

Supporting Information for

**Synthesis of luminescent coumarin-substituted phosphinoamide-bridged polynuclear gold(I) metallacycles and reactivity studies**

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## I. Synthesis and characterization

### I.1 General procedures

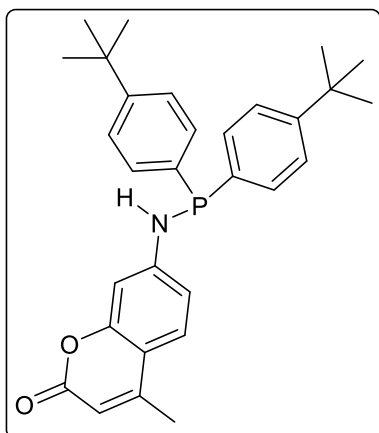
All air- and moisture-sensitive manipulations were performed under dry N<sub>2</sub> or Ar atmosphere using standard Schlenk techniques or in an argon-filled MBraun glovebox, unless otherwise stated. All solvents (Et<sub>2</sub>O and *n*-pentane) were dried using an MBraun solvent purification system (SPS-800) and degassed. THF and DCM were distilled under nitrogen from potassium benzophenone ketyl and P<sub>2</sub>O<sub>5</sub>, respectively. THF-*d*<sub>8</sub> was dried over Na-K alloy. CD<sub>2</sub>Cl<sub>2</sub> and CDCl<sub>3</sub> were dried over CaH<sub>2</sub>. The deuterated solvents were degassed by freeze-pump-thaw cycles. Bis(3,5-(di-*tert*-butyl)phenyl)chlorophosphine, and bis(4-(*tert*-butyl)phenyl)chlorophosphine were synthesized according to literature procedure.<sup>1</sup> [Au(tht)Cl] was synthesized by following the reported procedure.<sup>2</sup> All other chemicals were obtained from commercial sources and used without further purification.

Elemental analyses were carried out with an Elementar vario MICRO cube.

NMR spectra were recorded on Bruker spectrometers (Avance Neo 300 MHz, Avance Neo 400 MHz or Avance III 400 MHz). Chemical shifts are referenced internally using signals of the residual protio solvent (<sup>1</sup>H) or the solvent (<sup>13</sup>C{<sup>1</sup>H}) and are reported relative to tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}), H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). All NMR spectra were measured at 298 K, unless otherwise specified. The multiplicity of the signals is indicated as s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet and br = broad. Assignments were determined based on unambiguous chemical shifts, coupling patterns and <sup>13</sup>C-DEPT experiments.

Infrared (IR) spectra were recorded in the region 4000–400 cm<sup>-1</sup> on a Bruker Tensor 37 FTIR spectrometer equipped with a room temperature DLaTGS detector, a diamond attenuated total reflection (ATR) unit and a nitrogen-flushed chamber. In terms of their intensity, the signals were classified into different categories (vs = very strong, s = strong, m = medium, w = weak, and sh = shoulder).

### Synthesis of ligand 1:



7-amino-4-methylcoumarin (5.1 mmol, 900 mg) was dissolved in THF and triethylamine (5.1 mmol, 0.7 mL). It was followed by drop-wise addition of bis(4-(*tert*-butyl)phenyl)chlorophosphine (5.1 mmol, 1.7 g) dissolved in 20 mL of THF at -78 °C. The reaction mixture was stirred at room temperature for 2 days. The resulting colorless precipitate of HNEt<sub>3</sub>Cl was filtered off. The volume of the reaction mixture was reduced to one-third and an equal volume of *n*-pentane was added. On storing the mixture at -30 °C,

colorless solid was formed. The solid was washed with *n*-pentane thrice, dried under reduced pressure and characterized.

### Analytical data for 1:

Yield: 2.1 g (89 %), EA: Anal. Calcd for C<sub>30</sub>H<sub>34</sub>NO<sub>2</sub>P (471.58 g/mol): C, 76.41; H, 7.27; N, 2.97. Found: C, 76.90; H, 7.44; N, 3.47.

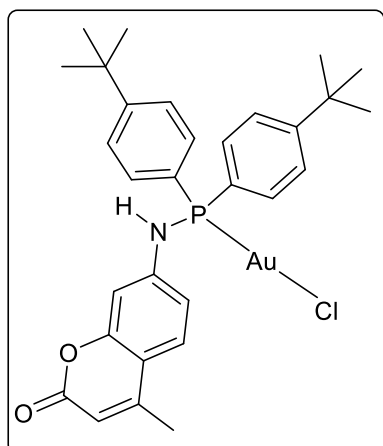
<sup>1</sup>H NMR (400 MHz, THF-d<sub>8</sub>):  $\delta$ (ppm) = 7.46 – 7.36 (m, 9H, Ph-*H*, Coum-*CH*), 7.06 (dd,  $J$  = 8.6, 2.4 Hz, 1H, Coum-*CH*), 6.93 (d,  $J$  = 2.2 Hz, 1H, Coum-*CH*), 6.67 (d,  $J$  = 8.6 Hz, 1H, Coum-*CH*), 5.91 (d,  $J$  = 1.2 Hz, 1H, N-*H*), 2.31 (d,  $J$  = 1.2 Hz, 3H, Coum-*CH*<sub>3</sub>), 1.31 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>).

<sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, 298 K, THF-d<sub>8</sub>):  $\delta$ (ppm) = 24.4 (s).

<sup>13</sup>C NMR (101 MHz, 298 K, THF-d<sub>8</sub>):  $\delta$ (ppm) = 160.6 (Coum-*C*), 156.7 (Coum-*C*), 153.0 (Ph-*C*), 152.8 (Coum-*C*), 137.3 (Coum-*C*), 137.2 (Coum-*C*), 132.3 (Ph-*C*), 132.0 (Ph-*CH*), 126.4 (Ph-*CH*), 113.1 (Coum-*CH*), 112.7 (Coum-*CH*), 111.1 (Coum-*CH*), 103.1 (Coum-*CH*), 35.5 (C(CH<sub>3</sub>)<sub>3</sub>), 31.5 (C(CH<sub>3</sub>)<sub>3</sub>), 18.3 (Coum-*CH*<sub>3</sub>).

IR (ATR):  $\tilde{\nu}$  (cm<sup>-1</sup>) = 3223 (br), 3083 (w), 3025 (w), 2957 (s), 2904 (m), 2866 (m), 2383 (w), 1694 (vs), 1606 (vs), 1561 (sh), 1498 (m), 1466 (m), 1388 (s), 1367 (m), 1300 (s), 1268 (m), 1226 (w), 1204 (m), 1150 (m), 1129 (m), 1091 (s), 1070 (m), 1017 (m), 995 (m), 934 (w), 912 (w), 864 (m), 831 (m), 798 (m), 750 (m), 719 (w), 685 (w), 640 (w), 598 (m), 561 (m), 544 (m), 521 (m), 470 (m), 446 (m).

## Synthesis of gold complex 2:



To a Schlenk flask containing ligand **1** (166 mg, 0.35 mmol, 1.0 eq) and [Au(tht)Cl] (113 mg, 0.35 mmol, 1.0 eq) 15 mL of DCM were added and stirred for an hour at rt. The volatiles were removed and the obtained solid was washed with *n*-pentane and was purified by crystallization. Single crystals for X-ray diffraction analysis were grown by slow evaporation of a toluene solution of complex **2**.

### Analytical data for 2:

Yield: 215 mg (87 %), EA: Anal. Calcd for C<sub>30</sub>H<sub>34</sub>NO<sub>2</sub>PAuCl (704.00 g/mol): C, 51.18; H, 4.87; N, 1.99. Found: C, 51.45; H, 4.95; N, 1.91.

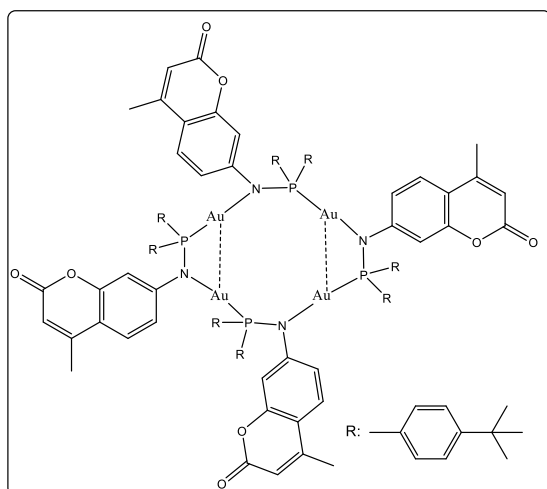
**<sup>1</sup>H NMR** (400 MHz, 298 K, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.75-7.65 (m, 4H, CH<sub>Ph</sub>), 7.52 (m, 4H, CH<sub>Ph</sub>), 7.44 (d, *J* = 8.6 Hz, 1H, Coum-CH), 7.02 (d, *J* = 8.6 Hz, 1H, Coum-CH), 6.86 (s, 1H, Coum-CH), 6.09 (s, 1H, Coum-CH), 5.24 (br, s, 1H, NH), 2.35 (s, 3H, Coum-CH<sub>3</sub>), 1.33 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (162 MHz, 298 K, CDCl<sub>3</sub>):  $\delta$  (ppm) = 57.2 (s).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, 298 K, CDCl<sub>3</sub>):  $\delta$  (ppm) = 161.2 (Coum-CO), 157.0 (Coum-C), 154.7 (Ph-C), 152.6 (Coum-C), 145.7 (Coum-C), 132.8 (Ph-CH), 132.6 (Coum-C), 126.8 (Ph-CH), 126.7 (Coum-CH), 126.1 (Ph-C), 113.9 (Coum-CH), 112.5 (Coum-CH), 105.2 (Coum-CH), 35.3 (C(CH<sub>3</sub>)<sub>3</sub>), 31.2 (C(CH<sub>3</sub>)<sub>3</sub>), 18.7 (Coum-CH<sub>3</sub>).

**IR (ATR):**  $\tilde{\nu}$  (cm<sup>-1</sup>) = 3223 (br, m), 3083 (w), 3025 (w), 2957 (s), 2904 (w), 2866 (w), 2383 (w), 1694 (vs), 1606 (vs), 1561 (m), 1498 (m), 1466 (m), 1388 (s), 1367 (m), 1300 (s), 1268 (m), 1226 (w), 1204 (m), 1150 (m), 1129 (m), 1091 (m), 1070 (m), 1017 (w), 995 (m), 934 (w), 912 (w), 864 (m), 831 (m), 798 (m), 750 (m), 719 (w), 685 (w), 640 (w), 598 (m), 561 (m), 544 (m), 521 (m), 470 (m), 446 (m).

### Synthesis of gold complex 3:



Complex **2** (132.2 mg, 0.19 mmol, 1.0 eq) was dissolved in 15 mL of DCM to which KO<sup>t</sup>Bu (42.8 mg, 0.37 mmol, 2.0 eq) was added in excess and the reaction mixture was stirred for 4 h. The volatiles were evaporated and the redissolved in DCM. The crude product was filtered and the volatiles were removed under reduced pressure. The crude product was dissolved in toluene and concentrated to obtain single crystals at room temperature.

### Analytical data for 3:

Yield: 60 mg, 48 % EA: Anal. Calcd for C<sub>120</sub>H<sub>132</sub>N<sub>4</sub>O<sub>8</sub>P<sub>4</sub>Au<sub>4</sub> (2670.16 g/mol): C, 53.98; H, 4.98; N, 2.10. Found: C, 53.93; H, 5.27; N, 1.46.

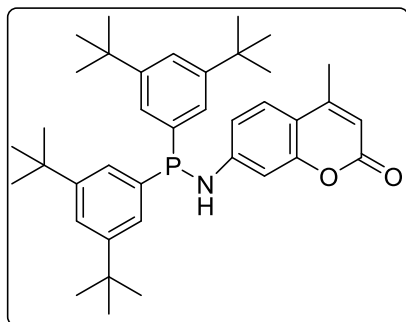
<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm) = 7.86-7.62 (m, 20H, CH<sub>Ph</sub>), 7.56-7.39 (m, 12H, CH<sub>Ph</sub>), 7.34-7.24 (m, 4H, Coum-CH), 6.99 (dd, *J* = 11.9, 8.4 Hz, 4H, Coum-CH), 6.84 (s, 4H, Coum-CH), 6.01 (s, 2H, Coum-CH), 5.83 (s, 2H, Coum-CH), 2.34 (s, 12H, Coum-CH<sub>3</sub>), 1.44 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.33 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.24 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0.77 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>).

<sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm) = 54.9 (s) and 60.8 (s).

<sup>13</sup>C{<sup>1</sup>H} NMR: Due to low solubility, clear signals in the aromatic region could not be recorded.

IR (ATR):  $\tilde{\nu}$  (cm<sup>-1</sup>) = 2959 (m), 2904 (w), 2867 (w), 1730 (sh), 1716 (s), 1598 (vs), 1496 (w), 1465 (w), 1389 (s), 1365 (m), 1325 (w), 1283 (sh), 1264 (s), 1197 (m), 1146 (s), 1086 (s), 1067 (s), 1008 (sh), 994 (m), 923 (m), 868 (m), 824 (s), 799 (s), 745 (m), 731 (m), 640 (w), 596 (vs), 559 (vs), 521 (s), 482 (m), 459 (m), 436 (m).

#### Synthesis of ligand 4:



7-Amino-4-methylcoumarin (800 mg, 1 eq) was dissolved in THF and triethylamine (0.6 mL, 1 eq). It was followed by dropwise addition of bis(3,5-(di-tert-butyl)phenyl)chlorophosphine (2.0 g, 1 eq) dissolved in 20 mL of THF at -78 °C. The reaction mixture was stirred at room temperature for 2 days. The volatiles were evaporated under reduced pressure. The crude product was

redissolved in 30 mL THF and the resulting colorless precipitate of HNEt<sub>3</sub>Cl was filtered off over a pad of celite. The volume of the reaction mixture was reduced to one-third and an equal volume of *n*-pentane was added. On storing the mixture at -30 °C, colorless solid was formed. The solid was washed with *n*-pentane thrice and dried under reduced pressure. To purify the product, the solid was dissolved in hot toluene and filtered through a canula filter. The product was obtained as a colorless solid.

#### Analytical data for 4:

Yield: 1.1 g (42.2 %). Anal. Calcd. for C<sub>38</sub>H<sub>50</sub>NO<sub>2</sub>P (583.8 g/mol): EA: C, 78.18; H, 8.63; N, 2.40; Found: C, 78.26; H, 8.41; N, 2.72.

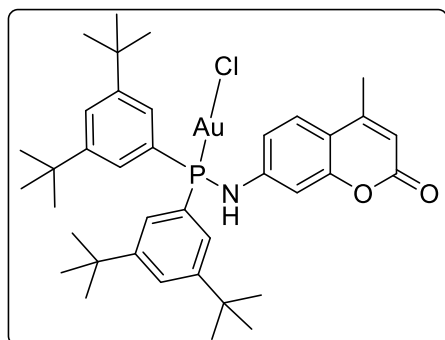
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.45 (s, 2H, Ph-CH), 7.40 (d, *J* = 8.6 Hz, 1H, Coum-CH), 7.26 (dd, *J* = 8.3, 1.8 Hz, 4H, Ph-CH), 7.03 (d, *J* = 8.7 Hz, 1H, Coum-CH), 6.97 (s, 1H, Coum-CH), 6.03 (s, 1H, Coum-CH), 4.89 (d, *J* = 7.1 Hz, 1H, NH), 2.35 (s, 3H, Coum-CH<sub>3</sub>), 1.28 (s, 36H, C(CH<sub>3</sub>)<sub>3</sub>).

<sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>): δ (ppm) = 32.7(s).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 161.9 (Coum-CO), 155.5 (Coum-C), 152.9 (Ph-C), 151.4 (Coum-C), 151.2 (Coum-C), 137.7 (Ph-C), 125.7 (Ph-CH), 125.6 (Coum-CH), 123.8 (Ph-CH), 113.0 (Coum-CH), 112.5 (Coum-C), 110.7 (Coum-CH), 102.9 (Coum-CH), 35.1 (C(CH<sub>3</sub>)<sub>3</sub>), 31.5 (C(CH<sub>3</sub>)<sub>3</sub>), 18.7 (Coum-CH<sub>3</sub>).

IR (ATR):  $\tilde{\nu}$  (cm<sup>-1</sup>) = 3439 (w), 3356 (w), 3310 (m), 3247 (w), 3073 (br), 2953 (s), 2903 (sh), 2866 (sh), 1696 (vs), 1610 (vs), 1557 (sh), 1502 (w), 1469 (w), 1420 (sh), 1390 (m), 1363 (w), 1320 (sh), 1302 (w), 1248 (w), 1203 (w), 1158 (sh), 1139 (w), 1068 (w), 1031 (w), 1014 (w), 988 (w), 898 (w), 870 (w), 841 (w), 781 (w), 709 (w), 684 (w), 647 (w), 605 (w), 575 (w), 544 (w), 528 (w), 468 (w), 443 (w), 420 (w).

### Synthesis of gold complex 5:



To a Schlenk flask containing ligand **4** (100 mg, 1 eq) and [Au(tht)Cl] (54.9 mg, 1 eq), 5 mL of THF were added and stirred for an hour at room temperature. The volatiles were removed and the obtained solid was washed with *n*-pentane and purified by crystallization. Single crystals were grown by layering a THF solution with *n*-pentane.

### Analytical data for 5:

Yield: 111 mg (79 %). Anal. Calcd. for C<sub>38</sub>H<sub>50</sub>AuClNO<sub>2</sub>P (816.21 g/mol): EA: C, 55.92; H, 6.17; N, 1.72; Found: C, 56.35; H, 6.34; N, 1.79.

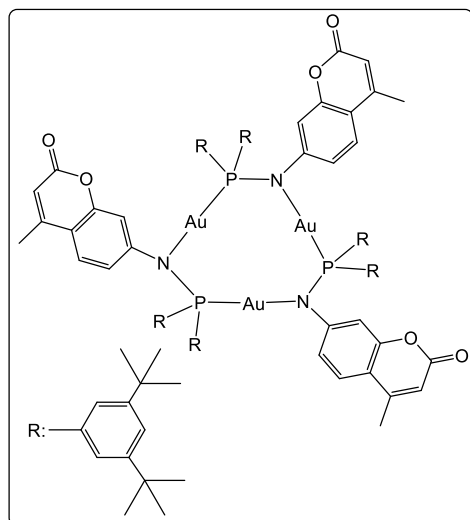
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 7.63 (m, 2H, Ph-CH), 7.52 (dd, *J* = 14.9, 1.8 Hz, 4H, Ph-CH), 7.43 (d, *J* = 8.6 Hz, 1H, Coum-CH), 7.03 (dd, *J* = 8.8, 2.4 Hz, 1H, Coum-CH), 6.88 (d, *J* = 2.3 Hz, 1H, Coum-CH), 6.10 (s, 1H, Coum-CH), 5.14 (d, *J* = 5.0 Hz 1H, NH), 2.35 (s, 3H, Coum-CH<sub>3</sub>), 1.29 (s, 36H, C(CH<sub>3</sub>)<sub>3</sub>).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (162 MHz, CDCl<sub>3</sub>): δ(ppm) = 60.1 (s).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>): δ(ppm) = 161.1 (Coum-CO), 154.7 (Coum-C), 152.5 (Ph-C), 145.7 (Coum-C), 129.6 (Coum-C), 128.9 (Ph-C), 127.4 (Ph-CH), 126.9 (Ph-CH), 126.0 (Coum-CH), 114.7 (Coum-C), 114.1 (Coum-CH), 112.6 (Coum-CH), 105.6 (Coum-CH), 35.3 (C(CH<sub>3</sub>)<sub>3</sub>), 31.4 (C(CH<sub>3</sub>)<sub>3</sub>), 18.7 (Coum-CH<sub>3</sub>).

**IR (ATR):**  $\tilde{\nu}$ (cm<sup>-1</sup>) = 3437 (w), 3354 (w), 3216 (br), 3075 (br), 3052 (w), 2954 (vs), 2904 (sh), 2865 (sh), 1698 (vs), 1613 (vs), 1561 (sh), 1547 (sh), 1501 (w), 1467 (w), 1421 (w), 1388 (m), 1362 (w), 1298 (s), 1266 (sh), 1247 (w), 1203 (w), 1144 (s), 1132 (sh), 1074 (w), 1018 (w), 996 (w), 914 (w), 897 (w), 865 (m), 806 (w), 794 (w), 781 (sh), 747 (w), 700 (w), 600 (w), 572 (w), 549 (w), 526 (w), 481 (w), 451 (w), 417 (w).

### Synthesis of gold complex 6:



Complex **5** (280 mg, 0.34 mmol, 1.0 eq) was dissolved in 15 mL of THF to which KO<sup>t</sup>-Bu (57.7 mg, 0.51 mmol, 1.5 eq) was added in excess and the reaction mixture was stirred overnight. The crude product was filtered and purified by crystallization. Crystals suitable for X-ray diffraction were obtained by layering *n*-pentane on a concentrated THF solution.

#### Analytical data for 6:

Yield: 208 mg (78 %, based on Au content). Anal. Calcd. for C<sub>114</sub>H<sub>147</sub>Au<sub>3</sub>N<sub>3</sub>O<sub>6</sub>P<sub>3</sub> (2339.27 g/mol):

EA: C, 58.53; H, 6.33; N, 1.80; Found: C, 58.75; H, 6.13; N, 1.56.

**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ(ppm) = 7.62 (d, *J* = 14.8 Hz, 12H, Ph-CH), 7.46 (s, 6H, Ph-CH), 7.13 – 6.95 (m, 6H, Coum-CH), 6.52 (s, 3H, Coum-CH), 5.84 (s, 3H, Coum-CH), 2.21 (s, 9H, Coum-CH<sub>3</sub>), 1.20 (s, 108H, C(CH<sub>3</sub>)<sub>3</sub>).

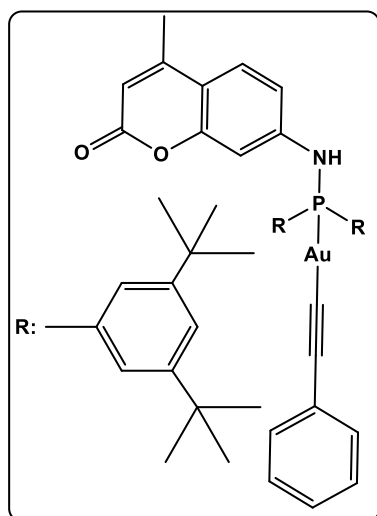
**<sup>31</sup>P{<sup>1</sup>H} NMR** (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ(ppm) = 59.4 (s).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ(ppm) = 161.5 (Coum-CO), 155.9 (Coum-C), 154.5 (Coum-C), 152.7 (Coum-C), 151.4 (Ph-C), 133.5 (Ph-C), 127.1 (Ph-CH), 125.4 (Ph-CH), 123.8 (Coum-CH), 120.8 (Coum-CH), 112.7 (Coum-C), 110.8 (Coum-CH), 109.6 (Coum-CH), 35.3 (C(CH<sub>3</sub>)<sub>3</sub>), 31.5 (C(CH<sub>3</sub>)<sub>3</sub>), 18.5 (Coum-CH<sub>3</sub>).

**IR (ATR):**  $\tilde{\nu}$ (cm<sup>-1</sup>) = 2955 (vs), 2904 (m), 2868 (m), 1731 (vs), 1598 (vs), 1537 (m), 1501 (m), 1477 (m), 1464 (m), 1419 (m), 1386 (s), 1363 (s), 1330 (w), 1275 (s), 1261 (s), 1248 (m), 1197 (s), 1142 (s), 1066 (s), 1010 (m), 990 (m), 937 (m), 896 (w), 872 (m), 844 (m), 816 (w), 793 (m), 739 (m), 705 (m), 680 (w), 640 (m), 617 (m), 576 (w), 548 (w), 528 (w), 518 (w), 481 (w), 456 (m), 433 (m).



### Synthesis of gold complex 7:



Complex **6** (26 mg) was dissolved in 1 mL of DCM and 100  $\mu\text{L}$  of phenylacetylene. The yellow colored solution turned colorless after 24 h. The volatiles were removed under reduced pressure. Crystalline solid can be obtained by layering a THF solution with *n*-pentane.

#### Analytical data for 7:

Yield: 20 mg. Anal. Calcd. for  $\text{C}_{46}\text{H}_{55}\text{AuNO}_2\text{P}$  (881.89 g/mol): EA: C, 62.65; H, 6.29; N, 1.59; Found: C, 62.52; H, 6.29; N, 1.25.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 7.60$  (s, 2H, Ph-CH), 7.53 (d,  $J = 1.8$  Hz, 2H, Ph-CH), 7.52 – 7.46 (m, 4H, Ph-CH), 7.43 (d,  $J = 8.6$  Hz, 1H, Coum-CH), 7.24 – 7.14 (m, 3H, Ph-CH), 7.07 (dd,  $J = 8.6, 2.4$  Hz, 1H, Coum-CH), 6.82 (d,  $J = 2.3$  Hz, 1H, Coum-CH), 6.10 (s, 1H, Coum-CH), 4.98 (d,  $J = 4.8$  Hz, 1H, N-H), 2.35 (s, 3H, Coum- $\text{CH}_3$ ), 1.29 (s, 36H,  $\text{C}(\text{CH}_3)_3$ ).

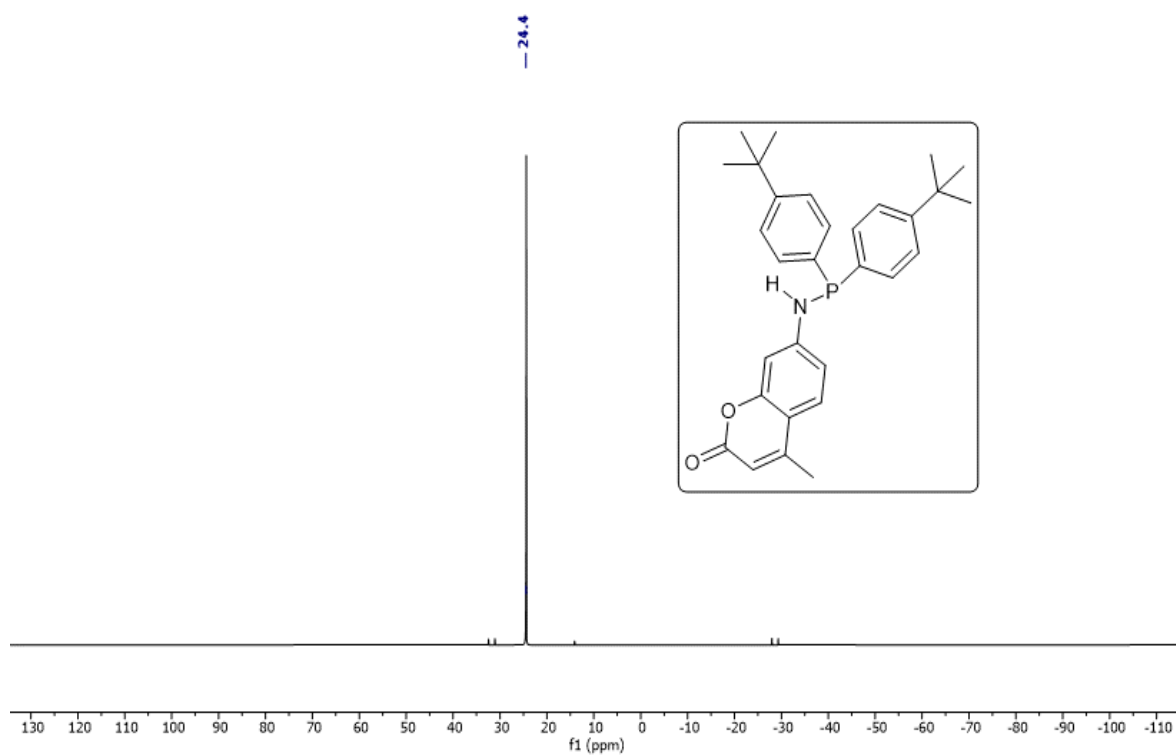
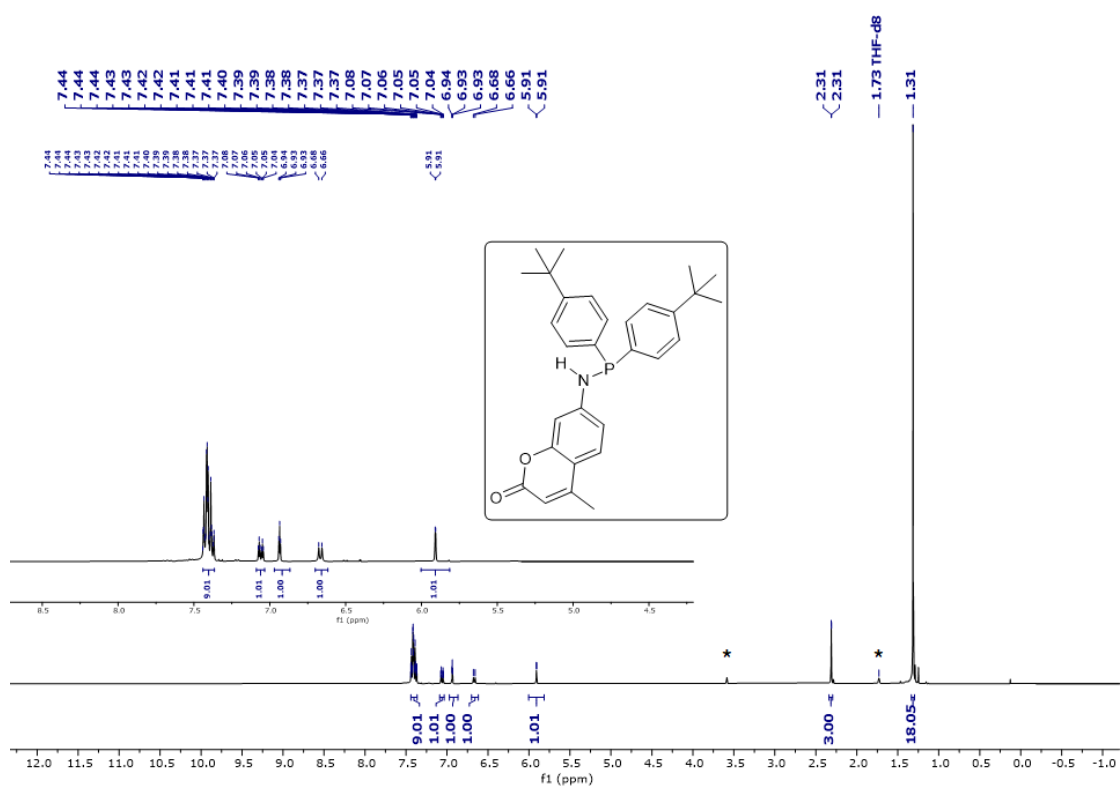
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 74.7$  (s).

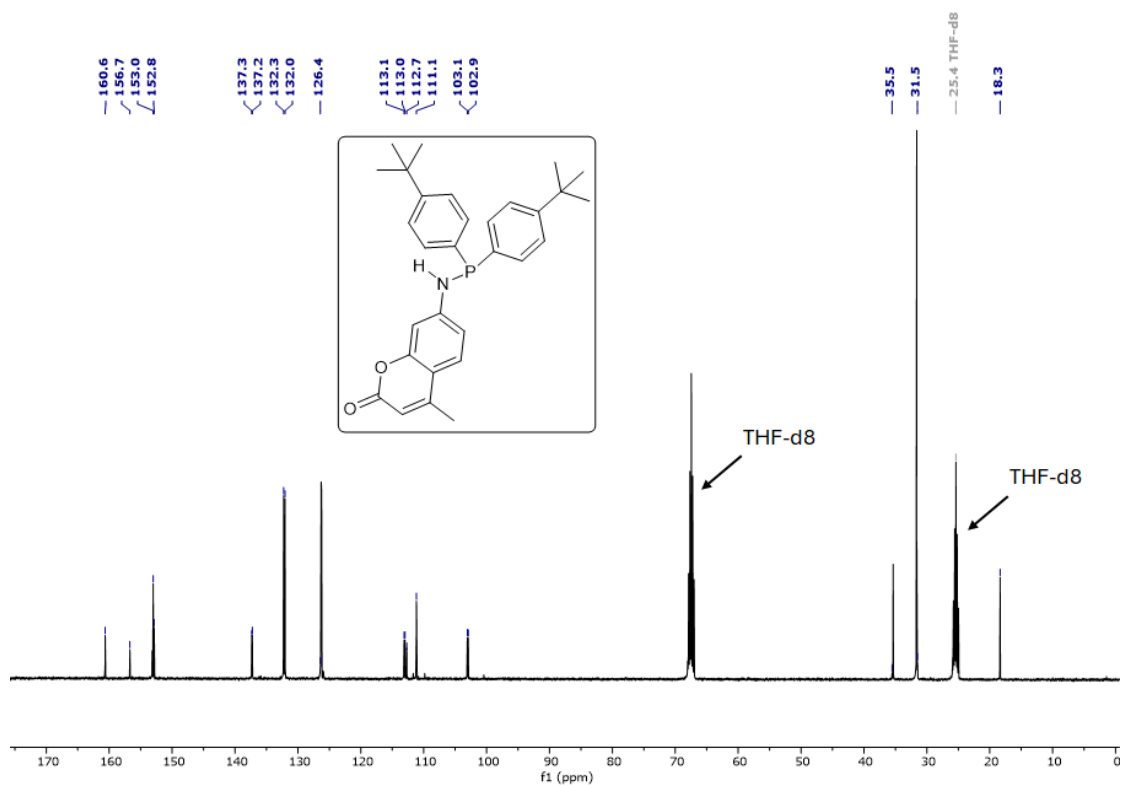
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 161.2$  (Coum-CO), 154.7 (Coum-C), 152.5 (Coum-C), 152.3 (Ph-C), 146.1 (Coum-C), 132.5 (Ph-CH), 130.6 (Ph-C), 130.0 (Ph-C), 128.1 (Ph-CH), 127.0 (Ph-CH), 126.9 (Ph-CH), 126.7 (Ph-CH), 126.0 (Coum-CH), 124.9 ( $\text{C}\equiv\text{C-Au}$ ), 114.5 ( $\text{C}\equiv\text{C-Au}$ ), 114.2 (Coum-C), 114.1 (Coum-CH), 112.5 (Coum-CH), 105.5 (Coum-CH), 35.3 ( $\text{C}(\text{CH}_3)_3$ ), 31.5 ( $\text{C}(\text{CH}_3)_3$ ), 18.7 (Coum- $\text{CH}_3$ ).

**IR (ATR):**  $\tilde{\nu}(\text{cm}^{-1}) = 3265$  (br), 2957 (vs), 2905 (m), 2868 (m), 2165 (w), 2103 (w), 1985 (w), 1720 (vs), 1613 (vs), 1562 (s), 1512 (m), 1462 (m), 1480 (m), 1423 (m), 1388 (s), 1364 (s), 1343 (m), 1250 (m), 1203 (m), 1142 (s), 1066 (m), 1014 (w), 986 (m), 901 (m), 842 (w), 798 (w), 782 (m), 755 (m), 707 (m), 693 (m), 588 (w), 562 (w), 528 (m), 494 (m), 444 (w), 423 (w).

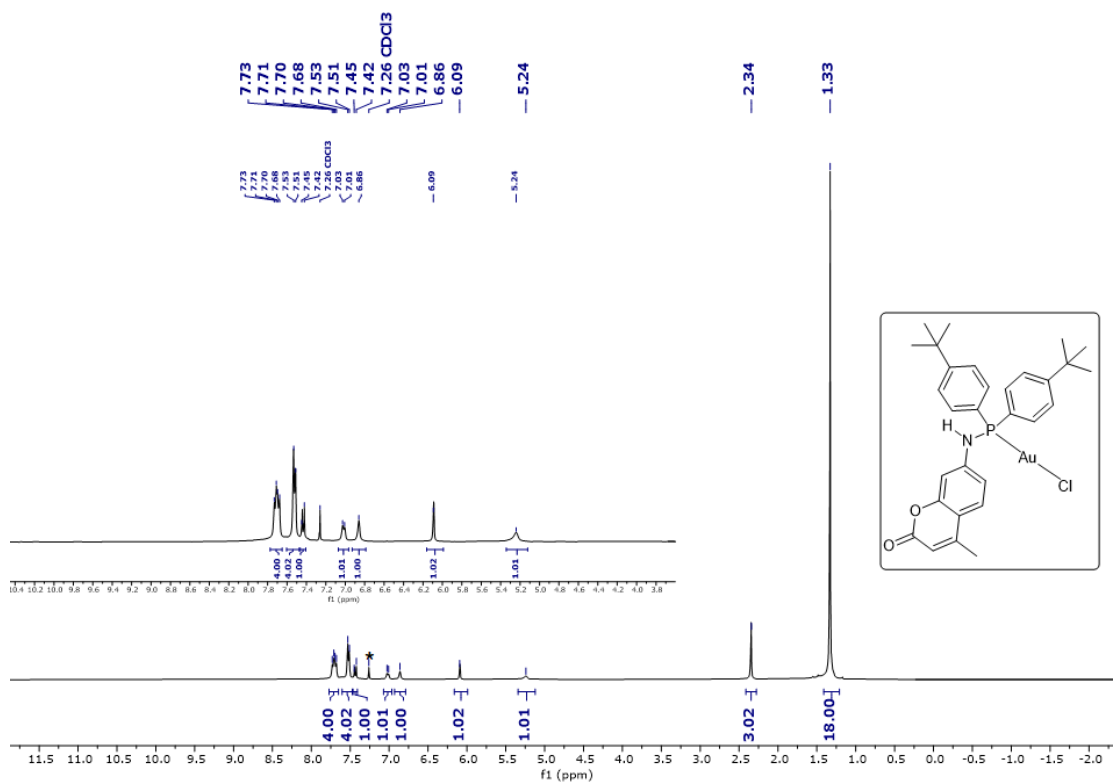
**Cell parameters:**  $a = 10.1413 \text{ \AA}$ ,  $b = 14.9946 \text{ \AA}$ ,  $c = 15.8207 \text{ \AA}$ ,  $\alpha = 86.276^\circ$ ,  $\beta = 72.712^\circ$ ,  $\gamma = 86.068^\circ$ ; volume = 2289.16  $\text{\AA}^3$ ; space group:  $P\bar{1}$ .

## II. NMR spectra





**Figure S3.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1** in THF-d<sub>8</sub> at room temperature.



**Figure S4.**  $^1\text{H}$  NMR spectrum of **2** in CDCl<sub>3</sub> at room temperature. \*, residual protio solvent signal.

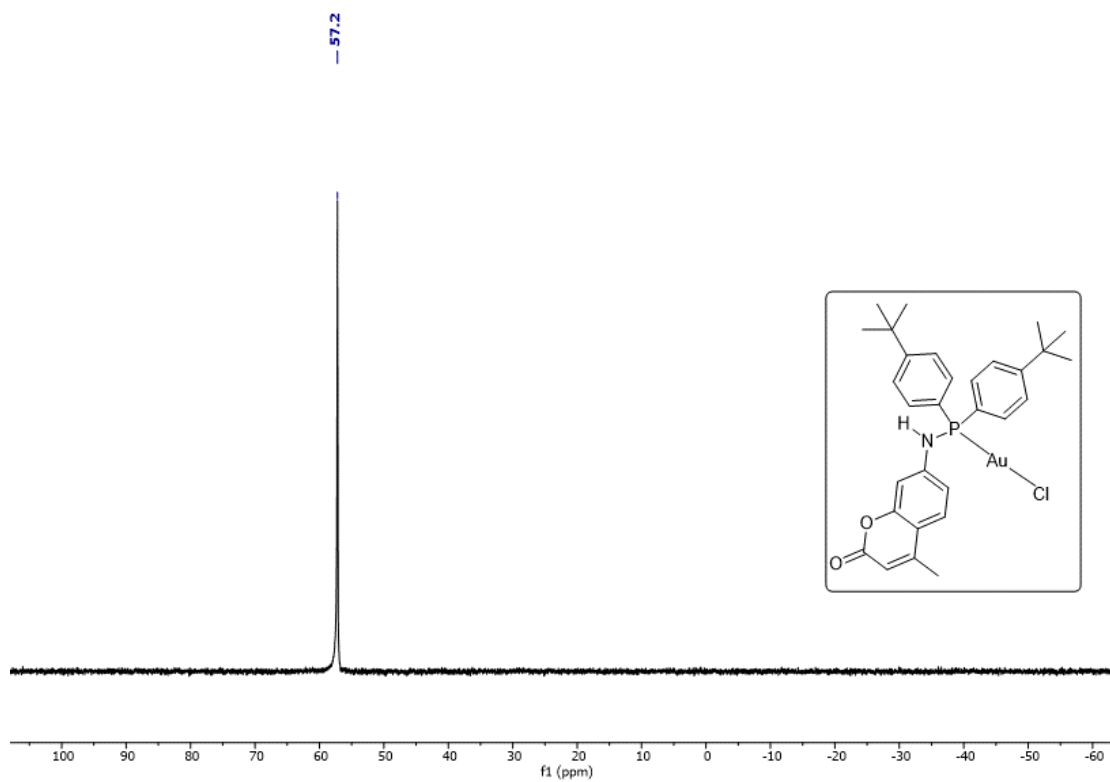


Figure S5.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{CDCl}_3$  at room temperature.

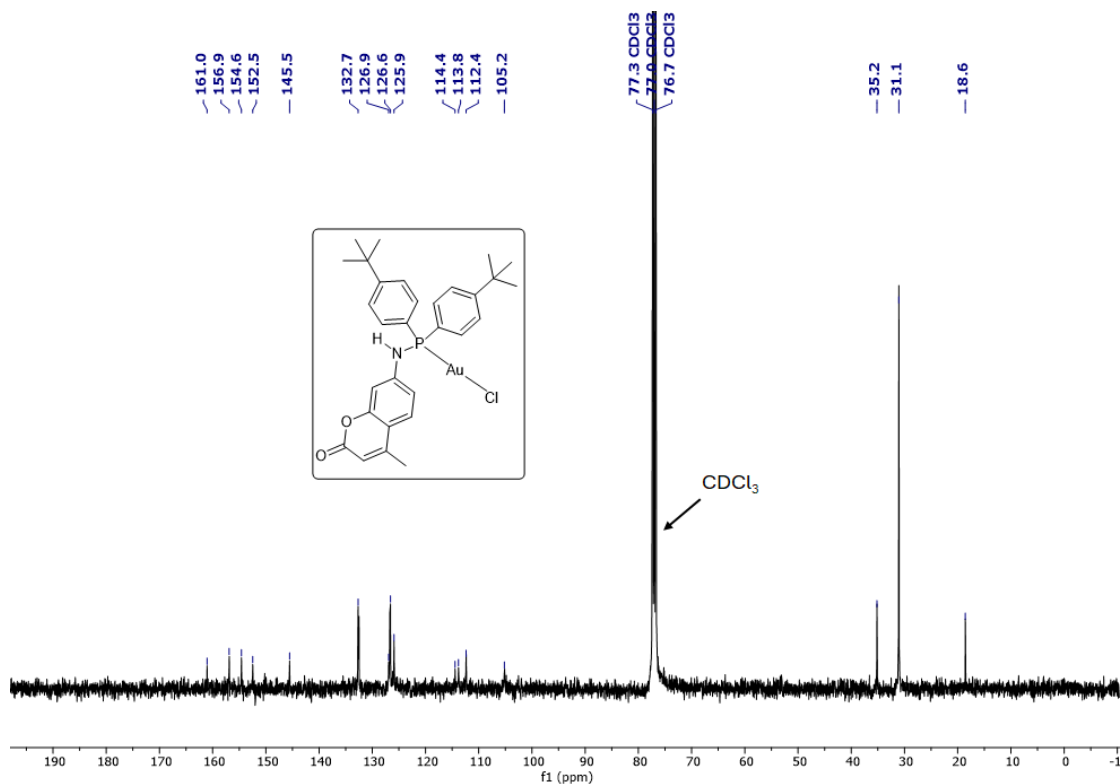
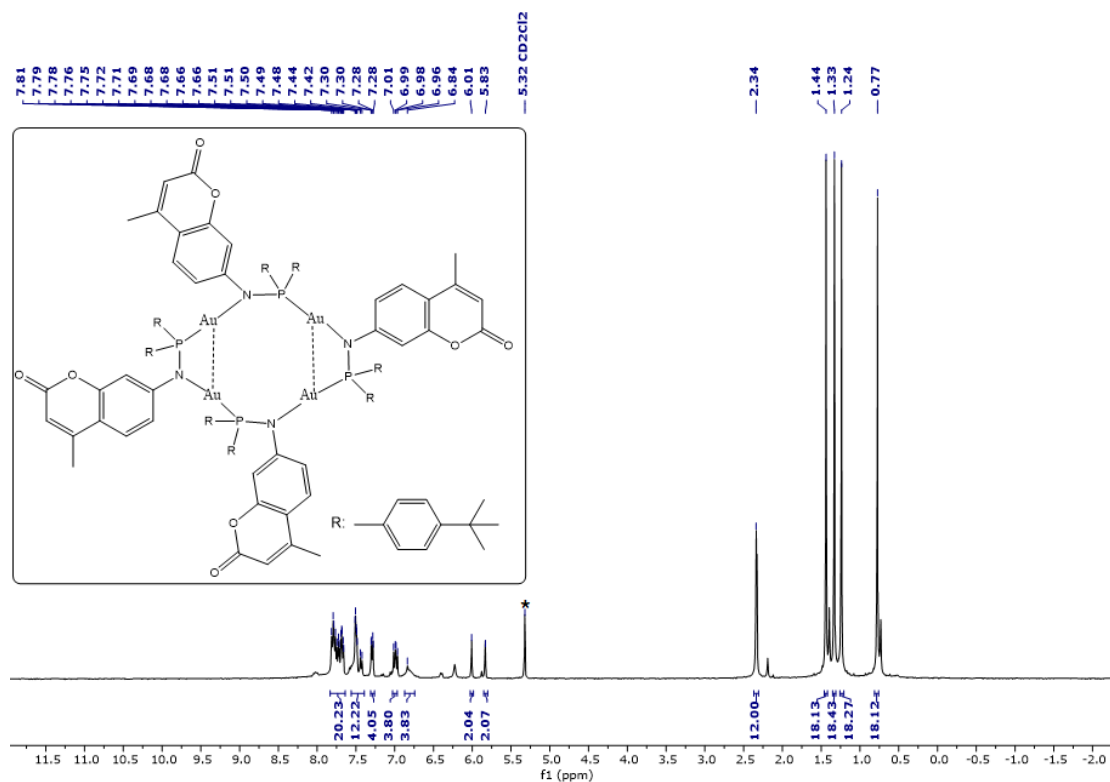
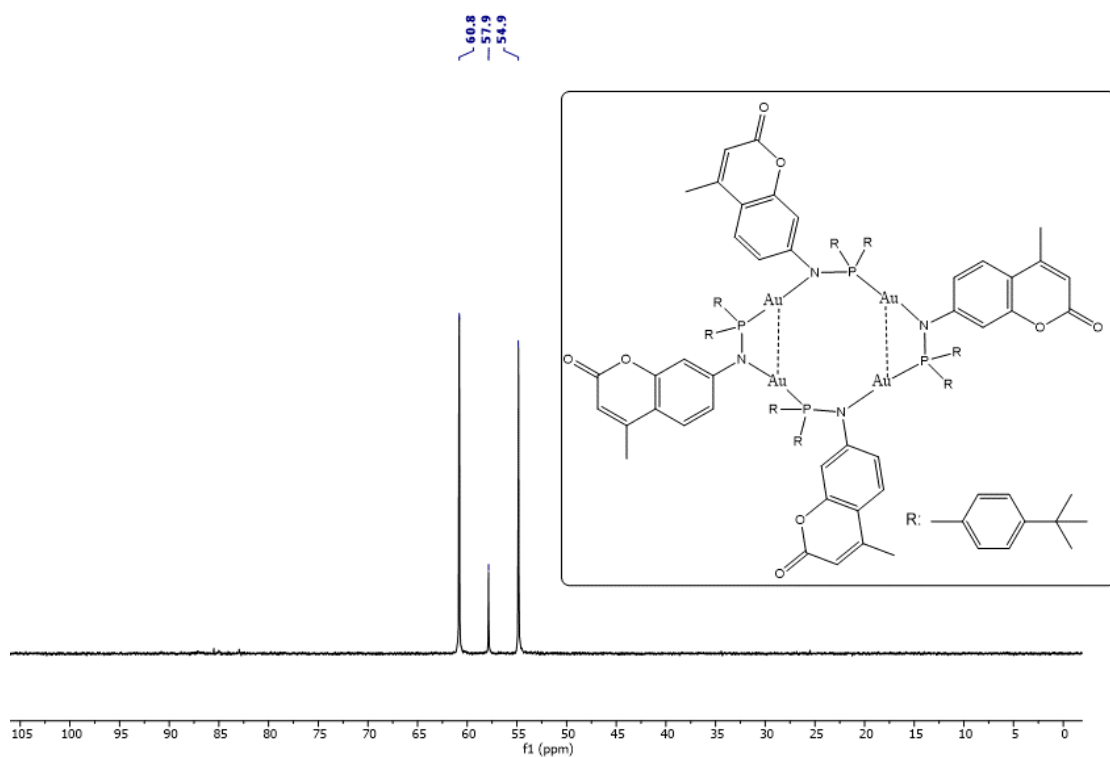


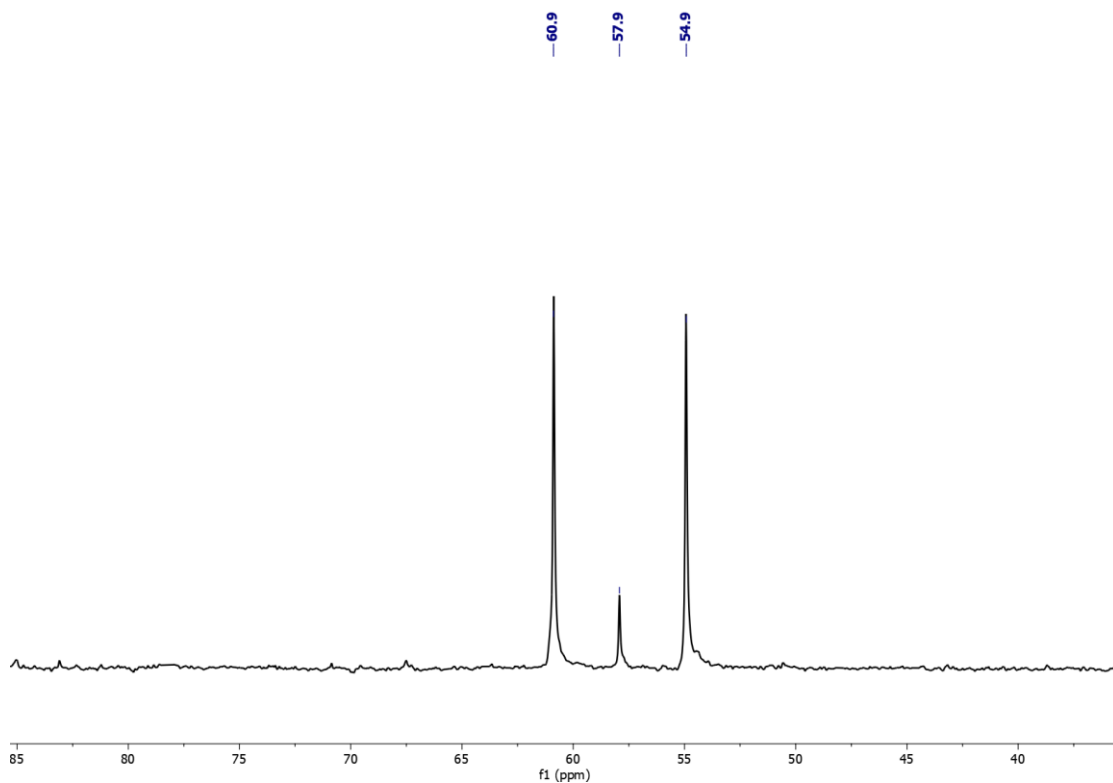
Figure S6.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{CDCl}_3$  at room temperature.



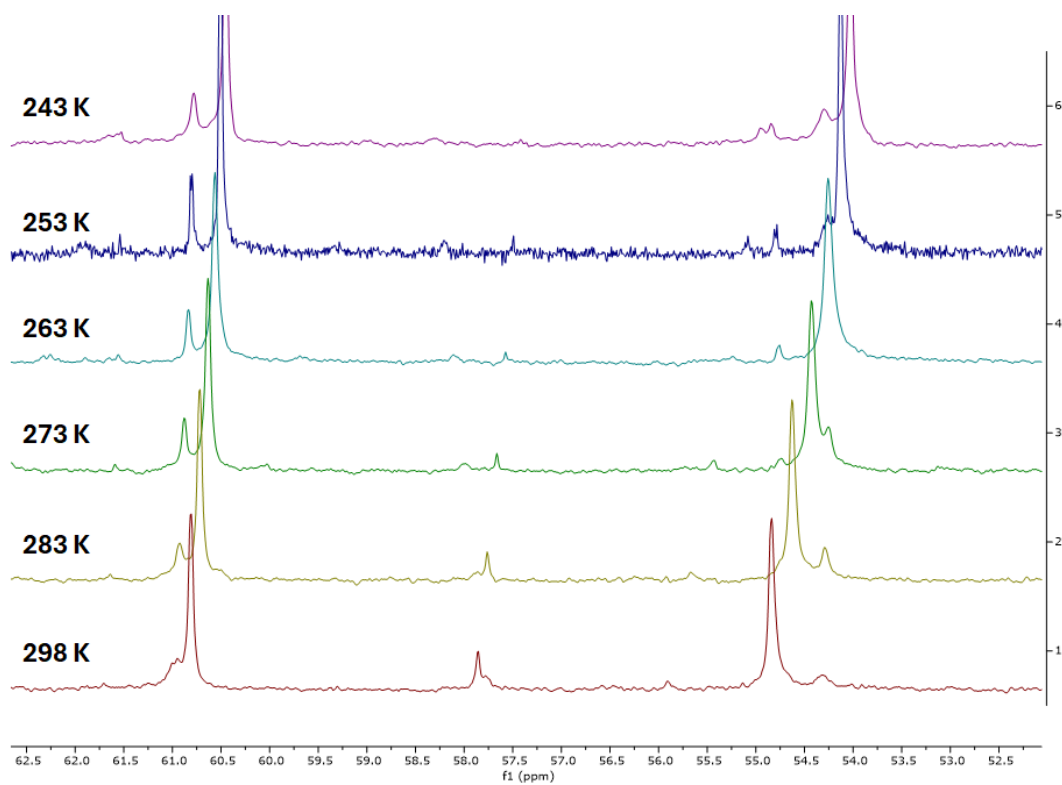
**Figure S7.**  $^1\text{H}$  NMR spectrum of **3** in  $\text{CD}_2\text{Cl}_2$  at room temperature. \*, residual protio solvent signal. Additional signals correspond to the trimer complex formed upon dissolution of crystals.



**Figure S8.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3** in  $\text{CD}_2\text{Cl}_2$  at room temperature. Additional signal at  $\delta = 57.9$  ppm correspond to the trimer formed upon dissolution of crystals.

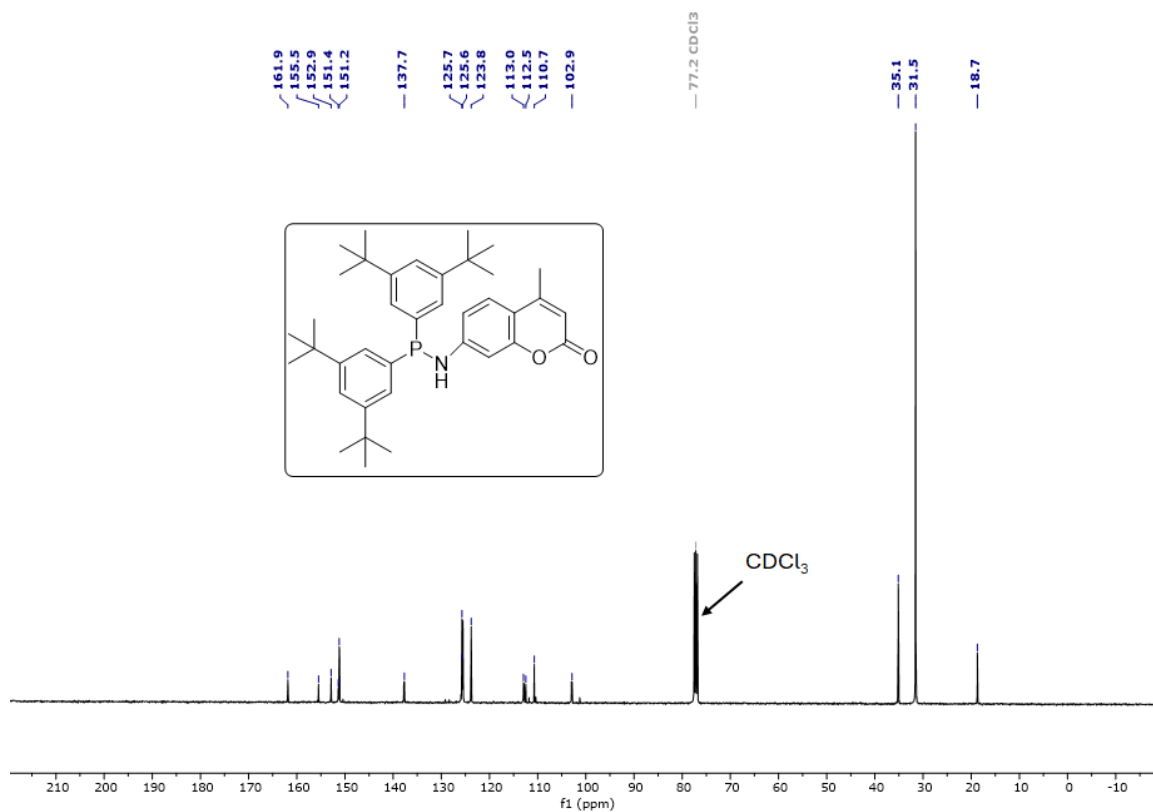


**Figure S9:**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3** in  $\text{CD}_2\text{Cl}_2$  at room temperature after 10 days.

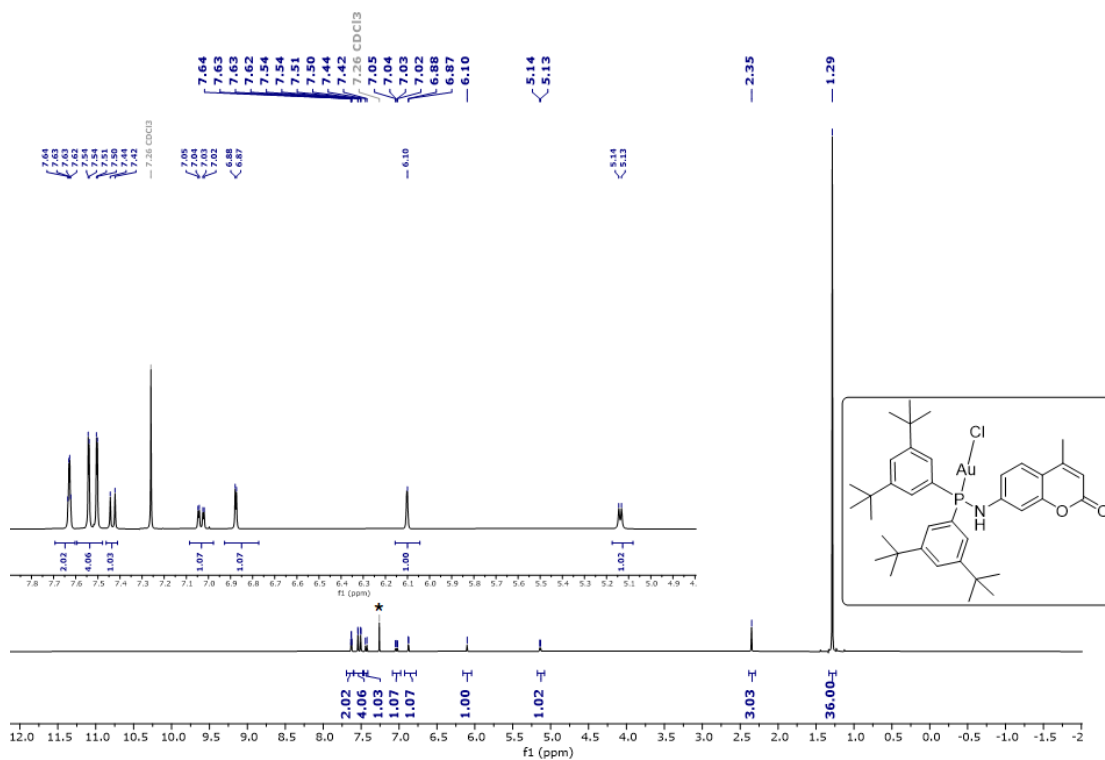


**Figure S10:** Variable temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3** in  $\text{CD}_2\text{Cl}_2$ .





**Figure S13.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 4 in  $\text{CDCl}_3$  at room temperature.



**Figure S14.**  $^1\text{H}$  NMR spectrum of 5 in  $\text{CDCl}_3$  at room temperature. \*, residual protio solvent signal.



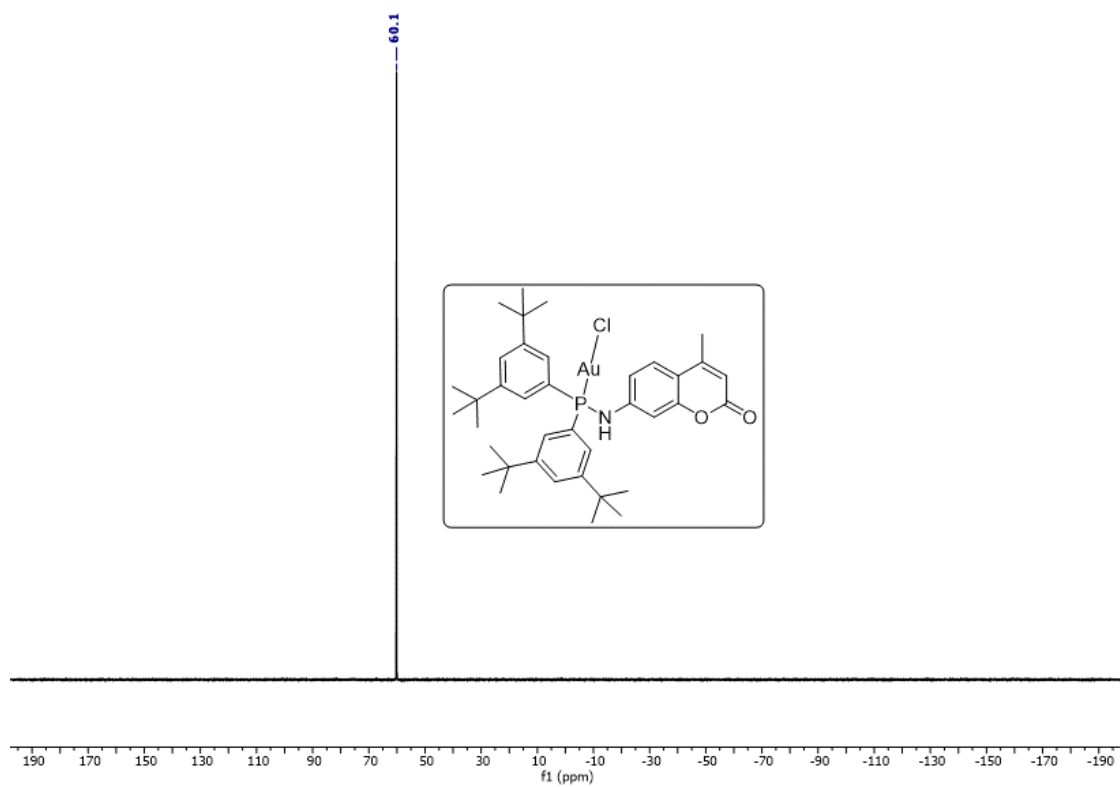


Figure S15.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of 5 in  $\text{CDCl}_3$  at room temperature.

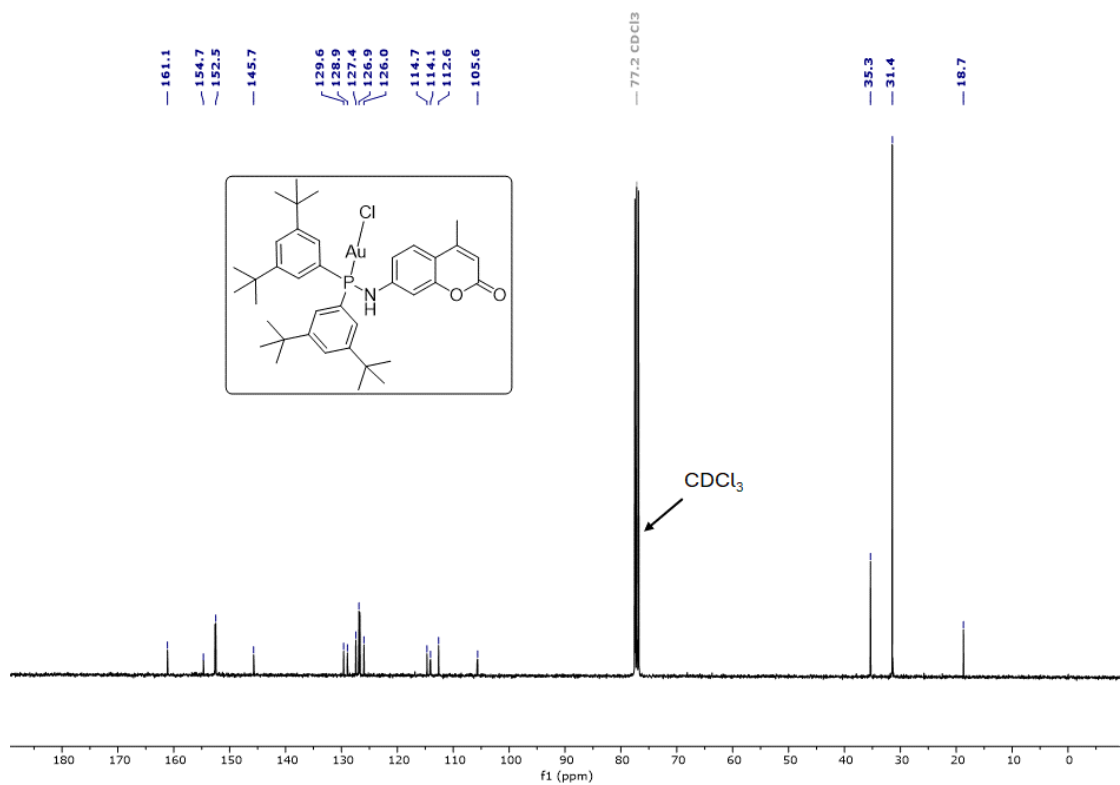
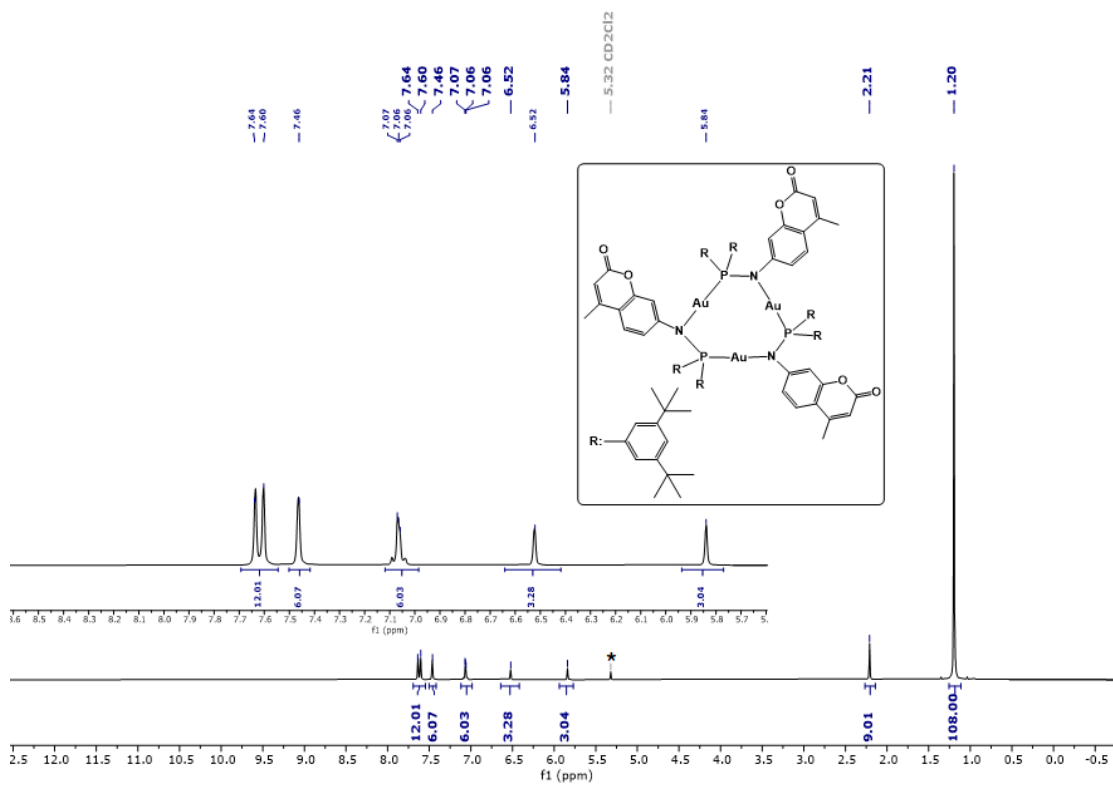
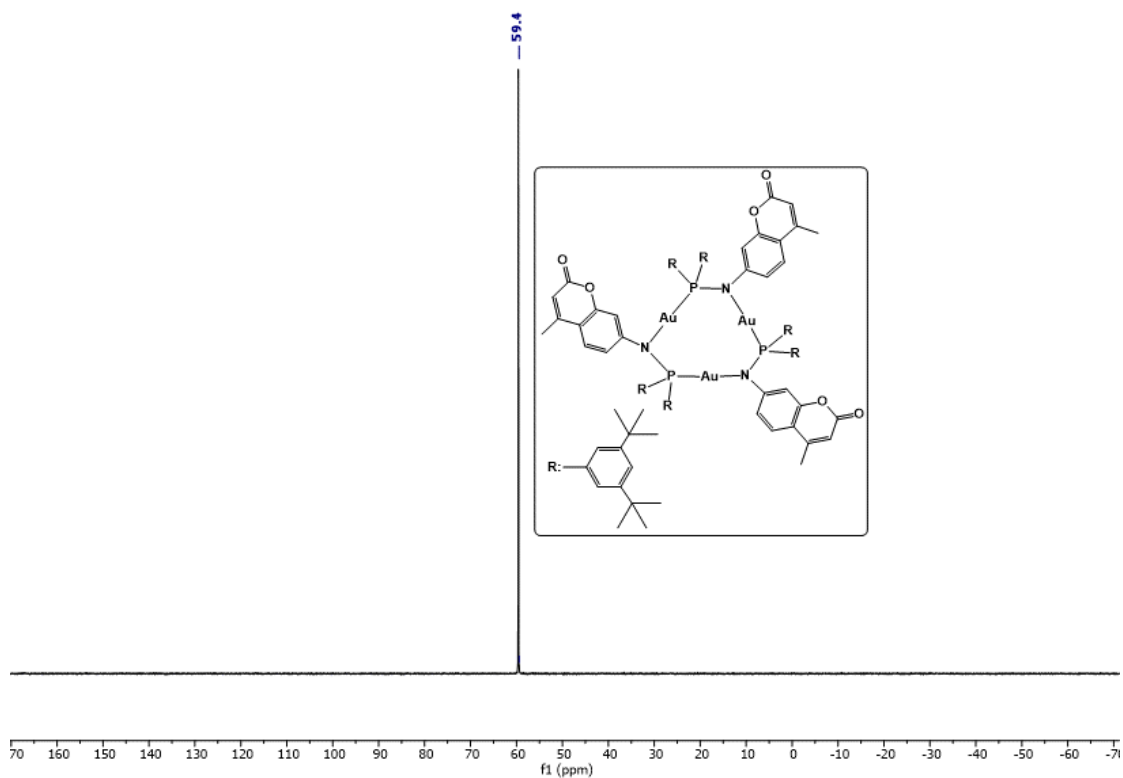


Figure S16.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 5 in  $\text{CDCl}_3$  at room temperature.



**Figure S17.**  $^1\text{H}$  NMR spectrum of **6** in  $\text{CD}_2\text{Cl}_2$  at room temperature. \*, residual protio solvent signal.



**Figure S18.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **6** in  $\text{CD}_2\text{Cl}_2$  at room temperature.

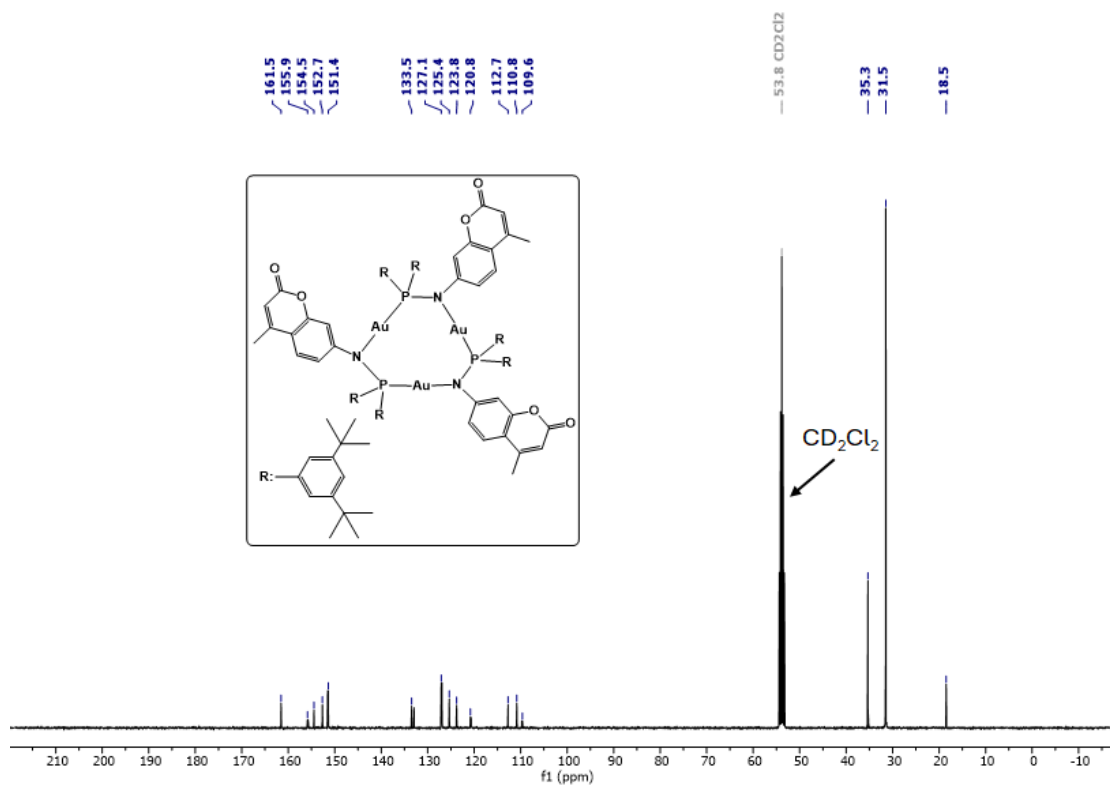


Figure S19.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **6** in  $\text{CD}_2\text{Cl}_2$  at room temperature.

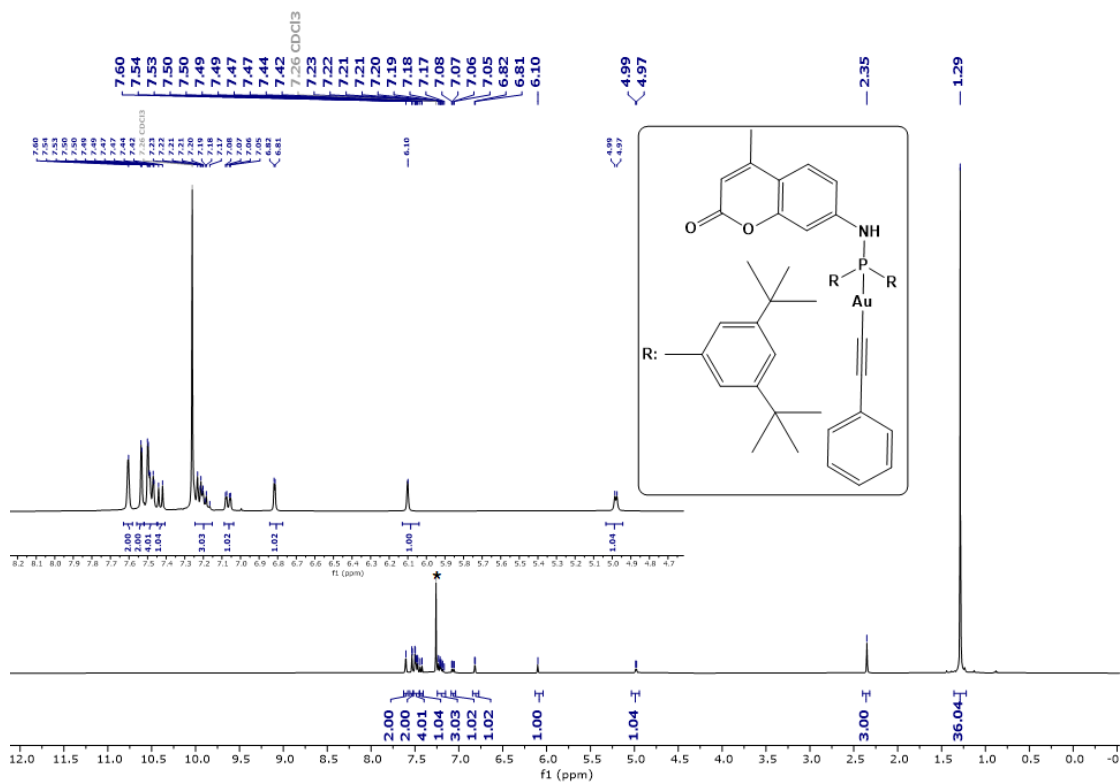


Figure S20.  $^1\text{H}$  NMR spectrum of **7** in  $\text{CDCl}_3$  at room temperature. \*, residual protio solvent signal.

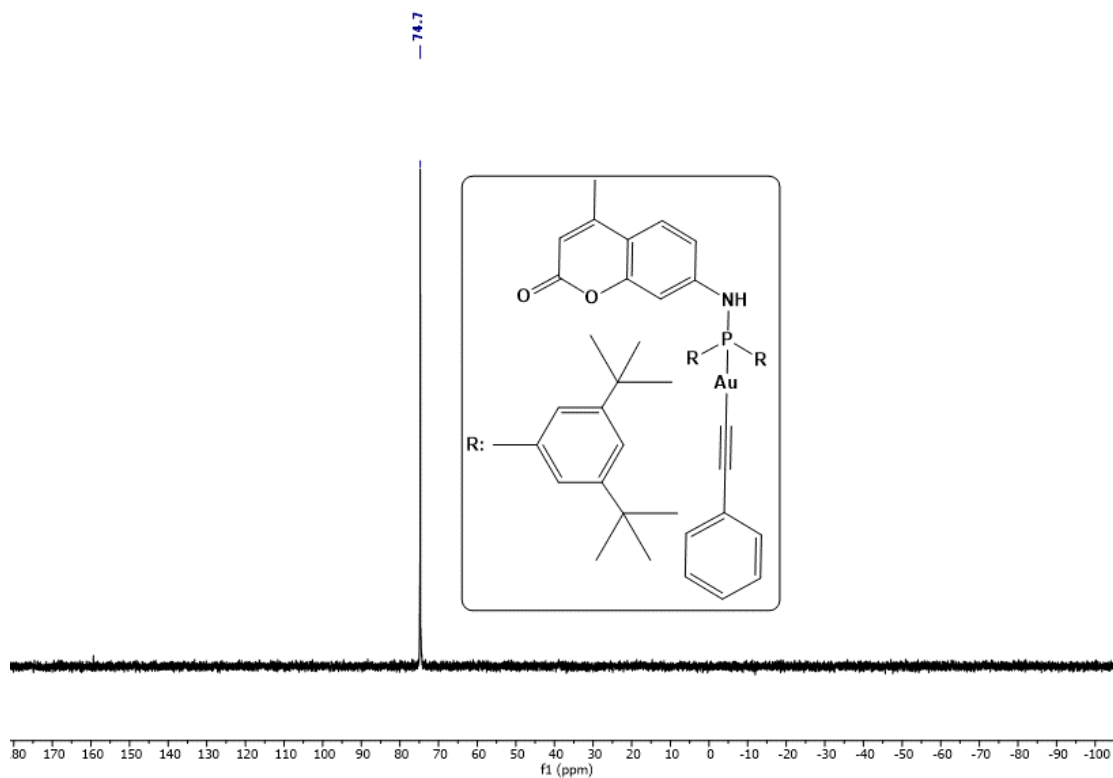


Figure S21.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **7** in  $\text{CDCl}_3$  at room temperature.

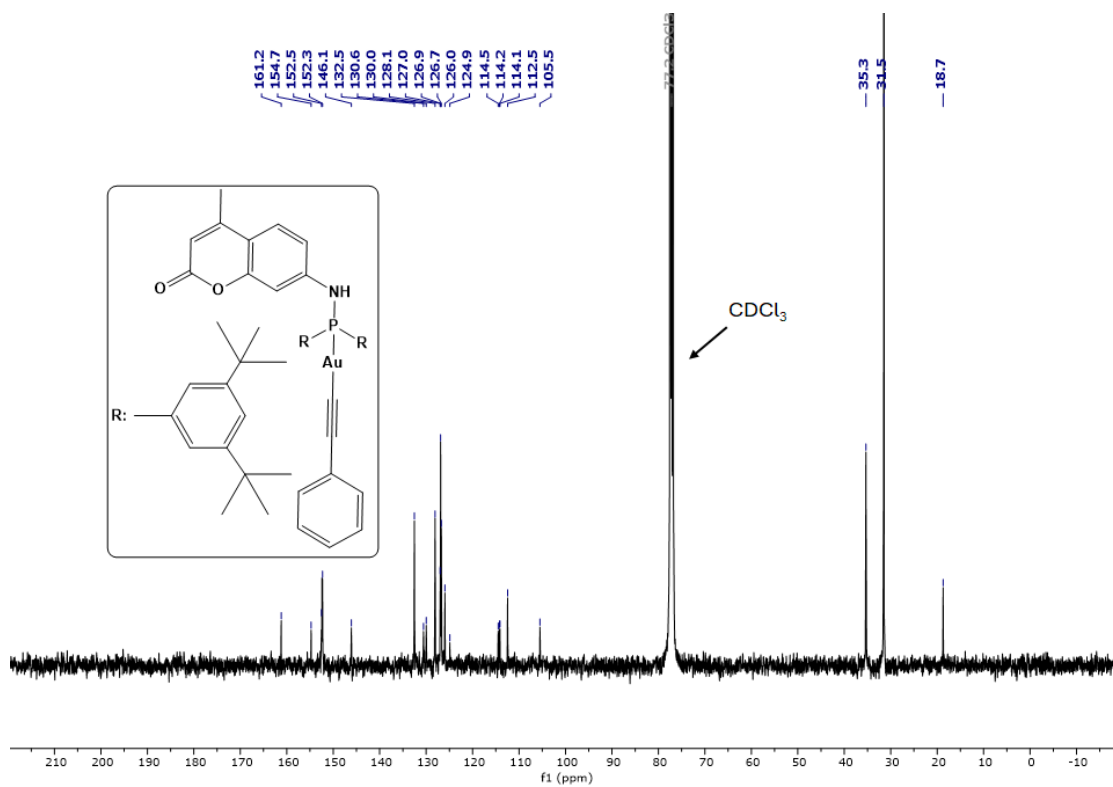
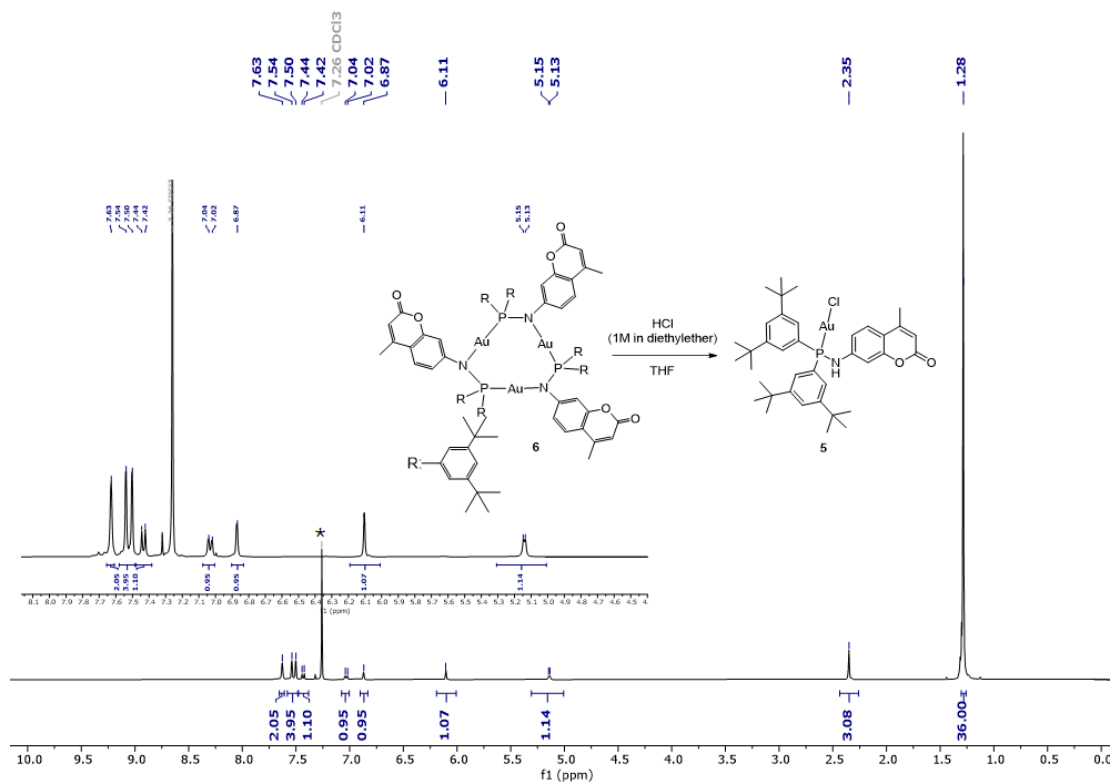
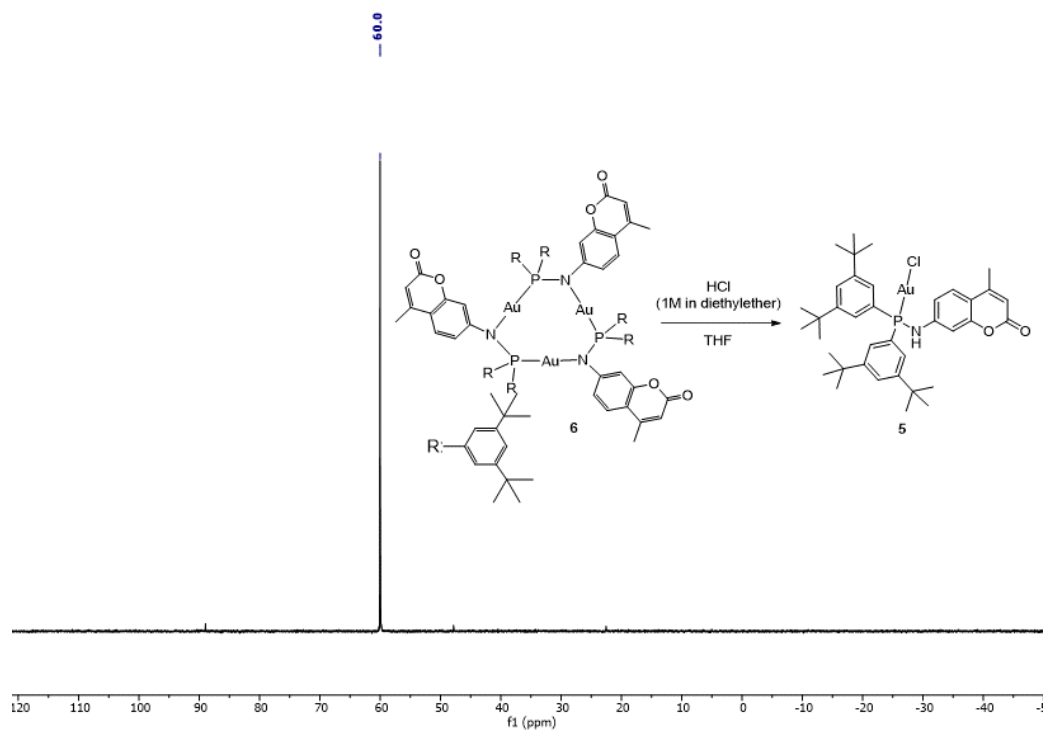


Figure S22.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **7** in  $\text{CDCl}_3$  at room temperature.



**Figure S23.**  $^1\text{H}$  NMR spectrum recorded in  $\text{CDCl}_3$  at room temperature after reacting complex 6 with HCl (1 M in diethylether) in THF for 15 min, followed by removal of volatiles. \*, residual protio solvent signal.



**Figure S24.**  $^1\text{H}$  NMR spectrum recorded in  $\text{CDCl}_3$  at room temperature after reacting complex 6 with HCl (1 M in diethylether) in THF for 15 min, followed by removal of volatiles.

### III. IR spectra

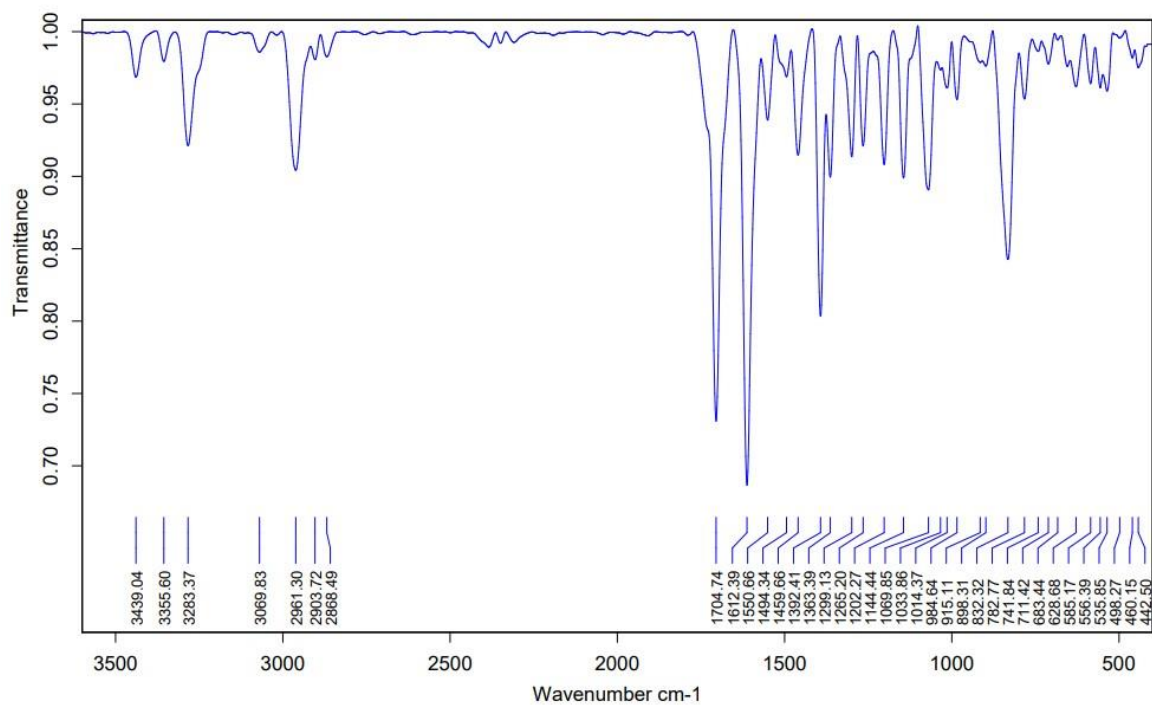


Figure S25. IR spectrum of complex 1.

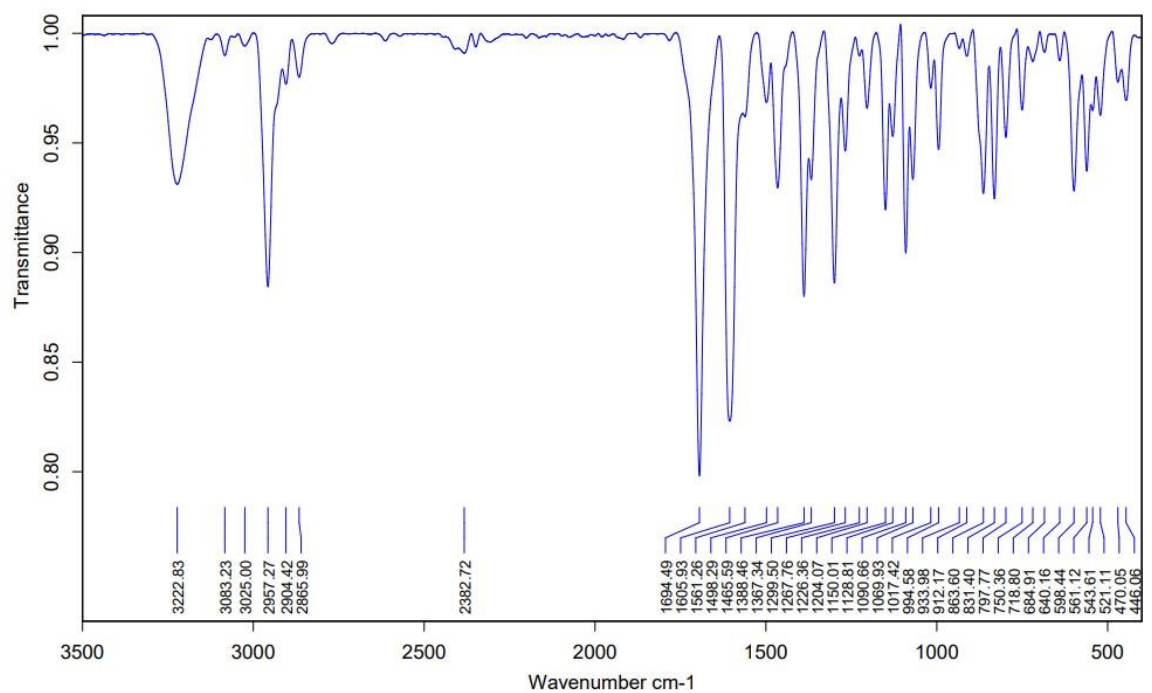


Figure S26. IR spectrum of complex 2.

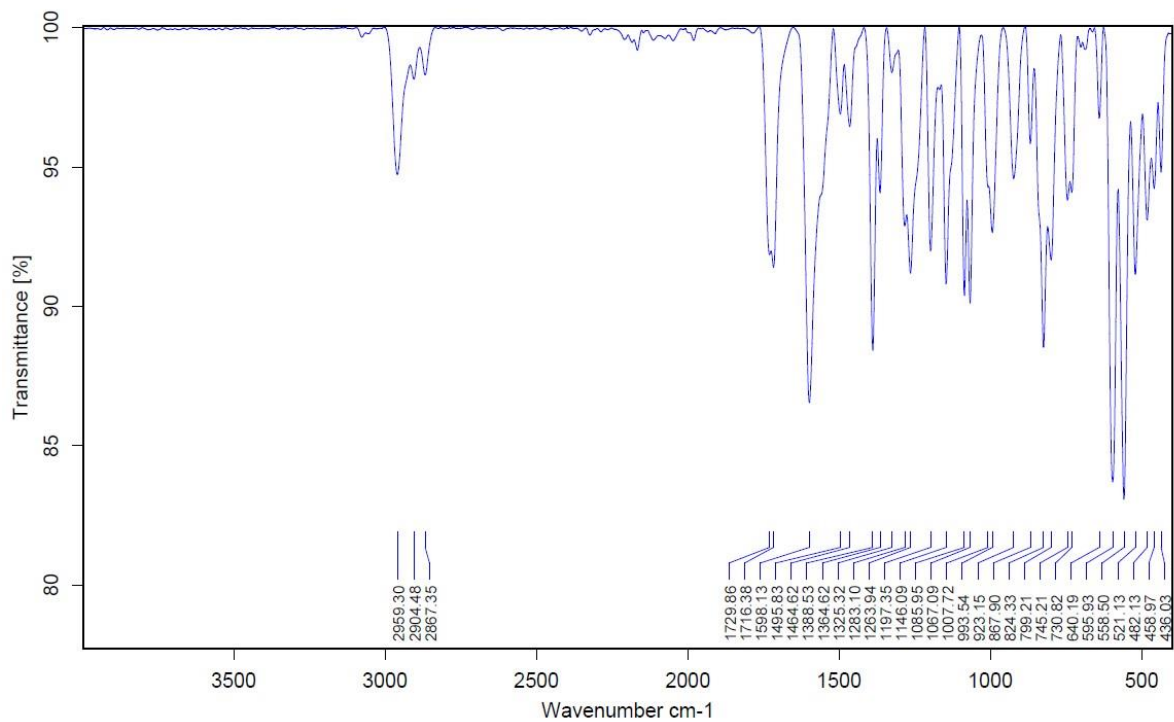


Figure S27. IR spectrum of complex 3

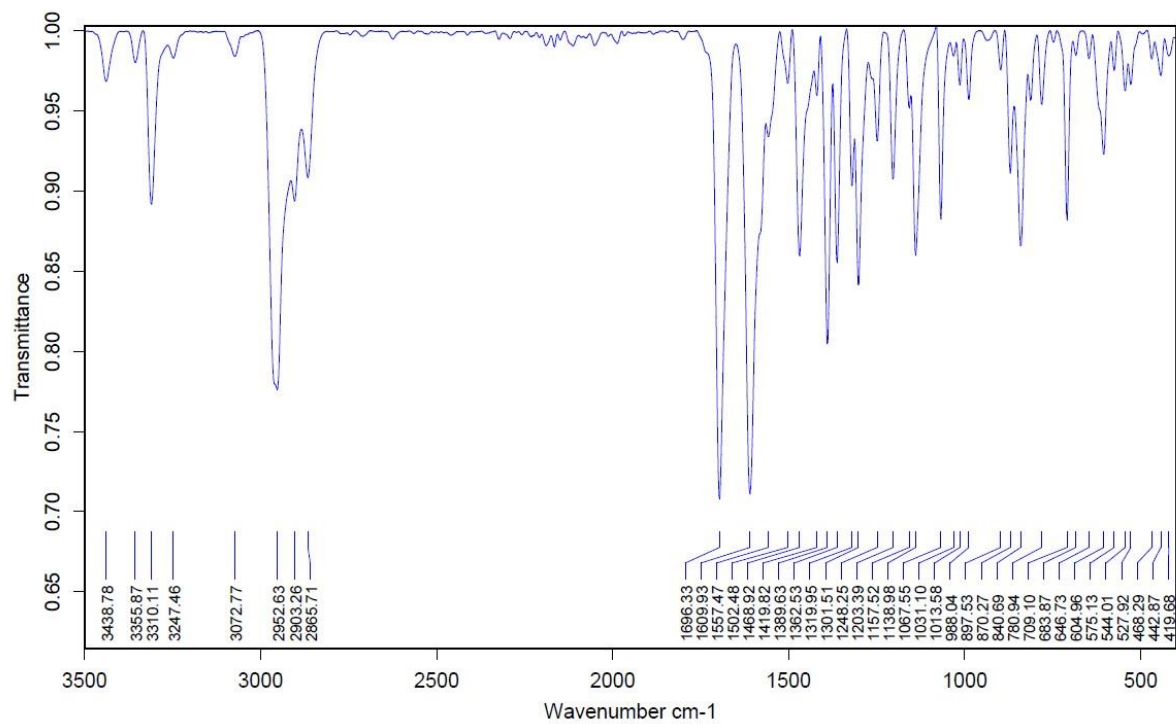


Figure S28. IR spectrum of complex 4.

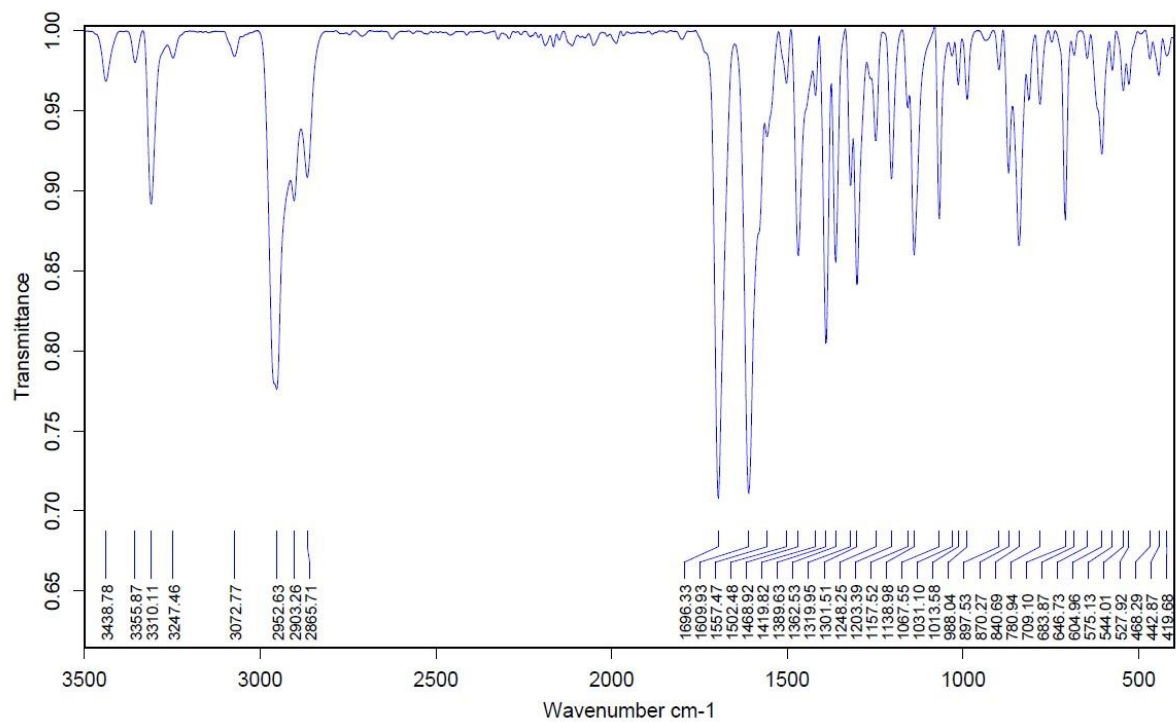


Figure S29. IR spectrum of complex 5.

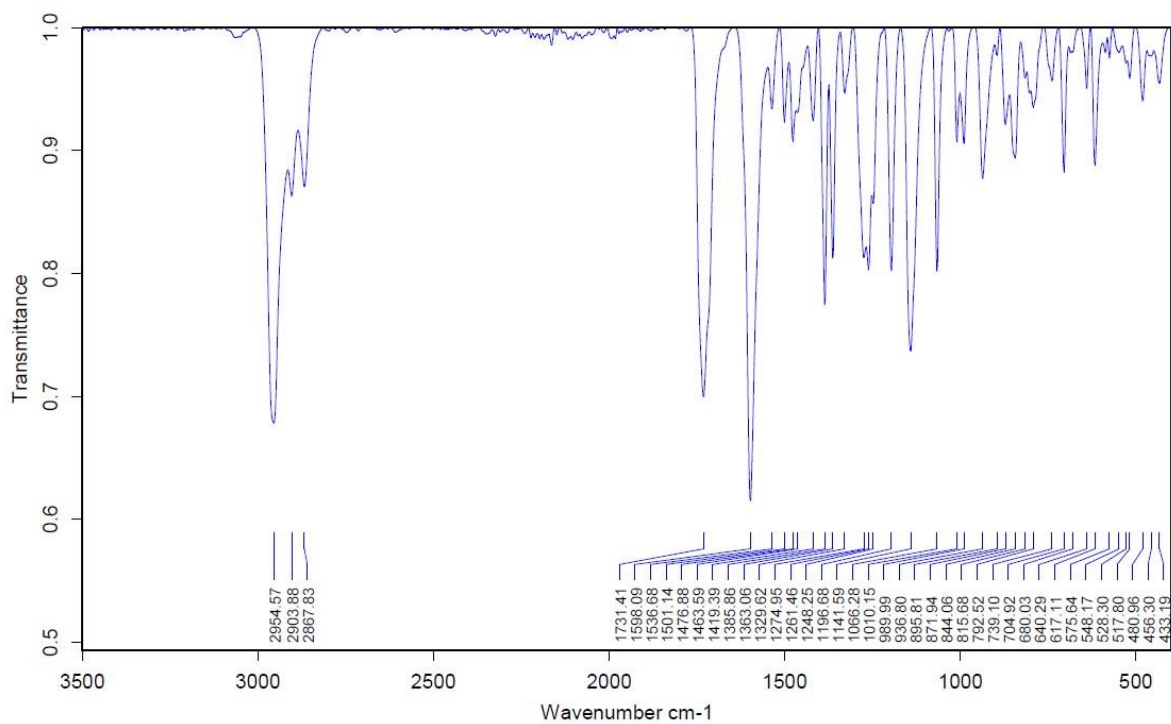
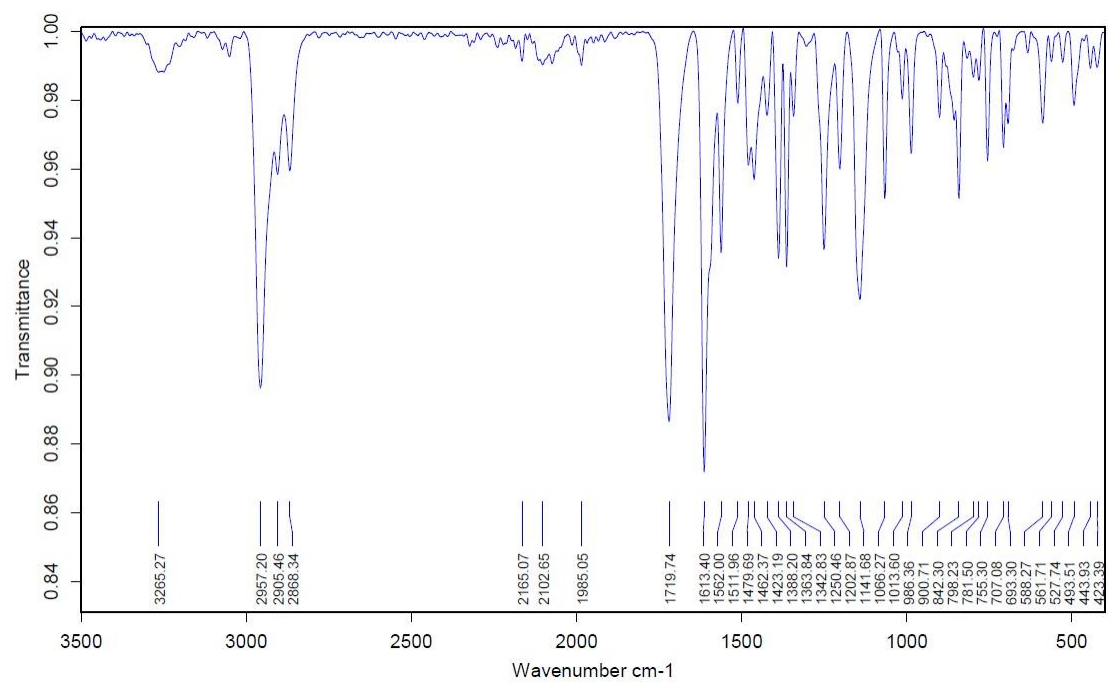


Figure S30. IR spectrum of complex 6.





**Figure S31.** IR spectrum of complex 7.

## IV. X-ray crystallography

### IV.1 General methods

Suitable crystals for the X-ray analysis of all compounds were obtained as described above. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fibre. The crystal was transferred directly to the cold stream of a STOE StadiVari (100 K or 150 K) diffractometer. All structures were solved by using the program SHELXS/T<sup>3,4</sup> and Olex2.<sup>5</sup> The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on  $F^2$  by using the program SHELXL.<sup>4,5</sup> The H-atoms were introduced into the geometrically calculated positions (SHELXL procedures) unless otherwise stated and refined riding on the corresponding parent atoms. In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance. Summary of the crystal data, data collection and refinement for all compounds are given in Table S1.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. 2362899-2362904. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

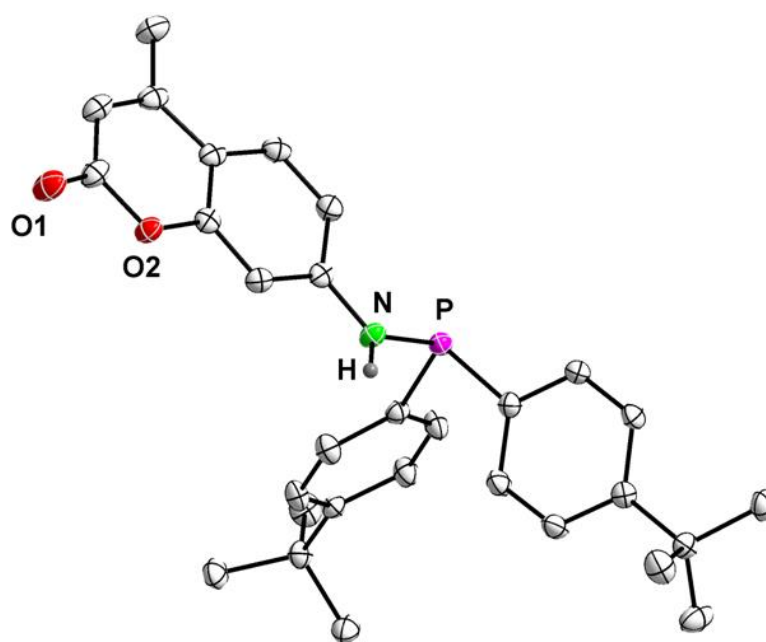
## V.2. Table S1: Summary of crystal data

Compound	1	2	3	4
Empirical	C <sub>30</sub> H <sub>34</sub> NO <sub>2</sub> P	C <sub>30</sub> H <sub>34</sub> AuClNO <sub>2</sub> P	C <sub>162</sub> H <sub>180</sub> Au <sub>4</sub> N <sub>4</sub> O <sub>8</sub> P <sub>4</sub>	C <sub>42</sub> H <sub>58</sub> NO <sub>3</sub> P
Formula weight	471.55	703.97	3222.84	655.86
Temperature/K	100	100	110	100
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	$P\bar{1}$	P2 <sub>1</sub> /n	$P\bar{1}$	$P\bar{1}$
a/Å	6.0275(4)	10.8340(4)	14.2081(10)	9.3543(14)
b/Å	11.5923(8)	14.4821(6)	17.4588(10)	10.0147(14)
c/Å	18.8673(12)	18.7055(6)	17.3078(13)	21.072(4)
α/°	77.543(5)	90	99.362(5)	78.064(13)
β/°	83.197(5)	101.538(3)	103.687(6)	84.654(13)
γ/°	89.080(6)	90	105.043(5)	81.201(11)
Volume/Å <sup>3</sup>	1278.15(15)	2875.57(19)	3911.9(5)	1904.8(5)
Z	2	4	1	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.225	1.626	1.368	1.144
μ/mm <sup>-1</sup>	0.135	5.291	3.833	0.110
F(000)	504.0	1392.0	1620.0	712.0
Crystal size/mm <sup>3</sup>	0.541 × 0.288 × 0.127	0.156 × 0.137 × 0.048	0.166 × 0.13 × 0.059	0.565 × 0.292 × 0.078
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2θ range for	6.3 to 59.982	3.584 to 60.17	3.92 to 63.714	3.96 to 50.496
Index ranges	-8 ≤ h ≤ 7, -16 ≤ k ≤	-15 ≤ h ≤ 12, -19 ≤ k	-19 ≤ h ≤ 19, -25 ≤ k	-11 ≤ h ≤ 11, -12 ≤
Reflections	16285	21126	57921	17468
Independent reflections	6206 [R <sub>int</sub> = 0.0220, R <sub>sigma</sub> = 0.0209]	7111 [R <sub>int</sub> = 0.0328, R <sub>sigma</sub> = 0.0424]	21641 [R <sub>int</sub> = 0.0480, R <sub>sigma</sub> = 0.0563]	6882 [R <sub>int</sub> = 0.0501, R <sub>sigma</sub> = 0.0634]
Data/restraints/	6206/0/314	7111/0/332	21641/1867/941	6882/468/545
Goodness-of-fit	1.036	0.991	1.104	1.008
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0378, wR <sub>2</sub> = 0.1012	R <sub>1</sub> = 0.0359, wR <sub>2</sub> = 0.0861	R <sub>1</sub> = 0.0531, wR <sub>2</sub> = 0.1337	R <sub>1</sub> = 0.0776, wR <sub>2</sub> = 0.2002
Final R indexes [all data]	R <sub>1</sub> = 0.0447, wR <sub>2</sub> = 0.1065	R <sub>1</sub> = 0.0542, wR <sub>2</sub> = 0.0935	R <sub>1</sub> = 0.0808, wR <sub>2</sub> = 0.1567	R <sub>1</sub> = 0.1159, wR <sub>2</sub> = 0.2293
Largest diff. peak/hole / e Å <sup>-3</sup>	0.34/-0.33	1.24/-2.49	2.33/-3.04	0.68/-0.42

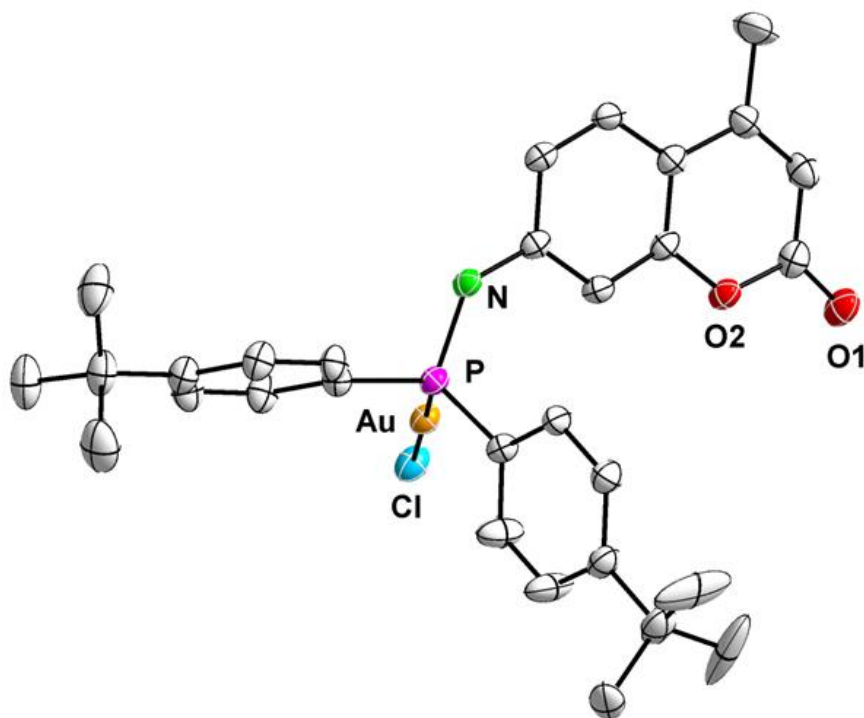
Compound	<b>5</b>	<b>6</b>
Empirical formula	C <sub>42</sub> H <sub>58</sub> AuCINO <sub>3</sub> P	C <sub>138</sub> H <sub>195</sub> Au <sub>3</sub> N <sub>3</sub> O <sub>12</sub> P <sub>3</sub>
Formula weight	888.28	2771.77
Temperature/K	100	100
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
a/Å	10.3094(6)	14.0902(2)
b/Å	11.1292(5)	19.6839(4)
c/Å	19.2381(10)	24.9846(4)
$\alpha$ /°	104.618(4)	99.2500(10)
$\beta$ /°	91.001(4)	96.0800(10)
$\gamma$ /°	102.302(4)	98.5200(10)
Volume/Å <sup>3</sup>	2080.86(19)	6703.9(2)
Z	2	2
$\rho_{\text{calc}}/\text{cm}^3$	1.418	1.373
$\mu/\text{mm}^{-1}$	3.674	3.368
F(000)	904.0	2844.0
Crystal size/mm <sup>3</sup>	0.181 × 0.138 × 0.092	0.219 × 0.140 × 0.034
Radiation	Mo K $\alpha$ ( $\lambda$ = 0.71073)	Mo K $\alpha$ ( $\lambda$ = 0.71073)
2 $\theta$ range for data	3.882 to 50.498	3.332 to 50.498
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -23 ≤ l ≤ 23	-16 ≤ h ≤ 16, -23 ≤ k ≤ 23, -29 ≤ l ≤ 29
Reflections collected	18799	73769
Independent reflections	7506 [R <sub>int</sub> = 0.0431, R <sub>sigma</sub> = 0.0750]	24205 [R <sub>int</sub> = 0.0376, R <sub>sigma</sub> = 0.0329]
Data/restraints/paramete	7506/0/455	24205/1277/1438
Goodness-of-fit on F <sup>2</sup>	0.971	1.045
Final R indexes [I > 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0402, wR <sub>2</sub> = 0.0809	R <sub>1</sub> = 0.0395, wR <sub>2</sub> = 0.0990
Final R indexes [all data]	R <sub>1</sub> = 0.0576, wR <sub>2</sub> = 0.0858	R <sub>1</sub> = 0.0470, wR <sub>2</sub> = 0.1036
Largest diff. peak/hole / e Å <sup>-3</sup>	1.21/-0.64	1.60/-1.92

Note: Cell parameters for complex **7**: a = 10.1413 Å, b = 14.9946 Å, c = 15.8207 Å,  $\alpha$  = 86.276°,  $\beta$  = 72.712°,  $\gamma$  = 86.068°; volume = 2289.16 Å<sup>3</sup>; space group: *P* $\bar{1}$ . These parameters are preliminary and not completely refined due to poor quality of the crystals.

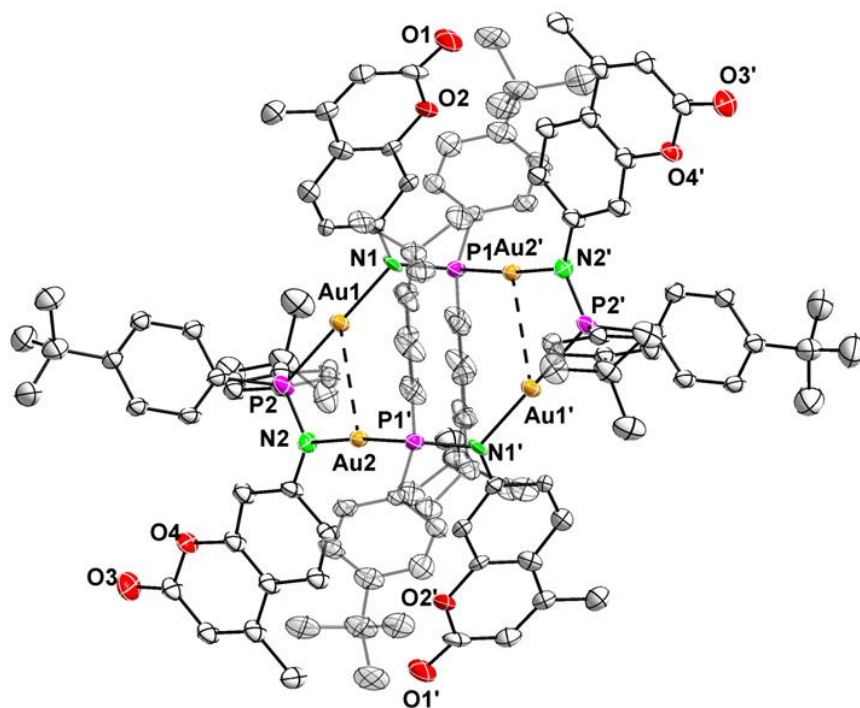
### V.3 Crystal structures



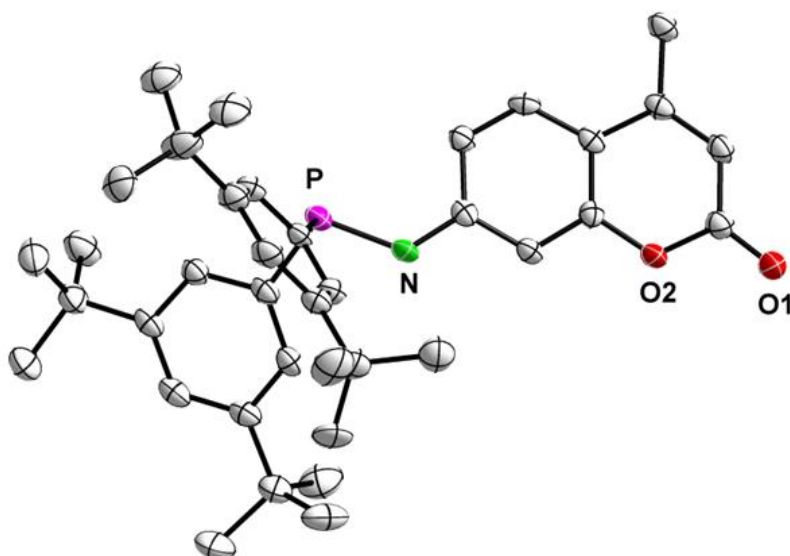
**Figure S32.** Molecular structure of ligand **1** in the solid state. Hydrogen atoms (except N-H) and non-coordinating solvents are removed for clarity. Selected bond distances (Å) and angles (°): N–P 1.7099(10); C1–N–P 123.79(8). Thermal ellipsoids are drawn at 50 % probability.



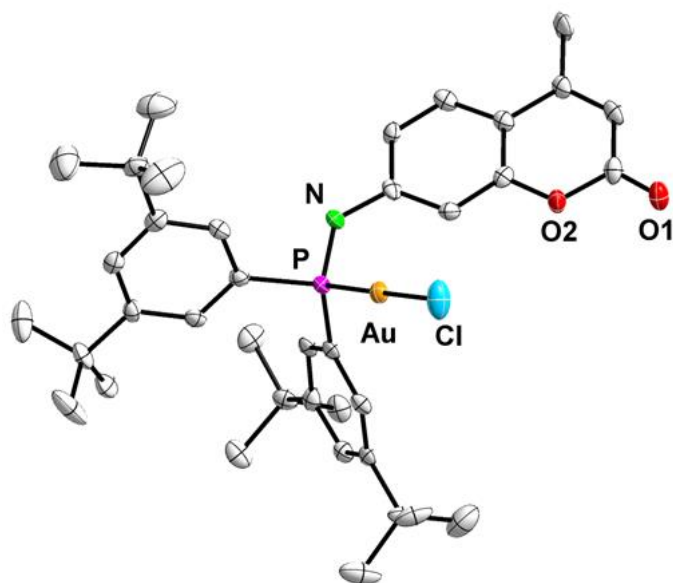
**Figure S33:** Molecular structure of complex **2** in the solid state. Hydrogen atoms and non-coordinating solvents are removed for clarity. Selected bond distances (Å) and angles (°): Au–Cl 2.2892(10), Au–P 2.2181(11), P–N 1.685(4); P–Au–Cl 178.85(4). Thermal ellipsoids are drawn at 50 % probability.



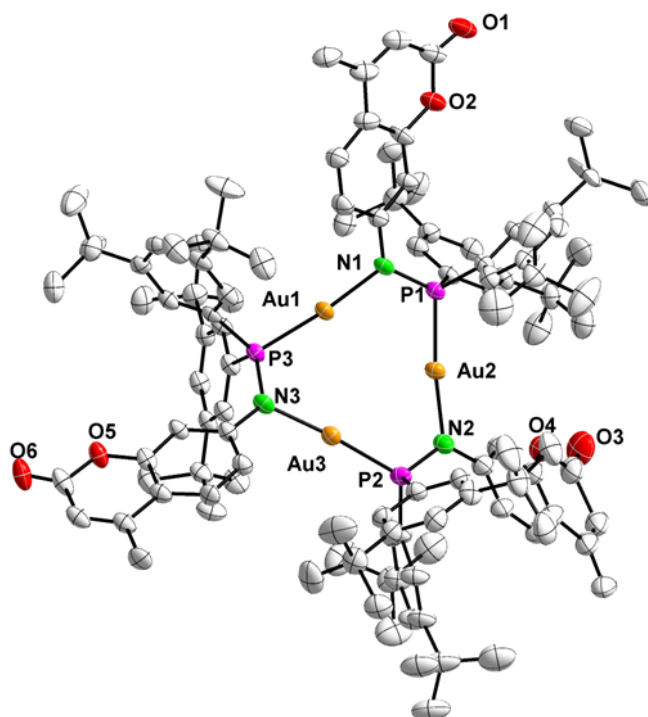
**Figure S34.** Molecular structure of polynuclear gold(I) complex **3** in the solid state. Selected bond distances (Å) and angles (°): Au1–Au2 3.2718(4), Au1–P2' 2.2253(15), P1–Au2 2.2195(15), Au1–N1 2.055(5), Au2–N2 2.072(4), N1–P1 1.632(5), N2–P2 1.655(6); P2–N2–Au2 119.7(3), P1–Au2–N2 177.4(2), P1–N1–Au1 113.8 (3), N1–Au1–P2' 175.04(14). Thermal ellipsoids are drawn at 50 % probability.



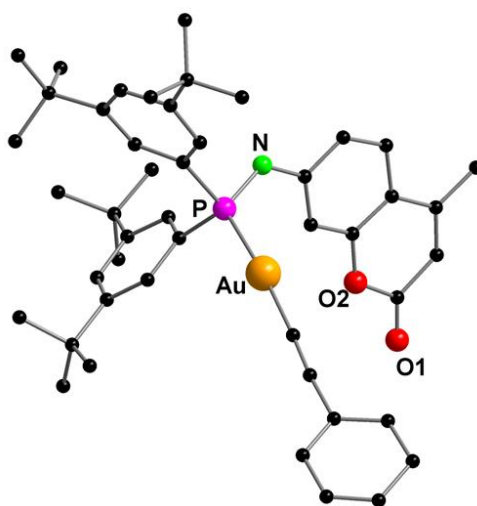
**Figure S35:** Molecular structure of ligand **4** in the solid state. Hydrogen atoms (except N-H) and non-coordinating solvents are removed for clarity. Selected bond distances (Å) and angles (°): N–P 1.705(3); C1–N–P 126.3(2). Thermal ellipsoids are drawn at 50 % probability.



**Figure S36:** Molecular structure of complex **5** in the solid state. Hydrogen atoms and non-coordinating solvents are removed for clarity. Selected bond distances (Å) and angles (°): Au–Cl 2.2742(14), Au–P 2.287(13), N–P 1.682(5); P–Au–Cl 179.26(6). Thermal ellipsoids are drawn at 50 % probability.



**Figure S37:** Molecular structure of trimeric gold(I) complex **6** in the solid state. Hydrogen atoms and non-coordinating solvents are removed for clarity. Selected bond distances (Å) and angles (°): Au1–N1 2.057(4), Au1–P3 2.2325(12), Au2–N2 2.082(4), Au2–P1 2.2414(13), Au3–N3 2.067(4), Au3–P2 2.2417(12), N1–P1 1.653(4), N2–P2 1.660(4), N3–P3 1.651(4); N1–Au1–P3 172.47(12), Au1–P3–N3 112.80(14), P3–N3–Au3 115.6(2), N3–Au3–P2 173.26(11), Au3–P2–N2 109.80(15), P2–N2–Au2 115.7, N2–Au2–P1 173.39(10), Au2–P1–N1 111.41(2), P1–N1–Au1 117.4(2). Thermal ellipsoids are drawn at 50 % probability.



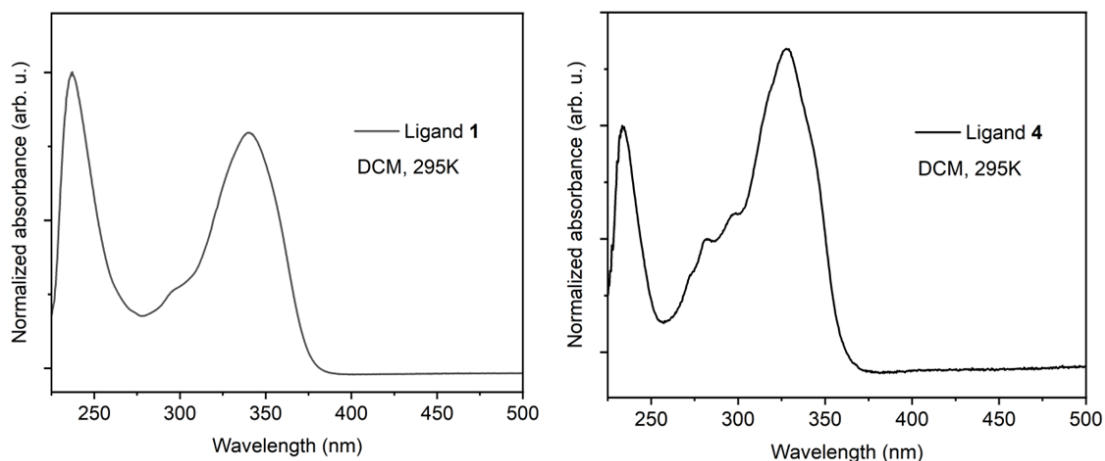
**Figure S38:** Molecular structure of the monomeric gold(I) complex **7** in the solid state.



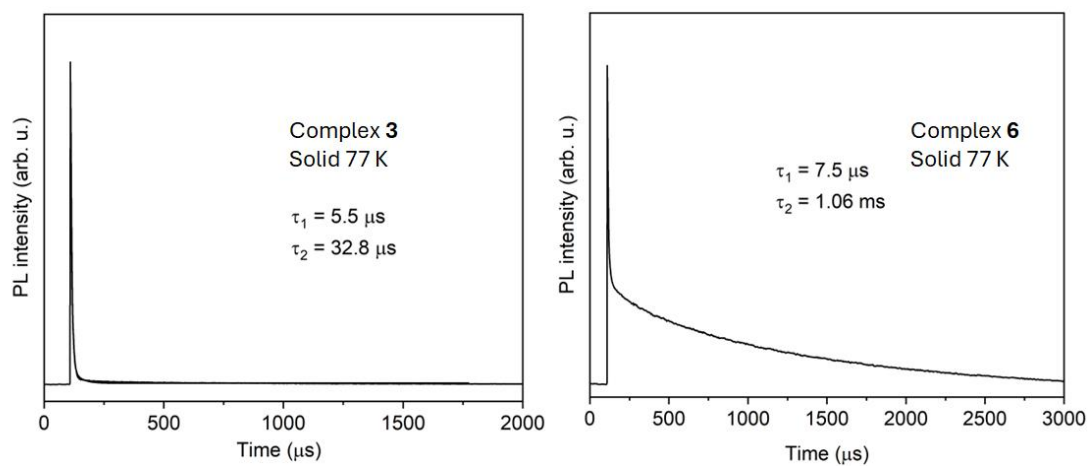
## VI. Photoluminescence data

PL measurements of the polycrystalline samples were performed with a Horiba Jobin Yvon Fluorolog-322 spectrometer, equipped with a closed-cycle optical cryostat (based on a Cryomech PT403 pulse tube cryocooler). A Hamamatsu R9910 photomultiplier (PMT) was used as a detector for the emission spectral range of about 300-830 nm. All emission spectra were corrected for the wavelength-dependent response of the spectrometer and detector (in relative photon flux units). Solid samples (crystalline powders) were measured as dispersions in a thin layer of viscous mineral oil (Sigma Aldrich) placed between two 1 mm thin quartz plates.

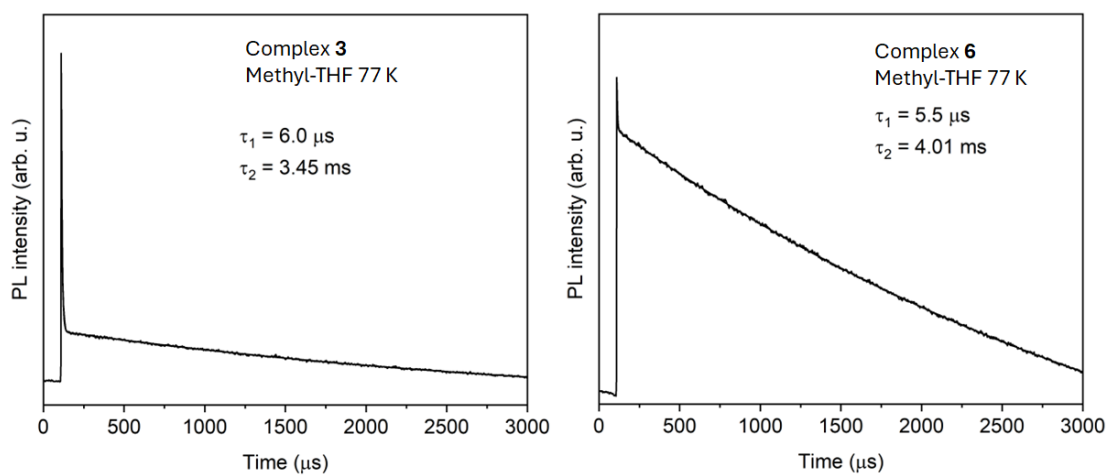
PL measurements of the solutions were carried out on a PTI QuantaMaster™ 8075-22 fluorometer with double excitation and emission monochromators (HORIBA Jobin Yvon GmbH). The samples were each sealed under inert atmosphere in NMR tubes with a J. Young valve (material Suprasil® quartz glass). The tube was placed in a glass dewar vessel (equipped with a suprasil finger on the bottom where spectroscopy takes place) which was filled with liquid nitrogen for measurements at 77 K. For emission detection, a R928 photomultiplier (250–800 nm) (HORIBA Jobin Yvon GmbH) was used. All spectra were corrected for the wavelength dependent response of the detector (in relative photon flux units) and the spectrometer. For detection of the emission decay traces, the sample was excited with either a Delta Diode™ (HORIBA Jobin Yvon GmbH, Model DD-370,  $\lambda_{exc} = 371$  nm, pulse <2 ns, 2  $\mu$ W) for fluorescence lifetimes or a PTI XenonFlash™ (set before the emission monochromators, frequency max. 300 Hz) for phosphorescence decay times. In case of using the Delta Diode, the signal was recorded until a satisfying signal-to-noise ratio was obtained. When using the Xenon Flash lamp, 10000 traces were recorded. Quantum yields were determined using integration sphere.



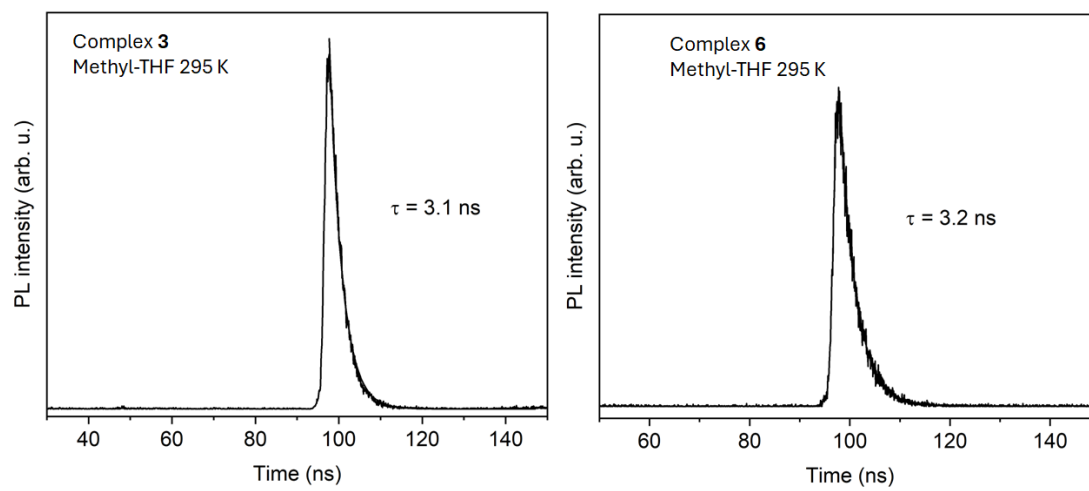
**Figure S39:** Normalized absorption spectra of ligand **1** and **4** in dichloromethane at room temperature.



**Figure S40.** Emission decay traces of solid samples of tetramer **3** and trimer **6** at 77 K.



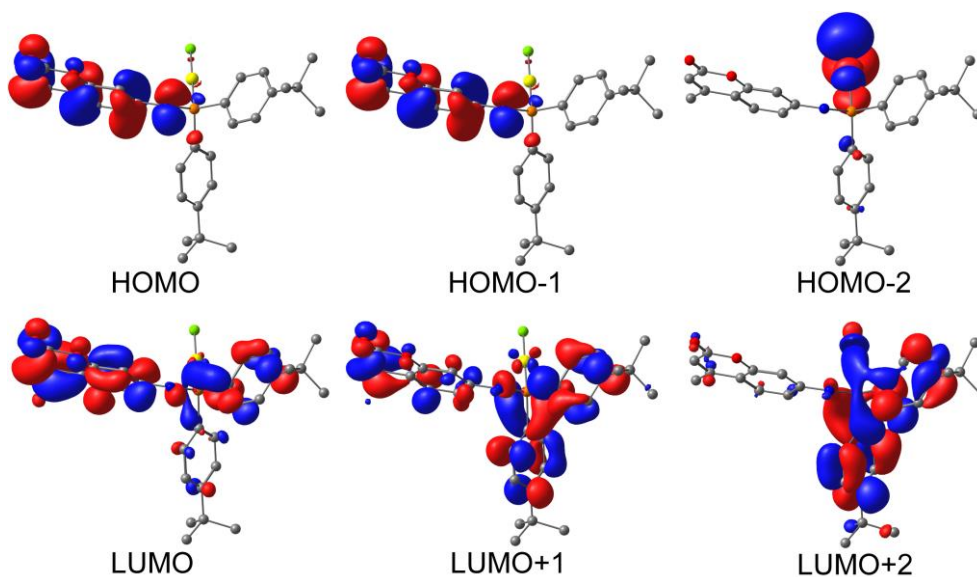
**Figure S41.** Emission decay traces of tetramer **3** and trimer **6** in frozen methyl-THF matrix at 77 K.



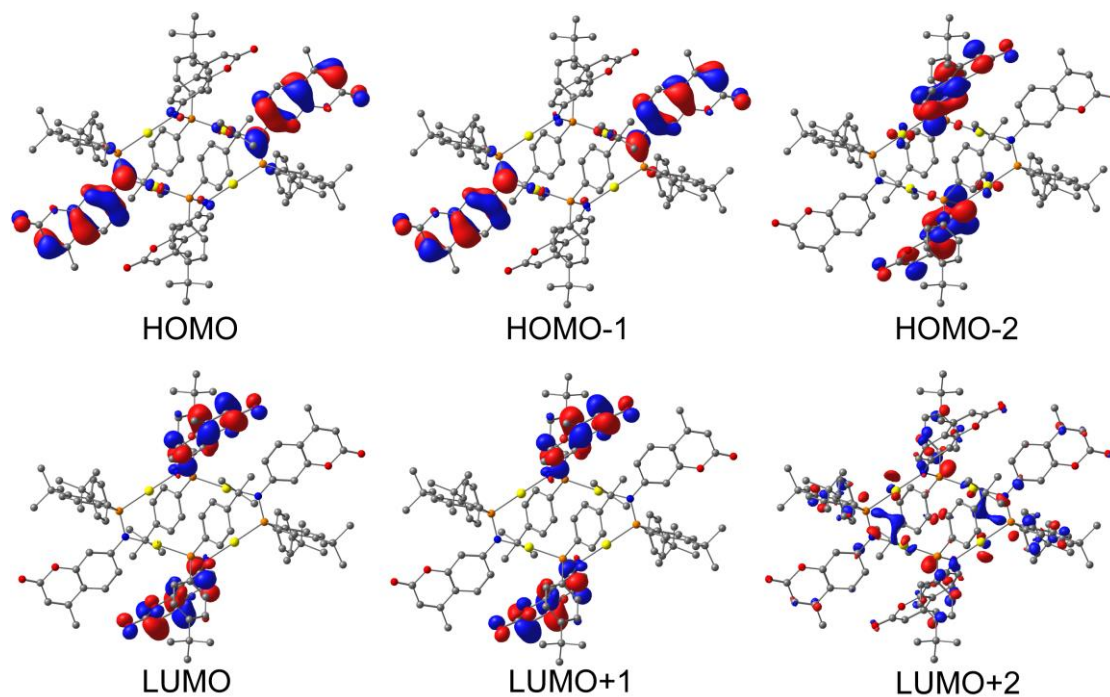
**Figure S42.** Emission decay traces of tetramer **3** and trimer **6** in methyl-THF at 295 K.

## VII. Quantum Chemical Calculations

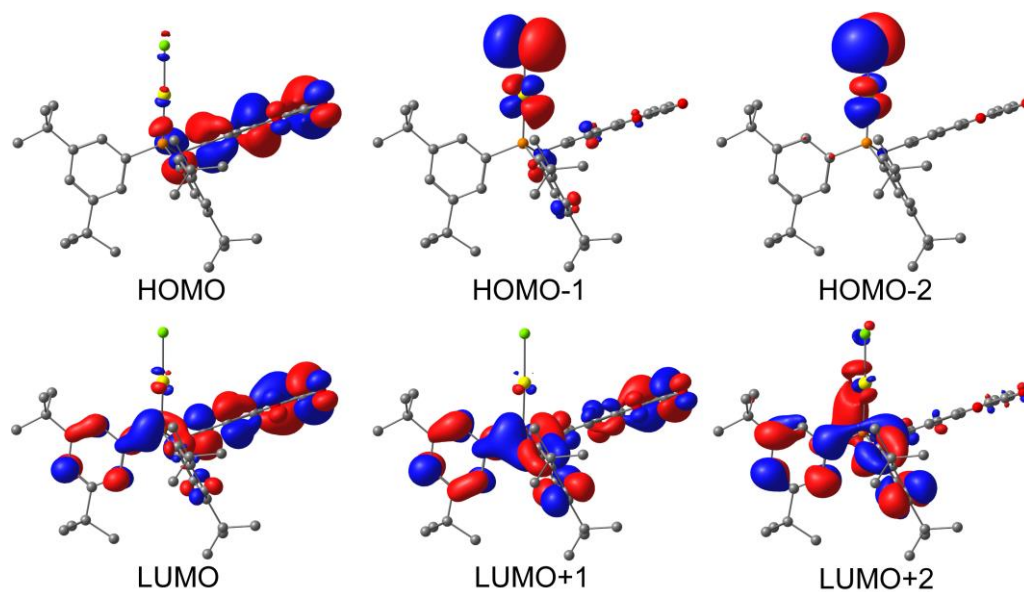
The geometry optimizations were initiated from the coordinates taken from the crystal structure of the complexes. All calculations were performed with the Gaussian 16, revision C.01, package.<sup>6</sup> The molecular geometries in the ground state ( $S_0$ ) and lowest singlet excited state ( $S_1$ ) were optimized via density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations, respectively. The spin-unrestricted DFT formalism (UDFT) was used to optimize geometries of the lowest triplet excited state ( $T_1$ ). Frequency calculations were also performed on all the optimized geometries to ensure that the optimized geometries did not have any imaginary frequencies. Geometry optimizations have been carried out using the density functional method CAM-B3LYP<sup>7</sup> functional which has been found good for long range electronic transition. The basis set was def2TZVP for the gold atom and 6-31G\*\* for C, N, O, P, Cl and H atoms. The excited singlet ( $S_n$ ) and triplet ( $T_n$ ) states were investigated using TD-DFT. Visualization of the molecular orbitals and the corresponding diagrams were done employing the Chemcraft software.<sup>8</sup>



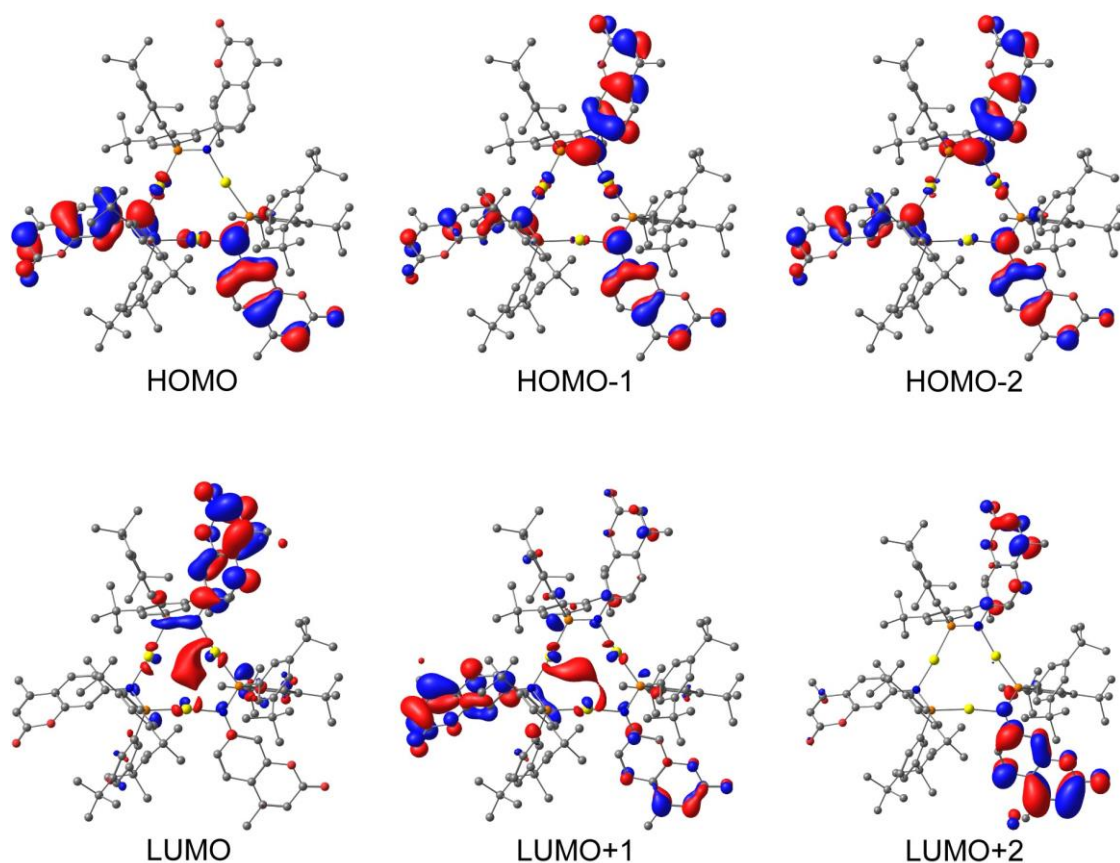
**Figure S43.** Selected Kohn-Sham orbitals of CAM-B3LYP/def2TZVP/6-31G\*\* optimized geometry of gold(I) complex **2**.



**Figure S44.** Selected Kohn-Sham orbitals of CAM-B3LYP/def2TZVP/6-31G\*\* optimized geometry of tertranuclear gold(I) complex **3**.



**Figure S45.** Selected Kohn-Sham orbitals of CAM-B3LYP/def2TZVP/6-31G\*\* optimized geometry of gold(I) complex **5**.



**Figure S46.** Selected Kohn-Sham orbitals of CAM-B3LYP/def2TZVP/6-31G\*\* optimized geometry of the trinuclear gold(I) complex **6**.

**Table S2:** TD-DFT Calculated (CAM-B3LYP/def2TZVP/6-31G\*\*) Energy Levels of  $S_1$  ( $E_{S1}$ ) and  $T_1$  ( $E_{T1}$ ) excited states and singlet-triplet Energy Gaps ( $\Delta E_{ST}$ ).

complex		$E_{S1}$	$E_{T1}$	$E_{T2}$	$E_{T3}$	$E_{T4}$	$E_{T5}$	$E_{T6}$	$E_{T7}$	$E_{T8}$	$E_{T9}$
2		2.75	1.99	2.02	2.05	2.48	3.06	3.17	3.47	3.50	3.57
	$\Delta E = E_{S1} - E_{Tn}$		0.76	0.73	0.70	0.27	-0.31	-0.42	-0.72	-0.75	-0.82
3		2.65	1.46	1.84	2.04	2.16	2.34	2.54	2.64	2.65	2.72
	$\Delta E = E_{S1} - E_{Tn}$		1.19	0.81	0.61	0.49	0.31	0.11	0.01	0.00	-0.07
5		2.75	1.29	2.01	2.30	2.75	2.77	2.92	3.08	3.11	3.17
	$\Delta E = E_{S1} - E_{Tn}$		1.46	0.74	0.45	0.00	-0.02	-0.17	-0.33	-0.36	-0.42
6		2.67	1.60	1.87	2.17	2.26	2.58	2.67	2.68	2.72	3.05
	$\Delta E = E_{S1} - E_{Tn}$		1.07	0.80	0.50	0.41	0.09	0.00	-0.01	-0.05	-0.38

**Table S3:** Selected excitation energies  $E$  (eV), wavelengths  $\lambda$  (nm) and main orbital configurations, of complexes **3** and **6** calculated with TD-DFT/CAM-B3LYP level. S1: Lowest singlet excited state, T1: lowest triplet excited state, and Tn: high-level triplet excited states, H:HOMO, L:LUMO.

Complex	ES	$E$	$\lambda$	configuration
<b>3</b>	S1	2.65	467	H-2→L+1 (33%) H-3→L (31%) H-30→L (4%)
	S18	3.39	365	H-2→L (41%) H-3→L+1 (40%) H-1→L+1 (3%)
	S21	3.87	321	H→L+3 (22%) H-1→L+5 (19%) H→L+6 (18%)
	T8	2.65	470	H-2→L+1 (65%) H-3→L (35%)
	T9	2.72	455	H-2→L+1 (5%)
<b>6</b>	S1	2.67	465	H-1→L (22%) H-2→L (20%) H-1→L+2 (6%) H-2→L+2 (5%)
	S13	3.34	371	H→L+1 (17%) H-2→L (14%) H-1→L (14%)
	S28	3.91	317	H→L (32%) H→L+3 (22%) H→L+2 (22%)
	T6	2.67	464	H-1→L+2 (15%) H-2→L (19%)
	T7	2.68	463	H-2→L+2 (20%) H-1→L+2 (7%)

## VII. References

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8. <http://www.chemcraftprog.com>.



### VIII Cartesian coordinates of the optimized geometries:

#### Complex 2 (CAMB-3LYP/6-31G\*\*/def2TZVP)

79	-0.067497814	-0.442652722	2.371794232	6	-1.973330733	-0.559586414	-0.920021707	6	0.770563531	3.458886404	-1.766950622
17	-0.652369596	-0.735107417	4.565126099	6	1.768541085	3.745099354	0.384812933	6	-3.971029814	0.529716158	-0.125652769
15	0.535959484	-0.139222020	0.204660030	6	2.473147688	-2.123714070	0.459398388	6	5.446994624	-3.395679331	-1.630131632
8	-4.835703412	-2.206987323	-2.388681082	6	-4.782627039	-0.343433650	-0.860168474	6	1.736203629	5.762435224	-1.154605923
8	-6.752422403	-3.025694616	-3.145163334	6	1.416554424	0.292012191	-0.855168495	6	-6.894816962	-1.203182389	-1.634671767
7	-0.580418768	-0.680488239	-0.975838403	6	2.003459149	-1.070025989	-0.321264624	6	3.570838381	-2.872678670	0.047589740
6	1.489421729	2.426104921	0.701003875	6	-6.234679510	-0.306618178	-0.874638710	6	5.128533601	-0.24523696	-2.998829473
2	-2.758101022	-1.436961044	-1.662764427	6	-6.219344535	-2.207155559	-2.442883618	6	-6.964936599	0.712739026	-0.051879470
6	0.853760778	1.597808840	-0.228176915	6	6.655282076	-2.451609952	-1.768334298	6	1.281751960	6.182085006	-2.557359051
6	-4.139940085	-1.319058533	-1.633024311	6	2.662582343	-0.774619944	-1.519633083	6	1.020730562	6.658075338	-0.126945185
6	0.491606756	2.129985974	-1.462585802	6	4.233299726	-2.594879189	-1.147734271	6	5.823808725	-4.520899105	-0.659510848
6	-2.593307702	0.442193133	-0.155604936	6	3.752634918	-1.528199891	-1.920041483	6	3.256688603	5.981828301	-1.054147110

#### Complex 3 (CAM-B3LYP/6-31G\*\*/def2TZVP)

79	2.577598000	1.163870000	-0.814545000	6	-2.647467000	-8.730036000	3.117963000	6	-5.380623000	-2.081356000	-0.538977000
79	2.159002000	-2.250620000	-0.376000000	6	-3.348324000	-7.501866000	5.167085000	6	-7.902459000	-1.252619000	0.185231000
15	-0.720006000	-2.454124000	1.195880000	6	8.971318000	3.208277000	0.819723000	6	-6.470970000	-2.858785000	-0.857896000
15	4.301101000	-1.522272000	-0.666861000	6	4.274353000	1.168810000	4.159945000	6	5.707612000	5.362850000	3.089696000
7	4.359178000	0.132299000	-0.468794000	6	8.863873000	4.513491000	1.550879000	6	-11.328032000	-0.958689000	0.669424000
7	0.160884000	-2.894848000	-0.179438000	6	10.163896000	2.708055000	0.430180000	6	-5.458825000	2.326966000	-0.496510000
8	-3.776416000	-4.700312000	-2.233759000	6	-0.969896000	-8.190519000	4.909545000	6	-6.682181000	2.884807000	-0.120643000
8	9.120910000	0.782031000	-0.572892000	6	9.450460000	-3.414977000	3.422363000	6	-7.510312000	3.469414000	-1.066570000
6	-0.495058000	-3.480267000	-1.257652000	6	7.550674000	-4.146448000	4.856390000	6	-7.158740000	3.523937000	-2.419527000
6	-1.837382000	-3.889505000	-1.222440000	6	8.351150000	-5.641259000	3.034000000	6	-5.920431000	2.969510000	-2.872687000
6	-2.450525000	-4.401986000	-2.356725000	6	8.110637000	-4.173127000	3.429385000	6	-5.092898000	2.383149000	-1.840968000
6	-1.770850000	-4.599891000	-3.561788000	6	4.902232000	-1.982737000	-2.332300000	6	-7.770575000	-2.459191000	-0.508522000
6	-0.412242000	-4.233166000	-3.577623000	6	4.924952000	-3.325144000	-2.731269000	6	4.526308000	5.186058000	3.282944000
6	0.202978000	-3.687449000	-2.476359000	6	5.323786000	-3.669984000	-4.011286000	6	-2.634467000	-0.360218000	-4.993374000
6	0.486281000	-1.663947000	2.305508000	6	5.705308000	-2.700696000	-4.949536000	6	2.502864000	5.155721000	4.678578000
6	0.638943000	-0.273711000	2.284036000	6	5.665122000	-1.368252000	-4.543639000	6	1.803990000	5.405938000	5.981968000
6	1.535473000	0.350425000	3.137102000	6	5.267951000	-1.010873000	-3.257082000	6	3.817656000	5.435643000	4.523222000
6	2.302505000	-0.377291000	4.055109000	6	6.521736000	-1.936809000	-7.236246000	6	2.210383000	7.679644000	-4.154730000
6	2.131740000	-1.762692000	4.077146000	6	6.141545000	-1.131460000	-6.353913000	6	-10.294973000	-1.455556000	0.293500000
6	1.240899000	-2.399523000	3.218509000	6	4.987357000	-3.887804000	-7.037064000	6	-4.044462000	0.597740000	-5.900170000
6	5.519299000	0.867211000	-0.168462000	6	7.365734000	-0.08434000	-6.244744000	6	-2.452392000	-1.317000000	-5.887006000
6	6.806513000	0.470584000	-0.533674000	79	-2.577585000	-1.163870000	0.814585000	6	2.647225000	8.730036000	-3.117963000
6	-0.500452000	-5.194970000	1.797866000	79	-2.150040000	2.250620000	0.376029000	6	3.348222000	7.501866000	-5.167085000
6	-1.174677000	-4.000517000	-2.058239000	15	0.719987000	2.454124000	-1.195799000	6	-8.971318000	-3.208277000	-0.819723000
6	-2.197912000	-4.004774000	3.003225000	15	-4.301101000	1.522272000	0.666861000	6	-4.274353000	-1.168810000	-4.159945000
6	-2.511037000	-5.171433000	3.682537000	7	-4.359178000	-0.132299000	0.468794000	6	-8.863873000	-4.513491000	-1.550879000
6	-1.863118000	-6.371823000	3.435414000	7	-0.160919000	2.898418000	0.179456000	6	-10.163896000	-2.708055000	-0.430180000
6	-0.842243000	-6.354313000	2.477493000	8	3.776423000	4.700326000	2.233600000	6	0.969896000	8.190519000	-4.909545000
6	5.380748000	2.081300000	0.538984000	8	-9.120927000	-0.782031000	0.572892000	6	-9.450460000	-3.414977000	3.422363000
6	7.902494000	1.252533000	-0.185494000	6	0.495058000	-3.480267000	1.257652000	6	1.837382000	3.889505000	1.222440000
6	6.471144000	2.858684000	0.857840000	6	1.837350000	3.889505000	1.222178000	6	-7.550674000	4.146448000	-4.856390000
6	-5.707573000	-5.362799000	-3.089960000	6	2.450542000	-4.401993000	2.356629000	6	-8.110637000	4.173127000	-3.429385000
8	11.328012000	0.958534000	-0.670037000	6	1.770916000	4.599980000	3.561718000	6	-4.920232000	-1.982737000	-2.332300000
6	5.458793000	-3.226292000	0.496598000	6	0.412318000	4.233166000	3.577622000	6	-4.920431000	3.324210000	2.731418000
6	6.682121000	-2.884843000	0.120745000	6	-0.202941000	3.687389000	2.476399000	6	-5.323888000	3.698200000	4.011447000
6	7.510263000	-3.469383000	1.066702000	6	-0.486250000	1.663965000	-2.305574000	6	-5.705394000	2.700478000	4.949647000
6	7.158726000	-3.523774000	2.419675000	6	-0.638941000	0.273733000	-2.284082000	6	-5.665175000	1.368055000	4.543686000
6	5.930441000	-2.969278000	2.782816000	6	-1.535452000	-0.35044000	-3.137165000	6	-5.267982000	1.010748000	3.257115000
6	5.092899000	-2.382895000	1.841067000	6	-2.302454000	0.377314000	-4.055201000	6	-6.521830000	1.936463000	7.236313000
6	7.770710000	2.459078000	0.507654000	6	-2.131651000	1.762707000	-4.077264000	6	-6.141642000	3.131164000	6.354064000
6	-4.526258000	-0.860110000	-3.283151000	6	-1.240809000	2.995400000	-3.218616000	6	-4.987462000	3.886757000	7.037244000
6	3.263564000	0.360250000	4.993228000	6	-5.519266000	-0.867252000	0.168417000	6	-7.365835000	4.058138000	6.244920000
6	-2.502754000	-5.155685000	-4.678687000	6	-6.806528000	-0.470642000	0.533497000				
6	-1.803830000	-5.405845000	-5.982061000	6	0.500333000	5.194968000	-1.797776000				
6	-3.817545000	-5.433824000	-4.523820000	6	1.174627000	4.000556000	-2.058157000				
6	-2.210537000	-7.679495000	4.154957000	6	2.197908000	4.004893000	-3.003095000				
6	0.1029503000	1.455412000	-0.293992000	6	2.531101000	5.171584000	-3.682362000				
6	4.044517000	-0.597690000	5.900690000	6	1.863005000	6.371934000	-3.435164000				
6	2.452589000	1.317131000	5.886840000	6	0.420289000	6.354347000	-2.477361000				

#### Complex 5 (CAM-B3LYP/6-31G\*\*/Def2TZVP)

79	0.155542327	-1.975274179	-1.517987236	6	-0.141461371	1.643551464	-1.780032201	6	1.267635623	4.107856084	2.516058947
15	-0.348570418	-0.415811886	0.053079146	6	-2.238661052	-1.548792194	0.647891656	6	0.092095803	5.790178347	1.107944968
17	0.609529084	-3.568177212	-3.098514925	6	0.483294596	3.882680460	-1.243915279	6	-0.511198544	2.224174121	-4.570682460
8	4.977482432	-0.376909980	0.187372298	6	2.750361080	-0.505568051	0.861095952	6	-3.456678412	2.722867998	3.130310059
8	7.060004879	-0.156058513	-0.543479333	6	6.338845564	-0.592184966	0.314703737	6	-4.970315488	1.107567535	4.100969000
6	0.424661729	-0.602893090	1.574013200	6	-2.574809954	0.577382100	1.436398005	6	6.379787373	-2.526179382	3.639502366
6	4.488367822	-1.498478683	2.261265536	6	-2.081597784	-0.437510376	0.606665287	6	-1.1248242019	4.498342819	-3.763042963
2	-2.960627029	-1.484262458	0.216664991	6	0.421289401	2.248763739	0.495444266	6	-6.541132034	-2.626532249	0.760387770
6	-4.693859043	-0.528910666	1.474836371	6	-5.119177642	-2.718819237	0.194971611	6	1.281774138	3.908886349	-1.341982190
6	3.487796268	-1.88044048	3.166247687	6	6.764611260	-1.331838026	1.493720395	6	-5.408926622	-2.720809091	-1.341982190
6	1.776724414	-0.902778897	1.771919331	6	-0.067968932	3.382596429	-3.669235186	6	-4.299395673	-0.041638209	0.672232201
6	0.408882323	-0.807837538	1.113139562	6	1.123145722	4.647573830	1.088175054	6	-5.667541572	2.302785243	2.067372367
6	2.160227998	-1.593803355	2.934342658	6	-4.481287171	1.63495387					

6	-5.314552988	-0.586963791	-4.510716581	6	-4.894664521	-7.896944420	0.530621125	6	-4.781939093	-0.009293332	-5.833887964
6	4.613101594	-4.824890442	5.043090098	6	-5.554063004	-6.329067533	-1.283491133	6	-5.647412357	0.583016002	-3.576658823
6	6.381894662	1.370636079	-4.364894149	6	-5.384560281	-6.468324018	0.234433251	6	-6.610724822	-1.372123448	-4.783105447
6	-2.881434411	-4.570054406	4.256358455	6	-6.759253710	-6.246757557	0.893318370	6	8.288371116	-1.257919553	-0.061101218
6	-3.582290438	-5.566059028	-5.421884528	6	-4.167280239	-0.624880383	0.899718705	6	8.256410291	-2.667983957	0.558178268
6	6.184719674	-1.045307675	-5.026342230	6	-5.235550577	-1.437281001	0.512287661	6	8.528507200	-0.220493943	1.051279335
6	-3.386936947	-3.259286885	4.886777615	6	-6.454098199	-1.361186768	1.171323352	6	9.463472698	-1.192446775	-1.043439955
6	-1.339328540	-5.561348663	-4.342029410	6	-6.696381474	-0.443940770	2.197663156	6	1.902858188	6.229609039	3.920173255
6	-1.359527151	-4.679084885	4.454795383	6	-5.629226758	0.397213435	2.555122218	8	-7.411297450	-2.237479347	0.756142212
6	-1.742308096	-4.109356011	-6.320832794	6	-4.401389593	0.307118331	1.938566899	8	-9.422510357	-3.145698480	0.944166292
6	-5.071314645	4.639980761	2.684207573	6	-8.008552558	-0.435140934	2.811415714	6	-8.317394953	0.546105100	3.903181469
6	-1.262691340	2.371193103	-5.123563177	6	-8.931514464	-1.323565080	2.383330211	6	-8.661047051	-2.297901143	1.339285164
6	-4.188932040	6.567938196	3.984828396	6	-2.676250732	7.651147832	-1.851369432	6	0.533022119	5.900278489	5.973039408
6	-4.316499074	4.286456565	5.030094129	6	-4.094462883	7.831421110	-2.421092395	6	1.778655620	3.970210176	5.014546621
6	-3.204699410	3.859126304	-5.589887933	6	-2.700576280	8.050106942	-0.370583822				
6	-0.857826267	4.697331769	-5.907175626	6	-1.701704226	8.594506504	-2.580776403				
6	-3.543473626	-5.742435763	4.989756169	6	0.985342119	5.242369015	4.664455859				