# Synthesis and Photophysical Properties of Linear Gold(I) Complexes Based on a CCC Carbene

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## SUPPORTING INOFORMATION

**Table S1.** UV-vis data for complexes **1** and **2** in toluene, THF and 1,2-difluorobenzene (DFB) solutions.

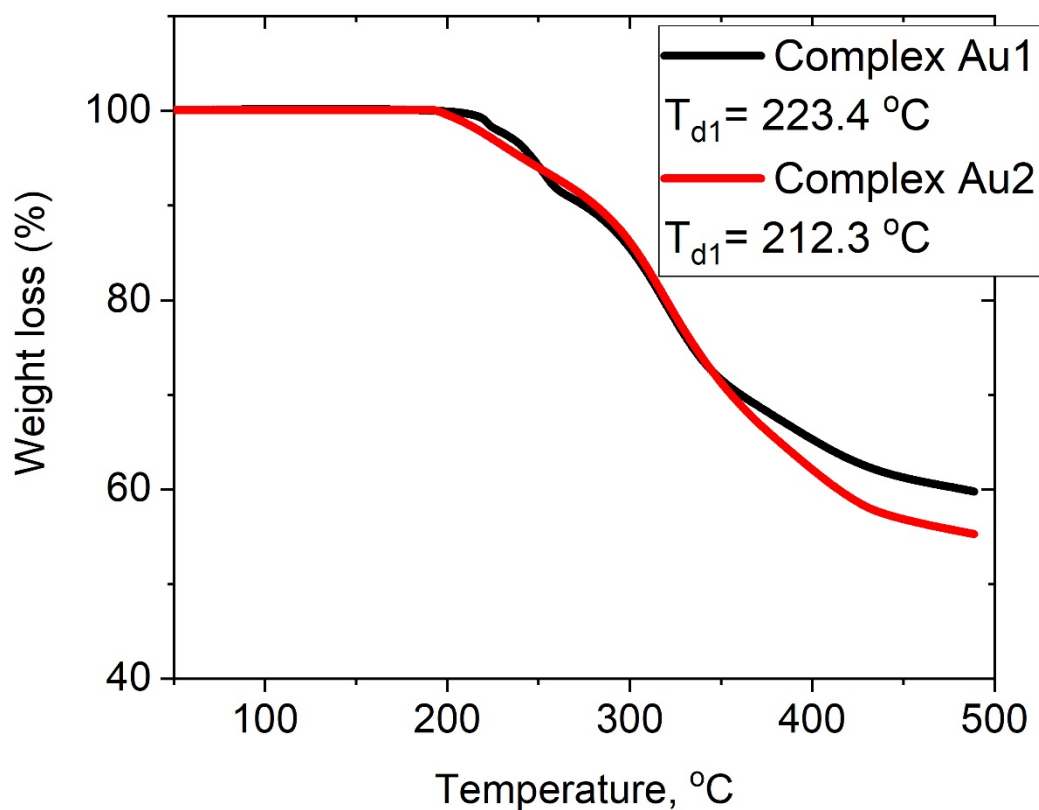| Complex | $\lambda_{abs}$ [nm], ($10^3 \, \varepsilon/M^{-1} \, cm^{-1}$) | | |
|---|---|---|---|
| | Toluene | THF | DFB |
| **1** | 305 (14.8), 409 (7.8) | 297 (15.7), 397 (8.7) | 298 (14.9), 394 (9.2) |
| **2** | 287 (25.4), 309 (16.1), 359 (7.1), 376 (9.0), 523 (4.2) | 290 (20.1), 309 (13.5), 358 (7.6), 376 (7.6), 477 (4.0) | 290 (20.4), 309 (13.3), 358 (7.8), 375 (7.4), 469 (4.3) |



**Figure S1.** Thermogravimetric plots for complexes **1** and **2**.

**X-Ray Crystallography.**

Crystals of complex **2** suitable for X-ray diffraction study were obtained by layering a 1:1 mixture of 1,2-difluorobenzene/$CH_2Cl_2$ solution with diethyl ether. Crystals were mounted in oil on glass fibers and fixed on the diffractometer in a cold nitrogen stream. Data were collected using an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer with graphite monochromated Mo K$_\alpha$ radiation ($\lambda$ = 0.71073 Å) at 140 K. Data were processed using the CrystAlisPro-CCD and –RED software.[1] The structure was solved by direct methods and refined by full-matrix least-squares against $F^2$ in an anisotropic (for non-hydrogen atoms) approximation. All hydrogen atom positions were refined in isotropic approximation in a "riding" model with the $U_{iso}(H)$ parameters equal to 1.2 $U_{eq}(C_i)$, for methyl groups equal to 1.5 $U_{eq}(C_{ii})$, where $U(C_i)$ and $U(C_{ii})$ are respectively the equivalent thermal parameters of the carbon atoms to which the corresponding H atoms are bonded. All calculations were performed using the SHELXTL software.[2]

The principal crystallographic data for complex **2**: CCDC number 2110631, $C_{40}H_{31}AuN_2$, Monoclinic, space group $P2_1/n$, $a$ = 15.6793(11) Å, $b$ = 12.7012(6) Å, $c$ = 15.9435(11) Å, $\beta$ = 110.255(8)°, $V$ = 2978.7(4) Å$^3$, $Z$ = 4, $d_{calc}$ = 1.643 g cm$^{-3}$, $\mu$ = 4.971 mm$^{-1}$, brown/block, crystal size 0.16 × 0.11 × 0.08 mm, $F(000)$ = 1456.0, $T_{min}/T_{max}$ 0.63178/1.00000, 29952 reflections measured (6.098 ° ≤ 2$\Theta$ ≤ 55.998°), 7179 unique ($R_{int}$ = 0.0414, $R_{sigma}$ = 0.0359) which were used in all calculations. The final $R_1$ was 0.0257 (I > 2σ(I)) and $wR_2$ was 0.0752 (all data), $GOF$ = 1.047, $\Delta\rho_{min}/\Delta\rho_{max}$ = 1.02/–0.96.
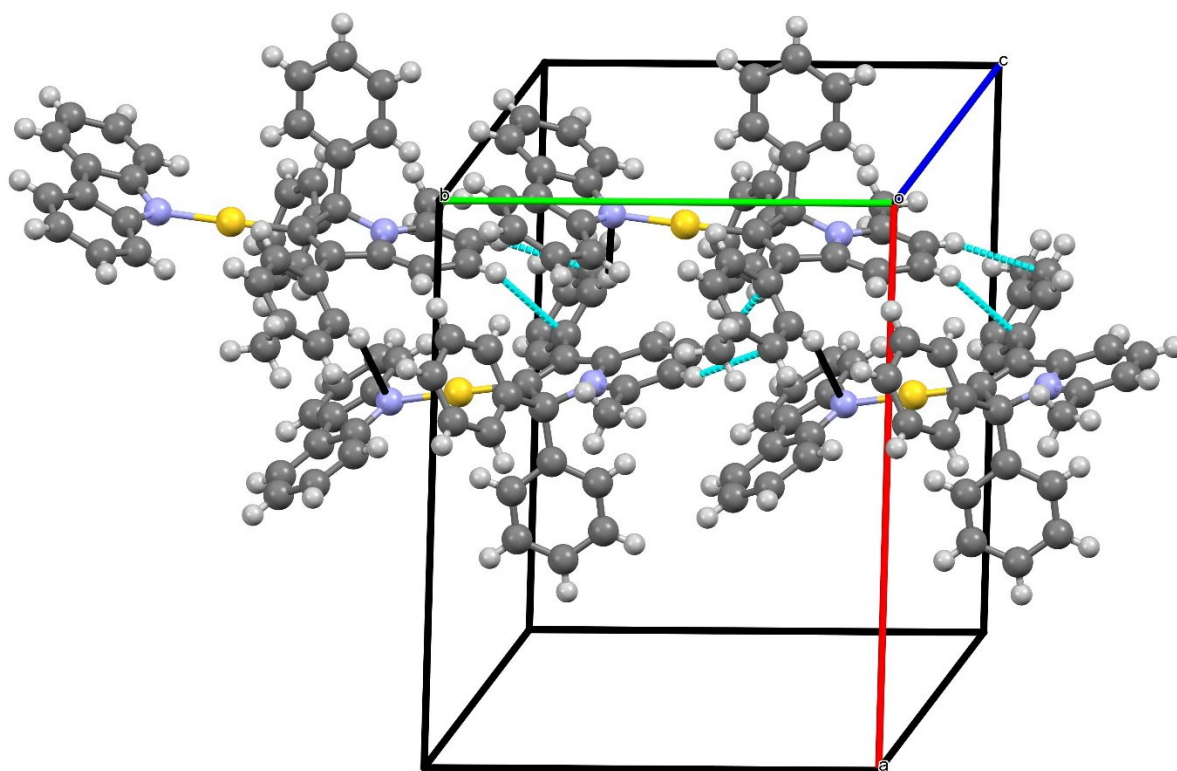
**Figure S2.** The crystal packing for complex **2** showing the major intermolecular contacts: multiple C-H···π (blue-green) and short C6A-H6A···N2(carbazole, black) contacts.

**Photophysical Characterisation**

Solution UV-visible absorption spectra were recorded using a Perkin-Elmer Lambda 35 UV/vis spectrometer for a wavelength range of 250-800 nm. Photoluminescence measurements in all media and temperatures were recorded on the Edinburgh Instruments FS5 spectrofluorimeter. Photoluminescent quantum yield was measured in an integrating sphere using an Edinburgh Instruments FS5 spectrofluorimeter. The solutions have been measured three times in a series of the dilution experiments to achieve the optical density 0.1 (for the LLCT band maximum) and eliminate self-absorption artifacts. 1,2-difluorobenzene (DFB) solutions have been prepared in a 1 cm screw-cap quartz cuvette inside a nitrogen glovebox from freshly distilled solvent with additional freeze-pump-thaw degassing procedure.

**Transient PL Measurements**

The time resolved fluorescence data for the solutions (DFB; with concentration to achieve optical density 0.1 for the lowest energy CT band), crystalline powder and

polystyrene host-guest films for gold complexes **1** and **2** at 298 K were collected on an Edinburgh Instruments FS5 spectrofluorimeter with a time-correlated single photon counting (TCSPC) technique. A NanoLED of 405 nm was used as excitation source, with an instrument response function width of 0.2 ns. The data were analyzed on an Edinburgh Instruments FS5 Fluoracle software.

The crystalline powder and polystyrene (2 wt%) host-guest films were investigated to acquire the time resolved fluorescence data at 77K on an Edinburgh Instruments FS5 spectrofluorimeter using the 5 W microsecond Xenon flash lamp with a repetition rate of 100 Hz (400 nm excitation wavelength).

**Table S2.** Mayer bond order analysis for gold complexes **1** and **2**.

|  | Au1-Cl | Au1-N2 | Au-C1 |
|---|---|---|---|
| 3CAuCl (**1**) | 0.87 | - | 0.86 |
| 3CAuCz (**2**) | - | 0.61 | 1.06 |

**Table S3.** Overlap integrals and HOMO-LUMO centroid distances

|  | Overlap integral of HOMO and LUMO | Centroid distance of HOMO and LUMO (Å) |
|---|---|---|
| 3CAuCl (**1**) | 0.45 | 7.8 |
| 3CAuCz (**2**) | 0.23 | 14.4 |

**Table S4.** Dipole moments of $S_0$ and $S_1$ states in $S_0$ geometry.

| | S0 | S1@S0 |
|---|---|---|
| 3CAuCl (**1**) |  13.8D |  7.2D |

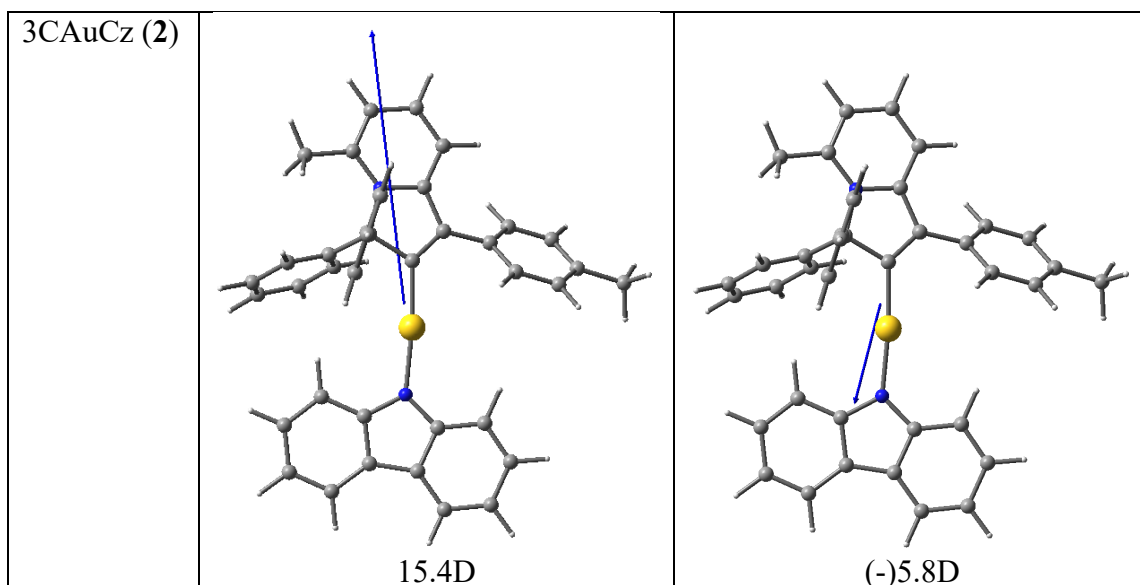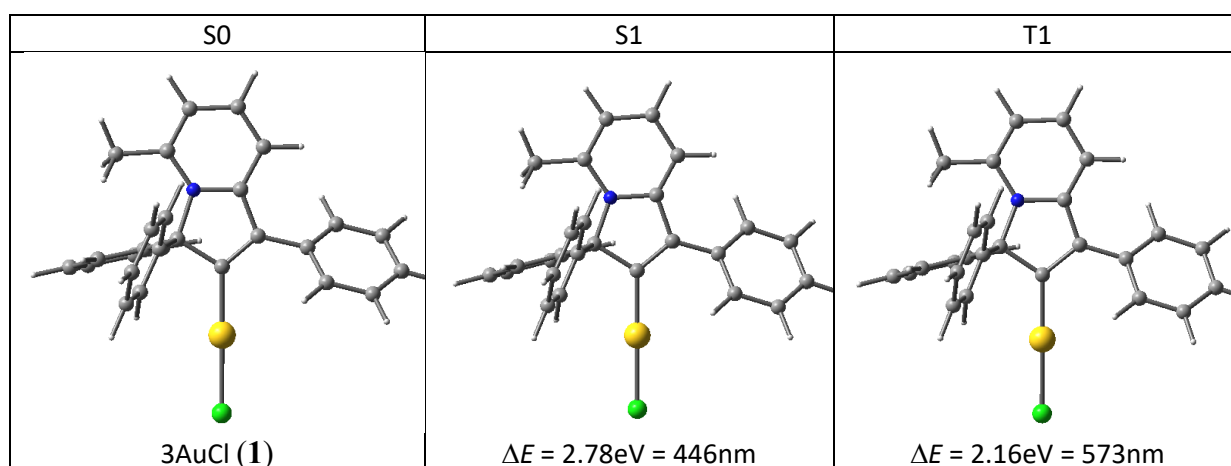| 3CAuCz (**2**) |  |  |
|---|---|---|
| | 15.4D | (-)5.8D |
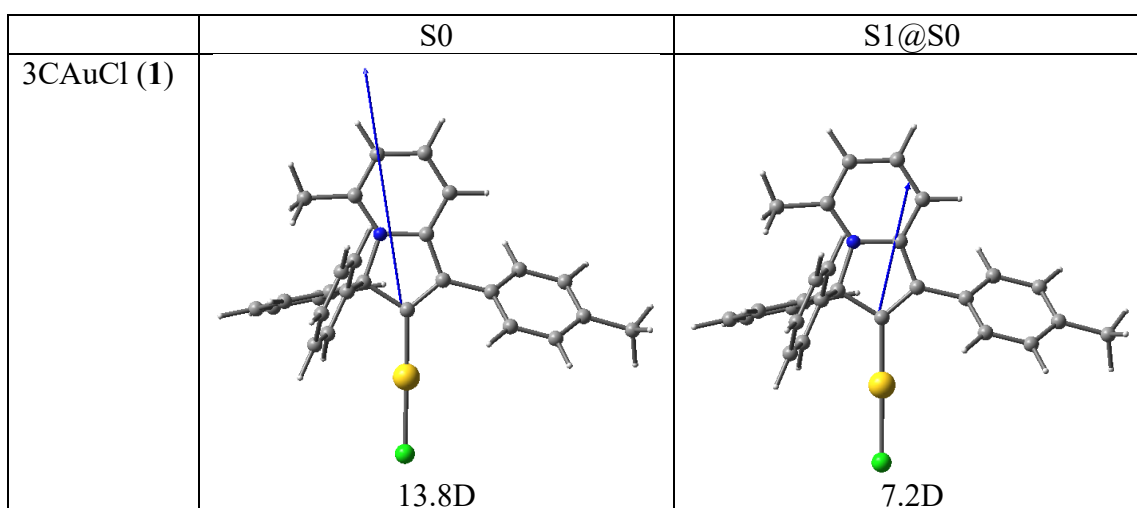
**Table S5.** Theoretically calculated $S_1$ and $T_1$ energy levels, orbital (HOMO, LUMO) contributions to vertical excitations ($S_0 \rightarrow S_1$) and oscillator strength coefficients for complexes **1** and **2**.

| | $S_1/T_1$ | $S_0$-$S_1$ character | $S_0$-$S_1$ oscillator strength |
|---|---|---|---|
| 3AuCl (**1**) | 3.06/2.39 | HOMO – LUMO (88%) | 0.1376 |
| 3AuCz (**2**) | 2.02/1.85 | HOMO – LUMO (98%) | 0.1328 |

**Table S6.** Optimized structures of ground and excited states for complexes **1** and **2**, where $\Delta E$ corresponds to the optimized $S_1$ or $T_1$ energies relative to the optimized $S_0$ state energy.

| S0 | S1 | T1 |
|---|---|---|
|  |  |  |
| 3AuCl (**1**) | $\Delta E$ = 2.78eV = 446nm | $\Delta E$ = 2.16eV = 573nm |

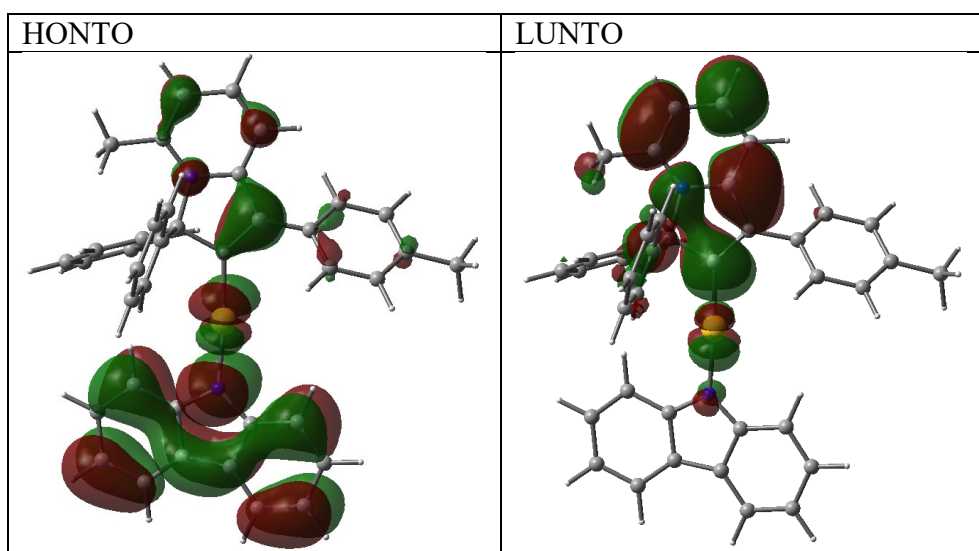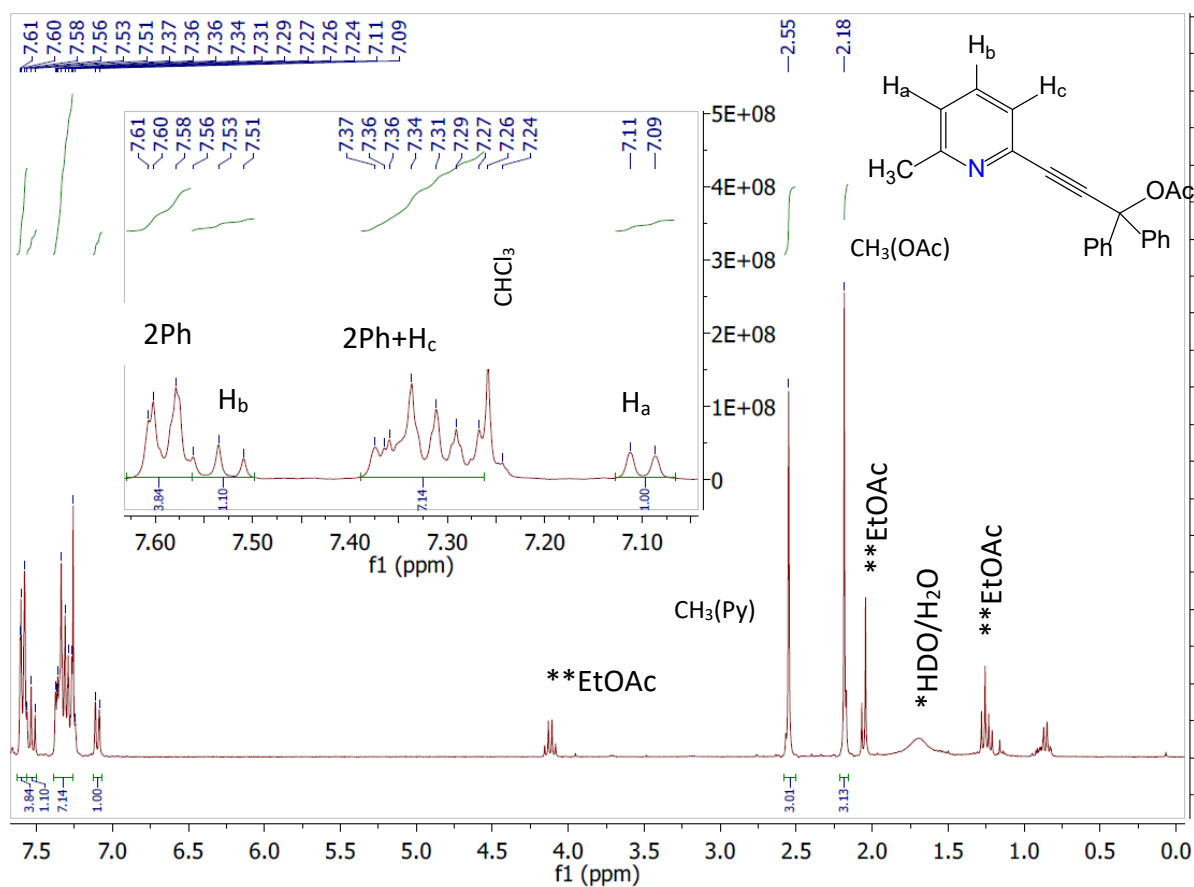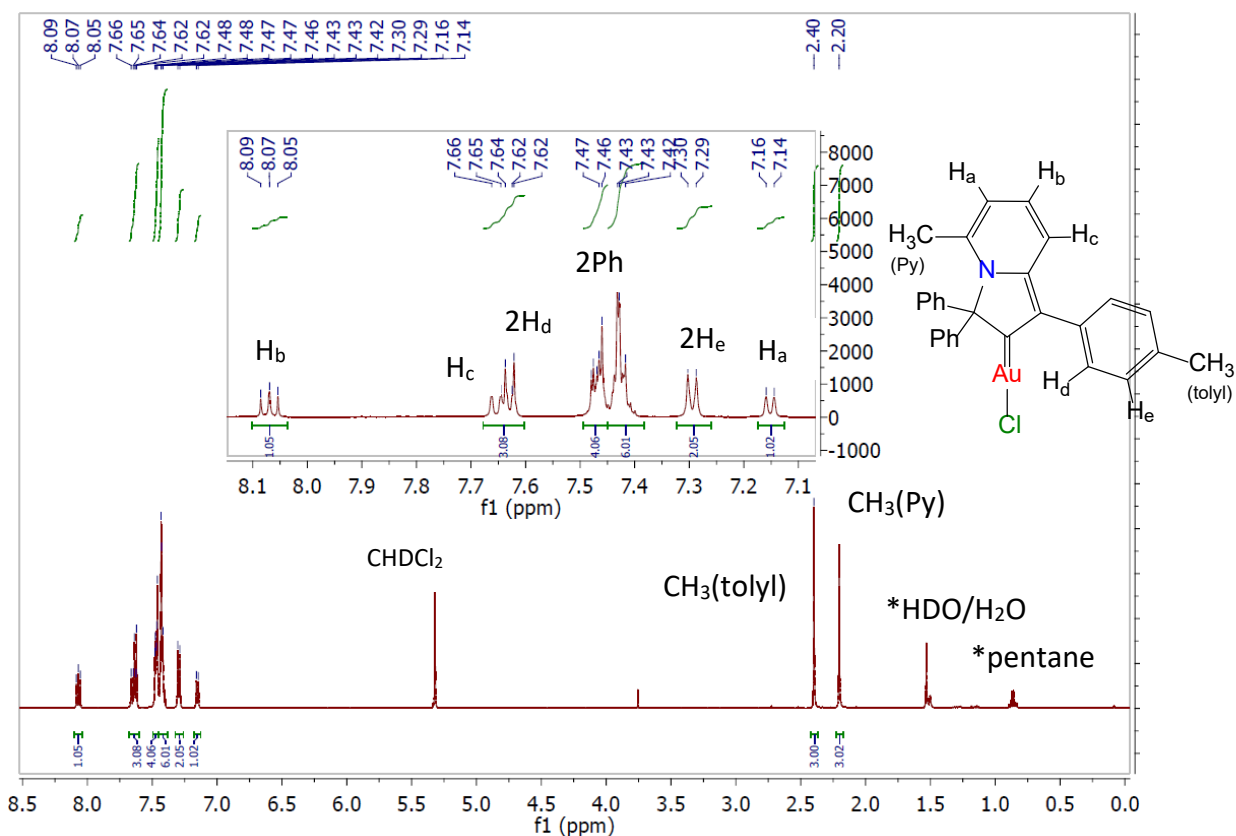| | ΔE (planar) = 1.82eV = 681nm | ΔE (planar) = 1.65eV = 750nm |
| 3AuCz (**2**) | ΔE (rotated) = 1.74eV = 712nm | ΔE (rotated) = 1.74eV = 712nm |
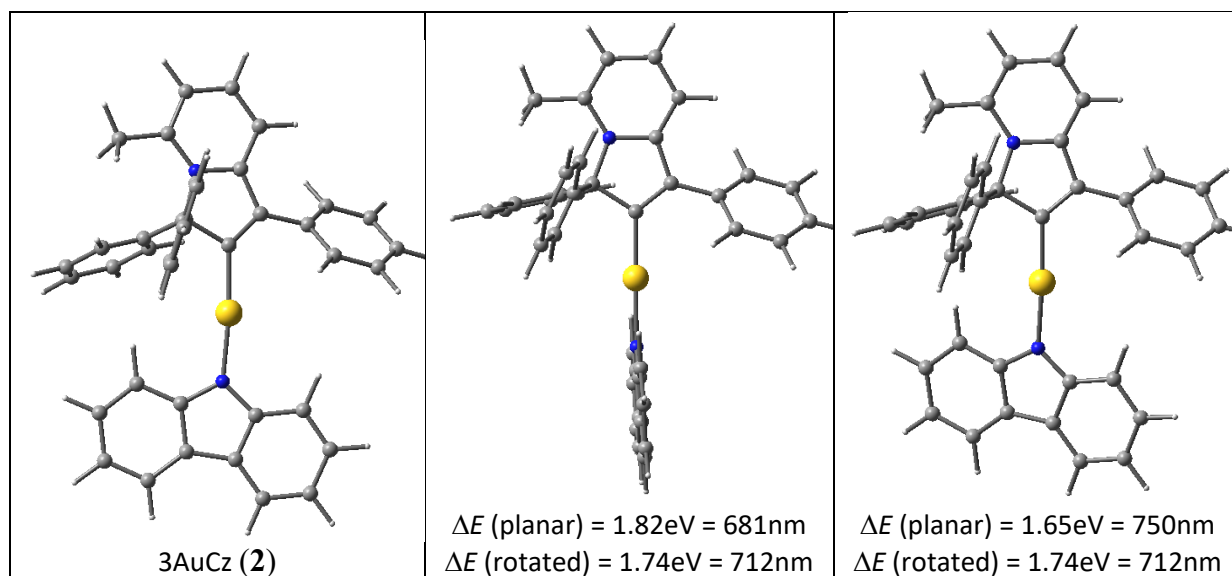
**Table S7.** Natural transition orbitals for $T_1$ state of gold complex 2 (transition coefficient is 0.997).
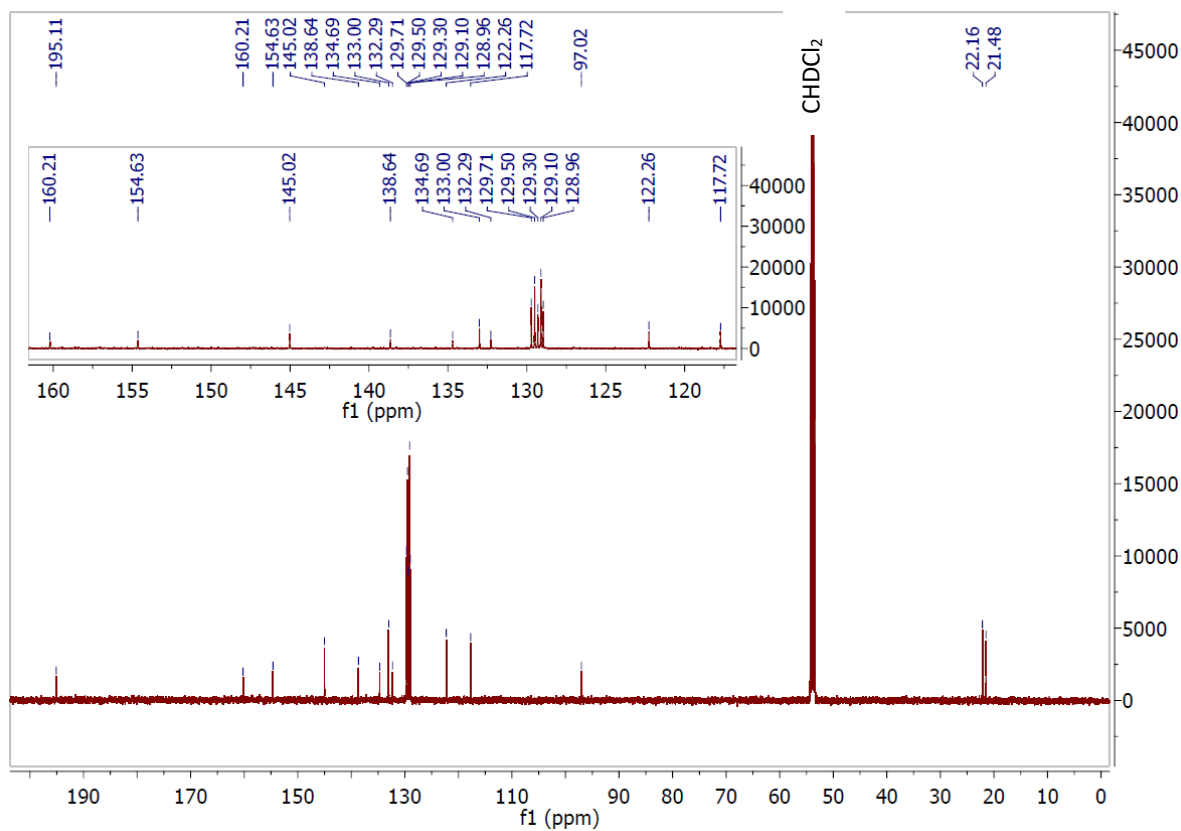

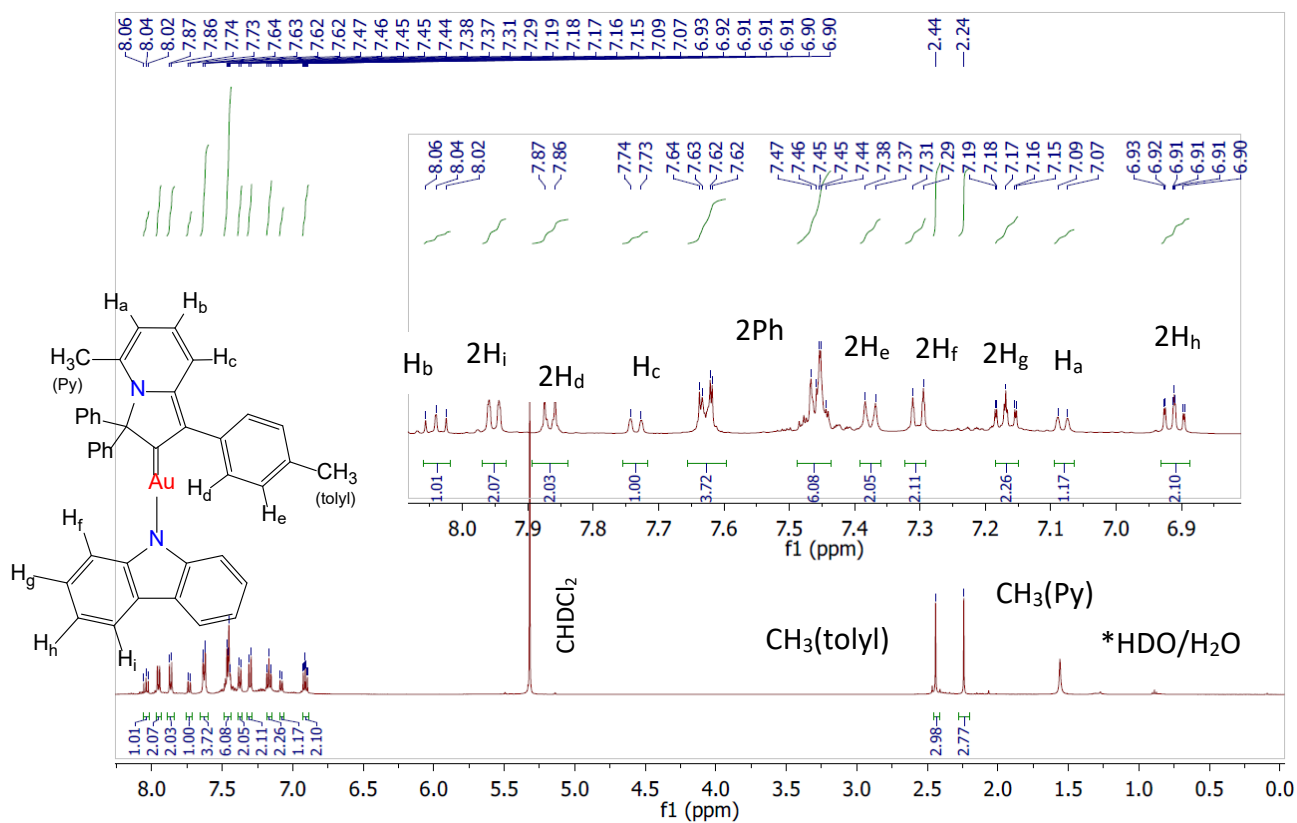
| HONTO | LUNTO |

## NMR and Mass Spectrometry Data



$^1$H NMR spectrum of 3-(6-methylpyridin-2-yl)-1,1-diphenylprop-2-yn-1-yl acetate(500 MHz, CDCl$_3$).

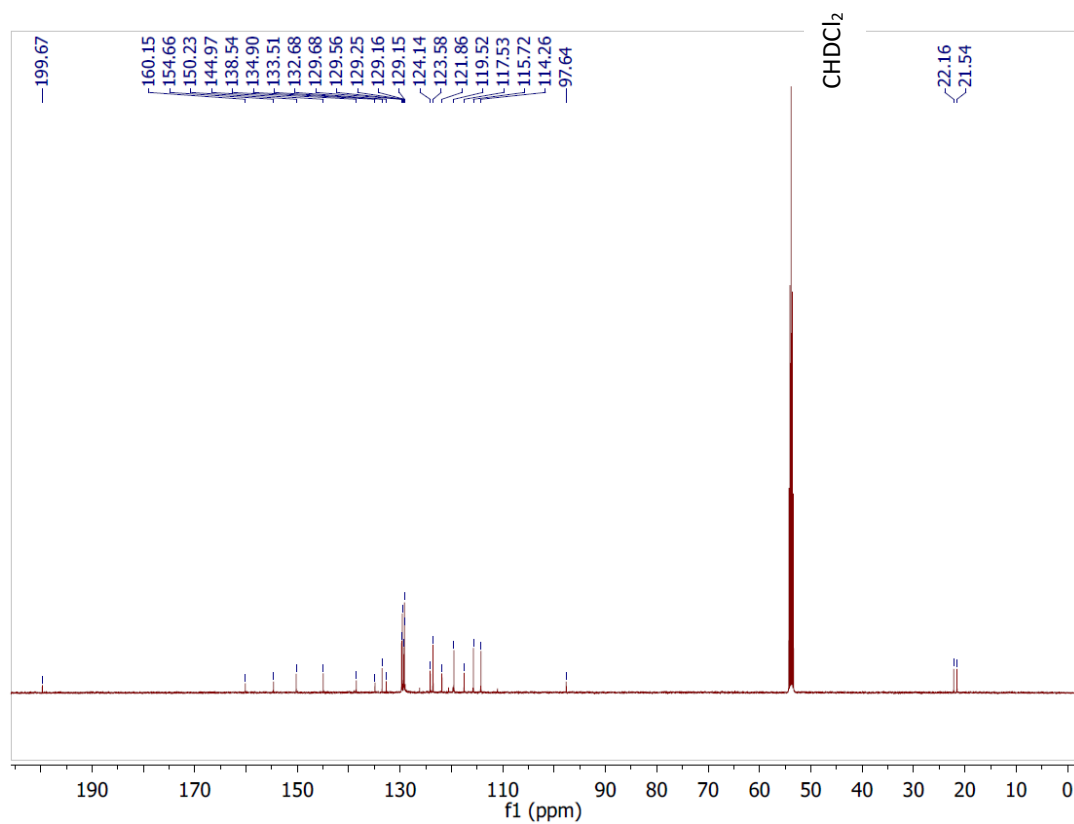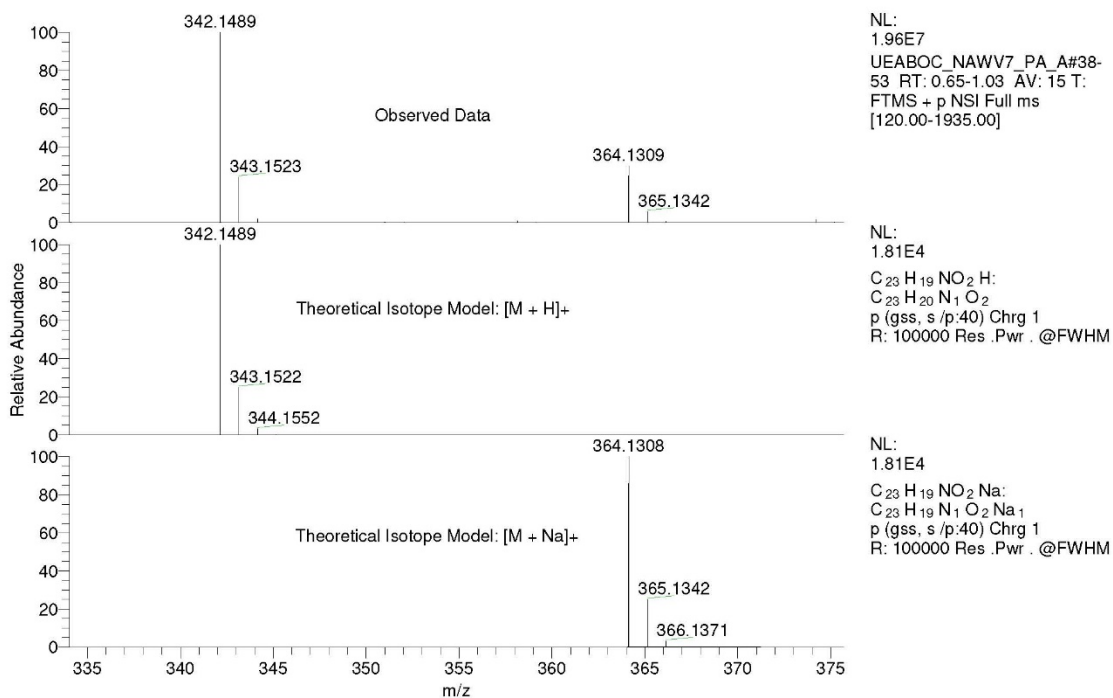$^1$H NMR spectrum for complex **1** (500 MHz, CD$_2$Cl$_2$).



$^{13}$C{$^1$H} NMR spectrum for complex **1** (125 MHz, CD$_2$Cl$_2$).

$^1$H NMR spectrum for complex **2** (500 MHz, CD$_2$Cl$_2$).



$^{13}$C{$^1$H} NMR spectrum for complex **2** (125 MHz, CD$_2$Cl$_2$).

HRMS for 3-(6-methylpyridin-2-yl)-1,1-diphenylprop-2-yn-1-yl acetate. $C_{23}H_{19}NO_2$ theoretical $[M+H]^+$ = 342.1489, HRMS (pNSI in $CH_2Cl_2$/MeOH+$NH_4$OAc): = 342.1489.
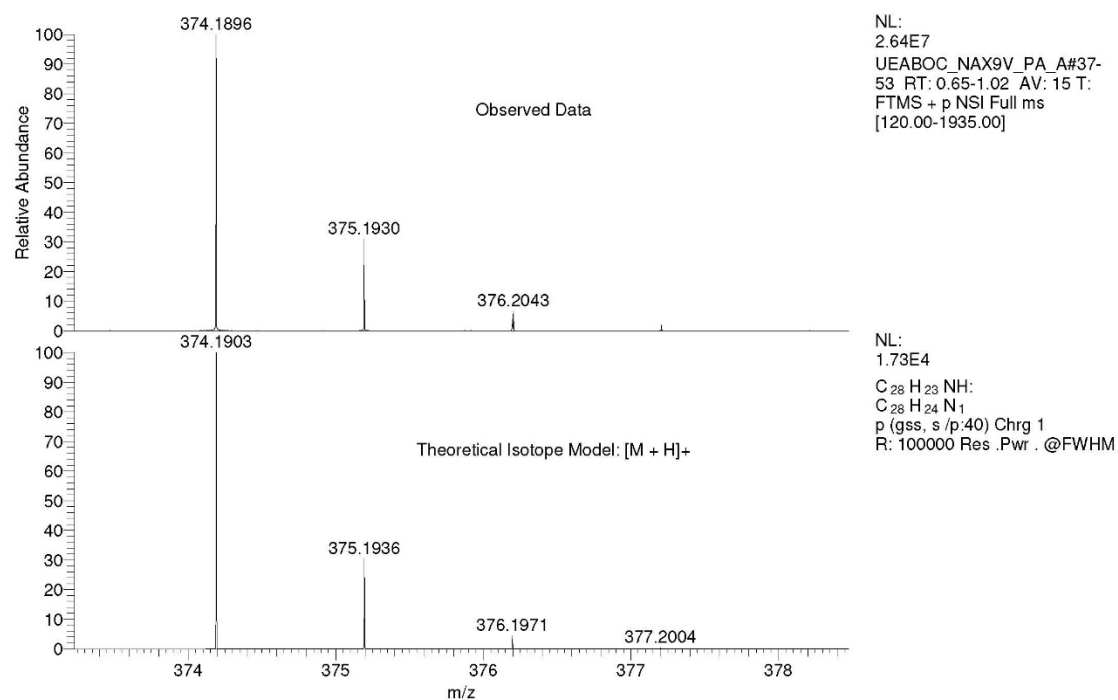
HRMS for ligand **L1**. $C_{28}H_{23}N$ theoretical $[M+H]^+$ = 374.1903, HRMS (pNSI in $CH_2Cl_2$/MeOH+NH$_4$OAc): = 374.1896.
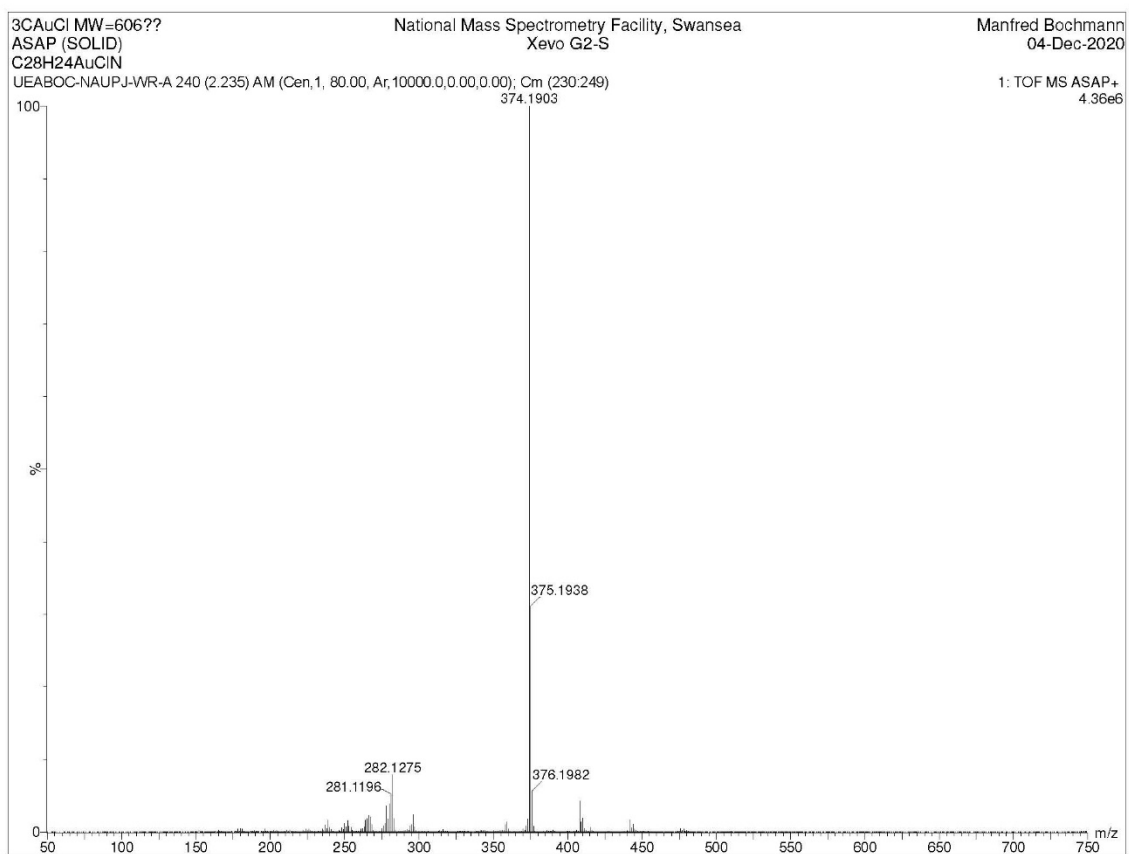
HRMS for gold complex **1**. $C_{28}H_{24}N$ theoretical $[M–AuCl]^+$ = 374.1909, HRMS (APCI(ASAP): = 374.1903.

Theoretical Isotope Pattern

Observed Data
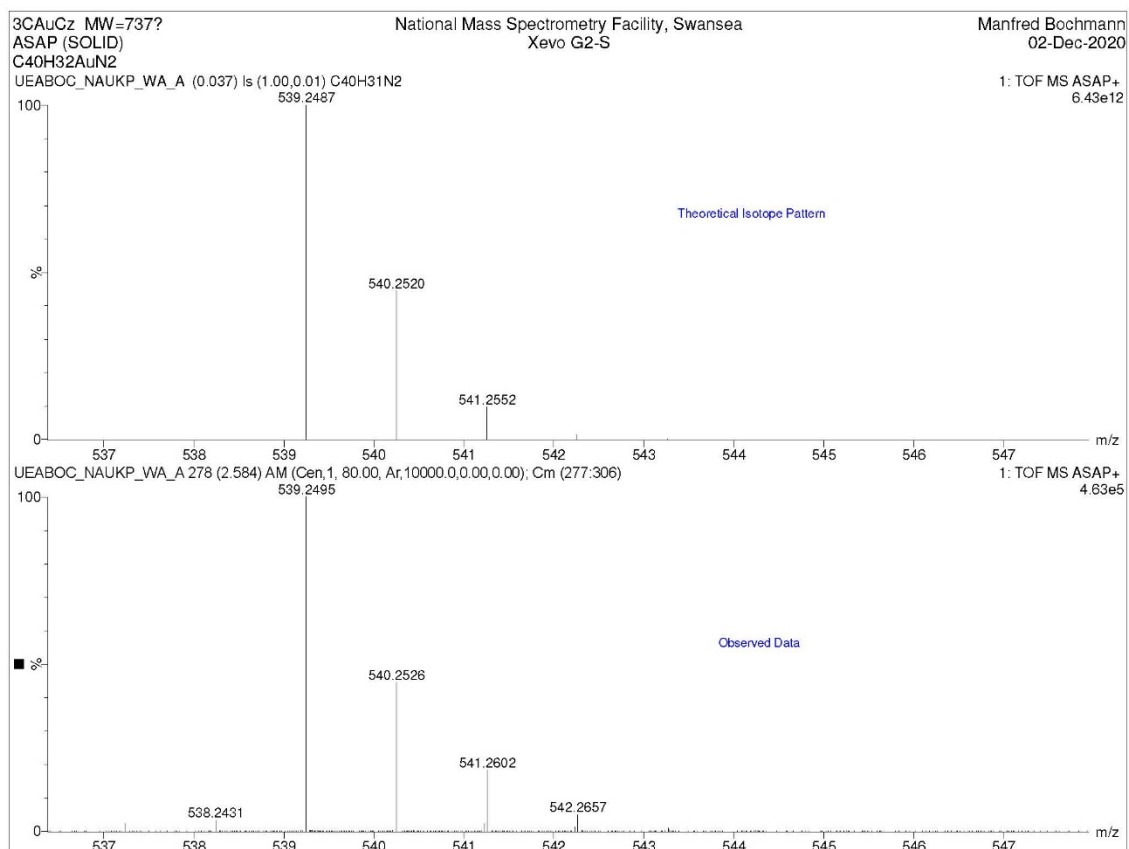
HRMS for gold complex **2**. HRMS $C_{40}H_{31}AuN_2$ theoretical $[M\text{-}Au]^+$ = 539.2487, HRMS (APCI(ASAP): = 539.2495.

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1 *Programs CrysAlisPro*, Oxford Diffraction Ltd., Abingdon, UK (2010).

2 (a) Sheldrick, G.M. SHELX-97 and SHELXL – Programs for crystal structure determination (SHELXS) and refinement (SHELXL), *Acta Cryst.* **2008**, *A64*, 112.

(b) G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", Acta Cryst., C71, 3-8 (Open Access).