

***Supporting Information***

**Phosphate Ligands in the Gold(I)-Catalysed Activation of Enynes**

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### General methods.

All commercially available reagents were used as received and handled under air. Unless otherwise stated, all reactions were run under Ar under anhydrous conditions. CH<sub>2</sub>Cl<sub>2</sub> was dried under N<sub>2</sub> using a solvent purification system (SPS). EtOH was distilled under Ar from CaH<sub>2</sub>. All other solvents were used as received. Thin layer chromatography was carried out using TLC-aluminum sheets with 0.2 mm of silica gel (Merck GF234). Chromatography purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 μm). NMR spectra were recorded at 23 °C on a Bruker Avance 400 Ultrashield and Bruker Avance 500 Ultrashield apparatus. Mass spectra were recorded on a Waters LCT Premier (ESI) and Waters GCT (EI, CI) spectrometers. Elemental analyses were performed on a LECO CHNS 932 micro-analyzer at the Universidad Complutense de Madrid. <sup>1</sup>H NMR chemical shifts are referenced to TMS. <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts are referenced to the solvent signal. <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts are referenced to an external standard (85% aqueous H<sub>3</sub>PO<sub>4</sub>).

The following compounds have been described: **10**,<sup>1</sup> **11**,<sup>2</sup> **12**,<sup>3</sup> **13**,<sup>4</sup> **14**,<sup>4</sup> **15**,<sup>5</sup> **16**,<sup>5</sup> **20**<sup>6</sup> and **21**<sup>6</sup>.

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<sup>1</sup> B. M. Trost, and R. Braslau, *Tetrahedron Lett.*, **1988**, 29, 1231–1234.

<sup>2</sup> T. R. Hoye and J. A. Suriano, *Organometallics*, **1992**, 11, 2044–2050.

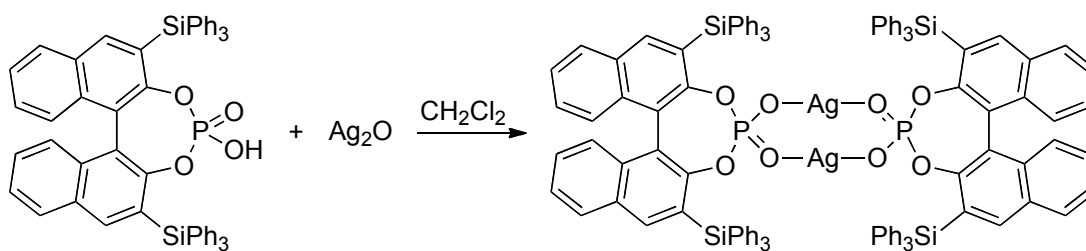
<sup>3</sup> J. W. Faller and P. P. Fontaine, *J. Org. Chem.*, **2006**, 691, 1912–1918.

<sup>4</sup> (a) C. Nieto-Oberhuber, S. Lopez and A. M. Echavarren, *J. Am. Chem. Soc.*, **2005**, 127, 6178–6179; (b) C. Nieto-Oberhuber, P. Pérez-Galán, E. Herrero-Gómez, T. Lauterbach, C. Rodríguez, S. López, C. Bour, A. Rosellón, D. J. Cárdenas and A. M. Echavarren, *J. Am. Chem. Soc.* **2008**, 130, 269–279.

<sup>5</sup> C. Nieto-Oberhuber, M. P. Muñoz, S. López, E. Jiménez-Núñez, C. Nevado, E. Herrero-Gómez, M. Raducan, and A.M. Echavarren, *Chem. Eur. J.*, **2006**, 12, 1677–1693.

<sup>6</sup> M. Méndez, M. P. Muñoz, and A. M. Echavarren, *J. Am. Chem. Soc.*, **2000**, 122, 11549–11550.

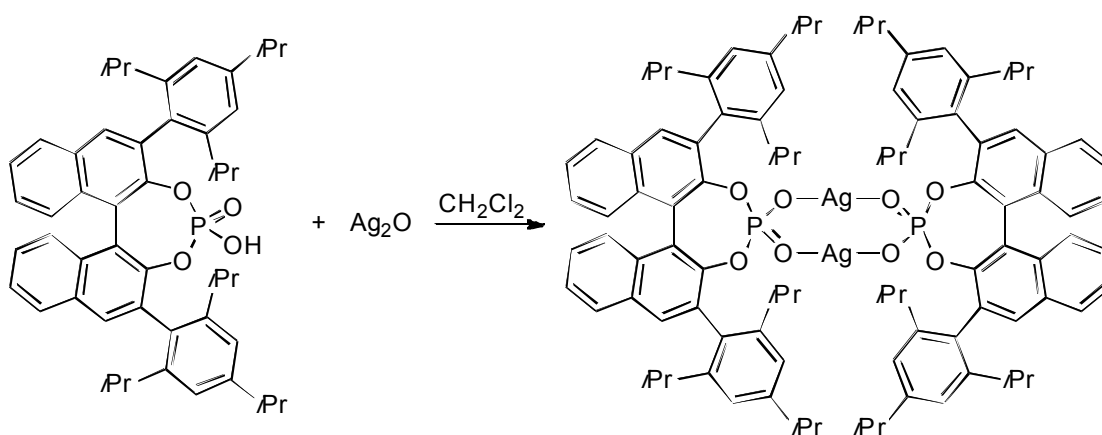
### Silver(I) Complex 5



Solid Ag<sub>2</sub>O (8.9 mg, 38 μmol) was added to a solution of the SiPh<sub>3</sub>-BINOL phosphoric acid **3** (44 mg, 51 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) and the mixture was stirred vigorously at room temperature for 4 h. The mixture was filtered into a vial through a small pad of Celite that was washed with CH<sub>2</sub>Cl<sub>2</sub> (4x1 mL). After evaporation of the solvent, the compound was precipitated from CH<sub>2</sub>Cl<sub>2</sub> (2 mL)/ MeCN (4 mL) and allowed to stand for 7 h during which time the precipitate became crystalline. Decantation and washing with MeCN (2x0.5 mL) yielded the desired compound as a off-white powder which was vacuum dried (50 °C, overnight) (46 mg, 92%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.98 (s, 4H), 7.80 (d, *J* = 8.2 Hz, 4H), 7.60-7.58 (m, 24H), 7.44 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 4H), 7.30 (ddd, *J* = 8.5, 6.7, 1.2 Hz, 4H), 7.25-7.20 (m, 16H), 7.16-7.13 (m, 24H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 152.85 (d, *J* = 9.3 Hz, C), 142.20 (C), 136.98 (CH), 135.25 (C), 134.72 (C), 130.99 (C), 128.98 (CH), 128.89 (CH), 127.78 (CH), 127.69 (CH), 127.50 (CH), 126.75 (d, *J* = 3.6 Hz, C), 125.54 (CH), 122.10 (d, *J* = 2.0 Hz, C); <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 12.7 (t, *J* = 17 Hz, 2P); MALDI-MS calcd. for C<sub>112</sub>H<sub>81</sub>Ag<sub>2</sub>O<sub>8</sub>P<sub>2</sub>Si<sub>4</sub> [M+H]<sup>+</sup>: 1943.3, found: 1943.4; other peaks: calcd. for [M+Ag]<sup>+</sup>: 2051.2, found: 2051.4; calcd. for [M/2+Ag]<sup>+</sup>: 1079.0, found: 1079.2; calcd. for [M/2+H]<sup>+</sup>: 973.1, found: 973.2.

Anal. Calcd. for C<sub>112</sub>H<sub>82</sub>Ag<sub>2</sub>O<sub>9</sub>P<sub>2</sub>Si<sub>4</sub> (M+H<sub>2</sub>O): C, 68.57; H, 4.21. Found: C, 68.69; H, 4.01.

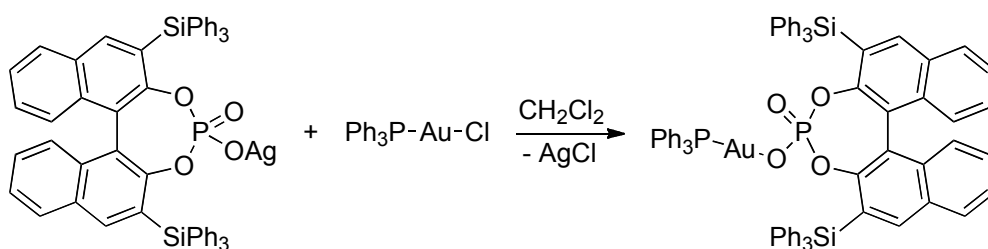
### Silver(I) Complex 6



Solid  $\text{Ag}_2\text{O}$  (21 mg, 91  $\mu\text{mol}$ ) was added to a solution of the  $i\text{Pr}_3\text{Ph}$ -BINOL phosphoric acid **4** (91 mg, 0.12 mmol) in  $\text{CH}_2\text{Cl}_2$  (2.4 mL) and the mixture was stirred vigorously at room temperature for 4 h. The mixture was filtered through a small pad of Celite, which was washed with  $\text{CH}_2\text{Cl}_2$  (5x2 mL). After evaporation of the solvent, the compound was precipitated from MeOH (1 mL)/  $\text{H}_2\text{O}$  (2 mL), filtered and washed with  $\text{H}_2\text{O}$  (2x4 mL). Vacuum drying (50  $^\circ\text{C}$ , overnight) yielded the desired compound as a white powder (77 mg, 74%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 5 mg/mL)  $\delta$  7.90 (d,  $J = 8.2$  Hz, 4H), 7.83 (s, 4H), 7.46 (ddd,  $J = 8.1, 6.0, 2.0$  Hz, 4H), 7.30-7.25 (m, 8H), 7.05 (s, 4H), 6.97 (s, 4H), 2.82 (septuplet,  $J = 7.0$  Hz, 4H), 2.68-2.61 (m, 8H), 1.21-1.13 (m, 60H), 0.93 (d,  $J = 6.8$  Hz, 12H);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  17.0 (t,  $J = 11$  Hz, 2P).

The compound is soluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{Et}_2\text{O}$ , hexane, MeCN, MeOH.  $^1\text{H}$  and  $^{31}\text{P}$  NMR data was in agreement with the literature<sup>9</sup>. Diluted solutions (5 mg/mL) in  $\text{CD}_2\text{Cl}_2$  showed a triplet that became a multiplet/broad singlet in more concentrated solutions. The  $^{31}\text{P}$  NMR spectrum in  $\text{CD}_3\text{CN}$  consisted of a broad singlet in the 238-338 K interval.

### Au(I) Complex 7



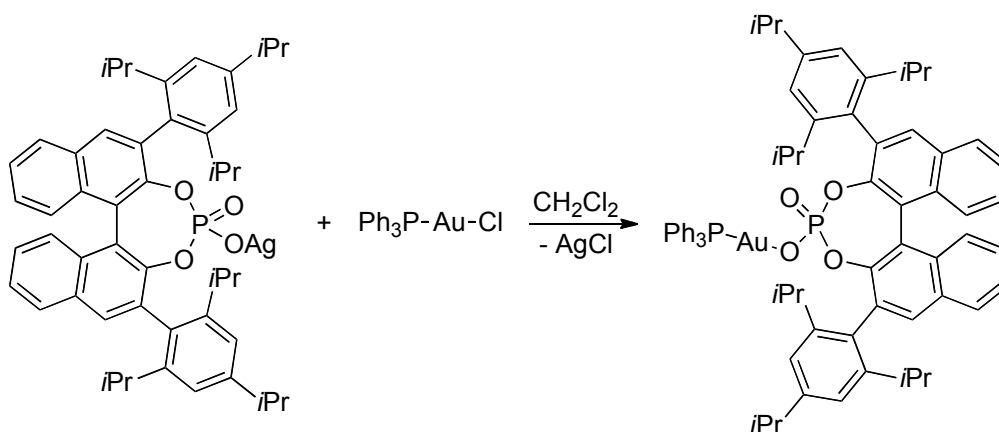
<sup>9</sup> G. L. Hamilton, E. J. Kang, M. Mba and F. D. Toste, *Science*, **2007**, 317, 496-499.

A mixture of [AuCl(PPh<sub>3</sub>)] (24 mg, 48 μmol) and silver complex **5** (39 mg, 40 μmol monomer) was stirred in CH<sub>2</sub>Cl<sub>2</sub> (1.6 mL) for 2 h. The resulting mixture was filtered through a pad of silica which was then washed with CH<sub>2</sub>Cl<sub>2</sub> (3x6.5 mL) and MeCN/CH<sub>2</sub>Cl<sub>2</sub> = 4 : 1 (2x6.5 mL). The MeCN containing washings were evaporated and vacuum dried to yield a white powder (48 mg, 90%). X-ray quality crystals were grown by layering a solution of the complex in CH<sub>2</sub>Cl<sub>2</sub> with MeOH or by layering a solution of CHCl<sub>3</sub> with EtOH.

<sup>1</sup>H{<sup>31</sup>P} NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.08 (s, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.68-7.66 (m, 12H), 7.52 (t, *J* = 7.5 Hz, 3H), 7.37 (t, *J* = 7.7 Hz, 6H), 7.30 (ddd, *J* = 8.1, 5.9, 2.1 Hz, 2H), 7.24-7.20 (m, 18H), 7.14-7.10 (m, 10H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 153.54 (d, *J* = 9.7 Hz, C), 141.67 (CH), 137.30 (CH), 135.12 (C), 134.58 (C), 134.46 (d, *J* = 13.5 Hz, CH), 132.36 (d, *J* = 2.7 Hz, CH), 130.63 (d, *J* = 1.0 Hz, C), 129.65 (CH), 129.43 (d, *J* = 12.1 Hz, CH), 128.74 (CH), 128.43 (d, *J* = 66.1 Hz, C), 127.94 (CH), 127.23 (CH), 127.11 (d, *J* = 3.1 Hz, C), 127.01 (CH), 125.07 (CH), 122.45 (d, *J* = 2.2 Hz, C); <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 29.8 (d, *J* = 3.6 Hz, 1P), 8.2 (d, *J* = 3.6 Hz, 1P); MALDI MS *m/z*: 1782.3 (calcd for [M + Au(PPh<sub>3</sub>)]<sup>+</sup>: 1782.3), 1417.1, 1409.1, 1322.3 (calcd for [M]<sup>+</sup>: 1322.3), 1260.1, 1245.2, 1066.1, 721.1, 645.1; HRMS calcd. for C<sub>74</sub>H<sub>55</sub>AuO<sub>4</sub>P<sub>2</sub>Si<sub>2</sub><sup>+</sup> [M]<sup>+</sup>: 1322.2774, found: 1322.2784.

Anal. calcd. for: C<sub>148</sub>H<sub>116</sub>Au<sub>2</sub>O<sub>11</sub>P<sub>4</sub>Si<sub>4</sub> (2M + 3H<sub>2</sub>O): C, 65.82; H, 4.33. Found: C, 65.78; H, 4.30.

### Au(I) Complex **8**



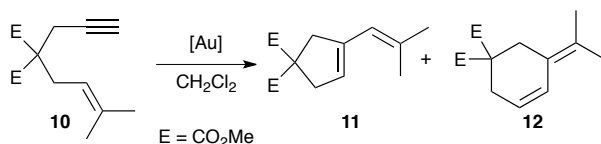
A mixture of [AuCl(PPh<sub>3</sub>)] (21 mg, 42 μmol) and silver complex **6** (30 mg, 35 μmol monomer) was stirred in CH<sub>2</sub>Cl<sub>2</sub> (1.4 mL) for 2 h. The resulting mixture was applied over a pad of silica and separated by flash chromatography (CH<sub>2</sub>Cl<sub>2</sub> to MeCN). After

vacuum drying (65 °C, 4 h), the desired complex was obtained as a white powder (42 mg, 98%).

$^1\text{H}\{^{31}\text{P}\}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.84 (d,  $J$  = 8.2 Hz, 2H), 7.79 (s, 2H), 7.52-7.47 (m, 3H), 7.39-7.35 (m, 8H), 7.24-7.12 (m, 12H), 7.03 (d,  $J$  = 1.6 Hz, 2H), 2.96 (br m, 2H), 2.88 (septuplet,  $J$  = 7.0 Hz, 2H), 2.67 (septuplet,  $J$  = 6.8 Hz, 2H), 1.27-1.24 (m, 18H), 1.17 (d,  $J$  = 6.8 Hz, 6H), 1.01 (d,  $J$  = 6.8 Hz, 6H), 0.88 (d,  $J$  = 6.8 Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  148.61 (C), 148.24 (br s, C), 148.04 (d,  $J$  = 9.2 Hz, C), 147.65 (br s, C), 134.35 (d,  $J$  = 13.6 Hz, CH), 133.13 (br s, C), 132.85 (C), 132.50 (CH), 132.35 (d,  $J$  = 2.7 Hz, CH), 130.98 (C), 129.49 (d,  $J$  = 12.1 Hz, CH), 128.43 (CH), 128.36 (d,  $J$  = 66.6 Hz, C), 127.42 (CH), 126.18 (CH), 125.34 (CH), 122.78 (d,  $J$  = 2.0 Hz, C), 121.66 (CH), 120.61 (CH), 34.61 (CH), 31.68 (br s, CH), 31.29 (CH), 26.61 ( $\text{CH}_3$ ), 24.97 ( $\text{CH}_3$ ), 24.28 ( $\text{CH}_3$ ), 24.13 ( $\text{CH}_3$ ), 24.04 (br s,  $\text{CH}_3$ ), 23.58 (br s,  $\text{CH}_3$ );  $^{31}\text{P}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ , -40 °C)  $\delta$  29.8 (d,  $J$  = 2.6 Hz, 1P), 10.1 (d,  $J$  = 2.6 Hz, 1P); HRMS calcd for  $\text{C}_{68}\text{H}_{71}\text{AuO}_4\text{P}_2^+ [\text{M}]^+$ : 1210.4488, found: 1210.4419; MALDI MS  $m/z$ : 1669.5 (calcd for  $[\text{M} + \text{Au}(\text{PPh}_3)]^+$ : 1669.5), 1417.2, 1409.1, 1227.2, 1210.4 (calcd for  $[\text{M}]^+$ : 1210.4), 1168.3, 1067.1, 1034.2, 721.1, 710.2.

Anal. calcd. for:  $\text{C}_{68}\text{H}_{71}\text{AuO}_4\text{P}_2$ : C, 67.43; H, 5.91. Found: C, 67.56; H, 5.99.

### Reaction of 1,6-enyne **10** with gold catalyst **7**



1,6-Enyne **10** (24 mg, 0.10 mmol) was added to a solution of **7** (6.6 mg, 5  $\mu\text{mol}$ ) and  $[\text{Ag}(\text{NCOMe})_2](\text{SbF}_6)$  (2.1 mg, 5  $\mu\text{mol}$ ) in  $\text{CD}_2\text{Cl}_2$  (0.5 mL). The progress of the reaction was monitored by  $^1\text{H}$  NMR. Conversion after 20 min: 100%, ratio **11:12** = 89 : 11.

*Control reaction performed in the absence of the gold complex.*

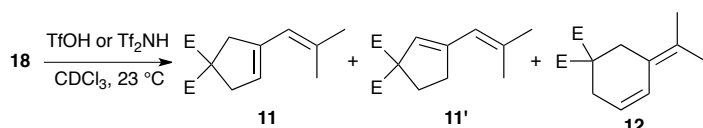
1,6-Enyne **10** (24 mg, 0.10 mmol) was dissolved in  $\text{CD}_2\text{Cl}_2$  (0.5 mL) and  $[\text{Ag}(\text{NCOMe})_2](\text{SbF}_6)$  (2.1 mg, 5  $\mu\text{mol}$ ) was added. The progress of the reaction was monitored by  $^1\text{H}$  NMR. Conversion after 20 min: 9%, ratio **11:12** = 45 : 55. Isolated yield = 6%.

A trace of hydroxycyclization (**20**) product<sup>6</sup> (3%) was also observed in both experiments.

*Control reaction performed with gold complex [Au(PPh<sub>3</sub>)(MeCN)](SbF<sub>6</sub>)*

[Au(PPh<sub>3</sub>)(MeCN)](SbF<sub>6</sub>) (2.8 mg, 5.25 μmol) was dissolved in CDCl<sub>3</sub> (0.5 mL). Then, enyne **10** (25 mg, 0.105 mmol) was added. <sup>1</sup>H NMR (5.5 h reaction time) showed a 1 : 2 : 1 mixture of **11** / **11'** / **12**. When (1 mol%) of [Au(PPh<sub>3</sub>)(MeCN)]SbF<sub>6</sub> was used, **11**, **11'**, and **12** (2:1:1 ratio) were obtained quantitatively in only 30 min. Identical results were obtained with [Au(NTf<sub>2</sub>)(PPh<sub>3</sub>)] (1 mol%).

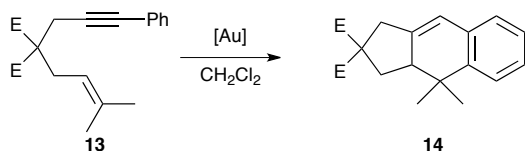
**Reaction of alkynyl gold(I) complex **18** with acids.**



Complex **18** (10 mg, 14.4 μmol) was dissolved in CDCl<sub>3</sub> (0.4 mL). Then, TfOH was added (1.3 μL, 14.4 μmol). <sup>1</sup>H NMR (30 min reaction time) showed a 4 : 4 : 1 mixture of **11** / **11'** / **12** (86%).

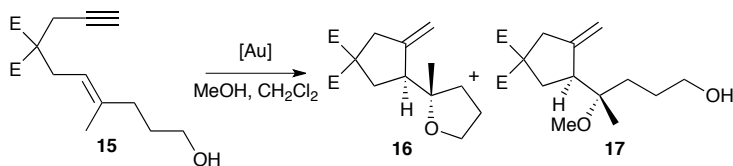
Complex **18** (10 mg, 14.4 μmol) was dissolved in CDCl<sub>3</sub> (0.4 mL). Then, Tf<sub>2</sub>NH was added (4.0 mg, 14.4 μmol). <sup>1</sup>H NMR (90 min reaction time) showed a 3 : 3 : 1 mixture of **11** / **11'** / **12** (80%).

**Reaction of 1,6-enyne **13** with gold catalyst **5**.**



Reaction of **13** with gold(I) complex **7** (5 mol%) and [Ag(NCMe)<sub>2</sub>]SbF<sub>6</sub><sup>10</sup> (5 mol%) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature for 6 h gave tricyclic compound **14**<sup>4</sup> (81%, < 1% ee).

**(R\*)-Dimethyl 3-methylene-4-((R\*)-2-methyltetrahydrofuran-2-yl)cyclopentane-1,1-dicarboxylate (**16**) and (R\*)-Dimethyl-3-((R\*)-5-hydroxy-2-methoxypentan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (**17**).**

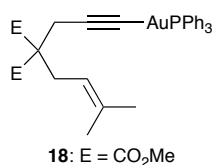


<sup>10</sup> M. Raducan, C. Rodríguez-Esrich, X. C. Cambeiro, E. Escudero-Adán, M. A. Pericàs and A. M. Echavarren, *Chem. Commun.*, **2011**, 47, 4893–4895.

A solution of enynol **15** (25 mg, 0.089 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.15 mL) was added to a solution of gold(I) complex **7** (5.9 mg, 4.43 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.15 mL). Then, MeOH (0.20 mL) was added and the mixture was stirred at room temperature for 24 h. The resulting mixture was filtered over a small pad of silica, the solvent was evaporated and the residue was chromatographed (hexane/EtOAc) to give known compound **16**<sup>s</sup> (4.8 mg, 19%) and **17** (12.4 mg, 44%).

**17**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.05 (s, 1H), 4.93 (s, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.68-3.59 (m, 2H), 3.19 (s, 2H), 2.98 – 2.84 (m, 2H), 2.61 – 2.47 (m, 1H), 2.24 – 1.86 (m, 2H), 1.27 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.98 (C), 171.86 (C), 147.91 (C), 110.76 (CH<sub>2</sub>), 78.48(C), 63.30 (CH<sub>2</sub>), 58.54 (C), 52.74 (C), 48.87 (CH<sub>3</sub>), 47.24 (CH<sub>3</sub>), 43.68 (CH<sub>2</sub>), 35.65 (CH<sub>2</sub>), 31.29 (CH<sub>3</sub>), 29.70 (CH<sub>2</sub>), 26.65 (CH<sub>2</sub>), 19.72 (CH<sub>2</sub>), 17.54 (CH<sub>3</sub>). HRMS-EI *m/z* calcd. for C<sub>16</sub>H<sub>26</sub>O<sub>6</sub>Na: 337.1627; found 337. 1618 [M+Na]<sup>+</sup>.

**(4,4-Bis(methoxycarbonyl)-7-methyl-6-octen-1-ynyl)(triphenylphosphine)gold (18).**



To a suspension of [AuCl(PPh<sub>3</sub>)] (100 mg, 0.202 mmol) in dry ethanol (4 mL) was added NaOEt [freshly prepared from Na (5 mg, 0.212 mmol) in ethanol (0.5 mL)] and enyne **10** (48 mg, 0.202 mmol). The solution was stirred at room temperature for 4.5 h. The solvent was partially evaporated, after which the white precipitate was filtered to give **18** (54 mg, 38% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.54 – 7.46 (m, 9H), 7.45 – 7.40 (m, 6H), 5.06-5.01 (m, 1H), 3.72 (s, 6H), 2.99 (d, *J* = 1.9 Hz, 2H), 2.91-2.87 (m, 2H), 1.67 (s, 3H), 1.68 (m, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 171.23 (C), 135.93 (C), 134.36 (CH), 134.25 (CH), 131.43 (CH), 131.41 (CH), 130.21 (C), 129.77 (C), 129.10 (CH), 129.01 (CH), 117.84 (CH), 98.25 (C), 98.03 (C), 57.86 (C), 52.51 (CH<sub>3</sub>), 30.88 (CH<sub>2</sub>), 26.06 (CH<sub>3</sub>), 24.17 (CH<sub>2</sub>), 18.02 (CH<sub>3</sub>). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 42.12. HRMS-EI *m/z* calcd. for C<sub>31</sub>H<sub>33</sub>O<sub>4</sub>PAu: 697.1782; found 697.1774 [M+H]<sup>+</sup>.

**Hydration of 1-octyne**

The gold phosphate complex **7** or **8** (5 μmol) was dissolved in CD<sub>3</sub>OD (0.5 mL) then 1-octyne (75 μL, 0.50 mmol) and D<sub>2</sub>O (36 μL, 2.0 mmol) were added. The reaction was



followed by  $^1\text{H}$  and  $^{31}\text{P}$  NMR. After 14 h deuteration of the alkyne proton was observed. In the case of complex **7** additional  $\text{CD}_2\text{Cl}_2$  (0.25 mL) was added in order to dissolve the gold complex. Conversions were determined by  $^1\text{H}$  NMR at 14 h, 42 h and 67 h.

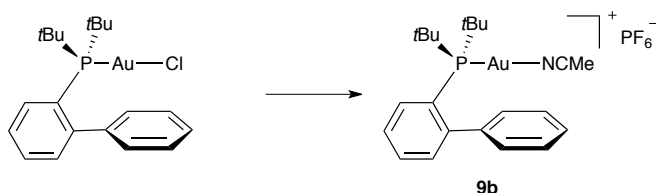
### Synthesis of gold complex [Au(OPOF<sub>2</sub>)(PPh<sub>3</sub>)] **19**.



$\text{PPh}_3\text{AuCl}$  (0.100 g, 0.202 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (10 mL). Then, solid  $\text{AgPF}_6$  (51.1 mg, 0.202 mmol) was added. The mixture was stirred at room temperature for 2.5 hours. The solution was filtered through a Celite pad and washed with  $\text{CH}_2\text{Cl}_2$ . The filtrate was concentrated to give **19** as a white solid (0.112 g, 99%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 – 7.44 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.16, 134.03, 132.46, 132.43, 129.51, 129.38, 127.82, 127.15.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  45.17 (s), 27.53 (s), -13.23 (t,  $J = 974.4$  Hz). Anal. Calcd. for  $\text{C}_{18}\text{H}_{15}\text{AuF}_2\text{O}_2\text{P}_2$ : C, 38.59; H, 2.70. Found: C, 38.67; H, 2.88.

In Chung's original report the difluorophosphate signal appeared at  $\delta$  -20.1 (t,  $J(^{31}\text{P}-^{19}\text{F}) = 972$  Hz).<sup>11</sup>

### Synthesis of gold complex **9b**.

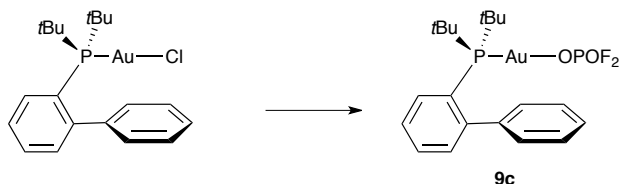


Chloro[(1,1'-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) (50 mg, 0.094 mmol) was dissolved in wet MeCN (0.75 mL). Then, solid  $\text{AgPF}_6$  (23.8 mg, 0.094 mmol) was added. The mixture was stirred at room temperature for 24 hours. The solution was filtered through a Celite pad and washed with MeCN. The filtrate was concentrated to give **9b** as a dark white solid (56 mg, 87%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 – 7.82 (m, 1H), 7.60 – 7.51 (m, 5H), 7.32 (ddd,  $J = 4.5, 3.6, 1.9$  Hz, 1H), 7.16 (dd,  $J = 7.8, 1.5$  Hz, 2H), 2.33 (s, 3H), 1.43 (s, 9H), 1.39 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  133.30, 133.22, 132.86, 131.28, 129.31, 128.97, 128.32, 128.24, 127.31, 127.24, 127.18, 38.14,

<sup>11</sup> S. M. Kim, J. H. Park and Y K. Chung, *Chem. Commun.*, **2011**, 47, 6717-6719.

37.86, 30.84, 30.78.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  57.23 (s), -144.23 (sept.,  $J = 711.9$  Hz).

### Synthesis of gold complex **9c**.

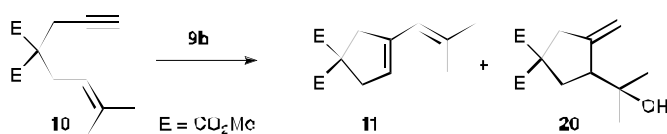


Chloro[(1,1'-biphenyl-2-yl)di-tert-butylphosphine]gold(I) (50 mg, 0.094 mmol) was dissolved in wet  $\text{CH}_2\text{Cl}_2$  (4.7 mL). Then, solid  $\text{AgPF}_6$  was added. The mixture was stirred at room temperature for 24 hours. The solution was filtered through a Celite pad and washed with  $\text{CH}_2\text{Cl}_2$ . The filtrate was concentrated to give **9c** as a white solid (53.5 mg, 90%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 – 7.83 (m, 1H), 7.58 – 7.43 (m, 5H), 7.36 – 7.31 (m, 1H), 7.15 (d,  $J = 7.2$  Hz, 2H), 1.42 (s, 9H), 1.38 (s, 8H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  133.19, 133.12, 132.81, 131.01, 129.17, 129.09, 128.93, 128.68, 128.63, 128.55, 38.06, 37.77, 30.85, 30.79.  $^{31}\text{P}$  NMR (202 MHz,  $\text{CDCl}_3$ )  $\delta$  56.62 (s), -13.49 (t,  $J = 971.5$  Hz).

### Reaction of 1,6-enyne **10** with **19**.

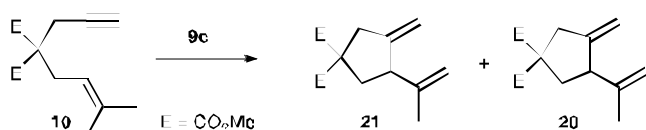
Complex **19** (3 mg, 5.25  $\mu\text{mol}$ ) was dissolved in  $\text{CDCl}_3$  (0.5 mL). Then, enyne **10** (25 mg, 0.105 mmol) was added. Conversion after 20 min: 7%.

### Reaction of 1,6-enyne **10** with **9b**.



Gold complex **9b** (3.6 mg, 5.25  $\mu\text{mol}$ ) was dissolved in  $\text{CDCl}_3$  (0.5 mL). Then, enyne **10** (25 mg, 0.105 mmol) was added.  $^1\text{H}$  NMR (35 min reaction time) showed a 7 : 1 mixture of **11** / **20**. A trace of compound **12** (3%) was also observed.

### Reaction of 1,6-enyne **10** with **9c**.



Gold complex **9c** (3.1 mg, 5.25  $\mu\text{mol}$ ) was dissolved in  $\text{CDCl}_3$  (0.5 mL). Then, enyne **10** (25 mg, 0.105 mmol) was added.  $^1\text{H}$  NMR (17 hours reaction time) showed a 1 : 1 mixture of **21** / **20**. A trace of compound **11** (5%) was also observed.

#### Reaction of 1,6-enyne **10** with acids.

Enyne **10** (0.105 mmol, 25 mg) was dissolved in  $\text{CDCl}_3$  (0.5 mL). Then, TfOH (1.05  $\mu\text{mol}$ ,  $9.3 \cdot 10^{-2}$   $\mu\text{mL}$ ) was added.  $^1\text{H}$  NMR (24 hours reaction time) showed no reaction.

Enyne **10** (0.105 mmol, 25 mg) was dissolved in  $\text{CDCl}_3$  (0.5 mL). Then, Tf<sub>2</sub>NH (1.05  $\mu\text{mol}$ ,  $3.0 \cdot 10^{-2}$   $\mu\text{mL}$ ) was added.  $^1\text{H}$  NMR (24 hours reaction time) showed no reaction.

Enyne **10** (0.105 mmol, 25 mg) was dissolved in  $\text{CDCl}_3$  (0.5 mL). Then, HBF<sub>4</sub> (1.05  $\mu\text{mol}$ ,  $6.6 \cdot 10^{-2}$   $\mu\text{mL}$ ) was added.  $^1\text{H}$  NMR (24 hours reaction time) showed no reaction.

#### Reaction of 1,6-enyne **13** with acids.

Enyne **13** (0.080 mmol, 25 mg) was dissolved in  $\text{CDCl}_3$  (0.38 mL). Then, TfOH (1.05  $\mu\text{mol}$ ,  $3.5 \cdot 10^{-1}$   $\mu\text{mL}$ ) was added.  $^1\text{H}$  NMR (24 hours reaction time) showed no reaction.

Enyne **13** (0.080 mmol, 25 mg) was dissolved in  $\text{CDCl}_3$  (0.38 mL). Then, Tf<sub>2</sub>NH (1.05  $\mu\text{mol}$ ,  $1.1 \cdot 10^{-1}$   $\mu\text{mL}$ ) was added.  $^1\text{H}$  NMR (24 hours reaction time) showed no reaction.

Enyne **13** (0.080 mmol, 25 mg) was dissolved in  $\text{CDCl}_3$  (0.38 mL). Then, HBF<sub>4</sub> (1.05  $\mu\text{mol}$ ,  $2.5 \cdot 10^{-1}$   $\mu\text{mL}$ ) was added.  $^1\text{H}$  NMR (24 hours reaction time) showed no reaction.

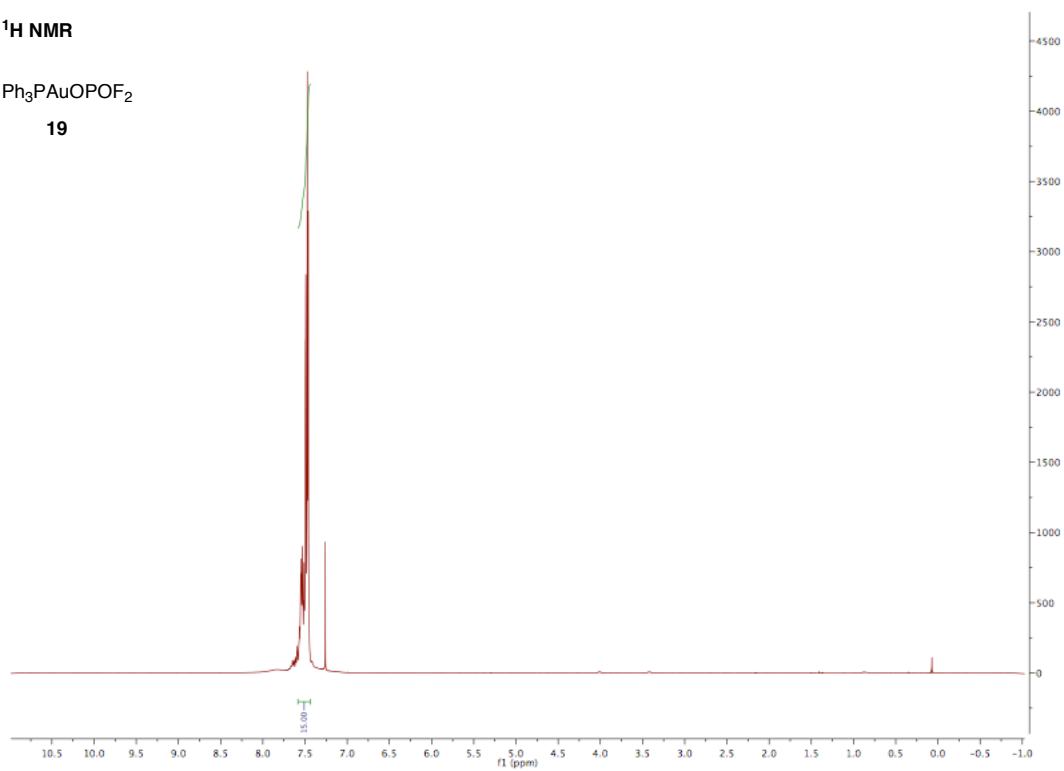
#### Reaction of 1,6-enyne **10** with [Au(NTf<sub>2</sub>)(PPh<sub>3</sub>)]

Complex PPh<sub>3</sub>AuNTf<sub>2</sub> (0.8 mg, 1.05  $\mu\text{mol}$ ) was dissolved in  $\text{CDCl}_3$  (0.5 mL) and 2,6-di-*tert*-butylpyridine was added (0.24  $\mu\text{L}$ , 1.05  $\mu\text{mol}$ ). Then enyne **10** (25 mg, 0.105 mmol) was added.  $^1\text{H}$  NMR (2 hours reaction time) showed a 4 : 1 : 2 mixture of **11** / **12** / **20**.

**<sup>1</sup>H NMR**

Ph<sub>3</sub>PAuOPOF<sub>2</sub>

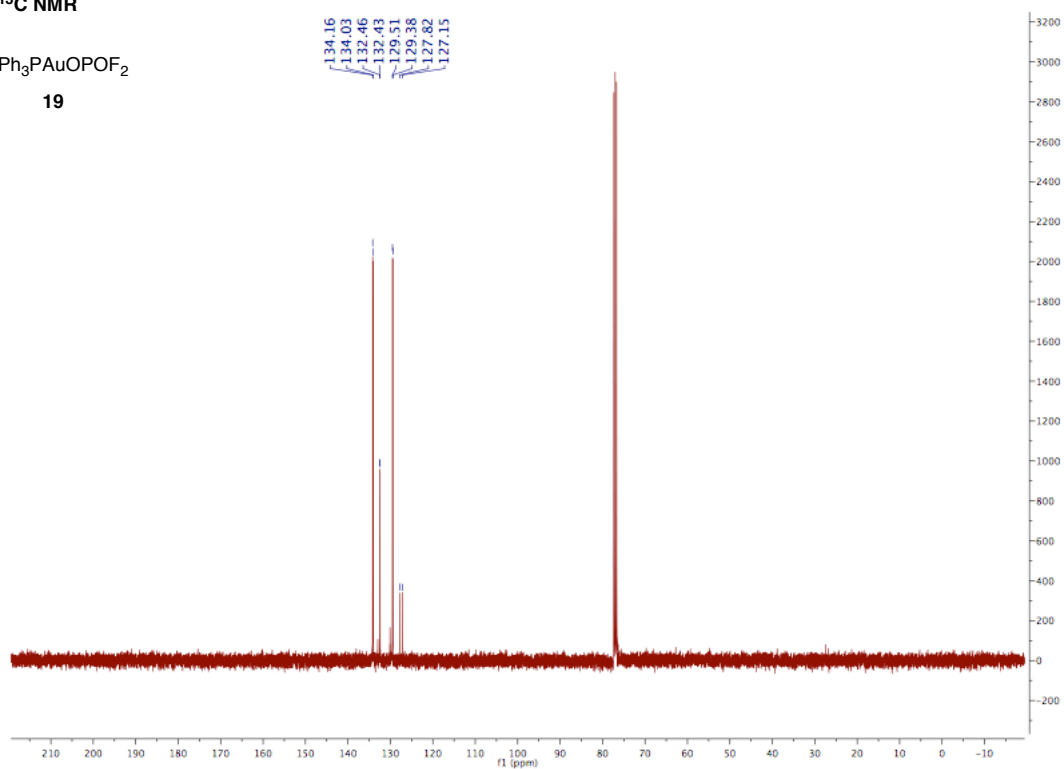
**19**

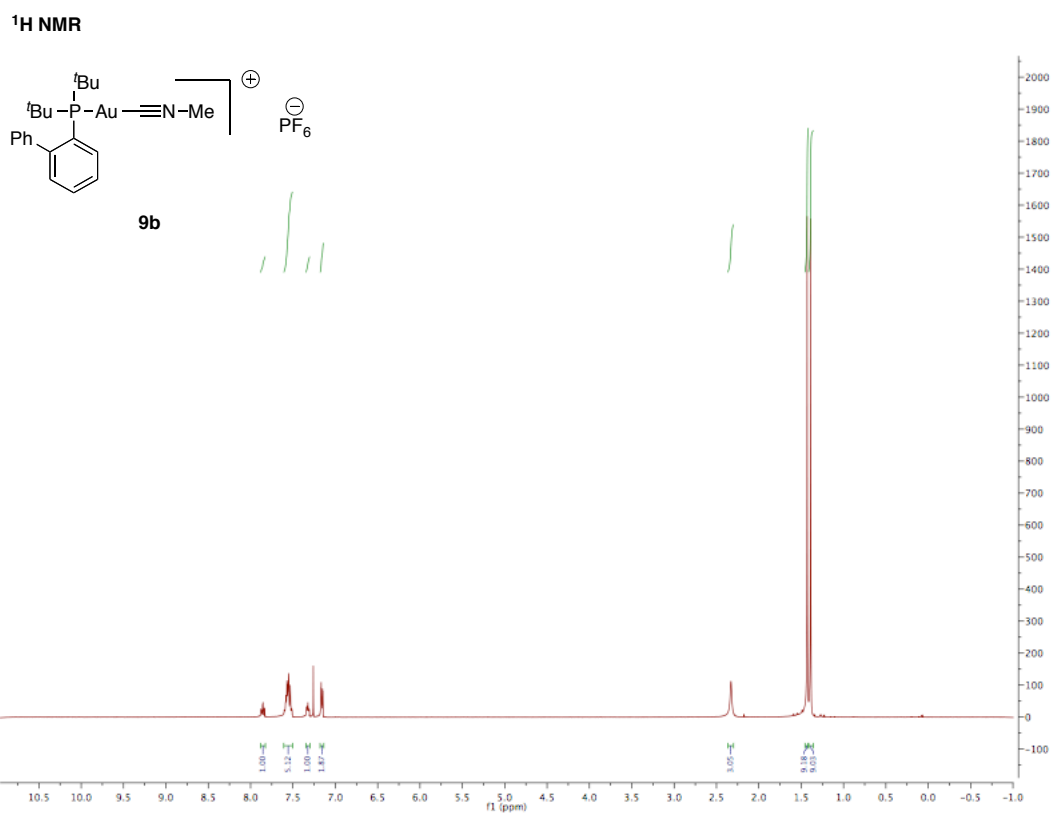
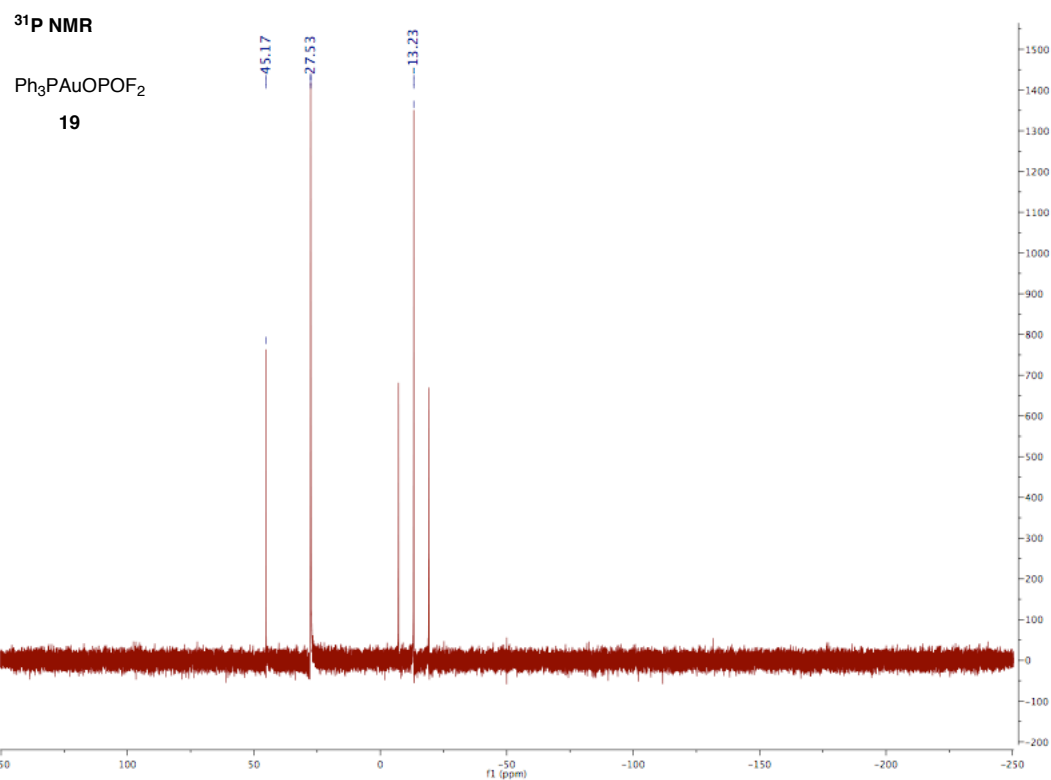


**<sup>13</sup>C NMR**

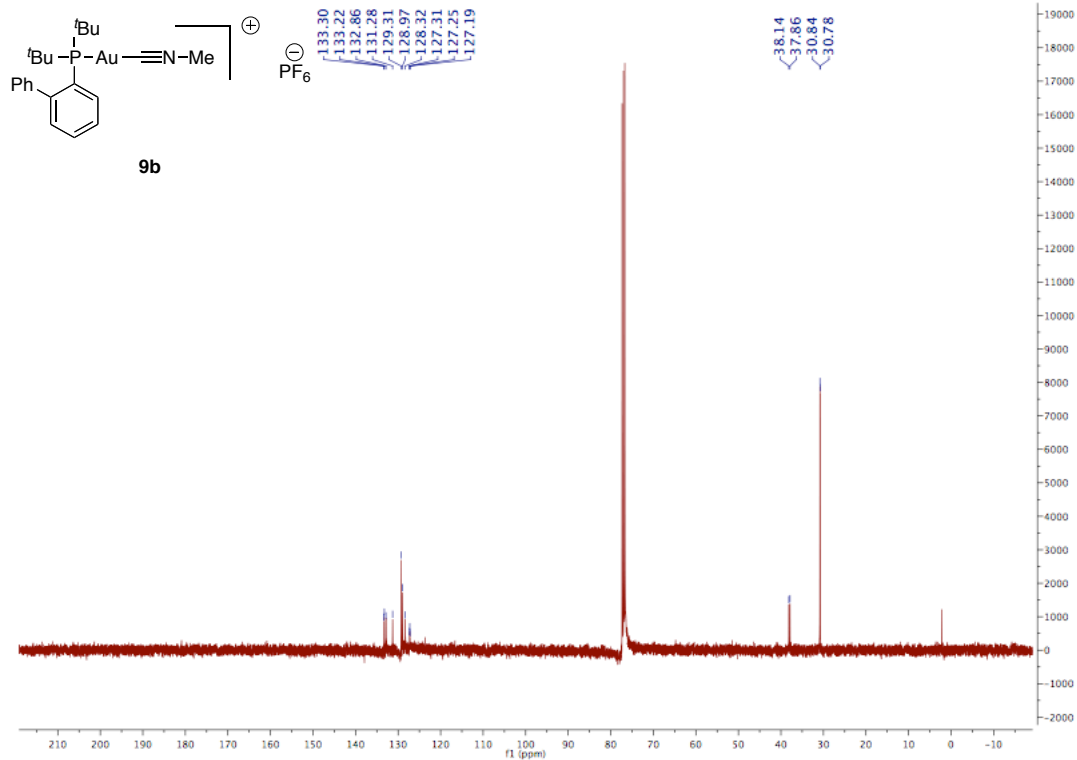
Ph<sub>3</sub>PAuOPOF<sub>2</sub>

**19**

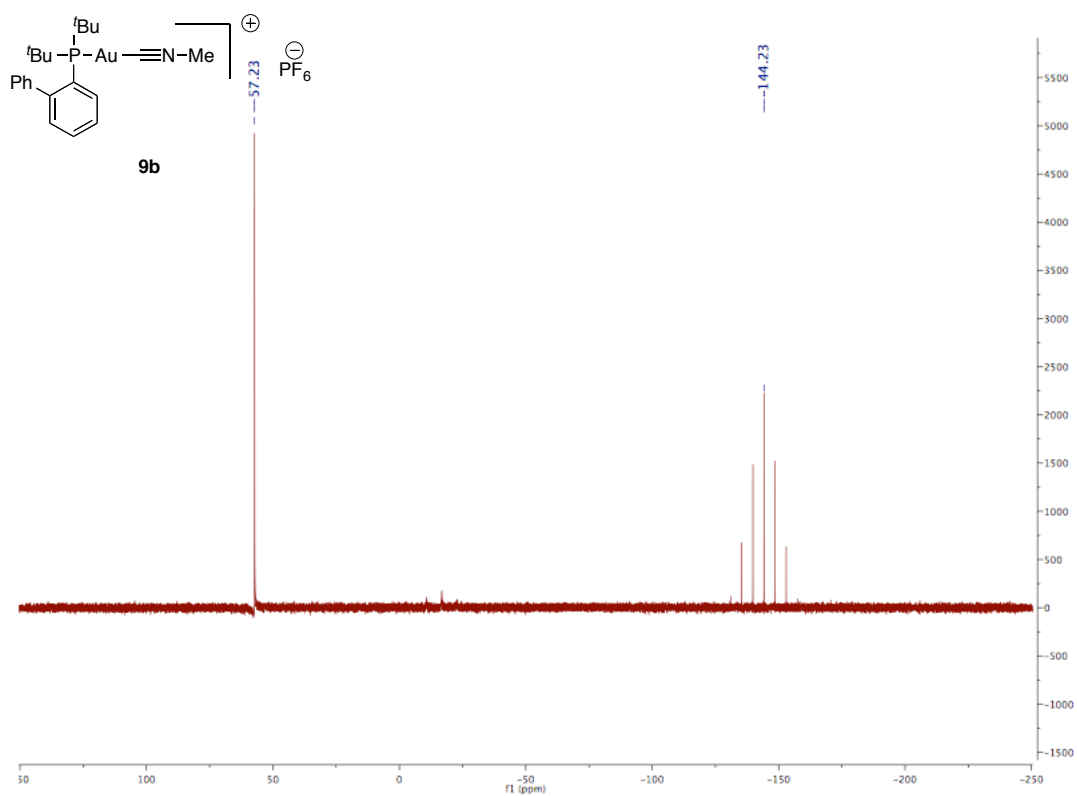




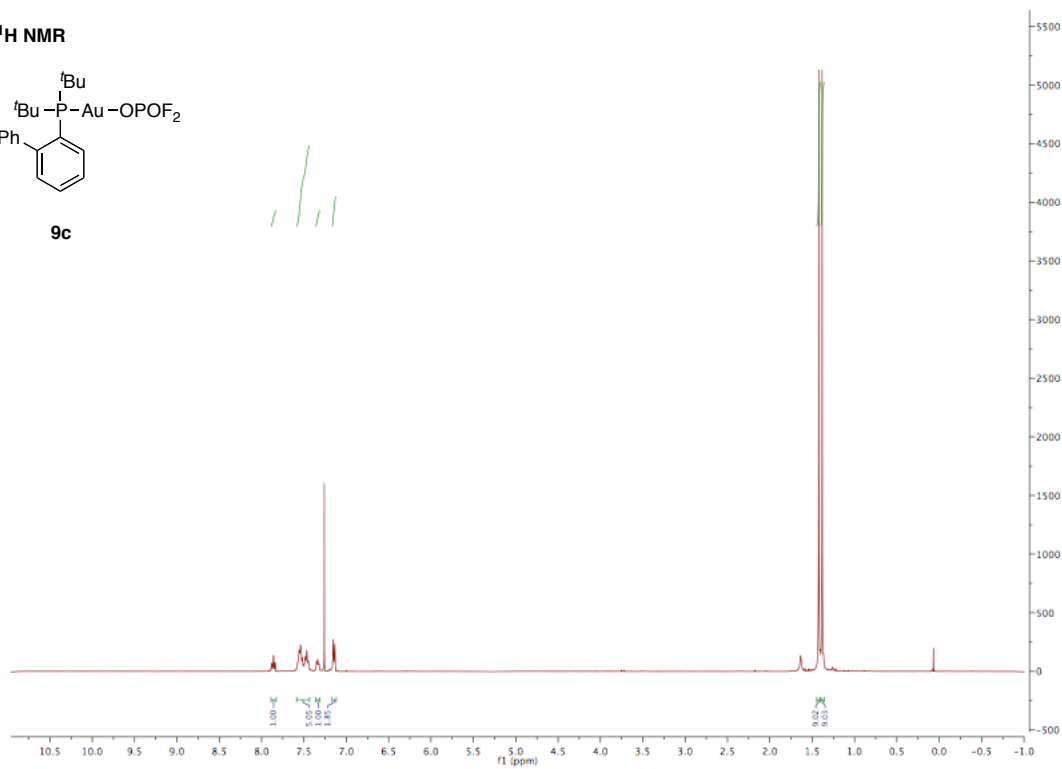
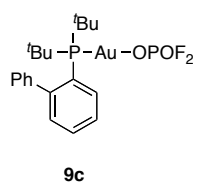
**<sup>13</sup>C NMR**



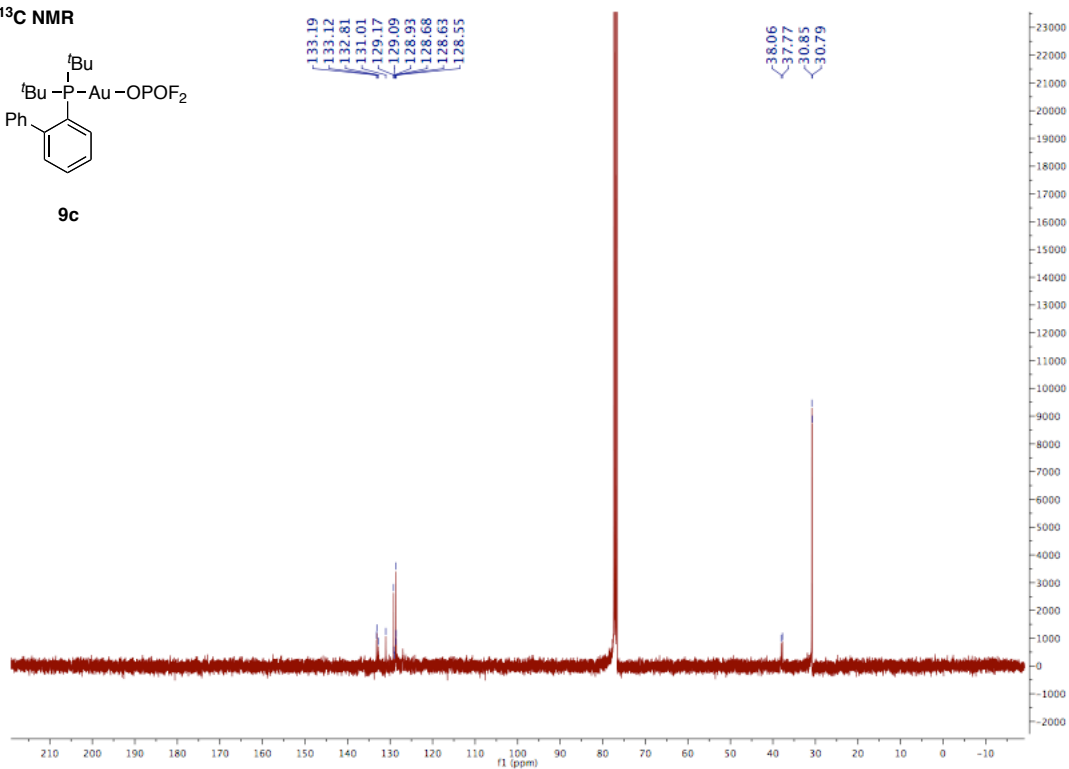
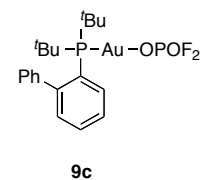
**<sup>31</sup>P NMR**

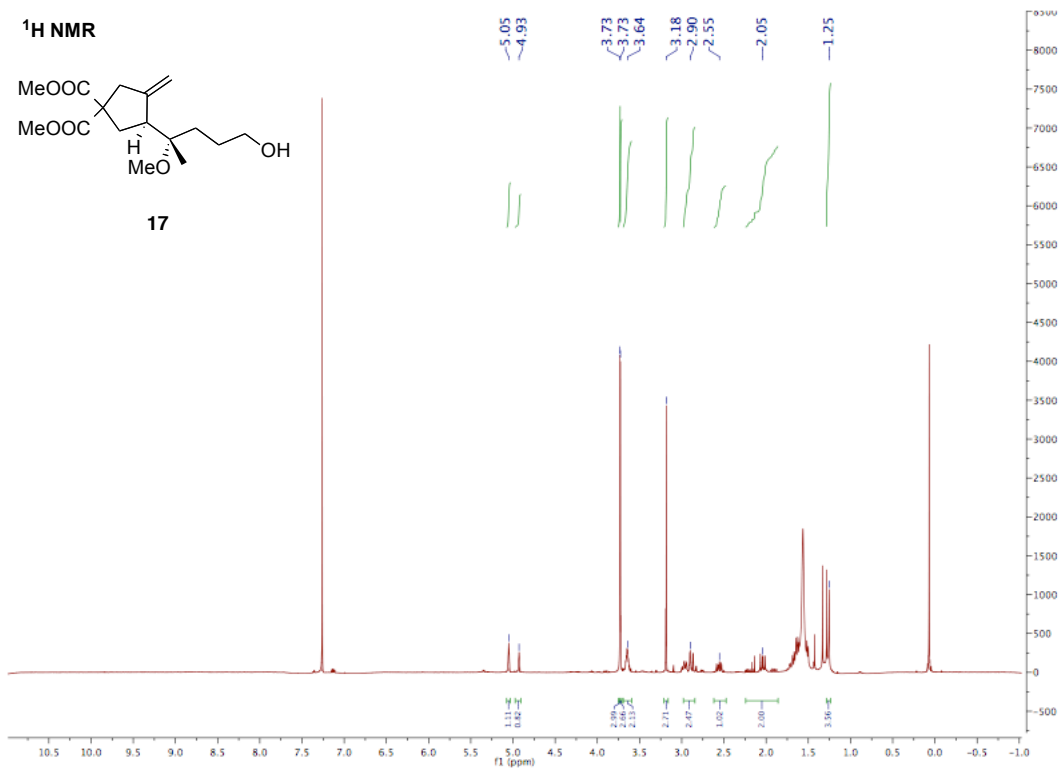
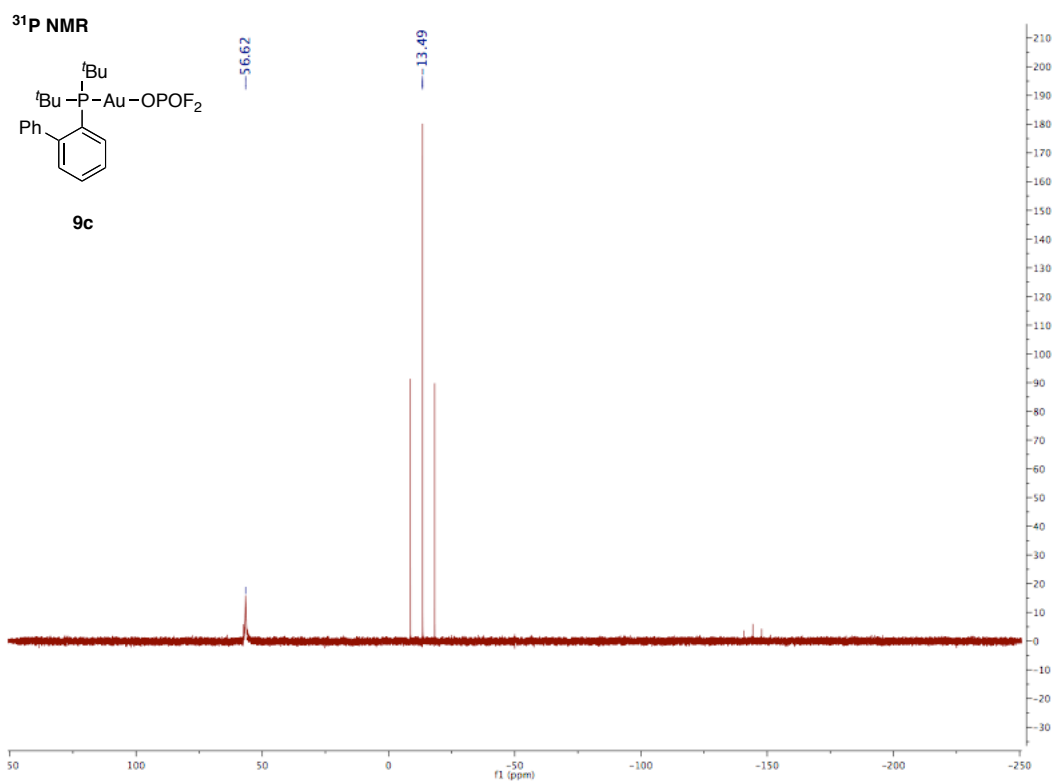


**<sup>1</sup>H NMR**

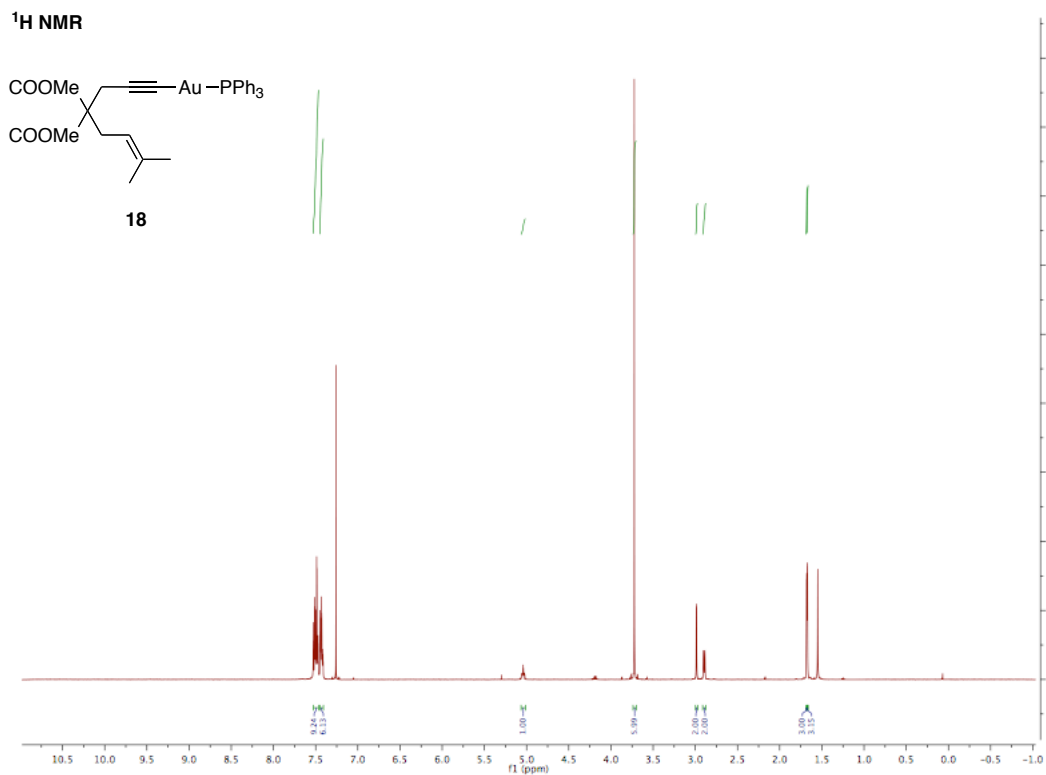
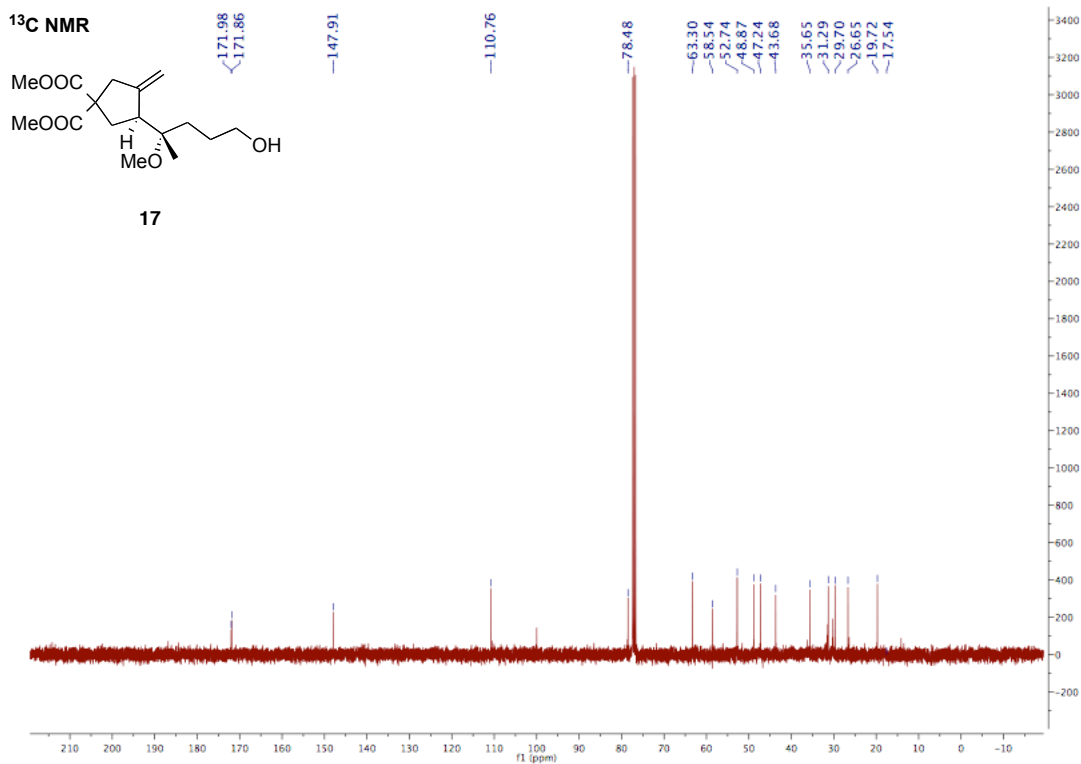


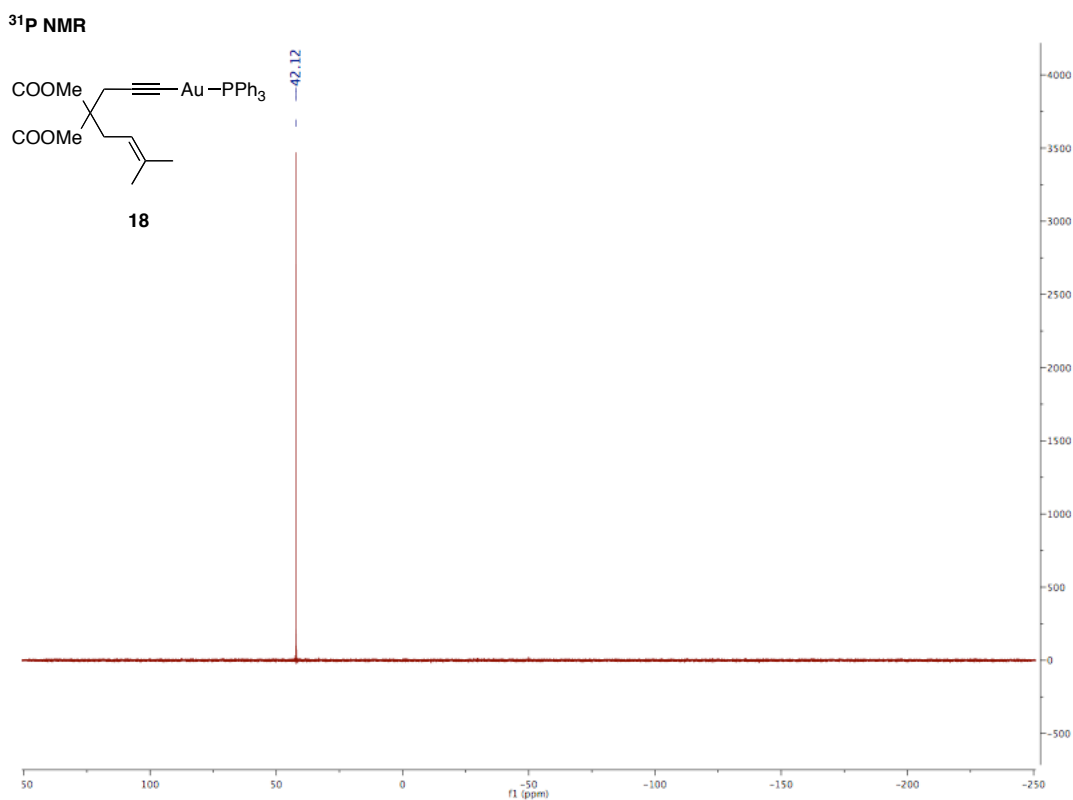
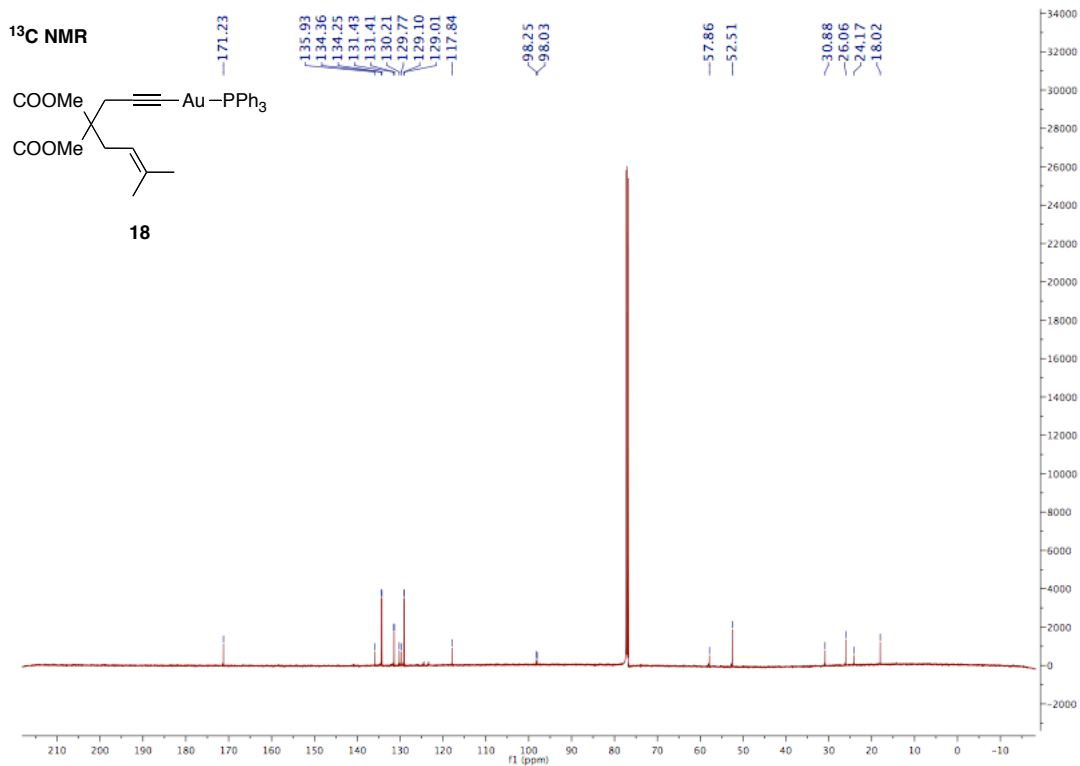
**<sup>13</sup>C NMR**











Crystal data and structure refinement for Ag(I) dimeric complex **5**.

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|                                    |   |              |
|------------------------------------|---|--------------|
| Empirical formula                  | C <sub>59.60</sub> H <sub>47.99</sub> Ag Cl <sub>2.39</sub> O <sub>4.84</sub> P Si <sub>2</sub> |              |
| Formula weight                     | 1121.30   |              |
| Temperature                        | 100(2) K  |              |
| Wavelength                         | 0.71073 Å   |              |
| Crystal system                     | Orthorhombic  |              |
| Space group                        | P2(1)2(1)2  |              |
| Unit cell dimensions               | a = 20.2597(6) Å  | ∠ = 90.00 °. |
|                                    | b = 16.3556(5) Å  | ∠ = 90.00 °. |
|                                    | c = 17.3458(5) Å  | ∠ = 90.00 °. |
| Volume                             | 5747.7(3) Å <sup>3</sup>  |              |
| Z                                  | 4   |              |
| Density (calculated)               | 1.296 Mg/m <sup>3</sup>   |              |
| Absorption coefficient             | 0.576 mm <sup>-1</sup>  |              |
| F(000)                             | 2300  |              |
| Crystal size                       | 0.20 x 0.15 x 0.05 mm <sup>3</sup>  |              |
| Theta range for data collection    | 1.17 to 36.51 °.  |              |
| Index ranges                       | -33 ≤ h ≤ 31, -27 ≤ k ≤ 26, -28 ≤ l ≤ 28  |              |
| Reflections collected              | 26827   |              |
| Independent reflections            | 17149 [R(int) = 0.0592]   |              |
| Completeness to theta = 36.51 °    | 0.984 %   |              |
| Absorption correction              | Empirical   |              |
| Max. and min. transmission         | 0.9717 and 0.8934   |              |
| Refinement method                  | Full-matrix least-squares on F <sup>2</sup>   |              |
| Data / restraints / parameters     | 26827 / 216 / 684   |              |
| Goodness-of-fit on F <sup>2</sup>  | 1.023   |              |
| Final R indices [I > 2σ(I)]        | R1 = 0.0692, wR2 = 0.1898   |              |
| R indices (all data)               | R1 = 0.1174, wR2 = 0.2312   |              |
| Absolute Structure Flack parameter | x = -0.06(3)  |              |
| Largest diff. peak and hole        | 1.835 and -0.881 e.Å <sup>-3</sup>  |              |

Bond lengths [Å] and angles [°] for **5**.

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Bond lengths----

|           |            |
|-----------|------------|
| Ag1-O3#1  | 2.1780(18) |
| Ag1-O3    | 2.1780(18) |
| Ag1-Ag2   | 3.0727(3)  |
| Ag2-O4    | 2.1901(18) |
| Ag2-O4#1  | 2.1901(18) |
| C1-C6     | 1.370(5)   |
| C1-C2     | 1.412(5)   |
| C1-Si1    | 1.920(4)   |
| C2-C3     | 1.419(5)   |
| C3-C4     | 1.370(6)   |
| C4-C5     | 1.360(7)   |
| C5-C6     | 1.470(6)   |
| C7-C8'    | 1.375(10)  |
| C7-C8     | 1.390(7)   |
| C7-C12    | 1.424(6)   |
| C7-C12'   | 1.481(17)  |
| C7-Si1    | 1.861(4)   |
| C8-C9     | 1.345(8)   |
| C9-C10    | 1.361(9)   |
| C10-C11   | 1.387(9)   |
| C11-C12   | 1.397(8)   |
| C8'-C9'   | 1.578(17)  |
| C9'-C10'  | 1.37(2)    |
| C10'-C11' | 1.25(3)    |
| C11'-C12' | 1.35(3)    |
| C13-C14   | 1.399(4)   |
| C13-C18   | 1.402(4)   |
| C13-Si1   | 1.877(3)   |
| C14-C15   | 1.409(5)   |
| C15-C16   | 1.386(5)   |
| C16-C17   | 1.370(5)   |
| C17-C18   | 1.395(4)   |
| C19-C20   | 1.381(3)   |
| C19-C28   | 1.422(3)   |
| C19-Si1   | 1.883(3)   |

|           |          |
|-----------|----------|
| C20-C21   | 1.412(4) |
| C21-C26   | 1.414(3) |
| C21-C22   | 1.420(4) |
| C22-C23   | 1.366(5) |
| C23-C24   | 1.409(5) |
| C24-C25   | 1.388(4) |
| C25-C26   | 1.412(4) |
| C26-C27   | 1.434(3) |
| C27-C28   | 1.377(3) |
| C27-C29   | 1.479(3) |
| C28-O1    | 1.388(3) |
| C29-C38   | 1.387(3) |
| C29-C30   | 1.432(3) |
| C30-C31   | 1.401(4) |
| C30-C35   | 1.444(4) |
| C31-C32   | 1.372(4) |
| C32-C33   | 1.406(5) |
| C33-C34   | 1.354(5) |
| C34-C35   | 1.426(4) |
| C35-C36   | 1.419(5) |
| C36-C37   | 1.357(4) |
| C37-C38   | 1.420(3) |
| C37-Si2   | 1.907(3) |
| C38-O2    | 1.395(3) |
| C39-C40   | 1.3900   |
| C39-C44   | 1.3900   |
| C39-Si2   | 1.993(2) |
| C40-C41   | 1.3900   |
| C41-C42   | 1.3900   |
| C42-C43   | 1.3900   |
| C43-C44   | 1.3900   |
| C39'-C40' | 1.3900   |
| C39'-C44' | 1.3900   |
| C39'-Si2  | 1.749(2) |
| C40'-C41' | 1.3900   |
| C41'-C42' | 1.3900   |
| C42'-C43' | 1.3900   |
| C43'-C44' | 1.3900   |

|             |            |
|-------------|------------|
| C45-C50     | 1.393(5)   |
| C45-C46     | 1.398(5)   |
| C45-Si2     | 1.868(3)   |
| C46-C47     | 1.403(5)   |
| C47-C48     | 1.349(6)   |
| C48-C49     | 1.364(6)   |
| C49-C50     | 1.401(5)   |
| C51-C52     | 1.3900     |
| C51-C56     | 1.3900     |
| C51-Si2     | 1.933(3)   |
| C52-C53     | 1.3900     |
| C53-C54     | 1.3900     |
| C54-C55     | 1.3900     |
| C55-C56     | 1.3900     |
| C51'-C52'   | 1.3900     |
| C51'-C56'   | 1.3900     |
| C51'-Si2    | 1.834(3)   |
| C52'-C53'   | 1.3900     |
| C53'-C54'   | 1.3900     |
| C53'-C53'#2 | 2.010(8)   |
| C54'-C55'   | 1.3900     |
| C55'-C56'   | 1.3900     |
| O1-P1       | 1.6146(16) |
| O2-P1       | 1.6052(17) |
| O3-P1       | 1.4845(18) |
| O4-P1       | 1.4811(18) |
| C1D-C11D    | 1.737(4)   |
| C1D-C11D#2  | 1.737(4)   |
| C1L-C11L    | 1.623(4)   |
| C1L-C12L    | 1.827(4)   |
| C1H-C2H     | 1.5457     |
| C2H-C3H     | 1.5451     |
| C3H-C4H     | 1.5415     |
| C4H-C5H     | 1.5405     |
| C5H-C6H     | 1.5385     |
| C1H'-C2H'   | 1.5593     |
| C2H'-C3H'   | 1.5581     |
| C3H'-C4H'   | 1.5397     |

|           |        |
|-----------|--------|
| C4H'-C5H' | 1.5372 |
| C5H'-C6H' | 1.5399 |
| C1E-C11E  | 1.6260 |
| C1E-C12E  | 1.8364 |

Angles-----

|               |           |
|---------------|-----------|
| O3-Ag1-O3#1   | 166.66(9) |
| O3-Ag1-Ag2#1  | 83.33(4)  |
| O3-Ag1-Ag2    | 83.33(4)  |
| O4-Ag2-O4#1   | 167.23(9) |
| O4-Ag2-Ag1    | 83.61(4)  |
| O4-Ag2-Ag1#1  | 83.61(4)  |
| C6-C1-C2      | 119.9(3)  |
| C6-C1-Si1     | 123.3(3)  |
| C2-C1-Si1     | 116.8(2)  |
| C1-C2-C3      | 121.0(3)  |
| C4-C3-C2      | 118.4(4)  |
| C5-C4-C3      | 122.3(4)  |
| C4-C5-C6      | 119.9(4)  |
| C1-C6-C5      | 118.4(4)  |
| C8'-C7-C8     | 12.6(5)   |
| C8'-C7-C12    | 122.6(5)  |
| C8-C7-C12     | 119.3(4)  |
| C8'-C7-C12'   | 100.3(9)  |
| C8-C7-C12'    | 90.9(9)   |
| C12-C7-C12'   | 40.3(10)  |
| C8'-C7-Si1    | 122.6(4)  |
| C8-C7-Si1     | 127.0(3)  |
| C12-C7-Si1    | 113.7(3)  |
| C12'-C7-Si1   | 131.7(7)  |
| C9-C8-C7      | 119.4(6)  |
| C8-C9-C10     | 122.3(6)  |
| C9-C10-C11    | 120.2(6)  |
| C10-C11-C12   | 119.2(5)  |
| C11-C12-C7    | 118.9(5)  |
| C7-C8'-C9'    | 124.3(9)  |
| C10'-C9'-C8'  | 113.0(14) |
| C11'-C10'-C9' | 122.0(14) |

|                |            |
|----------------|------------|
| C10'-C11'-C12' | 114.0(15)  |
| C11'-C12'-C7   | 129.7(16)  |
| C14-C13-C18    | 117.1(3)   |
| C14-C13-Si1    | 120.5(2)   |
| C18-C13-Si1    | 122.3(2)   |
| C13-C14-C15    | 122.3(3)   |
| C16-C15-C14    | 118.5(3)   |
| C17-C16-C15    | 120.3(3)   |
| C16-C17-C18    | 121.2(3)   |
| C17-C18-C13    | 120.6(3)   |
| C20-C19-C28    | 116.4(2)   |
| C20-C19-Si1    | 121.63(18) |
| C28-C19-Si1    | 122.01(17) |
| C19-C20-C21    | 122.6(2)   |
| C20-C21-C26    | 119.0(2)   |
| C20-C21-C22    | 121.7(2)   |
| C26-C21-C22    | 119.3(3)   |
| C23-C22-C21    | 120.9(3)   |
| C22-C23-C24    | 120.3(3)   |
| C25-C24-C23    | 119.8(3)   |
| C24-C25-C26    | 120.9(3)   |
| C25-C26-C21    | 118.8(2)   |
| C25-C26-C27    | 121.6(2)   |
| C21-C26-C27    | 119.5(2)   |
| C28-C27-C26    | 117.9(2)   |
| C28-C27-C29    | 120.7(2)   |
| C26-C27-C29    | 121.4(2)   |
| C27-C28-O1     | 118.98(18) |
| C27-C28-C19    | 123.7(2)   |
| O1-C28-C19     | 117.22(19) |
| C38-C29-C30    | 118.2(2)   |
| C38-C29-C27    | 120.6(2)   |
| C30-C29-C27    | 121.1(2)   |
| C31-C30-C29    | 123.2(2)   |
| C31-C30-C35    | 118.9(2)   |
| C29-C30-C35    | 117.9(2)   |
| C32-C31-C30    | 121.5(3)   |
| C31-C32-C33    | 120.0(3)   |



|                |            |
|----------------|------------|
| C34-C33-C32    | 120.5(3)   |
| C33-C34-C35    | 121.6(3)   |
| C36-C35-C34    | 122.5(3)   |
| C36-C35-C30    | 120.0(2)   |
| C34-C35-C30    | 117.5(3)   |
| C37-C36-C35    | 121.7(2)   |
| C36-C37-C38    | 117.9(3)   |
| C36-C37-Si2    | 121.1(2)   |
| C38-C37-Si2    | 120.9(2)   |
| C29-C38-O2     | 118.9(2)   |
| C29-C38-C37    | 123.5(2)   |
| O2-C38-C37     | 117.4(2)   |
| C40-C39-C44    | 120.0      |
| C40-C39-Si2    | 122.71(11) |
| C44-C39-Si2    | 116.93(11) |
| C41-C40-C39    | 120.0      |
| C40-C41-C42    | 120.0      |
| C43-C42-C41    | 120.0      |
| C42-C43-C44    | 120.0      |
| C43-C44-C39    | 120.0      |
| C40'-C39'-C44' | 120.0      |
| C40'-C39'-Si2  | 121.68(13) |
| C44'-C39'-Si2  | 118.31(13) |
| C39'-C40'-C41' | 120.0      |
| C42'-C41'-C40' | 120.0      |
| C43'-C42'-C41' | 120.0      |
| C44'-C43'-C42' | 120.0      |
| C43'-C44'-C39' | 120.0      |
| C50-C45-C46    | 118.0(3)   |
| C50-C45-Si2    | 119.5(3)   |
| C46-C45-Si2    | 122.5(3)   |
| C45-C46-C47    | 120.4(4)   |
| C48-C47-C46    | 119.9(4)   |
| C47-C48-C49    | 121.4(3)   |
| C48-C49-C50    | 119.7(3)   |
| C45-C50-C49    | 120.6(4)   |
| C52-C51-C56    | 120.0      |
| C52-C51-Si2    | 125.13(17) |

|                  |            |
|------------------|------------|
| C56-C51-Si2      | 114.87(17) |
| C51-C52-C53      | 120.0      |
| C54-C53-C52      | 120.0      |
| C55-C54-C53      | 120.0      |
| C54-C55-C56      | 120.0      |
| C55-C56-C51      | 120.0      |
| C52'-C51'-C56'   | 120.0      |
| C52'-C51'-Si2    | 120.6(2)   |
| C56'-C51'-Si2    | 118.7(2)   |
| C51'-C52'-C53'   | 120.0      |
| C54'-C53'-C52'   | 120.0      |
| C54'-C53'-C53'#2 | 98.0(5)    |
| C52'-C53'-C53'#2 | 120.0(5)   |
| C55'-C54'-C53'   | 120.0      |
| C56'-C55'-C54'   | 120.0      |
| C55'-C56'-C51'   | 120.0      |
| C28-O1-P1        | 120.68(14) |
| C38-O2-P1        | 120.51(15) |
| P1-O3-Ag1        | 126.57(10) |
| P1-O4-Ag2        | 125.76(11) |
| O4-P1-O3         | 120.66(10) |
| O4-P1-O2         | 111.22(10) |
| O3-P1-O2         | 104.28(10) |
| O4-P1-O1         | 103.88(9)  |
| O3-P1-O1         | 112.01(9)  |
| O2-P1-O1         | 103.69(9)  |
| C7-Si1-C13       | 105.48(14) |
| C7-Si1-C19       | 113.20(14) |
| C13-Si1-C19      | 109.33(12) |
| C7-Si1-C1        | 112.66(18) |
| C13-Si1-C1       | 108.23(13) |
| C19-Si1-C1       | 107.79(13) |
| C39'-Si2-C51'    | 90.47(14)  |
| C39'-Si2-C45     | 113.87(14) |
| C51'-Si2-C45     | 112.00(16) |
| C39'-Si2-C37     | 115.00(12) |
| C51'-Si2-C37     | 113.66(16) |
| C45-Si2-C37      | 110.57(13) |

|                 |            |
|-----------------|------------|
| C39'-Si2-C51    | 105.21(13) |
| C51'-Si2-C51    | 14.8       |
| C45-Si2-C51     | 106.11(15) |
| C37-Si2-C51     | 105.14(15) |
| C39'-Si2-C39    | 10.4       |
| C51'-Si2-C39    | 100.57(13) |
| C45-Si2-C39     | 111.58(13) |
| C37-Si2-C39     | 108.03(11) |
| C51-Si2-C39     | 115.23(13) |
| C11D-C1D-C11D#2 | 115.6(4)   |
| C11L-C1L-C12L   | 116.9(3)   |
| C3H-C2H-C1H     | 150.0      |
| C4H-C3H-C2H     | 150.9      |
| C5H-C4H-C3H     | 115.7      |
| C6H-C5H-C4H     | 103.7      |
| C3H'-C2H'-C1H'  | 141.3      |
| C4H'-C3H'-C2H'  | 146.7      |
| C5H'-C4H'-C3H'  | 118.3      |
| C4H'-C5H'-C6H'  | 103.8      |
| C11E-C1E-C12E   | 118.0      |

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Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+1, z

#2 -x+1, -y+1, z

Torsion angles [°] for **5**.

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|                    |            |
|--------------------|------------|
| O3#1-Ag1-Ag2-O4    | 178.43(7)  |
| O3-Ag1-Ag2-O4      | -1.57(7)   |
| O3#1-Ag1-Ag2-O4#1  | -1.58(7)   |
| O3-Ag1-Ag2-O4#1    | 178.42(7)  |
| C6-C1-C2-C3        | 1.1(5)     |
| Si1-C1-C2-C3       | -179.6(3)  |
| C1-C2-C3-C4        | -2.6(6)    |
| C2-C3-C4-C5        | 1.5(6)     |
| C3-C4-C5-C6        | 1.1(6)     |
| C2-C1-C6-C5        | 1.5(5)     |
| Si1-C1-C6-C5       | -177.8(2)  |
| C4-C5-C6-C1        | -2.6(5)    |
| C8'-C7-C8-C9       | 100(3)     |
| C12-C7-C8-C9       | -9.0(8)    |
| C12'-C7-C8-C9      | -38.9(11)  |
| Si1-C7-C8-C9       | 173.4(4)   |
| C7-C8-C9-C10       | 10.4(10)   |
| C8-C9-C10-C11      | -4.6(11)   |
| C9-C10-C11-C12     | -2.3(11)   |
| C10-C11-C12-C7     | 3.3(9)     |
| C8'-C7-C12-C11     | -11.9(9)   |
| C8-C7-C12-C11      | 2.3(8)     |
| C12'-C7-C12-C11    | 52.8(12)   |
| Si1-C7-C12-C11     | -179.9(5)  |
| C8-C7-C8'-C9'      | -41(2)     |
| C12-C7-C8'-C9'     | 37.4(14)   |
| C12'-C7-C8'-C9'    | 1.0(15)    |
| Si1-C7-C8'-C9'     | -155.7(10) |
| C7-C8'-C9'-C10'    | -26.6(19)  |
| C8'-C9'-C10'-C11'  | 21(3)      |
| C9'-C10'-C11'-C12' | 9(3)       |
| C10'-C11'-C12'-C7  | -47(4)     |
| C8'-C7-C12'-C11'   | 38(3)      |
| C8-C7-C12'-C11'    | 46(3)      |
| C12-C7-C12'-C11'   | -92(3)     |
| Si1-C7-C12'-C11'   | -169(2)    |

|                 |             |
|-----------------|-------------|
| C18-C13-C14-C15 | -1.3(5)     |
| Si1-C13-C14-C15 | 174.4(3)    |
| C13-C14-C15-C16 | 0.1(6)      |
| C14-C15-C16-C17 | 0.9(6)      |
| C15-C16-C17-C18 | -0.5(6)     |
| C16-C17-C18-C13 | -0.8(6)     |
| C14-C13-C18-C17 | 1.7(5)      |
| Si1-C13-C18-C17 | -174.0(3)   |
| C28-C19-C20-C21 | -0.6(3)     |
| Si1-C19-C20-C21 | 179.59(19)  |
| C19-C20-C21-C26 | 6.1(4)      |
| C19-C20-C21-C22 | -173.6(3)   |
| C20-C21-C22-C23 | 179.1(3)    |
| C26-C21-C22-C23 | -0.7(4)     |
| C21-C22-C23-C24 | 0.0(5)      |
| C22-C23-C24-C25 | 0.8(5)      |
| C23-C24-C25-C26 | -1.0(4)     |
| C24-C25-C26-C21 | 0.4(4)      |
| C24-C25-C26-C27 | -175.3(3)   |
| C20-C21-C26-C25 | -179.3(2)   |
| C22-C21-C26-C25 | 0.5(4)      |
| C20-C21-C26-C27 | -3.5(4)     |
| C22-C21-C26-C27 | 176.3(2)    |
| C25-C26-C27-C28 | 171.1(2)    |
| C21-C26-C27-C28 | -4.5(3)     |
| C25-C26-C27-C29 | -6.6(4)     |
| C21-C26-C27-C29 | 177.7(2)    |
| C26-C27-C28-O1  | -172.24(19) |
| C29-C27-C28-O1  | 5.5(3)      |
| C26-C27-C28-C19 | 10.7(3)     |
| C29-C27-C28-C19 | -171.5(2)   |
| C20-C19-C28-C27 | -8.2(3)     |
| Si1-C19-C28-C27 | 171.66(18)  |
| C20-C19-C28-O1  | 174.71(19)  |
| Si1-C19-C28-O1  | -5.5(3)     |
| C28-C27-C29-C38 | -55.5(3)    |
| C26-C27-C29-C38 | 122.2(3)    |
| C28-C27-C29-C30 | 122.9(3)    |

|                     |             |
|---------------------|-------------|
| C26-C27-C29-C30     | -59.4(3)    |
| C38-C29-C30-C31     | 172.9(2)    |
| C27-C29-C30-C31     | -5.6(4)     |
| C38-C29-C30-C35     | -6.3(3)     |
| C27-C29-C30-C35     | 175.3(2)    |
| C29-C30-C31-C32     | -178.9(3)   |
| C35-C30-C31-C32     | 0.2(4)      |
| C30-C31-C32-C33     | -0.9(5)     |
| C31-C32-C33-C34     | 0.5(5)      |
| C32-C33-C34-C35     | 0.6(5)      |
| C33-C34-C35-C36     | 179.6(3)    |
| C33-C34-C35-C30     | -1.3(5)     |
| C31-C30-C35-C36     | 180.0(3)    |
| C29-C30-C35-C36     | -0.8(4)     |
| C31-C30-C35-C34     | 0.8(4)      |
| C29-C30-C35-C34     | -180.0(3)   |
| C34-C35-C36-C37     | -175.9(3)   |
| C30-C35-C36-C37     | 5.0(4)      |
| C35-C36-C37-C38     | -1.8(4)     |
| C35-C36-C37-Si2     | -178.2(2)   |
| C30-C29-C38-O2      | -174.7(2)   |
| C27-C29-C38-O2      | 3.7(3)      |
| C30-C29-C38-C37     | 10.0(4)     |
| C27-C29-C38-C37     | -171.6(2)   |
| C36-C37-C38-C29     | -5.9(4)     |
| Si2-C37-C38-C29     | 170.50(19)  |
| C36-C37-C38-O2      | 178.7(2)    |
| Si2-C37-C38-O2      | -4.9(3)     |
| C44-C39-C40-C41     | 0.0         |
| Si2-C39-C40-C41     | -172.83(13) |
| C39-C40-C41-C42     | 0.0         |
| C40-C41-C42-C43     | 0.0         |
| C41-C42-C43-C44     | 0.0         |
| C42-C43-C44-C39     | 0.0         |
| C40-C39-C44-C43     | 0.0         |
| Si2-C39-C44-C43     | 173.24(13)  |
| C44'-C39'-C40'-C41' | 0.0         |
| Si2-C39'-C40'-C41'  | 178.71(15)  |

|                       |             |
|-----------------------|-------------|
| C39'-C40'-C41'-C42'   | 0.0         |
| C40'-C41'-C42'-C43'   | 0.0         |
| C41'-C42'-C43'-C44'   | 0.0         |
| C42'-C43'-C44'-C39'   | 0.0         |
| C40'-C39'-C44'-C43'   | 0.0         |
| Si2-C39'-C44'-C43'    | -178.75(15) |
| C50-C45-C46-C47       | -1.6(5)     |
| Si2-C45-C46-C47       | -179.0(3)   |
| C45-C46-C47-C48       | 0.8(6)      |
| C46-C47-C48-C49       | 0.1(6)      |
| C47-C48-C49-C50       | -0.2(5)     |
| C46-C45-C50-C49       | 1.4(5)      |
| Si2-C45-C50-C49       | 178.9(2)    |
| C48-C49-C50-C45       | -0.5(5)     |
| C56-C51-C52-C53       | 0.0         |
| Si2-C51-C52-C53       | 179.3(3)    |
| C51-C52-C53-C54       | 0.0         |
| C52-C53-C54-C55       | 0.0         |
| C53-C54-C55-C56       | 0.0         |
| C54-C55-C56-C51       | 0.0         |
| C52-C51-C56-C55       | 0.0         |
| Si2-C51-C56-C55       | -179.4(2)   |
| C56'-C51'-C52'-C53'   | 0.0         |
| Si2-C51'-C52'-C53'    | -170.1(2)   |
| C51'-C52'-C53'-C54'   | 0.0         |
| C51'-C52'-C53'-C53'#2 | 121.4(3)    |
| C52'-C53'-C54'-C55'   | 0.0         |
| C53'#2-C53'-C54'-C55' | -131.71(19) |
| C53'-C54'-C55'-C56'   | 0.0         |
| C54'-C55'-C56'-C51'   | 0.0         |
| C52'-C51'-C56'-C55'   | 0.0         |
| Si2-C51'-C56'-C55'    | 170.3(2)    |
| C27-C28-O1-P1         | 69.0(2)     |
| C19-C28-O1-P1         | -113.76(19) |
| C29-C38-O2-P1         | 69.6(3)     |
| C37-C38-O2-P1         | -114.8(2)   |
| O3#1-Ag1-O3-P1        | 1.44(12)    |
| Ag2-Ag1-O3-P1         | 1.44(12)    |

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|-----------------|-------------|
| O4#1-Ag2-O4-P1  | 2.37(12)    |
| Ag1-Ag2-O4-P1   | 2.38(12)    |
| Ag2-O4-P1-O3    | -2.10(18)   |
| Ag2-O4-P1-O2    | 120.42(12)  |
| Ag2-O4-P1-O1    | -128.64(11) |
| Ag1-O3-P1-O4    | -0.20(18)   |
| Ag1-O3-P1-O2    | -126.00(12) |
| Ag1-O3-P1-O1    | 122.52(12)  |
| C38-O2-P1-O4    | 66.84(19)   |
| C38-O2-P1-O3    | -161.60(17) |
| C38-O2-P1-O1    | -44.22(18)  |
| C28-O1-P1-O4    | -161.65(15) |
| C28-O1-P1-O3    | 66.55(17)   |
| C28-O1-P1-O2    | -45.30(16)  |
| C8'-C7-Si1-C13  | 130.1(6)    |
| C8-C7-Si1-C13   | 115.7(4)    |
| C12-C7-Si1-C13  | -62.0(4)    |
| C12'-C7-Si1-C13 | -18.5(14)   |
| C8'-C7-Si1-C19  | 10.6(6)     |
| C8-C7-Si1-C19   | -3.8(5)     |
| C12-C7-Si1-C19  | 178.5(3)    |
| C12'-C7-Si1-C19 | -138.0(14)  |
| C8'-C7-Si1-C1   | -112.1(6)   |
| C8-C7-Si1-C1    | -126.5(4)   |
| C12-C7-Si1-C1   | 55.8(4)     |
| C12'-C7-Si1-C1  | 99.3(14)    |
| C14-C13-Si1-C7  | -57.5(3)    |
| C18-C13-Si1-C7  | 118.0(3)    |
| C14-C13-Si1-C19 | 64.5(3)     |
| C18-C13-Si1-C19 | -120.0(3)   |
| C14-C13-Si1-C1  | -178.3(3)   |
| C18-C13-Si1-C1  | -2.8(3)     |
| C20-C19-Si1-C7  | 129.7(2)    |
| C28-C19-Si1-C7  | -50.1(2)    |
| C20-C19-Si1-C13 | 12.4(2)     |
| C28-C19-Si1-C13 | -167.39(19) |
| C20-C19-Si1-C1  | -105.0(2)   |
| C28-C19-Si1-C1  | 75.2(2)     |



|                    |             |
|--------------------|-------------|
| C6-C1-Si1-C7       | -9.5(3)     |
| C2-C1-Si1-C7       | 171.2(2)    |
| C6-C1-Si1-C13      | 106.7(3)    |
| C2-C1-Si1-C13      | -72.6(3)    |
| C6-C1-Si1-C19      | -135.2(3)   |
| C2-C1-Si1-C19      | 45.6(3)     |
| C40'-C39'-Si2-C51' | 125.88(18)  |
| C44'-C39'-Si2-C51' | -55.39(18)  |
| C40'-C39'-Si2-C45  | -119.71(16) |
| C44'-C39'-Si2-C45  | 59.02(17)   |
| C40'-C39'-Si2-C37  | 9.36(18)    |
| C44'-C39'-Si2-C37  | -171.91(15) |
| C40'-C39'-Si2-C51  | 124.53(17)  |
| C44'-C39'-Si2-C51  | -56.74(18)  |
| C40'-C39'-Si2-C39  | -40.27(5)   |
| C44'-C39'-Si2-C39  | 138.46(14)  |
| C52'-C51'-Si2-C39' | 117.6(2)    |
| C56'-C51'-Si2-C39' | -52.6(2)    |
| C52'-C51'-Si2-C45  | 1.5(3)      |
| C56'-C51'-Si2-C45  | -168.7(2)   |
| C52'-C51'-Si2-C37  | -124.7(2)   |
| C56'-C51'-Si2-C37  | 65.1(2)     |
| C52'-C51'-Si2-C51  | -67.47(12)  |
| C56'-C51'-Si2-C51  | 122.29(13)  |
| C52'-C51'-Si2-C39  | 120.2(2)    |
| C56'-C51'-Si2-C39  | -50.1(2)    |
| C50-C45-Si2-C39'   | 177.4(2)    |
| C46-C45-Si2-C39'   | -5.2(3)     |
| C50-C45-Si2-C51'   | -81.7(3)    |
| C46-C45-Si2-C51'   | 95.7(3)     |
| C50-C45-Si2-C37    | 46.2(3)     |
| C46-C45-Si2-C37    | -136.5(3)   |
| C50-C45-Si2-C51    | -67.3(3)    |
| C46-C45-Si2-C51    | 110.0(3)    |
| C50-C45-Si2-C39    | 166.4(2)    |
| C46-C45-Si2-C39    | -16.2(3)    |
| C36-C37-Si2-C39'   | 118.3(2)    |
| C38-C37-Si2-C39'   | -58.0(2)    |

|                     |             |
|---------------------|-------------|
| C36-C37-Si2-C51'    | 16.0(3)     |
| C38-C37-Si2-C51'    | -160.3(2)   |
| C36-C37-Si2-C45     | -111.0(2)   |
| C38-C37-Si2-C45     | 72.7(2)     |
| C36-C37-Si2-C51     | 3.1(3)      |
| C38-C37-Si2-C51     | -173.2(2)   |
| C36-C37-Si2-C39     | 126.7(2)    |
| C38-C37-Si2-C39     | -49.6(2)    |
| C52-C51-Si2-C39'    | 154.2(2)    |
| C56-C51-Si2-C39'    | -26.5(2)    |
| C52-C51-Si2-C51'    | 148.92(10)  |
| C56-C51-Si2-C51'    | -31.75(17)  |
| C52-C51-Si2-C45     | 33.2(3)     |
| C56-C51-Si2-C45     | -147.5(2)   |
| C52-C51-Si2-C37     | -84.0(2)    |
| C56-C51-Si2-C37     | 95.4(2)     |
| C52-C51-Si2-C39     | 157.2(2)    |
| C56-C51-Si2-C39     | -23.5(2)    |
| C40-C39-Si2-C39'    | 124.03(8)   |
| C44-C39-Si2-C39'    | -49.01(15)  |
| C40-C39-Si2-C51'    | 109.93(18)  |
| C44-C39-Si2-C51'    | -63.11(19)  |
| C40-C39-Si2-C45     | -131.15(15) |
| C44-C39-Si2-C45     | 55.82(16)   |
| C40-C39-Si2-C37     | -9.41(16)   |
| C44-C39-Si2-C37     | 177.55(14)  |
| C40-C39-Si2-C51     | 107.78(18)  |
| C44-C39-Si2-C51     | -65.26(19)  |
| C1H-C2H-C3H-C4H     | 45.1        |
| C2H-C3H-C4H-C5H     | 34.6        |
| C3H-C4H-C5H-C6H     | -118.9      |
| C1H'-C2H'-C3H'-C4H' | 96.4        |
| C2H'-C3H'-C4H'-C5H' | -146.5      |
| C3H'-C4H'-C5H'-C6H' | 148.0       |

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Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+1, z

#2 -x+1, -y+1, z

Crystal data and structure refinement for  $7 \cdot \text{CHCl}_3$

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|                                   |   |              |
|-----------------------------------|---|--------------|
| Empirical formula                 | C75.50 H58.50 Au Cl11.50 O4.50 P2 Si2       |              |
| Formula weight                    | 1405.98                                     |              |
| Temperature                       | 100(2) K                                    |              |
| Wavelength                        | 0.71073 Å                                   |              |
| Crystal system                    | Orthorhombic                                |              |
| Space group                       | P2(1)2(1)2(1)                               |              |
| Unit cell dimensions              | a = 11.5423(4) Å                            | ∠ = 90.00 °. |
|                                   | b = 14.3340(6) Å                            | ∠ = 90.00 °. |
|                                   | c = 40.0455(13) Å                           | ∠ = 90.00 °. |
| Volume                            | 6625.4(4) Å <sup>3</sup>                    |              |
| Z                                 | 4   |              |
| Density (calculated)              | 1.410 Mg/m <sup>3</sup>                     |              |
| Absorption coefficient            | 2.415 mm <sup>-1</sup>                      |              |
| F(000)                            | 2840  |              |
| Crystal size                      | 0.10 x 0.05 x 0.01 mm <sup>3</sup>          |              |
| Theta range for data collection   | 2.48 to 26.45 °.                            |              |
| Index ranges                      | -14 ≤ h ≤ 14, -12 ≤ k ≤ 17, -50 ≤ l ≤ 49    |              |
| Reflections collected             | 13548                                       |              |
| Independent reflections           | 10065 [R(int) = 0.1441 ]                    |              |
| Completeness to theta = 26.45 °   | 0.994 %                                     |              |
| Absorption correction             | Empirical                                   |              |
| Max. and min. transmission        | 0.9762 and 0.7942                           |              |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup> |              |
| Data / restraints / parameters    | 13548 / 176 / 839                           |              |
| Goodness-of-fit on F <sup>2</sup> | 1.022                                       |              |
| Final R indices [I > 2σ(I)]       | R1 = 0.0620, wR2 = 0.1398                   |              |
| R indices (all data)              | R1 = 0.0968, wR2 = 0.1598                   |              |
| Largest diff. peak and hole       | 1.908 and -1.288 e.Å <sup>-3</sup>          |              |

Bond lengths [Å] and angles [°] for 7·CHCl<sub>3</sub>.

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Bond lengths----

|           |           |
|-----------|-----------|
| Au1-O4    | 2.057(7)  |
| Au1-P2    | 2.200(3)  |
| C1-O1     | 1.388(10) |
| C1-C10    | 1.391(12) |
| C1-C2     | 1.415(11) |
| O1-P1     | 1.607(7)  |
| P1-O3     | 1.463(7)  |
| P1-O4     | 1.503(7)  |
| P1-O2     | 1.617(6)  |
| Si1-C21   | 1.864(9)  |
| Si1-C27   | 1.867(10) |
| Si1-C2    | 1.878(8)  |
| Si1-C33   | 1.885(10) |
| C2-C3     | 1.355(13) |
| O2-C20    | 1.402(11) |
| P2-C63    | 1.801(11) |
| P2-C57    | 1.810(10) |
| P2-C69    | 1.823(10) |
| Si2-C51   | 1.83(3)   |
| Si2-C45   | 1.89(3)   |
| Si2-C19   | 1.91(3)   |
| Si2-C39   | 1.95(2)   |
| Si2'-C45' | 1.85(3)   |
| Si2'-C39' | 1.86(3)   |
| Si2'-C19  | 1.91(3)   |
| Si2'-C51' | 1.94(3)   |
| C3-C4     | 1.433(13) |
| C4-C5     | 1.409(13) |
| C4-C9     | 1.415(12) |
| C5-C6     | 1.368(13) |
| C6-C7     | 1.407(13) |
| C7-C8     | 1.358(13) |
| C8-C9     | 1.445(12) |
| C9-C10    | 1.408(13) |
| C10-C11   | 1.499(12) |

|           |           |
|-----------|-----------|
| C11-C20   | 1.392(12) |
| C11-C12   | 1.407(13) |
| C12-C13   | 1.384(13) |
| C12-C17   | 1.422(11) |
| C13-C14   | 1.361(13) |
| C14-C15   | 1.418(13) |
| C15-C16   | 1.348(14) |
| C16-C17   | 1.408(13) |
| C17-C18   | 1.415(13) |
| C18-C19   | 1.381(13) |
| C19-C20   | 1.406(12) |
| C21-C26   | 1.389(14) |
| C21-C22   | 1.418(10) |
| C22-C23   | 1.359(13) |
| C23-C24   | 1.399(15) |
| C24-C25   | 1.385(14) |
| C25-C26   | 1.388(14) |
| C27-C32   | 1.389(13) |
| C27-C28   | 1.431(12) |
| C28-C29   | 1.381(14) |
| C29-C30   | 1.400(15) |
| C30-C31   | 1.375(13) |
| C31-C32   | 1.389(13) |
| C33-C34   | 1.379(13) |
| C33-C38   | 1.39(15)  |
| C34-C35   | 1.398(13) |
| C35-C36   | 1.407(16) |
| C36-C37   | 1.383(15) |
| C37-C38   | 1.380(14) |
| C39-C40   | 1.39      |
| C39-C44   | 1.39      |
| C40-C41   | 1.39      |
| C41-C42   | 1.39      |
| C42-C43   | 1.39      |
| C43-C44   | 1.39      |
| C39'-C40' | 1.39      |
| C39'-C44' | 1.39      |
| C40'-C41' | 1.39      |

|           |           |
|-----------|-----------|
| C41'-C42' | 1.39      |
| C42'-C43' | 1.39      |
| C43'-C44' | 1.39      |
| C45'-C46' | 1.39      |
| C45'-C50' | 1.39      |
| C46'-C47' | 1.39      |
| C47'-C48' | 1.39      |
| C48'-C49' | 1.39      |
| C49'-C50' | 1.39      |
| C45-C46   | 1.39      |
| C45-C50   | 1.39      |
| C46-C47   | 1.39      |
| C47-C48   | 1.39      |
| C48-C49   | 1.39      |
| C49-C50   | 1.39      |
| C57-C62   | 1.375(17) |
| C57-C58   | 1.426(15) |
| C58-C59   | 1.369(15) |
| C59-C60   | 1.410(2)  |
| C60-C61   | 1.383(19) |
| C61-C62   | 1.382(16) |
| C63-C64   | 1.367(16) |
| C63-C68   | 1.379(13) |
| C64-C65   | 1.390(17) |
| C65-C66   | 1.398(16) |
| C66-C67   | 1.352(16) |
| C67-C68   | 1.400(14) |
| C69-C70   | 1.336(13) |
| C69-C74   | 1.381(15) |
| C70-C71   | 1.386(15) |
| C71-C72   | 1.411(17) |
| C72-C73   | 1.314(19) |
| C73-C74   | 1.341(17) |
| C51-C52   | 1.39      |
| C51-C56   | 1.39      |
| C52-C53   | 1.39      |
| C53-C54   | 1.39      |
| C54-C55   | 1.39      |

|           |           |
|-----------|-----------|
| C55-C56   | 1.39      |
| C51'-C52' | 1.39      |
| C51'-C56' | 1.39      |
| C52'-C53' | 1.39      |
| C53'-C54' | 1.39      |
| C54'-C55' | 1.39      |
| C55'-C56' | 1.39      |
| C1S-C11S  | 1.68(3)   |
| C1S-C12S  | 1.73(2)   |
| C1S-C13S  | 1.85(3)   |
| O1W-C1W   | 1.427(10) |
| C1W-C2W   | 1.538(10) |

Angles-----

|             |            |
|-------------|------------|
| O4-Au1-P2   | 172.69(18) |
| O1-C1-C10   | 117.4(6)   |
| O1-C1-C2    | 118.3(7)   |
| C10-C1-C2   | 124.0(8)   |
| C1-O1-P1    | 121.3(6)   |
| O3-P1-O4    | 118.4(4)   |
| O3-P1-O1    | 113.4(4)   |
| O4-P1-O1    | 103.6(4)   |
| O3-P1-O2    | 107.1(4)   |
| O4-P1-O2    | 109.7(3)   |
| O1-P1-O2    | 103.9(3)   |
| C21-Si1-C27 | 111.0(4)   |
| C21-Si1-C2  | 107.0(4)   |
| C27-Si1-C2  | 108.1(4)   |
| C21-Si1-C33 | 106.3(4)   |
| C27-Si1-C33 | 111.6(4)   |
| C2-Si1-C33  | 112.8(4)   |
| C3-C2-C1    | 115.7(7)   |
| C3-C2-Si1   | 120.3(6)   |
| C1-C2-Si1   | 123.9(7)   |
| C20-O2-P1   | 119.1(6)   |
| C63-P2-C57  | 107.5(5)   |
| C63-P2-C69  | 103.7(4)   |
| C57-P2-C69  | 106.0(4)   |

|                |           |
|----------------|-----------|
| C63-P2-Au1     | 110.1(4)  |
| C57-P2-Au1     | 111.4(4)  |
| C69-P2-Au1     | 117.4(3)  |
| C51-Si2-C45    | 116.5(14) |
| C51-Si2-C19    | 117.9(16) |
| C45-Si2-C19    | 108.1(14) |
| C51-Si2-C39    | 100.5(14) |
| C45-Si2-C39    | 107.5(15) |
| C19-Si2-C39    | 104.8(12) |
| C45'-Si2'-C39' | 112.7(18) |
| C45'-Si2'-C19  | 106.5(15) |
| C39'-Si2'-C19  | 110.5(15) |
| C45'-Si2'-C51' | 111.4(15) |
| C39'-Si2'-C51' | 103.7(16) |
| C19-Si2'-C51'  | 112.2(17) |
| C2-C3-C4       | 124.5(8)  |
| C5-C4-C9       | 120.9(8)  |
| C5-C4-C3       | 122.3(8)  |
| C9-C4-C3       | 116.8(8)  |
| P1-O4-Au1      | 120.8(4)  |
| C6-C5-C4       | 120.8(8)  |
| C5-C6-C7       | 118.6(9)  |
| C8-C7-C6       | 122.8(8)  |
| C7-C8-C9       | 119.6(8)  |
| C10-C9-C4      | 120.9(8)  |
| C10-C9-C8      | 121.8(8)  |
| C4-C9-C8       | 117.2(8)  |
| C1-C10-C9      | 117.4(7)  |
| C1-C10-C11     | 120.8(8)  |
| C9-C10-C11     | 121.7(7)  |
| C20-C11-C12    | 119.9(8)  |
| C20-C11-C10    | 119.9(8)  |
| C12-C11-C10    | 119.8(8)  |
| C13-C12-C11    | 123.9(8)  |
| C13-C12-C17    | 118.3(8)  |
| C11-C12-C17    | 117.8(8)  |
| C14-C13-C12    | 122.3(9)  |
| C13-C14-C15    | 119.4(10) |



|              |           |
|--------------|-----------|
| C16-C15-C14  | 119.7(9)  |
| C15-C16-C17  | 121.5(8)  |
| C16-C17-C18  | 121.9(8)  |
| C16-C17-C12  | 118.7(8)  |
| C18-C17-C12  | 119.4(8)  |
| C19-C18-C17  | 122.8(8)  |
| C18-C19-C20  | 116.4(8)  |
| C18-C19-Si2' | 113.7(10) |
| C20-C19-Si2' | 129.8(10) |
| C18-C19-Si2  | 117.9(10) |
| C20-C19-Si2  | 125.2(10) |
| Si2'-C19-Si2 | 8.8(14)   |
| C11-C20-O2   | 119.8(8)  |
| C11-C20-C19  | 122.6(8)  |
| O2-C20-C19   | 117.5(8)  |
| C26-C21-C22  | 115.9(9)  |
| C26-C21-Si1  | 121.6(6)  |
| C22-C21-Si1  | 122.2(7)  |
| C23-C22-C21  | 121.0(9)  |
| C22-C23-C24  | 122.7(8)  |
| C25-C24-C23  | 116.8(10) |
| C24-C25-C26  | 120.8(10) |
| C25-C26-C21  | 122.6(8)  |
| C32-C27-C28  | 117.4(9)  |
| C32-C27-Si1  | 121.8(6)  |
| C28-C27-Si1  | 120.8(7)  |
| C29-C28-C27  | 120.2(9)  |
| C28-C29-C30  | 120.9(9)  |
| C31-C30-C29  | 119.2(9)  |
| C30-C31-C32  | 120.6(9)  |
| C31-C32-C27  | 121.7(8)  |
| C34-C33-C38  | 117.3(9)  |
| C34-C33-Si1  | 121.3(8)  |
| C38-C33-Si1  | 121.4(8)  |
| C33-C34-C35  | 122.1(10) |
| C34-C35-C36  | 118.9(9)  |
| C37-C36-C35  | 119.5(10) |
| C38-C37-C36  | 119.8(10) |

|                |           |
|----------------|-----------|
| C37-C38-C33    | 122.4(10) |
| C40-C39-C44    | 120.0     |
| C40-C39-Si2    | 123.8(12) |
| C44-C39-Si2    | 116.1(12) |
| C41-C40-C39    | 120.0     |
| C42-C41-C40    | 120.0     |
| C41-C42-C43    | 120.0     |
| C44-C43-C42    | 120.0     |
| C43-C44-C39    | 120.0     |
| C40'-C39'-C44' | 120.0     |
| C40'-C39'-Si2' | 118.3(14) |
| C44'-C39'-Si2' | 121.0(14) |
| C39'-C40'-C41' | 120.0     |
| C42'-C41'-C40' | 120.0     |
| C43'-C42'-C41' | 120.0     |
| C42'-C43'-C44' | 120.0     |
| C43'-C44'-C39' | 120.0     |
| C46'-C45'-C50' | 120.0     |
| C46'-C45'-Si2' | 116.4(13) |
| C50'-C45'-Si2' | 123.5(13) |
| C45'-C46'-C47' | 120.0     |
| C48'-C47'-C46' | 120.0     |
| C49'-C48'-C47' | 120.0     |
| C48'-C49'-C50' | 120.0     |
| C49'-C50'-C45' | 120.0     |
| C46-C45-C50    | 120.0     |
| C46-C45-Si2    | 122.4(10) |
| C50-C45-Si2    | 117.6(10) |
| C47-C46-C45    | 120.0     |
| C46-C47-C48    | 120.0     |
| C49-C48-C47    | 120.0     |
| C50-C49-C48    | 120.0     |
| C49-C50-C45    | 120.0     |
| C62-C57-C58    | 118.7(10) |
| C62-C57-P2     | 124.2(9)  |
| C58-C57-P2     | 117.0(8)  |
| C59-C58-C57    | 121.4(12) |
| C58-C59-C60    | 118.3(12) |

|                |           |
|----------------|-----------|
| C61-C60-C59    | 120.5(10) |
| C62-C61-C60    | 120.6(12) |
| C57-C62-C61    | 120.4(12) |
| C64-C63-C68    | 117.9(10) |
| C64-C63-P2     | 122.4(9)  |
| C68-C63-P2     | 119.4(8)  |
| C63-C64-C65    | 122.3(12) |
| C64-C65-C66    | 118.5(12) |
| C67-C66-C65    | 119.7(11) |
| C66-C67-C68    | 120.7(10) |
| C63-C68-C67    | 120.6(9)  |
| C70-C69-C74    | 117.9(10) |
| C70-C69-P2     | 124.0(8)  |
| C74-C69-P2     | 118.1(8)  |
| C69-C70-C71    | 123.0(10) |
| C70-C71-C72    | 117.1(11) |
| C73-C72-C71    | 118.4(10) |
| C72-C73-C74    | 123.9(12) |
| C73-C74-C69    | 119.7(12) |
| C52-C51-C56    | 120.0     |
| C52-C51-Si2    | 119.9(12) |
| C56-C51-Si2    | 117.4(12) |
| C53-C52-C51    | 120.0     |
| C54-C53-C52    | 120.0     |
| C53-C54-C55    | 120.0     |
| C56-C55-C54    | 120.0     |
| C55-C56-C51    | 120.0     |
| C52'-C51'-C56' | 120.0     |
| C52'-C51'-Si2' | 121.7(11) |
| C56'-C51'-Si2' | 118.2(11) |
| C53'-C52'-C51' | 120.0     |
| C52'-C53'-C54' | 120.0     |
| C55'-C54'-C53' | 120.0     |
| C54'-C55'-C56' | 120.0     |
| C55'-C56'-C51' | 120.0     |
| C11S-C1S-C12S  | 114.5(15) |
| C11S-C1S-C13S  | 109.1(13) |
| C12S-C1S-C13S  | 107.2(14) |

O1W-C1W-C2W            97(2)

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Torsion angles [°] for 7·CHCl<sub>3</sub>.

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|               |            |
|---------------|------------|
| C10-C1-O1-P1  | 69.8(10)   |
| C2-C1-O1-P1   | -115.0(8)  |
| C1-O1-P1-O3   | 67.3(7)    |
| C1-O1-P1-O4   | -163.2(6)  |
| C1-O1-P1-O2   | -48.6(7)   |
| O1-C1-C2-C3   | 178.6(8)   |
| C10-C1-C2-C3  | -6.6(15)   |
| O1-C1-C2-Si1  | -5.6(13)   |
| C10-C1-C2-Si1 | 169.3(8)   |
| C21-Si1-C2-C3 | 30.3(9)    |
| C27-Si1-C2-C3 | -89.4(9)   |
| C33-Si1-C2-C3 | 146.8(8)   |
| C21-Si1-C2-C1 | -145.4(8)  |
| C27-Si1-C2-C1 | 95.0(8)    |
| C33-Si1-C2-C1 | -28.9(10)  |
| O3-P1-O2-C20  | -162.4(6)  |
| O4-P1-O2-C20  | 68.0(7)    |
| O1-P1-O2-C20  | -42.2(7)   |
| O4-Au1-P2-C63 | 43.0(15)   |
| O4-Au1-P2-C57 | -76.2(15)  |
| O4-Au1-P2-C69 | 161.3(14)  |
| C1-C2-C3-C4   | 0.0(15)    |
| Si1-C2-C3-C4  | -176.0(7)  |
| C2-C3-C4-C5   | -179.7(10) |
| C2-C3-C4-C9   | 2.2(14)    |
| O3-P1-O4-Au1  | 154.8(4)   |
| O1-P1-O4-Au1  | 28.4(4)    |
| O2-P1-O4-Au1  | -82.0(5)   |
| P2-Au1-O4-P1  | -53.6(16)  |
| C9-C4-C5-C6   | 0.2(15)    |
| C3-C4-C5-C6   | -177.9(9)  |
| C4-C5-C6-C7   | -1.9(15)   |
| C5-C6-C7-C8   | 2.1(16)    |
| C6-C7-C8-C9   | -0.6(16)   |

|                  |           |
|------------------|-----------|
| C5-C4-C9-C10     | -176.3(9) |
| C3-C4-C9-C10     | 1.9(13)   |
| C5-C4-C9-C8      | 1.2(14)   |
| C3-C4-C9-C8      | 179.4(9)  |
| C7-C8-C9-C10     | 176.4(9)  |
| C7-C8-C9-C4      | -1.0(15)  |
| O1-C1-C10-C9     | -174.6(8) |
| C2-C1-C10-C9     | 10.5(15)  |
| O1-C1-C10-C11    | 7.6(14)   |
| C2-C1-C10-C11    | -167.3(9) |
| C4-C9-C10-C1     | -7.8(14)  |
| C8-C9-C10-C1     | 174.8(9)  |
| C4-C9-C10-C11    | 169.9(9)  |
| C8-C9-C10-C11    | -7.5(15)  |
| C1-C10-C11-C20   | -55.6(13) |
| C9-C10-C11-C20   | 126.8(10) |
| C1-C10-C11-C12   | 117.2(10) |
| C9-C10-C11-C12   | -60.5(12) |
| C20-C11-C12-C13  | 170.2(8)  |
| C10-C11-C12-C13  | -2.6(13)  |
| C20-C11-C12-C17  | -11.3(12) |
| C10-C11-C12-C17  | 175.9(8)  |
| C11-C12-C13-C14  | 177.6(9)  |
| C17-C12-C13-C14  | -0.9(13)  |
| C12-C13-C14-C15  | -0.4(14)  |
| C13-C14-C15-C16  | 2.1(14)   |
| C14-C15-C16-C17  | -2.6(14)  |
| C15-C16-C17-C18  | 178.8(9)  |
| C15-C16-C17-C12  | 1.3(13)   |
| C13-C12-C17-C16  | 0.5(12)   |
| C11-C12-C17-C16  | -178.1(8) |
| C13-C12-C17-C18  | -177.1(8) |
| C11-C12-C17-C18  | 4.3(12)   |
| C16-C17-C18-C19  | -175.4(9) |
| C12-C17-C18-C19  | 2.1(13)   |
| C17-C18-C19-C20  | -1.4(13)  |
| C17-C18-C19-Si1' | 179.7(12) |
| C17-C18-C19-Si2  | 171.1(11) |

|                   |            |
|-------------------|------------|
| C45'-Si2'-C19-C18 | -107.1(13) |
| C39'-Si2'-C19-C18 | 16(2)      |
| C51'-Si2'-C19-C18 | 130.8(12)  |
| C45'-Si2'-C19-C20 | 74.2(19)   |
| C39'-Si2'-C19-C20 | -163.1(12) |
| C51'-Si2'-C19-C20 | -47.9(19)  |
| C45'-Si2'-C19-Si2 | 13(10)     |
| C39'-Si2'-C19-Si2 | 135(12)    |
| C51'-Si2'-C19-Si2 | -109(11)   |
| C51-Si2-C19-C18   | 142.4(11)  |
| C45-Si2-C19-C18   | -82.7(12)  |
| C39-Si2-C19-C18   | 31.7(18)   |
| C51-Si2-C19-C20   | -45.8(18)  |
| C45-Si2-C19-C20   | 89.1(15)   |
| C39-Si2-C19-C20   | -156.5(11) |
| C51-Si2-C19-Si2'  | 79(11)     |
| C45-Si2-C19-Si2'  | -147(12)   |
| C39-Si2-C19-Si2'  | -32(10)    |
| C12-C11-C20-O2    | -171.6(7)  |
| C10-C11-C20-O2    | 1.1(12)    |
| C12-C11-C20-C19   | 12.5(13)   |
| C10-C11-C20-C19   | -174.7(8)  |
| P1-O2-C20-C11     | 70.3(9)    |
| P1-O2-C20-C19     | -113.7(8)  |
| C18-C19-C20-C11   | -5.9(13)   |
| Si2'-C19-C20-C11  | 172.7(13)  |
| Si2-C19-C20-C11   | -177.8(12) |
| C18-C19-C20-O2    | 178.2(7)   |
| Si2'-C19-C20-O2   | -3.2(17)   |
| Si2-C19-C20-O2    | 6.3(15)    |
| C27-Si1-C21-C26   | 160.7(8)   |
| C2-Si1-C21-C26    | 43.0(9)    |
| C33-Si1-C21-C26   | -77.8(8)   |
| C27-Si1-C21-C22   | -25.4(9)   |
| C2-Si1-C21-C22    | -143.2(8)  |
| C33-Si1-C21-C22   | 96.1(8)    |
| C26-C21-C22-C23   | 3.2(14)    |
| Si1-C21-C22-C23   | -171.0(8)  |

|                 |            |
|-----------------|------------|
| C21-C22-C23-C24 | -2.9(16)   |
| C22-C23-C24-C25 | 0.6(17)    |
| C23-C24-C25-C26 | 1.2(18)    |
| C24-C25-C26-C21 | -0.8(18)   |
| C22-C21-C26-C25 | -1.4(15)   |
| Si1-C21-C26-C25 | 172.9(9)   |
| C21-Si1-C27-C32 | -118.4(8)  |
| C2-Si1-C27-C32  | -1.3(9)    |
| C33-Si1-C27-C32 | 123.2(8)   |
| C21-Si1-C27-C28 | 61.7(8)    |
| C2-Si1-C27-C28  | 178.8(7)   |
| C33-Si1-C27-C28 | -56.6(8)   |
| C32-C27-C28-C29 | 2.2(13)    |
| Si1-C27-C28-C29 | -178.0(8)  |
| C27-C28-C29-C30 | -0.1(15)   |
| C28-C29-C30-C31 | -0.9(16)   |
| C29-C30-C31-C32 | -0.3(15)   |
| C30-C31-C32-C27 | 2.5(15)    |
| C28-C27-C32-C31 | -3.4(14)   |
| Si1-C27-C32-C31 | 176.8(8)   |
| C21-Si1-C33-C34 | -150.6(6)  |
| C27-Si1-C33-C34 | -29.4(7)   |
| C2-Si1-C33-C34  | 92.5(7)    |
| C21-Si1-C33-C38 | 30.3(7)    |
| C27-Si1-C33-C38 | 151.4(6)   |
| C2-Si1-C33-C38  | -86.7(7)   |
| C38-C33-C34-C35 | -0.7(11)   |
| Si1-C33-C34-C35 | -179.8(6)  |
| C33-C34-C35-C36 | 0.4(12)    |
| C34-C35-C36-C37 | -0.7(13)   |
| C35-C36-C37-C38 | 1.2(13)    |
| C36-C37-C38-C33 | -1.5(12)   |
| C34-C33-C38-C37 | 1.2(11)    |
| Si1-C33-C38-C37 | -179.6(6)  |
| C51-Si2-C39-C40 | 104.6(14)  |
| C45-Si2-C39-C40 | -18(2)     |
| C19-Si2-C39-C40 | -132.6(12) |
| C51-Si2-C39-C44 | -71.8(16)  |

|                     |            |
|---------------------|------------|
| C45-Si2-C39-C44     | 165.9(12)  |
| C19-Si2-C39-C44     | 51.0(18)   |
| C44-C39-C40-C41     | 0.0        |
| Si2-C39-C40-C41     | -176.3(17) |
| C39-C40-C41-C42     | 0.0        |
| C40-C41-C42-C43     | 0.0        |
| C41-C42-C43-C44     | 0.0        |
| C42-C43-C44-C39     | 0.0        |
| C40-C39-C44-C43     | 0.0        |
| Si2-C39-C44-C43     | 176.6(16)  |
| C45'-Si2'-C39'-C40' | -11(2)     |
| C19-Si2'-C39'-C40'  | -130.4(14) |
| C51'-Si2'-C39'-C40' | 109.2(16)  |
| C45'-Si2'-C39'-C44' | 178.1(14)  |
| C19-Si2'-C39'-C44'  | 59(2)      |
| C51'-Si2'-C39'-C44' | -61(2)     |
| C44'-C39'-C40'-C41' | 0.0        |
| Si2'-C39'-C40'-C41' | -170.5(19) |
| C39'-C40'-C41'-C42' | 0.0        |
| C40'-C41'-C42'-C43' | 0.0        |
| C41'-C42'-C43'-C44' | 0.0        |
| C42'-C43'-C44'-C39' | 0.0        |
| C40'-C39'-C44'-C43' | 0.0        |
| Si2'-C39'-C44'-C43' | 170(2)     |
| C39'-Si2'-C45'-C46' | -59(2)     |
| C19-Si2'-C45'-C46'  | 62.6(17)   |
| C51'-Si2'-C45'-C46' | -174.8(13) |
| C39'-Si2'-C45'-C50' | 124.5(16)  |
| C19-Si2'-C45'-C50'  | -114.2(14) |
| C51'-Si2'-C45'-C50' | 8(2)       |
| C50'-C45'-C46'-C47' | 0.0        |
| Si2'-C45'-C46'-C47' | -176.9(16) |
| C45'-C46'-C47'-C48' | 0.0        |
| C46'-C47'-C48'-C49' | 0.0        |
| C47'-C48'-C49'-C50' | 0.0        |
| C48'-C49'-C50'-C45' | 0.0        |
| C46'-C45'-C50'-C49' | 0.0        |
| Si2'-C45'-C50'-C49' | 176.7(17)  |



|                 |            |
|-----------------|------------|
| C51-Si2-C45-C46 | -156.4(11) |
| C19-Si2-C45-C46 | 68.0(14)   |
| C39-Si2-C45-C46 | -44.7(19)  |
| C51-Si2-C45-C50 | 24.3(19)   |
| C19-Si2-C45-C50 | -111.3(12) |
| C39-Si2-C45-C50 | 136.1(12)  |
| C50-C45-C46-C47 | 0.0        |
| Si2-C45-C46-C47 | -179.2(14) |
| C45-C46-C47-C48 | 0.0        |
| C46-C47-C48-C49 | 0.0        |
| C47-C48-C49-C50 | 0.0        |
| C48-C49-C50-C45 | 0.0        |
| C46-C45-C50-C49 | 0.0        |
| Si2-C45-C50-C49 | 179.3(13)  |
| C63-P2-C57-C62  | 21.1(11)   |
| C69-P2-C57-C62  | -89.4(10)  |
| Au1-P2-C57-C62  | 141.8(9)   |
| C63-P2-C57-C58  | -159.6(7)  |
| C69-P2-C57-C58  | 90.0(8)    |
| Au1-P2-C57-C58  | -38.9(8)   |
| C62-C57-C58-C59 | -3.0(15)   |
| P2-C57-C58-C59  | 177.6(9)   |
| C57-C58-C59-C60 | 3.5(16)    |
| C58-C59-C60-C61 | -3.9(18)   |
| C59-C60-C61-C62 | 3.9(19)    |
| C58-C57-C62-C61 | 2.8(16)    |
| P2-C57-C62-C61  | -177.9(9)  |
| C60-C61-C62-C57 | -3.3(19)   |
| C57-P2-C63-C64  | -74.1(11)  |
| C69-P2-C63-C64  | 38.0(11)   |
| Au1-P2-C63-C64  | 164.4(9)   |
| C57-P2-C63-C68  | 100.6(8)   |
| C69-P2-C63-C68  | -147.4(8)  |
| Au1-P2-C63-C68  | -21.0(8)   |
| C68-C63-C64-C65 | 5.5(19)    |
| P2-C63-C64-C65  | -179.7(10) |
| C63-C64-C65-C66 | -4(2)      |
| C64-C65-C66-C67 | 1.2(18)    |

|                     |            |
|---------------------|------------|
| C65-C66-C67-C68     | 0.8(16)    |
| C64-C63-C68-C67     | -3.5(15)   |
| P2-C63-C68-C67      | -178.4(7)  |
| C66-C67-C68-C63     | 0.4(15)    |
| C63-P2-C69-C70      | -116.9(9)  |
| C57-P2-C69-C70      | -3.9(10)   |
| Au1-P2-C69-C70      | 121.4(8)   |
| C63-P2-C69-C74      | 61.3(10)   |
| C57-P2-C69-C74      | 174.4(10)  |
| Au1-P2-C69-C74      | -60.4(10)  |
| C74-C69-C70-C71     | 1.6(17)    |
| P2-C69-C70-C71      | 179.8(9)   |
| C69-C70-C71-C72     | -3.2(18)   |
| C70-C71-C72-C73     | 4(2)       |
| C71-C72-C73-C74     | -4(2)      |
| C72-C73-C74-C69     | 2(3)       |
| C70-C69-C74-C73     | -1(2)      |
| P2-C69-C74-C73      | -179.3(12) |
| C45-Si2-C51-C52     | -149.3(12) |
| C19-Si2-C51-C52     | -18.1(16)  |
| C39-Si2-C51-C52     | 95.0(14)   |
| C45-Si2-C51-C56     | 49.3(16)   |
| C19-Si2-C51-C56     | -179.5(9)  |
| C39-Si2-C51-C56     | -66.4(14)  |
| C56-C51-C52-C53     | 0.0        |
| Si2-C51-C52-C53     | -160.9(12) |
| C51-C52-C53-C54     | 0.0        |
| C52-C53-C54-C55     | 0.0        |
| C53-C54-C55-C56     | 0.0        |
| C54-C55-C56-C51     | 0.0        |
| C52-C51-C56-C55     | 0.0        |
| Si2-C51-C56-C55     | 161.4(11)  |
| C45'-Si2'-C51'-C52' | -54(2)     |
| C39'-Si2'-C51'-C52' | -175.9(13) |
| C19-Si2'-C51'-C52'  | 64.8(18)   |
| C45'-Si2'-C51'-C56' | 123.2(14)  |
| C39'-Si2'-C51'-C56' | 2(2)       |
| C19-Si2'-C51'-C56'  | -117.5(13) |

|                     |            |
|---------------------|------------|
| C56'-C51'-C52'-C53' | 0.0        |
| Si2'-C51'-C52'-C53' | 177.6(18)  |
| C51'-C52'-C53'-C54' | 0.0        |
| C52'-C53'-C54'-C55' | 0.0        |
| C53'-C54'-C55'-C56' | 0.0        |
| C54'-C55'-C56'-C51' | 0.0        |
| C52'-C51'-C56'-C55' | 0.0        |
| Si2'-C51'-C56'-C55' | -177.7(17) |

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Crystal data and structure refinement for 7·MeOH/H<sub>2</sub>O

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|                                    |   |
|------------------------------------|---|
| Empirical formula                  | C76 H66 Au O7.50 P2 Si2   |
| Formula weight                     | 1414.37   |
| Temperature                        | 100(2) K  |
| Wavelength                         | 0.71073 Å   |
| Crystal system                     | Orthorhombic  |
| Space group                        | P2(1)2(1)2(1)   |
| Unit cell dimensions               | a = 11.7382(12) Å      <math>\langle = 90.00^\circ</math><br>b = 14.4403(14) Å      <math>\textcircled{R} = 90.00^\circ</math><br>c = 40.493(4) Å      <math>\textcircled{C} = 90.00^\circ</math> |
| Volume                             | 6863.7(12) Å <sup>3</sup>   |
| Z                                  | 4   |
| Density (calculated)               | 1.369 Mg/m <sup>3</sup>   |
| Absorption coefficient             | 2.279 mm <sup>-1</sup>  |
| F(000)                             | 2876  |
| Crystal size                       | 0.20 x 0.03 x 0.01 mm <sup>3</sup>  |
| Theta range for data collection    | 1.01 to 26.86 °.  |
| Index ranges                       | -13 <math>\leq h \leq 14</math> , -17 <math>\leq k \leq 10</math> , -50 <math>\leq l \leq 51</math>   |
| Reflections collected              | 39386   |
| Independent reflections            | 12587 [R(int) = 0.0658 ]  |
| Completeness to theta =26.86 °     | 0.967 %   |
| Absorption correction              | Empirical   |
| Max. and min. transmission         | 0.9776 and 0.6586   |
| Refinement method                  | Full-matrix least-squares on F <sup>2</sup>   |
| Data / restraints / parameters     | 12587 / 215 / 904   |
| Goodness-of-fit on F <sup>2</sup>  | 1.142   |
| Final R indices [I>2sigma(I)]      | R1 = 0.0588 , wR2 = 0.1424  |
| R indices (all data)               | R1 = 0.0644 , wR2 = 0.1464  |
| Absolute Structure Flack parameter | x =0.028(7)   |
| Largest diff. peak and hole        | 1.666 and -3.523 e.Å <sup>-3</sup>  |

Bond lengths [Å] and angles [°] for 7·MeOH/H<sub>2</sub>O.

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Bond lengths----

|         |            |
|---------|------------|
| Au1-O4  | 2.101(3)   |
| Au1-P1  | 2.2201(14) |
| C1-C6   | 1.380(9)   |
| C1-C2   | 1.423(7)   |
| C1-P1   | 1.830(5)   |
| C2-C3   | 1.426(6)   |
| C3-C4   | 1.378(8)   |
| C4-C5   | 1.393(8)   |
| C5-C6   | 1.393(8)   |
| C7-C12  | 1.396(8)   |
| C7-C8   | 1.438(7)   |
| C7-P1   | 1.825(5)   |
| C8-C9   | 1.396(7)   |
| C9-C10  | 1.359(9)   |
| C10-C11 | 1.456(9)   |
| C11-C12 | 1.396(8)   |
| C13-C14 | 1.364(7)   |
| C13-C18 | 1.406(6)   |
| C13-P1  | 1.858(5)   |
| C14-C15 | 1.435(7)   |
| C15-C16 | 1.408(9)   |
| C16-C17 | 1.386(8)   |
| C17-C18 | 1.383(7)   |
| C19-C28 | 1.377(5)   |
| C19-O1  | 1.412(5)   |
| C19-C20 | 1.426(5)   |
| C20-C21 | 1.387(5)   |
| C20-Si1 | 1.935(4)   |
| C21-C22 | 1.434(6)   |
| C22-C27 | 1.427(6)   |
| C22-C23 | 1.457(5)   |
| C23-C24 | 1.381(6)   |
| C24-C25 | 1.424(6)   |
| C25-C26 | 1.383(6)   |
| C26-C27 | 1.439(5)   |

|         |          |
|---------|----------|
| C27-C28 | 1.454(5) |
| C28-C29 | 1.515(5) |
| C29-C38 | 1.411(5) |
| C29-C30 | 1.456(6) |
| C30-C35 | 1.419(5) |
| C30-C31 | 1.433(6) |
| C31-C32 | 1.358(6) |
| C32-C33 | 1.416(6) |
| C33-C34 | 1.385(6) |
| C34-C35 | 1.425(6) |
| C35-C36 | 1.433(6) |
| C36-C37 | 1.382(6) |
| C37-C38 | 1.418(5) |
| C37-Si2 | 1.932(4) |
| C38-O2  | 1.428(5) |
| C39-C44 | 1.395(7) |
| C39-C40 | 1.437(6) |
| C39-Si1 | 1.910(4) |
| C40-C41 | 1.441(6) |
| C41-C42 | 1.408(8) |
| C42-C43 | 1.423(7) |
| C43-C44 | 1.397(7) |
| C45-C50 | 1.415(5) |
| C45-C46 | 1.425(7) |
| C45-Si1 | 1.904(4) |
| C46-C47 | 1.406(7) |
| C47-C48 | 1.400(7) |
| C48-C49 | 1.399(8) |
| C49-C50 | 1.383(6) |
| C51-C56 | 1.390(7) |
| C51-C52 | 1.417(5) |
| C51-Si1 | 1.896(5) |
| C52-C53 | 1.397(7) |
| C53-C54 | 1.401(7) |
| C54-C55 | 1.391(6) |
| C55-C56 | 1.416(7) |
| C57-C58 | 1.405(6) |
| C57-C62 | 1.416(8) |

|             |            |
|-------------|------------|
| C57-Si2     | 1.896(5)   |
| C58-C59     | 1.415(8)   |
| C59-C60     | 1.400(10)  |
| C60-C61     | 1.386(8)   |
| C61-C62     | 1.402(7)   |
| C63-C64     | 1.406(6)   |
| C63-C68     | 1.418(6)   |
| C63-Si2     | 1.915(4)   |
| C64-C65     | 1.362(7)   |
| C65-C66     | 1.401(8)   |
| C66-C67     | 1.381(9)   |
| C67-C68     | 1.405(7)   |
| C69-C70     | 1.3900     |
| C69-C74     | 1.3900     |
| C69-Si2     | 1.9015(18) |
| C70-C71     | 1.3900     |
| C71-C72     | 1.3900     |
| C72-C73     | 1.3900     |
| C73-C74     | 1.3900     |
| C69'-C70'   | 1.3900     |
| C69'-C74'   | 1.3900     |
| C69'-Si2    | 1.910(2)   |
| C70'-C71'   | 1.3900     |
| C71'-C72'   | 1.3900     |
| C72'-C73'   | 1.3900     |
| C73'-C74'   | 1.3900     |
| C69''-C70'' | 1.3900     |
| C69''-C74'' | 1.3900     |
| C69''-Si2   | 1.8978(19) |
| C70''-C71'' | 1.3900     |
| C71''-C72'' | 1.3900     |
| C72''-C73'' | 1.3900     |
| C73''-C74'' | 1.3900     |
| O1-P2       | 1.629(3)   |
| O2-P2       | 1.617(3)   |
| O3-P2       | 1.493(3)   |
| O4-P2       | 1.505(3)   |
| C1R-O1R     | 1.431(4)   |

|         |          |
|---------|----------|
| O1M-C1M | 1.425(4) |
| O1N-C1N | 1.437(4) |
| C1P-O1P | 1.414(4) |

Angles-----

|             |           |
|-------------|-----------|
| O4-Au1-P1   | 172.10(8) |
| C6-C1-C2    | 118.5(5)  |
| C6-C1-P1    | 124.0(4)  |
| C2-C1-P1    | 117.5(4)  |
| C1-C2-C3    | 119.1(5)  |
| C4-C3-C2    | 120.3(5)  |
| C3-C4-C5    | 120.5(5)  |
| C4-C5-C6    | 119.3(6)  |
| C1-C6-C5    | 122.3(6)  |
| C12-C7-C8   | 119.8(4)  |
| C12-C7-P1   | 122.1(4)  |
| C8-C7-P1    | 118.1(4)  |
| C9-C8-C7    | 118.3(5)  |
| C10-C9-C8   | 122.5(5)  |
| C9-C10-C11  | 120.0(5)  |
| C12-C11-C10 | 118.0(6)  |
| C7-C12-C11  | 121.4(5)  |
| C14-C13-C18 | 119.9(5)  |
| C14-C13-P1  | 117.1(4)  |
| C18-C13-P1  | 122.9(4)  |
| C13-C14-C15 | 120.7(5)  |
| C16-C15-C14 | 117.8(5)  |
| C17-C16-C15 | 121.0(5)  |
| C18-C17-C16 | 119.7(5)  |
| C17-C18-C13 | 120.7(5)  |
| C28-C19-O1  | 118.7(3)  |
| C28-C19-C20 | 123.0(3)  |
| O1-C19-C20  | 117.9(3)  |
| C21-C20-C19 | 117.8(3)  |
| C21-C20-Si1 | 118.6(3)  |
| C19-C20-Si1 | 123.6(3)  |
| C20-C21-C22 | 121.3(3)  |
| C27-C22-C21 | 120.1(3)  |



|             |          |
|-------------|----------|
| C27-C22-C23 | 118.9(4) |
| C21-C22-C23 | 121.0(4) |
| C24-C23-C22 | 120.5(4) |
| C23-C24-C25 | 120.0(4) |
| C26-C25-C24 | 120.9(4) |
| C25-C26-C27 | 120.7(4) |
| C22-C27-C26 | 118.8(3) |
| C22-C27-C28 | 118.0(3) |
| C26-C27-C28 | 123.2(3) |
| C19-C28-C27 | 119.0(3) |
| C19-C28-C29 | 119.7(3) |
| C27-C28-C29 | 121.2(3) |
| C38-C29-C30 | 117.9(3) |
| C38-C29-C28 | 122.1(4) |
| C30-C29-C28 | 120.0(3) |
| C35-C30-C31 | 118.5(4) |
| C35-C30-C29 | 118.4(4) |
| C31-C30-C29 | 123.1(3) |
| C32-C31-C30 | 120.5(4) |
| C31-C32-C33 | 121.6(4) |
| C34-C33-C32 | 119.3(4) |
| C33-C34-C35 | 120.4(4) |
| C30-C35-C34 | 119.6(4) |
| C30-C35-C36 | 119.7(4) |
| C34-C35-C36 | 120.7(3) |
| C37-C36-C35 | 123.4(3) |
| C36-C37-C38 | 116.0(4) |
| C36-C37-Si2 | 116.2(3) |
| C38-C37-Si2 | 127.6(3) |
| C29-C38-C37 | 124.3(4) |
| C29-C38-O2  | 116.6(3) |
| C37-C38-O2  | 119.1(3) |
| C44-C39-C40 | 118.0(4) |
| C44-C39-Si1 | 122.3(3) |
| C40-C39-Si1 | 119.6(4) |
| C39-C40-C41 | 121.0(5) |
| C42-C41-C40 | 118.5(4) |
| C41-C42-C43 | 120.1(4) |

|             |            |
|-------------|------------|
| C44-C43-C42 | 120.4(5)   |
| C39-C44-C43 | 121.9(4)   |
| C50-C45-C46 | 116.4(4)   |
| C50-C45-Si1 | 122.9(3)   |
| C46-C45-Si1 | 120.4(3)   |
| C47-C46-C45 | 121.8(4)   |
| C48-C47-C46 | 119.8(5)   |
| C49-C48-C47 | 119.0(5)   |
| C50-C49-C48 | 121.2(4)   |
| C49-C50-C45 | 121.8(4)   |
| C56-C51-C52 | 116.9(4)   |
| C56-C51-Si1 | 121.7(3)   |
| C52-C51-Si1 | 121.4(4)   |
| C53-C52-C51 | 122.1(4)   |
| C52-C53-C54 | 119.3(4)   |
| C55-C54-C53 | 120.2(5)   |
| C54-C55-C56 | 119.3(5)   |
| C51-C56-C55 | 122.2(4)   |
| C58-C57-C62 | 117.2(5)   |
| C58-C57-Si2 | 122.7(4)   |
| C62-C57-Si2 | 120.1(3)   |
| C57-C58-C59 | 120.4(6)   |
| C60-C59-C58 | 122.0(5)   |
| C61-C60-C59 | 117.4(5)   |
| C60-C61-C62 | 121.7(6)   |
| C61-C62-C57 | 121.3(5)   |
| C64-C63-C68 | 116.9(4)   |
| C64-C63-Si2 | 125.5(3)   |
| C68-C63-Si2 | 117.5(3)   |
| C65-C64-C63 | 122.3(4)   |
| C64-C65-C66 | 121.0(5)   |
| C67-C66-C65 | 118.3(5)   |
| C66-C67-C68 | 121.3(5)   |
| C67-C68-C63 | 120.1(4)   |
| C70-C69-C74 | 120.0      |
| C70-C69-Si2 | 116.60(16) |
| C74-C69-Si2 | 122.00(16) |
| C69-C70-C71 | 120.0      |

|                   |            |
|-------------------|------------|
| C72-C71-C70       | 120.0      |
| C71-C72-C73       | 120.0      |
| C72-C73-C74       | 120.0      |
| C73-C74-C69       | 120.0      |
| C70'-C69'-C74'    | 120.0      |
| C70'-C69'-Si2     | 112.24(16) |
| C74'-C69'-Si2     | 127.75(16) |
| C71'-C70'-C69'    | 120.0      |
| C70'-C71'-C72'    | 120.0      |
| C73'-C72'-C71'    | 120.0      |
| C72'-C73'-C74'    | 120.0      |
| C73'-C74'-C69'    | 120.0      |
| C70''-C69''-C74'' | 120.0      |
| C70''-C69''-Si2   | 115.83(16) |
| C74''-C69''-Si2   | 122.84(16) |
| C69''-C70''-C71'' | 120.0      |
| C70''-C71''-C72'' | 120.0      |
| C73''-C72''-C71'' | 120.0      |
| C74''-C73''-C72'' | 120.0      |
| C73''-C74''-C69'' | 120.0      |
| C19-O1-P2         | 120.6(3)   |
| C38-O2-P2         | 120.5(3)   |
| P2-O4-Au1         | 120.63(17) |
| C7-P1-C1          | 107.2(2)   |
| C7-P1-C13         | 104.9(2)   |
| C1-P1-C13         | 104.6(2)   |
| C7-P1-Au1         | 111.44(17) |
| C1-P1-Au1         | 110.65(18) |
| C13-P1-Au1        | 117.30(16) |
| O3-P2-O4          | 118.12(17) |
| O3-P2-O2          | 106.17(18) |
| O4-P2-O2          | 109.67(15) |
| O3-P2-O1          | 113.45(16) |
| O4-P2-O1          | 104.84(18) |
| O2-P2-O1          | 103.68(15) |
| C51-Si1-C45       | 110.51(18) |
| C51-Si1-C39       | 112.51(18) |
| C45-Si1-C39       | 106.7(2)   |

|               |            |
|---------------|------------|
| C51-Si1-C20   | 108.04(19) |
| C45-Si1-C20   | 106.74(17) |
| C39-Si1-C20   | 112.20(16) |
| C57-Si2-C69"  | 119.95(19) |
| C57-Si2-C69   | 111.25(19) |
| C69"-Si2-C69  | 8.7        |
| C57-Si2-C69'  | 103.01(19) |
| C69"-Si2-C69' | 17.2       |
| C69-Si2-C69'  | 8.6        |
| C57-Si2-C63   | 109.66(19) |
| C69"-Si2-C63  | 98.43(19)  |
| C69-Si2-C63   | 102.76(19) |
| C69'-Si2-C63  | 108.72(18) |
| C57-Si2-C37   | 108.0(2)   |
| C69"-Si2-C37  | 113.76(17) |
| C69-Si2-C37   | 118.92(17) |
| C69'-Si2-C37  | 121.39(17) |
| C63-Si2-C37   | 105.81(18) |

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Torsion angles [°] for 7·MeOH/H<sub>2</sub>O.

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|                 |           |
|-----------------|-----------|
| C6-C1-C2-C3     | 0.8(8)    |
| P1-C1-C2-C3     | -178.6(4) |
| C1-C2-C3-C4     | 0.7(7)    |
| C2-C3-C4-C5     | -1.6(8)   |
| C3-C4-C5-C6     | 0.9(9)    |
| C2-C1-C6-C5     | -1.4(9)   |
| P1-C1-C6-C5     | 177.9(5)  |
| C4-C5-C6-C1     | 0.6(10)   |
| C12-C7-C8-C9    | 0.5(7)    |
| P1-C7-C8-C9     | 179.7(4)  |
| C7-C8-C9-C10    | -0.3(7)   |
| C8-C9-C10-C11   | -1.6(8)   |
| C9-C10-C11-C12  | 3.3(9)    |
| C8-C7-C12-C11   | 1.4(8)    |
| P1-C7-C12-C11   | -177.8(5) |
| C10-C11-C12-C7  | -3.2(9)   |
| C18-C13-C14-C15 | -1.0(8)   |
| P1-C13-C14-C15  | -178.8(5) |
| C13-C14-C15-C16 | -0.2(9)   |
| C14-C15-C16-C17 | 0.7(10)   |
| C15-C16-C17-C18 | 0.1(10)   |
| C16-C17-C18-C13 | -1.3(8)   |
| C14-C13-C18-C17 | 1.8(8)    |
| P1-C13-C18-C17  | 179.4(4)  |
| C28-C19-C20-C21 | -8.6(7)   |
| O1-C19-C20-C21  | 178.6(4)  |
| C28-C19-C20-Si1 | 168.6(4)  |
| O1-C19-C20-Si1  | -4.2(6)   |
| C19-C20-C21-C22 | 1.6(7)    |
| Si1-C20-C21-C22 | -175.7(4) |
| C20-C21-C22-C27 | 2.5(7)    |
| C20-C21-C22-C23 | -177.5(5) |
| C27-C22-C23-C24 | 1.8(7)    |
| C21-C22-C23-C24 | -178.2(5) |
| C22-C23-C24-C25 | -3.1(8)   |
| C23-C24-C25-C26 | 1.5(8)    |

|                 |           |
|-----------------|-----------|
| C24-C25-C26-C27 | 1.5(8)    |
| C21-C22-C27-C26 | -178.9(4) |
| C23-C22-C27-C26 | 1.1(7)    |
| C21-C22-C27-C28 | -0.1(7)   |
| C23-C22-C27-C28 | 179.9(4)  |
| C25-C26-C27-C22 | -2.7(7)   |
| C25-C26-C27-C28 | 178.6(5)  |
| O1-C19-C28-C27  | -176.2(4) |
| C20-C19-C28-C27 | 11.0(7)   |
| O1-C19-C28-C29  | 5.7(7)    |
| C20-C19-C28-C29 | -167.1(4) |
| C22-C27-C28-C19 | -6.4(7)   |
| C26-C27-C28-C19 | 172.3(4)  |
| C22-C27-C28-C29 | 171.7(4)  |
| C26-C27-C28-C29 | -9.6(7)   |
| C19-C28-C29-C38 | -56.7(6)  |
| C27-C28-C29-C38 | 125.3(5)  |
| C19-C28-C29-C30 | 121.6(5)  |
| C27-C28-C29-C30 | -56.5(6)  |
| C38-C29-C30-C35 | -5.6(6)   |
| C28-C29-C30-C35 | 176.1(4)  |
| C38-C29-C30-C31 | 172.1(4)  |
| C28-C29-C30-C31 | -6.2(6)   |
| C35-C30-C31-C32 | -2.0(6)   |
| C29-C30-C31-C32 | -179.8(4) |
| C30-C31-C32-C33 | -1.0(7)   |
| C31-C32-C33-C34 | 2.7(7)    |
| C32-C33-C34-C35 | -1.3(6)   |
| C31-C30-C35-C34 | 3.4(6)    |
| C29-C30-C35-C34 | -178.8(4) |
| C31-C30-C35-C36 | -175.6(4) |
| C29-C30-C35-C36 | 2.2(6)    |
| C33-C34-C35-C30 | -1.7(6)   |
| C33-C34-C35-C36 | 177.3(4)  |
| C30-C35-C36-C37 | 1.6(6)    |
| C34-C35-C36-C37 | -177.4(4) |
| C35-C36-C37-C38 | -1.7(6)   |
| C35-C36-C37-Si2 | 173.7(3)  |

|                 |           |
|-----------------|-----------|
| C30-C29-C38-C37 | 5.8(6)    |
| C28-C29-C38-C37 | -175.9(4) |
| C30-C29-C38-O2  | -173.5(3) |
| C28-C29-C38-O2  | 4.7(6)    |
| C36-C37-C38-C29 | -2.2(6)   |
| Si2-C37-C38-C29 | -177.0(3) |
| C36-C37-C38-O2  | 177.2(4)  |
| Si2-C37-C38-O2  | 2.4(6)    |
| C44-C39-C40-C41 | 2.3(5)    |
| Si1-C39-C40-C41 | -179.0(3) |
| C39-C40-C41-C42 | -1.7(5)   |
| C40-C41-C42-C43 | 1.2(6)    |
| C41-C42-C43-C44 | -1.2(6)   |
| C40-C39-C44-C43 | -2.4(5)   |
| Si1-C39-C44-C43 | 179.0(3)  |
| C42-C43-C44-C39 | 1.9(6)    |
| C50-C45-C46-C47 | -1.4(7)   |
| Si1-C45-C46-C47 | 172.3(4)  |
| C45-C46-C47-C48 | 1.3(8)    |
| C46-C47-C48-C49 | 0.2(8)    |
| C47-C48-C49-C50 | -1.7(8)   |
| C48-C49-C50-C45 | 1.7(7)    |
| C46-C45-C50-C49 | -0.1(6)   |
| Si1-C45-C50-C49 | -173.6(3) |
| C56-C51-C52-C53 | 2.0(6)    |
| Si1-C51-C52-C53 | -174.9(3) |
| C51-C52-C53-C54 | -2.3(6)   |
| C52-C53-C54-C55 | 1.1(6)    |
| C53-C54-C55-C56 | 0.3(7)    |
| C52-C51-C56-C55 | -0.5(6)   |
| Si1-C51-C56-C55 | 176.4(3)  |
| C54-C55-C56-C51 | -0.6(7)   |
| C62-C57-C58-C59 | 0.5(7)    |
| Si2-C57-C58-C59 | 178.7(4)  |
| C57-C58-C59-C60 | 1.7(8)    |
| C58-C59-C60-C61 | -2.2(9)   |
| C59-C60-C61-C62 | 0.5(9)    |
| C60-C61-C62-C57 | 1.7(9)    |

|                         |             |
|-------------------------|-------------|
| C58-C57-C62-C61         | -2.2(7)     |
| Si2-C57-C62-C61         | 179.6(4)    |
| C68-C63-C64-C65         | 0.7(8)      |
| Si2-C63-C64-C65         | -174.7(5)   |
| C63-C64-C65-C66         | -1.7(9)     |
| C64-C65-C66-C67         | 3.1(9)      |
| C65-C66-C67-C68         | -3.6(9)     |
| C66-C67-C68-C63         | 2.7(9)      |
| C64-C63-C68-C67         | -1.1(8)     |
| Si2-C63-C68-C67         | 174.6(4)    |
| C74-C69-C70-C71         | 0.0         |
| Si2-C69-C70-C71         | 166.76(17)  |
| C69-C70-C71-C72         | 0.0         |
| C70-C71-C72-C73         | 0.0         |
| C71-C72-C73-C74         | 0.0         |
| C72-C73-C74-C69         | 0.0         |
| C70-C69-C74-C73         | 0.0         |
| Si2-C69-C74-C73         | -166.03(18) |
| C74'-C69'-C70'-C71'     | 0.0         |
| Si2-C69'-C70'-C71'      | 178.94(16)  |
| C69'-C70'-C71'-C72'     | 0.0         |
| C70'-C71'-C72'-C73'     | 0.0         |
| C71'-C72'-C73'-C74'     | 0.0         |
| C72'-C73'-C74'-C69'     | 0.0         |
| C70'-C69'-C74'-C73'     | 0.0         |
| Si2-C69'-C74'-C73'      | -178.76(19) |
| C74''-C69''-C70''-C71'' | 0.0         |
| Si2-C69''-C70''-C71''   | 167.18(17)  |
| C69''-C70''-C71''-C72'' | 0.0         |
| C70''-C71''-C72''-C73'' | 0.0         |
| C71''-C72''-C73''-C74'' | 0.0         |
| C72''-C73''-C74''-C69'' | 0.0         |
| C70''-C69''-C74''-C73'' | 0.0         |
| Si2-C69''-C74''-C73''   | -166.25(18) |
| C28-C19-O1-P2           | 69.8(5)     |
| C20-C19-O1-P2           | -117.1(4)   |
| C29-C38-O2-P2           | 69.6(4)     |
| C37-C38-O2-P2           | -109.8(4)   |



|                 |            |
|-----------------|------------|
| P1-Au1-O4-P2    | -56.1(7)   |
| C12-C7-P1-C1    | 24.8(5)    |
| C8-C7-P1-C1     | -154.4(4)  |
| C12-C7-P1-C13   | -86.1(4)   |
| C8-C7-P1-C13    | 94.8(4)    |
| C12-C7-P1-Au1   | 146.0(4)   |
| C8-C7-P1-Au1    | -33.2(4)   |
| C6-C1-P1-C7     | -80.4(5)   |
| C2-C1-P1-C7     | 98.9(4)    |
| C6-C1-P1-C13    | 30.7(6)    |
| C2-C1-P1-C13    | -150.0(4)  |
| C6-C1-P1-Au1    | 157.9(5)   |
| C2-C1-P1-Au1    | -22.8(4)   |
| C14-C13-P1-C7   | 172.6(4)   |
| C18-C13-P1-C7   | -5.1(5)    |
| C14-C13-P1-C1   | 59.9(5)    |
| C18-C13-P1-C1   | -117.8(4)  |
| C14-C13-P1-Au1  | -63.1(4)   |
| C18-C13-P1-Au1  | 119.2(4)   |
| O4-Au1-P1-C7    | -74.0(6)   |
| O4-Au1-P1-C1    | 45.2(6)    |
| O4-Au1-P1-C13   | 165.1(6)   |
| Au1-O4-P2-O3    | 157.41(17) |
| Au1-O4-P2-O2    | -80.8(2)   |
| Au1-O4-P2-O1    | 29.9(2)    |
| C38-O2-P2-O3    | -164.6(3)  |
| C38-O2-P2-O4    | 66.7(3)    |
| C38-O2-P2-O1    | -44.8(3)   |
| C19-O1-P2-O3    | 68.3(3)    |
| C19-O1-P2-O4    | -161.5(3)  |
| C19-O1-P2-O2    | -46.5(3)   |
| C56-C51-Si1-C45 | -116.0(3)  |
| C52-C51-Si1-C45 | 60.9(3)    |
| C56-C51-Si1-C39 | 124.9(3)   |
| C52-C51-Si1-C39 | -58.3(3)   |
| C56-C51-Si1-C20 | 0.5(4)     |
| C52-C51-Si1-C20 | 177.3(3)   |
| C50-C45-Si1-C51 | -26.1(4)   |

|                    |            |
|--------------------|------------|
| C46-C45-Si1-C51    | 160.7(3)   |
| C50-C45-Si1-C39    | 96.5(4)    |
| C46-C45-Si1-C39    | -76.7(4)   |
| C50-C45-Si1-C20    | -143.3(4)  |
| C46-C45-Si1-C20    | 43.5(4)    |
| C44-C39-Si1-C51    | 150.2(3)   |
| C40-C39-Si1-C51    | -28.3(3)   |
| C44-C39-Si1-C45    | 28.9(3)    |
| C40-C39-Si1-C45    | -149.7(3)  |
| C44-C39-Si1-C20    | -87.7(3)   |
| C40-C39-Si1-C20    | 93.8(3)    |
| C21-C20-Si1-C51    | -88.5(4)   |
| C19-C20-Si1-C51    | 94.4(4)    |
| C21-C20-Si1-C45    | 30.4(4)    |
| C19-C20-Si1-C45    | -146.7(4)  |
| C21-C20-Si1-C39    | 146.9(4)   |
| C19-C20-Si1-C39    | -30.2(5)   |
| C58-C57-Si2-C69"   | 25.4(5)    |
| C62-C57-Si2-C69"   | -156.4(4)  |
| C58-C57-Si2-C69    | 25.1(5)    |
| C62-C57-Si2-C69    | -156.8(4)  |
| C58-C57-Si2-C69'   | 22.5(4)    |
| C62-C57-Si2-C69'   | -159.4(4)  |
| C58-C57-Si2-C63    | 138.1(4)   |
| C62-C57-Si2-C63    | -43.8(5)   |
| C58-C57-Si2-C37    | -107.1(4)  |
| C62-C57-Si2-C37    | 71.1(4)    |
| C70"-C69"-Si2-C57  | 38.0(3)    |
| C74"-C69"-Si2-C57  | -155.3(2)  |
| C70"-C69"-Si2-C69  | 39.95(8)   |
| C74"-C69"-Si2-C69  | -153.27(9) |
| C70"-C69"-Si2-C69' | 47.74(9)   |
| C74"-C69"-Si2-C69' | -145.48(8) |
| C70"-C69"-Si2-C63  | -80.6(2)   |
| C74"-C69"-Si2-C63  | 86.2(2)    |
| C70"-C69"-Si2-C37  | 167.9(2)   |
| C74"-C69"-Si2-C37  | -25.3(2)   |
| C70-C69-Si2-C57    | 43.0(2)    |

|                    |            |
|--------------------|------------|
| C74-C69-Si2-C57    | -150.5(2)  |
| C70-C69-Si2-C69"   | -135.12(7) |
| C74-C69-Si2-C69"   | 31.36(11)  |
| C70-C69-Si2-C69'   | 60.36(8)   |
| C74-C69-Si2-C69'   | -133.16(9) |
| C70-C69-Si2-C63    | -74.2(2)   |
| C74-C69-Si2-C63    | 92.2(2)    |
| C70-C69-Si2-C37    | 169.4(2)   |
| C74-C69-Si2-C37    | -24.1(2)   |
| C70'-C69'-Si2-C57  | 70.5(2)    |
| C74'-C69'-Si2-C57  | -110.7(2)  |
| C70'-C69'-Si2-C69" | -100.83(6) |
| C74'-C69'-Si2-C69" | 78.01(12)  |
| C70'-C69'-Si2-C69  | -92.96(7)  |
| C74'-C69'-Si2-C69  | 85.88(12)  |
| C70'-C69'-Si2-C63  | -45.8(2)   |
| C74'-C69'-Si2-C63  | 133.0(2)   |
| C70'-C69'-Si2-C37  | -168.7(2)  |
| C74'-C69'-Si2-C37  | 10.1(3)    |
| C64-C63-Si2-C57    | -17.2(5)   |
| C68-C63-Si2-C57    | 167.5(4)   |
| C64-C63-Si2-C69"   | 108.9(5)   |
| C68-C63-Si2-C69"   | -66.5(4)   |
| C64-C63-Si2-C69    | 101.2(5)   |
| C68-C63-Si2-C69    | -74.1(4)   |
| C64-C63-Si2-C69'   | 94.8(5)    |
| C68-C63-Si2-C69'   | -80.6(4)   |
| C64-C63-Si2-C37    | -133.4(5)  |
| C68-C63-Si2-C37    | 51.3(4)    |
| C36-C37-Si2-C57    | -85.7(4)   |
| C38-C37-Si2-C57    | 89.1(4)    |
| C36-C37-Si2-C69"   | 138.6(3)   |
| C38-C37-Si2-C69"   | -46.6(4)   |
| C36-C37-Si2-C69    | 146.4(3)   |
| C38-C37-Si2-C69    | -38.8(4)   |
| C36-C37-Si2-C69'   | 156.0(3)   |
| C38-C37-Si2-C69'   | -29.2(5)   |
| C36-C37-Si2-C63    | 31.7(4)    |

C38-C37-Si2-C63

-153.5(4)

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