

## **C=O Scission and Reductive Coupling of Organic Carbonyls by a Redox-Active Diboraanthracene**

*Jordan W. Taylor and W. Hill Harman\**

Department of Chemistry, University of California, Riverside  
Riverside, CA 92521 (USA)

### **Contents**

General Considerationns.....	2
X-Ray Crystallography.....	2
Synthetic Procedures.....	2
NMR Spectra .....	5
FT-IR Spectra.....	28
X-ray Diffraction.....	30
References.....	36

**General considerations.** Unless otherwise noted, all manipulations were carried out using standard Schlenk or glovebox techniques under a N<sub>2</sub> atmosphere. Hexanes, benzene, toluene, and acetonitrile were dried and deoxygenated by argon sparge followed by passage through activated alumina in a solvent purification system from JC Meyer Solvent Systems followed by storage over 3 Å molecular sieves. THF and Et<sub>2</sub>O were distilled from sodium-benzophenone ketyl under N<sub>2</sub> followed by storage over 4 Å molecular sieves for at least 24 hours prior to use. Non-halogenated and non-nitrile containing solvents were tested with a standard purple solution of sodium benzophenone ketyl in THF to confirm effective oxygen and moisture removal prior to use. Hexamethyldisiloxane (HMDSO) was distilled from sodium metal and stored over 4 Å molecular sieves for 24 hours prior to use. Monomeric formaldehyde, anhydrous acetone and NaI•3(C<sub>6</sub>H<sub>7</sub>O) were obtained by literature procedures.<sup>1-3</sup> [Au(B<sub>2</sub>P<sub>2</sub>)] [K(18-c-6)] (**1**) was synthesized according to a literature procedure.<sup>4</sup> All other reagents were purchased from commercial suppliers and purified according to literature procedures. Elemental analyses were performed by Midwest Microlab, LLC, Indianapolis, IN. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc., degassed, and dried over activated 3 Å molecular sieves for at least 24 h prior to use. NMR spectra were recorded on Bruker NEO 400 MHz and Bruker Avance 600 MHz spectrometers. <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported in ppm relative to tetramethylsilane using residual solvent as an internal standard. <sup>11</sup>B chemical shifts are reported in ppm relative to BF<sub>3</sub>•Et<sub>2</sub>O. Original <sup>11</sup>B NMR spectra were processed using MestReNova 10.0.2 with a backwards-linear prediction applied to eliminate background signal from the borosilicate NMR tube.<sup>5</sup> For <sup>11</sup>B NMR spectra with peaks overlapping the borosilicate signal, a manual baseline correction was applied. IR spectra were recorded using a Bruker Alpha FT-IR with a universal sampling module collecting at 4 cm<sup>-1</sup> resolution with 32 scans.

**X-Ray Crystallography.** Single crystals were coated with paratone oil and mounted on cryo-loop glass fibers. X-ray intensity data were collected at 100(2) K on a Bruker APEX2<sup>6</sup> platform-CCD X-ray diffractometer system using fine-focus Mo K<sub>α</sub> radiation (λ = 0.71073 Å, 50kV/30mA power). The CCD detector was placed at 5.0600 cm from the crystal. Frames were integrated using the Bruker SAINT software package<sup>7</sup> and using a narrow-frame integration algorithm. Absorption corrections were applied to the raw intensity data using the SADABS program.<sup>8</sup> The Bruker SHELXTL software package<sup>9</sup> was used for phase determination and structure refinement. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F<sup>2</sup>. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. Relevant details for individual data collections are reported in Tables S1–S4.

## Synthetic Procedures

### [Au(B<sub>2</sub>P<sub>2</sub>)(OCH<sub>2</sub>OCH<sub>2</sub>)] [K(18-c-6)] (**2**).

(**2**) *Via paraformaldehyde:* A solution of [Au(B<sub>2</sub>P<sub>2</sub>)] [K(18-c-6)] (0.032 g, 0.030 mmol) in THF (2 mL) was added paraformaldehyde (0.010 g) at once. The reaction was stirred 1 hour before diluting with hexanes (4 mL) and filtering through celite. The filtrate was placed at –35 °C for 12 hours during which time the product precipitated as a colorless, crystalline solid. The solid was washed with hexanes (2 x 1mL) and dried *in vacuo*. Yield: 0.031 g, 94%.

(**2**) *Via gaseous formaldehyde from a modified literature procedure:* A Schlenk flask was charged with paraformaldehyde, (1.0 g, 30 mmol) Amberlite 126<sup>+</sup> Resin (0.030 g) and diethyl ether (10 mL). The mixture was stirred 30 minutes prior to slow distillation at 40 °C into a Schlenk flask

containing a stirring solution of  $[\text{Au}(\text{B}_2\text{P}_2)][\text{K}(18\text{-c-}6)]$  (0.032 g, 0.030 mmol) in THF (2 mL). As distillation commenced, a colorless solution began developing. Once distillation was finished, the flask containing the product had its volatiles removed *in vacuo*. The residue was washed with pentane (2 x 2 mL), dissolved in THF (1 mL), diluted with pentane (5 mL) and stored at  $-35\text{ }^\circ\text{C}$  for 12 hours during which time the product precipitated as a colorless, crystalline solid. The solid was washed with pentane (2 x 1 mL) and dried *in vacuo*. Yield: 0.023 g, 70%. A single-crystal suitable for XRD analysis was obtained by layering a concentrated benzene solution with HMDSO.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  9.30 (dd,  $J = 7.7, 3.6$  Hz, 1H), 8.35 (d,  $J = 4.6$  Hz, 1H), 7.74 (t,  $J = 7.3$  Hz, 2H), 7.60 (dt,  $J = 15.6, 7.6$  Hz, 4H), 7.48 (t,  $J = 7.3$  Hz, 2H), 7.35 (d,  $J = 7.3$  Hz, 2H), 7.29 (d,  $J = 7.1$  Hz, 2H), 7.12 (t,  $J = 6.9$  Hz, 2H), 7.07 (d,  $J = 6.4$  Hz, 2H), 4.80 (s, 2H), 4.21 (s, 2H), 3.14 (s, 24H), 2.41 (dh,  $J = 23.5, 7.4$  Hz, 4H), 1.06 (ddd,  $J = 12.6, 6.8, 3.3$  Hz, 12H), 0.94 (d,  $J = 7.1$  Hz, 3H), 0.89 (td,  $J = 6.8$  Hz, 6H), 0.85 (d,  $J = 7.3$  Hz, 3H).  $^{31}\text{P}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  48.72 (d,  $J = 266.7$  Hz), 45.54 (d,  $J = 270.9$  Hz).  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$   $-0.13, -12.28$ . FT-IR:  $\nu_{\text{max}}$   $\text{cm}^{-1}$  1116 (C-O).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  137.88, 137.77, 135.95, 135.83, 135.35, 134.94, 134.44, 134.10, 132.24, 131.83, 131.56, 130.79, 124.59, 123.78, 123.73, 123.50, 123.45, 123.31, 91.64, 69.77, 27.12, 26.92, 26.77, 26.57, 22.71, 22.66, 19.23, 18.93. Anal. Calcd for  $\text{C}_{50}\text{H}_{72}\text{AuB}_2\text{KO}_8\text{P}_2(1\text{x C}_4\text{H}_8\text{O})$ : C, 54.37 H, 6.76. Found: C, 53.92 H, 6.94.

**$[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_{14}\text{H}_{12}\text{O}_2)][\text{K}(18\text{-c-}6)(\text{THF})_2]$  (3).** A solution of  $[\text{Au}(\text{B}_2\text{P}_2)][\text{K}(18\text{-c-}6)]$  (0.031 g, 0.029 mmol) in toluene (4 mL) was added benzaldehyde (0.007g, 0.061 mmol) as a toluene solution (2 mL) dropwise. The reaction was stirred 1 hour during which time a colorless crystalline solid precipitated. The reaction was concentrated *in vacuo* (ca. 2 mL) before collecting the colorless crystalline solid on a filter. The solid was dissolved in THF and layered with pentane (4 mL) and allowed to stand overnight. The next day, colorless crystals had formed that were filtered, washed with pentane (2 x 1 mL) and dried *in vacuo*. An additional crop was obtained by layering the filtrate with pentane (ca. 3 mL). Yield: 0.036 g, 88 %. A single-crystal suitable for XRD analysis was obtained by vapor diffusion of pentane into a saturated THF solution.  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ )  $\delta$  8.93 – 8.85 (m, 2H), 7.47 (dt,  $J = 7.5, 4.1$  Hz, 2H), 7.25 (t,  $J = 7.2$  Hz, 2H), 7.07 (t,  $J = 7.3$  Hz, 2H), 6.86 (d,  $J = 7.1$  Hz, 4H), 6.77 (d,  $J = 6.9$  Hz, 2H), 6.64 – 6.57 (m, 6H), 6.56 – 6.47 (m, 6H), 4.06 (s, 2H), 3.47 (s, 24H), 2.47 (ddd,  $J = 11.8, 7.9, 4.6$  Hz, 2H), 2.38 (ddd,  $J = 11.8, 7.9, 4.6$  Hz, 2H), 1.14 (d,  $J = 7.8$  Hz, 6H), 1.11 (d,  $J = 7.0$  Hz, 6H), 0.72 (td,  $J = 16.6, 7.5$  Hz, 12H).  $^{31}\text{P}$  NMR (162 MHz, THF- $d_8$ )  $\delta$  44.43 (s).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz, THF- $d_8$ )  $\delta$   $-0.74$ .  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, THF- $d_8$ )  $\delta$  152.27, 138.00 (t,  $J = 7.3$  Hz), 133.35, 132.56, 130.40, 128.92, 128.10, 126.13, 124.14, 123.72, 123.39, 123.18, 85.73, 71.31, 30.82, 27.43 (d,  $J = 12.4$  Hz), 27.18 (d,  $J = 11.7$  Hz), 26.94 (d,  $J = 12.6$  Hz), 23.48 (t,  $J = 4.1$  Hz), 22.97, 19.65, 19.21. Anal. Calcd for  $\text{C}_{62}\text{H}_{80}\text{AuB}_2\text{KO}_8\text{P}_2$ : C, 58.50 H, 6.33. Found: C, 58.75 H, 6.38.

**$[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_7\text{H}_6\text{O})][\text{K}(18\text{-c-}6)]$  (4).** A solution of  $[\text{Au}(\text{B}_2\text{P}_2)][\text{K}(18\text{-c-}6)]$  (0.032 g, 0.030 mmol) in toluene (4 mL) was added benzaldehyde (3.07  $\mu\text{L}$ , 0.030 mmol) as a toluene solution (2 mL) dropwise. The reaction was stirred 15 minutes during which time a colorless solution appeared. The reaction had its volatiles removed *in vacuo* before washing the residue with pentane (3 x 1 mL). The colorless solid was then dissolved in benzene/pentane (1:3, 6 mL) and placed at  $-15\text{ }^\circ\text{C}$  overnight. The next day, colorless crystals had appeared that were collected on a filter, washed with pentane (2 x 1 mL) and dried *in vacuo*. Yield: 0.029 g, 83 %. A single-crystal suitable for XRD analysis was obtained by layering a saturated benzene solution with pentane  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.66 (ddd,  $J = 5.8, 4.2, 0.9$  Hz, 1H), 8.26 (ddt,  $J = 6.1, 4.0, 1.8$  Hz, 1H), 7.68 (q,  $J = 6.1$  Hz, 2H), 7.63 (t,  $J = 7.8$  Hz, 1H), 7.48 (dt,  $J = 20.4, 7.3$  Hz, 2H), 7.34 (t,  $J = 8.4$  Hz, 1H), 7.25 (t,  $J = 7.1$  Hz, 1H), 7.05 (ddd,  $J = 12.3, 8.0, 5.3$  Hz, 6H), 7.00 (d,  $J = 6.9$  Hz, 2H), 6.97 (t,  $J = 7.9$  Hz, 2H), 6.89 (t,  $J =$

7.2 Hz, 1H), 6.76 (d,  $J = 7.3$  Hz, 2H), 6.71 (d,  $J = 6.7$  Hz, 1H), 3.88 (s, 1H), 2.90 (s, 25H), 2.79 (dd,  $J = 16.2, 8.7$  Hz, 2H), 2.62 – 2.47 (m, 2H), 2.41 (ddd,  $J = 14.0, 7.0, 3.5$  Hz, 1H), 1.19 (d,  $J = 7.0$  Hz, 3H), 1.17 (d,  $J = 7.1$  Hz, 3H), 1.10 – 0.98 (m, 18H), 0.96 (d,  $J = 7.0$  Hz, 3H), 0.93 (d,  $J = 7.1$  Hz, 3H), 0.88 (t,  $J = 7.1$  Hz, 3H), 0.80 (d,  $J = 7.4$  Hz, 3H), 0.76 (d,  $J = 7.4$  Hz, 3H).  $^{31}\text{P}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  49.57 (d,  $J = 259.5$  Hz), 44.11 (d,  $J = 259.0$  Hz).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.03,  $-7.96$ .  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  171.23, 162.74, 156.24, 155.56, 154.42, 137.7 (d,  $J = 7.2$  Hz), 137.5 (d,  $J = 6.0$  Hz), 137.4 (d,  $J = 7.1$  Hz), 137.23 (d,  $J = 5.8$  Hz), 134.90 (d,  $J = 11.2$  Hz), 132.95 (d,  $J = 11.4$  Hz), 132.19, 131.84, 131.34, 129.58, 129.38, 128.59, 127.14, 126.49, 125.79, 124.23, 123.53, 123.24, 122.82 (t,  $J = 6.3$  Hz), 122.45, 121.86, 76.79, 69.67, 26.88 (d,  $J = 23.2$  Hz), 26.54 (d,  $J = 23.9$  Hz), 25.58 (d,  $J = 22.9$  Hz), 25.36, 24.97 (d,  $J = 2.1$  Hz), 24.91 (d,  $J = 2.1$  Hz), 22.24 (d,  $J = 6.7$  Hz), 22.13 (d,  $J = 7.5$  Hz), 20.51 (d,  $J = 8.8$  Hz), 20.35 (d,  $J = 8.1$  Hz), 17.94, 17.82.

### **[Au(B<sub>2</sub>P<sub>2</sub>)(C<sub>3</sub>H<sub>5</sub>)(OH)][K(18-c-6)] (5).**

(5) *Via acetone*: A solution of [Au(B<sub>2</sub>P<sub>2</sub>)]K(18-c-6) (0.036 g, 0.034 mmol) and acetone (7.5  $\mu\text{L}$ , 0.102 mmol) in benzene (5 mL) was heated at 60 °C for 10 hours. The pale yellow solution was diluted with pentane (5 mL), filtered through celite and stored at  $-15$  °C where a pale yellow solid appeared. The mother liquor was decanted and the solid washed with pentane (2 x 1 mL). The residue was dissolved in THF/benzene (1:1, 1 mL), diluted with pentane (6 mL) and stored at  $-15$  °C overnight. The next day, colorless crystals had formed that were separated by filtration, washed with pentane (2 x 1 mL) and dried *in vacuo*. Yield: 0.027 g, 71 %.

(5) *Via [NaI•3(C<sub>3</sub>H<sub>6</sub>O)]*: A solution of [Au(B<sub>2</sub>P<sub>2</sub>)]K(18-c-6) (0.030 g, 0.028 mmol) in THF (2 mL) was added NaI•3(C<sub>3</sub>H<sub>6</sub>O) (0.003 g, 0.030 mmol) as a THF solution (2 mL). The reaction was stirred 1 hour during which time a colorless solution appeared. The reaction had its volatiles removed *in vacuo* before washing the residue with pentane (1 x 1 mL). The colorless solid was then dissolved in benzene/pentane (1:3, 6 mL) and placed at  $-15$  °C overnight where pale yellow solid appeared. The residue was dissolved in THF/benzene (1:1, 1 mL), diluted with pentane (6 mL) and stored at  $-15$  °C overnight. The next day, colorless crystals had formed that were separated by filtration, washed with pentane (2 x 1 mL) and dried *in vacuo*. Yield: 0.020 g, 63 %. A single-crystal suitable for XRD analysis was obtained by layering a benzene solution with HMDSO.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.93 (ddd,  $J = 7.5, 3.4, 1.3$  Hz, 1H), 8.70 (s, 1H), 7.67 (t,  $J = 7.4$  Hz, 1H), 7.60 (q,  $J = 8.0$  Hz, 2H), 7.56 – 7.50 (m, 2H), 7.45 (t,  $J = 7.3$  Hz, 1H), 7.36 (s, 3H), 7.20 (s, 2H), 7.09 (s, 3H), 5.34 (s, 1H), 4.79 (d,  $J = 6.6$  Hz, 1H), 3.03 (s, 24H), 2.62 – 2.48 (m, 1H), 2.37 (s, 3H), 1.19 – 0.75 (m, 24H).  $^{31}\text{P}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  48.62 (d,  $J = 268.5$  Hz), 44.96 (d,  $J = 271.4$  Hz).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$   $-0.77, -7.93$ .  $^1\text{H}$  NMR (600 MHz, THF- $d_8$ )  $\delta$  8.60 (ddd,  $J = 7.4, 3.7, 1.3$  Hz, 1H), 7.85 (dd,  $J = 6.5, 4.0$  Hz, 1H), 7.54 (t,  $J = 7.7$  Hz, 1H), 7.51 (t,  $J = 7.6$  Hz, 1H), 7.32 (t,  $J = 7.8$  Hz, 1H), 7.20 (t,  $J = 7.4$  Hz, 1H), 7.12 (t,  $J = 7.4$  Hz, 1H), 7.08 (t,  $J = 7.4$  Hz, 1H), 6.82 (d,  $J = 6.9$  Hz, 1H), 6.65 – 6.62 (m, 1H), 6.61 – 6.51 (m, 6H), 4.78 (s, 1H), 4.05 – 3.98 (m, 1H), 2.46 (dddd,  $J = 24.0, 21.7, 10.7, 6.0$  Hz, 2H), 2.40 – 2.27 (m, 2H), 1.50 (s, 3H), 1.17 (dd,  $J = 12.8, 7.0$  Hz, 3H), 1.14 – 1.11 (m, 3H), 1.11 – 1.07 (m, 3H), 1.03 (dd,  $J = 14.3, 6.9$  Hz, 3H), 0.77 – 0.74 (m, 3H), 0.73 (dd,  $J = 7.2, 5.0$  Hz, 3H), 0.68 (dd,  $J = 17.4, 7.3$  Hz, 3H), 0.57 (dd,  $J = 16.7, 7.1$  Hz, 3H).  $^{31}\text{P}$  NMR (243 MHz, THF- $d_8$ )  $\delta$  46.31 (d,  $J = 269.6$  Hz), 42.84 (d,  $J = 271.2$  Hz).  $^{11}\text{B}\{^1\text{H}\}$  NMR (192 MHz, THF- $d_8$ )  $\delta$   $-3.33, -10.56$ .  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, THF- $d_8$ )  $\delta$  177.83 (m), 174.57 (m), 162.65 (m), 160.72 (m), 140.33 (d,  $J = 14.3$  Hz), 137.01 (d,  $J = 14.8$  Hz), 135.92 (d,  $J = 8.0$  Hz), 135.64 (d,  $J = 7.7$  Hz), 135.46 (d,  $J = 7.1$  Hz), 135.17 (d,  $J = 7.2$  Hz), 134.65 (d,  $J = 7.2$  Hz), 132.60 (d,  $J = 8.0$  Hz), 131.74, 131.28, 129.20, 128.83, 128.68, 128.51, 128.37, 123.49, 123.36 (d,  $J = 6.5$  Hz), 123.26, 123.12, 122.98, 115.8, 70.93, 29.36, 28.10 (d,  $J = 24.9$  Hz), 27.83 – 27.42 (m), 27.34, 26.98 (d,  $J = 24.8$  Hz), 26.56, 25.89 (d,  $J = 20.3$  Hz), 24.11 (d,  $J = 8.4$  Hz), 23.73 (d,  $J = 8.2$  Hz), 22.24 (d,  $J = 7.0$

Hz), 22.08 (d,  $J = 7.5$  Hz), 20.04 (d,  $J = 4.1$  Hz), 18.96 (d,  $J = 14.7$  Hz). FT-IR:  $\nu_{\max}$   $\text{cm}^{-1}$  3572 (O-H).  
Anal. Calcd for  $\text{C}_{51}\text{H}_{74}\text{AuB}_2\text{KO}_7\text{P}_2$ : C, 54.75 H, 6.67. Found: C, 54.07 H, 6.38.

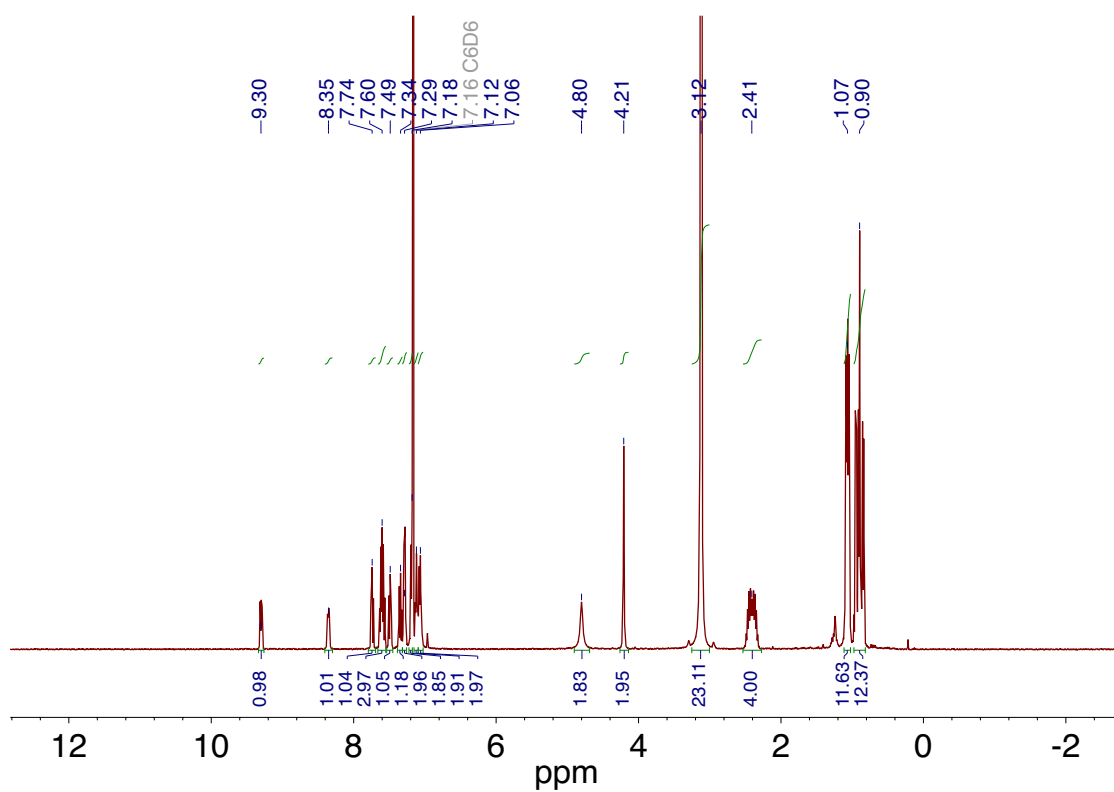


Fig. S1.  $^1\text{H}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{OCH}_2\text{OCH}_2)][\text{K}(18\text{-c-}6)]$  recorded at 400 MHz in  $\text{C}_6\text{D}_6$ .

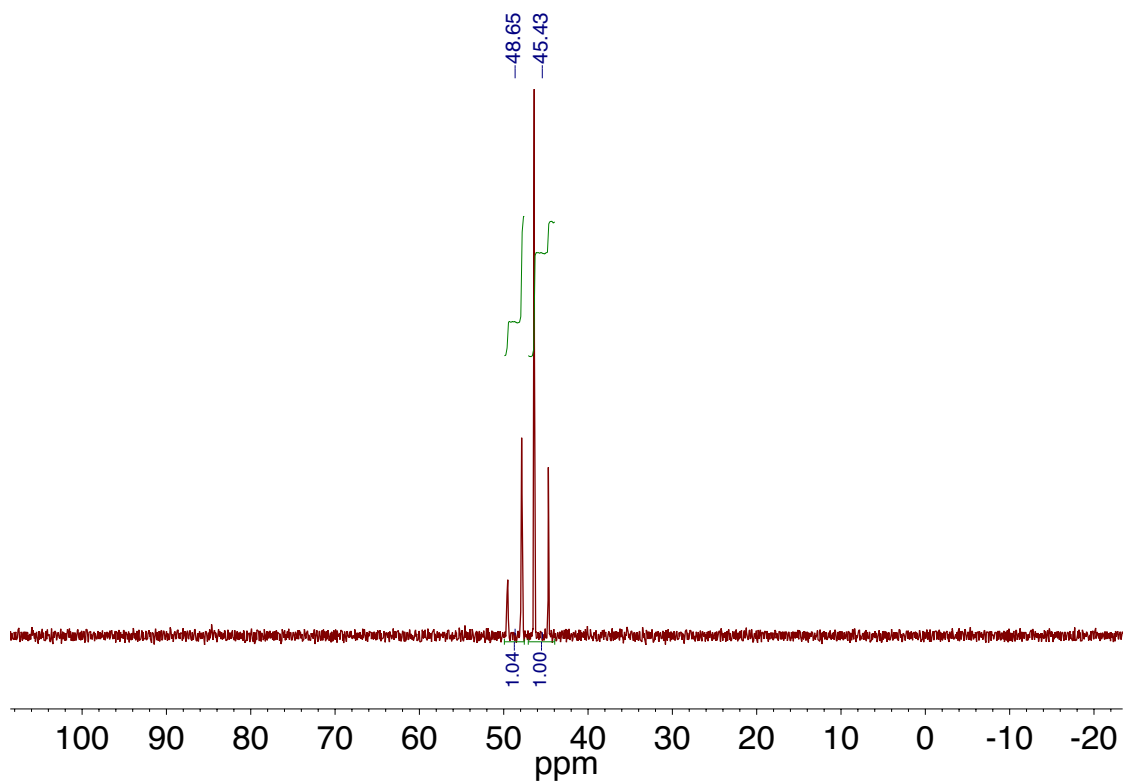


Fig. S2.  $^{31}\text{P}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{OCH}_2\text{OCH}_2)][\text{K}(18\text{-c-}6)]$  recorded at 162 MHz in  $\text{C}_6\text{D}_6$

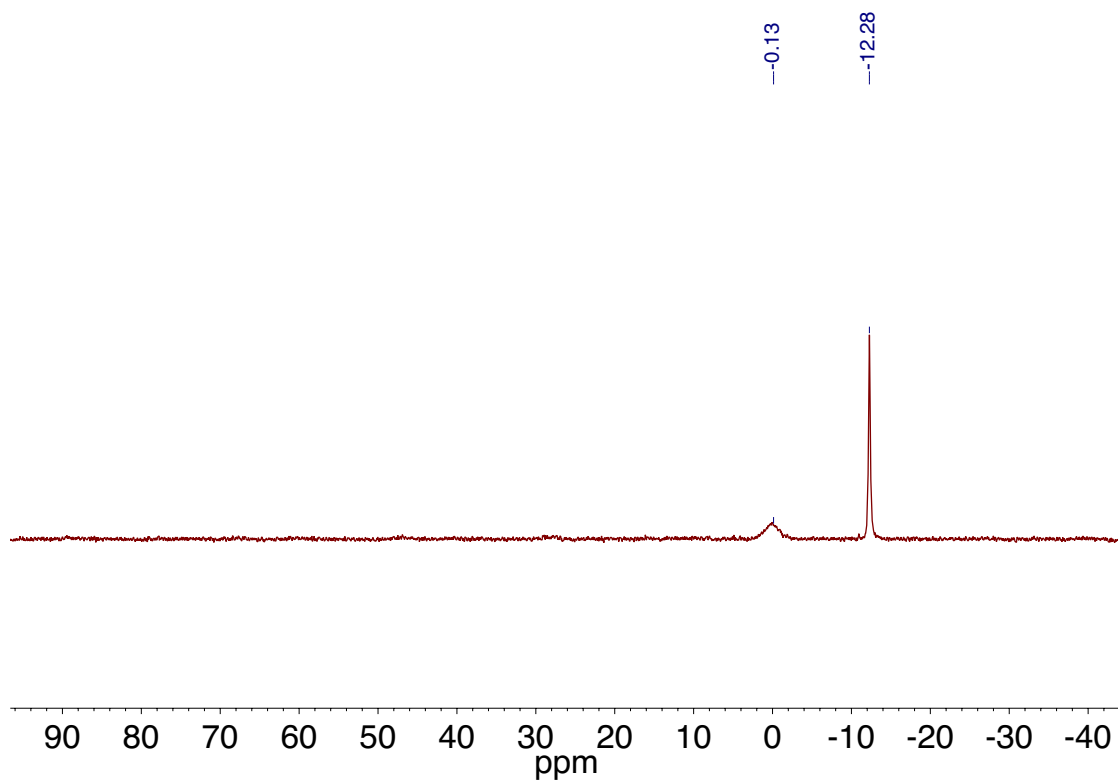


Fig. S3.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{OCH}_2\text{OCH}_2)][\text{K}(18\text{-c-}6)]$  recorded at 128 MHz in  $\text{C}_6\text{D}_6$ .

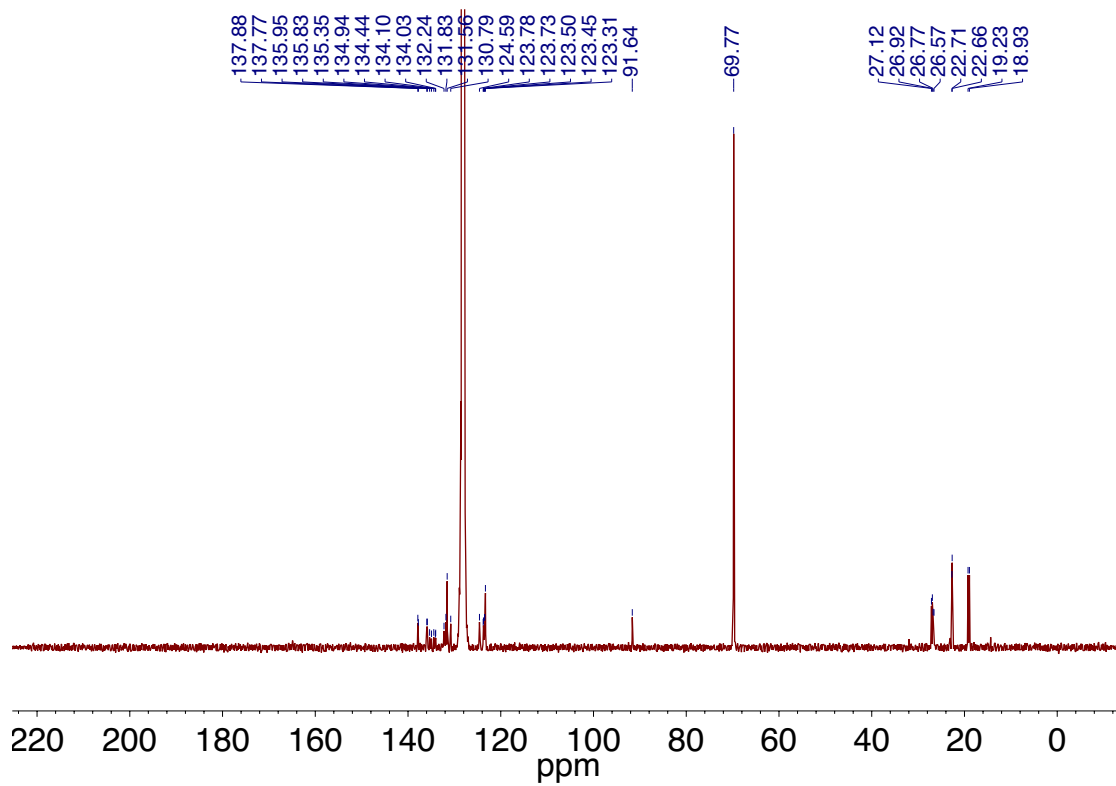


Fig. S4.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{OCH}_2\text{OCH}_2)][\text{K}(18\text{-c-}6)]$  recorded at 126 MHz in  $\text{C}_6\text{D}_6$ .

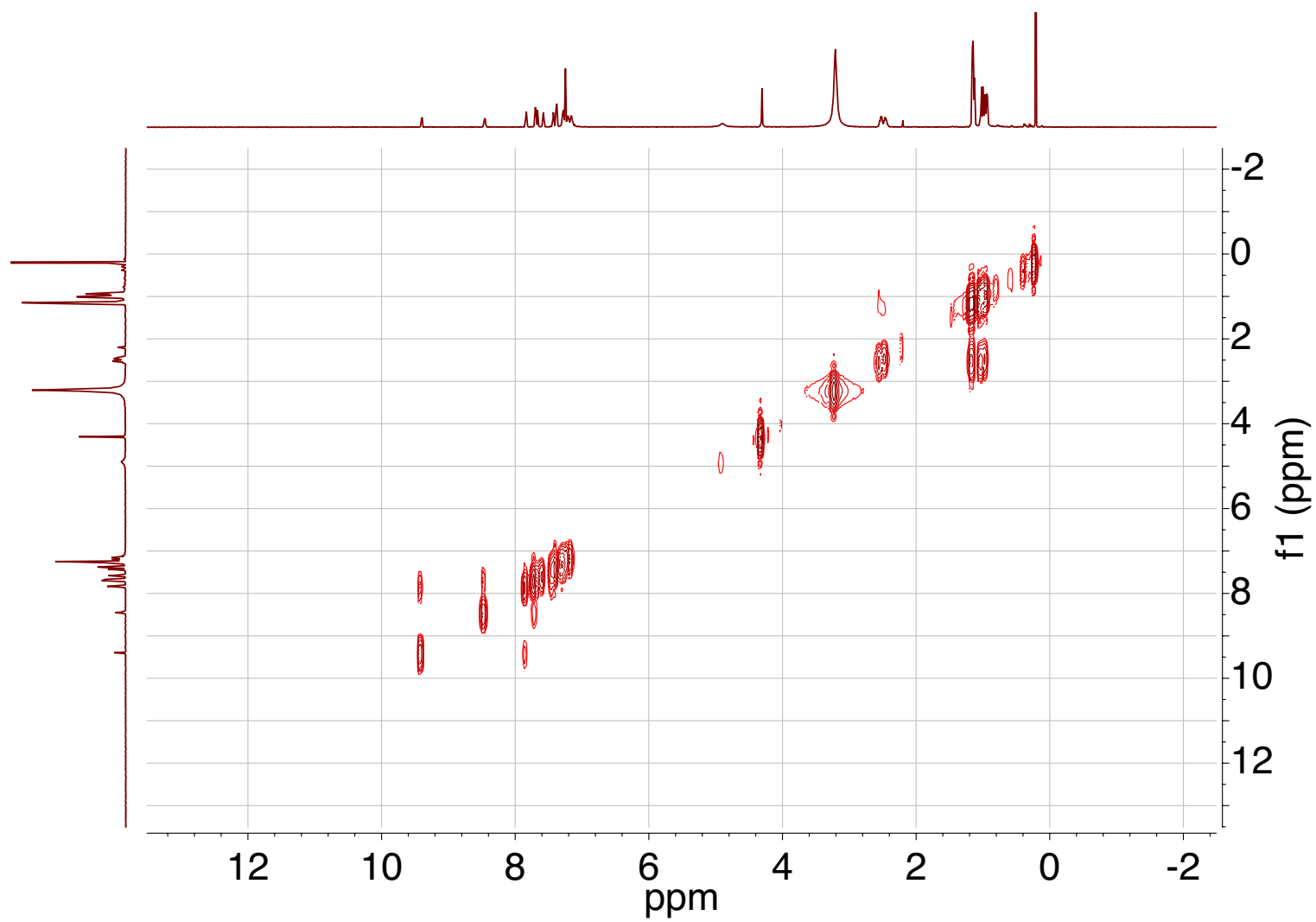


Fig. S5.  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{OCH}_2\text{OCH}_2)][\text{K}(18\text{-c-}6)]$  recorded at 400 MHz in  $\text{C}_6\text{D}_6$ .



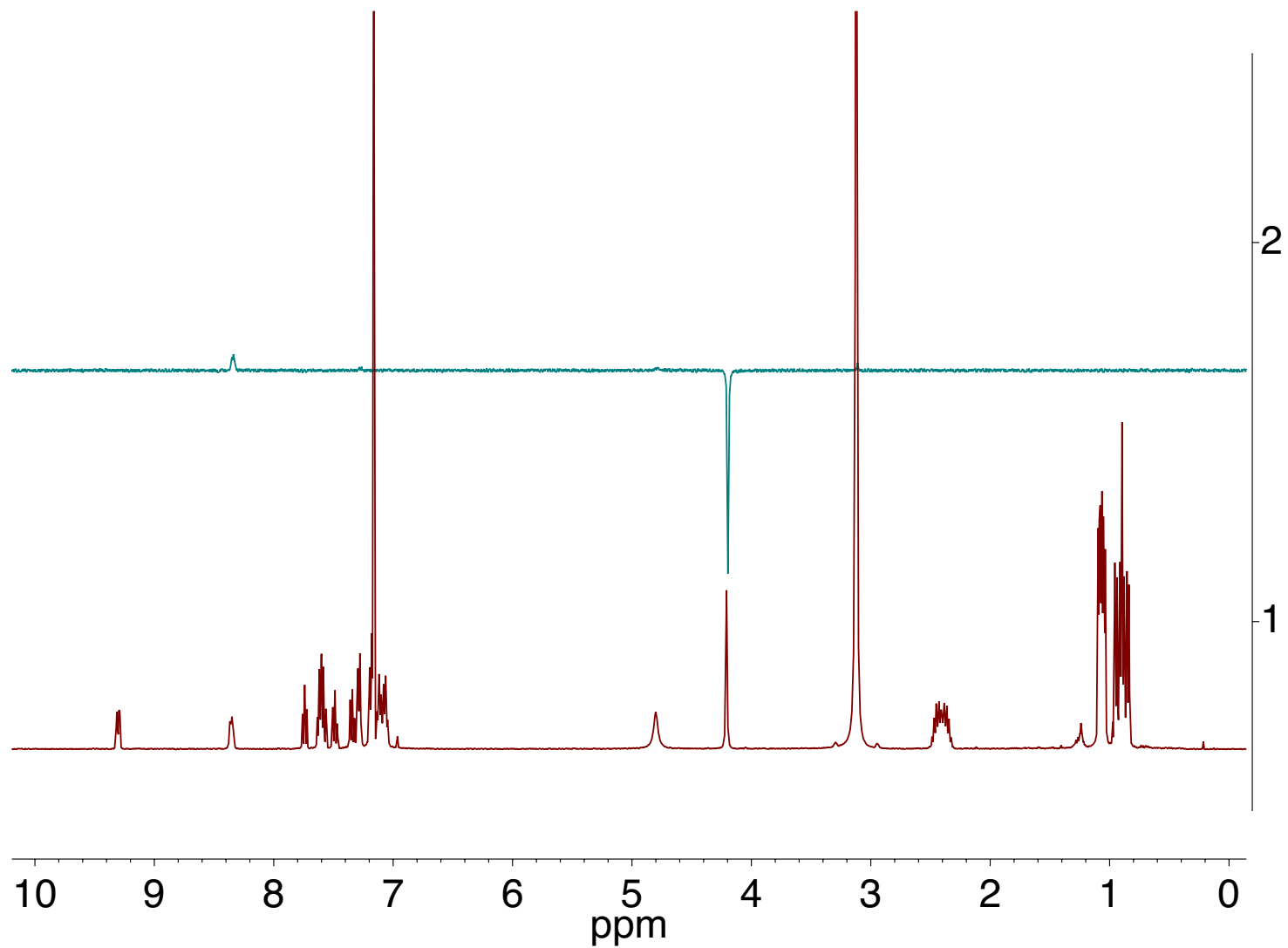


Fig. S6.  $^1\text{H}$ -1D NOE NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{OCH}_2\text{OCH}_2)][\text{K}(18\text{-c-}6)]$  recorded at 400 MHz in  $\text{C}_6\text{D}_6$ .

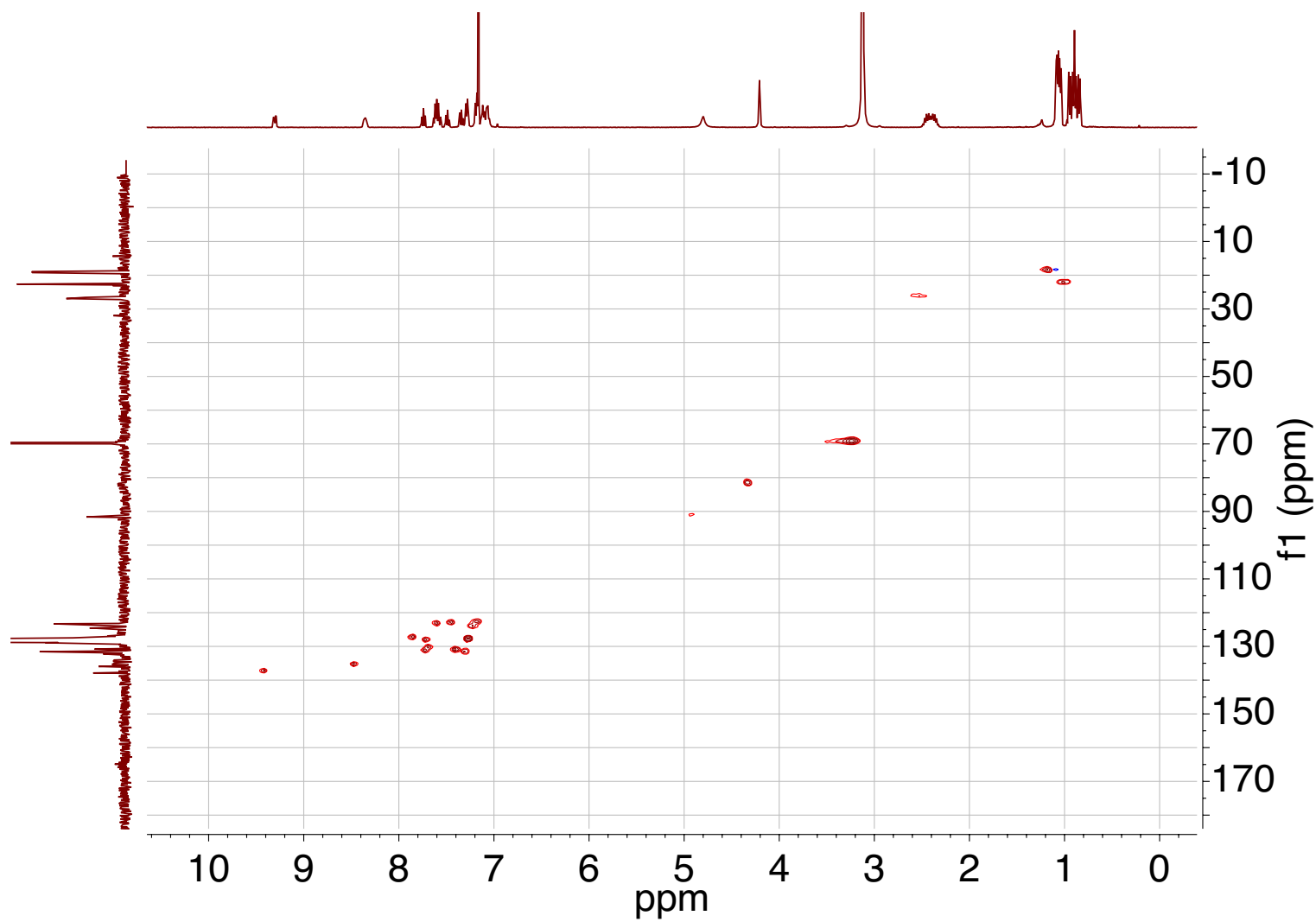


Fig. S7. <sup>1</sup>H-<sup>13</sup>C HSQC NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{OCH}_2\text{OCH}_2)][\text{K}(18\text{-c-}6)]$  recorded at 400 (<sup>1</sup>H) MHz in C<sub>6</sub>D<sub>6</sub>.

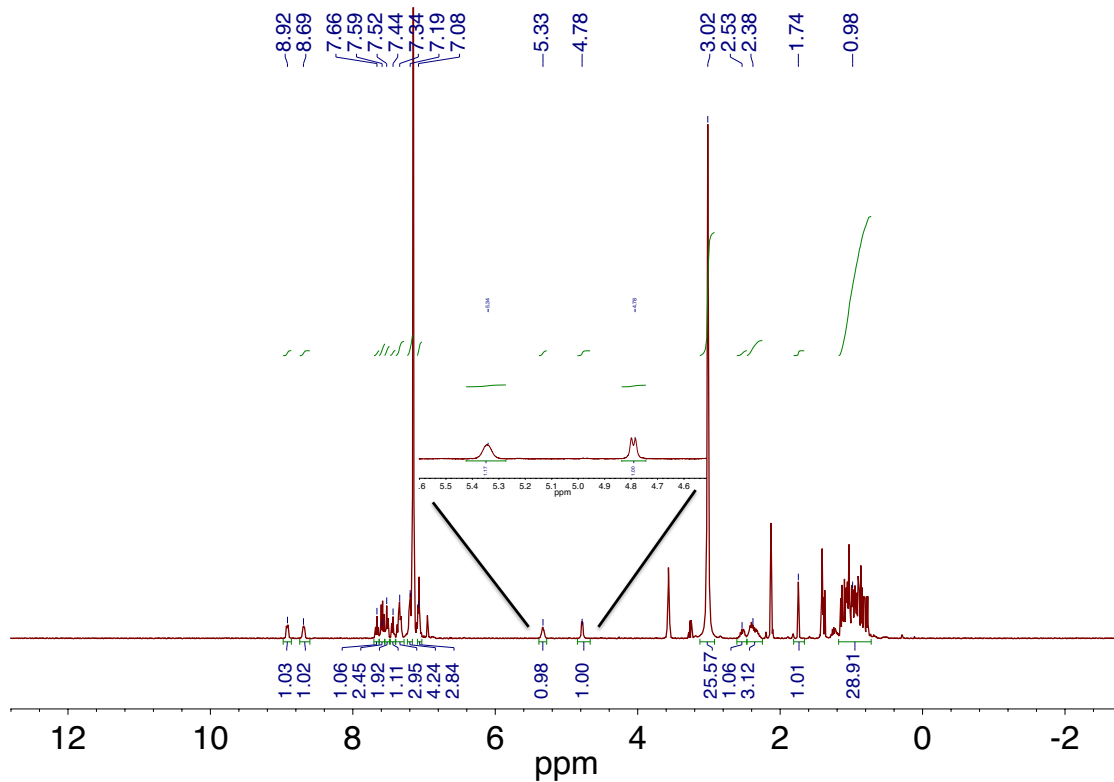


Fig. S8.  $^1\text{H}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_3\text{H}_5)(\text{OH})][\text{K}(18\text{-c-}6)]$  recorded at 400 MHz in  $\text{C}_6\text{D}_6$ .

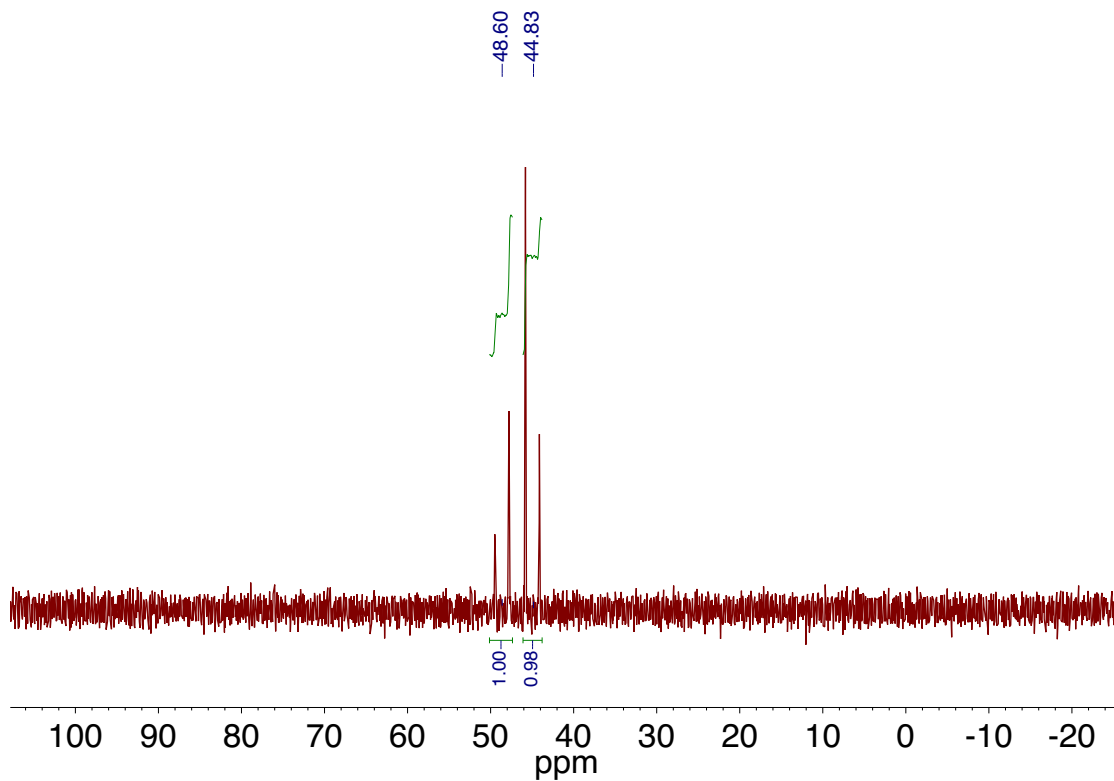
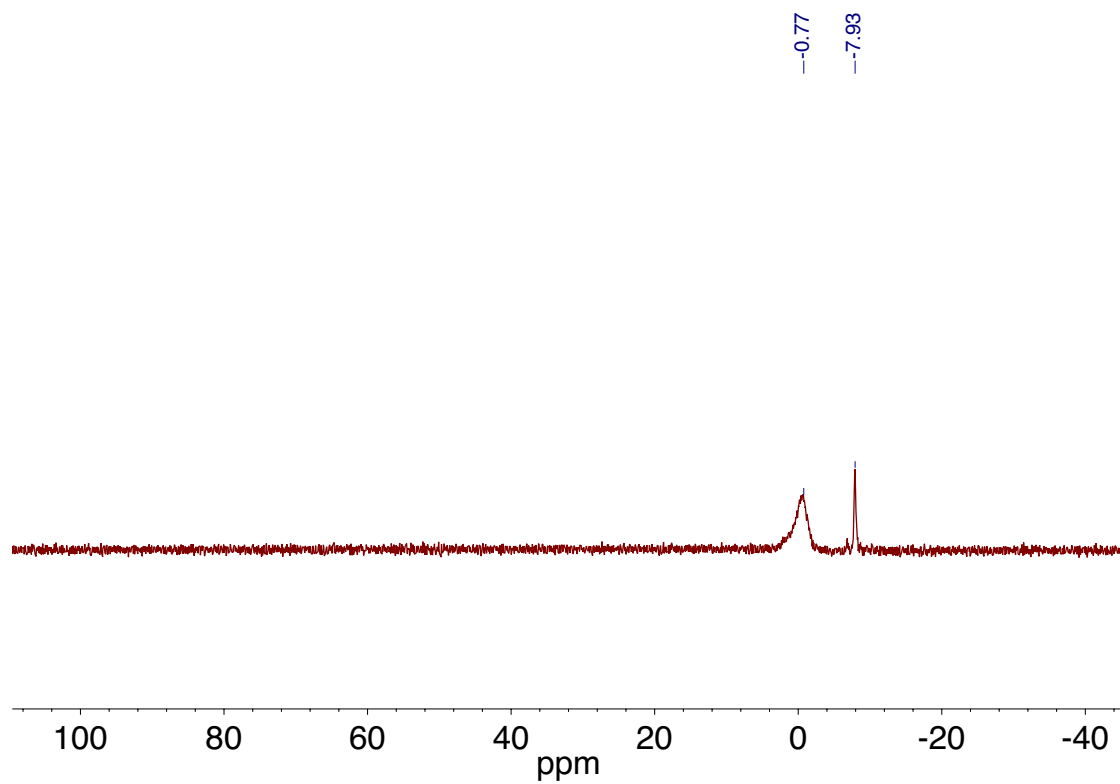
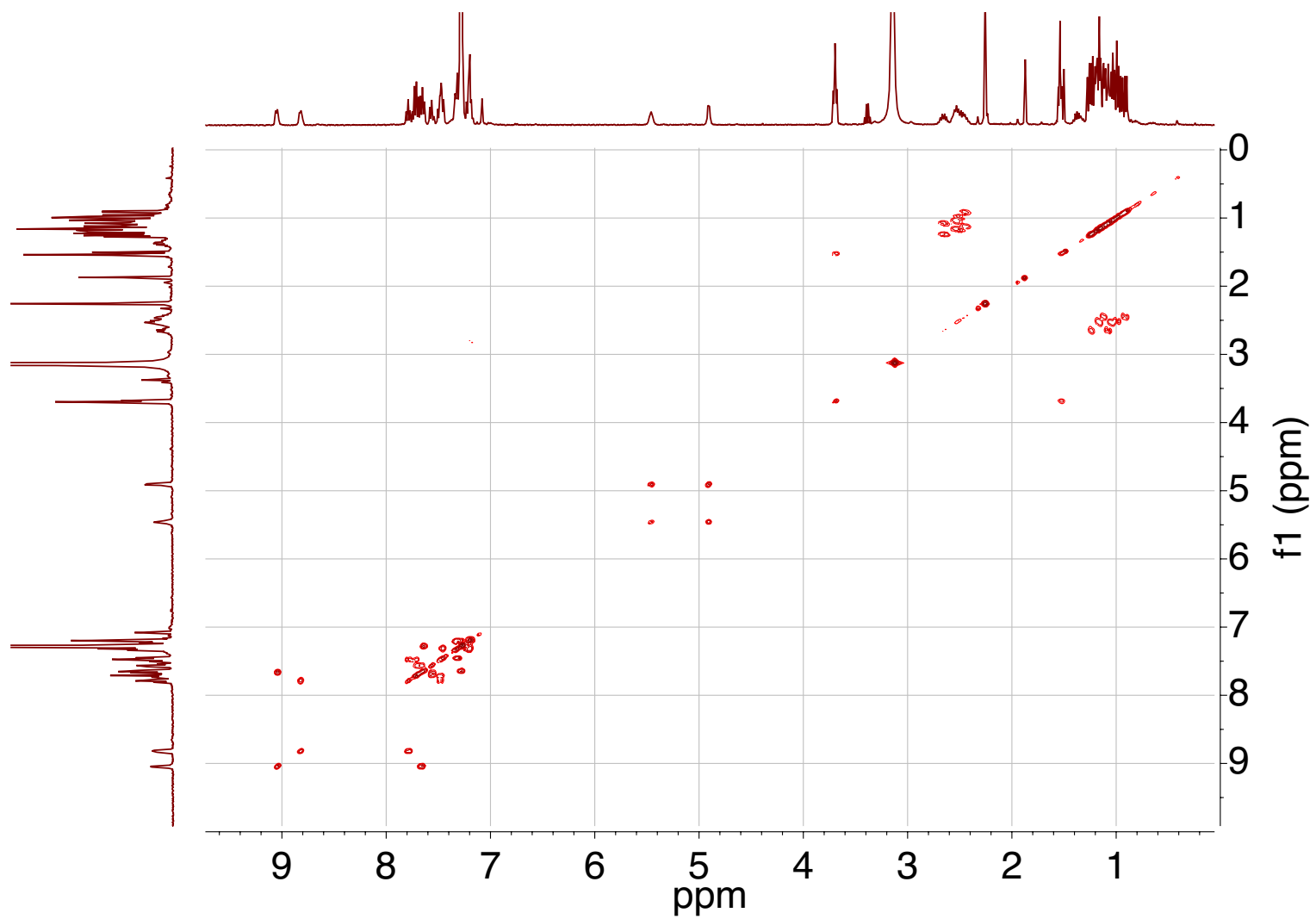


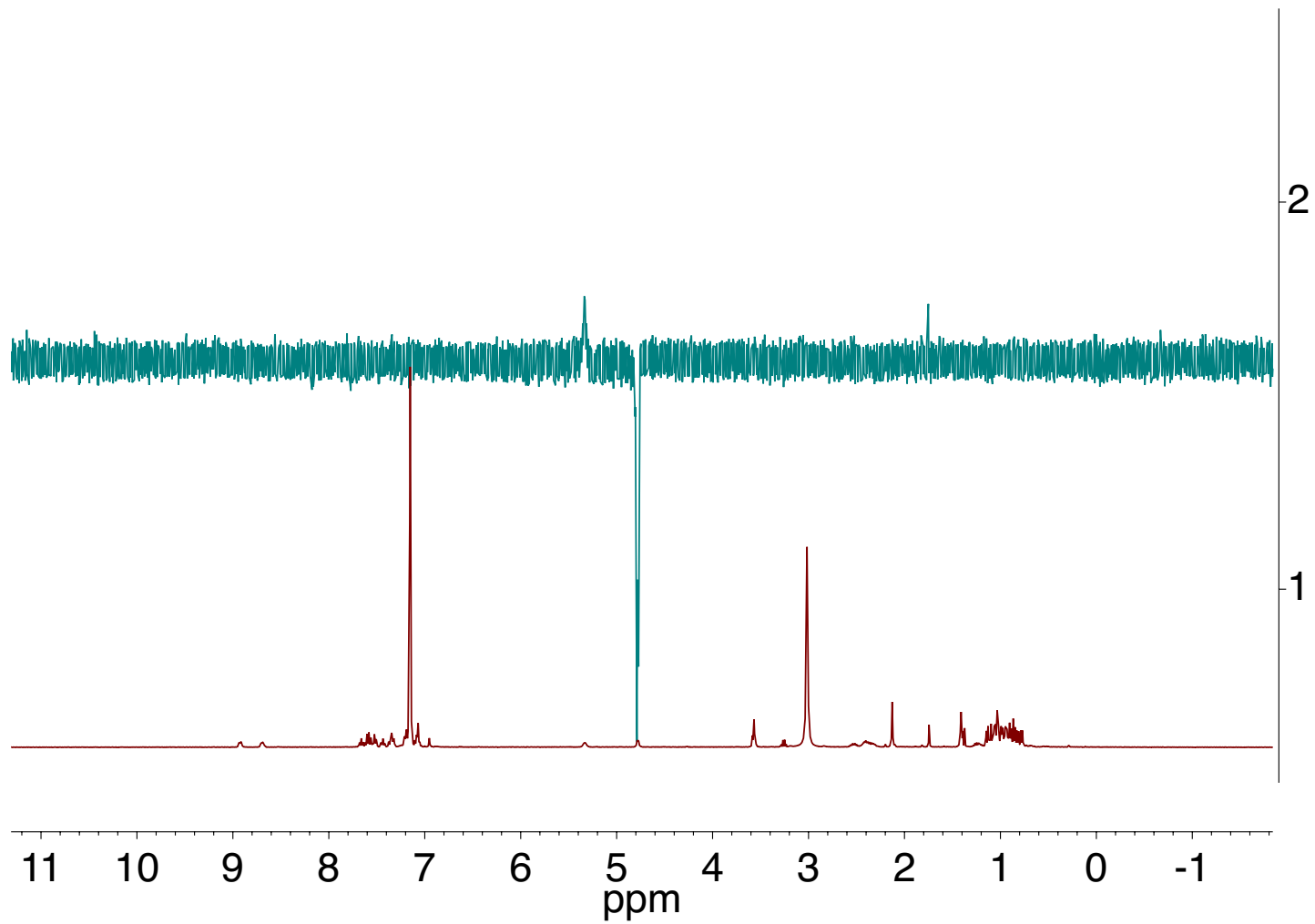
Fig. S9.  $^{31}\text{P}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_3\text{H}_5)(\text{OH})][\text{K}(18\text{-c-}6)]$  recorded at 162 MHz in  $\text{C}_6\text{D}_6$ .



**Figure S10.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_3\text{H}_5)(\text{OH})][\text{K}(\text{18-c-6})]$  recorded at 128 MHz in  $\text{C}_6\text{D}_6$ .



**Figure S11.** <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_3\text{H}_5)(\text{OH})][\text{K}(\text{18-c-6})]$  recorded at 500 MHz in  $\text{C}_6\text{D}_6$ .



**Figure S12.**  $^1\text{H}$ -1D NOE NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_3\text{H}_5)(\text{OH})][\text{K}(\text{18-c-6})]$  recorded at 400 MHz in  $\text{C}_6\text{D}_6$ .

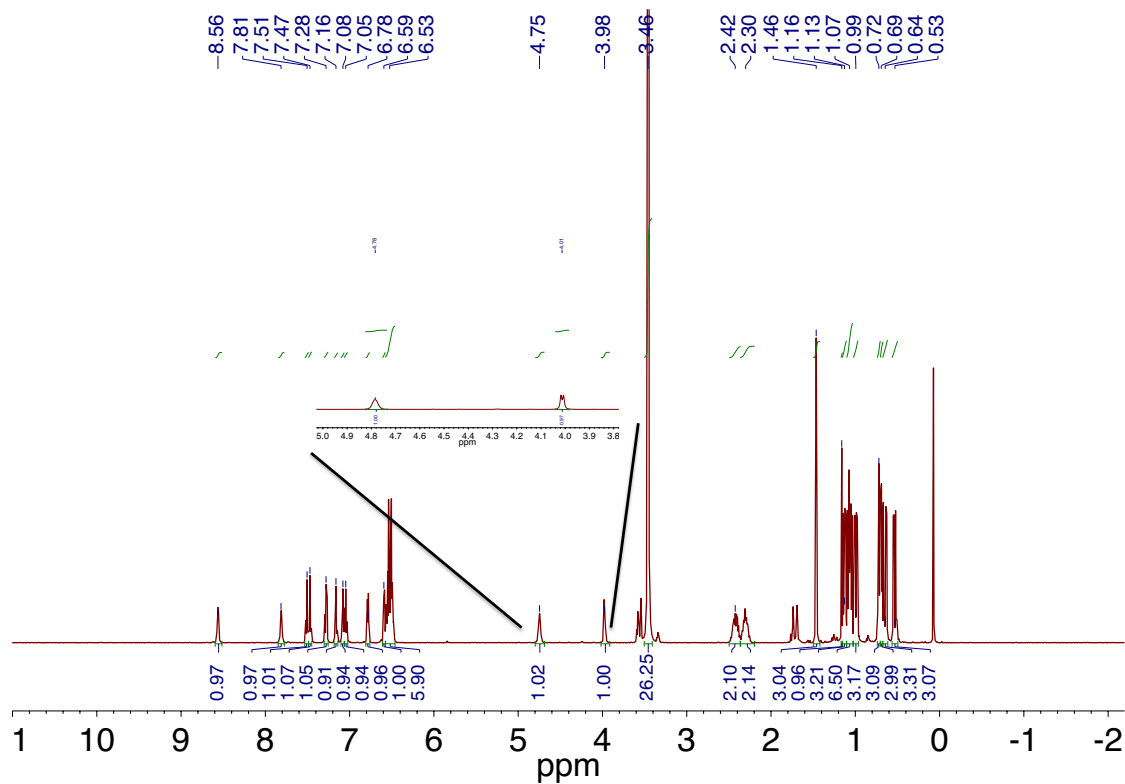


Figure S13.  $^1\text{H}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_3\text{H}_5)(\text{OH})][\text{K}(18\text{-c-}6)]$  recorded at 600 MHz in  $\text{THF-}d_8$ .

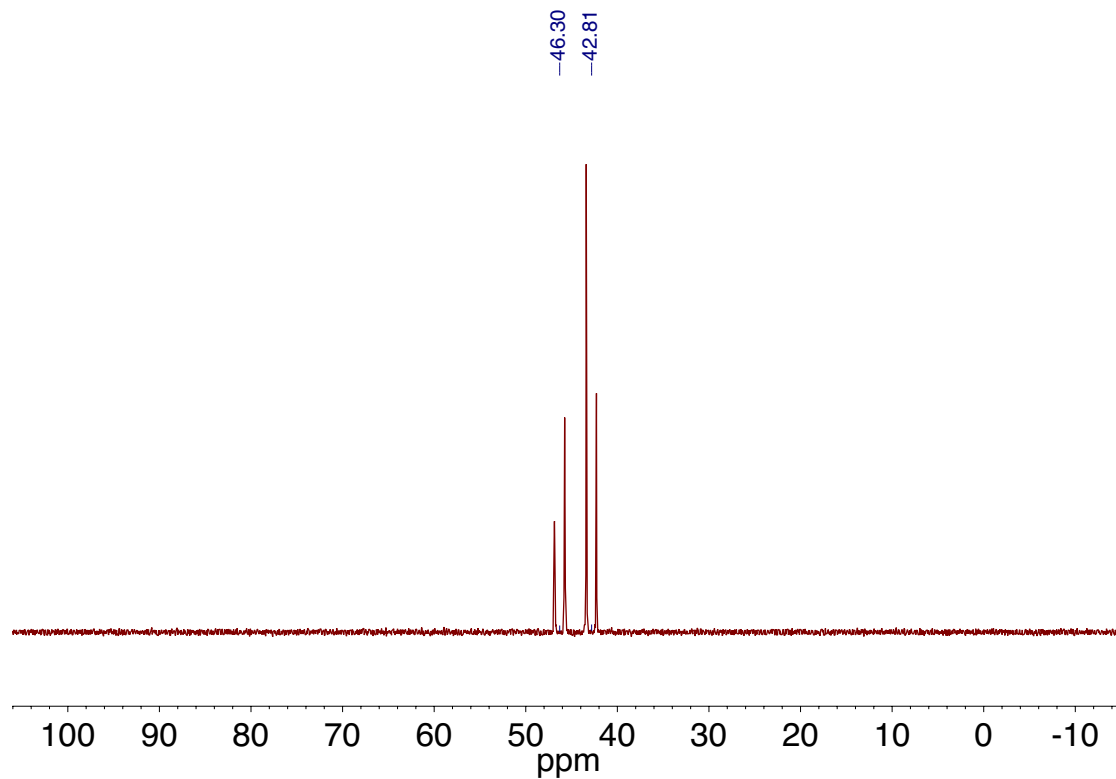


Figure S14.  $^{31}\text{P}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_3\text{H}_5)(\text{OH})][\text{K}(18\text{-c-}6)]$  recorded at 243 MHz in  $\text{THF-}d_8$ .

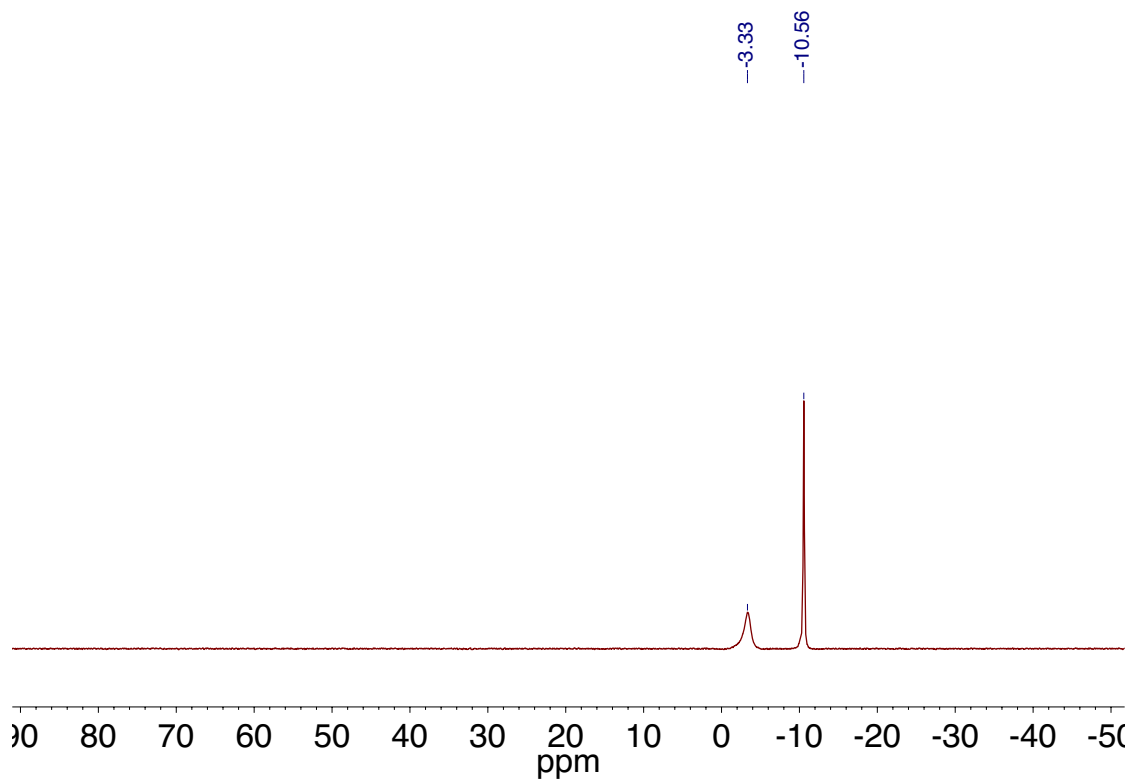


Figure S15.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_3\text{H}_5)(\text{OH})][\text{K}(\text{18-c-6})]$  recorded at 192 MHz in  $\text{THF-}d_8$ .

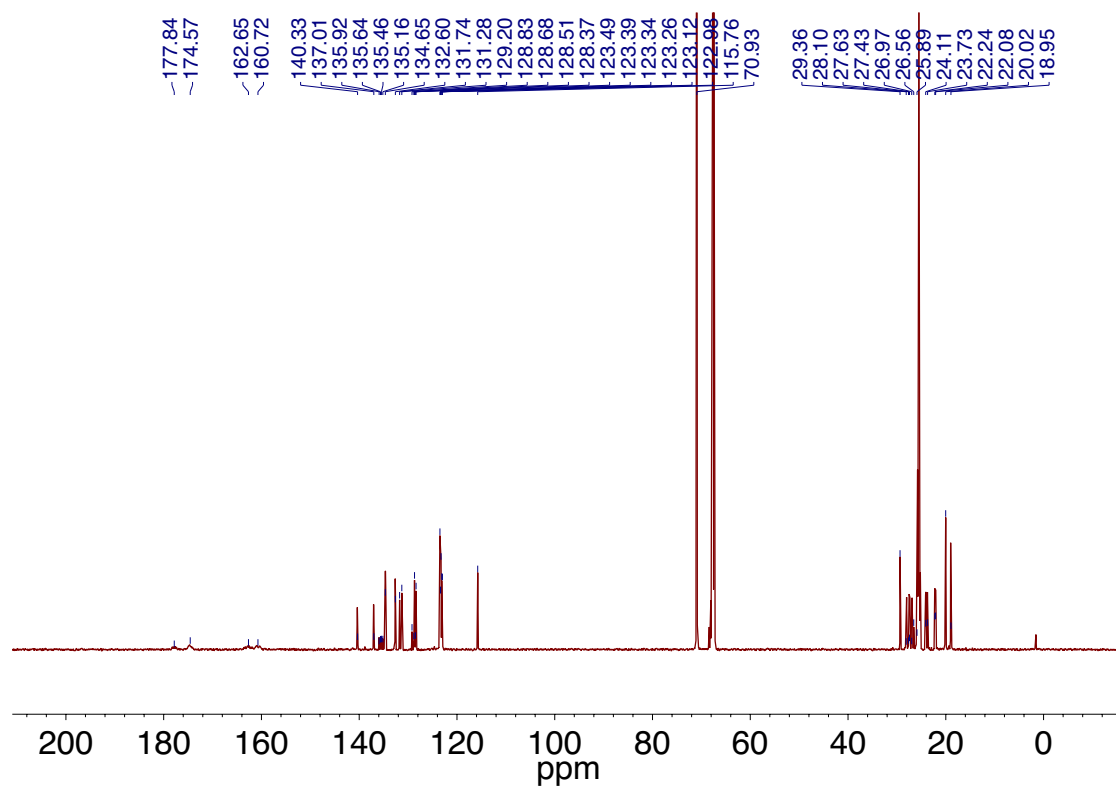
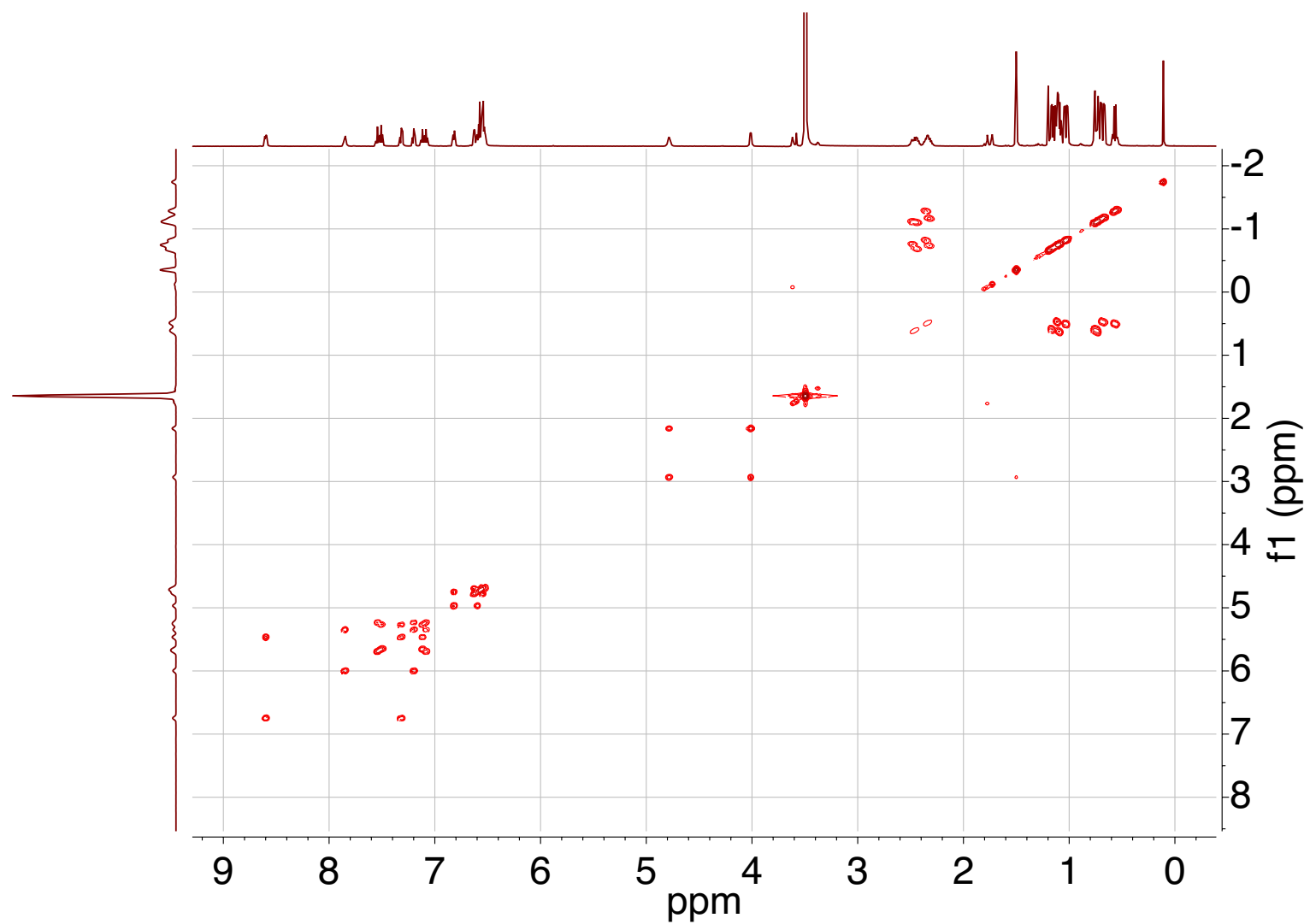
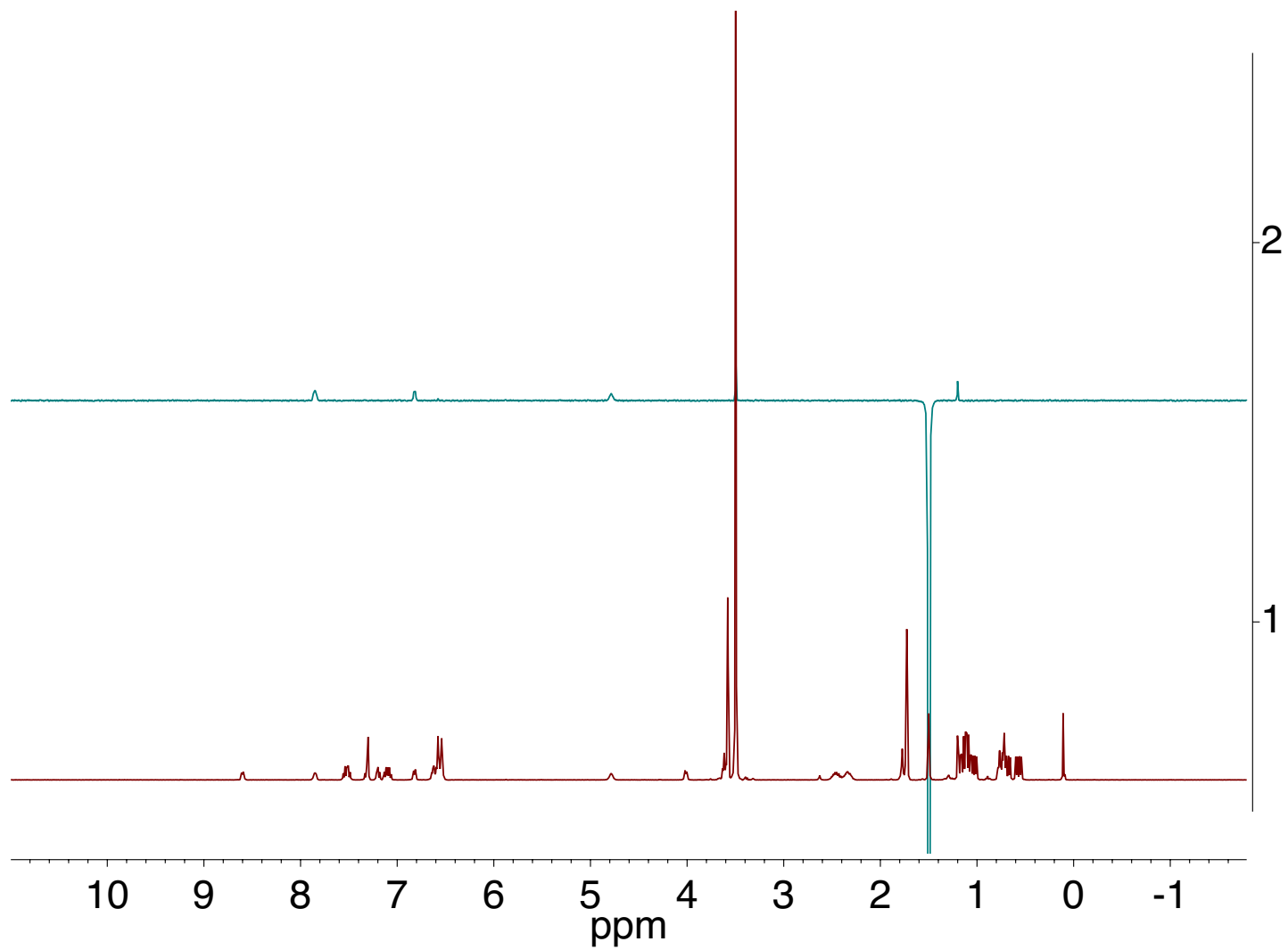


Figure S16.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_3\text{H}_5)(\text{OH})][\text{K}(\text{18-c-6})]$  recorded at 151 MHz in  $\text{THF-}d_8$ .





**Figure S17.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_3\text{H}_5)(\text{OH})][\text{K}(18\text{-c-}6)]$  recorded at 600 MHz in  $\text{THF-}d_8$ .



**Figure S18.**  $^1\text{H}$ -1D NOE NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_3\text{H}_5)(\text{OH})][\text{K}(\text{18-c-6})]$  recorded at 400 MHz in  $\text{THF-}d_8$ .

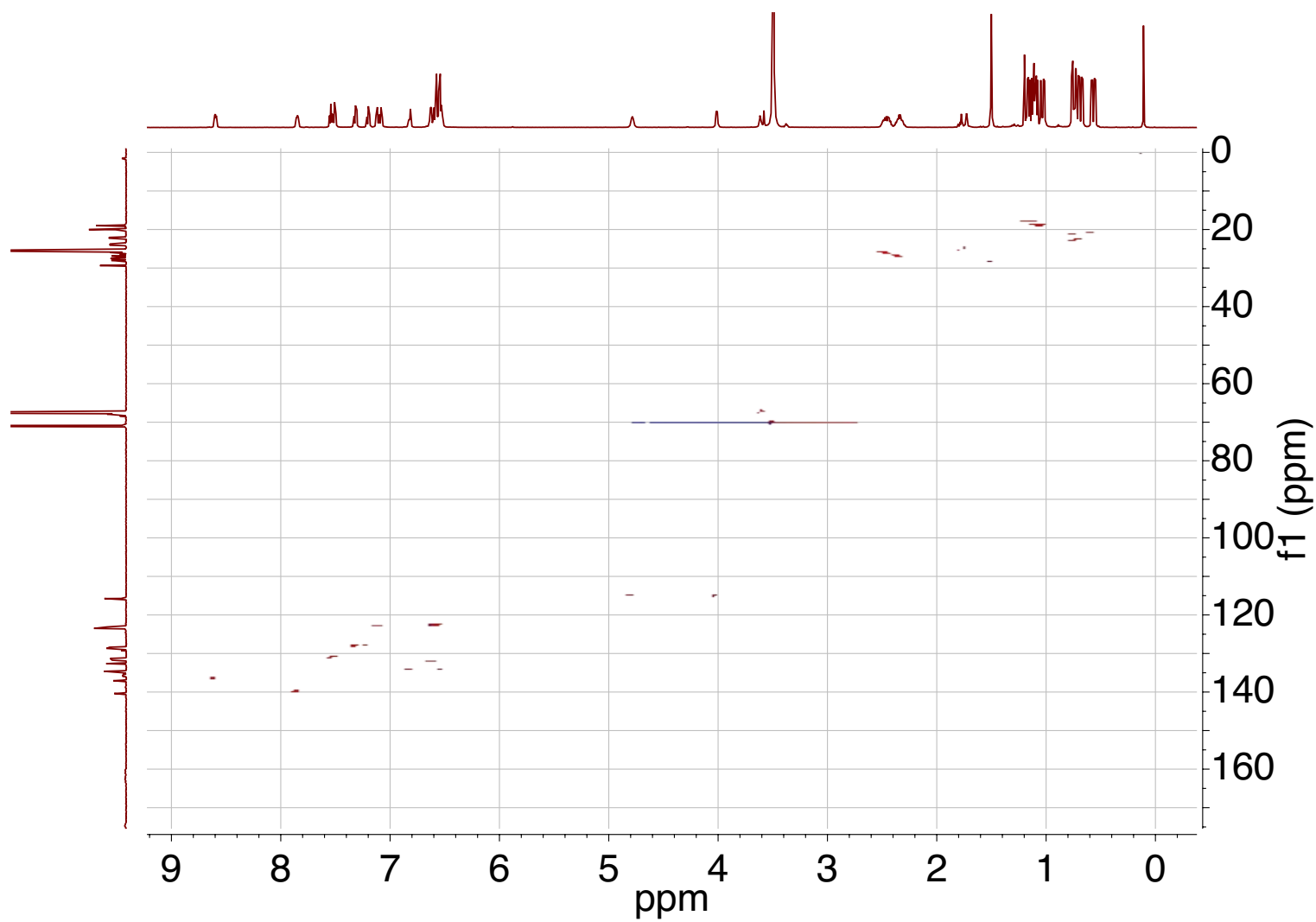


Figure S19.  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_3\text{H}_5)(\text{OH})][\text{K}(18\text{-c-}6)]$  recorded at 600 ( $^1\text{H}$ ) MHz in  $\text{THF-}d_8$ .

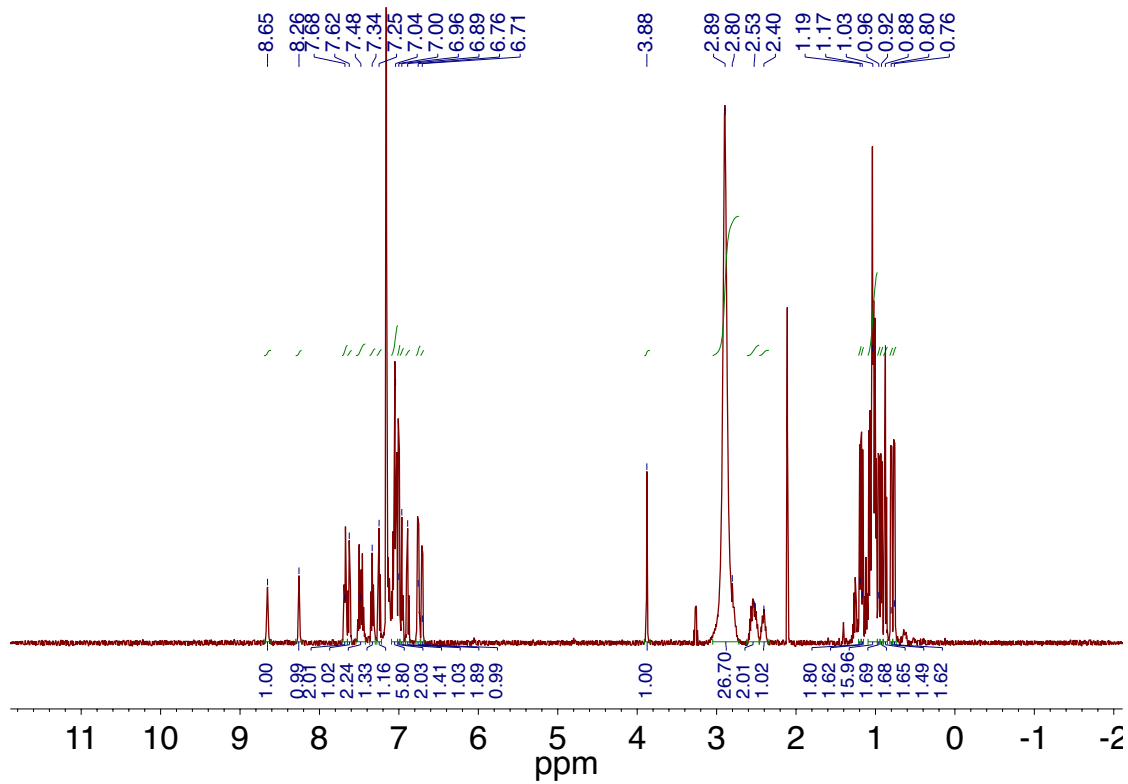


Figure S20.  $^1\text{H}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_7\text{H}_6\text{O})][\text{K}(18\text{-c-}6)]$  recorded at 400 MHz in  $\text{C}_6\text{D}_6$ .

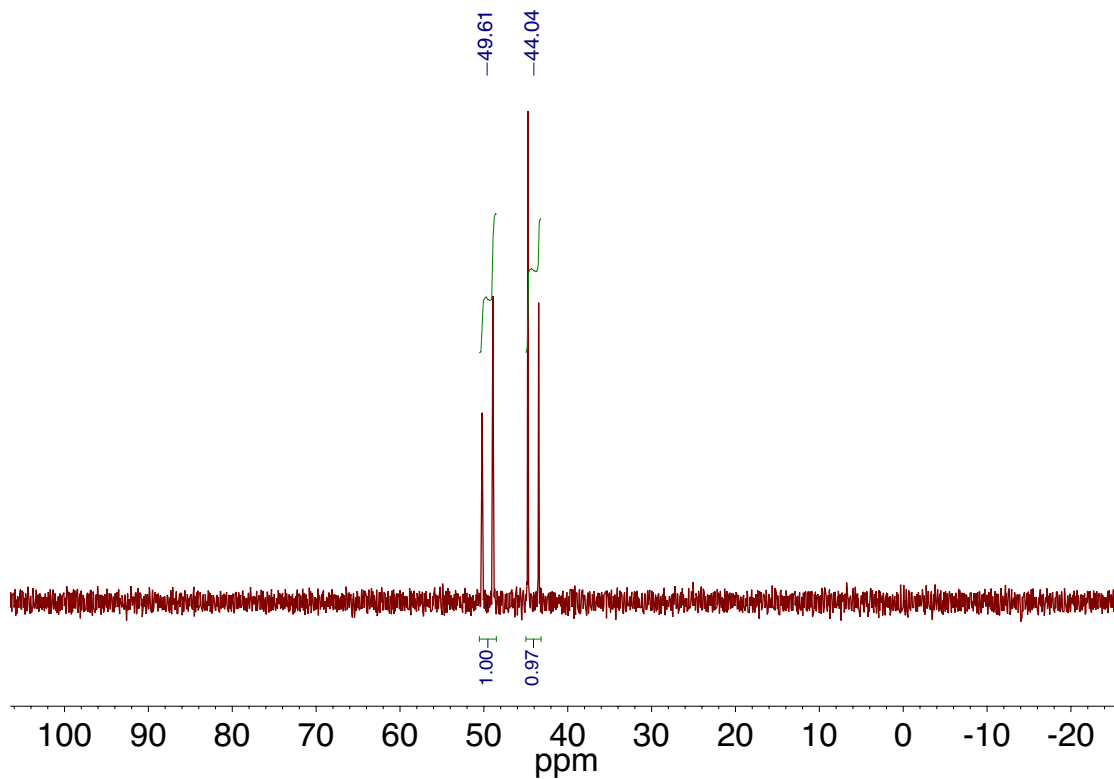


Figure S21.  $^{31}\text{P}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_7\text{H}_6\text{O})][\text{K}(18\text{-c-}6)]$  recorded at 202 MHz in  $\text{C}_6\text{D}_6$ .

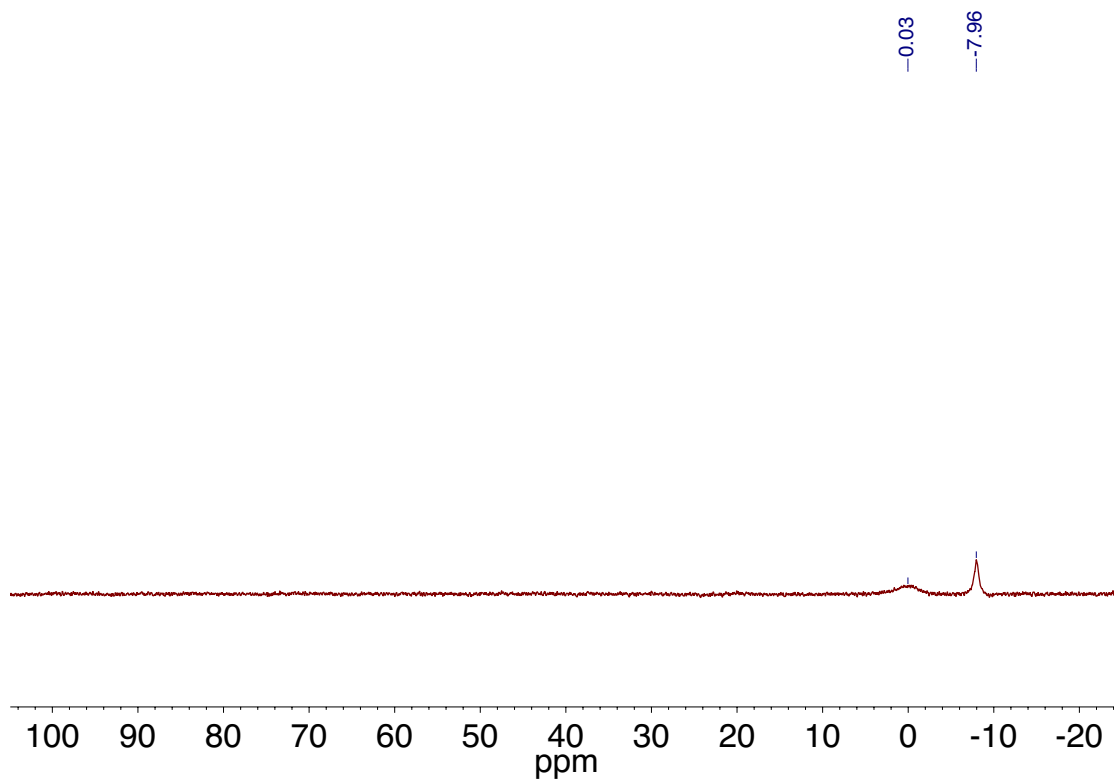


Figure S22.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_7\text{H}_6\text{O})][\text{K}(18\text{-c-6})]$  recorded at 160 MHz in  $\text{C}_6\text{D}_6$ .

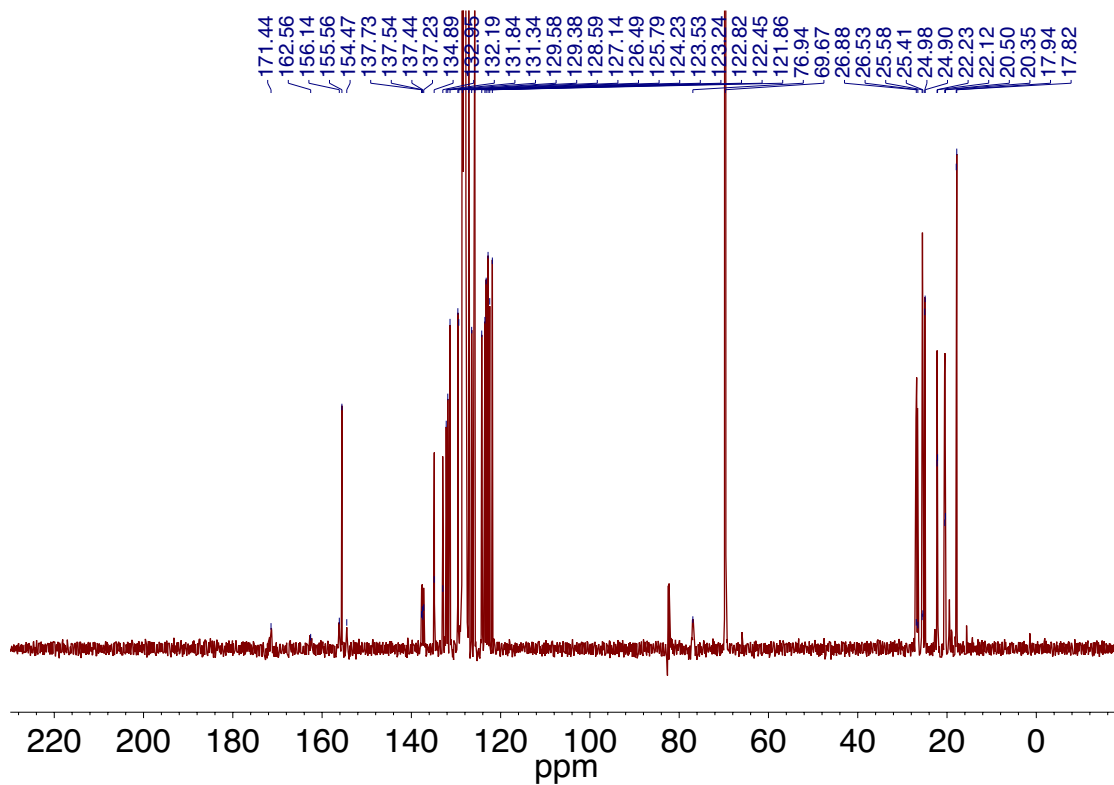


Figure S23.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_7\text{H}_6\text{O})][\text{K}(18\text{-c-6})]$  recorded at 151 MHz in  $\text{C}_6\text{D}_6$ .

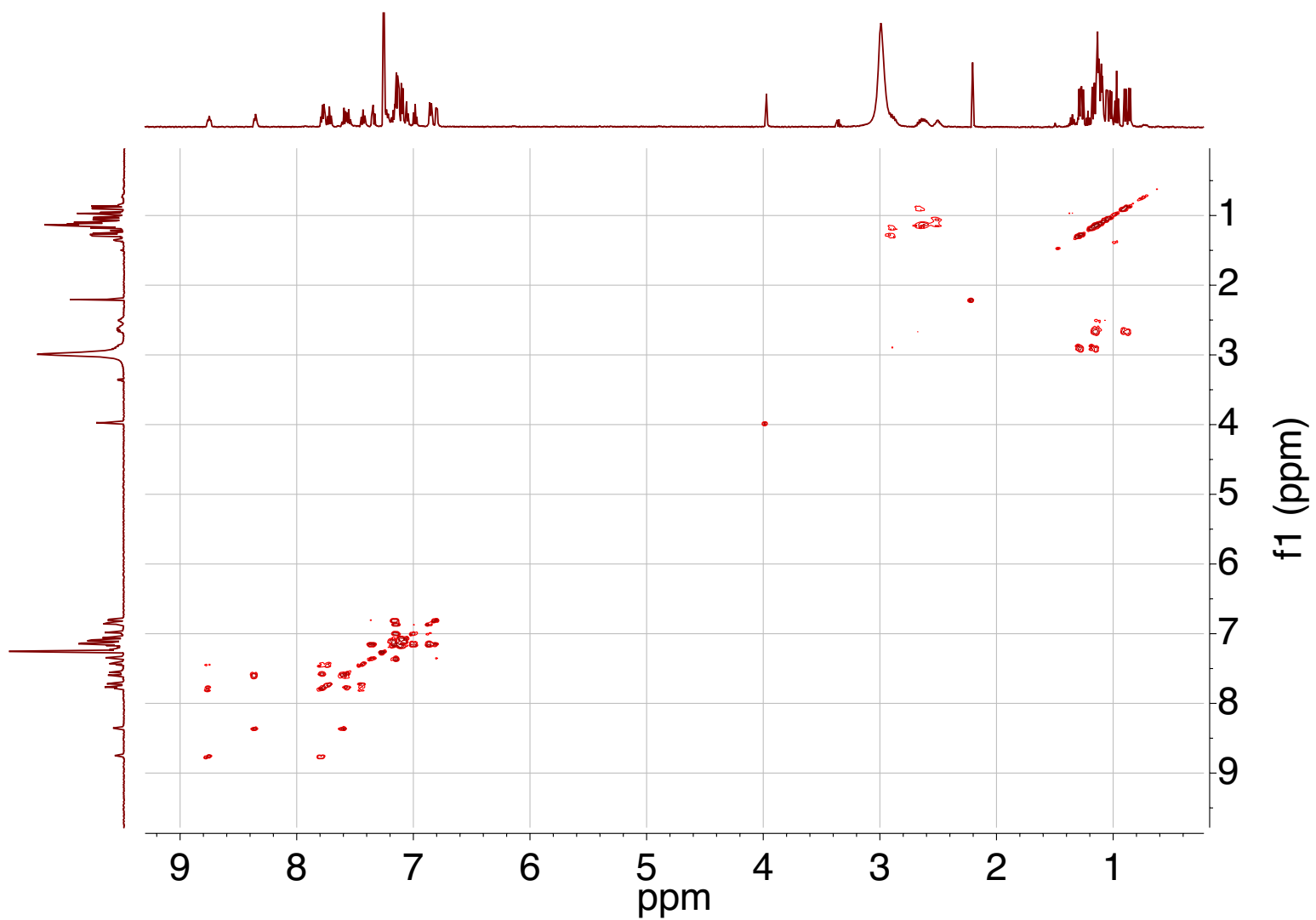


Figure S24.  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_7\text{H}_6\text{O})][\text{K}(\text{18-c-6})]$  recorded at 500 MHz in  $\text{C}_6\text{D}_6$ .

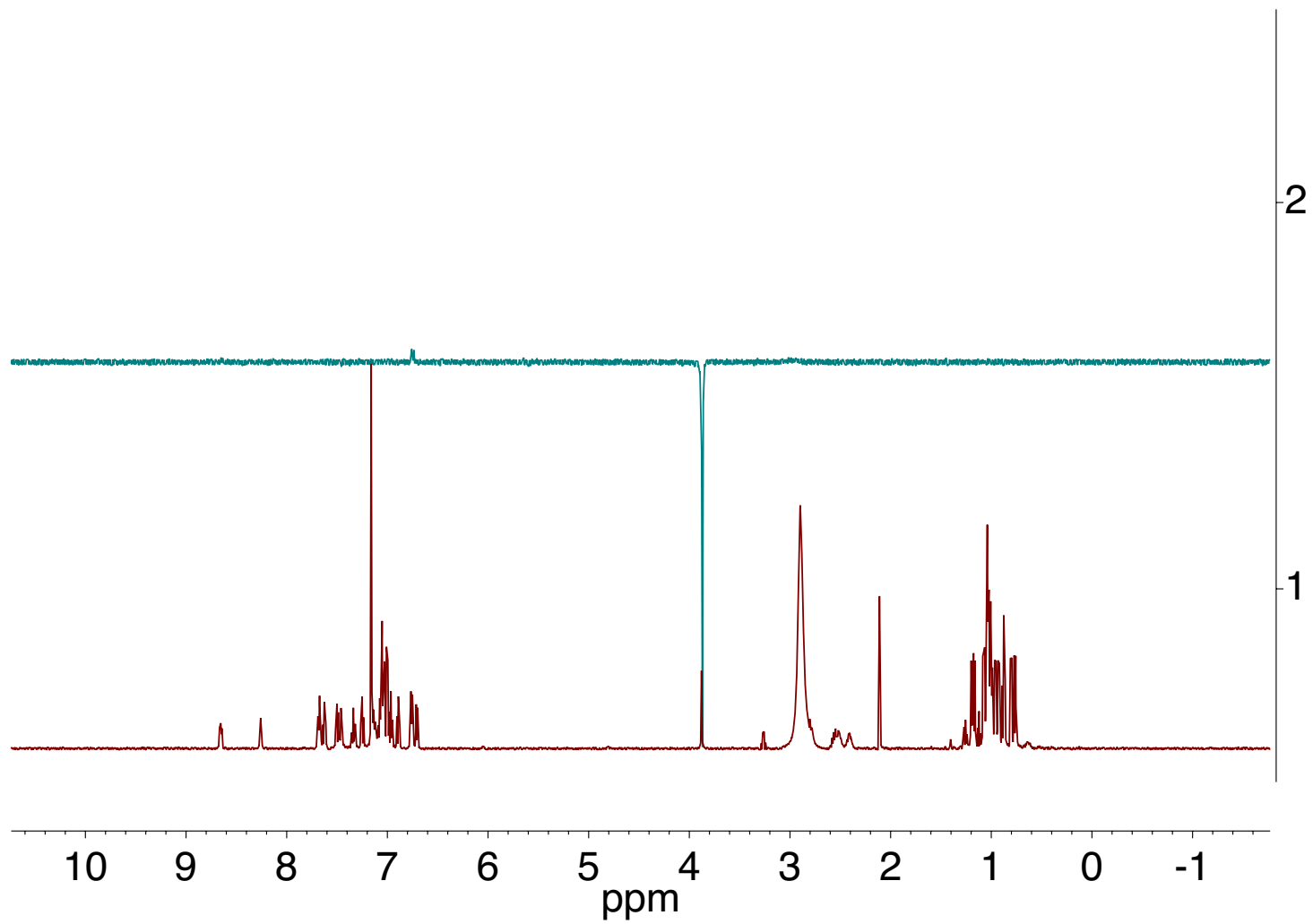


Figure S25.  $^1\text{H}$ -1D NOE spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_7\text{H}_6\text{O})][\text{K}(18\text{-c-}6)]$  recorded at 400 MHz in  $\text{C}_6\text{D}_6$ .

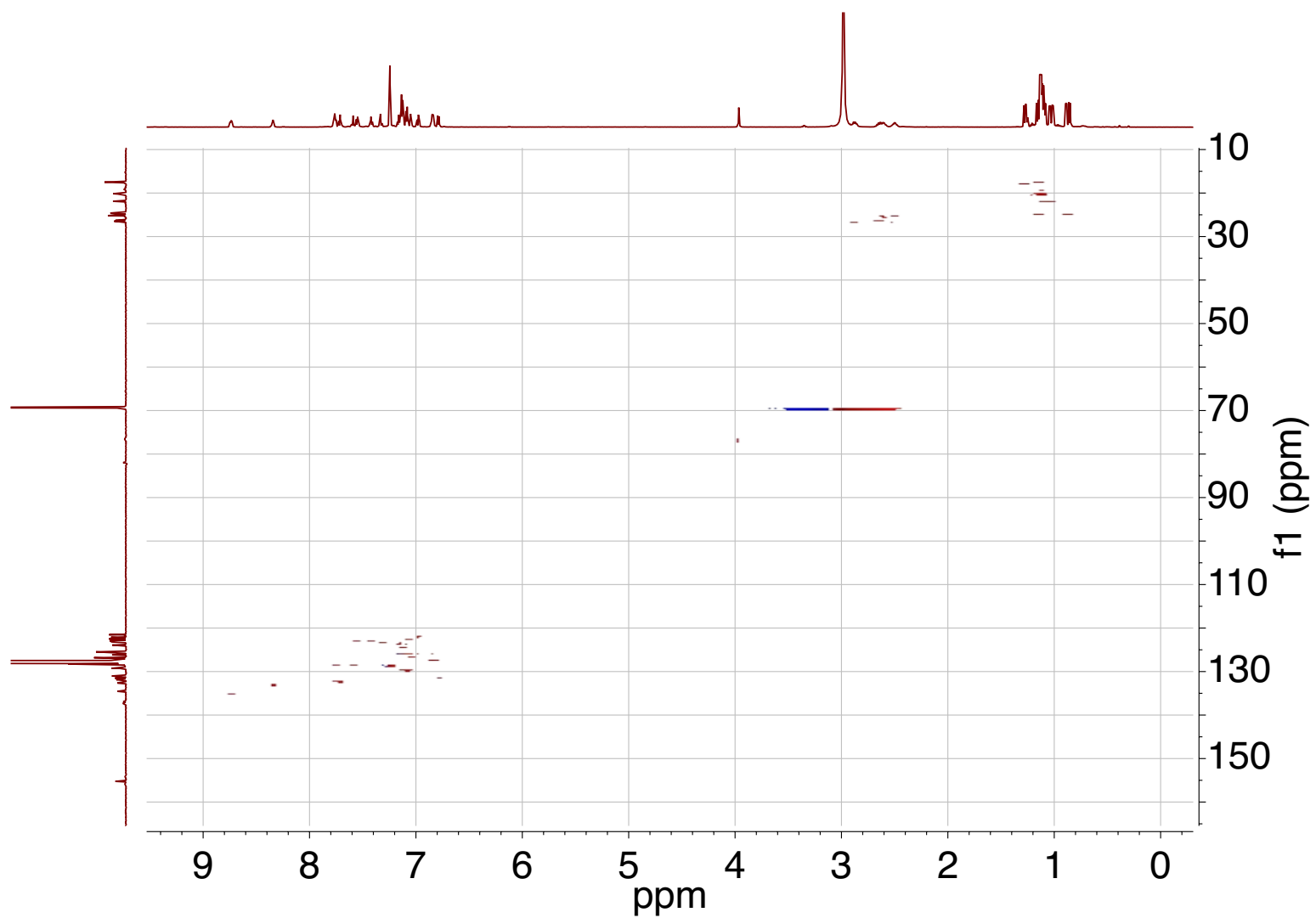


Figure S26.  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_7\text{H}_6\text{O})][\text{K}(18\text{-c-}6)]$  recorded on a 600 MHz spectrometer in  $\text{C}_6\text{D}_6$ .



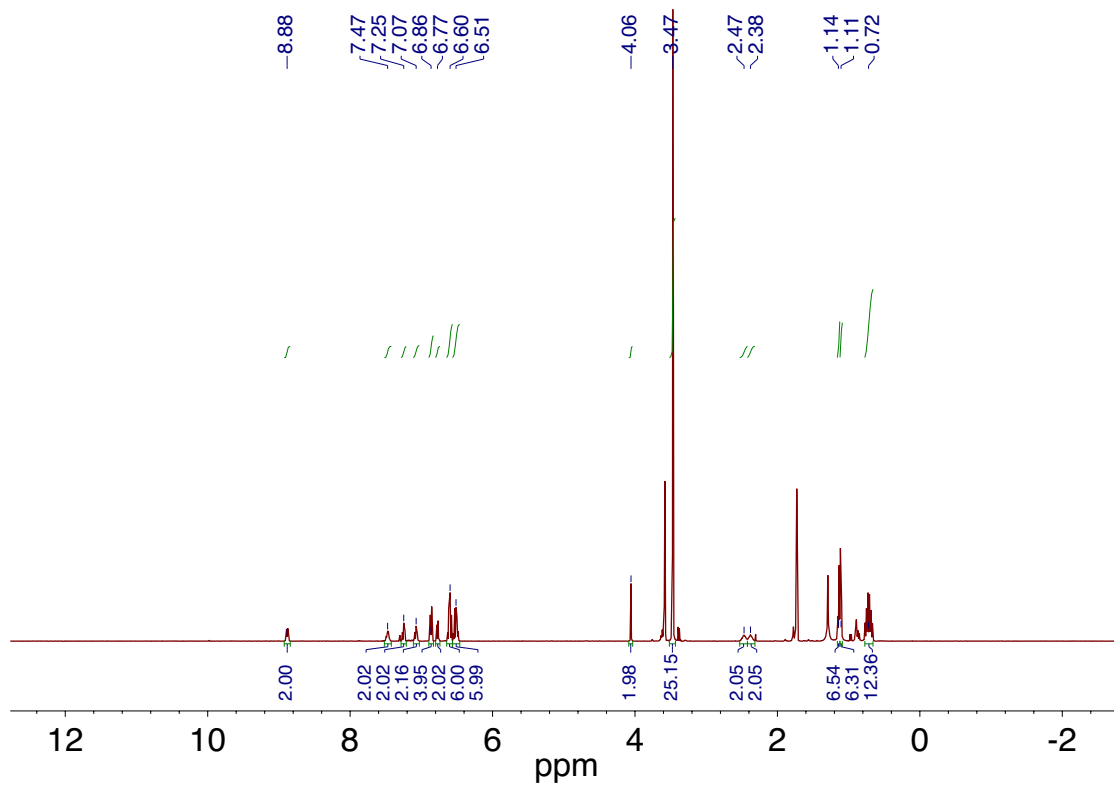


Figure S27.  $^1\text{H}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_{14}\text{H}_{12}\text{O}_2)][\text{K}(\text{18-c-6})(\text{THF})_2]$  recorded at 500 MHz in  $\text{THF-d}_8$ .

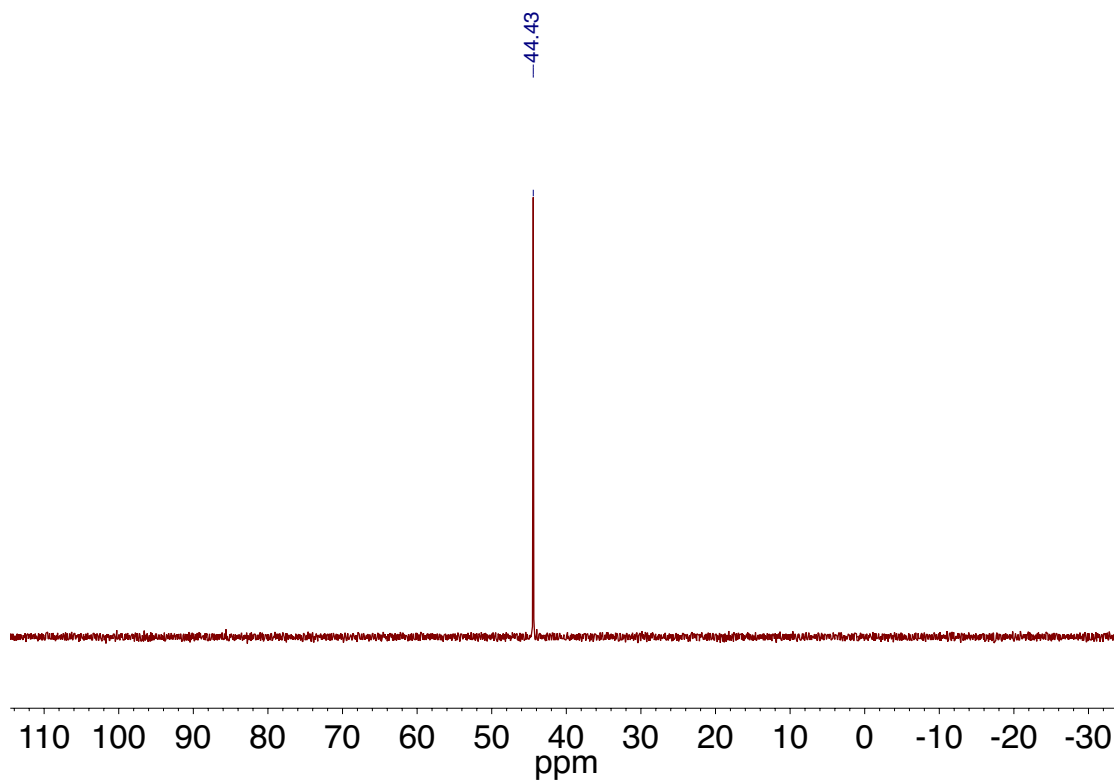


Figure S28.  $^{31}\text{P}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_{14}\text{H}_{12}\text{O}_2)][\text{K}(\text{18-c-6})(\text{THF})_2]$  recorded at 162 MHz in  $\text{THF-d}_8$ .

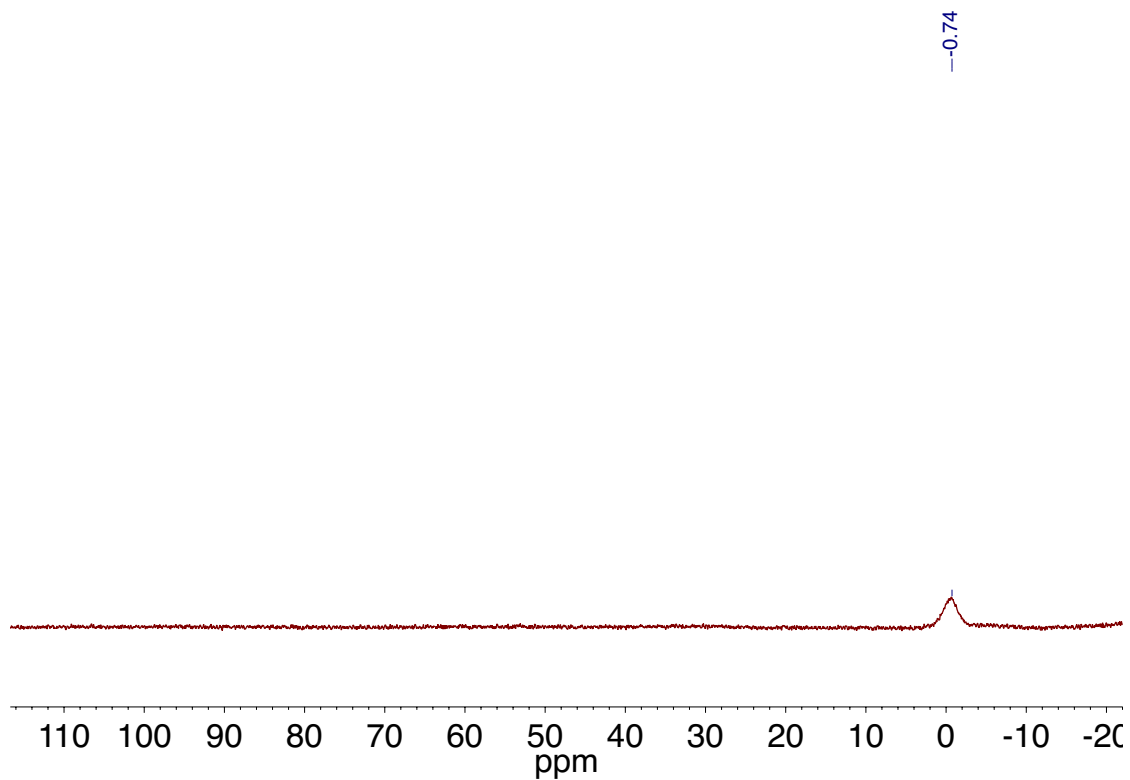


Figure S29.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_{14}\text{H}_{12}\text{O}_2)][\text{K}(18\text{-c-6})(\text{THF})_2]$  recorded at 128 MHz in  $\text{THF-}d_8$ .

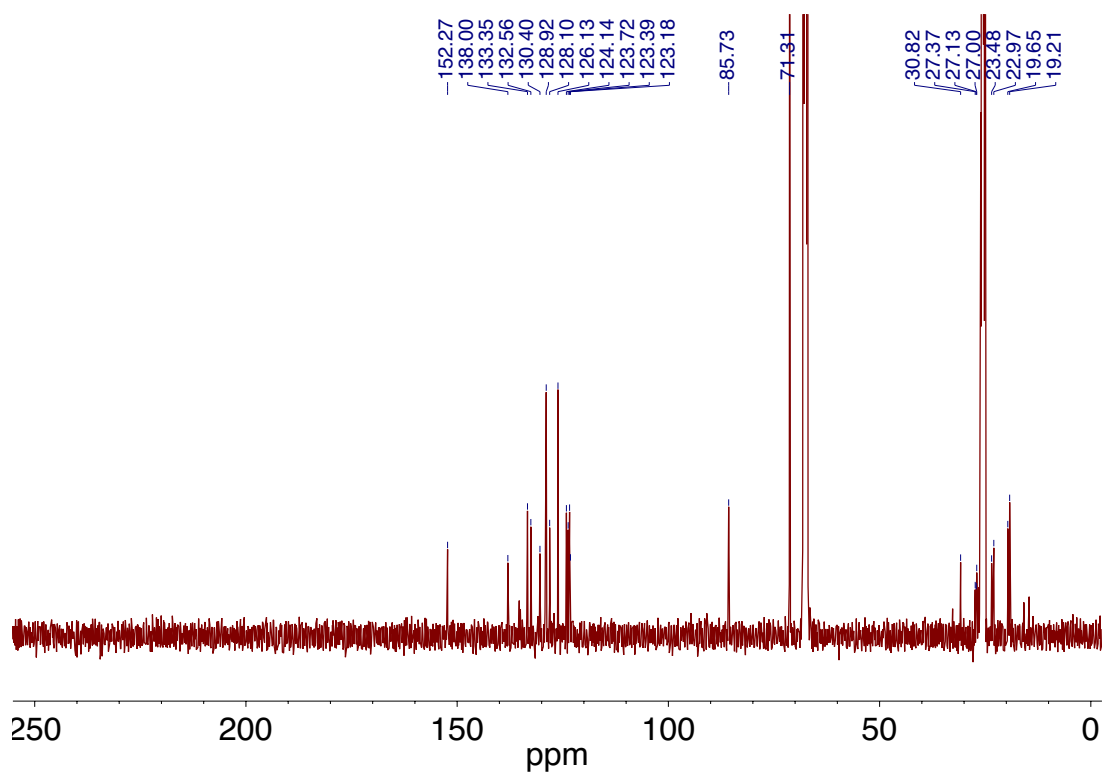


Figure S30.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_{14}\text{H}_{12}\text{O}_2)][\text{K}(18\text{-c-6})(\text{THF})_2]$  recorded at 101 MHz in  $\text{THF-}d_8$ .

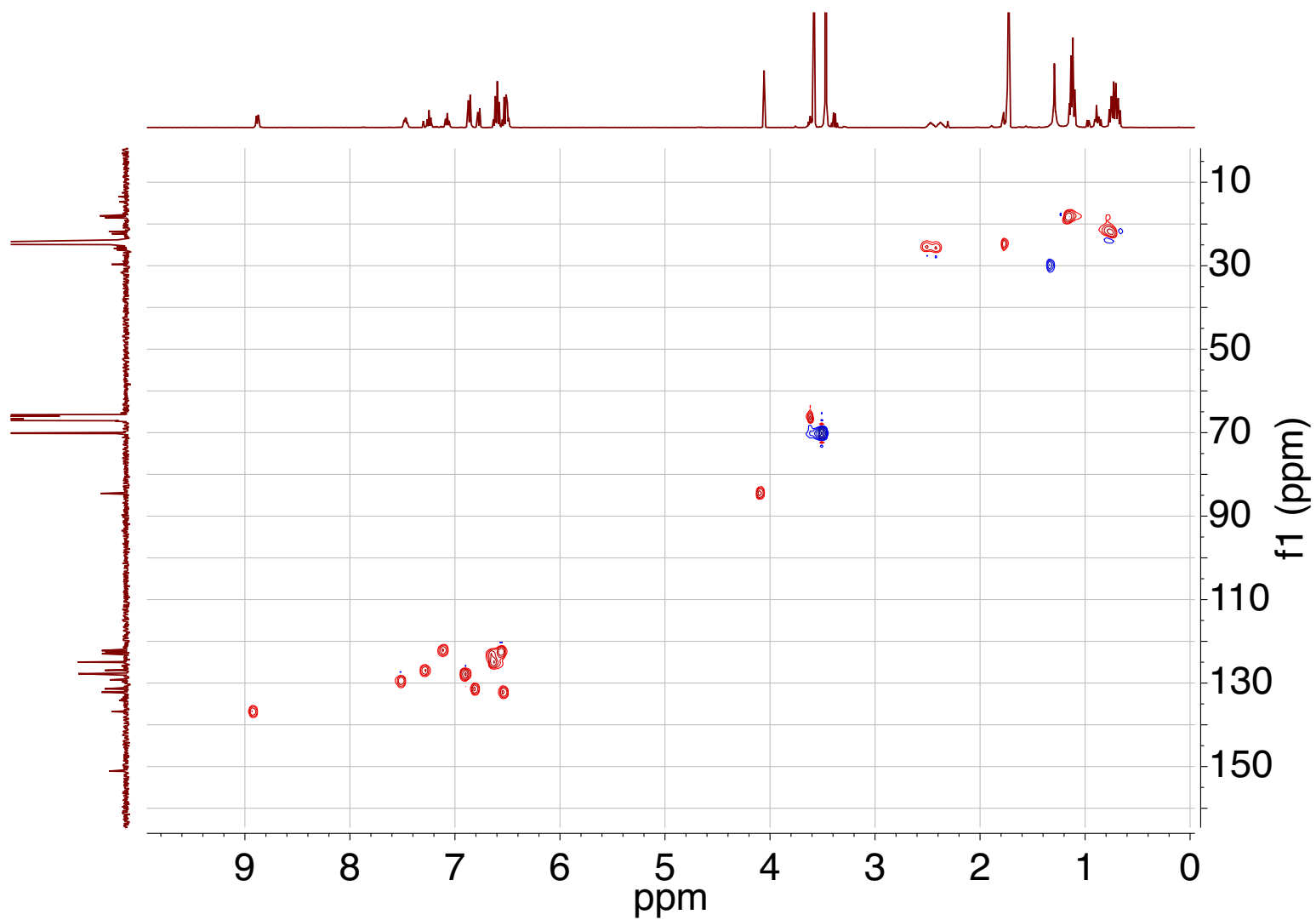


Figure S31. <sup>1</sup>H-<sup>13</sup>C HSQC NMR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_{14}\text{H}_{12}\text{O}_2)][\text{K}(18\text{-c-}6)(\text{THF})_2]$  recorded at 400 (<sup>1</sup>H) MHz in C<sub>6</sub>D<sub>6</sub>.

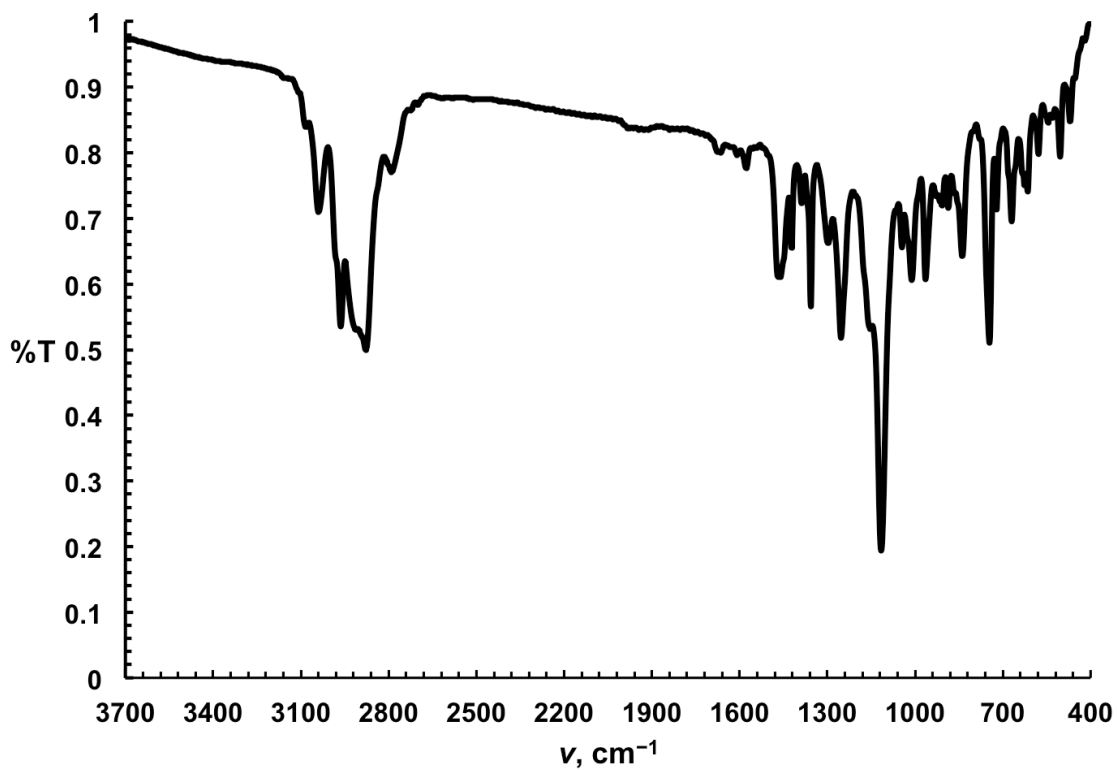


Figure S32. FT-IR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{OCH}_2\text{OCH}_2)][\text{K}(18\text{-c-}6)]$ .

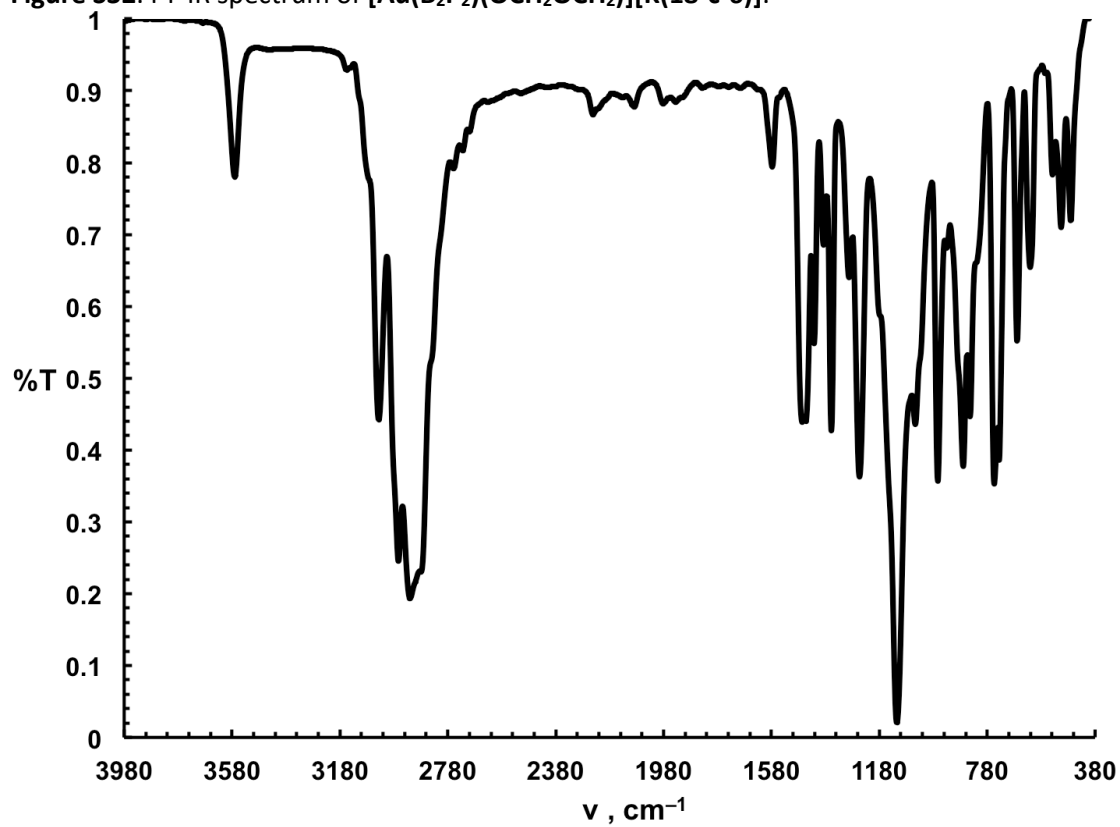


Figure S33. FT-IR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_3\text{H}_5)(\text{OH})][\text{K}(18\text{-c-}6)]$ .

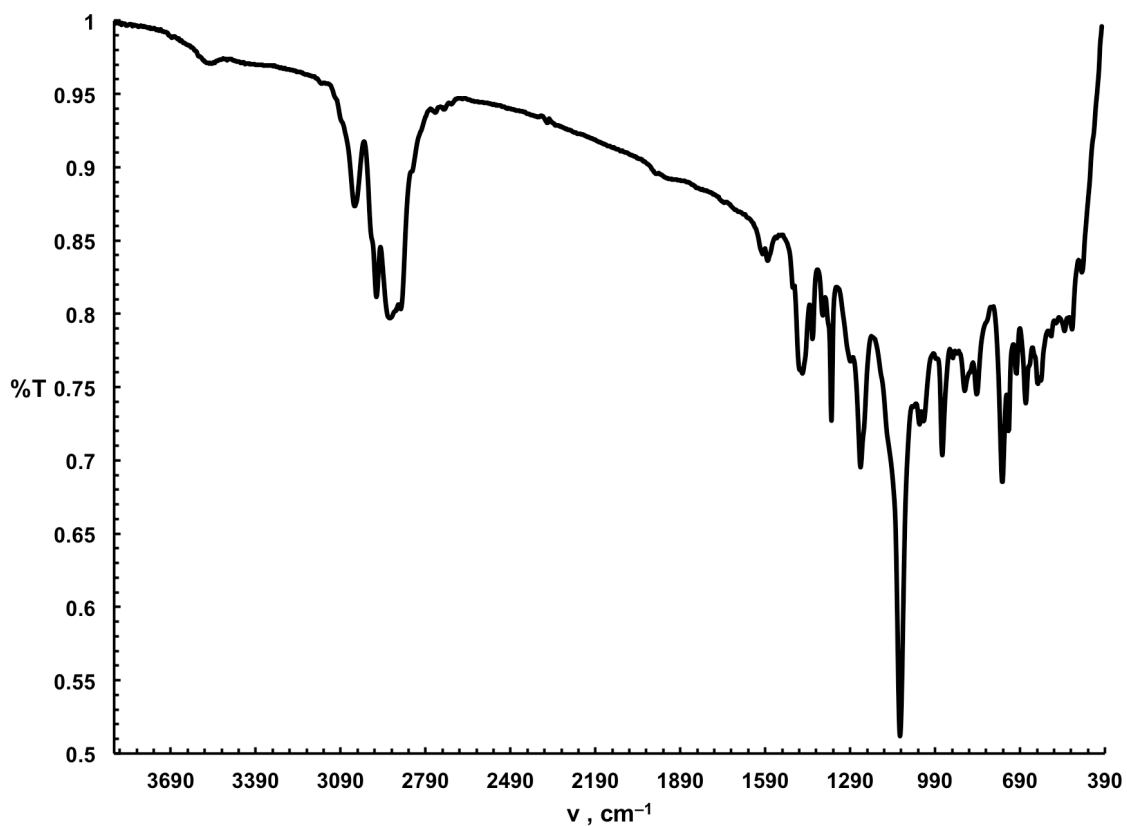


Figure S34. FT-IR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_7\text{H}_6\text{O})][\text{K}(18\text{-c-}6)]$ .

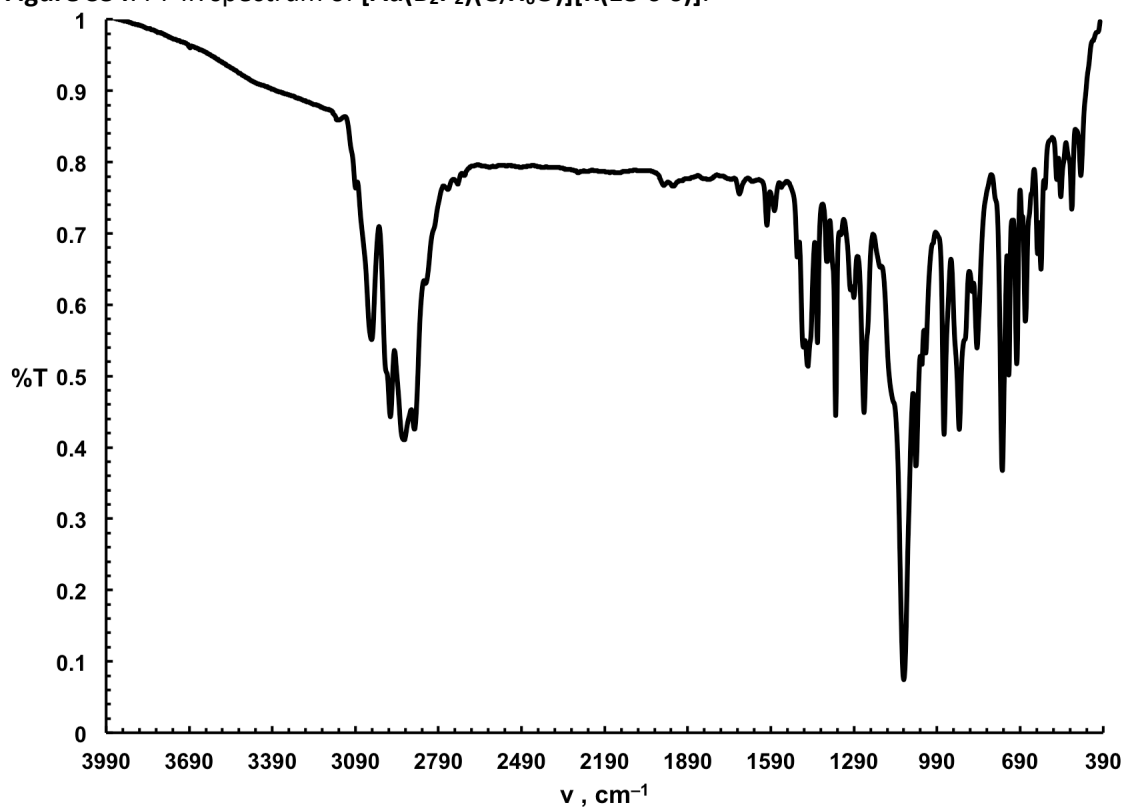


Figure S35. FT-IR spectrum of  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_{14}\text{H}_{12}\text{O}_2)][\text{K}(18\text{-c-}6)(\text{THF})_2]$ .

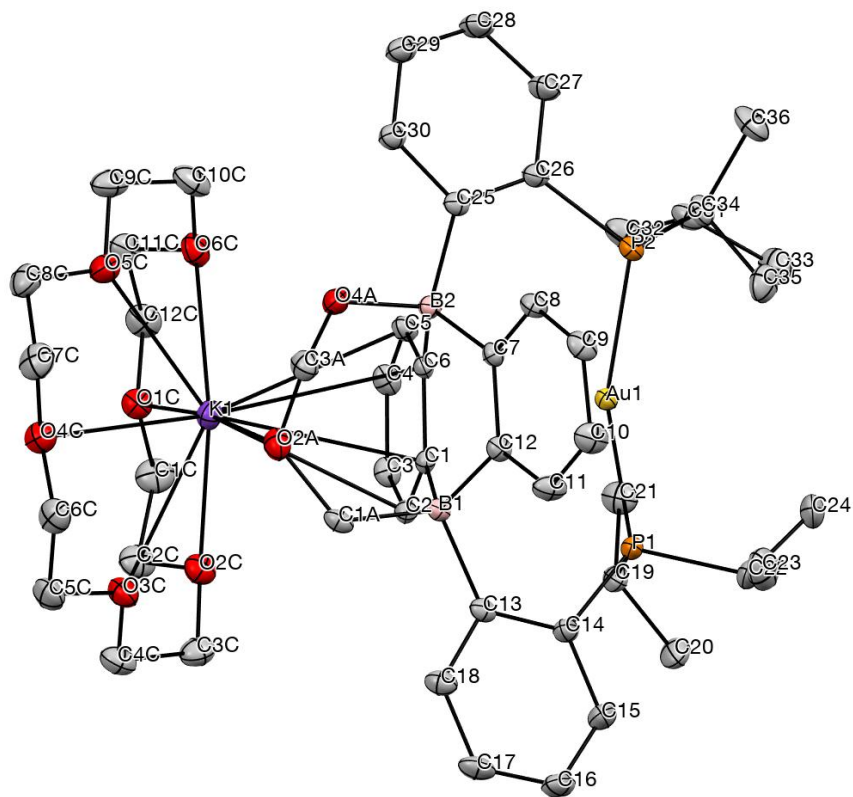


Figure S36. Labeled thermal ellipsoid plot (50%) for  $[\text{Au}(\text{B}_2\text{P}_2)(\text{OCH}_2\text{OCH}_2)][\text{K}(18\text{-c-}6)]$ .

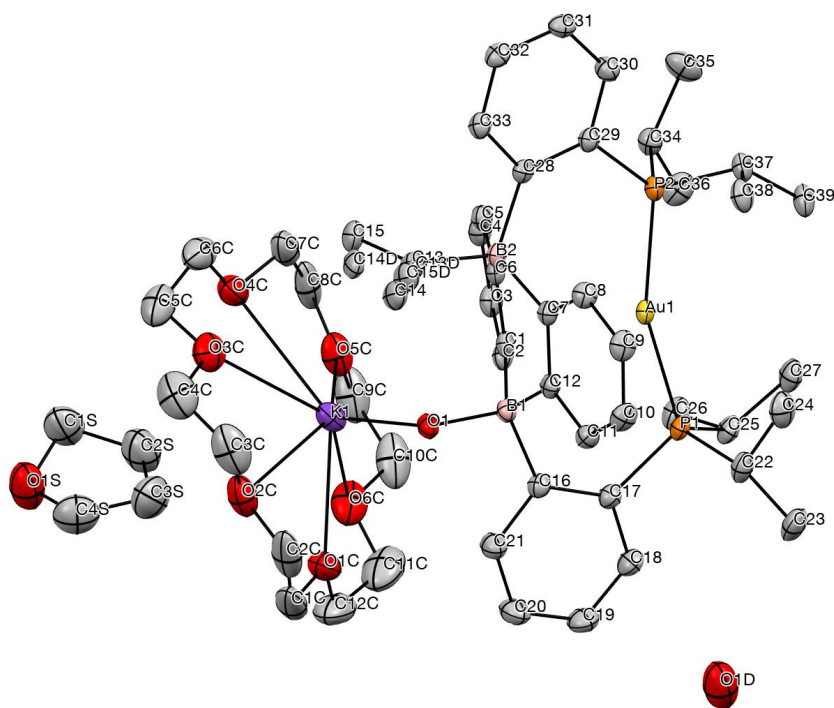


Figure S37. Labeled thermal ellipsoid plot (50%) for  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_3\text{H}_5)(\text{OH})][\text{K}(18\text{-c-}6)]$ .

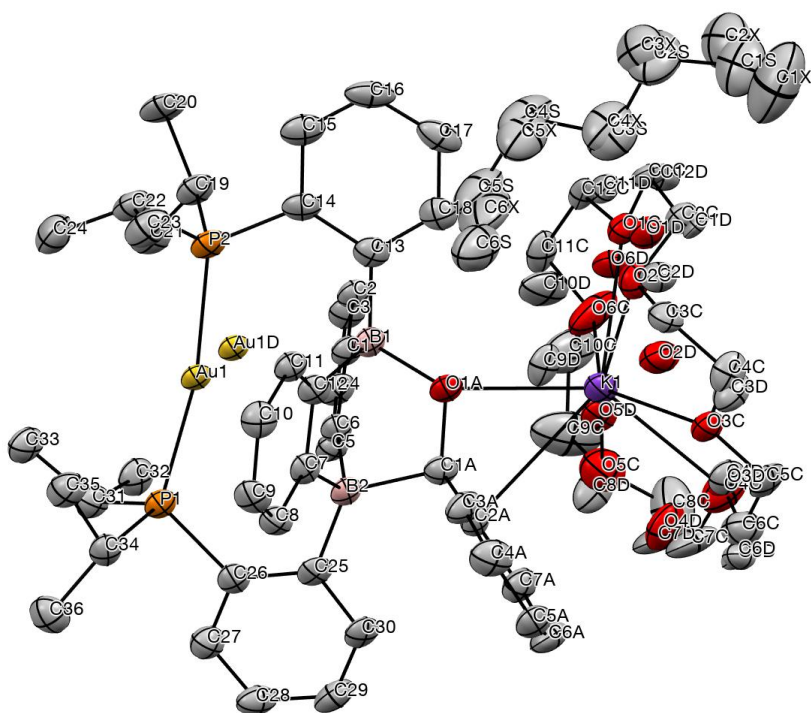


Figure S38. Labeled thermal ellipsoid plot (30%) for  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_7\text{H}_6\text{O})][\text{K}(\text{18-c-6})]$ .

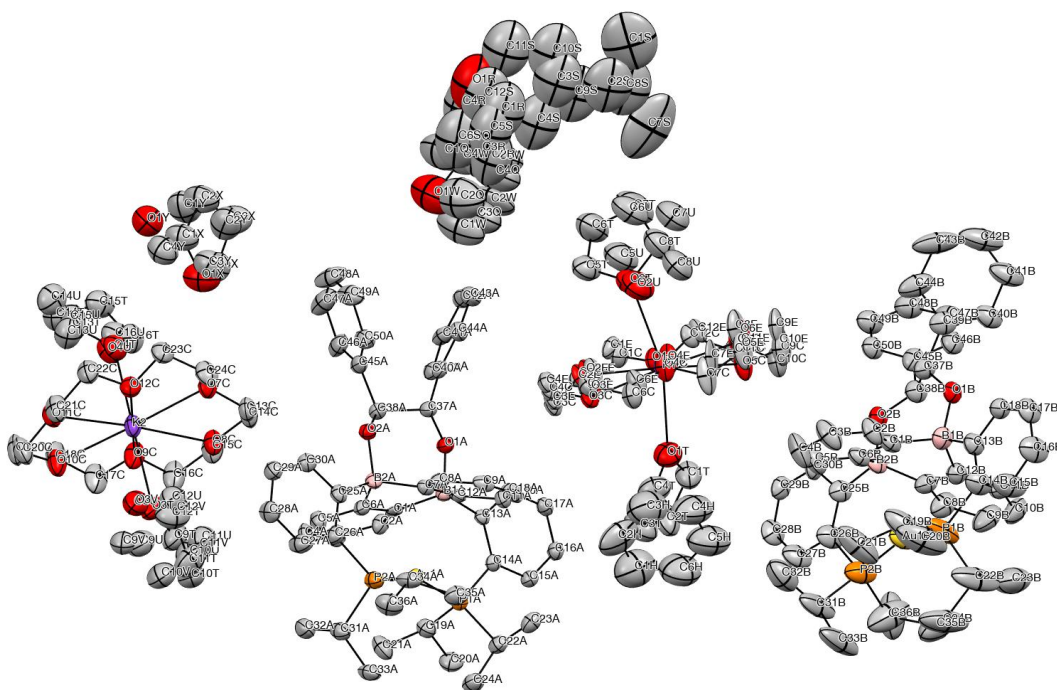


Figure S39. Labeled thermal ellipsoid plot (30%) for  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_{14}\text{H}_{12}\text{O}_2)][\text{K}(\text{18-c-6})(\text{THF})_2]$ .

**Table S1.** Crystal data and structure refinement for **[Au(B<sub>2</sub>P<sub>2</sub>)(OCH<sub>2</sub>OCH<sub>2</sub>)] [K(18-c-6)]**.

Identification code	hh248JT123_0m	
Empirical formula	C <sub>50</sub> H <sub>72</sub> AuB <sub>2</sub> KO <sub>8</sub> P <sub>2</sub>	
Formula weight	1120.70 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P $\bar{1}$	
Unit cell dimensions	$a = 10.0837(2)$ Å	$\alpha = 81.7553(5)^\circ$ .
	$b = 14.1067(2)$ Å	$\beta = 84.4017(5)^\circ$ .
	$c = 18.4824(3)$ Å	$\gamma = 73.8383(5)^\circ$ .
Volume	2494.48(7) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.492 mg/m <sup>3</sup>	
Absorption coefficient	3.148 mm <sup>-1</sup>	
$F(000)$	1148	
Crystal size	0.584 x 0.571 x 0.514 mm <sup>3</sup>	
$\vartheta$ range for data collection	1.768 to 28.700°.	
Index ranges	$-13 \leq h \leq 13, -19 \leq k \leq 19, -24 \leq l \leq 24$	
Reflections collected	98727	
Independent reflections	12884 [ $R_{\text{int}} = 0.0199$ ]	
Completeness to $\vartheta = 25.242^\circ$	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	12884 / 0 / 585	
Goodness-of-fit on $F^2$	1.078	
Final $R$ indices [ $I > 2\sigma_I$ ]	$R_1 = 0.0149, wR_2 = 0.0370$	
$R$ indices (all data)	$R_1 = 0.0154, wR_2 = 0.0372$	
Largest diff. peak and hole	1.277 and $-0.446$ e/Å <sup>3</sup>	



**Table S2.** Crystal data and structure refinement for **[Au(B<sub>2</sub>P<sub>2</sub>)(C<sub>3</sub>H<sub>5</sub>)(OH)][K(18-c-6)]**.

Identification code	hh191JT94r_0m	
Empirical formula	C <sub>55</sub> H <sub>82</sub> AuB <sub>2</sub> KO <sub>8</sub> P <sub>2</sub>	
Formula weight	1190.83 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	$a = 19.9307(6)$ Å	$\alpha = 90^\circ$ .
	$b = 14.7178(4)$ Å	$\beta = 110.8122(5)^\circ$ .
	$c = 20.3785(6)$ Å	$\gamma = 90^\circ$ .
Volume	5587.7(3) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.416 mg/m <sup>3</sup>	
Absorption coefficient	2.815 mm <sup>-1</sup>	
$F(000)$	2456	
Crystal size	0.384 x 0.284 x 0.167 mm <sup>3</sup>	
$\vartheta$ range for data collection	1.749 to 29.130°.	
Index ranges	$-27 \leq h \leq 27, -20 \leq k \leq 20, -27 \leq l \leq 27$	
Reflections collected	121534	
Independent reflections	15037 [ $R_{\text{int}} = 0.0221$ ]	
Completeness to $\vartheta = 25.242^\circ$	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	15037 / 18 / 667	
Goodness-of-fit on $F^2$	1.039	
Final $R$ indices [ $I > 2\sigma$ ]	$R_1 = 0.0186, wR_2 = 0.0446$	
$R$ indices (all data)	$R_1 = 0.0212, wR_2 = 0.0457$	
Largest diff. peak and hole	0.941 and $-0.581$ e/Å <sup>3</sup>	

**Notes:** This structure contains several badly disordered solvent molecules in the asymmetric unit, along with one disordered cation (out of two) leading to several high-level CheckCIF alerts. However, the anionic portions contain the chemical interesting aspects of this compound and are themselves well-ordered.

**Table S3.** Crystal data and structure refinement for **[Au(B<sub>2</sub>P<sub>2</sub>)(C<sub>7</sub>H<sub>6</sub>O)][K(18-c-6)]**.

Identification code	hh257JT128_0m
Empirical formula	C <sub>61</sub> H <sub>88</sub> AuB <sub>2</sub> KO <sub>7</sub> P <sub>2</sub>
Formula weight	1252.94 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions	$a = 11.3469(11)$ Å $\alpha = 103.9421(14)^\circ$ . $b = 13.0442(13)$ Å $\beta = 95.7811(14)^\circ$ . $c = 21.464(2)$ Å $\gamma = 101.0043(15)^\circ$ .
Volume	2990.5(5) Å <sup>3</sup>
Z	2
Density (calculated)	1.391 mg/m <sup>3</sup>
Absorption coefficient	2.633 mm <sup>-1</sup>
$F(000)$	1296
Crystal size	0.324 x 0.108 x 0.051 mm <sup>3</sup>
$\vartheta$ range for data collection	1.650 to 26.371°.
Index ranges	$-14 \leq h \leq 14$ , $-16 \leq k \leq 16$ , $-26 \leq l \leq 26$
Reflections collected	53298
Independent reflections	12231 [ $R_{\text{int}} = 0.0692$ ]
Completeness to $\vartheta = 25.242^\circ$	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	12231 / 1064 / 895
Goodness-of-fit on $F^2$	1.058
Final $R$ indices [ $I > 2\sigma_I$ ]	$R_1 = 0.0509$ , $wR_2 = 0.1149$
$R$ indices (all data)	$R_1 = 0.0715$ , $wR_2 = 0.1245$
Largest diff. peak and hole	2.593 and $-2.471$ e/Å <sup>3</sup>

**Notes:** The [(18-c-6)K]<sup>+</sup> cation and a molecule of n-hexane are disordered over two positions, giving rise to the observed CheckCIF alerts.

**Table S4.** Crystal data and structure refinement for  $[\text{Au}(\text{B}_2\text{P}_2)(\text{C}_{14}\text{H}_{12}\text{O}_2)][\text{K}(\text{18-c-6})(\text{THF})_2]$ .

Identification code	hh256JT127_0m	
Empirical formula	$\text{C}_{79.12}\text{H}_{112.34}\text{AuB}_2\text{KO}_{11.15}\text{P}_2$	
Formula weight	1561.53 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	$a = 14.6392(19)$ Å	$\alpha = 90^\circ$ .
	$b = 45.535(6)$ Å	$\beta = 96.0286(16)^\circ$ .
	$c = 23.842(3)$ Å	$\gamma = 90^\circ$ .
Volume	$15805(3)$ Å <sup>3</sup>	
Z	8	
Density (calculated)	1.312 mg/m <sup>3</sup>	
Absorption coefficient	2.011 mm <sup>-1</sup>	
$F(000)$	6514	
Crystal size	0.469 x 0.392 x 0.046 mm <sup>3</sup>	
$\vartheta$ range for data collection	1.593 to 25.350°.	
Index ranges	$-17 \leq h \leq 17, -54 \leq k \leq 54, -28 \leq l \leq 28$	
Reflections collected	211642	
Independent reflections	28913 [ $R_{\text{int}} = 0.0852$ ]	
Completeness to $\vartheta = 25.242^\circ$	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	28913 / 1966 / 2252	
Goodness-of-fit on $F^2$	1.041	
Final $R$ indices [ $I > 2\sigma_I$ ]	$R1 = 0.0609, wR2 = 0.1362$	
$R$ indices (all data)	$R1 = 0.0837, wR2 = 0.1472$	
Largest diff. peak and hole	3.450 and $-2.397$ e/Å <sup>3</sup>	

**Notes:** There is a disordered molecule of THF in the lattice responsible for the Level C CheckCIF alert.

## References

- [1] Schlosser, M.; Jenny, T.; Guggisberg, Y. *Synlett* **1990**, *11*, 704.
- [2] Burfield, D. R.; Smithers, R. H. *J. Org. Chem.*, **1978**, *43*, 3966–3968.
- [3] Shipsey, K.; Werner, E. A. *J. Chem. Soc., Trans.*, **1913**, *103*, 1255-1257.
- [4] Taylor, J. W.; McSkimming, A.; Moret, M.-E.; Harman, W. H. *Angew. Chem. Int. Ed.* **2017**, *56*, 10413-10417.
- [5] Led, J. J.; Gesmar, H., *Chem. Rev.* **1991**, *91*, 1413-1426.
- [6] *APEX 2*, version 2014.1-1, Bruker (2014), Bruker AXS Inc., Madison, Wisconsin, USA.
- [7] *SAINT*, version V8.34A, Bruker (2012), Bruker AXS Inc., Madison, Wisconsin, USA.
- [8] *SADABS*, version 2012/1, Bruker (2012), Bruker AXS Inc., Madison, Wisconsin, USA.
- [9] *SHELXTL*, version 2013/4, Bruker (2013), Bruker AXS Inc., Madison, Wisconsin, USA.