Electronic Supplementary Information (ESI)

N-Heterocyclic Carbene-Stabilized Gold Nanoparticles with Tunable Sizes

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1. X-ray crystal structures determination

	1-AuX$_4$	**2-AuX$_4$**
Formula	$C_{27}H_{53}N_2 \cdot AuBrCl_3$	$C_{31}H_{55}N_2 \cdot AuBr_{0.93}Cl_{3.07}$
M / (g/mol)	789.53	835.23
cryst system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
a, b, c / Å	8.4845 (4), 42.119 (2), 9.4482 (5)	9.1187 (2), 10.1455 (3), 39.2531 (10)
β / °	102.912 (2)	90.211 (1)
V / Å^3	3291.0 (3)	3631.43 (16)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	5.95	5.33
Crystal size (mm)	0.25 × 0.22 × 0.08	0.32 × 0.26 × 0.17
T_{min}, T_{max}	0.495, 0.746	0.426, 0.739
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27789, 5785, 5469	104767, 10687, 8429
R_{int}	0.023	0.049
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.595	0.706
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.057, 1.30	0.068, 0.125, 1.44
No. of reflections	5785	10687
No. of parameters	309	349
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.53, -2.43	1.42, -2.20

Table S1. Crystal data and structure refinement for **1-AuX$_4$** and **2-AuX$_4$**

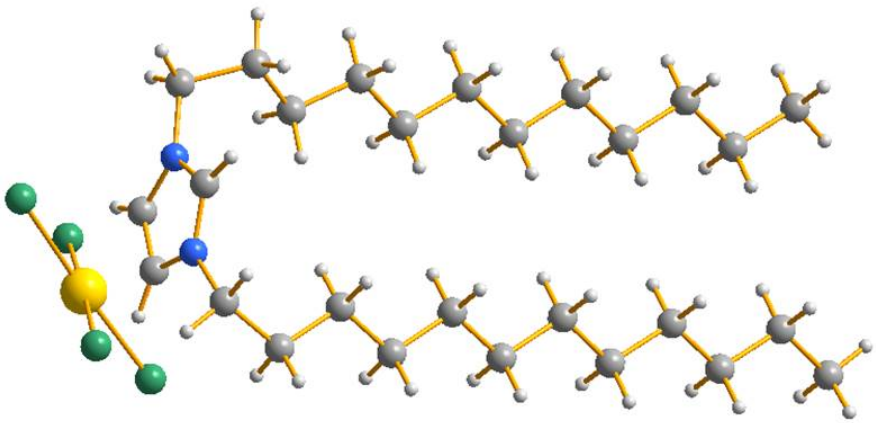


Figure S1. Molecular structure of **1-AuX$_4$** (color code: Au = yellow, Cl/Br = green, N = blue, C = grey, H = light grey).

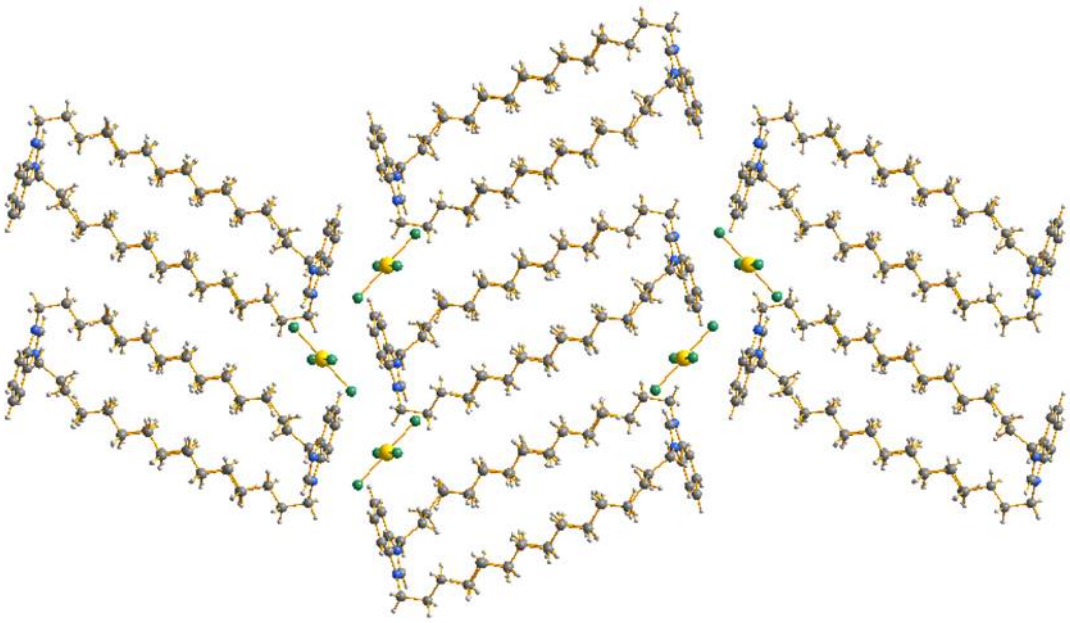


Figure S2. Crystal packing of **2-AuX$_4$** (color code: Au = yellow, Cl/Br = green, N = blue, C = grey, H = light grey).

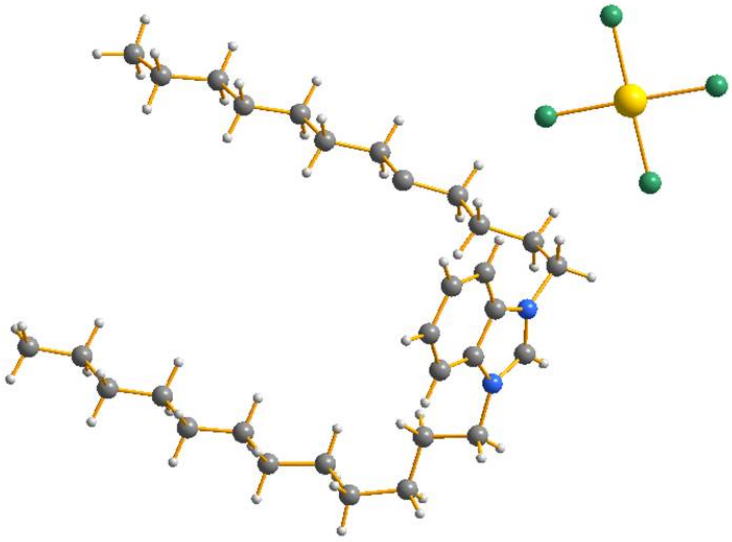


Figure S3. Molecular structure of **2-AuX$_4$** (color code: Au = yellow, Cl/Br = green, N = blue, C = grey, H = light grey).

2. NaH free vs. NaH containing protocol

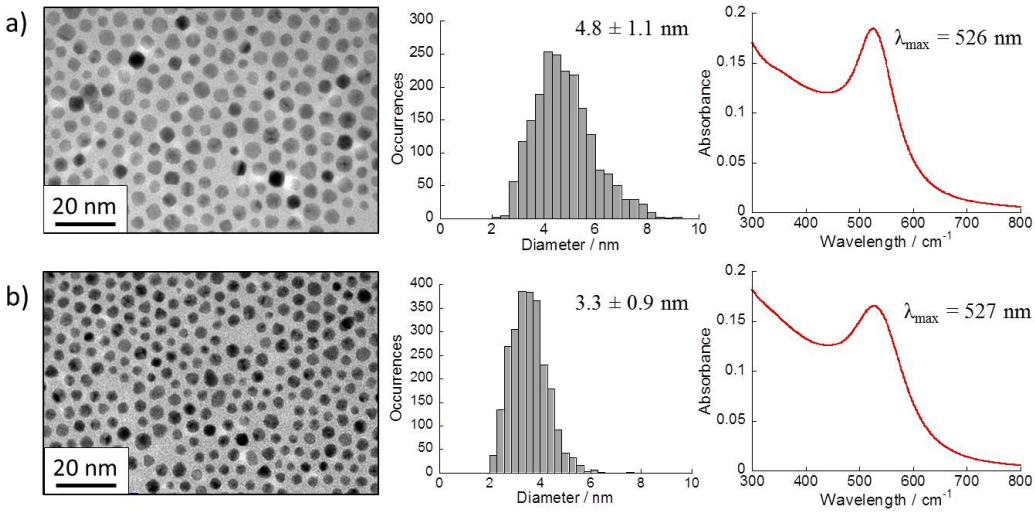


Figure S4. TEM images, corresponding size distributions and UV-visible absorption spectra of gold nanoparticles prepared with NaH and $NaBH_4$:
a) **1-AuX$_4$** only; b) **1-AuX$_4$** + 4 **1**-Br

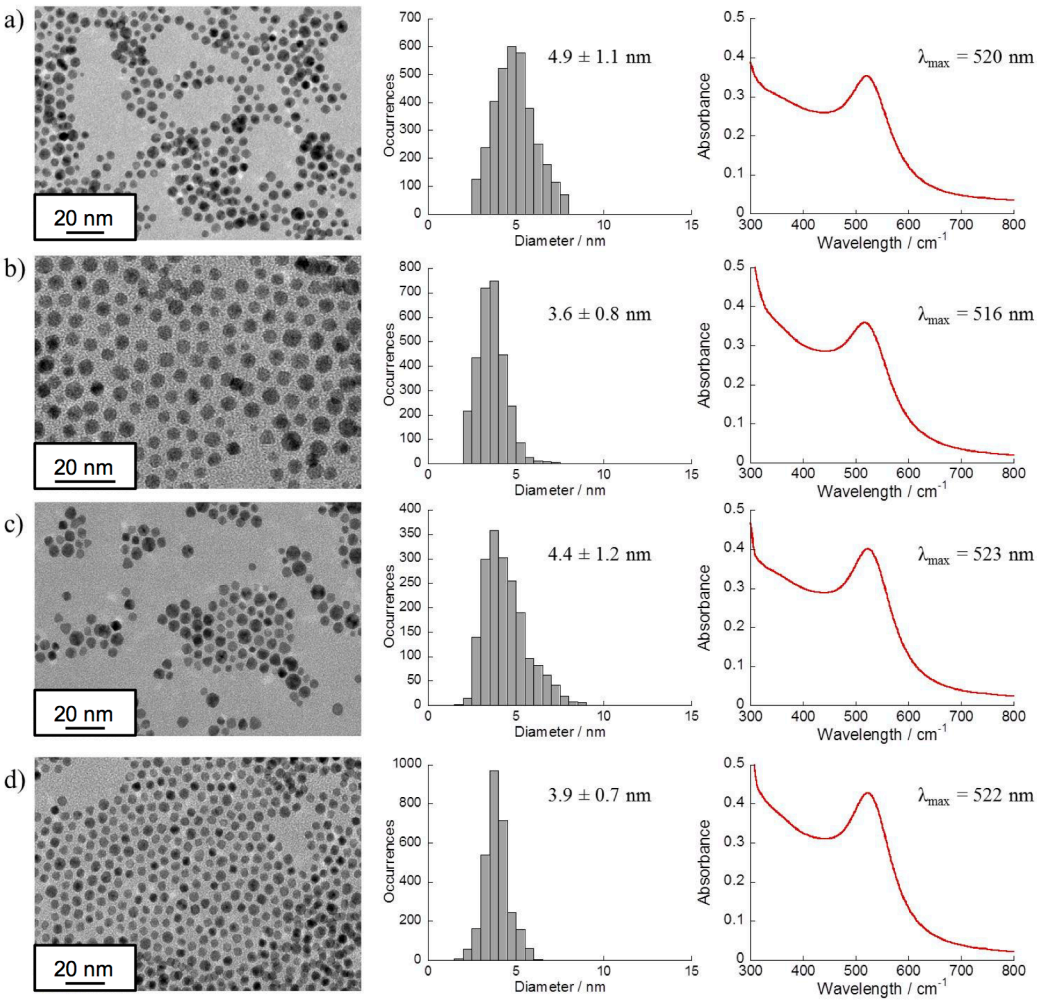


Figure S5. TEM images, corresponding size distributions and UV-visible absorption spectra of gold nanoparticles prepared from **2-AuX$_4$**:
a) $NaBH_4$ only; b) $NaBH_4$ only and **2**-Br addition;
c) NaH + $NaBH_4$; d) NaH + $NaBH_4$ and **2**-Br addition

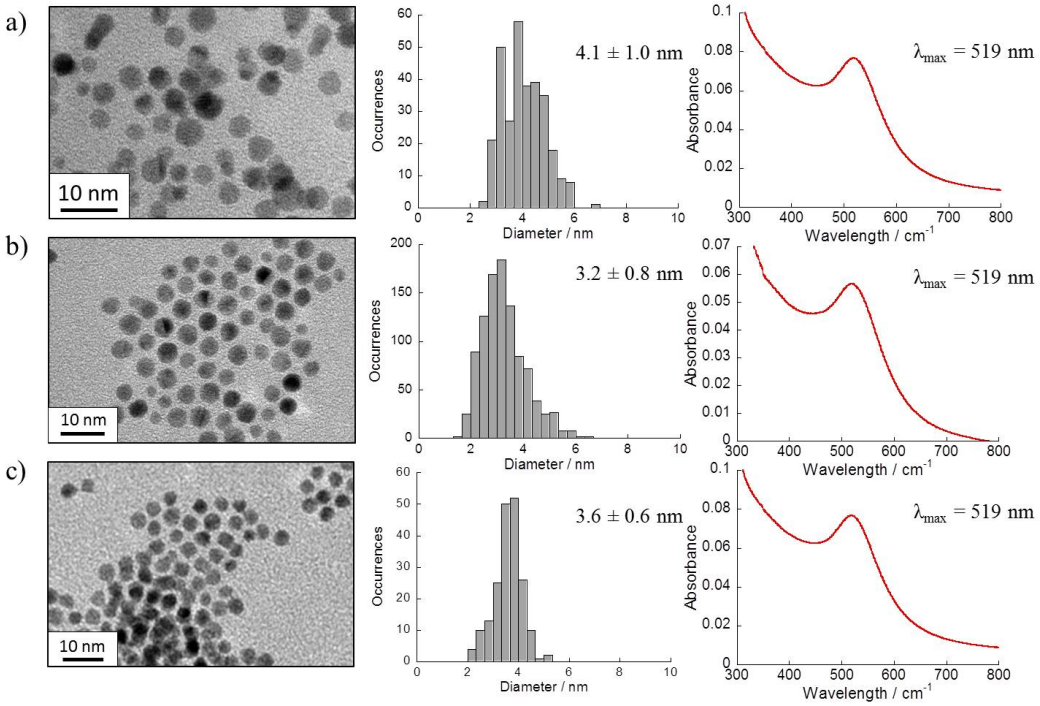


Figure S6. TEM images, corresponding size distributions and UV-visible absorption spectra of gold nanoparticles prepared from **3-AuX$_4$**:
a) $NaBH_4$ only and **3**-Br addition;
b) NaH + $NaBH_4$; c) NaH + $NaBH_4$ and **3**-Br addition

3. Infrared spectroscopy

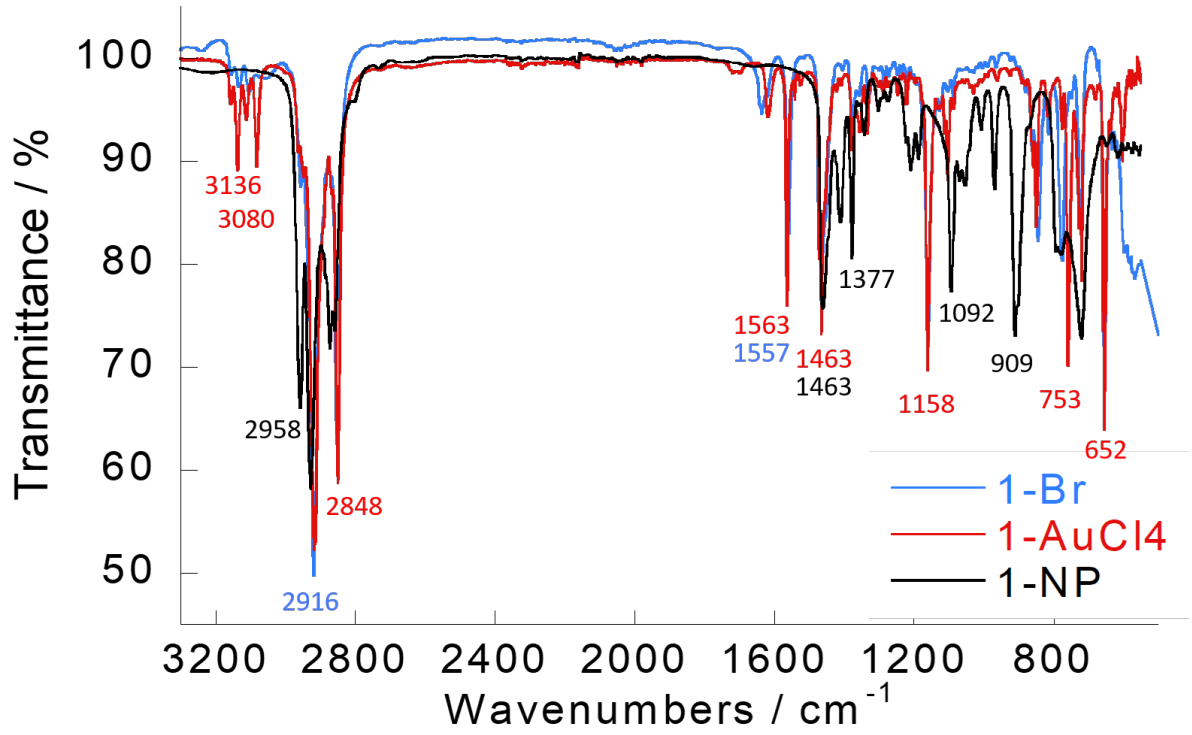


Figure S7. IR spectra of **1**-Br (blue curve), **1-AuX$_4$** (red curve) and **1-AuNPs** (black curve)

4. Mass spectrometry

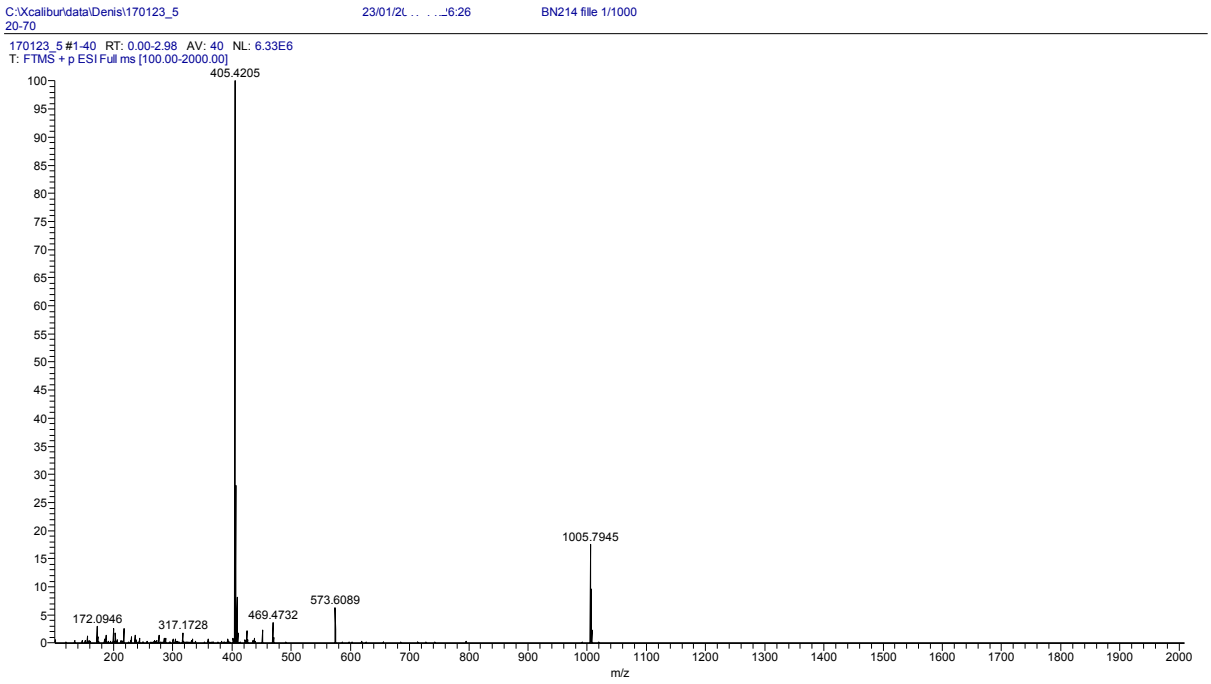


Figure S8. Mass spectrum of **1-AuNPs**: m/z = 405.42 = $\mathbf{1}^+$; m/z = 1005.79 = $[Au(\mathbf{NHC1})_2]^+$.

5. X-ray photoelectron spectroscopy

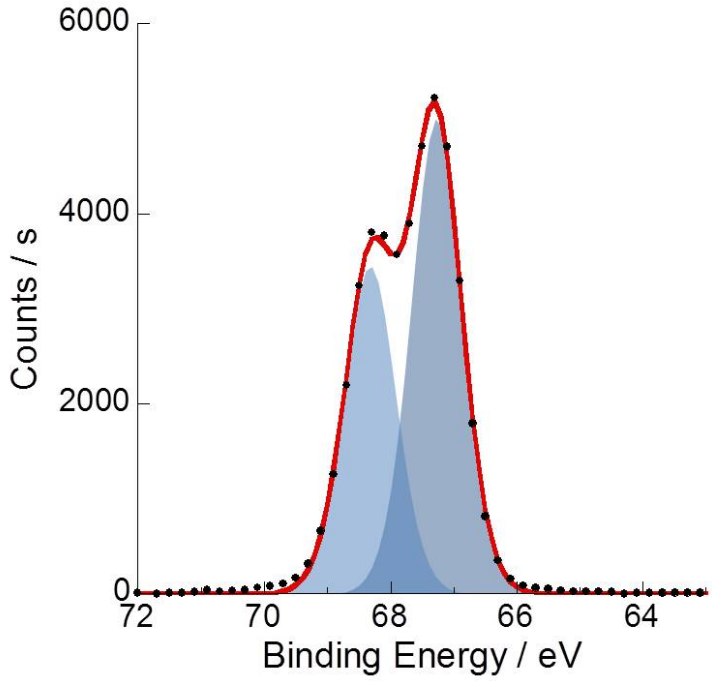


Figure S9. Br3d photopeak for **1**-Br

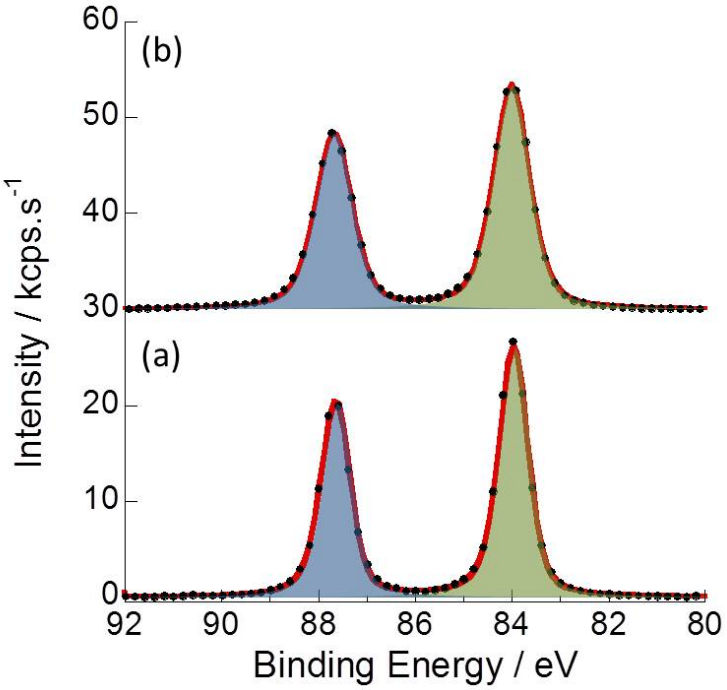


Figure S10. Au4f photoelectron peak for **1-AuNPs** (top trace) and a planar gold substrate (bottom trace)

6. NPs synthesized from AuCl

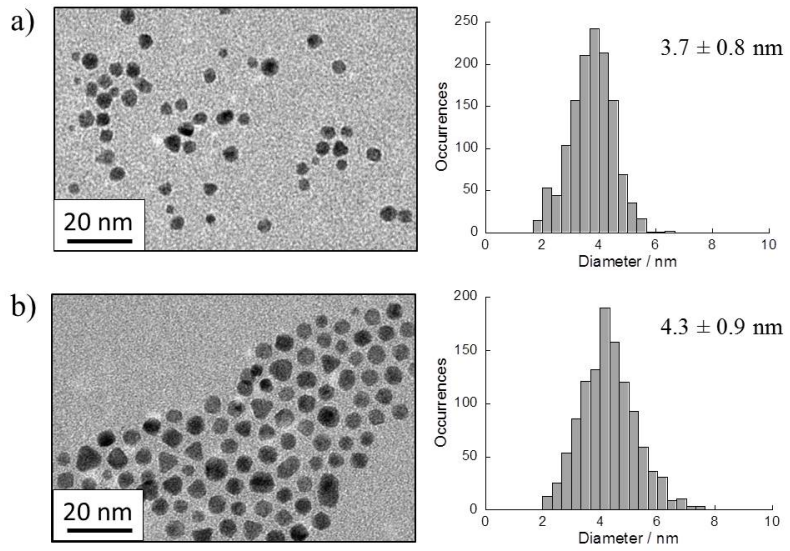
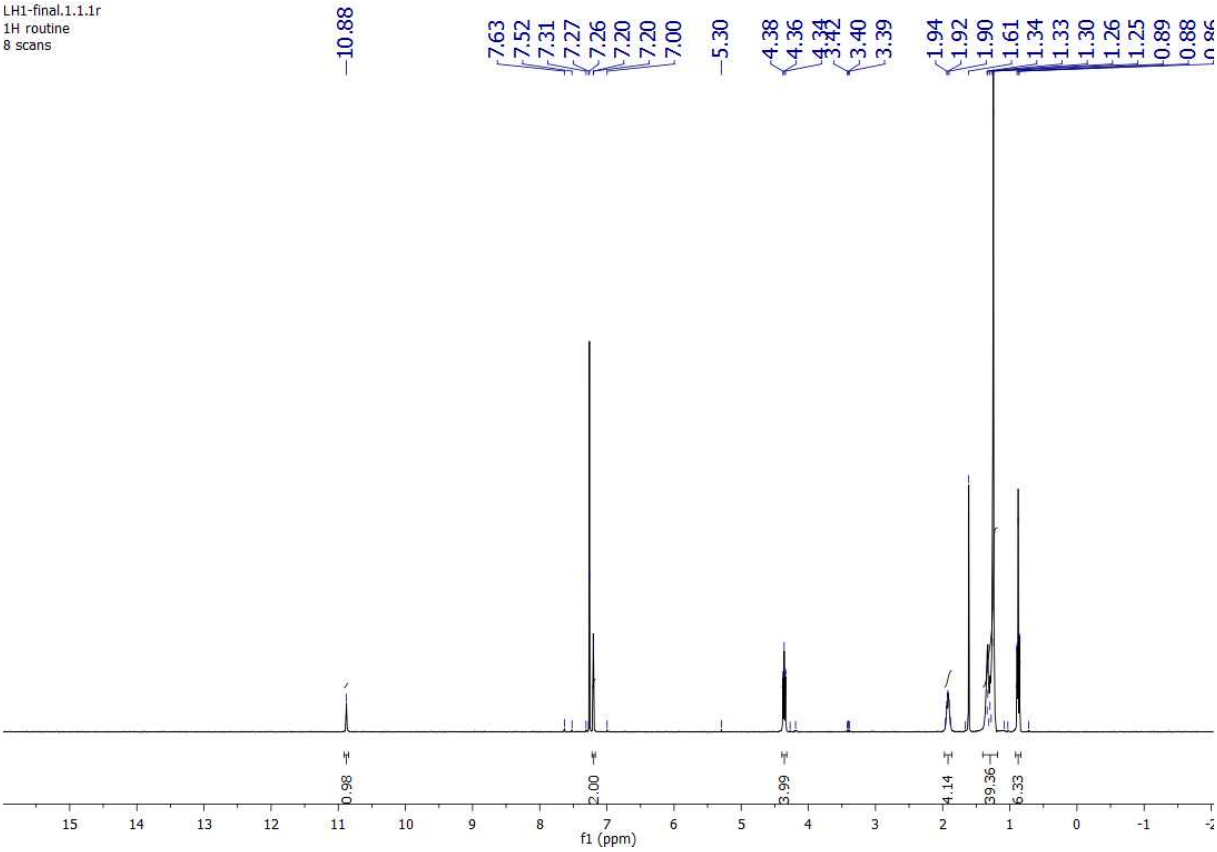


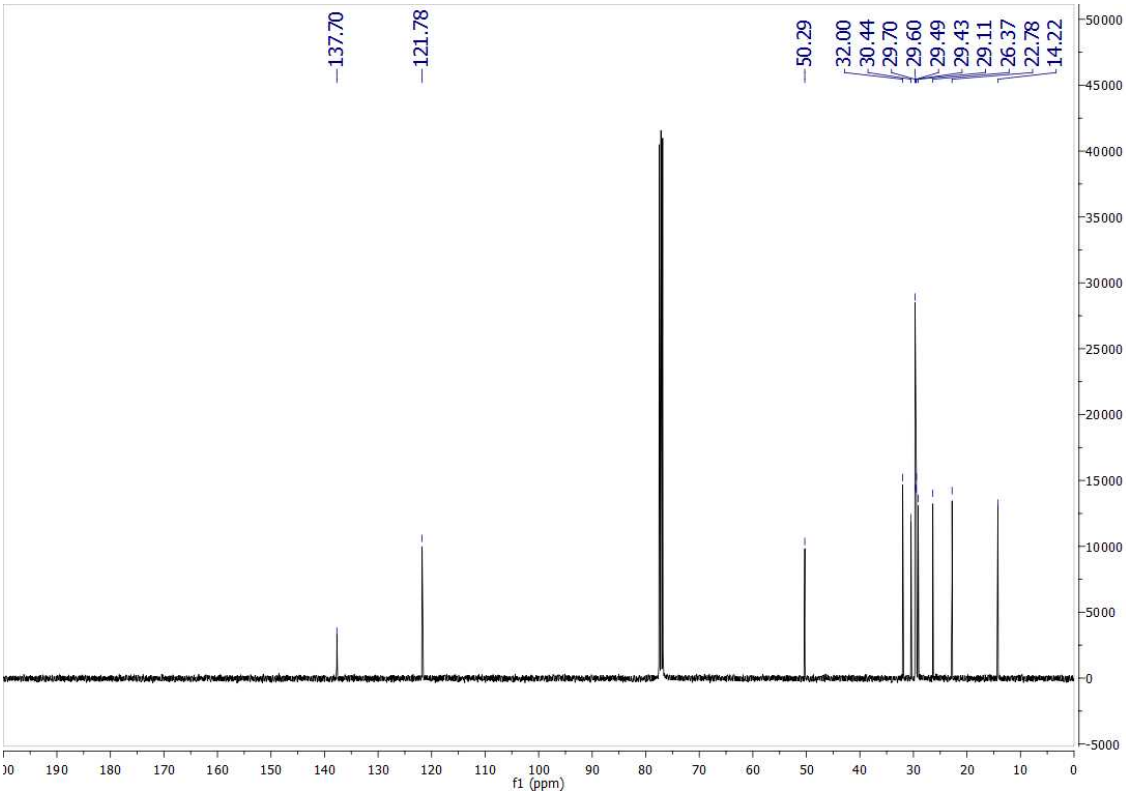
Figure S11. TEM images and corresponding size distributions of gold nanoparticles:
a) AuCl + **3**-Br, $NaBH_4$ only (λ_{max} = 532 nm); b) AuCl + **1**-Br, NaH + $NaBH_4$ (λ_{max} = 535 nm)

7. NMR spectra

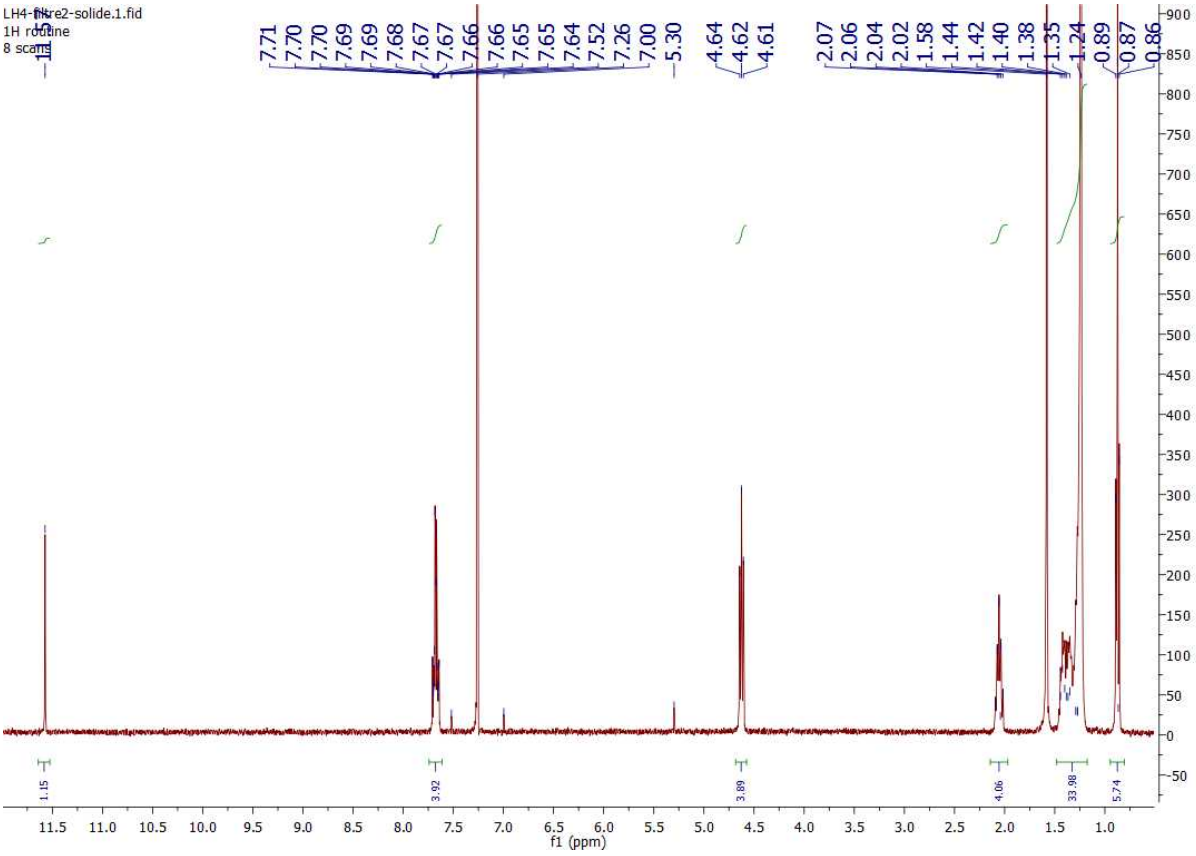
a) 1-Br ^{1}H



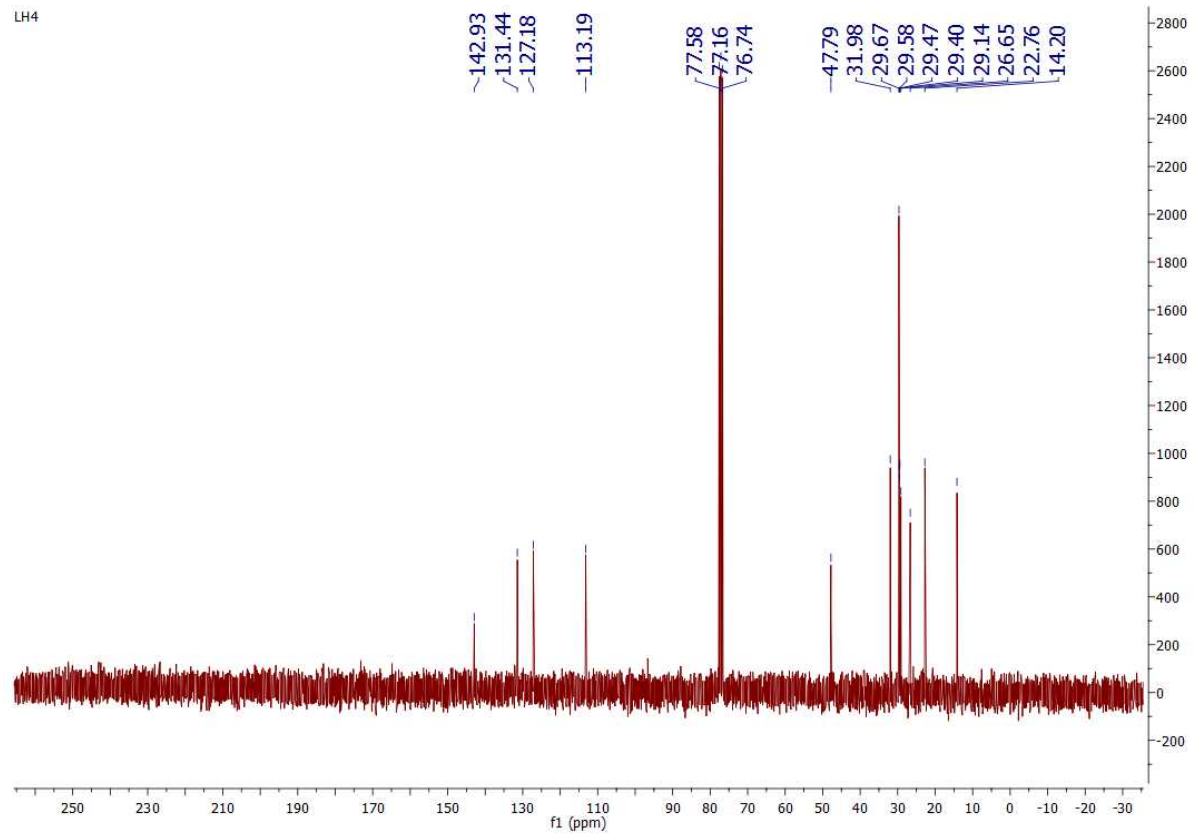
b) 1-Br ^{13}C



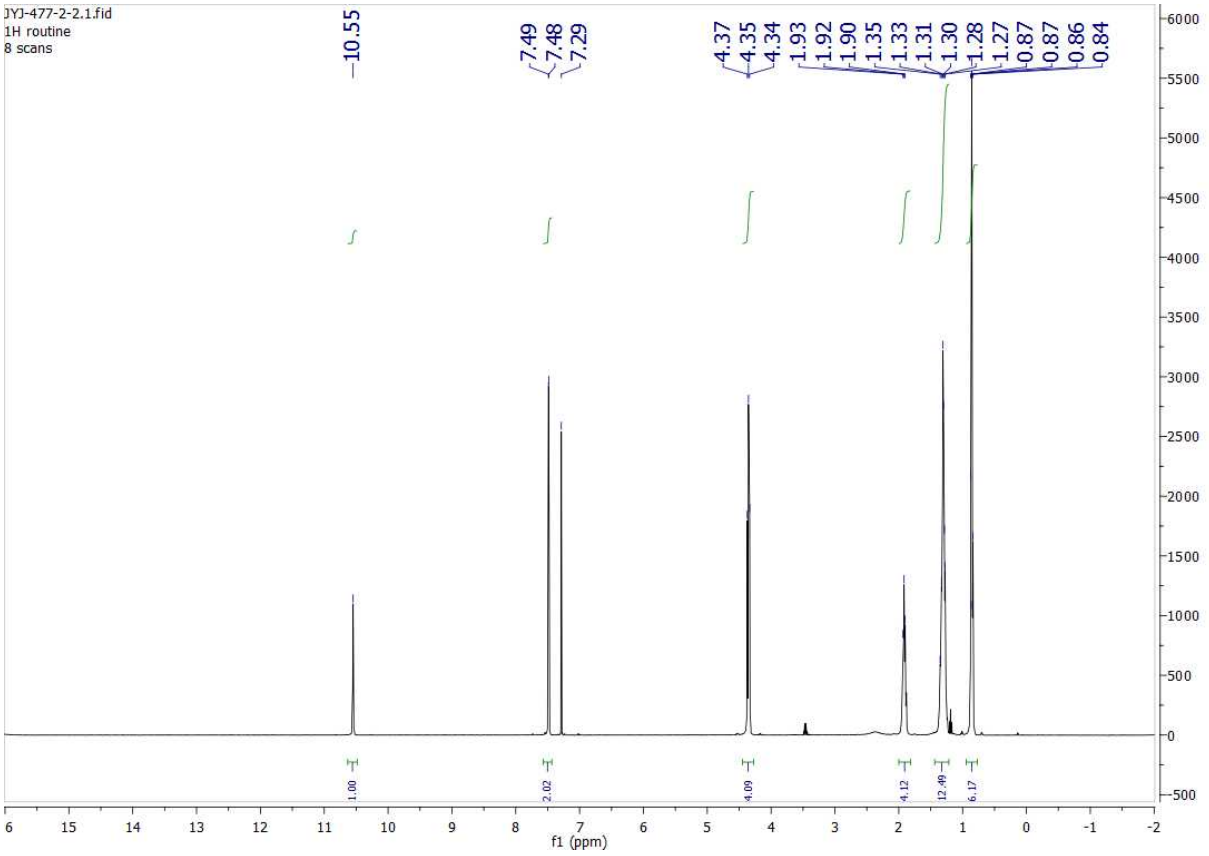
c) 2-Br ^{1}H



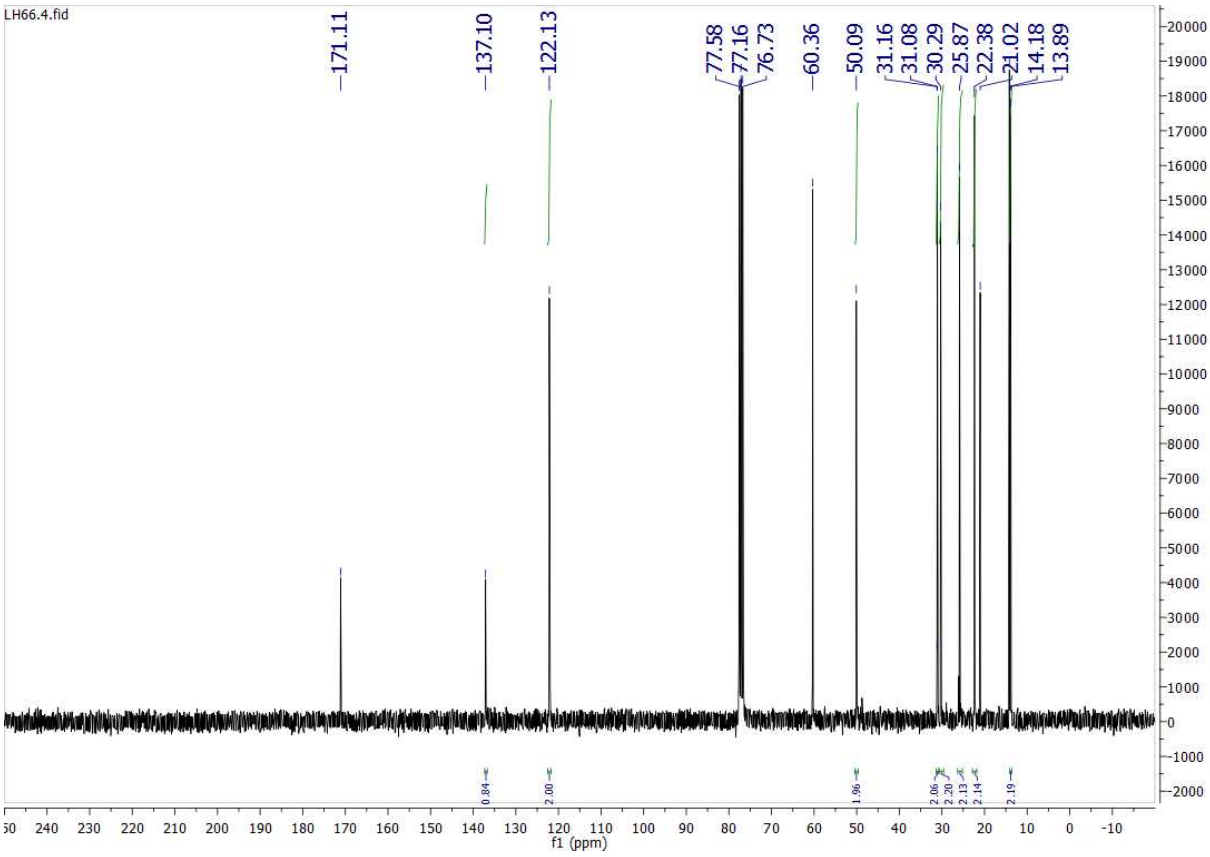
d) 2-Br ^{13}C



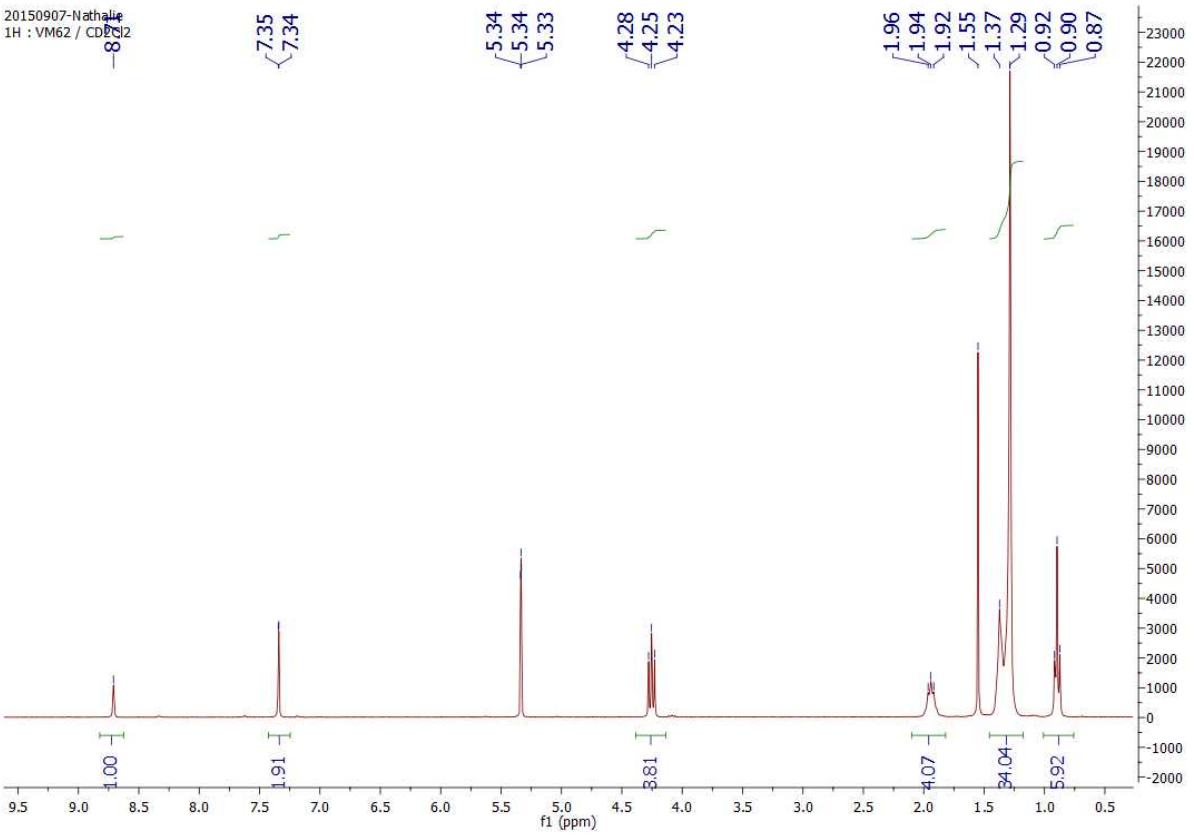
e) 3-Br ^{1}H



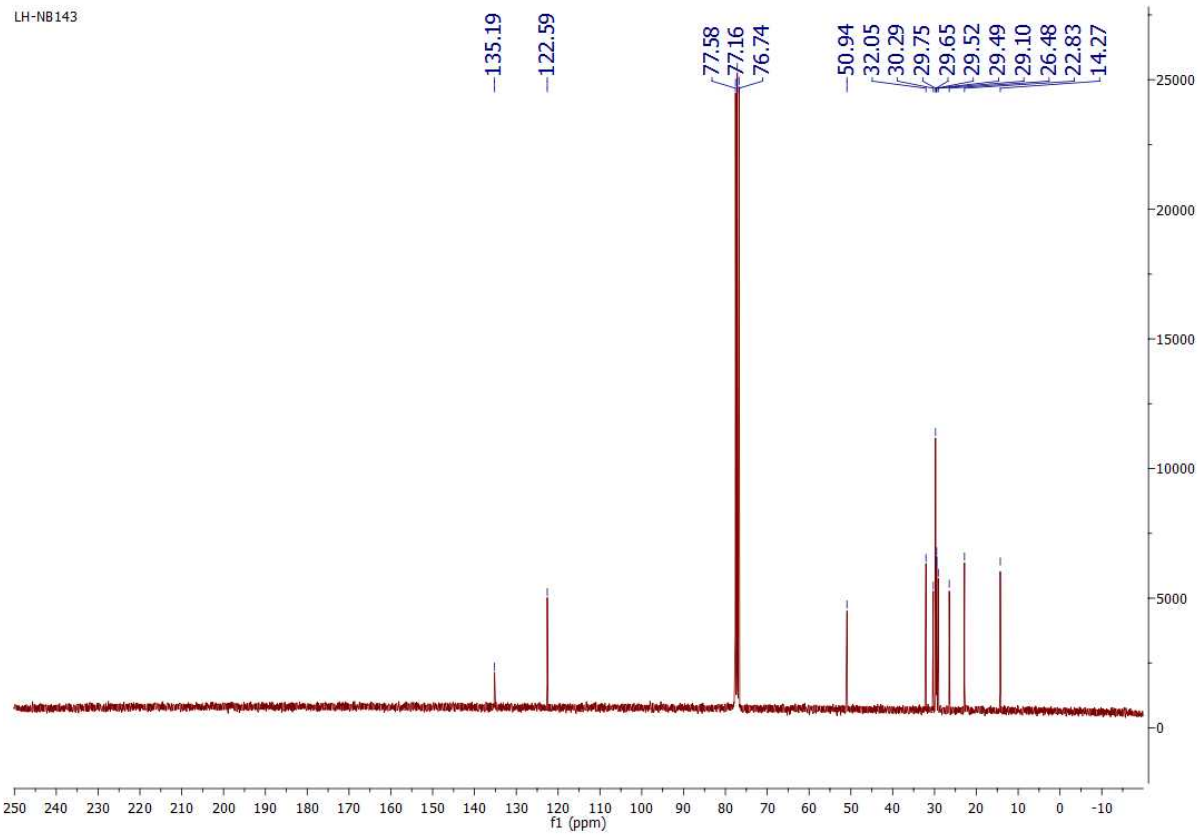
f) 3-Br ^{13}C



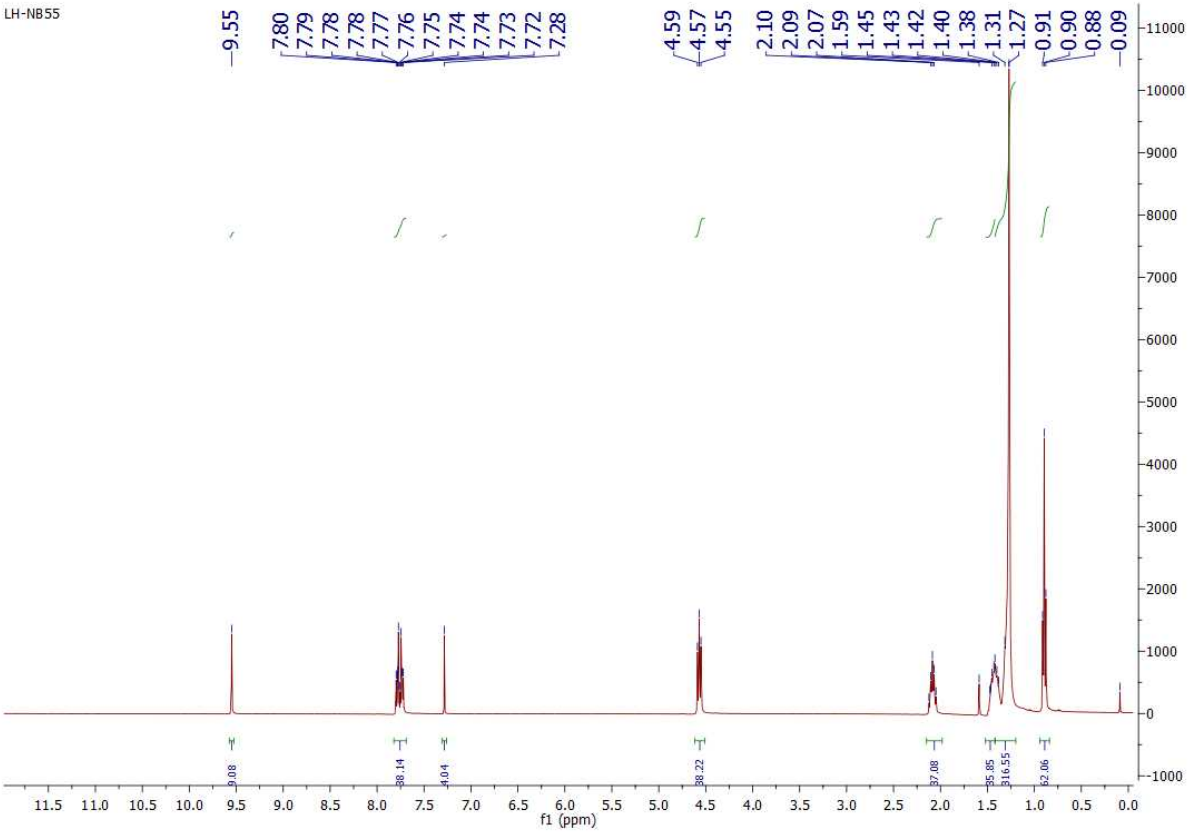
g) 1-AuX$_4$ ^{1}H



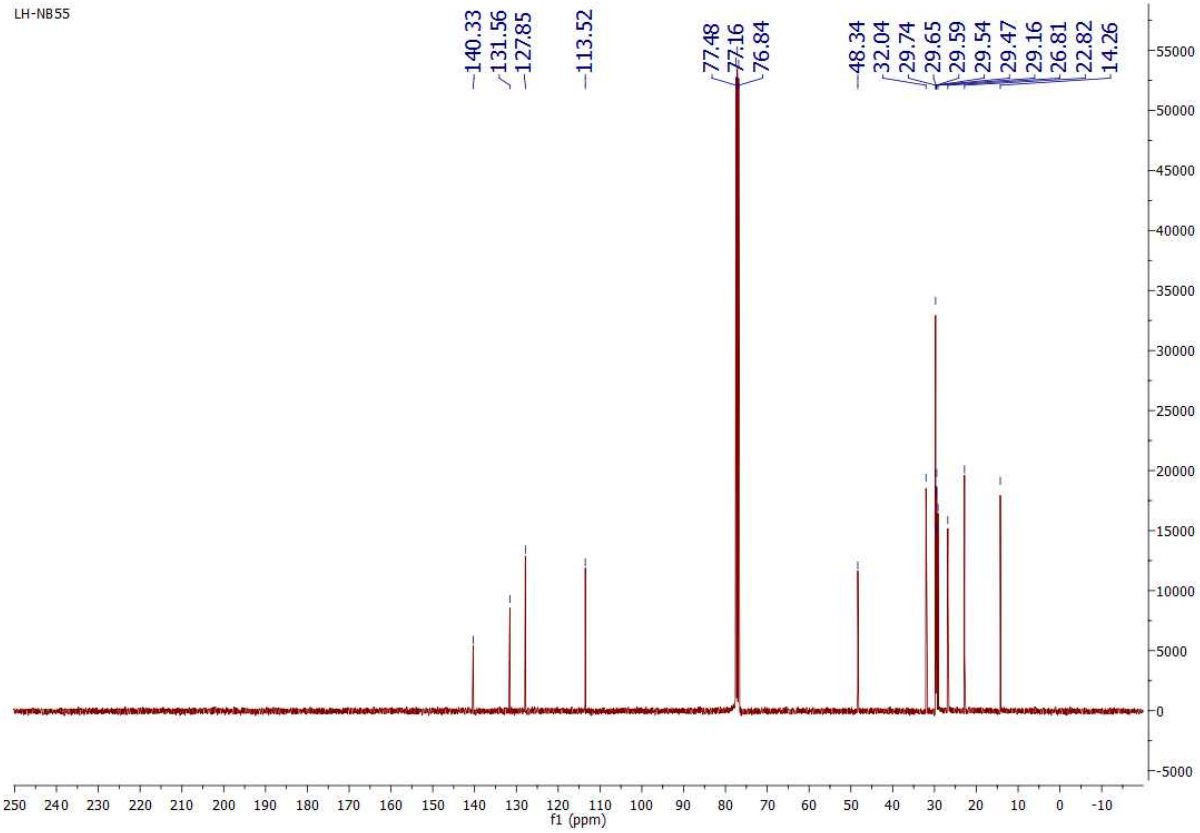
h) 1-AuX$_4$ ^{13}C



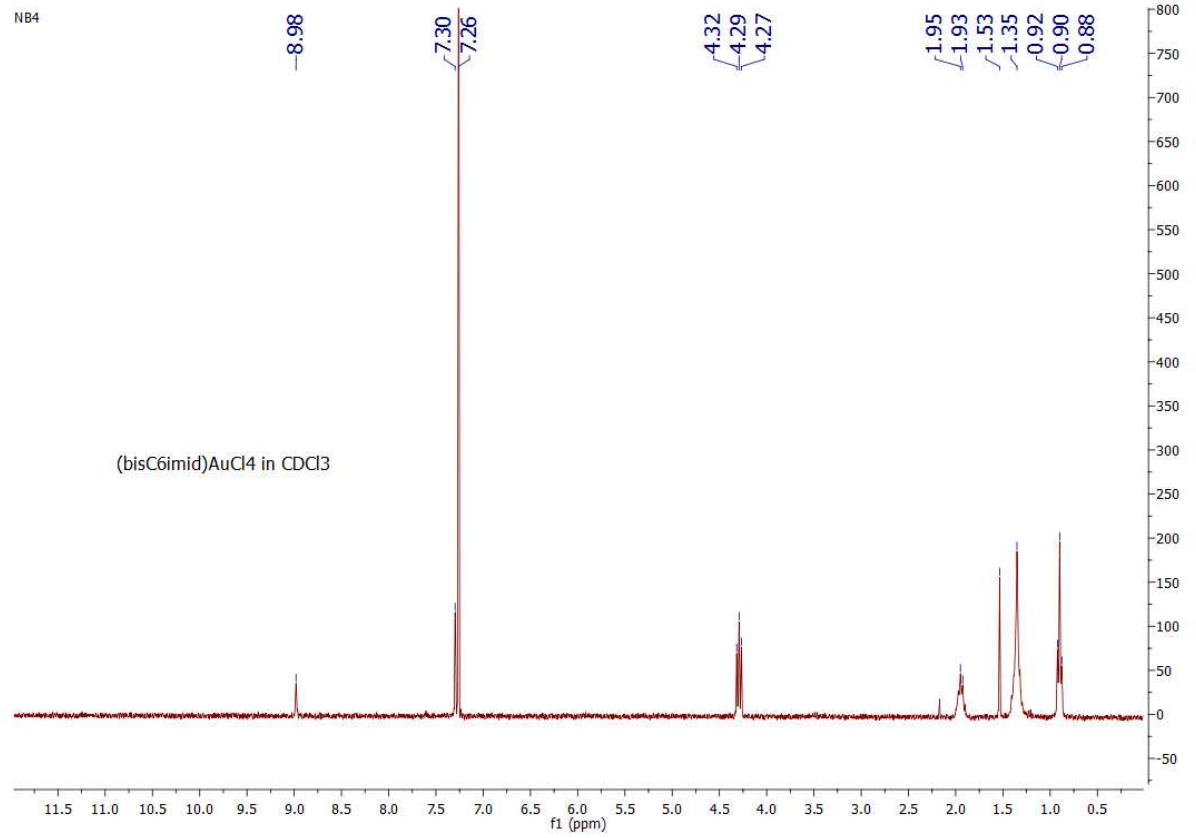
i) 2-AuX$_4$ ^{1}H



j) 2-AuX$_4$ ^{13}C



k) 3-AuX$_4$ ^{1}H



l) 3-AuX$_4$ ^{13}C