

Supporting Information for:

**[Ni₃₀S₁₆(PEt₃)₁₁]: An Open-shell Nickel Sulfide Nanocluster with a “Metal-like”
Core**

Alexander J. Touchton, Guang Wu, Trevor W. Hayton*

*Department of Chemistry and Biochemistry, University of California, Santa Barbara,
California 93106, United States*

*hayton@chem.ucsb.edu

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Experimental Details

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions in the glovebox under an atmosphere of dinitrogen, unless otherwise noted. Tetrahydrofuran (THF) was distilled twice, first from calcium hydride and then from sodium benzophenone ketyl and stored over 3 Å molecular sieves for 24 h prior to use. 1,2-dimethoxyethane (DME) was distilled from sodium benzophenone ketyl and stored over 3 Å molecular sieves for 24 h prior to use. Hexanes, diethyl ether, and toluene were dried by passage over activated molecular sieves using a Vacuum Atmospheres DRI-SOLV solvent purification system and stored over 3 Å molecular sieves for 24 h prior to use. Pentane and methylene chloride were dried on an MBraun solvent purification system and stored over activated 3 Å molecular sieves for 24 h prior to use. Acetonitrile was dried over activated 3 Å molecular sieves for 24 h, degassed by bubbling dry N₂ into the solvent for 30 min, cannula transferred into a new vessel, and dried again over 3 Å molecular sieves for 24 h prior to use. Benzene-*d*₆ and toluene-*d*₈ were purchased from Cambridge Isotope Laboratories and dried over activated 3 Å molecular sieves for 24 h prior to use. *Bis*(1,5-cyclooctadiene)nickel(0) (98+%) was purchased from Strem Chemicals and used as received. Triethylphosphine, 99%, was purchased from Sigma-Aldrich and used as received. All other reagents were used as received.

NMR spectra were collected at 25 °C unless otherwise noted. ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on a Bruker Avance NEO 500 MHz spectrometer. ¹H and ¹³C{¹H} NMR spectra were referenced to external SiMe₄ using the residual protio solvent resonances as internal standards.^{1, 2} ³¹P{¹H} NMR spectra were

referenced indirectly to the ^1H chemical shift of SiMe_4 at 0 ppm.^{1,2} Mass spectra were collected at the Materials Research Laboratory Shared Experimental Facilities at the University of California, Santa Barbara, using an electrospray ionization (ESI) source in positive ion mode with a Waters Xevo G2-XS TOF Time-of-Flight mass spectrometer. Model mass spectra were generated in MassLynx V4.1 software with the isotope clusters displayed with a minimum abundance of 0.1%. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer. Elemental analyses were performed by the Micro-Mass Facility at the University of California, Berkeley.

Magnetism Measurements. Magnetic properties were recorded using a Quantum Design Magnetic Property Measurement 5XL Super Conducting Quantum Interference Device (MPMS 5XL SQUID) magnetometer. All loading equipment, including quartz wool and borosilicate glass NMR tubes, were oven-dried at 120 °C for 24 h prior to use. Complex **1** (18.0 mg, 0.00504 mmol) was sandwiched between two plugs of high purity quartz wool (72.4 mg total) in a 5 mm borosilicate glass NMR tube that was flame-sealed at one end, and tightly packed to a length of ~ 2 cm. Nitrile gloves were worn over glovebox gloves during sample loading, and contact with quartz wool was minimized to prevent contamination. A vacuum adaptor was attached to the open end of the borosilicate glass NMR tube, and the sample was subsequently flame-sealed under static vacuum. The experiments for complex **1** were performed between 2 and 300 K at an applied field of 10,000 Oe. Diamagnetic correction was made using Pascal's constants ($\chi_{\text{dia}} = -2.02945 \times 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1}$).³ Data were not corrected for the contribution of the straw sample holder, borosilicate glass NMR tube, or quartz wool.

Synthesis of $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]$ (1). A 20 mL scintillation vial equipped with a magnetic stir bar was charged with $[\text{Ni}(1,5\text{-cod})_2]$ (0.5153 g, 1.873 mmol), toluene (5 mL), and triethylphosphine (0.42 mL, 2.9 mmol). To this solution was added a suspension of S_8 (0.0300 g, 0.117 mmol) in toluene (2 mL), which resulted in an immediate color change to dark brown. Additional portions of toluene (2×1 mL) were used to transfer all of the S_8 . After stirring for 5 min, the reaction mixture was pipetted into a 50 mL Cajon flask equipped with a Teflon rototflow valve. Additional portions of toluene (3×1.5 mL) were used to transfer all the residue from the vial to the flask; the stir bar was also added to the flask. The flask was sealed and removed from the glovebox, whereupon the solution was heated in an oil bath at 115 °C for 16 h with stirring. After 16 h, the flask was brought back into the glovebox and transferred to a 20 mL scintillation vial. The volatiles were removed in vacuo to provide a brown solid. The solid was then rinsed with acetonitrile (10 mL) and the rinsings (containing the majority of the Et_3PS) were discarded. The remaining undissolved solid was dried *in vacuo*, dissolved in a mixture of THF and hexanes (5 mL THF/5 mL hexanes), and filtered through a Celite column supported on glass wool (0.5 cm \times 5 cm) to provide a deep brown filtrate. Additional portions of THF/hexanes (1:1 v/v solution, 3×2 mL) and then portions of THF (2×0.5 mL) were used to rinse the Celite plug. The filtrate was then concentrated in vacuo to 3 mL. Storage of this solution at -25 °C for 15 d resulted in the deposition of a black, crystalline solid, which was isolated by decanting the supernatant (0.0184 g, 8% yield by $[\text{Ni}(1,5\text{-cod})_2]$). An additional crop of crystals was obtained by concentrating the supernatant further (2 mL), followed by storage at -25 °C for 6 d (0.0118 g; 0.0302 g total, 14% total yield by

[Ni(1,5-cod)₂]]. Crystals of **1** suitable for X-ray crystallography were grown from the slow evaporation of a toluene/diethyl ether (1:10 v:v) solution of **1** that was permitted to slowly evaporate over the course of three weeks at -25 °C. Anal. Calcd for C₆₆H₁₆₅Ni₃₀P₁₁S₁₆: C, 22.18; H, 4.65. Found: C, 21.79; H, 4.65. ¹H NMR (500 MHz, 25 °C, benzene-*d*₆): δ 9.43 (br s, P(CH₂CH₃)₃, 12 H), 5.05 (br m, P(CH₂CH₃)₃, 18 H), 3.40 (br m, P(CH₂CH₃)₃, 24 H), 2.13 (br s, P(CH₂CH₃)₃, 36 H), 1.51 (br s, P(CH₂CH₃)₃, 18 H), 1.30 (br s, P(CH₂CH₃)₃, 12 H), 1.15 (br s, P(CH₂CH₃)₃, 27 H), 0.58 (br s, P(CH₂CH₃)₃, 18 H). ¹³C{¹H} NMR (126 MHz, 25 °C, benzene-*d*₆): δ 43.82 (s, P(CH₂CH₃)₃), 35.29 (s, P(CH₂CH₃)₃), 29.86 (s, P(CH₂CH₃)₃), 25.18 (s, P(CH₂CH₃)₃), 22.72 (s, P(CH₂CH₃)₃ overlapping with an *n*-pentane resonance), 21.93 (s, P(CH₂CH₃)₃), 15.40 (s, P(CH₂CH₃)₃), 11.86 (s, P(CH₂CH₃)₃). ³¹P{¹H} NMR (203 MHz, 25 °C, C₆D₆): δ 2050 (2P), 836 (3P), 238 (2P), 25 (4P). ³¹P{¹H} NMR (203 MHz, 25 °C, C₇D₈): δ 2054 (2P), 842 (3P), 246 (2P), 30 (4P). ³¹P{¹H} NMR (203 MHz, 15 °C, C₇D₈): δ 2071 (2P), 850 (3P), 235 (2P), 9.54 (4P). ³¹P{¹H} NMR (203 MHz, 5 °C, C₇D₈): δ 2086 (2P), 859 (3P), 221 (2P), -17.92 (4P). ³¹P{¹H} NMR (203 MHz, -5 °C, C₇D₈): δ 2100 (2P), 870 (3P), 209 (2P), -47.2 (4P). ³¹P{¹H} NMR (203 MHz, -15 °C, C₇D₈): δ 2110 (2P), 881 (3P), 200 (2P), -78.4 (4P). ³¹P{¹H} NMR (203 MHz, -25 °C, C₇D₈): δ 2120 (2P), 894 (3P), 193 (2P), -112 (4P). Evans' method (500 MHz, 423.0 mg of benzene-*d*₆, 33.8 mg of PhF, 15.1 mg of **1**, 25 °C): Δν = 163.0 Hz, 4.64 μB, 2.70 cm³ K/mol. (. ESI-MS (THF, positive ion mode, 2.50 kV): 3572.43 *m/z* ([Ni₃₀S₁₆(PEt₃)₁₁]⁺, [**1**]⁺, calcd 3572.57 *m/z*), 1786.20 *m/z* ([Ni₃₀S₁₆(PEt₃)₁₁]²⁺, [**1**]²⁺, calcd 1787.30 *m/z*). IR (KBr pellet, cm⁻¹): 411 (s), 611 (s), 702 (m), 723 (m), 756 (s), 989 (s), 1024 (s), 1120 (w), 1171 (w), 1240 (s), 1369 (m), 1402 (s), 1448 (s), 2870 (vs), 2922 (vs), 2951 (vs).

Isolation of $[\text{Ni}_{26}\text{S}_{14}(\text{PEt}_3)_{10}]$ (2**).** A 20 mL scintillation vial equipped with a magnetic stir bar was charged with $[\text{Ni}(1,5\text{-cod})_2]$ (437.0 mg, 1.589 mmol), toluene (7 mL), and triethylphosphine (0.24 mL, 1.62 mmol). To this solution was added a suspension of S_8 (25.5 mg, 0.0994 mmol) in toluene (1 mL), which resulted in an immediate color change to dark brown. Additional portions of toluene (2×1 mL) were used to transfer all of the S_8 . After stirring for 5 min, the reaction mixture was pipetted into a 50 mL Cajon flask equipped with a Teflon rototflow valve. Additional portions of toluene (3×1.5 mL) were used to transfer the remaining residue from the vial to the flask; the stir bar was also added to the flask. The flask was sealed and removed from the glovebox, whereupon the solution was heated in an oil bath at 95 °C for 5 h. After 5 h, the flask was brought back into the glovebox and the solution was filtered through a Celite column supported on glass wool (0.5 cm \times 5 cm) to provide a deep brown filtrate. An aliquot (1 mL) was removed from the filtrate, dried *in vacuo*, re-dissolved in benzene- d_6 (0.5 mL), and assayed by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Figure S37). The aliquot was then returned to the filtrate, and the volume of the solution was reduced *in vacuo* to 1 mL and the solution was layered with pentane (19 mL). Storage of this solution at -25 °C for 3 d resulted in the deposition of a mixture of black solids and colorless crystals (65 mg), which were isolated by decanting the supernatant. The solids were dried *in vacuo* and then rinsed acetonitrile (8 mL). The rinsings were discarded. The remaining undissolved solids were dissolved in toluene (5 mL) and filtered through a Celite column supported on glass wool (0.5 cm \times 5 cm) to provide a dark brown filtrate. The filtrate was dried *in vacuo* to provide a dark brown solid (40 mg), which consisted of a mixture of **2** and **1** in a 1:1 ratio (as assayed

by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy). This solid was then redissolved in toluene (5 mL) and filtered through a Celite column supported on glass wool (0.5 cm \times 5 cm) to provide a pale brown filtrate. The filtrate was concentrated *in vacuo* to 1 mL and layered with pentane (19 mL). Storage of this solution at $-25\text{ }^\circ\text{C}$ for 5 d resulted in the deposition of deep brown crystalline solids (8.8 mg, 5% yield by Ni). Crystals of **2** suitable for X-ray crystallography were grown from a toluene/pentane (0.5 mL/3.5 mL) solution left to slowly evaporate for one week at $-25\text{ }^\circ\text{C}$. ^1H NMR (500 MHz, $25\text{ }^\circ\text{C}$, C_6D_6): δ 21.38 (s, $\text{P}(\text{CH}_2\text{CH}_3)_3$, 12 H), 6.04 (q, $J_{\text{HH}} = 7.4\text{ Hz}$, $\text{P}(\text{CH}_2\text{CH}_3)_3$, 12 H), 5.54 (q, $J_{\text{HH}} = 7.4\text{ Hz}$, $\text{P}(\text{CH}_2\text{CH}_3)_3$, 12 H), 4.60 (q, $J_{\text{HH}} = 7.5\text{ Hz}$, $\text{P}(\text{CH}_2\text{CH}_3)_3$, 12 H), 2.77 (q, $J_{\text{HH}} = 7.6\text{ Hz}$, $\text{P}(\text{CH}_2\text{CH}_3)_3$, 12H), 1.84 (t, $J_{\text{HH}} = 7.4\text{ Hz}$, $\text{P}(\text{CH}_2\text{CH}_3)_3$, 18H), 1.77 (t, $J_{\text{HH}} = 7.4\text{ Hz}$, $\text{P}(\text{CH}_2\text{CH}_3)_3$, 36H), 1.16 (t, $J_{\text{HH}} = 7.1\text{ Hz}$, $\text{P}(\text{CH}_2\text{CH}_3)_3$, 18H), 1.00 (m, $\text{P}(\text{CH}_2\text{CH}_3)_3$, 18H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, $25\text{ }^\circ\text{C}$, C_6D_6): δ 5730 (2P), 912 (2P), 606 (2P), 179 (4P). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): δ 73.44 ($\text{P}(\text{CH}_2\text{CH}_3)_3$), 35.47 ($\text{P}(\text{CH}_2\text{CH}_3)_3$), 32.59 ($\text{P}(\text{CH}_2\text{CH}_3)_3$), 26.19 ($\text{P}(\text{CH}_2\text{CH}_3)_3$), 22.73 ($\text{P}(\text{CH}_2\text{CH}_3)_3$), 15.04 ($\text{P}(\text{CH}_2\text{CH}_3)_3$), 14.84 ($\text{P}(\text{CH}_2\text{CH}_3)_3$), 13.86 ($\text{P}(\text{CH}_2\text{CH}_3)_3$). ESI-MS (THF, positive ion mode, 2.50 kV): 3155.05 m/z ($[\text{Ni}_{26}\text{S}_{14}(\text{PEt}_3)_{10}]^+$, [**2**] $^+$, calcd 3154.80 m/z), 1577.55 m/z ($[\text{Ni}_{26}\text{S}_{14}(\text{PEt}_3)_{10}]^{2+}$, [**2**] $^{2+}$, calcd 1577.40 m/z).

***In situ* Monitoring of the Formation of 1.** A 20 mL scintillation vial equipped with a magnetic stir bar was charged with $[\text{Ni}(1,5\text{-cod})_2]$ (0.0862 g, 0.313 mmol), toluene- d_8 (6 mL), PEt_3 (0.069 mL, 0.468 mmol), and S_8 (0.0050 g, 0.019 mmol). After stirring for 2 min, triphenylphosphine oxide (0.0255 g, 0.0916 mmol) was added to the reaction mixture as an internal standard. An aliquot (1 mL) was then removed from the reaction mixture and dried *in vacuo*. The resulting solid was re-dissolved in

C₆D₆ (1 mL) and analyzed by ¹H and ³¹P{¹H} NMR spectroscopies. A second aliquot (0.5 mL) was also removed from the reaction mixture at this time, and dried *in vacuo*. This solid was re-dissolved in THF and analyzed by ESI-MS. The remaining reaction mixture was transferred to a 50 mL Cajon flask equipped with a Teflon rotoflow valve, removed from the glovebox, and heated to 115 °C in an oil bath temperature. After 15 min at 115 °C, the flask was returned to the glovebox, and additional aliquots were removed for analysis by NMR spectroscopy and ESI-MS. Subsequently, the flask was removed from the glovebox and returned to the oil bath at 115 °C. Additional aliquots were taken at 45 min, 105 min, 225 min, and 17 h, and similarly analyzed. ¹H NMR (initial aliquot, C₆D₆, 25 °C): 0.89 (m, [(1,5-cod)Ni(PEt₃)₂], CH₃, 18H), 1.42 (m, [(1,5-cod)Ni(PEt₃)₂], CH₂, 12H), 2.20 (s, 1,5-cod, allylic H), 2.35 (m, [(1,5-cod)Ni(PEt₃)₂], allylic H, 8H), 4.32 (m, [(1,5-cod)Ni(PEt₃)₂], vinylic H, 4H), 5.53 (s, vinylic H, 1,5-cod, 4H), 7.12 – 6.95 (overlapping phenyl resonances assignable to toluene and triphenylphosphine oxide), 7.68 (m, o-Ph, OPPh₃, 6H). ¹H NMR (aliquot taken after 15 min at 115 °C, C₆D₆, 25 °C): 0.99 (m, unassigned ethyl resonances, P(CH₂CH₃)₃), 2.20 (s, 1,5-cod, allylic H), 5.53 (s, vinylic H, 1,5-cod, 4H), 7.68 (m, o-Ph, OPPh₃, 6H), 8.46 (s, unassigned), 8.66 (s, unassigned), 9.34 (br s, P(CH₂CH₃)₃, 12 H, [Ni₃₀S₁₆(PEt₃)₁₁] (**1**)), 9.91 (s, unassigned), 11.56 (s, unassigned), 12.05 (s, unassigned), 12.10 (s, unassigned), 12.53 (s, unassigned), 13.21 (s, unassigned), 14.39 (s, unassigned), 21.51 (s, P(CH₂CH₃)₃, 12H, [Ni₂₆S₁₄(PEt₃)₁₀] (**2**)), 26.47 (s, unassigned). ¹H NMR (aliquot taken after 45 min at 115 °C, C₆D₆, 25 °C): 0.99 (m, unassigned ethyl resonances, P(CH₂CH₃)₃), 2.20 (s, 1,5-cod, allylic H), 5.53 (s, vinylic H, 1,5-cod, 4H), 7.68 (m, o-Ph, OPPh₃, 6H), 9.34 (br s, P(CH₂CH₃)₃, 12 H, [Ni₃₀S₁₆(PEt₃)₁₁] (**1**)), 21.51

(s, P(CH₂CH₃)₃), 12H, [Ni₂₆S₁₄(PEt₃)₁₀] (**2**)). ¹H NMR (aliquot taken after 105 min at 115 °C, C₆D₆, 25 °C): 0.99 (m, unassigned ethyl resonances, P(CH₂CH₃)₃), 2.20 (s, 1,5-cod, allylic H), 5.53 (s, vinylic H, 1,5-cod, 4H), 7.68 (m, o-Ph, OPPh₃, 6H), 9.34 (br s, P(CH₂CH₃)₃, 12 H, [Ni₃₀S₁₆(PEt₃)₁₁] (**1**)), 21.49 (s, P(CH₂CH₃)₃), 12H, [Ni₂₆S₁₄(PEt₃)₁₀] (**2**)). ¹H NMR (aliquot taken after 225 min at 115 °C, C₆D₆, 25 °C): 0.99 (m, unassigned ethyl resonances, P(CH₂CH₃)₃), 2.20 (s, 1,5-cod, allylic H), 5.53 (s, vinylic H, 1,5-cod, 4H), 7.68 (m, o-Ph, OPPh₃, 6H), 9.34 (br s, P(CH₂CH₃)₃, 12 H, [Ni₃₀S₁₆(PEt₃)₁₁] (**1**)). ¹H NMR (aliquot taken after 17 h at 115 °C, C₆D₆, 25 °C): 0.99 (m, unassigned ethyl resonances, P(CH₂CH₃)₃), 2.20 (s, 1,5-cod, allylic H), 5.53 (s, vinylic H, 1,5-cod, 4H), 7.68 (m, o-Ph, OPPh₃, 6H), 9.34 (br s, P(CH₂CH₃)₃, 12 H, [Ni₃₀S₁₆(PEt₃)₁₁] (**1**)). ³¹P{¹H} NMR (initial aliquot, C₆D₆, 25 °C): -4.30 (s, PEt₃, 4P, [Ni₈S₅(PEt₃)₇]), 7.16 (s, unassigned), 9.72 (s, unassigned), 12.94 (s, PEt₃, 2P, [Ni₈S₅(PEt₃)₇]), 13.46 (s, PEt₃, 1P, [Ni₈S₅(PEt₃)₇]), 15.52 (s, unassigned), 15.95 (s, unassigned), 17.72 (s, unassigned, overlapping with [Ni(1,5-cod)(PEt₃)₂]), 18.15 (s, [Ni(1,5-cod)(PEt₃)₂], overlapping with unassigned resonance), 19.58 (s, unassigned), 19.97 (s, unassigned), 24.55 (s, OPPh₃), 30.94 (s, unassigned), 45.04 (s, unassigned), 52.88 (s, SPEt₃), 229.68 (s, unassigned). ³¹P{¹H} NMR (aliquot taken after 15 min at 115 °C, C₆D₆, 25 °C): -4.66 (s, PEt₃, 4P, [Ni₈S₅(PEt₃)₇]), 9.28 (s, unassigned), 13.06 (s, PEt₃, 2P, [Ni₈S₅(PEt₃)₇]), 15.09 (s, PEt₃, 1P, [Ni₈S₅(PEt₃)₇]), 24.55 (s, OPPh₃), 30.44 (s, PEt₃, 4P, [Ni₃₀S₁₆(PEt₃)₁₁] (**1**)), 52.44 (s, SPEt₃), 159.42 (s, unassigned), 246.22 (s, PEt₃, 2P, [Ni₃₀S₁₆(PEt₃)₁₁] (**1**)). ³¹P{¹H} NMR (aliquot taken after 45 min at 115 °C, C₆D₆, 25 °C): 9.24 (s, unassigned), 24.55 (s, OPPh₃), 30.44 (s, PEt₃, 4P, [Ni₃₀S₁₆(PEt₃)₁₁] (**1**)), 52.44 (s, SPEt₃), 246.22 (s, PEt₃, 2P, [Ni₃₀S₁₆(PEt₃)₁₁] (**1**)). ³¹P{¹H} NMR (aliquot taken after 105 min at 115 °C,

C_6D_6 , 25 °C): 9.24 (s, unassigned), 24.55 (s, $OPPh_3$), 30.19 (s, PEt_3 , 4P, $[Ni_{30}S_{16}(PEt_3)_{11}]$ (**1**)), 52.44 (s, $SPEt_3$), 246.22 (s, PEt_3 , 2P, $[Ni_{30}S_{16}(PEt_3)_{11}]$ (**1**)). $^{31}P\{^1H\}$ NMR (aliquot taken after 225 min at 115 °C, C_6D_6 , 25 °C): 9.24 (s, unassigned), 24.55 (s, $OPPh_3$), 30.19 (s, PEt_3 , 4P, $[Ni_{30}S_{16}(PEt_3)_{11}]$ (**1**)), 52.44 (s, $SPEt_3$), 246.22 (s, PEt_3 , 2P, $[Ni_{30}S_{16}(PEt_3)_{11}]$ (**1**)). $^{31}P\{^1H\}$ NMR (aliquot taken after 17 h at 115 °C, C_6D_6 , 25 °C): 9.24 (s, unassigned), 24.55 (s, $OPPh_3$), 30.19 (s, PEt_3 , 4P, $[Ni_{30}S_{16}(PEt_3)_{11}]$ (**1**)), 52.44 (s, $SPEt_3$), 246.22 (s, PEt_3 , 2P, $[Ni_{30}S_{16}(PEt_3)_{11}]$ (**1**)). ESI-MS (initial aliquot, THF, positive ion mode, 2.50 kV): 1455.9746 m/z ($[Ni_8S_5(PEt_3)_7]^+$, calcd 1455.9733 m/z), 1548.8735 m/z ($[Ni_{12}S_8(PEt_3)_5]^+$, calcd 1549.4364 m/z), 1935.2334 m/z ($[Ni_{16}S_9(PEt_3)_6]^+$, calcd 1935.2368 m/z). ESI-MS (aliquot taken after 15 min at 115 °C, THF, positive ion mode, 2.50 kV): 775.3942 m/z ($[Ni_5S_4(PEt_3)_3]^+$, calcd 775.8306 m/z), 1455.9589 m/z ($[Ni_8S_5(PEt_3)_7]^+$, calcd 1455.9733 m/z), 1548.8735 m/z ($[Ni_{12}S_8(PEt_3)_5]^+$, calcd 1549.4364 m/z), 1786.2678 m/z ($[Ni_{30}S_{16}(PEt_3)_{11}]^{2+}$ (**[1]**)²⁺, calcd 1786.2880 m/z), 3154.8130 m/z ($[Ni_{26}S_{14}(PEt_3)_{10}]^+$ (**[2]**)⁺, calcd 3154.8032 m/z), 3572.5762 m/z ($[Ni_{30}S_{16}(PEt_3)_{11}]^+$ (**[1]**)⁺, calcd 3572.5681 m/z). ESI-MS (aliquot taken after 45 min at 115 °C, THF, positive ion mode, 2.50 kV): 1396.0408 m/z ($[Ni_7S_5(PEt_3)_7]^+$, calcd 1396.0380 m/z), 1455.9746 m/z ($[Ni_8S_5(PEt_3)_7]^+$, calcd 1455.9733 m/z), 1548.8735 m/z ($[Ni_{12}S_8(PEt_3)_5]^+$, calcd 1549.4364 m/z), 1786.2678 m/z ($[Ni_{30}S_{16}(PEt_3)_{11}]^{2+}$ (**[1]**)²⁺, calcd 1786.2880 m/z), 1983.9646 m/z ($[Ni_{32}S_{21}(PEt_3)_{12}]^{2+}$, calcd 1984.1973 m/z), 2384.9607 m/z ($[Ni_{20}S_{12}(PEt_3)_7]^+$, calcd 2384.9814 m/z), 2508.8269 m/z ($[Ni_{21}S_{14}(PEt_3)_7]^+$, calcd 2506.8608 m/z), 2624.9739 m/z ($[Ni_{21}S_{14}(PEt_3)_8]^+$, calcd 2624.9521 m/z), 3154.7900 m/z ($[Ni_{26}S_{14}(PEt_3)_{10}]^+$ (**[2]**)⁺, calcd 3154.8032 m/z), 3572.5273 m/z ($[Ni_{30}S_{16}(PEt_3)_{11}]^+$ (**[1]**)⁺, calcd

3572.5681 m/z). ESI-MS (aliquot taken after 105 min at 115 °C, THF, positive ion mode, 2.50 kV): 1200.0392 m/z (unidentified Ni₆ cluster), 1396.0408 m/z ([Ni₇S₅(PEt₃)₇]⁺, calcd 1396.0380 m/z), 1786.2678 m/z ([Ni₃₀S₁₆(PEt₃)₁₁]²⁺ (**[1]**²⁺), calcd 1786.2880 m/z), 2384.9607 m/z ([Ni₂₀S₁₂(PEt₃)₇]⁺, calcd 2384.9814 m/z), 2506.8179 m/z ([Ni₂₁S₁₄(PEt₃)₇]⁺, calcd 2506.8608 m/z), 2624.9111 m/z ([Ni₂₁S₁₄(PEt₃)₈]⁺, calcd 2624.9521 m/z), 2860.0703 m/z ([Ni₂₃S₁₄(PEt₃)₉]⁺, calcd 2860.9102 m/z), 3154.8130 m/z ([Ni₂₆S₁₄(PEt₃)₁₀]⁺ (**[2]**⁺), calcd 3154.8032 m/z), 3572.5029 m/z ([Ni₃₀S₁₆(PEt₃)₁₁]⁺ (**[1]**⁺), calcd 3572.5681 m/z). ESI-MS (aliquot taken after 225 min at 115 °C, THF, positive ion mode, 2.50 kV): 1200.0392 m/z (unidentified Ni₆ cluster), 1786.2678 m/z ([Ni₃₀S₁₆(PEt₃)₁₁]²⁺ (**[1]**²⁺), calcd 1786.2880 m/z), 2624.9319 m/z ([Ni₂₁S₁₄(PEt₃)₈]⁺, calcd 2624.9521 m/z), 3572.5273 m/z ([Ni₃₀S₁₆(PEt₃)₁₁]⁺ (**[1]**⁺), calcd 3572.5681 m/z). ESI-MS (aliquot taken after 17 h at 115 °C, THF, positive ion mode, 2.50 kV): 1200.0392 m/z (unidentified Ni₆ cluster), 1786.2678 m/z ([Ni₃₀S₁₆(PEt₃)₁₁]²⁺ (**[1]**²⁺), calcd 1786.2880 m/z), 3572.5029 m/z ([Ni₃₀S₁₆(PEt₃)₁₁]⁺ (**[1]**⁺), calcd 3572.5681 m/z). The prominent peak at 1200.0392 m/z in the 17 h, 225 min, and 105 min spectra could not be definitively assigned; however, the molecular weight and isotope pattern suggests it is a Ni₆ cluster. Resonances assigned to [(1,5-cod)Ni(PEt₃)₂], 1,5-cod, and SPEt₃ are consistent with those previously reported for [(1,5-cod)Ni(PEt₃)₂],⁴ 1,5-cod,⁵ SPEt₃.^{6,7}

X-ray Crystallography. Data for **1**·Et₂O and **2**·C₅H₁₂ was collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a MoK α X-ray source ($\alpha = 0.71073 \text{ \AA}$). Crystals of **1**·Et₂O and **2**·C₅H₁₂ were mounted on a cryoloop under Paratone-N oil. Data for **1**·Et₂O

and $2 \cdot \text{C}_5\text{H}_{12}$ were collected at 100(2) K and 116(2) K, respectively, using an Oxford nitrogen gas cryostream system. Data for $1 \cdot \text{Et}_2\text{O}$ and $2 \cdot \text{C}_5\text{H}_{12}$ were collected utilizing frame exposures of 30 s and 60 s, respectively. Data collection and cell parameter determination were conducted using the SMART program.⁸ Integration of the data frames and final cell parameter refinement were performed using SAINT software.⁹ Absorption correction of the data was carried out using the multi-scan method SADABS.¹⁰ Subsequent calculations were carried out using SHELXTL.¹¹ Structure determination was done using the intrinsic phasing method in SHELXTL embedded in APEX2.¹¹ All hydrogen atom positions were idealized, and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.¹¹ Ball and stick graphics for $1 \cdot \text{Et}_2\text{O}$ and $2 \cdot \text{C}_5\text{H}_{12}$ were generated using VESTA, version 3.5.7.¹²

For $1 \cdot \text{Et}_2\text{O}$ and $2 \cdot \text{C}_5\text{H}_{12}$, the EADP command was used to constrain anisotropic (or isotropic) displacement parameters of the methylene and methyl carbons of the triethylphosphine ligands. The SADI command was further used to constrain the ethyl groups of the triethylphosphine ligands.

For $1 \cdot \text{Et}_2\text{O}$, the diethyl ether solvate molecule was constrained using the EADP and SADI commands. Additionally, the DFIX command was used to fix the C-O and C-C distances in the diethyl ether solvate molecule, as well as the P1-C2 and C1-C2 distances (2.75 Å and 1.52 Å, respectively).

For $2 \cdot \text{C}_5\text{H}_{12}$, the crystal was badly twinned; however, integrating and refining the data to include two or more domains did not improve the structure quality. As such,

the disorder on the ethyl groups of the PEt_3 ligands was not resolved, and these carbon atoms were only refined isotropically. Additionally, the carbon atoms of the pentane solvate molecule were constrained using the EADP and SADI commands. The DFIX command was used to fix the C-C bonds of the pentane solvate molecule as well as the P1-C2 and C1-C2 distances (2.8 Å and 1.5 Å, respectively). Hydrogen atoms were not assigned to the pentane solvate.

Further crystallographic details can be found in Table S1. Complexes **1**·Et₂O and **2**·C₅H₁₂ have been deposited in the Cambridge Structural Database (**1**·Et₂O: CCDC 2150613; **2**·C₅H₁₂: CCDC 2150614).

Table S1. X-ray Crystallographic Data for **1**·Et₂O and **2**·C₅H₁₂

	[Ni ₃₀ S ₁₆ (PEt ₃) ₁₁]·Et ₂ O (1 ·Et ₂ O)	[Ni ₂₆ S ₁₄ (PEt ₃) ₁₀]·C ₅ H ₁₂ (2 ·C ₅ H ₁₂)
empirical formula	Ni ₃₀ S ₁₆ P ₁₁ O ₇₀ H ₁₇₅	Ni ₂₆ S ₁₄ P ₁₀ C ₆₅ H ₁₆₂
crystal habit, color	Plate, black	Plate, black
crystal size (mm)	0.25 × 0.20 × 0.05	0.20 × 0.15 × 0.10
crystal system	Monoclinic	Monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
volume (Å ³)	12191(6)	11374(16)
<i>a</i> (Å)	19.050(6)	19.007(15)
<i>b</i> (Å)	33.432(10)	25.85(2)
<i>c</i> (Å)	21.256(6)	23.475(19)
<i>α</i> (deg)	90	90
<i>β</i> (deg)	115.771(4)	99.628(7)
<i>γ</i> (deg)	90	90
<i>Z</i>	4	4
formula weight (g/mol)	3648.02	3228.94
density (calculated) (Mg/m ³)	1.988	1.886
absorption coefficient (mm ⁻¹)	4.957	4.615
<i>F</i> ₀₀₀	7456	6616
<i>R</i> _{int}	0.0488	0.2698
total no. reflections	68292	41853
unique reflections	23848	18613
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0948 w <i>R</i> ₂ = 0.2530	<i>R</i> ₁ = 0.1338 w <i>R</i> ₂ = 0.2944
largest diff. peak and hole (e·Å ⁻³)	2.484 and -1.804	1.270 and -1.092
GOF	1.173	0.919

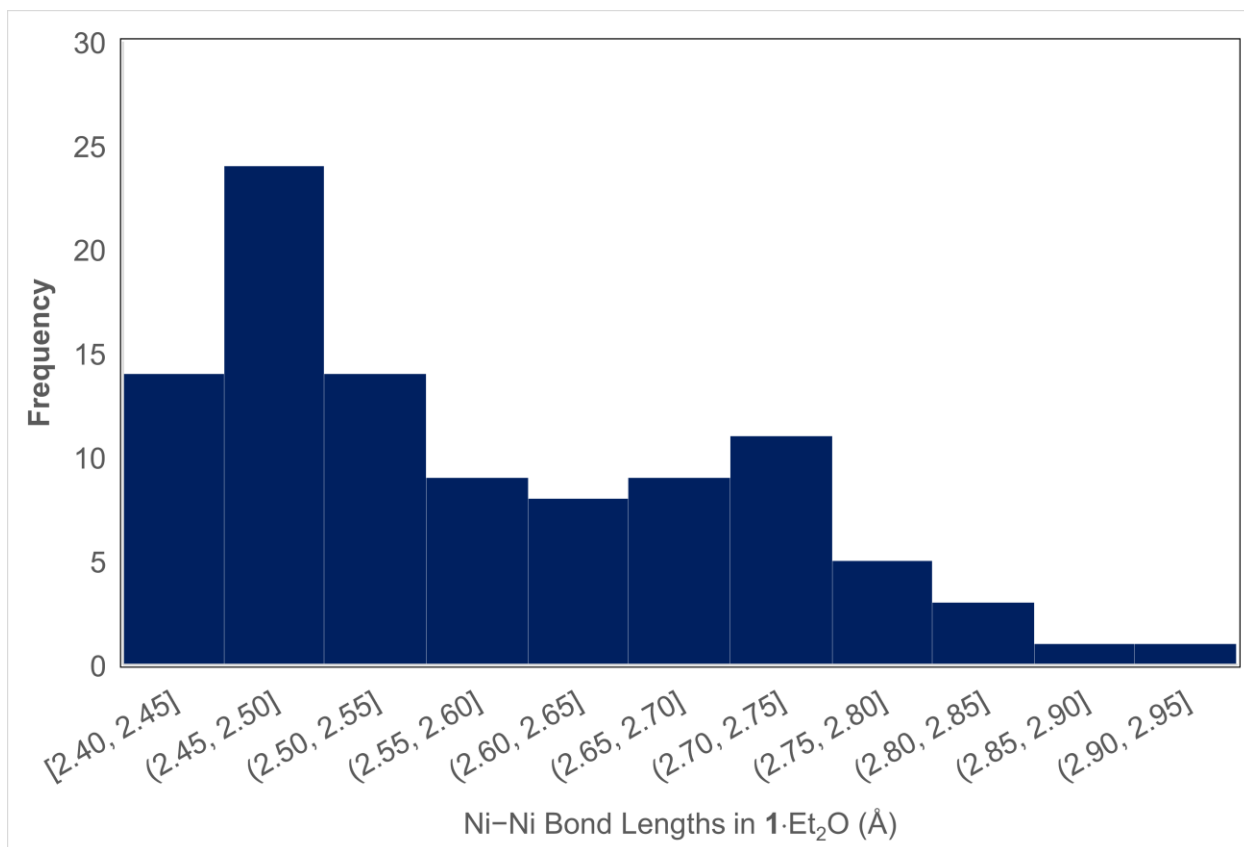


Figure S1. Histogram depicting the distribution of Ni-Ni bond distances in **1·Et₂O**.

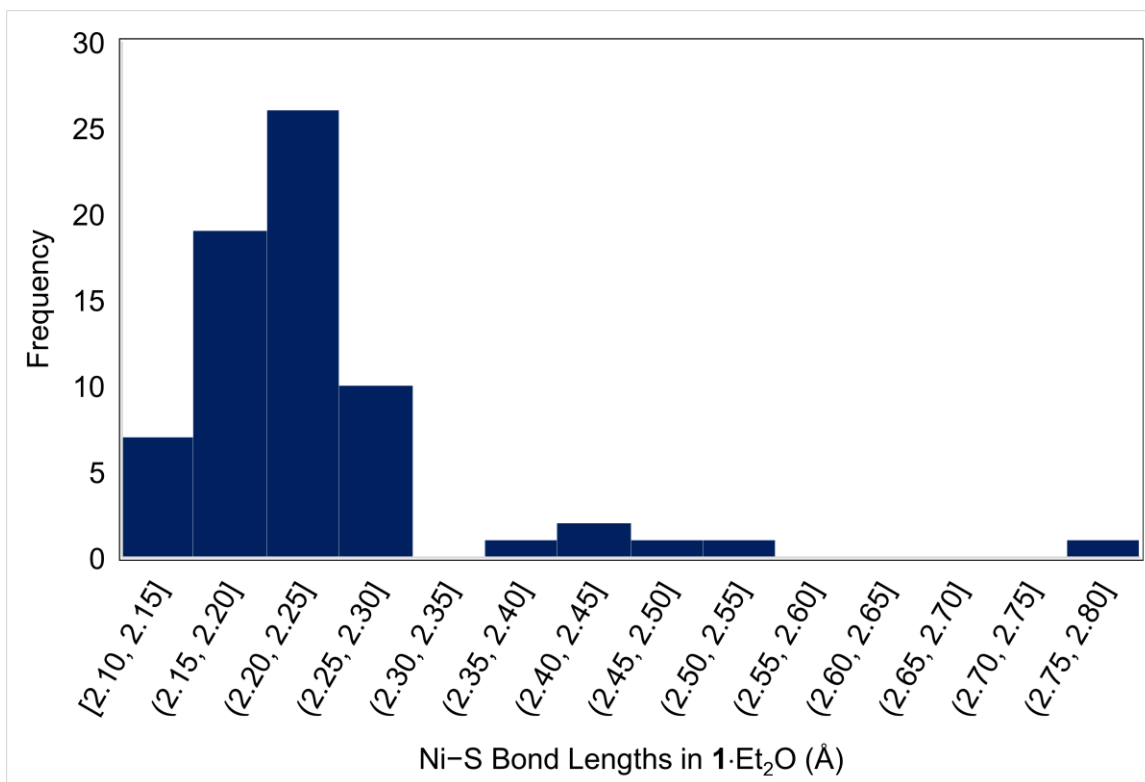


Figure S2. Histogram depicting the distribution of Ni-S bond distances in 1·Et₂O.

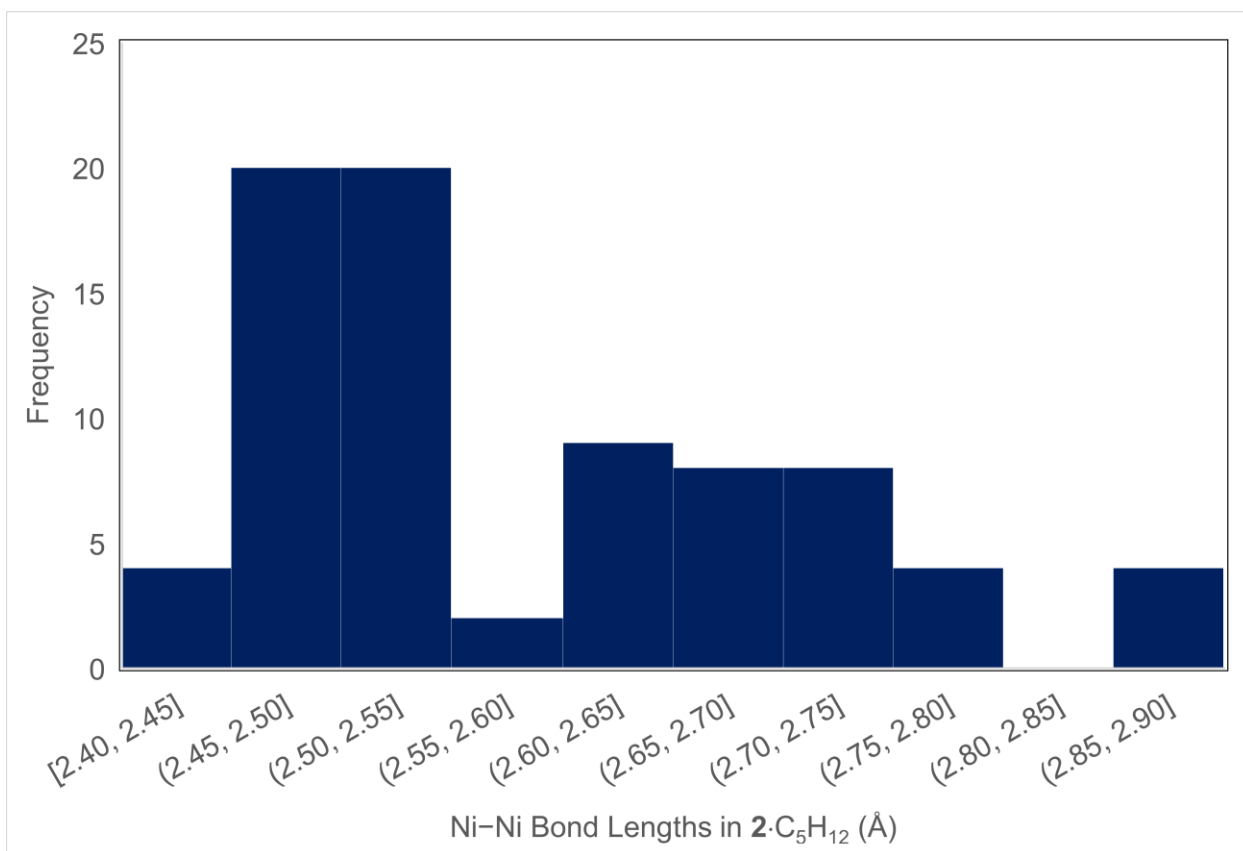


Figure S3. Histogram depicting the distribution of Ni–Ni bond distances in $2 \cdot C_5H_{12}$.

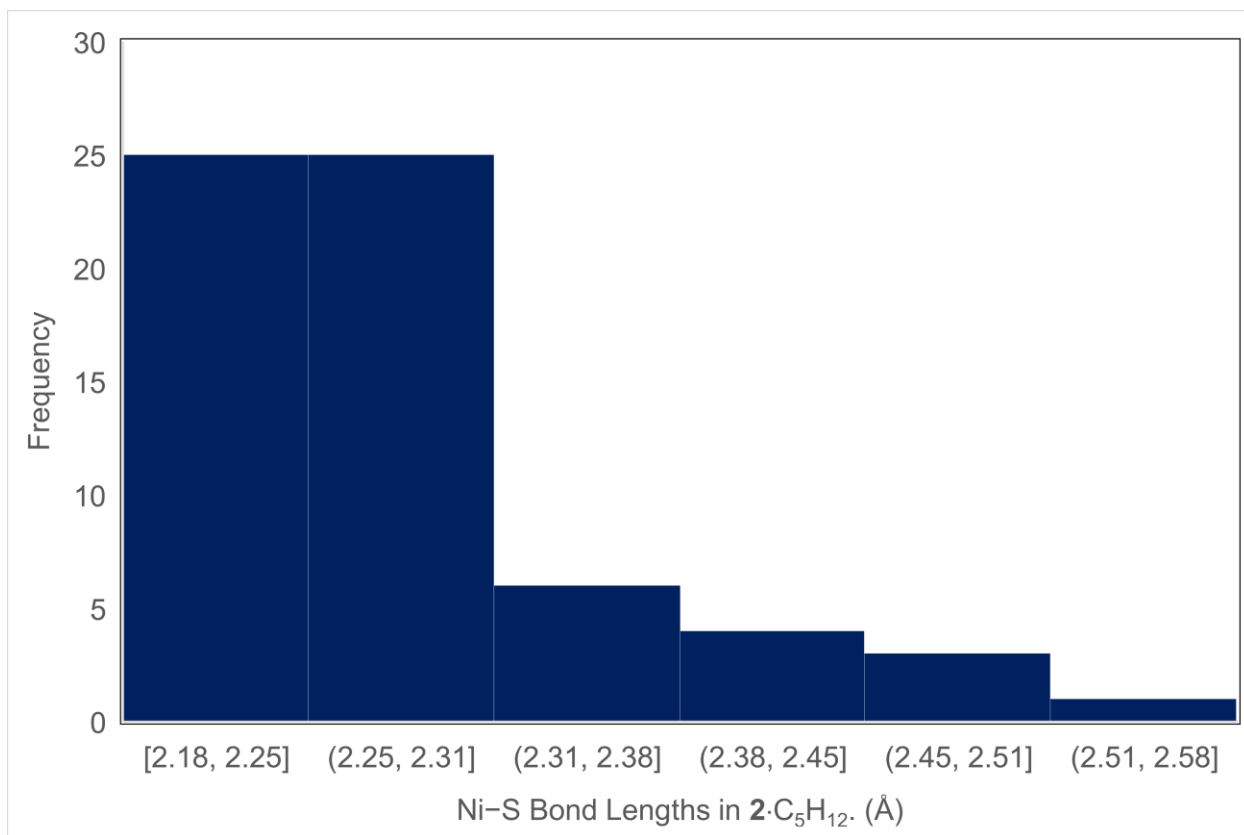


Figure S4. Histogram depicting the distribution of Ni-S bond distances in 2·C₅H₁₂.

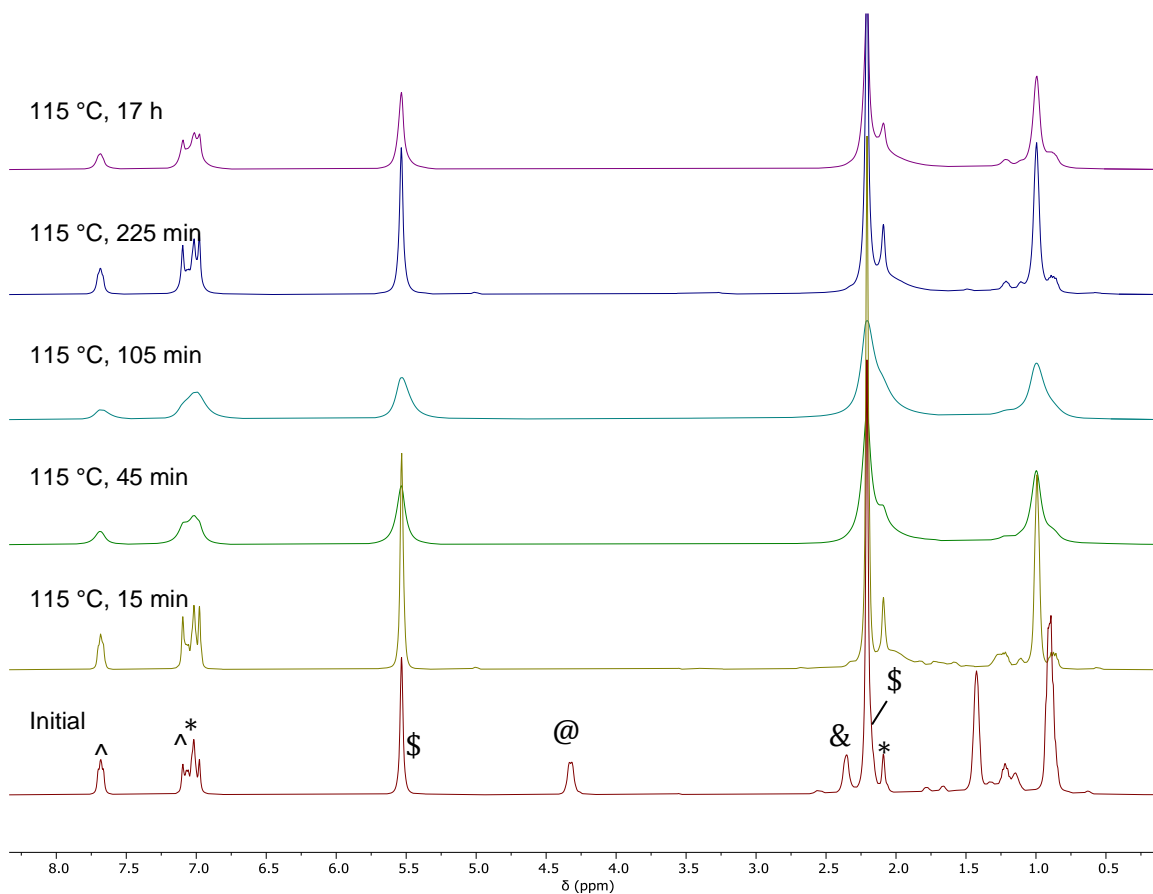


Figure S5. Partial ^1H NMR (25 °C, toluene- d_8) spectra of the reaction of $[\text{Ni}(1,5\text{-cod})_2]$ with PEt_3 (1.5 equiv) and S_8 (0.06 equiv). For experimental details, see pages S8–S12. ($\$$) indicates a resonance assignable to free 1,5-cod. (\wedge) indicates a resonance assigned to triphenylphosphine oxide. ($@$) indicates a resonance assignable to $[\text{Ni}(1,5\text{-cod})_2]$. ($*$) indicates a resonance assignable to toluene. ($\&$) indicates a resonance tentatively assigned to $[\text{Ni}(1,5\text{-cod})(\text{PEt}_3)_2]$.

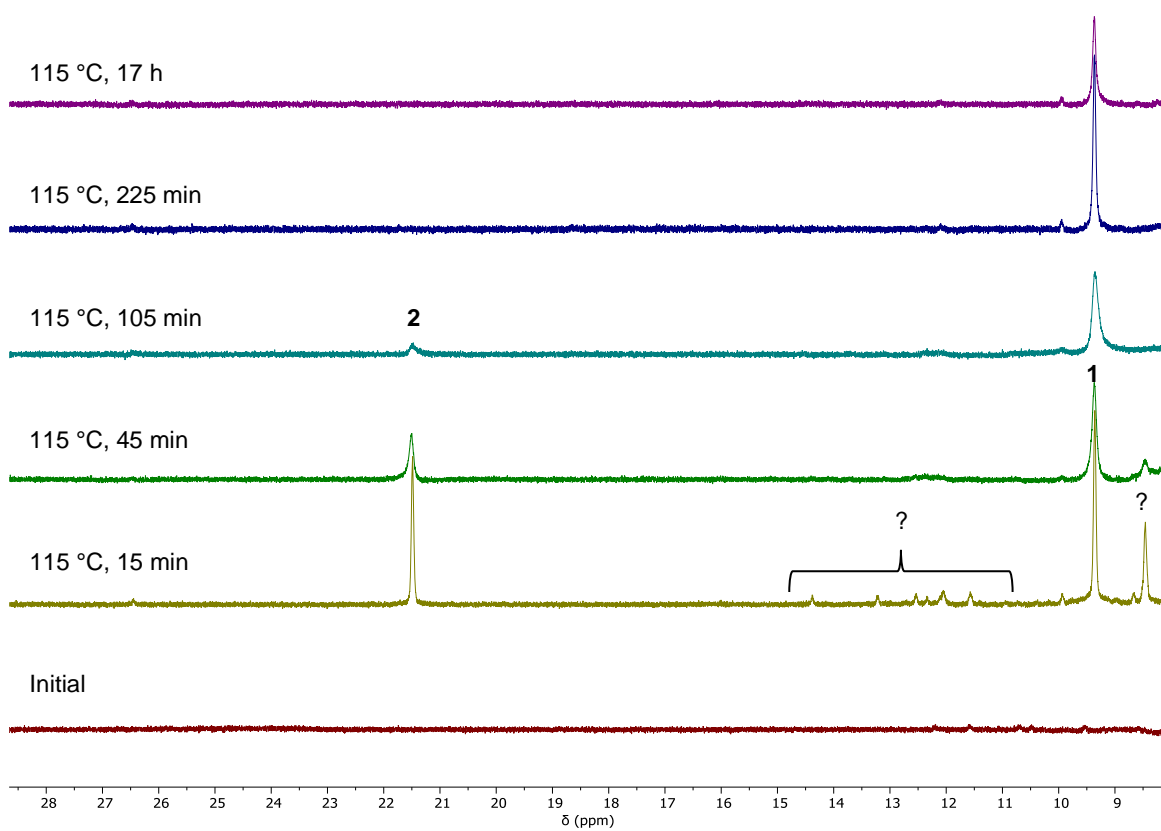


Figure S6. Partial ¹H NMR (25 °C, toluene-*d*₈) spectra of the reaction of [Ni(1,5-cod)₂] with PEt₃ (1.5 equiv) and S₈ (0.06 equiv). For experimental details, see pages S8–S12. (?) indicates resonances that remains unassigned.

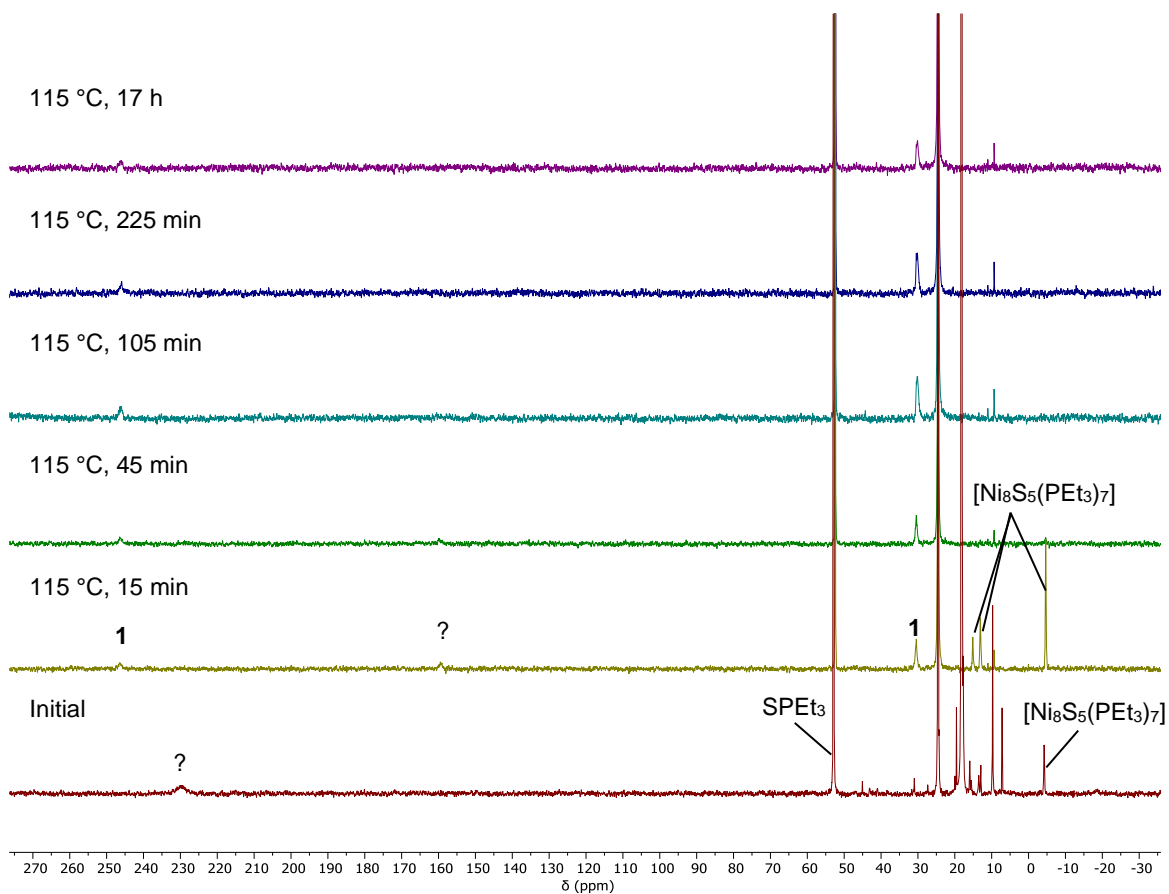


Figure S7. $^{31}\text{P}\{^1\text{H}\}$ NMR (25 °C, toluene- d_8) spectra of the reaction of $[\text{Ni}(1,5\text{-cod})_2]$ with PEt_3 (1.5 equiv) and S_8 (0.06 equiv). For experimental details, see pages S8–S12.

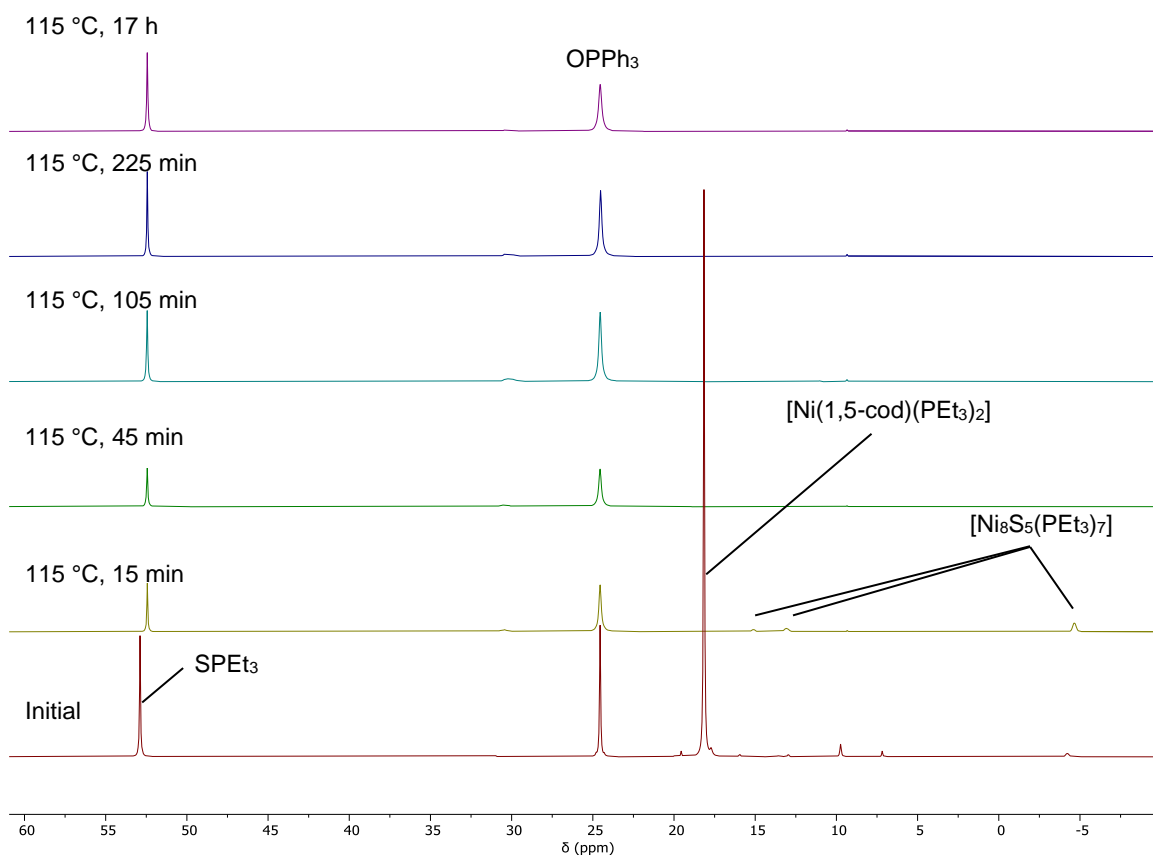


Figure S8. Partial $^{31}\text{P}\{^1\text{H}\}$ NMR (25 °C, toluene- d_8) spectra of the reaction of $[\text{Ni}(1,5\text{-cod})_2]$ with PEt_3 (1.5 equiv) and S_8 (0.06 equiv). For experimental details, see pages S8–S12.

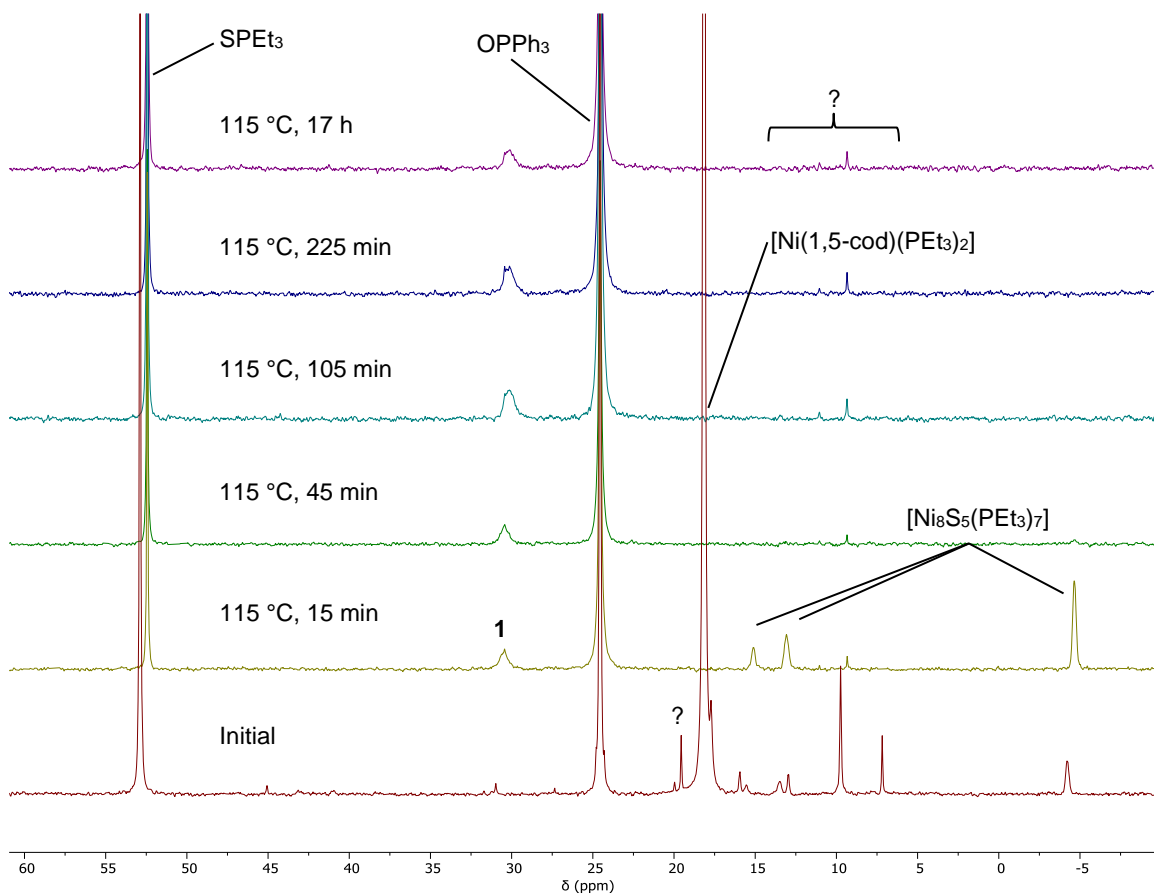


Figure S9. Partial $^{31}\text{P}\{^1\text{H}\}$ NMR (25 °C, toluene- d_8) spectra of the reaction of $[\text{Ni}(1,5\text{-cod})_2]$ with PEt_3 (1.5 equiv) and S_8 (0.06 equiv). For experimental details, see pages S8–S12.

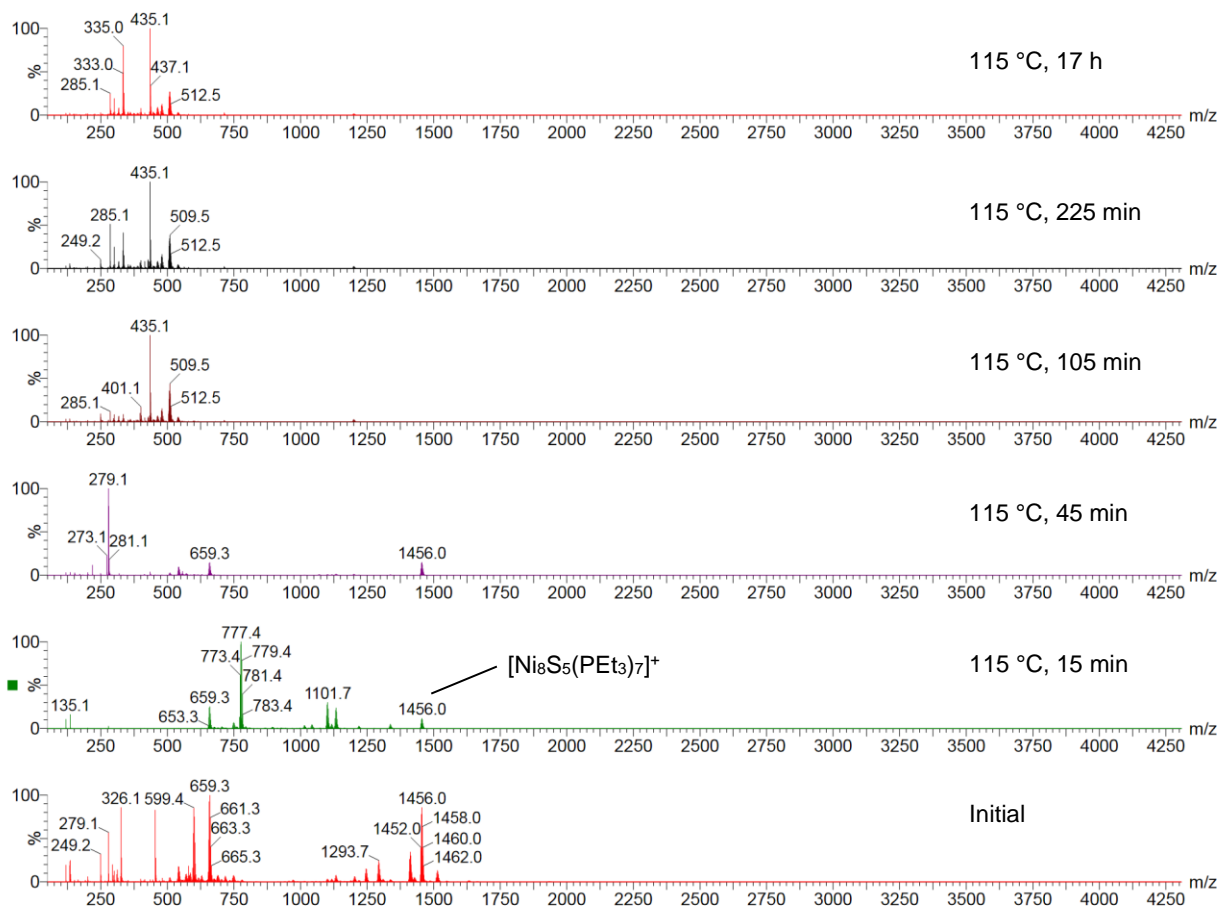


Figure S10. ESI-MS (THF, positive ion mode, 2.50 kV) of the reaction of $[\text{Ni}(1,5\text{-cod})_2]$ with PEt_3 (1.5 equiv) and S_8 (0.06 equiv). For experimental details, see pages S8–S12.

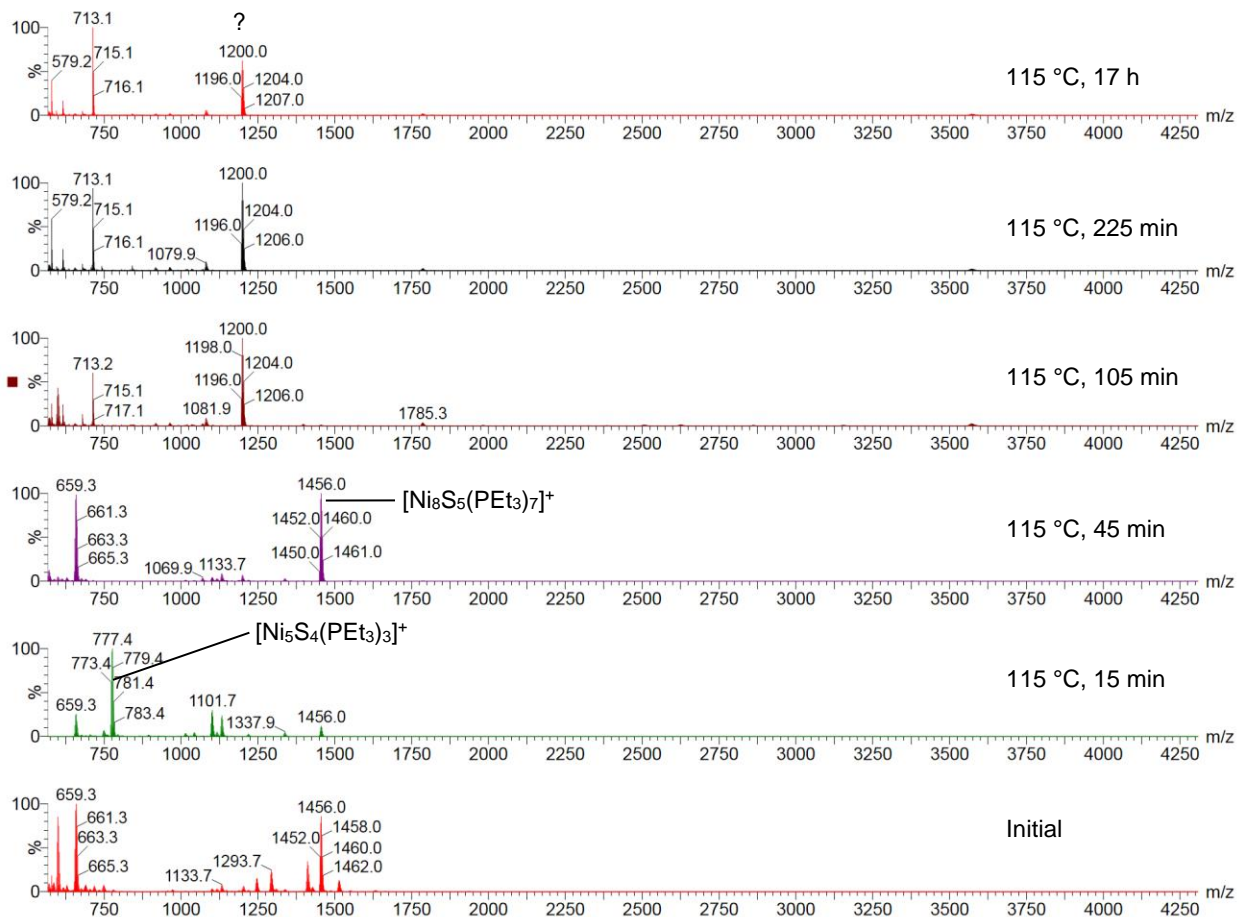


Figure S11. Partial ESI-MS (THF, positive ion mode, 2.50 kV) spectra of the reaction of $[\text{Ni}(1,5\text{-cod})_2]$ with PEt_3 (1.5 equiv) and S_8 (0.06 equiv). Each spectrum is of a dried aliquot of the reaction mixture dissolved in THF. The prominent peak (marked with a ?) at 1200.0 m/z in the 17 h, 225 min, and 105 min spectra could not be definitively assigned; however, the molecular weight and isotope pattern suggests it is a Ni_6 cluster. For experimental details, see pages S8–S12.

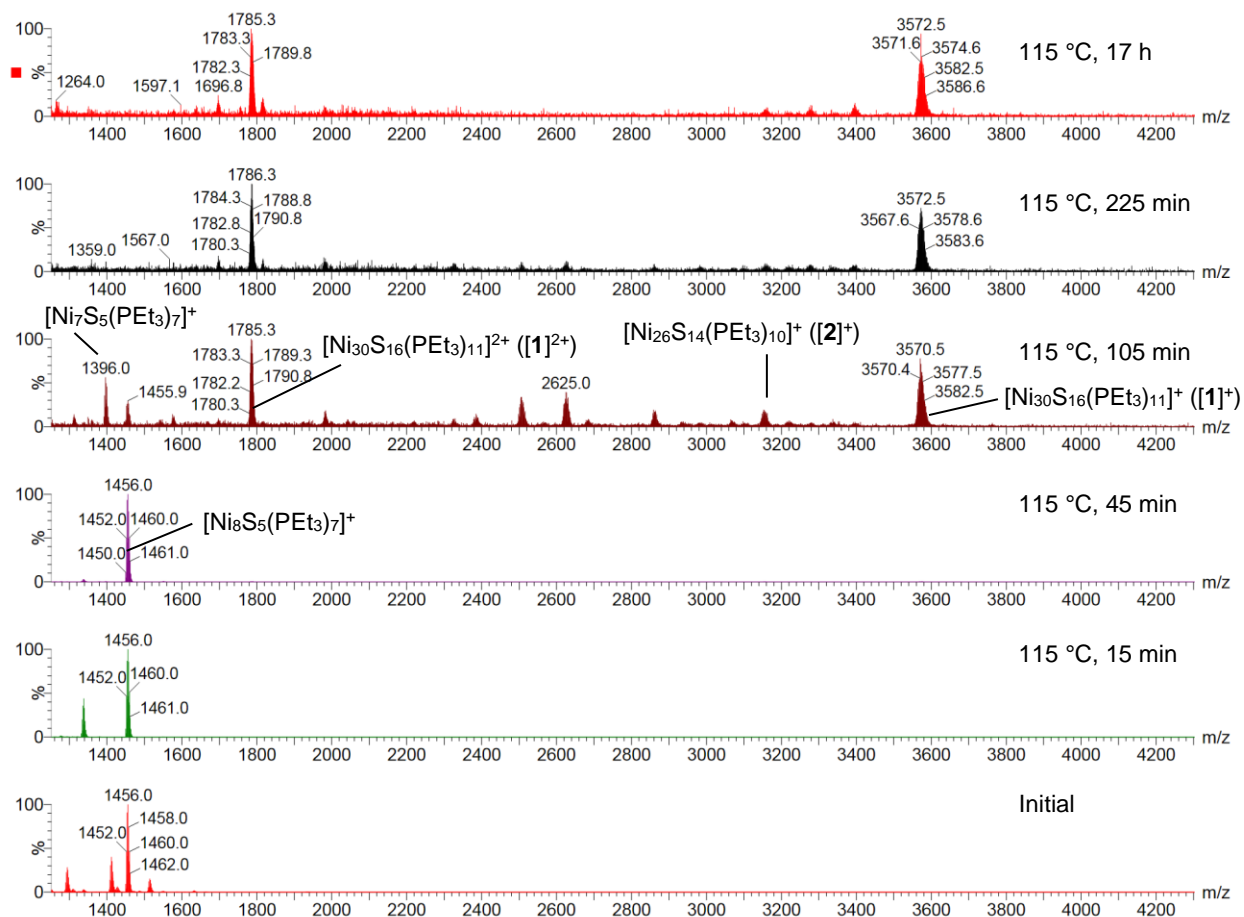


Figure S12. Partial ESI-MS (THF, positive ion mode, 2.50 kV) spectra of the reaction of $[\text{Ni}(\text{1,5-cod})_2]$ with PEt_3 (1.5 equiv) and S_8 (0.06 equiv). For experimental details, see pages S8–S12.

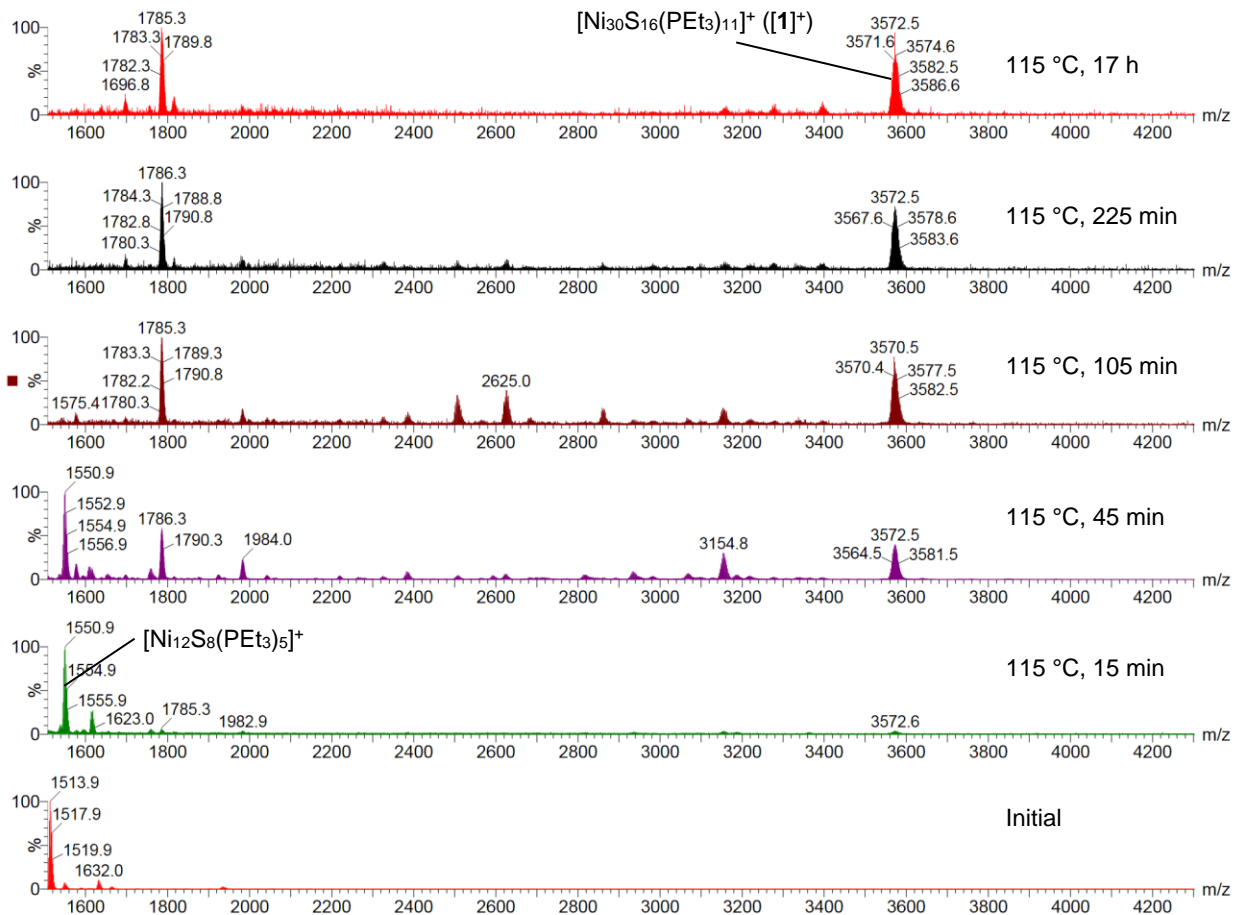


Figure S13. Partial ESI-MS (THF, positive ion mode, 2.50 kV) spectra of the reaction of $[\text{Ni}(1,5\text{-cod})_2]$ with PEt_3 (1.5 equiv) and S_8 (0.06 equiv). For experimental details, see pages S8–S12.

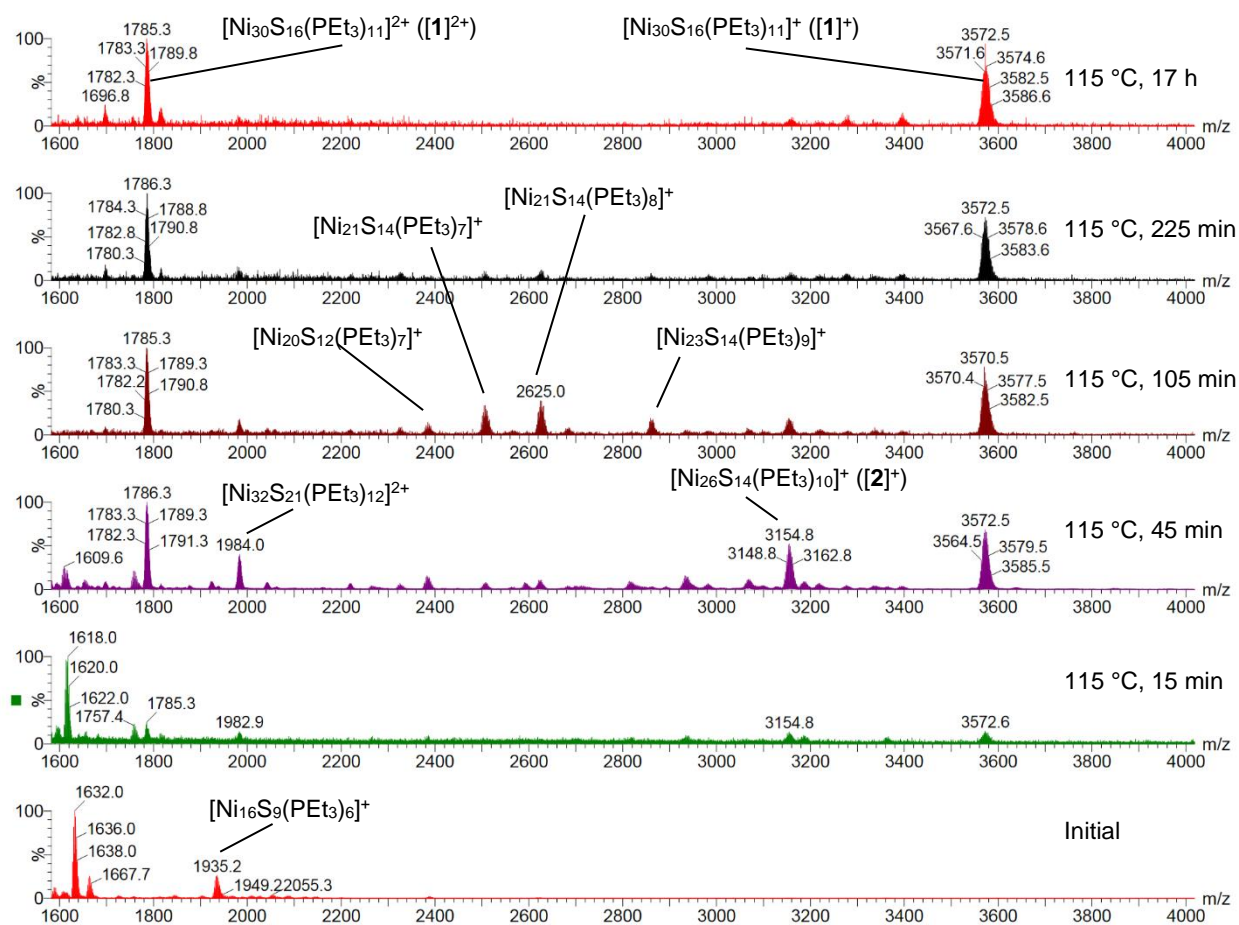


Figure S14. Partial ESI-MS (THF, positive ion mode, 2.50 kV) spectra of the reaction of $[\text{Ni}(1,5\text{-cod})_2]$ with PEt_3 (1.5 equiv) and S_8 (0.06 equiv). For experimental details, see pages S8–S12.

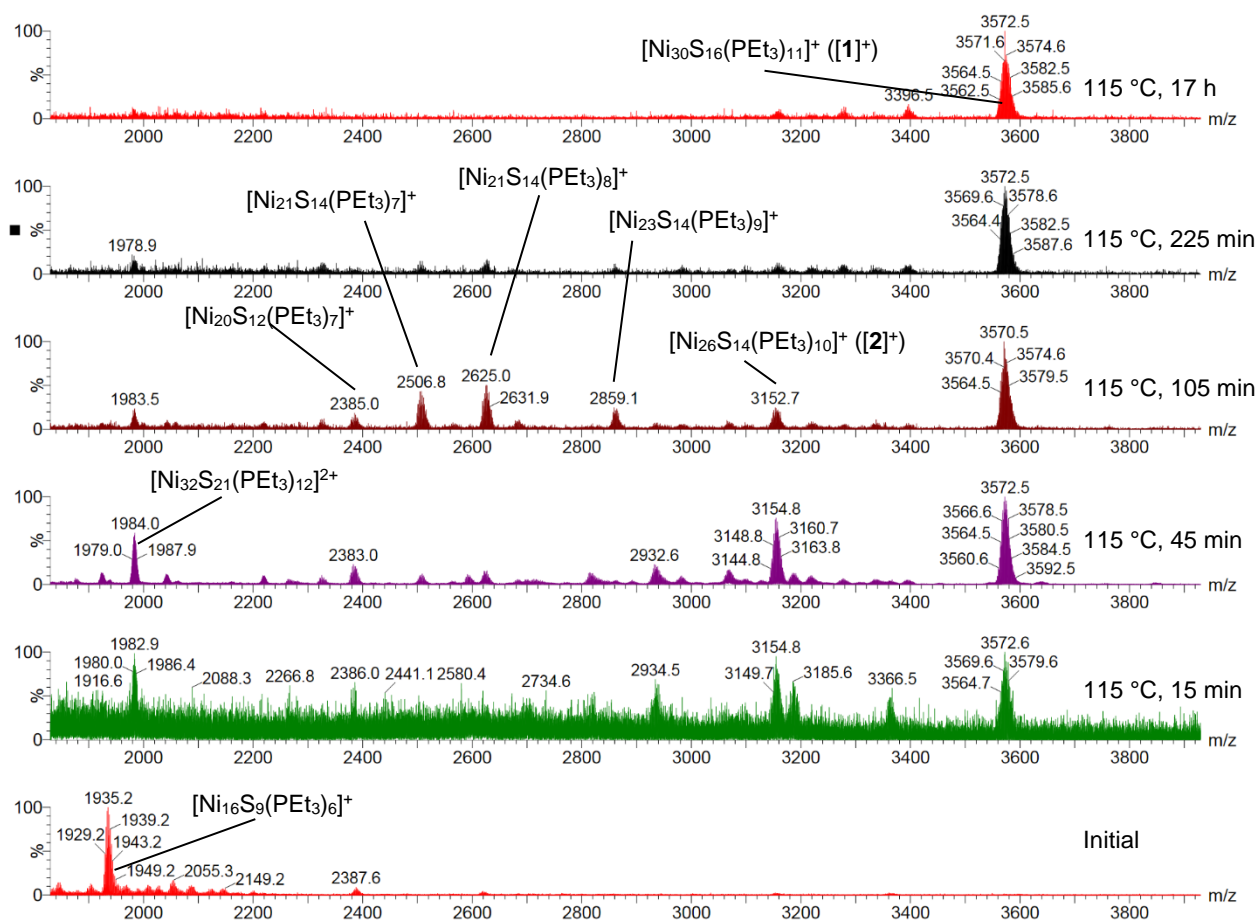


Figure S15. Partial ESI-MS (THF, positive ion mode, 2.50 kV) spectra of the reaction of $[\text{Ni}(1,5\text{-cod})_2]$ with PEt_3 (1.5 equiv) and S_8 (0.06 equiv). For experimental details, see pages S8–S12.

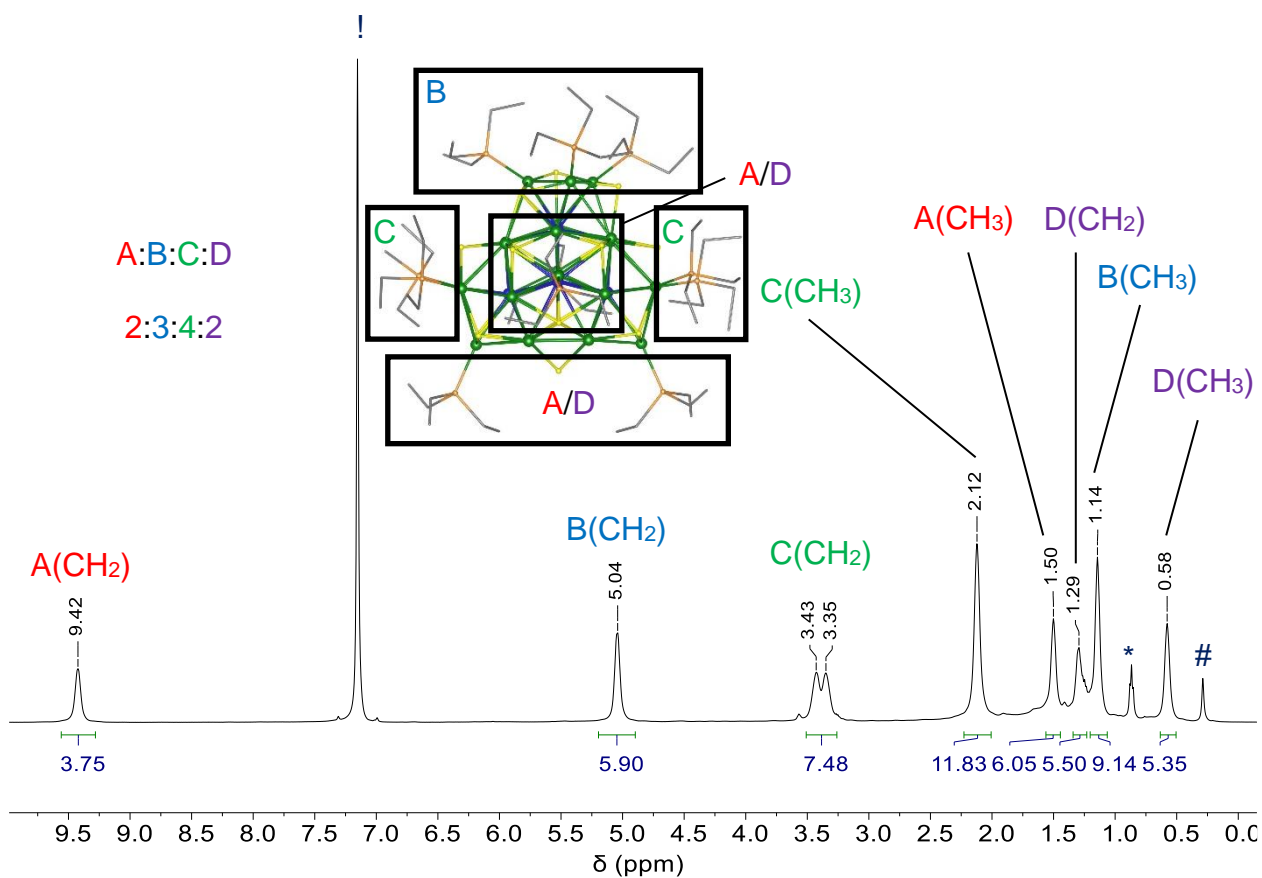


Figure S16. ^1H NMR (500 MHz, 25 °C, benzene- d_6) spectrum of $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]$ (**1**).

(*) indicates the presence of *n*-pentane.¹³ (#) indicates the presence of silicone grease.¹³ (!) indicates a resonance assignable to benzene.¹³

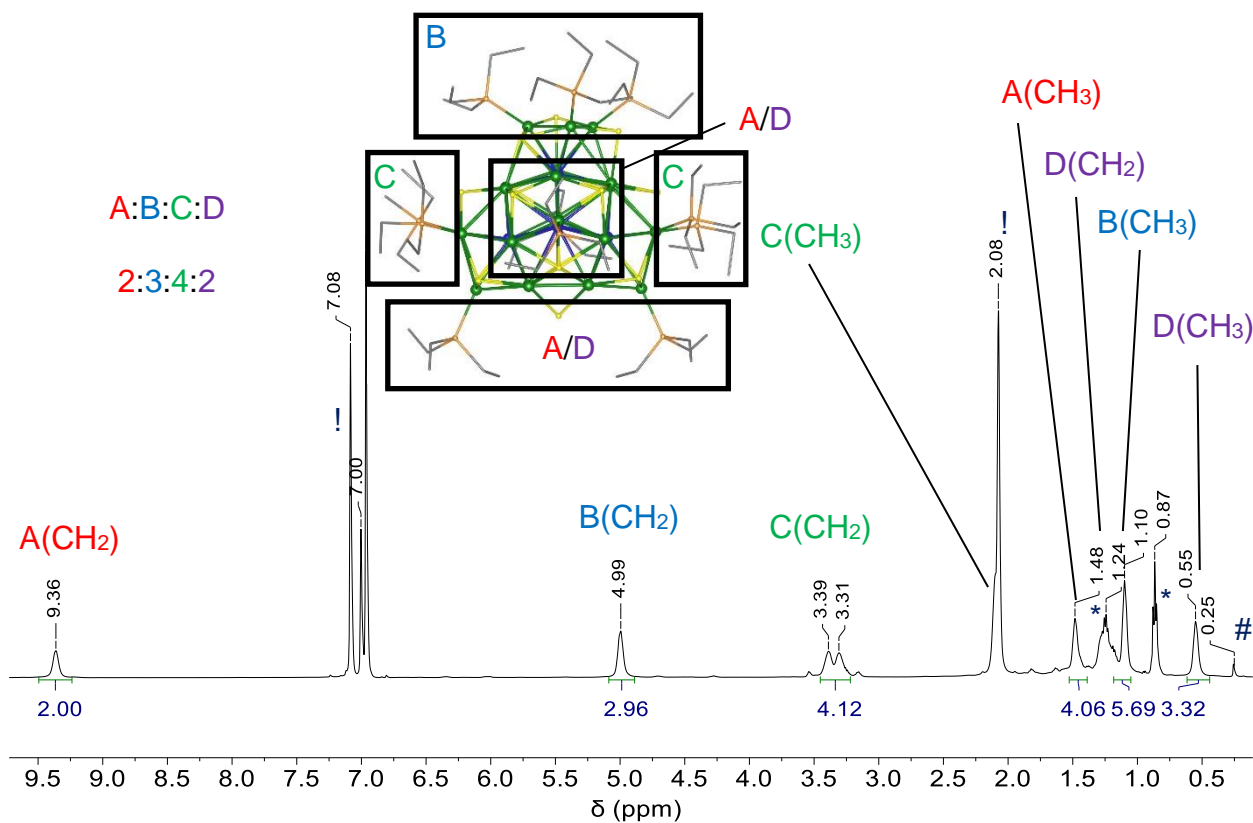


Figure S17. ^1H NMR (500 MHz, 25 °C, $\text{toluene-}d_8$) spectrum of $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]$ (1).

(*) indicates the presence of *n*-pentane.¹³ (#) indicates the presence of silicone grease.¹³ (!) indicates resonances assignable to toluene.¹³

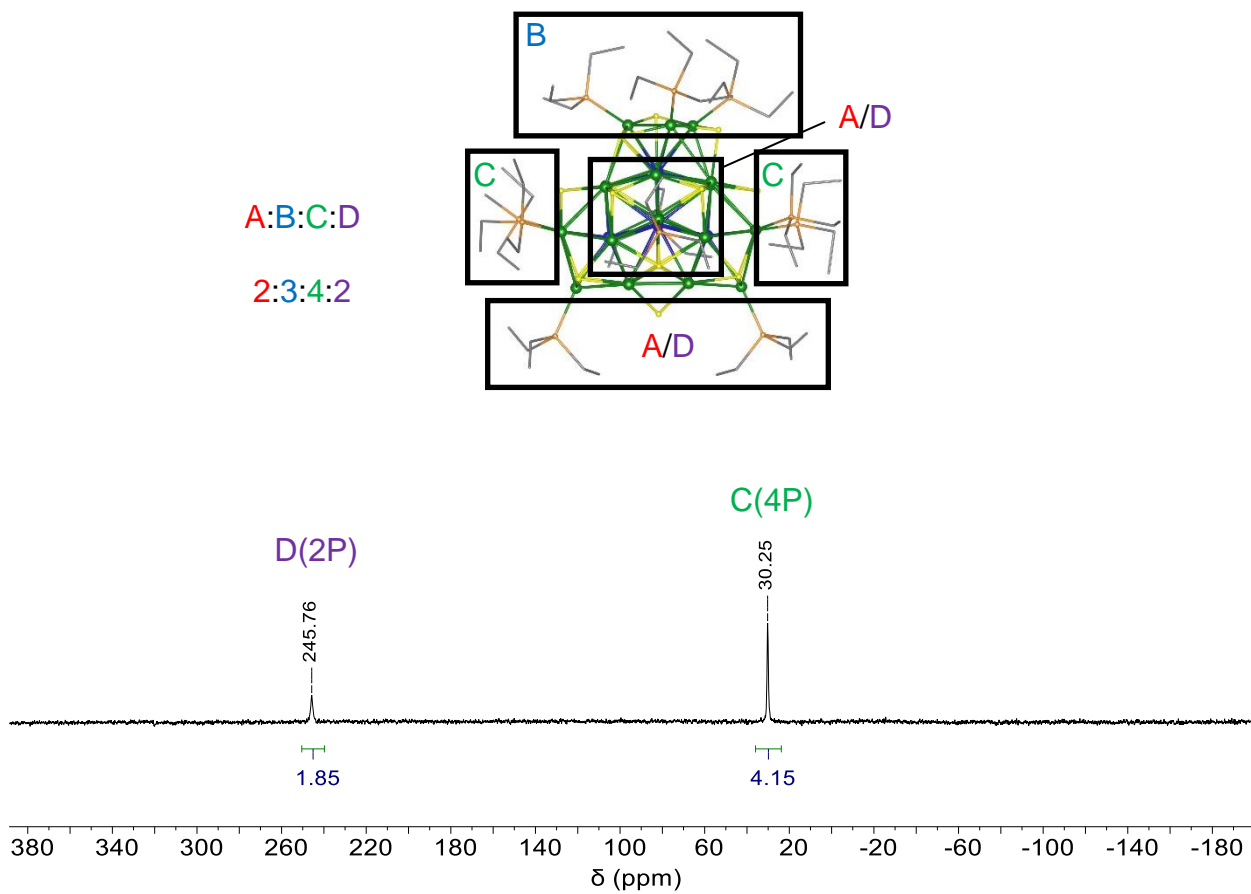


Figure S 18. Partial $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 25 °C, toluene- d_8) spectrum of $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]$ (**1**) from -200 ppm to 400 ppm.

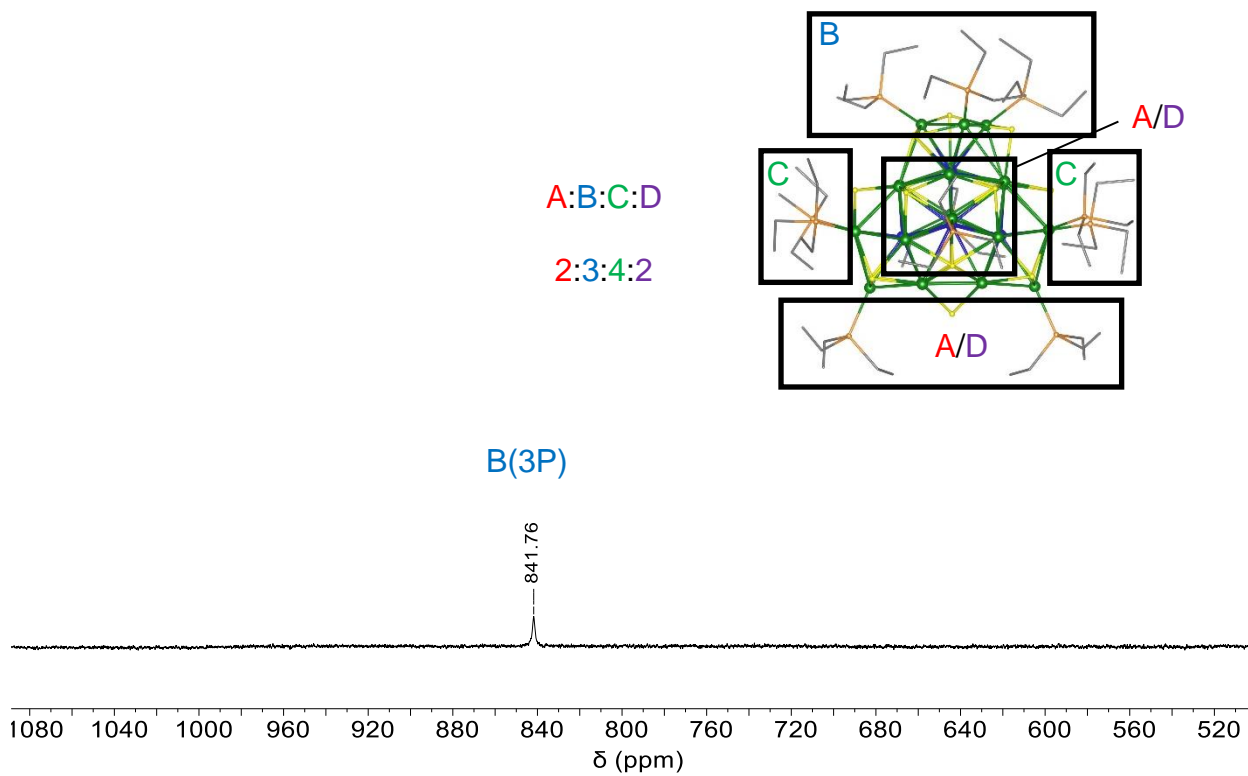


Figure S 19. Partial $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 25 °C, toluene- d_8) spectrum of $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]$ (**1**) from 500 ppm to 1100 ppm.

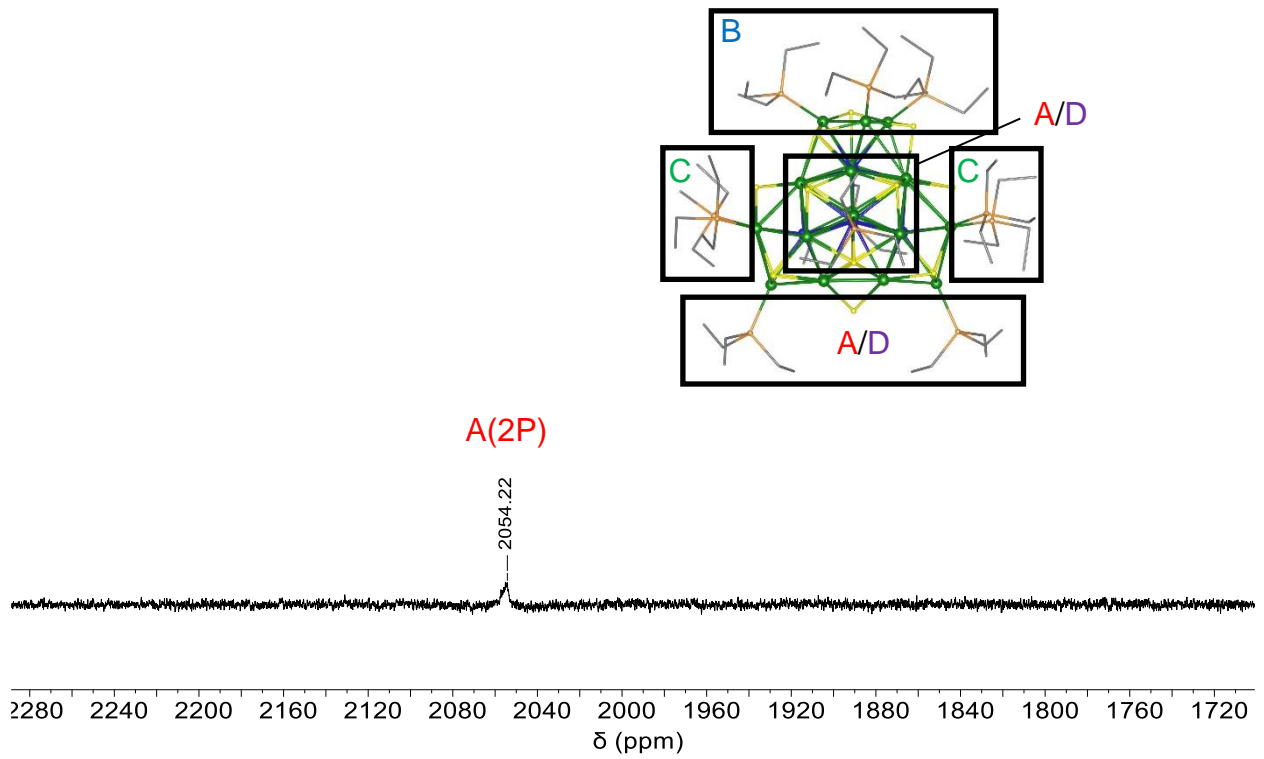


Figure S 20. Partial $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 25 °C, toluene- d_8) spectrum of $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]$ (**1**) from 1700 ppm to 2289 ppm.

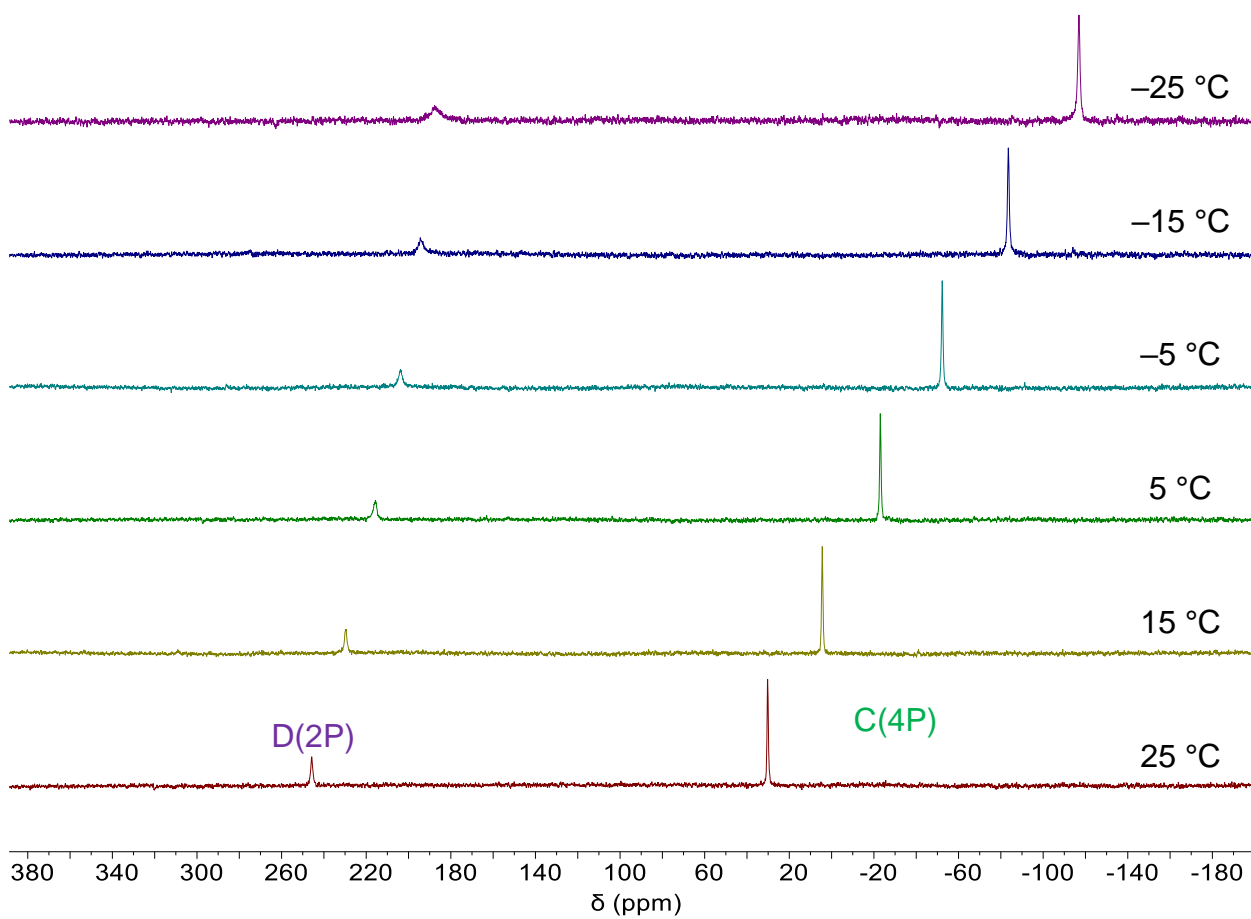


Figure S 21. Variable temperature partial $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, toluene- d_8) spectrum of $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]$ (**1**) from -200 ppm to 400 ppm and from 25 °C to -25 °C.

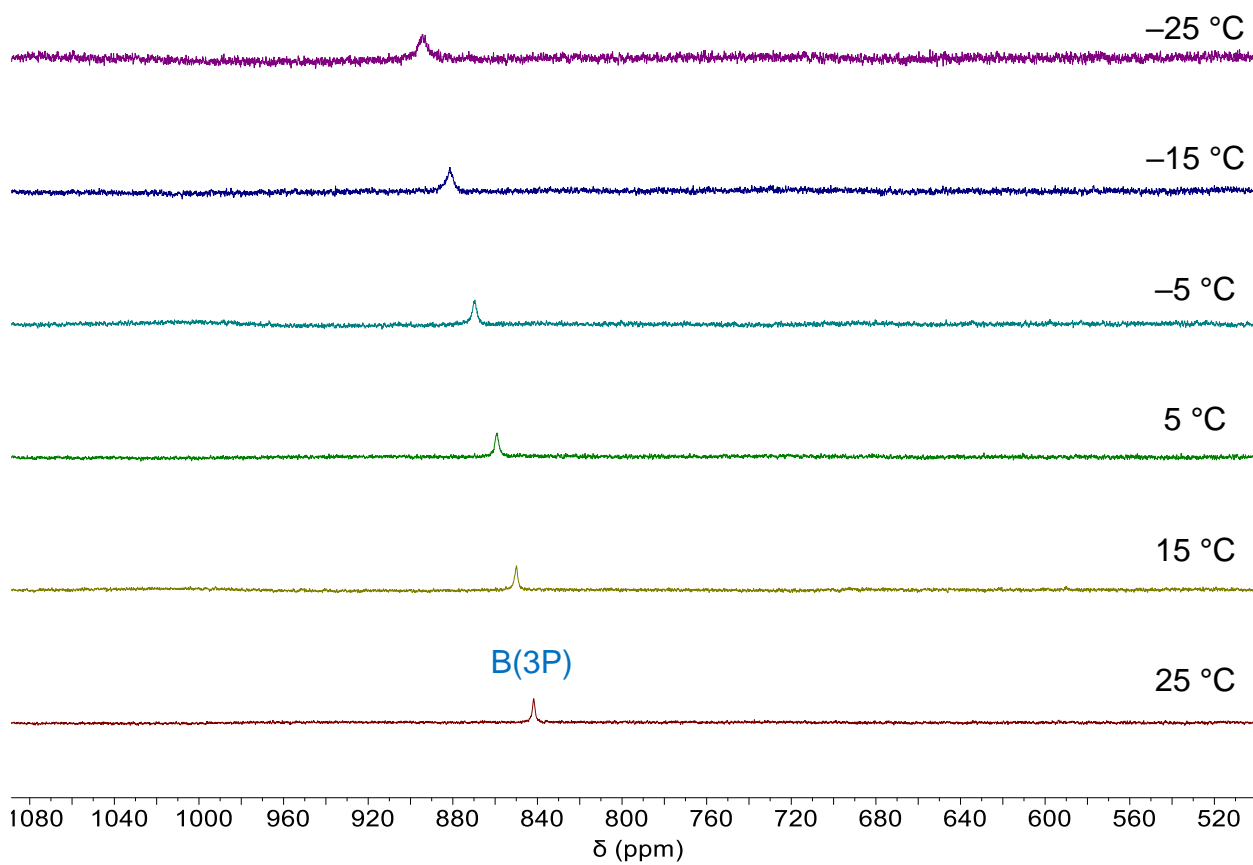


Figure S 22. Variable temperature partial $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, $\text{toluene-}d_8$) spectrum of $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]$ (**1**) from 500 ppm to 1100 ppm and from $25\text{ }^\circ\text{C}$ to $-25\text{ }^\circ\text{C}$.

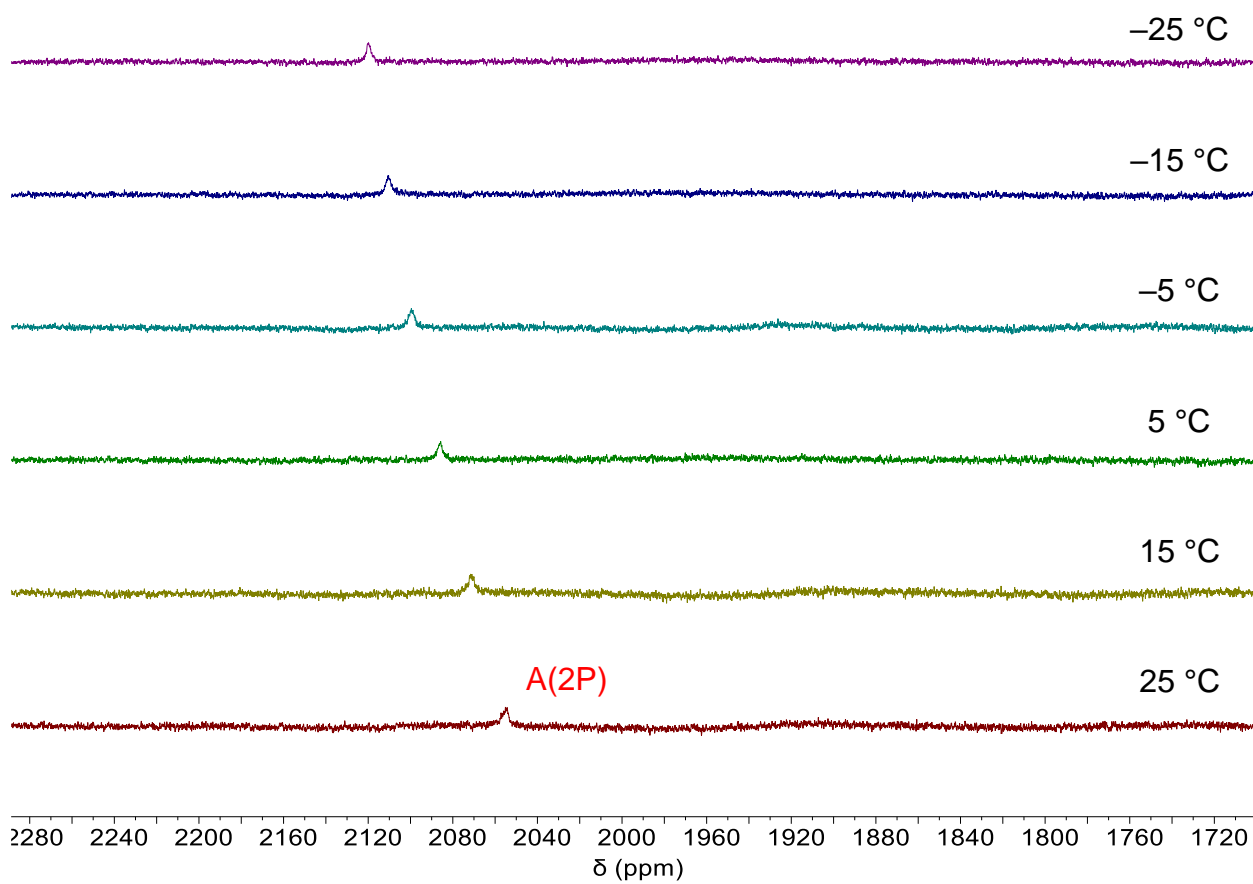


Figure S 23. Variable temperature partial $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, toluene- d_8) spectrum of $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]$ (**1**) from 1700 ppm to 2289 ppm and from $25\text{ }^\circ\text{C}$ to $-25\text{ }^\circ\text{C}$.

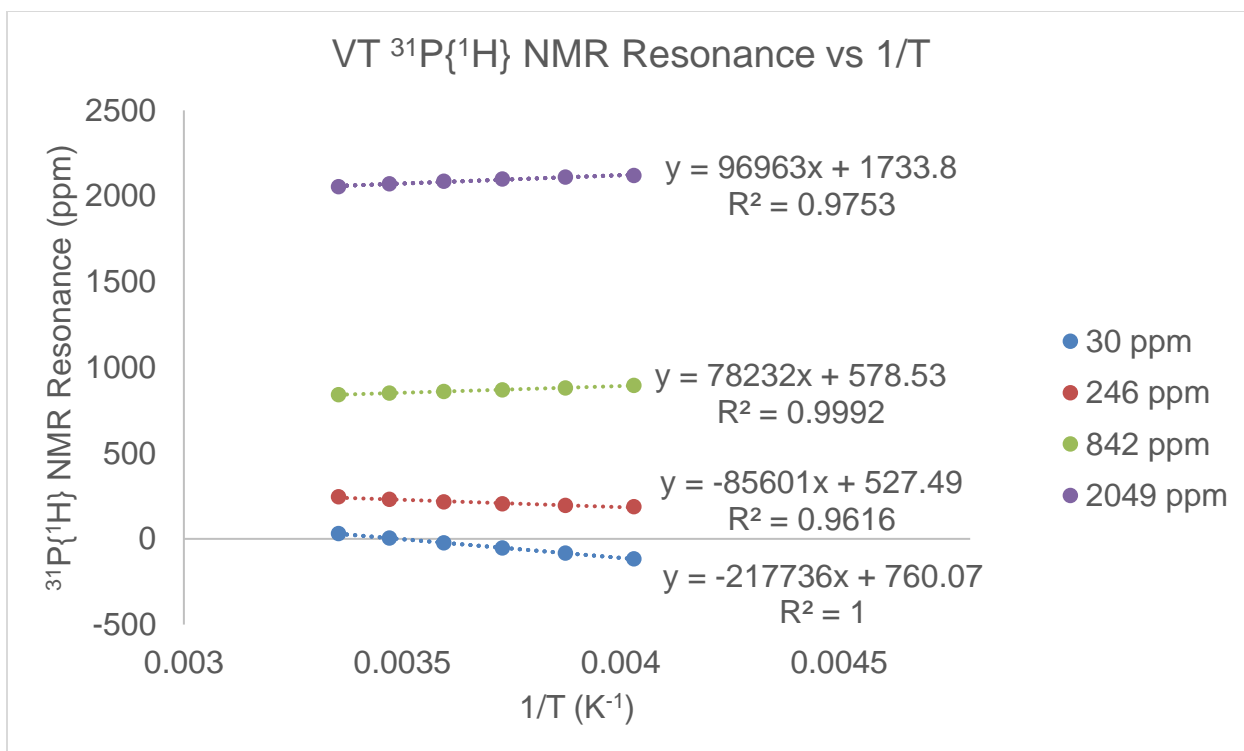


Figure S24. A plot of $^{31}\text{P}\{^1\text{H}\}$ NMR resonances of **1** in toluene- d_8 from 25 °C to -25 °C versus $1/T$. Linear trendlines are displayed for each ^{31}P NMR assignment.

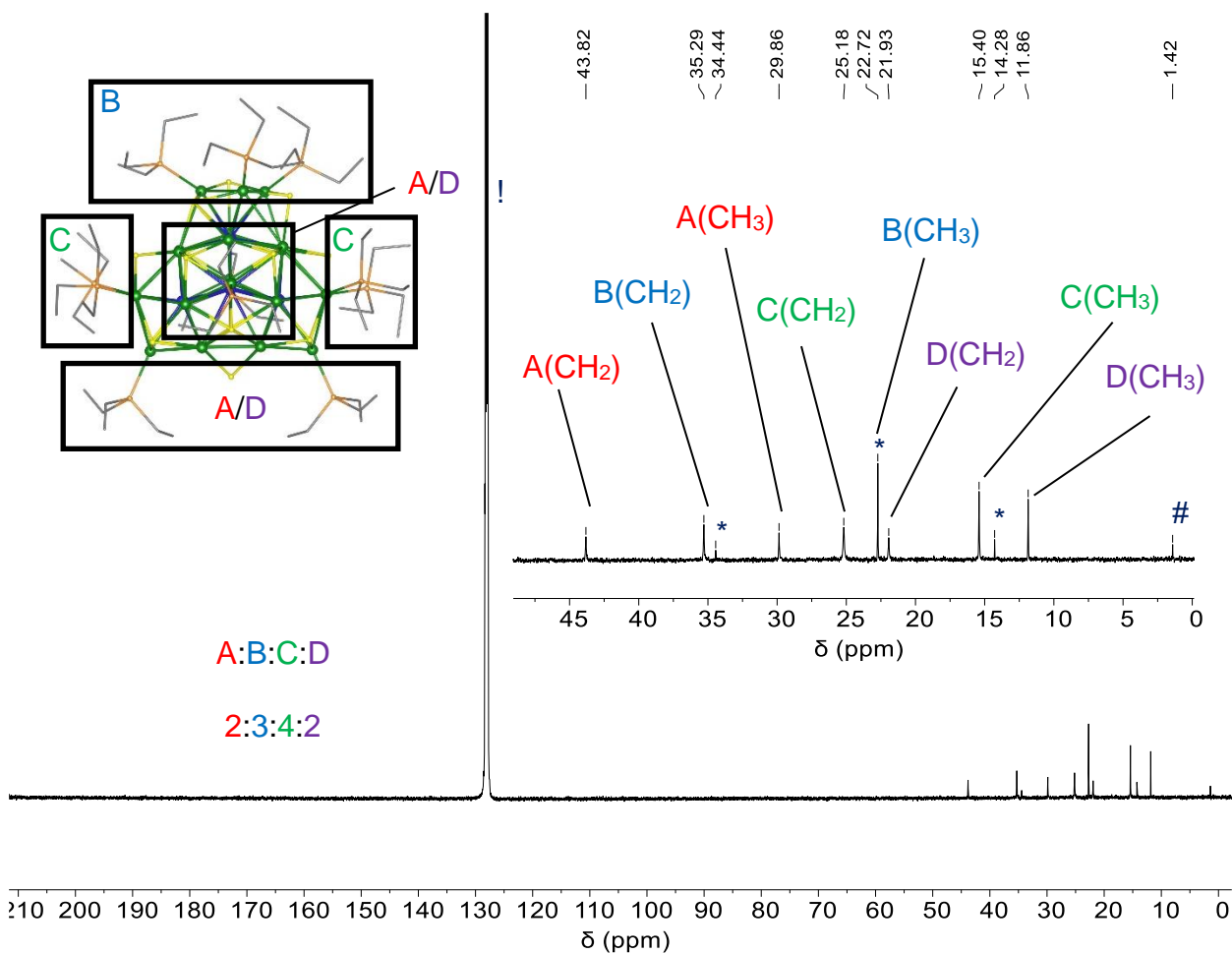


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 25 °C, benzene- d_6) spectrum of $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]$ (**1**). The inset above shows a partial $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum 0 to 49 ppm. (*) indicates the presence of *n*-pentane.¹³ (#) indicates the presence of silicone grease.¹³ (!) indicates a resonance assignable to benzene- d_6 .¹³ The resonance at 22.72 ppm is assignable to $\text{P}(\text{CH}_2\text{CH}_3)_3$ (*B*) overlapping with an *n*-pentane resonance.¹³

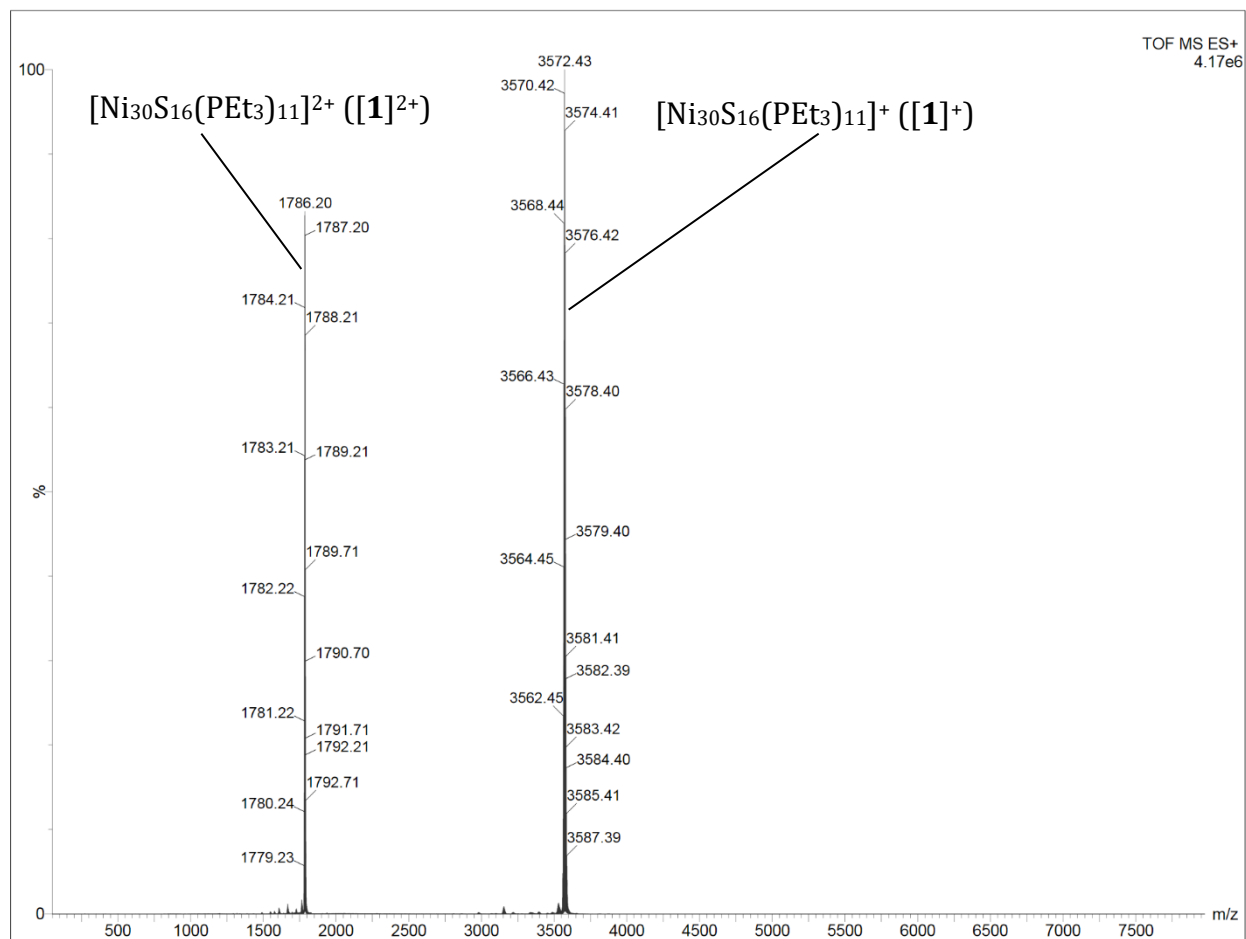


Figure S26. ESI-MS (positive ion mode) spectrum of $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]$ (**1**) taken in THF at a capillary voltage of 2.50 kV.

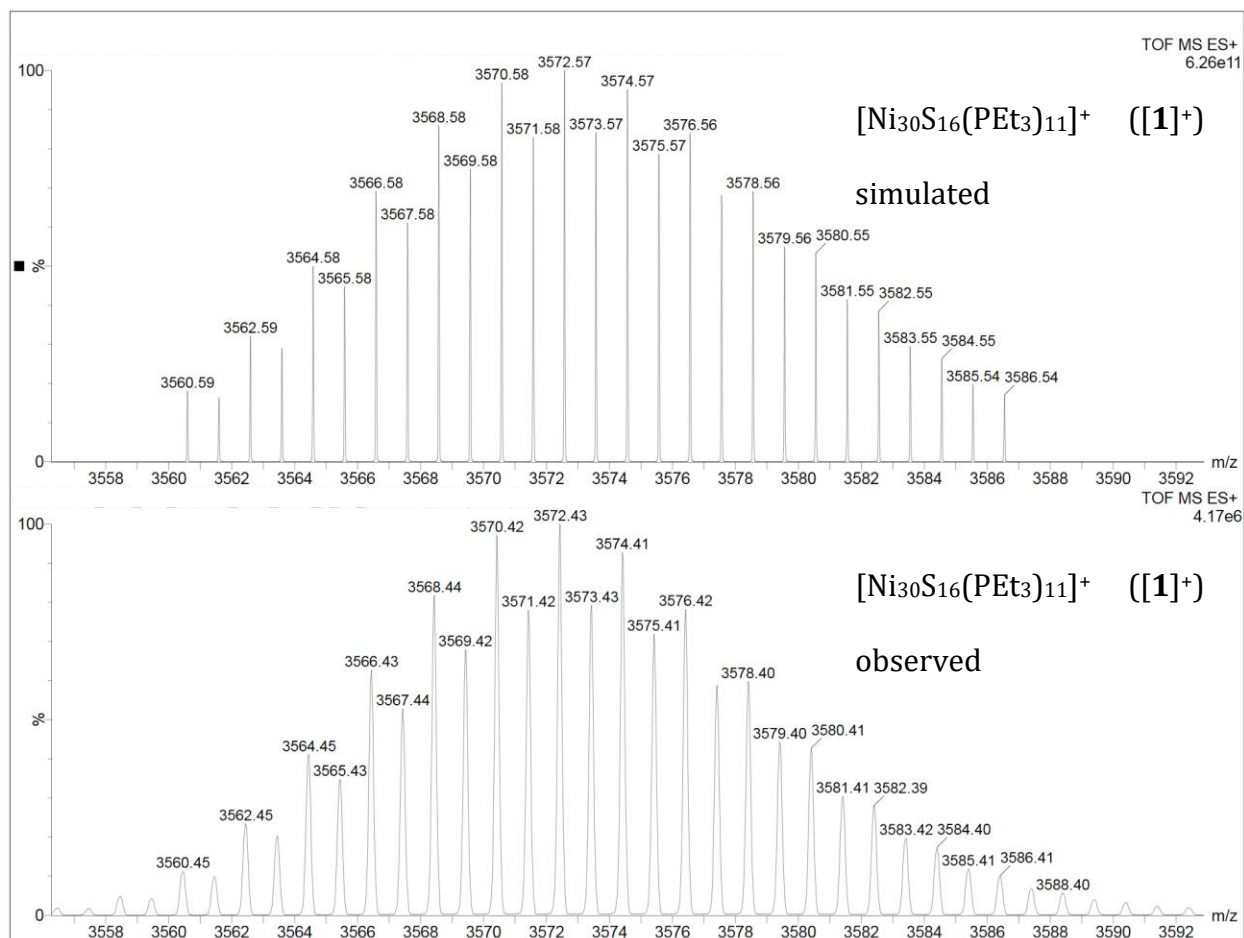


Figure S27. Partial ESI-MS (positive ion mode) spectrum of $[\text{Ni}_{30}\text{S}_{16}(\text{PET}_3)_{11}]$ (**1**) taken in THF at a capillary voltage of 2.50 kV. Only the peak at 3572.43 m/z is displayed (bottom spectrum) with the simulated spectrum for $[\text{Ni}_{30}\text{S}_{16}(\text{PET}_3)_{11}]^+$ ($[\mathbf{1}]^+$) displayed above (top spectrum).

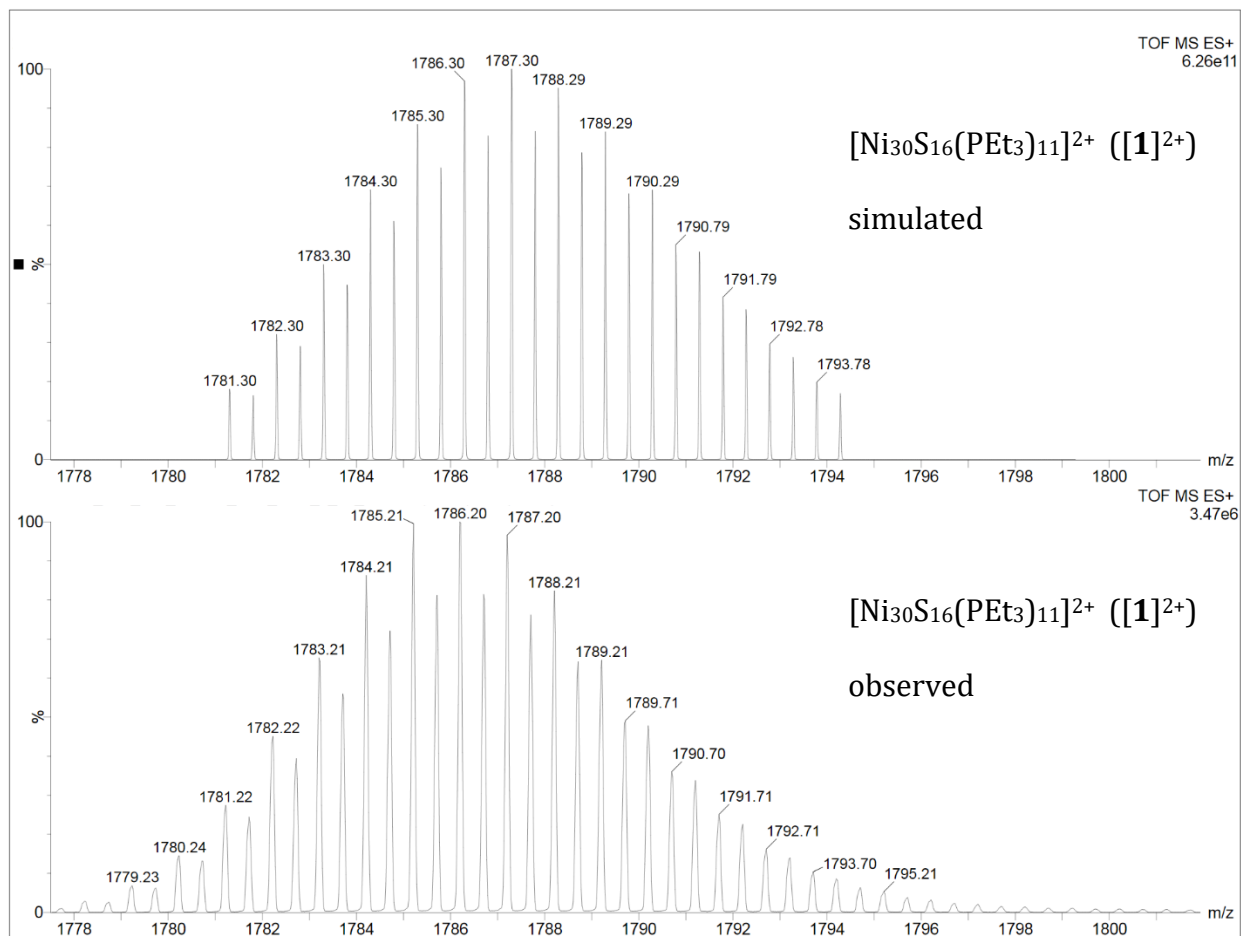


Figure S28. Partial ESI-MS (positive ion mode) spectrum of $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]$ (**1**) taken in THF at a capillary voltage of 2.50 kV. Only the peak at 1786.20 m/z is displayed (bottom spectrum) with the simulated spectrum for $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]^{2+}$ ($[\mathbf{1}]^{2+}$) displayed above (top spectrum).

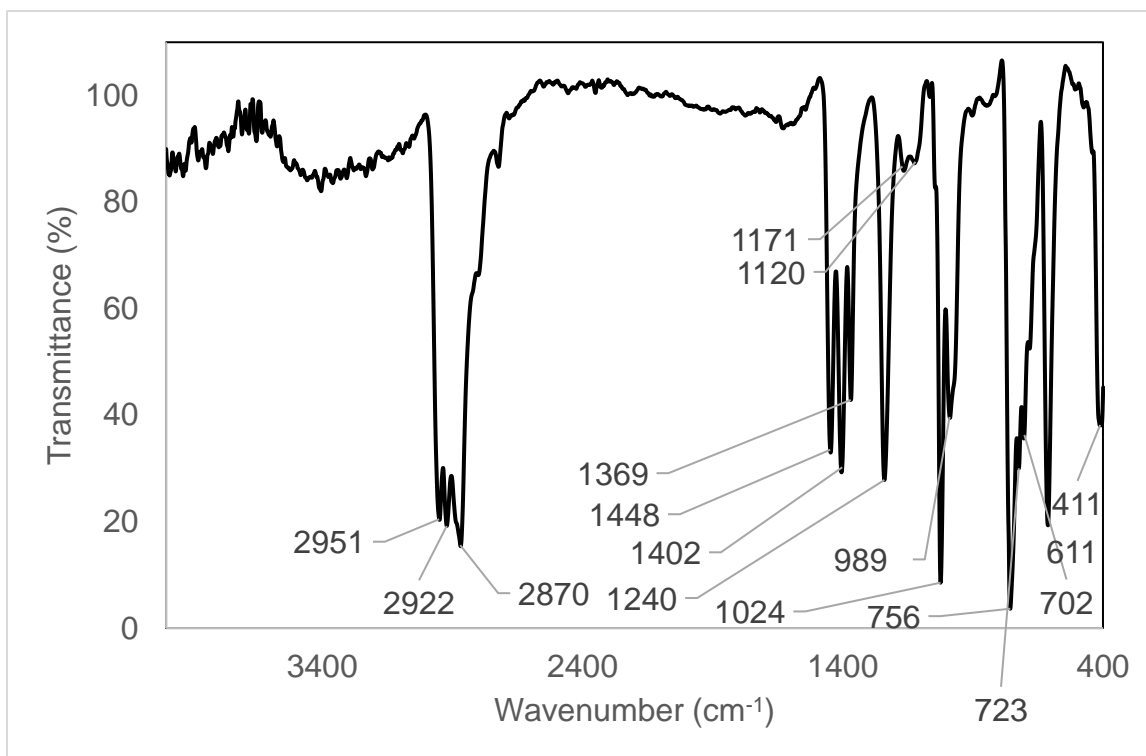


Figure S29. IR spectrum of $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]$ (**1**) (KBr pellet).

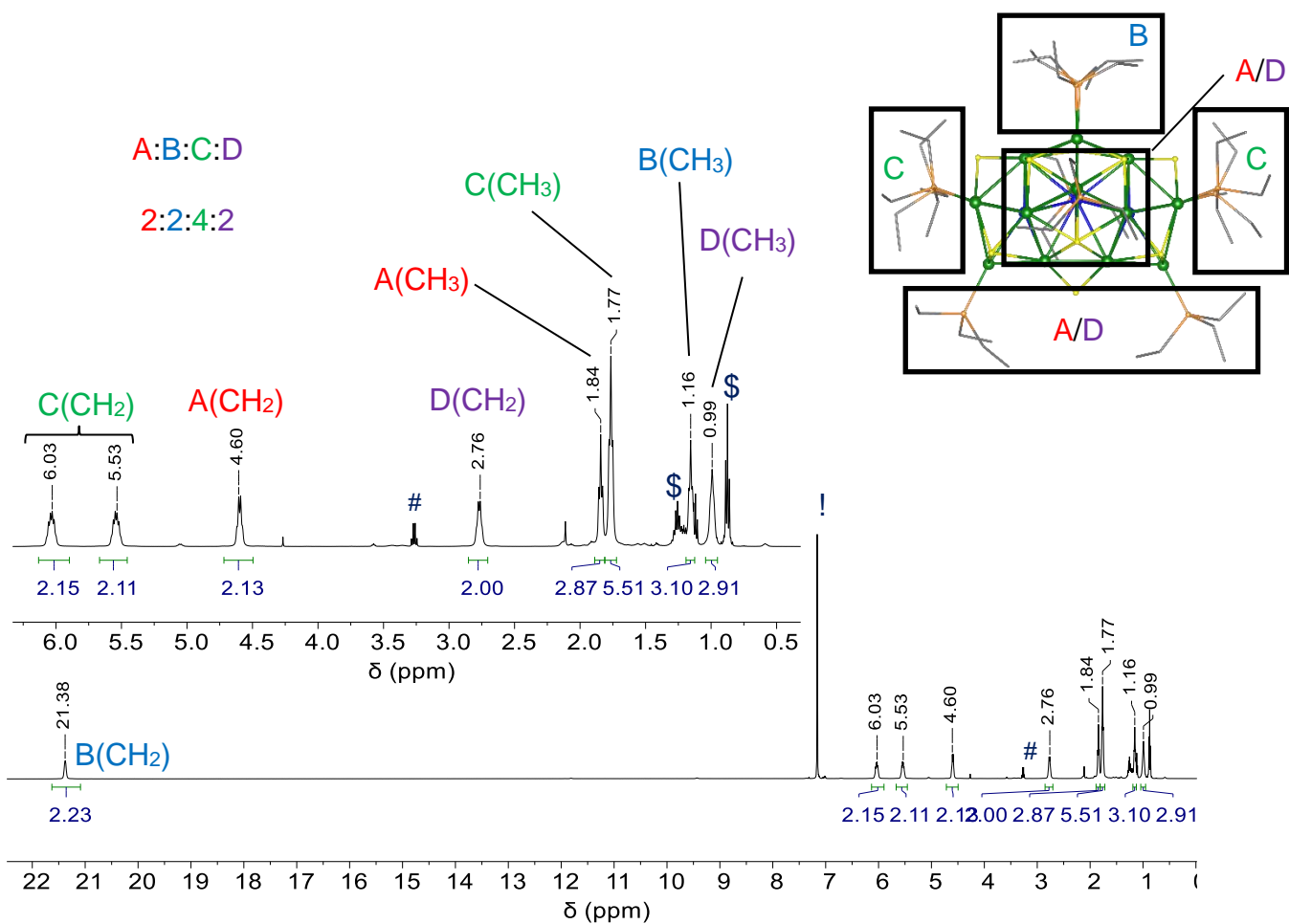


Figure S30. ^1H NMR (500 MHz, 25 °C, benzene- d_6) spectrum of $[\text{Ni}_{26}\text{S}_{14}(\text{PEt}_3)_{10}]$ (**2**).

(\$) indicates the presence of *n*-pentane.¹³ (!) indicates a resonance assignable to benzene.¹³ (#) indicates a resonance assignable to diethyl ether.¹³

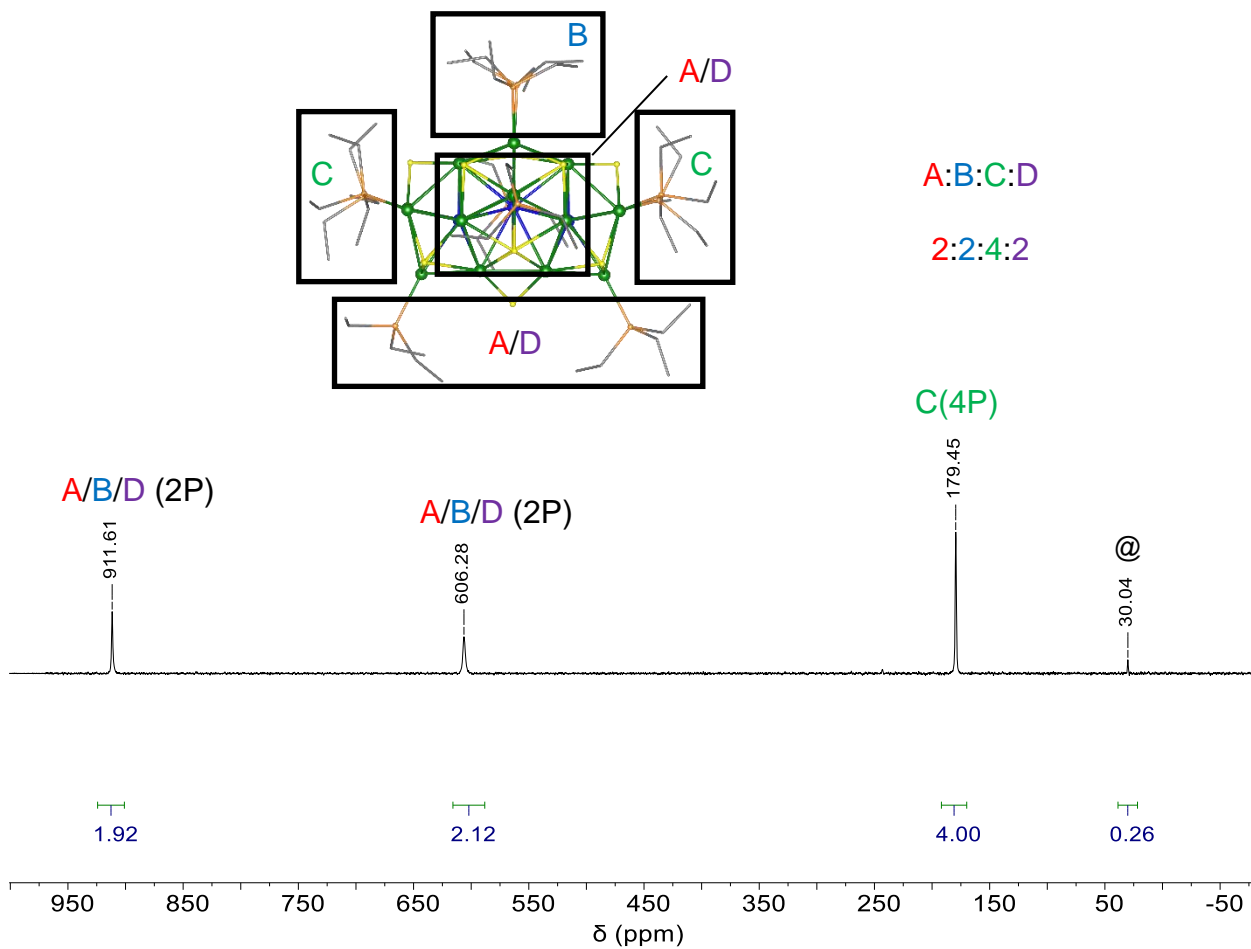


Figure S 31. Partial $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 25 °C, benzene- d_6) spectrum of $[\text{Ni}_{26}\text{S}_{14}(\text{PEt}_3)_{10}]$ (**2**) from -65 ppm to 1000 ppm. (@) indicates a resonance assignable to **1**.

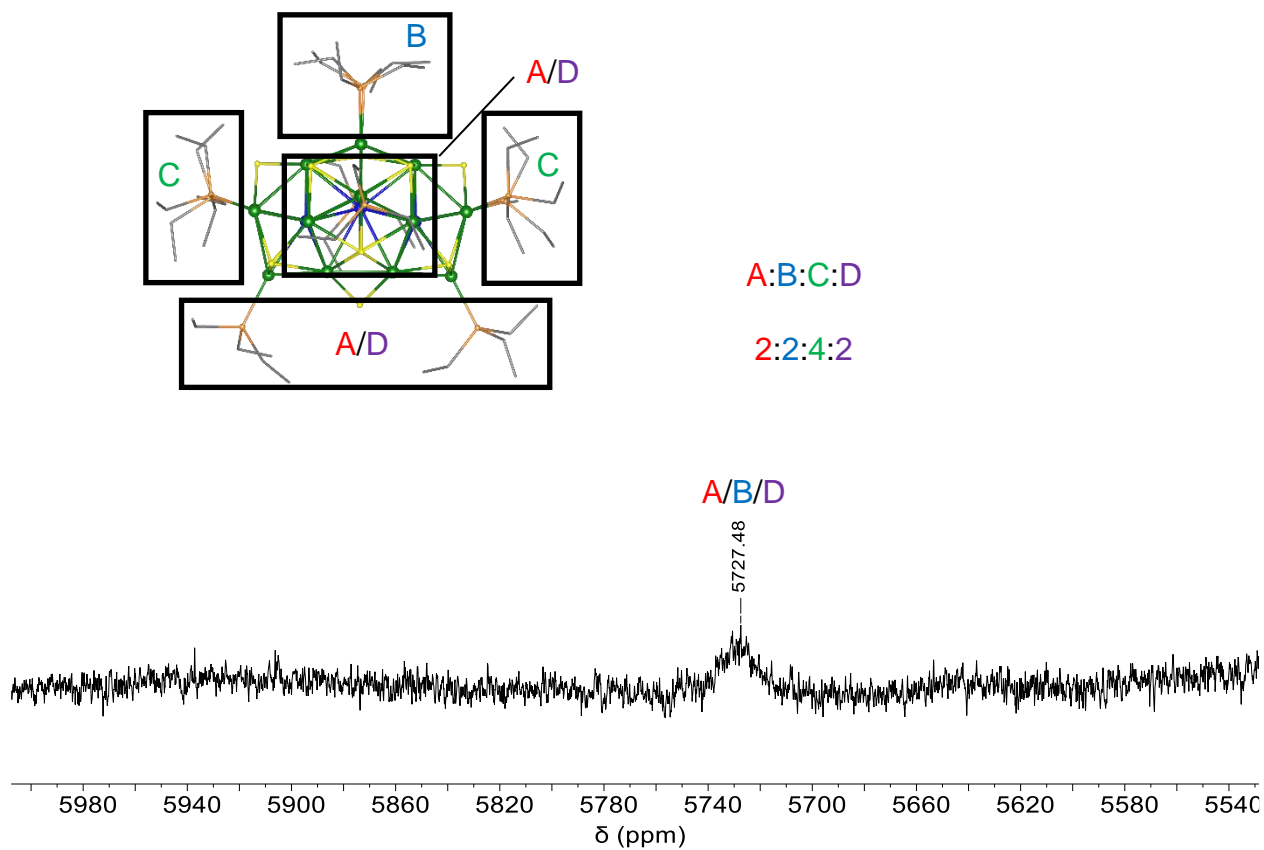


Figure S 32. Partial ³¹P{¹H} NMR (202 MHz, 25 °C, benzene-*d*₆) spectrum of [Ni₂₆S₁₄(PEt₃)₁₀] (**2**) from 5540 ppm to 6000 ppm.

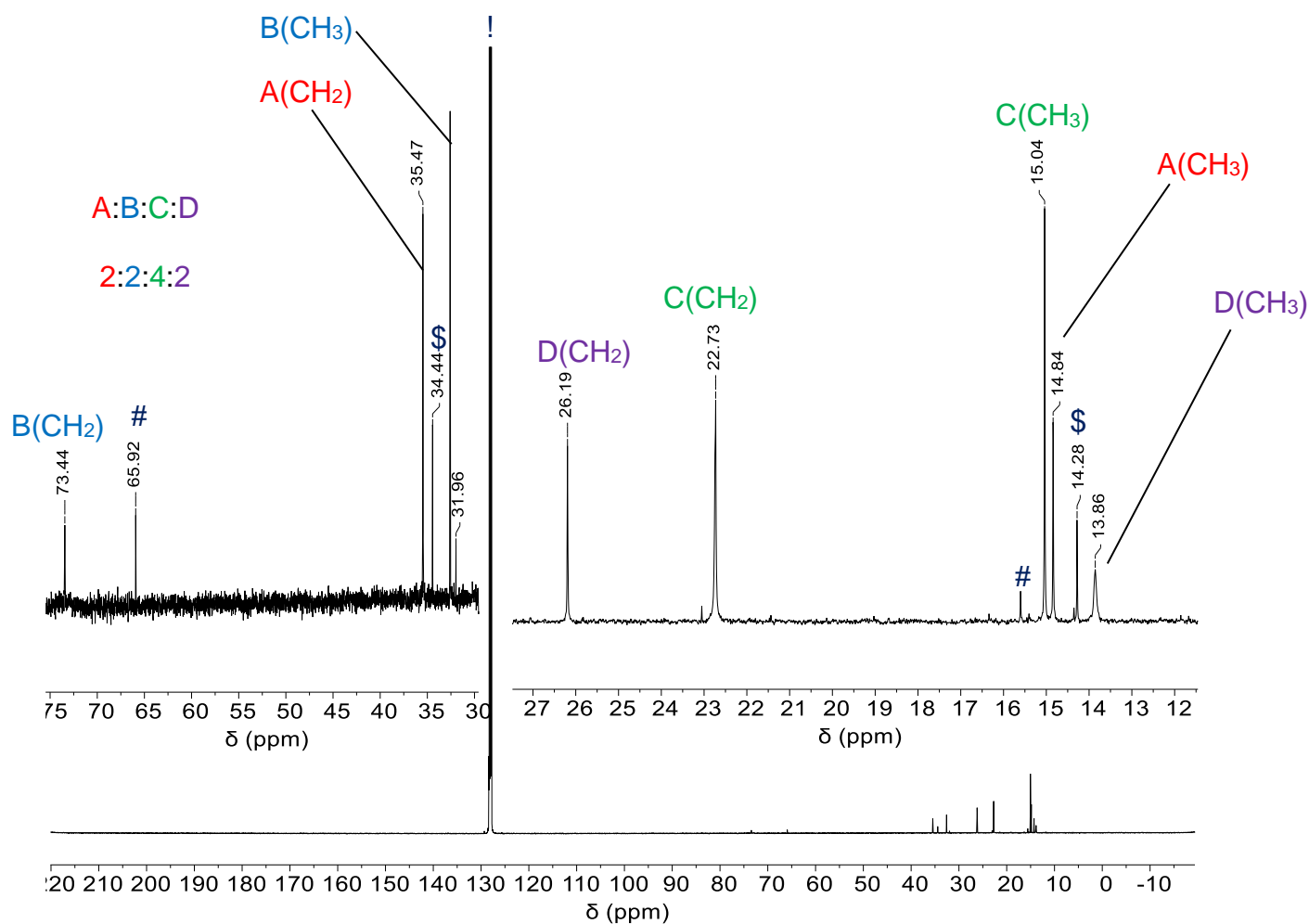


Figure S33. $^{13}C\{^1H\}$ NMR (126 MHz, 25 °C, benzene- d_6) spectrum of 2. The inset above shows a partial $^{13}C\{^1H\}$ NMR spectrum 0 to 49 ppm. (\$) indicates the presence of *n*-pentane.¹³ (#) indicates the presence of silicone grease.¹³ (!) indicates a resonance assignable to benzene- d_6 .¹³

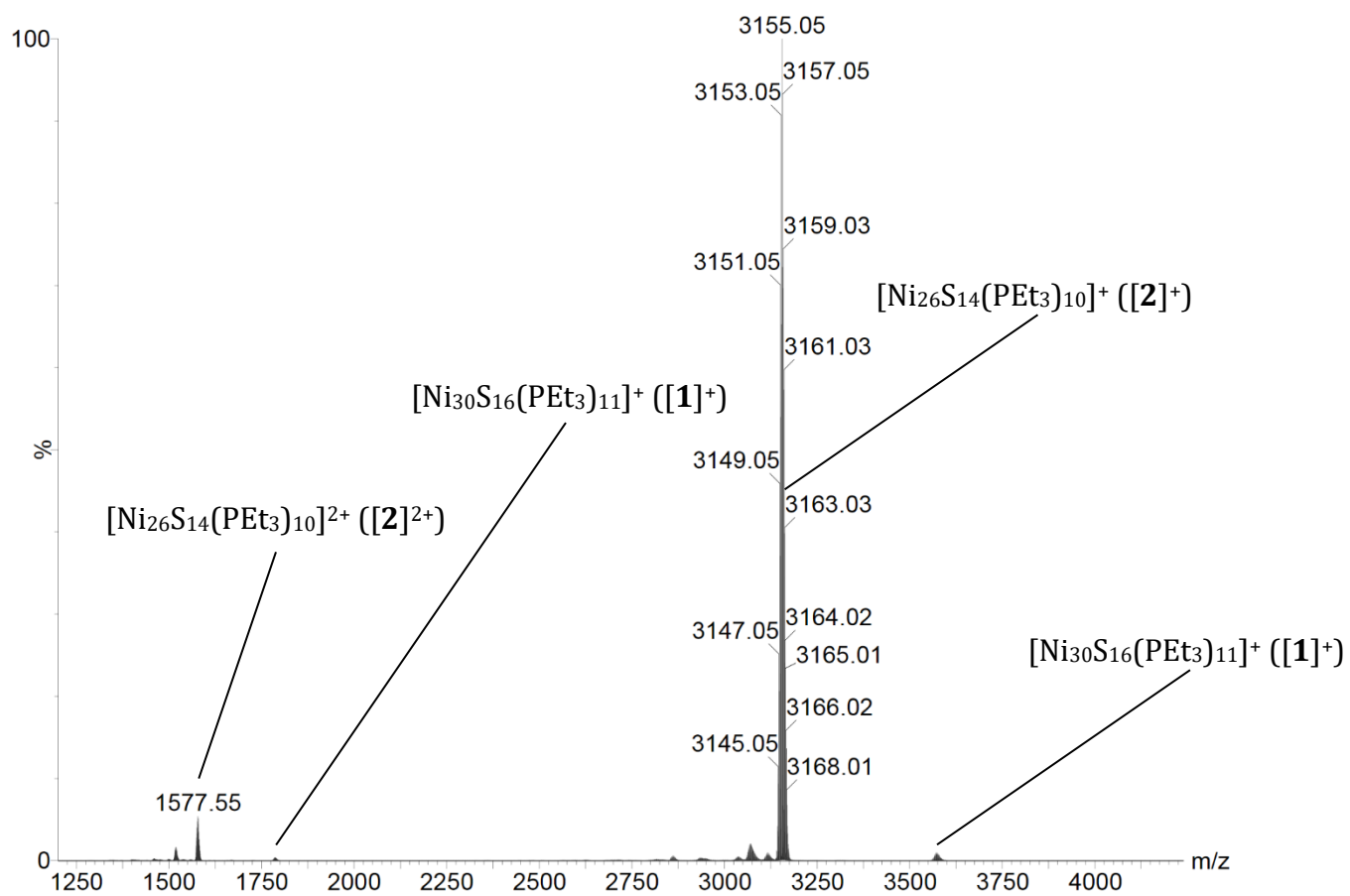


Figure S34. ESI-MS (positive ion mode) spectrum of $[\text{Ni}_{26}\text{S}_{14}(\text{PEt}_3)_{10}]$ (**2**) taken in THF at a capillary voltage of 2.50 kV.

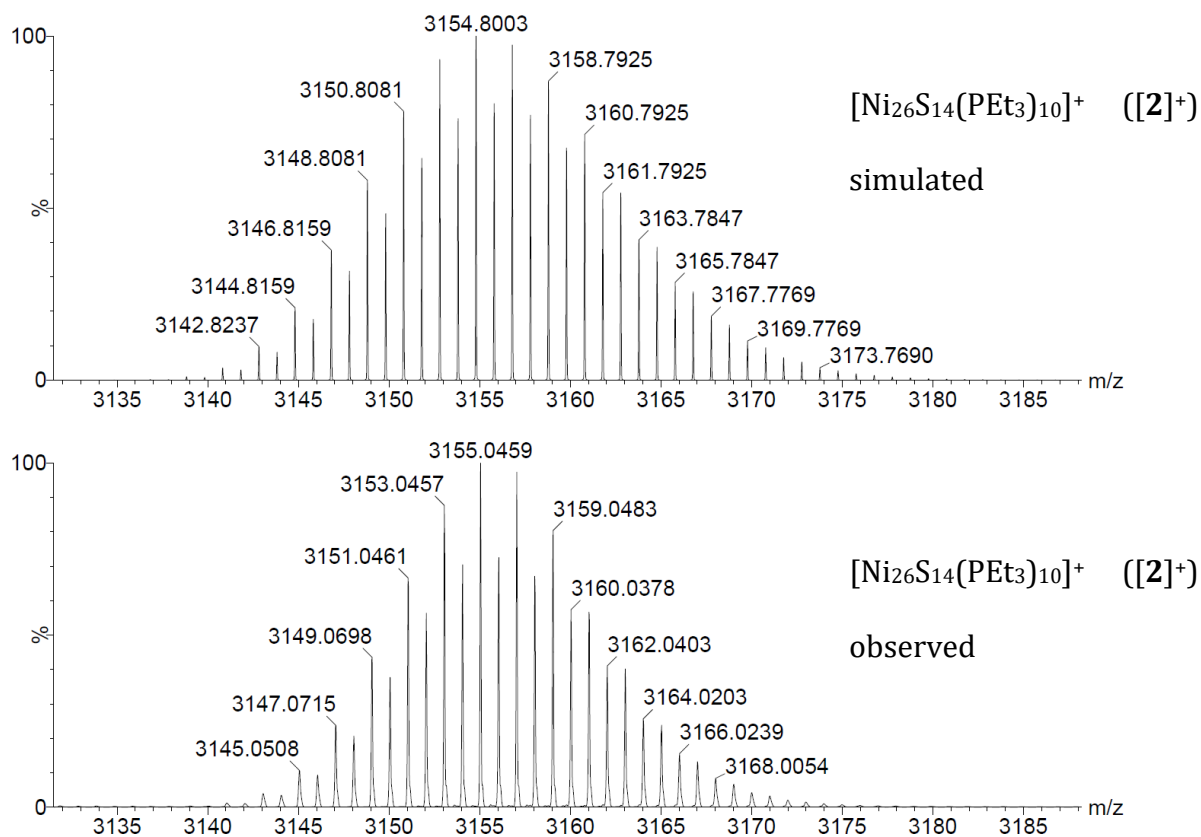


Figure S35. Partial ESI-MS (positive ion mode) spectrum of $[\text{Ni}_{26}\text{S}_{14}(\text{PEt}_3)_{10}] \quad (2)$ taken in THF at a capillary voltage of 2.50 kV. Only the peak at 3155.05 m/z is displayed (bottom spectrum) with the simulated spectrum for $[\text{Ni}_{26}\text{S}_{14}(\text{PEt}_3)_{10}]^+ \quad ([2]^+)$ displayed above (top spectrum).

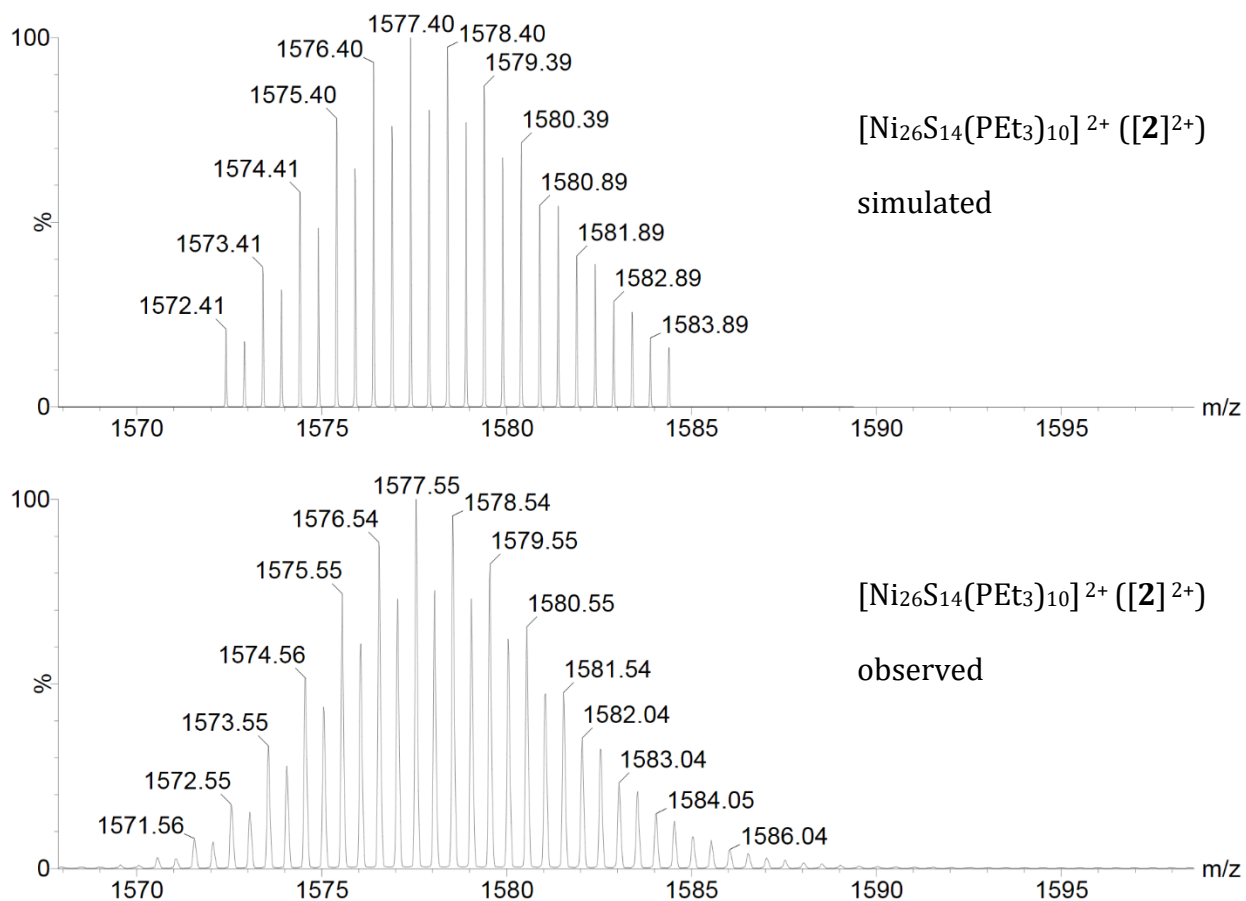


Figure S36. Partial ESI-MS (positive ion mode) spectrum of $[\text{Ni}_{26}\text{S}_{14}(\text{PEt}_3)_{10}]$ ($\mathbf{2}$) taken in THF at a capillary voltage of 2.50 kV. Only the peak at 1577.55 m/z is displayed (bottom spectrum) with the simulated spectrum for $[\text{Ni}_{26}\text{S}_{14}(\text{PEt}_3)_{10}]^{2+}$ ($[\mathbf{2}]^{2+}$) displayed above (top spectrum).

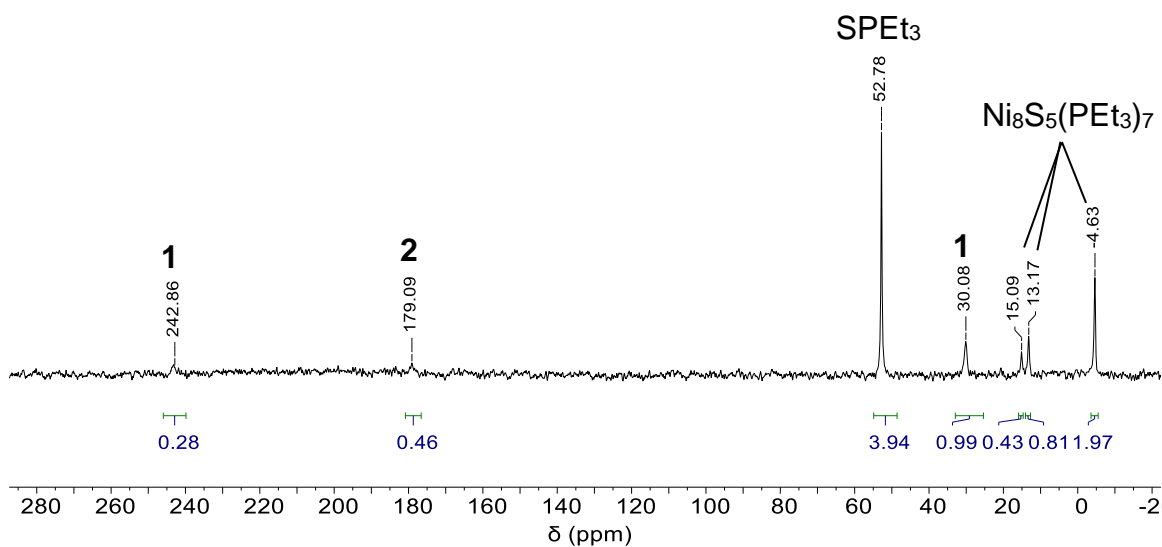


Figure S37. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 25 °C, benzene-*d*₆) spectrum of an aliquot taken from the reaction of [Ni(1,5-cod)₂] (30 equiv), PEt₃ (31 equiv), and S₈ (1.9 equiv) after thermolysis at 95 °C for 5 h. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C₆D₆): δ 242.86 (**1**, 2P), 179.09 (**2**, 4P), 52.78 (SPEt₃), 30.08 (**1**, 4P), 15.09 (Ni₈S₅(PEt₃)₇, 1P), 13.17 (Ni₈S₅(PEt₃)₇, 2P), -4.63 (Ni₈S₅(PEt₃)₇, 4P).

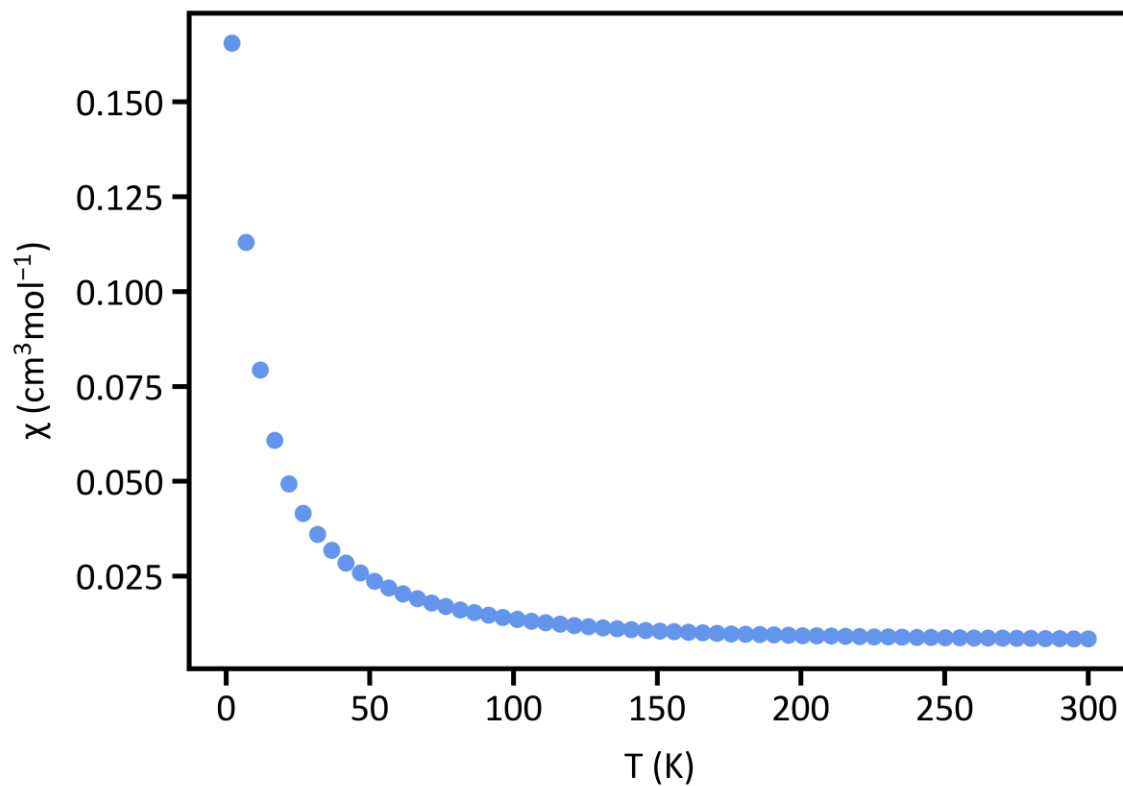


Figure S38. Variable-temperature magnetic susceptibility (χ) data for **1** collected at 1 T (10,000 Oe). For experimental details, see page S4.

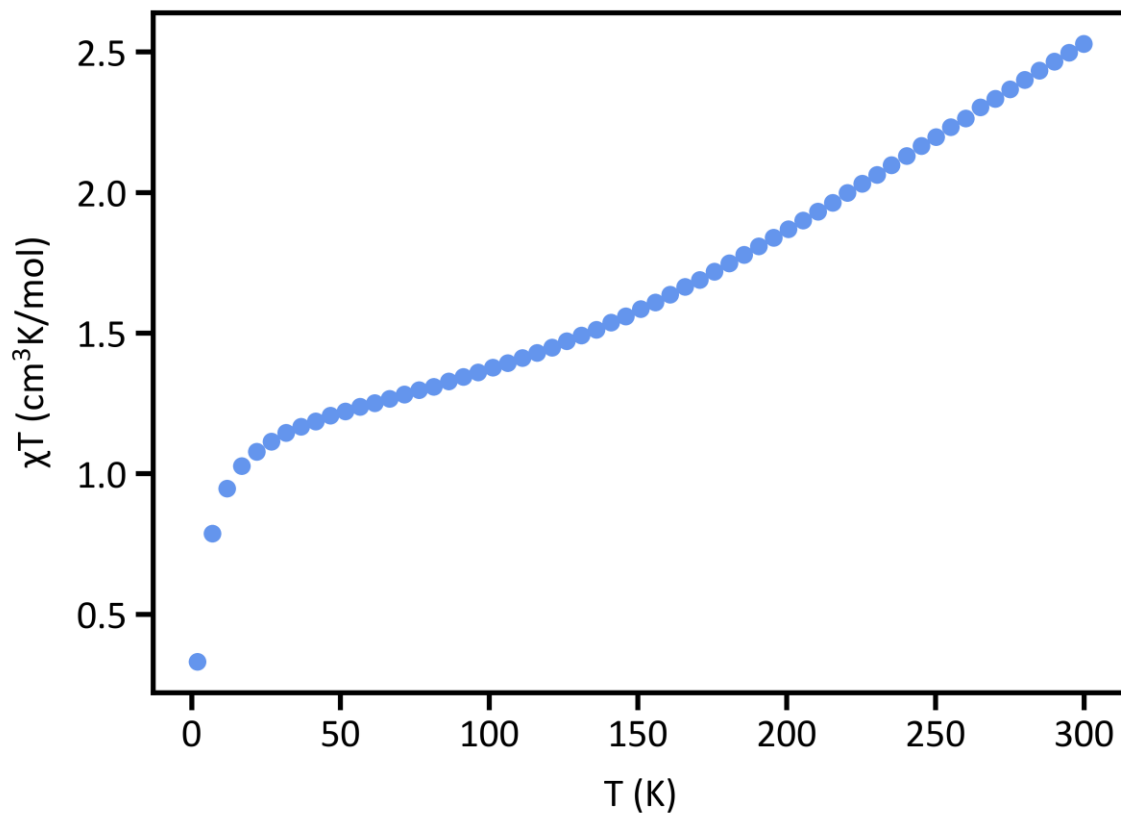


Figure S39. Variable-temperature magnetic susceptibility (χT) data for **1** collected at 1 T (10,000 Oe). For experimental details, see page S4.

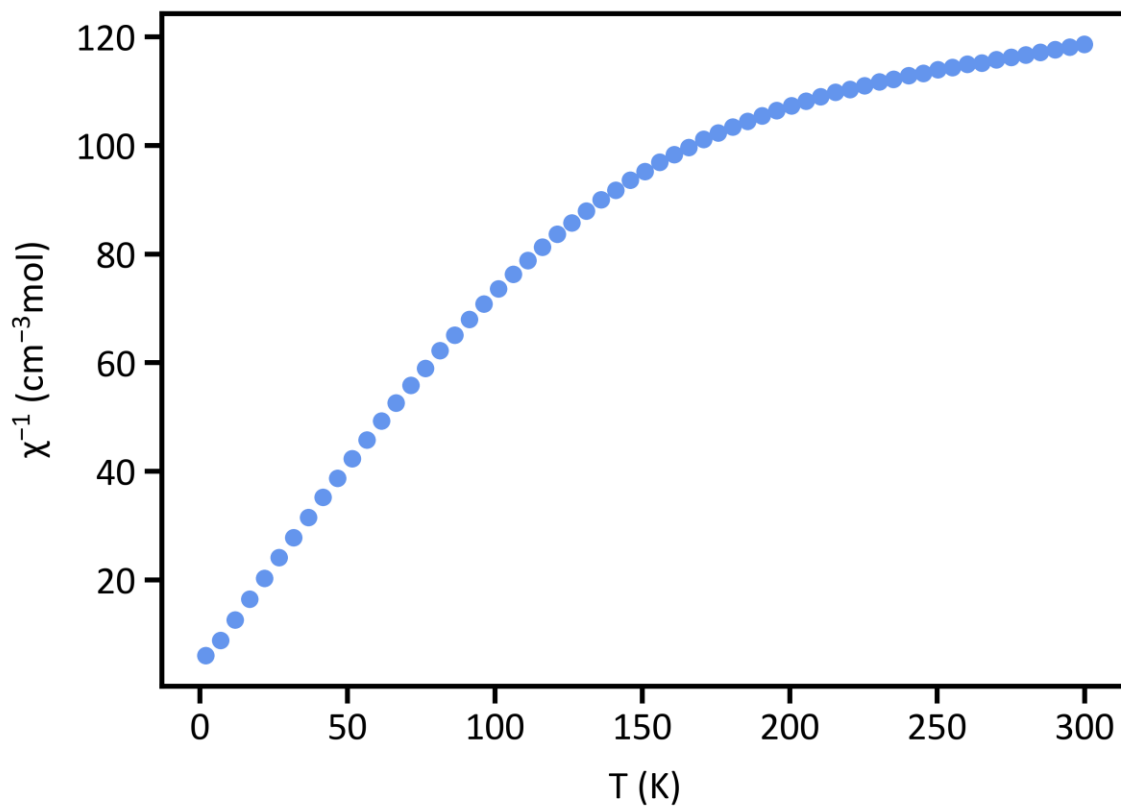


Figure S40. Variable-temperature magnetic susceptibility (χ^{-1}) data for **1** collected at 1 T (10,000 Oe). For experimental details, see page S4.

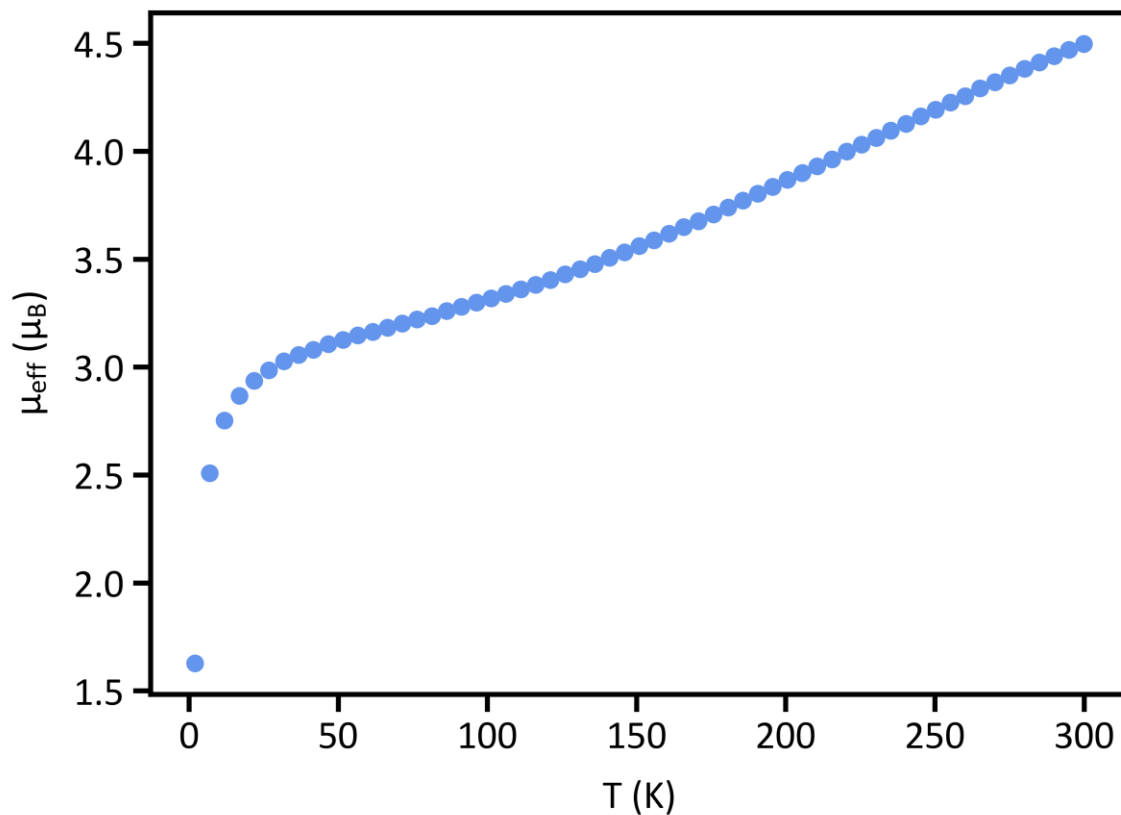


Figure S41. Effective magnetic moment of **1** collected at 1 T (10,000 Oe). For experimental details, see page S4.

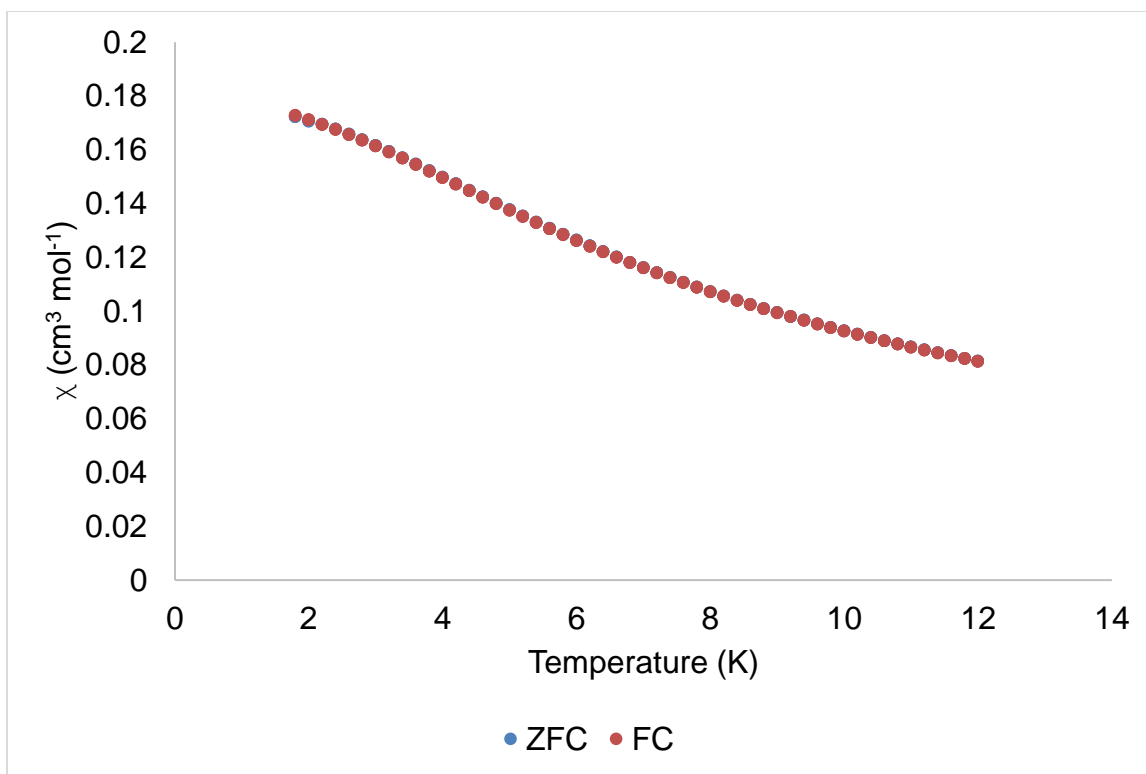


Figure S42. Zero-field cooled and field-cooled low-temperature susceptibility of **1** collected at 1 T (10,000 Oe) from 1.8 K to 12 K. For experimental details, see page S4.

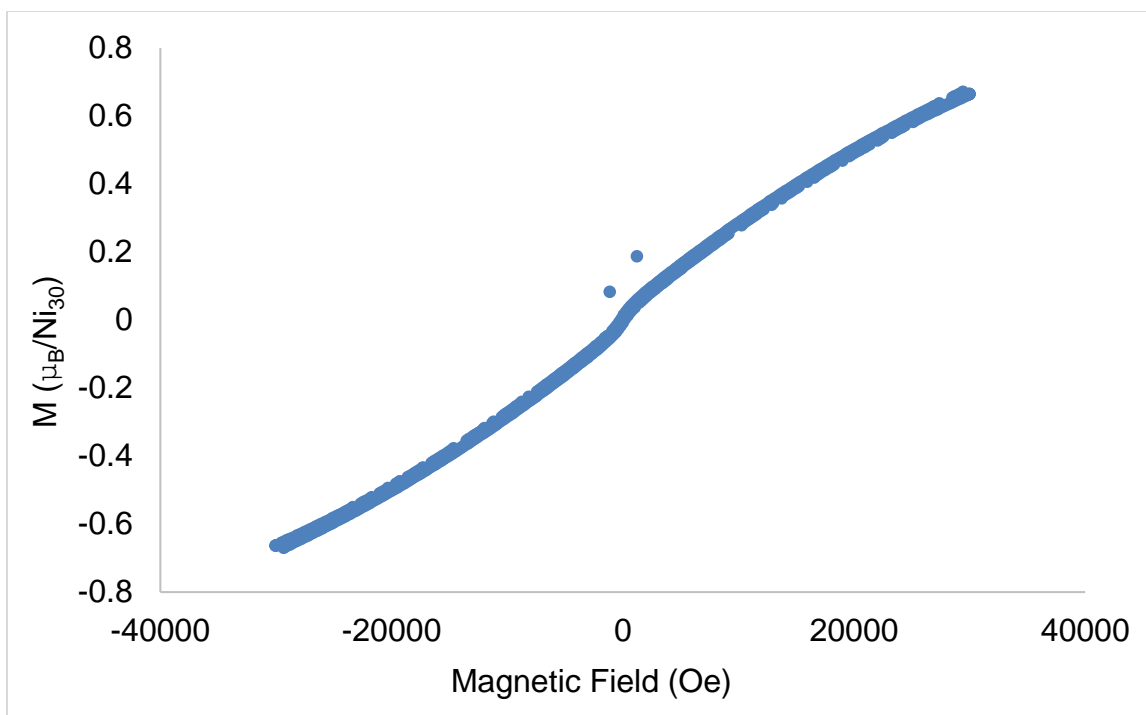


Figure S43. Magnetization versus magnetic field for **1** collected at 2 K from -40,000 Oe (-4 T) to 40,000 Oe (4 T) at a sweep rate of 200 Oe/s. For experimental details, see page S4.

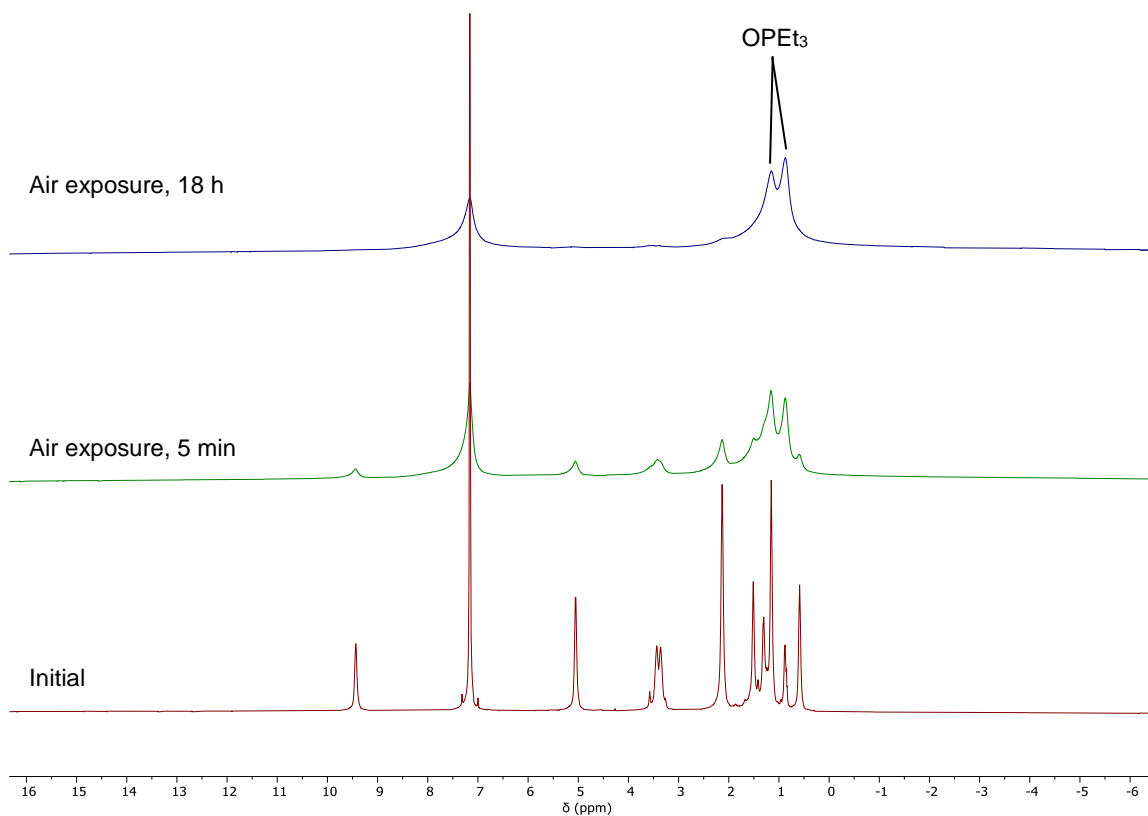


Figure S44. ^1H NMR (25 $^\circ\text{C}$, benzene- d_6) spectra of a solution of $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]$ (**1**) exposed to air. **Experimental Details:** $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]$ (**1**) (5 mg, 0.0014 mmol) was dissolved in benzene- d_6 (0.7 mL) and transferred to a borosilicate NMR tube and sealed. A ^1H NMR spectrum was recorded for the sample. The NMR tube was then unsealed, exposed to air for 1 min, and re-sealed, whereupon dark solids began to deposit in the NMR tube, although no color change was noted. The ^1H NMR spectrum was re-recorded. After 18 h, another ^1H NMR spectrum was recorded.

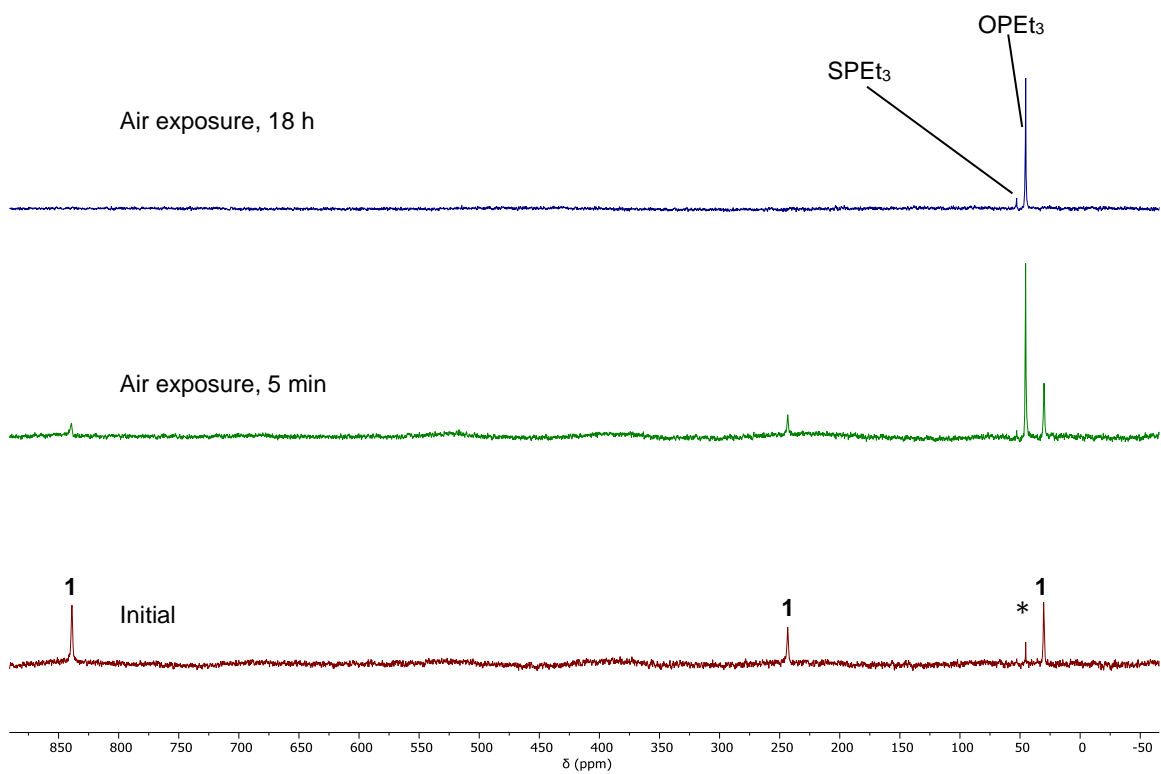


Figure S45. $^{31}\text{P}\{^1\text{H}\}$ NMR (25 °C, benzene- d_6) spectra of a solution of $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}]$ (**1**) exposed to air. **Experimental Details:** See Page S59. A small amount of Et_3PO was present as an impurity in this sample of **1** before exposure to air (*).

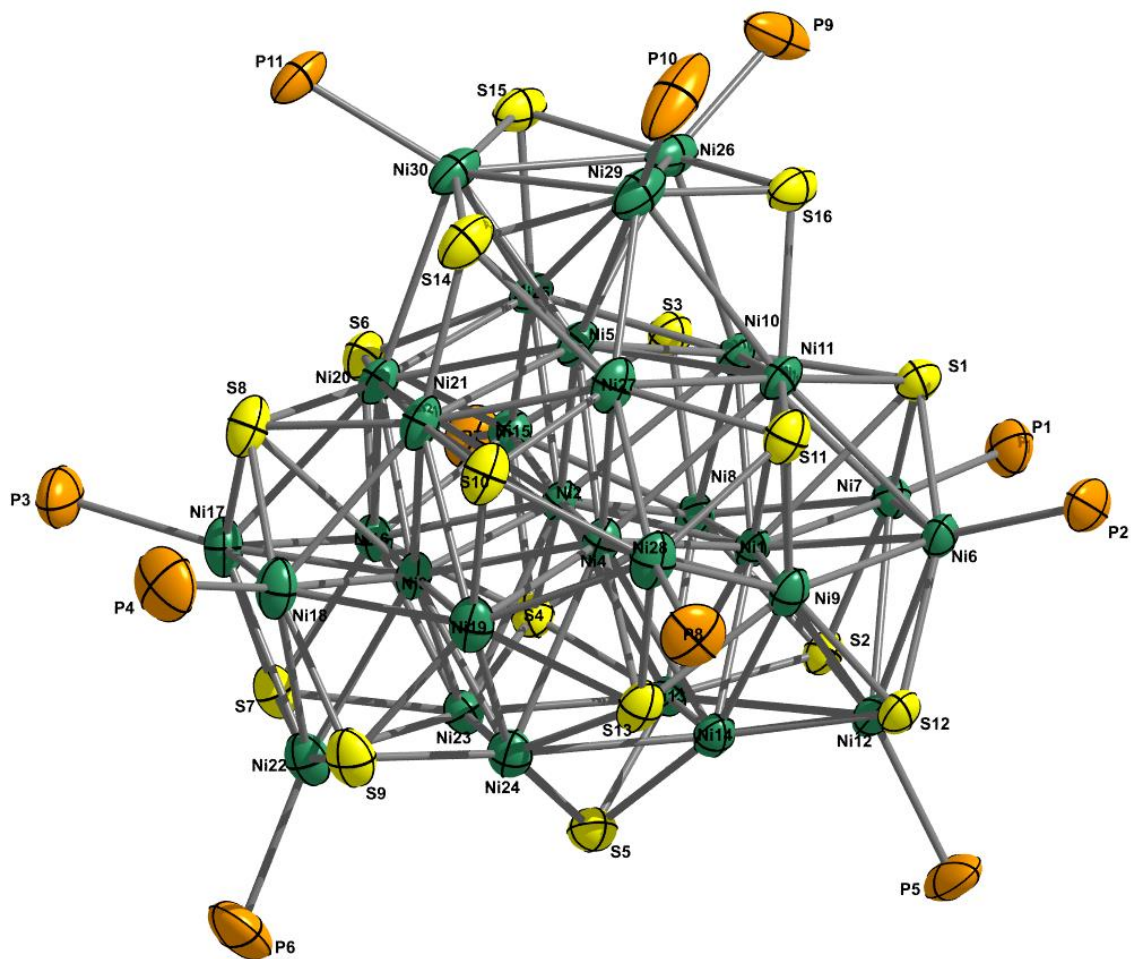


Figure S46. ORTEP diagram of $[\text{Ni}_{30}\text{S}_{16}(\text{PEt}_3)_{11}] \cdot \text{OC}_4\text{H}_{10}$ (**1**·Et₂O) with 50% thermal ellipsoids shown for non-carbon atoms. Hydrogen atoms, carbon atoms, and diethyl ether solvate are omitted for clarity.

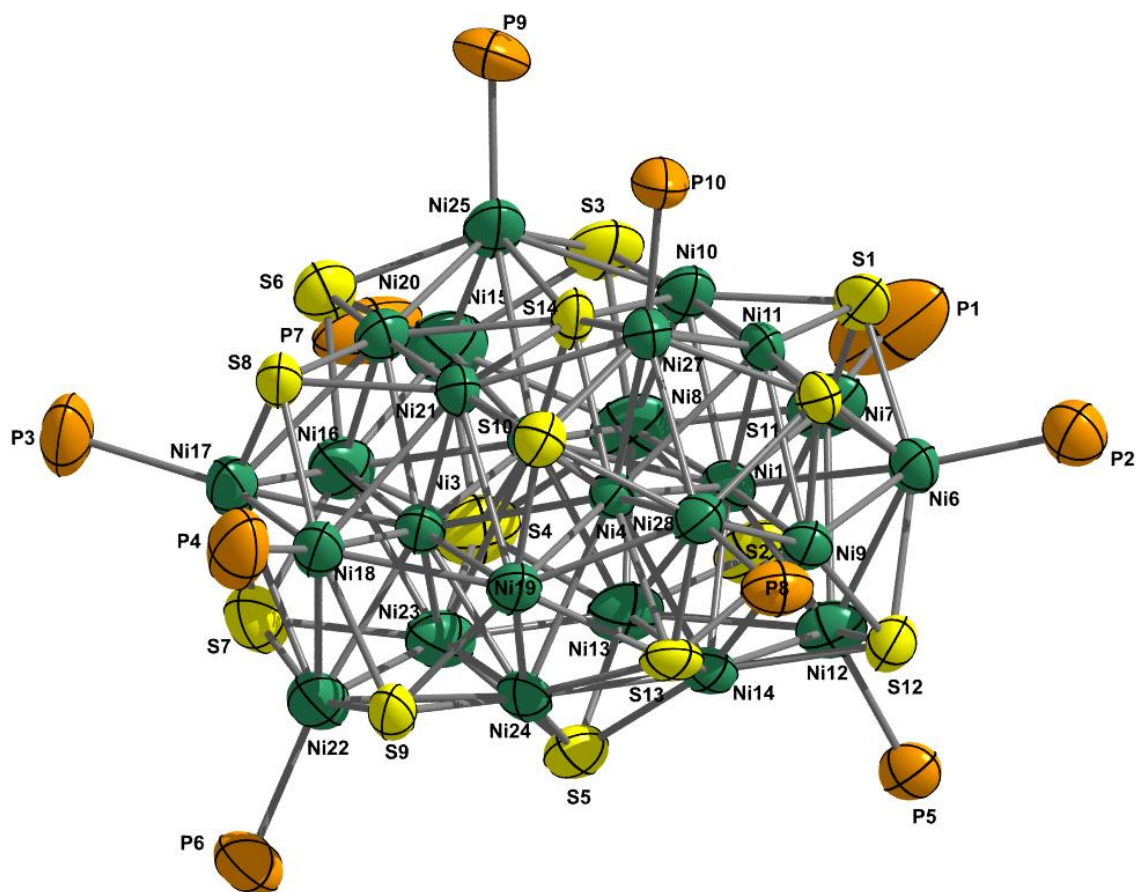


Figure S47. ORTEP diagram of $[\text{Ni}_{26}\text{S}_{14}(\text{PET}_3)_{10}] \cdot \text{C}_5\text{H}_{12}$ ($2 \cdot \text{C}_5\text{H}_{12}$) with 50% thermal ellipsoids shown for non-carbon atoms. Hydrogen atoms, carbon atoms, and diethyl ether solvate are omitted for clarity.

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