SUPPORTING INFORMATION

Capping *nido*-Nonagermanide Clusters with *M*-PPh_3 and Dynamics in Solution: Synthesis and Structure of *closo*-$[(Me_3Si)_3Si]_3Et[Ge_9M](PPh_3)$ (*M* = Ni, Pt)

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Content

1 Crystallographic details on **1** and **2**

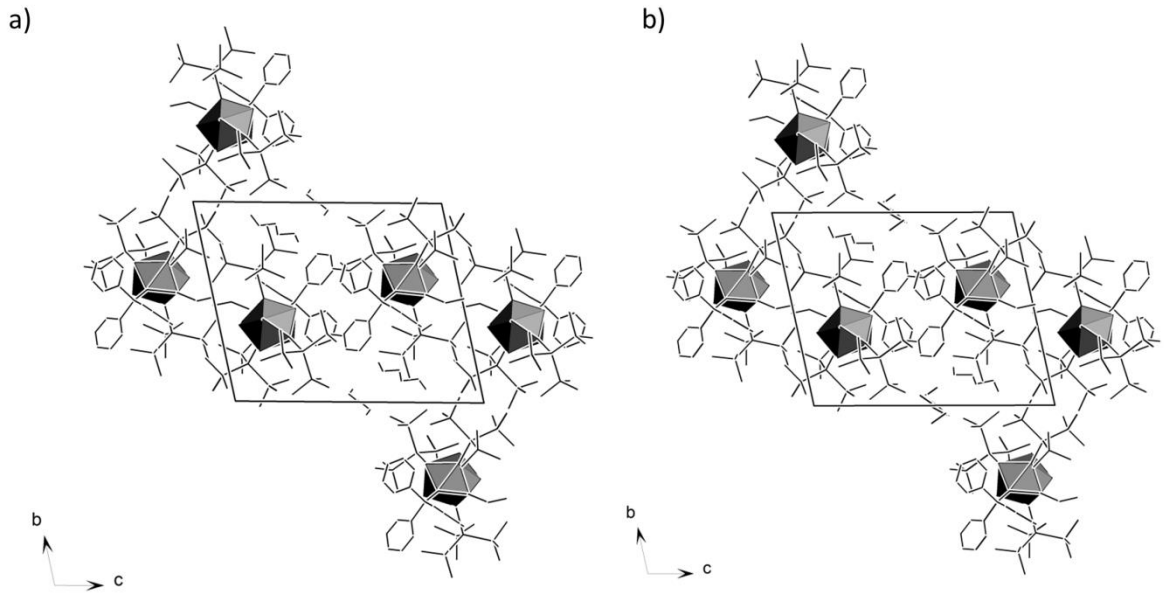

Figure S1. Illustration of the unit cells of a) **1** and b) **2**. [MGe$_9$] cluster cores (M = Ni, Pt) are shown as dark-grey polyhedra. Functionalities and solvent molecules are shown schematically. Hydrogen atoms are omitted for clarity.

Table S1. Selected bond lengths [Å] in **1**.

Ge1 – Ge2	2.4682(6)	Ge3 – Si5	2.422(1)
Ge1 – Ge5	2.5662(6)	Ge3 – Ni	2.6317(6)
Ge1 – Ge7	2.5660(6)	Ge4 – Ge5	2.7638(6)
Ge1 – Ge8	2.7772(7)	Ge4 – Ge6	2.5503(6)
Ge1 – Si1	2.415(1)	Ge4 – Ni	2.4135(6)
Ge1 – Ni	2.6217(7)	Ge5 – Ge6	2.5376(6)
Ge2 – Ge3	2.4730(6)	Ge5 – Ni	2.3984(6)
Ge2 – Ge8	2.7181(6)	Ge6 – Ge7	2.5511(7)
Ge2 – C1	1.983(4)	Ge6 – Ge9	2.5513(6)
Ge2 – Ni	2.3158(6)	Ge6 – Si9	2.398(1)
Ge3 – Ge4	2.5537(6)	Ge7 – Ge8	2.6040(6)
Ge3 – Ge8	2.8020(6)	Ge7 – Ge9	2.7785(6)
Ge3 – Ge9	2.5685(6)	Ge8 – Ge9	2.6111(6)

Table S2. Selected bond lengths [Å] in **2**.

Ge1 – Ge2	2.4756(8)	Ge3 – Si5	2.407(2)
Ge1 – Ge5	2.6032(8)	Ge3 – Pt	2.7676(7)
Ge1 – Ge7	2.5637(8)	Ge4 – Ge5	2.8885(9)
Ge1 – Ge8	2.7613(9)	Ge4 – Ge6	2.5457(8)
Ge1 – Si1	2.404(2)	Ge4 – Pt	2.4990(7)

Ge1 – Pt	2.7672(7)	Ge5 – Ge6	2.5348(8)
Ge2 – Ge3	2.4772(9)	Ge5 – Pt	2.4902(6)
Ge2 – Ge8	2.7432(8)	Ge6 – Ge7	2.5468(9)
Ge2 – C1	1.981(5)	Ge6 – Ge9	2.5460(8)
Ge2 – Pt	2.4365(6)	Ge6 – Si9	2.396(2)
Ge3 – Ge4	2.5880(8)	Ge7 – Ge8	2.5988(8)
Ge3 – Ge8	2.7890(9)	Ge7 – Ge9	2.7497(9)
Ge3 – Ge9	2.5657(8)	Ge8 – Ge9	2.6037(9)

Table S3. Selected bond angles [°] in **1**.

Ni – Ge1 – Ge8	95.26(2)	Ni – Ge2 – Ge8	104.59(2)
Ni – Ge3 – Ge8	94.45(2)	Ge5 – Ge4 – Ge9	90.76(2)
Ge1 – Ni – Ge3	88.02(2)	Ge5 – Ge7 – Ge9	88.83(2)
Ge1 – Ge8 – Ge3	81.72(2)	Ge5 – Ge6 – Ge9	114.87(2)
Ge1 – Ge2 – Ge3	95.24(2)	Ge4 – Ge6 – Ge7	115.07(2)

Table S4. Selected bond angles [°] in **2**.

Pt – Ge1 – Ge8	97.59(2)	Pt – Ge2 – Ge8	106.69(2)
Pt – Ge3 – Ge8	96.93(2)	Ge5 – Ge4 – Ge9	89.34(2)
Ge1 – Pt – Ge3	82.66(2)	Ge5 – Ge7 – Ge9	90.25(2)
Ge1 – Ge8 – Ge3	82.38(2)	Ge5 – Ge6 – Ge9	115.99(3)
Ge1 – Ge2 – Ge3	95.12(3)	Ge4 – Ge6 – Ge7	116.12(3)

2 NMR Spectroscopic Characterization of $[(Me_3Si)_3Si]_3Ge_9Et$

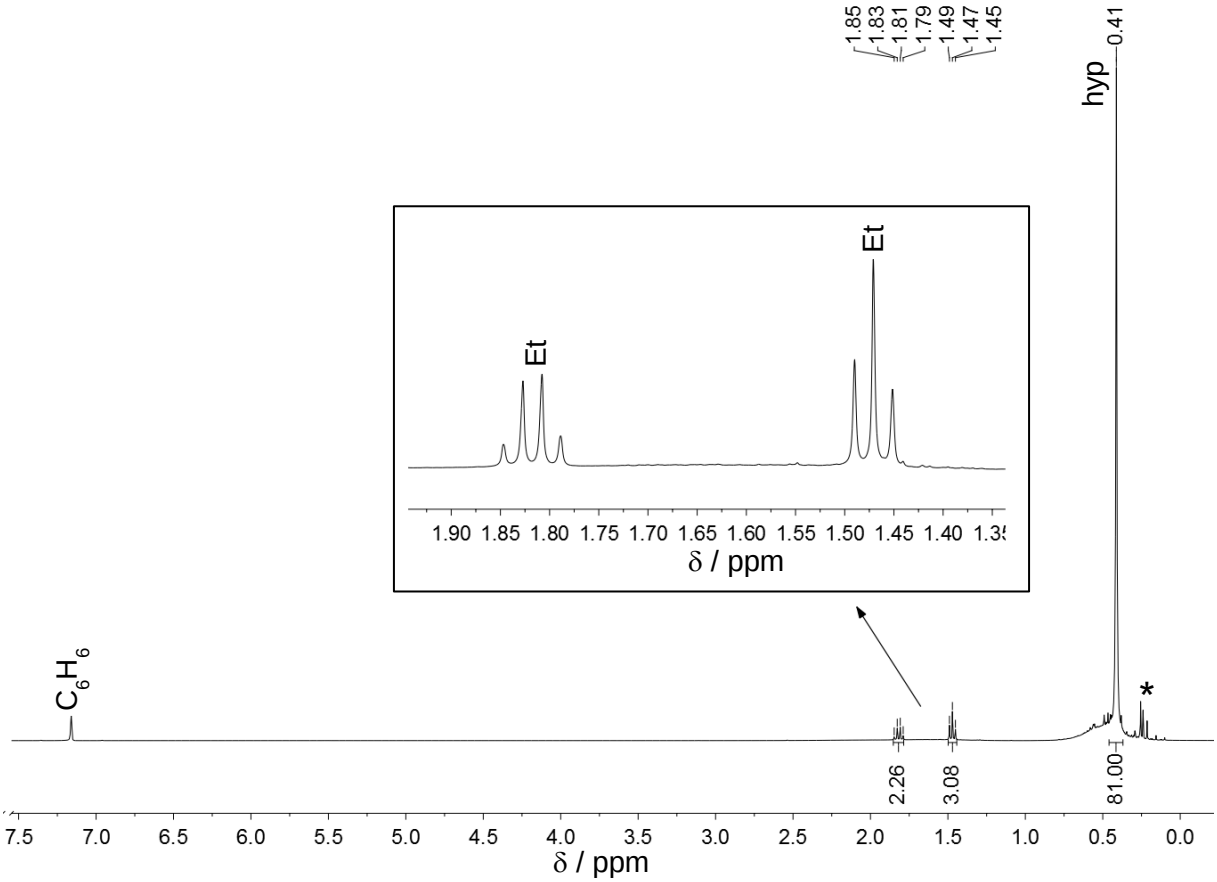

Figure S2. ^{1}H NMR spectrum of the crude product of $[(Me_3Si)_3Si]_3Ge_9Et$ recorded in $[D_6]$benzene at r.t. Signals marked with * could not be assigned.

3 NMR Spectroscopic Characterization of **1**

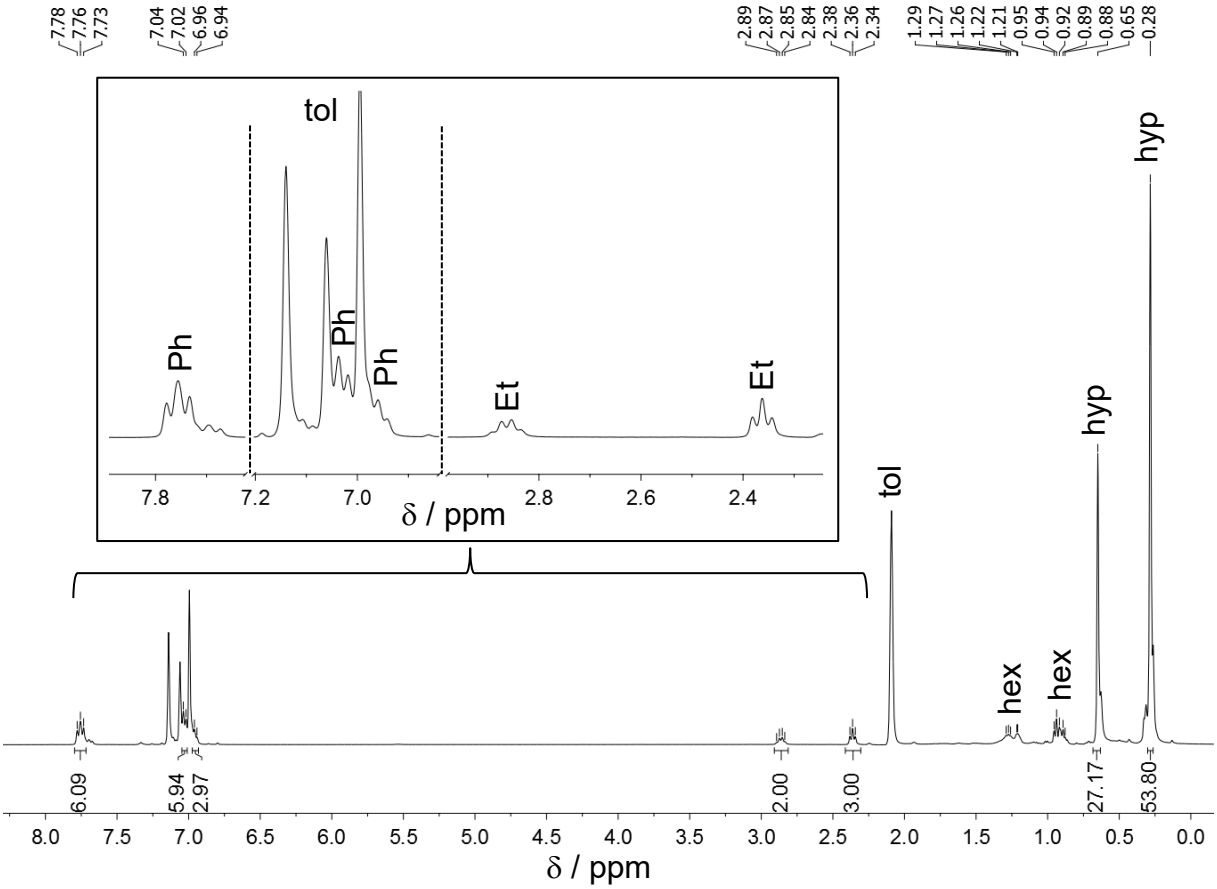

Figure S3. ^{1}H NMR spectrum of dissolved crystals of **1** recorded in [D_8]toluene at −40 °C. The crystals were dissolved at −78 °C to avoid decomposition of the compound. The regions of the phenyl and ethyl groups are shown enlarged. The signals of the hypersilyl groups are marked with hyp, the signals of hexane are marked with “hex”.

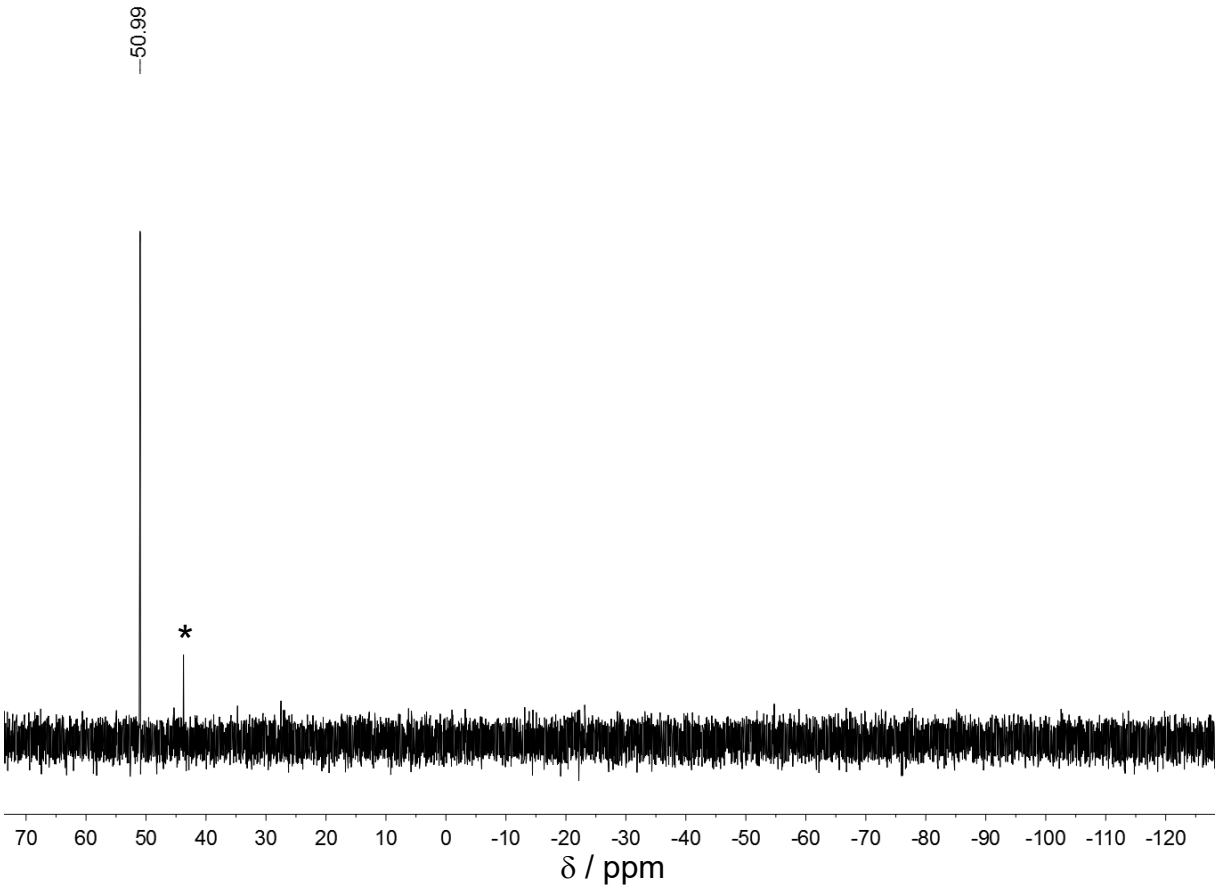

Figure S4. ^{31}P NMR spectrum of dissolved crystals of **1** recorded in [D_8]toluene at −40 °C. The signal marked with * could not be assigned.

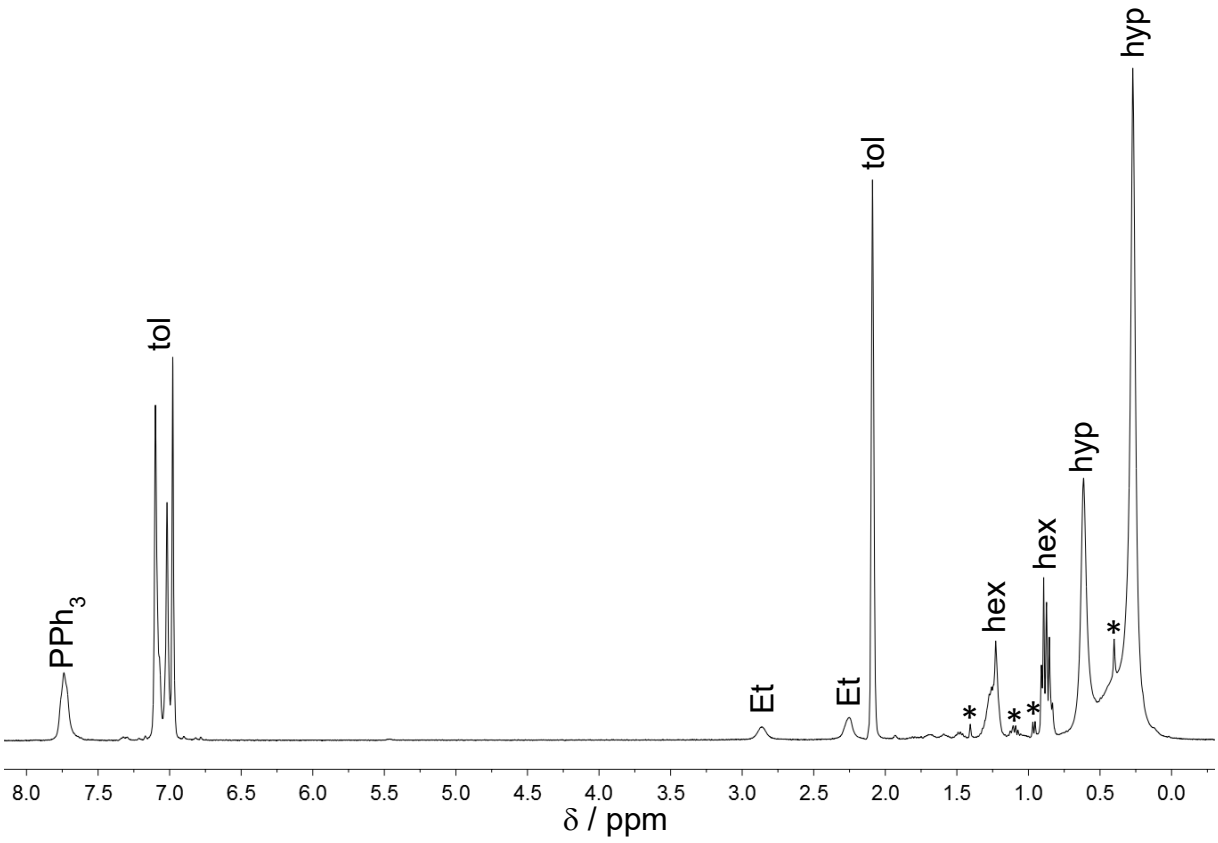

Figure S5. ^{1}H NMR spectrum of dissolved crystals of **1** recorded in [D_8]toluene at 20 °C. The crystals were dissolved at −78 °C.

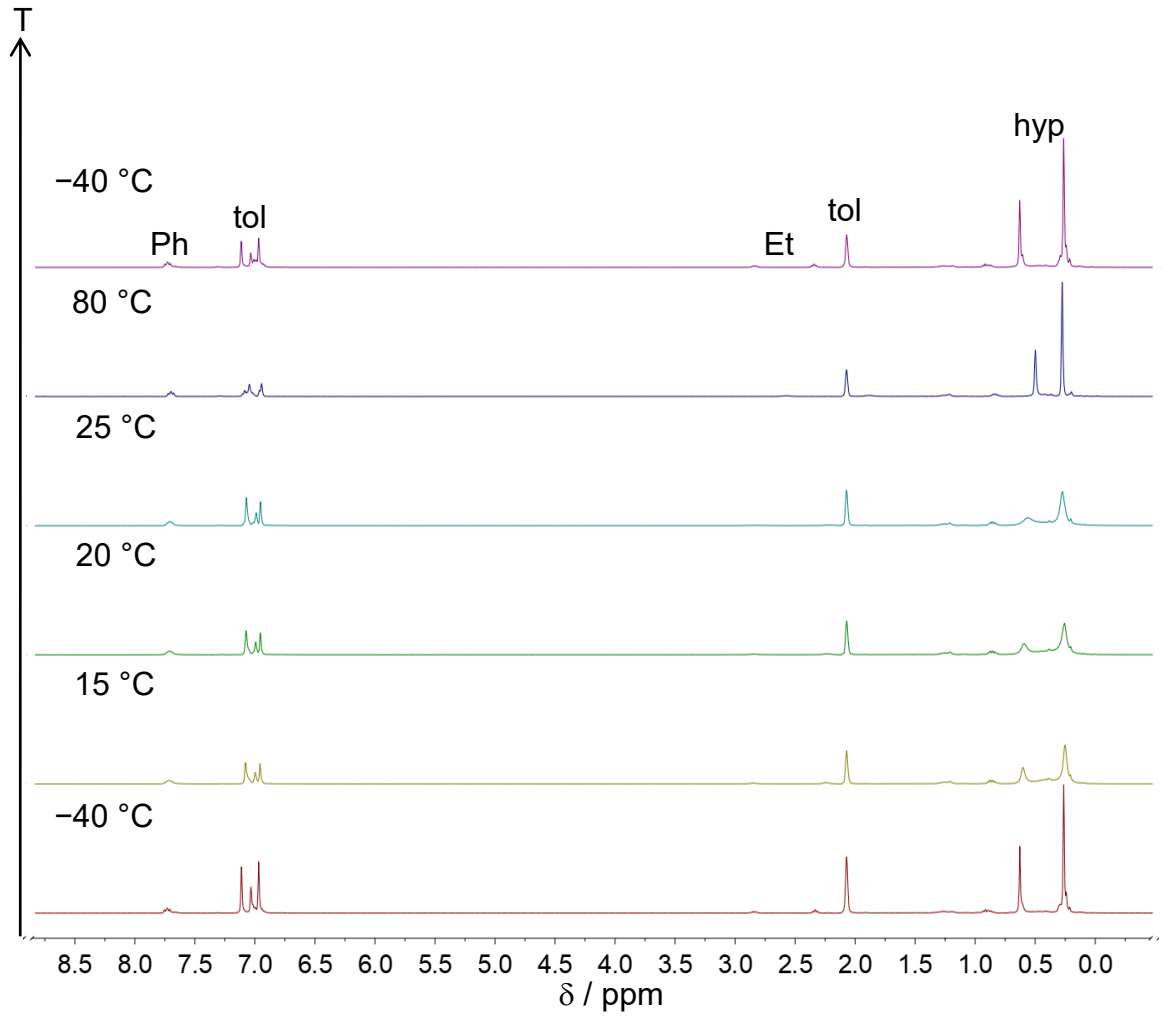

Figure S6. Temperature-dependent ^{1}H NMR spectra of dissolved crystals of **1** recorded in [D_8]toluene.

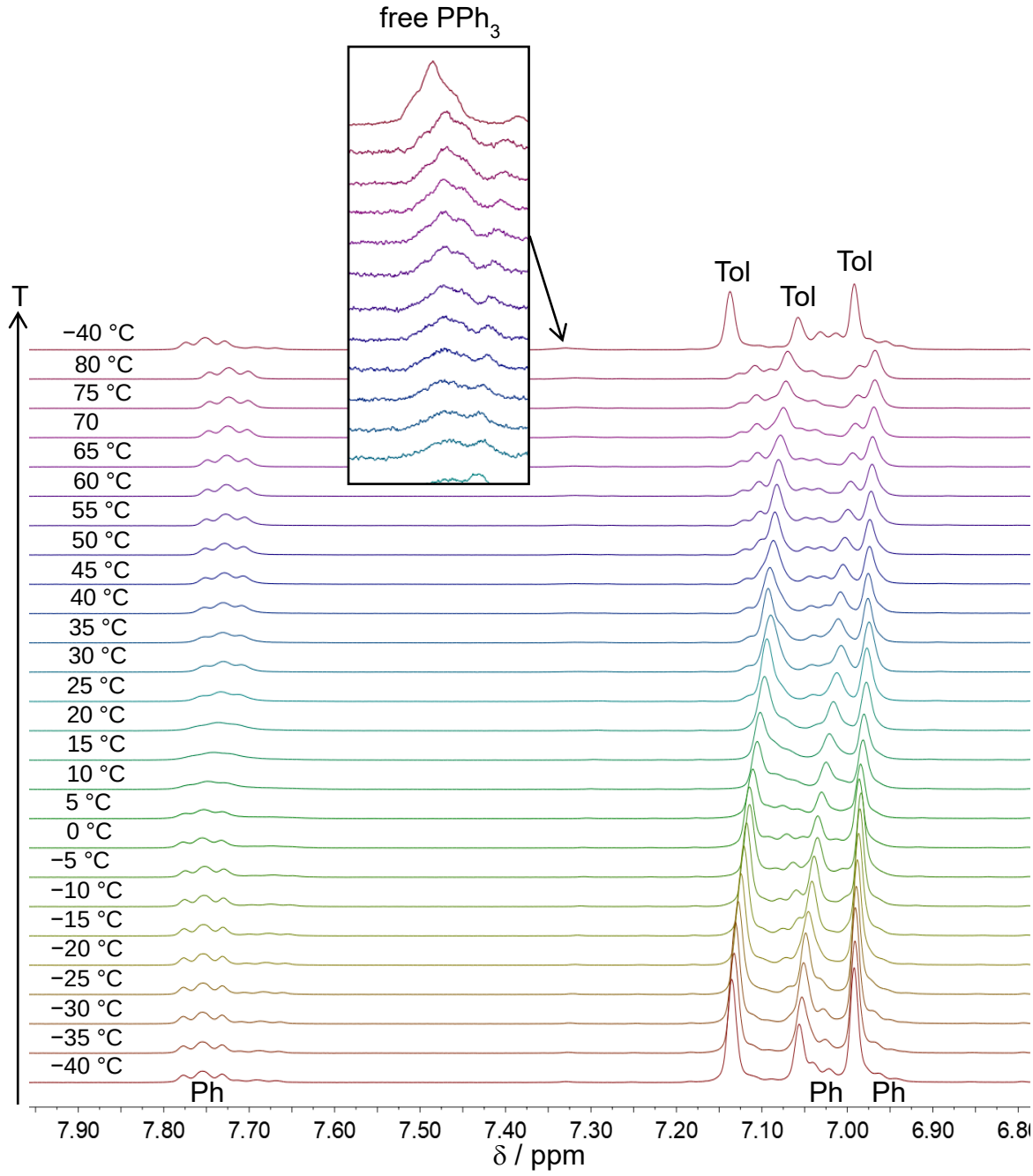

Figure S7. Variable temperature ^{1}H NMR study of crystals of **1** in [D_8]toluene in the range from −40 °C to 80 °C and subsequent cooling to −40 °C. For reasons of clarity only the signals of the triphenylphosphine ligand are shown.

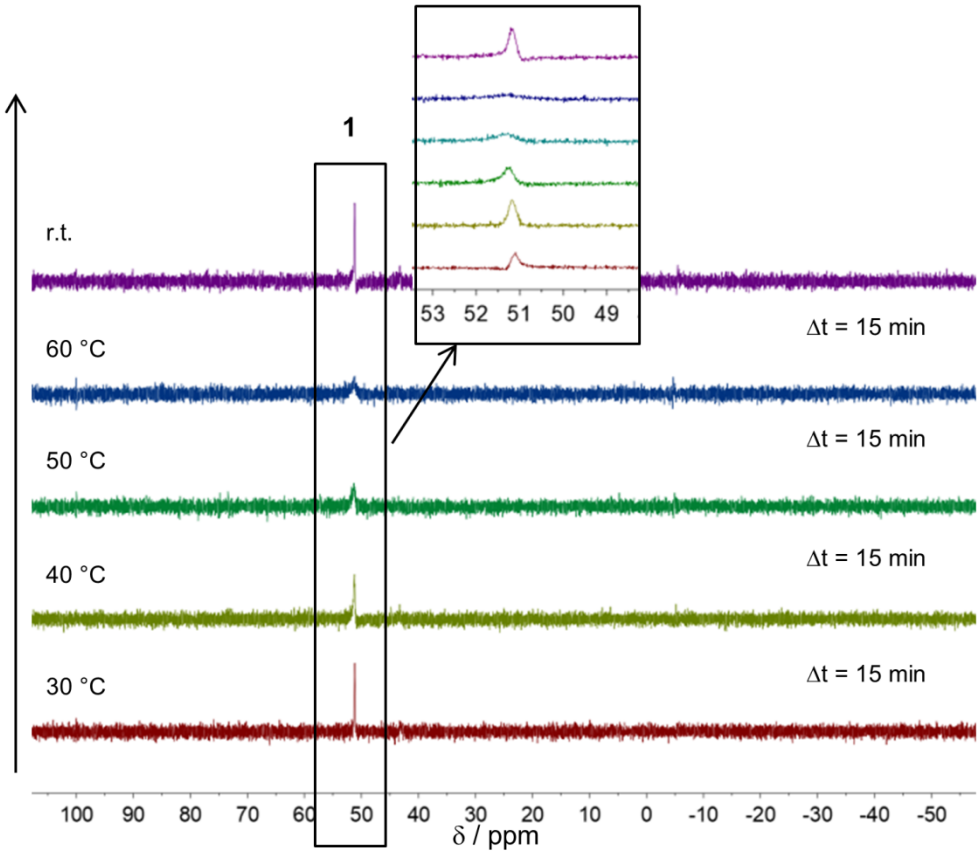

Figure S8. Variable temperature ^{31}P NMR study of crystals of **1** in [D_8]toluene in the range from 30 °C to 60 °C and subsequent cooling to r.t.

4 NMR Spectroscopic Characterization of **2**

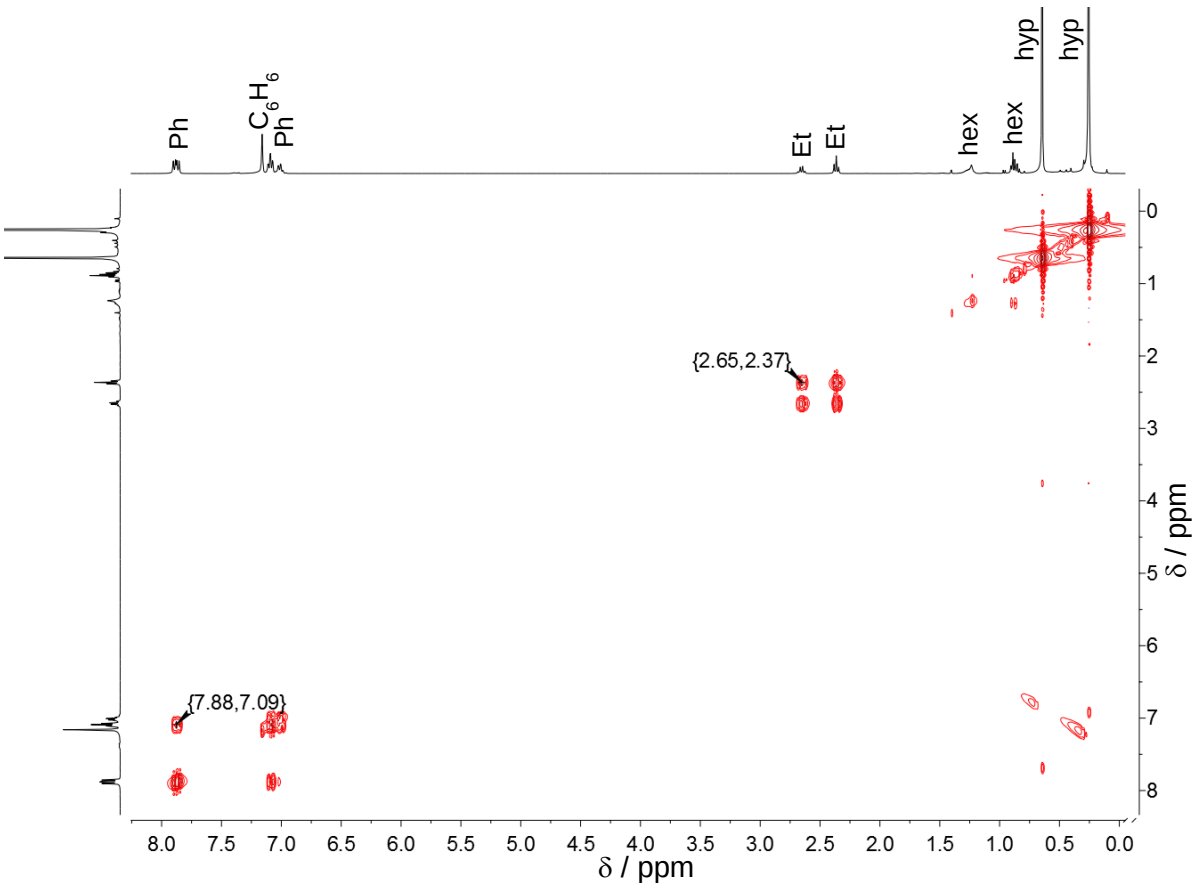

Figure S9. ^{1}H ^{1}H COSY NMR spectrum of dissolved crystals of **2** recorded in [D_6]benzene at r.t.

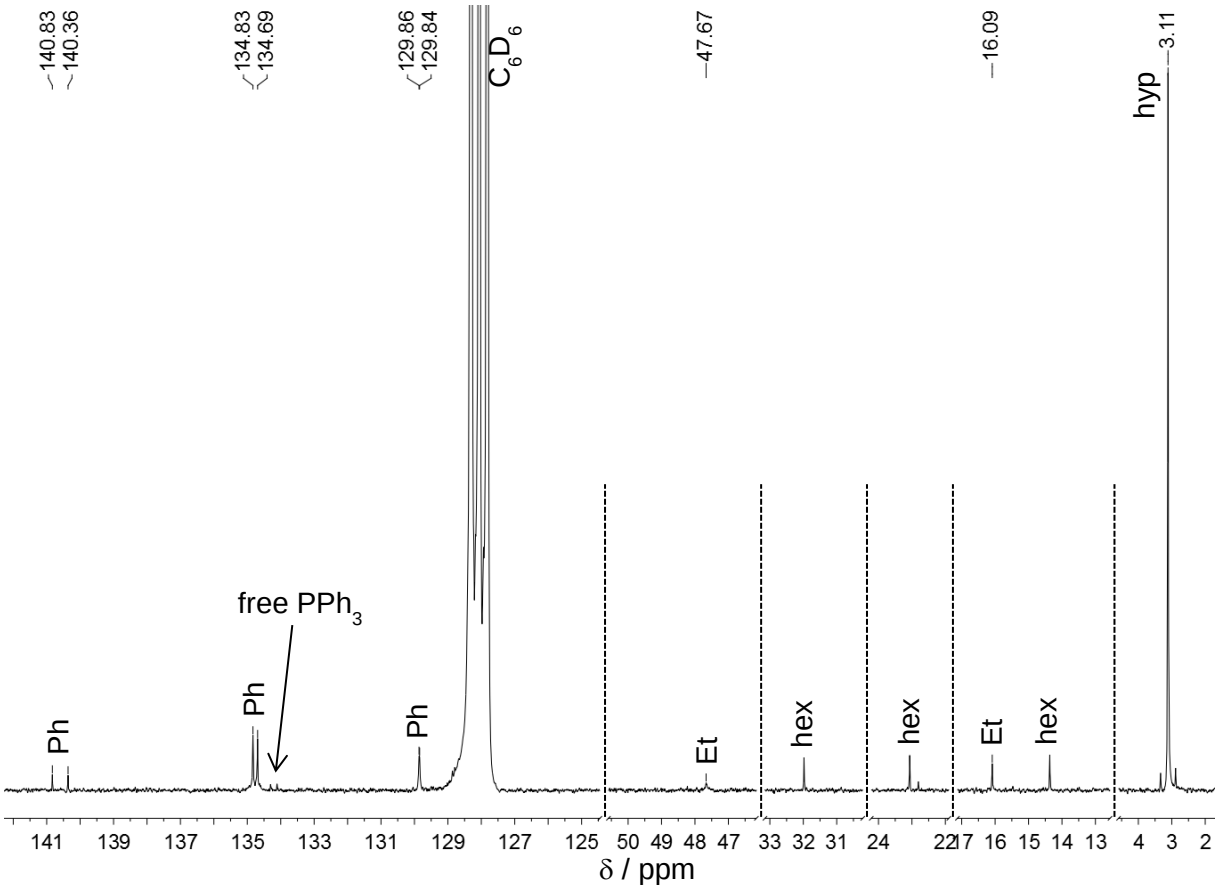

Figure S10. ^{13}C NMR spectrum of dissolved crystals of compound **2** recorded in [D_6]benzene at r.t. Only the relevant regions are depicted for clarity.

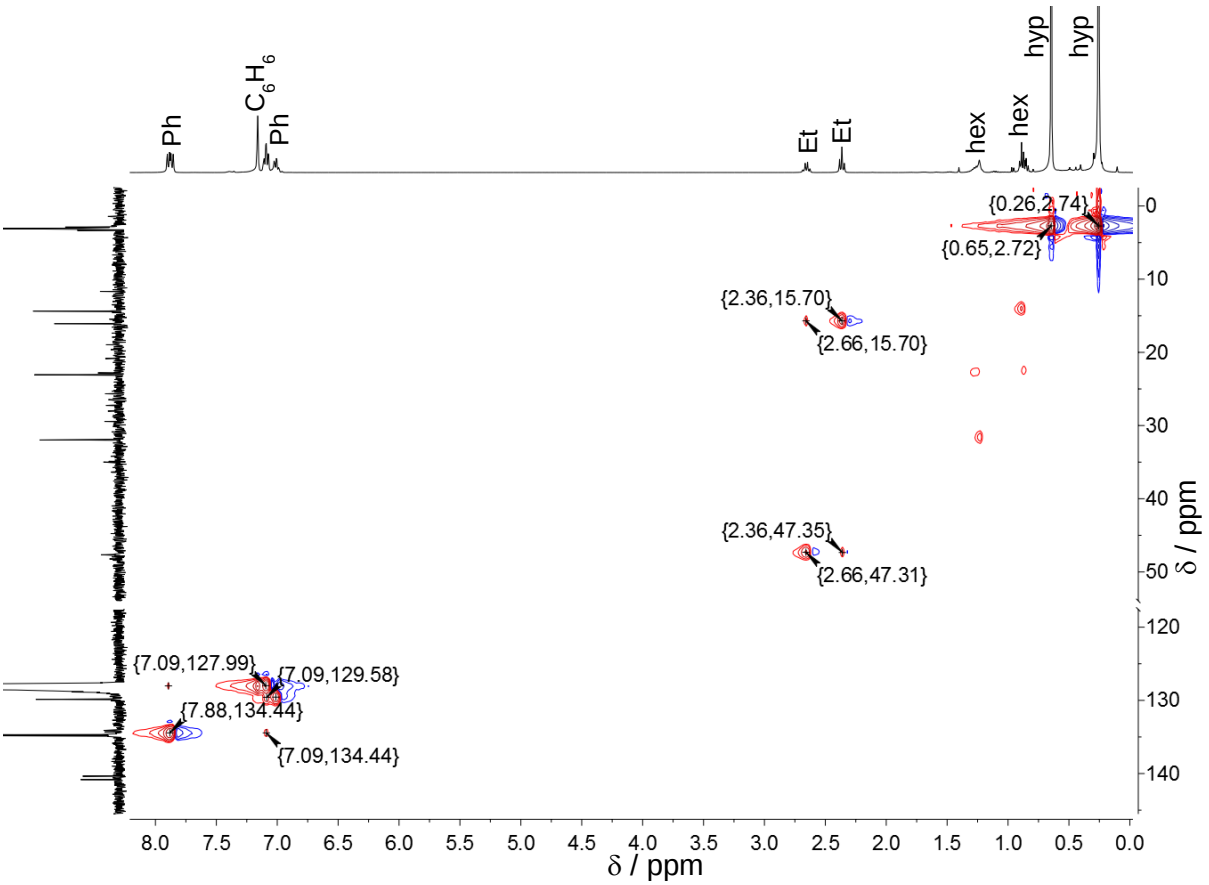

Figure S11. ^{1}H ^{13}C HSQC NMR spectrum of dissolved crystals of **2** recorded in [D_6]benzene at r.t.

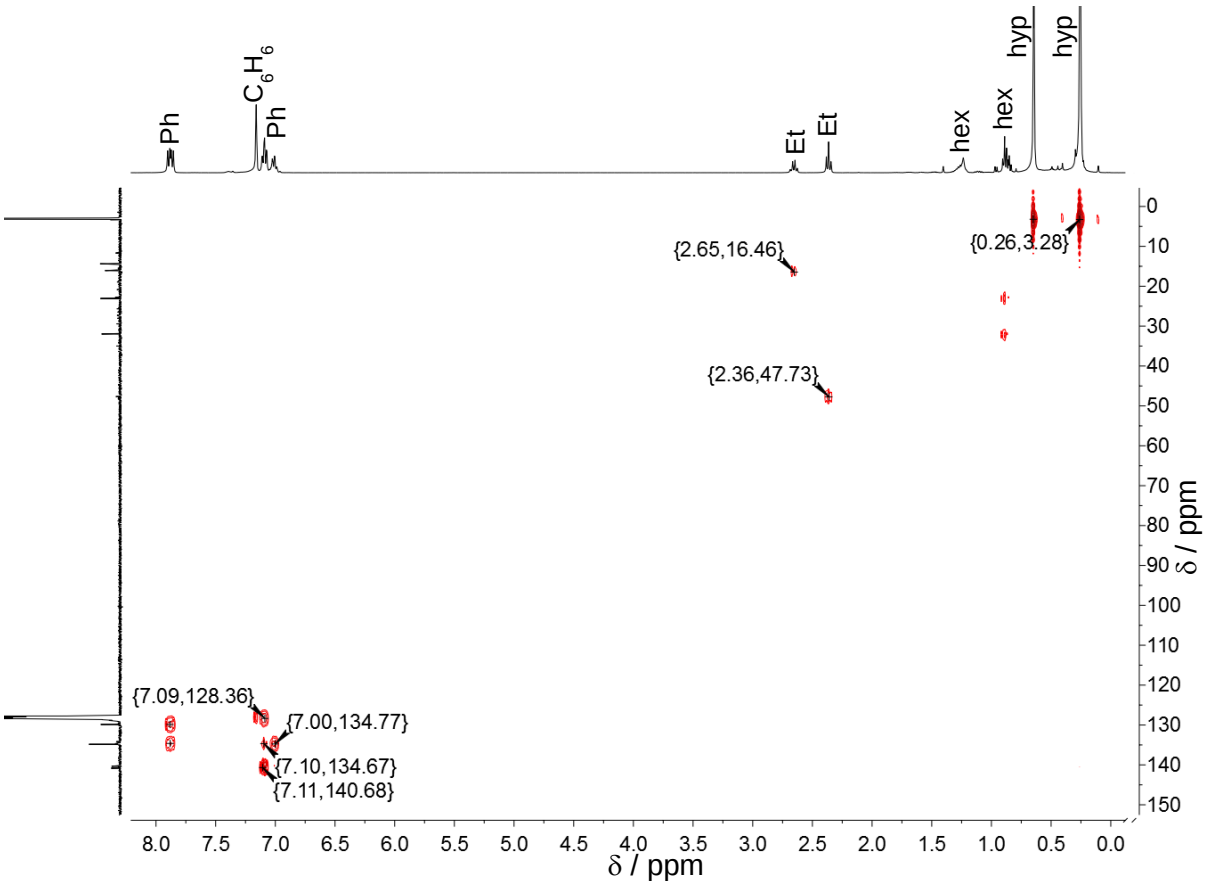

Figure S12. ^{1}H ^{13}C HMBC NMR spectrum of dissolved crystals of **2** recorded in [D_6]benzene at r.t.

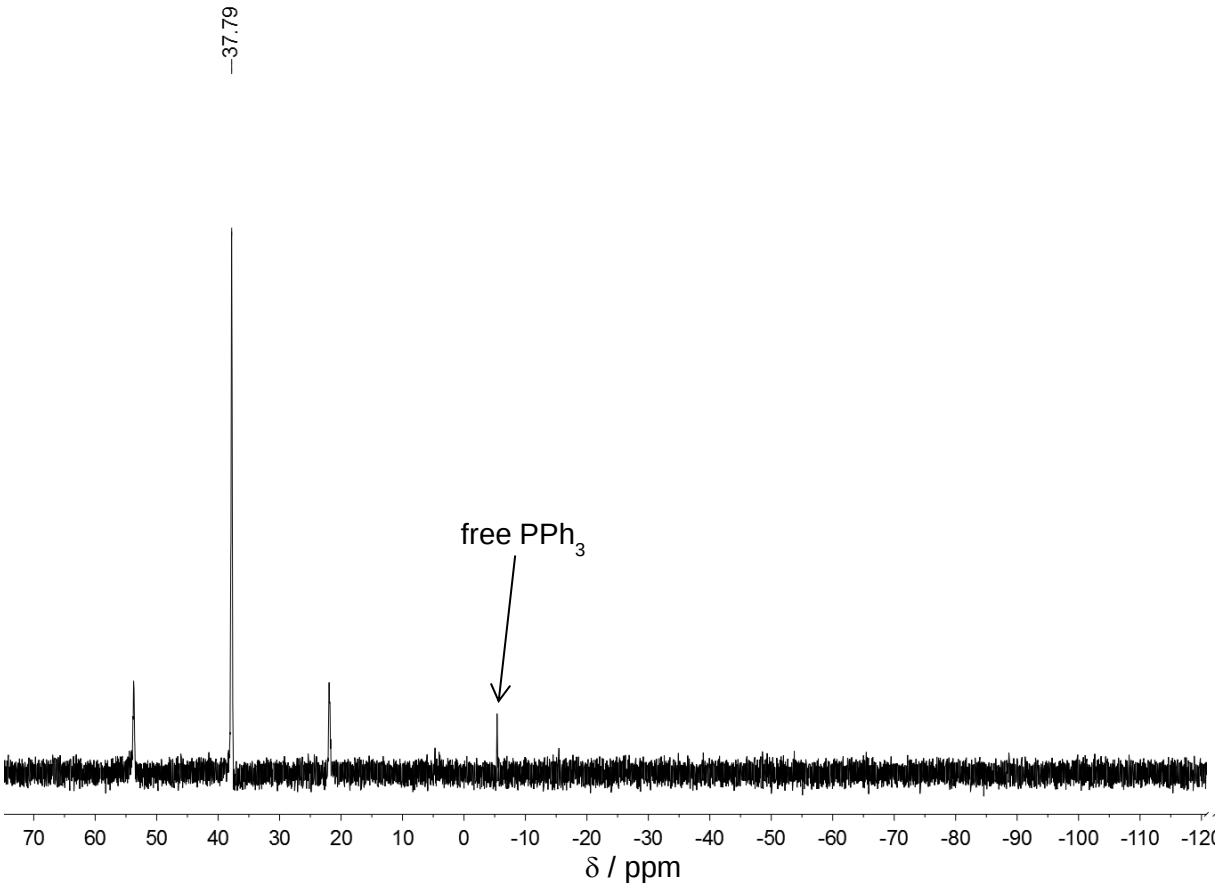

Figure S13. ^{31}P NMR spectrum of dissolved crystals of compound **2** recorded in [D_6]benzene at r.t. The spectrum also shows the coupling of ^{31}P to ^{195}Pt with ^{1}J = 2567 Hz, which is typical for platinum-phosphine complexes.[1]

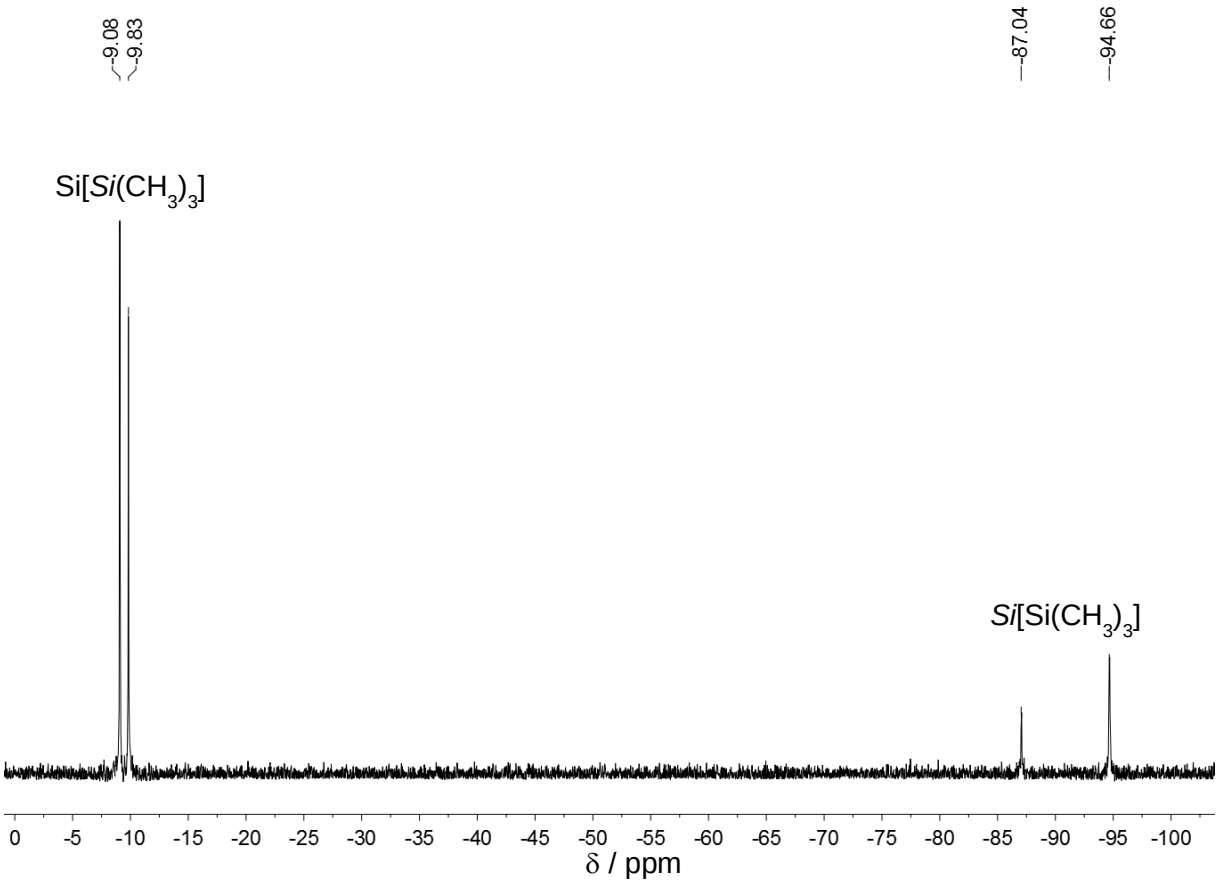

Figure S14. ^{29}Si NMR spectrum of dissolved crystals of compound **2** recorded in [D_6]benzene at r.t.

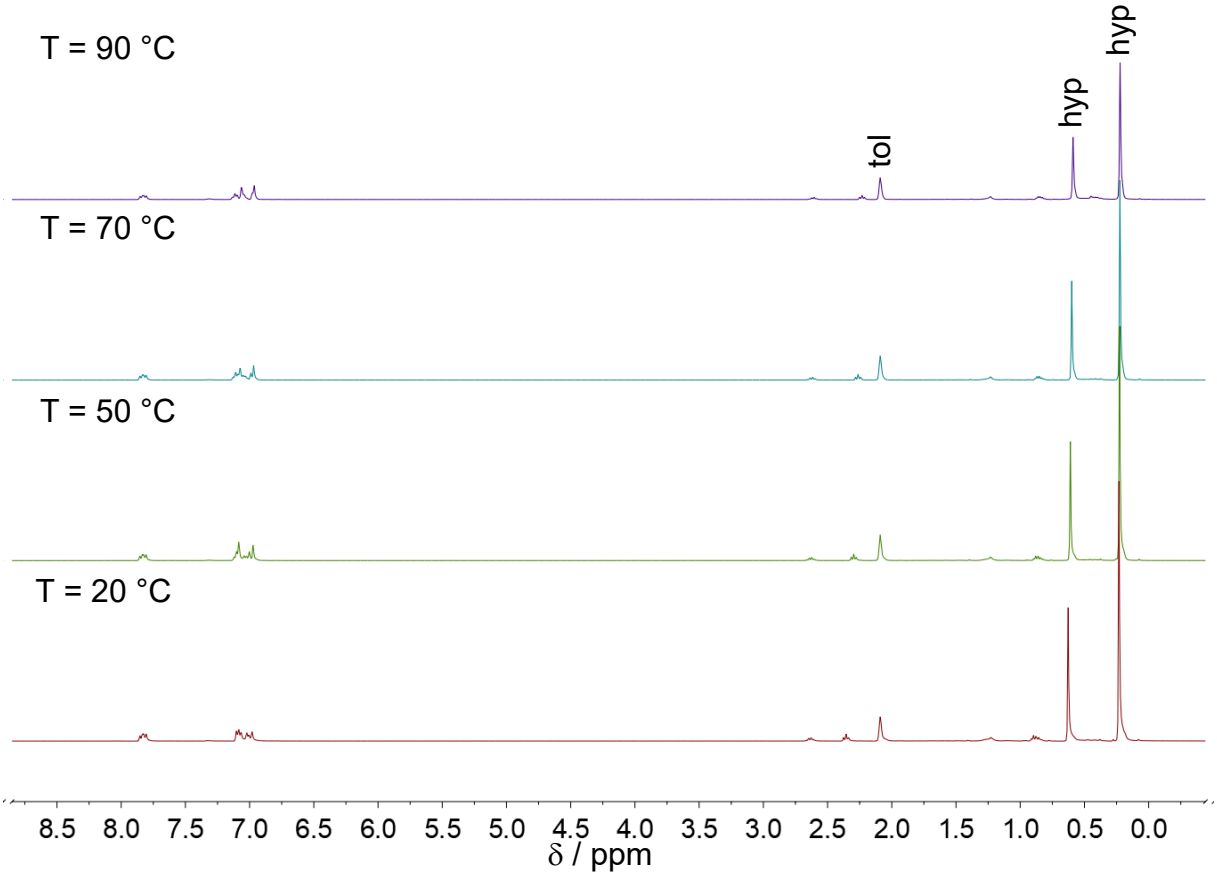

Figure S15. T-resolved ^{1}H NMR study of dissolved crystals of **2** recorded in [D_8]toluene.

5 References

(1) Pidcock, A. *Advances in Chemistry* **1982**, *196*, 1.
(2) Klinger, M.; Schenk, C.; Henke, F.; Clayborne, A.; Schnepf, A.; Unterreiner, A.-N. *Chem. Commun.* **2015**, *51*, 12278.