

## Electronic Supplementary Information

### Seeking a Au-C stretch on gold nanoparticles with <sup>13</sup>C-labeled N-heterocyclic carbenes

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## Synthesis and Functionalization of Nanoparticles

60 nm quasi-spherical citrate-capped gold nanoparticles (AuNPs) were synthesized according to a modified Frens method from the Sharma group.<sup>1, 2</sup> In short, 180 mL of  $2.5 \times 10^{-4}$  M tetrachloroaurate trihydrate salt solution was prepared from a 25 mM gold aurate salt (Sigma Aldrich, Lot MKCP6119,  $\geq 49.0$  Au basis). The solution was boiled, and 1.2 mL of  $3.44 \times 10^{-4}$  M trisodium citrate (Sigma Aldrich, Lot SLCG2942, ACS Reagent,  $\geq 99.0\%$ ) was rapidly added to it. This reaction was left to boil for 30 minutes, and the color changed from a faint yellow to a deep red with some yellow. After it cooled slowly, the suspension was diluted to 180 mL using ultrapure water. The AuNPs were characterized with UV-vis spectroscopy and TEM.

Functionalization of the AuNPs with NHCs were done by our established method of ligand exchange.<sup>3</sup> 5  $\mu$ L of the NHCs (dissolved in  $\text{CH}_2\text{Cl}_2$  to make 10 and 1 mM solutions) were added to 5 mL of the synthesized AuNPs and mixed for 30 minutes to form 10 and 1  $\mu$ M samples of NHCs on AuNPs. They were allowed to self-aggregate before SERS measurements were done. **1-AuCl**, **2-AuCl**, and **(2-H)(Br)** were all functionalized on AuNPs using this method.

For Raman measurements of the NHC complexes, the 10 mM NHC solution in  $\text{CH}_2\text{Cl}_2$  was drop casted on a clean glass slide and allowed to dry completely.

## Synthesis of Compounds

### General Considerations for Synthesis:

All reactions and workups were conducted under air unless otherwise stated. All glassware for air and water sensitive reactions were dried at 160 °C overnight before use. All reactions were stirred vigorously with magnetic stirrers. Synthesis of the NHC-metal complex was performed using an Mbraun Unilab Glovebox with  $\text{N}_2$  atmosphere. Solvents used under  $\text{N}_2$  atmosphere were dried on an Innovative Technologies (Newburyport, MA) Pure Solv MD-7 Solvent Purification System, degassed by three freeze-pump-thaw cycles on a Schlenk line to remove dioxygen and stored over activated 4 Å molecular sieves prior to use. Celite was dried at 240 °C under vacuum overnight and stored in a dinitrogen glovebox. For flash chromatography, the following solid phase materials were used: Silica Gel, Standard Grade, 40-63  $\mu\text{m}$ , 60 Å (Sorbtech);  $\text{C}_{18}$  Silica Gel, Enhanced Grade, Endcapped, 40-63  $\mu\text{m}$ , 60 Å (Sorbtech); Aluminum Oxide, neutral, Brockman I, 40-300  $\mu\text{m}$ , 60 Å (Acros Organics); and Spherical Silica Gel, Premium Rf, 40-75  $\mu\text{m}$ , 70 Å (Sorbtech). All other compounds were purchased from commercial vendors at the highest available purity and used without any further purification.

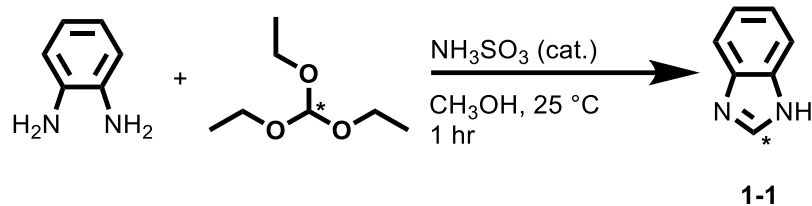
Compound **1-1** was previously reported synthesized and described by Liu and coworkers utilizing an entirely different synthetic route.<sup>4</sup> Compound **(1-H)(I)** was also previously reported by Crudden and coworkers utilizing a similar synthetic route to the one given here.<sup>5</sup> Compound **1-AuCl** was utilized as a reagent by Young and coworkers, but no synthetic details nor spectroscopic characterization were provided.<sup>6</sup>

### General Considerations for Molecular Characterization:

Solution  $^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  NMR were performed on a Bruker Avance 500 MHz narrow-bore broadband system at 298 K.  $^1\text{H}$  was referenced to the residual solvent and  $^{13}\text{C}$  was referenced to solvent. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 with a Smart iTR accessory for attenuated total reflectance (ATR) using the neat compounds.

Mass spectrometry analysis of **1-AuCl** was conducted at the Biological and Small Molecule Mass Spectrometry Core Facility located in the Department of Chemistry at the University of Tennessee and performed using a Waters Synapt G2- Si qTOF instrument with LDI ion source. The reflector was set to positive mode and data were collected from 100-1000 Daltons. Mass spectrometry analysis of **(1-H)(I)** was conducted at the Biological and Small Molecule Mass Spectrometry Core Facility located in the Department of Chemistry at the University of Tennessee and performed using a Waters Synapt G2-Si qTOF instrument with ESI ion source. The reflector was set to positive mode and data were collected from 100-1000 Daltons. Analysis of **1-1** was performed using a JEOL AccuTOF-D time-of-flight (TOF) mass spectrometer with a DART (direct analysis in real time) ionization source from JEOL USA, Inc. (Peabody, MA). Solutions for mass spectrometry were prepared in acetonitrile for all compounds.

### Synthesis of benzimidazole (imidazole-<sup>13</sup>C), 1-1.



This compound was prepared according to previously published procedure for the nonlabelled compound with additional modifications.<sup>7</sup> *o*-Phenylene diamine (0.659 g, 6.09 mmol) and sulfamic acid (0.0314 g, 0.323 mmol) were added to 12 mL of methanol and stirred, forming a clear yellow solution. While stirring, triethyl orthoformate (formyl-<sup>13</sup>C) (0.910 g, 6.10 mmol) was added, turning the solution a clear orange. The reaction was stirred for 1 hr after completion of the addition of triethyl orthoformate. The reaction was then dried on a Schlenk line and the product was extracted with 15 mL ethyl acetate and 15 mL DI water three times. The organic layer was dried and then purified on a silica column with 0-5% isopropanol gradient in ethyl acetate, then again with a second column of C<sub>18</sub> silica with pure acetonitrile as the mobile phase. The solvent was then removed under reduced pressure yielding a pale, off-white solid (0.295 g, 40.6%).

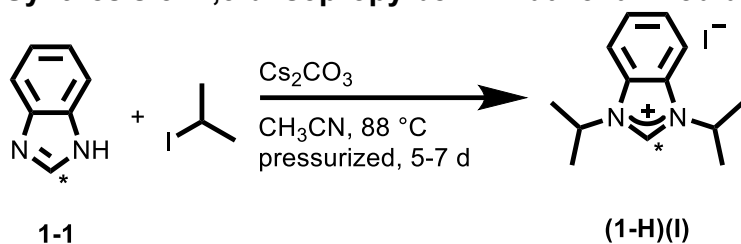
**<sup>1</sup>H NMR:** (500 MHz, CDCl<sub>3</sub>) δ 8.10 (d, *J*<sup>13</sup><sub>CH</sub> = 206.4 Hz, 1H), 7.68 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.31 (dd, *J* = 6.1, 3.2 Hz, 2H), 5.17 (br s, 1H).

**<sup>13</sup>C NMR:** (126 MHz, CDCl<sub>3</sub>) δ 141.73 (trace <sup>13</sup>C-labelled impurity, 3% by integration), 140.47\*, 137.61, 123.20, 115.70.

\* demarcates <sup>13</sup>C labeled peak

**HR-MS:** [M+H]<sup>+</sup> 120.06373 (found), [C<sub>6</sub><sup>13</sup>CH<sub>6</sub>N<sub>2</sub>+H]<sup>+</sup> 120.06352 (calculated)

### Synthesis of 1,3-diisopropylbenzimidazolium iodide (imidazolium-<sup>13</sup>C), (1-H)(I)



This compound was prepared according to previously published procedure for the non-<sup>13</sup>C labeled compound with deuterated isopropyls with modifications.<sup>8</sup> **1-1** 0.295 g (2.48 mmol), 2-iodopropane 2.64 g (15.5 mmol), and cesium carbonate 1.01 g (3.10 mmol) were added to a pressure vial with 20 mL of acetonitrile. The pressure vial was sealed and stirred, and then heated to 100 °C for one week. Pressure was vented from the reaction and it was cooled to room temperature. The solvent was then removed under reduced pressure. The product was extracted with 10 mL dichloromethane and filtered over Celite. Then the solvent was removed under vacuum and product was dissolved in minimal (< 5 mL) acetonitrile. The solution was then triturated with 100 mL diethyl ether and filtered over a 30 mL fine frit, yielding a pale cream solid (0.694 g, 84.6%).

**<sup>1</sup>H NMR:** (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 10.80 (d,  $J^{13\text{C}\text{H}} = 216.6$  Hz, 1H), 7.80 (dd,  $J = 6.3, 3.2$  Hz, 2H), 7.67 (dd,  $J = 6.4, 3.2$  Hz, 2H), 5.16 (dq,  $J = 13.6, 6.9$  Hz, 2H), 1.87 (d,  $J = 6.8$  Hz, 12H).

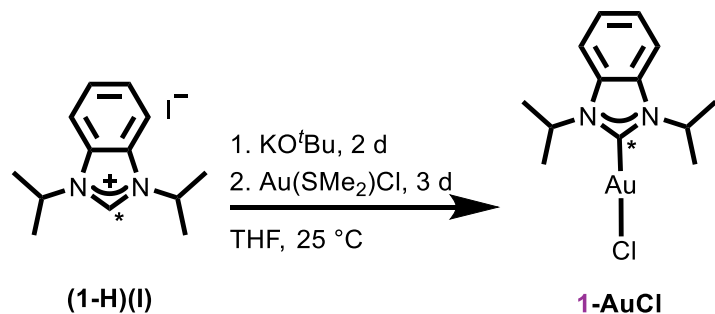
**<sup>13</sup>C NMR:** (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 139.93\*, 131.39, 127.39, 114.23, 52.82, 22.46.

\* demarcates <sup>13</sup>C labeled peak

**IR:** 3159, 3019, 2985, 1607, 1534, 1481, 1443, 1418, 1380, 1368, 1347, 1329, 1311, 1244, 1203, 1187, 1174, 1140, 1127, 1112, 1079, 1018, 982, 953, 815, 780, 763, 623, 605, 574 cm<sup>-1</sup>.

**HR-MS:** [M]<sup>+</sup> 204.1576 (found), [C<sub>12</sub><sup>13</sup>CH<sub>19</sub>N<sub>2</sub>]<sup>+</sup> 204.1576 (calculated)

**Synthesis of (1,3-diisopropylbenzimidazolium (imidazolium-<sup>13</sup>C))gold(I) chloride, 1-AuCl**



Under inert  $\text{N}_2$  atmosphere in a glovebox, 1,3-diisopropylbenzimidazolium iodide (benzimidazolium-<sup>13</sup>C) (0.500 g, 1.51 mmol) was added to a vial with 8 mL tetrahydrofuran and a stir bar and stirred at room temperature. Potassium *tert*-butoxide (0.166 g, 1.48 mmol) was added to a second vial with 5 mL tetrahydrofuran. The potassium *tert*-butoxide and tetrahydrofuran mixture was added slowly to the stirring benzimidazolium solution. The reaction was stirred for 48 hours at room temperature, then filtered over Celite, which removed potassium salts from the very pale-yellow solution of free carbene. The free carbene solution was then added dropwise to a stirring solution of dimethylsulfidegold(I) chloride (0.339 g, 1.58 mmol) in 5 mL tetrahydrofuran and stirred for 3 days at room temperature. The vial was then removed from the glovebox and solvent was removed under vacuum. The product was extracted with 15 mL dichloromethane and filtered over Celite, then concentrated to approximately 2 mL and triturated with 50 mL of hexanes. The solid was collected over a 30 mL fine frit and purified via flash chromatography on spherical silica gel packed with pure dichloromethane then run through with 2:1 ratio of dichloromethane to isopropanol. The solvent was then removed, yielding a pale, off-white solid (0.244 g, 36.4%).

**<sup>1</sup>H NMR:** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (dd,  $J = 6.2, 3.2$  Hz, 2H), 7.37 (dd,  $J = 6.3, 3.1$  Hz, 2H), 5.51 (m, 2H), 1.74 (d,  $J = 7.0$  Hz, 12H).

**<sup>13</sup>C NMR:** (126 MHz,  $\text{CDCl}_3$ )  $\delta$  187.01 (trace amount  $[(1)_2\text{Au}]^+$ , ~1-2% by integration), 176.33\*, 132.57, 123.99, 113.26, 54.53, 21.83.

\* demarcates <sup>13</sup>C labeled peak

**IR:** 2974, 2930, 1478, 1427, 1410, 1386, 1372, 1304, 1296, 1227, 1173, 1142, 1093, 1025, 937, 894, 855, 812, 747, 734, 649, 616, 548  $\text{cm}^{-1}$ .

**HR-MS:** 1-AuCl  $[\text{M-Cl}]^+$  400.1170 (found),  $[\text{C}_{12}^{13}\text{CH}_{19}\text{N}_2\text{Au}]^+$  400.1164 (calculated); (12-Au)<sup>+</sup>  $[\text{M}]^+$  603.2669 (found),  $[\text{C}_{24}^{13}\text{C}_2\text{H}_{36}\text{N}_4\text{Au}]^+$  603.2267 (calculated)

## Instrumentation for Spectroscopic Measurements

We measured surface-enhanced Raman spectra using a home-built Raman setup consisting of a 633 nm HeNe laser (Thor Labs) directed on the samples using an inverted microscope (Nikon Eclipse Ti-U) and focused with an objective (Nikon, 20x, NA=0.5). The power at the objective was 1.30 mW, and acquisition times were 300 s for the **(2-H)(Br)** on AuNP, and 600 s for **1-AuNP** and **2-AuNP**. Backscattered light was collected using the same objective, filtered through a Rayleigh rejection filter (Semrock), dispersed with a spectrometer (Princeton Instruments Acton SP2300, 1200 g/mm) and detected with a back-illuminated, deep-depletion CCD (Princeton Instruments, PIXIS, Spec-10). Spectra was recorded using Winspec32 software (Princeton Instruments), and background subtracted, normalized, plotted and analyzed on MATLAB R2023a.

For the Raman of the NHC complexes, 3mW power (at the objective) and 300s acquisition times were used.

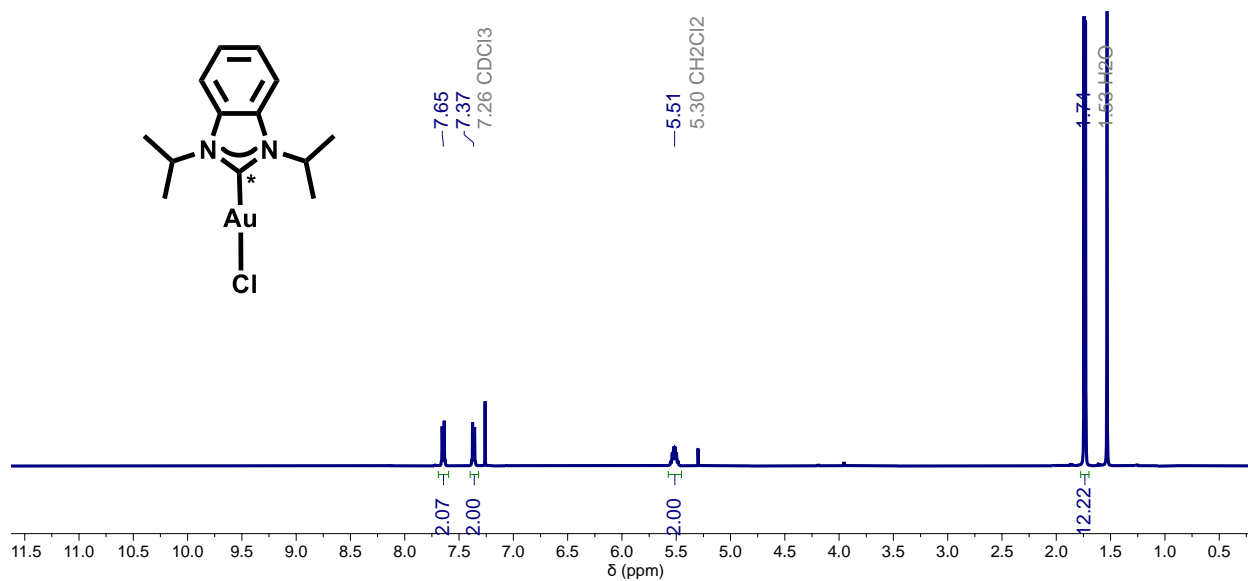
To get the entire wavenumber range (from 60 to 1860  $\text{cm}^{-1}$ ) with the 1200 g/mm grating, the spectrograph was positioned at center wavelengths 665 nm and 690 nm, and the raw spectra background subtracted, then collaged together to form the final spectra. Multiple measurements were taken on several aggregates with multiple calibrations to ensure reproducibility.

## Theory Calculations

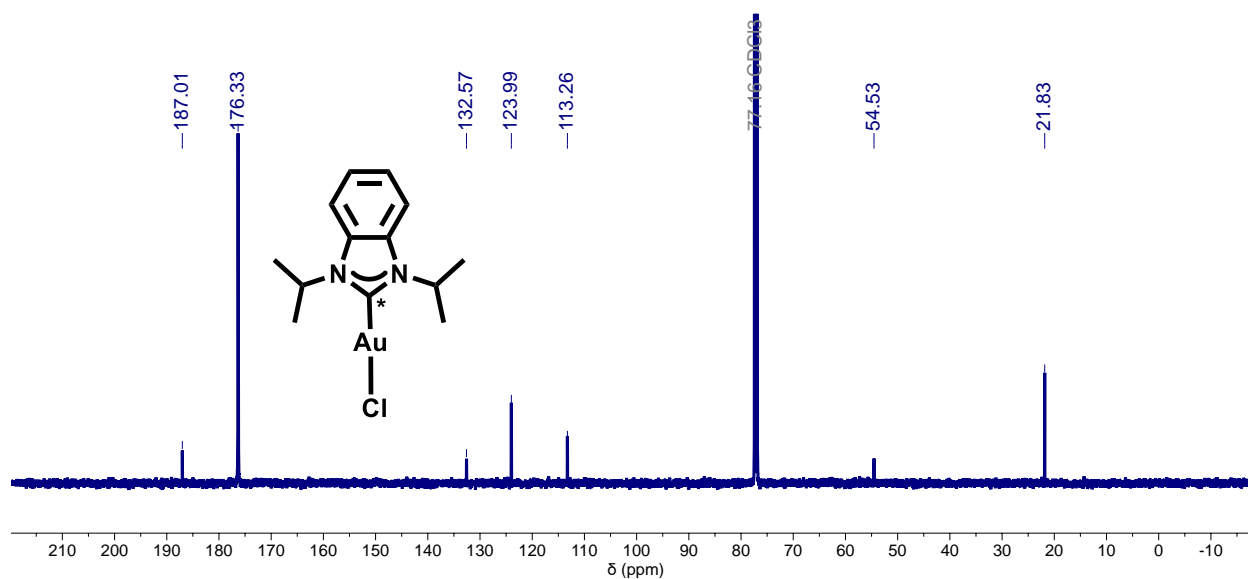
For each model system, carbene molecule was bound to a gold cluster. All calculations were performed using a local version of Amsterdam density functional (ADF)<sup>9, 10</sup> engine from Amsterdam Modeling Suite (AMS).<sup>11</sup> The Becke-Perdew (BP86) XC functional<sup>12, 13</sup> with dispersion correction Grimme3 BJDAMP<sup>14</sup> was used. The triple- $\zeta$  polarized Slater type (TZP) basis set with small frozen cores from the ADF basis set library was used.<sup>15</sup> The zeroth-order regular approximation (ZORA) was used for scalar relativistic effects.<sup>16, 17</sup> All geometry optimizations were performed with constraint that only adatom and carbene molecules were relaxed. Based on optimized geometry, mobile block Hessian frequency calculations were performed.<sup>18, 19</sup>

The vibrational frequencies and normal modes were calculated within the harmonic approximation. Polarizability calculations were performed using the AOResponse module with the Adiabatic Local Density Approximation (ALDA) at static limit.<sup>20</sup> The polarizability derivatives were calculated by numerical differentiation with respect to the normal mode displacements. For all systems, z-axis was set to be perpendicular to metal surface and only the zz components of polarizabilities were considered. The structures and normal modes of the models systems were plotted with PyMOL.<sup>21</sup>

## Spectral Characterization of Complex 1-AuCl

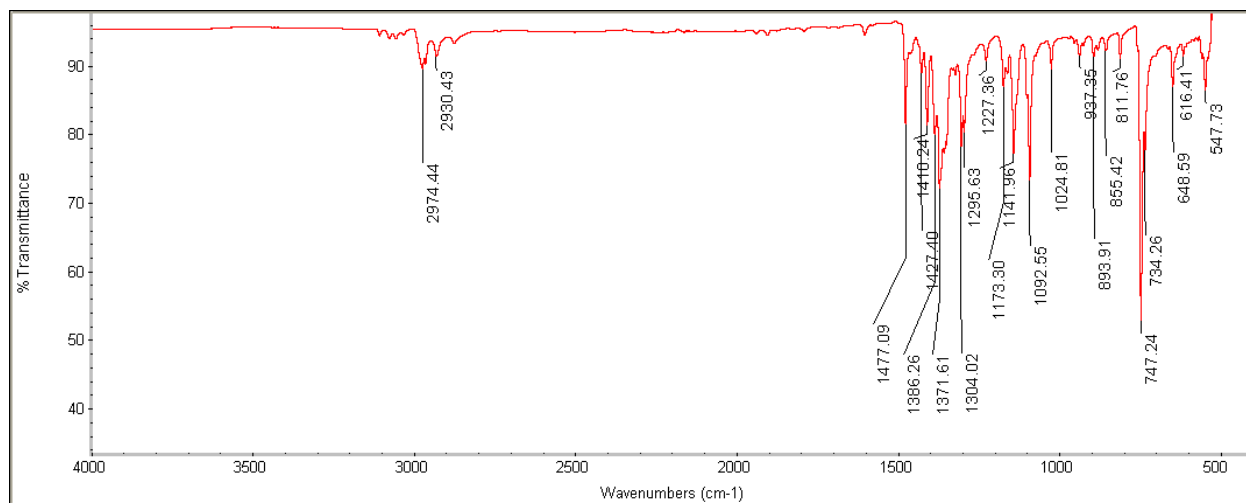


**Figure S1.** <sup>1</sup>H NMR in CDCl<sub>3</sub> of (1,3-diisopropylbenzimidazolium (imidazolium-<sup>13</sup>C))gold(I) chloride, **1-AuCl**.

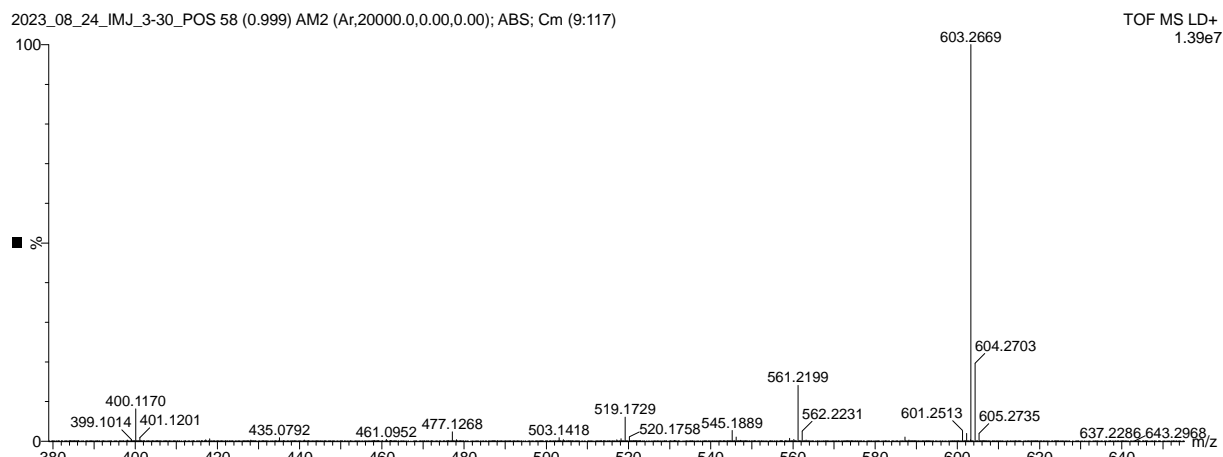


**Figure S2.** <sup>13</sup>C NMR in CDCl<sub>3</sub> of (1,3-diisopropylbenzimidazolium (imidazolium-<sup>13</sup>C))gold(I) chloride, **1-AuCl**. Resonance at 187.01 ppm represents labeled carbene signal from [(**1**)<sub>2</sub>Au<sup>+</sup>] ~1-2% by integration.



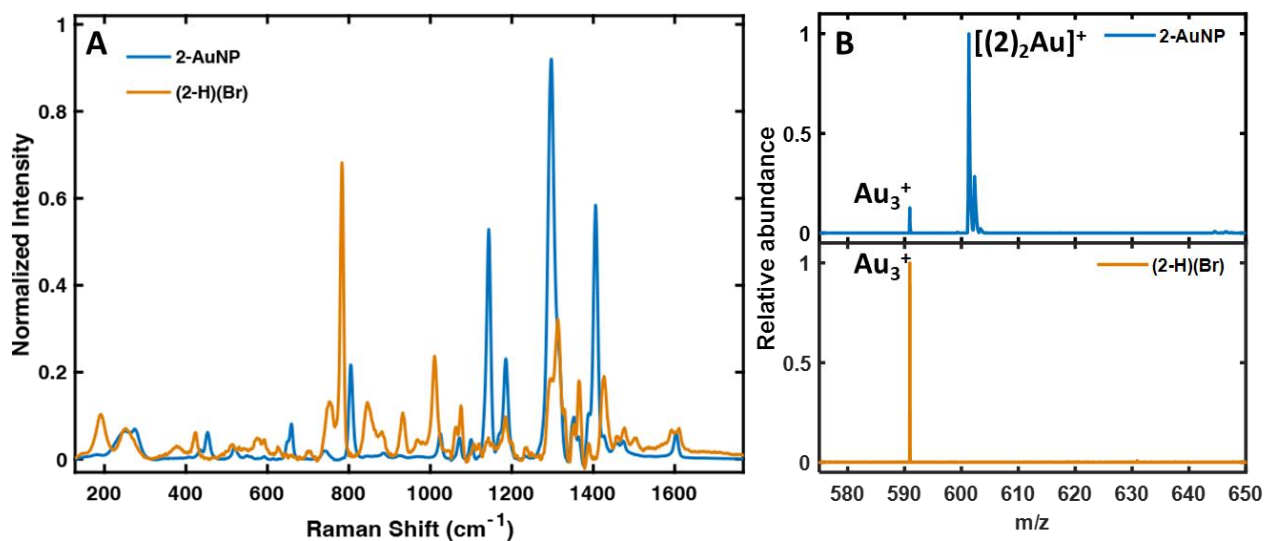


**Figure S3.** IR of (1,3-diisopropylbenzimidazolium (imidazolium-<sup>13</sup>C))gold(I) chloride, **1-AuCl**.



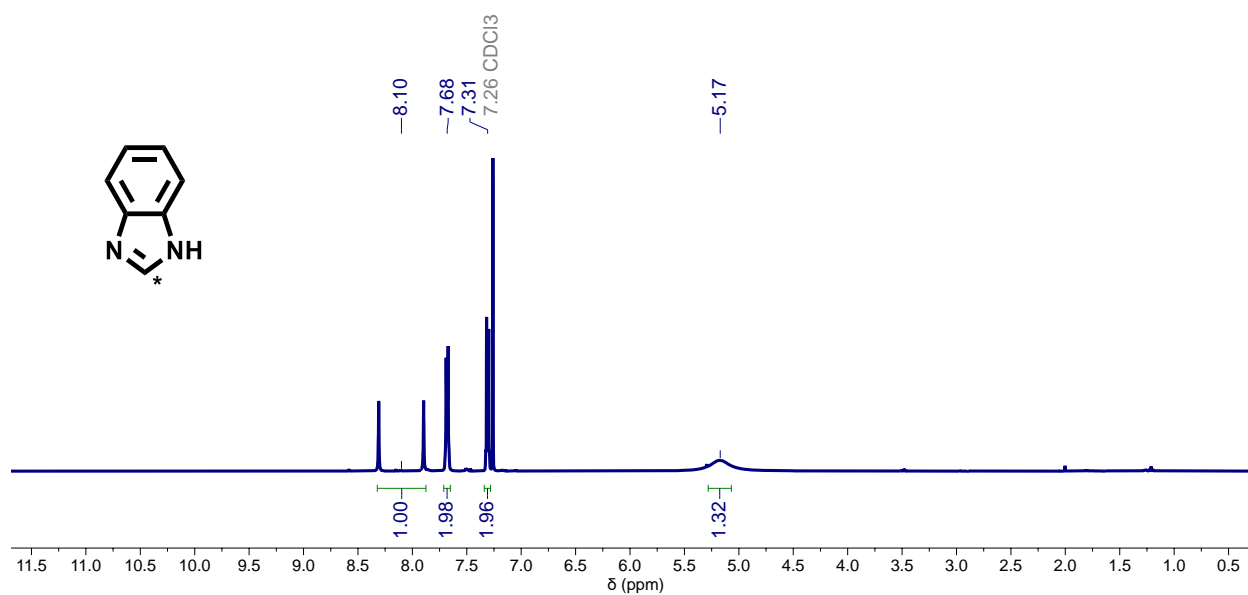
**Figure S4.** LDI-MS of (1,3-diisopropylbenzimidazolium (imidazolium-<sup>13</sup>C))gold(I) chloride, **1-AuCl**.

## Characterization of Physisorbed vs Chemisorbed NHC

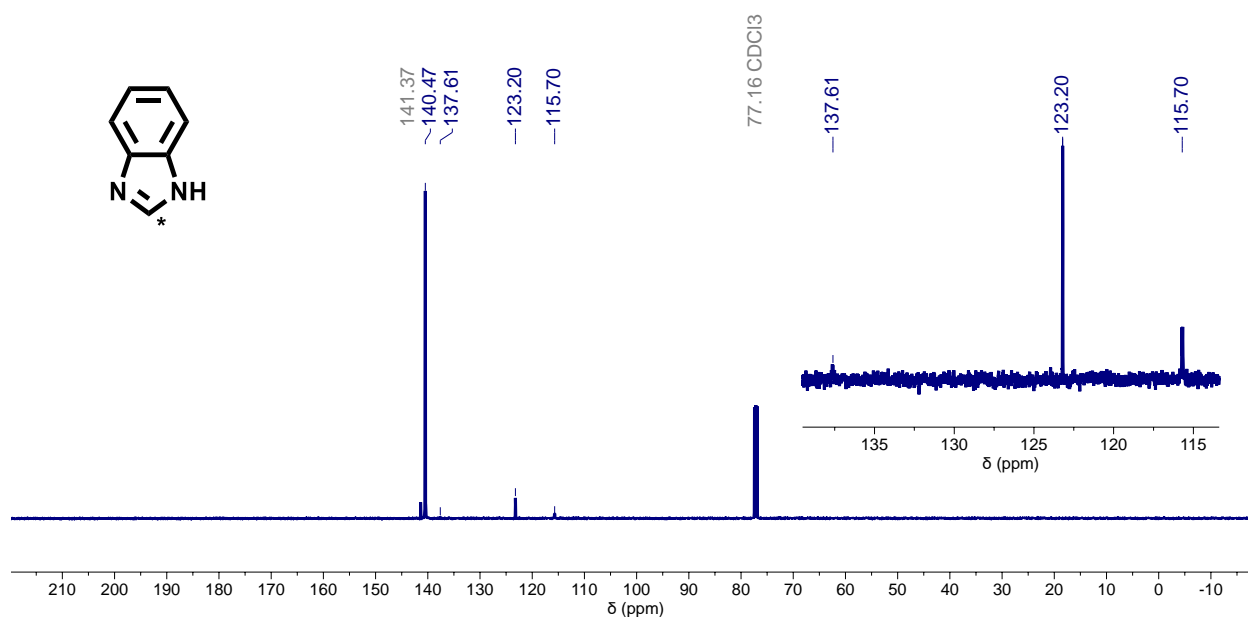


**Figure S5.** (A) SERS spectra of the natural abundance NHC-functionalized gold nanoparticle, **2-AuNP**, showing NHC chemisorption to the gold surface (blue), and the diisopropyl benzimidazolium bromide salt **(2-H)(Br)**, which physisorbs to the gold surface (orange). (B) LDI-MS spectra of **2-AuNP** (blue) and **(2-H)(Br)** on AuNP (orange), with **2-AuNP** giving predominantly [(2)<sub>2</sub>Au]<sup>+</sup> at 601 m/z, which indicates that the NHC is chemisorbed to the surface with an Au-C bond.<sup>22</sup> This peak is missing in the physisorbed case.

## Spectra of Previously Characterized Compounds

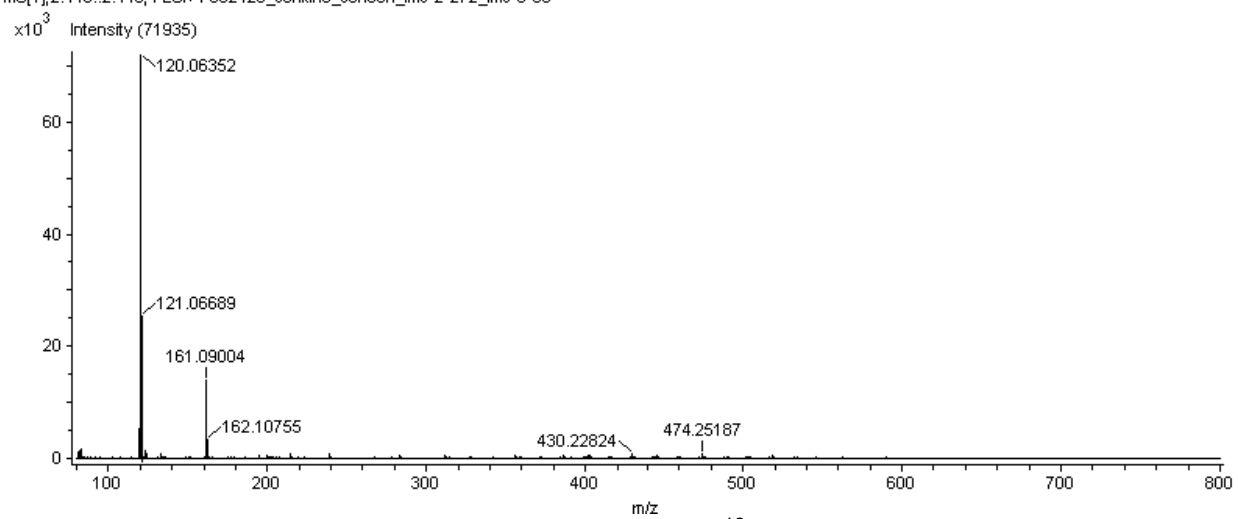


**Figure S6.**  $^1\text{H}$  NMR in  $\text{CDCl}_3$  of benzimidazole (imidazole- $^{13}\text{C}$ ), **1-1**.

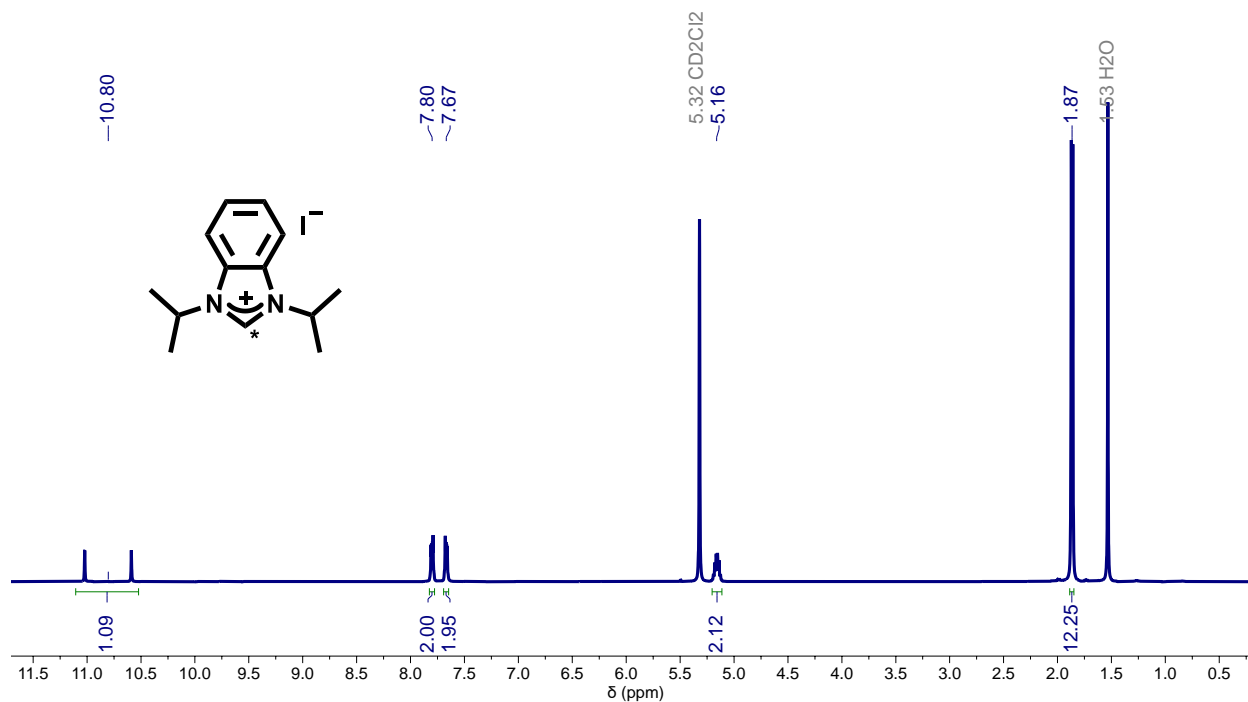


**Figure S7**  $^{13}\text{C}$  NMR in  $\text{CDCl}_3$  of benzimidazole (imidazole- $^{13}\text{C}$ ), **1-1**. Resonance at 141.73 ppm is trace  $^{13}\text{C}$ -labelled impurity, 3% by integration.

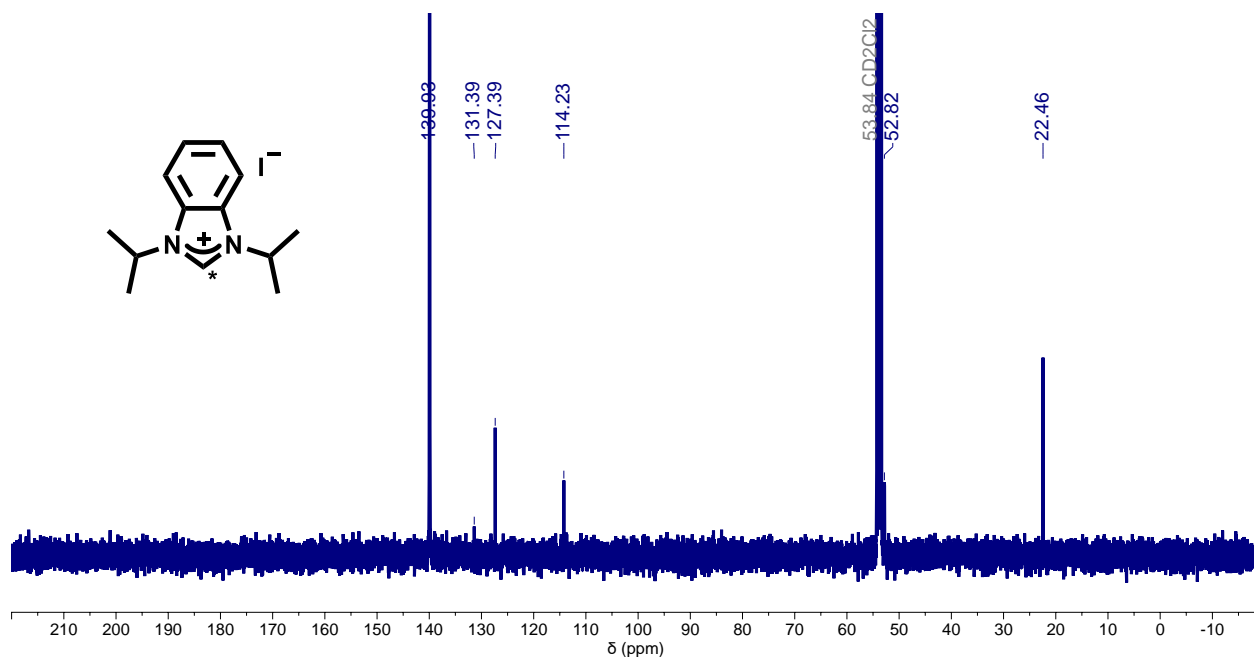
MS[1];2.443..2.449; /ESI+ /082423\_Jenkins\_Jensen\_IMJ-2-272\_IMJ-3-30



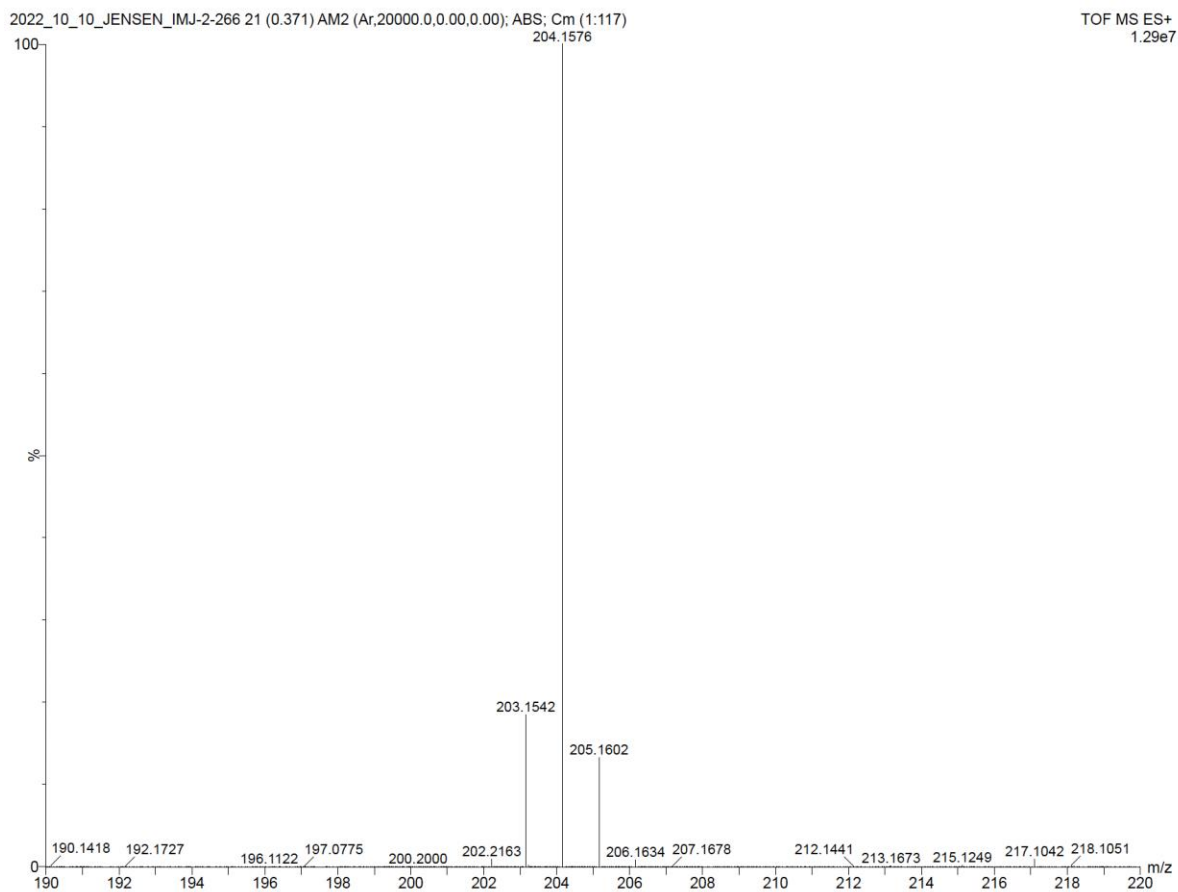
**Figure S8.** DART-MS of benzimidazole (imidazole- $^{13}\text{C}$ ), **1-1**.



**Figure S9.**  $^1\text{H}$  NMR in  $\text{CD}_2\text{Cl}_2$  of 1,3-diisopropylbenzimidazolium iodide (imidazolium- $^{13}\text{C}$ ), **(1-H)(I)**.



**Figure S10.**  $^{13}\text{C}$  NMR in  $\text{CD}_2\text{Cl}_2$  of 1,3-diisopropylbenzimidazolium iodide (imidazolium- $^{13}\text{C}$ ), (1-H)(I).



**Figure S11.** ESI-MS of 1,3-diisopropylbenzimidazolium iodide (imidazolium- $^{13}\text{C}$ ), (1-H)(I).

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