

# Electronic Supplementary Information for Poly(phosphonate)-mediated Horner-Wadsworth-Emmons Reactions

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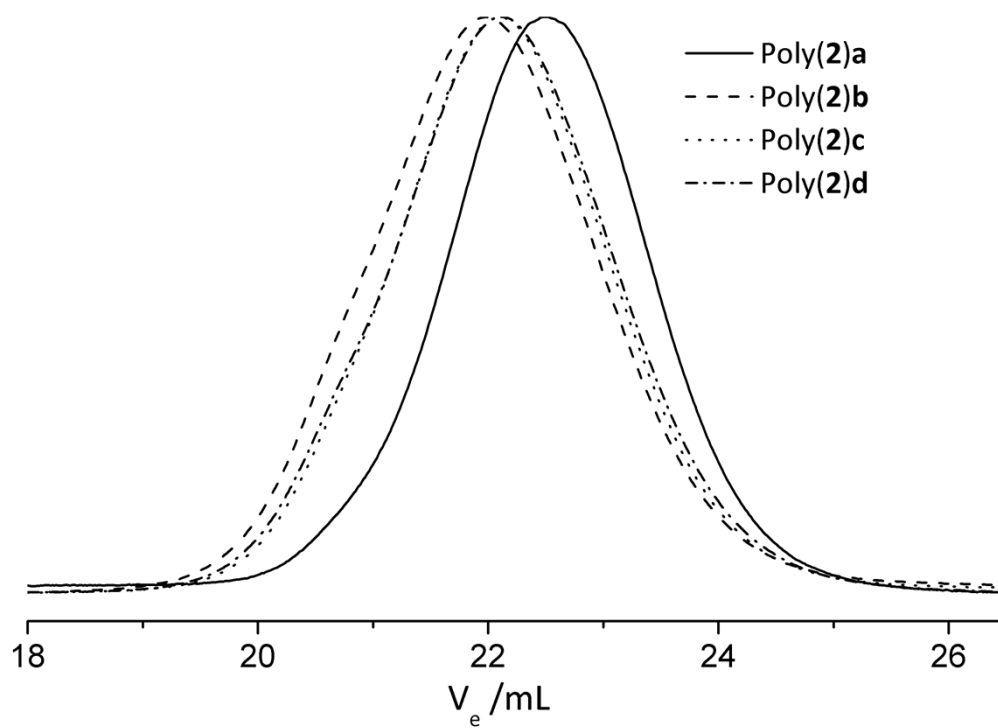
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330.*

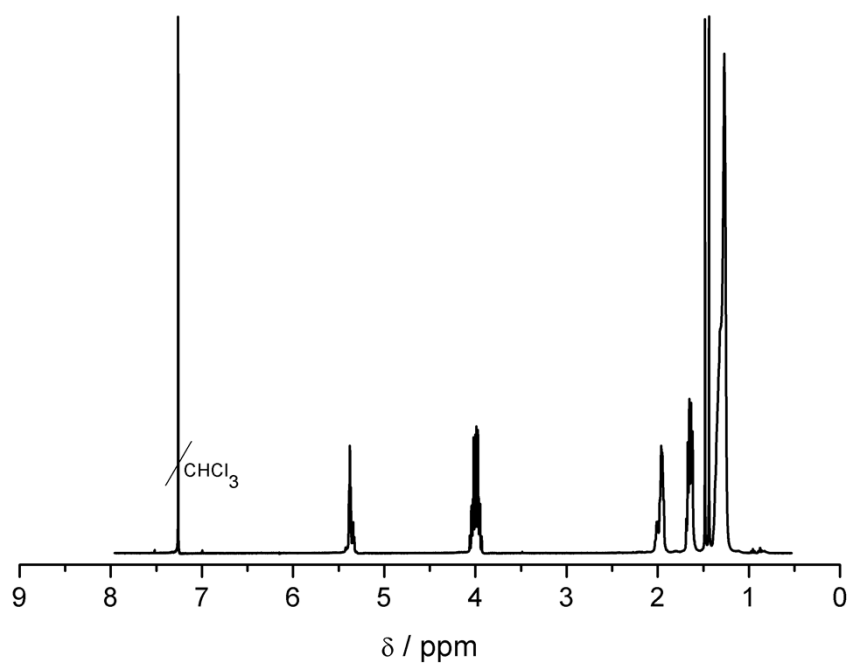
## **Content**

1. SEC elugrams and  $^1\text{H}$ ,  $^{13}\text{C}\{\text{H}\}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}\{\text{H}\}$  and 2D NMR spectra.
2. Base-screening for the poly(phosphonate)-mediated HWE reaction.

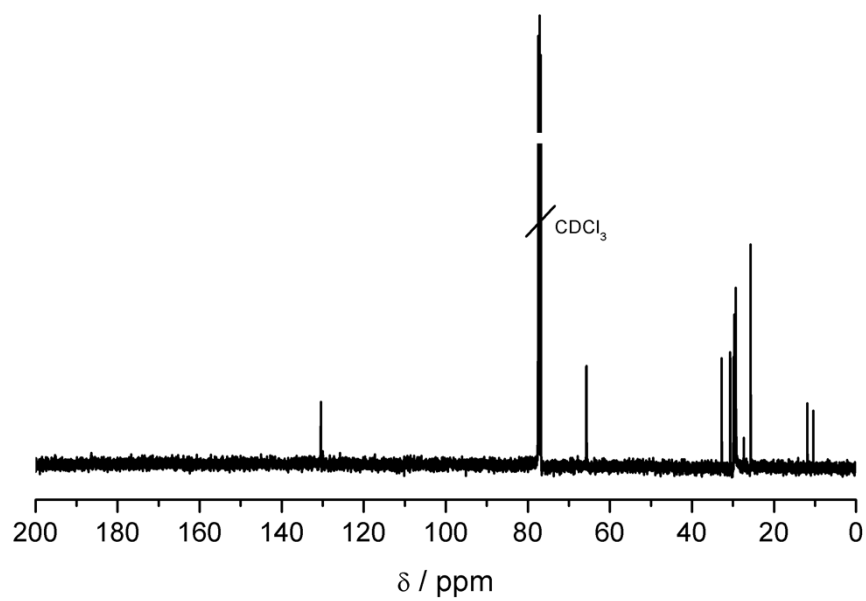
**1. SEC elugrams and  $^1\text{H}$ ,  $^{13}\text{C}\{\text{H}\}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}\{\text{H}\}$  and 2D NMR spectra.**



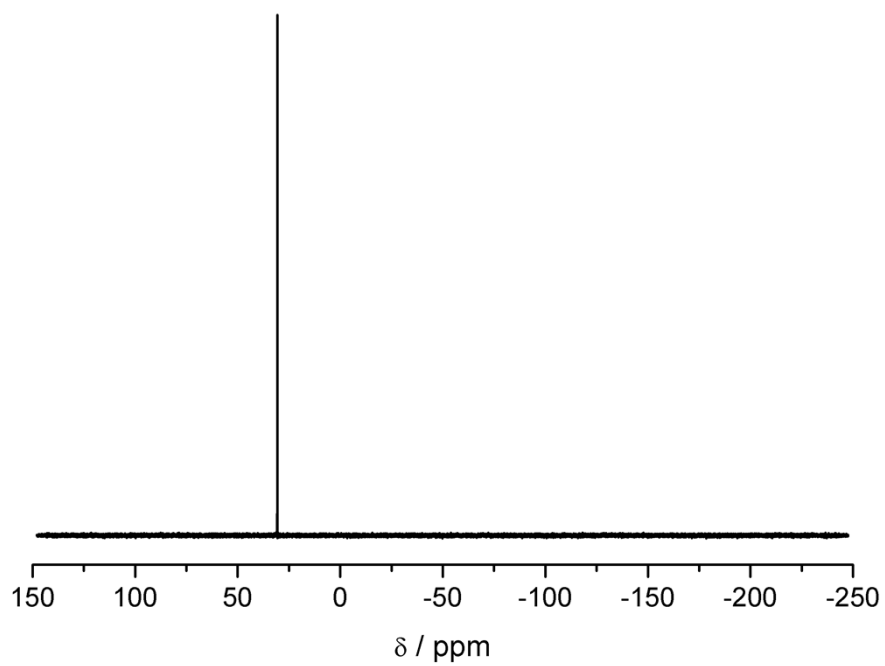
**Figure S1.** SEC elugrams of poly(2)a-d in THF.



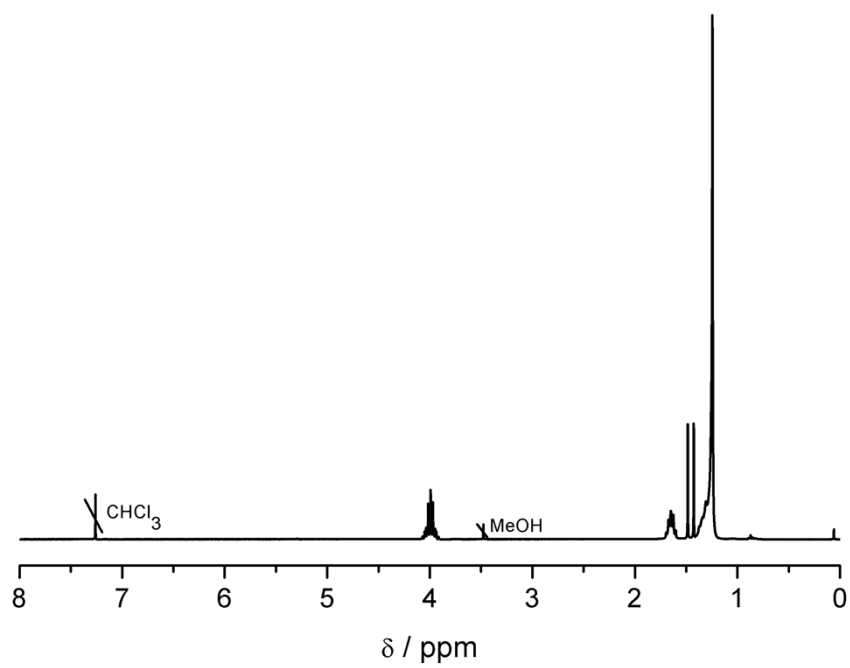
**Figure S2.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298K) of poly(**2**)**d**.



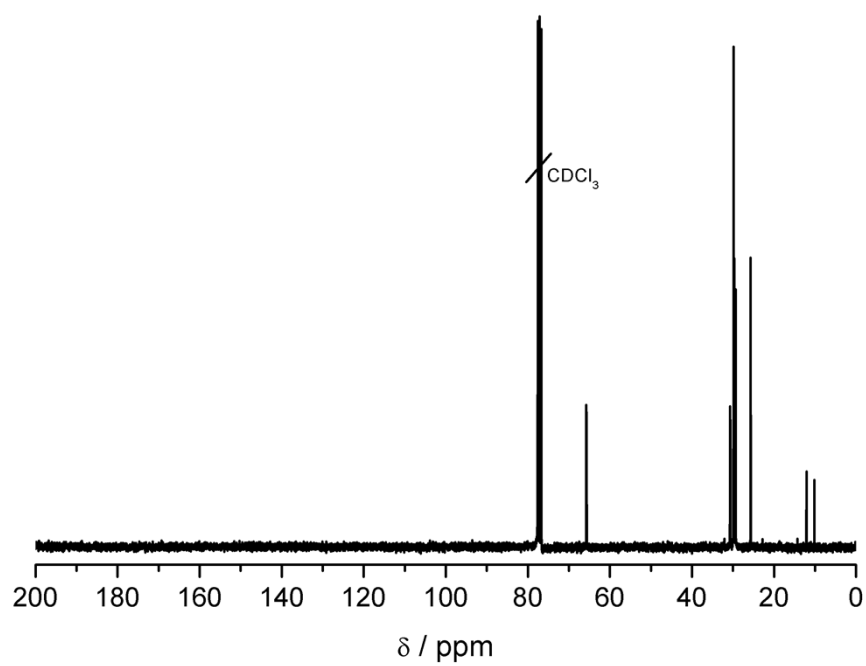
**Figure S3.**  $^{13}\text{C}\{\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 298K) of poly(**2**)**d**.



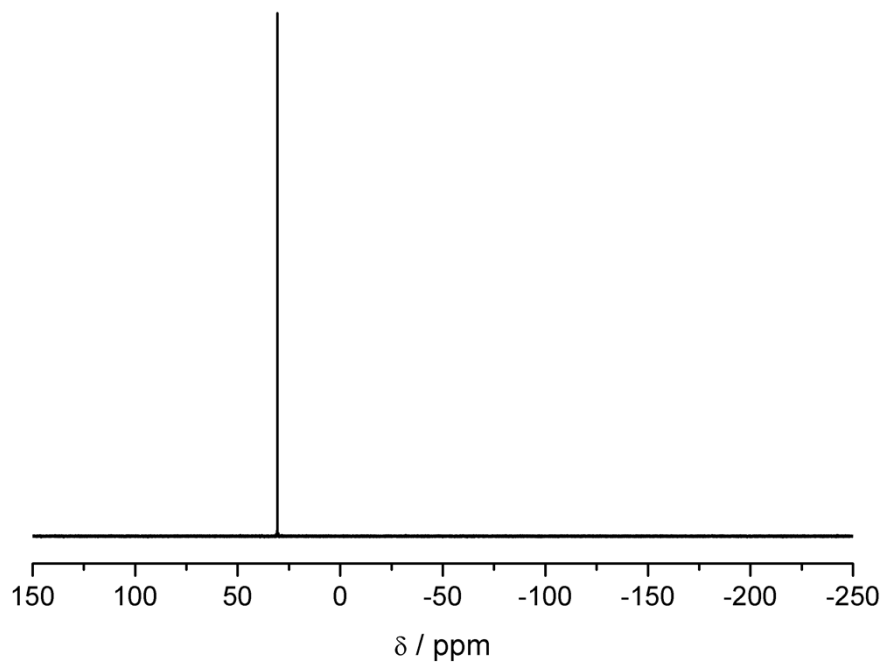
**Figure S4.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ , 298K) of poly(2)d.



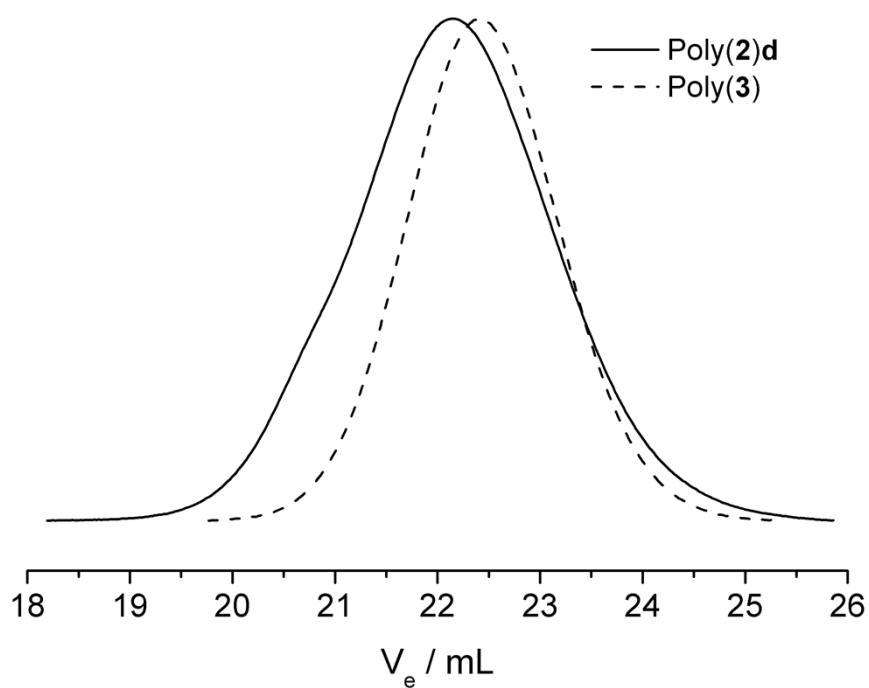
**Figure S5.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298K) of poly(3).



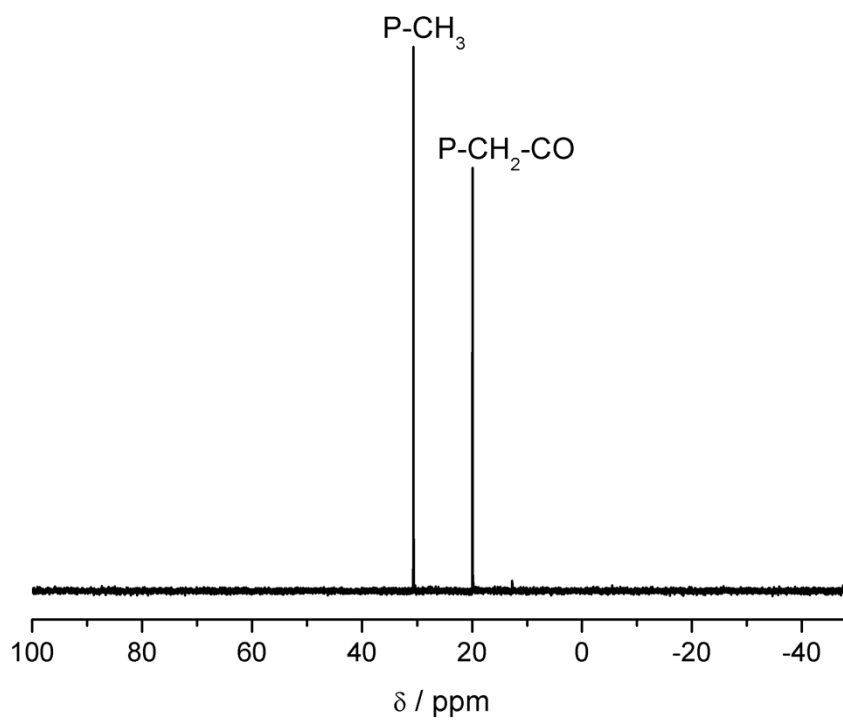
**Figure S6.**  $^{13}\text{C}\{\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 298K) of poly(**3**).



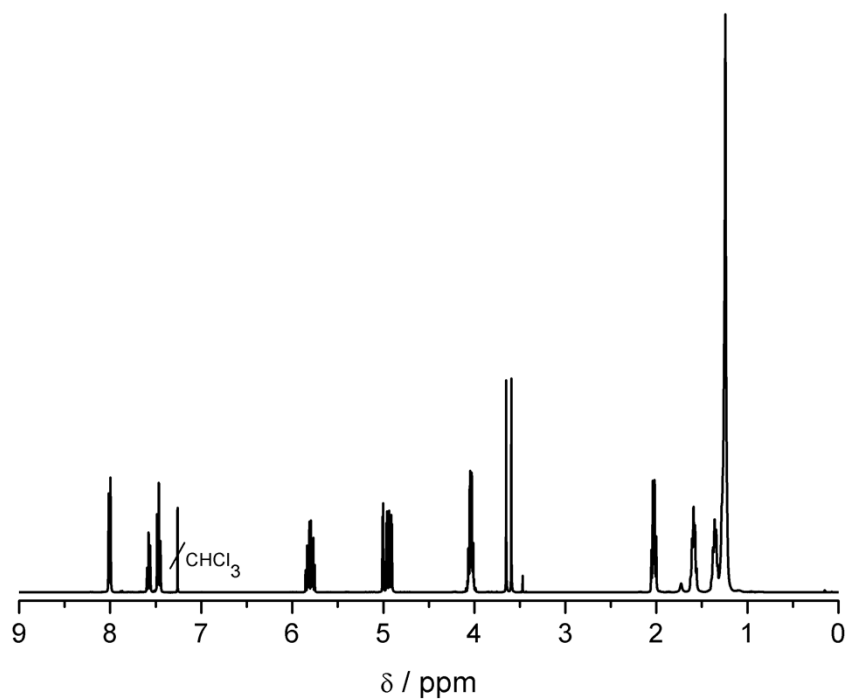
**Figure S7.**  $^{31}\text{P}\{\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ , 298K) of poly(**3**).



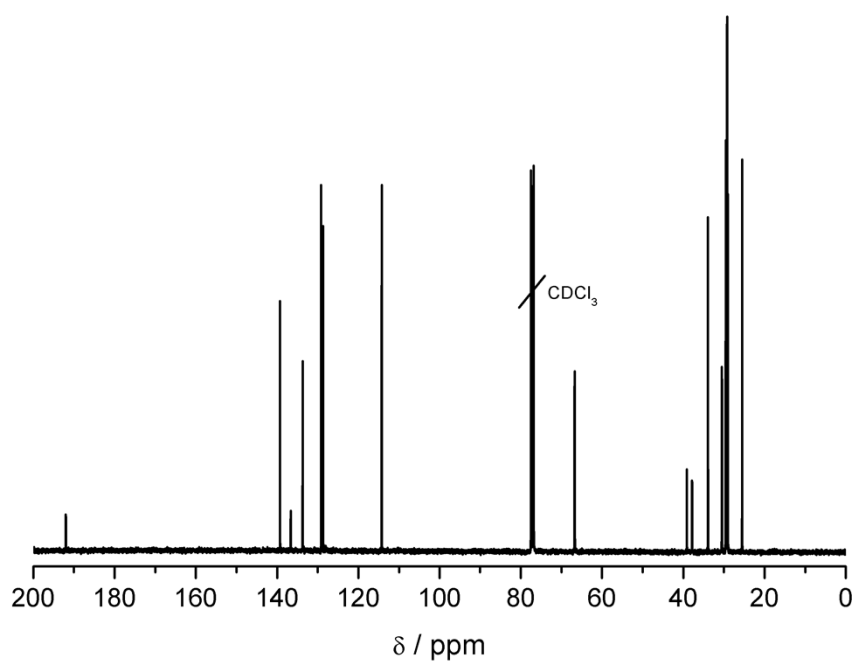
**Figure S8.** SEC elugrams of the unsaturated poly(**2**)**d** and the saturated poly(**3**) in THF.



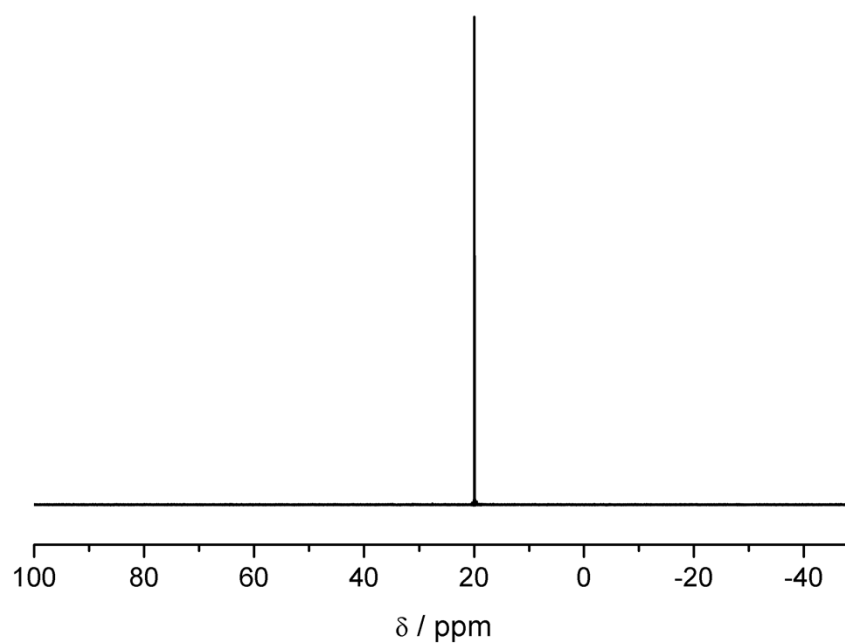
**Figure S9.**  $^{31}\text{P}\{\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ , 298K) of poly(**3-co-4**).



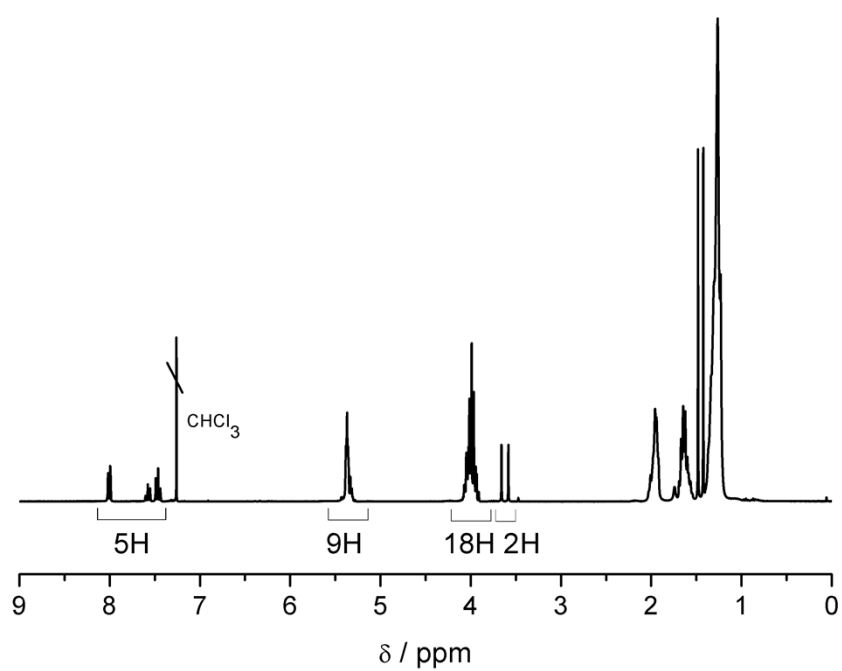
**Figure S10.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298K) of the phenacyl phosphonate monomer **5**.



**Figure S11.**  $^{13}\text{C}\{\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 298K) of the phenacyl phosphonate monomer **5**.

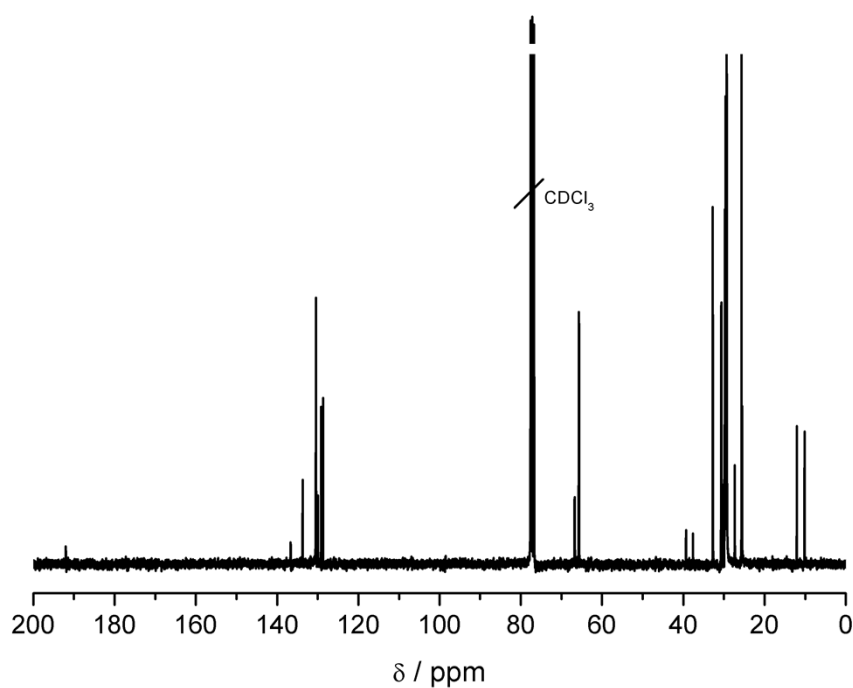


**Figure S12.**  $^{31}\text{P}\{\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ , 298K) of the phenacyl phosphonate monomer **5**.

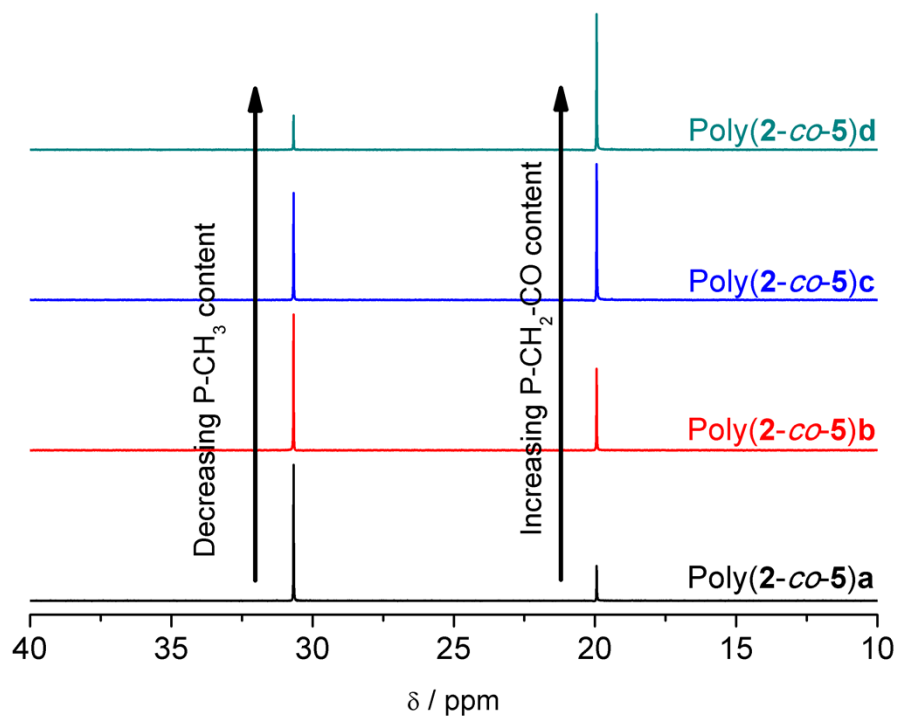




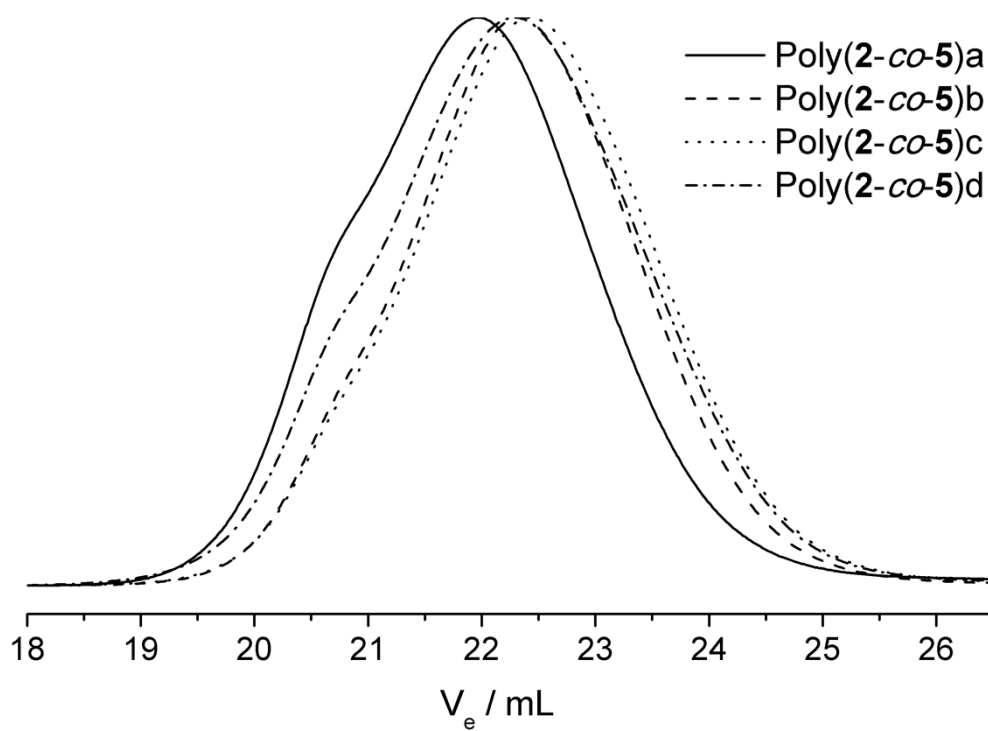
**Figure S13.** Representative  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298K) spectrum of poly(**2-co-5**)**a**. Integrals of the aromatic protons from 8.01 to 7.76 ppm, the multiplet from 5.40 to 5.29 and the multiplet from 4.09 to 3.91 ppm are given to allow calculation of phenacyl phosphonate content. The integral of the doublet at 3.62 ppm is also given to allow verification of the calculated ratio.



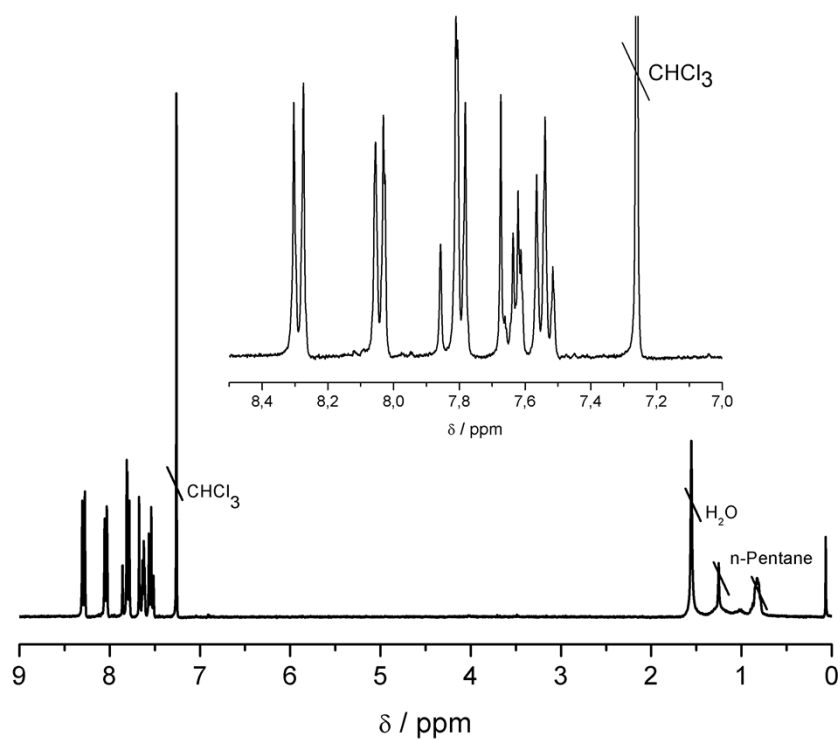
**Figure S14.** Representative  $^{13}\text{C}\{\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 298K) spectrum of poly(**2-co-5**)**a**.



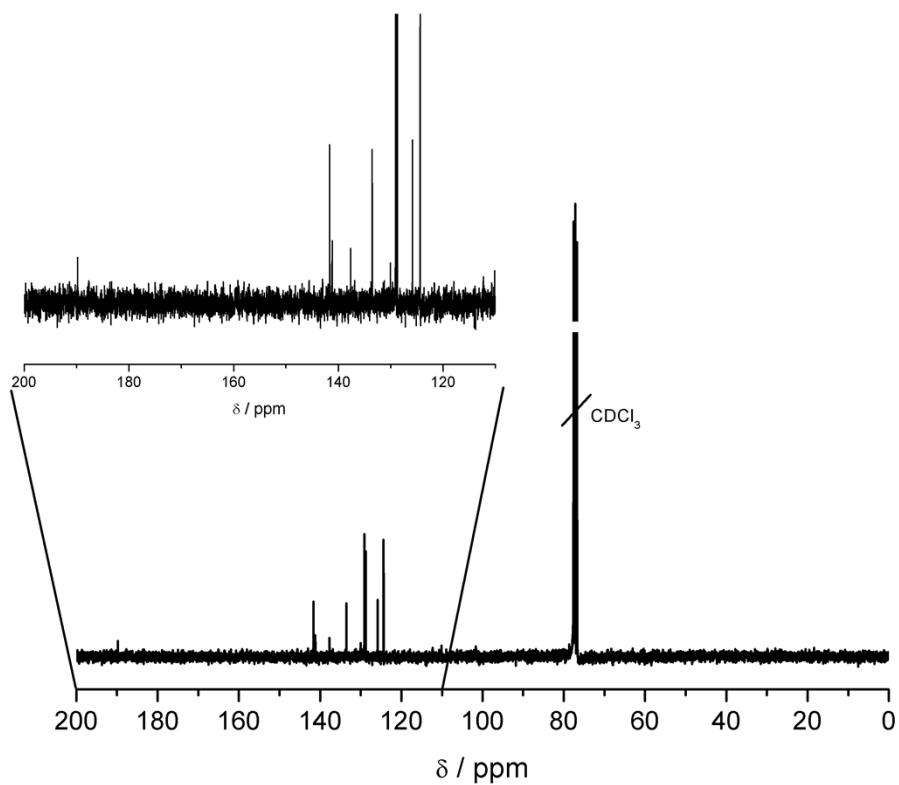
**Figure S15.**  $^{31}\text{P}\{\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ , 298K) spectra of poly(2-co-5)a-d. Increasing phenacyl phosphonate content and decreasing methyl phosphonate content can be observed qualitatively.



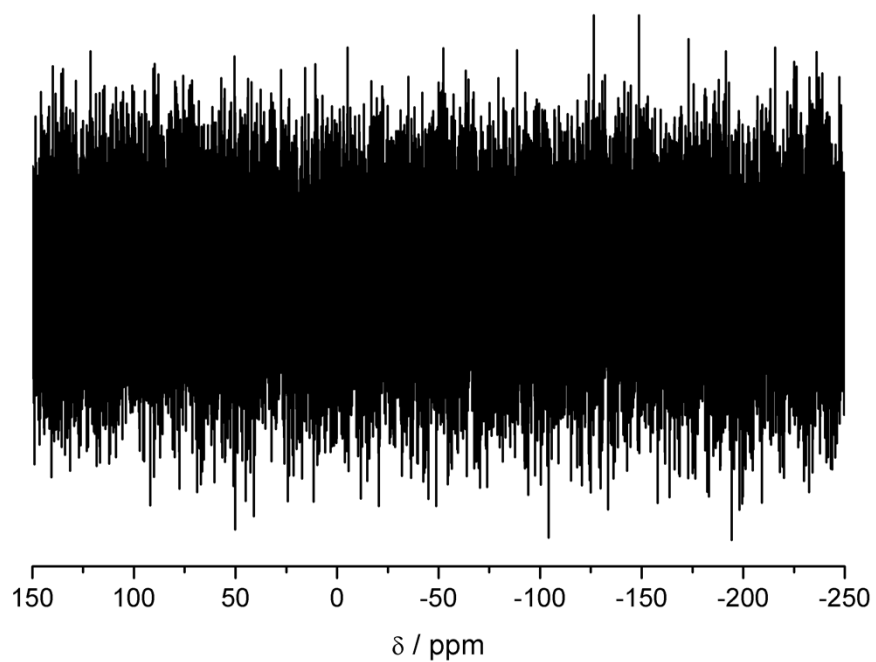
**Figure S16.** SEC elugrams of copolymers poly(2-co-5)a-d in THF.



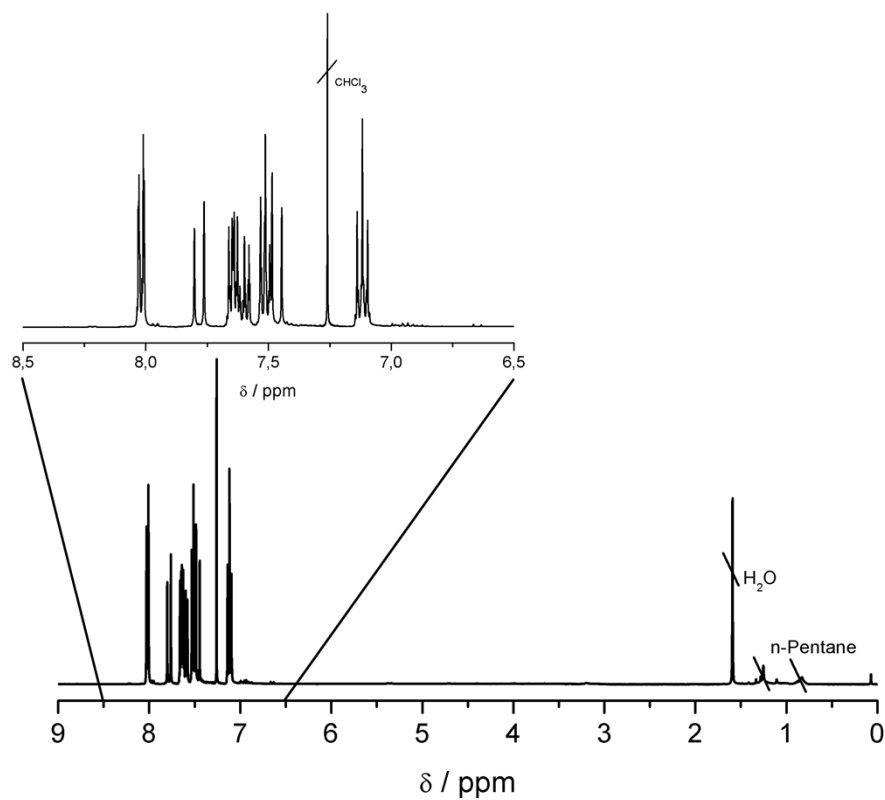
**Figure S17.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298K) of **7a**. The region from 8.5 to 7.0 ppm is magnified to aid clarity.



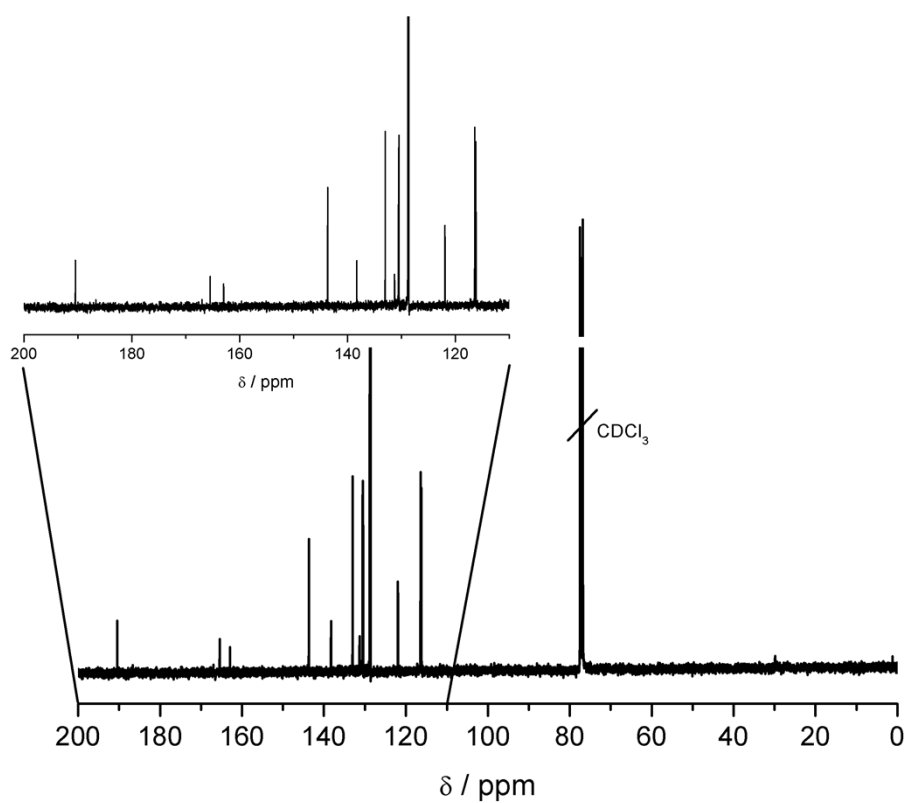
**Figure S18.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 298K) of **7a**. The region from 200 to 110 ppm is magnified to aid clarity.



**Figure S19.**  $^{31}\text{P}\{\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ , 298K) of **7a**. The absence of any signal proves the complete removal of all poly(phosphonate).

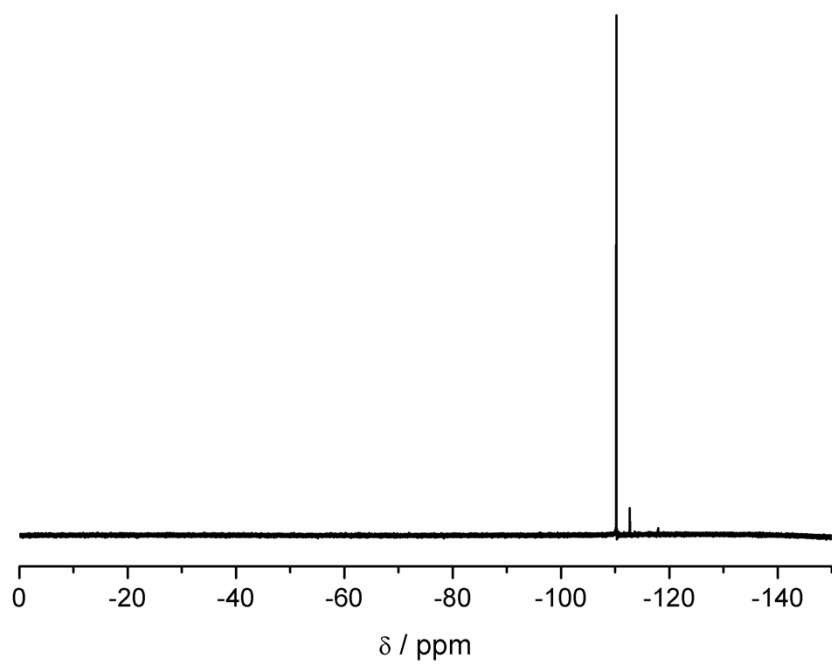


**Figure S20.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298K) of **7b**. The region from 8.5 to 6.5 ppm is magnified to aid clarity.

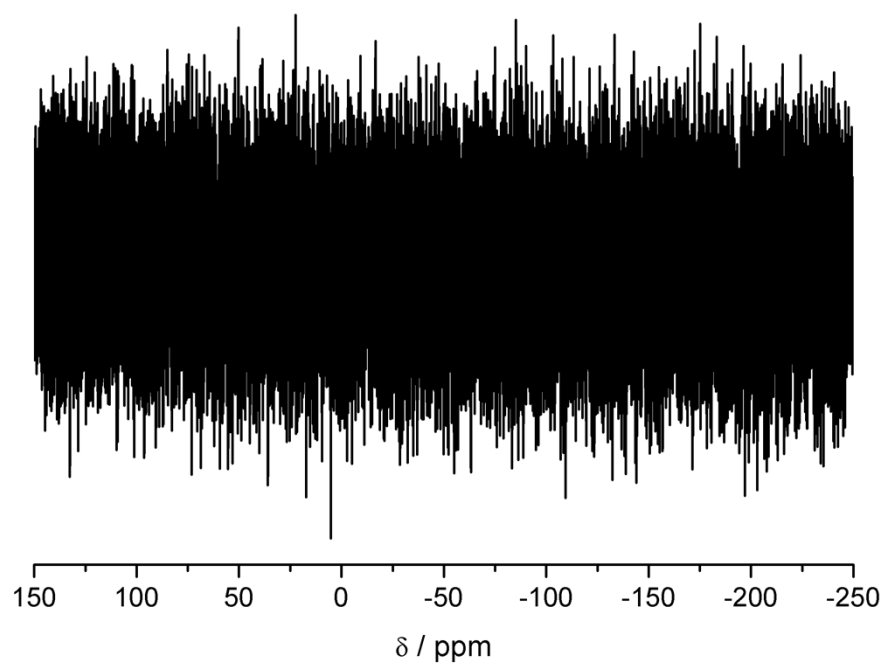


**Figure S21.**  $^{13}\text{C}\{\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 298K) of **7b**. The region from 200 to 110 ppm is magnified to aid clarity.

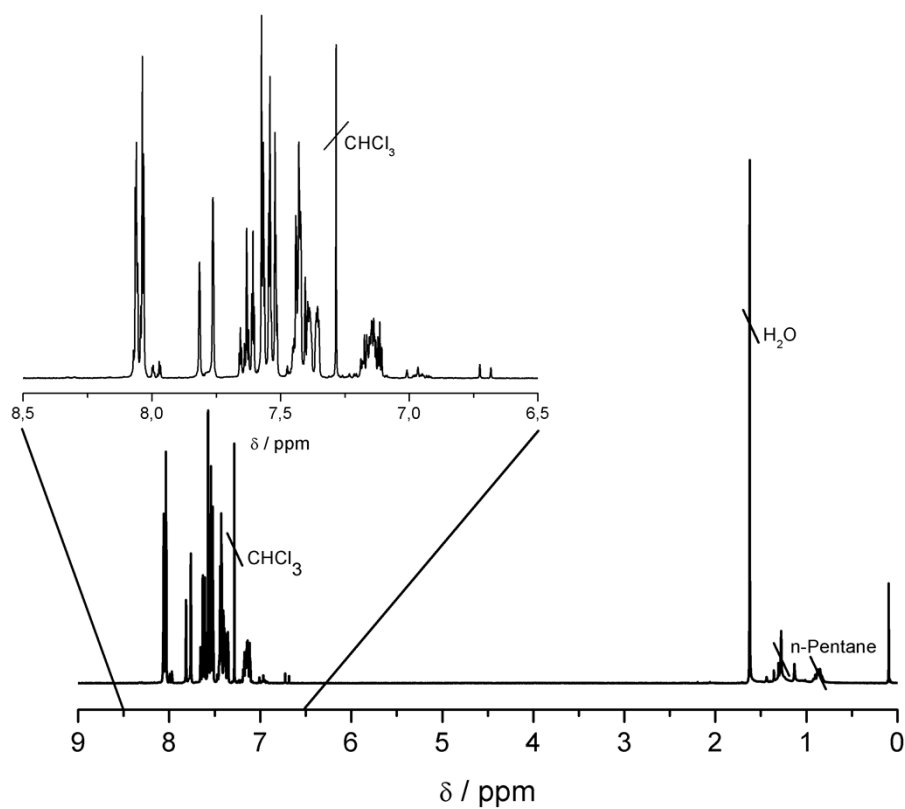




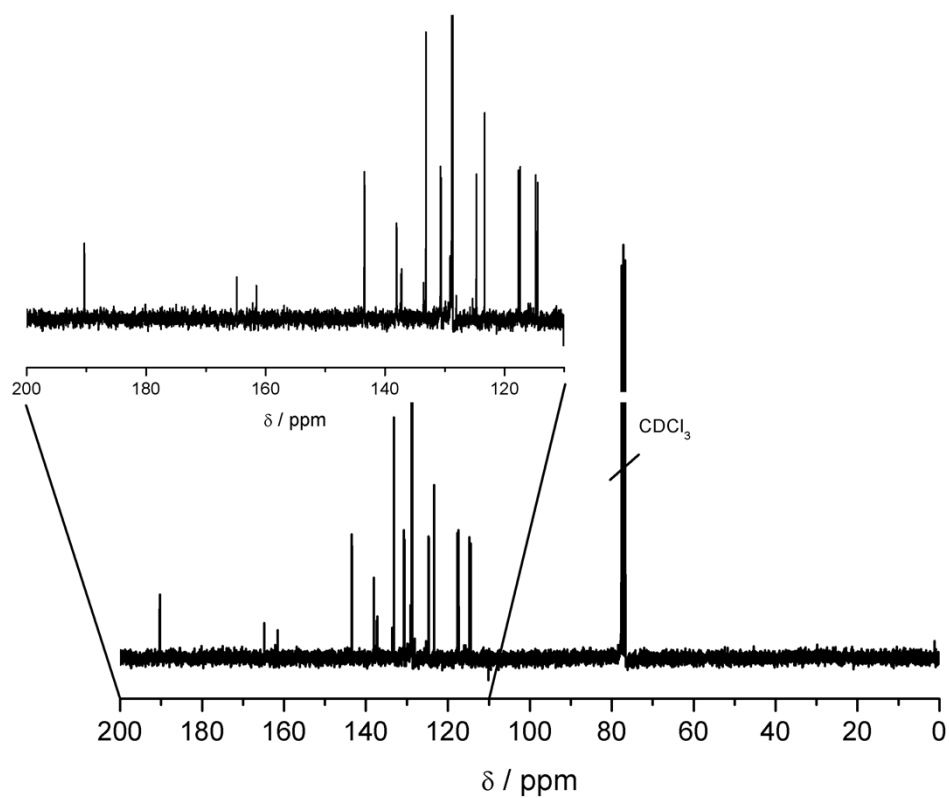
**Figure S22.**  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ , 298K) of **7b**.



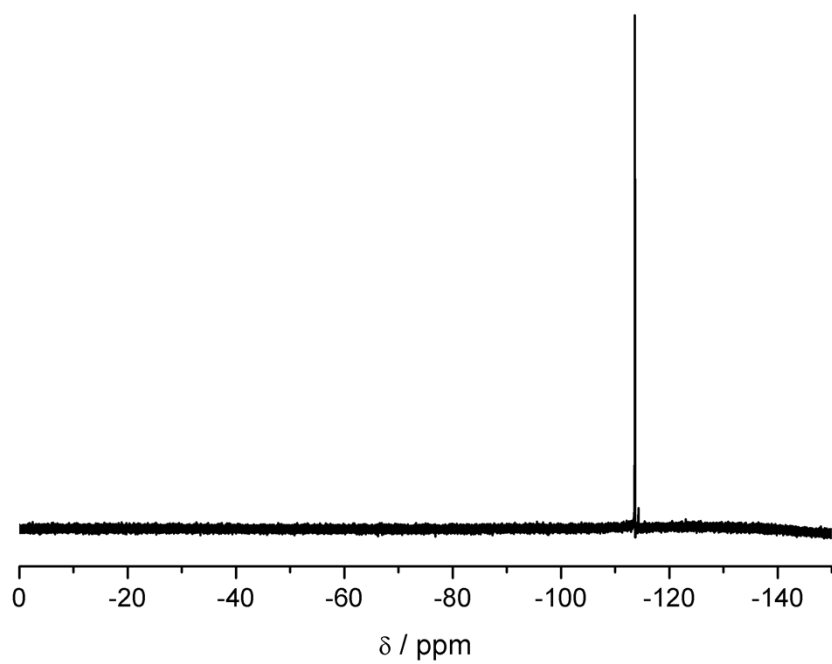
**Figure S23.**  $^{31}\text{P}\{\text{H}\}$  NMR(121 MHz,  $\text{CDCl}_3$ , 298K) of **7b**. The absence of any signal proves the complete removal of all poly(phosphonate).



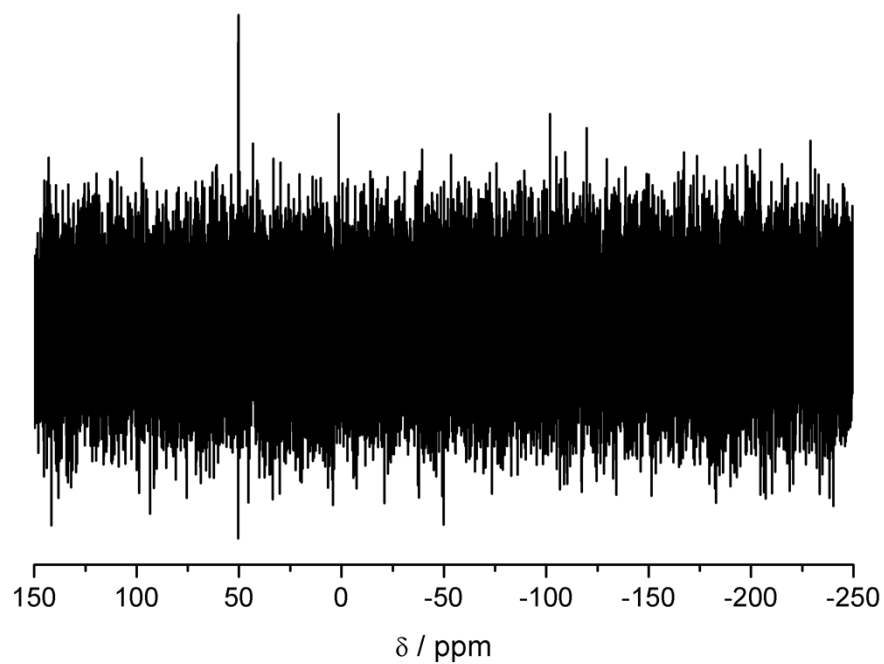
**Figure S24.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298K) of **7c**. The region from 8.5 to 6.5 ppm is magnified to aid clarity.



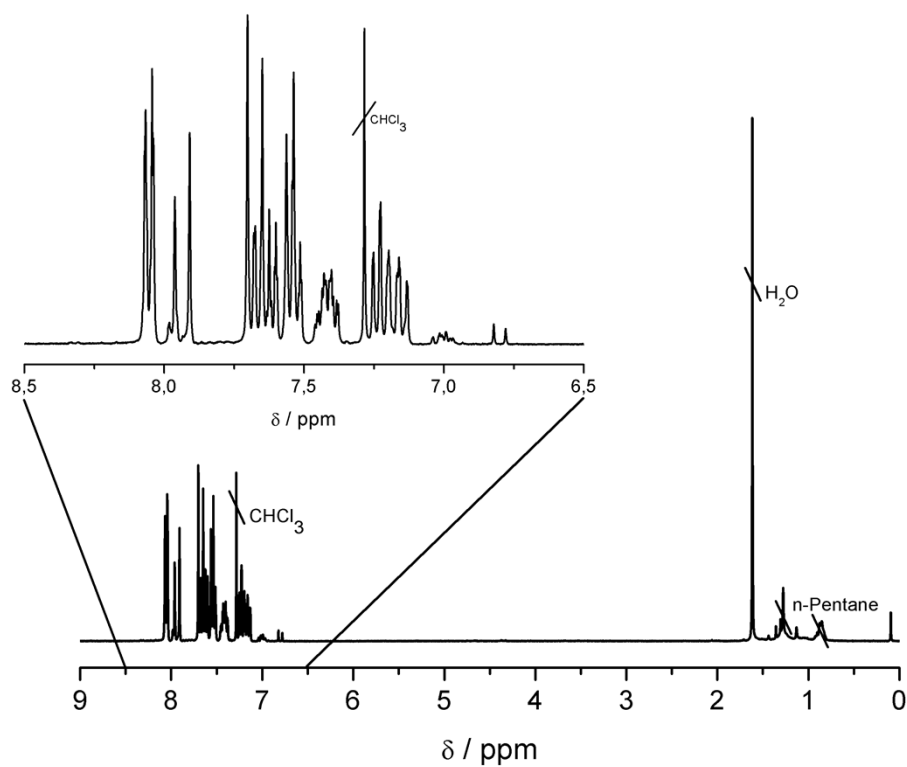
**Figure S25.**  $^{13}\text{C}\{\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 298K) of **7c**. The region from 200 to 110 ppm is magnified to aid clarity.



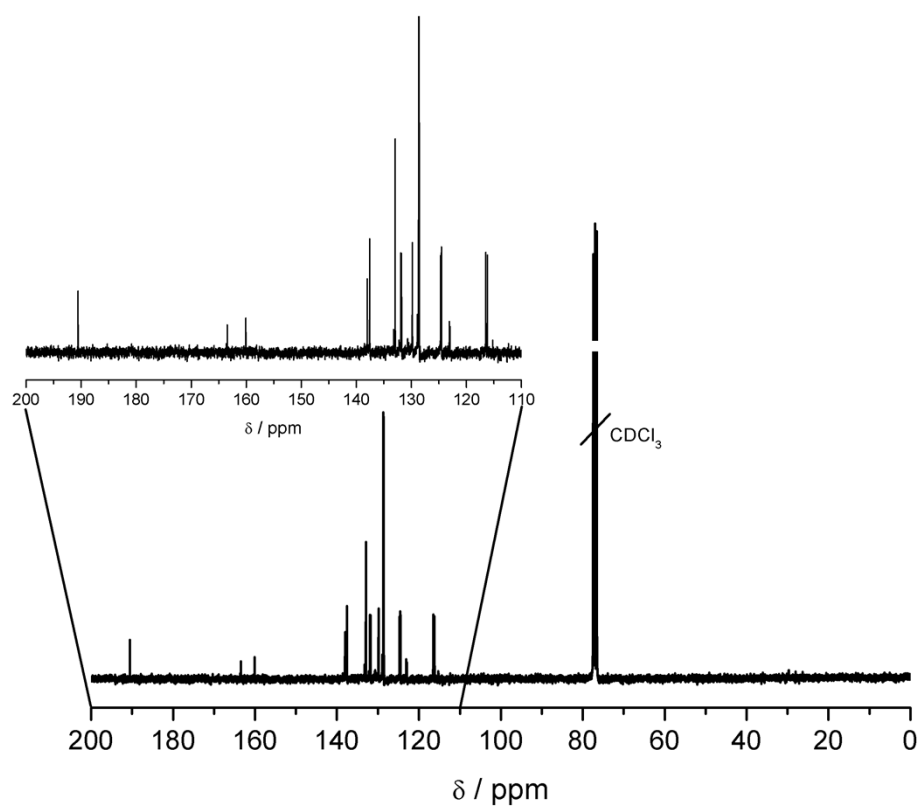
**Figure S26.**  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ , 298K) of **7c**.



**Figure S27.**  $^{31}\text{P}\{\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ , 298K) of **7c**. The absence of any signal proves the complete removal of all poly(phosphonate).

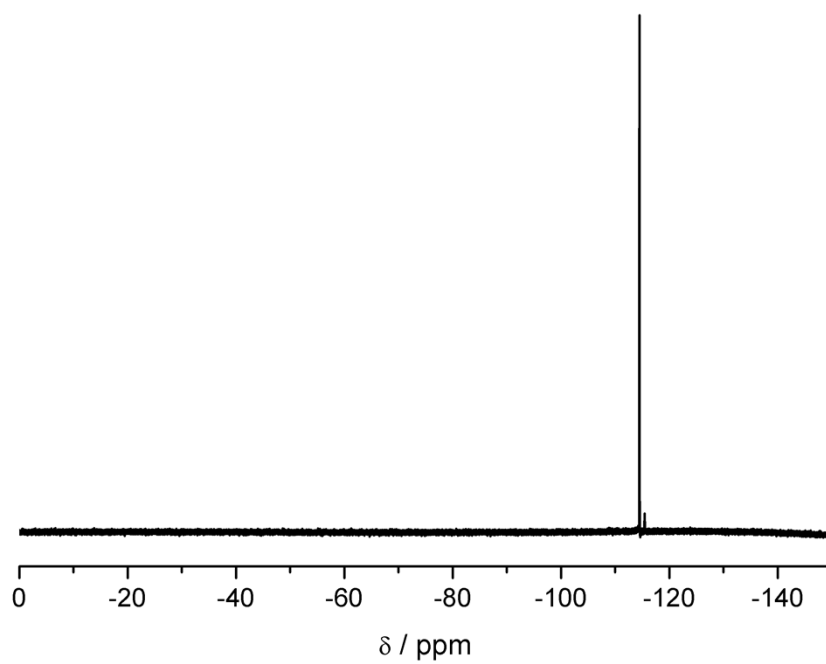


**Figure S28.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298K) of **7d**. The region from 8.5 to 6.5 ppm is magnified to aid clarity.

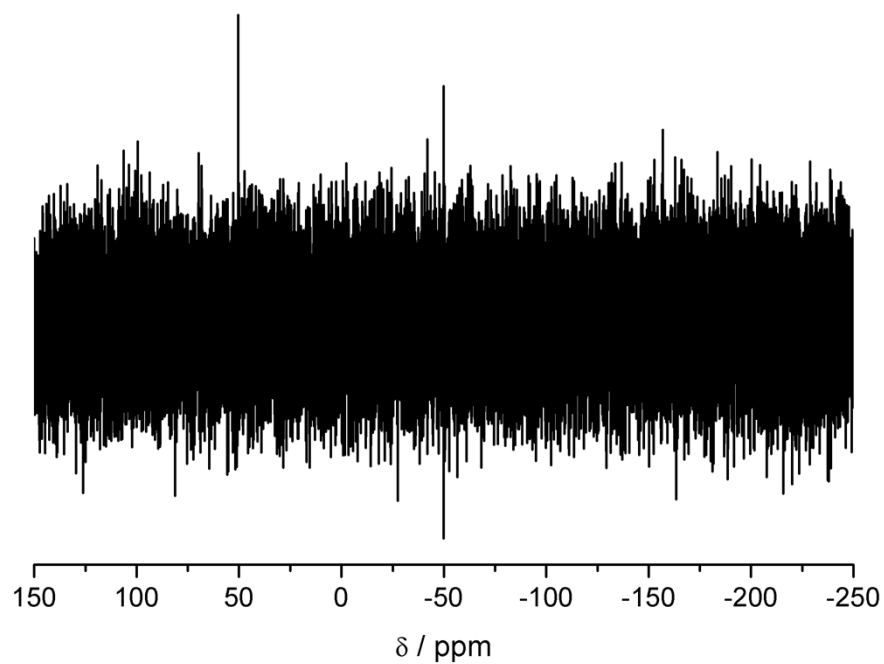


**Figure S29.**  $^{13}\text{C}\{\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 298K) of **7d**. The region from 200 to 110 ppm is magnified to aid clarity.

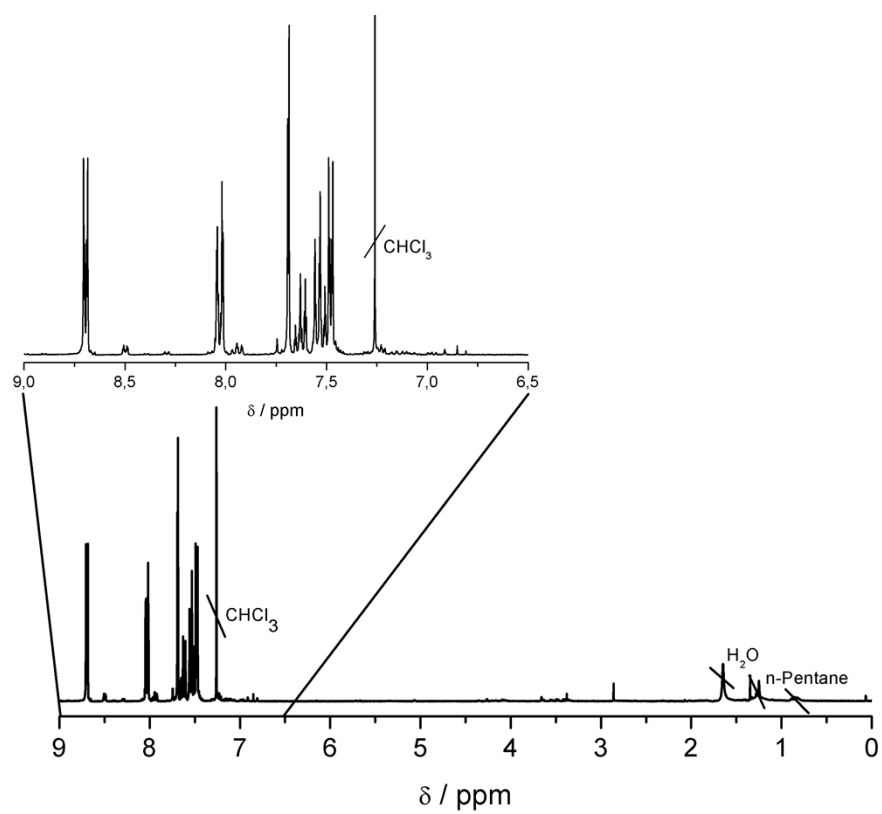




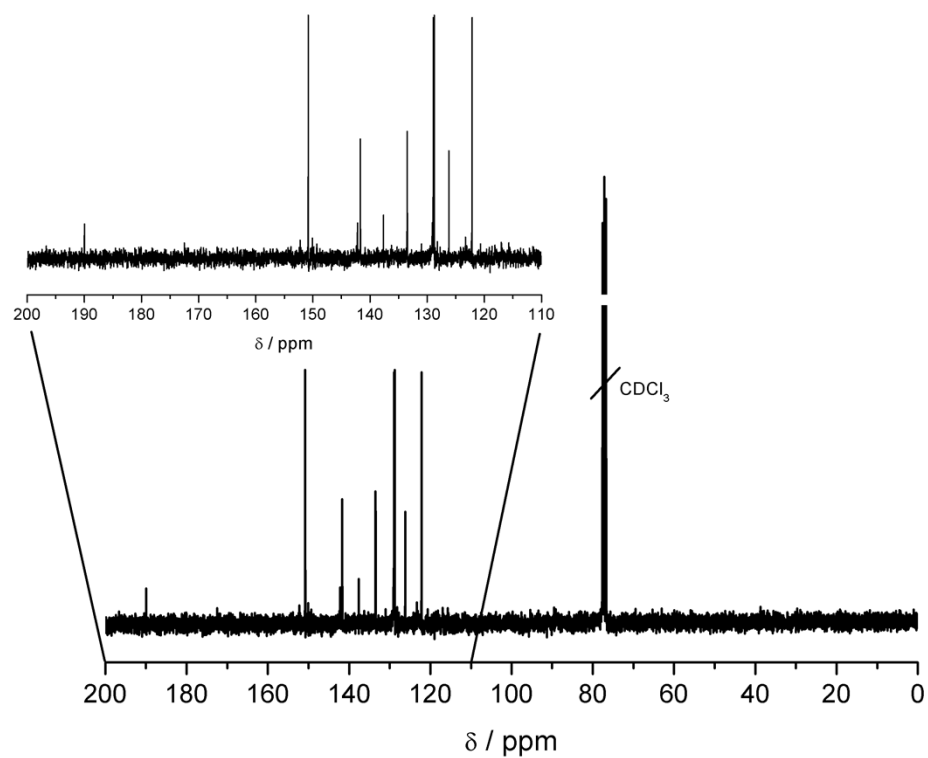
**Figure S30.**  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ , 298K) of **7d** in  $\text{CDCl}_3$ .



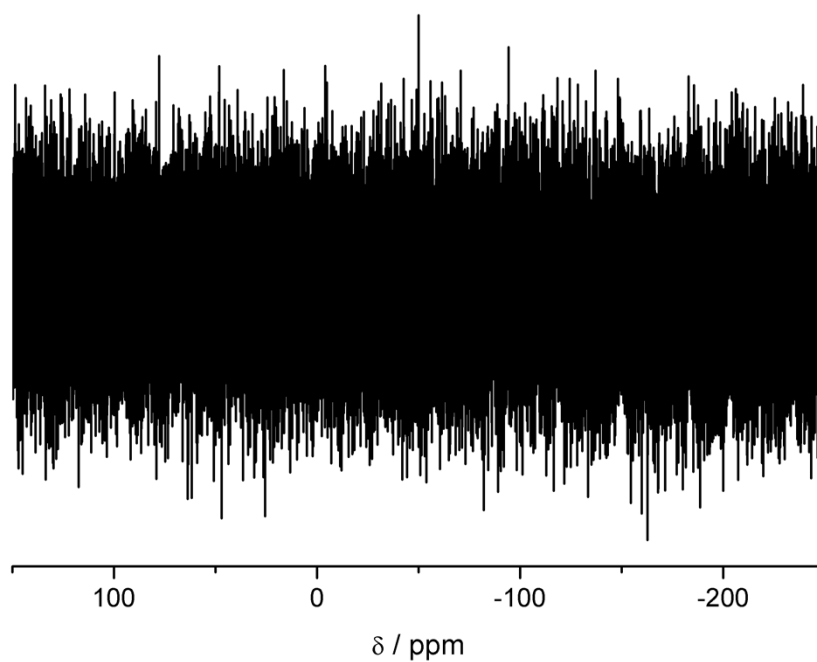
**Figure S31.**  $^{31}\text{P}\{\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ , 298K) of **7d**. The absence of any signal proves the complete removal of all poly(phosphonate).



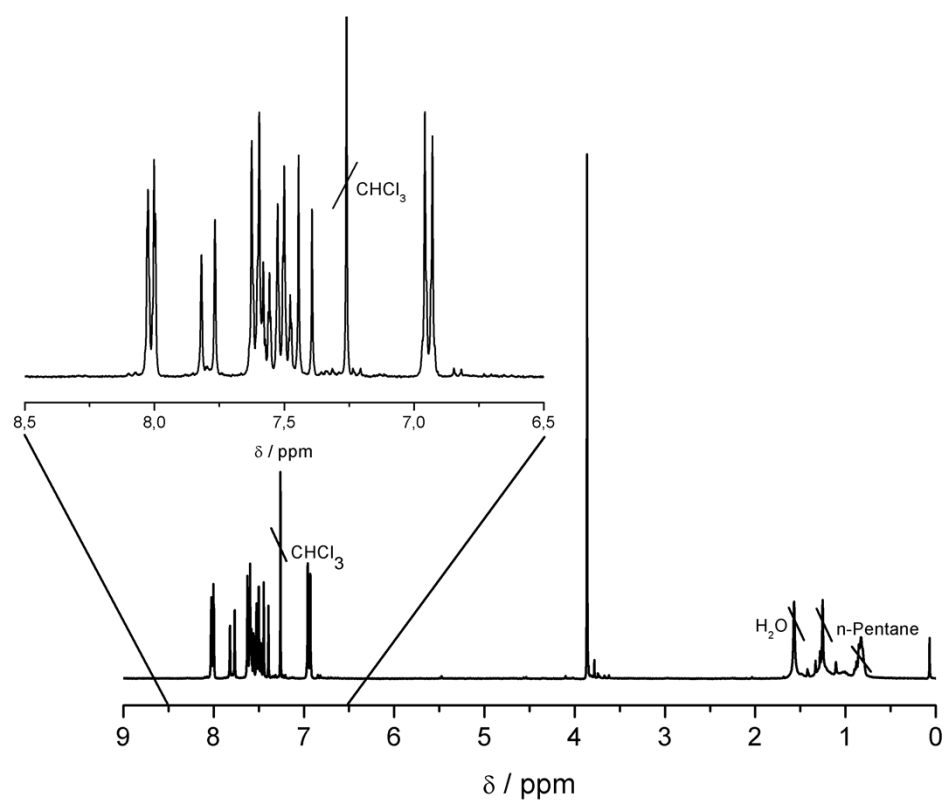
**Figure S32.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298K) of **7e**. The region from 9.0 to 6.5 ppm is magnified to aid clarity.



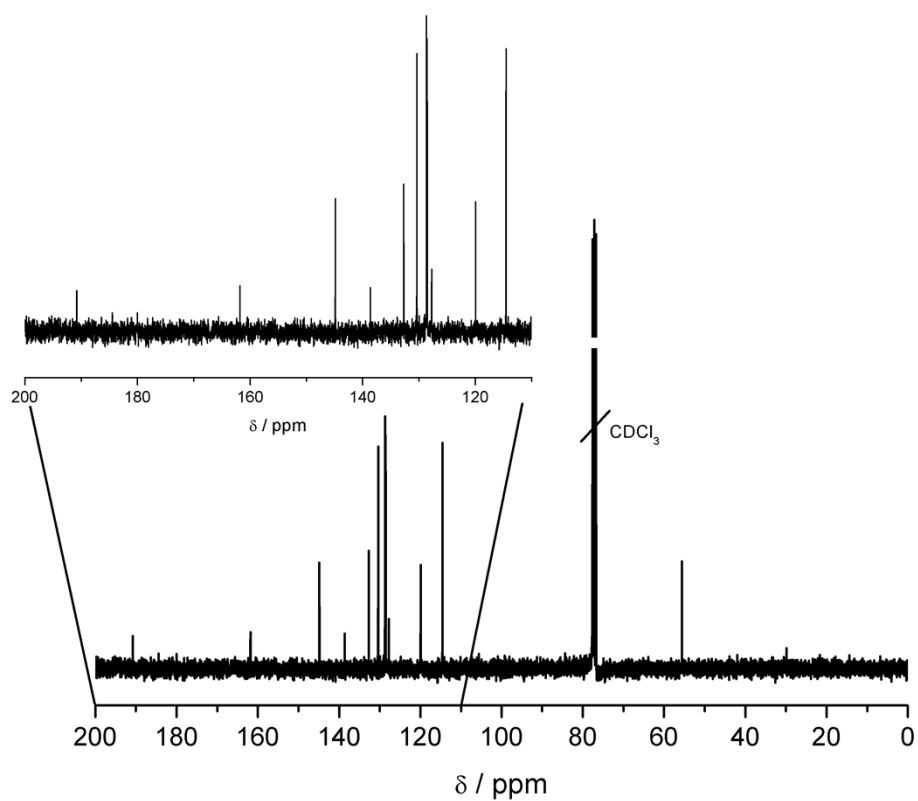
**Figure S33.**  $^{13}\text{C}\{^1\text{H}\}$  NMR(75 MHz,  $\text{CDCl}_3$ , 298K) of **7e**. The region from 200 to 110 ppm is magnified to aid clarity.



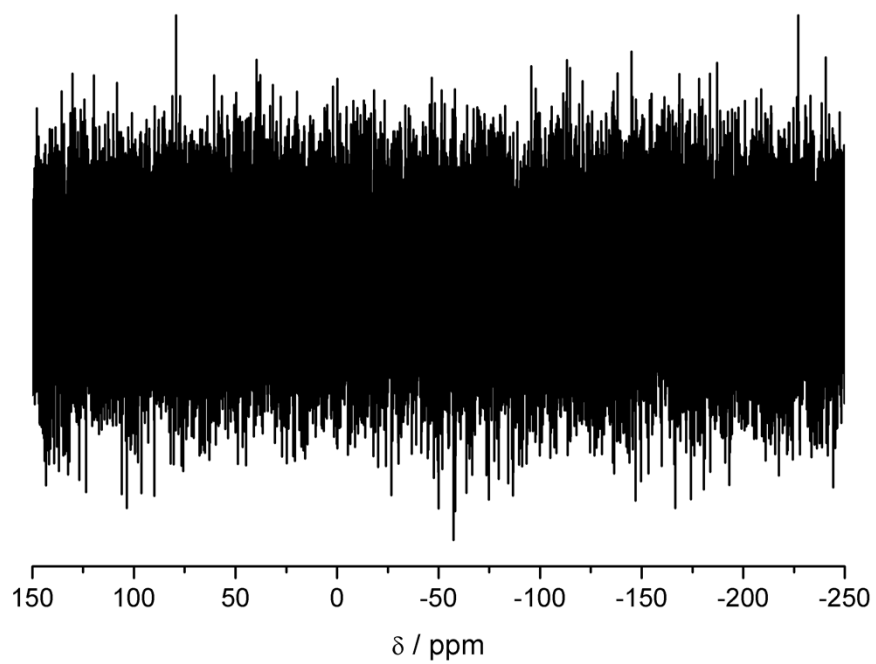
**Figure S34.**  $^{31}\text{P}\{\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ , 298K) of **7e**. The absence of any signal proves the complete removal of all poly(phosphonate).



**Figure S35.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298K) of **7f**. The region from 8.5 to 6.5 ppm is magnified to aid clarity.

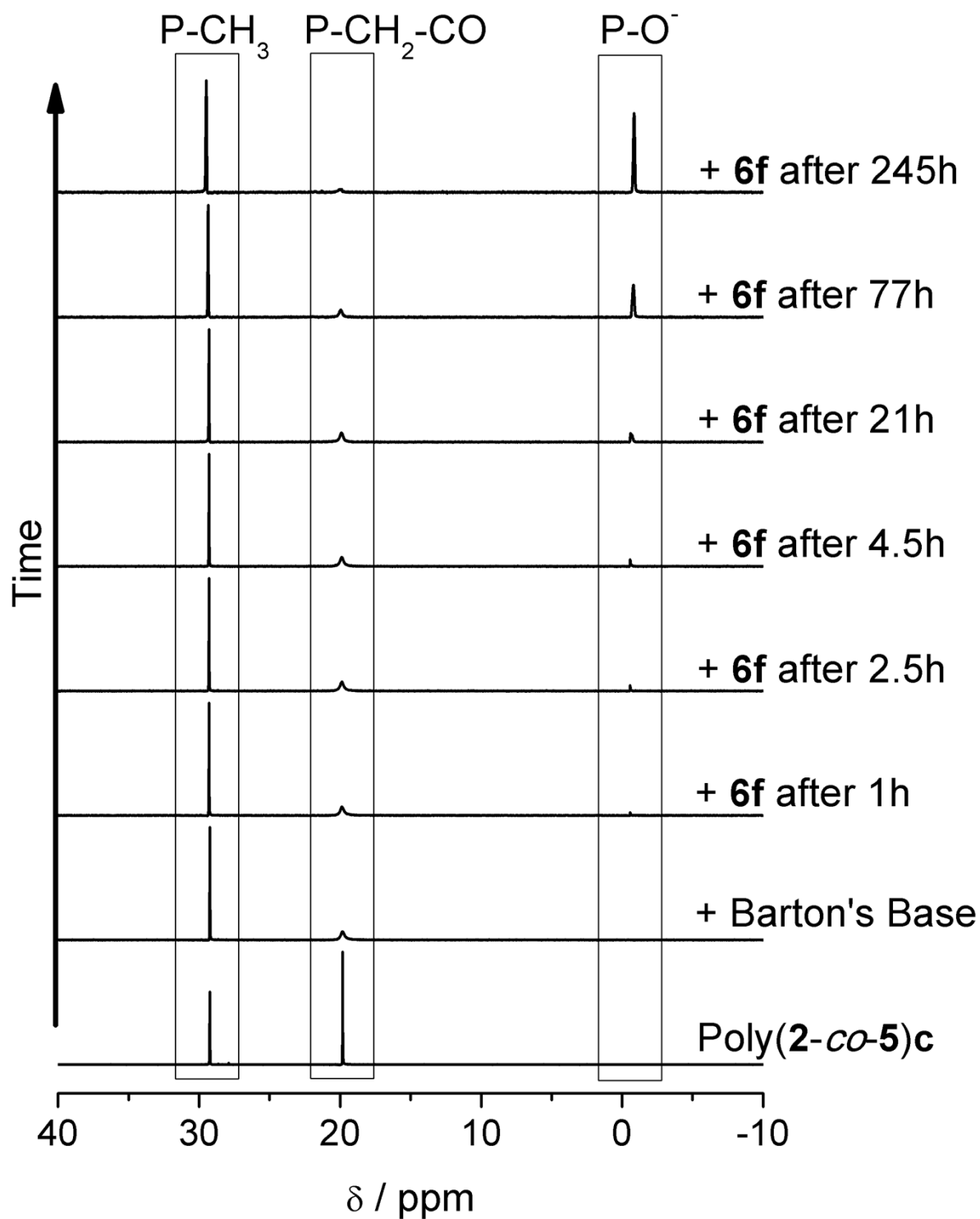


**Figure S36.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 298K) of **7f**. The region from 200 to 110 ppm is magnified to aid clarity.

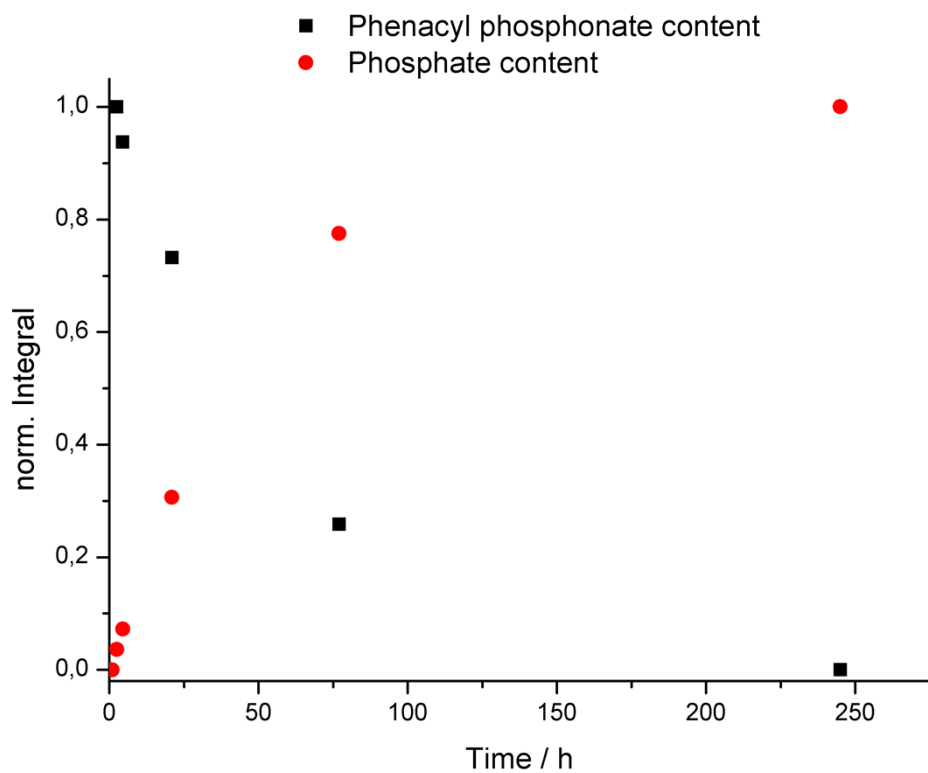


**Figure S37.**  $^{31}\text{P}\{\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ , 298K) of **7f**. The absence of any signal proves the complete removal of all poly(phosphonate).

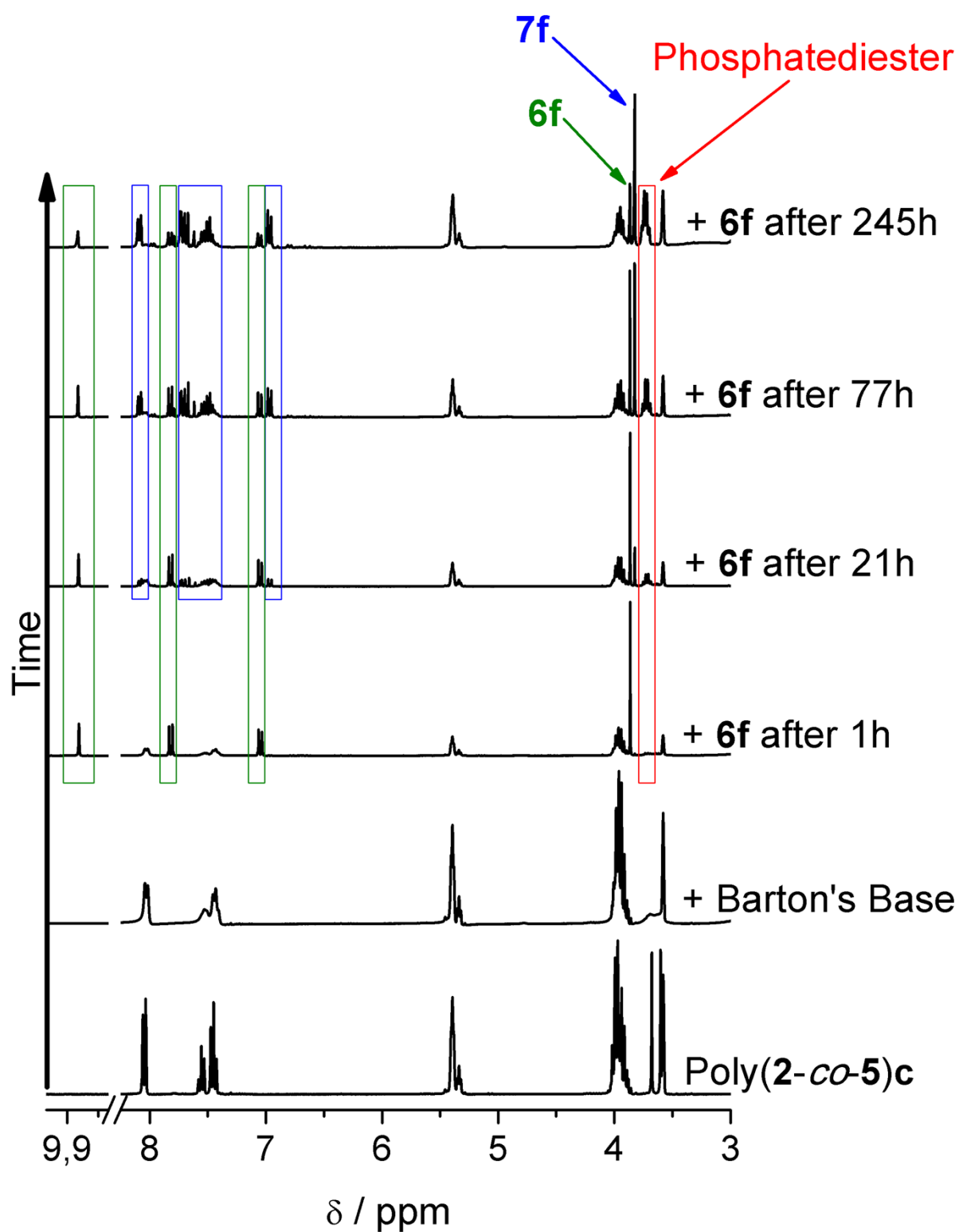




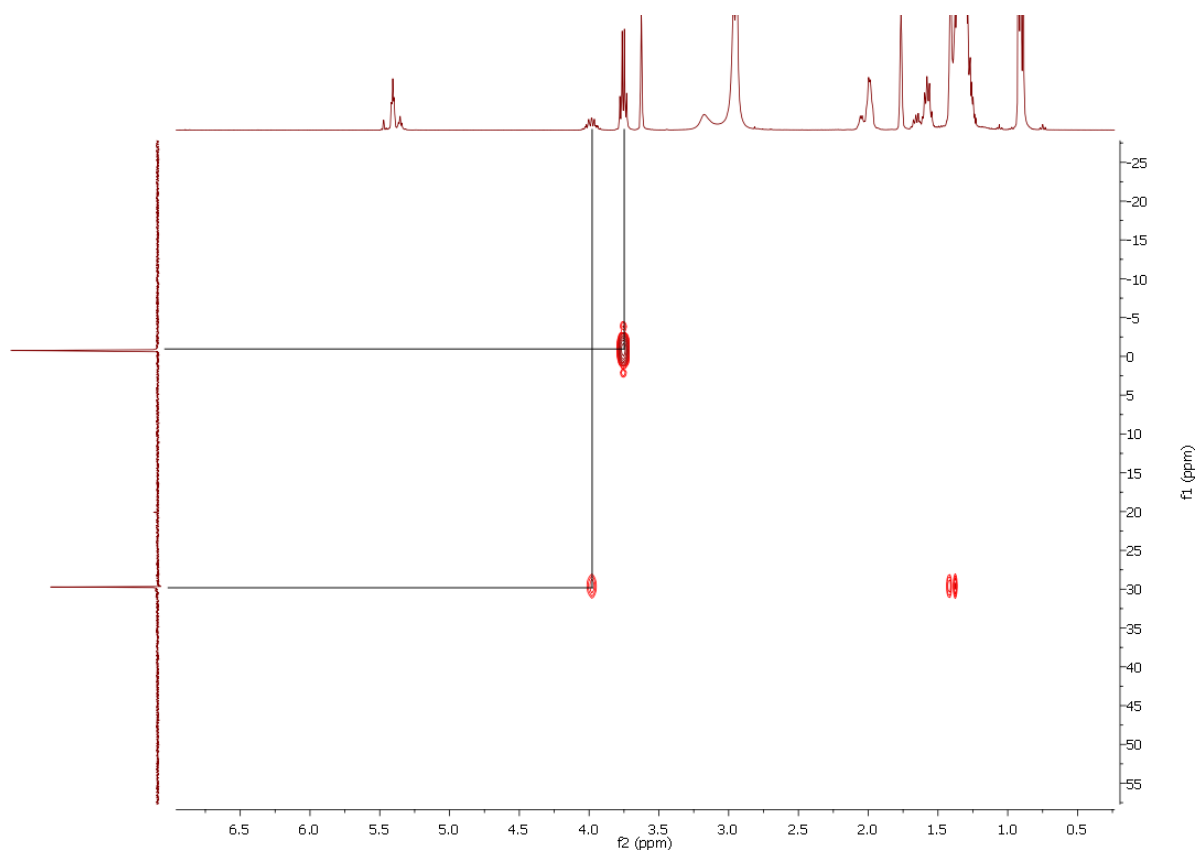
**Figure S38.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{THF-}d_8$ , 298K) spectra of the HWE reaction **6f** to **7f** (run 6).



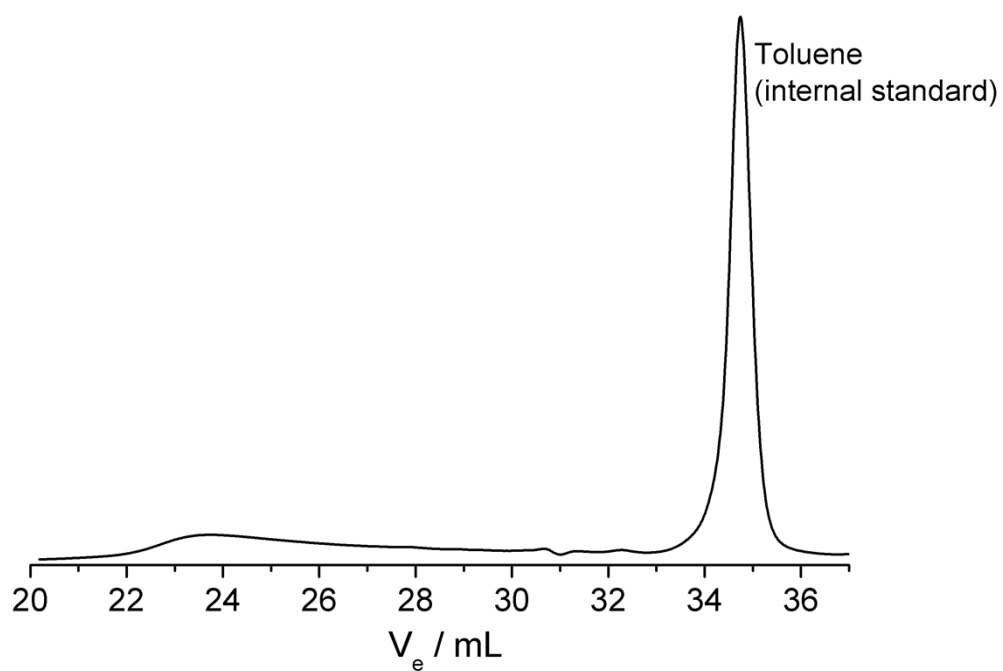
**Figure S39.** Reaction kinetics of run 6 (**6f** to **7f**) as determined from  $^{31}\text{P}\{\text{H}\}$  NMR spectra in  $\text{THF-}d_8$ . Both signals were normalized and compared to the methyl phosphonate signal which does not take part in the HWE reaction.



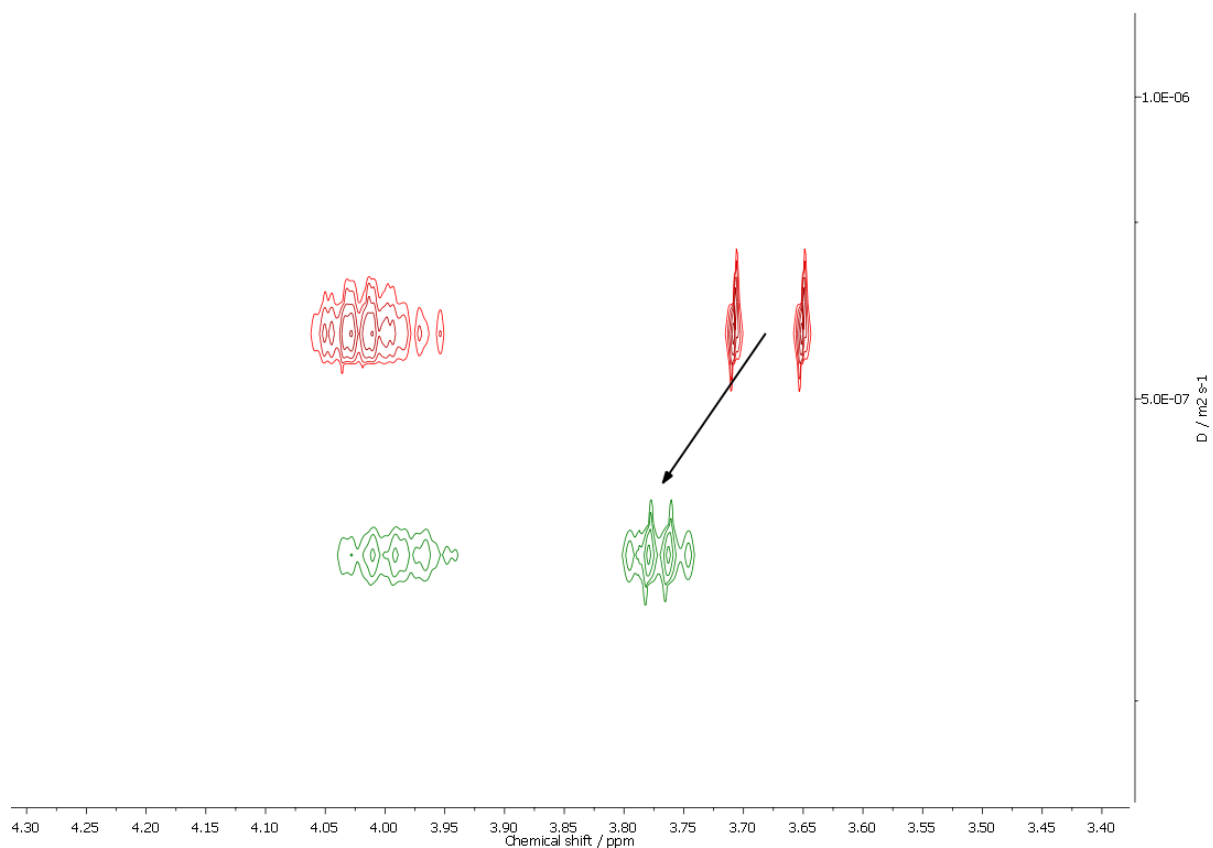
**Figure S40.**  $^1\text{H}$  NMR spectra (300 MHz,  $\text{THF-d}_8$ , 298K) of the HWE reaction (run 6) **6f** (green) to **7f** (blue).



**Figure S41.**  $^1\text{H}^{31}\text{P}$  HMBC (400 MHz,  $\text{THF-}d_8$ , 298K) of the polymeric residue of run 6. Cross-correlation between the phosphate signal at -0.8 ppm and the multiplet at 3.79 – 3.66 ppm verifies that these proton signals, which evolved during the HWE reaction, belong to the phosphate backbone. The methyl phosphonate backbone (30.6 ppm) is represented as two cross-correlations at 4.04 – 3.86 ppm (P-O-CH<sub>2</sub>) and at 1.46 ppm (doublet, P-CH<sub>3</sub>).



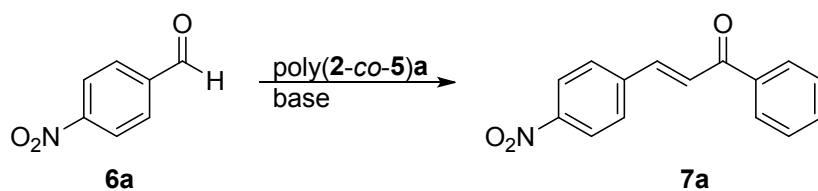
**Figure S42.** SEC elugram of poly(2-co-8)**b** in THF. The phosphonate poly(2-co-5) was converted into a phosphonate-phosphate copolymer during the HWE reaction. The ionic nature of the copolymer causes interaction with the SEC columns, leading to a broad signal.



**Figure S43.** Magnification of the  $^1\text{H}$ -DOSY NMR spectra (400 MHz,  $\text{THF-}d_8$ , 298K) of Figure 4. The resonances of poly(**2-co-5**)**b** are depicted in red, the reaction mixture after the HWE reaction is shown in green. The doublet at 3.62 ppm of the phenacyl phosphonate units of the polymer has transformed to a multiplet at 3.77 ppm indicating the formation of a phosphate diester.

## 2. Screening of bases for the HWE reaction.

Deprotonation of the functionalized polymer was studied by screening different bases with 4-nitrobenzaldehyde (**6a**) as an electron-deficient substrate (Scheme S1). The results are summarized in Table S1.



**Scheme S1.** HWE reaction with 4-nitrobenzaldehyde, deprotonation was conducted with different bases.

**Table S1.** Bases screened for the HWE reaction of poly(2-co-5)a with 4-nitrobenzaldehyde in THF.

Run	Base	Temperature	Equivalents of Base <sup>a</sup>	Time / h	Conversion to <b>7a</b> <sup>b</sup>	Conversion to phosphate <sup>c</sup>
1	<i>n</i> -BuLi <sup>d</sup>	-21°C	1.0	3	no reaction	no reaction
2	NaH <sup>e</sup>	20°C	1.0	4	n.d.	<5%
3	NaH <sup>e</sup>	20°C	2.0	4	n.d.	<10%
4	Barton base <sup>f</sup>	20°C	1.0	4	72%	>99%

<sup>a</sup> Equivalents in respect to phenacyl phosphonate units. <sup>b</sup> Determined via <sup>1</sup>H NMR spectroscopy. <sup>c</sup> Determined via <sup>31</sup>P{H} NMR

spectroscopy. <sup>d</sup> 1.6 M solution in hexane. <sup>e</sup> Sodium hydride, dry 95%. <sup>f</sup> *N*-*tert*-Butyl-*N'*,*N''*,*N'''*-tetramethylguanidine.

It is well known that lithium bases catalyze the HWE reaction as the lithium cation is able to stabilize the deprotonated phosphonate. The usage of *n*-butyl lithium, however, did not produce a reaction product. Deprotonation of poly(**2-co-5**)**a** was accomplished by sodium hydride. After addition of the aldehyde and workup, the desired product **7a** was obtained. However, the degree of phenacyl phosphonate units which were transformed into phosphates (from  $^{31}\text{P}\{\text{H}\}$  NMR spectroscopy) remained rather low and conversion to **7a** was not increased also if two equivalents of base were added.