

Gold (I) and Gold (III) compounds as selective catalysts for hydroboration of alkynes vs. alkenes.

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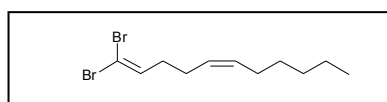
Experimental Section.

General.

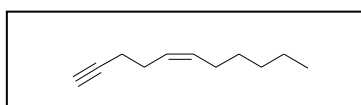
Phenylacetylene, styrene, 2-methyl-but-1-en-3-yne **16**, AuClPPh₃ and catecholborane were obtained from Aldrich Co. Phenylethynylstyrene **19** was synthesised according to a reported procedure.¹ The rest of reagents and solvents were obtained from commercial sources and used without further purification otherwise specified. ¹H, ¹³C, DEPT and ³¹P-NMR were recorded in a 300 MHz instrument using the corresponding deuterated solvent containing TMS as internal standard. Gas chromatographic analyses were performed in an instrument equipped with a 25 m capillary column of 5% phenylmethylsilicone. GC/MS analyses were performed on a spectrometer equipped with the same column as the GC and operated under the same conditions. IR spectra were recorded on a spectrophotometer by impregnating the windows with the neat compound and analysing. Accurate masses were obtained by ESI technique.

Syntheses of AuCl₃PPh₃ and Substrates.

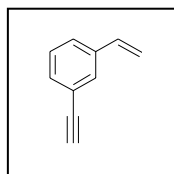
AuCl₃PPh₃.² Chlorine gas, generated *in situ* by addition of HCl (conc., 124 ml) over KMnO₄ (20 g),³ was slowly bubbled through a CHCl₃ (10 ml) solution containing 124 mg (0.25 mmol) of AuClPPh₃ under magnetical stirring. The originally colourless solution turned bright yellow. This solution was filtered, concentrated by rotary evaporation, *n*-hexanes was slowly added and the mixture was cooled to 0 °C. The precipitate was isolated by filtration, washed with anhydrous diethyl ether, and vacuum dried to yield 119 mg (84 %) of a bright yellow solid, pure compound as assessed by NMR. ¹H NMR δ: 7.75 (9H, m), 7.55 (6H, m). ¹³C NMR δ: 135.1, 133.8, 129.2, 123.7, 122.8. ³¹P NMR δ: 44.0.



1,1-Dibromo-undeca-1,5-diene. Zn dust (1.96 g, 30 mmol) was added to a solution of triphenylphosphine (7.87 g, 30 mmol) in CH₂Cl₂ (100 ml) and the mixture was cooled to 0 °C. Carbon tetrabromide (9.95 g, 30 mmol) was added and the green mixture was stirred for 15 min. The ice-bath was removed and, after stirring for another 15 min, a solution of 4-decenal (1.82 ml, 10 mmol) in CH₂Cl₂ (40 ml) was added. The mixture was stirred for 2 h. After this time, *n*-hexanes (120 ml) was added whereupon a precipitate was formed. The mixture was filtered and the filtrate was washed with *n*-hexanes (120 ml). The solvent was removed *in vacuo* and the resulting crude was redissolved in *n*-hexanes (120 ml) and placed in the fridge for 3h. After this time, the mixture was filtered once more and the solvent removed *in vacuo* to yield the pure compound as a yellow solid (3.1 g, quantitative). IR (neat, cm⁻¹): 3008, 2923, 2854, 1620, 1450, 810, 771, 671. ¹H NMR δ: 6.35 (1H, t), 5.35 (2H, m), 2.15 (4H, m), 2.0 (2H, m), 1.2 (6H, m), 0.85 (3H, t). ¹³C NMR δ: 138.2, 132.0, 127.5, 88.9, 33.1, 31.6, 29.3, 27.2, 25.4, 22.7, 14.1. HRMS (ESI) *m/z* 307.9771 [(M+Na)⁺; calculated for C₁₁H₁₈Br₂: 307,9775]; major peaks: 229.0596, 198.8591, 149.1352, 69.0683.



Undec-5-en-1-yne (17). *n*-BuLi (15.6 ml, 25.0 mmol, 1.6 M in hexanes) was added dropwise over 15 min to a solution of 1,1-dibromo-undeca-1,5-diene (3.1 g, 10.0 mmol) in THF (100 ml) at -78 °C. The solution was allowed to return to r.t. over 30 min, after which NH₄Cl (aq.) (60 ml) was added and the aqueous layer was extracted with ether (2 x 100 ml). The organic fractions were combined and washed with water (2 x 80 ml) and brine (80 ml), then dried over MgSO₄, filtered and concentrated *in vacuo*. The resulting crude was purified by flash column chromatography (*n*-hexanes) to give **17** as a pale yellow oil (900 mg, 6 mmol, 60 %). R_f (*n*-hexanes): 0.55. IR (neat, cm⁻¹): 3309, 3008, 2924, 2862, 2121, 1458, 1250, 717, 632. ¹H NMR δ: 5.45 (2H, m), 2.25 (4H, m), 2.05 (2H, m), 1.95 (1H, t), 1.3 (6H, m), 0.85 (3H, t). ¹³C NMR δ: 132.7, 127.3, 84.2, 68.2, 31.5, 29.3, 27.3, 26.4, 22.4, 18.8, 14.0. HRMS (ESI) *m/z* 150.1411 [(M+Na)⁺; calculated for C₁₁H₁₈: 150,1409]; major peaks: 149.1377, 91.0620, 69.0741, 55.0599.



1-Ethynyl-3-vinylbenzene (18). Following Bestmann and co-workers' procedure,⁴ a solution of dimethyl-1-diazo-2-oxopropylphosphonate (540 mg, 2.9 mmol) in dry methanol (12 ml) was added over a magnetically stirred dispersion of 3-ethynylbenzaldehyde (305 μ l, 2.4 mmol) and K_2CO_3 (662 mg, 4.8 mmol) in dry methanol (24 ml) under nitrogen atmosphere. The stirring was continued for 4 h, observing that the inorganic base was dissolved. After this time, the solution was extracted with ether (35 ml, 4 times) and the combined organic fractions washed with brine (50 ml), then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting crude was purified by flash column chromatography (pentane) to give **18** as a colorless liquid (186 mg, 1.45 mmol, 61 %). R_f (*n*-hexanes): 0.56. IR (neat, cm^{-1}): 3293, 3085, 3062, 3016, 2106, 1828, 1628, 1589, 1481, 1419, 1304, 1273, 1242, 987, 910, 802, 710, 656, 625. 1H NMR δ : 7.46 (1H, t), 7.30 (2H, m), 7.17 (1H, m), 6.58 (1H, dd), 5.67 (1H, d), 5.20 (1H, d), 2.99 (1H, s). ^{13}C NMR δ : 137.8, 136.0, 131.4, 130.0, 128.5, 126.6, 122.5, 114.8, 83.5, 77.1. HRMS (ESI) m/z 128.0630 [$(M+Na)^+$]; calculated for $C_{10}H_8$: 128,0626]; major peaks: 128.0630, 57.0602.

1 T. Ishizone, G. Uehara, A. Hirao and S. Nakahama, *Macromolecules* 1998, **31(12)**, 3764.

2 S. Attar, J. H. Nelson, W. H. Bearden, N. W. Alcock, L. Solujic and E. B. Milosavljevic, *Polyhedron* 1991, **10(16)**, 1939.

3 *Vogel's Textbook of Practical Organic Chemistry*, Fifth ed.; 1989; pp. 424

4 S. Müller, B. Liepold, G. J. Roth and H. J. Bestmann, *Synlett* 1996, 521.

Experimental Procedures.

Kinetics in deuterated solvents.

The following is a typical procedure (Figure 1, curve A): AuClPh₃ (14.8 mg, 1.5 mol%) was placed in a previously dehydrated 10 ml round bottomed flask. The air was evacuated and the flask was backfilled with nitrogen and closed with a rubber septum. A nitrogen balloon was coupled with a needle. Subsequently, CDCl₃ (4 ml), phenylacetylene **1** (219 μ l, 2 mmol) and catecholborane **3** (256 μ l, 2.4 mmol) were added *via* syringe. The reaction mixture was magnetically stirred at room temperature. Periodic samples were taken and analysed by ¹H-NMR. For competitive experiments, the corresponding amount of styrene **2** was added after addition of **1**.

Kinetics in solvent-free conditions.

Hydroboration of phenylacetylene 1 (Figure 2a). Phenylacetylene **1** (219 μ l, 2 mmol) and pinacolborane **6** (348 μ l, 2.4 mmol, 1.2 eq., **A** and **C-F**; 580 μ l, 4 mmol, 2 eq., **B**) were placed in a round-bottomed flask together with the corresponding amount of catalyst: none (**A** and **B**), AuCl (23.2 mg, 5 mol%, **C**), AuCl₃ (30.4 mg, 5 mol%, **D**), AuClPPh₃ + AgOTf (49.3 + 25.7 mg, 5 mol%, **E**), AuCl₃ (60.8 mg, 10 mol%, **F**). Then, the mixture was placed in a pre-heated oil bath at 70 °C under magnetical stirring. Aliquots were periodically taken and analysed by CG.

Hydroboration of styrene 2 (Figure 2b). Styrene **2** (229 μ l, 2 mmol) and pinacolborane **6** (348 μ l, 2.4 mmol, 1.2 eq.) were placed in a round-bottomed flask together with the corresponding amount of catalyst: none (**A**) or AuCl₃ (30.4 mg, 5 mol%, **B**) under nitrogen atmosphere. Then, the mixture was placed in a pre-heated oil bath at 70 °C under magnetical stirring. Aliquots were periodically taken and analysed by CG.

Studies about the mechanism.

NMR measurements of the reaction mixture. AuPPh₃Cl was dissolved in CD₂Cl₂ and **1** was added. The mixture was cooled to – 40 °C and followed by ¹H-, ³¹P- and ¹¹B-

NMR, leaving to reach room temperature. No new signals were observed. Then, catecholborane **3** was added and the reaction followed during one week.

Interaction between AuPPh₃Cl and catecholborane 3. AuPPh₃Cl (99 mg, 0.2 mmol) was dissolved in CD₂Cl₂ (2 ml) under nitrogen atmosphere. Then, **3** (106 μ l, 1 mmol) was added and the reaction followed by ¹H- and ³¹P-NMR.

Control experiments for ³¹P-NMR studies. A) Neat PPh₃ (52 mg, 0.2 mmol, δ = -4.3 ppm) and POPh₃ (56 mg, 0.2 mmol, δ = 28.5 ppm) were dissolved in CD₂Cl₂ (0.75 ml) and analysed. HCl in ether (2.0 M, 200 μ l, 1 eq.) was added and the resulting mixture analysed (δ = -4.3 and a broad signal \sim 39 ppm). B) AuCl (11.6 mg, 0.05 mmol) was dissolved in CD₂Cl₂ (0.75 ml) and POPh₃ (55 mg, 0.2 mmol) was added (δ = 29.3 from the free phosphine oxide and a small signal \sim 58 ppm from, tentatively, the gold-phosphine oxide complex). C) **3** and PPh₃ were dissolved in CD₂Cl₂ and analysed (no signal obtained).

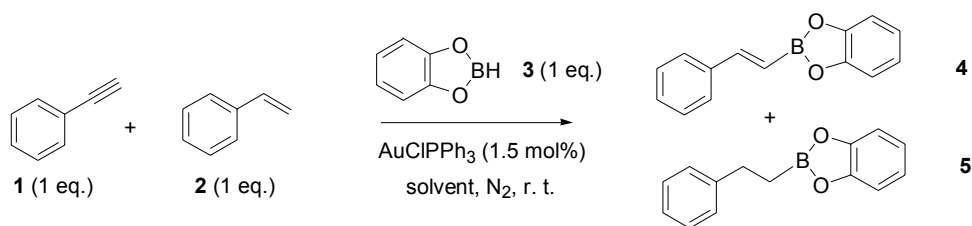
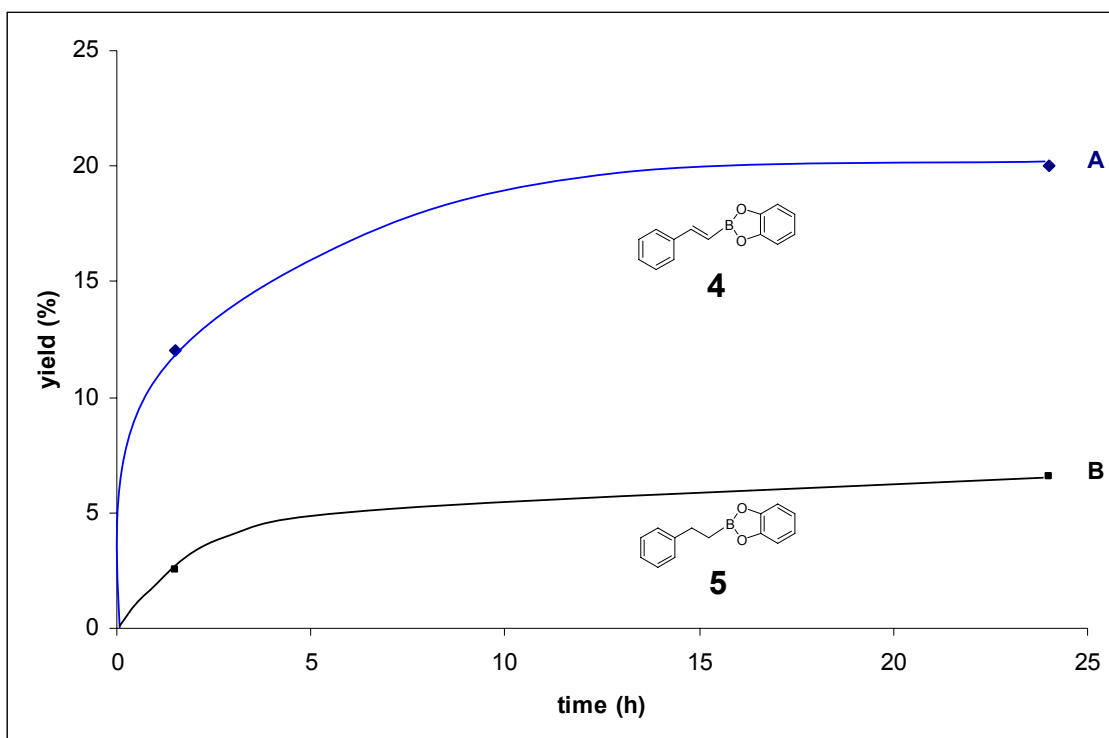


Figure S1. Time yield plot for the competitive hydroboration of phenylacetylene **1** (164 μ l, 1.5 mmol) and styrene **2** (172 μ l, 1.5 mmol) with catecholborane **3** (160 μ l, 1.5 mmol) in the presence of AuClPPh₃ (11.1 mg, 1.5 mol%) as catalyst, at room temperature under nitrogen atmosphere, using 3 ml of CDCl₃ as solvent (curve **A** shows the yield of **4**; curve **B** shows the yield of **5**). A similar procedure was followed when CD₃CN or toluene-*d*⁸ were used as solvents.



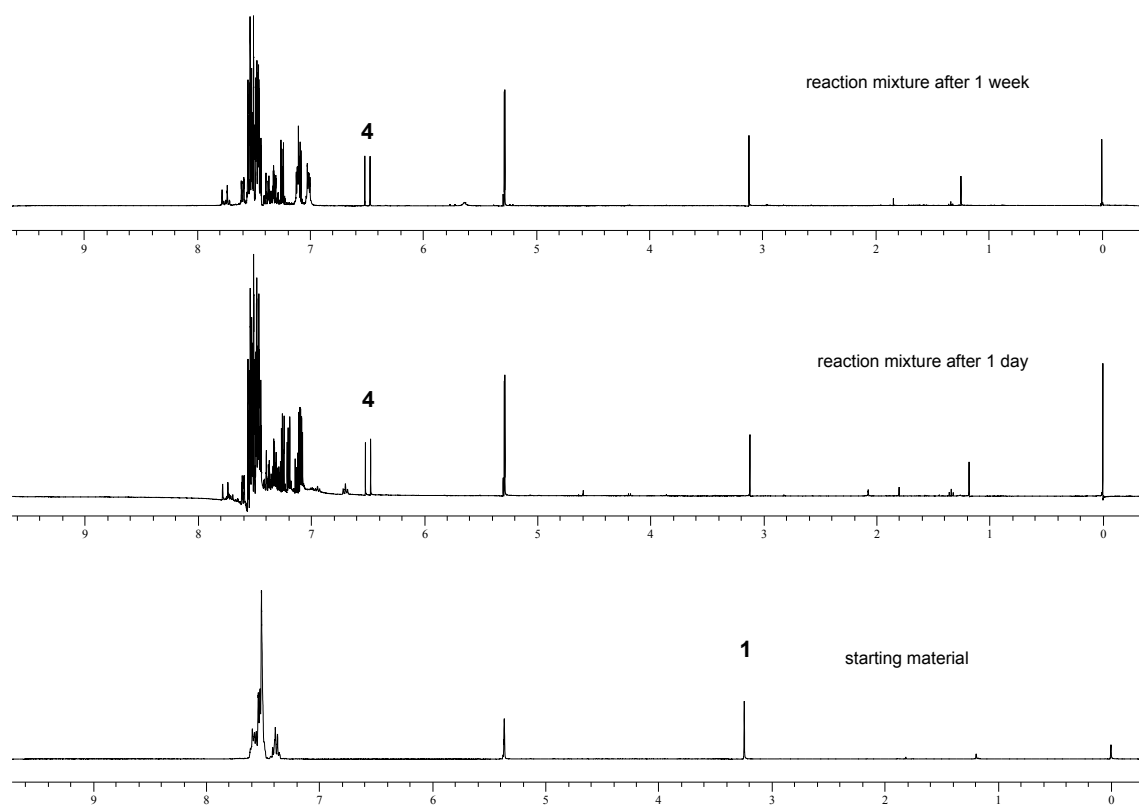


Figure S2. *In situ* $^1\text{H-NMR}$ spectra for the hydroboration of phenylacetylene **1** with catecholborane **3**, using AuClPPh_3 as catalyst in CD_2Cl_2 . From bottom to top: reaction time = 0, 1 and 7 days.

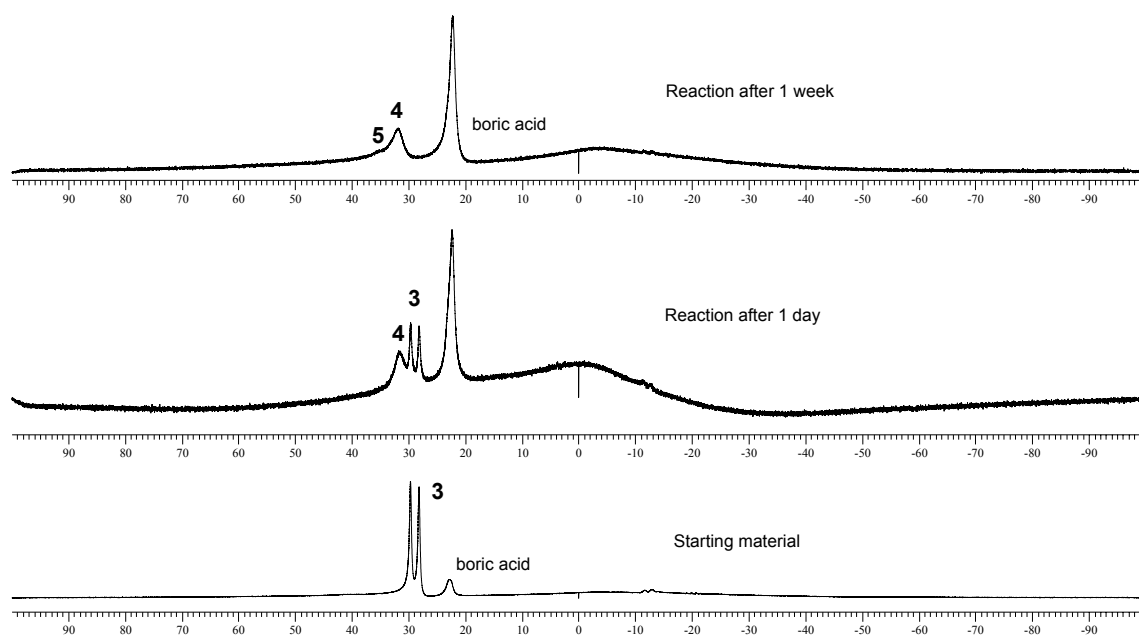


Figure S3. *In situ* ^{11}B -NMR spectra for the hydroboration of phenylacetylene **1** with catecholborane **3**, using AuClPPh_3 as catalyst in CD_2Cl_2 . From bottom to top: reaction time = 0, 1 and 7 days.

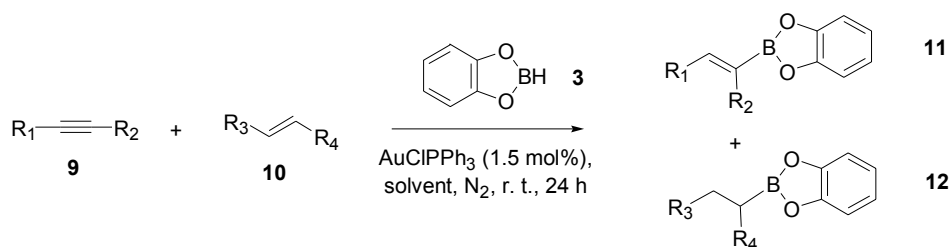


Table S1. Final product ratios in the competitive hydroboration of aromatic alkynes and/or alkenes (1.5 mmol) with catecholborane **3** (160 μ l, 1.5 mmol) in the presence of AuClPPh₃ (11.1 mg, 1.5 mol%) as catalyst, at room temperature under nitrogen atmosphere, using 3 ml of solvent (0.5 M solutions).

Entry	Substrate	Solvent	11 : 12
1	 $\mathbf{1} \quad \mathbf{2}$	CDCl ₃	3.0 ^a
2		Toluene- <i>d</i> ⁸	3.0
3		CD ₃ CN	2.7
4			1.9 ^b
5	 $\mathbf{18}$	CDCl ₃	8.6 ^c

^a No reaction with pinacolborane **6** ^b 3.5 eq. of catecholborane **3**

^c 3 mol% of catalyst, 96 h.

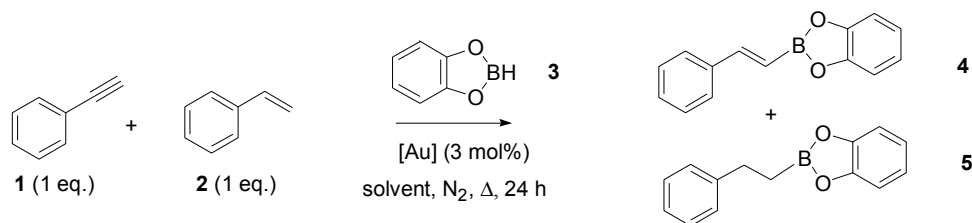


Table S2. Final yields obtained for the competitive hydroboration of phenylacetylene **1** (164 μl, 1.5 mmol) and styrene **2** (172 μl, 1.5 mmol) with catecholborane **3** in the presence or not of gold complexes (3 mol%) as catalysts, using 3 ml of solvent (0.5 M solutions) under nitrogen atmosphere.

Entry	Au catalyst	Solvent	T (°C)	3 (eq.)	4 yield (%) ^a	5 yield (%) ^a
1	AuCIPPh ₃	CDCl ₃	25	3.5	39	19 ^{b,c}
2	AuCIPPh ₃	CDCl ₃	50	1	10	4 ^d
3	AuCl ₃ PPh ₃			1	22	8
4	AuCIPPh ₃	CD ₃ CN	25	1	12	5
5	AuCIPPh ₃		25	3.5	86	46 ^b
6	AuCIPPh ₃		50	2	44	33
7	none			2	36	26
8	AuCIPPh ₃		80	1	40	14
9	none			1	32	14
10	AuCIPPh ₃	Toluene- <i>d</i> ⁸	100	1	[58]	[12]
11	AuCl ₃ PPh ₃			1	[45]	[9]
12	AuCIPPh ₃	none	50	1.5	77	44
13	none	none	50	1.5	80	41

^a [isolated yield] ^b 1.5 mol % of catalyst ^c 48 h ^d No reaction with pinacolborane **6**

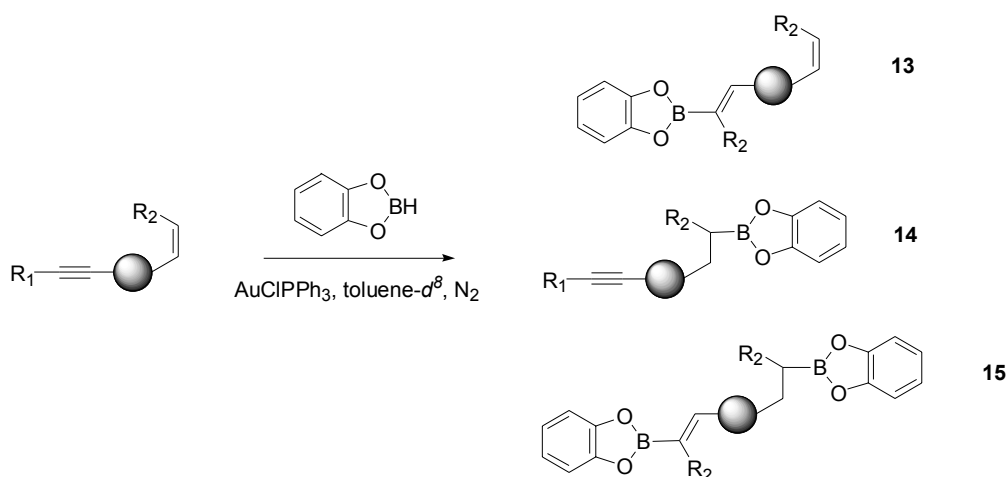


Table S3. Competitive hydroboration with catecholborane **3** (1 eq.) of different compounds, containing both alkynyl and alkenyl functionalities, in the presence or not of AuClPPh₃ as catalyst, using 3 ml of toluene-*d*⁸ (0.5 M solutions) as solvent under nitrogen atmosphere.

Entry	Substrate	Catalyst (mol%)	T (°C)	Time (h)	Starting material	13	14 + 15
1	16	none	25	72	-	90	10
2	17	none	25	72	30	70	-
3			100	24	-	85	15
4		AuClPPh ₃ (3)	100	24	-	70	30
5	18	AuClPPh ₃ (3)	25	96	83	15	2
6			100	24	30	50	19
7		none	100	24	38	47	15
8	19	AuClPPh ₃ (3)	60	24	60	10	30
9			100	24	40	20	40
10			100	24	10	35	55 ^a
11		AuClPPh ₃ (10)	80	24	10	45	45 ^a
12			100	24	<5	40	55 ^a

^a 2 eq. of **3**.