### Supporting Information

# A Multipurpose Gold(I) Precatalyst

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#### **General methods**

The Au(I) complexes: [tris(2,4-di-*tert*-butylphenyl)phosphite](benzonitrile)gold(I) hexafluoroantimonate and complex 7 were synthesized according to described procedures<sup>-1</sup>

AuCl, AgSbF<sub>6</sub>, dry PhCN (reagent) and dry MeCN (reagent) were stored and handled under an atmosphere of dry N<sub>2</sub> or dry Ar. 2,4,6-trimetoxybenzonitrile (tmbn) from Alfa Aesar (yellow) was purified by short column flash chromatography ( $CH_2Cl_2$ ) to yield a white crystalline solid. All other commercially available reagents were used as received and handled under air.

Unless otherwise specified: all experiments were performed under ambient conditions (atmosphere, lighting, temperature) in closed flasks or vials using magnetic stirring.  $CH_2Cl_2$  and  $Et_2O$  were dried under  $N_2$  using a solvent purification system (SPS). 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  $GF_{234}$ ). Chromatography purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 µm) or automated flash cromatographer CombyFlash Companion.

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. NMR chemical shifts ( $\delta$ ) are expressed in ppm. <sup>1</sup>H NMR chemical shifts are referenced to TMS (in the case of CDCl<sub>3</sub>) or to the solvent residual signal (in the case of other NMR solvents). <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>).

<sup>1.</sup> C. H. M. Amijs, V. López-Carrillo, M. Raducan, P. Pérez-Galán, C. Ferrer, A. M. Echavarren, *J. Org. Chem.* **2008**, *73*, 7721-7730.

#### Bis(benzonitrile)gold(I) hexafluoroantimonate

AuCl + PhCN + AgSbF<sub>6</sub> 
$$\xrightarrow{CH_2Cl_2}$$
 PhCN Au-NCPh<sup>+</sup> SbF<sub>6</sub><sup>-</sup>

This complex was synthesized and stored under Ar. Dry PhCN (0.31 mL, 3.0 mmol) was added over a suspension of AuCl (116 mg, 0.500 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) resulting in an immediate color change from orange to yellow. The suspension was stirred vigorously for 5 min in the dark then a solution of  $AgSbF_6$  (175 mg, 0.500 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added. The mixture was stirred vigorously at room temperature for 43 h in the absence of light and under positive Ar pressure. The precipitate was filtered off (suction through Teflon) then over the resulting CH<sub>2</sub>Cl<sub>2</sub> solution (aprox. 5 mL) Et<sub>2</sub>O (10 mL) was added. The resulting white precipitate was decanted under Ar, washed with Et<sub>2</sub>O (2x5 mL) and vacuum dried. It turned pale purple during vacuum drying and subsequent storage in the glovebox. Yield 188 mg (59%). IR: 2296 cm<sup>-1</sup> (CN); <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.97 (d, J = 7.7 Hz, 4H), 7.92 (t, J= 7.7 Hz, 2H), 7.69 (t, J = 8.0 Hz, 4H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  137.38 (CH), 134.56 (CH), 130.49 (CH), 119.85 (CN), 106.57 (C). MS (TOF MS ES+) peak  $[Au(PhCN)_3]^+$  observed corresponding to at 506.0. Anal. calcd. for C<sub>14</sub>H<sub>10</sub>AuF<sub>6</sub>N<sub>2</sub>Sb·0.5H<sub>2</sub>O: C, 25.95; H, 1.71; N, 4.32; found: C, 25.78; H, 1.61; N, 4.87; **Bis(2,4,6-trimethoxybenzonitrile)gold(I) hexafluoroantimonate (1)** 



Under an Ar atmosphere, AuCl (466 mg, 2.00 mmol) and tmbn (2.77 g, 14.0 mmol) were vigorously stirred in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) in the dark for 10 min then a solution of AgSbF<sub>6</sub> (703 mg, 2.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added. The mixture was stirred in the dark for 20 min, then it was filtered through 2 Teflon filters (under air) and CHCl<sub>3</sub> (comerial grade, 40 mL) and Et<sub>2</sub>O (40 mL) were added. The precipitate was filtered, air dried and vacuum dried (65 °C, overnight) to yield a white solid (1.23-1.37 g, 75-83%). mp 226-231 (dec); IR: 2278 cm<sup>-1</sup> (CN); <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  6.16 (s, 4H), 3.94 (s, 12H), 3.93 (s, 6H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  169.91 (C), 166.61 (C), 118.89 (CN), 91.57 (CH), 78.30 (C), 57.19 (CH<sub>3</sub>), 56.85 (CH<sub>3</sub>); MALDI-MS calcd. for C<sub>20</sub>H<sub>22</sub>AuN<sub>2</sub>O<sub>6</sub><sup>+</sup> [M-SbF<sub>6</sub>]<sup>+</sup>: 583.1; found: 583.1. Anal. calcd. for: C<sub>20</sub>H<sub>22</sub>AuF<sub>6</sub>N<sub>2</sub>O<sub>6</sub>Sb: C, 29.33; H, 2.71; N, 3.42;. Found: C, 29.26; H, 2.87; N, 3.47.

Phosphine test: the nitrile complex (7.3 mg for tmbn or 5.5 mg for PhCN) and 6.6 mg 2-(di-*t*-Bu-phosphino)biphenyl were dissolved in 0.5 mL CDCl<sub>3</sub> and the ratio Au:Ag was determined by integration of the <sup>31</sup>P NMR spectra. The results were in concordance with the ones obtained by integration of the <sup>1</sup>H NMR spectra.

Recovery of the desired complex from a sample contaminated with Ag(I) complex **2a**: 1.18 g sample prepared as above was found to contain silver (mol ratio Au : Ag = 3 : 1). This solid was precipitated from  $CH_2Cl_2$  (40 mL)/CHCl<sub>3</sub> (40 mL)/Et<sub>2</sub>O (20 mL) and dried as above in order to obtain the desired complex, free of silver (0.63 g, 39%).

#### **Bis(2,4,6-trimethoxybenzonitrile)silver(I) hexafluoroantimonate (2a)**



2,4,6-Trimethoxybenzonitrile (213 mg, 1.10 mmol) was dissolved in a solution of AgSbF<sub>6</sub> (176 mg, 0.500 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) then the mixture was filtered (Teflon) and Et<sub>2</sub>O (10 mL) was added. The resulting precipitate was filtered and vacuum dried (50 °C, 5 h) to give **2a** (315 mg, 86%) bright white solid. X-ray quality crystals were obtained by slow diffusion of Et<sub>2</sub>O over a solution of the complex in CH<sub>2</sub>Cl<sub>2</sub>. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  6.15 (s, 4H), 3.92 (s, 12H), 3.91 (s, 6H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  168.56 (C), 165.73 (C), 118.77 (C), 91.33 (CH), 80.09 (C), 56.98 (CH<sub>3</sub>), 56.61 (CH<sub>3</sub>); MS ESI calcd for C<sub>20</sub>H<sub>22</sub>AgN<sub>2</sub>O<sub>6</sub> (M-SbF<sub>6</sub>): 493.1, found: 493.0. Anal. calcd for C<sub>20</sub>H<sub>22</sub>AgF<sub>6</sub>N<sub>2</sub>O<sub>6</sub>Sb: C, 32.91; H, 3.04; N, 3.84; found: C, 33.05; H, 3.11; N, 3.92.

#### Bis(acetonitrile)silver(I) hexafluoroantimonate (2b)

$$Ag^+SbF_6^- \xrightarrow{MeCN} [Ag(NCMe)_2]^+(SbF_6)^-$$

The following operations were performed in a glovebox, under Ar. A solution of  $AgSbF_6$  (0.702 g, 2.00 mmol) in dry  $CH_2Cl_2$  10 mL, was suction filtered (through a Teflon HPLC filter) and transferred to a vial, then 0.23 mL dry MeCN (0.23 mL, 4.4 mmol) was added. The resulting clear solution was carefully layered with pentane (10 mL) and allowed to stand. After 24 hours large crystals had formed. The mixture was shaken until the liquid phase homogenized, and the turbid solution was allowed to stand over the large crystals for another 24 h. The resulting crop of crystals were separated by decantation and vacuum dried (739 mg, 90%). The crystalline complex did not change in aspect or NMR properties after being stored for a week under ambient moisture and

lighting. It was stored in a aluminum covered vial in a desiccator and weighed under air when needed. At least one of the resulting crystals was of X-ray quality. <sup>1</sup>H NMR (500 MHz,  $CD_2Cl_2$ )  $\delta$  2.29 (s, 6H); <sup>13</sup>C NMR (125 MHz,  $CD_2Cl_2$ )  $\delta$  120.38 (C), 2.62 (CH<sub>3</sub>); Anal. calcd. for C<sub>4</sub>H<sub>6</sub>AgF<sub>6</sub>N<sub>2</sub>Sb: C, 11.29; H, 1.42; N, 6.58; found: C, 10.86; H, 1.40; N, 6.56.

# (Tris(perfluorophenyl)phosphine)(2,4,6-trimethoxybenzonitrile)gold(I) hexafluoroantimonate (3)

 $[Au(tmbn)_2](SbF_6) + C_6F_5 - P \xrightarrow{C_6F_5} CH_2Cl_2 \xrightarrow{C_6F_5} C_6F_5 \xrightarrow{MeO} SbF_6$ 

A solution of tris(pentafluorophenyl)phosphine (27 mg, 0.05 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.25 mL) was added over a stirred solution of [Au(tmbn)<sub>2</sub>](SbF<sub>6</sub>) (1) (41 mg, 0.05 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) then Et<sub>2</sub>O was added (3.75 mL) and the solution was allowed to stand overnight in a closed vial. The resulting precipitate was filtered and vacuum dried (50 °C, 5 h) to yield the desired complex as a white solid (46mg, 79% yield). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  6.16 (s, 2H), 3.94 (s, 6H), 3.93 (s, 3H); <sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -127.5 (br s, 6F), -140.0 (br s, 3F), -156.50 (br s, 6F); <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -37.1 (br s, 1P); ESI-MS calcd. for C<sub>28</sub>H<sub>11</sub>AuF<sub>15</sub>NO<sub>3</sub>P<sup>+</sup> [M-SbF<sub>6</sub>]: 922.0; found: 921.8. Anal. calcd. for C<sub>28</sub>H<sub>11</sub>AuF<sub>21</sub>NO<sub>3</sub>PSb: C, 29.04; H, 0.96; N, 1.21; found: C, 28.96; H, 1.01; N, 1.38.

#### [Au(JohnPHOS)(2,4,6-trimethoxybenzonitrile)](SbF<sub>6</sub>) (4)

Method A.



A mixture of the cationic complex [Au(JohnPhos)(NCMe)](SbF<sub>6</sub>) (77 mg, 0.10 mmol) and 2,4,6-trimethoxybenzonitrile (20 mg, 0.10 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 mL). After evaporation and vacuum drying (50 °C, 5 h) **4** was obtained as a white foamy solid (93 mg, 100%). <sup>1</sup>H{<sup>31</sup>P} NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.91-7.89 (m, 1H), 7.62-7.58 (m, 2H), 7.49-7.45 (m, 2H), 7.42-7.38 (m, 1H), 7.35-7.33 (m, 1H), 7.20 (d, *J* = 7.2 Hz, 2H), 6.21 (s, 2H), 4.01 (s, 6H), 3.96 (s, 3H), 1.45 (s, 18H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.01 (C), 165.75 (C), 149.15 (d, *J* = 12.1 Hz, C), 142.52 (d, *J* = 6.8 Hz, C), 133.33 (d, *J* = 5.4 Hz, CH), 133.27 (d, *J* = 1.9 Hz, CH), 131.67 (d, *J* = 2.4 Hz, CH), 129.60 (CH), 129.09 (CH), 128.44 (CH), 127.83 (d, *J* = 7.7 Hz, CH), 123.95 (d, *J* =

51.2 Hz, C), 117.05 (br s, C), 91.40 (CH), 77.36 (C), 56.81 (CH<sub>3</sub>), 56.62 (CH<sub>3</sub>), 38.23 (d, J = 27.3 Hz, C), 31.02 (d, J = 6.1 Hz, CH<sub>3</sub>); <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  60.6 (s, 1P); HRMS ESI calcd. for C<sub>30</sub>H<sub>38</sub>AuNO<sub>3</sub>P (M-SbF<sub>6</sub>): 688.2, found: 688.0; Anal. calcd. for C<sub>30</sub>H<sub>38</sub>AuF<sub>6</sub>NO<sub>3</sub>PSb: C, 38.98; H, 4.14; N, 1.52; found: C, 39.42; H, 4.03; N, 1.70. *Method B*.



A solution of 2-di-*t*Bu-phosphinobiphenyl (30 mg, 0.10 mmol) in  $CH_2Cl_2$  was added dropwise with shaking over a solution of  $[Au(tmbn)_2](SbF_6)$  (1) (82 mg, 0.10 mmol) in  $CH_2Cl_2$  (2 mL), then  $Et_2O$  was added until turbidity was observed (15 mL). The mixture was allowed to stand overnight at room temperature, then 4 h at 10 °C (fridge) then 24 h at room temperature. The resulting white microcrystalline powder was filtered and vacuum dried (50 °C, 5 h) to give 4 (76 mg, 90% yield).

# (Tris(2,4-di-*tert*-butylphenyl)phosphite)(2,4,6-trimethoxybenzonitrile)gold(I) hexafluoroantimonate (5)



A solution of AgSbF<sub>6</sub> (70.2 mg, 0.200 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added over a solution of gold (I) chloro(tris(2,4-di-*tert*-butylphenyl)phosphite) (176 mg, 0.200 mmol) and 2,4,6-trimethoxybenzonitrile (38.7 mg, 0.2 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (2 mL). A white precipitate appeared immediately. After stirring for 5 min, the mixture was filtered (double Teflon filter), evaporated and vacuum dried. (60 °C, 2 h). The cationic complex **5** was obtained as a light purple solid which contained solvated CH<sub>2</sub>Cl<sub>2</sub> (1:1 complex/CH<sub>2</sub>Cl<sub>2</sub> = 1:1) (239 mg, 88%). <sup>1</sup>H{<sup>31</sup>P} NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.50 (d, *J* = 2.5 Hz, 3H), 7.35 (d, *J* = 8.6 Hz, 3H), 7.21 (dd, *J* = 8.6, 2.5 Hz, 3H), 6.18 (s, 2H), 5.30 (s, 2H), 3.95 (s, 3H), 3.93 (s, 6H), 1.47 (s, 27 H), 1.31 (s, 27 H); <sup>13</sup>C NMR (PENDANT, 101 MHz, CDCl<sub>3</sub>)  $\delta$  169.92 (C), 166.24 (C), 149.39 (C), 147.06 (d, *J* = 6.6 Hz, C), 139.38 (d, *J* = 7.2 Hz, C), 126.10 (CH), 124.65 (CH), 121.37 (C), 119.03 (d, *J* = 8.4 Hz, CH), 91.63 (CH), 77.23 (C), 56.99 (CH<sub>3</sub>), 56.83 (CH<sub>3</sub>), 35.29 (C), 34.91 (C), 31.46 (CH<sub>3</sub>), 30.72 (CH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  91.8 (s, 1P); MS ESI

Calcd for C<sub>52</sub>H<sub>74</sub>AuNO<sub>6</sub>P (M-SbF<sub>6</sub>): 1036.5, found: 1036.1. Anal. calcd. for C<sub>52.5</sub>H<sub>75</sub>AuClF<sub>6</sub>NO<sub>6</sub>PSb (M+0.5CH<sub>2</sub>Cl<sub>2</sub>): C, 47.94; H, 5.75; N, 1.06; found: C, 47.95; H, 5.62; N, 1.25.

[1,3-Bis(2,4,6-trimethyl-phenyl)imidazol-2-ylidene](2,4,6-trimethoxybenzonitrile)gold(I) hexafluoroantimonate (6)



A solution of [AgCl(IMes)] (27 mg, 60 µmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.6 mL) was added over a solution of  $[Au(tmbn)_2](SbF_6)$  (1) (49 mg, 60 µmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.2 mL). After shaking for 5 min, the mixture was filtered through a Teflon HPLC filter, then Et<sub>2</sub>O (7.2 mL) was added and the mixture was allowed to stand overnight.  $[(IMes)Au(tmbn)](SbF_6)^1$  was obtained as colorless needles which were separated by decantation, washed with Et<sub>2</sub>O (3x1.2 mL) and vacuum dried (39 mg, 70%).

[1,3-Bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene](2,4,6trimethoxybenzonitrile)gold(I) hexafluoroantimonate (7)



A solution of [AgCl(IMes)] (82 mg, 0.15 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL + 0.5 mL rinsing) was added over a solution of [Au(tmbn)<sub>2</sub>](SbF<sub>6</sub>) (1) (123 mg, 0.15 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) then the mixture was stirred for 5 min. The resulting AgCl was filtered off (through 2 HPLC Teflon filters) then the mixture was evaporated to dryness. Precipitation from CHCl<sub>3</sub> (3 mL) /Et<sub>2</sub>O (6 mL) yielded **7** as white crystals which were filtered and vacuum dried at 50 °C for 4 h (130 mg, 86% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.59 (t, *J* = 7.8 Hz, 2H), 7.40 (s, 2H), 7.36 (d, *J* = 7.8 Hz, 4H), 6.08 (s, 2H), 3.89 (s, 3H), 3.83 (s, 6H), 2.51 (septuplet, *J* = 6.8 Hz, 4H), 1.32 (d, *J* = 6.8 Hz, 12H), 1.27 (d, *J* = 6.8 Hz, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.26 (C), 167.06 (C), 165.76 (C), 145.80 (C), 133.38 (C), 131.39 (CH), 124.99 (CH), 124.66 (CH), 119.07 (C), 91.25 (CH), 78.10

(C), 56.75 (CH<sub>3</sub>), 56.62 (CH<sub>3</sub>), 29.02 (CH), 24.71 (CH<sub>3</sub>), 24.15 (CH<sub>3</sub>); ESI-MS calcd for  $C_{37}H_{47}AuN_3O_3^+$  [M-SbF<sub>6</sub>]<sup>+</sup>: 778.3; found: 778.2. Anal. calcd. for  $C_{37}H_{47}AuF_6N_3O_3Sb$ : C, 43.80; H, 4.67; N, 4.14; found: C, 43.95; H, 4.61; N, 4.28. [Au<sub>2</sub>((*R*)-DTBM-MeO-BIPHEP)(tmbn)<sub>2</sub>](SbF<sub>6</sub>)<sub>2</sub> (8)



A solution of (R)-DTBM-MeO-BIPHEP (58 mg, 50 µmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was added with shaking over a solution of  $[Au(tmbn)_2](SbF_6)$  (1) (82 mg, 0.10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) then Et<sub>2</sub>O (10 mL) and was added. After 24 h the mixture was homogenized by sonication and a small amount of solid  $[Au(tmbn)_2](SbF_6)$  (<0.1 mg) was added then the mixture was allowed to stand for 24 h. The resulting small needles were separated by decantation, washed with Et<sub>2</sub>O (2x1 mL) and vacuum dried at 50 °C, overnight (78 mg, 65% yield). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.66 (td, J = 8.1, 2.9 Hz, 2H), 7.36 (d, J = 14.7 Hz, 4H), 7.18 (d, J = 14.6 Hz, 4H), 7.13 (d, J = 8.5 Hz, 2H), 7.04 (dd, J = 11.2, 7.7 Hz, 2H), 6.14 (s, 4H), 3.93 (s, 6H), 3.86 (s, 12H), 3.75 (s, 6H), 3.52 (s, 2H), 3.75 (s, 2H),6H), 2.85 (s, 6H), 1.38 (s, 36H), 1.29 (s, 36H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 169.97 (br s, C), 166.23 (br s, C), 164.12 (d, J = 3.0 Hz, C), 163.66 (d, J = 2.9 Hz, C), 160.01 (d, J = 12.7 Hz, C), 146.33 (d, J = 12.7 Hz, C), 146.06 (d, J = 12.3 Hz, C), 133.31 (d, J)= 15.9 Hz, CH), 133.01 (d, J = 15.4 Hz, CH), 131.06 (d, J = 11.9 Hz, CH), 129.95-129.73 (m, C), 128.08 (d, J = 68.1 Hz, C), 127.15 (d, J = 6.3 Hz, CH), 121.92 (d, J =70.1 Hz, C), 120.10 (d, J = 72.8 Hz, C), 118.94 (C), 115.24 (d, J = 1.9 Hz, CH), 91.75 (CH), 77.90 (br s, C), 65.30 (CH<sub>3</sub>), 64.86 (CH<sub>3</sub>), 57.10 (CH<sub>3</sub>), 56.97 (CH<sub>3</sub>), 54.77 (CH<sub>3</sub>), 36.54 (C), 36.34 (C), 31.95 (CH<sub>3</sub>); <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 20.8 (s, 2P); ESI-MS calcd. for  $C_{94}H_{126}Au_2F_6N_2O_{12}P_2Sb^+$  [M-SbF<sub>6</sub>]<sup>+</sup>: 2167.7, found: 2167.4. Anal. calcd. for C<sub>94</sub>H<sub>126</sub>Au<sub>2</sub>F<sub>12</sub>N<sub>2</sub>O<sub>12</sub>P<sub>2</sub>Sb<sub>2</sub>: C, 46.98; H, 5.28; N, 1.17; found: C, 46.79; H, 5.06; N, 1.33.

#### [Au<sub>2</sub>((*R*)-DTBM-SEGPHOS)(tmbn)<sub>2</sub>](SbF<sub>6</sub>)<sub>2</sub> (9)



A solution of (R)-DTBM-SEGPHOS (35.4 mg, 30 µmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.3 mL), was added dropwise with shaking over a solution of  $[Au(tmbn)_2](SbF_6)$  (1) (49 mg, 60 umol) in CH<sub>2</sub>Cl<sub>2</sub> (1.2 mL) then Et<sub>2</sub>O (commercial grade, 6 mL) was added and the turbid mixture was allowed to stand overnight in a capped vial. The resulting small colorless needles were filtered and vacuum dried (50 °C, overnight) (52 mg, 71% yield). X-ray quality crystals were obtained by slow counter diffusion of Et<sub>2</sub>O into a solution of the complex in CH<sub>2</sub>Cl<sub>2</sub>. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.36 (d, J = 14.9 Hz, 4H), 7.31 (d, J = 14.8 Hz, 4H), 7.07 (dd, J = 8.1, 1.6 Hz, 2H), 6.97 (dd, J = 12.1, 8.1 Hz, 2H),6.14 (s, 4H), 5.77 (d, J = 1.3 Hz, 2H), 4.75 (d, J = 1.3 Hz, 2H), 3.92 (s, 6H), 3.86 (s, 12H), 3.74 (s, 6H), 3.51 (s, 6H), 1.35 (s, 36H), 1.30 (s, 36H); <sup>13</sup>C NMR (125 MHz,  $CD_2Cl_2$ )  $\delta$  170.05 (C), 166.24 (C), 164.44 (C), 164.25 (C), 152.01 (C), 149.91 (d, J = 14.2 Hz, C), 146.20 (d, J = 13.1 Hz, C), 146.08 (d, J = 12.9 Hz, C), 133.98 (d, J = 16.5Hz, CH), 133.42 (d, J = 16.9 Hz, CH), 131.32 (d, J = 7.4 Hz, CH), 120.80 (d, J = 42.8Hz, C), 120.23 (d, J = 42.1 Hz, C), 119.58 (d, J = 72.8 Hz, C), 119.66-119.56 (m, C), 117.89-117.70 (m, C), 109.95 (d, J = 12.5 Hz, CH), 103.01 (CH<sub>2</sub>), 91.80 (CH), 77.86 (C), 65.36 (CH<sub>3</sub>), 64.93 (CH<sub>3</sub>), 57.18 (CH<sub>3</sub>), 57.02 (CH<sub>3</sub>), 36.47 (C), 36.38 (C), 31.87 (CH<sub>3</sub>), 31.81 (CH<sub>3</sub>); <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 23.1 (s, 2P); ESI-MS calcd for  $C_{94}H_{122}Au_{2}F_{6}N_{2}O_{14}P_{2}Sb^{+}$  [M-SbF<sub>6</sub>]<sup>+</sup>: 2195.7, found: 2195.5. Anal. calcd. for: C<sub>94</sub>H<sub>122</sub>Au<sub>2</sub>F<sub>12</sub>N<sub>2</sub>O<sub>14</sub>P<sub>2</sub>Sb<sub>2</sub>: C, 46.44; H, 5.06; N, 1.15; found: C, 46.31; H, 4.93; N, 1.31.

## General procedure for Addition of Dibenzoylmethane to Enyne 12 (Table 1)<sup>1,2</sup>

To a solution of  $[Au(tmbn)_2](SbF_6)$  (1) (9.8 mg, 12 µmol) and additive in CH<sub>2</sub>Cl<sub>2</sub> (0.3 mL) a solution of the ligand (14 µmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.3 mL) was added then the resulting mixture was added to a solution of enyne 10 (65 mg, 0.20 mmol) and dibenzoylmethane (224 mg, 1.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.4 mL). The reaction mixture was stirred at room

<sup>2.</sup> C. H. M. Amijs, C. Ferrer, A. M. Echavarren, Chem. Commun. 2007, 698-700.

temperature for the time indicated in Table. The mixture was filtered trough silica gel, which was further eluted with CH<sub>2</sub>Cl<sub>2</sub> several times.

Determination of the yield by NMR: a precisely weighed quantity of internal standard (1,3,5 trimethoxybenzene or BHT) was added to the  $CH_2Cl_2$  solution and a sample of the homogeneous mixture was evaporated and analyzed by H NMR (CDCl<sub>3</sub>). Compounds **11a/11b** were described previously.<sup>1,2</sup>

Isolated yield: The  $CH_2Cl_2$  solution was concentrated over Florisil and purified by flash chromatography chromatography (hexane/EtOAc = 5:1, 3x15 cm silica) to give a mixture of products **11a/11b** as a white solid. Ratios and yield in the table. When the mixture contained traces of contaminants (dibenzoylmethane,  $CH_2Cl_2$ , EtOAc,), the purity of the cyclized compound was determined by <sup>1</sup>H NMR and the yield was corrected accordingly.

#### Synthesis of Supported Gold(I) Complexes

#### PS1-PAu

In a flame-dried round bottom flask, commercially available polystyrene bound triphenylphosphine ( $f = 1.6 \text{ mmol} \cdot \text{g}^{-1}$ , 55 mg, 0.087 mmol) was introduced, the system was purged with a gentle stream of Ar and the resin was swollen with 1 mL of dry CH<sub>2</sub>Cl<sub>2</sub>. In another flask, [Au(tmbn)<sub>2</sub>]SbF<sub>6</sub> (1) (75 mg, 0.091 mmol) was introduced, and transferred via cannula and under inert atmosphere to the flask containing the resin dissolved in 1 mL CH<sub>2</sub>Cl<sub>2</sub> (+1 mL rinse). The mixture obtained was shaken for 45 minutes at room temperature and then it was filtered under inert atmosphere, washed with CH<sub>2</sub>Cl<sub>2</sub> (3 x 10 mL) and dried under reduced pressure, to give *PS<sub>1</sub>*-PAu as a purple solid.

IR: 3057, 2920, 2246, 1602, 1437 cm<sup>-1</sup>. <sup>31</sup>P NMR: Broad singlets at 49.8 and 31.8 ppm. Anal. calcd. for  $f_{\text{max}} = 0.800 \text{ mmol} \cdot \text{g}^{-1}$ : N, 1.12%; found: C, 58.94%; H, 4.84%; N, 0.52%.  $f = 0.372 \text{ mmol} \cdot \text{g}^{-1}$  (46% yield of functionalization).<sup>3</sup>

#### *PS*<sub>1</sub>-P

Hydroxymethyl polystyrene (f = 1.0 mmol/g, 3.0 g, 3.0 mmol) was introduced in a 50mL Schlenk flask and the system was purged by a gentle Ar stream. The resin was washed with dry and degassed THF (2 x 20 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL). Then it was swollen with 20 mL of CH<sub>2</sub>Cl<sub>2</sub>, and Et<sub>3</sub>N (0.84 mL 6.0 mmol) was added. After shaking the mixture for 5 min, a solution of pinacol chlorophosphite<sup>4</sup> (0.822 g, 4.5 mmol) in 4 mL of CH<sub>2</sub>Cl<sub>2</sub> was added via cannula and the resulting mixture was stirred overnight at room temperature. Then, liquid phase was removed by filtration and the resin was washed with CH<sub>2</sub>Cl<sub>2</sub> (2 x 20 mL), THF (2 x 20 mL), CH<sub>2</sub>Cl<sub>2</sub> and dried under reduced pressure.

IR: 3024.5, 2919.6, 1600.6, 1510.4, 1451.0 cm<sup>-1</sup>. <sup>31</sup>P NMR: broad singlet at 151.6 ppm.

#### PS<sub>2</sub>-PAu

The phosphite-functionalized resin ( $f_{\text{max}} = 0.87 \text{ mmol/g}$ , 0.86 g, 0.75 mmol) was introduced in a 50-mL Schlenk flask, purged with Ar and 20 mL of CH<sub>2</sub>Cl<sub>2</sub> were added.

<sup>3.</sup> C and H consistent with 0.372 mmol·g<sup>-1</sup> [Au(PR<sub>3</sub>)(tmbn)]SbF<sub>6</sub> plus 0.344 mmol·g<sup>-1</sup> of presumably inactive [Au(PR<sub>3</sub>)<sub>2</sub>]SbF<sub>6</sub> complex, this explaining also the presence of two <sup>31</sup>P NMR signals.

<sup>4.</sup> A. Zwierzak, Can. J. Chem. 1967, 45, 2501-2512.

In a separate flask,  $[Au(tmbn)_2]SbF_6$  (1) (674 mg, 0.82 mmol) was introduced and purged under a gentle stream of Ar. Then, it was dissolved with 10 mL of CH<sub>2</sub>Cl<sub>2</sub> (+5 mL rinse) and transferred via cannula to the flask containing the resin and shaken for 45 min, whereupon the resin turned purple. Then, the liquid phase was removed by filtration and the resin was washed with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL) and dried under reduced pressure to afford the resin as a pale purple solid.

IR: 3024, 2247, 1603, 1576 cm<sup>-1</sup>. <sup>31</sup>P NMR: broad singlet at 119.7 ppm. Anal. calcd. for  $f_{\text{max}} = 0.56 \text{ mmol} \cdot \text{g}^{-1}$ : N, 0.789; found: C, 66.72%; H, 5.93%; N 0.75%  $f = 0.53 \text{ mmol} \cdot \text{g}^{-1}$  (96% yield of functionalization over the two steps) *PS*<sub>3</sub>-**P** 

$$\bigcirc OH + CI - P'_{O} \longrightarrow \underbrace{Et_{3}N}_{CH_{2}CI_{2}, rt} \bigcirc O'_{P'_{O}}$$

Hydroxymethyl polystyrene (*f* 1.0 mmol/g, 1.5 g, 1.50 mmol) was introduced in a 50-mL Schlenk flask and the system was purged by a gentle Ar stream. The resin was washed with dry and degassed THF (2 x 10 mL) and  $CH_2Cl_2$  (10 mL). Then it was swollen with 10 mL of  $CH_2Cl_2$ , and  $Et_3N$  (0.42 mL 3.00 mmol) was added. After shaking the mixture for 5 min, a solution of catechol chlorophosphite<sup>5</sup> (0.393 g, 2.25 mmol) in 2 mL of  $CH_2Cl_2$  was added via cannula and the resulting mixture was stirred overnight at room temperature. Then, the liquid phase was removed by filtration and the resin was washed with  $CH_2Cl_2$  (2 x 20 mL), THF (2 x 20 mL),  $CH_2Cl_2$  (2 x 20 mL) and dried under reduced pressure.

IR: 3059, 3024, 2921, 2489, 1601, 1492, 1476, 1451 cm<sup>-1</sup>. <sup>31</sup>P NMR: broad singlet at 130.8 ppm.

#### PS3-PAu

The phosphite-functionalized resin ( $f_{max}$  0.87 mmol/g, 0.300 g, 0.26 mmol) was introduced in a 50-mL Schlenk flask, purged with Ar and 2 mL of CH<sub>2</sub>Cl<sub>2</sub> were added. In a separate flask, [Au(tmbn)<sub>2</sub>]SbF<sub>6</sub> (1) (0.187 g, 0.29 mmol) was introduced and purged under a gentle stream of Ar. Then, it was dissolved with 3 mL of CH<sub>2</sub>Cl<sub>2</sub> (+1 mL rinse) and transferred via canula to the flask containing the resin and shaken for 45 min, whereupon the resin turned purple. Then, the liquid phase was removed by filtration and the resin was washed with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL) and dried under reduced pressure to afford the resin as a purple solid.

<sup>5.</sup> P: C. Crofts, J. H. H. Markes, H. N. Rydon, J. Chem Soc. 1958, 4251.

IR: 3059, 3024, 2929, 2848, 2251, 1600, 1509, 1451 cm<sup>-1</sup>. <sup>31</sup>P NMR: broad singlet at 99.7 ppm. Anal. calcd. for  $f_{\text{max}} = 0.57 \text{ mmol} \cdot \text{g}^{-1}$ : N, 0.798%; found: C, 78.10%; H, 6.54%; N, 0.50%  $f = 0.36 \text{ mmol} \cdot \text{g}^{-1}$  (63% yield of functionalization over the two steps)

# Gold-Catalyzed Reactions with *PS*<sub>2</sub>-PAu

#### **Skeletal Rearrangement of Enyne 12a<sup>6</sup>**

The PS-supported gold complex  $PS_2$ -PAu ( $f 0.53 \text{ mmol} \cdot \text{g}^{-1}$ , 7.9 mg, 0.0042 mmol) was introduced in a vial, purged under a gentle stream of Ar and suspended in 1 mL of CH<sub>2</sub>Cl<sub>2</sub>. A solution of propargyl prenyl dimethylmalonate (**21a**) (50 mg, 0.210 mmol) in 1 mL of CH<sub>2</sub>Cl<sub>2</sub> was added and the mixture was shaken at room temperature for 5 min. Then, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure to give **13a** (49.2 mg, 98% yield) without need for a further purification.

### **Skeletal Rearrangement of Enyne 12b<sup>6</sup>**

The PS-supported gold complex  $PS_2$ -PAu ( $f 0.53 \text{ mmol} \cdot \text{g}^{-1}$ , 6.6 mg, 0.0035 mmol) was introduced in a vial, purged under a gentle stream of Ar and suspended in 1 mL of CH<sub>2</sub>Cl<sub>2</sub>. A solution of propargyl cinnamyl dimethylmalonate (**12b**) (50 mg, 0.175 mmol) in 1 mL of CH<sub>2</sub>Cl<sub>2</sub> was added and the mixture was shaken at room temperature for 30 min. Then, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The crude mixture was purified by silica gel chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 70:30) to give a 1.6:1 mixture of **13b** and **14b** (34.6 mg, 69% yield).

## Skeletal Rearrangement of Enyne 21n<sup>6</sup>

The PS-supported gold complex  $PS_2$ -PAu ( $f 0.53 \text{ mmol} \cdot \text{g}^{-1}$ , 17.9 mg, 0.0095 mmol) was introduced in a vial, purged under a gentle stream of Ar and suspended in 1 mL of CH<sub>2</sub>Cl<sub>2</sub>. A solution of propargyl allyl dimethylmalonate (**12c**) (50 mg, 0.238 mmol) in 1 mL of CH<sub>2</sub>Cl<sub>2</sub> was added and the mixture was shaken at room temperature for 8 h. Then, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The crude mixture was purified by silica gel chromatography (hexanes/EtOAc 90:10) to give a 1:9.3 mixture of the **13c** and **13c** (40.6 mg, 81%).

#### **Methoxycyclization of 21a<sup>6</sup>**

The PS-supported gold complex  $PS_2$ -PAu ( $f 0.53 \text{ mmol} \cdot \text{g}^{-1}$ , 15.8 mg, 0.0084 mmol) was introduced in a vial, purged under a gentle stream of Ar and suspended in 1 mL of

<sup>6.</sup> C. Nieto-Oberhuber, M. P. Muñoz, S. López, E. Jiménez-Núñez, C. Nevado, E. Herrero-Gómez, M. Raducan, A. M. Echavarren, *Chem. Eur. J.* **2006**, *12*, 1677-1693.

CH<sub>2</sub>Cl<sub>2</sub>:MeOH (1:1). A solution of propargyl prenyl dimethylmalonate (**12a**) (50 mg, 0.210 mmol) in 1 mL of CH<sub>2</sub>Cl<sub>2</sub>:MeOH (1:1) was added and the mixture was shaken at room temperature for 4 h. Then, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The crude mixture was purified by silica gel chromatography (CH<sub>2</sub>Cl<sub>2</sub>/EtOAc 98:2) to give **15a** (35.3 mg, 62% yield).

#### **Methoxycyclization of 12b**<sup>6</sup>

The PS-supported gold complex  $PS_2$ -PAu (f 0.53 mmol·g<sup>-1</sup>, 13.2 mg, 0.0070 mmol) was introduced in a vial, purged under a gentle stream of Ar and suspended in 1 mL of CH<sub>2</sub>Cl<sub>2</sub>:MeOH (1:1). A solution of propargyl cinnamyl dimethylmalonate (50 mg, 0.175 mmol) in 1 mL of CH<sub>2</sub>Cl<sub>2</sub>:MeOH (1:1) was added and the mixture was shaken at room temperature for 24 h. Then, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The crude mixture was purified by silica gel chromatography (from hexanes/CH<sub>2</sub>Cl<sub>2</sub> 50:50 to CH<sub>2</sub>Cl<sub>2</sub>) to give **15b** (44.9 mg, 81% yield).

#### X-Ray Crystal Data

## Bis(2,4,6-trimethoxybenzonitrile)gold(I) hexafluoroantimonate (1)

CCDC-805890	C1 C2 C7 C1 C1 C1 C1 C1 C1 C1 C1 C1 C1 C1 C1 C1	
Empirical formula	C20 H22 Au F6 N2 O6 Sb	
Formula weight	819.11	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.4956(3)  Å	<b>a</b> = 98.076(2)°.
	b = 8.7019(3)  Å	b = 106.973(2) °.
	c = 10.6582(4)  Å	$g = 103.527(2)^{\circ}$ .
Volume	629.96(4) Å <sup>3</sup>	
Z	1	
Density (calculated)	2.159 $Mg/m^3$	
Absorption coefficient	6.970 mm <sup>-1</sup>	
F(000)	388	
Crystal size	$0.20 \ x \ 0.15 \ x \ 0.02 \ mm^3$	
Theta range for data collection	2.05 to 36.50°.	
Index ranges	-11 <=h<=12 ,-14 <=k<=12 ,-	17 <=l<=17
Reflections collected	5390	
Independent reflections	5124 [R(int) = 0.0337 ]	
Completeness to theta =36.50 $^{\circ}$	0.869 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8732 and 0.3362	
Refinement method	Full-matrix least-squares on F	72
Data / restraints / parameters	5390 / 0 / 169	

Goodness-of-fit on F <sup>2</sup>	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0281, $wR2 = 0.0728$
R indices (all data)	R1 = 0.0306, $wR2 = 0.0751$
Largest diff. peak and hole	2.704 and -1.728 $e.Å^{-3}$

# **Bis(2,4,6-trimethoxybenzonitrile)silver(I) hexafluoroantimonate (2a)** CCDC-805790



Empirical formula	C15 H16.50 Ag0.75 F4.50 N1.50 O4.50 Sb0.75	
Formula weight	547.51	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.2042(8)  Å	$\alpha = 111.6910(10)$ °.
	b = 13.0515(4)  Å	$\beta = 107.540(2)$ °.
	c = 13.7709(5)  Å	$\gamma = 97.984(2)$ °.
Volume	1864.24(15) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.951 Mg/m <sup>3</sup>	
Absorption coefficient	1.958 mm <sup>-1</sup>	
F(000)	1068	
Crystal size	$0.40 \ x \ 0.20 \ x \ 0.10 \ mm^3$	
Theta range for data collection	1.75 to 30.50°.	
Index ranges	-17 <=h<=17 ,-18 <=k<=18 ,-1	18 <=l<=19
Reflections collected	10737	
Independent reflections	10205 [R(int) = 0.0195 ]	
Completeness to theta =30.50 $^{\circ}$	0.944 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8283 and 0.5081	

Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	10737 / 0 / 499
Goodness-of-fit on F <sup>2</sup>	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0183, $wR2 = 0.0484$
R indices (all data)	R1 = 0.0195, $wR2 = 0.0491$
Largest diff. peak and hole	$0.737~and$ -0.608 $~e.{\ensuremath{\text{A}^{-3}}}$

#### Bis(acetonitrile)silver(I) hexafluoroantimonate (2b)

#### CCDC-805794



2410 [R(int) = 0.0309 ]
0.948 %
Empirical
0.4621 and 0.2625
Full-matrix least-squares on $F^2$
2410 / 0 / 68
1.079
R1 = 0.0235, $wR2 = 0.0645$
R1 = 0.0278, $wR2 = 0.0680$
1.598 and -0.896 $e.Å^{-3}$

# [Au<sub>2</sub>((*R*)-DTBM-SEGPHOS)(tmbn)<sub>2</sub>](SbF<sub>6</sub>)<sub>2</sub> (9)

CCDC-805792 (9)



Empirical formula

C188 H244 Au4 F24 N4 O28 P4 Sb4

Formula weight	4862.62	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 18.0870(8)  Å	$\alpha$ = 90.00 °.
	b = 12.98300(6)  Å	$\beta = 93.39$ °.
	c = 51.7750(19)  Å	$\gamma = 90.00^{\circ}.$
Volume	12136.7(7) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.331 Mg/m <sup>3</sup>	
Absorption coefficient	2.944 mm <sup>-1</sup>	
F(000)	4840	
Crystal size	$0.15 \text{ x } 0.05 \text{ x } 0.02 \text{ mm}^3$	
Theta range for data collection	0.82 to 29.60°.	
Index ranges	-24 <=h<=24 ,-17 <=k<=17 ,-6	68 <=l<=64
Reflections collected	103594	
Independent reflections	57720 [R(int) = 0.0940 ]	
Completeness to theta =29.60 $^{\circ}$	0.959 %	
Absorption correction	Empirical	
Max. and min. transmission	0.88 and 0.94	
Refinement method	Full-matrix least-squares on F	2
Data / restraints / parameters	57720 / 3287 / 2284	
Goodness-of-fit on F <sup>2</sup>	1.090	
Final R indices [I>2sigma(I)]	R1 = 0.1023, $wR2 = 0.2732$	
R indices (all data)	R1 = 0.1494, w $R2 = 0.2947$	
Absolute Structure Flack parameter	x =0.093(7)	
Largest diff. peak and hole	3.745 and $-4.834$ e.Å <sup>-3</sup>	



# [Au(NCPh)<sub>2</sub>](SbF<sub>6</sub>) <sup>1</sup>H NMR



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210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2011









 $[Au(JohnPhos)(tmbn)](SbF_6) (4) \ ^1H\{ \ ^{31}P\} \ NMR$ 







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

# [Au(tris(2,4-di-*tert*-butylphenyl)phosphite)(tmbn)](SbF<sub>6</sub>) (**5**) <sup>31</sup>P{<sup>1</sup>H} NMR

















