Electronic Supplementary Material (ESI) for ChemComm.

Pnictogen bonding at the service of gold catalysis: The case of a phosphinostiborane gold complex

Supporting Information

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Contents

1 Techniques and methods

All the air and moisture-sensitive experiments were carried out under a dry nitrogen atmosphere using either the glove box or standard Schlenk techniques. 4,5-Dibromo-2,7-*tert*-butyl-9,9-dimethylxanthene[1] and **4**-AuCl [2] were synthesized following literature procedures. All other chemicals were obtained from commercial suppliers and used without further purification. Solvents were dried by refluxing over Na/K (Et_2O, THF), or CaH_2 (CH_2Cl_2, $CDCl_3$). All other solvents were ACS reagent grade and used as received. Elemental analyses were performed by Atlantic Microlab (Norcross, GA).

1.1 NMR spectroscopy

NMR spectra were recorded at room temperature using a Varian Inova 500 FT NMR spectrometer, a Bruker Avance 500 NMR spectrometer, or a Bruker Ascend 400 NMR spectrometer. Chemical shifts are given in ppm. ^{1}H and ^{13}C signals were referenced to residual solvent signals.[3]

The following abbreviations are used in the compilation of NMR data provided for each compound:

s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; td, triplet of doublets; tt, triplet of triplets; dm, doublet of multiplets.

$^{m}J_{X\text{-}Y}$, coupling constant between nucleus X and Y separated by m bonds.

1.2 Single crystal X-ray diffraction measurement

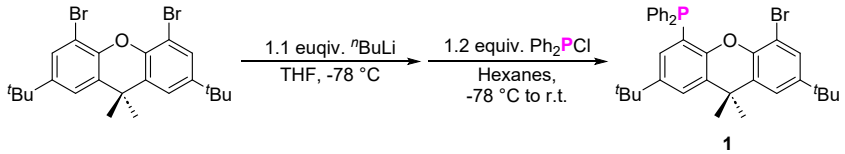
The crystallographic measurements were performed at 110 K using a Bruker D8 Quest (Mo source) or a Bruker APEX 22 diffractometer equipped with Photon III detectors. Semi-empirical absorption corrections were applied using the Bruker SADABS software package.[4] The structures were solved by direct methods with SHELXT[5] to locate all non-hydrogen atoms. Subsequent refinement using a difference map on F^2 with the SHEXL package[6] allowed for the location of the remaining non-hydrogen atoms which were refined anisotropically. H atoms were added in calculated positions using a riding model. CCDC 2299051-2299054 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk.

1.3 Quantum chemical computations

All calculations were conducted with the ORCA 5.0.2 program.[7] Gas-phase optimizations and frequency calculations were performed using r^{2}SCAN-3c composite method[8] and mixed basis sets: def2-SVP[9] for C, H, O, F, Cl and def2-TZVP[9-11] for Sb and Au. Frequency calculations were carried out to verify the nature of the local minima with no imaginary frequency being found except for the adduct of **3**-AuCl and **6**. In this case, a small negative frequency of -2.14 cm^{-1} remained and was ignored because of its low value. Single point calculations on the optimized structure were performed with PWPB95-D3(BJ) method[12] and def2-QZVPP basis set.[9, 10, 13, 14] Electrostatic potential (ESP) maps were plotted using Multiwfn software package[15, 16] and VMD software.[17, 18]

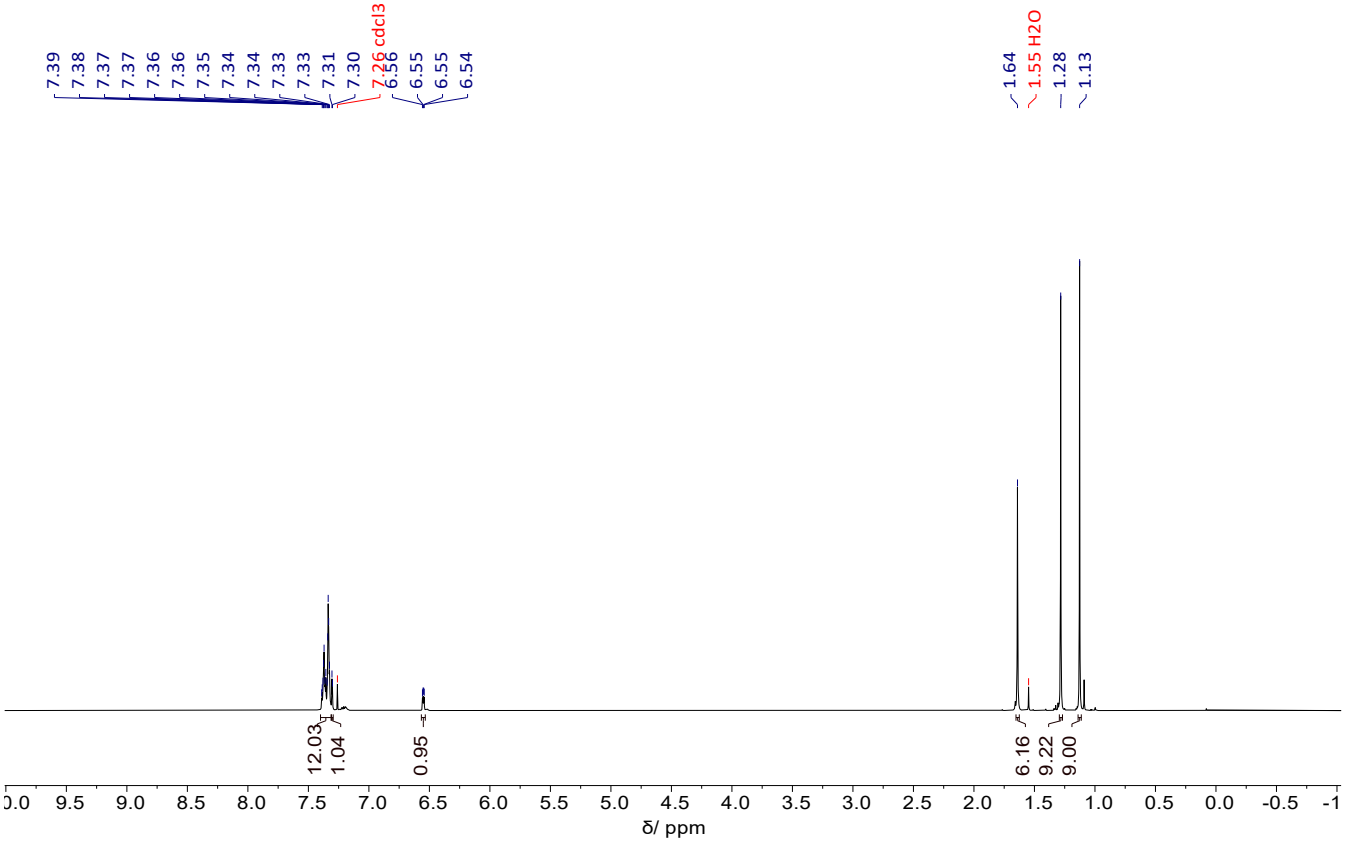
2 Experimental Procedures

2.1 Syntheses and NMR spectra

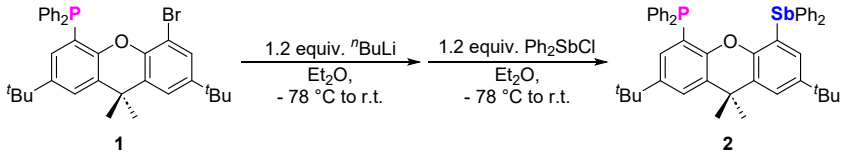


1

4-diphenylphosphino-5-bromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (1): The synthesis was adapted from a known literature procedure.[19] Under a N_2 atmosphere, a solution of ^{n}BuLi (2.5 M in hexanes, 3.3 mL, 8.25 mmol) was added dropwise to a solution of 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (3.60 g, 7.50 mmol) in anhydrous THF (80 mL) cooled at -78 °C. The resulting mixture was stirred at -78 °C for 2 h. To this mixture was added dropwise a solution of Ph_2PCl (1.67 mL, 1.99 g, 9.00 mmol) in anhydrous hexanes (10 mL). The afforded mixture was slowly warmed up to room temperature and kept at room temperature overnight. The resulting suspension was quenched with H_2O (100 mL). The resulting mixture was extracted with CH_2Cl_2 (100 mL × 3). The organic fractions were combined, dried over anhydrous $MgSO_4$, filtered, and brought to dryness under reduced pressure to afford a light yellow oil as the crude product. This oil was triturated with a mixture of CH_2Cl_2/MeOH (5 mL/25 mL), affording **1** as a colorless powder (2.34g). This crude product was used in the next step without further purification.



^{1}H NMR ($CDCl_3$, 500.1 MHz): δ 7.39-7.31 (m, 12H, Xan-*H* & Ph-*H*), 7.30 (d, $^4J_{H\text{-}H}$ = 2.2 Hz, 1H, Xan-*H*), 6.55 (dd, $^3J_{P\text{-}H}$ = 4.8 Hz, $^4J_{H\text{-}H}$ = 2.2 Hz, 2H, Xan-3-*H*), 1.64 (s, 6H, C(CH_3)$_2$), 1.28 (s, 9H, C(CH_3)$_3$), 1.13 (s, 9H, C(CH_3)$_3$).



4-diphenylphosphino-5-diphenylstibino-2,7-di-*tert*-butyl-9,9-dimethylxanthene (2): Under a N_2 atmosphere, a solution of ^{n}BuLi (2.5 M in hexanes, 1.9 mL, 4.75 mmol) was added dropwise to a solution of **1** in anhydrous Et_2O (50 mL) cooled at -78 °C. The resulting light yellow solution was stirred at -78 °C for 30 min, and then warmed up to room temperature and kept at room temperature for 1h. The resulting solution was cooled to -78 °C and treated with Ph_2SbCl (1.50 g, 4.82 mmol) suspended in anhydrous Et_2O (10 mL). The resulting white suspension was slowly warmed to room temperature and kept at room temperature overnight. The reaction mixture was brought to dryness under reduced pressure. The residue was extracted with CH_2Cl_2 (100 mL) and filtered through a pad of celite. The filtrate was brought to dryness under reduced pressure to afford a sticky colorless solid as the crude product. The crude solid was triturated with pentane (20 mL), affording compound **2** as a colorless powder (2.12 g, 69%). Single crystals suitable for X-ray diffraction were grown by slow evaporation of a CH_2Cl_2 solution of **2**.

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ample No. 2

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rofessor/Supervisor: Francois Gabbai
O# / CC# AB0856762

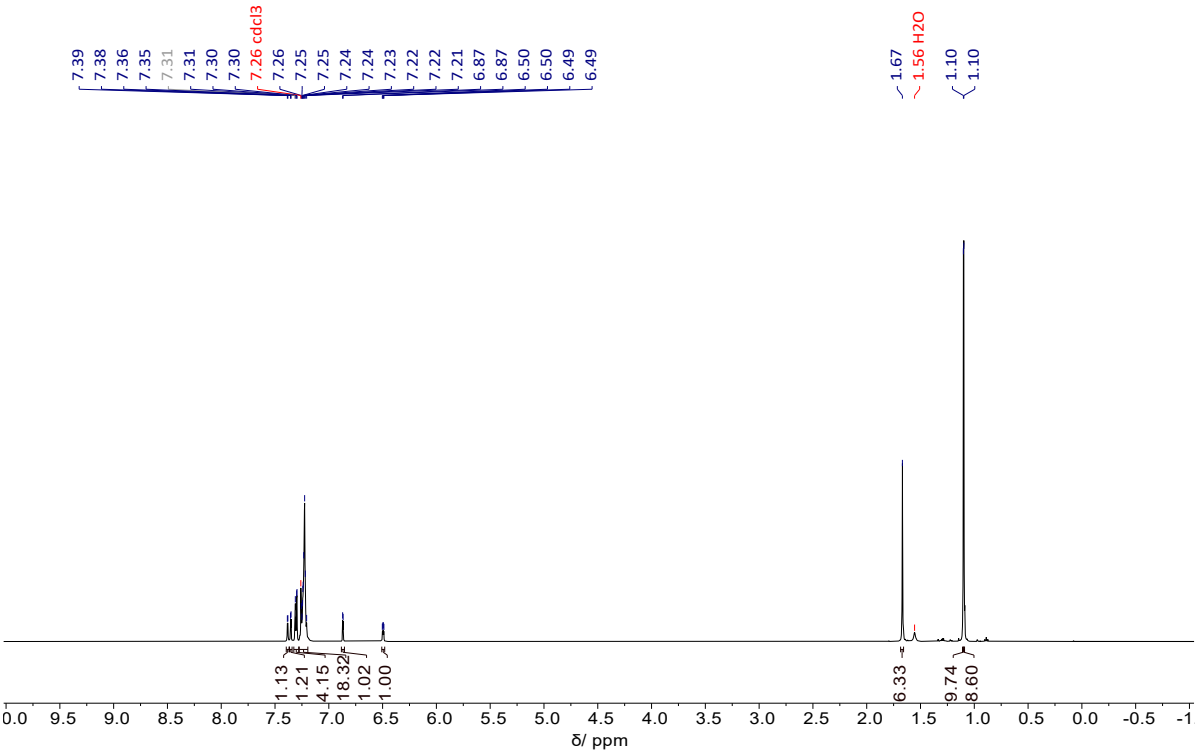
Name Benyu Zhou Date 10/04/2023
Phone (281) 935-6107

Element	Theory	Found	
C	72.22	72.31	
H	6.18	6.27	

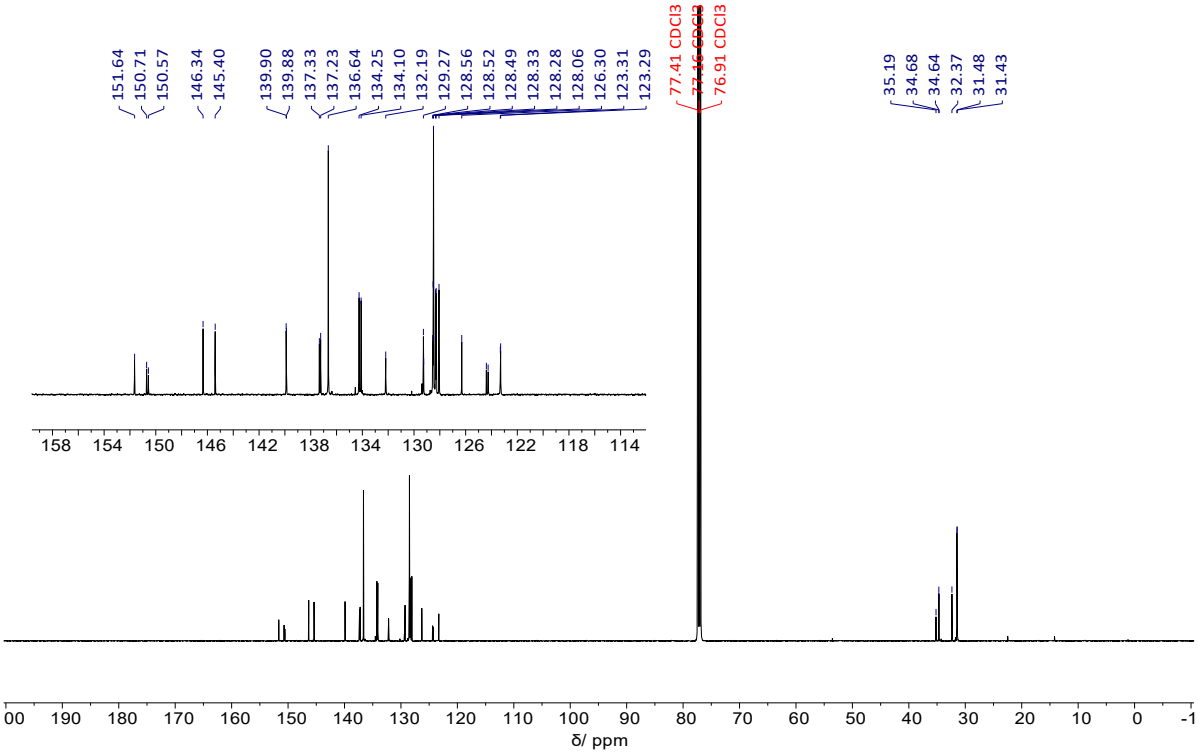
Single ☒ Duplicate ☐
Elements Present: C H O P Sb
Analyze for: C H
Hygroscopic ☐ Explosive ☐
M.P. _____ B.P. _____
To be dried: Yes ☒ No ☐
Temp. _____ Vac. _____ Time _____
Rush Service ☐ Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.
Include Email Address or FAX # Below
benyuzhou1995@tamu.edu

Date Received OCT 16 2023 Date Completed OCT 17 2023
Remarks:

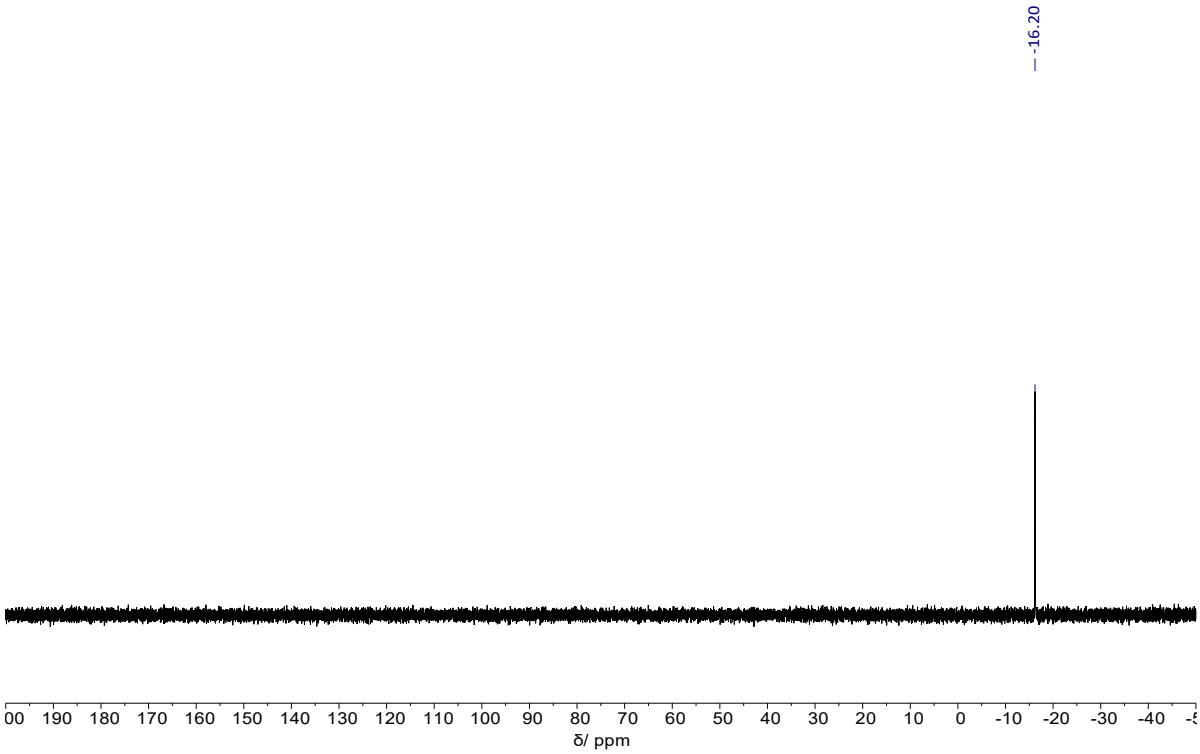
Elemental Analysis: Calculated for $C_{47}H_{48}OPSb$: C 72.22, H, 6.19; Found: C 72.31, H 6.27



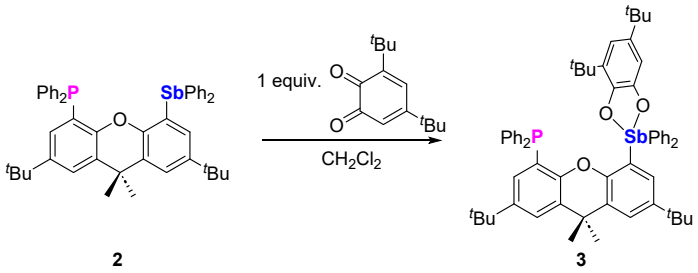
^{1}H NMR ($CDCl_3$, 500.1 MHz): δ 7.38 (d, $^{4}J_{H\text{-}H}$ = 2.4 Hz, 1H, Xan-*H*), 7.35 (d, $^{4}J_{H\text{-}H}$ = 2.4 Hz, 1H, Xan-*H*), 7.32-7.28 (m, 4H, Ph-*H*), 7.27-7.20 (partially overlapping with the $CHCl_3$ solvent peak, m, 16H, Ph-*H*), 6.87 (d, $^{4}J_{H\text{-}H}$ = 2.2 Hz, 1H, Xan-1-*H*), 6.49 (dd, $^{3}J_{P\text{-}H}$ = 4.8 Hz, $^{4}J_{H\text{-}H}$ = 2.2 Hz, 1H, Xan-3-*H*), 1.67 (s, 6H, $C(CH_3)_2$), 1.10 (s, 9H, $C(CH_3)_3$), 1.10 (s, 9H, $C(CH_3)_3$).



^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 151.6 (s), 150.7 (s), 150.6 (s), 146.3 (s), 145.4 (s), 139.9 (s), 139.9 (s), 137.3 (s), 137.2 (s), 136.6 (s), 134.2 (s), 134.1 (s), 132.2 (s), 129.3 (s), 128.5 (s), 128.5 (s), 128.3 (s), 128.3 (s), 128.28 (s), 128.1 (s), 126.3(s), 123.3 (s), 123.2 (s), 35.2 (s), 34.7 (s), 34.6 (s), 32.4 (s), 31.5 (s), 31.4 (s).



$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202.1 MHz): δ -16.20 (s).



Compound 3: A solution of 3,5-di-tert-butyl-o-benzoquinone (56.4 mg, 0.256 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of **2** (200 mg, 0.256 mmol) in CH_2Cl_2 (5 mL). The resulting yellow solution was stirred for 30 min. The reaction solution was brought to dryness under reduced pressure. The residue was triturated with pentane (10 mL) to afford compound **3** as a yellow powder (213 mg, 83%). Single crystals suitable for X-ray diffraction were grown by slow evaporation of a $CHCl_3$/MeOH solution of **3**.

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Sample No. 3

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Professor/Supervisor: Francois Gabbai
Name Benyu Zhou Date 10/04/2023
PO# / CC# AB08545O5
Phone (281) 935-6107

Element	Theory	Found	
C	73.11	72.86	
H	6.84	6.92	

Single ☒ Duplicate ☐
Elements Present: C H O P Sb
Analyze for: C H
Hygroscopic ☐ Explosive ☐
M.P. _____ B.P. _____
To be dried: Yes ☒ No ☐
Temp. _____ Vac. _____ Time _____
Rush Service ☐ Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.
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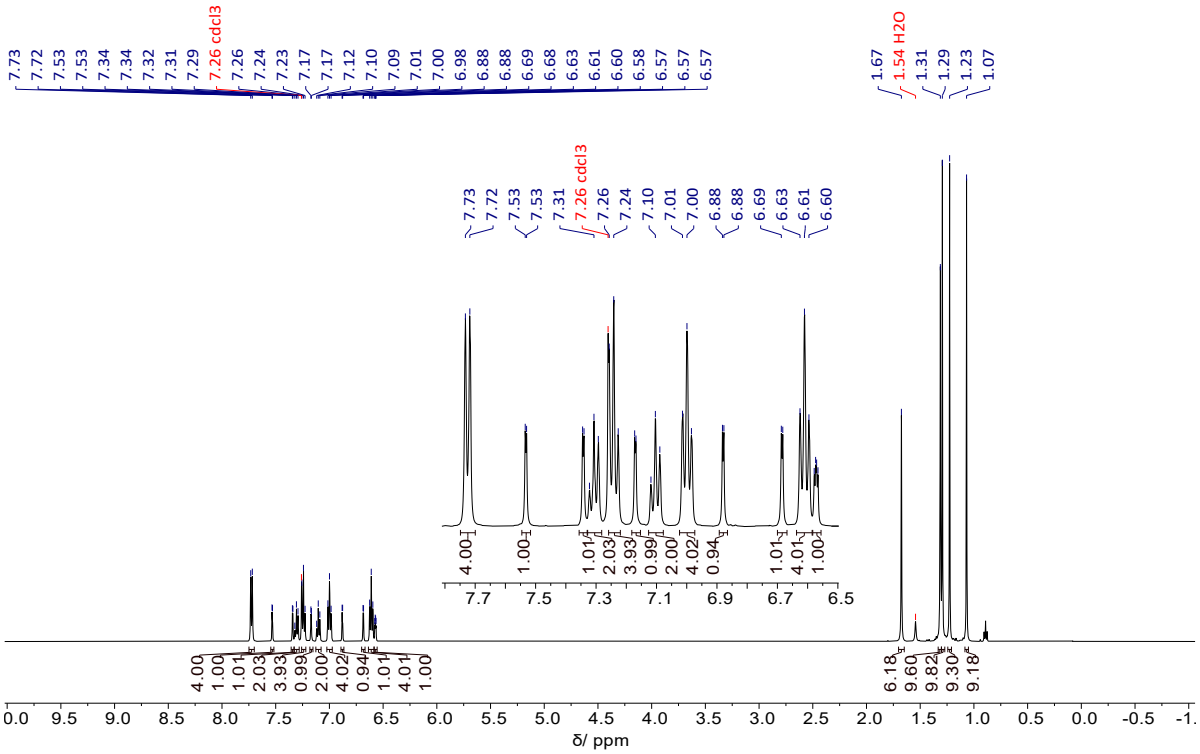
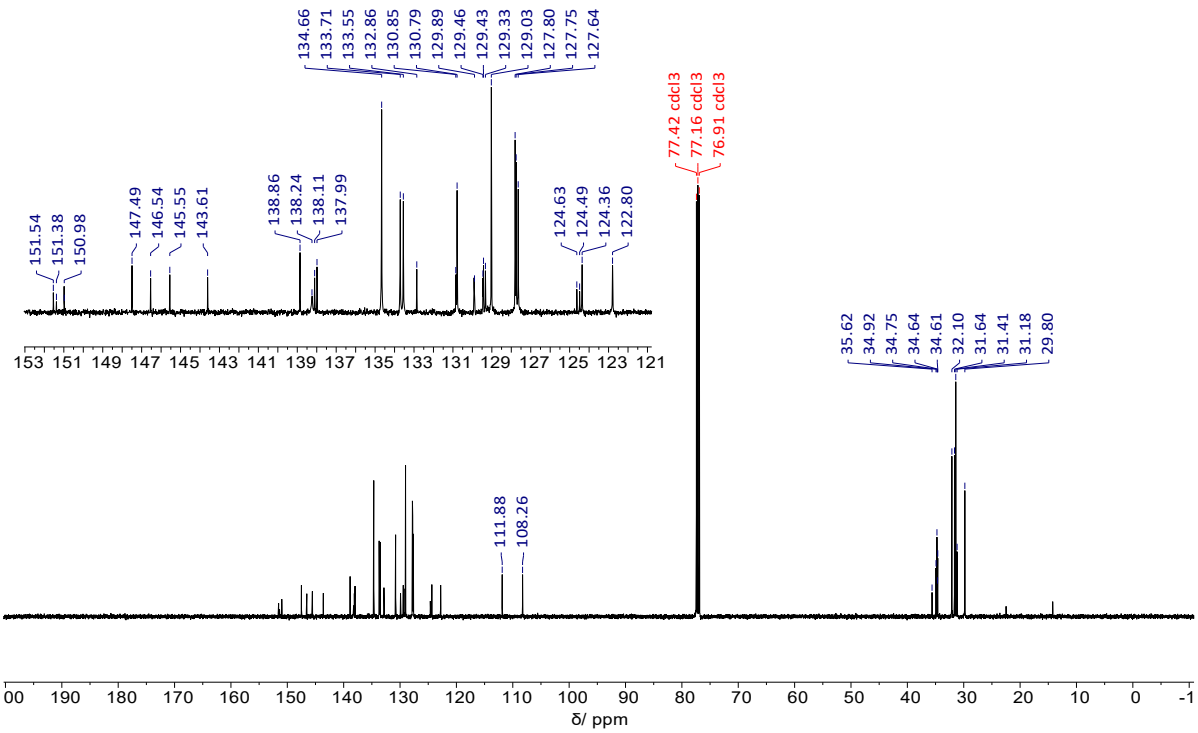
benyuzhou1995@tamu.edu

Date Received OCT 0 9 2023 Date Completed OCT 1 0 2023
Remarks:

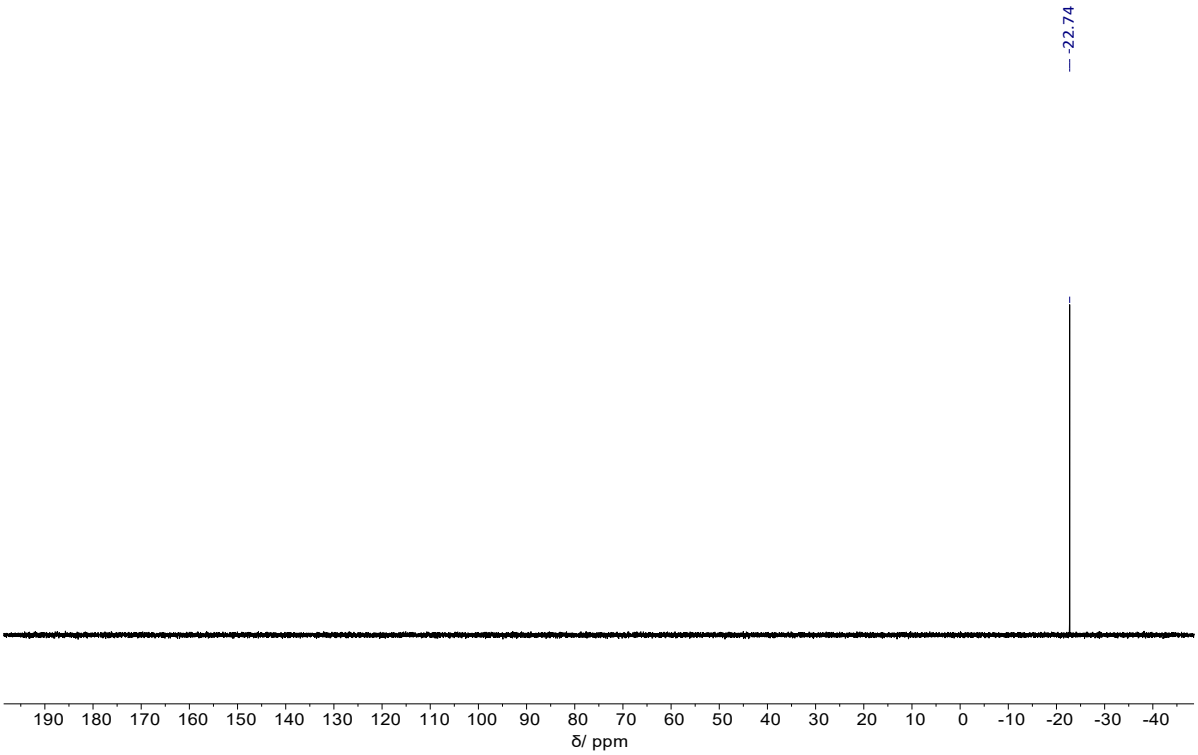
Elemental Analysis: Calculated for $C_{61}H_{68}O_3PSb$: C 73.12, H, 6.84; Found: C 72.86, H 6.92



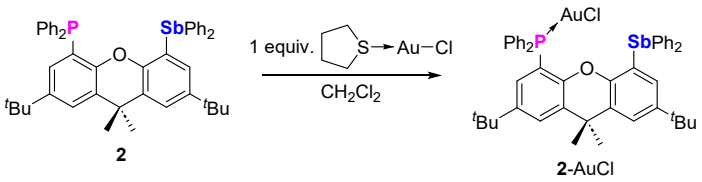
^{1}H NMR ($CDCl_3$, 500.1 MHz): δ 7.72 (d, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 4H, Ph-*H*), 7.53 (d, $^{4}J_{H\text{-}H}$ = 2.3 Hz, 1H, Xanthene-*H* or Catecholate-*H*), 7.34 (d, $^{4}J_{H\text{-}H}$ = 2.3 Hz, 1H, Xanthene-*H* or Catecholate-*H*), 7.31 (t, $^{3}J_{H\text{-}H}$ = 7.4 Hz, 2H, Ph-4-*H*), 7.24 (t, $^{3}J_{H\text{-}H}$ = 7.4 Hz, 4H, Ph-3,5-*H*), 7.17 (d, $^{4}J_{H\text{-}H}$ = 2.2 Hz, 1H, Xanthene-*H*), 7.10 (t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 2H, Ph-4-*H*), 7.00 (t, $^{3}J_{H\text{-}H}$ = 7.4 Hz, 4H, Ph-3,5-*H*), 6.88 (d, $^{4}J_{H\text{-}H}$ = 2.4 Hz, 1H, Xanthene-*H*), 6.68 (d, $^{4}J_{H\text{-}H}$ = 2.4 Hz, 1H, Xanthene-*H*), 6.61 (t, $^{3}J_{H\text{-}H}$ = 7.4 Hz, 4H, Ph-3,5-*H*), 6.57 (dd, $^{4}J_{P\text{-}H}$ = 4.0 Hz, $^{4}J_{H\text{-}H}$ = 2.3 Hz, 4H, Ph-3,5-*H*), 1.67 (s, 6H, $C(CH_3)_2$), 1.31 (s, 9H, $C(CH_3)_3$), 1.29 (s, 9H, $C(CH_3)_3$), 1.23 (s, 9H, $C(CH_3)_3$), 1.07 (s, 9H, $C(CH_3)_3$).



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 151.5 (s), 151.4 (s), 151.0 (s), 147.5 (s), 146.5 (s), 145.6 (s), 143.6 (s), 138.9 (s), 138.2 (s), 138.1 (s), 138.0 (s), 134.7 (s), 133.7 (s), 133.6 (s), 132.9 (s), 130.9 (s), 130.8 (s), 129.9 (s), 129.5 (s), 129.4 (s), 127.8 (s), 127.8 (s), 127.6 (s), 124.6 (s), 124.5 (s), 124.4 (s), 122.8 (s), 111.9 (s), 108.3 (s), 35.6 (s), 34.9 (s), 34.8 (s), 34.7 (s), 32.6 (s), 32.1 (s), 31.6 (s), 31.4 (s), 31.2 (s), 29.8 (s).



$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202.4 MHz): δ -22.74 (s)



Compound 2-AuCl: Compound **2** (400 mg, 0.512 mmol) and chloro(tetrahydrothiophene)gold (I) (164 mg, 0.512 mmol) were combined in CH_2Cl_2 (10 mL). The resulting solution was stirred in the absence of light for 30 min, and then filtered through a celite plug. The colorless filtrate was brought to dryness to afford a colorless solid as the crude product. This solid was redissolved in $CHCl_3$ (5 mL) and precipitated with MeOH (20 mL) to obtain a colorless solid. This solid was further washed with Et_2O to afford compound **2**-AuCl as a colorless powder (391 mg, 75%). Single crystals suitable for X-ray diffraction were grown by slow vapor diffusion of Et_2O into a $CHCl_3$ solution of **2**-AuCl.

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Professor/Supervisor: Francois Gabbai
PO# / CC# AB0856762

Name Benyu Zhou Date 10/04/2023
Phone (281) 935-6107

Element	Theory	Found	
C	55.67	55.93	
H	4.77	4.87	

Single ☒ Duplicate ☐

Elements Present: C H O P Cl Sb Zu

Analyze for: C H

Hygroscopic ☐ Explosive ☐
M.P. _____ B.P. _____

To be dried: Yes ☒ No ☐
Temp. _____ Vac. _____ Time _____

Rush Service ☐ Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.

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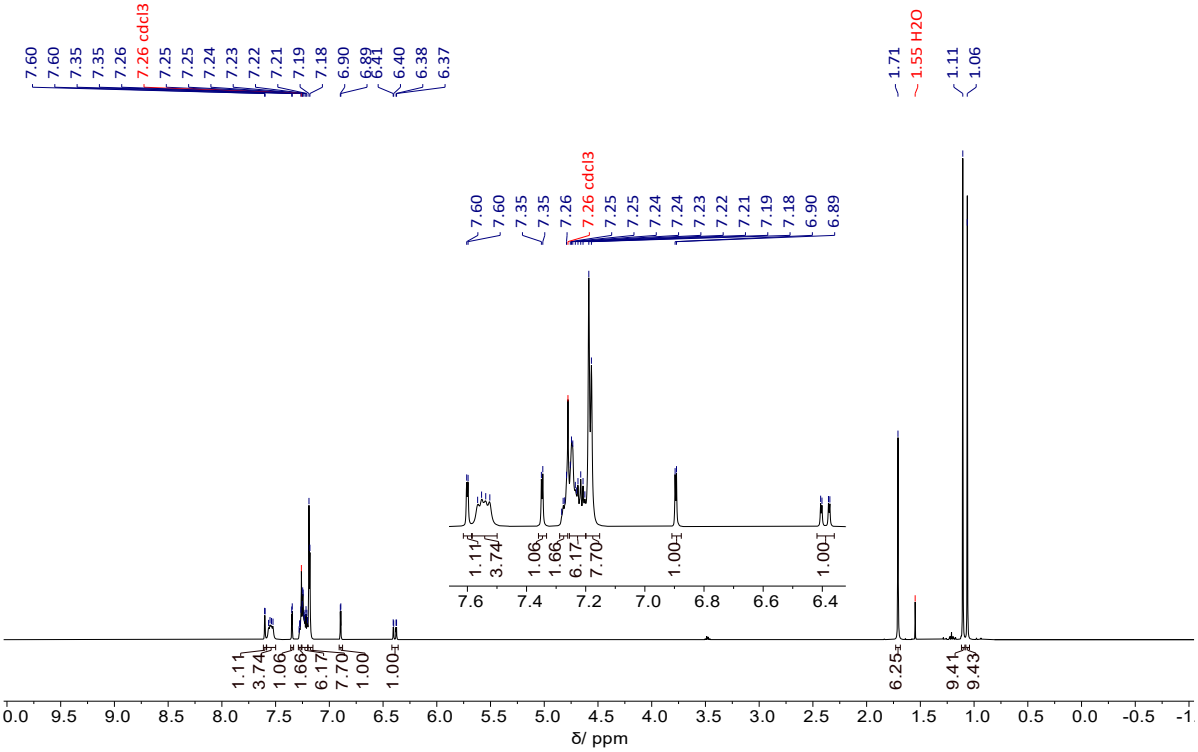
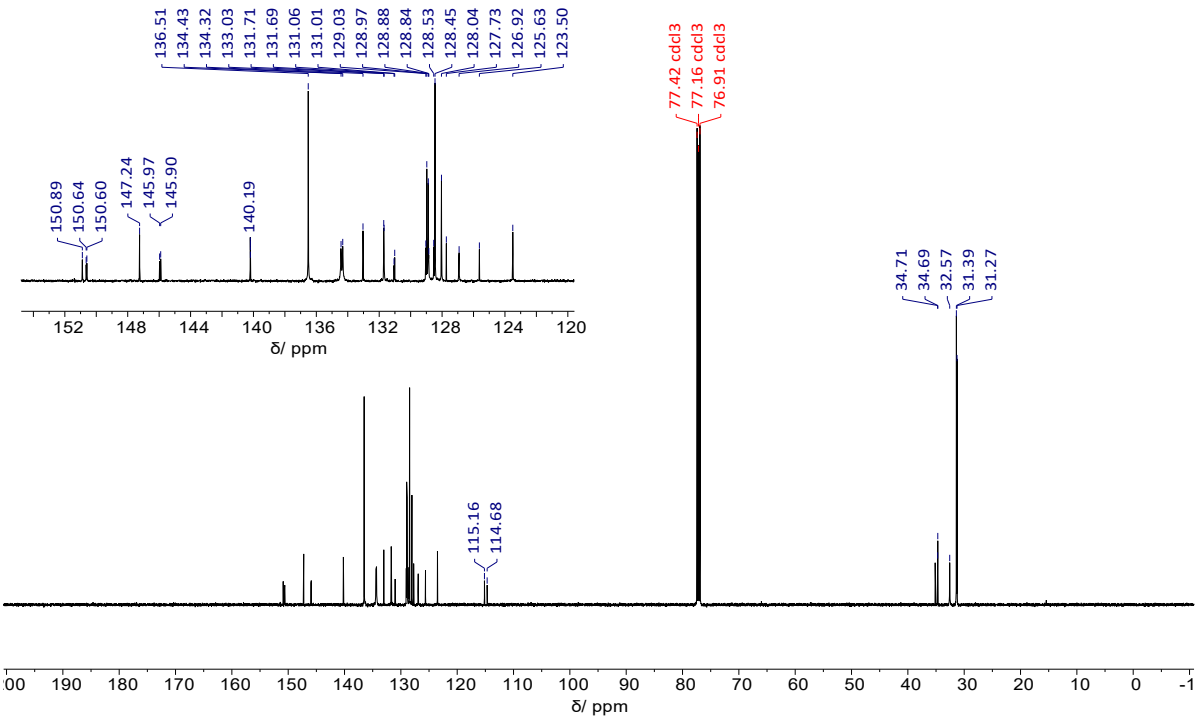
Date Received OCT 16 2023 Date Completed OCT 17 2023

Remarks:

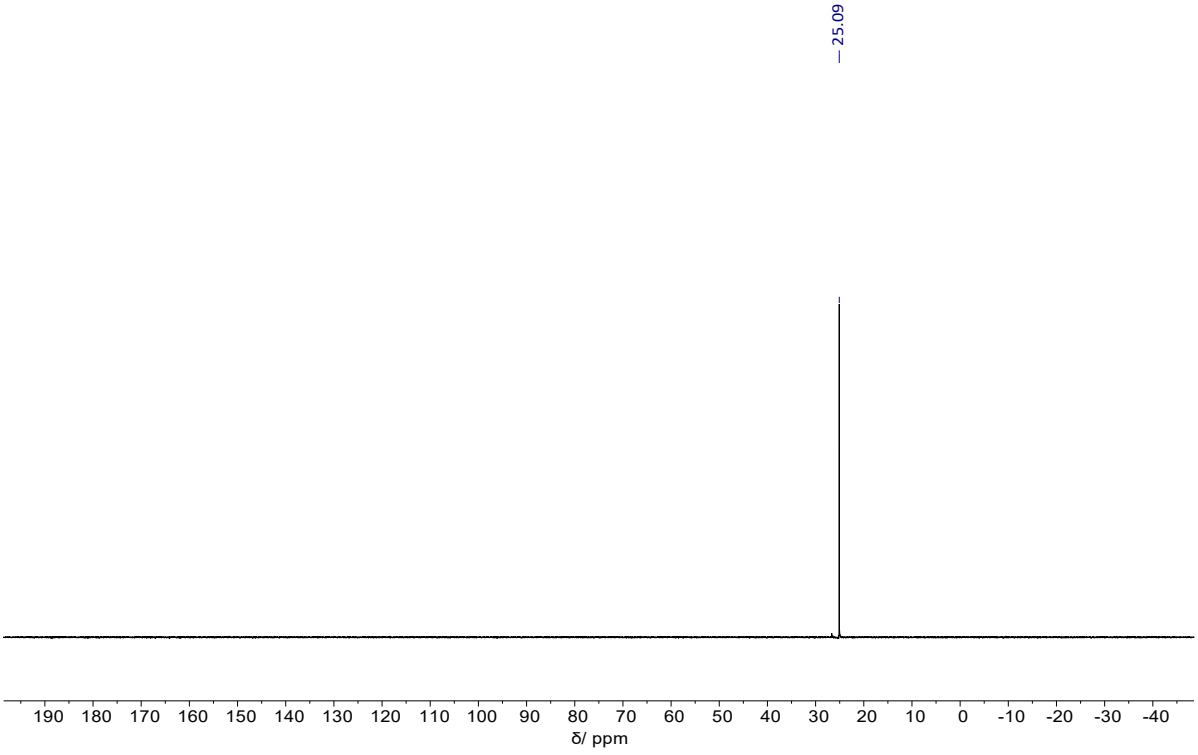
Elemental Analysis: Calculated for $C_{47}H_{48}OPClSbAu$: C 55.67, H, 4.77; Found: C 55.93, H 4.87.



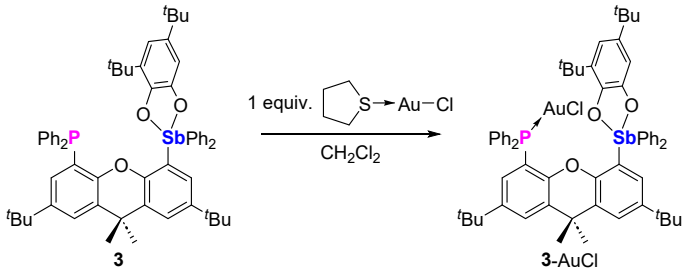
^{1}H NMR ($CDCl_3$, 500.1 MHz): δ 7.60 (d, $^{4}J_{H\text{-}H}$ = 2.3 Hz, 1H, Xan-*H*), 7.58-7.50 (m, 4H, Ph-*H*), 7.35 (d, $^{4}J_{H\text{-}H}$ = 2.3 Hz, 1H, Xan-*H*), 7.29-7.20 (m, 8H, Ph-*H*), 7.20-7.16 (m, 8H, Ph-*H*), 6.90 (d, $^{4}J_{H\text{-}H}$ = 2.4 Hz, 1H, Xan-1-*H*), 6.39 (dd, $^{3}J_{H\text{-}H}$ = 13.3 Hz, $^{4}J_{H\text{-}H}$ = 2.4 Hz, 1H, Xan-3-*H*), 1.71 (s, 6H, $C(CH_3)_2$), 1.11 (s, 9H, $C(CH_3)_3$), 1.06 (s, 9H, $C(CH_3)_3$).



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 150.9 (s), 150.64 (s), 150.60 (s), 147.2 (s), 146.0 (s), 145.9 (s), 140.2 (s), 136.5 (s), 134.4 (s), 134.3 (s), 133.0 (s), 131.7 (s), 131.7 (s), 131.1 (s), 131.0 (s), 129.0 (s), 129.0 (s), 128.9 (s), 128.8 (s), 128.5 (s), 128.4 (s), 128.0 (s), 127.7 (s), 126.9 (s), 125.6 (s), 123.5 (s), 34.7 (s), 34.7 (s), 32.6 (s), 31.4 (s), 31.3 (s).



$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202.4 MHz): δ 25.09 (s)



Compound 3-AuCl: Compound **3** (50 mg, 0.0500 mmol) and chloro(tetrahydrothiophene)gold (I) (16.0 mg, 0.0500 mmol) were combined in CH_2Cl_2 (5 mL). The resulting solution was stirred in the absence of light for 5 min, and then the solution was brought to dryness to afford a yellow solid as crude product. This solid was washed with Pentane (10 mL) to afford compound **3**-AuCl as a yellow powder (59.1 mg, 96%). Single crystals suitable for X-ray diffraction were grown by slow vapor diffusion of Et_2O into a $CHCl_3$ solution of **3**-AuCl.

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Sample No. 3-AuCl

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Name Benyu Zhou Date 10/04/2023
Phone (281) 935-6107

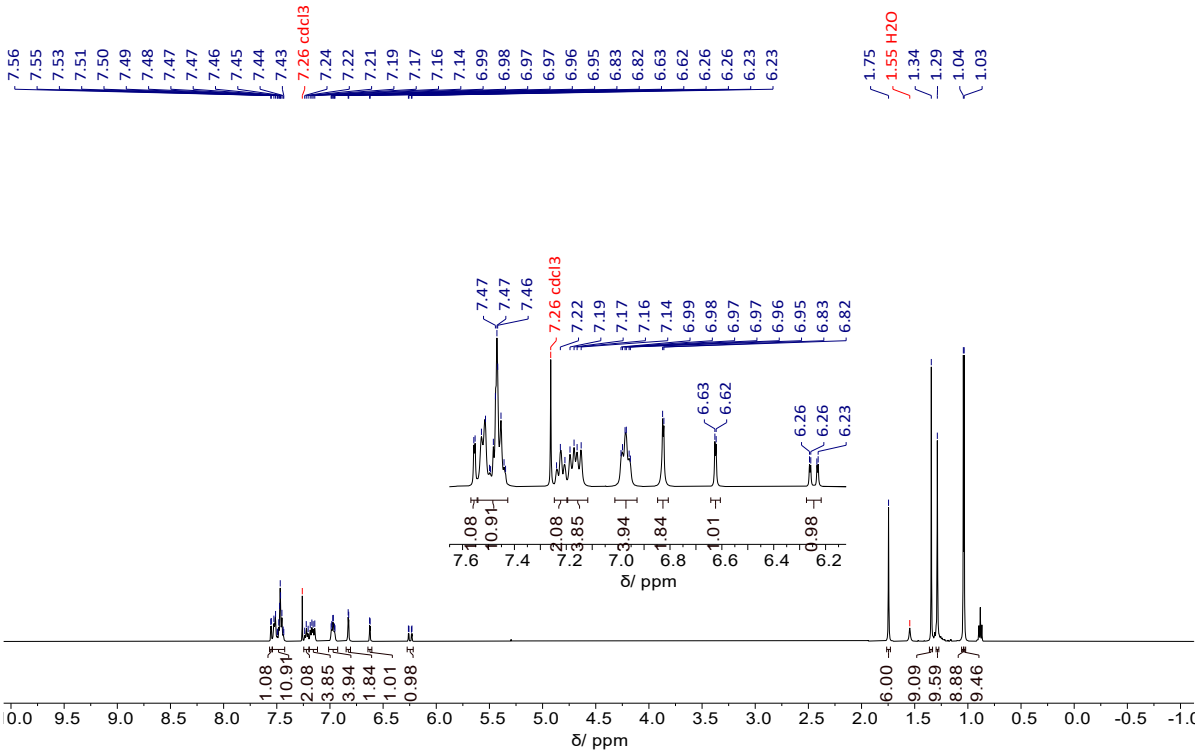
Professor/Supervisor: Francois Gabbai
PO# / CC# AB0854505

Element	Theory	Found	
C	59.36	59.35	
H	5.55	5.51	

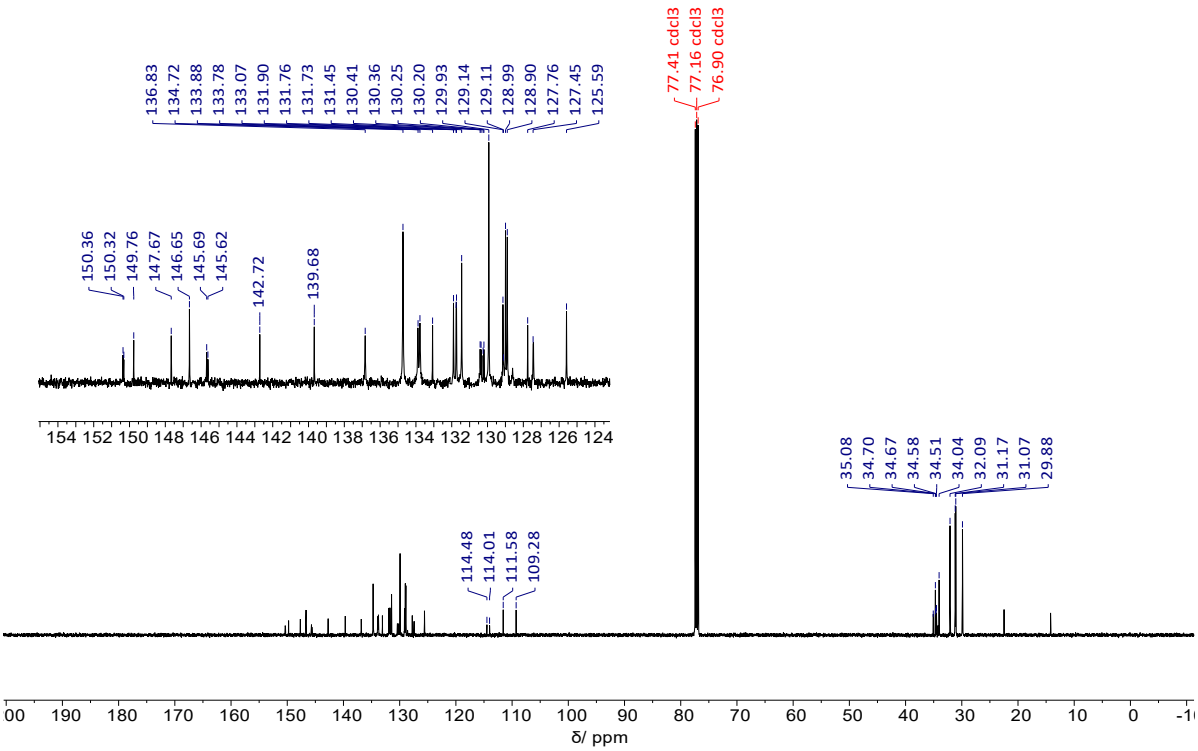
Single ☒ Duplicate ☐
Elements Present: C H O P Cl Sb Zu
Analyze for: C H
Hygroscopic ☐ Explosive ☐
M.P. B.P.
To be dried: Yes ☒ No ☐
Temp. Vac. Time
Rush Service ☐ Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.
Include Email Address or FAX # Below
benyuzhou1995@tamu.edu

Date Received OCT 0 9 2023 Date Completed OCT 1 0 2023
Remarks:

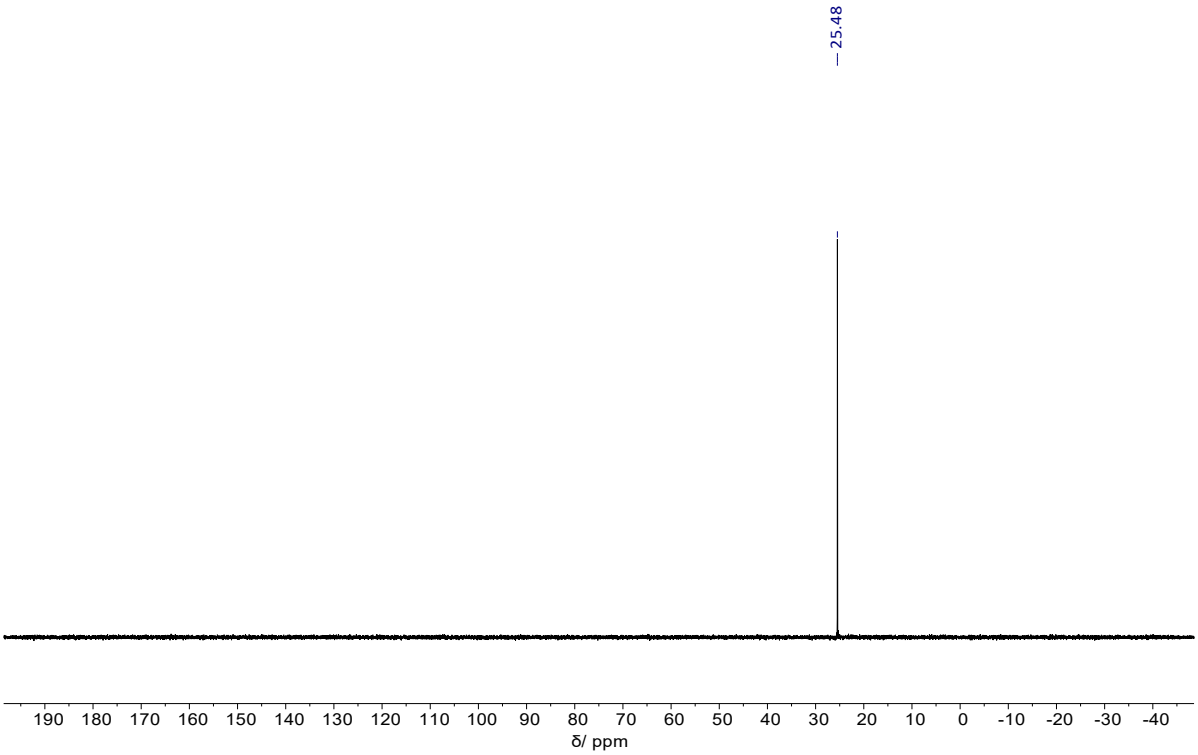
Elemental Analysis: Calculated for $C_{61}H_{68}O_3PClSbAu$: C 59.33, H, 5.55; Found: C 59.35, H 5.51.



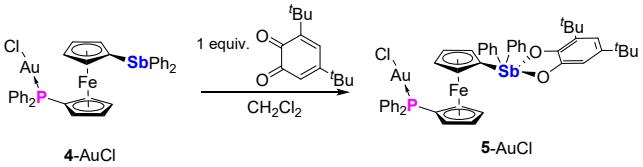
^{1}H NMR ($CDCl_3$, 500.1 MHz): δ 7.55 (d, $^{4}J_{H\text{-}H}$ = 2.4 Hz, 1H,), 7.54-7.43 (m, 11H, Ph-*H*), 7.22 (t, $^{3}J_{H\text{-}H}$=7.3 Hz, Ph-4-*H*), 7.16 (dd, $^{3}J_{P\text{-}H}$=13.7 Hz, $^{3}J_{H\text{-}H}$=7.8 Hz, 4H, PPh_2-2,6-*H*), 7.00-6.94(m, 4H, Ph-*H*), 6.83(d, $^{4}J_{H\text{-}H}$ = 2.4 Hz, 2H, Xanthene-*H* or Catecholate-*H*), 6.62 (d, $^{4}J_{H\text{-}H}$ = 2.4 Hz, 1H, Xanthene-*H*), 6.25 (dd, $^{3}J_{H\text{-}H}$ = 14.2 Hz, $^{4}J_{H\text{-}H}$ =2.4 Hz, 1H, Xanthene-4-*H*), 1.75 (s, 6H, $C(CH_3)_2$), 1.34 (s, 9H, $C(CH_3)_3$), 1.29 (s, 9H, $C(CH_3)_3$), 1.04 (s, 9H, $C(CH_3)_3$), 1.03 (s, 9H, $C(CH_3)_3$).



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 150.4 (s), 150.3 (s), 149.8 (s), 147.7 (s), 146.6 (s), 145.7 (s), 145.6 (s), 142.7 (s), 139.7 (s), 136.8 (s), 134.7 (s), 133.9 (s), 133.8 (s), 133.1 (s), 131.9 (s), 131.8 (s), 131.7 (s), 131.4 (s), 130.4 (s), 130.4 (s), 130.3 (s), 130.2 (s), 129.9 (s), 129.1 (s), 129.0 (s), 128.9 (s), 127.8 (s), 127.5 (s), 127.4 (s), 125.6 (s), 114.5 (s), 114.0 (s), 111.6 (s), 109.3 (s), 35.1 (s), 34.7 (s), 34.7 (s), 34.6 (s), 34.5 (s), 34.0 (s), 32.1 (s), 31.2 (s), 31.1 (s), 29.9 (s).



$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202.4 MHz): δ 25.48 (s)



Compound 5-AuCl: A solution of 3,5-di-*tert*-butyl-*o*-benzoquinone (33.6 mg, 0.152mmol) in CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of **4**-AuCl (134 mg, 0.152mmol) in CH_2Cl_2 (5 mL). The resulting yellow solution was stirred for 30 min. The reaction solution was brought to dryness under reduced pressure. This solid was redissolved in CH_2Cl_2 (3 mL) and precipitated with hexane (20 mL) to obtain a pale yellow solid. This solid was further washed with pentane to afford **5**-AuCl as a yellow powder (134 mg, 80%).

Atlantic Microlab, Inc.

Sample No. 5-AuCl

6180 Atlantic Blvd. Suite M
Norcross, GA 30071
www.atlanticmicrolab.com

Company/School Texas A&M University
Dept. Chemistry
Address 580 Ross Street
City, State, Zip College Station, TX 77843
Name Benyu Zhou Date 10/04/2023
Phone (281) 935-6107

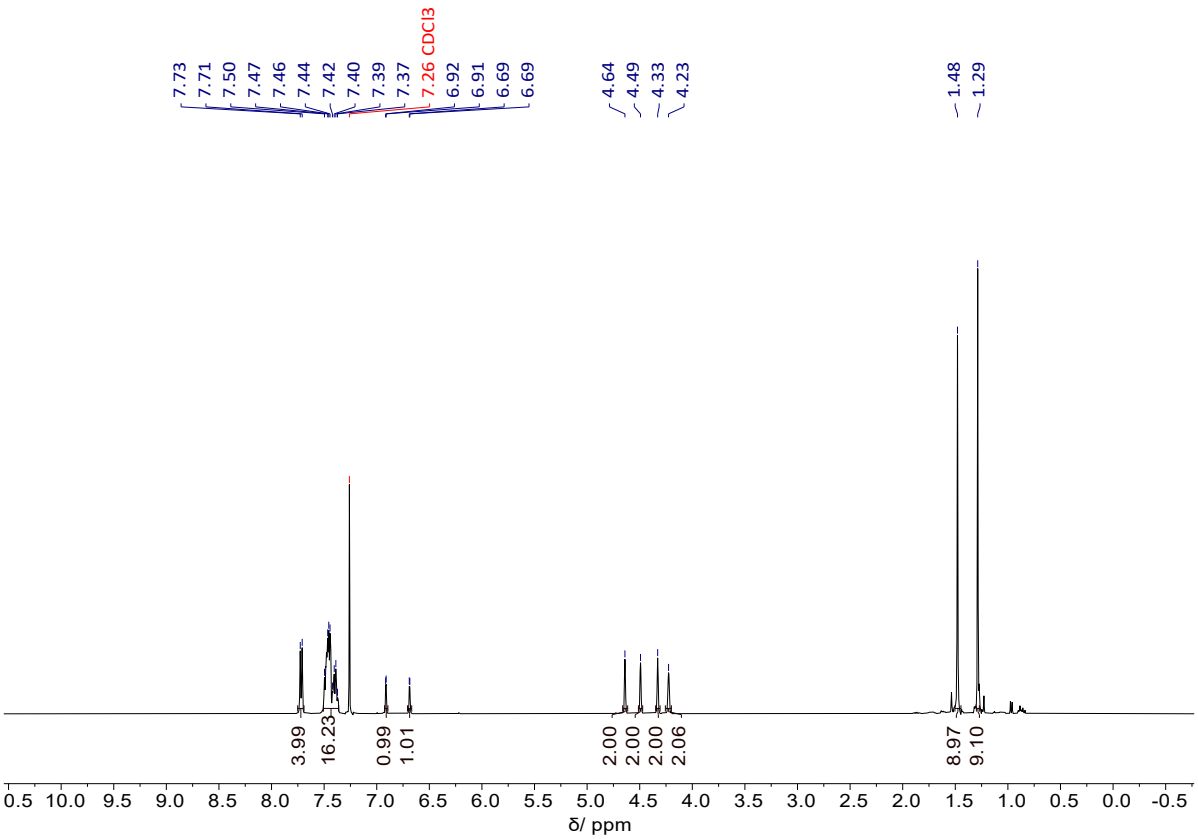
Professor/Supervisor: Francois Gabbai
PO# / CC# AB0854505

Element	Theory	Found	
C	52.51	52.77	
H	4.41	4.58	

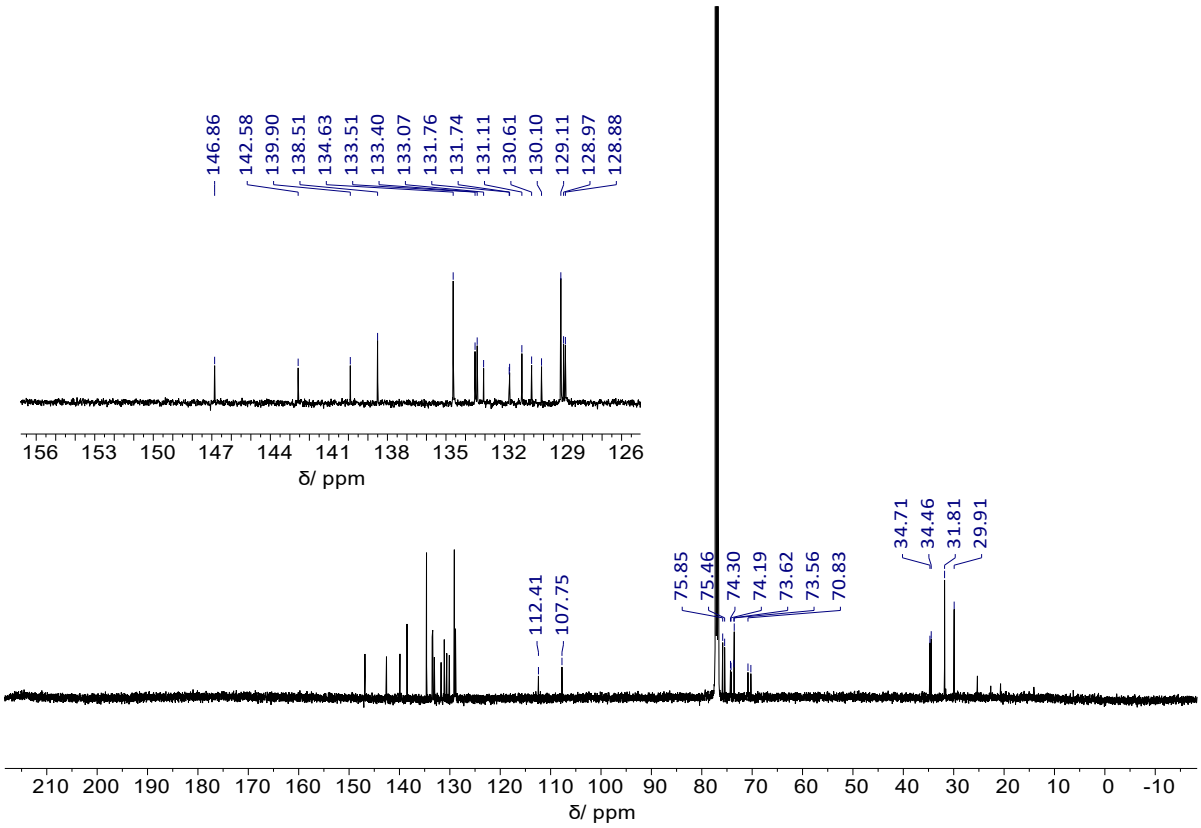
Single ☒ Duplicate ☐
Elements Present: C H O Fe P Cl Sb Zu
Analyze for: C H
Hygroscopic ☐ Explosive ☐
M.P. _____ B.P. _____
To be dried: Yes ☒ No ☐
Temp. _____ Vac. _____ Time _____
Rush Service ☐ Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.
Include Email Address or FAX # Below
benyuzhou1995@tamu.edu

Date Received OCT 0 9 2023 Date Completed OCT 1 0 2023
Remarks:

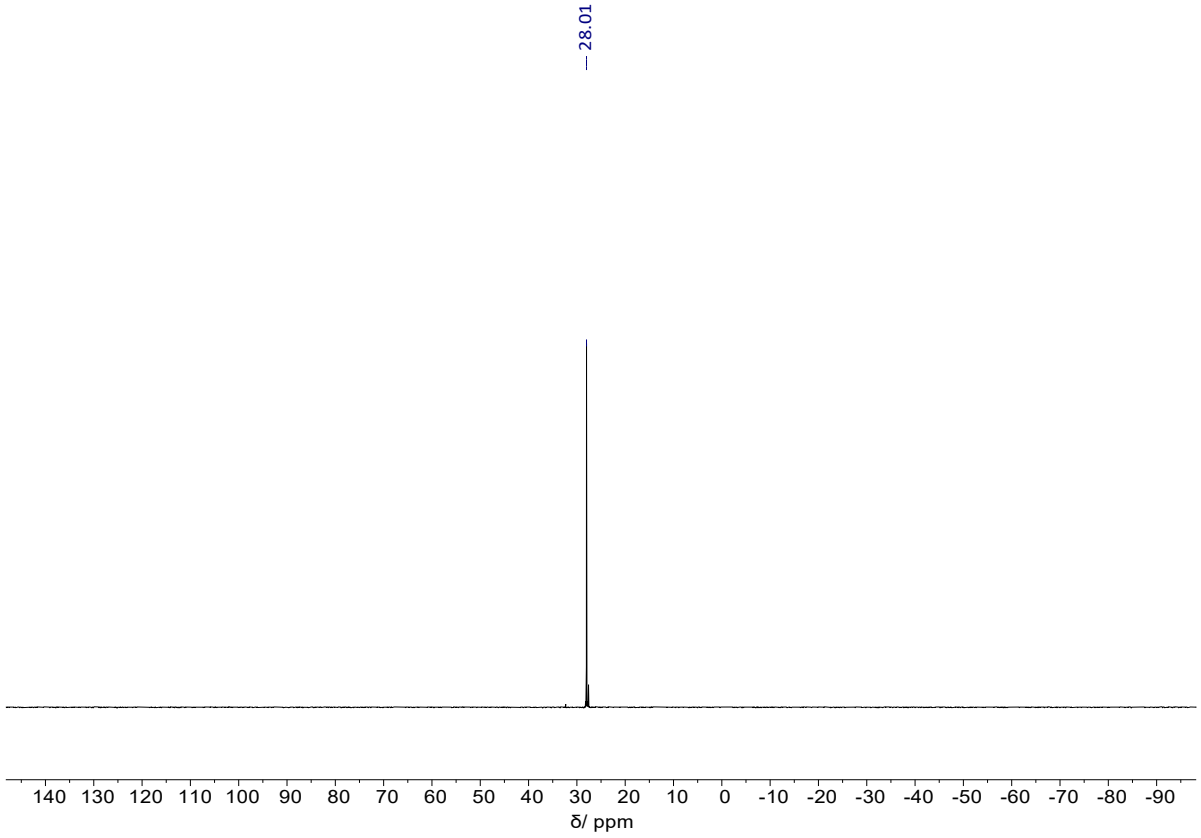
Elemental Analysis: Calculated for $C_{48}H_{48}O_2PClFeSbAu$: C 52.51, H, 4.41; Found: C 52.77, H 4.58.



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, $^{3}J_{H\text{-}H}$=7.4 Hz, 4H), 7.50-6.69 (m, 16H, Ph-*H*), 6.91(d, $^{4}J_{H\text{-}H}$ = 2.1 Hz, 1H, Catecholate-*H*), 6.61 (d, $^{4}J_{H\text{-}H}$ = 2.1 Hz, 1H, Catecholate-*H*), 4.64 (s, 1H, Ferrocene-*H*), 4.49 (s, 1H, Ferrocene-*H*), 4.33 (s, 1H, Ferrocene-*H*), 4.23 (s, 1H, Ferrocene-*H*), 1.48 (s, 9H, $C(CH_3)_2$), 1.29 (s, 9H, $C(CH_3)_3$).

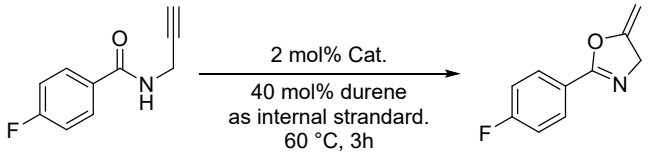


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.8 MHz): δ 146.9 (s), 142.6(s), 139.9 (s), 138.5 (s), 134.6 (s), 133.5 (s), 133.4 (s), 133.07 (s), 131.8 (s), 131.7 (s), 131.1 (s), 130.6 (s), 130.1 (s), 129.1 (s), 129.0 (s), 128.9 (s), 112.4 (s), 107.8 (s), 75.8 (s), 75.5 (s), 74.3 (s), 74.2 (s), 73.6 (s), 73.6 (s), 70.8 (s), 70.3 (s), 34.7 (s), 34.5 (s), 31.8 (s), 29.9 (s).



$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202.4 MHz): δ 28.01 (s)

3 Catalytic isomerization of propargylic amides



Under an N_2 atmosphere, a $CDCl_3$ solution (0.7 mL) of the gold catalyst (0.0040 mmol) and durene (0.0800 mmol, internal standard) was added to a J-Young NMR tube containing the substrate (0.200 mmol). The resulting solution was heated at 50 °C for 3 h. For the first 2 h, the *in situ* ^{1}H NMR spectra of the reaction solution were recorded periodically, and then a final spectrum was recorded at 3 h. The conversions were calculated by integrating the characteristic methylene peaks of the product and the starting substrate respectively. The results are summarized in **Figure S1-S4** and **Table S1**.

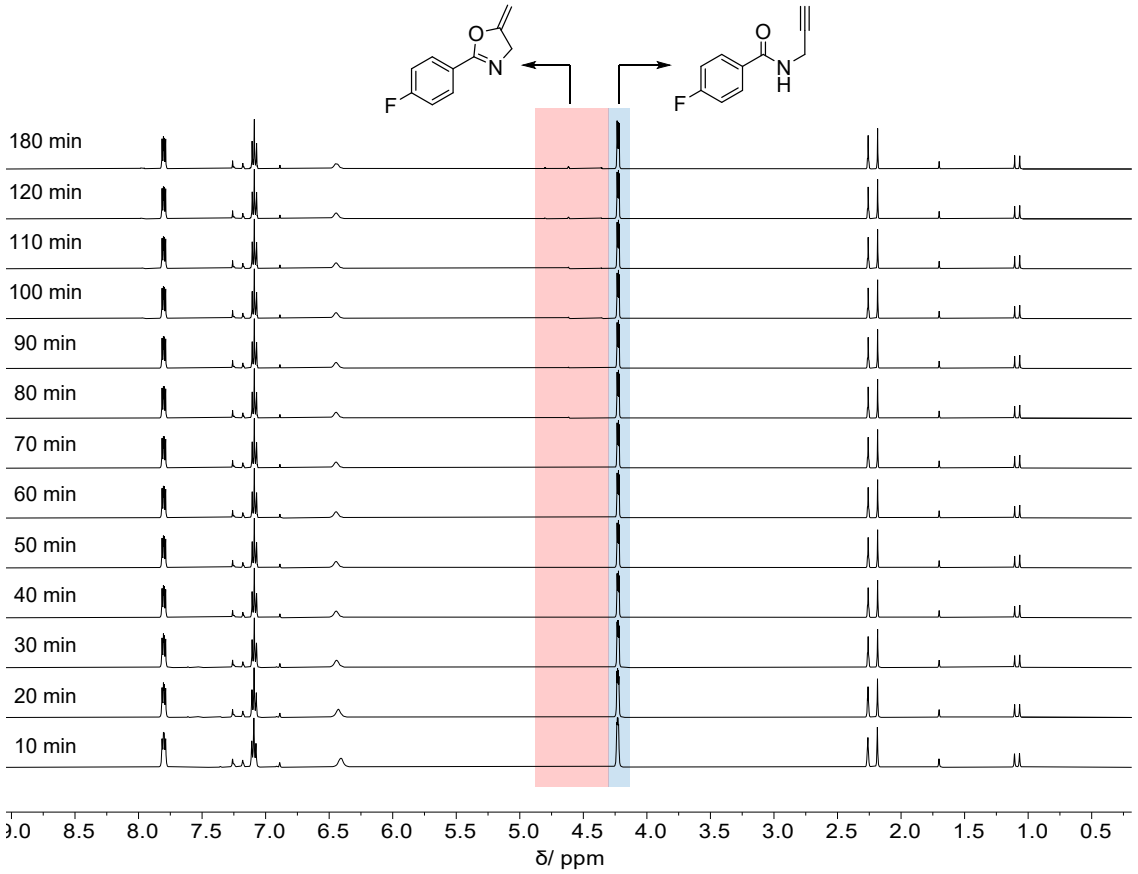


Figure S1. ^{1}H NMR spectra recorded *in situ* during the course of catalysis using **2**-AuCl as the catalyst.

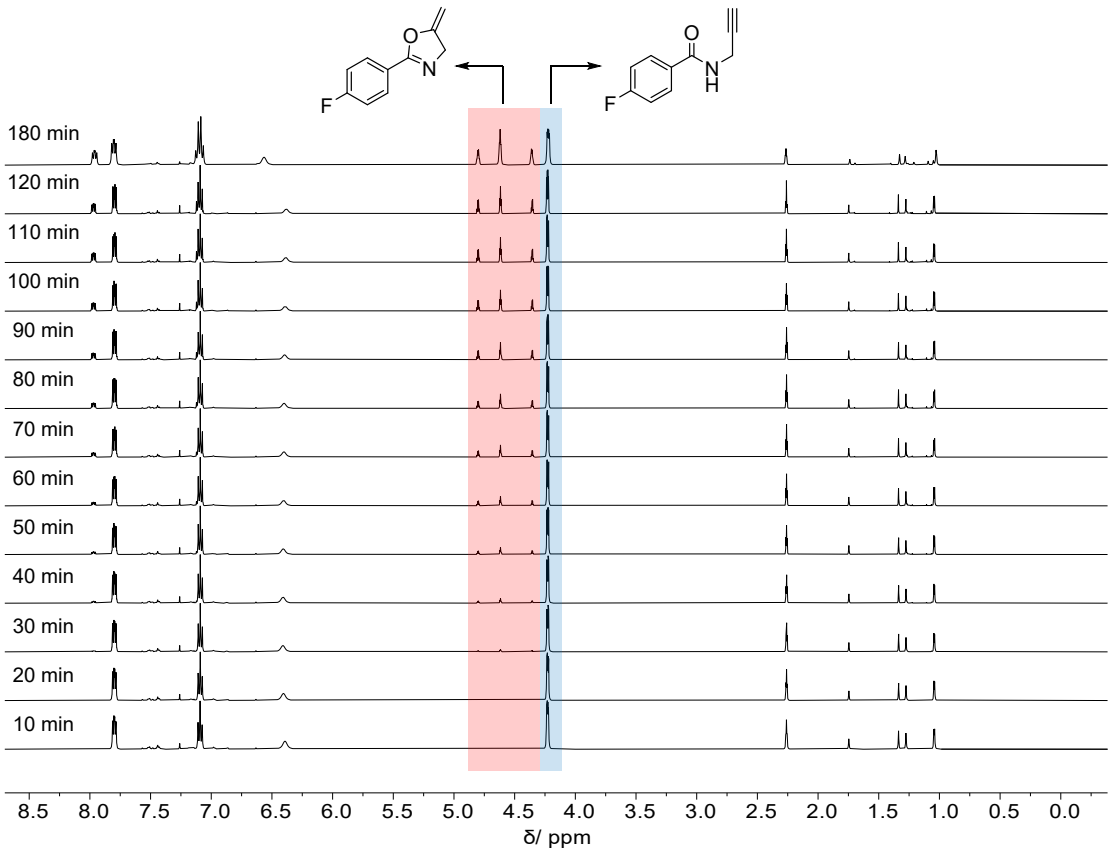


Figure S2. ^{1}H NMR spectra recorded *in situ* during the course of catalysis using **3**-AuCl as the catalyst.

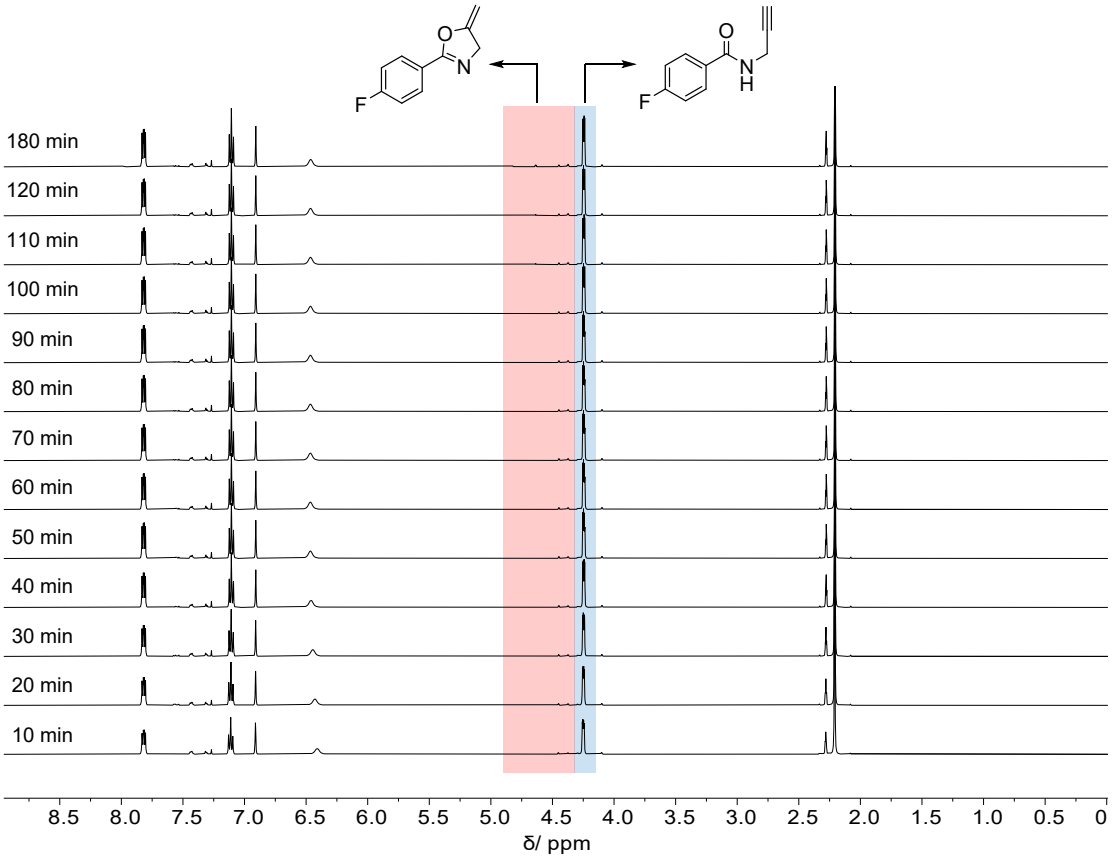


Figure S3. ^{1}H NMR spectra recorded *in situ* during the course of catalysis using **4**-AuCl as the catalyst.

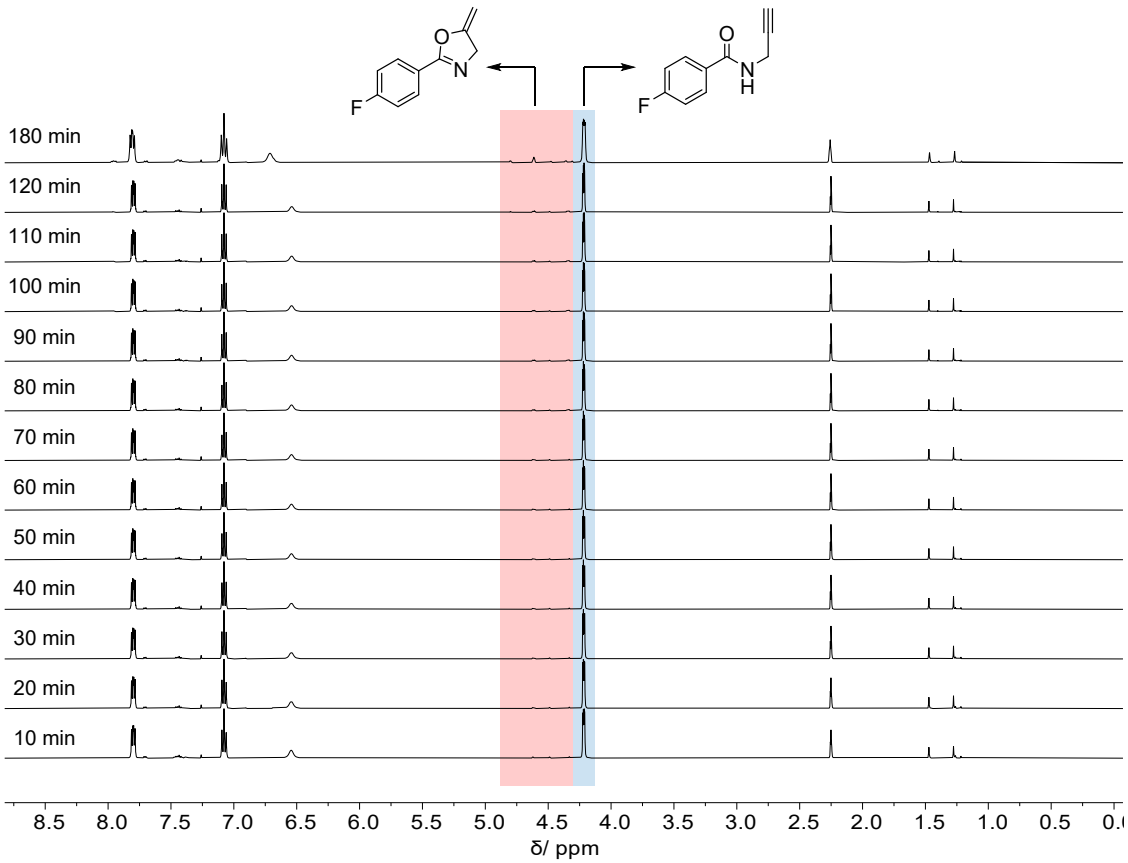


Figure S4. [1]H NMR spectra recorded *in situ* during the course of catalysis using **5**-AuCl as the catalyst.

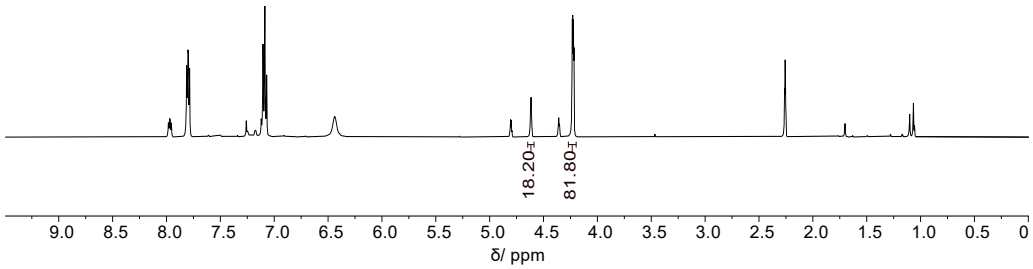


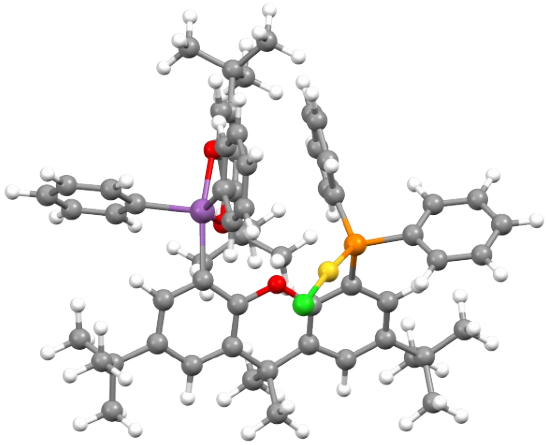
Figure S5. [1]H NMR spectra recorded *in situ* after 2 hours of catalysis reaction using **2**-AuCl/AgOTf as the catalyst.

Table S1. Catalytic results for the isomerization of propargyl amide 6 after 3 h.

Entry	Catalyst	Conversion
1	**2**-AuCl	4%
2	**3**-AuCl	39%
3	**4**-AuCl	2%
4	**5**-AuCl	6%

4 Computational results

4.1 Cartesian Coordinates for the optimized structure of **3**-AuCl in gas phase



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Sb	9.13390447715088	9.65320767214329	12.82366264706481
Cl	5.21635560070618	8.67940487094291	17.59451749747783
P	6.60432193049341	12.64882302616172	15.85446941549307
O	10.42709217373625	11.19541553847681	13.07917922246952
O	8.77544873613386	10.76258511428386	11.11976388344268
O	9.10494235406336	11.11044420146304	15.76660171815426
C	11.64220134931935	8.69188207835856	16.87722874329178
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C	7.94400238197428	13.93470196912159	12.19318082104428
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H	9.05997762282498	15.62425449662627	8.92093829480959
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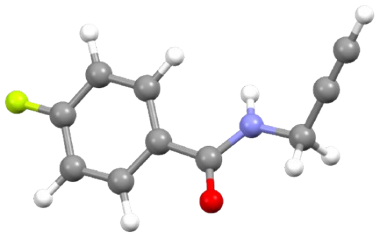
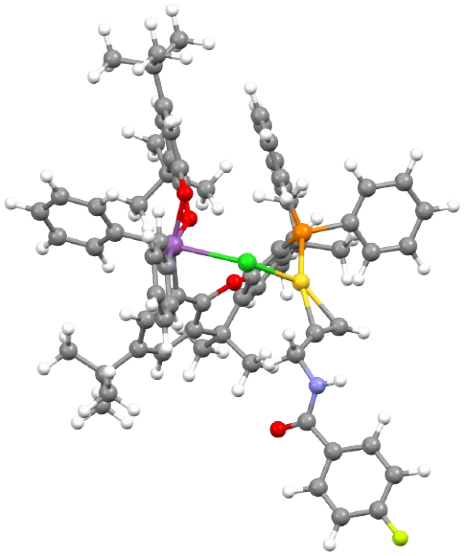
4.2 Cartesian Coordinates for the optimized structure of **6** in gas phase



C	-1.98708616752844	0.23128841822637	0.56793872757902
C	-0.70873059356555	-0.15814520337334	0.16437673552448
C	0.23298238405610	0.79562996769322	-0.25729488814071
C	-0.13604666470422	2.15060973753853	-0.29112558037699
C	-1.40452316763506	2.55624150448802	0.11772902591658
C	-2.31214647549313	1.58680790378915	0.54539230782720
H	-2.73683250197589	-0.49705942096637	0.88653244850375
H	-0.47016397288859	-1.22601131842740	0.14653110068780
H	0.59779719863823	2.87733603459617	-0.64908488299405
H	-1.70539212071832	3.60688245120195	0.10701805991443
F	-3.53320849934720	1.96705847538044	0.93597916420405
C	1.61516021935345	0.45090603612031	-0.72937076725867
N	2.11652564599726	-0.74276350155773	-0.27999537641738
H	1.62398587004711	-1.26871472516716	0.43015752003653
C	3.42917070204261	-1.21258603875802	-0.69076390659618
H	4.19931640626565	-0.98759417560477	0.07556576535022
H	3.70927536097257	-0.63197152769998	-1.58775560893512
C	3.43424835204691	-2.64455136231312	-0.97351698164707
C	3.43292759774467	-3.83911353759991	-1.19064725950199
H	3.43796648508251	-4.89442912199442	-1.39146705364830
O	2.25157394160927	1.19727940442809	-1.46179855002762

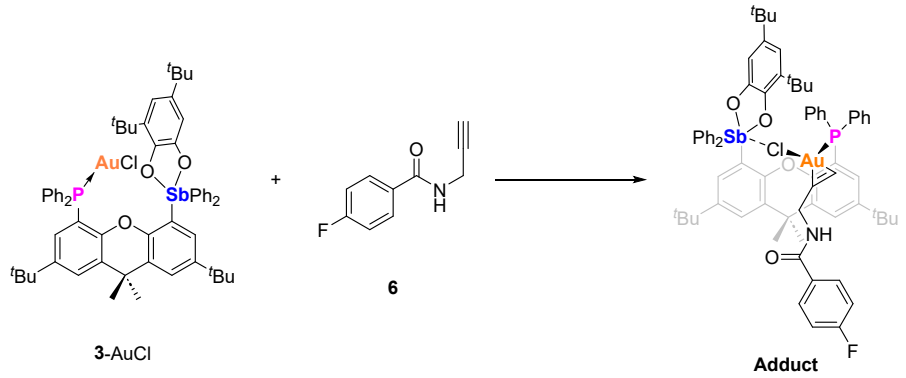
4.3 Cartesian Coordinates for the optimized structure of the adduct between **3**-AuCl and **6** in gas phase



Au	5.68638341912743	11.07471591254811	16.09384432621546	H	11.89650893978317	16.51973276036935	19.87646588984816
Sb	8.94249277714644	9.42284411079715	12.99670926192972	H	12.41616115226528	15.08146848551420	18.96560469975486
Cl	6.25485970900579	9.81977834364061	14.05307453687795	C	10.73773951725538	16.64966200698860	17.43302593405372
P	6.73930094725957	13.12639182676530	15.61679188272530	H	11.54342766695565	16.20719625313467	16.82434872412166
O	9.66776948597368	11.31709597773741	13.43571337600213	H	11.09078171250276	17.61821810967572	17.82678504443854
O	8.21160437922452	10.51076099104202	11.42734845169020	H	9.88414429319112	16.85026038891819	16.76521597551020
O	8.70507155801116	10.87678033222977	16.06123652310529	C	10.75448275969926	8.89403831658228	11.96434674234503
C	11.08064028593855	8.33827073106474	17.24795144192520	C	11.99070171595314	8.77467842493449	12.61503507501338
H	11.70051758594046	8.14093660530342	18.12216509574899	H	12.06389075802393	8.93077232833769	13.69523282451632
C	11.01334740137600	7.38323657417802	16.22752562916459	C	13.14761536180879	8.46257196655051	11.89218493739672
C	10.25116705322555	7.71493812628985	15.09329509923006	H	14.10530797981057	8.36938194894496	12.41437634576659
H	10.25675693598762	7.03622125988953	14.23339064594649	C	13.08155247473514	8.27987875095944	10.50776690283301
C	9.53150149370719	8.90786834791421	14.99807873143526	H	13.98675198607199	8.03950563804617	9.94157359637136
C	8.32876176618603	13.17540498786012	16.52411301508850	C	11.85580642834997	8.41338865661777	9.84815687652337
C	8.77321477116582	14.35460721414614	17.13471363321944	H	11.79879848609054	8.28398725965216	8.76290457147707
H	8.22739467456531	15.28037347197706	16.93377716384359	C	10.69932160384329	8.71829765415741	10.57274803664858
C	9.86919849812902	14.37330424824656	18.00906825391289	H	9.74919040188458	8.83329606427696	10.04367295089323
C	10.43465358823491	13.13646900970673	18.35525933527704	C	7.75412510844690	7.72422313357898	12.42613032837637
H	11.21955922973877	13.10455949364339	19.11045667693244	C	7.28716656149743	7.59428228120503	11.11087007092833
C	10.37183072441685	10.55168714562431	18.35019253962256	H	7.46299441128124	8.39304423487424	10.38664458345566
C	10.35885071410430	9.54163948257147	17.20430608421201	C	6.56540105575982	6.45476579317976	10.73589277576654
C	9.53508405827220	9.78014659108838	16.09689003912056	H	6.20018427573829	6.36020006782784	9.70833709849043
C	9.03358632972934	11.98103032840715	16.78288420975183	C	6.30464888409139	5.44593042859088	11.66753929447809
C	10.00628397520079	11.92747137162057	17.79156536429197	H	5.74186010857005	4.55569768365969	11.37018922232178
C	9.24692579861333	10.15758121553701	19.34374011669869	C	6.75269627666393	5.58497457965065	12.98547858632342
H	9.18966134117167	10.88609128272335	20.17045636261803	H	6.53582671952335	4.80810124213489	13.72565567427902
H	9.44112439963784	9.15514075736762	19.76067910947530	C	7.46886590277125	6.72435772284500	13.36614511233412
H	8.26789245794401	10.13158543107289	18.83714243752305	H	7.78210609050158	6.83904731670606	14.40872236753720
C	11.71670935551569	10.56726483980086	19.08585952222936	C	6.98805587340064	13.61555377741038	13.88564169206601
H	11.69546909989576	11.27988005548361	19.92435237018954	C	6.18737602576294	13.04964922631742	12.88068416377116
H	12.54160716125673	10.84088451252955	18.40829583216528	H	5.49201654584103	12.24221485150221	13.11911477800571
H	11.93652609212083	9.58405082192428	19.52730542781885	C	6.30768960532410	13.50230159355190	11.56547077708485
C	11.74735005314703	6.03758450665855	16.27982891007861	H	5.69942601452884	13.04366520742280	10.78099297693453
C	10.71605437138496	4.90199845771021	16.11909422217919	C	7.22199535193126	14.50958760000341	11.24739002793820
H	9.96981851787078	4.93431928688737	16.93044048268968	H	7.32667964097133	14.84376714078130	10.21196539731568
H	11.21855807131155	3.91998814645802	16.14922053479961	C	8.02335290939674	15.07211959825057	12.24589796808561
H	10.17657785946085	4.97383311783188	15.16076730958436	H	8.75778891078568	15.84173157540925	11.99217977558448
C	12.77423333106306	5.96969491956271	15.13135950828058	C	7.90369519755201	14.63052489945094	13.56446165589850
H	12.29564791958619	6.06523127246330	14.14331674426207	H	8.52565140814842	15.07296199656505	14.34663400351237
H	13.31057780456624	5.00540972986632	15.15388998574398	C	5.81973265476261	14.53316255647592	16.36005280208584
H	13.51791569999951	6.77937044000959	15.22303182769112	C	5.29624802673382	15.57647666493679	15.58295963504378
C	12.48755704989720	5.83654130454839	17.60901186567418	H	5.46129804661695	15.58928926896103	14.50195222329515
H	13.27358389278324	6.59521264088740	17.76047805583688	C	4.56420462775279	16.60408213048989	16.19057685845828
H	12.97672700093598	4.84867780931004	17.61523586920434	H	4.15891141039633	17.41304200838957	15.57557066088707
H	11.79783645949466	5.87290852243559	18.46877580024902	C	4.35596924648161	16.60151765499822	17.57125655065176
C	10.34698185968481	15.70976559196509	18.59131571755540	H	3.78843361397294	17.40906812701244	18.04299485282217
C	9.20687549036279	16.34715012018955	19.41146002336901	C	4.87382203439367	15.55888839441031	18.35107160883457
H	8.31318392694673	16.53643072409191	18.79453567067851	H	4.71403305110044	15.55096651456970	19.43350711603974
H	9.53234472001649	17.31255076478753	19.83582580144369	C	5.59233238255330	14.52615352787940	17.74932975565010
H	8.90733092488241	15.68826874826891	20.24390677275585	H	5.99657574859415	13.71148983616503	18.35998207494056
C	11.56793969107770	15.53552939041275	19.50446022441794	C	9.85320200194048	11.97975769975199	12.27529560991025
H	11.33973609814539	14.91040205377004	20.38381057583184	C	9.03697182098409	11.55502277304261	11.19508090596436

C	9.13517446653488	12.14897695622642	9.93590280159799
H	8.47827693795841	11.77480832811182	9.14856413726427
C	10.05651472072166	13.18356185710575	9.72117047836415
C	10.89213245500576	13.55620057204695	10.78834806629699
H	11.64051565315413	14.32837923341870	10.60643827850313
C	10.84415815436014	12.96582416047193	12.06428457319213
C	11.86546578941935	13.32173729881602	13.15890323720559
C	12.63683560690146	12.04976037530892	13.56625770996404
H	11.96301687251195	11.31204548556114	14.02361531579428
H	13.42387421772423	12.30370289036650	14.29857580059058
H	13.11406034463680	11.58335788629198	12.68855174854610
C	11.16099061784441	13.89955360143796	14.39890405192949
H	10.75372284709020	14.90138714550527	14.18204020219444
H	11.87656949101860	13.99991328362074	15.23483086719370
H	10.33703809987814	13.25158719791956	14.72882833906806
C	12.89239120486933	14.35759797932503	12.67785679009297
H	13.48228076300058	13.98704209456049	11.82308254956267
H	13.59535855671815	14.58153857250249	13.49808897786023
H	12.41347278782014	15.30677743857657	12.38401599347937
C	10.22999466570227	13.86114485865145	8.35265721990735
C	10.12349271379361	15.39191354495527	8.49879094199986
H	9.13996749516977	15.68046371735898	8.90634244259414
H	10.24428831209333	15.88470317626832	7.51802676960761
H	10.89615096521030	15.79462466936868	9.17278621297293
C	9.16623291783461	13.40388610046285	7.34487280513191
H	9.23736365403416	12.32364183352279	7.13820828317830
H	9.30226377488435	13.93523663793212	6.38795465885778
H	8.14622399664183	13.61585709648277	7.70764478905619
C	11.61928084567454	13.50045816995990	7.78792228437608
H	12.42513229946279	13.84560465375484	8.45570546498173
H	11.77400680415255	13.96396938139534	6.79707493824160
H	11.72054100495041	12.40752000984773	7.68132217018351
C	4.65711882576971	9.61291965491113	17.21515058940469
C	4.61864417718536	10.70386432060108	17.86815759617375
H	4.33649959024857	11.33014325645522	18.70723913709985
C	4.43310473780677	8.18310458725186	16.91290794886700
H	4.10483397871699	8.07927572943658	15.86289019762123
H	5.39662818849663	7.64848242962345	16.99087441164776
N	3.50663018504168	7.54966278621415	17.82788122989035
H	2.52461343062718	7.77979154774177	17.75267032931767
C	3.92985136757752	6.65650537454445	18.78037696262149
O	5.08871014643113	6.27194554590069	18.85534523419986
C	2.87068276349750	6.15411310859063	19.71783967286912
C	1.69163258460610	6.85785915976918	20.01578558458976
C	3.11458724514191	4.92982090288515	20.36244238888797
C	0.76151169367700	6.34325567471625	20.92058066717856
H	1.49733375714387	7.84011517220988	19.57404245296621
C	2.19155759238689	4.39734230051036	21.25946504137551
H	4.04917393475183	4.40750799301114	20.14206621995887
C	1.02392700387503	5.11402290980894	21.52342304496070
H	-0.15466815643235	6.88226091637650	21.17396397082723
H	2.36057345969515	3.44163150143188	21.76199810771200
F	0.13496586354459	4.61366585036466	22.38796780114220

4.4 Thermodynamic parameters of the optimized structures. All energies are in Hartree.



Compound	Single point energy	Free energy correction	Free energy
3-AuCl	-3767.866721213	1.03546675	-3766.831254
6	-615.5334972	0.11876002	-615.4147371
Adduct	-4383.3870069911	1.18199565	-4382.205011

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