Supporting Information

Mono-alkyl-substituted phosphinoboranes (HRP–BH_2–NMe_3) as precursors for poly(alkylphosphinoborane)s: improved synthesis and comparative study

Felix Lehnfeld [1], Tim Oswald [2], Rüdiger Beckhaus [2] and Manfred Scheer [1,*]

[1] Institut für Anorganische Chemie, Universität Regensburg, 93040 Regensburg, Germany; felix.lehnfeld@chemie.uni-regensburg.de
[2] Institut für Chemie, Carl von Ossietzky Universität Oldenburg, Carl-von-Ossietzky Straße 9–11, 26129 Oldenburg, Germany; tim.oswald@uni-oldenburg.de (T.O.); ruediger.beckhaus@uni-oldenburg.de (R.B.)
* Correspondence: manfred.scheer@ur.de

NMR spectra

1.1 Compound 1a

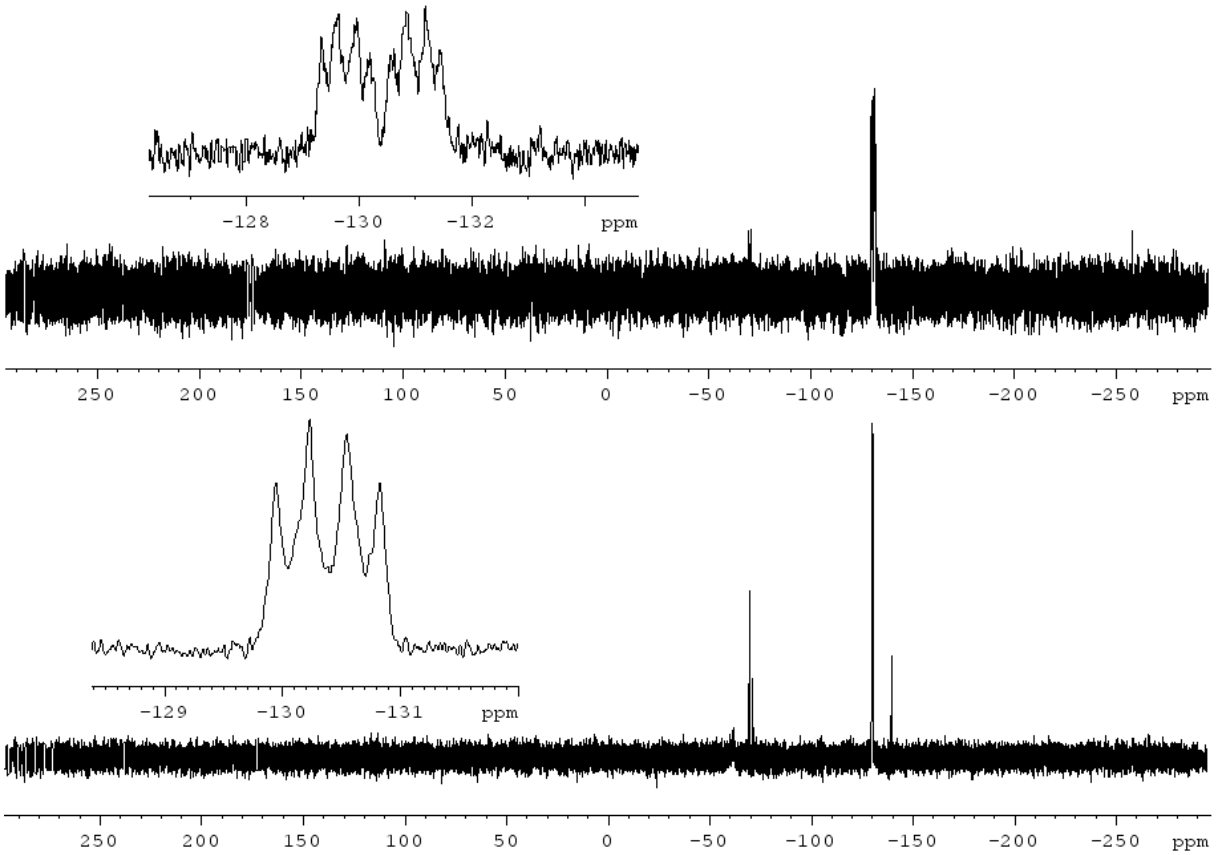

Figure S1. ^{31}**P** NMR (top) and ^{31}**P**{^{1}H} NMR (bottom) spectra of **1a** in *n*-hexane

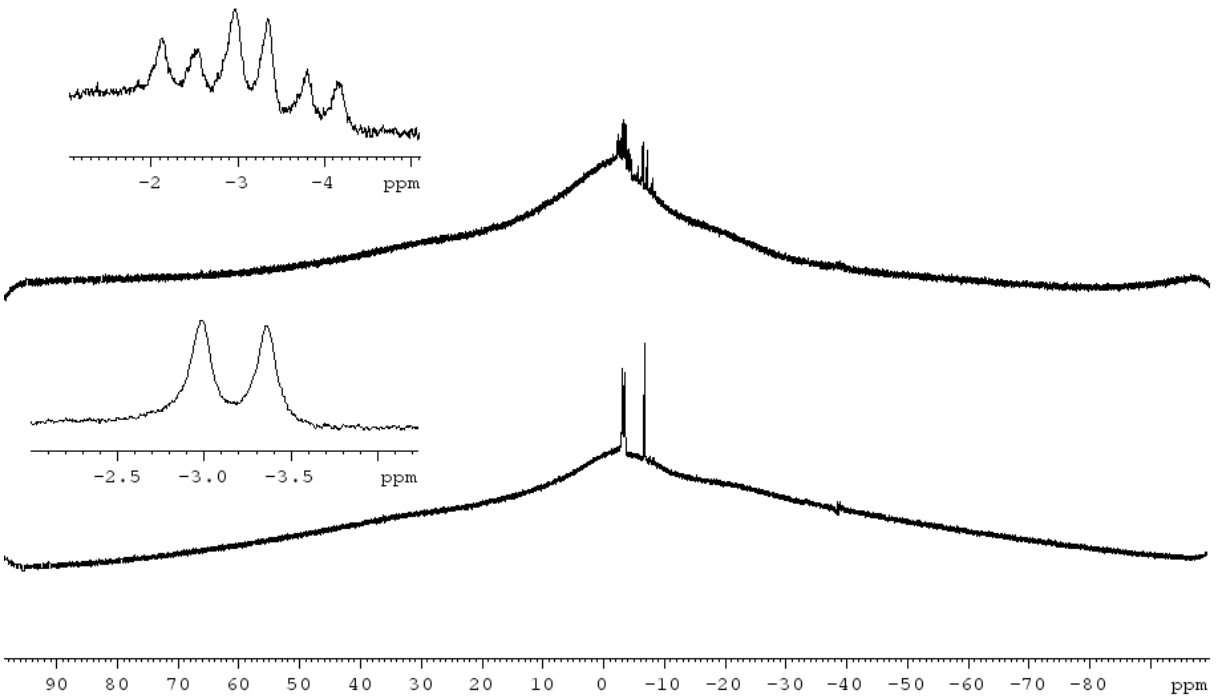

Figure S2. ^{11}B NMR (top) and ^{11}B{^{1}H} NMR (bottom) spectra of **1a** in *n*-hexane

1.2 Compound 1b

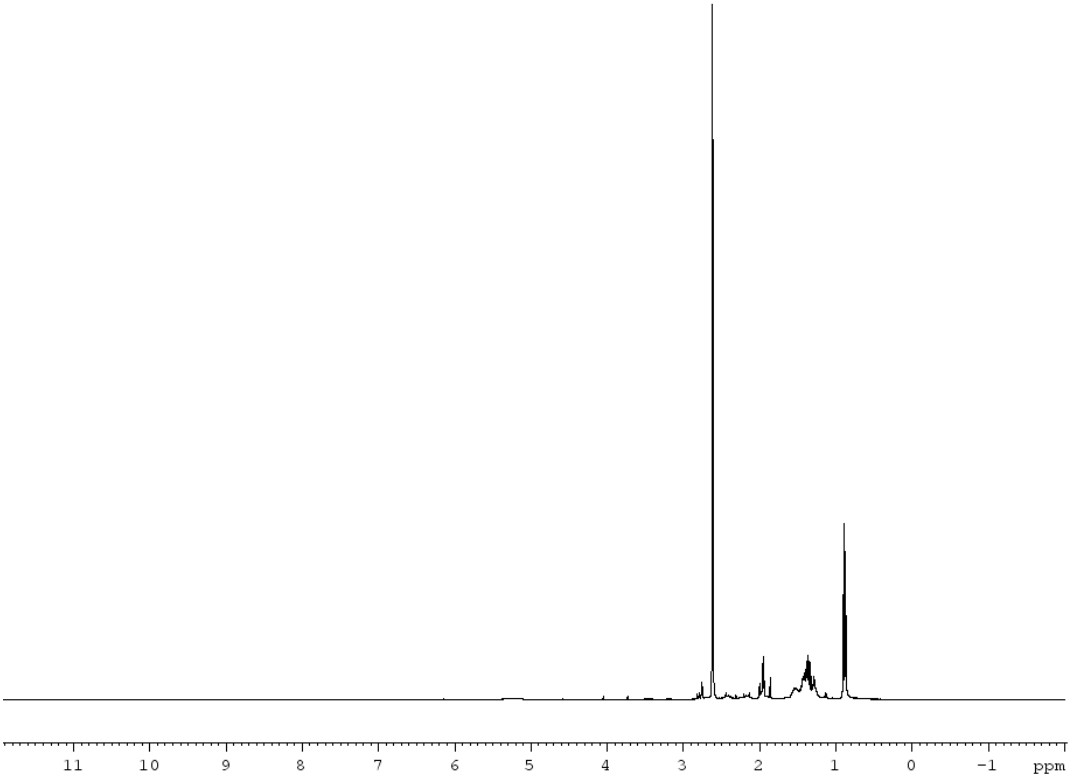

Figure S3. ^{1}H NMR spectr**um** of **1b** in CD_3CN

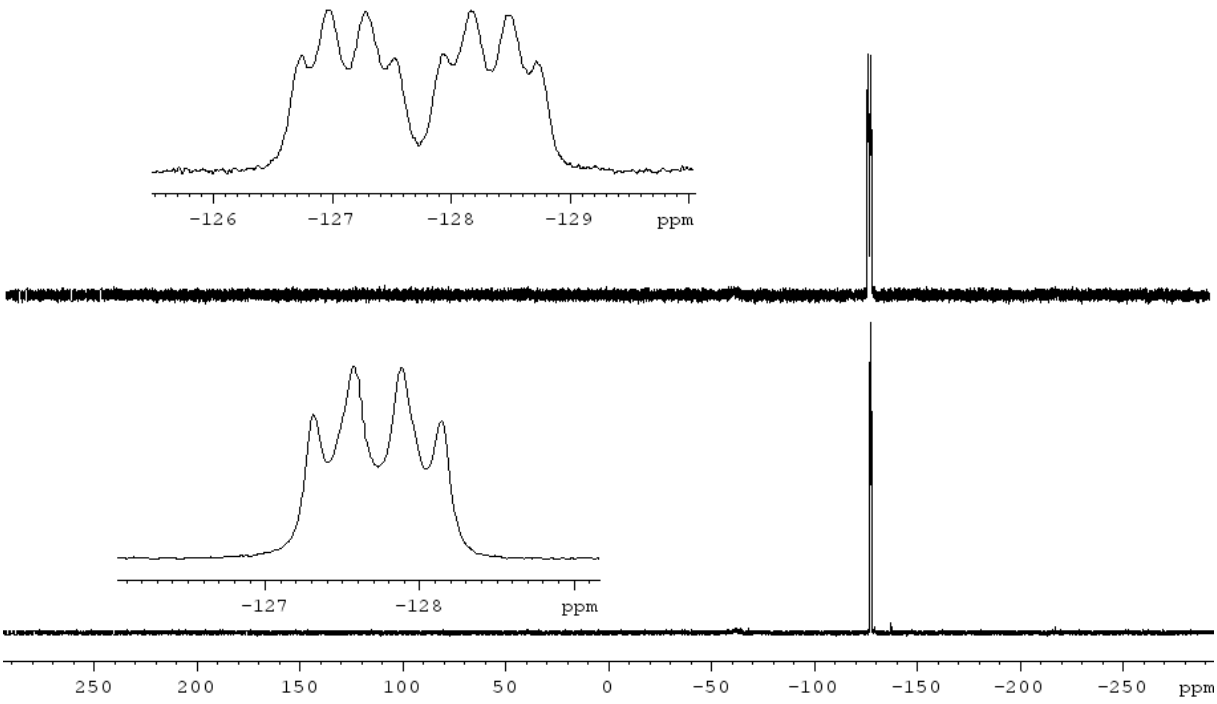

Figure S4. ^{31}**P** NMR (top) and ^{31}**P**{^{1}H} NMR (bottom) spectra of **1b** in CD_3CN

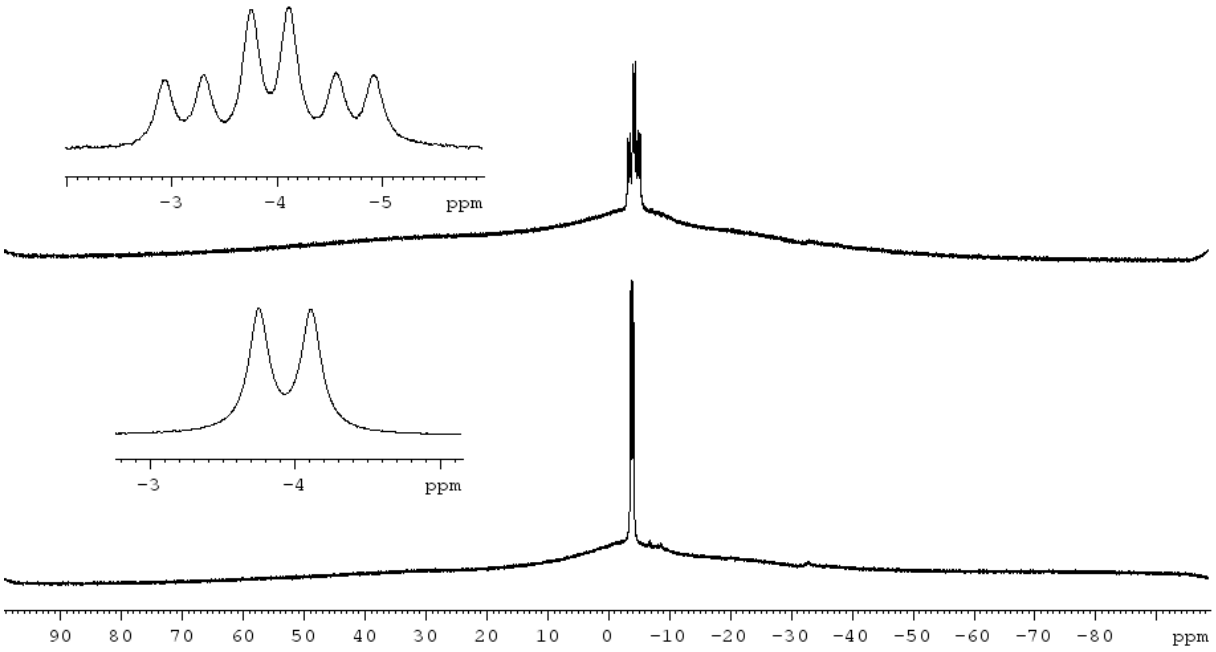

Figure S5. ^{11}B NMR (top) and $^{11}B\{^{1}H\}$ NMR (bottom) spectra of **1b** in CD_3CN

2. Compound 1c

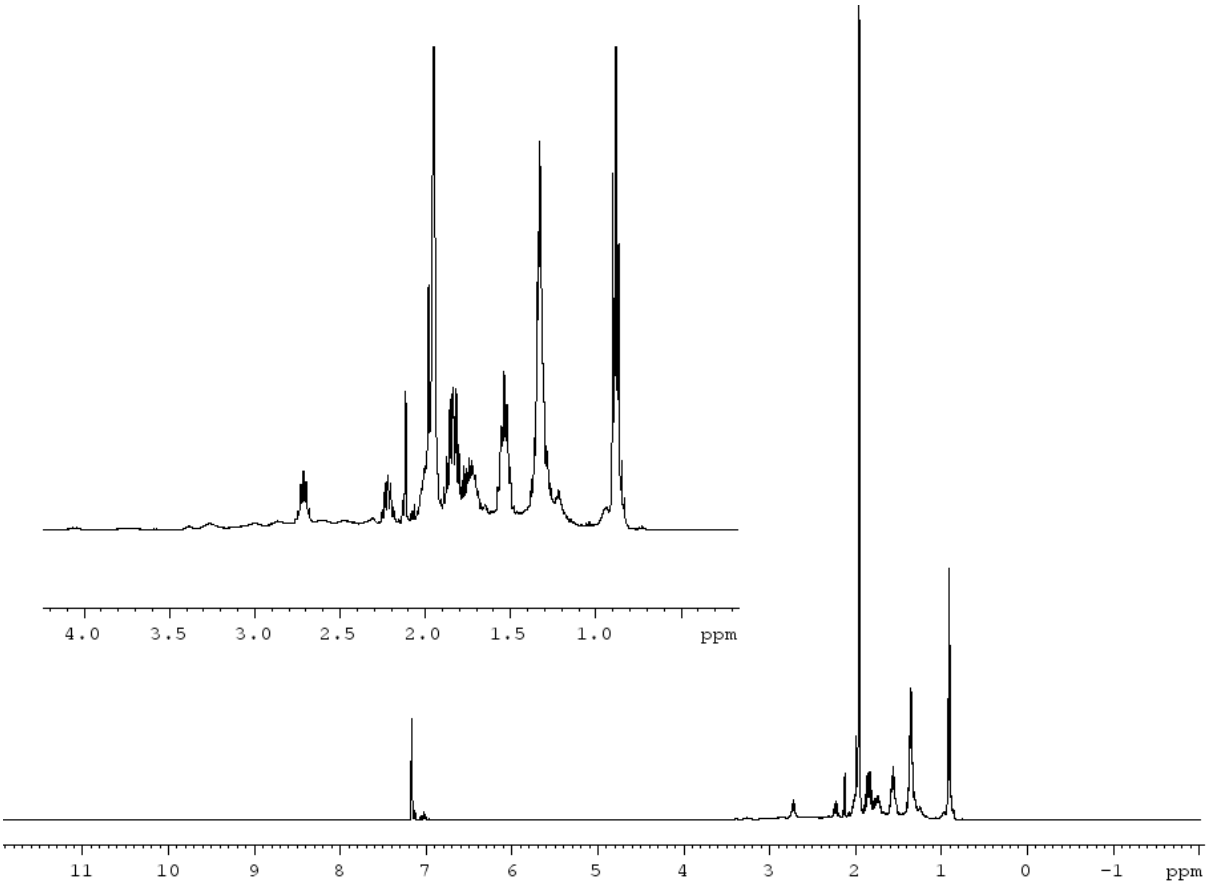

Figure S6. ^{1}H NMR spectr**um** of **1c** in C_6D_6

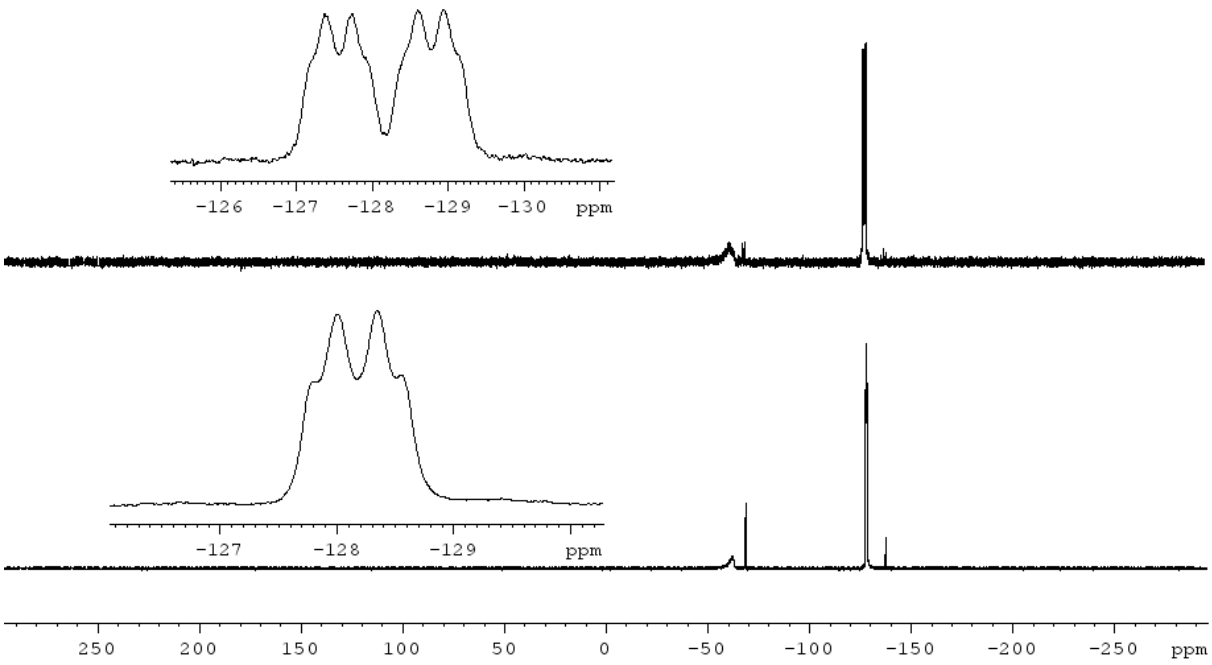

Figure S7. ^{31}P NMR (top) and $^{31}P\{^{1}H\}$ NMR (bottom) spectra of **1c** in C_6D_6

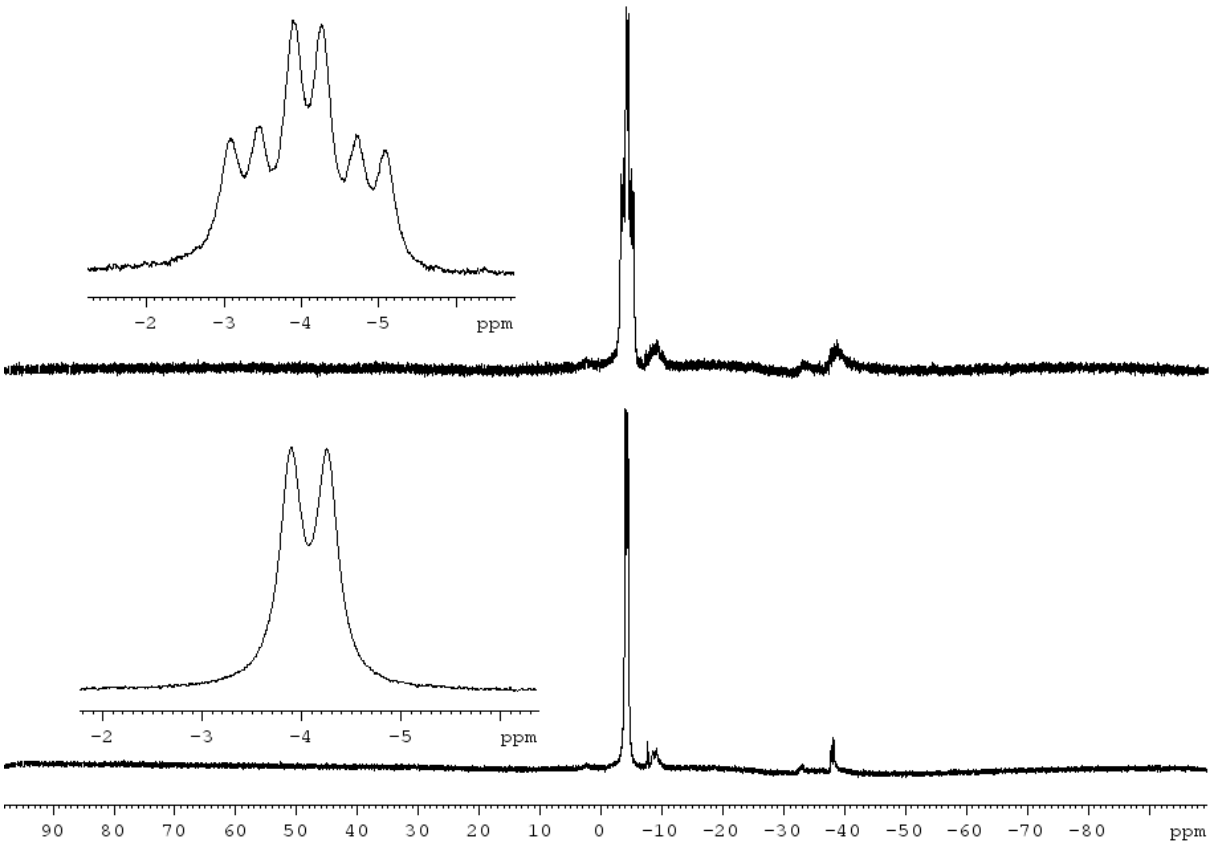

Figure S8. ^{11}B NMR (top) and $^{11}B\{^{1}H\}$ NMR (bottom) spectra of **1c** in C_6D_6

Compound 2

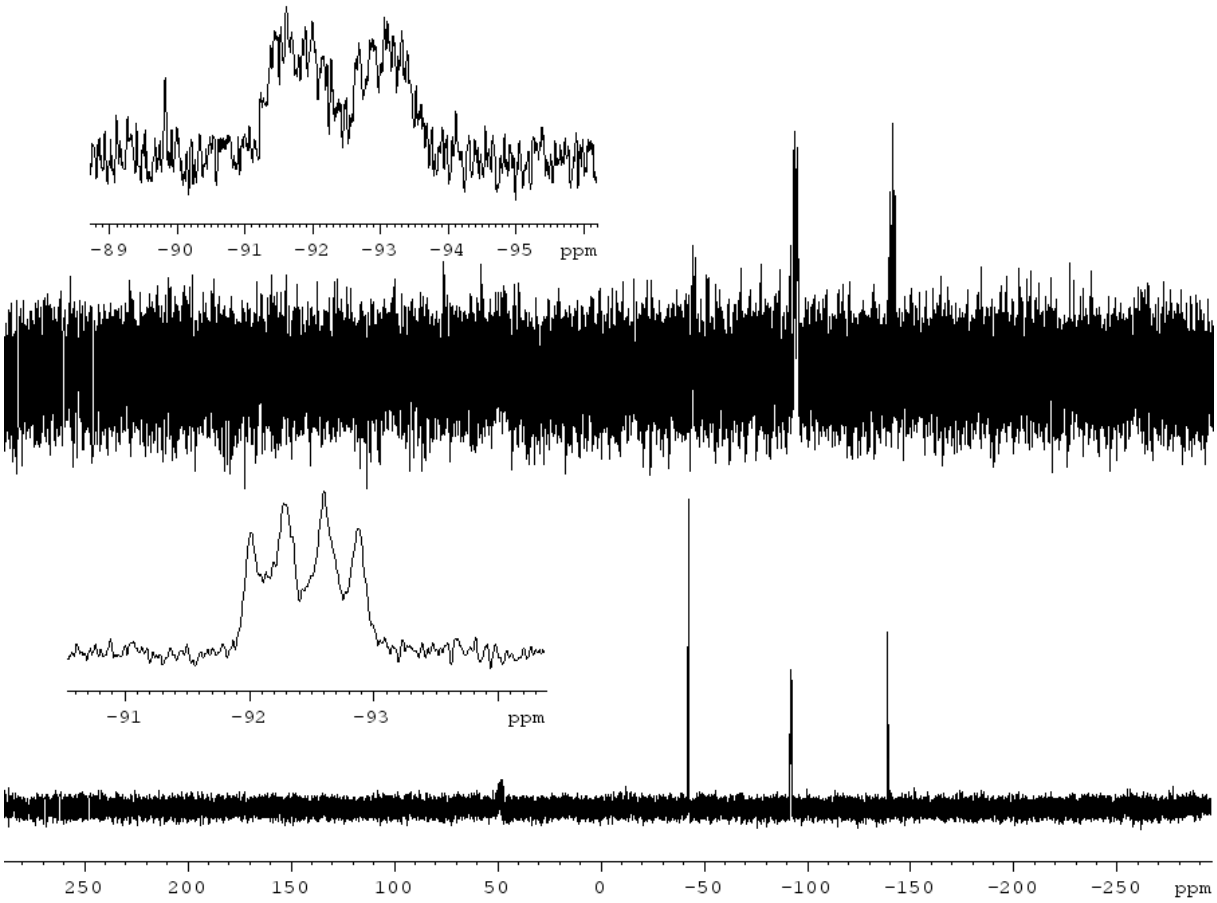

Figure S9. ^{31}P NMR (top) and $^{31}P\{^{1}H\}$ NMR (bottom) spectra of **2** in *n*-hexane

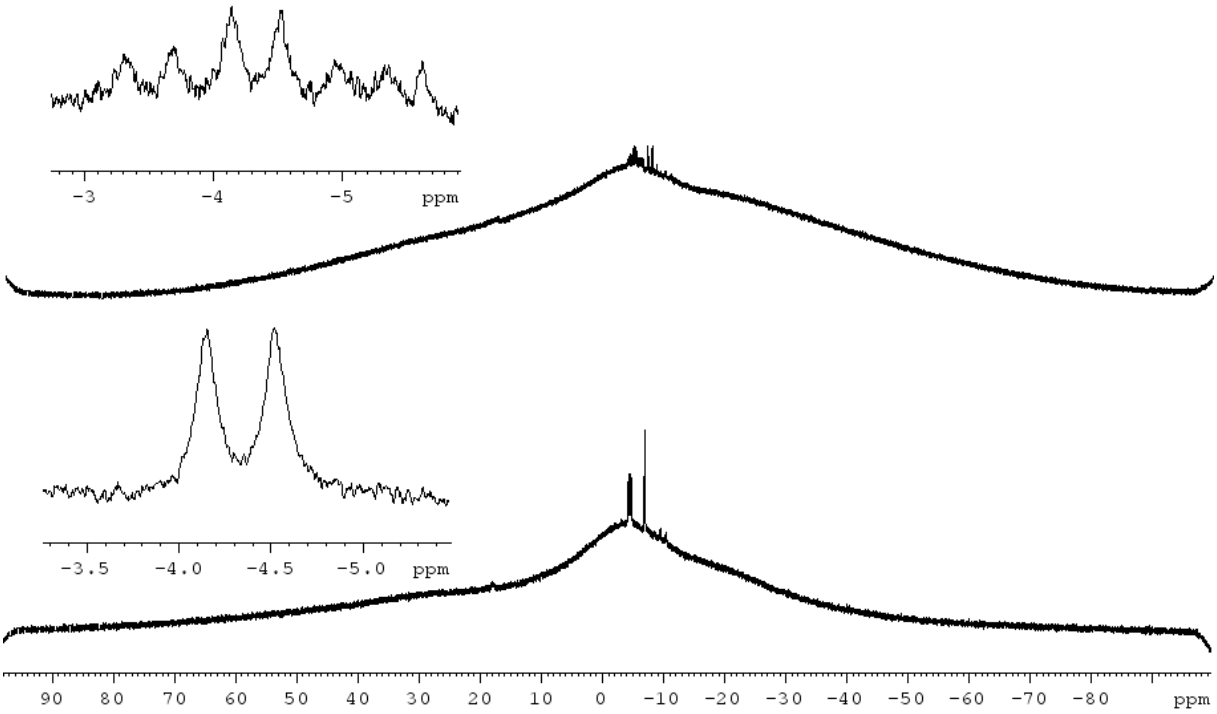

Figure S10. ^{11}B NMR (top) and $^{11}B\{^{1}H\}$ NMR (bottom) spectra of **2** in *n*-hexane

3. Compound 3a und 3b

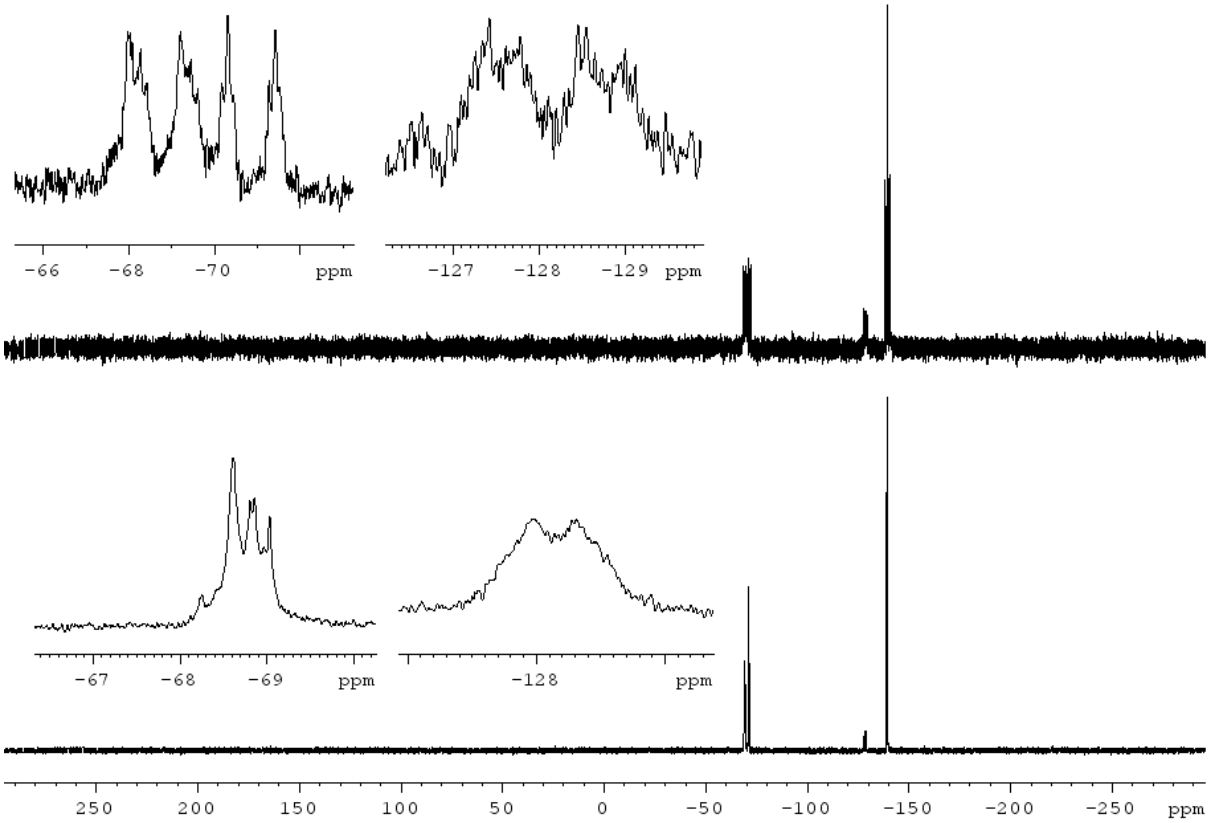

Figure S11. ^{31}P NMR (top) and $^{31}P\{^{1}H\}$ NMR (bottom) spectra of **3a** and **3b** in THF

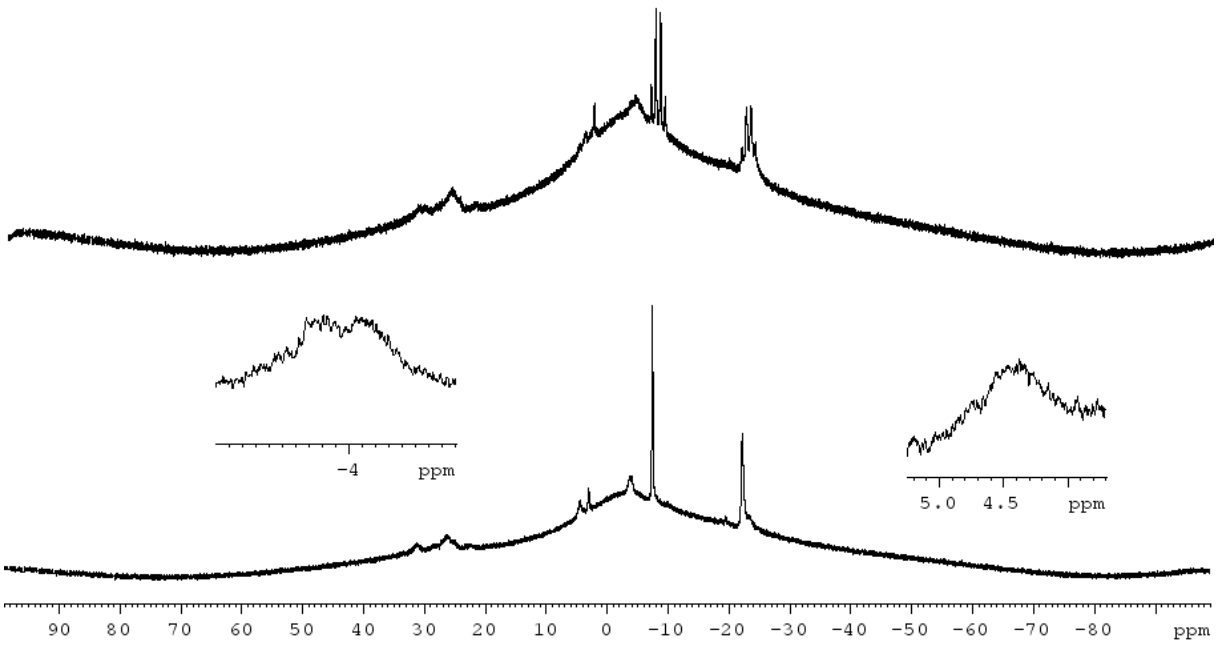

Figure S12. ^{11}B NMR (top) and $^{11}B\{^{1}H\}$ NMR (bottom) spectra of **3a** and **3b** in THF

3.1 Polymerization reactions

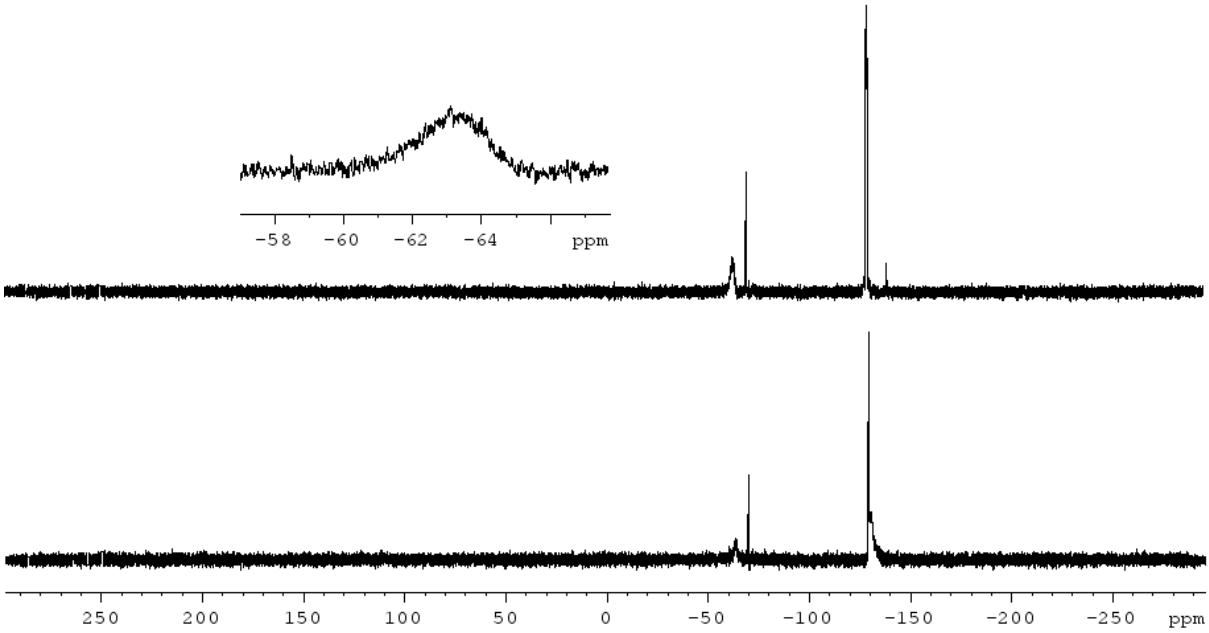

Figure S13. $^{31}P\{^{1}H\}$ NMR spectra of **1a** (c = 0.089 mol/L) after stirring at r.t. for 90 min (bottom) and 24 h (top)

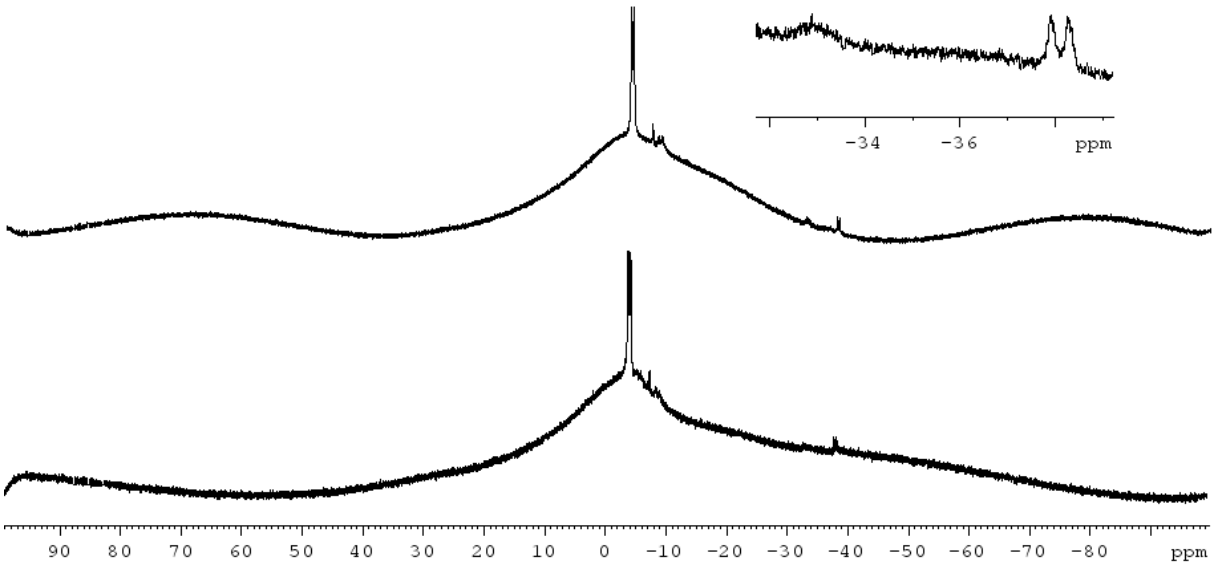

Figure S14. $^{11}B\{^{1}H\}$ NMR spectra of **1a** (c = 0.089 mol/L) after stirring at r.t. for 90 min (bottom) and 24 h (top)

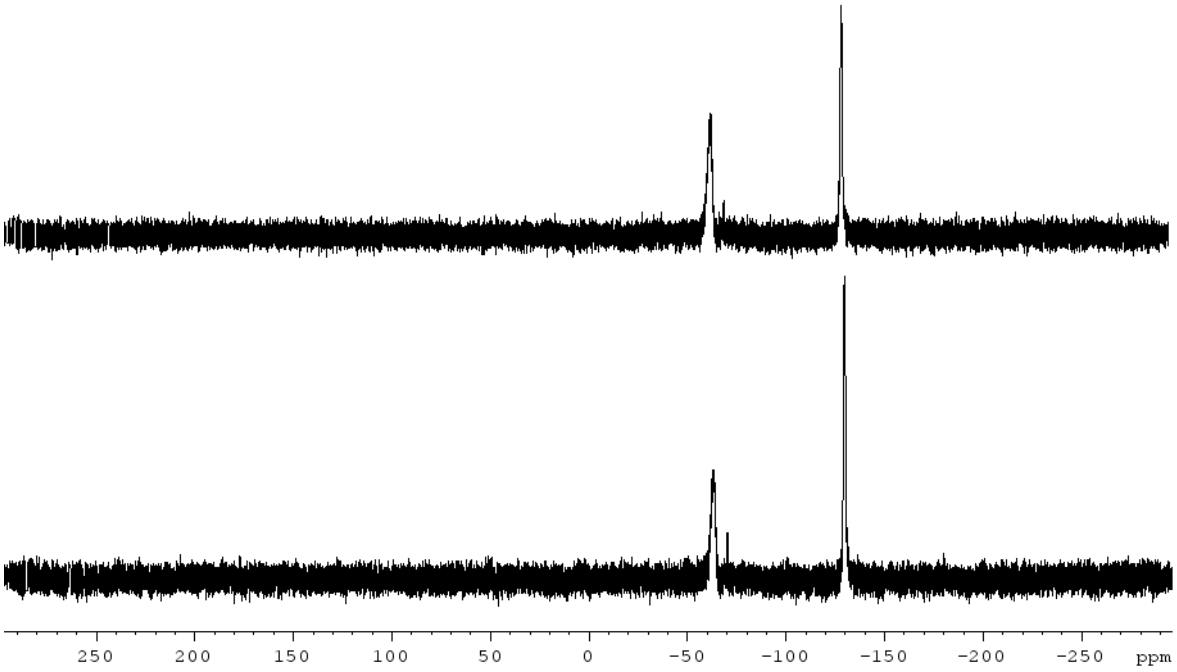

Figure S15. $^{31}P\{^{1}H\}$ NMR spectra of **1a** (c = 0.089 mol/L) after stirring at r.t. for 90 min (bottom) and 24 h (top) in the presence of 5 mol% of $[(\eta^5{:}\eta^1\text{-}C_5H_4C_{10}H_{14})_2Ti]$.

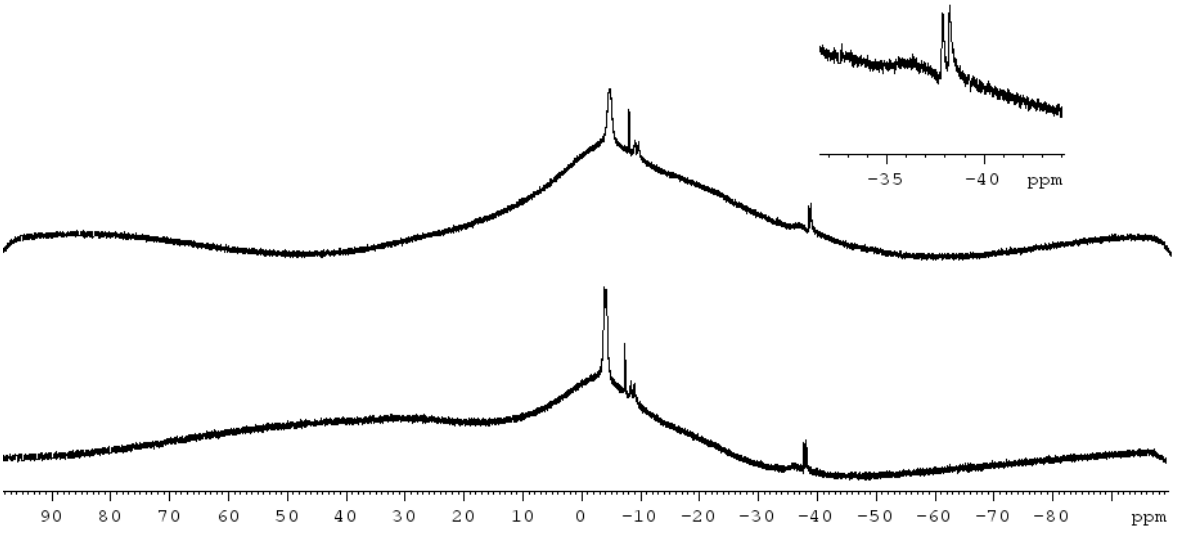

Figure S16. $^{11}B\{^{1}H\}$ NMR spectra of **1a** (c = 0.089 mol/L) after stirring at r.t. for 90 min (bottom) and 24 h (top) in the presence of 5 mol% of $[(\eta^5{:}\eta^1\text{-}C_5H_4C_{10}H_{14})_2Ti]$.

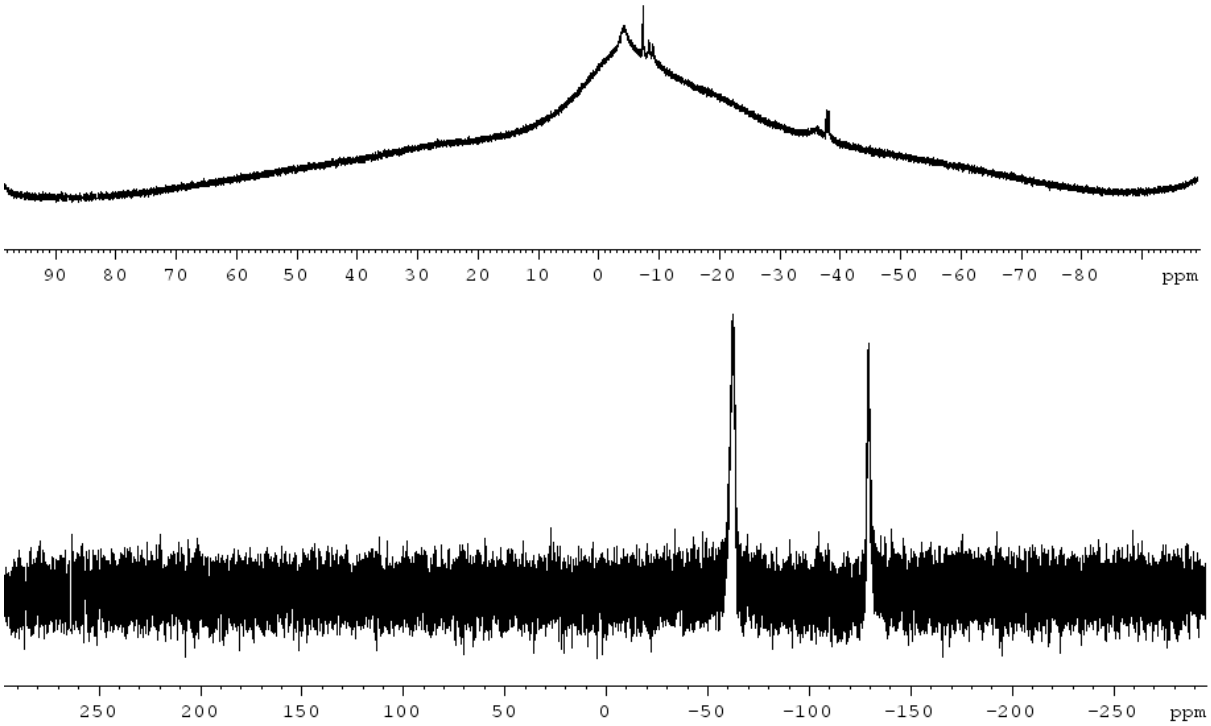

Figure S16. $^{31}P\{^{1}H\}$ NMR and $^{11}B\{^{1}H\}$ NMR (top) spectra of **1a** (c = 0.089 mol/L) after stirring at r.t. for 24 h in the presence of 10 mol% of $[(\eta^5{:}\eta^1\text{-}C_5H_4C_{10}H_{14})_2Ti]$.

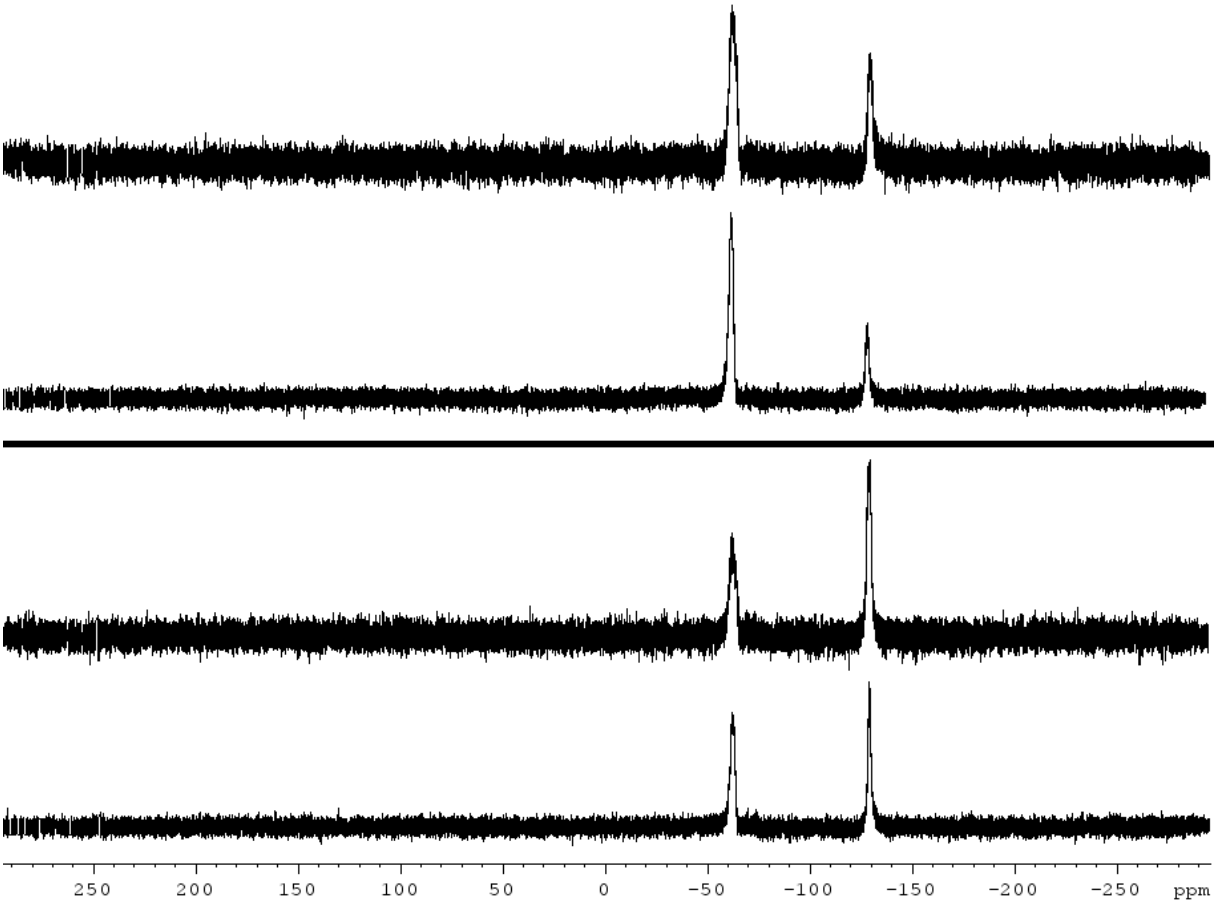

Figure S17. ^{31}P NMR (top) and $^{31}P\{^{1}H\}$ NMR (bottom) spectra of **1a** (c = 0.03 mol/L) after stirring at r.t. for 210 min (lower half) and 42 h (upper half) in the presence of 10 mol% of $[(\eta^5{:}\eta^1\text{-}C_5H_4C_{10}H_{14})_2Ti]$.

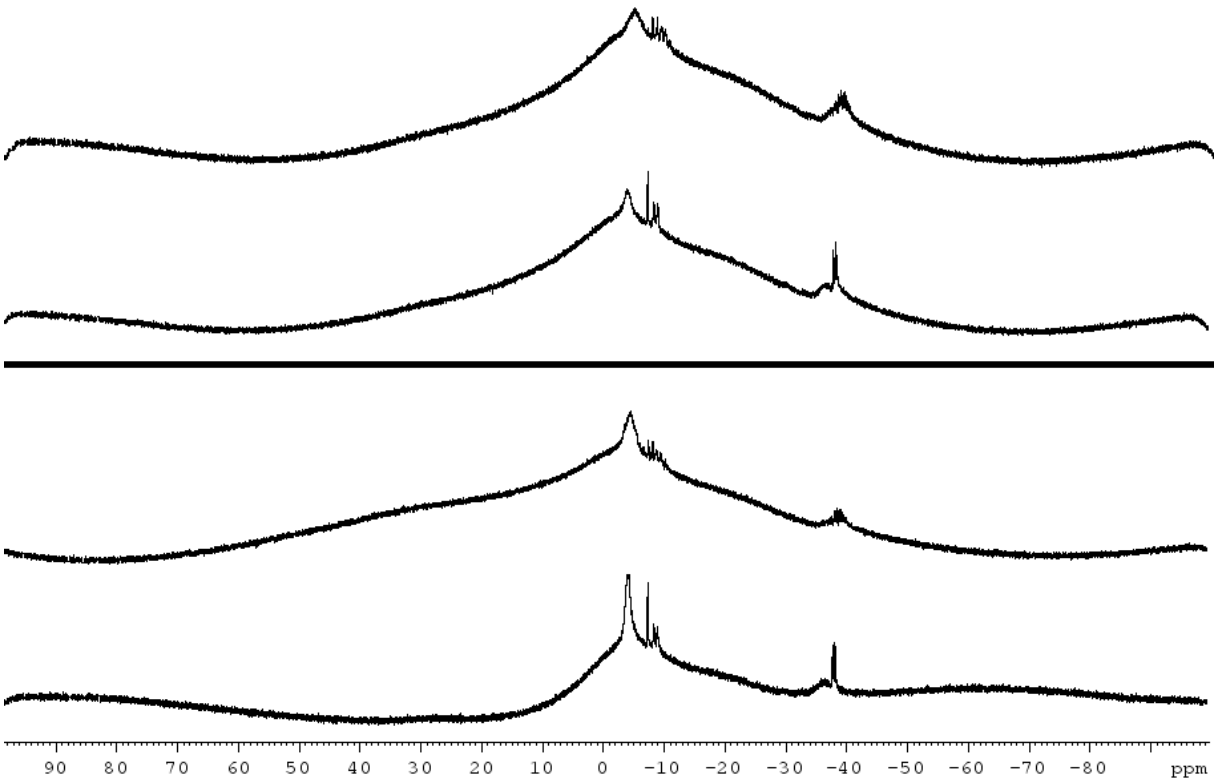

Figure S18. ^{11}B NMR (top) and $^{11}B\{^1H\}$ NMR (bottom) spectra of **1a** (c = 0.03 mol/L) after stirring at r.t. for 210 min (lower half) and 42 h (upper half) in the presence of 10 mol% of $[(\eta^5{:}\eta^1\text{-}C_5H_4C_{10}H_{14})_2Ti]$.

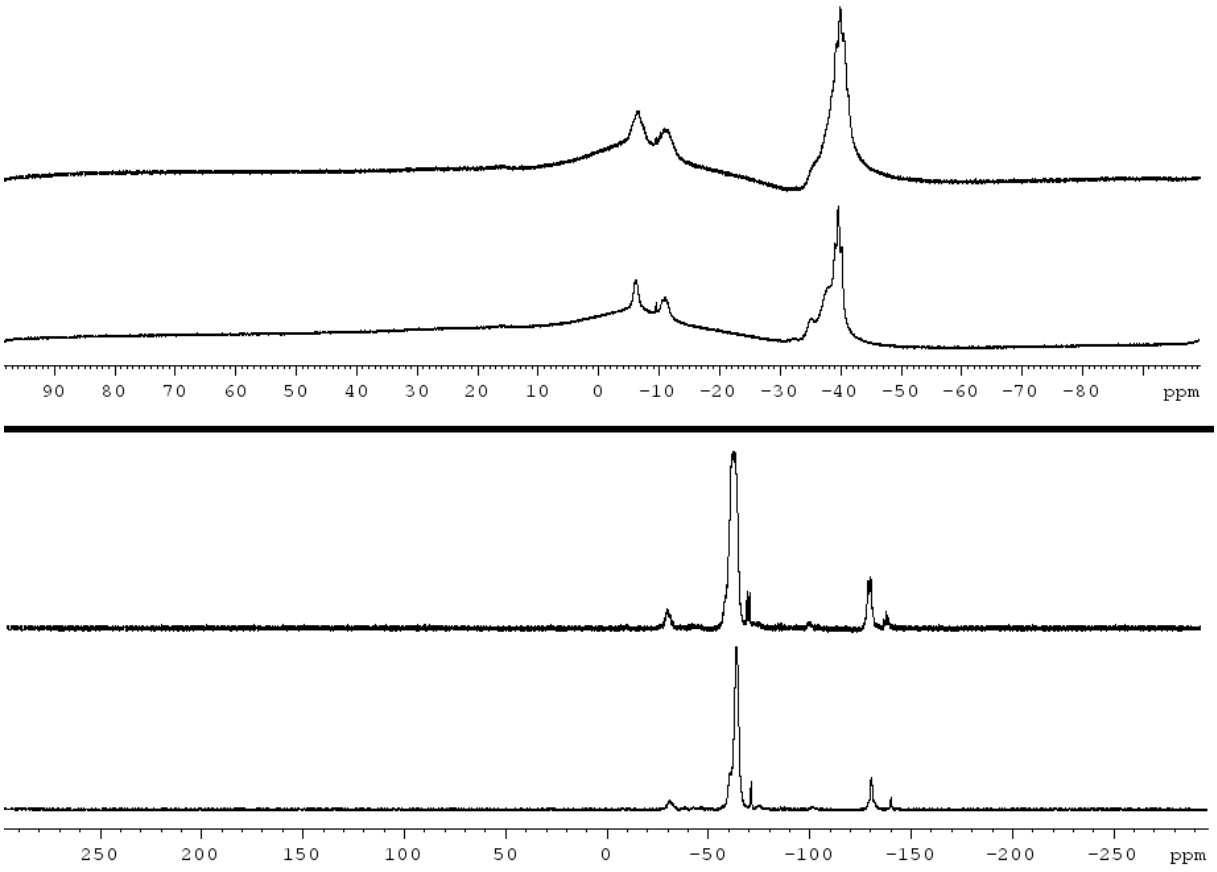

Figure S19. ^{11}B NMR (top, upper half), $^{11}B\{^1H\}$ NMR (bottom, upper half), ^{31}P NMR (top, lower half), and $^{31}P\{^1H\}$ NMR (bottom, lower half) spectra of **1b** (c = 0.5 mol/L) after stirring at r.t. for 21 d in the presence of 5 mol% of $[(\eta^5{:}\eta^1\text{-}C_5H_4C_{10}H_{14})_2Ti]$.

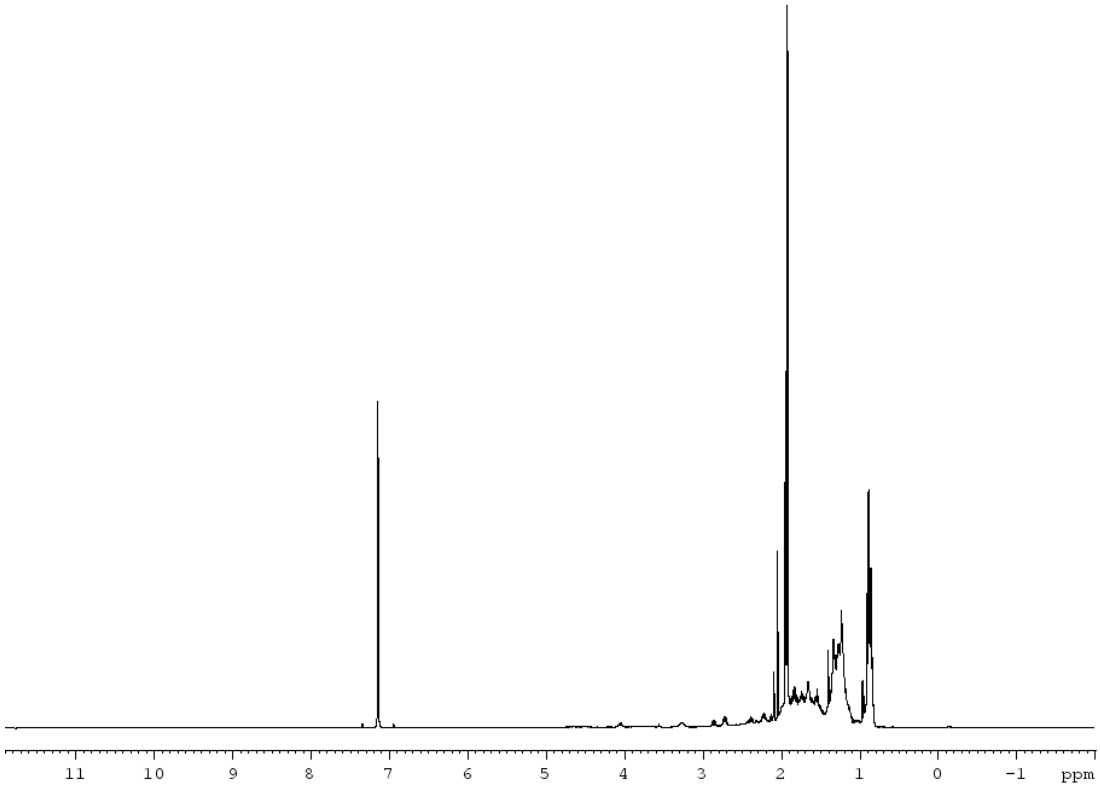

Figure S20. ^{1}H NMR spectrum of neat **1c** after stirring at r.t. for 4 d

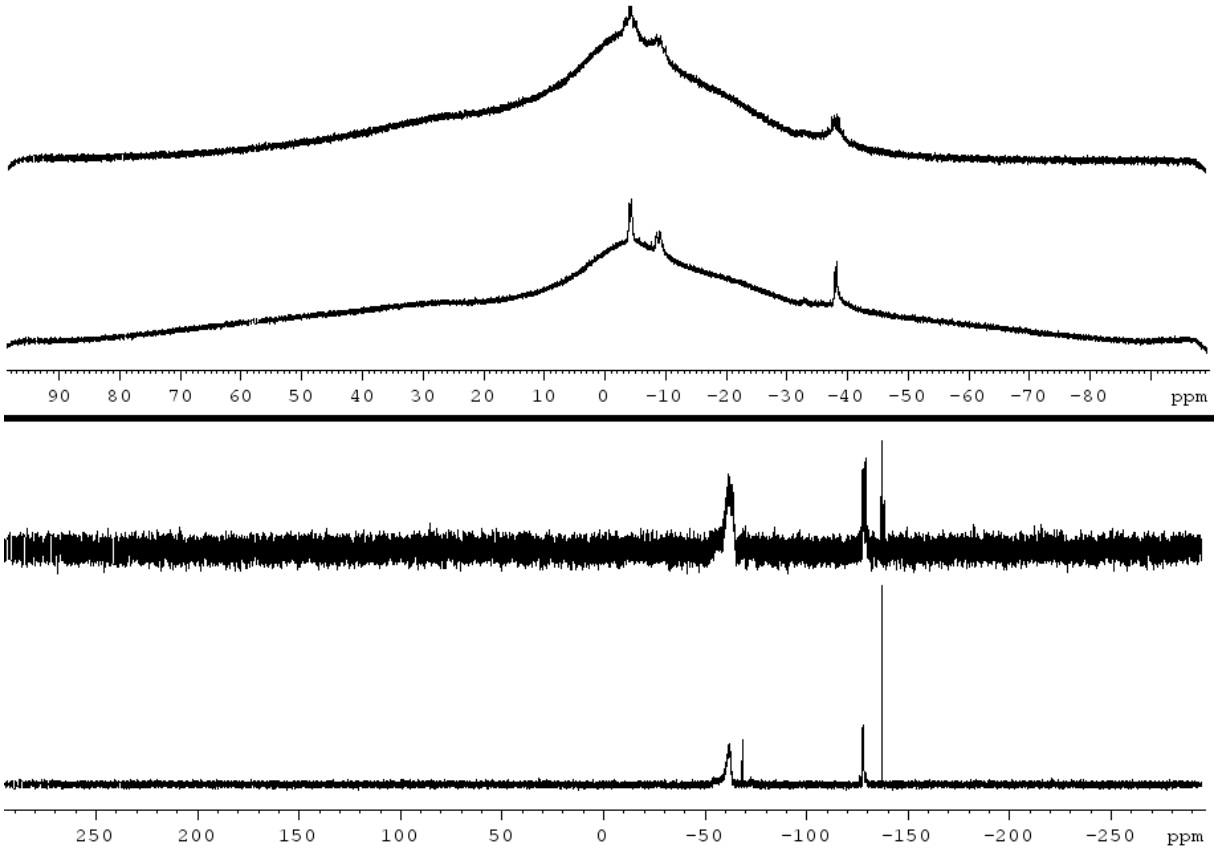

Figure S21. ^{11}B NMR (top, upper half), ^{11}B{^{1}H} NMR (bottom, upper half), ^{31}P NMR (top, lower half), and ^{31}P{^{1}H} NMR (bottom, lower half) spectra of **1c** (neat) after stirring at r.t. for 4 d

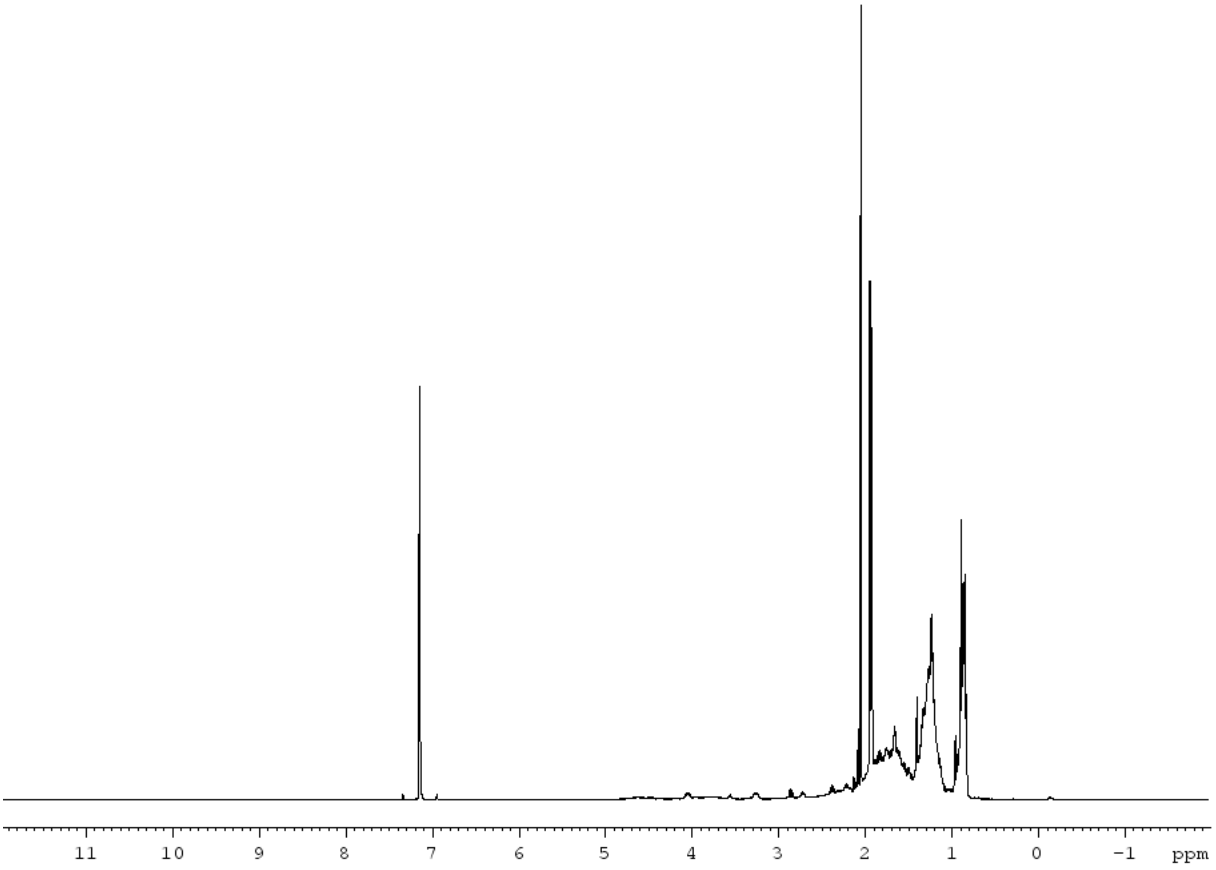

Figure S22. ^{1}H NMR spectrum of neat **1c** after stirring for 16h at 323 K

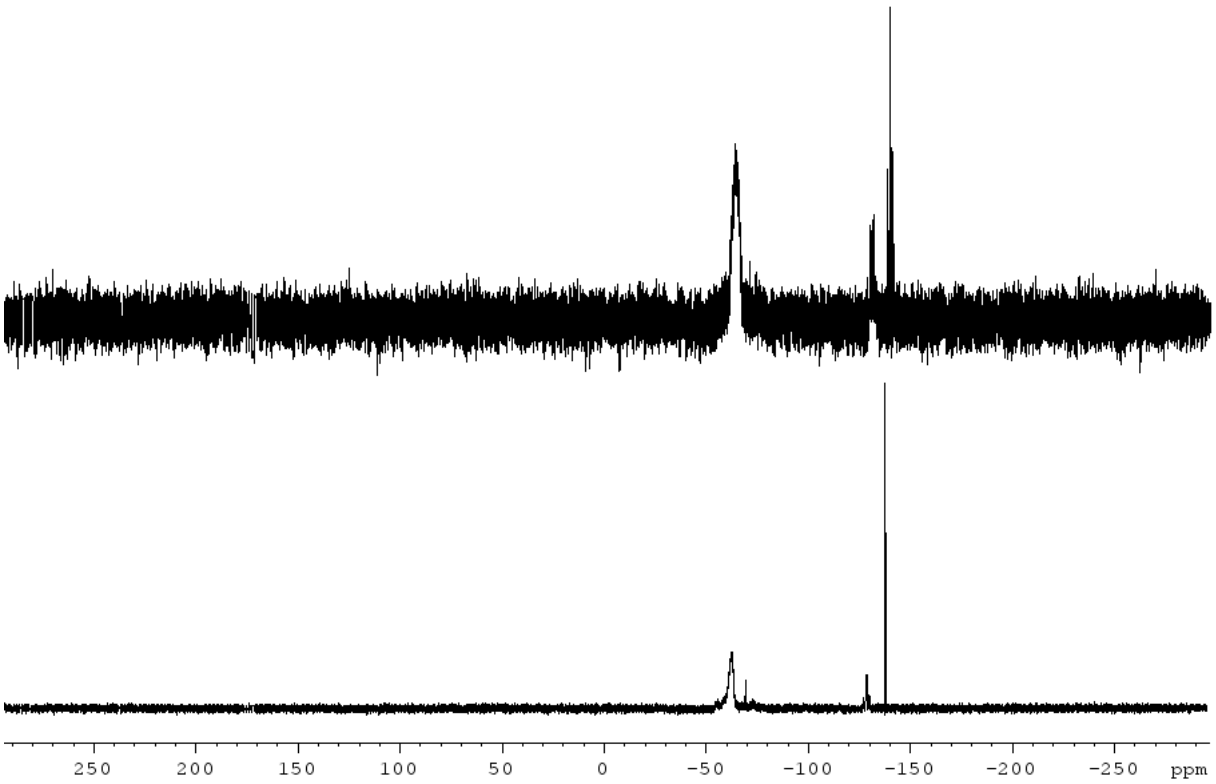

Figure S23. ^{31}P NMR (top) and $^{31}P\{^{1}H\}$ NMR (bottom) spectra of **1c** (neat) after stirring for 16h at 323 K

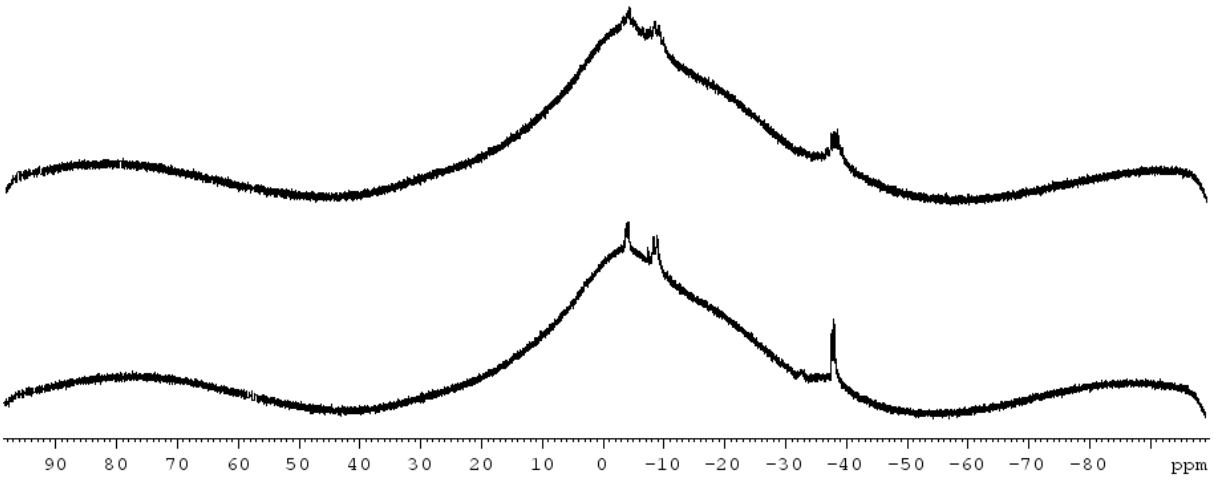

Figure S24. ^{11}B NMR (top) and $^{11}B\{^{1}H\}$ NMR (bottom) spectra of **1c** (neat) after stirring for 16h at 323 K

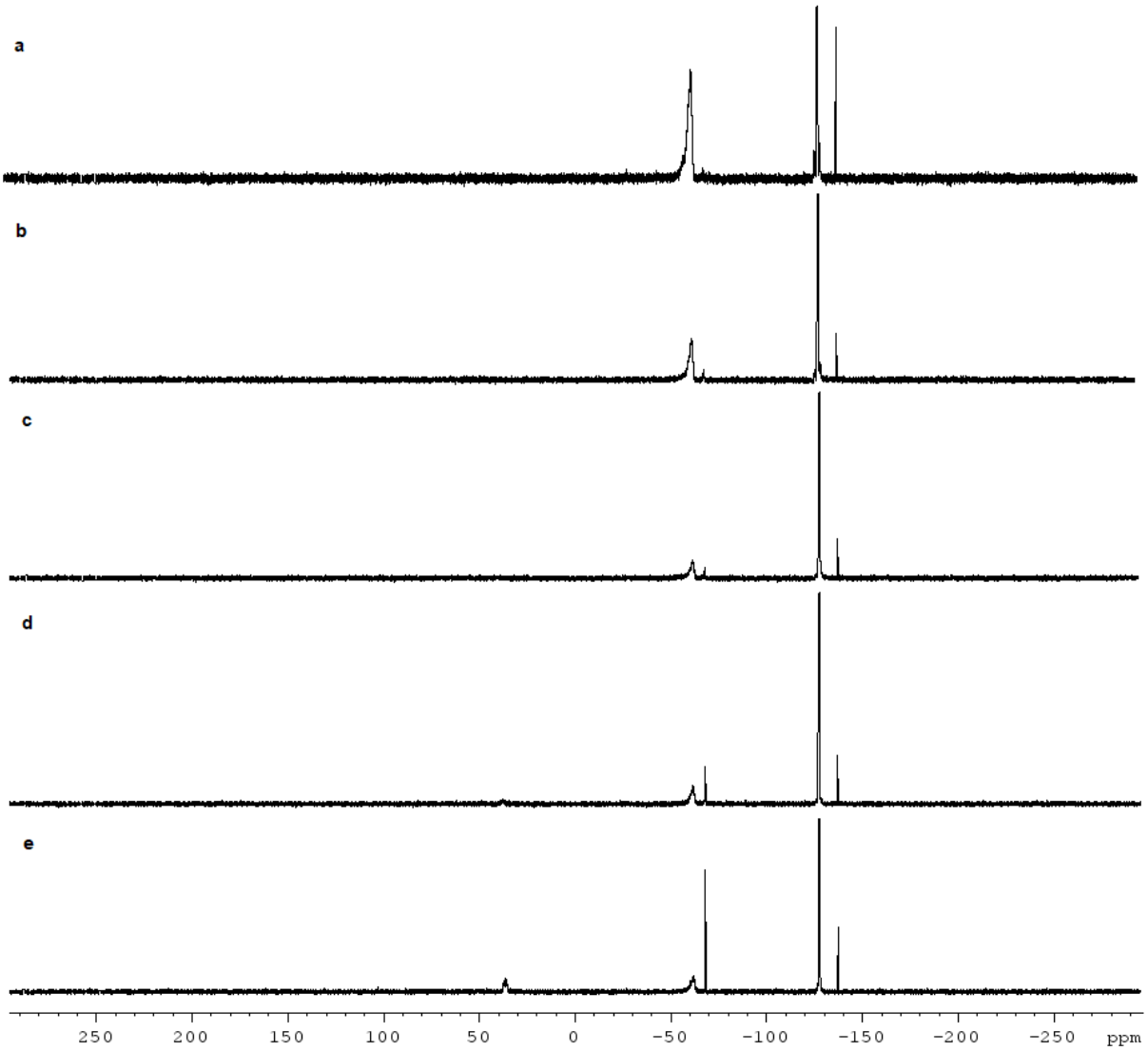

Figure S25. $^{31}P\{^{1}H\}$ NMR spectra of **1c** (c = 0.4 mol/L) after stirring for 21d (a), 7d (b), 16h (c), 90 min (d), 30 min (e) at r.t. in the presence of 4 mol% of $[(\eta^5{:}\eta^1\text{-}C_5H_4C_{10}H_{14})_2Ti]$.

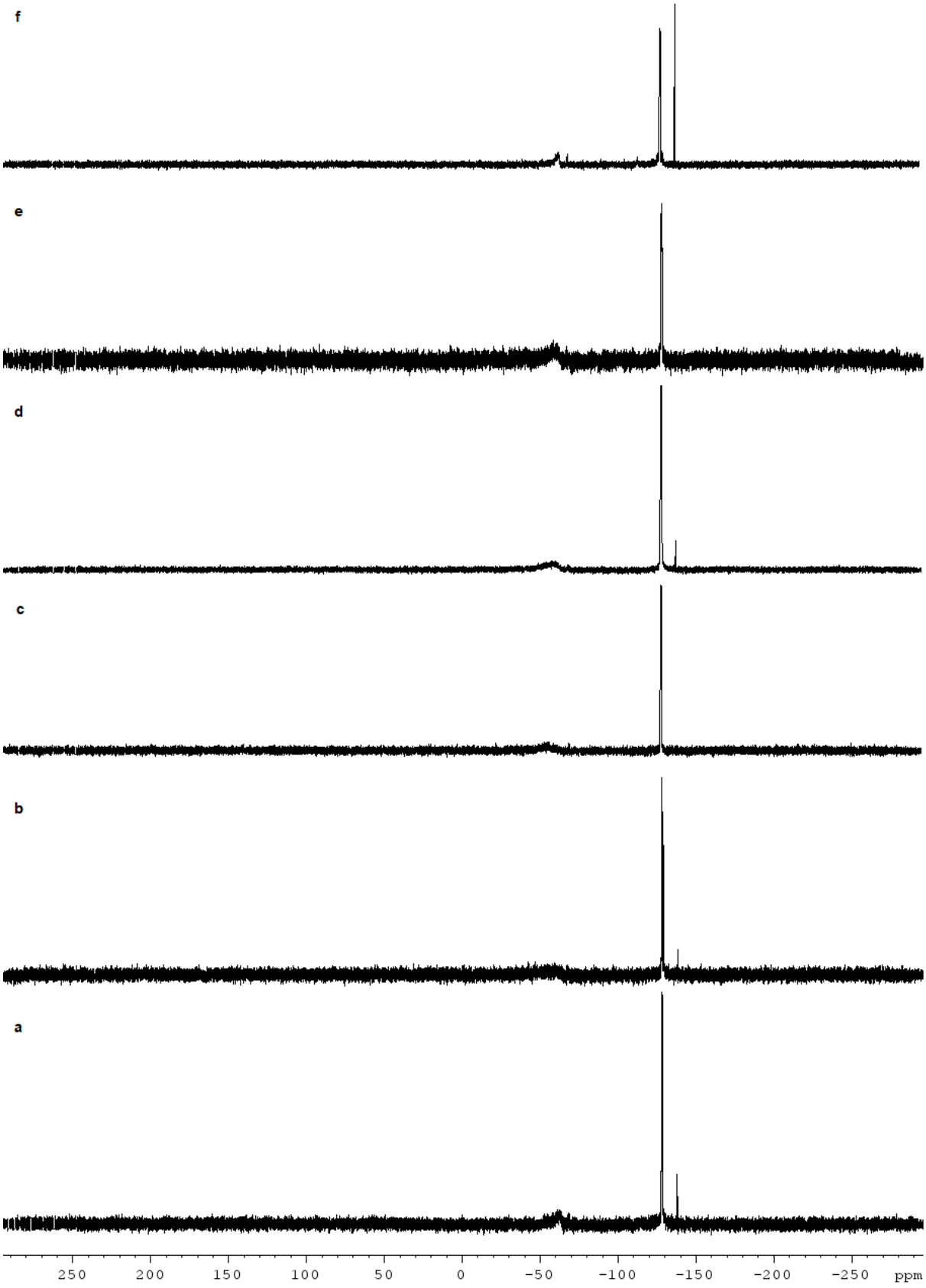

Figure S26. $^{31}P\{^{1}H\}$ NMR spectra of **1c** in toluene at.r.t for 3h under different conditions: a) 5 mol% [Ti], c (**1c**) = 0.1 mol/L; b) 10 mol% [Ti], c (**1c**) = 0.1 mol/L; c) 10 mol% [Ti], c (**1c**) = 0.1 mol/L, in 1:1 mixture of THF and toluene; d) 10 mol% [Ti], c (**1c**) = 0.2 mol/L; e) 25 mol% [Ti], c (**1c**) = 0.1 mol/L; f) in absence of [Ti], c (**1c**) = 0.1 mol/L

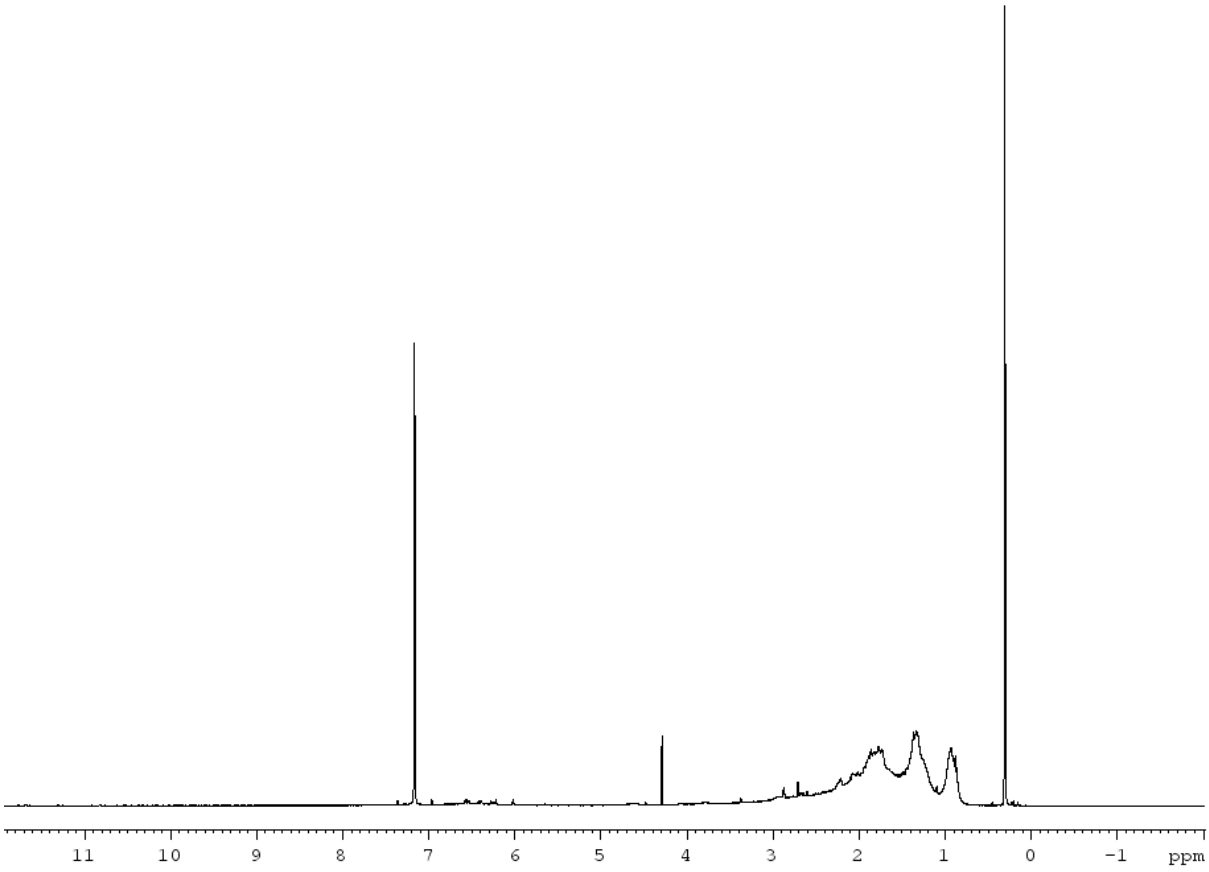

Figure S27. ^{1}H NMR spectrum of isolated poly-**1c** in C_6D_6

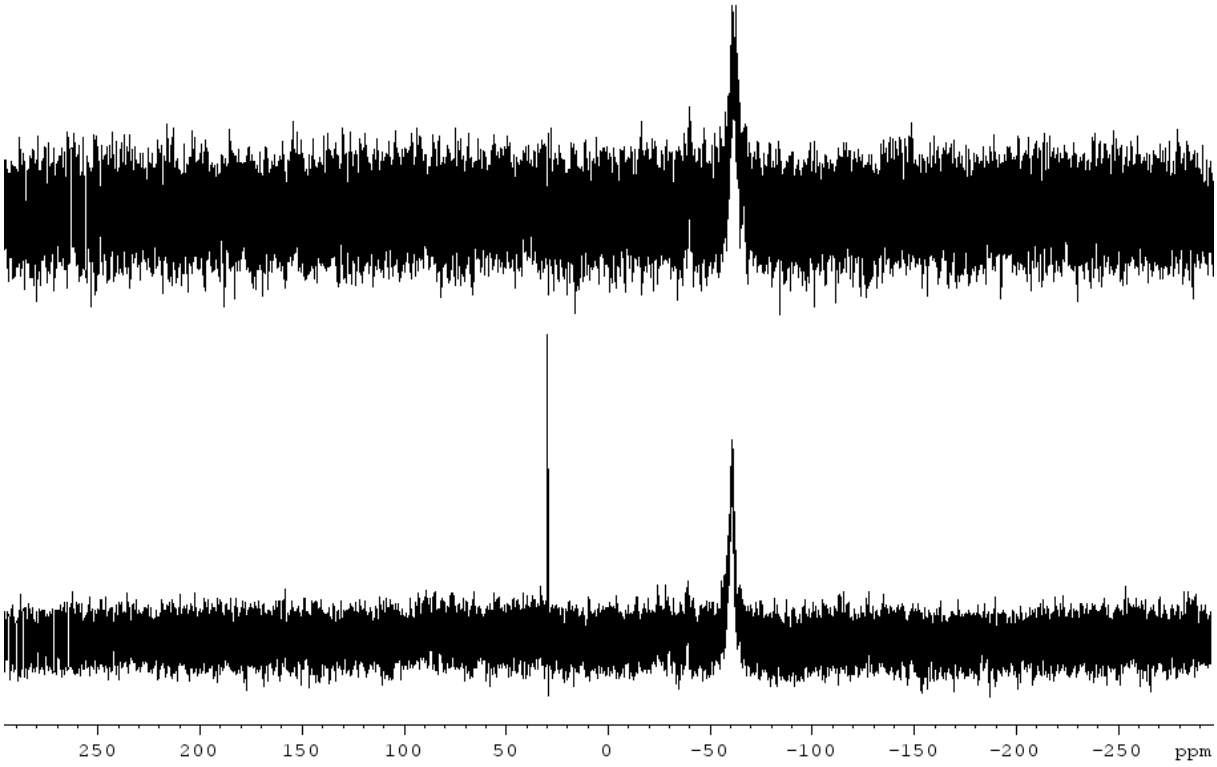

Figure S28. ^{31}P NMR (top) and $^{31}P\{^{1}H\}$ NMR (bottom) spectra of isolated poly-**1c** in C_6D_6

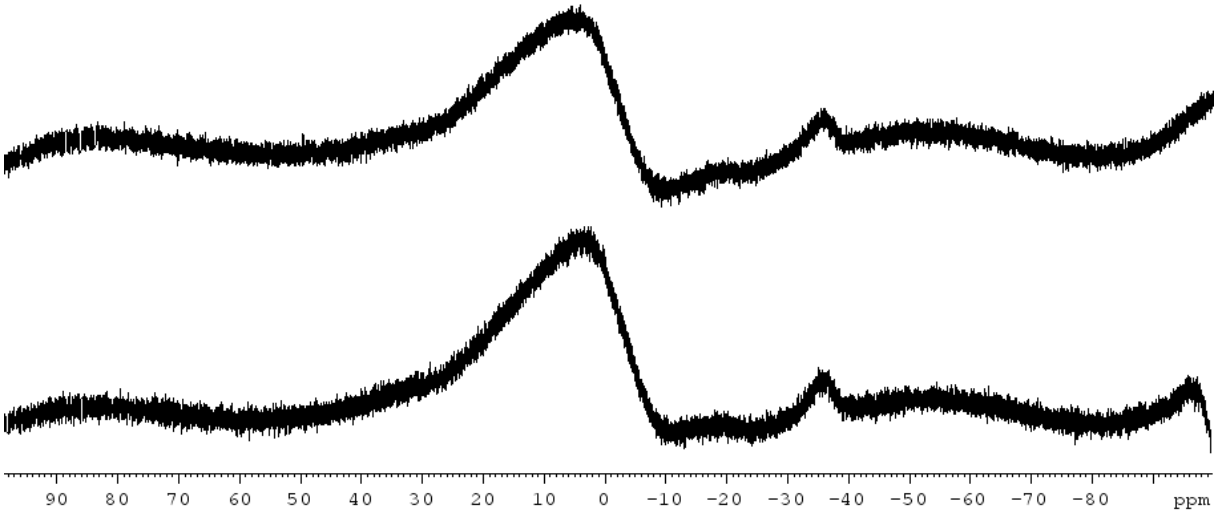

Figure S29. ^{11}B NMR (top) and $^{11}B\{^1H\}$ NMR (bottom) spectra of isolated poly-**1c** in C_6D_6

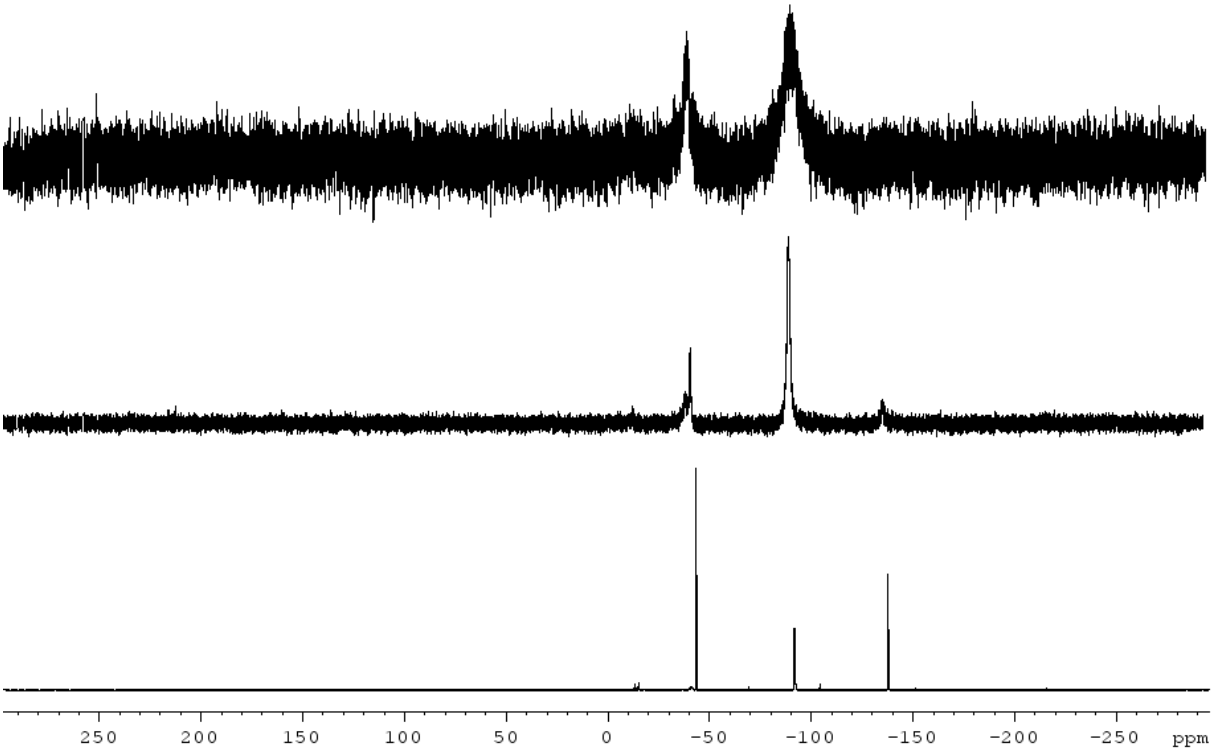

Figure S30. $^{31}P\{^1H\}$ NMR spectra of **2** in toluene after 3h at r.t. in the absence of [Ti] (bottom), in the presence of 5mol% [Ti] (middle) and in the presence of 10 mol% [Ti] (top)

References.

1. Stauber, A.; Jurca, T.; Marquardt, C.; Fleischmann, M.; Seidl, M.; Whittell, G.R.; Manners, I.; Scheer, M. A Convenient Route to Monoalkyl‐Substituted Phosphanylboranes (HRP–BH2–NMe3): Prospective Precursors to Poly [(alkylphosphino) boranes]. *Eur. J. Inorg. Chem.* **2016**, *2016*, 2684–2687.