51678151	1	-0.65725559	2.84914446	0.31448150
6	-2.77515554	-2.08915567	0.48008150	1	-1.64215553	2.22664452	1.22628140
1	-3.02345562	-3.13285565	0.71508151	8	-1.39575553	3.11994433	0.88608152
8	-1.23145556	-0.43555552	-1.24361861	1	-3.25205564	-1.43115556	1.21818149
6	-1.44125557	0.75694448	-1.98411858	1	-2.11705565	0.49074447	-2.80651855
1	-1.90945554	1.53874445	-1.37671852	6	2.77964449	-0.87045550	-0.28581852
1	-0.50265557	1.14464438	-2.39361835	1	2.25234437	1.66274440	0.30668148
8	0.69664443	-1.17515552	0.81508148	8	4.08714437	-0.30635554	-0.10451852
8	0.35764441	1.00034440	-0.13651852	1	2.33154440	-0.54245555	-1.23311853
6	1.88424444	-0.41225553	0.85788149	1	2.82494450	-1.96805561	-0.27991849
6	1.44954443	1.04494441	0.72948152	1	4.58134413	-0.45715553	-0.92071849
1	2.39054441	-0.60985553	1.81158149				

E1



Zero-point vibrational energy	563672.8 (Joules/Mol)
	134.72104 (Kcal/Mol)
Zero-point correction=	0.214692 (Hartree/Particle)
Thermal correction to Energy=	0.231244
Thermal correction to Enthalpy=	0.232189
Thermal correction to Gibbs Free Energy=	0.169407
Sum of electronic and zero-point Energies=	-1066.512346
Sum of electronic and thermal Energies=	-1066.495793
Sum of electronic and thermal Enthalpies=	-1066.494849
Sum of electronic and thermal Free Energies=	-1066.557630

Cartesian

8	-1.87306666	-1.14941108	-1.59576666	1	2.88953328	0.15758888	-1.48386669
15	-1.50896657	-0.40051112	-0.34726667	8	2.62913346	-1.65641117	-0.52376664
8	-1.23286664	1.23708880	-0.31156665	6	3.72903347	0.23068888	0.47753334
6	-2.26586652	2.20698905	-0.31246665	1	1.71373343	-1.82611120	-0.83736664
1	-1.77426660	3.16578889	-0.52126664	1	-0.24786660	-1.58951116	0.90263331
8	-3.07226658	-0.11271112	0.33553332	8	-1.12726665	-1.21031117	1.06393337
6	-3.96026659	-1.20211112	0.36293334	1	-3.01056671	2.00948906	-1.08986664
1	-4.10256672	-1.62701118	-0.63906664	1	-4.92516661	-0.83731109	0.74283338
1	-3.60476661	-1.99961114	1.03273332	8	5.02723360	0.09818889	-0.11256665
8	0.32203338	-0.49401110	-0.71816665	1	3.65443349	-0.37021112	1.39473331
6	1.27443337	0.28648889	-0.05436666	1	3.53963327	1.28548884	0.73493338
6	2.65723348	-0.23731112	-0.48146665	1	5.67773342	0.21168889	0.59323335
1	1.17843342	0.21278889	1.04783332	1	1.19013333	1.35208881	-0.31376666
1	-2.77696657	2.25818896	0.65373337				

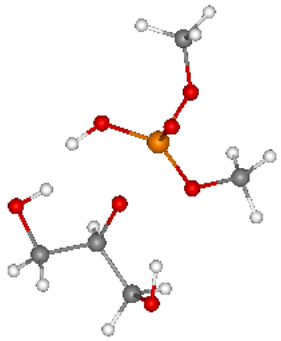
E1_alt

Zero-point vibrational energy	563471.9 (Joules/Mol)
	134.67303 (Kcal/Mol)
Zero-point correction=	0.214615 (Hartree/Particle)
Thermal correction to Energy=	0.231233
Thermal correction to Enthalpy=	0.232178
Thermal correction to Gibbs Free Energy=	0.169087
Sum of electronic and zero-point Energies=	-1066.515416
Sum of electronic and thermal Energies=	-1066.498798
Sum of electronic and thermal Enthalpies=	-1066.497853
Sum of electronic and thermal Free Energies=	-1066.560944

Cartesian

8	1.69911480	-1.35091853	1.35344076	1	-2.92218542	0.25568148	1.40454078
15	1.24531484	-0.52001852	0.18964076	8	-2.80378532	-1.64051855	0.58394074
8	1.20591486	1.14358151	0.27044076	6	-3.88358521	0.20788148	-0.50115925
6	2.37541461	1.91238141	0.46944076	1	-1.87228525	-1.85521853	0.80024076
1	2.03591466	2.91708136	0.75014073	1	1.65261483	-1.11721849	-1.78035927
8	2.92411470	-0.40051851	-0.65695930	8	0.80001473	-1.07491851	-1.30705917
6	4.08671474	-0.85251856	-0.02235924	1	2.98911476	1.51388144	1.28594077
1	4.65991449	-0.01981851	0.43044075	1	4.74701452	-1.33161855	-0.76495928
1	3.85661459	-1.57271850	0.77204072	8	-5.14288521	0.18598148	0.18154076
8	-0.44278526	-0.50821853	0.61704075	1	-3.89518523	-0.47141850	-1.36425924
6	-1.40518522	0.19278148	-0.12885925	1	-3.67138529	1.22788143	-0.86075926
6	-2.77078533	-0.23051850	0.42674077	1	-5.83648539	0.20698148	-0.49085924
1	-1.33708525	-0.06431851	-1.19685924	1	-1.28128517	1.28088140	-0.02455924
1	2.98711467	1.96548152	-0.43655923				

E2

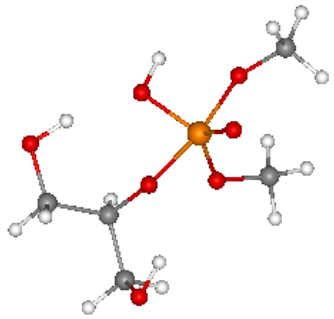


Zero-point vibrational energy	567762.0 (Joules/Mol)
	135.69837 (Kcal/Mol)
Zero-point correction=	0.216249 (Hartree/Particle)
Thermal correction to Energy=	0.232082
Thermal correction to Enthalpy=	0.233026
Thermal correction to Gibbs Free Energy=	0.172508
Sum of electronic and zero-point Energies=	-1066.524960
Sum of electronic and thermal Energies=	-1066.509128
Sum of electronic and thermal Enthalpies=	-1066.508184
Sum of electronic and thermal Free Energies=	-1066.568701

Cartesian

8	-1.28034437	-0.58804446	-1.86447036	1	1.28265560	-0.10844445	1.36392963
15	-1.05824435	-0.29274446	-0.40997037	1	1.68245566	2.07255554	0.54552966
8	-0.71154439	1.21935558	0.17972963	1	-2.26654458	1.92405546	1.38382959
6	-1.69564438	2.19385576	0.49042964	1	1.78865564	1.02455556	-1.64417040
1	-1.14344442	3.12405562	0.67142963	1	3.33515549	1.40515554	0.62372965
8	-2.67414451	-0.12364445	0.15192963	1	3.57785559	-0.90134448	-0.48317039
6	-3.59424448	-1.10584438	-0.25897038	8	2.24875546	-2.43194437	-0.03187037
1	-3.63094449	-1.18494451	-1.35267043	1	3.36285543	-1.29054451	1.24272954
1	-3.34434462	-2.09334445	0.15622963	1	1.60625565	-2.17294431	-0.72787035
8	0.82655561	-0.37274444	-0.65007037	1	0.02445562	-1.89574444	0.59252965
8	2.54605556	1.51745558	-1.25867045	8	-0.85654438	-1.50224447	0.71282965
6	1.75525558	-0.08374445	0.36972964	1	-2.39404440	2.34565568	-0.33777037
6	2.35635543	1.31135559	0.13112964	1	-4.58354425	-0.81234449	0.11782964
6	2.84025550	-1.17744446	0.28612965				

E2_alt

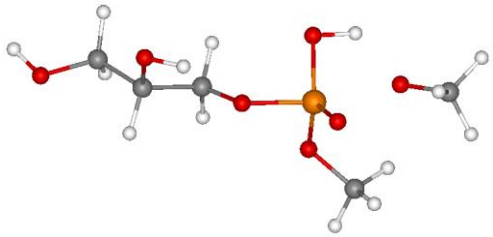


Zero-point vibrational energy	566686.0 (Joules/Mol)
	135.44121 (Kcal/Mol)
Zero-point correction=	0.215839 (Hartree/Particle)
Thermal correction to Energy=	0.231889
Thermal correction to Enthalpy=	0.232833
Thermal correction to Gibbs Free Energy=	0.171961
Sum of electronic and zero-point Energies=	-1066.528970
Sum of electronic and thermal Energies=	-1066.512921
Sum of electronic and thermal Enthalpies=	-1066.511977
Sum of electronic and thermal Free Energies=	-1066.572849

Cartesian

8	1.24745929	0.06751843	-1.88072228	1	-1.44414067	0.16531843	1.25277770
15	0.82025921	0.30231842	-0.46212223	1	-1.86324072	-2.05458164	0.57757783
8	0.67495930	-0.94918156	0.62697780	1	2.38295913	-1.16178155	1.80727780
6	1.78725934	-1.70608163	1.06887770	1	-1.96424067	-1.24488163	-1.69212222
1	1.37335932	-2.61548138	1.52097774	1	-3.50084090	-1.35078156	0.62407780
8	2.49775910	0.66481841	0.21737778	1	-3.29424095	1.13791847	-0.96942222
6	3.60325909	0.60801840	-0.64612222	8	-2.30794072	2.48841858	0.26997778
1	3.78315926	-0.40458155	-1.03842223	1	-3.71354079	1.09771848	0.75907779
1	3.49195910	1.26781845	-1.51772225	1	-1.35044074	2.39521837	0.09087777
8	-0.89074075	0.16321842	-0.76162219	1	1.31995928	2.09041834	0.58567774
8	-2.74944091	-1.63218153	-1.25282228	8	0.46115926	1.77771842	0.24427778
6	-1.88264072	0.07321843	0.25057778	1	2.43835926	-1.99628150	0.23677778
6	-2.52984095	-1.31328154	0.11367777	1	4.49145937	0.91951841	-0.07432222
6	-2.88204074	1.20991838	0.04857779				

TS1-alt

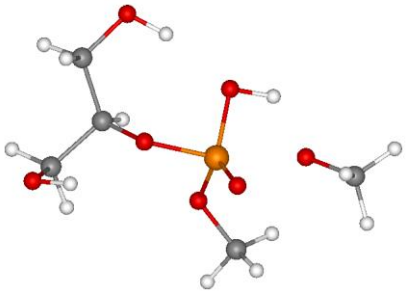


Zero-point vibrational energy	558927.1 (Joules/Mol)
	133.58678 (Kcal/Mol)
Zero-point correction=	0.212884 (Hartree/Particle)
Thermal correction to Energy=	0.229172
Thermal correction to Enthalpy=	0.230116
Thermal correction to Gibbs Free Energy=	0.167638
Sum of electronic and zero-point Energies=	-1066.514651
Sum of electronic and thermal Energies=	-1066.498363
Sum of electronic and thermal Enthalpies=	-1066.497419
Sum of electronic and thermal Free Energies=	-1066.559897

Cartesian

8	1.71802223	-1.07663333	1.50011110	1	-2.97987771	0.49816668	1.27991116
15	1.13882220	-0.41173333	0.29901111	8	-2.90867782	-1.51633334	0.80721110
8	1.19552219	1.22526658	0.18981113	6	-3.93987775	0.13316669	-0.59248888
6	2.38382220	1.92376661	0.54091114	1	-2.00057769	-1.71613336	1.10701108
1	2.07282233	2.94256663	0.80091113	1	1.86802220	-1.07193339	-1.45398891
8	3.07272220	-0.35043332	-0.74448889	8	0.90002227	-1.10553336	-1.14378881
6	4.19442225	-0.91713333	-0.15548888	1	2.86812234	1.46376657	1.40821111
1	4.84322214	-0.15473333	0.32811111	1	4.82902241	-1.42843342	-0.90708888
1	3.93842220	-1.65133333	0.62681115	8	-5.19537783	0.25756669	0.08181113
8	-0.51197773	-0.40523332	0.68241113	1	-3.96517777	-0.68843329	-1.32098889
6	-1.46667778	0.13386668	-0.20868888	1	-3.70537782	1.06776667	-1.12648892
6	-2.83797765	-0.15663332	0.40511113	1	-5.89087772	0.20106669	-0.58678889
1	-1.37867773	-0.34253332	-1.19498885	1	-1.32727778	1.21736658	-0.32608888
1	3.08542228	1.92886662	-0.29598886				

TS2-alt

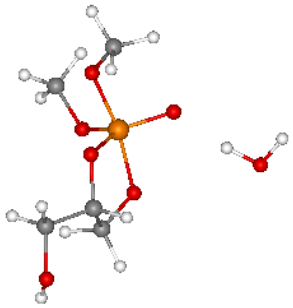


Zero-point vibrational energy	560842.1 (Joules/Mol)
	134.04449 (Kcal/Mol)
Zero-point correction=	0.213613 (Hartree/Particle)
Thermal correction to Energy=	0.229383
Thermal correction to Enthalpy=	0.230328
Thermal correction to Gibbs Free Energy=	0.169686
Sum of electronic and zero-point Energies=	-1066.527438
Sum of electronic and thermal Energies=	-1066.511668
Sum of electronic and thermal Enthalpies=	-1066.510724
Sum of electronic and thermal Free Energies=	-1066.571366

Cartesian

8	1.22766280	-0.22027409	-1.84218156	1	-1.46773720	0.20792592	1.25751841
15	0.68106288	0.14342591	-0.50538152	1	-2.10483718	-1.99167407	0.66021848
8	0.66466290	-0.98437411	0.68561852	1	2.51096272	-1.26627409	1.59191847
6	1.81366277	-1.78807402	0.93391854	1	-2.33833718	-1.30157399	-1.62118161
1	1.44446278	-2.70757413	1.40251839	1	-3.65333724	-1.12897408	0.83611852
8	2.63766289	0.68642586	0.28991848	1	-3.22393727	1.29812598	-0.98248148
6	3.74936271	0.66202587	-0.54588151	8	-2.13453722	2.56522584	0.25941849
1	4.33646297	-0.27187407	-0.42508155	1	-3.67243719	1.32552600	0.73631847
1	3.47876287	0.72862589	-1.61208153	1	-1.18593717	2.40312576	0.07581848
8	-0.98253715	0.02742592	-0.76918149	1	1.54136276	1.76472592	0.33691847
8	-3.12533712	-1.52757406	-1.09008157	8	0.55096287	1.65632594	0.08501847
6	-1.95233715	0.11502592	0.27761847	1	2.32576275	-2.03967428	0.00041848
6	-2.73793721	-1.19857407	0.23691846	1	4.43856287	1.49642599	-0.31328154
6	-2.82213712	1.34612596	0.04061848				

D1-aq

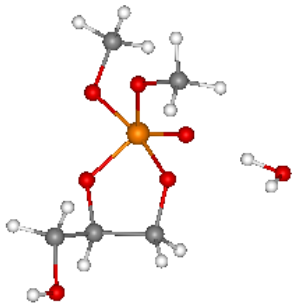


Zero-point vibrational energy	560032.5 (Joules/Mol)
	133.85098 (Kcal/Mol)
Zero-point correction=	0.213305 (Hartree/Particle)
Thermal correction to Energy=	0.229619
Thermal correction to Enthalpy=	0.230563
Thermal correction to Gibbs Free Energy=	0.168942
Sum of electronic and zero-point Energies=	-1066.625079
Sum of electronic and thermal Energies=	-1066.608765
Sum of electronic and thermal Enthalpies=	-1066.607821
Sum of electronic and thermal Free Energies=	-1066.669442

Cartesian

8	-1.81811106	1.21427786	-0.06480739	1	1.88708889	1.33477783	-0.77380735
15	-0.85091114	0.06307778	0.21959262	1	-1.60781109	-2.87152219	0.93349266
8	-1.08231103	-0.93132222	1.52469265	1	-2.07721114	4.16697741	-0.57000738
6	-1.96461105	-2.05502224	1.56529260	6	2.91688895	-0.54232228	-0.54000735
1	-1.97751105	-2.38162208	2.60899258	1	-1.52301109	2.87477779	0.09589262
8	-1.59741104	-1.11212218	-0.79310739	8	-1.45281112	3.87077785	0.10689262
6	-1.89561105	-0.75822222	-2.12920737	1	-2.97921109	-1.78652215	1.26069260
1	-2.58101106	0.09657778	-2.17570734	1	-2.37511110	-1.62302220	-2.60100746
1	-0.98961115	-0.51252222	-2.69950747	8	4.17508888	0.04577778	-0.20970739
8	0.15198889	1.03557777	1.30359268	1	2.94868898	-0.74502218	-1.61340737
8	0.55168891	-0.23932222	-0.67250735	1	2.77448893	-1.49892223	-0.01980738
6	1.50578892	0.67077780	1.24679267	1	4.27368879	0.03317778	0.75369263
6	1.75228894	0.38937777	-0.23030739	1	1.71168888	-0.23132223	1.84979260
1	2.12288880	1.49287784	1.62349260				

D2-aq

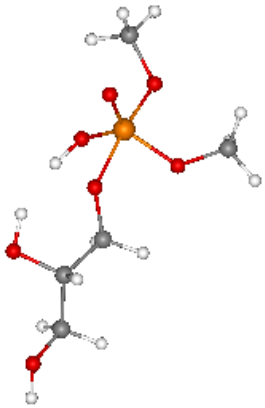


Zero-point vibrational energy	561229.6 (Joules/Mol)
	134.13709 (Kcal/Mol)
Zero-point correction=	0.213761 (Hartree/Particle)
Thermal correction to Energy=	0.230665
Thermal correction to Enthalpy=	0.231609
Thermal correction to Gibbs Free Energy=	0.168821
Sum of electronic and zero-point Energies=	-1066.625737
Sum of electronic and thermal Energies=	-1066.608833
Sum of electronic and thermal Enthalpies=	-1066.607889
Sum of electronic and thermal Free Energies=	-1066.670678

Cartesian

8	-1.57825184	0.50390744	1.29871488	1	1.16954815	1.61730731	1.53771472
15	-0.73785186	-0.35099259	0.34611481	1	-3.20655203	-1.85219264	-0.39558518
8	-1.41265190	-1.89529264	0.67571485	1	-0.75435185	3.22580743	0.26681483
6	-2.82055187	-2.02689266	0.61701483	1	-1.51245189	2.19610739	1.09621477
1	-3.06475186	-3.05359268	0.91001481	8	-1.45415187	3.17910743	0.93461484
8	-1.27845180	-0.53429258	-1.21368527	1	-3.31935191	-1.33459270	1.30641484
6	-1.38005185	0.53930742	-2.14988518	1	-2.05055189	0.18810740	-2.93948531
1	-1.80685186	1.43660736	-1.69258523	6	2.79854798	-0.90819257	-0.17388517
1	-0.40715188	0.78760743	-2.58028531	1	2.21334791	1.66960740	0.09191483
8	0.66884816	-1.09659266	0.90491486	8	4.06964827	-0.27359259	-0.02978517
8	0.31434816	0.96340746	-0.23888516	1	2.37444806	-0.72639257	-1.17058516
6	1.86964810	-0.33269259	0.88571483	1	2.88194799	-1.99259269	-0.02528517
6	1.42974818	1.10020733	0.60151482	1	4.64814806	-0.60549259	-0.73178518
1	2.34574795	-0.42369258	1.86831474				

E1-aq

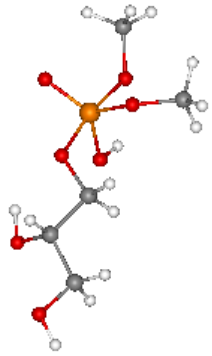


Zero-point vibrational energy	564465.0 (Joules/Mol)
	134.91038 (Kcal/Mol)
Zero-point correction=	0.214993 (Hartree/Particle)
Thermal correction to Energy=	0.231393
Thermal correction to Enthalpy=	0.232337
Thermal correction to Gibbs Free Energy=	0.170376
Sum of electronic and zero-point Energies=	-1066.609660
Sum of electronic and thermal Energies=	-1066.593260
Sum of electronic and thermal Enthalpies=	-1066.592316
Sum of electronic and thermal Free Energies=	-1066.654278

Cartesian

8	-1.85121107	-1.18534446	-1.62189996	1	2.83778906	0.02105553	-1.51010001
15	-1.49401104	-0.40774447	-0.37100002	8	2.62268901	-1.68664443	-0.35990000
8	-1.25371110	1.22595549	-0.37820002	6	3.72858906	0.30555552	0.40899998
6	-2.26441097	2.22485542	-0.22820002	1	1.73348892	-1.92564452	-0.68730003
1	-1.76331103	3.17805552	-0.41949999	1	-0.23431103	-1.56864452	0.95840001
8	-3.06851101	-0.14794447	0.27709997	8	-1.13211107	-1.20914447	1.04970002
6	-3.95001101	-1.25064445	0.35380000	1	-3.07491088	2.09305549	-0.94910002
1	-4.13961077	-1.68404448	-0.63550001	1	-4.89701080	-0.88934445	0.76990002
1	-3.56261086	-2.03954458	1.01250005	8	5.00188923	-0.02084446	-0.15150002
8	0.29638895	-0.49324447	-0.74930000	1	3.63278913	-0.10754447	1.42209995
6	1.26008892	0.28885552	-0.07420002	1	3.60348916	1.39565551	0.46810001
6	2.63348913	-0.26254445	-0.46550000	1	5.68218899	0.34025556	0.43610001
1	1.13978899	0.23065552	1.02149999	1	1.19458890	1.34695554	-0.35790002
1	-2.68151093	2.22795558	0.78090000				

E1-alt-aq

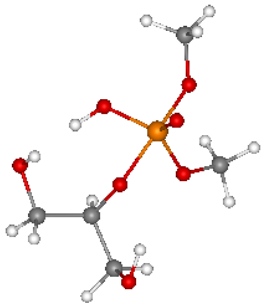


Zero-point vibrational energy	564455.4 (Joules/Mol)
	134.90807 (Kcal/Mol)
Zero-point correction=	0.214990 (Hartree/Particle)
Thermal correction to Energy=	0.231320
Thermal correction to Enthalpy=	0.232264
Thermal correction to Gibbs Free Energy=	0.171000
Sum of electronic and zero-point Energies=	-1066.611666
Sum of electronic and thermal Energies=	-1066.595335
Sum of electronic and thermal Enthalpies=	-1066.594391
Sum of electronic and thermal Free Energies=	-1066.655655

Cartesian

8	1.75054812	-1.88247406	1.06155550	1	-2.88615179	-0.59087408	1.48055553
15	1.34174812	-0.73957407	0.15485558	8	-2.65875173	-1.77947402	-0.20024443
8	1.36174810	0.82162595	0.72755557	6	-3.74805188	0.36722592	-0.21974441
6	2.01854825	1.90202582	0.06685558	1	-1.74775195	-2.09287405	-0.03274442
1	1.61934805	2.81652570	0.51465559	1	1.57894814	-0.86607409	-1.97374439
8	2.92674828	-0.51397407	-0.63834441	8	0.78994817	-0.89317405	-1.40294445
6	4.09734821	-0.65107405	0.13855559	1	3.10184813	1.87642586	0.21105558
1	4.07524824	-0.03017411	1.04635561	1	4.94794798	-0.32607409	-0.47244442
1	4.26034832	-1.68997407	0.45015559	8	-5.02965164	-0.12897409	0.17395559
8	-0.34455186	-0.82357407	0.66135561	1	-3.64115191	0.34222588	-1.31244445
6	-1.28535187	0.14902592	0.24775559	1	-3.61975169	1.40562594	0.11615558
6	-2.66745186	-0.48637408	0.40575558	1	-5.70155191	0.41702589	-0.26044440
1	-1.12765193	0.43132588	-0.80214441	1	-1.21655190	1.05542588	0.86375558
1	1.80404806	1.91022599	-1.00564444				

E2-aq

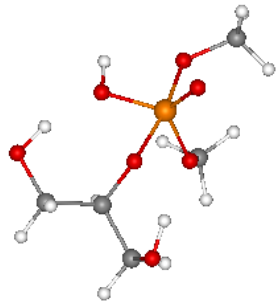


Zero-point vibrational energy	566565.7 (Joules/Mol)
	135.41245 (Kcal/Mol)
Zero-point correction=	0.215793 (Hartree/Particle)
Thermal correction to Energy=	0.231874
Thermal correction to Enthalpy=	0.232819
Thermal correction to Gibbs Free Energy=	0.172011
Sum of electronic and zero-point Energies=	-1066.613024
Sum of electronic and thermal Energies=	-1066.596944
Sum of electronic and thermal Enthalpies=	-1066.595999
Sum of electronic and thermal Free Energies=	-1066.656807

Cartesian

8	-1.28947413	-0.35751483	-1.98878515	1	1.18792593	0.04128516	1.25601482
15	-1.03597414	-0.16361484	-0.50578517	1	1.86322594	2.11828518	0.37231481
8	-0.72417414	1.32278514	0.15271480	1	-2.10167408	1.73768508	1.67671478
6	-1.67107403	2.18908525	0.78001481	1	2.01202583	0.99468517	-1.77348518
1	-1.10687411	3.08358502	1.05971479	1	3.41612601	1.28218508	0.60911483
8	-2.66737413	-0.04121484	0.04081480	1	3.35052586	-1.19651484	-0.51468521
6	-3.57307410	-1.06011486	-0.33198518	8	1.89322591	-2.47211480	0.24601482
1	-3.63297415	-1.17011487	-1.42188513	1	3.20002604	-1.27511489	1.25301480
1	-3.29647398	-2.03021479	0.10261481	1	1.64102590	-2.57731485	-0.68488520
8	0.78062588	-0.21881485	-0.77278519	1	0.04472587	-1.82691491	0.45681483
8	2.79412603	1.39148510	-1.33818519	8	-0.85787416	-1.45111489	0.52761483
6	1.70122588	-0.03291484	0.28771478	1	-2.47837400	2.47028518	0.09971480
6	2.47592592	1.26868510	0.04651479	1	-4.56227446	-0.78141487	0.04851480
6	2.63692594	-1.24501491	0.31651485				

E2-alt-aq



Zero-point vibrational energy	565327.3 (Joules/Mol)
	135.11647 (Kcal/Mol)
Zero-point correction=	0.215322 (Hartree/Particle)
Thermal correction to Energy=	0.231458
Thermal correction to Enthalpy=	0.232403
Thermal correction to Gibbs Free Energy=	0.171487
Sum of electronic and zero-point Energies=	-1066.616103
Sum of electronic and thermal Energies=	-1066.599966
Sum of electronic and thermal Enthalpies=	-1066.599022
Sum of electronic and thermal Free Energies=	-1066.659938

Cartesian

8	1.20457780	0.19551113	-2.10372233	1	-1.32212222	0.11591114	1.13197780
15	0.88287783	0.34631115	-0.63232219	1	-1.74652219	-2.09138870	0.41557774
8	0.78997779	-0.98208892	0.35627779	1	1.59697783	-0.30878884	2.16847777
6	1.59307778	-1.18818891	1.51917779	1	-2.00512218	-1.23818886	-1.82752216
1	1.13277781	-2.02398872	2.05317760	1	-3.37682223	-1.40378892	0.59497774
8	2.52447772	0.72271115	-0.07702224	1	-3.31552219	1.09911120	-0.96232224
6	3.61957788	0.11231114	-0.72952223	8	-2.24392223	2.45761132	0.18847775
1	3.51087785	-0.97888887	-0.80142224	1	-3.60142231	1.04941118	0.78977776
1	3.75487781	0.50191116	-1.74522221	1	-1.28502226	2.35401130	0.02357778
8	-0.85342222	0.17351115	-0.90412223	1	1.33407784	2.18441129	0.43187776
8	-2.75742221	-1.62728882	-1.34032226	8	0.49807784	1.78231108	0.13237777
6	-1.80442226	0.04411114	0.14877775	1	2.62377787	-1.44958889	1.26747775
6	-2.44572210	-1.34218884	0.02257776	1	4.51967812	0.32721114	-0.14192224
6	-2.82822227	1.16801107	0.02087778				

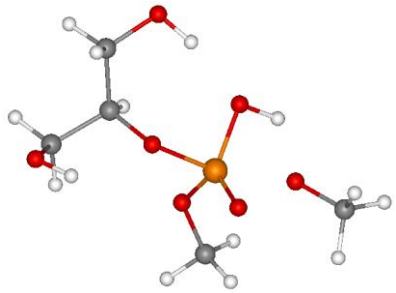
TS1-alt-aq

Zero-point vibrational energy	557805.4 (Joules/Mol)
	133.31869 (Kcal/Mol)
Zero-point correction=	0.212457 (Hartree/Particle)
Thermal correction to Energy=	0.228792
Thermal correction to Enthalpy=	0.229736
Thermal correction to Gibbs Free Energy=	0.167724
Sum of electronic and zero-point Energies=	-1066.606702
Sum of electronic and thermal Energies=	-1066.590368
Sum of electronic and thermal Enthalpies=	-1066.589423
Sum of electronic and thermal Free Energies=	-1066.651435

Cartesian

8	1.72211111	-0.97137409	1.57028890	1	-2.99298906	0.29562587	1.37868881
15	1.13581109	-0.36797410	0.32998890	8	-2.85548902	-1.60287416	0.55938888
8	1.23541105	1.24272585	0.10718890	6	-3.94068909	0.23632587	-0.53381109
6	2.43471098	1.97372591	0.39088890	1	-1.98468888	-1.82797420	0.93308890
1	2.11531091	2.97542596	0.68978894	1	1.85301113	-1.17267418	-1.36411119
8	3.05681109	-0.43767411	-0.73581111	8	0.87871104	-1.18447411	-1.04371119
6	4.14111090	-1.09177411	-0.14891109	1	2.99371099	1.51202583	1.20768893
1	4.56901121	-0.51757413	0.69238889	1	4.95311117	-1.23357415	-0.88391113
1	3.88801098	-2.08987403	0.25118890	8	-5.19648886	0.04392590	0.11758890
8	-0.49258897	-0.31767410	0.74478889	1	-3.88348913	-0.35997412	-1.45401108
6	-1.46608889	0.25032592	-0.12881111	1	-3.80208898	1.29352582	-0.79811108
6	-2.82798910	-0.18477412	0.40178889	1	-5.89268923	0.29012591	-0.50931108
1	-1.32178891	-0.11917411	-1.15101111	1	-1.38868892	1.34362590	-0.12911110
1	3.06891108	2.02202606	-0.49411109				

TS2-alt-aq



Zero-point vibrational energy	557913.1 (Joules/Mol)
	133.34444 (Kcal/Mol)
Zero-point correction=	0.212498 (Hartree/Particle)
Thermal correction to Energy=	0.228562
Thermal correction to Enthalpy=	0.229507
Thermal correction to Gibbs Free Energy=	0.168474
Sum of electronic and zero-point Energies=	-1066.610506
Sum of electronic and thermal Energies=	-1066.594442
Sum of electronic and thermal Enthalpies=	-1066.593498
Sum of electronic and thermal Free Energies=	-1066.654531

Cartesian

8	1.22764444	-0.14802593	-1.85232222	1	-1.46735561	0.17537408	1.26887774
15	0.69154435	0.13427407	-0.48212224	1	-2.12275553	-2.00242591	0.55637777
8	0.67544436	-1.04602599	0.63747782	1	2.43184447	-1.45042598	1.68077779
6	1.80794442	-1.88502586	0.89967781	1	-2.48525548	-1.29392588	-1.68062222
1	1.40024436	-2.84472585	1.22687769	1	-3.62735558	-1.11642599	0.88217777
8	2.65284443	0.62917405	0.30987775	1	-3.19925570	1.35267401	-0.94892222
6	3.74204445	0.72117406	-0.56292224	8	-2.06435561	2.57187414	0.29767776
1	4.08354425	-0.27172592	-0.90292221	1	-3.63355565	1.35847402	0.77167779
1	3.52374434	1.30727410	-1.47162223	1	-1.11815560	2.38007426	0.13657777
8	-0.96185565	0.04417408	-0.76192218	1	1.59414446	1.69797409	0.41297781
8	-3.25025558	-1.42392588	-1.09402227	8	0.59044433	1.62877405	0.15847777
6	-1.94715559	0.11807407	0.28457779	1	2.40874434	-2.03342581	0.00037779
6	-2.75865555	-1.17322588	0.22027777	1	4.59694433	1.20177412	-0.05822222
6	-2.79115558	1.36817408	0.07087778				

Table S1. Free energies and free enthalpies of key intermediates and transition states

	D1	D2 (**GS**)	E1	E1 alt	E2	E2 alt	TS1	TS2
Gas phase								
G, a.e.u.	-1066.577	-1066.575	-1066.558	-1066.561	-1066.569	-1066.573	-1066.560	-1066.571
H, a.e.u.	-1066.511	-1066.514	-1066.495	-1066.498	-1066.508	-1066.512	-1066.497	-1066.511
G,kcal/mol	-669286.406	-669285.666	-669274.512	-669276.591	-669281.459	-669284.062	-669275.934	-669283.131
H,kcal/mol	-669245.431	-669246.957	-669235.116	-669237.001	-669243.484	-669245.864	-669236.729	-669245.078
ΔG^{D2}			**11.15**	**9.08**	**4.21**	**1.60**	**9.73**	**2.54**
ΔH^{D2}			**11.84**	**9.96**	**3.47**	**1.09**	**-1.61**	**-9.96**
Water, IEFPCM model								
G, a.e.u.	-1066.669	-1066.671	-1066.654	-1066.656	-1066.657	-1066.660	-1066.651	-1066.655
H, a.e.u.	-1066.608	-1066.608	-1066.592	-1066.594	-1066.596	-1066.599	-1066.589	-1066.593
G,kcal/mol	-669344.675	-669345.450	-669335.159	-669336.023	-669336.746	-669338.711	-669333.375	-669335.318
H,kcal/mol	-669306.007	-669306.050	-669296.278	-669297.580	-669298.589	-669300.486	-669294.462	-669297.019
ΔG^{D2}			**10.29**	**9.43**	**8.70**	**6.74**	**12.08**	**10.13**
ΔH^{D2}			**9.77**	**8.47**	**7.46**	**5.56**	**11.59**	**9.03**