Supporting information for

Aminophosphine Ligands as a Privileged Platform for Development of Antitumoral Ruthenium(II) Arene Complexes

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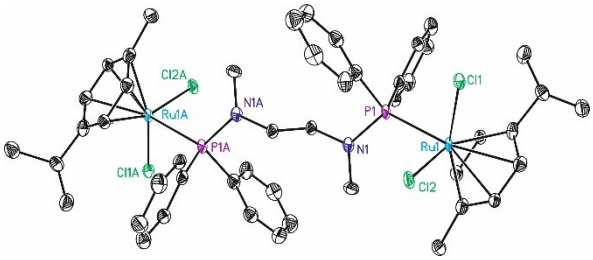
1. Equipment for general procedure.

Routine NMR spectra were recorded on a Bruker-Avance-400-Ultrashield spectrometer equipped with a BBFO plus SmartProbe. ^{1}H- and $^{13}C\{1H\}$-NMR chemical shifts (δ) are given in ppm relative to TMS. Routine GC-MS analyses were recorded on an Agilent 7890B chromatograph equipped with an Agilent 5977A MSD detector. Additional mass spectra were recorded on a Waters Micromass LCT Premier (ESI). A Bruker-Nonius diffractometer equipped with an Apex II 4K CCD area detector was used for single-crystal diffraction.

2. X-ray crystallographic structure determination.

Table S1. Crystallographic details for **Ru1**



Crystal data and structure refinement for LB135_25.

Identification code	LB135_25	
Empirical formula	C52 H62 Cl16 N2 P2 Ru2	
Formula weight	1546.31	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.9333(17)Å	α= 69.559(4)°.
	b = 11.2468(15)Å	β = 77.274(5)°.
	c = 14.0128(17)Å	γ = 84.437(5)°.
Volume	1574.5(4) $Å^3$	
Z	1	
Density (calculated)	1.631 Mg/m^3	
Absorption coefficient	1.246 mm^{-1}	
F(000)	778	
Crystal size	0.06 x 0.05 x 0.02 mm^3	
Theta range for data collection	1.583 to 25.164°.	
Index ranges	-12<=h<=13,-12<=k<=13,0<=l<=16	
Reflections collected	5477	
Independent reflections	5477[R(int) = 0.0724]	
Completeness to theta =25.164°	97.2%	
Absorption correction	Empirical	
Max. and min. transmission	0.976 and 0.733	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5477/ 312/ 375	
Goodness-of-fit on F^2	1.144	
Final R indices [I>2sigma(I)]	R1 = 0.0885, wR2 = 0.2374	
R indices (all data)	R1 = 0.1087, wR2 = 0.2490	
Largest diff. peak and hole	1.950 and -2.003 e.$Å^-$	

Table S2. Crystallographic details for **Ru3**

Crystal data and structure refinement for mo_LB353Cb-055.

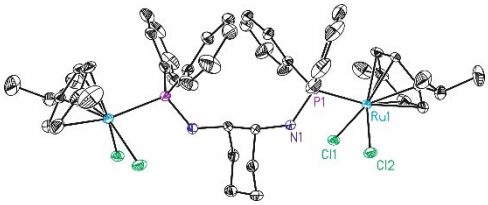
Identification code	mo_LB353Cb-055	
Empirical formula	$C_{41}H_{78}Cl_{12}N_2P_2Ru_2$	
Formula weight	1288.53	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 18.725(2)Å	α= 90°.
	b = 13.2472(18)Å	β = 93.657(5)°.
	c = 22.395(3)Å	γ = 90°.
Volume	5543.9(13) $Å^3$	
Z	4	
Density (calculated)	1.544 Mg/m^3	
Absorption coefficient	1.212 mm^{-1}	
F(000)	2640	
Crystal size	0.12 x 0.12 x 0.03 mm^3	
Theta range for data collection	1.822 to 27.225°.	
Index ranges	-24<=h<=24,-16<=k<=16,-28<=l<=28	
Reflections collected	17328	
Independent reflections	17328[R(int) =?]	
Completeness to theta =27.225°	96.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.965 and 0.742	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17328/ 644/ 721	
Goodness-of-fit on F^2	1.075	
Final R indices [I>2sigma(I)]	R1 = 0.0768, wR2 = 0.2078	
R indices (all data)	R1 = 0.0814, wR2 = 0.2148	
Flack parameter	x =-1.2(2)	
Largest diff. peak and hole	1.283 and -0.956 e.$Å^{-3}$	

Table S3. Crystallographic details for **Ru5**

Crystal data and structure refinement for mo_LB337_04.

Identification code	mo_LB337_04	
Empirical formula	$C_{50}H_{61}Cl_7N_2P_2Ru_2$	
Formula weight	1202.23	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.2885(16)Å	α= 90°.
	b = 36.990(7)Å	β = 104.031(5)°.
	c = 13.802(2)Å	γ = 90°.
Volume	5095.8(15) $Å^3$	
Z	4	
Density (calculated)	1.567 Mg/m^3	
Absorption coefficient	1.060 mm^{-1}	
F(000)	2448	
Crystal size	0.08 x 0.03 x 0.03 mm^3	
Theta range for data collection	1.101 to 24.818°.	
Reflections collected	8537	
Independent reflections	8537[R(int) =?]	
Completeness to theta =24.818°	97.1%	
Absorption correction	Empirical	
Max. and min. transmission	0.969 and 0.526	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8537/ 312/ 670	
Goodness-of-fit on F^2	0.908	
Final R indices [I>2sigma(I)]	R1 = 0.0793, wR2 = 0.1620	
R indices (all data)	R1 = 0.1823, wR2 = 0.1997	
Largest diff. peak and hole	1.476 and -1.867 $e.Å^{-3}$	

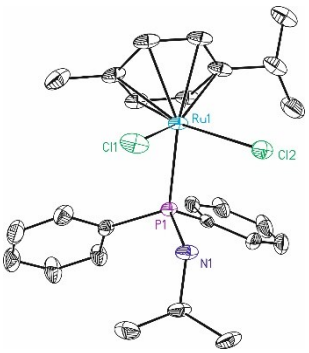
Table S4. Crystallographic details for **Ru8**



Crystal data and structure refinement for mo_LB326_0m.

Identification code	mo_LB326_0m	
Empirical formula	$C_{50}H_{60}Cl_4N_2P_2Ru_2$	
Formula weight	1094.88	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 19.7175(12)Å	α= 90°.
	b = 13.6257(8)Å	β = 111.7051(15)°.
	c = 19.4388(12)Å	γ = 90°.
Volume	4852.2(5) $Å^3$	
Z	4	
Density (calculated)	1.499 Mg/m^3	
Absorption coefficient	0.945 mm^{-1}	
F(000)	2240	
Crystal size	0.25 x 0.10 x 0.07 mm^3	
Theta range for data collection	1.863 to 34.889°.	
Index ranges	-26<=h<=31,-21<=k<=21,-28<=l<=30	
Reflections collected	50883	
Independent reflections	10063[R(int) = 0.0232]	
Completeness to theta =34.889°	94.9%	
Absorption correction	Empirical	
Max. and min. transmission	0.937 and 0.86	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10063/ 17/ 304	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0282, wR2 = 0.0677	
R indices (all data)	R1 = 0.0356, wR2 = 0.0734	
Largest diff. peak and hole	1.534 and -0.625 $e.Å^{-3}$	

Table S5. Crystallographic details for **Ru9**



Crystal data and structure refinement for LB327b-05.

Identification code	LB327b-05	
Empirical formula	C25 H32 Cl2 N P Ru	
Formula weight	549.45	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.0527(5)Å	α= 90°.
	b = 14.1683(7)Å	β = 100.4265(14)°.
	c = 17.5477(9)Å	γ = 90°.
Volume	2458.0(2) $Å^3$	
Z	4	
Density (calculated)	1.485 Mg/m^3	
Absorption coefficient	7.860 mm^{-1}	
F(000)	1128	
Crystal size	0.15 x 0.15 x 0.10 mm^3	
Theta range for data collection	4.037 to 68.287°.	
Index ranges	-11<=h<=11,0<=k<=16,0<=l<=21	
Reflections collected	4276	
Independent reflections	4276[R(int) =?]	
Completeness to theta =68.287°	95.1%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.507 and 0.39	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4276/ 13/ 280	
Goodness-of-fit on F^2	1.115	
Final R indices [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.0933	
R indices (all data)	R1 = 0.0336, wR2 = 0.0948	
Largest diff. peak and hole	0.931 and -0.935 $e.Å^{-3}$	

Table S6. Crystallographic details for **Ru11.**

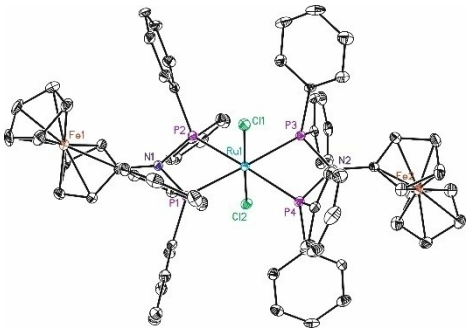
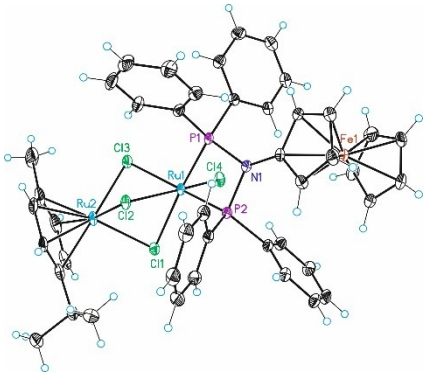


Table 1. Crystal data and structure refinement for **Ru11**.

Identification code	LB133	
Empirical formula	$C_{68}H_{58}Cl_2Fe_2N_2P_4Ru$	
Formula weight	1310.71	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 24.374(2) Å	α= 90.00 °.
	b = 11.4323(10) Å	β = 108.050(3) °.
	c = 21.033(2) Å	γ = 90.00 °.
Volume	5572.5(9) $Å^3$	
Z	4	
Density (calculated)	1.562 Mg/m^3	
Absorption coefficient	1.039 mm^{-1}	
F(000)	2680	
Crystal size	0.12 x 0.06 x 0.04 mm^3	
Theta range for data collection	0.88 to 29.68 °.	
Index ranges	-25 <=h<=33 ,-9 <=k<=15 ,-29 <=l<=24	
Reflections collected	51897	
Independent reflections	15625 [R(int) = 0.0771]	
Completeness to theta =29.68 °	99.0%	
Absorption correction	Empirical	
Max. and min. transmission	0.9596 and 0.8855	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15625 / 0 / 712	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0490 , wR2 = 0.0907	
R indices (all data)	R1 = 0.0928 , wR2 = 0.1070	
Largest diff. peak and hole	0.724 and -0.809 $e.Å^{-3}$	

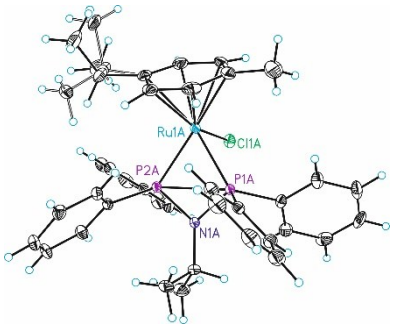
Table S7. Crystallographic details for **Ru13**



Crystal data and structure refinement for **Ru13.**

Identification code	LB129_0m	
Empirical formula	$C_{46}H_{45}Cl_{10}FeNP_2Ru_2$	
Formula weight	1286.26	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.3629(7)Å	α= 82.317(2)°.
	b = 13.5134(9)Å	β = 84.668(2)°.
	c = 18.8728(13)Å	γ = 74.300(2)°.
Volume	2517.0(3) $Å^3$	
Z	2	
Density (calculated)	1.697 Mg/m^3	
Absorption coefficient	1.505 mm^{-1}	
F(000)	1284	
Crystal size	0.15 x 0.10 x 0.04 mm^3	
Theta range for data collection	1.575 to 30.570°.	
Index ranges	-14<=h<=10,-18<=k<=19,-26<=l<=22	
Reflections collected	32494	
Independent reflections	14486[R(int) = 0.0274]	
Completeness to theta =30.570°	93.9%	
Absorption correction	Empirical	
Max. and min. transmission	0.942 and 0.779	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14486/ 36/ 634	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.0963	
R indices (all data)	R1 = 0.0521, wR2 = 0.1051	
Largest diff. peak and hole	1.696 and -1.288 e.$Å^{-3}$	

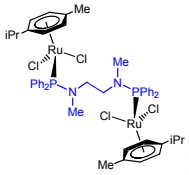
Table S8. Crystallographic details for **Ru14**



Crystal data and structure refinement for mo_LB96_0m.

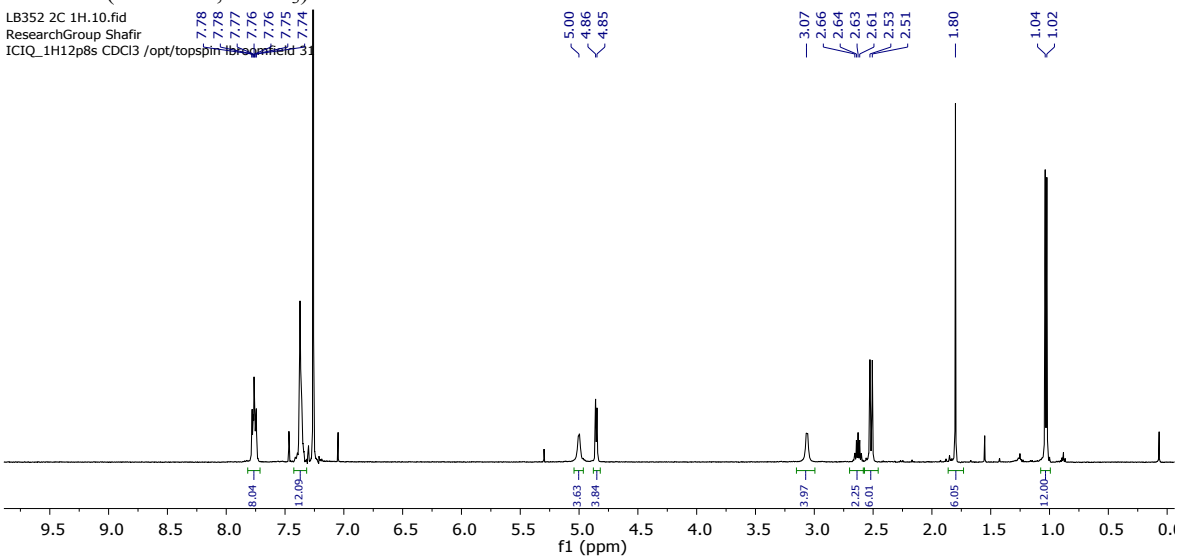
Identification code	mo_LB96_0m	
Empirical formula	$C_{75}H_{86}B_2Cl_2F_8N_2OP_4Ru_2$	
Formula weight	1601.99	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.3175(8)Å	α= 90°.
	b = 19.2105(12)Å	β = 90°.
	c = 36.437(3)Å	γ = 90°.
Volume	7221.9(9) $Å^3$	
Z	4	
Density (calculated)	1.473 Mg/m^3	
Absorption coefficient	0.647 mm^{-1}	
F(000)	3288	
Crystal size	0.20 x 0.08 x 0.08 mm^3	
Theta range for data collection	1.540 to 30.168°.	
Index ranges	-13<=h<=14,-25<=k<=27,-50<=l<=50	
Reflections collected	130627	
Independent reflections	19482[R(int) = 0.0395]	
Completeness to theta =30.168°	93.6%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.950 and 0.874	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19482/ 471/ 993	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0252, wR2 = 0.0527	
R indices (all data)	R1 = 0.0285, wR2 = 0.0540	
Flack parameter	x =-0.022(5)	
Largest diff. peak and hole	0.435 and -0.366 e.$Å^{-3}$	

3. NMR spectra

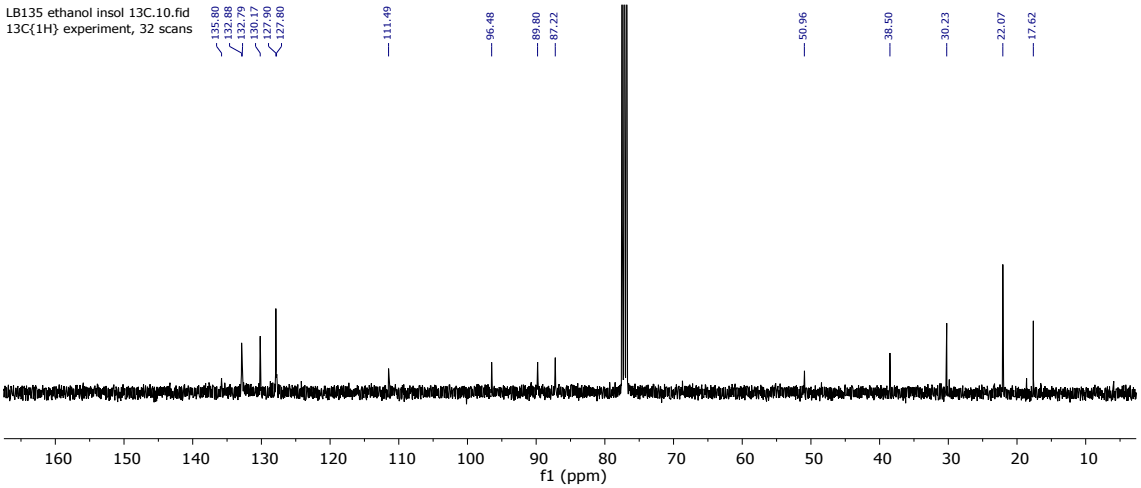


Ru1

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$)

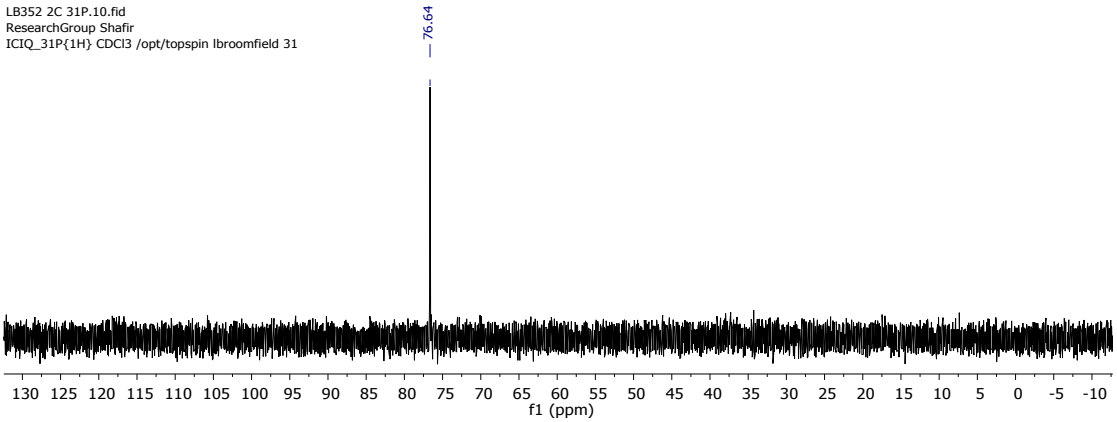
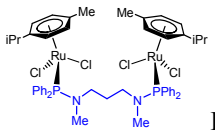
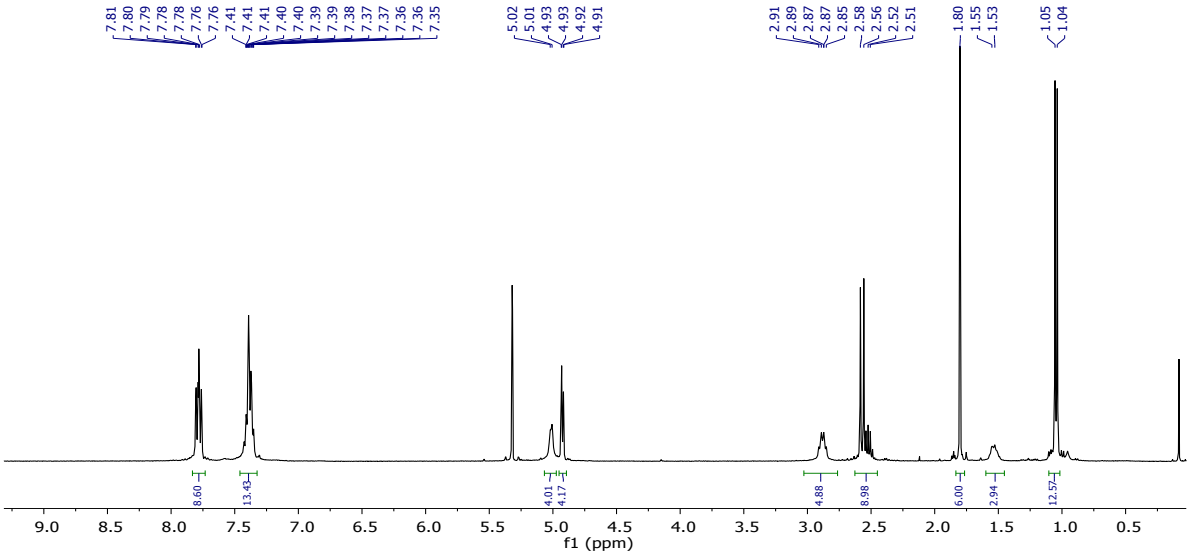


Figure S1

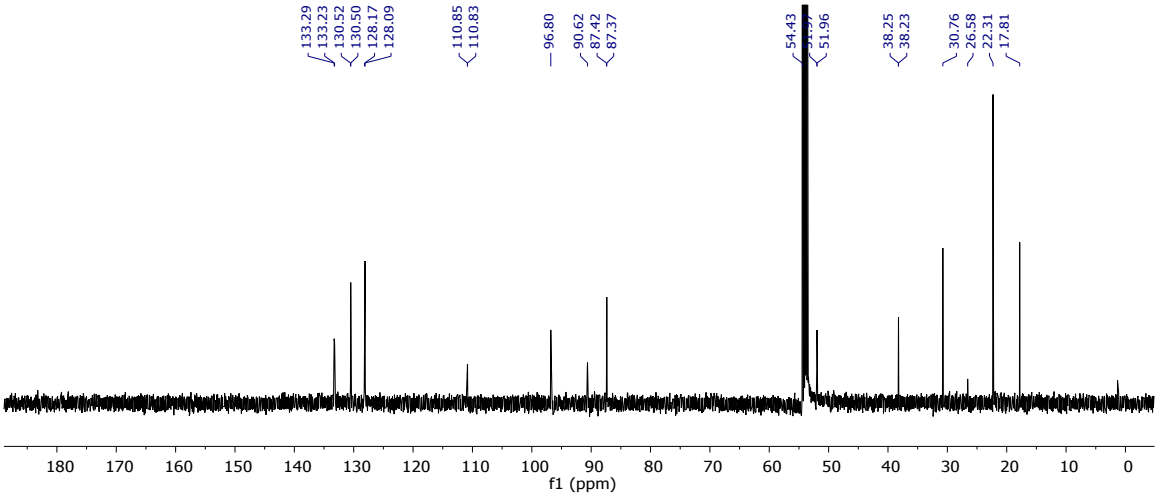


Ru2

^{1}H NMR (400 MHz, CD_2Cl_2)



^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2)



^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2)

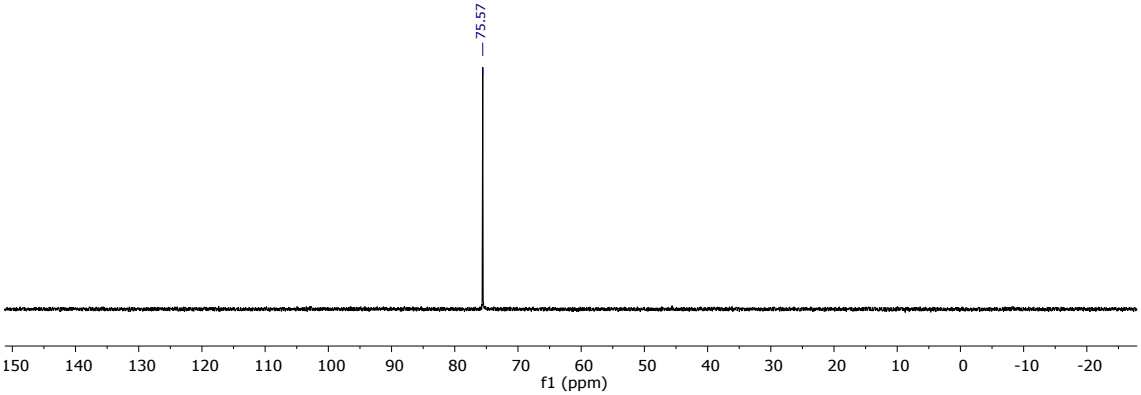
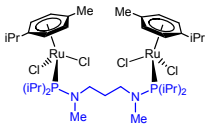
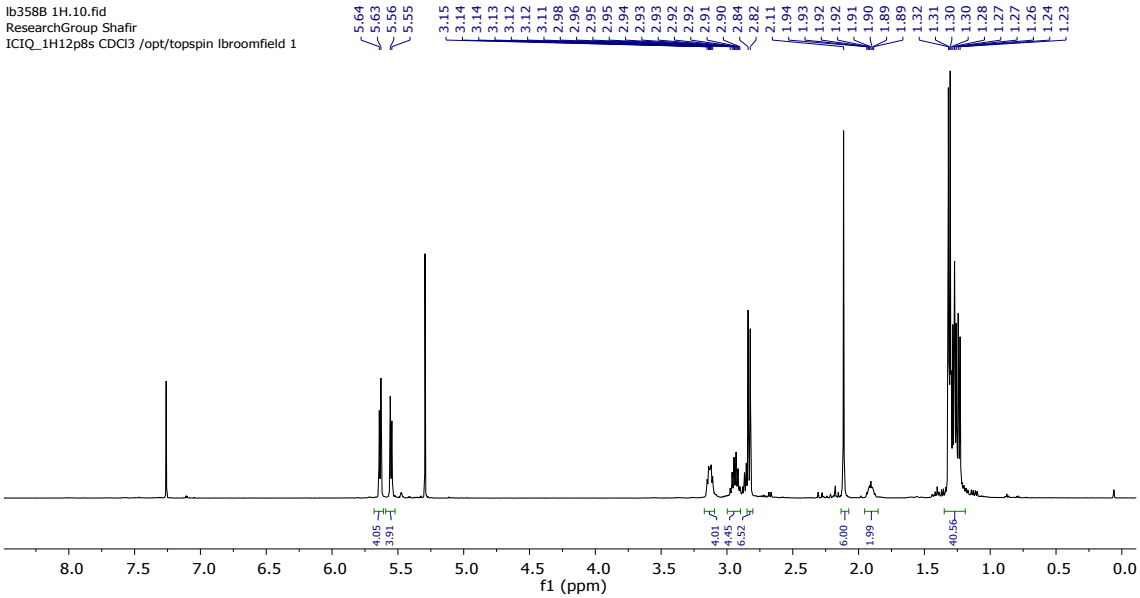


Figure S2

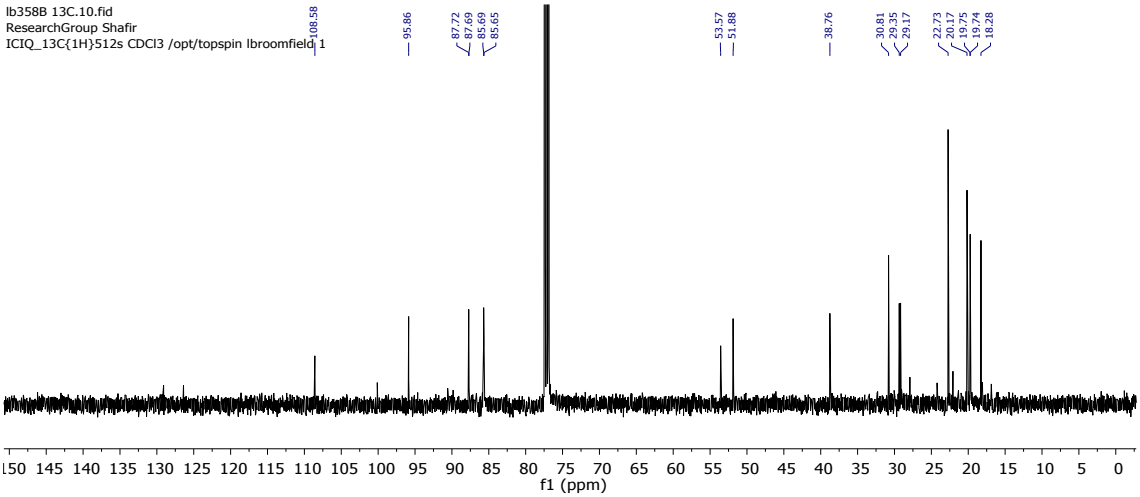


Ru3

^{1}H NMR (500 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)

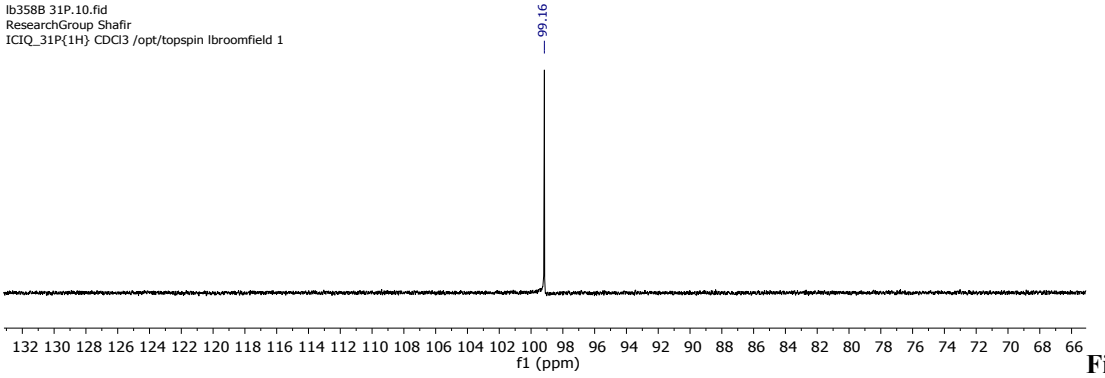
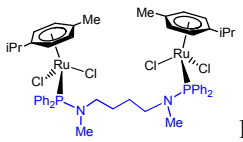
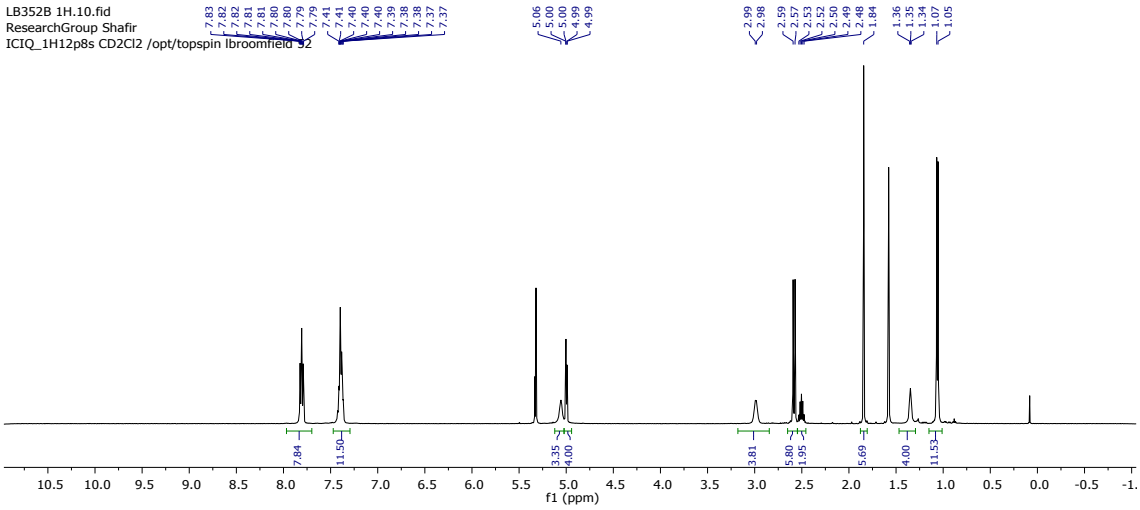


Figure S3

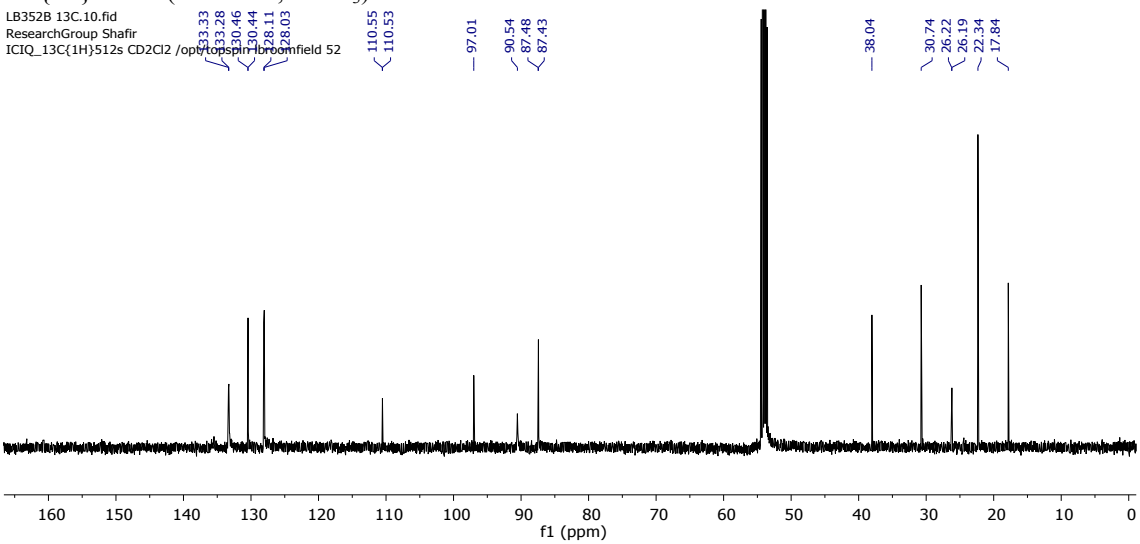


Ru4

^{1}H NMR (500 MHz, CD_2Cl_2)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)

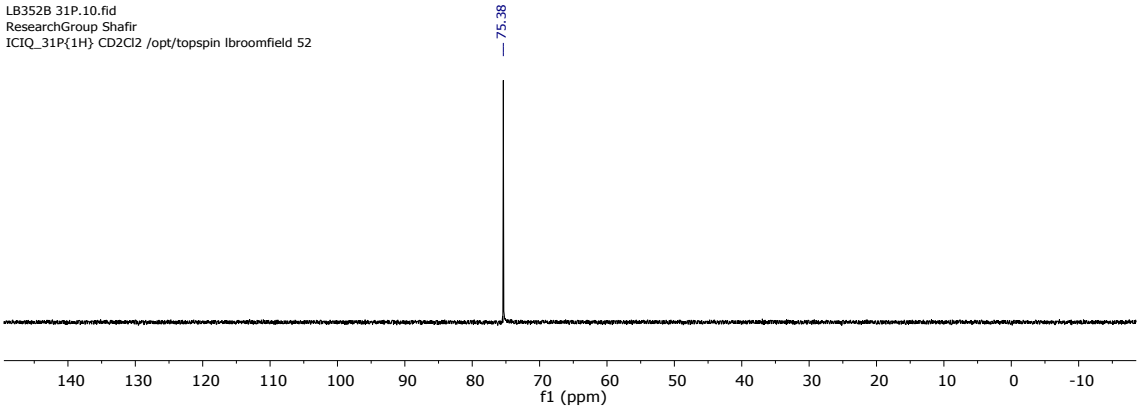
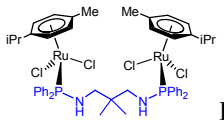
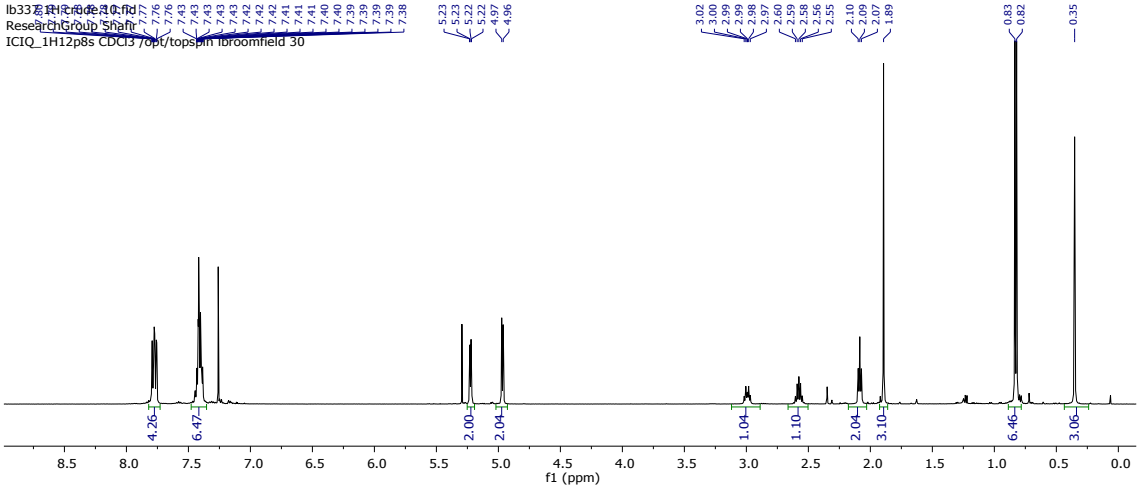


Figure S4

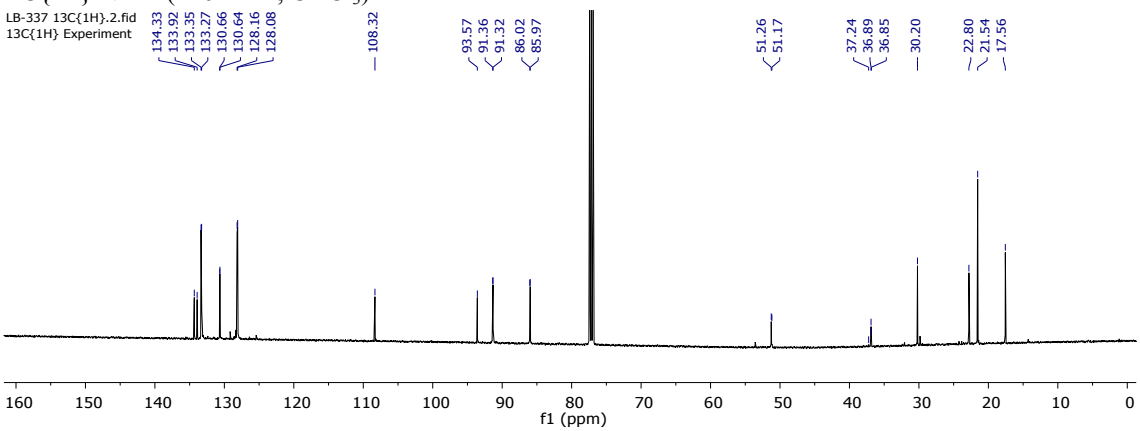


Ru5

^{1}H NMR (500 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



$^{31}P\{^{1}H\}$ NMR ($CDCl_3$)

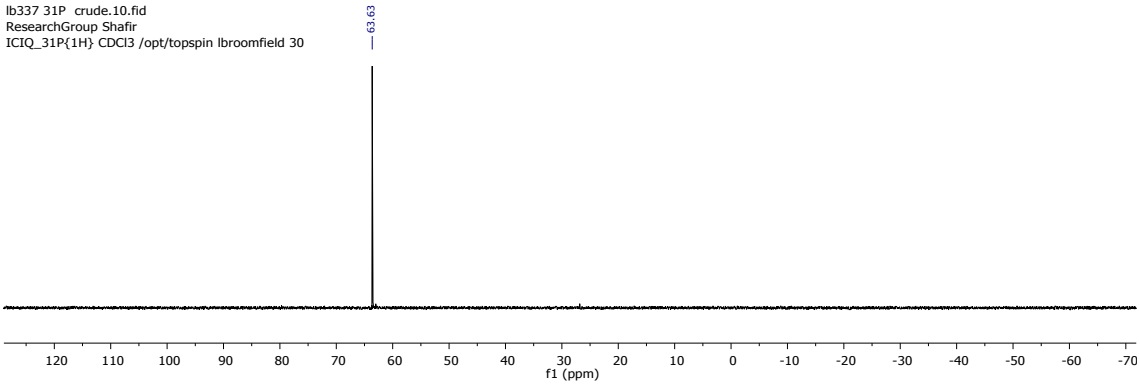
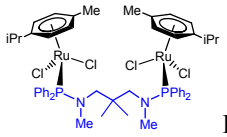
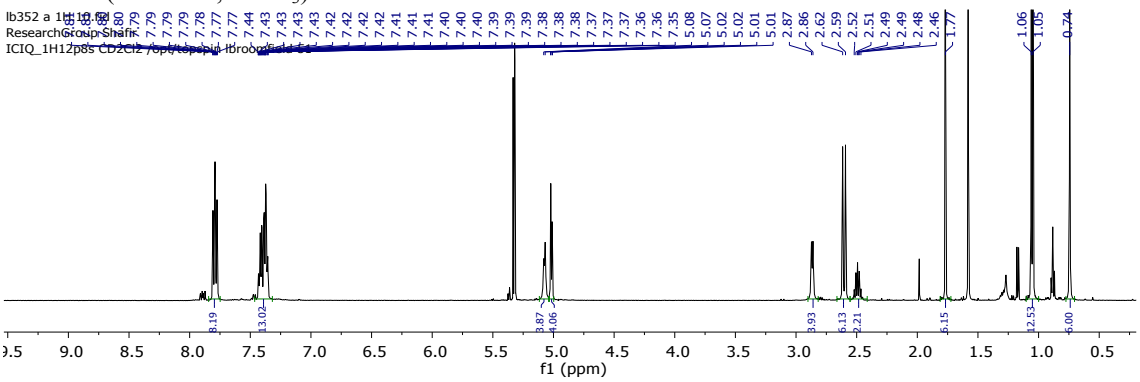


Figure S5

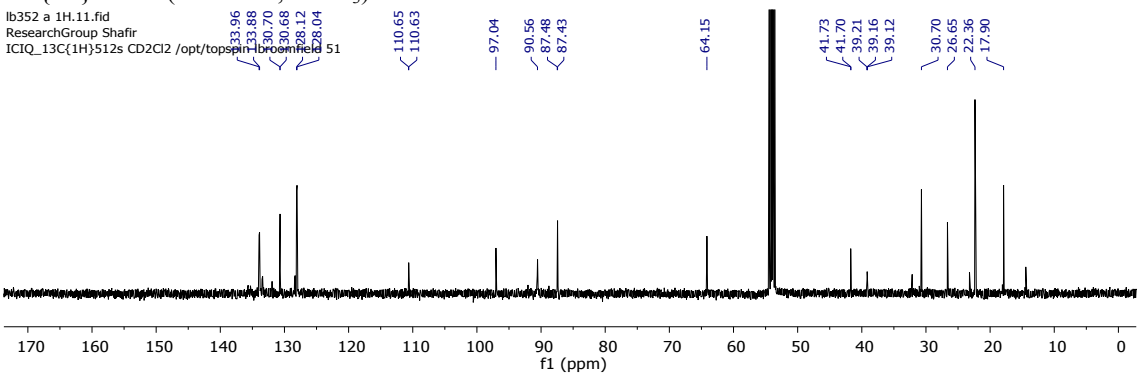


Ru6

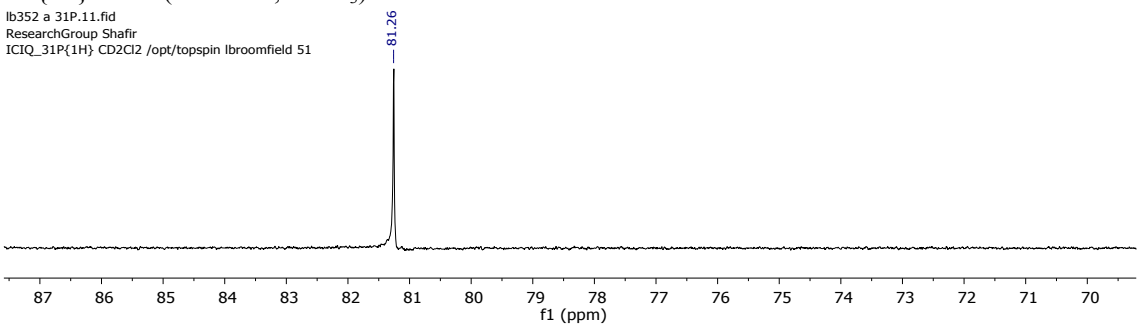
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$)



2DgHSQCped ($CDCl_3$)

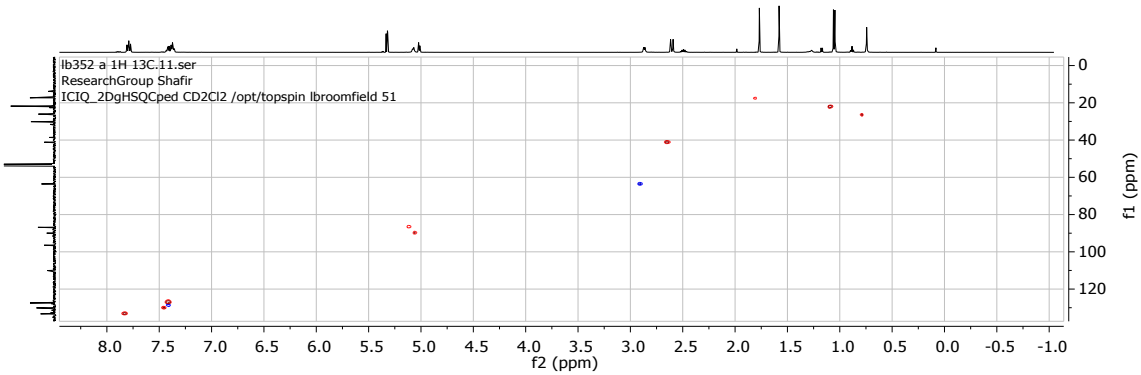
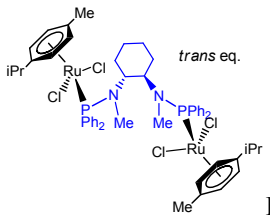
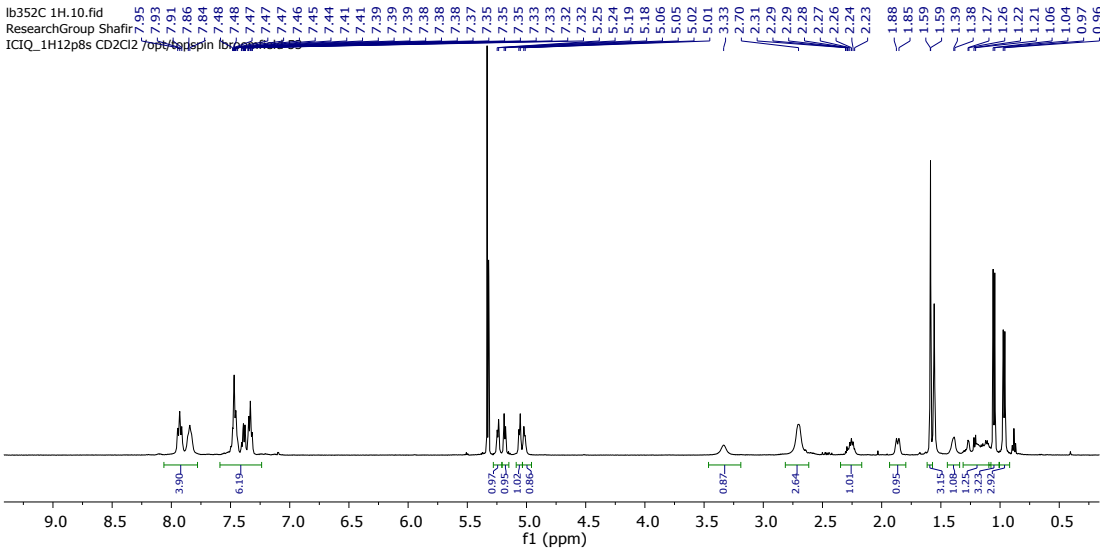


Figure S6

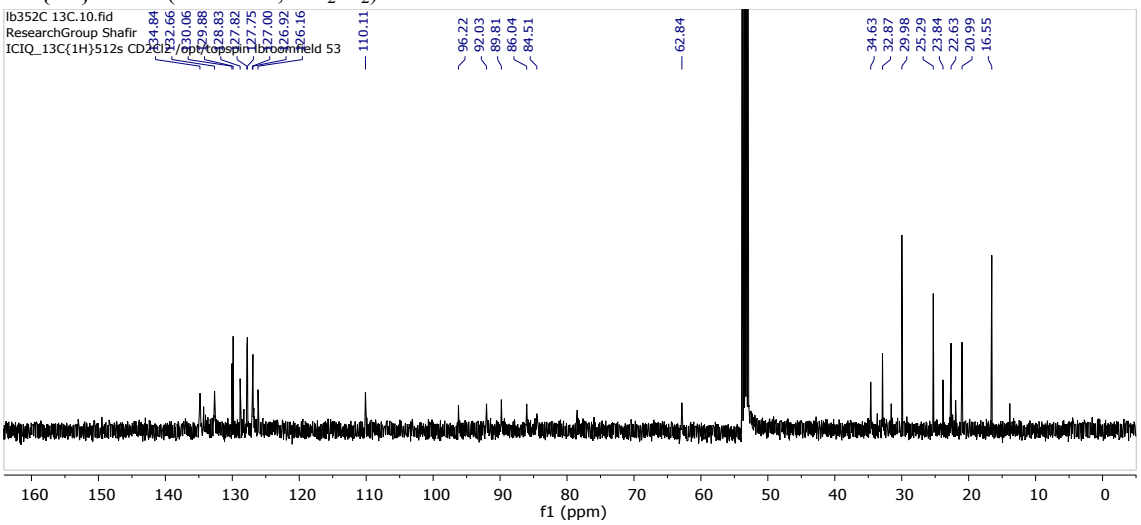


Ru7

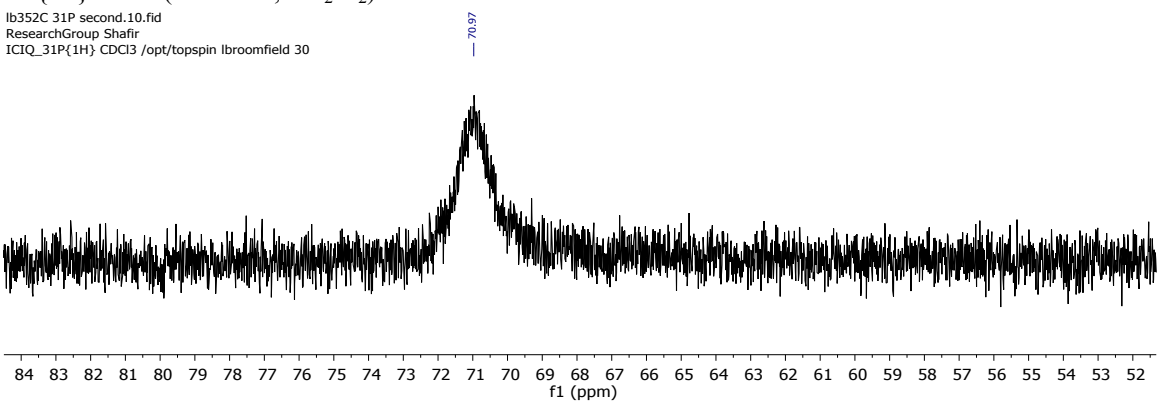
^{1}H NMR (500 MHz, CD_2Cl_2)



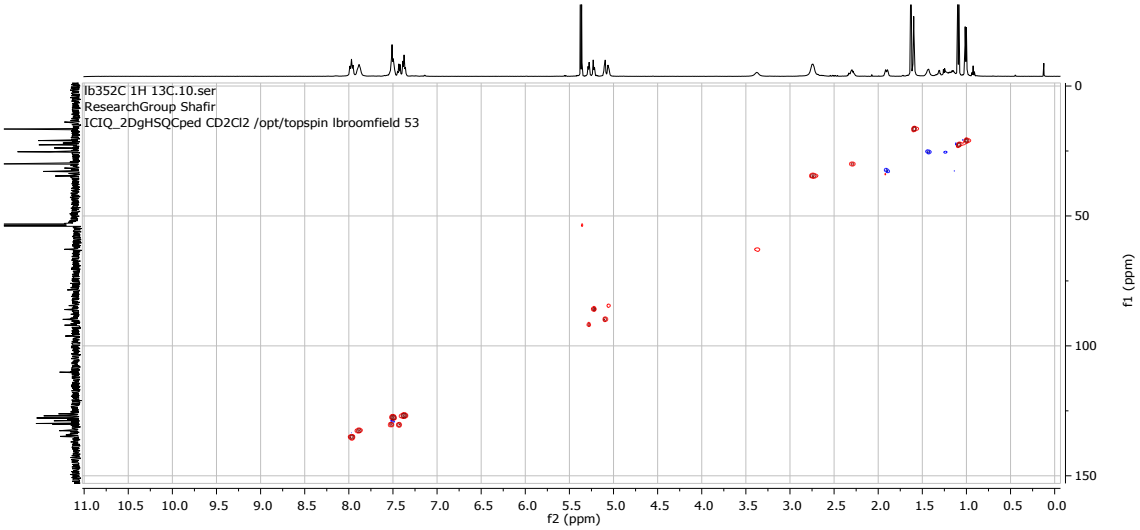
$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2)



$^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2)



2DgHSQCped (CD_2Cl_2)



VT ^{1}H NMR (500 MHz, $CDCl_3$)

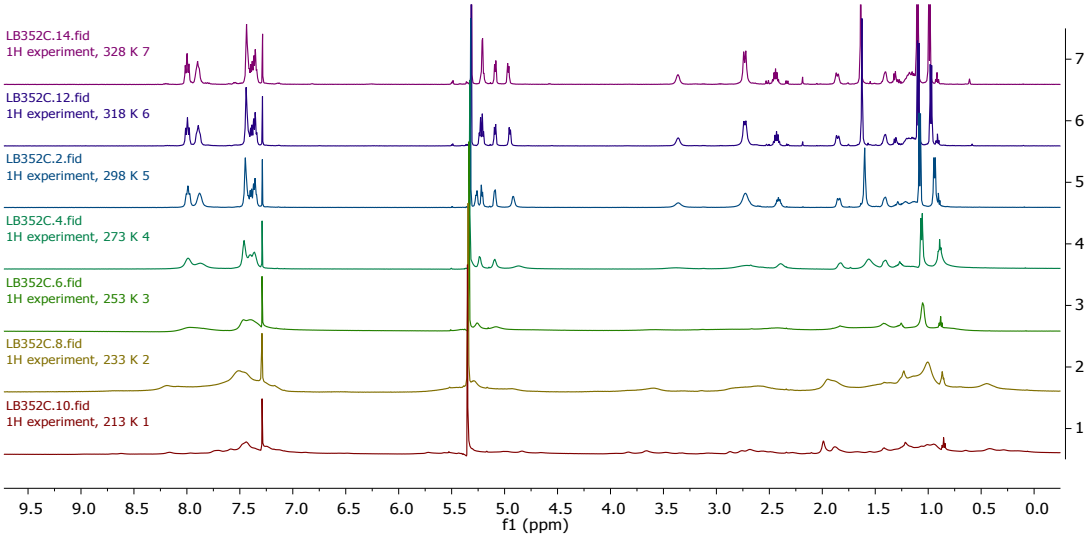
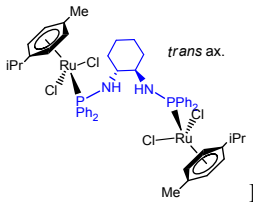
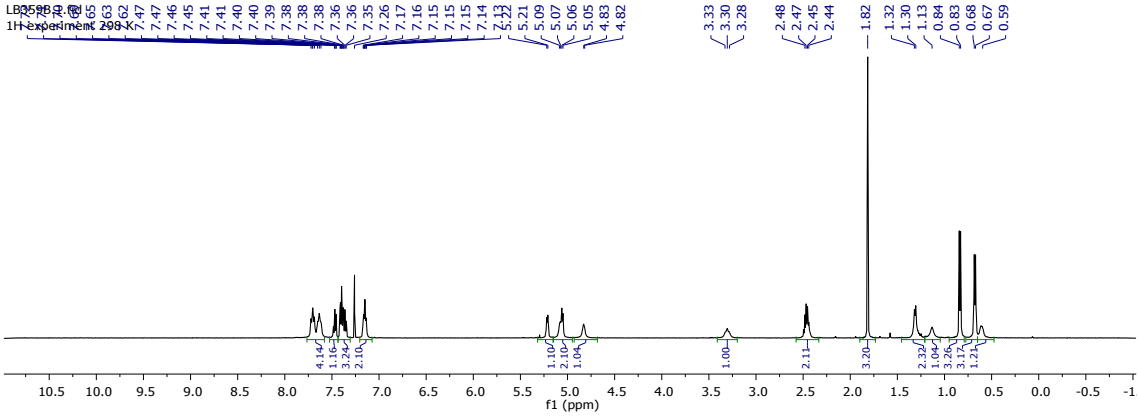


Figure S7

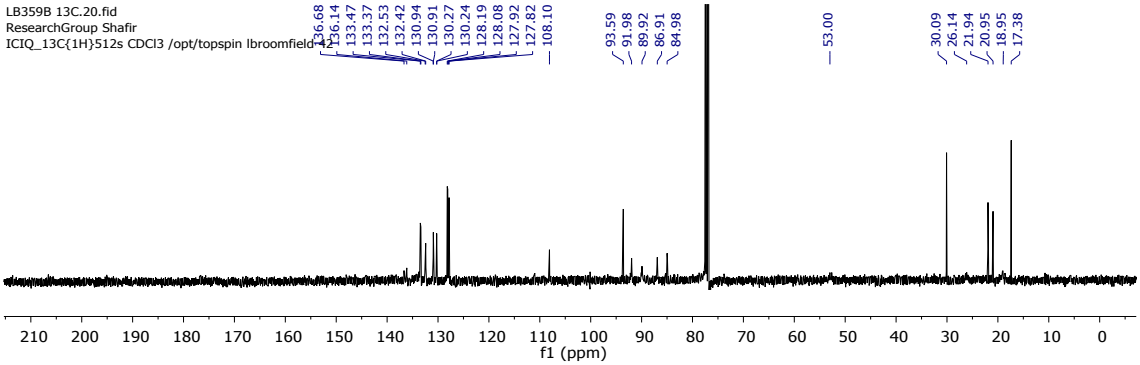


Ru8

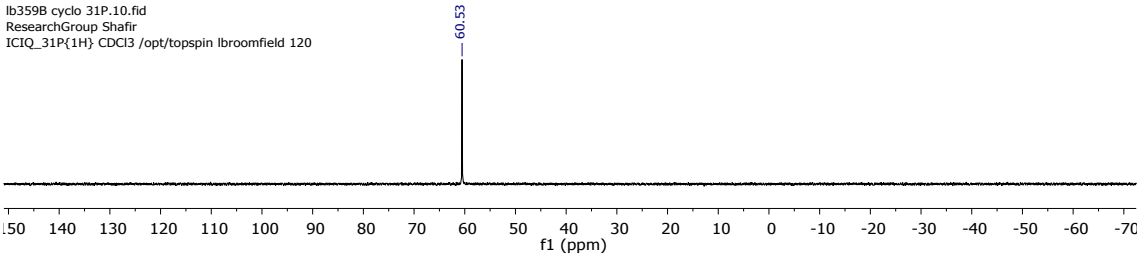
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$)



2DgHSQCped ($CDCl_3$)

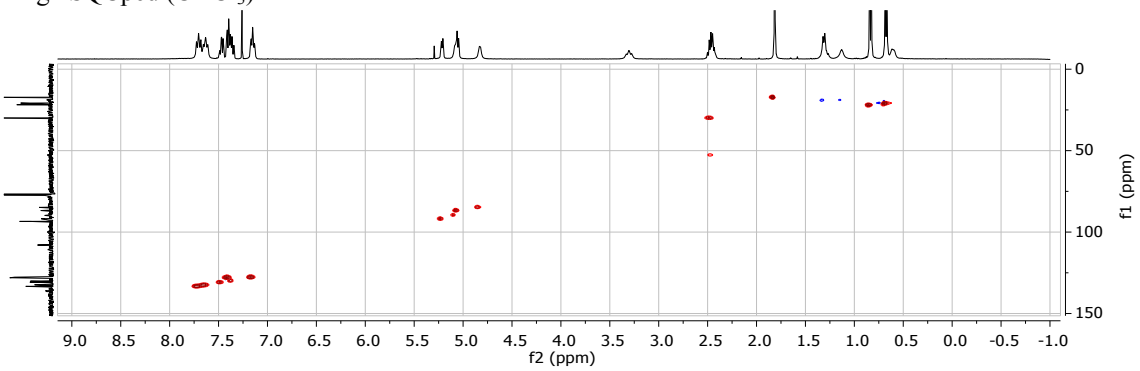
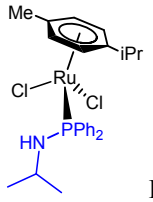
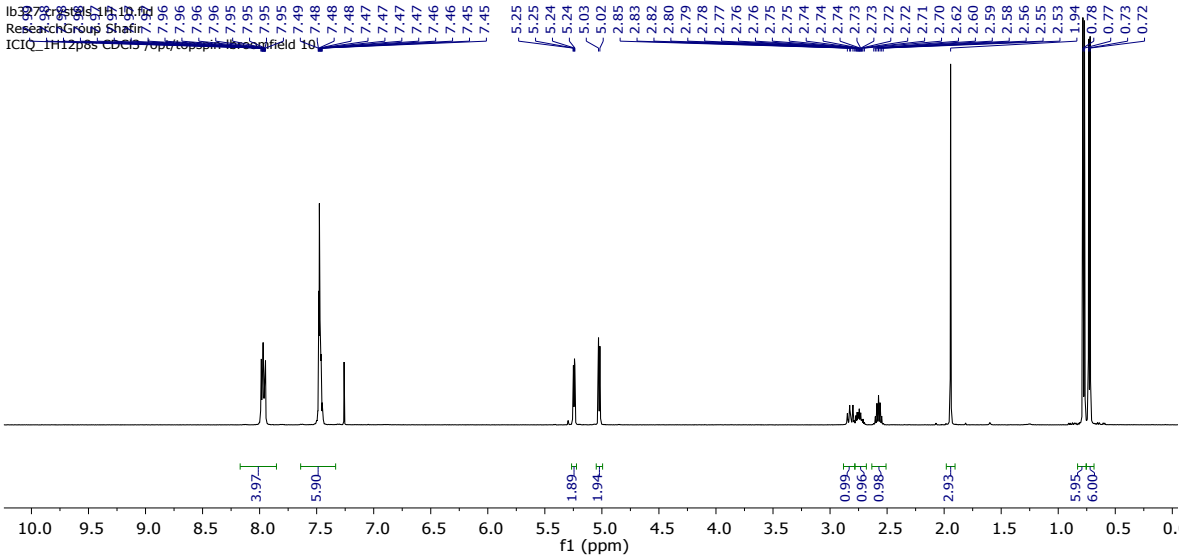


Figure S8

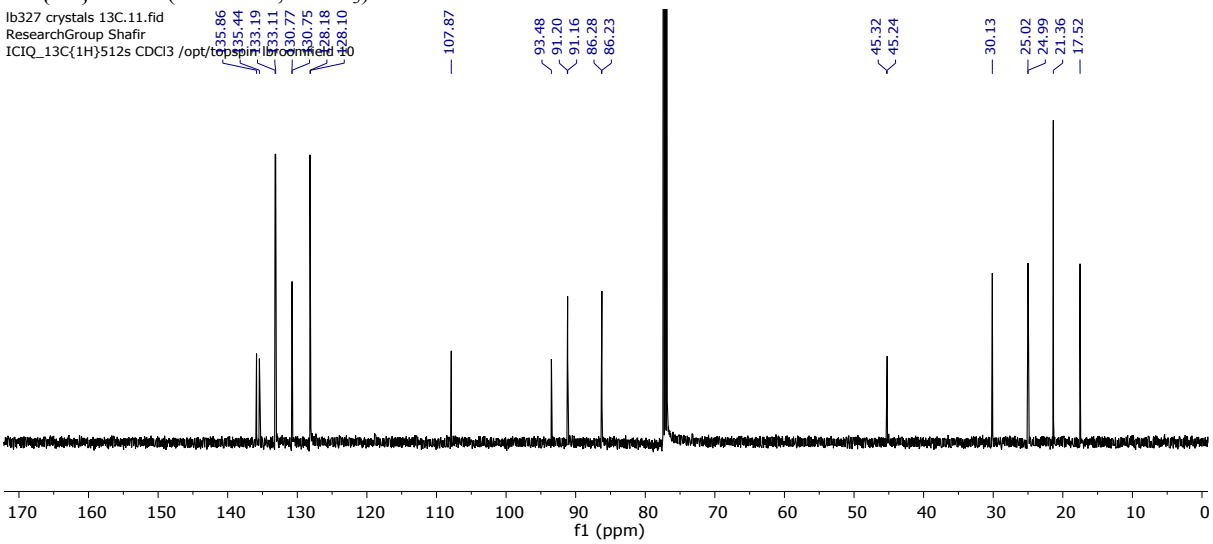


Ru9

^{1}H NMR (500 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)

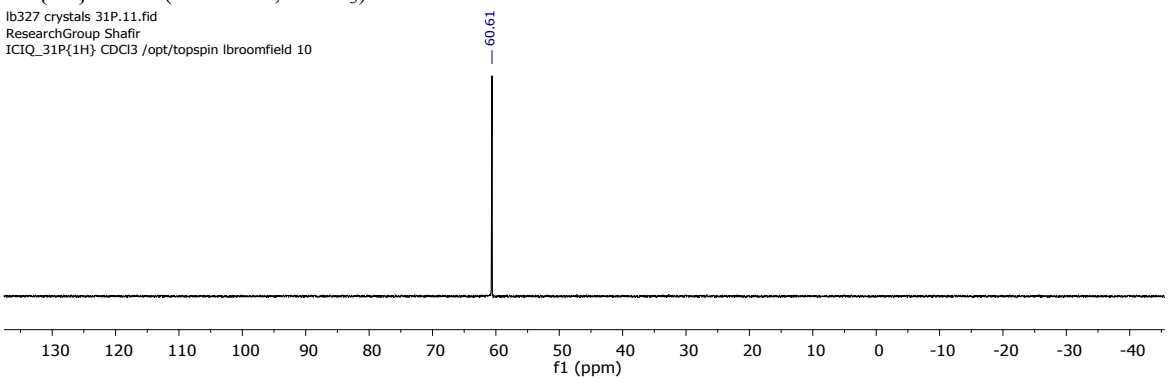
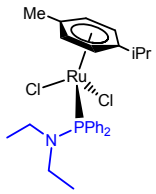
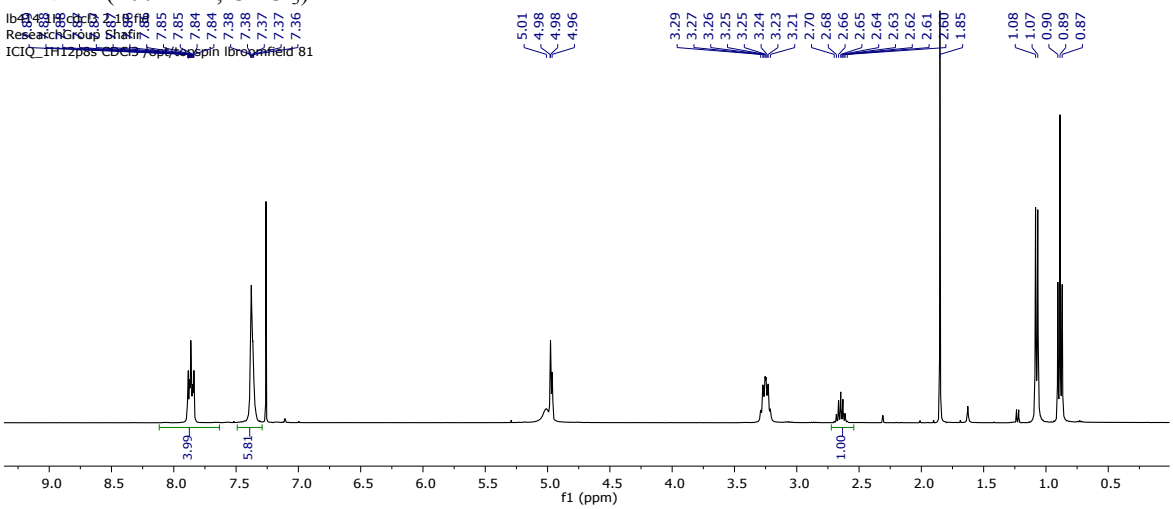


Figure S9

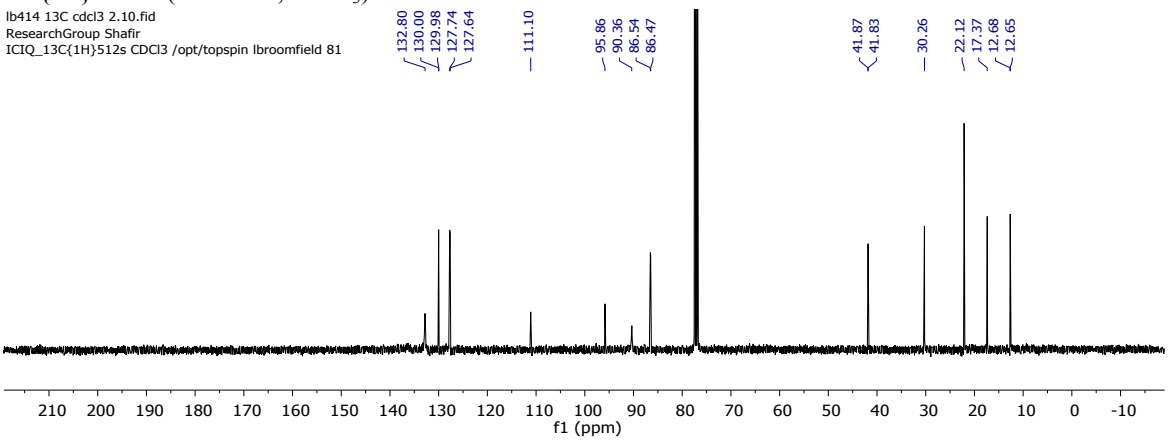


Ru10

^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



$^{31}P\{^{1}H\}$ NMR ($CDCl_3$)

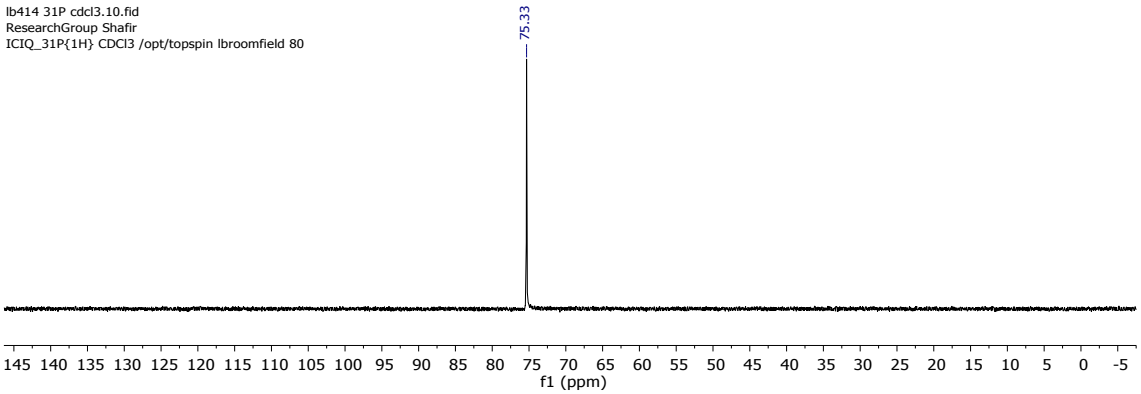
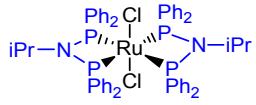
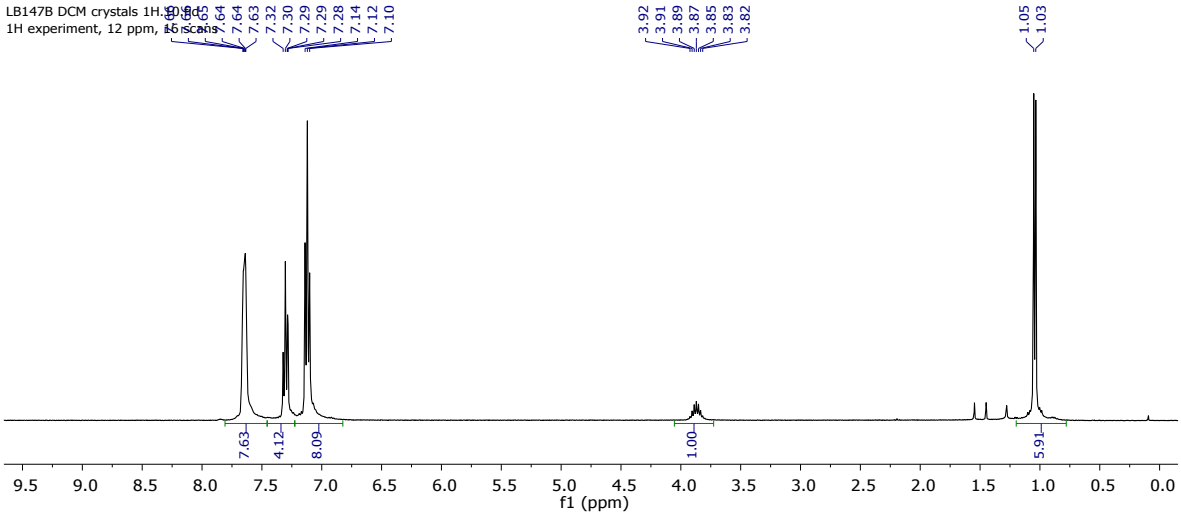


Figure S10

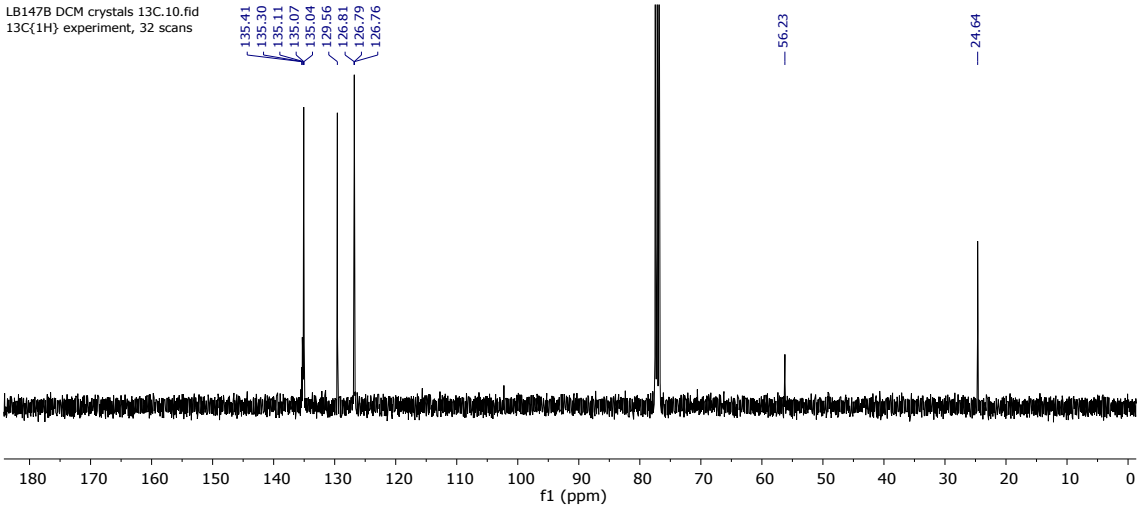


Ru11

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$)

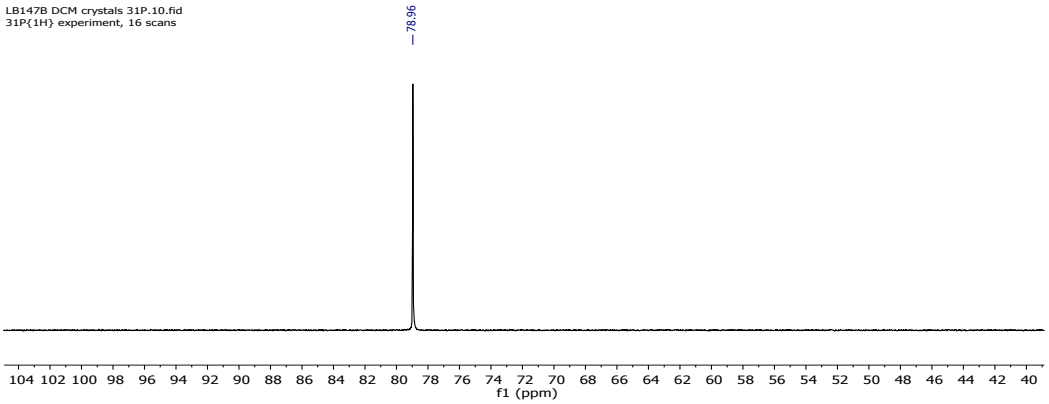
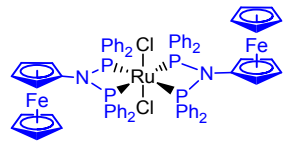
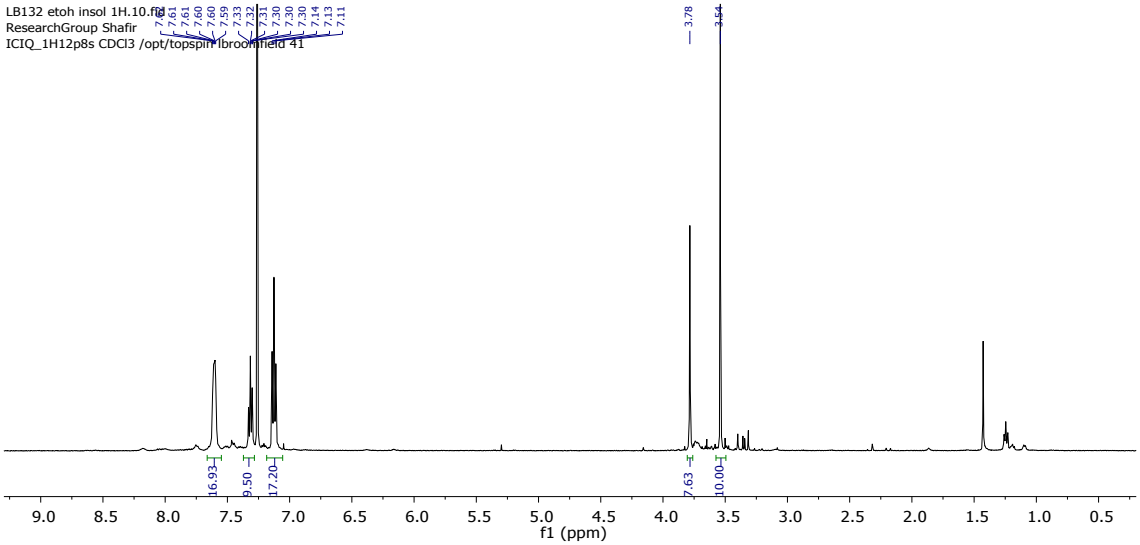


Figure S11

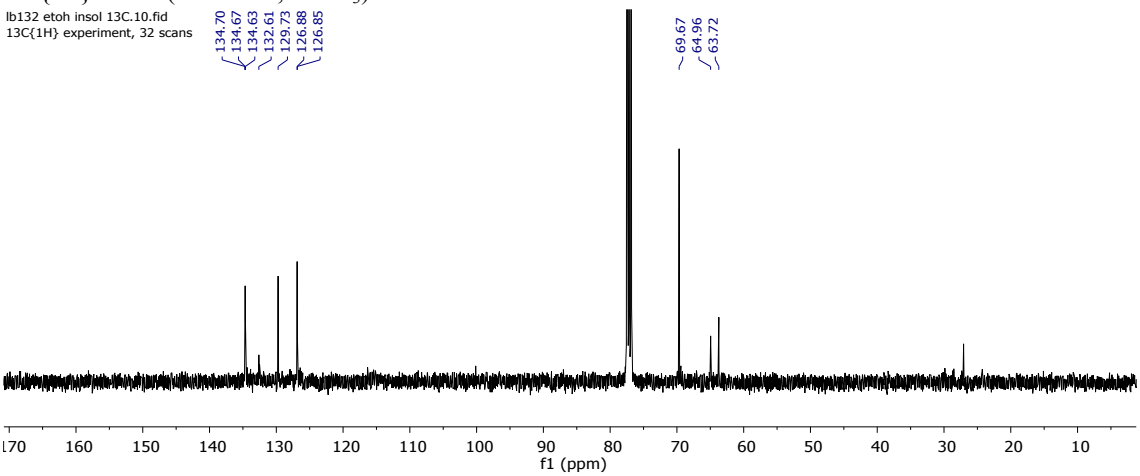


Ru12

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$)

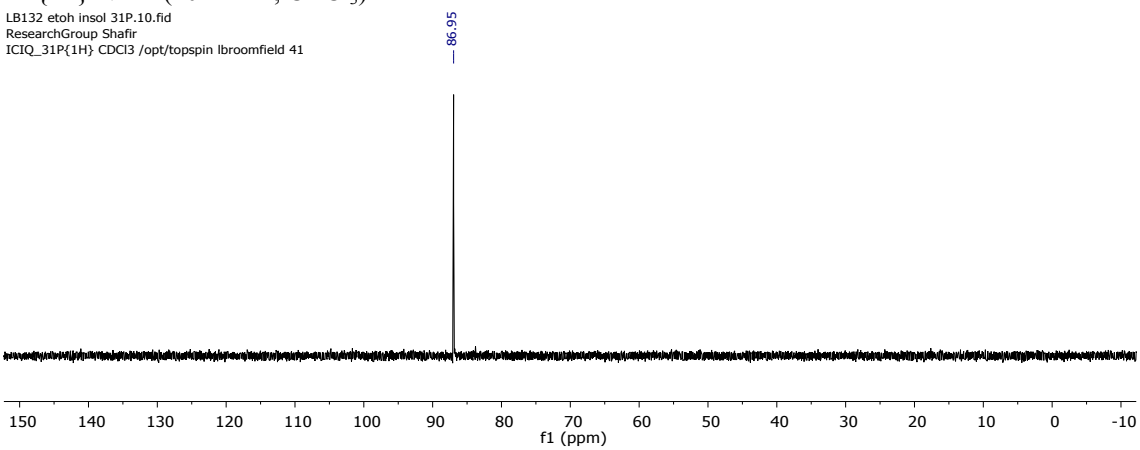
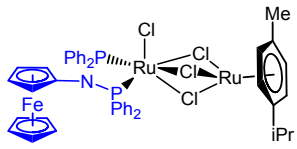
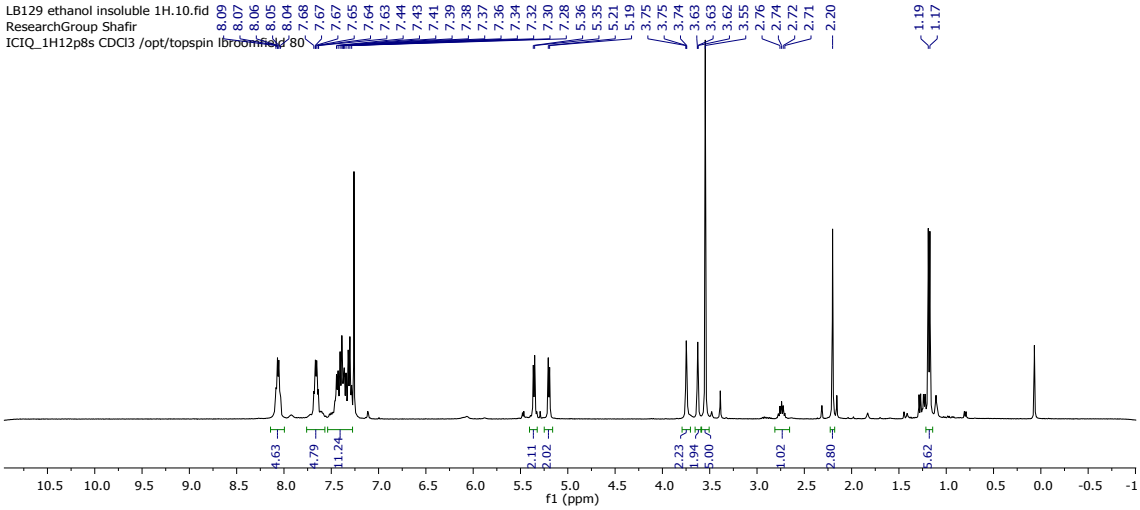


Figure S12

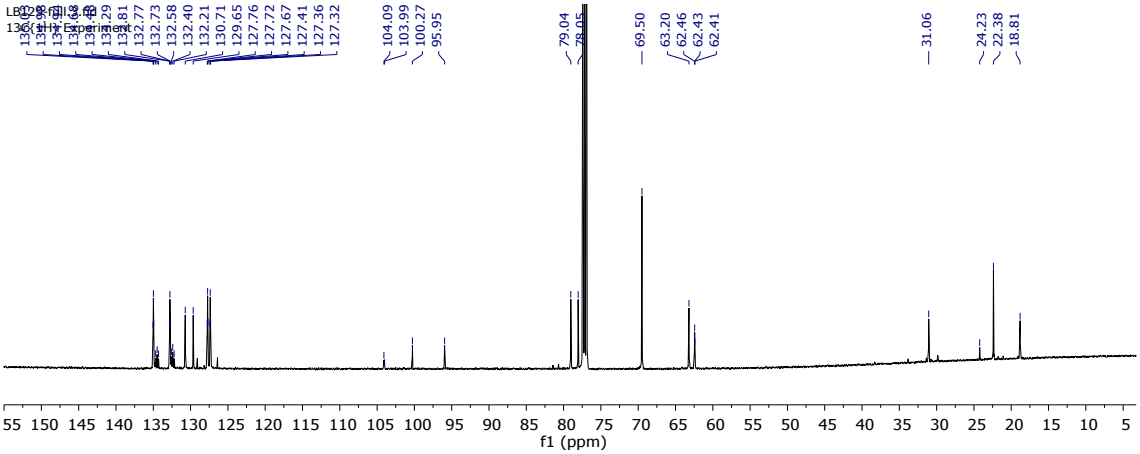


Ru13

^{1}H NMR (400 MHZ, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)

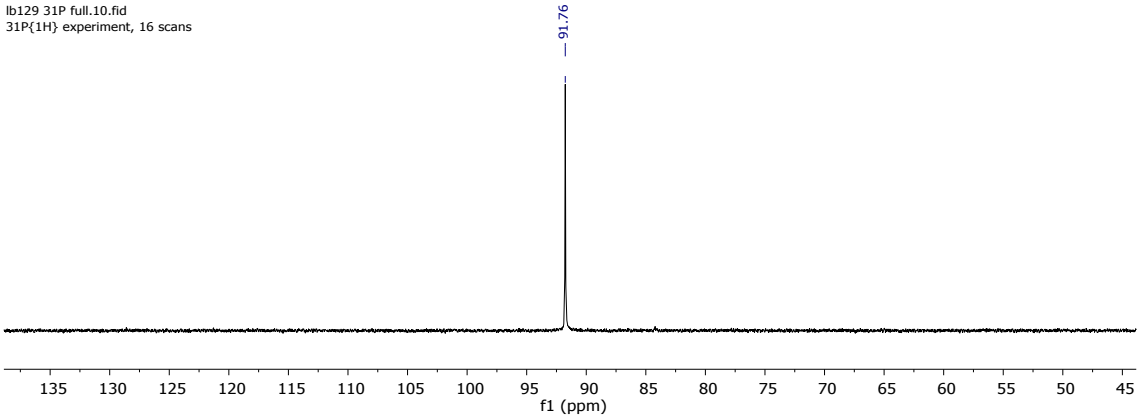
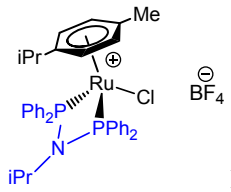
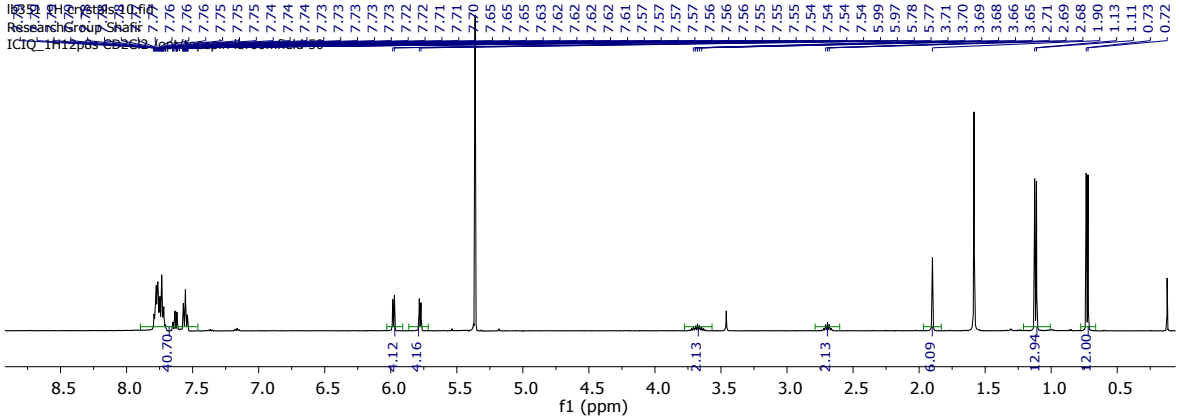


Figure S13

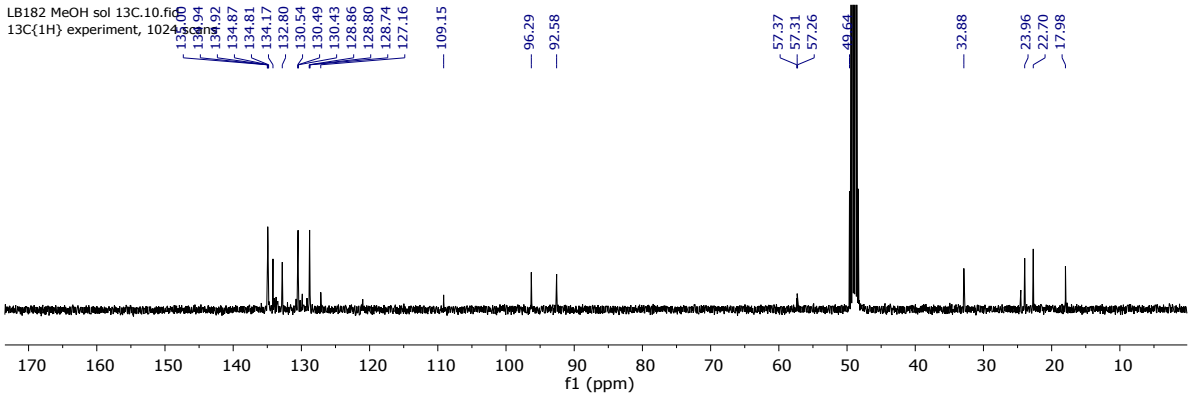


Ru14

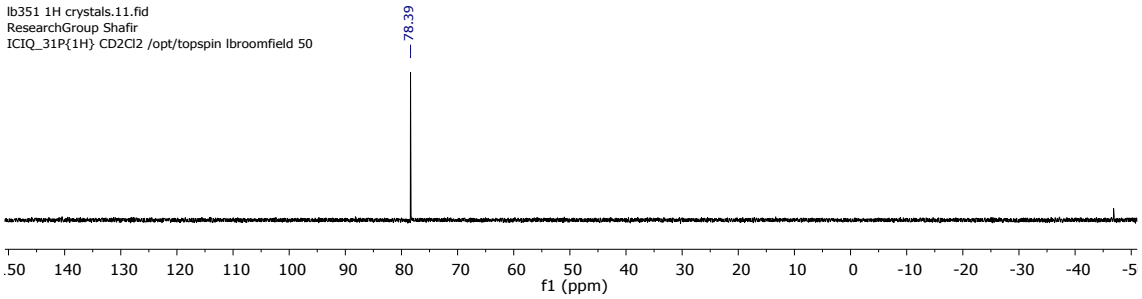
^{1}H NMR (500 MHz, CD_2Cl_2)



$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD)



$^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2)



$^{19}F\{^{1}H\}$ NMR (376 MHz, CD_3OD)

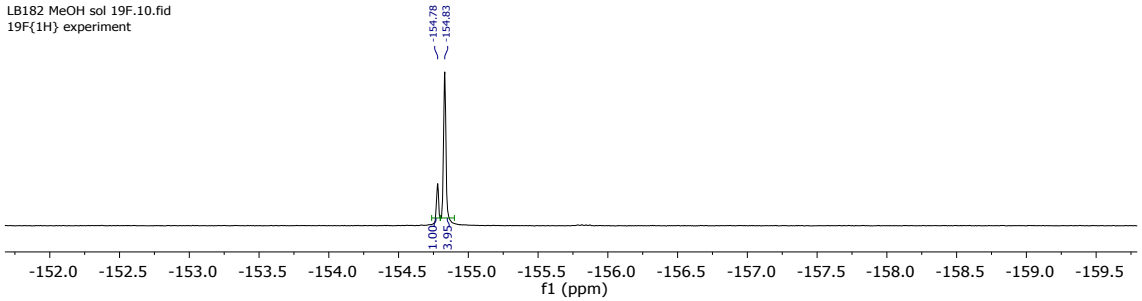
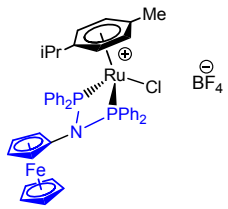
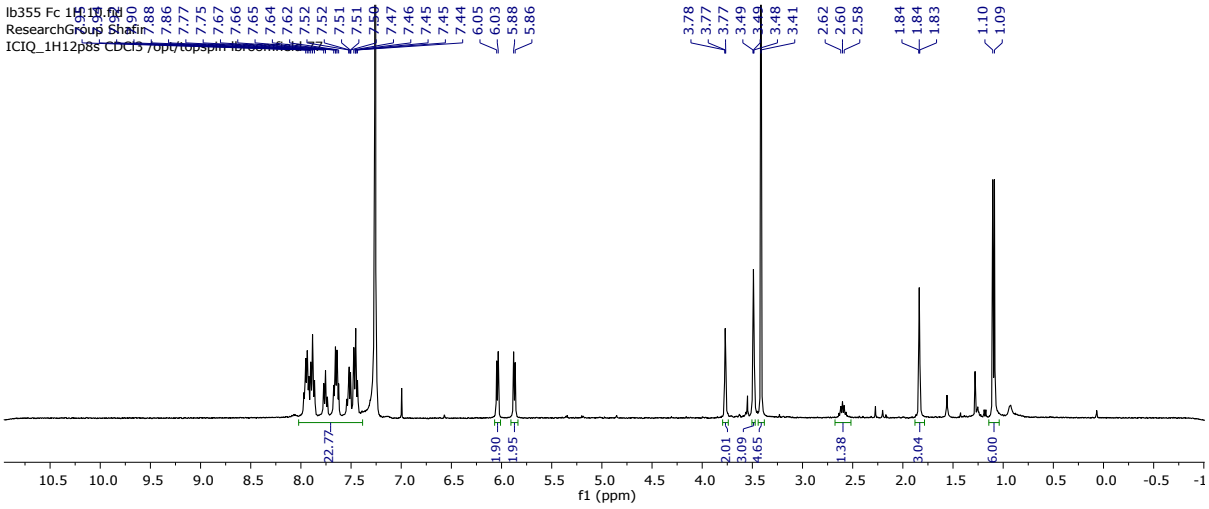


Figure S14

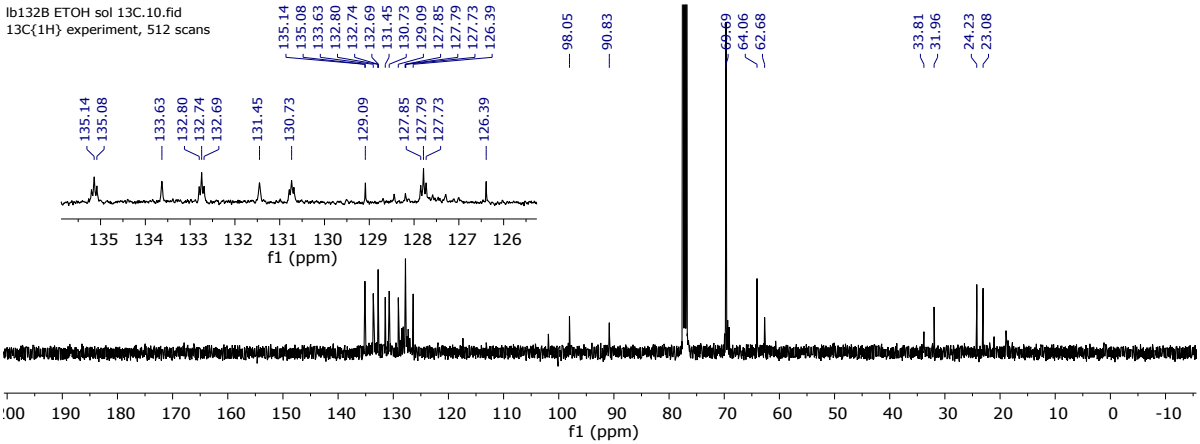


Ru15

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$)

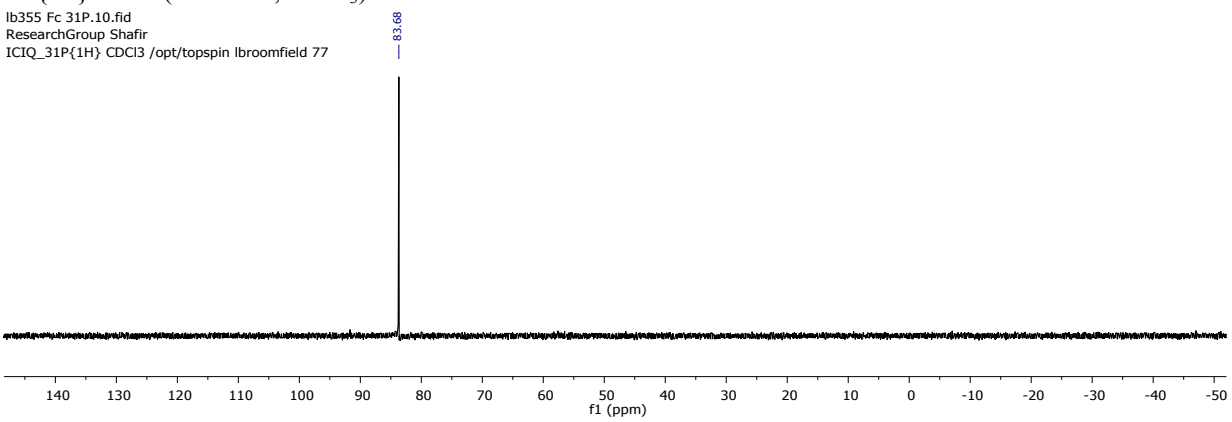


Figure S15

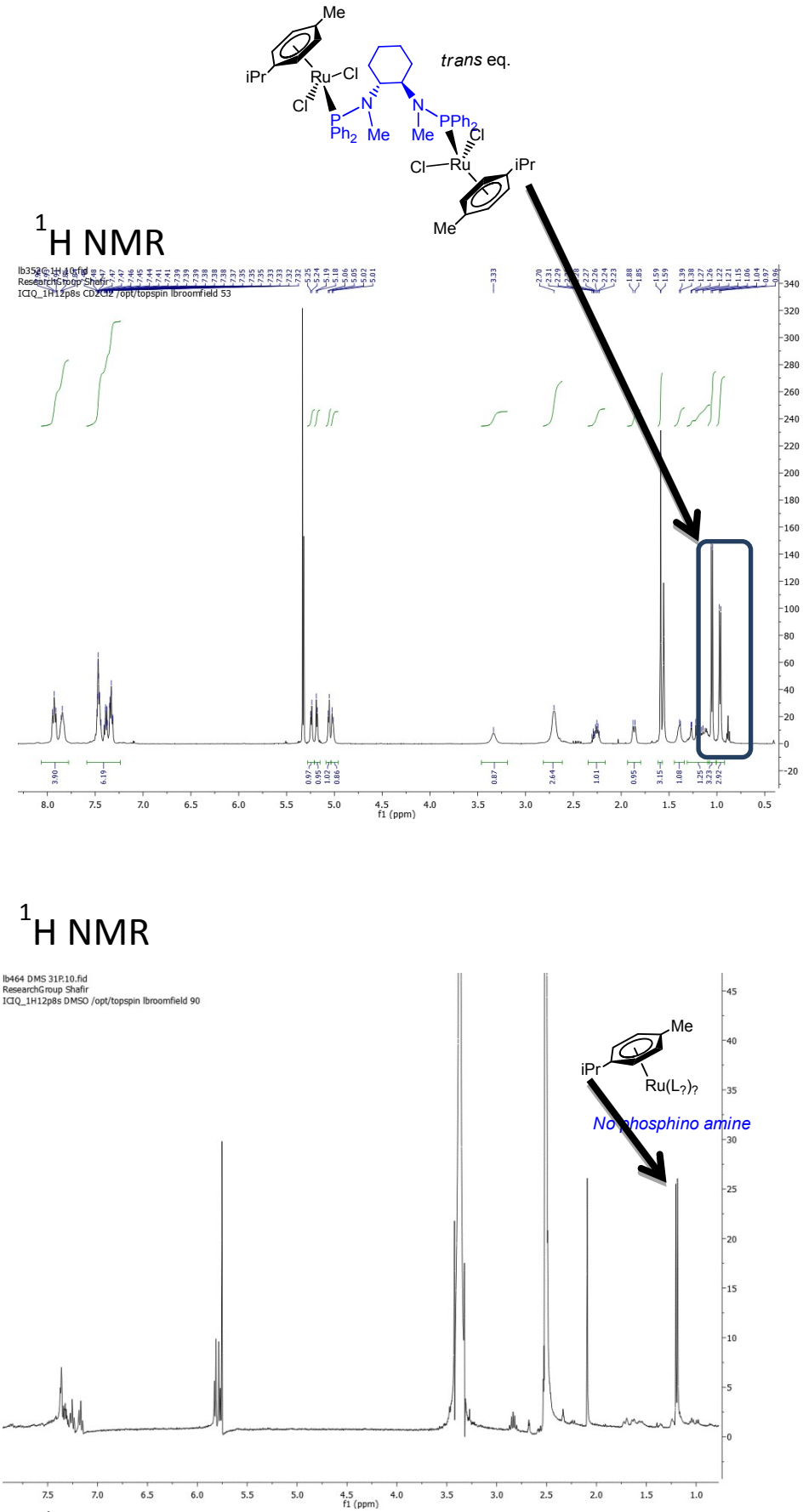


Figure S16. [1]H-NMR data for the disproportion reaction of **Ru7**.

4. HRMS spectra

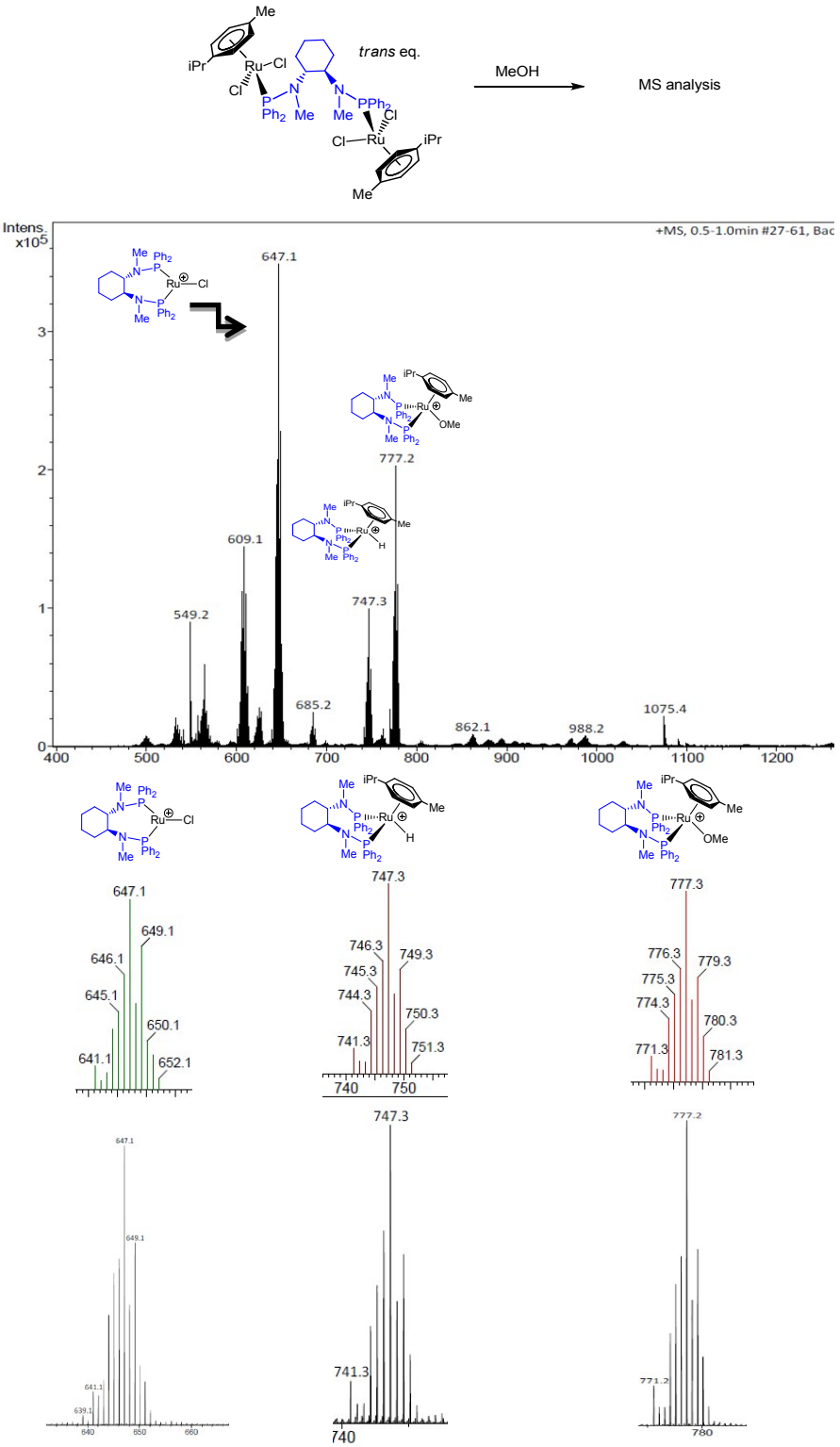


Figure S17. Analysis of a MeCN solution of **Ru7** by HRMS.