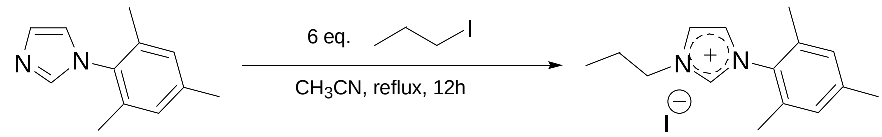
Supporting information

Dissymmetric gold(I) N-heterocyclic carbene complexes: a key unexpected structural parameter for highly efficient catalysts in the addition of alcohols to internal alkynes

Synthesis of 1-(propyl)-3-(mesityl)imidazolium iodide [1]



1

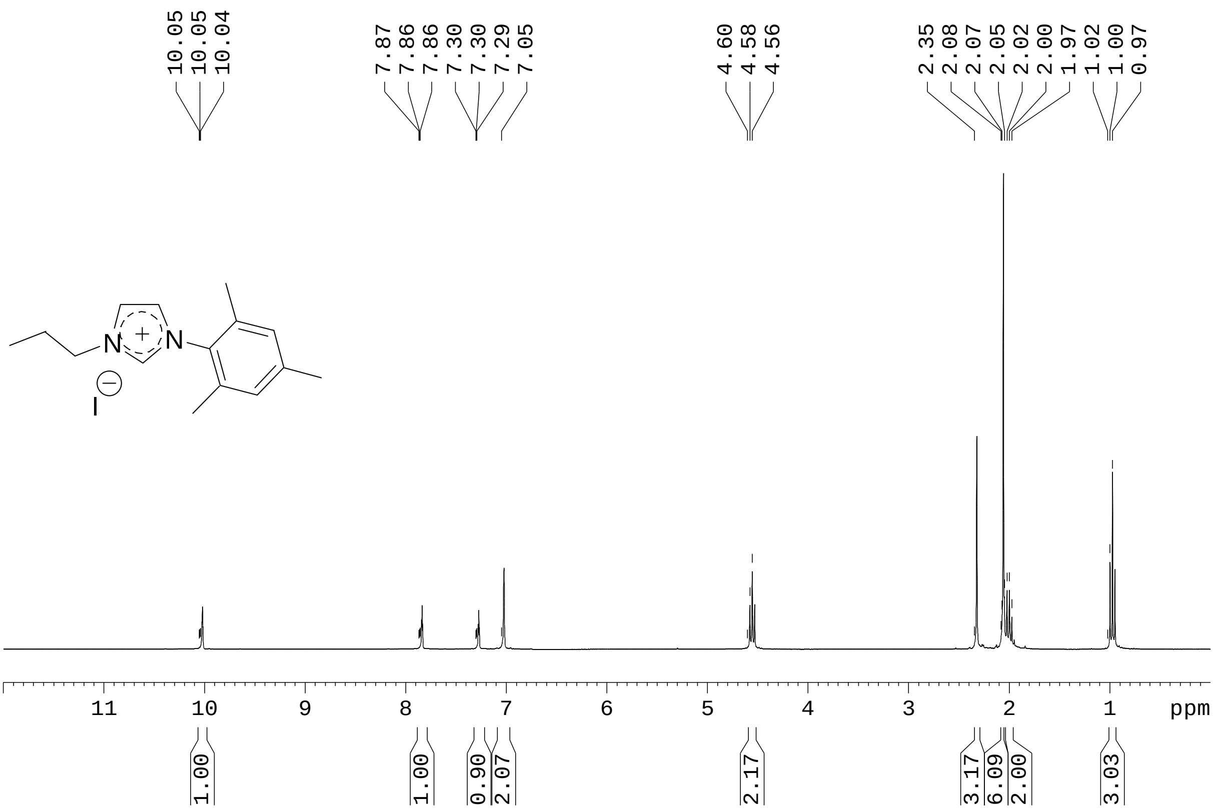


Figure S1 : ^{1}H NMR spectra of 1.

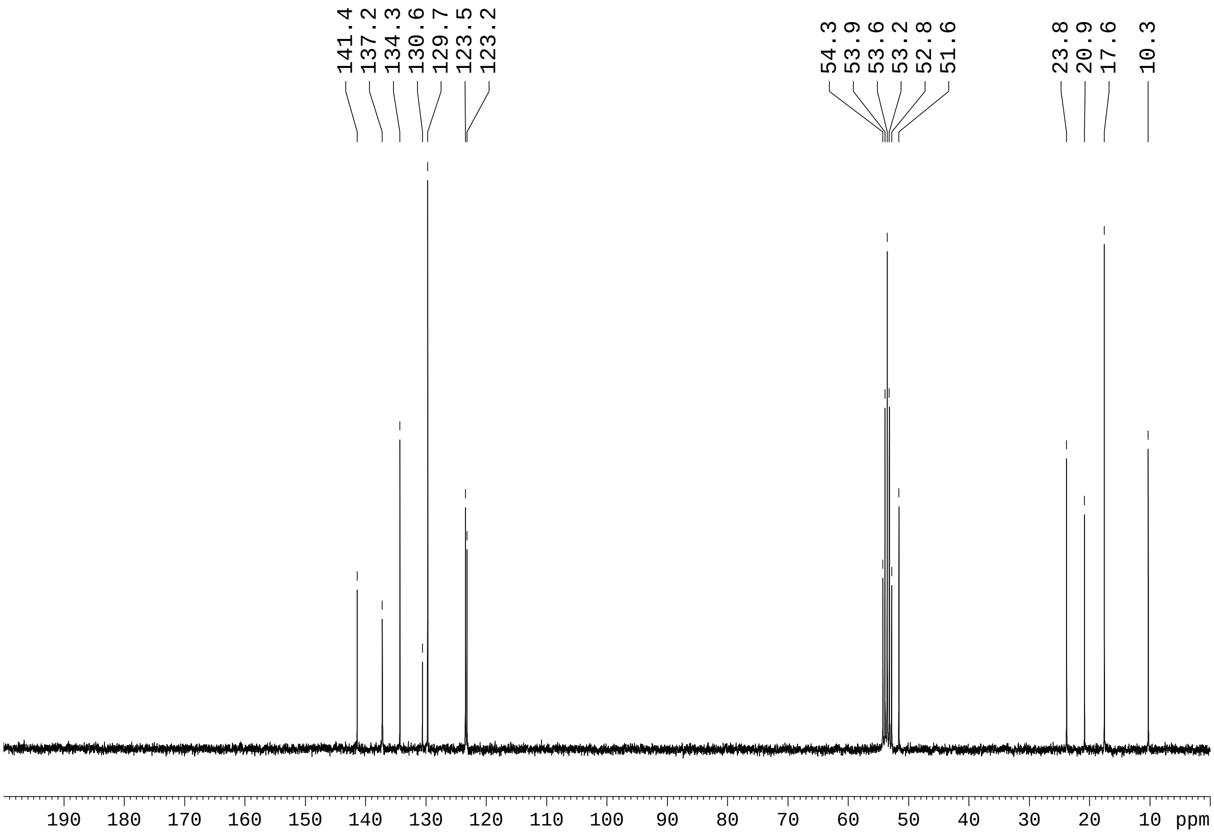
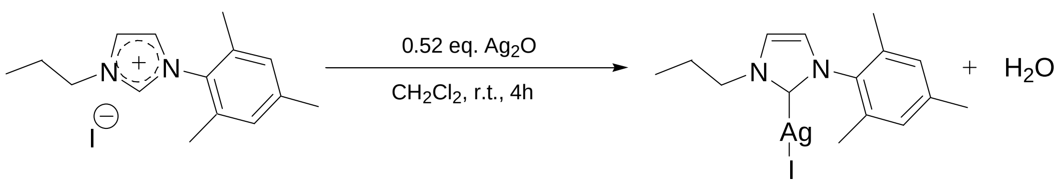


Figure S2 : ^{13}C NMR spectra of 1.

Synthesis of Silver (1-(propyl)-3-(mesityl)imidazol-2-ylidene) iodide [1-Ag]



1 **1-Ag**

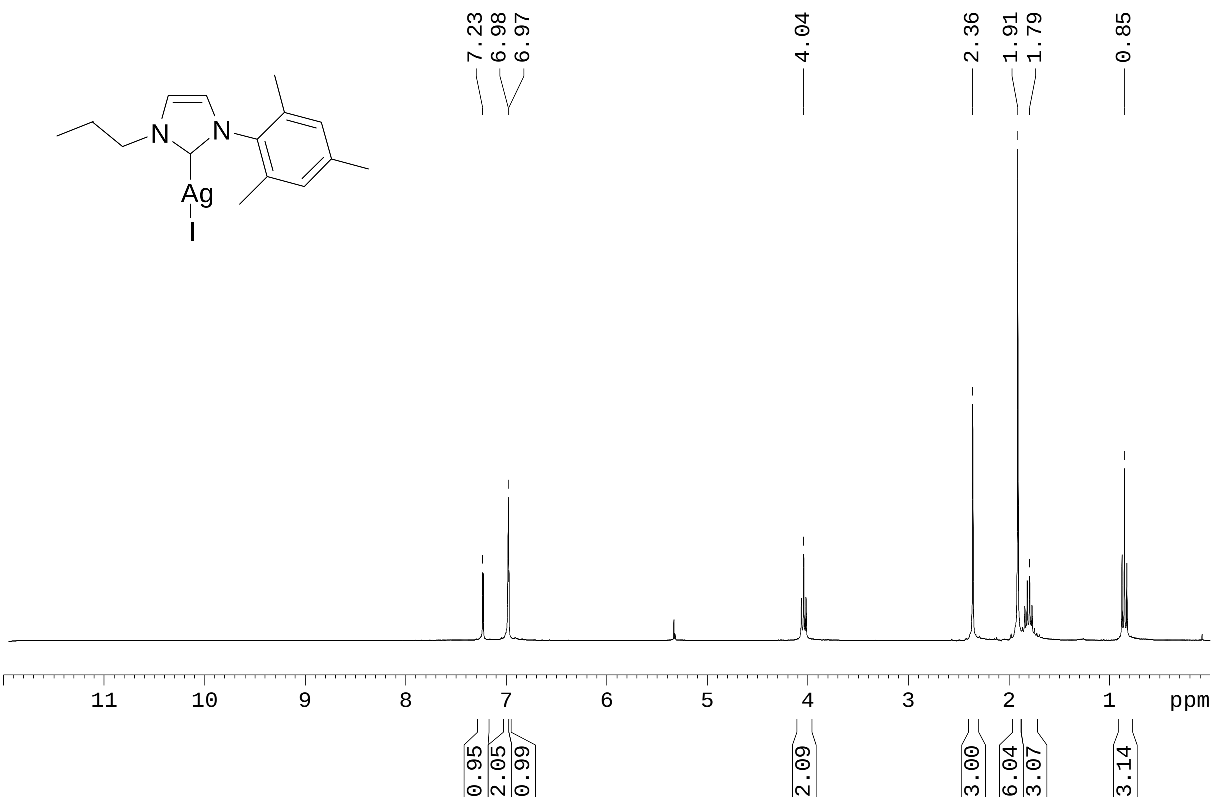


Figure S3 : ^{1}H NMR spectra of 1-Ag.

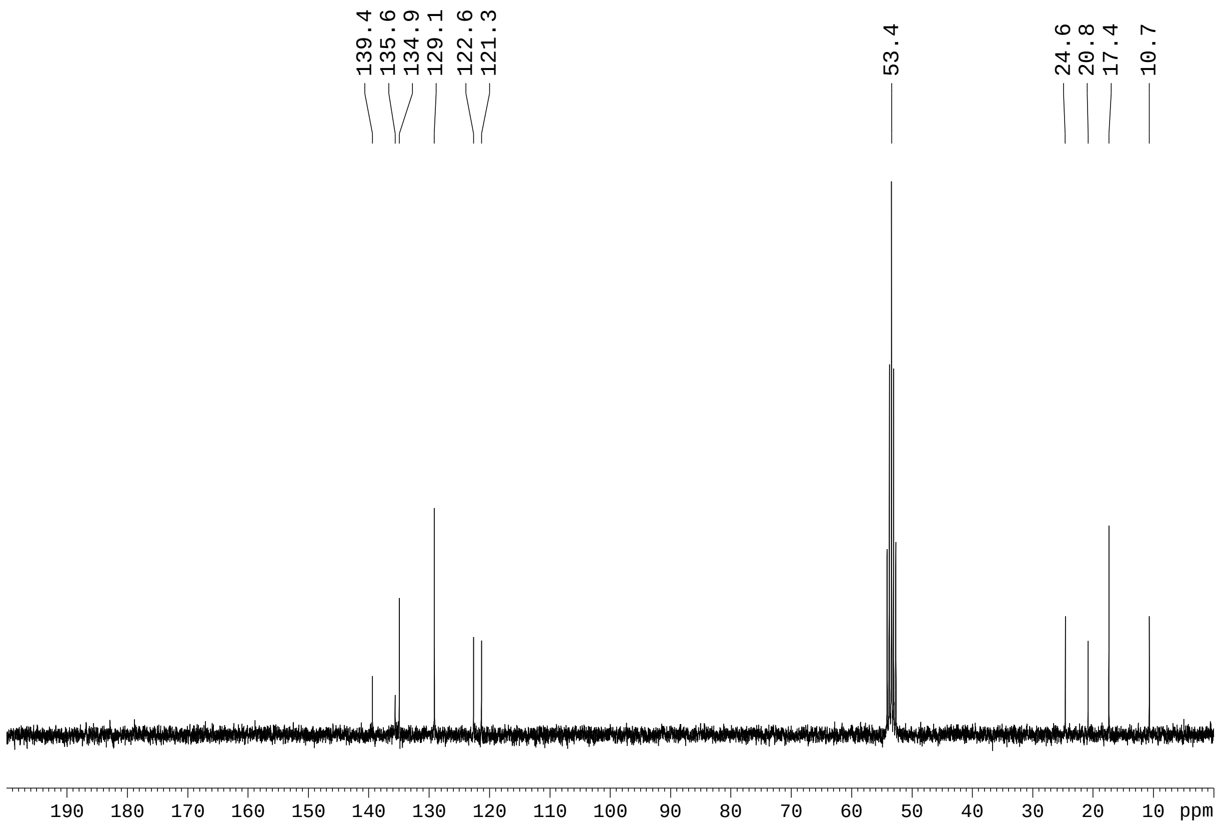
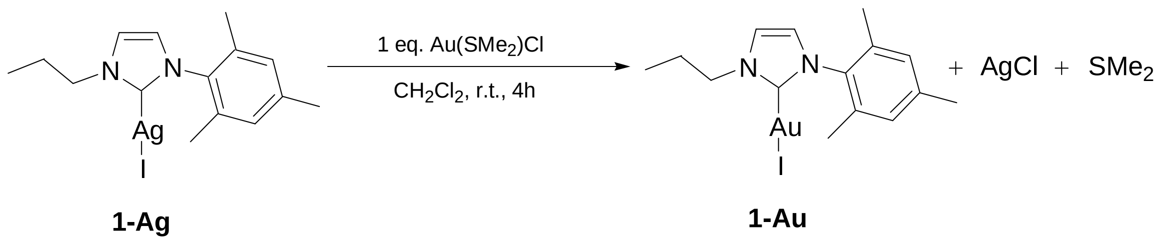


Figure S4 : ^{13}C NMR spectra of 1-Ag.

Synthesis of Gold (1-(propyl)-3-(mesityl)imidazol-2-ylidene) iodide [1-Au]



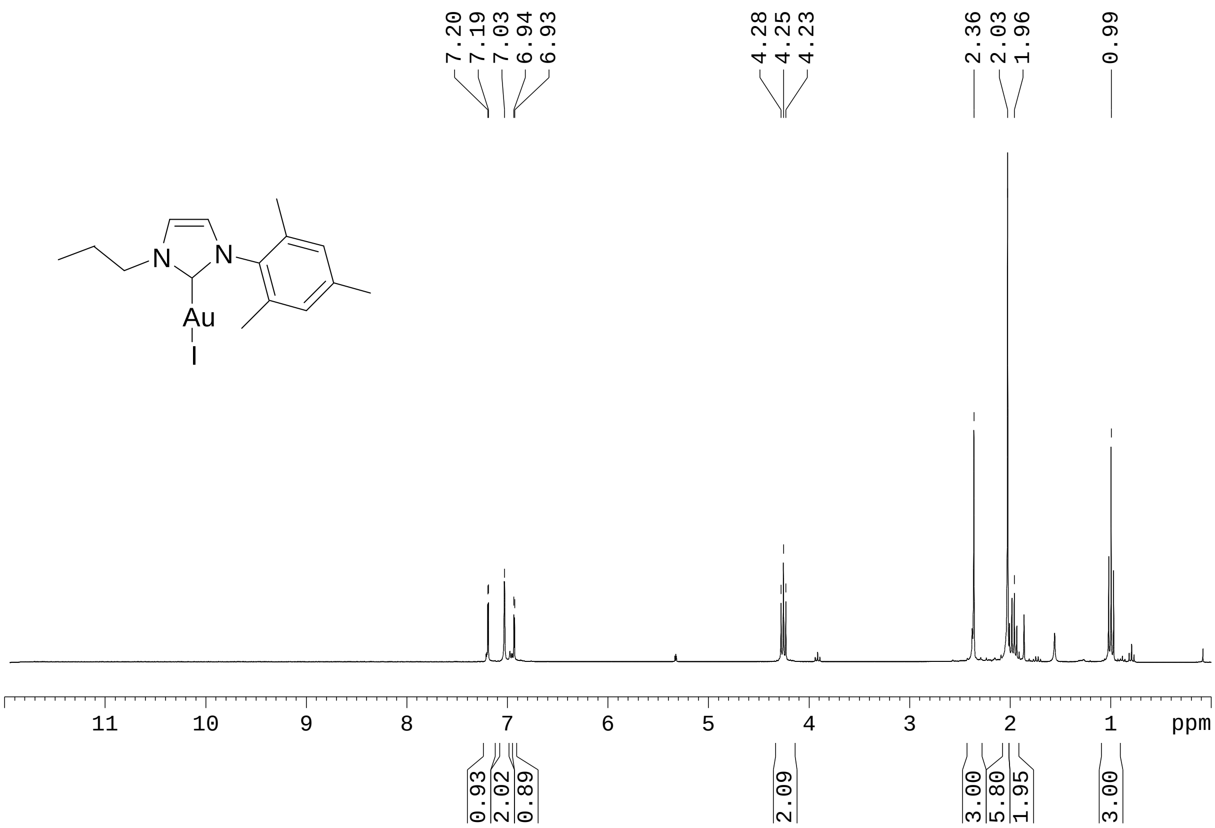


Figure S5 : ^{1}H NMR spectra of 1-Au.

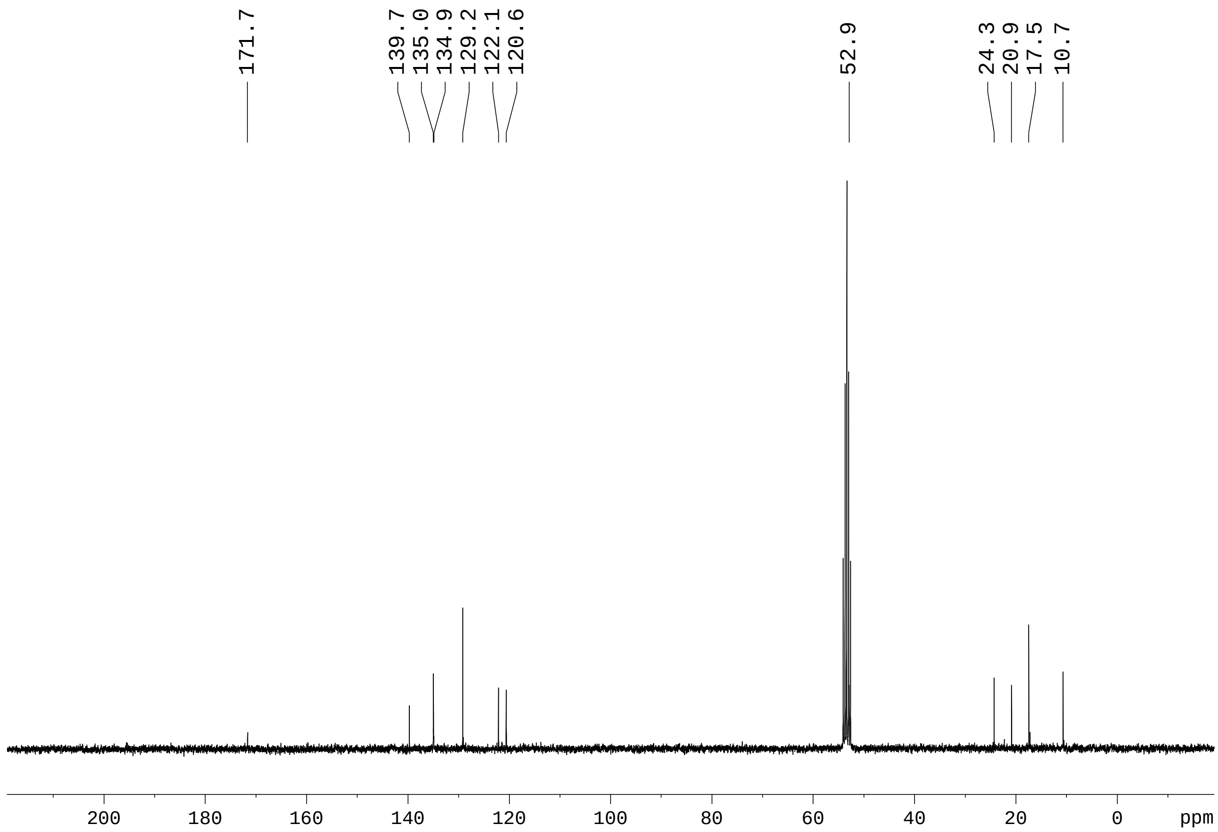
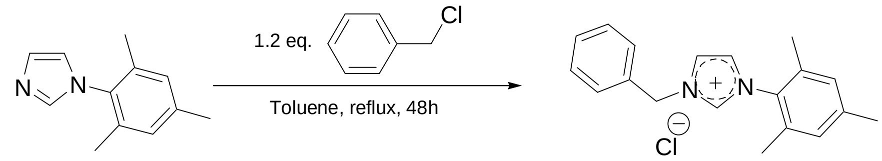


Figure S6 : ^{13}C NMR spectra of 1-Au.

Synthesis of 1-(benzyl)-3-(mesityl)imidazolium chloride [2]



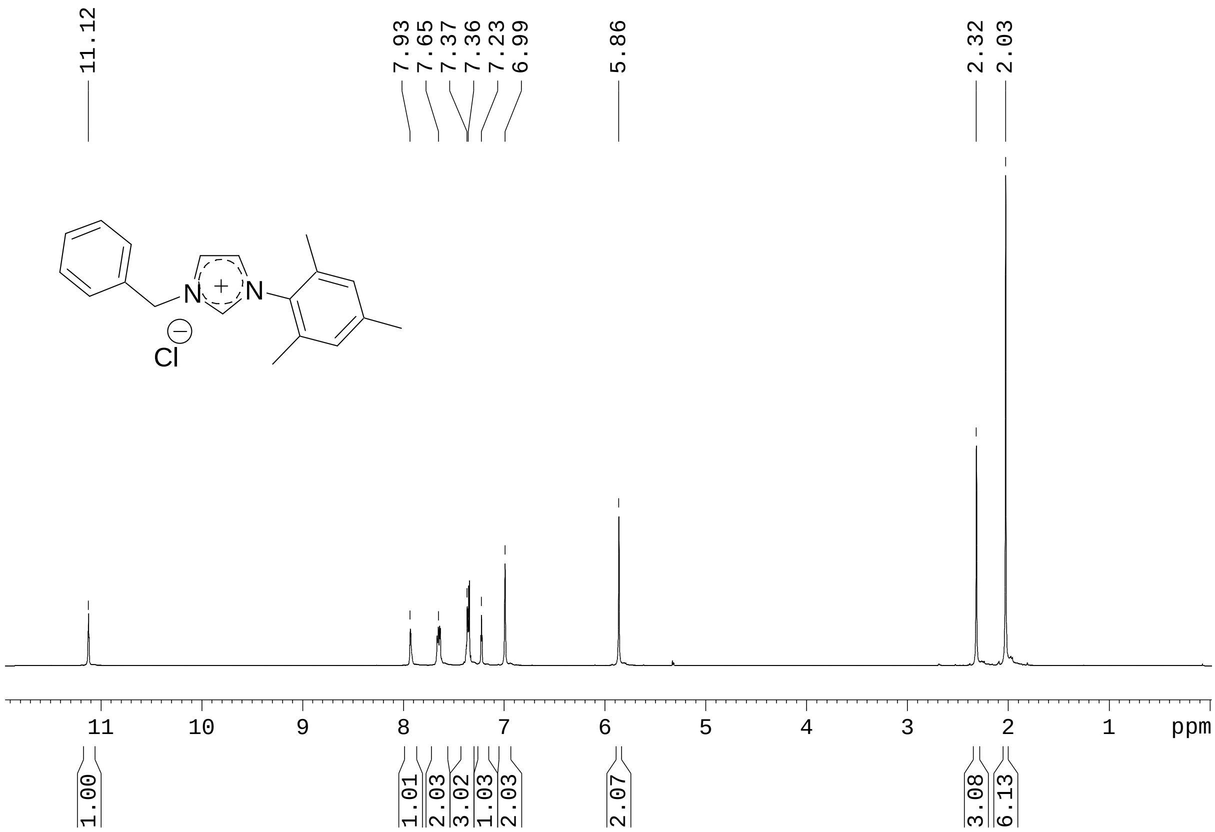


Figure S7 : ^{1}H NMR spectra of 2.

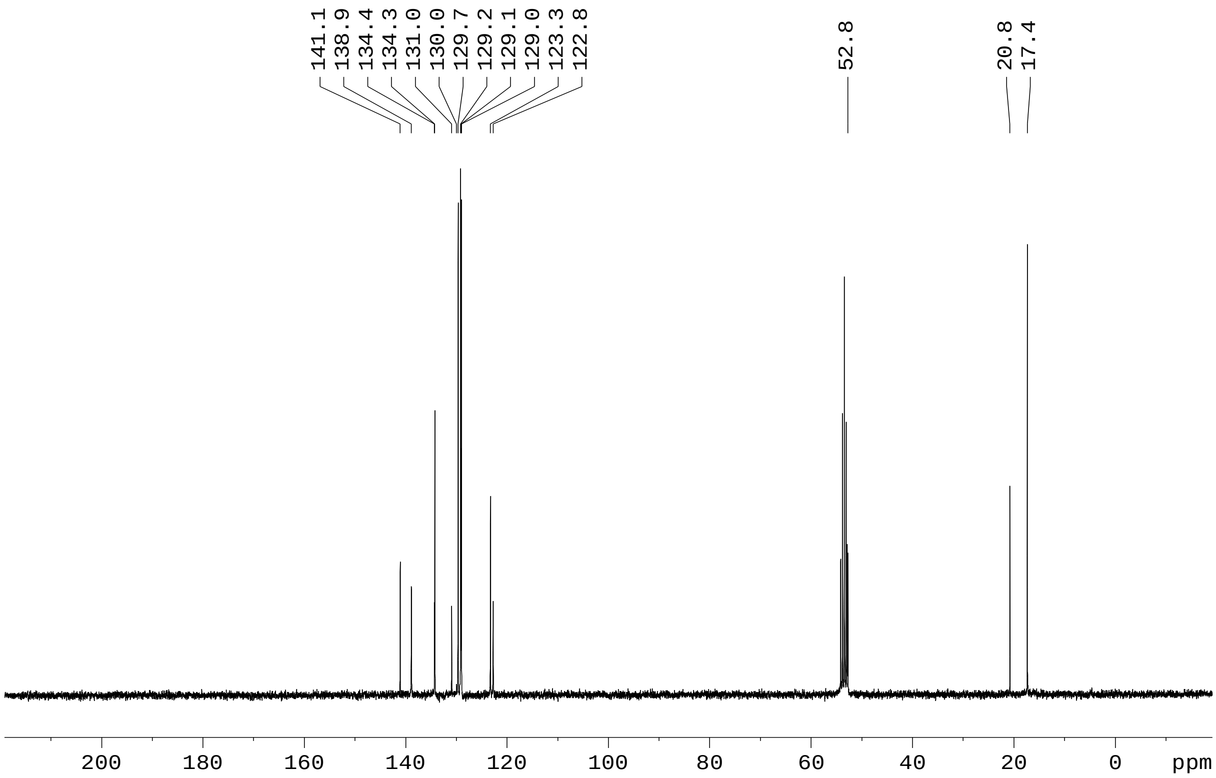
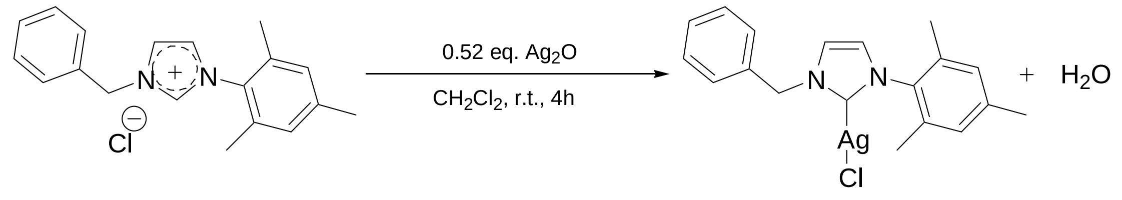


Figure S8 : ^{13}C NMR spectra of 2.

Synthesis of Silver(1-(benzyl)-3-(mesityl)imidazol-2-ylidene) chloride [2-Ag]



2 **2-Ag**

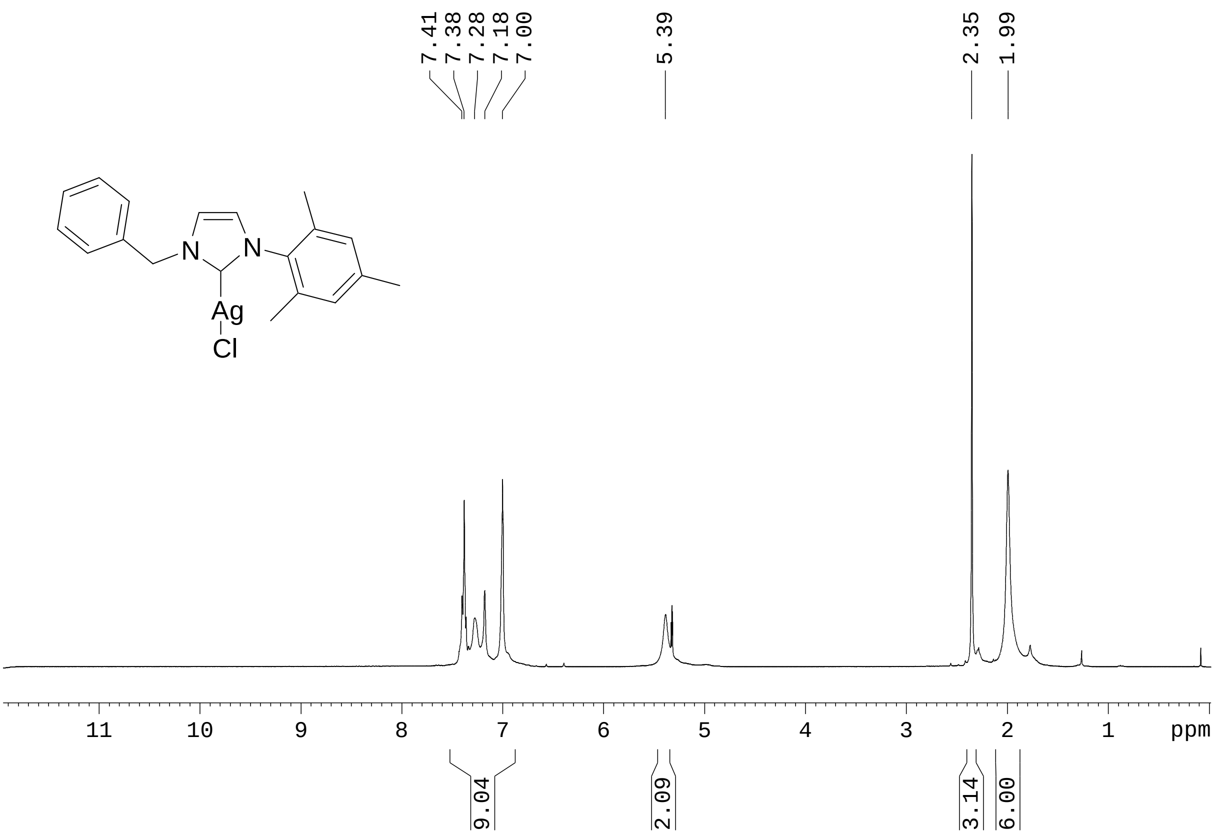


Figure S9 : ^{1}H NMR spectra of 2-Ag.

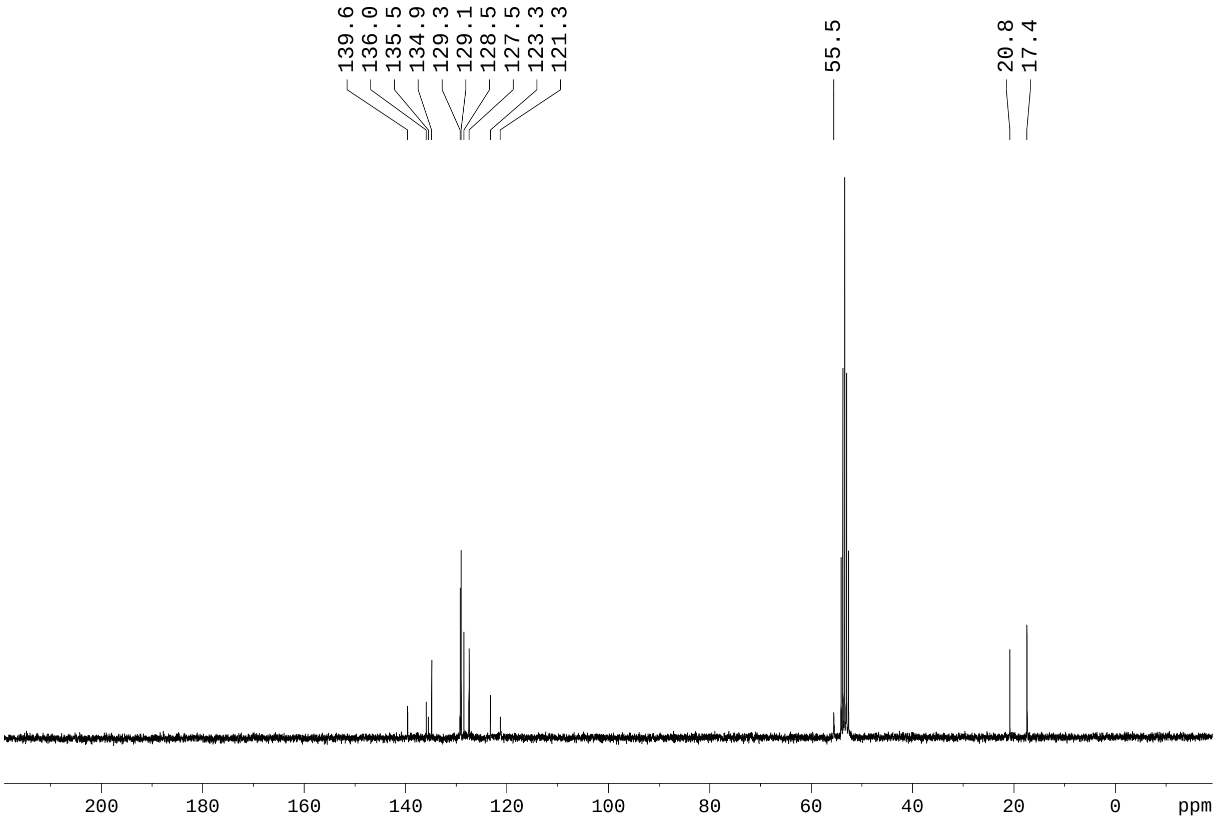
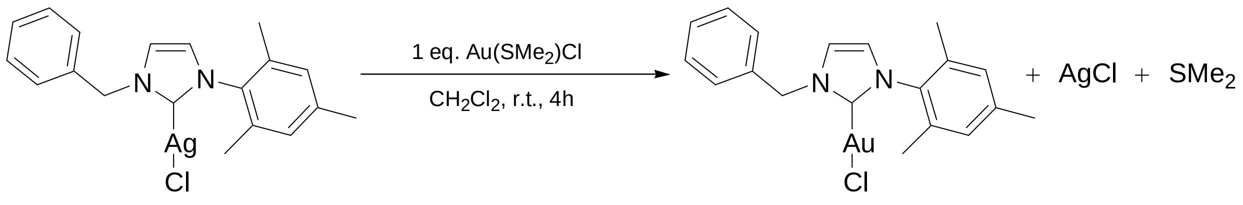


Figure S10 : ^{13}C NMR spectra of 2-Ag.

Synthesis of Gold (1-(benzyl)-3-(mesityl)imidazol-2-ylidene) chloride [2-Au]



2-Ag **2-Au**

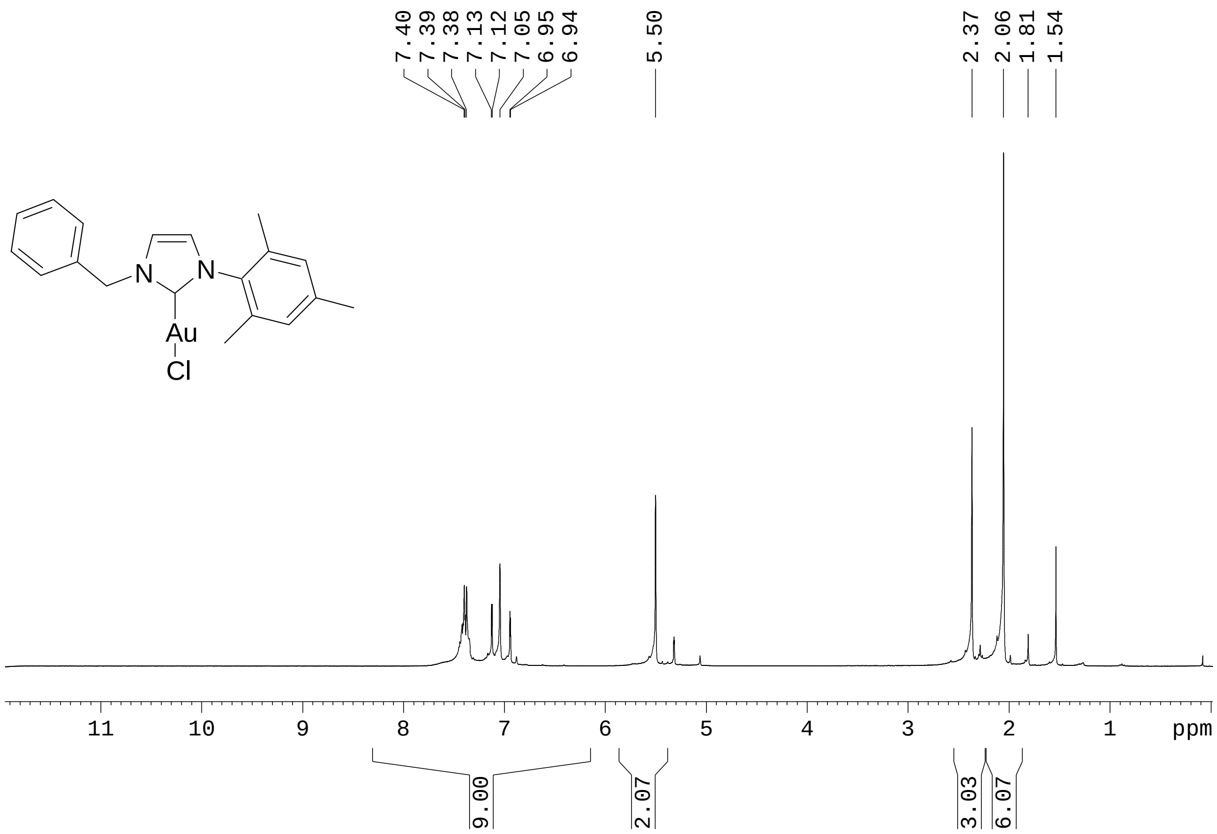


Figure S12 : ^{1}H NMR spectra of 2-Au.

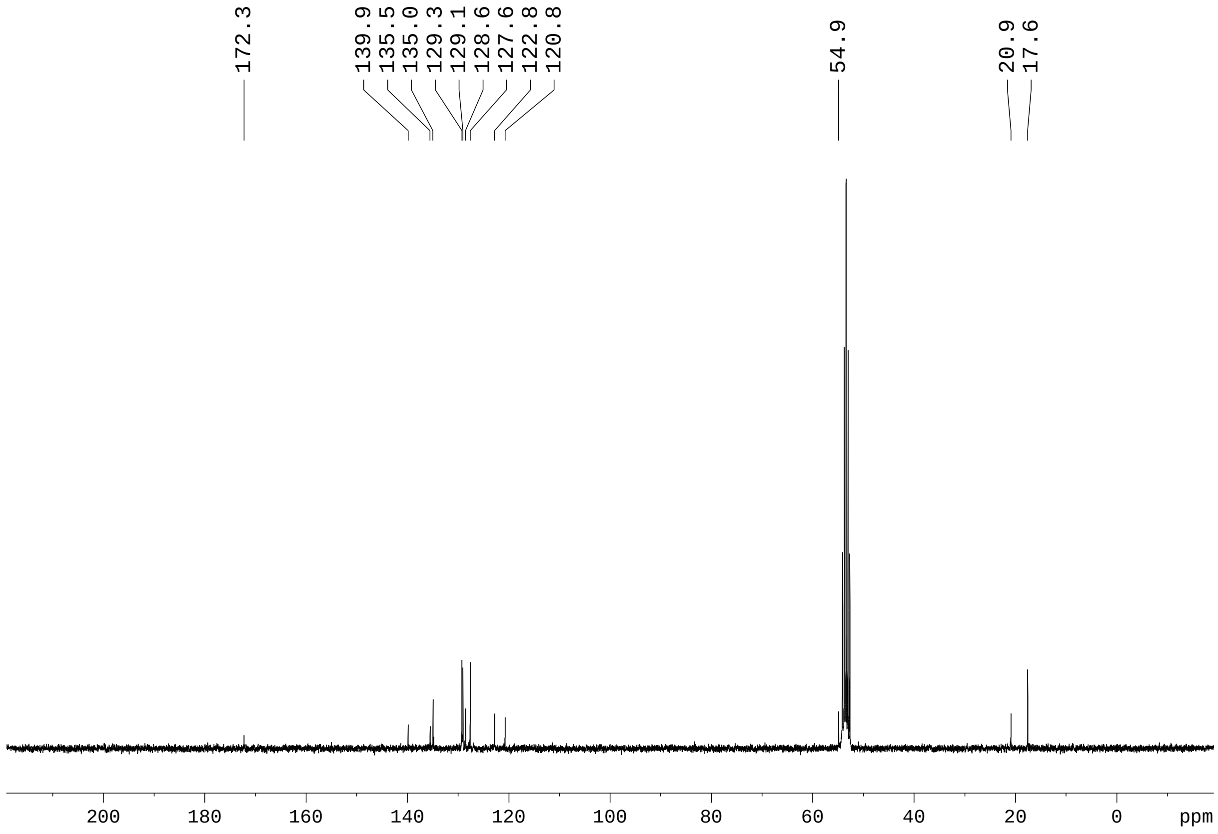


Figure S13 : ^{13}C NMR spectra of 2-Au.

Table S1 : Crystal Data and Experimental Details for 2-Au.

Crystal data

$C_{19}H_{20}AuClN_2$	$Z = 2$
$M_r = 508.80$	$D_x = 1.850$ Mg m^{-3}
Monoclinic, *P*1*c*1	Mo *K*α radiation
$a = 9.4696$ (2) Å	Cell parameters from 2284 reflections
$b = 11.5952$ (2) Å	θ = 0.7–27.9°
$c = 9.5469$ (2) Å	μ = 8.20 mm^{-1}
β = 119.3890 (10)°	$T = 293$ K
$V = 913.36$ (3) Å^3	Block, colorless

Data collection

Nonius KappaCCD diffractomer	3785 reflections with $I > 2.0\sigma(I)$
φ & ω scans	$R_{int} = 0.000$
Absorption correction: multi-scan (based on symmetry-related measurements)	$\theta_{max} = 27.9°$
$T_{min} = 0.05$, $T_{max} = 0.14$	$h = -12 \rightarrow 12$
3881 measured reflections	$k = 0 \rightarrow 15$
3881 independent reflections	$l = -12 \rightarrow 12$

Refinement

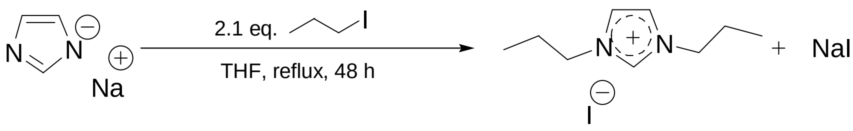
Refinement on F^2	No H atoms present
$R[F^2 > 2\sigma(F^2)] = 0.022$	Calculated weights Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.05P)^2 + 1.02P]$,where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$wR(F^2) = 0.057$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.27$	$\Delta\rho_{max} = 0.89$ e Å^{-1}
3873 reflections	$\Delta\rho_{min} = -1.78$ e Å^{-1}
210 parameters	Extinction correction: None

Geometric parameters (Å, °) for 1

Au1—Cl2	2.2815 (17)	C12—C13	1.337 (9)
Au1—C3	1.953 (7)	C13—N14	1.380 (6)
C3—N4	1.373 (7)	N14—C15	1.444 (7)
C3—N14	1.336 (8)	C15—C16	1.405 (7)
N4—C5	1.462 (7)	C15—C20	1.394 (8)
N4—C12	1.389 (7)	C16—C17	1.397 (11)
C5—C6	1.513 (8)	C16—C23	1.500 (12)
C6—C7	1.378 (8)	C17—C18	1.354 (14)
C6—C11	1.397 (7)	C18—C19	1.387 (10)
C7—C8	1.396 (8)	C18—C22	1.520 (9)
C8—C9	1.392 (9)	C19—C20	1.405 (8)
C9—C10	1.378 (9)	C20—C21	1.495 (8)
C10—C11	1.370 (8)		

Cl2—Au1—C3	178.7 (2)	C13—N14—C3	112.6 (5)
Au1—C3—N4	126.7 (5)	C13—N14—C15	122.8 (4)
Au1—C3—N14	130.0 (4)	C3—N14—C15	124.6 (4)
N4—C3—N14	103.2 (5)	N14—C15—C16	119.7 (5)
C3—N4—C5	125.8 (5)	N14—C15—C20	117.9 (4)
C3—N4—C12	111.2 (5)	C16—C15—C20	122.3 (6)
C5—N4—C12	122.8 (5)	C15—C16—C17	117.7 (7)
N4—C5—C6	111.8 (4)	C15—C16—C23	119.6 (7)
C5—C6—C7	120.4 (5)	C17—C16—C23	122.7 (8)
C5—C6—C11	120.5 (5)	C16—C17—C18	121.7 (8)
C7—C6—C11	119.1 (5)	C17—C18—C19	119.8 (6)
C6—C7—C8	120.7 (5)	C17—C18—C22	120.5 (8)
C7—C8—C9	119.5 (5)	C19—C18—C22	119.7 (9)
C8—C9—C10	119.3 (6)	C18—C19—C20	121.8 (7)
C9—C10—C11	121.3 (6)	C19—C20—C15	116.7 (5)
C6—C11—C10	120.1 (5)	C19—C20—C21	121.0 (6)
N4—C12—C13	106.3 (5)	C15—C20—C21	122.2 (5)
C12—C13—N14	106.7 (5)		

Synthesis of N,N'-bis(propyl)imidazolium iodide [3]



3

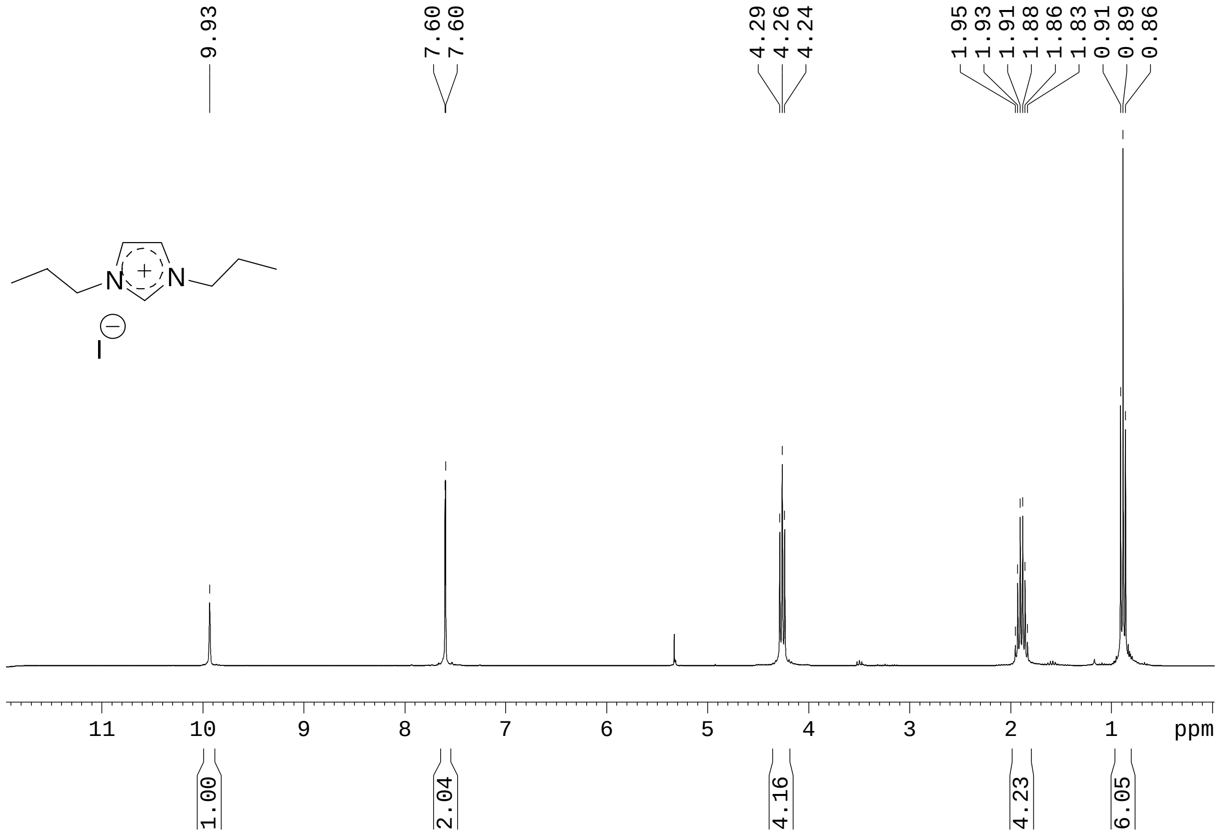
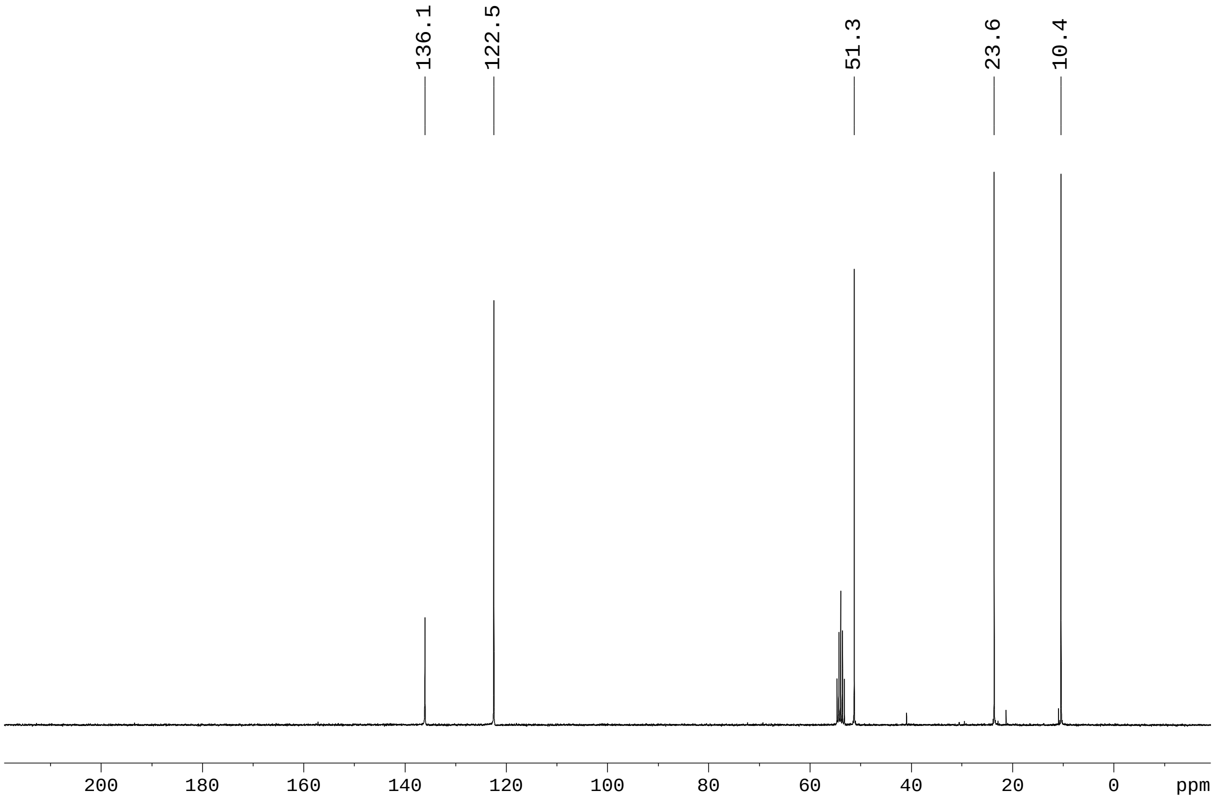
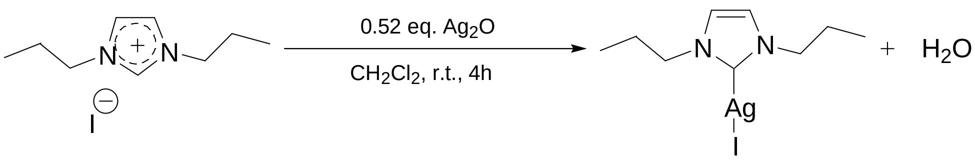


Figure S14 : ^{1}H NMR spectra of 3.



igure S15 : ^{13}C NMR spectra of 3.

Synthesis of Silver (N,N'-bis(propyl)imidazol-2-ylidene) iodide [3-Ag]



3 **3-Ag**

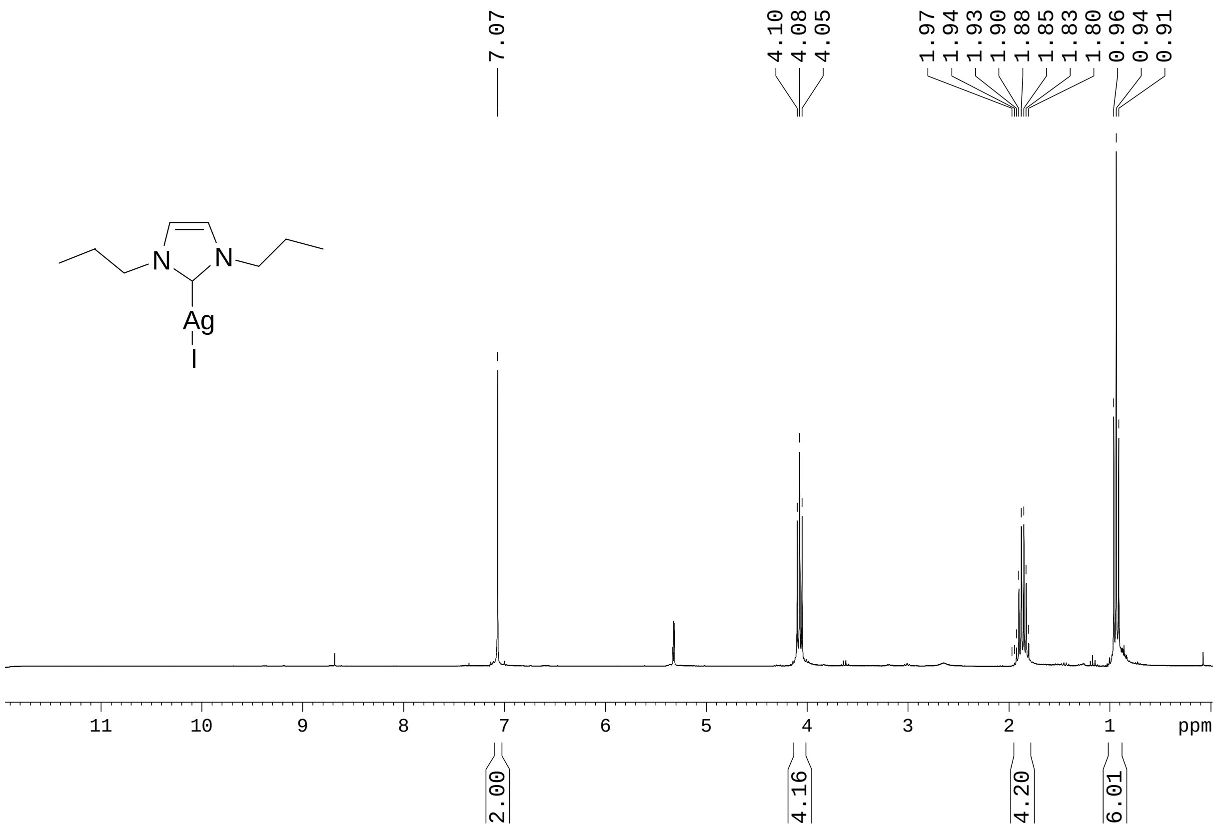


Figure S16 : ^{1}H NMR spectra of 3-Ag.

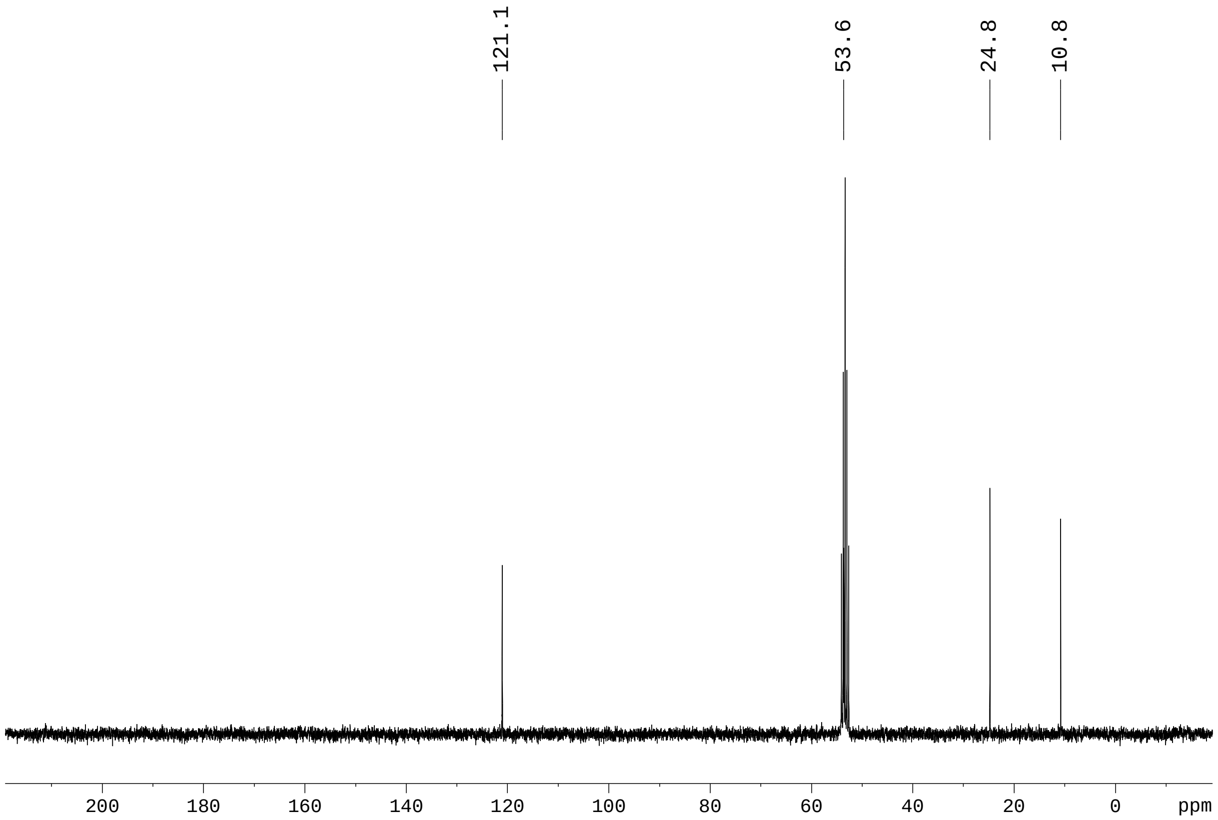
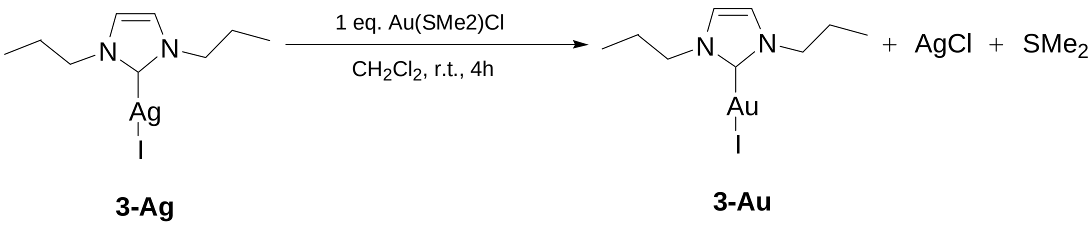


Figure S17 : ^{13}C NMR spectra of 3-Ag.

Synthesis of Gold (N,N'-bis(propyl)imidazol-2-ylidene) iodide [3-Au]



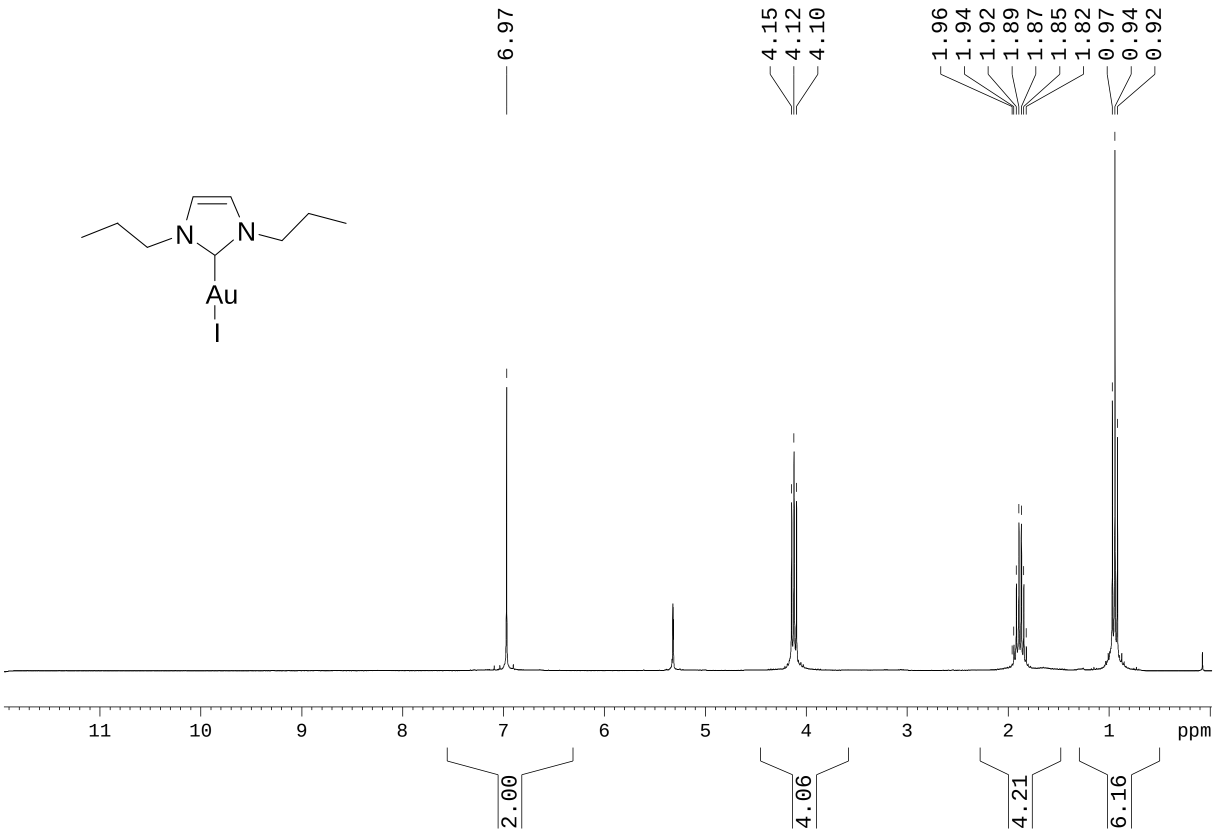


Figure S18 : ^{1}H NMR spectra of 3-Au.

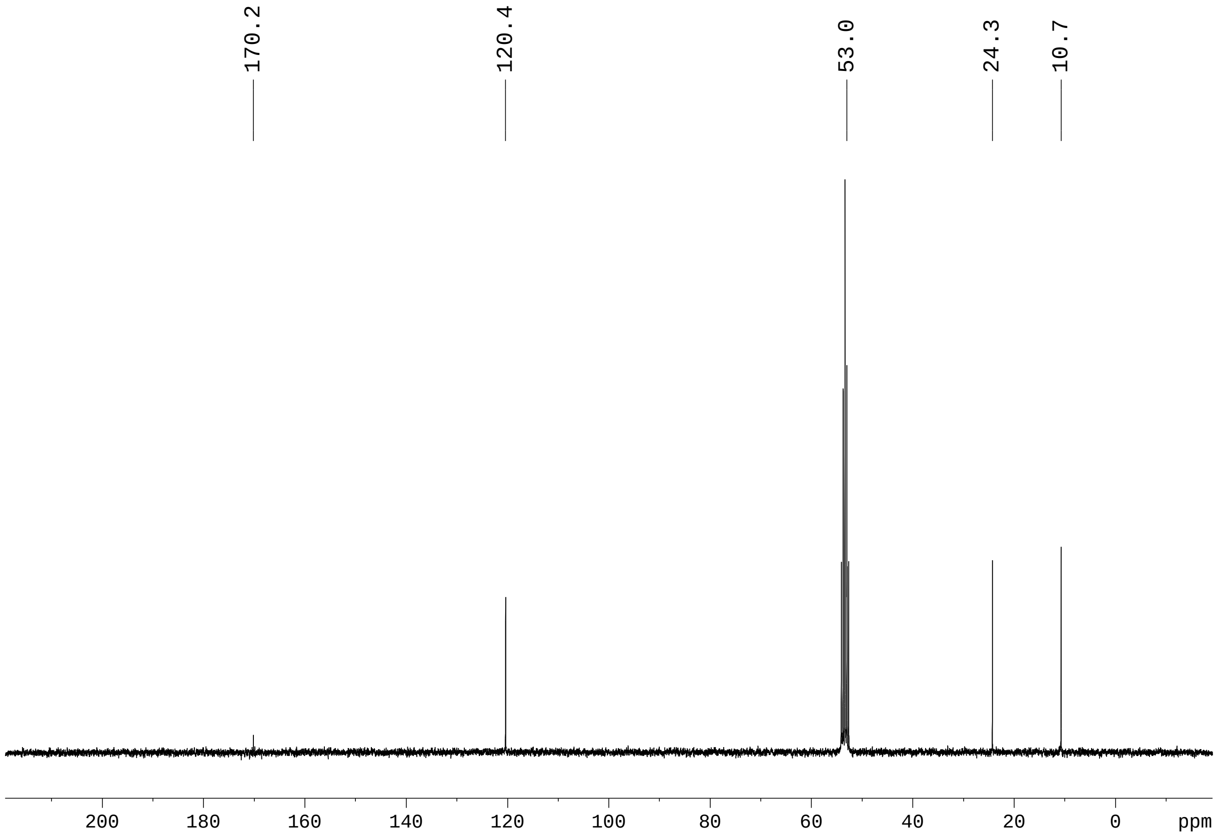
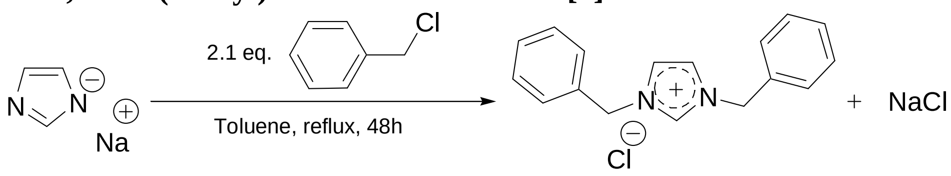


Figure S19 : ^{13}C NMR spectra of 3-Au.

Synthesis of N,N'-bis(benzyl)imidazolium chloride [4]



4

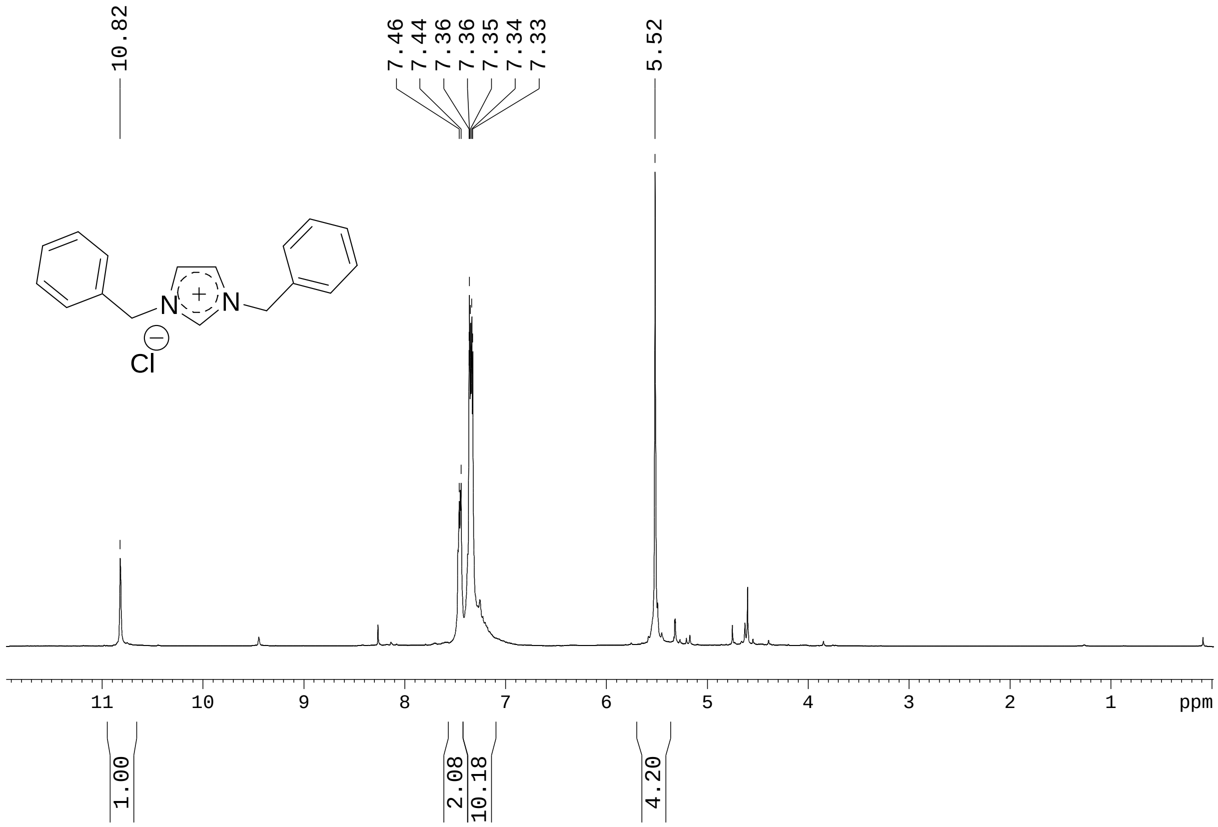


Figure S20 : ^{1}H NMR spectra of 4.

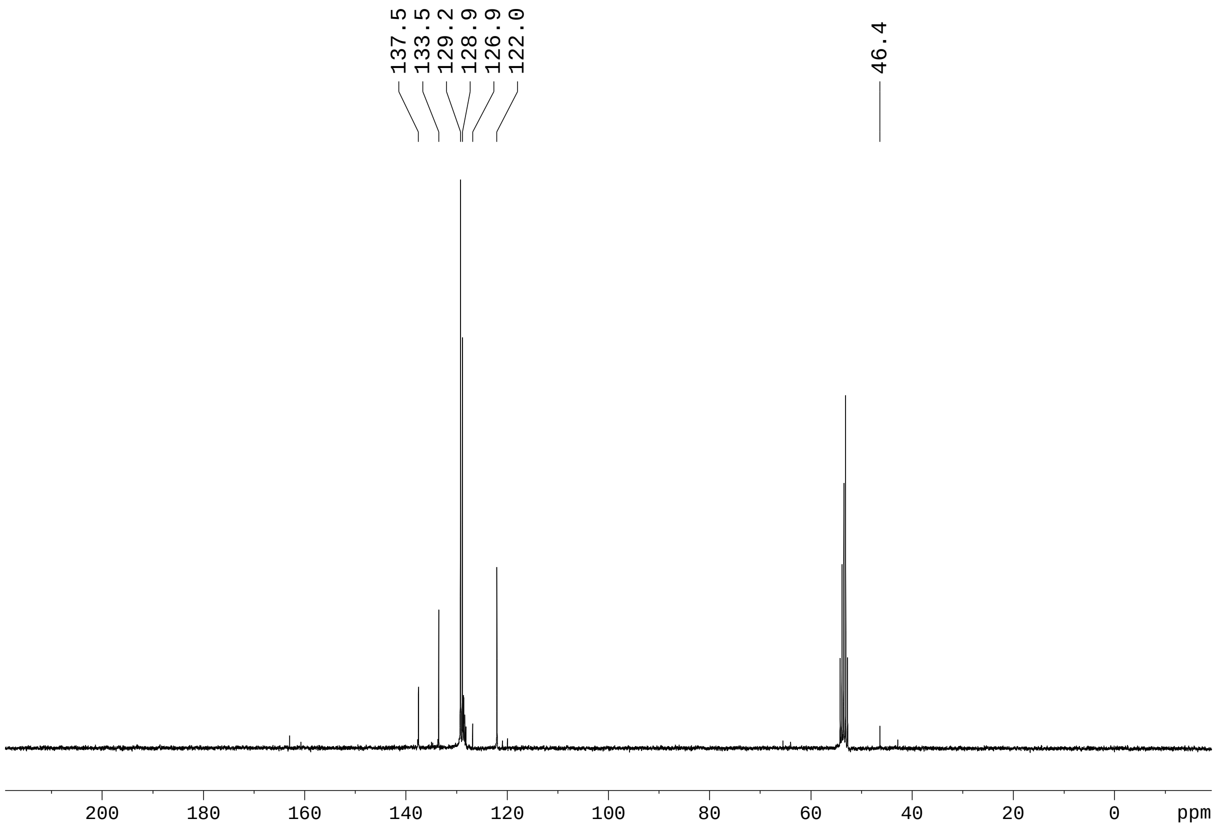
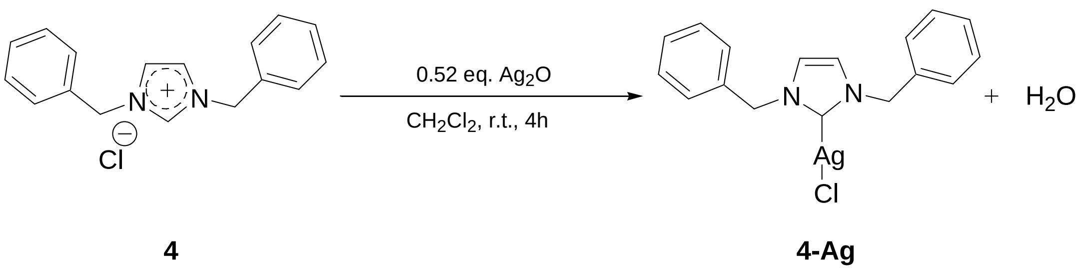


Figure S21 : ^{13}C NMR spectra of 4.

Synthesis of Silver (N,N-bis(benzyl)imidazol-2-ylidene) chloride [4-Ag]



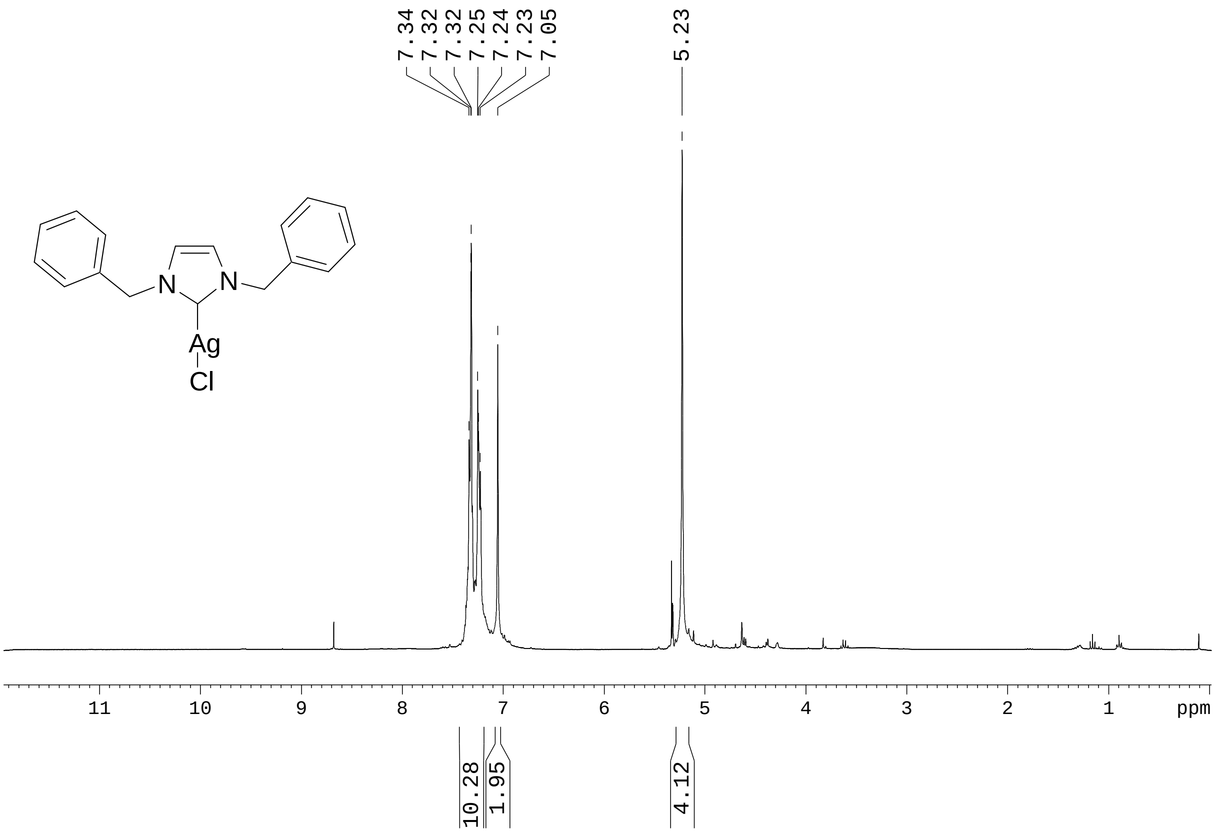


Figure S22 : ^{1}H NMR spectra of 4-Ag.

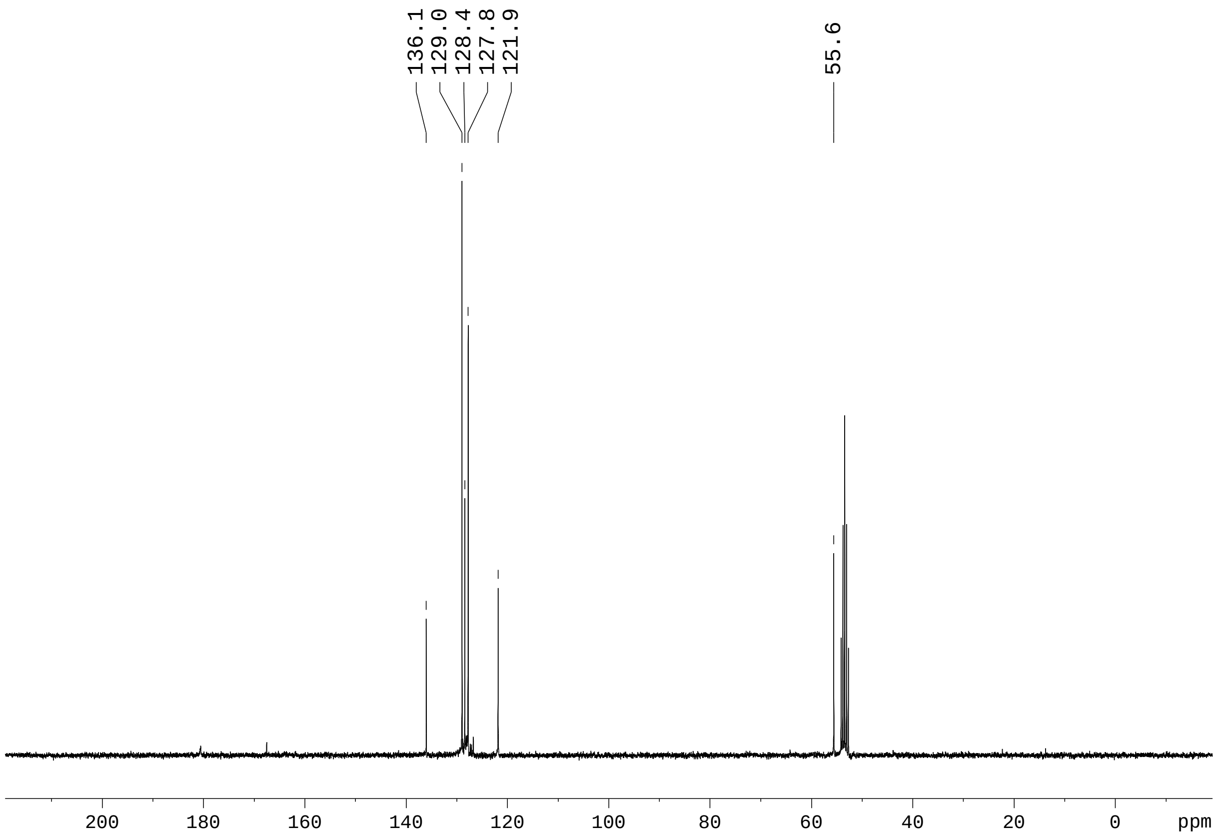
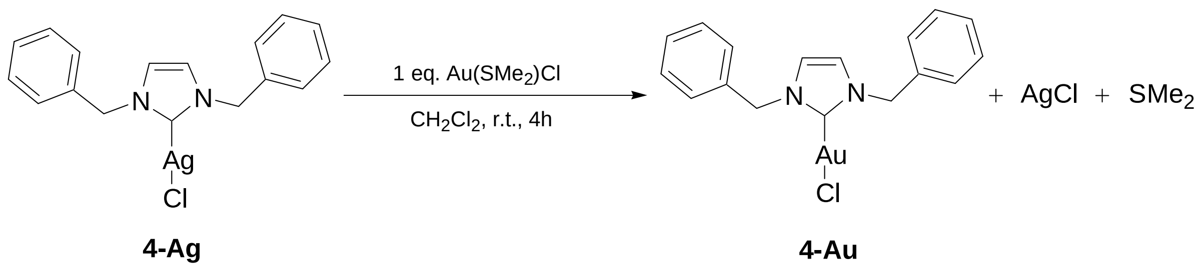


Figure S23 : ^{13}C NMR spectra of 4-Ag.

Synthesis of Gold (N,N-bis(benzyl)imidazol-2-ylidene) chloride [4-Au]



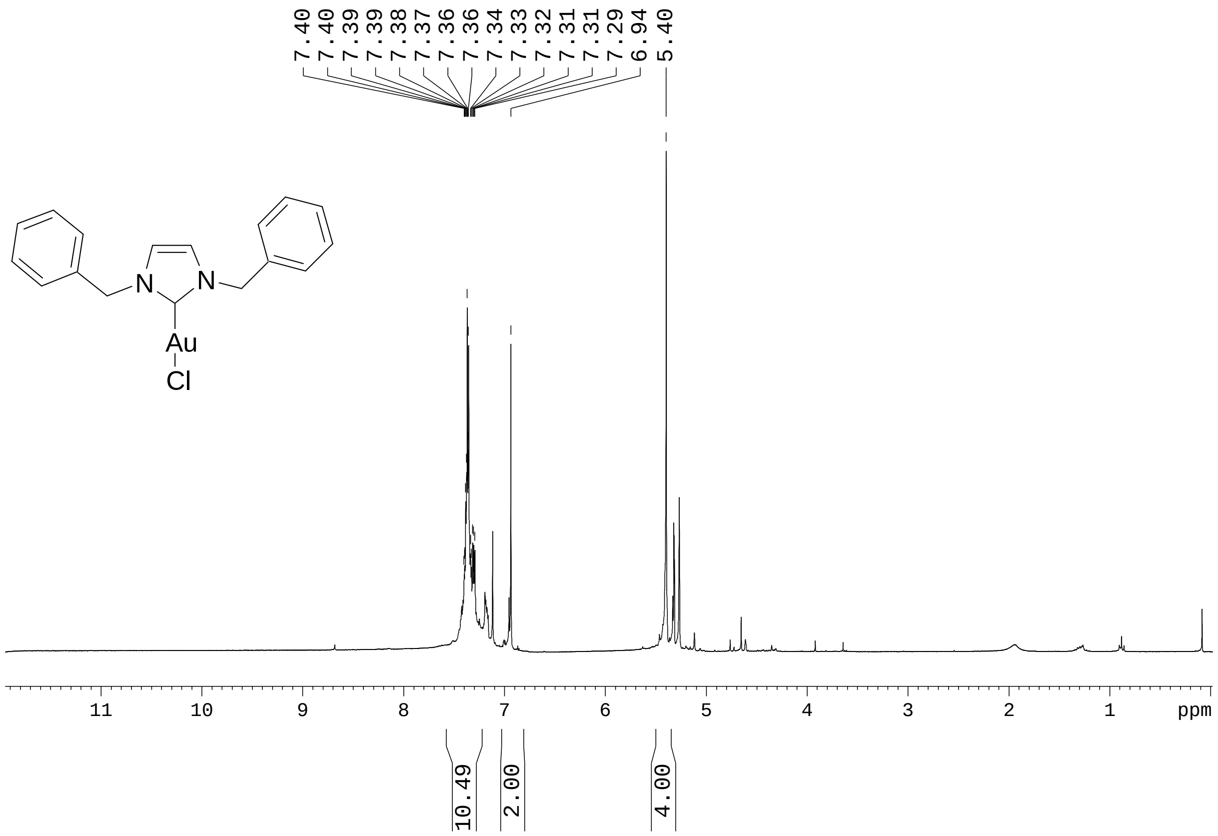


Figure S24 : ^{1}H NMR spectra of 4-Au.

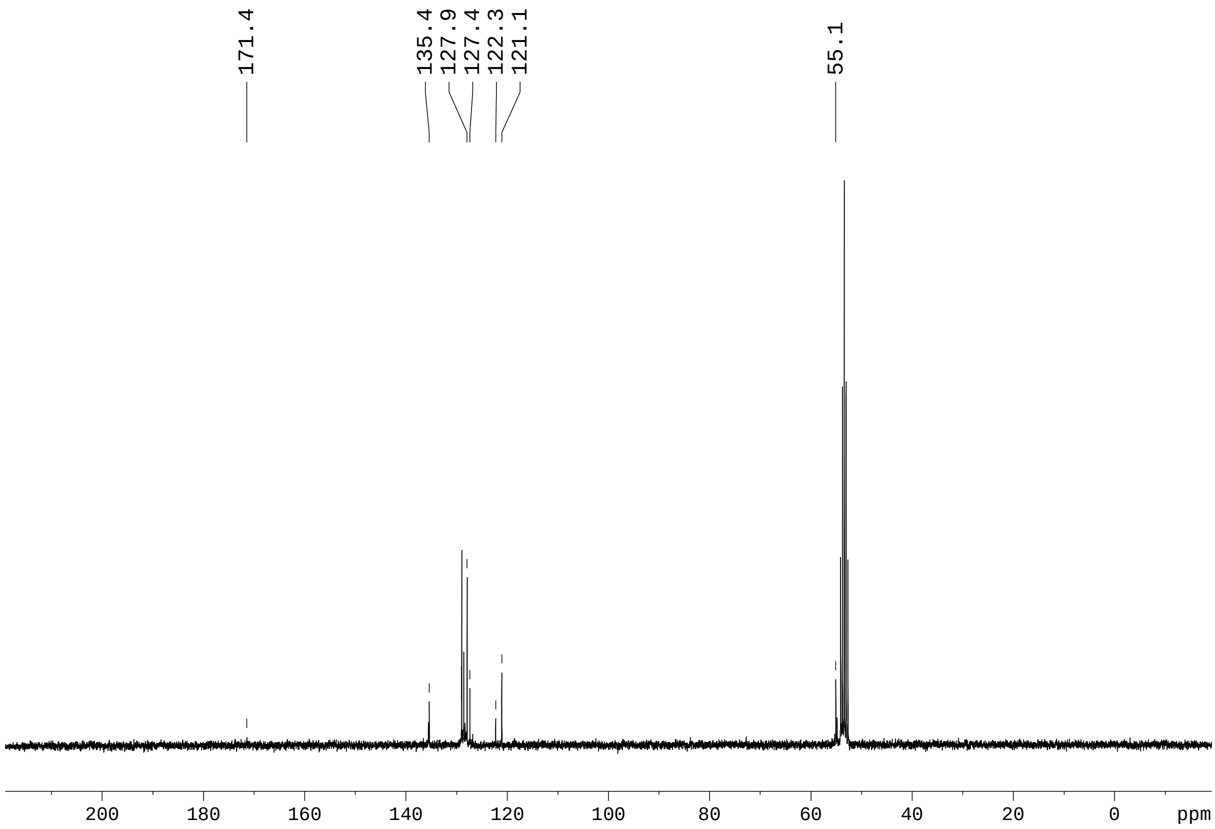


Figure S25 : ^{13}C NMR spectra of 4-Au.

Homogeneous catalysis

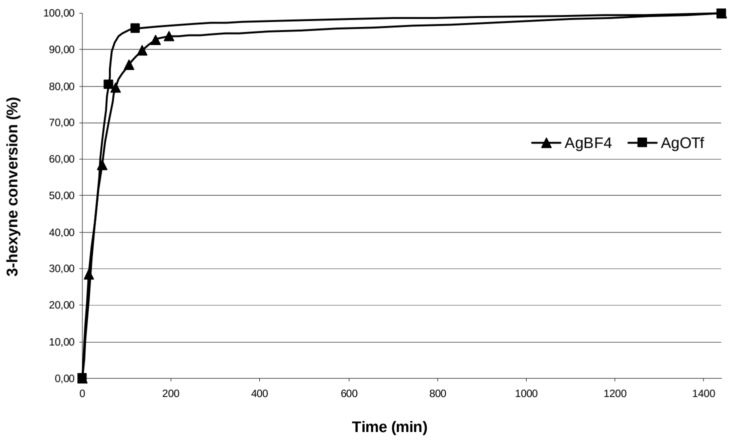


Figure S26 : 3-hexyne conversion versus time using 0,4 mol% Au (Table V.1, entries 3 and 4).

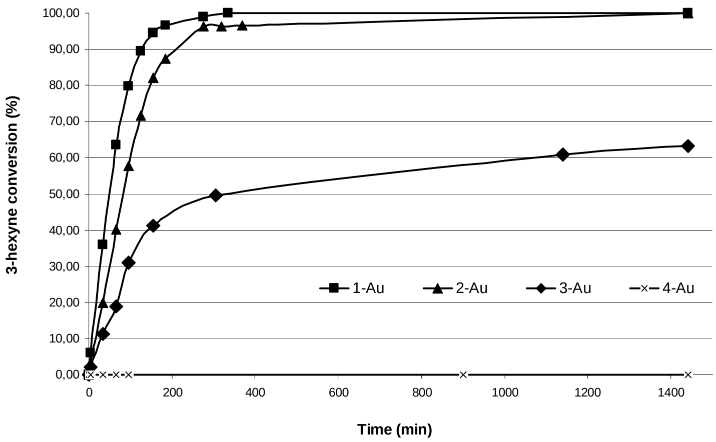


Figure S27 : 3-hexyne conversion versus time using 0,01 mol% Au (Table V.1, entries 7, 8, 9 and 10).

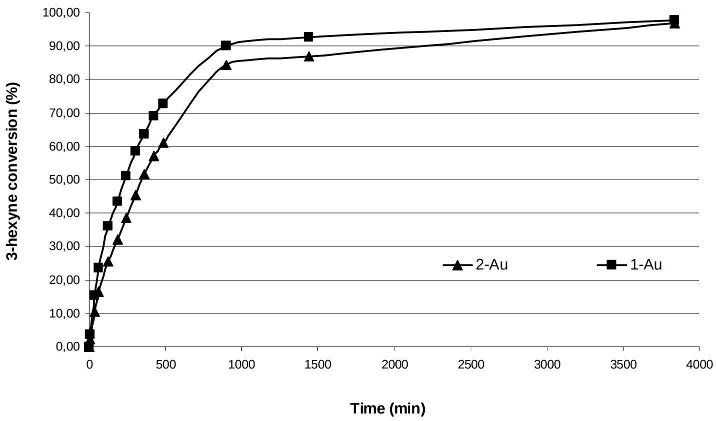


Figure S28 : 3-hexyne conversion versus time using 0,001 mol% Au (Table V.1, entries 13 and 14).

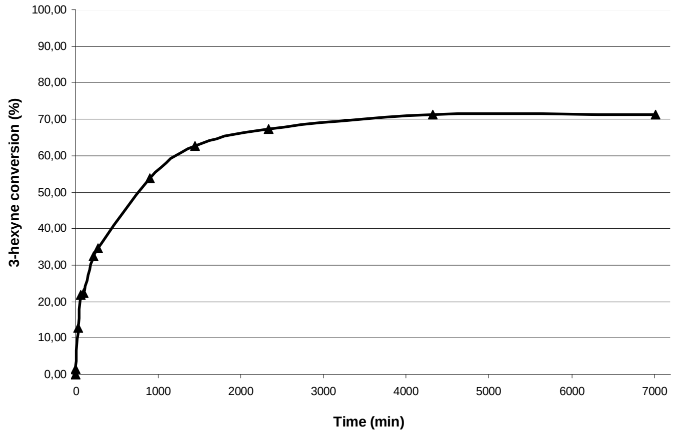


Figure S29 : 3-hexyne conversion versus time using 0,0001 mol% Au (Table V.1, entry 16).

Catalyst 1-Au

Catalyst 2-Au

Catalyst 3-Au

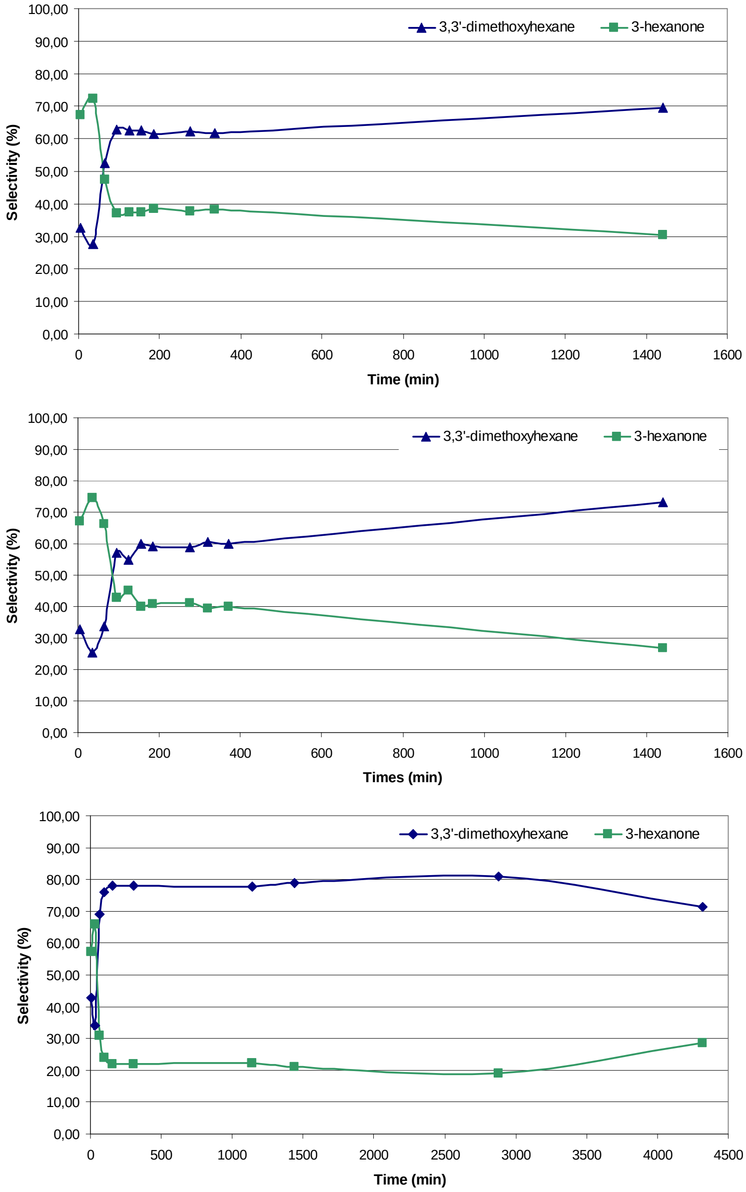
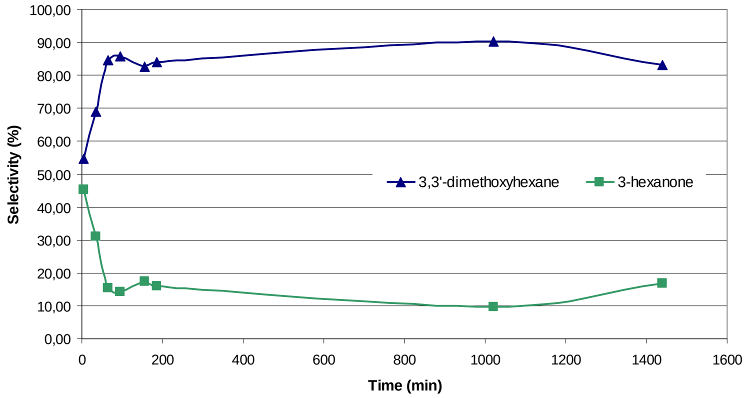


Figure S30 : Products selectivity versus time using 0,01 mol% Au (Table V.1, entries 7, 8 and 9).

Catalyst 1-Au



Catalyst 2-Au

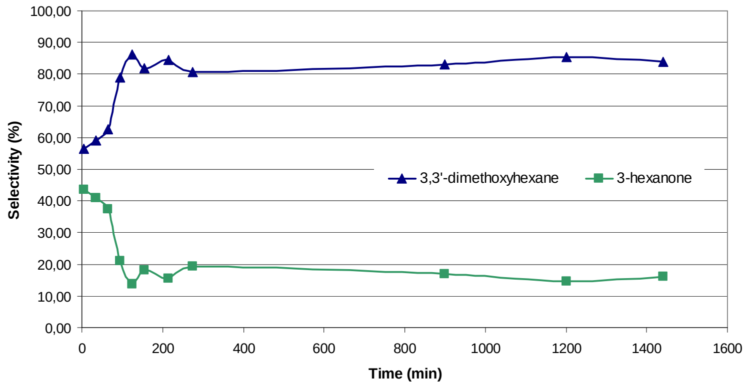
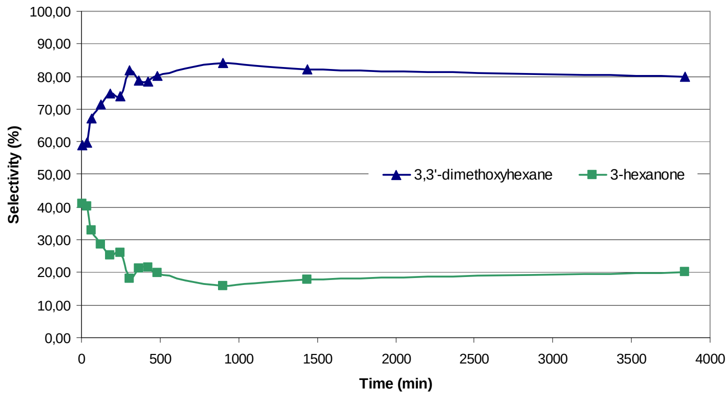


Figure S31 : Products selectivity versus time using 0,01 mol% Au (Table V.1, entries 11 and 12).

Catalyst 1-Au



Catalyst 2-Au

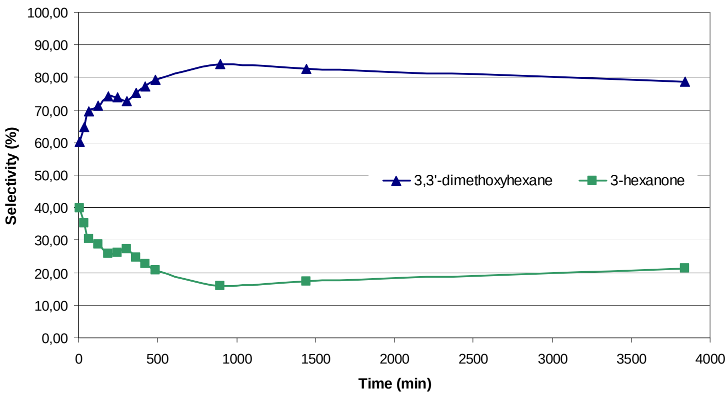
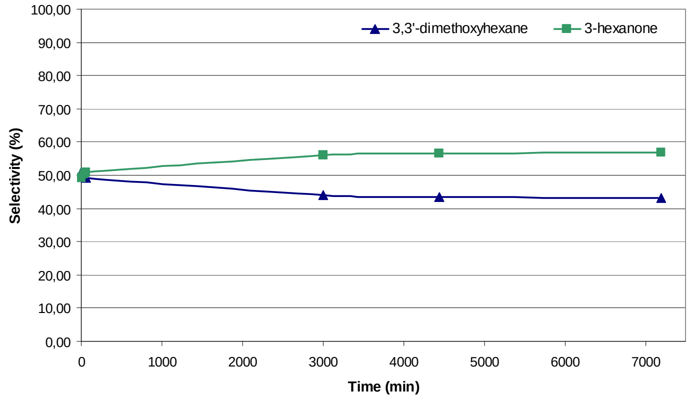


Figure S32 : Products selectivity versus time using 0,001 mol% Au (Table V.1, entries 13 and 14).

Catalyst 1-Au



Catalyst 2-Au

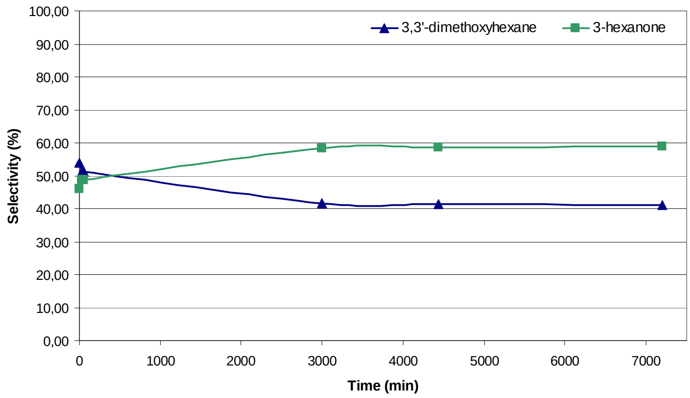


Figure S33 : Products selectivity versus time using 0,0001 mol% Au (Table V.1, entries 15 and 16).