Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis and catalytic activity of heterobimetallic Au/M (M = Rh^{III}, Ir^{III}) complexes with ditopic mono- and triphosphane ligands

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Electronic Supplementary Information

Table of Contents

Characterisation of complexes

Spectra of ligand **L1**H

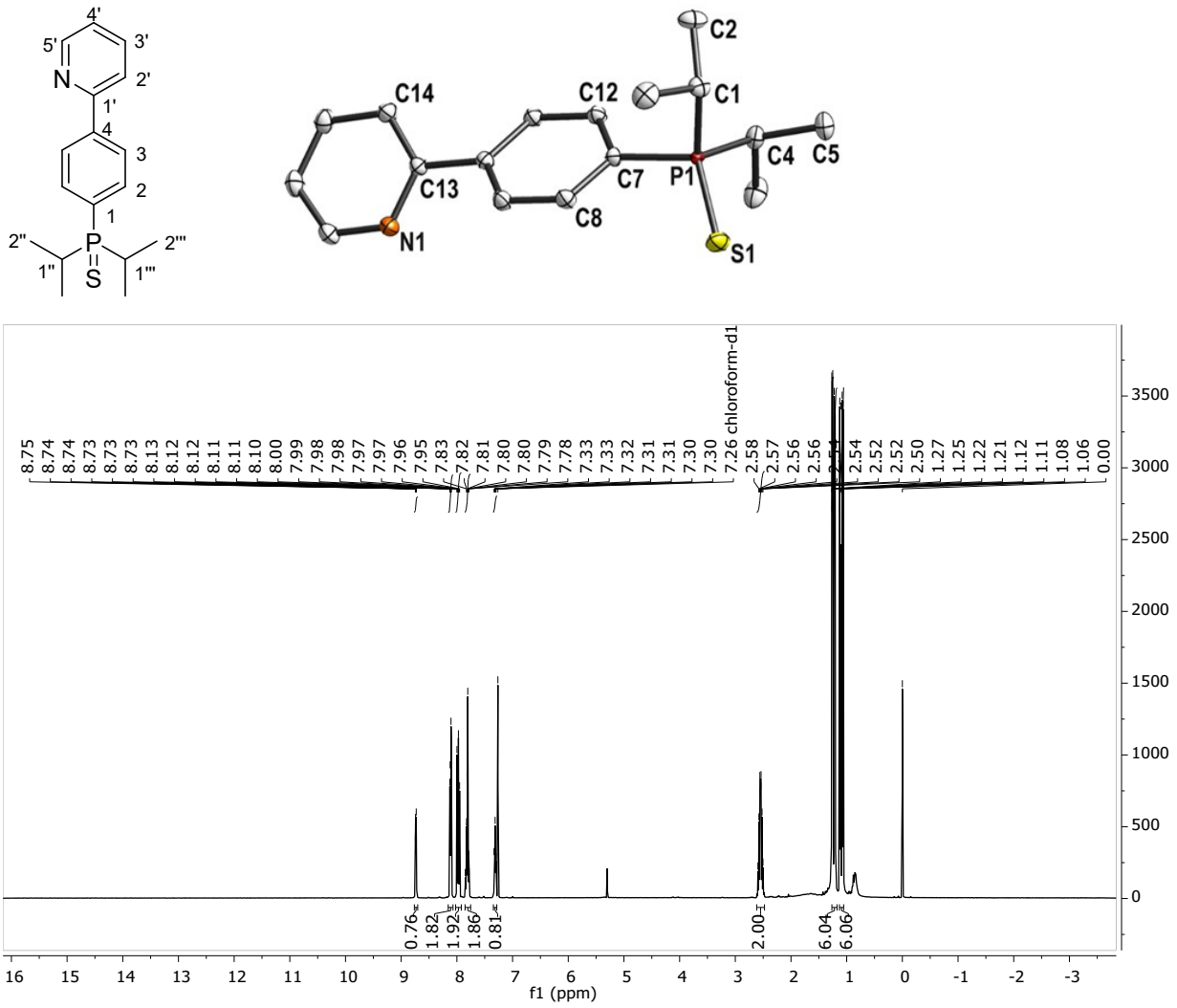


Figure S1. ^{1}H NMR spectrum of **L1**H in $CDCl_3$.

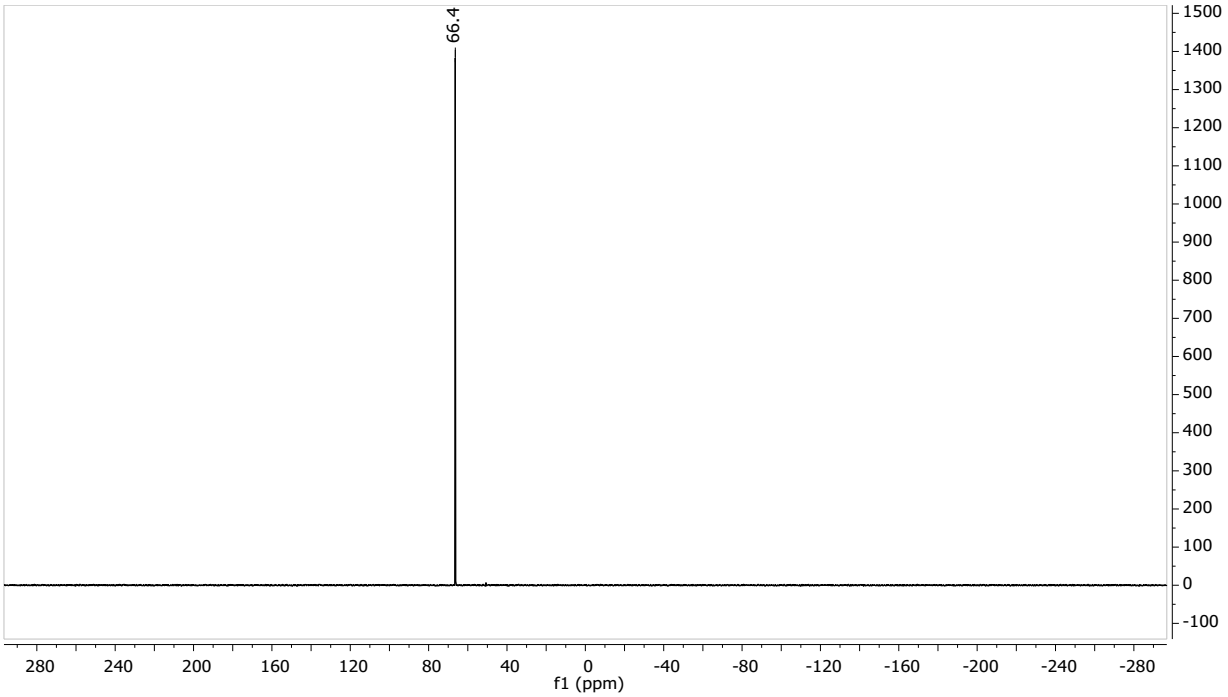


Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum of **L1**H in $CDCl_3$.

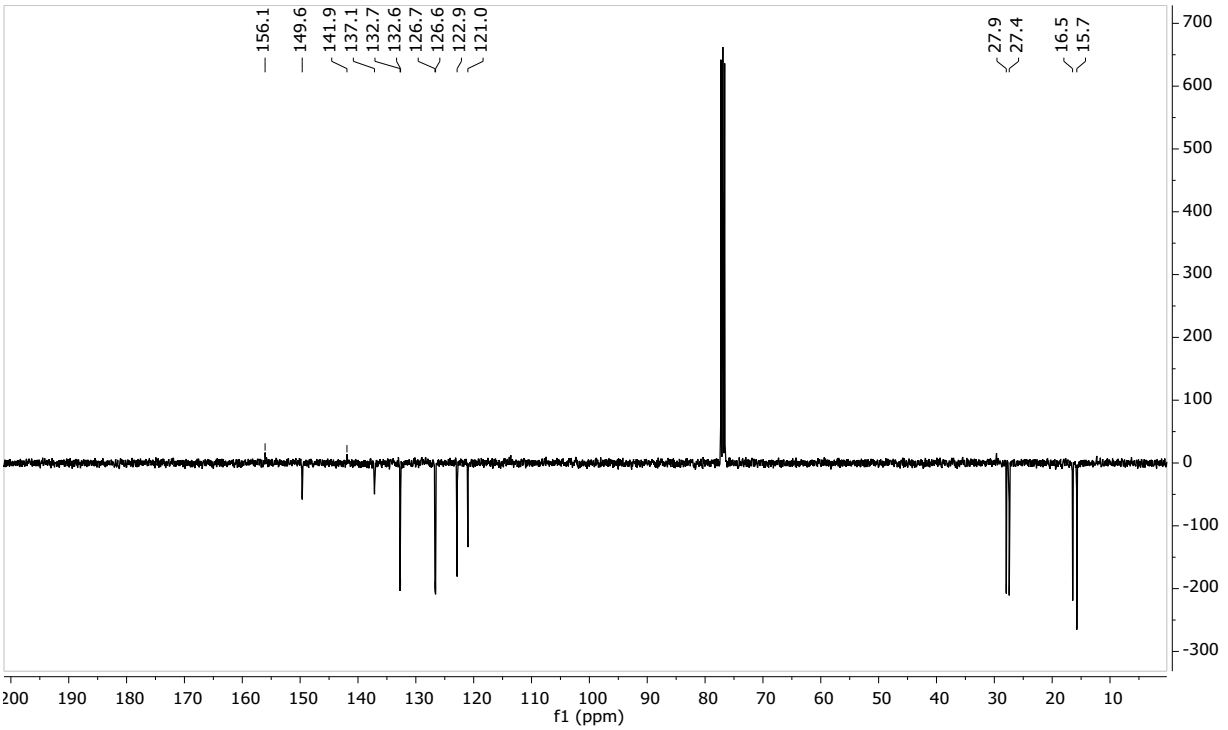


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **L1**H in $CDCl_3$.

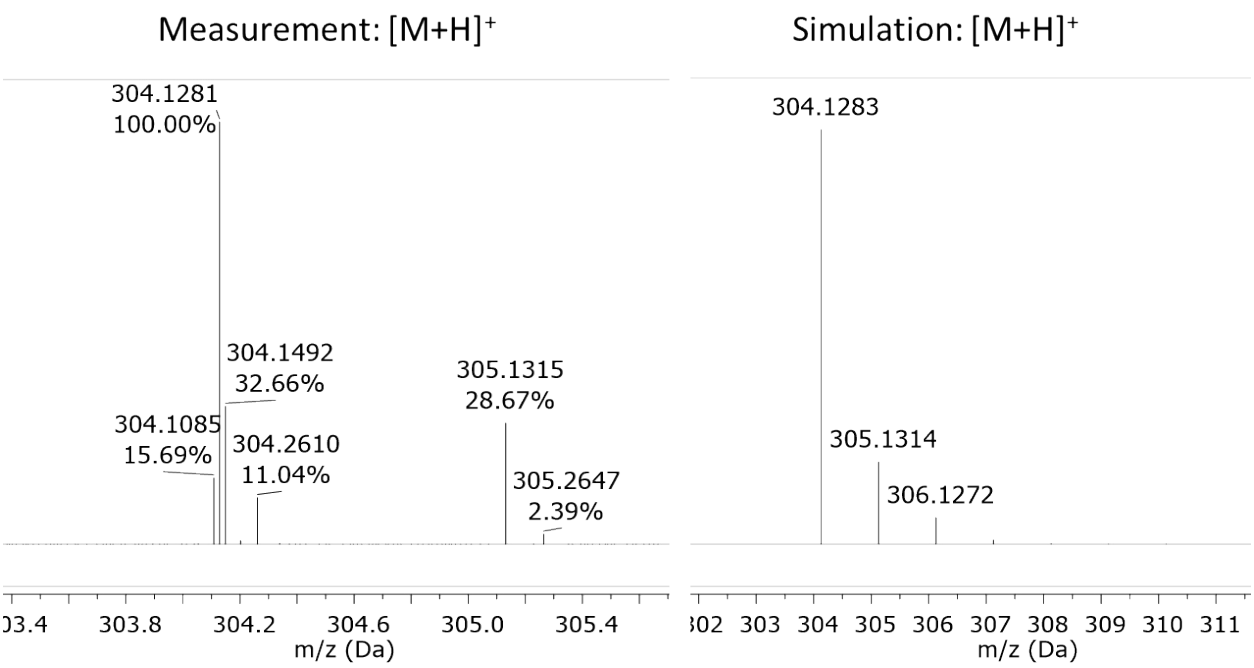
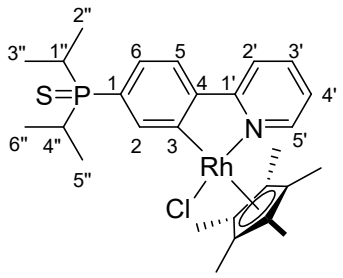


Figure S4. HR-ESI-MS (positive mode, CH_3OH) of **L1**, *m/z* $[M+H]^+$.

Spectra of complex **1**



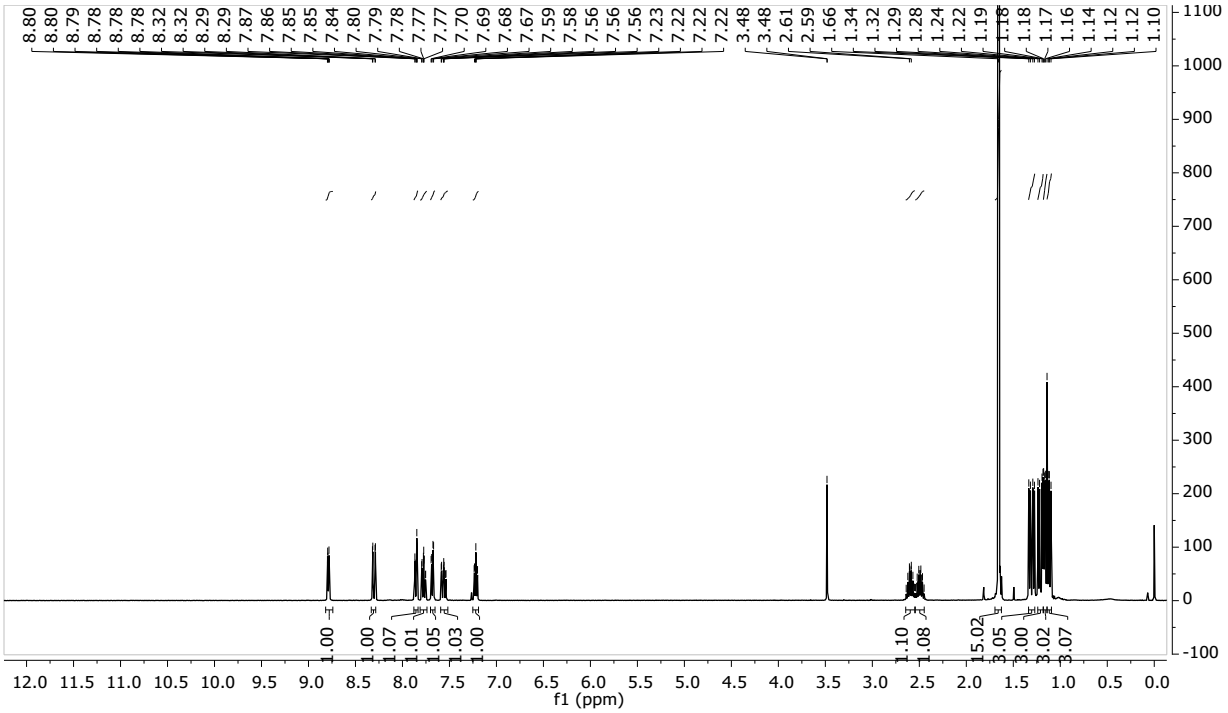


Figure S5. ^{1}H NMR spectrum of **1** in $CDCl_3$.

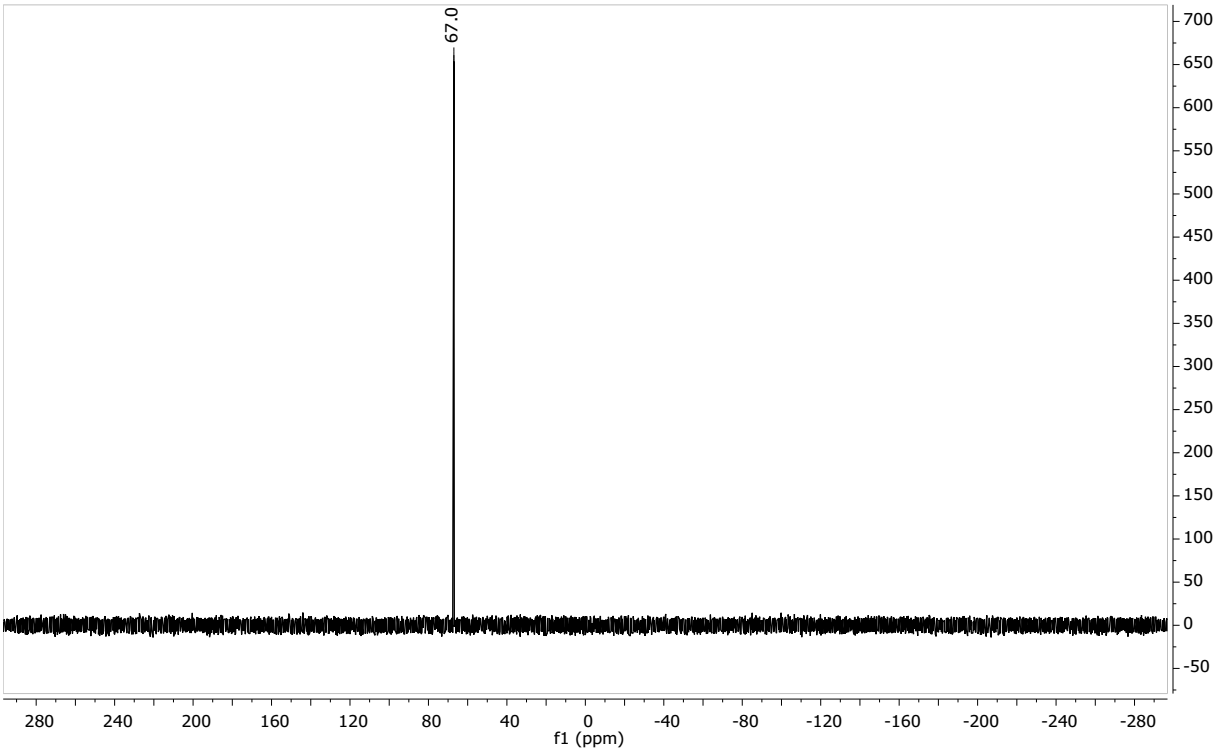


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$.

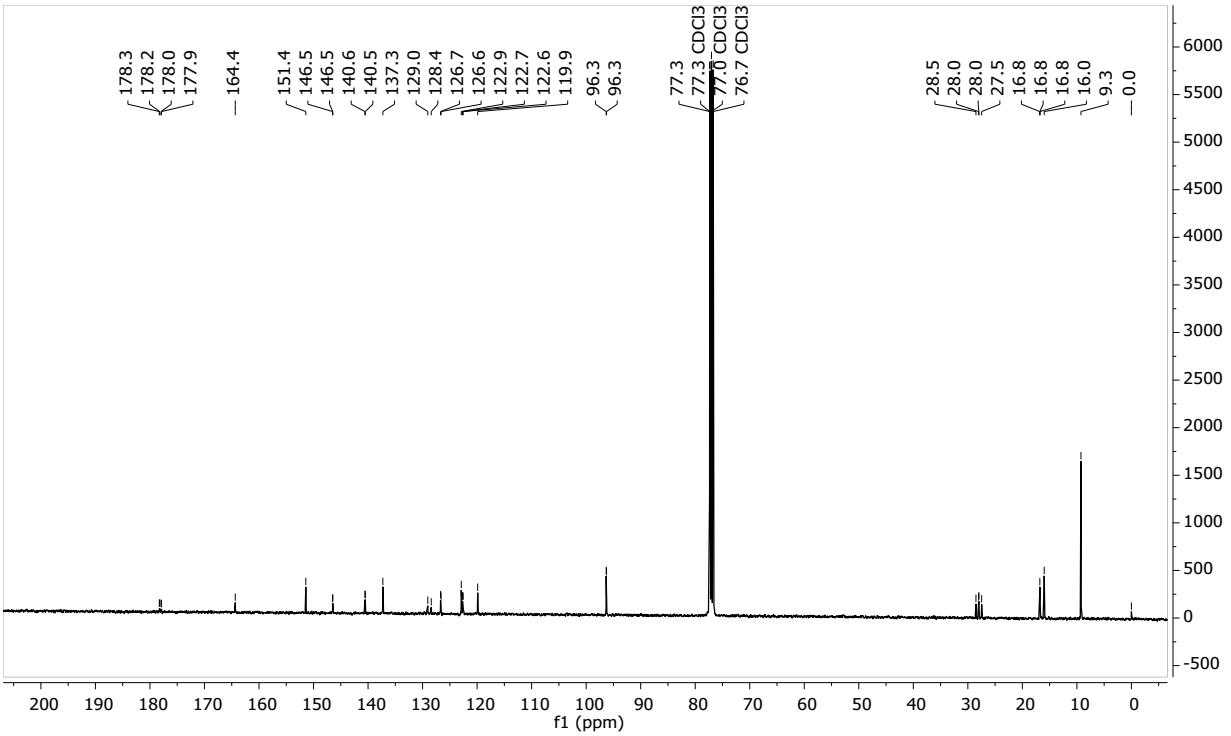
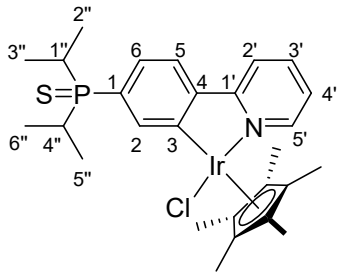


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$.

Spectra of complex **2**



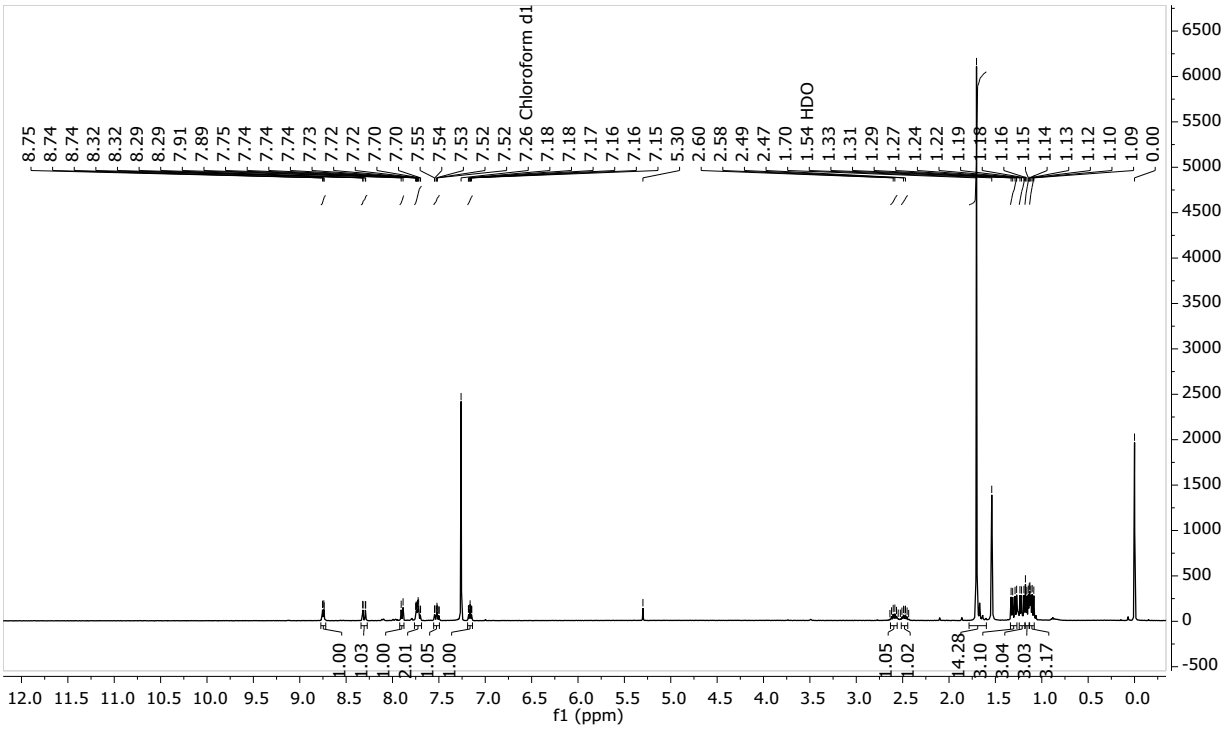


Figure S8. ^{1}H NMR spectrum of **2** in $CDCl_3$.

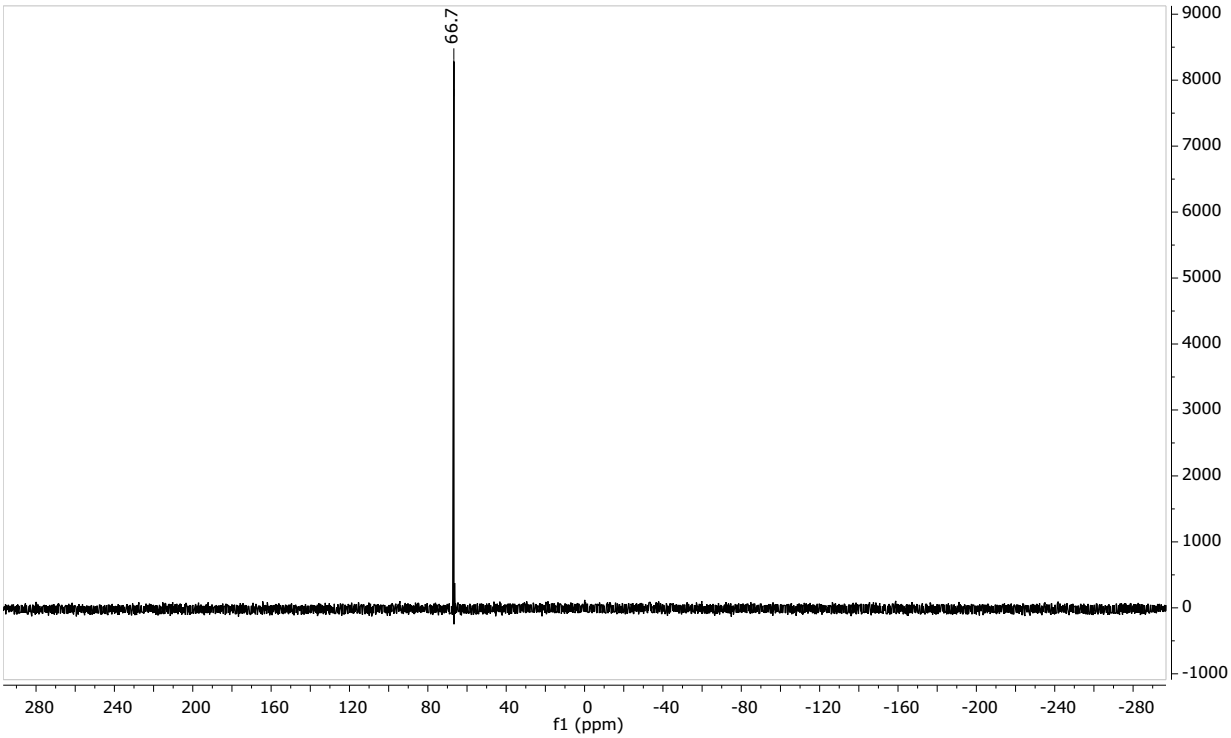


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$.

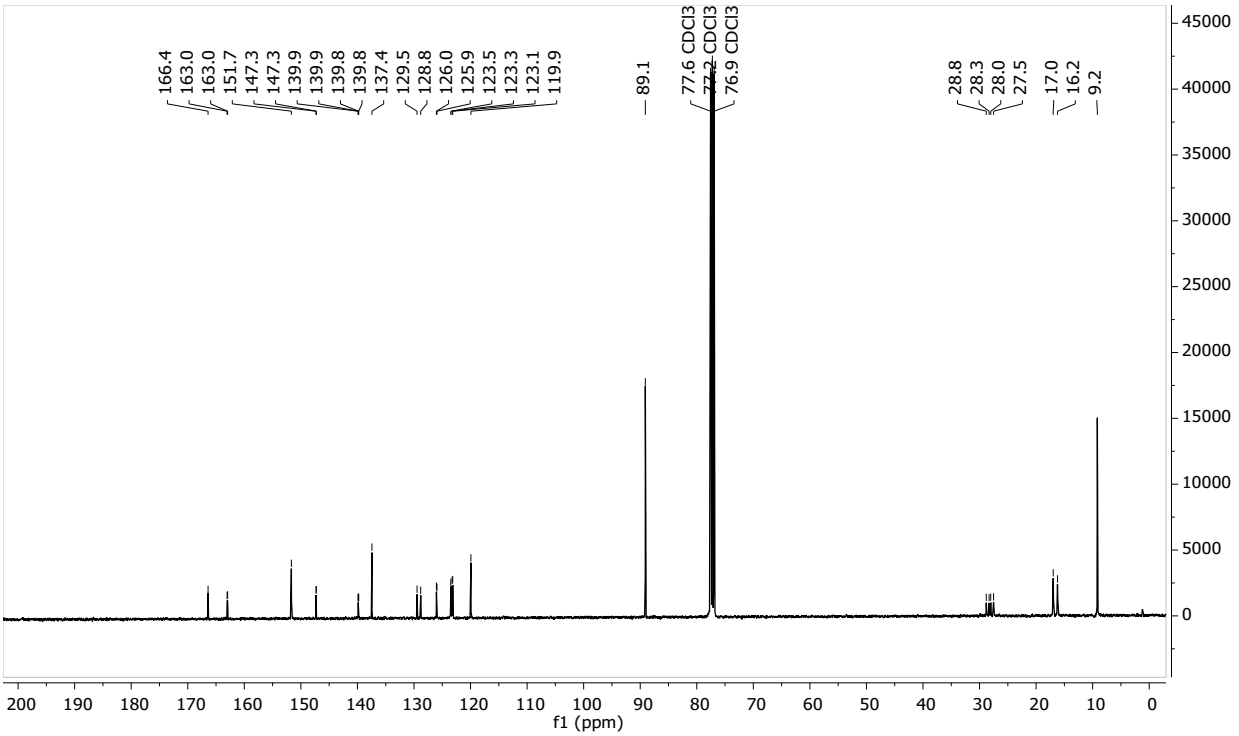


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$.

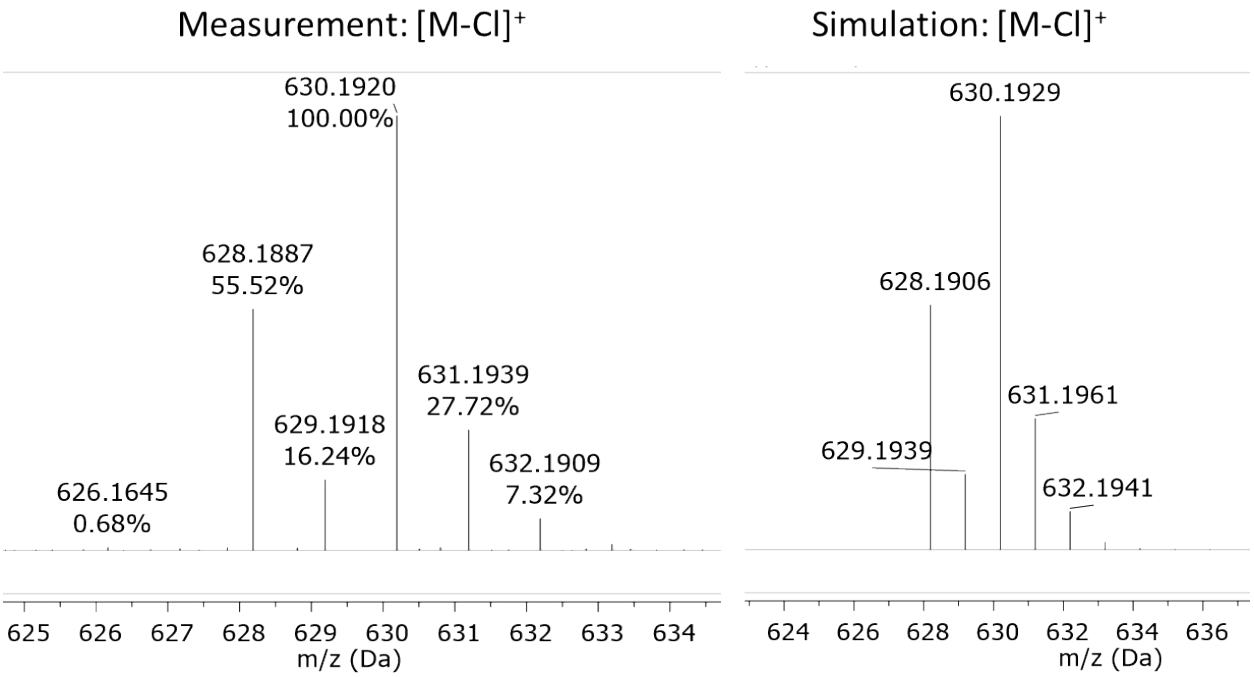
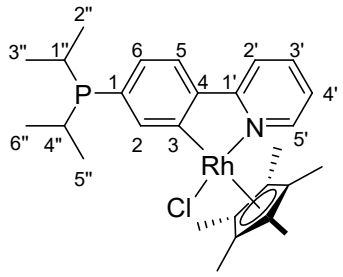


Figure S11. HR-ESI-MS (positive mode, CH_3OH) of **2**, *m/z* $[M\text{-}Cl]^+$.

Spectra of complex **3**



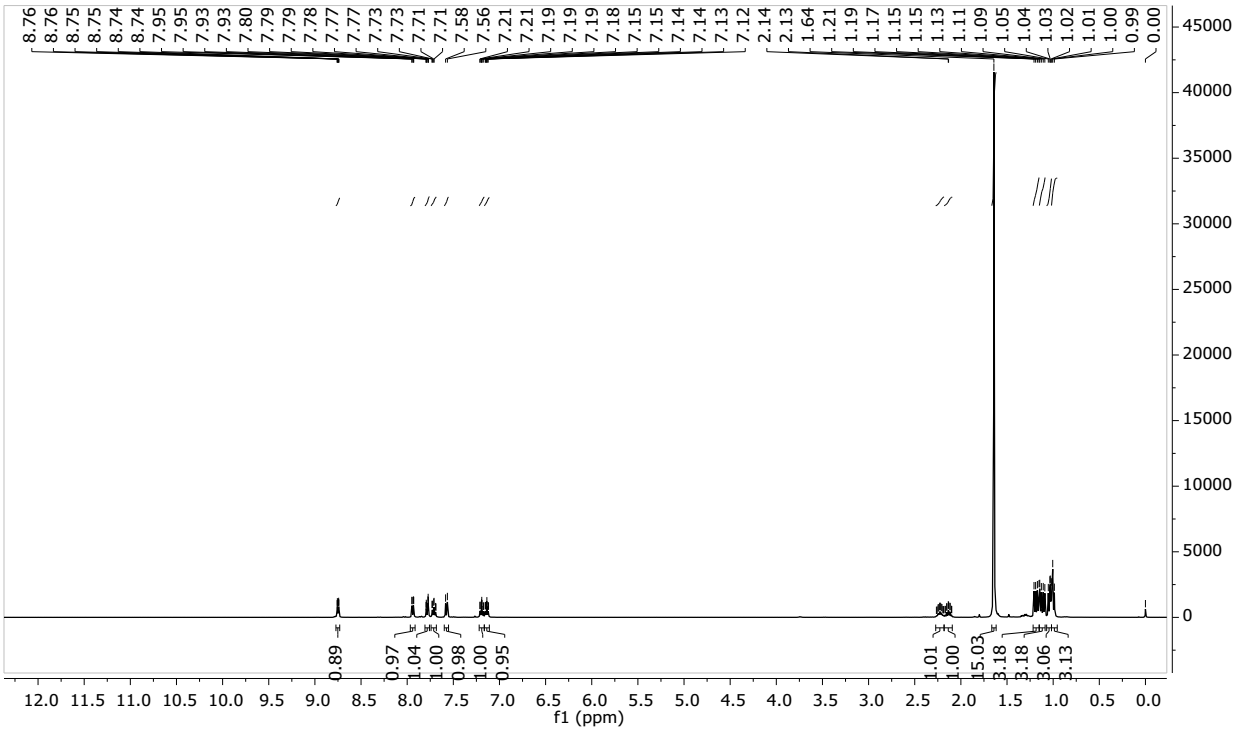


Figure S12. ^{1}H NMR spectrum of **3** in $CDCl_3$.

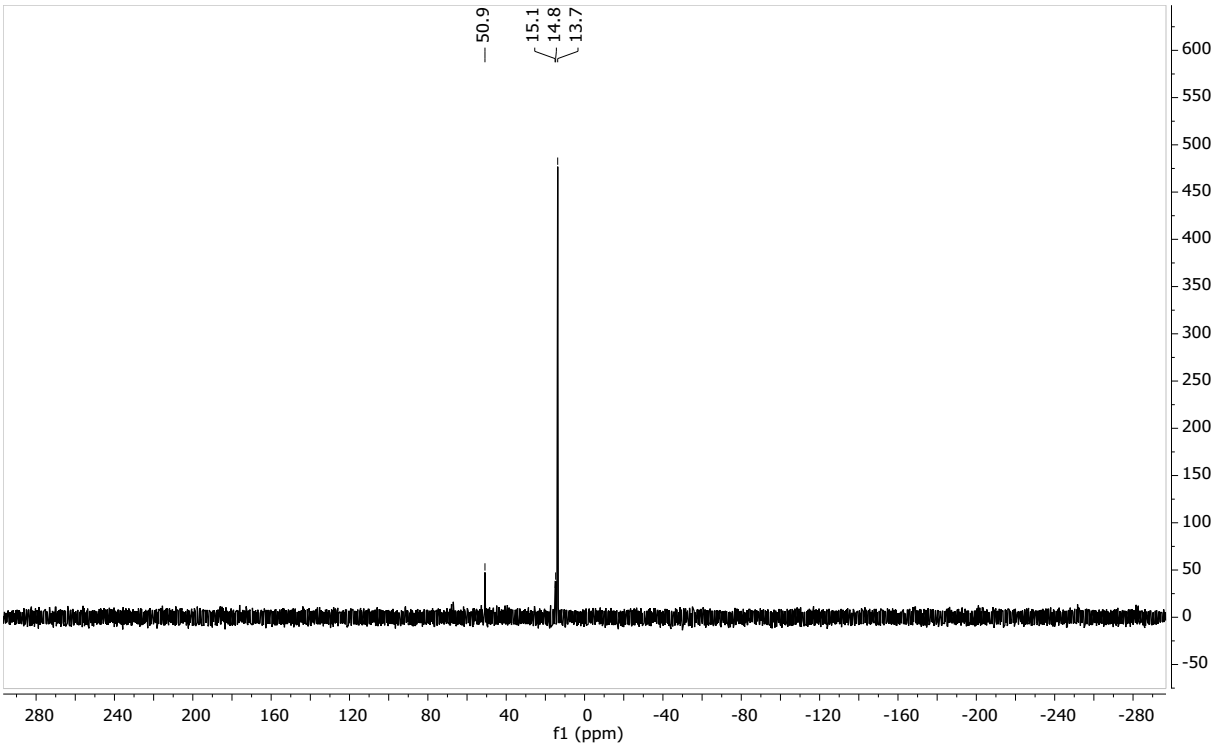


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

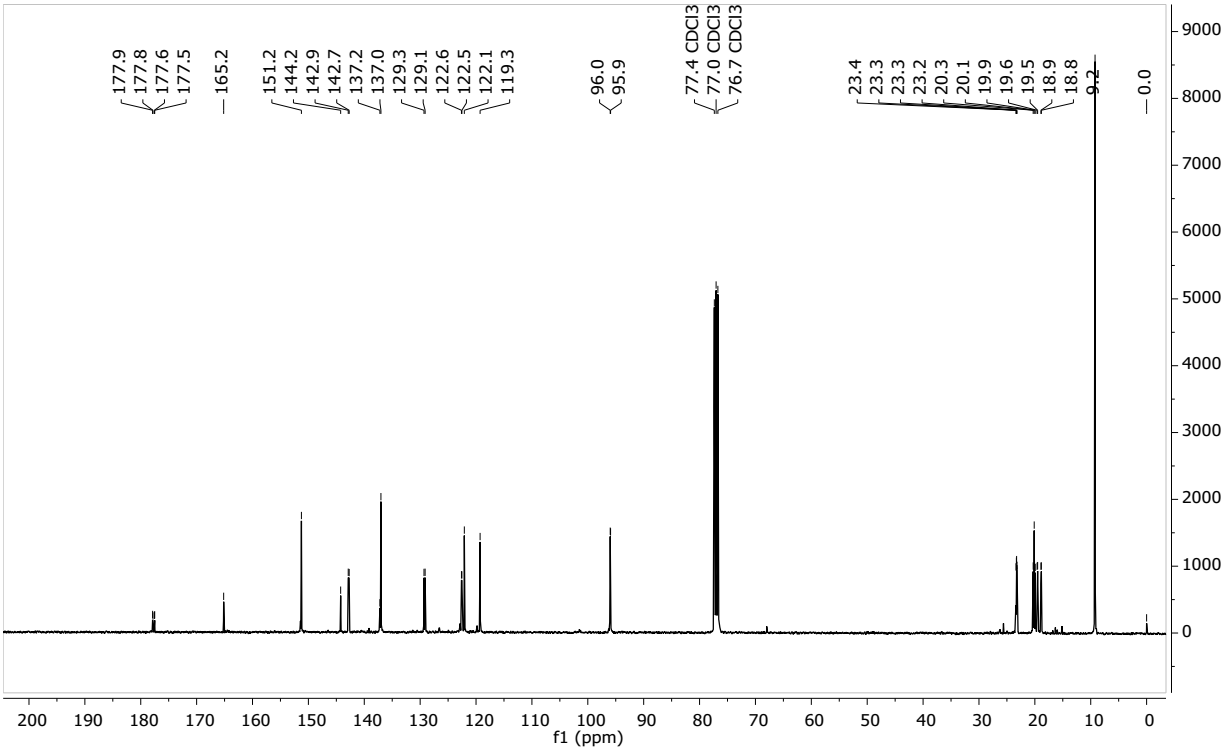


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

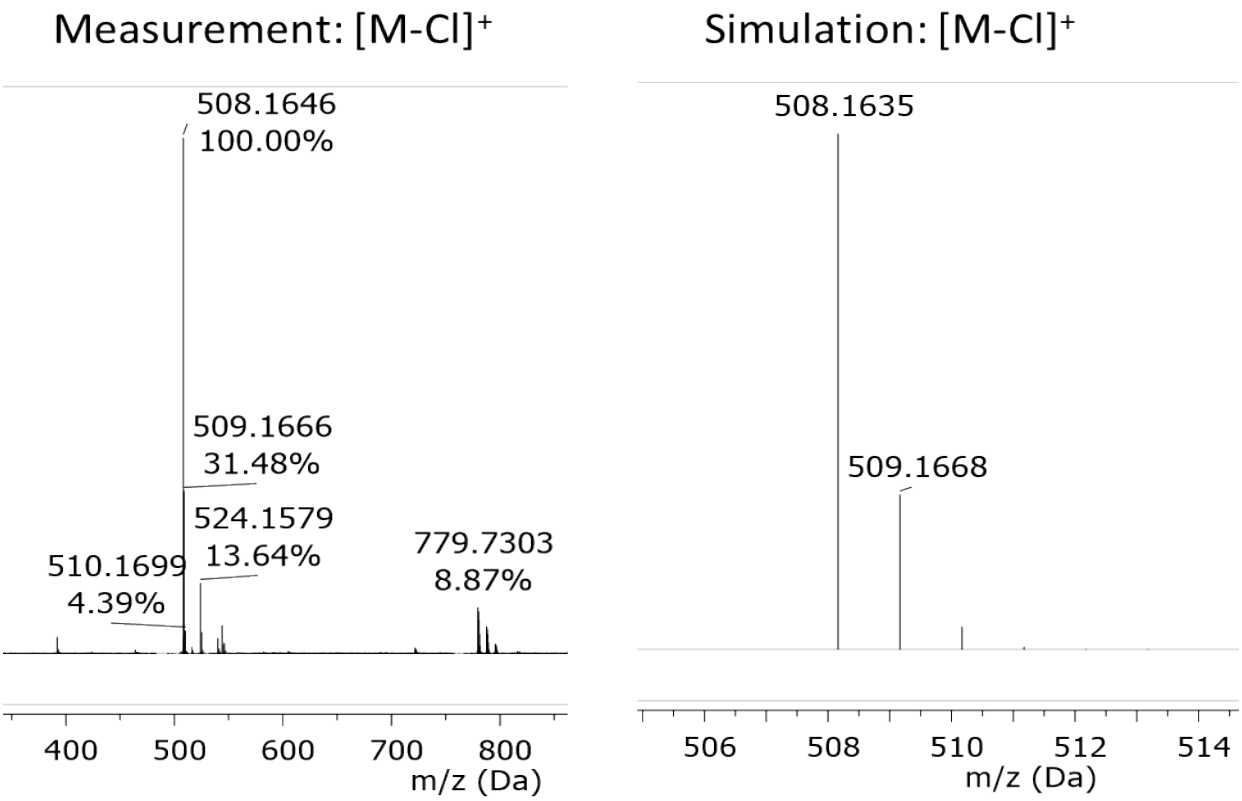


Figure S15. HR-ESI-MS (positive mode, CH_3OH) of **3**, *m/z* $[M\text{-}Cl]^+$.

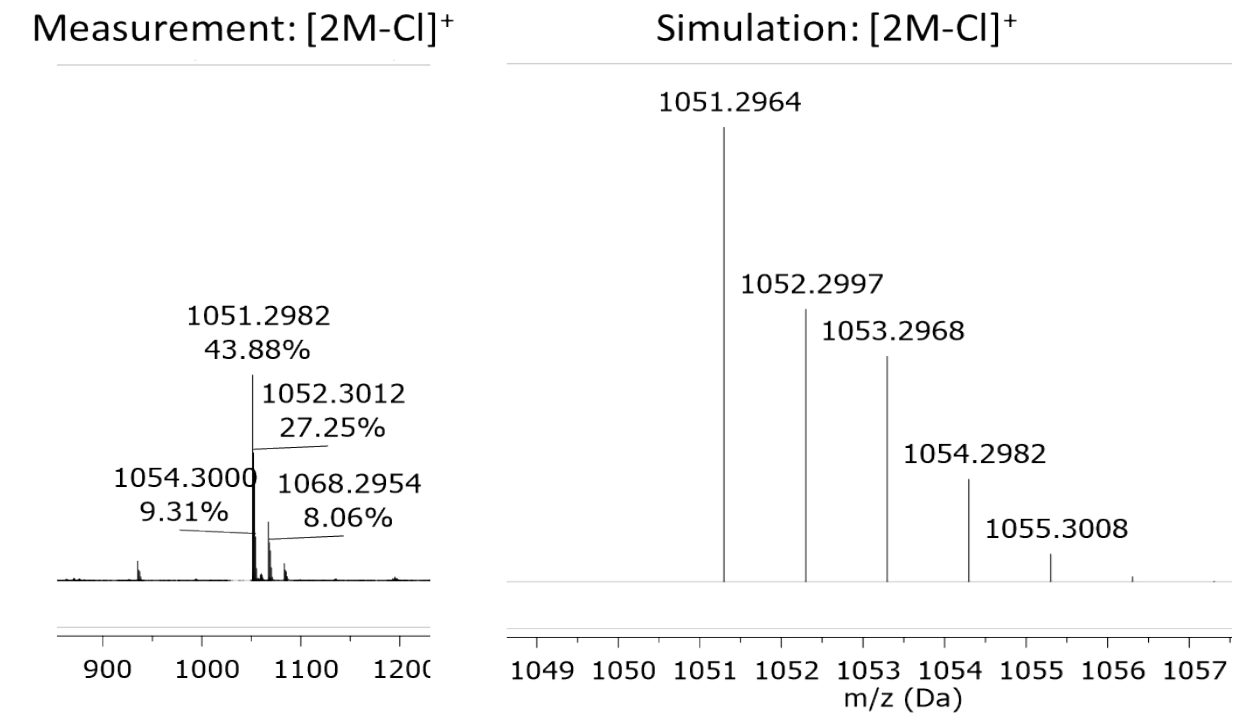
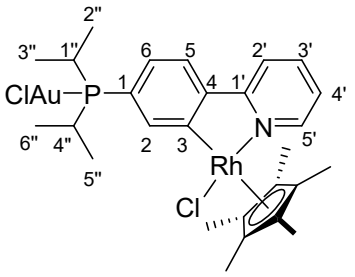


Figure S16. HR-ESI-MS (positive mode, CH_3OH) of **3**, *m/z* $[2M\text{-}Cl]^+$.

Spectra of complex **5**



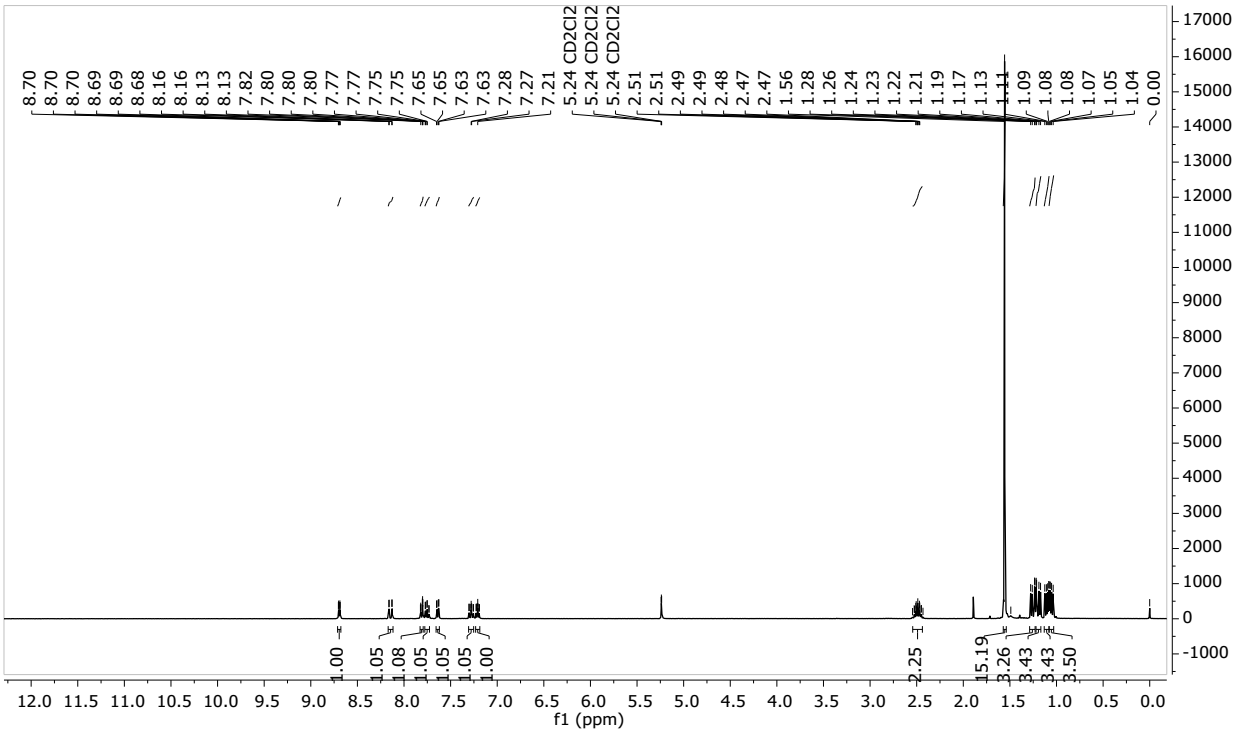


Figure S17. ^{1}H NMR spectrum of **5** in CD_2Cl_2.

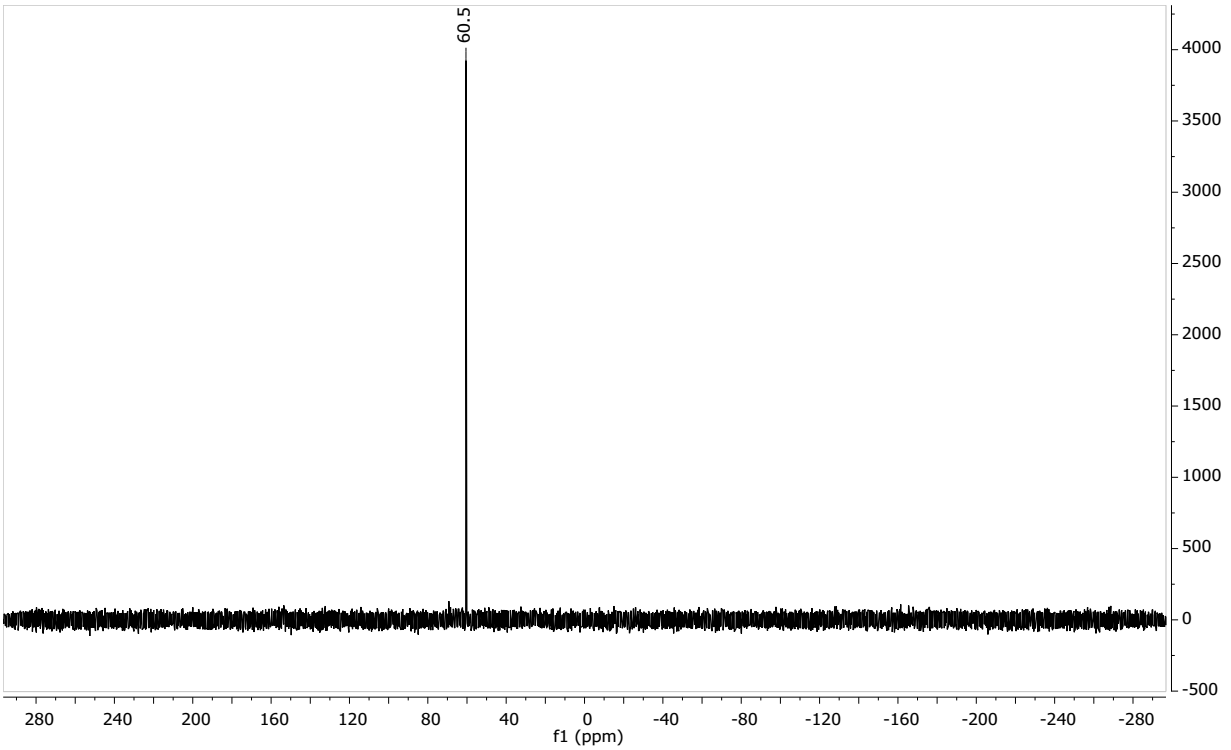


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of **5** in CD_2Cl_2.

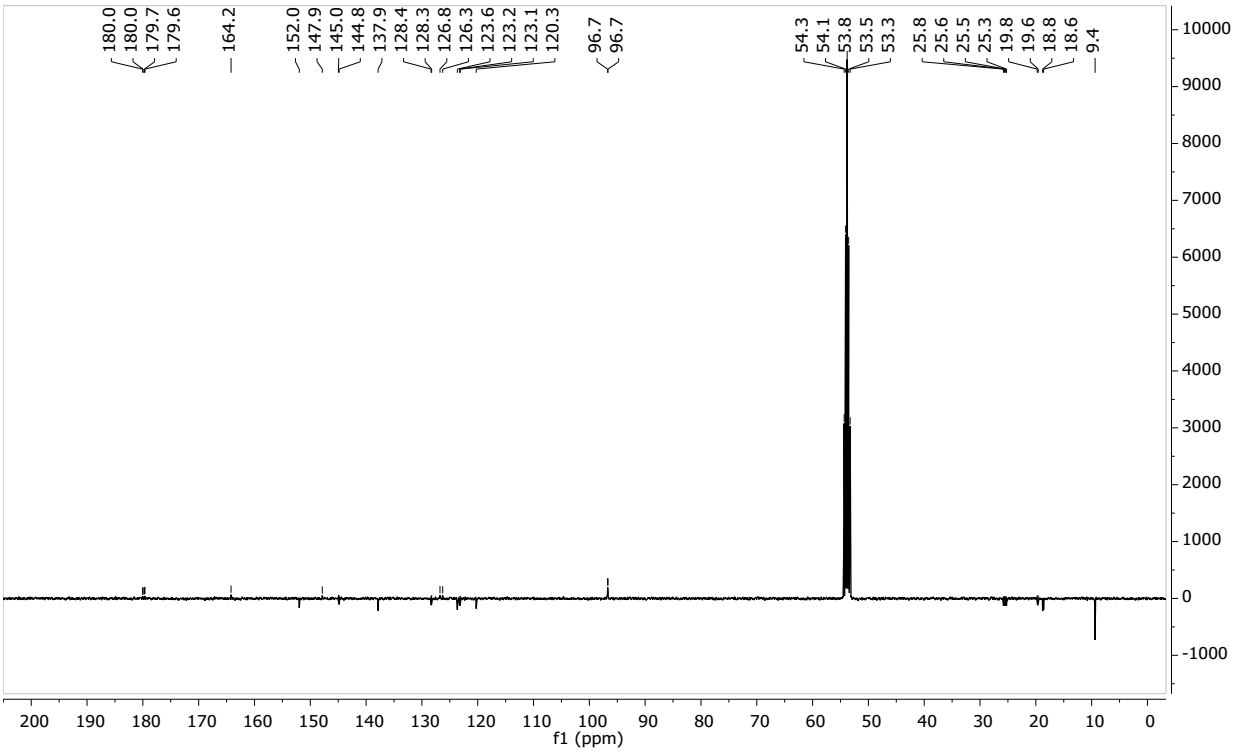


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in CD_2Cl_2.

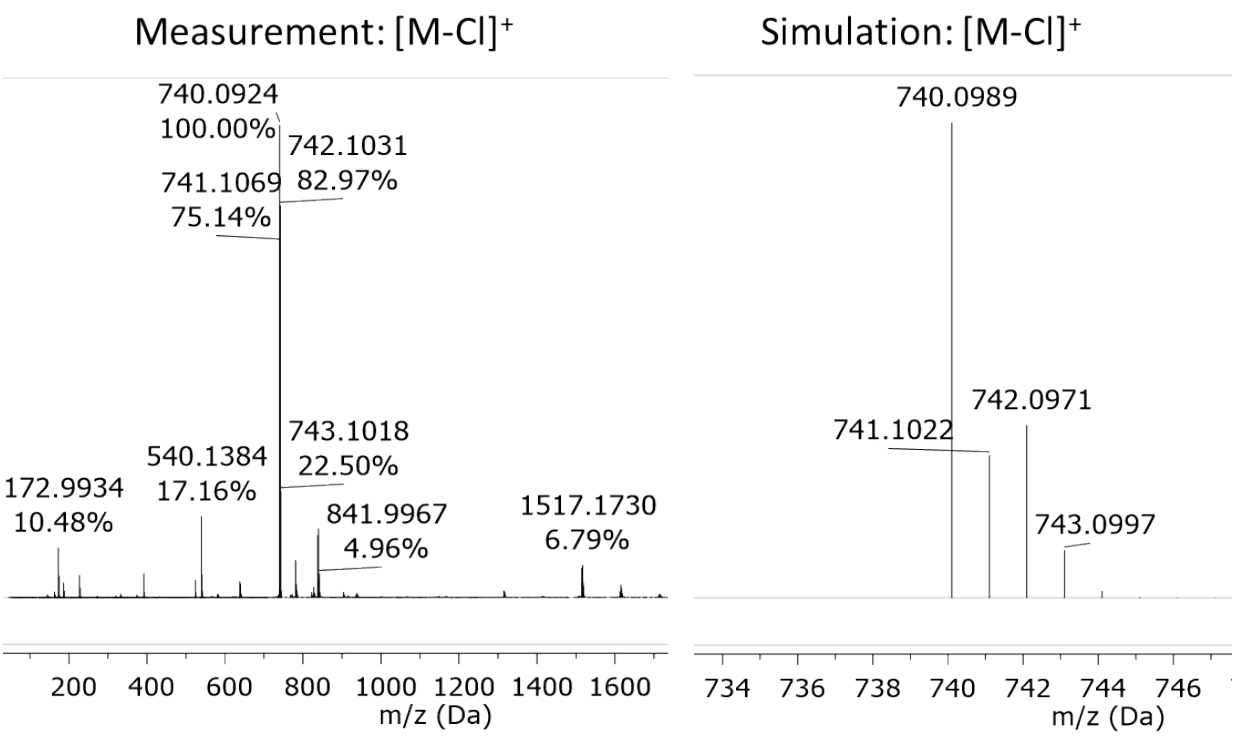
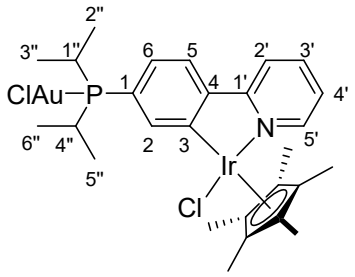


Figure S20. HR-ESI-MS (positive mode, CH_3OH) of **5**, *m/z* $[M\text{-}Cl]^+$.

Spectra of complex **6**



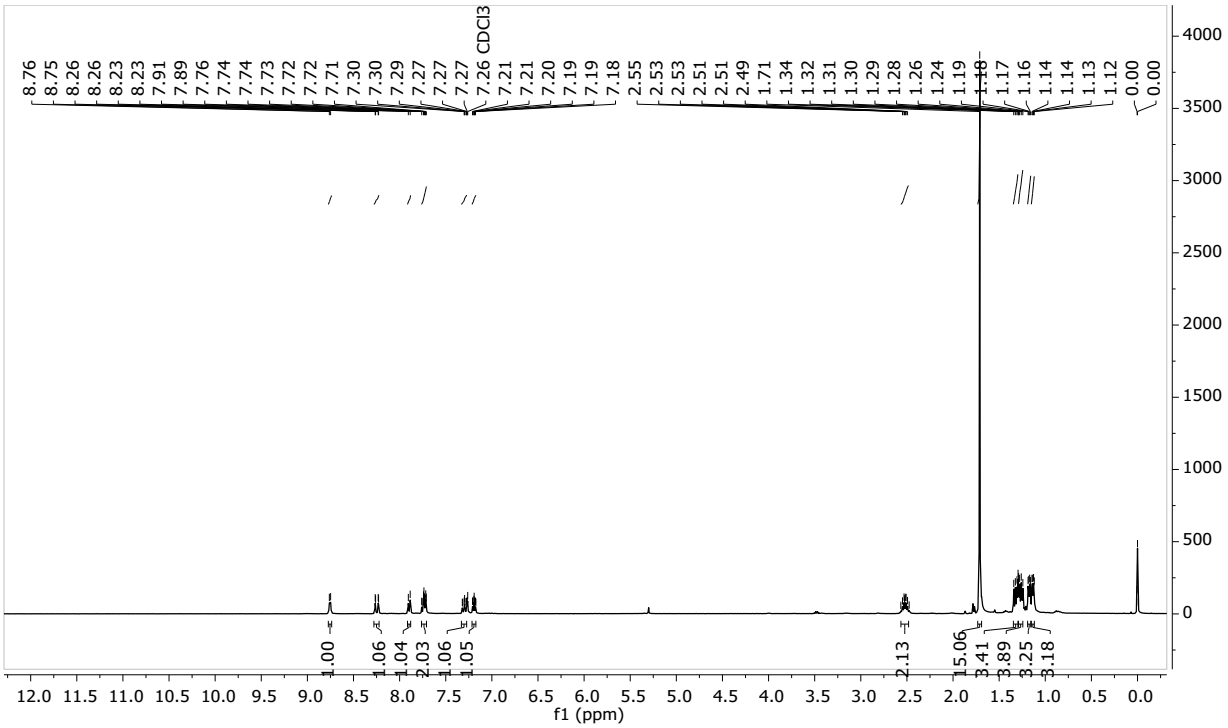


Figure S21. ^{1}H NMR spectrum of **6** in $CDCl_3$.

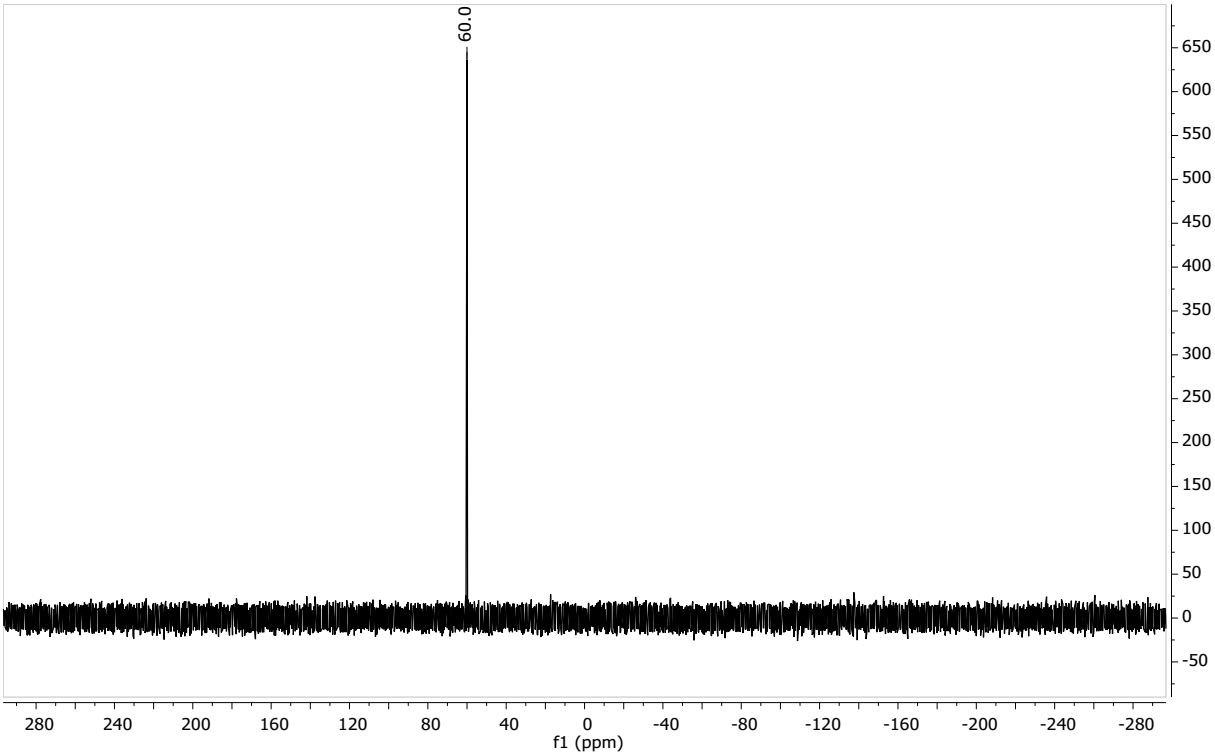


Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$.

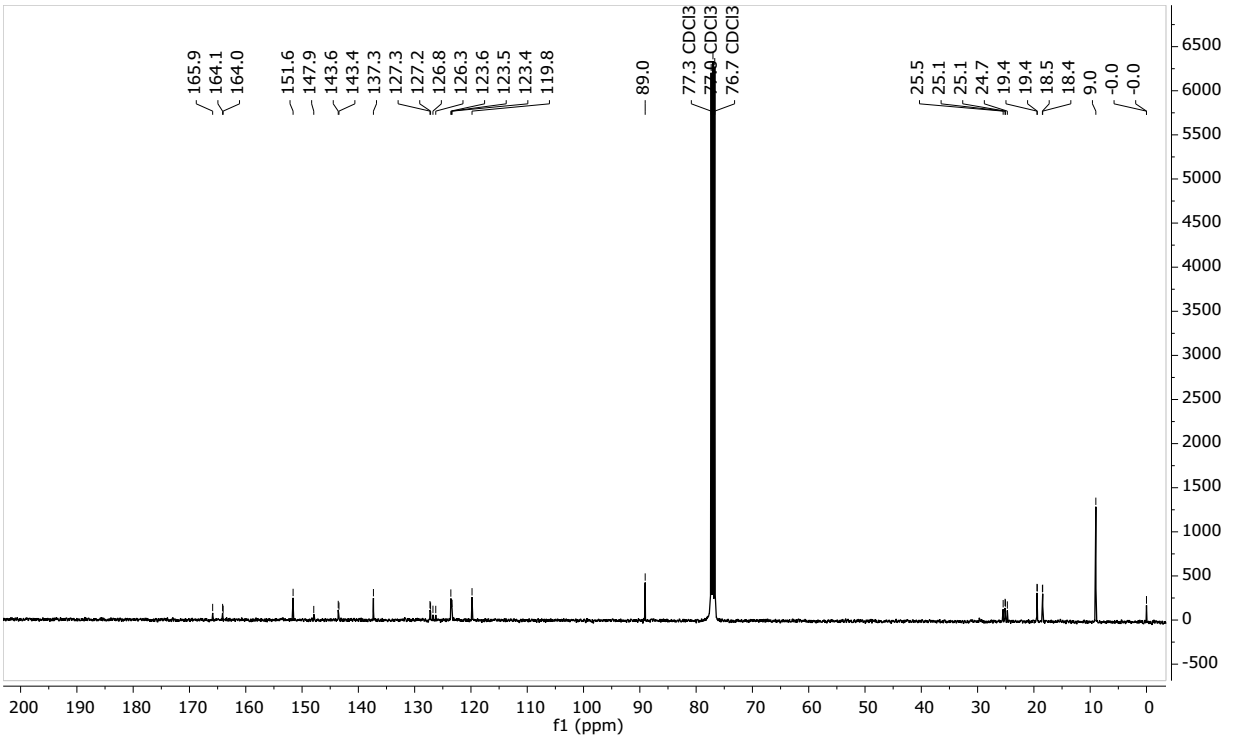


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$.

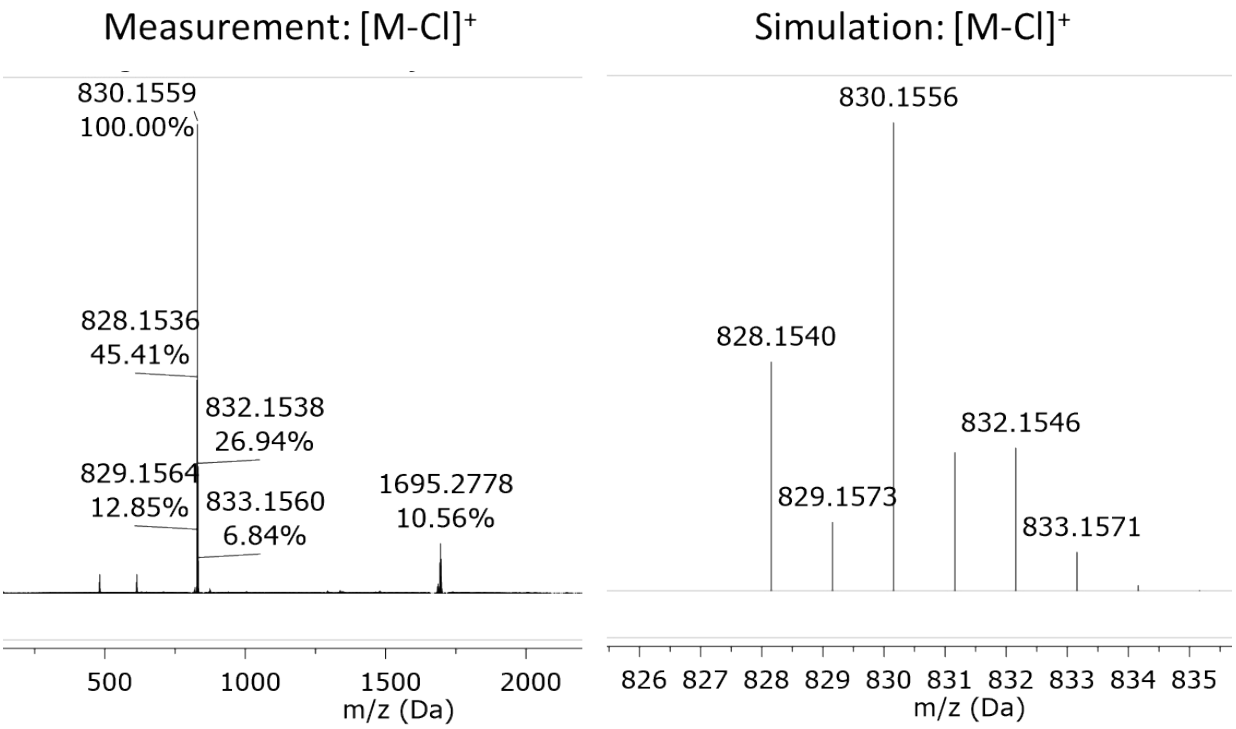
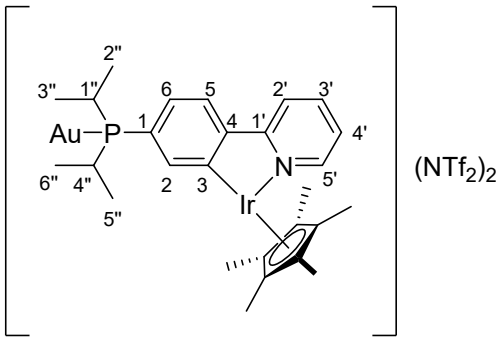


Figure S24. HR-ESI-MS (positive mode, CH_3OH) of **6**, *m/z* $[M\text{-}Cl]^+$.

Spectra of complex **7**



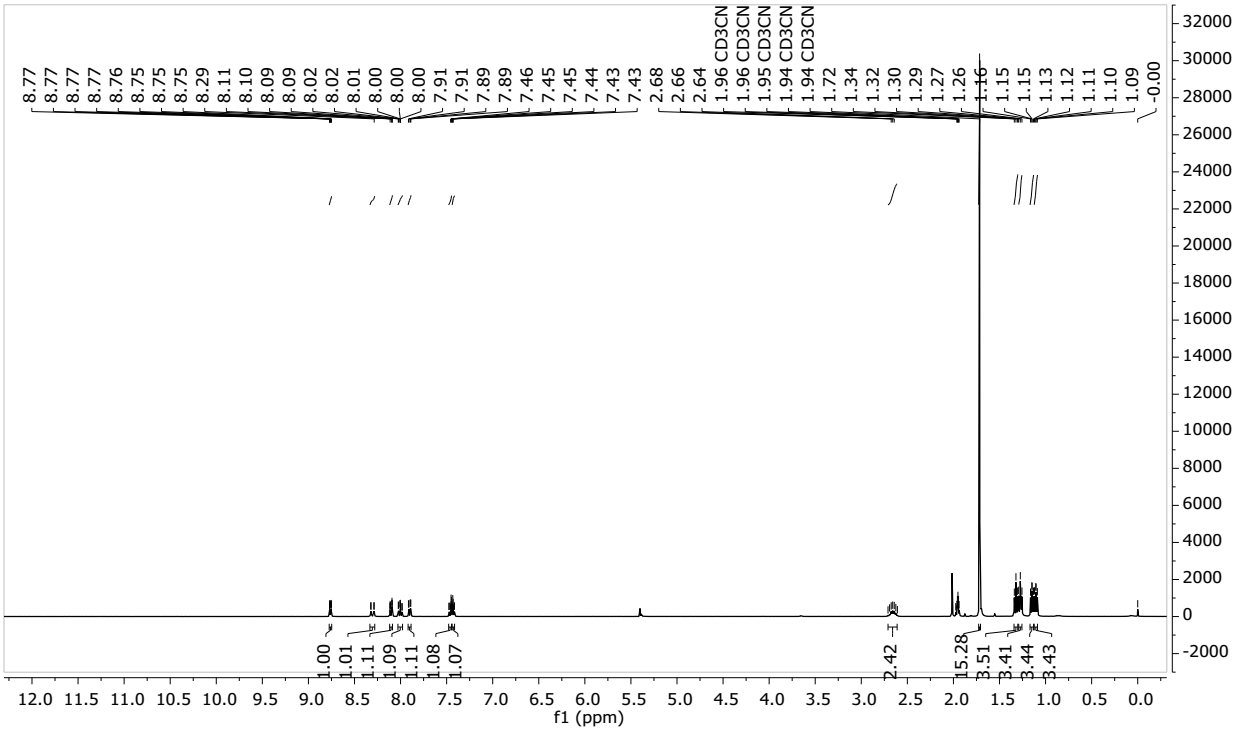


Figure S25. ^{1}H NMR spectrum of **7** in CD_3CN/CD_2Cl_2.

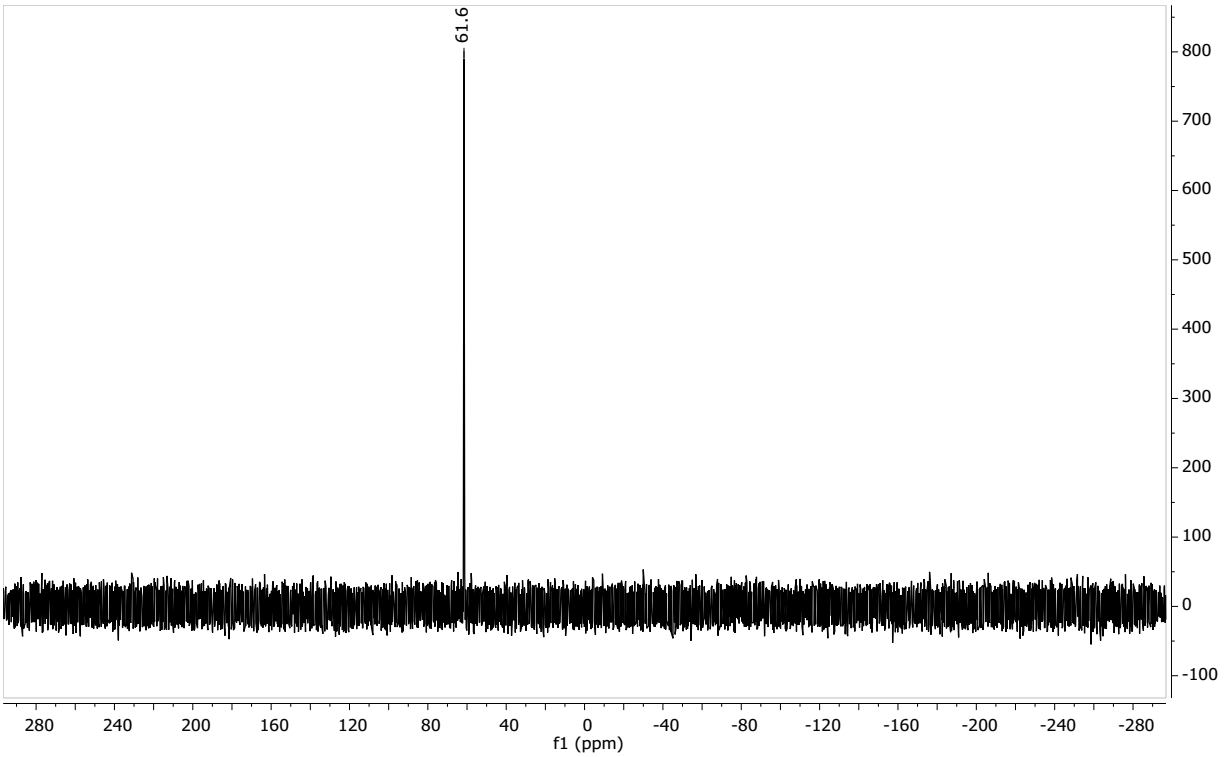


Figure S26. $^{31}P\{^{1}H\}$ NMR spectrum of **7** in CD_3CN/CD_2Cl_2.

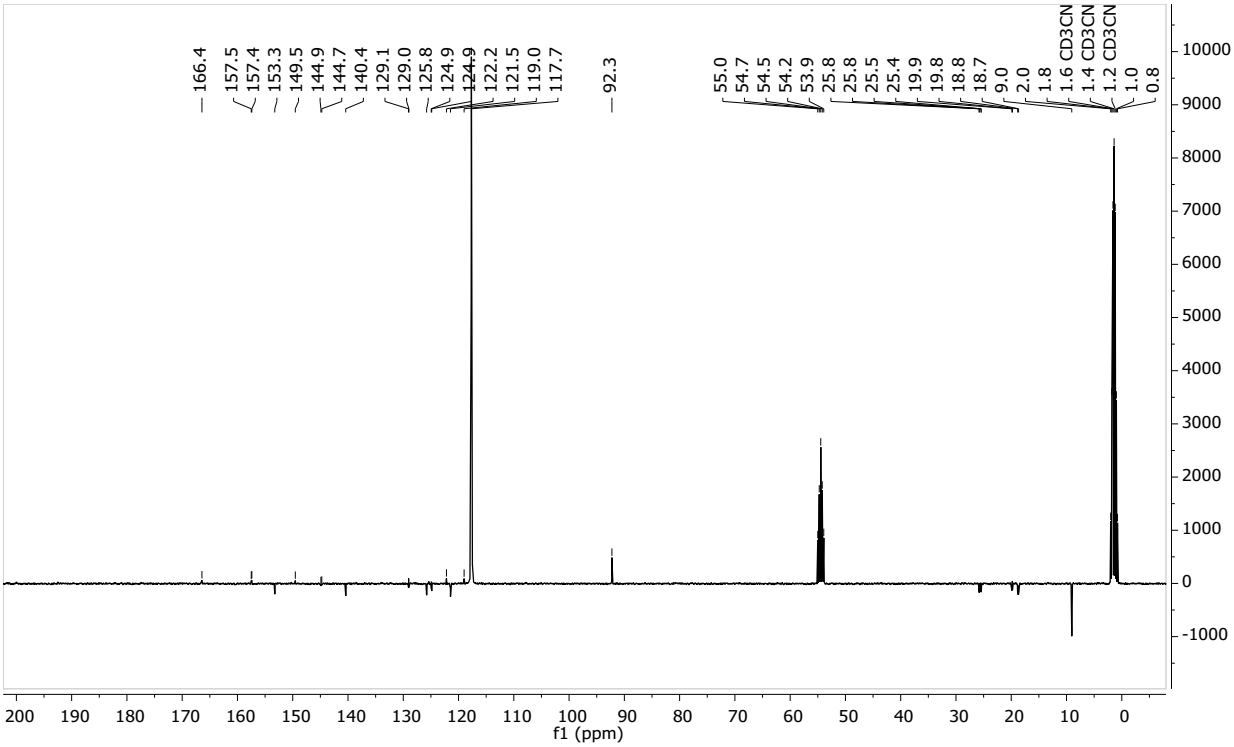


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in CD_3CN/CD_2Cl_2.

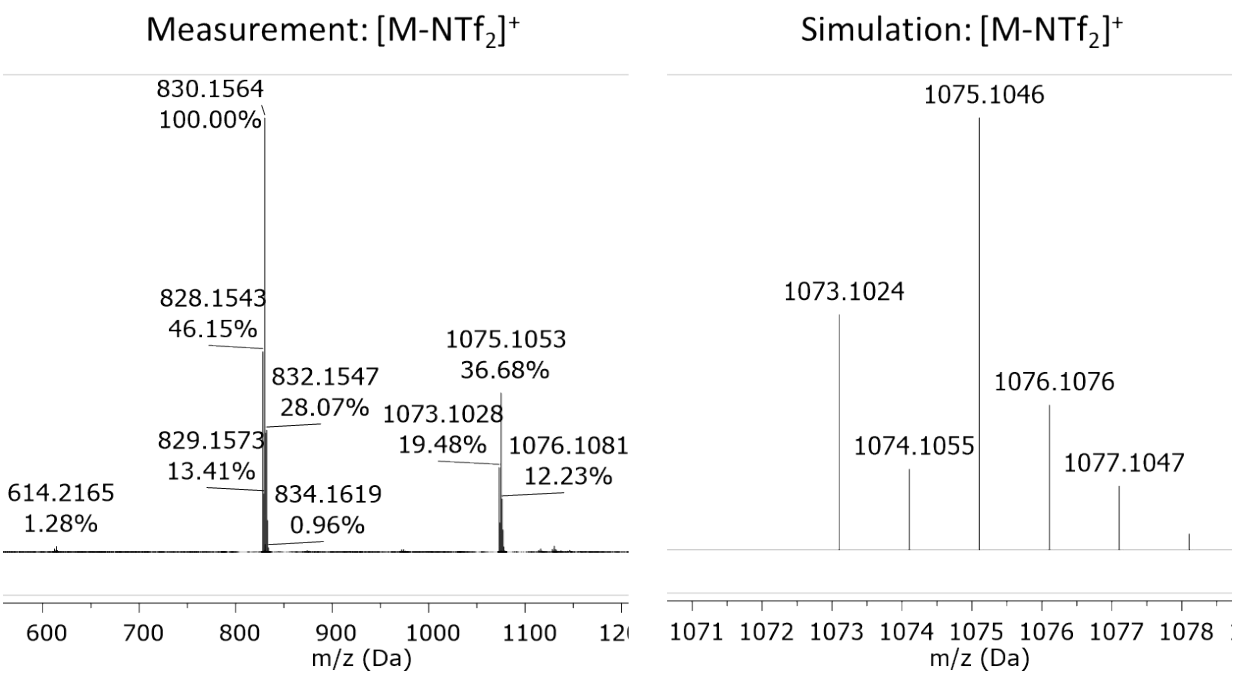
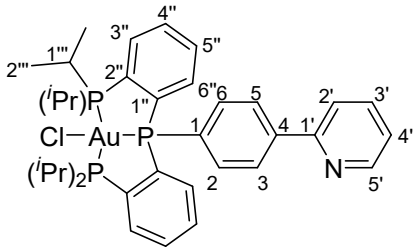


Figure S28. HR-ESI-MS (positive mode, CH_3OH) of **7**, *m/z* $[M\text{-}NTf_2]^+$. The signal at 830.1564 can be assigned to $[MCl]^+$ (see Figure S24), indicating the presence of **6** ($[M\text{-}Cl]^+$) or the monocationic complex with one NTf_2 anion ($[M\text{-}NTf_2]^+$) as an impurity.

Spectra of complex **8**



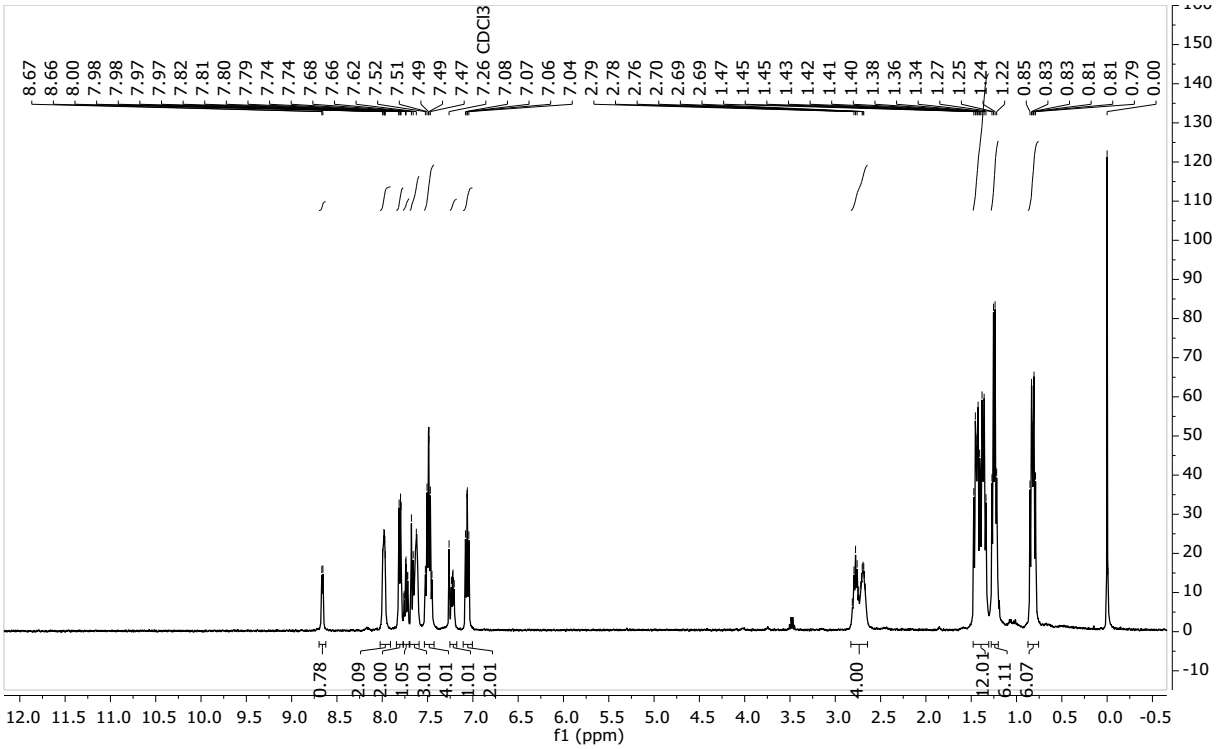


Figure S29. ^{1}H NMR spectrum of **8** in $CDCl_3$.

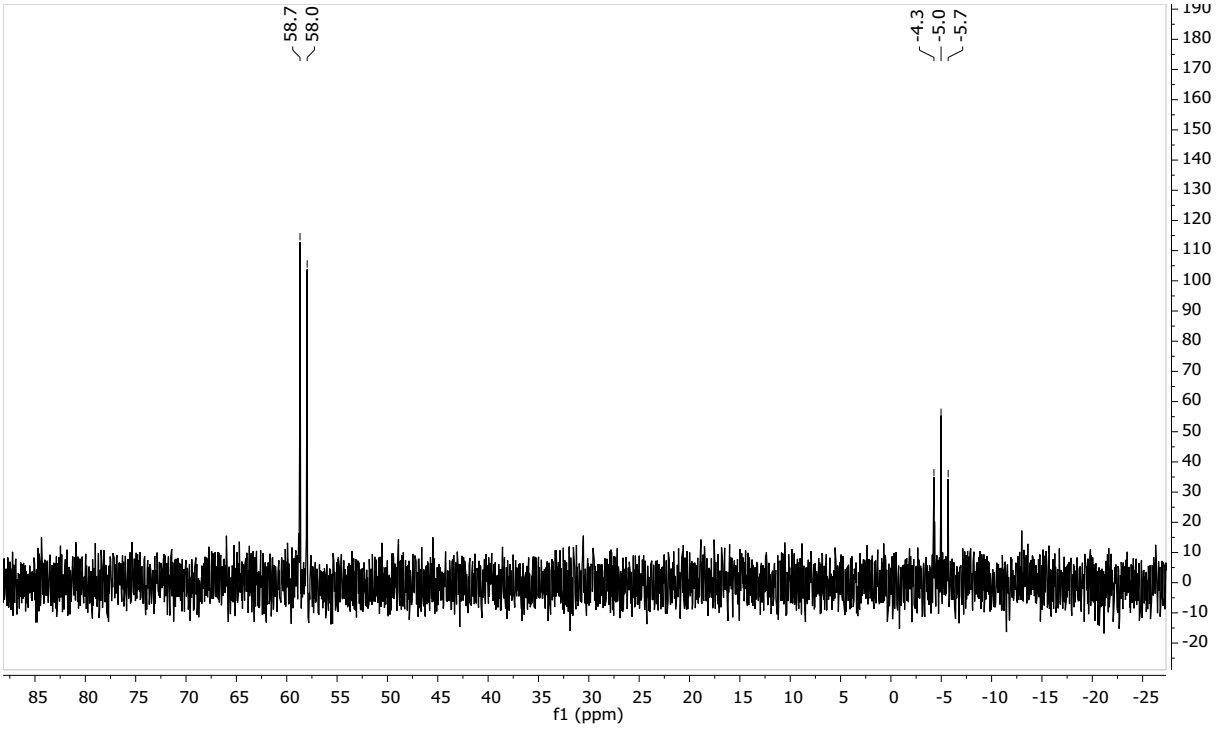


Figure S30. $^{31}P\{^{1}H\}$ NMR spectrum of **8** in $CDCl_3$.

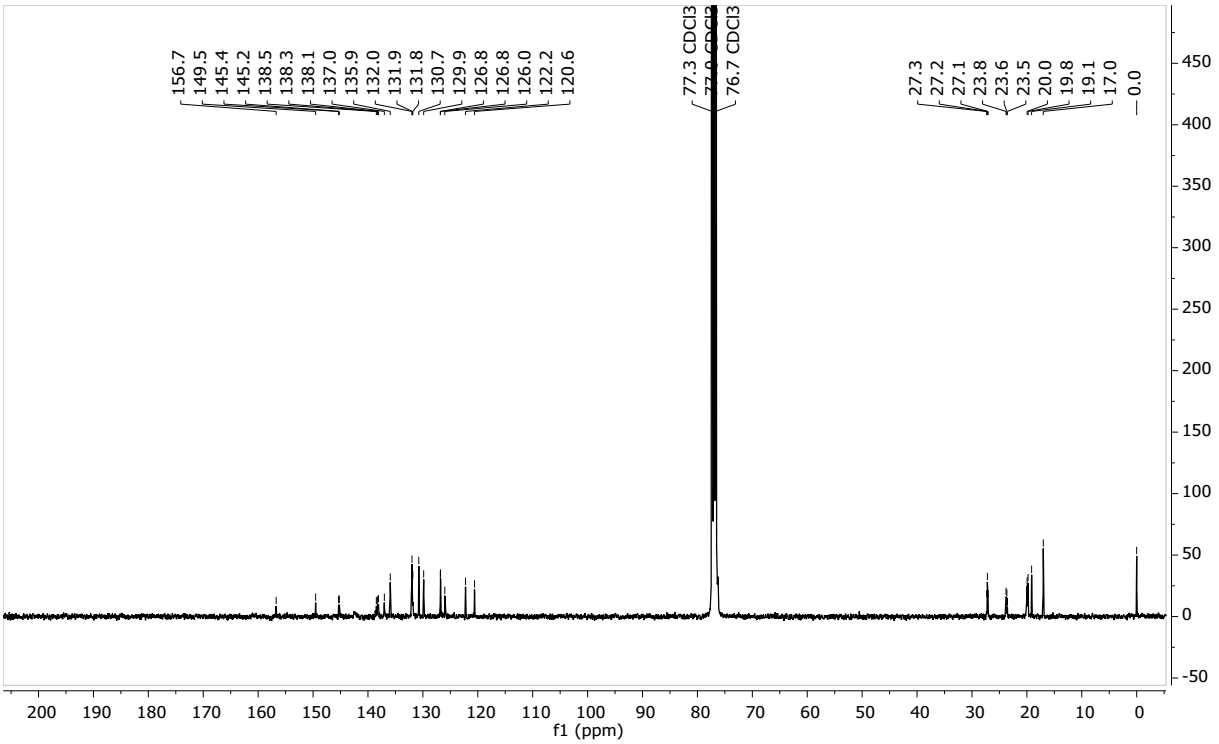


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of **8** in $CDCl_3$.

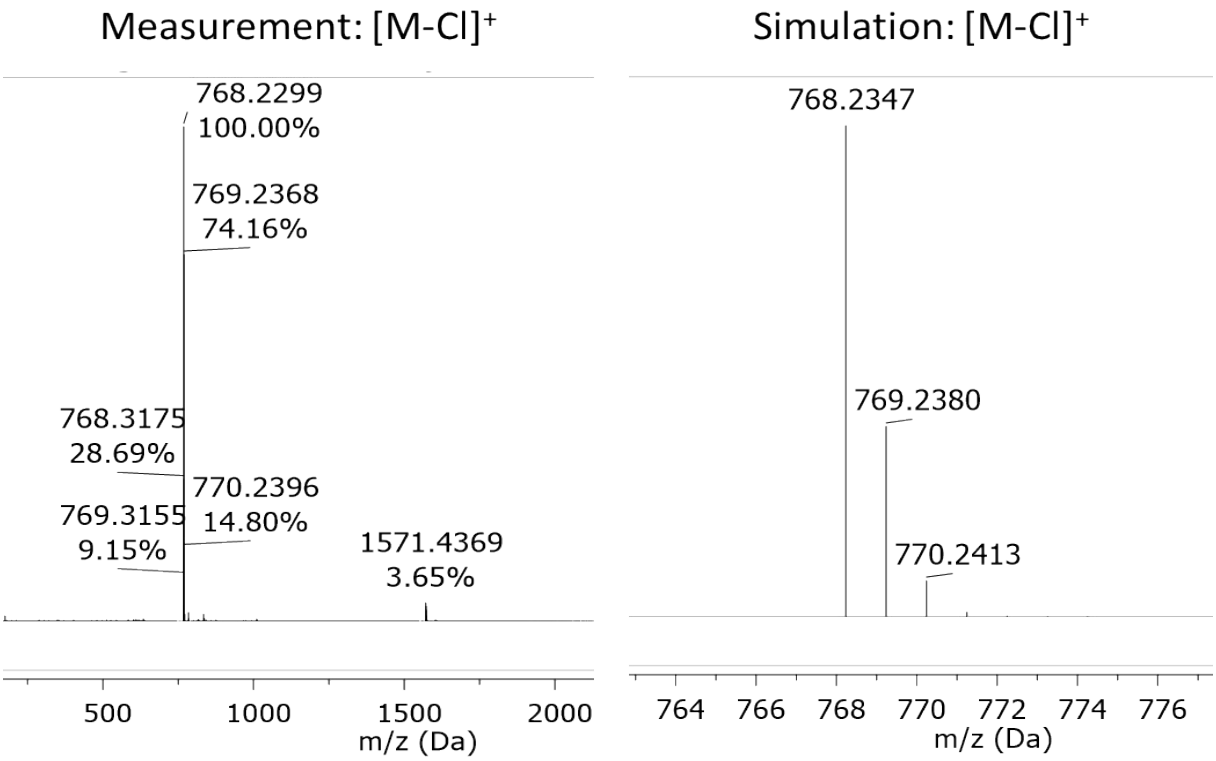
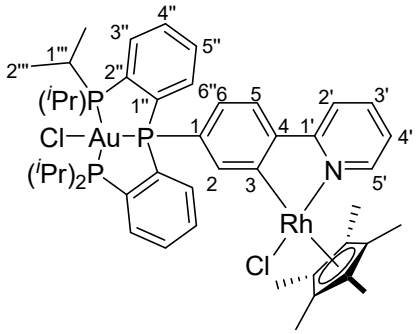


Figure S32. HR-ESI-MS (positive mode, CH_3OH) of **8**, *m/z* $[M\text{-}Cl]^+$.

Spectra of complex **9**



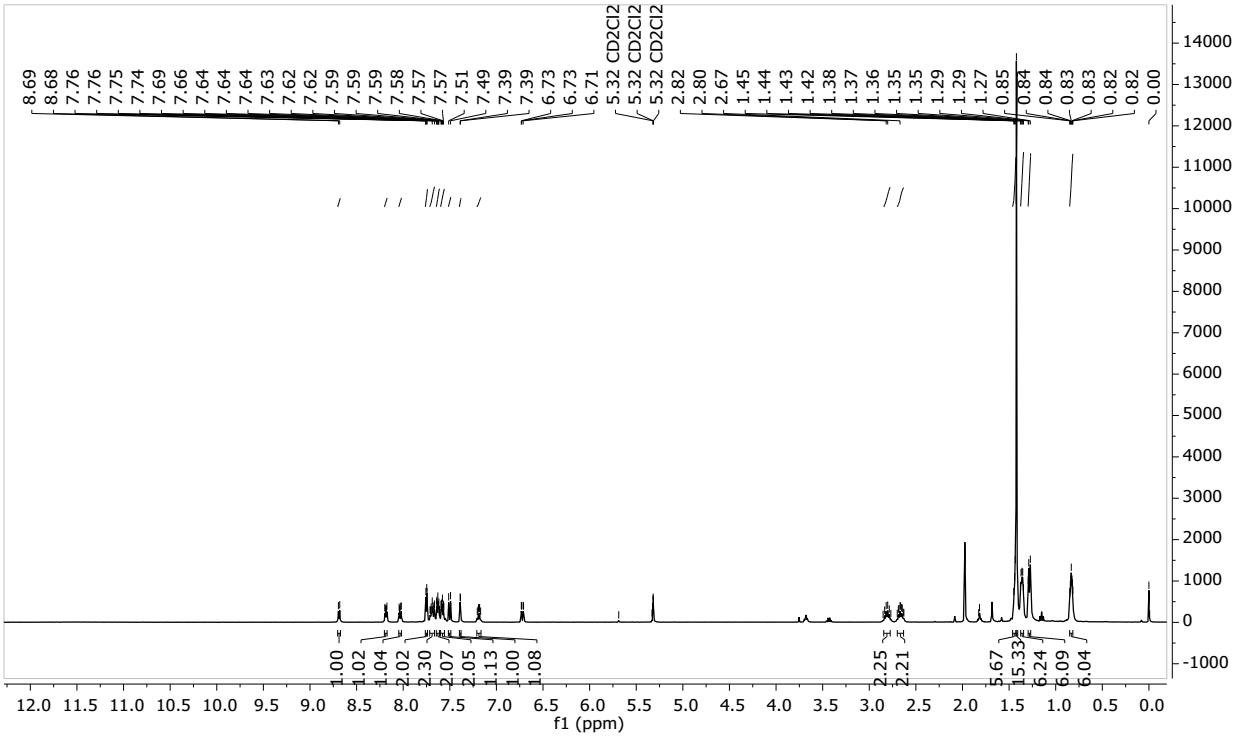


Figure S33. ^{1}H NMR spectrum of **9** in CD_2Cl_2.

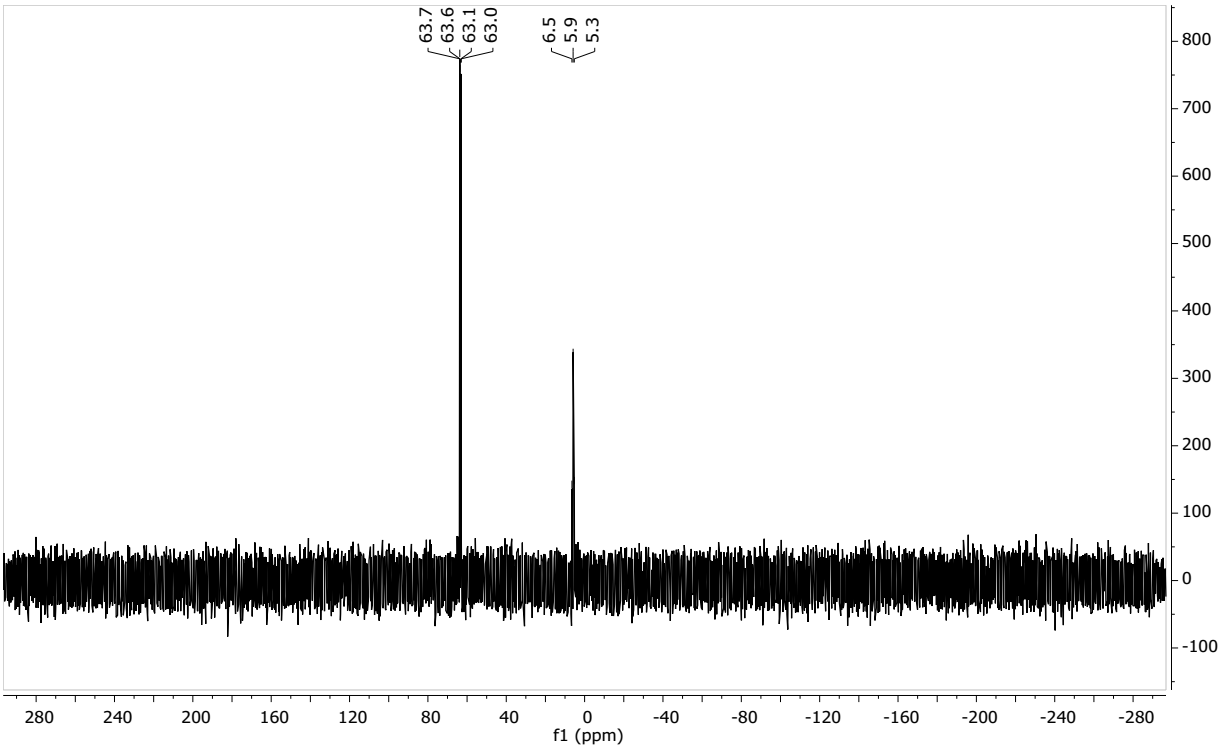


Figure S34. $^{31}P\{^{1}H\}$ NMR spectrum of **9** in CD_2Cl_2.

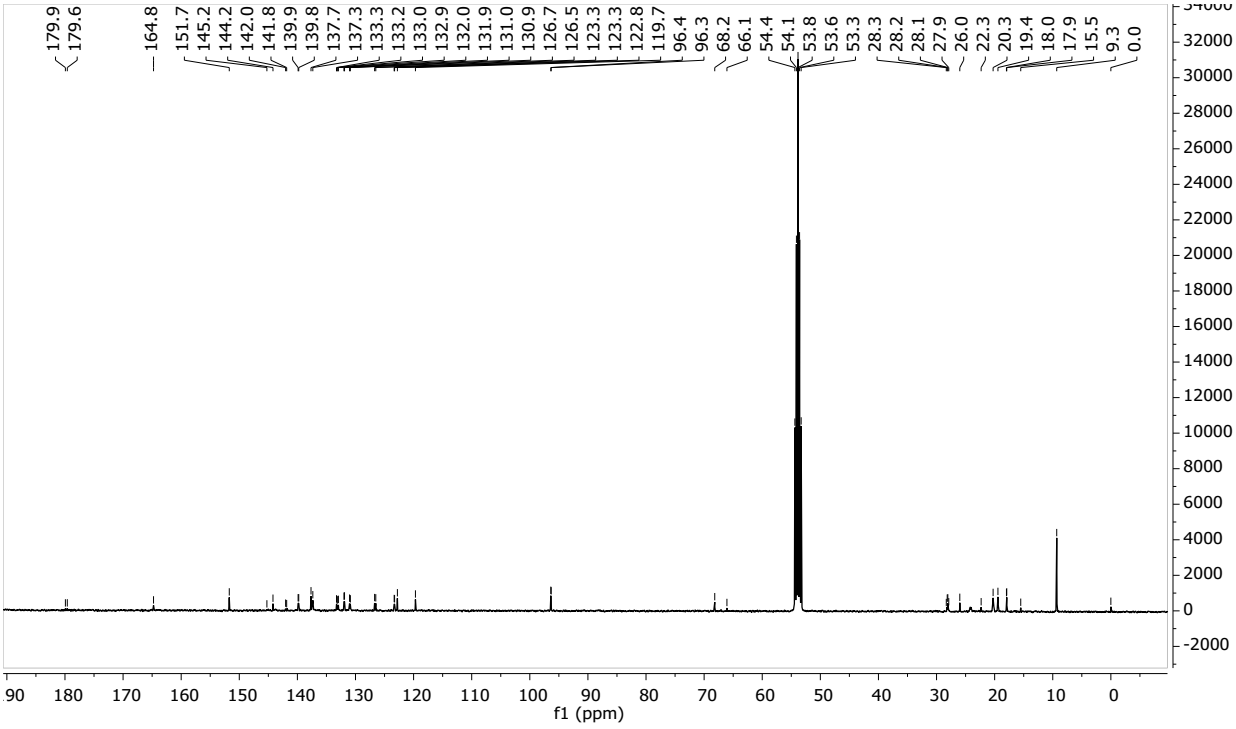


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **9** in CD_2Cl_2.

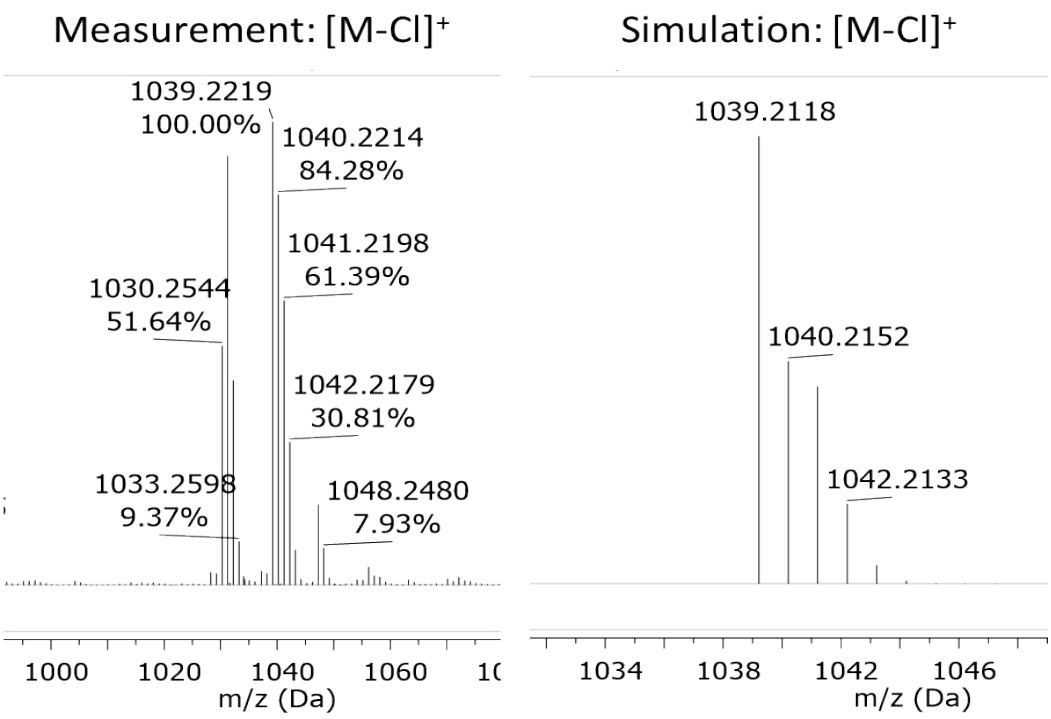
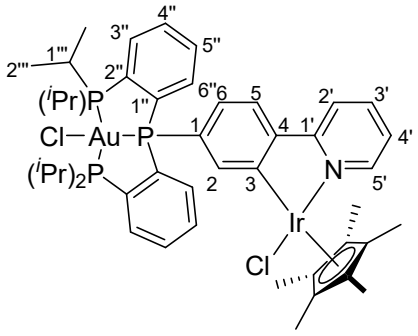


Figure S36. HR-ESI-MS (positive mode, CH_3OH) of **9**, *m/z* $[M\text{-}Cl]^+$.

Spectra of complex **10**



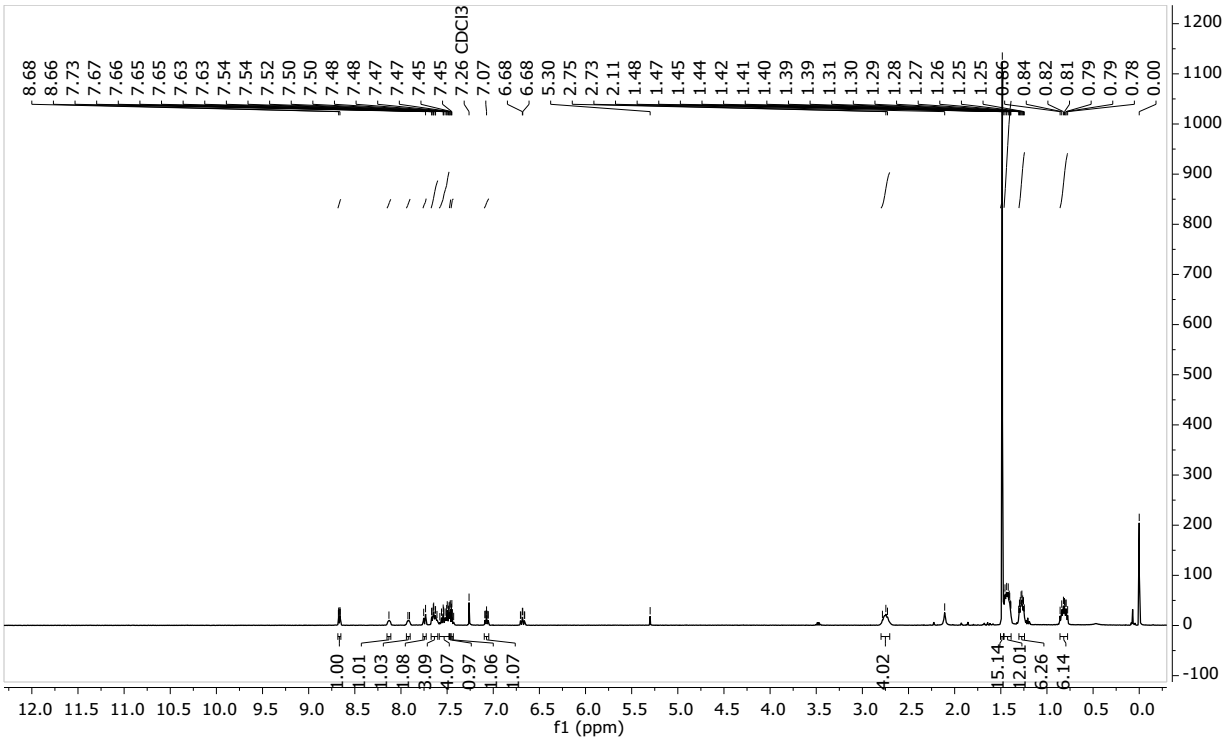


Figure S37. ^{1}H NMR spectrum of **10** in $CDCl_3$.

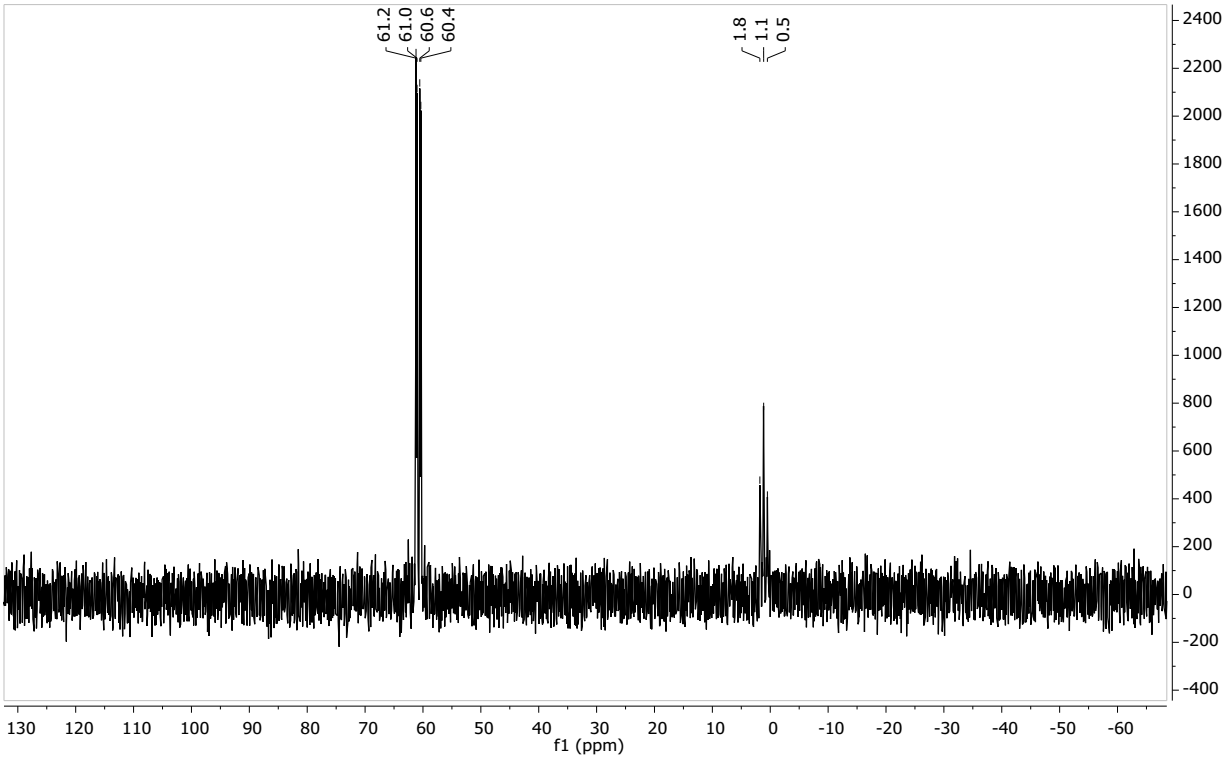


Figure S38. $^{31}P\{^{1}H\}$ NMR spectrum of **10** in $CDCl_3$.

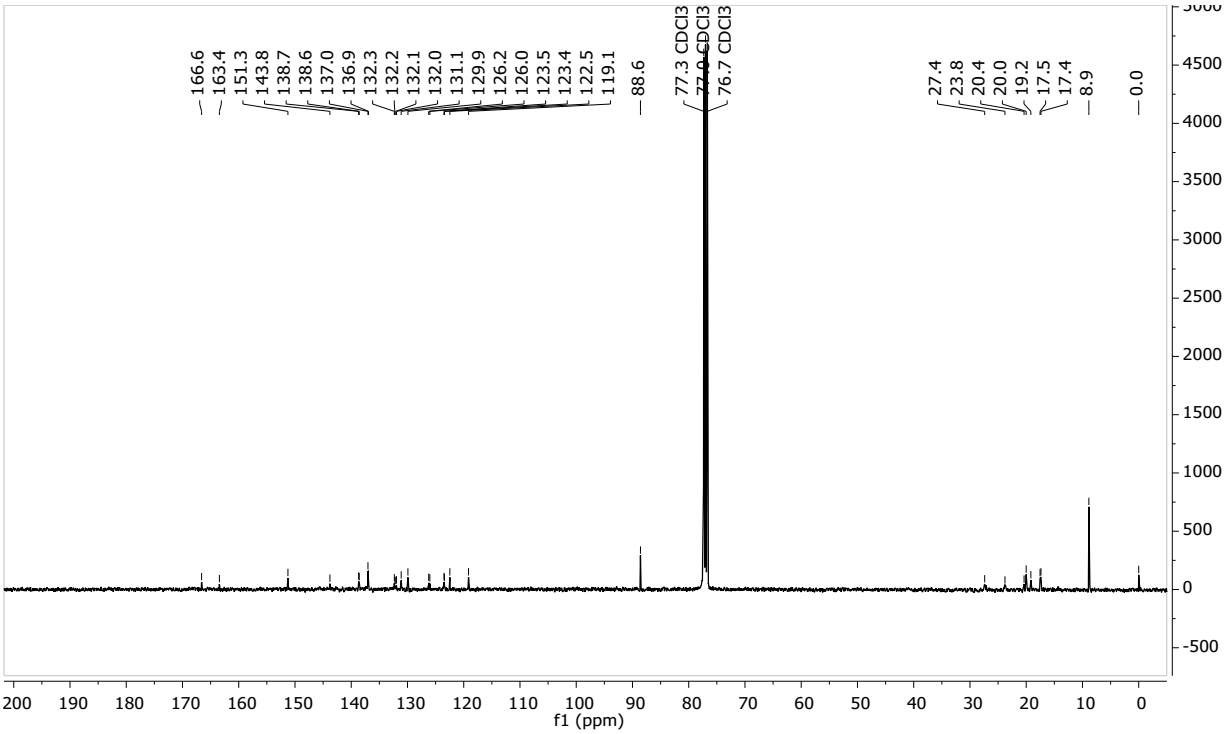


Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of **10** in $CDCl_3$.

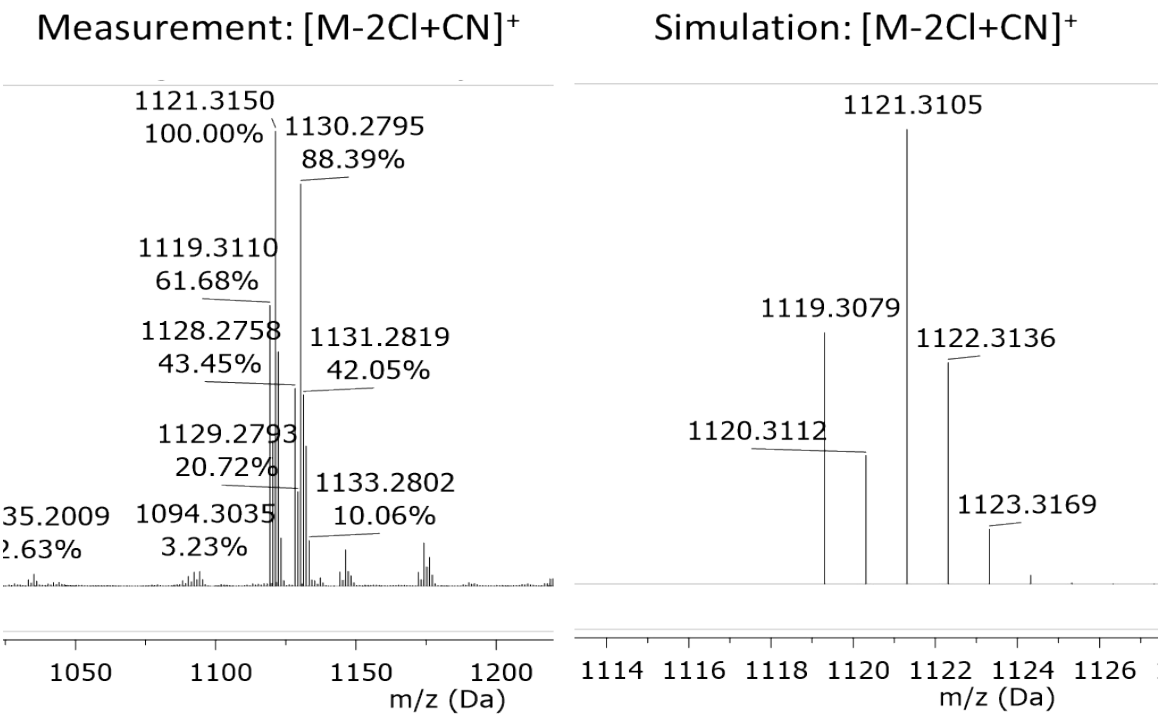


Figure S40. HR-ESI-MS (positive mode, CH_3OH) of **10**, *m/z* $[M\text{-}2Cl+CN]^+$.

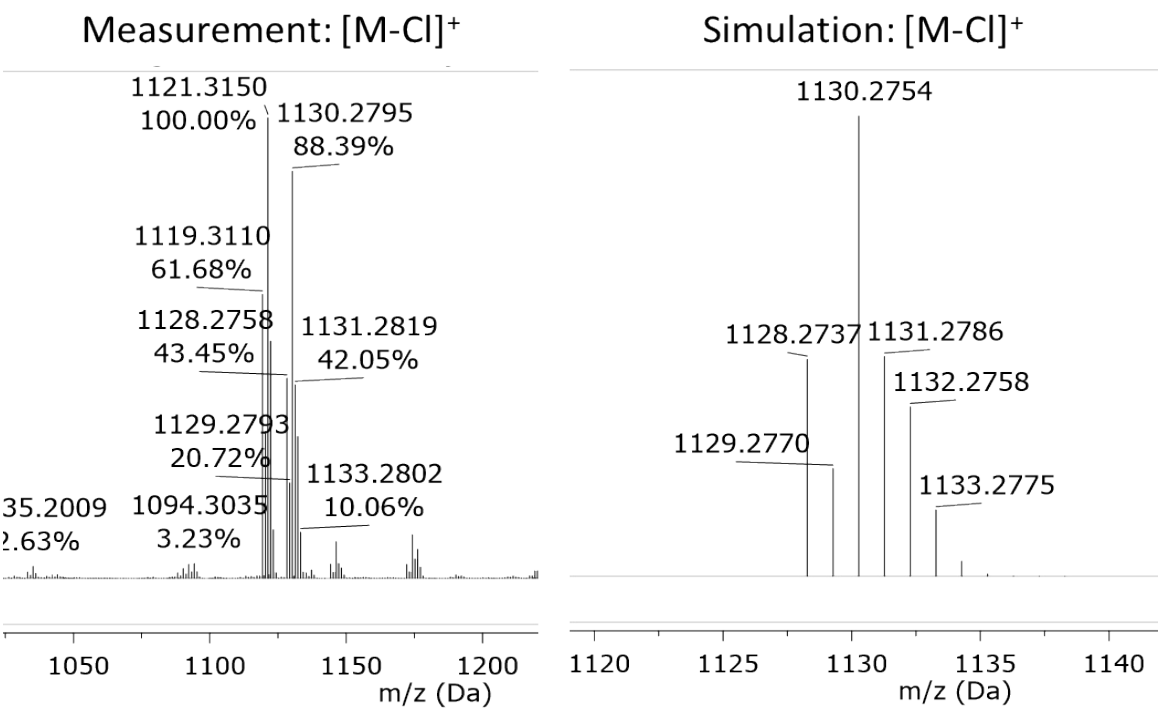


Figure S41. HR-ESI-MS (positive mode, CH_3OH) of **10**, *m/z* $[M\text{-}Cl]^+$.

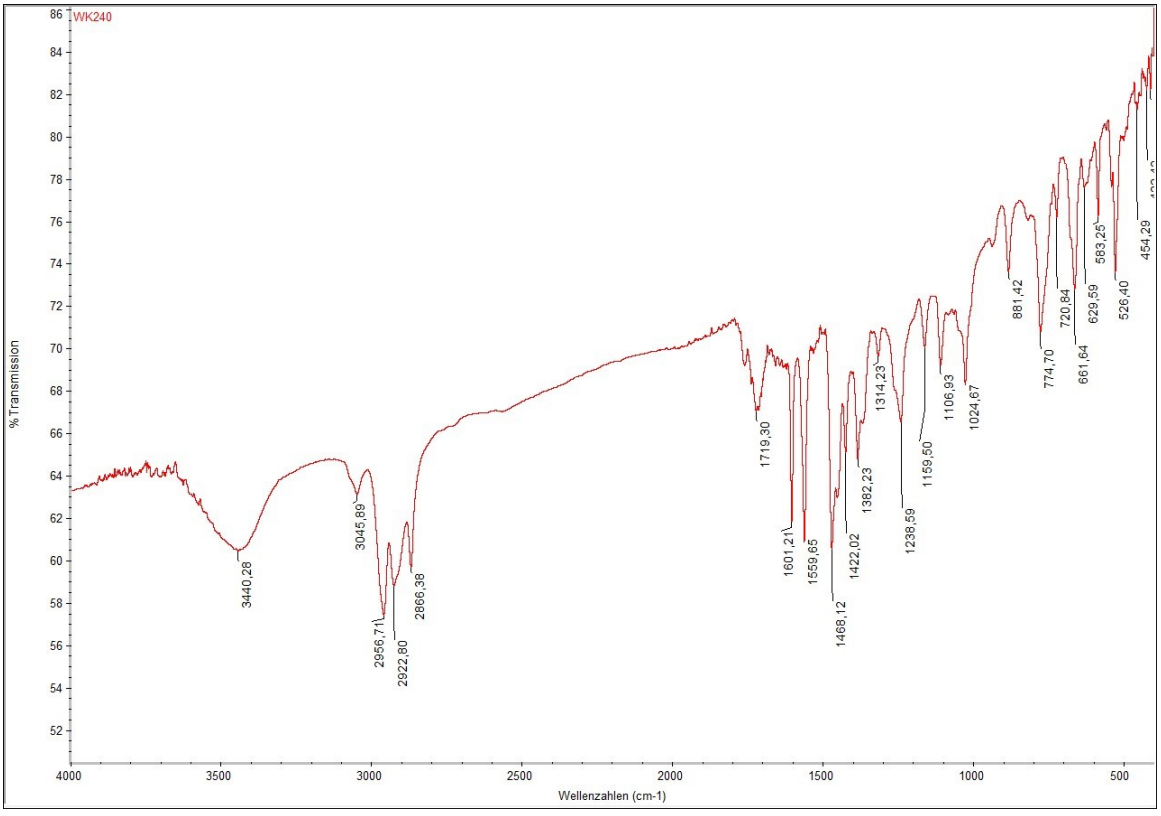
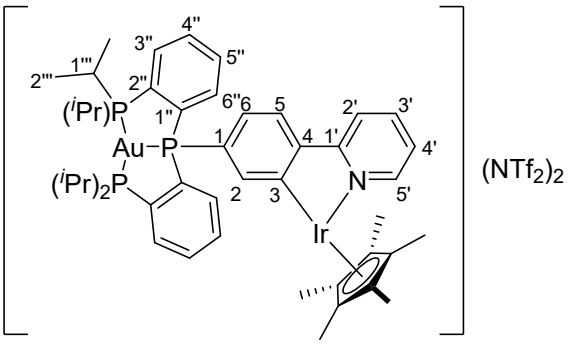


Figure S42. FT-IR (KBr) spectrum of **10**: ν (cm^{-1}).

Spectra of complex **11**



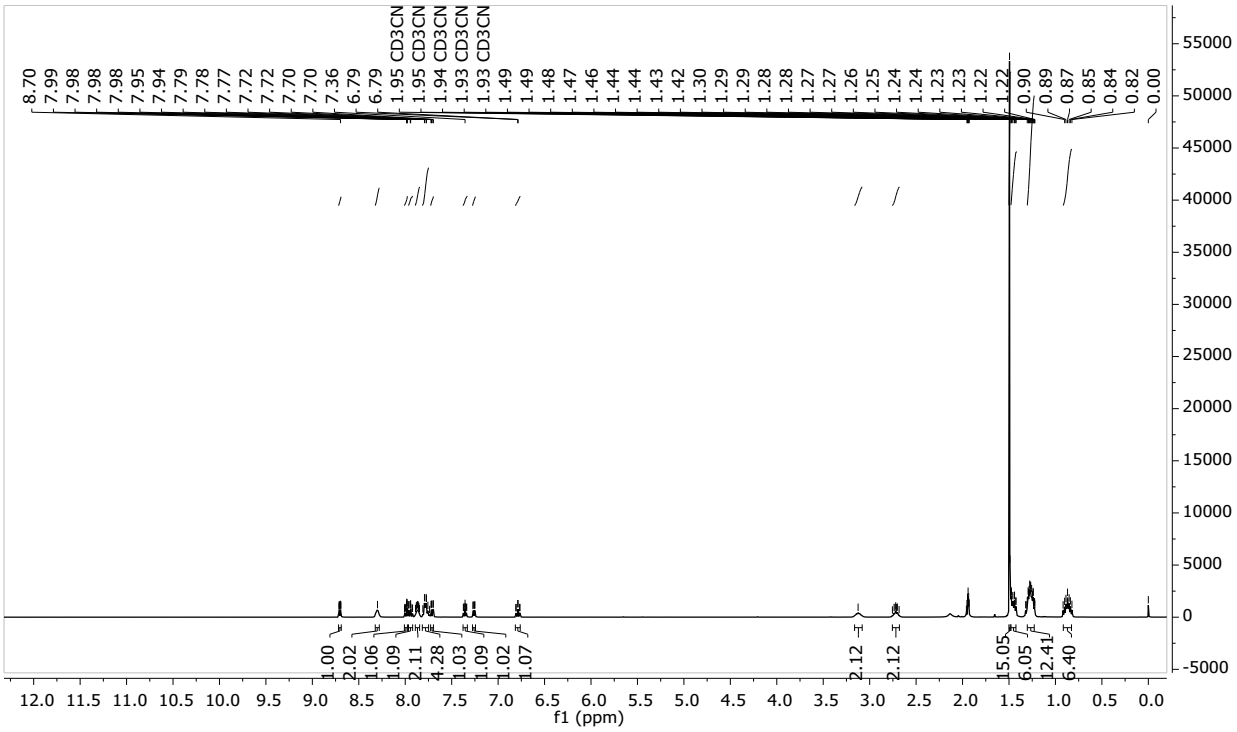


Figure S43. ^{1}H NMR spectrum of **11** in CD_3CN.

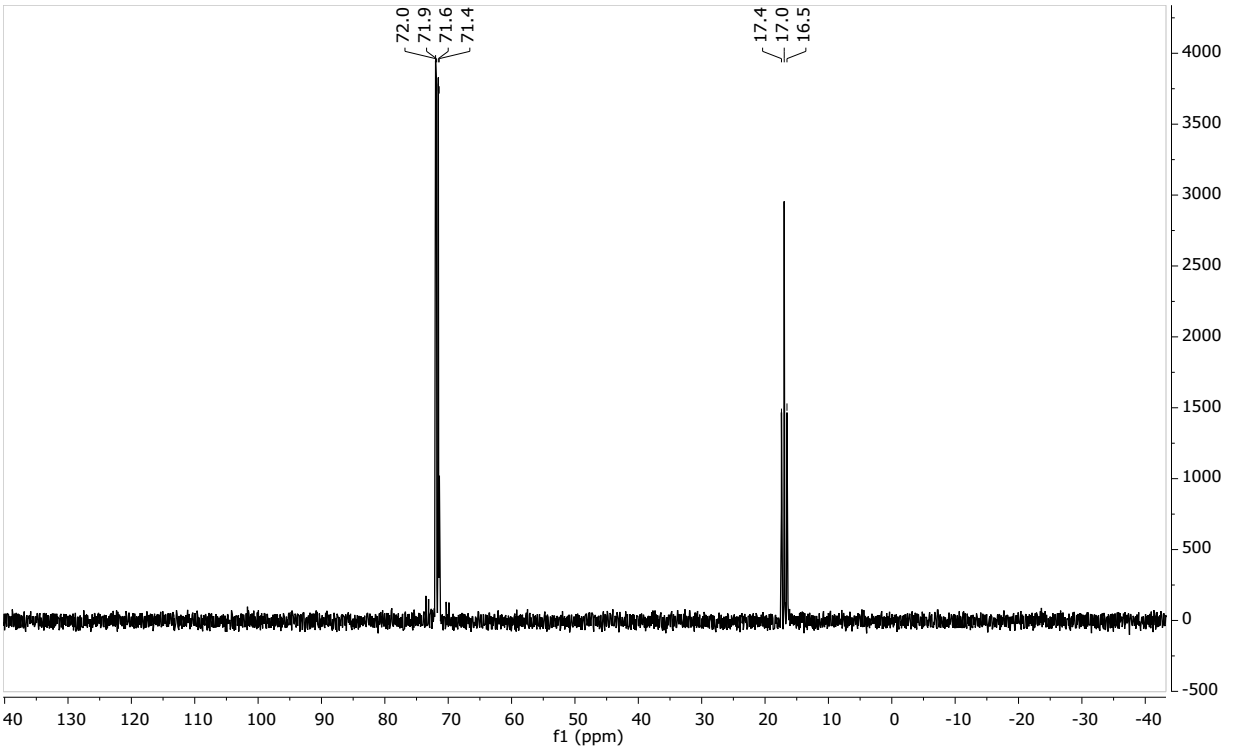


Figure S44. $^{31}P\{^{1}H\}$ NMR spectrum of **11** in CD_3CN.

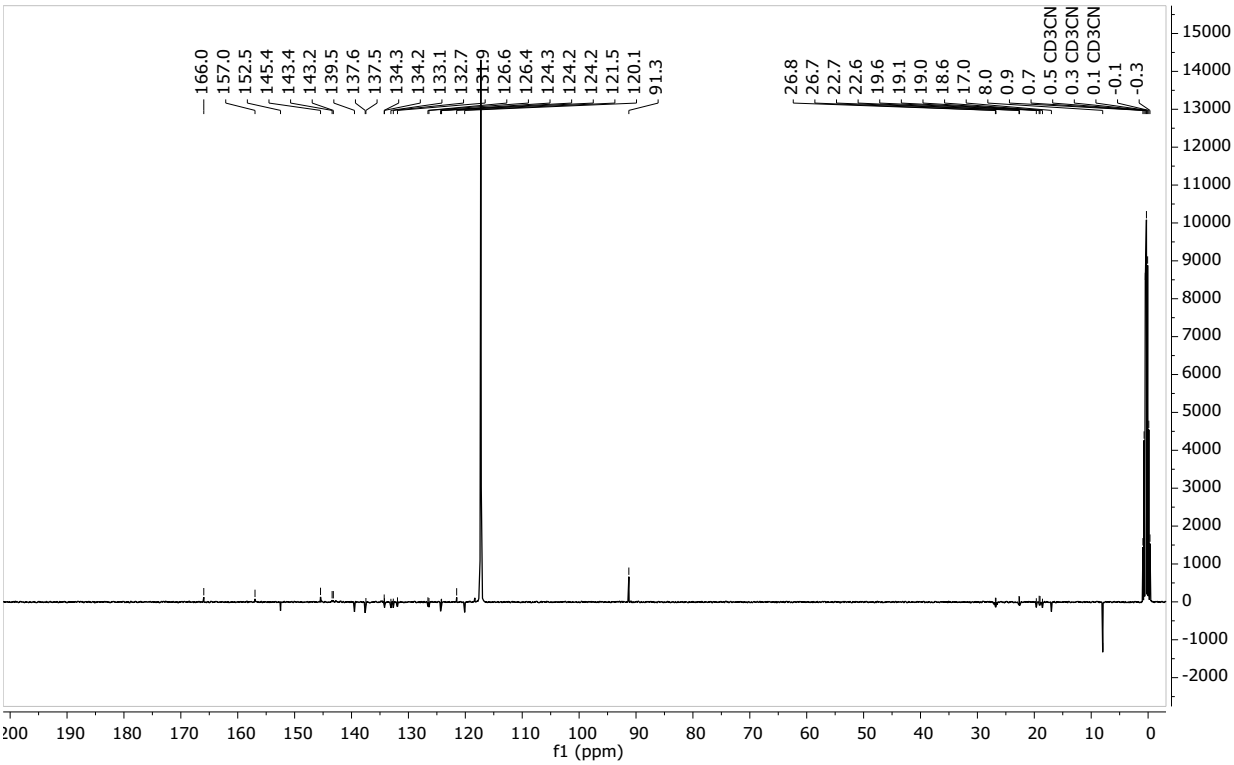


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of **11** in CD_3CN/CD_2Cl_2.

Crystallographic data

Table S0. Fundamental structure parameters

Compound	**L1H**	**1**	**2**
Empirical formula	$C_{17}H_{22}NPS$	$C_{28}H_{40}ClNOPRhS$	$C_{27}H_{36}ClIrNPS$
Formula weight	303.38	608.00	665.25
Temperature [K]	130(2)	130(2)	130(2)
Wavelength [pm]	71.073	71.073	71.073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	P $2_1/c$	P 2_1	P $na2_1$
Unit cell dimensions			
a [pm]	1802.95(3)	773.990(10)	2331.45(3)
b [pm]	843.470(10)	1463.08(3)	1396.26(2)
c [pm]	1120.42(2)	1296.09(3)	794.840(10)
α [deg]	90	90	90
β [deg]	106.352(2)	104.194(2)	90
γ [deg]	90	90	90
Volume [nm^3]	1.63494(5)	1.42290(5)	2.58745(6)
Z	4	2	4
$\rho_{(calculated)}$ [Mg/m^3]	1.233	1.419	1.708
μ [mm^{-1}]	0.286	0.845	5.422
F(000)	648	632	1320
Crystal size [mm^3]	0.65 · 0.61 · 0.23	0.25 · 0.23 · 0.03	0.43 · 0.34 · 0.29
Θ_{Min} / Θ_{Max} [deg]	2.687 / 32.395	2.136 / 32.495	1.700 / 32.450
Index ranges	-26 ≤ h ≤ 26 -12 ≤ k ≤ 12 -16 ≤ l ≤ 16	-11 ≤ h ≤ 11 -21 ≤ k ≤ 21 -19 ≤ l ≤ 19	-33 ≤ h ≤ 33 -20 ≤ k ≤ 21 -11 ≤ l ≤ 11
Reflections collected	44011	19745	37668
Indp. reflections (R_{int})	5635 (0.0156)	9324 (0.0478)	8190 (0.0357)
Completeness (Θ_{Max})	100.0 % (30.51)	100.0 % (30.51)	100.0 % (30.51)
T_{Max} / T_{Min}	1.00000 / 0.89608	1.00000 / 0.95405	0.450 / 0.275
Restraints / parameters	0 / 269	1 / 318	1 / 298
Gof on F^2	1.147	0.963	1.044
R1 / wR2 (I>2σ(I))	0.0322 / 0.0819	0.0440 / 0.0634	0.0287 / 0.0572
R1 / wR2 (all data)	0.0357 / 0.0843	0.0650 / 0.0693	0.0338 / 0.0591
Absolute structure parameter	-	0.00(2)	-0.023(5)
Residual electron density [$e \cdot Å^{-3}$]	0.491 / -0.300	1.026 / -1.014	1.768 / -0.907
Comments	†[1]	-	-
CCDC No	2322723	2322724	2322725

Table S1. continued

Compound	**3**	**5**	**6**
Empirical formula	$C_{27}H_{36}ClNPRh$	$C_{27}H_{36}AuCl_2NPRh$	$C_{27}H_{36}AuCl_2IrNP$
Formula weight	543.90	776.31	865.60
Temperature [K]	130(2)	130(2)	130(2)
Wavelength [pm]	71.073	71.073	71.073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 2_1/n	P 2_1	P 2_1
Unit cell dimensions			
a [pm]	782.150(10)	769.39(2)	770.690(10)
b [pm]	2815.60(2)	1491.64(2)	1483.63(2)
c [pm]	1164.770(10)	1263.49(3)	1263.76(2)
α [deg]	90	90	90
β [deg]	93.1230(10)	105.388(2)	105.505(2)
γ [deg]	90	90	90
Volume [nm^3]	2.56127(4)	1.39806(5)	1.39242(4)
Z	4	2	2
$\rho_{(calculated)}$ [Mg/m^3]	1.410	1.844	2.065
μ [mm^{-1}]	0.848	6.095	10.301
F(000)	1128	756	820
Crystal size [mm^3]	0.24 · 0.19 · 0.13	0.48 · 0.29 · 0.05	0.41 · 0.26 · 0.10
Θ_{Min} / Θ_{Max} [deg]	1.894 / 32.015	2.158 / 32.331	2.164 / 32.549
Index ranges	-11 ≤ h ≤ 11 -41 ≤ k ≤ 41 -17 ≤ l ≤ 17	-11 ≤ h ≤ 11 -21 ≤ k ≤ 21 -18 ≤ l ≤ 18	-11 ≤ h ≤ 11 -21 ≤ k ≤ 22 -19 ≤ l ≤ 18
Reflections collected	57522	21571	18502
Indp. reflections (R_{int})	8446 (0.0299)	9169 (0.0333)	9105 (0.0264)
Completeness (Θ_{Max})	100.0 % (30.51)	100.0 % (30.51)	100.0 % (30.51)
T_{Max} / T_{Min}	1.00000 / 0.93328	0.779 / 0.245	0.420 / 0.149
Restraints / parameters	0 / 289	1 / 307	1 / 307
Gof on F^2	1.111	1.038	1.052
R1 / wR2 (I>2σ(I))	0.0298 / 0.0610	0.0302 / 0.0571	0.0257 / 0.0508
R1 / wR2 (all data)	0.0353 / 0.0631	0.0336 / 0.0586	0.0275 / 0.0516
Absolute structure parameter	-	-0.027(2)	-0.023(4)
Residual electron density [$e \cdot Å^{-3}$]	0.903 / -0.488	1.834 / -0.830	1.316 / -1.329
Comments	-	†[2]	†[2]
CCDC No	2322726	2322727	2322728

Table S1. continued

Compound	**8**	**9**	**10**
Empirical formula	$C_{36}H_{46}AuCl_3NP_3$	$C_{48}H_{64}AuCl_8NP_3Rh$	$C_{49}H_{64}AuCl_2IrN_3P_3$
Formula weight	888.96	1331.38	1248.00
Temperature [K]	130(2)	130(2)	130(2)
Wavelength [pm]	71.073	71.073	71.073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P $2_1/c$	P $2_1/c$	$P\bar{1}$
Unit cell dimensions			
a [pm]	1550.06(2)	1453.20(2)	1066.370(10)
b [pm]	2356.07(3)	1262.62(2)	1080.08(2)
c [pm]	2105.85(3)	2977.51(3)	2172.68(3)
α [deg]	90	90	82.6960(10)
β [deg]	105.0630(10)	92.7690(10)	86.8970(10)
γ [deg]	90	90	83.7420(10)
Volume [nm^3]	7.42642(17)	5.45687(13)	2.46526(6)
Z	8	4	2
$\rho_{(calculated)}$ [Mg/m^3]	1.590	1.621	1.681
μ [mm^{-1}]	4.333	3.501	5.910
F(000)	3552	2656	1228
Crystal size [mm^3]	0.42 · 0.31 · 0.15	0.11 · 0.09 · 0.05	0.56 · 0.14 · 0.05
Θ_{Min} / Θ_{Max} [deg]	1.701 / 30.495	1.752 / 27.406°.	2.520 / 34.691
Index ranges	-21 ≤ h ≤ 21 -31 ≤ k ≤ 33 -29 ≤ l ≤ 28	-18 ≤ h ≤ 18 -15 ≤ k ≤ 16 -36 ≤ l ≤ 35	-16 ≤ h ≤ 16 -17 ≤ k ≤ 17 -34 ≤ l ≤ 34
Reflections collected	80851	39789	72977
Indp. reflections (R_{int})	20407 (0.0569)	11249 (0.0507)	19938 (0.0312)
Completeness (Θ_{Max})	100.0 % (28.29)	100.0 % (25.35)	99.9 % (33.14)
T_{Max} / T_{Min}	0.599 / 0.324	0.843 / 0.684	0.754 / 0.217
Restraints / parameters	0 / 816	78 / 622	0 / 547
Gof on F^2	1.059	1.027	1.059
R1 / wR2 (I>2σ(I))	0.0427 / 0.0745	0.0384, 0.0633	0.0262 / 0.0448
R1 / wR2 (all data)	0.0809 / 0.0862	0.0614, 0.0692	0.0361 / 0.0475
Absolute structure parameter	-	-	-
Residual electron density [$e \cdot Å^{-3}$]	2.714 / -1.293	0.573 / -0.872	2.607 / -0.896
Comments	†[3]	†[4]	-
CCDC No	2322729	2322730	2322731

†[1]: Nitrogen atom N(1) localised with bond length and displacement parameter analysis. †[2]: Structures of compounds **5** and **6** are isotyp. †[3]: The complex molecules are most likely marginally disordered with a ratio of 0.9845(4) : 0.0155(4). This disorder is only detectable for the most electron rich atoms Au(1) and Au(2). †[4]: Two of the three CH_2Cl_2 solvent molecules are disordered with a ratio of 0.806(4) : 0.194(4) (Cl(5), Cl(6), C(47)) and 0.53(1) : 0.47(1) (Cl(7), Cl(8), C(48)).

Table S1. Selected bond lengths [Å] and angles [°] of complexes **1** and **2** compared to their parent 2-phenylpyridyl complexes.

M, R =	Rh, H Ref.[30]	Rh, P(S)iPr$_2$ **1**	Ir, H Ref.[30]	Ir, P(S)iPr$_2$ **2**
M1–C9	2.036(1)	2.017(4)	2.045(2)	2.032(5)
M1–Cl1	2.392(1)	2.402(1)	2.397(1)	2.392(1)
M1–N1	2.092(1)	2.095(3)	2.080(2)	2.087(4)
C9–M1–N1	78.71(5)	78.7(2)	77.89(9)	77.7(2)
C9–M1–Cl1	88.34(4)	86.8(1)	88.64(7)	85.6(2)
N1–M1–Cl1	87.87(3)	85.54(9)	86.19(6)	83.0(1)

Table S2. Comparison of selected bond lengths [Å] and torsion angles [°] of **5** and **6** with their precursor complexes.

M1, R =	Rh, S	Rh, electron pair *	Rh, AuC	Ir, S	Ir, AuCl
	1	**3**	**5**	**2**	**6**
M1–C9	2.017(4)	2.020(1)	2.014(5)	2.032(5)	2.031(6)
M1–Cl2	2.402(1)	2.389(4)	2.393(1)	2.392(1)	2.394(2)
M1–N1	2.095(3)	2.079(1)	2.091(4)	2.087(4)	2.081(6)
Cp*(cen)–M1···P1–R	15.53(6)	59.28(3)	15.10(5)	11.15(6)	-14.50(5)

* The geometric position of the lone pair of electrons at P1 was estimated by determining the line through P1 and a centroid of the pendant carbon atoms (C1, C4 and C7). Cen = centre of the C_5 ring.

Table S3. Comparison of selected intramolecular distances [Å] and torsion angles [°] of **5** and **6**, with analogous complexes from reference[42].

	Au/Rh	Au/Ir		
	5	**6**		
M1···Au1	6.2471(6)	6.2344(4)	7.278(2)	7.303(1)
Cl1···Cl2	8.025(3)	8.047(3)	7.802(2)	7.849(1)
Cl2–M1···Au1–Cl1	110.34(6)	111.32(6)	40.56(7)	40.52(2)

Table S4. Selected bond lengths [Å] and angles [°] of gold(I) complex **8** and the heterobimetallic complexes **9** and **10**.

	Au **8**	Au/Rh **9**	Au/Ir **10**
Au1-P1	2.554(1)	2.542(1)	2.5164(5)
Au1-P2	2.293(1)	2.312(1)	2.3009(6)
Au1-P3	2.299(1)	2.294(1)	2.3155(6)
Au1-Cl1	2.636(1)	2.610(1)	2.5806(6)
M1-Cl2	/	2.387(1)	2.3889(5)
M1-N1	/	2.100(4)	2.090(2)
M1-C15	/	2.022(4)	2.037(2)
Cl1-Au1-P1	118.58(4)	114.49(4)	113.64(2)
P1-Au1-P2	86.65(4)	85.23(4)	87.68(2)
P1-Au1-P3	85.14(4)	87.26(4)	86.71(2)
P2-Au1-P3	150.11(4)	142.37(4)	139.24(2)
C15-M1-N1	/	78.8(2)	77.97(7)
C15-M1-Cl2	/	86.8(2)	88.74(6)