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SUPPORTING INFORMATION

AUROPHILICITY VS THIOPHILICITY: DIRECTING THE CRYSTALLINE SUPRAMOLECULAR ARRANGEMENT IN LUMINESCENT GOLD COMPOUNDS

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X-ray crystallography. Experimental 2
NMR spectra 32
Solution UV-absorption spectra 43
References 44

X-ray crystallography. Experimental section

Crystals of **1 - 7** mounted on glass fiber were studied with Oxford Diffraction Gemini "A" diffractometer with a CCD area detector ($\lambda_{MoK\alpha}$ = 0.71073 Å, monochromator: graphite) source equipped with a sealed tube X-ray source at 130 K. Unit cell constants were determined with a set of 15/3 narrow frame/runs (1° in ω) scans. A data sets consisted of 427, 510, 420, 221, 505, 227 and 411 frames of intensity data collected for **1 - 7** compounds respectively with a frame width of 1° in ω, to detector distance of 55.00 mm. The double pass method of scanning was used to exclude any noise. The collected frames were integrated by using an orientation matrix determined from the narrow frame scans. CrysAlisPro and CrysAlis RED software packages[1] were used for data collection and data integration. Analysis of the integrated data did not reveal any decay. Final cell constants were determined by a global refinement. Collected data were corrected for absorbance by using Analytical numeric absorption correction[2] using a multifaceted crystal model based on expressions upon the Laue symmetry using equivalent reflections. Structure solution and refinement were carried out with the SHELXS-2014[3]. and SHELXL-2014[4], WinGX v2014.1 software was used to prepare material for publication[5]. Full-matrix least-squares refinement was carried out by minimising $(Fo^2–Fc^2)^2$. All non-hydrogen atoms were refined anisotropically. H atoms attached to C atoms were placed in geometrically idealized positions and refined as riding on their parent atoms, with C–H = 0.95, 0.99 Å and with Uiso(H) = 1.2Ueq(C) for aromatic and methylene groups. Crystal data and experimental details of the structure determinations are listed in Tables S1A-7B. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center as supplementary material number CCDC 1584418-1584424. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail:deposit@ccdc.cam.ac.uk.

Table SXX1A. Crystal data and structure refinement for compound 1 [Au2(SC6F5)2(μ-dppe)].

Identification code	[Au2(SC6F5)2(μ-dppe)]	
Empirical formula	C19 H12 Au Cl0 F5 P S	
Formula weight	595.28	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.9864(5) Å	α= 91.560(4)°.
	b = 11.0902(4) Å	β= 113.048(5)°.
	c = 11.4091(6) Å	γ = 105.140(4)°.
Volume	999.18(9) $Å^3$	
Z	2	
Density (calculated)	1.979 Mg/m^3	
Absorption coefficient	7.591 mm^{-1}	
F(000)	562	
Crystal size	0.560 x 0.300 x 0.060 mm^3	
Theta range for data collection	3.443 to 29.459°.	
Index ranges	-11<=h<=11, -14<=k<=14, -14<=l<=15	
Reflections collected	10918	
Independent reflections	4715 [R(int) = 0.0423]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4715 / 0 / 244	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0290, wR2 = 0.0569	
R indices (all data)	R1 = 0.0354, wR2 = 0.0605	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.627 and -1.332 $e.Å^{-3}$	

Table SXX1b. Bond lengths [Å] and angles [°] for compound 1 [Au2(SC6F5)2(μ-dppe)].

C(1)-C(6)	1.385(6)		C(16)-C(17)	1.370(7)
C(1)-C(2)	1.393(6)		C(16)-H(16)	0.9500
C(1)-S(1)	1.753(4)		C(17)-C(18)	1.380(7)
C(2)-F(5)	1.346(5)		C(17)-H(17)	0.9500
C(2)-C(3)	1.381(6)		C(18)-C(19)	1.373(6)
C(3)-F(4)	1.342(5)		C(18)-H(18)	0.9500
C(3)-C(4)	1.371(6)		C(19)-H(19)	0.9500
C(4)-F(3)	1.343(5)		Au(1)-P(1)	2.2590(11)
C(4)-C(5)	1.364(6)		Au(1)-S(1)	2.3130(11)
C(5)-F(2)	1.337(5)			
C(5)-C(6)	1.392(6)		C(6)-C(1)-C(2)	114.3(4)
C(6)-F(1)	1.353(5)		C(6)-C(1)-S(1)	127.3(3)
C(7)-C(7)#1	1.539(8)		C(2)-C(1)-S(1)	118.4(3)
C(7)-P(1)	1.828(4)		F(5)-C(2)-C(3)	117.3(4)
C(7)-H(7A)	0.9900		F(5)-C(2)-C(1)	119.6(4)
C(7)-H(7B)	0.9900		C(3)-C(2)-C(1)	123.1(4)
C(8)-C(9)	1.389(6)		F(4)-C(3)-C(4)	119.9(4)
C(8)-C(13)	1.391(6)		F(4)-C(3)-C(2)	120.0(4)
C(8)-P(1)	1.810(4)		C(4)-C(3)-C(2)	120.1(4)
C(9)-C(10)	1.392(6)		F(3)-C(4)-C(5)	120.3(4)
C(9)-H(9)	0.9500		F(3)-C(4)-C(3)	120.4(4)
C(10)-C(11)	1.360(7)		C(5)-C(4)-C(3)	119.4(4)
C(10)-H(10)	0.9500		F(2)-C(5)-C(4)	121.4(4)
C(11)-C(12)	1.389(7)		F(2)-C(5)-C(6)	119.2(4)
C(11)-H(11)	0.9500		C(4)-C(5)-C(6)	119.4(4)
C(12)-C(13)	1.393(6)		F(1)-C(6)-C(1)	121.1(4)
C(12)-H(12)	0.9500		F(1)-C(6)-C(5)	115.3(4)
C(13)-H(13)	0.9500		C(1)-C(6)-C(5)	123.6(4)
C(14)-C(19)	1.383(6)		C(7)#1-C(7)-P(1)	110.7(4)
C(14)-C(15)	1.389(6)		C(7)#1-C(7)-H(7A)	109.5
C(14)-P(1)	1.820(4)		P(1)-C(7)-H(7A)	109.5
C(15)-C(16)	1.383(6)		C(7)#1-C(7)-H(7B)	109.5
C(15)-H(15)	0.9500		P(1)-C(7)-H(7B)	109.5

H(7A)-C(7)-H(7B)	108.1
C(9)-C(8)-C(13)	118.8(4)
C(9)-C(8)-P(1)	118.0(3)
C(13)-C(8)-P(1)	123.1(3)
C(8)-C(9)-C(10)	120.3(4)
C(8)-C(9)-H(9)	119.8
C(10)-C(9)-H(9)	119.8
C(11)-C(10)-C(9)	120.1(5)
C(11)-C(10)-H(10)	119.9
C(9)-C(10)-H(10)	119.9
C(10)-C(11)-C(12)	121.1(4)
C(10)-C(11)-H(11)	119.5
C(12)-C(11)-H(11)	119.5
C(11)-C(12)-C(13)	118.8(5)
C(11)-C(12)-H(12)	120.6
C(13)-C(12)-H(12)	120.6
C(8)-C(13)-C(12)	120.8(4)
C(8)-C(13)-H(13)	119.6
C(12)-C(13)-H(13)	119.6
C(19)-C(14)-C(15)	118.8(4)
C(19)-C(14)-P(1)	119.7(3)
C(15)-C(14)-P(1)	121.5(3)
C(16)-C(15)-C(14)	120.4(5)

C(16)-C(15)-H(15)	119.8
C(14)-C(15)-H(15)	119.8
C(17)-C(16)-C(15)	120.1(5)
C(17)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
C(16)-C(17)-C(18)	119.8(4)
C(16)-C(17)-H(17)	120.1
C(18)-C(17)-H(17)	120.1
C(19)-C(18)-C(17)	120.4(5)
C(19)-C(18)-H(18)	119.8
C(17)-C(18)-H(18)	119.8
C(18)-C(19)-C(14)	120.5(4)
C(18)-C(19)-H(19)	119.7
C(14)-C(19)-H(19)	119.7
P(1)-Au(1)-S(1)	178.27(4)
C(8)-P(1)-C(14)	104.80(18)
C(8)-P(1)-C(7)	106.34(19)
C(14)-P(1)-C(7)	104.15(19)
C(8)-P(1)-Au(1)	114.54(14)
C(14)-P(1)-Au(1)	113.28(14)
C(7)-P(1)-Au(1)	112.81(13)
C(1)-S(1)-Au(1)	109.85(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table S2A. Crystal data and structure refinement for compound 2 [Au2(SC6F4H)2(μ-dppe)].

Identification code	[Au2(SC6F4H)2(μ-dppe)]	
Empirical formula	C38 H26 Au2 F8 P2 S2	
Formula weight	1154.58	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.9700(5) Å	α= 75.894(5)°.
	b = 10.9988(7) Å	β= 67.698(5)°.
	c = 11.4532(7) Å	γ = 75.461(5)°.
Volume	997.96(11) $Å^3$	
Z	1	
Density (calculated)	1.921 Mg/m^3	
Absorption coefficient	7.590 mm^{-1}	
F(000)	546	
Crystal size	0.570 x 0.200 x 0.030 mm^3	
Theta range for data collection	3.420 to 29.508°.	
Index ranges	-12<=h<=12, -15<=k<=15, -15<=l<=15	
Reflections collected	13255	
Independent reflections	4826 [R(int) = 0.0738]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4826 / 15 / 223	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0402, wR2 = 0.0821	
R indices (all data)	R1 = 0.0525, wR2 = 0.0892	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.527 and -1.377 $e.Å^{-3}$	

Table S2B. Bond lengths [Å] and angles [°] for compound 2 [Au2(SC6F4H)2(μ-dppe)].

C(1)-C(2)	1.383(9)		C(16)-C(17)	1.375(10)
C(1)-C(6)	1.404(8)		C(16)-H(16)	0.9500
C(1)-S(1)	1.749(6)		C(17)-C(18)	1.375(10)
C(2)-F(1)	1.350(7)		C(17)-H(17)	0.9500
C(2)-C(3)	1.392(9)		C(18)-C(19)	1.399(9)
C(3)-C(4)	1.360(9)		C(18)-H(18)	0.9500
C(3)-F(2)	1.364(7)		C(19)-H(19)	0.9500
C(4)-C(5)	1.368(9)		Au(1)-P(1)	2.2603(15)
C(4)-H(4)	0.9500		Au(1)-S(1)	2.3113(16)
C(5)-F(3)	1.346(7)			
C(5)-C(6)	1.384(9)		C(2)-C(1)-C(6)	114.4(5)
C(6)-F(4)	1.358(7)		C(2)-C(1)-S(1)	127.4(5)
C(7)-C(7)#1	1.546(11)		C(6)-C(1)-S(1)	118.1(5)
C(7)-P(1)	1.833(6)		F(1)-C(2)-C(1)	121.0(5)
C(7)-H(7A)	0.9900		F(1)-C(2)-C(3)	117.3(6)
C(7)-H(7B)	0.9900		C(1)-C(2)-C(3)	121.6(6)
C(8)-C(13)	1.382(8)		C(4)-C(3)-F(2)	119.7(6)
C(8)-C(9)	1.396(8)		C(4)-C(3)-C(2)	123.5(6)
C(8)-P(1)	1.816(6)		F(2)-C(3)-C(2)	116.8(6)
C(9)-C(10)	1.372(9)		C(3)-C(4)-C(5)	115.7(6)
C(9)-H(9)	0.9500		C(3)-C(4)-H(4)	122.1
C(10)-C(11)	1.380(10)		C(5)-C(4)-H(4)	122.1
C(10)-H(10)	0.9500		F(3)-C(5)-C(4)	120.6(6)
C(11)-C(12)	1.366(10)		F(3)-C(5)-C(6)	117.2(6)
C(11)-H(11)	0.9500		C(4)-C(5)-C(6)	122.1(6)
C(12)-C(13)	1.418(8)		F(4)-C(6)-C(5)	118.7(6)
C(12)-H(12)	0.9500		F(4)-C(6)-C(1)	118.7(5)
C(13)-H(13)	0.9500		C(5)-C(6)-C(1)	122.6(6)
C(14)-C(15)	1.388(9)		C(7)#1-C(7)-P(1)	109.6(5)
C(14)-C(19)	1.397(8)		C(7)#1-C(7)-H(7A)	109.7
C(14)-P(1)	1.808(6)		P(1)-C(7)-H(7A)	109.7
C(15)-C(16)	1.389(9)		C(7)#1-C(7)-H(7B)	109.7
C(15)-H(15)	0.9500		P(1)-C(7)-H(7B)	109.7

H(7A)-C(7)-H(7B)	108.2
C(13)-C(8)-C(9)	120.2(6)
C(13)-C(8)-P(1)	123.1(5)
C(9)-C(8)-P(1)	116.7(5)
C(10)-C(9)-C(8)	119.2(6)
C(10)-C(9)-H(9)	120.4
C(8)-C(9)-H(9)	120.4
C(9)-C(10)-C(11)	121.1(7)
C(9)-C(10)-H(10)	119.5
C(11)-C(10)-H(10)	119.5
C(12)-C(11)-C(10)	120.8(6)
C(12)-C(11)-H(11)	119.6
C(10)-C(11)-H(11)	119.6
C(11)-C(12)-C(13)	119.0(7)
C(11)-C(12)-H(12)	120.5
C(13)-C(12)-H(12)	120.5
C(8)-C(13)-C(12)	119.7(6)
C(8)-C(13)-H(13)	120.1
C(12)-C(13)-H(13)	120.1
C(15)-C(14)-C(19)	119.3(6)
C(15)-C(14)-P(1)	120.0(5)
C(19)-C(14)-P(1)	120.7(5)
C(14)-C(15)-C(16)	121.0(6)
C(14)-C(15)-H(15)	119.5
C(16)-C(15)-H(15)	119.5
C(17)-C(16)-C(15)	119.4(6)
C(17)-C(16)-H(16)	120.3
C(15)-C(16)-H(16)	120.3
C(18)-C(17)-C(16)	120.6(6)
C(18)-C(17)-H(17)	119.7
C(16)-C(17)-H(17)	119.7
C(17)-C(18)-C(19)	120.6(6)
C(17)-C(18)-H(18)	119.7
C(19)-C(18)-H(18)	119.7
C(14)-C(19)-C(18)	119.1(6)
C(14)-C(19)-H(19)	120.4
C(18)-C(19)-H(19)	120.4
P(1)-Au(1)-S(1)	177.44(5)
C(14)-P(1)-C(8)	104.6(3)
C(14)-P(1)-C(7)	105.0(3)
C(8)-P(1)-C(7)	105.4(3)
C(14)-P(1)-Au(1)	113.5(2)
C(8)-P(1)-Au(1)	115.0(2)
C(7)-P(1)-Au(1)	112.43(19)
C(1)-S(1)-Au(1)	110.4(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table S3A. Crystal data and structure refinement for compound 3 [Au2(SC6F2H3-3,5)2(μ-dppe)].

Identification code	[Au2(SC6F2H3-3,5)2(μ-dppe)]	
Empirical formula	C38 H30 Au2 F4 P2 S2	
Formula weight	1082.61	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.9850(5) Å	α= 76.038(4)°.
	b = 10.8789(5) Å	β= 67.746(5)°.
	c = 11.1836(6) Å	γ = 75.977(4)°.
Volume	967.88(10) $Å^3$	
Z	1	
Density (calculated)	1.857 Mg/m^3	
Absorption coefficient	7.805 mm^{-1}	
F(000)	514	
Crystal size	0.510 x 0.240 x 0.120 mm^3	
Theta range for data collection	3.412 to 29.461°.	
Index ranges	-11<=h<=11, -15<=k<=14, -15<=l<=15	
Reflections collected	10742	
Independent reflections	4596 [R(int) = 0.0326]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4596 / 0 / 217	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0247, wR2 = 0.0486	
R indices (all data)	R1 = 0.0288, wR2 = 0.0507	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.738 and -1.652 e.$Å^{-3}$	

Table S3b. Bond lengths [Å] and angles [°] for compound 3 [Au2(SC6F2H3-3,5)2(μ-dppe)].

C(1)-C(6)	1.391(5)		C(16)-C(17)	1.368(6)
C(1)-C(2)	1.394(6)		C(16)-H(16)	0.9500
C(1)-S(1)	1.763(4)		C(17)-C(18)	1.368(6)
C(2)-C(3)	1.363(6)		C(17)-H(17)	0.9500
C(2)-H(2)	0.9500		C(18)-C(19)	1.384(5)
C(3)-F(1)	1.353(5)		C(18)-H(18)	0.9500
C(3)-C(4)	1.389(5)		C(19)-H(19)	0.9500
C(4)-C(5)	1.362(6)		Au(1)-P(1)	2.2582(8)
C(4)-H(4)	0.9500		Au(1)-S(1)	2.3037(9)
C(5)-F(2)	1.363(4)			
C(5)-C(6)	1.368(6)		C(6)-C(1)-C(2)	118.8(4)
C(6)-H(6)	0.9500		C(6)-C(1)-S(1)	117.2(3)
C(7)-C(7)#1	1.526(6)		C(2)-C(1)-S(1)	124.0(3)
C(7)-P(1)	1.824(4)		C(3)-C(2)-C(1)	119.5(4)
C(7)-H(7A)	0.9900		C(3)-C(2)-H(2)	120.3
C(7)-H(7B)	0.9900		C(1)-C(2)-H(2)	120.3
C(8)-C(9)	1.383(5)		F(1)-C(3)-C(2)	118.8(4)
C(8)-C(13)	1.389(5)		F(1)-C(3)-C(4)	118.0(4)
C(8)-P(1)	1.812(3)		C(2)-C(3)-C(4)	123.3(4)
C(9)-C(10)	1.396(5)		C(5)-C(4)-C(3)	115.1(4)
C(9)-H(9)	0.9500		C(5)-C(4)-H(4)	122.4
C(10)-C(11)	1.371(6)		C(3)-C(4)-H(4)	122.4
C(10)-H(10)	0.9500		C(4)-C(5)-F(2)	117.5(4)
C(11)-C(12)	1.368(6)		C(4)-C(5)-C(6)	124.7(4)
C(11)-H(11)	0.9500		F(2)-C(5)-C(6)	117.7(4)
C(12)-C(13)	1.396(5)		C(5)-C(6)-C(1)	118.6(4)
C(12)-H(12)	0.9500		C(5)-C(6)-H(6)	120.7
C(13)-H(13)	0.9500		C(1)-C(6)-H(6)	120.7
C(14)-C(19)	1.375(5)		C(7)#1-C(7)-P(1)	110.3(3)
C(14)-C(15)	1.387(5)		C(7)#1-C(7)-H(7A)	109.6
C(14)-P(1)	1.818(3)		P(1)-C(7)-H(7A)	109.6
C(15)-C(16)	1.395(5)		C(7)#1-C(7)-H(7B)	109.6
C(15)-H(15)	0.9500		P(1)-C(7)-H(7B)	109.6

H(7A)-C(7)-H(7B)	108.1	C(14)-C(15)-H(15)	120.1
C(9)-C(8)-C(13)	119.9(3)	C(16)-C(15)-H(15)	120.1
C(9)-C(8)-P(1)	123.2(3)	C(17)-C(16)-C(15)	120.0(4)
C(13)-C(8)-P(1)	116.9(3)	C(17)-C(16)-H(16)	120.0
C(8)-C(9)-C(10)	119.9(4)	C(15)-C(16)-H(16)	120.0
C(8)-C(9)-H(9)	120.1	C(16)-C(17)-C(18)	120.3(4)
C(10)-C(9)-H(9)	120.1	C(16)-C(17)-H(17)	119.9
C(11)-C(10)-C(9)	120.0(4)	C(18)-C(17)-H(17)	119.9
C(11)-C(10)-H(10)	120.0	C(17)-C(18)-C(19)	120.3(4)
C(9)-C(10)-H(10)	120.0	C(17)-C(18)-H(18)	119.9
C(12)-C(11)-C(10)	120.5(4)	C(19)-C(18)-H(18)	119.9
C(12)-C(11)-H(11)	119.8	C(14)-C(19)-C(18)	120.2(4)
C(10)-C(11)-H(11)	119.8	C(14)-C(19)-H(19)	119.9
C(11)-C(12)-C(13)	120.4(4)	C(18)-C(19)-H(19)	119.9
C(11)-C(12)-H(12)	119.8	P(1)-Au(1)-S(1)	176.56(3)
C(13)-C(12)-H(12)	119.8	C(8)-P(1)-C(14)	104.93(15)
C(8)-C(13)-C(12)	119.3(4)	C(8)-P(1)-C(7)	106.28(15)
C(8)-C(13)-H(13)	120.3	C(14)-P(1)-C(7)	103.99(16)
C(12)-C(13)-H(13)	120.3	C(8)-P(1)-Au(1)	113.20(11)
C(19)-C(14)-C(15)	119.5(3)	C(14)-P(1)-Au(1)	114.64(11)
C(19)-C(14)-P(1)	121.8(3)	C(7)-P(1)-Au(1)	112.90(11)
C(15)-C(14)-P(1)	118.7(3)	C(1)-S(1)-Au(1)	109.00(12)
C(14)-C(15)-C(16)	119.8(3)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z+1

Table S4A. Crystal data and structure refinement for compound 4 [Au2(SC6F2H3-2,4)2(μ-dppe)].

Identification code	[Au2(SC6F2H3-2,4)2(μ-dppe)]	
Empirical formula	C38 H30 Au2 F4 P2 S2	
Formula weight	1082.61	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 11.8084(7) Å	α= 90°.
	b = 19.9316(10) Å	β= 110.408(6)°.
	c = 15.9884(8) Å	γ = 90°.
Volume	3526.8(4) $Å^3$	
Z	4	
Density (calculated)	2.039 Mg/m^3	
Absorption coefficient	8.568 mm^{-1}	
F(000)	2056	
Crystal size	0.500 x 0.190 x 0.090 mm^3	
Theta range for data collection	3.577 to 29.515°.	
Index ranges	-16<=h<=15, -19<=k<=27, -20<=l<=21	
Reflections collected	19964	
Independent reflections	8367 [R(int) = 0.0345]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8367 / 0 / 433	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.0586	
R indices (all data)	R1 = 0.0493, wR2 = 0.0660	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.233 and -1.071 e.$Å^{-3}$	

Table S4B. Bond lengths [Å] and angles [°] for compound 4 [Au2(SC6F2H3-2,4)2(μ-dppe)].

C(1)-C(2)	1.391(6)	C(15)-P(2)	1.808(4)
C(1)-C(6)	1.393(7)	C(16)-C(17)	1.382(6)
C(1)-S(1)	1.770(5)	C(16)-H(16)	0.9500
C(2)-F(1)	1.351(5)	C(17)-C(18)	1.383(7)
C(2)-C(3)	1.372(7)	C(17)-H(17)	0.9500
C(3)-C(4)	1.376(7)	C(18)-C(19)	1.386(7)
C(3)-H(3)	0.9500	C(18)-H(18)	0.9500
C(4)-F(2)	1.364(5)	C(19)-C(20)	1.384(6)
C(4)-C(5)	1.377(7)	C(19)-H(19)	0.9500
C(5)-C(6)	1.385(6)	C(20)-H(20)	0.9500
C(5)-H(5)	0.9500	C(21)-C(22)	1.386(6)
C(6)-H(6)	0.9500	C(21)-C(26)	1.387(6)
C(7)-C(8)	1.518(6)	C(21)-P(2)	1.823(5)
C(7)-P(1)	1.829(4)	C(22)-C(23)	1.388(7)
C(7)-H(7A)	0.9900	C(22)-H(22)	0.9500
C(7)-H(7B)	0.9900	C(23)-C(24)	1.369(7)
C(8)-P(2)	1.823(4)	C(23)-H(23)	0.9500
C(8)-H(8A)	0.9900	C(24)-C(25)	1.380(7)
C(8)-H(8B)	0.9900	C(24)-H(24)	0.9500
C(9)-C(10)	1.376(6)	C(25)-C(26)	1.388(6)
C(9)-C(14)	1.394(7)	C(25)-H(25)	0.9500
C(9)-S(2)	1.772(5)	C(26)-H(26)	0.9500
C(10)-F(3)	1.352(5)	C(27)-C(32)	1.391(6)
C(10)-C(11)	1.380(6)	C(27)-C(28)	1.393(6)
C(11)-C(12)	1.381(7)	C(27)-P(1)	1.815(4)
C(11)-H(11)	0.9500	C(28)-C(29)	1.393(7)
C(12)-F(4)	1.359(6)	C(28)-H(28)	0.9500
C(12)-C(13)	1.359(7)	C(29)-C(30)	1.372(7)
C(13)-C(14)	1.386(7)	C(29)-H(29)	0.9500
C(13)-H(13)	0.9500	C(30)-C(31)	1.383(7)
C(14)-H(14)	0.9500	C(30)-H(30)	0.9500
C(15)-C(20)	1.397(6)	C(31)-C(32)	1.384(6)
C(15)-C(16)	1.399(6)	C(31)-H(31)	0.9500

C(32)-H(32)	0.9500
C(33)-C(34)	1.389(6)
C(33)-C(38)	1.397(6)
C(33)-P(1)	1.813(5)
C(34)-C(35)	1.382(7)
C(34)-H(34)	0.9500
C(35)-C(36)	1.374(7)
C(35)-H(35)	0.9500
C(36)-C(37)	1.378(7)
C(36)-H(36)	0.9500
C(37)-C(38)	1.373(7)
C(37)-H(37)	0.9500
C(38)-H(38)	0.9500
Au(1)-P(1)	2.2576(12)
Au(1)-S(1)	2.3145(12)
Au(1)-Au(2)#1	3.1034(3)
Au(2)-P(2)	2.2588(12)
Au(2)-S(2)	2.3137(12)
C(2)-C(1)-C(6)	115.9(4)
C(2)-C(1)-S(1)	124.6(4)
C(6)-C(1)-S(1)	119.3(4)
F(1)-C(2)-C(3)	116.1(4)
F(1)-C(2)-C(1)	120.0(4)
C(3)-C(2)-C(1)	123.9(5)
C(2)-C(3)-C(4)	117.0(5)
C(2)-C(3)-H(3)	121.5
C(4)-C(3)-H(3)	121.5
F(2)-C(4)-C(3)	118.5(4)
F(2)-C(4)-C(5)	118.5(4)
C(3)-C(4)-C(5)	123.0(4)
C(4)-C(5)-C(6)	117.4(5)
C(4)-C(5)-H(5)	121.3
C(6)-C(5)-H(5)	121.3
C(5)-C(6)-C(1)	122.8(5)
C(5)-C(6)-H(6)	118.6
C(1)-C(6)-H(6)	118.6
C(8)-C(7)-P(1)	111.7(3)
C(8)-C(7)-H(7A)	109.3
P(1)-C(7)-H(7A)	109.3
C(8)-C(7)-H(7B)	109.3
P(1)-C(7)-H(7B)	109.3
H(7A)-C(7)-H(7B)	107.9
C(7)-C(8)-P(2)	111.0(3)
C(7)-C(8)-H(8A)	109.4
P(2)-C(8)-H(8A)	109.4
C(7)-C(8)-H(8B)	109.4
P(2)-C(8)-H(8B)	109.4
H(8A)-C(8)-H(8B)	108.0
C(10)-C(9)-C(14)	116.5(4)
C(10)-C(9)-S(2)	123.7(4)
C(14)-C(9)-S(2)	119.7(4)
F(3)-C(10)-C(9)	119.1(4)
F(3)-C(10)-C(11)	116.6(4)
C(9)-C(10)-C(11)	124.2(5)
C(10)-C(11)-C(12)	116.4(5)
C(10)-C(11)-H(11)	121.8
C(12)-C(11)-H(11)	121.8
F(4)-C(12)-C(13)	120.1(5)
F(4)-C(12)-C(11)	117.5(5)
C(13)-C(12)-C(11)	122.4(5)
C(12)-C(13)-C(14)	119.3(5)
C(12)-C(13)-H(13)	120.4
C(14)-C(13)-H(13)	120.4
C(13)-C(14)-C(9)	121.1(5)
C(13)-C(14)-H(14)	119.4
C(9)-C(14)-H(14)	119.4
C(20)-C(15)-C(16)	119.3(4)
C(20)-C(15)-P(2)	116.9(3)
C(16)-C(15)-P(2)	123.8(3)

C(17)-C(16)-C(15)	120.3(4)
C(17)-C(16)-H(16)	119.9
C(15)-C(16)-H(16)	119.9
C(16)-C(17)-C(18)	120.0(4)
C(16)-C(17)-H(17)	120.0
C(18)-C(17)-H(17)	120.0
C(17)-C(18)-C(19)	120.3(4)
C(17)-C(18)-H(18)	119.9
C(19)-C(18)-H(18)	119.9
C(20)-C(19)-C(18)	120.2(4)
C(20)-C(19)-H(19)	119.9
C(18)-C(19)-H(19)	119.9
C(19)-C(20)-C(15)	119.9(4)
C(19)-C(20)-H(20)	120.0
C(15)-C(20)-H(20)	120.0
C(22)-C(21)-C(26)	119.9(4)
C(22)-C(21)-P(2)	119.9(4)
C(26)-C(21)-P(2)	120.1(3)
C(21)-C(22)-C(23)	119.5(4)
C(21)-C(22)-H(22)	120.2
C(23)-C(22)-H(22)	120.2
C(24)-C(23)-C(22)	120.4(5)
C(24)-C(23)-H(23)	119.8
C(22)-C(23)-H(23)	119.8
C(23)-C(24)-C(25)	120.6(5)
C(23)-C(24)-H(24)	119.7
C(25)-C(24)-H(24)	119.7
C(24)-C(25)-C(26)	119.5(5)
C(24)-C(25)-H(25)	120.2
C(26)-C(25)-H(25)	120.2
C(21)-C(26)-C(25)	120.1(4)
C(21)-C(26)-H(26)	119.9
C(25)-C(26)-H(26)	119.9
C(32)-C(27)-C(28)	119.2(4)
C(32)-C(27)-P(1)	123.0(3)

C(28)-C(27)-P(1)	117.6(3)
C(29)-C(28)-C(27)	119.9(5)
C(29)-C(28)-H(28)	120.1
C(27)-C(28)-H(28)	120.1
C(30)-C(29)-C(28)	120.3(5)
C(30)-C(29)-H(29)	119.8
C(28)-C(29)-H(29)	119.8
C(29)-C(30)-C(31)	120.1(5)
C(29)-C(30)-H(30)	120.0
C(31)-C(30)-H(30)	120.0
C(30)-C(31)-C(32)	120.2(5)
C(30)-C(31)-H(31)	119.9
C(32)-C(31)-H(31)	119.9
C(31)-C(32)-C(27)	120.3(4)
C(31)-C(32)-H(32)	119.9
C(27)-C(32)-H(32)	119.9
C(34)-C(33)-C(38)	118.4(4)
C(34)-C(33)-P(1)	121.5(3)
C(38)-C(33)-P(1)	120.1(3)
C(35)-C(34)-C(33)	119.9(4)
C(35)-C(34)-H(34)	120.1
C(33)-C(34)-H(34)	120.1
C(36)-C(35)-C(34)	121.1(5)
C(36)-C(35)-H(35)	119.5
C(34)-C(35)-H(35)	119.5
C(35)-C(36)-C(37)	119.5(5)
C(35)-C(36)-H(36)	120.2
C(37)-C(36)-H(36)	120.2
C(38)-C(37)-C(36)	120.0(5)
C(38)-C(37)-H(37)	120.0
C(36)-C(37)-H(37)	120.0
C(37)-C(38)-C(33)	121.1(4)
C(37)-C(38)-H(38)	119.5
C(33)-C(38)-H(38)	119.5
P(1)-Au(1)-S(1)	176.65(4)

P(1)-Au(1)-Au(2)#1	105.91(3)	C(7)-P(1)-Au(1)	109.89(15)
S(1)-Au(1)-Au(2)#1	76.01(3)	C(15)-P(2)-C(8)	106.9(2)
P(2)-Au(2)-S(2)	174.63(4)	C(15)-P(2)-C(21)	103.0(2)
P(2)-Au(2)-Au(1)#2	106.58(3)	C(8)-P(2)-C(21)	104.7(2)
S(2)-Au(2)-Au(1)#2	77.65(3)	C(15)-P(2)-Au(2)	115.90(15)
C(33)-P(1)-C(27)	102.9(2)	C(8)-P(2)-Au(2)	110.24(15)
C(33)-P(1)-C(7)	104.4(2)	C(21)-P(2)-Au(2)	115.13(15)
C(27)-P(1)-C(7)	105.8(2)	C(1)-S(1)-Au(1)	109.49(15)
C(33)-P(1)-Au(1)	116.34(15)	C(9)-S(2)-Au(2)	103.04(15)
C(27)-P(1)-Au(1)	116.34(15)		

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+1/2,z-1/2 #2 x+1/2,-y+1/2,z+1/2

Table S5A. Crystal data and structure refinement for compound 5 [Au2(SC6H4(CF3)-2)2(μ-dppe)].

Identification code	[Au2(SC6H4(CF3)-2)2(μ-dppe)]	
Empirical formula	C80 H64 Au4 F12 P4 S4	
Formula weight	2293.29	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.5426(5) Å	α= 84.665(3)°.
	b = 12.7737(4) Å	β= 67.650(4)°.
	c = 13.3107(5) Å	γ = 74.963(3)°.
Volume	1904.80(13) $Å^3$	
Z	1	
Density (calculated)	1.999 Mg/m^3	
Absorption coefficient	7.945 mm^{-1}	
F(000)	1092	
Crystal size	0.530 x 0.240 x 0.170 mm^3	
Theta range for data collection	3.529 to 29.475°.	
Index ranges	-16<=h<=17, -17<=k<=16, -18<=l<=17	
Reflections collected	25313	
Independent reflections	9157 [R(int) = 0.0541]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9157 / 0 / 469	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.0813	
R indices (all data)	R1 = 0.0573, wR2 = 0.0929	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.634 and -2.278 e.$Å^{-3}$	

Table S5B. Bond lengths [Å] and angles [°] for compound 5 [Au2(SC6H4(CF3)-2)2(μ-dppe)].

C(1)-C(28)	1.397(9)		C(15)-C(16)	1.378(8)
C(1)-C(2)	1.402(8)		C(15)-C(20)	1.390(8)
C(1)-S(1)	1.756(6)		C(15)-P(1)	1.824(5)
C(2)-C(4)	1.394(9)		C(16)-C(17)	1.385(8)
C(2)-C(3)	1.488(10)		C(16)-H(16)	0.9500
C(3)-F(1)	1.341(8)		C(17)-C(18)	1.378(9)
C(3)-F(3)	1.345(7)		C(17)-H(17)	0.9500
C(3)-F(2)	1.353(8)		C(18)-C(19)	1.372(8)
C(4)-C(5)	1.351(11)		C(18)-H(18)	0.9500
C(4)-H(4)	0.9500		C(19)-C(20)	1.385(8)
C(5)-C(6)	1.396(11)		C(19)-H(19)	0.9500
C(5)-H(5)	0.9500		C(20)-H(20)	0.9500
C(6)-C(28)	1.385(8)		C(21)-C(27)	1.387(9)
C(6)-H(6)	0.9500		C(21)-C(22)	1.412(8)
C(7)-C(8)	1.526(7)		C(21)-S(2)	1.766(6)
C(7)-P(1)	1.836(5)		C(22)-C(24)	1.394(9)
C(7)-H(8A)	0.9900		C(22)-C(23)	1.485(10)
C(7)-H(8B)	0.9900		C(23)-F(4)	1.325(8)
C(8)-P(2)	1.831(5)		C(23)-F(5)	1.339(8)
C(8)-H(28A)	0.9900		C(23)-F(6)	1.352(9)
C(8)-H(28B)	0.9900		C(24)-C(25)	1.373(11)
C(9)-C(10)	1.384(8)		C(24)-H(24)	0.9500
C(9)-C(14)	1.386(9)		C(25)-C(26)	1.382(10)
C(9)-P(1)	1.820(6)		C(25)-H(25)	0.9500
C(10)-C(11)	1.392(9)		C(26)-C(27)	1.388(9)
C(10)-H(10)	0.9500		C(26)-H(26)	0.9500
C(11)-C(12)	1.351(10)		C(27)-H(27)	0.9500
C(11)-H(11)	0.9500		C(28)-H(7)	0.9500
C(12)-C(13)	1.384(9)		C(29)-C(34)	1.391(8)
C(12)-H(12)	0.9500		C(29)-C(30)	1.398(9)
C(13)-C(14)	1.385(9)		C(29)-P(2)	1.818(6)
C(13)-H(13)	0.9500		C(30)-C(31)	1.372(10)
C(14)-H(14)	0.9500		C(30)-H(30)	0.9500

C(31)-C(32)	1.381(11)
C(31)-H(31)	0.9500
C(32)-C(33)	1.379(11)
C(32)-H(32)	0.9500
C(33)-C(34)	1.385(10)
C(33)-H(33)	0.9500
C(34)-H(34)	0.9500
C(35)-C(36)	1.379(8)
C(35)-C(40)	1.391(8)
C(35)-P(2)	1.818(6)
C(36)-C(37)	1.382(9)
C(36)-H(36)	0.9500
C(37)-C(38)	1.361(10)
C(37)-H(37)	0.9500
C(38)-C(39)	1.370(10)
C(38)-H(38)	0.9500
C(39)-C(40)	1.404(9)
C(39)-H(39)	0.9500
C(40)-H(40)	0.9500
Au(1)-P(1)	2.2541(14)
Au(1)-S(1)	2.3009(15)
Au(1)-Au(2)#1	3.1331(3)
Au(2)-P(2)	2.2557(15)
Au(2)-S(2)	2.3037(15)
C(28)-C(1)-C(2)	117.6(6)
C(28)-C(1)-S(1)	121.7(5)
C(2)-C(1)-S(1)	120.6(5)
C(4)-C(2)-C(1)	119.3(7)
C(4)-C(2)-C(3)	119.5(6)
C(1)-C(2)-C(3)	121.2(6)
F(1)-C(3)-F(3)	106.0(6)
F(1)-C(3)-F(2)	105.7(6)
F(3)-C(3)-F(2)	104.9(5)
F(1)-C(3)-C(2)	113.6(5)
F(3)-C(3)-C(2)	112.2(6)
F(2)-C(3)-C(2)	113.6(6)
C(5)-C(4)-C(2)	122.3(7)
C(5)-C(4)-H(4)	118.9
C(2)-C(4)-H(4)	118.9
C(4)-C(5)-C(6)	119.6(7)
C(4)-C(5)-H(5)	120.2
C(6)-C(5)-H(5)	120.2
C(28)-C(6)-C(5)	118.9(7)
C(28)-C(6)-H(6)	120.6
C(5)-C(6)-H(6)	120.6
C(8)-C(7)-P(1)	111.1(3)
C(8)-C(7)-H(8A)	109.4
P(1)-C(7)-H(8A)	109.4
C(8)-C(7)-H(8B)	109.4
P(1)-C(7)-H(8B)	109.4
H(8A)-C(7)-H(8B)	108.0
C(7)-C(8)-P(2)	112.4(3)
C(7)-C(8)-H(28A)	109.1
P(2)-C(8)-H(28A)	109.1
C(7)-C(8)-H(28B)	109.1
P(2)-C(8)-H(28B)	109.1
H(28A)-C(8)-H(28B)	107.9
C(10)-C(9)-C(14)	119.8(6)
C(10)-C(9)-P(1)	119.9(5)
C(14)-C(9)-P(1)	120.3(4)
C(9)-C(10)-C(11)	119.9(6)
C(9)-C(10)-H(10)	120.1
C(11)-C(10)-H(10)	120.1
C(12)-C(11)-C(10)	120.1(6)
C(12)-C(11)-H(11)	120.0
C(10)-C(11)-H(11)	120.0
C(11)-C(12)-C(13)	120.7(7)
C(11)-C(12)-H(12)	119.6
C(13)-C(12)-H(12)	119.6

C(12)-C(13)-C(14)	119.9(7)
C(12)-C(13)-H(13)	120.0
C(14)-C(13)-H(13)	120.0
C(13)-C(14)-C(9)	119.6(6)
C(13)-C(14)-H(14)	120.2
C(9)-C(14)-H(14)	120.2
C(16)-C(15)-C(20)	119.9(5)
C(16)-C(15)-P(1)	119.4(4)
C(20)-C(15)-P(1)	120.6(4)
C(15)-C(16)-C(17)	119.8(6)
C(15)-C(16)-H(16)	120.1
C(17)-C(16)-H(16)	120.1
C(18)-C(17)-C(16)	120.5(6)
C(18)-C(17)-H(17)	119.7
C(16)-C(17)-H(17)	119.7
C(19)-C(18)-C(17)	119.5(5)
C(19)-C(18)-H(18)	120.3
C(17)-C(18)-H(18)	120.3
C(18)-C(19)-C(20)	120.8(6)
C(18)-C(19)-H(19)	119.6
C(20)-C(19)-H(19)	119.6
C(19)-C(20)-C(15)	119.4(5)
C(19)-C(20)-H(20)	120.3
C(15)-C(20)-H(20)	120.3
C(27)-C(21)-C(22)	117.0(6)
C(27)-C(21)-S(2)	123.2(5)
C(22)-C(21)-S(2)	119.7(5)
C(24)-C(22)-C(21)	120.4(7)
C(24)-C(22)-C(23)	117.9(6)
C(21)-C(22)-C(23)	121.6(6)
F(4)-C(23)-F(5)	105.3(7)
F(4)-C(23)-F(6)	105.2(6)
F(5)-C(23)-F(6)	105.6(6)
F(4)-C(23)-C(22)	115.1(6)
F(5)-C(23)-C(22)	112.4(6)
F(6)-C(23)-C(22)	112.3(7)
C(25)-C(24)-C(22)	120.9(7)
C(25)-C(24)-H(24)	119.6
C(22)-C(24)-H(24)	119.6
C(24)-C(25)-C(26)	119.6(6)
C(24)-C(25)-H(25)	120.2
C(26)-C(25)-H(25)	120.2
C(25)-C(26)-C(27)	119.8(7)
C(25)-C(26)-H(26)	120.1
C(27)-C(26)-H(26)	120.1
C(21)-C(27)-C(26)	122.2(6)
C(21)-C(27)-H(27)	118.9
C(26)-C(27)-H(27)	118.9
C(6)-C(28)-C(1)	122.2(7)
C(6)-C(28)-H(7)	118.9
C(1)-C(28)-H(7)	118.9
C(34)-C(29)-C(30)	120.7(6)
C(34)-C(29)-P(2)	119.1(5)
C(30)-C(29)-P(2)	120.0(5)
C(31)-C(30)-C(29)	119.3(7)
C(31)-C(30)-H(30)	120.3
C(29)-C(30)-H(30)	120.3
C(30)-C(31)-C(32)	120.1(7)
C(30)-C(31)-H(31)	119.9
C(32)-C(31)-H(31)	119.9
C(33)-C(32)-C(31)	120.8(7)
C(33)-C(32)-H(32)	119.6
C(31)-C(32)-H(32)	119.6
C(32)-C(33)-C(34)	120.1(7)
C(32)-C(33)-H(33)	120.0
C(34)-C(33)-H(33)	120.0
C(33)-C(34)-C(29)	118.9(7)
C(33)-C(34)-H(34)	120.5
C(29)-C(34)-H(34)	120.5
C(36)-C(35)-C(40)	119.0(6)

C(36)-C(35)-P(2)	121.2(5)	P(2)-Au(2)-S(2)	172.52(5)
C(40)-C(35)-P(2)	119.6(4)	P(2)-Au(2)-Au(1)#1	110.81(4)
C(35)-C(36)-C(37)	121.0(7)	S(2)-Au(2)-Au(1)#1	74.06(4)
C(35)-C(36)-H(36)	119.5	C(9)-P(1)-C(15)	105.6(3)
C(37)-C(36)-H(36)	119.5	C(9)-P(1)-C(7)	105.6(3)
C(38)-C(37)-C(36)	120.0(7)	C(15)-P(1)-C(7)	105.2(2)
C(38)-C(37)-H(37)	120.0	C(9)-P(1)-Au(1)	113.17(19)
C(36)-C(37)-H(37)	120.0	C(15)-P(1)-Au(1)	112.81(18)
C(37)-C(38)-C(39)	120.4(7)	C(7)-P(1)-Au(1)	113.73(19)
C(37)-C(38)-H(38)	119.8	C(35)-P(2)-C(29)	105.5(3)
C(39)-C(38)-H(38)	119.8	C(35)-P(2)-C(8)	104.8(2)
C(38)-C(39)-C(40)	120.2(7)	C(29)-P(2)-C(8)	104.0(3)
C(38)-C(39)-H(39)	119.9	C(35)-P(2)-Au(2)	110.10(19)
C(40)-C(39)-H(39)	119.9	C(29)-P(2)-Au(2)	115.13(19)
C(35)-C(40)-C(39)	119.3(7)	C(8)-P(2)-Au(2)	116.21(19)
C(35)-C(40)-H(40)	120.4	C(1)-S(1)-Au(1)	108.7(2)
C(39)-C(40)-H(40)	120.4	C(21)-S(2)-Au(2)	108.6(2)
P(1)-Au(1)-S(1)	177.88(5)	_____	
P(1)-Au(1)-Au(2)#1	102.16(4)	_____	
S(1)-Au(1)-Au(2)#1	77.48(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z+1

Table S6A. Crystal data and structure refinement for compound 6 [Au2(SC6H4F-3)2(μ-dppe)].

Identification code	[Au2(SC6H4F-3)2(μ-dppe)]	
Empirical formula	C38 H32 Au2 F2 P2 S2	
Formula weight	1046.63	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 11.5947(5) Å	α= 90°.
	b = 19.9982(10) Å	β= 108.857(5)°.
	c = 15.8994(7) Å	γ = 90°.
Volume	3488.8(3) $Å^3$	
Z	4	
Density (calculated)	1.993 Mg/m^3	
Absorption coefficient	8.650 mm^{-1}	
F(000)	1992	
Crystal size	0.400 x 0.290 x 0.130 mm^3	
Theta range for data collection	3.576 to 29.556°.	
Index ranges	-16<=h<=13, -27<=k<=26, -19<=l<=21	
Reflections collected	20116	
Independent reflections	8324 [R(int) = 0.0562]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8324 / 0 / 392	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0552, wR2 = 0.1113	
R indices (all data)	R1 = 0.0780, wR2 = 0.1239	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.450 and -2.747 $e.Å^{-3}$	

Table S6B. Bond lengths [Å] and angles [°] for compound 6 [Au2(SC6H4F-3)2(μ-dppe)].

Au(1)-P(1)	2.253(2)	C(20)-C(21)	1.384(11)
Au(1)-S(1)	2.305(2)	C(20)-H(20)	0.9500
Au(1)-Au(2)	3.0151(4)	C(21)-C(22)	1.359(13)
Au(2)-P(2)	2.267(2)	C(21)-H(21)	0.9500
Au(2)-S(2)	2.306(12)	C(22)-C(23)	1.379(13)
Au(2)-S(2P)	2.35(2)	C(22)-H(22)	0.9500
C(32)-C(12)	1.375(12)	C(23)-C(24)	1.394(13)
C(32)-C(25)	1.396(13)	C(23)-H(23)	0.9500
C(32)-S(1)	1.756(10)	C(24)-H(24)	0.9500
C(25)-C(9)	1.381(15)	C(8)-C(7)#1	1.525(11)
C(25)-H(8)	0.9500	C(8)-P(2)	1.821(8)
C(9)-C(10)	1.351(15)	C(8)-H(25A)	0.9900
C(9)-H(9)	0.9500	C(8)-H(25B)	0.9900
C(10)-C(11)	1.363(16)	C(26)-C(31)	1.391(12)
C(10)-H(10)	0.9500	C(26)-C(27)	1.394(11)
C(11)-C(12)	1.377(15)	C(26)-P(1)	1.817(8)
C(11)-F(1)	1.382(12)	C(27)-C(28)	1.374(12)
C(12)-H(12)	0.9500	C(27)-H(27)	0.9500
C(13)-C(14)	1.387(12)	C(28)-C(29)	1.381(14)
C(13)-C(18)	1.401(11)	C(28)-H(28)	0.9500
C(13)-P(2)	1.808(8)	C(29)-C(30)	1.359(14)
C(14)-C(15)	1.385(13)	C(29)-H(29)	0.9500
C(14)-H(14)	0.9500	C(30)-C(31)	1.379(13)
C(15)-C(16)	1.359(13)	C(30)-H(30)	0.9500
C(15)-H(15)	0.9500	C(31)-H(31)	0.9500
C(16)-C(17)	1.385(14)	C(7)-P(1)	1.831(7)
C(16)-H(16)	0.9500	C(7)-H(32A)	0.9900
C(17)-C(18)	1.379(12)	C(7)-H(32B)	0.9900
C(17)-H(17)	0.9500	C(33)-C(38)	1.370(12)
C(18)-H(18)	0.9500	C(33)-C(34)	1.374(12)
C(19)-C(24)	1.382(12)	C(33)-P(1)	1.807(8)
C(19)-C(20)	1.383(11)	C(34)-C(35)	1.402(13)
C(19)-P(2)	1.811(8)	C(34)-H(34)	0.9500

C(35)-C(36)	1.378(14)
C(35)-H(35)	0.9500
C(36)-C(37)	1.365(14)
C(36)-H(36)	0.9500
C(37)-C(38)	1.376(12)
C(37)-H(37)	0.9500
C(38)-H(38)	0.9500
C(1)-C(2)	1.3900
C(1)-C(6)	1.3900
C(1)-S(2)	1.758(10)
C(2)-C(3)	1.3900
C(2)-H(2)	0.9500
C(3)-C(4)	1.3900
C(3)-H(3)	0.9500
C(4)-C(5)	1.3900
C(4)-H(4)	0.9500
C(5)-F(2)	1.287(12)
C(5)-C(6)	1.3900
C(6)-H(6)	0.9500
C(1P)-C(2P)	1.3900
C(1P)-C(6P)	1.3900
C(1P)-S(2P)	1.79(2)
C(2P)-C(3P)	1.3900
C(2P)-H(2P)	0.9500
C(3P)-C(4P)	1.3900
C(3P)-H(3P)	0.9500
C(4P)-C(5P)	1.3900
C(4P)-H(4P)	0.9500
C(5P)-C(6P)	1.3900
C(5P)-F(2P)	1.40(2)
C(6P)-H(6P)	0.9500
P(1)-Au(1)-S(1)	177.49(9)
P(1)-Au(1)-Au(2)	103.20(5)
S(1)-Au(1)-Au(2)	75.69(6)

P(2)-Au(2)-S(2)	172.8(3)
P(2)-Au(2)-S(2P)	175.1(5)
P(2)-Au(2)-Au(1)	104.72(5)
S(2)-Au(2)-Au(1)	78.13(19)
S(2P)-Au(2)-Au(1)	70.5(4)
C(12)-C(32)-C(25)	119.2(10)
C(12)-C(32)-S(1)	124.0(8)
C(25)-C(32)-S(1)	116.7(8)
C(9)-C(25)-C(32)	120.0(10)
C(9)-C(25)-H(8)	120.0
C(32)-C(25)-H(8)	120.0
C(10)-C(9)-C(25)	121.4(10)
C(10)-C(9)-H(9)	119.3
C(25)-C(9)-H(9)	119.3
C(9)-C(10)-C(11)	117.5(11)
C(9)-C(10)-H(10)	121.2
C(11)-C(10)-H(10)	121.2
C(10)-C(11)-C(12)	124.0(11)
C(10)-C(11)-F(1)	120.4(11)
C(12)-C(11)-F(1)	115.6(11)
C(32)-C(12)-C(11)	117.8(10)
C(32)-C(12)-H(12)	121.1
C(11)-C(12)-H(12)	121.1
C(14)-C(13)-C(18)	119.0(8)
C(14)-C(13)-P(2)	121.3(7)
C(18)-C(13)-P(2)	119.7(7)
C(15)-C(14)-C(13)	120.6(9)
C(15)-C(14)-H(14)	119.7
C(13)-C(14)-H(14)	119.7
C(16)-C(15)-C(14)	119.8(9)
C(16)-C(15)-H(15)	120.1
C(14)-C(15)-H(15)	120.1
C(15)-C(16)-C(17)	120.9(9)
C(15)-C(16)-H(16)	119.6
C(17)-C(16)-H(16)	119.6

C(18)-C(17)-C(16)	120.0(9)
C(18)-C(17)-H(17)	120.0
C(16)-C(17)-H(17)	120.0
C(17)-C(18)-C(13)	119.7(9)
C(17)-C(18)-H(18)	120.1
C(13)-C(18)-H(18)	120.1
C(24)-C(19)-C(20)	118.5(8)
C(24)-C(19)-P(2)	123.6(6)
C(20)-C(19)-P(2)	117.9(7)
C(19)-C(20)-C(21)	121.1(8)
C(19)-C(20)-H(20)	119.5
C(21)-C(20)-H(20)	119.5
C(22)-C(21)-C(20)	119.7(8)
C(22)-C(21)-H(21)	120.2
C(20)-C(21)-H(21)	120.2
C(21)-C(22)-C(23)	120.9(9)
C(21)-C(22)-H(22)	119.5
C(23)-C(22)-H(22)	119.5
C(22)-C(23)-C(24)	119.2(9)
C(22)-C(23)-H(23)	120.4
C(24)-C(23)-H(23)	120.4
C(19)-C(24)-C(23)	120.6(9)
C(19)-C(24)-H(24)	119.7
C(23)-C(24)-H(24)	119.7
C(7)#1-C(8)-P(2)	109.3(6)
C(7)#1-C(8)-H(25A)	109.8
P(2)-C(8)-H(25A)	109.8
C(7)#1-C(8)-H(25B)	109.8
P(2)-C(8)-H(25B)	109.8
H(25A)-C(8)-H(25B)	108.3
C(31)-C(26)-C(27)	118.2(8)
C(31)-C(26)-P(1)	123.9(6)
C(27)-C(26)-P(1)	117.8(6)
C(28)-C(27)-C(26)	120.7(9)
C(28)-C(27)-H(27)	119.7
C(26)-C(27)-H(27)	119.7
C(27)-C(28)-C(29)	120.2(8)
C(27)-C(28)-H(28)	119.9
C(29)-C(28)-H(28)	119.9
C(30)-C(29)-C(28)	119.8(9)
C(30)-C(29)-H(29)	120.1
C(28)-C(29)-H(29)	120.1
C(29)-C(30)-C(31)	120.9(10)
C(29)-C(30)-H(30)	119.6
C(31)-C(30)-H(30)	119.6
C(30)-C(31)-C(26)	120.3(9)
C(30)-C(31)-H(31)	119.9
C(26)-C(31)-H(31)	119.9
C(8)#2-C(7)-P(1)	111.5(6)
C(8)#2-C(7)-H(32A)	109.3
P(1)-C(7)-H(32A)	109.3
C(8)#2-C(7)-H(32B)	109.3
P(1)-C(7)-H(32B)	109.3
H(32A)-C(7)-H(32B)	108.0
C(38)-C(33)-C(34)	119.2(8)
C(38)-C(33)-P(1)	120.5(7)
C(34)-C(33)-P(1)	120.3(7)
C(33)-C(34)-C(35)	119.9(9)
C(33)-C(34)-H(34)	120.0
C(35)-C(34)-H(34)	120.0
C(36)-C(35)-C(34)	120.0(10)
C(36)-C(35)-H(35)	120.0
C(34)-C(35)-H(35)	120.0
C(37)-C(36)-C(35)	119.2(9)
C(37)-C(36)-H(36)	120.4
C(35)-C(36)-H(36)	120.4
C(36)-C(37)-C(38)	120.8(9)
C(36)-C(37)-H(37)	119.6
C(38)-C(37)-H(37)	119.6
C(33)-C(38)-C(37)	120.8(9)

C(33)-C(38)-H(38)	119.6
C(37)-C(38)-H(38)	119.6
C(33)-P(1)-C(26)	103.5(4)
C(33)-P(1)-C(7)	104.8(4)
C(26)-P(1)-C(7)	104.8(4)
C(33)-P(1)-Au(1)	116.0(3)
C(26)-P(1)-Au(1)	116.1(2)
C(7)-P(1)-Au(1)	110.4(3)
C(13)-P(2)-C(19)	103.7(4)
C(13)-P(2)-C(8)	104.3(4)
C(19)-P(2)-C(8)	106.6(4)
C(13)-P(2)-Au(2)	116.9(3)
C(19)-P(2)-Au(2)	115.4(3)
C(8)-P(2)-Au(2)	109.1(3)
C(32)-S(1)-Au(1)	108.1(3)
C(2)-C(1)-C(6)	120.0
C(2)-C(1)-S(2)	123.7(7)
C(6)-C(1)-S(2)	116.3(7)
C(1)-C(2)-C(3)	120.0
C(1)-C(2)-H(2)	120.0
C(3)-C(2)-H(2)	120.0
C(4)-C(3)-C(2)	120.0
C(4)-C(3)-H(3)	120.0
C(2)-C(3)-H(3)	120.0
C(3)-C(4)-C(5)	120.0
C(3)-C(4)-H(4)	120.0
C(5)-C(4)-H(4)	120.0

F(2)-C(5)-C(6)	122.8(8)
F(2)-C(5)-C(4)	117.2(8)
C(6)-C(5)-C(4)	120.0
C(5)-C(6)-C(1)	120.0
C(5)-C(6)-H(6)	120.0
C(1)-C(6)-H(6)	120.0
C(1)-S(2)-Au(2)	111.4(5)
C(2P)-C(1P)-C(6P)	120.0
C(2P)-C(1P)-S(2P)	113.1(14)
C(6P)-C(1P)-S(2P)	126.9(14)
C(1P)-C(2P)-C(3P)	120.0
C(1P)-C(2P)-H(2P)	120.0
C(3P)-C(2P)-H(2P)	120.0
C(4P)-C(3P)-C(2P)	120.0
C(4P)-C(3P)-H(3P)	120.0
C(2P)-C(3P)-H(3P)	120.0
C(3P)-C(4P)-C(5P)	120.0
C(3P)-C(4P)-H(4P)	120.0
C(5P)-C(4P)-H(4P)	120.0
C(4P)-C(5P)-C(6P)	120.0
C(4P)-C(5P)-F(2P)	124.9(15)
C(6P)-C(5P)-F(2P)	114.7(15)
C(5P)-C(6P)-C(1P)	120.0
C(5P)-C(6P)-H(6P)	120.0
C(1P)-C(6P)-H(6P)	120.0
C(1P)-S(2P)-Au(2)	105.0(11)

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+1/2,z-1/2 #2 x+1/2,-y+1/2,z+1/2

Table S7A. Crystal data and structure refinement for compound 7 [Au2(SC6H4(CF3)-4)2(μ-dppe)].

Identification code	[Au2(SC6H4(CF3)-4)2(μ-dppe)]	
Empirical formula	C40 H32 Au2 F6 P2 S2	
Formula weight	1146.65	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.7553(4) Å	α= 64.407(6)°.
	b = 14.6526(8) Å	β= 77.001(5)°.
	c = 15.2724(10) Å	γ = 83.625(4)°.
Volume	1918.2(2) $Å^3$	
Z	2	
Density (calculated)	1.985 Mg/m^3	
Absorption coefficient	7.890 mm^{-1}	
F(000)	1092	
Crystal size	0.480 x 0.180 x 0.170 mm^3	
Theta range for data collection	3.518 to 29.473°.	
Index ranges	-12<=h<=13, -18<=k<=20, -19<=l<=20	
Reflections collected	20777	
Independent reflections	9176 [R(int) = 0.0378]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9176 / 0 / 469	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.0787	
R indices (all data)	R1 = 0.0569, wR2 = 0.0904	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.932 and -1.640 $e.Å^{-3}$	

Table S7B. Bond lengths [Å] and angles [°] for compound 7 [Au2(SC6H4(CF3)-4)2(μ-dppe)].

C(1)-C(9)	1.398(8)	C(14)-F(4)	1.339(8)
C(1)-C(2)	1.417(8)	C(15)-C(16)	1.381(8)
C(1)-S(1)	1.758(6)	C(15)-H(15)	0.9500
C(2)-C(3)	1.384(7)	C(16)-H(16)	0.9500
C(2)-H(2)	0.9500	C(17)-C(18)	1.383(8)
C(3)-C(4)	1.379(8)	C(17)-C(22)	1.403(8)
C(3)-H(3)	0.9500	C(17)-P(2)	1.806(5)
C(4)-C(6)	1.390(9)	C(18)-C(19)	1.388(8)
C(4)-C(5)	1.492(8)	C(18)-H(18)	0.9500
C(5)-F(3)	1.313(7)	C(19)-C(20)	1.365(8)
C(5)-F(1)	1.321(7)	C(19)-H(19)	0.9500
C(5)-F(2)	1.331(8)	C(20)-C(21)	1.379(8)
C(6)-C(9)	1.386(8)	C(20)-H(20)	0.9500
C(6)-H(6)	0.9500	C(21)-C(22)	1.383(8)
C(7)-C(8)	1.522(7)	C(21)-H(21)	0.9500
C(7)-P(1)	1.830(5)	C(22)-H(22)	0.9500
C(7)-H(8A)	0.9900	C(23)-C(28)	1.392(8)
C(7)-H(8B)	0.9900	C(23)-C(24)	1.404(7)
C(8)-P(2)	1.848(5)	C(23)-P(2)	1.817(5)
C(8)-H(9A)	0.9900	C(24)-C(25)	1.389(9)
C(8)-H(9B)	0.9900	C(24)-H(24)	0.9500
C(9)-H(7)	0.9500	C(25)-C(26)	1.374(10)
C(10)-C(11)	1.373(8)	C(25)-H(25)	0.9500
C(10)-C(16)	1.396(8)	C(26)-C(27)	1.369(10)
C(10)-S(2)	1.769(6)	C(26)-H(26)	0.9500
C(11)-C(12)	1.389(9)	C(27)-C(28)	1.398(9)
C(11)-H(11)	0.9500	C(27)-H(27)	0.9500
C(12)-C(13)	1.377(9)	C(28)-H(28)	0.9500
C(12)-H(12)	0.9500	C(29)-C(30)	1.397(8)
C(13)-C(15)	1.362(9)	C(29)-C(34)	1.398(8)
C(13)-C(14)	1.484(9)	C(29)-P(1)	1.815(5)
C(14)-F(5)	1.317(9)	C(30)-C(31)	1.397(8)
C(14)-F(6)	1.325(8)	C(30)-H(30)	0.9500

C(31)-C(32)	1.374(8)
C(31)-H(31)	0.9500
C(32)-C(33)	1.364(9)
C(32)-H(32)	0.9500
C(33)-C(34)	1.388(8)
C(33)-H(33)	0.9500
C(34)-H(34)	0.9500
C(35)-C(36)	1.385(8)
C(35)-C(40)	1.390(8)
C(35)-P(1)	1.820(6)
C(36)-C(37)	1.395(9)
C(36)-H(36)	0.9500
C(37)-C(38)	1.371(10)
C(37)-H(37)	0.9500
C(38)-C(39)	1.369(9)
C(38)-H(38)	0.9500
C(39)-C(40)	1.381(9)
C(39)-H(39)	0.9500
C(40)-H(40)	0.9500
Au(1)-P(1)	2.2555(15)
Au(1)-S(1)	2.3237(14)
Au(2)-P(2)	2.2615(14)
Au(2)-S(2)	2.3207(14)
C(9)-C(1)-C(2)	118.3(5)
C(9)-C(1)-S(1)	117.8(4)
C(2)-C(1)-S(1)	123.9(4)
C(3)-C(2)-C(1)	120.0(5)
C(3)-C(2)-H(2)	120.0
C(1)-C(2)-H(2)	120.0
C(4)-C(3)-C(2)	121.1(6)
C(4)-C(3)-H(3)	119.4
C(2)-C(3)-H(3)	119.4
C(3)-C(4)-C(6)	119.3(5)
C(3)-C(4)-C(5)	121.8(6)
C(6)-C(4)-C(5)	118.9(6)
F(3)-C(5)-F(1)	107.1(6)
F(3)-C(5)-F(2)	104.8(6)
F(1)-C(5)-F(2)	106.0(5)
F(3)-C(5)-C(4)	112.9(5)
F(1)-C(5)-C(4)	112.6(6)
F(2)-C(5)-C(4)	112.9(6)
C(9)-C(6)-C(4)	120.7(6)
C(9)-C(6)-H(6)	119.6
C(4)-C(6)-H(6)	119.6
C(8)-C(7)-P(1)	111.2(3)
C(8)-C(7)-H(8A)	109.4
P(1)-C(7)-H(8A)	109.4
C(8)-C(7)-H(8B)	109.4
P(1)-C(7)-H(8B)	109.4
H(8A)-C(7)-H(8B)	108.0
C(7)-C(8)-P(2)	109.6(3)
C(7)-C(8)-H(9A)	109.7
P(2)-C(8)-H(9A)	109.7
C(7)-C(8)-H(9B)	109.7
P(2)-C(8)-H(9B)	109.7
H(9A)-C(8)-H(9B)	108.2
C(6)-C(9)-C(1)	120.5(6)
C(6)-C(9)-H(7)	119.7
C(1)-C(9)-H(7)	119.7
C(11)-C(10)-C(16)	118.3(5)
C(11)-C(10)-S(2)	124.1(4)
C(16)-C(10)-S(2)	117.6(4)
C(10)-C(11)-C(12)	120.7(6)
C(10)-C(11)-H(11)	119.7
C(12)-C(11)-H(11)	119.7
C(13)-C(12)-C(11)	120.6(6)
C(13)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7
C(15)-C(13)-C(12)	118.9(6)

C(15)-C(13)-C(14)	122.3(6)
C(12)-C(13)-C(14)	118.8(6)
F(5)-C(14)-F(6)	104.8(6)
F(5)-C(14)-F(4)	105.0(6)
F(6)-C(14)-F(4)	105.3(6)
F(5)-C(14)-C(13)	114.2(6)
F(6)-C(14)-C(13)	113.7(6)
F(4)-C(14)-C(13)	112.9(6)
C(13)-C(15)-C(16)	121.2(6)
C(13)-C(15)-H(15)	119.4
C(16)-C(15)-H(15)	119.4
C(15)-C(16)-C(10)	120.2(6)
C(15)-C(16)-H(16)	119.9
C(10)-C(16)-H(16)	119.9
C(18)-C(17)-C(22)	118.7(5)
C(18)-C(17)-P(2)	118.9(4)
C(22)-C(17)-P(2)	122.4(4)
C(17)-C(18)-C(19)	120.3(5)
C(17)-C(18)-H(18)	119.8
C(19)-C(18)-H(18)	119.8
C(20)-C(19)-C(18)	120.4(6)
C(20)-C(19)-H(19)	119.8
C(18)-C(19)-H(19)	119.8
C(19)-C(20)-C(21)	120.4(6)
C(19)-C(20)-H(20)	119.8
C(21)-C(20)-H(20)	119.8
C(20)-C(21)-C(22)	119.9(6)
C(20)-C(21)-H(21)	120.1
C(22)-C(21)-H(21)	120.1
C(21)-C(22)-C(17)	120.3(5)
C(21)-C(22)-H(22)	119.8
C(17)-C(22)-H(22)	119.8
C(28)-C(23)-C(24)	118.4(5)
C(28)-C(23)-P(2)	122.9(4)
C(24)-C(23)-P(2)	118.7(4)

C(25)-C(24)-C(23)	120.3(6)
C(25)-C(24)-H(24)	119.9
C(23)-C(24)-H(24)	119.9
C(26)-C(25)-C(24)	120.0(6)
C(26)-C(25)-H(25)	120.0
C(24)-C(25)-H(25)	120.0
C(27)-C(26)-C(25)	120.8(7)
C(27)-C(26)-H(26)	119.6
C(25)-C(26)-H(26)	119.6
C(26)-C(27)-C(28)	119.9(7)
C(26)-C(27)-H(27)	120.1
C(28)-C(27)-H(27)	120.1
C(23)-C(28)-C(27)	120.4(6)
C(23)-C(28)-H(28)	119.8
C(27)-C(28)-H(28)	119.8
C(30)-C(29)-C(34)	118.6(5)
C(30)-C(29)-P(1)	123.3(4)
C(34)-C(29)-P(1)	118.0(4)
C(31)-C(30)-C(29)	120.1(5)
C(31)-C(30)-H(30)	120.0
C(29)-C(30)-H(30)	120.0
C(32)-C(31)-C(30)	120.1(6)
C(32)-C(31)-H(31)	120.0
C(30)-C(31)-H(31)	120.0
C(33)-C(32)-C(31)	120.4(6)
C(33)-C(32)-H(32)	119.8
C(31)-C(32)-H(32)	119.8
C(32)-C(33)-C(34)	120.6(6)
C(32)-C(33)-H(33)	119.7
C(34)-C(33)-H(33)	119.7
C(33)-C(34)-C(29)	120.2(6)
C(33)-C(34)-H(34)	119.9
C(29)-C(34)-H(34)	119.9
C(36)-C(35)-C(40)	118.5(5)
C(36)-C(35)-P(1)	119.1(4)

C(40)-C(35)-P(1)	122.4(4)
C(35)-C(36)-C(37)	120.2(6)
C(35)-C(36)-H(36)	119.9
C(37)-C(36)-H(36)	119.9
C(38)-C(37)-C(36)	119.9(6)
C(38)-C(37)-H(37)	120.1
C(36)-C(37)-H(37)	120.1
C(39)-C(38)-C(37)	120.8(6)
C(39)-C(38)-H(38)	119.6
C(37)-C(38)-H(38)	119.6
C(38)-C(39)-C(40)	119.4(6)
C(38)-C(39)-H(39)	120.3
C(40)-C(39)-H(39)	120.3
C(39)-C(40)-C(35)	121.2(6)
C(39)-C(40)-H(40)	119.4
C(35)-C(40)-H(40)	119.4
P(1)-Au(1)-S(1)	165.34(5)
P(2)-Au(2)-S(2)	174.33(5)
C(29)-P(1)-C(35)	103.5(2)
C(29)-P(1)-C(7)	105.9(2)
C(35)-P(1)-C(7)	103.0(2)
C(29)-P(1)-Au(1)	119.35(18)
C(35)-P(1)-Au(1)	112.32(19)
C(7)-P(1)-Au(1)	111.19(19)
C(17)-P(2)-C(23)	108.1(2)
C(17)-P(2)-C(8)	105.5(2)
C(23)-P(2)-C(8)	99.3(2)
C(17)-P(2)-Au(2)	116.69(19)
C(23)-P(2)-Au(2)	112.84(17)
C(8)-P(2)-Au(2)	112.85(17)
C(1)-S(1)-Au(1)	105.0(2)
C(10)-S(2)-Au(2)	106.75(19)

NMR spectra

General note. ^{1}H-NMR spectra may present the following solvent or environmental (water) residual signals: water, 1.56 ppm; acetone, 2.17 ppm; dichloromethane, 5.30 ppm.

Compound 1 *[$Au_2(SC_6F_5)_2(\mu$-dppe)].*

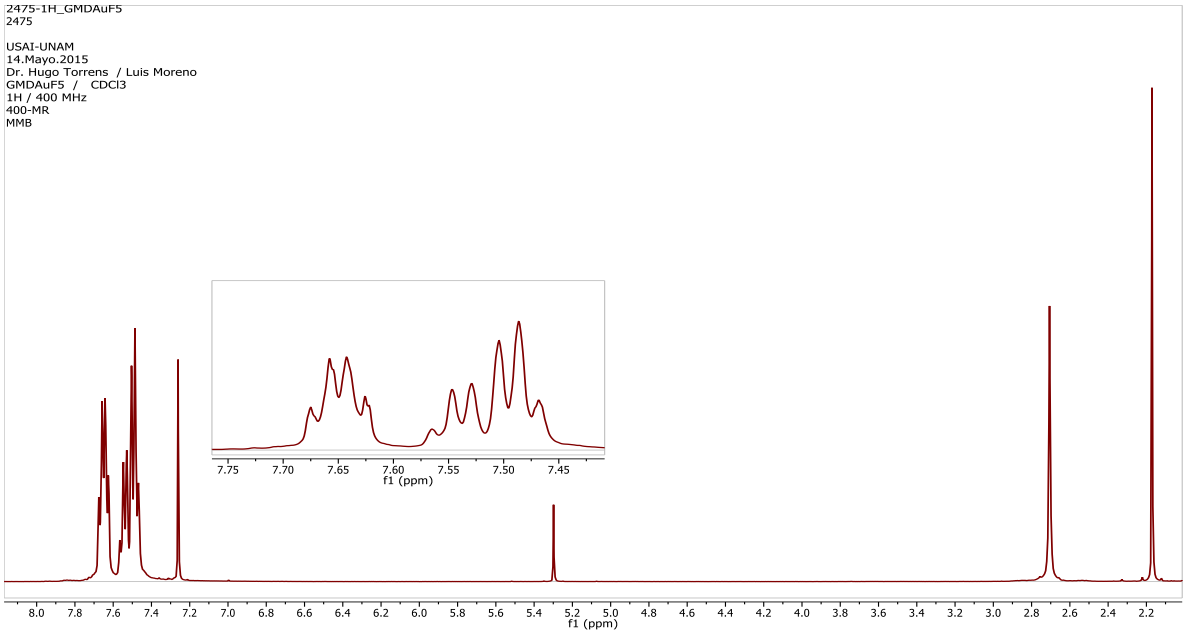

Figure S 1- ^{1}H-NMR-Spectrum of Compound 1 [$Au_2(SC_6F_5)_2(\mu$-dppe)].

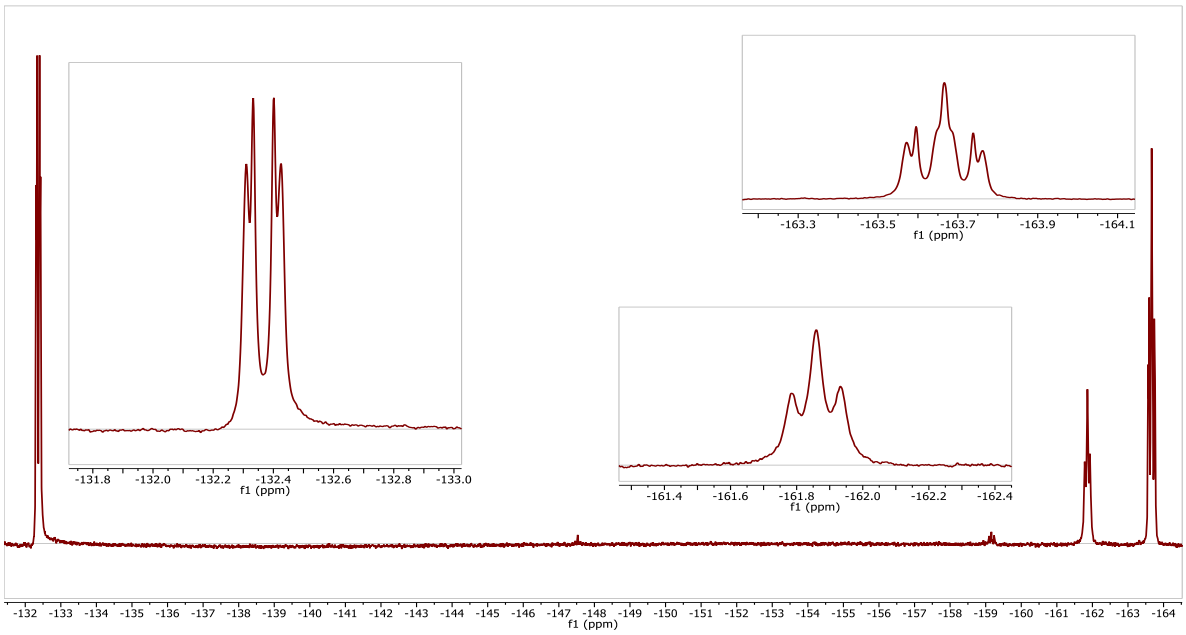

Figure S 2- ^{19}F-NMR-Spectrum of Compound 1 [$Au_2(SC_6F_5)_2(\mu$-dppe)].

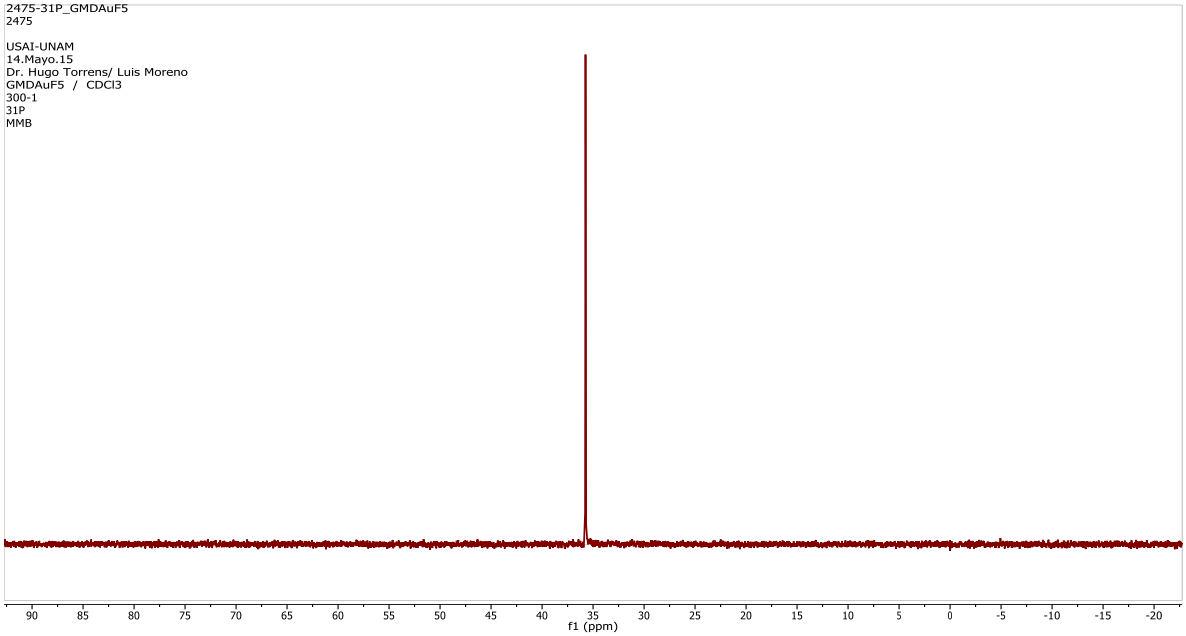

Figure S 3-^{31}P-NMR-Spectrum of Compound 1 [$Au_2(SC_6F_5)_2$(μ-dppe)].

Compound 2

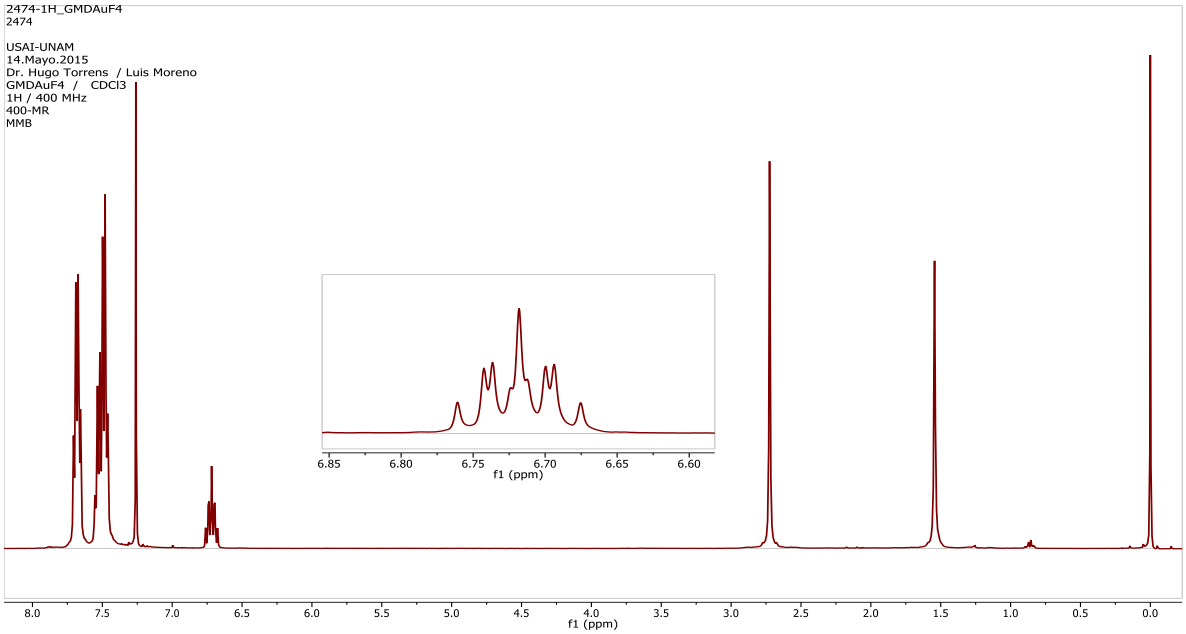

Figure S 4-^{1}H-NMR-Spectrum of Compound 2 [$Au_2(SC_6F_4H)_2$(μ-dppe)].

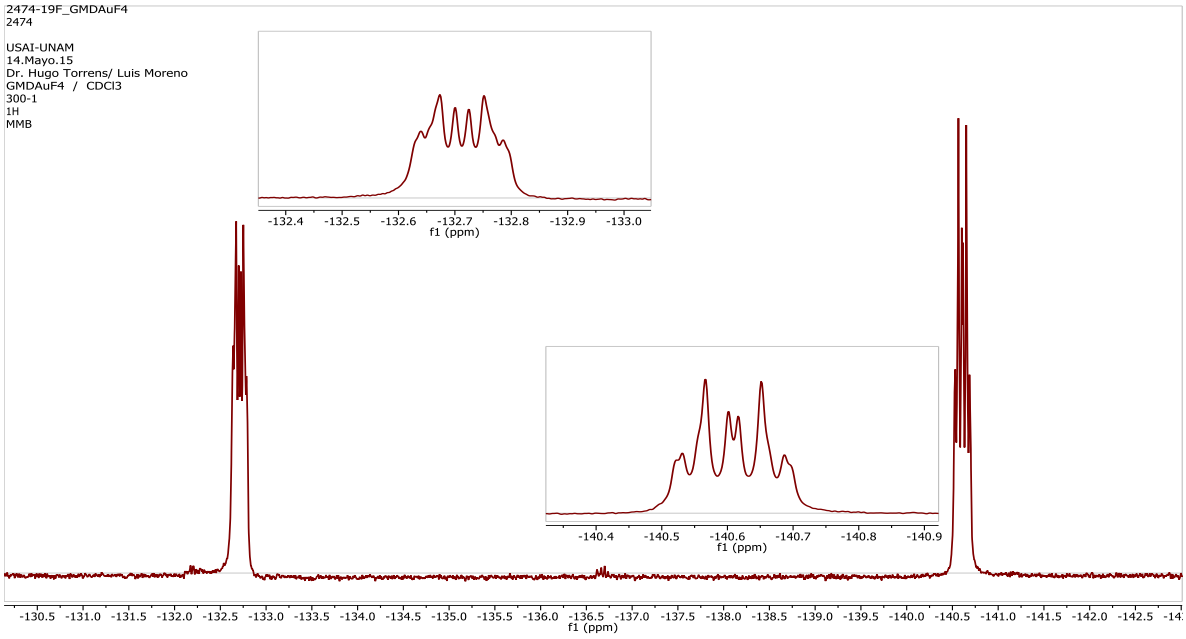

Figure S 5-^{19}F-NMR-Spectrum of Compound 2 [$Au_2(SC_6F_4H)_2$(μ-dppe)].

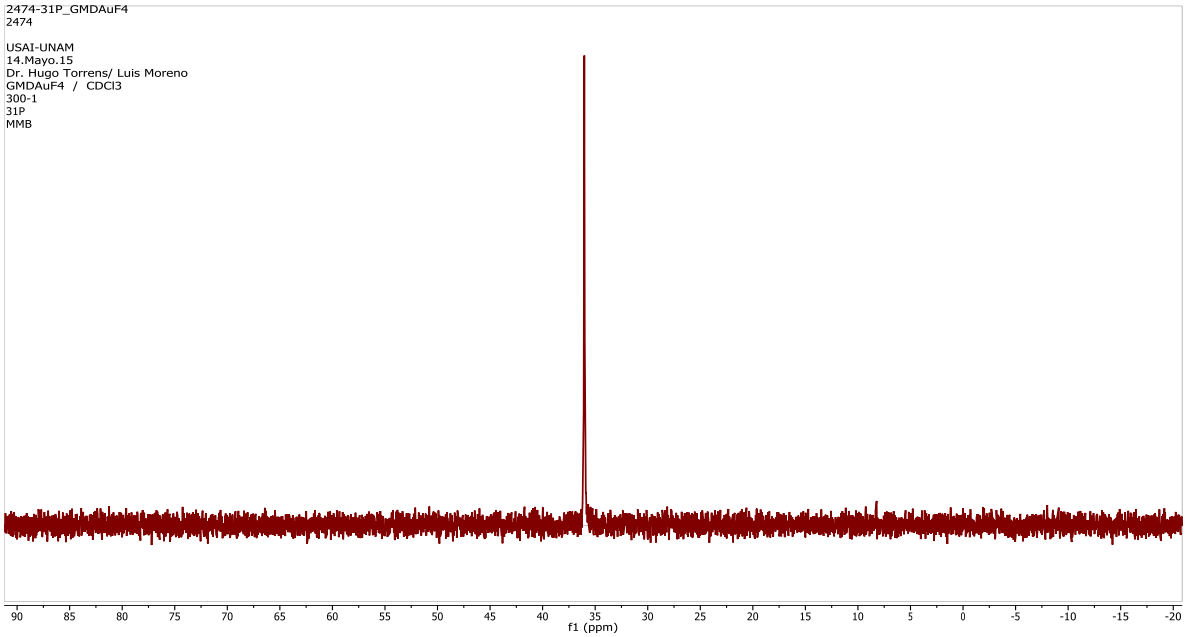

Figure S 6-^{31}P-NMR-Spectrum of Compound 2 [$Au_2(SC_6F_4H)_2$(μ-dppe)].

Compound 3

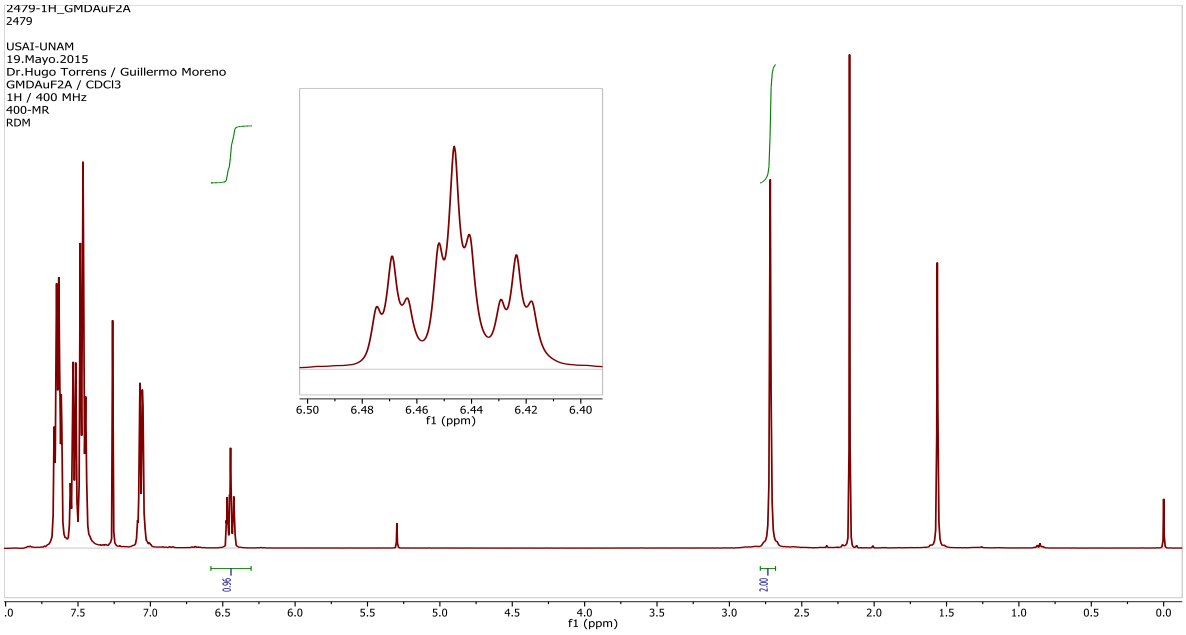

Figure S 7-^{1}H-NMR-Spectrum of Compound 3 [$Au_2(SC_6F_2H_3$-3,5$)_2$(μ-dppe)].

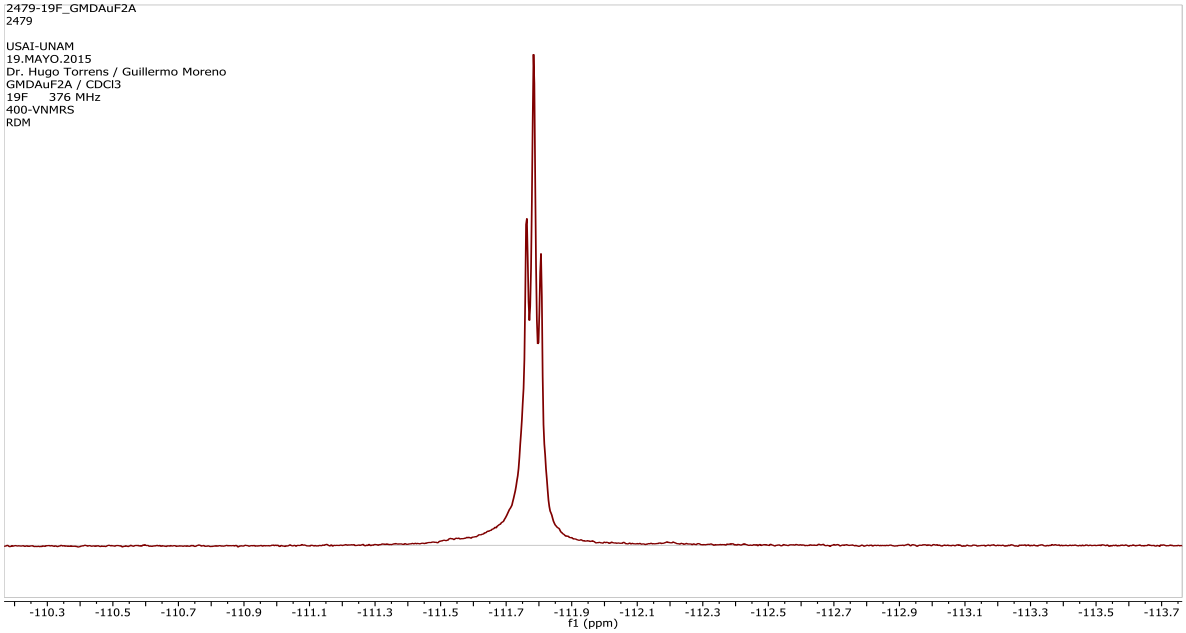

Figure S 8- ^{19}F NMR-Spectrum of Compound 3 [$Au_2(SC_6F_2H_3$-3,5$)_2$(μ-dppe)].

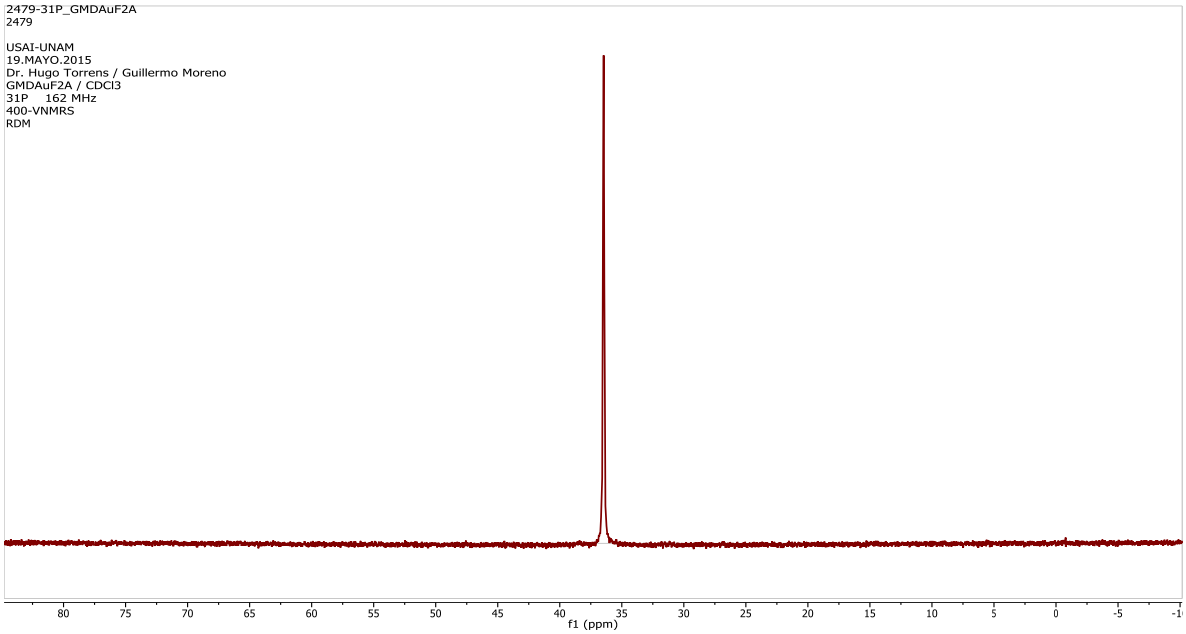

Figure S 9-^{31}P NMR-Spectrum of Compound 3 [$Au_2(SC_6F_2H_3$-3,5$)_2$(μ-dppe)].

Compound 4

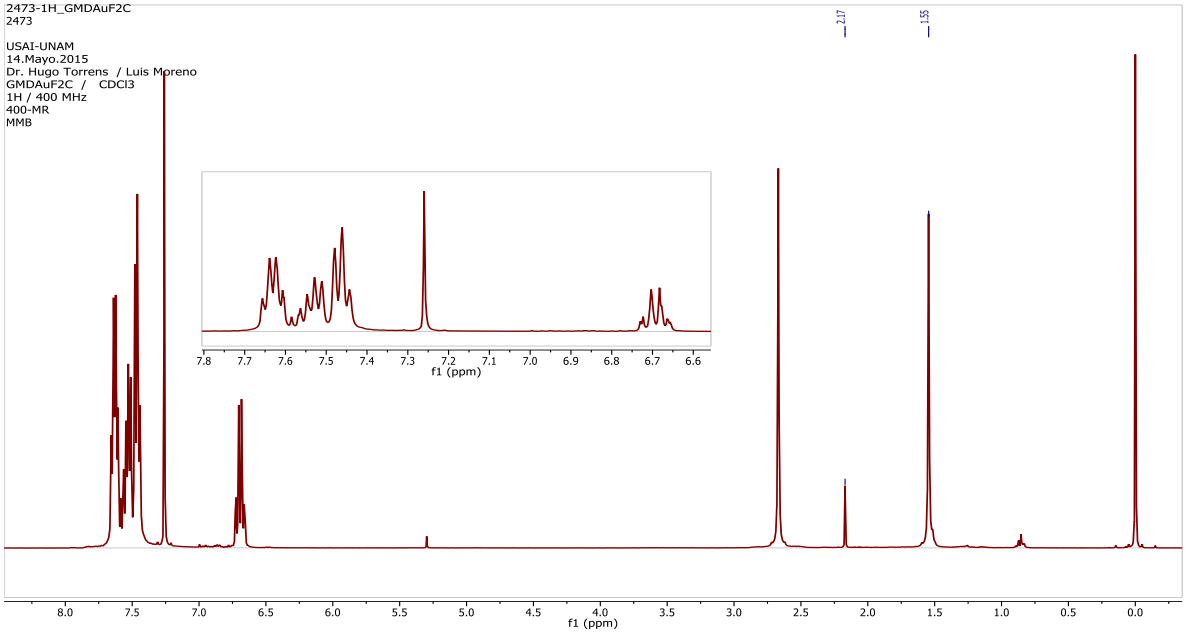

Figure S 10-^{1}H-NMR-Spectrum of Compound 4 [$Au_2(SC_6F_2H_3$-2,4$)_2$(μ-dppe)].

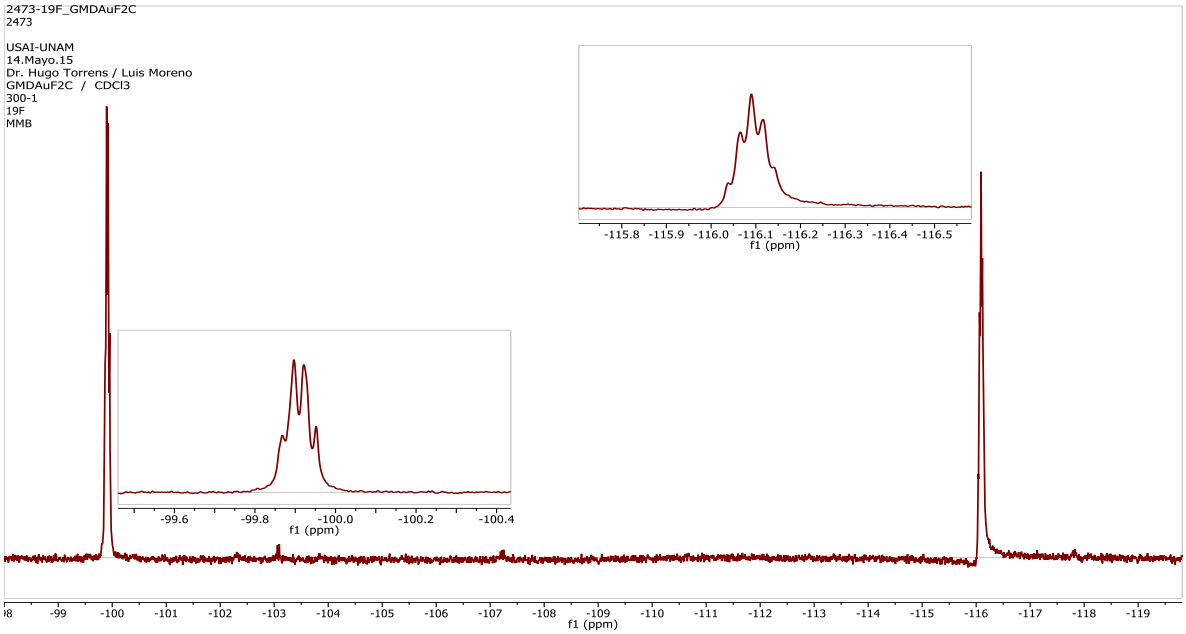

Figure S 11- ^{19}F-NMR-Spectrum of Compound 4 [$Au_2(SC_6F_2H_3$-2,4$)_2$(μ-dppe)].

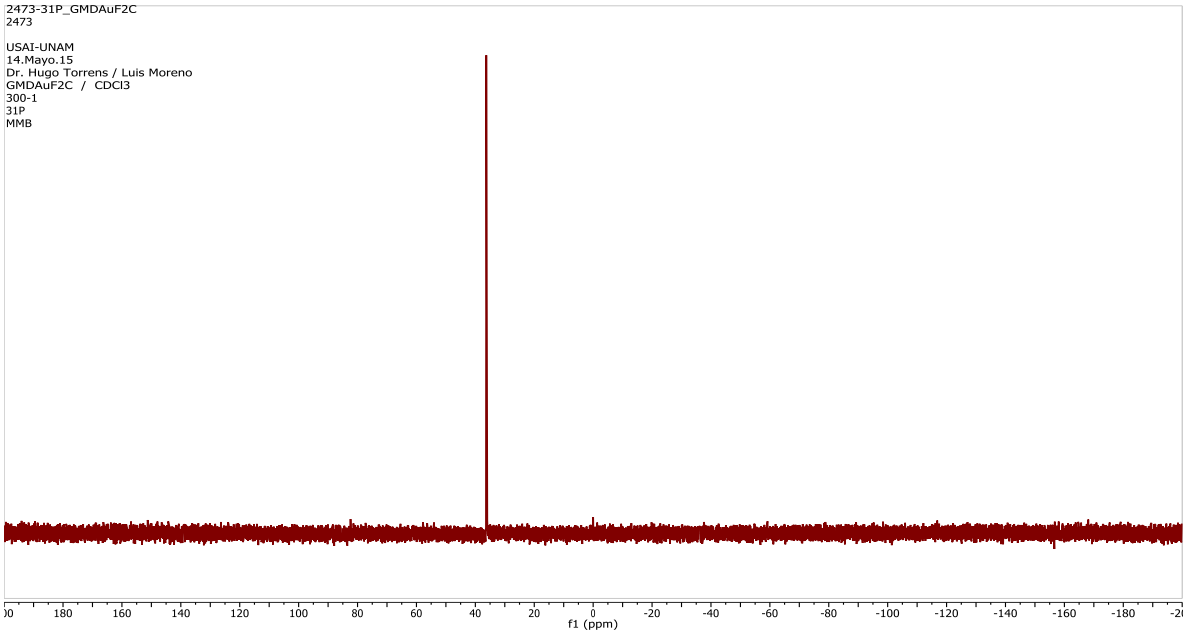

Figure S 12- ^{31}P-NMR-Spectrum of Compound 4 [$Au_2(SC_6F_2H_3$-2,4$)_2$(μ-dppe)].

Compound 5

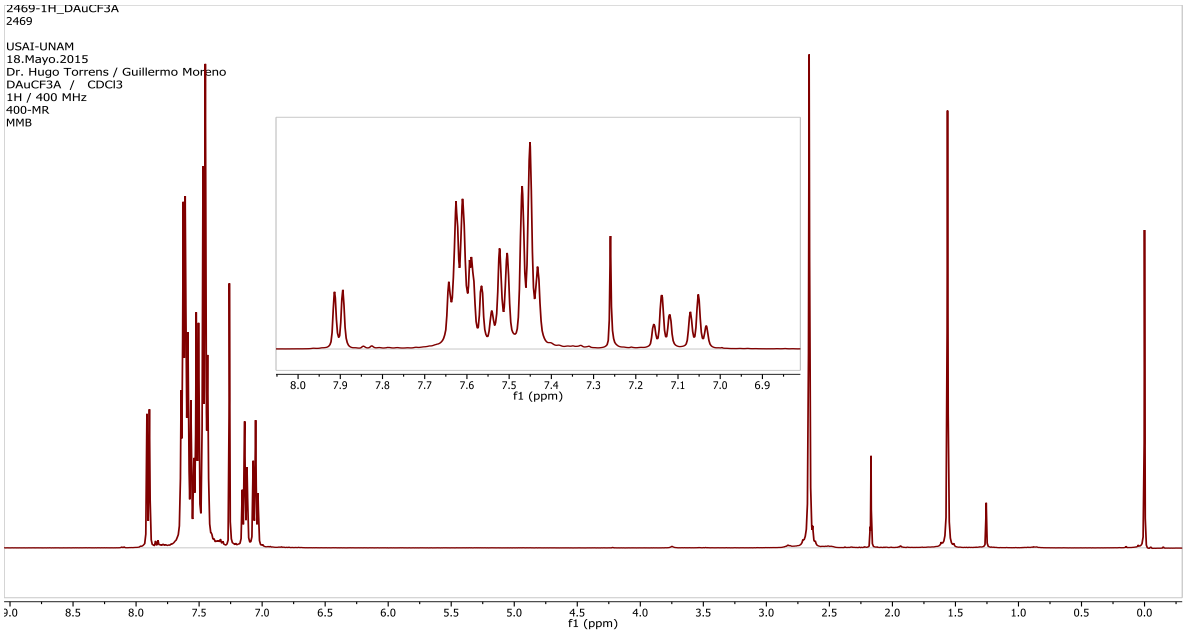

Figure S 13- ^{1}H-NMR-Spectrum of Compound 5 [$Au_2(SC_6H_4(CF_3)\text{-}2)_2(\mu\text{-dppe})$].

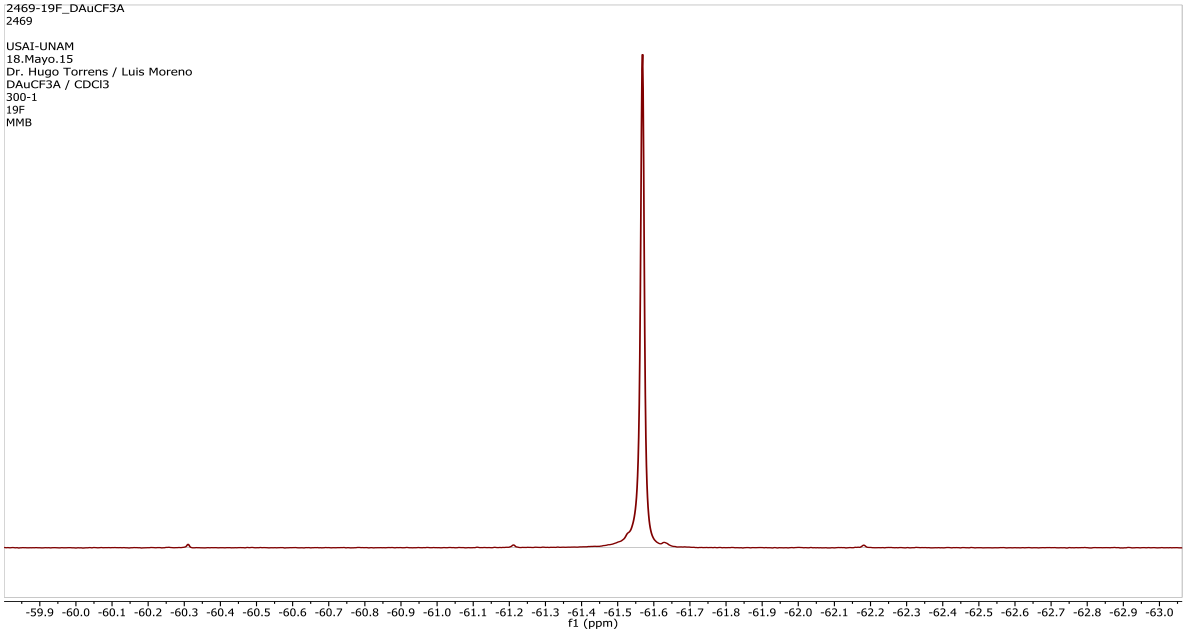

Figure S 14- ^{19}F-NMR-Spectrum of Compound 5 [$Au_2(SC_6H_4(CF_3)\text{-}2)_2(\mu\text{-dppe})$].

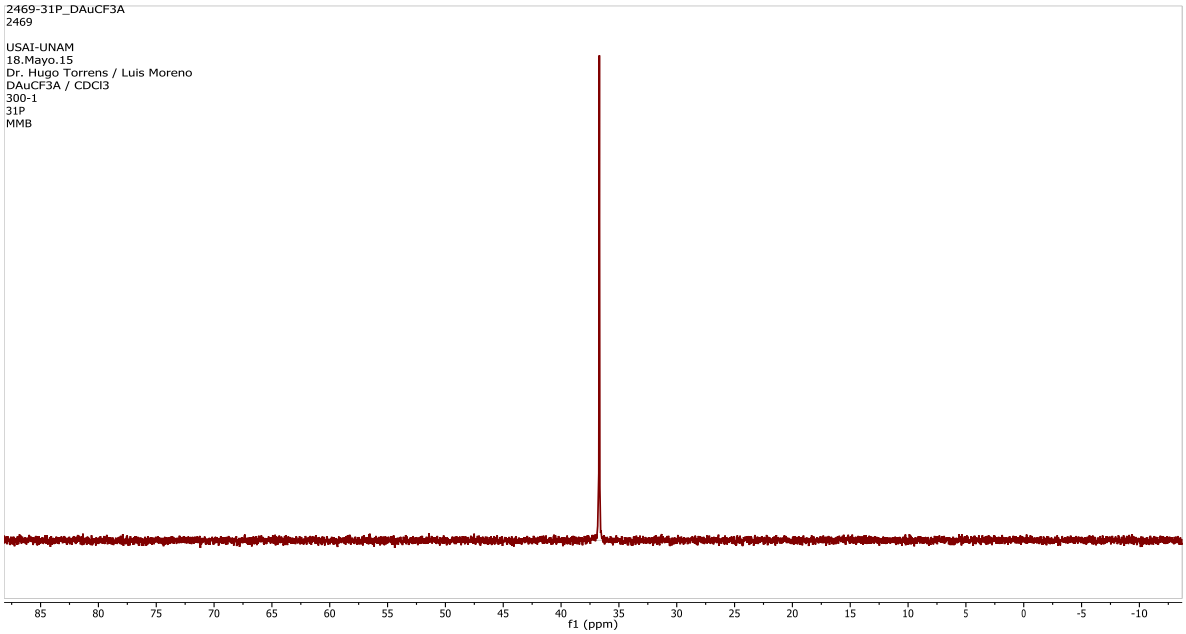

Figure S 15- ^{31}P-NMR-Spectrum of Compound 5 [$Au_2(SC_6H_4(CF_3)$-2)$_2$(μ-dppe)].

Compound 6

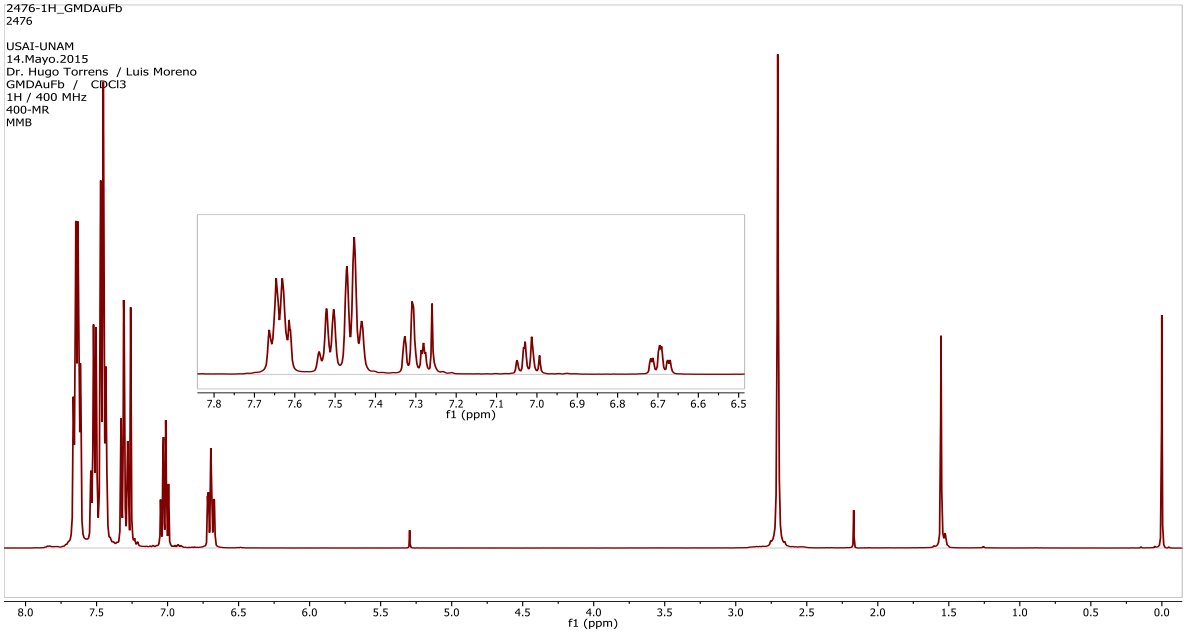

Figure S 16- ^{1}H-NMR-Spectrum of Compound 6 [$Au_2(SC_6H_4F$-3)$_2$(μ-dppe)].

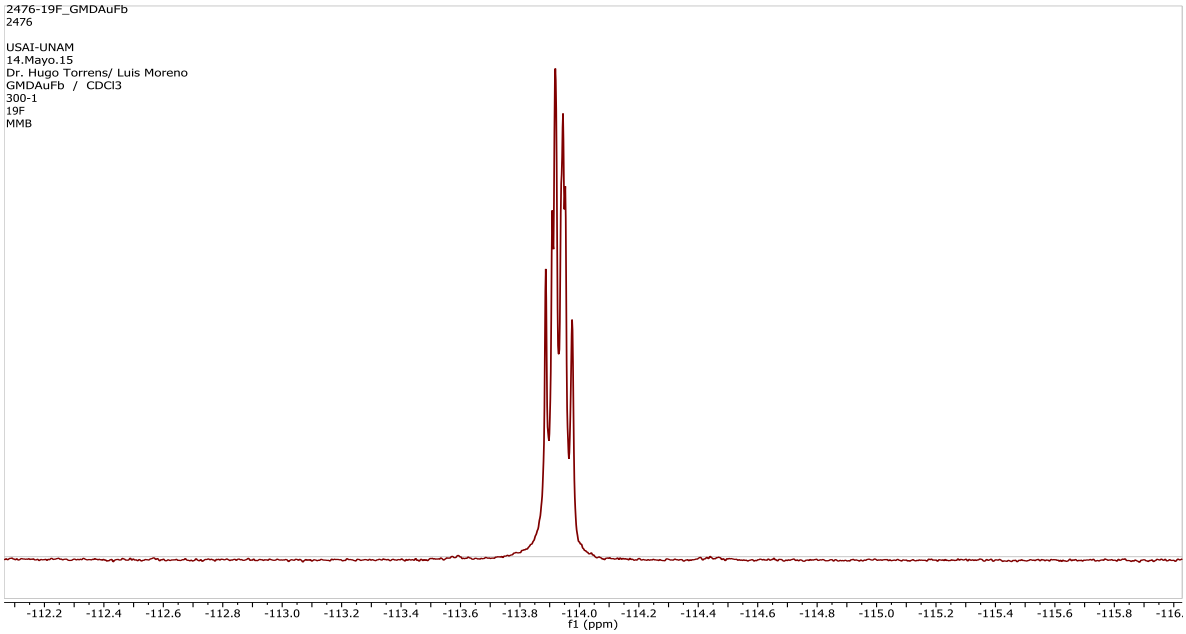

Figure S 17- ^{19}F-NMR-Spectrum of Compound 6 [$Au_2(SC_6H_4F\text{-}3)_2(\mu\text{-}dppe)$].

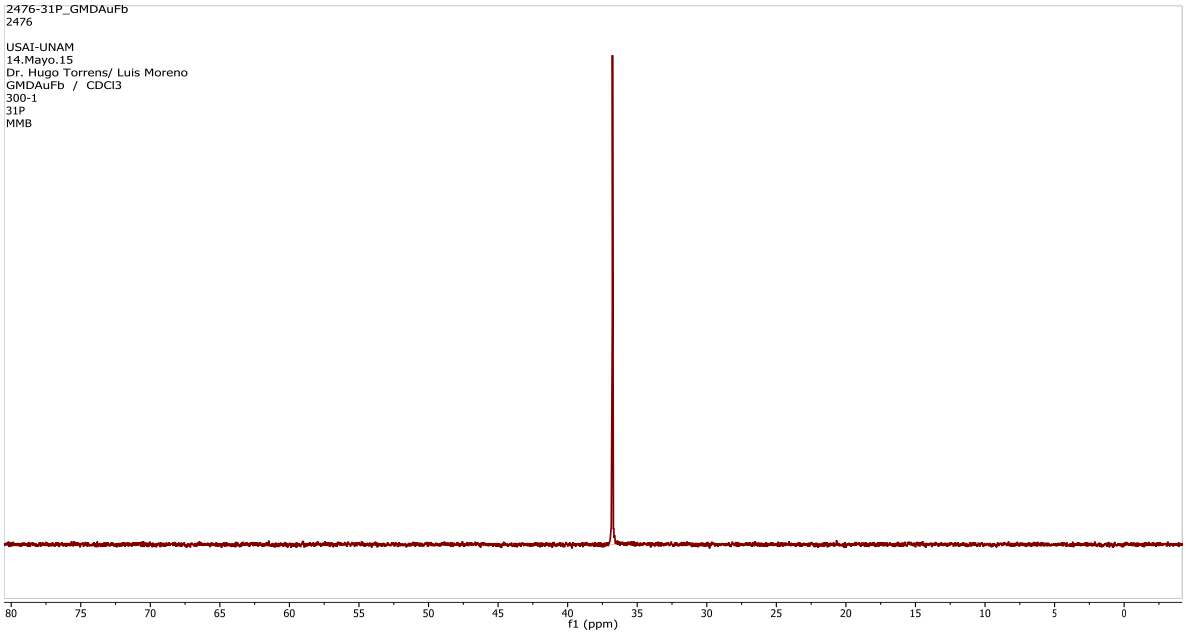

Figure S 18- ^{31}P-NMR-Spectrum of Compound 6 [$Au_2(SC_6H_4F\text{-}3)_2(\mu\text{-}dppe)$].

Compound 7

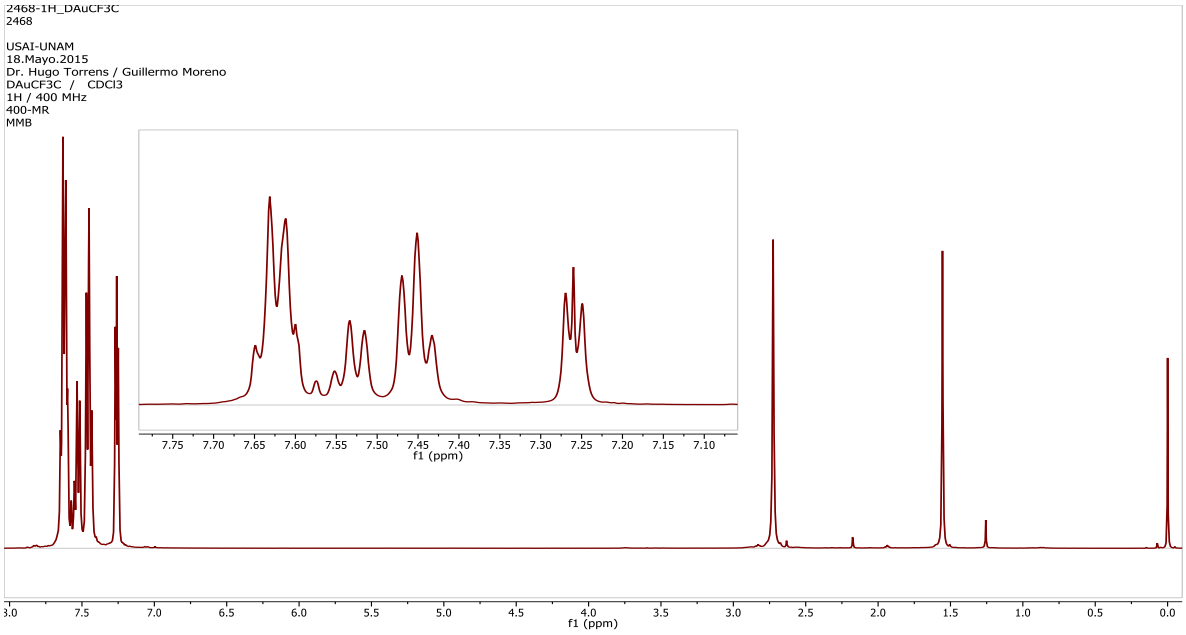

Figure S 19- ^{1}H-NMR-Spectrum of Compound 7 [$Au_2(SC_6H_4(CF_3)\text{-}4)_2(\mu\text{-dppe})$].

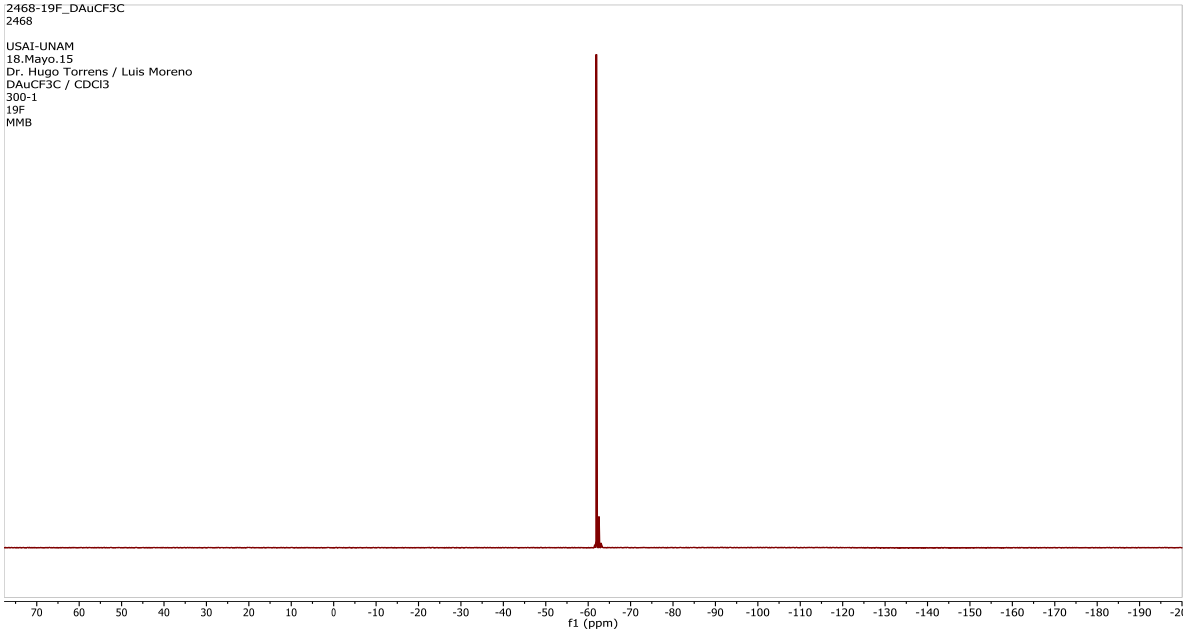

Figure S 20- ^{19}F-NMR-Spectrum of Compound 7 [$Au_2(SC_6H_4(CF_3)\text{-}4)_2(\mu\text{-dppe})$].

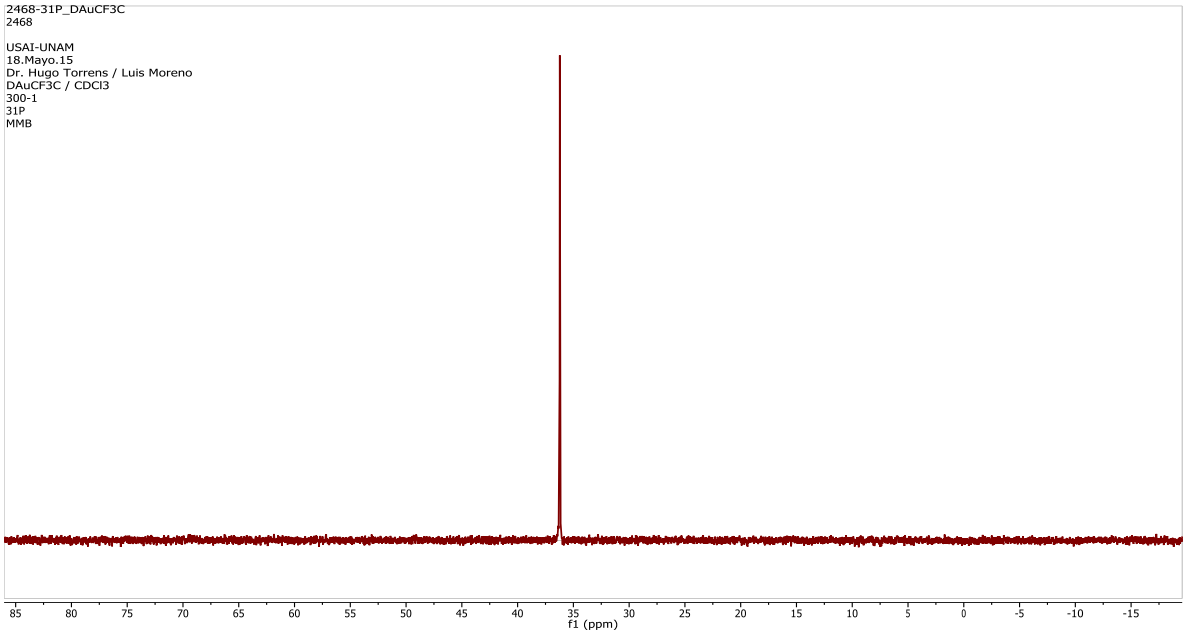

Figure S 21- ^{31}P-NMR-Spectrum of Compound 7 [$Au_2(SC_6H_4(CF_3)\text{-}4)_2(\mu\text{-dppe})$].

Solution UV-absorption spectrum

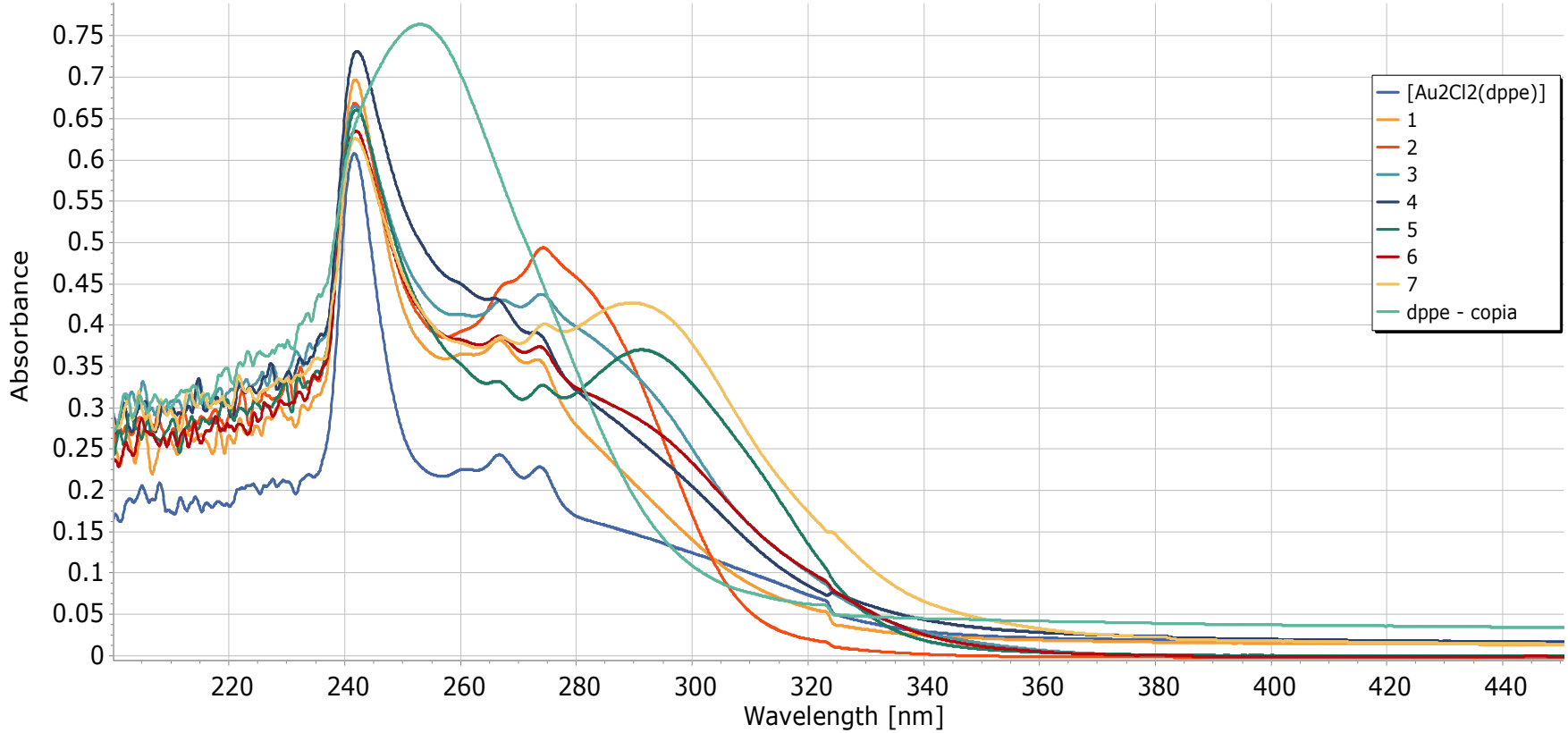

Figure S 22- Uncorrected spectra acquired in chloroform solutions in a UV/Visible lambda 2, Perkin Elmer spectrophotometer.

References

1 A. T. Agilent CrysAlis PRO and CrysAlis RED, 2013.

2 R. C. Clark and J. S. Reid, *Acta Crystallogr. Sect. A Found. Crystallogr.*, 1995, **51**, 887–897.

3 G. M. Sheldrick, *Acta Cryst*, 2015, **71**, 3–8.

4 G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 3–8.

5 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.

6 M. Levy and J. P. Perdew, *J. Chem. Phys.*, 1986, **84**, 4519–4523.

7 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100.

8 E. Van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1993, **99**, 4597–4610.

9 D. A. Pantazis, X.-Y. Chen, C. R. Landis and F. Neese, *J. Chem. Theory Comput.*, 2008, **4**, 908–919.

10 F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2012, **2**, 73–78.

11 M. El-Hamdi, M. Solà, G. Frenking and J. Poater, *J. Phys. Chem. A*, 2013, **117**, 8026–8034.

12 M. Palusiak, C. Fonseca Guerra and F. M. Bickelhaupt, *Int. J. Quantum Chem.*, 2009, **109**, 2507–2519.

13 C. F. Matta, R. J. Boyd and Wiley InterScience (Online service), *The quantum theory of atoms in molecules: from solid state to DNA and drug design*, Wiley-VCH, 2007.

14 P. Macchi and A. Sironi, *Coord. Chem. Rev.*, 2003, **238**, 383–412.

15 J. S. M. Anderson and P. W. Ayers, *J. Phys. Chem. A*, 2011, **115**, 13001–13006.

16 T. A. Keith, 2016, AIMAll (version 12.06.03) 2016.

17 E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen and W.

Yang, *J. Am. Chem. Soc.*, 2010, **132**, 6498–6506.

18 J. Contreras-García, E. R. Johnson, S. Keinan, R. Chaudret, J. P. Piquemal, D. N. Beratan and W. Yang, *J. Chem. Theory Comput.*, 2011, **7**, 625–632.

19 W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graph.*, 1996, **14**, 33–38.

20 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.