

Supporting Information

Excited State Turn-On of Auophilicity and Tunability of Relativistic Effects in a Series of Digold Triazolates Synthesized via iClick

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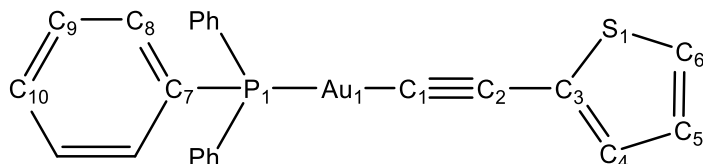
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1. Syntheses, NMR and X-ray Crystallography Data

Synthesis of $\text{PPh}_3\text{AuC}\equiv\text{CTh}$.



74.4 % Yield (0.37 mmol, 209.6 mg). ^1H NMR (500 MHz, CDCl_3): δ 6.89 (dd, $^3J_{\text{HH}} = 3.5$, 5.1 Hz, 1H, $\text{C}_5\text{-H}$), 7.08 (dd, $^3J_{\text{HH}} = 5.2$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 1H, $\text{C}_4\text{-H}$), 7.15 (dd, $^3J_{\text{HH}} = 3.7$ Hz, $^3J_{\text{HH}} = 1.3$ Hz, 1H, $\text{C}_6\text{-H}$), 7.43-7.56 (m, 15H, aromatic). $^{13}\text{C}\{^1\text{H}\}$ NMR (indirect detection through ^1H - ^{13}C gHMBC and ^1H - ^{13}C gHSQC (126 MHz, CDCl_3)): δ 125.1 (C_4), 125.2 (C_3), 126.5 (C_5), 129.1 (d, $^4J_{\text{CP}} = 11$ Hz, C_{10}), 129.6 (d, $^1J_{\text{CP}} = 56$ Hz, C_7), 131.1 (C_6), 131.5 (d, $^3J_{\text{CP}} = 3$ Hz, C_9), 134.3 (d, $^2J_{\text{CP}} = 14$ Hz, C_8). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3): δ 42.52. ESI-MS: m/z calculated for $\text{C}_{24}\text{H}_{18}\text{AuPS}$ $[\text{M}+\text{Na}]^+$ 589.0430, found 589.0408. Anal. Calcd. for $\text{C}_{24}\text{H}_{18}\text{AuPS}$: C, 50.89; H, 3.20. Found: C, 50.60; H, 3.11; N, -0.23.

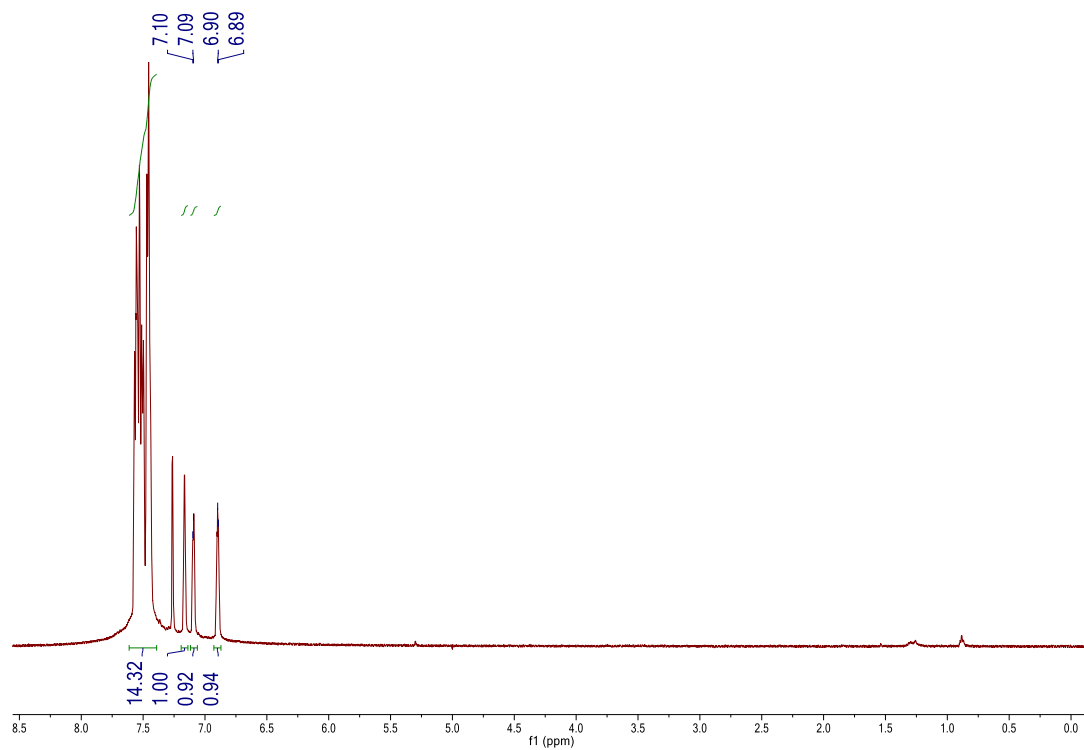


Figure S1. ¹H NMR spectrum of **PPh₃AuC≡CTh** (CDCl₃, 500 MHz, 25 °C).

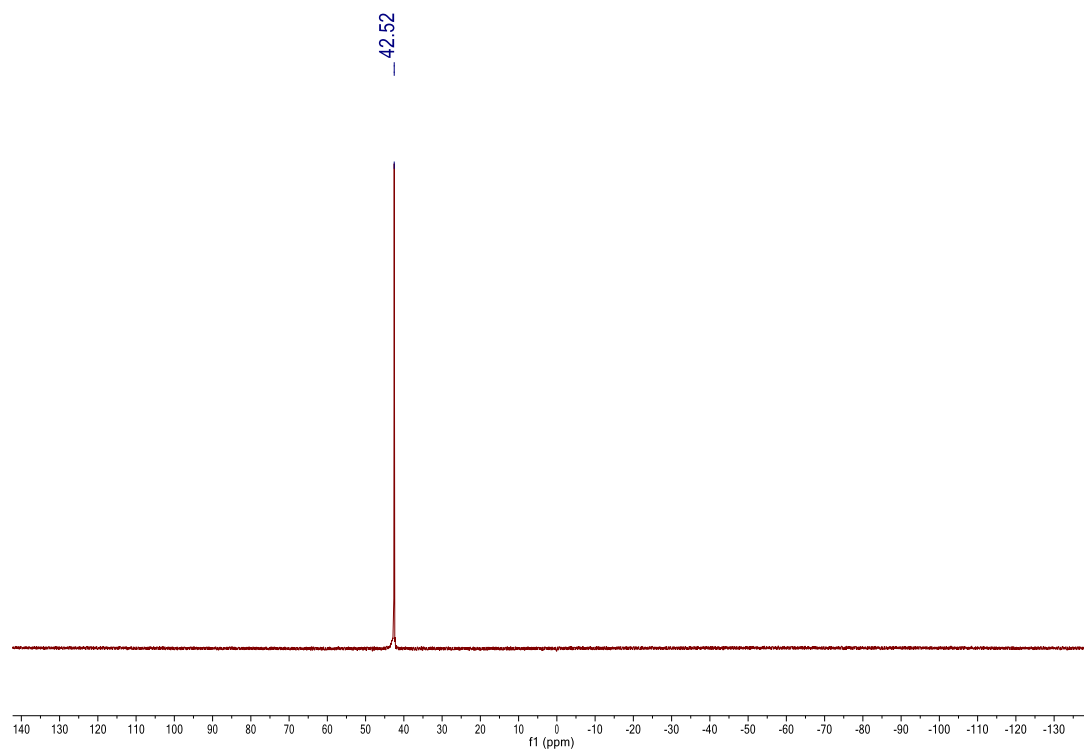


Figure S2. ³¹P{¹H} NMR spectrum of **PPh₃AuC≡CTh** (CDCl₃, 121 MHz, 25 °C).

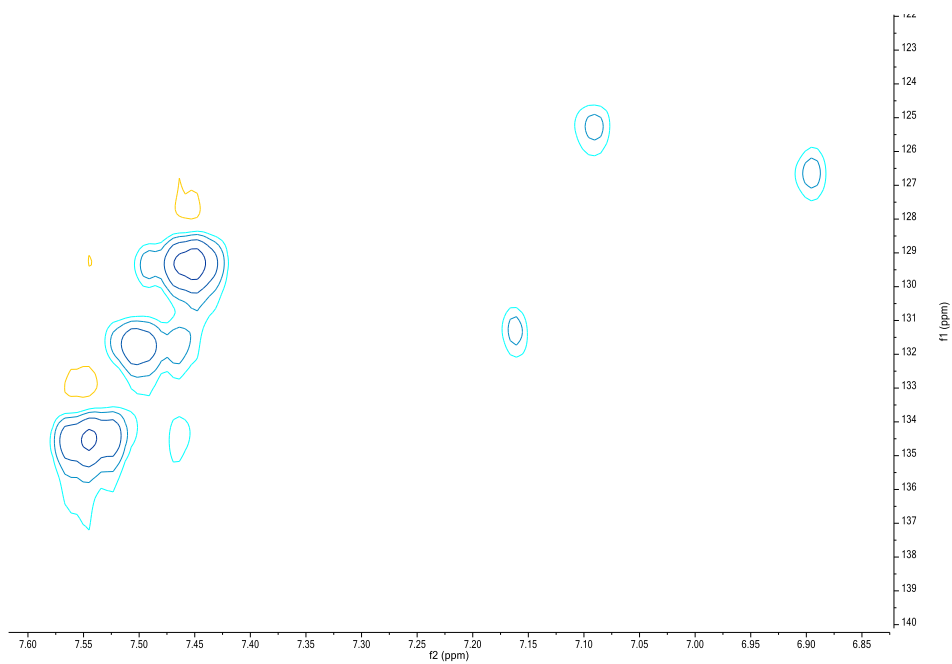


Figure S3. ^1H - ^{13}C gHSQC spectrum of **$\text{PPh}_3\text{AuC}\equiv\text{CTh}$** (CDCl_3 , 500 MHz, 25 $^\circ\text{C}$).

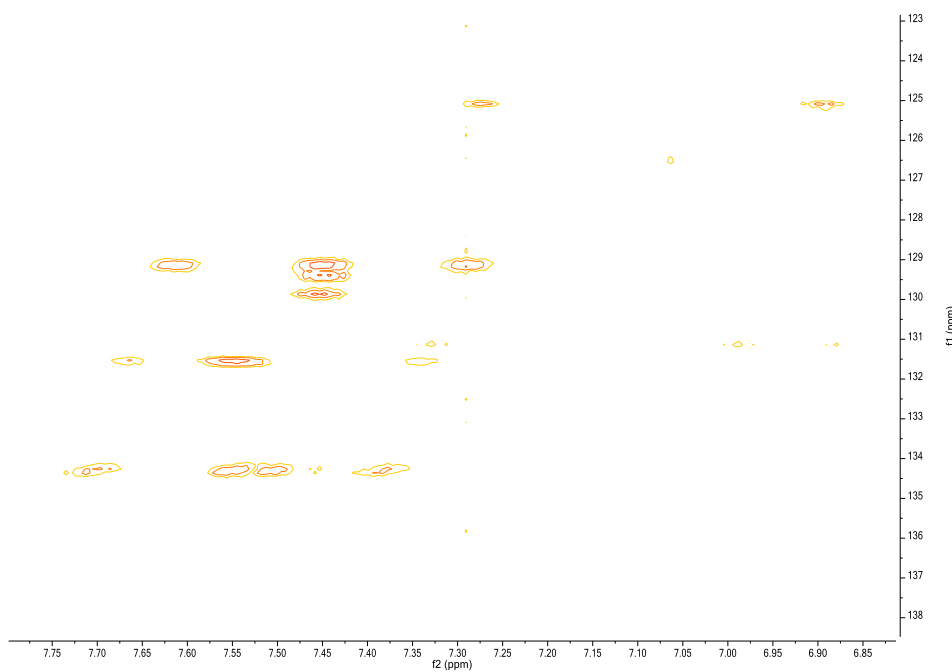


Figure S4. ^1H - ^{13}C gHMBC spectrum of **$\text{PPh}_3\text{AuC}\equiv\text{CTh}$** (CDCl_3 , 500 MHz, 25 $^\circ\text{C}$).

X-Ray Crystallography of **PPh₃AuC≡CTh**.

X-Ray Intensity data were collected at 100 K on a Bruker D8 Venture diffractometer using MoK α radiation ($\lambda = 0.71073$ Å) and a Photon III area detector. Raw data frames were read by program SAINT⁶ and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces. The structure was solved and refined in *SHELXTL2014*, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. One of the thiophene rings is disordered and refined in two parts. In the final cycle of refinement, 14010 reflections (of which 13274 are observed with $I > 2 \sigma(I)$) were used to refine 488 parameters and the resulting R_1 , wR_2 and S (goodness of fit) were 1.79%, 4.18% and 1.049, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized.

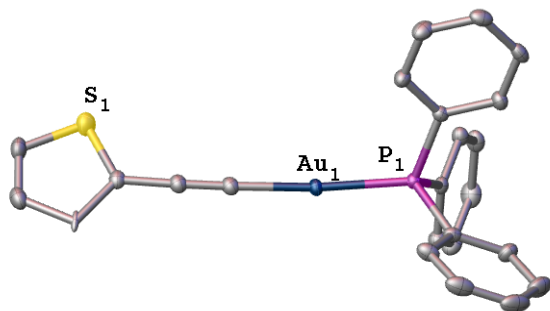


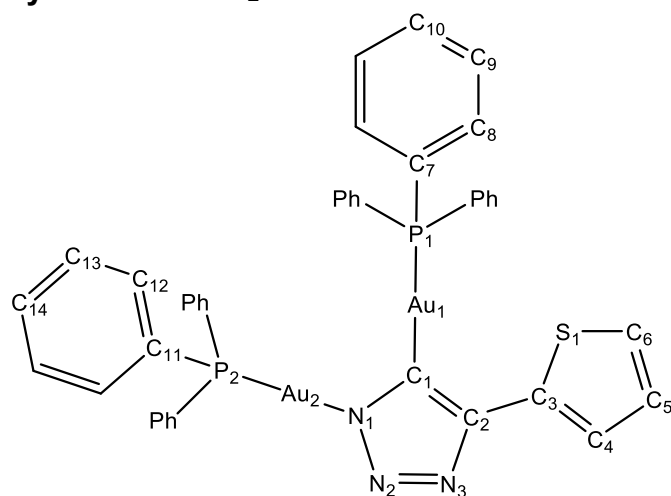
Figure S5. Molecular structure of **PPh₃AuC≡CTh** (All hydrogen atoms removed for clarity).

Table S1. Crystal data and structure refinement for shen3.

Identification code	shen3	
Empirical formula	C ₄₈ H ₃₆ Au ₂ P ₂ S ₂	
Formula weight	1132.76	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.4948(4) Å b = 12.7123(5) Å c = 13.9821(6) Å	a = 96.6190(10)°. b = 93.3830(10)°. c = 92.2090(10)°.
Volume	2023.86(14) Å ³	
Z	2	
Density (calculated)	1.859 Mg/m ³	
Absorption coefficient	7.457 mm ⁻¹	
F(000)	1088	

Crystal size	0.223 x 0.205 x 0.126 mm ³
Theta range for data collection	2.701 to 33.108°.
Index ranges	-17≤h≤17, -18≤k≤19, -20≤l≤21
Reflections collected	117239
Independent reflections	14010 [R(int) = 0.0226]
Completeness to theta = 25.000°	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5628 and 0.3433
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	14010 / 18 / 488
Goodness-of-fit on F ²	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0179, wR2 = 0.0418 [13274]
R indices (all data)	R1 = 0.0198, wR2 = 0.0427
Extinction coefficient	n/a
Largest diff. peak and hole	1.406 and -1.449 e.Å ⁻³

Synthesis of Au₂-Th.



93.8% Yield (0.047 mmol, 50.1 mg). ¹H NMR (500 MHz, CDCl₃): δ 6.85-6.90 (m, 2H, C₅-H and C₆-H), 7.12-7.21 (m, 12H, C₉-H and C₁₃-H), 7.28-7.30 (m, 6H, C₁₀-H and C₁₄-H), 7.38-7.43 (m, 12H, C₈-H and C₁₂-H), 7.60-7.62 (m, 1H, C₄-H). ¹³C{¹H} NMR (indirect detection through ¹H-¹³C gHMBC and ¹H-¹³C gHSQC (126 MHz, CDCl₃)): δ 120.7 (C₄), 121.1 (C₅), 127.1 (C₆), 129.1 (d, ³J_{CP} = 11 Hz, C₉ and C₁₃), 131.5 (d, ⁴J_{CP} = 12 Hz, C₁₀ and C₁₄), 134.3 (d, ²J_{CP} = 14 Hz, C₈ and C₁₂), 140.2 (C₃). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 44.59 (s, P1), 31.50 (s, P2). ESI-MS: m/z calculated for C₄₂H₃₃Au₂N₃P₂S [M+H]⁺ 1068.1280, found 1068.1252.

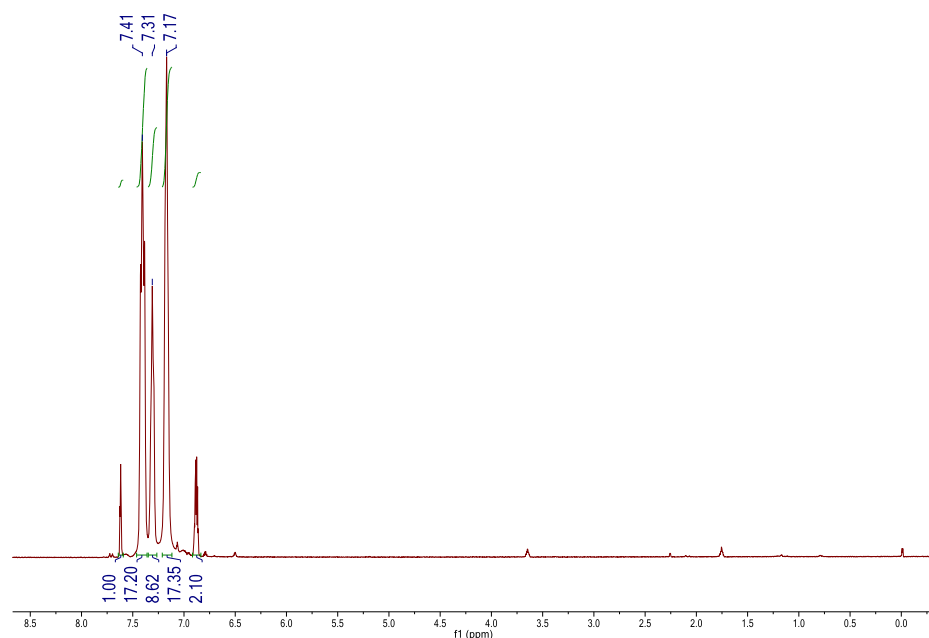


Figure S6. ¹H NMR spectrum of **Au₂-Th** (CDCl₃, 500 MHz, 25 °C).

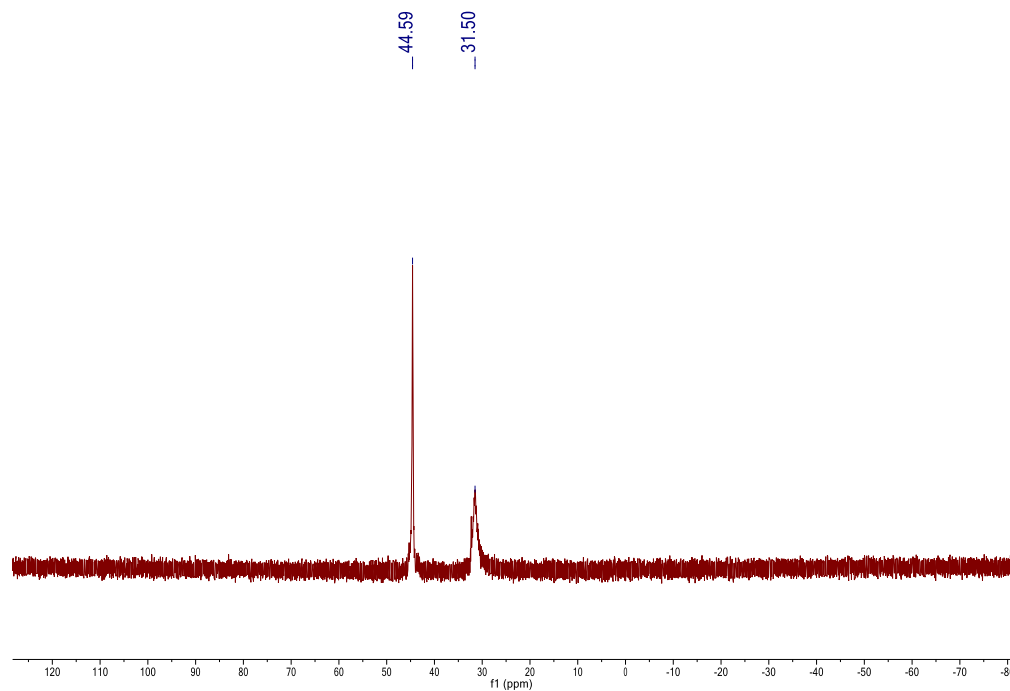


Figure S7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Au}_2\text{-Th}$ (CDCl_3 , 121 MHz, 25 °C).

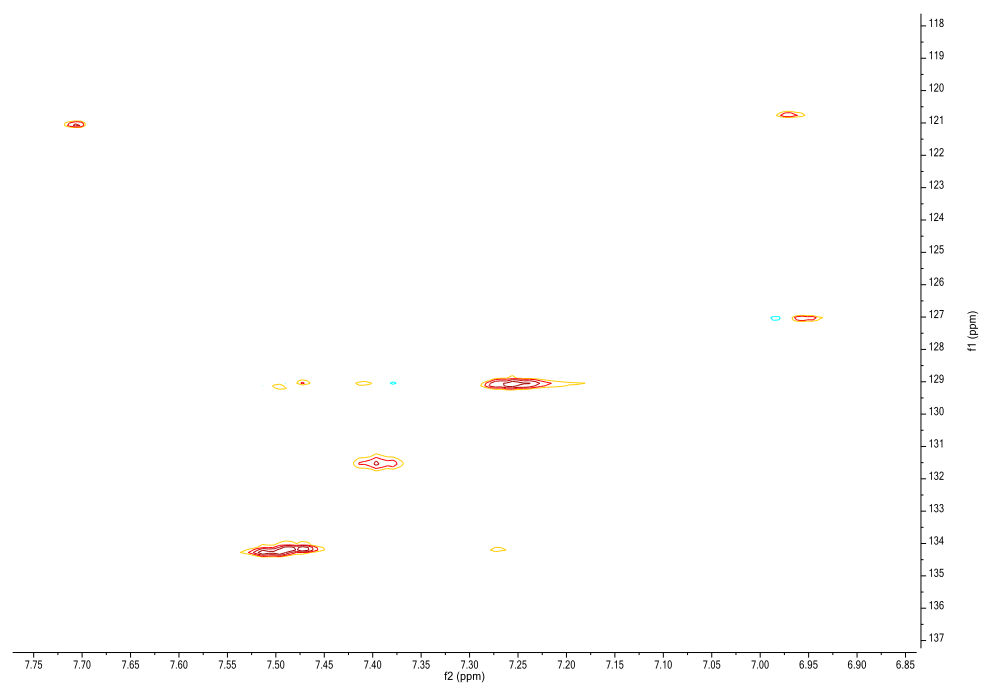


Figure S8. $^1\text{H}\text{-}^{13}\text{C}$ gHSQC spectrum of $\text{Au}_2\text{-Th}$ (CDCl_3 , 500 MHz, 25 °C).

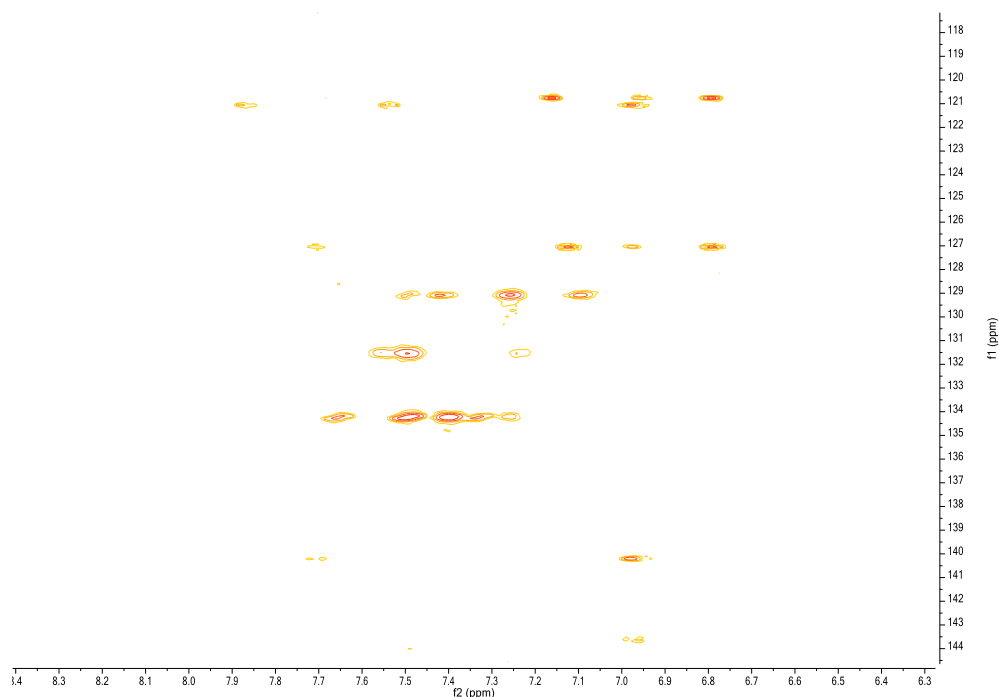


Figure S9. ^1H - ^{13}C gHMBC spectrum of **Au₂-Th** (CDCl_3 , 500 MHz, 25 °C).

X-Ray Crystallography of **Au₂-Th**.

X-Ray Intensity data were collected at 100 K on a Bruker D8 Venture diffractometer using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and a Photon III area detector. Raw data frames were read by program SAINT⁶ and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces. The structure was solved and refined in *SHELXTL2014*, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The asymmetric unit consists of the digold complex and two dichloromethane solvent molecules. Each of the solvent molecules were disordered and refined in two parts. In the final cycle of refinement, 11561 reflections (of which 10035 are observed with $I > 2\sigma(I)$) were used to refine 491 parameters and the resulting R_1 , wR_2 and S (goodness of fit) were 3.77%, 9.33% and 1.067, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized.

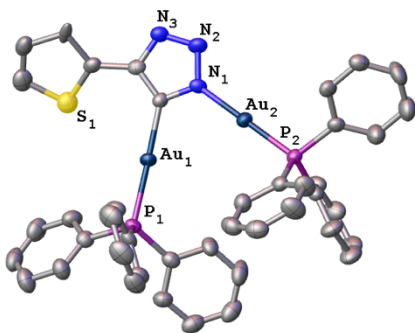
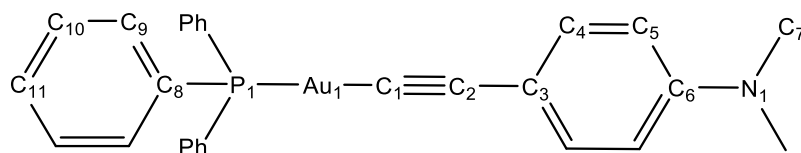


Figure S10. Molecular structure of **Au₂-Th** (All hydrogen atoms removed for clarity).

Table S2. Crystal data and structure refinement for shen4.

Identification code	shen4
Empirical formula	C _{43.50} H ₃₆ Au ₂ Cl ₃ N ₃ P ₂ S
Formula weight	1195.03
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P n a 21
Unit cell dimensions	a = 17.4021(16) Å a = 90° b = 22.787(2) Å b = 90° c = 11.8185(10) Å c = 90°
Volume	4686.6(8) Å ³
Z	4
Density (calculated)	1.694 Mg/m ³
Absorption coefficient	6.569 mm ⁻¹
F(000)	2292
Crystal size	0.11 x 0.03 x 0.02 mm ³
Theta range for data collection	2.267 to 28.309°.
Index ranges	-23 ≤ h ≤ 23, -30 ≤ k ≤ 30, -15 ≤ l ≤ 15
Reflections collected	55101
Independent reflections	11561 [R(int) = 0.0587]
Completeness to theta = 25.242°	99.9 %
Absorption correction	"multi-scan"
Max. and min. transmission	0.2907 and 0.2004
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11561 / 391 / 491
Goodness-of-fit on F ²	1.067
Final R indices [I > 2sigma(I)]	R1 = 0.0377, wR2 = 0.0933 [10035]
R indices (all data)	R1 = 0.0488, wR2 = 0.0989
Absolute structure parameter	0.020(4)
Extinction coefficient	n/a
Largest diff. peak and hole	1.945 and -1.046 e.Å ⁻³

Synthesis of $\text{PPh}_3\text{AuC}\equiv\text{CPhNMe}_2$.



62.3 % Yield (0.31 mmol, 187.9 mg). ^1H NMR (500 MHz, CDCl_3): δ 2.91 (s, 6H, $\text{C}_7\text{-H}$), 6.57 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H, $\text{C}_5\text{-H}$), 7.35-7.55 (m, 17H, $\text{C}_4\text{-H}$ and aromatic). $^{13}\text{C}\{^1\text{H}\}$ NMR (indirect detection through $^1\text{H}\text{-}^{13}\text{C}$ gHMBC and $^1\text{H}\text{-}^{13}\text{C}$ gHSQC (126 MHz, CDCl_3)): δ 40.3 (C_7), 111.8 (C_5), 112.1 (C_3), 129.1 (d, $^4J_{\text{CP}} = 11$ Hz, C_{11}), 130.0 (d, $^1J_{\text{CP}} = 55$ Hz, C_8), 131.4 (d, $^3J_{\text{CP}} = 2$ Hz, C_{10}), 133.4 (C_4), 134.3 (d, $^2J_{\text{CP}} = 14$ Hz, C_9), 149.2 (C_6). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3): δ 42.52. ESI-MS: m/z calculated for $\text{C}_{28}\text{H}_{25}\text{AuNP}$ $[\text{M}+\text{H}]^+$ 604.1468, found 604.1438.

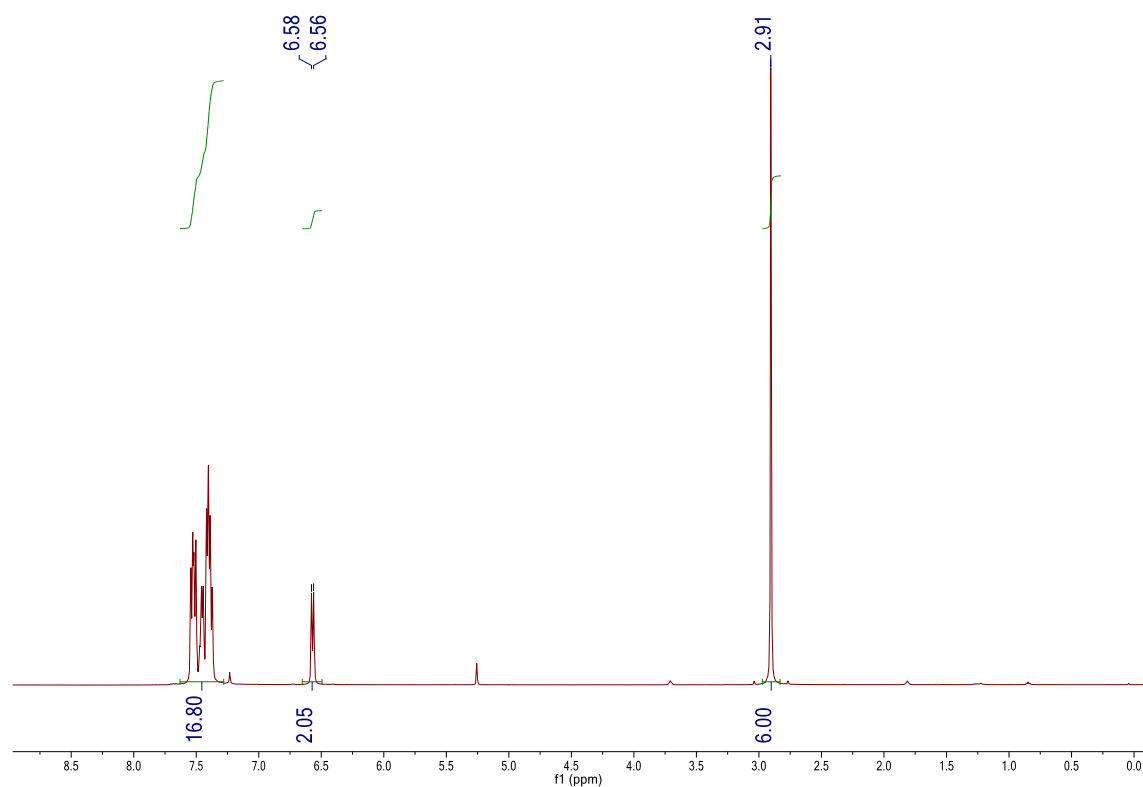


Figure S11. ^1H NMR spectrum of $\text{PPh}_3\text{AuC}\equiv\text{CPhNMe}_2$ (CDCl_3 , 500 MHz, 25 °C).

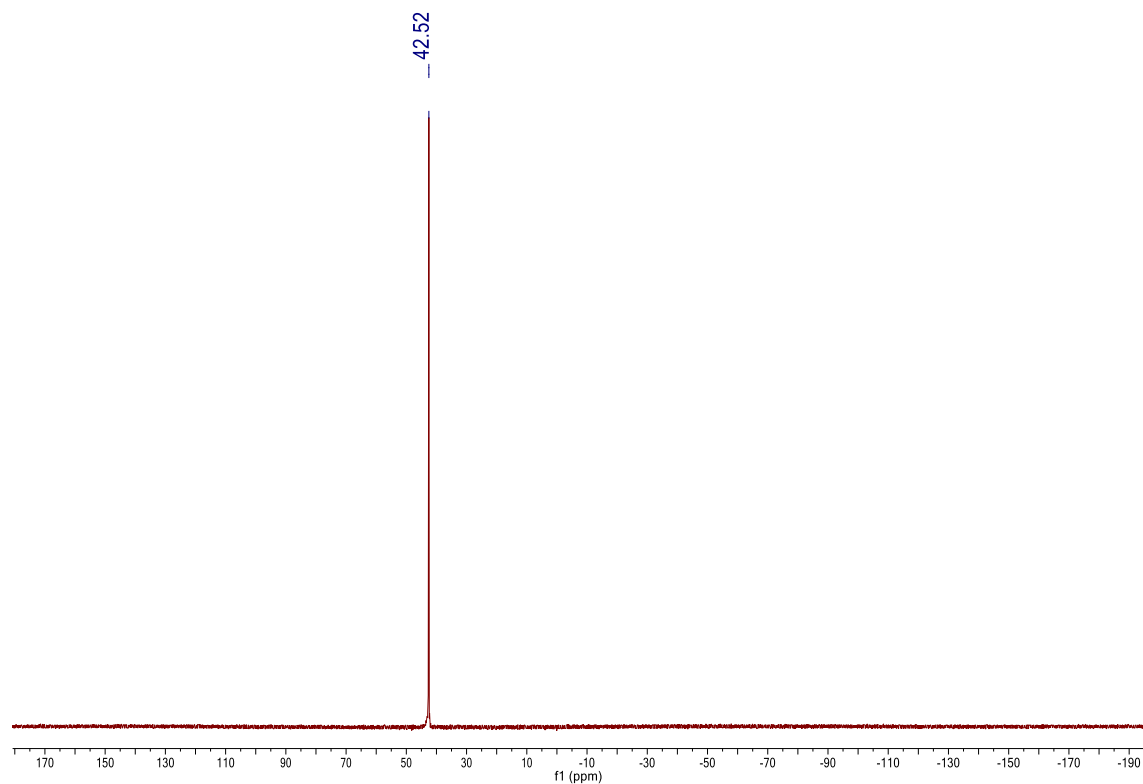


Figure S12. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{PPh}_3\text{AuC}\equiv\text{CPhNMe}_2$ (CDCl_3 , 121 MHz, 25 °C).

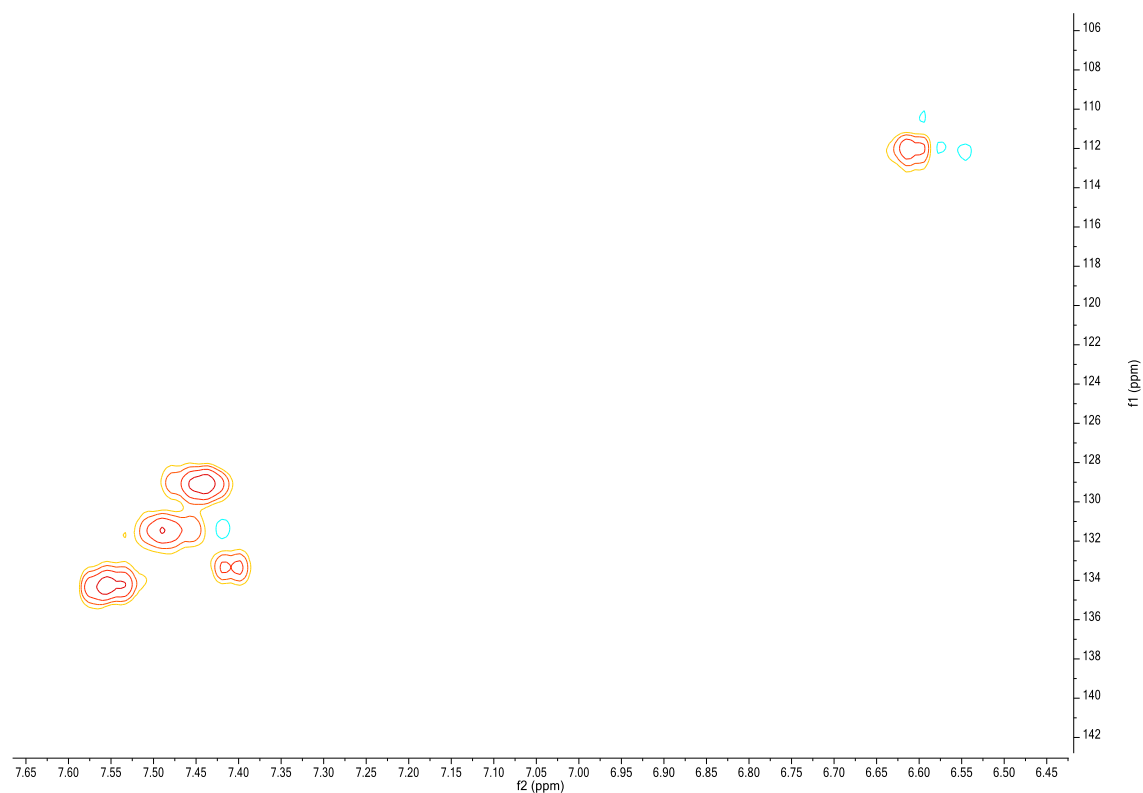


Figure S13. ^1H - ^{13}C gHSQC spectrum of $\text{PPh}_3\text{AuC}\equiv\text{CPhNMe}_2$ (CDCl_3 , 500 MHz, 25 °C).

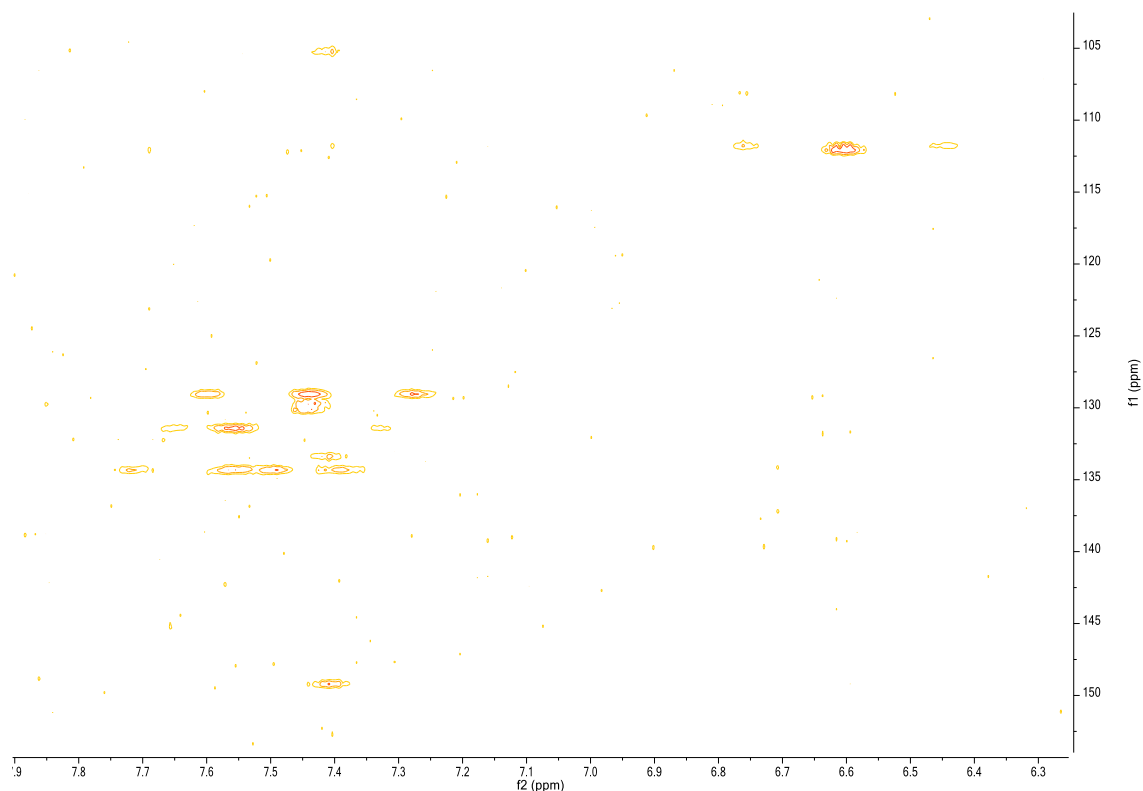


Figure S14. ^1H - ^{13}C gHMBC spectrum of $\text{PPh}_3\text{AuC}\equiv\text{CPhNMe}_2$ (CDCl_3 , 500 MHz, 25 °C).

X-Ray Crystallography of $\text{PPh}_3\text{AuC}\equiv\text{CPhNMe}_2$.

X-Ray Intensity data were collected at 100 K on a Bruker DV8 Venture diffractometer using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and a Photon III area detector. Raw data frames were read by program SAINT⁶ and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces. The structure was solved and refined in *SHELXTL2014*, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The asymmetric unit consists of the Au complex and a THF solvent molecule refined at 50% occupancy. In the final cycle of refinement, 8961 reflections (of which 8821 are observed with $I > 2\sigma(I)$) were used to refine 327 parameters and the resulting R_1 , wR_2 and S (goodness of fit) were 1.49%, 3.43% and 1.132, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized.

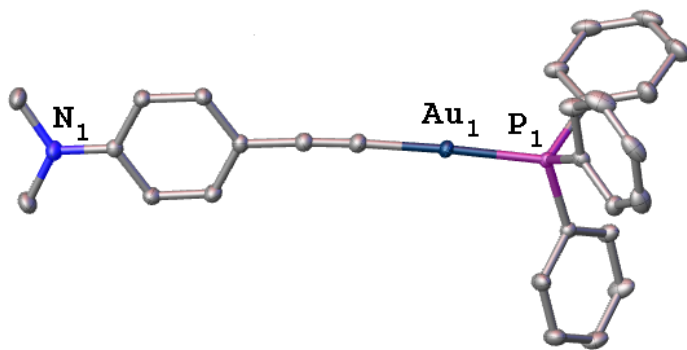
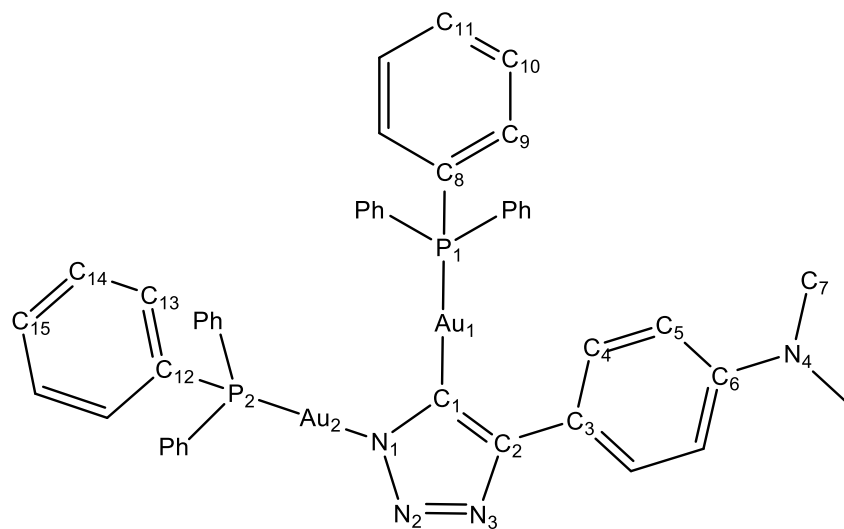


Figure S15. Molecular structure of **PPh₃AuC≡CPhNMe₂** (All hydrogen atoms removed for clarity).

Table S3. Crystal data and structure refinement for shen1.

Identification code	shen1	
Empirical formula	C ₃₀ H ₂₉ Au ₁ N ₁ O _{0.5} P ₁	
Formula weight	1278.95	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.1947(4) Å	a = 68.8680(10)°.
	b = 12.5315(5) Å	b = 72.2030(10)°.
	c = 12.6998(5) Å	c = 72.2960(10)°.
Volume	1268.24(9) Å ³	
Z	2	
Density (calculated)	1.675 Mg/m ³	
Absorption coefficient	5.884 mm ⁻¹	
F(000)	628	
Crystal size	0.106 x 0.096 x 0.091 mm ³	
Theta range for data collection	2.384 to 33.403°.	
Index ranges	-14 ≤ h ≤ 13, -18 ≤ k ≤ 19, -19 ≤ l ≤ 19	
Reflections collected	76385	
Independent reflections	8961 [R(int) = 0.0276]	
Completeness to theta = 25.000°	97.1 %	
Absorption correction	Integration	
Max. and min. transmission	0.6119 and 0.4821	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8961 / 0 / 327	
Goodness-of-fit on F ²	1.132	
Final R indices [I > 2sigma(I)]	R1 = 0.0149, wR2 = 0.0343 [8821]	
R indices (all data)	R1 = 0.0153, wR2 = 0.0344	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.980 and -0.857 e.Å ⁻³	

Synthesis of Au₂-PhNMe₂.



92.5 % Yield (0.046 mmol, 51.1 mg). ¹H NMR (500 MHz, CDCl₃): δ 2.89 (s, 6H, C₇-H), 6.69 (d, ³J_{HH} = 8.3 Hz, 2H, C₅-H), 7.18-7.21 (m, 12H, C₁₀-H and C₁₄-H), 7.33-7.35 (m, 6H, C₁₁-H and C₁₅-H), 7.43-7.47 (m, 12H, C₉-H and C₁₃-H), 8.24 (d, ³J_{HH} = 8.2 Hz, 2H, C₄-H). ¹C{¹H} NMR (indirect detection through ¹H-¹³C gHMBC and ¹H-¹³C gHSQC (126 MHz, CDCl₃)): δ 41.0 (C₇), 112.8 (C₅), 126.1 (C₃), 127.3 (C₄), 129.0 (d, ³J_{CP} = 11 Hz, C₁₀ and C₁₄), 131.4 (C₁₁ and C₁₅), 134.2 (d, ²J_{CP} = 14 Hz, C₉ and C₁₃), 136.5 (C₈ and C₁₂), 149.2 (C₆), 151.7 (C₂). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 44.61 (s, P1), 31.17 (s, P2). ESI-MS: m/z calculated for C₄₆H₄₀Au₂N₄P₂ [M+H]⁺ 1105.2138, found 1105.2104.

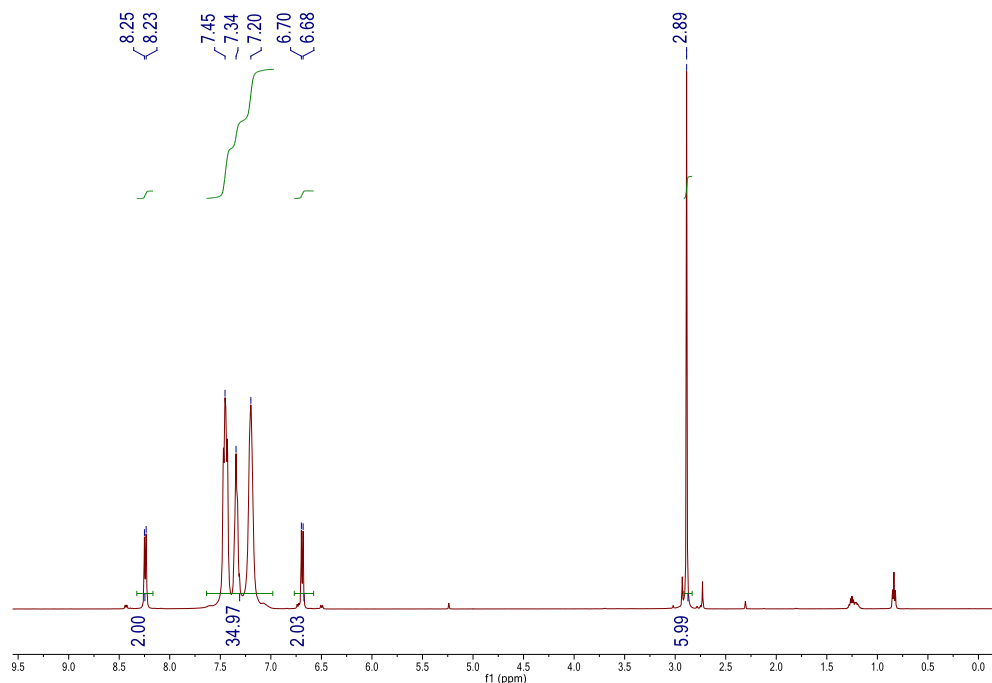


Figure S16. ¹H NMR spectrum of Au₂-PhNMe₂ (CDCl₃, 500 MHz, 25 °C).

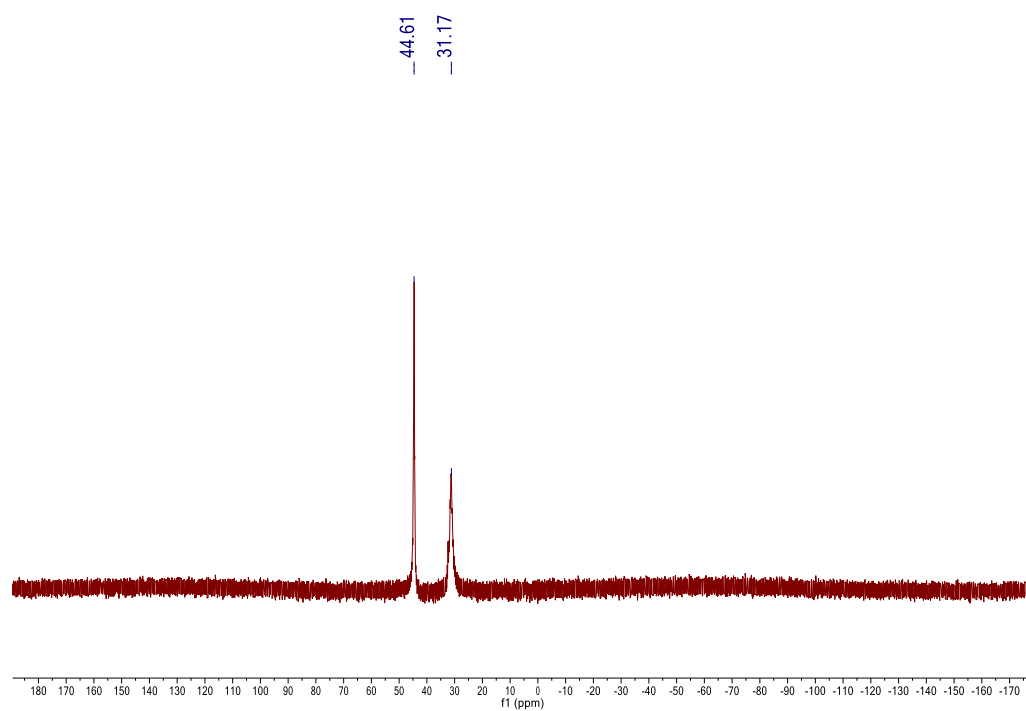


Figure S17. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **Au₂-PhNMe₂** (CDCl_3 , 121 MHz, 25 °C).

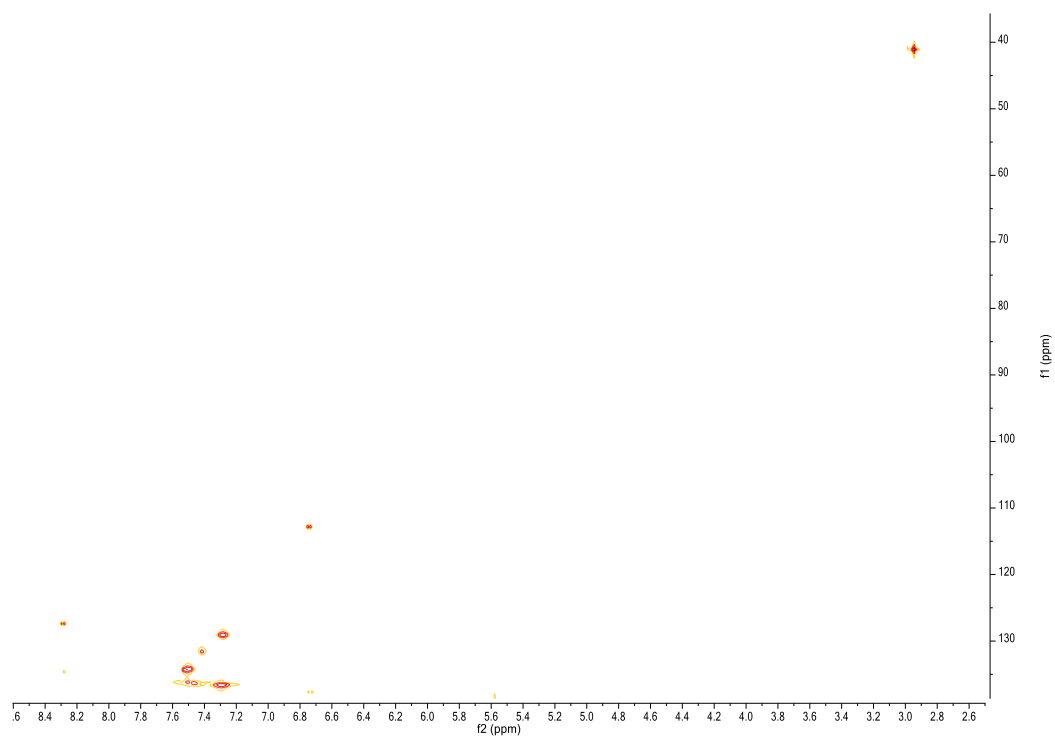


Figure S18. ^1H - ^{13}C gHSQC spectrum of **Au₂-PhNMe₂** (CDCl_3 , 500 MHz, 25 °C).

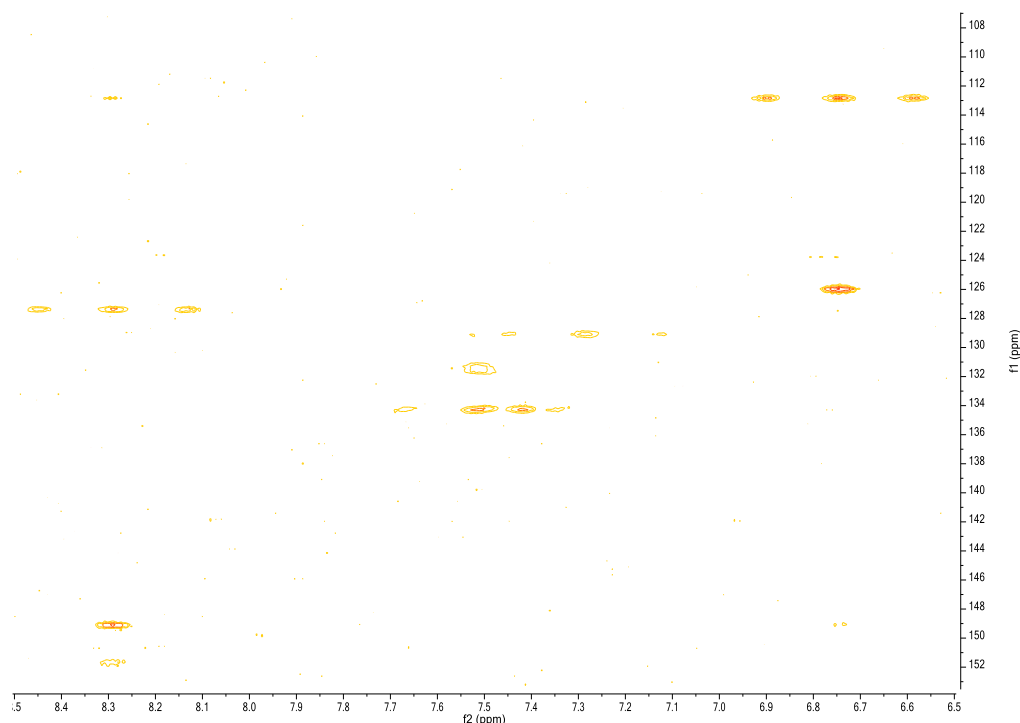


Figure S19. ^1H - ^{13}C gHMBC spectrum of **Au₂-PhNMe₂** (CDCl_3 , 500 MHz, 25 °C).

X-Ray Crystallography of **Au₂-PhNMe₂**.

X-Ray Intensity data were collected at 100 K on a Bruker DV8 Venture diffractometer using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and a Photon III area detector. Raw data frames were read by program SAINT⁶ and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces. The structure was solved and refined in *SHELXTL2014*, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The asymmetric unit consists of the gold complex and three dichloromethane molecules. The solvent molecules were disordered and could not be modeled properly, thus program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. In the final cycle of refinement, 10827 reflections (of which 10235 are observed with $I > 2\sigma(I)$) were used to refine 489 parameters and the resulting R_1 , wR_2 and S (goodness of fit) were 2.69%, 6.51% and 1.080, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized. The structure was solved and refined in *SHELXTL6.1*, using full-matrix least-squares refinement.

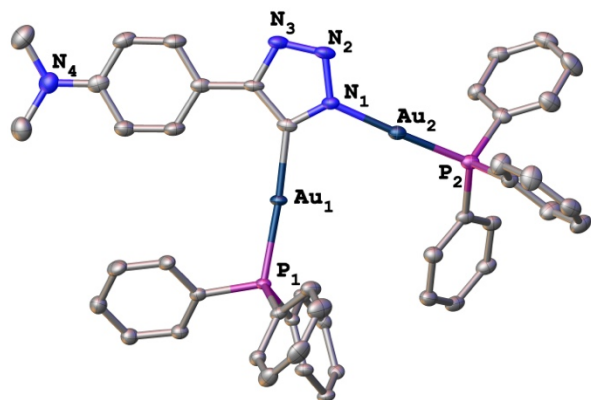
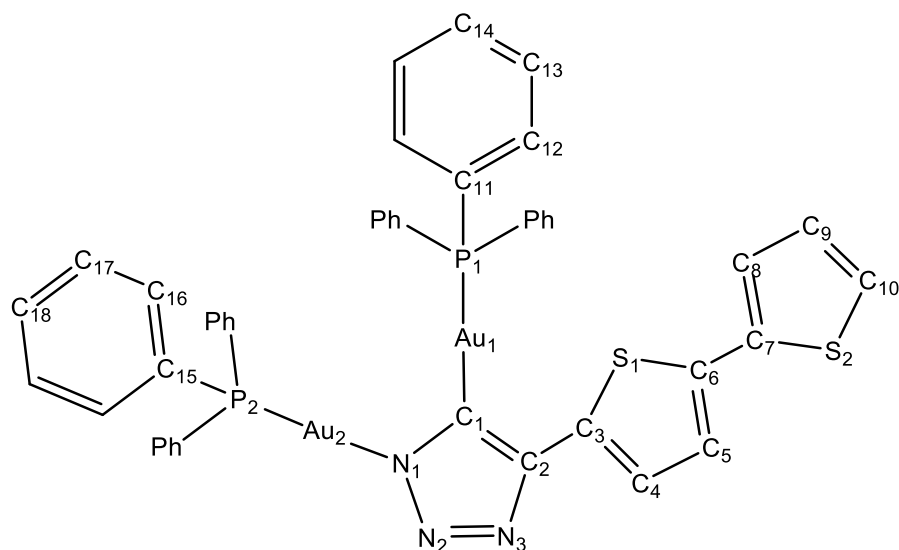


Figure S20. Molecular structure of **PPh₃AuC≡CPhNMe₂** (All hydrogen atoms removed for clarity).

Table S4. Crystal data and structure refinement for shen2.

Identification code	shen2	
Empirical formula	C ₄₉ H ₄₆ Au ₂ Cl ₆ N ₄ P ₂	
Formula weight	1359.47	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.3232(5) Å	a = 108.3241(13)°.
	b = 14.8436(6) Å	b = 110.0928(11)°.
	c = 15.9362(7) Å	c = 91.3270(13)°.
Volume	2361.95(18) Å ³	
Z	2	
Density (calculated)	1.912 Mg/m ³	
Absorption coefficient	6.652 mm ⁻¹	
F(000)	1316	
Crystal size	0.319 x 0.193 x 0.103 mm ³	
Theta range for data collection	2.300 to 27.499°.	
Index ranges	-14 ≤ h ≤ 14, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20	
Reflections collected	138984	
Independent reflections	10827 [R(int) = 0.0276]	
Completeness to theta = 25.000°	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10827 / 0 / 489	
Goodness-of-fit on F ²	1.080	
Final R indices [I > 2σ(I)]	R1 = 0.0269, wR2 = 0.0651 [10235]	
R indices (all data)	R1 = 0.0290, wR2 = 0.0673	
Extinction coefficient	n/a	
Largest diff. peak and hole	4.799 and -1.861 e.Å ⁻³	

Synthesis of Au₂-biTh.



95.3% Yield (0.089 mmol, 102 mg). ¹H-NMR (600MHz, CDCl₃), δ (ppm): 6.91 (dd, ³J_{HH} = 3.5 Hz, ⁴J_{HH} = 1.0 Hz, 1H, C₈-H), 6.95 (dd, ³J_{HH} = 3.6, 5.0 Hz, 1H, C₉-H), 7.09 (d, ³J_{HH} = 3.7 Hz, 1H, C₅-H), 7.12 (d, ³J_{HH} = 4.8 Hz, 1H, C₁₀-H), 7.24-7.38 (m, 12H, C₁₃-H and C₁₇-H), 7.40-7.49 (m, 6H, C₁₄-H and C₁₈-H), 7.48-7.60 (m, 12H, C₁₂-H and C₁₆-H), 7.61 (d, ³J_{HH} = 3.7 Hz, 1H, C₄-H). ¹³C{¹H} NMR (indirect detection through ¹H-¹³C gHMBC and ¹H-¹³C gHSQC) (600 MHz, CDCl₃), δ (ppm): 121.78 (C₄), 122.42 (C₈), 122.94 (C₁₀), 124.25 (C₅), 127.41 (C₉), 128.48 (d, ¹J_{CP} = 12 Hz, C₁₁ and C₁₅), 129.12 (d, ³J_{CP} = 11 Hz, C₁₃ and C₁₇), 131.56 (m, C₁₄ and C₁₈), 132.07 (C₆), 134.25 (d, ²J_{CP} = 14 Hz, C₁₂ and C₁₆), 138.80 (C₇), 145.56 (C₂). ³¹P{¹H} NMR (242.9 MHz, CDCl₃), δ (ppm): 44.58 (s, P₁), 31.18 (s, P₂). ESI-MS: m/z calculated for C₄₆H₃₅Au₂N₃P₂S₂ [M+H]⁺ 1150.1157, found 1150.1122.

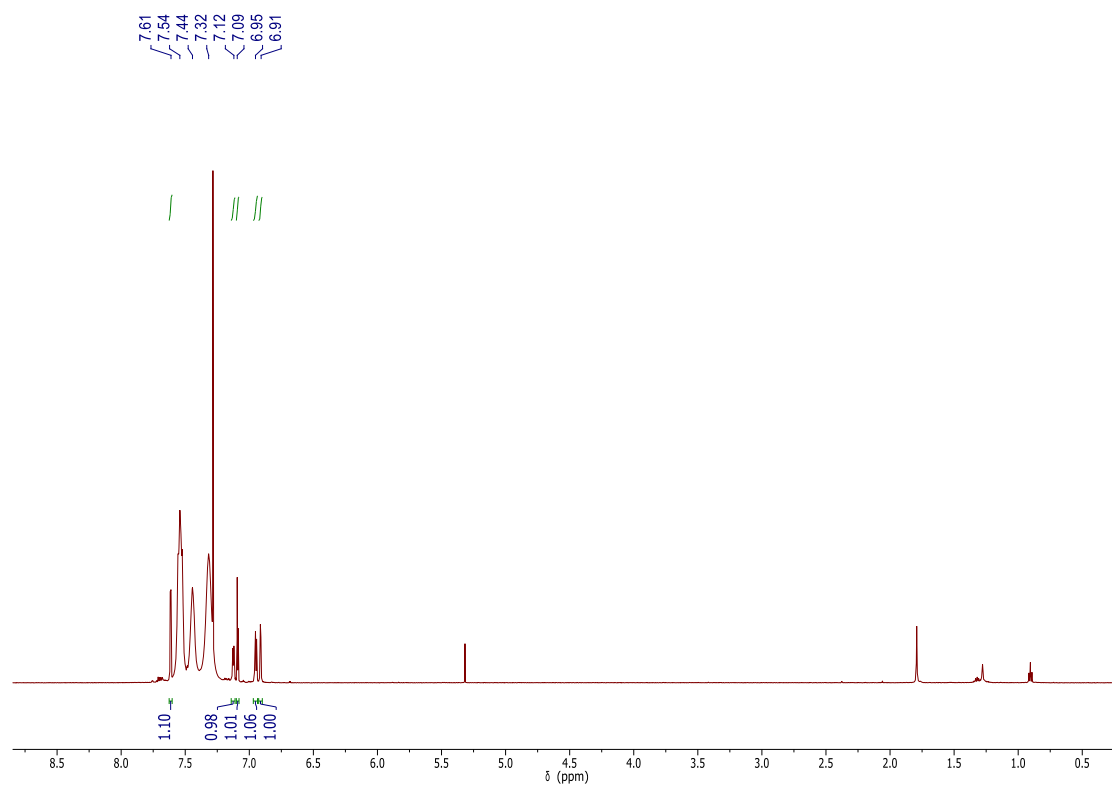


Figure S21. ¹H NMR spectrum of **Au₂-biTh** (CDCl₃, 600 MHz, 25 °C).

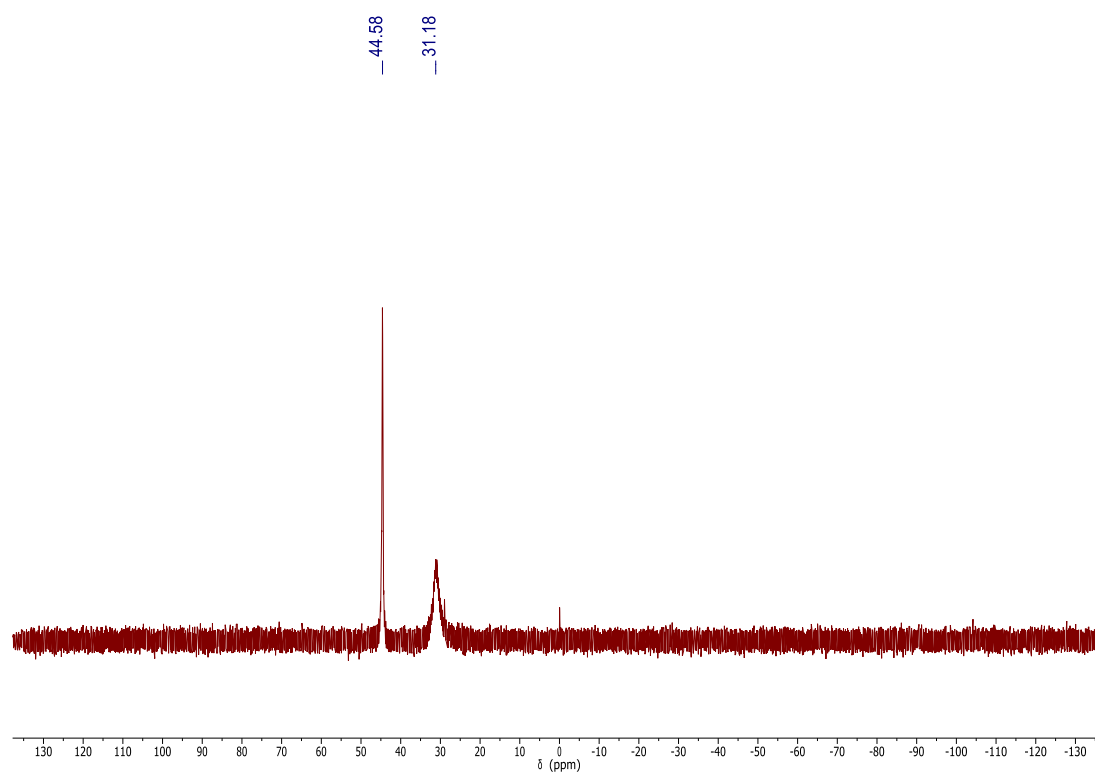


Figure S22. ³¹P{¹H} NMR spectrum of **Au₂-biTh** (CDCl₃, 243 MHz, 25 °C).

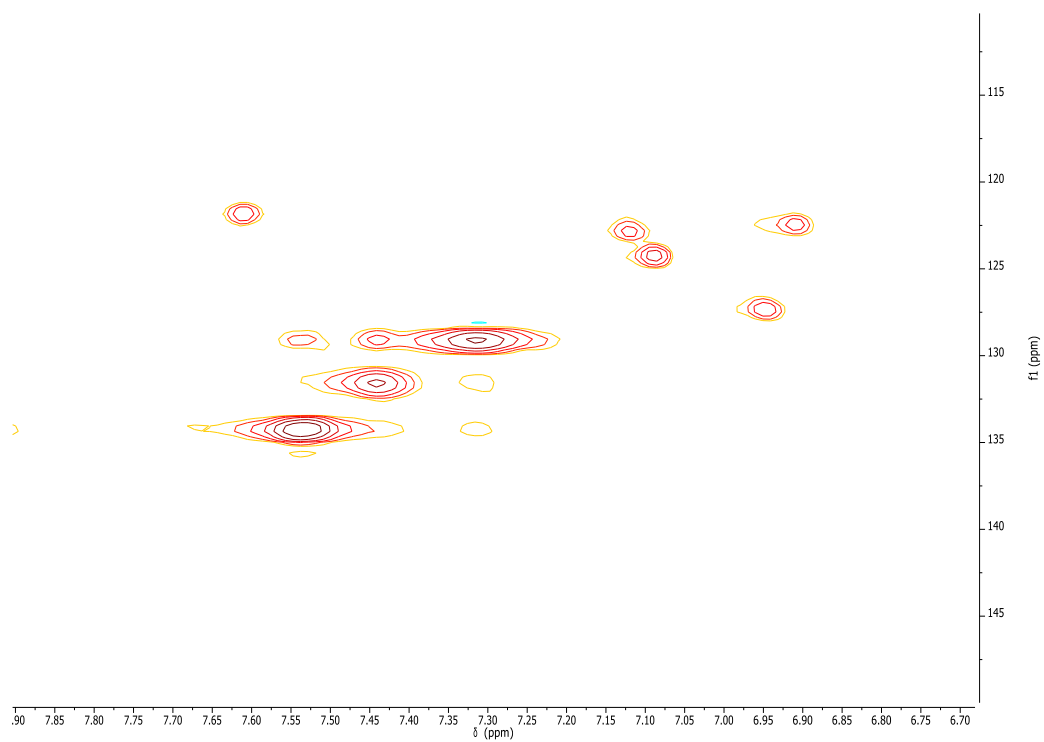


Figure S23. ^1H - ^{13}C gHSQC spectrum of **Au₂-biTh** (CDCl_3 , 600 MHz, 25 °C).

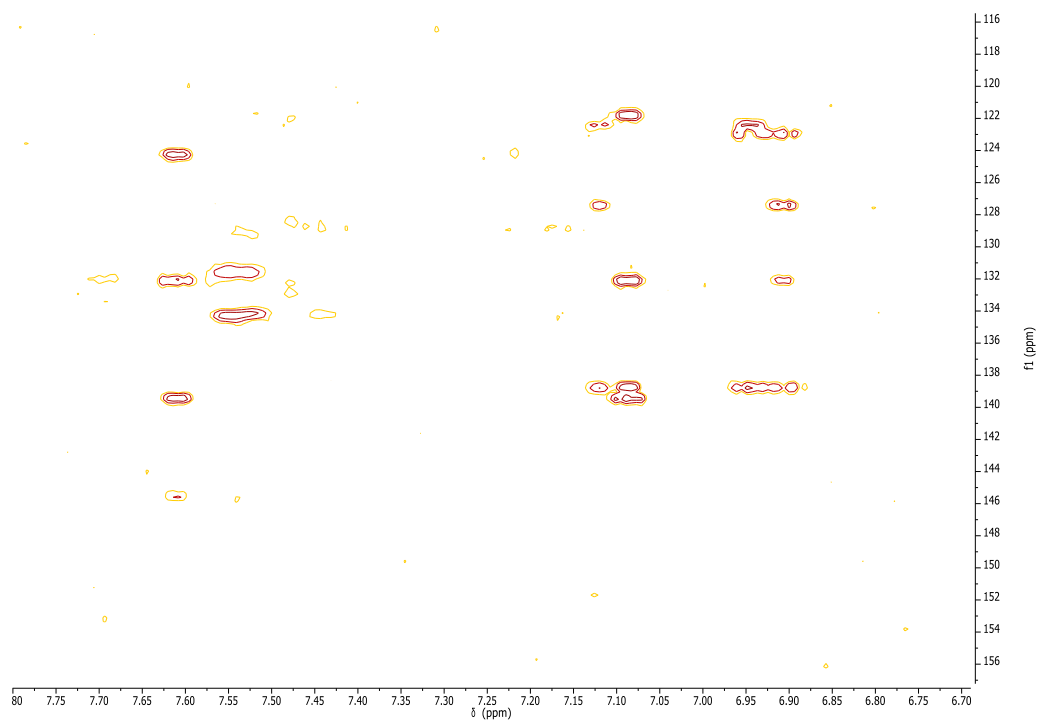


Figure S24. ^1H - ^{13}C gHMBC spectrum of **Au₂-biTh** (CDCl_3 , 600 MHz, 25 °C).

X-Ray Crystallography of **Au₂-biTh**.

X-Ray Intensity data were collected at 100 K on a Bruker D8 Venture diffractometer using MoK α radiation ($\lambda = 0.71073$ Å) and a Photon III area detector. Raw data frames were read by program SAINT⁶ and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces. The structure was solved and refined in SHELXTL2014, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The Au₂ complex has one thiophene ring disordered and was refined in two parts with their site occupation factors and geometries dependently refined. In the final cycle of refinement, 9551 reflections (of which 8312 are observed with $I > 2\sigma(I)$) were used to refine 497 parameters and the resulting R_1 , wR_2 and S (goodness of fit) were 5.75 %, 13.81 % and 1.070, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized.

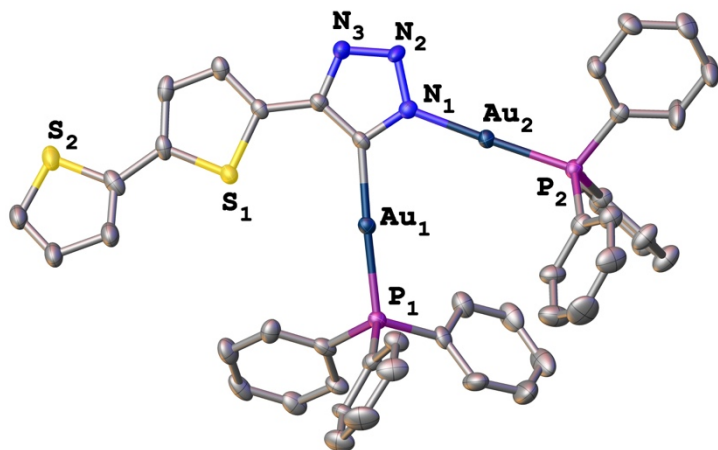
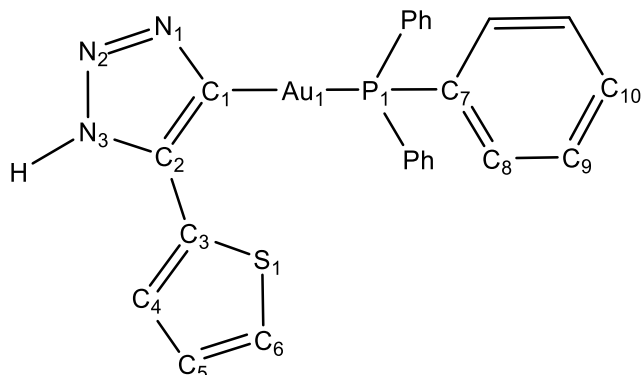


Figure S25. Molecular structure of **Au₂-biTh** (All hydrogen atoms removed for clarity).

Table S5. Crystal data and structure refinement for jh1.

Identification code	jh1	
Empirical formula	$C_{46}H_{35}Au_2N_3P_2S_2$	
Formula weight	1149.76	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	$a = 12.5803(14)$ Å	$a = 90^\circ$.
	$b = 13.1347(14)$ Å	$b = 100.260(2)^\circ$.
	$c = 25.578(3)$ Å	$c = 90^\circ$.
Volume	$4158.8(8)$ Å ³	
Z	4	
Density (calculated)	1.836 Mg/m ³	
Absorption coefficient	7.261 mm ⁻¹	
F(000)	2208	
Crystal size	$0.170 \times 0.073 \times 0.023$ mm ³	
Theta range for data collection	1.958 to 27.500° .	
Index ranges	$-16 \leq h \leq 16$, $-17 \leq k \leq 17$, $-33 \leq l \leq 33$	
Reflections collected	127998	
Independent reflections	9551 [$R(\text{int}) = 0.0977$]	
Completeness to $\theta = 25.000^\circ$	99.9 %	
Absorption correction	"multi-scan"	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9551 / 6 / 497	
Goodness-of-fit on F^2	1.070	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0575$, $wR2 = 0.1381$ [8312]	
R indices (all data)	$R1 = 0.0668$, $wR2 = 0.1442$	
Largest diff. peak and hole	6.033 and -2.002 e.Å ⁻³	

Synthesis of 4,5-Au₁-Th.



H-C≡C-Th (0.05 mmol) and PPh₃Au-N₃ (0.05 mmol) were added into 2 mL of DCM. The solution was stirred in the dark for 5 h then solvents was removed *in vacuo*. Crystals were grown through pentane diffusion into a methylene chloride solution of the triazolate at -25 °C. 91.1% Yield (0.046 mmol, 27.77 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.00 (dd, ³J_{HH} = 3.5, 5.0 Hz, 1H, C₅-H), 7.06 (dd, ³J_{HH} = 5.0 Hz, ⁴J_{HH} = 1.2 Hz, 1H, C₄-H), 7.74 (dd, ³J_{HH} = 3.6 Hz, ⁴J_{HH} = 1.2 Hz, 1H, C₆-H), 7.49-7.63 (m, 15H, C₈-H, C₉-H and C₁₀-H). ¹³C{¹H} NMR (indirect detection through ¹H-¹³C gHMBC and ¹H-¹³C gHSQC (101 MHz, CDCl₃)): δ 122.1 (C₄), 122.6 (C₆), 127.4 (C₅), 129.3 (d, ³J_{CP} = 11 Hz, C₉), 129.7 (d, ¹J_{CP} = 55 Hz, C₇), 131.7 (d, ⁴J_{CP} = 2 Hz, C₁₀), 134.3 (d, ²J_{CP} = 13 Hz, C₈), 137.8 (C₈), 148.1 (C₉). ³¹P{¹H} NMR (161 MHz, CDCl₃): δ 43.50. ESI-MS: m/z calculated for C₂₄H₁₉AuN₃PS [M+H]⁺ 610.0781, found 610.0762.

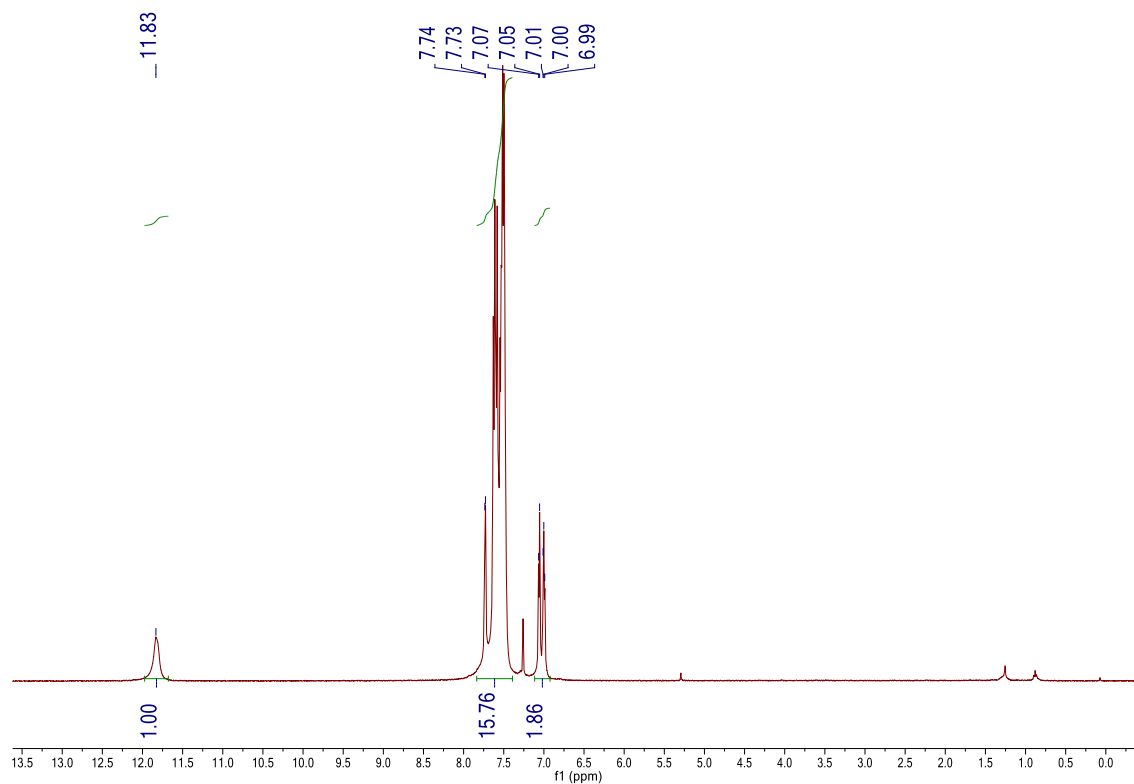


Figure S26. ¹H NMR spectrum of **4,5-Au₁-Th** (CDCl₃, 400 MHz, 25 °C).

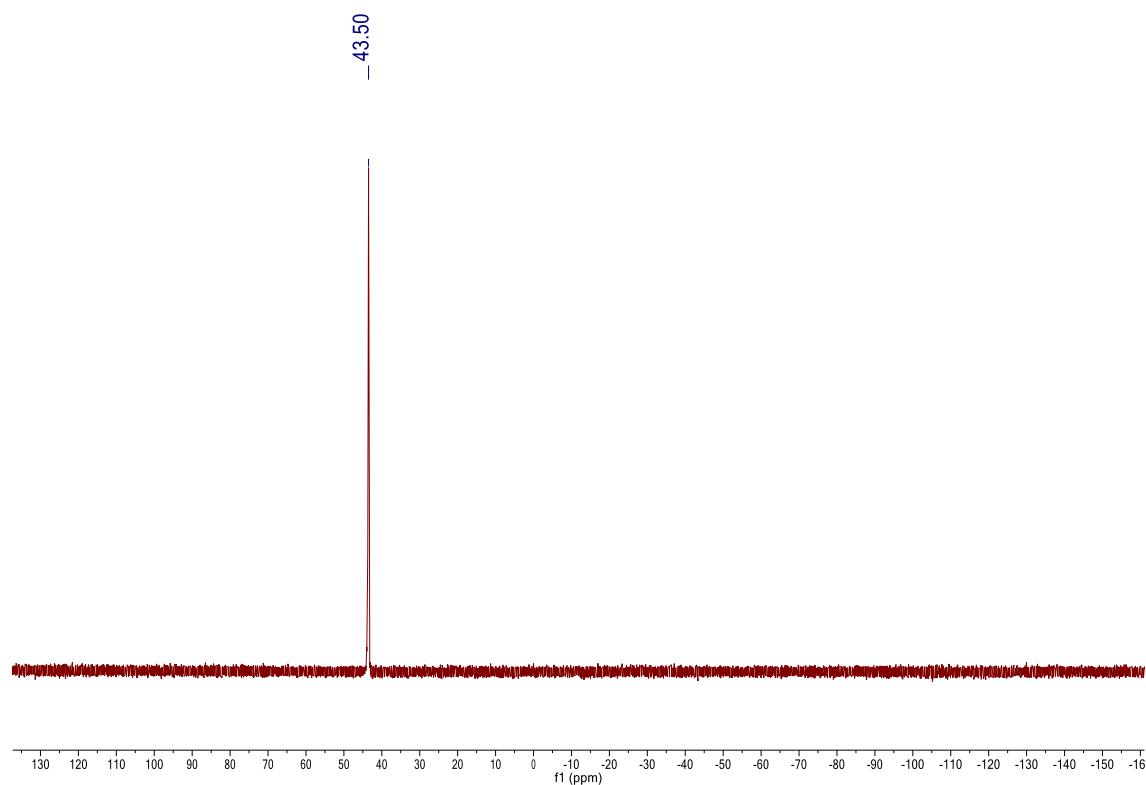


Figure S27. ³¹P{¹H} NMR spectrum of **4,5-Au₁-Th** (CDCl₃, 161 MHz, 25 °C).

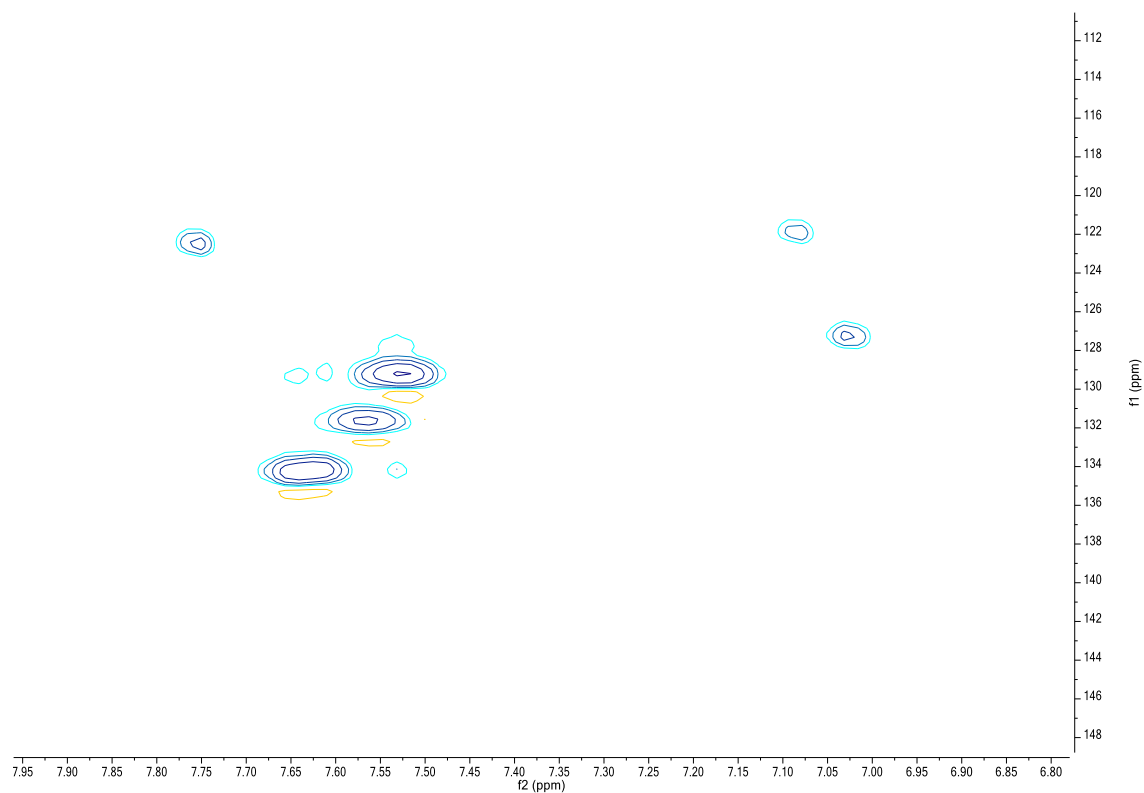


Figure S28. ^1H - ^{13}C gHSQC spectrum of **4,5-Au₁-Th** (CDCl_3 , 400 MHz, 25 °C).

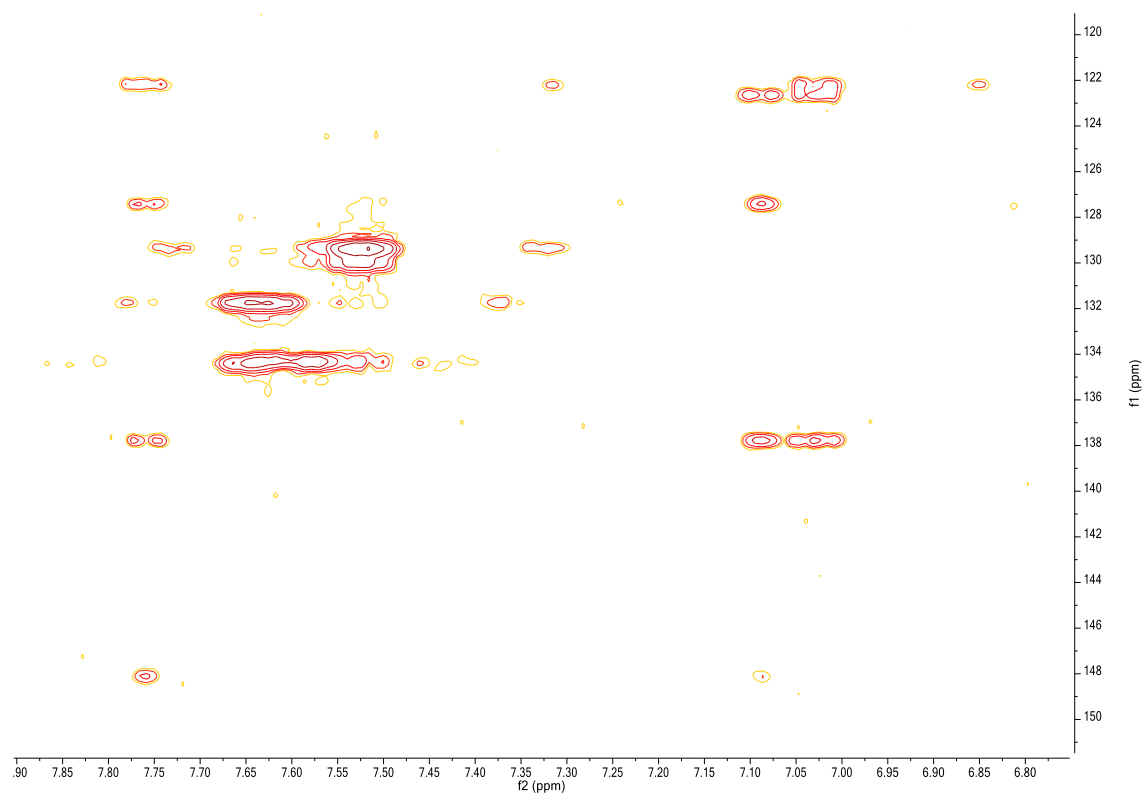


Figure S29. ^1H - ^{13}C gHMBC spectrum of **4,5-Au₁-Th** (CDCl_3 , 400 MHz, 25 °C).

X-Ray Crystallography of **4,5-Au₁-Th**.

X-Ray Intensity data were collected at 173(2) K on a Bruker DV8 Venture diffractometer using MoK α radiation ($\lambda = 0.71073$ Å) and a Photon III area detector. Raw data frames were read by program SAINT⁶ and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces. The structure was solved and refined in *SHELXTL2014*, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The asymmetric unit consists of two Au complexes and three dichloromethane solvent molecules. There are three disordered regions. A phenyl ring in molecule A and part of the thiophene in molecule B where both disorders were refined in two parts in each case. Additionally, one of the dichloromethane molecules is also refined in two parts. The protons on the nitrogen atoms in both molecules were obtained from a Difference Fourier map and refined freely. In the final cycle of refinement, 19408 reflections (of which 16243 are observed with $I > 2 \sigma(I)$) were used to refine 585 parameters and the resulting R_1 , wR_2 and S (goodness of fit) were 3.86 %, 8.78 % and 1.044, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized.

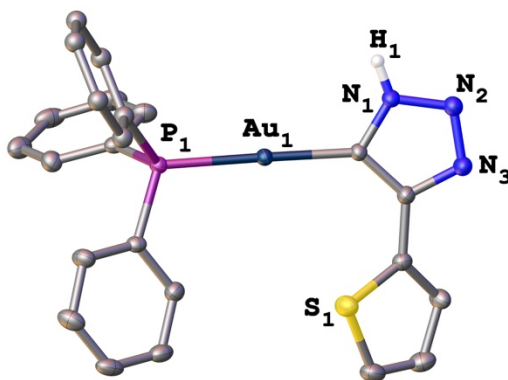


Figure S30. Molecular structure of **4,5-Au₁-Th** (Hydrogen atoms removed for clarity).

Table S6. Crystal data and structure refinement for shen5.

Identification code	shen5	
Empirical formula	C _{25.50} H ₂₂ AuCl ₃ N ₃ PS	
Formula weight	736.81	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 14.4013(5) Å b = 22.8626(8) Å c = 17.4326(5) Å	a = 90°. b = 111.0532(11)°. c = 90°.
Volume	5356.6(3) Å ³	
Z	8	
Density (calculated)	1.827 Mg/m ³	
Absorption coefficient	5.950 mm ⁻¹	
F(000)	2856	
Crystal size	0.202 x 0.084 x 0.037 mm ³	
Theta range for data collection	1.815 to 33.291°.	
Index ranges	-21 ≤ h ≤ 22, -35 ≤ k ≤ 35, -26 ≤ l ≤ 25	
Reflections collected	188156	
Independent reflections	19408 [R(int) = 0.0534]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Integration	
Max. and min. transmission	0.8588 and 0.5166	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	19408 / 8 / 585	
Goodness-of-fit on F ²	1.044	
Final R indices [I > 2sigma(I)]	R1 = 0.0386, wR2 = 0.0878 [16243]	
R indices (all data)	R1 = 0.0507, wR2 = 0.0939	
Extinction coefficient	n/a	
Largest diff. peak and hole	5.391 and -2.311 e.Å ⁻³	

2. Fluorescence of Au₂-Th and 4,5-Au₁-Th

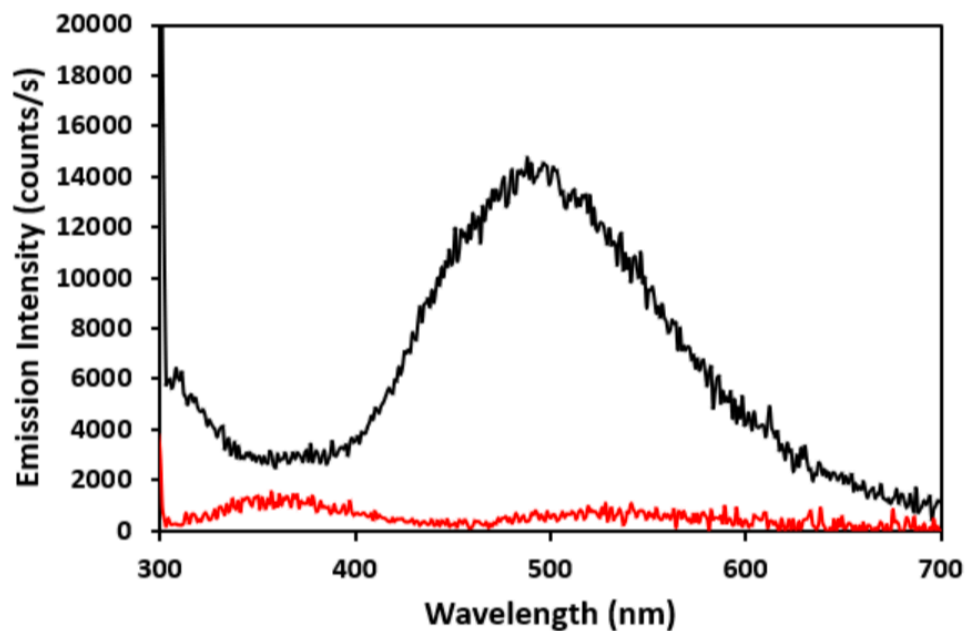


Figure S31. Photoluminescence spectra of **Au₂-Th** (black line) and **4,5-Au₁-Th** (red line) at room temperature in THF under air saturated conditions, showing trace fluorescence that is indicative of an aurophilic interaction in the digold compound that is not present in the monogold triazolate.

3. Computational Results

Validation of Trimethyl Phosphine Ligands

For the modeling of all compounds, triphenyl phosphine ligands were reduced to trimethyl phosphine ligands to reduce computational costs. Considering that the aryl ligands themselves may contribute as photophysically active chromophores, it is necessary to validate that this reduction in molecular complexity does not impact the computational results described herein. For this purpose, a model compound of $\text{Au}_2\text{-Th}$ with triphenyl phosphine ligands was subjected to the same computational interrogation as the reduced species described in the main text. The results found minimal discrepancies, with the charge difference densities (CDDs), maintaining LMCT character (albeit with a newfound contribution from the triphenyl phosphine ligands) and the calculated absorption spectrum showing no shift with respect to the trimethyl phosphine variety of **Au₂-Th**. Additionally, the bulkier triphenyl phosphine ligands do not appear to preclude aurophilic bonding in the relaxed excited state geometry.

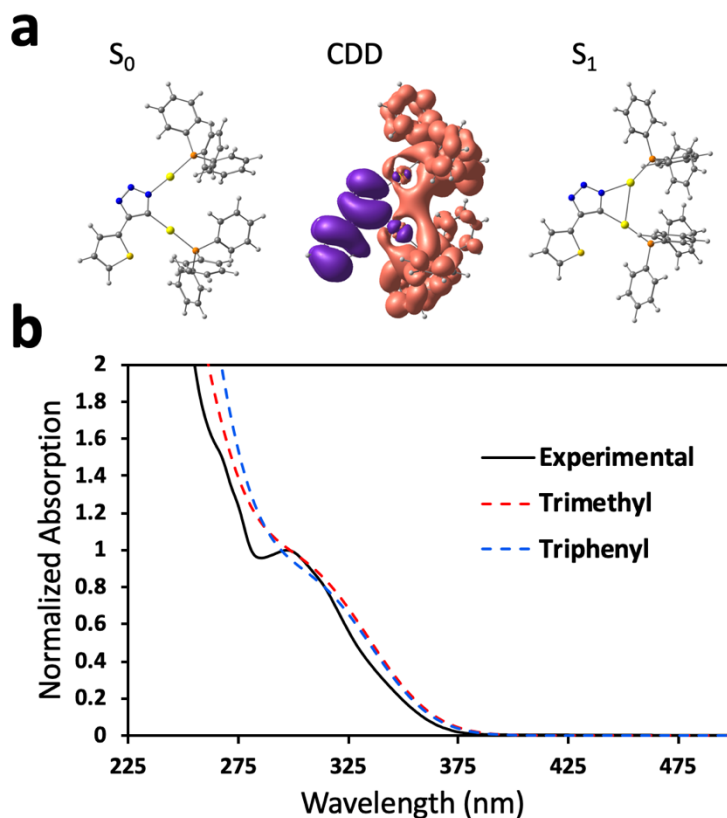


Figure S32. Shown here are the results of CAM-B3LYP calculations to produce the optimized ground state geometry, CDD, and relaxed excited state geometry (a) of **Au₂-Th** with triphenyl phosphine ligands; and the calculated absorption spectrum (b) compared to experiment and to **Au₂-Th** using trimethyl phosphine ligands.

Calculated Absorption Spectra

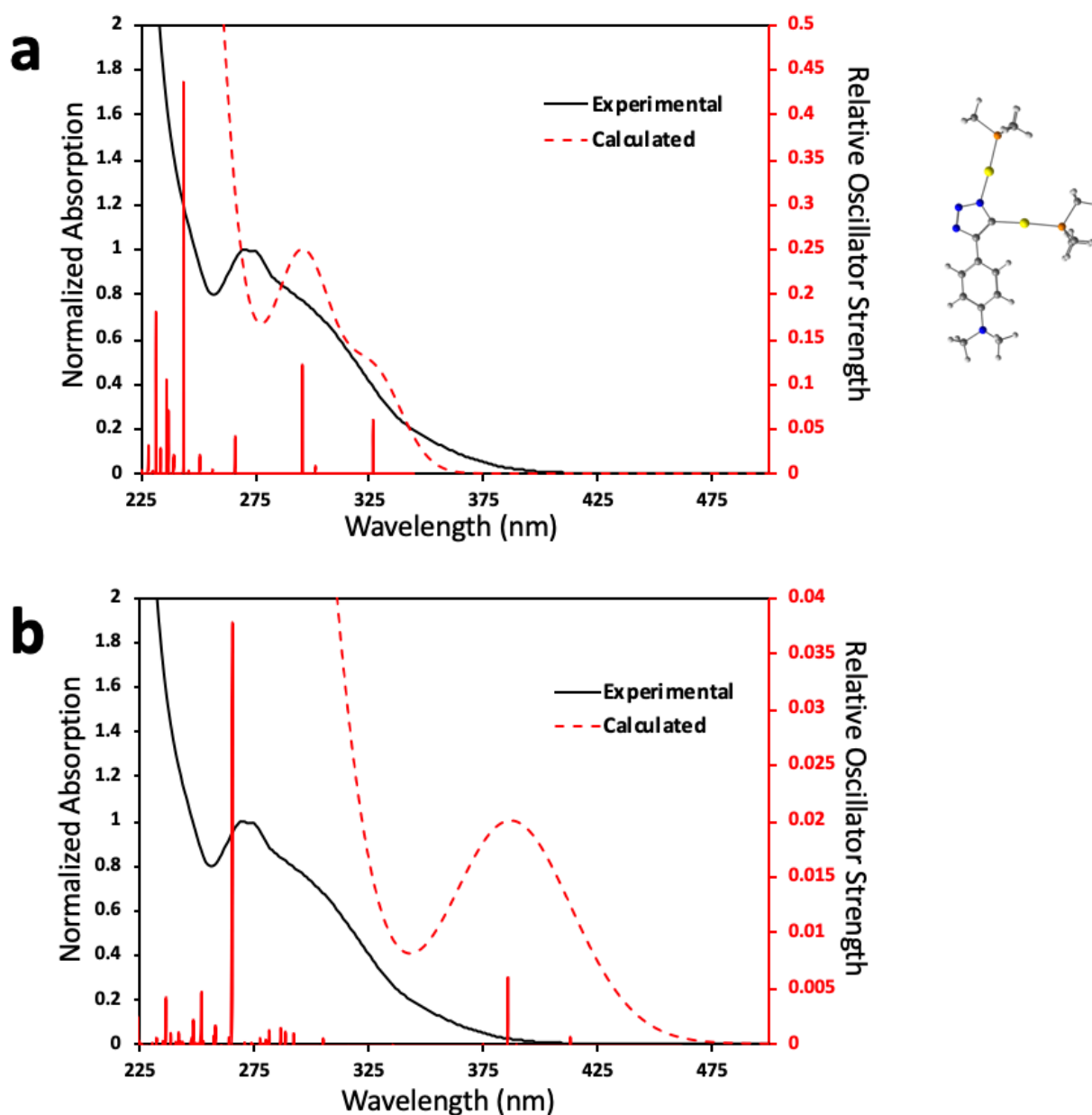


Figure S33. Experimental (black line) and calculated (red lines) absorption spectra of $\text{Au}_2\text{-PhNMe}_2$ using CAM-B3LYP (a) and with B3LYP (b). The dashed line shows artificially broadened spectra using gaussian functions (FWHM = 25 nm for a and 50 nm for b).

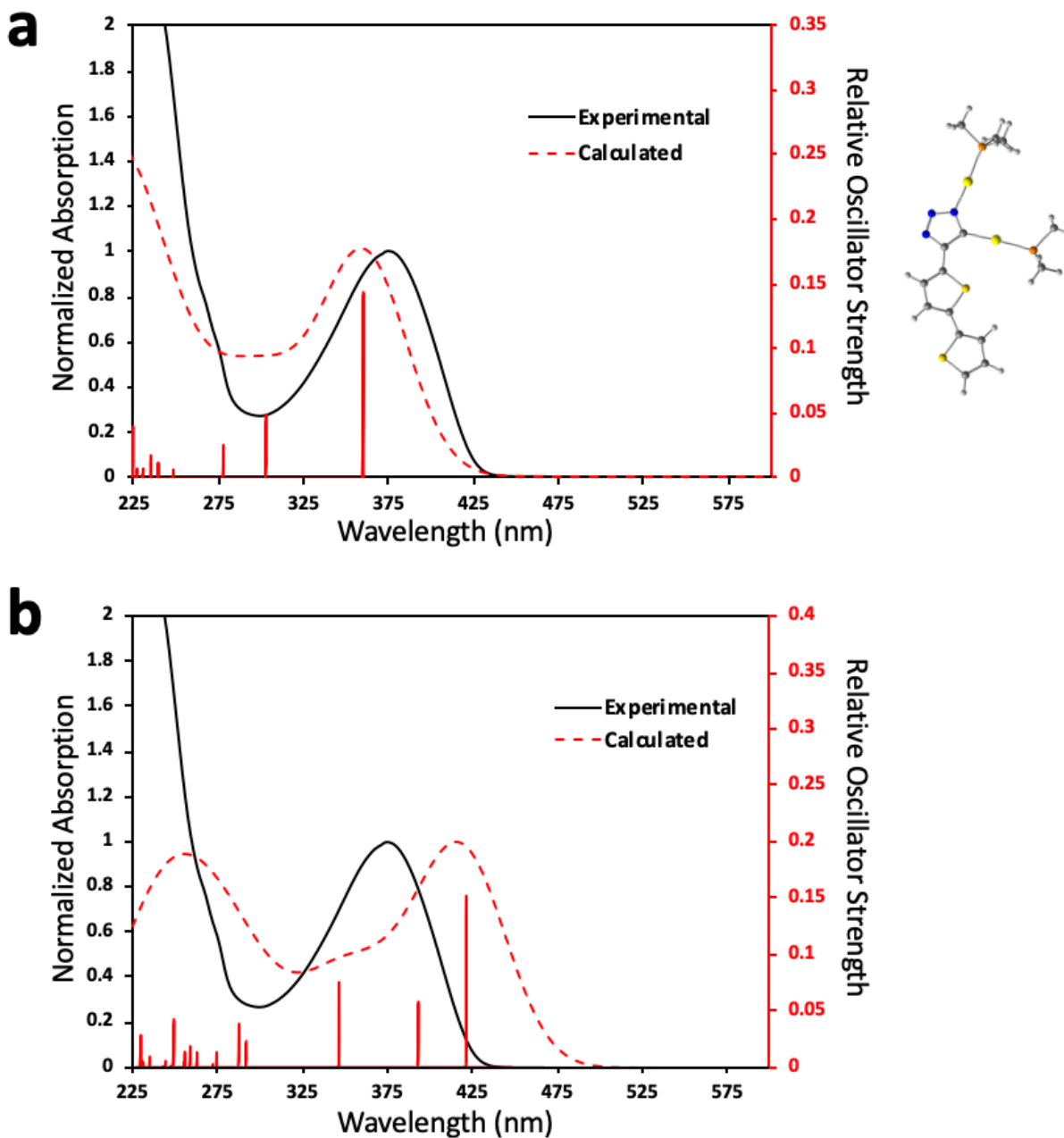


Figure S34. Experimental (black line) and calculated (red lines) absorption spectra of $\text{Au}_2\text{-biTh}$ using CAM-B3LYP (a) and with B3LYP (b). The dashed line shows artificially broadened spectra using gaussian functions (FWHM = 50 nm).

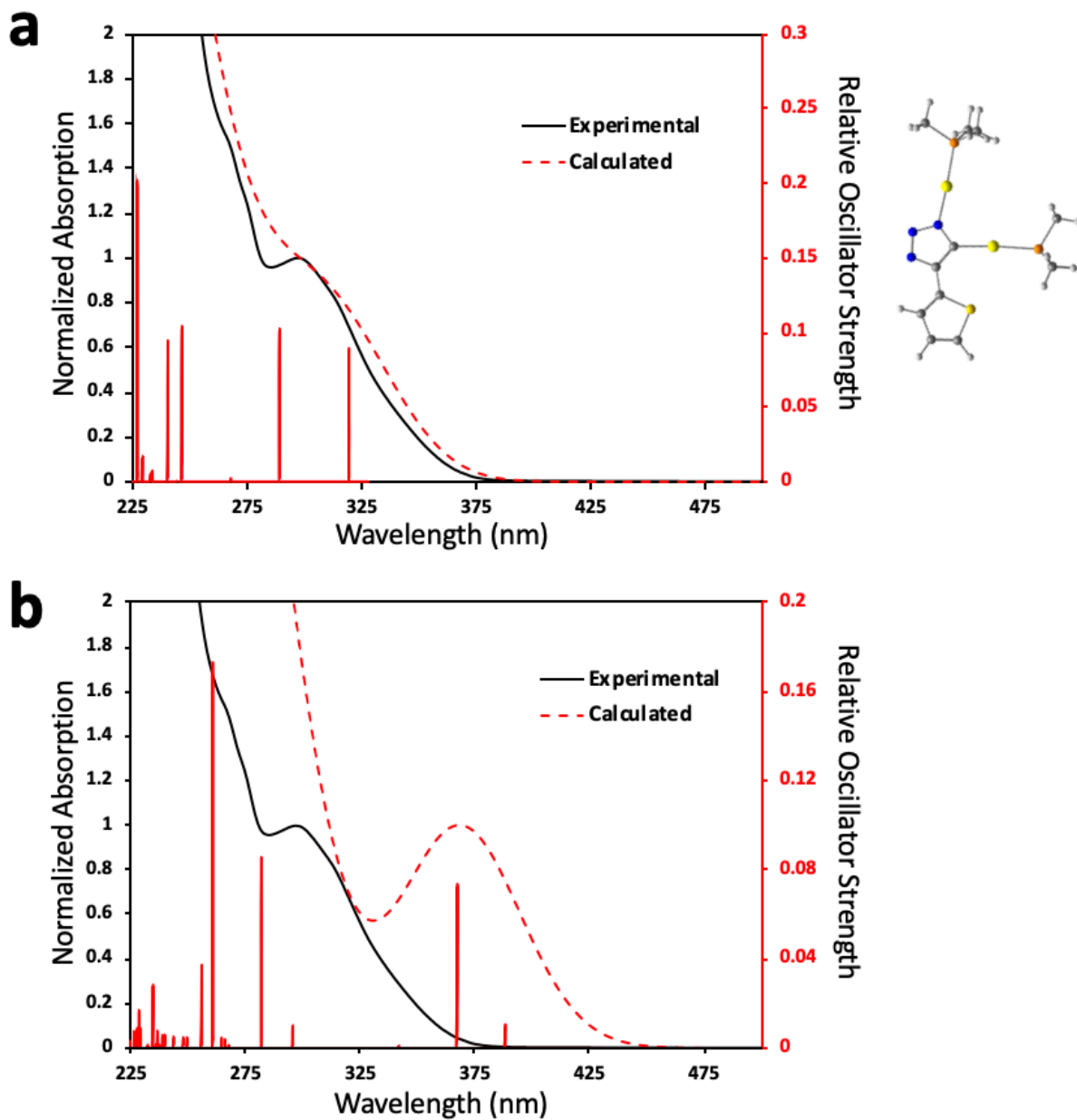


Figure S35. Experimental (black line) and calculated (red lines) absorption spectra of $\text{Au}_2\text{-Th}$ using CAM-B3LYP (a) and with B3LYP (b). The dashed line shows artificially broadened spectra using gaussian functions (FWHM = 50 nm).

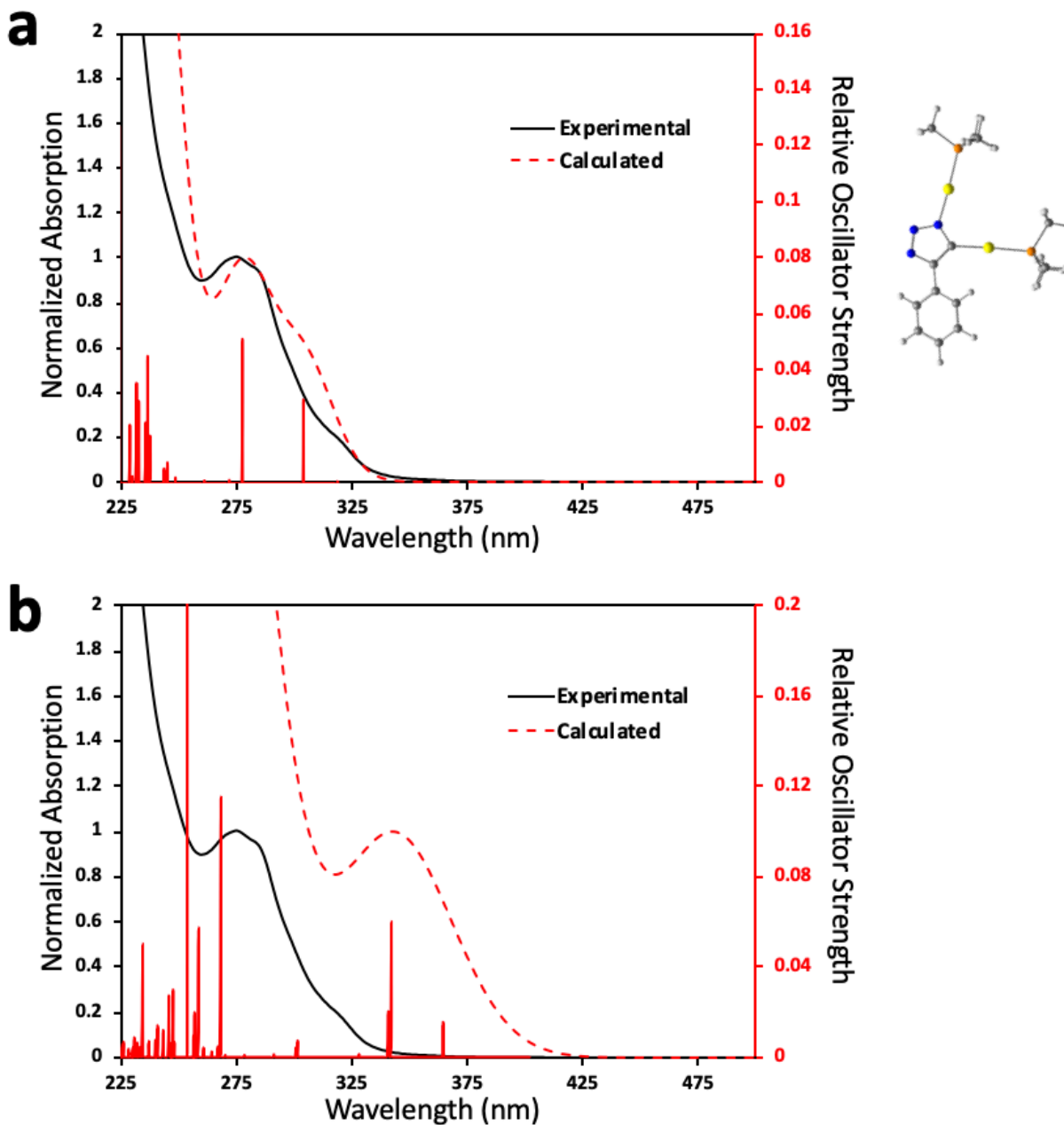


Figure S36. Experimental (black line) and calculated (red lines) absorption spectra of $\text{Au}_2\text{-Ph}$ using CAM-B3LYP (a) and with B3LYP (b). The dashed line shows artificially broadened spectra using gaussian functions (FWHM = 25 nm for a and 50 nm for b).

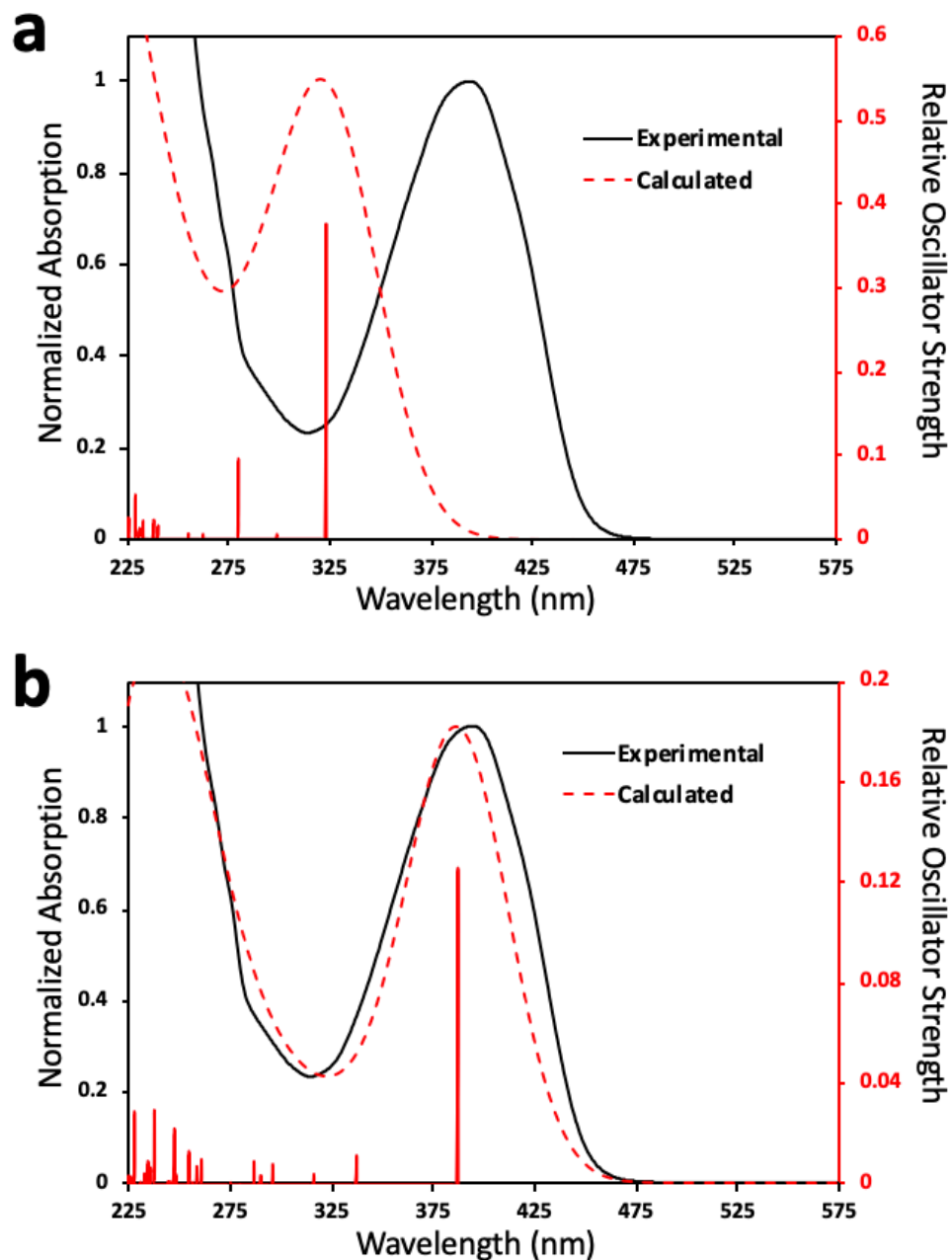


Figure S37. Experimental (black line) and calculated (red lines) absorption spectra of $\text{Au}_2\text{-PhNO}_2$ using CAM-B3LYP (a) and with B3LYP (b). The dashed line shows artificially broadened spectra using gaussian functions (FWHM = 50 nm).

Full Disclosure

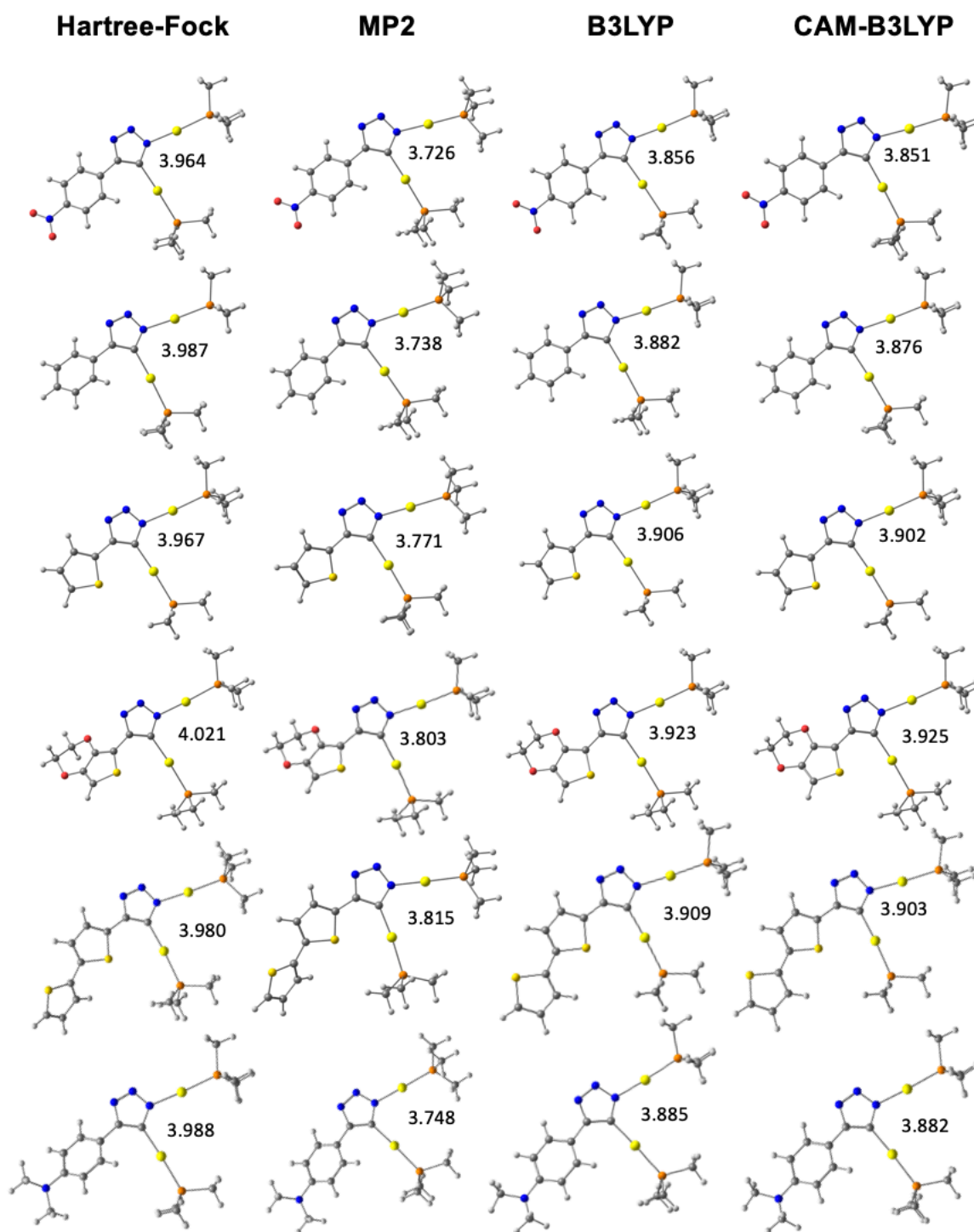


Figure S38. Optimized ground state (S_0) geometries of digold triazolates by different levels of theory. The numbers show interatomic Au(I)-Au(I) distances in Angstroms. Shown in descending order are **Au₂-PhNO₂**, **Au₂-Ph**, **Au₂-Th**, **Au₂-EDOT**, **Au₂-biTh**, and **Au₂-PhNMe₂**.

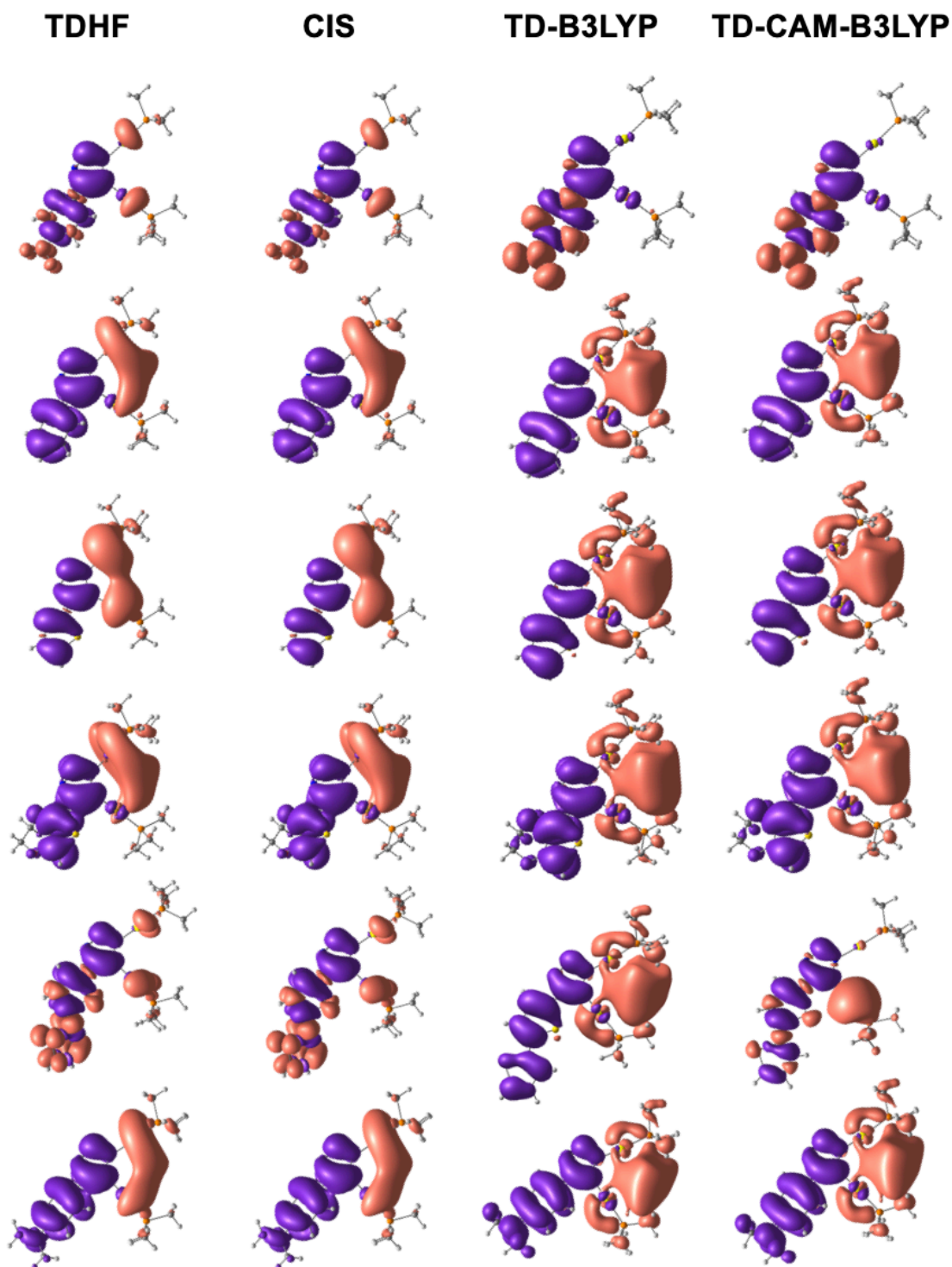


Figure S39. Charge difference densities (CDDs) of the lowest energy electronic excited state (S_1) of digold triazoles by different methods. Shown in descending order are **Au₂-PhNO₂**, **Au₂-Ph**, **Au₂-Th**, **Au₂-EDOT**, **Au₂-biTh**, and **Au₂-PhNMe₂**.

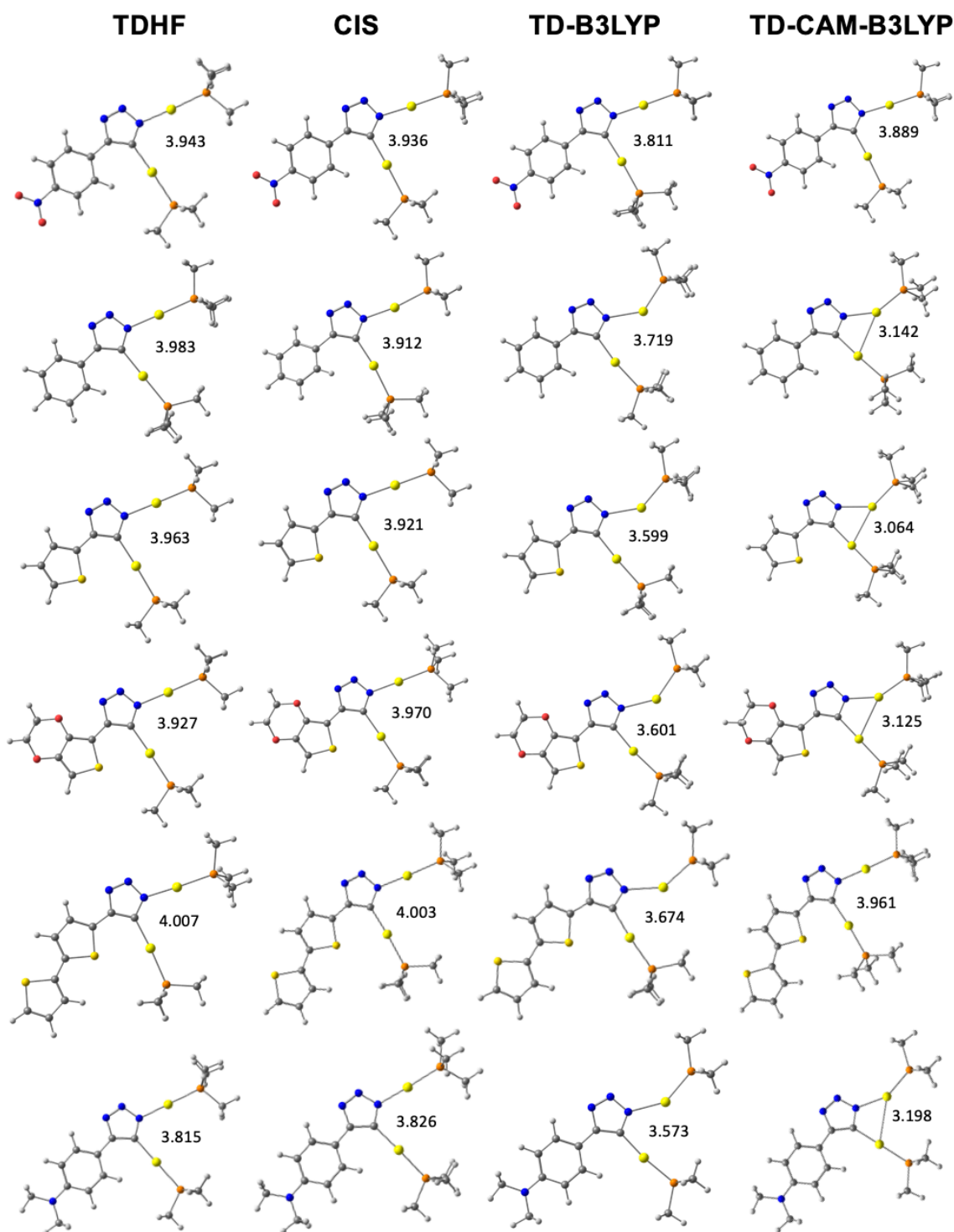


Figure S40. Optimized excited state (S_1) geometries of digold triazolates by different levels of theory. The numbers show interatomic Au(I)-Au(I) distances in Angstroms. Shown in descending order are **Au₂-PhNO₂**, **Au₂-Ph**, **Au₂-Th**, **Au₂-EDOT**, **Au₂-biTh**, and **Au₂-PhNMe₂**.

Orbital Analysis

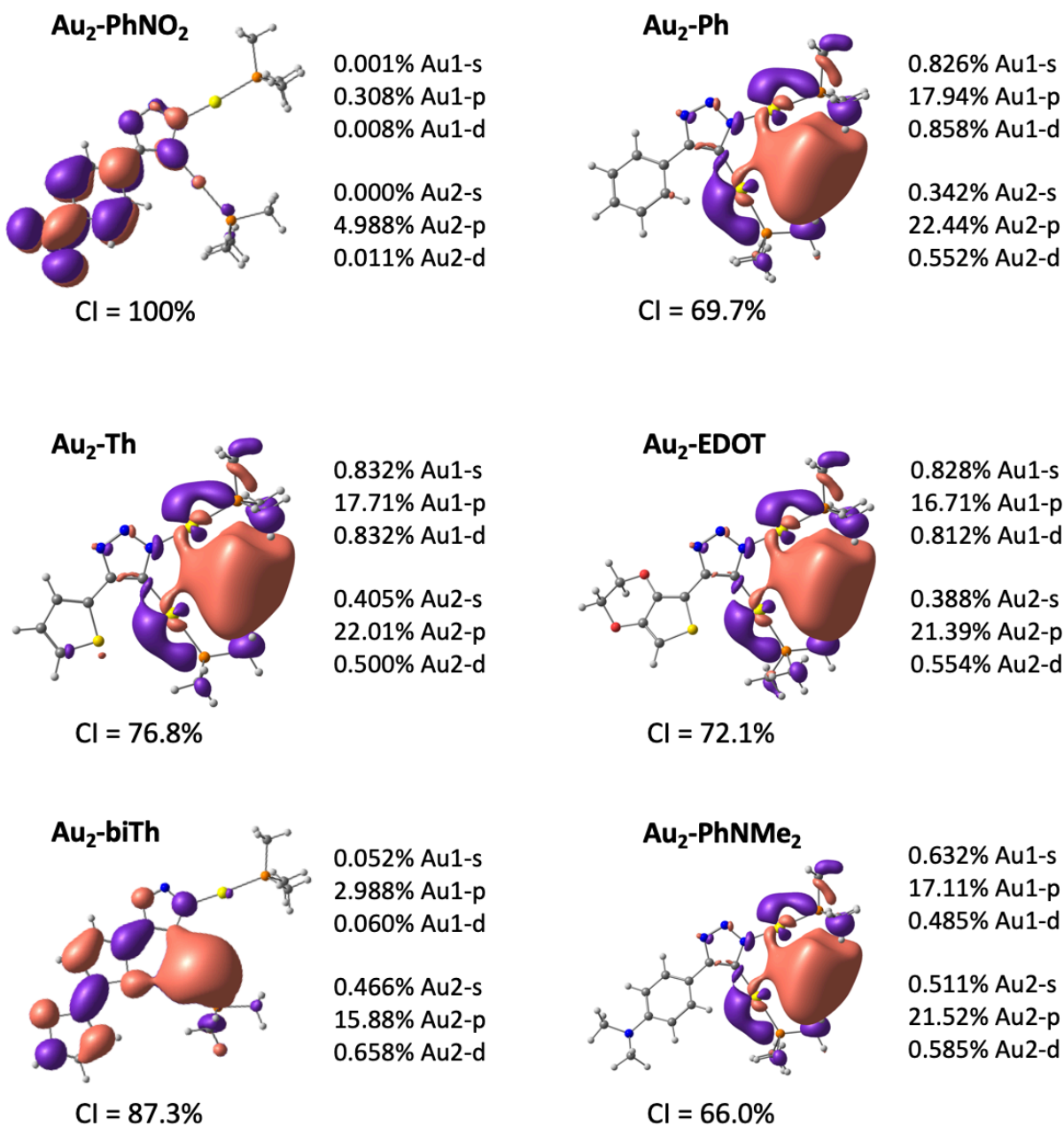


Figure S41. Shown here are the unoccupied (virtual) molecular orbitals (MOs) from the results of CAM-B3LYP calculations that contributed most heavily to the configuration interaction (CI) of the excited state, S_1 , for all compounds. Written below each MO is the percent contribution (CI = X%) of one-electron transitions to this orbital. The atomic orbital compositions from Au atoms are displayed to the right of each MO, divided into percent s, p, and d character.

Triplet States

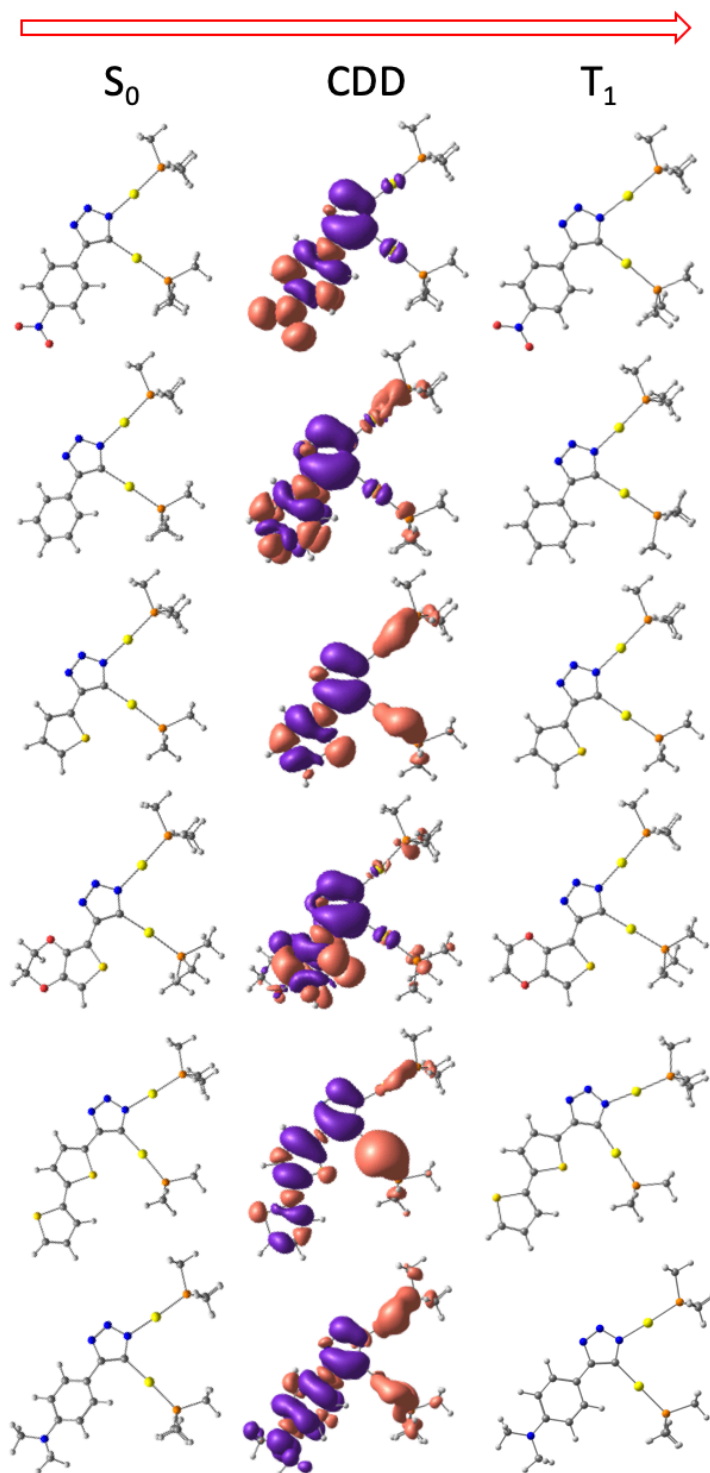


Figure S42. The results of a geometry optimizations of the singlet multiplicity ground state (S_0), the CDD of the lowest lying excited triplet state identified by TDDFT, and the relaxed geometry of that excited state using CAM-B3LYP.

4. References

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