

- *Electronic Supplementary Information* -

**Fragmentation, Catenation, and Direct Functionalisation of White Phosphorus by a
Uranium(IV)-Silyl-Phosphino-Carbene Complex**

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Experimental Details

General

All manipulations were carried out using Schlenk techniques, or an MBraun UniLab glovebox, under an atmosphere of dry nitrogen or argon. Solvents were dried by passage through activated alumina towers and degassed before use. All solvents were subsequently further dried and stored over NaK₂. Deuterated solvents were dried over NaK₂, distilled and stored over NaK₂. Tetramethylethylenediamine (TMEDA) was dried over CaH₂ and distilled immediately prior to use. Glassware used for all reactions was silylated with hexamethyldisilazane under reduced pressure. Crystals were examined using a Rigaku FR-X diffractometer, equipped with a HyPix 6000HE photon counting pixel array detector with mirror-monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$) or Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation. Intensities were integrated from a sphere of data recorded on narrow (1.0°) frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Gaussian grid face-indexed absorption corrections with a beam profile correction were applied. The structures were solved either by direct methods and all non-hydrogen atoms were refined by full-matrix least-squares

on all unique F^2 values with anisotropic displacement parameters with exceptions noted in the respective cif files. Except where noted, Hydrogen atoms were refined with constrained geometries and riding thermal parameters. CrysAlisPro¹ was used for control and integration, SHELXT² was used for structure solution, and SHELXL³ and Olex2⁴ were employed for structure refinement. ORTEP-3⁵ and POV-Ray⁶ were employed for molecular graphics. FTIR spectra were recorded on a Bruker Alpha spectrometer with Platinum-ATR module. Variable-temperature magnetic moment data were recorded in an applied dc field of 0.5 T on a Quantum Design MPMS XL7 superconducting quantum interference device magnetometer using powdered samples. Care was taken to ensure complete thermalisation of the sample before each data point was measured and samples were immobilised in an eicosane matrix to prevent sample reorientation during measurements. Specifically, 41.2 mg of finely ground **4** was immobilised in a matrix of 19.8 mg of eicosane within a 4 mm diameter tube sealed under vacuum. The sample holder background was subtracted using data from a blank and a diamagnetic correction was applied using Pascal Table of Constants. Elemental microanalyses were carried out by Mr Martin Jennings at the Micro Analytical Laboratory, Department of Chemistry, University of Manchester. The compounds $[U\{C(SiMe_3)(PPh_2)\}(BIPM^{TMS})(\mu-Cl)Li(TMEDA)(\mu-TMEDA)_{0.5}\}_2$ (**1**),⁷ P_4 ,⁸ $[Li\{CH(Ph)(SiMe_3)\}(TMEDA)]$,⁹ and $[Li\{CH(SiMe_3)(PPh_2)\}(THF)]$ ¹⁰ were prepared as described previously.

Preparation of $[P_5\{C(SiMe_3)(PPh_2)\}_2][Li(TMEDA)_2]$ (2) and $[U\{BIPM^{TMS}\}\{Cl\}\{\mu-Cl\}_2\{Li(TMEDA)\}]$ (3) from $[U\{C(SiMe_3)(PPh_2)\}(BIPM^{TMS})(\mu-Cl)Li(TMEDA)(\mu-TMEDA)_{0.5}\}_2$ (1)

To a Young's ampoule equipped with a glass stirrer bar was added a solid mixture of **1** (100 mg, 0.038 mol) and P_4 (5 mg, 0.038 mol). Toluene (5 ml) was distilled into the vessel *in vacuo* at -196 °C. The red mixture was allowed to warm to room temperature and stirred for 10 hours.

Stirring was ceased and the solution was allowed to stand at room temperature for 14 hours, leading to the formation of a crop of orange crystals of **2**. The mother liquor decanted into a separate vessel *via* canula filtration and the crystals washed with toluene (3 × 5 ml) and dried *in vacuo*. The decanted mother liquor was cooled to 5 °C for 1 hour, leading to the formation of a crop of yellow crystals of **3**, which were washed with pentane (3 × 5 ml). Crystals of **2** suitable for X-ray diffraction were obtained by layering a concentrated toluene solution with SiMe₄ in an NMR tube and storage at room temperature overnight. Crystals of **3** suitable for X-ray diffraction were obtained by evaporation of a concentrated toluene solution over the course of 48 hours inside a glovebox. [P₅{C(SiMe₃)(PPh₂)}₂][Li(TMEDA)₂] (**2**): Yield: 9 mg, 32% (based on P). Anal. Calcd for C₄₄H₆₆Li₄P₇Si₂: C 56.77; H 7.15; N 6.02%. Found: C 57.12; H 7.64; N 5.33%. ATR-IR ν/cm⁻¹: 3049 (w), 2961 (w), 2881 (w), 2323 (w), 2255 (w), 1509 (w), 1432 (w), 1349 (m), 1252 (w), 1178 (m), 1103 (w), 1083 (s), 1055 (m), 985 (s), 934 (w), 831 (m), 752 (m), 742 (w), 725 (w), 707 (s), 694 (s), 678 (s), 658 (m), 634 (s), 600 (m), 520 (m), 505 (m), 483 (s), 450 (m), 441 (m), 421 (m), 409 (w). [U{BIPM^{TMS}}{Cl}{μ-Cl}₂{Li(TMEDA)}] (**3**): Yield: 20 mg, 26% (based on U). Anal. Calcd for C₃₇H₅₄Cl₃Li₄P₂Si₂U: C 43.39; H 5.31; N 5.47%. Found: C 43.05; H 5.22; N 5.86%. ¹H NMR (C₆D₆, 298 K): δ -5.43 (br, 18H, (-SiCH₃)₃), -0.44 (s, 2 H), 0.27 (s, 4H), 1.26 (s, 4H), 3.32 (br, 6H), 7.03 (s), 7.36 (br), 7.54 (br), 7.68 (br), 10.28 (br, 4H), 14.86 (s, 2H). ³¹P NMR (C₆D₆, 298 K): δ -365.13 (br, U=C(PNSiMe₃Ph₂)₂). ATR-IR ν/cm⁻¹: 3052 (w), 2951 (w), 2872 (w), 2835 (w), 2792 (w), 1699 (w), 1461 (w), 1436 (w), 1343 (m), 1288 (w), 1245 (m), 1180 (w), 1159 (w), 1108 (m), 1060 (s), 1036 (s), 947 (m), 895 (m), 830 (s), 772 (m), 753 (m), 729 (s), 714 (s), 692 (s), 675 (m), 650 (m), 618 (m), 604 (m), 548 (w), 525 (s), 508 (s), 442 (m), 418 (m).

Preparation of $[\{U(BIPM^{TMS})([\mu-\eta^2:\eta^2-P_2]C[SiMe_3][PPh_2])\}_2]$ (4**)**

To a Young's ampoule equipped with a glass stirrer bar was added a solid mixture of **1** (100 mg, 0.038 mol) and P_4 (5 mg, 0.038 mol). Toluene (5 ml) was distilled into the vessel *in vacuo* at $-196\text{ }^\circ\text{C}$. The red mixture was allowed to warm to $-35\text{ }^\circ\text{C}$ and stirred for 4 hours. Stirring was ceased and the solution was allowed to stand at $-35\text{ }^\circ\text{C}$ for 14 hours, leading to the formation of a crop of orange crystals of **4**. The crystals were washed with toluene (3×5 ml) and dried *in vacuo*. Yield: 39 mg, 46%. Single crystals of **4** suitable for X-ray diffraction were obtained by storage of a concentrated toluene solution of **4** at $-35\text{ }^\circ\text{C}$ overnight. $[\{U(BIPM^{TMS})([\mu-\eta^2:\eta^2-P_2]C[SiMe_3][PPh_2])\}_2]$ (**4**): Anal. Calcd for $C_{94}H_{114}N_4P_{10}Si_6U_2$: C 50.08; H 5.10; N 2.49%. Found: C 50.25; H 5.16; N 2.01%. ATR-IR ν/cm^{-1} : 3051 (w), 2946 (m), 2885 (m), 2834 (m), 2792 (w), 1460 (m), 1434 (m), 1287 (m), 1241 (s), 1181 (w), 1158 (w), 1104 (s), 1025 (s), 996 (s), 948 (s, br), 899 (s), 827 (s), 766 (s), 740 (s), 711 (s), 690 (s), 644 (s), 602 (s), 551 (s), 504 (s), 486 (s), 443 (s).

Preparation of $[P_5\{C(SiMe_3)(PPh_2)\}_2][Li(TMEDA)_2]$ (2**) and $[U\{BIPM^{TMS}\}_2\{Cl\}_2\{Li(TMEDA)\}]$ (**3**) from $[\{U(BIPM^{TMS})([\mu-\eta^2:\eta^2-P_2]C[SiMe_3][PPh_2])\}_2]$ (**4**)**

To a Young's ampoule equipped with a glass stirrer bar was added a solid mixture of **4** (30 mg, 0.013 mmol) and LiCl (3 mg, 0.067 mmol, 5 equiv.). Toluene (2.5 ml) and TMEDA (8 mg, 0.067 mol, 5 equiv.) were distilled into the vessel *in vacuo* at $-196\text{ }^\circ\text{C}$. The red mixture was allowed to warm to room temperature and stirred for 10 hours. Stirring was ceased and the solution was allowed to stand at room temperature for 14 hours, leading to the formation of a crop of orange crystals of **2**. The mother liquor decanted into a separate vessel *via* canula filtration and the crystals washed with toluene (3×2 ml) and dried *in vacuo*. The decanted mother liquor was cooled to $5\text{ }^\circ\text{C}$ for 1 hour, leading to the formation of a crop of yellow crystals, which were washed with pentane (3×5 ml). $[P_5\{C(SiMe_3)(PPh_2)\}_2][Li(TMEDA)_2]$

(2): Yield: 7 mg, 66% (based on P). $[\text{U}\{\text{BIPM}^{\text{TMS}}\}\{\text{Cl}\}\{\mu\text{-Cl}\}_2\{\text{Li}(\text{TMEDA})\}]$ (3): Yield: 15 mg, 54% (based on U).

Preparation of $[\text{U}\{\text{C}(\text{SiMe}_3)(\text{PPh}_2)\}\{\text{BIPM}^{\text{TMS}}\}(\mu\text{-Cl})\text{Li}(\text{TMEDA})(\mu\text{-TMEDA})_{0.5}]_2$ (1) from $[\text{U}\{\text{BIPM}^{\text{TMS}}\}\{\text{Cl}\}\{\mu\text{-Cl}\}_2\{\text{Li}(\text{TMEDA})\}]$ (3)

To a Young's ampoule equipped with a glass stirrer bar was added solid **3** (75 mg, 0.073 mmol). Toluene (5 ml) was distilled into the vessel *in vacuo* at -196 °C. The mixture was warmed to -78 °C and $[\text{Li}\{\text{CH}(\text{Ph})(\text{SiMe}_3)\}\{\text{TMEDA}\}]$ (21 mg, 0.066 mmol, 0.9 equiv.) in toluene (5 ml) was added dropwise over the course of one hour with stirring. The mixture was allowed to warm to room temperature and stirred for 1 hour. The red solution was cooled to -78 °C and $[\text{Li}\{\text{CH}(\text{SiMe}_3)(\text{PPh}_2)\}\{\text{THF}\}]$ (26 mg, 0.059 mmol, 0.8 equiv.) in toluene (5 ml) was added dropwise over the course of 30 minutes with stirring. The dark red mixture was allowed to warm to room temperature and stirred for 14 hours. The mixture was then filtered, concentrated to approximately 1 ml, and transferred to an NMR tube inside a glovebox. The concentrated solution was layered with pentane and left to stand at room temperature for 48 hours, leading to the formation of a crop of dark red crystals, which were washed with toluene (1.5 ml) and pentane (3×3 ml). Yield: 38 mg, 39%. All analytical data for **1** matched that previously reported for the compound.

Crystallographic Structures

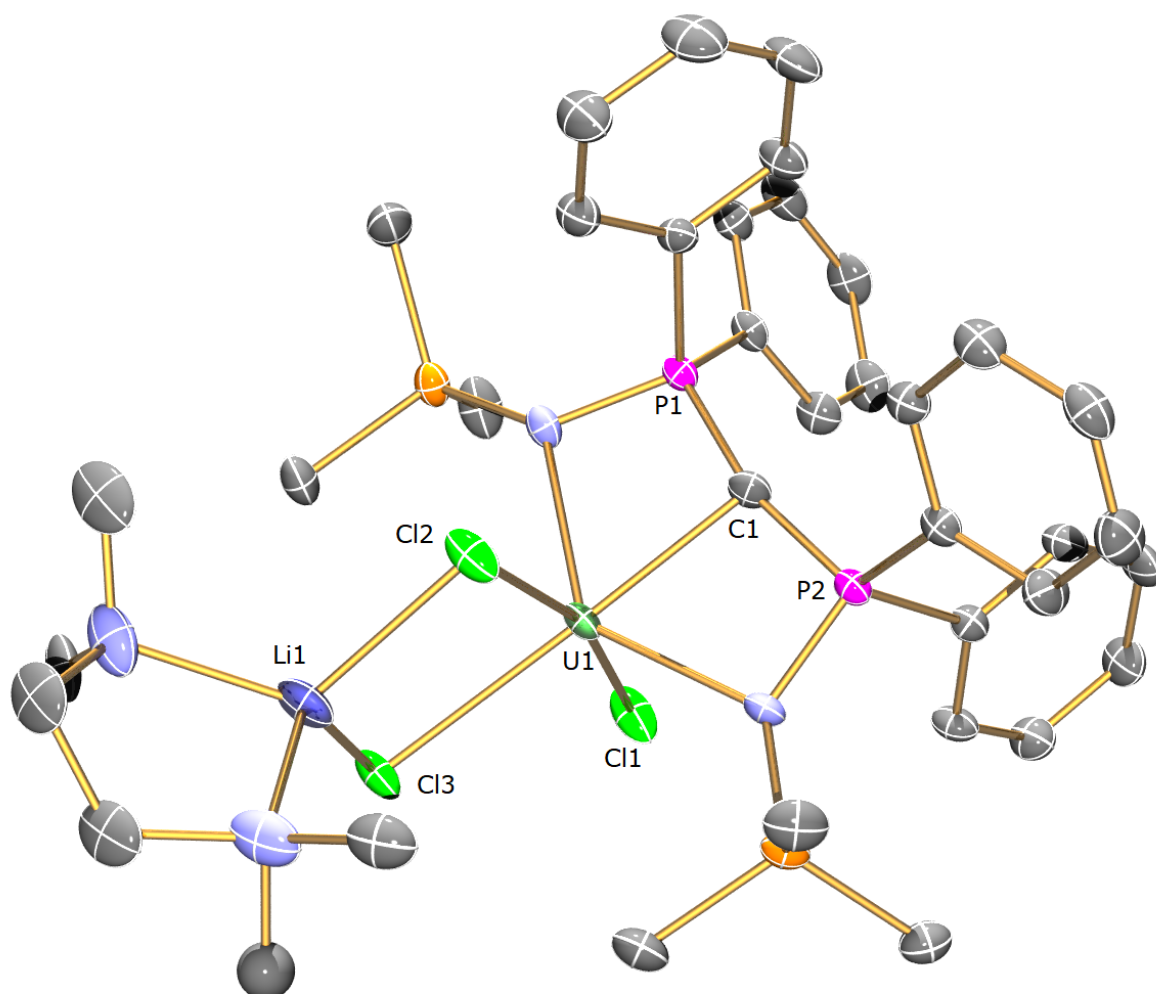


Figure S1. Molecular structure of 3 at 150 K. Thermal ellipsoids set at 30% probability.

Hydrogen atoms and disordered elements are omitted for clarity.

Spectroscopic Data

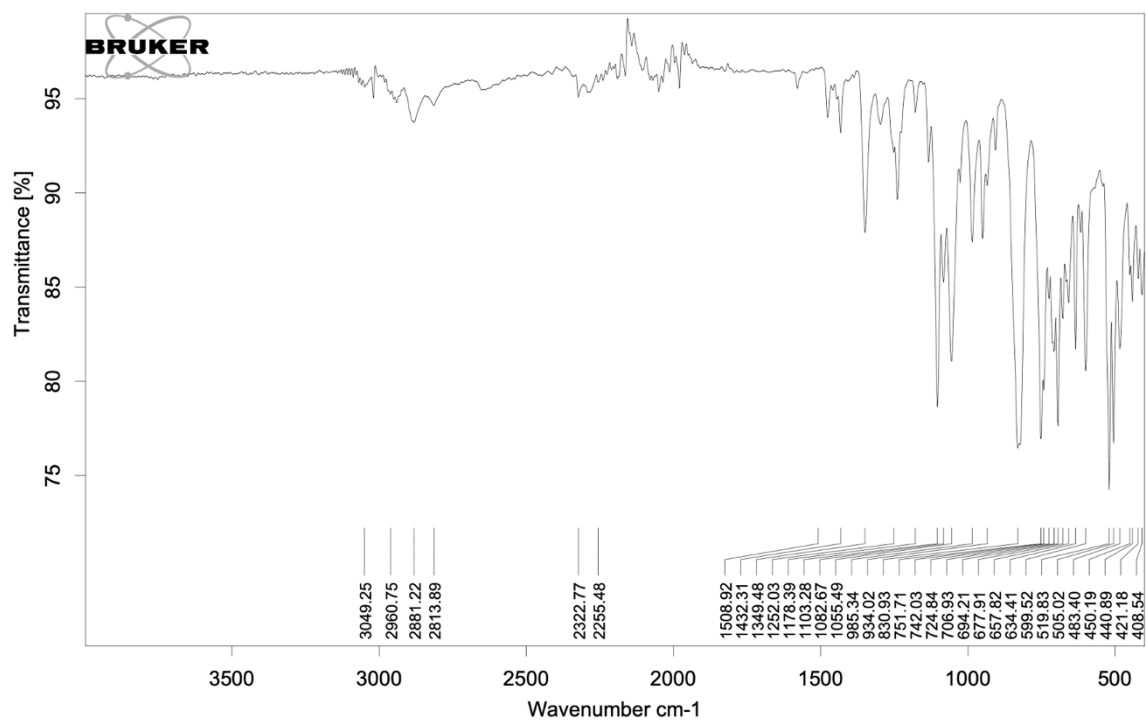


Figure S2. ATIR Spectrum of 2.

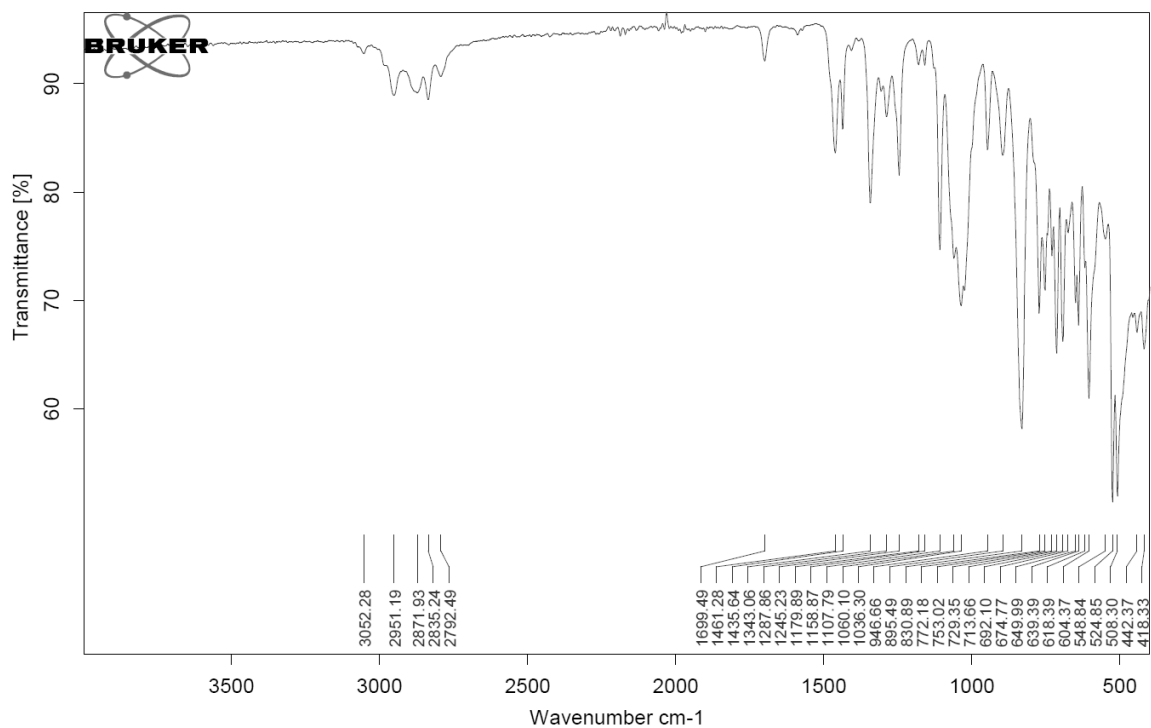


Figure S3. ATIR Spectrum of 3.

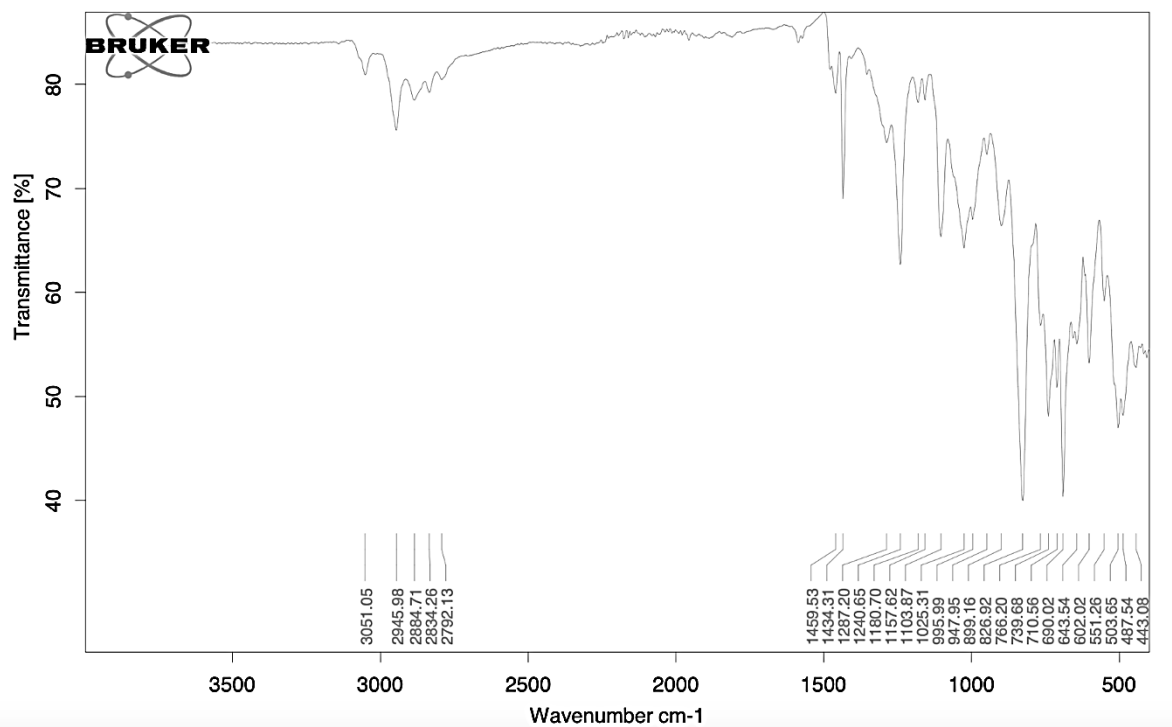


Figure S4. ATIR Spectrum of 4.

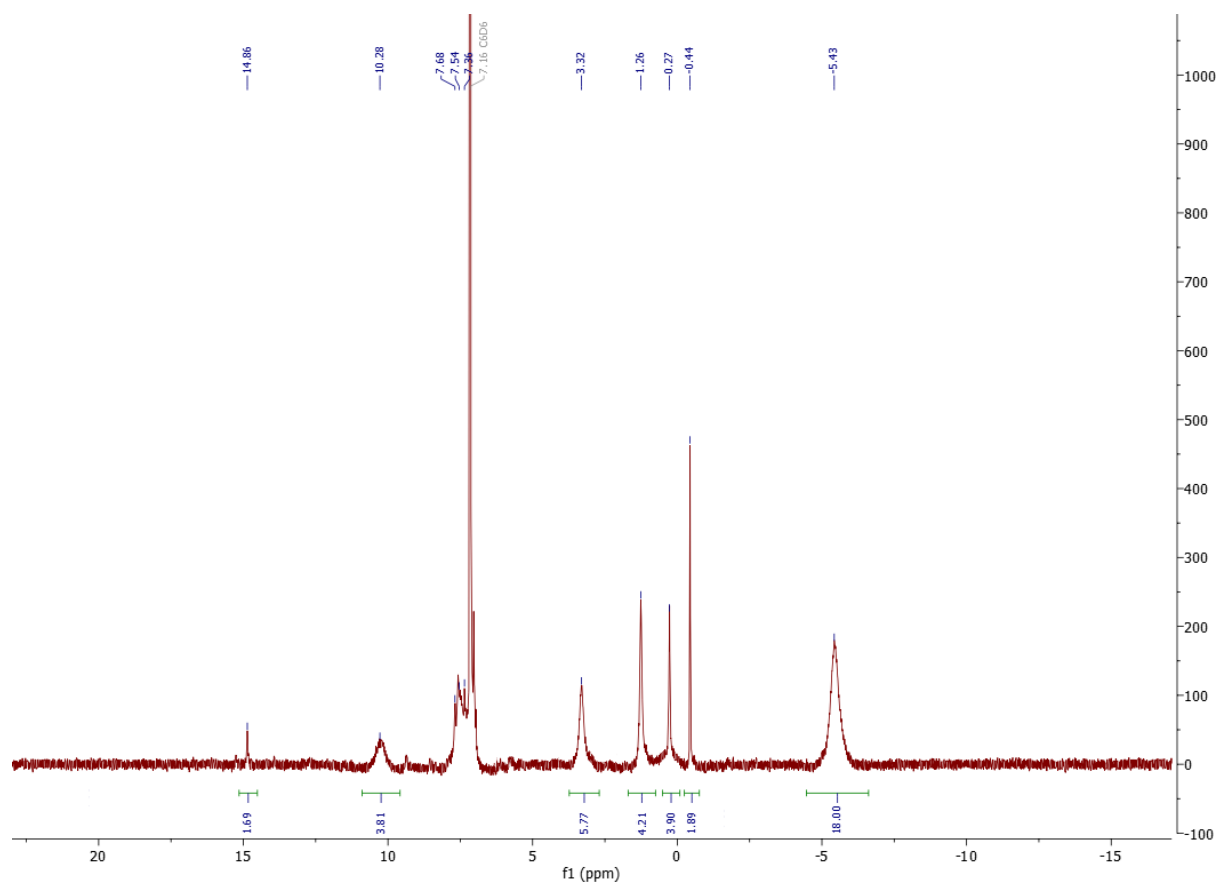


Figure S5. ¹H NMR spectrum of 3 in C₆D₆.

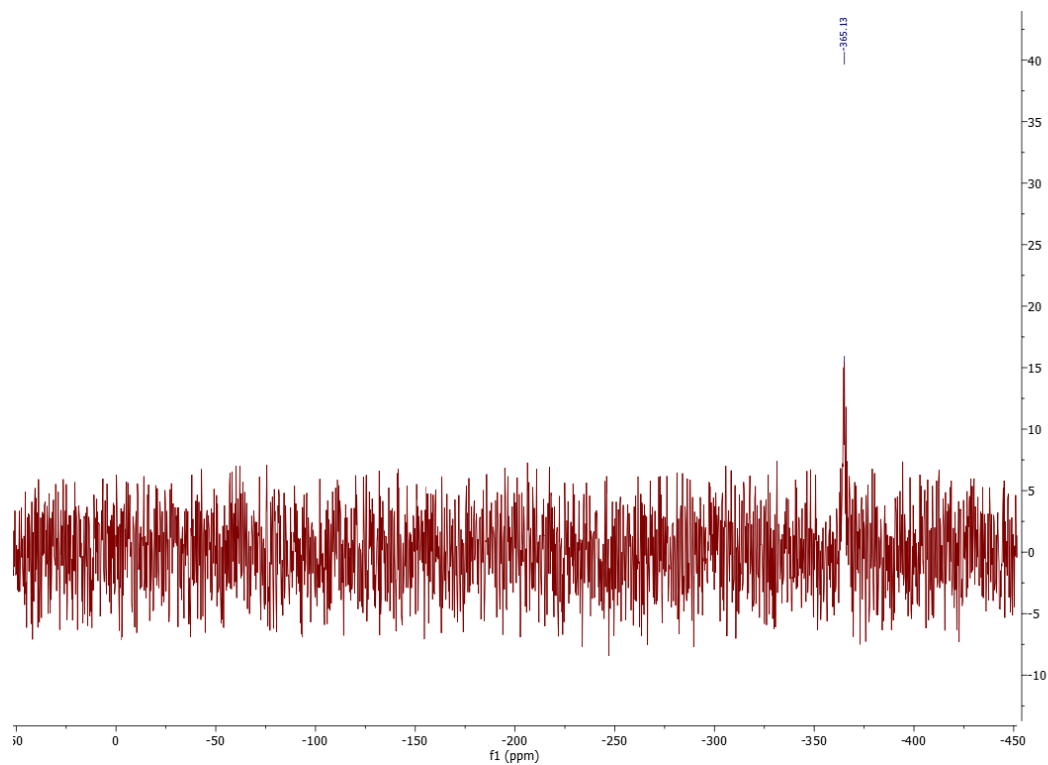


Figure S6. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** in C_6D_6 .

Magnetometric Data

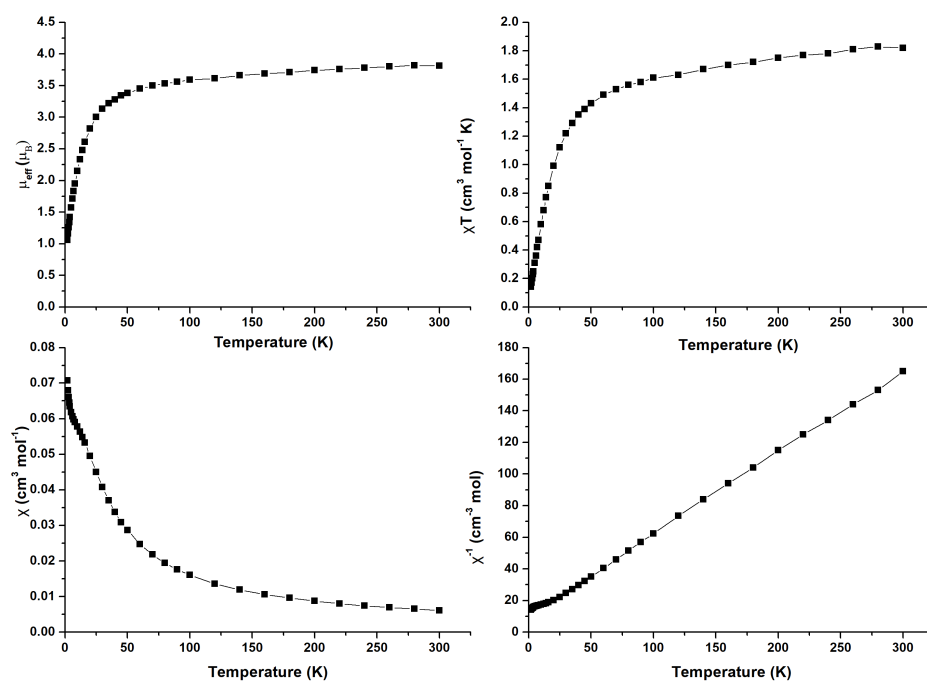


Figure S7. Variable-temperature SQUID data of a powdered sample of **4**. Lines are a guide to the eye only.

References

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