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Controlled ring-opening polymerisation of cyclic phosphates, phosphonates and phosphoramidates catalysed by hereroleptic BHT-alkoxy magnesium complexes

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S1. General experimental remarks

All of the synthetic and polymerization experiments were conducted under an argon atmosphere. Toluene, diethyl ether, THF and triethylamine were refluxed with Na/benzophenone/dibenzo-18-crown-6 and distilled prior to use. Heptane was refluxed for 10 h over sodium and then distilled and stored under an argon atmosphere over sodium. Methanol was refluxed and distilled over magnesium methoxide. 2,6-Di-*tert*-butyl-4-methylphenol (BHT, Sigma-Aldrich, ≥99%), di-n-butylmagnesium (Sigma-Aldrich, 1.0 M solution in heptane), trimethylaluminium (Sigma-Aldrich, 1.0 M solution in toluene), diethylzinc (Sigma-Aldrich, 1.0 M solution in toluene), 1,8-diazabicyclo[5.4.0]undec-7-ene (**DBU**, Sigma-Aldrich, 99%) and acetic acid (Acros, ≥99.9%) were used as purchased. Benzyl alcohol (Acros, 99 %) was distilled over BaO and stored under argon. $Mg(BHT)_2(THF)_2$ (**Mg2**),[1] $Ca(BHT)_2(THF)_3$ (**Ca1**),[2] $EtZn(BHT)(THF)_2$ (**Zn1**),[3] $Me_2Al(BHT)(THF)_2$ (**Al1**),[4] 1,5,7-triazabicyclo[4.4.0]undec-5-ene (**TBD**),[5] *N*-[3,5-bis(trifluoromethyl)phenyl]-*N*'-cyclohexyl thiourea (**TU**)[6] were prepared according to the described methods.

$CDCl_3$ (Cambridge Isotope Laboratories, Inc., D 99.8 atom %) was used as purchased. THF-d_8 (Aldrich, ≥99.5 atom % ^2H) and toluene-d_8 (Aldrich, ≥99.6 atom % ^2H) were stored over sodium/benzophenone and condensed into NMR tubes using the Schlenk technique. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400 MHz) at 20 °C. The ^1H homodecoupling spectra were recorded on a Agilent 400-MR spectrometer (400 MHz) at 20 °C in $CDCl_3$. The chemical shifts are reported in ppm relative to the solvent residual peaks.

GPC mesaurements of the polymers were performed in DMF (containing 0.1 g/L 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.

Elemental analysis (C, H) was performed on a Perkin Elmer Series II CHNS/O Analyser 2400.

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S2. Preparation of BHT-derived magnesium complexes

S2.1. Syntesis of BuMg(BHT)(THF)$_2$ (Mg1)

BHT (0.22 g, 1 mmol) was placed into an ampoule filled with argon. Heptane (1 mL) was injected with a syringe through a septum. Upon ionol dissolution, the ampoule was cooled to -10 °C. Dibutylmagnesium (1 mL of 1 M in heptane, 1 mmol) was transferred into the ampoule while stirring the solution. After warming to room temperature and stirring for 4 h, the as-formed crystals were washed with 2 mL of heptane and dried under vacuum. The obtained solid was dissolved in THF (2 mL). The resulting solution was evaporated under reduced pressure to a residual volume of 0.5 mL. The as-formed crystalline precipitate was filtered, washed with 1 mL of a 1:1 (v/v) THF/heptane mixture, and dried under vacuum. The yield was 0.38 g (86 %).

^{1}H NMR (400 MHz, THF-d$_8$, 20 °C): δ 6.72 (s, 2H, CH$_{Ar}$); 2.09 (s, 3H, Me$_{Ar}$); 1.51 (m, 2H, CH$_3$CH$_2$C*H*$_2$); 1.36 (s, 18H, ^{tert}Bu); 1.24 (sext, ^3J = 7.3 Hz, 2H, CH$_3$C*H*$_2$); 0.84 (t, ^3J = 7.3 Hz, 3H, C*H*$_3$CH$_2$); 0.49 (m, 2H, C*H*$_2$Mg).

^{13}C{^{1}H} NMR (101 MHz, THF-d$_8$, 20 °C): δ 161.86 (C-O(Ar)); 137.35 (Ar); 125.36 (Ar); 119.58 (Ar); 35.43 ((CH$_3$)$_3$*C*); 33.86 (CH$_2$CH$_2$); 32.87 (CH$_2$CH$_2$); 31.02 ((*C*H$_3$)C); 21.63 (Me(Ar)); 14.50 (Me(Bu)); 8.52 (CH$_2$Mg).

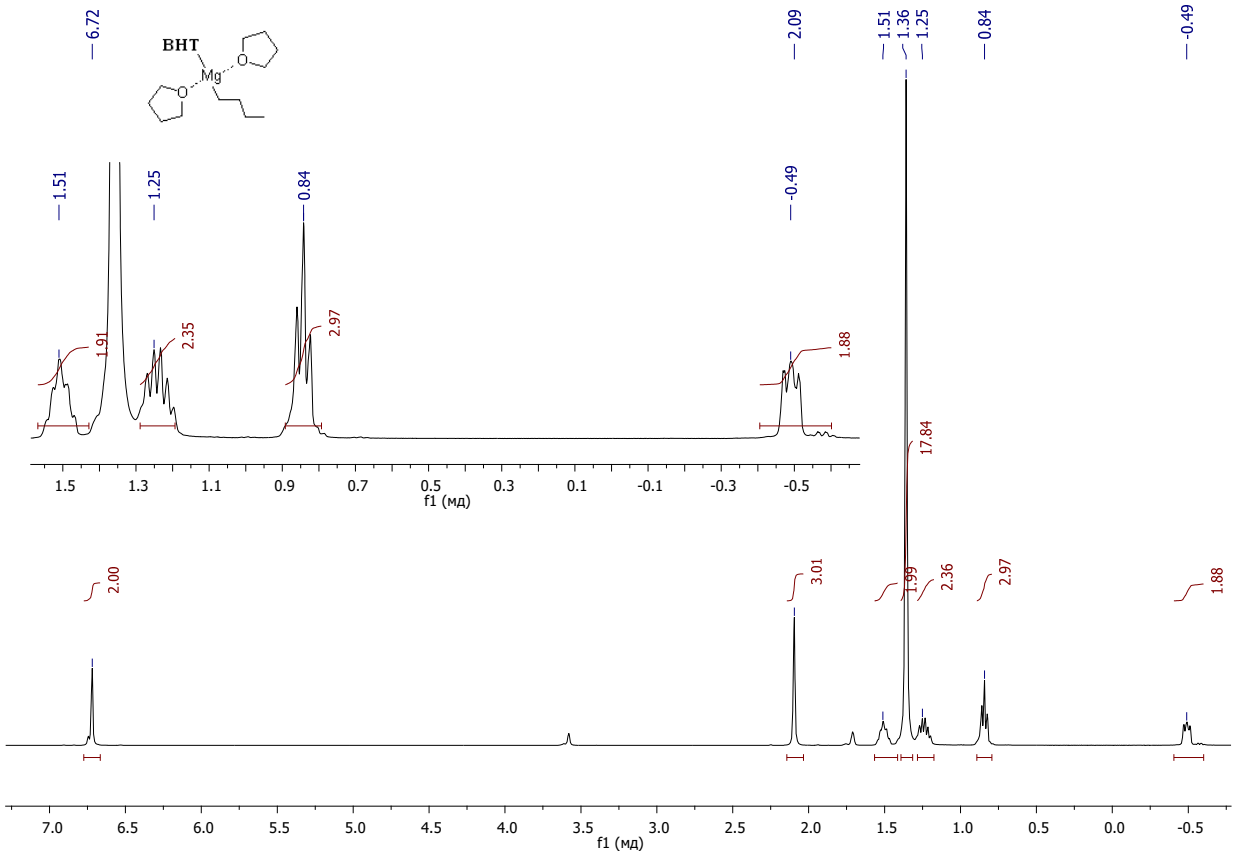


Fig. S1. ^{1}H NMR spectrum (400 MHz, THF-d$_8$, 20 °C) of BuMg(BHT)(THF)$_2$ (**Mg1**)

S2.2. Syntesis of [(BHT)Mg(μ-PhCH$_2$O)(THF)]$_2$ (Mg3)

A solution Bu_2Mg in heptane (20 mL, 1 M, 20 mmol) was dropwise added to a stirred solution of BHT (4.410 g, 20 mmol) in a toluene/THF mixture (8 mL and 4.5 mL, correspondingly). After 40 min, a solution of $PhCH_2OH$ (2.168 g, 20 mmol) in THF (1 mL) was dropwise added to the stirred reaction mixture. The formed solution was then stirred for 3 min. After 5 min, crystals of **4** started to form. Two hours later, the mother liquor was decanted. Some of formed crystals were taken for the X-ray diffraction studies. The remaining crystals were washed with toluene (2×5 mL) and hexane (2×5 mL), dried under dynamic vacuum till the constant mass. The yield was 6.785 g (8.02 mmol, 80%).

Anal. found (calcd for $C_{26}H_{38}MgO_3$): C, 73.96 (73.85%); H, 9.22 (9.06%).

^{1}H NMR (400 MHz, THF-d$_8$, 20 °C): δ 7.37 (d, ^3J = 7.7 Hz, 2H, o-H$_{Ph}$); 7.20 (t, ^3J = 7.6 Hz, 2H, m-H$_{Ph}$); 7.13 (t, ^3J = 7.6 Hz, 1H, p-H$_{Ph}$); 6.77 (s, 2H, m-H$_{BHT}$); 5.02 (s, 2H, O-C*H*$_2$-Ph); 3.64-3.59 (m, 4H, CH$_2$C*H*$_2$O$_{THF}$); 2.13 (s, 3H, -C*H*$_{3\ BHT}$); 1.80-1.75 (m, 4H, C*H*$_2$CH$_2$O$_{THF}$); 1.37 (s, 18H, 2,6-^{t}*Bu*$_{2\ BHT}$).

^{13}C{^{1}H} NMR (101 MHz, THF-d$_8$, 20 °C): δ 161.4 (ipso-*C*-O$_{BHT}$); 145.8 (ipso-*C*-CH$_{2\ BnO}$); 137.7 (o-*C*-^{t}Bu$_{BHT}$); 129.1 (o-*C*$_{BnO}$); 128.1 (m-*C*$_{BHT}$); 127.6 (p-*C*$_{BnO}$); 125.7 (m-*C*$_{BnO}$); 121.0 (p-*C*-Me$_{BHT}$); 68.4 (CH$_2$*C*H$_2$O$_{THF}$); 66.6 (Ph-*C*H$_2$-O); 35.7 (-*C*Me$_{3\ BHT}$); 31.4 (-C(*C*H$_3$)$_{3\ BHT}$); 26.5 (*C*H$_2$CH$_2$O$_{THF}$); 21.6 (p-CH$_{3\ BHT}$).

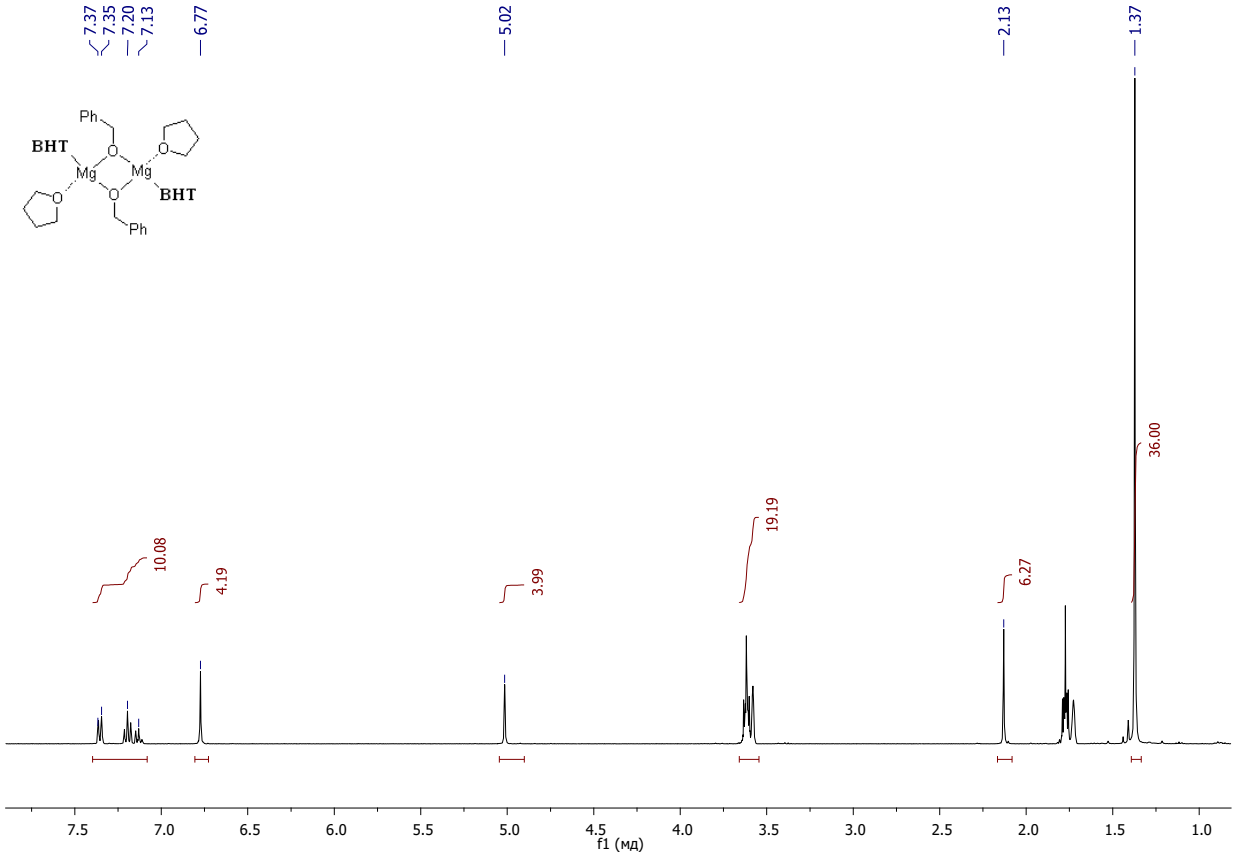
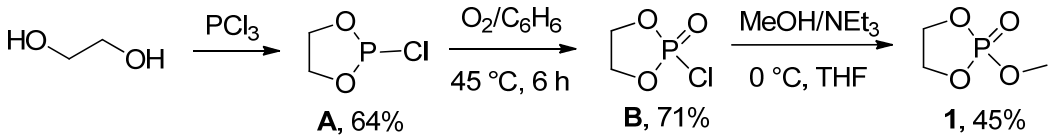


Fig. S2. ^{1}H NMR spectrum (400 MHz, THF-d$_8$, 20 °C) of [(μ-PhCH$_2$O)Mg(BHT)(THF)]$_2$ (**Mg3**)

S3. Synthesis and characterization of monomers 1-6

S3.1. Syntesis of 2-methoxy-2-oxo-1,3,2-dioxaphospholane 1 (methyl ethylene phosphate, MeOEP)



*2-Chloro-1,3,2-dioxaphospholane (**A**).*

The compound was synthesized via a modified literature protocol.[1] 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 purified twice by distillation under reduced pressure. The yield was 80.7 g (64%). B. p. 83-84 °C (79-81 Torr), colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.44 (m, 2H, OCH_2CH_2O); 4.22 (m, 2H, OCH_2CH_2O). ^{31}P{H} NMR (162 MHz, $CDCl_3$, 20 °C): δ 167.61.

*2-Chloro-2-oxo-1,3,2-dioxaphospholane (**B**).*

The compound was synthesized according to a modified literature procedure.[1]. 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 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 (71.3%). B. p. 79-80 °C (0.4 Torr), colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.63-4.46 (m, 4H, OCH_2CH_2O). ^{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.

2-Methoxy-2-oxo-1,3,2-dioxaphospholane **1** *(MeOEP).*

A flame-dried 1000 mL three-neck flask, equipped with a dropping funnel, was charged with dry methanol (4.8 g, 0.15 mol), dry triethylamine (21 mL, 0.15 mol) and dry THF (300 mL). A solution of 2-chloro-2-oxo-1,3,2-dioxaphospholane (21.3 g, 0.15 mol) in dry THF (60 mL) was added dropwise under stirring at -20 °C. After 12 h of stirring at -20 °C, triethylammonium chloride was filtered off, the filtrate was concentrated *in vacuo*. The residue was purified by distillation under reduced pressure. The yield was 8.95 g (45%). B. p. 92-93°C (0.4 Torr), colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.42 (m, 2H, OCH_2CH_2O); 4.35 (m, 2H, OCH_2CH_2O); 3.76 (d, $^{2}J_{HP}$ = 11.8 Hz, 3H, OCH_3). ^{13}C{H} NMR (101 MHz, $CDCl_3$, 20 °C): δ 66.13 (s, 2C, OCH_2CH_2O); 55.22 (d, $^{2}J_{CP}$ = 6.4 Hz, 1C, O-CH_3). ^{31}P{H} NMR (162 MHz, $CDCl_3$, 20 °C): δ 18.60.

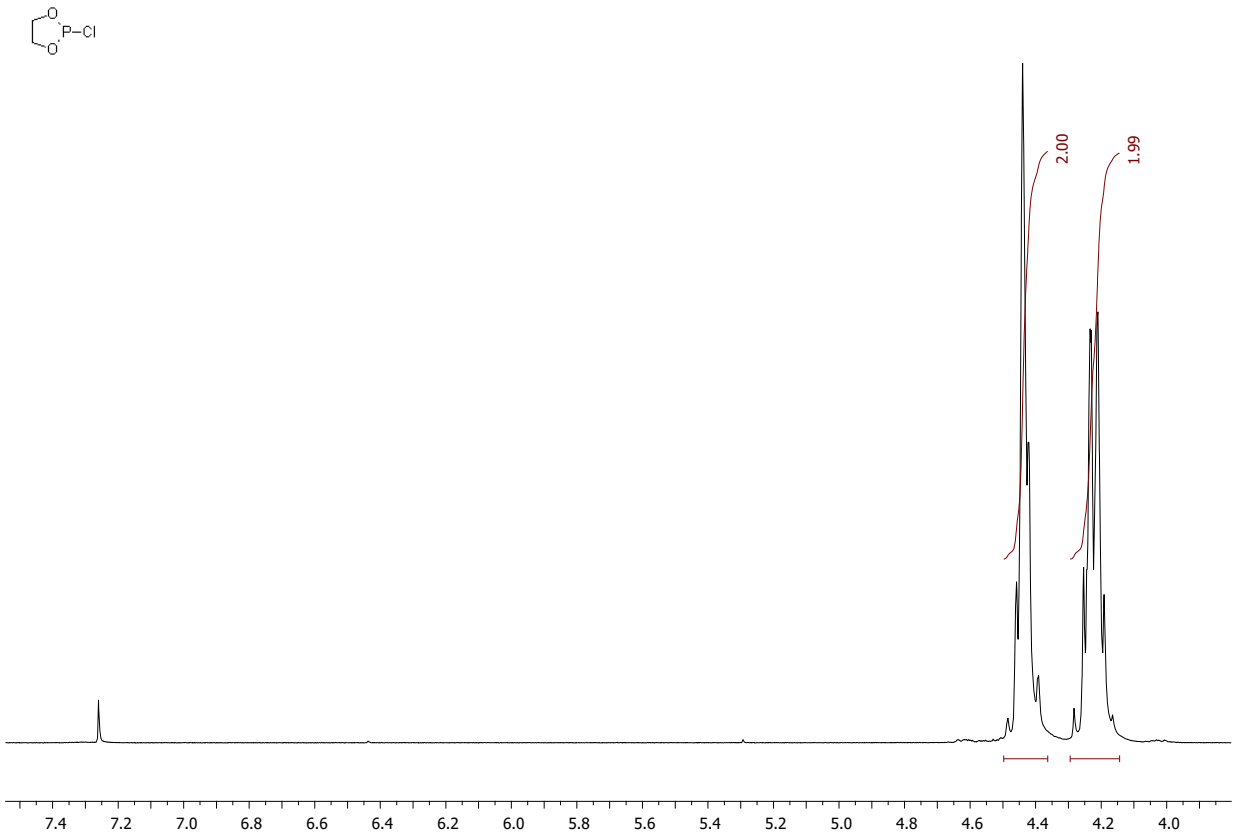


Fig. S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of 2-chloro-1,3,2-dioxaphospholane

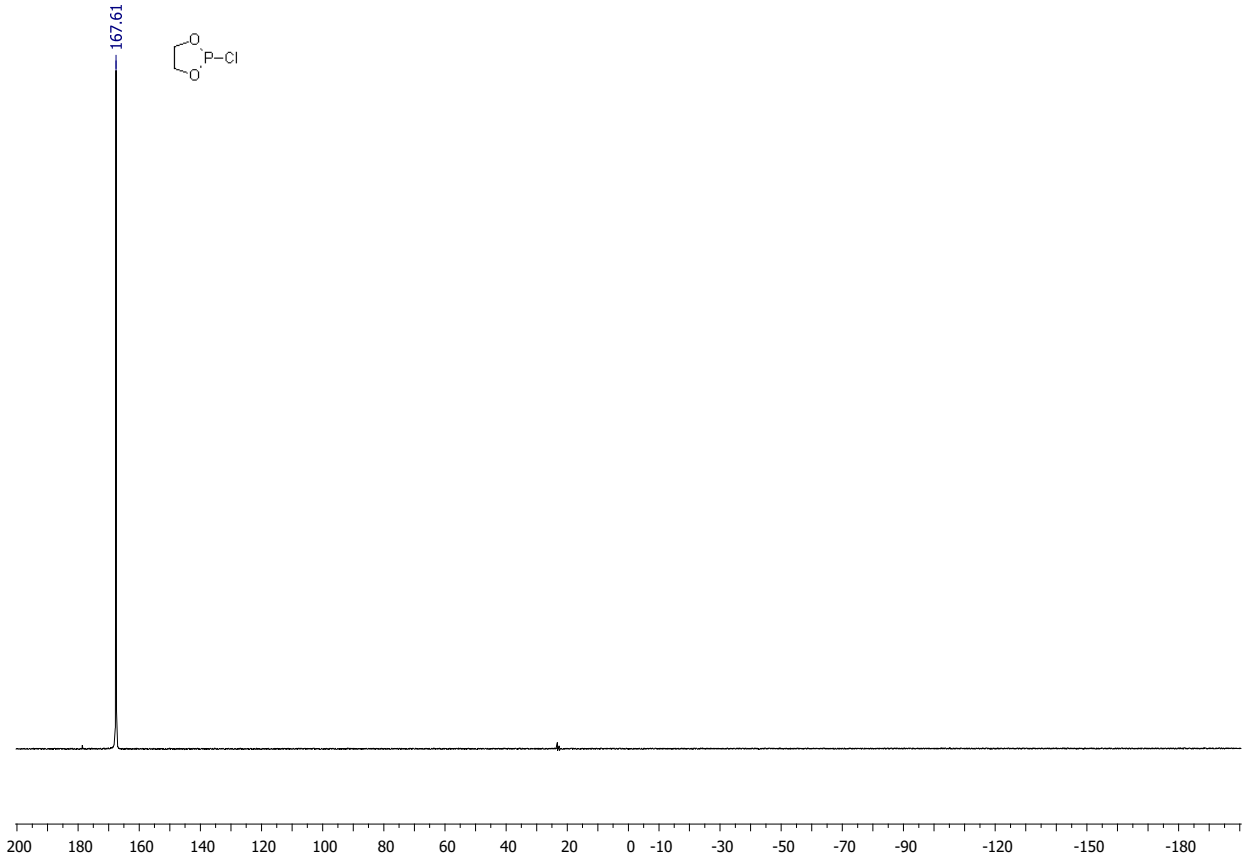


Fig. S4. ^{31}P{H} NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of 2-chloro-1,3,2-dioxaphospholane

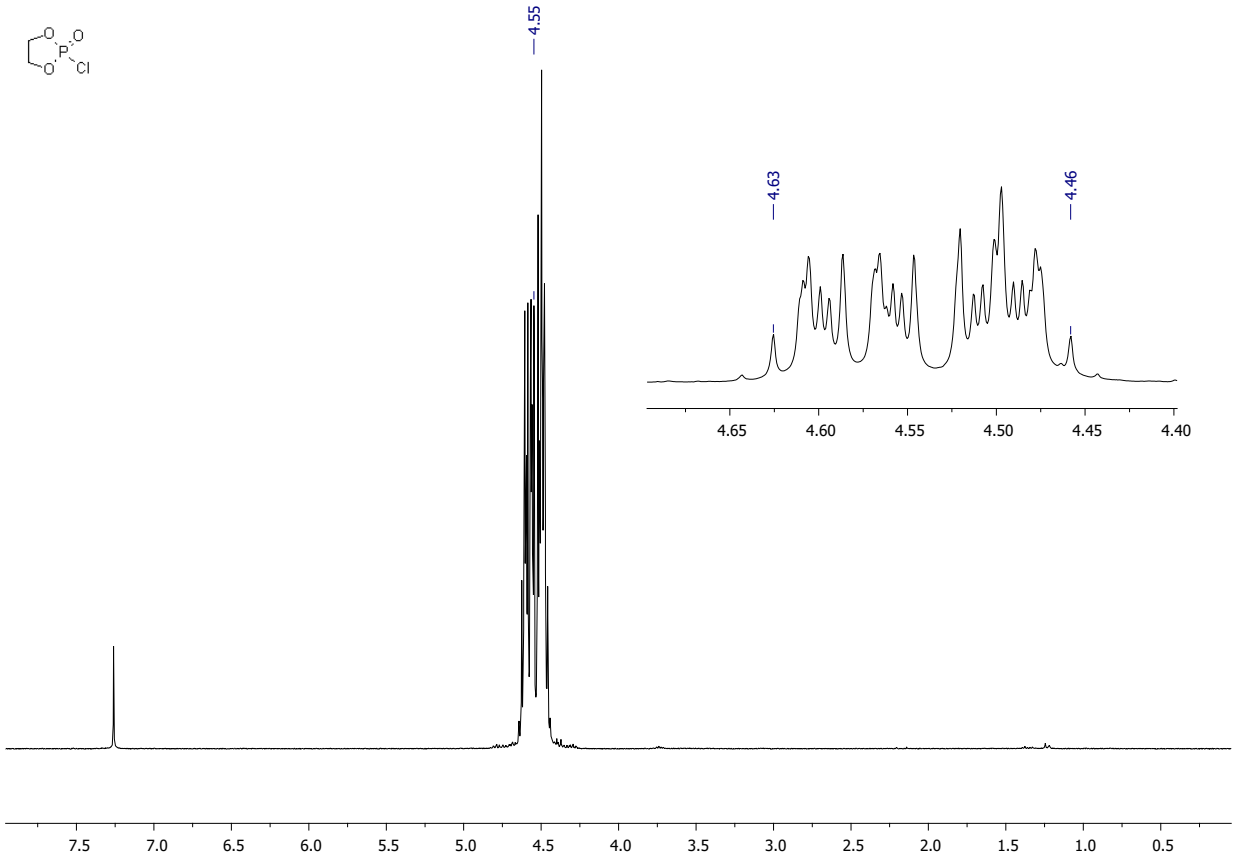


Fig. S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of 2-chloro-2-oxo-1,3,2-dioxaphospholane

Fig. S6. ^{31}P{^{1}H} NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of 2-chloro-2-oxo-1,3,2-dioxaphospholane

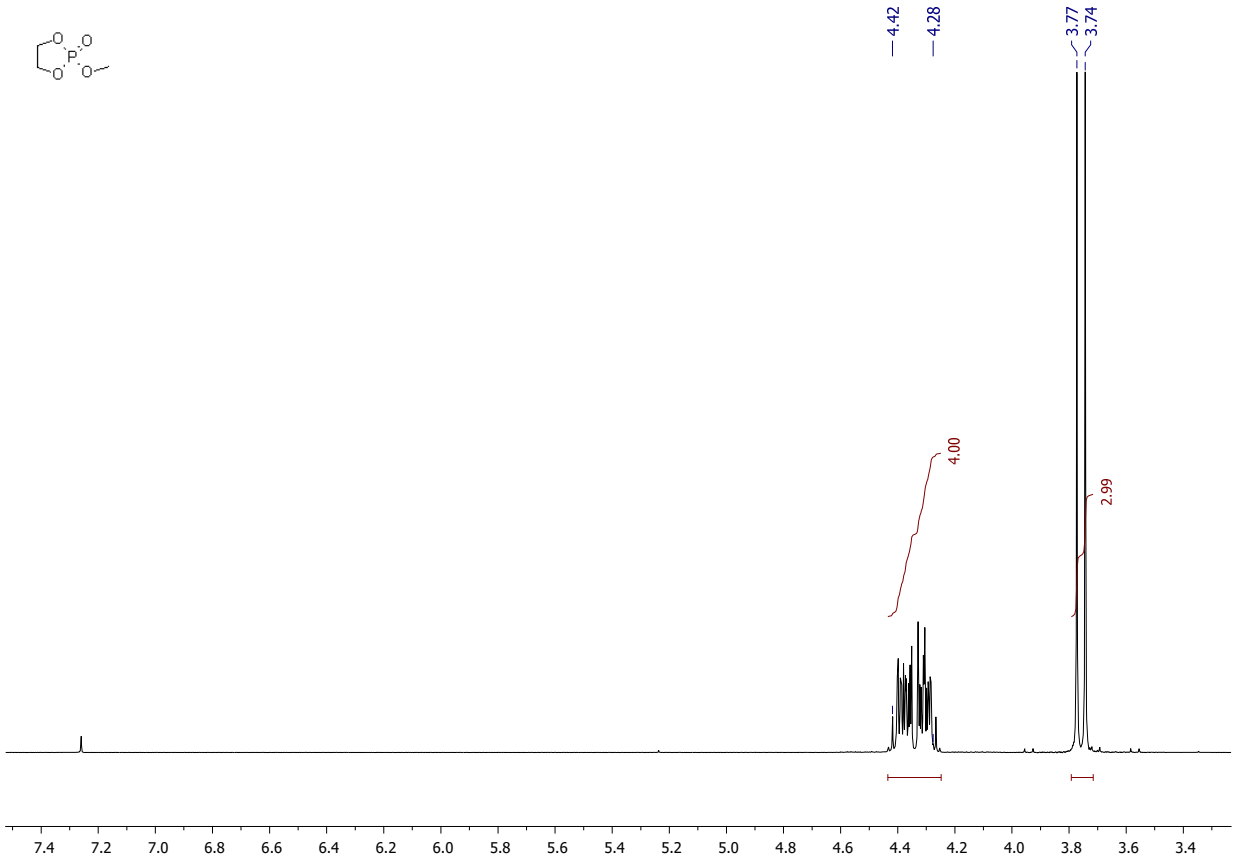


Fig. S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of **MeOEP** (**1**)

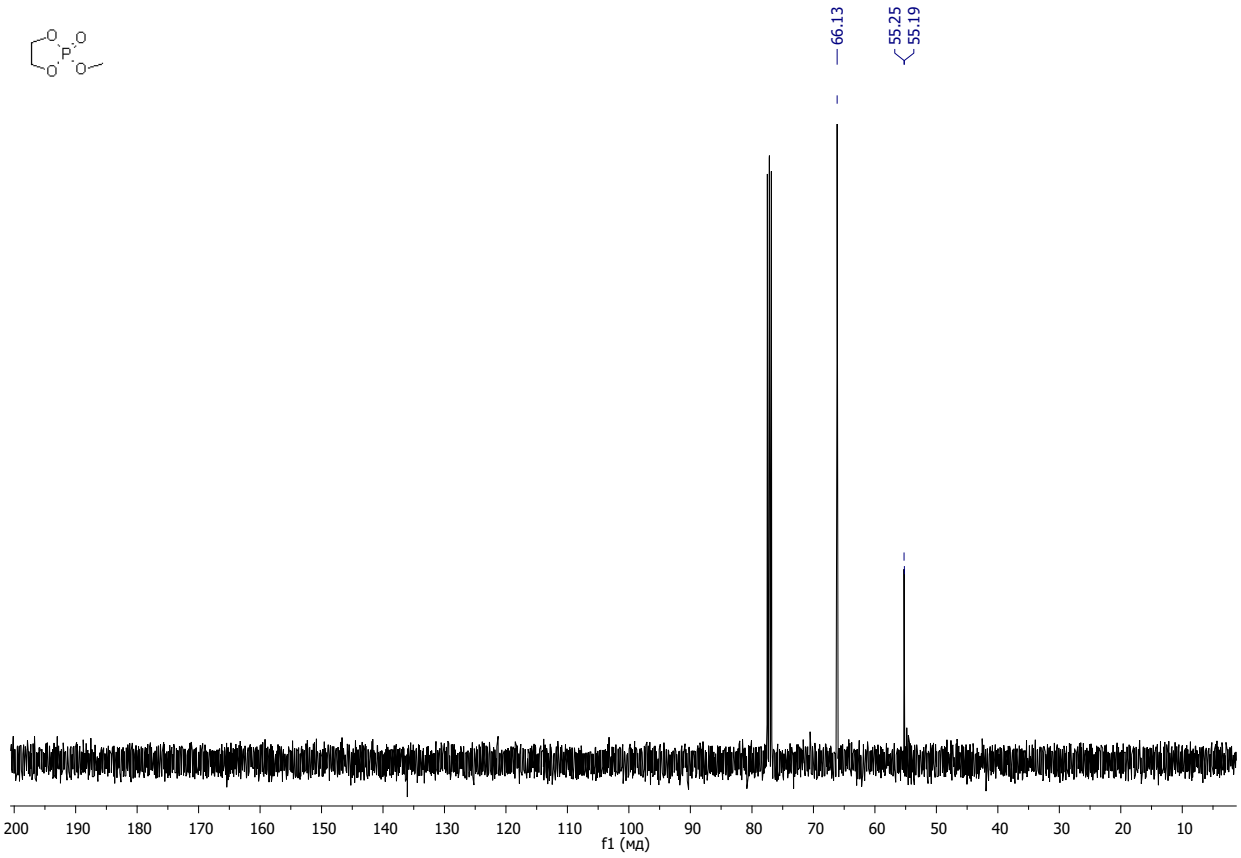


Fig. S8. ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of **MeOEP** (**1**)

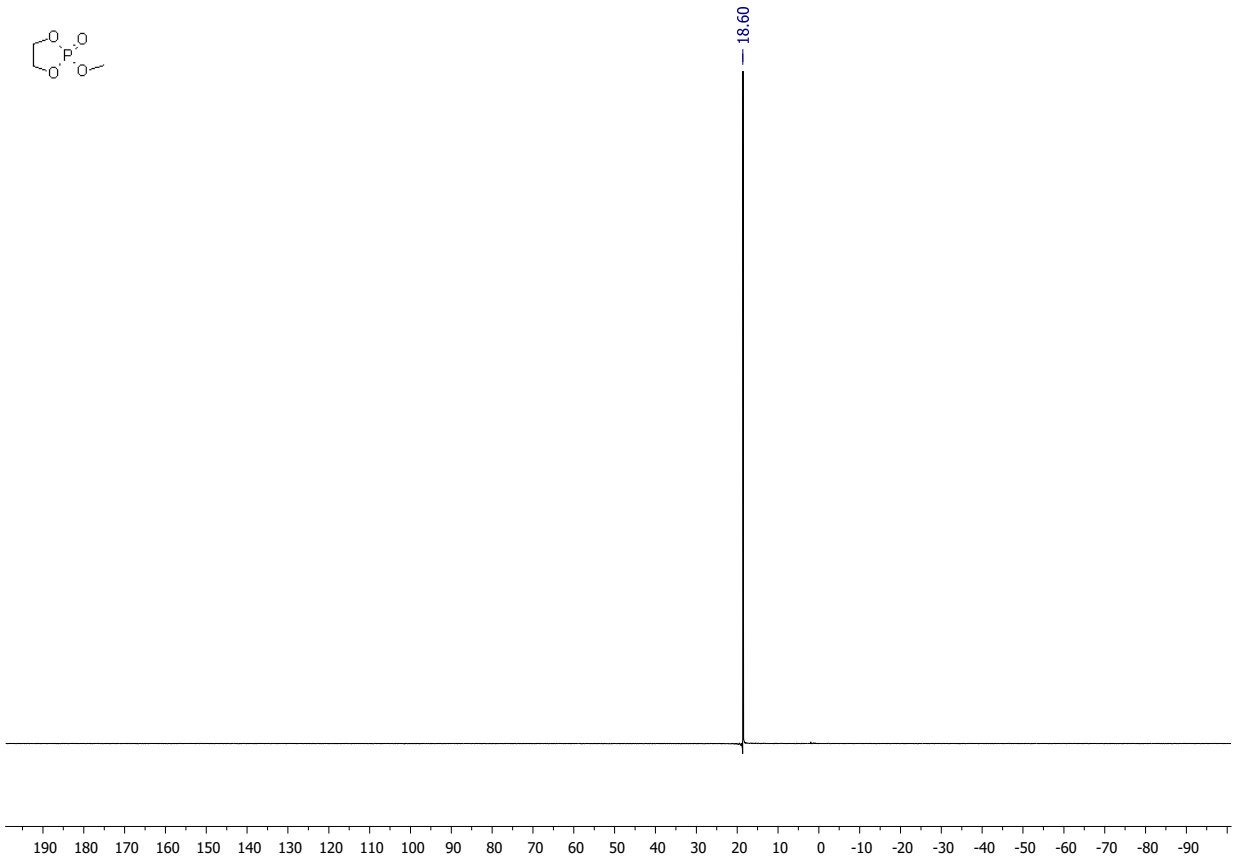
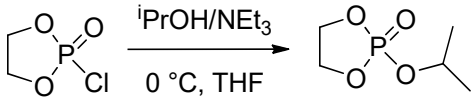


Fig. S9. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of **MeOEP** (**1**)

S3.2. Syntesis of 2-isopropoxy-2-oxo-1,3,2-dioxaphospholane 2 (isopropyl ethylene phosphate, ^{i}PrOEP)



2, 42%

The compound was synthesized via a modified literature protocol.[2] A flame-dried 500 mL three-neck flask, equipped with a dropping funnel, was charged with dry isopropanol (12 g, 0.2 mol), dry triethylamine (28 mL, 0.2 mol) and dry THF (80 mL). A solution of 2-chloro-2-oxo-1,3,2-dioxaphospholane (28.4 g, 0.2 mol) in dry THF (20 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 purified by distillation under reduced pressure. The yield was 14.1 g (42%). B. p. 88-90 °C (0.4 Torr), colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.72 (sept. of d, $^{3}J_{HH}$ = $^{3}J_{HP}$ = 6.6 Hz, 1H, O-C*H*$(CH_3)_2$); 4.40 (m, 2H, OCH_2CH_2O); 4.33 (m, 2H, OCH_2CH_2O); 1.33 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, O-CH(CH_3)$_2$). $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$, 20 °C): δ 74.21 (d, $^{2}J_{CP}$ = 6.0 Hz, 1C, O-*C*HMe_2); 65.91 (d , $^{2}J_{CP}$ = 2.6 Hz, 2C, O*C*H_2*C*H_2O); 23.61 (s, 2C, O-CH(*C*H_3)$_2$). $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$, 20 °C): δ 16.75 (s).

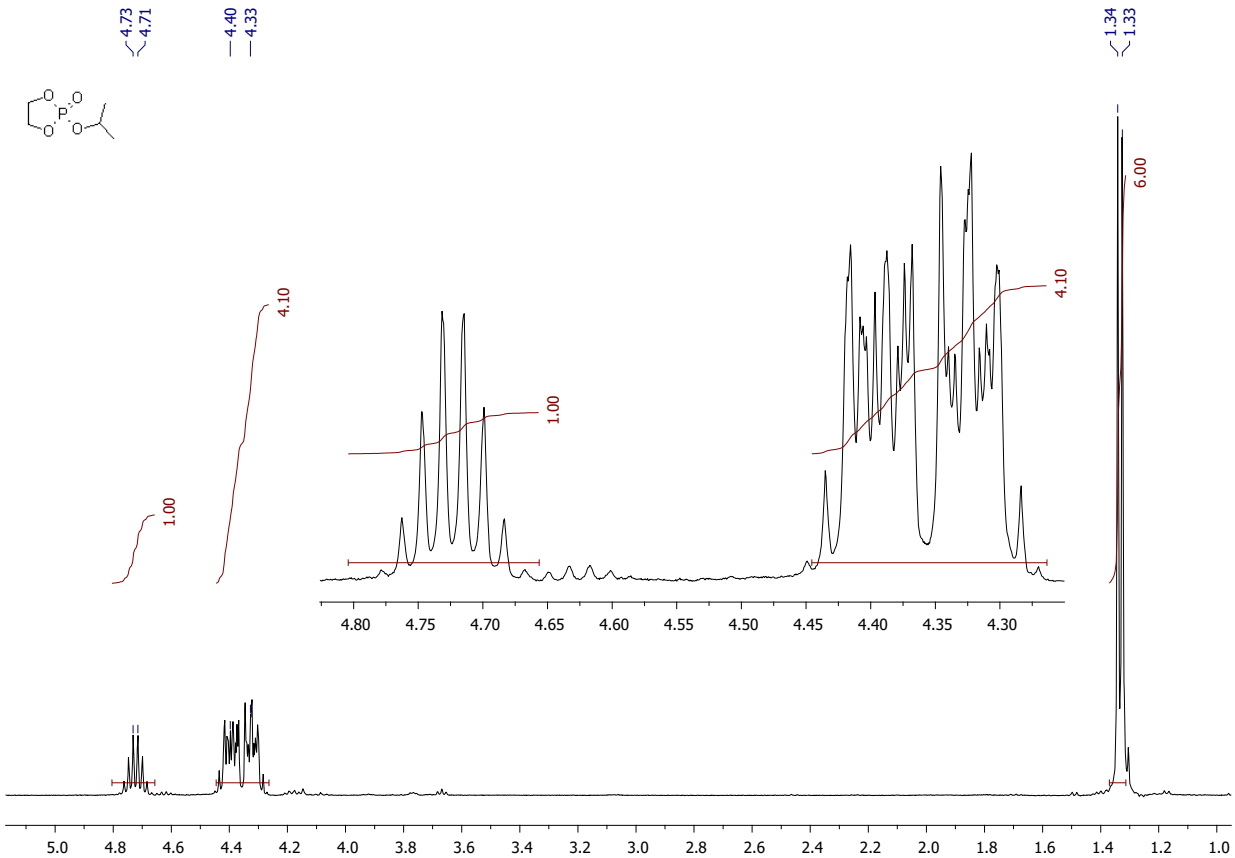


Fig. S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of **^{i}PrOEP** (**2**)

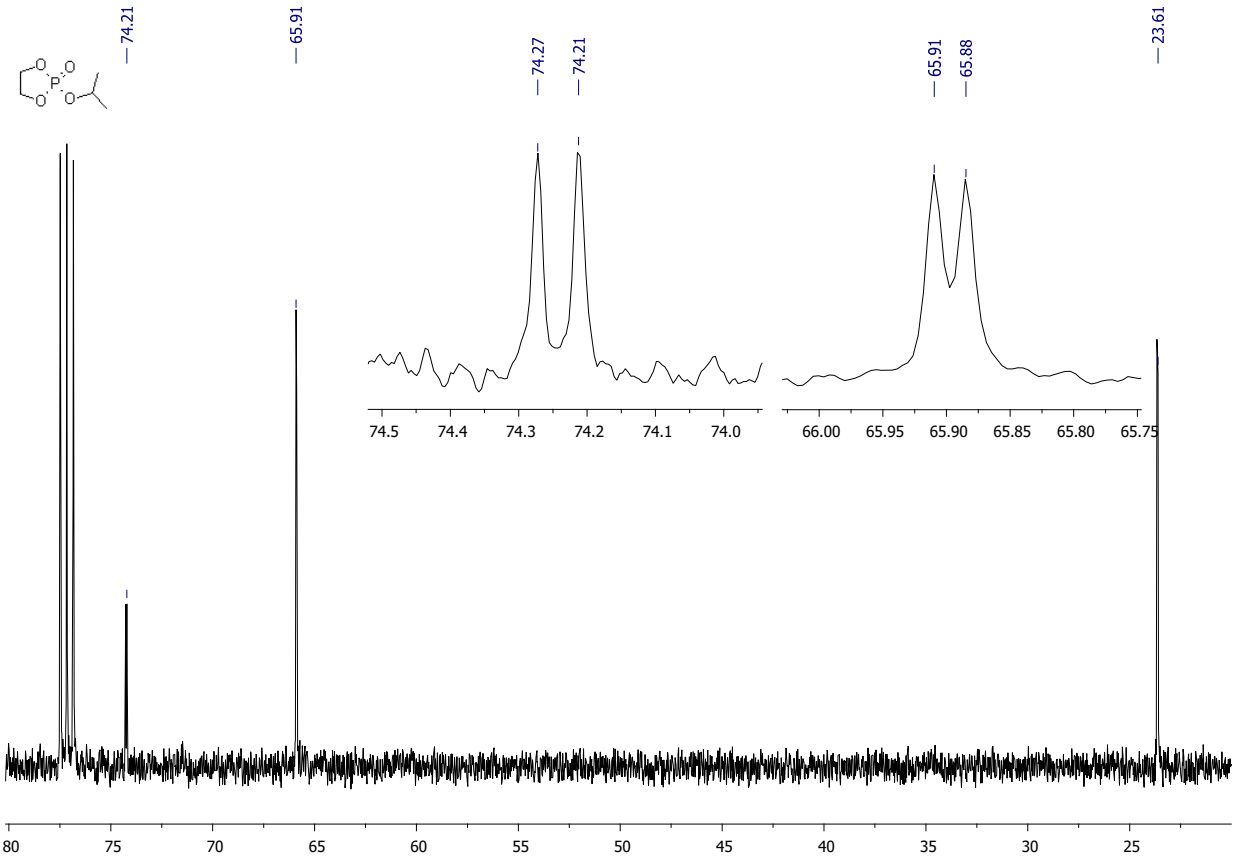


Fig. S11. ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of **^{i}PrOEP** (**2**)

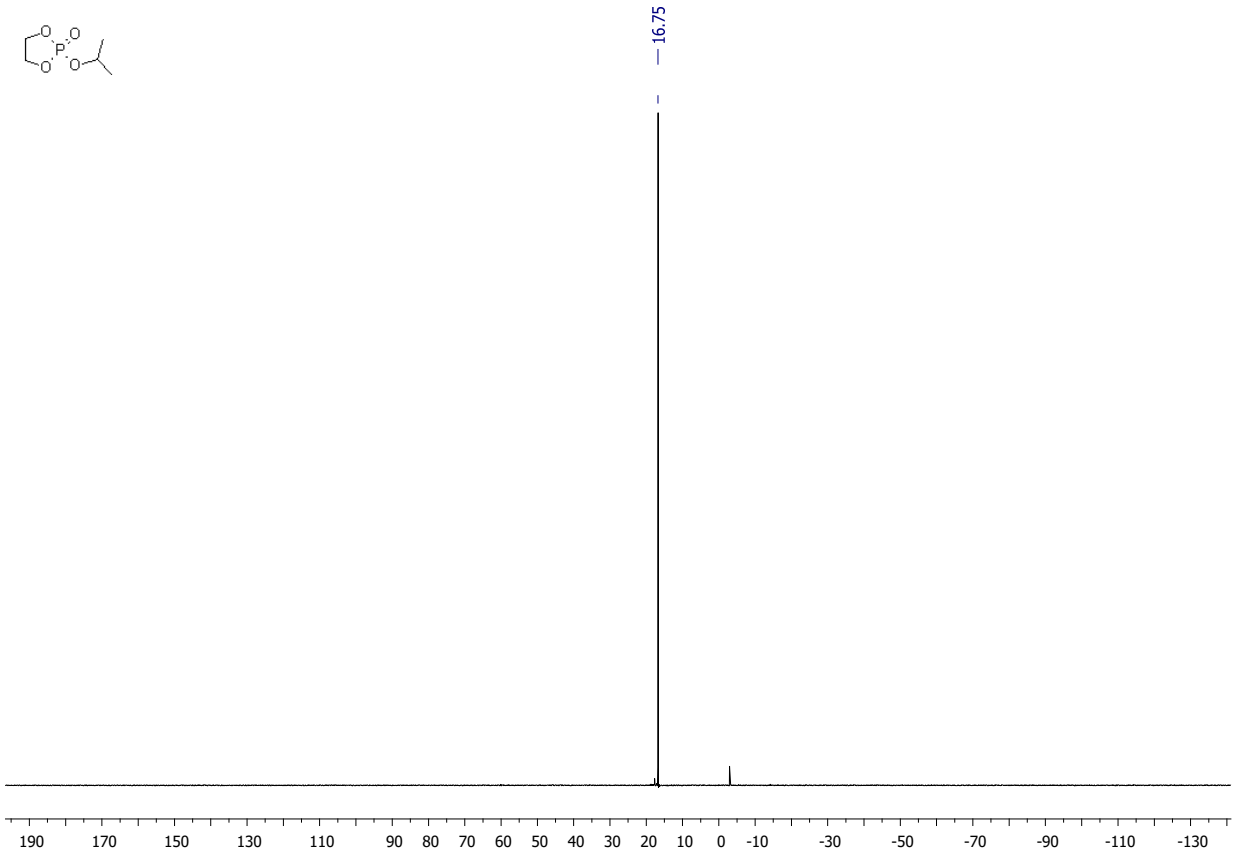
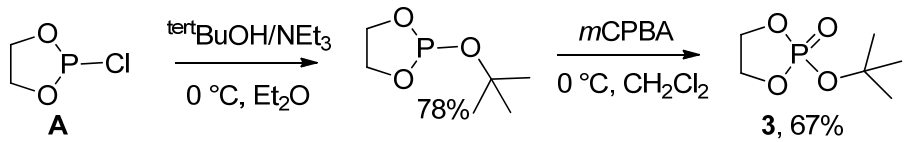


Fig. S12. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of **^{i}PrOEP** (**2**)

S3.3. Syntesis of 2-*tert*-butoxy-2-oxo-1,3,2-dioxaphospholane 4 (*tert*-butyl ethylene phosphate, ^{t}BuOEP)



2-tert-Butoxy-1,3,2-dioxaphospholane.

A flame-dried 1000 mL three-neck flask, equipped with a dropping funnel, was charged with dry tert-butanol (38.6 g, 0.52 mol), dry triethylamine (78 mL, 0.52 mol) and dry diethyl ether (500 mL). A solution of 2-chloro-oxo-1,3,2-dioxaphospholane (66.0 g, 0.52 mol) in dry ether (60 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 purified by distillation under reduced pressure. The yield was 67.1 g (78%). B. p. 70-75°C (13 Torr), colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.14 (m, 2H, OCH_2CH_2O); 3.88 (m, 2H, OCH_2CH_2O); 1.35 (s, 9H, O-C(CH_3)$_3$. $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$, 20 °C): δ 134.57 (s).

2-tert-Butoxy-2-oxo-1,3,2-dioxaphospholane **3** *(tBuOEP).*

A flame-dried 500 mL three-neck flask, equipped with a dropping funnel, was charged with 2-*tert*-butoxy-1,3,2-dioxaphospholane (8.2 g, 0.05 mol) in dry dichloromethane (100 mL). A solution of meta-

chloroperbenzoic acid (~0.055 mol) prepared by drying of the mixture of commercial 70-77% meta-chloroperbenzoic acid (13 g) in 100 mL of dichloromethane over $MgSO_4$, was added dropwise under stirring at 0 °C within 3 hours. The resulting precipitate of meta-chlorobenzoic acid was removed by filtration. The filtrate was treated with the aq. solutions of 15 % K_2CO_3 (2×40 mL) and 20% sodium thiosulfate (2×30 mL), dried over $MgSO_4$ and concentrated *in vacuo* to give a low-melting (M. p. = 28 °C) white crystalline substance. The yield was 6.1g (67%).

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.33 (m, 2H, OCH_2CH_2O); 4.26 (m, 2H, OCH_2CH_2O); 1.47 (s, 9H, O-C(CH_3)$_3$. ^{13}C{H} NMR (101 MHz, $CDCl_3$, 20 °C): δ 84.08 (d, $^2J_{CP}$ = 7.2 Hz, 1C, O-*C*(CH_3)$_3$); 65.52 (d, $^2J_{CP}$ = 2.3 Hz, 2C, O*C*H_2*C*H_2O); 29.67 (d, $^3J_{CP}$ = 4.4 Hz, 3C, O-C(*C*H_3)$_3$). ^{31}P{H} NMR (162 MHz, $CDCl_3$, 20 °C): δ 13.21 (s). For $C_6H_{13}O_4P$ Calc.: C, 40.00; H, 7.27; O, 35.53. Found: C, 40.11; H, 7.20; O, 44.36.

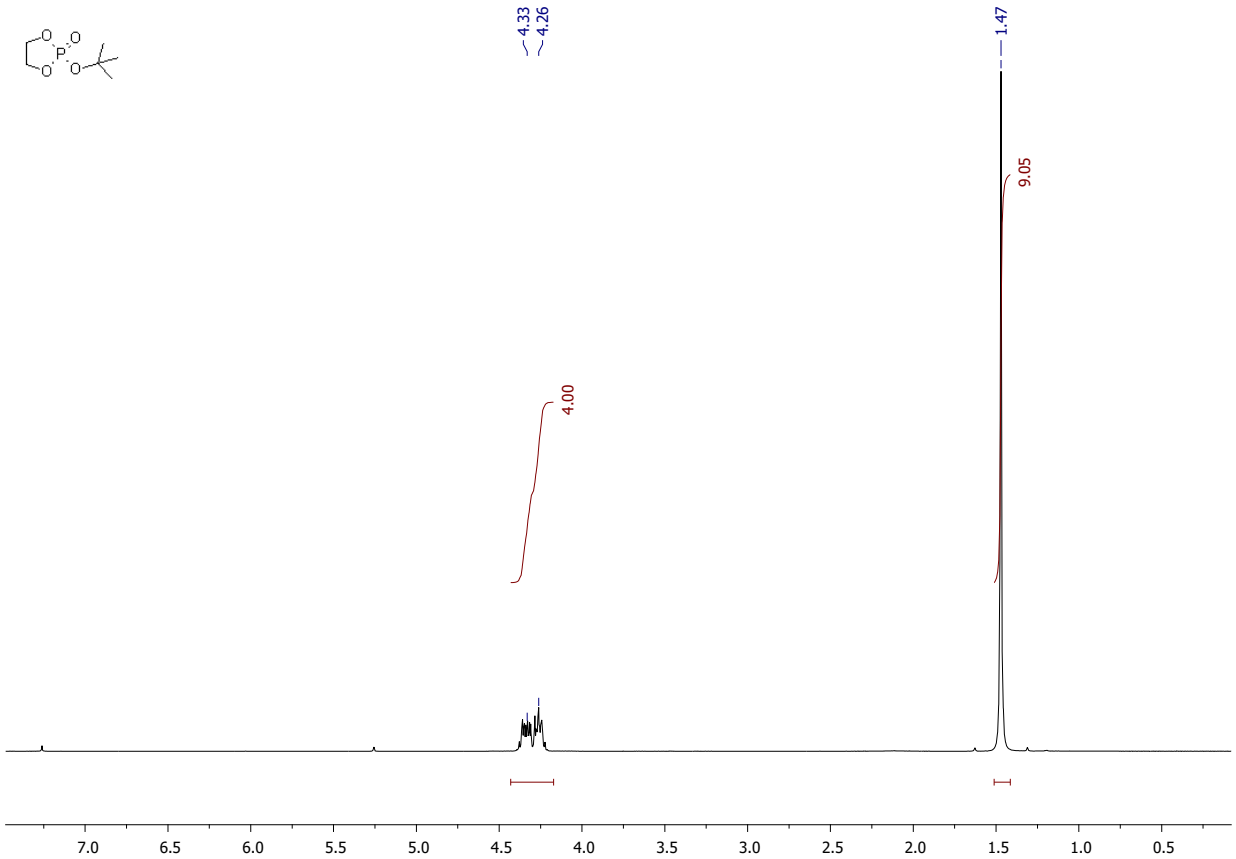


Fig. S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of **^{t}BuOEP** (**3**)

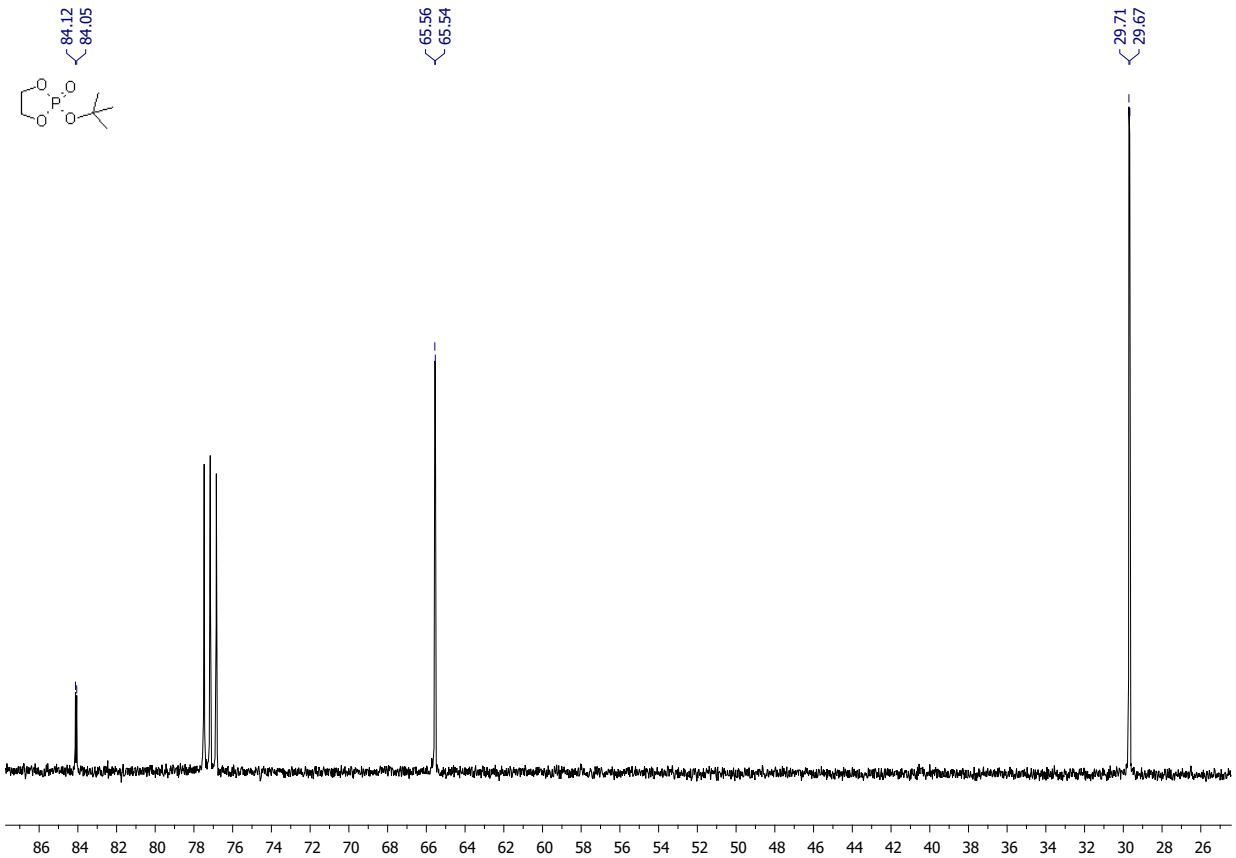


Fig. S14. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of **^{t}BuOEP** (**4**)

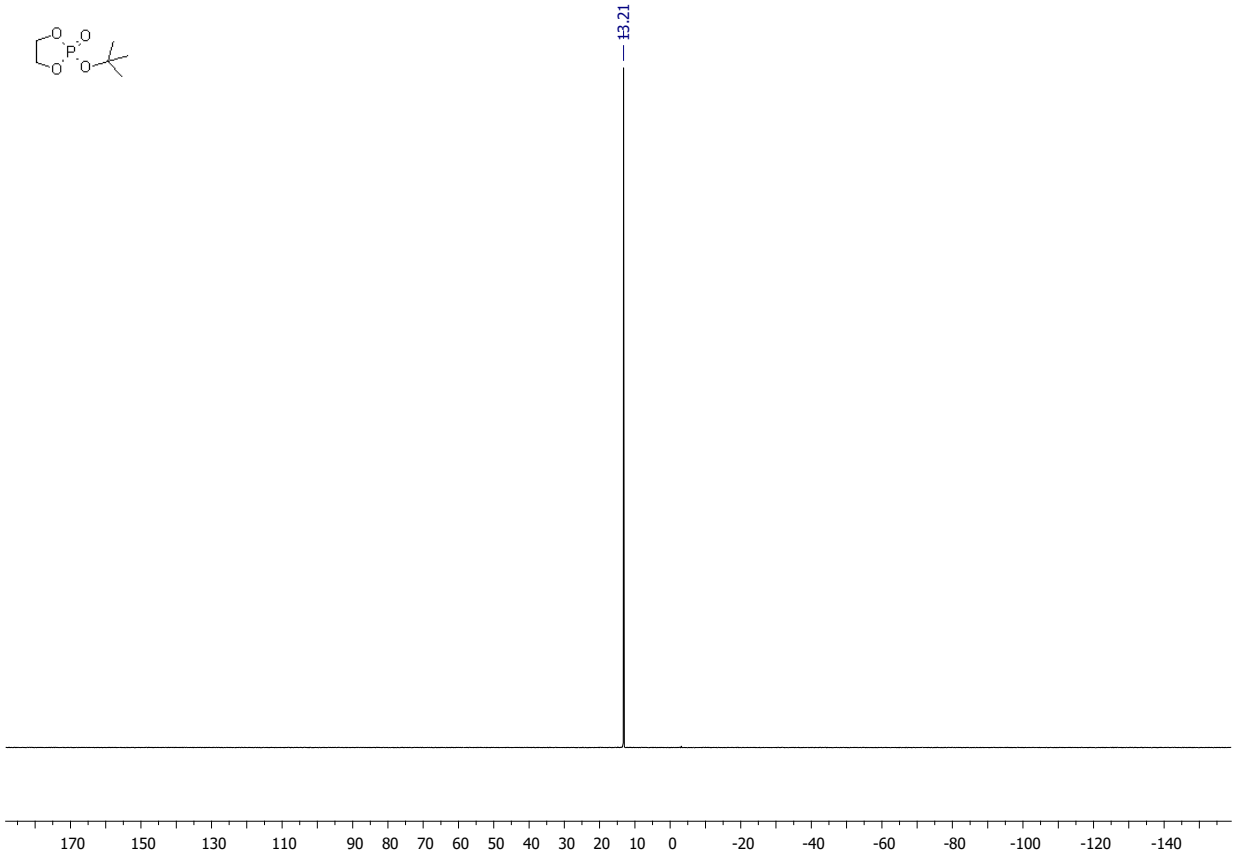
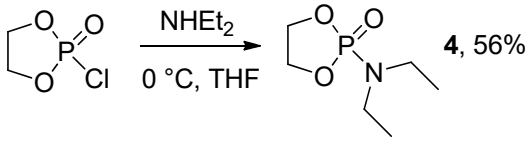


Fig. S15. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of **^{t}BuOEP** (**4**)

S3.4. Syntesis of 2-diethylamino-2-oxo-1,3,2-dioxaphospholane 4 (N,N-diethyl ethylene phosphoramidate, Et_2NEP)



A flame-dried 500 mL three-neck flask, equipped with a dropping funnel, was charged with dry diethylamine (10.4 mL, 0.1 mol) in dry ether (100 mL). A solution of 2-chloro-2-oxo-1,3,2-dioxaphospholane (7.1 g, 0.05 mol) in dry ether (10 mL) was added dropwise under stirring at 0 °C. The mixture was allowed to warm to room temperature and stirred for 2 h. Diethylammonium chloride was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was purified by distillation under reduced pressure. The yield was 5.1 g (56%). B. p. 118-122 °C / 0.8 Torr, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.38 (m, 2H, OCH_2CH_2O), 4.25 (m, 2H, OCH_2CH_2O); 3.04 (qd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HP}$ = 7.2 Hz, 4H, NCH_2CH_3); 1.09 (t, $^3J_{HH}$ = 7.3 Hz, 6H, NCH_2CH_3). ^{13}C{H} NMR (101 MHz, $CDCl_3$, 20 °C): δ 65.44 (d, $^2J_{CP}$ = 2.1 Hz, 2C, OCH_2CH_2O), 40.06 (d, $^2J_{CP}$ = 5.2 Hz, 2C, NCH_2CH_3), 14.28 (d, 2C NCH_2CH_3). ^{31}P{H} NMR (162 MHz, $CDCl_3$, 20 °C): δ 26.69 (s). For $C_6H_{14}NO_3P$ Calc.: C, 40.22; H, 7.88; N, 7.82; O, 26.79. Found: C, 40.28; H, 7.94; N, 7.79; O, 26.72.

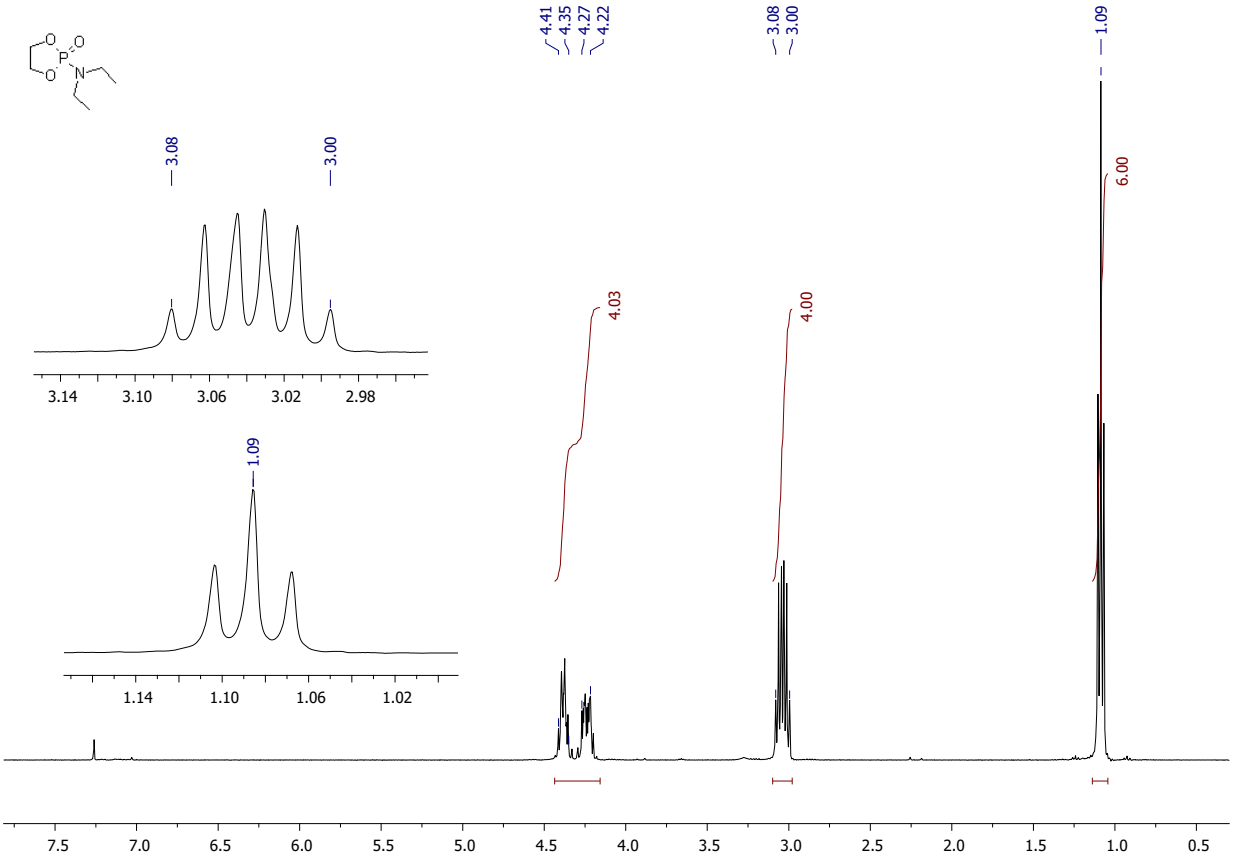


Fig. S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of **Et_2NEP (4)**

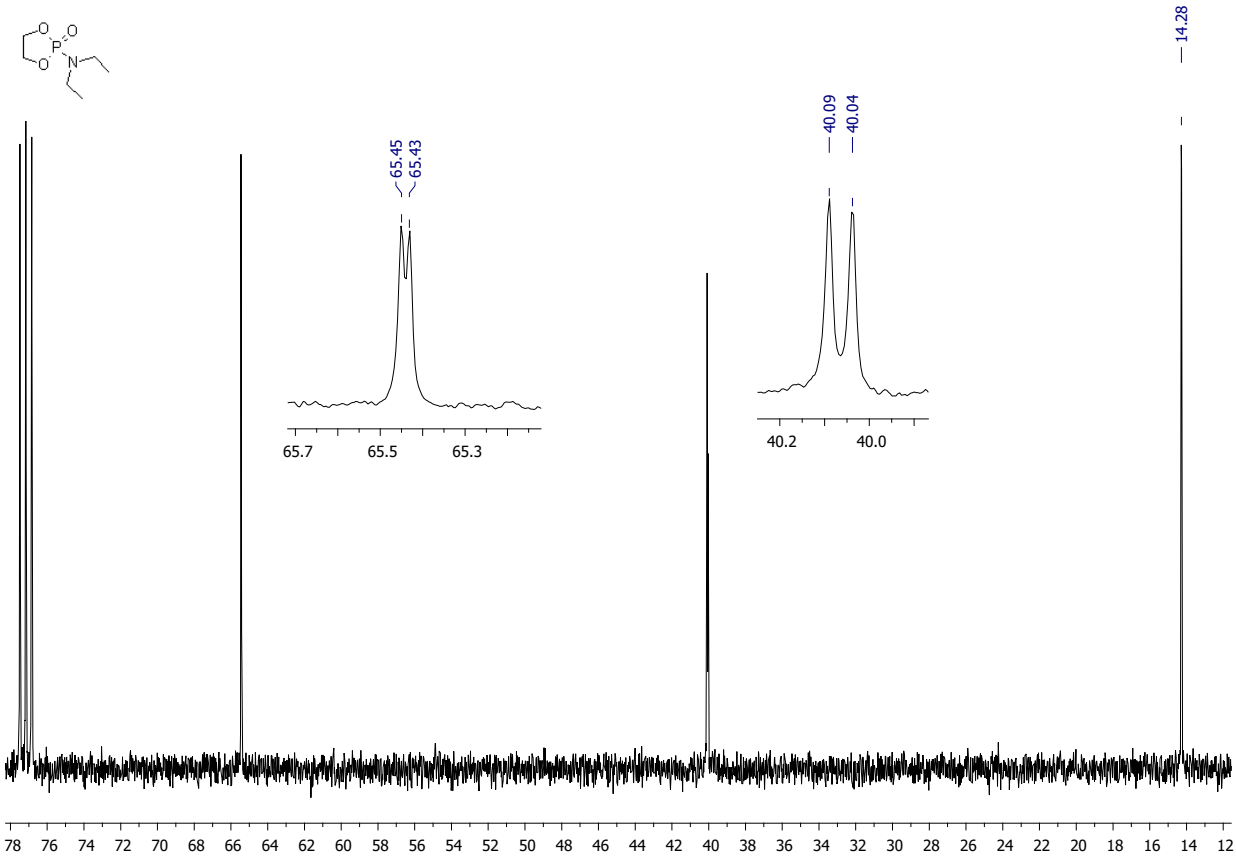


Fig. S17. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of **Et_2NEP** (**4**)

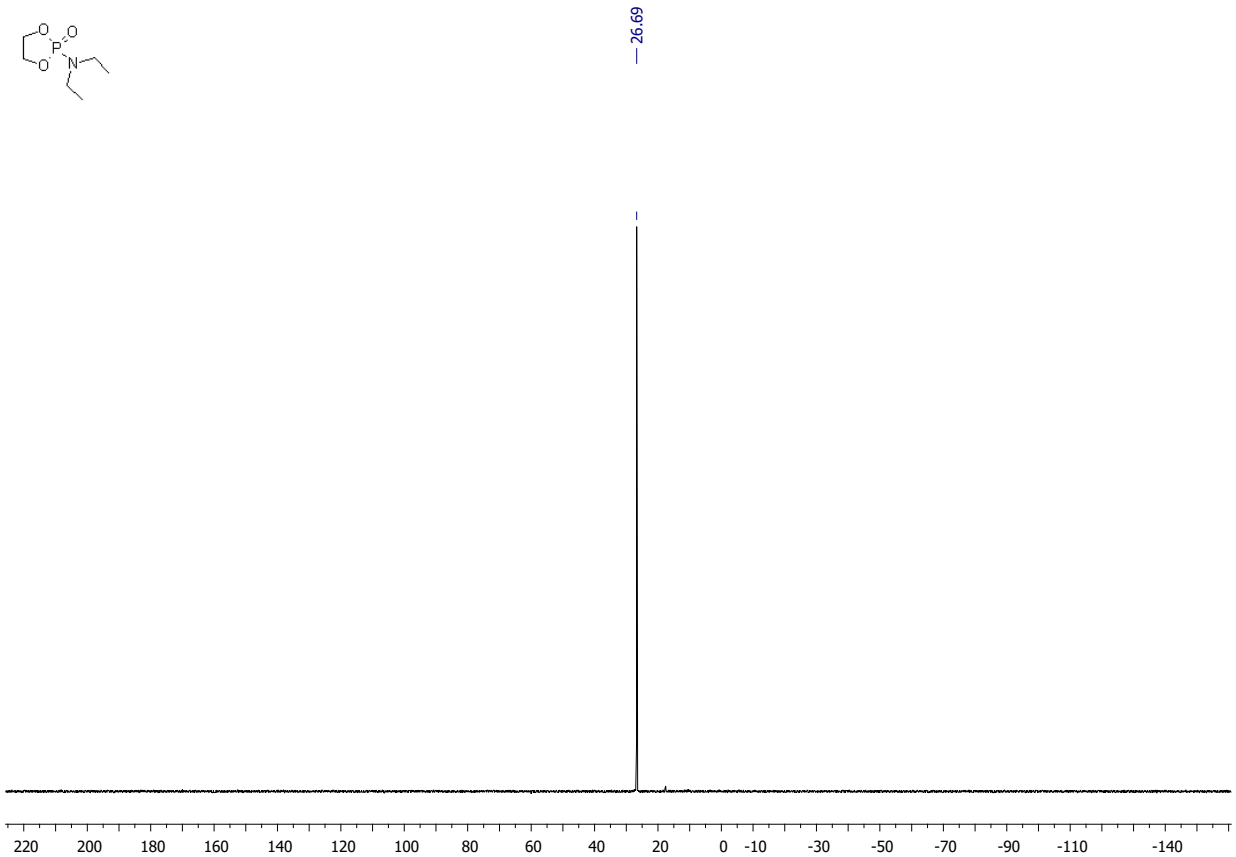
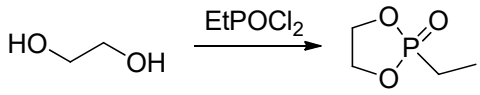


Fig. S18. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of **Et_2NEP** (**4**)

S3.5. Syntesis of 2-ethyl-2-oxo-1,3,2-dioxaphospholane 5 (ethyl ethylene phosphonate, EtPPn)



5, 64%

A flame-dried flask, equipped with two dropping funnels, was charged with 80 mL of dry THF and cooled to −20 °C. Ethylphosphonic acid dichloride (15.6 g, 0.1 mol) was dissolved in dry THF (80 mL) and transferred into one dropping funnel. A solution of dry ethylene glycol (6.6 g, 0.1 mol) and dry pyridine (16.9 g, 0.2 mol) in THF (60 mL) was transferred into the second dropping funnel. Dropping speed was adjusted to be approximately equal for both mixtures. After complete addition the solution was stirred at −20 °C within 20 h. The precipitate of the pyridinium hydrochloride was removed by filtration, the filtrate was concentrated to one half of the initial volume and cooled to −50 °C. The new portion of the pyridinium hydrochloride was removed by filtration, after that the filtrate was evaporated. The residue was purified by distillation under reduced pressure. The yield was 8.6 g (yield: 64%). B. p. 106-108 °C / 0.36 Torr, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.44 (m, 2H, OCH_2CH_2O); 4.23 (m, 2H, OCH_2CH_2O); 1.94 (dq, $^{3}J_{HH}$ = 7.9 Hz, $^{2}J_{HP}$ = 18.1 Hz, 2H, CH_2CH_3); 1.16 (dt, $^{3}J_{HH}$ = 7.9 Hz, $^{3}J_{HP}$ = 21.3 Hz, 3H, CH_2CH_3).
^{13}C{H} NMR (101 MHz, $CDCl_3$, 20 °C): δ 66.39 (bs, 2C, OCH_2CH_2O); 19.58 & 18.25 (d, $^{1}J_{CP}$ = 135 Hz, 1C, CH_2CH_3); 6.85 (d, $^{2}J_{CP}$ = 7.0 Hz, 1C, CH_2CH_3). ^{31}P{H} NMR (162 MHz, $CDCl_3$, 20 °C): δ 52.64 (s).

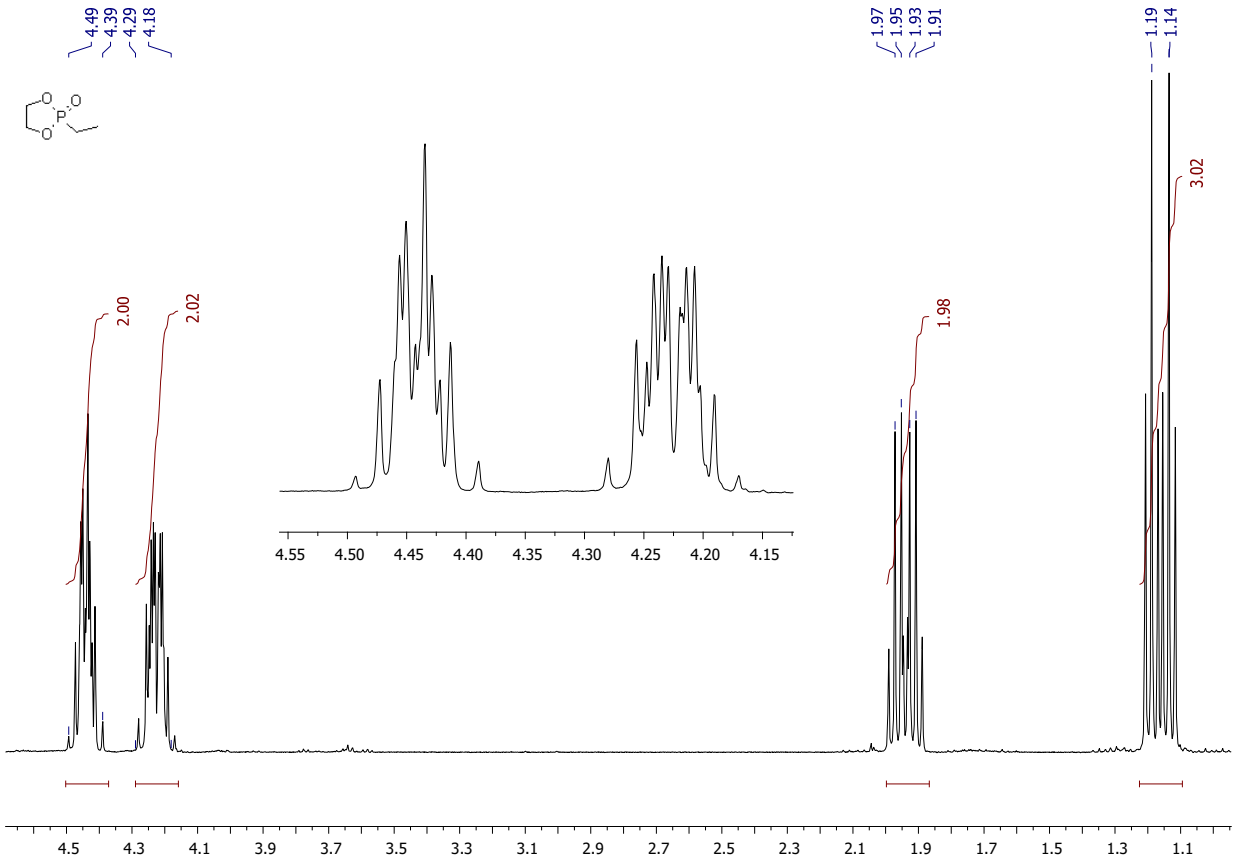


Fig. S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of **EtPPn** (**5**)

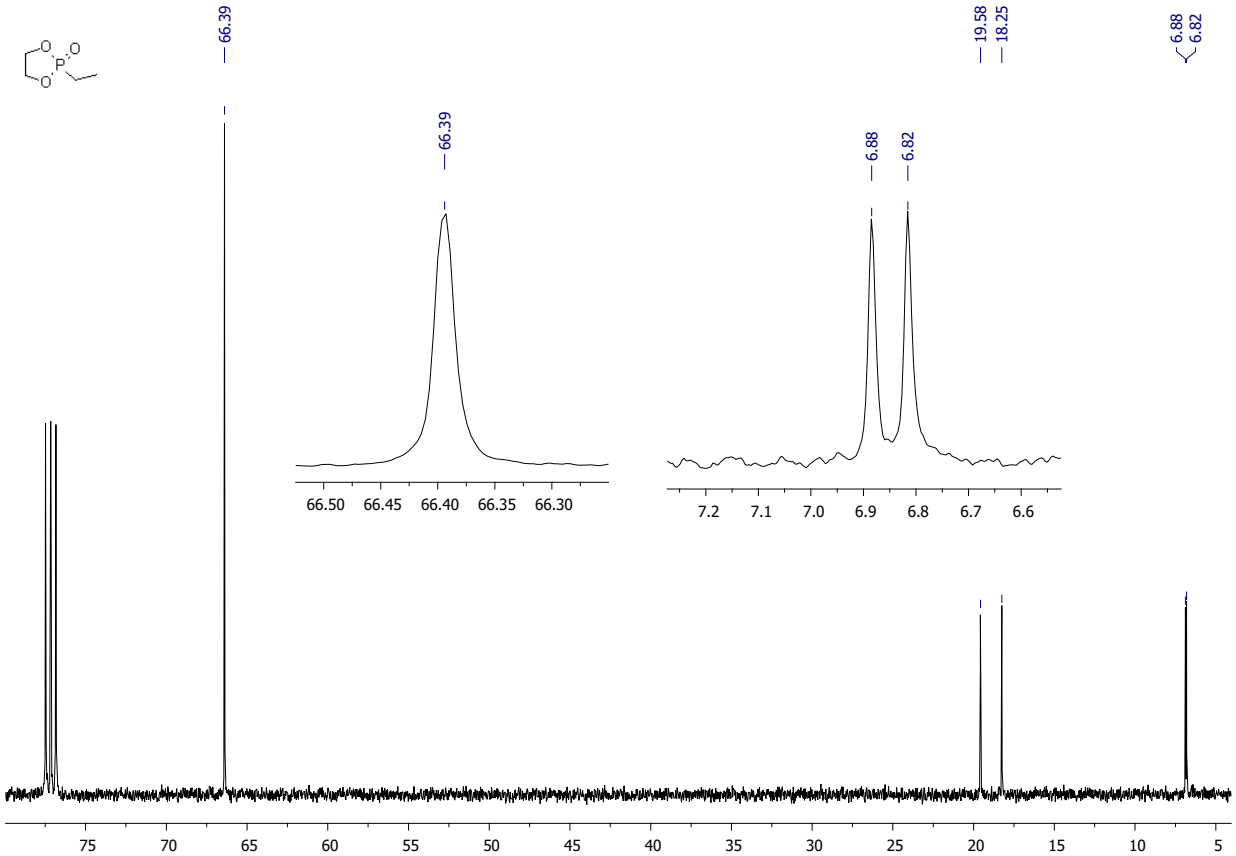


Fig. S20. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of **EtPPn** (**5**)

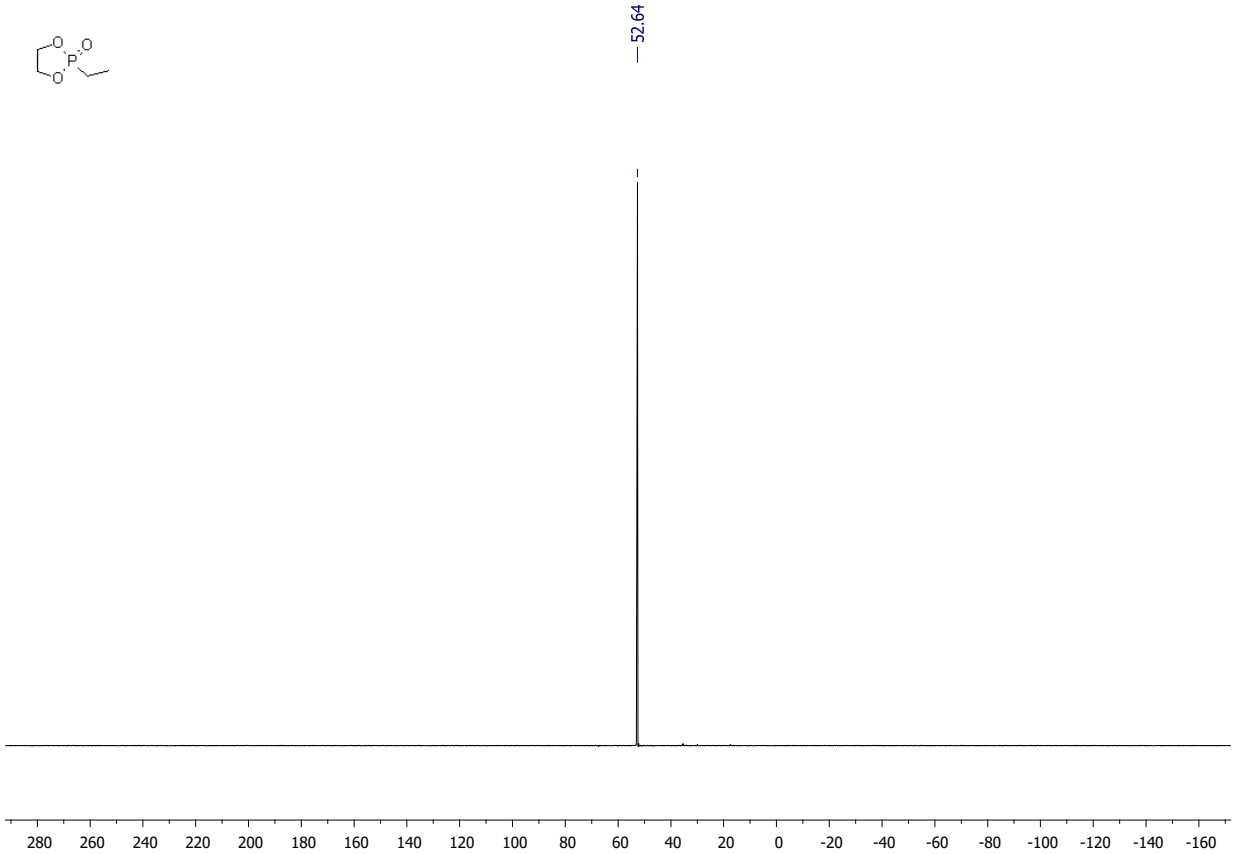


Fig. S21. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of **EtPPn** (**5**)

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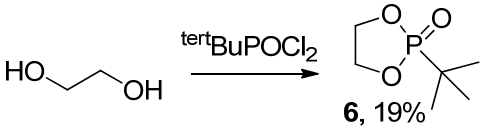
S3.6. Syntesis of 2-*tert*-butyl-2-oxo-1,3,2-dioxaphospholane 6 (*tert*-butyl ethylene phosphonate, tBuPPn)



A flame-dried flask was charged with dry *tert*-butyldichlorophosphate (12.5 g, 70 mmol), ethylene glycol (4.34 g, 70 mmol) and dry THF (150 mL). Sodium hydride (60% suspension, 5.6 g, 0.14 mol) was added by portions, the mixture was stirred at 40 °C within 2 hours and at 20 °C overnight. The resulting suspension was treated with 500 mL of water, and extracted three times with 50 mL of dichloromethane. The organic phase was separated, dried and concentrated *in vacuo*. The residue was recrystallyzed twice from hexane to give **tBuEP** as a white crystalline solid. The yield was 4.6 g, 19%.

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.49 (m, 2H, OCH_2CH_2O); 4.24 (m, 2H, OCH_2CH_2O); 1.25 (d, $^{2}J_{HP}$ = 17.6 Hz, 9H, $C(CH_3)_3$.

^{13}C{H} NMR (101 MHz, $CDCl_3$, 20 °C): δ 66.70 (d, $^{2}J_{CP}$ = 2.3 Hz, 2C, OCH_2CH_2O); 32.95 & 31.65 (d, $^{1}J_{CP}$ = 129.7 Hz, 1C, $C(CH_3)_3$); 24.98 (d, $^{2}J_{CP}$ = 2.0 Hz, 3C, $C(CH_3)_3$).

^{31}P{H} NMR (162 MHz, $CDCl_3$, 20 °C): δ 57.52 (s).

For $C_6H_{13}O_3P$ Calc.: C, 43.90; H, 7.98; O, 29.24. Found: C, 43.95; H, 8.02; O, 29.19.

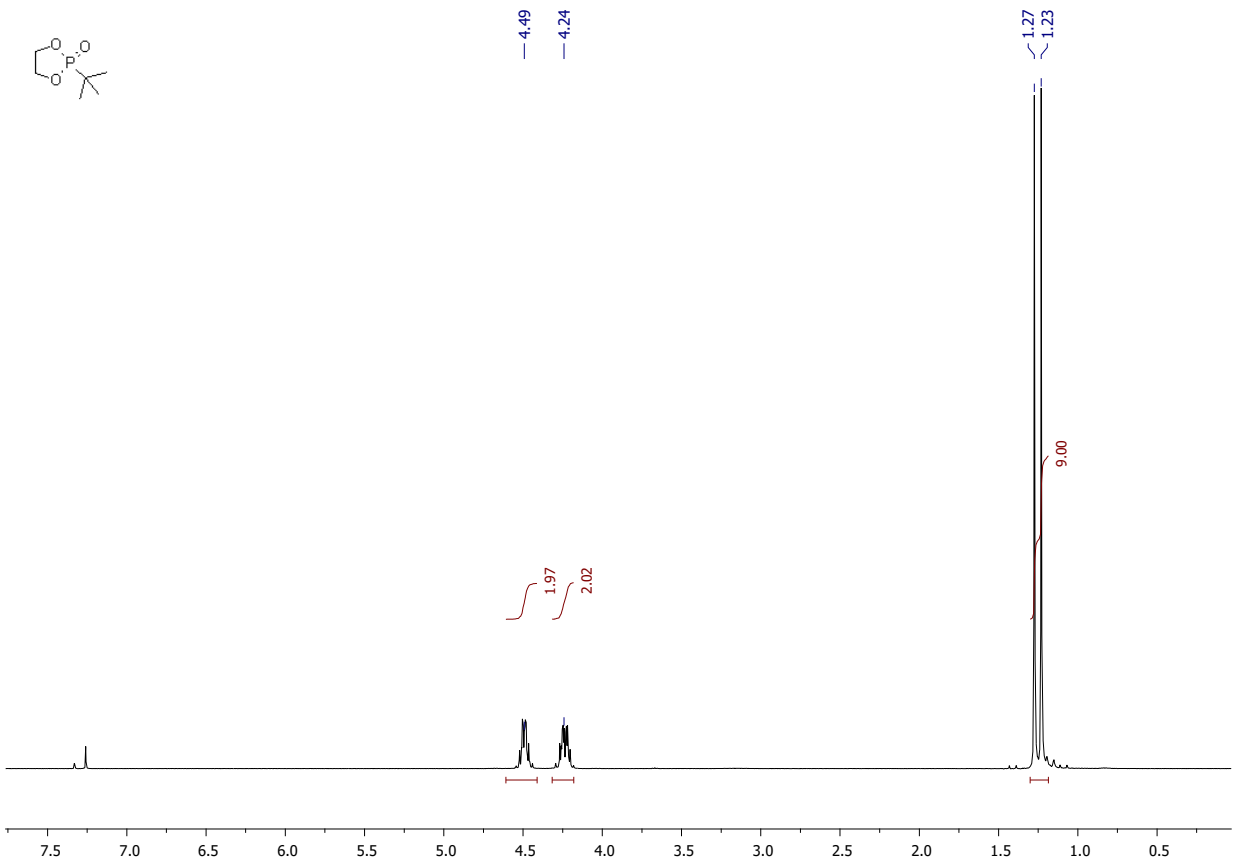


Fig. S22. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of **^{t}BuPPn** (**6**)

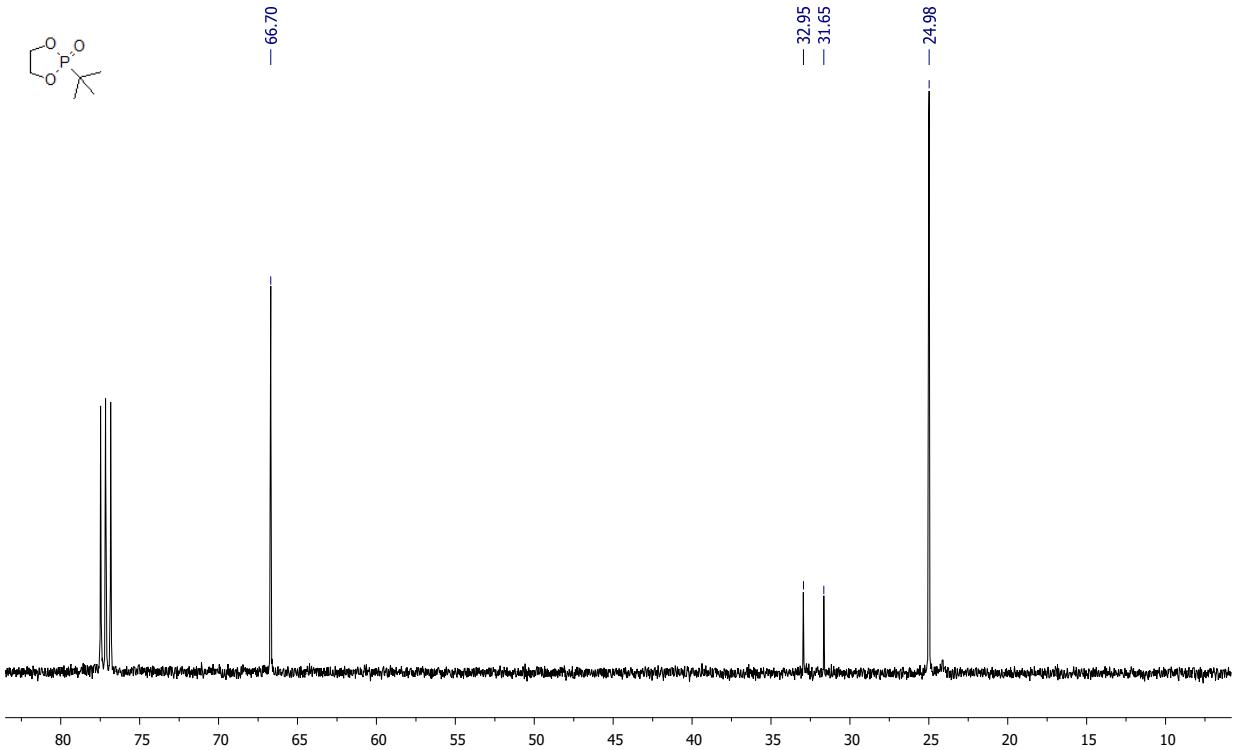


Fig. S23. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of **^{t}BuPPn** (**6**)

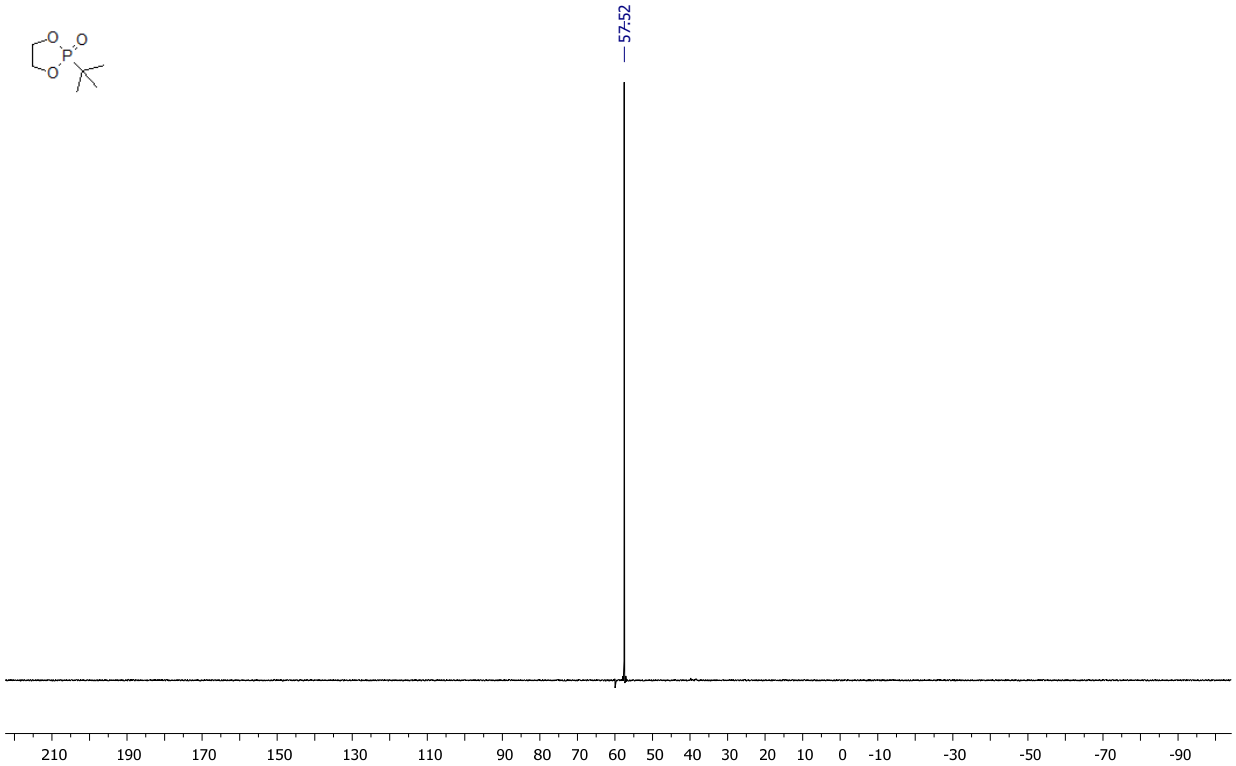


Fig. S24. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of **^{t}BuPPn** (**6**)

References

1. S. Schöttler, G. Becker, S. Winzen, T. Steinbach, K. Mohr, K. Landfester, V. Mailänder and F. R. Wurm, *Nature Nanotech.* 2016, *11*, 372−377.

2. T. S. Stukenbroeker, D. Solis-Ibarra and R. M. Waymouth, *Macromolecules* 2014, *47*, 8224−8230.

S4. Homopolymer synthesis and characterization

S4.1. Polymerization of ^{i}PrOEP

Polymerization of ***^{i}PrOEP*** *using* ***Mg3*** *as the catalyst (Table 1, Run 3).*

^{i}PrOEP (0.977 g, $5.88\cdot10^{-3}$ mol) was introduced into a vial equipped with magnetic stirrer and septum, 0.46 mL dry CH_2Cl_2 was added to **^{i}PrOEP**. A stock solution of **Mg3** in dry THF (317 mg, $7.50\cdot10^{-4}$ mol Mg in 8.2 mL solution) was prepared. The polymerization was started by rapid addition of the stock solution of **5** (0.4 mL solution, $7.31\cdot10^{-5}$ mol Mg) to the stirred solution of **^{i}PrOEP** by a syringe to give a total reaction concentration of 2M **^{i}PrOEP**. The polymerization was terminated after the required time by the addition of an excess of acetic acid in CH_2Cl_2. The monomer conversion was determined using ^{31}P NMR spectroscopy by integration of the monomer (δ 16.7 ppm) and polymer (δ –2.15 ppm) resonance signals. The polymer was purified by precipitation using a 5-fold volume excess of dry diethyl ether and subsequent centrifugation (5 min, 4000 rpm), supernatant was decanted and redissolved in dry CH_2Cl_2, then precipitated and centrifugated again. The polymer obtained was dissolved in dry CH_2Cl_2, the solvent was removed *in vacuo*. The yield was 0.85 g (87%).

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 5.00 (d, $^{3}J_{HP}$ = 7.9 Hz, PhCH_2); 4.61 (d of sept, $^{3}J_{HP}$ = $^{3}J_{HH}$ = 6.3 Hz, 1H); 4.16 (dd, $^{3}J_{HP}$ = 4.3 Hz, 4H); 3.72 (d, $^{3}J_{HH}$ = 6.3 Hz, 3H), 1.28 (d, $^{3}J_{HH}$ = 6.3 Hz, 6H).

^{13}C{H} NMR (101 MHz, $CDCl_3$, 20 °C): δ 73.50 (d, $^{2}J_{CP}$ = 6.1 Hz); 65.99 (dd, $^{2}J_{CP}$ ~ $^{3}J_{CP}$ ~ 6.5 Hz); 23.60 (d, $^{3}J_{CP}$ = 5.5 Hz).

^{31}P{H} NMR (162 MHz, $CDCl_3$, 20 °C): δ –2.15.

M_n (NMR) of polyphosphates were calculated using integral intensities of Ph$C\underline{H_2}$O (5.0 ppm, 2H), [$PhCH_2O$]; –$OC\underline{H_2}C\underline{H_2}O$– (4.16 ppm, 4H), [$OCH_2CH_2O$] and –$C\underline{H_2}OH$ (3.7 ppm, 2H) [CH_2OH] by the formula:

$$M_n(NMR) = \frac{I[OCH_2CH_2O] + I[CH_2OH]}{I[PhCH_2O] + I[CH_2OH]} \times M_{Sub} + 108.13$$

where 108.13 is MW of $PhCH_2OH$.

M_n (theor) was calculated by formula

$$M_n(theor) = \frac{[Sub]}{[Cat]} \times M_{Sub} + 108.13$$

For example, poly(^{i}PrOEP) obtained by polymerization of **^{i}PrOEP** in the presence of **Mg3** (monomer/Mg ratio 80), is characterized by M_n(NMR) = $1.38\cdot10^{4}$ Da (Table 1 Run 3 in the main text of the article, for ^{1}H NMR spectrum see Figure S25).

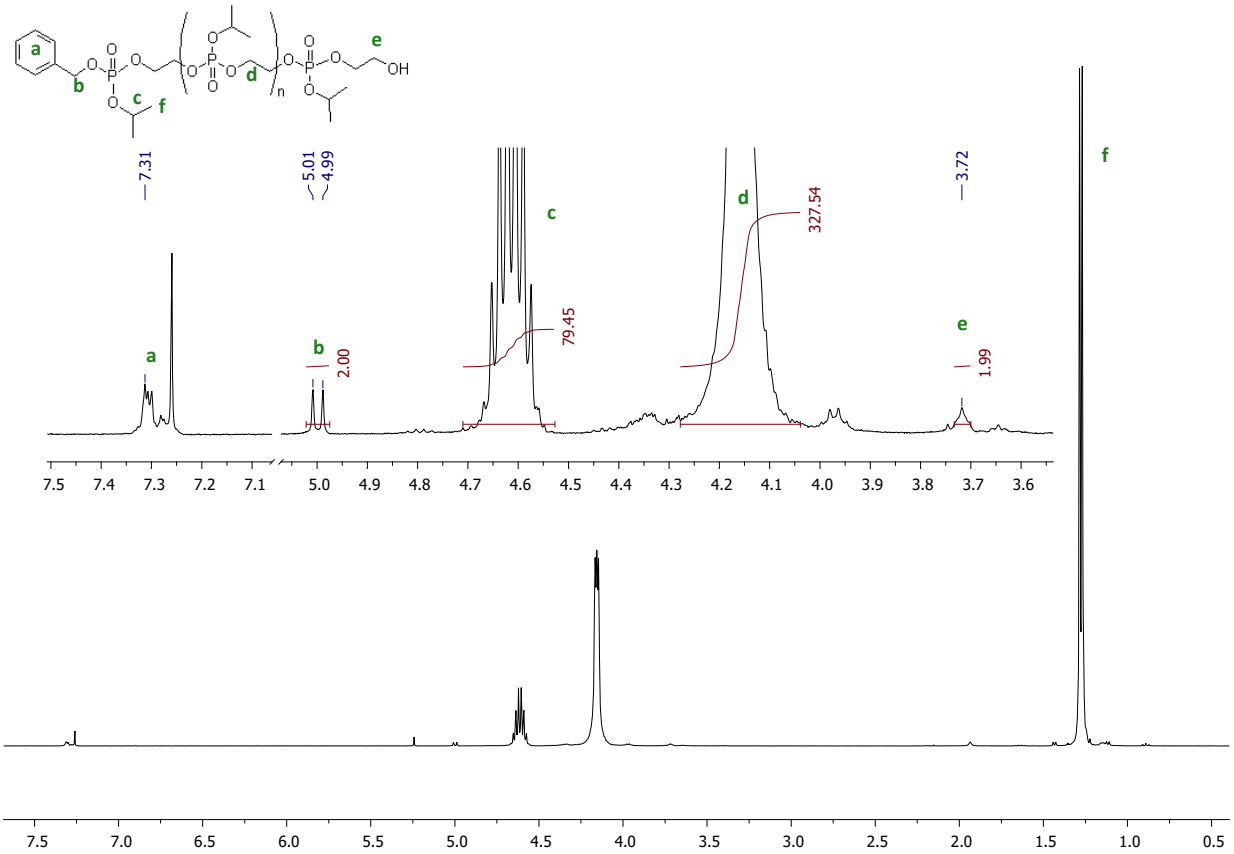


Fig. S25. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of poly(iPrOEP) prepared using **Mg3** as the catalyst at 20 °C, [*Sub*]/[Cat] = 80 (Table 1, Run 3)

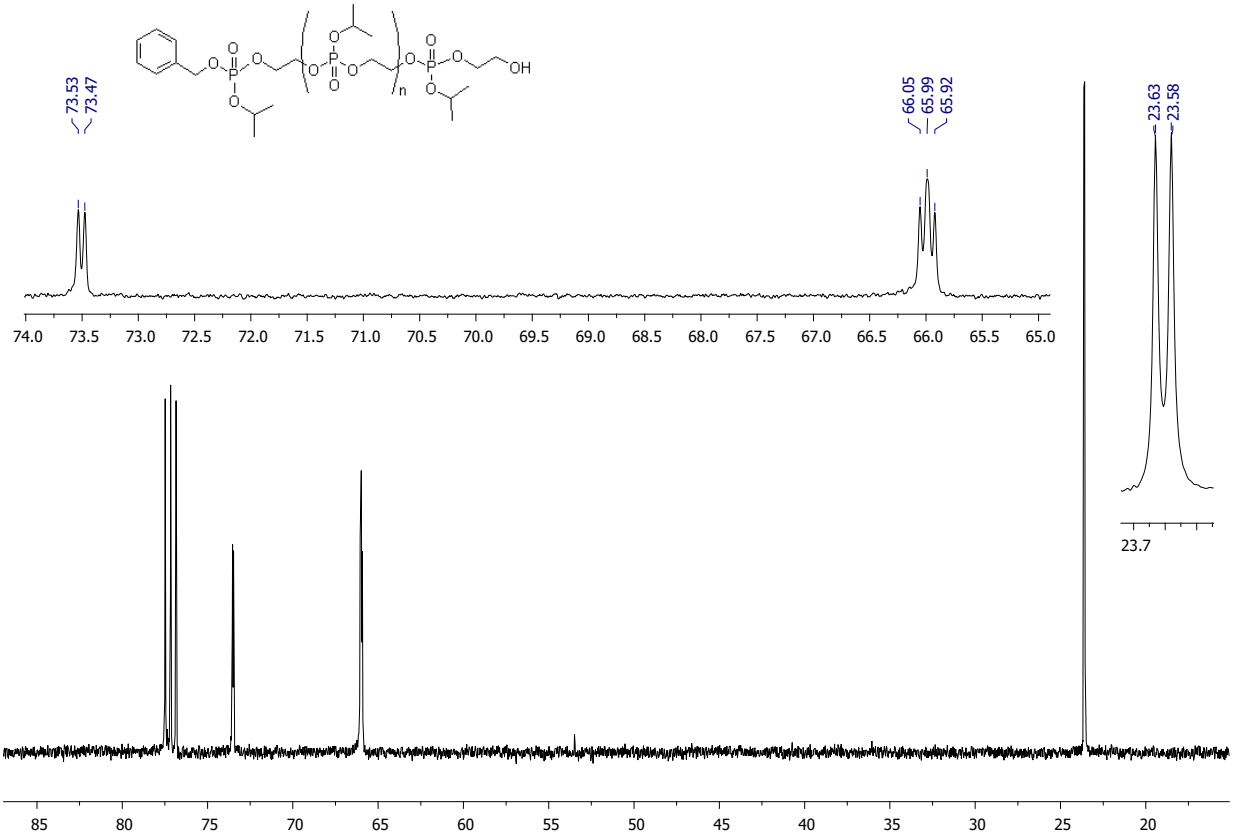


Fig. S26. ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of poly(iPrOEP) (Table 1, Run 3)

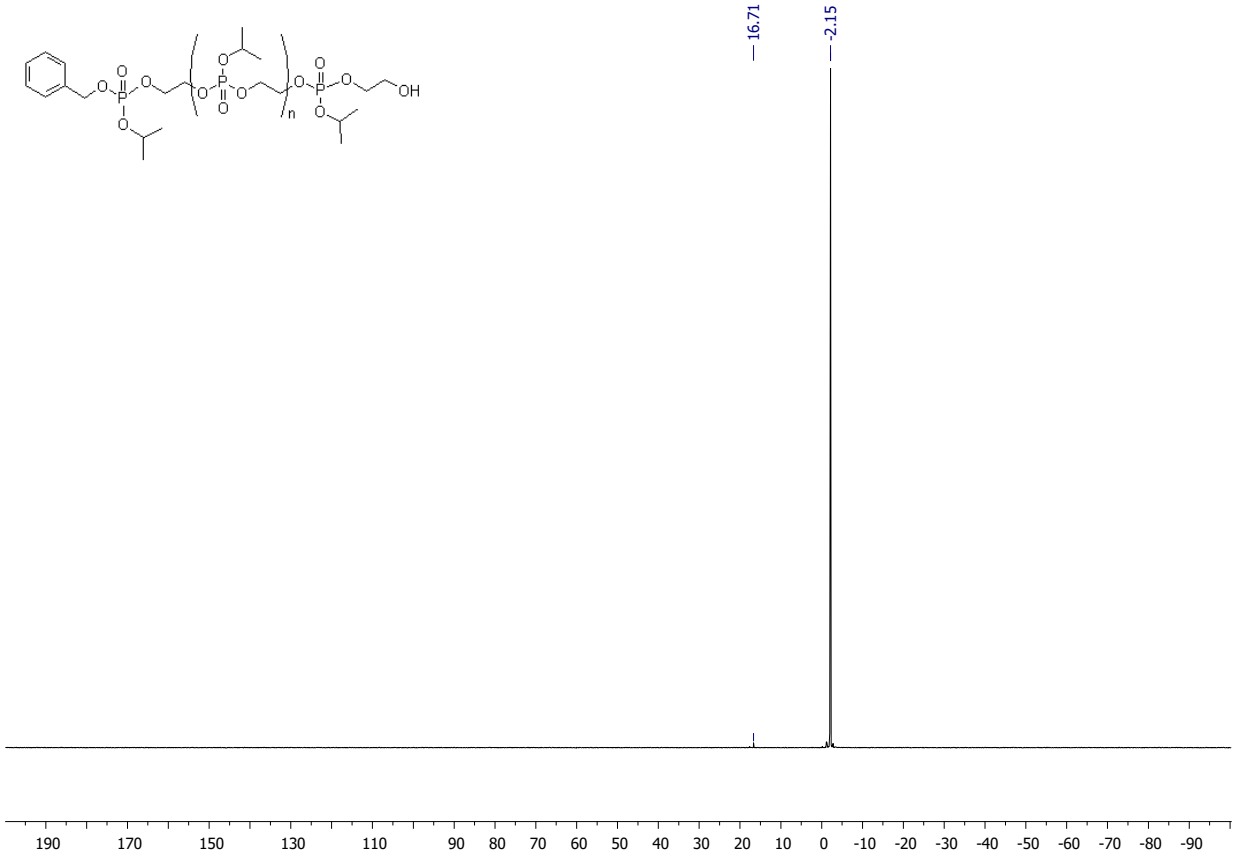


Fig. S27. $^{31}P\{^{1}H\}$NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of poly(iPrOEP) (Table 1, Run 3)

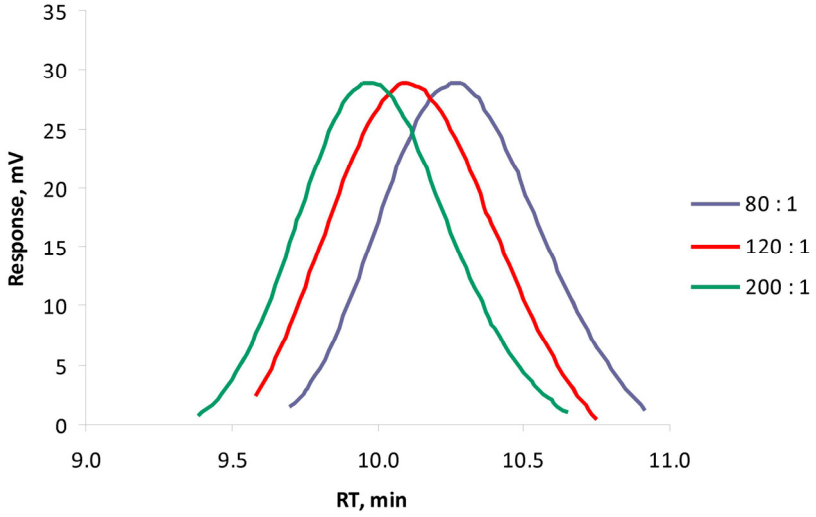


Fig. S28. SEC traces of poly(^{i}PrOEP) samples obtained in the presence of **Mg3** for different monomer/catalyst ratios (Table 1, Runs 3-5)

S4.2. Polymerization of MeOEP

*Polymerization of MeOEP using **Mg3** as the catalyst at 20 °C (Table 2, Run 1).*

MeOEP (0.252 g, 0.181 mL, $1.82\cdot10^{-3}$ mol) was introduced into a vial equipped with magnetic stirrer and septum, 0.53 mL dry CH_2Cl_2 was added to MeOEP. A stock solution of **Mg3** in dry THF (317 mg, $7.50\cdot10^{-4}$ mol Mg in 8.2 mL solution) was prepared. The polymerization was started by rapid addition of the stock solution of **5** (0.2 mL solution, $1.82\cdot10^{-5}$ mol Mg) to the stirred solution of MeOEP by a syringe

to give a total reaction concentration of 2M MeOEP. The polymerization was terminated after 1 hour by the addition of an excess of acetic acid in CH_2Cl_2. The monomer conversion was determined using ^{31}P NMR spectroscopy by integration of the monomer (δ 18.6 ppm) and polymer (δ –0.19 ppm) resonance signals. The polymer was precipitated twice using a 5-fold volume excess of dry diethyl ether. The precipitated polymer was redissolved in dry CH_2Cl_2, the solvent was removed *in vacuo*. The yield was 0.21 g (84%). The amount of branches in polymer chain was determined using ^{31}P NMR spectroscopy by integration of the resonance signals of branched (δ –1.47 ppm) and unbranched (δ –0.19 ppm) phosphorus atoms, see Fig. S31.

*Polymerization of MeOEP using **TBD** as the catalyst at 20 °C (Table 2, Run 2).*

MeOEP (0.496 g, 0.357 mL, $3.59\cdot10^{-3}$ mol) was introduced into a vial equipped with magnetic stirrer and septum, 0.85 mL dry CH_2Cl_2 was added to MeOEP. A stock solution of TBD in dry toluene (0.50 g, $3.59\cdot10^{-3}$ mol in 40.0 mL solution) and a stock solution of the $PhCH_2OH$ (initiator) in dry CH_2Cl_2 (39 mg benzyl alcohol, $3.61\cdot10^{-4}$ mol in 2.0 mL solution) were prepared. 0.2 mL of the stock solution of the initiator ($3.61\cdot10^{-5}$ mol) was added to the stirred solution of MeOEP. The polymerization was started by rapid addition of the stock solution of TBD (0.4 mL solution, $3.59\cdot10^{-5}$ mol) to the to the reaction mixture by a syringe to give a total reaction concentration of 2M MeOEP. The polymerization was terminated after 1 hour by the addition of an excess of acetic acid in CH_2Cl_2. The monomer conversion was determined using ^{31}P NMR spectroscopy by integration of the monomer (δ 18.6 ppm) and polymer (δ –0.19 ppm) resonance signals. The polymer was precipitated twice using a 5-fold volume excess of dry diethyl ether. The precipitated polymer was redissolved in dry CH_2Cl_2, the solvent was removed *in vacuo*. The yield was 0.44 g (88%). The amount of branches in polymer chain was determined using ^{31}P NMR spectroscopy by integration of the resonance signals of branched (δ –1.47 ppm) and unbranched (δ –0.19 ppm) phosphorus atoms, see Fig. S33.

*Polymerization of MeOEP using **TBD** as the catalyst at 20 °C (Table 2, Run 3).*

The same experimental was performed. Reaction time was 24 h.

*Polymerization of MeOEP using **DBU/TU** as the catalyst at 20 °C (Table 2, Runs 4-6).*

MeOEP (1.39 g, 1.0 mL, $1.01\cdot10^{-2}$ mol) and TU (0.187 g, $5.05\cdot10^{-4}$ mol) were introduced into a vial equipped with magnetic stirrer and septum. 3.65 mL dry CH_2Cl_2 was added to MeOEP and TU. A stock solution of DBU in dry CH_2Cl_2 (0.769 g, $5.05\cdot10^{-3}$ mol in 2.0 mL solution) and a stock solution of the $PhCH_2OH$ (initiator) in dry CH_2Cl_2 (0.109 g, $1.01\cdot10^{-3}$ mol in 2.0 mL solution) were prepared. 0.2 mL of the stock solution of the initiator ($1.01\cdot10^{-4}$ mol) was added to the stirred solution of MeOEP and TU. The polymerization was started by rapid addition of the stock solution of DBU (0.2 mL, $5.05\cdot10^{-4}$ mol) to the reaction mixture by a syringe to give a total reaction concentration of 2M MeOEP. The polymerization was terminated after 1 hour by the addition of an excess of acetic acid in toluene. The monomer conversion was determined using ^{31}P NMR spectroscopy by integration of the monomer (δ 18.6 ppm) and polymer (δ –0.19 ppm) resonance signals. The polymer was precipitated twice using a 5-fold volume excess of dry diethyl ether. The precipitated polymer was redissolved in dry CH_2Cl_2, the solvent was removed *in vacuo*. The yield was 1.20 g (86%). The amount of branches in polymer chain was determined using ^{31}P NMR spectroscopy by integration of the resonance signals of branched (δ –1.47 ppm) and unbranched (δ – 0.19 ppm) phosphorus atoms, see Fig. S34.

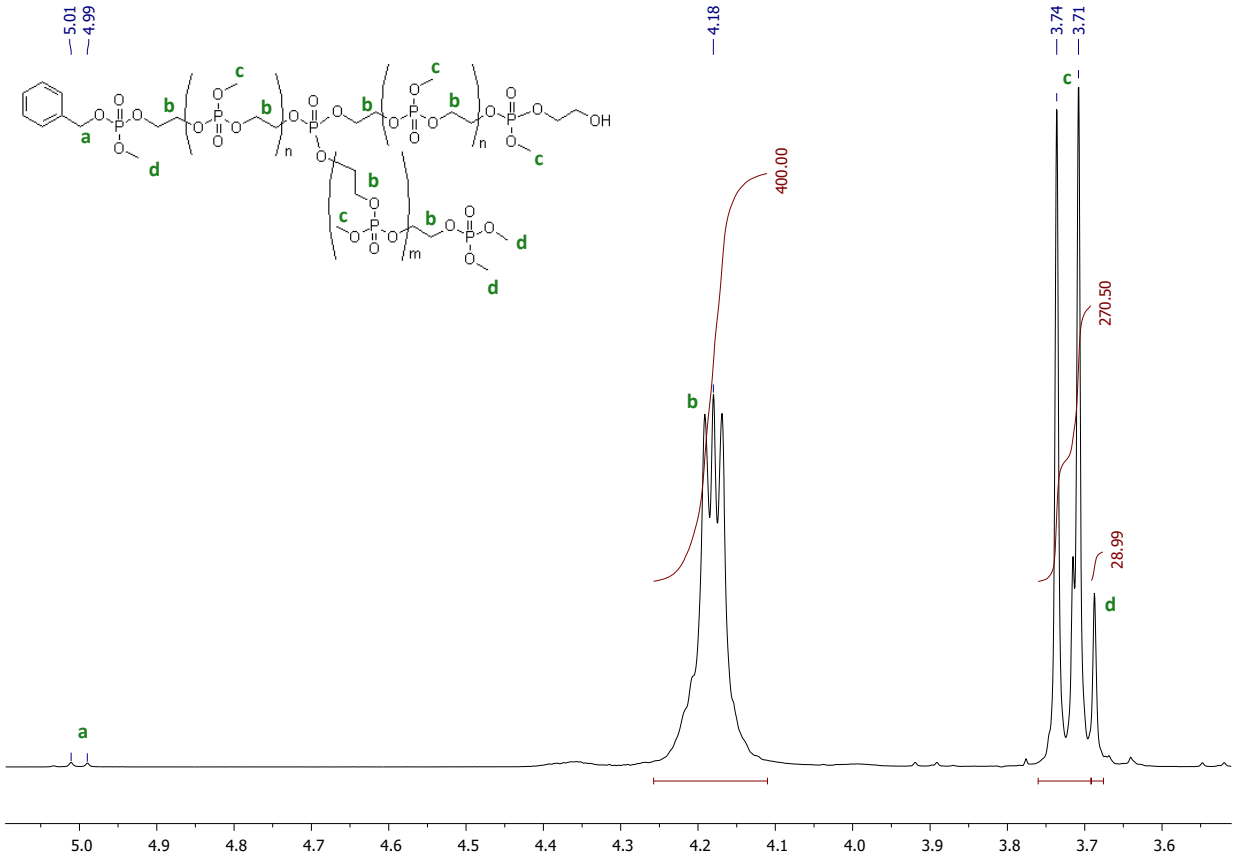


Fig. S29. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of partially branched poly(MeOEP) prepared using **Mg3** as the catalyst at 20 °C (Table 2, Run 1)

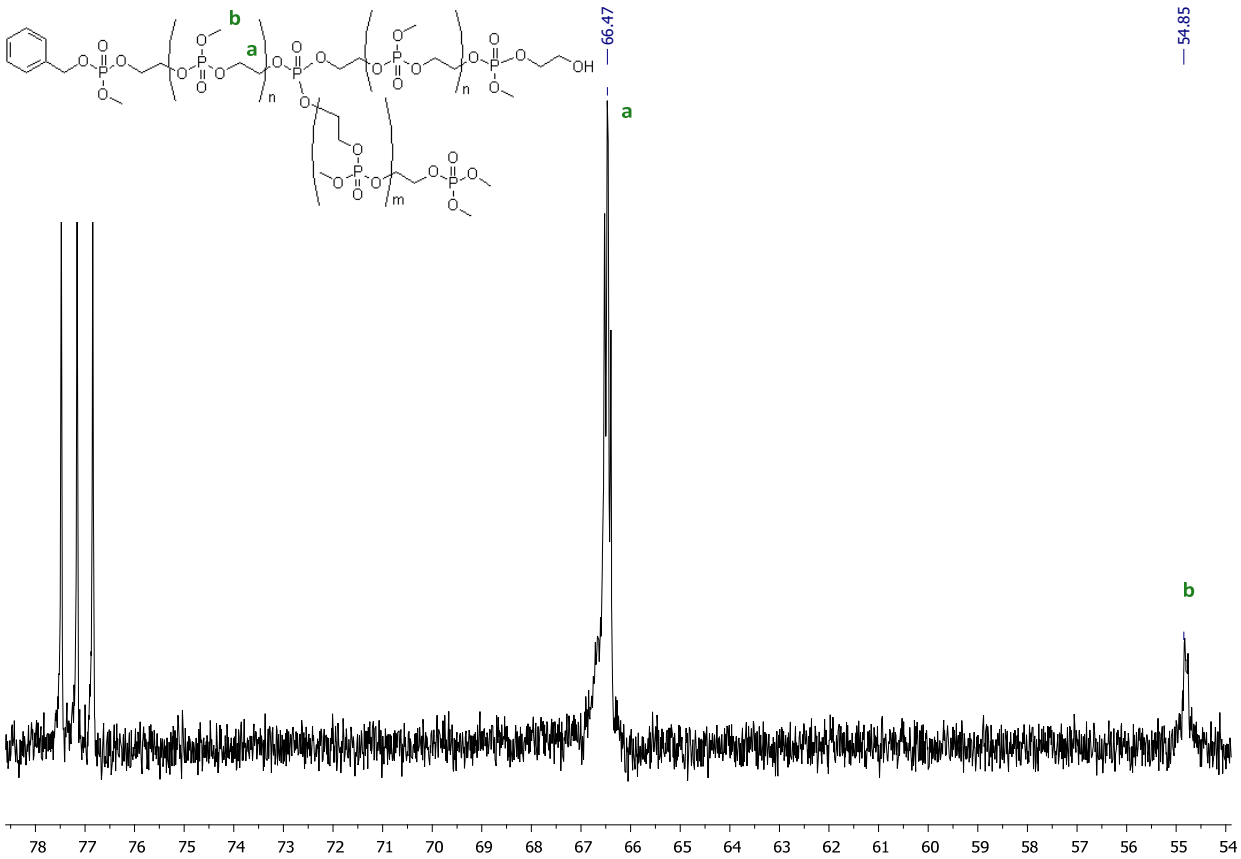


Fig. S30. ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of partially branched poly(MeOEP) prepared using **Mg3** as the catalyst at 20 °C (Table 2, Run 1)

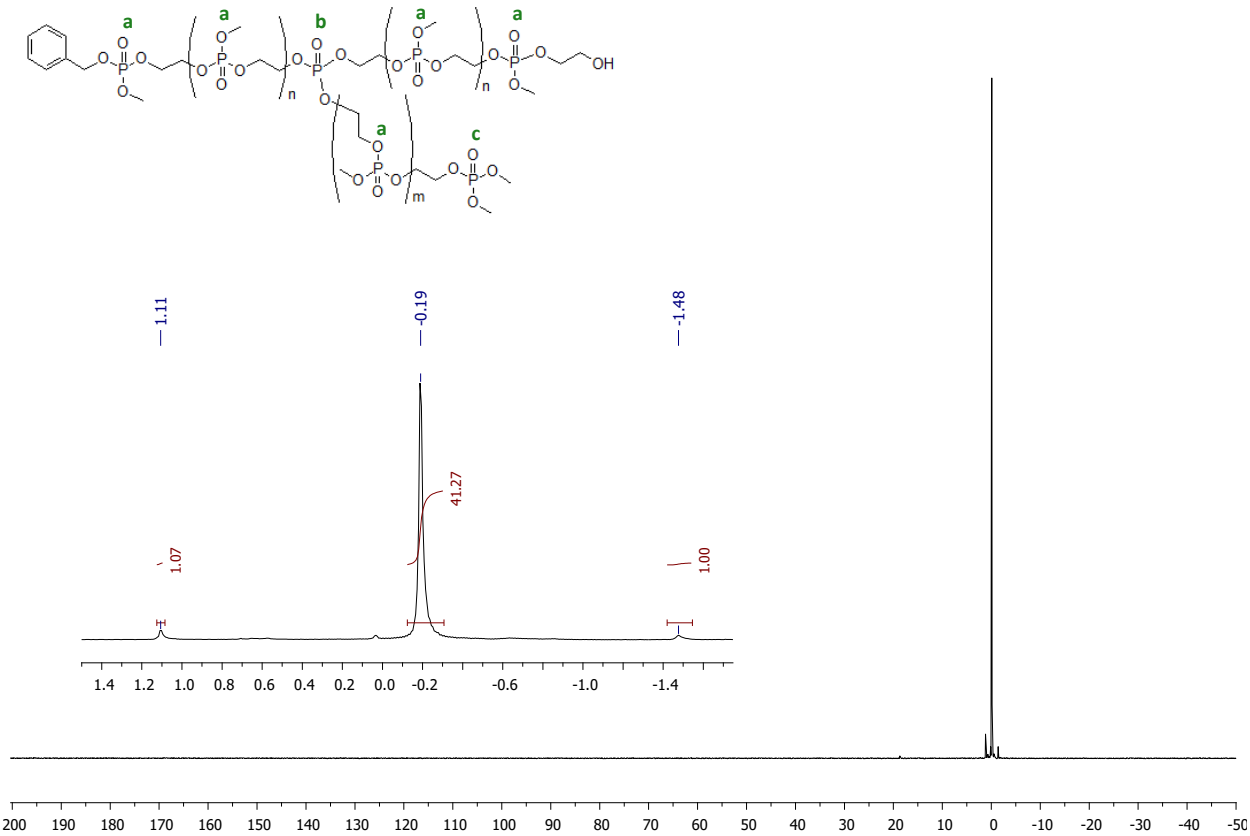


Fig. S31. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of partially branched poly(MeOEP) prepared using **Mg3** as the catalyst at 20 °C (Table 2, Run 1).

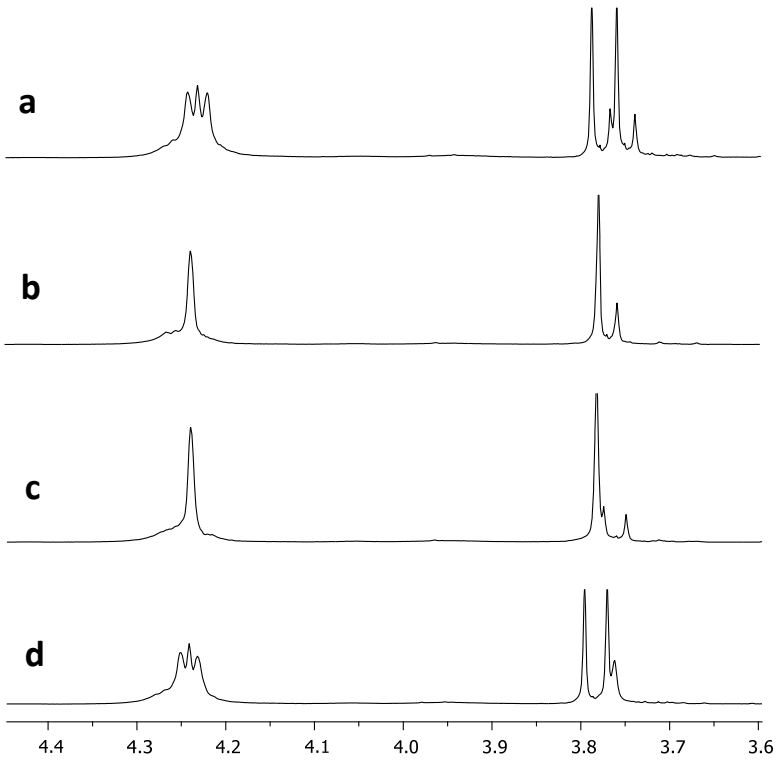


Fig. S32. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 20 °C) of partially branched poly(MeOEP) (Table 2, Run 2): a) without H–P decoupling; b) full H–P decoupling; c) H–P decoupling at 1.1 ppm of ^{31}P scale; d) ; H–P decoupling at -1.5 ppm of ^{31}P scale.

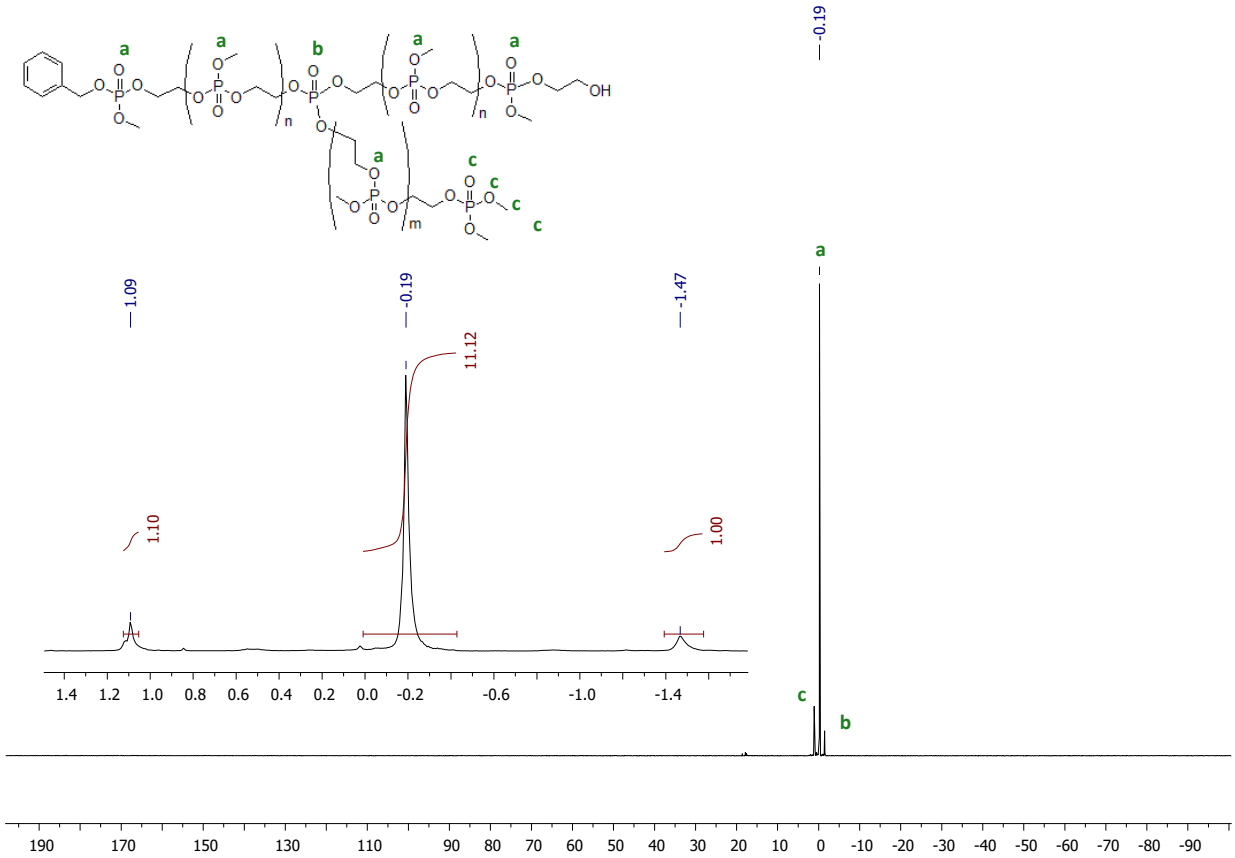


Fig. S33. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of partially branched poly(MeOEP) prepared using **TBD** as the catalyst at 20 °C, reaction time 1 h (Table 2, Run 2).

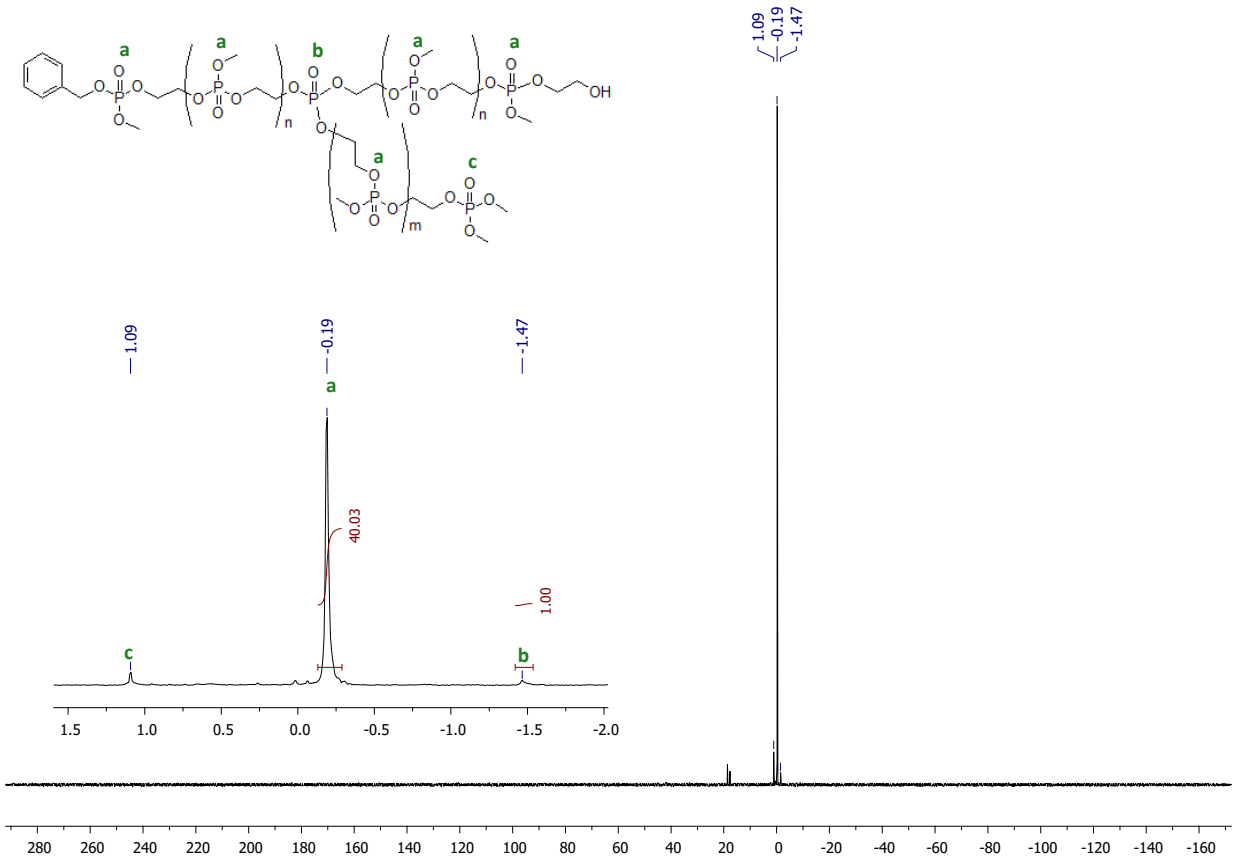


Fig. S34. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of partially branched poly(MeOEP) prepared using **DBU/TU** as the catalyst at 20 °C, reaction time 1 h (Table 2, Run 6).

*Polymerization of MeOEP using **Mg3** as the catalyst at -20 °C (Table 2, Run 10).*

MeOEP (0.252 g, 0.181 mL, $1.82 \cdot 10^{-3}$ mol) was introduced into a vial equipped with magnetic stirrer and septum, 0.53 mL dry CH_2Cl_2 was added to MeOEP. A stock solution of **Mg3** in dry THF (317 mg, $7.50 \cdot 10^{-4}$ mol Mg in 8.2 mL solution) was prepared. All solutions were cooled down to –20 °C. The polymerization was started by rapid addition of the stock solution of **Mg3** (0.2 mL solution, $1.82 \cdot 10^{-5}$ mol Mg) to the stirred solution of MeOEP by a syringe to give a total reaction concentration of 2M MeOEP. Probes of the reaction mixture after 1, 5, 15 and 60 min were collected using a syringe and immediately poured into NMR tubes containing 2.0 µL AcOH in 600 µL of $CDCl_3$. The polymerization was terminated in 1 hour by the addition of an excess of acetic acid in CH_2Cl_2. The monomer conversion was determined using ^{31}P NMR spectroscopy by integration of the monomer (δ 18.6 ppm) and polymer (δ –0.19 ppm). The polymer was precipitated twice using a 5-fold volume excess of dry diethyl ether. The precipitated polymer was redissolved in dry CH_2Cl_2, the solvent was removed *in vacuo*. The yield was 0.22 g (88%). The amount of branches in polymer chain was determined using ^{31}P NMR spectroscopy by integration of the resonance signals of branched (δ –1.47 ppm) and unbranched (δ –0.19 ppm) phosphorus atoms, see Fig. S37.

*Polymerization of MeOEP using **Mg3** as the catalyst at -50 °C (Table 2, Run 15).*

MeOEP (0.252 g, 0.181 mL, $1.82 \cdot 10^{-3}$ mol) was introduced into a vial equipped with magnetic stirrer and septum, 0.53 mL dry CH_2Cl_2 was added to MeOEP. A stock solution of **Mg3** in dry THF (317 mg, $7.50 \cdot 10^{-4}$ mol Mg in 8.2 mL solution) was prepared. All solutions were cooled down to -50 °C. The polymerization was started by rapid addition of the stock solution of **Mg3** (0.2 mL solution, $1.82 \cdot 10^{-5}$ mol Mg) to the stirred solution of MeOEP by a syringe to give a total reaction concentration of 2M MeOEP. The polymerization was terminated in 1 hour by the addition of an excess of acetic acid in CH_2Cl_2. The monomer conversion was determined using ^{31}P NMR spectroscopy by integration of the monomer (δ 18.6 ppm) and polymer (δ –0.19 ppm) resonance signals. The polymer was precipitated twice using a 5-fold volume excess of dry diethyl ether. The precipitated polymer was redissolved in dry CH_2Cl_2, the solvent was removed *in vacuo*. The yield was 0.23 g (91%). The polymer obtained at –50 °C is linear, see Fig. S38.

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 5.04 (d, $^3J_{HP}$ = 8.3 Hz, PhCH_2); 4.22 (dd, $^3J_{HP}$ = 4.6 Hz, 4H); 3.77 (d, $^3J_{HP}$ = 11.0 Hz, 3H).

^{13}C{H} NMR (101 MHz, $CDCl_3$, 20 °C): δ 66.36 (dd, $^2J_{CP}$ = $^3J_{CP}$ = 6.5 Hz); 54.70 (d, $^2J_{CP}$ = 6.6 Hz).

^{31}P{H} NMR (162 MHz, $CDCl_3$, 20 °C): δ –0.19.

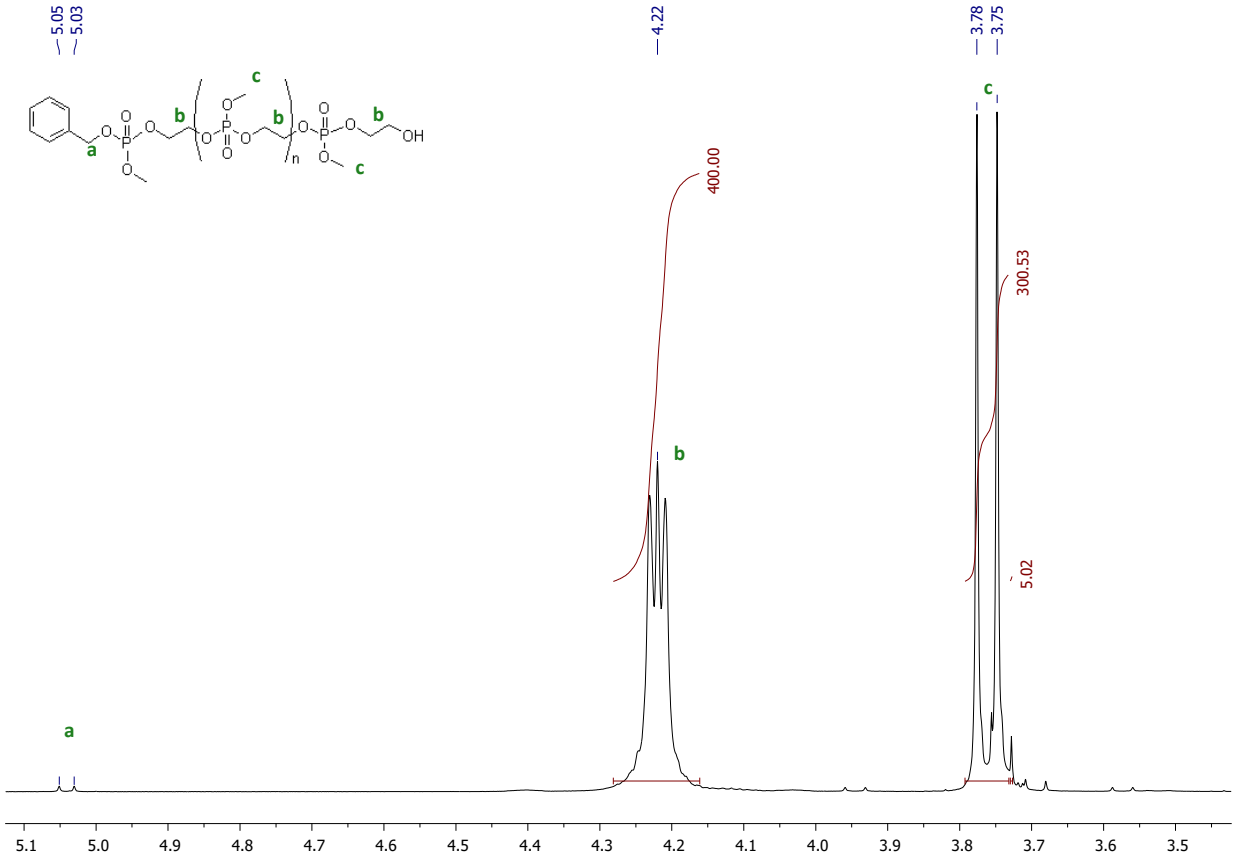


Fig. S35. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of poly(MeOEP) prepared using **Mg3** as the catalyst at –20 °C (Table 2, Run 10)

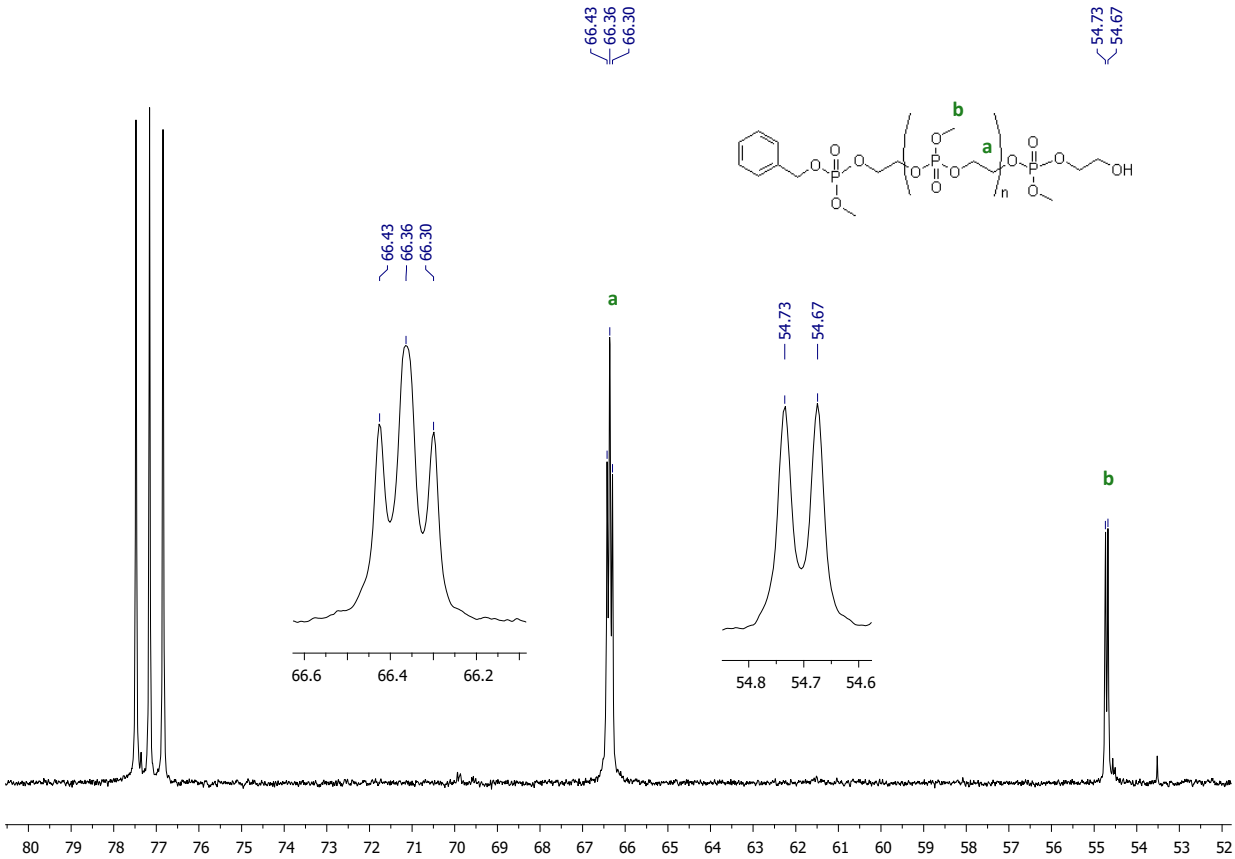


Fig. S36. ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of poly(MeOEP) prepared using **Mg3** as the catalyst at –20 °C (Table 2, Run 10)

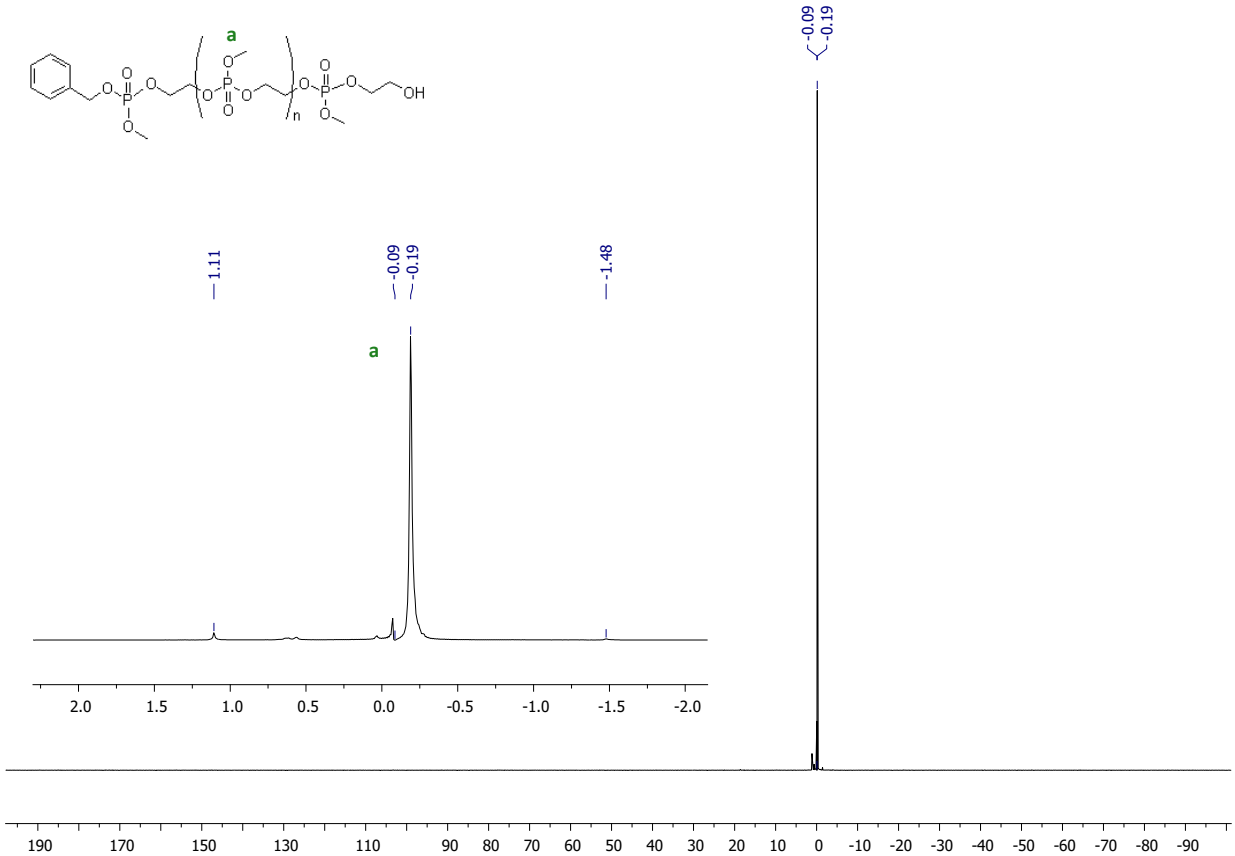


Fig. S37. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of poly(MeOEP) prepared using **Mg3** as the catalyst at –20 °C (Table 2, Run 10)

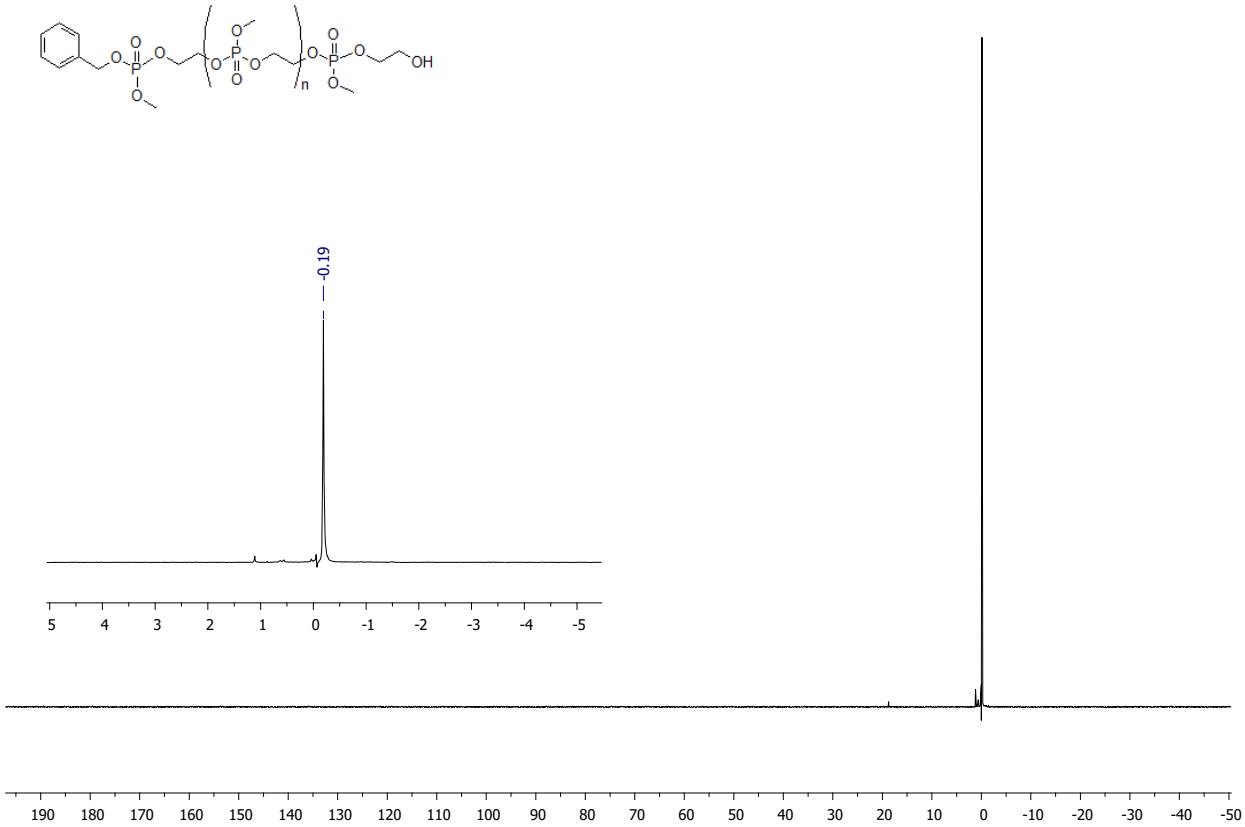


Fig. S38. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of poly(MeOEP) prepared using **Mg3** as the catalyst at –50 °C (Table 2, Run 15)

S4.3. Polymerization of ^{t}BuOEP

*Polymerization of tBuOEP using **Mg3** as the catalyst at 20 °C (Table 3, Run 4).*

^{t}BuOEP (0.660 g, $3.66 \cdot 10^{-3}$ mol) was introduced into a vial equipped with magnetic stirrer and septum, dry CH_2Cl_2 was added to give a total reaction volume of 1.4 mL. A stock solution of **Mg3** in dry THF (317 mg, $7.50 \cdot 10^{-4}$ mol Mg in 4.1 mL solution) was prepared. The polymerization was started by rapid addition of the stock solution of **Mg3** (0.4 mL solution, $7.31 \cdot 10^{-5}$ mol Mg) to the stirred solution of tBuOEP by a syringe to give a total reaction concentration of 2M **^{t}BuOEP**. The polymerization was terminated after 18 hours by the addition of an excess of acetic acid in CH_2Cl_2. The monomer conversion was determined using ^{31}P NMR spectroscopy by integration of the monomer (δ = 13.2 ppm) and polymer (δ = –5.8 ppm) resonance signals. The polymer was purified by precipitation using a 5-fold volume excess of dry diethyl ether and subsequent centrifugation (5 min, 4000 rpm), supernatant was decanted and redissolved in dry CH_2Cl_2, then precipitated and centrifugated again. The polymer obtained was dissolved in dry CH_2Cl_2, the solvent was removed *in vacuo*. The yield was 0.58 g (88%).

*Polymerization of tBuOEP using **TBD** as the catalyst at 20 °C (Table 3, Run 6).*

^{t}BuOEP (0.971 g, $5.39 \cdot 10^{-3}$ mol) was introduced into a vial equipped with magnetic stirrer and septum, dry CH_2Cl_2 was added to give a total reaction volume of 2.3 mL. A stock solution of **TBD** in dry toluene (1.00 g, $7.18 \cdot 10^{-3}$ mol in 10.0 mL solution) and a stock solution of the initiator in dry CH_2Cl_2 (23 mg benzyl alcohol, $2.13 \cdot 10^{-3}$ mol in 1.0 mL solution) were prepared. 0.1 mL of the stock solution of the initiator ($2.13 \cdot 10^{-4}$ mol) was added to the stirred solution of **^{t}BuOEP**. The polymerization was started by rapid addition of the stock solution of **TBD** (0.3 mL solution, $2.15 \cdot 10^{-4}$ mol) to the to the reaction mixture by a syringe to give a total reaction concentration of 2M tBuOEP. The polymerization was terminated after 22 hours by the addition of an excess of acetic acid in CH_2Cl_2. The monomer conversion was determined using ^{31}P NMR spectroscopy by integration of the monomer (δ=13.2 ppm) and polymer (δ=-5.8 ppm) resonance signals. The polymer was purified by precipitation using a 5-fold volume excess of dry diethyl ether and subsequent centrifugation (5 min, 4000 rpm), supernatant was decanted and redissolved in dry CH_2Cl_2, then precipitated and centrifugated again. The polymer obtained was dissolved in dry CH_2Cl_2, the solvent was removed *in vacuo*. The yield was 0.76 g (78%).

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.07 (m, 4H); 1.39 (bs, 9H).
^{13}C{H} NMR (101 MHz, $CDCl_3$, 20 °C): δ 84.14 (d, $^{2}J_{CP}$ = 7.1 Hz); 65.83 (dd, J_{CP} = 6.0 & 8.1 Hz); 29.90 (d, $^{3}J_{CP}$ = 4.1 Hz).
^{31}P{H} NMR (162 MHz, $CDCl_3$, 20 °C): δ –5.76.

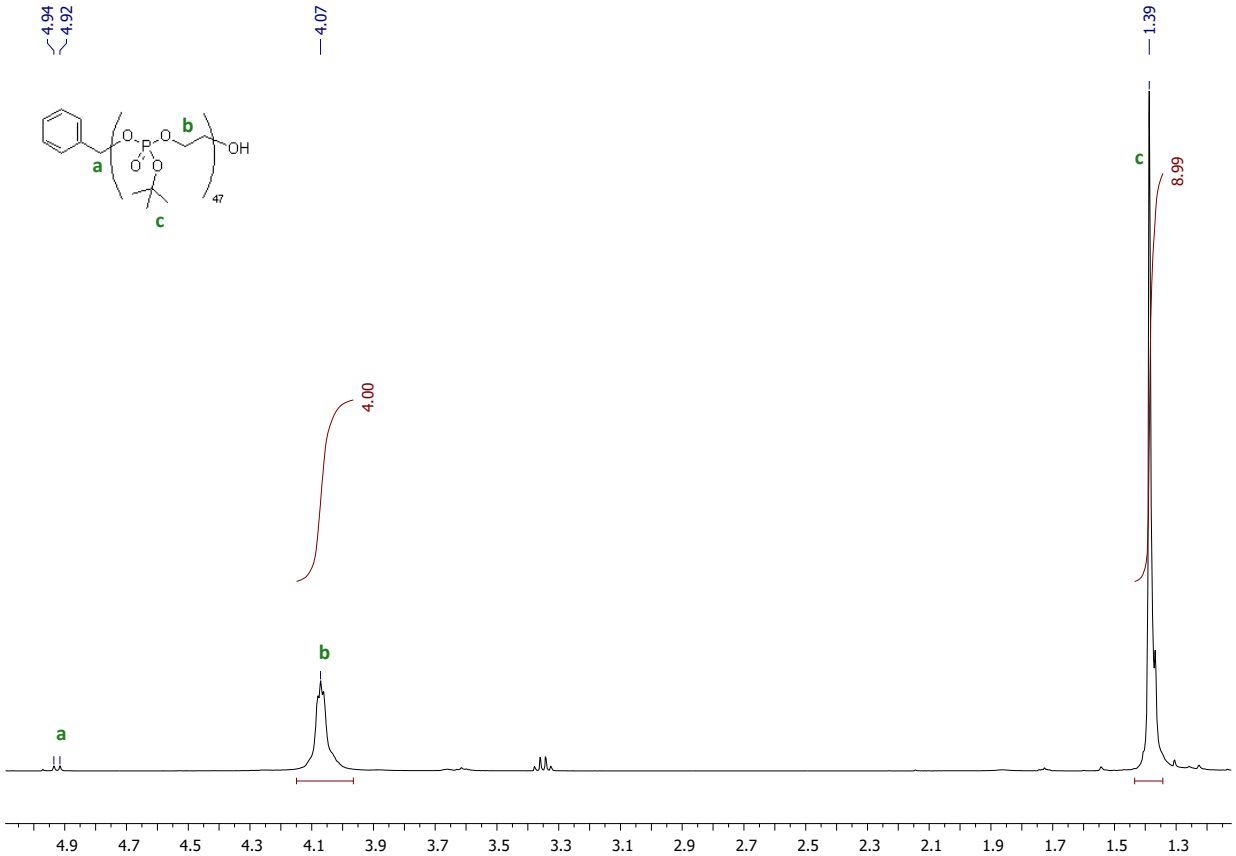


Fig. S39. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of poly(^{t}BuOEP) prepared using **Mg3** as the catalyst at 20 °C (Table 3, Run 1)

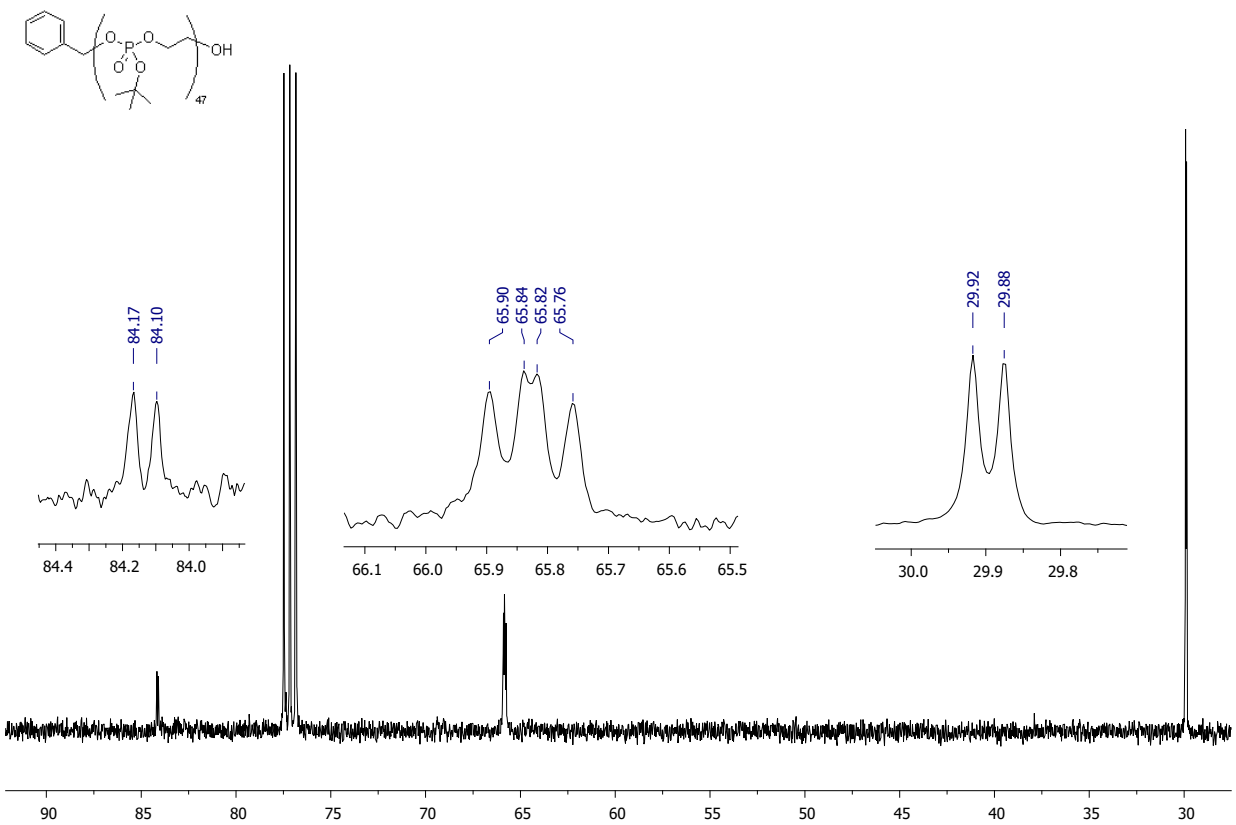


Fig. S40. ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of poly(^{t}BuOEP) prepared using **Mg3** as the catalyst at 20 °C (Table 3, Run 1)

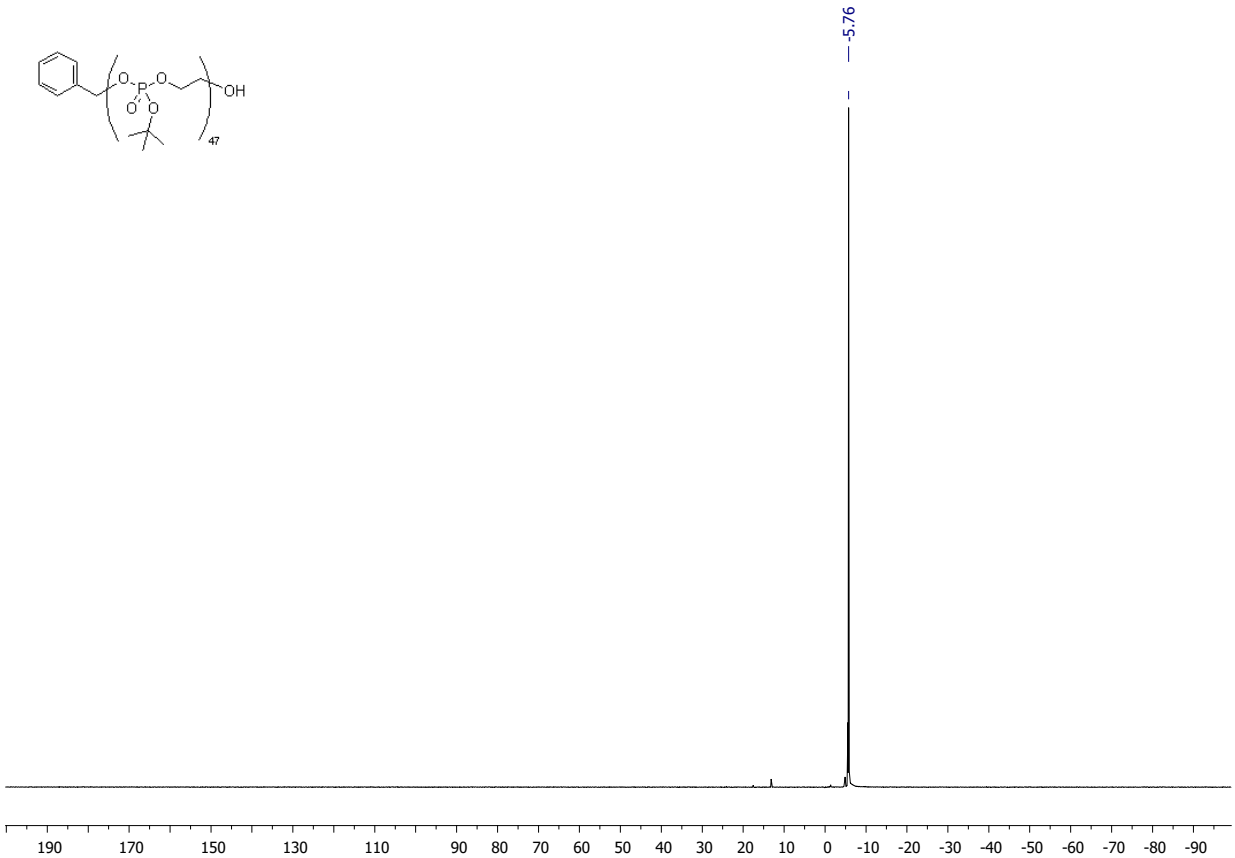


Fig. S41. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of poly(^{t}BuOEP) prepared using **Mg3** as the catalyst at 20 °C (Table 3, Run 1)

S4.4. Polymerization of Et_2NEP

Polymerization of Et_2NEP using **Mg3** *as the catalyst at 100 °C (Table 3, Run 7).*

Et_2NEP (0.448 g, $2.5\cdot10^{-3}$ mol) was introduced into a vial equipped with magnetic stirrer and septum, the vial was heated up to 100 °C. A stock solution of **Mg3** in dry toluene (22 mg, $5.20\cdot10^{-5}$ mol Mg in 0.5 mL solution) was prepared. The polymerization was started by rapid addition of the stock solution of **5** (0.25 mL solution, $2.6\cdot10^{-5}$ mol Mg) to the stirred solution of Et_2NEP by a syringe and the temperature kept at 100 °C. The polymerization was terminated after 1 hour by the addition of an excess of acetic acid in CH_2Cl_2. The monomer conversion was determined using ^{31}P NMR spectroscopy by integration of the monomer (δ 26.7 ppm) and polymer (δ 10.4 ppm) resonance signals. The polymer was precipitated twice using a 5-fold volume excess of dry diethyl ether. The precipitated polymer was redissolved in dry CH_2Cl_2, the solvent was removed *in vacuo*. The yield was 0.29 g (64%).

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.08 (m, 4H, –OCH_2CH_2O–); 3.05 (qd, $^{3}J_{HH}$ = 6.8 Hz, $^{3}J_{HP}$ = 5.2 Hz, 4H, –CH_2CH$_3$); 1.07 (t, $^{3}J_{HH}$ = 6.8 Hz, 6H, –CH$_2$CH_3).

$^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$, 20 °C): δ 64.74 (m); 39.79 (d, $^{2}J_{CP}$ = 4.7 Hz); 14.23.

$^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$, 20 °C): δ 10.62.

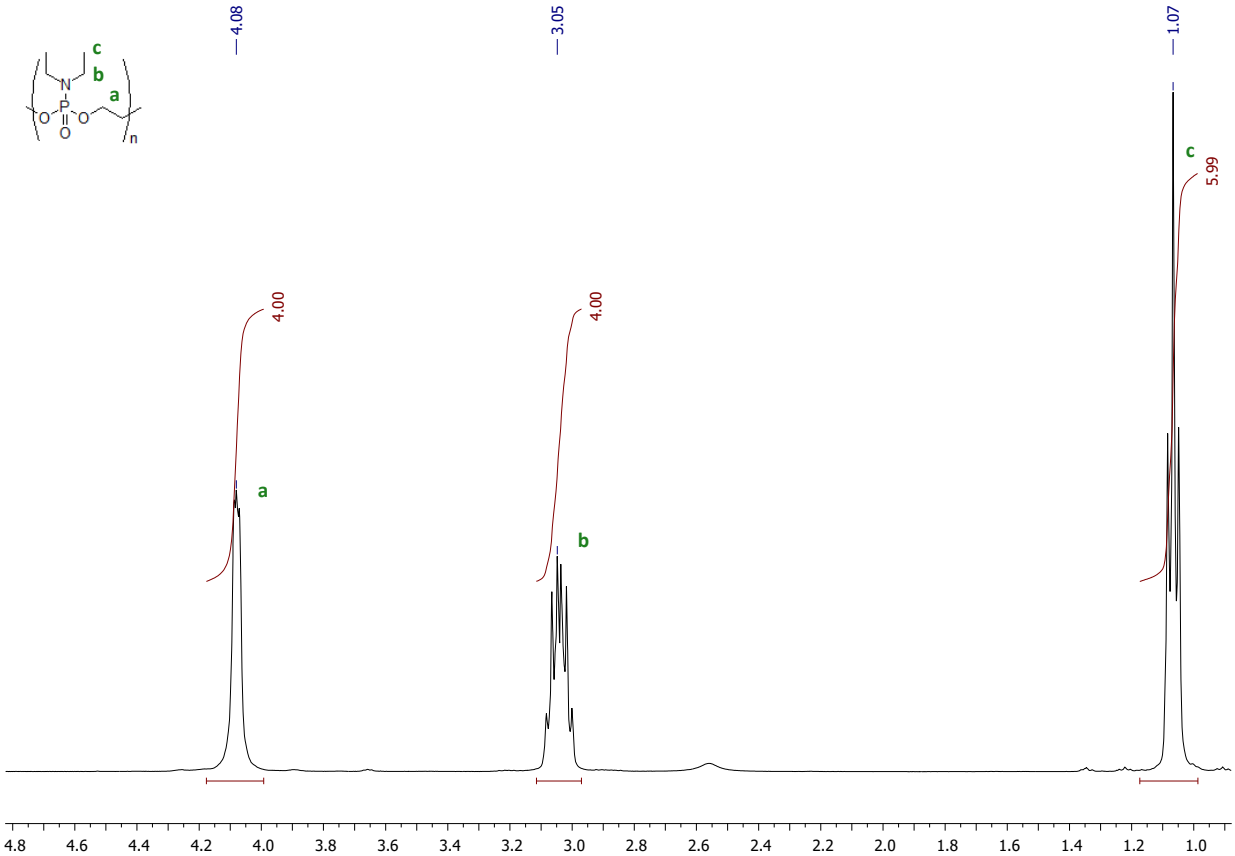


Fig. S42. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of poly(Et_2NEP) prepared using **Mg3** as the catalyst at 100 °C (Table 3, Run 4)

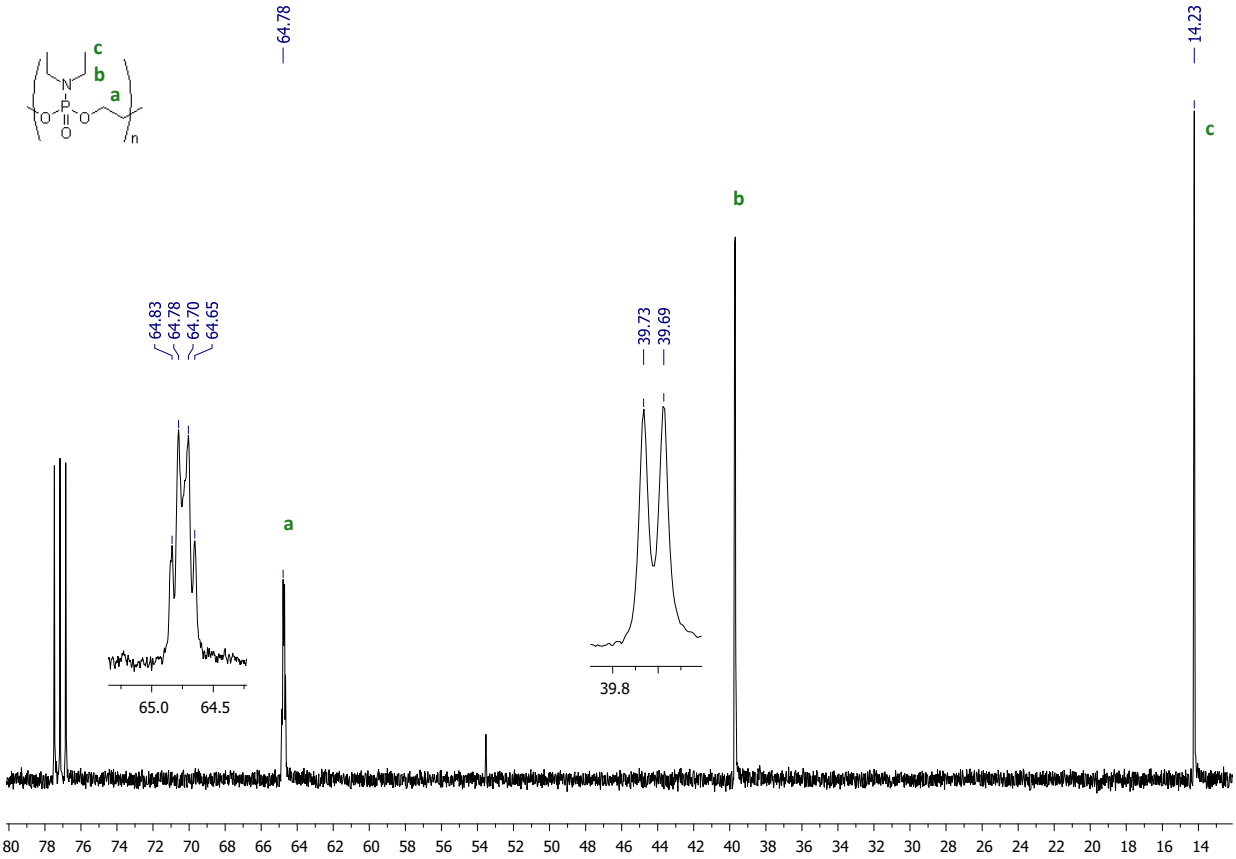


Fig. S43. ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of poly(Et_2NEP) prepared using **Mg3** as the catalyst at 100 °C (Table 3, Run 4)

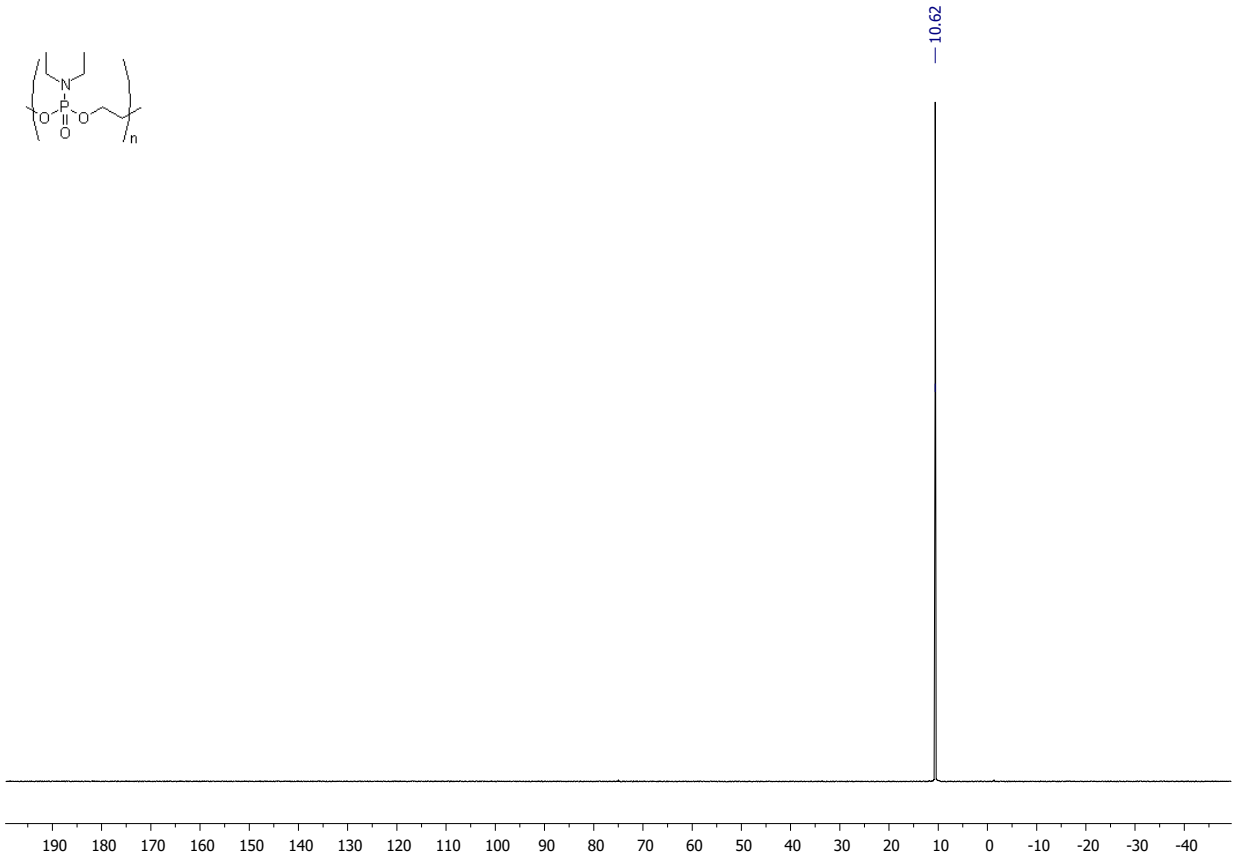


Fig. S44. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of poly(Et_2NEP) prepared using **Mg3** as the catalyst at 100 °C (Table 3, Run 4)

S4.5. Polymerization of EtPPn

*Polymerization of EtPPn using **Mg3** as the catalyst at 20 °C (Table 3, Run 9).*

EtPPn (0.50 g, $3.66 \cdot 10^{-3}$ mol) was introduced into a vial equipped with magnetic stirrer and septum, dry CH_2Cl_2 was added to give a total reaction volume of 1.4 mL, the mixture was cooled to –20 ℃. A stock solution of **Mg3** in dry THF (317 mg, $7.50 \cdot 10^{-4}$ mol Mg in 4.1 mL solution) was prepared. The polymerization was started by rapid addition of the stock solution of **Mg3** (0.4 mL solution, $7.31 \cdot 10^{-5}$ mol Mg) to the stirred solution of **EtPPn** by a syringe to give a total reaction concentration of 2M **EtPPn**. The polymerization was terminated after 1 h of the stirring at –20 ℃ by the addition of an excess of acetic acid in CH_2Cl_2. The monomer conversion was determined using ^{31}P NMR spectroscopy by integration of the monomer (δ = 52.6 ppm) and polymer (δ = 35.3 ppm) resonance signals. The polymer was purified by precipitation using a 5-fold volume excess of dry diethyl ether and subsequent centrifugation (5 min, 4000 rpm), supernatant was decanted and redissolved in dry CH_2Cl_2, then precipitated and centrifugated again. The polymer obtained was dissolved in dry CH_2Cl_2, the solvent was removed *in vacuo*. The yield was 0.45 g (89%).

^{1}H-NMR (400 MHz, $CDCl_3$, 20 °C): δ 5.05 (d, $^{3}J_{HP}$ = 8.0 Hz, PhCH_2); 4.24 (m, 2H); 4.16 (m, 2H); 1.78 (qd, $^{3}J_{HH}$ = 7.8 Hz, $^{2}J_{HP}$ = 18.3 Hz, 2H, –CH_2CH$_3$); 1.14 (td, $^{3}J_{HH}$ = 7.8 Hz, $^{3}J_{HP}$ = 20.4 Hz, 3H, –CH$_2$CH_3).

^{13}C{H} NMR (101 MHz, $CDCl_3$, 20 °C): δ 64.09 (dd, $^{2}J_{CP}$ ~ $^{3}J_{CP}$ ~ 6.5 Hz); 19.09 & 17.67 (d, $^{1}J_{CP}$ = 142 Hz); 6.05 (d, $^{2}J_{CP}$ = 7.1 Hz).

^{31}P{H} NMR (162 MHz, $CDCl_3$, 20 °C): δ 35.29.

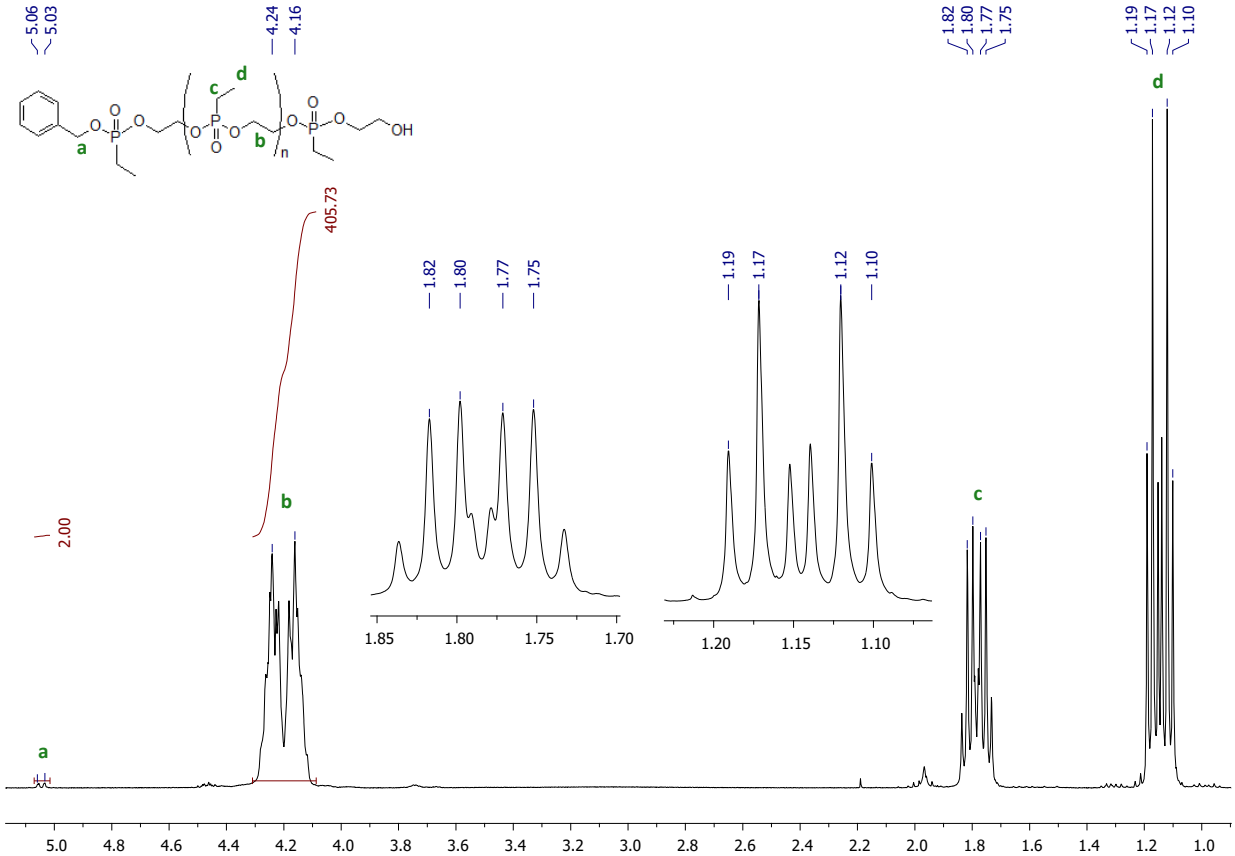


Fig. S45. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of poly(EtPPn) prepared using **Mg3** as the catalyst at 20 °C (Table 3, Run 6)

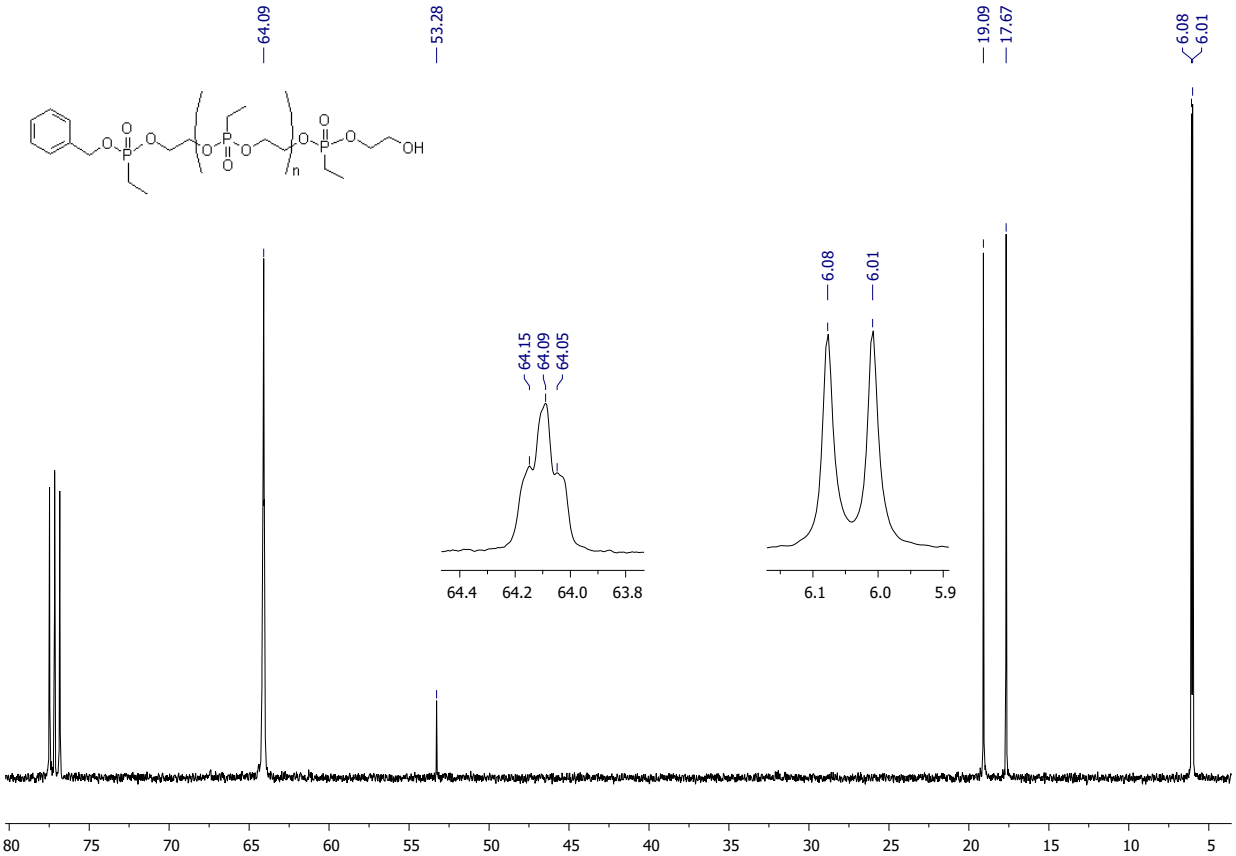


Fig. S46. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of poly(EtPPn) prepared using **Mg3** as the catalyst at 20 °C (Table 3, Run 6)

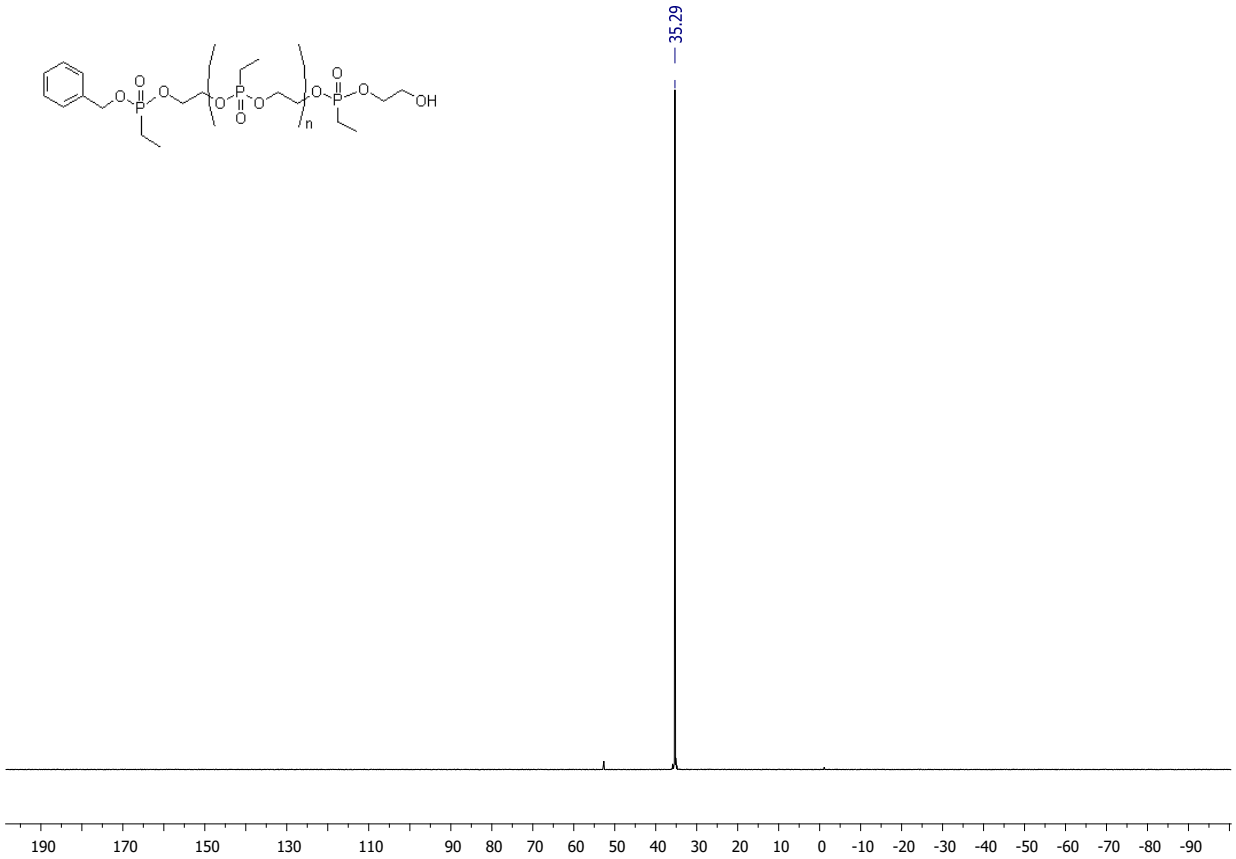


Fig. S47. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of poly(EtPPn) prepared using **Mg3** as the catalyst at 20 °C (Table 3, Run 6)

S4.8. Polymerization of ^{t}BuPPn

*Polymerization of ^{t}BuPPn using **Mg3** as the catalyst at 100 °C (Table 3, Run 10).*

^{t}BuPPn (0.410 g, $2.5 \cdot 10^{-3}$ mol) was introduced into a vial equipped with magnetic stirrer and septum, the vial was heated up to 100 °C. A stock solution of **Mg3** in dry toluene (22 mg, $5.20 \cdot 10^{-5}$ mol Mg in 0.5 mL solution) was prepared. The polymerization was started by rapid addition of the stock solution of **5** (0.25 mL solution, $2.6 \cdot 10^{-5}$ mol Mg) to the stirred solution of **iBuPPn** by a syringe and the temperature kept at 100 °C. The polymerization was terminated after 1 hour by the addition of an excess of acetic acid in CH_2Cl_2. The monomer conversion was determined using ^{31}P NMR spectroscopy by integration of the monomer (δ 57.7 ppm) and polymer (δ 38.3 ppm) resonance signals. The polymer was precipitated twice using a 5-fold volume excess of dry diethyl ether. The precipitated polymer was redissolved in dry CH_2Cl_2, the solvent was removed *in vacuo*. The yield was 0.30 g (74%).

^{1}H-NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.22 (m, 4H, –OCH_2CH_2O–); 1.17 (d, $^{2}J_{HP}$ = 17.2 Hz, 9H, –C(CH_3)$_3$).

^{13}C{H}-NMR (101 MHz, $CDCl_3$, 20 °C): δ 64.94 (m); 32.39 & 30.98 (d, $^{1}J_{CP}$ = 148.5 Hz); 24.69.

^{31}P{H}-NMR (162 MHz, $CDCl_3$, 20 °C): δ 38.31.

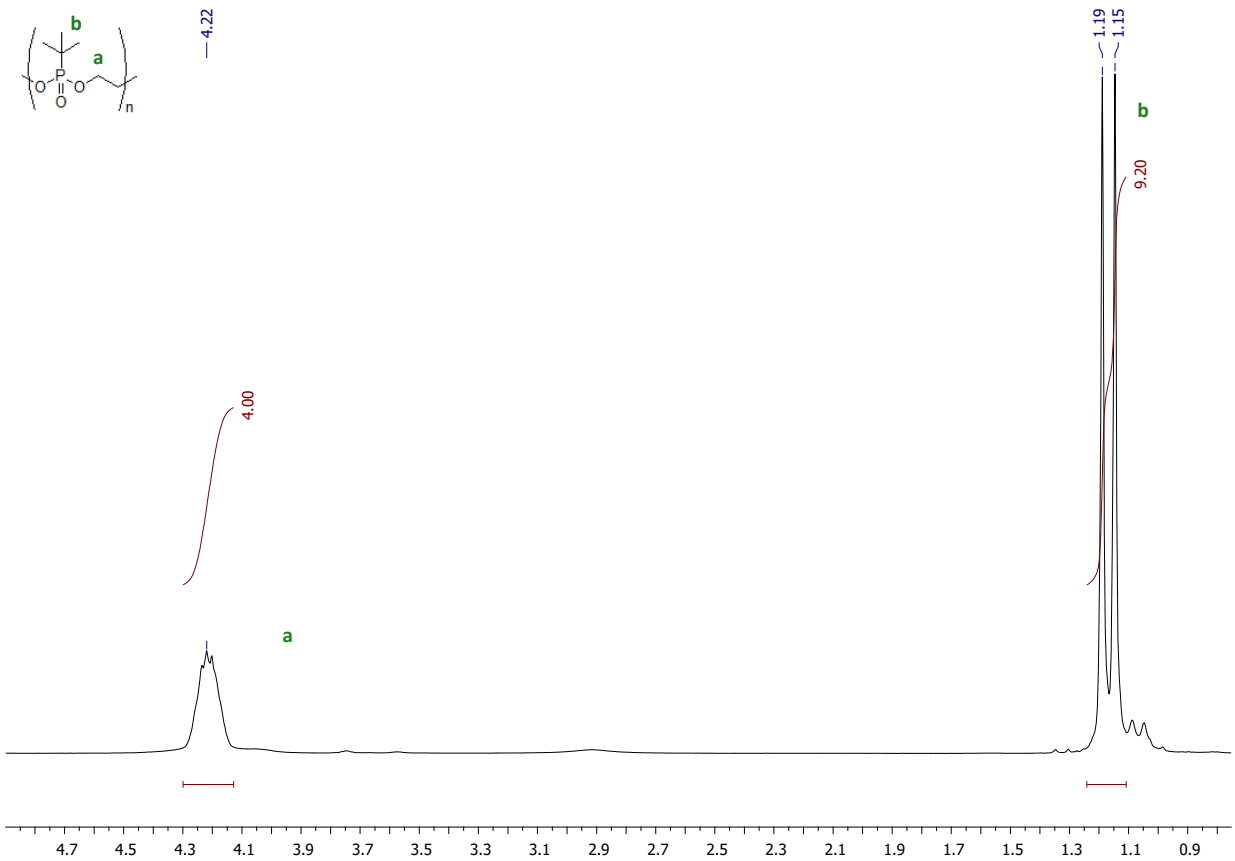


Fig. S48. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of poly(^{t}BuPPn) prepared using **Mg3** as the catalyst at 100 °C (Table 3, Run 7)

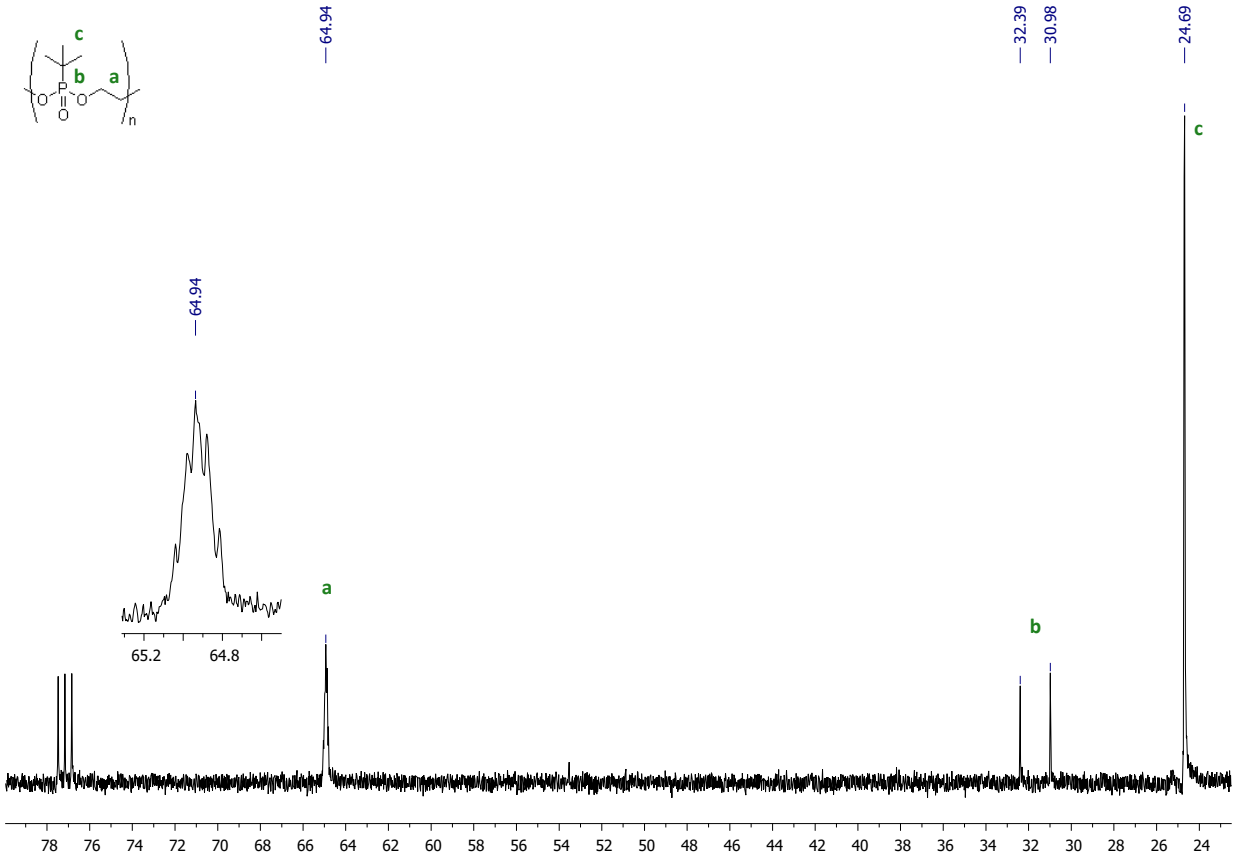


Fig. S49. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of poly(^{t}BuPPn) prepared using **Mg3** as the catalyst at 100 °C (Table 3, Run 7)

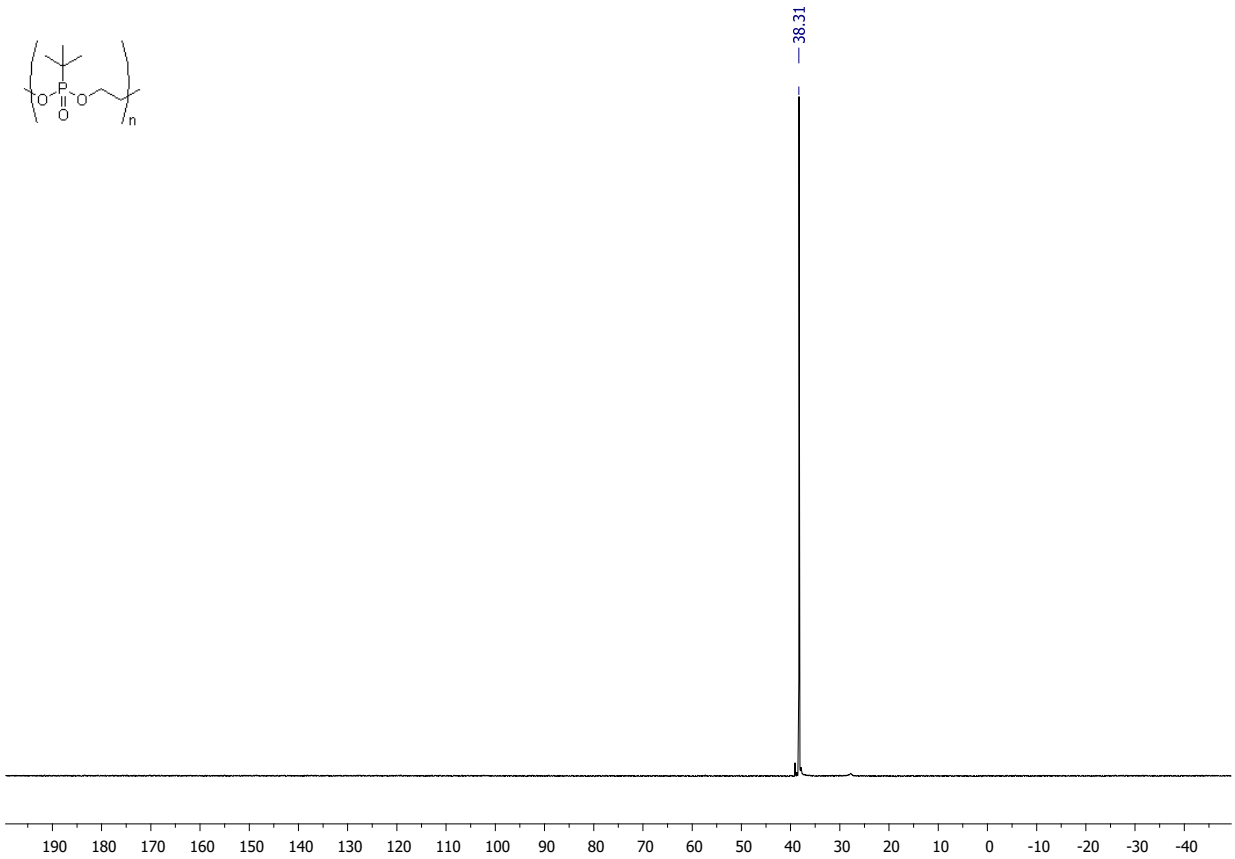


Fig. S50. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of poly(^{t}BuPPn) prepared using **Mg3** as the catalyst at 100 °C (Table 3, Run 7)