# SUPPORTING INFORMATION

Gold(I) Triazolyls: Organometallic Synthesis in Air and Aqueous Media James E. Heckler, Nihal Deligonul, Arnold Rheingold, and Thomas G. Gray\*

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## EXPERIMENTAL

MATERIALS AND METHODS. Experimental procedures requiring air- and moisture-free conditions were performed under argon using Schlenk-line techniques or in a nitrogen-filled MBraun glovebox. Acetonitrile, pentane, diethyl ether, and methylene chloride were purchased from Fisher and were dried in an MBraun solvent purification system in which the solvent had passed over two columns of activated molecular sieves; hexanes, ethyl acetate, methanol, chloroform, and tert-butanol were purchased from Fisher and used as received; anhydrous benzene was purchased from Sigma Aldrich. Deuterated solvents ( $CDCl_3$ ,  $C_6D_6$ , and  $DMSO-d_6$ ) were obtained from Cambridge Isotope Laboratories *via* Fisher Scientific and used as received. Solvents were degassed by freeze-pump-thaw procedures. <sup>1</sup>H NMR spectra experiments were performed on Varian-400 FT NMR and -300 FT NMR spectrometers operating at 399.7 MHz and 299.8 MHz, respectively. Chemical shifts are reported in parts per million  $(\delta)$ , measured from tetramethylsilane (0 ppm) and referenced to the residual solvent peaks. Highresolution electrospray ionization mass-spectrometry (Hi-res ESI-MS) was performed on an IonSpec HiRes ESI-FTICRMS at the University of Cincinnati Mass Spectrometry facility. UV-Vis absorption and luminescence experiments were performed on a Cary 5G UV-Vis-NIR spectrometer and Cary Eclipse spectrometer, respectively. Combustion analyses were performed by Robertson Microlit Laboratories (Ledgewood, NJ) or Midwest Microlab, LLC (Indianapolis, IN).

Chemicals from commercial sources were used as received. 7-methoxy-4-bromomethylcoumarin, adamantyl azide, 4-azidoanisole (~0.5M in TBME), 1-bromooctane, azidomethyl phenyl sulfide, *N*-Boc-4-azido-L-homoalanine (dicyclohexylammonium) salt, 3,3-dimethylbut-1-yne, 1-ethynylnaphthalene, methyl propiolate, sodium azide, copper(I) iodide and copper turnings were purchased from Sigma Aldrich; benzyl azide and 2-(4-biphenyl)-2-propanol were purchased from Alfa Aesar; trifluoroacetic acid was purchased from Fisher Scientific; chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) was purchased from Strem Chemicals, Inc.

Chloro(4,5-dichloro-1,3-dimethylimidazol-2-ylidene)gold(I) was synthesized by transmetalation from the silver salt, which was synthesized according to literature procedure.<sup>1</sup> Bis[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) tetrafluoroborate was synthesized according to literature procedure,<sup>2</sup> as was 1-azidooctane.<sup>3</sup>

### SYNTHESIS OF ORGANOAZIDES

*CAUTION:* Organic azides are potentially explosive and great care should be taken when handling them. All azides used in this study obeyed the "# carbons  $> 2 \times #$  nitrogens" rule of thumb, which the exception of sodium azide. In our hands, the synthesized azides appear to be stable and have not decomposed.



**4-(azidomethyl)-7-methoxycoumarin.** Prepared according to a modified literature procedure of Sun et al.<sup>4</sup> In a 100 mL round-bottom flask was suspended 4-bromomethyl-7-methoxycoumarin (0.104 g, 0.387 mmol) and sodium azide (0.252 g, 3.87 mmol, approx. 10 equiv.) in a 8 mL of a 1:1 (v/v) mixture of acetone and acetonitrile. The mixture was stirred and refluxed at 85 °C for 4 h, at which point it was cooled to room temperature. The mixture was then concentrated to half volume and to this was added 30 mL of ethyl acetate to give an orange suspension, which was filtered to give a pale golden solution. The solution was dried with magnesium sulfate, filtered again, and concentrated to dryness to give a light yellow residue. The crude solid was recrystallized from hot methanol to give bright yellow crystals, which were washed with cold methanol and pentane and dried *in vacuo*. Yield: 0.050 mg (56%).



**2-(4-biphenyl)-2-azidopropane.** Prepared analogously to a literature procedure of Rogawski *et al.*<sup>5</sup> In a 100 mL round-bottom flask was dissolved 2-(4-biphenyl)-2-propanol (2.049 g, 9.650 mmol) in 20 mL of chloroform at 5 °C. To this was added an excess of sodium azide (1.876 g, 28.85 mmol, 3 equiv.) and the pale yellow slurry was stirred for 5 minutes. Following this, trifluoroacetic acid (5.5 g, 48 mmol, approx. 5 equiv.) was very slowly added dropwise, causing the mixture to change color to dark yellow and then to raspberry. The mixture was allowed to warm to room temperature while stirring for 12 h. The orange mixture was poured into a separatory funnel containing 50 mL of diethyl ether and 50 mL of water. The organic layer was washed with 50 mL of water twice and then slowly with 80 mL of 1N ammonium hydroxide (*caution: exothermic*). The organic layer was collected, dried with magnesium sulfate, filtered, and concentrated to give a golden oil. Yield: 1.763 g (77%).

### SYNTHESIS OF (NHC)GOLD(I) ALKYNYLS.

*Note:* Compounds **1a-1d** were prepared according to a previously described method<sup>6</sup> with a slight modification: during the filtration over Celite, the filtrate was a solution of dichloromethane instead of diethyl ether



(3,3-dimethylbutynyl)(1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)gold(I) (1a). Starting with 0.821 g (1.32 mmol) of IPrAuCl. Yield: 0.823 g (93%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>),  $\delta$  7.12 (t, 2H, *J* = 7.6 Hz), 6.99-6.97 (d, 4H, *J* = 8 Hz), 6.19 (s, 2H), 2.54 (sept., 4H, *J* = 6.8 Hz), 1.39-1.38 (d, 12H, *J* = 6.8 Hz), 1.19 (s, 9H), 1.03-1.01 (d, 12H, *J* = 6.8 Hz). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  7.48 (t, 2H, *J* = 8 Hz), 7.27 (d, 4H, *J* = 8 Hz), 7.06 (s, 2H), 2.61 (sept., 4H, *J* = 7.2 Hz), 1.35-1.33 (d, 12H, *J* = 6.8 Hz), 1.19-1.17 (d, 12H, *J* = 6.8 Hz).



(1-napthylethynyl)(1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)gold(I) (1b). Starting with 0.788 g (1.269 mmol) of IPrAuCl. Yield: 0.906 g (97%). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ),  $\delta$  8.88-8.85 (m, 1H), 7.55 (dd, 1H, J = 7.2, 1.2 Hz), 7.48-7.46 (m, 1H), 7.30 (d, 1H, J = 8.4 Hz), 7.12-7.06 (m, 4H), 7.04 (s, 3H), 7.02 (s, 2H), 6.25 (s, 2H), 2.60 (sept., 4H, J = 6.8 Hz), 1.46 (d, 12H, J = 6.8 Hz), 1.06 (d, 12H, J = 6.8 Hz).



(Methylpropiolyl)(1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)gold(I). Starting with 0.350 g (0.564 mmol) of IPrAuCl. Yield: 0.335 g (89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  7.49 (t, 2H, *J* = 8 Hz), 7.29-7.27 (d, 4H, *J* = 8 Hz), 7.14 (s, 2H), 3.59 (s, 3H), 2.52 (sept., 4H, *J* = 6.8 Hz), 1.33-1.31 (d, 12H, *J* = 6.8 Hz), 1.22-1.20 (d, 12H, *J* = 6.8 Hz).



(3,3-dimethylbutynyl)(4,5-dichloro-1,3-dimethylimidazol-2-ylidene)gold(I). Starting with 0.210 g (0.529 mmol) of ( $Cl_2Me_2Im$ )AuCl. Yield: 0.195 g (83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  3.81 (s, 6H), 1.32 (s, 9H). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>),  $\delta$  2.69 (s, 6H), 1.58 (s, 9H).

### SYNTHESIS OF 5-GOLD-1,4-DISUBSTITUTED-1,2,3-TRIAZOLES

CuAAC = copper-catalyzed azide alkynyl cycloaddition



# (1-benzyl-4-(*tert*-butyl)-1,2,3-triazol-5-yl)(1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)gold(I) (2a). *Method A (CuI, 5 mol %):* In separate 100 mL oven/vacuum-dried round-bottom flasks, under argon, were added 1a (0.107 g, 0.160 mmol) and cuprous iodide (0.002 g, 0.008 mmol, 5 mol %). To each flask was added 5 mL of dry degassed acetonitrile and each solution stirred. To the flask containing the gold alkynyl was added benzyl azide (0.06 mL, 0.480 mmol, 3 equiv.) *via* syringe, and to this solution

was transferred the copper-containing solution *via* cannulation. The resultant pale golden solution was stirred for 6 h, at which point the solvent was removed *in vacuo* to yield a pale brown residue. In a glovebox, the residue was dissolved in 5 mL of benzene and filtered over Celite to yield a golden solution, which was evaporated to dryness, leaving behind a pale golden residue. Trituration with pentane, followed by filtration of the solid and washing with pentane (3 x 25 mL) yielded a light tan solid. Drying *in vacuo* led to isolation of analytically pure product. Yield: 0.087 g (68%). Anal. Calcd: C, 60.07; H, 6.55; N, 8.76. Found: C, 60.03; H, 6.68; N, 8.74 %.

*Method B (copper turnings):* In a 100 mL round-bottom flask was added **1a** (0.208 g, 0.311 mmol), which was suspended in 7 mL of a 2:1 (v/v) mixture of *tert*-butanol and water and stirred. Benzyl azide (0.12 mL, 0.960 mmol, approx. 3 equiv.) was added drop wise, followed by the addition of an excess of copper turnings. The mixture stirred for 6 h, at which point it was diluted by the addition of 25 mL of water and the resultant solid filtered off. After washing with water (3 x 25 mL) and hexanes (3 x 25 mL), the tan solid was dried *in vacuo* to yield analytically pure material. Yield: 0.188 g (76%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>),  $\delta$  7.23 (t, 2H), 7.06 (d, 4H), 7.00-6.96 (m, 8 H), 6.89-6.84 (m, 3 H), 6.30 (s, 2H), 5.19 (s, 2H), 2.50 (sept., 4H, *J* = 8.4 Hz), 1.44 (s, 9H), 1.25 (d, 12H, *J* = 9.2 Hz), 1.03 (d, 12H, *J* = 8.8 Hz). Anal. Calcd: C, 60.07; H, 6.55; N, 8.76. Found: C, 60.32; H, 6.57; N, 8.72 %.



#### (1-benzyl-4-(carboxymethyl)-1,2,3-triazol-5-yl)(1,3-bis(2,6-diisopropylphenyl)imidazol-2-

**ylidene**)**gold(I).** *Method B:* In a 50 mL round-bottom flask was added **1c** (0.059 g, 0.089 mmol), which was suspended in 5 mL of a 2:1 (v/v) mixture of *tert*-butanol and water and stirred. Benzyl azide (0.03 mL, 0.240 mmol, approx. 2.8 equiv.) was added drop wise, followed by the addition of an excess of copper turnings. The mixture stirred for 12 h, at which point a gray solid was collected by filtration. After rinsing the solid with water (5 mL) and then with pentane (3 x 20 mL), the gray solid was dried *in vacuo*. Yield: 0.057 g (81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  7.47 (t, 2H, *J* = 7.6 Hz), 7.25 (d, 4H), 7.19 (s, 2H), 5.02 (s, 2H), 3.37 (s, 3H), 2.59 (q, 4H, J = 7.2 Hz), 1.24 (d, 12H, *J* = 6.8 Hz), 1.21 (d, 12H, *J* = 7.2 Hz).



(4-(*tert*-butyl)-1-octyl-1,2,3-triazol-5-yl) (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)gold(I) (3a). *Method A*: In separate 100 mL oven/vacuum-dried round-bottom flasks, under argon, were added 1a (0.139 g, 0.208 mmol) and CuI (0.002 g, 0.011 mmol, 5 mol %). To each flask was added 5 mL of dry degassed acetonitrile and the solutions stirred. To the flask containing the gold alkynyl was added 1-azidooctane (0.064 g, 0.413 mmol, approx. 2 equiv.) by syringe. To the resultant solution was added the copper-containing solution *via* cannulation. The resultant pale golden solution was stirred for 4 h, after which time the solvent was removed *in vacuo* to yield a white residue. Inside a glovebox, the residue was removed *in vacuo* to give an off-white solid, which was triturated with pentane, collected by filtration, and washed with pentane (3 x 20 mL). Drying *in vacuo* led to isolation of an analytically pure white solid. Yield: 0.115 g (67%). Anal. Calcd: C, 59.91; H, 7.60; N, 8.52. Found: C, 59.80; H, 7.60; N, 8.58 %.

*Method B:* To a 100 mL round-bottom flask was added **1a** (0.072 g, 0.108 mmol). The solid was suspended in 5 mL of a 2:1 (v/v) mixture of *tert*-butanol and water. To this was added 1-azidooctane (0.075 g, 0.48 mmol, approx. 4.5 equiv.), followed by an excess of copper turnings. The mixture was stirred for 5 h, after which it was diluted with 25 mL of water, the copper removed and the solid filtered off. Washing the solid with water (3 x 25 mL) and hexanes (3 x 25 mL), followed by drying *in vacuo*, led to isolation of an analytically pure white solid. Yield: 0.070 g (82%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>),  $\delta$  7.23 (t, 2H, *J* = 7.6 Hz), 7.06 (d, 4H, *J* = 8 Hz), 6.32 (s, 2H), 4.01 (t, 2H, *J* = 7.2 Hz), 2.56 (sept., 4H, *J* = 7.2 Hz), 1.53 (t, 2H, *J* = 7.6 Hz), 1.44 (s, 9H), 1.36 (d, 12H, *J* = 6.8 Hz), 1.29 (quin, 2H, *J* = 6.8 Hz), 1.26-1.08 (m, 8H), 1.06 (d, 12H, *J* = 6.8 Hz), 0.92 (t, 3H, *J* = 7.2 Hz). Anal. Calcd: C, 59.91; H, 7.60; N, 8.52. Found: C, 59.86; H, 7.50; N, 8.54 %.



(4-(*tert*-butyl)-1-((phenylthio)methyl)-1,2,3-triazol-5-yl) (1,3-bis(2,6-diisopropylphenyl)imidazol-2ylidene)gold(I) (4a). *Method A:* In separate 100 mL oven/vacuum-dried round-bottom flasks, under an argon atmosphere, were added 1a (0.135 g, 0.2019 mmol) and CuI (0.002 g, 0.0105 mmol, 5.2 mol %). To each flask was added 5 mL of dry degassed acetonitrile and the solutions stirred. To the flask containing the gold alkynyl was added azidomethyl phenyl sulfide (0.06 mL, 0.424 mmol, approx. 2.1 equiv.), and the CuI solution was introduced to this mixture *via* cannulation. The resultant golden solution was stirred for 6 h, at which point the solvent was removed *in vacuo* to give a rose-colored residue. In a glovebox, the residue was dissolved in 3 mL of benzene and filtered over Celite to give a pale golden solution, which was dried *in vacuo* to give a white solid. Trituration with pentane, followed by filtration and washing with pentane (3 x 20 mL), lead to the isolation of an analytically pure white solid. Yield: 0.085 g (51%). Anal. Calcd: C, 57.75; H, 6.30; N, 8.42. Found: C, 58.15; H, 6.19; N, 8.66 %.

*Method B*: In a 100 mL round-bottom flask was suspended **1a** (0.121 g, 0.182 mmol) and azidomethyl phenyl sulfide (0.07 mL, 0.495 mmol, approx. 2.7 equiv.) in 8 mL of a 1:1 (v/v) mixture of water and *tert*-butanol. An excess of copper turnings was added, and the mixture was stirred for 4 h. The product had some solubility in the reaction mixture, so it was poured into a separatory funnel containing 20 mL of methylene chloride. The product was extracted 3 times into methylene chloride, and the combined organic fractions were washed with brine. The solution was concentrated to half volume, dried with magnesium sulfate, and filtered. Concentration via rotary evaporation led to a dark, semi-crystalline residue, which was triturated with pentane, collected by filtration, and washed with pentane (3 x 20 mL). Drying the gray solid *in vacuo* led to isolation of analytically pure material. Yield: 0.133 g (88%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>),  $\delta$  7.51 (dt, 2H, *J* = 7.2, 1.2 Hz), 7.29 (t, 2H, *J* = 7.6 Hz), 7.11-7.09 (d, 4H, *J* = 7.6 Hz), 6.97-6.93 (tt, 3H, *J* = 7.6, 2 Hz), 6.33 (s, 2H), 5.27 (s, 2H), 2.58 (sept., 4H, *J* = 6.8 Hz ), 1.40 (s, 9H), 1.39-1.37 (d, 12H, *J* = 6.8 Hz ), 1.08-1.06 (d, 12H, *J* = 6.8 Hz). Anal. Calcd: C, 57.75; H, 6.30; N, 8.42. Found: C, 57.82; H, 6.23; N, 8.09 %.



(4-(*tert*-butyl)-1-anisyl-1,2,3-triazol-5-yl) (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)gold(I) (5a). *Method B:* In a 100 mL round-bottom flask was charged with 1a (0.148 g, 0.222 mmol). The solid was suspended in 5 mL of a 2:1 (v/v) mixture of *tert*-butanol and water and to this mixture was added 1-azido-4-methoxybenzene (1.3 mL, 0.65 mmol, approx. 2.9 equiv.). An excess of copper turnings was added, and the mixture was stirred for 7 h. The reaction mixture was then diluted with 30 mL of water, the copper turnings removed, and the resultant solid filtered off to give a white solid which was washed with water (3 x 20 mL) and pentane (3 x 20 mL). Drying the white solid *in vacuo* led to isolation of analytically pure material. Yield: 0.117 g (65%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>),  $\delta$  7.51-7.49 (d, 2H, *J* = 8.8 Hz), 7.28 (t, 2H, *J* = 8 Hz), 7.02-7.00 (d, 4H, *J* = 8 Hz), 6.33-6.31 (d, 2H, *J* = 8.8 Hz), 6.22 (s, 2H), 3.37 (s, 3H), 2.52 (sept., 4H, *J* = 6.8 Hz), 1.49 (s, 9H), 1.24-1.22 (d, 12H, *J* = 6.8 Hz), 1.03-1.01 (d, 12H, *J* = 6.8 Hz). Anal. Calcd: C, 58.89; H, 6.42; N, 8.58. Found: C, 58.69; H, 6.23; N, 8.63 %.



# (1-((7-methoxycoumarin-4-yl)methyl)-4-(*tert*-butyl)-1,2,3-triazol-5-yl)(1,3-bis(2,6diisopropylphenyl)imidazol-2-ylidene)gold(I) (6a). *Method A:* In a 100 mL oven/vacuum-dried roundbottom flask was added 1a (0.109 g, 0.163 mmol) and 7-methoxy-4-azidomethylcoumarin (0.038 g, 0.163

mmol) under argon. A separate flask was charged with copper(I) iodide (0.002 g, 0.012 mmol, 7 mol %) under argon. To each flask was added 5 mL of dry degassed acetonitrile and the solutions were stirred. The solution of copper(I) iodide was transferred *via* cannula to the other flask, and the resultant golden solution was stirred for 6 h. The solvent was then removed *in vacuo* to yield a yellow residue. Inside a glovebox, the residue was dissolved in 5 mL of benzene and filtered over Celite to give a dark golden solution, which was evaporated to dryness to yield a golden solid. Trituration with pentane, followed by filtration and washing with pentane (3 x 25 mL), and finally drying *in vacuo* led to isolation of a golden solid powder. Crystallization *via* vapor diffusion of diethyl ether into a saturated solution of the product in THF yielded crystals suitable for both x-ray diffraction and combustion analysis. Yield: 0.118 g (80%). Anal. Calcd: C, 58.86; H, 6.06; N, 7.80. Found: C, 58.90; H, 6.00; N, 7.81 %.

*Method B:* In a 100 mL round-bottom flask was added **1a** (0.075 g, 0.113 mmol) and 7-methoxy-4azidomethylcoumarin (0.035 g, 0.150 mmol). The solids was suspended in 5 mL of a 2:1 (v/v) mixture of *tert*-butanol and water and stirred. An excess of copper turnings was added to the mixture, which was left to stir for 8 h. The mixture was diluted with 25 mL of water and the suspended solid collected by filtration. After washing with water 3 x 15 mL and pentane (3 x 20 mL), the yellow solid was dried *in vacuo* to yield analytically pure material. Yield: 0.090 g (89%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>),  $\delta$  7.01-6.88 (m, 7H), 6.61 (td, 2H, J = 9.6, 2.4 Hz), 6.25 (s, 2H), 5.49 (s, 1H), 5.09 (s, 2H), 3.23 (s, 3H), 2.46 (sept., 4H, J = 6.8 Hz), 1.43 (s, 9H), 1.32 (d, 12H, J = 6.8 Hz), 1.00 (d, 12H, J = 6.8 Hz). Anal. Calcd: C, 58.86; H, 6.06; N, 7.80. Found: C, 59.01; H, 5.78; N, 7.58 %.



(1-((7-methoxycoumarin-4-yl)methyl)-4-(1-naphthyl)-1,2,3-triazol-5-yl)(1,3-bis(2,6diisopropylphenyl)imidazol-2-ylidene)gold(I) (6b). *Method B:* In a 100 mL round-bottom flask was added 1b (0.115 g, 0.211 mmol) and 7-methoxy-4-azidomethylcoumarin (0.048 g, 0.209 mmol). The

solids was suspended in 5 mL of a 2:1 (v/v) mixture of *tert*-butanol and water and stirred. An excess of copper turnings was added, and the mixture stirred for 8 h. The mixture was then diluted by addition of 25 mL of water, the copper turnings removed, and the suspended solid collected by filtration. After washing with water (3 x 25 mL) and pentane (3 x 25 mL), the peach colored solid was dried *in vacuo* to yield analytically pure product. Yield: 0.188 g (92%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>),  $\delta$  8.87 (d, 1H, *J* = 7.2 Hz), 7.55 (dd, 1H, *J* = 7.2, 1.2 Hz), 7.47 (d, 1H, *J* = 7.2 Hz), 7.29 (d, 2H, *J* = 8 Hz), 7.18 (t, 2H, *J* = 7.6 Hz), 7.10 (m, 2H), 7.03 (d, 4H, *J* = 7.6 Hz), 6.93 (t, 1H, *J* = 7.6 Hz), 6.62 (d, 1H, *J* = 8.8 Hz), 6.52 (dd, 1H, *J* = 8.8, 2.4 Hz), 6.43 (d, 1H, *J* = 7.2 Hz), 1.06 (d, 12H, *J* = 6.8 Hz). Anal. Calcd: C, 62.04; H, 5.41; N, 7.24. Found: C, 61.99; H, 5.46; N, 6.90 %.



#### (1-(3-((Boc)amino)-3-carboxypropyl)-4-(tert-butyl)-1,2,3-triazol-5-yl)(1,3-bis(2,6-

**diisopropylphenyl)imidazol-2-ylidene)gold(I)** (7a). *Method A:* To an oven/vacuum dried 100 mL round-bottom flask containing a stir bar was added **1a** (0.115 g, 0.173 mmol) and *N*-Boc-4-azido-L-homoalanine (dicyclohexylammonium) salt (0.078 g, 0.182 mmol). In a separate oven/vacuum dried 100 mL oven/vacuum-dried round-bottom flask containing a stir bar was charged copper(I) iodide (0.002 g, 0.009 mmol, 5 mol %). To each flask was added, with stirring, 3 mL dry, degassed acetonitrile. The copper-containing solution was transferred *via* cannulation to the flask containing the reactants. The resultant golden solution was stirred for 6 h. The solvent was removed *in vacuo* to yield a dark residue. Inside a glovebox, the residue was dissolved in benzene and filtered through Celite to give a pale golden solution. The solvent was removed *in vacuo* to yield a light yellow powder which was triturated with pentane and collected by filtration. Rinsing the solid with pentane (3 x 20 mL) and drying *in vacuo* led to isolation of a pale yellow solid powder. Yield: 0.152 g (97%). Electrospray mass spectrum (M+H<sup>+</sup>): Calcd. for  $C_{42}H_{62}AuN_6O_4^+$ : 911.449. Found: 911.450. Anal Calcd.: C, 55.38; H, 6.75; N, 9.23. Found: C, 58.16; H, 7.55; N, 9.12 %.

*Method B*: In a 20 mL scintillation vial was charged with **1a** (0.023 g, 0.034 mmol) and *N*-Boc-4-azido-Lhomoalanine (dicyclohexylammonium) salt (0.015 g, 0.035 mmol), and a small stir bar. To this solid mixture was added 2 mL of a 2:1 (v/v) mixture of *tert*-butanol and water. Anexcess of copper metal turnings was added. The mixture was stirred for 24 h. The product was slightly soluble in the reaction medium. The copper metal was first removed, followed by evaporation of the solvent *in vacuo* to yield an off-white solid residue with a tinge of green color. The residue was dissolved in toluene, filtered through Celite, and concentrated to an off-white solid, which was dried *in vacuo*. Yield: 0.028 g (89 %). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>,  $\delta$  7.51 (m, 2H), 7.27-7.20 (m, 4H), 6.31 (s, 2H), 4.47 (m, 1H), 2.53 (sept., 4H, *J* = 7.2 Hz), 1.49 (s, 9H), 1.43 (s, 9H), 1.38 (d, 12H, *J* = 6.8 Hz), 1.10 (d, 12H, *J* = 6.8, 2.8 Hz). Electrospray mass spectrum (M+H<sup>+</sup>): Calcd. for C<sub>42</sub>H<sub>62</sub>AuN<sub>6</sub>O<sub>4</sub><sup>+</sup>: 911.449. Found: 911.450. Anal. Calcd.: C, 55.38; H, 6.75; N, 9.23. Found: C, 56.42; H, 7.13; N, 8.80 %.



(1-(2-deoxyribos-1-yl)-4-(*tert*-butyl)-1,2,3-triazol-5-yl)(1,3-bis(2,6-diisopropylphenyl)imidazol-2ylidene)gold(I) (8a). *Method B:* In a 100 mL oven/vacuum-dried round-bottom flask with a stir bar was added 1a (0.125 g, 0.187 mmol) and 2-deoxy-3,5-di-O-(p-toluoyl)-D-ribofuranosyl azide (0.080 g, 0.203 mmol). The solids was suspended in 5 mL of a 2:1 (v/v) mixture of *tert*-butanol and water, followed by an excess of copper metal turnings. The suspension was stirred for 24 h, after which it was a clear solution. The product was extracted into CH<sub>2</sub>Cl<sub>2</sub> (3 x 10 mL); the organic layer washed with brine (1 x 30 mL), dried over magnesium sulfate, and filtered to yield a colorless solution. The solution was concentrated by evaporation to a pale green residue, which was triturated with pentane and collected by filtration. The solid was washed with pentane (3 x 10 mL) and dried *in vacuo* to yield a pale green solid, which was crystallized by vapor diffusion of pentane into chloroform to yield chunky white crystals. Yield: 0.127 g (64%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  7.98 (d, 2H, *J* = 8.2 Hz), 7.91 (d, 2H, *J* = 8.2 Hz), 7.49 (t, 2H, *J* = 7.9 Hz), 7.32 (m, 3H), 7.23 (s, 2H) 7.19 (m, 5H), 5.49 (dd, 1H, *J* = 7.8, 4.6 Hz), 5.40, (q, 1H, *J* = 7.0 Hz),

4.82 (m, 1H), 4.64 (dd, 1H, *J* = 11.6, 4.0 Hz), 4.35 (dd, 1H, *J* = 13.2, 6.8 Hz), 2.75 (m, 1H), 2.55 (m, 5H), 2.41 (s, 3H), 2.39 (s, 3H), 1.27 (d, 12H, *J* = 6.8 Hz), 1.20 (dd, 12 H, *J* = 13.2, 6.8 Hz), 0.99 (s, 9H). Anal. Calcd: C, 61.07; H, 6.26; N, 6.59. Found: C, 60.80; H, 6.16; N, 6.59 %.

[5,5-bis(IPrAu)- $\mu$ -(4-carboxymethyl-1,2,3-triazol-5-yl)][NTf<sub>2</sub>]. In a 50-mL round-bottom flask were charged IPrAu(carboxymethylethynyl) (0.033 g, 0.049 mmol) and IPrAu(triflimide) (0.043 g, 0.049 mmol). The solids were suspended in 3 mL of acetonitrile and stirred, and to this yellow solution was dropwise added benzyl azide (0.015 mL, 0.120 mmol). An excess of copper turnings were added, and the mixture was stirred for 6 h. The mixture was filtered over celite and the filtrate concentrated in vacuo to give a pale golden oil. The oil was redissolved in a minimal amount of acetonitrile, and diethyl ether was layered on. After 2 days, pale green dendritic crystals were isolated, rinsed with diethyl ether, and dried in vacuo. Yield: 0.058 mg (70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  7.45 (t, 2H, *J* = 7.7 Hz), 7.44 (t, 2H, *J* = 7.7 Hz), 7.26 (d, 4H), 7.24 (s, 2H), 7.22 (s, 2H), 7.15 (t, 3H, *J* = 7.6 Hz), 6.63 (d, 2H, *J* = 8 Hz), 4.81 (s, 2H), 3.08 (s, 3H), 2.53 (sept., 4H, *J* = 7.2 Hz), 2.50 (sept., 4H, *J* = 7.2 Hz), 1.49 (s, 9H), 1.21 (d, 24H, *J* = 6.8 Hz), 1.18 (d, 24H, *J* = 6.8 Hz). Anal. Calcd: C, 48.26; H, 4.96; N, 6.72. Found: C, 48.34; H, 4.93; N, 6.60 %.

Alternatively, the digold compound can be prepared by reacting a prepared gold triazolate **2c** with one equivalent of IPrAu(triflimide): in a 25 mL round-bottomed flash were charged (4-carboxymethyl-1-benzyl-1,2,3-triazol-5-yl)(IPrAu) (0.015 g, 0.019 mmol) and IPrAu(triflimide) (0.017 g, 0.019 mmol). The solids were dissolved in dichloromethane and stirred for 2 h. The solvent was



stripped on the rotavap to yield an off-white solid, which was rinsed with pentane and dried in vacuo to yield a white lustrous solid. Yield: 0.030 mg (96%). The NMR analysis was identical to above.



**Figure S1.** Thermal ellipsoid depiction (50% probability) of the triflimidate salt of a di-gold cation. Hydrogen atoms are omitted for clarity. A line drawing of the cation appears at the top right. Selected interatomic distances (Å): Au1–C30 1.991(12); Au1–C64 2.033(11); Au2–C3 1.977(12); Au2–N8 2.047(9).



Figure S2. Absorption (solid) and emission spectra (dashed) of 6a in chloroform.



Figure S3. Absorption (solid) and emission spectra (dashed) of 6b in chloroform.

# Table S1. Crystallographic Data for 6a.

	nd072012_0m						
Crystal data							
Chemical formula	$C_{53}H_{63}AuN_5O_3$						
$M_{ m r}$	1015.05						
Crystal system, space group	Monoclinic, $P2_1/c$						
Temperature (K)	160						
a, b, c (Å)	18.156 (2), 14.8551 (16), 20.079 (2)						
β (°)	116.059 (1)						
$V(\text{\AA}^3)$	4865.0 (9)						
Ζ	4						
Radiation type	Μο Κα						
$\mu$ (mm <sup>-1</sup> )	3.07						
Crystal size (mm <sup>3</sup> )	0.34  imes 0.08  imes 0.05						
Data collection							
Diffractometer	AXScale in APEX II CCD area detector diffractometer						
Absorption correction	Multi-scan AXScale in APEX 2 (Bruker, 2004)						
$T_{\min}, T_{\max}$	0.423, 0.857						
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	61121, 12140, 9142						
<i>R</i> <sub>int</sub>	0.054						
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.671						
Refinement							
$R[F^2 > 2\sigma(F^2)],$ $wR(F^2), S$	0.032, 0.084, 1.08						
No. of reflections	12140						
No. of parameters	529						
No. of restraints	48						
H-atom treatment	H-atom parameters constrained						
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	0.94, -1.07						

## Table S2. Crystallographic data for

## [5,5-bis(IPrAu)-µ-(4-carboxymethyl-1,2,3-triazol-5-yl)][NTf<sub>2</sub>].

	gray22						
Crystal data							
Chemical formula	$C_{67}H_{82}Au_2F_6N_8O_6S_2$						
M <sub>r</sub>	1667.46						
Crystal system, space group	Triclinic, $P^{-1}$						
Temperature (K)	100						
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.5547 (8), 16.6467 (11), 18.4622 (11)						
$\alpha, \beta, \gamma$ (°)	84.620 (4), 72.861 (3), 80.747 (4)						
$V(\text{\AA}^3)$	3634.8 (4)						
Ζ	2						
Radiation type	Μο Κα						
$\mu$ (mm <sup>-1</sup> )	4.16						
Crystal size (mm)	0.30  imes 0.22  imes 0.07						
Data collection							
Diffractometer	Bruker diffractometer	APEX-II	Ι		CCD		
Absorption correction	Multi-scan SADABS						
$T_{\min}, T_{\max}$	0.321, 0.482						
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	53380, 12849, 8105						
R <sub>int</sub>	0.099						
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.608						
Refinement							
$R[F^2 > 2\sigma(F^2)],$ wR(F <sup>2</sup> ), S	0.062, 0.156, 1.07						
No. of reflections	12849						
No. of parameters	831						
No. of restraints	0						
H-atom treatment	H-atom parameters constrained						
	$w = 1/[\sigma^2(F_o^2)]$ where $P = (F_o^2 + 2F_c^2)/3$	+	$(0.054P)^2$	+	31.P]		
$\Delta\rho_{max}, \Delta\rho_{min}  (e \ \text{\AA}^{-3})$	2.32, -3.40						

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