# Cationic gold catalyses *@*-bromination of terminal alkynes and subsequent hydroaddition reactions.

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## General.

Glassware was dried in an oven at 175 °C before use. Reagents and solvents were obtained from commercial sources and were used without further purification otherwise indicated. Gold (I) complexes AuPR<sub>3</sub>NTf<sub>2</sub><sup>1,2</sup> and **6a-c<sup>3</sup>** were prepared as previously reported, and complex 4a was prepared following a standard procedure for similar compounds.<sup>4</sup> All the products obtained were characterised by GC-MS, <sup>1</sup>H- and <sup>13</sup>C-NMR, and DEPT. When available, the characterisation given in the literature was used for comparison. Gas chromatographic analyses were performed in an instrument equipped with a 25 m capillary column of 5% phenylmethylsilicone. Nitrobenzene was used as external standard. GC/MS analyses were performed on a spectrometer equipped with the same column as the GC and operated under the same conditions. Column chromatography and TLC were performed over SiO<sub>2</sub>. <sup>1</sup>H, <sup>13</sup>C, DEPT and <sup>31</sup>P-NMR were recorded in a 300 MHz instrument using CD<sub>3</sub>CN,  $1.4-d^8$ -dioxane, CD<sub>2</sub>Cl<sub>2</sub> or CDCl<sub>3</sub> as solvents, containing TMS as internal standard. IR spectra of the compounds were recorded on a spectrophotometer as self-supported wafers or by impregnating the windows with a dichloromethane solution of the compound and leaving to evaporate before analysis.

#### **Reaction Procedures.**

*Catalyst screening (Table 1).* AuP<sup>t</sup>Bu<sub>3</sub>NTf<sub>2</sub> (3.4 mg, 0.005 mmol) and NBS **2a** (97.8 mg, 0.55 mmol) were placed in a 2 ml vial equipped with a magnetic stirrer. CH<sub>3</sub>CN or DCM (0.5 ml) and phenylacetylene **1a** (55  $\mu$ l, 0.5 mmol) were added, the vial was sealed and the resulting mixture was stirred for 20 h at room temperature. Then, ~200  $\mu$ l of the reaction mixture were taken and submitted to GC and GC-MS analysis after a) precipitation in a *n*-hexane : DCM mixture (3 : 1 in volume, 1 ml) and filtration if CH<sub>3</sub>CN was the solvent of the reaction or b) precipitation in *n*-hexane (1 ml) and filtration if DCM was the solvent.

*Isotopic experiments (Tables 2 and 3, and Schemes 2 and 3).* The corresponding metal complex or substrate (typically 0.1 mmol), the corresponding succinimide and the catalyst (if proceeded) were placed in a 2 ml vial equipped with a magnetic bar.  $CD_3CN$  was added and then H<sub>2</sub>O (if proceeded) or HNTf<sub>2</sub> (if proceeded) and the vial was sealed.

The reaction mixture was magnetically stirred at rt for the indicated time after which additional  $CD_3CN$  was added to analyse the mixture immediately by NMR spectroscopy.

*Kinetics (Figure 1).* AuP'Bu<sub>3</sub>NTf<sub>2</sub> (17 mg, 0.025 mmol) and NBS **2a** (978 mg, 5.5 mmol) were placed in a vial equipped with a magnetic stirrer. DCM (5 ml) and phenylacetylene **1a** (550  $\mu$ l, 5 mmol) were added, the vial was closed with a septum cap and the resulting mixture was placed in a pre-heated oil bath at 28 °C and stirred for the indicated time. Aliquots (100-200  $\mu$ l) were periodically taken and submitted to GC analysis after precipitation in *n*-hexane (1 ml) and filtration.

Reaction procedure for the synthesis of 1-bromophenylacetylene **3a** (Table 4, entry 1). AuP<sup>*i*</sup>Bu<sub>3</sub>NTf<sub>2</sub> (13.6 mg, 0.02 mmol) and NBS **2a** (355.6 mg, 2 mmol) were placed in a vial equipped with a magnetic stirrer. DCM (2 ml) and phenylacetylene **1a** (220 µl, 2 mmol) were added, the vial was closed with a septum cap and the resulting mixture was stirred for 24 h at room temperature. Then, an aliquot was taken for GC analysis and *n*-hexane (20 ml) was added to the reaction mixture. The resulting suspension was stirred for 15 min, filtered and concentrated under vacuum to give **3a** (330 mg, >90 % purity, 83 % yield). Column chromatography of the reaction mixture lead to the analytically pure compound but significant weight loss was observed, probably by decomposition of the product on column. R<sub>f</sub> (*n*-hexane): 0.56. MS (*m*/*z*, relative intensity): 182 (100), 180 (100), 101 (48), 75 (26). IR ( $\nu$ , cm<sup>-1</sup>): 2369-2320 (several peaks), 2200, 1697, 1221, 1176. <sup>1</sup>H NMR ( $\delta$ , ppm): 7.37 (aromatic CH, 2H, mult), 7.26-7.23 (aromatic CH, 3H, mult). <sup>13</sup>C NMR ( $\delta$ , ppm): 132.0 (aromatic, 2CH), 128.7 (aromatic, CH), 128.3 (aromatic, 2CH), 122.7 (aromatic, C), 80.0 (alkyne, C), 49.7 (alkyne, C-Br).

*Cascade reaction* (7*a*, *Scheme 5*). AuP<sup>t</sup>Bu<sub>3</sub>NTf<sub>2</sub> (34 mg, 0.05 mmol) and NBS 2**a** (177.8 mg, 1 mmol) were placed in a vial equipped with a magnetic stirrer. DCM (1 ml) and phenylacetylene 1**a** (110  $\mu$ l, 1 mmol) were added, the vial was closed with a septum cap and the resulting mixture was stirred for 8 h at room temperature. Then, ethylene glycol (55.5  $\mu$ l, 1 mmol) was added and the vial stirred in a preheated oil bath at 35 °C for 24 h. The mixture was analyzed by GC and GC-MS.

#### Characterisation.

R<sub>f</sub> (*n*-hexane): 0.56. MS (*m/z*, relative intensity): 182 (100), 180 (100), 101 (48), 75 (26). IR ( $\nu$ , cm<sup>-1</sup>): 2200, 1697, 1221, 1176. <sup>1</sup>H NMR ( $\delta$ , ppm): 7.37 (aromatic CH, 2H, mult), 7.26-7.23 (aromatic CH, 3H, mult). <sup>13</sup>C NMR ( $\delta$ , ppm): 132.0 (aromatic, 2CH), 128.7 (aromatic, CH), 128.3 (aromatic, 2CH), 122.7 (aromatic, C), 80.0 (alkyne, C), 49.7 (alkyne, C-Br).

R<sub>f</sub> (*n*-hexane): 0.38. MS (*m*/*z*, relative intensity): 228 (100), 101 (38), 75 (31). IR (υ, cm<sup>-1</sup>): 2169, 1751, 1689, 1596, 1487, 1441, 1220. <sup>1</sup>H NMR (δ, ppm): 7.35 (aromatic CH, 2H, mult), 7.25-7.20 (aromatic CH, 3H, mult). <sup>13</sup>C NMR (δ, ppm): 132.3 (aromatic, 2CH), 128.8 (aromatic, CH), 128.2 (aromatic, 2CH), 123.3 (aromatic, C), 94.1 (alkyne, C), 6.2 (alkyne, C-I).

R<sub>f</sub> (*n*-hexane): 0.52. MS (*m*/*z*, relative intensity): 218 (62), 216 (100), 214 (100), 137 (18), 135 (57), 99 (71), 74 (38). IR (υ, cm<sup>-1</sup>): 2197, 1489, 1397. <sup>1</sup>H NMR (δ, ppm; *J*, Hz): 7.29 (aromatic CH, 2H, dt, J= 8.8, 2.2), 7.20 (aromatic CH, 2H, dt, J= 8.8, 2.2). <sup>13</sup>C NMR (δ, ppm): 134.8 (aromatic, C), 133.2 (aromatic, 2CH), 128.7 (aromatic, 2CH), 121.1 (aromatic, C), 78.9 (alkyne, C), 51.0 (alkyne, C-Br).

R<sub>f</sub> (*n*-hexane: AcOEt, 8:2): 0.71. MS (*m*/*z*, relative intensity): 227 (100), 195 (33), 179 (44), 167 (36), 100 (54), 88 (10), 74 (39). IR (υ, cm<sup>-1</sup>): 2195, 1591, 1507, 1403, 1350. <sup>1</sup>H NMR (δ, ppm; *J*, Hz): 8.13 (aromatic *CH*, 2H, dt, *J*= 9.1, 2.3), 7.64 (aromatic *CH*, 2H, dt, *J*= 9.1, 2.3). <sup>13</sup>C NMR (δ, ppm): 149.5 (aromatic, C), 134.9 (aromatic, 2CH), 131.0 (aromatic, C), 125.6 (aromatic, 2CH), 80.1 (alkyne, C), 58.4 (alkyne, C-Br).

R<sub>f</sub> (*n*-hexane): 0.49. MS (*m*/*z*, relative intensity): 262 (100), 260 (100), 258 (100), 181 (53), 179 (54), 100 (53), 74 (38). IR (υ, cm<sup>-1</sup>): 2198, 1485, 1392. <sup>1</sup>H NMR (δ, ppm; *J*, Hz): 7.37 (aromatic CH, 2H, dt, *J*= 8.8, 2.2), 7.23 (aromatic CH, 2H, dt, *J*= 8.8, 2.2). <sup>13</sup>C NMR (δ, ppm): 133.4 (aromatic, 2CH), 131.6 (aromatic, 2CH), 123.0 (aromatic, C), 121.6 (aromatic, C), 79.0 (alkyne, C), 51.2 (alkyne, C-Br).

R<sub>f</sub> (*n*-hexane): 0.51. MS (*m*/*z*, relative intensity): 196 (100), 194 (100), 115 (100), 89 (32). IR (υ, cm<sup>-1</sup>): 2195, 1488, 1455. <sup>1</sup>H NMR (δ, ppm; *J*, Hz): 7.33 (aromatic *CH*, 1H, dmult, *J*= 7.5), 7.15 (aromatic *CH*, 1H, td, *J*= 7.2, 1.5), 7.10 (aromatic *CH*, 1H, dmult, *J*= 7.5), 7.04 (aromatic *CH*, 1H, tmult, *J*= 7.2), 2.35 (*CH*<sub>3</sub>, 3H, s). <sup>13</sup>C NMR (δ, ppm): 140.8 (aromatic, C), 132.3 (aromatic, CH), 129.4 (aromatic, CH), 128.6 (aromatic, CH), 125.5 (aromatic, CH), 122.5 (aromatic, C), 79.1 (alkyne, C), 52.8 (alkyne, C-Br), 20.5 (methyl, CH<sub>3</sub>).

R<sub>f</sub> (*n*-hexane): 0.62. MS (*m/z*, relative intensity): 274 (<5), 272 (<5), 193 (<5), 162 (10), 161 (10), 160 (10), 159 (10), 95 (100), 81 (100), 67 (92), 55 (88). IR (υ, cm<sup>-1</sup>): 2925, 2854, 2220, 1466. <sup>1</sup>H NMR (δ, ppm; *J*, Hz): 2.12 (CH<sub>2</sub>, 2H, t, *J*= 7.0), 1.42 (CH<sub>2</sub>, 2H, quint, *J*= 7.1), 1.32-1.16 (9CH<sub>2</sub>s, 18H, mult), 0.81 (CH<sub>3</sub>, 3H, t, *J*= 6.7). <sup>13</sup>C NMR (δ, ppm): 80.5 (alkyne, C), 37.4 (alkyne, C-Br), 31.9 (CH<sub>2</sub>), 29.6 (3CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 28.8 (CH<sub>2</sub>), 28.3 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 19.7 (CH<sub>2</sub>), 14.1 (methyl, CH<sub>3</sub>).

IR ( $\upsilon$ , cm<sup>-1</sup>): 3050-2850 (several peaks), 2114, 1484. <sup>1</sup>H NMR ( $\delta$ , ppm; *J*, Hz): 7.43 (aromatic C*H*, 2H, mult), 7.18-7.08 (aromatic C*H*, 3H, mult), 1.46 (3<sup>t</sup>Bu, 27H, d, *J*<sub>H-P</sub>= 13.2). <sup>13</sup>C NMR ( $\delta$ , ppm; *J*<sub>C-P</sub>, Hz): 136.4, 134.7, 132.2 (2C), 127.6 (2C), 126.3, 103.1 (*J*<sub>C-P</sub>= 23.1), 38.9 (3C, *J*<sub>C-P</sub>= 18.1), 32.3 (9C, *J*<sub>C-P</sub>= 4.4). <sup>31</sup>P NMR ( $\delta$ , ppm): 91.48.

<sup>1</sup>H NMR (CD<sub>3</sub>CN, δ, ppm; *J*, Hz): 2.47 (cyclic C*H*<sub>2</sub>, 4H, s), 1.49 (3<sup>*t*</sup>Bu, 27H, d, *J*<sub>H-P</sub>= 13.6). <sup>13</sup>C NMR (CD<sub>3</sub>CN, δ, ppm; *J*<sub>C-P</sub>, Hz): 188.2 (2C), 39.8 (3C, *J*<sub>C-P</sub>= 21.4), 32.4 (9C, *J*<sub>C-P</sub>= 4.4), 32.2 (2C, *J*<sub>C-P</sub>= 3.2). <sup>31</sup>P NMR (δ, ppm): 87.47.

# **References.**

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# Table S1.



Table S1. Results for the metal-catalyzed formation of 3a in different solvents.

	<b>Conversion</b> (%) <sup>a)</sup>			
Catalyst /	$AuP^{t}Bu_{3}NTf_{2}$ (1 mol%)	AgNO <sub>3</sub>		
Solvent		1 mol%	10 mol%	
DCM	100 <sup>b)</sup>	61 <sup>b)</sup>	100	
CH <sub>3</sub> CN	98	10	100	
H <sub>2</sub> O	99	0	100	
1,4-dioxane	91	0 <sup>c)</sup>	0 <sup>c)</sup>	
Diethyl ether	94	0 <sup>c)</sup>	8 <sup>c)</sup>	
Acetone	33	100	100	
<i>n</i> -hexane	0	0	0	

<sup>a)</sup> GC yield. Selectivity to **3a** typically accounts for >80 %. <sup>b)</sup> For 0.1 mol% catalyst, AuP'Bu<sub>3</sub>NTf<sub>2</sub>: 22 %,

 $AgNO_{3}: 17 \ \%; \ AuP'Bu_{3}NTf_{2} + AgNO_{3} \ (0.1 \ mol\% \ each). \ 40 \ \%. \ ^{c)} \ Bromination \ of \ the \ solvent \ was \ found.$ 

Spectra.







200 175 150 125 100 75 50 25 0















S16





















