## Supplementary Information Available

# Comparative biological evaluation and G-quadruplex interaction studies of two new families of organometallic gold(I) complexes featuring N-heterocyclic carbene and alkynyl ligands

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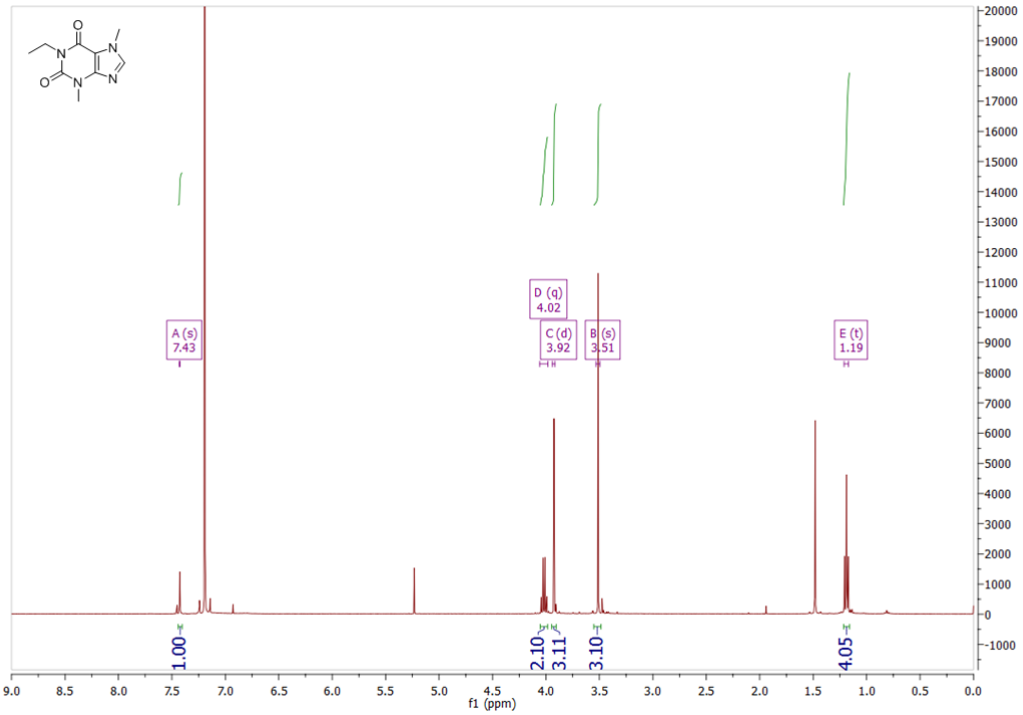



**Figure S1**. $^{1}$H NMR spectrum of **1a** in $CDCl_3$.

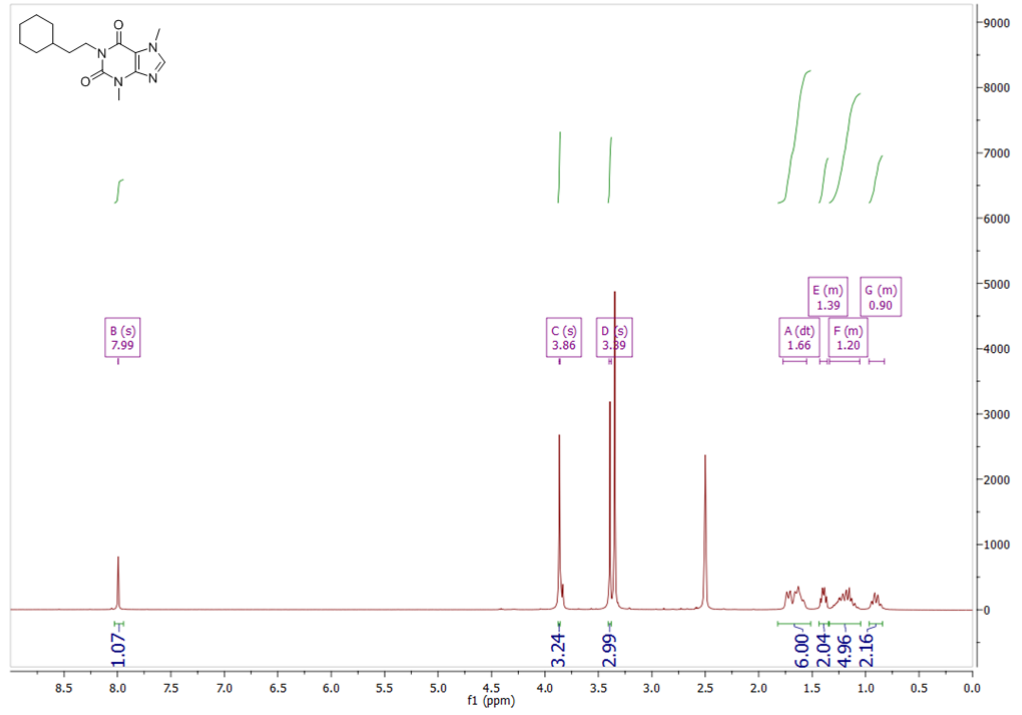



**Figure S2**. $^{1}$H NMR spectrum of **1b** in DMSO.

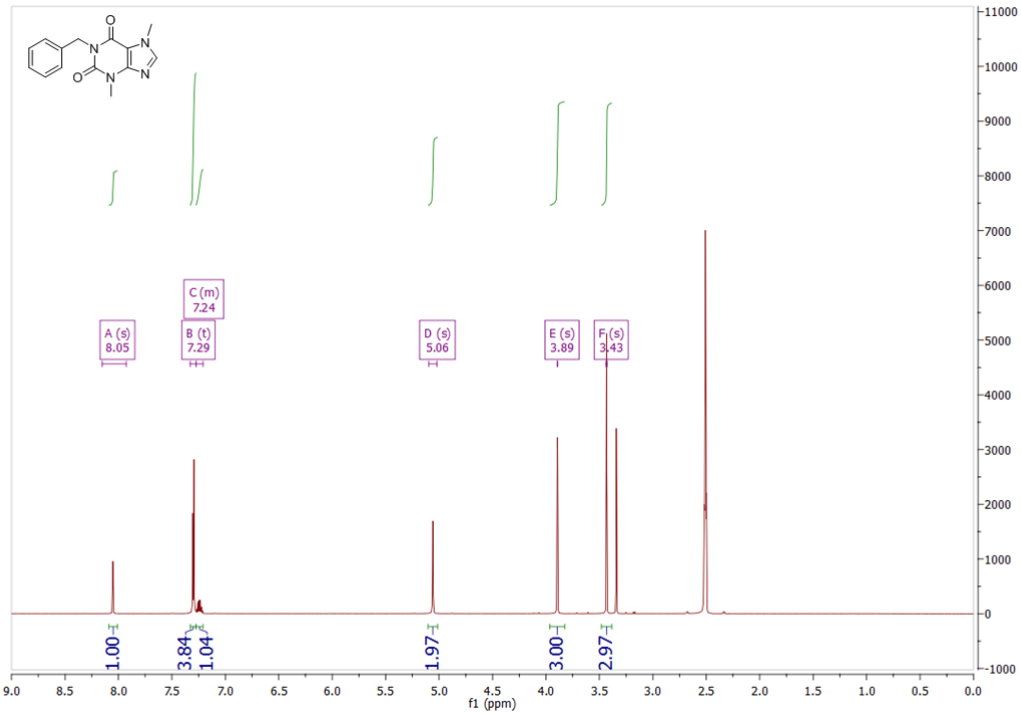



**Figure S3**. $^{1}$H NMR spectrum of **1c** in DMSO.

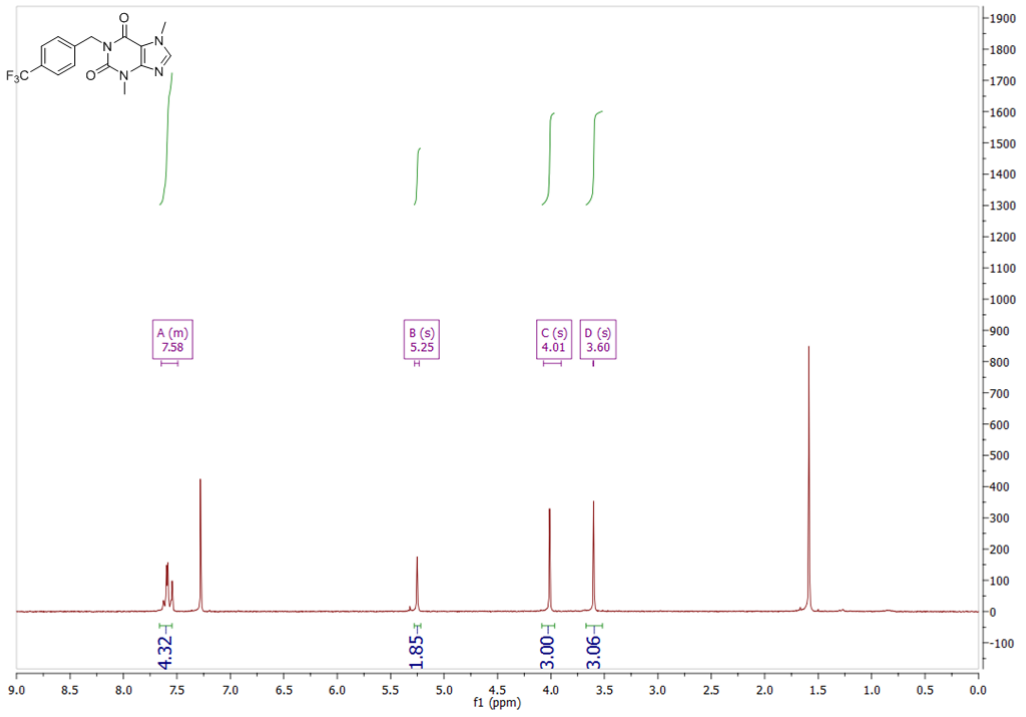



**Figure S4**. $^{1}$H NMR spectrum of **1d** in $CDCl_3$.

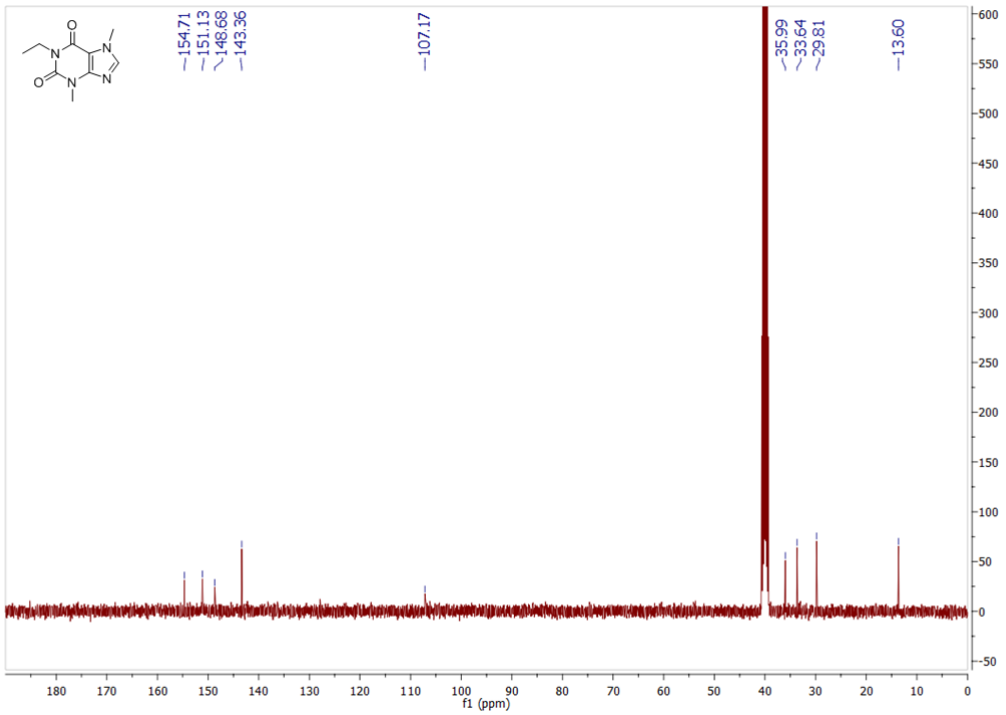



**Figure S5**. $^{13}C$ NMR spectrum of **1a** in $CDCl_3$.

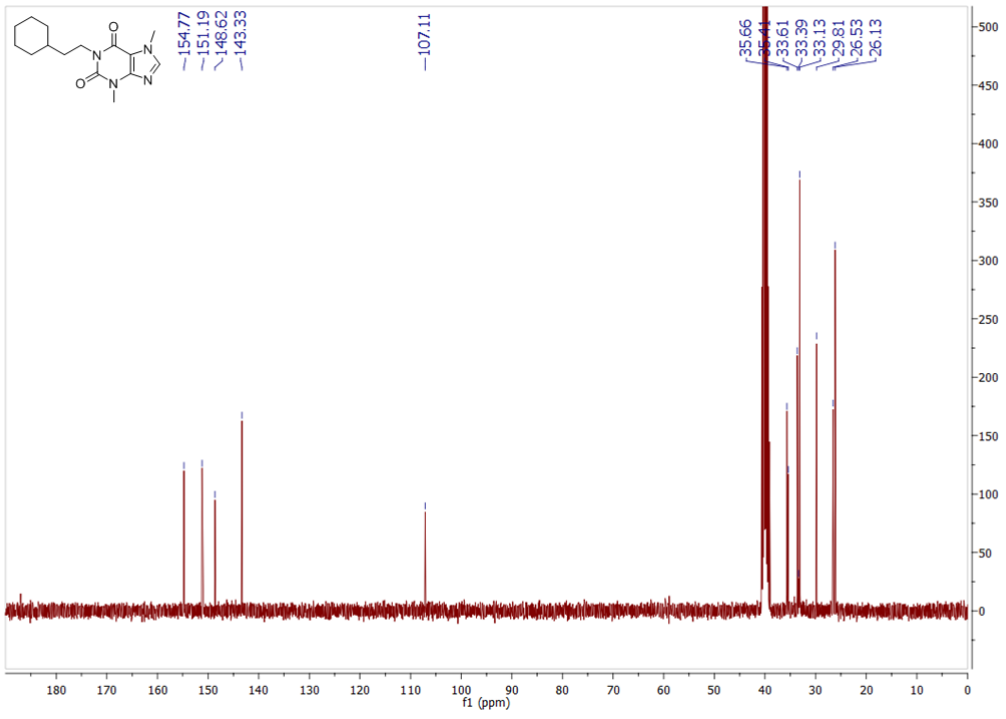



**Figure S6**. $^{13}C$ NMR spectrum of **1b** in DMSO.

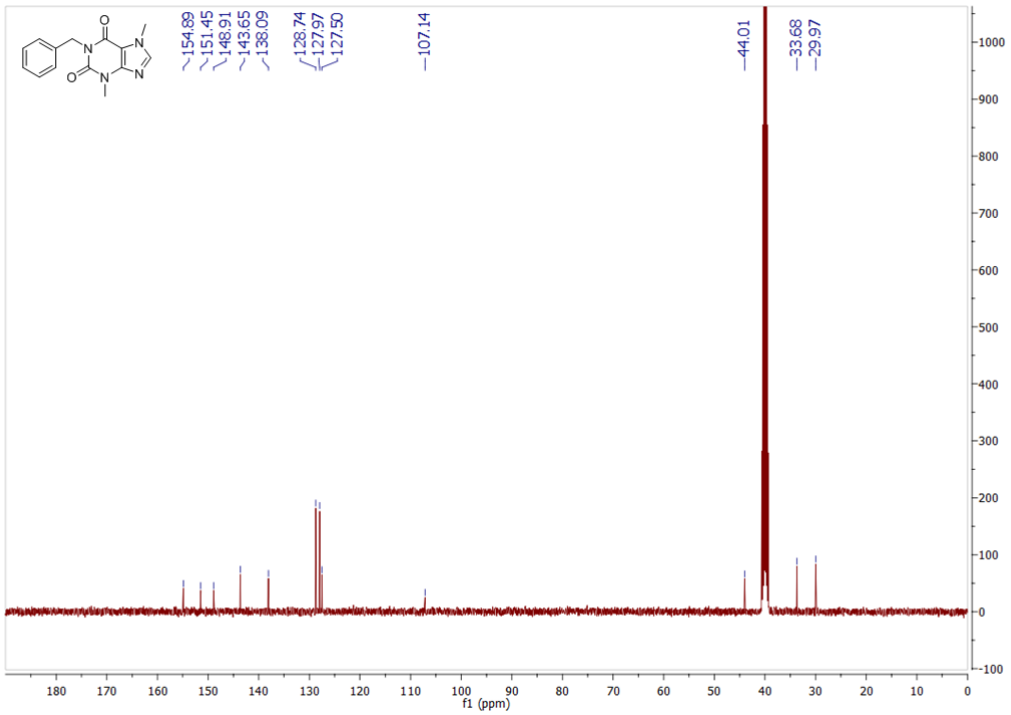



**Figure S7**. $^{13}$C NMR spectrum of **1c** in DMSO.

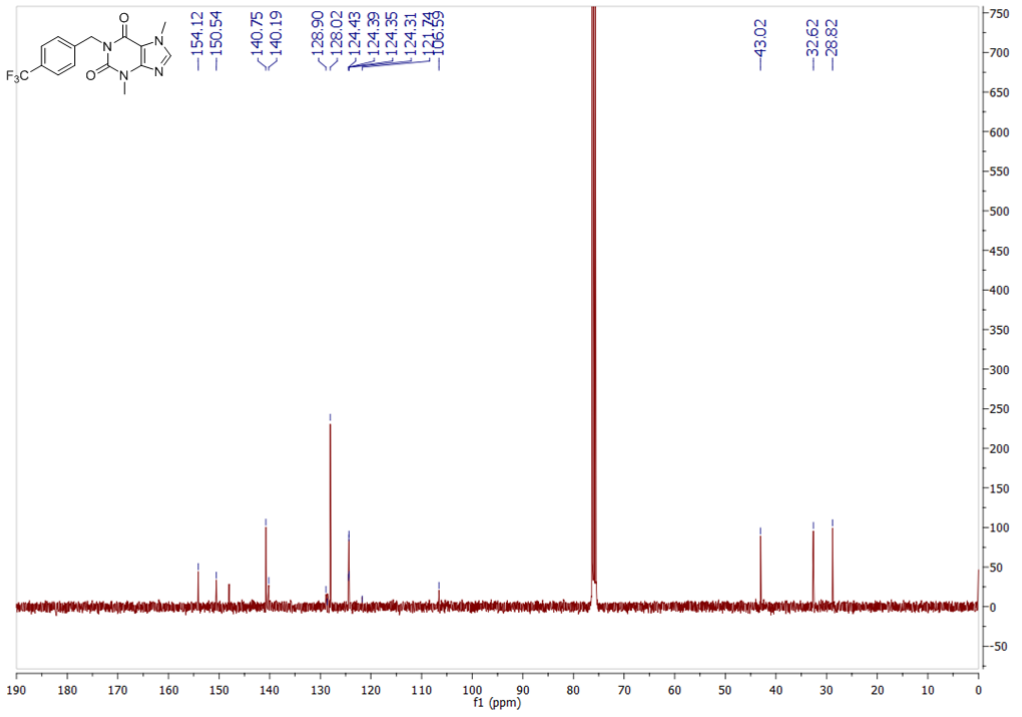



**Figure S8**. $^{13}$C NMR spectrum of **1d** in $CDCl_3$.

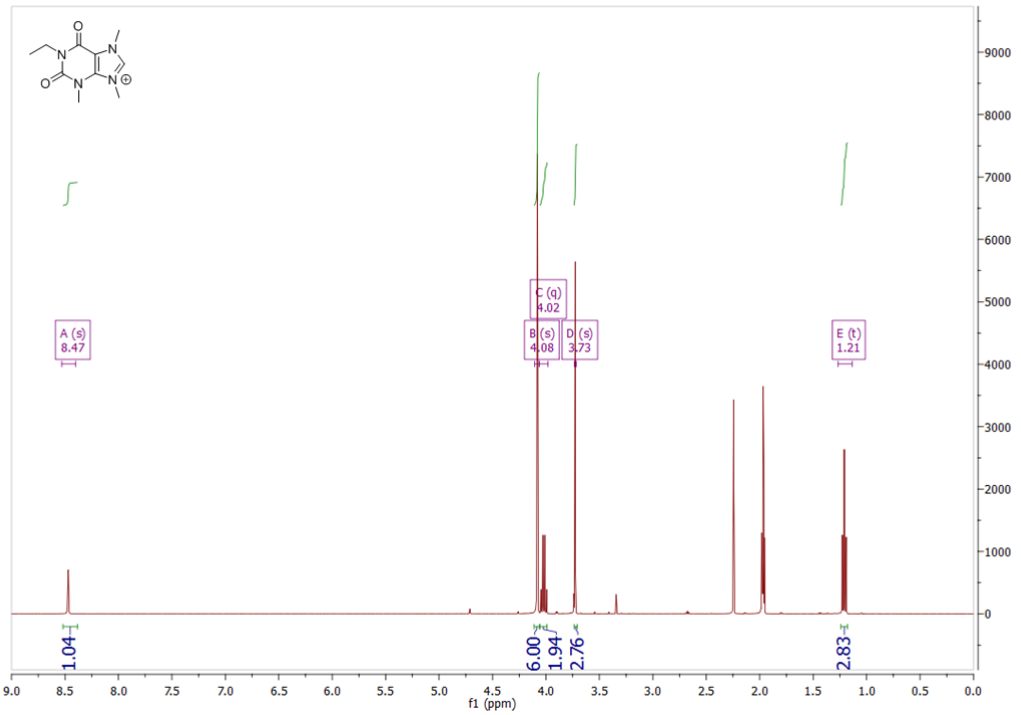



**Figure S9**. $^{1}$H NMR spectrum of **2a** in $CD_3CN$.

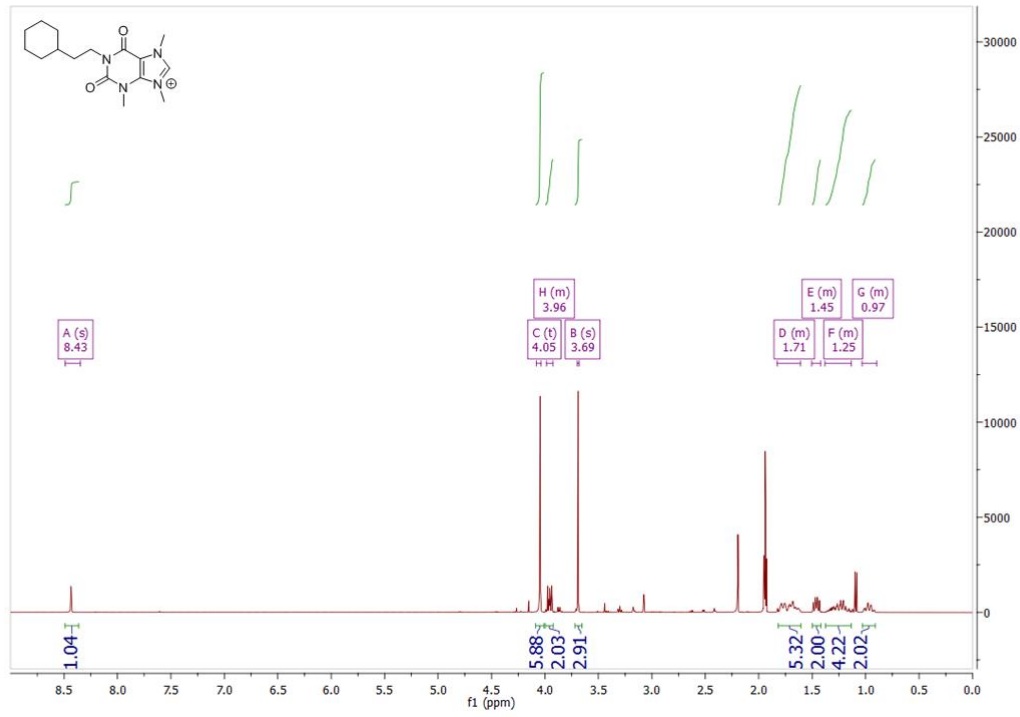



**Figure S10.** $^{1}$H NMR spectrum of **2b** in $CD_3CN$.

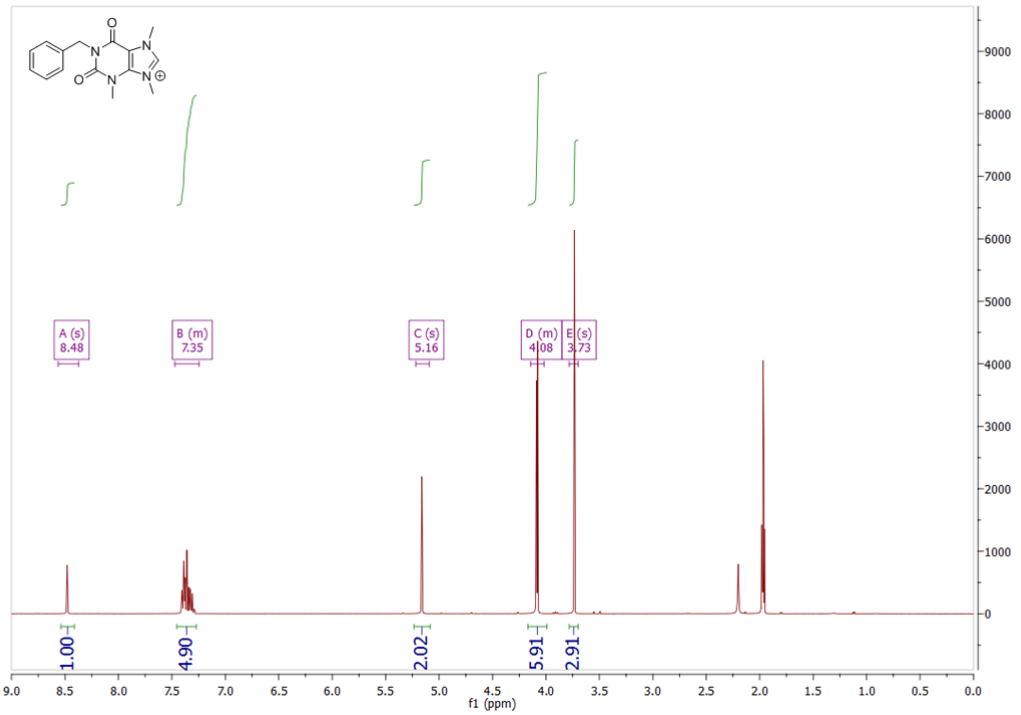



**Figure S11.** $^{1}$H NMR spectrum of **2c** in $CD_3CN$.

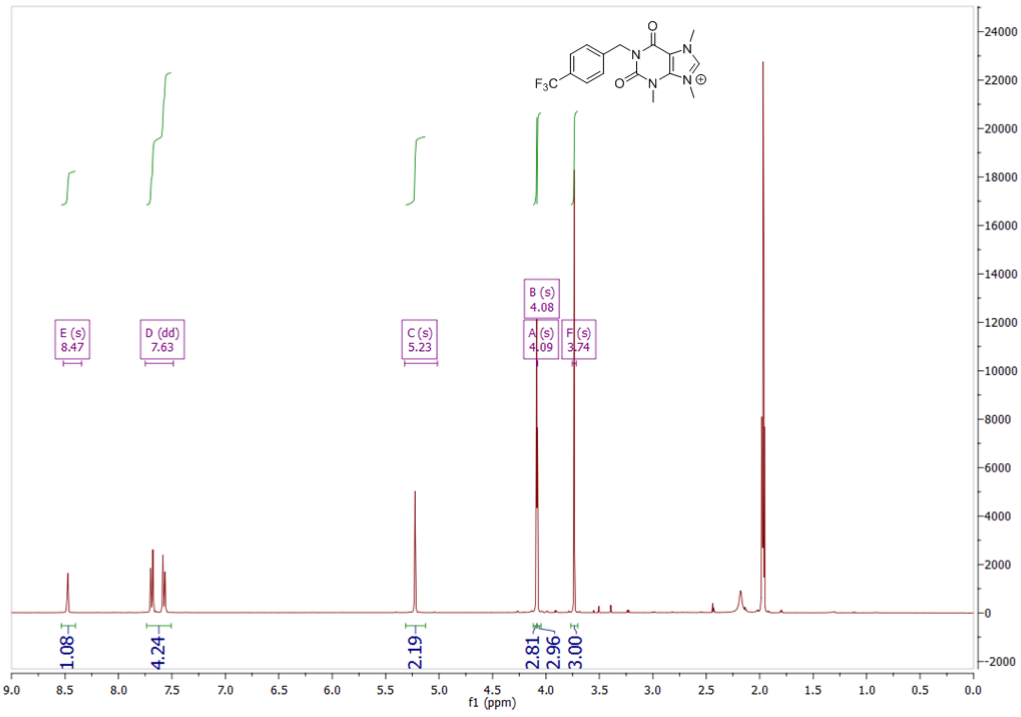



**Figure S12.** $^{1}$H NMR spectrum of **2d** in $CD_3CN$.

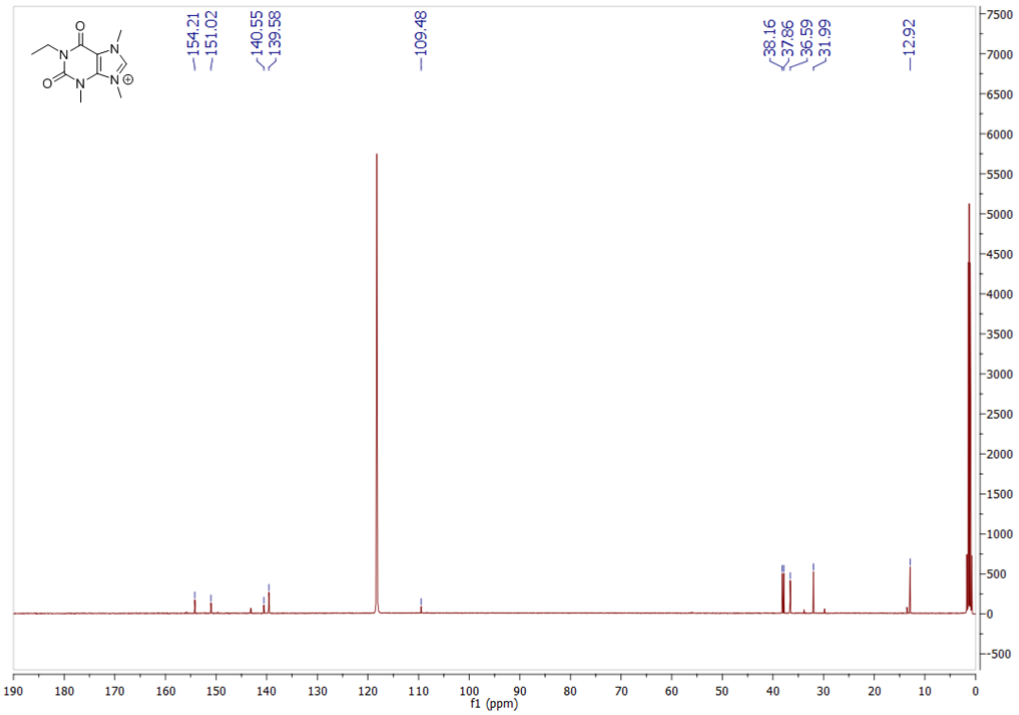



**Figure S13**. $^{13}C$ NMR spectrum of **2a** in $CD_3CN$.

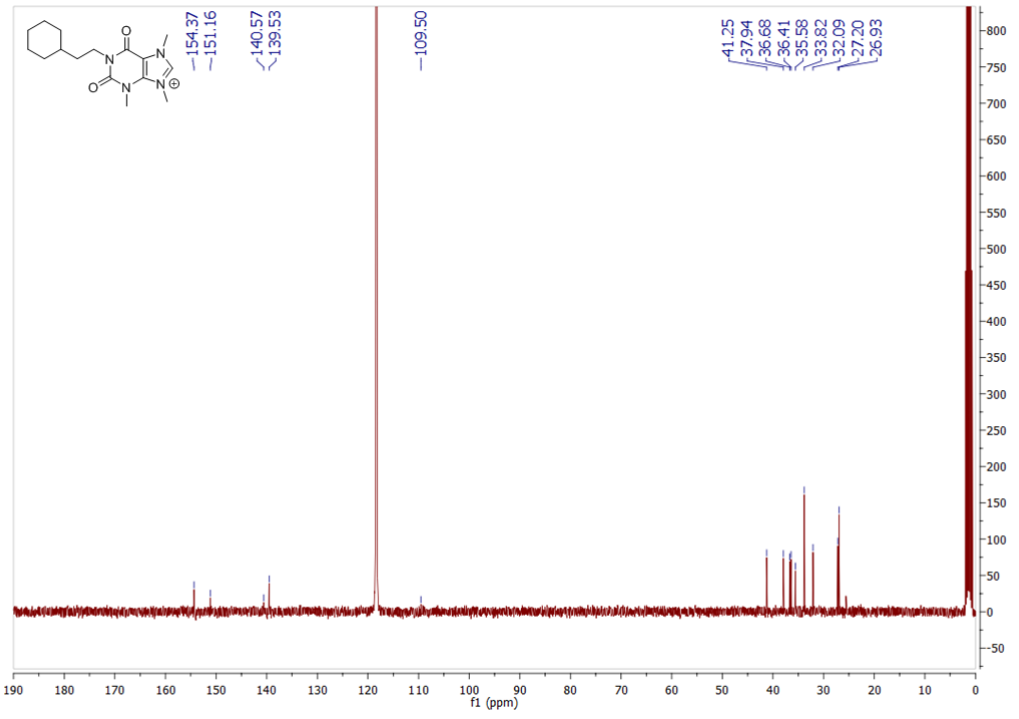



**Figure S14.** $^{13}C$ NMR spectrum of **2b** in $CD_3CN$.

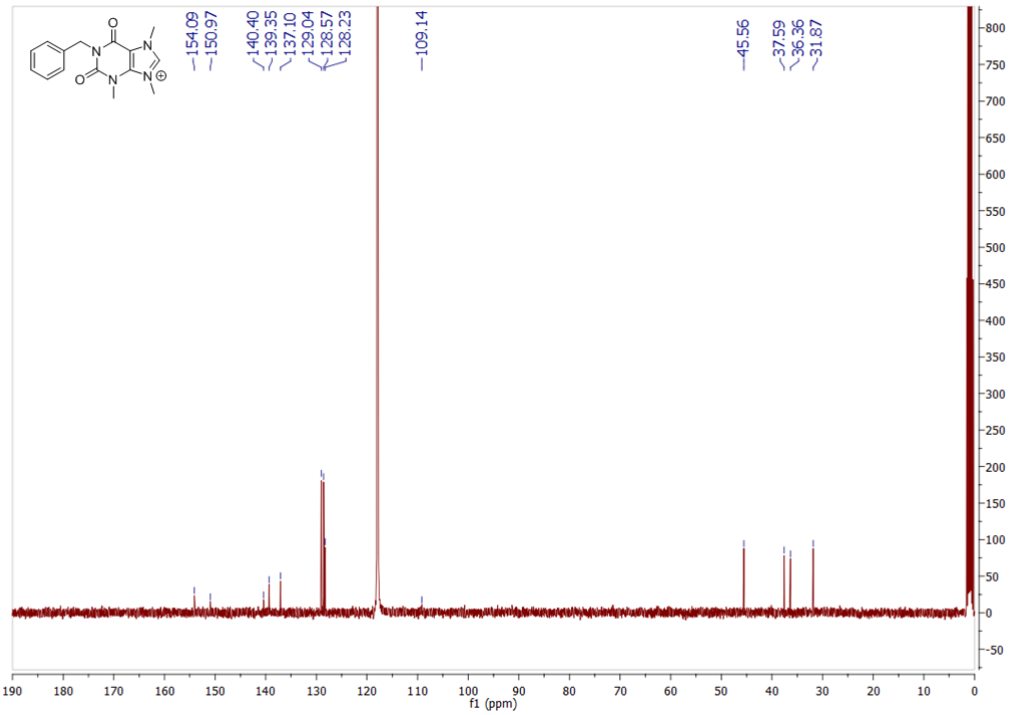



**Figure S15.** $^{1}$H NMR spectrum of **2c** in $CD_3CN$.

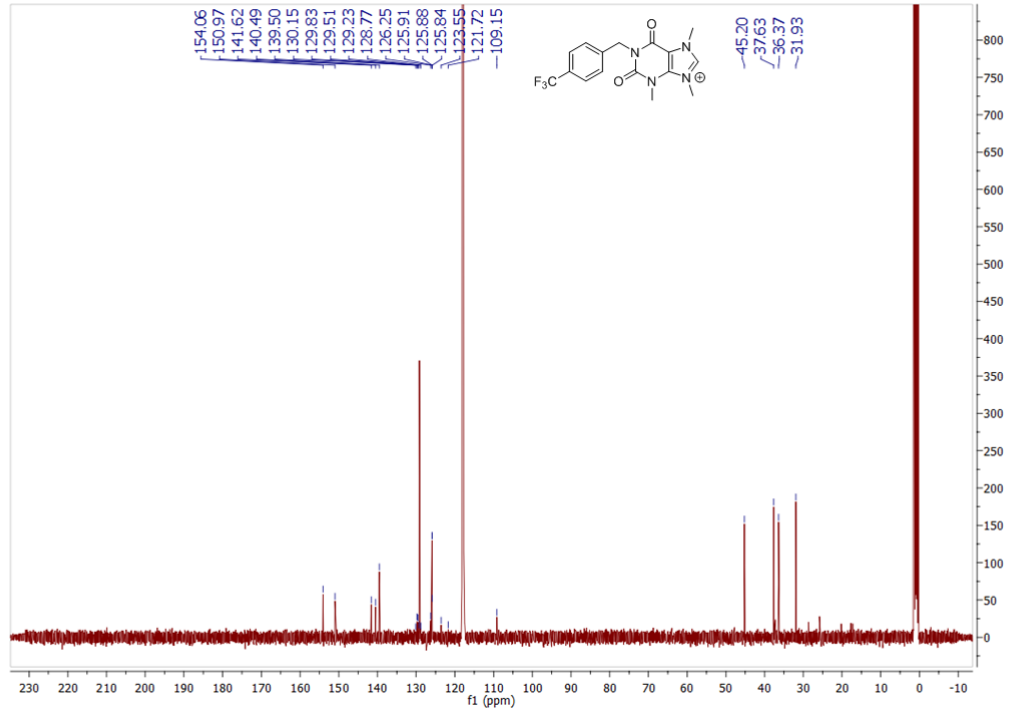



**Figure S16.** $^{13}$C NMR spectrum of **2d** in $CD_3CN$.

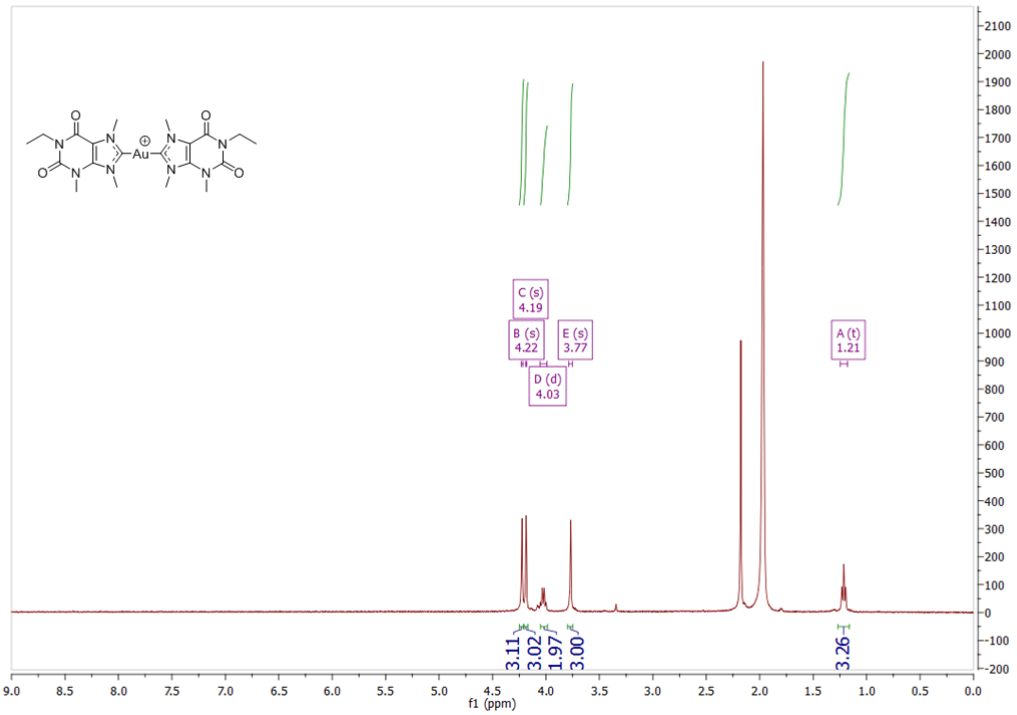



**Figure S17.** $^{1}$H NMR spectrum of **3a** in $CD_3CN$.

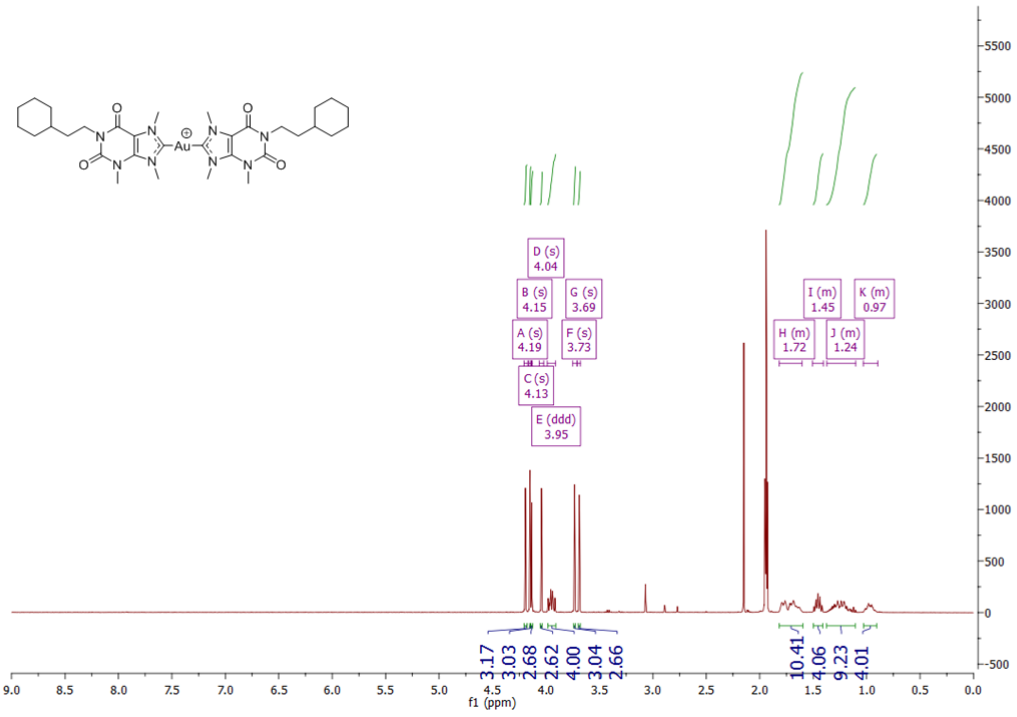



**Figure S18.** $^{1}$H NMR spectrum of **3b** in $CD_3CN$.

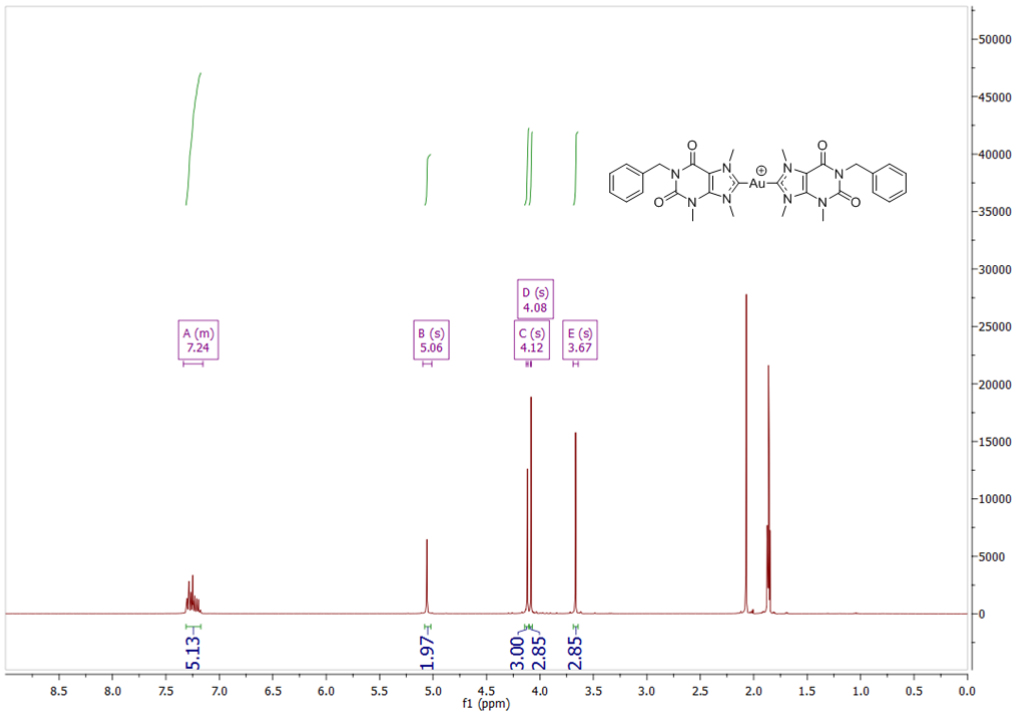



**Figure S19.** $^{1}$H NMR spectrum of **3c** in $CD_3CN$

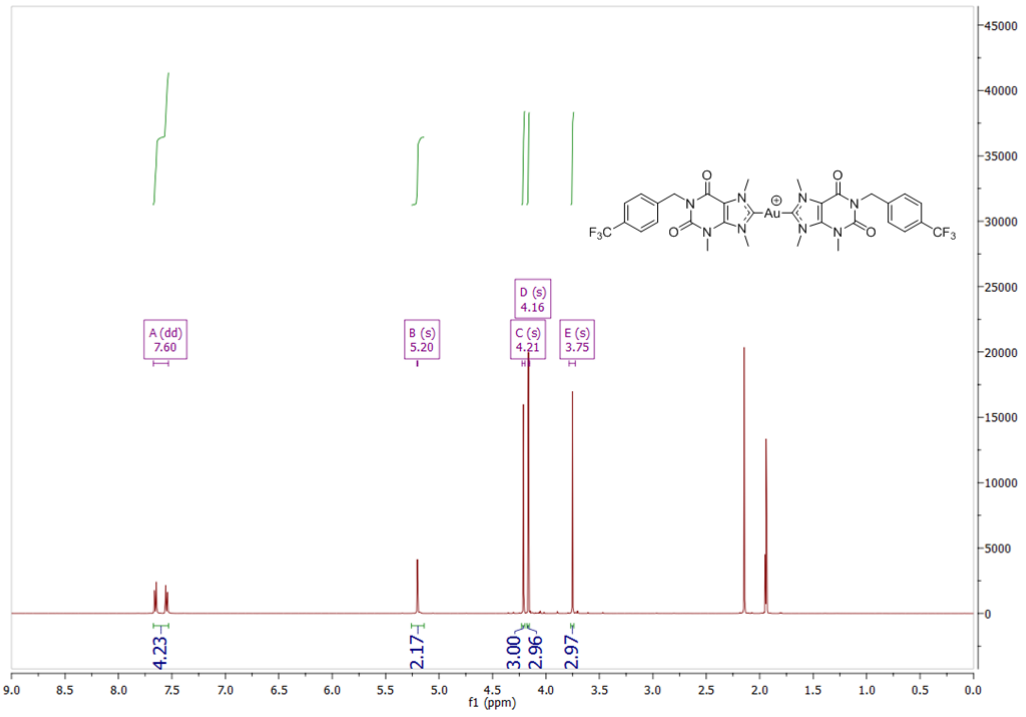



**Figure S20.** $^{1}$H NMR spectrum of **3d** in $CD_3CN$.

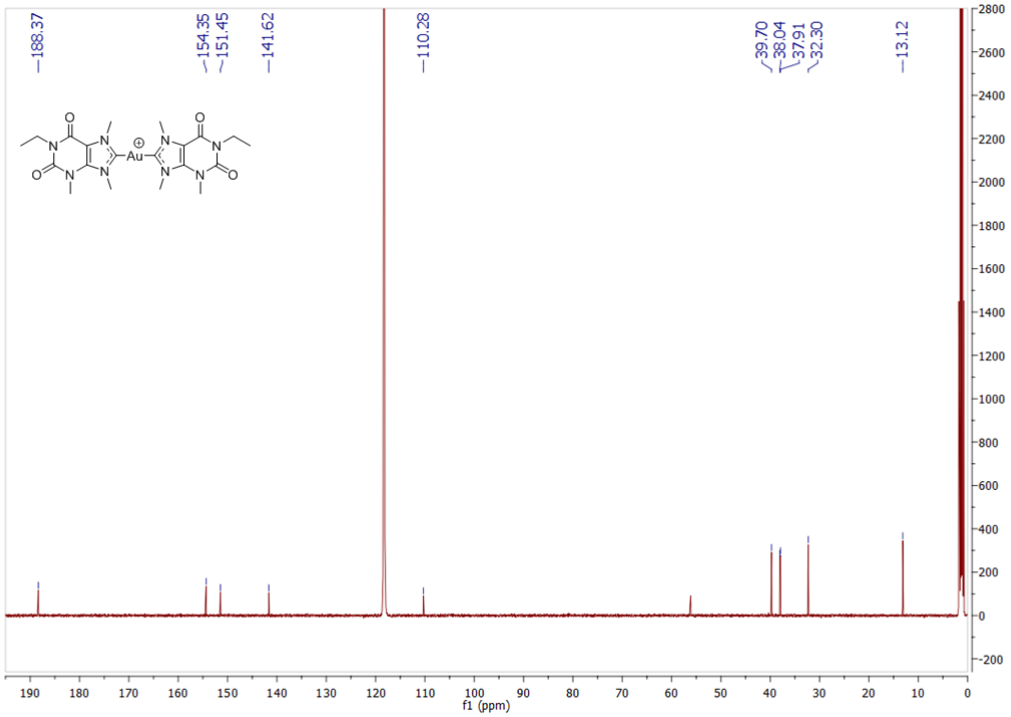



**Figure S21.** $^{13}$C NMR spectrum of **3a** in $CD_3CN$.

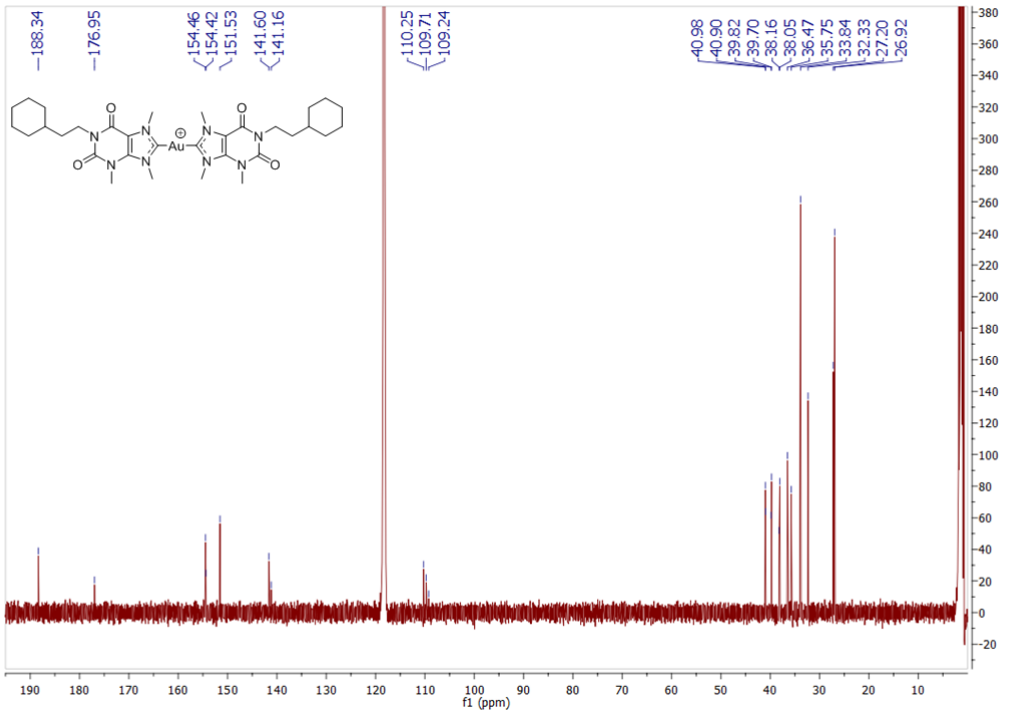



**Figure S22.** $^{13}$C NMR spectrum of **3b** in $CD_3CN$.

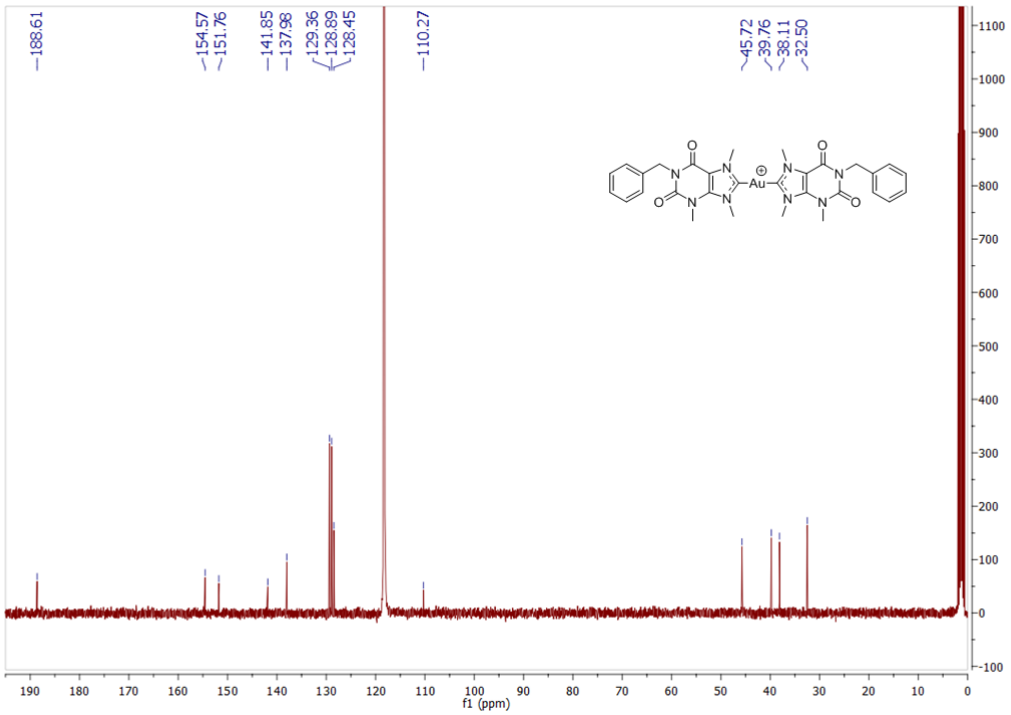



**Figure S23.** $^{13}$C NMR spectrum of **3c** in $CD_3CN$.

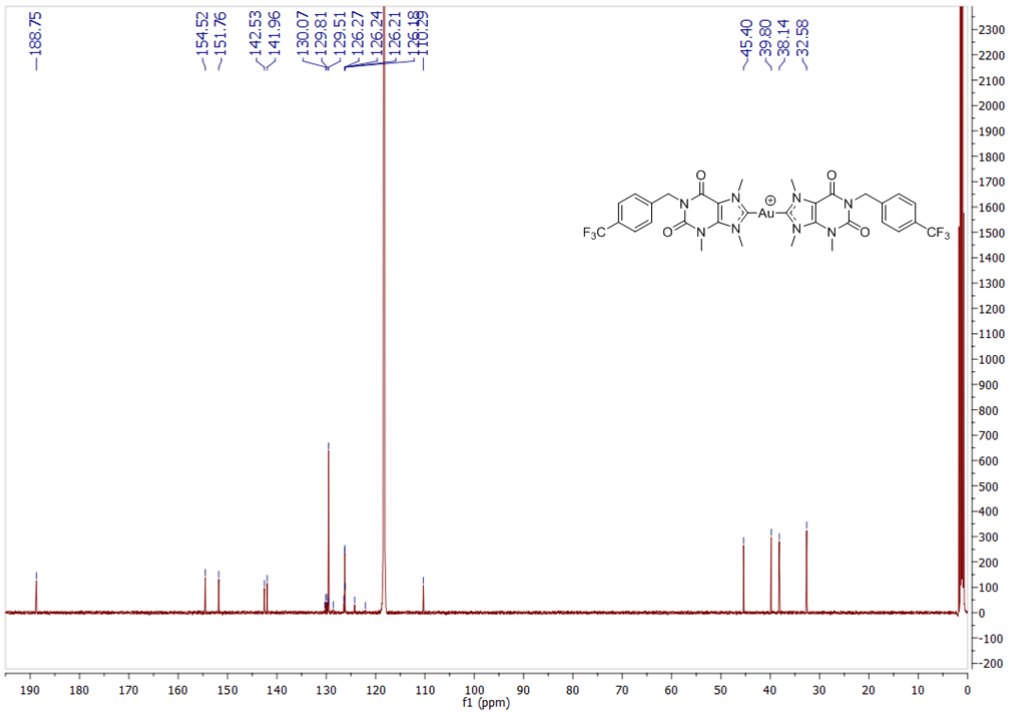



**Figure S24.** $^{13}$C NMR spectrum of **3d** in $CD_3CN$.

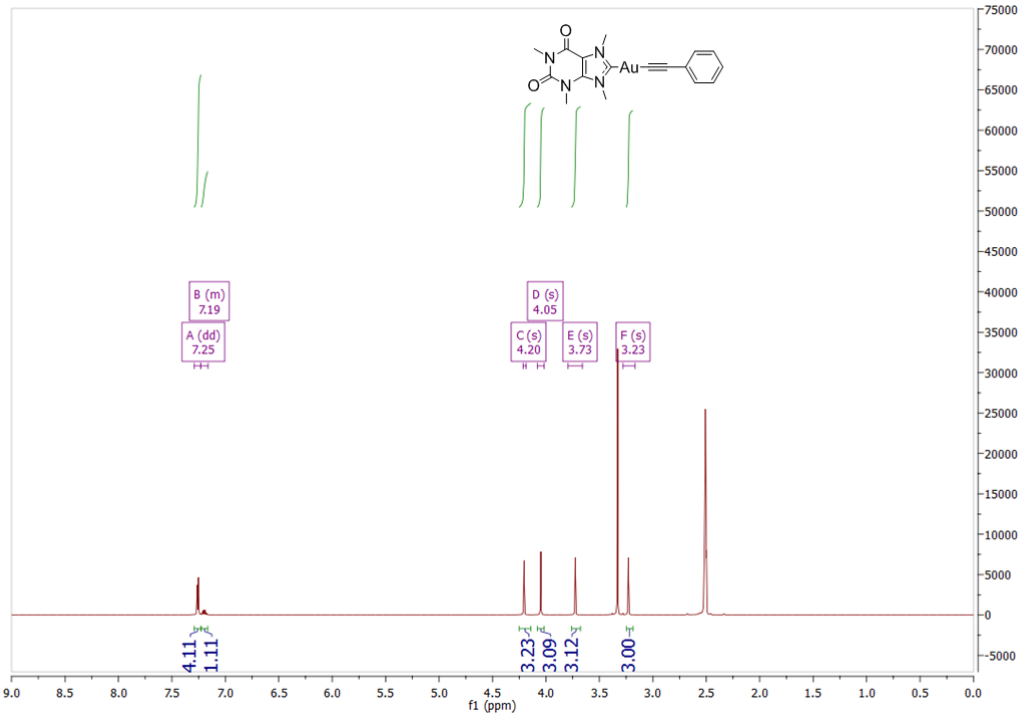



**Figure S25.** $^{1}$H NMR spectrum of **4a** in DMSO.

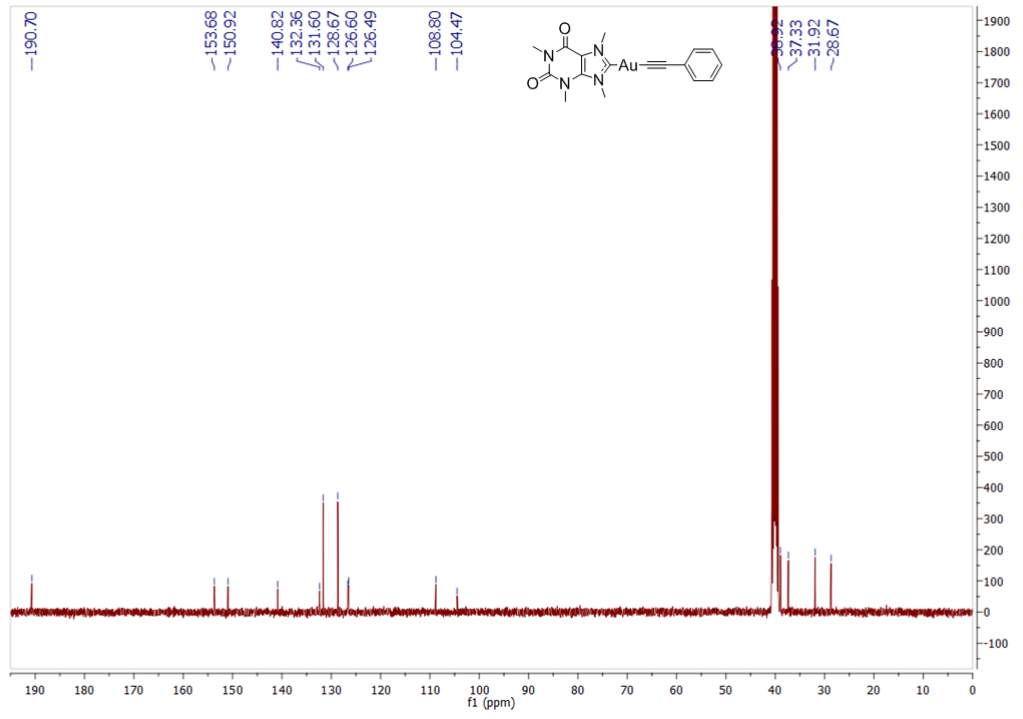



**Figure S26.** $^{13}$C NMR spectrum of **4a** in DMSO.

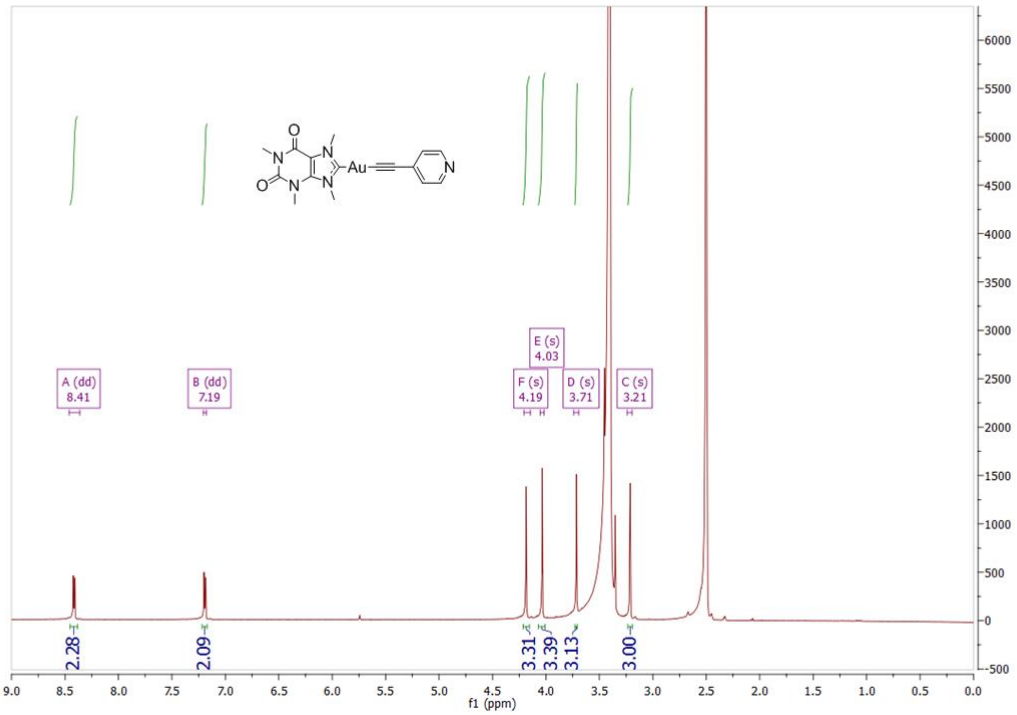



**Figure S27.** $^{1}$H NMR spectrum of **4b** in DMSO.

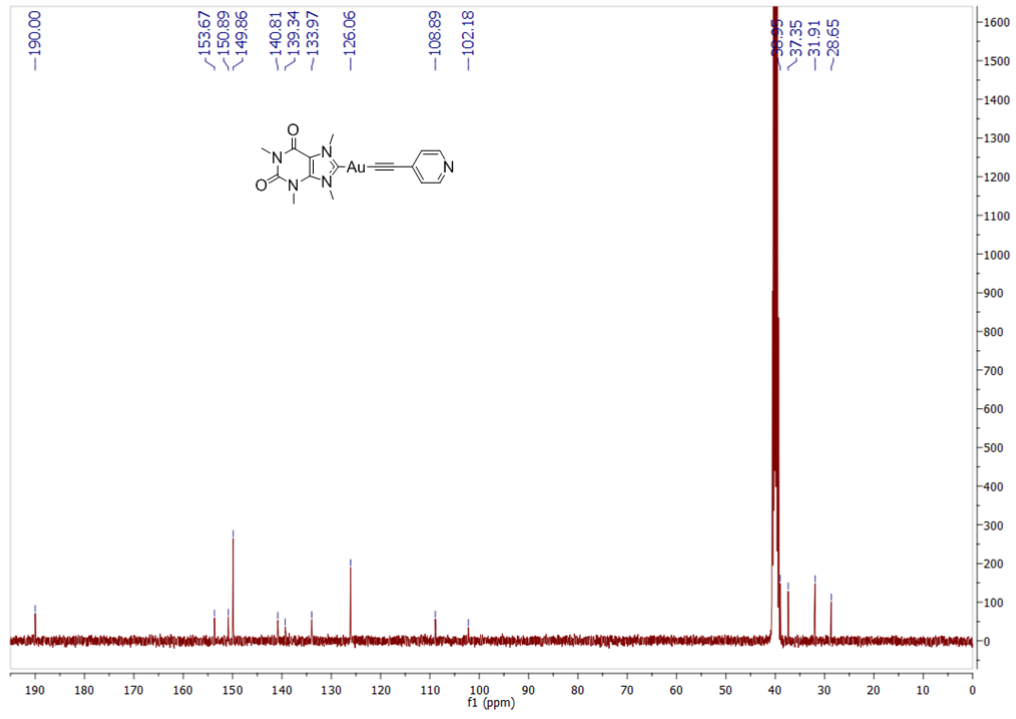



**Figure S28.** $^{13}$C NMR spectrum of **4b** in DMSO.

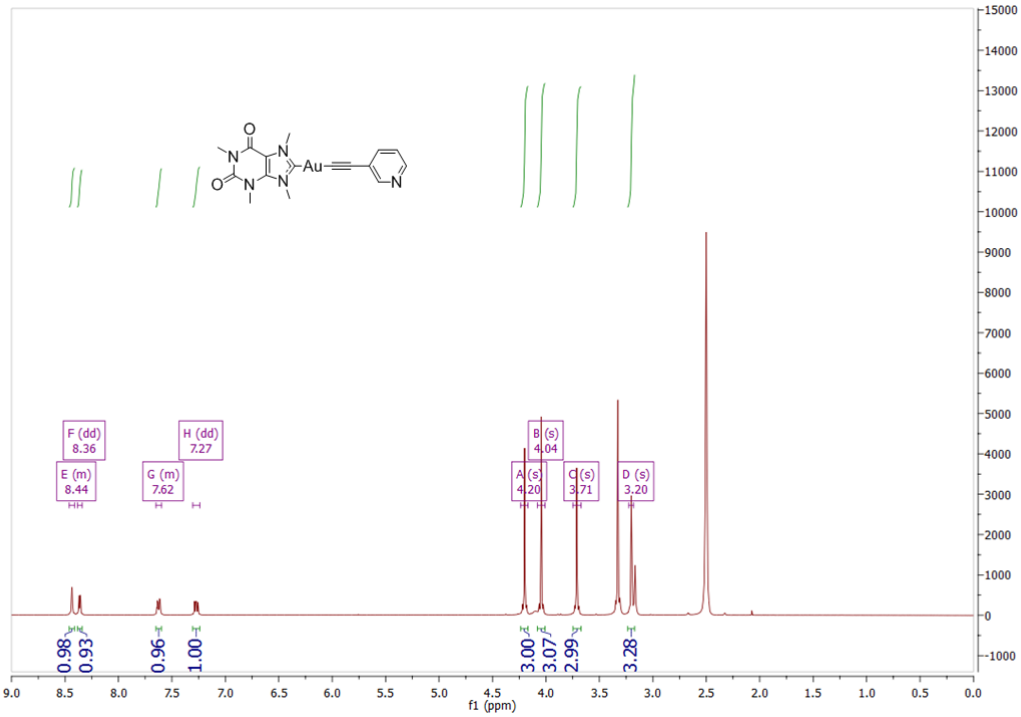



**Figure S29.** $^{1}$H NMR spectrum of **4c** in DMSO.

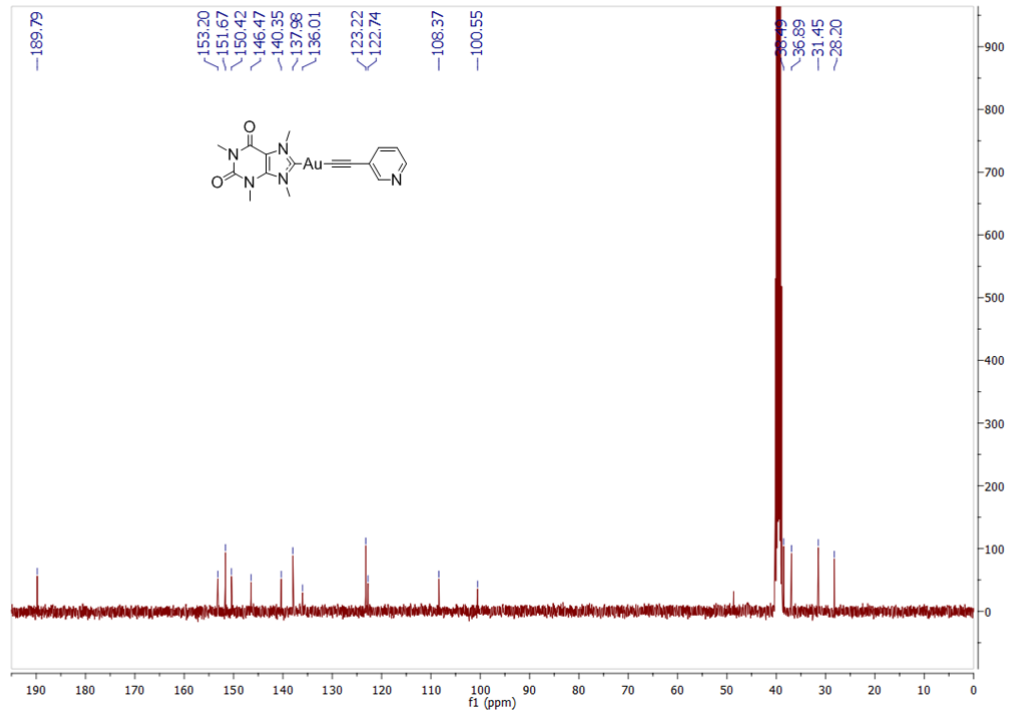



**Figure S30.** $^{13}$C NMR spectrum of **4c** in DMSO.

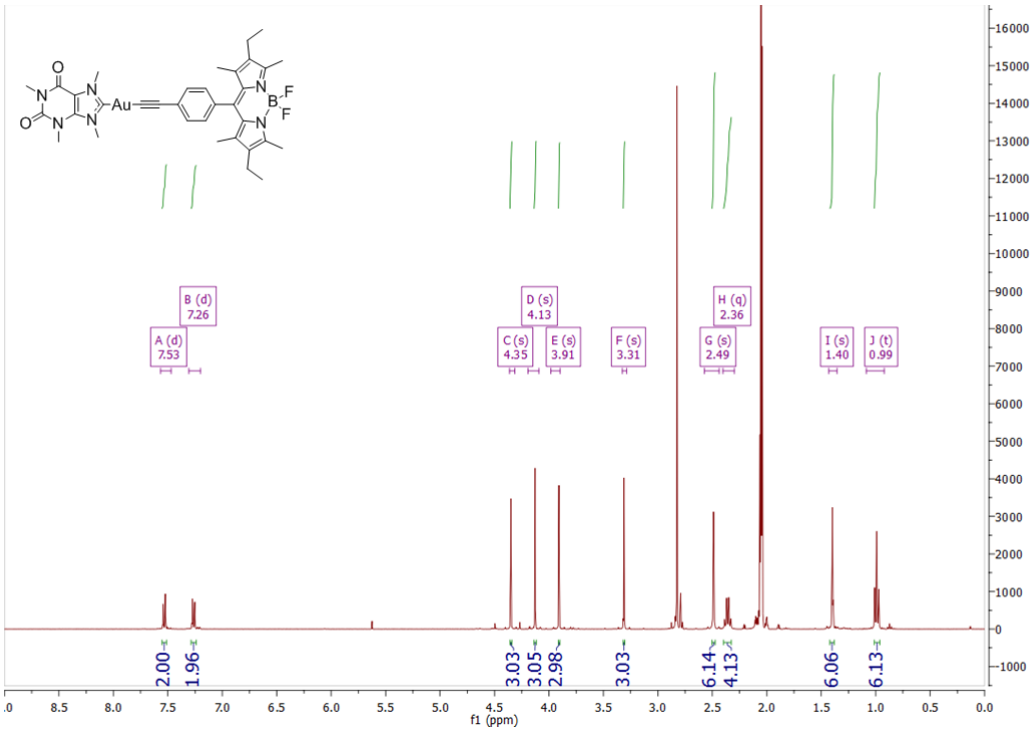



**Figure S31.** $^{1}$H NMR spectrum of **4d** in acetone.

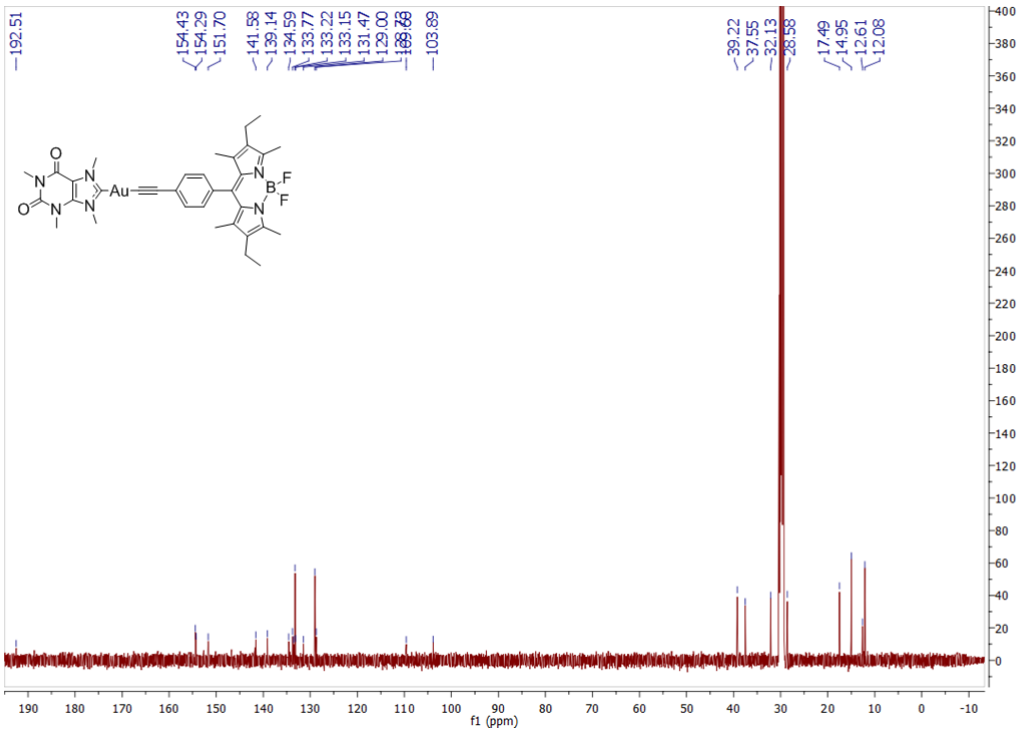



**Figure S32.** $^{13}$C NMR spectrum of **4d** in acetone.

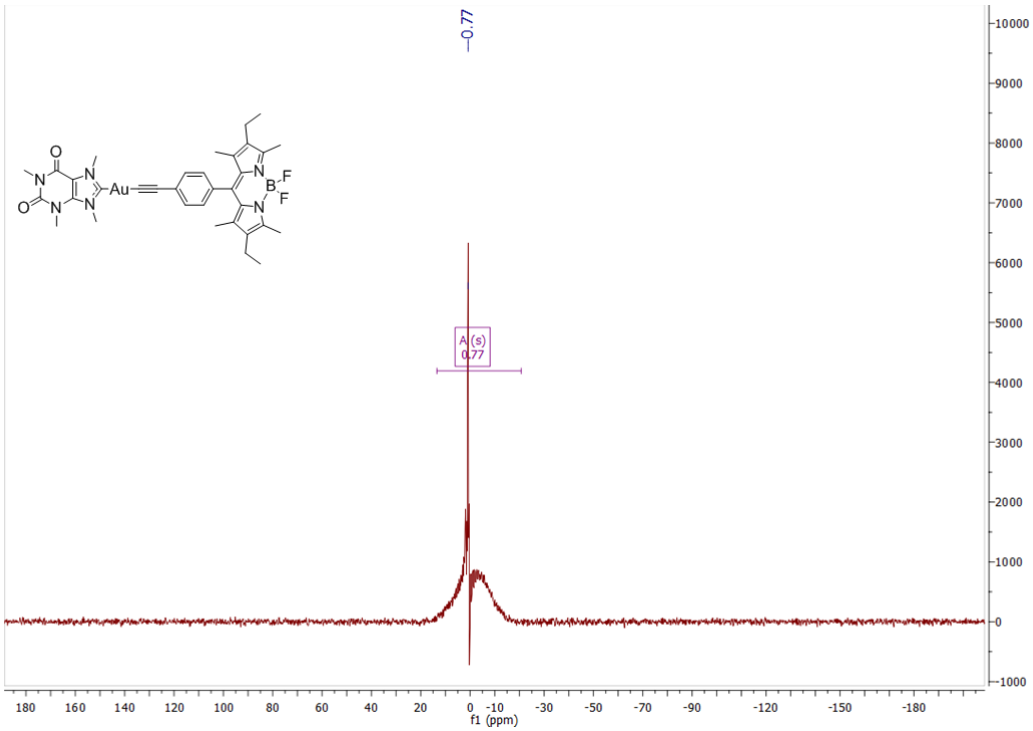



**Figure S33.** $^{11}$B NMR spectrum of **4d** in acetone.

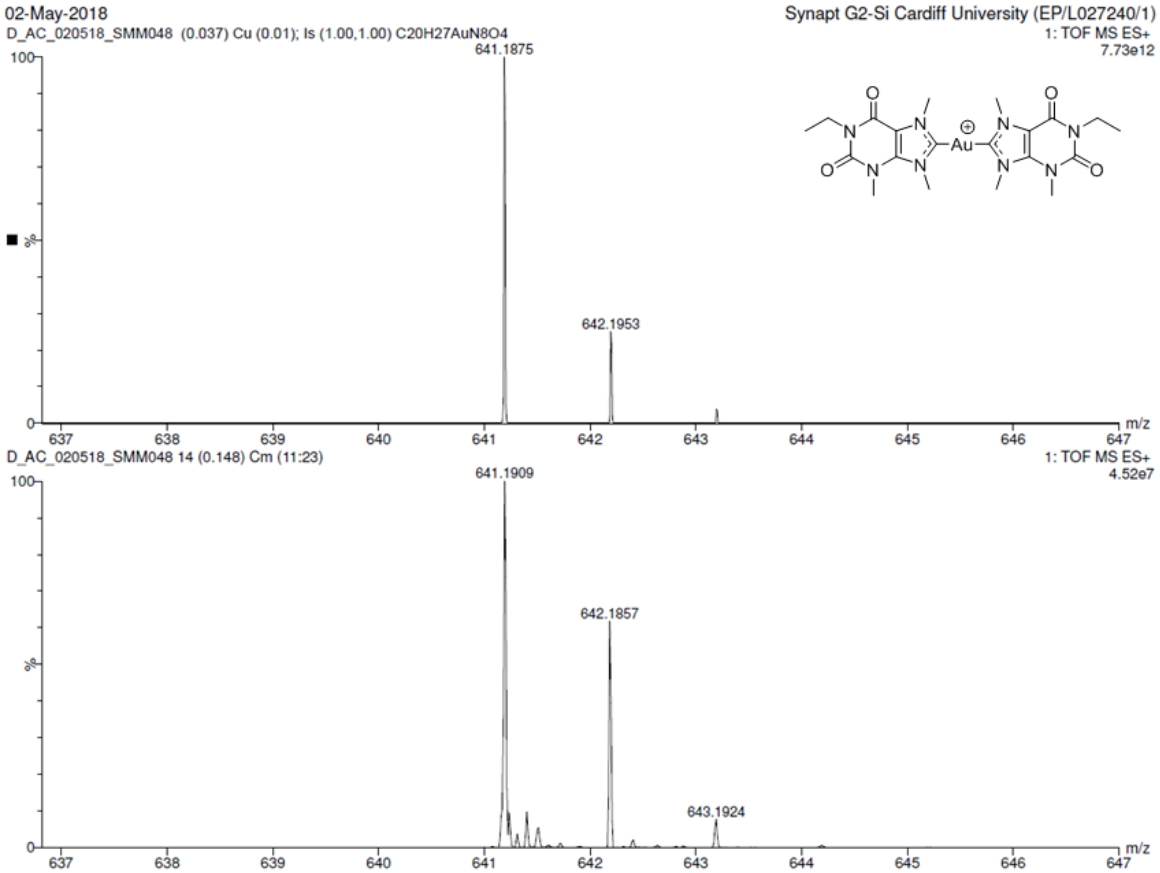



**Figure S34.** ESI-MS simulated (top) and experimental (below) spectra of **3a**.

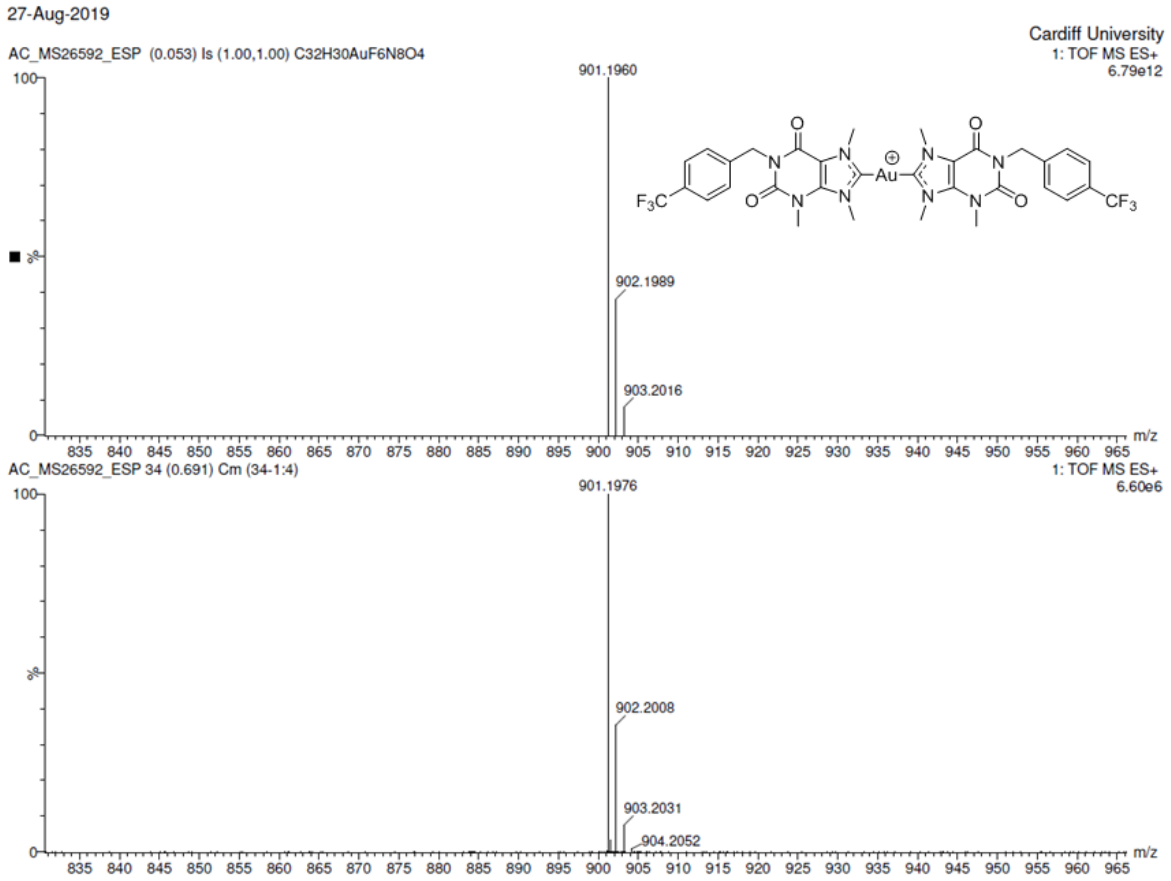



**Figure S35.** ESI-MS simulated (top) and experimental (below) spectra of **3d**.

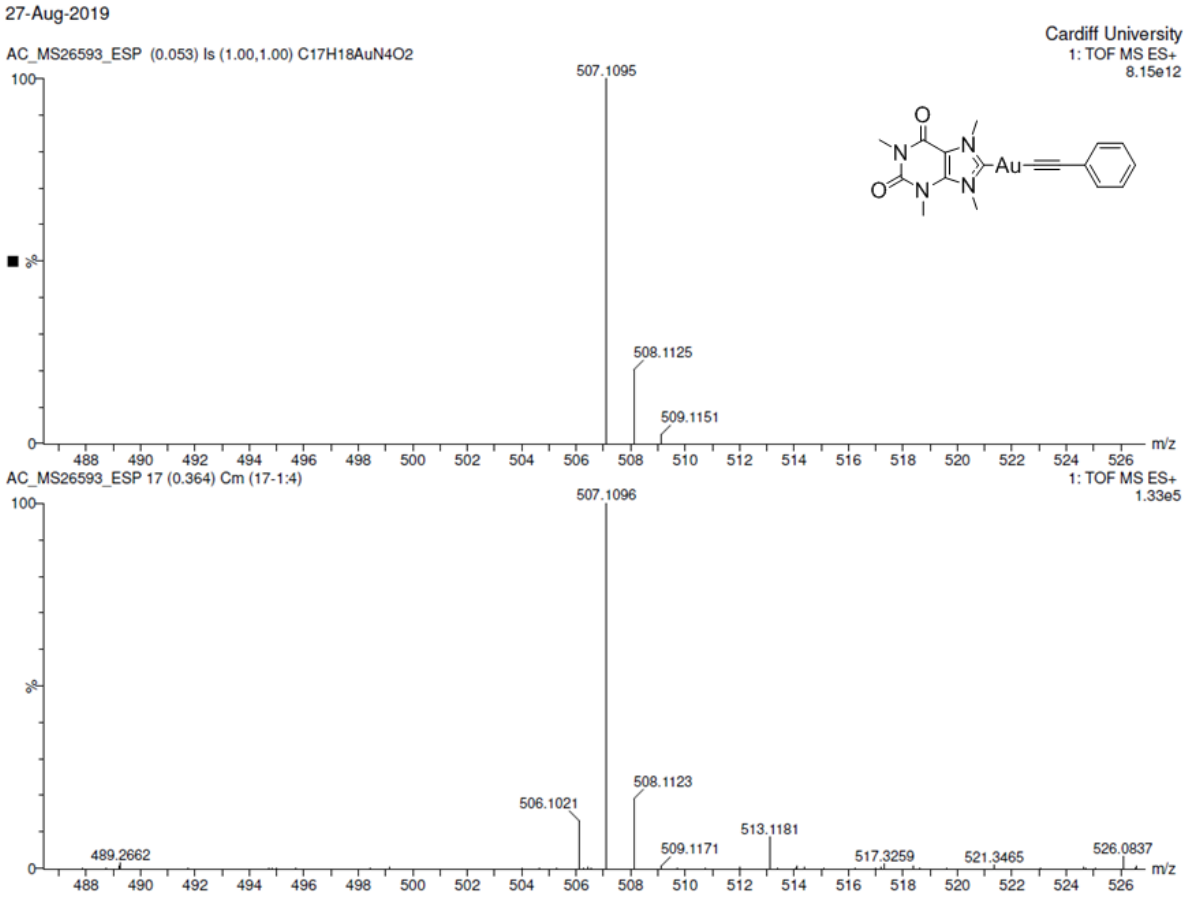



**Figure S36.** ESI-MS simulated (top and middle) and experimental (below) spectra of **4a**.

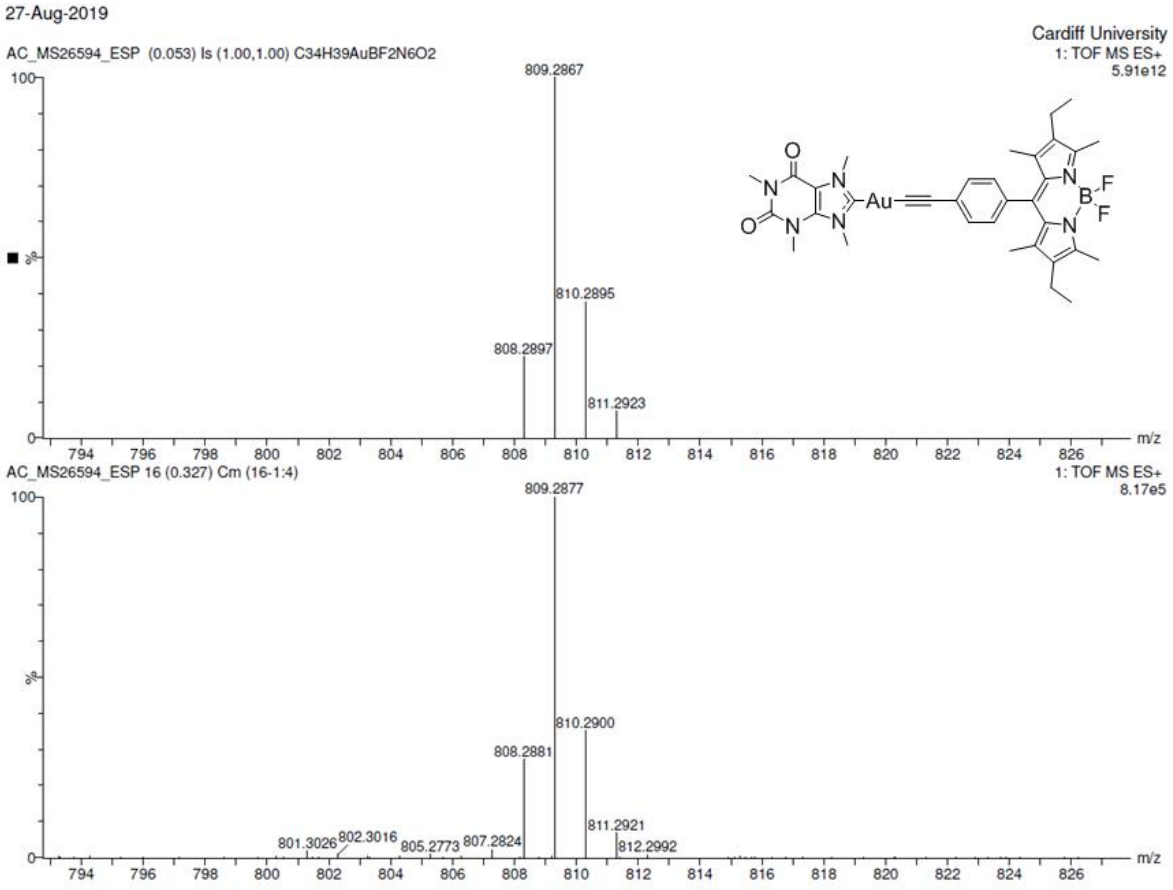



**Figure S37.** ESI-MS simulated (top) and experimental (below) spectra of **4d**.

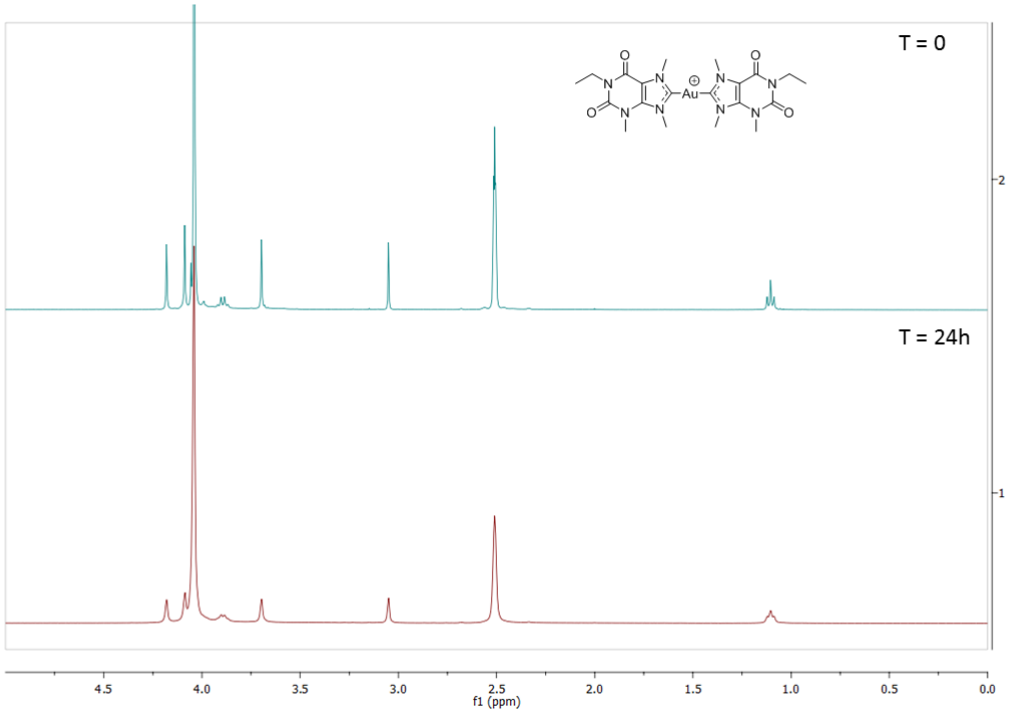



**Figure S38.** $^{1}$H NMR spectra of **3a** at t = 0 (top) and t = 24 h (below) in DMSO-$d_6$ : $D_2O$ (80 : 20).

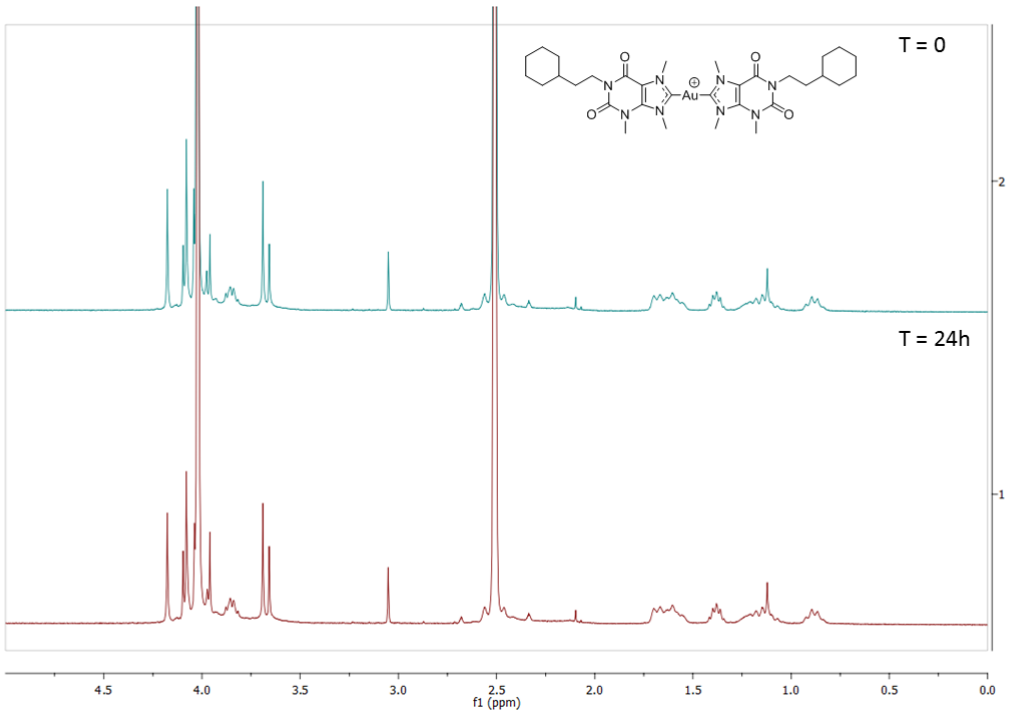



**Figure S39.** $^{1}$H NMR spectra of **3b** at t = 0 (top) and t = 24 h (below) in DMSO-$d_6$ : $D_2O$ (80 : 20).

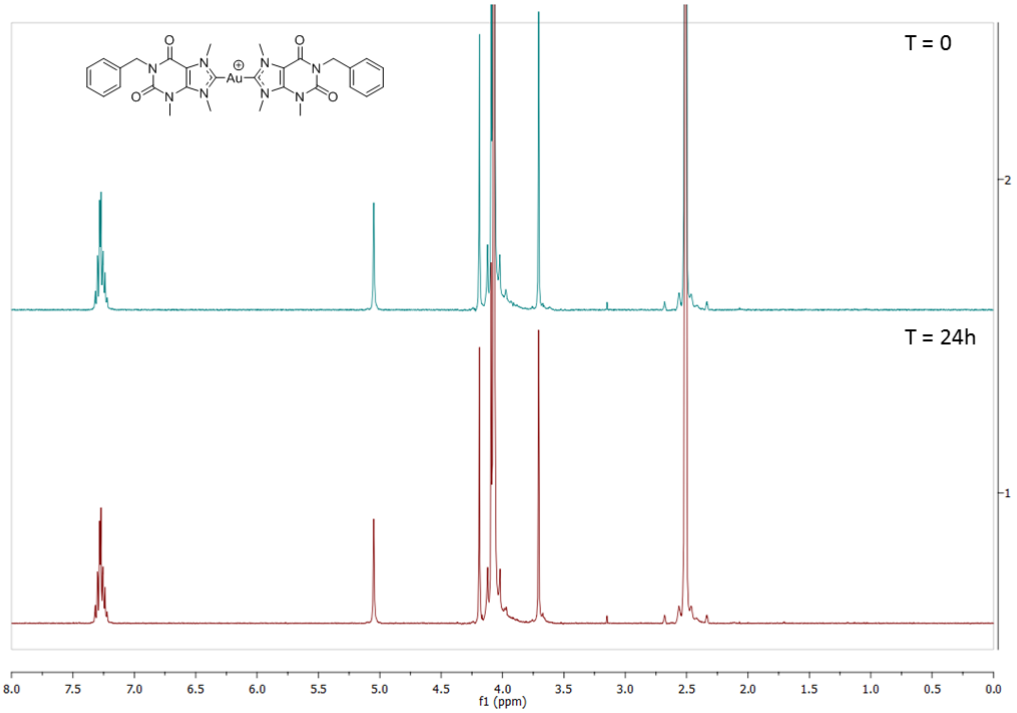



**Figure S40.** $^{1}$H NMR spectra of **3c** at t = 0 (top) and t = 24 h (below) in DMSO-$d_6$ : $D_2O$ (80 : 20).

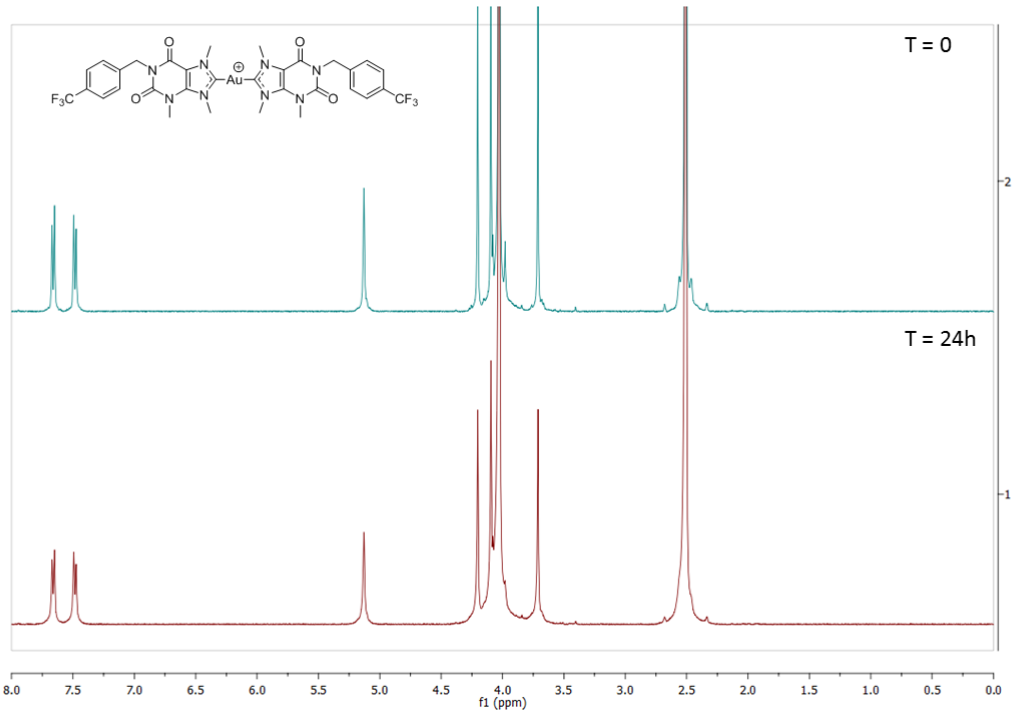



**Figure S41.** $^{1}$H NMR spectra of **3d** at t = 0 (top) and t = 24 h (below) in DMSO-$d_6$ : $D_2O$ (80 : 20).

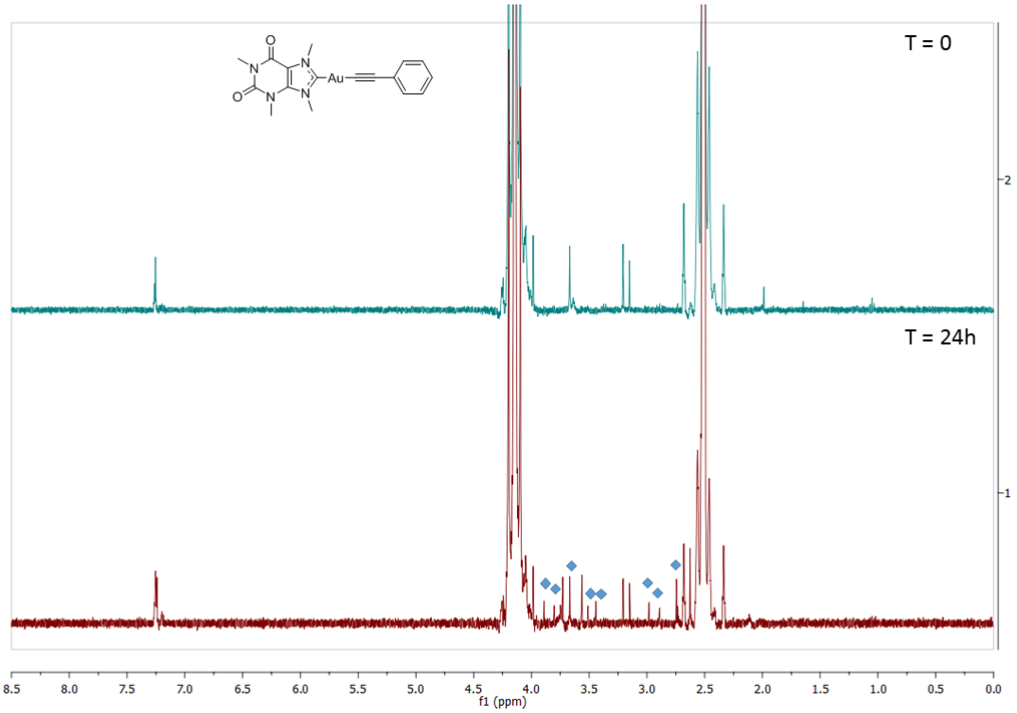



**Figure S42.** $^{1}$H NMR spectra of **4a** at t = 0 (top) and t = 24 h (below) in DMSO-$d_6$ : $D_2O$ (80 : 20). Blue diamonds represent newly formed peaks after 24 hours.

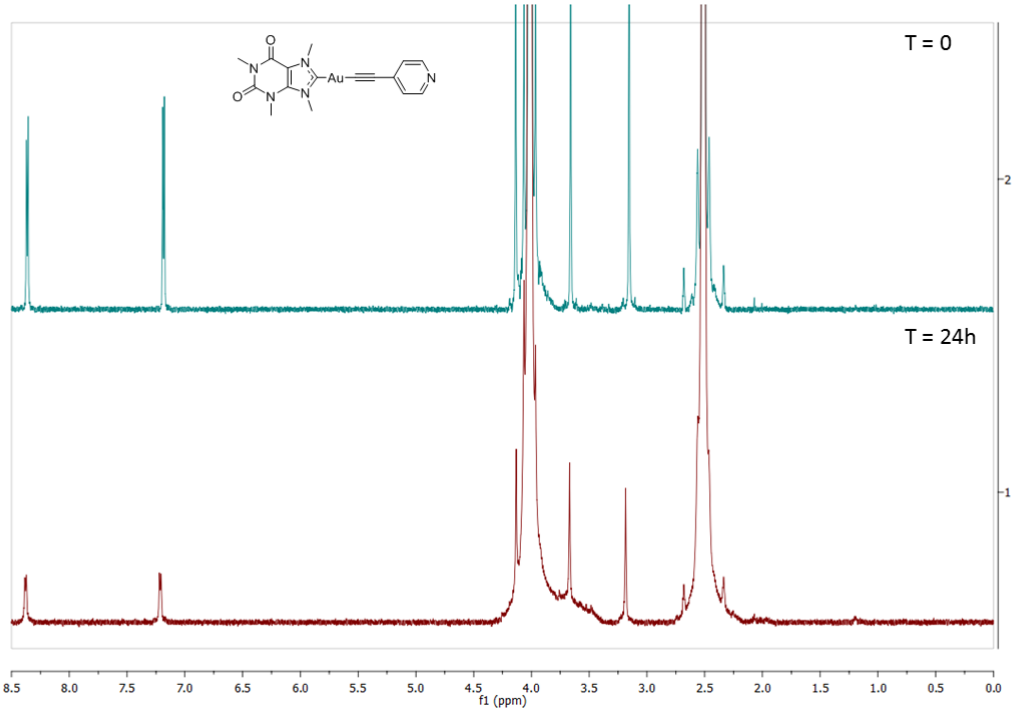



**Figure S43.** $^{1}$H NMR spectra of **4b** at t = 0 (top) and t = 24 h (below) in DMSO-$d_6$ : $D_2O$ (80 : 20).

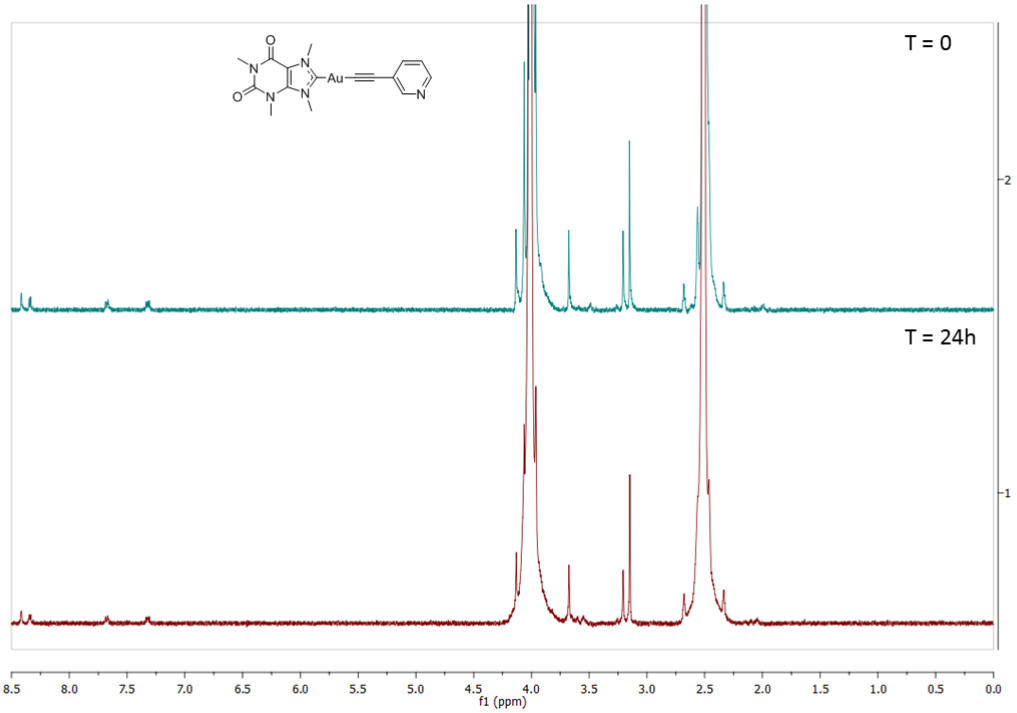



**Figure S44.** $^{1}$H NMR spectra of **4c** at t = 0 (top) and t = 24 h (below) in DMSO-$d_6$ : $D_2O$ (80 : 20).

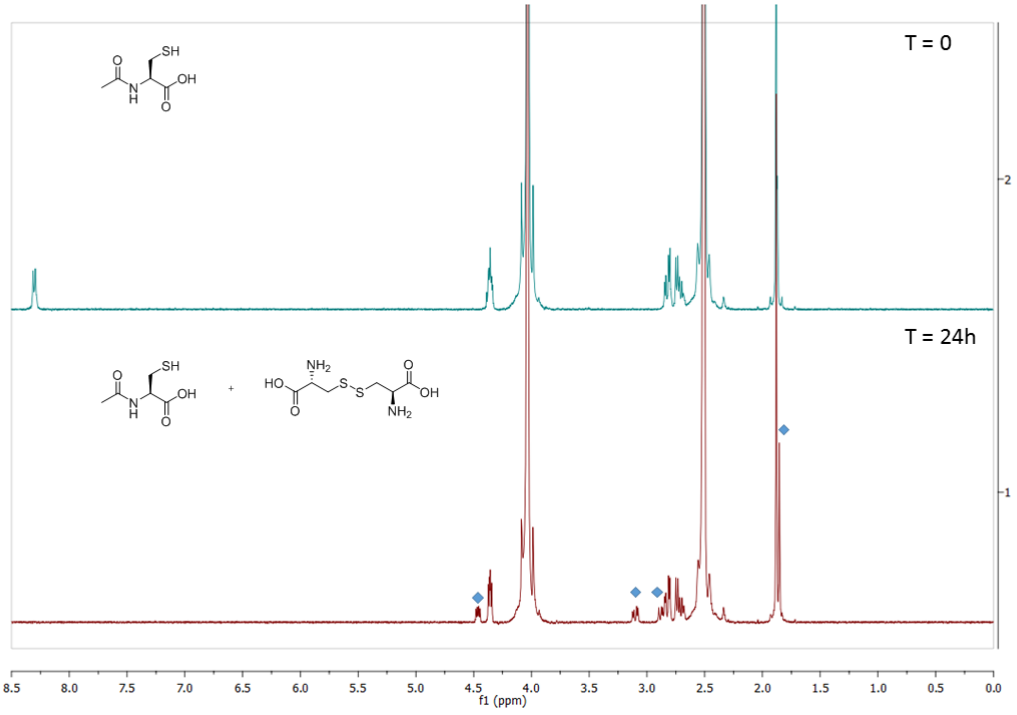



**Figure S45.** $^{1}$H NMR spectra of **N-acetyl cysteine** at t = 0 (top) and t = 24 h (below) in DMSO-$d_6$ : $D_2O$ (80 : 20). Blue diamonds represent newly formed peaks after 24 hours.

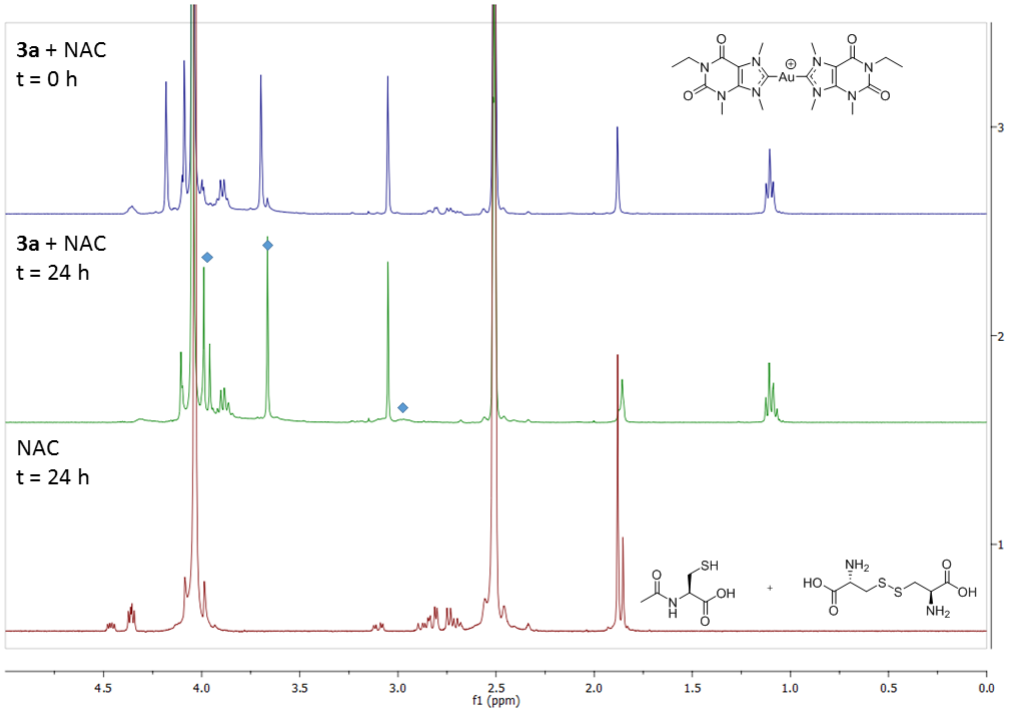



**Figure S46.** $^{1}$H NMR spectra of **3a** in presence of an equimolar amount of N-acetyl cysteine at t = 0 (top) and t = 24 h (middle). For comparison, $^{1}$H NMR spectrum of N-acetyl cysteine after 24 hours is shown below. Blue diamonds represent newly formed peaks after 24 hours.

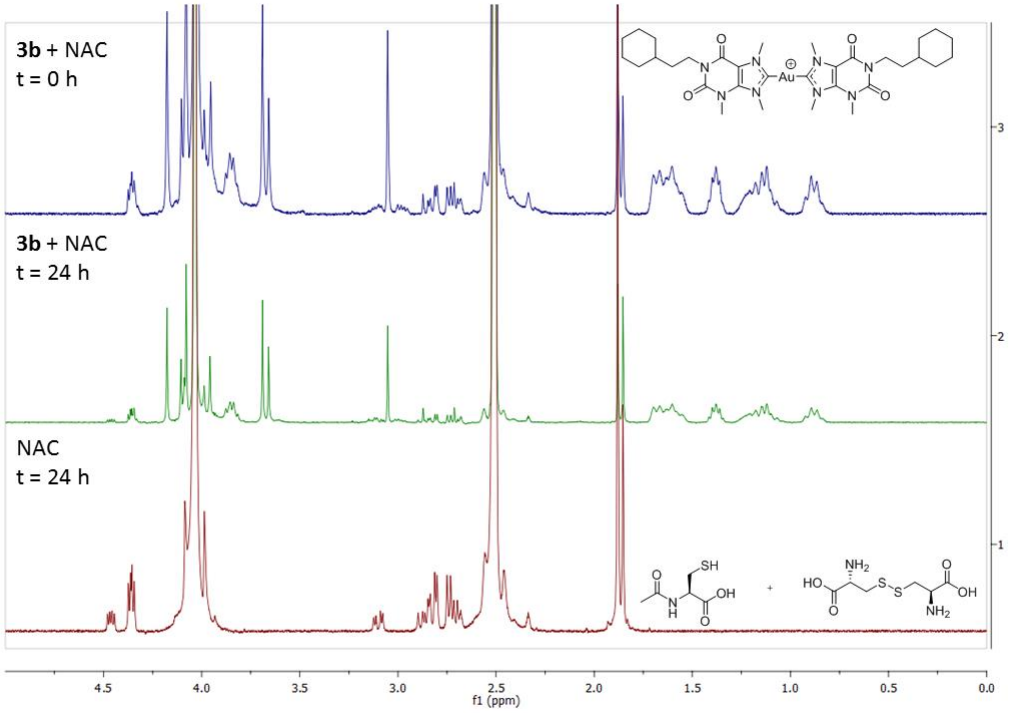



**Figure S47.** $^{1}$H NMR spectra of **3b** in presence of an equimolar amount of N-acetyl cysteine at t = 0 (top) and t = 24 h (middle). For comparison, $^{1}$H NMR spectrum of N-acetyl cysteine after 24 hours is shown below.

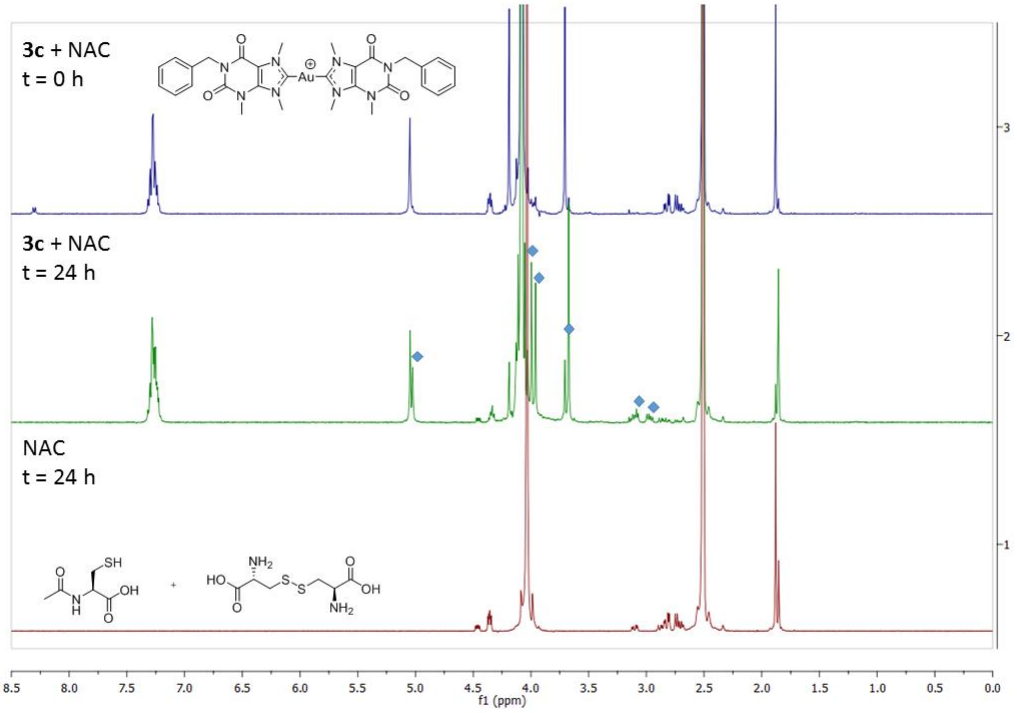



**Figure S48.** $^{1}$H NMR spectra of **3c** in presence of an equimolar amount of N-acetyl cysteine at t = 0 (top) and t = 24 h (middle). For comparison, $^{1}$H NMR spectrum of N-acetyl cysteine after 24 hours is shown below. Blue diamonds represent newly formed peaks after 24 hours.

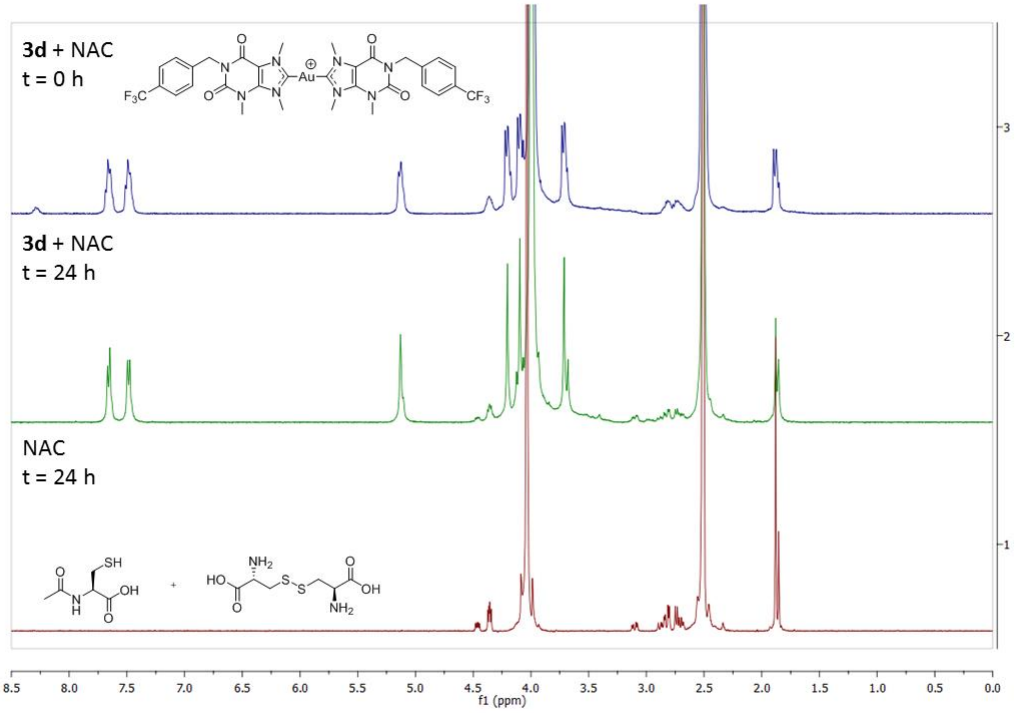



**Figure S49.** $^{1}$H NMR spectra of **3d** in presence of an equimolar amount of N-acetyl cysteine at T = 0 (top) and T = 24h (middle). For comparison, $^{1}$H NMR spectrum of N-acetyl cysteine after 24 hours is shown below.

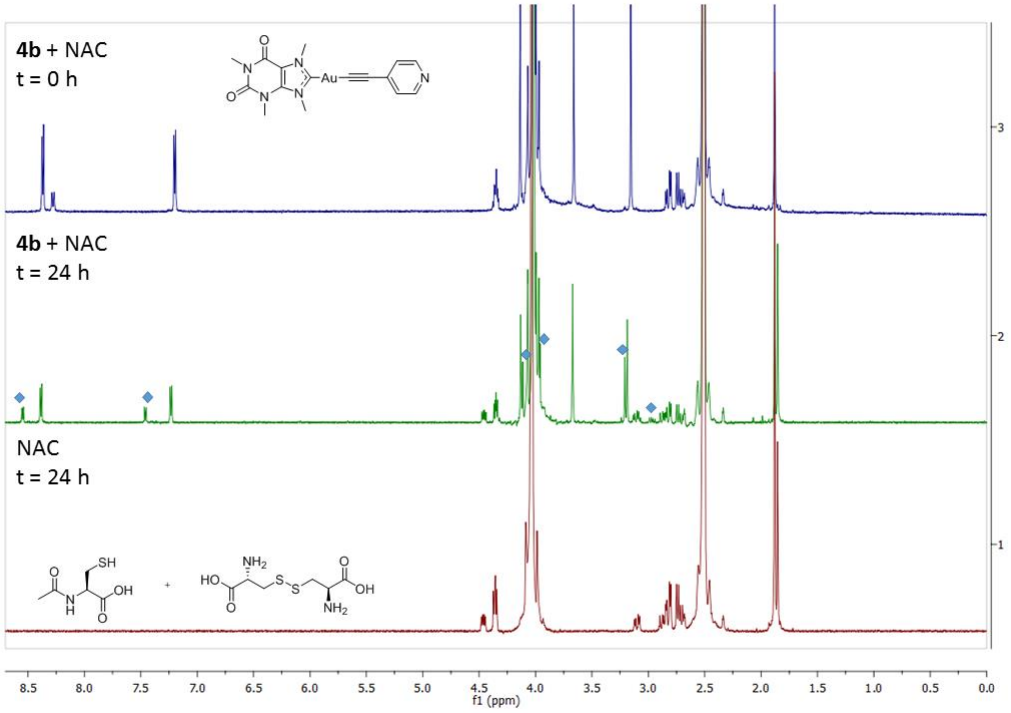



**Figure S50.** $^{1}$H NMR spectra of **4b** in presence of an equimolar amount of N-acetyl cysteine at t = 0 (top) and t = 24 h (middle). For comparison, $^{1}$H NMR spectrum of N-acetyl cysteine after 24 hours is shown below. Blue diamonds represent newly formed peaks after 24 hours.

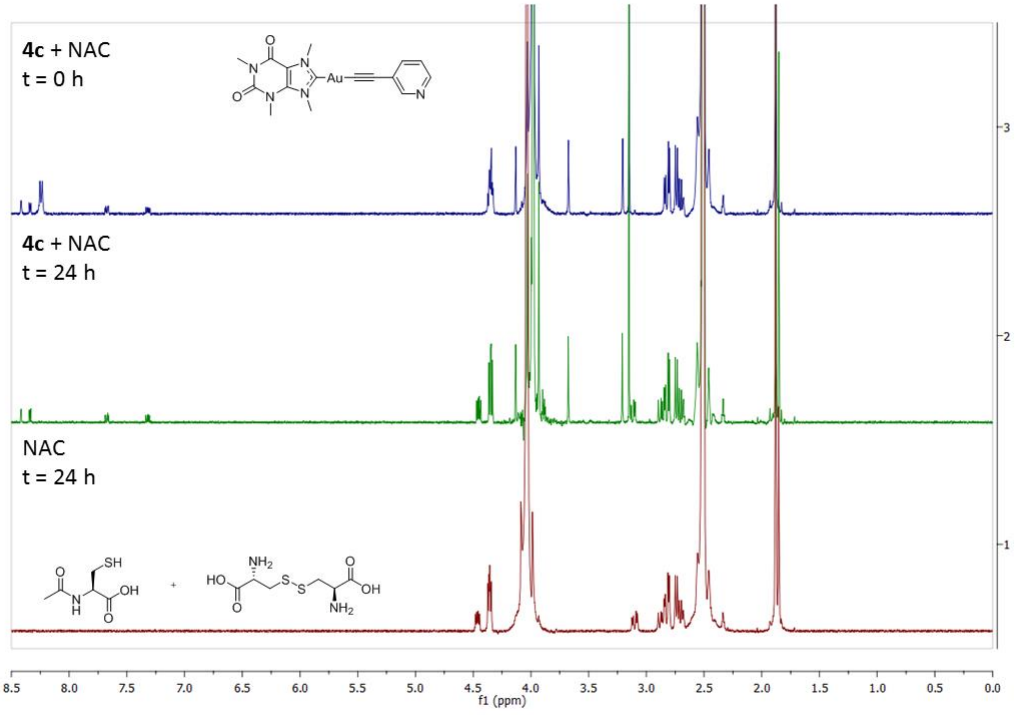



**Figure S51.** $^{1}$H NMR spectra of **4c** in presence of an equimolar amount of N-acetyl cysteine at t = 0 (top) and t = 24 h (middle). For comparison, $^{1}$H NMR spectrum of N-acetyl cysteine after 24 hours is shown below.

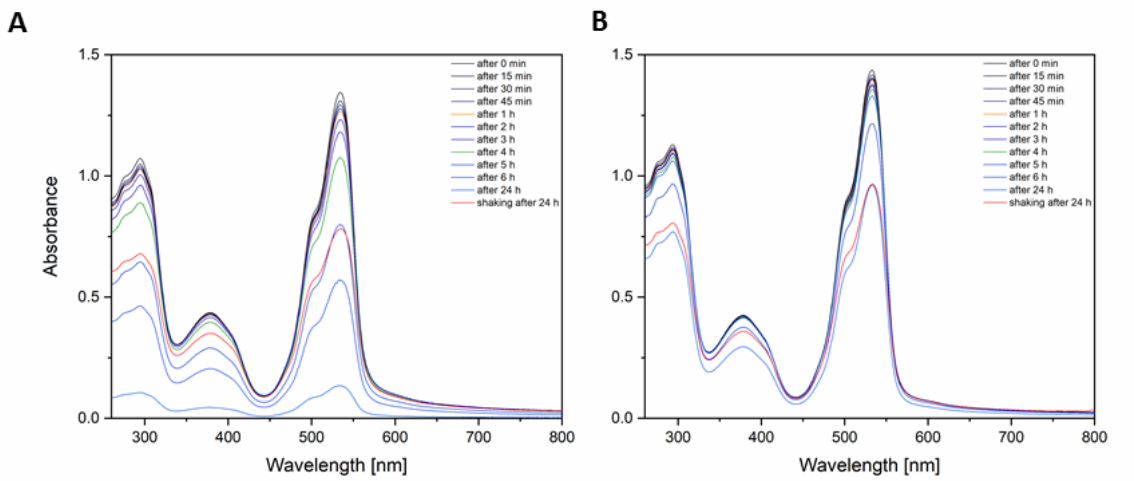



**Figure S52**. UV-visible spectra of **4d** (40.5 µM) in 1x PBS (left); and in water (right) recorded over 24 h and shaken cuvette afterwards.

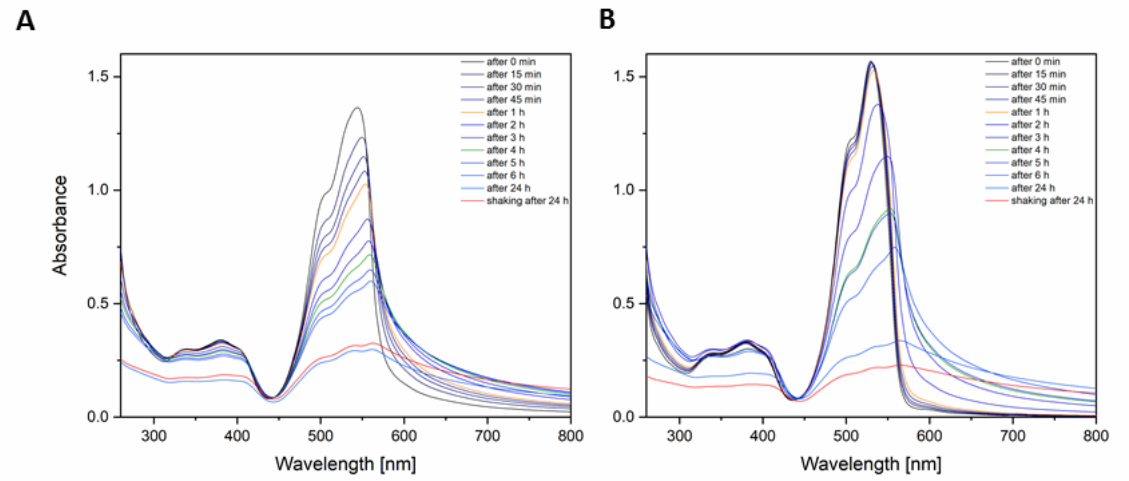



**Figure S53**. UV-visible spectra of BODIPY-alkyne ligand (60 µM) in 1x PBS (left); and in biological water (right) recorded over 24 h and shaken cuvette afterwards.

**Table S1.** $\Delta T_m$ of the investigated Au(I) NHC complexes for the selected DNA G-quadruplexes.

/ means no variation with respect to the DNA melting temperature.

| | $\Delta T_m$ (°C ) | | |
|---|---|---|---|
| | hTelo | *C-KIT1* | *hTERT* |
| **AuTMX$_2$** | 13.1 ± 1.8 | 8.8 ± 1.8 | 2.1 ± 0.3 |
| **AuTMXI** | 3.2 ± 0.6 | 4.0 ± 0.1 | 1.5 ± 0.2 |
| **3a** | 5.7 ± 1.0 | 3.4 ± 1.2 | 1.6 ± 0.02 |
| **3b** | / | / | / |
| **3c** | 2.1 ± 0.4 | / | / |
| **3d** | / | / | / |
| **4a** | / | / | / |
| **4b** | / | / | / |
| **4c** | / | / | / |

Sample ID: **3a**

# Crystal Data and Experimental

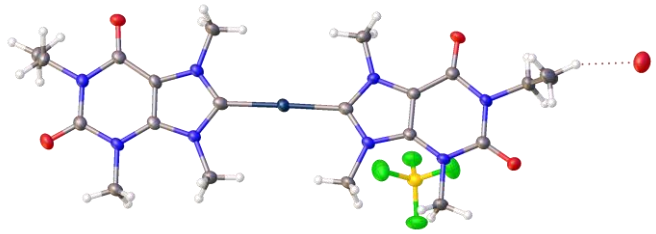


**Figure S54:** Thermal ellipsoids drawn at the 50% probability level.

**Crystal Data.** $C_{20}H_{28}AuBF_4N_8O_{4.11}$, $M_r$ = 730.04, monoclinic, $P2_1/n$ (No. 14), a = 10.67910(10) Å, b = 15.81980(10) Å, c = 15.46860(10) Å, $\beta$ = 104.5940(10)°, $\alpha = \gamma = 90°$, $V$ = 2528.97(3) Å$^3$, $T$ = 100.0(7) K, $Z$ = 4, $Z'$ = 1, $\mu$(Cu$K_\alpha$) = 11.607 mm$^{-1}$, 44235 reflections measured, 4513 unique ($R_{int}$ = 0.0549) which were used in all calculations. The final $wR_2$ was 0.0662 (all data) and $R_1$ was 0.0250 (I > 2(I)).

**Table S2**

| **Compound** | **3a** |
|---|---|
| Formula | $C_{20}H_{28}AuBF_4N_8O_{4.11}$ |
| $D_{calc.}$/ g cm$^{-3}$ | 1.917 |
| $\mu$/mm$^{-1}$ | 11.607 |
| Formula Weight | 730.04 |
| Colour | colourless |
| Shape | irregular |
| Size/mm$^3$ | 0.260×0.110×0.060 |
| $T$/K | 100.0(7) |
| Crystal System | monoclinic |
| Space Group | $P2_1/n$ |
| $a$/Å | 10.67910(10) |
| $b$/Å | 15.81980(10) |
| $c$/Å | 15.46860(10) |
| $\alpha$/° | 90 |
| $\beta$/° | 104.5940(10) |
| $\gamma$/° | 90 |
| V/Å$^3$ | 2528.97(3) |
| $Z$ | 4 |
| $Z'$ | 1 |
| Wavelength/Å | 1.54184 |
| Radiation type | Cu$K_\alpha$ |
| $\Theta_{min}$/° | 4.546 |
| $\Theta_{max}$/° | 67.075 |
| Measured Refl. | 44235 |
| Independent Refl. | 4513 |
| Reflections with I > 2(I) | 4491 |
| $R_{int}$ | 0.0549 |
| Parameters | 361 |
| Restraints | 0 |
| Largest Peak | 1.556 |
| Deepest Hole | -0.710 |
| GooF | 1.150 |
| $wR_2$ (all data) | 0.0662 |
| $wR_2$ | 0.0661 |
| $R_1$ (all data) | 0.0251 |
| $R_1$ | 0.0250 |

## Structure Quality Indicators

| | | | | |
|---|---|---|---|---|
| **Reflections:** | d min (Cu) 0.84 | I/σ 48.7 | Rint 5.49% | complete 100% (IUCr) 100% |
| **Refinement:** | Shift 0.001 | Max Peak 1.6 | Min Peak -0.7 | GooF 1.150 |

A colourless irregular-shaped crystal with dimensions 0.260×0.110×0.060 $mm^3$ was mounted on a MITIGEN holder in perfluoroether oil. Data were collected using a Rigaku 007HF diffractometer equipped with Varimax confocal mirrors and an AFC11 goniometer and HyPix 6000HE detector, and equipped with an Oxford Cryosystems low-temperature device operating at $T$ = 100.0(7) K.

Data were measured using $\omega$ scans of 0.5 ° per frame for 0.5 s using $CuK_\alpha$ radiation. The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.40.39a, 2019). The maximum resolution that was achieved was $\Theta$ = 67.075° (0.84 Å).

The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.40.39a, 2019) and the unit cell was refined using **CrysAlisPro** (Rigaku, V1.171.40.39a, 2019) on 32078 reflections, 73% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku, V1.171.40.39a, 2019). The final completeness is 99.80 % out to 67.075° in $\Theta$.

A multi-scan absorption correction was performed using CrysAlisPro 1.171.40.39a (Rigaku Oxford Diffraction, 2019) using spherical harmonics as implemented in SCALE3 ABSPACK. The absorption coefficient $\mu$ of this material is 11.607 $mm^{-1}$ at this wavelength ($\lambda$ = 1.54184 Å) and the minimum and maximum transmissions are 0.331 and 1.000.

The structure was solved and the space group $P2_1/n$ (# 14) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2014/7 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. There was a little density left in between some molecules, and this was assumed to be some water. The occupancy of the water oxygen atom was refined to about 0.11(1). The water hydrogen atoms were omitted.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

## Reflection Statistics

| | | | |
|---|---|---|---|
| Total reflections (after filtering) | 45307 | Unique reflections | 4513 |
| Completeness | 0.998 | Mean I/$\sigma$ | 46.71 |
| $hkl_{max}$ collected | (12, 18, 18) | $hkl_{min}$ collected | (-12, -18, -18) |
| $hkl_{max}$ used | (12, 18, 18) | $hkl_{min}$ used | (-12, 0, 0) |
| Lim $d_{max}$ collected | 100.0 | Lim $d_{min}$ collected | 0.77 |
| $d_{max}$ used | 15.82 | $d_{min}$ used | 0.84 |
| Friedel pairs | 6315 | Friedel pairs merged | 1 |
| Inconsistent equivalents | 69 | $R_{int}$ | 0.0549 |
| $R_{sigma}$ | 0.0205 | Intensity transformed | 0 |
| Omitted reflections | 0 | Omitted by user (OMIT hkl) | 0 |
| Multiplicity | (3852, 3830, 2820, 1699, 1339, 891, 483, 221, 112, 33, 1) | Maximum multiplicity | 25 |
| Removed systematic absences | 1072 | Filtered off (Shel/OMIT) | 0 |

**Table S3**: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **3a**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$.

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| Au1 | 6703.3(2) | 4830.7(2) | 4419.9(2) | 20.10(7) |
| O1 | 1210(2) | 8069.8(16) | 2908.3(16) | 32.2(5) |
| O2 | 4547(2) | 8112.5(15) | 5430.9(15) | 29.7(5) |
| O3 | 10730(2) | 878.5(16) | 4102.3(16) | 32.9(6) |
| O4 | 11546(2) | 2926.6(15) | 6251.8(15) | 29.0(5) |
| N1 | 2845(3) | 8064.1(17) | 4187.1(17) | 22.7(5) |
| N2 | 2572(3) | 6937.5(17) | 3130.8(17) | 22.0(5) |
| N3 | 4338(2) | 5871.9(16) | 3535.4(16) | 19.2(5) |
| N4 | 5458(3) | 6476.1(17) | 4753.7(17) | 21.7(5) |
| N5 | 11091(3) | 1871.1(17) | 5195.5(17) | 23.7(6) |
| N6 | 9175(3) | 1883.9(17) | 3997.9(17) | 21.6(5) |
| N7 | 7809(2) | 3144.0(17) | 4050.7(16) | 20.0(5) |
| N8 | 9046(2) | 3746.3(17) | 5223.4(16) | 20.1(5) |
| C1 | 2158(3) | 7718(2) | 3378(2) | 23.8(7) |
| C2 | 4000(3) | 7751(2) | 4743(2) | 23.3(7) |
| C3 | 4384(3) | 6978(2) | 4411(2) | 21.2(6) |
| C4 | 3697(3) | 6601(2) | 3647(2) | 19.9(6) |
| C5 | 5435(3) | 5802(2) | 4230(2) | 22.1(6) |
| C6 | 2442(3) | 8912(2) | 4428(2) | 27.8(7) |
| C7 | 3282(4) | 9598(2) | 4187(2) | 30.1(7) |
| C8 | 1891(3) | 6583(2) | 2257(2) | 27.6(7) |
| C9 | 3968(4) | 5215(2) | 2848(2) | 26.0(7) |
| C10 | 6478(3) | 6658(2) | 5563(2) | 28.2(7) |
| C11 | 10359(3) | 1508(2) | 4408(2) | 25.0(7) |
| C12 | 10824(3) | 2633(2) | 5577(2) | 22.4(7) |
| C13 | 9637(3) | 2997(2) | 5082(2) | 20.0(6) |
| C14 | 8861(3) | 2630(2) | 4337(2) | 20.1(6) |
| C15 | 7934(3) | 3844(2) | 4588(2) | 22.0(6) |
| C16 | 12294(3) | 1421(2) | 5640(2) | 32.3(8) |
| C17 | 12018(5) | 643(3) | 6125(3) | 46.7(11) |
| C18 | 8471(3) | 1542(2) | 3124(2) | 29.6(7) |
| C19 | 9580(3) | 4355(2) | 5929(2) | 27.1(7) |
| C20 | 6721(3) | 3042(2) | 3252(2) | 26.1(7) |
| F1 | 9337(2) | 3814.9(16) | 2994.5(15) | 42.5(5) |
| F2 | 11336(2) | 4218.1(14) | 2919.2(13) | 34.3(5) |
| F3 | 10971(2) | 2852.0(15) | 3252.1(16) | 42.6(5) |
| F4 | 10133(2) | 3347.6(16) | 1857.3(14) | 40.7(5) |
| B1 | 10436(4) | 3562(3) | 2754(2) | 24.7(7) |
| O5 | 14250(30) | -582(17) | 6698(19) | 48(10) |

**Table S4**: Anisotropic Displacement Parameters (×10⁴) **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Au1 | 20.54(10) | 19.70(11) | 18.76(10) | 1.86(4) | 2.52(6) | 2.20(4) |
| O1 | 26.6(12) | 34.8(13) | 29.7(12) | 0.0(11) | -3.1(10) | 10.2(11) |
| O2 | 38.8(13) | 26.0(12) | 19.0(11) | -2.8(9) | -2.8(10) | 4.6(10) |
| O3 | 37.4(14) | 30.2(13) | 25.3(12) | -8.6(10) | -3.0(10) | 11.8(11) |
| O4 | 28.7(12) | 29.3(12) | 21.4(11) | -5.5(10) | -7.9(9) | 3.6(10) |
| N1 | 24.3(13) | 22.8(13) | 19.8(13) | 1.5(11) | 3.6(11) | 5.6(11) |
| N2 | 20.6(13) | 23.7(13) | 18.1(12) | 1.6(11) | -1.5(10) | 2.2(11) |
| N3 | 20.9(12) | 18.9(12) | 16.1(12) | 1.3(10) | 1.3(10) | 1.1(10) |
| N4 | 22.1(13) | 21.0(13) | 18.9(12) | 1.6(10) | -0.6(10) | 0.9(11) |
| N5 | 23.7(14) | 23.1(13) | 19.6(13) | -1.6(11) | -3.0(11) | 5.5(11) |
| N6 | 22.9(13) | 22.3(13) | 16.0(12) | -2.5(10) | -1.5(10) | 1.0(11) |
| N7 | 19.7(12) | 20.7(13) | 17.0(12) | 0.9(10) | -0.2(10) | 0.5(10) |
| N8 | 22.0(13) | 19.3(12) | 16.8(12) | -3.4(10) | 1.1(10) | 2.1(10) |
| C1 | 22.9(16) | 25.1(16) | 22.9(15) | 2.1(13) | 4.7(13) | 2.8(13) |
| C2 | 27.1(16) | 23.6(16) | 18.2(15) | 3.7(13) | 3.6(13) | 2.2(13) |
| C3 | 21.1(15) | 19.5(15) | 20.8(15) | 4.5(12) | 1.1(12) | 1.4(12) |
| C4 | 20.9(15) | 20.2(15) | 18.4(14) | 4.9(12) | 4.5(12) | -0.2(12) |
| C5 | 25.5(16) | 20.6(15) | 18.1(14) | 1.8(12) | 1.5(12) | -3.4(13) |
| C6 | 29.8(17) | 29.0(18) | 24.1(16) | -1.7(14) | 5.8(13) | 9.8(14) |
| C7 | 40(2) | 22.3(16) | 25.6(17) | 0.5(14) | 3.3(15) | 9.2(16) |
| C8 | 27.4(17) | 32.0(18) | 19.3(15) | -1.6(13) | -1.8(13) | 4.4(14) |
| C9 | 28.9(18) | 24.6(18) | 21.3(17) | -2.8(12) | 0.5(14) | 1.2(13) |
| C10 | 29.3(17) | 26.3(17) | 21.8(16) | -2.0(13) | -6.8(13) | 3.5(14) |
| C11 | 27.7(17) | 26.2(17) | 18.9(15) | 0.1(13) | 2.0(13) | 4.6(14) |
| C12 | 25.7(16) | 21.6(16) | 18.5(15) | 0.6(13) | 3.0(13) | 2.0(13) |
| C13 | 21.7(15) | 20.4(14) | 16.5(14) | -0.7(12) | 2.5(12) | 0.0(12) |
| C14 | 23.3(15) | 20.5(15) | 15.5(14) | 1.4(12) | 3.3(12) | 0.8(12) |
| C15 | 21.7(15) | 25.7(16) | 17.5(14) | 0.7(12) | 2.9(12) | -1.6(13) |
| C16 | 31.5(18) | 29.1(18) | 28.0(17) | -5.6(14) | -8.0(14) | 10.9(15) |
| C17 | 65(3) | 27.1(19) | 34(2) | 0.2(16) | -12.9(19) | 10.1(19) |
| C18 | 34.3(18) | 27.6(17) | 20.7(16) | -6.4(13) | -4.8(13) | 4.9(15) |
| C19 | 33.7(18) | 23.8(16) | 21.0(15) | -4.3(13) | 1.6(13) | 2.1(14) |
| C20 | 22.6(16) | 31.0(17) | 19.8(15) | -2.8(13) | -4.1(12) | 3.8(13) |
| F1 | 35.0(11) | 55.9(14) | 41.5(12) | 11.0(11) | 19.1(10) | 9.7(10) |
| F2 | 36.9(11) | 34.8(11) | 29.0(10) | -3.4(9) | 4.0(8) | -8.7(9) |
| F3 | 32.6(11) | 36.1(12) | 54.8(14) | 9.3(11) | 3.1(10) | -0.2(9) |
| F4 | 37.4(12) | 54.9(14) | 26.8(10) | -12.7(10) | 2.7(9) | -7.8(10) |
| B1 | 23.0(17) | 28.7(19) | 21.6(17) | -2.0(15) | 4.3(14) | -2.7(15) |
| O5 | 58(19) | 33(15) | 51(17) | 2(12) | 10(13) | 13(12) |

**Table S5**: Bond Lengths in Å for **3a**.

| Atom | Atom | Length/Å |
|---|---|---|
| Au1 | C5 | 2.020(3) |
| Au1 | C15 | 2.015(3) |
| O1 | C1 | 1.221(4) |
| O2 | C2 | 1.219(4) |
| O3 | C11 | 1.211(4) |
| O4 | C12 | 1.223(4) |
| N1 | C1 | 1.394(4) |
| N1 | C2 | 1.404(4) |
| N1 | C6 | 1.484(4) |
| N2 | C1 | 1.397(4) |
| N2 | C4 | 1.371(4) |
| N2 | C8 | 1.474(4) |
| N3 | C4 | 1.375(4) |
| N3 | C5 | 1.380(4) |
| N3 | C9 | 1.467(4) |
| N4 | C3 | 1.386(4) |
| N4 | C5 | 1.335(4) |
| N4 | C10 | 1.465(4) |
| N5 | C11 | 1.395(4) |
| N5 | C12 | 1.402(4) |
| N5 | C16 | 1.478(4) |
| N6 | C11 | 1.396(4) |
| N6 | C14 | 1.367(4) |
| N6 | C18 | 1.475(4) |
| N7 | C14 | 1.368(4) |
| N7 | C15 | 1.371(4) |
| N7 | C20 | 1.476(4) |
| N8 | C13 | 1.386(4) |
| N8 | C15 | 1.347(4) |
| N8 | C19 | 1.460(4) |
| C2 | C3 | 1.426(5) |
| C3 | C4 | 1.362(4) |
| C6 | C7 | 1.514(5) |
| C12 | C13 | 1.427(4) |
| C13 | C14 | 1.367(4) |
| C16 | C17 | 1.509(6) |
| F1 | B1 | 1.377(4) |
| F2 | B1 | 1.394(4) |
| F3 | B1 | 1.400(5) |
| F4 | B1 | 1.384(4) |

**Table S6**: Bond Angles in ° for **3a**.

| Atom | Atom | Atom | Angle/° |
|---|---|---|---|
| C15 | Au1 | C5 | 178.55(12) |
| C1 | N1 | C2 | 126.5(3) |
| C1 | N1 | C6 | 117.4(3) |
| C2 | N1 | C6 | 115.5(3) |
| C1 | N2 | C8 | 118.0(3) |
| C4 | N2 | C1 | 118.3(3) |
| C4 | N2 | C8 | 122.9(3) |
| C4 | N3 | C5 | 108.7(3) |
| C4 | N3 | C9 | 129.3(3) |
| C5 | N3 | C9 | 121.9(3) |
| C3 | N4 | C10 | 125.4(3) |
| C5 | N4 | C3 | 109.8(3) |
| C5 | N4 | C10 | 124.8(3) |
| C11 | N5 | C12 | 126.4(3) |
| C11 | N5 | C16 | 116.0(3) |
| C12 | N5 | C16 | 117.6(3) |
| C11 | N6 | C18 | 117.0(3) |
| C14 | N6 | C11 | 118.3(3) |
| C14 | N6 | C18 | 123.4(3) |
| C14 | N7 | C15 | 109.8(3) |
| C14 | N7 | C20 | 128.0(3) |
| C15 | N7 | C20 | 122.1(3) |
| C13 | N8 | C19 | 125.1(3) |
| C15 | N8 | C13 | 109.6(3) |
| C15 | N8 | C19 | 125.2(3) |
| O1 | C1 | N1 | 121.7(3) |
| O1 | C1 | N2 | 120.8(3) |
| N1 | C1 | N2 | 117.5(3) |
| O2 | C2 | N1 | 121.5(3) |
| O2 | C2 | C3 | 126.7(3) |
| N1 | C2 | C3 | 111.7(3) |
| N4 | C3 | C2 | 129.7(3) |
| C4 | C3 | N4 | 107.1(3) |
| C4 | C3 | C2 | 123.2(3) |
| N2 | C4 | N3 | 130.0(3) |
| C3 | C4 | N2 | 122.5(3) |
| C3 | C4 | N3 | 107.5(3) |
| N3 | C5 | Au1 | 125.5(2) |
| N4 | C5 | Au1 | 127.6(2) |
| N4 | C5 | N3 | 106.9(3) |
| N1 | C6 | C7 | 111.0(3) |
| O3 | C11 | N5 | 120.9(3) |
| O3 | C11 | N6 | 121.4(3) |
| N5 | C11 | N6 | 117.7(3) |
| O4 | C12 | N5 | 122.3(3) |
| O4 | C12 | C13 | 126.0(3) |
| N5 | C12 | C13 | 111.6(3) |
| N8 | C13 | C12 | 129.7(3) |
| C14 | C13 | N8 | 107.0(3) |
| C14 | C13 | C12 | 123.2(3) |
| N6 | C14 | N7 | 130.5(3) |
| N6 | C14 | C13 | 122.4(3) |
| C13 | C14 | N7 | 107.1(3) |
| N7 | C15 | Au1 | 126.0(2) |
| N8 | C15 | Au1 | 127.6(2) |
| N8 | C15 | N7 | 106.4(3) |
| N5 | C16 | C17 | 111.6(3) |
| F1 | B1 | F2 | 109.2(3) |
| F1 | B1 | F3 | 109.9(3) |
| F1 | B1 | F4 | 110.0(3) |
| F2 | B1 | F3 | 109.2(3) |
| F4 | B1 | F2 | 110.1(3) |
| F4 | B1 | F3 | 108.3(3) |

**Table S7**: Torsion Angles in ° for **3a**.

| Atom | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|
| O2 | C2 | C3 | N4 | -2.6(6) |
| O2 | C2 | C3 | C4 | 178.0(3) |
| O4 | C12 | C13 | N8 | 1.4(6) |
| O4 | C12 | C13 | C14 | -179.0(3) |
| N1 | C2 | C3 | N4 | 179.3(3) |
| N1 | C2 | C3 | C4 | -0.1(4) |
| N4 | C3 | C4 | N2 | -179.5(3) |
| N4 | C3 | C4 | N3 | 0.9(3) |
| N5 | C12 | C13 | N8 | -178.7(3) |
| N5 | C12 | C13 | C14 | 1.0(4) |
| N8 | C13 | C14 | N6 | 178.7(3) |
| N8 | C13 | C14 | N7 | -1.2(3) |
| C1 | N1 | C2 | O2 | 178.2(3) |
| C1 | N1 | C2 | C3 | -3.6(4) |
| C1 | N1 | C6 | C7 | -97.4(3) |
| C1 | N2 | C4 | N3 | -177.0(3) |
| C1 | N2 | C4 | C3 | 3.4(4) |
| C2 | N1 | C1 | O1 | -174.7(3) |
| C2 | N1 | C1 | N2 | 7.1(5) |
| C2 | N1 | C6 | C7 | 73.8(3) |
| C2 | C3 | C4 | N2 | 0.1(5) |
| C2 | C3 | C4 | N3 | -179.6(3) |
| C3 | N4 | C5 | Au1 | -177.3(2) |
| C3 | N4 | C5 | N3 | 0.5(3) |
| C4 | N2 | C1 | O1 | 175.2(3) |
| C4 | N2 | C1 | N1 | -6.5(4) |
| C4 | N3 | C5 | Au1 | 177.9(2) |
| C4 | N3 | C5 | N4 | 0.0(3) |
| C5 | N3 | C4 | N2 | 179.8(3) |
| C5 | N3 | C4 | C3 | -0.6(3) |
| C5 | N4 | C3 | C2 | 179.6(3) |
| C5 | N4 | C3 | C4 | -0.9(4) |
| C6 | N1 | C1 | O1 | -4.5(5) |
| C6 | N1 | C1 | N2 | 177.2(3) |
| C6 | N1 | C2 | O2 | 7.9(4) |
| C6 | N1 | C2 | C3 | -173.9(3) |
| C8 | N2 | C1 | O1 | 4.5(5) |
| C8 | N2 | C1 | N1 | -177.2(3) |
| C8 | N2 | C4 | N3 | -6.8(5) |
| C8 | N2 | C4 | C3 | 173.6(3) |
| C9 | N3 | C4 | N2 | -3.4(5) |
| C9 | N3 | C4 | C3 | 176.3(3) |
| C9 | N3 | C5 | Au1 | 0.8(4) |
| C9 | N3 | C5 | N4 | -177.1(3) |
| C10 | N4 | C3 | C2 | -1.0(5) |
| C10 | N4 | C3 | C4 | 178.5(3) |
| C10 | N4 | C5 | Au1 | 3.3(5) |
| C10 | N4 | C5 | N3 | -178.8(3) |
| C11 | N5 | C12 | O4 | -176.8(3) |
| C11 | N5 | C12 | C13 | 3.2(5) |
| C11 | N5 | C16 | C17 | -76.2(4) |
| C11 | N6 | C14 | N7 | 177.0(3) |
| C11 | N6 | C14 | C13 | -2.9(5) |
| C12 | N5 | C11 | O3 | 174.4(3) |
| C12 | N5 | C11 | N6 | -7.1(5) |
| C12 | N5 | C16 | C17 | 106.6(4) |
| C12 | C13 | C14 | N6 | -1.0(5) |
| C12 | C13 | C14 | N7 | 179.1(3) |
| C13 | N8 | C15 | Au1 | -177.3(2) |
| C13 | N8 | C15 | N7 | 1.1(3) |

| Atom | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|
| C14 | N6 | C11 | O3 | -175.0(3) |
| C14 | N6 | C11 | N5 | 6.6(4) |
| C14 | N7 | C15 | Au1 | 176.5(2) |
| C14 | N7 | C15 | N8 | -1.9(3) |
| C15 | N7 | C14 | N6 | -177.9(3) |
| C15 | N7 | C14 | C13 | 2.0(3) |
| C15 | N8 | C13 | C12 | 179.7(3) |
| C15 | N8 | C13 | C14 | 0.1(3) |
| C16 | N5 | C11 | O3 | -2.5(5) |
| C16 | N5 | C11 | N6 | 176.0(3) |
| C16 | N5 | C12 | O4 | 0.0(5) |
| C16 | N5 | C12 | C13 | -179.9(3) |
| C18 | N6 | C11 | O3 | -7.1(5) |
| C18 | N6 | C11 | N5 | 174.5(3) |
| C18 | N6 | C14 | N7 | 9.9(5) |
| C18 | N6 | C14 | C13 | -170.0(3) |
| C19 | N8 | C13 | C12 | 2.5(5) |
| C19 | N8 | C13 | C14 | -177.2(3) |
| C19 | N8 | C15 | Au1 | 0.0(5) |
| C19 | N8 | C15 | N7 | 178.4(3) |
| C20 | N7 | C14 | N6 | -2.6(5) |
| C20 | N7 | C14 | C13 | 177.3(3) |
| C20 | N7 | C15 | Au1 | 0.9(4) |
| C20 | N7 | C15 | N8 | -177.5(3) |

**Table S8**: Hydrogen Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **3a**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$.

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| H6A | 2505 | 8931 | 5064 | 33 |
| H6B | 1546 | 9011 | 4115 | 33 |
| H7A | 3254 | 9562 | 3563 | 45 |
| H7B | 4158 | 9527 | 4534 | 45 |
| H7C | 2968 | 10141 | 4313 | 45 |
| H8A | 2448 | 6606 | 1858 | 41 |
| H8B | 1123 | 6907 | 2013 | 41 |
| H8C | 1660 | 6006 | 2332 | 41 |
| H9A | 4643 | 4799 | 2930 | 39 |
| H9B | 3840 | 5467 | 2268 | 39 |
| H9C | 3180 | 4950 | 2897 | 39 |
| H10A | 6852 | 7200 | 5505 | 42 |
| H10B | 7135 | 6231 | 5642 | 42 |
| H10C | 6114 | 6662 | 6070 | 42 |
| H16A | 12851 | 1798 | 6062 | 39 |
| H16B | 12749 | 1258 | 5196 | 39 |
| H17A | 11518 | 251 | 5702 | 70 |
| H17B | 11541 | 799 | 6550 | 70 |
| H17C | 12819 | 383 | 6431 | 70 |
| H18A | 7566 | 1502 | 3101 | 44 |
| H18B | 8800 | 991 | 3043 | 44 |
| H18C | 8588 | 1911 | 2657 | 44 |
| H19A | 9759 | 4077 | 6499 | 41 |
| H19B | 8966 | 4802 | 5916 | 41 |
| H19C | 10366 | 4588 | 5837 | 41 |
| H20A | 7051 | 2990 | 2732 | 39 |
| H20B | 6165 | 3527 | 3190 | 39 |
| H20C | 6240 | 2543 | 3315 | 39 |

**Table S9**: Atomic Occupancies for all atoms that are not fully occupied in **3a**.

| Atom | Occupancy |
|---|---|
| O5 | 0.110(12) |

Sample ID: **4b**

**Table S10**

| **Compound** | **4b** |
|---|---|
| Formula | $C_{48}H_{48}Au_3N_{15}O_6$ |
| $D_{calc.}$/ g cm$^{-3}$ | 1.807 |
| $\mu$/mm$^{-1}$ | 14.974 |
| Formula Weight | 1521.91 |
| Colour | colourless |
| Shape | plate |
| Size/mm$^3$ | 0.150×0.080×0.020 |
| $T$/K | 100.01(10) |
| Crystal System | triclinic |
| Space Group | $P$-1 |
| $a$/Å | 12.4804(2) |
| $b$/Å | 14.5714(2) |
| $c$/Å | 16.2958(2) |
| $\alpha$/° | 105.5230(10) |
| $\beta$/° | 94.9850(10) |
| $\gamma$/° | 98.6460(10) |
| V/Å$^3$ | 2797.70(7) |
| $Z$ | 2 |
| $Z'$ | 1 |
| Wavelength/Å | 1.54184 |
| Radiation type | CuK$_\alpha$ |
| $\Theta_{min}$/° | 2.840 |
| $\Theta_{max}$/° | 67.076 |
| Measured Refl. | 47307 |
| Independent Refl. | 9932 |
| Reflections with I > 2(I) | 9183 |
| $R_{int}$ | 0.0463 |
| Parameters | 661 |
| Restraints | 0 |
| Largest Peak | 1.344 |
| Deepest Hole | -2.146 |
| GooF | 1.080 |
| $wR_2$ (all data) | 0.1027 |
| $wR_2$ | 0.1010 |
| $R_1$ (all data) | 0.0404 |
| $R_1$ | 0.0379 |

**Crystal Data.** $C_{48}H_{48}Au_3N_{15}O_6$, $M_r$ = 1521.91, triclinic, $P$-1 (No. 2), a = 12.4804(2) Å, b = 14.5714(2) Å, c = 16.2958(2) Å, $\alpha$ = 105.5230(10)°, $\beta$ = 94.9850(10)°, $\gamma$ = 98.6460(10)°, $V$ = 2797.70(7) Å$^3$, $T$ = 100.01(10) K, $Z$ = 2, $Z'$ = 1, $\mu$(CuK$_\alpha$) = 14.974 mm$^{-1}$, 47307 reflections measured, 9932 unique ($R_{int}$ = 0.0463) which were used in all calculations. The final $wR_2$ was 0.1027 (all data) and $R_1$ was 0.0379 (I > 2(I)).

## Structure Quality Indicators

| | | | | |
|---|---|---|---|---|
| **Reflections:** | d min (Cu) 0.84 | I/σ 31.9 | Rint 4.63% | complete 99% (IUCr) 99% |
| **Refinement:** | Shift 0.001 | Max Peak 1.3 | Min Peak -2.1 | GooF 1.080 |

A colourless plate-shaped crystal with dimensions 0.150×0.080×0.020 mm$^3$ was mounted on a MITIGEN holder in perfluoroether oil. Data were collected using a Rigaku 007HF diffractometer equipped with Varimax confocal mirrors and an AFC11 goniometer and HyPix 6000HE detector, and equipped with an Oxford Cryosystems low-temperature device operating at $T$ = 100.01(10) K.

Data were measured using $\omega$ scans of 0.5 ° per frame for 2 s using CuK$_\alpha$ radiation (Rotating-anode X-ray tube, 40 kV, 30 mA). The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.40.39a, 2019). The maximum resolution that was achieved was $\Theta$ = 67.076° (0.84 Å).

Cell parameters were retrieved using the **CrysAlisPro** (Rigaku, V1.171.39.46, 2018) software and refined using **CrysAlisPro** (Rigaku, V1.171.39.46, 2018) on 20201 reflections, 43% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku, V1.171.40.39a, 2019). The final completeness is 99.40 % out to 67.076° in $\Theta$.

A multi-scan absorption correction was performed using CrysAlisPro 1.171.40.39a (Rigaku Oxford Diffraction, 2019) using spherical harmonics as implemented in SCALE3 ABSPACK. The absorption coefficient $\mu$ of this material is 14.974 mm$^{-1}$ at this wavelength ($\lambda$ = 1.54184 Å) and the minimum and maximum transmissions are 0.566 and 1.000.

The structure was solved and the space group $P$-1 (# 2) determined by the ShelXD (Sheldrick, 2008) structure solution program using Dual Space and refined by Least Squares using version 2014/7 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. There is still a cavity of about 550 Å$^3$ available for solvents. No solvents were identified, so the structure was SQUEEZEd.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

## Reflection Statistics

| | | | |
|---|---|---|---|
| Total reflections (after filtering) | 47320 | Unique reflections | 9932 |
| Completeness | 0.994 | Mean I/$\sigma$ | 21.68 |
| $hkl_{max}$ collected | (14, 17, 19) | $hkl_{min}$ collected | (-14, -17, -19) |
| $hkl_{max}$ used | (14, 16, 19) | $hkl_{min}$ used | (-14, -17, 0) |
| Lim $d_{max}$ collected | 100.0 | Lim $d_{min}$ collected | 0.77 |
| $d_{max}$ used | 15.56 | $d_{min}$ used | 0.84 |
| Friedel pairs | 6844 | Friedel pairs merged | 1 |
| Inconsistent equivalents | 8 | $R_{int}$ | 0.0463 |
| $R_{sigma}$ | 0.0314 | Intensity transformed | 0 |
| Omitted reflections | 0 | Omitted by user (OMIT hkl) | 13 |
| Multiplicity | (3994, 4561, 3342, 2300, 1312, 706, 372, 150, 34, 5, 2) | Maximum multiplicity | 13 |
| Removed systematic absences | 0 | Filtered off (Shel/OMIT) | 0 |

**Table S11**: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **4b**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$.

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| Au1 | 8034.0(2) | 9304.3(2) | 5035.5(2) | 41.23(8) |
| Au2 | 6416.9(2) | 7335.4(2) | 3806.0(2) | 42.65(8) |
| Au3 | 4657.0(2) | 5471.1(2) | 2530.6(2) | 50.94(9) |
| O1 | 10839(6) | 9894(7) | 2312(5) | 116(3) |
| O2 | 12255(5) | 7084(6) | 2210(4) | 110(2) |
| O3 | 2307(3) | 7996(3) | 5450(3) | 56.6(11) |
| O4 | 3792(5) | 7534(4) | 7940(3) | 69.5(13) |
| O5 | 7534(4) | 4404(4) | -269(4) | 79.3(15) |
| O6 | 7273(5) | 7142(5) | -1064(4) | 92.7(19) |
| N1 | 3617(5) | 10303(4) | 7735(4) | 62.4(15) |
| N2 | 9559(4) | 9431(3) | 3704(3) | 45.5(11) |
| N3 | 9678(3) | 8176(3) | 4155(3) | 41.6(10) |
| N4 | 10996(4) | 7452(5) | 3176(4) | 65.8(16) |
| N5 | 11542(5) | 8466(6) | 2277(4) | 82(2) |
| N6 | 9987(4) | 6975(5) | 354(4) | 64.0(16) |
| N7 | 4478(3) | 7673(3) | 4781(3) | 37.5(10) |
| N8 | 5788(4) | 7355(3) | 5574(3) | 38.6(10) |
| N9 | 4872(4) | 7456(3) | 6880(3) | 48.0(11) |
| N10 | 3053(5) | 7732(4) | 6682(3) | 51.7(12) |
| N11 | 1849(5) | 5263(4) | 6341(4) | 70.6(17) |
| N12 | 6019(4) | 5074(4) | 1070(3) | 49.7(12) |
| N13 | 5367(4) | 6388(4) | 1159(3) | 50.6(12) |
| N14 | 6275(5) | 6885(4) | -4(4) | 66.3(16) |
| N15 | 7373(5) | 5770(5) | -668(4) | 72.9(18) |
| C1 | 3605(5) | 10453(5) | 6963(4) | 53.2(15) |
| C2 | 4418(5) | 10304(4) | 6462(4) | 49.0(14) |
| C3 | 5343(5) | 10001(4) | 6773(4) | 44.6(13) |
| C4 | 5381(6) | 9871(5) | 7583(4) | 56.6(16) |
| C5 | 4509(6) | 10013(5) | 8031(5) | 61.8(17) |
| C6 | 6217(5) | 9831(4) | 6263(4) | 45.5(13) |
| C7 | 6923(5) | 9657(4) | 5807(4) | 48.5(14) |
| C8 | 9170(4) | 8953(4) | 4255(4) | 45.4(14) |
| C9 | 10345(4) | 8163(4) | 3521(4) | 43.5(13) |
| C10 | 10285(5) | 8929(5) | 3257(4) | 49.5(14) |
| C11 | 10860(5) | 9154(5) | 2618(4) | 50.9(15) |
| C12 | 11592(5) | 7674(6) | 2567(4) | 55.3(17) |
| C13 | 9469(5) | 7456(4) | 4628(4) | 53.2(15) |
| C14 | 9229(5) | 10337(4) | 3634(5) | 59.0(17) |
| C15 | 11005(5) | 6637(4) | 3375(4) | 54.5(17) |
| C16 | 12132(5) | 8663(7) | 1699(5) | 80(3) |
| C17 | 9865(5) | 6306(5) | 768(4) | 57.8(17) |
| C18 | 9192(5) | 6317(4) | 1412(4) | 51.3(15) |
| C19 | 8617(5) | 7074(4) | 1646(4) | 44.2(13) |
| C20 | 8763(5) | 7778(5) | 1206(4) | 52.0(15) |
| C21 | 9443(6) | 7684(6) | 578(5) | 61.9(18) |
| C22 | 7926(5) | 7138(5) | 2301(4) | 48.9(14) |
| C23 | 7343(5) | 7205(4) | 2859(4) | 48.6(14) |
| C24 | 5498(5) | 7469(4) | 4780(4) | 42.2(12) |
| C25 | 4950(4) | 7496(4) | 6051(4) | 39.5(12) |
| C26 | 4118(5) | 7682(4) | 5561(4) | 39.9(12) |
| C27 | 3095(4) | 7826(4) | 5846(4) | 42.1(12) |
| C28 | 3888(6) | 7574(4) | 7199(4) | 52.4(15) |
| C29 | 3829(5) | 7800(4) | 4043(4) | 46.9(13) |
| C30 | 6887(5) | 7201(4) | 5831(4) | 50.5(14) |
| C31 | 5770(7) | 7345(5) | 7455(4) | 64.9(18) |
| C32 | 2043(6) | 7836(5) | 7050(5) | 63.6(18) |
| C33 | 1370(6) | 5462(7) | 5662(6) | 86(3) |
| C34 | 1850(6) | 5471(7) | 4934(6) | 77(2) |
| C35 | 2910(5) | 5279(4) | 4888(4) | 52.1(15) |

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| C36 | 3423(5) | 5083(4) | 5602(4) | 53.3(15) |
| C37 | 2856(6) | 5077(4) | 6300(5) | 62.3(17) |
| C38 | 3463(5) | 5284(4) | 4142(5) | 54.3(16) |
| C39 | 3904(5) | 5322(4) | 3523(5) | 55.0(16) |
| C40 | 5384(5) | 5636(4) | 1511(4) | 48.7(14) |
| C41 | 6032(5) | 6296(5) | 520(4) | 54.3(16) |
| C42 | 6435(5) | 5465(5) | 447(4) | 53.4(15) |
| C43 | 7148(6) | 5133(6) | -168(5) | 63.7(18) |
| C44 | 7009(6) | 6630(6) | -604(5) | 72(2) |
| C45 | 6304(6) | 4207(5) | 1268(5) | 63.8(18) |
| C46 | 4779(7) | 7171(5) | 1493(5) | 66.1(19) |
| C47 | 5932(8) | 7814(6) | 105(6) | 89(3) |
| C48 | 8106(6) | 5493(8) | -1325(5) | 88(3) |

**Table S12**: Anisotropic Displacement Parameters (×10⁴) **4b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Au1 | 28.67(13) | 35.19(13) | 48.68(14) | -1.79(10) | -6.69(9) | 3.21(9) |
| Au2 | 29.44(13) | 38.57(14) | 49.10(15) | 1.09(10) | -3.61(10) | -1.46(10) |
| Au3 | 39.84(15) | 37.96(14) | 62.06(17) | 3.67(11) | -13.74(11) | -1.82(10) |
| O1 | 86(5) | 160(7) | 102(5) | 55(5) | 4(4) | -6(5) |
| O2 | 70(4) | 154(7) | 88(4) | -2(4) | -4(3) | 36(4) |
| O3 | 42(2) | 49(2) | 73(3) | 12(2) | 2(2) | 6.7(19) |
| O4 | 91(4) | 66(3) | 54(3) | 21(2) | 12(3) | 14(3) |
| O5 | 61(3) | 77(4) | 82(4) | 0(3) | 2(3) | 2(3) |
| O6 | 77(4) | 118(5) | 74(4) | 45(4) | -31(3) | -18(3) |
| N1 | 48(3) | 48(3) | 80(4) | 2(3) | 15(3) | 0(2) |
| N2 | 32(2) | 39(3) | 51(3) | 0(2) | -11(2) | -5.4(19) |
| N3 | 25(2) | 32(2) | 54(3) | -2.4(19) | -9.0(19) | -1.6(17) |
| N4 | 32(3) | 83(4) | 58(3) | -9(3) | -13(2) | 0(3) |
| N5 | 36(3) | 126(6) | 53(4) | -7(4) | -11(3) | -7(4) |
| N6 | 38(3) | 90(5) | 50(3) | 6(3) | -1(2) | -1(3) |
| N7 | 27(2) | 28(2) | 49(3) | 5.9(18) | -7.3(18) | -3.9(17) |
| N8 | 32(2) | 28(2) | 47(2) | 4.1(18) | -9.2(19) | 0.9(17) |
| N9 | 57(3) | 37(2) | 45(3) | 8(2) | -4(2) | 8(2) |
| N10 | 56(3) | 40(3) | 58(3) | 10(2) | 12(3) | 7(2) |
| N11 | 53(4) | 54(3) | 82(4) | -11(3) | 6(3) | -2(3) |
| N12 | 40(3) | 43(3) | 56(3) | 6(2) | -15(2) | 1(2) |
| N13 | 44(3) | 42(3) | 52(3) | 4(2) | -21(2) | -1(2) |
| N14 | 53(3) | 63(4) | 71(4) | 18(3) | -23(3) | -6(3) |
| N15 | 49(3) | 94(5) | 59(4) | 13(3) | -19(3) | -9(3) |
| C1 | 33(3) | 47(3) | 66(4) | 0(3) | 0(3) | 0(2) |
| C2 | 41(3) | 39(3) | 53(3) | 1(3) | -6(3) | -4(2) |
| C3 | 37(3) | 30(3) | 52(3) | -6(2) | -1(2) | 0(2) |
| C4 | 59(4) | 44(3) | 62(4) | 7(3) | 1(3) | 12(3) |
| C5 | 66(5) | 50(4) | 64(4) | 10(3) | 6(3) | 7(3) |
| C6 | 42(3) | 31(3) | 54(3) | 3(2) | -9(3) | 2(2) |
| C7 | 37(3) | 38(3) | 57(4) | -2(3) | -11(3) | 3(2) |
| C8 | 33(3) | 41(3) | 51(3) | 3(3) | -9(3) | -2(2) |
| C9 | 26(3) | 43(3) | 43(3) | -13(2) | -8(2) | 4(2) |
| C10 | 37(3) | 59(4) | 43(3) | 3(3) | 1(2) | 1(3) |
| C11 | 35(3) | 66(4) | 40(3) | 12(3) | -7(2) | -14(3) |
| C12 | 28(3) | 85(5) | 36(3) | -9(3) | -4(2) | 10(3) |
| C13 | 41(3) | 48(3) | 69(4) | 19(3) | -4(3) | 3(3) |
| C14 | 50(4) | 45(3) | 73(4) | 18(3) | -18(3) | -8(3) |
| C15 | 35(3) | 41(3) | 66(4) | -18(3) | -15(3) | 18(3) |
| C16 | 27(3) | 143(8) | 54(4) | 21(4) | -1(3) | -20(4) |
| C17 | 39(3) | 71(4) | 52(4) | -2(3) | -5(3) | 13(3) |
| C18 | 46(3) | 45(3) | 48(3) | -2(3) | -13(3) | 3(3) |
| C19 | 30(3) | 47(3) | 42(3) | -1(2) | -7(2) | -1(2) |
| C20 | 36(3) | 51(4) | 57(4) | 3(3) | -9(3) | 2(3) |
| C21 | 49(4) | 70(5) | 59(4) | 22(3) | -9(3) | -9(3) |
| C22 | 37(3) | 51(3) | 45(3) | 1(3) | -12(3) | -4(3) |
| C23 | 35(3) | 46(3) | 49(3) | -5(3) | -5(3) | -3(2) |
| C24 | 37(3) | 32(3) | 49(3) | 2(2) | -5(2) | 2(2) |
| C25 | 36(3) | 30(3) | 46(3) | 5(2) | -2(2) | 1(2) |
| C26 | 42(3) | 29(3) | 42(3) | 7(2) | -7(2) | 2(2) |
| C27 | 35(3) | 32(3) | 54(3) | 8(2) | -2(2) | 3(2) |
| C28 | 62(4) | 42(3) | 51(4) | 10(3) | 7(3) | 9(3) |
| C29 | 38(3) | 49(3) | 48(3) | 12(3) | -8(2) | 2(2) |
| C30 | 36(3) | 44(3) | 65(4) | 11(3) | -10(3) | 5(2) |
| C31 | 86(5) | 56(4) | 50(4) | 14(3) | -9(3) | 18(4) |
| C32 | 53(4) | 60(4) | 75(5) | 8(3) | 22(3) | 13(3) |
| C33 | 31(4) | 98(6) | 99(7) | -18(5) | -5(4) | 16(4) |
| C34 | 33(4) | 101(6) | 80(5) | 1(4) | -12(4) | 13(4) |
| C35 | 34(3) | 33(3) | 73(4) | -5(3) | -7(3) | 0(2) |

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C36 | 39(3) | 39(3) | 73(4) | 3(3) | -3(3) | 6(2) |
| C37 | 61(4) | 38(3) | 75(5) | -2(3) | 9(4) | 4(3) |
| C38 | 38(3) | 33(3) | 78(5) | 1(3) | -11(3) | 2(2) |
| C39 | 41(3) | 38(3) | 70(4) | -1(3) | -14(3) | 2(3) |
| C40 | 35(3) | 33(3) | 62(4) | 1(3) | -21(3) | -6(2) |
| C41 | 44(3) | 47(3) | 57(4) | 7(3) | -27(3) | -8(3) |
| C42 | 38(3) | 53(4) | 56(4) | 9(3) | -17(3) | -6(3) |
| C43 | 45(4) | 63(4) | 63(4) | 1(3) | -21(3) | -4(3) |
| C44 | 56(4) | 74(5) | 67(5) | 18(4) | -32(4) | -20(4) |
| C45 | 59(4) | 40(3) | 81(5) | 7(3) | -13(4) | 8(3) |
| C46 | 81(5) | 50(4) | 61(4) | 11(3) | -14(4) | 18(4) |
| C47 | 84(6) | 78(6) | 105(7) | 46(5) | -19(5) | -4(5) |
| C48 | 46(4) | 129(8) | 69(5) | 8(5) | 1(4) | -6(4) |

**Table S13**: Bond Lengths in Å for **4b**.

| Atom | Atom | Length/Å |
|---|---|---|
| Au1 | Au2 | 3.2860(3) |
| Au1 | C7 | 1.985(7) |
| Au1 | C8 | 2.018(6) |
| Au2 | Au3 | 3.3036(3) |
| Au2 | C23 | 1.993(7) |
| Au2 | C24 | 2.023(6) |
| Au3 | C39 | 1.984(8) |
| Au3 | C40 | 2.013(7) |
| O1 | C11 | 1.306(10) |
| O2 | C12 | 1.338(9) |
| O3 | C27 | 1.221(7) |
| O4 | C28 | 1.240(8) |
| O5 | C43 | 1.209(9) |
| O6 | C44 | 1.223(9) |
| N1 | C1 | 1.333(9) |
| N1 | C5 | 1.344(9) |
| N2 | C8 | 1.356(8) |
| N2 | C10 | 1.384(8) |
| N2 | C14 | 1.470(8) |
| N3 | C8 | 1.359(7) |
| N3 | C9 | 1.379(8) |
| N3 | C13 | 1.465(8) |
| N4 | C9 | 1.439(8) |
| N4 | C12 | 1.367(9) |
| N4 | C15 | 1.313(9) |
| N5 | C11 | 1.441(10) |
| N5 | C12 | 1.368(11) |
| N5 | C16 | 1.310(10) |
| N6 | C17 | 1.325(10) |
| N6 | C21 | 1.309(10) |
| N7 | C24 | 1.350(7) |
| N7 | C26 | 1.382(7) |
| N7 | C29 | 1.459(7) |
| N8 | C24 | 1.372(7) |
| N8 | C25 | 1.365(7) |
| N8 | C30 | 1.466(7) |
| N9 | C25 | 1.378(7) |
| N9 | C28 | 1.391(8) |
| N9 | C31 | 1.453(8) |
| N10 | C27 | 1.411(8) |
| N10 | C28 | 1.369(9) |
| N10 | C32 | 1.453(8) |
| N11 | C33 | 1.332(12) |
| N11 | C37 | 1.329(9) |
| N12 | C40 | 1.340(8) |
| N12 | C42 | 1.393(9) |
| N12 | C45 | 1.469(8) |
| N13 | C40 | 1.368(8) |
| N13 | C41 | 1.378(9) |
| N13 | C46 | 1.459(9) |
| N14 | C41 | 1.385(9) |
| N14 | C44 | 1.413(11) |
| N14 | C47 | 1.450(11) |
| N15 | C43 | 1.404(10) |
| N15 | C44 | 1.378(11) |
| N15 | C48 | 1.482(10) |
| C1 | C2 | 1.363(9) |
| C2 | C3 | 1.399(8) |
| C3 | C4 | 1.380(9) |
| C3 | C6 | 1.439(9) |
| C4 | C5 | 1.374(10) |
| C6 | C7 | 1.213(9) |
| C9 | C10 | 1.310(9) |
| C10 | C11 | 1.395(9) |
| C17 | C18 | 1.399(10) |
| C18 | C19 | 1.392(9) |
| C19 | C20 | 1.399(9) |
| C19 | C22 | 1.424(9) |
| C20 | C21 | 1.377(10) |
| C22 | C23 | 1.206(9) |
| C25 | C26 | 1.359(8) |
| C26 | C27 | 1.422(8) |
| C33 | C34 | 1.377(13) |
| C34 | C35 | 1.398(9) |
| C35 | C36 | 1.396(10) |
| C35 | C38 | 1.450(11) |
| C36 | C37 | 1.391(10) |
| C38 | C39 | 1.201(10) |
| C41 | C42 | 1.359(9) |
| C42 | C43 | 1.433(11) |

**Table S14**: Bond Angles in ° for **4b**

| Atom | Atom | Atom | Angle/° |
|---|---|---|---|
| C7 | Au1 | Au2 | 93.66(16) |
| C7 | Au1 | C8 | 179.7(2) |
| C8 | Au1 | Au2 | 86.68(15) |
| Au1 | Au2 | Au3 | 175.328(9) |
| C23 | Au2 | Au1 | 93.39(16) |
| C23 | Au2 | Au3 | 87.57(16) |
| C23 | Au2 | C24 | 179.1(2) |
| C24 | Au2 | Au1 | 86.05(15) |
| C24 | Au2 | Au3 | 93.04(15) |
| C39 | Au3 | Au2 | 90.29(17) |
| C39 | Au3 | C40 | 178.3(2) |
| C40 | Au3 | Au2 | 90.26(15) |
| C1 | N1 | C5 | 116.6(6) |
| C8 | N2 | C10 | 108.8(5) |
| C8 | N2 | C14 | 122.9(5) |
| C10 | N2 | C14 | 128.3(6) |
| C8 | N3 | C9 | 109.2(5) |
| C8 | N3 | C13 | 123.3(5) |
| C9 | N3 | C13 | 127.4(5) |
| C12 | N4 | C9 | 113.5(6) |
| C15 | N4 | C9 | 125.3(6) |
| C15 | N4 | C12 | 121.1(6) |
| C12 | N5 | C11 | 121.5(6) |
| C16 | N5 | C11 | 116.2(9) |
| C16 | N5 | C12 | 122.3(8) |
| C21 | N6 | C17 | 116.7(6) |
| C24 | N7 | C26 | 110.1(5) |
| C24 | N7 | C29 | 124.6(5) |
| C26 | N7 | C29 | 125.2(5) |
| C24 | N8 | C30 | 121.5(5) |
| C25 | N8 | C24 | 109.1(4) |
| C25 | N8 | C30 | 129.1(5) |
| C25 | N9 | C28 | 117.9(5) |
| C25 | N9 | C31 | 124.0(6) |
| C28 | N9 | C31 | 118.0(5) |
| C27 | N10 | C32 | 117.8(5) |
| C28 | N10 | C27 | 126.3(5) |
| C28 | N10 | C32 | 115.9(6) |
| C37 | N11 | C33 | 116.6(7) |
| C40 | N12 | C42 | 110.7(5) |
| C40 | N12 | C45 | 124.2(6) |
| C42 | N12 | C45 | 124.9(6) |
| C40 | N13 | C41 | 109.2(5) |
| C40 | N13 | C46 | 122.0(6) |
| C41 | N13 | C46 | 128.6(6) |
| C41 | N14 | C44 | 118.2(7) |
| C41 | N14 | C47 | 123.4(7) |
| C44 | N14 | C47 | 117.9(7) |
| C43 | N15 | C48 | 116.0(8) |
| C44 | N15 | C43 | 127.3(7) |
| C44 | N15 | C48 | 116.6(8) |
| N1 | C1 | C2 | 124.0(6) |
| C1 | C2 | C3 | 119.1(6) |
| C2 | C3 | C6 | 120.9(6) |
| C4 | C3 | C2 | 117.5(6) |
| C4 | C3 | C6 | 121.6(6) |
| C5 | C4 | C3 | 119.3(6) |
| N1 | C5 | C4 | 123.5(7) |
| C7 | C6 | C3 | 177.3(6) |
| C6 | C7 | Au1 | 177.1(5) |

| Atom | Atom | Atom | Angle/° |
|---|---|---|---|
| N2 | C8 | Au1 | 126.8(4) |
| N2 | C8 | N3 | 105.9(5) |
| N3 | C8 | Au1 | 127.3(4) |
| N3 | C9 | N4 | 128.4(6) |
| C10 | C9 | N3 | 107.8(5) |
| C10 | C9 | N4 | 123.8(6) |
| N2 | C10 | C11 | 128.0(6) |
| C9 | C10 | N2 | 108.3(5) |
| C9 | C10 | C11 | 123.7(6) |
| O1 | C11 | N5 | 118.7(7) |
| O1 | C11 | C10 | 127.7(7) |
| C10 | C11 | N5 | 113.7(7) |
| O2 | C12 | N4 | 119.5(8) |
| O2 | C12 | N5 | 116.6(7) |
| N5 | C12 | N4 | 123.9(6) |
| N6 | C17 | C18 | 123.9(7) |
| C19 | C18 | C17 | 118.9(6) |
| C18 | C19 | C20 | 116.4(6) |
| C18 | C19 | C22 | 122.0(6) |
| C20 | C19 | C22 | 121.6(6) |
| C21 | C20 | C19 | 119.3(6) |
| N6 | C21 | C20 | 124.8(7) |
| C23 | C22 | C19 | 179.1(7) |
| C22 | C23 | Au2 | 178.4(5) |
| N7 | C24 | Au2 | 127.4(4) |
| N7 | C24 | N8 | 106.2(5) |
| N8 | C24 | Au2 | 126.4(4) |
| N8 | C25 | N9 | 129.7(5) |
| C26 | C25 | N8 | 108.2(5) |
| C26 | C25 | N9 | 122.1(5) |
| N7 | C26 | C27 | 130.2(5) |
| C25 | C26 | N7 | 106.4(5) |
| C25 | C26 | C27 | 123.3(5) |
| O3 | C27 | N10 | 120.7(5) |
| O3 | C27 | C26 | 127.6(6) |
| N10 | C27 | C26 | 111.6(5) |
| O4 | C28 | N9 | 119.3(6) |
| O4 | C28 | N10 | 122.0(6) |
| N10 | C28 | N9 | 118.7(5) |
| N11 | C33 | C34 | 124.1(7) |
| C33 | C34 | C35 | 119.6(8) |
| C34 | C35 | C38 | 122.3(7) |
| C36 | C35 | C34 | 116.7(7) |
| C36 | C35 | C38 | 121.1(6) |
| C37 | C36 | C35 | 119.0(6) |
| N11 | C37 | C36 | 124.0(8) |
| C39 | C38 | C35 | 177.3(7) |
| C38 | C39 | Au3 | 176.5(6) |
| N12 | C40 | Au3 | 127.8(5) |
| N12 | C40 | N13 | 106.2(6) |
| N13 | C40 | Au3 | 125.9(5) |
| N13 | C41 | N14 | 129.8(6) |
| C42 | C41 | N13 | 108.0(6) |
| C42 | C41 | N14 | 122.2(7) |
| N12 | C42 | C43 | 131.0(7) |
| C41 | C42 | N12 | 105.9(6) |
| C41 | C42 | C43 | 123.1(7) |
| O5 | C43 | N15 | 121.7(8) |
| O5 | C43 | C42 | 126.6(8) |
| N15 | C43 | C42 | 111.7(7) |

| Atom | Atom | Atom | Angle/° |
|---|---|---|---|
| O6 | C44 | N14 | 120.6(9) |
| O6 | C44 | N15 | 122.0(9) |
| N15 | C44 | N14 | 117.3(7) |

**Table S15**: Torsion Angles in ° for **4b**.

| Atom | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|
| N1 | C1 | C2 | C3 | -1.9(9) |
| N2 | C10 | C11 | O1 | 0.6(11) |
| N2 | C10 | C11 | N5 | -179.3(5) |
| N3 | C9 | C10 | N2 | -1.4(6) |
| N3 | C9 | C10 | C11 | 179.7(5) |
| N4 | C9 | C10 | N2 | 177.9(5) |
| N4 | C9 | C10 | C11 | -1.1(9) |
| N6 | C17 | C18 | C19 | -0.6(9) |
| N7 | C26 | C27 | O3 | -1.7(10) |
| N7 | C26 | C27 | N10 | 177.1(5) |
| N8 | C25 | C26 | N7 | -1.2(6) |
| N8 | C25 | C26 | C27 | 177.4(5) |
| N9 | C25 | C26 | N7 | 179.7(5) |
| N9 | C25 | C26 | C27 | -1.7(8) |
| N11 | C33 | C34 | C35 | -1.0(14) |
| N12 | C42 | C43 | O5 | 0.8(11) |
| N12 | C42 | C43 | N15 | -179.1(6) |
| N13 | C41 | C42 | N12 | -1.4(6) |
| N13 | C41 | C42 | C43 | 179.1(5) |
| N14 | C41 | C42 | N12 | -179.9(5) |
| N14 | C41 | C42 | C43 | 0.6(9) |
| C1 | N1 | C5 | C4 | 0.1(10) |
| C1 | C2 | C3 | C4 | -0.1(8) |
| C1 | C2 | C3 | C6 | 179.6(5) |
| C2 | C3 | C4 | C5 | 1.9(9) |
| C3 | C4 | C5 | N1 | -2.0(10) |
| C5 | N1 | C1 | C2 | 1.9(9) |
| C6 | C3 | C4 | C5 | -177.9(6) |
| C8 | N2 | C10 | C9 | 0.1(6) |
| C8 | N2 | C10 | C11 | 178.9(6) |
| C8 | N3 | C9 | N4 | -177.0(5) |
| C8 | N3 | C9 | C10 | 2.2(6) |
| C9 | N3 | C8 | Au1 | 176.1(4) |
| C9 | N3 | C8 | N2 | -2.1(6) |
| C9 | N4 | C12 | O2 | 178.3(5) |
| C9 | N4 | C12 | N5 | -3.0(8) |
| C9 | C10 | C11 | O1 | 179.3(7) |
| C9 | C10 | C11 | N5 | -0.6(8) |
| C10 | N2 | C8 | Au1 | -176.9(4) |
| C10 | N2 | C8 | N3 | 1.3(6) |
| C11 | N5 | C12 | O2 | -179.7(5) |
| C11 | N5 | C12 | N4 | 1.6(9) |
| C12 | N4 | C9 | N3 | -178.1(5) |
| C12 | N4 | C9 | C10 | 2.8(8) |
| C12 | N5 | C11 | O1 | -179.5(6) |
| C12 | N5 | C11 | C10 | 0.4(8) |
| C13 | N3 | C8 | Au1 | -0.6(7) |
| C13 | N3 | C8 | N2 | -178.8(5) |
| C13 | N3 | C9 | N4 | -0.4(8) |
| C13 | N3 | C9 | C10 | 178.8(5) |
| C14 | N2 | C8 | Au1 | 3.5(7) |
| C14 | N2 | C8 | N3 | -178.3(5) |
| C14 | N2 | C10 | C9 | 179.6(5) |
| C14 | N2 | C10 | C11 | -1.5(9) |

| Atom | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|
| C15 | N4 | C9 | N3 | 5.0(9) |
| C15 | N4 | C9 | C10 | -174.0(6) |
| C15 | N4 | C12 | O2 | -4.7(9) |
| C15 | N4 | C12 | N5 | 174.0(6) |
| C16 | N5 | C11 | O1 | 2.6(9) |
| C16 | N5 | C11 | C10 | -177.5(6) |
| C16 | N5 | C12 | O2 | -2.0(9) |
| C16 | N5 | C12 | N4 | 179.3(6) |
| C17 | N6 | C21 | C20 | 0.1(10) |
| C17 | C18 | C19 | C20 | 0.1(8) |
| C17 | C18 | C19 | C22 | -179.4(5) |
| C18 | C19 | C20 | C21 | 0.4(8) |
| C19 | C20 | C21 | N6 | -0.5(10) |
| C21 | N6 | C17 | C18 | 0.5(9) |
| C22 | C19 | C20 | C21 | 179.9(5) |
| C24 | N7 | C26 | C25 | 1.0(6) |
| C24 | N7 | C26 | C27 | -177.5(5) |
| C24 | N8 | C25 | N9 | -180.0(5) |
| C24 | N8 | C25 | C26 | 1.0(6) |
| C25 | N8 | C24 | Au2 | -179.5(4) |
| C25 | N8 | C24 | N7 | -0.3(6) |
| C25 | N9 | C28 | O4 | 179.4(5) |
| C25 | N9 | C28 | N10 | -0.6(8) |
| C25 | C26 | C27 | O3 | -179.9(5) |
| C25 | C26 | C27 | N10 | -1.1(7) |
| C26 | N7 | C24 | Au2 | 178.8(4) |
| C26 | N7 | C24 | N8 | -0.4(6) |
| C27 | N10 | C28 | O4 | 177.4(6) |
| C27 | N10 | C28 | N9 | -2.6(9) |
| C28 | N9 | C25 | N8 | -176.3(5) |
| C28 | N9 | C25 | C26 | 2.6(8) |
| C28 | N10 | C27 | O3 | -177.8(6) |
| C28 | N10 | C27 | C26 | 3.4(8) |
| C29 | N7 | C24 | Au2 | 2.5(7) |
| C29 | N7 | C24 | N8 | -176.7(4) |
| C29 | N7 | C26 | C25 | 177.3(5) |
| C29 | N7 | C26 | C27 | -1.2(9) |
| C30 | N8 | C24 | Au2 | 5.7(7) |
| C30 | N8 | C24 | N7 | -175.1(4) |
| C30 | N8 | C25 | N9 | -5.7(9) |
| C30 | N8 | C25 | C26 | 175.2(5) |
| C31 | N9 | C25 | N8 | 6.8(9) |
| C31 | N9 | C25 | C26 | -174.2(5) |
| C31 | N9 | C28 | O4 | -3.5(9) |
| C31 | N9 | C28 | N10 | 176.5(5) |
| C32 | N10 | C27 | O3 | 0.4(8) |
| C32 | N10 | C27 | C26 | -178.5(5) |
| C32 | N10 | C28 | O4 | -0.8(9) |
| C32 | N10 | C28 | N9 | 179.2(5) |
| C33 | N11 | C37 | C36 | 0.3(10) |
| C33 | C34 | C35 | C36 | 0.1(11) |
| C33 | C34 | C35 | C38 | -179.6(7) |
| C34 | C35 | C36 | C37 | 0.9(9) |
| C35 | C36 | C37 | N11 | -1.1(9) |
| C37 | N11 | C33 | C34 | 0.8(12) |
| C38 | C35 | C36 | C37 | -179.4(5) |
| C40 | N12 | C42 | C41 | 0.1(6) |
| C40 | N12 | C42 | C43 | 179.5(6) |
| C40 | N13 | C41 | N14 | -179.4(5) |
| C40 | N13 | C41 | C42 | 2.3(6) |
| C41 | N13 | C40 | Au3 | 174.7(4) |
| C41 | N13 | C40 | N12 | -2.3(6) |

| Atom | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|
| C41 | N14 | C44 | O6 | -177.9(6) |
| C41 | N14 | C44 | N15 | 4.6(8) |
| C41 | C42 | C43 | O5 | -179.9(6) |
| C41 | C42 | C43 | N15 | 0.3(8) |
| C42 | N12 | C40 | Au3 | -175.6(4) |
| C42 | N12 | C40 | N13 | 1.4(6) |
| C43 | N15 | C44 | O6 | 178.5(6) |
| C43 | N15 | C44 | N14 | -4.1(9) |
| C44 | N14 | C41 | N13 | 178.8(6) |
| C44 | N14 | C41 | C42 | -3.1(8) |
| C44 | N15 | C43 | O5 | -178.3(6) |
| C44 | N15 | C43 | C42 | 1.6(9) |
| C45 | N12 | C40 | Au3 | -0.2(8) |
| C45 | N12 | C40 | N13 | 176.7(5) |
| C45 | N12 | C42 | C41 | -175.3(5) |
| C45 | N12 | C42 | C43 | 4.2(10) |
| C46 | N13 | C40 | Au3 | -1.1(7) |
| C46 | N13 | C40 | N12 | -178.1(5) |
| C46 | N13 | C41 | N14 | -3.9(10) |
| C46 | N13 | C41 | C42 | 177.8(6) |
| C47 | N14 | C41 | N13 | 7.2(10) |
| C47 | N14 | C41 | C42 | -174.7(6) |
| C47 | N14 | C44 | O6 | -5.8(9) |
| C47 | N14 | C44 | N15 | 176.7(6) |
| C48 | N15 | C43 | O5 | 0.0(9) |
| C48 | N15 | C43 | C42 | 179.9(5) |
| C48 | N15 | C44 | O6 | 0.1(9) |
| C48 | N15 | C44 | N14 | 177.6(6) |

**Table S16**: Hydrogen Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **4b**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$.

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| H1 | 2993 | 10677 | 6749 | 64 |
| H2 | 4357 | 10405 | 5909 | 59 |
| H4 | 6003 | 9685 | 7827 | 68 |
| H5 | 4537 | 9901 | 8580 | 74 |
| H13A | 9045 | 6852 | 4238 | 80 |
| H13B | 9056 | 7701 | 5099 | 80 |
| H13C | 10167 | 7334 | 4862 | 80 |
| H14A | 8817 | 10226 | 3065 | 88 |
| H14B | 9882 | 10834 | 3710 | 88 |
| H14C | 8769 | 10555 | 4079 | 88 |
| H15A | 11288 | 6780 | 3985 | 82 |
| H15B | 11475 | 6260 | 3024 | 82 |
| H15C | 10260 | 6264 | 3266 | 82 |
| H16A | 11881 | 8172 | 1145 | 121 |
| H16B | 12902 | 8661 | 1877 | 121 |
| H16C | 12054 | 9303 | 1640 | 121 |
| H17 | 10257 | 5788 | 618 | 69 |
| H18 | 9128 | 5815 | 1686 | 62 |
| H20 | 8397 | 8315 | 1339 | 62 |
| H21 | 9523 | 8168 | 286 | 74 |
| H29A | 4287 | 7818 | 3587 | 70 |
| H29B | 3553 | 8409 | 4217 | 70 |
| H29C | 3212 | 7258 | 3831 | 70 |
| H30A | 7250 | 7000 | 5319 | 76 |
| H30B | 6832 | 6696 | 6127 | 76 |
| H30C | 7314 | 7805 | 6218 | 76 |
| H31A | 5905 | 6680 | 7269 | 97 |
| H31B | 5580 | 7484 | 8041 | 97 |
| H31C | 6430 | 7797 | 7441 | 97 |
| H32A | 2148 | 8456 | 7497 | 95 |
| H32B | 1839 | 7306 | 7302 | 95 |
| H32C | 1460 | 7817 | 6599 | 95 |
| H33 | 654 | 5606 | 5681 | 103 |
| H34 | 1462 | 5608 | 4465 | 93 |
| H36 | 4147 | 4955 | 5612 | 64 |
| H37 | 3212 | 4930 | 6777 | 75 |
| H45A | 7051 | 4361 | 1571 | 96 |
| H45B | 6258 | 3689 | 733 | 96 |
| H45C | 5794 | 3994 | 1633 | 96 |
| H46A | 4409 | 7048 | 1970 | 99 |
| H46B | 4235 | 7206 | 1036 | 99 |
| H46C | 5296 | 7786 | 1699 | 99 |
| H47A | 5133 | 7713 | -18 | 133 |
| H47B | 6263 | 8137 | -291 | 133 |
| H47C | 6168 | 8218 | 698 | 133 |
| H48A | 8393 | 4922 | -1260 | 132 |
| H48B | 8715 | 6031 | -1249 | 132 |
| H48C | 7696 | 5342 | -1900 | 132 |

**Table S17**: Solvent masking (Olex2) information for **4b**.

| No | x | y | z | V | e | Content |
|---|---|---|---|---|---|---|
| 1 | -0.040 | 0.000 | 0.000 | 551.7 | 176.5 | ? |

# Crystal Data and Experimental

**Crystal Data.** $C_{34}H_{38}AuBF_2N_6O_2$, $M_r$ = 808.48, triclinic, *P*-1 (No. 2), a = 7.45010(10) Å, b = 23.1052(5) Å, c = 23.6290(7) Å, $\alpha$ = 90.528(2)°, $\beta$ = 90.954(2)°, $\gamma$ = 93.994(2)°, $V$ = 4056.74(16) Å$^3$, $T$ = 30(2) K, $Z$ = 4, $Z'$ = 2, $\mu$ = 3.385 mm$^{-1}$, 127294 reflections measured, 13129 unique ($R_{int}$ = 0.162) which were used in all calculations. The final $wR_2$ was 0.3057 (all data) and $R_1$ was 0.0999 (I > 2(I)).

**Table S18**

| **Compound** | **4d** |
|---|---|
| Formula | $C_{34}H_{38}AuBF_2N_6O_2$ |
| $D_{calc.}$/ g cm$^{-3}$ | 1.324 |
| $\mu$/mm$^{-1}$ | 3.385 |
| Formula Weight | 808.48 |
| Colour | orange |
| Shape | plate |
| Size/mm$^3$ | 0.100×0.040×0.010 |
| $T$/K | 30(2) |
| Crystal System | triclinic |
| Space Group | *P*-1 |
| $a$/Å | 7.45010(10) |
| $b$/Å | 23.1052(5) |
| $c$/Å | 23.6290(7) |
| $\alpha$/° | 90.528(2) |
| $\beta$/° | 90.954(2) |
| $\gamma$/° | 93.994(2) |
| V/Å$^3$ | 4056.74(16) |
| $Z$ | 4 |
| $Z'$ | 2 |
| Wavelength/Å | 0.6889 |
| Radiation type | ? |
| $\Theta_{min}$/° | 2.381 |
| $\Theta_{max}$/° | 23.905 |
| Measured Refl. | 127294 |
| Independent Refl. | 13129 |
| Reflections with I > 2(I) | . |
| $R_{int}$ | 0.162 |
| Parameters | 852 |
| Restraints | 0 |
| Largest Peak | 4.481 |
| Deepest Hole | -1.879 |
| GooF | 1.127 |
| $wR_2$ (all data) | 0.3057 |
| $wR_2$ | 0.2804 |
| $R_1$ (all data) | 0.1427 |
| $R_1$ | 0.0999 |

## Structure Quality Indicators

| | | | | |
|---|---|---|---|---|
| **Reflections:** | d min (0.6889) 0.85 | I/σ 12.7 | Rint 16.23% | complete 95% |
| **Refinement:** | Shift -0.001 | Max Peak 4.5 | Min Peak -1.9 | GooF 1.127 |

The unit cell was refined using DIALS (Winter, 2010, 2018).

Data reduction, scaling and absorption corrections were performed. The final completeness is 94.90 % out to 23.905° in $\Theta$. An empirical absorption correction was performed using CCP4 7.0.75 (Winn, 2011), AIMLESS Evans, 2013), version 0.7.4. The absorption coefficient $\mu$ of this material is 3.385 $mm^{-1}$ at this wavelength ($\lambda$ = 0.6889 Å) and the minimum and maximum transmissions are 0.983 and 1.000.

The value of Z' is 2. This means that there are two independent molecules in the asymmetric unit.

The structure forms “square” channels in the *a*-direction.

## Table S19 - Reflection Statistics

| | | | |
|---|---|---|---|
| Total reflections (after filtering) | 127294 | Unique reflections | 13129 |
| Completeness | 0.95 | Mean I/$\sigma$ | 10.12 |
| $hkl_{max}$ collected | (8, 27, 28) | $hkl_{min}$ collected | (-8, -28, -28) |
| $hkl_{max}$ used | (8, 27, 27) | $hkl_{min}$ used | (-8, -27, 0) |
| Lim $d_{max}$ collected | 10.0 | Lim $d_{min}$ collected | 0.85 |
| $d_{max}$ used | 8.29 | $d_{min}$ used | 0.85 |
| Friedel pairs | 12917 | Friedel pairs merged | 1 |
| Inconsistent equivalents | 116 | $R_{int}$ | 0.1623 |
| $R_{sigma}$ | 0.0786 | Intensity transformed | 0 |
| Omitted reflections | 0 | Omitted by user (OMIT hkl) | 0 |
| Multiplicity | (3174, 2164, 2106, 2699, 4360, 5321, 4856, 1695, 273) | Maximum multiplicity | 18 |
| Removed systematic absences | 0 | Filtered off (Shel/OMIT) | 1057 |

**Table S20**: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **4d.** $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$.

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| Au1 | 9164.8(8) | 1216.5(3) | 4930.5(2) | 48.6(3) |
| Au2 | 4338.9(9) | 5180.2(3) | 1189.2(3) | 51.9(3) |
| F1 | 9110(10) | 3431(4) | 9891(3) | 45(2) |
| F2 | 12122(10) | 3490(4) | 9827(4) | 49(2) |
| F3 | 2263(10) | 228(4) | 3535(3) | 48(2) |
| F4 | 5255(10) | 193(4) | 3505(3) | 43(2) |
| O1 | 8378(16) | -130(5) | 1950(4) | 60(3) |
| O2 | 9035(15) | 1781(5) | 2454(5) | 59(3) |
| O3 | 4297(15) | 8145(5) | -267(5) | 54(3) |
| O4 | 5093(14) | 7772(5) | 1606(5) | 52(3) |
| N1 | 10397(16) | 3582(5) | 8967(5) | 42(3) |
| N2 | 10480(15) | 2627(5) | 9444(5) | 36(3) |
| N3 | 8841(15) | 459(6) | 3875(5) | 38(3) |
| N4 | 8629(15) | 73(5) | 2884(5) | 40(3) |
| N5 | 8750(15) | 818(6) | 2211(5) | 41(3) |
| N6 | 9069(16) | 1371(6) | 3677(5) | 42(3) |
| N7 | 4100(17) | 1126(5) | 3667(5) | 42(3) |
| N8 | 3803(15) | 646(5) | 2733(5) | 37(3) |
| N9 | 4333(15) | 6220(5) | 403(5) | 37(3) |
| N10 | 4424(15) | 7199(5) | -23(5) | 37(3) |
| N11 | 4669(16) | 7953(5) | 657(6) | 43(3) |
| N12 | 4632(16) | 6482(5) | 1274(5) | 42(3) |
| C1 | 10220(20) | 3285(7) | 8448(6) | 45(4) |
| C2 | 10030(20) | 3699(7) | 8010(7) | 58(5) |
| C3 | 9770(30) | 3609(8) | 7379(7) | 73(6) |
| C4 | 10150(30) | 4243(7) | 8285(7) | 60(5) |
| C5 | 9940(40) | 4829(9) | 7993(10) | 101(8) |
| C6 | 11710(40) | 5036(12) | 7699(13) | 130(10) |
| C7 | 10360(20) | 4156(7) | 8870(7) | 55(5) |
| C8 | 10550(20) | 4606(7) | 9315(7) | 58(5) |
| C9 | 10630(20) | 2215(7) | 9838(6) | 43(4) |
| C10 | 10720(20) | 2352(7) | 10459(6) | 53(4) |
| C11 | 10638(19) | 1668(6) | 9583(6) | 39(4) |
| C12 | 10830(20) | 1105(7) | 9895(7) | 52(4) |
| C13 | 9060(20) | 796(7) | 10057(7) | 54(4) |
| C14 | 10480(20) | 1747(7) | 9007(6) | 43(4) |
| C15 | 10490(20) | 1272(7) | 8560(6) | 51(4) |
| C16 | 10375(19) | 2349(6) | 8917(6) | 38(4) |
| C17 | 10234(19) | 2675(7) | 8422(6) | 43(4) |
| C18 | 10070(20) | 2377(6) | 7858(6) | 43(4) |
| C19 | 8380(20) | 2174(8) | 7646(7) | 55(5) |
| C20 | 8200(20) | 1932(8) | 7119(8) | 64(5) |
| C21 | 9690(20) | 1886(7) | 6774(6) | 46(4) |
| C22 | 11360(20) | 2060(7) | 6992(7) | 55(5) |
| C23 | 11530(20) | 2311(7) | 7533(6) | 50(4) |
| C24 | 9500(20) | 1647(7) | 6205(7) | 53(4) |
| C25 | 9360(20) | 1457(8) | 5744(7) | 60(5) |
| C26 | 9030(20) | 998(7) | 4095(6) | 40(4) |
| C27 | 8730(20) | -66(7) | 4222(6) | 42(4) |
| C28 | 8788(19) | 502(7) | 3294(6) | 37(4) |
| C29 | 8500(20) | -553(7) | 3008(7) | 53(4) |
| C30 | 8600(20) | 228(7) | 2327(6) | 44(4) |
| C31 | 8720(20) | 988(8) | 1621(6) | 57(5) |
| C32 | 8930(20) | 1282(8) | 2608(7) | 46(4) |
| C33 | 8938(18) | 1071(7) | 3177(6) | 38(4) |
| C34 | 9270(20) | 2015(7) | 3727(7) | 60(5) |
| C35 | 4230(20) | 1669(7) | 3402(7) | 50(4) |
| C36 | 4450(30) | 2121(8) | 3821(7) | 72(6) |
| C37 | 4640(40) | 2774(8) | 3730(8) | 96(8) |

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| C38 | 4470(30) | 1838(8) | 4331(7) | 76(6) |
| C39 | 5200(50) | 2179(15) | 4961(12) | 153(16) |
| C40 | 3520(50) | 2283(18) | 5099(14) | 190(20) |
| C41 | 4220(20) | 1224(8) | 4226(7) | 57(5) |
| C42 | 4140(20) | 754(7) | 4650(7) | 60(5) |
| C43 | 3555(19) | 238(6) | 2309(6) | 37(4) |
| C44 | 3440(20) | -407(7) | 2423(7) | 53(4) |
| C45 | 3470(20) | 508(7) | 1789(6) | 42(4) |
| C46 | 3150(20) | 202(7) | 1234(7) | 52(4) |
| C47 | 4850(20) | 165(7) | 890(7) | 57(5) |
| C48 | 3690(20) | 1100(6) | 1886(6) | 41(4) |
| C49 | 3720(20) | 1570(7) | 1444(6) | 52(4) |
| C50 | 3890(19) | 1192(6) | 2483(6) | 38(4) |
| C51 | 4090(20) | 1699(6) | 2809(7) | 43(4) |
| C52 | 4150(20) | 2284(7) | 2533(6) | 45(4) |
| C53 | 2590(30) | 2563(8) | 2440(8) | 66(5) |
| C54 | 2620(30) | 3082(8) | 2175(8) | 67(5) |
| C55 | 4220(30) | 3361(7) | 1987(7) | 53(4) |
| C56 | 5800(20) | 3091(7) | 2090(7) | 54(4) |
| C57 | 5760(20) | 2559(7) | 2356(7) | 57(5) |
| C58 | 4240(20) | 3910(7) | 1702(7) | 58(5) |
| C59 | 4260(30) | 4370(8) | 1488(8) | 63(5) |
| C60 | 4440(20) | 6017(6) | 932(7) | 44(4) |
| C61 | 4120(20) | 5825(6) | -94(7) | 46(4) |
| C62 | 4449(18) | 6812(6) | 414(7) | 38(4) |
| C63 | 4280(20) | 7026(7) | -613(6) | 49(4) |
| C64 | 4470(20) | 7798(7) | 103(7) | 41(4) |
| C65 | 4740(20) | 8578(6) | 797(7) | 54(4) |
| C66 | 4862(18) | 7589(7) | 1125(7) | 42(4) |
| C67 | 4680(19) | 6984(6) | 954(7) | 41(4) |
| C68 | 4840(20) | 6461(7) | 1887(7) | 57(5) |
| B1 | 10550(20) | 3298(8) | 9546(7) | 42(4) |
| B2 | 3860(20) | 538(8) | 3364(7) | 40(4) |

**Table S21**: Anisotropic Displacement Parameters (×10⁴) **4d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Au1 | 53.8(5) | 55.7(5) | 37.0(4) | -5.7(3) | -6.3(3) | 10.5(3) |
| Au2 | 64.2(5) | 28.5(4) | 64.2(5) | 11.8(3) | 4.2(4) | 9.9(3) |
| F1 | 41(5) | 43(5) | 51(5) | -4(4) | 1(4) | 11(4) |
| F2 | 39(5) | 47(6) | 60(6) | -14(4) | -5(4) | -1(4) |
| F3 | 36(5) | 52(6) | 58(5) | 16(4) | 1(4) | 2(4) |
| F4 | 40(5) | 43(5) | 46(5) | 9(4) | -5(4) | 8(4) |
| O1 | 83(9) | 64(8) | 35(6) | -7(6) | -9(6) | 30(7) |
| O2 | 65(8) | 56(9) | 56(7) | 20(6) | -7(6) | 6(6) |
| O3 | 68(8) | 28(6) | 67(8) | 12(6) | 15(6) | 10(5) |
| O4 | 56(7) | 43(7) | 58(7) | -9(6) | 0(6) | 9(5) |
| N1 | 52(8) | 30(8) | 43(8) | -6(6) | 5(6) | 2(6) |
| N2 | 41(7) | 31(7) | 36(7) | 1(6) | 0(5) | 4(6) |
| N3 | 32(7) | 50(9) | 32(7) | -2(6) | -2(5) | 5(6) |
| N4 | 38(7) | 43(8) | 40(7) | 6(6) | -1(6) | 11(6) |
| N5 | 40(7) | 56(9) | 29(7) | 8(6) | -6(5) | 17(6) |
| N6 | 43(8) | 44(8) | 39(8) | -9(7) | -7(6) | 5(6) |
| N7 | 57(8) | 34(8) | 37(7) | 5(6) | -3(6) | 4(6) |
| N8 | 41(7) | 31(7) | 39(7) | 10(6) | -2(5) | 6(6) |
| N9 | 45(8) | 23(7) | 44(8) | 3(6) | 1(6) | 10(6) |
| N10 | 42(7) | 23(7) | 48(8) | 3(6) | 7(6) | 3(5) |
| N11 | 38(7) | 25(7) | 68(10) | 8(7) | 7(6) | 3(6) |
| N12 | 40(8) | 33(8) | 56(8) | 8(7) | 2(6) | 11(6) |
| C1 | 52(10) | 42(10) | 43(9) | -3(8) | 1(7) | 8(8) |
| C2 | 78(13) | 44(11) | 51(10) | 4(9) | -2(9) | 3(9) |
| C3 | 115(17) | 50(12) | 55(12) | 3(9) | 0(11) | 11(11) |
| C4 | 103(15) | 27(10) | 49(11) | 5(8) | 1(10) | 2(9) |
| C5 | 150(20) | 63(15) | 88(16) | -9(13) | 42(16) | -7(15) |
| C6 | 130(20) | 100(20) | 160(30) | 30(19) | -20(20) | 13(18) |
| C7 | 68(12) | 35(11) | 62(12) | -5(9) | 1(9) | 1(9) |
| C8 | 81(13) | 44(11) | 47(10) | -2(8) | -4(9) | -10(9) |
| C9 | 43(9) | 40(10) | 45(9) | -4(8) | -1(7) | 2(7) |
| C10 | 70(12) | 40(10) | 50(10) | 1(8) | 0(8) | 14(9) |
| C11 | 44(9) | 29(9) | 46(10) | -1(7) | -2(7) | 10(7) |
| C12 | 60(11) | 45(11) | 51(10) | 4(8) | -3(8) | 6(9) |
| C13 | 58(11) | 58(12) | 46(10) | 6(8) | 1(8) | 11(9) |
| C14 | 45(10) | 37(10) | 46(10) | -5(8) | -3(7) | 1(7) |
| C15 | 68(11) | 39(10) | 44(9) | -9(8) | 10(8) | -3(8) |
| C16 | 37(9) | 33(9) | 44(9) | 1(7) | 4(7) | 4(7) |
| C17 | 41(9) | 42(10) | 45(9) | -7(8) | 9(7) | -7(7) |
| C18 | 64(11) | 32(9) | 35(9) | -3(7) | 1(8) | 4(8) |
| C19 | 58(11) | 61(12) | 45(10) | -9(9) | 5(8) | 3(9) |
| C20 | 47(11) | 83(15) | 65(12) | -26(11) | -14(9) | 24(10) |
| C21 | 58(11) | 39(10) | 41(9) | -3(7) | -17(8) | 7(8) |
| C22 | 68(12) | 55(11) | 42(10) | -1(8) | 8(9) | -2(9) |
| C23 | 63(11) | 51(11) | 34(9) | -9(8) | -6(8) | 2(9) |
| C24 | 79(13) | 51(11) | 32(10) | -1(8) | 0(8) | 17(9) |
| C25 | 79(13) | 65(13) | 41(11) | 9(9) | 1(9) | 32(10) |
| C26 | 48(10) | 56(11) | 18(7) | 10(8) | -6(6) | 16(8) |
| C27 | 51(10) | 46(10) | 30(8) | 7(7) | -7(7) | 5(8) |
| C28 | 37(9) | 41(10) | 34(9) | 3(7) | 1(6) | 10(7) |
| C29 | 67(11) | 45(11) | 47(10) | -2(8) | -6(8) | 14(9) |
| C30 | 46(10) | 52(11) | 35(9) | 6(9) | -4(7) | 20(8) |
| C31 | 59(11) | 73(13) | 40(9) | 13(9) | -5(8) | 11(9) |
| C32 | 48(10) | 43(11) | 49(10) | 15(9) | 4(8) | 15(8) |
| C33 | 31(8) | 46(11) | 37(9) | 2(8) | 1(6) | 6(7) |
| C34 | 76(13) | 49(12) | 56(11) | -12(9) | -2(9) | 9(9) |
| C35 | 62(11) | 39(10) | 48(10) | 5(8) | -1(8) | 8(8) |
| C36 | 133(18) | 41(11) | 42(10) | 3(9) | 9(11) | 5(11) |
| C37 | 180(20) | 45(13) | 62(13) | -12(10) | 12(14) | -8(14) |

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C38 | 135(19) | 60(14) | 31(10) | -10(9) | -1(11) | -1(12) |
| C39 | 200(30) | 170(30) | 110(20) | 80(20) | 90(20) | 110(30) |
| C40 | 210(40) | 220(40) | 130(30) | 50(30) | -70(30) | -110(40) |
| C41 | 73(13) | 43(11) | 54(11) | 0(9) | -1(9) | 1(9) |
| C42 | 77(13) | 49(11) | 53(11) | 7(9) | 8(9) | 1(9) |
| C43 | 40(9) | 32(9) | 38(9) | 6(7) | -4(7) | 2(7) |
| C44 | 70(12) | 39(10) | 47(10) | 9(8) | -10(8) | -2(9) |
| C45 | 43(9) | 35(10) | 47(10) | 3(8) | -9(7) | -2(7) |
| C46 | 65(11) | 40(10) | 52(10) | 7(8) | 1(9) | -5(8) |
| C47 | 80(13) | 44(11) | 44(10) | -5(8) | -2(9) | -3(9) |
| C48 | 46(9) | 34(10) | 43(9) | 6(7) | -6(7) | 1(7) |
| C49 | 71(12) | 45(10) | 39(9) | 11(8) | -14(8) | -5(9) |
| C50 | 43(9) | 27(9) | 44(9) | 13(7) | -2(7) | 6(7) |
| C51 | 45(9) | 32(9) | 53(10) | 13(8) | 2(7) | 5(7) |
| C52 | 61(11) | 30(9) | 45(9) | 8(7) | 1(8) | 5(8) |
| C53 | 64(12) | 44(11) | 92(14) | 29(10) | 18(10) | 13(9) |
| C54 | 70(14) | 48(12) | 85(14) | 17(10) | 5(10) | 24(10) |
| C55 | 80(13) | 25(9) | 55(10) | 5(8) | 5(9) | 8(9) |
| C56 | 61(12) | 36(10) | 63(11) | 18(8) | -3(9) | -6(9) |
| C57 | 57(12) | 43(11) | 71(12) | 22(9) | -9(9) | 6(9) |
| C58 | 84(14) | 31(11) | 61(11) | 17(9) | 5(9) | 11(9) |
| C59 | 77(13) | 41(12) | 71(12) | 7(10) | 3(10) | 16(9) |
| C60 | 41(9) | 27(9) | 68(12) | 2(9) | 2(8) | 18(7) |
| C61 | 52(10) | 27(9) | 59(10) | 5(8) | 2(8) | 9(7) |
| C62 | 31(8) | 23(9) | 60(11) | 4(8) | 3(7) | 4(6) |
| C63 | 63(11) | 29(9) | 58(11) | 11(8) | 8(8) | 15(8) |
| C64 | 39(9) | 30(10) | 54(11) | 2(9) | 13(8) | 6(7) |
| C65 | 57(11) | 30(10) | 76(12) | -6(8) | 5(9) | 11(8) |
| C66 | 24(8) | 40(10) | 63(11) | 4(9) | 3(7) | 11(7) |
| C67 | 41(9) | 27(9) | 57(11) | 7(8) | 6(8) | 8(7) |
| C68 | 66(12) | 44(11) | 61(12) | 6(9) | 5(9) | 3(9) |
| B1 | 39(11) | 44(11) | 42(10) | 0(9) | -5(8) | 3(9) |
| B2 | 31(10) | 43(11) | 48(11) | 11(9) | -3(8) | 8(9) |

**Table S22**: Bond Lengths in Å for **4d**.

| Atom | Atom | Length/Å |
|---|---|---|
| Au1 | C25 | 1.997(18) |
| Au1 | C26 | 2.033(13) |
| Au2 | C59 | 2.005(19) |
| Au2 | C60 | 2.028(15) |
| F1 | B1 | 1.405(19) |
| F2 | B1 | 1.382(19) |
| F3 | B2 | 1.412(19) |
| F4 | B2 | 1.393(19) |
| O1 | C30 | 1.213(18) |
| O2 | C32 | 1.211(18) |
| O3 | C64 | 1.204(18) |
| O4 | C66 | 1.214(17) |
| N1 | C1 | 1.400(18) |
| N1 | C7 | 1.35(2) |
| N1 | B1 | 1.53(2) |
| N2 | C9 | 1.347(19) |
| N2 | C16 | 1.393(17) |
| N2 | B1 | 1.56(2) |
| N3 | C26 | 1.344(19) |
| N3 | C27 | 1.469(19) |
| N3 | C28 | 1.377(17) |
| N4 | C28 | 1.377(18) |
| N4 | C29 | 1.477(19) |
| N4 | C30 | 1.367(18) |
| N5 | C30 | 1.39(2) |
| N5 | C31 | 1.453(18) |
| N5 | C32 | 1.41(2) |
| N6 | C26 | 1.315(19) |
| N6 | C33 | 1.363(17) |
| N6 | C34 | 1.49(2) |
| N7 | C35 | 1.41(2) |
| N7 | C41 | 1.34(2) |
| N7 | B2 | 1.53(2) |
| N8 | C43 | 1.371(18) |
| N8 | C50 | 1.398(18) |
| N8 | B2 | 1.51(2) |
| N9 | C60 | 1.342(19) |
| N9 | C61 | 1.480(18) |
| N9 | C62 | 1.365(17) |
| N10 | C62 | 1.374(19) |
| N10 | C63 | 1.447(18) |
| N10 | C64 | 1.410(19) |
| N11 | C64 | 1.356(19) |
| N11 | C65 | 1.476(18) |
| N11 | C66 | 1.41(2) |
| N12 | C60 | 1.339(18) |
| N12 | C67 | 1.389(19) |
| N12 | C68 | 1.45(2) |
| C1 | C2 | 1.43(2) |
| C1 | C17 | 1.41(2) |
| C2 | C3 | 1.51(2) |
| C2 | C4 | 1.40(2) |
| C4 | C5 | 1.54(3) |
| C4 | C7 | 1.41(2) |
| C5 | C6 | 1.54(3) |
| C7 | C8 | 1.47(2) |
| C9 | C10 | 1.50(2) |
| C9 | C11 | 1.40(2) |
| C11 | C12 | 1.52(2) |
| C11 | C14 | 1.38(2) |
| C12 | C13 | 1.51(2) |
| C14 | C15 | 1.52(2) |
| C14 | C16 | 1.42(2) |
| C16 | C17 | 1.40(2) |
| C17 | C18 | 1.49(2) |
| C18 | C19 | 1.40(2) |
| C18 | C23 | 1.36(2) |
| C19 | C20 | 1.36(2) |
| C20 | C21 | 1.40(2) |
| C21 | C22 | 1.37(2) |
| C21 | C24 | 1.45(2) |
| C22 | C23 | 1.40(2) |
| C24 | C25 | 1.17(2) |
| C28 | C33 | 1.34(2) |
| C32 | C33 | 1.43(2) |
| C35 | C36 | 1.43(2) |
| C35 | C51 | 1.41(2) |
| C36 | C37 | 1.52(3) |
| C36 | C38 | 1.38(2) |
| C38 | C39 | 1.74(4) |
| C38 | C41 | 1.44(2) |
| C39 | C40 | 1.34(4) |
| C41 | C42 | 1.48(2) |
| C43 | C44 | 1.51(2) |
| C43 | C45 | 1.39(2) |
| C45 | C46 | 1.49(2) |
| C45 | C48 | 1.38(2) |
| C46 | C47 | 1.52(2) |
| C48 | C49 | 1.51(2) |
| C48 | C50 | 1.43(2) |
| C50 | C51 | 1.39(2) |
| C51 | C52 | 1.50(2) |
| C52 | C53 | 1.38(2) |
| C52 | C57 | 1.38(2) |
| C53 | C54 | 1.36(2) |
| C54 | C55 | 1.40(2) |
| C55 | C56 | 1.39(2) |
| C55 | C58 | 1.44(2) |
| C56 | C57 | 1.38(2) |
| C58 | C59 | 1.18(2) |
| C62 | C67 | 1.34(2) |
| C66 | C67 | 1.45(2) |

**Table S23**: Bond Angles in ° for **4d**.

| Atom | Atom | Atom | Angle/° |
|---|---|---|---|
| C25 | Au1 | C26 | 177.9(7) |
| C59 | Au2 | C60 | 176.8(7) |
| C1 | N1 | B1 | 125.3(13) |
| C7 | N1 | C1 | 108.6(13) |
| C7 | N1 | B1 | 126.1(13) |
| C9 | N2 | C16 | 107.4(12) |
| C9 | N2 | B1 | 126.9(12) |
| C16 | N2 | B1 | 125.6(12) |
| C26 | N3 | C27 | 123.3(12) |
| C26 | N3 | C28 | 108.0(12) |
| C28 | N3 | C27 | 128.7(13) |
| C28 | N4 | C29 | 123.8(12) |
| C30 | N4 | C28 | 119.0(13) |
| C30 | N4 | C29 | 117.2(12) |
| C30 | N5 | C31 | 117.5(13) |
| C30 | N5 | C32 | 127.2(12) |
| C32 | N5 | C31 | 115.3(14) |
| C26 | N6 | C33 | 108.8(13) |
| C26 | N6 | C34 | 126.8(13) |
| C33 | N6 | C34 | 124.4(13) |
| C35 | N7 | B2 | 125.5(13) |
| C41 | N7 | C35 | 107.2(13) |
| C41 | N7 | B2 | 127.3(13) |
| C43 | N8 | C50 | 107.7(11) |
| C43 | N8 | B2 | 127.1(13) |
| C50 | N8 | B2 | 125.0(13) |
| C60 | N9 | C61 | 121.6(12) |
| C60 | N9 | C62 | 109.9(12) |
| C62 | N9 | C61 | 128.5(13) |
| C62 | N10 | C63 | 123.5(12) |
| C62 | N10 | C64 | 119.0(13) |
| C64 | N10 | C63 | 117.4(12) |
| C64 | N11 | C65 | 117.4(13) |
| C64 | N11 | C66 | 128.0(13) |
| C66 | N11 | C65 | 114.6(13) |
| C60 | N12 | C67 | 109.7(13) |
| C60 | N12 | C68 | 124.8(13) |
| C67 | N12 | C68 | 125.5(13) |
| N1 | C1 | C2 | 108.4(14) |
| N1 | C1 | C17 | 120.8(14) |
| C17 | C1 | C2 | 130.8(14) |
| C1 | C2 | C3 | 130.0(15) |
| C4 | C2 | C1 | 105.5(14) |
| C4 | C2 | C3 | 124.5(16) |
| C2 | C4 | C5 | 125.2(17) |
| C2 | C4 | C7 | 108.5(15) |
| C7 | C4 | C5 | 126.1(16) |
| C4 | C5 | C6 | 111(2) |
| N1 | C7 | C4 | 109.0(14) |
| N1 | C7 | C8 | 124.1(16) |
| C4 | C7 | C8 | 126.9(16) |
| N2 | C9 | C10 | 122.4(13) |
| N2 | C9 | C11 | 110.4(13) |
| C11 | C9 | C10 | 127.1(15) |
| C9 | C11 | C12 | 125.1(14) |
| C14 | C11 | C9 | 107.1(14) |
| C14 | C11 | C12 | 127.8(14) |
| C13 | C12 | C11 | 114.2(14) |
| C11 | C14 | C15 | 125.5(15) |
| C11 | C14 | C16 | 107.2(13) |
| C16 | C14 | C15 | 127.2(14) |
| N2 | C16 | C14 | 107.9(13) |
| N2 | C16 | C17 | 120.0(13) |
| C17 | C16 | C14 | 132.1(13) |
| C1 | C17 | C18 | 119.0(14) |
| C16 | C17 | C1 | 120.9(13) |
| C16 | C17 | C18 | 120.1(14) |
| C19 | C18 | C17 | 120.0(14) |
| C23 | C18 | C17 | 121.5(14) |
| C23 | C18 | C19 | 118.5(14) |
| C20 | C19 | C18 | 120.6(15) |
| C19 | C20 | C21 | 121.0(16) |
| C20 | C21 | C24 | 121.6(15) |
| C22 | C21 | C20 | 118.2(14) |
| C22 | C21 | C24 | 120.2(15) |
| C21 | C22 | C23 | 120.2(16) |
| C18 | C23 | C22 | 121.2(16) |
| C25 | C24 | C21 | 180(2) |
| C24 | C25 | Au1 | 174.0(17) |
| N3 | C26 | Au1 | 126.5(11) |
| N6 | C26 | Au1 | 124.9(12) |
| N6 | C26 | N3 | 108.6(12) |
| N3 | C28 | N4 | 130.0(14) |
| C33 | C28 | N3 | 106.6(13) |
| C33 | C28 | N4 | 123.3(13) |
| O1 | C30 | N4 | 121.7(15) |
| O1 | C30 | N5 | 121.1(14) |
| N4 | C30 | N5 | 117.1(14) |
| O2 | C32 | N5 | 121.0(14) |
| O2 | C32 | C33 | 127.8(16) |
| N5 | C32 | C33 | 111.1(14) |
| N6 | C33 | C32 | 129.8(15) |
| C28 | C33 | N6 | 107.9(13) |
| C28 | C33 | C32 | 122.3(14) |
| N7 | C35 | C36 | 109.8(14) |
| N7 | C35 | C51 | 119.7(14) |
| C51 | C35 | C36 | 130.5(15) |
| C35 | C36 | C37 | 128.1(16) |
| C38 | C36 | C35 | 105.0(16) |
| C38 | C36 | C37 | 126.9(16) |
| C36 | C38 | C39 | 122.8(18) |
| C36 | C38 | C41 | 108.8(15) |
| C41 | C38 | C39 | 126.9(18) |
| C40 | C39 | C38 | 92(3) |
| N7 | C41 | C38 | 109.2(15) |
| N7 | C41 | C42 | 123.3(15) |
| C38 | C41 | C42 | 127.5(16) |
| N8 | C43 | C44 | 122.4(12) |
| N8 | C43 | C45 | 109.9(13) |
| C45 | C43 | C44 | 127.6(13) |
| C43 | C45 | C46 | 125.0(14) |
| C48 | C45 | C43 | 107.7(13) |
| C48 | C45 | C46 | 127.3(14) |
| C45 | C46 | C47 | 113.6(13) |
| C45 | C48 | C49 | 126.7(14) |
| C45 | C48 | C50 | 107.7(13) |
| C50 | C48 | C49 | 125.6(13) |
| N8 | C50 | C48 | 107.0(12) |
| C51 | C50 | N8 | 121.4(13) |
| C51 | C50 | C48 | 131.6(13) |

| Atom | Atom | Atom | Angle/° |
|---|---|---|---|
| C35 | C51 | C52 | 119.1(14) |
| C50 | C51 | C35 | 120.2(14) |
| C50 | C51 | C52 | 120.6(14) |
| C53 | C52 | C51 | 120.8(15) |
| C53 | C52 | C57 | 117.6(15) |
| C57 | C52 | C51 | 121.6(15) |
| C54 | C53 | C52 | 121.5(17) |
| C53 | C54 | C55 | 121.5(17) |
| C54 | C55 | C58 | 121.5(17) |
| C56 | C55 | C54 | 117.5(15) |
| C56 | C55 | C58 | 121.0(16) |
| C57 | C56 | C55 | 120.5(16) |
| C56 | C57 | C52 | 121.4(16) |
| C59 | C58 | C55 | 177.5(19) |
| C58 | C59 | Au2 | 175.2(17) |
| N9 | C60 | Au2 | 128.5(11) |
| N12 | C60 | Au2 | 125.2(12) |
| N12 | C60 | N9 | 106.3(13) |
| N9 | C62 | N10 | 130.0(14) |
| C67 | C62 | N9 | 107.8(13) |
| C67 | C62 | N10 | 122.2(13) |

| Atom | Atom | Atom | Angle/° |
|---|---|---|---|
| O3 | C64 | N10 | 120.7(15) |
| O3 | C64 | N11 | 122.7(14) |
| N11 | C64 | N10 | 116.6(14) |
| O4 | C66 | N11 | 123.0(14) |
| O4 | C66 | C67 | 126.0(15) |
| N11 | C66 | C67 | 110.9(14) |
| N12 | C67 | C66 | 130.8(15) |
| C62 | C67 | N12 | 106.3(13) |
| C62 | C67 | C66 | 122.9(14) |
| F1 | B1 | N1 | 110.8(13) |
| F1 | B1 | N2 | 109.3(12) |
| F2 | B1 | F1 | 107.4(12) |
| F2 | B1 | N1 | 111.3(13) |
| F2 | B1 | N2 | 110.7(13) |
| N1 | B1 | N2 | 107.3(12) |
| F3 | B2 | N7 | 110.7(13) |
| F3 | B2 | N8 | 110.7(12) |
| F4 | B2 | F3 | 105.9(13) |
| F4 | B2 | N7 | 110.8(13) |
| F4 | B2 | N8 | 110.7(13) |
| N8 | B2 | N7 | 108.1(13) |

**Table S24**: Torsion Angles in ° for **4d**.

| Atom | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|
| O2 | C32 | C33 | N6 | -1(3) |
| O2 | C32 | C33 | C28 | 178.9(15) |
| O4 | C66 | C67 | N12 | 3(3) |
| O4 | C66 | C67 | C62 | -179.1(14) |
| N1 | C1 | C2 | C3 | -178.9(18) |
| N1 | C1 | C2 | C4 | 1(2) |
| N1 | C1 | C17 | C16 | 2(2) |
| N1 | C1 | C17 | C18 | -179.0(13) |
| N2 | C9 | C11 | C12 | 178.6(13) |
| N2 | C9 | C11 | C14 | -0.4(17) |
| N2 | C16 | C17 | C1 | 1(2) |
| N2 | C16 | C17 | C18 | -178.3(13) |
| N3 | C28 | C33 | N6 | -0.3(15) |
| N3 | C28 | C33 | C32 | -179.9(13) |
| N4 | C28 | C33 | N6 | -180.0(13) |
| N4 | C28 | C33 | C32 | 0(2) |
| N5 | C32 | C33 | N6 | -179.4(13) |
| N5 | C32 | C33 | C28 | 0(2) |
| N7 | C35 | C36 | C37 | -180(2) |
| N7 | C35 | C36 | C38 | 1(2) |
| N7 | C35 | C51 | C50 | -2(2) |
| N7 | C35 | C51 | C52 | 177.2(14) |
| N8 | C43 | C45 | C46 | -177.9(14) |
| N8 | C43 | C45 | C48 | 0.7(17) |
| N8 | C50 | C51 | C35 | 1(2) |
| N8 | C50 | C51 | C52 | -178.9(13) |
| N9 | C62 | C67 | N12 | -2.2(16) |
| N9 | C62 | C67 | C66 | 179.8(13) |
| N10 | C62 | C67 | N12 | -180.0(12) |
| N10 | C62 | C67 | C66 | 2(2) |
| N11 | C66 | C67 | N12 | -174.4(14) |
| N11 | C66 | C67 | C62 | 3(2) |
| C1 | N1 | C7 | C4 | 0.4(19) |
| C1 | N1 | C7 | C8 | -178.9(16) |
| C1 | N1 | B1 | F1 | -118.8(15) |
| C1 | N1 | B1 | F2 | 121.7(15) |
| C1 | N1 | B1 | N2 | 0(2) |
| C1 | C2 | C4 | C5 | -177.3(19) |
| C1 | C2 | C4 | C7 | -1(2) |
| C1 | C17 | C18 | C19 | -92.7(19) |
| C1 | C17 | C18 | C23 | 85(2) |
| C2 | C1 | C17 | C16 | -177.7(16) |
| C2 | C1 | C17 | C18 | 1(3) |
| C2 | C4 | C5 | C6 | -80(3) |
| C2 | C4 | C7 | N1 | 1(2) |
| C2 | C4 | C7 | C8 | 179.8(18) |
| C3 | C2 | C4 | C5 | 3(3) |
| C3 | C2 | C4 | C7 | 179.2(18) |
| C5 | C4 | C7 | N1 | 176.5(19) |
| C5 | C4 | C7 | C8 | -4(3) |
| C7 | N1 | C1 | C2 | -1.2(18) |
| C7 | N1 | C1 | C17 | 179.2(14) |
| C7 | N1 | B1 | F1 | 59(2) |
| C7 | N1 | B1 | F2 | -60(2) |
| C7 | N1 | B1 | N2 | 178.5(14) |
| C7 | C4 | C5 | C6 | 105(2) |
| C9 | N2 | C16 | C14 | -0.4(16) |
| C9 | N2 | C16 | C17 | -179.1(13) |
| C9 | N2 | B1 | F1 | -62.0(19) |
| C9 | N2 | B1 | F2 | 56.1(19) |

| Atom | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|
| C9 | N2 | B1 | N1 | 177.7(13) |
| C9 | C11 | C12 | C13 | 91.3(19) |
| C9 | C11 | C14 | C15 | 177.7(14) |
| C9 | C11 | C14 | C16 | 0.1(17) |
| C10 | C9 | C11 | C12 | -3(3) |
| C10 | C9 | C11 | C14 | 178.1(15) |
| C11 | C14 | C16 | N2 | 0.1(16) |
| C11 | C14 | C16 | C17 | 178.7(15) |
| C12 | C11 | C14 | C15 | -1(3) |
| C12 | C11 | C14 | C16 | -178.8(15) |
| C14 | C11 | C12 | C13 | -89.9(19) |
| C14 | C16 | C17 | C1 | -177.7(15) |
| C14 | C16 | C17 | C18 | 3(2) |
| C15 | C14 | C16 | N2 | -177.4(14) |
| C15 | C14 | C16 | C17 | 1(3) |
| C16 | N2 | C9 | C10 | -178.1(14) |
| C16 | N2 | C9 | C11 | 0.4(17) |
| C16 | N2 | B1 | F1 | 122.5(14) |
| C16 | N2 | B1 | F2 | -119.3(14) |
| C16 | N2 | B1 | N1 | 2.3(19) |
| C16 | C17 | C18 | C19 | 86(2) |
| C16 | C17 | C18 | C23 | -95.5(18) |
| C17 | C1 | C2 | C3 | 1(3) |
| C17 | C1 | C2 | C4 | -178.9(17) |
| C17 | C18 | C19 | C20 | 176.2(16) |
| C17 | C18 | C23 | C22 | -176.5(15) |
| C18 | C19 | C20 | C21 | -1(3) |
| C19 | C18 | C23 | C22 | 2(2) |
| C19 | C20 | C21 | C22 | 4(3) |
| C19 | C20 | C21 | C24 | -177.9(17) |
| C20 | C21 | C22 | C23 | -4(3) |
| C21 | C22 | C23 | C18 | 2(3) |
| C23 | C18 | C19 | C20 | -2(3) |
| C24 | C21 | C22 | C23 | 177.5(16) |
| C26 | N3 | C28 | N4 | 179.3(14) |
| C26 | N3 | C28 | C33 | -0.3(16) |
| C26 | N6 | C33 | C28 | 0.9(16) |
| C26 | N6 | C33 | C32 | -179.6(15) |
| C27 | N3 | C26 | Au1 | -1(2) |
| C27 | N3 | C26 | N6 | -179.5(12) |
| C27 | N3 | C28 | N4 | 0(2) |
| C27 | N3 | C28 | C33 | -179.9(13) |
| C28 | N3 | C26 | Au1 | 179.4(10) |
| C28 | N3 | C26 | N6 | 0.9(16) |
| C28 | N4 | C30 | O1 | -176.5(14) |
| C28 | N4 | C30 | N5 | 0.6(19) |
| C29 | N4 | C28 | N3 | -1(2) |
| C29 | N4 | C28 | C33 | 178.6(14) |
| C29 | N4 | C30 | O1 | 4(2) |
| C29 | N4 | C30 | N5 | -178.8(12) |
| C30 | N4 | C28 | N3 | 179.6(14) |
| C30 | N4 | C28 | C33 | -1(2) |
| C30 | N5 | C32 | O2 | -179.2(14) |
| C30 | N5 | C32 | C33 | 0(2) |
| C31 | N5 | C30 | O1 | -3(2) |
| C31 | N5 | C30 | N4 | 179.9(12) |
| C31 | N5 | C32 | O2 | 1(2) |
| C31 | N5 | C32 | C33 | 179.7(12) |
| C32 | N5 | C30 | O1 | 177.1(14) |
| C32 | N5 | C30 | N4 | 0(2) |
| C33 | N6 | C26 | Au1 | -179.6(10) |
| C33 | N6 | C26 | N3 | -1.1(16) |

| Atom | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|
| C34 | N6 | C26 | Au1 | 2(2) |
| C34 | N6 | C26 | N3 | -179.7(13) |
| C34 | N6 | C33 | C28 | 179.5(14) |
| C34 | N6 | C33 | C32 | -1(2) |
| C35 | N7 | C41 | C38 | -1(2) |
| C35 | N7 | C41 | C42 | -179.8(16) |
| C35 | N7 | B2 | F3 | -120.9(15) |
| C35 | N7 | B2 | F4 | 121.9(15) |
| C35 | N7 | B2 | N8 | 0(2) |
| C35 | C36 | C38 | C39 | 165.2(19) |
| C35 | C36 | C38 | C41 | -1(2) |
| C35 | C51 | C52 | C53 | -89(2) |
| C35 | C51 | C52 | C57 | 91.8(19) |
| C36 | C35 | C51 | C50 | 179.8(18) |
| C36 | C35 | C51 | C52 | -1(3) |
| C36 | C38 | C39 | C40 | 96(3) |
| C36 | C38 | C41 | N7 | 2(2) |
| C36 | C38 | C41 | C42 | -179.8(19) |
| C37 | C36 | C38 | C39 | -15(4) |
| C37 | C36 | C38 | C41 | 179(2) |
| C39 | C38 | C41 | N7 | -164(2) |
| C39 | C38 | C41 | C42 | 14(3) |
| C41 | N7 | C35 | C36 | 0(2) |
| C41 | N7 | C35 | C51 | -178.0(15) |
| C41 | N7 | B2 | F3 | 59(2) |
| C41 | N7 | B2 | F4 | -58(2) |
| C41 | N7 | B2 | N8 | -179.9(15) |
| C41 | C38 | C39 | C40 | -100(3) |
| C43 | N8 | C50 | C48 | -0.2(15) |
| C43 | N8 | C50 | C51 | 178.4(13) |
| C43 | N8 | B2 | F3 | -56.7(19) |
| C43 | N8 | B2 | F4 | 60.4(19) |
| C43 | N8 | B2 | N7 | -178.1(12) |
| C43 | C45 | C46 | C47 | -103.0(18) |
| C43 | C45 | C48 | C49 | 179.3(15) |
| C43 | C45 | C48 | C50 | -0.8(17) |
| C44 | C43 | C45 | C46 | 3(3) |
| C44 | C43 | C45 | C48 | -178.3(15) |
| C45 | C48 | C50 | N8 | 0.6(16) |
| C45 | C48 | C50 | C51 | -177.9(16) |
| C46 | C45 | C48 | C49 | -2(3) |
| C46 | C45 | C48 | C50 | 177.7(15) |
| C48 | C45 | C46 | C47 | 79(2) |
| C48 | C50 | C51 | C35 | 178.9(15) |
| C48 | C50 | C51 | C52 | -1(3) |
| C49 | C48 | C50 | N8 | -179.4(14) |
| C49 | C48 | C50 | C51 | 2(3) |
| C50 | N8 | C43 | C44 | 178.8(13) |
| C50 | N8 | C43 | C45 | -0.3(16) |
| C50 | N8 | B2 | F3 | 119.2(15) |
| C50 | N8 | B2 | F4 | -123.8(15) |
| C50 | N8 | B2 | N7 | -2.2(19) |
| C50 | C51 | C52 | C53 | 90(2) |
| C50 | C51 | C52 | C57 | -89(2) |
| C51 | C35 | C36 | C37 | -1(4) |
| C51 | C35 | C36 | C38 | 178.8(19) |
| C51 | C52 | C53 | C54 | -177.7(17) |
| C51 | C52 | C57 | C56 | 178.5(16) |
| C52 | C53 | C54 | C55 | -1(3) |
| C53 | C52 | C57 | C56 | -1(3) |
| C53 | C54 | C55 | C56 | -1(3) |
| C53 | C54 | C55 | C58 | 179.6(18) |

| Atom | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|
| C54 | C55 | C56 | C57 | 2(3) |
| C55 | C56 | C57 | C52 | -1(3) |
| C57 | C52 | C53 | C54 | 1(3) |
| C58 | C55 | C56 | C57 | -178.9(16) |
| C60 | N9 | C62 | N10 | 179.1(14) |
| C60 | N9 | C62 | C67 | 1.6(16) |
| C60 | N12 | C67 | C62 | 2.2(16) |
| C60 | N12 | C67 | C66 | 179.9(15) |
| C61 | N9 | C60 | Au2 | 0(2) |
| C61 | N9 | C60 | N12 | 179.9(12) |
| C61 | N9 | C62 | N10 | -1(2) |
| C61 | N9 | C62 | C67 | -178.6(13) |
| C62 | N9 | C60 | Au2 | 179.6(10) |
| C62 | N9 | C60 | N12 | -0.2(16) |
| C62 | N10 | C64 | O3 | -173.8(13) |
| C62 | N10 | C64 | N11 | 4.7(19) |
| C63 | N10 | C62 | N9 | -1(2) |
| C63 | N10 | C62 | C67 | 176.2(14) |
| C63 | N10 | C64 | O3 | 4(2) |
| C63 | N10 | C64 | N11 | -177.6(12) |
| C64 | N10 | C62 | N9 | 176.6(13) |
| C64 | N10 | C62 | C67 | -6(2) |
| C64 | N11 | C66 | O4 | 177.5(14) |
| C64 | N11 | C66 | C67 | -5(2) |
| C65 | N11 | C64 | O3 | -2(2) |
| C65 | N11 | C64 | N10 | 179.4(12) |
| C65 | N11 | C66 | O4 | -1(2) |
| C65 | N11 | C66 | C67 | 176.8(12) |
| C66 | N11 | C64 | O3 | 179.3(14) |
| C66 | N11 | C64 | N10 | 1(2) |
| C67 | N12 | C60 | Au2 | 179.0(10) |
| C67 | N12 | C60 | N9 | -1.2(16) |
| C68 | N12 | C60 | Au2 | 1(2) |
| C68 | N12 | C60 | N9 | -178.8(13) |
| C68 | N12 | C67 | C62 | 179.7(14) |
| C68 | N12 | C67 | C66 | -3(2) |
| B1 | N1 | C1 | C2 | 177.2(14) |
| B1 | N1 | C1 | C17 | -3(2) |
| B1 | N1 | C7 | C4 | -177.9(15) |
| B1 | N1 | C7 | C8 | 3(3) |
| B1 | N2 | C9 | C10 | 6(2) |
| B1 | N2 | C9 | C11 | -175.6(13) |
| B1 | N2 | C16 | C14 | 175.8(13) |
| B1 | N2 | C16 | C17 | -3(2) |
| B2 | N7 | C35 | C36 | -179.9(15) |
| B2 | N7 | C35 | C51 | 2(2) |
| B2 | N7 | C41 | C38 | 179.0(16) |
| B2 | N7 | C41 | C42 | 0(3) |
| B2 | N8 | C43 | C44 | -5(2) |
| B2 | N8 | C43 | C45 | 176.2(13) |
| B2 | N8 | C50 | C48 | -176.8(13) |
| B2 | N8 | C50 | C51 | 2(2) |

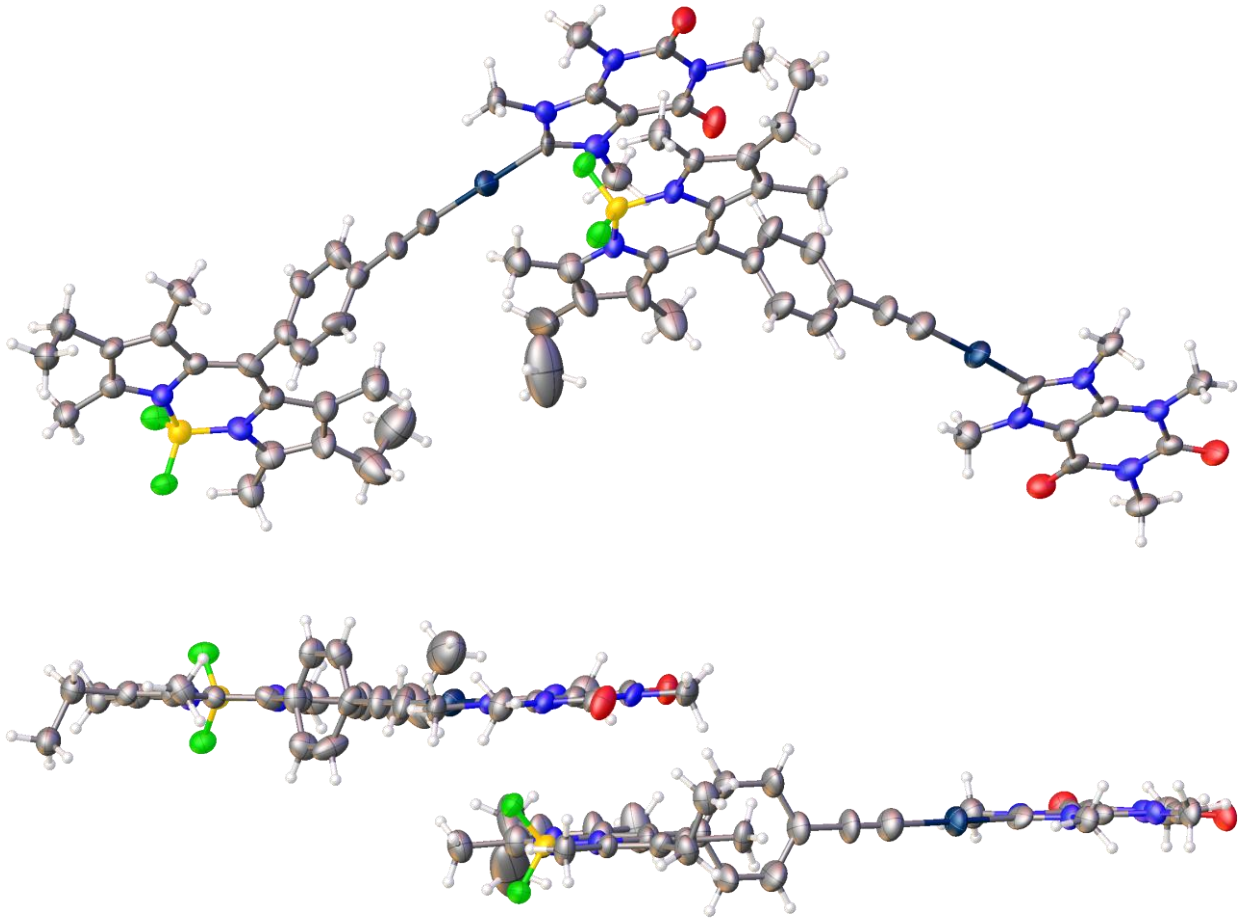
**Table S25**: Hydrogen Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **4d**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$.

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| H3A | 10908 | 3512 | 7213 | 109 |
| H3B | 9383 | 3966 | 7209 | 109 |
| H3C | 8851 | 3292 | 7307 | 109 |
| H5A | 9640 | 5121 | 8278 | 121 |
| H5B | 8950 | 4786 | 7709 | 121 |
| H6A | 12005 | 4747 | 7416 | 195 |
| H6B | 12685 | 5087 | 7981 | 195 |
| H6C | 11550 | 5407 | 7513 | 195 |
| H8A | 10630 | 4422 | 9686 | 87 |
| H8B | 9498 | 4839 | 9303 | 87 |
| H8C | 11641 | 4858 | 9253 | 87 |
| H10A | 11852 | 2231 | 10619 | 79 |
| H10B | 9705 | 2145 | 10646 | 79 |
| H10C | 10659 | 2771 | 10517 | 79 |
| H12A | 11484 | 842 | 9652 | 62 |
| H12B | 11563 | 1188 | 10242 | 62 |
| H13A | 8414 | 651 | 9714 | 80 |
| H13B | 8336 | 1067 | 10257 | 80 |
| H13C | 9294 | 470 | 10304 | 80 |
| H15A | 9360 | 1255 | 8341 | 76 |
| H15B | 10623 | 898 | 8744 | 76 |
| H15C | 11502 | 1356 | 8306 | 76 |
| H19 | 7346 | 2206 | 7872 | 66 |
| H20 | 7037 | 1791 | 6984 | 77 |
| H22 | 12401 | 2009 | 6776 | 66 |
| H23 | 12695 | 2439 | 7675 | 59 |
| H27A | 7594 | -292 | 4140 | 64 |
| H27B | 8790 | 45 | 4624 | 64 |
| H27C | 9740 | -301 | 4135 | 64 |
| H29A | 7388 | -655 | 3209 | 79 |
| H29B | 9537 | -646 | 3244 | 79 |
| H29C | 8506 | -775 | 2652 | 79 |
| H31A | 9145 | 675 | 1386 | 86 |
| H31B | 9510 | 1341 | 1573 | 86 |
| H31C | 7490 | 1062 | 1505 | 86 |
| H34A | 10414 | 2159 | 3563 | 90 |
| H34B | 9253 | 2130 | 4127 | 90 |
| H34C | 8274 | 2182 | 3524 | 90 |
| H37A | 5635 | 2869 | 3475 | 143 |
| H37B | 4876 | 2972 | 4095 | 143 |
| H37C | 3518 | 2900 | 3563 | 143 |
| H39A | 5775 | 1918 | 5227 | 183 |
| H39B | 5981 | 2537 | 4903 | 183 |
| H40A | 2952 | 2487 | 4790 | 289 |
| H40B | 3542 | 2522 | 5444 | 289 |
| H40C | 2825 | 1914 | 5165 | 289 |
| H42A | 2951 | 726 | 4824 | 90 |
| H42B | 5067 | 840 | 4943 | 90 |
| H42C | 4347 | 385 | 4464 | 90 |
| H44A | 4406 | -587 | 2227 | 79 |
| H44B | 2271 | -581 | 2285 | 79 |
| H44C | 3552 | -471 | 2831 | 79 |
| H46A | 2267 | 408 | 1010 | 63 |
| H46B | 2625 | -195 | 1302 | 63 |

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| H47A | 4556 | -55 | 540 | 85 |
| H47B | 5743 | -32 | 1112 | 85 |
| H47C | 5335 | 556 | 798 | 85 |
| H49A | 2737 | 1821 | 1512 | 78 |
| H49B | 3569 | 1392 | 1067 | 78 |
| H49C | 4873 | 1801 | 1468 | 78 |
| H53 | 1481 | 2388 | 2566 | 79 |
| H54 | 1516 | 3260 | 2115 | 80 |
| H56 | 6917 | 3274 | 1978 | 64 |
| H57 | 6848 | 2378 | 2418 | 69 |
| H61A | 5208 | 5861 | -320 | 68 |
| H61B | 3085 | 5929 | -326 | 68 |
| H61C | 3912 | 5424 | 34 | 68 |
| H63A | 5164 | 6741 | -692 | 74 |
| H63B | 4523 | 7367 | -851 | 74 |
| H63C | 3068 | 6853 | -696 | 74 |
| H65A | 3555 | 8679 | 925 | 81 |
| H65B | 5065 | 8803 | 460 | 81 |
| H65C | 5638 | 8666 | 1098 | 81 |
| H68A | 6094 | 6564 | 1995 | 86 |
| H68B | 4484 | 6069 | 2016 | 86 |
| H68C | 4065 | 6737 | 2061 | 86 |

**Table S26**: Solvent masking (Olex2) information for **2019ncs0295**.

| No | x | y | z | V | e | Content |
|---|---|---|---|---|---|---|
| 1 | -0.373 | 0.500 | 0.500 | 1094.1 | 396.1 | ? |



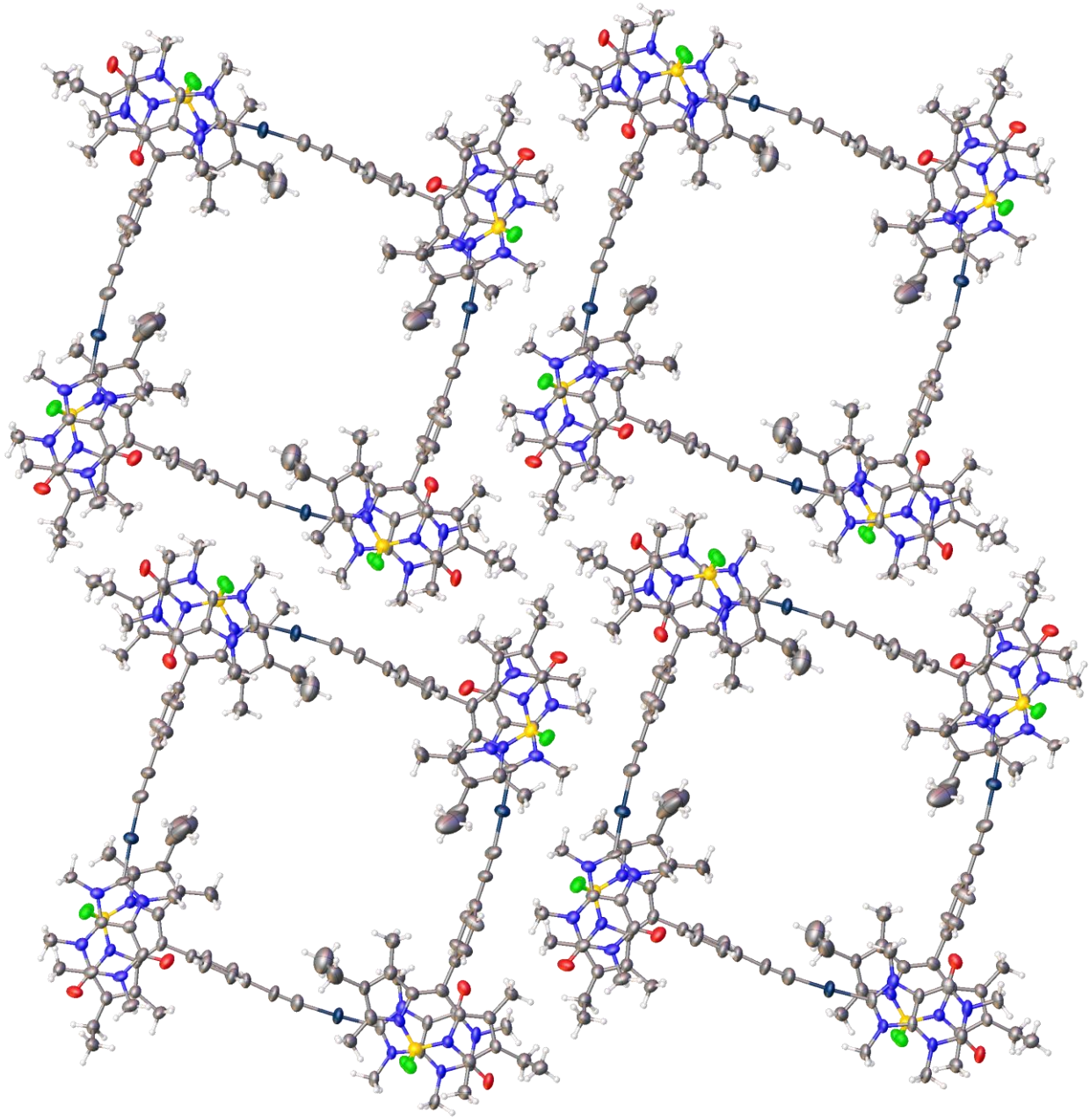


**Figure S55**