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SUPPLEMENTARY MATERIAL

Palladacycle Promoted Asymmetric P-H Addition of Diphenylphosphine to 3-Benzylidene-2,4-pentadione: Catalyst inactivation via unexpected P,O chelation

In memory of Emeritus Professor Brice Bosnich for his contributions to the field of organophosphorus chemistry and in catalysis. LPH is grateful to Professor Bosnich for his guidance during his stay at the University of Toronto and the University of Chicago

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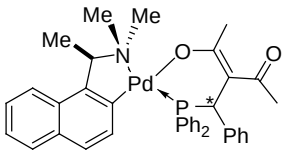
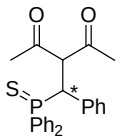
1. Characterization of Reaction Products



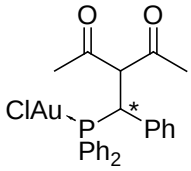
9

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 50.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68-7.55 (m, 21H), 5.17-5.22 (d, J = 20.1 Hz, 1H)). 4.48-4.52 (m, 1H), 3.00 – 3.01 (d, *J* = 3.3 Hz, 3H), 2.86 (s, 3H), 2.36 (s, 3H), 2.24 (s, 3H), 1.94-1.95 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 123.98-134.60, 70.96, 50.90, 45.18, 41.18, 30.76, 30.07, 29.79, 24.81, 23.48. HRMS of **9**: Calculated for $C_{38}H_{39}NO_2PPd$= 678.1753, found= 678.1729.



11

$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) δ 50.64. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14-7.17 (m, 15H), 5.19-5.24 (dd, J = 13.1, 10.9 Hz, 1H), 4.94-5.00 (dd, J = 10.8, 9.1 Hz, 1H), 2.04 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.92-127.83, 70.21, 46.70, 31.42, 29.02. HRMS of **11**: Calculated for $C_{24}H_{24}O_2PS$=407.1235, found=407.1231.



Au-phosphine adduct

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 49.65. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-8.04 (m, 15H), 4.90-5.01 (m, 2H), 1.92 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 128.46-135.72, 72.59, 43.94, 31.22, 28.79.

2. NMR Spectra

Figure 1A. ^{31}P NMR of **9.**

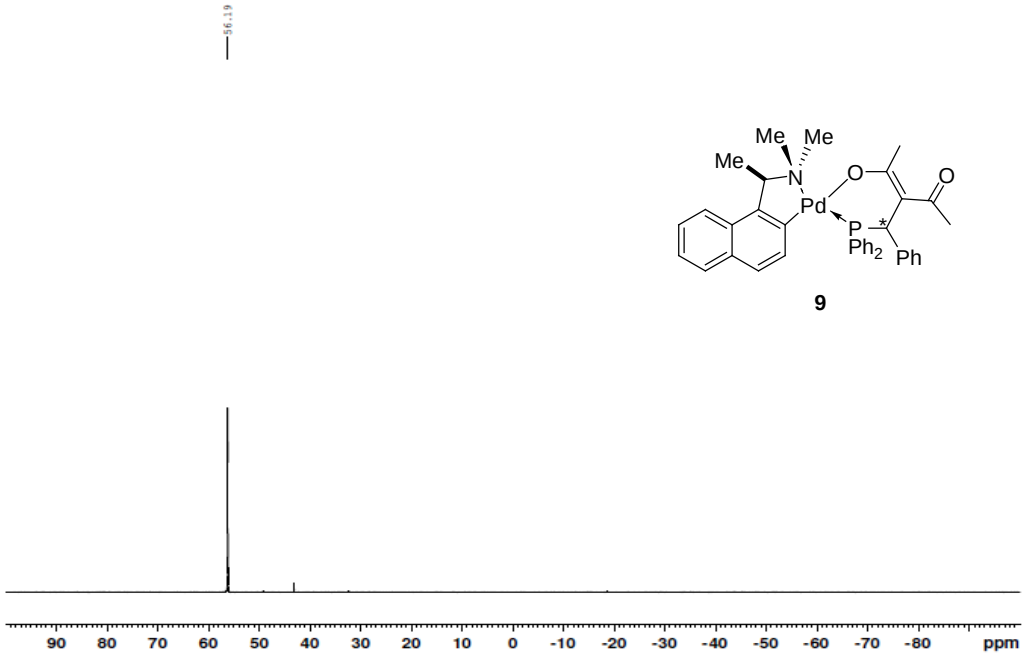


Figure 1B. ^{1}H NMR of **9.**

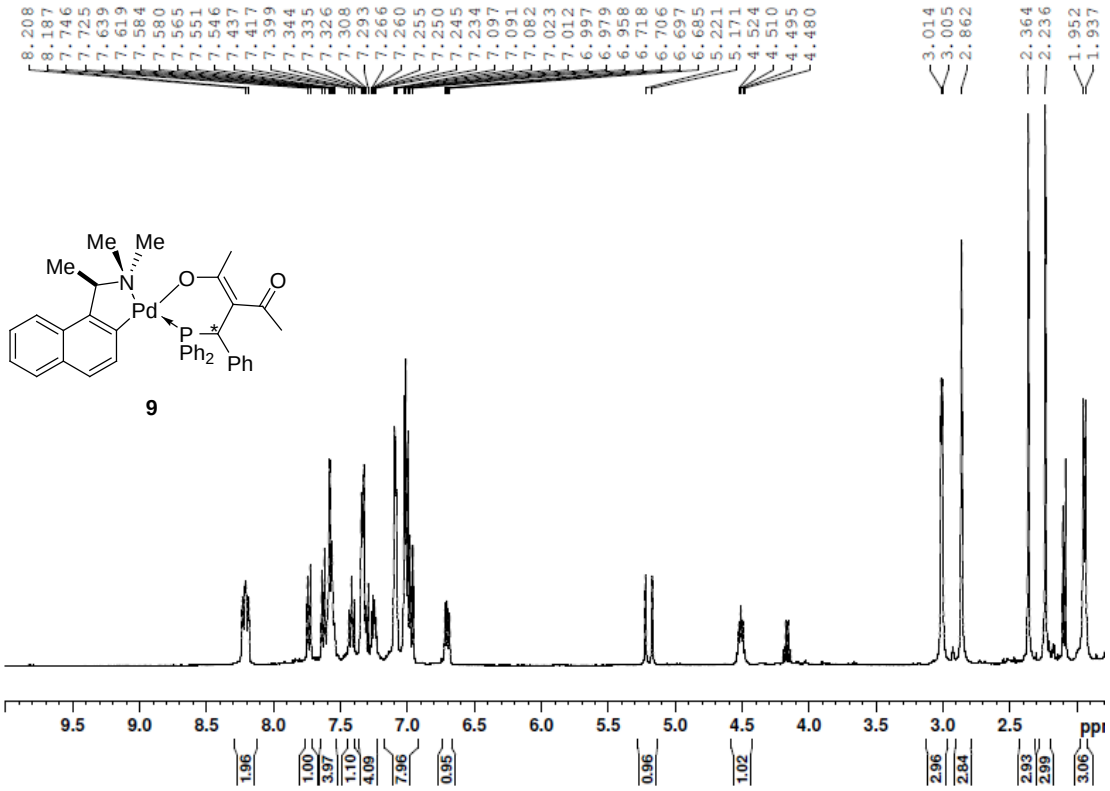


Figure 1C. ^{13}C NMR of **9.**

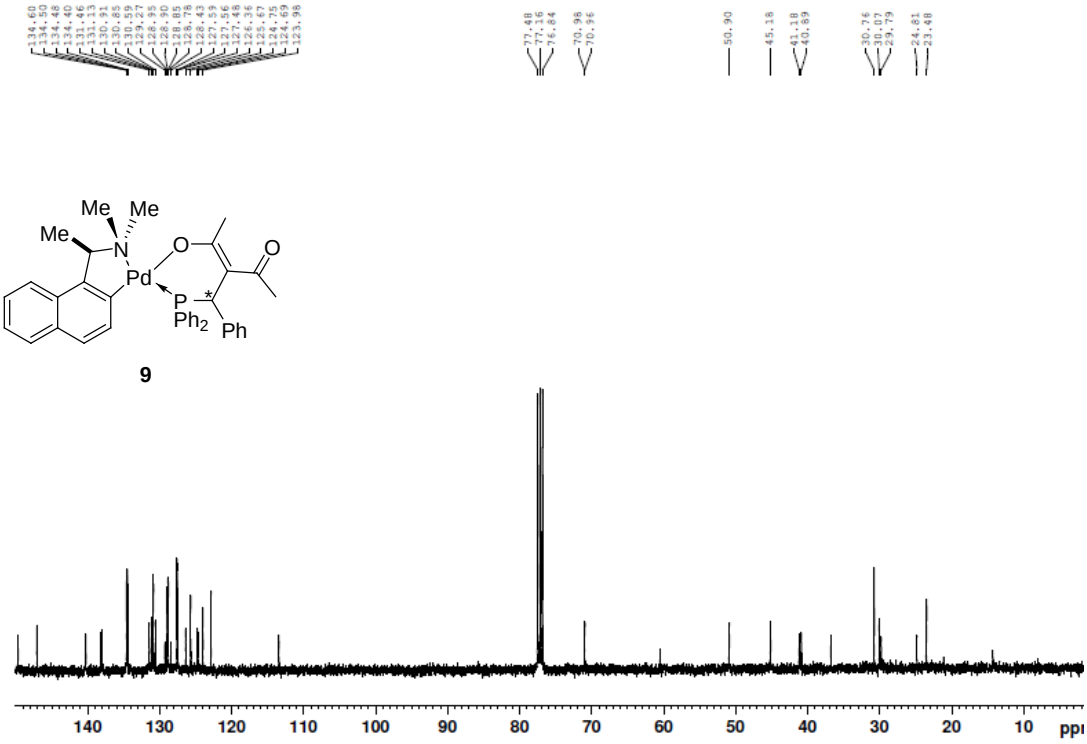


Figure 1D. HRMS of **9.**

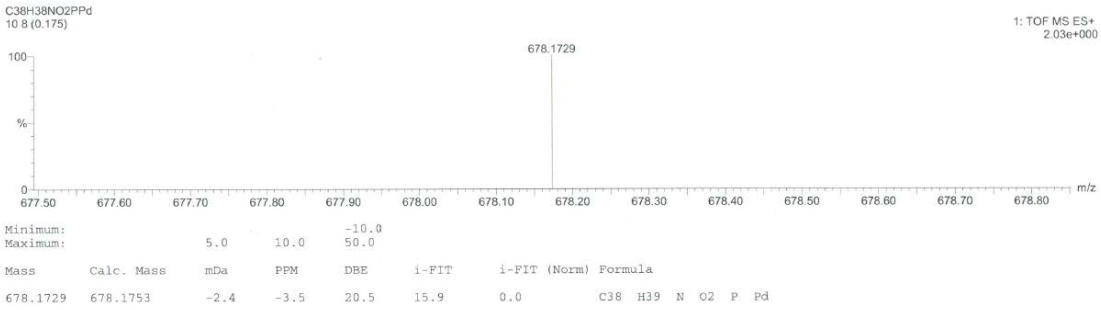


Figure 2A. ^{31}P NMR of **11.**

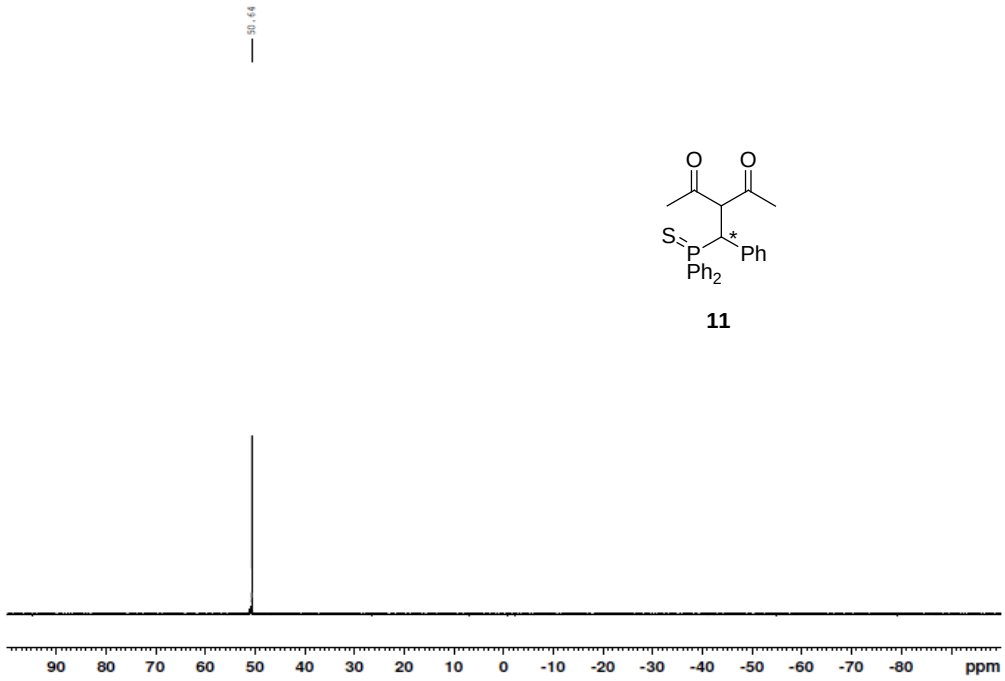


Figure 2B. ^{1}H NMR of **11.**

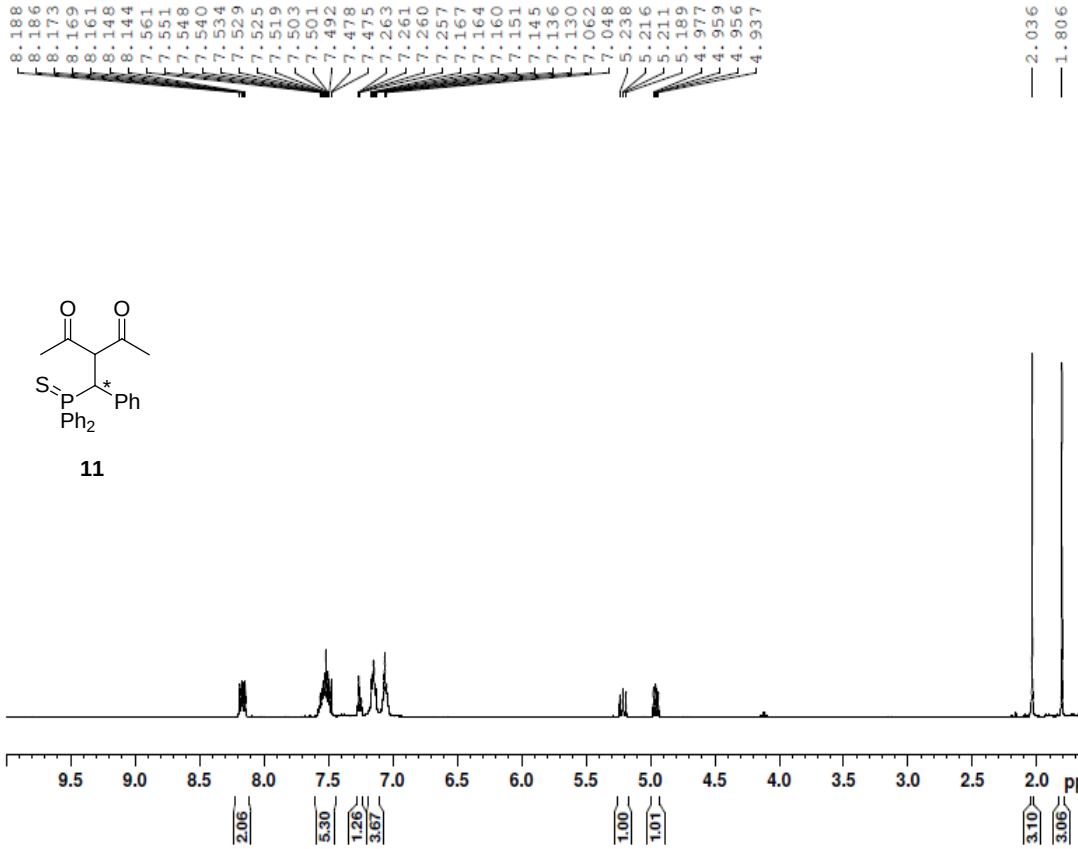


Figure 1C. ^{13}C NMR of **11.**

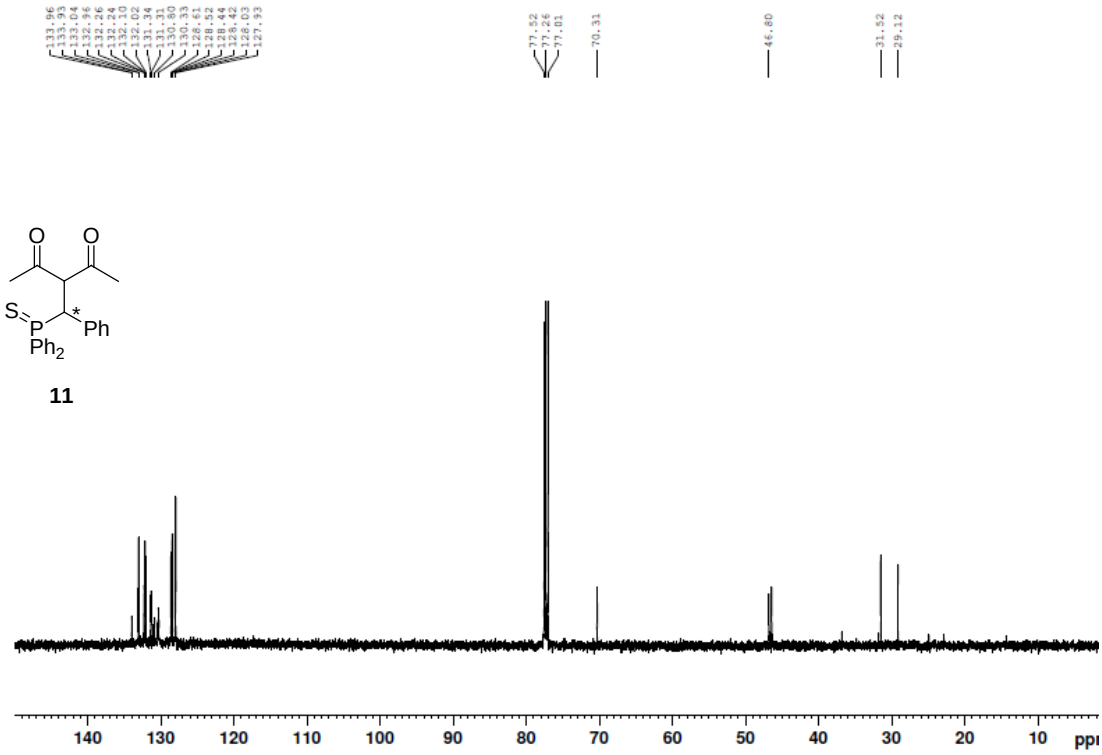
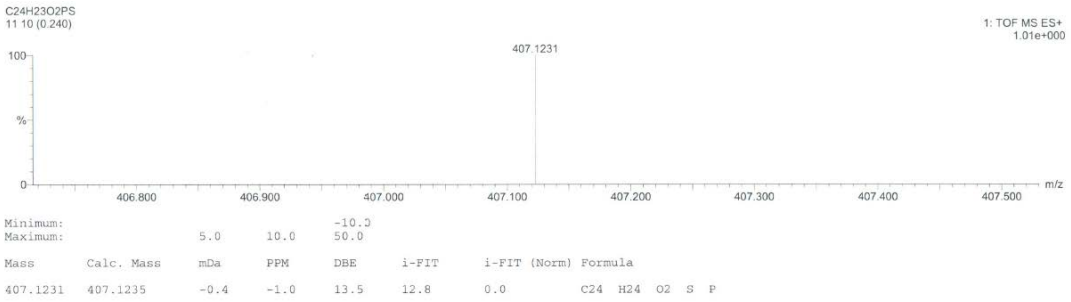


Figure 1D. HRMS of **11.**



Minimum:				-10.0			
Maximum:		5.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
407.1231	407.1235	-0.4	-1.0	13.5	12.8	0.0	C24 H24 O2 S P

Figure 3A. ^{31}P NMR of **gold(I)-phosphine adduct.**

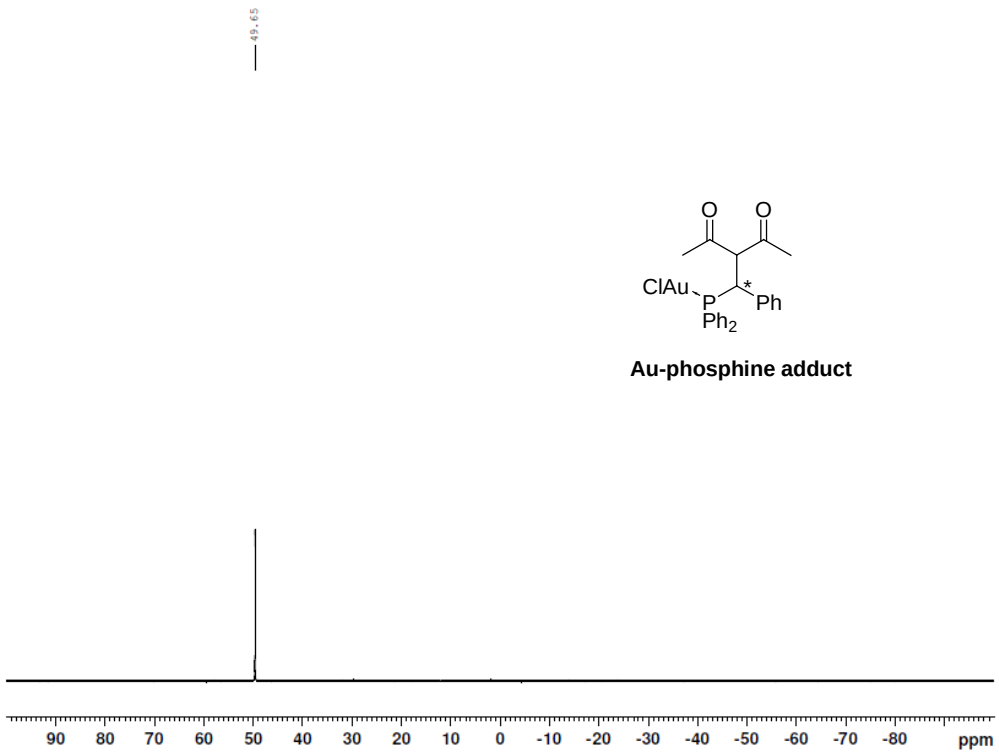


Figure 3B. ^{1}H NMR of **gold(I)-phosphine adduct.**

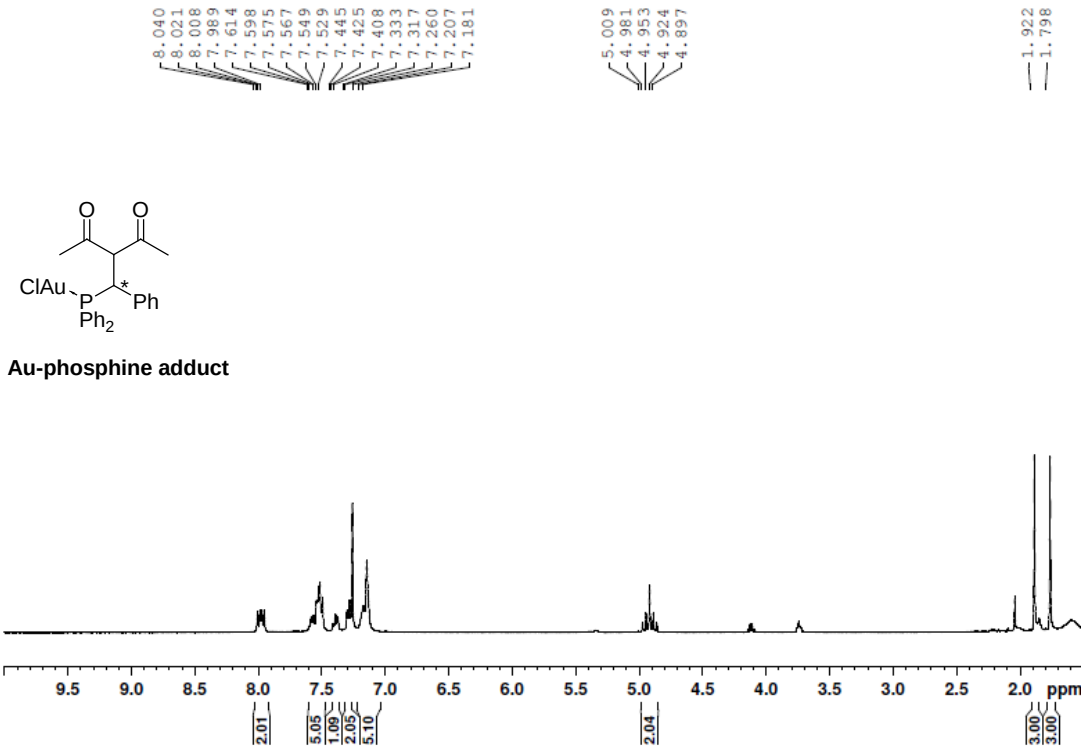
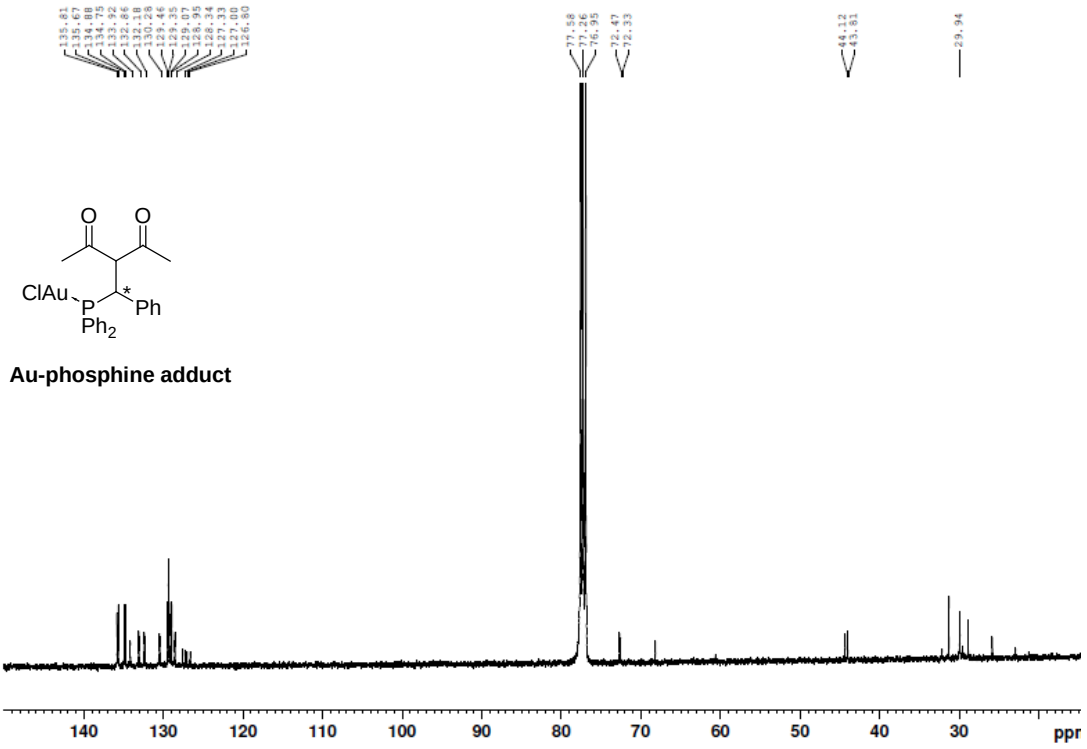
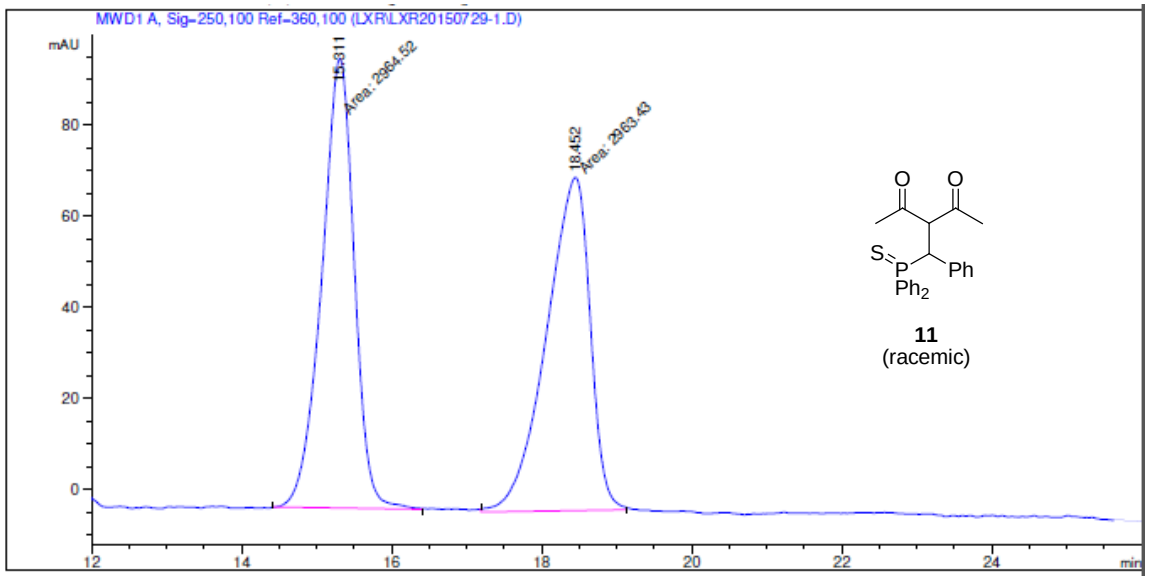


Figure 3C. ^{13}C NMR of **gold(I)-phosphine adduct.**

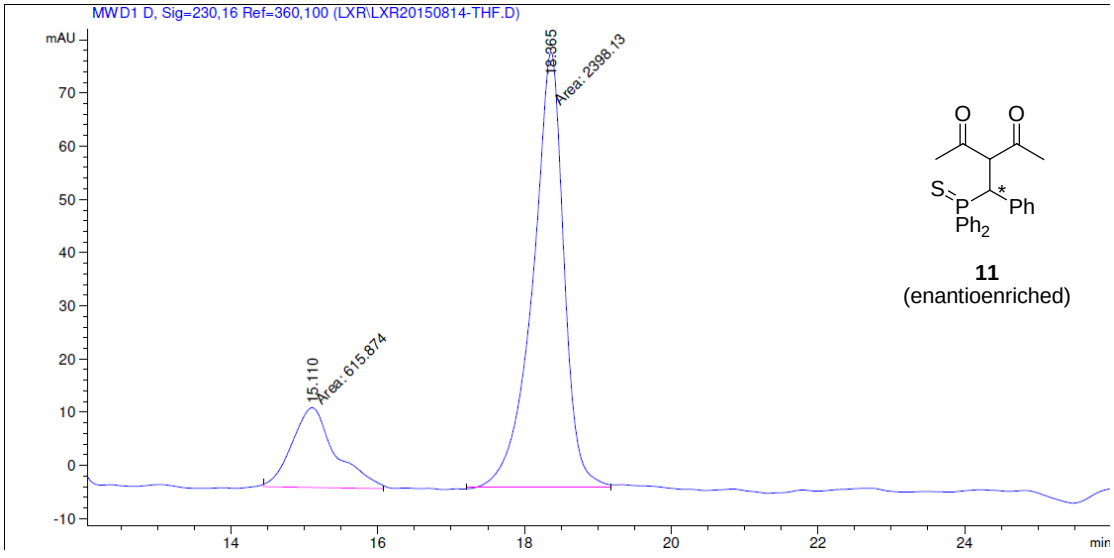


3. Chiral HPLC Analyses of products under different conditions



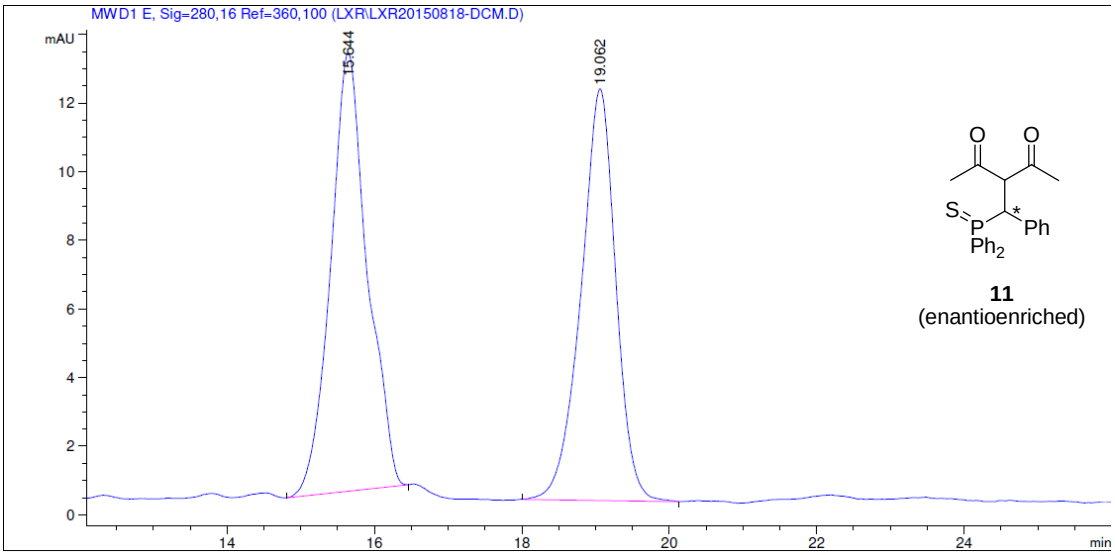
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.311	MM	0.5010	2964.52051	98.62655	50.0092
2	18.452	MM	0.6755	2963.43164	73.12206	49.9908

Table 1, entry 1 (Tetrahydrofuran as solvent at room temperature)



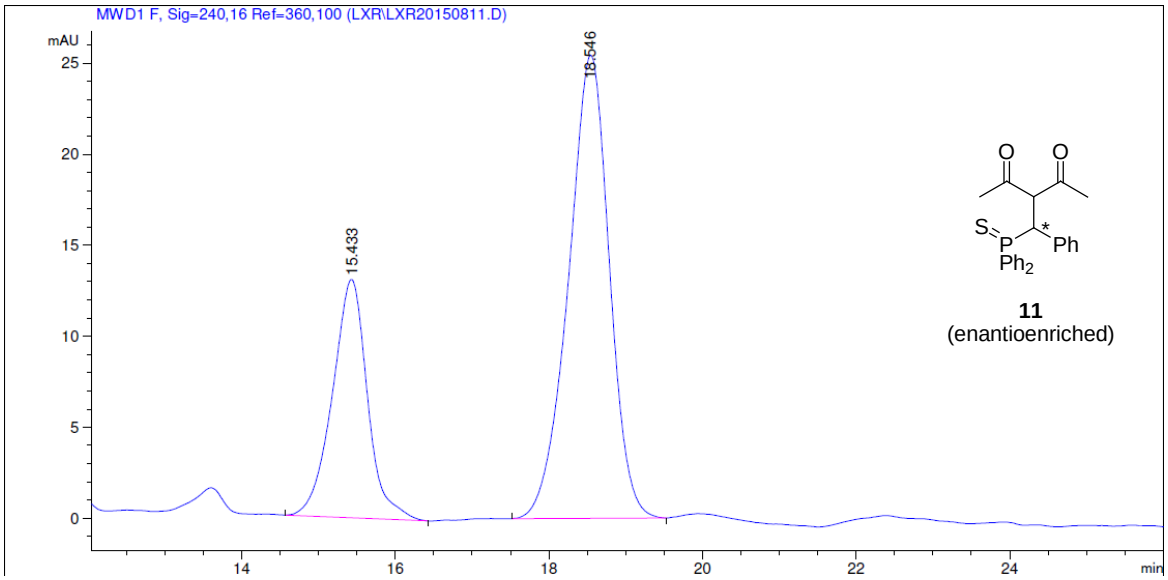
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.110	MM	0.6857	615.87433	14.97012	20.4338
2	18.365	MM	0.4893	2398.13086	81.67802	79.5662

Table 1, entry 2 (Dichloromethane as solvent at room temperature)



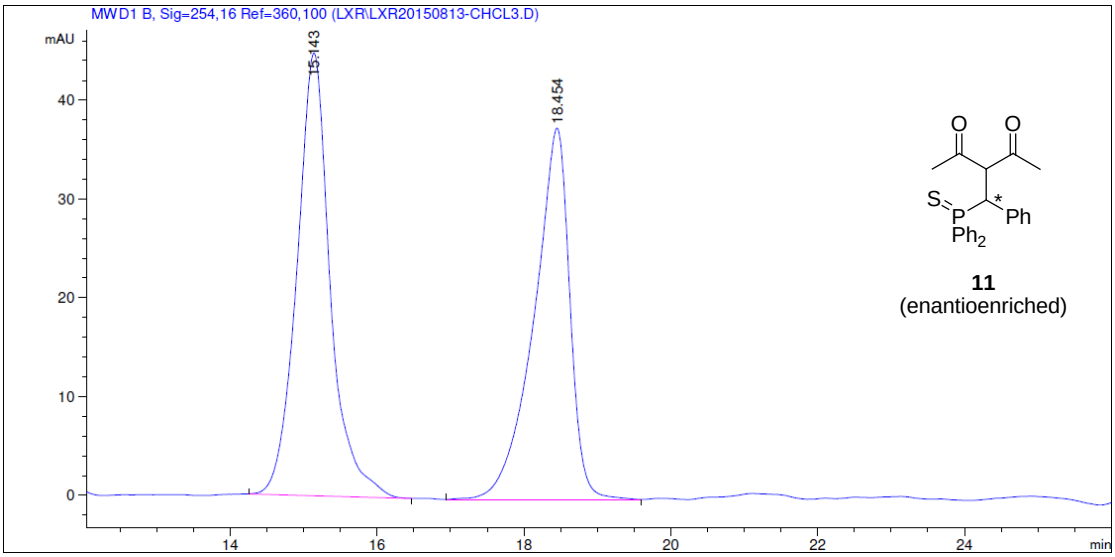
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.644	BB	0.5033	441.50262	12.77122	52.8945
2	19.062	BB	0.4825	393.18219	11.99196	47.1055

Table 1, entry 3 (Acetone as solvent at room temperature)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.433	BB	0.4720	415.52829	13.10120	30.6537
2	18.546	BB	0.5570	940.02625	25.44585	69.3463

Table 1, entry 4 (Chloroform as solvent at room temperature)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.143	BB	0.4623	1414.45032	44.80695	52.5470
2	18.454	BB	0.4844	1277.33179	37.59084	47.4530

4. Single Crystal X-ray Diffraction Data

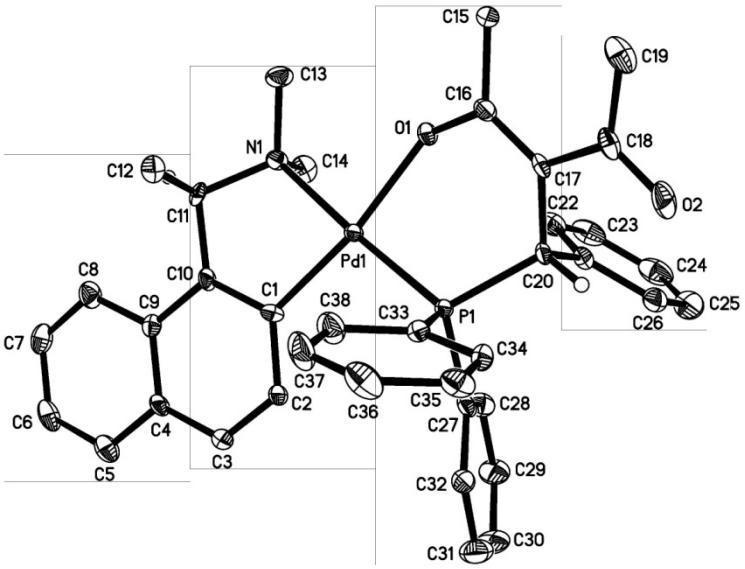


Figure 7: Molecular structure and absolute stereochemistry of chelate **9** with 50% thermal ellipsoids shown. Hydrogen atoms except those on the chiral centre are omitted for clarity. CCDC 1424966 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Structure Report

A yellow block-like specimen of $C_{38}H_{38}NO_2PPd$, approximate dimensions 0.180 mm x 0.400 mm x 0.420 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 0.24 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 60896 reflections to a maximum θ angle of 33.78° (0.64 Å resolution), of which 25236 were independent (average redundancy 2.413, completeness = 99.6%, R_{int} = 10.73%, R_{sig} = 14.78%) and 18985 (75.23%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.8563(8) Å, b = 15.4239(10) Å, c = 17.5713(12) Å, β = 96.314(2)°, volume = 3193.8(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 5975 reflections above 20 σ(I) with 5.360° < 2θ < 50.34°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.798. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7670 and 0.8900.

The final anisotropic full-matrix least-squares refinement on F^2 with 924 variables converged at R1 = 6.50%, for the observed data and wR2 = 14.22% for all data. The goodness-of-fit was 0.989. The largest peak in the final difference electron density synthesis was 1.476 $e^-/Å^3$ and the

largest hole was -1.282 $e^-/Å^3$ with an RMS deviation of 0.139 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.410 g/cm^3 and F(000), 1400 e^-.

Table 1. Sample and crystal data for leung872s.

Identification code	leung872s	
Chemical formula	$C_{38}H_{38}NO_2PPd$	
Formula weight	678.06 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.180 x 0.400 x 0.420 mm	
Crystal habit	yellow block	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 11.8563(8) Å	α = 90°
	b = 15.4239(10) Å	β = 96.314(2)°
	c = 17.5713(12) Å	γ = 90°
Volume	3193.8(4) $Å^3$	
Z	4	
Density (calculated)	1.410 g/cm^3	
Absorption coefficient	0.666 mm^{-1}	
F(000)	1400	

Table 2. Data collection and structure refinement for leung872s.

Theta range for data collection	1.98 to 33.78°
Index ranges	-18<=h<=18, -24<=k<=24, -26<=l<=27
Reflections collected	60896
Independent reflections	25236 [R(int) = 0.1073]
Coverage of independent reflections	99.6%
Absorption correction	multi-scan
Max. and min. transmission	0.8900 and 0.7670
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	25236 / 806 / 924
Goodness-of-fit on F^2	0.989
Δ/σ_{max}	0.001

Final R indices	18985 data; R1 = 0.0650, wR2 = 0.1249 I>2σ(I) all data R1 = 0.0942, wR2 = 0.1422
Weighting scheme	$w=1/[\sigma^2(F_o^2)]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	-0.0(0)
Largest diff. peak and hole	1.476 and -1.282 eÅ^{-3}
R.M.S. deviation from mean	0.139 eÅ^{-3}

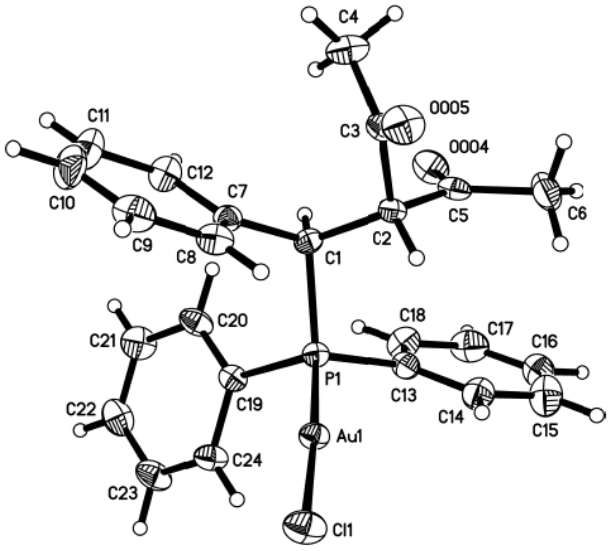


Figure 8: Molecular structure of the gold(I)-phosphine adduct with 50% thermal ellipsoids. CCDC 1424965 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Structure Report

A colorless block-like specimen of $C_{24}H_{23}AuClO_2P$, approximate dimensions 0.100 mm x 0.140 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 0.63 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 44175 reflections to a maximum θ angle of 36.49° (0.60 Å resolution), of which 11409 were independent (average redundancy 3.872, completeness = 99.0%, R_{int} = 10.12%, R_{sig} = 9.98%) and 7841 (68.73%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.9394(4) Å, b = 11.1972(4) Å, c = 11.8538(4) Å, α = 116.6194(19)°, β = 92.541(2)°, γ = 93.610(3)°, volume = 1173.18(8) $Å^3$, are based upon the refinement of the XYZ-centroids of 4570 reflections above 20 σ(I) with 5.41° < 2θ < 50.07°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.715. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.3580 and 0.5640.

The final anisotropic full-matrix least-squares refinement on F^2 with 264 variables converged at R1 = 4.60%, for the observed data and wR2 = 9.08% for all data. The goodness-of-fit was 0.971. The largest peak in the final difference electron density synthesis was 1.429 $e^-/Å^3$ and

the largest hole was -2.508 $e^-/Å^3$ with an RMS deviation of 0.233 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.718 g/cm^3 and F(000), 588 e^-.

Table 1. Sample and crystal data for leung881.

Identification code	leung881	
Chemical formula	$C_{24}H_{23}AuClO_2P$	
Formula weight	606.81 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.140 x 0.200 mm	
Crystal habit	colorless block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.9394(4) Å	α = 116.6194(19)°
	b = 11.1972(4) Å	β = 92.541(2)°
	c = 11.8538(4) Å	γ = 93.610(3)°
Volume	1173.18(8) $Å^3$	
Z	2	
Density (calculated)	1.718 g/cm^3	
Absorption coefficient	6.468 mm^{-1}	
F(000)	588	

Table 2. Data collection and structure refinement for leung881.

Theta range for data collection	2.71 to 36.49°
Index ranges	-16<=h<=16, -18<=k<=18, -19<=l<=19
Reflections collected	44175
Independent reflections	11409 [R(int) = 0.1012]
Coverage of independent reflections	99.0%
Absorption correction	multi-scan
Max. and min. transmission	0.5640 and 0.3580
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	11409 / 0 / 264
Goodness-of-fit on F^2	0.971
Δ/σ_{max}	0.002

	7841
Final R indices	data; R1 = 0.0460, wR2 = 0.0780
	$I>2\sigma(I)$
	all data R1 = 0.0865, wR2 = 0.0908
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0289P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.429 and -2.508 $eÅ^{-3}$
R.M.S. deviation from mean	0.233 $eÅ^{-3}$