Synthesis of Novel Heteroleptic Delocalised Cationic Pyrazole Gold Complexes as Potent HepG2 Cytotoxic Agents

Fatai Afolabi,[a] *Wided Souissi,*[b] *Guillaume Rivière, Clément Lemaitre, S. Mark Roe,*[a] *Neil Crickmore*[b]* *and Eddy M. E. Viseux*[a]*

[a]*Department of Chemistry, School of Life Sciences, University of Sussex, Brighton, BN1 9QJ, UK. E-mail: E.M.E.Viseux@sussex.ac.uk; Tel: +44 (0) 1273 678621*

[b]*Department of Biochemistry, School of Life Sciences, University of Sussex, Brighton, BN1 9QJ, UK. E-mail: N.Crickmore@sussex.ac.uk; Tel: +44 (0) 1273 678917*

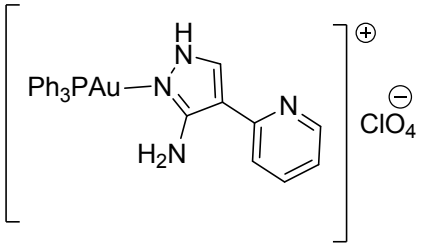
I. Experimental Procedures

Methods and Materials

The starting materials and solvents were used without further purification from commercially available sources unless otherwise stated and purchased. All operations were conducted using oven-dried glassware, a nitrogen atmosphere and Schlenk techniques, unless stated otherwise. The solutions of silver(I) salts and the mixtures of silver(I) salt and gold(I) were protected from the light until the filtration of the residual silver chloride.

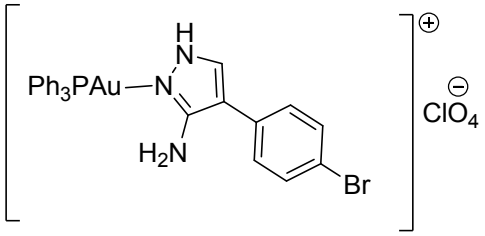
The NMR spectra were recorded on a Varian 400 (400 MHz) or Varian 600 (600 MHz). Chemical shifts were reported in parts per million (ppm) referenced to residual solvent resonances or external 85% H_3PO_4 as appropriate. The IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer, equipped with a diamond top plate. Mass spectra were obtained using VG Autospec Magnetic Sector MS and Bruker Daltonic FT-ICR-MS Apex III 4.7 Tesla instruments, using electrospray ionisation (ESI).

For the X-ray data collection, a selected crystal was placed on a Xcalibur, Eos, Gemini ultra-diffractometer. The crystal was kept at 173.0 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.



Triphenylphosphine(5-amino-4-(pyridin-2-yl)-1H-pyrazole)gold(I) perchlorate (6)

$AgClO_4$ (4.2 mg, 0.020 mmol, 1 eq.) and Ph_3PAuCl (10.0 mg, 0.020 mmol, 1 eq.) were dissolved in methanol (0.5 mL) yielding a white precipitate instantly. The mixture was stirred for 30 minutes. The completion of the reaction was monitored by ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.5 ppm. A solution of 5-amino-4-(pyridin-2-yl)-1H-pyrazole (3.2 mg, 0.020 mmol, 1 eq.) in CH_2Cl_2 (0.6 ml) was added to the previous solution and stirred for a further 30 minutes. The mixture was filtered over a glass microfiber filter placed in a syringe and into an NMR Schlenk flask, under nitrogen. The solution was dried under reduced pressure and $CDCl_3$ (0.5 mL) was added. ^{31}P, ^{1}H and^{13}C NMR analyses were recorded. The material was concentrated under reduced pressure to obtain the title complex as a brown solid (11.9 mg, 83%). MP:165.6-168.2 $^{o}C$$^{1}H$ NMR (600 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 4.7 Hz, 1H), 7.85 (s, 1H), 7.64 (td, *J* = 7.8, 1.9 Hz, 2H), 7.42-7.62 (m, 14H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.06 (dd, *J* = 7.5, 4.9Hz, 1H), 6.39 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.7, 148.6, 136.5, 134.3, 134.2, 132.5, 132.4, 129.6, 128.0, 127.1, 120.1, 118.4. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 30.0 HRMS (ESI) calculated for $C_8H_8N_4AuPh_3P^+$: 619.44. Found: 619.1320. Error: 0.12 ppm. IR (diamond, cm^{-1}): 3073.97 (NH_2), 2923.29 (CH), 1621.74 (C=C), 1514.68 (benzene ring).

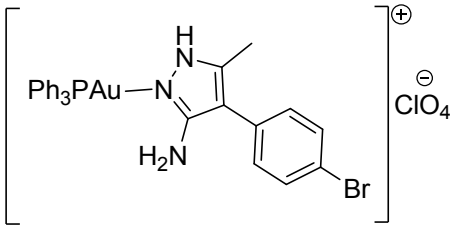


Triphenylphosphine(5-Amino-4-(4-bromophenyl)-pyrazole) gold(I) perchlorate (7)

$AgClO_4$ (4.2 mg, 0.020 mmol, 1 eq.) and Ph_3PAuCl (10.0 mg, 0.020 mmol, 1 eq.) were dissolved in methanol (0.5 mL) yielding a white precipitate instantly. The mixture was stirred for 30 minutes. The completion of the reaction was monitored by ^{31}P NMR (^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.5 ppm). A solution of 5-amino-4-(4-bromophenyl)-pyrazole (4.8 mg, 0.020 mmol, 1 eq.) in CH_2Cl_2 (0.6 ml,) was added to the solution of cationic gold prepared previously and stirred for 30 minutes. The mixture was filtered over a glass microfiber filter placed in a syringe and into an NMR Schlenk flask, under nitrogen. Solution was dried under reduced pressure and $CDCl_3$ (0.5 mL) was added. ^{31}P, ^{1}H and^{13}C NMR analyses were recorded with this solution. The material was concentrated under reduced

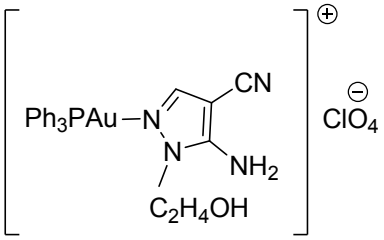
pressure to obtain the corresponding complex as a light brown solid (15.0 mg, 94%). MP: 142.4-144.6°C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 12.21 (broad s, 1H), 7.52–7.62 (m, 21H), 7.24 (s, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 134.3, 134.2, 132.5, 132.5, 132.4, 129.8, 129.7, 129.6, 128.3, 127.4, 127.0, 120.9. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 31.0. HRMS (ESI) calculated for $C_9H_8BrN_3AuPh_3P^+$:697.35. Found: 696.0473. Error: -5.22 ppm. IR (diamond, cm^{-1}): 3356.99 (NH_2), 2921.62 (CH), 1621.58 (C=C), 1598.78 (benzene ring).

X-ray: available see the appendix (material was concentrated under reduced pressure at ambient temperature. The residue was recrystalised from a minimal amount of CH_2Cl_2:n-Hexane (1:1).



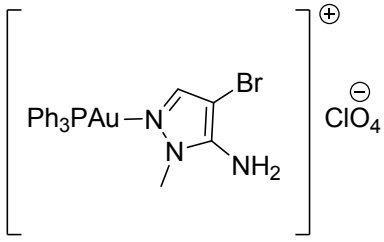
Triphenylphosphine(5-Amino-4-(4-bromophenyl)-3-methylpyrazole) gold(I) perchlorate (8)

$AgClO_4$ (4.2 mg, 0.020 mmol, 1 eq.) and Ph_3PAuCl (10.0 mg, 0.020 mmol, 1 eq.) were dissolved in methanol (0.5 mL) yielding a white precipitate instantly. The mixture was stirred for 30 minutes. The completion of the reaction was monitored by ^{31}P NMR (^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.5 ppm). A solution of 5-amino-4-(4-bromophenyl)-3-methylpyrazole (5.0 mg, 0.020 mmol, 1 eq.) in CH_2Cl_2 (0.6 ml) was added to the solution of cationic gold prepared previously and stirred for 30 minutes. The mixture was filtered over a glass microfiber filter placed in a syringe and into an NMR Schlenk flask, under nitrogen. Solution was dried under reduced pressure and $CDCl_3$ (0.5 mL) was added. ^{31}P, ^{1}H and^{13}C NMR analyses were recorded with this solution. The material was concentrated under reduced pressure to afford the title complex as a grey solid (14.3 mg, 88 %). MP:148.0-149.6°C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 11.86 (broad s, 2H), 7.51–7.62 (m, 16H), 7.45 (d, J = 8.7 Hz, 1H), 7.16 (d, J = 8.3 Hz, 2H), 3.72 (q, J = 7.0 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 134.4, 134.2, 132.5, 132.4, 130.5, 130.4, 129.7, 129.6, 127.6, 127.1, 121.2, 13.8. ^{31}P NMR (162 MHz, Chloroform-*d*) δ31.50 HRMS (ESI) calculated for $C_{10}H_{10}BrN_3AuPh_3P^+$:711.38. Found: 710. 0630.Error: -2.01ppm IR (diamond, cm^{-1}): 3316.13 (NH_2), 2924.07 (CH), 1598.28 (benzene ring). X-ray: available see the appendix (material was concentrated under reduced pressure at ambient temperature. The residue was recrystalised from a minimal amount of CH_2Cl_2:n-Hexane (1:1).



Triphenylphosphine(5-Amino-4-cyano-1-(2-hydroxyethyl)-pyrazole gold(I) perchlorate (9)

$AgClO_4$ (4.2 mg, 0.020 mmol, 1 eq.) and Ph_3PAuCl (10.0 mg, 0.020 mmol, 1 eq.) were dissolved in methanol (0.5 mL). yielding a white precipitate instantly. The completion of the reaction was monitored by ^{31}P NMR (^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.5 ppm). A solution of 5-Amino-4-cyano-1-(2-hydroxyethyl)-pyrazole (3.0mg, 0.020 mmol, 1 eq.) in CH_2Cl_2 (0.6 ml) was added to the solution of cationic gold prepared previously and stirred for 30 minutes. The mixture was filtered over a glass microfiber filter placed in a syringe and into an NMR Schlenk flask, under nitrogen. Solution was dried under reduced pressure and $CDCl_3$ (0.5 mL) was added. ^{31}P, ^{1}H and^{13}C NMR analyses were recorded with this solution. The material was concentrated under reduced pressure to give the corresponding complex as a yellow solid. (13.5 mg, 95%). MP: 126.3-127.4 ^{o}C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.45 – 7.63 (m, 16H), 5.86 (s, 2H), 4.44 (t, *J* = 5.0 Hz, 2H), 4.10 (t, *J* = 5.1 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.9, 134.1, 134.0, 132.8, 129.9, 129.8, 109.9, 78.0, 60.5, 52.7. ^{31}P NMR (162 MHz, Chloroform-*d*) δ29.70 HRMS (ESI) calculated for $C_6H_8N_4OAuPh_3P^+$:611.42. Found: 611.1270 Error: 2.76 ppm. IR (diamond, cm^{-1}): 3339.28 (NH_2), 3214.86 (OH) 2924.76 (CH), 2224.58 (CN), 1645.18 (C=C), 1583.90 (benzene ring). X-ray: available see the appendix (material was concentrated under reduced pressure at ambient temperature. The residue was recrystalised from a minimal amount of CH_2Cl_2:n-Hexane (1:1).



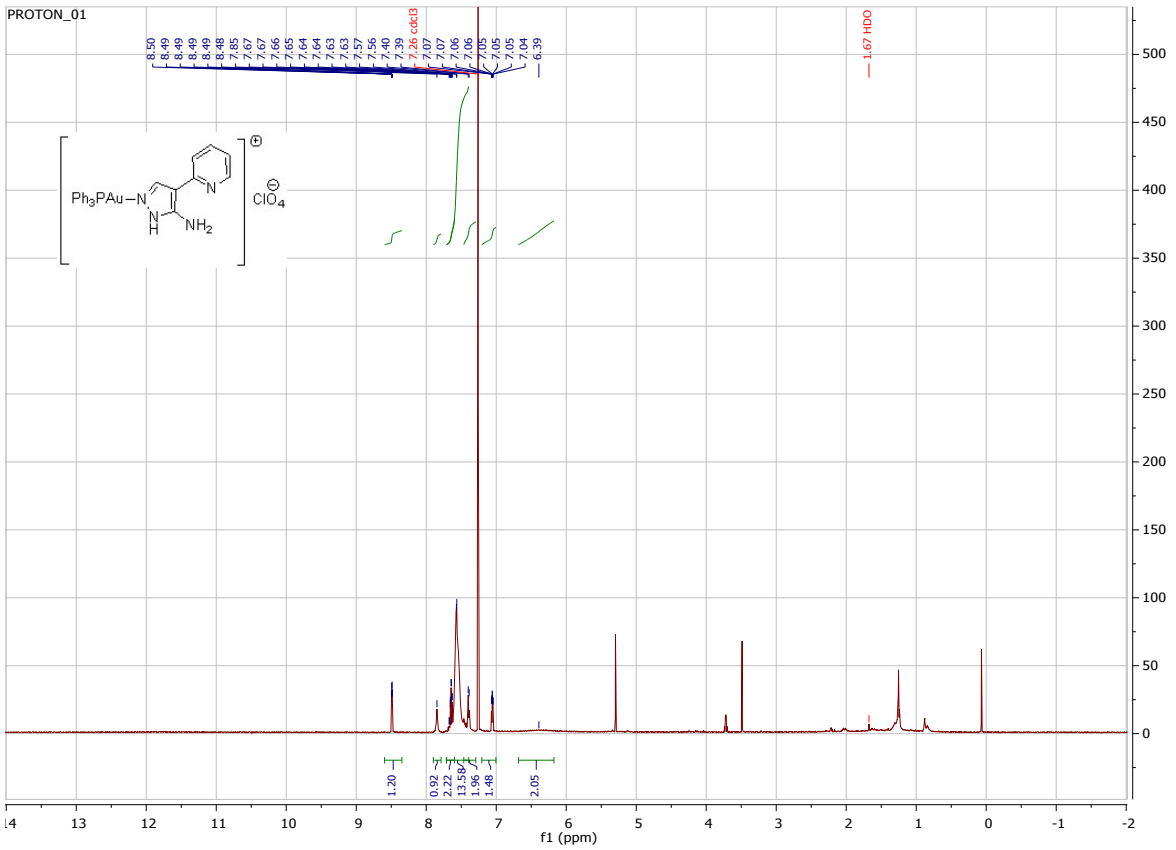
Triphenylphosphine(3-Amino-4-bromo-2-methylpyrazol) gold(I) perchlorate (10)

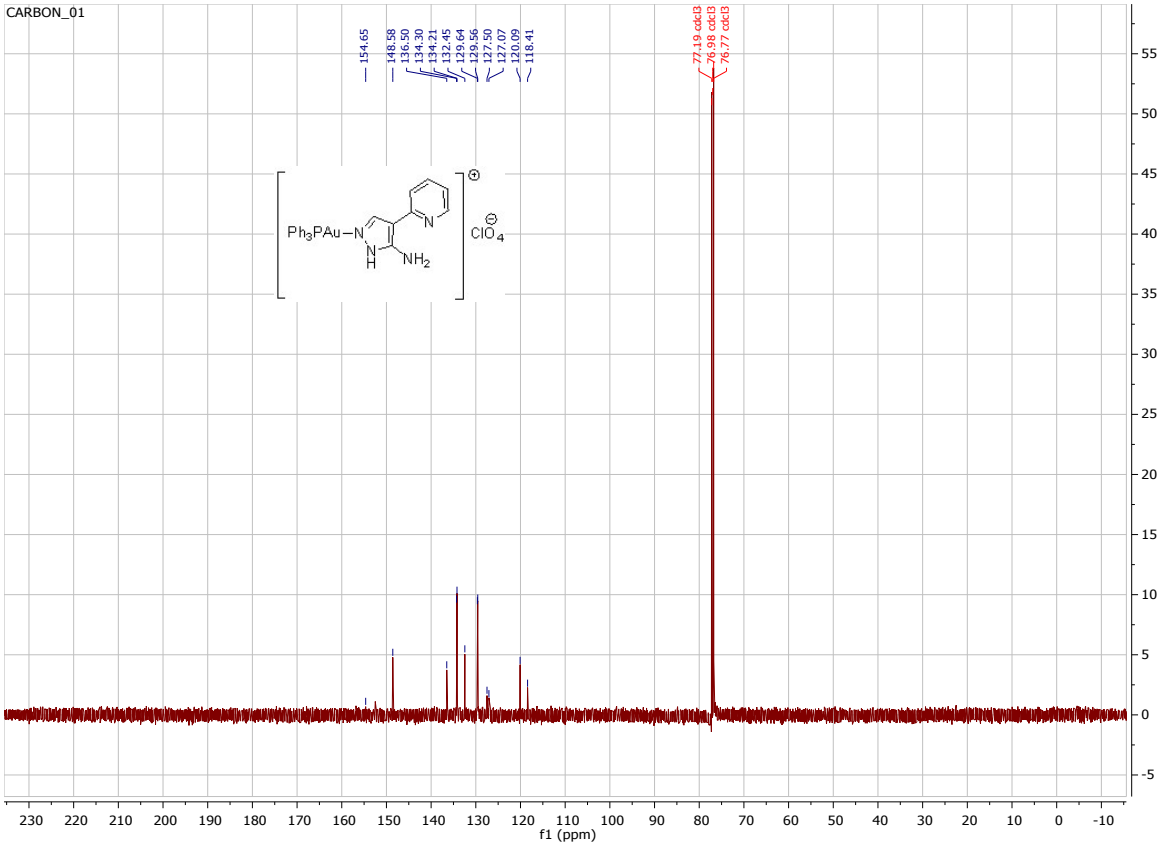
$AgClO_4$ (4.2 mg, 0.020 mmol, 1 eq.) and Ph_3PAuCl (10.0 mg, 0.020 mmol, 1 eq.) were dissolved in methanol (0.5 mL). yielding a white precipitate instantly. The mixture was stirred for 30 minutes. The

completion of the reaction was monitored by ^{31}P NMR (^{31}P NMR (162 MHz, Chloroform-*d*) δ 28.5 ppm). A solution of 3-amino-4-bromo-2-methylpyrazol (3.6mg, 0.020 mmol, 1 eq.) in CH_2Cl_2 (0.6 ml) was added to the solution of cationic gold prepared previously and stirred for 30 minutes. The mixture was filtered over a glass microfiber filter placed in a syringe and into an NMR Schlenk flask, under nitrogen. Solution was dried under reduced pressure and $CDCl_3$ (0.5 mL) was added. ^{31}P, ^{1}H and ^{13}C NMR analysis were recorded with this solution. The material was concentrated under reduced pressure to give the corresponding complex as a dark brown solid (12.8 mg, 87%). MP: 172.2-174.3 ^{o}C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 – 7.66 (m, 3H), 7.47 – 7.60 (m, 12H), 7.35 (s, 1H), 4.97 (s, 2H), 3.98 (s, 3H) ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.2, 134.0, 133.9, 132.9, 129.8, 127.0, 78.5, 36.8. ^{31}P NMR (162 MHz, Chloroform-*d*) δ30.0. HRMS (ESI) calculated for $C_4H_6BrN_3AuPh_3P^+$:635.28. Found: 634.0317 Error: 0.95 ppm IR (diamond, cm^{-1}): 3337.43 (NH_2), 2925.08 (CH), 1645.83 (C=C), 1579.65 (benzene ring). X-ray: available see the appendix (material was concentrated under reduced pressure at ambient temperature. The residue was recrystalised from a minimal amount of CH_2Cl_2:n-Hexane (1 : 1).

II. Spectra Data

Triphenylphosphine(5-Amino-4-(pyridin-2-yl)-1H-pyrazole) gold(I) perchlorate

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154.65
148.58
136.50
134.30
134.21
132.45
129.64
129.56
127.50
127.07
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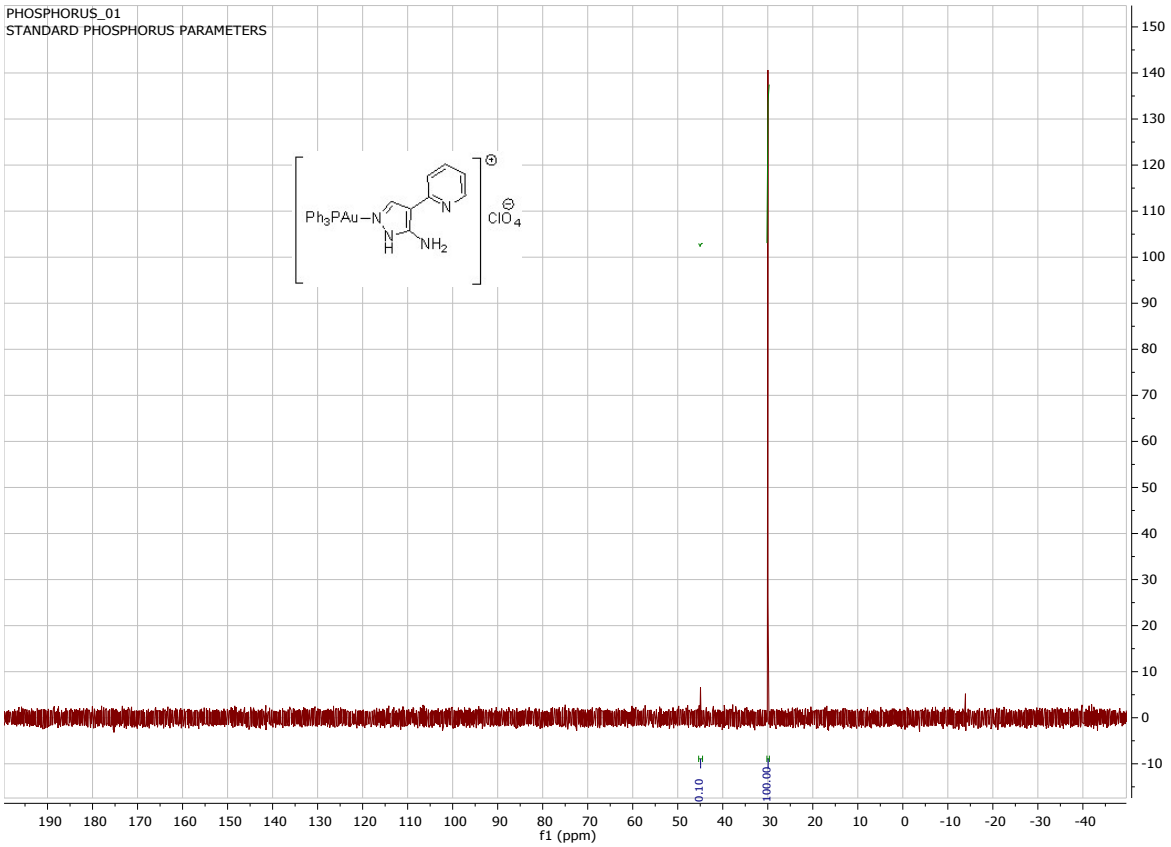
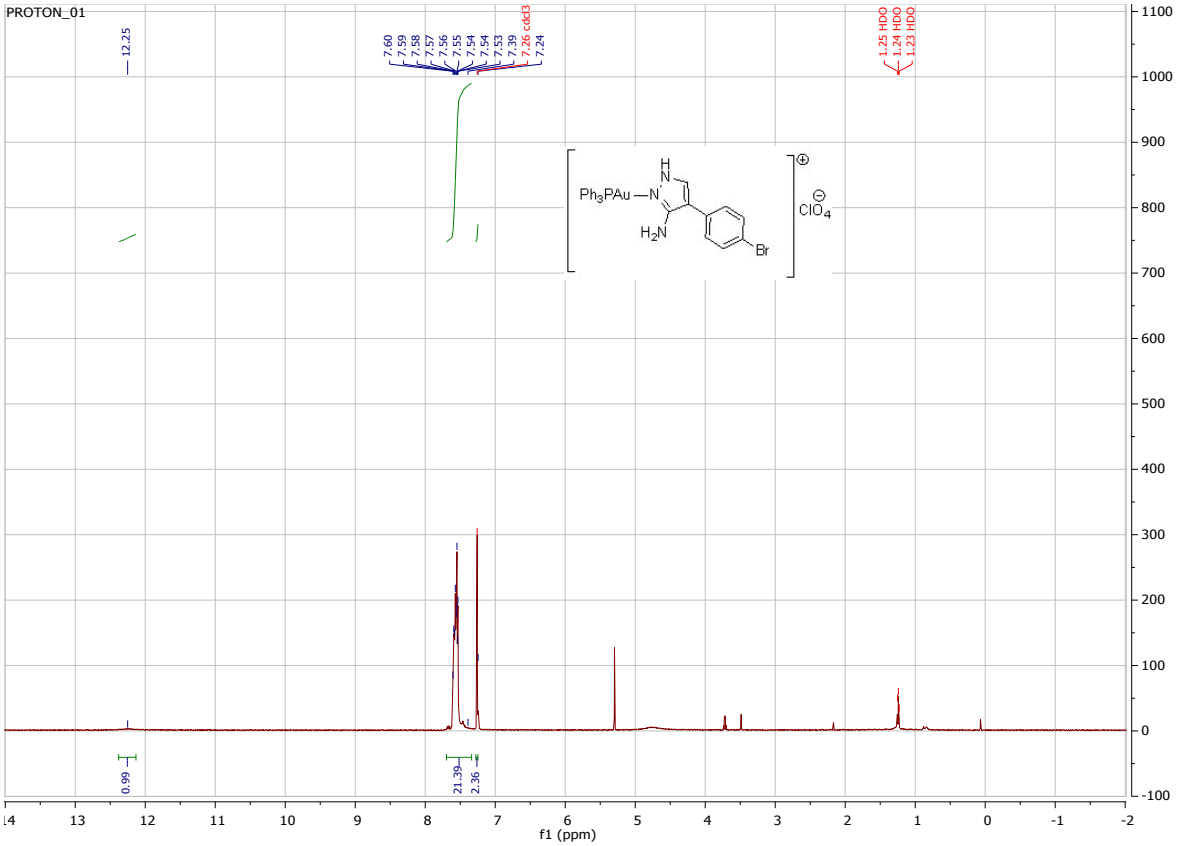
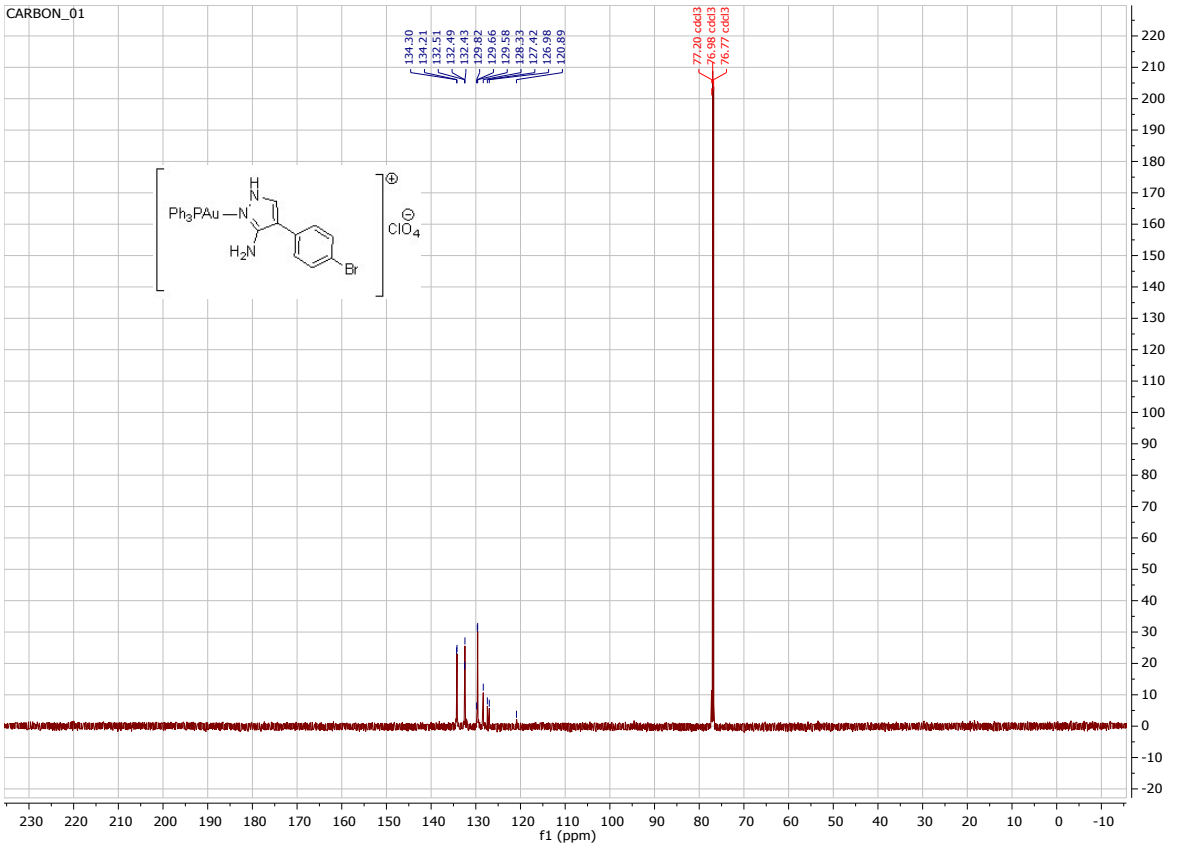
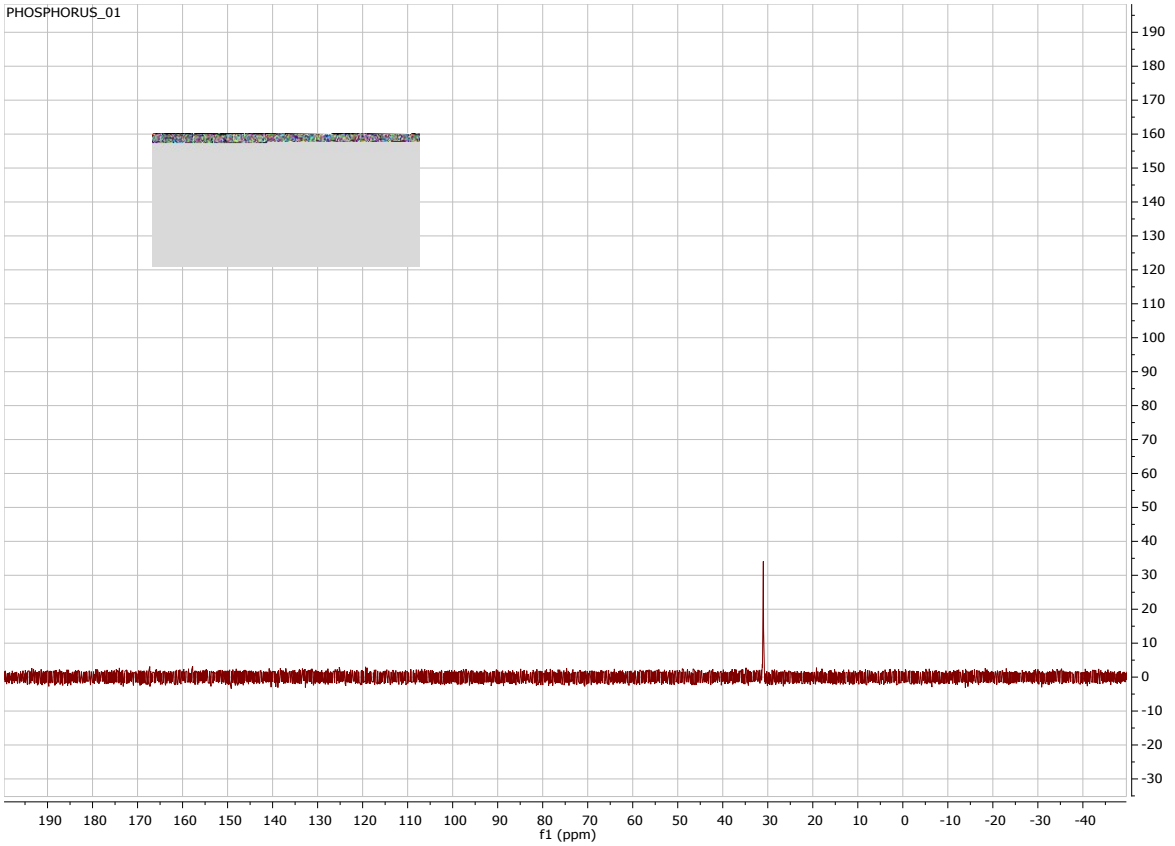
76.98 cdcl3
76.77 cdcl3
Ph3PAu
NH2
ClO4
f1 (ppm)


PHOSPHORUS_01
STANDARD PHOSPHORUS PARAMETERS
Ph3PAu
NH2
ClO4
0.10
100.00
f1 (ppm)

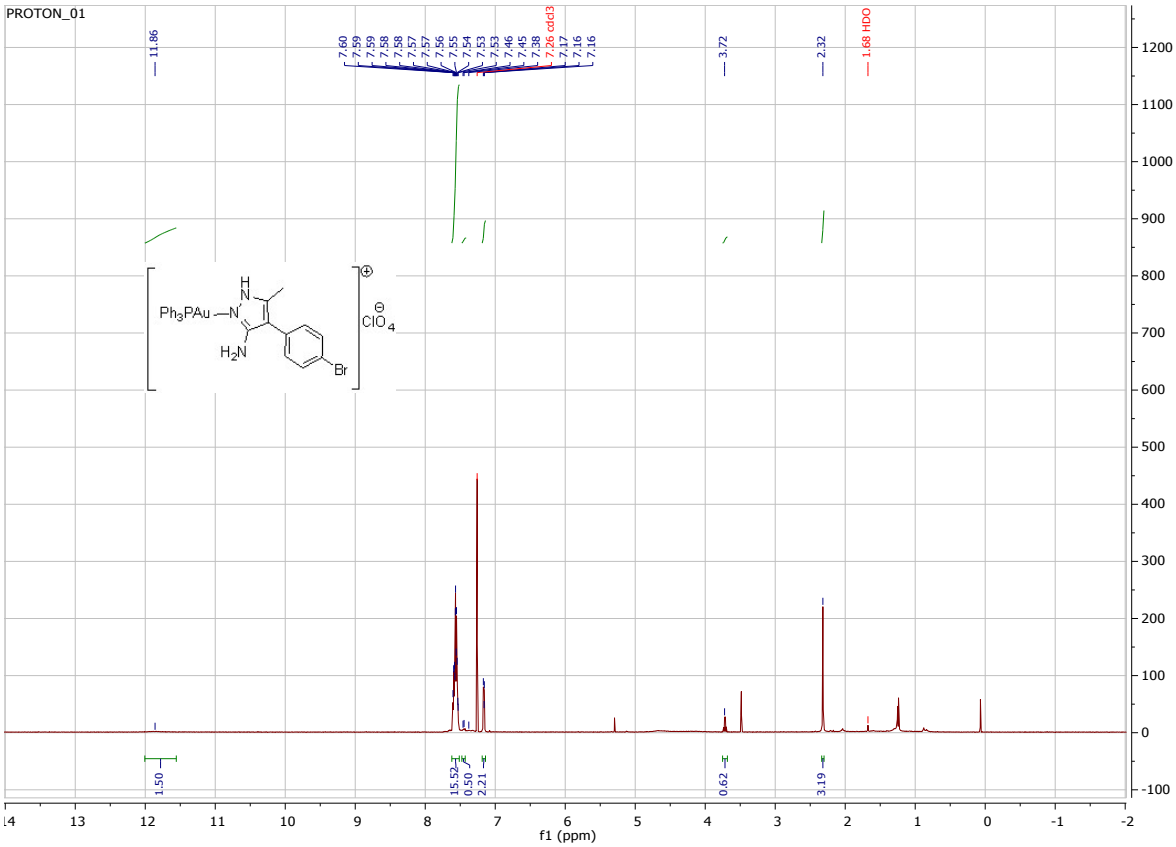
Triphenylphosphine(5-Amino-4-(4-bromophenyl)-pyrazole) gold(I) perchlorate

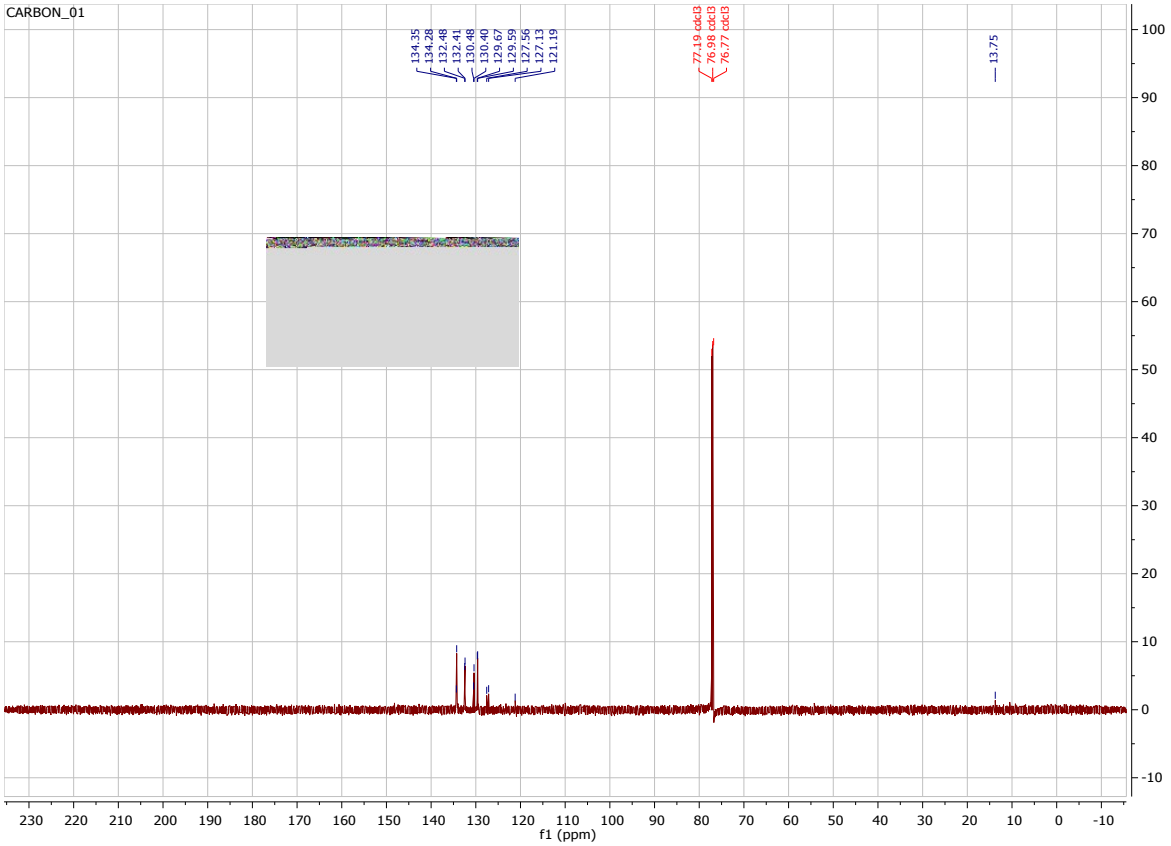






Triphenylphosphine(5-Amino-4-(4-bromophenyl)3-methyl-pyrazole) gold(I) perchlorate




CARBON_01
134.35
134.28
132.48
132.41
130.48
130.40
129.07
128.99
127.56
127.13
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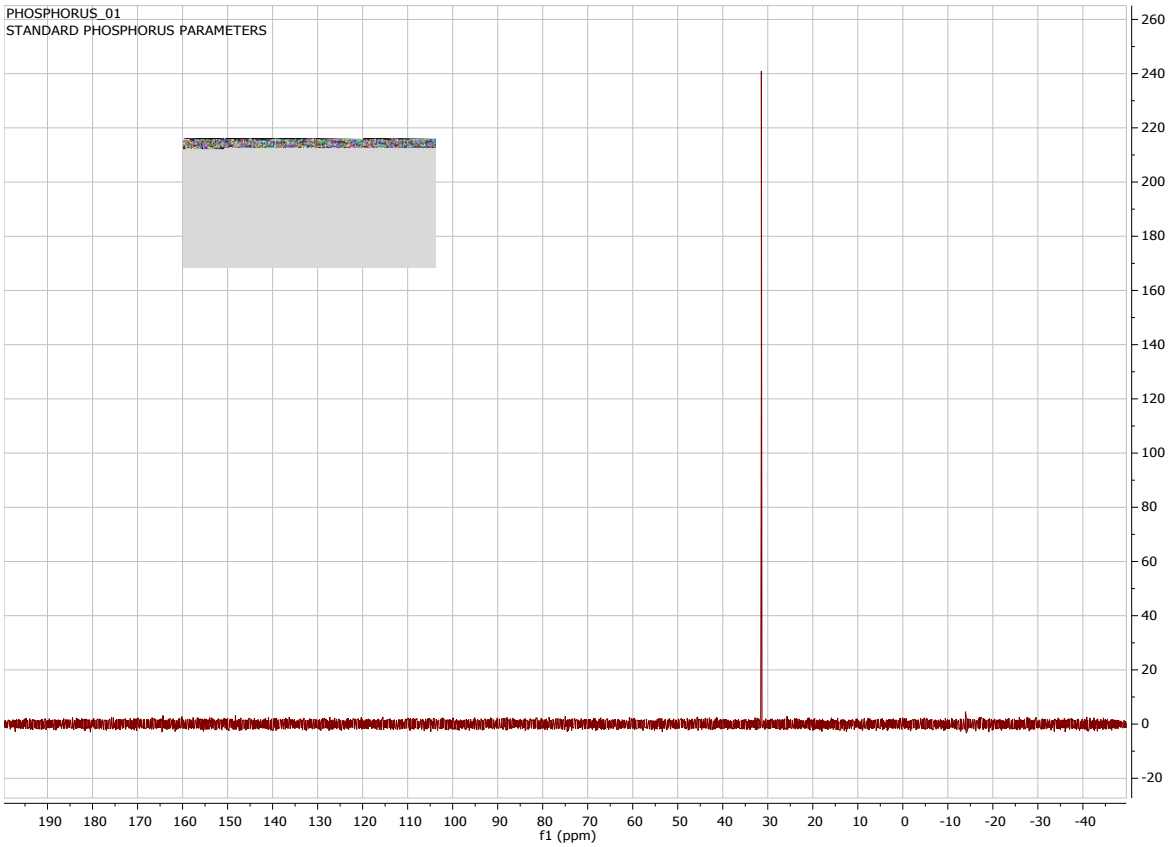
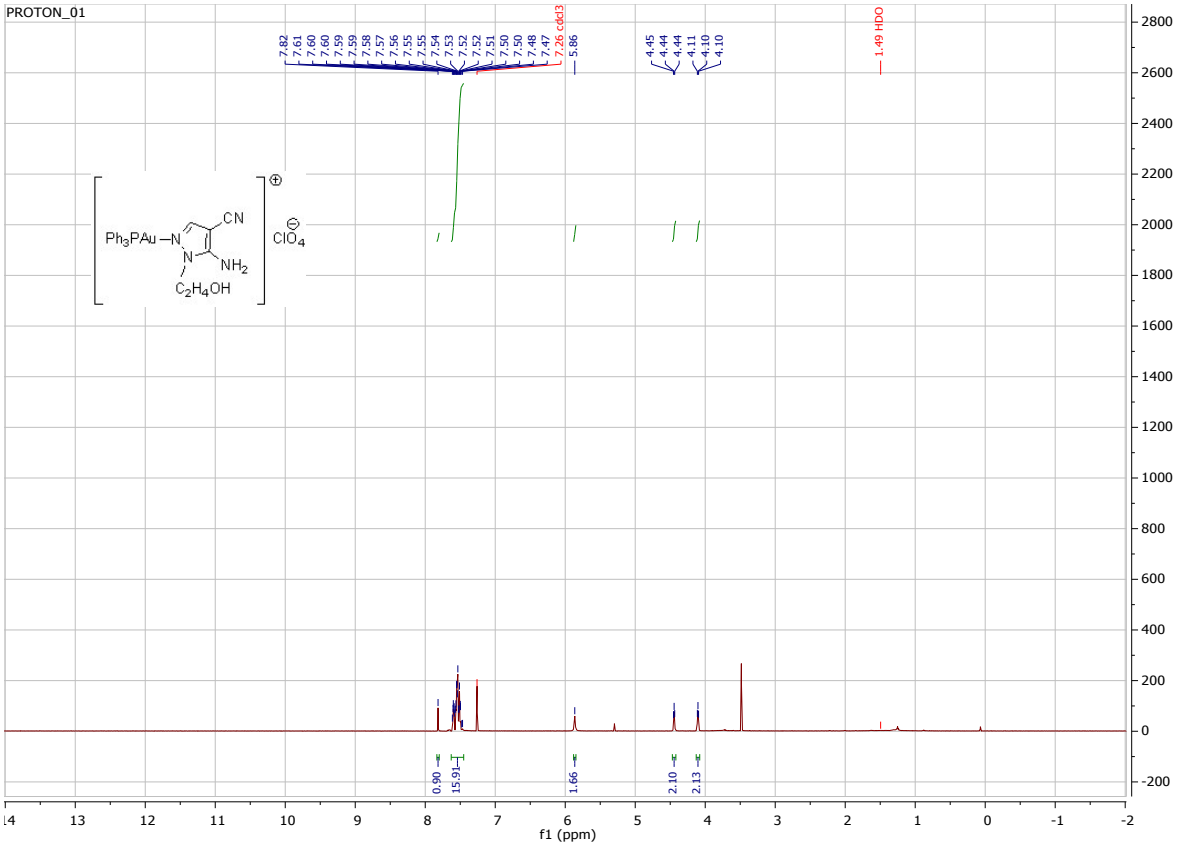
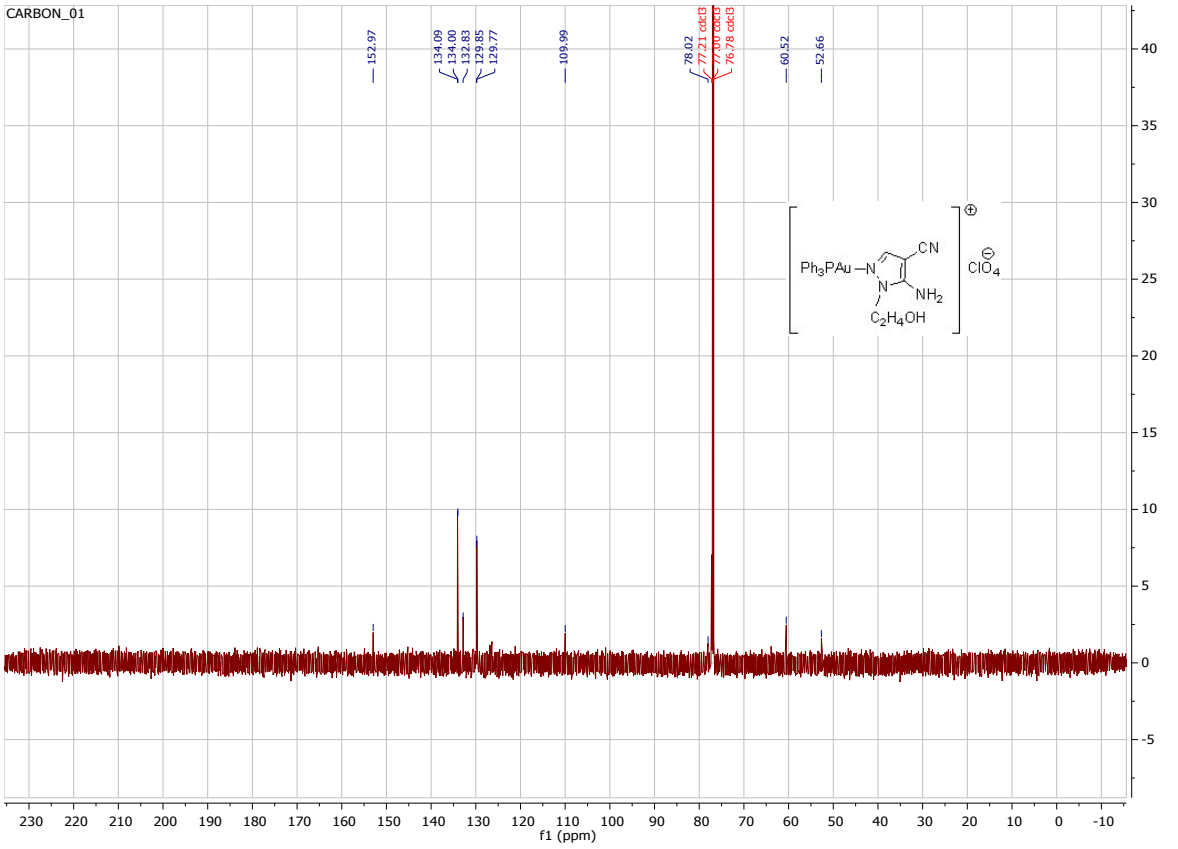
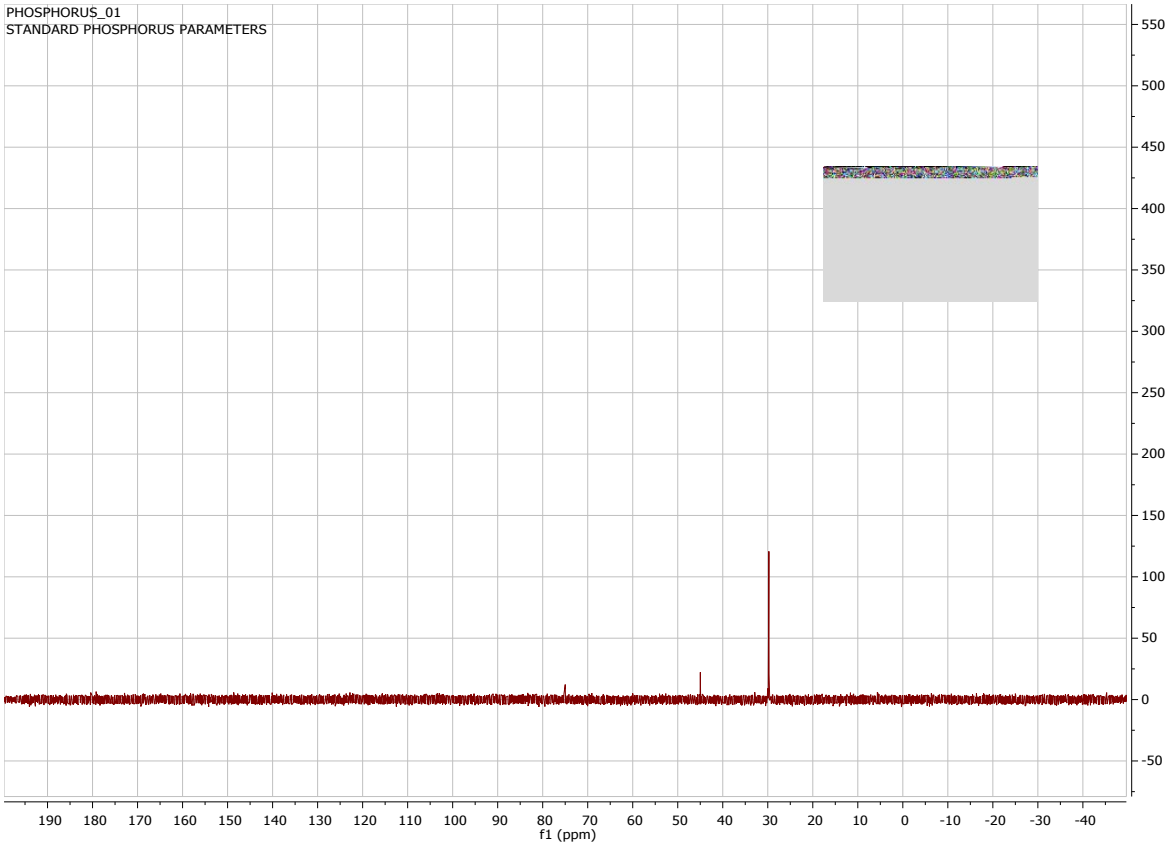
76.98 cdcl3
76.77 cdcl3
13.75
f1 (ppm)


PHOSPHORUS_01
STANDARD PHOSPHORUS PARAMETERS
f1 (ppm)

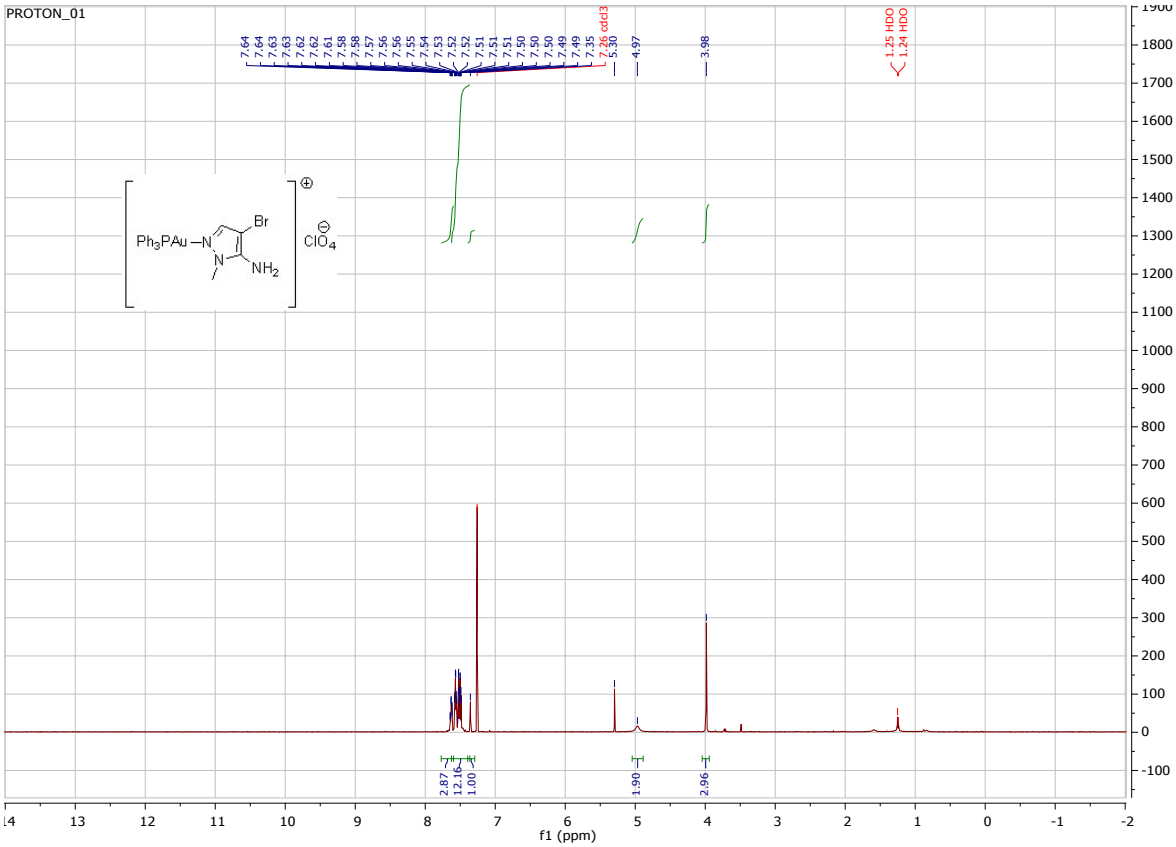
Triphenylphosphine(5-Amino-4-cyano-1-(2-hydroxyethyl)-pyrazole gold(I) perchlorate

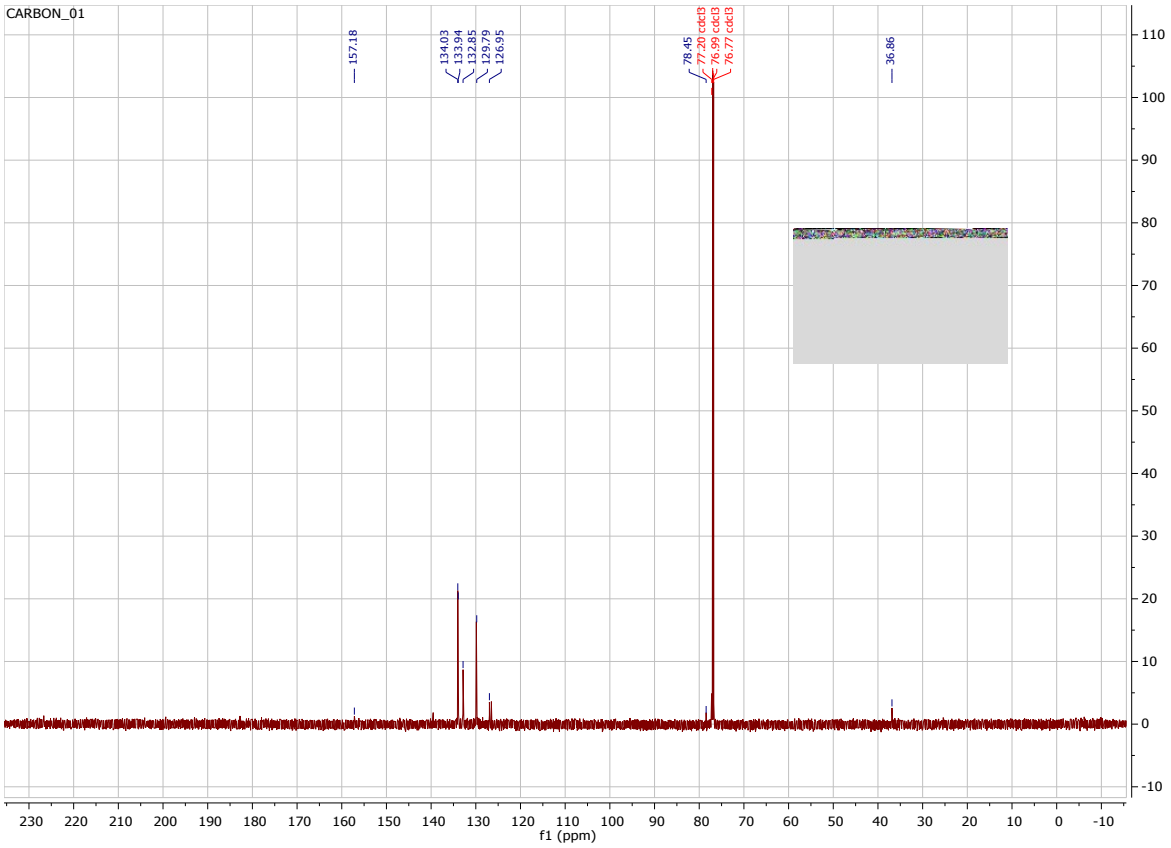


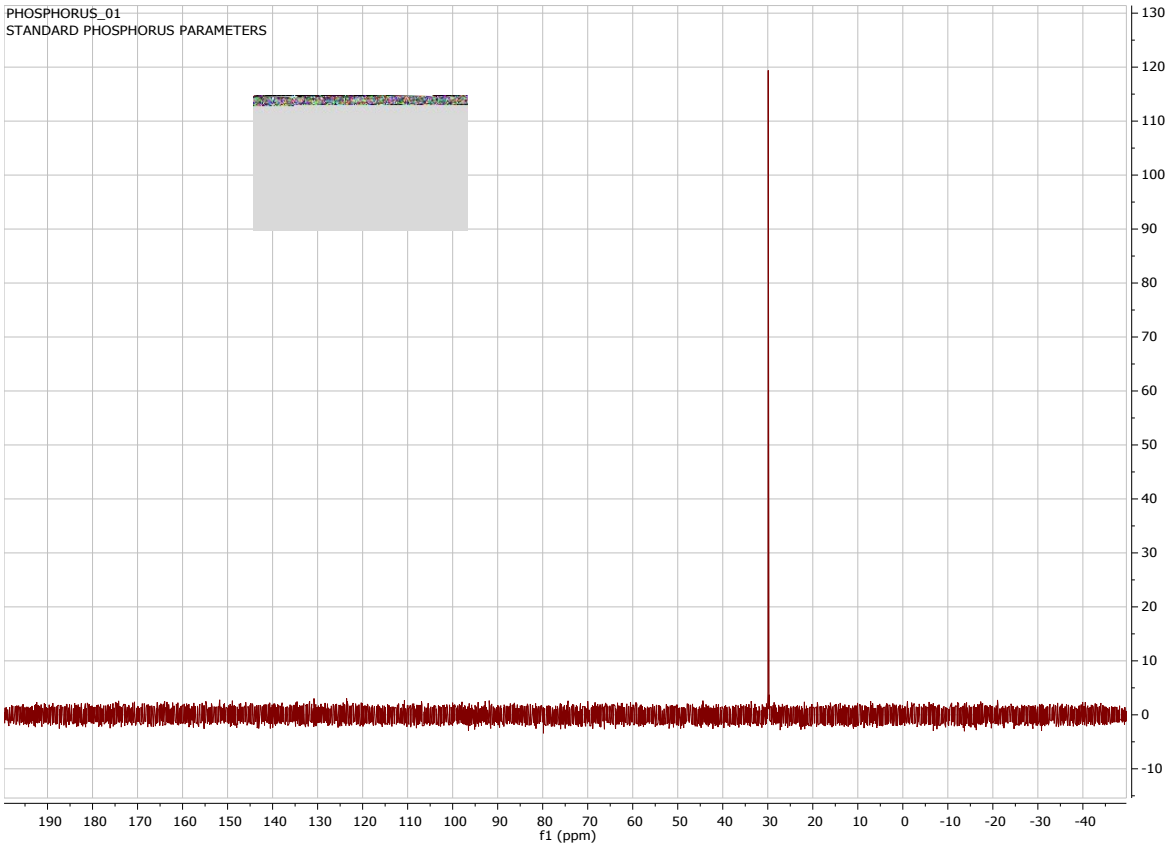




Triphenylphosphine(4-Bromo-1-methyl-1*H*-pyrazol-5-amine) gold(I) perchlorate




CARBON_01
157.18
134.03
133.94
132.85
129.79
126.95
78.45
77.20 cdcl3
76.99 cdcl3
76.77 cdcl3
36.86
f1 (ppm)


PHOSPHORUS_01
STANDARD PHOSPHORUS PARAMETERS
f1 (ppm)

III. X-Ray Data

Figure S1. ORTEP plot for Triphenylphosphine(5-Amino-4-(4-bromophenyl)-pyrazole) gold(I) perchlorate **7**

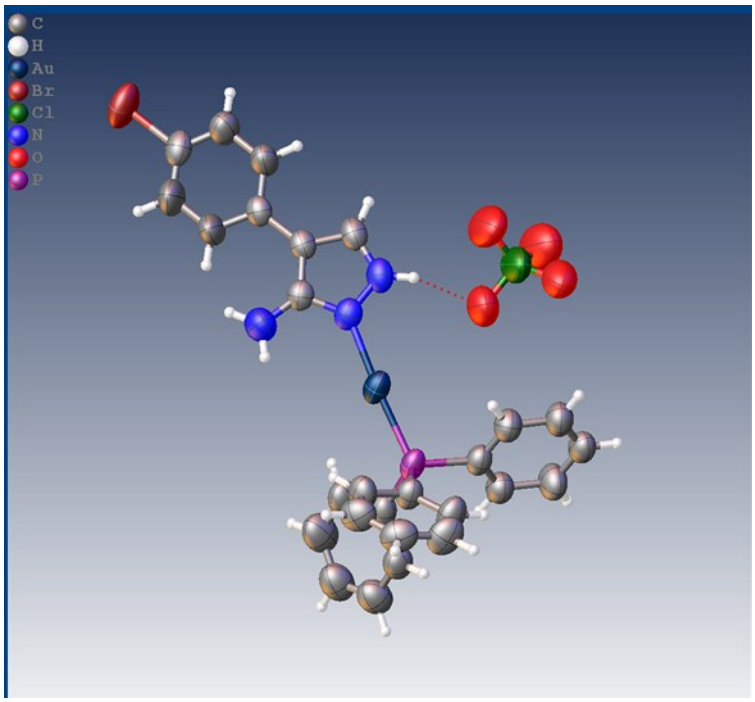


Table S1 Crystal data and structure refinement for **7.**

Identification code	V01GR34
Empirical formula	$C_{27}H_{23}AuBrClN_3O_4P$
Formula weight	796.78
Temperature/K	173.0
Crystal system	orthorhombic
Space group	Pbcn
a/Å	18.9094(6)
b/Å	16.3880(5)
c/Å	17.9115(5)

α/°	90
β/°	90
γ/°	90
Volume/Å^3	5550.6(3)
Z	8
ρ_{calc}g/cm^3	1.907
μ/mm^{-1}	13.404
F(000)	3072.0
Crystal size/mm^3	0.22 × 0.12 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.138 to 136.496
Index ranges	-22 ≤ h ≤ 12, -18 ≤ k ≤ 19, -19 ≤ l ≤ 21
Reflections collected	10573
Independent reflections	5023 [R_{int} = 0.0393, R_{sigma} = 0.0507]
Data/restraints/parameters	5023/331/343
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0755, wR_2 = 0.2012
Final R indexes [all data]	R_1 = 0.0911, wR_2 = 0.2157
Largest diff. peak/hole / e Å^{-3}	2.10/-1.10

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **7**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)

Au1	3010.4(3)	4520.4(3)	4809.1(3)	67.2(2)
Br1	7946.3(11)	2325.1(14)	3740.8(14)	117.4(7)
P1	1842.5(17)	4730(2)	4719.2(18)	62.5(7)
N1	4327(6)	4206(6)	5670(6)	68(2)
N2	4073(5)	4279(6)	4974(6)	61(2)
N6	4512(7)	4076(10)	3772(7)	101(4)
C3	4602(6)	4058(6)	4507(6)	57(2)
C4	5185(6)	3828(6)	4922(6)	54(2)
C5	4983(7)	3935(7)	5656(7)	65(2)
C7	5859(6)	3496(6)	4625(6)	56(2)
C9	1446(6)	4689(7)	5634(7)	63(2)
C10	1599(7)	5705(7)	4327(7)	64(3)
C11	1408(7)	4004(8)	4125(7)	69(3)
C12	5924(9)	3218(14)	3917(9)	112(7)
C13	6555(10)	2920(16)	3653(11)	136(9)
C14	7101(7)	2816(8)	4097(8)	73(3)
C15	7060(9)	3063(12)	4802(9)	94(5)
C16	6434(8)	3413(11)	5057(8)	86(4)
C17	1724(8)	5192(9)	6176(8)	76(3)
C18	1454(8)	5179(10)	6899(8)	82(3)
C19	911(8)	4670(9)	7085(8)	76(3)
C20	634(9)	4146(11)	6542(8)	90(4)
C21	921(7)	4171(9)	5799(8)	74(3)
C22	1112(8)	6227(8)	4655(8)	80(4)

C23	968(9)	6974(9)	4317(10)	94(4)
C24	1300(8)	7188(9)	3670(9)	86(4)
C25	1783(8)	6690(9)	3355(9)	86(4)
C26	1952(7)	5940(9)	3678(7)	74(3)
C27	682(8)	4087(9)	3952(8)	81(3)
C28	364(10)	3523(10)	3494(9)	93(4)
C29	737(10)	2917(11)	3191(10)	99(4)
C30	1444(11)	2846(11)	3318(11)	107(5)
C31	1769(9)	3377(10)	3785(9)	88(4)
Cl1	3603(3)	4841(5)	7442(3)	146(2)
O1	4283(9)	5047(15)	7300(10)	198(6)
O2	3607(11)	4294(16)	7979(11)	200(6)
O3	3197(9)	5462(13)	7820(10)	162(5)
O4	3309(9)	4736(13)	6736(8)	155(5)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **7.** The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au1	66.6(4)	63.3(4)	71.7(4)	14.0(2)	18.5(2)	13.0(2)
Br1	110.4(14)	118.0(15)	123.9(16)	-2.6(12)	46.9(12)	37.6(11)
P1	62.1(16)	64.3(16)	61.1(16)	13.9(13)	17.3(13)	18.1(13)
N1	85(5)	60(5)	59(4)	4(4)	15(4)	-5(4)
N2	69(4)	48(4)	65(4)	10(3)	10(3)	2(4)
N6	92(8)	139(12)	71(5)	6(5)	0(5)	12(8)

C3	66(5)	46(5)	58(4)	5(4)	7(3)	1(4)
C4	68(4)	42(4)	51(4)	2(3)	3(3)	-4(3)
C5	82(5)	59(6)	53(4)	-2(4)	6(4)	-7(4)
C7	70(5)	48(5)	51(4)	5(4)	6(3)	-2(4)
C9	63(5)	66(5)	59(4)	10(4)	11(4)	11(4)
C10	67(6)	62(5)	63(5)	13(4)	10(4)	15(4)
C11	80(5)	68(5)	59(5)	11(4)	11(4)	16(4)
C12	83(7)	191(18)	63(6)	-41(8)	-3(5)	26(8)
C13	98(7)	230(20)	80(7)	-47(9)	10(6)	47(10)
C14	79(6)	67(7)	74(6)	-2(5)	24(4)	-6(5)
C15	89(7)	116(12)	76(6)	-4(6)	2(5)	36(7)
C16	83(6)	114(11)	61(6)	-7(6)	-1(4)	29(6)
C17	77(7)	85(7)	68(5)	1(5)	13(5)	-1(6)
C18	84(7)	94(8)	67(6)	1(5)	12(5)	7(6)
C19	73(6)	94(8)	60(6)	12(5)	9(5)	11(5)
C20	96(8)	106(9)	67(6)	6(5)	18(5)	-13(7)
C21	73(6)	84(7)	63(5)	5(5)	8(4)	3(5)
C22	82(7)	67(6)	91(7)	13(5)	25(6)	21(5)
C23	95(9)	68(6)	119(9)	19(6)	13(7)	23(6)
C24	86(8)	66(6)	105(8)	21(6)	-7(6)	2(5)
C25	92(8)	78(7)	87(8)	28(6)	-4(6)	4(6)
C26	86(8)	76(6)	60(5)	15(5)	9(5)	9(5)
C27	84(6)	84(7)	75(7)	-2(6)	6(5)	20(5)
C28	106(8)	88(7)	85(8)	1(6)	-13(6)	16(6)

C29	125(8)	90(8)	84(9)	-1(7)	-9(7)	22(6)
C30	129(9)	93(9)	99(10)	-19(8)	-9(7)	35(7)
C31	99(7)	86(7)	81(8)	-6(6)	7(6)	30(6)
Cl1	91(3)	277(7)	71(2)	10(3)	18(2)	2(4)
O1	101(6)	369(18)	124(11)	17(11)	28(6)	-18(8)
O2	146(12)	328(13)	126(9)	59(9)	22(8)	6(9)
O3	99(8)	284(12)	104(9)	-35(8)	9(7)	-20(8)
O4	123(8)	263(16)	79(5)	-5(6)	14(5)	18(9)

Table S4. Bond Lengths for **7**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	P1	2.241(3)	C12	C13	1.37(2)
Au1	N2	2.068(10)	C13	C14	1.31(2)
Br1	C14	1.899(13)	C14	C15	1.33(2)
P1	C9	1.803(12)	C15	C16	1.39(2)
P1	C10	1.805(12)	C17	C18	1.392(19)
P1	C11	1.795(15)	C18	C19	1.36(2)
N1	N2	1.341(15)	C19	C20	1.40(2)
N1	C5	1.317(16)	C20	C21	1.438(19)
N2	C3	1.354(15)	C22	C23	1.392(19)
N6	C3	1.327(17)	C23	C24	1.36(2)
C3	C4	1.382(16)	C24	C25	1.35(2)
C4	C5	1.379(16)	C25	C26	1.396(19)
C4	C7	1.484(16)	C27	C28	1.37(2)

C7	C12	1.353(17)	C28	C29	1.33(2)
C7	C16	1.343(19)	C29	C30	1.36(3)
C9	C17	1.378(19)	C30	C31	1.36(2)
C9	C21	1.341(18)	Cl1	O1	1.355(18)
C10	C22	1.388(17)	Cl1	O2	1.31(2)
C10	C26	1.394(17)	Cl1	O3	1.442(19)
C11	C27	1.41(2)	Cl1	O4	1.392(16)
C11	C31	1.376(18)			

Table S5. Bond Angles for **7**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	Au1	P1	175.3(3)	C31	C11	C27	117.2(14)
C9	P1	Au1	109.8(4)	C7	C12	C13	121.4(15)
C9	P1	C10	106.3(5)	C14	C13	C12	121.4(16)
C10	P1	Au1	114.5(4)	C13	C14	Br1	120.8(12)
C11	P1	Au1	113.1(4)	C13	C14	C15	119.3(14)
C11	P1	C9	108.9(6)	C15	C14	Br1	119.8(12)
C11	P1	C10	103.8(6)	C14	C15	C16	119.1(15)
C5	N1	N2	110.5(10)	C7	C16	C15	122.9(14)
N1	N2	Au1	119.9(8)	C9	C17	C18	120.4(14)
N1	N2	C3	106.5(10)	C19	C18	C17	120.9(15)
C3	N2	Au1	133.0(9)	C18	C19	C20	119.2(13)
N2	C3	C4	109.3(10)	C19	C20	C21	118.9(14)
N6	C3	N2	120.7(12)	C9	C21	C20	120.1(14)

N6	C3	C4	129.9(12)	C10	C22	C23	119.2(14)
C3	C4	C7	126.2(10)	C24	C23	C22	120.4(15)
C5	C4	C3	104.9(10)	C25	C24	C23	120.7(14)
C5	C4	C7	128.8(11)	C24	C25	C26	121.0(15)
N1	C5	C4	108.8(11)	C10	C26	C25	118.6(13)
C12	C7	C4	122.6(12)	C28	C27	C11	119.4(14)
C16	C7	C4	121.7(11)	C29	C28	C27	120.8(17)
C16	C7	C12	115.6(13)	C28	C29	C30	121.0(18)
C17	C9	P1	117.4(10)	C31	C30	C29	119.6(17)
C21	C9	P1	122.1(11)	C30	C31	C11	121.9(16)
C21	C9	C17	120.4(12)	O1	Cl1	O3	114.7(14)
C22	C10	P1	123.4(10)	O1	Cl1	O4	103.8(11)
C22	C10	C26	120.0(12)	O2	Cl1	O1	107.6(13)
C26	C10	P1	116.5(9)	O2	Cl1	O3	98.1(13)
C27	C11	P1	120.7(10)	O2	Cl1	O4	125.6(16)
C31	C11	P1	122.0(12)	O4	Cl1	O3	107.6(11)

Table S6. Torsion Angles for **7.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Au1	P1	C9	C17	54.0(11)	C9	P1	C11	C27	63.3(12)
Au1	P1	C9	C21	-123.3(11)	C9	P1	C11	C31	-120.7(12)
Au1	P1	C10	C22	-130.2(12)	C9	C17	C18	C19	0(2)
Au1	P1	C10	C26	47.0(13)	C10	P1	C9	C17	-70.4(12)
Au1	P1	C11	C27	-174.3(10)	C10	P1	C9	C21	112.3(11)

Au1	P1	C11	C31	1.7(13)		C10	P1	C11	C27	-49.6(12)	
Au1	N2	C3	N6	10.4(18)		C10	P1	C11	C31	126.4(12)	
Au1	N2	C3	C4	-169.0(8)		C10	C22	C23	C24	0(3)	
Br1	C14	C15	C16	-179.2(14)		C11	P1	C9	C17	178.3(10)	
P1	C9	C17	C18	-178.6(11)		C11	P1	C9	C21	1.0(13)	
P1	C9	C21	C20	178.4(11)		C11	P1	C10	C22	106.0(14)	
P1	C10	C22	C23	178.8(13)		C11	P1	C10	C26	-76.8(12)	
P1	C10	C26	C25	-179.9(12)		C11	C27	C28	C29	-3(2)	
P1	C11	C27	C28	179.9(12)		C12	C7	C16	C15	0(3)	
P1	C11	C31	C30	-177.8(14)		C12	C13	C14	Br1	175.1(19)	
N1	N2	C3	N6	-179.3(12)		C12	C13	C14	C15	-5(4)	
N1	N2	C3	C4	1.3(12)		C13	C14	C15	C16	1(3)	
N2	N1	C5	C4	0.6(13)		C14	C15	C16	C7	2(3)	
N2	C3	C4	C5	-0.9(12)		C16	C7	C12	C13	-4(3)	
N2	C3	C4	C7	175.9(10)		C17	C9	C21	C20	1(2)	
N6	C3	C4	C5	179.7(14)		C17	C18	C19	C20	1(2)	
N6	C3	C4	C7	-3(2)		C18	C19	C20	C21	-1(2)	
C3	C4	C5	N1	0.2(12)		C19	C20	C21	C9	0(2)	
C3	C4	C7	C12	-14(2)		C21	C9	C17	C18	-1(2)	
C3	C4	C7	C16	169.1(13)		C22	C10	C26	C25	-3(2)	
C4	C7	C12	C13	179.4(19)		C22	C23	C24	C25	-1(3)	
C4	C7	C16	C15	176.5(15)		C23	C24	C25	C26	0(3)	
C5	N1	N2	Au1	170.7(8)		C24	C25	C26	C10	2(2)	
C5	N1	N2	C3	-1.2(13)		C26	C10	C22	C23	2(2)	

C5	C4	C7	C12	161.6(15)	C27	C11	C31 C30 -2(2)
C5	C4	C7	C16	-14.8(19)	C27	C28	C29 C30 -1(3)
C7	C4	C5	N1	-176.5(10)	C28	C29	C30 C31 3(3)
C7	C12	C13	C14	7(4)	C29	C30	C31 C11 -2(3)
C9	P1	C10	C22	-8.7(15)	C31	C11	C27 C28 4(2)
C9	P1	C10	C26	168.4(11)			

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **7.**

Atom	x	y	z	U(eq)
H1	4089	4322	6078	82
H6A	4104	4233	3584	121
H6B	4860	3931	3474	121
H5	5269	3830	6081	78
H12	5525	3229	3595	135
H13	6598	2785	3139	163
H15	7453	3002	5128	113
H16	6414	3601	5558	103
H17	2102	5550	6056	92
H18	1650	5529	7267	98
H19	724	4671	7577	91
H20	261	3779	6662	107
H21	737	3819	5424	88
H22	879	6077	5104	96
H23	636	7336	4538	113

H24	1190	7695	3439	103
H25	2011	6852	2907	103
H26	2301	5597	3461	89
H27	417	4530	4149	97
H28	-128	3564	3393	112
H29	506	2529	2881	119
H30	1708	2427	3080	128
H31	2260	3315	3881	106

Figure S2. ORTEP plot for Triphenylphosphine(5-Amino-4-(4-bromophenyl)3-methyl-pyrazole) gold(I) perchlorate **8**

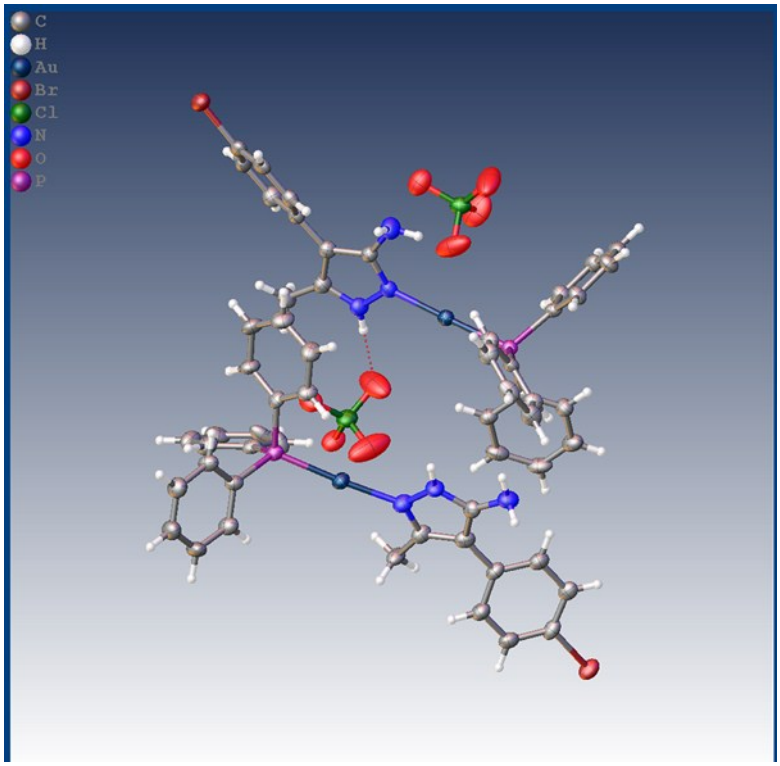


Table S8. Crystal data and structure refinement for **8.**

Identification code	exp_67
Empirical formula	$C_{28}H_{25}AuBrClN_3O_4P$
Formula weight	810.80
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	12.7645(4)
b/Å	15.6061(5)
c/Å	16.4732(4)
α/°	105.959(2)
β/°	93.268(2)
γ/°	112.402(3)
Volume/Å^3	2868.22(16)
Z	4
ρ_{calc}g/cm^3	1.878
μ/mm^{-1}	12.982
F(000)	1568.0
Crystal size/mm^3	0.14 × 0.12 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.674 to 136.624
Index ranges	-15 ≤ h ≤ 14, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19
Reflections collected	31051

Independent reflections	10158 [R_{int} = 0.0544, R_{sigma} = 0.0420]
Data/restraints/parameters	10158/60/707
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0612, wR_2 = 0.1639
Final R indexes [all data]	R_1 = 0.0618, wR_2 = 0.1649
Largest diff. peak/hole / e $Å^{-3}$	5.17/-2.72

Table S9. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **8** U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
Au1	137.1(2)	7986.1(2)	6324.7(2)	25.65(12)
Br1	1486.5(9)	3085.1(7)	1467.1(6)	45.3(2)
P1	-777.9(15)	8869.3(12)	6982.1(11)	24.9(4)
N1	961(5)	7183(4)	5695(4)	27.2(12)
N2	1894(5)	7117(5)	6087(4)	31.2(13)
N3	-288(6)	6381(6)	4311(5)	44.7(17)
C1	660(6)	6523(5)	4896(5)	26.4(14)
C2	2165(6)	6447(6)	5565(5)	31.6(16)
C3	1411(6)	6053(5)	4780(5)	29.5(15)
C4	3115(7)	6248(6)	5850(6)	40.1(18)
C5	1428(6)	5324(5)	4002(5)	29.2(15)
C6	2469(7)	5380(6)	3740(6)	36.7(17)
C7	2491(7)	4712(6)	2997(5)	35.9(17)

C8	1474(7)	3985(5)	2511(5)	33.3(16)
C9	417(7)	3897(5)	2738(5)	31.7(16)
C10	402(6)	4564(5)	3484(5)	31.8(16)
C11	-2222(6)	8099(5)	7060(4)	24.7(14)
C12	-2711(6)	8351(6)	7768(5)	32.0(16)
C13	-3812(6)	7699(6)	7825(6)	38.4(18)
C14	-4405(6)	6831(6)	7157(5)	35.8(18)
C15	-3923(6)	6597(6)	6455(6)	36.4(17)
C16	-2830(7)	7225(5)	6400(5)	33.3(16)
C17	-19(6)	9670(5)	8057(4)	25.8(14)
C18	-181(7)	10513(5)	8446(5)	33.5(16)
C19	408(8)	11102(6)	9263(5)	41.3(19)
C20	1149(7)	10866(6)	9703(5)	42(2)
C21	1320(7)	10038(6)	9326(5)	38.9(18)
C22	733(6)	9437(6)	8495(5)	30.3(15)
C23	-922(6)	9665(5)	6400(4)	24.5(13)
C24	75(7)	10388(6)	6304(5)	33.5(16)
C25	-1(6)	10972(5)	5819(5)	30.3(15)
C26	-1075(7)	10827(5)	5436(5)	31.2(16)
C27	-2065(6)	10110(6)	5515(5)	33.0(16)
C28	-2001(6)	9528(5)	6014(5)	31.3(15)
Au2	-3498.2(2)	3901.6(2)	8411.0(2)	29.92(12)
Br2	-2908.3(7)	9943.5(6)	13095.0(5)	38.8(2)
P2	-3013.5(15)	2705.1(13)	7696.5(12)	27.6(4)

N4	-3939(5)	5021(5)	9003(4)	33.9(14)
N5	-4863(5)	5139(4)	8671(4)	31.7(13)
N6	-5897(6)	6138(5)	8987(4)	37.6(15)
C29	-4985(6)	5907(5)	9192(5)	30.5(15)
C30	-3471(6)	5748(6)	9749(5)	33.1(16)
C31	-4104(6)	6329(6)	9907(5)	33.7(16)
C32	-2438(7)	5847(6)	10266(5)	35.7(17)
C33	-3862(6)	7181(5)	10674(5)	29.7(15)
C34	-4080(6)	7981(6)	10614(5)	34.5(16)
C35	-3812(6)	8814(5)	11346(5)	33.3(16)
C36	-3340(6)	8811(5)	12109(5)	32.8(16)
C37	-3130(7)	8032(6)	12190(5)	34.5(16)
C38	-3411(7)	7212(6)	11481(5)	34.4(17)
C39	-3454(6)	1629(5)	8040(5)	29.1(15)
C40	-3159(7)	1761(6)	8904(5)	37.9(17)
C41	-3431(9)	959(7)	9184(5)	44(2)
C42	-4051(8)	24(6)	8611(6)	45(2)
C43	-4353(8)	-107(6)	7758(6)	42.5(19)
C44	-4053(7)	690(6)	7459(5)	34.7(16)
C45	-3645(6)	2283(5)	6572(5)	27.1(15)
C46	-4712(6)	2306(6)	6362(5)	32.7(16)
C47	-5235(7)	1996(6)	5499(5)	40.8(19)
C48	-4709(7)	1635(7)	4863(5)	44(2)
C49	-3640(7)	1618(6)	5067(5)	38.6(18)

C50	-3117(7)	1953(6)	5926(5)	33.1(16)
C51	-1465(6)	3105(5)	7765(4)	30.0(15)
C52	-797(7)	4080(6)	7902(6)	41(2)
C53	406(7)	4391(7)	7924(6)	43(2)
C54	881(7)	3717(7)	7836(5)	42.0(19)
C55	217(7)	2757(6)	7714(5)	39.3(18)
C56	-954(7)	2444(6)	7669(5)	39.6(18)
Cl1	2846.4(17)	7622.7(15)	8366.3(12)	41.4(4)
O1	3938(5)	8013(5)	8935(4)	46.5(14)
O2	2562(6)	6646(4)	7840(4)	50.4(15)
O3	1979(7)	7648(10)	8858(6)	112(4)
O4	2892(10)	8193(6)	7832(6)	101(3)
Cl2	-3407.9(15)	6015.7(13)	3582.9(11)	34.2(4)
O5	-3089(6)	5285(5)	3040(5)	55.1(16)
O6	-2462(7)	6931(5)	3902(6)	84(3)
O7	-3792(9)	5716(6)	4273(5)	88(3)
O8	-4302(10)	6062(8)	3078(6)	101(3)

Table S10. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **8** The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au1	22.85(18)	20.89(18)	27.26(19)	7.26(13)	2.68(13)	3.41(13)
Br1	66.0(6)	39.1(5)	34.6(4)	9.9(4)	13.1(4)	26.5(5)
P1	20.7(8)	19.9(8)	25.6(9)	5.9(7)	1.3(7)	1.0(7)

N1	21(3)	25(3)	31(3)	11(2)	3(2)	4(2)
N2	23(3)	31(3)	33(3)	9(3)	2(3)	5(3)
N3	40(4)	43(4)	45(4)	7(3)	-5(3)	18(3)
C1	25(3)	23(3)	27(3)	7(3)	4(3)	6(3)
C2	26(3)	30(4)	35(4)	9(3)	5(3)	7(3)
C3	23(3)	29(4)	32(4)	10(3)	4(3)	6(3)
C4	31(4)	44(5)	44(5)	15(4)	-4(3)	15(4)
C5	26(3)	26(4)	34(4)	12(3)	4(3)	7(3)
C6	27(4)	32(4)	43(4)	11(3)	2(3)	5(3)
C7	40(4)	42(4)	37(4)	18(4)	13(4)	24(4)
C8	42(4)	30(4)	33(4)	18(3)	14(3)	15(3)
C9	36(4)	25(4)	32(4)	15(3)	3(3)	6(3)
C10	29(4)	27(4)	39(4)	17(3)	6(3)	7(3)
C11	24(3)	25(3)	25(3)	12(3)	2(3)	7(3)
C12	20(3)	29(4)	35(4)	8(3)	0(3)	0(3)
C13	23(4)	39(4)	50(5)	21(4)	8(3)	5(3)
C14	15(3)	33(4)	49(5)	20(4)	-5(3)	-4(3)
C15	24(4)	26(4)	45(5)	9(3)	1(3)	-2(3)
C16	30(4)	22(4)	34(4)	5(3)	-1(3)	0(3)
C17	23(3)	20(3)	23(3)	7(3)	1(3)	-3(3)
C18	33(4)	27(4)	33(4)	7(3)	-1(3)	7(3)
C19	51(5)	30(4)	32(4)	6(3)	6(4)	8(4)
C20	39(4)	39(5)	24(4)	3(3)	-2(3)	-4(4)
C21	32(4)	47(5)	29(4)	17(4)	0(3)	6(4)

C22	27(4)	30(4)	26(4)	5(3)	3(3)	6(3)
C23	24(3)	22(3)	21(3)	6(3)	4(3)	3(3)
C24	27(4)	30(4)	36(4)	11(3)	0(3)	5(3)
C25	31(4)	20(3)	32(4)	7(3)	7(3)	4(3)
C26	41(4)	26(4)	22(3)	5(3)	4(3)	12(3)
C27	28(4)	34(4)	36(4)	16(3)	1(3)	8(3)
C28	24(3)	29(4)	36(4)	12(3)	-1(3)	6(3)
Au2	28.34(19)	26.08(19)	26.73(19)	1.97(13)	1.56(13)	7.26(14)
Br2	31.7(4)	29.5(4)	36.4(4)	-5.5(3)	-0.8(3)	5.3(3)
P2	24.4(8)	23.4(9)	26.4(9)	4.1(7)	1.9(7)	3.9(7)
N4	26(3)	30(3)	31(3)	2(3)	-1(3)	4(3)
N5	29(3)	28(3)	26(3)	2(3)	-5(3)	5(3)
N6	32(3)	39(4)	31(3)	8(3)	-1(3)	8(3)
C29	31(4)	20(3)	33(4)	7(3)	4(3)	4(3)
C30	23(3)	30(4)	35(4)	4(3)	5(3)	4(3)
C31	27(4)	34(4)	32(4)	10(3)	7(3)	4(3)
C32	33(4)	38(4)	25(4)	-4(3)	-5(3)	15(3)
C33	25(3)	22(3)	30(4)	0(3)	6(3)	3(3)
C34	29(4)	35(4)	31(4)	5(3)	6(3)	8(3)
C35	28(4)	25(4)	37(4)	7(3)	9(3)	2(3)
C36	25(3)	21(3)	39(4)	-1(3)	6(3)	3(3)
C37	33(4)	36(4)	27(4)	7(3)	7(3)	9(3)
C38	34(4)	29(4)	31(4)	3(3)	6(3)	9(3)
C39	25(3)	32(4)	24(3)	7(3)	2(3)	6(3)

C40	40(4)	30(4)	33(4)	6(3)	4(3)	7(3)
C41	66(6)	43(5)	27(4)	15(4)	12(4)	24(5)
C42	60(6)	36(4)	42(5)	16(4)	12(4)	19(4)
C43	46(5)	28(4)	44(5)	7(4)	5(4)	9(4)
C44	36(4)	28(4)	30(4)	8(3)	6(3)	4(3)
C45	25(3)	18(3)	28(4)	1(3)	2(3)	2(3)
C46	26(4)	31(4)	27(4)	3(3)	-2(3)	2(3)
C47	33(4)	39(4)	37(4)	2(3)	-7(3)	9(4)
C48	37(4)	45(5)	30(4)	1(4)	-5(3)	6(4)
C49	40(4)	42(5)	28(4)	6(3)	10(3)	14(4)
C50	32(4)	36(4)	22(3)	3(3)	1(3)	8(3)
C51	28(4)	27(4)	21(3)	1(3)	0(3)	2(3)
C52	28(4)	33(4)	58(5)	25(4)	-2(4)	4(3)
C53	25(4)	52(5)	54(5)	38(4)	5(3)	3(4)
C54	28(4)	61(6)	31(4)	19(4)	-4(3)	11(4)
C55	29(4)	47(5)	34(4)	3(4)	-1(3)	16(4)
C56	36(4)	35(4)	34(4)	2(3)	4(3)	7(4)
Cl1	40.8(10)	41.3(10)	29.5(9)	0.7(8)	-4.8(8)	12.9(9)
O1	32(3)	46(3)	40(3)	-2(3)	-3(2)	7(3)
O2	55(4)	37(3)	40(3)	3(2)	-11(3)	8(3)
O3	47(4)	168(9)	61(5)	-22(5)	-1(3)	25(5)
O4	154(9)	47(4)	60(4)	2(3)	-42(5)	15(5)
Cl2	29.0(8)	31.0(9)	29.7(9)	7.7(7)	1.0(7)	0.7(7)
O5	44(3)	39(3)	66(4)	7(3)	13(3)	7(3)

O6	64(4)	35(3)	109(6)	1(4)	17(4)	-10(3)
O7	120(7)	50(4)	54(4)	7(3)	38(4)	-4(4)
O8	135(7)	104(7)	57(5)	-25(4)	-34(5)	83(6)

Table S11. Bond Lengths for **8**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	P1	2.2332(18)	P2	C45	1.808(7)
Au1	N1	2.042(6)	P2	C51	1.818(8)
Br1	C8	1.903(8)	N4	N5	1.368(9)
P1	C11	1.811(7)	N4	C30	1.337(10)
P1	C17	1.816(7)	N5	C29	1.338(10)
P1	C23	1.817(7)	N6	C29	1.393(10)
N1	N2	1.374(8)	C29	C31	1.393(11)
N1	C1	1.355(9)	C30	C31	1.412(11)
N2	C2	1.330(10)	C30	C32	1.460(10)
N3	C1	1.410(10)	C31	C33	1.477(10)
C1	C3	1.405(10)	C33	C34	1.405(11)
C2	C3	1.396(11)	C33	C38	1.399(11)
C2	C4	1.445(10)	C34	C35	1.419(11)
C3	C5	1.470(11)	C35	C36	1.364(11)
C5	C6	1.399(11)	C36	C37	1.380(11)
C5	C10	1.408(10)	C37	C38	1.383(11)
C6	C7	1.382(12)	C39	C40	1.389(11)
C7	C8	1.368(11)	C39	C44	1.393(11)

C8	C9	1.387(11)	C40	C41	1.380(12)
C9	C10	1.382(11)	C41	C42	1.387(13)
C11	C12	1.387(11)	C42	C43	1.372(13)
C11	C16	1.388(10)	C43	C44	1.390(11)
C12	C13	1.413(10)	C45	C46	1.402(10)
C13	C14	1.387(12)	C45	C50	1.379(11)
C14	C15	1.368(12)	C46	C47	1.402(11)
C15	C16	1.391(11)	C47	C48	1.383(13)
C17	C18	1.394(10)	C48	C49	1.398(12)
C17	C22	1.381(10)	C49	C50	1.393(11)
C18	C19	1.379(11)	C51	C52	1.376(11)
C19	C20	1.374(13)	C51	C56	1.396(11)
C20	C21	1.375(13)	C52	C53	1.417(11)
C21	C22	1.398(11)	C53	C54	1.381(13)
C23	C24	1.394(10)	C54	C55	1.360(12)
C23	C28	1.396(10)	C55	C56	1.374(11)
C24	C25	1.392(10)	Cl1	O1	1.443(6)
C25	C26	1.383(11)	Cl1	O2	1.423(6)
C26	C27	1.375(11)	Cl1	O3	1.415(9)
C27	C28	1.402(10)	Cl1	O4	1.402(9)
Au2	P2	2.2382(19)	Cl2	O5	1.449(7)
Au2	N4	2.048(7)	Cl2	O6	1.405(7)
Br2	C36	1.909(7)	Cl2	O7	1.389(8)
P2	C39	1.815(8)	Cl2	O8	1.410(9)

Table S12 Bond Angles for **8**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Au1	P1	178.56(17)	C51	P2	Au2	112.7(2)
C11	P1	Au1	111.8(2)	N5	N4	Au2	123.3(5)
C11	P1	C17	108.0(3)	C30	N4	Au2	131.1(5)
C11	P1	C23	106.7(3)	C30	N4	N5	105.5(6)
C17	P1	Au1	112.8(2)	C29	N5	N4	111.6(6)
C17	P1	C23	105.8(3)	N5	C29	N6	120.8(7)
C23	P1	Au1	111.3(2)	N5	C29	C31	107.5(7)
N2	N1	Au1	123.4(5)	N6	C29	C31	131.6(7)
C1	N1	Au1	130.3(5)	N4	C30	C31	110.7(7)
C1	N1	N2	105.6(6)	N4	C30	C32	119.6(7)
C2	N2	N1	111.1(6)	C31	C30	C32	129.6(7)
N1	C1	N3	121.2(6)	C29	C31	C30	104.6(7)
N1	C1	C3	110.1(6)	C29	C31	C33	129.2(7)
C3	C1	N3	128.7(7)	C30	C31	C33	126.2(7)
N2	C2	C3	108.2(6)	C34	C33	C31	121.0(7)
N2	C2	C4	120.5(7)	C38	C33	C31	120.8(7)
C3	C2	C4	131.3(7)	C38	C33	C34	118.3(7)
C1	C3	C5	128.2(7)	C33	C34	C35	121.0(7)
C2	C3	C1	104.9(6)	C36	C35	C34	117.8(7)
C2	C3	C5	126.9(7)	C35	C36	Br2	118.9(6)
C6	C5	C3	120.8(7)	C35	C36	C37	122.5(7)

C6	C5	C10	117.8(7)	C37	C36	Br2	118.5(6)
C10	C5	C3	121.3(7)	C36	C37	C38	119.7(7)
C7	C6	C5	121.1(7)	C37	C38	C33	120.6(7)
C8	C7	C6	119.2(7)	C40	C39	P2	118.2(6)
C7	C8	Br1	119.7(6)	C40	C39	C44	120.1(7)
C7	C8	C9	122.1(7)	C44	C39	P2	121.6(6)
C9	C8	Br1	118.1(6)	C41	C40	C39	119.9(8)
C10	C9	C8	118.4(7)	C40	C41	C42	120.0(8)
C9	C10	C5	121.3(7)	C43	C42	C41	120.1(8)
C12	C11	P1	121.6(5)	C42	C43	C44	120.7(8)
C12	C11	C16	119.9(7)	C43	C44	C39	119.1(7)
C16	C11	P1	118.4(6)	C46	C45	P2	117.8(6)
C11	C12	C13	119.6(7)	C50	C45	P2	122.7(6)
C14	C13	C12	119.4(8)	C50	C45	C46	119.5(7)
C15	C14	C13	120.5(7)	C45	C46	C47	120.2(7)
C14	C15	C16	120.6(7)	C48	C47	C46	119.3(8)
C11	C16	C15	120.0(8)	C47	C48	C49	120.8(7)
C18	C17	P1	121.3(5)	C50	C49	C48	119.2(8)
C22	C17	P1	119.2(6)	C45	C50	C49	120.9(7)
C22	C17	C18	119.5(7)	C52	C51	P2	118.5(6)
C19	C18	C17	119.7(7)	C52	C51	C56	120.0(7)
C20	C19	C18	120.8(8)	C56	C51	P2	121.4(6)
C19	C20	C21	120.1(7)	C51	C52	C53	118.9(8)
C20	C21	C22	119.7(8)	C54	C53	C52	119.4(8)

C17	C22	C21	120.2(7)	C55	C54	C53	121.4(8)
C24	C23	P1	118.7(5)	C54	C55	C56	119.6(8)
C24	C23	C28	120.1(6)	C55	C56	C51	120.7(8)
C28	C23	P1	121.2(5)	O2	Cl1	O1	110.7(4)
C25	C24	C23	120.2(7)	O3	Cl1	O1	109.3(5)
C26	C25	C24	119.2(7)	O3	Cl1	O2	110.0(6)
C27	C26	C25	121.3(7)	O4	Cl1	O1	110.3(5)
C26	C27	C28	120.0(7)	O4	Cl1	O2	108.4(5)
C23	C28	C27	119.1(7)	O4	Cl1	O3	108.1(8)
N4	Au2	P2	176.68(19)	O6	Cl2	O5	111.3(5)
C39	P2	Au2	116.4(3)	O6	Cl2	O8	111.2(7)
C39	P2	C51	104.1(3)	O7	Cl2	O5	108.3(5)
C45	P2	Au2	109.3(2)	O7	Cl2	O6	108.6(6)
C45	P2	C39	106.5(3)	O7	Cl2	O8	110.6(7)
C45	P2	C51	107.3(3)	O8	Cl2	O5	106.8(5)

Table S13. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **8**.

Atom	x	y	z	U(eq)
H2	2263	7472	6615	37
H3A	-844	5801	4230	54
H3B	-537	6836	4522	54
H4A	3841	6743	5799	60
H4B	3020	5598	5494	60

H4C	3128	6270	6451	60
H6	3173	5887	4078	44
H7	3203	4757	2825	43
H9	-279	3390	2389	38
H10	-315	4509	3650	38
H12	-2309	8959	8212	38
H13	-4143	7854	8317	46
H14	-5151	6395	7188	43
H15	-4338	6001	6000	44
H16	-2500	7056	5911	40
H18	-695	10680	8149	40
H19	301	11678	9526	50
H20	1544	11276	10268	51
H21	1833	9875	9629	47
H22	853	8867	8232	36
H24	808	10482	6570	40
H25	677	11465	5752	36
H26	-1128	11231	5111	37
H27	-2792	10008	5232	40
H28	-2684	9046	6088	38
H5	-5322	4756	8177	38
H6A	-6290	5748	8470	45
H6B	-6359	6058	9365	45
H32A	-2660	5423	10626	53

H32B	-2015	6529	10632	53
H32C	-1946	5655	9887	53
H34	-4411	7963	10076	41
H35	-3957	9356	11305	40
H37	-2794	8059	12731	41
H38	-3296	6664	11542	41
H40	-2771	2403	9302	46
H41	-3193	1047	9769	53
H42	-4268	-526	8809	54
H43	-4771	-750	7368	51
H44	-4254	596	6867	42
H46	-5081	2532	6804	39
H47	-5944	2034	5354	49
H48	-5078	1396	4279	52
H49	-3276	1382	4626	46
H50	-2385	1953	6068	40
H52	-1135	4536	7979	49
H53	880	5056	7999	52
H54	1689	3929	7862	50
H55	560	2305	7659	47
H56	-1420	1771	7571	48

Table S14. Solvent masks information for **8**.

Number	X	Y	Z	Volume	Electron count	Content

1	0.000	0.500	0.000	105.8	13.7	MeOH

Figure S3. ORTEP plot for Triphenylphosphine(5-Amino-4-cyano-1-(2-hydroxyethyl)-pyrazole gold(I) perchlorate **9**

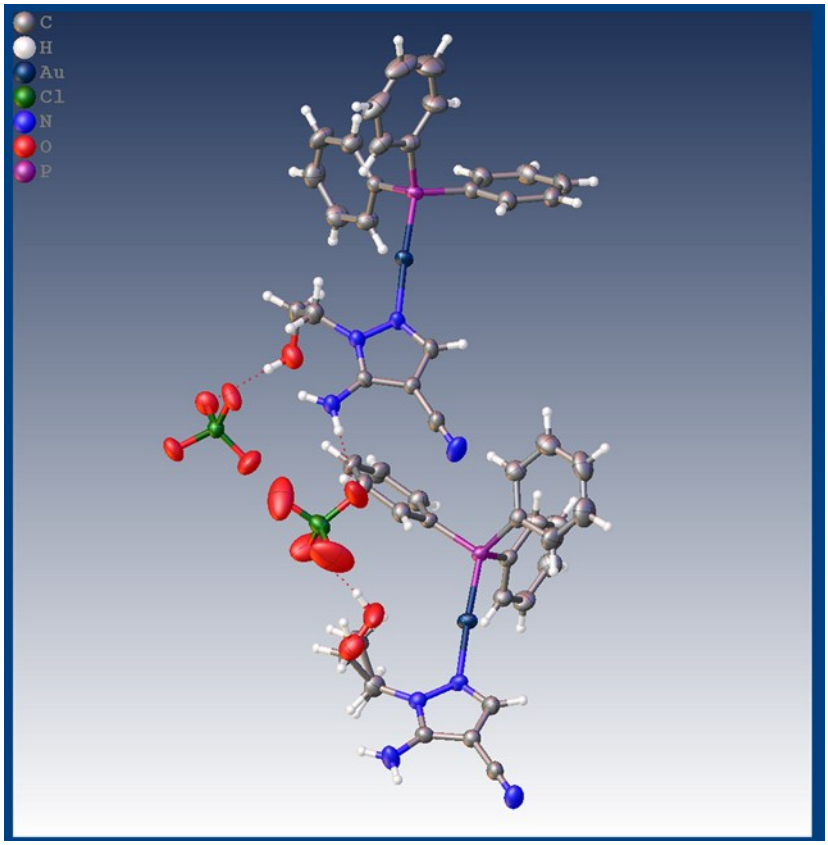


Table S15. Crystal data and structure refinement for **9**.

Identification code	V04AF71D
Empirical formula	$C_{24}H_{23}AuClN_4O_5P$
Formula weight	710.85
Temperature/K	173
Crystal system	triclinic

Space group	P-1
a/Å	13.2511(11)
b/Å	14.8189(13)
c/Å	15.7353(12)
α/°	66.312(8)
β/°	74.845(7)
γ/°	66.970(8)
Volume/Å^3	2584.0(4)
Z	4
ρ_{calc}g/cm^3	1.827
μ/mm^{-1}	12.601
F(000)	1384.0
Crystal size/mm^3	0.32 × 0.1 × 0.04
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.884 to 134.13
Index ranges	-12 ≤ h ≤ 15, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18
Reflections collected	15895
Independent reflections	9215 [R_{int} = 0.0310, R_{sigma} = 0.0415]
Data/restraints/parameters	9215/8/671
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0338, wR_2 = 0.0906
Final R indexes [all data]	R_1 = 0.0376, wR_2 = 0.0939
Largest diff. peak/hole / e Å^{-3}	1.25/-1.83

Table S16. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **9** U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
Au1	11834.0(2)	3463.6(2)	3321.0(2)	32.39(7)
P1	10772.5(9)	4993.7(8)	2458.6(7)	27.2(2)
O1	10408(6)	1864(7)	4334(6)	70(3)
N1	12797(3)	2087(3)	4194(3)	32.2(8)
N2	12694(3)	1125(3)	4452(3)	31.0(7)
N3	13283(4)	-544(3)	5615(3)	49.9(11)
N4	14996(4)	293(3)	6676(3)	45.9(10)
C1	13422(4)	2012(3)	4769(3)	34.2(9)
C2	13732(4)	1011(3)	5406(3)	30.1(8)
C3	13260(4)	449(3)	5182(3)	31.1(8)
C4	14430(4)	612(3)	6110(3)	32.9(9)
C5	12135(4)	899(4)	3915(3)	41.3(10)
C6	11013(9)	850(10)	4344(9)	49(3)
C7	9647(3)	4895(3)	2087(3)	29.3(8)
C8	9437(4)	5341(4)	1164(3)	39.1(10)
C9	8516(4)	5287(4)	933(4)	46.0(11)
C10	7821(4)	4804(4)	1621(4)	45.8(11)
C11	8032(4)	4352(4)	2542(4)	43(1)
C12	8950(4)	4395(3)	2774(3)	37.1(9)

C13	11524(3)	5668(3)	1410(3)	29.1(8)
C14	11128(4)	6747(4)	1012(4)	44.8(12)
C15	11713(5)	7257(4)	207(4)	53.1(13)
C16	12672(5)	6688(4)	-203(3)	47.7(12)
C17	13066(4)	5618(4)	202(4)	42.2(10)
C18	12488(4)	5107(4)	1006(3)	35.2(9)
C19	10126(4)	5904(3)	3095(3)	32.2(8)
C20	9115(4)	6678(4)	2901(3)	40.4(10)
C21	8700(5)	7428(4)	3329(4)	51.7(12)
C22	9296(6)	7386(5)	3958(4)	58.9(15)
C23	10273(6)	6614(6)	4163(4)	62.9(16)
C24	10697(5)	5863(5)	3740(4)	50.1(12)
Au2	3640.8(2)	8712.9(2)	1923.2(2)	31.95(7)
P2	2611.9(9)	10202.1(8)	1000.5(7)	28.2(2)
O2	4842(4)	5666(3)	1539(3)	53.9(9)
N5	4659(3)	7368(3)	2753(3)	33.9(8)
N6	4566(3)	6395(3)	3035(3)	33.7(8)
N7	5413(3)	4683(3)	4013(3)	36.6(8)
N8	7353(5)	5533(4)	4844(4)	58.7(13)
C25	5457(4)	7275(3)	3182(3)	34.7(9)
C26	5895(4)	6247(3)	3728(3)	29.6(8)
C27	5319(4)	5693(3)	3611(3)	28.3(8)
C28	6716(4)	5841(3)	4330(3)	37.1(10)
C29	3646(5)	6247(4)	2802(4)	45.4(11)

C30	3815(5)	6362(4)	1787(4)	44.7(11)
C31	2406(4)	10096(3)	-41(3)	30.8(8)
C32	3320(4)	9565(4)	-542(4)	42.6(10)
C33	3205(5)	9464(4)	-1341(4)	48.5(12)
C34	2172(5)	9874(5)	-1640(4)	52.2(13)
C35	1256(5)	10396(5)	-1152(4)	53.4(13)
C36	1383(5)	10499(4)	-352(4)	45.3(11)
C37	1260(4)	10734(4)	1565(3)	37.1(9)
C38	738(4)	10069(5)	2265(4)	46.7(12)
C39	-313(5)	10469(7)	2700(4)	67(2)
C40	-835(5)	11536(8)	2420(5)	77(2)
C41	-314(7)	12189(7)	1729(7)	84(2)
C42	725(5)	11810(5)	1298(5)	59.2(15)
C43	3260(4)	11196(3)	640(3)	31.7(8)
C44	3399(4)	11847(3)	-280(3)	39.1(10)
C45	3863(4)	12611(4)	-481(4)	46.1(11)
C46	4163(4)	12743(4)	225(4)	46.9(12)
C47	4024(4)	12101(4)	1142(4)	45.6(11)
C48	3589(4)	11317(4)	1345(4)	39.8(10)
Cl1	7519.7(10)	2206.3(8)	5261.5(8)	40.5(2)
O3	7257(6)	3261(3)	5132(5)	93(2)
O4	8055(8)	1627(5)	6071(5)	127(3)
O5	8188(4)	1940(6)	4482(4)	90.7(19)
O6	6524(6)	2031(7)	5334(6)	117(3)

Cl2	5290.5(9)	3053.8(7)	2647.9(7)	32.9(2)
O7	6371(4)	3005(4)	2659(4)	67.8(12)
O8	4515(4)	3587(3)	3266(3)	52.1(9)
O9	4977(4)	3622(3)	1716(3)	51.2(9)
O10	5228(4)	2017(3)	2937(3)	48.9(9)
O1A	10598(11)	776(10)	5159(9)	57(4)
C6A	10867(13)	1319(16)	4174(13)	38(5)

Table S17. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **9**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au1	28.92(11)	28.56(11)	31.3(1)	-2.91(7)	-8.42(7)	-5.25(7)
P1	25.2(5)	26.7(5)	27.8(5)	-6.4(4)	-8.4(4)	-6.0(4)
O1	37(4)	80(5)	116(7)	-62(5)	5(4)	-23(4)
N1	28.5(18)	26.1(16)	36.0(18)	0.2(14)	-12.4(15)	-8.3(14)
N2	28.2(18)	29.6(17)	33.7(17)	-7.8(14)	-6.9(14)	-8.7(14)
N3	73(3)	28.7(19)	54(2)	-2.8(17)	-32(2)	-18(2)
N4	57(3)	42(2)	44(2)	-6.8(17)	-22(2)	-20(2)
C1	34(2)	30(2)	37(2)	-7.0(17)	-7.2(18)	-12.7(17)
C2	31(2)	29.7(19)	28.4(19)	-8.8(15)	-5.4(16)	-9.0(16)
C3	31(2)	26.4(19)	33(2)	-8.8(15)	-8.4(16)	-4.6(16)
C4	36(2)	27.7(19)	37(2)	-8.4(16)	-9.0(18)	-12.2(17)
C5	48(3)	47(2)	33(2)	-14.1(18)	-11(2)	-14(2)
C6	40(5)	48(7)	75(7)	-26(6)	-23(5)	-15(5)

C7	24.5(19)	28.2(18)	37(2)	-14.3(16)	-8.5(16)	-3.4(15)
C8	41(3)	41(2)	36(2)	-9.9(18)	-9.7(19)	-14(2)
C9	44(3)	55(3)	44(3)	-17(2)	-19(2)	-12(2)
C10	33(2)	51(3)	64(3)	-26(2)	-15(2)	-13(2)
C11	36(2)	48(3)	54(3)	-24(2)	-2(2)	-17(2)
C12	39(2)	37(2)	39(2)	-16.3(18)	-4.3(18)	-12.6(19)
C13	26(2)	34(2)	26.9(18)	-7.4(15)	-5.1(15)	-9.9(16)
C14	36(3)	34(2)	41(2)	-1.1(19)	1(2)	-3(2)
C15	50(3)	40(3)	45(3)	4(2)	-4(2)	-10(2)
C16	49(3)	53(3)	34(2)	-7(2)	0(2)	-21(2)
C17	32(2)	55(3)	42(2)	-25(2)	4.2(19)	-11(2)
C18	32(2)	37(2)	37(2)	-15.5(18)	-2.5(18)	-10.2(18)
C19	35(2)	34(2)	30.7(19)	-9.2(15)	-6.5(16)	-14.2(18)
C20	40(3)	46(2)	38(2)	-20.0(19)	-2.2(19)	-11(2)
C21	50(3)	48(3)	54(3)	-25(2)	5(2)	-11(2)
C22	79(4)	61(3)	55(3)	-39(3)	10(3)	-34(3)
C23	80(4)	77(4)	54(3)	-35(3)	-12(3)	-32(4)
C24	54(3)	59(3)	47(3)	-22(2)	-21(2)	-14(3)
Au2	35.62(12)	23.35(10)	34.76(11)	-6.90(7)	-13.71(8)	-4.43(7)
P2	28.5(5)	23.1(4)	30.5(5)	-9.1(4)	-9.3(4)	-2.3(4)
O2	64(2)	41.1(18)	60(2)	-15.4(17)	-9.6(19)	-21.1(18)
N5	44(2)	21.6(16)	40.2(19)	-5.6(14)	-23.3(17)	-7.9(15)
N6	40(2)	25.1(16)	39.6(19)	-8.8(14)	-16.3(16)	-9.3(15)
N7	44(2)	26.8(17)	43(2)	-7.1(14)	-19.0(17)	-11.1(16)

N8	67(3)	52(2)	66(3)	-2(2)	-42(3)	-25(2)
C25	42(2)	29(2)	41(2)	-13.5(17)	-11.6(19)	-12.9(18)
C26	33(2)	29.5(19)	29.9(19)	-11.7(15)	-9.4(16)	-8.2(16)
C27	34(2)	23.8(18)	27.7(18)	-9.0(14)	-8.7(16)	-7.0(16)
C28	44(3)	31(2)	42(2)	-7.8(17)	-16(2)	-15.8(19)
C29	48(3)	39(2)	52(3)	-11(2)	-18(2)	-14(2)
C30	55(3)	38(2)	48(3)	-14(2)	-19(2)	-15(2)
C31	33(2)	25.6(18)	35(2)	-11.3(15)	-8.9(17)	-6.0(16)
C32	38(3)	45(2)	43(2)	-19(2)	-10(2)	-5(2)
C33	51(3)	54(3)	43(3)	-29(2)	-4(2)	-8(2)
C34	65(4)	63(3)	42(3)	-22(2)	-13(2)	-25(3)
C35	44(3)	72(3)	50(3)	-22(3)	-22(2)	-11(3)
C36	41(3)	50(3)	46(3)	-20(2)	-13(2)	-8(2)
C37	32(2)	45(2)	35(2)	-19.4(18)	-8.7(17)	-3.8(19)
C38	35(3)	71(3)	36(2)	-18(2)	-7(2)	-18(2)
C39	39(3)	131(7)	48(3)	-45(4)	6(2)	-35(4)
C40	34(3)	139(7)	76(4)	-80(5)	-3(3)	-3(4)
C41	59(4)	83(5)	110(6)	-64(5)	-10(4)	10(4)
C42	44(3)	53(3)	77(4)	-35(3)	-7(3)	2(3)
C43	34(2)	25.2(18)	36(2)	-12.7(16)	-8.2(17)	-4.6(16)
C44	46(3)	31(2)	38(2)	-10.9(17)	-9.5(19)	-8.8(19)
C45	46(3)	34(2)	49(3)	-6.9(19)	-1(2)	-13(2)
C46	40(3)	32(2)	72(3)	-24(2)	0(2)	-13(2)
C47	40(3)	46(3)	63(3)	-31(2)	-10(2)	-11(2)

C48	44(3)	35(2)	43(2)	-15.0(18)	-11(2)	-9.8(19)
Cl1	49.7(6)	30.7(5)	38.3(5)	-12.8(4)	-6.7(5)	-8.1(4)
O3	121(5)	38(2)	136(5)	-25(3)	-82(4)	-4(3)
O4	181(8)	81(4)	76(4)	-9(3)	-72(5)	19(4)
O5	61(3)	143(5)	72(3)	-69(4)	-1(2)	-8(3)
O6	107(5)	172(7)	135(6)	-107(6)	53(4)	-94(5)
Cl2	34.6(5)	30.7(4)	37.8(5)	-13.9(4)	-8.1(4)	-10.2(4)
O7	43(2)	78(3)	96(3)	-36(3)	-19(2)	-19(2)
O8	69(3)	44.5(18)	54(2)	-28.5(16)	12.6(18)	-30.0(18)
O9	68(3)	40.4(18)	43.6(18)	-7.5(14)	-19.3(17)	-15.2(17)
O10	70(3)	28.3(15)	52(2)	-14.7(14)	-18.1(18)	-12.5(16)
O1A	53(7)	67(8)	50(7)	-10(5)	-5(5)	-27(6)
C6A	52(11)	28(10)	39(8)	-21(8)	-16(7)	-1(10)

Table S18. Bond Lengths for **9**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	P1	2.2342(10)	P2	C43	1.814(4)
Au1	N1	2.075(3)	O2	C30	1.420(7)
P1	C7	1.812(4)	N5	N6	1.374(5)
P1	C13	1.819(4)	N5	C25	1.333(6)
P1	C19	1.813(5)	N6	C27	1.343(6)
O1	C6	1.395(14)	N6	C29	1.476(6)
N1	N2	1.368(5)	N7	C27	1.337(6)
N1	C1	1.325(6)	N8	C28	1.154(7)

N2	C3	1.351(6)	C25	C26	1.383(6)
N2	C5	1.458(6)	C26	C27	1.407(6)
N3	C3	1.342(6)	C26	C28	1.418(6)
N4	C4	1.146(6)	C29	C30	1.500(7)
C1	C2	1.384(6)	C31	C32	1.400(7)
C2	C3	1.402(6)	C31	C36	1.383(7)
C2	C4	1.419(6)	C32	C33	1.378(7)
C5	C6	1.481(12)	C33	C34	1.386(8)
C5	C6A	1.551(15)	C34	C35	1.384(8)
C7	C8	1.386(6)	C35	C36	1.387(7)
C7	C12	1.394(6)	C37	C38	1.388(8)
C8	C9	1.399(7)	C37	C42	1.398(8)
C9	C10	1.380(8)	C38	C39	1.392(8)
C10	C11	1.383(8)	C39	C40	1.385(12)
C11	C12	1.389(7)	C40	C41	1.371(13)
C13	C14	1.391(6)	C41	C42	1.372(10)
C13	C18	1.378(6)	C43	C44	1.392(6)
C14	C15	1.397(7)	C43	C48	1.390(6)
C15	C16	1.382(8)	C44	C45	1.384(7)
C16	C17	1.381(8)	C45	C46	1.378(8)
C17	C18	1.392(7)	C46	C47	1.384(9)
C19	C20	1.390(7)	C47	C48	1.384(7)
C19	C24	1.386(7)	Cl1	O3	1.400(5)
C20	C21	1.387(7)	Cl1	O4	1.407(6)

C21	C22	1.388(9)	Cl1	O5	1.412(5)
C22	C23	1.361(10)	Cl1	O6	1.409(6)
C23	C24	1.382(8)	Cl2	O7	1.410(4)
Au2	P2	2.2233(10)	Cl2	O8	1.444(4)
Au2	N5	2.055(4)	Cl2	O9	1.444(4)
P2	C31	1.805(4)	Cl2	O10	1.446(3)
P2	C37	1.801(5)	O1A	C6A	1.45(2)

Table S19. Bond Angles for **9.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Au1	P1	176.01(11)	C43	P2	Au2	109.91(14)
C7	P1	Au1	113.42(14)	N6	N5	Au2	125.1(3)
C7	P1	C13	106.79(19)	C25	N5	Au2	127.6(3)
C7	P1	C19	105.5(2)	C25	N5	N6	107.0(3)
C13	P1	Au1	113.86(14)	N5	N6	C29	121.1(4)
C19	P1	Au1	111.98(14)	C27	N6	N5	110.4(3)
C19	P1	C13	104.55(19)	C27	N6	C29	128.0(4)
N2	N1	Au1	125.7(3)	N5	C25	C26	109.8(4)
C1	N1	Au1	125.7(3)	C25	C26	C27	106.3(4)
C1	N1	N2	106.8(3)	C25	C26	C28	127.0(4)
N1	N2	C5	121.7(4)	C27	C26	C28	126.6(4)
C3	N2	N1	110.4(3)	N6	C27	C26	106.4(3)
C3	N2	C5	127.6(4)	N7	C27	N6	124.0(4)
N1	C1	C2	110.5(4)	N7	C27	C26	129.4(4)

C1	C2	C3	105.8(4)	N8	C28	C26	177.1(6)
C1	C2	C4	127.6(4)	N6	C29	C30	110.6(4)
C3	C2	C4	126.5(4)	O2	C30	C29	111.9(4)
N2	C3	C2	106.5(4)	C32	C31	P2	118.4(3)
N3	C3	N2	124.5(4)	C36	C31	P2	122.7(4)
N3	C3	C2	128.9(4)	C36	C31	C32	118.9(4)
N4	C4	C2	179.7(5)	C33	C32	C31	120.5(5)
N2	C5	C6	114.7(6)	C32	C33	C34	119.6(5)
N2	C5	C6A	109.6(8)	C35	C34	C33	120.8(5)
O1	C6	C5	103.9(8)	C34	C35	C36	119.1(5)
C8	C7	P1	122.2(3)	C31	C36	C35	121.1(5)
C8	C7	C12	120.1(4)	C38	C37	P2	119.7(4)
C12	C7	P1	117.6(3)	C38	C37	C42	119.6(5)
C7	C8	C9	119.3(4)	C42	C37	P2	120.7(4)
C10	C9	C8	120.2(5)	C37	C38	C39	120.3(6)
C9	C10	C11	120.8(4)	C40	C39	C38	119.3(7)
C10	C11	C12	119.3(5)	C41	C40	C39	120.1(6)
C11	C12	C7	120.4(4)	C40	C41	C42	121.5(8)
C14	C13	P1	120.4(4)	C41	C42	C37	119.2(7)
C18	C13	P1	119.8(3)	C44	C43	P2	123.8(3)
C18	C13	C14	119.8(4)	C48	C43	P2	116.4(3)
C13	C14	C15	119.9(5)	C48	C43	C44	119.8(4)
C16	C15	C14	120.0(5)	C45	C44	C43	119.5(5)
C17	C16	C15	119.8(5)	C46	C45	C44	120.4(5)

C16	C17	C18	120.4(5)	C45	C46	C47	120.5(5)
C13	C18	C17	120.1(4)	C48	C47	C46	119.5(5)
C20	C19	P1	121.4(3)	C47	C48	C43	120.3(5)
C24	C19	P1	118.5(4)	O3	Cl1	O4	107.1(4)
C24	C19	C20	120.0(5)	O3	Cl1	O5	112.4(5)
C21	C20	C19	119.8(5)	O3	Cl1	O6	107.3(4)
C20	C21	C22	119.3(6)	O4	Cl1	O5	111.0(4)
C23	C22	C21	120.8(5)	O4	Cl1	O6	113.4(6)
C22	C23	C24	120.5(5)	O6	Cl1	O5	105.6(4)
C23	C24	C19	119.6(6)	O7	Cl2	O8	110.2(3)
N5	Au2	P2	176.98(11)	O7	Cl2	O9	110.1(3)
C31	P2	Au2	113.15(14)	O7	Cl2	O10	110.4(3)
C31	P2	C43	107.9(2)	O8	Cl2	O9	108.1(2)
C37	P2	Au2	113.82(16)	O8	Cl2	O10	109.4(2)
C37	P2	C31	106.7(2)	O9	Cl2	O10	108.5(2)
C37	P2	C43	104.8(2)	O1A	C6A	C5	108.4(12)

Table S20. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **9**

Atom	x	y	z	U(eq)
H1	9730	1953	4401	105
H3A	12912	-794	5426	60
H3B	13668	-945	6089	60
H1A	13628	2568	4748	41

H5AA	12594	224	3828	50
H5AB	12081	1441	3287	50
H5BC	12374	138	4052	50
H5BD	12333	1232	3237	50
H6A	10698	642	3974	59
H6B	11025	350	4992	59
H8	9913	5679	693	47
H9	8370	5583	301	55
H10	7190	4783	1460	55
H11	7554	4015	3011	52
H12	9103	4083	3404	44
H14	10462	7137	1286	54
H15	11452	7995	-59	64
H16	13059	7032	-761	57
H17	13736	5229	-69	51
H18	12759	4370	1276	42
H20	8710	6692	2476	48
H21	8016	7966	3193	62
H22	9019	7903	4248	71
H23	10667	6591	4600	76
H24	11375	5321	3890	60
H2	4803	5061	1747	81
H7A	4964	4444	3905	44
H7B	5923	4258	4385	44

H25	5690	7831	3122	42
H29A	2941	6768	2939	55
H29B	3599	5545	3192	55
H30A	3208	6227	1653	54
H30B	3786	7086	1400	54
H32	4025	9272	-328	51
H33	3830	9116	-1686	58
H34	2091	9796	-2187	63
H35	551	10679	-1362	64
H36	757	10853	-12	54
H38	1099	9338	2449	56
H39	-668	10014	3183	81
H40	-1555	11817	2707	93
H41	-680	12920	1544	101
H42	1076	12274	823	71
H44	3177	11767	-766	47
H45	3976	13046	-1110	55
H46	4468	13279	81	56
H47	4226	12198	1628	55
H48	3515	10859	1971	48
H1AA	9914	1002	5312	86
H6AA	10627	2077	4053	46
H6AB	10480	1198	3790	46

Table S21. Atomic Occupancy for **9**.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
O1	0.661(14)	H1	0.661(14)	H5AA	0.661(14)
H5AB	0.661(14)	H5BC	0.339(14)	H5BD	0.339(14)
C6	0.661(14)	H6A	0.661(14)	H6B	0.661(14)
O1A	0.339(14)	H1AA	0.339(14)	C6A	0.339(14)
H6AA	0.339(14)	H6AB	0.339(14)		

Figure S4. ORTEP plot for Triphenylphosphine(4-Bromo-1-methyl-1H-pyrazol-5-amine) gold(I) perchlorate **10**

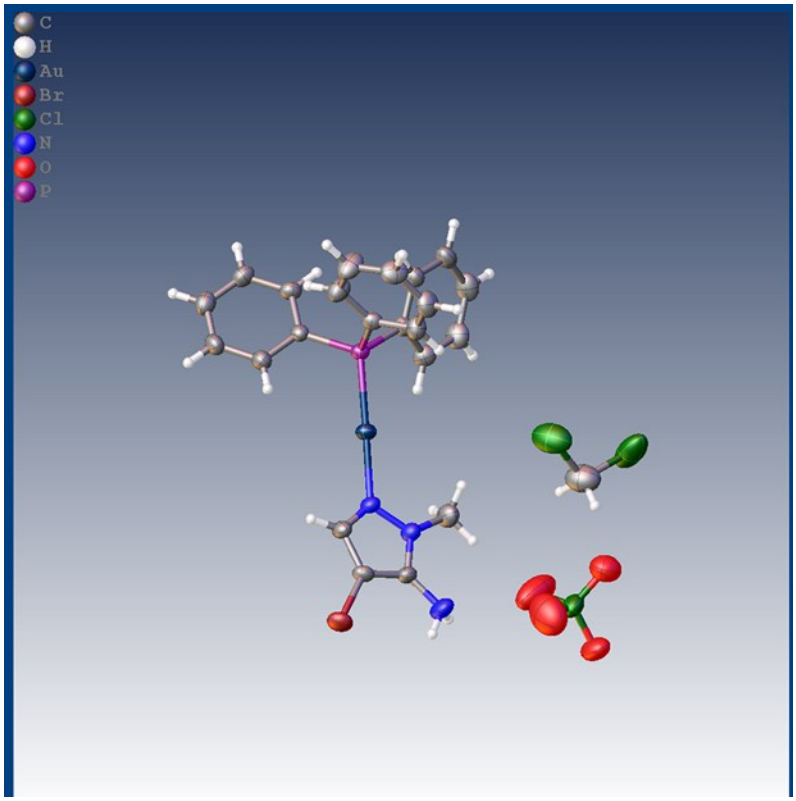


Table S22, Crystal data and structure refinement for **10.**

Identification code	V04AF77D
Empirical formula	$C_{23}H_{23}AuBrCl_3N_3O_4P$
Formula weight	819.64
Temperature/K	173
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.8129(4)
b/Å	6.9184(2)
c/Å	29.6985(9)

α/°	90
β/°	103.268(3)
γ/°	90
Volume/Å^3	2762.33(14)
Z	4
ρ_{calc}g/cm^3	1.971
μ/mm^{-1}	15.222
F(000)	1576.0
Crystal size/mm^3	0.36 × 0.08 × 0.06
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.886 to 136.47
Index ranges	-16 ≤ h ≤ 16, -8 ≤ k ≤ 6, -35 ≤ l ≤ 35
Reflections collected	16828
Independent reflections	5048 [R_{int} = 0.0394, R_{sigma} = 0.0366]
Data/restraints/parameters	5048/39/327
Goodness-of-fit on F^2	1.151
Final R indexes [I>=2σ (I)]	R_1 = 0.0497, wR_2 = 0.1424
Final R indexes [all data]	R_1 = 0.0554, wR_2 = 0.1452
Largest diff. peak/hole / e Å^{-3}	3.26/-1.29

Table S23. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **10**.U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)

Au1	2214.9(3)	3461.4(6)	6020.7(2)	32.31(14)
Br1	1071.9(9)	-3626.1(16)	4915.5(4)	47.2(3)
P1	2098.7(16)	5726(3)	6541.8(7)	27.9(4)
N1	2248(6)	1235(11)	5566(3)	34.8(17)
N2	3092(6)	289(12)	5525(3)	36.1(17)
N3	3514(7)	-2730(16)	5225(4)	58(3)
C1	1485(7)	140(15)	5373(3)	37(2)
C2	1821(7)	-1553(13)	5204(3)	33.5(19)
C3	2857(7)	-1409(14)	5298(3)	36(2)
C4	4059(8)	1195(17)	5679(4)	51(3)
C5	3245(7)	7050(14)	6752(3)	33.4(19)
C6	3399(7)	8086(14)	7171(3)	38(2)
C7	4271(8)	9126(15)	7324(4)	45(2)
C8	4984(8)	9123(16)	7064(4)	47(3)
C9	4855(8)	8091(17)	6660(4)	47(3)
C10	3970(7)	7029(14)	6499(4)	38(2)
C11	1098(6)	7418(14)	6325(3)	31.0(18)
C12	256(7)	6692(15)	6026(3)	39(2)
C13	-566(7)	7906(17)	5882(4)	44(2)
C14	-545(8)	9786(16)	6030(4)	44(2)
C15	289(7)	10483(15)	6331(4)	41(2)
C16	1123(7)	9329(14)	6478(3)	36(2)
C17	1813(7)	4700(13)	7059(3)	30.7(18)
C18	981(8)	5266(16)	7212(4)	45(2)

C19	802(9)	4499(19)	7617(4)	55(3)
C20	1445(9)	3178(16)	7869(4)	48(3)
C21	2271(8)	2577(17)	7706(4)	47(2)
C22	2447(7)	3334(15)	7305(4)	41(2)
Cl1	6459(2)	-2610(5)	5619.3(10)	58.5(7)
O1	6010(14)	-980(20)	5421(6)	142(5)
O2	6959(9)	-2357(19)	6081(4)	90(3)
O3	7032(8)	-3584(17)	5359(4)	89(3)
O4	5624(11)	-3810(30)	5626(6)	138(5)
Cl2	8322(3)	3502(6)	6582(2)	110.2(18)
Cl3	6250(3)	2857(7)	6578.3(16)	94.5(14)
C23	7185(12)	2560(30)	6280(6)	80(4)

Table S24. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **10**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au1	37.0(2)	29.6(2)	30.9(2)	-6.95(15)	8.80(15)	-0.98(15)
Br1	52.6(6)	38.6(6)	48.5(6)	-15.8(5)	7.7(5)	-8.4(5)
P1	30.4(10)	26.3(11)	26.9(10)	-4.1(8)	6.2(8)	-0.5(9)
N1	34(4)	36(4)	35(4)	-9(3)	10(3)	5(3)
N2	31(4)	39(4)	40(4)	-9(4)	10(3)	1(3)
N3	43(5)	63(6)	69(6)	-27(5)	14(5)	13(5)
C1	30(5)	45(6)	37(5)	-13(4)	9(4)	2(4)
C2	39(5)	30(5)	32(4)	-9(4)	8(4)	-5(4)

C3	38(5)	36(5)	33(5)	-9(4)	5(4)	9(4)
C4	33(5)	55(7)	63(7)	-15(6)	8(5)	-5(5)
C5	30(4)	37(5)	33(4)	0(4)	6(4)	-1(4)
C6	36(5)	38(5)	37(5)	-4(4)	5(4)	-3(4)
C7	46(6)	38(5)	43(5)	-6(4)	-5(4)	-2(4)
C8	42(5)	37(5)	61(7)	10(5)	5(5)	-12(4)
C9	38(5)	53(7)	54(6)	9(5)	16(5)	-7(5)
C10	42(5)	31(5)	43(5)	0(4)	14(4)	-5(4)
C11	30(4)	35(5)	27(4)	-5(4)	6(3)	2(4)
C12	35(5)	43(6)	37(5)	-7(4)	4(4)	2(4)
C13	32(5)	57(7)	40(5)	-12(5)	0(4)	-1(5)
C14	41(5)	48(6)	42(5)	7(5)	11(4)	9(5)
C15	44(5)	32(5)	48(5)	0(4)	14(4)	6(4)
C16	42(5)	30(5)	35(5)	-6(4)	9(4)	-2(4)
C17	35(4)	26(4)	31(4)	-3(4)	8(4)	-6(4)
C18	46(6)	42(6)	49(6)	9(5)	18(5)	9(5)
C19	59(7)	63(8)	54(7)	17(6)	34(6)	14(6)
C20	66(7)	45(6)	38(5)	10(5)	22(5)	-3(5)
C21	49(6)	45(6)	46(6)	14(5)	6(5)	3(5)
C22	34(5)	42(6)	45(5)	6(5)	7(4)	1(4)
Cl1	49.4(14)	72.7(19)	53.4(15)	-8.9(14)	11.8(12)	21.2(14)
O1	189(12)	138(8)	109(9)	18(7)	55(8)	92(8)
O2	98(7)	98(8)	69(5)	-19(5)	8(4)	14(6)
O3	63(5)	106(8)	96(7)	-50(6)	17(5)	16(5)

O4	94(7)	188(11)	130(11)	-12(8)	21(7)	-24(7)
Cl2	73(2)	68(2)	188(5)	-45(3)	25(3)	6.6(19)
Cl3	99(3)	110(3)	87(3)	-22(2)	46(2)	-42(3)
C23	88(7)	85(10)	76(8)	-12(8)	36(6)	-19(7)

Table S25. Bond Lengths for **10**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	P1	2.234(2)	C11	C12	1.386(13)
Au1	N1	2.056(7)	C11	C16	1.396(13)
Br1	C2	1.859(9)	C12	C13	1.398(14)
P1	C5	1.812(9)	C13	C14	1.371(16)
P1	C11	1.813(9)	C14	C15	1.373(15)
P1	C17	1.816(9)	C15	C16	1.387(14)
N1	N2	1.367(11)	C17	C18	1.386(13)
N1	C1	1.317(12)	C17	C22	1.379(14)
N2	C3	1.357(12)	C18	C19	1.386(15)
N2	C4	1.451(13)	C19	C20	1.372(16)
N3	C3	1.340(13)	C20	C21	1.401(16)
C1	C2	1.395(13)	C21	C22	1.371(15)
C2	C3	1.398(13)	Cl1	O1	1.358(15)
C5	C6	1.409(13)	Cl1	O2	1.398(11)
C5	C10	1.382(13)	Cl1	O3	1.398(10)
C6	C7	1.387(14)	Cl1	O4	1.425(16)
C7	C8	1.383(16)	Cl2	C23	1.746(17)

C8	C9	1.372(17)	Cl3	C23	1.738(15)
C9	C10	1.412(14)			

Table S26. Bond Angles for **10.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Au1	P1	175.3(2)	C8	C9	C10	119.7(10)
C5	P1	Au1	113.4(3)	C5	C10	C9	119.3(10)
C5	P1	C11	109.3(4)	C12	C11	P1	116.9(7)
C5	P1	C17	104.4(4)	C12	C11	C16	120.4(9)
C11	P1	Au1	112.2(3)	C16	C11	P1	122.4(7)
C11	P1	C17	104.9(4)	C11	C12	C13	118.8(10)
C17	P1	Au1	112.1(3)	C14	C13	C12	121.0(9)
N2	N1	Au1	124.4(6)	C13	C14	C15	119.7(10)
C1	N1	Au1	125.5(6)	C14	C15	C16	121.0(10)
C1	N1	N2	107.4(8)	C15	C16	C11	119.1(9)
N1	N2	C4	120.5(8)	C18	C17	P1	121.7(7)
C3	N2	N1	110.3(8)	C22	C17	P1	118.8(7)
C3	N2	C4	128.9(8)	C22	C17	C18	119.5(9)
N1	C1	C2	109.9(8)	C19	C18	C17	120.2(10)
C1	C2	Br1	128.2(7)	C20	C19	C18	120.4(10)
C1	C2	C3	106.2(8)	C19	C20	C21	119.1(10)
C3	C2	Br1	125.6(7)	C22	C21	C20	120.4(10)
N2	C3	C2	106.1(8)	C21	C22	C17	120.3(10)
N3	C3	N2	125.3(9)	O1	Cl1	O2	113.3(10)

N3	C3	C2	128.3(9)	O1	Cl1	O3	114.9(9)
C6	C5	P1	120.2(7)	O1	Cl1	O4	101.6(11)
C10	C5	P1	119.6(7)	O2	Cl1	O3	112.7(7)
C10	C5	C6	120.2(9)	O2	Cl1	O4	106.2(9)
C7	C6	C5	119.8(10)	O3	Cl1	O4	106.8(9)
C8	C7	C6	119.5(10)	Cl3	C23	Cl2	112.3(9)
C9	C8	C7	121.5(10)				

Table S27. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **10**

Atom	x	y	z	U(eq)
H3A	3206	-3744	5072	70
H3B	3900	-2204	5057	70
H1	807	455	5353	45
H4A	4065	2433	5520	76
H4B	4573	346	5609	76
H4C	4193	1418	6014	76
H6	2907	8072	7348	45
H7	4378	9836	7605	53
H8	5577	9851	7168	57
H9	5359	8091	6490	57
H10	3874	6308	6220	45
H12	238	5393	5920	47
H13	-1149	7420	5679	53

H14	-1104	10602	5925	52
H15	296	11776	6439	49
H16	1702	9832	6681	43
H18	533	6183	7040	54
H19	230	4891	7720	66
H20	1333	2678	8150	58
H21	2713	1638	7874	57
H22	3008	2917	7197	49
H23A	6986	3219	5976	96
H23B	7265	1170	6222	96