

# Gold(I) Triphenylphosphine Complexes Incorporating Pentaarylfulleride Ligands

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- Pages 1-2. Experimental section
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**General:** All reactions are performed under argon and in the absence of light. The freeze-pump-thaw method was used to remove traces of O<sub>2</sub>. The reactions were worked up quickly with minimal exposure to air as an excess *t*-BuOK in the solution tends to quickly decompose the product. THF was freshly distilled from Na benzophenone ketyl. Anhydrous grade CS<sub>2</sub> was used as purchased. Pentaarylhydro[60]fullerenes, C<sub>60</sub>Ar<sub>5</sub>H were prepared according to previous work.<sup>1</sup> Potassium *t*-butoxide and triphenylphosphine gold(I) chloride were purchased from Alfa Aesar and Strem and used as received. Silica gel (60 Å porosity, 200x400 mesh) was purchased from Sorbent Technologies.

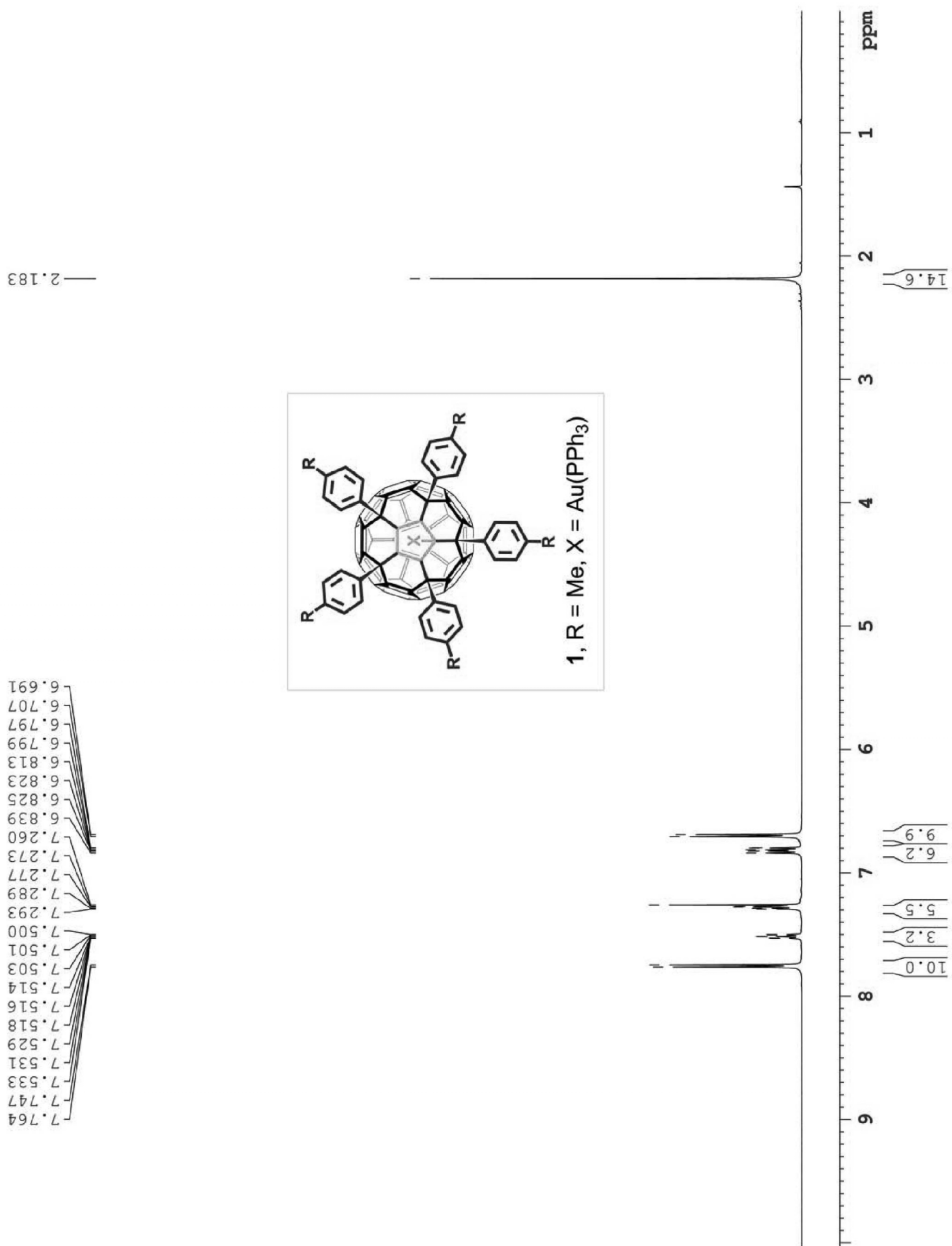
<sup>1</sup>H (500 MHz), <sup>13</sup>C (126 MHz), <sup>31</sup>P (203 MHz) NMR spectra were measured on a Bruker DRX500 spectrometer. <sup>1</sup>H NMR spectra are referenced to residual CHCl<sub>3</sub> in chloroform-*d* (δ 7.26 ppm). <sup>13</sup>C{<sup>1</sup>H} NMR spectra are referenced to the chloroform-*d* solvent signal (δ 77.00 ppm). <sup>31</sup>P NMR spectra were referenced externally to 85% H<sub>3</sub>PO<sub>4</sub>, δ 0.0 ppm. UV-Vis absorption spectra were measured with a Shimadzu UV-3101PC spectrometer. Low-resolution mass spectra were measured using an Applied Biosystems Voyager DE-STR MALDI-TOF. IR spectra were recorded on a Jasco FT/IR-420 spectrometer. Elemental analyses were carried out by Midwest MicroLab LLC, Indianapolis, Indiana 46250.

**(PPh<sub>3</sub>)Au[C<sub>60</sub>(4-Me(C<sub>6</sub>H<sub>4</sub>)<sub>5</sub>] (1):** A suspension of *t*-BuOK (14.0 mg, 0.13 mmol) in THF (4 mL) was added to a suspension of C<sub>60</sub>(4-tolyl)<sub>5</sub>H (75.0 mg, 0.064 mmol) in THF (4 mL). The mixture was stirred for 15 minutes, during which time it became a dark brown-black, homogenous solution. The solution was added to a solution of triphenylphosphine gold(I) chloride (41.0 mg, 0.083 mmol) in THF (2 mL) and the resulting solution was stirred for 60 min at 25 °C. The progress of the reaction was monitored by HPLC (Nakalai Tesque Buckyprep, 4.6x250 mm, toluene/2-propanol 7:3, ret: 4.5 min). After completion of the reaction, the solvent was removed under vacuum. The residue was redissolved in CS<sub>2</sub>, filtered through a Millex filter (0.45 μm porosity), and then chromatographed on a short silica gel column using a solvent gradient, beginning with neat CS<sub>2</sub> and ending with 8% v/v of CH<sub>2</sub>Cl<sub>2</sub> in CS<sub>2</sub>. The red band was collected to afford a crystalline reddish brown powder of pure **1** (70% yield). <sup>1</sup>H NMR (500 MHz, CS<sub>2</sub>/CDCl<sub>3</sub> 1:1) δ (ppm): 2.18 (s, 15H, *Me*), 6.70 (d, *J* = 8.1 Hz, 10H, *m*-C<sub>6</sub>H<sub>4</sub>),<sup>2</sup> 6.82 (ddd, *J* = 12.8 Hz, 7.7 Hz, 1.1 Hz, 6H, *o*-Ph), 7.28 (td, *J* = 8.0 Hz, 2.2 Hz, 6H, *m*-Ph), 7.52 (tdt, *J* = 7.5 Hz, 2.1 Hz, 1.2 Hz, 3H, *p*-Ph), 7.76 (d, *J* = 8.1 Hz, 10H, *o*-C<sub>6</sub>H<sub>4</sub>);<sup>2</sup> <sup>13</sup>C NMR (126 MHz, CS<sub>2</sub>/CDCl<sub>3</sub> 1:1) δ (ppm): 20.97, 60.00, 128.42, 128.66, 128.70 (d, <sup>3</sup>*J*<sub>C-P</sub> = 9.6 Hz,<sup>3</sup> *m*-Ph), 128.96 (d, <sup>2</sup>*J*<sub>C-P</sub> = 5.5 Hz, C<sub>60</sub>(Cp)), 129.75 (d, <sup>1</sup>*J*<sub>C-P</sub> = 55.4 Hz, *ipso*-Ph), 130.76 (d, <sup>4</sup>*J*<sub>C-P</sub> = 2.3

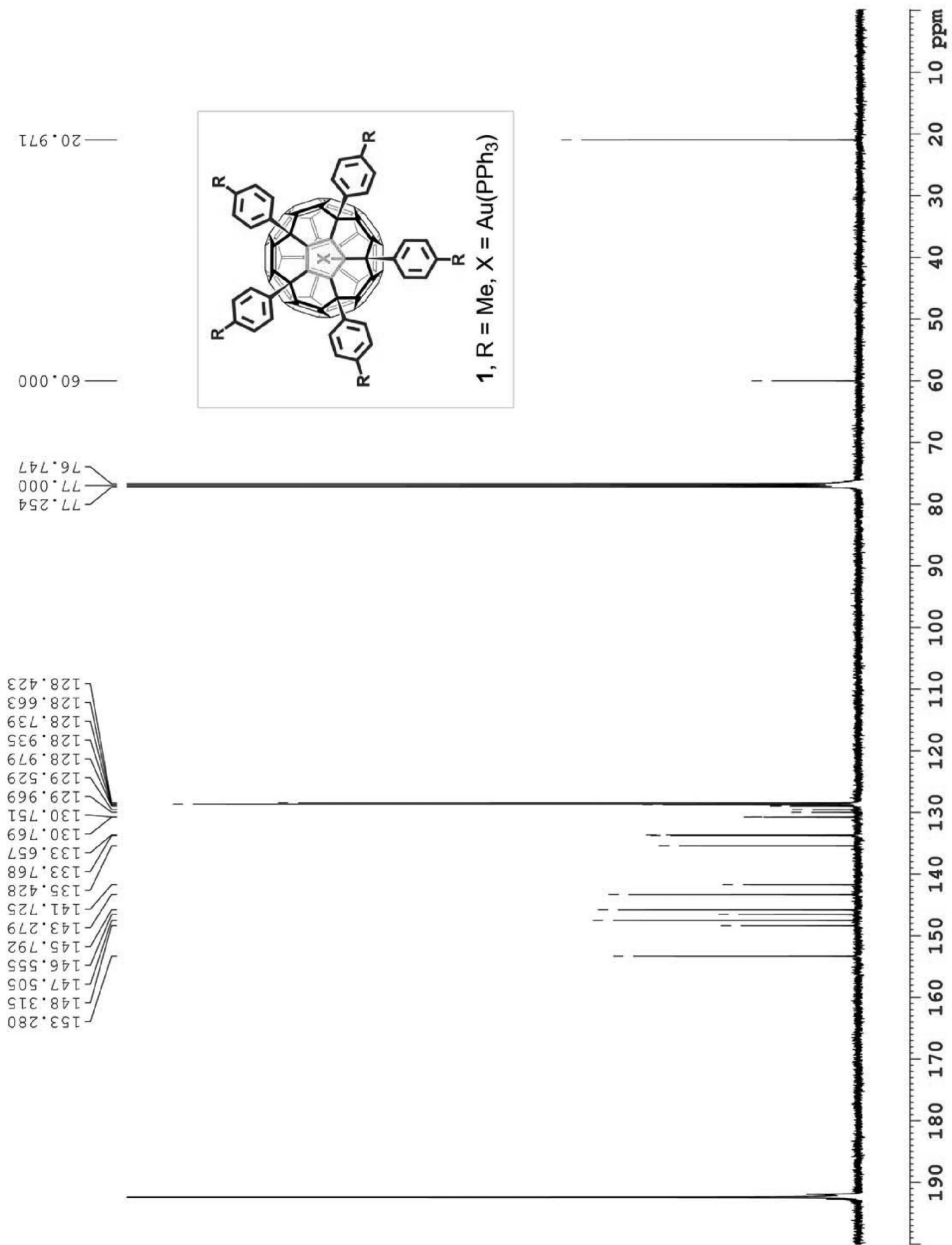
Hz, *p*-Ph), 133.72 (d,  $^2J_{C-P}$  = 13.9 Hz, *o*-Ph), 133.43, 141.73, 143.28, 145.79, 146.55, 147.51, 148.32, 153.28;  $^{31}\text{P}$  NMR  $\{^1\text{H}\}$  (203 MHz,  $\text{CS}_2/\text{CDCl}_3$  1:1)  $\delta$  (ppm): 31.83; FTIR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3078(w), 3051(w), 3026(w), 2956(s), 2900(w), 2864(m), 1608(w), 1571(w), 1508(m), 1477(w), 1458(m), 1437(m), 1394(w), 1362(m), 1267(m), 1234(w), 1120(w), 1103(m), 1018(m), 960(w), 895(w), 818(m), 771(w), 746(m), 692(m), 636(w), 588(m), 565(m), 536(s), 503(m); UV-Vis ( $\text{CHCl}_3$ )  $\lambda$  (nm) 358 ( $\epsilon$  = 49,240) 399 (22,710); Anal. Calcd for  $\text{C}_{113}\text{H}_{50}\text{PAu}$ : C, 82.98; H, 3.08; P, 1.89; Found C, 81.14; H, 3.05; P, 2.00; MALDI-TOF-MS (+) anthracene matrix,  $m/z$  1634.1 [ $\text{M}^+$ ], calcd for  $\text{C}_{113}\text{H}_{50}\text{PAu}$ : 1634.3.

**(PPh<sub>3</sub>)Au[C<sub>60</sub>(4-*t*-Bu(C<sub>6</sub>H<sub>4</sub>)<sub>5</sub>] (2):** To a solution of triphenylphosphine gold(I) chloride (35.0 mg, 0.070 mmol) in THF (2 mL) was added a solution of C<sub>60</sub>(4-*t*-butylphenyl)<sub>5</sub> anion prepared from C<sub>60</sub>(4-*t*-butylphenyl)<sub>5</sub>H (75.0 mg, 0.054 mmol) and *t*-BuOK (8.0 mg, 0.071 mmol) in THF (5 mL) at 25 °C. The solution was stirred for 90 min at 25 °C. The progress of the reaction was monitored by HPLC (Nakalai Tesque Buckyprep, 4.6x250 mm, toluene/2-propanol 7:3, ret: 4.1 min). After completion of the reaction, the solvent was removed under vacuum. The residue was redissolved in  $\text{CS}_2$ , filtered through a Millex filter (0.45  $\mu\text{m}$  porosity), and then chromatographed on a short silica gel column using a solvent gradient, beginning with neat  $\text{CS}_2$  and ending with 8% v/v of  $\text{CH}_2\text{Cl}_2$  in  $\text{CS}_2$ . The red band was collected to afford **2** as a crystalline red powder (95% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CS}_2/\text{CDCl}_3$  1:1)  $\delta$  (ppm): 1.13 (s, 45H,  $\text{CMe}_3$ ), 6.89 (d,  $J$  = 8.3 Hz, 6H, *o*-Ph), 6.91 (d,  $J$  = 8.3 Hz, 10H, *m*-C<sub>6</sub>H<sub>4</sub>), 7.29 (td,  $J$  = 7.7 Hz, 2.1 Hz, 6H, *m*-Ph), 7.48 (td,  $J$  = 7.4 Hz, 0.9 Hz, 3H, *p*-Ph), 7.81 (d,  $J$  = 8.3 Hz, 10H, *o*-C<sub>6</sub>H<sub>4</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CS}_2/\text{CDCl}_3$  1:1)  $\delta$  (ppm): 31.09, 33.86, 59.90, 124.84, 128.10, 128.81(d,  $^3J_{C-P}$  = 11.5 Hz, *m*-Ph), 128.88 (d,  $^2J_{C-P}$  = 6.2 Hz, C<sub>60</sub>(Cp)), 129.77 (d,  $^1J_{C-P}$  = 55.0 Hz, *ipso*-Ph), 130.74 (s, *p*-Ph), 133.90 (d,  $^2J_{C-P}$  = 14.0 Hz, *o*-Ph), 143.24, 145.75, 146.53, 147.48, 148.26, 148.50, 153.24;  $^{31}\text{P}\{^1\text{H}\}$  NMR (203 MHz,  $\text{CS}_2/\text{CDCl}_3$  1:1)  $\delta$  (ppm): 31.76; FTIR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3053 (w), 3018 (w), 2916 (w), 2860 (w), 1610(w), 1572 (w), 1508(s), 1456(w), 1435(w), 1377(w), 1279 (w), 1184(m), 1099(m), 1020(w), 958(w), 893(w), 837(w), 806(m), 752(s), 692(m), 648(w), 617(w), 582(w), 561(w), 536(s), 501(m); UV-Vis ( $\text{CHCl}_3$ )  $\lambda$  (nm) 355 ( $\epsilon$  = 28,450) 400 (12,320); Anal. Calcd for  $\text{C}_{128}\text{H}_{80}\text{PAu}$ : C, 83.28; H, 4.37; P, 1.68; Found C, 83.09; H, 4.32; P, 1.81; MALDI-TOF-MS (+) anthracene matrix,  $m/z$  1844.0 [ $\text{M}^+$ ], calcd for  $\text{C}_{128}\text{H}_{80}\text{PAu}$ : 1844.6.

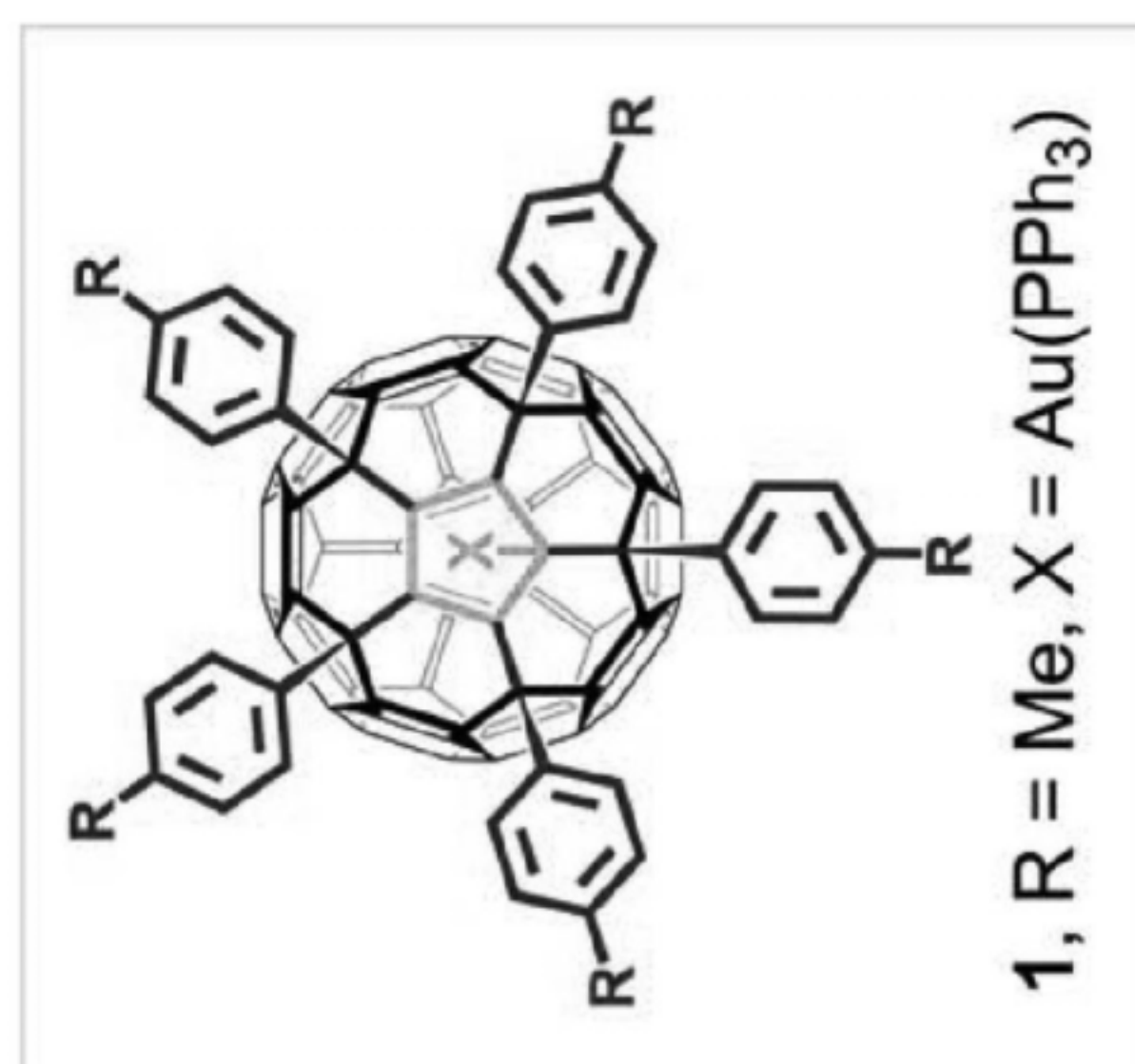
# <sup>1</sup>H NMR Spectrum for compound 1:



<sup>13</sup>C NMR Spectrum for compound 1:



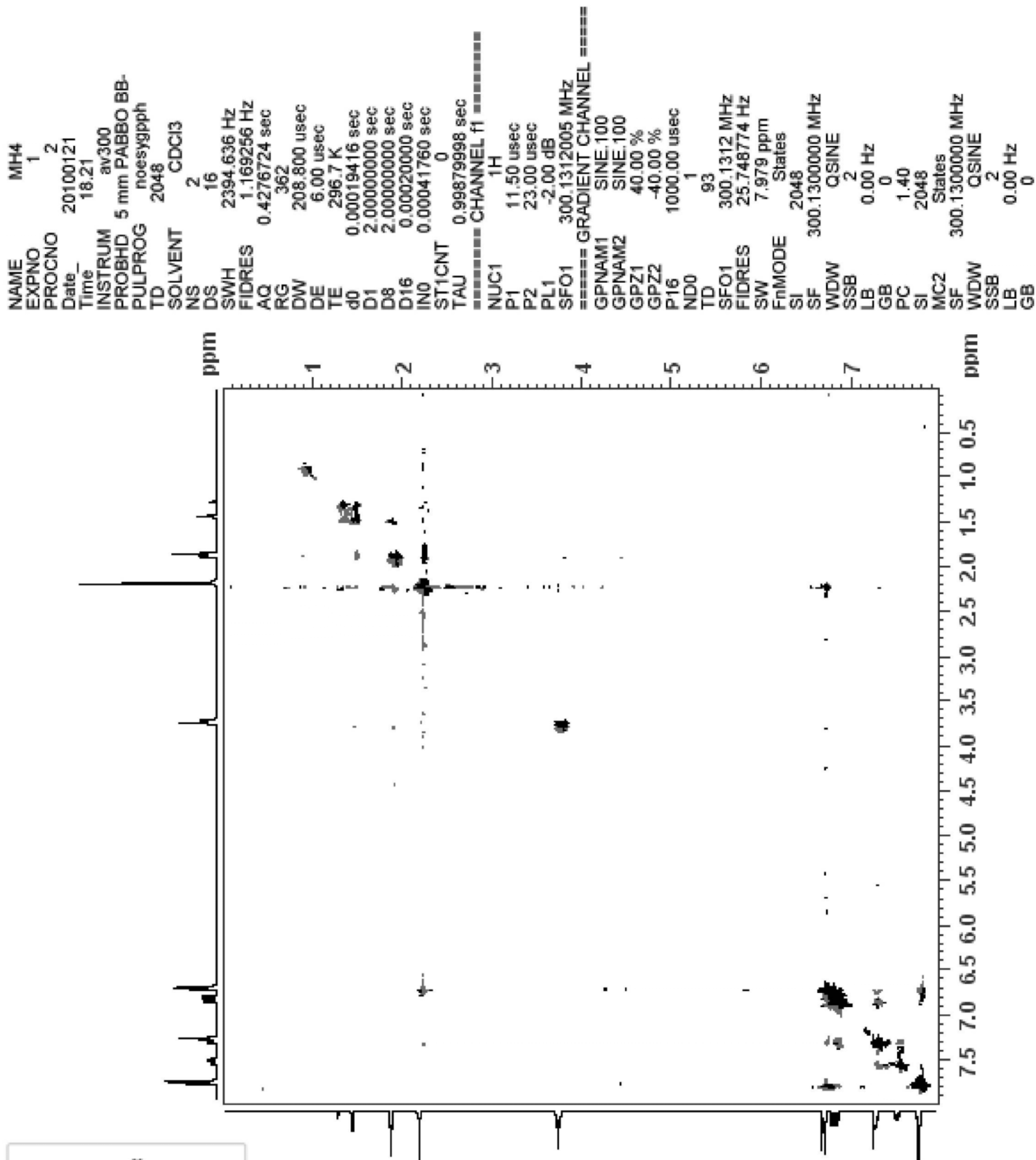
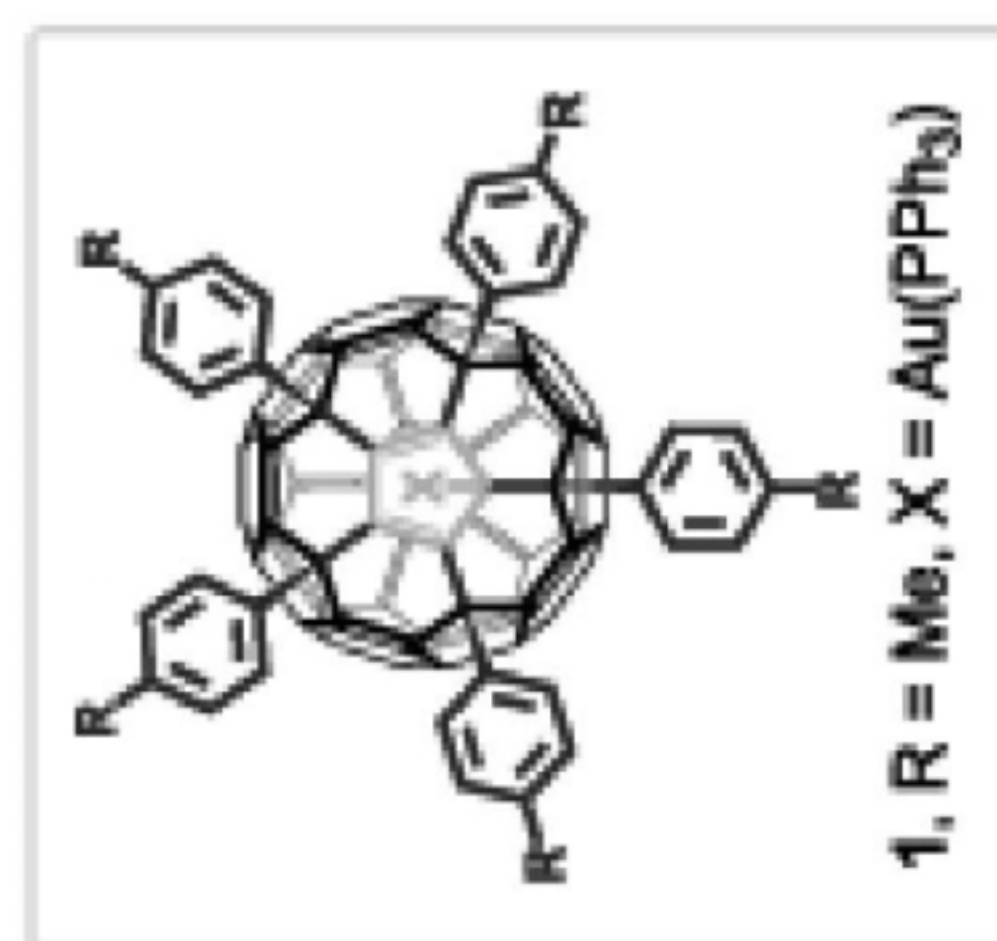
**$^{31}\text{P}$  NMR Spectrum for compound 1:**



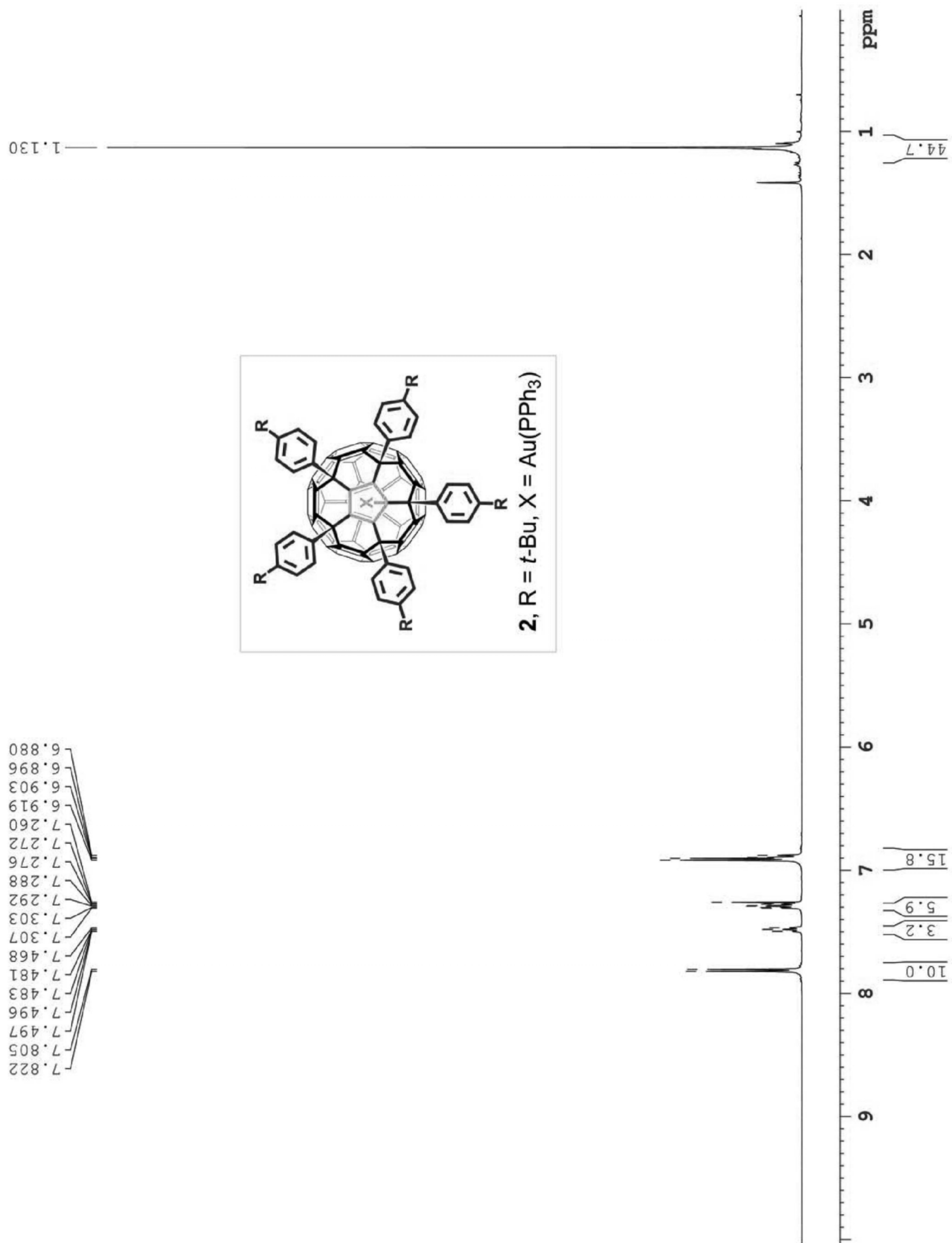
— 31.834

200 150 100 50 0 -50 -100 -150 -200 ppm

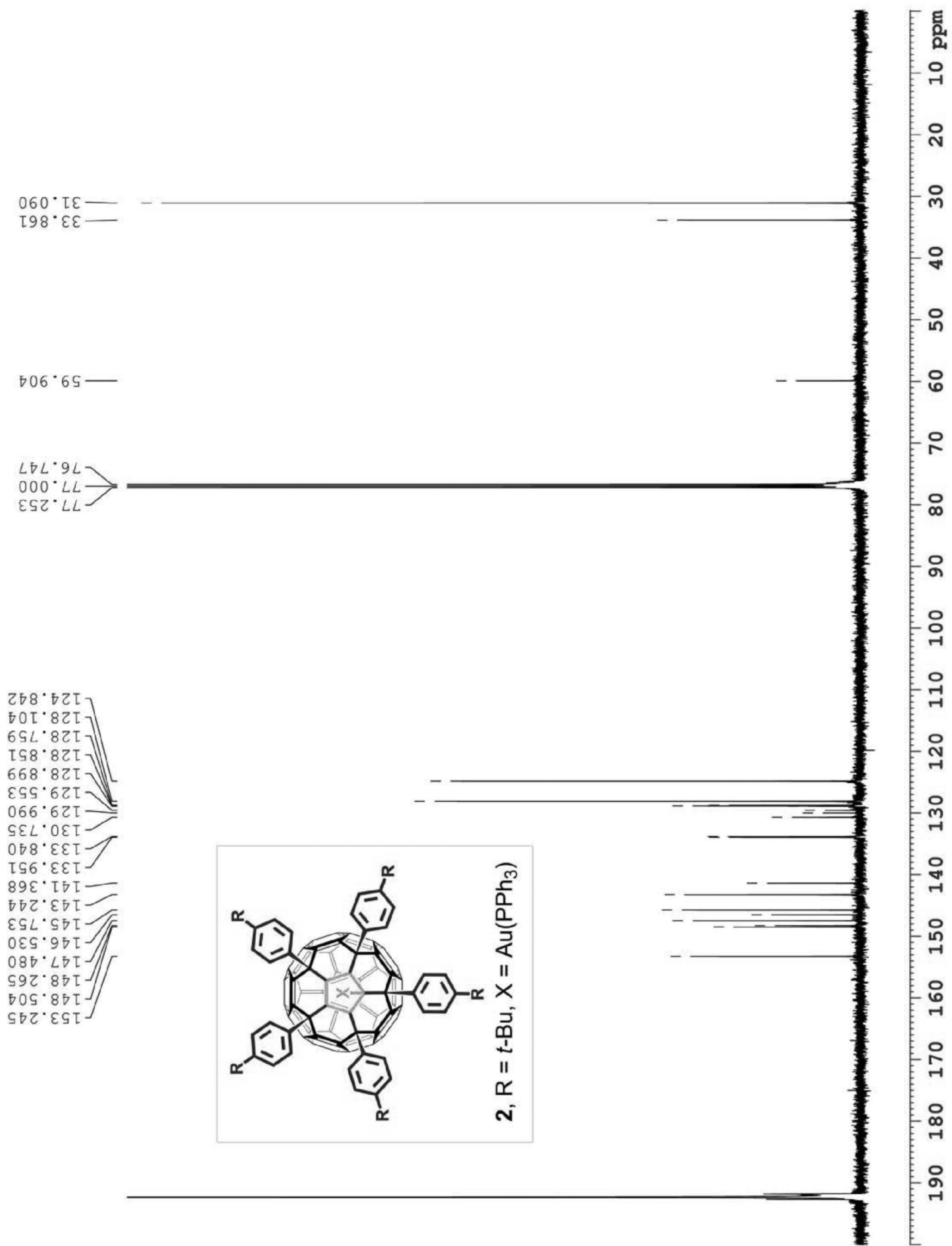
2D NOESY Spectrum for compound 1:



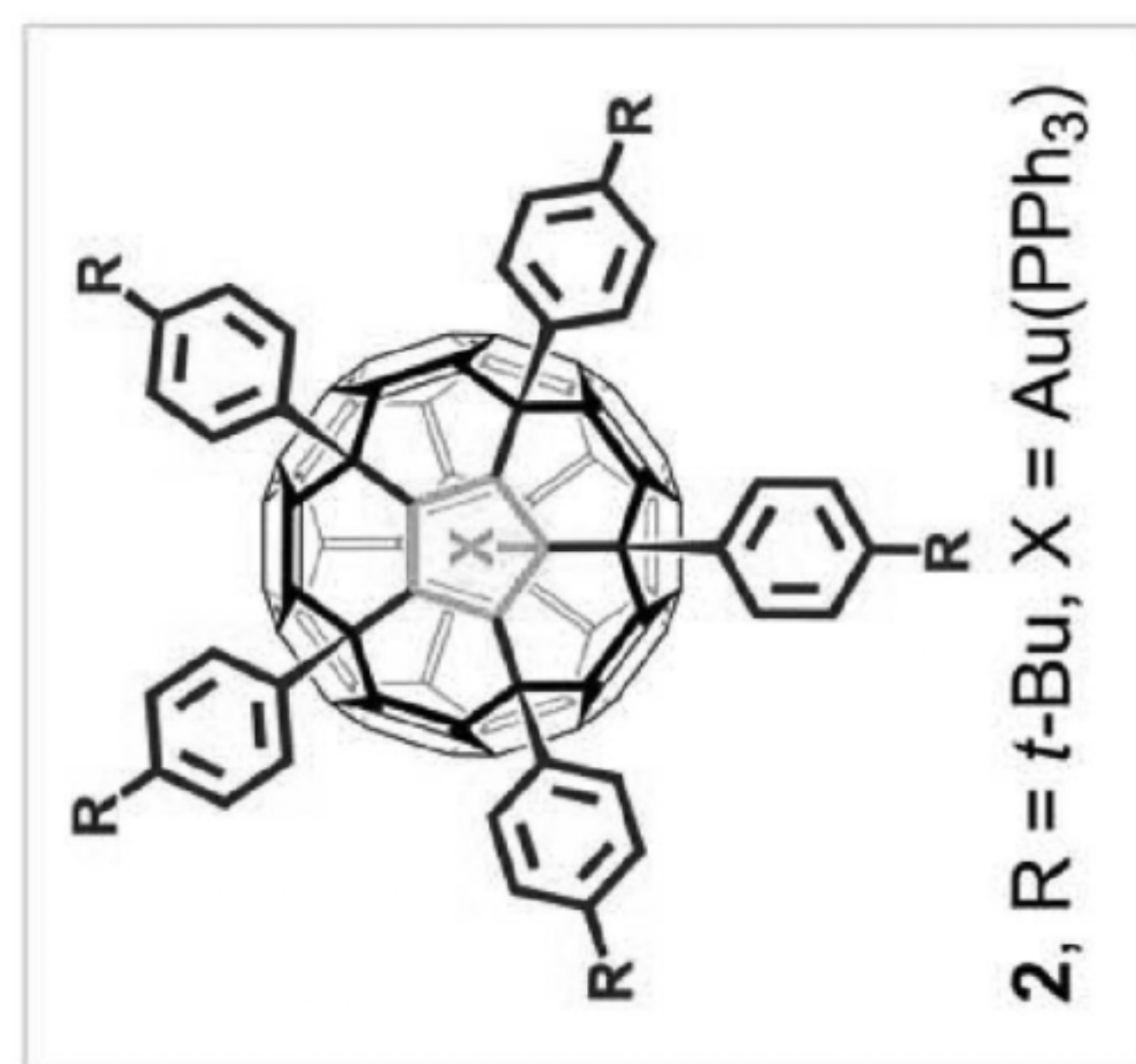
<sup>1</sup>H NMR Spectrum for compound 2:



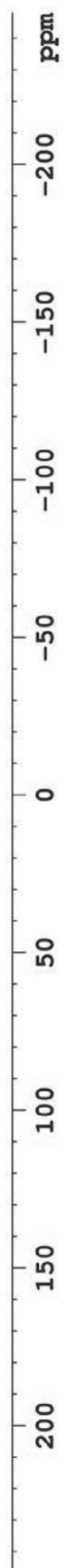
<sup>13</sup>C NMR Spectrum for compound 2:



**$^{31}\text{P}$  NMR Spectrum for compound 2:**



— 31.757



## Crystallography

The X-ray intensity data were measured at 100K on a Bruker SMART APEX2 CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ( $\lambda = 0.71073 \text{ \AA}$ ) operated at 2250 watts power. The detector was placed at a distance of 6.000 cm from the crystal. A total of 1800 frames were collected with a scan width of  $0.3^\circ$  in  $\omega$ , with an exposure time ranging from 30 to 90 sec/frame. The data frames were collected using the program APEX2 and processed using the program SAINT routine within APEX2.<sup>4</sup> Data were corrected for absorption based on the multi-scan technique as implemented in SADABS. Structure solution and refinement were performed using Bruker SHELXTL (Version 6.12) Software Package. Mercury CSD 2.2 (Build RC5) and Diamond (Version 2.1c) were used to visualize the crystal structures.

**Table S1.** Crystal data and refinement information.

	<b>1·(ODCB)<sub>2</sub></b>	<b>1·(CHCl<sub>3</sub>)<sub>2</sub>(CS<sub>2</sub>)</b>	<b>2·(CHCl<sub>3</sub>)<sub>3</sub></b>
chemical formula	C <sub>125</sub> H <sub>58</sub> AuCl <sub>4</sub> P	C <sub>116</sub> H <sub>52</sub> AuCl <sub>6</sub> PS <sub>2</sub>	C <sub>131</sub> H <sub>83</sub> AuCl <sub>9</sub> P
formula weight	1929.45	1950.33	2203.96
crystal description	red platelet	red block	red needle
crystal size (mm)	0.13 × 0.07 × 0.04	0.40 × 0.30 × 0.15	0.10 × 0.05 × 0.02
crystal system	triclinic	monoclinic	triclinic
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	15.9259(14)	37.699(6)	15.1223(16)
<i>b</i> (Å)	16.3684(14)	20.948(4)	15.9245(17)
<i>c</i> (Å)	18.8575(16)	20.166(3)	23.844(3)
$\alpha$ (°)	89.7740(10)	90.00	88.4870(10)
$\beta$ (°)	69.3100(10)	97.111(2)	86.7880(10)
$\gamma$ (°)	63.8850(10)	90.00	72.517(2)
<i>V</i> (Å <sup>3</sup> )	4061.5(6)	15803(5)	5467.9(11)
<i>Z</i>	2	8	2
<i>T</i> (K)	100(2)	100(2)	100(2)
radiation	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$
$\lambda$ (Å)	0.71073	0.71073	0.71073
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.578	1.640	1.339
$\mu$ (cm <sup>-1</sup> )	2.024	2.198	1.630
F(000)	1940	7808	2232
$\theta_{\min}$ , $\theta_{\max}$ (°)	3.67, 28.34	3.80, 29.12	3.64, 28.02
reflections collected	51229	103204	66872
unique reflections	19762	21137	25781
<i>R</i> <sub>int</sub>	0.0984	0.0497	0.1013
observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	12821	17161	16015
paramaters/restraints	1173/0	1160/36	1299/106
<i>R</i> <sub>1</sub> (on <i>F</i> <sub>o</sub> , obs. data)	0.0616	0.0464	0.0859
<i>wR</i> <sub>2</sub> (on <i>F</i> <sub>o</sub> <sup>2</sup> , all data)	0.1316	0.1228	0.2422
GOF	0.989	1.101	1.000
$\Delta$ (e Å <sup>-3</sup> )	-1.401, 1.583	-2.759, 2.731	-2.020, 2.412

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**References:**

- <sup>1</sup> Kennedy, R. D.; Ayzner, A. L.; Wanger, D. D.; Day, C. T.; Halim, M.; Khan, S.I.; Tolbert, S.; Schwartz, B.; Rubin, Y. *J. Am. Chem. Soc.* **2008**, *130*, 17290.
- <sup>2</sup> These assignments were determined from a 2D NOESY experiment., see spectrum on page 6.
- <sup>3</sup> For C-P coupling constants in similar complexes, see: Kang, J. G.; Cho, H. K.; Park, C.; Yun, S. S.; Kim, J. K.; Broker, G. A.; Smyth, D. R.; Tiekink, E. R. *Inorg. Chem.*, **2007**, *46*, 8228.
- <sup>4</sup> APEX2 v2.2-0 and SAINT v7.34A data collection and data processing programs, respectively. Bruker Analytical X-ray Instruments, Inc., Madison, WI; SADABS v2008/1 semi-empirical absorption correction program. G.M. Sheldrick, University of Göttingen, Germany.