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Electronic Supporting Information

1,3,2-Diheterophospholane complexes: access to new tuneable precursors of phosphanoxyl complexes and P-functional polymers

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Experimental Procedures

The synthesis of all compounds were performed under an argon atmosphere, using common Schlenk techniques and dry solvents. Tetrahydrofuran (THF), diethyl ether, petrol ether (40/60) and n-pentane were dried over sodium wire/benzophenone, CH_2Cl_2 over CaH_2, toluene over sodium and further purified by subsequent distillation. The diamines, diols, 2-aminoethanol were used as received as was $Li[AlH_4]$. TEMPO was resublimed before usage. Styrene and acrylonitrile were freshly distilled and then stored in the dark at 4 °C. Acetonitrile(pentacarbonyl)tungsten(0) and tetrabutylammonium penta-carbonyl hydrido tungstate(-1) were synthesised according to literature. All NMR spectra were recorded on a Bruker AVI-300 (300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C, 59.6 MHz for ^{29}Si and 121.5 MHz for ^{31}P), Bruker AVI-400 (400.1 MHz for ^{1}H, 100.6 MHz for ^{13}C, 79.5 MHz for ^{29}Si and 162.0 MHz for ^{31}P) and Bruker AV III HD Prodigy 500 (500.2 MHz for ^{1}H, 125.8 MHz for ^{13}C, 99.3 MHz for ^{29}Si, and 202.5 MHz for ^{31}P) spectrometers at 25 °C if not specified otherwise. The ^{1}H and ^{13}C NMR spectra were referenced to the residual proton resonances and the ^{13}C NMR signals of the deuterated solvents; ^{31}P NMR spectra were referenced to 85% H_3PO_4 as an external standard, respectively. Chemical shift δ for all spectra is given in ppm. Melting points were determined in one-side melted off capillaries using a Büchi Type S or a Carl Roth Type MPM-2 apparatus and are uncorrected. Elemental analyses were carried out on a Vario EL gas chromatograph. Mass spectrometric data were collected on a MAT 90 Thermo Finnigan sector instrument equipped with a LIFDI ion source from Linden CMS GmbH.

X-ray data were collected with a STOE IPDS-2T. The structures were solved by Patterson methods (SHELXS-97) and refined by full-matrix least squares on F2 (SHELXL-97). CCDC 2132109-2132114 contain the supplementary crystallographic data (see ESI p. 23).

The 2-Chlor-1,3-diisopropyl-1,3,2-diazaphospholidine **1** and 2-Chlor-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane **5b** were synthesised according to the literature.[1,2]

Synthesis of Pentacarbonyl(2-chlor-1,3-diisopropyl-1,3,2-diazaphospholidine-κ*P*)tungsten 2

In a dried 100 mL *Schlenk* tube 2.19 g (6 mmol, 1 eq.) $W(NCMe)(CO)_5$ were dissolved in 15 mL of THF. A solution of 0.92 g (4.4 mmol, 0.73 eq.) **1** in 10 mL of THF was added via a transfer cannula and rinsed two times with 5 mL of THF. The reaction was stirred for 20 h. After removing the solvent at reduced pressure ($3\cdot10^{-2}$ mbar) the crude product was extracted with three times 15 mL of *n*-pentane. The n-pentane solution was filtered through silica (Ø = 2 cm, h = 1.5 cm) and the solid phase was washed with additional 90 mL of *n*-pentane. The product was obtained as a yellow solid (0.61 g, 26 %, m.p. 125 °C).

^{1}H-NMR (500.1 MHz, 298 K, C_6D_6): 4.06 – 3.96 (m, 2H, $CH(^{i}Pr)_2$), 2.70 – 2.65 (m, 2H, CH_2), 2.50 – 2.43 (m, 2H, CH_2), 1.08 (d, $^{3}J_{H,H}$ = 6.6 Hz, 6H, CH_3), 0.93 (d, $^{3}J_{H,H}$ = 6.8 Hz, 6H, CH_3); **^{13}C{^{1}H}-NMR** (125.8 MHz, 298 K, C_6D_6): 198.8 (d_{sat}, $^{2}J_{P,C}$ = 42 Hz, $^{1}J_{W,C}$ = 141 Hz, *trans*-CO), 195.9 (d_{sat}, $^{2}J_{P,C}$ = 9 Hz, $^{1}J_{W,C}$ = 126 Hz, *cis*-CO), 46.2 (d, $^{2}J_{P,C}$ = 12 Hz, $CH(^{i}Pr)_2$), 40.2 (d, $^{2}J_{P,C}$ = 6 Hz, CH_2), 21.3 (d, $^{3}J_{P,C}$ = 12 Hz, CH_3), 18.6 (s, CH_3); **^{31}P{^{1}H}-NMR** (202.5 MHz, 298 K, C_6D_6): 130.9 (s_{sat}, $^{1}J_{W,P}$ = 369 Hz, $^{2}J_{P,C}$ = 42 Hz); **MS** (EI, 70 eV): *m/z* (%) = 532.0 (0.2) $[M]^{+\bullet}$, 516.0 (3) $[M\text{-}CO]^{+\bullet}$, 497.0 (10) $[M\text{-}2CO]^{+\bullet}$, 469.0 (6) $[M\text{-}3CO]^{+\bullet}$, 441.0 (5) $[M\text{-}5CO]^{+\bullet}$, 173.2 (100) $[M\text{-}W(CO)_5Cl]^{+\bullet}$; **IR** (ATR diamond) $\tilde{\nu}$ in cm^{-1} = 2971 (w, ν(C-H)), 2938(w, ν(C-H)), 2883 (w, ν(C-H)), 2078 (w, ν(C=O)), 1902 (vs, ν(C=O)); **Anal. calc.** for $C_{13}H_{18}N_2O_5PWCl$, C 29.32 H 3.41 N 5.26, **found** C 29.26 H 3.52 N 5.26.

Synthesis of Pentacarbonyl(1,3-diisopropyl-1,3,2-diazaphospholidine-κ*P*)tungsten 3

In a dried 100 mL *Schlenk* tube 0.53 g (1 mmol, 1 eq.) of **2** were dissolved in 10 mL of Et_2O. The solution was cooled in an ice bath and a cooled suspension of 38.0 mg (1 mmol, 1 eq.) of $Li[AlH_4]$ in 5 mL of Et_2O

was added with a transfer cannula, which was rinsed two times with 15 mL of Et_2O. The mixture was allowed to warm to room temperature and after 3 h the solvent was removed under reduced pressure ($3 \cdot 10^{-2}$ mbar). The product was extracted five times with 10 mL of *n*-pentane. After removing the solvent at reduced pressure ($3 \cdot 10^{-2}$ mbar) the product was obtained as a bright yellow solid (0.34 g, 69 %, m.p. 69 °C). **^{1}H-NMR** (300.1 MHz, 298 K, C_6D_6): 7.70 (d_{sat}, $^1J_{P,H}$ = 272.9 Hz, $^2J_{W,H}$ = 17.4 Hz, 1H, P-H), 3.78 – 3.65 (m, 2H, $CH(^iPr)_2$), 2.66 – 2.55 (m, 2H, CH_2), 2.36 – 2.29 (m, 2H, CH_2), 1.00 (d, $^3J_{H,H}$ = 6.6 Hz, CH_3), 0.83 (d, $^3J_{H,H}$ = 6.6 Hz, CH_3); **^{13}C{^{1}H}-NMR** (75.5 MHz, 298 K, C_6D_6): 198.9 (d, $^2J_{P,C}$ = 26 Hz, *trans*-CO), 196.2 (d_{sat}, $^2J_{P,C}$ = 9 Hz, $^1J_{W,C}$ = 125 Hz, *cis*-CO), 45.2 (d, $^2J_{P,C}$ = 11 Hz, $CH(^iPr)_2$), 41.6 (d, $^2J_{P,C}$ = 5 Hz, CH_2), 21.1 (d, $^3J_{P,C}$ = 11 Hz, CH_3), 17.3 (d, $^3J_{P,C}$ = 2.0 Hz, CH_3); **^{31}P{^{1}H}-NMR** (121.5 MHz, 298 K, C_6D_6): 78.7 (s_{sat}, $^1J_{W,P}$ = 295 Hz); **^{31}P-NMR** (121.5 MHz, 298 K, C_6D_6): 78.7 (dm_{sat}, $^1J_{P,H}$ = 273 Hz, $^1J_{W,P}$ = 295 Hz); **MS** (EI, 70 eV): *m/z* (%) = 498.1 (0.5) $[M]^{+\bullet}$, 441.1 (0.5) $[M\text{-}H\text{-}2CO]^{+\bullet}$, 173.2 (100) $[M\text{-}HW(CO)_5]^{+\bullet}$; **IR** (ATR diamond) $\tilde{\nu}$ in cm^{-1} = 2974 (w, ν(C-H)), 2935 (w, ν(C-H)), 2878 (w, ν(C-H)), 2368 (w, ν(P-H)), 2072 (w, ν(C=O)), 1893 (vs, ν(C-H)) ; **Anal. calc.** for $C_{13}H_{19}N_2O_5PW$, C 31.35 H 3.84 N 5.62, **found** C 31.31 H 3.65 N 5.65.

Synthesis of Pentacarbonyl(1,3-diisopropyl-2-(2,2,6,6-tetramethylpiperidin-1-oxyl)-1,3,2-diazaphospholidine-κ*P*)tungsten 4

In a 100 mL *Schlenk* tube 0.4 g (0.80 mmol, 1 eq.) **3** were dissolved in 15 mL Et_2O. The colourless solution was cooled with an ice bath and with a transfer cannula a solution of 0.25 g (1.60 mmol, 2 eq.) TEMPO in 5 mL Et_2O was added. After addition the cannula was rinsed with 5 mL Et_2O. After 3 hours the solvent was removed under reduced pressure ($3 \cdot 10^{-2}$ mbar). The obtained yellow solid was purified via column chromatography (Al_2O_3, argon, -20 °C, Ø = 3 cm, h = 4 cm, petrol ether (40/65)). After the first fraction (50 mL petrol ether) the product was obtained in the second fraction (20 mL PE, 30 mL PE with 20 % Et_2O, 55 mL PE with 50 % Et_2O and 35 mL PE: Et_2O (1:1). All solutions had to be kept cold at around 0 °C. After removing solvent under reduced pressure ($3 \cdot 10^{-2}$ mbar) and 0 °C the product was obtained as a thermal labile yellow powder in almost quantitative yields. **^{1}H-NMR** (300.1 MHz, 263 K, $CDCl_3$): 4.07- 3.93 (m, 2H, CH^iPr_2), 3.29 – 3.21 (m, 2H NCH_2), 3.12 – 3.02 (m, 2H, NCH_2), 1.61 – 1.45 (m, 6H, CH_2-CH_2-CH_2), 1.26 (s, 6H, CCH_3 (TEMP-moiety)), 1.23 (d, $^3J_{H,H}$ = 6.6 Hz, 6H, N-$CH(CH_3)_2$), 1.15 (d, $^3J_{H,H}$ = 6.5 Hz, 6H, N-$CH(CH_3)_2$), 1.07 (s, 6H, CCH_3 (TEMP-moiety)); **^{13}C{^{1}H}-NMR** (75.5 MHz, 263 K, $CDCl_3$): 198.8 (d, $^2J_{P,C}$ = 32 Hz, *trans*-CO), 198.4 (d, $^2J_{P,C}$ = 9 Hz, *cis*-CO), 61.0 (d, $^3J_{P,C}$ = 2 Hz, N$\underline{C}(CH_2)(CH_3)_2$ (TEMP-moiety)), 46.1 (d, $^2J_{P,C}$ = 14 Hz, CH^iPr_2), 41.1 (d, $^2J_{P,C}$ = 3 Hz, N-CH_2), 40.0 (s, $\underline{C}H_2$-CH_2-$\underline{C}H_2$), 33.2 ($NC(CH_2)(\underline{C}H_3)_2$ (TEMP-moiety)), 21.7 (d, $^3J_{P,C}$ = 2 Hz, $NCH(\underline{C}H_3)_2$), 20.9 (s, $NC(CH_2)(\underline{C}H_3)_2$ (TEMP-moiety)), 20.8 (d, $^3J_{P,C}$ = 5 Hz, $NCH(\underline{C}H_3)_2$), 16.8 (s, CH_2-$\underline{C}H_2$-CH_2 (TEMP-moiety)); **^{31}P{^{1}H}-NMR** (121.5 MHz, 263 K, $CDCl_3$): 140.6 (br. s); **Anal. calc.** for $C_{22}H_{36}N_3O_6PW$, C 40.44 N 6.43 H 5.55, **found** C 41.05 N 6.07 H 5.98.

Synthesis of 2-Chlor-3-isopropyl-1,3,2-oxazaphospholidine 5a[3]

To a dried 250 mL three necked round bottom flask with vacuum adapter and two 50 mL dropping funnels, 50 mL Et_2O were added. In one of the dropping funnels 25 mL Et_2O, 7 mL NEt_3 (50 mmol, 1 eq.) and 5.75 mL (50 mmol, 1 eq.) N-isopropyl-2-aminoethanol were mixed. The second dropping funnel was filled with 25 mL Et_2O and 4.4 mL (50 mmol, 1 eq.) PCl_3. The flask was cooled to -30 °C in a cooling bath and kept at this temperature for the duration of the addition. While stirring, the two solutions were simultaneously added dropwise. After 30 minutes the addition was completed. To the reaction mixture 7 mL NEt_3 (50 mmol, 1 eq.) in 20 mL Et_2O were added dropwise. The reaction mixture was stirred for 30 minutes, after which the cooling bath was removed. The precipitated salt was filtered off through a frit (P3) and washed eight times with 20 mL Et_2O each. The solvent was removed from the filtrate under reduced pressure (26 mbar, 25 °C) and the crude product was obtained as a yellow oil. The crude product was distilled (T: 130 °C, b.p.: 107-108 °C, 21 mbar) to obtain the pure product as a

colourless liquid (3.165 g, 38 %). **^{1}H-NMR** (300.1 MHz, 298 K, $CDCl_3$): 4.47 (br. s, 2H, OCH_2), 3.51 (m, 1H, CH^iPr_2), 3.21 (m, 2H, NCH_2), 1.33 (d, $^2J_{H,H}$ = 6.4 Hz, 6 H, CH_3); **^{31}P{^{1}H}-NMR** (121.5 MHz, 298 K, $CDCl_3$): δ 168.4 (s).

Synthesis of Pentacarbonyl(3-isopropyl-1,3,2-oxazaphospholidine-κ*P*)tungsten 6a

In a 100 mL *Schlenk* tube 0.45 g (1 mmol, 1 eq.) $NEt_4[W(CO)_5H]$ were suspended in 15 mL THF. While stirring, a solution of 0.17 g (1.04 mmol, 1.05 eq.) **5a** in 5 mL THF was added with a transfer canula, which was rinsed with 5 mL THF after addition. After 2.5 hours the solvent was removed under reduced pressure ($3\cdot10^{-2}$ mbar). The product was extracted from the sticky yellow residue by extraction with five times 10 mL Et_2O. After removing the solvent from the filtrate under reduced pressure ($3\cdot10^{-2}$ mbar) the product was obtained as an off-white powder (0.19 g, 41.5 %, m.p.: 91 C). **^{1}H-NMR** (500.1 MHz, 298 K, C_6D_6): 7.71 (d_{sat}, $^1J_{P,H}$ = 321 Hz, $^2J_{W,H}$ = 18.4 Hz, 1H, PH), 3.72 – 3.6 (m, 1H, CH^iPr_2), 3.46 – 3.39 (m, 1H, OCH_2), 3.37 – 3.32 (m, 1H, OCH_2), 2.36 – 2.28 (m, 1H, NCH_2), 2.06 – 2.00 (m, 1H, NCH_2), 0.89 (d, $^3J_{H,H}$ = 6.6 Hz, 3H, CH_3), 0.72 (d, $^3J_{H,H}$ = 6.6 Hz, 3H, CH_3); **^{13}C{^{1}H}-NMR** (125.8 MHz, 298 K, C_6D_6): 198.7 (d_{sat}, $^2J_{P,C}$ = 28.1 Hz, $^1J_{W,C}$ = 138 Hz, *trans*-CO), 195.6 (d_{sat}, $^2J_{P,C}$ = 9 Hz, $^1J_{W,C}$ = 125 Hz, *cis*-CO), 69.1 (d, $^2J_{P,C}$ = 10 Hz, OCH_2), 45.6 (d, $^2J_{P,C}$ = 11 Hz, CH^iPr_2), 41.1 (s, NCH_2), 21.6 (d, $^3J_{P,C}$ = 8 Hz, CH_3), 19.4 (d, $^3J_{P,C}$ = 4 Hz, CH_3); **^{31}P{^{1}H}-NMR** (202.5 MHz, 298 K, C_6D_6): 121 (s_{sat}, $^1J_{W,P}$ = 305 Hz); **^{31}P-NMR** (202.5 MHz, 298 K, C_6D_6): 121 (dm_{sat}, $^1J_{P,H}$ = 321 Hz, $^1J_{W,P}$ = 305 Hz); **MS** (EI, 70 eV): *m/z* = 457.0 $[M]^{+\bullet}$, 429.0 $[M\text{-}CO]^{+\bullet}$, 399.0 $[M\text{-}2CO\text{-}H_2]^{+\bullet}$, 371.0 $[M\text{-}3CO\text{-}H_2]^{+\bullet}$, 343.0 $[M\text{-}4CO\text{-}H_2]^{+\bullet}$, 132.1 $[M\text{-}H\text{-}WCO_5]^{+\bullet}$; **IR** (ATR diamond) $\tilde{\nu}$ in cm^{-1} 2963 (w, ν(C-H)), 2216 (w, ν(P-H)), 2076 (w, ν(C=O)), 1880 (vs, ν(C=O)); **Anal. calc.** for $C_{10}H_{12}NO_6PW$, C 26.28 H 2.65 N 3.06, **found** C 26.26 H 2.89 N 3.24.

Synthesis of Pentacarbonyl(4,4,5,5-tetramethyl-1,3,2-dioxaphospholane-κ*P*)tungsten 6b

In a 100 mL *Schlenk* tube 0.69 g (1.51 mmol, 1 eq.) $NEt_4[W(CO)_5H]$ were suspended in 15 mL THF. While stirring a solution of 0.29 g (1.59 mmol, 1.05 eq.) **5b** in 5 mL THF was added with a transfer canula, which was rinsed with two times with 2.5 mL THF after addition. After 1.5 hours the solvent was removed under reduced pressure ($3\cdot10^{-2}$ mbar). The product was extracted from the sticky yellow residue by extraction with five times 10 mL Et_2O. The solvent was removed under reduced pressure to give the pure product as an off-white powder. To increase the yield the residue from the filtration was purified via column chromatography (SiO_2, argon, -20 °C, Ø = 1 cm, h = 10 cm, petrol ether (40/65) with 2.5 % NEt_3). The product was obtained in the first fraction. After removing the solvent under reduced pressure ($3\cdot10^{-2}$ mbar) the product was obtained as an off-white powder (0.27 g, 38.6 %, m.p.: 63 °C). **^{1}H-NMR** (500.1 MHz, 298 K, C_6D_6): δ in ppm 8.49 (dsat, $^1J_{P,H}$ = 349.7 Hz, $^2J_{W,H}$ = 22 Hz, 1H, PH), 0.96 (s, 3H, CH_3) 0.75 (s, 6H, CH_3); **^{13}C{^{1}H}-NMR** (125.8 MHz, 298 K, C_6D_6): δ in ppm 198.6 (d_{sat}, $^2J_{P,C}$ = 30.7 Hz, $^1J_{W,C}$ = 137 Hz, *trans*-CO), 195.3 (d_{sat}, $^2J_{P,C}$ = 9 Hz, $^1J_{W,C}$ = 125 Hz, *cis*-CO), 87.0 (d, $^2J_{P,C}$ = 6 Hz, $(H_3C)_2\underline{C}O$), 24.5 (d, $^3J_{P,C}$ = 5 Hz, CH_3), 21.5 (d, $^3J_{P,C}$ = 4 Hz, CH_3); **^{31}P{^{1}H}-NMR** (202.5 MHz, 298 K, C_6D_6): δ in ppm 146.3 (s_{sat}, $^1J_{W,P}$ = 325 Hz); **^{31}P-NMR** (202.5 MHz, 298 K, C_6D_6): δ in ppm 146.3 (d_{sat}, $^1J_{P,H}$ = 350 Hz, $^1J_{W,P}$ = 325 Hz); **MS** (EI, 70 eV): *m/z* = 472.0 $[M]^{+\bullet}$, 444.0 $[M\text{-}CO]^{+\bullet}$, 416.0 $[M\text{-}2CO]^{+\bullet}$; **IR** (ATR diamond) $\tilde{\nu}$ in cm^{-1} 2993 (w, ν(C-H)), 2280 (w, ν(P-H)), 2076 (w, ν(C=O)), 1906 (vs, ν(C=O)); **Anal. calc.** for $C_{11}H_{13}O_7PW$, C 27.99 H 2.78, **found** C 28.00 H 2.91.

Synthesis of Pentacarbonyl(3-isopropyl-2-(2,2,6,6-tetramethylpiperidin-1-oxyl)-1,3,2-oxazaphospholidine-κ*P*)tungsten 7a

In a 10 mL *Schlenk* tube 122 mg (0.27 mmol, 1 eq.) **6a** was dissolved in 3 mL THF. A solution of 84 mg (0.53 mmol, 2 eq.) TEMPO in 1 mL THF was added to the solution of **6b** with a transfer cannula. The cannula was rinsed with 1 mL THF. The reaction mixture was stirred for 7 hours and all volatiles were removed under reduced pressure ($4\cdot10^{-2}$ mbar) to obtain the product as a beige powder (0.16 g, 97 %).

^{1}H-NMR (500.14 MHz, 298 K, THF-d8): δ in ppm 4.35 – 4.26 (m, 2H, OCH_2), 3.95 (dh, $^{3}J_{P,H}$ = 10.3 Hz, $^{3}J_{H,H}$ = 6.6 Hz, $NC\underline{H}^{i}Pr_2$), 3.37 – 3.27 (m, 1H, NCH_2) 3.20 – 3.10 (m, 1H, NCH_2), 1.69 – 1.51 (m , 5H, CH_2-CH_2-CH_2 (TEMP-moiety)), 1.41 (s, 3H, $NC(CH_2)(\underline{C}H_3)_2$), 1.33 (d, $^{3}J_{H,H}$ = 6.7 Hz, 3H, $NCH(CH_3)_2$), 1.32 (s, 3H, $NC(CH_2)(\underline{C}H_3)_2$), 1.27 (d, $^{3}J_{H,H}$ = 6.6 Hz, 3H, $NCH(CH_3)_2$), 1.18 (s, 3H, $NC(CH_2)(\underline{C}H_3)_2$), 1.14 (s, 3H, $NC(CH_2)(\underline{C}H_3)_2$); **^{13}C{^{1}H}-NMR** (125.78 MHz, 298 K, THF-d8): δ in ppm 199.6 (d_{sat}, $^{2}J_{P,C}$ = 37 Hz, $^{1}J_{W,C}$ = 140 Hz*, trans*-CO), 198.0 (d_{sat}, $^{2}J_{P,C}$ = 9 Hz, $^{1}J_{W,C}$ = 126 Hz, *cis*-CO), 67.8 (d, $^{2}J_{P,C}$ = 9 Hz, OCH_2), 62.6 (d, $^{2}J_{P,C}$ = 5 Hz, $N\underline{C}(CH_2)(CH_3)_2$), 62.0 (s, $NC(CH_2)(\underline{C}H_3)_2$), 45.3 (d, $^{2}J_{P,C}$ = 13 Hz, $N\underline{C}H^{i}Pr_2$), 41.2 (s, $N\underline{C}(CH_2)(CH_3)_2$), 41.1 (s, $N\underline{C}(CH_2)(CH_3)_2$), 40.4 (s, NCH_2), 34.3 (s, $NC(CH_2)(\underline{C}H_3)_2$), 33.81 (s, $NC(CH_2)(\underline{C}H_3)_2$), 22.1 (s, $NCH(C\underline{H}_3)_2$), 21.5 (s, $NC(CH_2)(\underline{C}H_3)_2$), 21.4 (s, $NC(CH_2)(\underline{C}H_3)_2$), 20.9 (d, $^{3}J_{P,C}$ = 7 Hz, $NCH(C\underline{H}_3)_2$); **^{31}P-NMR** (202.5 MHz, 298 K, THF-d8): δ in ppm 151.0 (s_{sat}, $^{1}J_{W,P}$ = 366.7 Hz); **MS** (EI, 70 eV): *m/z* = 612.2 $[M]^{+\bullet}$, 456.0 $[M\text{-}TEMPO]^{+\bullet}$, 428.0 $[M\text{-}TEMPO\text{-}CO]^{+\bullet}$, 140.1 $[TEMP]^{+\bullet}$, 132.1 $[M\text{-}TEMPO\text{-}W(CO)_5]^{+\bullet}$, 126.1 $[TEMP\text{-}N]^{+\bullet}$; **IR** (ATR diamond) ṽ in cm^{-1}; **Anal. calc.** for $C_{19}H_{29}N_2O_7PW$, C 37.27 N 4.58 H 4.77, **found** C 37.62 N 4.53 H 5.23.

Synthesis of Pentacarbonyl(4,4,5,5-tetramethyl-2-(2,2,6,6-tetramethylpiperidin-1-oxyl)-1,3,2-dioxaphospholane-κ*P*)tungsten 7b

In a 10 mL *Schlenk* tube 99 mg (0.21 mmol, 1 eq.) **6a** was dissolved in 6 mL THF. A solution of 71 mg (0.44 mmol, 2.1 eq.) TEMPO in 2 mL THF was added to the solution of **6b** with a transfer cannula. The cannula was rinsed twice with 1 mL THF. The solution was stirred for a week until a mixture of presumably **7b**, **6b** and an unknown complex were formed in a ratio of 7:1.5:1. Via column chromatography (SiO_2, argon, -20 °C, Ø = 2 cm, h = 10 cm, Et_2O) **6b** was removed from the mixture. From a saturated Et_2O solution at 4 °C single crystals were grown. **^{31}P{^{1}H}-NMR** (162.0 MHz, 298 K, THF): δ in ppm 161.9 (s_{sat}, $^{1}J_{W,P}$ = 387.8 Hz, **7b**), 146.1 (s_{sat}, $^{1}J_{W,P}$ = 325 Hz, **6b**), 131.1(s_{sat}, $^{1}J_{W,P}$ = 391.5 Hz).

General procedure for the synthesis of the polymers

A 25 mL *Schlenk* tube was charged with around 25-50 mg of **4** cooled in an ice bath. 10 mL precooled toluene were added. Freshly distilled monomer (styrene: 500 eq.; acrylonitrile: 1000 eq., 300 eq.) was added to the yellow solution. The whole setup was covered in tin foil and stirred for 3 days. Alongside a reference sample was prepared under the exact same conditions but without addition of **4**.

Work up of polystyrene

After 3 days the toluene solution is added to 50 mL methanol. The turbid suspension was allowed to set for 1 hour, until it was possible to filter the suspension. The solid was dissolved in 10 mL toluene and again precipitated in 50 mL methanol. This process was repeated one more time. After filtration the solid was dried in a 20 mL *Schlenk* tube under reduced pressure ($3\cdot10^{-2}$ mbar). The solid was obtained as a colourless flaky solid, which was grinded to a colourless free flowing powder. (81.9 mg, 2.1 %).

Work up of polyacrylonitrile

After 3 days the toluene solution is added to 25 methanol. The reaction vessel is rinsed with 10 mL methanol. The two portions are combined and stirred for five minutes, upon they are filtered. The pale-yellow solid is washed with 5 mL of methanol and then dimethylformamide (DMF) is added until everything is dissolved. The solution is added to 20 mL Et_2O, stirred for five minutes and filtered. The solid is washed with two times 20 mL Et_2O and then redissolved in just enough DMF to dissolve the solid. The solution is poured into 3 mL water. The precipitated polymer is filtered and washed with two times 10 mL water. Dissolving in DMF and precipitation in water is repeated two times. The product is then added to a 50 mL *Schlenk* flask and dried under reduced pressure ($3\cdot10^{-2}$ mbar). The polymer is obtained as pale-yellow flakes, which can be grinded into fine powder. (483 mg, 80 %).

NMR Data:

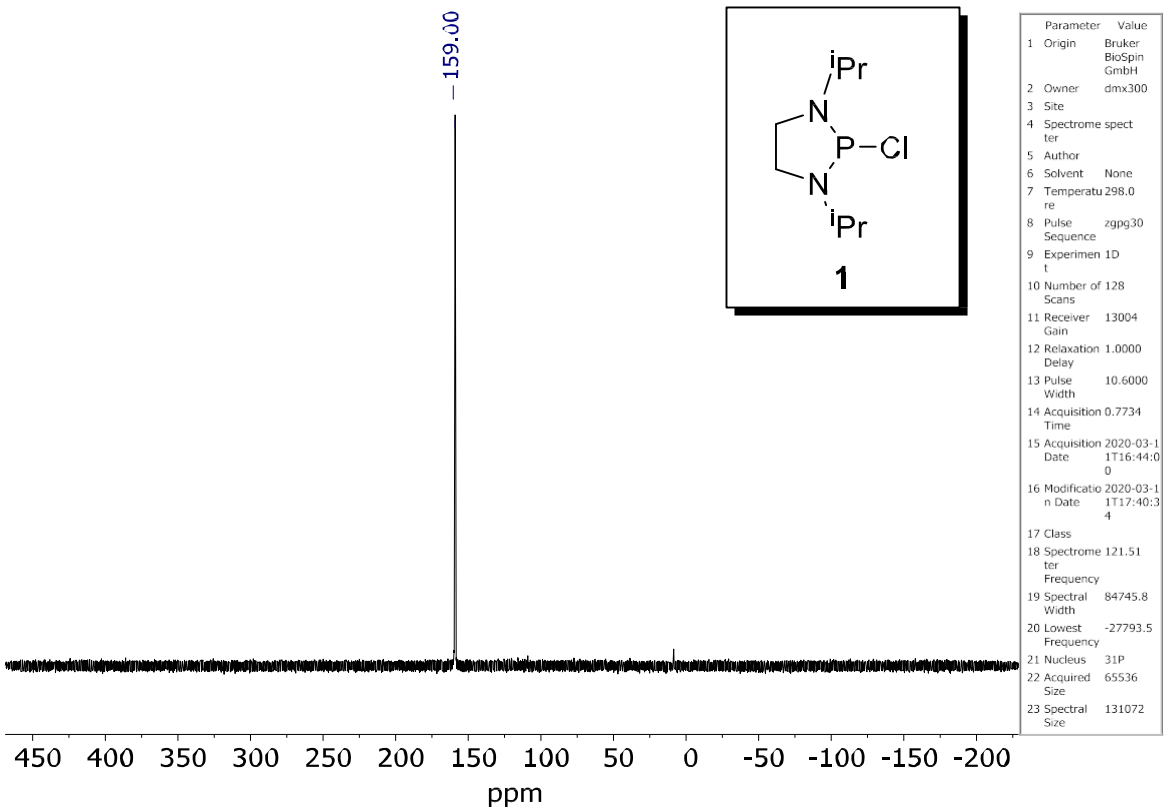

*Figure 1 $^{31}P\{^{1}H\}$-NMR spectrum of **1** in toluene*

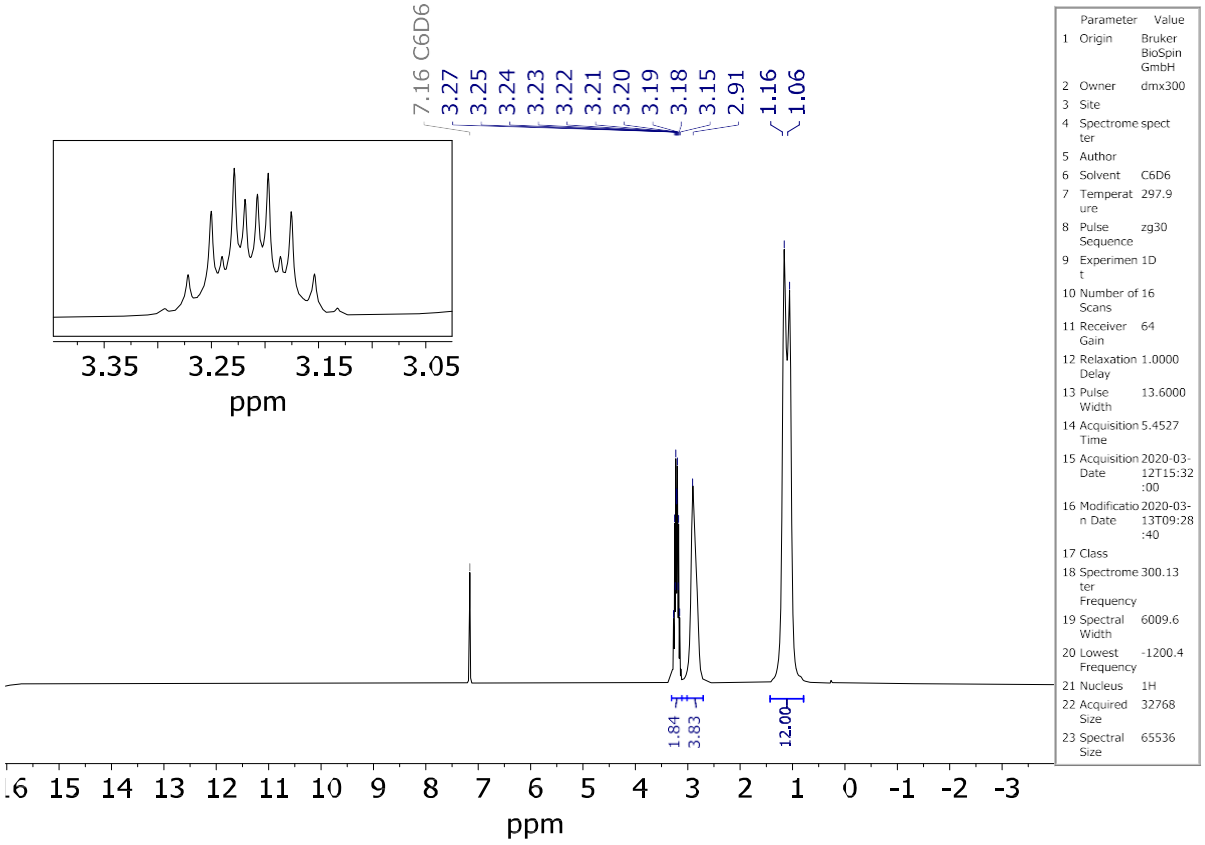

*Figure 2 ^{1}H-NMR spectrum of **1** in C6D6.*

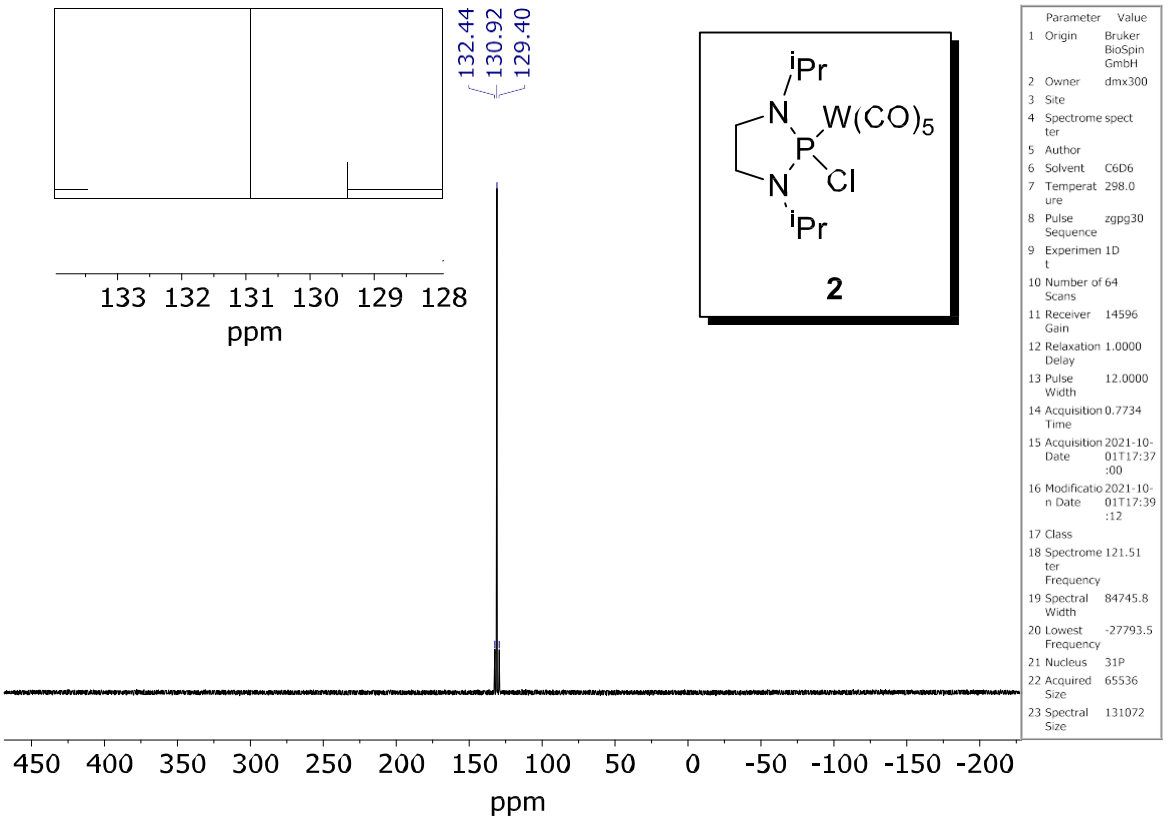

*Figure 3 $^{31}P\{^{1}H\}$-NMR spectrum of **2** in C_6D_6.*

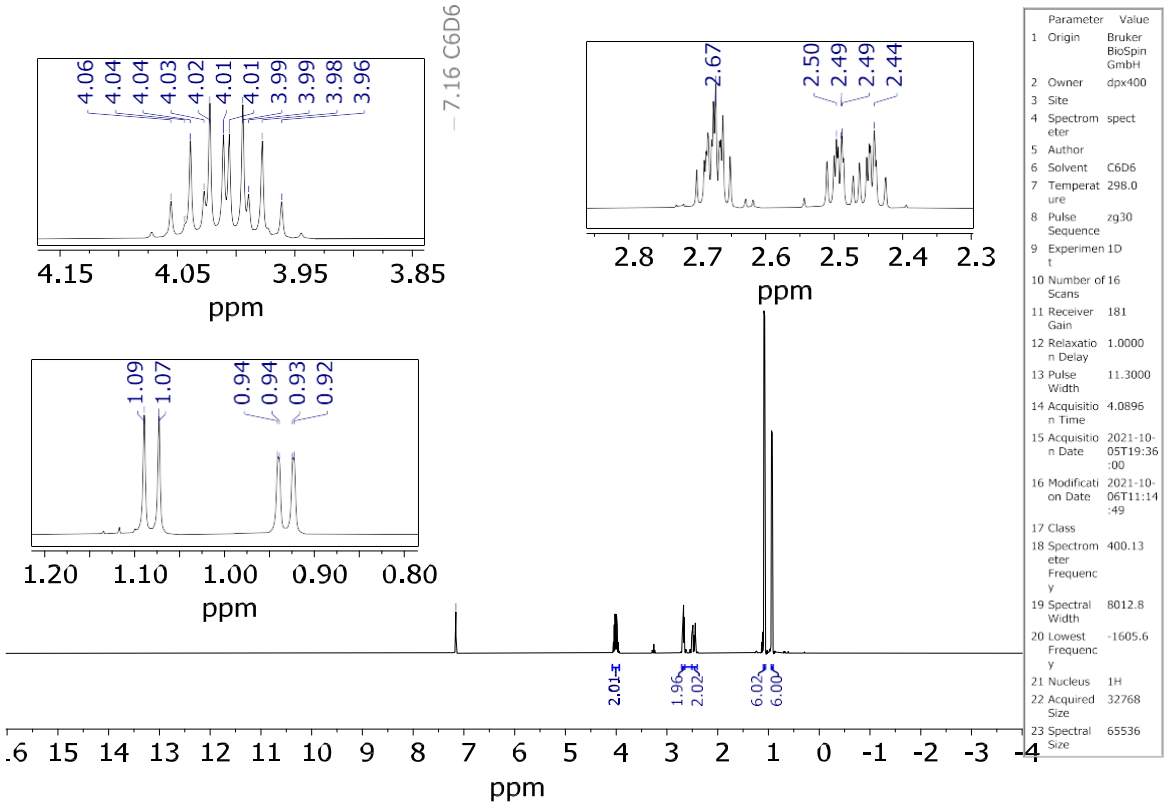

*Figure 4 ^{1}H-NMR spectrum of **2** in C_6D_6.*

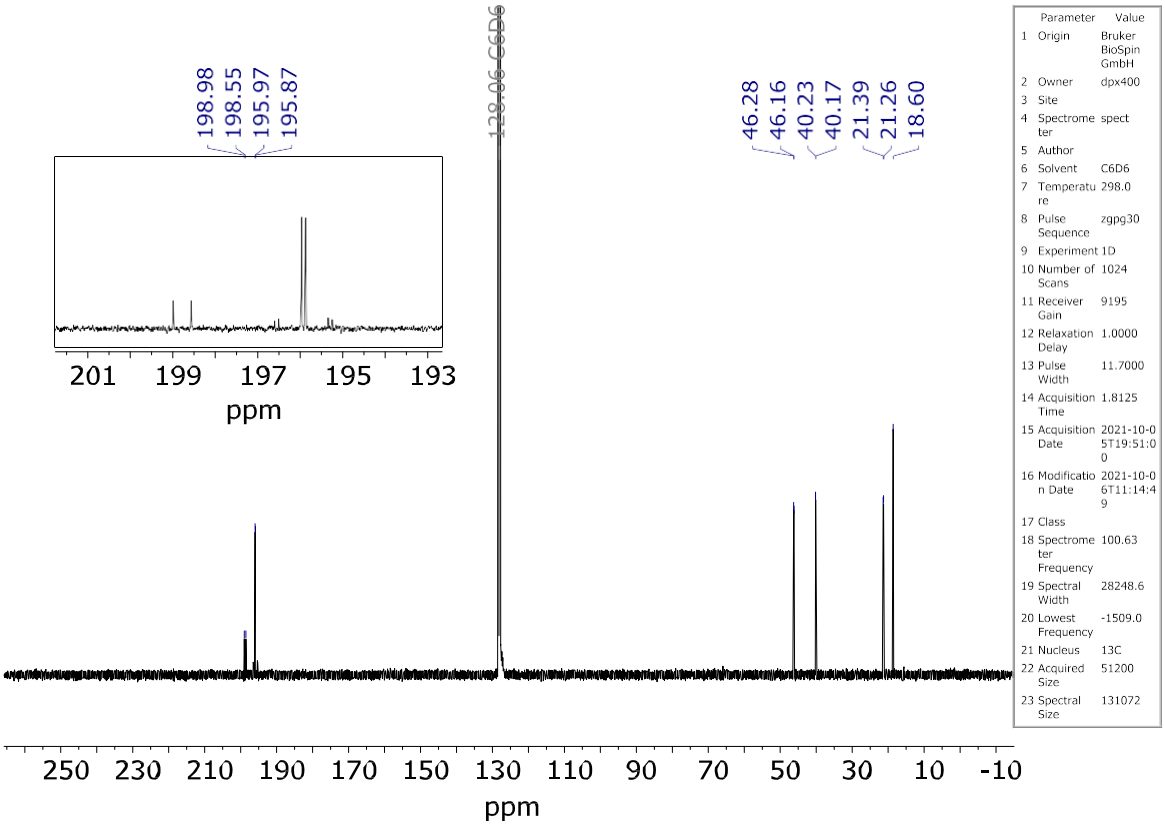

*Figure 5 $^{13}C\{^1H\}$-NMR spectrum of **2** in C_6D_6.*

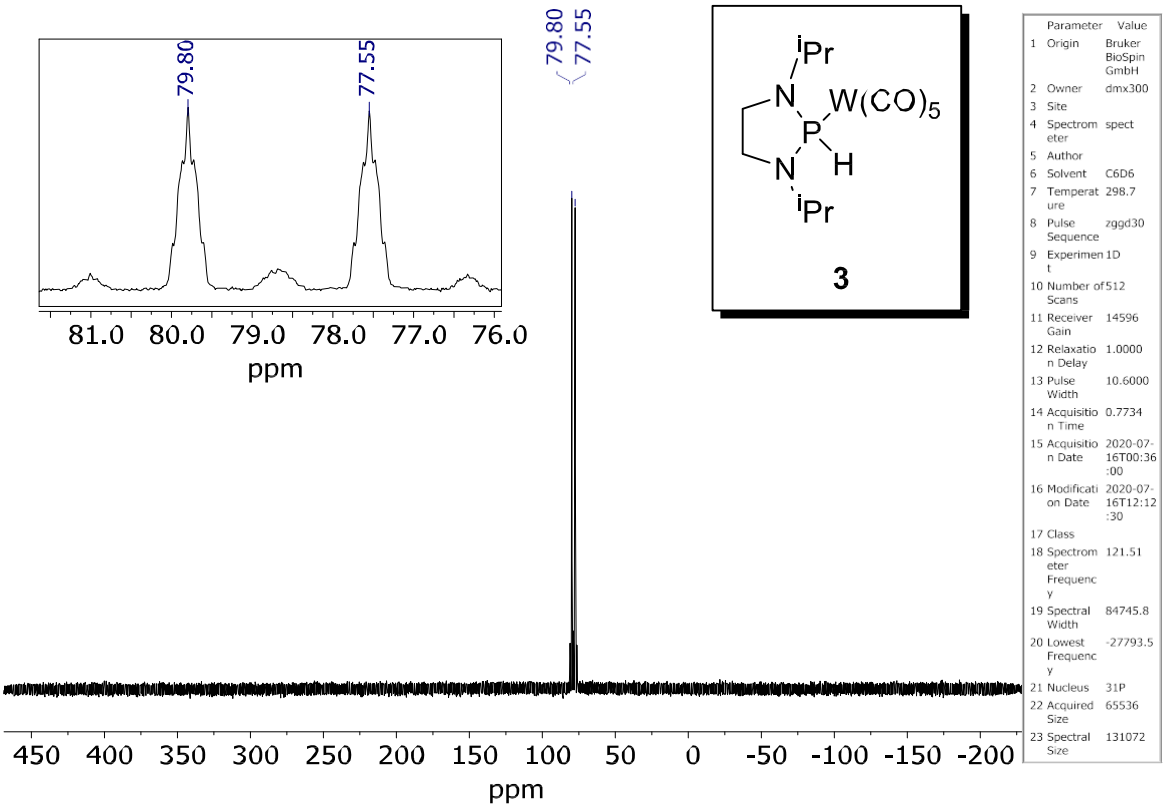

*Figure 6 ^{31}P-NMR spectrum of **3** in C_6D_6.*

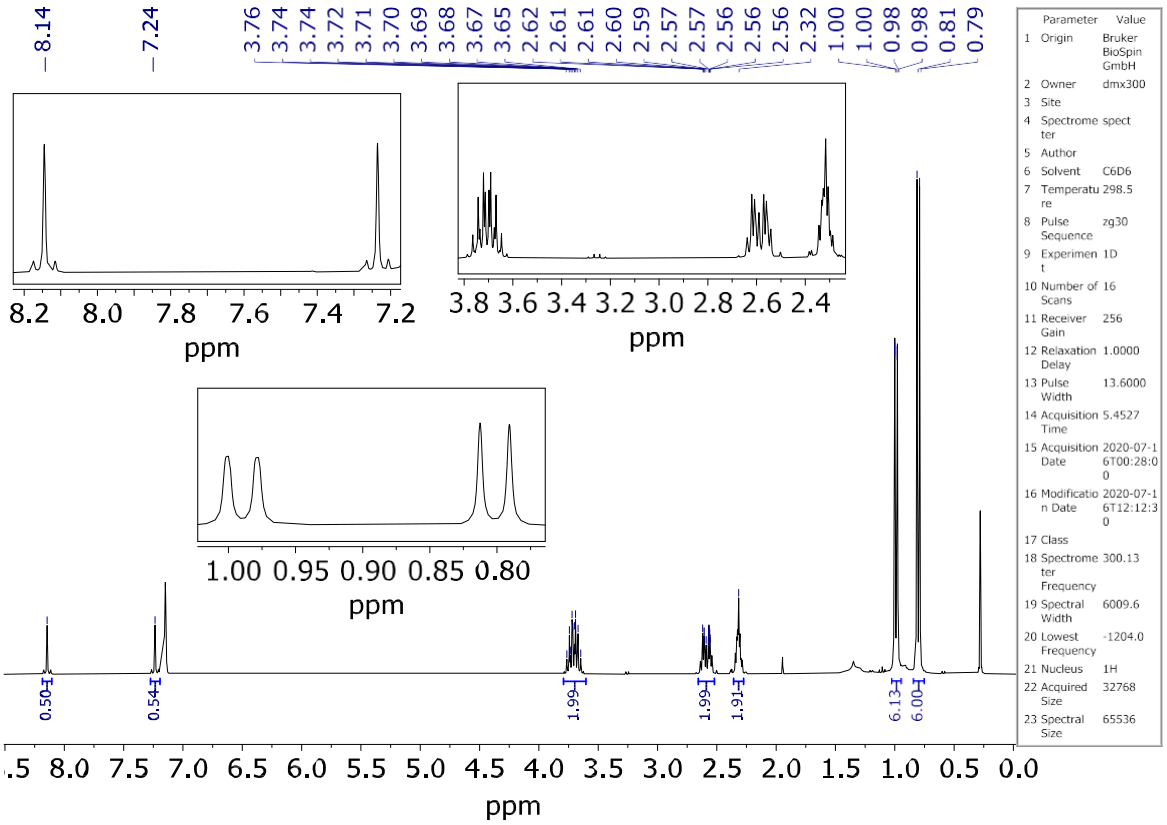

*Figure 7 ^{1}H-NMR spectrum of **3** in C_6D_6*

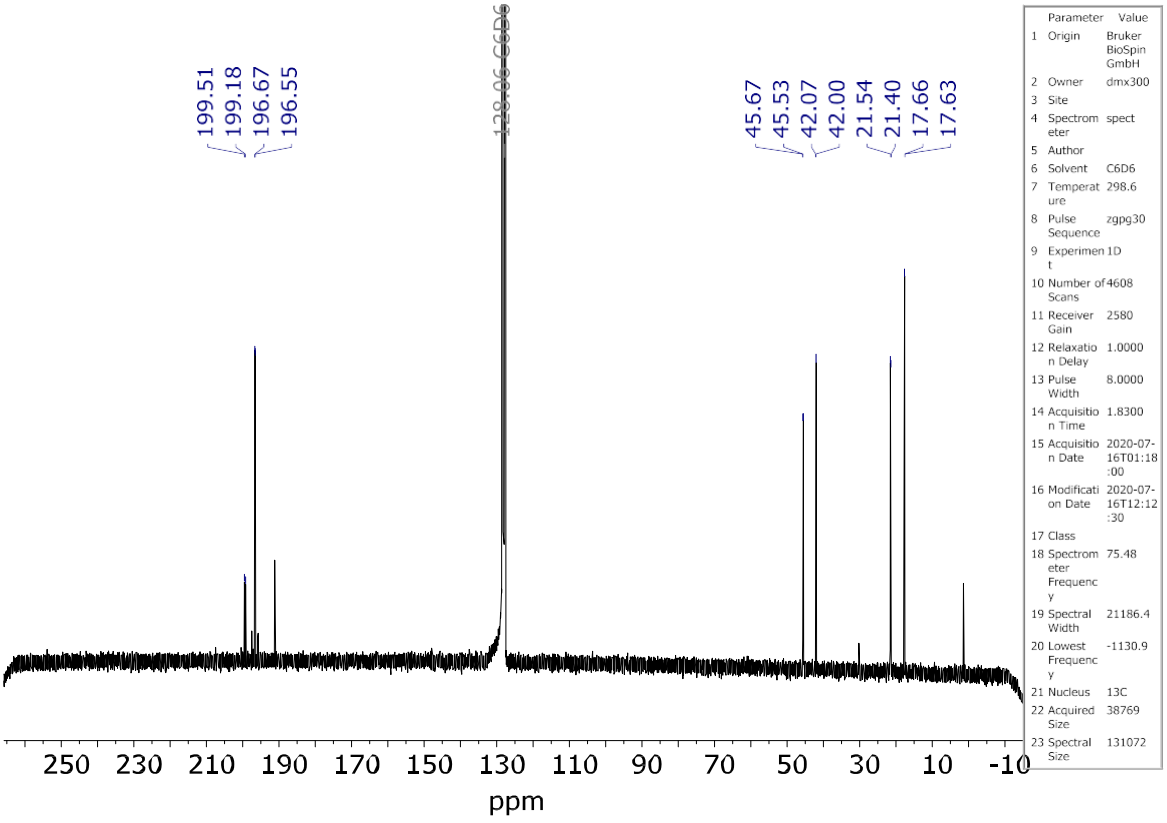

*Figure 8 $^{13}C\{^{1}H\}$-NMR spectrum of **3** in C_6D_6*

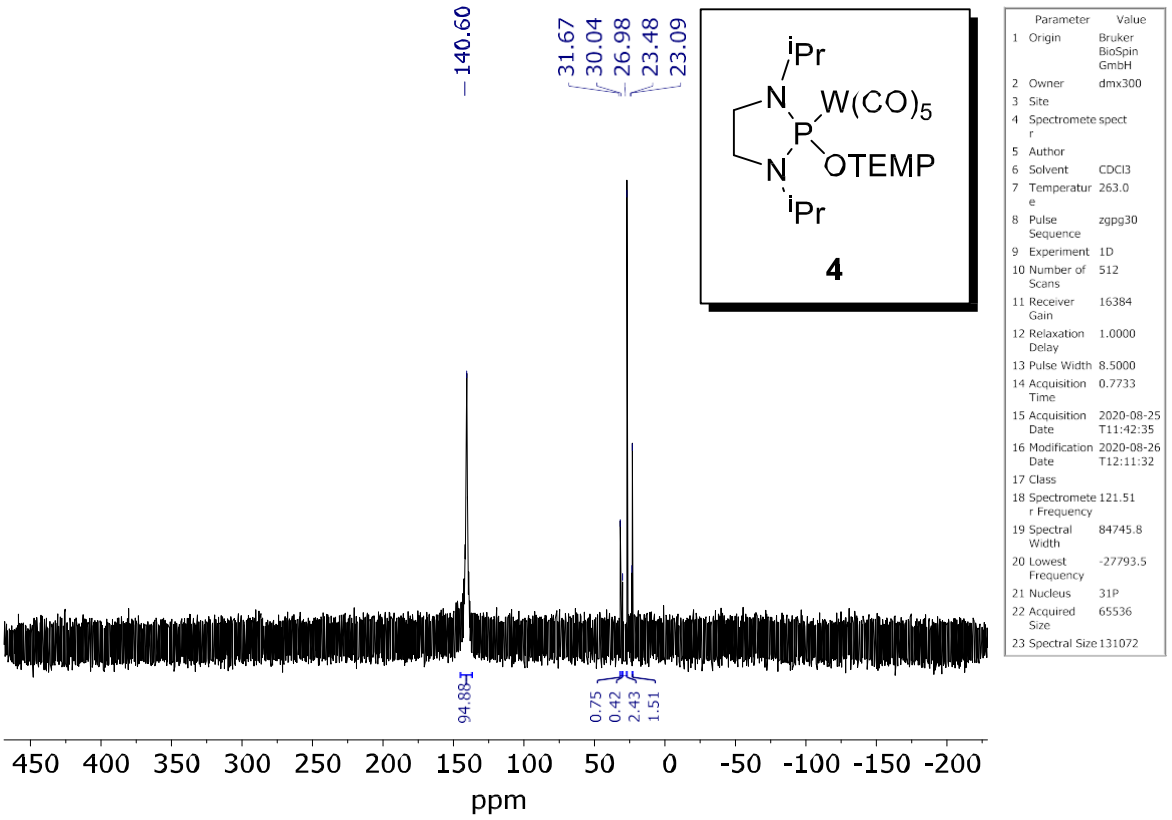

*Figure 9 $^{31}P\{^{1}H\}$-NMR spectrum of **4** in $CDCl_3$ at -10 °C.*

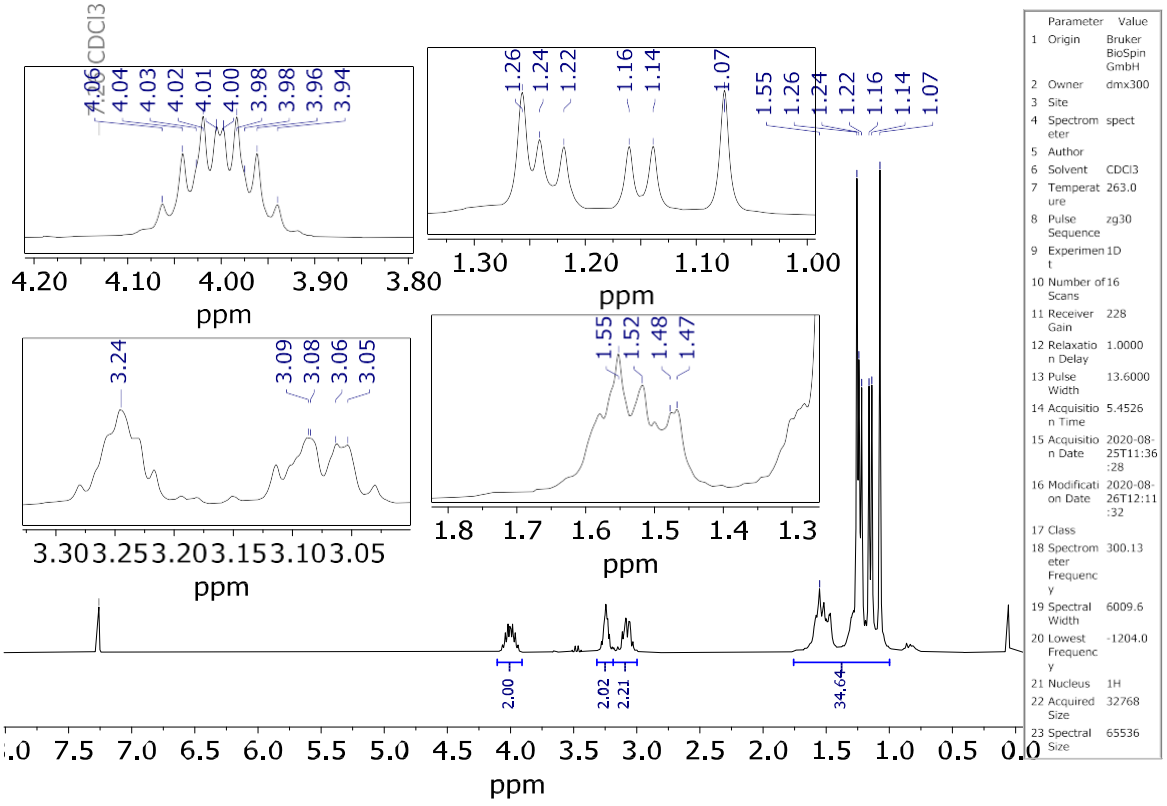

*Figure 10 ^{1}H-NMR spectrum of **4** in $CDCl_3$ at - 10 °C.*

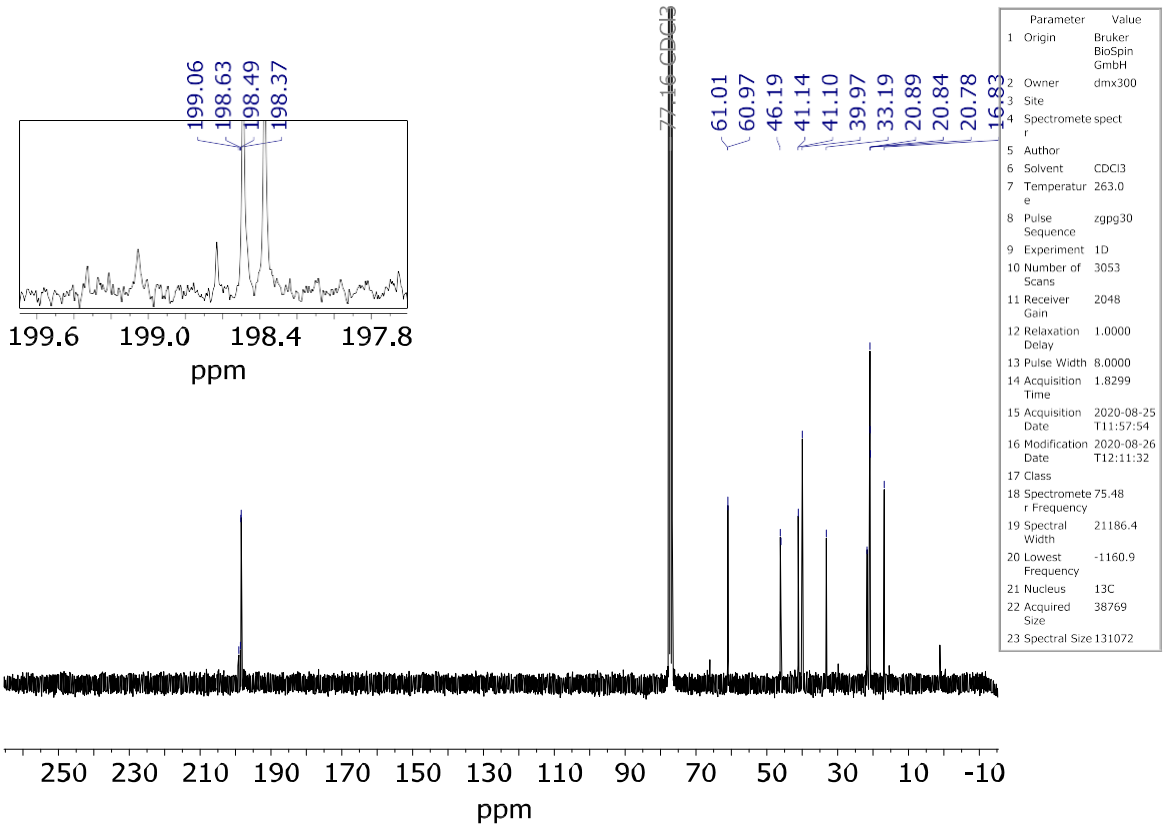

*Figure 11 $^{13}C\{^1H\}$-NMR spectrum of **4** in $CDCl_3$ at - 10 °C.*

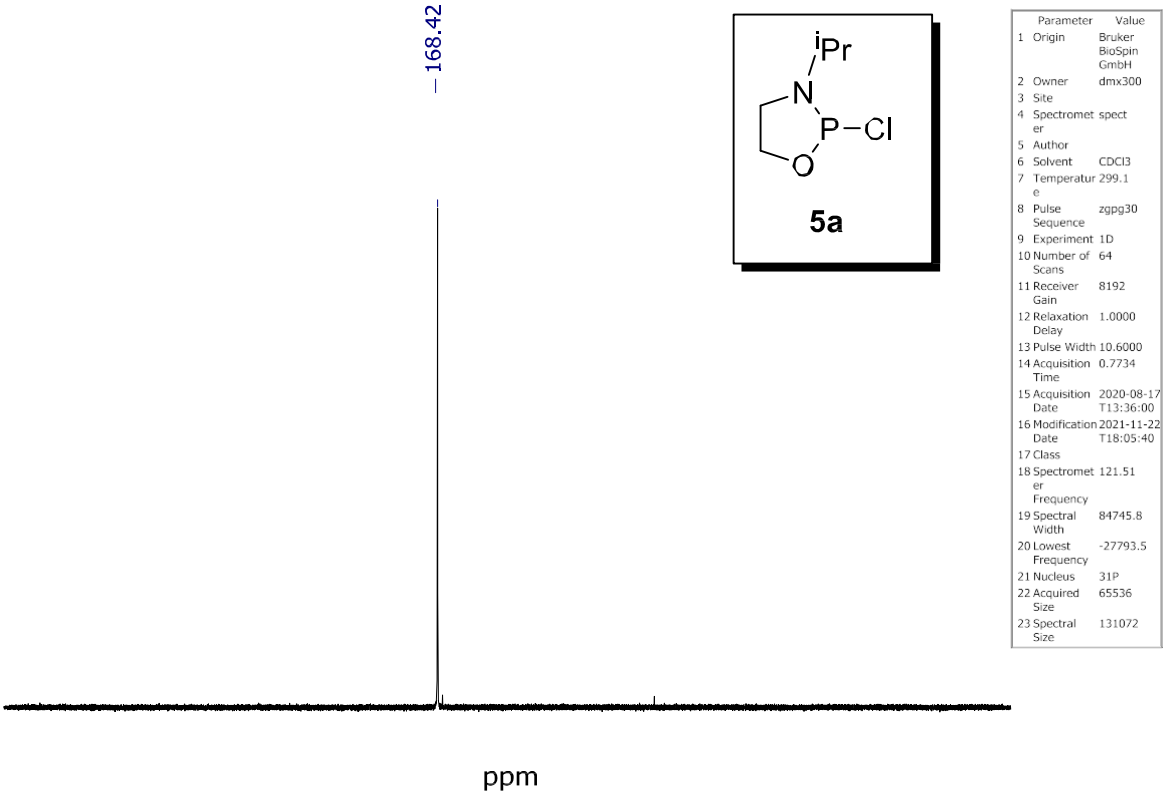

*Figure 12 $^{31}P\{^1H\}$-NMR spectrum of **5a** in $CDCl_3$.*

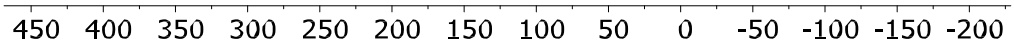

*Figure 12 $^{31}P\{^{1}H\}$-NMR spectrum of **5a** in $CDCl_3$.*

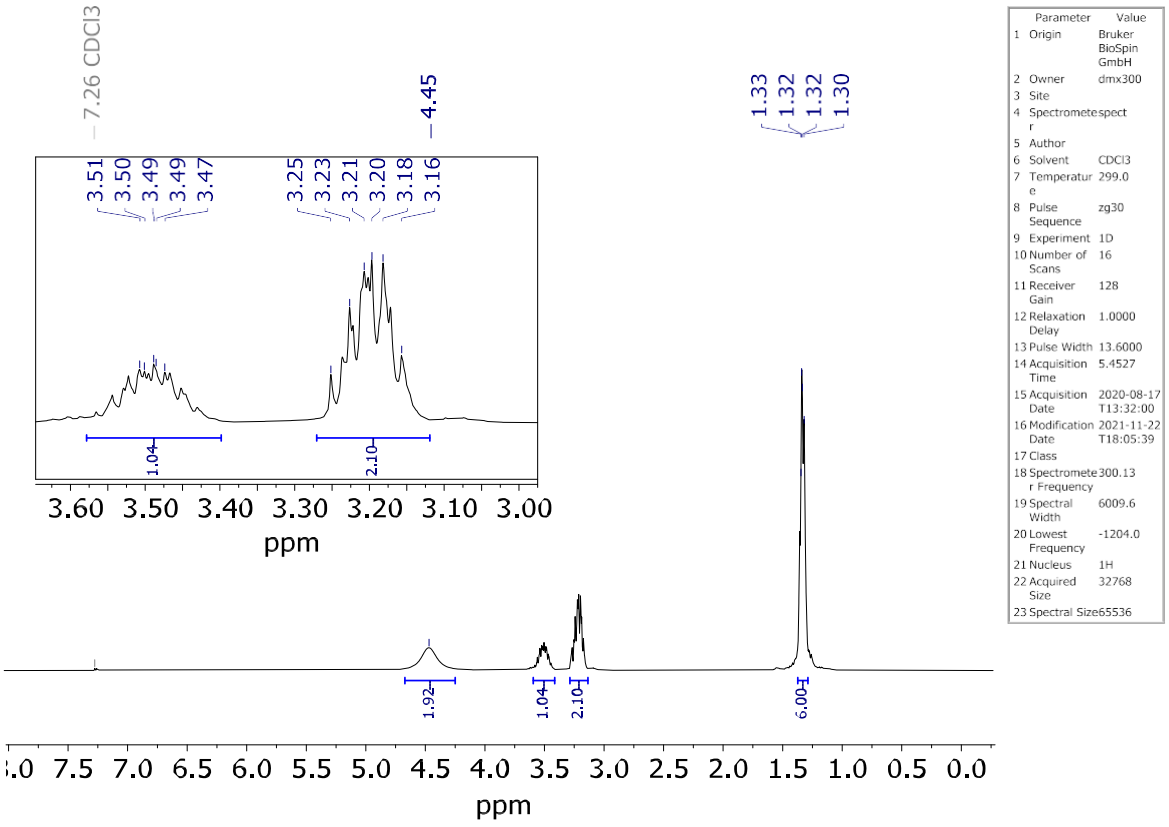

*Figure 13 ^{1}H-NMR spectrum of **5a** in $CDCl_3$.*

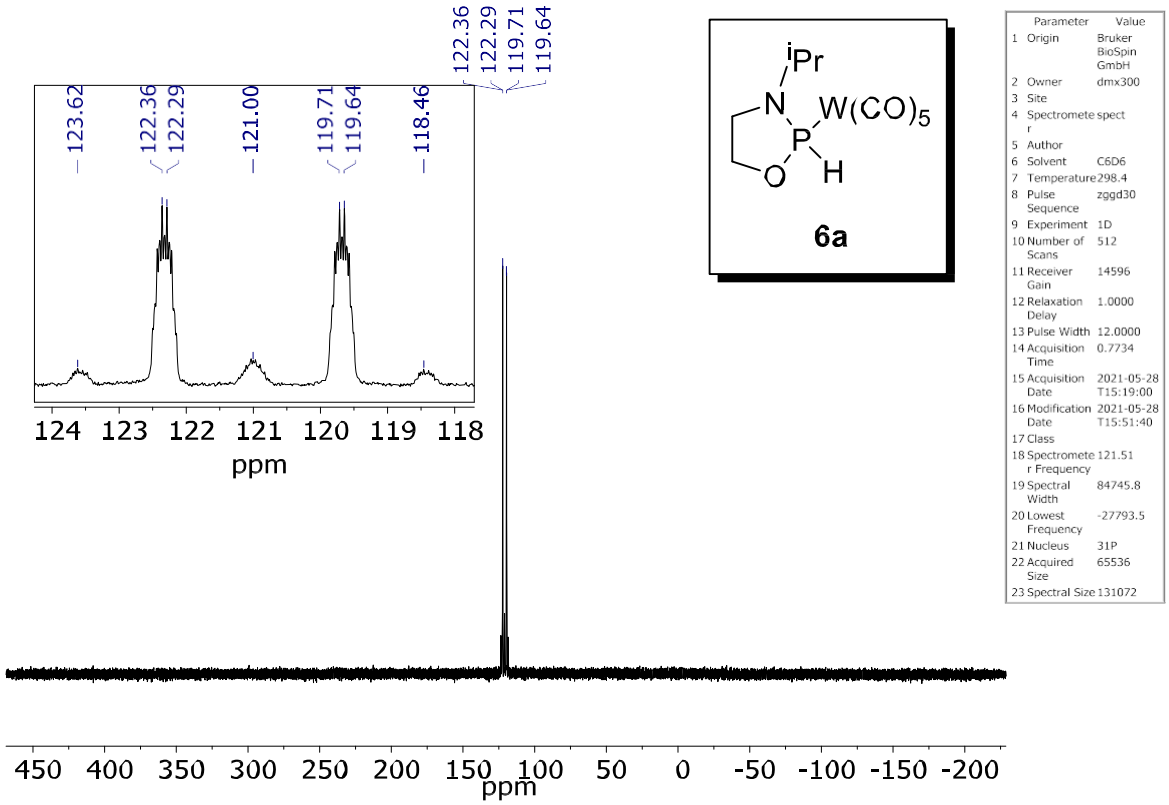

*Figure 14 ^{31}P-NMR spectrum of **6a** in C_6D_6.*

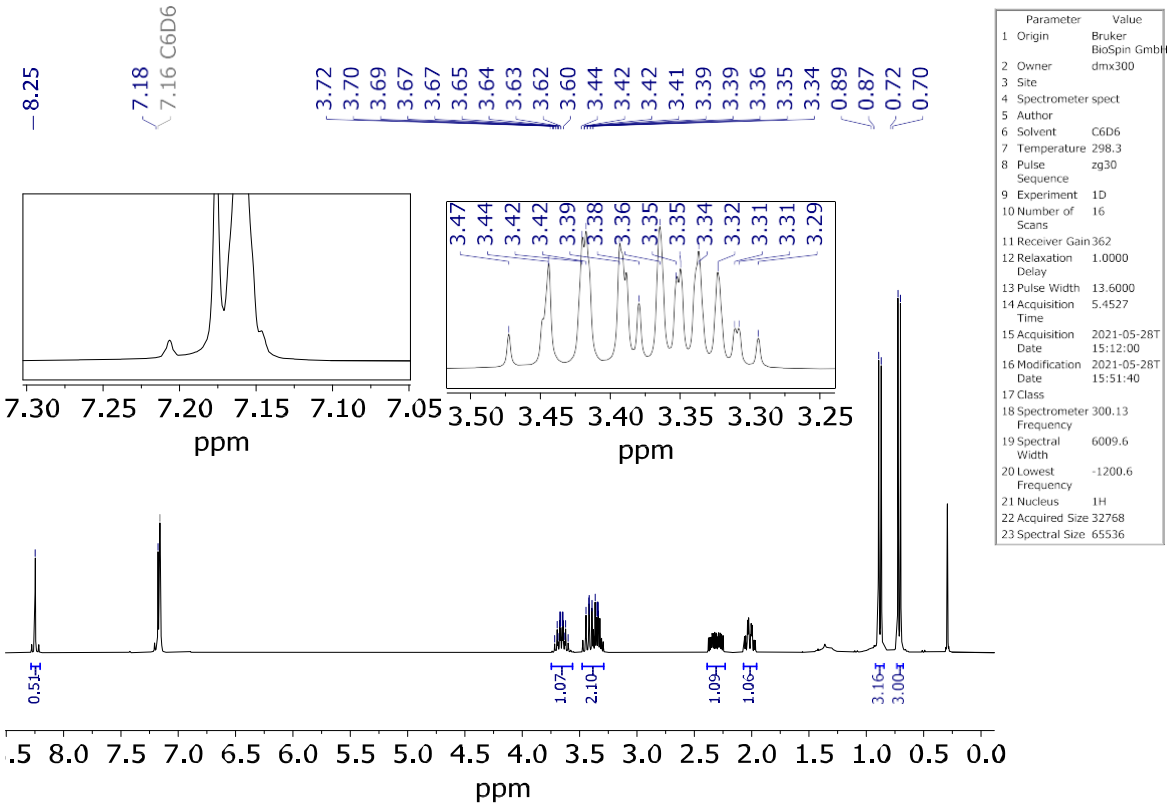

*Figure 15 ^{1}H-NMR spectrum of **6a** in C_6D_6.*

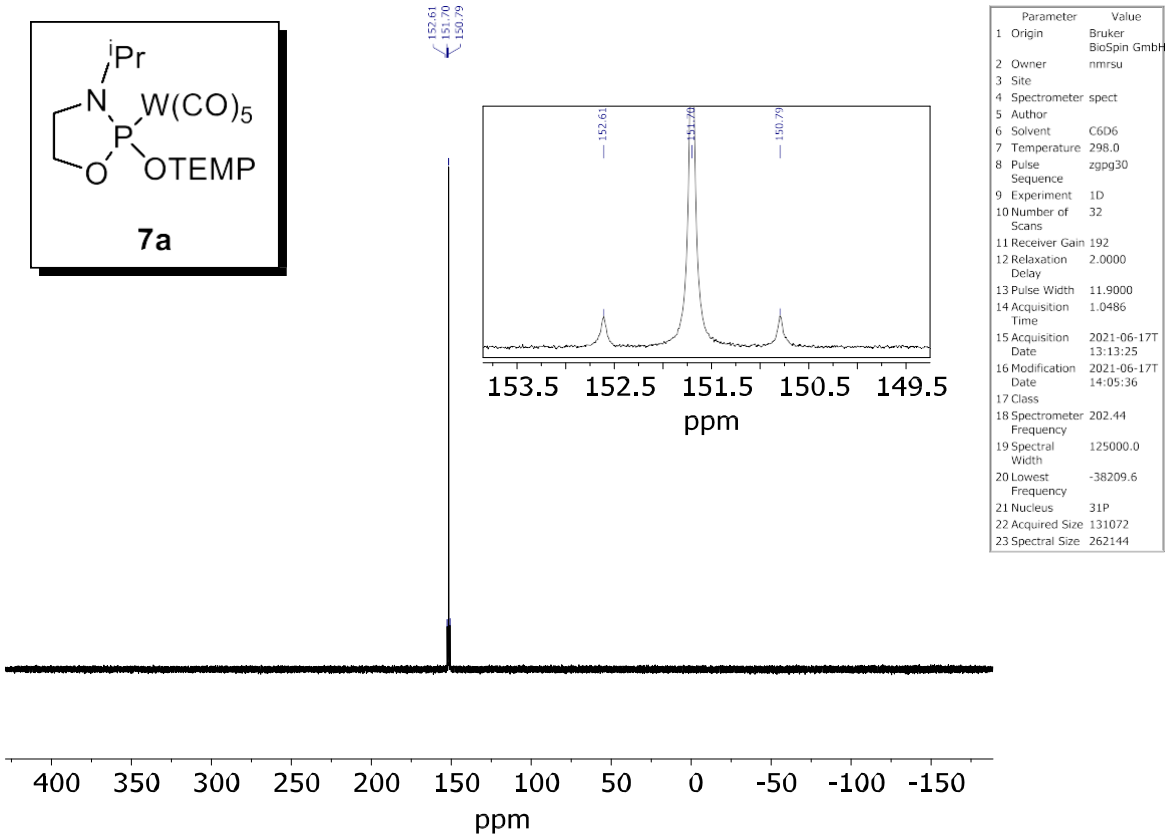

*Figure 16 ^{31}P{^{1}H}-NMR spectrum of **7a** in C_6D_6.*

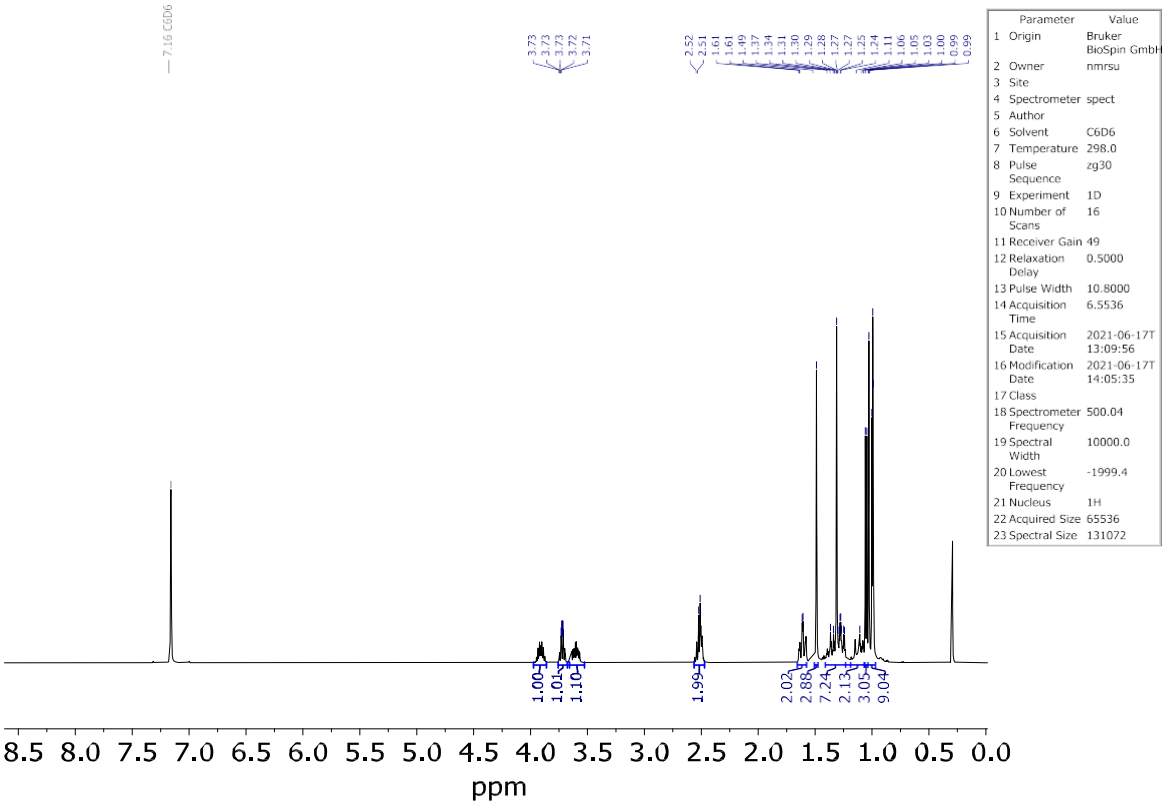

*Figure 17 ^{1}H-NMR spectrum of **7a** in C_6D_6.*

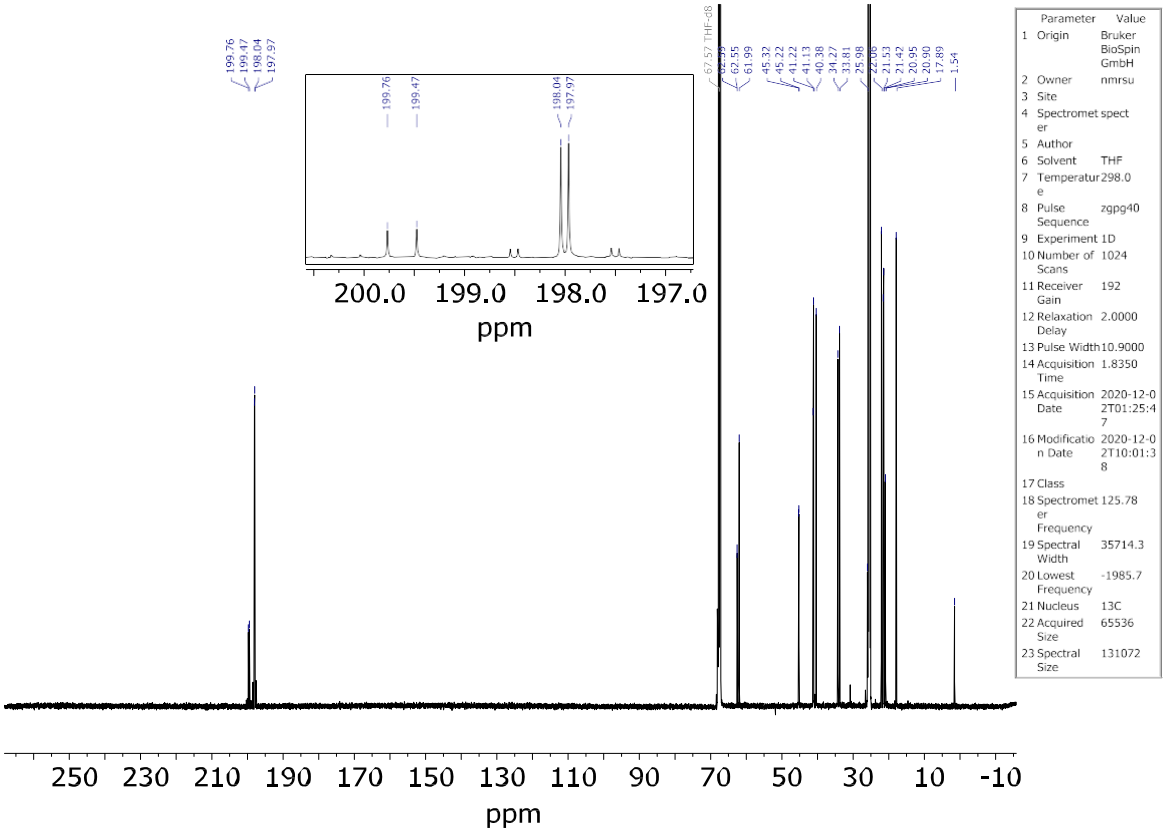

*Figure 18 $^{13}C\{^{1}H\}$-NMR spectrum of **7a** in THF-d8.*

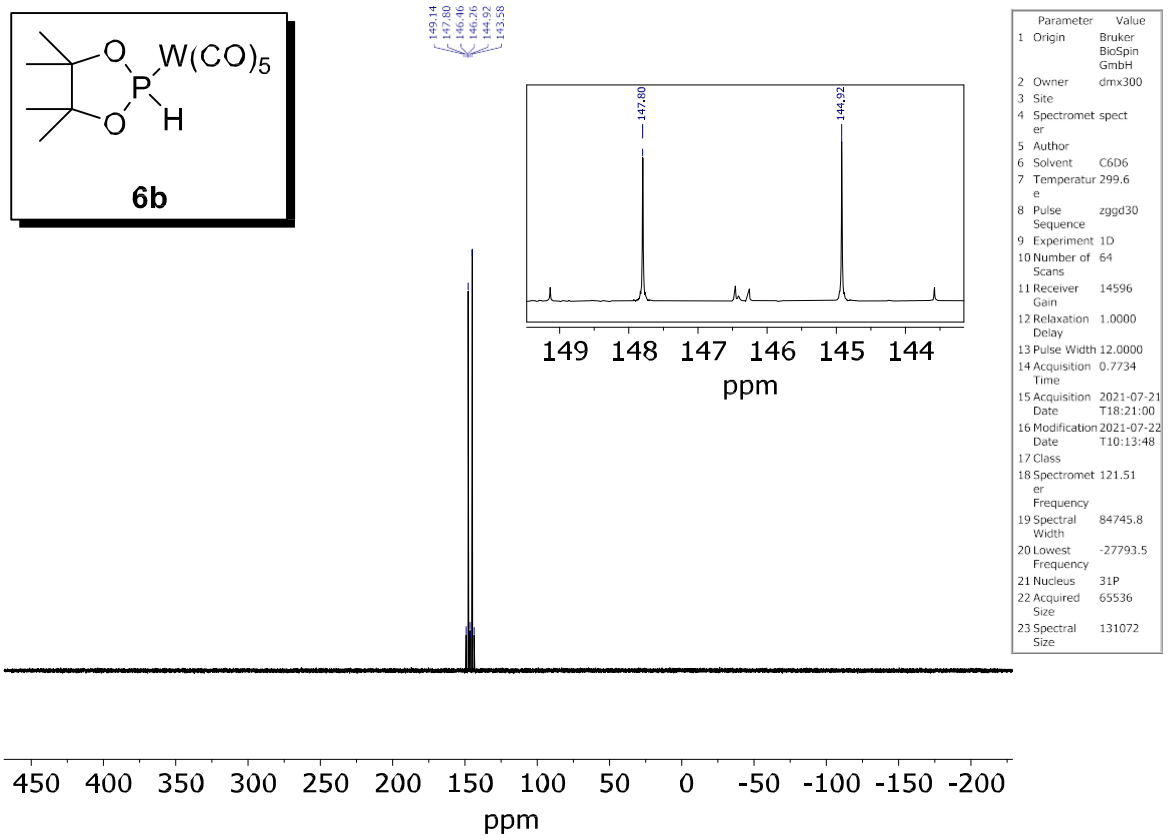

*Figure 19 ^{31}P-NMR spectrum of **6b** in C_6D_6.*

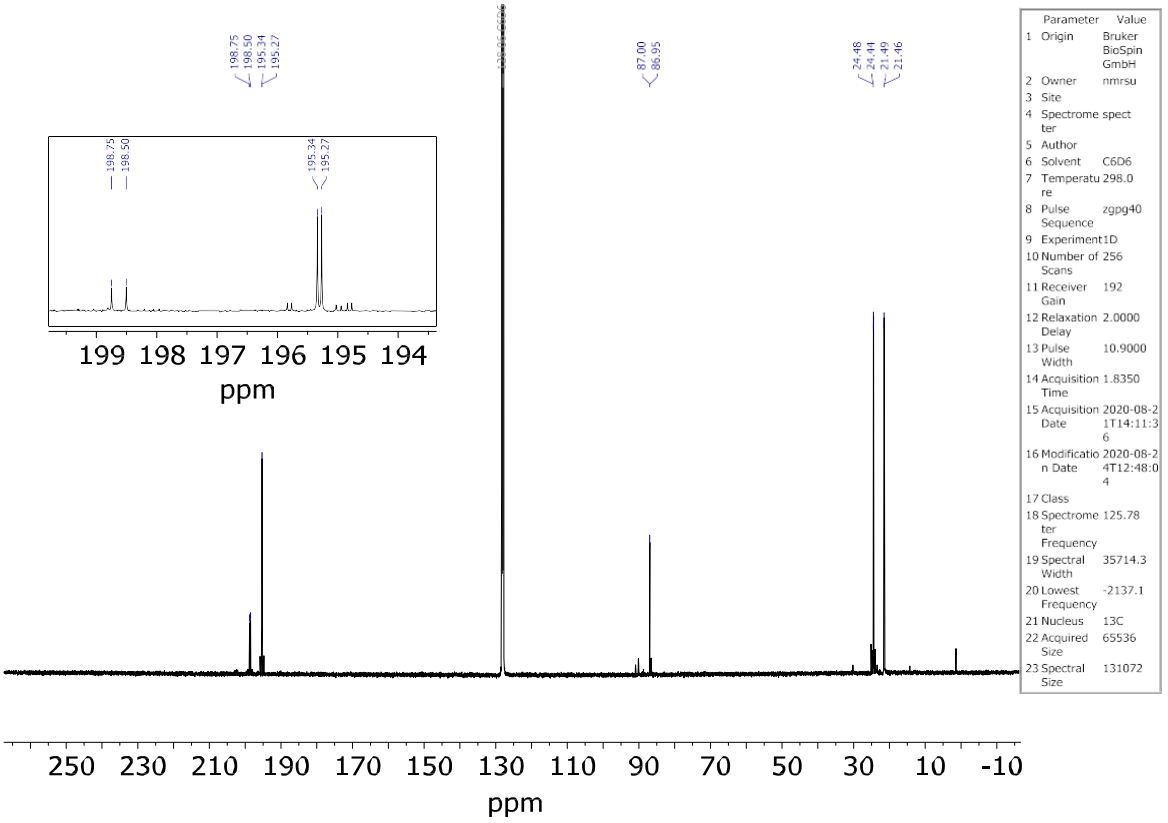

*Figure 20 $^{13}C\{^1H\}$-NMR spectrum of **6b** in C_6D_6.*

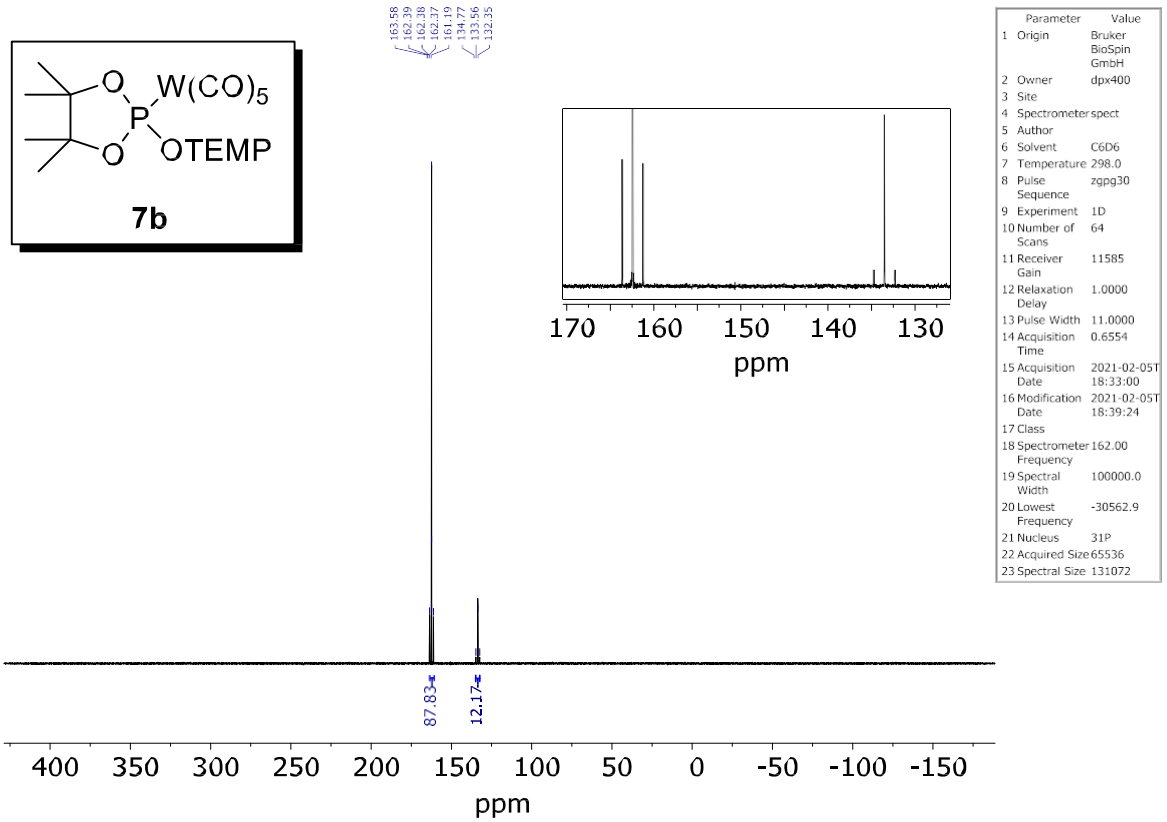

*Figure 21 $^{31}P\{^{1}H\}$-NMR spectrum of **7b** with the impurity at 133.6 ppm in C_6D_6 after purfication attempt via column chromatography.*

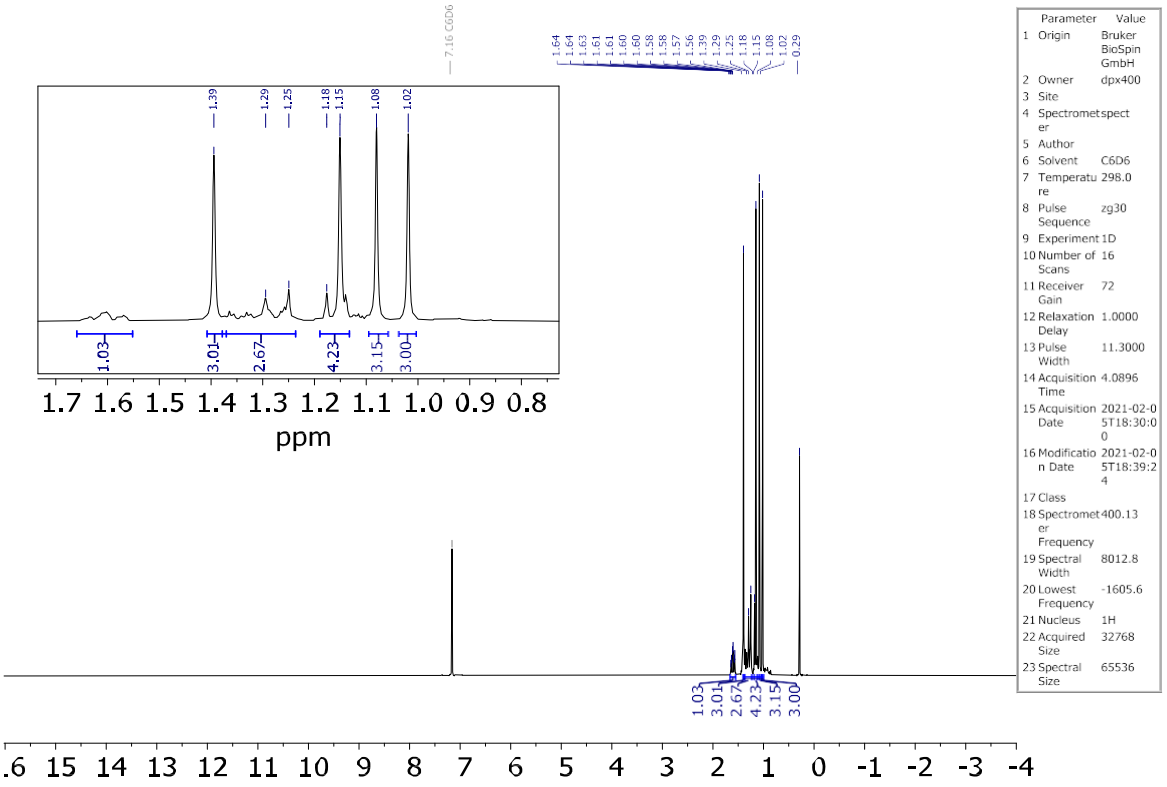

*Figure 22 ^{1}H-NMR spectrum of **7b** with impurity in C_6D_6 after purification attempt via column chromatography.*

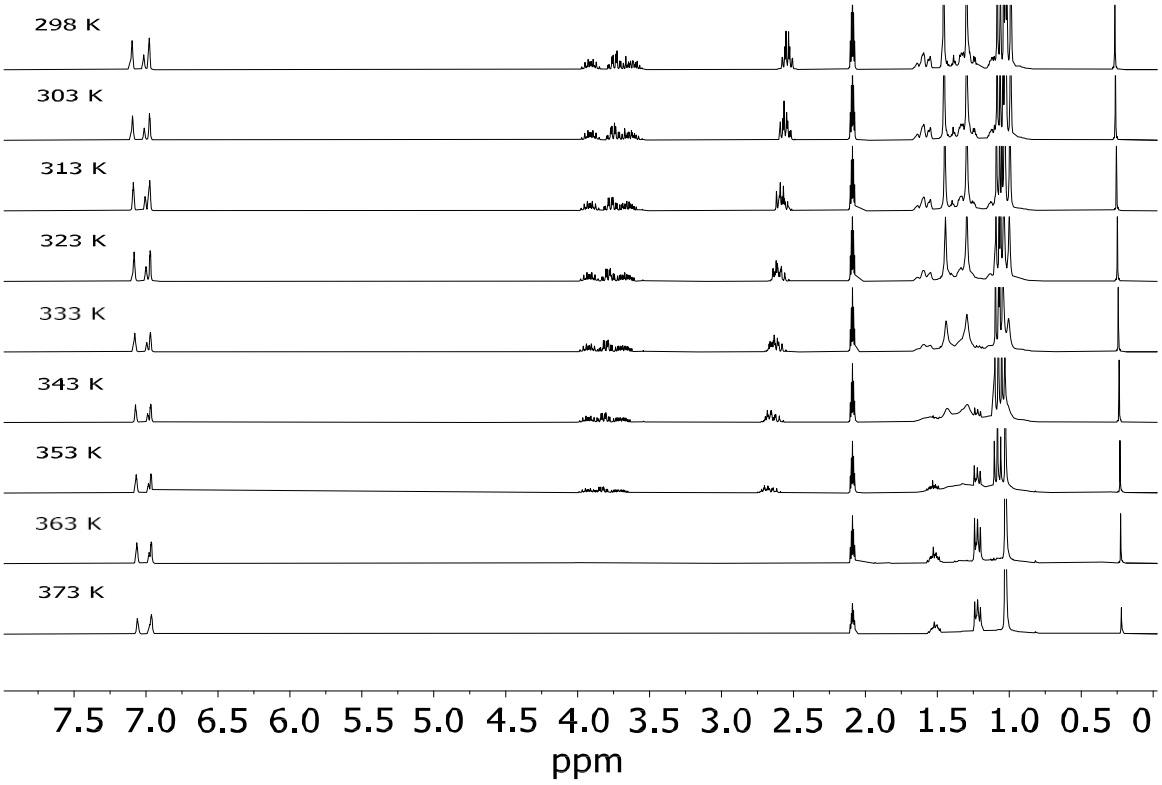

*Figure 23 VT- ^{1}H-NMR spectra of **7a** in toluene-d8 in 10 °C steps from r.t. to 100 °C.*

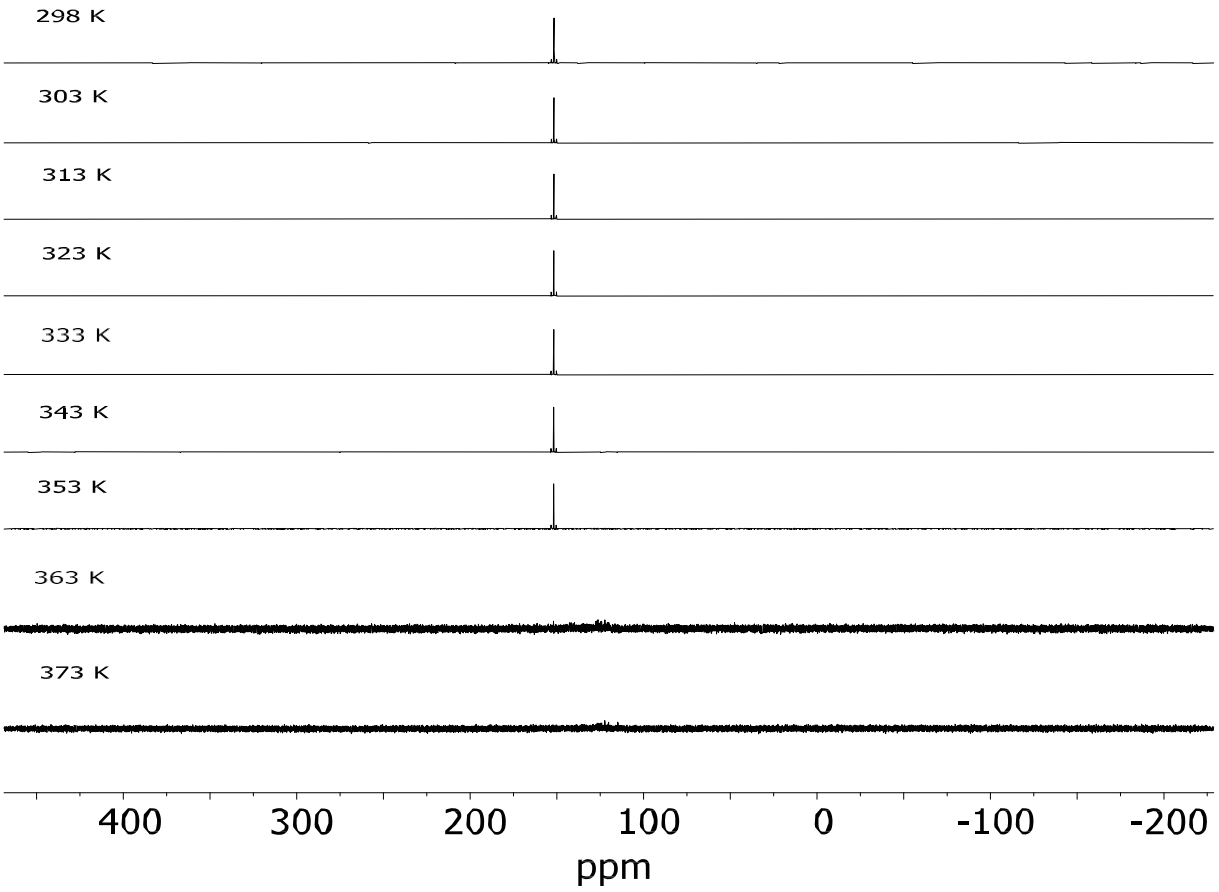

*Figure 24 VT-^{31}P{ ^{1}H}-NMR spectra of **7a** in toluene-d8 in 10 °C steps from r.t. to 100 °C.*

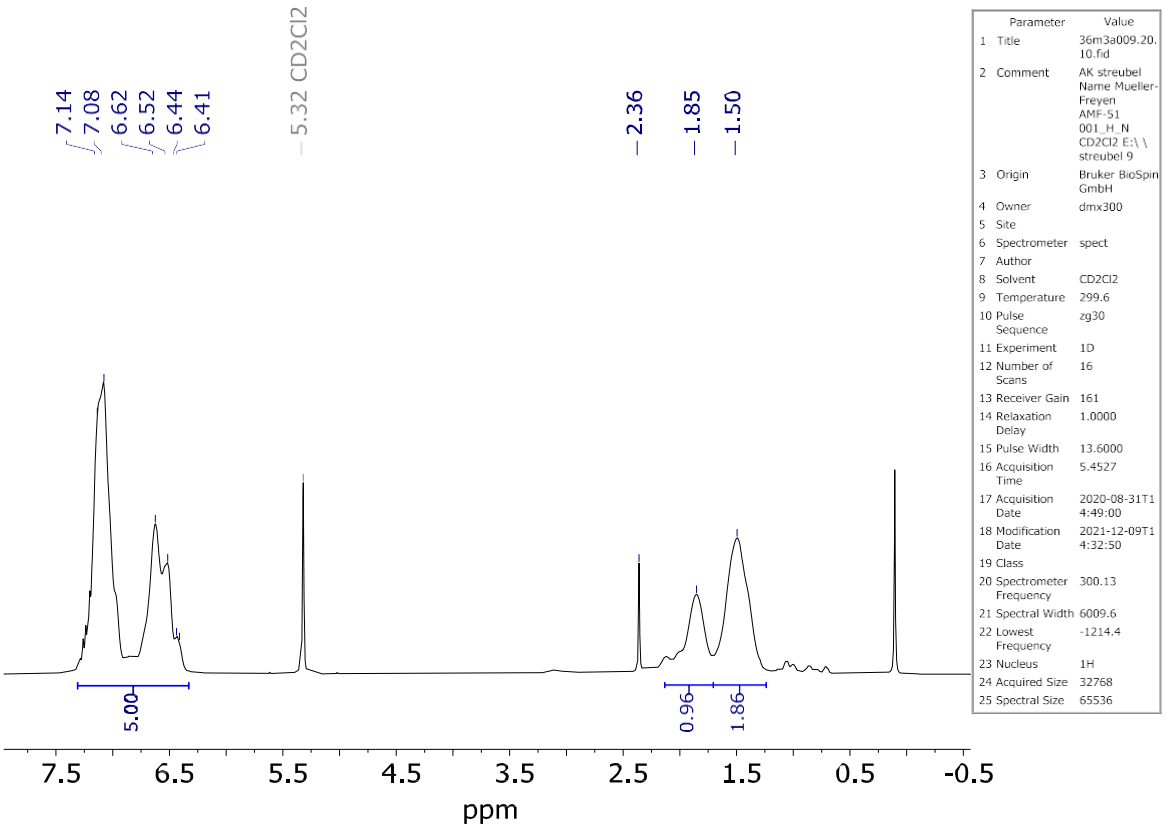

*Figure 25 ^{1}H-NMR spectrum of polystyrene in CD_2Cl_2 for which **4'** was used (in the form of **4**) as an initiator.*

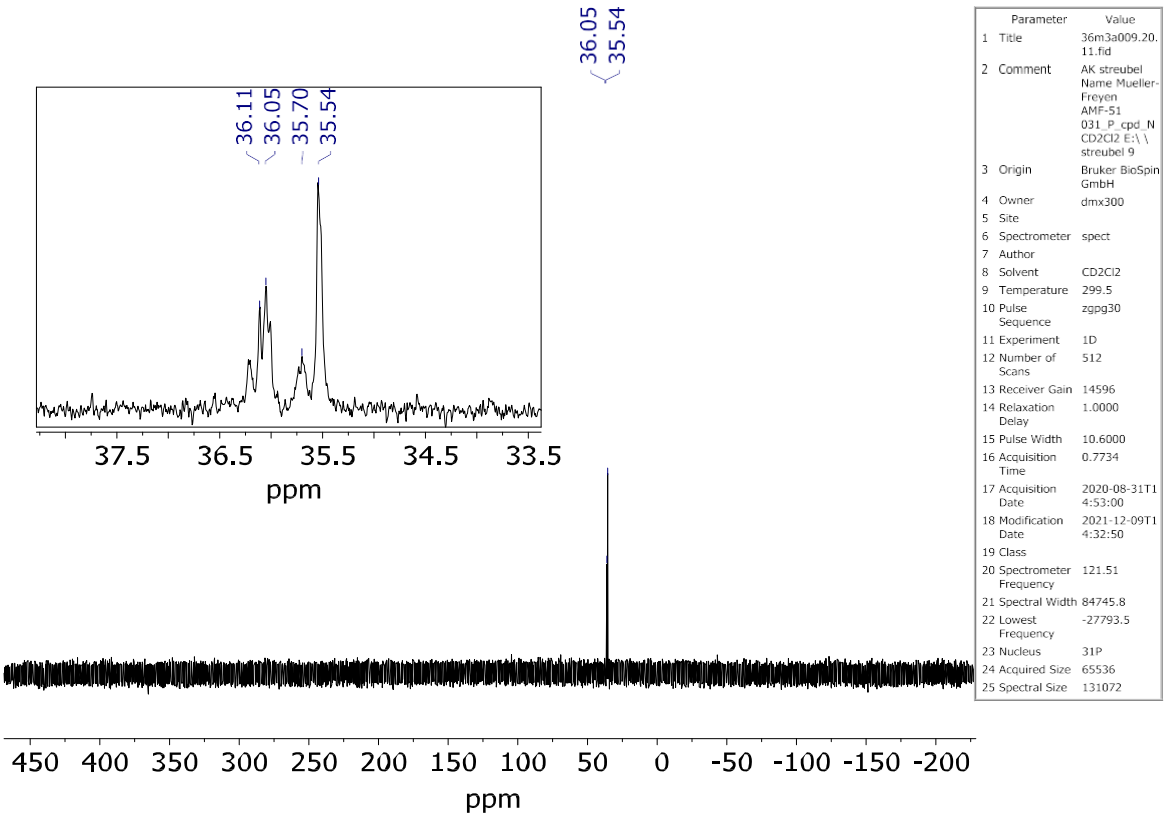

*Figure 26 ^{31}P{^{1}H}-NMR spectrum of polystyrene in CD_2Cl_2 for which **4'** was used (in the form of **4**) as an initiator.*

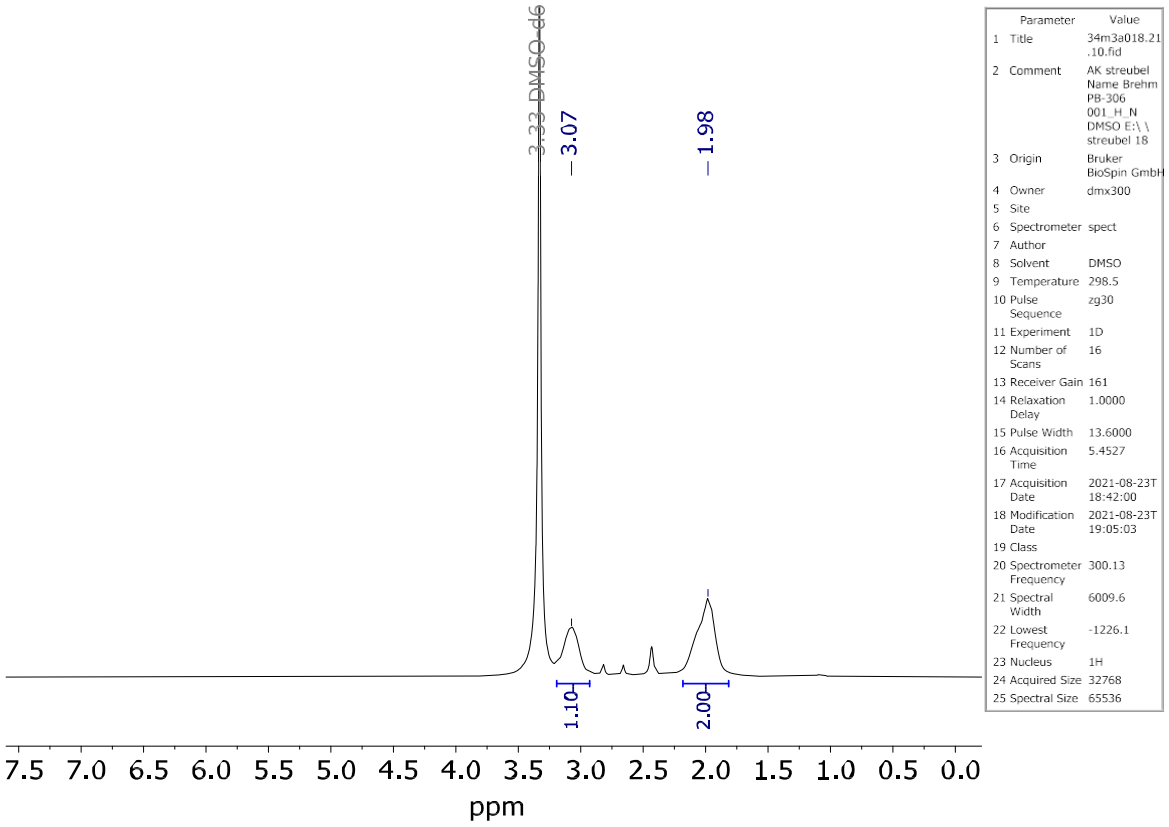

*Figure 27 ^{1}H-NMR spectrum of polyacrylonitrile in DMSO-d6 for which **4'** was used (in the form of **4**) as an initiator.*

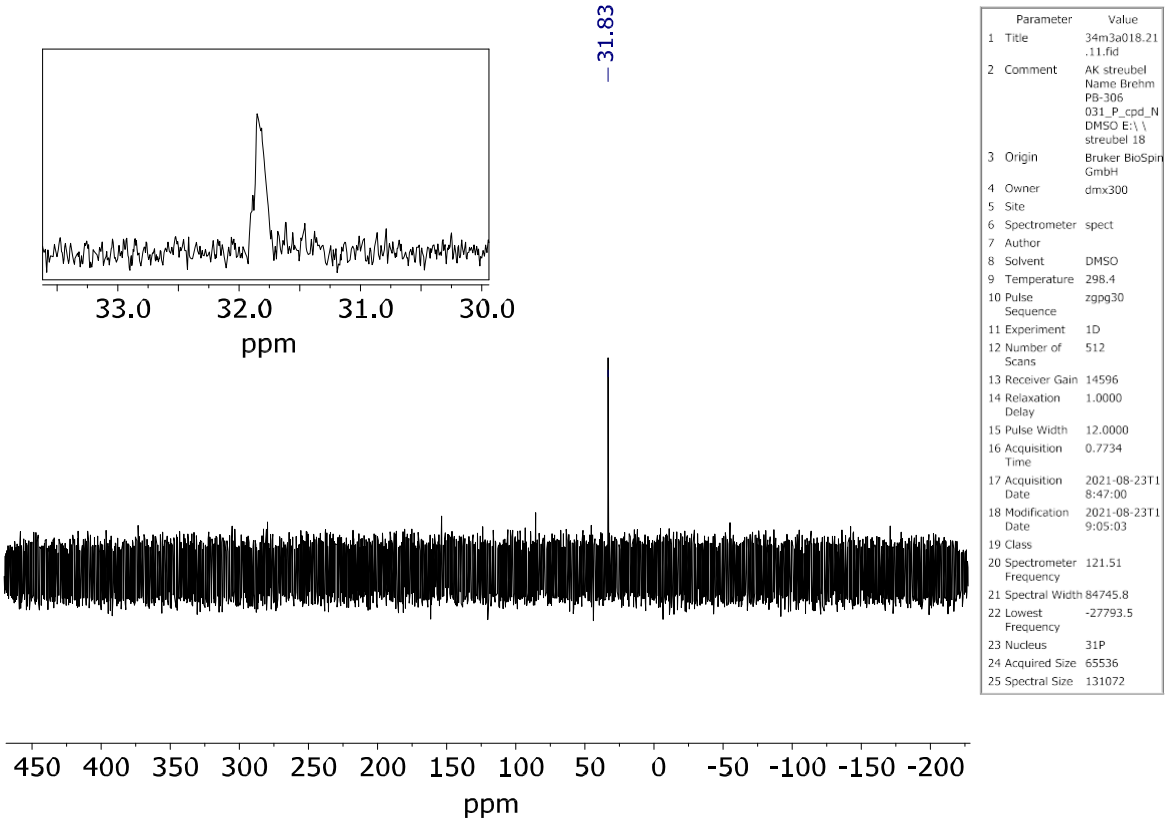

*Figure 28 ^{31}P{^{1}H}-NMR spectrum of polystyrene in DMSO-d6 for which **4'** was used (in the form of **4**) as an initiator.*

MALDI-MS:

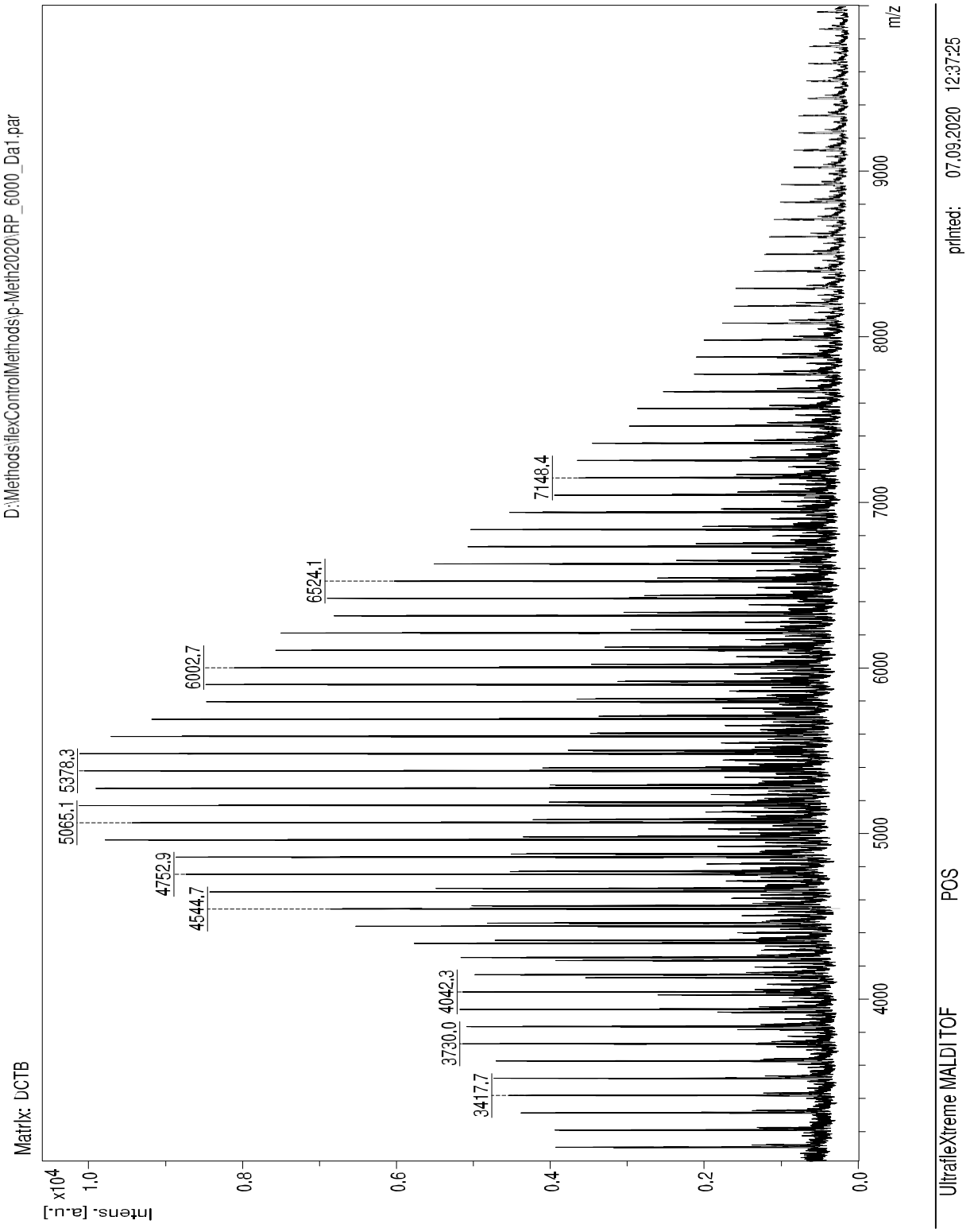

*Figure 29 MALDI-MS of polystyrene obtained from polymerisation with **4**.*

5800

5300

4800

4300

3800

3300

2800

*Figure 30 MALDI-MS of polyacrylonitrile obtained from polymerisation with **4**.*

Crystallograpic Data:

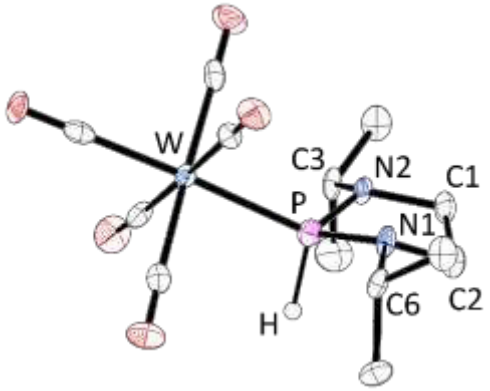

*Figure 31 Crystal Structure for **3**: Suitable single crystals of **3** were obtained from a concentrated diethylether solution at 4 °C. All hydrogens, except the* P *bound, are omitted for clarity. Ellipsoids are set at 50% probability level.*

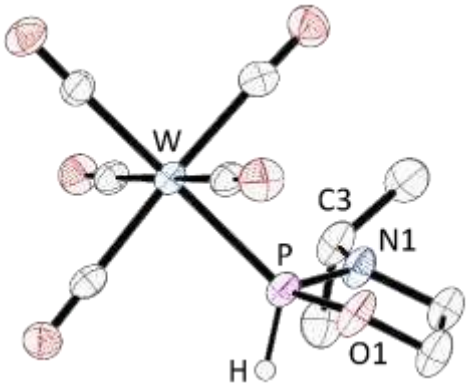

*Figure 32 Crystal Structure for **6a**: Suitable single crystals of **6a** were obtained from a concentrated n-pentane solution at 4 °C. All hydrogens, except the* P *bound, are omitted for clarity. Ellipsoids are set at 50% probability level.*

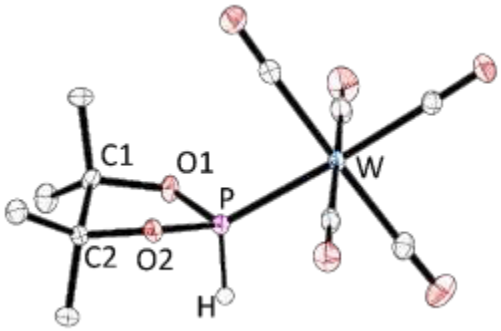

*Figure 33 Crystal Structure for **6a:** Suitable single crystals of **6a** were obtained by slow evaporation of an n-pentane solution at r.t. All hydrogens, except the* P *bound, are omitted for clarity. Ellipsoids are set at 50% probability level.*

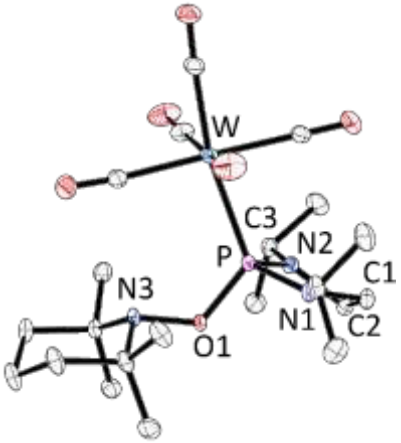

*Figure 34 Crystal Structure for **4**: Suitable single crystals of **4** were obtained from a concentrated diethylether solution at -30 °C. All hydrogens are omitted for clarity. Ellipsoids are set at 50% probability level.*

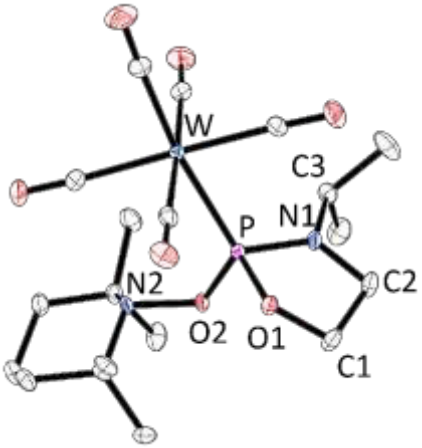

*Figure 35 Crystal Structure for **7a**: Suitable single crystals of **7a** were obtained from a concentrated n-pentane solution at -30 °C. All hydrogens are omitted for clarity. Ellipsoids are set at 50% probability level.*

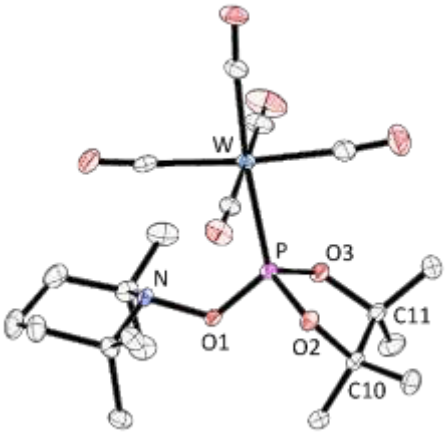

*Figure 36 Crystal Structure for **7b**: Suitable single crystals of **7b** were obtained from a concentrated diethylether solution at 4 °C. All hydrogens are omitted for clarity. Ellipsoids are set at 50% probability level.*

Crystal structures were generated with *Olex2*[4]

	3	**6a**	**6b**
Empirical formula	$C_{13}H_{19}N_2O_5PW$	$C_{10}H_{12}NO_6PW$	$C_{11}H_{13}O_7PW$
Formula weight	498.12 g mol^{-1}	457.03 g mol^{-1}	472.03 g mol^{-1}
Temperature	123.0 K	123.0 K	123.0 K
Wavelength	0.71973 Å	0.71073 Å	0.71073 Å
Crystal system, space group	orthorhombic, $P2_12_12_1$	monoclinic, $P2_1/n$	triclinic, P-1
Unit cell dimensions	a = 8.3463(4) Å b = 9.9319(5) Å c = 21.1509(13) Å α = 90 ° β = 90 ° γ = 90 °	a = 6.169(11) Å b = 18.469(4) Å c = 12.033(2) Å α = 90 ° β = 102.033(2) ° γ = 90 °	a = 7.0371(3) Å b = 10.1674(4) Å c = 10.6647(4) Å α = 99.282(3) ° β = 101.783(3) ° γ = 91.016(3) °
Volume	1753.30(16) Å^3	1414.8(4) Å^3	736.17(5) Å^3
Z, calculated density	4, 1.887 g cm^{-3}	4, 2.146 g cm^{-3}	2, 2.129 g cm^{-3}
Absorption coefficient	6.701 mm^{-1}	8.297 mm^{-1}	7.980 mm^{-1}
F(*000*)	960	864	448
Crystal size	0.12 x 0.1 x 0.06 mm^3	0.15 x 0.12 x 0.08 mm^3	0.14 x 0.12 x 0.12 mm^3
2θ-range for data collection	5.246 – 53.994 °	5.61 – 55.994 °	5.922 – 55.988 °
Limiting indices	-10 ≤ h ≤ 10 -12 ≤ k ≤ 12 -21 ≤ l ≤ 26	-8 ≤ h ≤ 5 -24 ≤ k ≤ 22 -15 ≤ l ≤ 15	-9 ≤ h ≤ 8 -13 ≤ k ≤ 13 -14 ≤ l ≤ 14
Reflections collected / unique	9246 / 3768 [R_{int} = 0.0402]	7225 / 3401 [R_{int} = 0.0378]	25605 / 3563 [R_{int} = 0.0583]
Completeness to θ_{max}	99.7 %	99.3 %	99.9 %
Absorption correction	Integration	Integration	Integration
Max. / min. transmission	0.5198/ 0.3326	0.0396/ 0.0104	0.3962/ 0.1271
Data/ restraints/ parameters	3768/0/207	3401/0/177	3563/0/190
Goodness-of-fit on F^2	0.641	0.876	1.167
Final R indices [I>σ(I)]	R_1 = 0.0230, wR_2 = 0.0314	R_1 = 0.0268, wR_2 = 0.0542	R_1 = 0.0147, wR_2 = 0.0347
R indices (all data)	R_1 = 0.0347, wR_2 = 0.0327	R_1 = 0.0433, wR_2 = 0.0566	R_1 = 0.0156, wR_2 = 0.0350
Largest diff. peak /hole	0.73/ -0.67 e Å^{-3}	1.32/ -1.63 e Å^{-3}	1.47/ -0.80 e Å^{-3}
CCDC number	2132109	2132111	2132112

	4	**7a**	**7b**
Empirical formula	$C_{22}H_{36}N_3O_6PW$	$C_{19}H_{29}N_2O_7PW$	$C_{20}H_{30}NO_8PW$
Formula weight	653.36 g mol^{-1}	612.26 g mol^{-1}	627.27 g mol^{-1}
Temperature	123.0 K	100.0 K	123.0 K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/n$	triclinic, P-1	monoclinic, $P2_1/n$
Unit cell dimensions	a = 12.1269(3) Å b = 10.9786(2) Å c = 20.1204(5) Å α = 90 ° β = 102.575(2) ° γ = 90 °	a = 8.2932(3) Å b = 10.1104(3) Å c = 15.3182(5) Å α = 73.319(2) ° β = 74.659(3) ° γ = 71.740(3) °	a = 11.1040(2) Å b = 14.0762(2) Å c = 15.5766(3) Å α = 90 ° β = 93.904(2) ° γ = 90 °
Volume	2614.50(11) $Å^3$	1146.66(7) $Å^3$	2429.01(7) $Å^3$
Z, calculated density	4, 1.660 g cm^{-3}	2, 1.773 g cm^{-3}	4, 1.715 g cm^{-3}
Absorption coefficient	4.519 mm^{-1}	5.148 mm^{-1}	4.864 mm^{-1}
F(*000*)	1304	604	1240
Crystal size	0.25 x 0.15 x 0.1 mm^3	0.3 x 0.15 x 0.12 mm^3	0.25 x 0.21 x 0.18 mm^3
2θ-range for data collection	5.566 – 55.994 °	5.482 – 55.996 °	5.24 – 55.988 °
Limiting indices	-14 ≤ h ≤ 16 -14 ≤ k ≤ 14 -26 ≤ 1 ≤ 26	-10 ≤ h ≤ 10 -13 ≤ k ≤ 13 -20 ≤ 1 ≤ 20	-14 ≤ h ≤ 13 -18 ≤ k ≤ 18 -20 ≤ 1 ≤ 20
Reflections collected / unique	36816 / 6301 [R_{int} = 0.0622]	19824 / 5540 [R_{int} = 0.0643]	38270 / 5876 [R_{int} = 0.0583]
Completeness to θ_{max}	98.2 %	99.9 %	99.9 %
Absorption correction	Integration	Integration	Integration
Max. / min. transmission	0.6122/ 0.3373	0.6833/ 0.3164	0.8542/ 0.4419
Data/ restraints/ parameters	6301/5/306	5540/0/277	5876/0/288
Goodness-of-fit on F^2	0.982	1.018	1.043
Final R indices [I>σ(I)]	R_1 = 0.0185, wR_2 = 0.0380	R_1 = 0.0175, wR_2 = 0.0418	R_1 = 0.0243, wR_2 = 0.0598
R indices (all data)	R_1 = 0.0240, wR_2 = 0.0391	R_1 = 0.0197, wR_2 = 0.0423	R_1 = 0.0280, wR_2 = 0.0611
Largest diff. peak /hole	0.79/ -1.00 e $Å^{-3}$	1.10/ -1.90 e $Å^{-3}$	3.05/ -1.74 e $Å^{-3}$
CCDC number	2132110	2132113	2132114

Computational Details:

All structures were set up with the open-source molecular builder and visualization tool *Avogadro 1.2.0.*[5]

Coordinates of the calculated structures are given in a separate ESI (.txt) file.

The quantum chemical DFT calculations have been performed using the ORCA[6] 4.0.1.2. For optimisation of the structures the TPSS-D3BJ/def2-TZVP + cPCM(THF) level of theory, which combines the TPSS[7] meta-GGA density functional with the BJ-damped DFT-D3[8,9] dispersion correction and the def2-TZVP[10] basis set, using the conductor-like polarisable continuum model (cPCM)[11] solvation model for THF as a solvent (ε = 7.25). The density-fitting RI-J (def2/J)[12] approach is used to accelerate the geometry optimization and numerical harmonic frequency calculations. The DFT Grid is set to Grid4, for the final energy FinalGrid5 is chosen (if not mentioned otherwise). The optimized structures are characterised by frequency analysis to identify the nature of located stationary points (no imaginary frequency below - 25 cm^{-1} for true minima and only one imaginary frequency (or another below - 15 cm^{-1}) for transition states) and to provide thermal corrections (at 298.15 K and 1 atm) according to the modified ideal gas-rigid rotor-harmonic oscillator model.

For the calculation of transition states relaxed potential energy surface (PES) were performed along the important bond (breaking or forming) and from the highest energy structure we transition state frequency was taken and the structure was then optimised under the restrain to keep that imaginary vibration.

The final free energies in THF are computed on the RI-PWPB95-D3BJ/def2-QZVPP + cPCM(THF), which combines the double-hybrid-meta-GGA PWPB95[13] functional with the BJ-damped DFT-D3 dispersion correction and the def2-QZVPP[10] basis set using the conductor-like polarisable continuum model (cPCM) solvation model for THF as a solvent (ε = 7.25). The density-fitting RI-JK (def2/JK)[14] approach is used to accelerate the calculation and the def2-QZVPP/C[15] auxiliary basis set is used. The final reaction Gibbs free energies (ΔG) are determined from the electronic single-point energies on the RI-PWPB95-D3BJ/def2-QZVPP + cPCM(THF) level plus the thermal corrections from the TPSS-D3BJ/def2-TZVP + cPCM(THF).

The graphical representations of the calculated structures were generated with the free software *UCSF Chimera 1.15*.[16]

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Computed Structures:

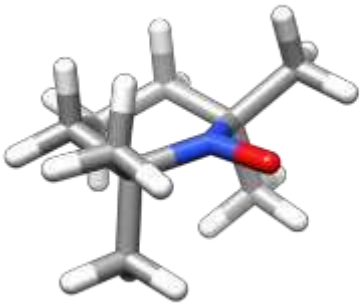

Figure 37 Calculated structure of TEMPO.

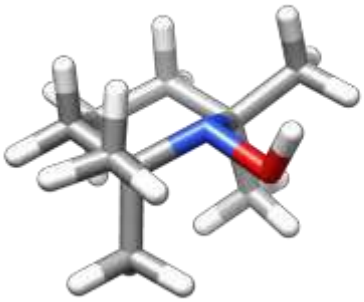

Figure 38 Calculated structure of TEMPOH.

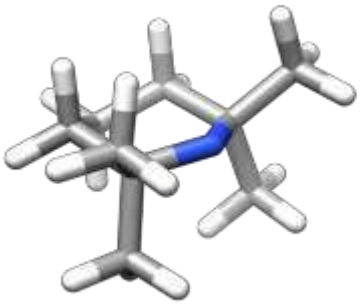

Figure 39 Calculated structure of TEMP.

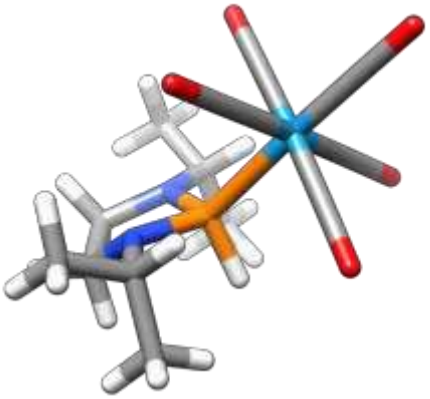

*Figure 40 Calculated structure for **3**.*

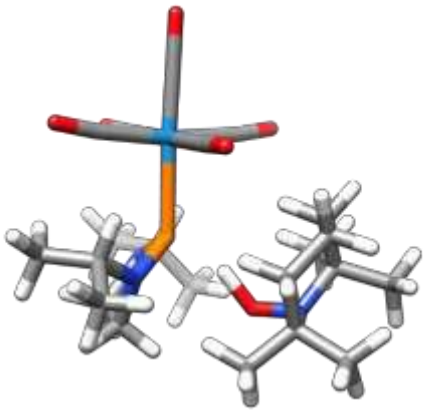

*Figure 41 Calculated transition state (TS) structure **TS{3+TEMPO}** for **3** to **3'**.*

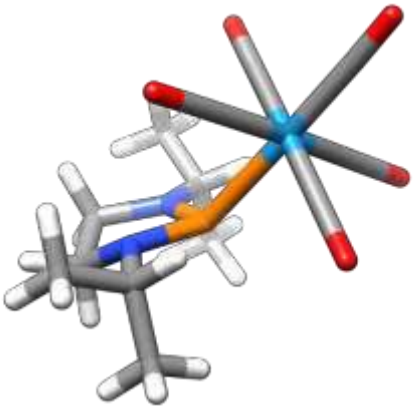

*Figure 42 Calculated structure for **3'**.*

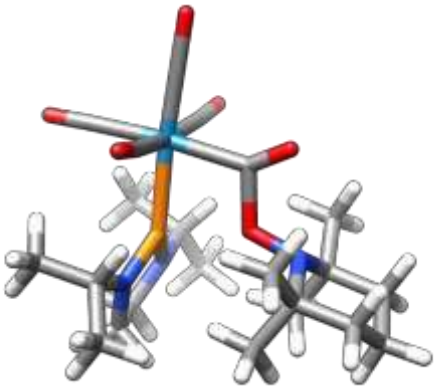

*Figure 43 Calculated TS structure **TS{3'+TEMPO}** for **3'** to **4**.*

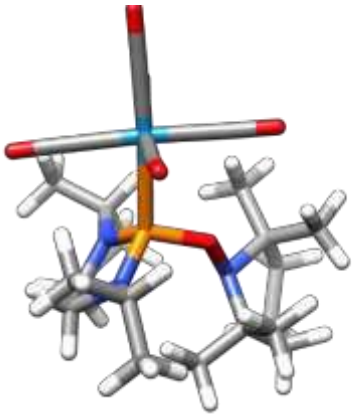

*Figure 44 Calculated structure for **4**.*

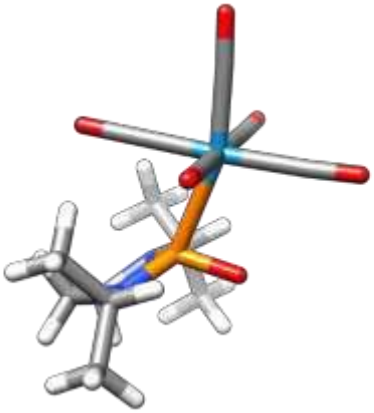

*Figure 45 Calculated structure for **4'**.*

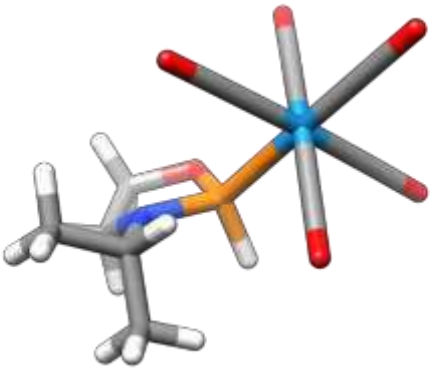

*Figure 46 Calculated structure for **6a**.*

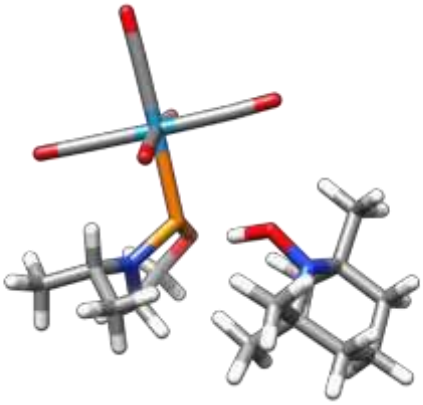

*Figure 47 Calculated transition state (TS) structure **TS{6a+TEMPO}** for **6a** to **6a'.***

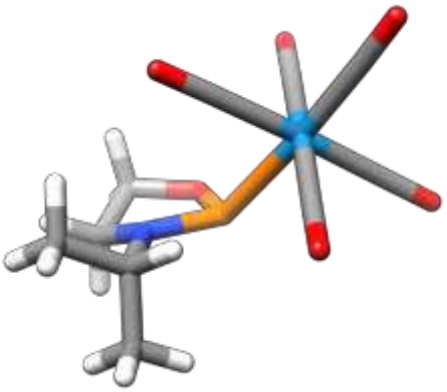

*Figure 48 Calculated structure for **6a'.***

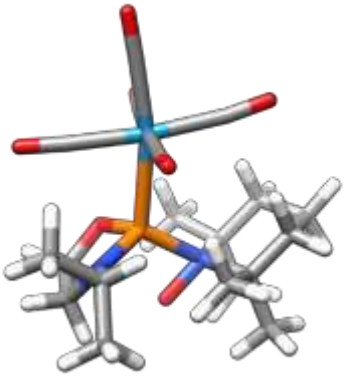

*Figure 49 Calculated TS structure **TS{6a'+TEMPO}** for **6a'** to **7a**.*

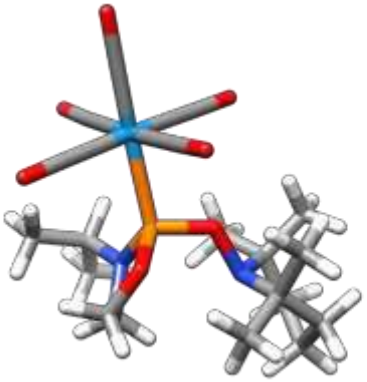

*Figure 50 Calculated structure for **7a**.*

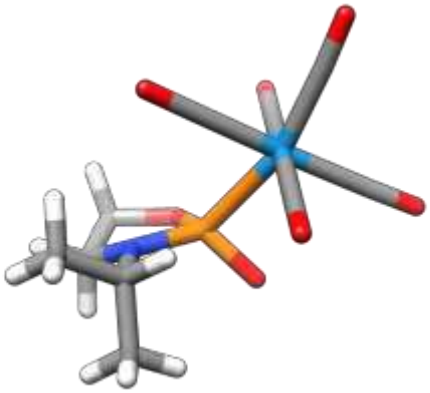

*Figure 51 Calculated structure for **7a'**.*

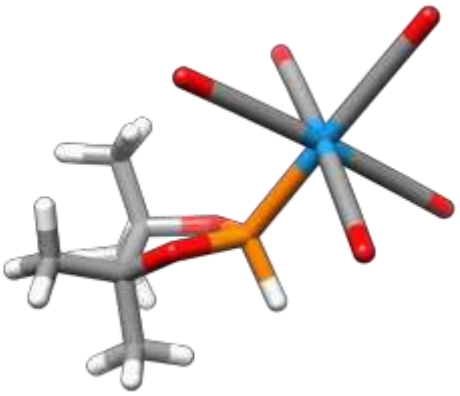

*Figure 52 Calculated structure for **6b**.*

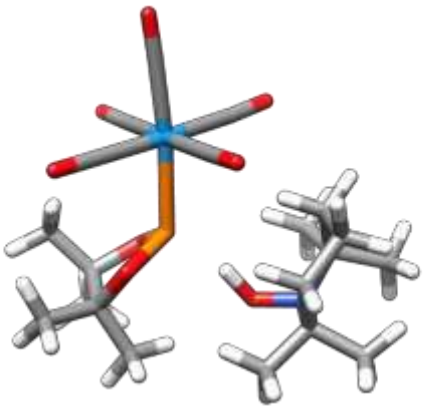

*Figure 53 Calculated TS structure **TS{6b+OTEMP}** for **6b** to **6b'**.*

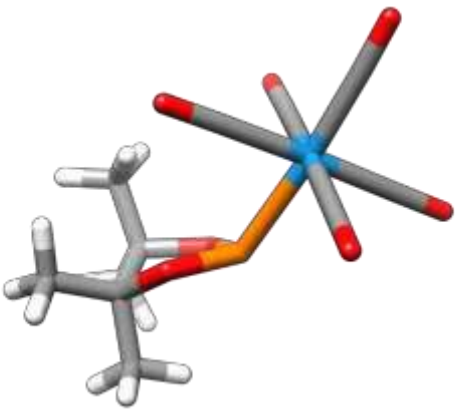

*Figure 54 Calculated structure for **6b'**.*

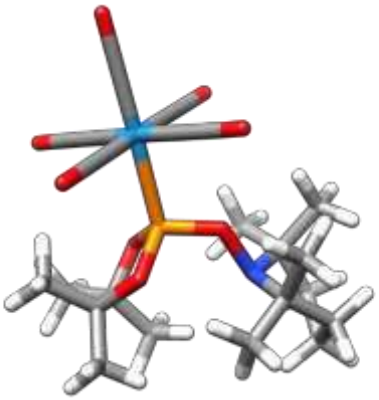

*Figure 55 Calculated structure of **7b**.*

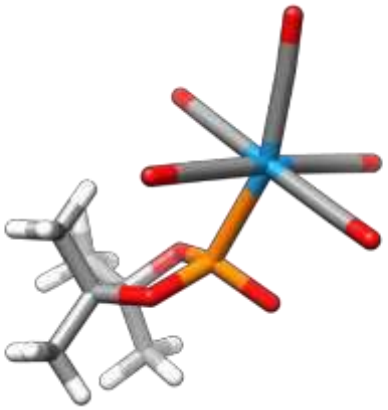

*Figure 56 Calculated structure of **7b'**.*