Supporting Information

Small-molecule activation at Au(III): metallacycle construction from ethylene, water, and acetonitrile

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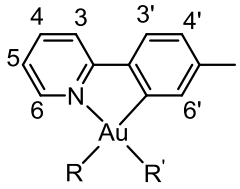
Experimental Section

General procedures. Gold(III) complexes **1** and **2** and AuBrMe(tpy) were prepared by previously reported procedures.[1,2] Distilled water was used. CH_3CN and CH_2Cl_2 were purified using a MB SPS-800 solvent purifying system from MBraun. The gold(III) complexes studied here are not sensitive to air, so inert atmosphere was not utilized, except for the synthesis of **9**. NMR spectra were recorded on Bruker Avance DPX200, AVII400, DRX500, AVII600 and AV600 instruments at ambient temperature. ^{1}H and ^{13}C spectra have been referenced relative to the residual solvent signals. ^{19}F has been referenced to $CFCl_3$ by using C_6F_6 (-164.9 ppm with respect to $CFCl_3$ at 0 ppm) as an internal standard. The ^{15}N chemical shifts have been calibrated using $MeNO_2$ as an external standard at 0 ppm. The peaks in the ^{1}H NMR and ^{13}C NMR spectra were assigned by the aid of 2D NMR techniques such as HSQC, HMBC, COSY, NOESY, and ^{1}H-^{15}N HMBC according to the numbering scheme shown below. Mass spectra (ESI) were obtained on a Micromass QTOF II spectrometer and a Bruker Daltronics maXisII spectrometer. Elemental analysis was performed by Microanalytisches Laboratorium Kolbe, Mülheim an der Ruhr, Germany.

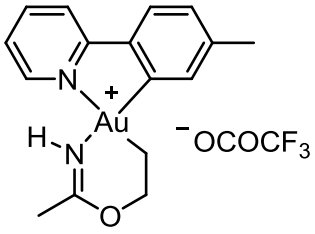


Numbering scheme used for reporting the NMR data.

[1] E. Langseth, C. H. Görbitz, R. H. Heyn and M. Tilset, *Organometallics*, 2012, **31**, 6567-6571.

[2] E. Langseth, A. Nova, E. A. Tråseth, F. Rise, S. Øien, R. H. Heyn and M. Tilset, *J. Am. Chem. Soc*., 2014, **136**, 10104-10115.

Preparation of [Au(tpy)(C–N)$^+$][$^-$OCOCF$_3$] (3).



3

Preparation of 3 from 1. Au(tpy)(OCOCF$_3$)$_2$ (50.1 mg, 0.0847 mmol, 1.0 equiv.) was dissolved in acetonitrile (3 mL). Water (10 µL, 0.55 mmol, 6.5 equiv.) was added. Ethylene was bubbled through the solution at ambient pressure for two minutes, and the flask was sealed with a glass stopper. The reaction mixture was stirred at ambient temperature in the absence of light for 7 days. The reaction mixture was filtered and the volatiles were removed under reduced pressure furnishing **3** as a white solid (38.1 mg, 0.0675 mmol, 80%).

Preparation of 3 from 2. Au(tpy)(CH$_2$CH$_2$OCOCF$_3$)(OCOCF$_3$) (50.1 mg, 0.0809 mmol, 1.0 equiv.) was dissolved in acetonitrile (3 mL). Water (10 µL, 0.55 mmol, 6.8 equiv.) was added. Ethylene was bubbled through the solution at ambient pressure for two minutes, and the flask was sealed with a glass stopper. The reaction mixture was stirred at ambient temperature in the absence of light for 5 days. The reaction mixture was filtered and the volatiles were removed under reduced pressure furnishing **3** as a white solid (35.8 mg, 0.0634 mmol, 78%).

^{1}H NMR (600 MHz, CD_2Cl_2): δ 10.28 (bs, 1H, N**H**), 9.33 (d, 1H, *J* = 5.4 Hz, **H^6**), 8.08 (ddd, 1H, *J* = 8.0, 7.5, 1.4 Hz, **H^4**), 7.96 (d, 1H, *J* = 8.0 Hz, **H^3**), 7.71 (d, 1H, *J* = 7.7 Hz, **H$^{3'}$**), 7.58 (ddd, 1H, *J* = 7.5, 5.6, 1.1 Hz, **H^5**), 7.23-7.25 (m, 2H, **H$^{4'}$** and **H$^{6'}$**), 4.34 (m, 2H, OC**H$_2$**), 2.73 (m, 2H, AuC**H$_2$**), 2.51 (s, 3H, OCC**H$_3$**), 2.44 (s, 3H, ArC**H$_3$**).

^{1}H NMR (400 MHz, CD_3CN): δ 9.03 (bs, 1H, N**H**), 8.94 (d, 1H, *J* = 5.4 Hz, **H^6**), 8.15 (ddd, 1H, *J* = 8.0, 7.6, 1.5 Hz, **H^4**), 8.08 (d, 1H, *J* = 8.1 Hz, **H^3**), 7.77 (d, 1H, *J* = 8.4 Hz, **H$^{3'}$**), 7.58 (ddd, 1H, *J* = 7.3, 5.7, 1.3 Hz, **H^5**), 7.22-7.24 (m, 2H, **H$^{4'}$** and **H$^{6'}$**), 4.32 (m, 2H, OC**H$_2$**), 2.69 (m, 2H, AuC**H$_2$**), 2.43 (s, 3H, OCC**H$_3$**), 2.39 (s, 3H, ArC**H$_3$**).

^{13}C NMR (150 MHz, CD_2Cl_2): δ 175.2, 161.7, 149.8, 142.4, 142.3, 142.0, 141.9, 131.2, 129.4, 126.0, 124.9, 120.2, 66.5, 28.6, 22.0, 21.6. $^-$OCOCF$_3$ was not observed by ^{13}C NMR.

^{15}N{^{1}H} NMR (600 MHz, CD_2Cl_2): δ -129 (**N**(tpy)), -212 (**N**H, $|J|$ = 78 Hz), as observed by ^{1}H-^{15}N HMBC (see **Figure S12**).

^{19}F NMR (188 MHz, CD_2Cl_2): δ -78.1 (bs, C**F**$_3$).

MS (ESI^+, MeCN): *m/z* (rel. %): 451 ($[M\text{-}OCOCF_3]^+$, 100).

MS (ESI^-, MeCN): *m/z* (rel. %): 113 ($[OCOCF_3]^-$, 100) was observed among other unidentified peaks.

HRMS (ESI^+, MeCN): Found: 451.1068; calcd for $C_{16}H_{18}AuN_2O$: 451.1084 (+0.0016).

HRMS (ESI^-, MeCN): Found: 112.9859; calcd for $C_2F_3O_2$: 112.9856 (–0.0003).

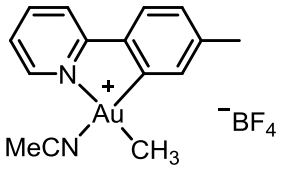
Elemental analysis: Anal. Calcd for $C_{18}H_{18}AuF_3N_2O_3$: C, 38.31; H, 3.22; N, 4.96. Found: C, 37.81; H, 3.19; N, 4.59.

Comments to the ^{1}H-^{15}N HMBC Spectrum

In the ^{1}H-^{15}N HMBC spectrum, see **Figure S12**, signals arising from two different N atoms are clearly observed. One signal at $\delta(^{15}N\{^{1}H\})$ = -212 arises from the chelate NH and correlates with the broadened ^{1}H signal of the NH group at $\delta(^{1}H)$ = 10.28 and with the signal from the metallacycle methyl group at $\delta(^{1}H)$ = 2.51. No correlation of NH with OCH_2CH_2 was observed which is in agreement with the proposed structure **3**. The chemical shift of NH is in the range of what has been observed for Pt(II) imine complexes[3,4] and is shifted upfield compared to free 2-methyl-2-oxazoline ($\delta(^{15}N)$ = -167 ppm)[5] probably due to the coordination of N to Au. The $|{}^{1}J(^{1}H\text{-}^{15}N)|$ coupling constant of 78 Hz is within the range of what is observed for ketimines and protonated ketimines.[6] The other ^{15}N signal at $\delta(^{15}N\{^{1}H\})$ = -129 arises from the N atom in the tpy ligand and has a correlation with the signal arising from the CH proton α to the pyridyl-N atom at $\delta(^{1}H)$ = 9.33. This chemical shift is similar to what is observed for $Au(ppy)Cl_2$ (ppy = 2-phenylpyridine)[7] and Au(III) acetylpyridine and benzoylpyridine complexes[8] and is within the region where ^{15}N NMR shifts for azines are usually found and lies in the region between pyridine and protonated pyridine.[9,10]

[3] B. Longato, D. Montagner, G. Bandoli and E. Zangrando, *Inorg. Chem*., 2006, **45**, 1805-1814.
[4] T. Chivers, K. McGregor and M. Parvez, *Inorg. Chem*., 1993, **32**, 5119-5125.
[5] M. Witanowski, I. Stefaniak and G. A. Webb, *Annu. Rep. NMR Spectrosc.*, 1987, **18**, 213-737.
[6] M. Witanowski and G. A. Webb, eds., *Nitrogen NMR*, Springer US, Boston, MA, 1973.
[7] L. Pazderski, T. Pawlak, J. Sitkowski, L. Kozerski and E. Szłyk, *Magn. Reson. Chem*., 2009, **47**, 932-941.
[8] D. Niedzielska, T. Pawlak, T Czubachowski and L. Pazderski, *J. Spectrosc.*, 2013, **2013**, Article ID 982832. DOI: 10.1155/2013/982832.
[9] W. von Philipsborn and R. Müller, *Angew. Chem. Int. Ed.*, 1986, **25**, 383-413.
[10] M. Witanowski, I. Stefaniak and G. A. Webb, *Annu. Rep. NMR Spectrosc.*, 1978, **7**, 117-244.

Preparation of [Au(tpy)(NCMe)Me$^+$][BF$_4^-$] (9).



9

A solution of AuBrMe(tpy) (49 mg, 0.11 mmol, 1.0 equiv.) in CH_2Cl_2 (5 mL) was cooled to –78 °C. A solution of $AgBF_4$ (53 mg, 0.27 mmol, 2.5 equiv.) in acetonitrile (500 μL) was added. Stirring was continued for 5 minutes, and the solution was warmed to ambient temperature. The solvents were removed from the grayish mixture under reduced pressure. The pale greyish solid was dissolved in acetonitrile (10 mL) and filtered to furnish a clear, colorless solution. The solvent was removed under reduced pressure, leaving a light grey solid. Recrystallization by slow diffusion of ether layered on top of a concentrated solution of **9** in acetonitrile provided material for the single-crystal structure determination and for the spectroscopic characterization.

^{1}H NMR (CD_3CN, 500 MHz): δ 8.72 (d, *J* = 5.4 Hz, 1H, **H^6**), 8.18 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H, **H^4**), 8.08 (d, *J* = 8.2 Hz, 1H, **H^3**), 7.76 (d, *J* = 8.3 Hz, 1H, **H$^{3'}$**), 7.61 (dd, *J* = 6.6, 6.6 Hz, 1H, **H^5**), 7.27 (s, 1H, **H$^{6'}$**), 7.26 (d, *J* = 7.2 Hz, 1H, **H$^{4'}$**), 2.39 (s, 3H, ArC**H$_3$**), 1.97 (s, 3H, NCC**H$_3$**), 1.51 (s, 3H, AuC**H$_3$**).

^{13}C NMR (CD_3CN, 150 MHz): δ 160.5, 148.7, 143.5, 143.4, 142.5, 136.6, 132.1, 130.7, 127.3, 126.1, 121.6, 21.8, 12.1, 1.3.

MS (ESI^+, MeCN): *m*/*z* (rel. %): 421([M-BF_4]$^+$,100).

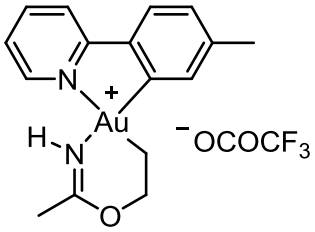
HRMS (MeCN): Found: 421.0973, calcd for $C_{15}H_{16}N_2Au$ 421.0979 (–1.4 ppm).

Mechanistic experiments on the role of acetamide.

Experiment in scheme 4A: A CH_2Cl_2 solution of **2** (1.0 equiv.) and acetamide (1.9 equiv.) were stirred for 6 days at ambient temperature. Volatiles were removed under reduced pressure and the remaining solid was investigated by ^{1}H NMR spectroscopy, which revealed that Au(III) complex **3** was not formed.

Experiment in scheme 4B: The metallacycle complex **3** was synthesized from **2** as already described, but in acetonitrile-d_3 with acetamide (3.1 equiv.) and water (6.6 equiv.) added. After 5 days the volatiles were removed under reduced pressure. The remaining solid was dissolved in CH_2Cl_2, filtered and CH_2Cl_2 was removed under reduced pressure yielding a white solid. Inspection of the white solid by ^{1}H NMR spectroscopy revealed that **3-*d*$_3$** was formed as the major product, together with minor amounts of **3** (ca 8% by ^{1}H-NMR integration) as inferred by the metallacycle-methyl resonance at δ 2.51 (CD_2Cl_2) in the ^{1}H NMR spectrum (see **Figure S14**).

Complex **3**



3

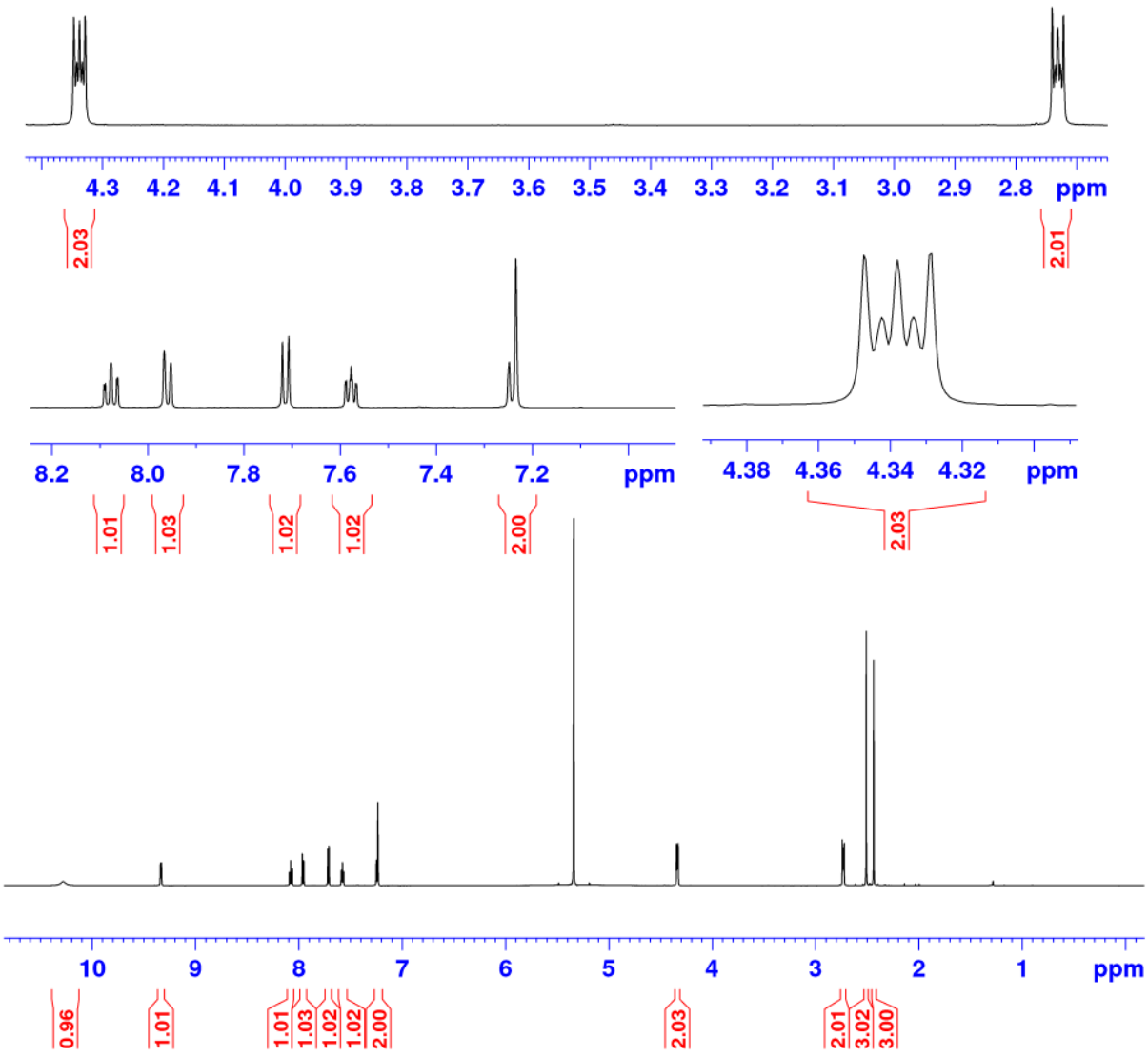


Figure S1. ^{1}H NMR (600 MHz, CD_2Cl_2) of Au(III) complex **3**.

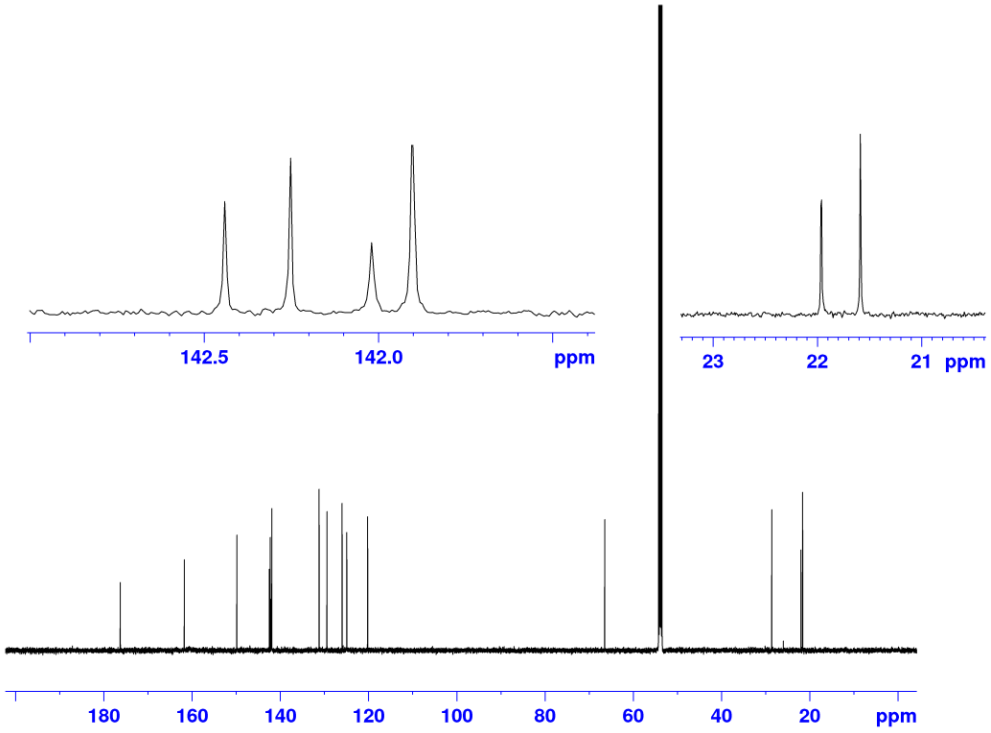


Figure S2. ^{13}C NMR(150 MHz, CD_2Cl_2, d1 = 10 s) of Au(III) complex **3**.

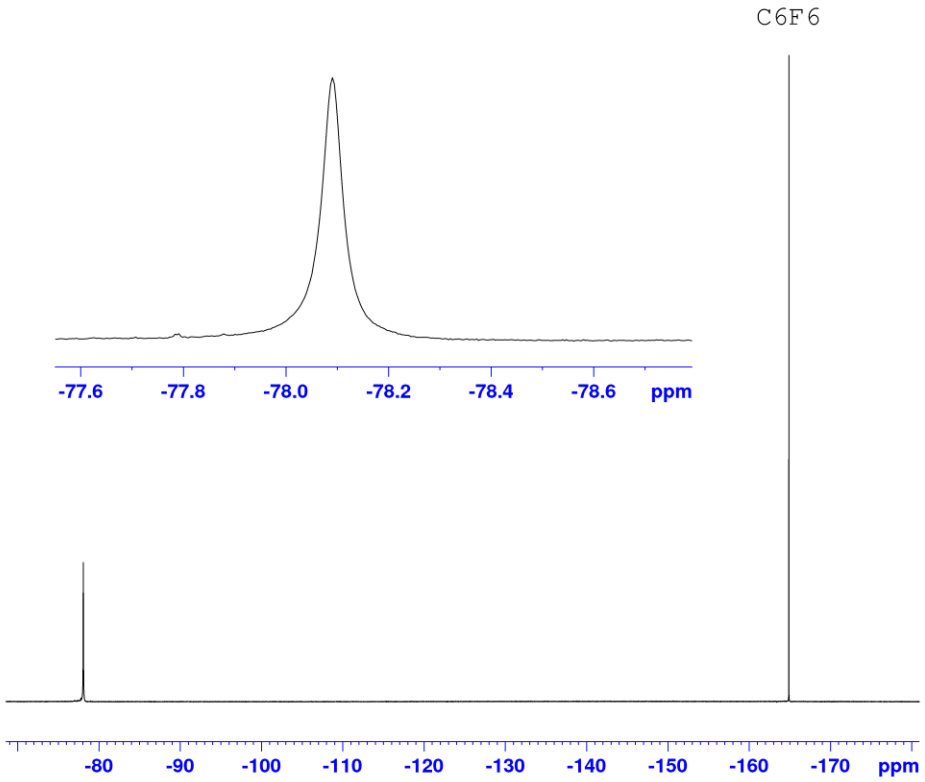


Figure S3. ^{19}F NMR (188 MHz, CD_2Cl_2) of Au(III) complex **3**.

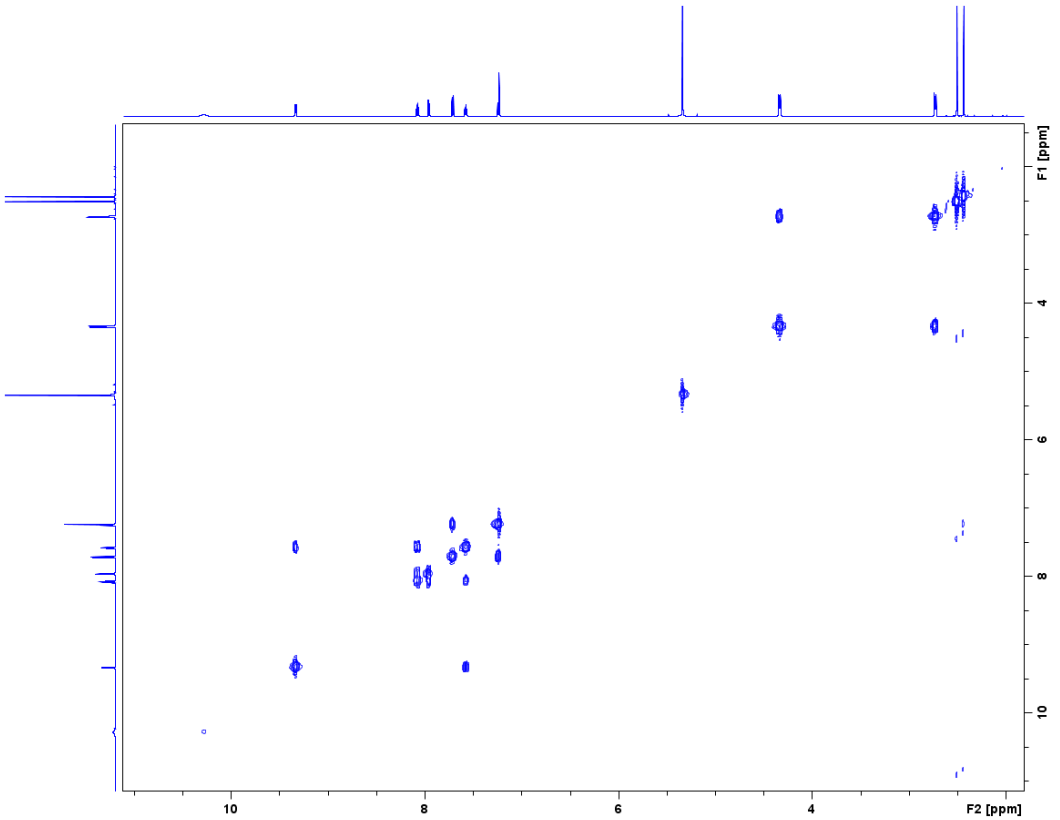


Figure S4. COSY (600 MHz, CD_2Cl_2) of Au(III) complex **3**.

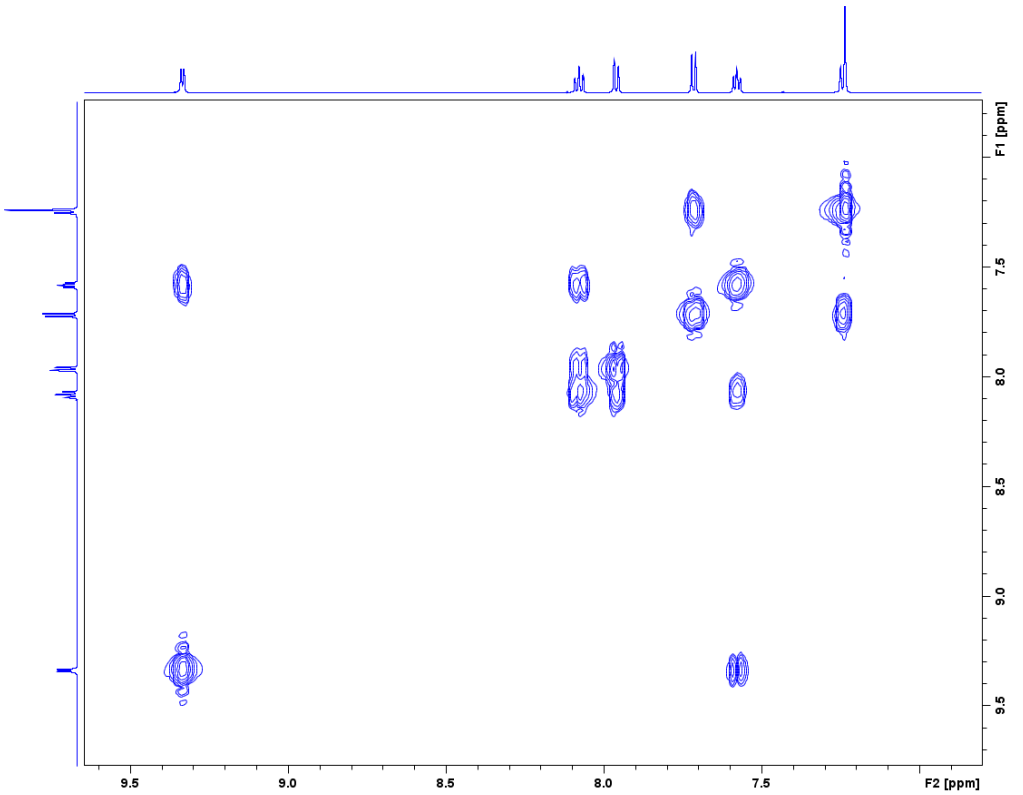


Figure S5. COSY (600 MHz, CD_2Cl_2) of Au(III) complex **3**. Close-up of the aromatic region.

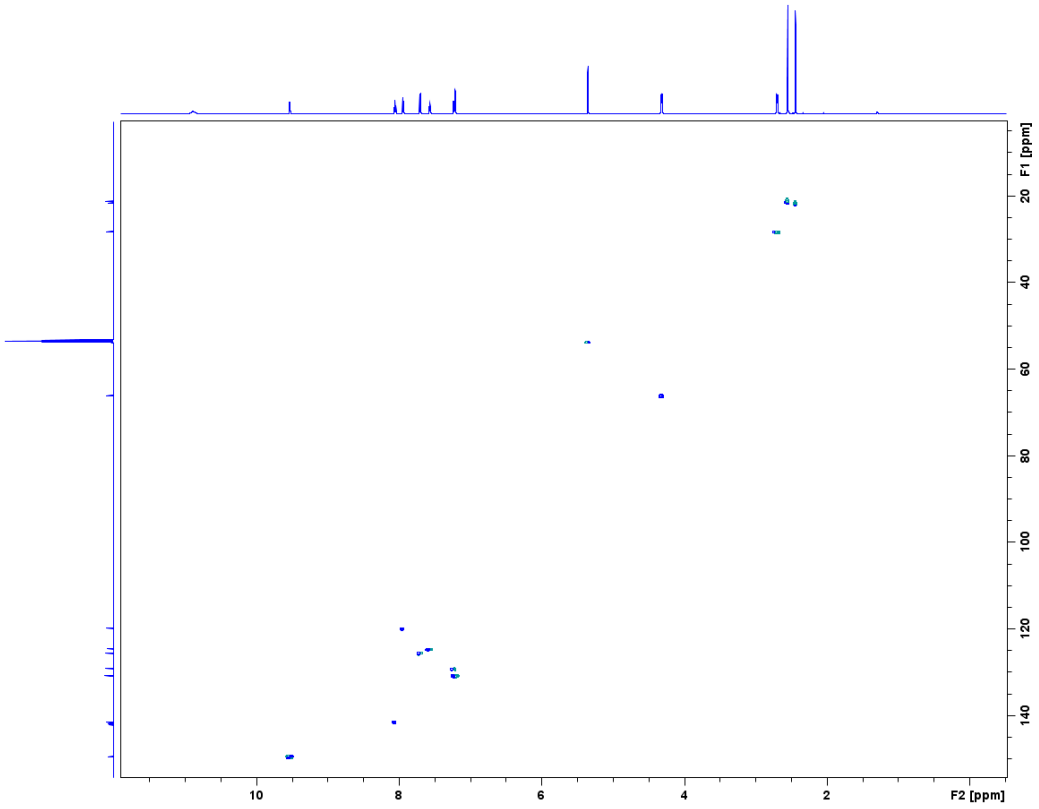


Figure S6. HSQC (600 MHz, CD_2Cl_2) of Au(III) complex **3**.

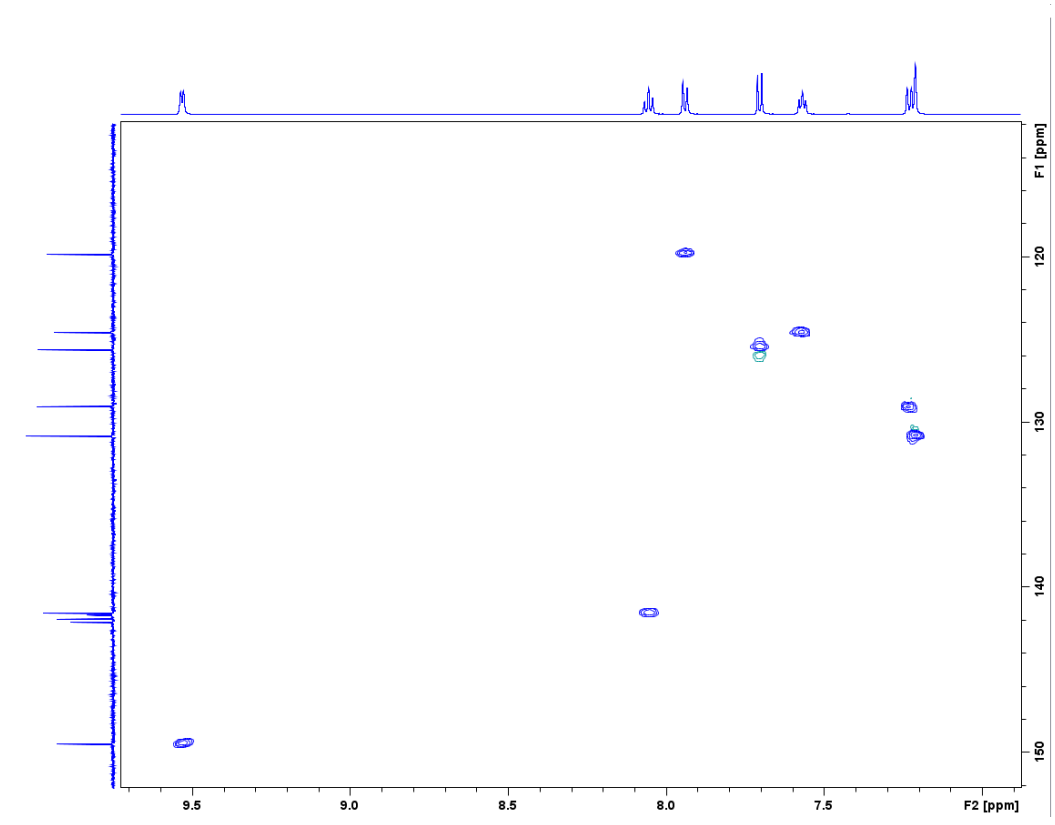


Figure S7. HSQC (600 MHz, CD_2Cl_2) of Au(III) complex **3**. Close-up of the aromatic region.

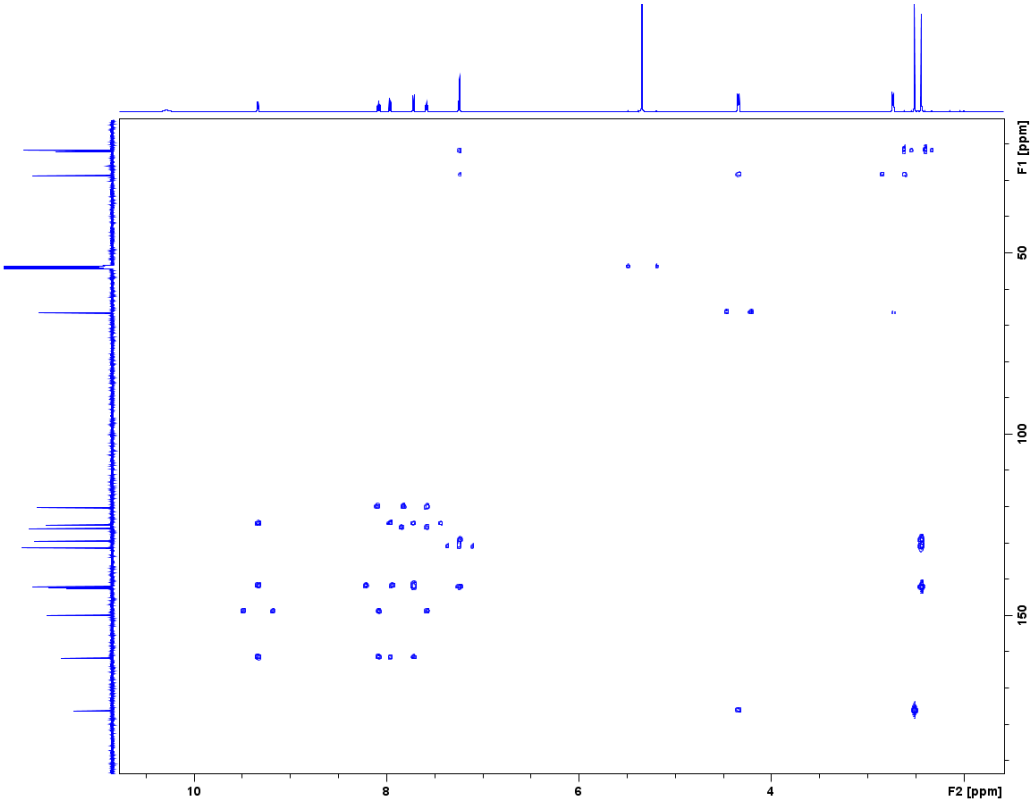


Figure S8. HMBC (600 MHz, CD_2Cl_2, no decoupling) of Au(III) complex **3**.

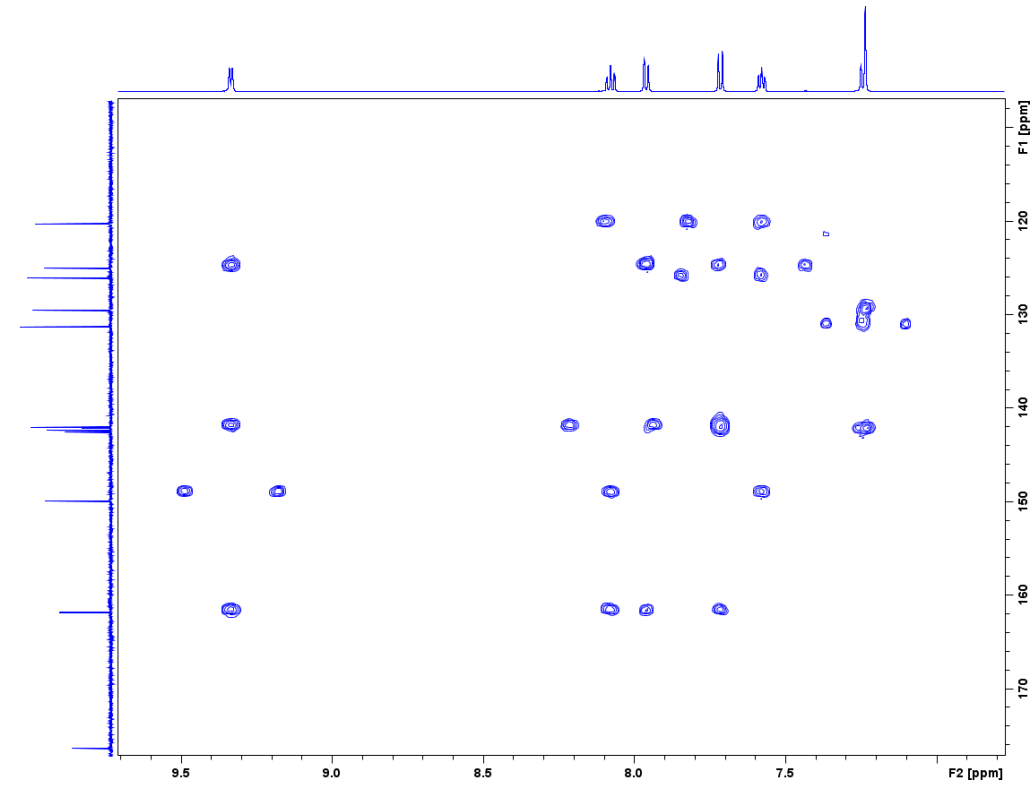


Figure S9. HMBC (600 MHz, CD_2Cl_2, no decoupling) of Au(III) complex **3**. Close-up of the aromatic region.

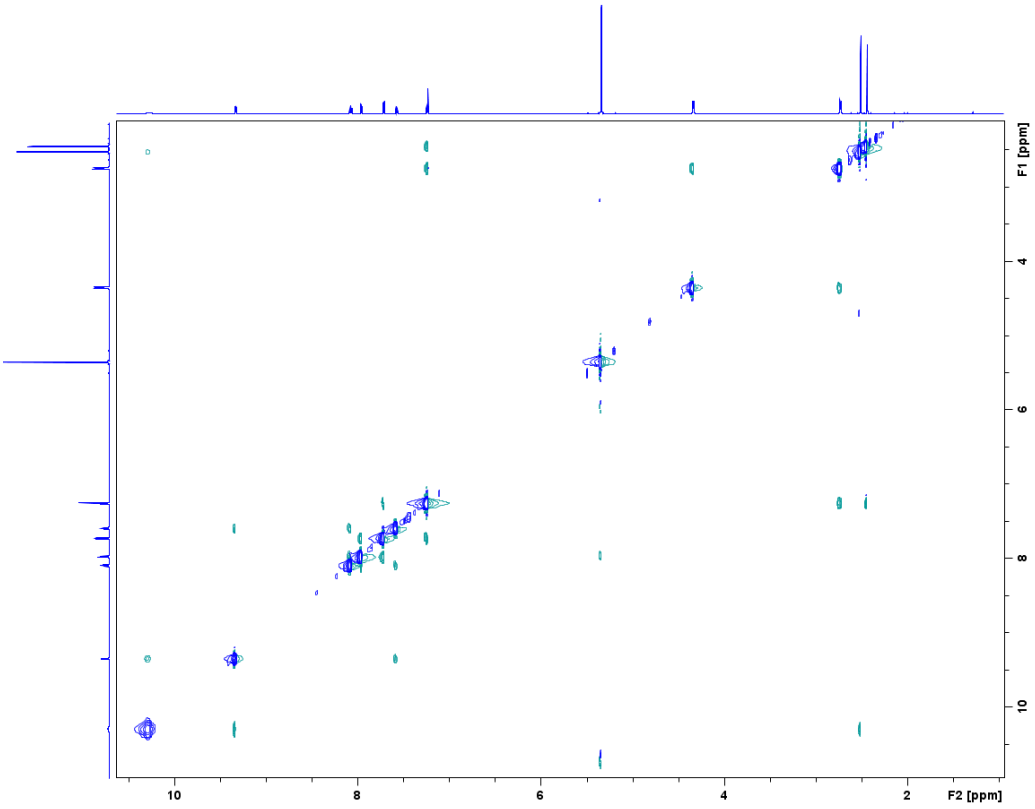


Figure S10. NOESY (600 MHz, CD_2Cl_2, mixing time = 1 s) of Au(III) complex **3**.

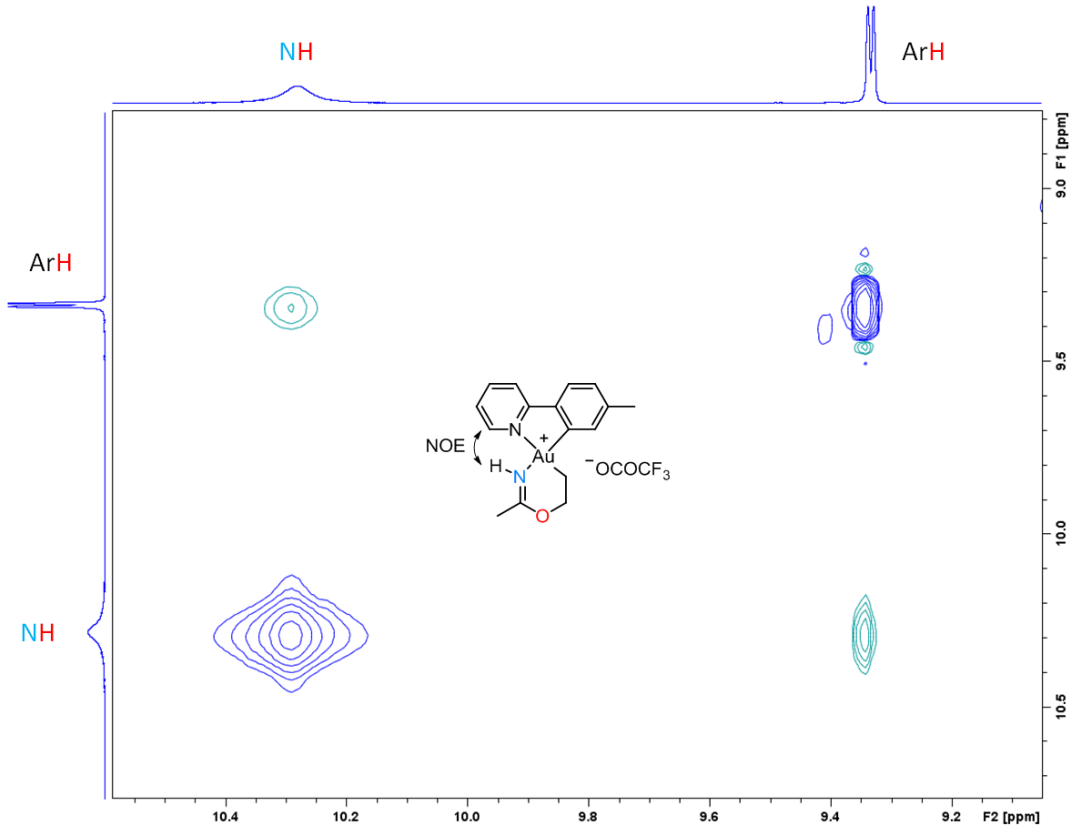


Figure S11. NOESY (600 MHz, CD_2Cl_2, mixing time = 1 s) of Au(III) complex **3**. Close-up of the NOE correlation between NH and tpy.

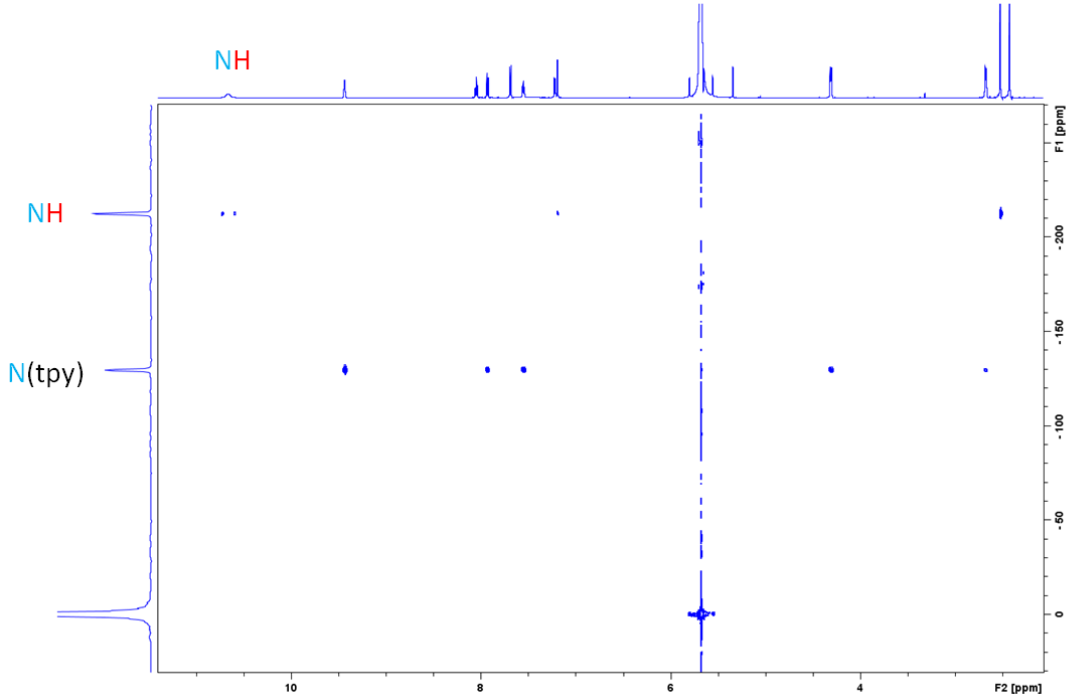


Figure S12. ^{1}H-^{15}N HMBC (600 MHz, CD_2Cl_2, no decoupling) of Au(III) complex **3**. The ^{15}N chemical shifts have been calibrated using $MeNO_2$ as an external standard at 0 ppm.

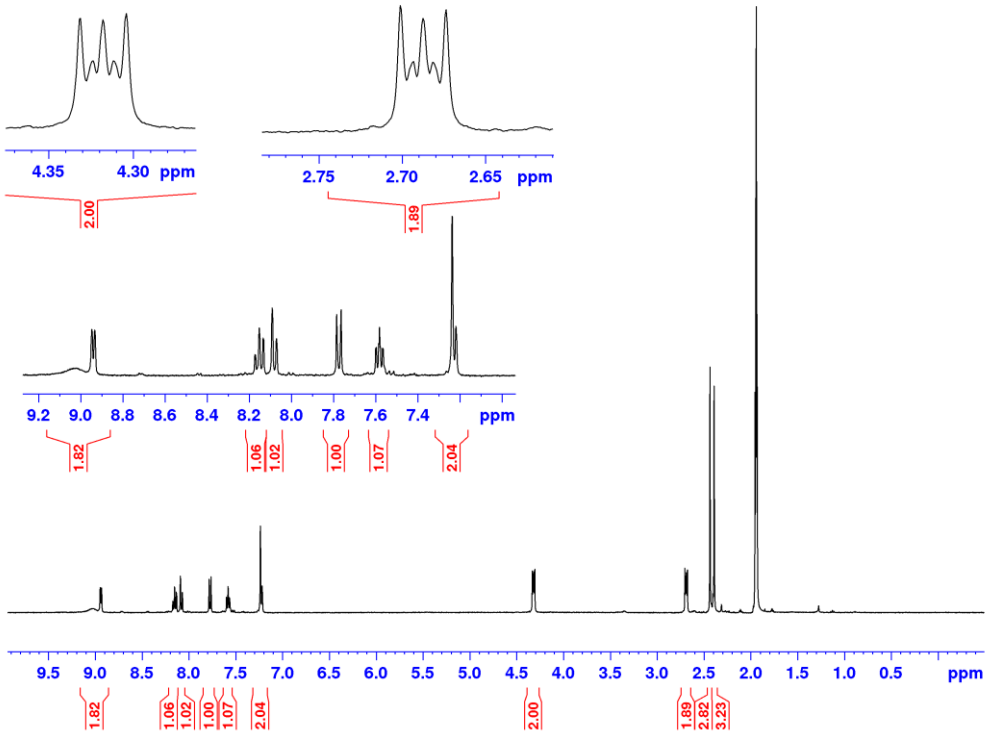


Figure S13: ^{1}H NMR (400 MHz, CD_3CN) of Au(III) complex **3**.

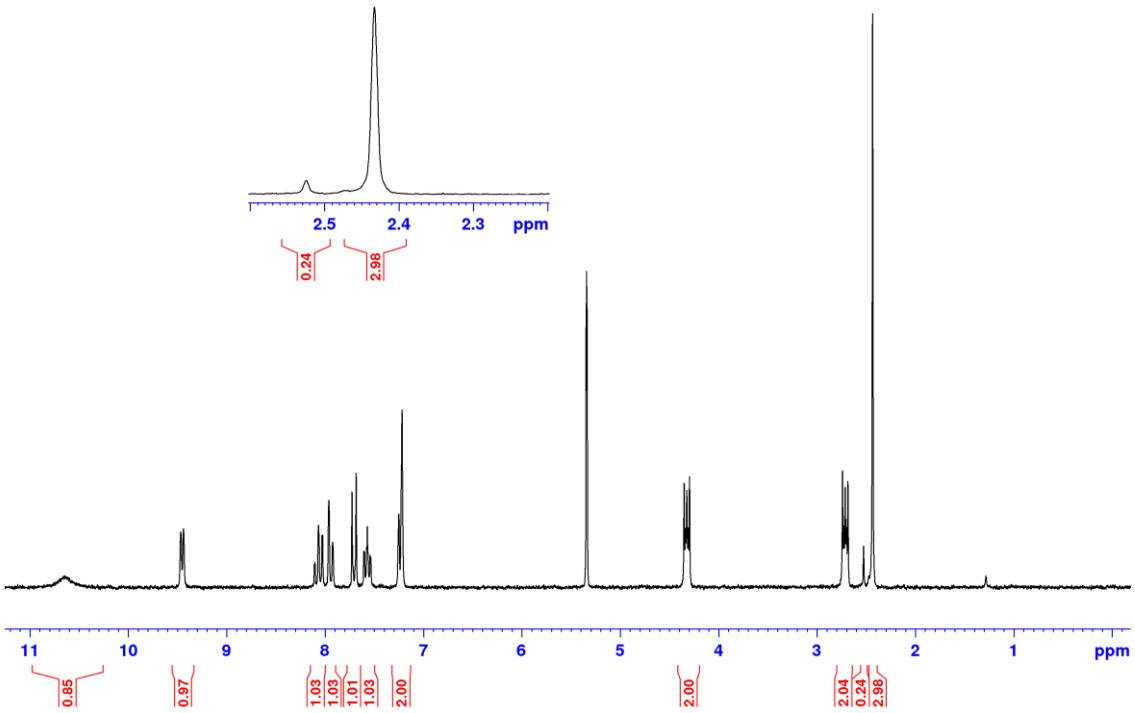


Figure S14: ^{1}H NMR (200 MHz, CD_2Cl_2) of Au(III) complex **3-*d*$_3$**. Small amounts of **3** (ca 8% by integration) can also be observed.

Complex **9**

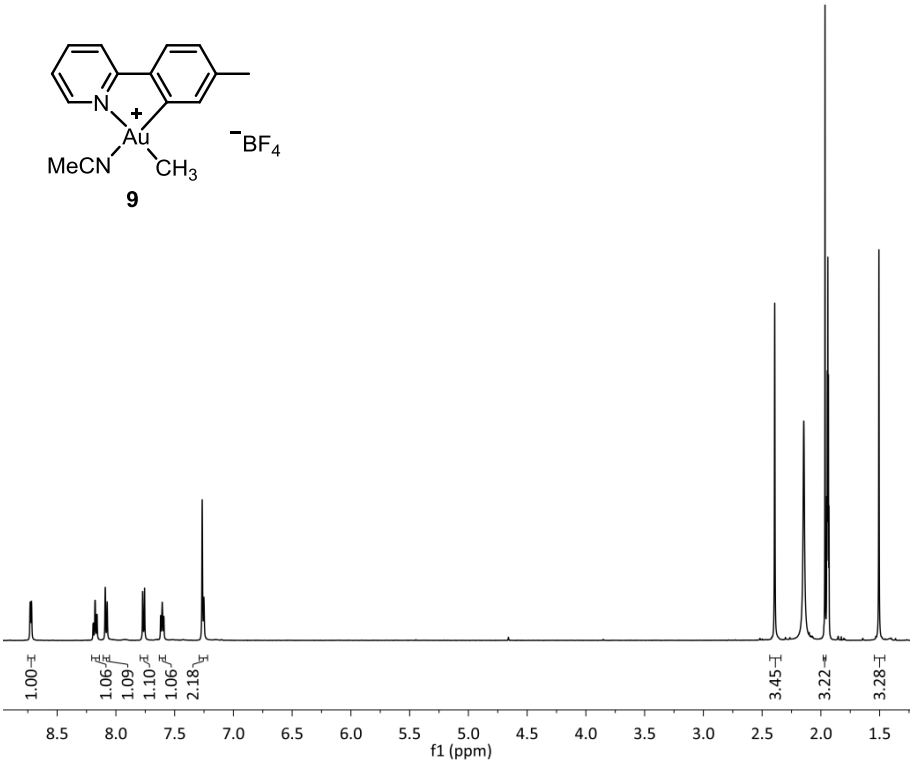


Figure S15. ^{1}H NMR (500 MHz, CD_3CN) of **9**.

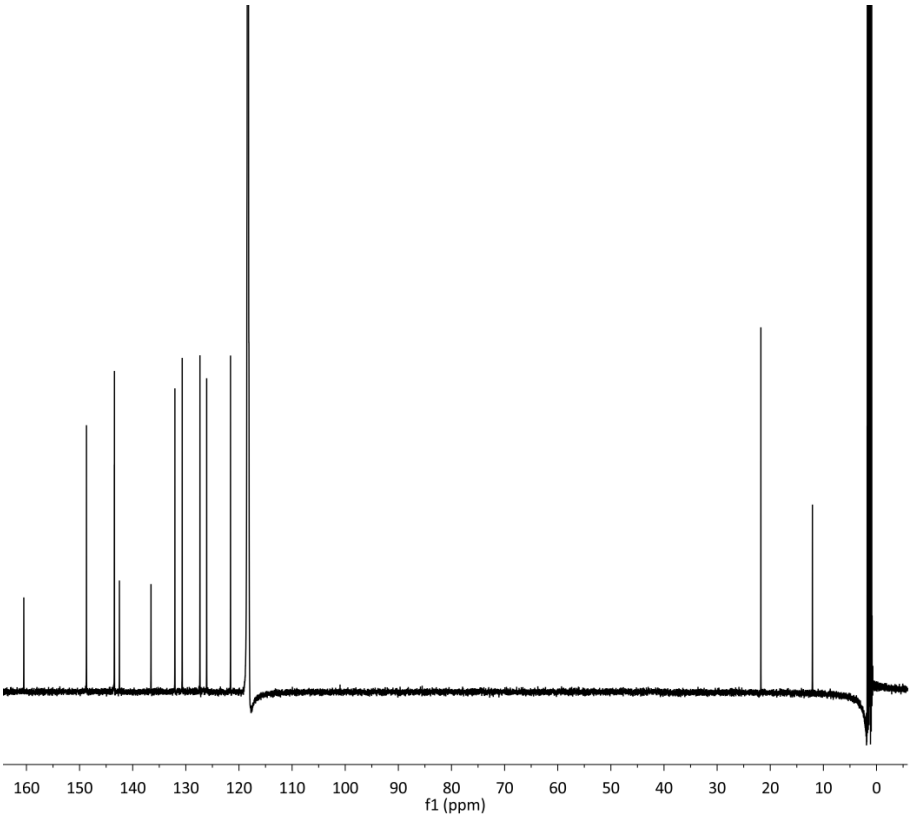


Figure S16. ^{13}C NMR (150 MHz, CD_3CN) of **9**.

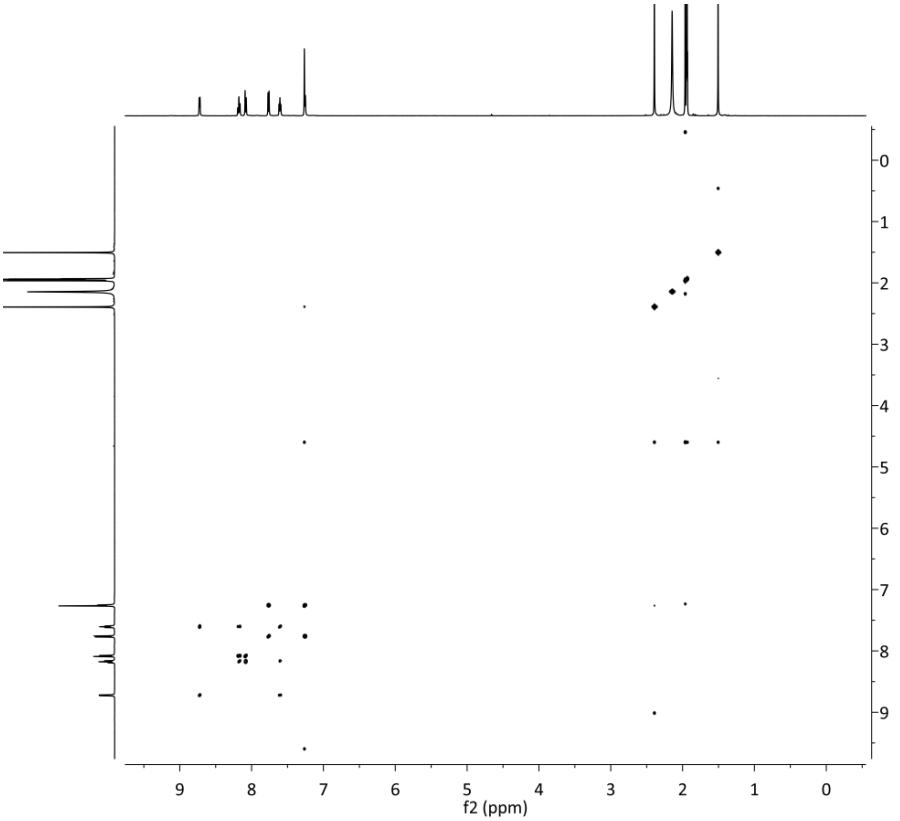


Figure S17. COSY (500 MHz, CD_3CN) of **9**.

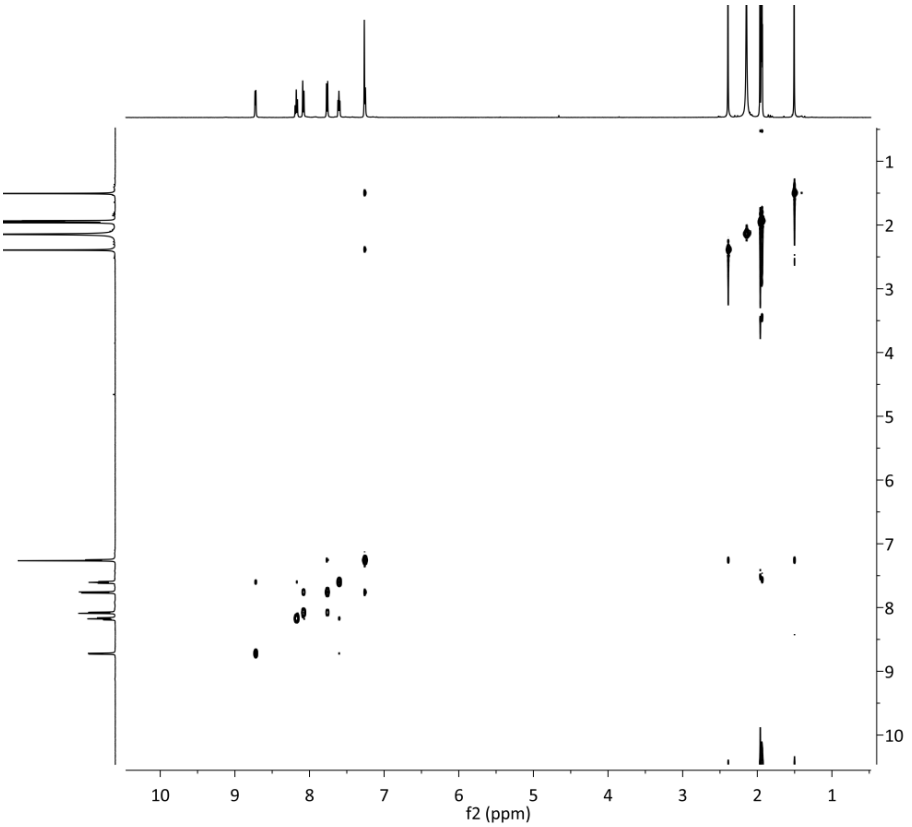


Figure S18. NOESY (500 MHz, CD_3CN) of **9**.

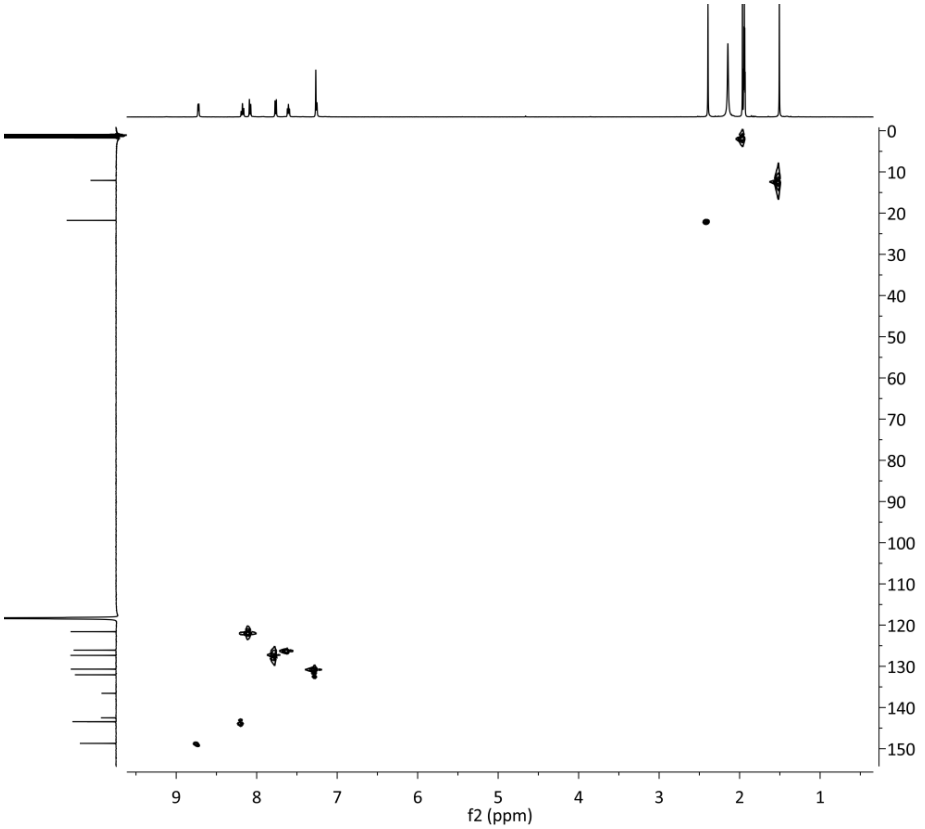


Figure S19. HSQC (600 MHz, CD_3CN) of **9**.

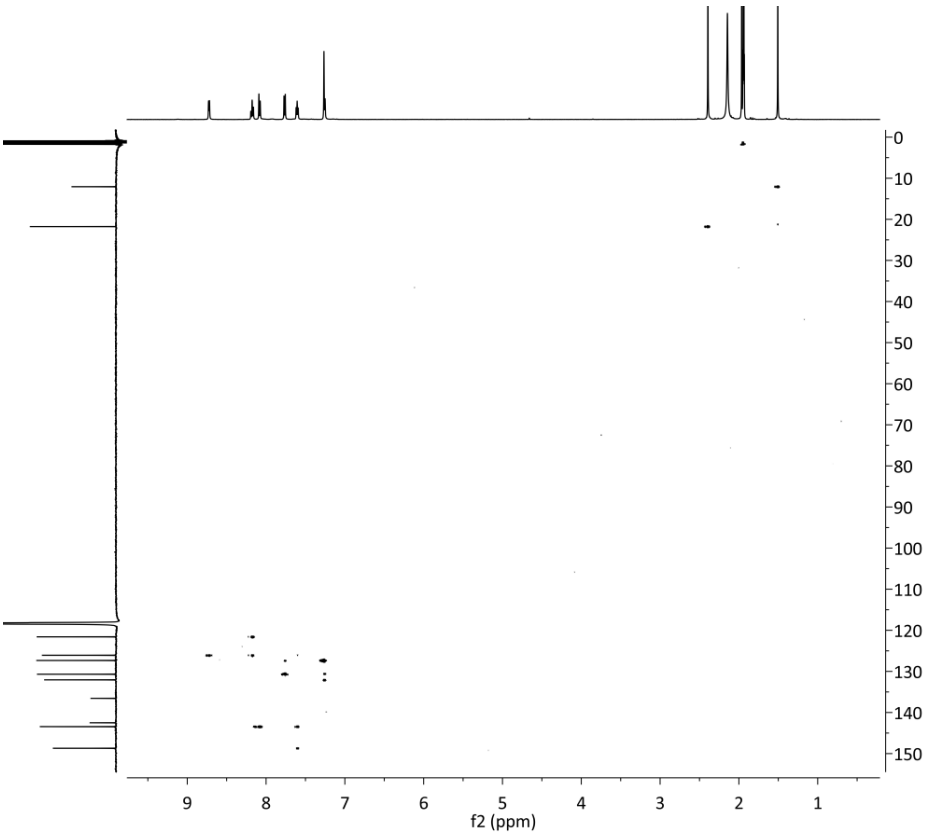


Figure S20. H2BC (500 MHz, CD_3CN) of **9**.

Crystallographic methods

Crystals of **3** were grown by the vapor diffusion technique. A small vial with a reaction mixture containing **2** dissolved in acetonitrile was placed in a larger vial containing pentane slowly affording crystals of **3**. Crystals of **9** were grown by slow diffusion of ether layered on top of a concentrated solution of **9** in acetonitrile.

The data were acquired using a Bruker D8 Venture diffractometer with the APEX2 suite, integrated with SAINT V8.32B, solved with SHELXT[11] in the OLEX2 GUI[12], and refined with SHELXL[13]. The cif files were edited with enCIFer v1.4[14], and molecular graphics were produced with Diamond v4.1.2.[15]

All metric data are contained in the respective cif files, available as ESI and from https://www.ccdc.cam.ac.uk/ (CCDC numbers 1443528 for **3;** 1443527 for **9**).

[11] G. Sheldrick, *Acta Crystallogr., Sect. A,* 2015, **71**, 3-8.
[12] O. V. Dolomanov, L. J. Bourhis, R. J Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr*. 2009, **42**, 339-341.
[13] G. Sheldrick, *Acta Crystallogr., Sect. C,* 2015, **71**, 3-8.
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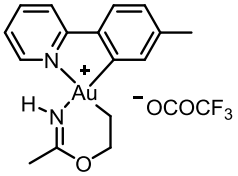
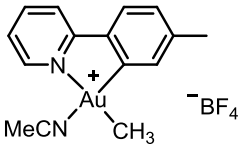
Table S1. Crystal and structure refinement data for **3** and **9**.

Compound	 **3**	 **9**
CCDC no	1443528	1443527
Identification code	msh-246-mp_sx	EAT-156-P1_b
Empirical formula	$C_{18}H_{18}AuF_3N_2O_3$	$C_{15}H_{16}AuBF_4N_2$
Formula weight	564.31	508.07
Temperature/K	100	100
Crystal system	monoclinic	monoclinic
Space group	$P11_2/n$	$P2_1/m$
a/Å	7.1906(6)	10.2527(5)
b/Å	12.6491(10)	6.6903(3)
c/Å	19.3960(16)	12.3307(6)
α/°	90	90
β/°	89.9973(16)	109.737(2)
γ/°	90	90
Volume/Å^3	1764.2(2)	796.12(7)
Z	4	4
ρ_{calc}g/cm^3	2.125	2.119
μ/mm^{-1}	8.391	9.279
F(000)	1080	960
Crystal size/mm^3	0.472 × 0.123 × 0.077	0.2 × 0.15 × 0.08
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.292 to 63.234	4.22 to 52.896
Index ranges	-10 ≤ h ≤ 10, -18 ≤ k ≤ 18, -28 ≤ l ≤ 28	-12 ≤ h ≤ 12, -8 ≤ k ≤ 8, -15 ≤ l ≤ 15
Reflections collected	28613	12713
Independent reflections	5951 [R_{int} = 0.0480, R_{sigma} = 0.0353]	1786 [R_{int} = 0.0380, R_{sigma} = 0.0222]
Data/restraints/parameters	5951/0/247	1786/0/142
Goodness-of-fit on F^2	1.05	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0187, wR_2 = 0.0415	R_1 = 0.0221, wR_2 = 0.0504
Final R indexes [all data]	R_1 = 0.0214, wR_2 = 0.0424	R_1 = 0.0229, wR_2 = 0.0507
Largest diff. peak/hole / e Å^{-3}	0.79/-1.51	1.13/-0.73

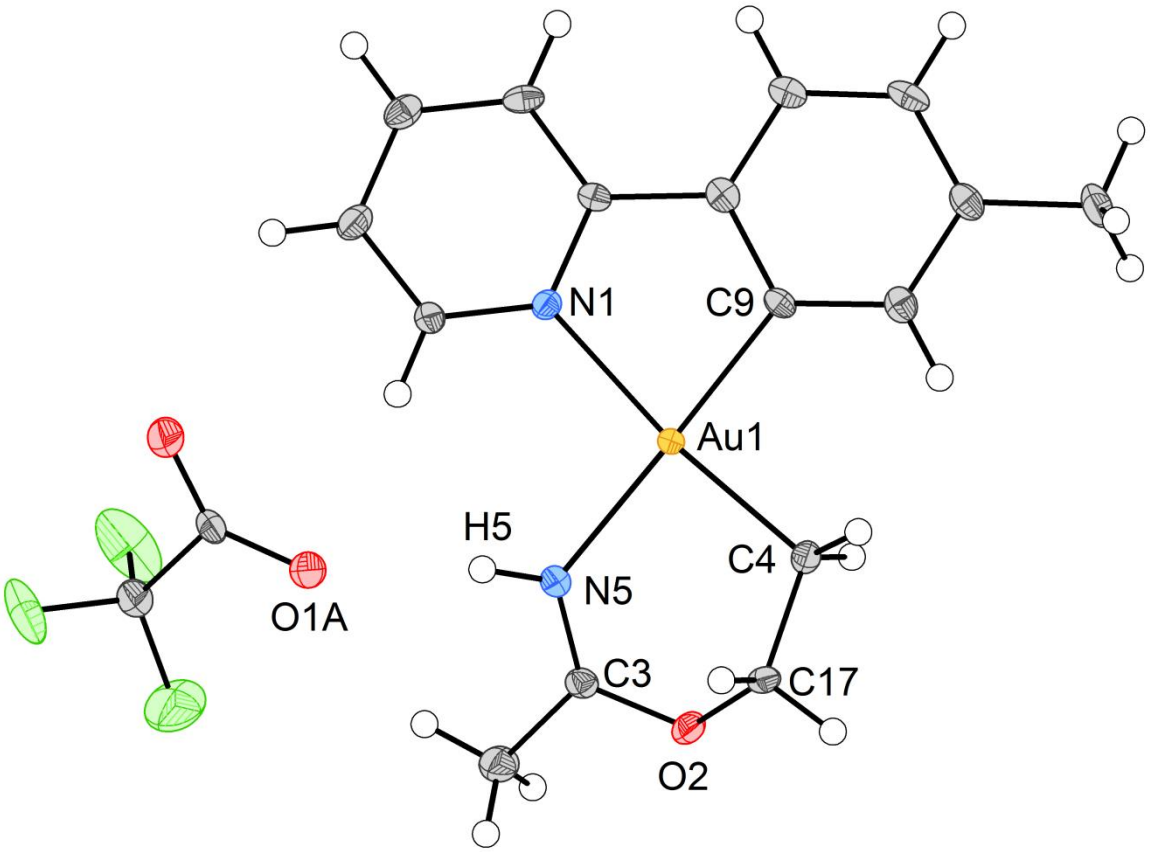


Figure S21. ORTEP plot of **3** with 50% ellipsoids. Selected bond distances and angles: Au1-C4, 2.042(3); Au1-C9, 2.019(3); Au1-N1, 2.126(2); Au1-N5, 2.092(3); C3-N5, 1.284(4); C3-O2, 1.332(3); C17-O2, 1.449(4); C4-C17, 1.510(4); O1A···N5, 2.8708(2); C4-Au1-C9, 92.39(12); C4-Au1-N5, 89.54(11); C9-Au1-N1, 80.60(10); N1-Au1-N5, 97.43(9); C4-Au1-N1, 172.99(11); C9-Au1-N5, 174.24(12); C3-O2-C17-C4, -70.8(4); Au1-C4-C17-O2, 60.2(3); Au1-N5-C3-O2, 26.5(5); C17-O2-C3-N5, 21.8(5).

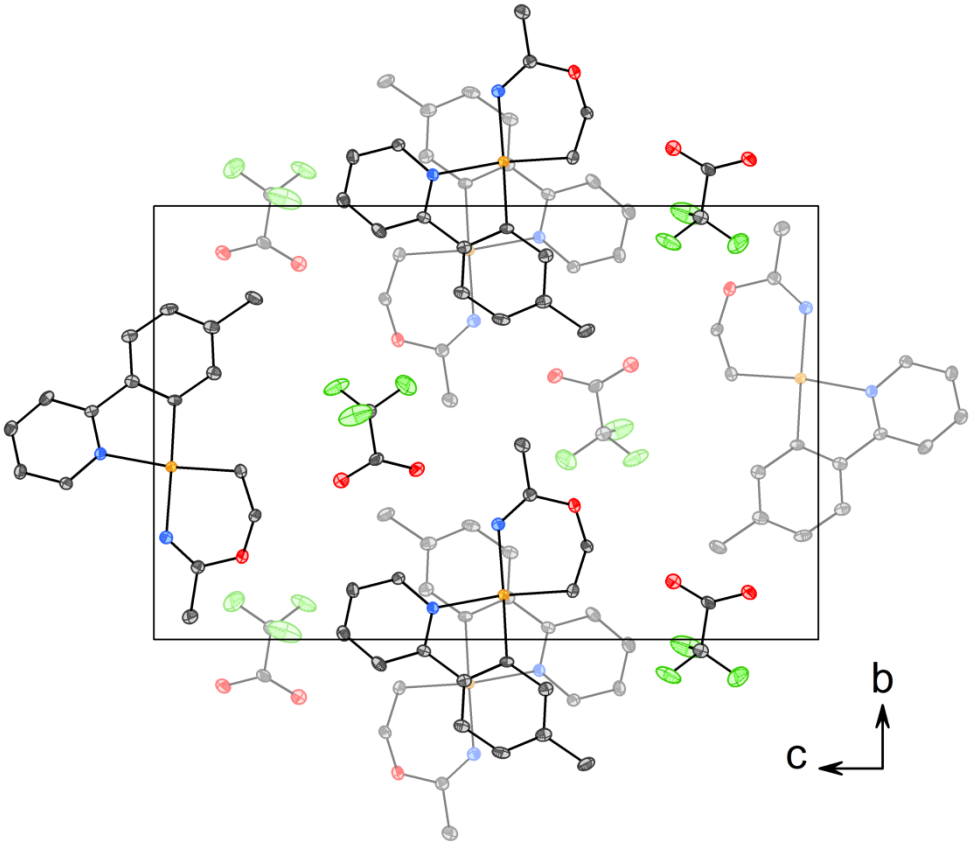


Figure S 22. Packing diagram of **1** viewed along the *a* axis showing stacking between the tpy ligands. The thermal ellipsoids are displayed at 50 % probability, and H atoms are omitted for clarity.

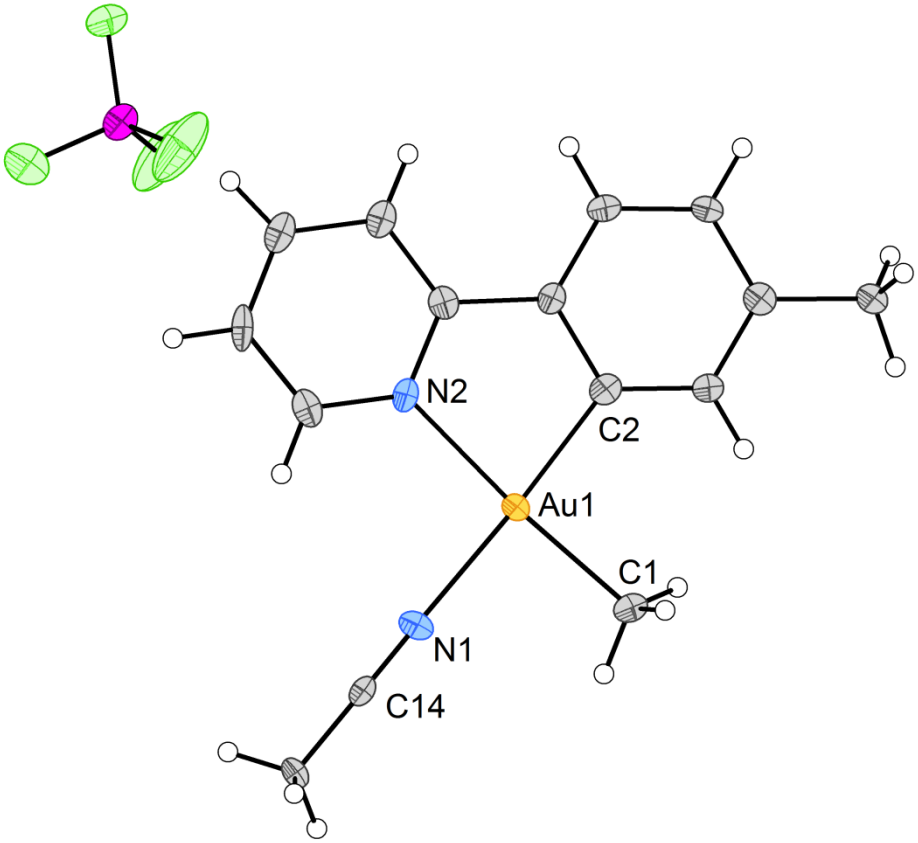


Figure S23. ORTEP plot of **9** with 50% ellipsoids. Selected bond distances and angles: Au1-C1, 2.049(6); Au1-C2, 2.002(6); Au1-N1, 2.088(5); Au1-N2, 2.113(5); C14-N1, 1.144(8); C1-Au1-C2, 93.6(2); C1-Au1-N1, 89.3(2); C2-Au1-N2, 82.2(2); N1-Au1-N2, 94.87(19); C1-Au1-N2, 175.8(2); C2-Au1-N1, 177.0 (2); Au1-N1-C14, 179.0(5).

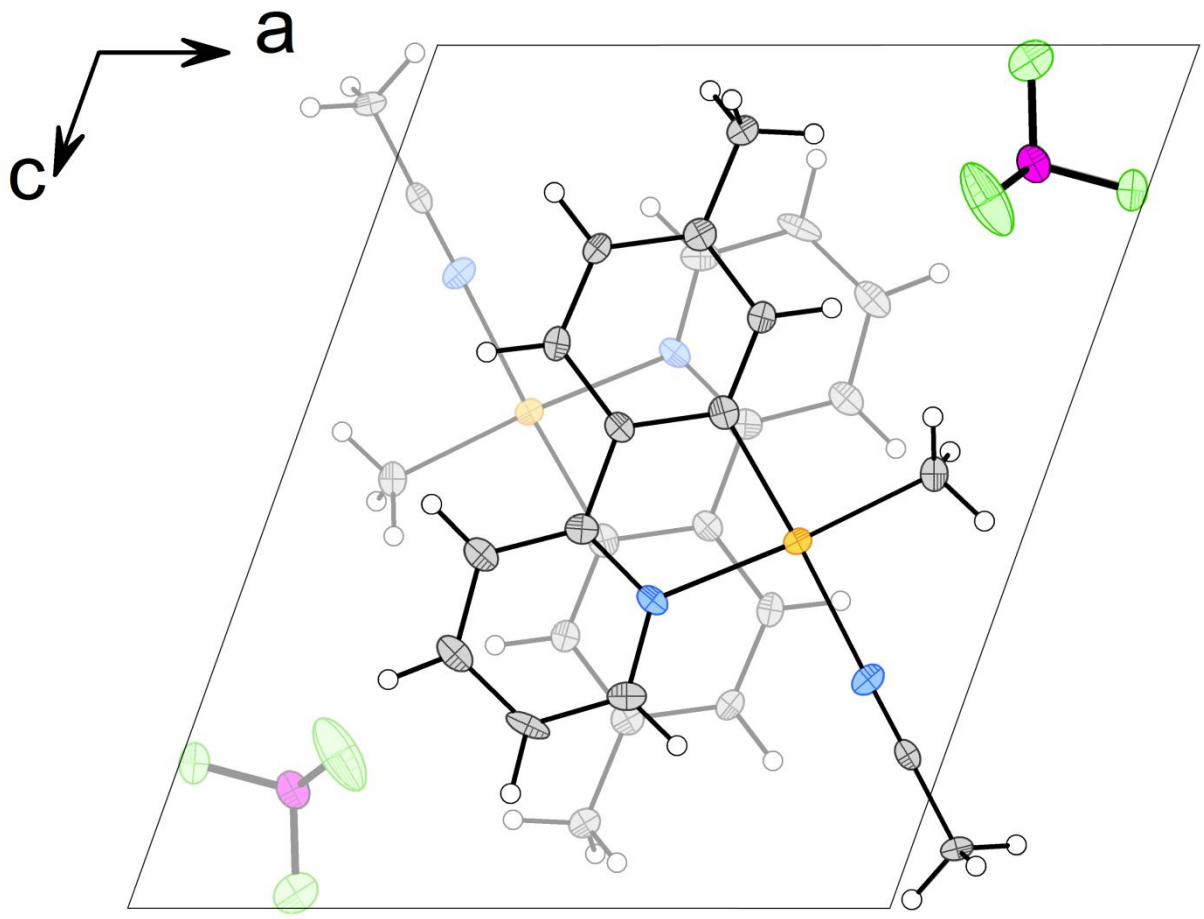


Figure S 24. Packing diagram of **9** viewed along the *b* axis showing stacking between the tpy ligands. The thermal ellipsoids are displayed at 50 % probability. All non-H atoms in **9** are confined to the mirror plane b=0.25. The structure displays parallel displaced π –π –stacking along the *b* axis, with an interplanar distance of 3.345(3) Å. This packing is rather close due to the perfect planarity of the molecule.

Computational Details

Calculations were carried out at the DFT level as implemented in the Gaussian09 software package.[16] The hybrid PBE0+GD3 functional[17,18] including Grimme's model for dispersion forces was used to optimize all geometries. This methodology was selected because previous studies have proven its solid performance in the modeling of Au(III) alkene complexes.[19] C, H, N and O were described with the all-electron triple-ζ 6-311+G** basis set,[20] whereas Au was described with the Stuttgart–Köln basis set including a small-core quasi-relativistic pseudopotential.[21] Geometries were fully optimized without any constraint. Vibrational frequencies were computed analytically to verify that the stationary points found were energy minima or transition states. All optimizations needed for the mechanism proposal were carried out in solvent (acetonitrile) using the SMD solvation model.[22] Complexes **3**, **4** and **5** were optimized in gas phase with the aim of comparing their geometries with an X-Ray crystal structure. Gibbs energies were obtained for T = 298.15 K and p = 1 atm. In the bimolecular steps, these energies were corrected for the 1M standard state (T = 298.15 K and p = 24.465 atm).

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[22] A. V. Marenich, C. J Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378-6396.

Comparison of the X-Ray geometry with the optimized 3, 4 and 5 geometries.

The fully DFT-optimized geometries of **3**, **4** and **5** were compared to the X-Ray crystal structure (Table S1). The selected bond distances, including all involved in covalent bonds to the metal center, yield the lowest RMSD value for complex **3**.

Table S 2: Bond distances (d) and root-mean-square deviations (RMSD), in Å.

d	X-Ray	DFT **3**	DFT **4**	DFT **5**
Au-C	2.042	2.040	2.038	2.037
C-C	1.509	1.504	1.517	1.508
C-X[a]	1.449	1.443	1.460	1.451
X-C	1.333	1.306	1.325	1.303
C-CH_3	1.504	1.488	1.492	1.485
C-Y[a]	1.284	1.292	1.256	1.239
Y-Au	2.093	2.118	2.143	2.166
Au-C'	2.019	2.010	1.999	1.997
Au-N	2.127	2.136	2.114	2.113
RMSD		0.015	0.022	0.032

[a]X = N and Y = O in **3**; X = O and Y = N in **4**; X = Y = O in **5**.

Optimized coordinates and energies

See **Scheme 5** for the labels used for all intermediates and TS.

1
E : -1705.0796184
G : -1704.896934

Au	-0.192386	-0.248599	-0.008542
N	-1.051644	-2.052941	-0.223527
C	-0.347201	-3.172845	-0.423614
H	0.729864	-3.069569	-0.458297
C	-0.981462	-4.388541	-0.584548
H	-0.388528	-5.280080	-0.744746
C	-2.370518	-4.428807	-0.537986
H	-2.895106	-5.369586	-0.663399
C	-3.087317	-3.261243	-0.332356
H	-4.169395	-3.272430	-0.294205
C	-2.409618	-2.059527	-0.173441
C	-2.997697	-0.749649	0.050337
C	-4.361215	-0.481425	0.149366
H	-5.086715	-1.282718	0.053657
C	-4.795804	0.818964	0.370204
H	-5.860072	1.019347	0.442850
C	-3.892912	1.874941	0.502064
C	-2.518630	1.606444	0.400478
H	-1.808828	2.420057	0.504405
C	-2.091523	0.316128	0.176311
C	-4.362005	3.274006	0.751605
H	-5.451821	3.335368	0.730178
H	-3.959952	3.961446	0.000908
H	-4.017824	3.629020	1.728860
O	0.557508	1.605833	0.295331
C	0.861031	2.301347	-0.744428
O	0.718661	2.042403	-1.914795
C	1.481319	3.651681	-0.307105
F	0.605610	4.367325	0.413525
F	2.568774	3.462175	0.451202
F	1.839894	4.386539	-1.356762
O	1.798168	-0.917625	-0.319035
C	2.534535	-1.095912	0.709218
O	2.252917	-1.030555	1.887359
C	3.984003	-1.449953	0.289796
F	4.526446	-0.469263	-0.448075
F	4.777753	-1.644926	1.342833
F	4.012680	-2.570187	-0.450162

2
E: -1783.625807
G : -1783.38686

Au	-0.779820	-0.114270	-0.287779

F	-0.806928	4.615821	-1.050769
N	-2.772605	-0.780711	-0.059852
O	3.254834	1.005124	0.566504
F	-1.525352	5.045511	0.937937
O	-1.352128	1.912494	-0.584268
F	-2.864201	4.201477	-0.527624
O	-0.781198	2.562329	1.499755
O	4.029874	-1.068092	0.107940
C	1.173587	0.417397	-0.542942
H	1.650512	-0.303995	-1.208852
H	1.147362	1.392050	-1.038227
F	5.899561	1.518083	1.038701
F	6.445070	-0.047688	-0.344062
C	-1.193834	2.740352	0.370608
C	1.886170	0.522310	0.778345
H	1.444190	1.279435	1.422863
H	1.945166	-0.425559	1.314418
C	-2.871986	-2.114459	0.131383
C	-1.592031	-2.825550	0.134089
C	-3.855890	-0.001909	-0.091904
H	-3.682214	1.056016	-0.253066
F	5.387171	1.695516	-1.053478
C	4.153869	0.119392	0.224012
C	-0.417096	-2.065962	-0.063343
C	0.814523	-2.698178	-0.073193
H	1.728729	-2.134191	-0.223124
C	0.922008	-4.083469	0.112040
C	-4.126441	-2.694136	0.300963
H	-4.217357	-3.761758	0.454378
C	5.499366	0.832355	-0.037120
C	-0.243603	-4.823167	0.304614
H	-0.179418	-5.897556	0.447158
C	-5.126536	-0.522821	0.069681
H	-5.987175	0.133958	0.038505
C	-1.486095	-4.204604	0.314918
H	-2.375234	-4.808106	0.465561
C	-5.256607	-1.892671	0.269461
H	-6.237613	-2.336831	0.399794
C	2.270220	-4.736250	0.113266
H	2.856707	-4.413743	0.980676
H	2.841662	-4.461342	-0.778703
H	2.184256	-5.824382	0.147424
C	-1.604366	4.170290	-0.065232

3

E: -940.2051276

G: -939.941861

Au	-0.542827	-0.149075	-0.062616
O	-3.665483	-1.496045	-0.040845
N	-2.537620	0.483520	0.112694

N	0.385373	1.785231	-0.046436
C	2.289117	0.366426	0.061663
C	-3.598693	-0.225974	0.282818
C	-1.256095	-2.051404	-0.210844
H	-0.582909	-2.612272	-0.860970
H	-1.257315	-2.507902	0.783152
C	3.251213	-2.269574	0.175344
C	0.459175	4.160049	-0.162544
H	-0.081550	5.095427	-0.236492
C	3.760355	-3.677916	0.204254
H	3.010136	-4.364943	0.603461
H	4.668203	-3.759603	0.807337
H	4.010157	-4.015862	-0.808438
C	1.385824	-0.715063	-0.000100
C	1.880223	-2.010690	0.064927
H	1.206749	-2.861124	0.039020
C	2.488426	2.893047	-0.014136
H	3.569321	2.845466	0.025370
C	1.846749	4.117475	-0.092924
H	2.426857	5.033881	-0.107690
C	4.130939	-1.187453	0.235034
H	5.197552	-1.367220	0.330613
C	1.735251	1.720536	0.004942
C	3.657849	0.113956	0.181038
H	4.364320	0.935111	0.240541
C	-4.865205	0.297826	0.853399
H	-4.762414	1.339905	1.153838
H	-5.143030	-0.307134	1.720764
H	-5.663247	0.203184	0.112025
C	-2.616836	-2.079075	-0.844557
H	-2.623600	-1.576556	-1.816224
H	-2.952872	-3.109262	-0.981778
C	-0.234609	2.964612	-0.139380
H	-1.315936	2.951970	-0.206442
H	-2.679575	1.440298	0.417929

3-gas

E: -940.117608

Au	2.106105	10.205169	1.304317
O	2.753987	12.243805	3.943766
N	2.324899	10.067653	3.406800
N	1.836218	8.122821	0.912085
C	1.416304	9.048813	-1.234294
C	2.381022	11.033463	4.263213
C	2.467012	12.204732	1.481692
H	2.991716	12.526832	0.581121
H	1.513870	12.736928	1.546116
C	1.186884	11.385238	-2.776826
C	1.839547	5.796521	1.420094
H	1.979461	5.012936	2.153725

C	1.085716	12.631212	-3.600654
H	0.884461	13.507273	-2.980865
H	0.295233	12.549340	-4.349638
H	2.024740	12.812281	-4.135144
C	1.676912	10.307192	-0.656792
C	1.550090	11.450555	-1.426850
H	1.720024	12.431874	-0.998260
C	1.352325	6.551816	-0.802062
H	1.104913	6.344486	-1.834746
C	1.503836	5.514638	0.099016
H	1.369086	4.488792	-0.225669
C	0.942612	10.132350	-3.339232
H	0.654595	10.060019	-4.382809
C	1.527267	7.870787	-0.381419
C	1.052564	8.980858	-2.580458
H	0.842560	8.024153	-3.045884
C	2.038938	10.896626	5.704682
H	1.676909	9.897625	5.944697
H	1.271299	11.631704	5.958775
H	2.919966	11.124237	6.309591
C	3.356307	12.502035	2.657880
H	4.295038	11.941700	2.613592
H	3.589861	13.567188	2.708640
C	1.998712	7.118858	1.779380
H	2.278822	7.386801	2.791590
H	2.024261	9.205365	3.843146

4

E: -940.222680

G: -939.95941

Au	-0.515351	-0.229829	-0.085195
N	0.226091	1.762873	-0.029873
C	2.242938	0.520411	0.039691
C	-3.515256	-0.303677	0.266057
C	-1.111137	-2.173044	-0.198823
H	-0.424594	-2.712484	-0.852343
H	-1.059373	-2.598233	0.808316
C	3.416131	-2.030468	0.207354
C	0.057430	4.127028	-0.099821
H	-0.570648	5.008810	-0.129793
C	4.037808	-3.391836	0.266018
H	3.353899	-4.123097	0.703552
H	4.962453	-3.382083	0.848521
H	4.290685	-3.740366	-0.742263
C	1.436910	-0.637540	0.021400
C	2.026477	-1.888388	0.111827
H	1.418871	-2.786859	0.114107
C	2.210262	3.061793	-0.055108
H	3.291285	3.120900	-0.057215
C	1.445113	4.216862	-0.096976

H	1.931728	5.185804	-0.128194
C	4.204794	-0.878947	0.219565
H	5.283805	-0.968963	0.300818
C	1.574867	1.823262	-0.017196
C	3.628462	0.379266	0.139865
H	4.266416	1.256493	0.166926
C	-4.694624	0.311595	0.932436
H	-4.367096	0.800407	1.853218
H	-5.469806	-0.420969	1.156941
H	-5.103336	1.082399	0.273278
C	-2.506905	-2.274513	-0.777441
H	-2.528578	-1.880920	-1.798863
H	-2.807490	-3.324279	-0.823632
C	-0.517778	2.869417	-0.068523
H	-1.592307	2.722527	-0.073803
O	-2.539924	0.435968	-0.046138
N	-3.527720	-1.596609	0.008623
H	-4.345381	-2.121518	0.286757

4-gas

E: -940.138076

Au	2.096975	10.302778	1.262959
N	1.829852	8.229625	0.949179
C	1.443922	9.070085	-1.229756
C	2.351272	10.946780	4.223150
C	2.403353	12.309294	1.449956
H	2.931448	12.664051	0.564193
H	1.429345	12.804926	1.503585
C	1.181537	11.367728	-2.832402
C	1.798192	5.944701	1.581586
H	1.900367	5.197510	2.358247
C	1.062648	12.591109	-3.687592
H	0.784978	13.467330	-3.098128
H	0.318123	12.454870	-4.474540
H	2.018784	12.810036	-4.175528
C	1.657437	10.352440	-0.686029
C	1.516771	11.476981	-1.477421
H	1.655138	12.469450	-1.064228
C	1.392173	6.583751	-0.698155
H	1.173611	6.322114	-1.725265
C	1.515501	5.596139	0.264643
H	1.391634	4.554503	-0.010663
C	0.985564	10.095164	-3.367954
H	0.721996	9.990271	-4.415208
C	1.553493	7.919240	-0.336663
C	1.111600	8.963644	-2.580486
H	0.938308	7.989860	-3.025505
C	1.929854	10.609850	5.613753
H	0.927469	10.177488	5.585716
H	1.936343	11.471430	6.281515

H	2.606725	9.846636	6.005757
C	3.256890	12.619515	2.665253
H	4.246664	12.161320	2.567374
H	3.409167	13.699628	2.742654
C	1.950497	7.284168	1.884477
H	2.172363	7.635210	2.886332
O	2.398872	10.029086	3.367014
N	2.672803	12.199750	3.935702
H	2.614499	12.877021	4.680037

5-gas

Au	-0.50573400	-0.21783500	-0.08971200
N	0.23838500	1.75894800	-0.04751100
C	2.24957000	0.51375800	0.03824800
C	-3.52185900	-0.31381900	0.27941700
C	-1.13838900	-2.15094500	-0.19665800
H	-0.48350300	-2.69731700	-0.87822400
H	-1.07543500	-2.60932700	0.79435100
C	3.39761400	-2.05240400	0.19900400
C	0.07214200	4.12431800	-0.09163300
H	-0.55254200	5.00785100	-0.12378200
C	4.00708500	-3.41836600	0.26283900
H	3.32205400	-4.14337200	0.70706500
H	4.93043800	-3.41421500	0.84542600
H	4.25609800	-3.77196900	-0.74370200
C	1.44293800	-0.64021200	0.01868200
C	2.00874100	-1.89721600	0.10696800
H	1.39184400	-2.78827400	0.11449900
C	2.22199200	3.05531900	-0.01505400
H	3.30235400	3.11272300	0.01158200
C	1.46029300	4.21112900	-0.05579700
H	1.94769100	5.17987900	-0.06004000
C	4.19473100	-0.90810600	0.20600000
H	5.27243200	-1.00833700	0.28070200
C	1.58839000	1.81520800	-0.01067000
C	3.63252300	0.35474800	0.12924200
H	4.28176600	1.22322900	0.15022800
C	-4.74947000	0.23351500	0.90991400
H	-4.50575600	1.10924900	1.50930500
H	-5.24917500	-0.52943500	1.50548100
H	-5.43164000	0.54113700	0.11003000
C	-2.53725700	-2.21932400	-0.75521500
H	-2.60748400	-1.76354800	-1.74647700
H	-2.88196900	-3.25258500	-0.82190400
C	-0.50409300	2.86874000	-0.08721800
H	-1.57827600	2.72233500	-0.11495500
O	-2.57691400	0.41619600	-0.05060200
O	-3.54862400	-1.60116200	0.08207600

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E: -1257.567175
G : -1257.349083

Au	0.076123	-0.414571	-0.010211
N	0.329629	1.630435	0.011929
C	-0.685400	2.500686	0.017073
H	-1.682342	2.079783	-0.022347
C	-0.449308	3.860714	0.067311
H	-1.287075	4.546614	0.068924
C	0.865787	4.308364	0.115803
H	1.081134	5.370379	0.158957
C	1.907268	3.393856	0.108119
H	2.937205	3.726211	0.145649
C	1.622137	2.035808	0.052444
C	2.588061	0.949916	0.022536
C	3.970216	1.132931	0.023154
H	4.381216	2.136054	0.060649
C	4.822086	0.041082	-0.023192
H	5.895482	0.201212	-0.015338
C	4.323281	-1.260251	-0.082607
C	2.933578	-1.450440	-0.081098
H	2.563166	-2.468096	-0.127868
C	2.086803	-0.362481	-0.023072
C	5.243368	-2.436655	-0.172113
H	6.180406	-2.244062	0.355760
H	5.492027	-2.645828	-1.219027
H	4.782080	-3.335501	0.243224
C	-0.133372	-2.558281	-0.579978
C	0.011782	-2.515650	0.787813
H	0.705175	-2.767353	-1.236324
H	-1.123510	-2.591977	-1.025173
H	0.973203	-2.675487	1.263948
H	-0.869293	-2.489118	1.421804
O	-2.019249	-0.102905	-0.142686
C	-2.989609	-0.843758	0.233692
O	-2.987633	-1.906174	0.816482
C	-4.341500	-0.205099	-0.182196
F	-4.442809	1.057591	0.256554
F	-4.454956	-0.175456	-1.519819
F	-5.381930	-0.884333	0.296234

7

E: -1333.544496
G: -1333.314879

Au	-0.739966	-0.033929	-0.266681
F	-0.540982	4.707505	-0.953326
N	-2.799391	-0.541348	-0.073379
O	3.349574	0.636923	0.770435
F	-1.233056	5.133982	1.044738
O	-1.128743	2.036707	-0.557092
F	-2.614041	4.379858	-0.431231

O	-0.736707	2.588045	1.595801
C	1.260173	0.334910	-0.432102
H	1.691853	-0.395689	-1.122818
H	1.335065	1.328699	-0.884640
C	-1.027458	2.822737	0.439540
C	1.966690	0.312097	0.905960
H	1.548392	1.067730	1.574223
H	1.855321	-0.664013	1.394283
C	-3.000838	-1.863515	0.114135
C	-1.780626	-2.674721	0.109013
C	-3.820742	0.316611	-0.098254
H	-3.569817	1.359097	-0.258223
C	-0.545403	-2.012677	-0.072576
C	0.625645	-2.751516	-0.098409
H	1.583500	-2.263185	-0.241945
C	0.614859	-4.144132	0.057325
C	-4.295360	-2.347463	0.287471
H	-4.466223	-3.405978	0.438468
C	-0.609680	-4.784757	0.239184
H	-0.638273	-5.863241	0.360467
C	-5.127278	-0.105359	0.068065
H	-5.935509	0.615246	0.043262
C	-1.793389	-4.060858	0.264047
H	-2.732379	-4.586209	0.403262
C	-5.361136	-1.461851	0.264926
H	-6.372544	-1.830086	0.400012
C	1.900944	-4.911683	0.035072
H	2.531326	-4.638522	0.888159
H	2.474224	-4.691597	-0.871003
H	1.721435	-5.988141	0.075873
C	-1.353864	4.281222	0.026234
H	3.748399	-0.027858	0.199721

8

E: -940.168725

G : -939.913382

Au	-0.786384	-0.077117	-0.353806
N	-2.796311	-0.763823	-0.122881
O	3.212057	1.051849	0.619793
C	1.190635	0.426159	-0.566561
H	1.681334	-0.346236	-1.163145
H	1.204700	1.361246	-1.132837
C	1.864434	0.614104	0.774736
H	1.364537	1.396423	1.351614
H	1.829970	-0.309112	1.366249
C	-2.873594	-2.093992	0.098375
C	-1.585856	-2.791014	0.109323
C	-3.896183	-0.007730	-0.161806
H	-3.752447	1.050109	-0.346857
C	-0.414385	-2.026340	-0.090729

C	0.819387	-2.654800	-0.070576
H	1.732625	-2.088459	-0.215128
C	0.934176	-4.035796	0.138901
C	-4.116001	-2.691697	0.296132
H	-4.185112	-3.756730	0.477453
C	-0.229111	-4.779118	0.328398
H	-0.160966	-5.850524	0.490011
C	-5.156015	-0.545999	0.024909
H	-6.028007	0.095161	-0.012501
C	-1.473687	-4.165841	0.315354
H	-2.361881	-4.769392	0.468877
C	-5.260717	-1.912299	0.259784
H	-6.231780	-2.370407	0.414099
C	2.285014	-4.682633	0.156062
H	2.912039	-4.258112	0.946984
H	2.809031	-4.518936	-0.791278
H	2.206663	-5.759037	0.322528
H	3.689629	0.361469	0.148420
N	-1.266842	1.955482	-0.563740
C	-1.498405	3.074287	-0.669759
C	-1.790620	4.472857	-0.805171
H	-1.822930	4.732516	-1.865945
H	-2.758128	4.686153	-0.344567
H	-1.010315	5.054537	-0.308463

11

E: -939.716239

G: -939.466593

Au	-0.556005	-0.231298	0.013316
O	-3.689408	-1.432759	0.023571
N	-2.431839	0.567453	0.135895
N	0.362912	1.707316	0.040780
C	2.300313	0.331477	0.043155
C	-3.503583	-0.087177	0.223253
C	-1.315665	-2.112882	-0.076232
H	-0.646373	-2.724765	-0.686273
H	-1.331319	-2.521817	0.940349
C	3.332186	-2.276686	0.118697
C	0.347544	4.078880	-0.002694
H	-0.221482	5.000653	-0.009685
C	3.878776	-3.672265	0.131573
H	3.150289	-4.380589	0.533927
H	4.794513	-3.737284	0.725424
H	4.127948	-3.998765	-0.885115
C	1.411001	-0.767478	0.033504
C	1.952178	-2.048638	0.074215
H	1.295526	-2.915053	0.078494
C	2.425592	2.874128	-0.018005
H	3.508049	2.864208	-0.043136
C	1.738247	4.077664	-0.030418

H	2.287507	5.012816	-0.062157
C	4.188419	-1.172816	0.128779
H	5.262942	-1.325770	0.172208
C	1.712295	1.676349	0.021331
C	3.680375	0.116849	0.092710
H	4.369865	0.954993	0.113118
C	-4.826961	0.524917	0.583768
H	-4.706399	1.583893	0.810119
H	-5.250839	0.015568	1.455244
H	-5.538091	0.406436	-0.239880
C	-2.683436	-2.135903	-0.699263
H	-2.648242	-1.748660	-1.725374
H	-3.059743	-3.163302	-0.740159
C	-0.305733	2.859453	0.031033
H	-1.387813	2.764328	0.053746

TS8-11

E: -1466.171110

G : -1465.898626

Au	-1.104162	-0.109786	-0.080236
N	-2.620014	-1.620654	-0.028109
C	0.191697	1.465471	-0.186070
H	-0.246945	2.194205	-0.871149
H	0.246746	1.907389	0.813599
C	-3.947049	0.346191	0.046072
C	-2.734768	1.068801	0.024050
C	-3.872653	-1.117872	0.008755
C	-3.986801	3.152840	0.174173
C	-5.177631	2.421930	0.178371
H	-6.128582	2.943659	0.235205
C	-4.963091	-1.985536	0.018497
H	-5.972110	-1.594168	0.045899
C	2.819067	-2.239295	0.292287
H	2.520929	-3.277962	0.442193
H	3.379050	-1.880549	1.158791
H	3.468453	-2.170077	-0.584249
C	-5.159587	1.038343	0.118637
H	-6.100199	0.497569	0.134428
C	-2.777246	2.455278	0.098559
H	-1.858209	3.032716	0.100074
C	1.613573	-1.428989	0.087934
C	1.559243	1.116988	-0.701828
H	2.161038	2.032189	-0.755401
C	-2.402226	-2.935802	-0.053453
H	-1.362509	-3.243500	-0.081607
C	-3.444782	-3.845054	-0.042232
H	-3.236445	-4.907815	-0.060874
C	-4.745141	-3.354053	-0.006716
H	-5.588976	-4.035814	0.002013
C	-4.008409	4.649412	0.243317

H	-4.580198	4.994536	1.110598
H	-4.486443	5.074238	-0.646013
H	-2.998006	5.058298	0.313217
F	7.205701	-0.310448	-1.218253
F	7.927765	0.013683	0.788445
F	7.178788	1.675862	-0.363454
O	5.418615	-0.383215	1.555023
O	4.664686	0.490709	-0.382255
C	5.539205	0.123468	0.448053
C	6.979007	0.375132	-0.081414
N	0.437195	-1.501055	-0.091208
O	2.264263	0.225319	0.163838
H	3.294398	0.294954	-0.029386
H	1.511297	0.687310	-1.708955

$Ac^{F}O^{-}$

E: -526.002908

G: -526.006242

O	1.520722	-1.133568	0.003053
C	1.045924	0.011766	0.000031
O	1.581873	1.126773	-0.003380
C	-0.519009	0.014452	0.000164
F	-1.017601	-0.625820	1.080990
F	-1.071872	1.238910	0.000730
F	-1.017215	-0.624675	-1.081633

$Ac^{F}OH$

E: -526.453018

G: -526.446089

O	-1.509299	-1.037878	-0.006387
O	-1.487809	1.217449	0.004867
F	0.999571	-0.723598	-1.047920
F	1.177905	1.186907	-0.057925
F	0.998839	-0.619798	1.111143
C	-0.945028	0.153095	-0.002710
C	0.592016	-0.000633	-0.001479
H	-2.477817	-0.937344	0.001879

MeCN

E: -132.640805

G: -132.618458

C	-1.102241	-0.546218	0.000000
N	0.051100	-0.546218	0.000000
C	-2.546584	-0.546219	0.000000
H	-2.915503	-0.063555	0.907758
H	-2.915503	-0.001409	-0.871878
H	-2.915503	-1.573692	-0.035880

Ethylene

E: -78.508293

G: -78.478906

C	-3.012604	-0.394081	0.000000
H	-2.495437	-1.350340	0.000000
H	-4.099320	-0.424833	0.000000
C	-2.348536	0.756733	0.000000
H	-2.865703	1.712992	0.000000
H	-1.261820	0.787485	0.000000

H_2O

E: -76.381036

G: -76.3772

O	-0.875293	-0.201809	0.000000
H	0.085543	-0.158009	0.000000
H	-1.154738	0.718535	0.000000