Versatile Methods for Preparation of New Cyclometalated Gold(III) Complexes

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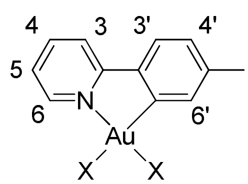
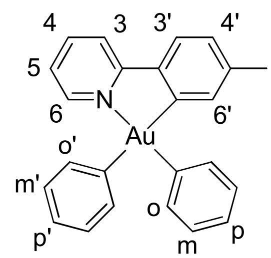
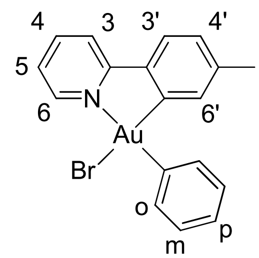
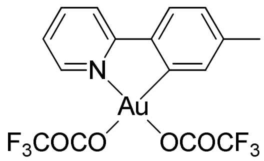
Supporting Information

General Experimental Methods. MeLi, PhLi, MeMgBr, EtMgBr and PhMgBr were purchased from Sigma-Aldrich and used as received. TFA and NMR-solvents were used as received. CH_2Cl_2 and THF were dried by use of the solvent purification system MB SPS-800 from MBraun. $AuCl_2$(tpy) was prepared as previously reported (Shaw, A. P.; Tilset, M.; Heyn, R. H.; Jakobsen, S. *J. Coord. Chem.* **2011**, *64*, 38-47). All reactions were performed with magnetic stirring, including microwave reaction. The microwave oven used was of the type Milestone MicroSYNTH with a rotor of the type SK-10. All reactions were performed under argon, except when performed in the microwave. In the Grignard reactions neutral distilled water neutralized with $NaHCO_3$ was used for washing,. Elemental analyses were performed by School of Chemistry, University of Birmingham, England (compounds **1** and **2**) and Mikroanalytisches Laboratorium Kolbe, Mülheim an der Ruhr, Germany (compounds **3-6**). NMR spectra were recorded on a Bruker Avance DPX200 operating at 200 MHz (^{1}H), DPX300 operating at 300 MHz (^{1}H) and AVII400 operating on at 400 MHz (^{1}H). ^{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. ^{1}H NMR assignments were made on the basis of COSY and NOESY experiments and refer to the numbering schemes shown below. Mass spectrometry was performed with Waters ProSpec (EI) and Q-TOF-2 (ESI) instruments.





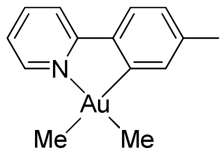




Compound 1: $Au(OCOCF_3)_2(tpy)$

A solution of $Au(OAc)_3$ (0.384 g, 1.03 mmol, 1.00 equiv.) and 2-(*p*-tolyl)pyridine (186 μL, 1.09 mmol, 1.06 equiv.) in a 1:1 mixture of water (15.0 mL) and trifluoroacetic acid (15.0 mL) was heated in the microwave oven at 120 ^{0}C for 30 min. After the reaction, the light yellow solution was cooled at room temperature for 15-30 min and then decanted over to an Erlenmeyer flask. If the product had started to precipitate out, TFA was added to redissolve the product before decanting, in order to remove a small amount of unreacted $Au(OAc)_3$. The product can be precipitated by either addition of water (20-50 mL), by cooling to 0 °C, or by combined water addition and cooling. The precipitate was collected on a fine frit and washed with water (3 x 5 mL) and diethyl ether (5 mL) and dried under a stream of air for 30-40 min. The product was obtained in 94 % yield (0.572 g).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.42 (d, 6-C*H*, *J* = 5.8 Hz, 1H), 8.19 (t, 4-C*H*, *J* = 7.7 Hz, 1H), 7.92 (d, 3-C*H*, *J* = 8.0 Hz, 1H), 7.50-7.42 (m, 5,3′-C*H*, 2H), 7.23 (d, 4′-C*H*, *J* = 7.8 Hz, 1H), 6.71 (s, 6′-C*H*, 1H), 2.37 (s, ArCH_3, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 165.0, 147.7, 144.3, 144.2, 142.7, 138.2, 131.2, 129.1, 125.9, 124.2, 121.5, 22.4 (For the CF_3 and CO signals, coupling to ^{19}F was not observed).
^{19}F NMR (377 MHz, CD_2Cl_2): δ -76.1 (s, CF_3 *(trans to N)*, 3F), -77.0 (s, CF_3 *(cis to N)*, 3F).
MS (ESI in CH_3CN): *m/z* = 859.1, 614.1 (63 % $[M+Na^+]^+$), 478.1 (100 % $[M-OCOCF_3]^+$).
MS-HR (CH_3CN): 614.0067, calculated for $C_{16}H_{10}AuF_6NNaO_4$ 614.0077 (-1.68 ppm).
Anal. Calcd for $C_{16}H_{10}AuF_6NO_4$: C, 32.51; H, 1.7; N, 2.37. Found: C, 32.69; H, 1.61; N, 2.48.



Compound 2: $AuMe_2$(tpy)

A solution of $Au(OCOCF_3)_2$(tpy) (**1**) (0.150 g, 0.253 mmol, 1.00 equiv.) in THF (5.0 mL) was cooled in a dry ice/acetone bath and then MeLi (1.6 M in Et_2O, 0.560 mL, 0.896 mmol, 3.54 equiv.) was added. No change in color was observed upon addition. The reaction was stirred for 1 h at -78 °C and then allowed to warm up to rt. The solution turned purple upon warming up. THF was removed *in vacuo*. The resulting solid was dissolved in dry CH_2Cl_2 and filtered through Celite to give a light yellow solution. In case of a continued purple solution, filter solution again. CH_2Cl_2 was removed *in vacuo* to give a white powder of compound **2** (0.093 g, 93 %)

$AuMe_2$(tpy) (**2**) could also be synthesized from $AuCl_2$(tpy) (0.104 g, 0.239 mmol, 1.00 equiv.) and MeLi (1.6 M in Et_2O, 0.500 mL, 0.800 mmol, 3.34 equiv) using the same procedure (except stirring at -78 °C for 3.5 h), yielding 0.085 g (89 %) of **2**.

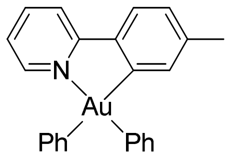
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, 6-C*H*, *J* = 5.5 Hz, 1H), 7.98-7.81 (m, 3,4-C*H*, 2H), 7.67 (d, 3´-C*H*, *J* = 7.9 Hz, 1H), 7.56 (s, 6´-C*H*, 1H), 7.30-7.24 (m, 5-C*H*, 1H), 7.07 (dd, 4´-C*H*, *J* = 7.9, 1.0 Hz, 1H), 2.41 (s, ArCH_3, 3H), 1.38 (s, AuCH_3 *(trans to N)*, 3H), 0.44 (s, AuCH_3 *(cis to N)*, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.2, 167.4, 146.5, 143.8, 141.0, 139.7, 132.9, 126.6, 124.7, 122.4, 119.8, 22.1, 13.2, 1.6.

MS (EI in CH_3CN): *m/z* = 395 (11 % $[M]^+$), 380 (84 % $[M\text{-}Me]^+$), 182 (100 %).

MS-HR (CH_3CN): 395.093983, calculated for $C_{14}H_{16}AuN$ 395.094835 (+2.2 ppm).

Anal. Calcd for $C_{14}H_{16}AuN$: C, 42.54; H, 4.08; N, 3.54. Found: C, 42.27; H, 3.99; N, 3.48.



Compound 3: AuPh$_2$(tpy)

A solution of Au(OCOCF$_3$)$_2$(tpy) (**1**) (0.154 g, 0.261 mmol, 1.00 equiv.) in THF (5.0 mL) was cooled in a dry ice/acetone bath and then PhLi (1.8 M in Et$_2$O, 0.490 mL, 0.896 mmol, 3.39 equiv.) was added. The solution turned orange upon addition. The reaction was stirred for 1 h at -78 °C and then was warmed up to rt. THF was removed *in vacuo*. The resulting brown oil was dissolved in dry CH$_2$Cl$_2$ and filtered through Celite to give a light brown solution. In case of a continued purple solution, the solution was filtered again. CH$_2$Cl$_2$ was removed *in vacuo* and gave a brown powder (0.126 g, 93 %)

AuPh$_2$(tpy) (**3**) could also be synthesized from AuCl$_2$(tpy) (0.101 g, 0.231 mmol, 1.00 equiv.) and PhLi (1.8 M in Et$_2$O, 0.450 mL, 0.810 mmol, 3.51 equiv) using the same procedure (except stirring at -78 °C for 2 h), yielding 0.096 g (80 %) of **3**.

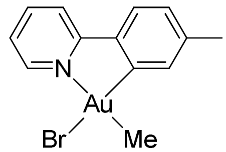
^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.09 (d, 6-C*H*, *J* = 5.3 Hz, 1H), 7.97-7.84 (m, 3,4-C*H*, 2H), 7.70 (d, 3′-C*H*, *J* = 7.9 Hz, 1H), 7.48 (d, o′-C*H*, *J* = 7.3 Hz, 2H), 7.43 (d, o-C*H*, *J* = 7.6 Hz, 2H), 7.23 (t, m′-C*H*, *J* = 7.3 Hz, 2H), 7.18-7.11 (m, m,5-C*H*, 3H), 7.09-7.01 (m, p,p′,4′-C*H*, 3H), 6.82 (s, 6′-C*H*, 1H), 2.21 (s, ArC*H$_3$*, 3H).

^{13}C NMR (101 MHz, CD$_2$Cl$_2$): δ 169.8, 167.9, 167.3, 149.6, 143.9, 142.8, 141.8, 140.9, 137.0, 135.8, 133.0, 129.3, 129.3, 127.6, 125.2, 124.7, 124.7, 123.4, 120.4, 22.2.

MS (ESI in CH$_3$CN): *m/z* = 558.1 (100 % [M+K]$^+$).

MS-HR (CH$_3$CN): 558.0880, calculated for C$_{24}$H$_{20}$AuKN 558.0898 (-3.30 ppm).

Anal. Calcd for C$_{24}$H$_{20}$AuN: C, 55.50; H, 3.88; N, 2.70. Found: C, 55.69; H, 4.01; N, 2.51.



Compound 4: AuBrMe(tpy)

A solution of $Au(OCOCF_3)_2$(tpy) (**1**) (0.100 g, 0.169 mmol, 1.00 equiv.) in THF (10.0 mL) was cooled in a dry ice/acetone bath and MeMgBr (3.0 M in Et_2O, 0.080 mL, 0.240 mmol, 1.42 equiv.) was added. The solution formed an off-white, milky suspension shortly after addition. The reaction was stirred for 1 h at -78 °C and then at rt for 1 h. While warming to ambient temperature, the reaction cleared up to a light yellow solution. THF was removed *in vacuo*. The resulting off-white solid was dissolved in CH_2Cl_2 (25 mL) and washed with distilled water (pH=7, 3 x 25 mL), and the organic phase turned slightly purple. The organic phase was dried over $MgSO_4$ and filtered through Celite to give a light yellow solution and solvent was removed *in vacuo* to yield **4** as an off-white powder, 0.068 g (87 %).

Compound **4** could be synthesized from $AuCl_2$(tpy), but was not isolated. $AuCl_2$(tpy) (0.076 g, 0.175 mmol, 1.00 equiv.) and MeMgBr (3.0 M in Et_2O, 0.170 mL, 0.510 mmol, 2.92 equiv) using the same procedure. The ^{1}H NMR spectrum is shown.

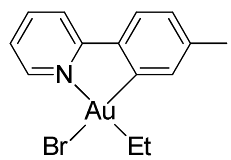
^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.53 (d, 6-C*H*, *J* = 5.4 Hz, 1H), 7.98 (td, 4-C*H*, *J* = 7.7, 1.5 Hz, 1H), 7.91 (d, 3-C*H*, *J* = 8.0 Hz, 1H), 7.68 (d, 3′-C*H*, *J* = 7.9 Hz, 1H), 7.45-7.42 (m, 5-C*H*, 1H), 7.32 (s, 6′-C*H*, 1H), 7.20 (d, 4′-C*H*, *J* = 8.0 Hz, 1H), 2.43 (s, ArCH_3, 3H), 1.62 (s, AuCH_3, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 162.2, 149.2, 147.9, 142.4, 141.8, 141.1, 130.5, 128.9, 125.9, 124.5, 120.0, 22.2, 8.4, 1.3.

MS (EI in CH_3CN): *m/z* = 460.9 (10 % $[M(^{81}Br)]^+$), 458.9 (11 % $[M(^{79}Br)]^+$), 445.9 (9 % $[M(^{81}Br)$-$Me]^+$), 443.9 (9 % $[M(^{79}Br)$-$Me]^+$), 380.0 (55 % $[M$-$Br]^+$), 365.0 (9 % $[M$-Br-$Me)]^+$), 182.0 (100%).

MS-HR (CH_3CN): 458.990018, calculated for $C_{13}H_{13}Au^{79}BrN$ 458.989696 (-0.7 ppm).

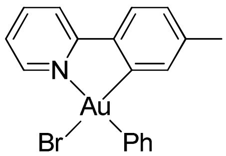
Anal. Calcd for $C_{13}H_{13}AuBrN$: C, 33.93; H, 2.85; N, 3. 40. Found: C, 33.91; H, 2.87; N, 3.03.



Compound 5: AuBrEt(tpy)

A solution of $Au(OCOCF_3)_2(tpy)$ (**1**) (0.101 g, 0.171 mmol, 1.00 equiv.) in THF (10.0 mL) was cooled in a dry ice/acetone bath and then EtMgBr (3.0 M in Et_2O, 0.080 mL, 0.240 mmol, 1.41 equiv.) was added. No color change was observed upon addition. The reaction was stirred for 1 h at -78 °C and then at rt for 1 h. During warming to rt, the reaction cleared up to a light yellow solution. THF was removed *in vacuo*. The resulting off-white solid was dissolved in CH_2Cl_2 (25 mL) and washed with distilled water (pH=7, 3 x 25 mL), and the organic phase turned slightly purple. The organic phase was dried over $MgSO_4$ and filtered through Celite to give a light yellow solution and solvent was removed *in vacuo* to yield **5** as a light yellow powder, 0.053 g (66 %).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.48 (d, 6-C*H*, *J* = 4.8 Hz, 1H), 7.96 (td, 4-C*H*, *J* = 7.7, 1.6 Hz, 1H), 7.91 (d, 3-C*H*, *J* = 7.9 Hz, 1H), 7.69 (d, 3′-C*H*, *J* = 7.9 Hz, 1H), 7.46-7.39 (m, 5,6′-C*H*, 2H), 7.20 (d, 4′-C*H*, *J* = 8.4 Hz, 1H), 2.53 (q, AuCH_2, *J* = 7.6 Hz, 2H), 2.46 (s, ArCH_3, 3H), 1.40 (t, CH_2CH_3, *J* = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, CD_2Cl_2): δ 161.9, 149.4, 149.4, 142.7, 141.7, 141.0, 130.7, 128.8, 125.7, 124.3, 120.0, 27.7, 22.3, 16.6.
MS (EI in CH_3CN): *m/z* = 475.0 (2 % $[M(^{81}Br)]^+$), 473.0 (2 % $[M(^{79}Br)]^+$), 445.9 (10 % $[M(^{81}Br)\text{-}Et]^+$), 443.9 (11 % $[M(^{79}Br)\text{-}Et]^+$), 394.0 (7 % $[M\text{-}Br]^+$), 365.0 (12 % $[M\text{-}Et\text{-}Br]^+$), 196 (100 %).
MS-HR (CH_3CN): 473.005165, calculated for $C_{14}H_{15}Au^{79}BrN$ 473.005346 (+0.4 ppm).
Anal. Calcd for $C_{14}H_{15}AuBrN$: C, 35.46; H, 3.19; N, 2. 95. Found: C, 35.36; H, 3.19; N, 2.87.



Compound 6: AuBrPh(tpy)

A solution of $Au(OCOCF_3)_2$(tpy) (**1**) (0.100 g, 0.169 mmol, 1.00 equiv.) in THF (10.0 mL) was cooled in a dry ice/acetone bath and then PhMgBr (1.0 M in THF, 0.350 mL, 0.350 mmol, 2.07 equiv.) was added. No color change was observed upon addition. The reaction was stirred for 1 h at -78 °C and then at rt for 1 h. The solution was light yellow. THF was removed *in vacuo*. The resulting white solid was dissolved in CH_2Cl_2 (25 mL) and washed with distilled water (pH=7, 3 x 25 mL), and the organic phase turned slightly purple. The organic phase was dried over $MgSO_4$ and filtered through Celite to give a light yellow solution and solvent was removed *in vacuo* to yield **6** as an white powder, 0.083 g (94 %).

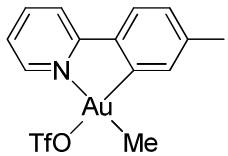
^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.61 (d, 6-C*H*, *J* = 5.1 Hz, 1H), 8.03 (td, 4-C*H*, *J* = 8.0, 1.4 Hz, 1H), 7.94 (d, 3-C*H*, *J* = 8.1 Hz, 1H), 7.63 (d, 3′-C*H*, *J* = 8.0 Hz, 1H), 7.52-7.40 (m, 5,o-C*H*, 3H), 7.25 (t, m-C*H*, *J* = 7.3 Hz, 2H), 7.19 (m, p-C*H*, 1H), 7.14 (d, 4′-C*H*, *J* = 7.8 Hz, 1H), 6.55 (s, 6′-C*H*, 1H), 2.18 (s, ArC*H₃*, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 163.1, 150.8, 149.7, 143.3, 142. 8, 141.6, 140.9, 134.8, 133.6, 129.8, 128.9, 126.2, 125.3, 124.4, 120.3, 22.1.

MS (EI in CH_3CN): *m/z* = 522.9 (0.6 % $[M(^{81}Br)]^+$), 521.0 (0.7 % $[M(^{79}Br)]^+$), 442.0 (0.1 % $[M\text{-}Br]^+$), 365.0 (4 % $[M\text{-}Ph\text{-}Br]^+$), 245.1 (31 %), 244.1 (100 %).

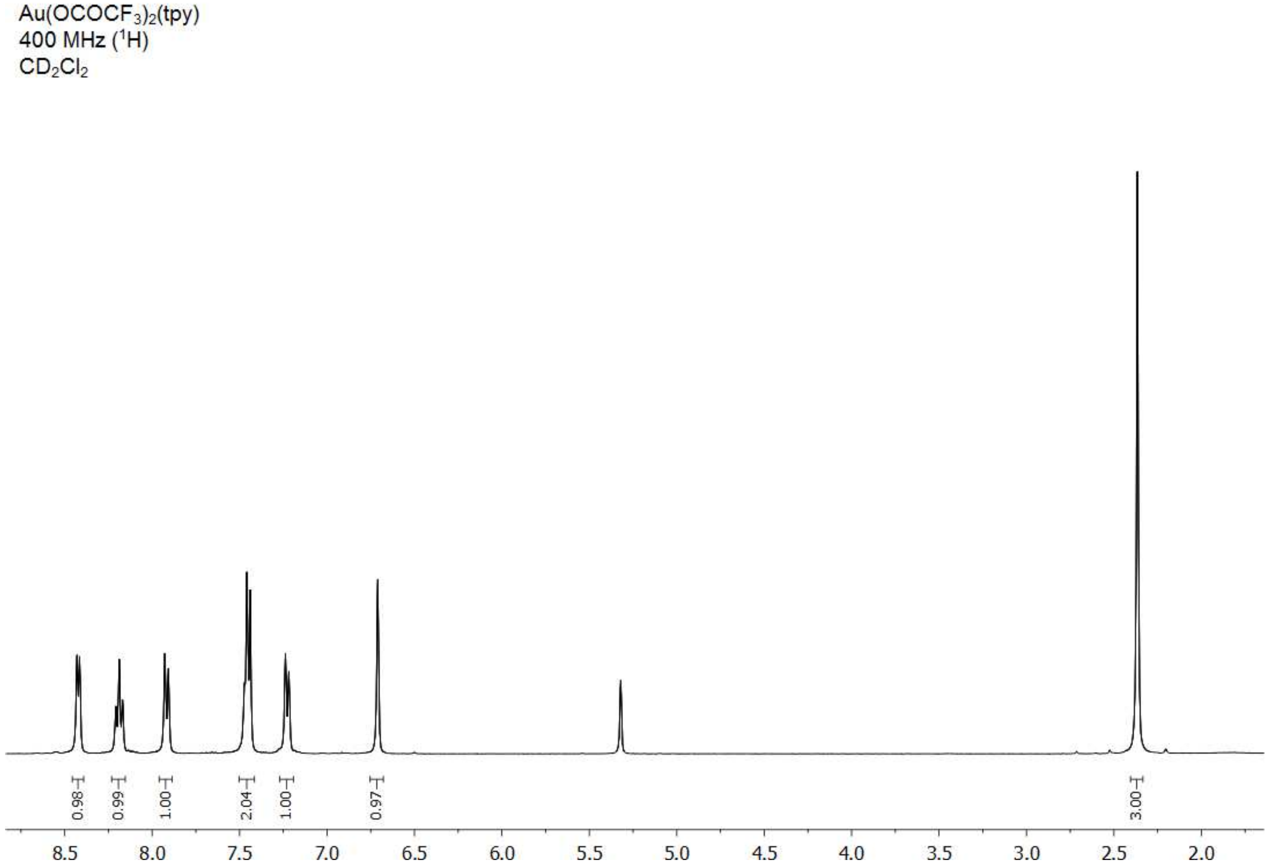
MS-HR (CH_3CN): 521.006245, calculated for $C_{18}H_{15}Au^{79}BrN$ 521.005346 (-1.7 ppm).

Anal. Calcd for $C_{18}H_{15}AuBrN$: C, 41.40; H, 2.90; N, 2.68. Found: C, 41.91; H, 3.40; N, 2.63.

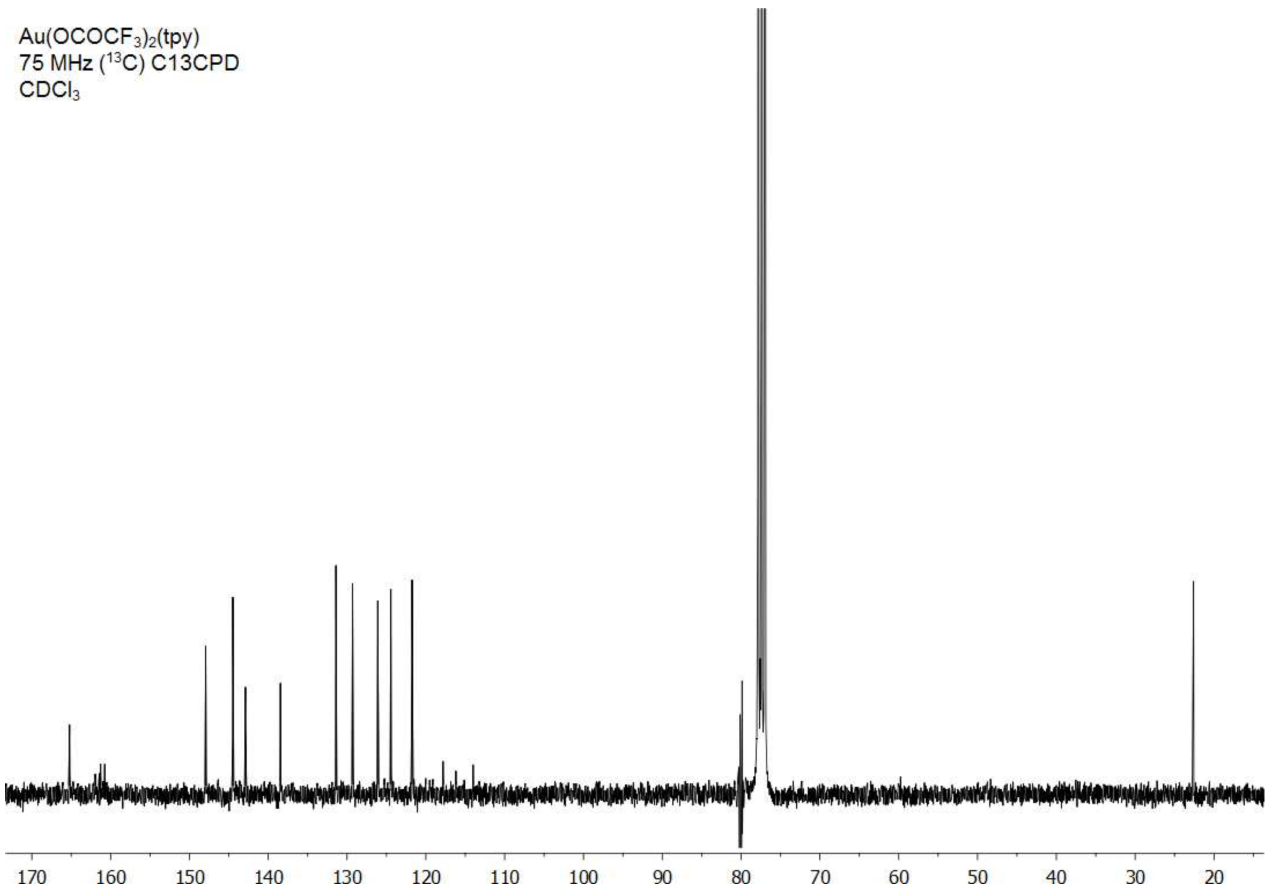


Compound 7: AuMe(OTf)(tpy)

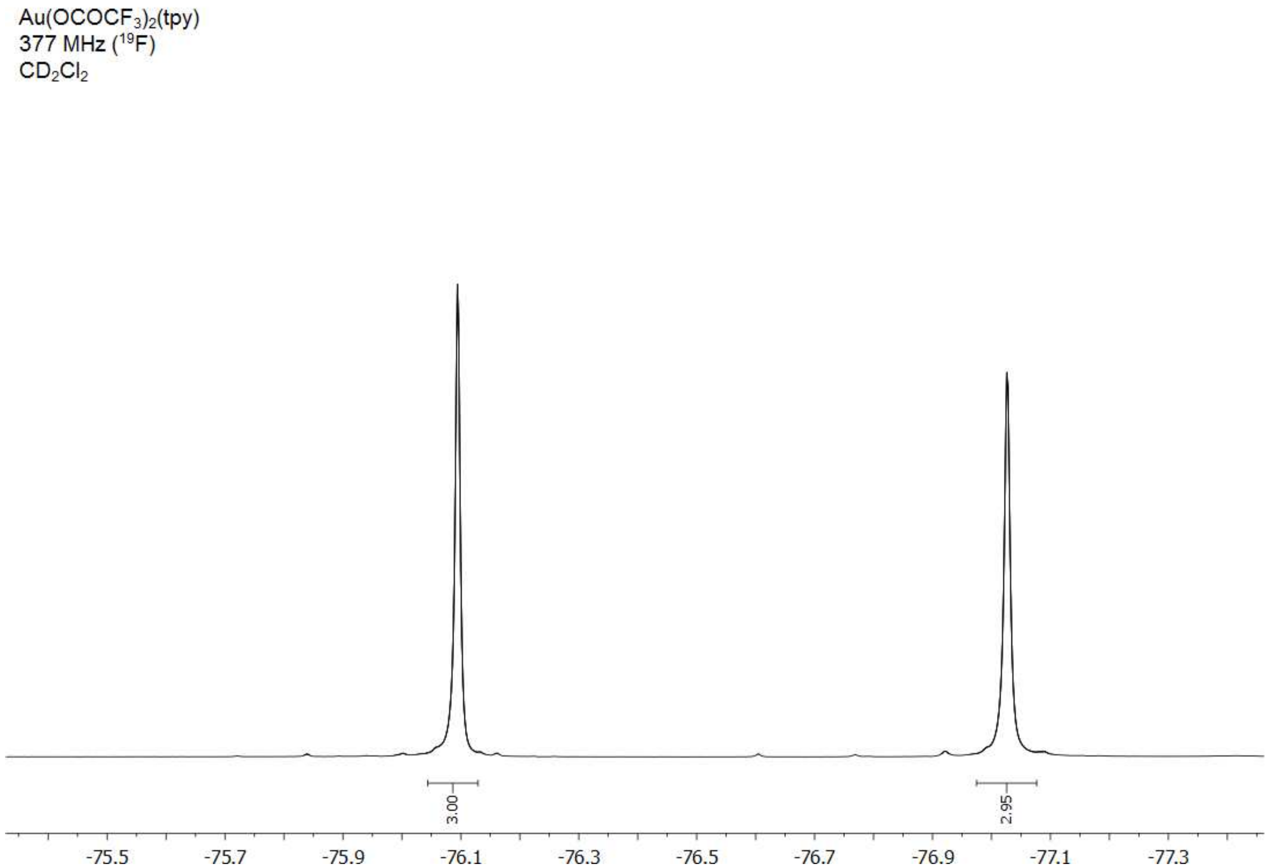
In an NMR tube, AuBrMe(tpy) (**4**), an excess of AgOTf and $CDCl_3$ was added. ^{1}H NMR spectra was acquired after approximately 24 hours. The only observed species was AuMe(OTf)(tpy) (**7**).
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (d, 6-C*H*, *J* = 5.6 Hz, 1H), 8.03 (td, 4-C*H*, *J* = 8.1, 1.6 Hz, 1H), 7.92 (d, 3-C*H*, *J* = 8.1 Hz, 1H), 7.61 (d, 3´-C*H*, *J* = 7.9 Hz, 1H), 7.57-7.50 (m, 5-C*H*, 1H), 7.22 (s, 6´-C*H*, 1H), 7.19 (d, 4´-C*H*, *J* = 7.9 Hz, 1H), 2.42 (s, ArCH_3, 3H), 1.66 (s, AuCH_3, 3H).



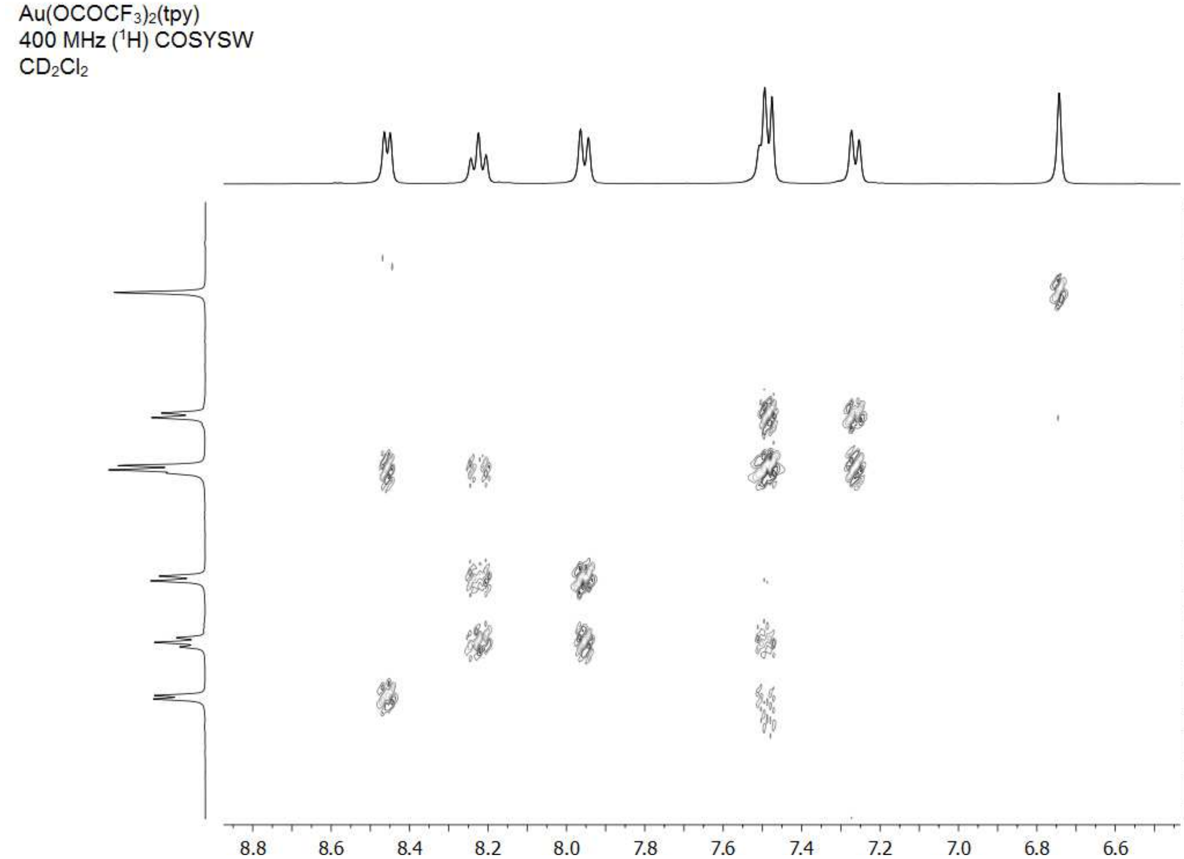
[1]H NMR spectrum of $Au(OCOCF_3)_2$(tpy) (**1**)



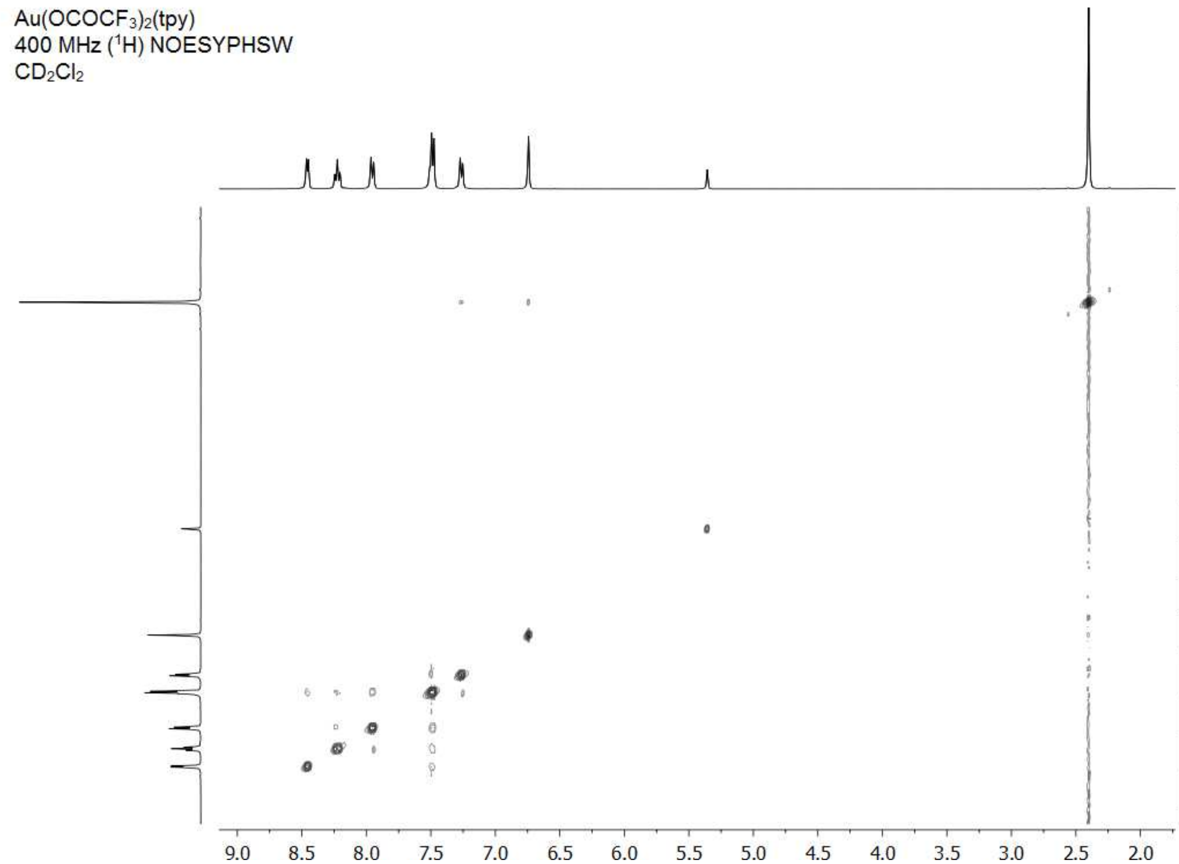
[13]C NMR spectrum of $Au(OCOCF_3)_2$(tpy) (**1**)



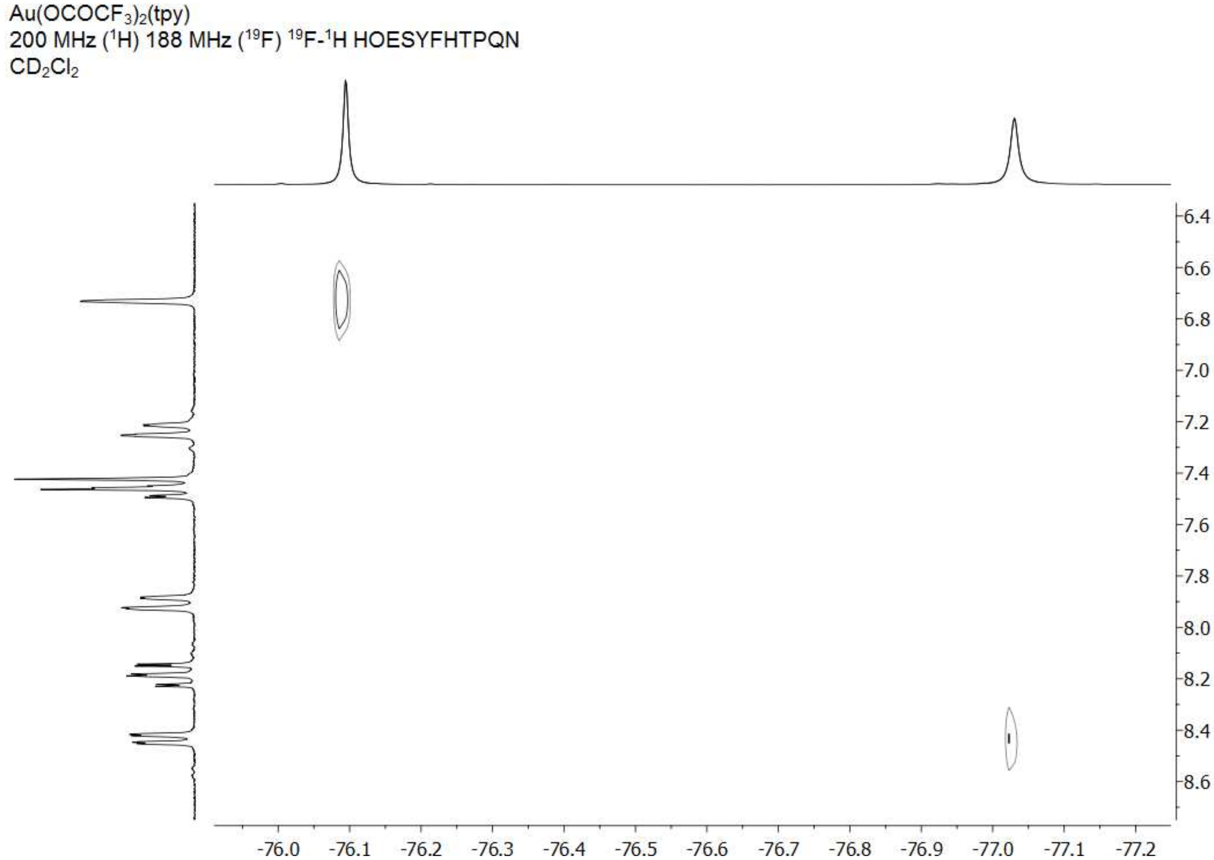
[19]F NMR spectrum of Au($OCOCF_3$)$_2$(tpy) (**1**)



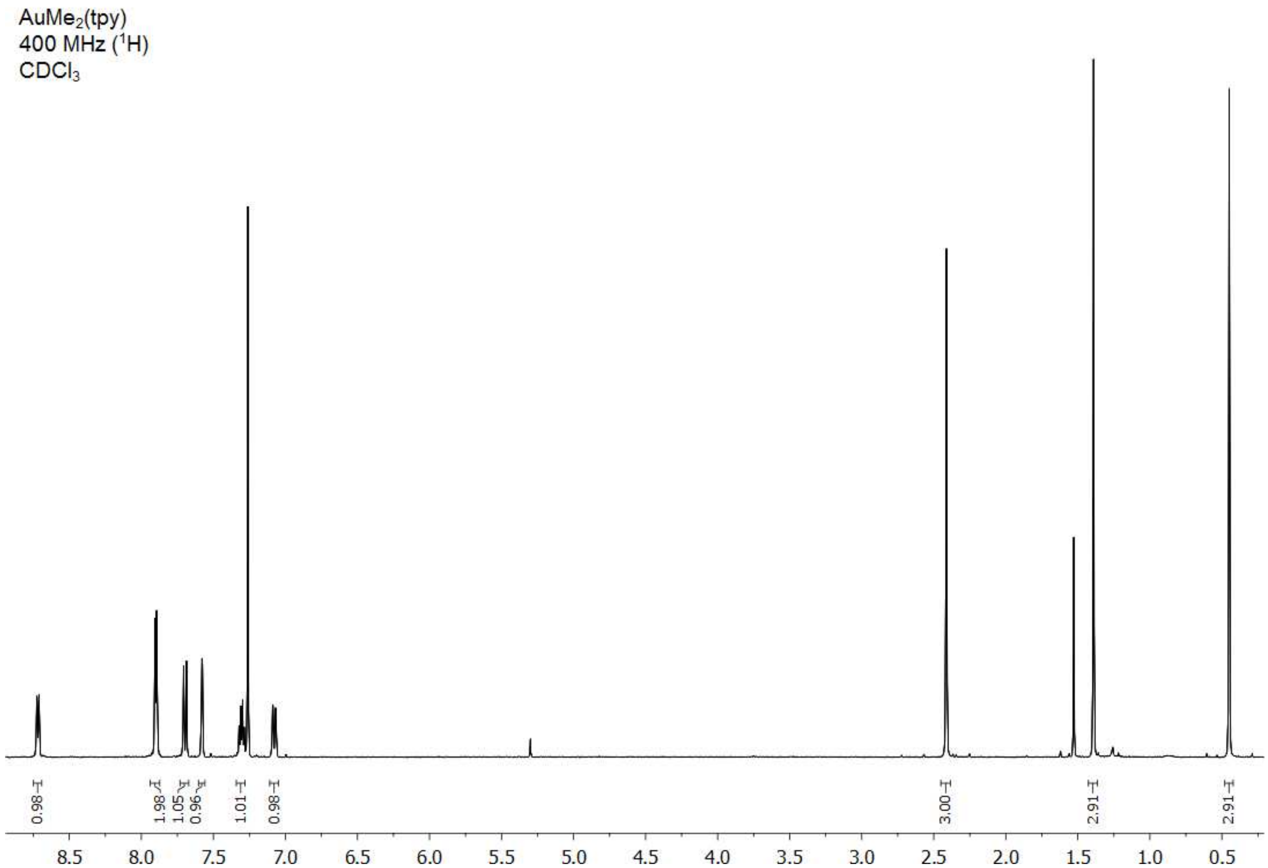
^1H COSY NMR spectrum of $Au(OCOCF_3)_2(tpy)$ (**1**)



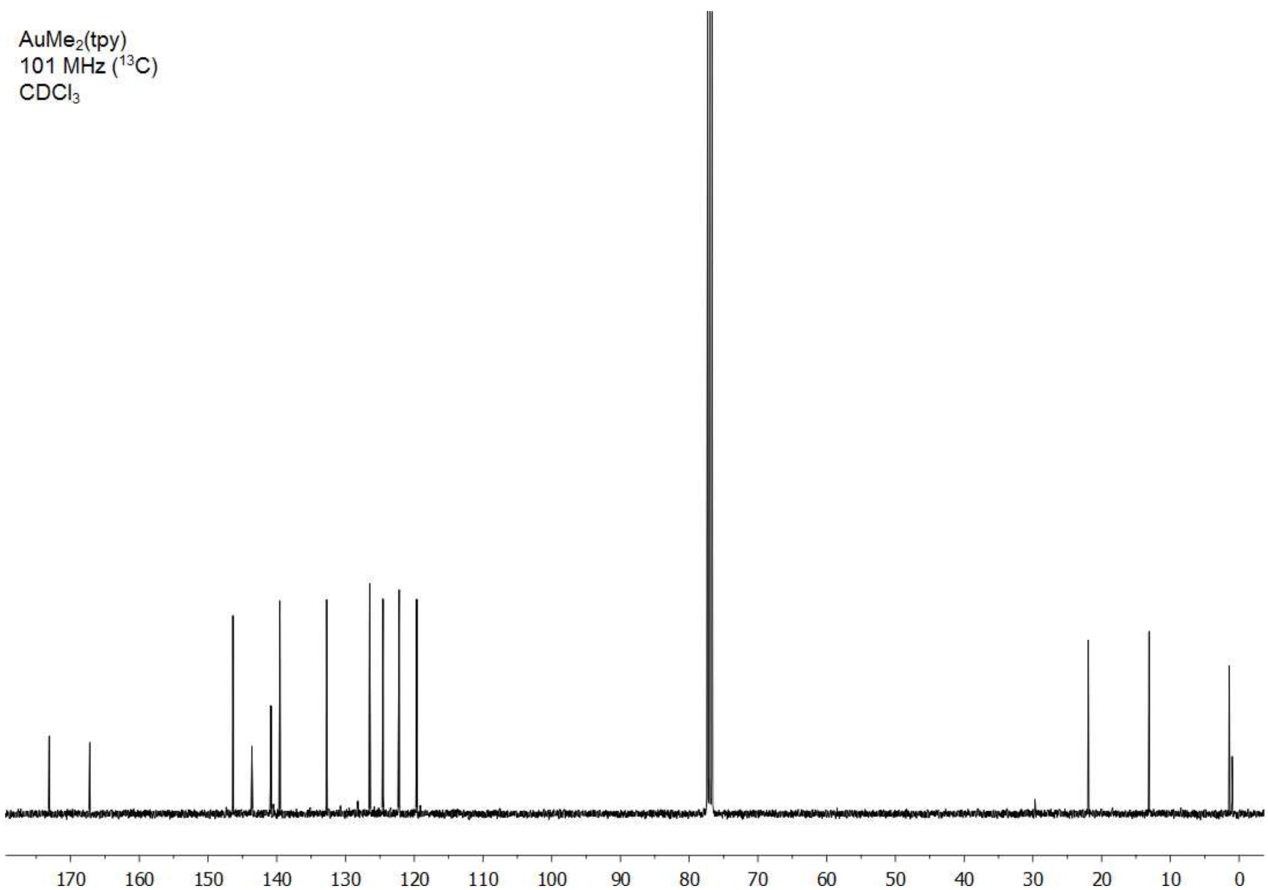
[1]H NOESY NMR spectrum of $Au(OCOCF_3)_2(tpy)$ (**1**)



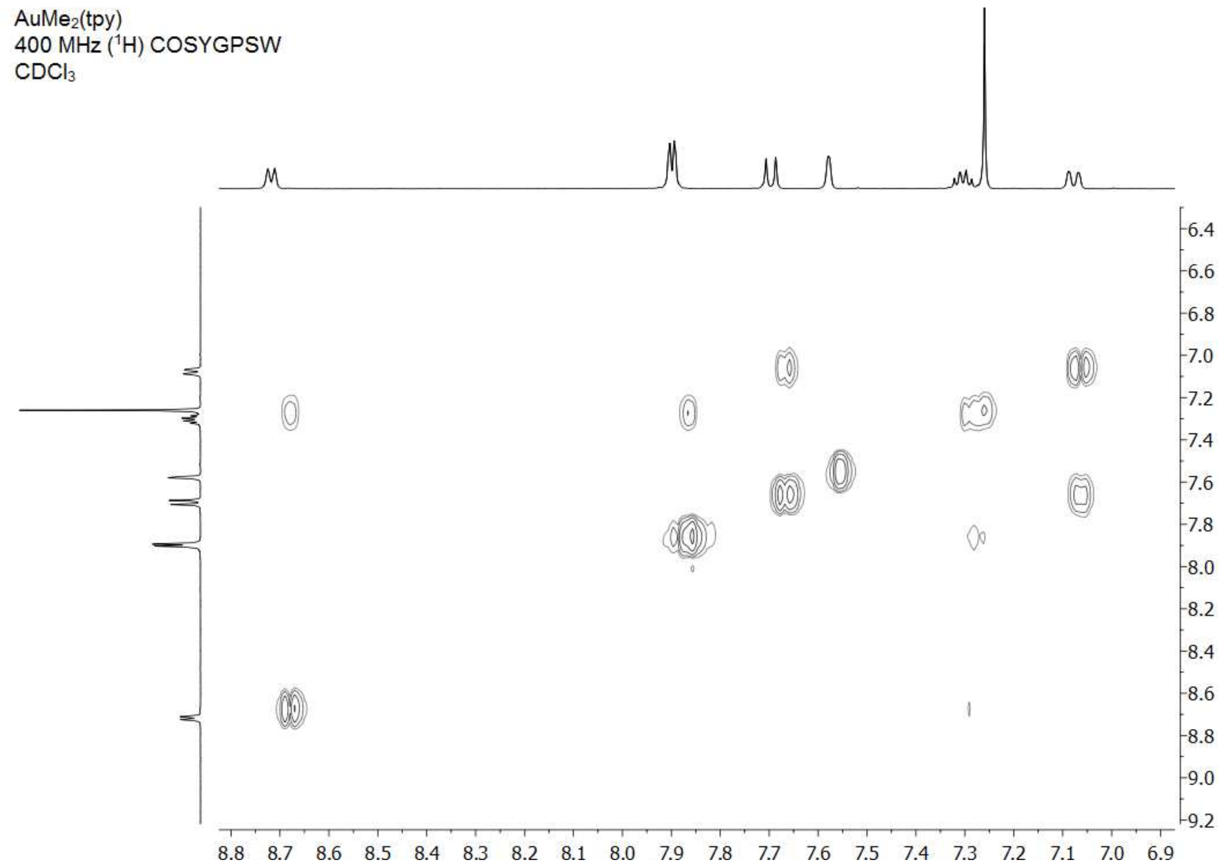
^{19}F-^{1}H HOESY NMR spectrum of $Au(OCOCF_3)_2(tpy)$ (**1**)



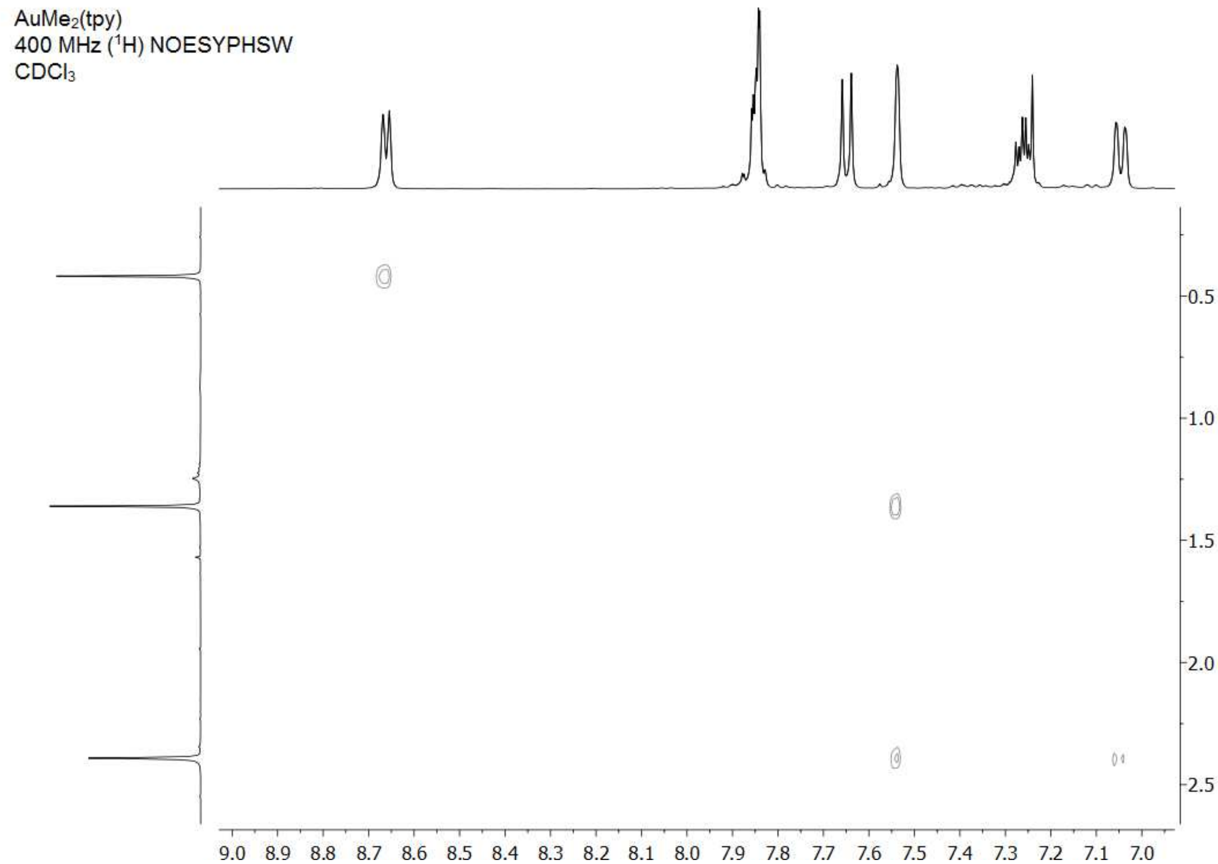
^{1}H NMR spectrum of $AuMe_2$(tpy) (**2**)



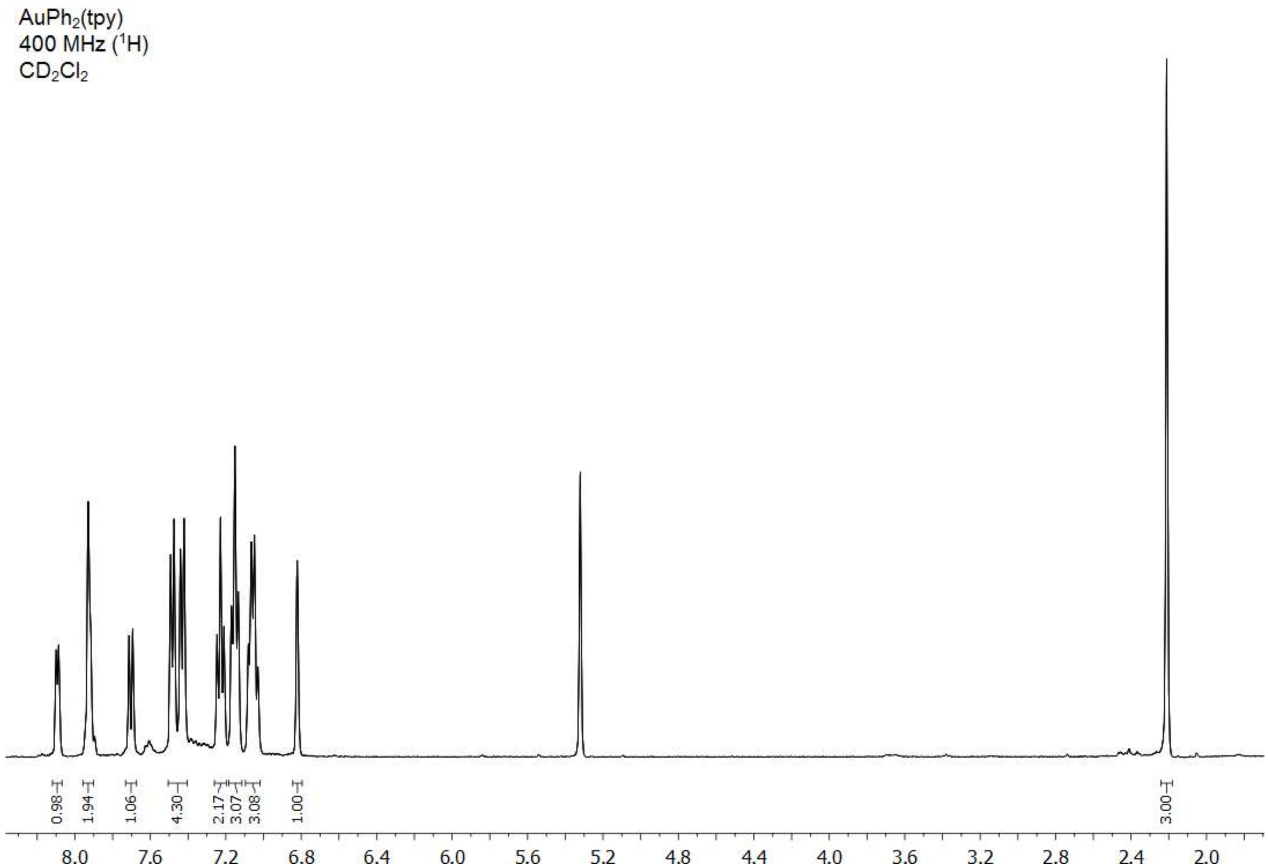
^{13}C NMR spectrum of AuMe$_2$(tpy) (**2**)



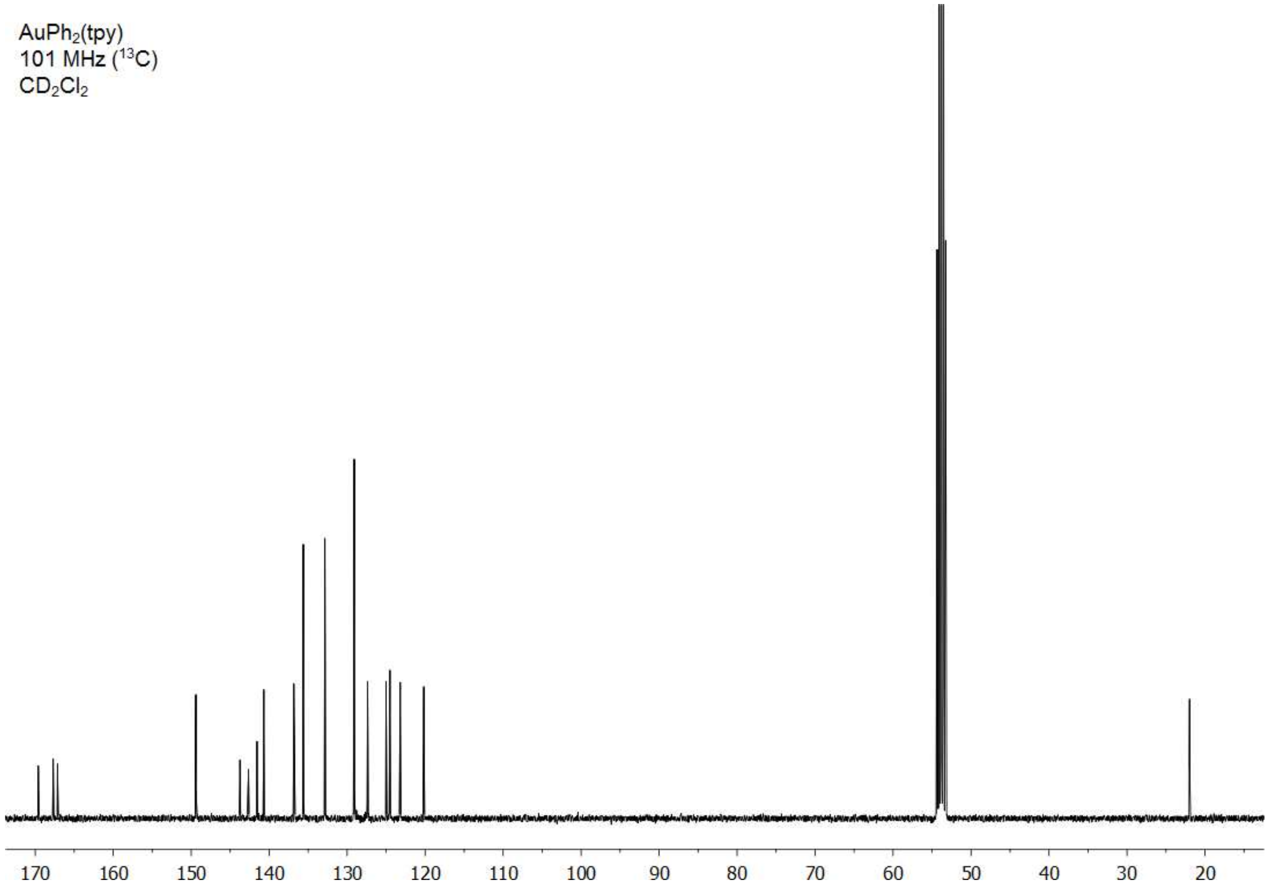
[1]H COSY NMR spectrum of $AuMe_2$(tpy) (**2**)



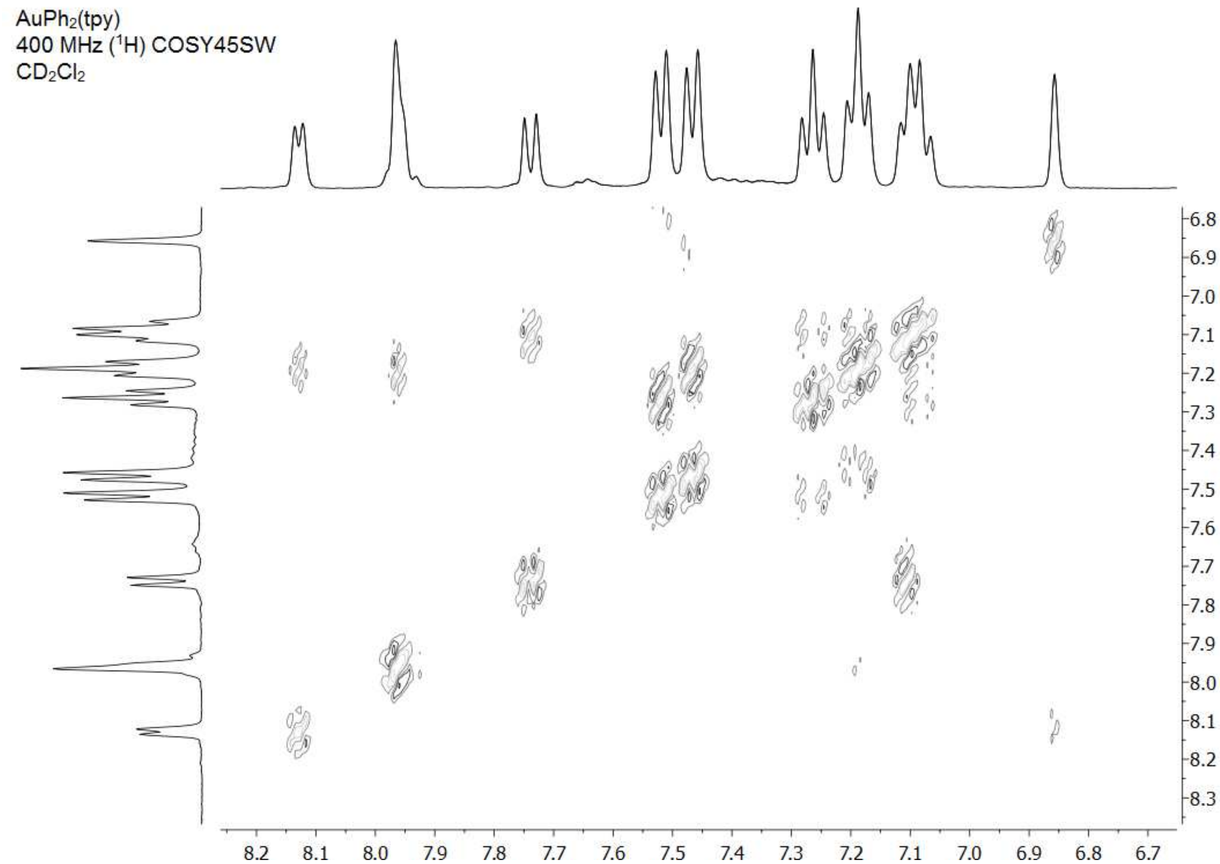
^{1}H NOESY NMR spectrum of $AuMe_2$(tpy) (**2**)



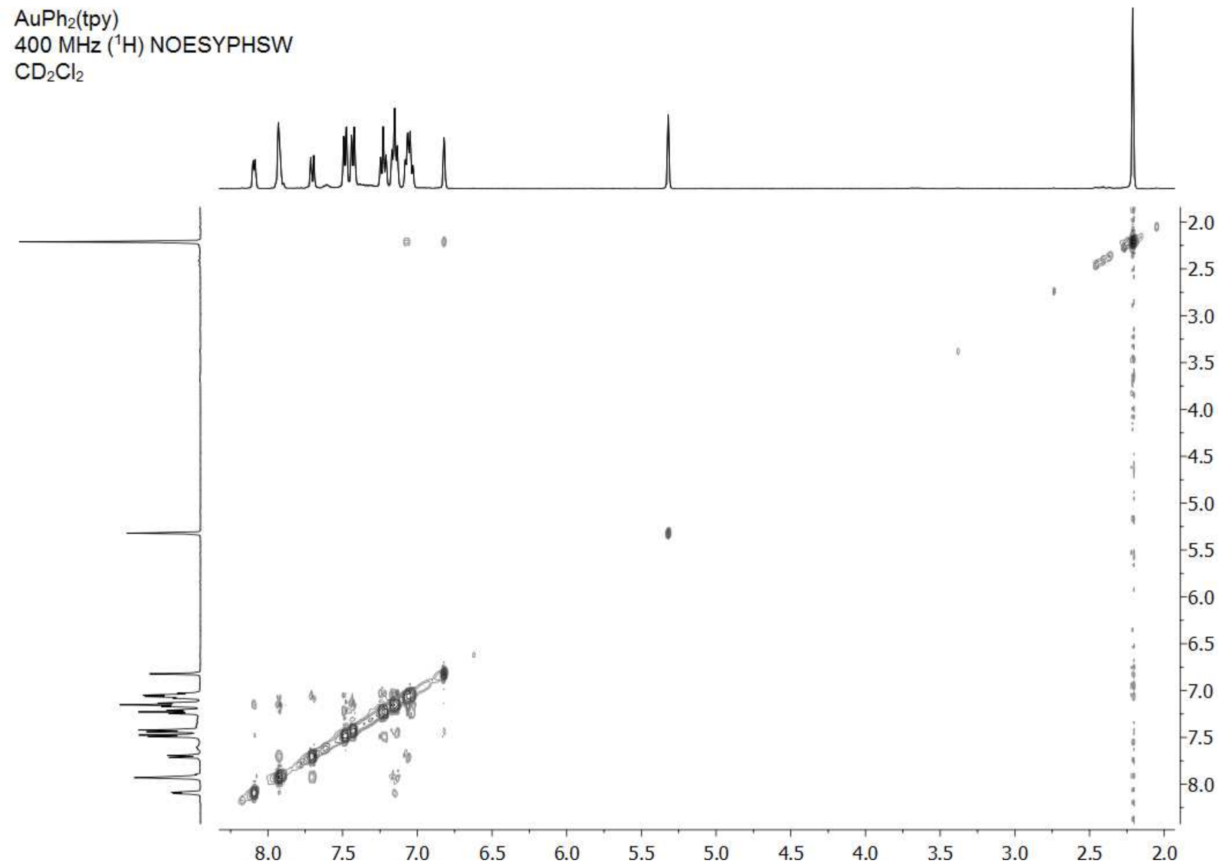
^{1}H NMR spectrum of $AuPh_2$(tpy) (**3**)



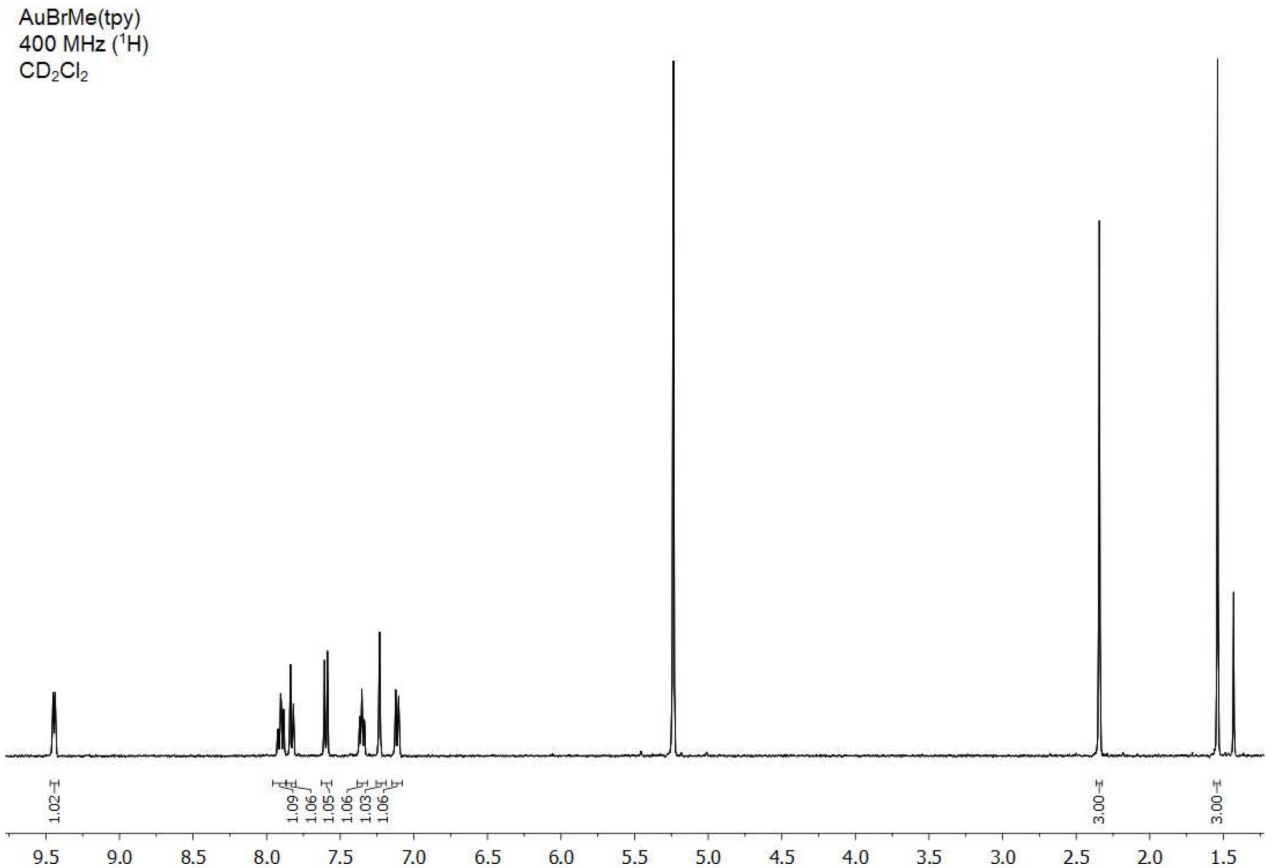
^{13}C NMR spectrum of $AuPh_2$(tpy) (**3**)



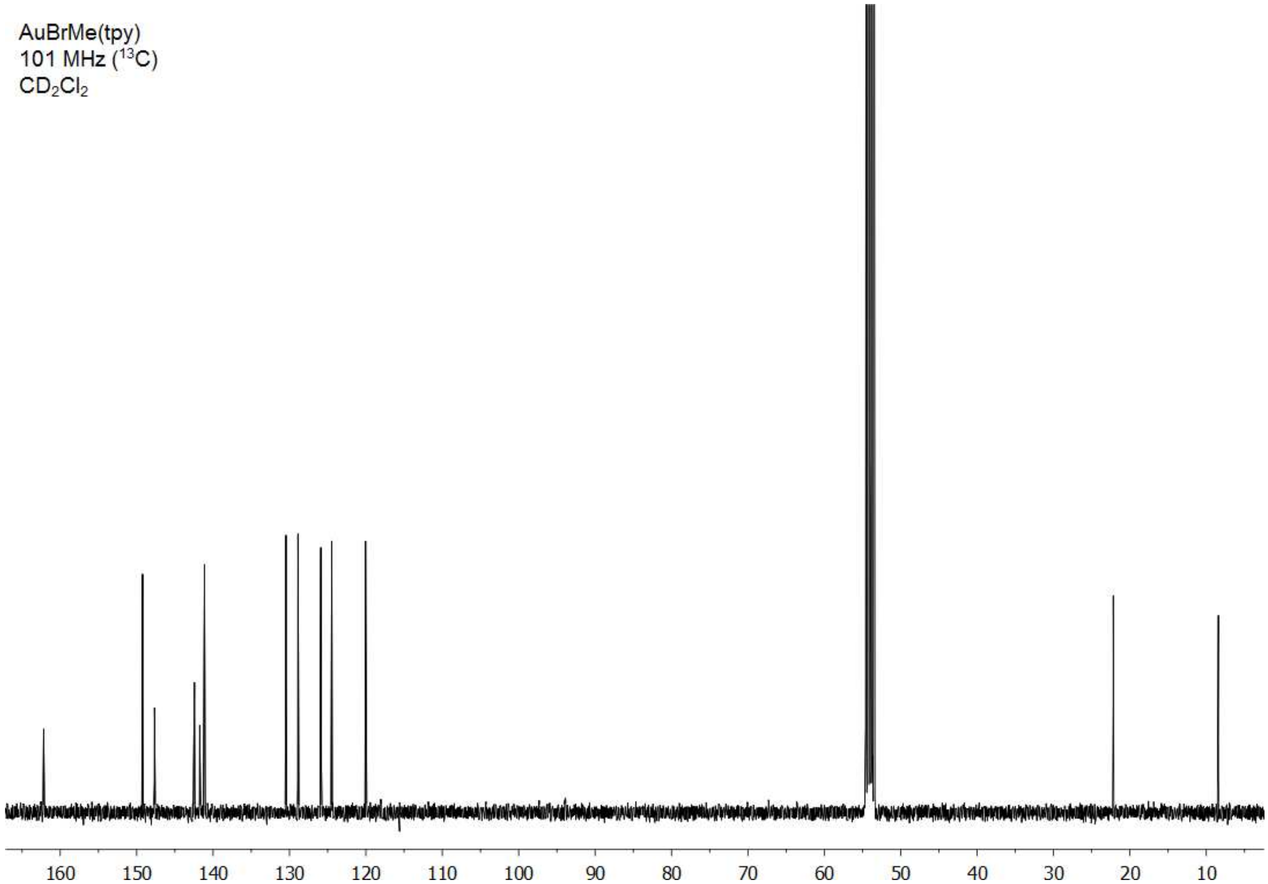
^{1}H COSY NMR spectrum of $AuPh_2$(tpy) (**3**)



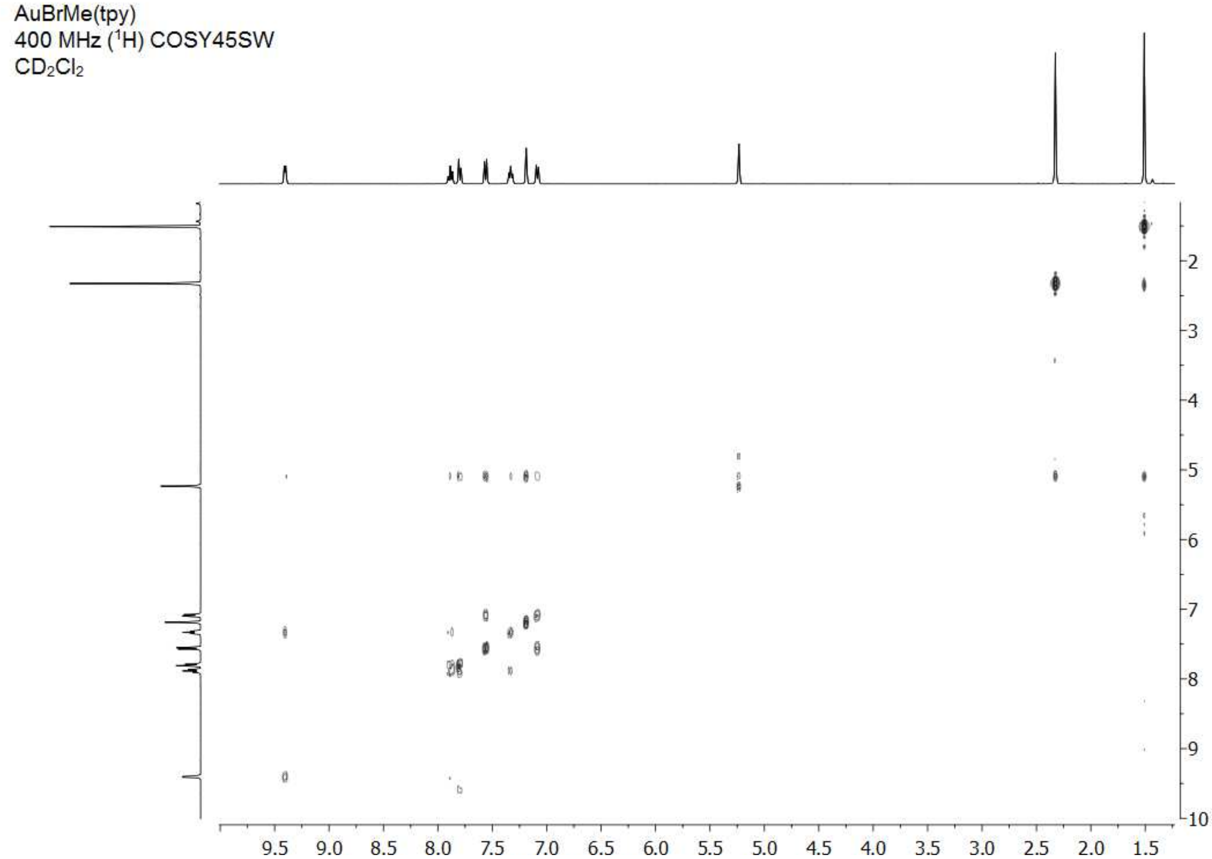
[1]H NOESY NMR spectrum of $AuPh_2$(tpy) (**3**)



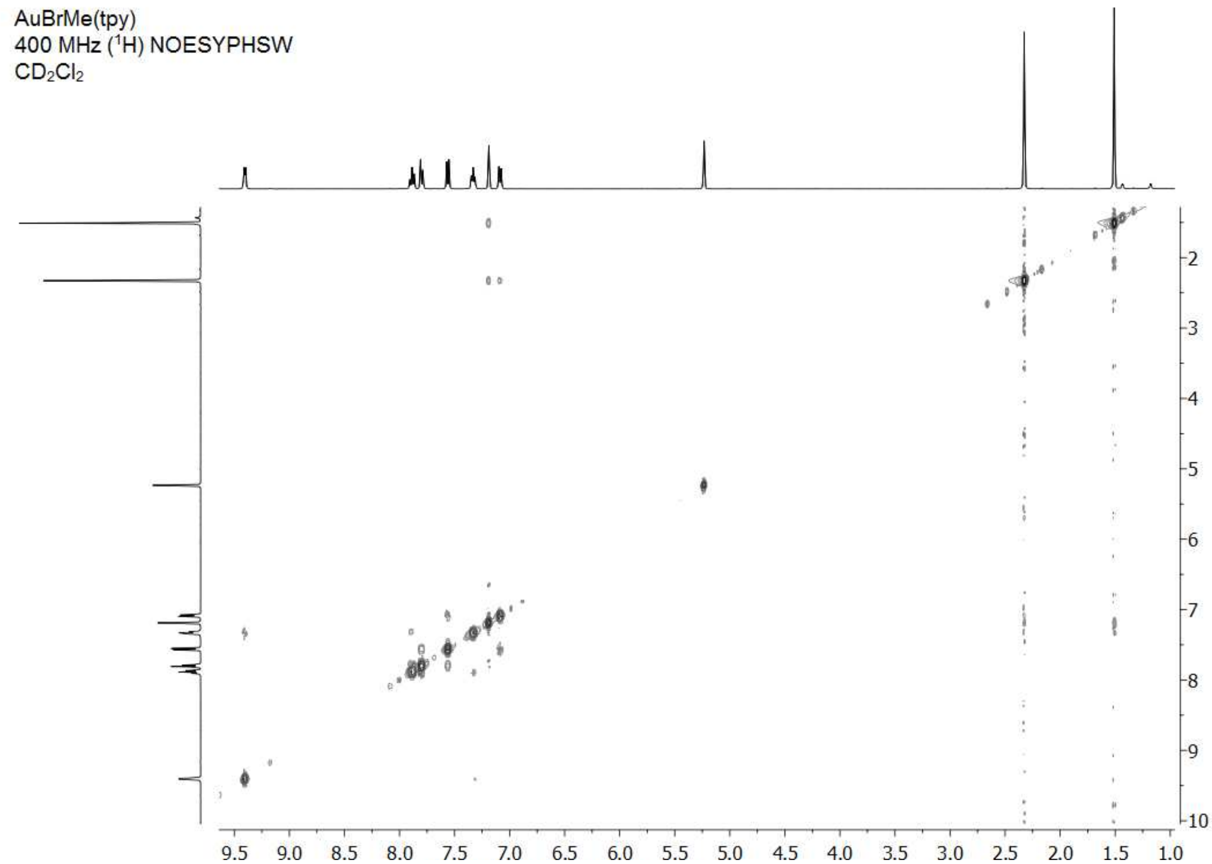
^{1}H NMR spectrum of AuBrMe(tpy) (**4**)



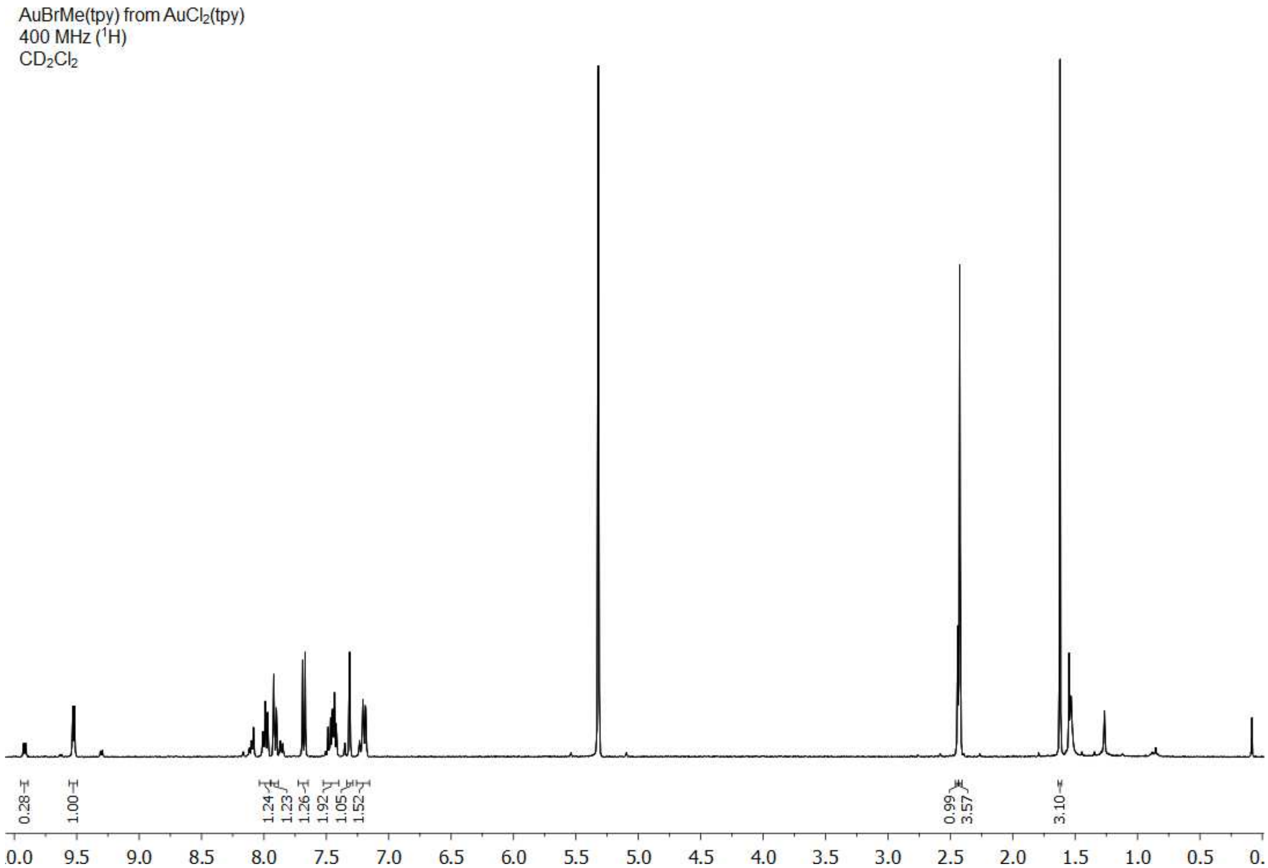
^{13}C NMR spectrum of AuBrMe(tpy) (**4**)



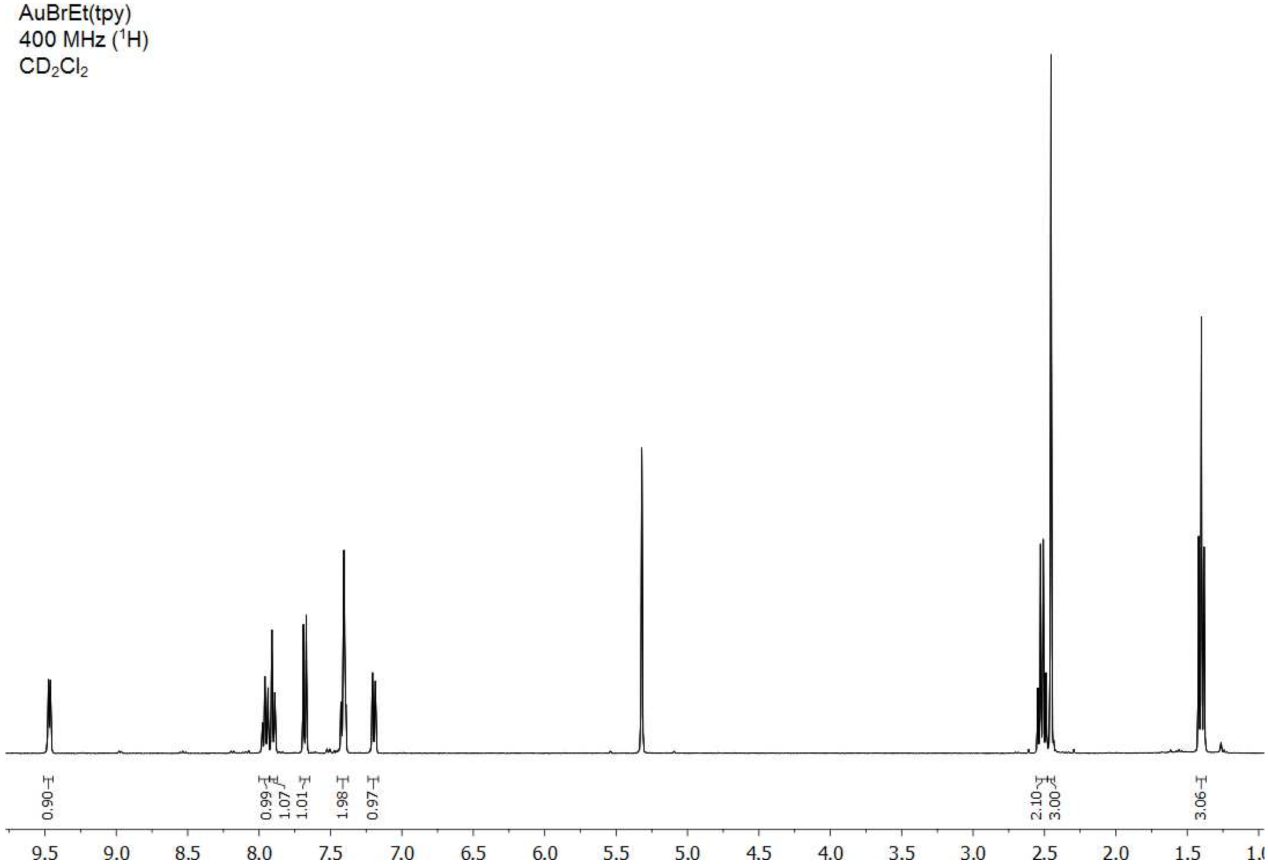
[1]H COSY NMR spectrum of AuBrMe(tpy) (**4**)



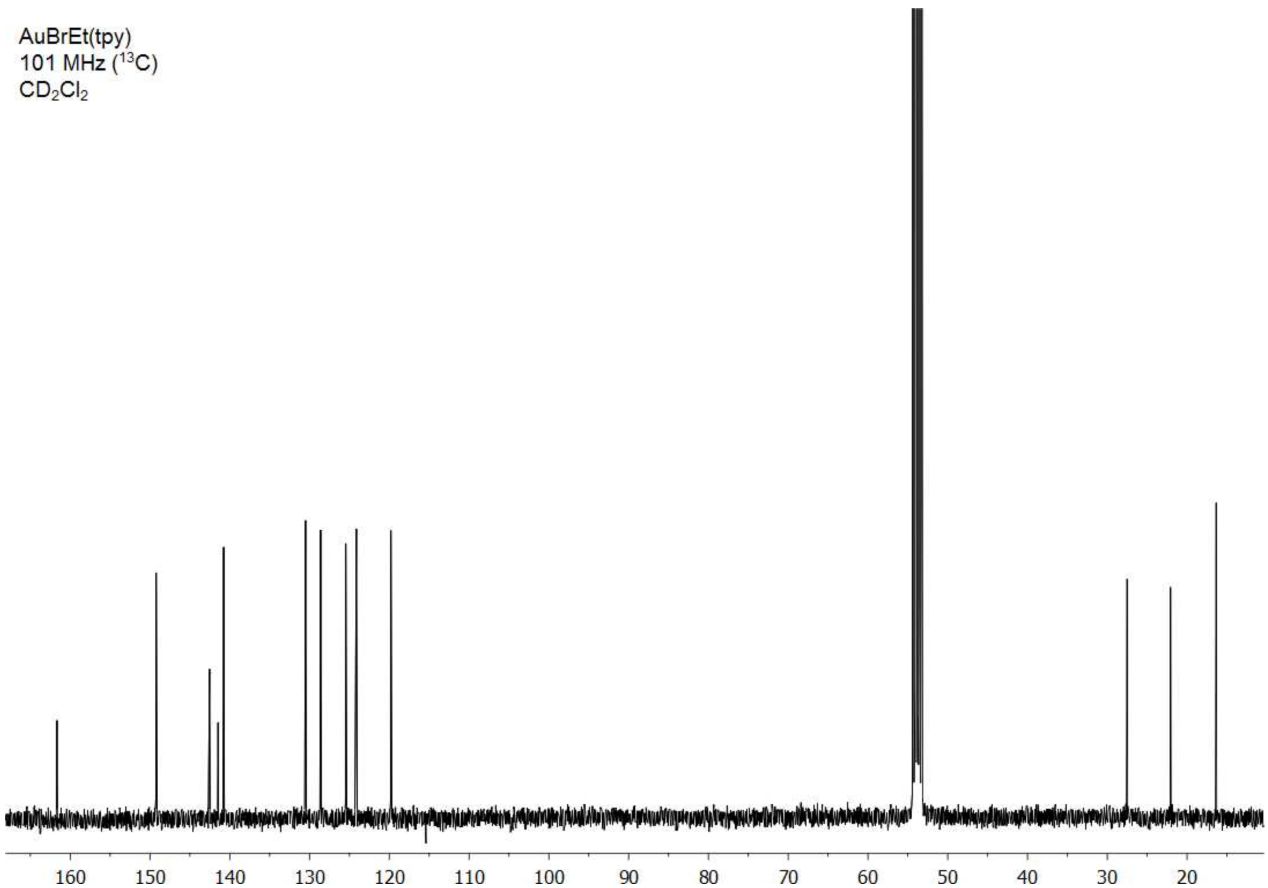
^{1}H NOESY NMR spectrum of AuBrMe(tpy) (**4**)



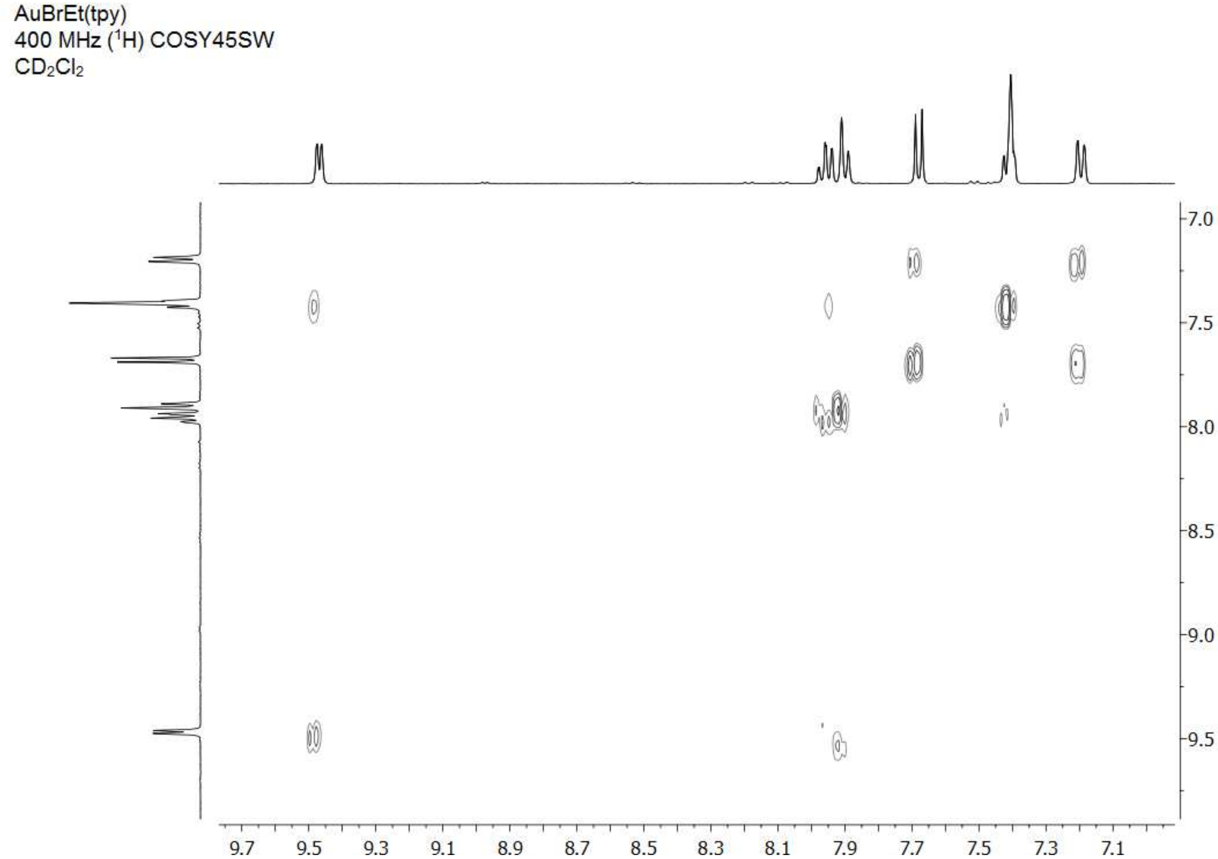
^1H NMR spectrum of AuBrMe(tpy) (**4**) when attempted synthesis from $AuCl_2$(tpy)



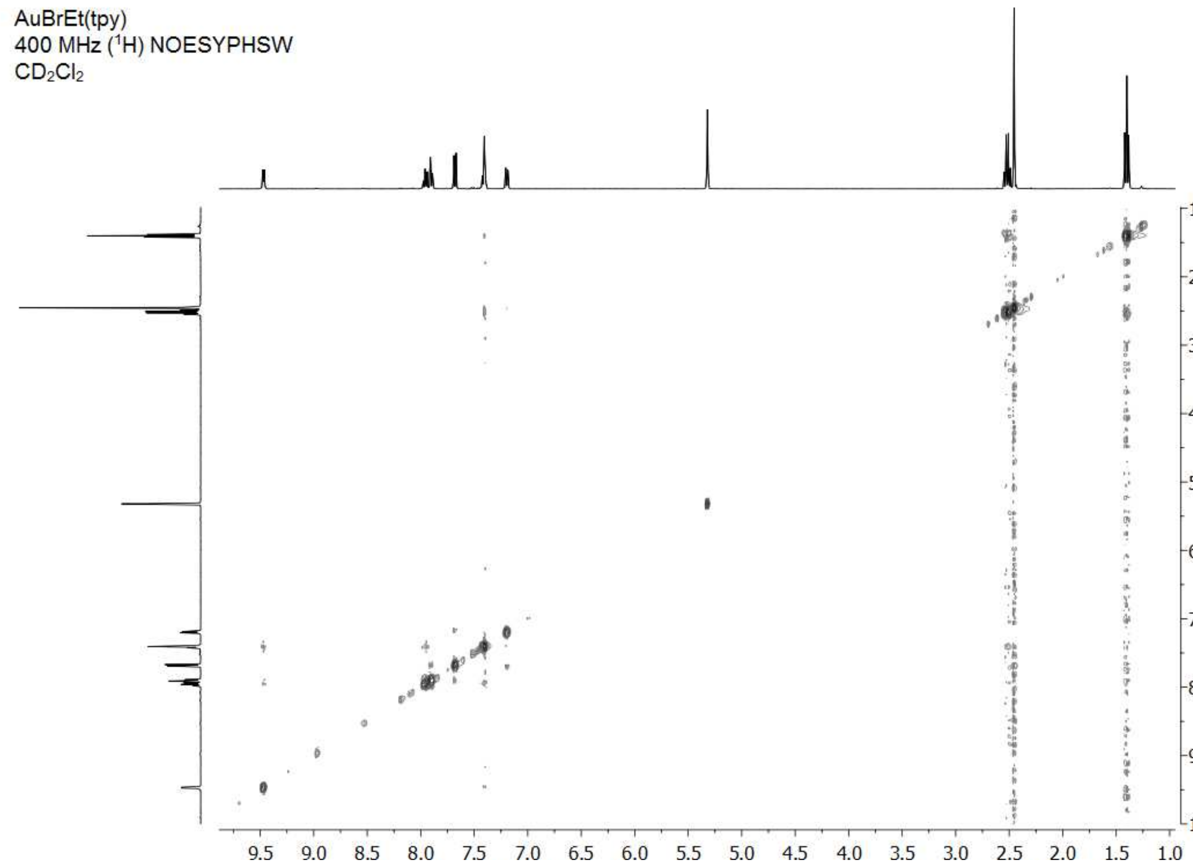
^{1}H NMR spectrum of AuBrEt(tpy) (**5**)



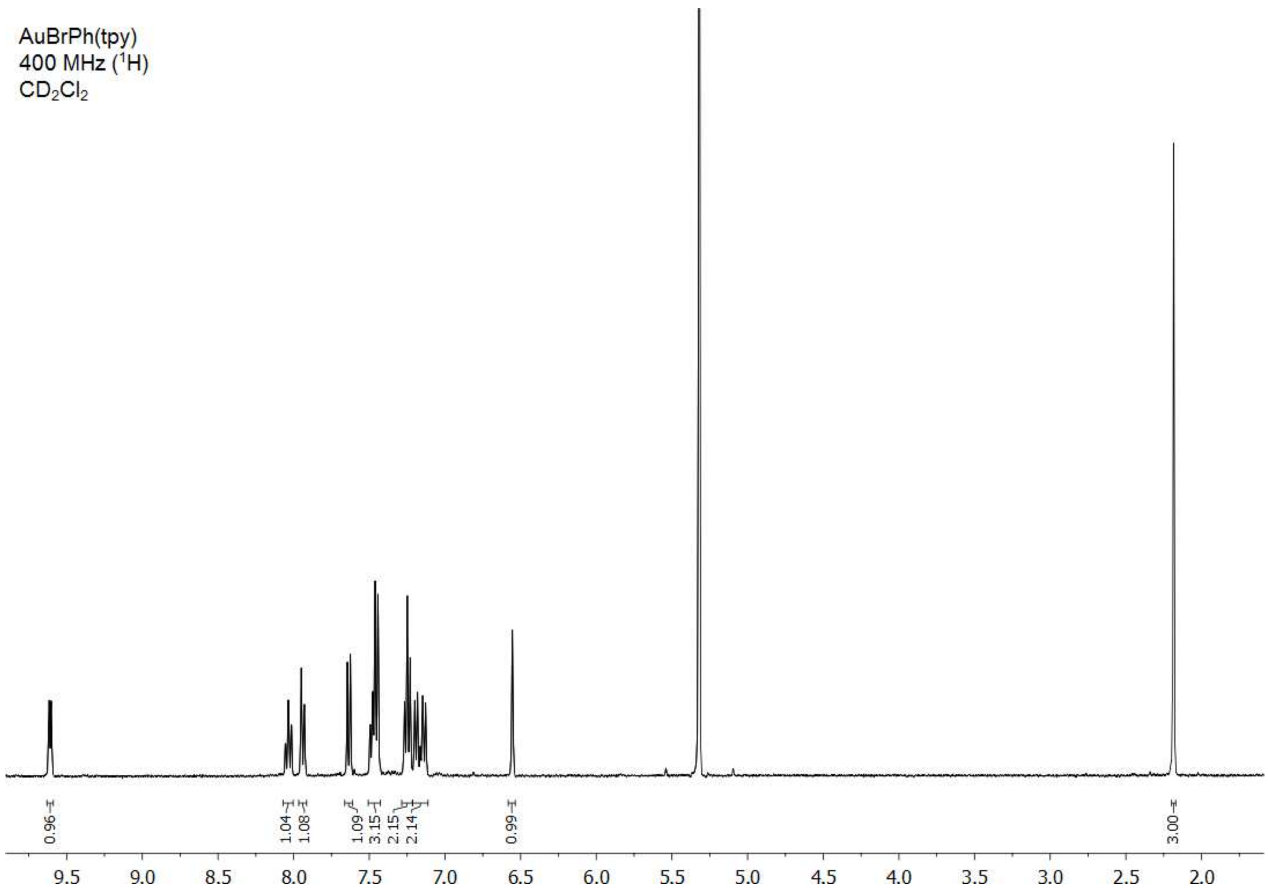
^{13}C NMR spectrum of AuBrEt(tpy) (**5**)



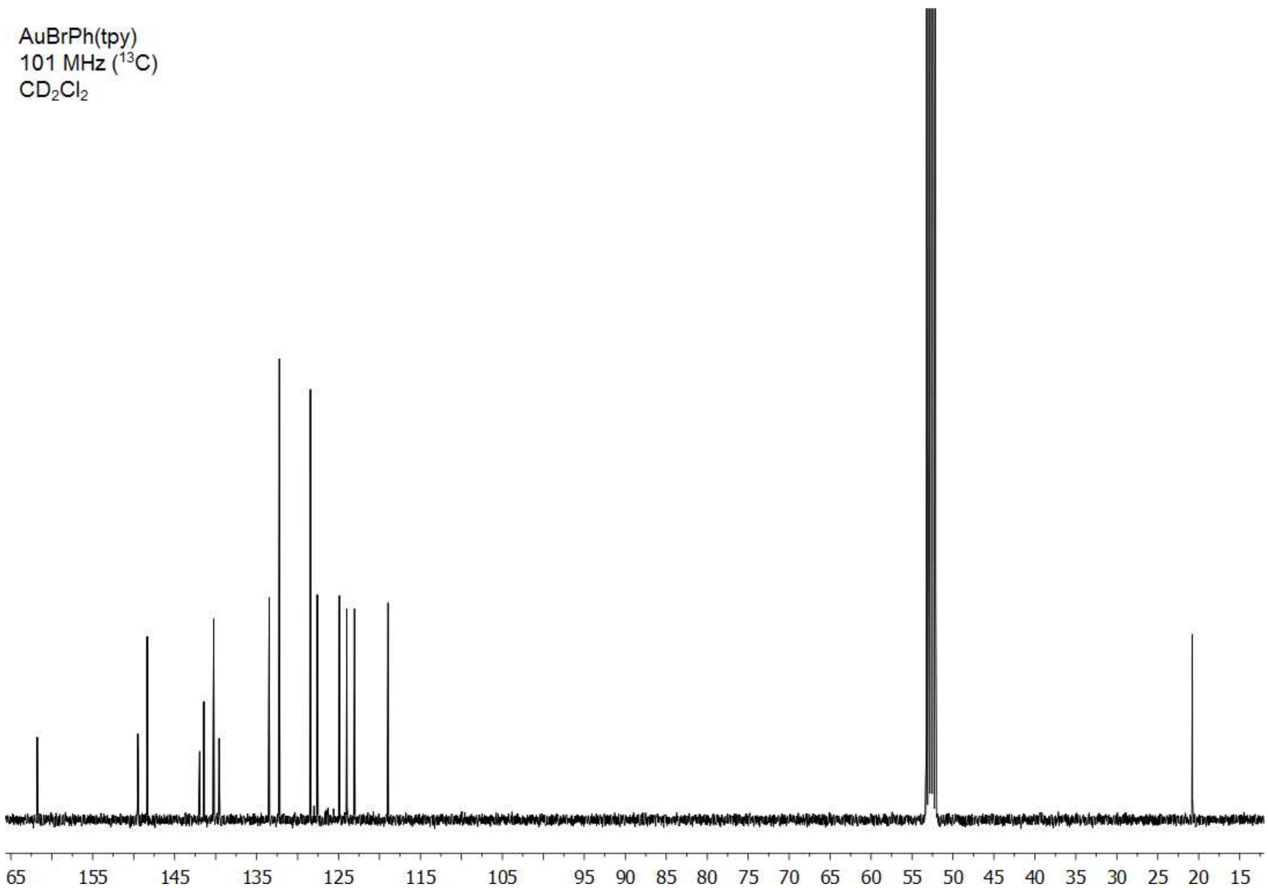
^{1}H COSY NMR spectrum of AuBrEt(tpy) (**5**)



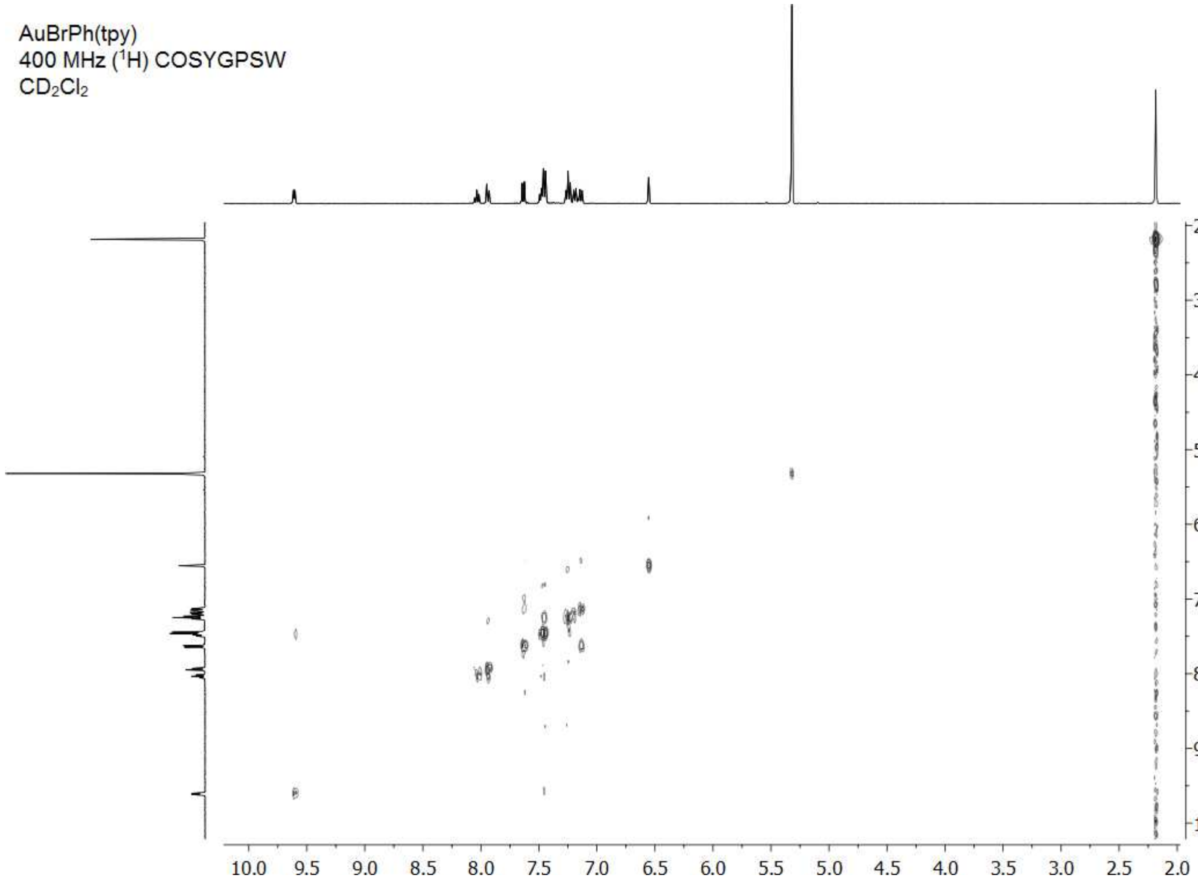
^{1}H NOESY NMR spectrum of AuBrEt(tpy) (**5**)



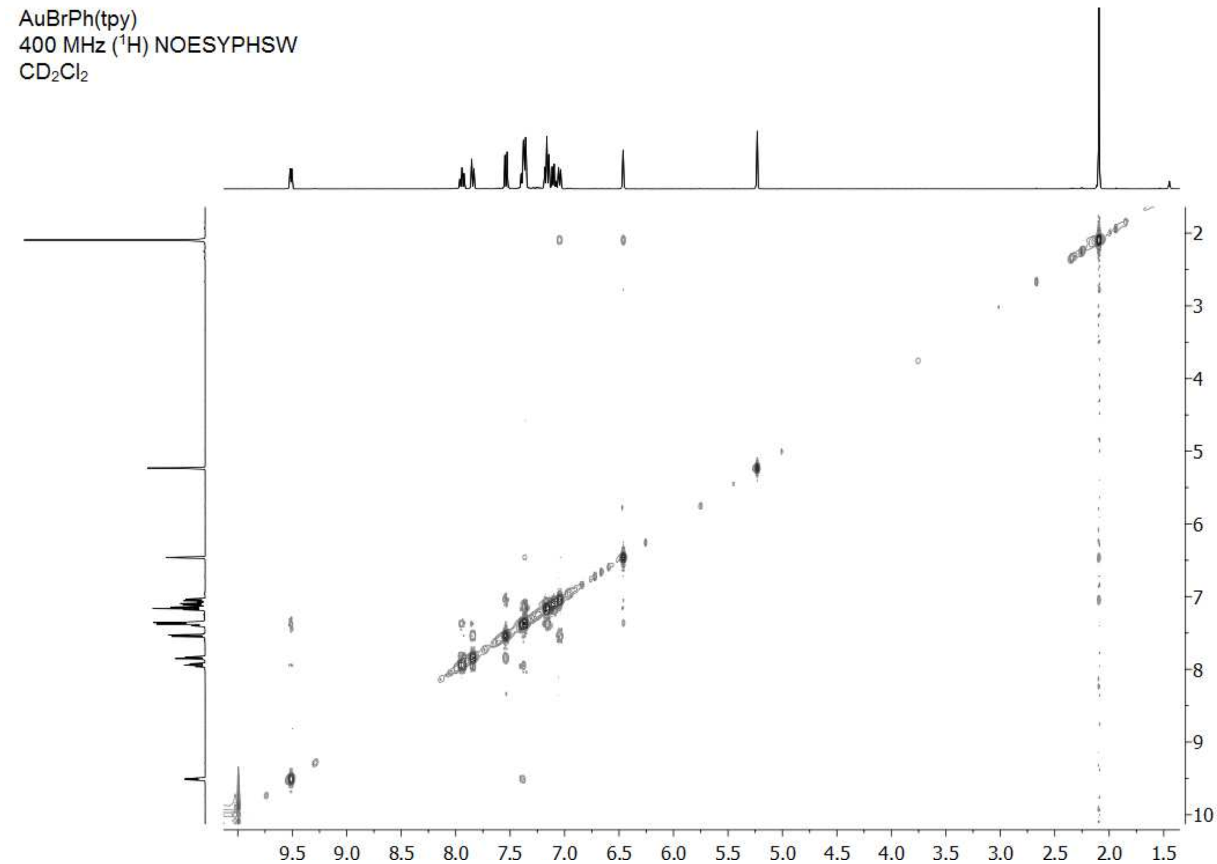
^{1}H NMR spectrum of AuBrPh(tpy) (**6**)



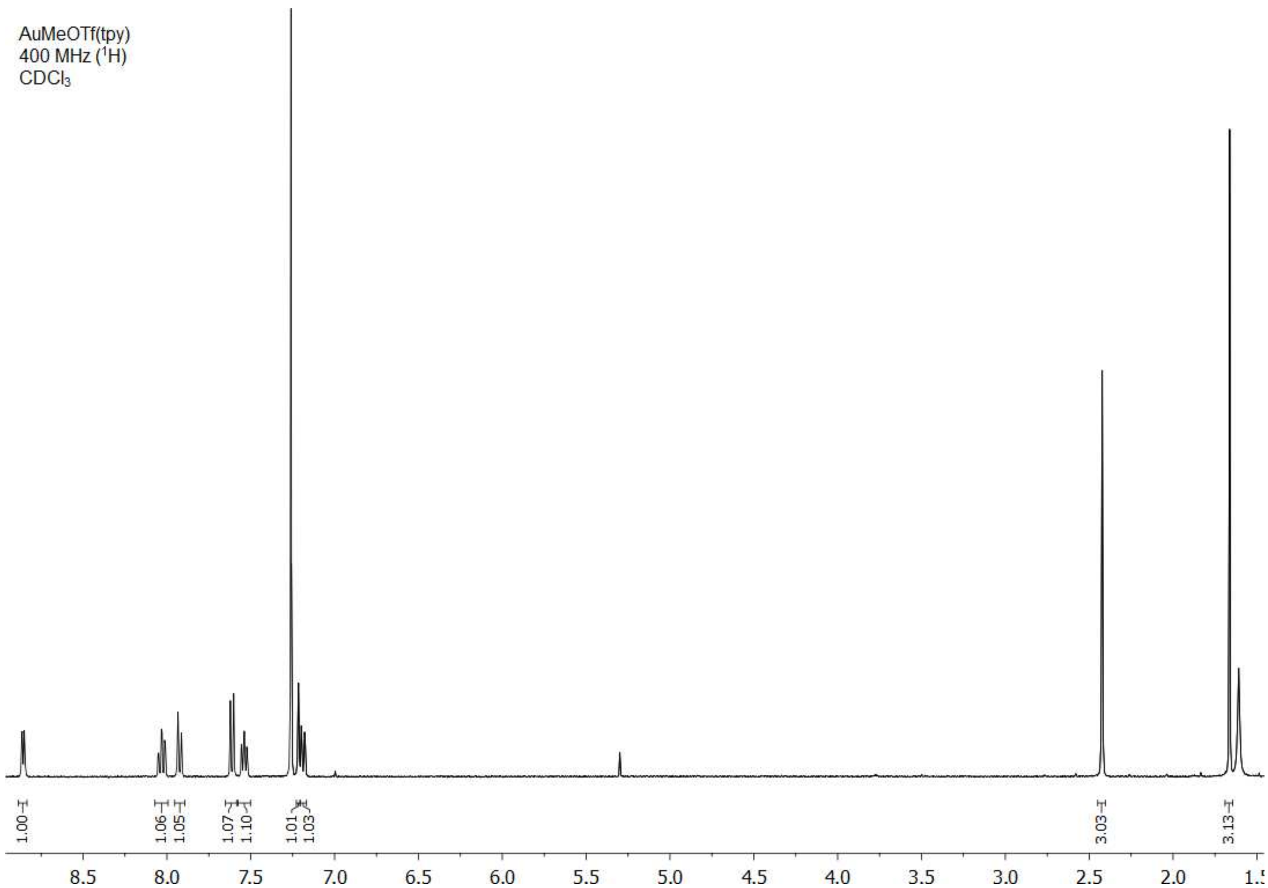
^{13}C NMR spectrum of AuBrPh(tpy) (**6**)



[1]H COSY NMR spectrum of AuBrPh(tpy) (**6**)



[1]H NOESY NMR spectrum of AuBrPh(tpy) (**6**)



[1]H NMR spectrum of AuMeOTf(tpy) (**7**)

Crystallographic Methods. Date collection was performed on a Bruker Apex II CCD Diffractometer. Data integration and cell refinement with SAINT-Plus (Bruker AXS, Inc. SAINT-Plus; Bruker AXS, Inc.: Madison, Wisconsin, USA, 2007), absorption correction by SADABS (Bruker AXS, Inc. SADABS; Bruker AXS, Inc.: Madison, Wisconsin, USA, 2007), structure solution by SHELXTL (Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2008**, *64*, 112-122). Crystals of **1** and **2** were grown from dichloromethane layered with pentane.

Compound **1** Crystallographic Data

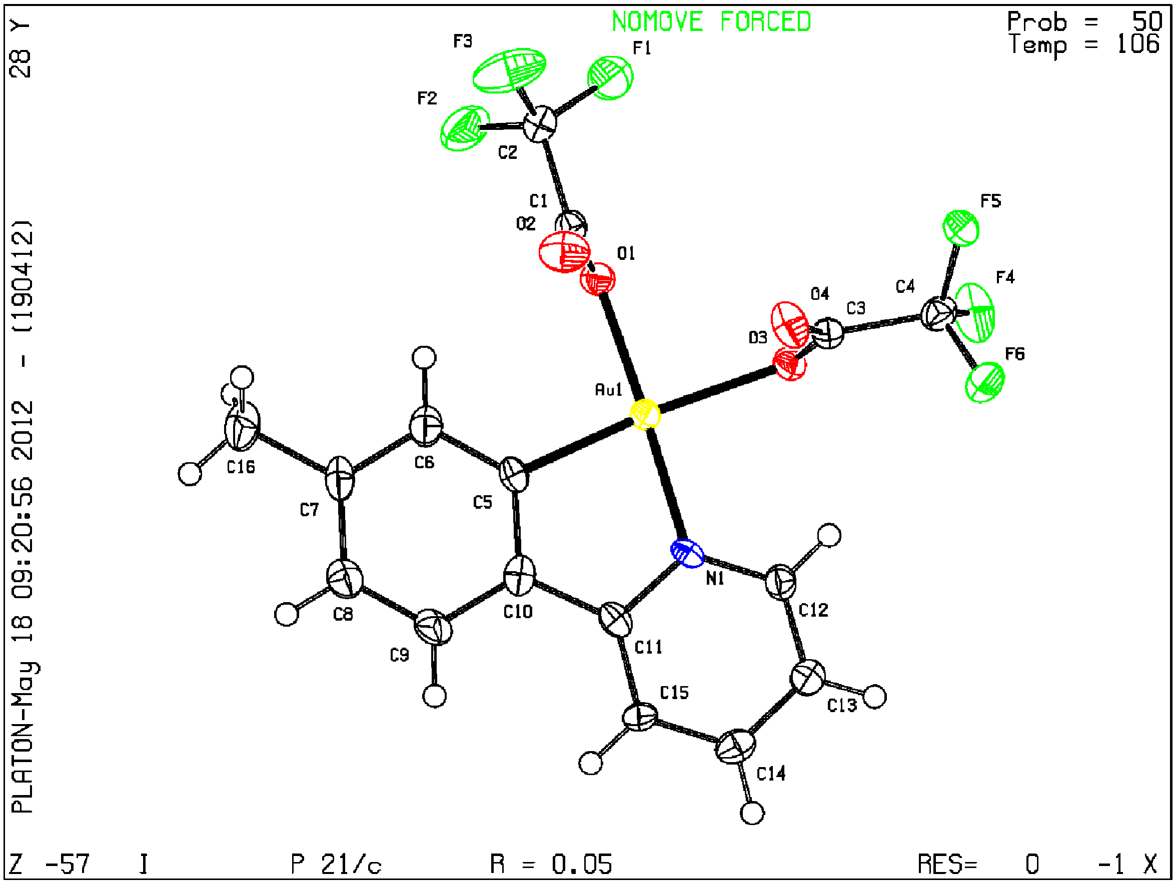


Table 1. Crystal data and structure refinement for **1**.

Identification code	el358	
Empirical formula	$C_{16}H_{10}AuF_6NO_4$	
Formula weight	591.22	
Temperature	106(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.230(3) Å	α = 90.00°
	b = 21.745(7) Å	β = 100.924(3) °
	c = 9.403(3) Å	γ = 90.00°
Volume	1652.2(9) $Å^3$	
Z	4	
Density (calculated)	2.385 Mg/m^{-3}	
Absorption coefficient	8.994 mm^{-1}	
F(000)	1120	
Crystal size	1.2 x 0.3 x 0.05 mm^3	
Theta range for date collection	2.40 to 28.78°	
Index ranges	-11<=h<=10, -25<=k<=28, -12<=l<=12	
Reflections collected	13129	
Independent reflections	3984 [R_{int} = 0.0509]	
Completeness to theta = 27.29°	99.1 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.638 and 0.158	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3984 / 0 / 254	
Goodness-of-fit on F^2	1.139	
Final R indices [I>2sigma(I)]	R_1 = 0.0480, wR_2 = 0.1362	
R indices (all data)	R_1 = 0.0561, wR_2 = 0.1425	
Largest diff. peak and hole	2.274 and -3.087 e.$Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **1**.

Au(1)-N(1)	1.991(6)
Au(1)- O(1)	1.993(5)
Au(1)-C(5)	1.995(7)
Au(1)-O(3)	2.111(5)
F(1)-C(2)	1.304(10)
F(2)-C(2)	1.342(10)
F(3)-C(2)	1.302(10)
F(4)-C(4)	1.315(9)
F(5)-C(4)	1.333(9)
F(6)-C(4)	1.333(9)
O(1)-C(1)	1.309(9)
O(2)-C(1)	1.196(9)
O(3)-C(3)	1.287(9)
O(4)-C(3)	1.210(9)
N(1)-C(12)	1.342(11)
N(1)-C(11)	1.369(9)
C(1)-C(2)	1.544(11)
C(3)-C(4)	1.542(11)
C(5)-C(6)	1.371(11)
C(5)-C(10)	1.400(11)
C(6)-C(7)	1.396(11)
C(6)-H(6)	0.9500
C(7)-C(8)	1.387(12)
C(7)-C(16)	1.512(12)
C(8)-C(9)	1.374(12)
C(8)-H(8)	0.9500
C(9)-C(10)	1.396(11)
C(9)-H(9)	0.9500
C(10)-C(11)	1.443(10)
C(11)-C(15)	1.380(11)
C(12)-C(13)	1.366(11)
C(12)-H(12)	0.9500
C(13)-C(14)	1.406(11)
C(13)-H(13)	0.9500

C(14)-C(15)	1.368(11)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
N(1)-Au(1)-O(1)	175.5(2)
N(1)-Au(1)-C(5)	81.8(3)
O(1)-Au(1)-C(5)	96.4(3)
N(1)-Au(1)-O(3)	93.1(2)
O(1)-Au(1)-O(3)	88.8(2)
C(5)-Au(1)-O(3)	174.8(3)
C(1)-O(1)-Au(1)	117.8(5)
C(3)-O(3)-Au(1)	112.5(4)
C(12)-N(1)-C(11)	120.6(7)
C(12)-N(1)-Au(1)	123.2(5)
C(11)-N(1)-Au(1)	116.2(5)
O(2)-C(1)-O(1)	129.6(8)
O(2)-C(1)-C(2)	120.1(7)
O(1)-C(1)-C(2)	110.2(6)
F(3)-C(2)-F(1)	109.1(8)
F(3)-C(2)-F(2)	105.7(7)
F(1)-C(2)-F(2)	106.0(7)
F(3)-C(2)-C(1)	112.9(7)
F(1)-C(2)-C(1)	112.3(7)
F(2)-C(2)-C(1)	110.3(7)
O(4)-C(3)-O(3)	128.5(7)
O(4)-C(3)-C(4)	117.3(7)
O(3)-C(3)-C(4)	114.1(6)
F(4)-C(4)-F(6)	108.5(7)
F(4)-C(4)-F(5)	107.9(7)
F(6)-C(4)-F(5)	106.8(6)
F(4)-C(4)-C(3)	114.7(7)
F(6)-C(4)-C(3)	107.8(6)

F(5)-C(4)-C(3)	110.9(6)
C(6)-C(5)-C(10)	121.7(7)
C(6)-C(5)-Au(1)	126.2(6)
C(10)-C(5)-Au(1)	112.1(6)
C(5)-C(6)-C(7)	119.5(8)
C(5)-C(6)-H(6)	120.2
C(7)-C(6)-H(6)	120.2
C(8)-C(7)-C(6)	119.2(8)
C(8)-C(7)-C(16)	120.8(8)
C(6)-C(7)-C(16)	120.1(8)
C(9)-C(8)-C(7)	121.3(8)
C(9)-C(8)-H(8)	119.4
C(7)-C(8)-H(8)	119.4
C(8)-C(9)-C(10)	120.1(8)
C(8)-C(9)-H(9)	120.0
C(10)-C(9)-H(9)	120.0
C(9)-C(10)-C(5)	118.2(7)
C(9)-C(10)-C(11)	124.3(8)
C(5)-C(10)-C(11)	117.4(7)
N(1)-C(11)-C(15)	119.1(7)
N(1)-C(11)-C(10)	112.5(7)
C(15)-C(11)-C(10)	128.4(7)
N(1)-C(12)-C(13)	121.8(7)
N(1)-C(12)-H(12)	119.1
C(13)-C(12)-H(12)	119.1
C(12)-C(13)-C(14)	118.4(7)
C(12)-C(13)-H(13)	120.8
C(14)-C(13)-H(13)	120.8
C(15)-C(14)- C(13)	119.3(8)
C(15)-C(14)-H(14)	120.4
C(13)-C(14)-H(14)	120.4
C(14)-C(15)-C(11)	120.7(8)
C(14)-C(15)-H(15)	119.7
C(11)-C(15)-H(15)	119.7
C(7)-C(16)-H(16A)	109.5

C(7)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(7)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

Table 3. Torsion angles [°] for **1**.

N(1)-Au(1)-O(1)-C(1)	143(3)
C(5)-Au(1)-O(1)-C(1)	77.0(6)
O(3)-Au(1)-O(1)-C(1)	-102.7(5)
N(1)-Au(1)-O(3)-C(3)	-95.8(5)
O(1)-Au(1)-O(3)-C(3)	88.3(5)
C(5)-Au(1)-O(3)-C(3)	-88(3)
O(1)-Au(1)-N(1)-C(12)	110(3)
C(5)-Au(1)-N(1)-C(12)	176.2(6)
O(3)-Au(1)-N(1)-C(12)	-4.5(5)
O(1)-Au(1)-N(1)-C(11)	-69(3)
C(5)-Au(1)-N(1)-C(11)	-2.2(5)
O(3)-Au(1)-N(1)-C(11)	177.1(5)
Au(1)-O(1)-C(1)-O(2)	-5.0(12)
Au(1)-O(1)-C(1)-C(2)	177.9(5)
O(2)-C(1)-C(2)-F(3)	0.3(11)
O(1)-C(1)-C(2)-F(3)	177.7(7)
O(2)-C(1)-C(2)-F(1)	124.2(9)
O(1)-C(1)-C(2)-F(1)	-58.4(9)
O(2)-C(1)-C(2)-F(2)	-117.7(9)
O(1)-C(1)-C(2)-F(2)	59.7(9)
Au(1)-O(3)-C(3)-O(4)	-5.7(10)
Au(1)-O(3)-C(3)-C(4)	169.4(5)
O(4)-C(3)-C(4)-F(4)	-172.7(7)
O(3)-C(3)-C(4)-F(4)	11.6(10)
O(4)-C(3)-C(4)-F(6)	66.3(9)
O(3)-C(3)-C(4)-F(6)	-109.3(7)
O(4)-C(3)-C(4)-F(5)	-50.2(9)
O(3)-C(3)-C(4)-F(5)	134.1(7)

N(1)-Au(1)-C(5)-C(6)	-178.4(7)
O(1)-Au(1)-C(5)-C(6)	-2.5(7)
O(3)-Au(1)-C(5)-C(6)	174(2)
N(1)-Au(1)-C(5)-C(10)	2.5(5)
O(1)-Au(1)-C(5)-C(10)	178.3(5)
O(3)-Au(1)-C(5)-C(10)	-5(3)
C(10)-C(5)-C(6)-C(7)	-1.5(11)
Au(1)-C(5)-C(6)-C(7)	179.4(6)
C(5)-C(6)-C(7)-C(8)	1.6(11)
C(5)-C(6)-C(7)-C(16)	-179.6(7)
C(6)-C(7)-C(8)-C(9)	-1.7(12)
C(16)-C(7)-C(8)-C(9)	179.5(8)
C(7)-C(8)-C(9)-C(10)	1.7(12)
C(8)-C(9)-C(10)-C(5)	-1.5(11)
C(8)-C(9)-C(10)-C(11)	-178.1(7)
C(6)-C(5)-C(10)-C(9)	1.5(10)
Au(1)-C(5)-C(10)-C(9)	-179.4(5)
C(6)-C(5)-C(10)-C(11)	178.3(7)
Au(1)-C(5)-C(10)-C(11)	-2.5(8)
C(12)-N(1)-C(11)-C(15)	3.8(10)
Au(1)-N(1)-C(11)-C(15)	-177.8(5)
C(12)-N(1)-C(11)-C(10)	-177.0(6)
Au(1)-N(1)-C(11)-C(10)	1.4(7)
C(9)-C(10)-C(11)-N(1)	177.4(6)
C(5)-C(10)-C(11)-N(1)	0.8(9)
C(9)-C(10)-C(11)-C(15)	-3.5(12)
C(5)-C(10)-C(11)-C(15)	179.9(7)
C(11)-N(1)-C(12)-C(13)	-3.9(10)
Au(1)-N(1)-C(12)-C(13)	177.8(5)
N(1)-C(12)-C(13)-C(14)	1.5(11)
C(12)-C(13)-C(14)-C(15)	0.9(11)
C(13)-C(14)-C(15)-C(11)	-1.0(11)
N(1)-C(11)-C(15)-C(14)	-1.4(11)
C(10)-C(11)-C(15)-C(14)	179.6(7)

Compound **2** Crystallographic Data

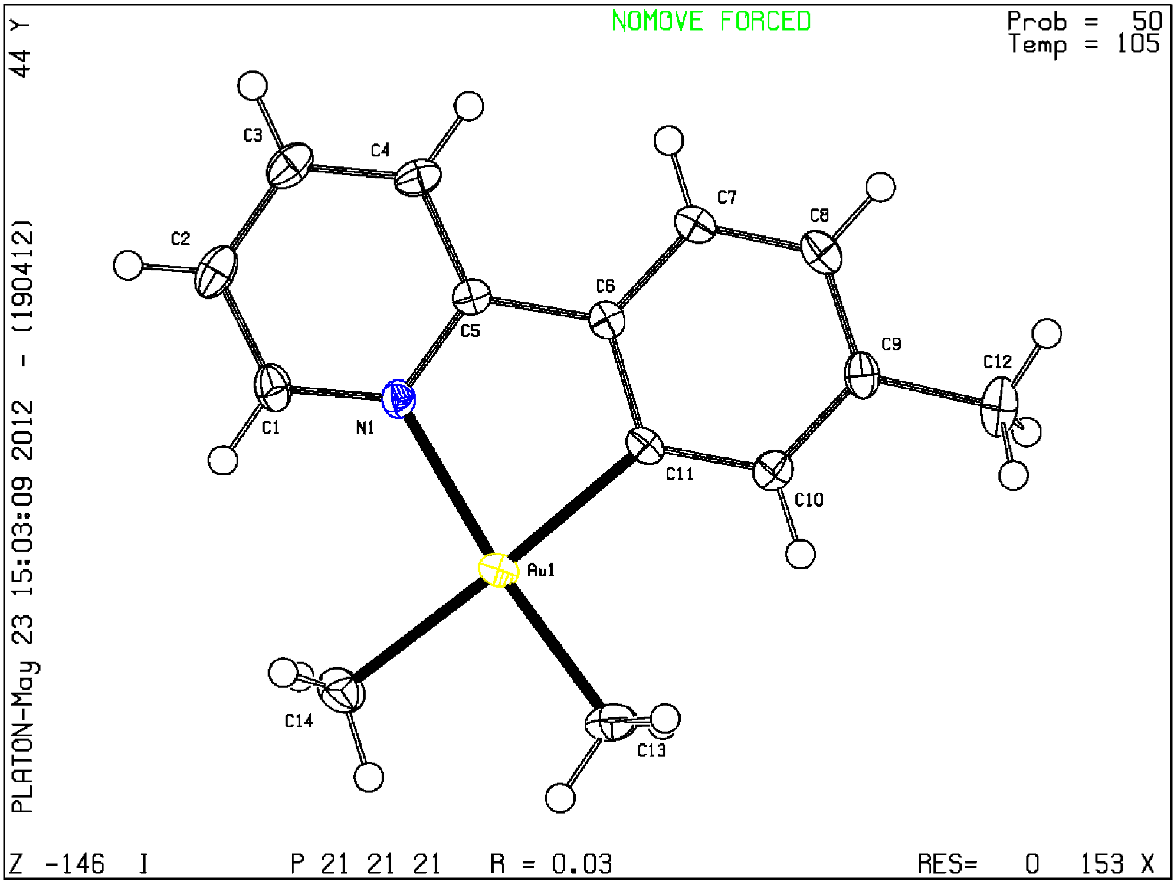


Table 4. Crystal data and structure refinement for **2**.

Identification code	el323	
Empirical formula	$C_{14}H_{16}AuN$	
Formula weight	395.26	
Temperature	105	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 4.9545(3) Å	α = 90.00°
	b = 8.5064(5) Å	β = 90.00°
	c = 28.8920(17) Å	γ = 90.00°
Volume	1217.65(13)	
Z	4	
Density (calculated)	2.156 Mg/m^{-3}	
Absorption coefficient	12.053 mm^{-1}	
F(000)	744	
Crystal size	1.75 x 0.10 x 0.07 mm^3	
Theta range for date collection	2.50 to 37.09°	
Index ranges	-8<=h<=8, -14<=k<=14, -48<=l<=48	
Reflections collected	24687	
Independent reflections	6192 [R_{int} = 0.0460]	
Completeness to theta = 37.09°	99.5 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.207 and 0.430	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6192 / 0 / 148	
Goodness-of-fit on F^2	1.098	
Final R indices [I>2sigma(I)]	R_1 = 0.0316, wR_2 = 0.0548	
R indices (all data)	R_1 = 0.0424, wR_2 = 0.0570	
Largest diff. peak and hole	2.865 and -1.976 e.$Å^{-3}$	

Table 5. Bond lengths [Å] and angles [°] for **2**.

Au(1)-C(13)	2.038(4)
Au(1)-C(11)	2.062(4)
Au(1)-N(1)	2.130(3)
Au(1)-C(14)	2.134(4)
N(1)-C(1)	1.352(5)
N81)-C(5)	1.352(4)
C(1)-C(2)	1.387(6)
C(1)-H(11)	0.9500
C(2)-C(3)	1.388(7)
C(2)-H(21)	0.9500
C(3)-C(4)	1.380(6)
C(3)-H(31)	0.9500
C(4)-C(5)	1.404(5)
C(4)-H(41)	0.9500
C(5)-C(6)	1.472(5)
C(6)-C(7)	1.403(5)
C(6)-C(11)	1.415(5)
C(7)-C(8)	1.385(5)
C(7)-H(71)	0.9500
C(8)-C(9)	1.395(5)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.402(5)
C(9)-C(12)	1.514(5)
C(10)-C(11)	1.401(5)
C(10)-H(101)	0.9500
C(12)-H(121)	0.9800
C(12)-H(122)	0.9800
C(12)-H(123)	0.9800
C(13)-H(131)	0.9800
C(13)-H(132)	0.9800
C(13)-H(133)	0.9800
C(14)-H(141)	0.9800
C(14)-H(142)	0.9800
C(14)-H(143)	0.9800

C(13)-Au(1)-C(11)	93.86(16)
C(13)-Au(1)-N(1)	173.78(14)
C(11)-Au(1)-N(1)	80.01(13)
C(13)-Au(1)-C(14)	89.13(17)
C(11)-Au(1)-C(14)	176.03(17)
N(1)-Au(1)-C(14)	97.04(15)
C(1)-N(1)-C(5)	120.4(3)
C(1)-N(1)-Au(1)	125.6(3)
C(5)-N/(1)-Au(1)	114.0(2)
N(1)-C(1)-C(2)	121.4(4)
N(1)-C(1)-H(11)	119.3
C(2)-C(1)-H(11)	119.3
C(1)-C(2)-C(3)	119.1(4)
C(1)-C(2)-H(21)	120.5
C(3)-C(2)-H(21)	120.5
C(4)-C(3)-C(2)	119.3(4)
C(4)-C(3)-H(31)	120.4
C(2)-C(3)-H(31)	120.4
C(3)-C(4)-C(5)	119.9(4)
C(3)-C(4)-H(41)	120.0
C(5)-C(4)-H(41)	120.0
N(1)-C(5)-C(4)	119.9(3)
N(1)-C(5)-C(6)	115.8(3)
C(4)-C(5)-C(6)	124.2(3)
C(7)-C(6)-C(11)	120.4(3)
C(7)-C(6)-C(5)	123.0(3)
C(11)-C(6)-C(5)	116.6(3)
C(8)-C(7)-C(6)	120.4(3)
C(8)-C(7)-H(71)	119.8
C(6)-C(7)-H(71)	119.8
C(7)-C(8)-C(9)	120.6(3)
C(7)-C(8)-H(8A)	119.7
C(9)-C(8)-H(8A)	119.7
C(8)-C(9)-C(10)	118.8(3)

C(8)-C(9)-C(12)	121.2(4)
C(10)-C(9)-C(12)	119.9(4)
C(11)-C(10)-C(9)	122.1(3)
C(11)-C(10)-H(101)	118.9
C(9)-C(10)-H(101)	118.9
C(10)-C(11)-C(6)	117.7(3)
C(10)-C(11)-Au(1)	128.9(3)
C(6)-C(11)-Au(1)	113.4(2)
C(9)-C(12)-H(121)	109.5
C(9)-C(12)-H(122)	109.5
H(121)-C(12)-H(122)	109.5
C(9)-C(12)-H(123)	109.5
H(121)-C(12)-H(123)	109.5
H(122)-C(12)-H(123)	109.5
Au(1)-C(13)-H(131)	109.5
Au(1)-C(13)-H(132)	109.5
H(131)-C813)-H(132)	109.5
Au(1)-C(13)-H(133)	109.5
H(131)-C(13)-H(133)	109.5
H(132)-C(13)-H(133)	109.5
Au(1)-C(14)-H(141)	109.5
Au(1)-C(14)-H(142)	109.5
H(141)-C(14)-H(142)	109.5
Au(1)-C(14)-H(143)	109.5
H(141)-C(14)-H(143)	109.5
H(142)-C(14)-H(143)	109.5

Table 6. Torsion angles [°] for **2**.

C(13)-Au(1)-N(1)-C(1)	-168.3(13)
C(11)-Au(1)-N(1)-C(1)	-177.7(3)
C(14)-Au(1)-N(1)-C(1)	5.0(3)
C(13)-Au(1)-N(1)-C(5)	10.5(16)
C(11)-Au(1)-N(1)-C(5)	1.2(3)
C(14)-Au(1)-N(1)-C(5)	-176.1(3)
C(5)-N(1)-C(1)-C(2)	-0.6(6)

Au(1)-N(1)-C(1)-C(2)	178.2(3)
N(1)-C(1)-C(2)-C(3)	0.4(6)
C(1)-C(2)-C(3)-C(4)	-0.1(6)
C(2)-C(3)-C(4)-C(5)	0.0(6)
C(1)-N(1)-C(5)-C(4)	0.5(5)
Au(1)-N(1)-C(5)-C(4)	-178.4(3)
C(1)-N(1)-C(5)-C(6)	179.8(3)
Au(1)-N(1)-C(5)-C(6)	0.9(4)
C(3)-C(4)-C(5)-N(1)	-0.2(5)
C(3)-C(4)-C(5)-C(6)	-179.5(3)
N(1)-C(5)-C(6)-C(7)	175.2(3)
C(4)-C(5)-C(6)-C(7)	-5.5(5)
N(1)-C(5)-C(6)-C(11)	-3.7(5)
C(4)-C(5)-C(6)-C(11)	175.6(3)
C(1)-C(6)-C(7)-C(8)	-1.2(5)
C(5)-C(6)-C(7)-C(8)	179.9(3)
C(6)-C(7)-C(8)-C(9)	-0.7(6)
C(7)-C(8)-C(9)-C(10)	1.5(5)
C(7)-C(8)-C(9)-C(12)	-178.2(4)
C(8)-C(9)-C(10)-C(11)	-0.5(6)
C(12)-C(9)-C(10)-C(11)	179.3(4)
C(9)-C(10)-C(11)-C(6)	-1.4(5)
C(9)-C(10)-C(11)-Au(1)	174.5(3)
C(7)-C(6)-C(11)-C(10)	2.2(5)
C(5)-C(6)-C(11)-C(10)	-178.9(3)
C(7)-C(6)-C(11)-Au(1)	-174.3(3)
C(5)-C(6)-C(11)-Au(1)	4.6(4)
C(13)-Au(1)-C(11)-C(10)	1.9(4)
N(1)-Au(1)-C(11)-C(10)	-179.2(4)
C(14)-Au(1)-C(11)-C(10)	-137(2)
C(13)-Au(1)-C(11)-C(6)	177.9(3)
N(1)-Au(1)-C(11)-C(6)	-3.1(2)
C(14)-Au(1)-C(11)-C(6)	39(2)