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Synthesis and ring-opening polymerization of glycidyl ethylene phosphate with a formation of linear and branched polyphosphates

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S1. A generalized representation of the NMR studies

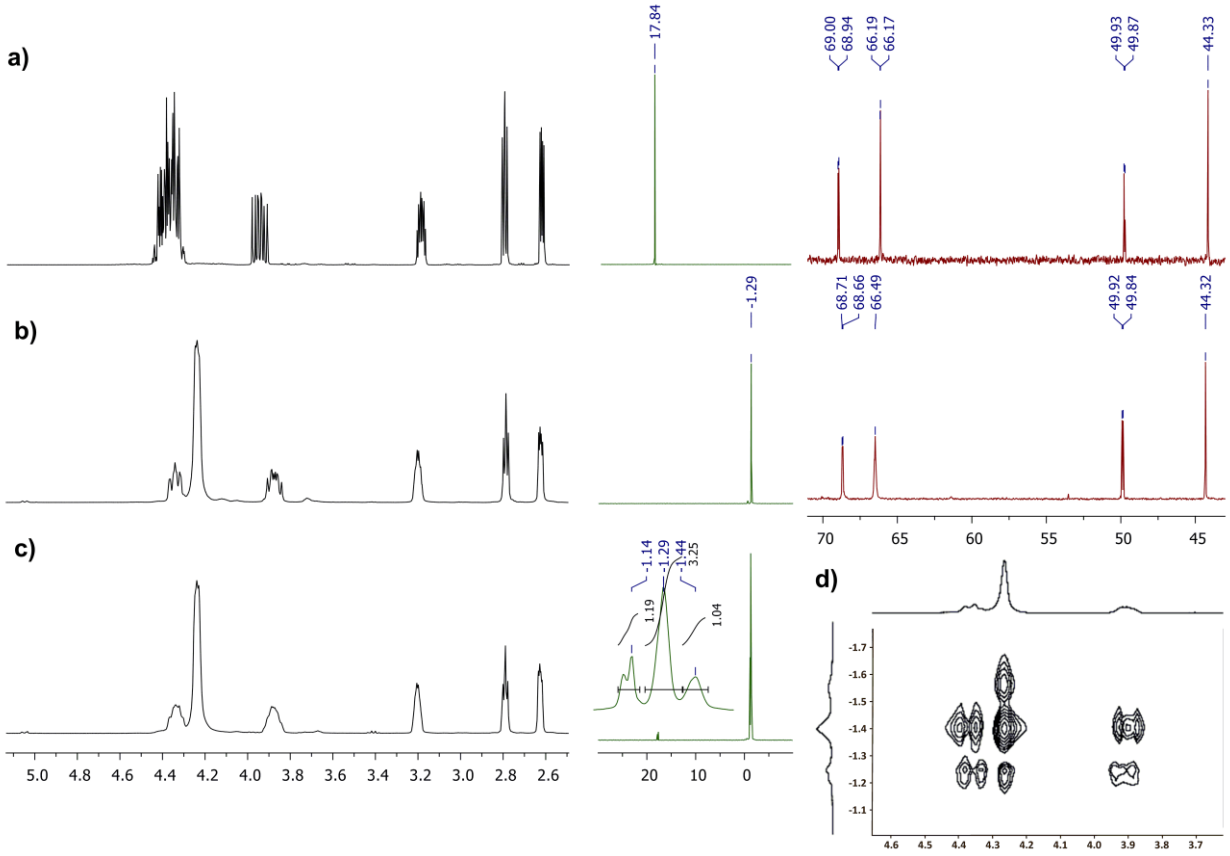


Fig S1 ^{1}H (left), ^{31}P (middle) and ^{13}C (right) NMR spectra of monomer **1** ("GlyOEP") (a), linear (b) and branched (c) polymers; ^{1}H-^{31}P NMR correlation spectra of branched poly-**1** (d, Table 1, run 1)

S2. General experimental remarks

All synthetic and polymerization experiments were conducted under an argon atmosphere. Toluene, diethyl ether, THF and triethylamine were refluxed over 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 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), acetic acid (Acros, ≥99.9%) were used as purchased. Benzyl alcohol (Acros, 99 %) was distilled over BaO and stored under argon. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (**TBD**), was prepared according to the described method.[1]

$CDCl_3$ (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 dm^{-3} lithium bromide as additive) with a flow rate of 1 ml min^{-1} 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.

S3. Preparation of BHT-derived magnesium complex BTH-Mg

A solution Bu_2Mg in heptane (20 ml, 1 *M*, 20 mmol) was added dropwise to a stirred solution of 2,6-di-*tert*-butyl-4-methylphenol (**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 om stirring. The formed solution was then stirred for 3 min. After 5 min, crystals of $[(\mu\text{-}PhCH_2O)Mg(BHT)(THF)]_2$ (**BTH-Mg**) 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, 1H, O-CH_2-Ph); 3.64-3.59 (m, 4H, $CH_2CH_2O_{THF}$); 2.13 (s, 3H, -$CH_{3\ BHT}$); 1.80-1.75 (m, 4H, $CH_2CH_2O_{THF}$); 1.37 (s, 18H, 2,6-$^tBu_{2\ BHT}$).

^{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*-$^tBu_{\ BHT}$); 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 ($CH_2CH_2O_{THF}$); 66.6 (Ph-CH_2-O); 35.7 (-*C*$Me_{3\ BHT}$); 31.4 (-C(*C*$H_3)_{3\ BHT}$); 26.5 ($CH_2CH_2O_{THF}$); 21.6 (p-$CH_{3\ BHT}$).

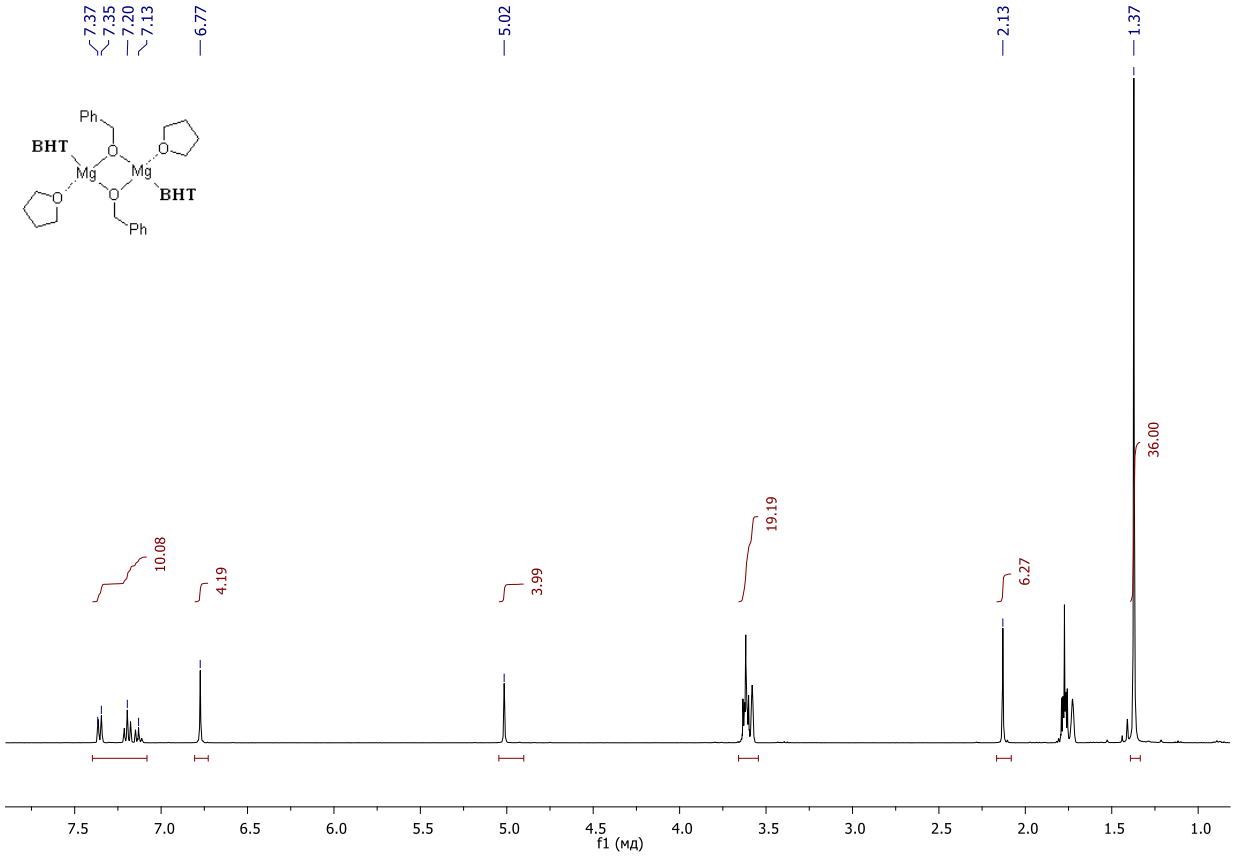


Fig. S2. ^{1}H NMR spectrum (400 MHz, THF-d_8, 20 °C) of $[(\mu\text{-}PhCH_2O)Mg(BHT)(THF)]_2$ **BTH-Mg**

S4. Synthesis and characterization of monomer 1

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

The compound was synthesized via a modified literature protocol [I. Nifant'ev, A. Shlyakhtin, V. Bagrov, B. Lozhkin, G. Zakirova, P. Ivchenko, O. Legon'kova. *Reac. Kinet. Mech. Cat.* **2016**, *117*, 447-476]. 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, 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 **2**.*

The compound **2** was synthesized according to a modified literature procedure [I. Nifant'ev, A. Shlyakhtin, V. Bagrov, B. Lozhkin, G. Zakirova, P. Ivchenko, O. Legon'kova. *Reac. Kinet. Mech. Cat.* **2016**, *117*, 447-476]. 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%). 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, 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.

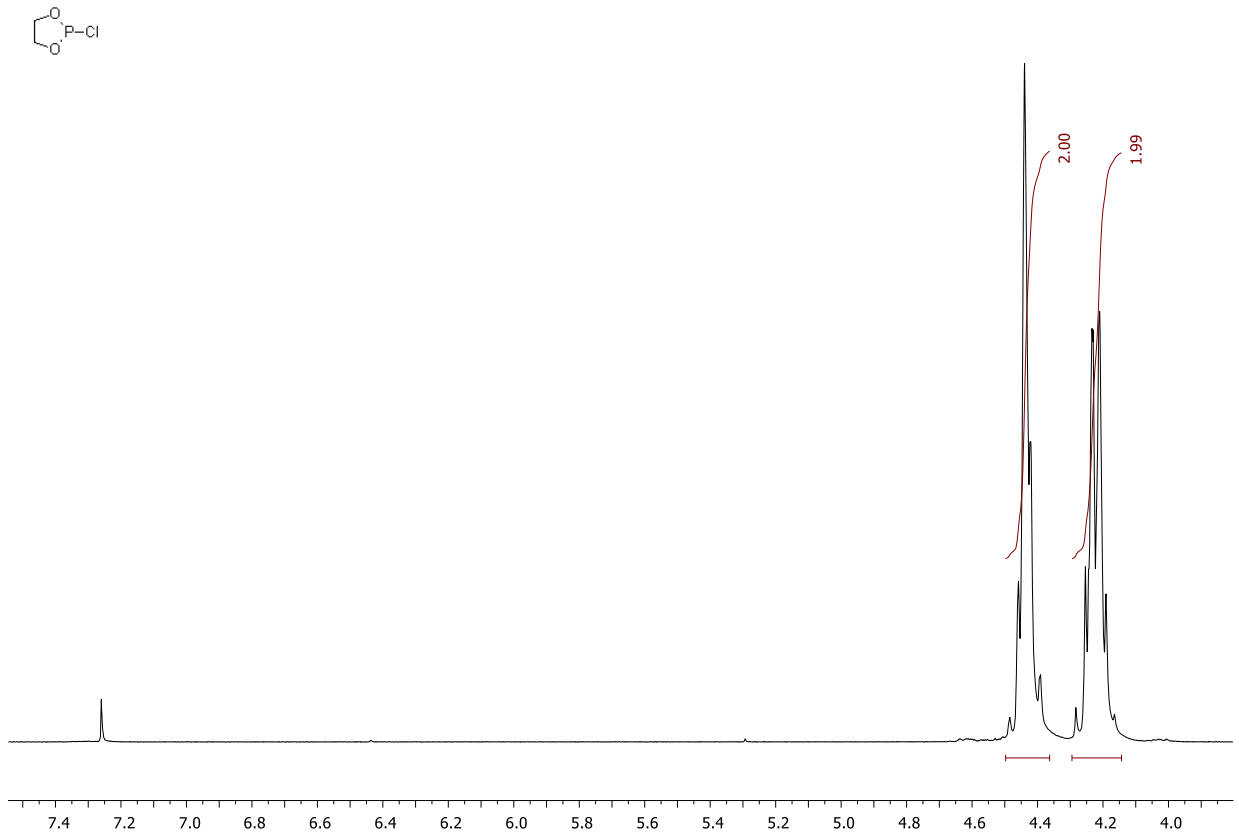


Fig. S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of 2-chloro-1,3,2-dioxaphospholane

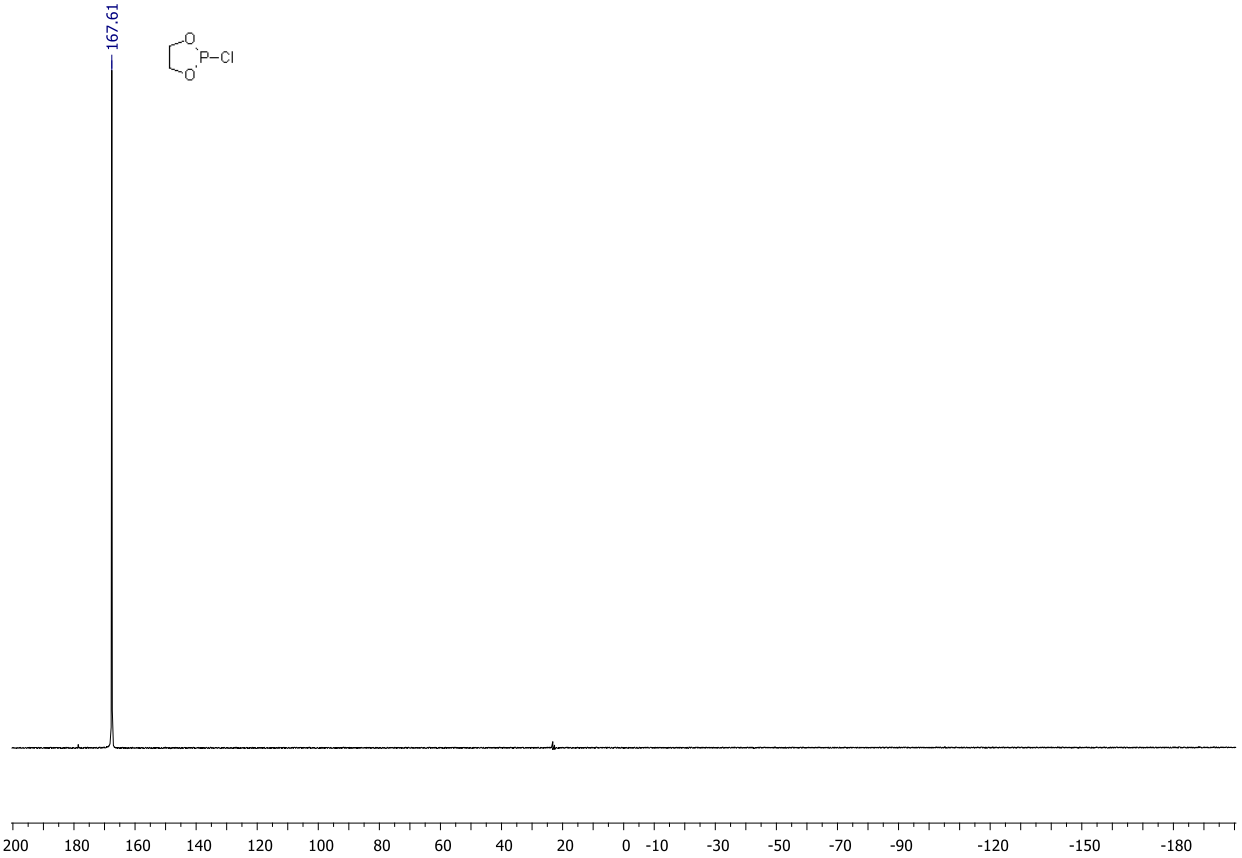


Fig. S4. ^{31}P{H} NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of 2-chloro-1,3,2-dioxaphospholane

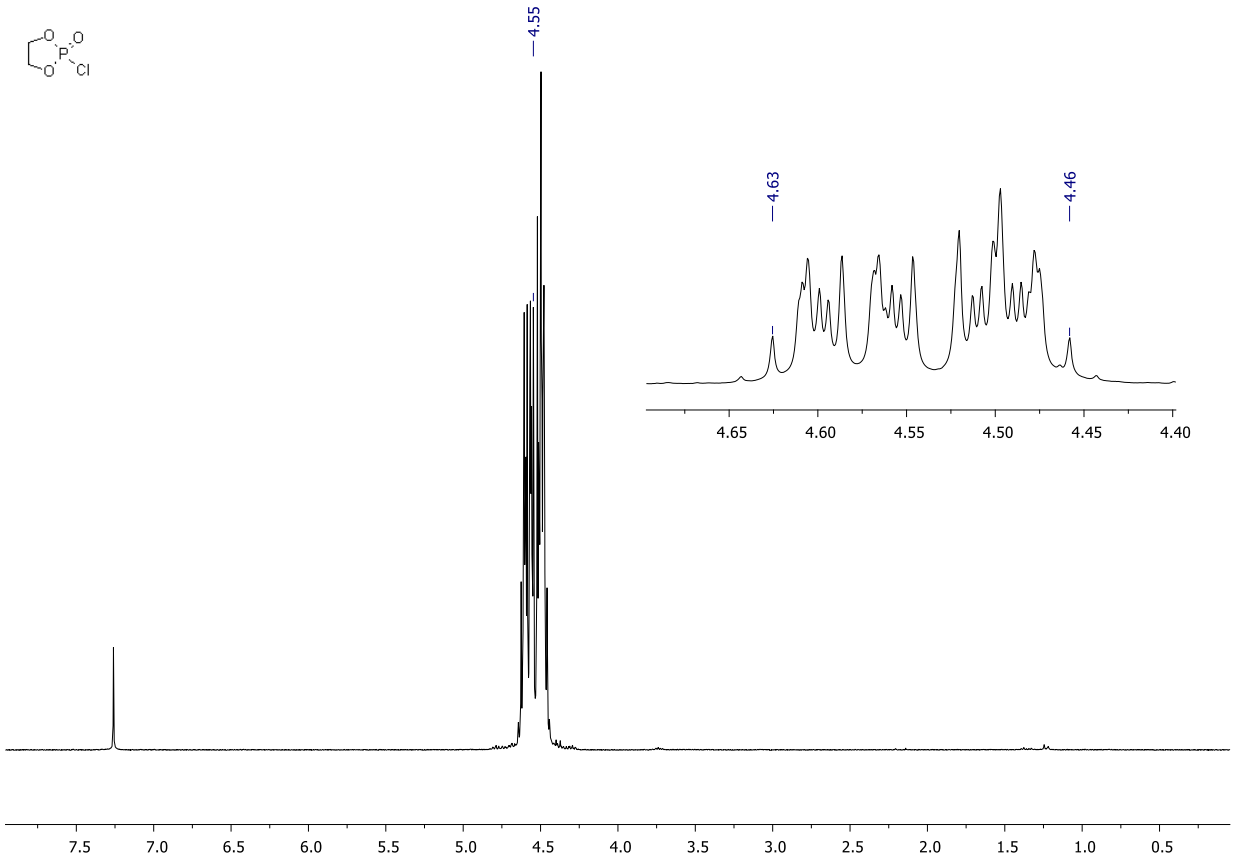
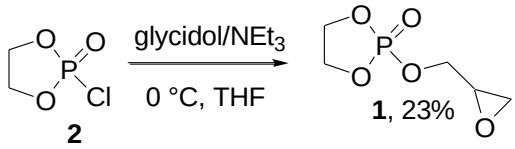


Fig. S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of 2-chloro-1,3,2-dioxaphospholane 2-oxide

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

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



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 **2** (35.5 g, 0.25 mol) in dry THF (70 ml) was added dropwise under stirring at 0 °C. The mixture was allowed to reach room temperature and it was 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, the combined extracts were concentrated *in vacuo*. The residue was divided into two portions which were distilled separately under reduced pressure. The total yield was 9.5 g (23%). B. p. 150-155 °C (0.5 Torr), colorless 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.

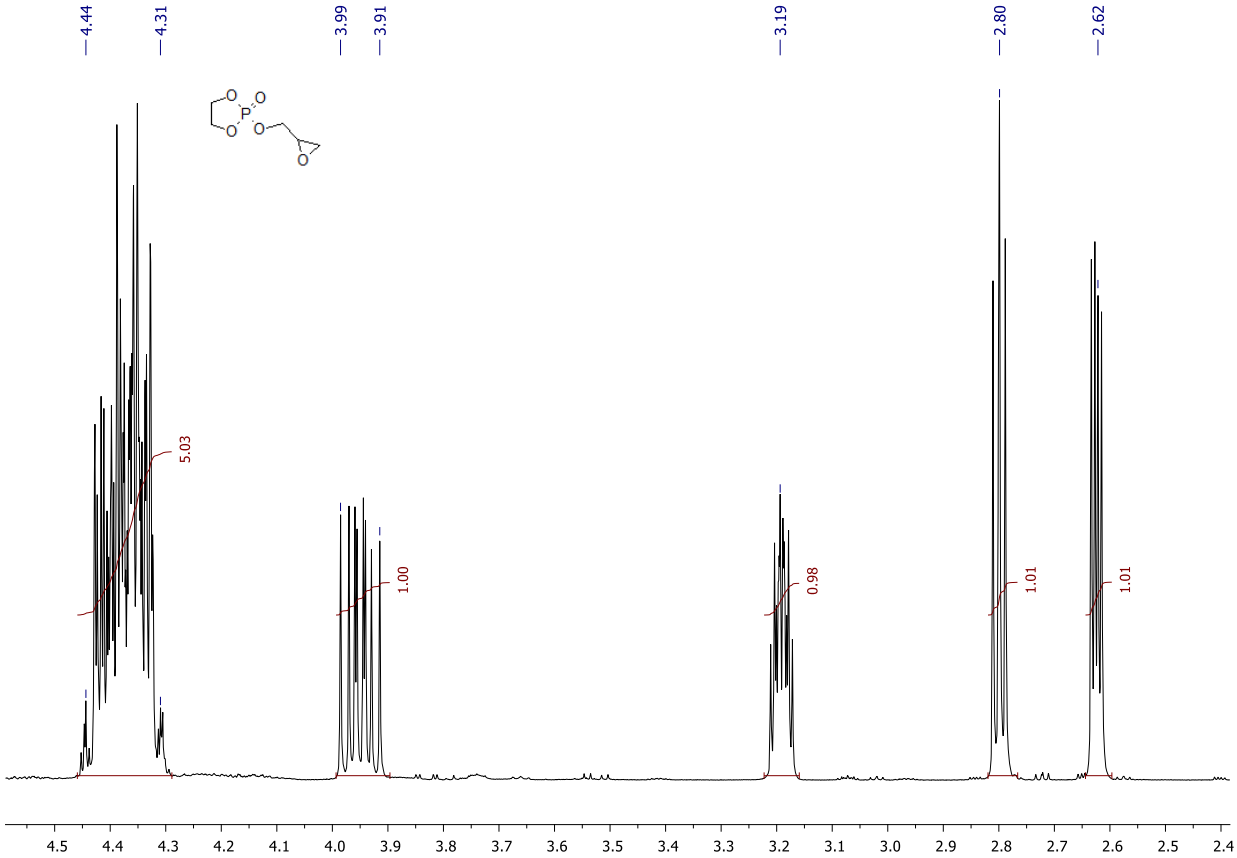


Fig. S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of **1**

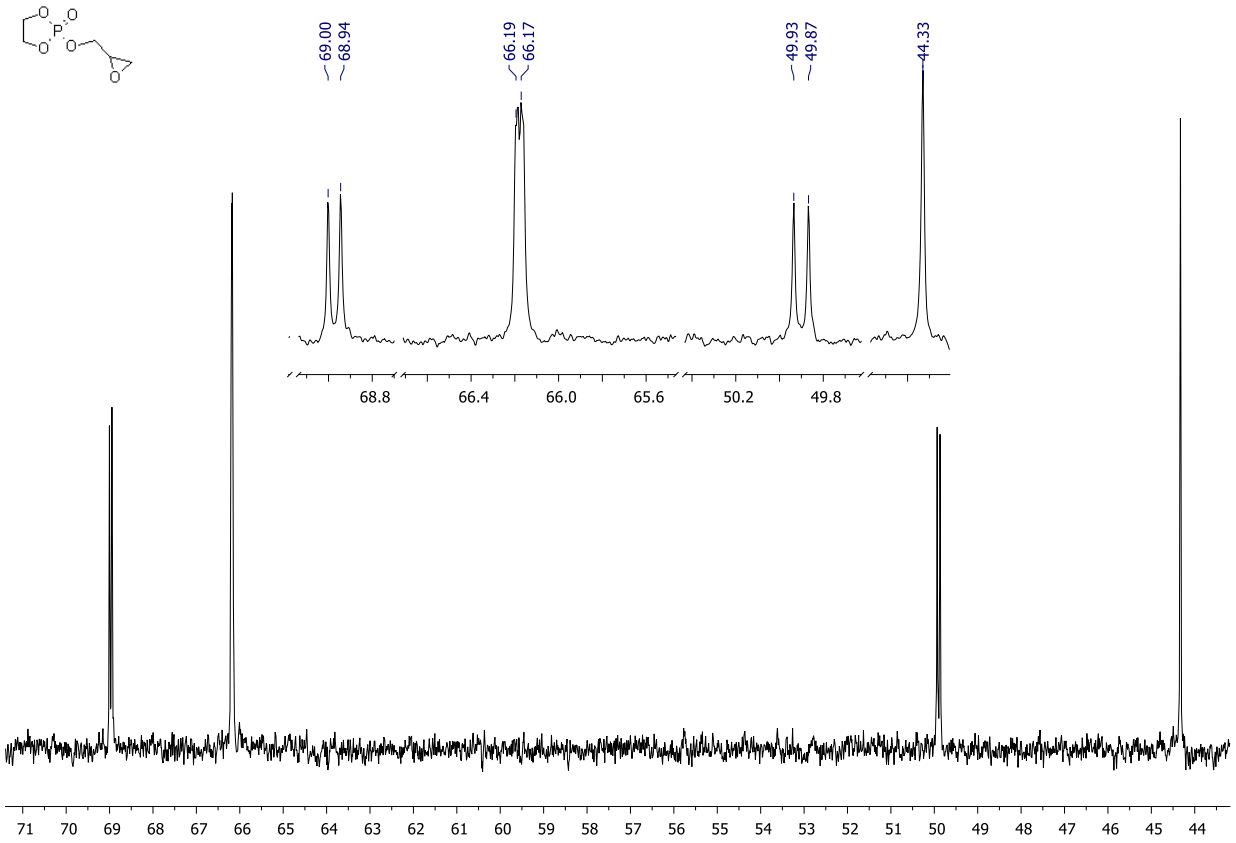


Fig. S8. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of **1**

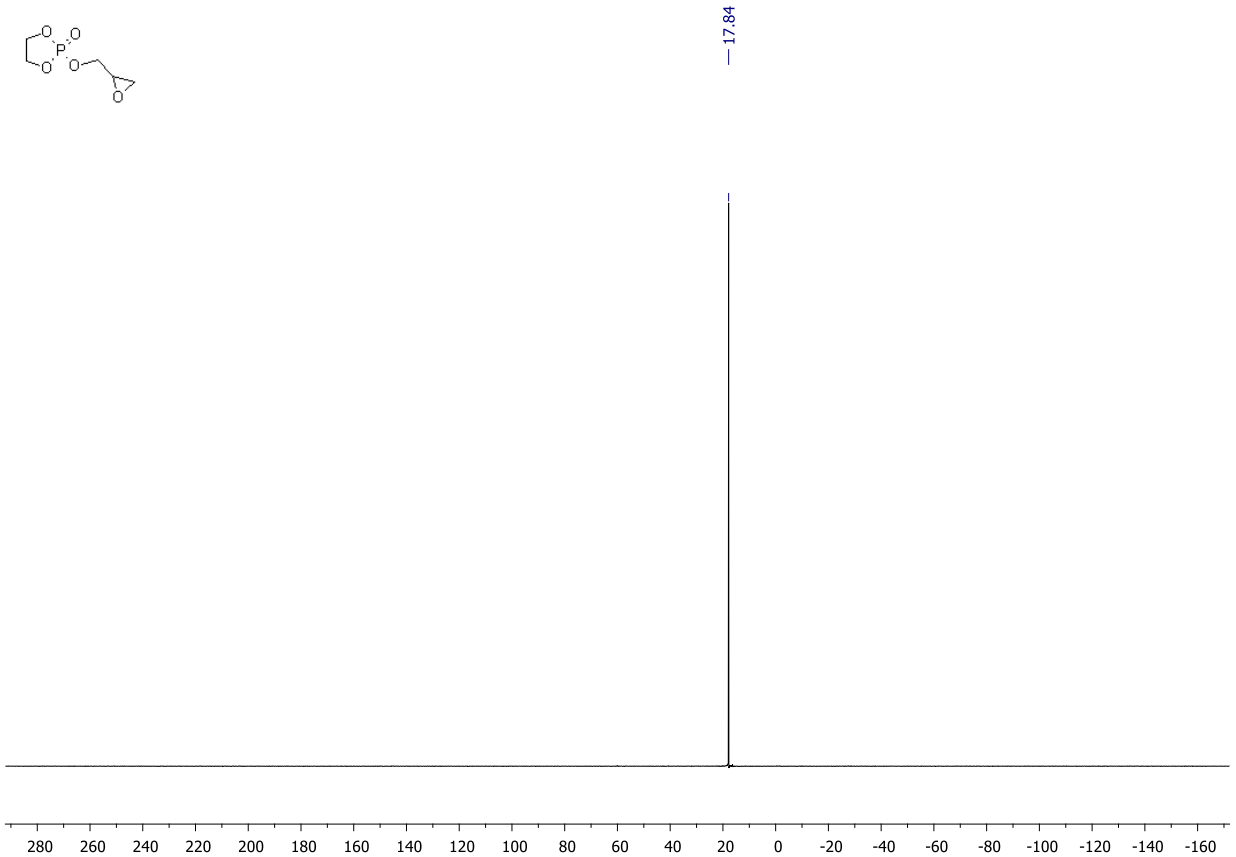


Fig. S9. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of **1**

S5. Polymer synthesis and characterization

*Polymerization of GlyO-EP using **BHT-Mg** as the catalyst at 20 °C (Table 3, Run 1).*

Monomer **1** (1.320 g, $7.33 \cdot 10^{-3}$ 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 3.3 ml. A stock solution of **BHT-Mg** in dry THF (317 mg, $7.50 \cdot 10^{-4}$ mol Mg in 8.2 ml solution) was prepared. The polymerization was started by rapid injection of the stock solution of **BHT-Mg** (0.4 ml solution, $7.31 \cdot 10^{-5}$ mol Mg) to the stirred solution of **1** to reach a total reaction concentration of [**1**] of 2 *M*. 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=17.9 ppm) and polymer (δ=-1.2 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), the supernatant was decanted and re-dissolved 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 1.08 g (82%). The amount of branches in polymer chain was determined using ^{31}P NMR spectroscopy by integration of the resonance signals of branched (δ –1.44 ppm) and unbranched (δ –1.29 ppm) phosphorus atoms, see Fig. S12.

*Polymerization of **1** using **BHT-Mg** as the catalyst at -50 °C (Table 1, Run 2).*

Monomer **1** (0.329 g, $1.83 \cdot 10^{-3}$ 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 0.7 ml. A stock solution of **BHT-Mg** 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 injection of the stock solution of **BHT-Mg** (0.2 ml solution, $1.82 \cdot 10^{-5}$ mol Mg) to the stirred solution of **1** to reach a total reaction concentration of [**1**] of 2 *M*. 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=17.9 ppm) and polymer (δ= –1.2 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), the supernatant was decanted and re-dissolved 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 0.28 g (86%).

Linear homopolymer containing only traces of branches was obtained, see Fig. S15.

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 5.05 (d, $^3J_{HP}$ = 8.1 Hz, PhCH_2); 4.34 (m, 1H); 4.24 (dd, $^3J_{HP}$ = 4.3 Hz, 4H, –OCH_2CH_2O–); 3.89 (m, 1H) {–CH_2CHOCH$_2$}; 3.20 (m, 1H, –CH$_2$CHOCH$_2$); 2.79 (m, 1H); 2.63 (m, 1H) {–CH$_2$CHOCH_2}.

^{13}C{H} NMR (101 MHz, $CDCl_3$, 20 °C): δ 68.68 (d, $^2J_{CP}$ = 5.4 Hz); 66.49 (dd, $^2J_{CP}$ = 6.3 Hz); 49.88 (d, $^3J_{CP}$ = 7.5 Hz); 44.32.

^{31}P{H} NMR (162 MHz, $CDCl_3$, 20 °C): δ –1.29.

*Polymerization of **1** using **TBD** as the catalyst at 20 °C (Table 3, Run 3).*

Monomer **1** (1.294 g, $7.18 \cdot 10^{-3}$ 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 3.4 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 (78 mg benzyl alcohol, $7.21 \cdot 10^{-4}$ mol in 1.0 ml solution) were prepared. The initiator (0.1 ml of the stock solution, $7.21 \cdot 10^{-5}$ mol) was added to the stirred solution of monomer **1**. The polymerization was started by rapid injection of the stock solution of **TBD** (0.1 ml of solution, $7.18 \cdot 10^{-5}$ mol) to the to the reaction mixture to reach total reaction concentration of [**1**] of 2 *M*. 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=17.9 ppm) and polymer (δ=-1.2 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), the supernatant was decanted and re-dissolved 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 0.96 g (74%). The amount of branches in polymer chain was determined using ^{31}P NMR spectroscopy by integration of the resonance signals of branched (δ –1.44 ppm) and unbranched (δ –1.29 ppm) phosphorus atoms, see Fig. S16.

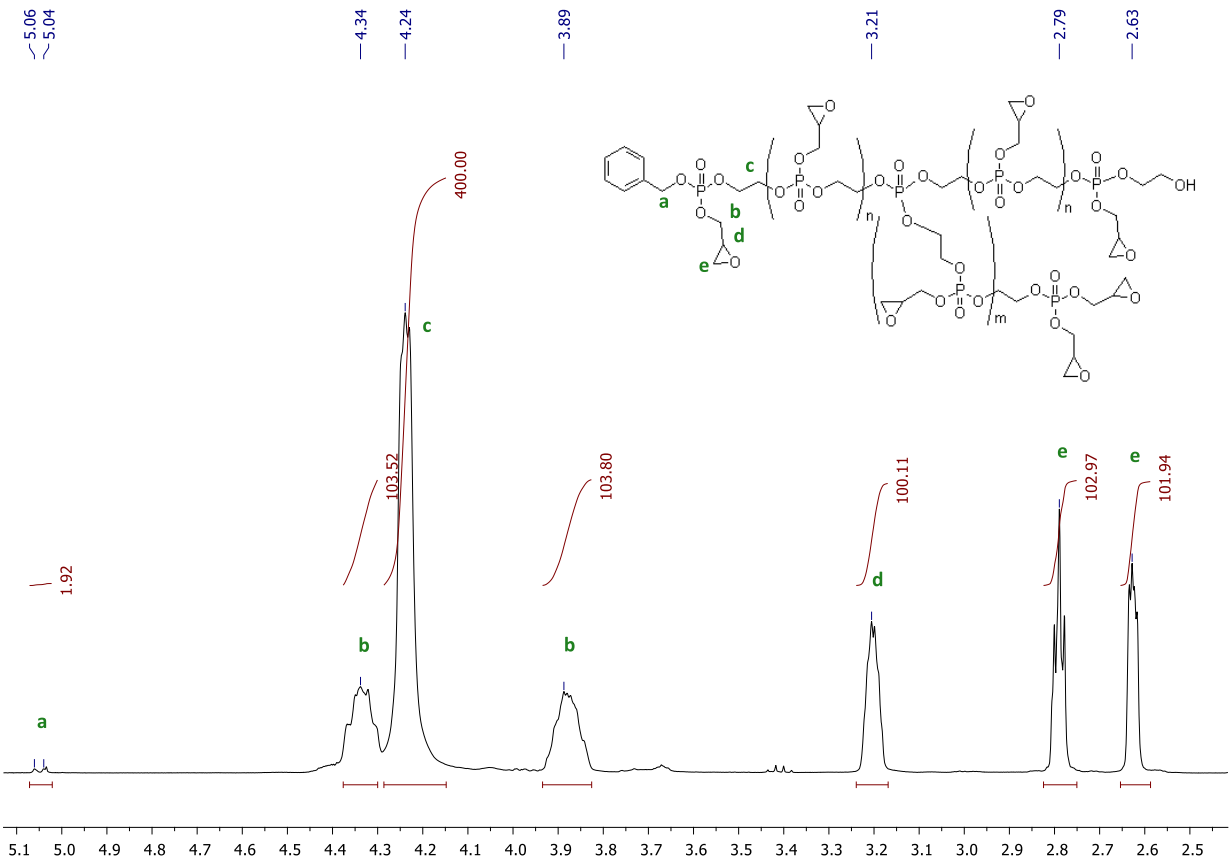


Fig. S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of poly-**1** prepared using **BHT-Mg** as the catalyst at 20 °C (Table 3, Run 1)

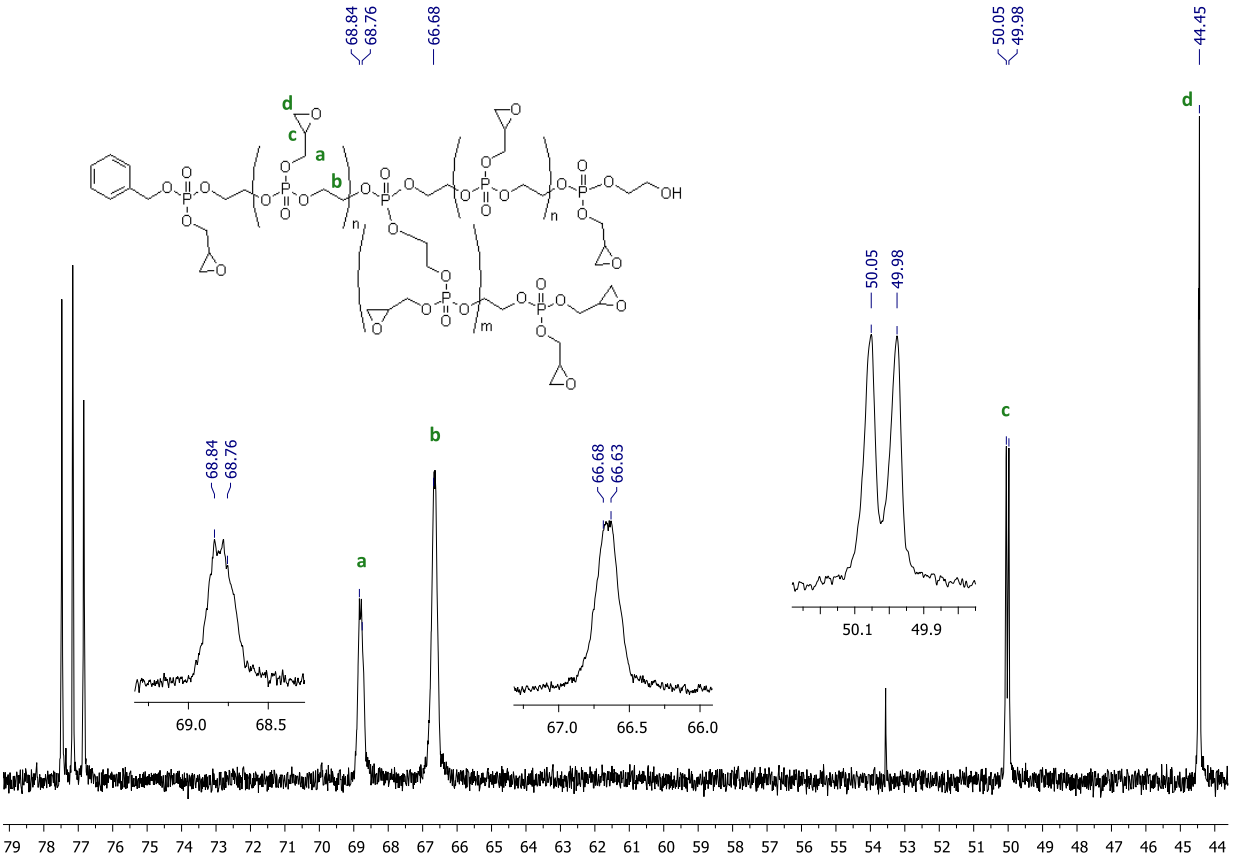


Fig. S11. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of poly-**1** prepared using **BHT-Mg** as the catalyst at 20 °C Table 3, Run 1)

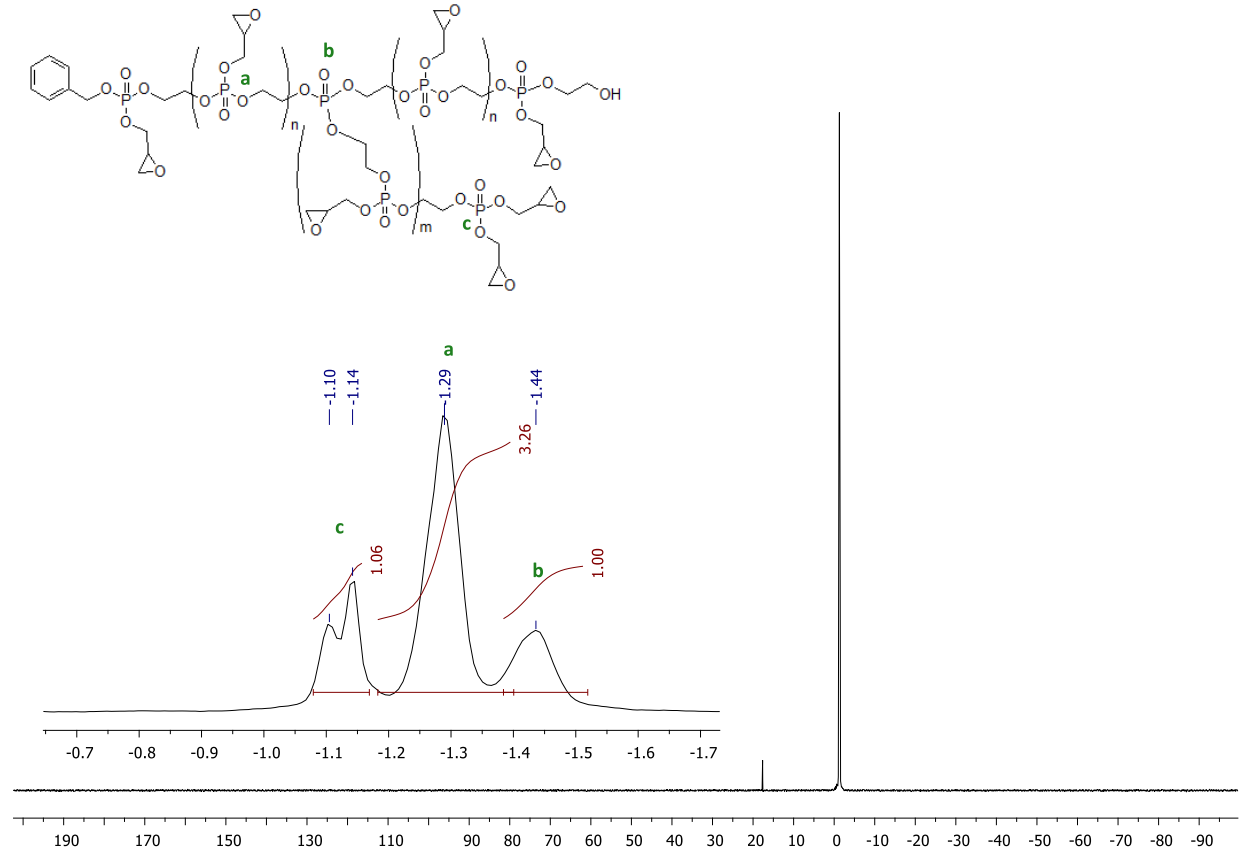


Fig. S12. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of poly-**1** prepared using **Mg3** as the catalyst at 20 °C (Table 3, Run 1)

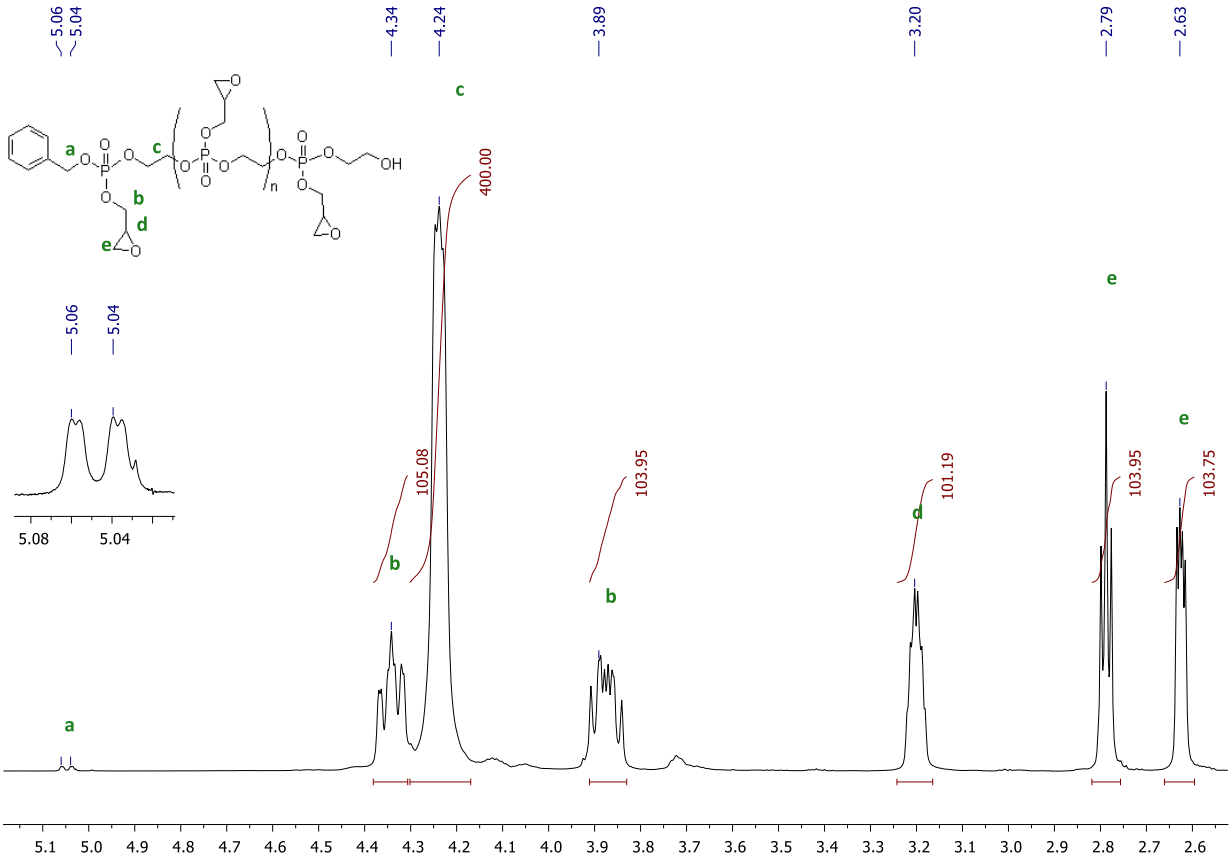


Fig. S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of poly-**1** prepared using **Mg3** as the catalyst at –50 °C (Table 3, Run 2)

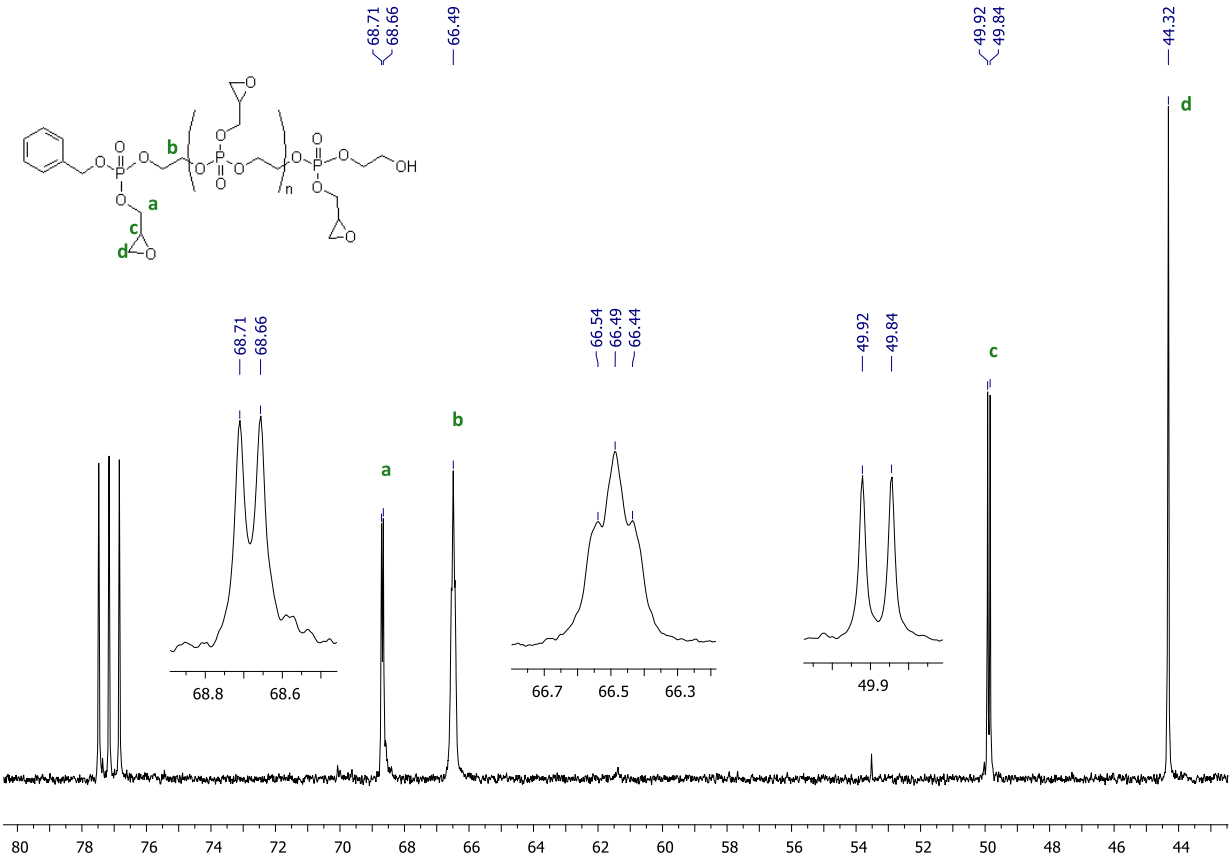


Fig. S14. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of poly-**1** prepared using **Mg3** as the catalyst at –50 °C (Table 3, Run 2)

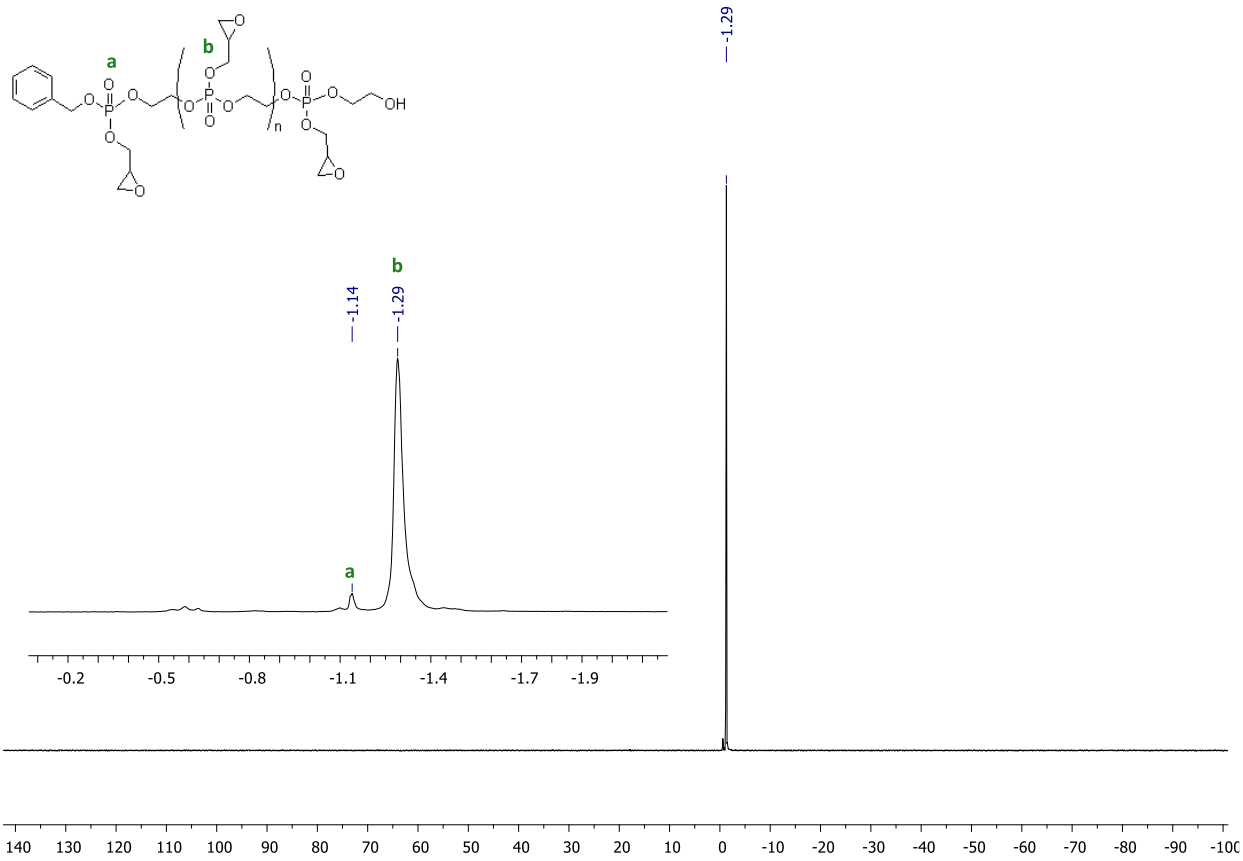


Fig. S15. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of poly-**1** prepared using **Mg3** as the catalyst at –50 °C (Table 3, Run 2)

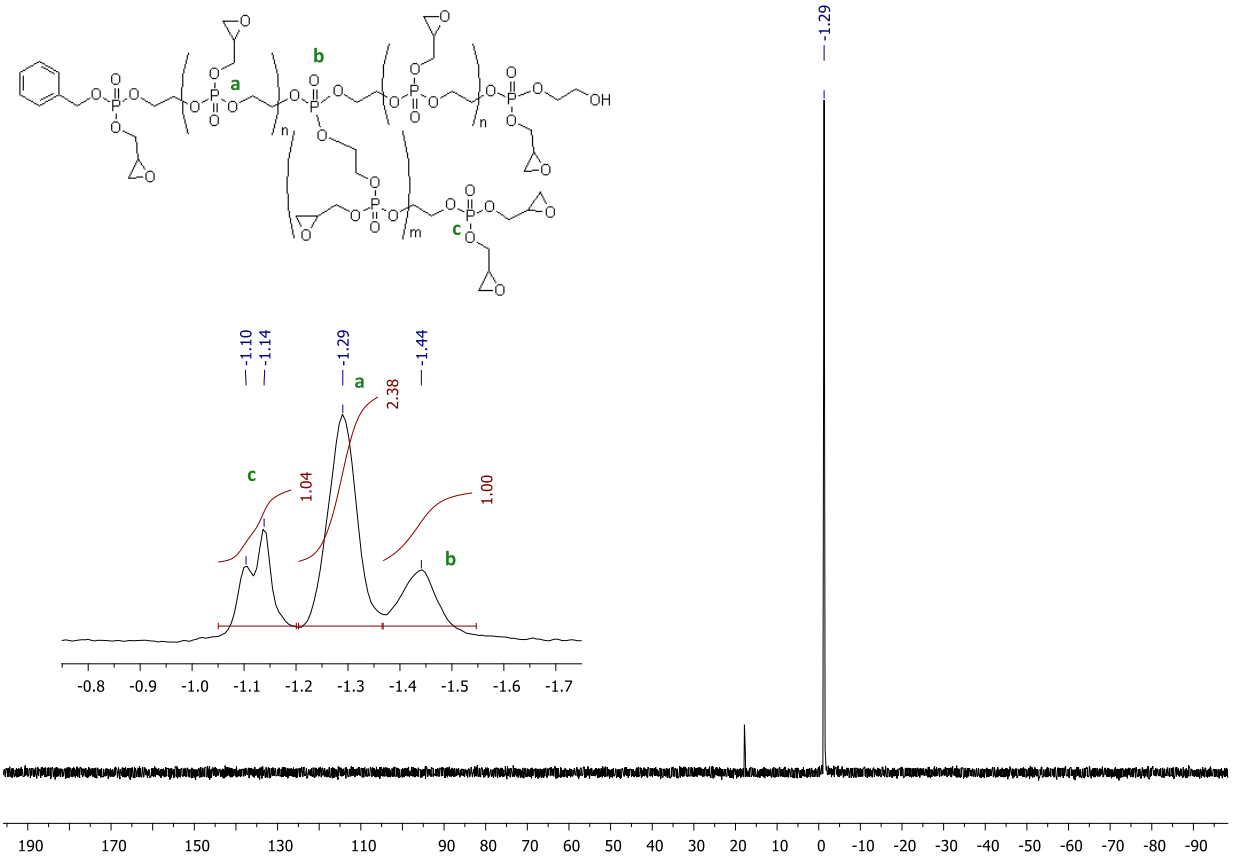


Fig. S16. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 20 °C) of poly-**1** prepared using **TBD** as the catalyst at 20 °C (Table 3, Run 3)