

Supplementary Information for

Structure and Dynamic Behavior of Rhodium Complexes Supported by Lewis Acidic Group 13 Metallatranes

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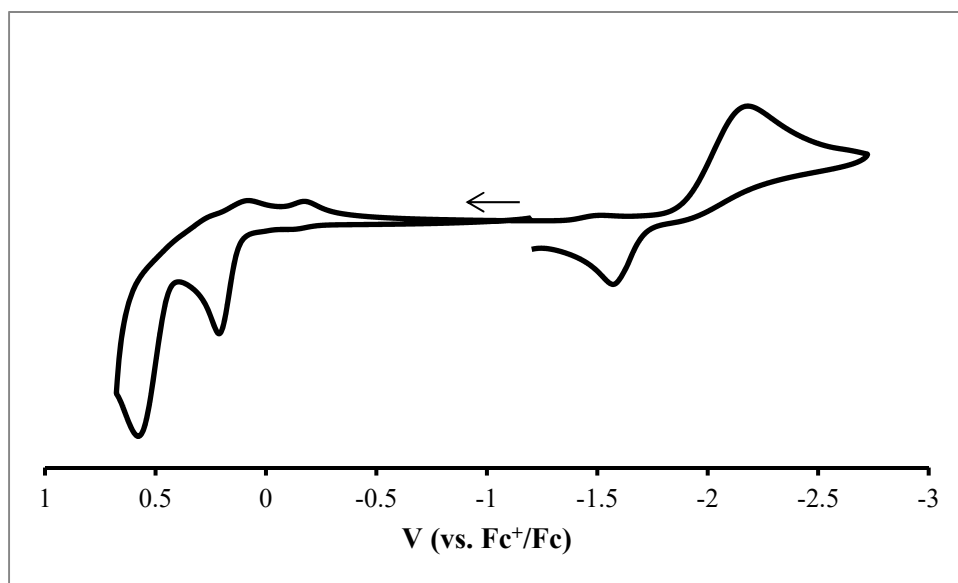


Figure S1. Full cyclic voltammogram of **1-Cl** (100 mV/s) in 0.1 M TBAPF₆ in THF referenced to the Fc/Fc⁺ redox couple. First oxidation $E_{pa} = 0.21$ V; second oxidation $E_{pa} = 1.00$ V.

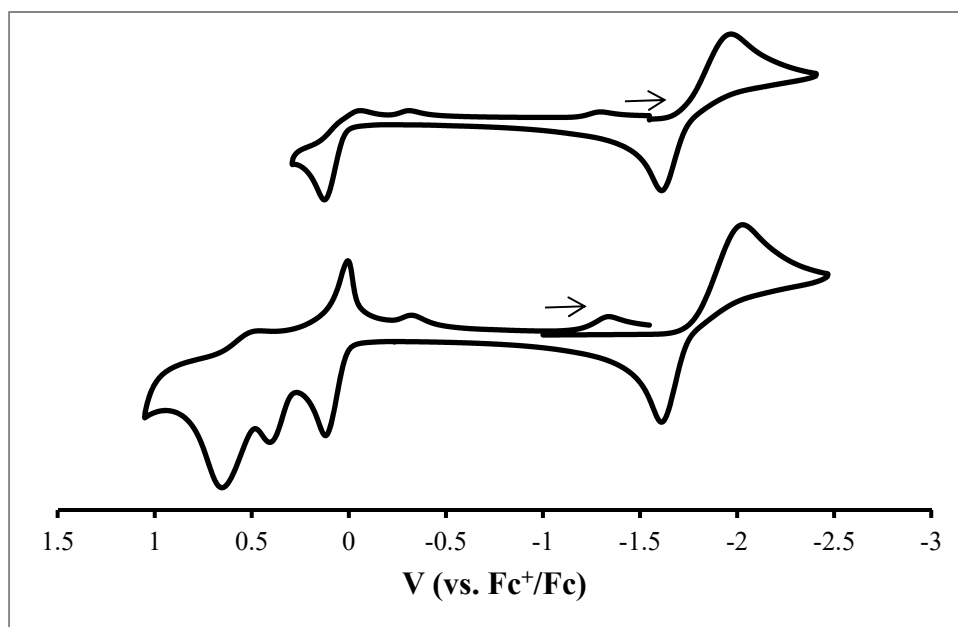


Figure S2. Cyclic voltammogram of **2-Cl** (100 mV/s) in 0.1 M TBAPF₆ in THF referenced to the Fc/Fc⁺ redox couple. First oxidation $E_{pa} = 0.12$ V; second oxidation $E_{pa} = 0.41$ V; third oxidation $E_{pa} = 0.65$. The return reduction at $E_{pc} = 0.81$ V is absent in the top CV, demonstrating that it is an electrochemical event not related to the first oxidation.

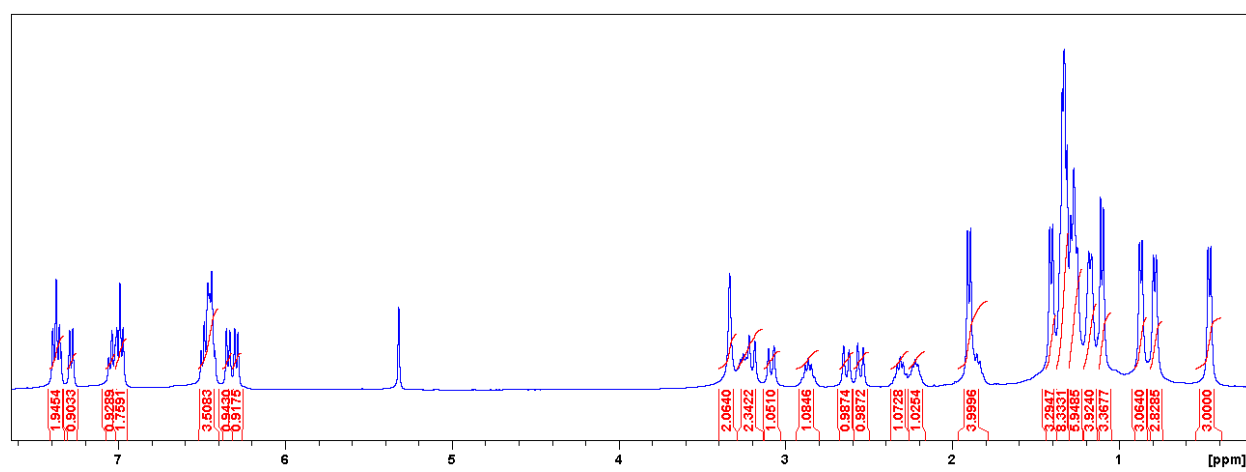
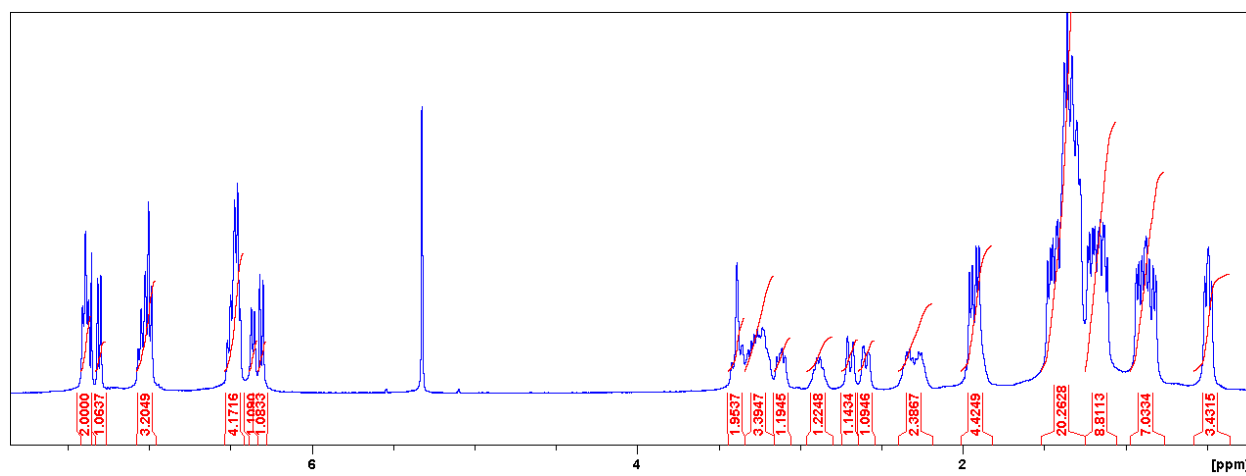


Figure S3. ^1H (top) and $^1\text{H}\{^{31}\text{P}\}$ (bottom) NMR spectra of **1-Cl** (400 MHz) in CD_2Cl_2 at -18°C .

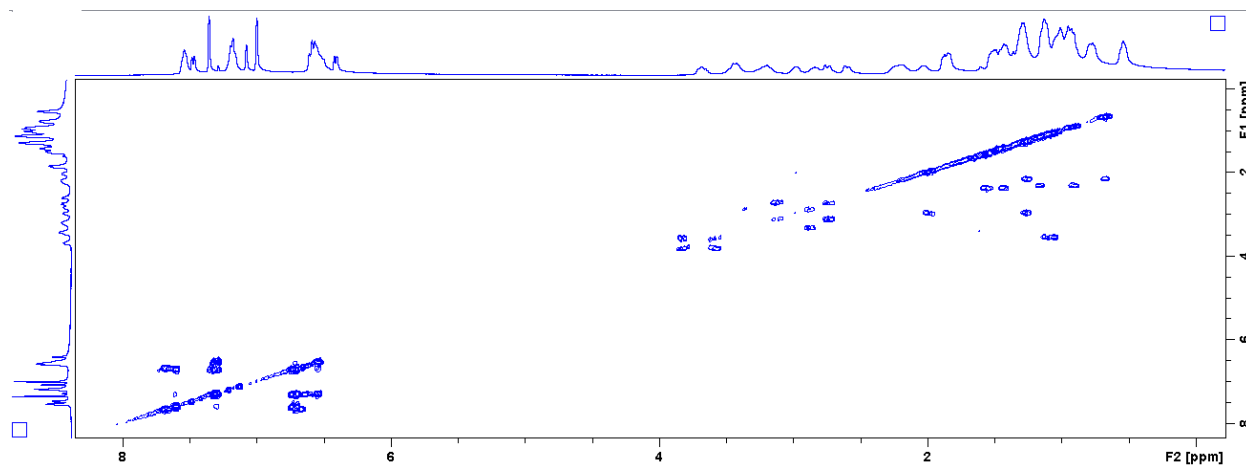


Figure S4. ^1H COSY NMR spectrum of **1-Cl** (400 MHz) in $\text{C}_6\text{D}_5\text{Br}$ at 0°C .

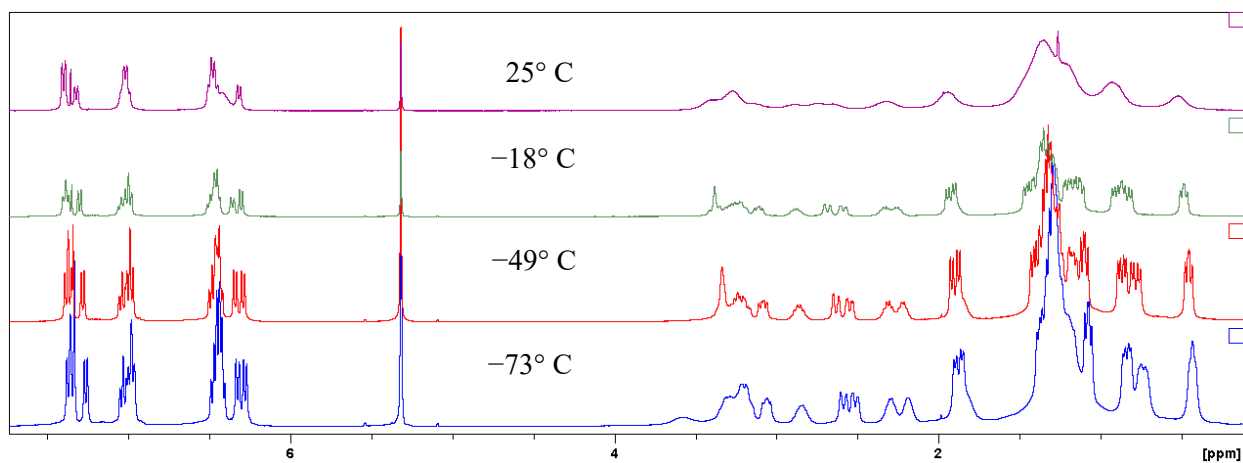


Figure S5. Low temperature VT ^1H NMR spectrum of **1-Cl** (400 MHz) in CD_2Cl_2 . In order from bottom to top: -73°C , -49°C , -18°C , and 25°C .

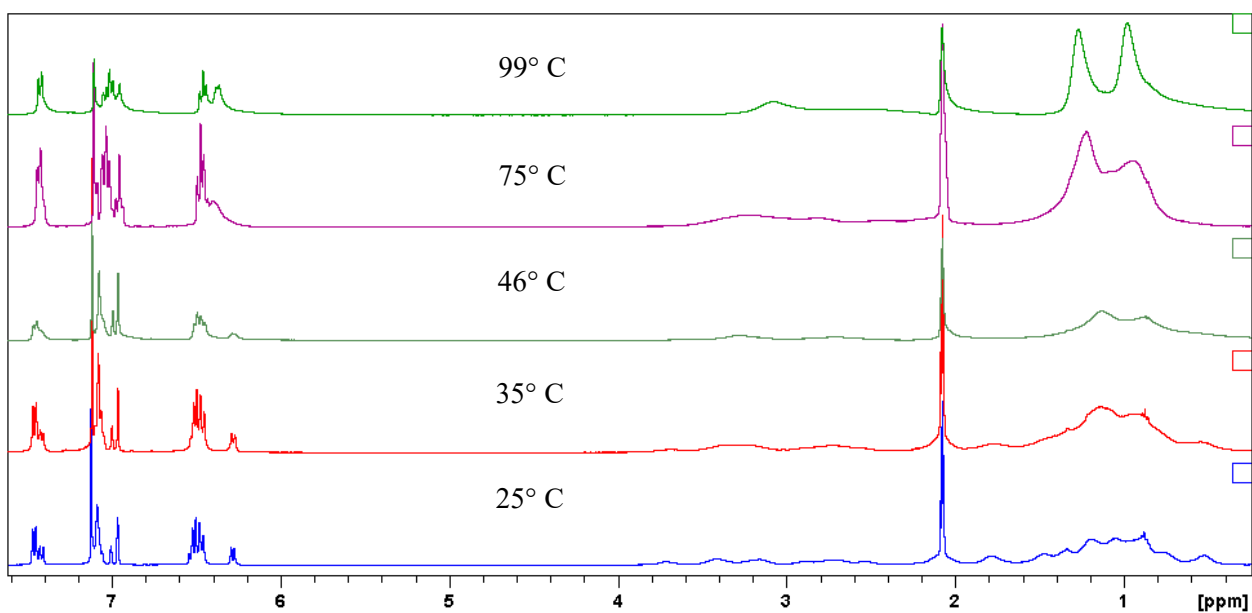


Figure S6. High temperature VT ^1H NMR spectrum of **1-Cl** (400 MHz) in toluene- d_8 .

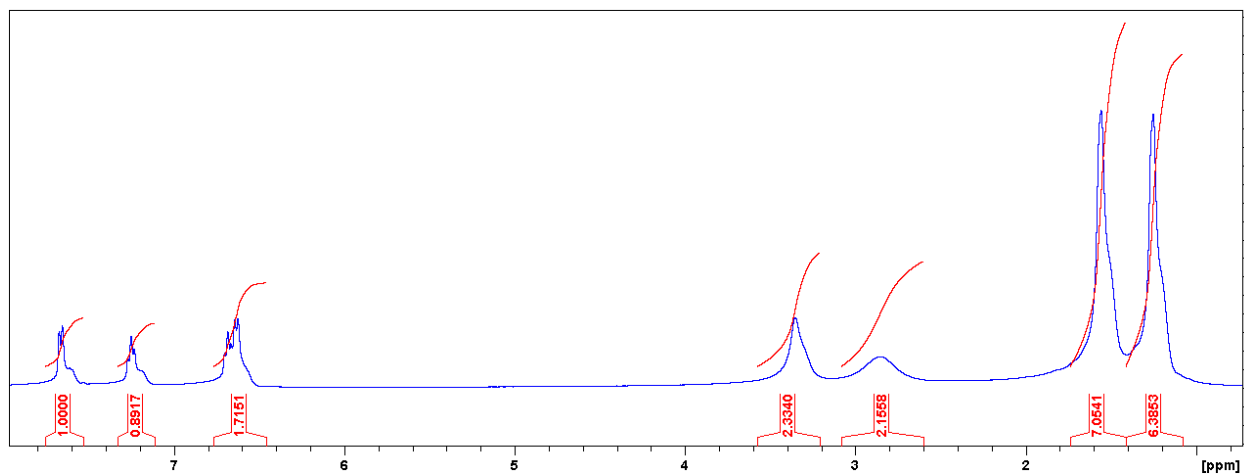


Figure S7. ^1H NMR spectrum of **1-Cl** (400 MHz) in $\text{C}_6\text{D}_5\text{Br}$ at 115°C . The bad shims are an effect of the shimming coils being at an elevated temperature.

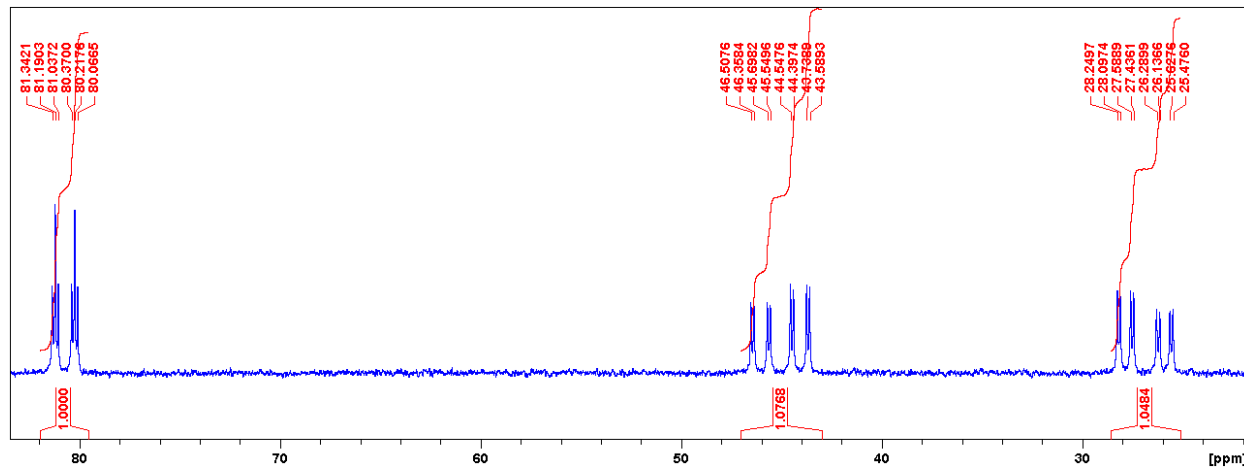


Figure S8. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1-Cl** (162 MHz) in CD_2Cl_2 at -18°C .

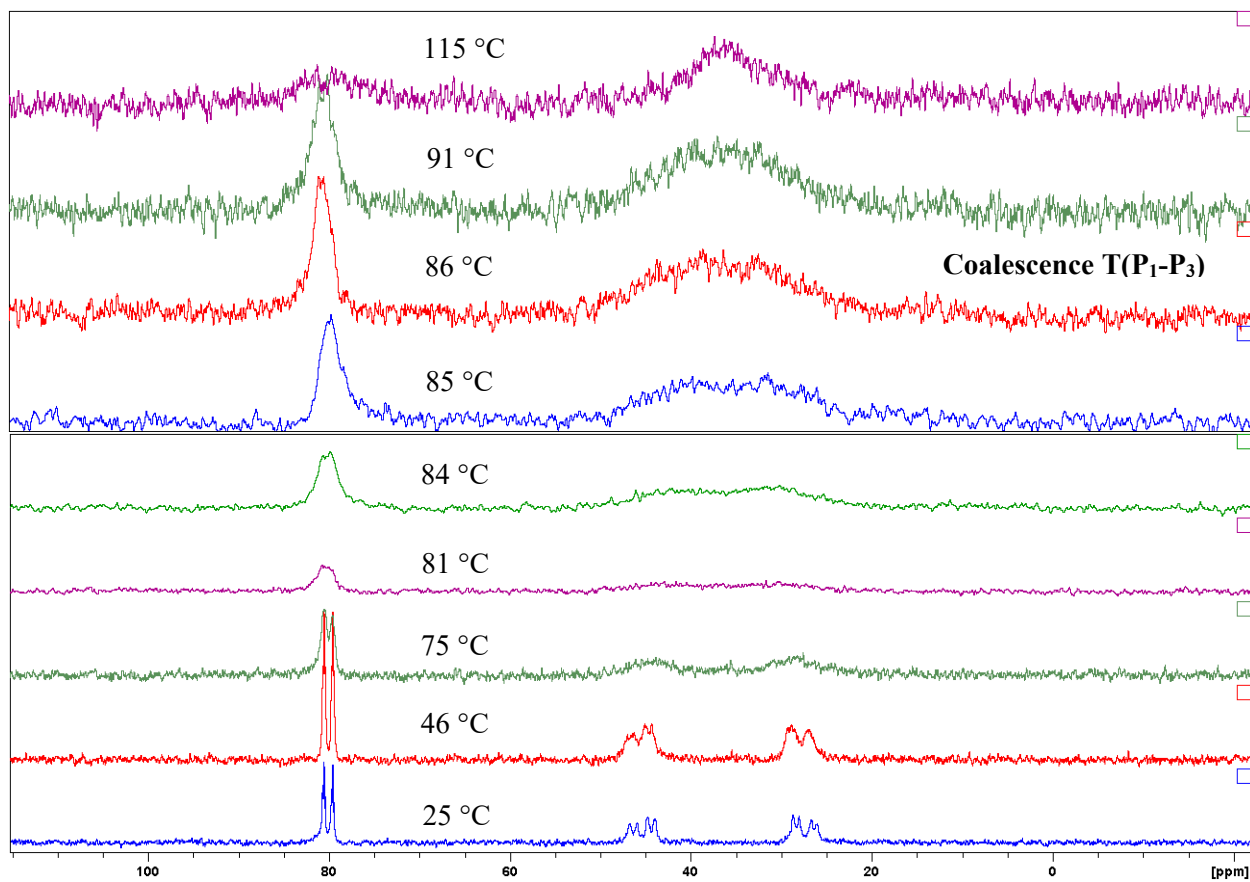


Figure S9. High temperature VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1-Cl** (162 MHz) in $\text{C}_6\text{D}_5\text{Br}$.

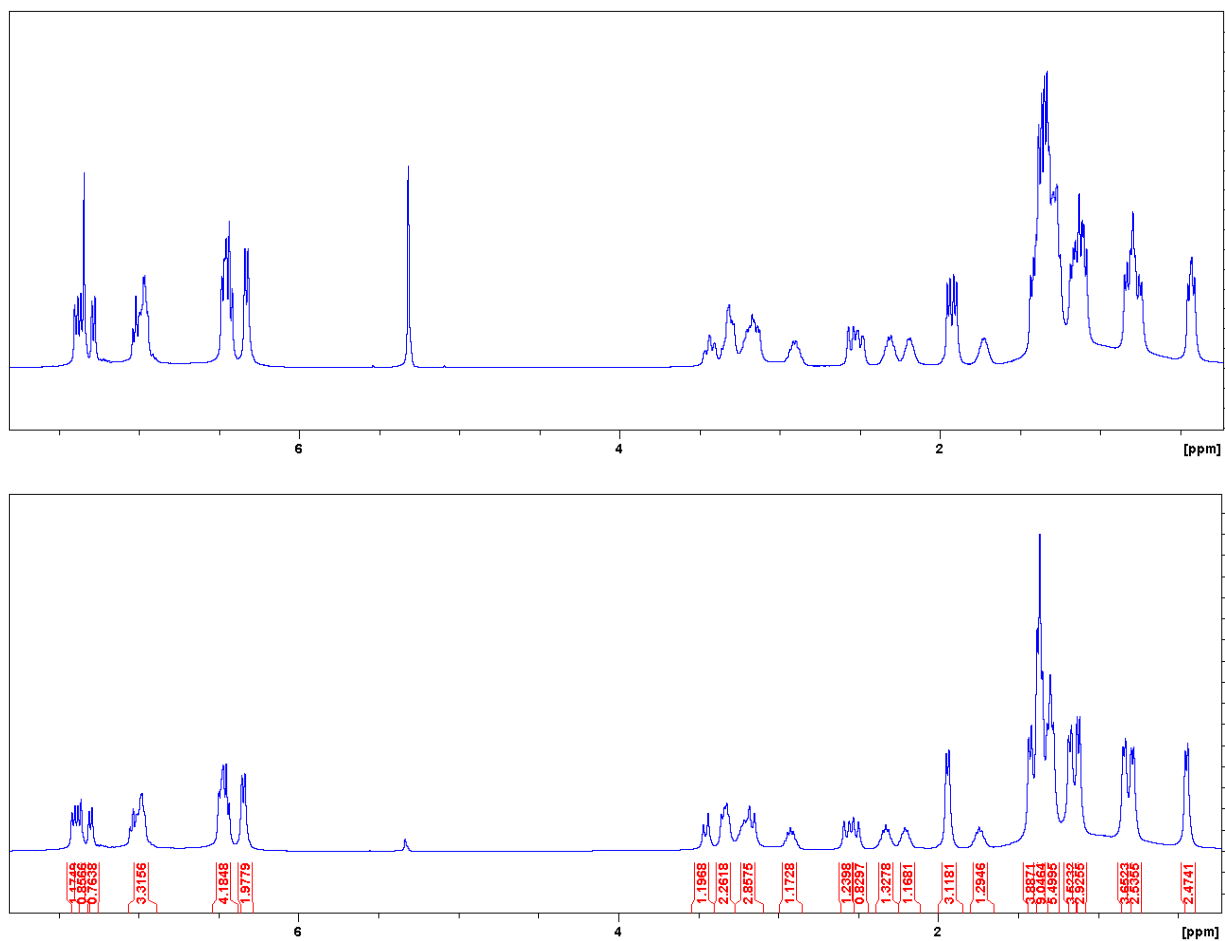


Figure S10. ^1H (top) and $^1\text{H}\{^{31}\text{P}\}$ (bottom) NMR spectra of 2-Cl (400 MHz) in CD_2Cl_2 at -49°C .

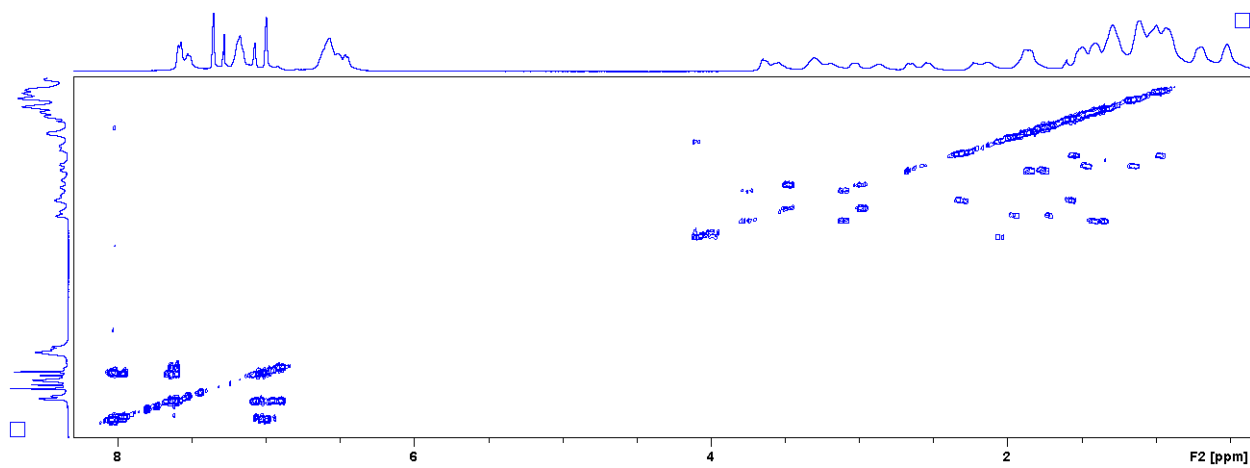


Figure S11. ^1H COSY NMR spectrum of 2-Cl (400 MHz) in $\text{C}_6\text{D}_5\text{Br}$ at 0°C .

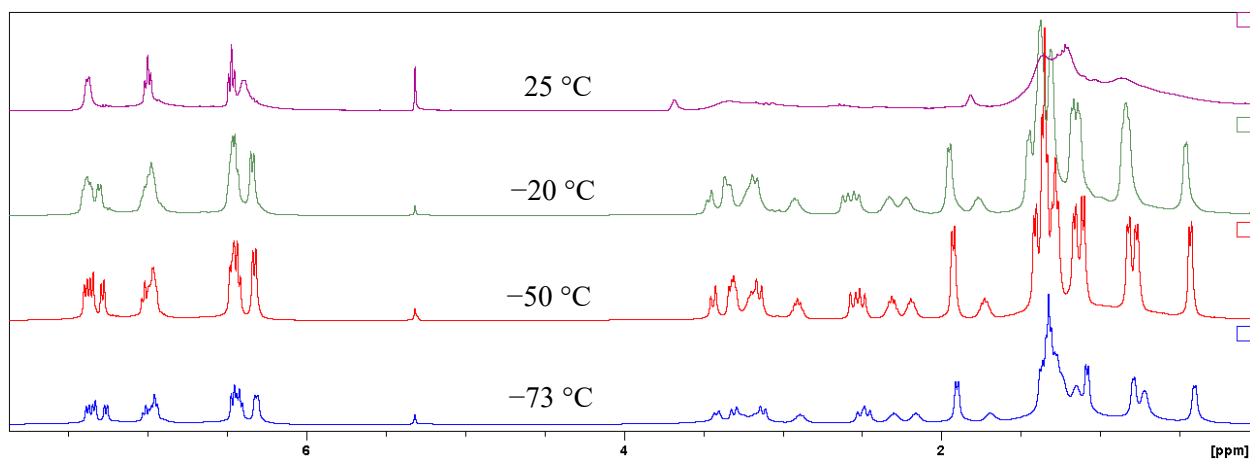


Figure S12. Low temperature VT ^1H NMR spectrum of **2-Cl** (400 MHz) in CD_2Cl_2 .

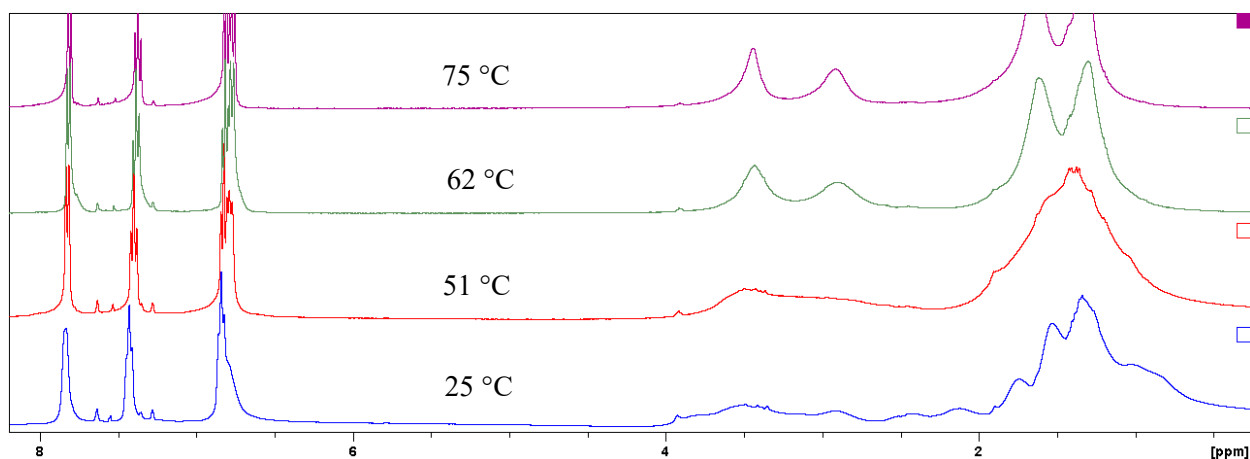


Figure S13. High temperature VT ^1H NMR spectrum of **2-Cl** (400 MHz) in $\text{C}_6\text{D}_5\text{Br}$.

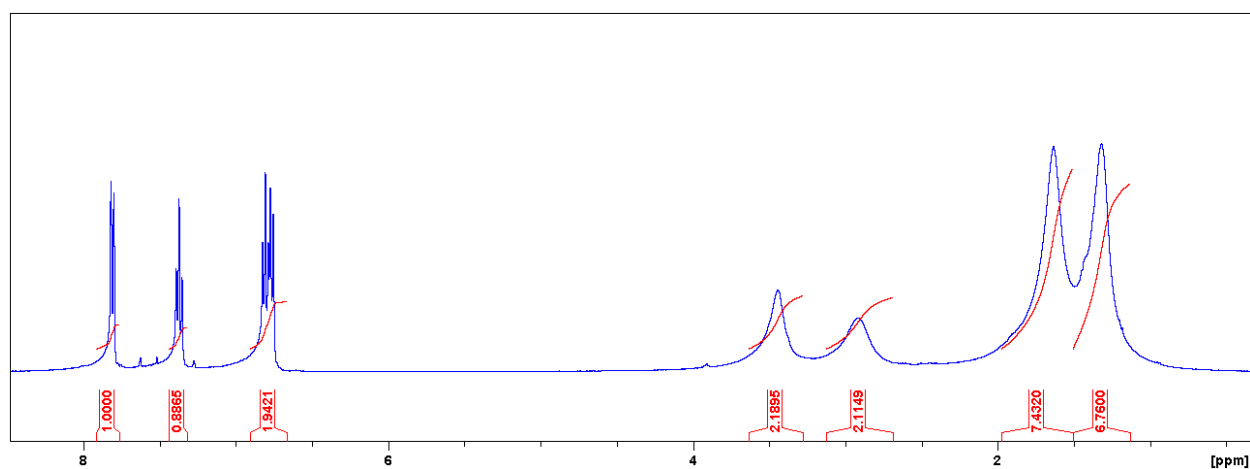


Figure S14. ^1H NMR spectrum of **2-Cl** (400 MHz) in $\text{C}_6\text{D}_5\text{Br}$ at 75°C .

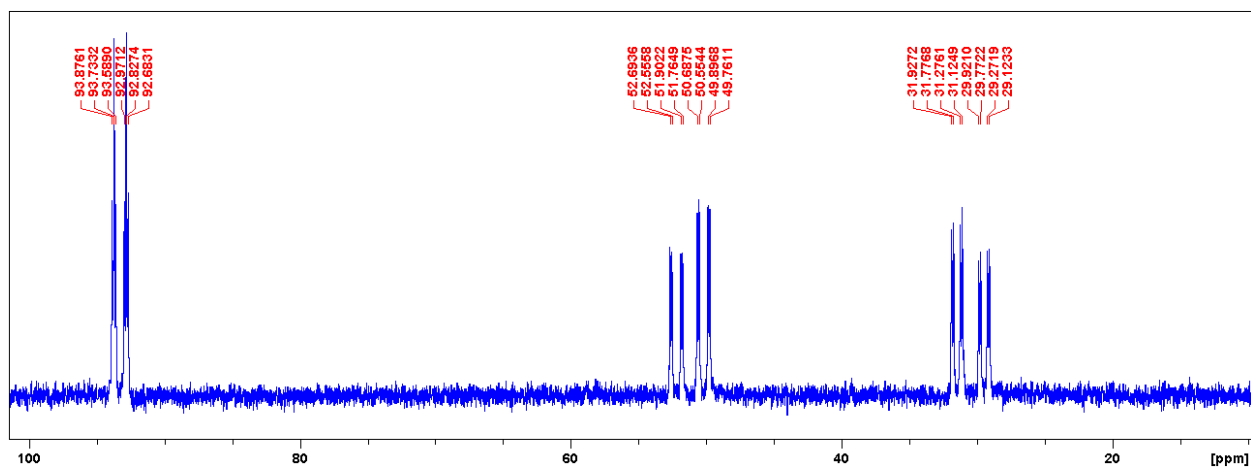


Figure S15. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2-Cl** (162 MHz) in CD_2Cl_2 at -18°C .

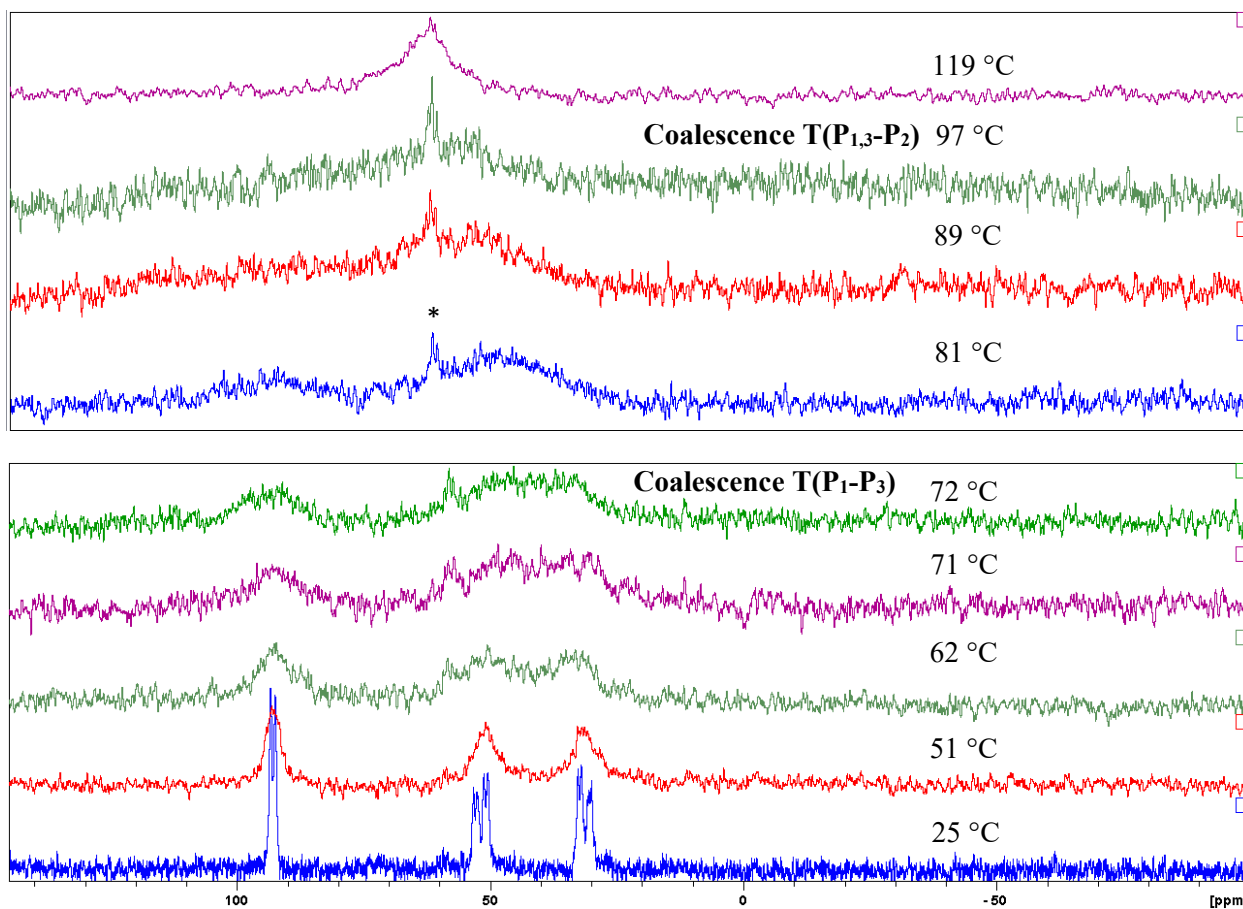


Figure S16. High temperature VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2-Cl** (162 MHz) in $\text{C}_6\text{D}_5\text{Br}$. * denote a minor impurity. Note: The average of the three peaks at -18°C : $(93.3 + 51.2 + 30.5)/3 = 58.3$ ppm, which is close to the 58.6 ppm shift observed at high temperatures.

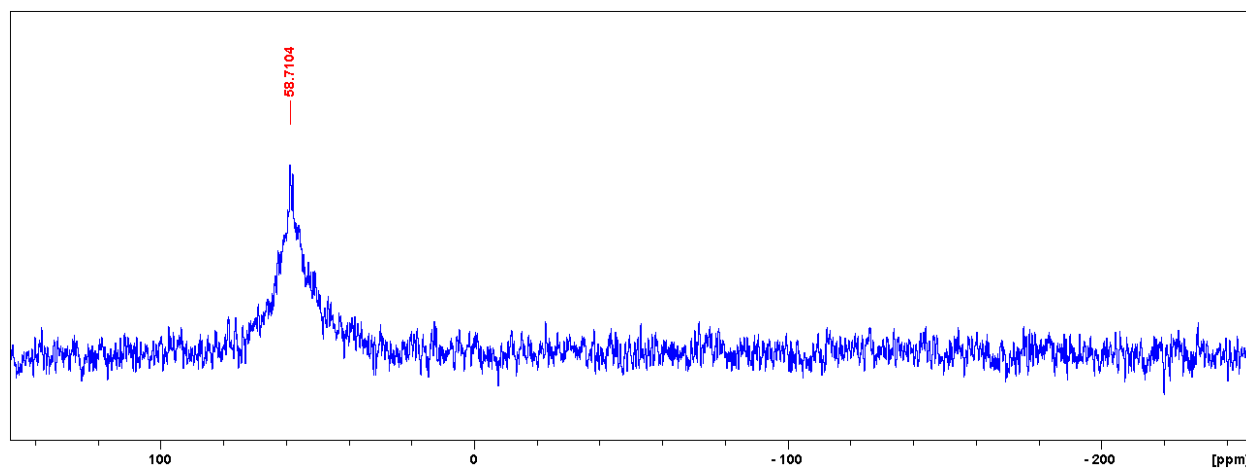


Figure S17. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2-Cl** (162 MHz) in $\text{C}_6\text{D}_5\text{Br}$ at 107°C .

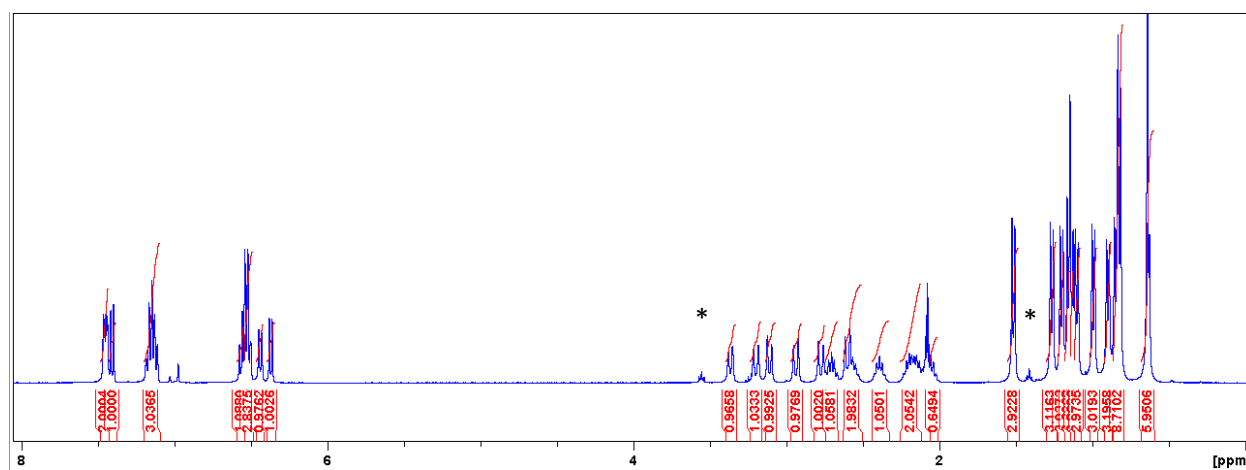
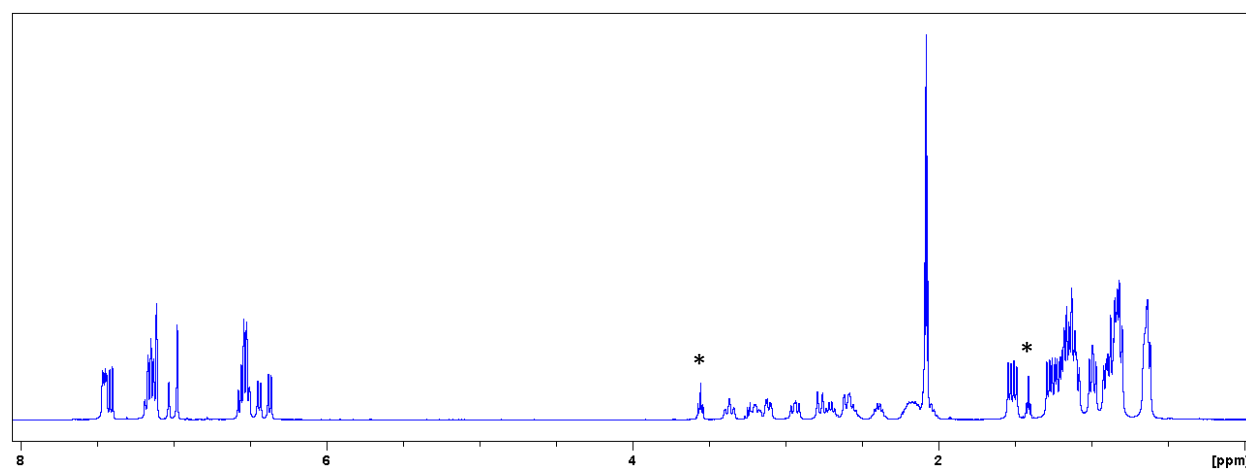


Figure S18. ^1H (top) and $^1\text{H}\{^{31}\text{P}\}$ (bottom) NMR spectra of **1-CH₃** (400 MHz) in $\text{toluene-}d_8$ at -18°C . * denotes residual THF.

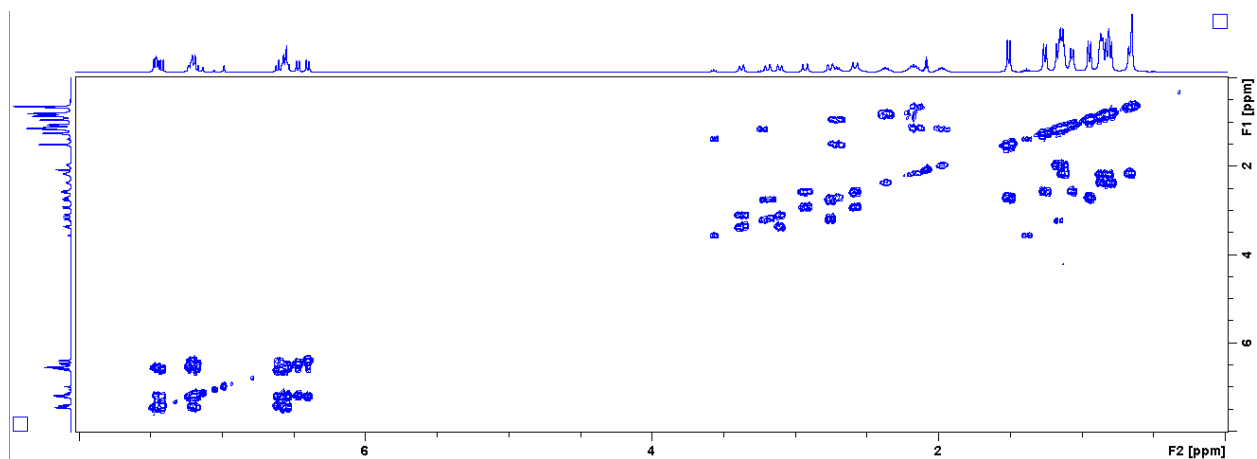


Figure S19. ^1H COSY NMR spectrum of **1-CH₃** (400 MHz) in toluene- d_8 at -18°C .

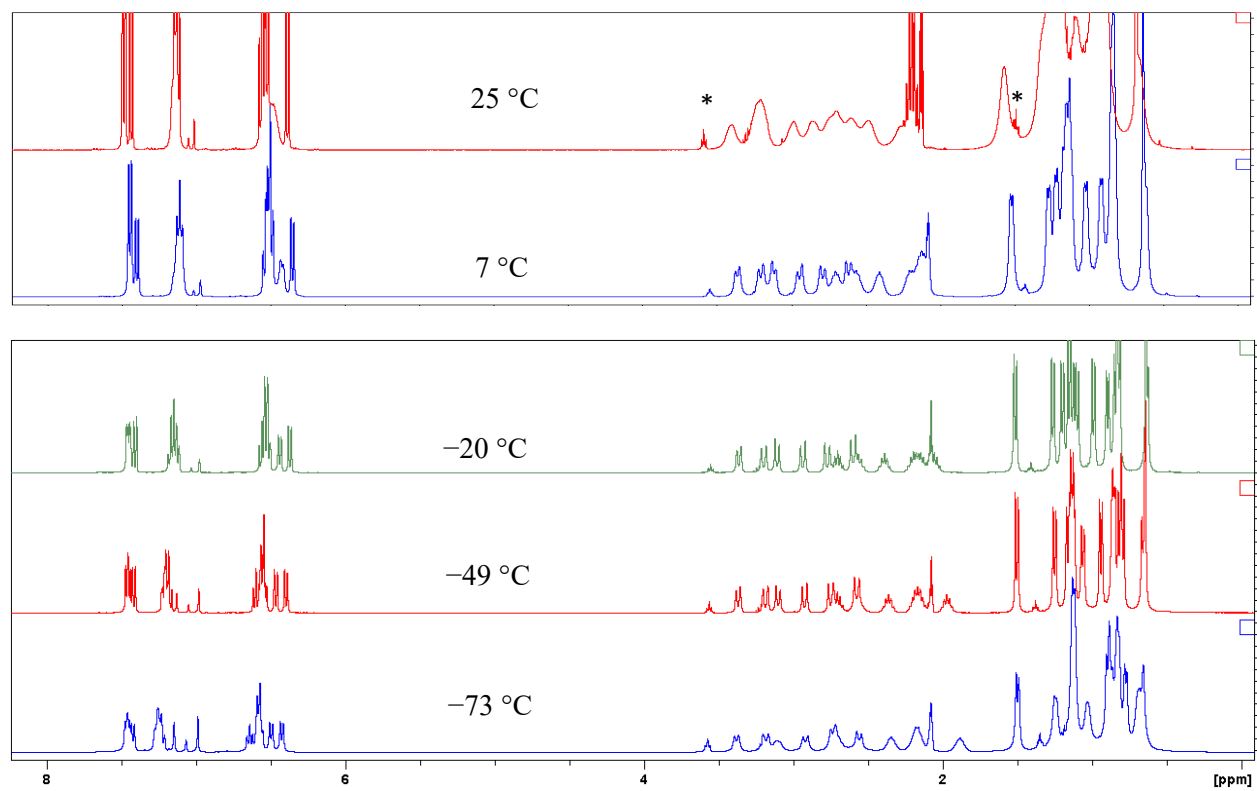


Figure S20. Low temperature VT $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of **1-CH₃** (400 MHz) in toluene- d_8 . * denotes residual THF.

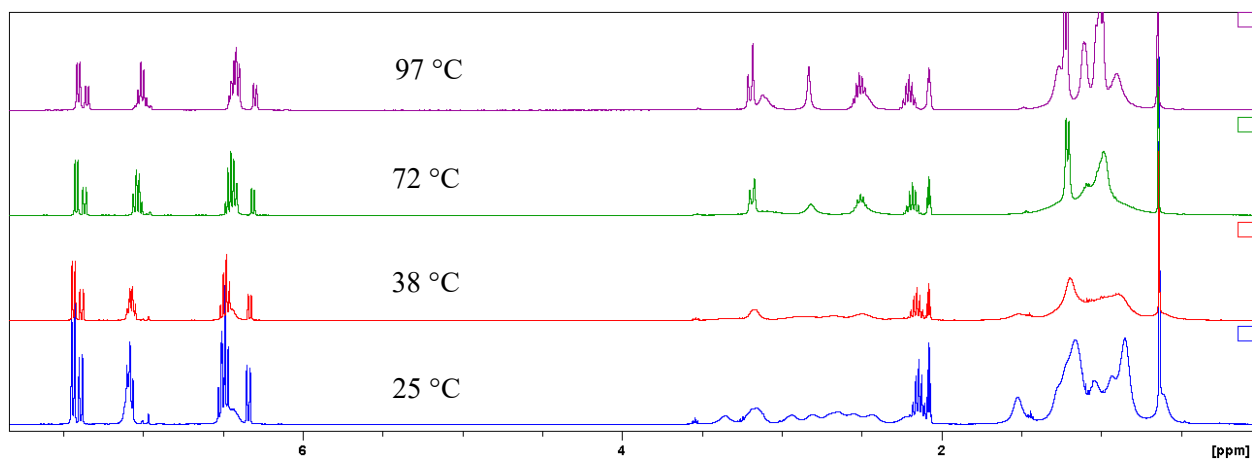


Figure S21. High temperature VT ^1H NMR spectrum of **1-CH₃** (400 MHz) in toluene- d_8 .

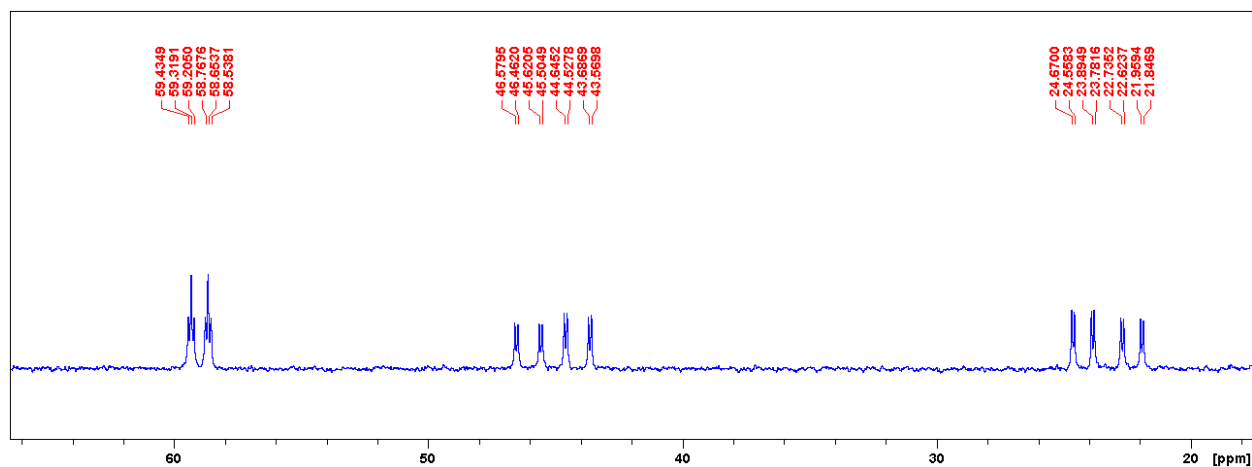


Figure S22. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1-CH₃** (162 MHz) in toluene- d_8 at -18°C .

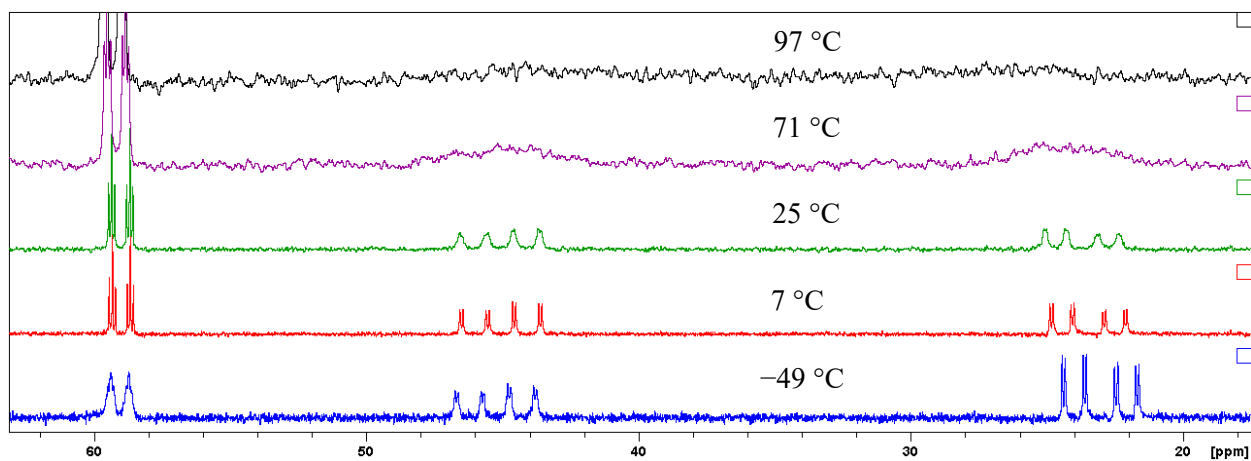


Figure S23. VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1-CH₃** (162 MHz) in toluene-*d*₈.

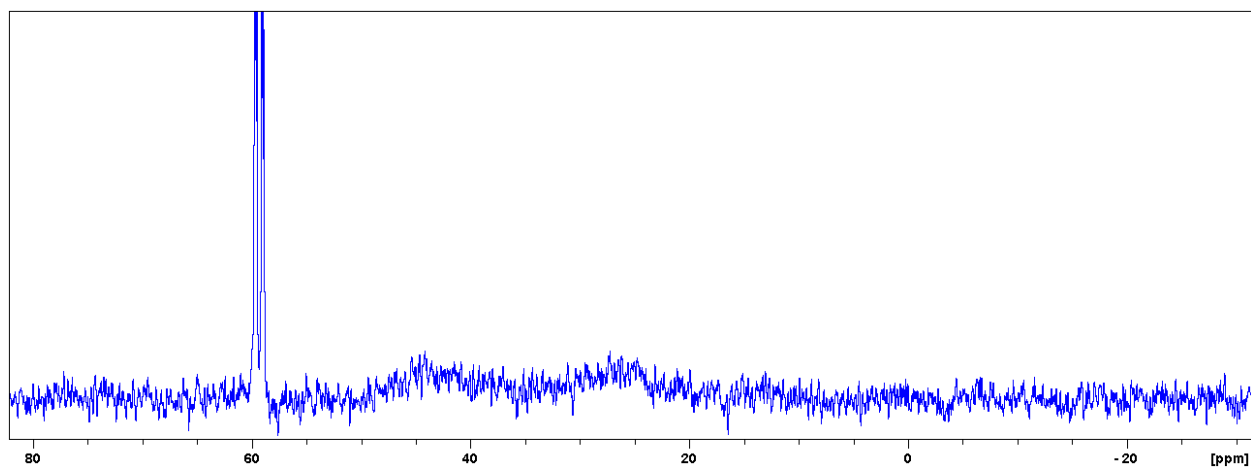


Figure S24. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1-CH₃** (162 MHz) in toluene-*d*₈ at 97°C. The peaks for P_1 and P_3 have not yet coalesced at this temperature.

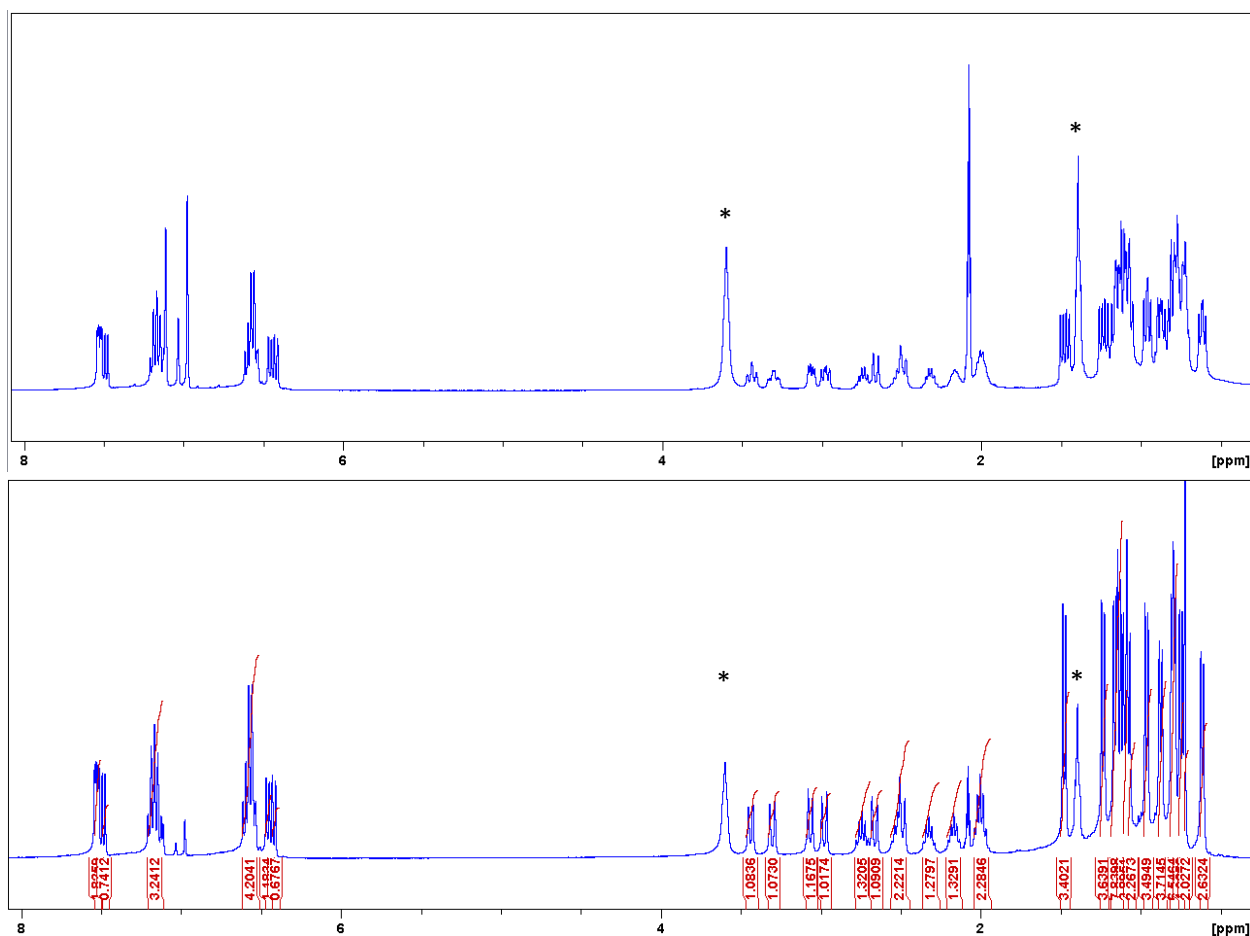


Figure S25. ¹H (top) and ¹H{³¹P} (bottom) NMR spectra of **2-CH₃** (400 MHz) in toluene-*d*₈ at -13°C. * denotes residual THF.

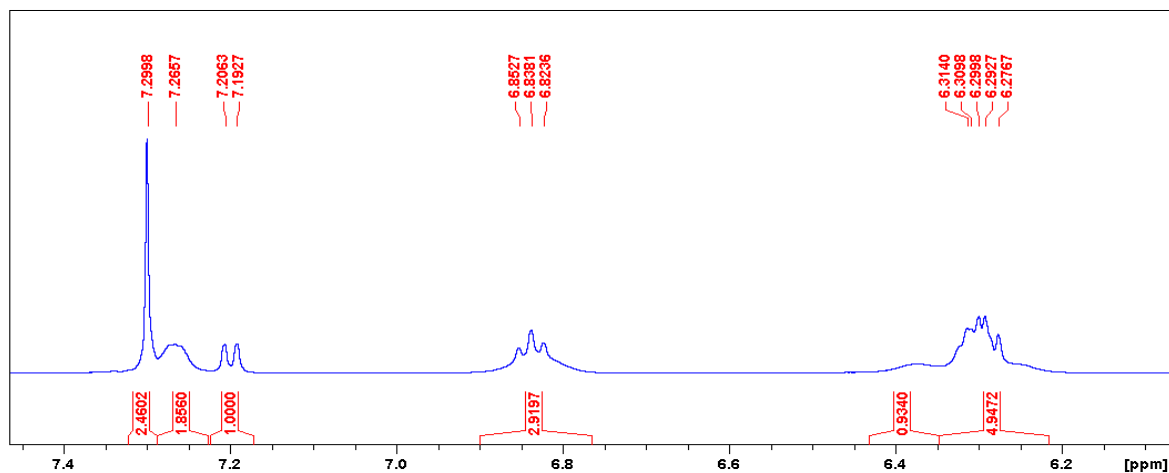


Figure S26. ¹H NMR spectrum of **2-CH₃** sample sent for elemental analysis in THF-*d*₈. Crystals of **2-CH₃**(C₆H₆) was subjected to vacuum prior to elemental analysis (EA). The NMR of the aryl region for the EA sample shows that the relative integration of C₆H₆ to **2-CH₃** is 0.5 to 1.

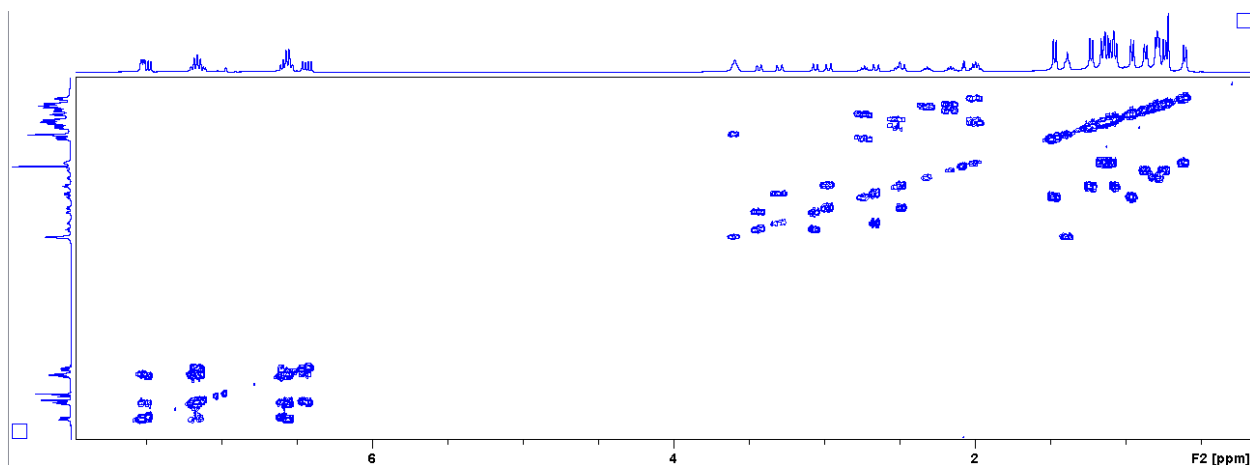


Figure S27. ^1H COSY NMR spectrum of **2-CH₃** (400 MHz) in toluene- d_8 at -13°C .

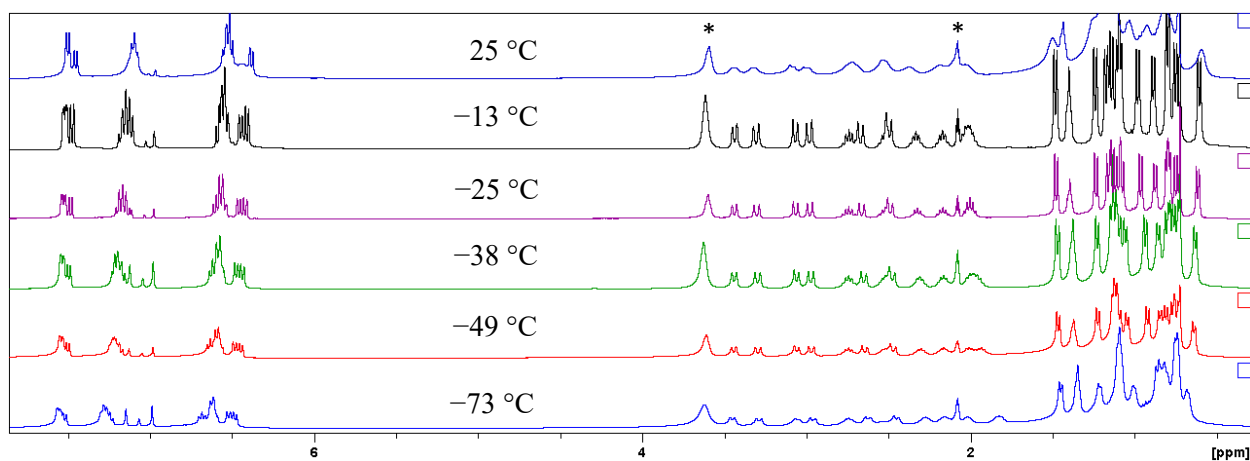


Figure S28. Low temperature VT $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of **2-CH₃** (400 MHz) in toluene- d_8 . * denotes residual THF.

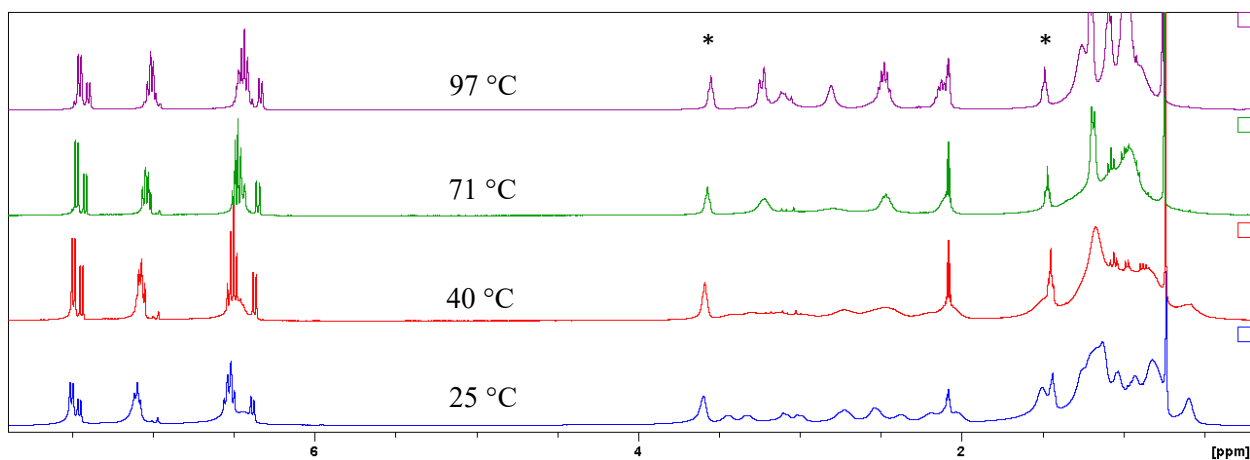


Figure S29. High temperature VT $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of **2-CH₃** (400 MHz) in toluene- d_8 . * denotes residual THF.

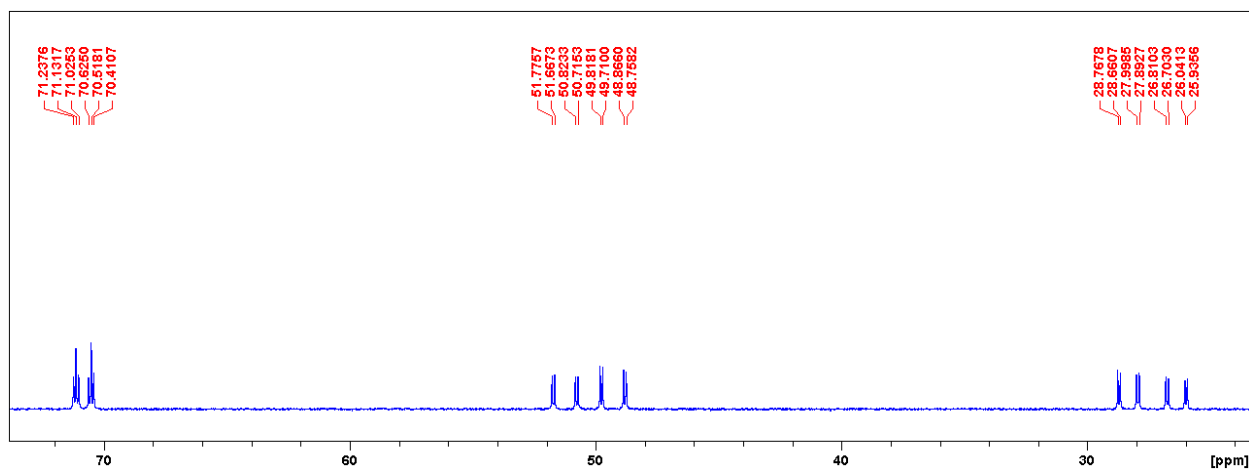


Figure S30. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2-CH₃** (162 MHz) in toluene-*d*₈ at 3°C.

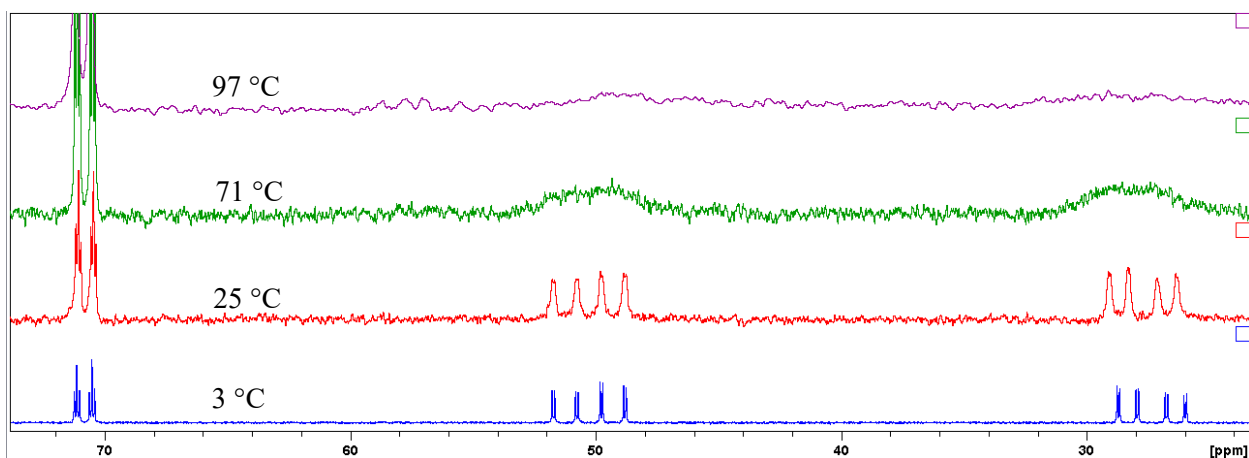


Figure S31. VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2-CH₃** (162 MHz) in toluene-*d*₈.

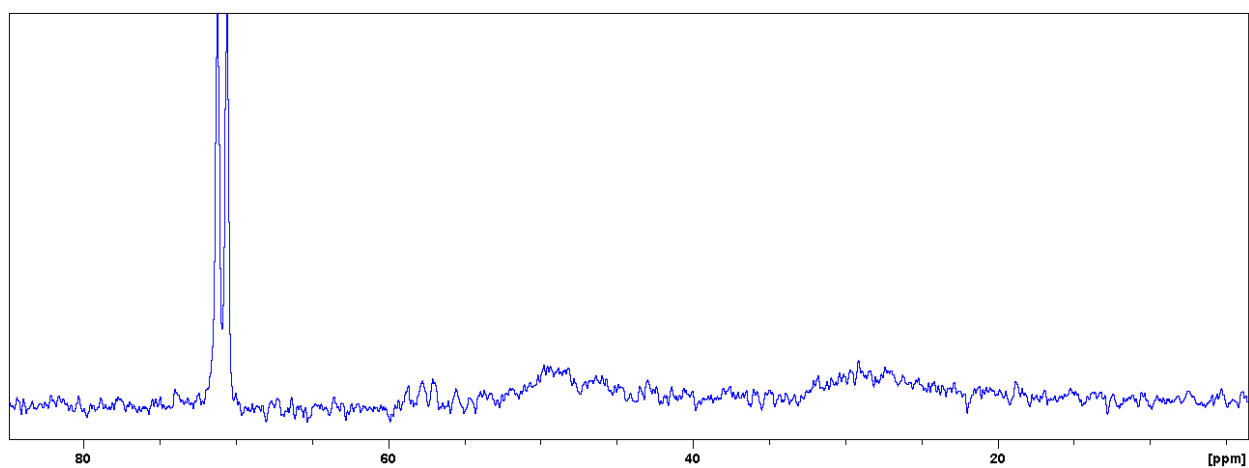


Figure S32. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2-CH₃** (162 MHz) in toluene-*d*₈ at 97°C. The peaks for *P*₁ and *P*₃ have not yet coalesced at this temperature.

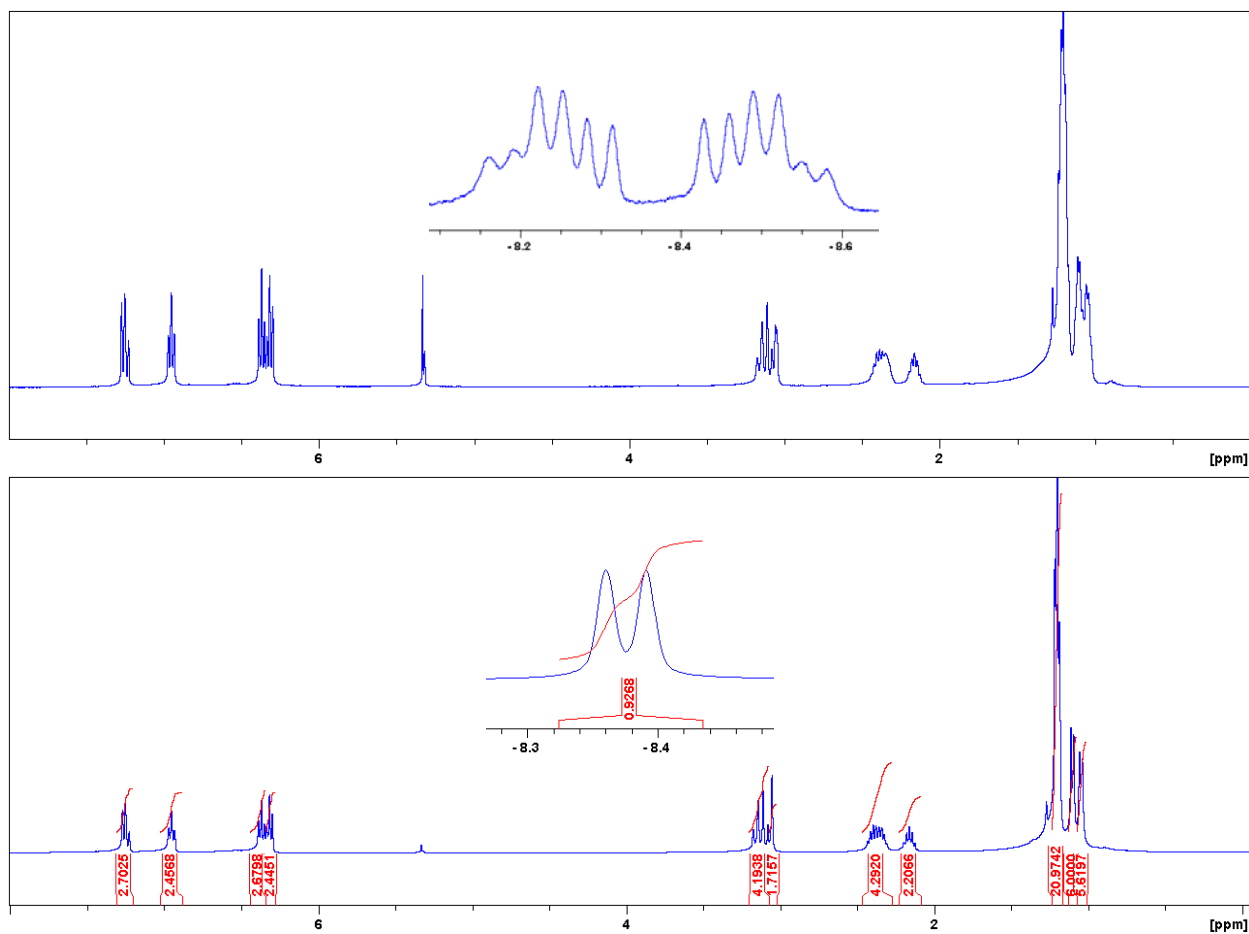


Figure S33. ^1H (top) and $^1\text{H}\{^{31}\text{P}\}$ (bottom) NMR spectra of **1-H** (400 MHz) in CD_2Cl_2 at 25°C .

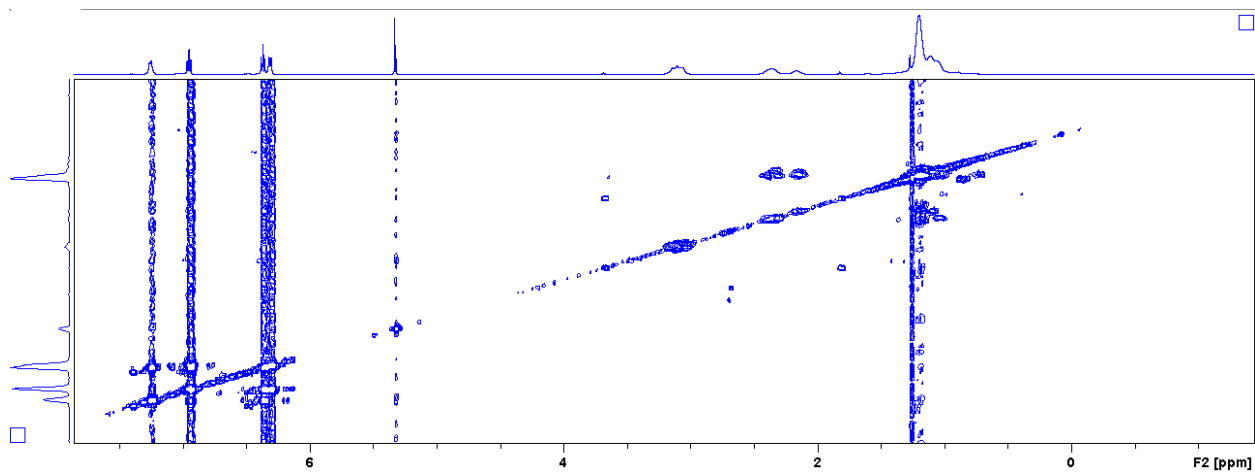


Figure S34. ^1H COSY NMR spectrum of **1-H** (500 MHz) in CD_2Cl_2 at 25°C .

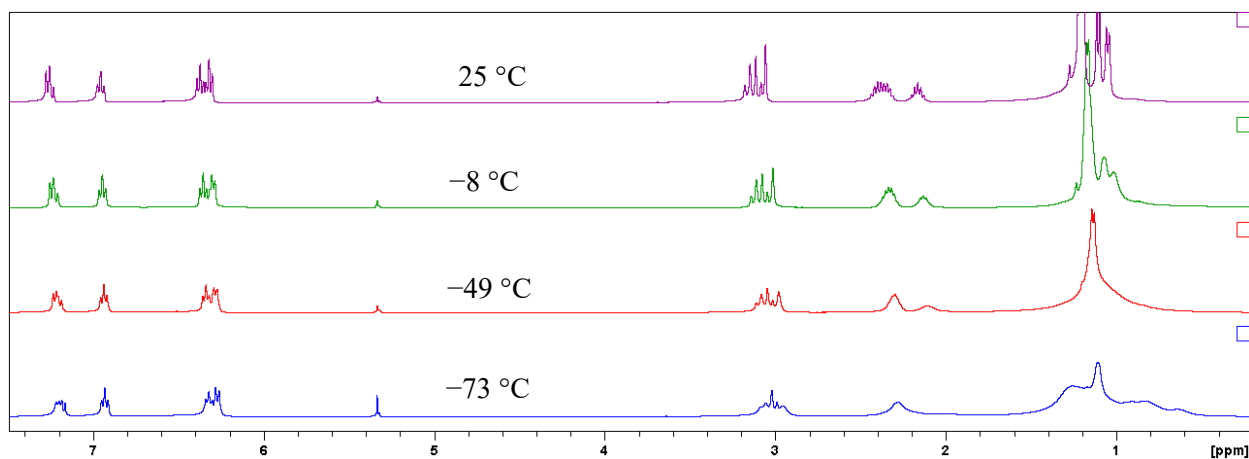


Figure S35. Low temperature VT $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of **1-H** (400 MHz) in CD_2Cl_2 .

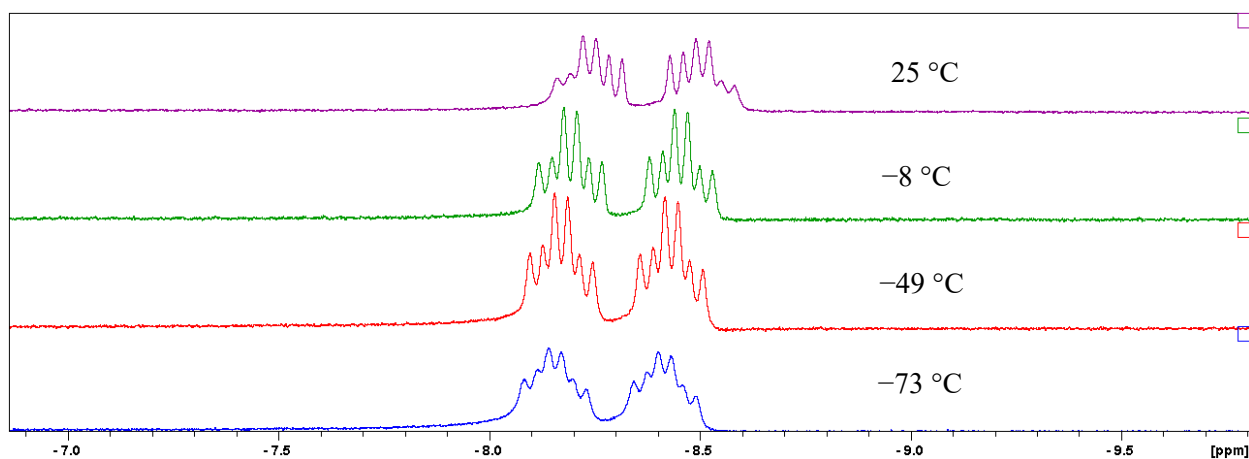


Figure S36. Low temperature VT $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of **1-H** (400 MHz) in CD_2Cl_2 in hydride region. In order from bottom to top: -73°C , -49°C , -8°C and 25°C .

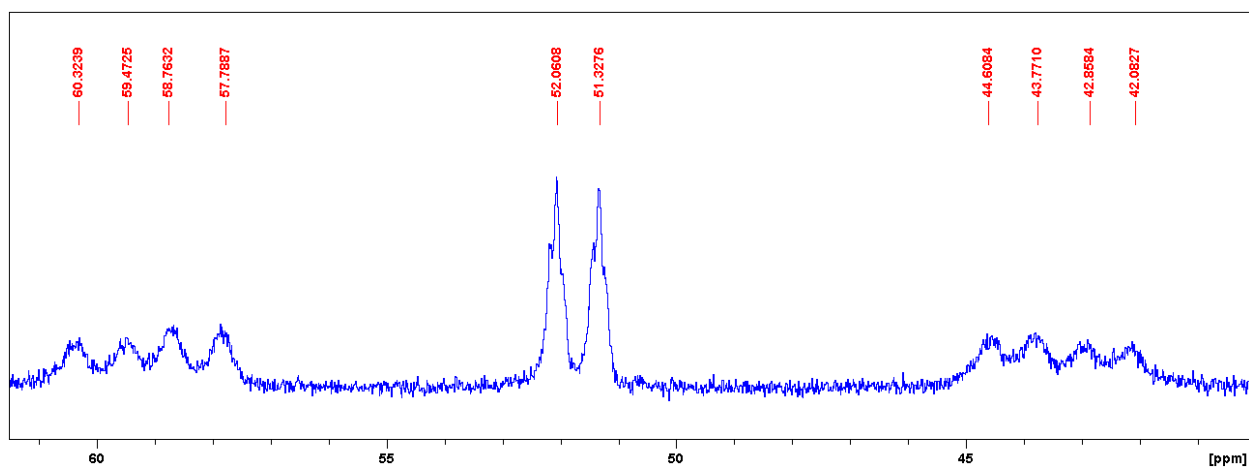


Figure S37. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1-H** (162 MHz) in CD_2Cl_2 at -73°C .

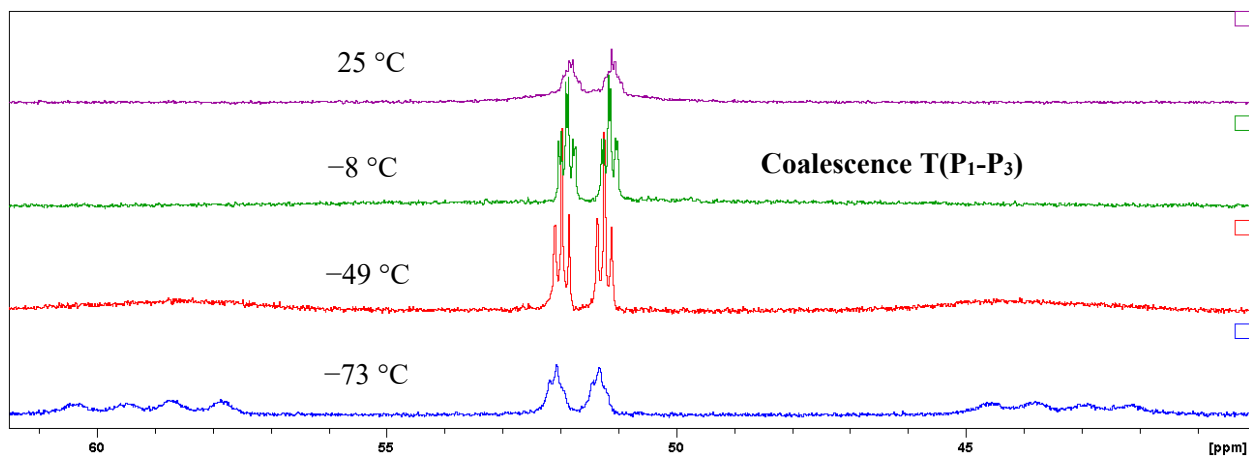


Figure S38. VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1-H** (162 MHz) in CD_2Cl_2 .

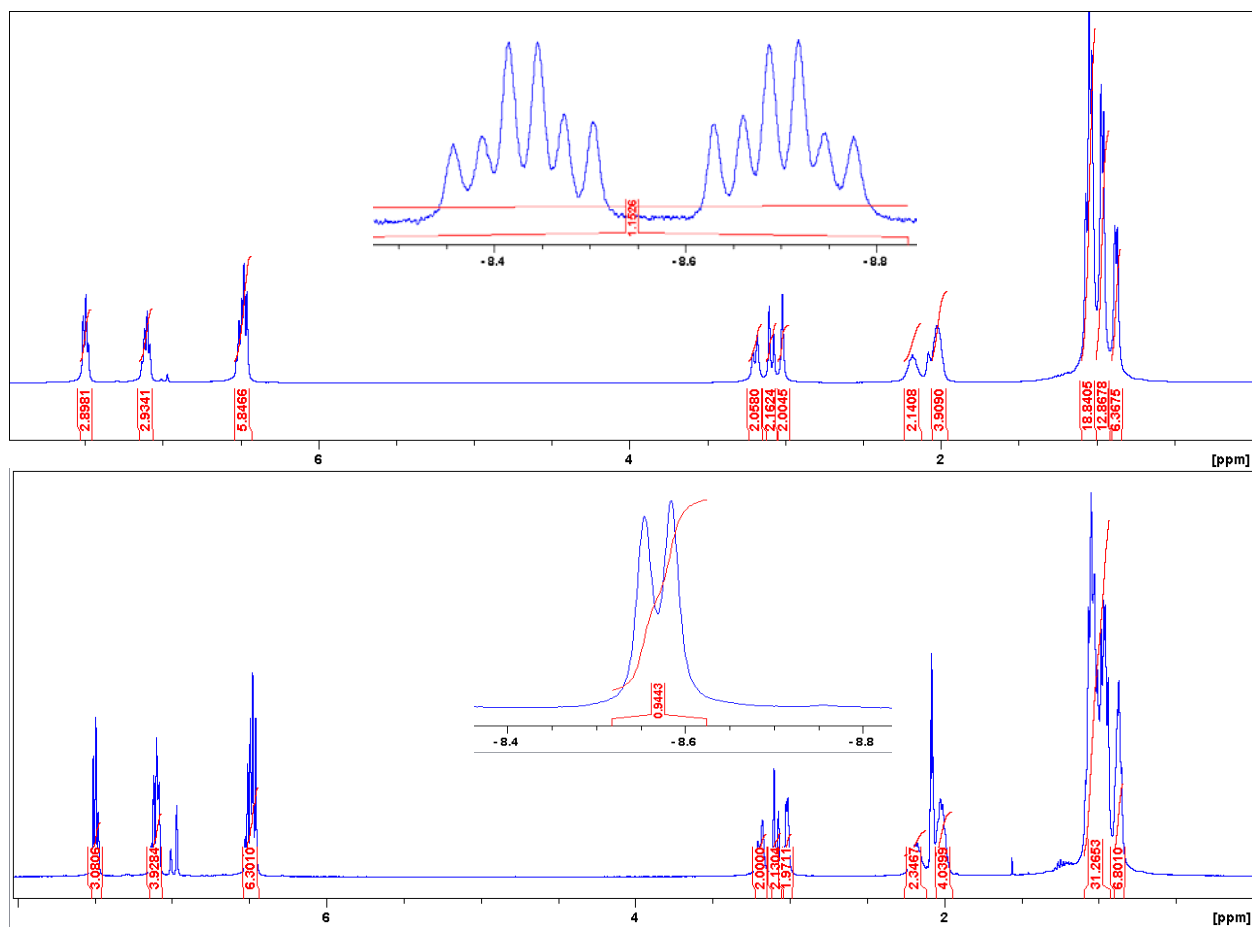


Figure S39. ^1H (top) and $^1\text{H}\{^{31}\text{P}\}$ (bottom) NMR spectra of **2-H** (400 MHz) in $\text{toluene-}d_8$ at 25°C .

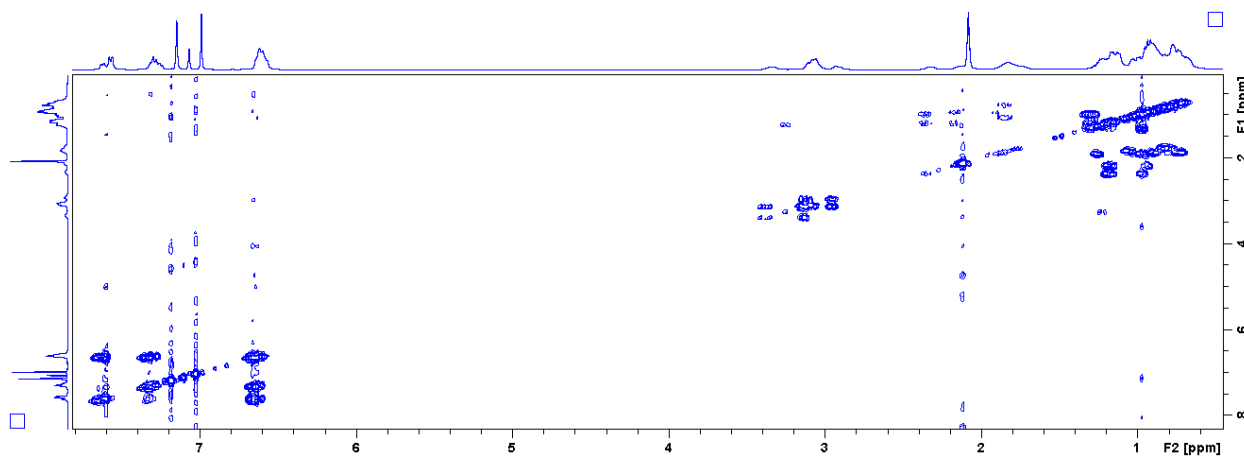


Figure S40. ^1H COSY NMR spectrum of **2-H** (400 MHz) in toluene- d_8 at -73°C .

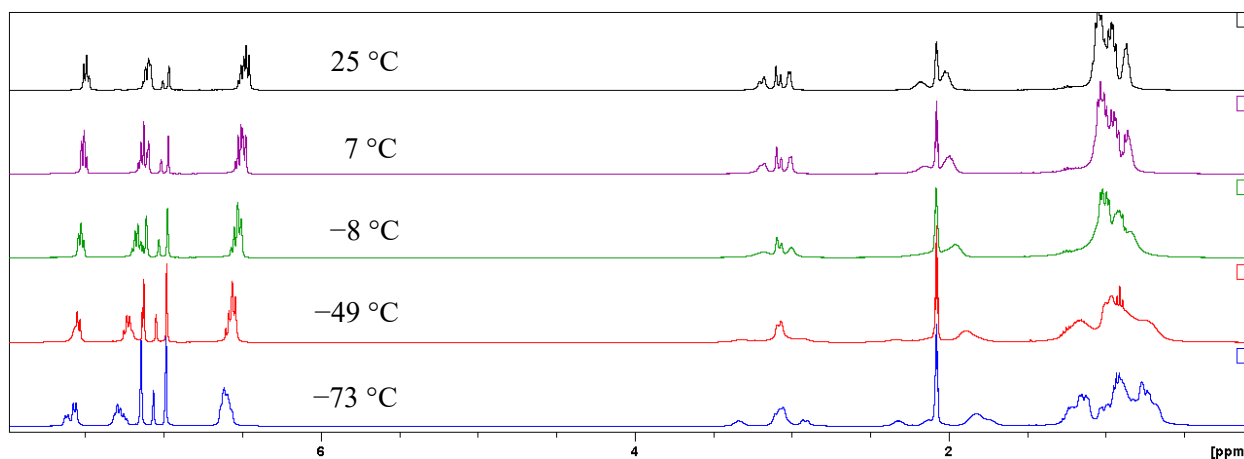


Figure S41. Low temperature VT $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of **2-H** (400 MHz) in toluene- d_8 .

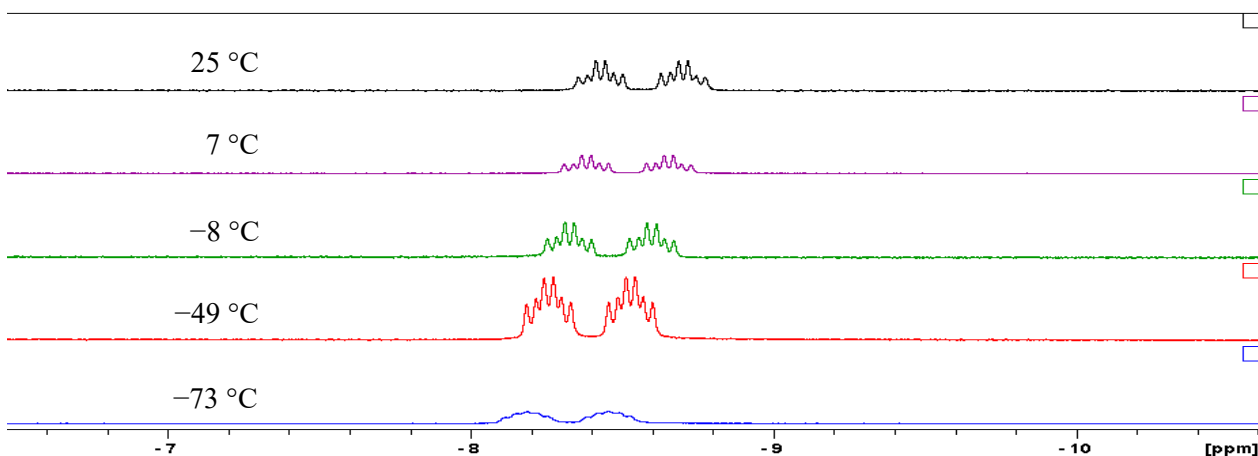


Figure S42. Low temperature VT $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of **2-H** (400 MHz) in toluene- d_8 in hydride region.

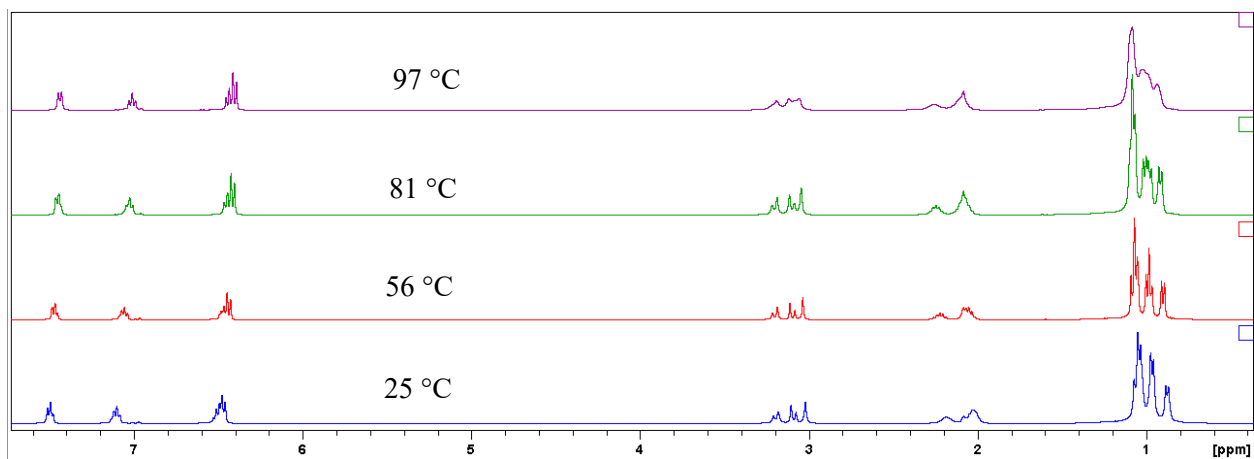


Figure S43. High temperature VT $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of **2-H** (400 MHz) in $\text{toluene-}d_8$.

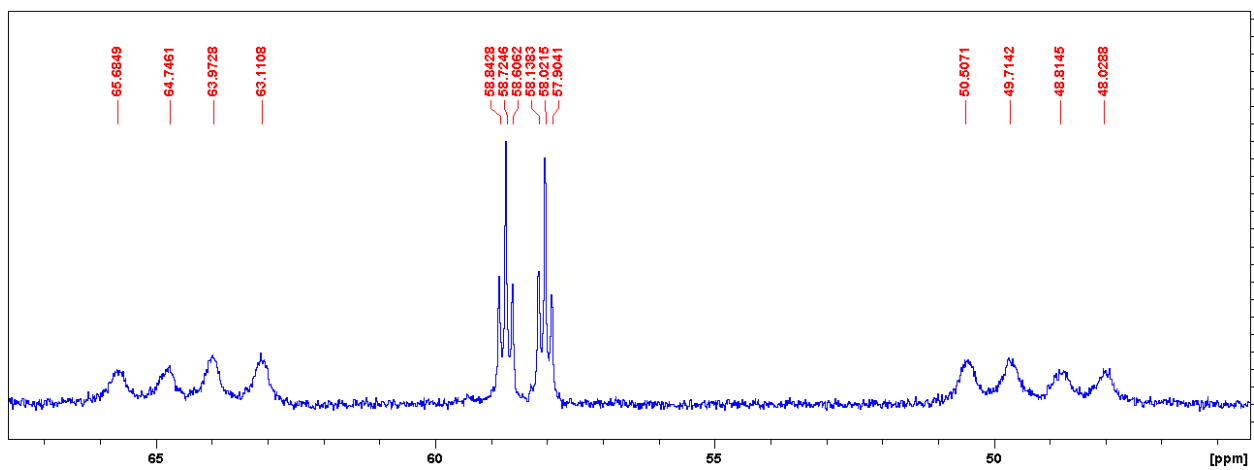


Figure S44. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2-H** (162 MHz) in $\text{toluene-}d_8$ at -49°C .

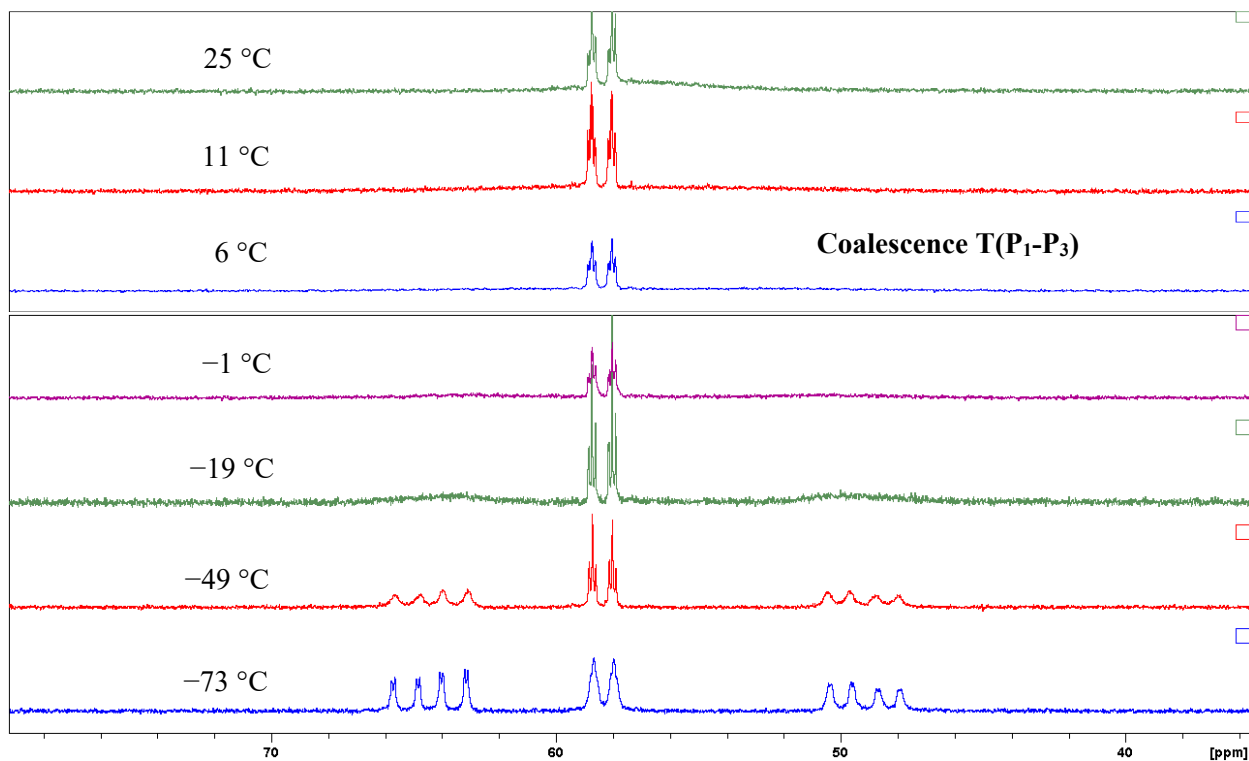


Figure S45. Low temperature VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2-H** (162 MHz) in toluene- d_8 .

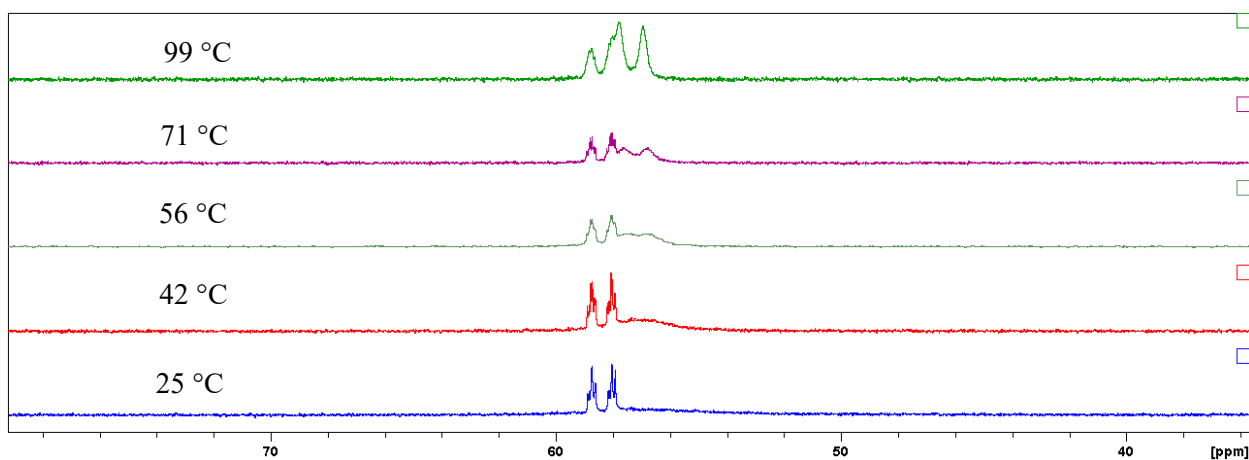


Figure S46. High temperature VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2-H** (162 MHz) in toluene- d_8 . At room temperature, the only visible phosphorus signal corresponds to the phosphine *trans* to the hydride ligand (labeled as P_2 in main text). The other two phosphorus nuclei are not visible at room temperature because they are near coalescence (labeled as P_1 and P_3 in main text). At higher temperatures the two phosphines *cis* to the hydride are equivalent and appear as a doublet, corresponding to both $\text{P}_{1,3}$.

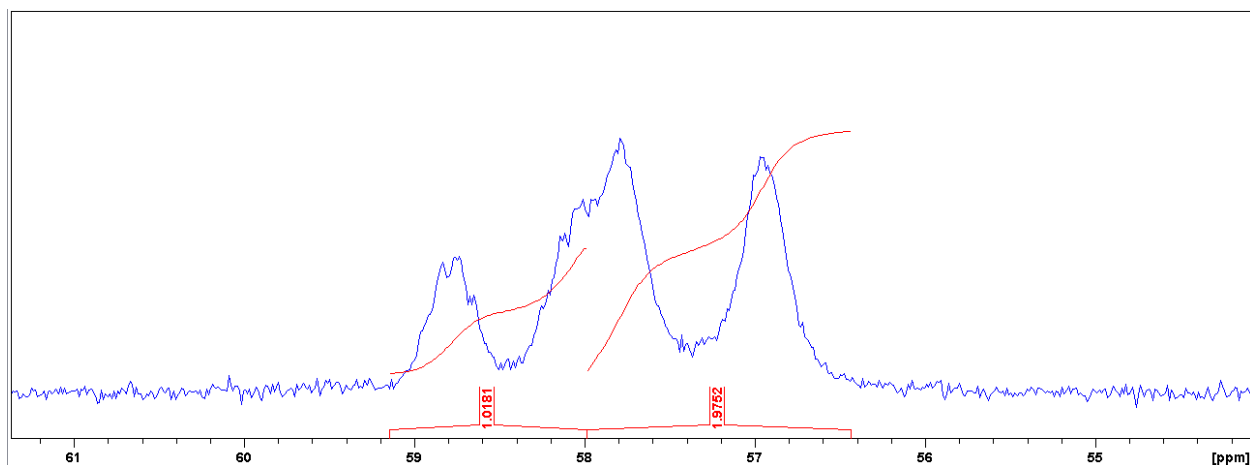


Figure S47. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2-H** (162 MHz) in toluene- d_8 at 97°C.

Table S1. Calculation of approximate rate constants and energy barriers for the fluxional processes that equilibrate P_1 and P_3 for all complexes.

	1-Cl	2-Cl	1-CH3	2-CH3	1-H	2-H
T_c (K)	359	345	>370	>370	265	279
Δ (Hz)	2905.7	3338.9	3493.7	3749.6	2562.8	2482.4
J (Hz)	317	325	314	317	265	273
k_c (s^{-1})	6681	7625	7947	8506	5873	5711
ΔG^\ddagger (kcal/mol)	14.9	14.2	>15.2	>15.2	10.9	11.5

where $k_c = (\pi/\sqrt{2}) \times (\sqrt{\Delta\nu^2 + 6J^2})^{-1}$ for a coupled system and Eyring relationship, $\Delta G^\ddagger = RT_c[23.76 + \ln(T_c/k_c)]$.

References

1. D. Kost; E. H. Carlson; M. Raban. *J. Chem. Soc. D*, **1971**, 13, 656.