Electronic Supplementary Material (ESI) for Dalton Transactions.

$Ru(O_2CCF_3)_2(PPh_3)_2$ and ruthenium phosphine complexes bearing fluoroacetate ligands: synthesis, characterization and catalytic activity

Daniela A. Hey[a,#], Pauline J. Fischer[a,#], Walter Baratta[b,*], Fritz E. Kühn[a,*]

[#]D.A.H. and P.J.F. contributed equally to this work.

[a] *Molecular Catalysis, Catalysis Research Center and Department of Chemistry, Technische Universität München, Lichtenbergstr. 4, 85747 Garching bei München, Germany*

[b] *Dipartimento di Scienze AgroAlimentari, Ambientali e Animali (DI4A), Università di Udine, Via Cotonificio 108, I-33100 Udine, Italy*

Supporting Information

Table of contents

1. Crystallographic data

1.1 Crystallographic data for complex 1a.

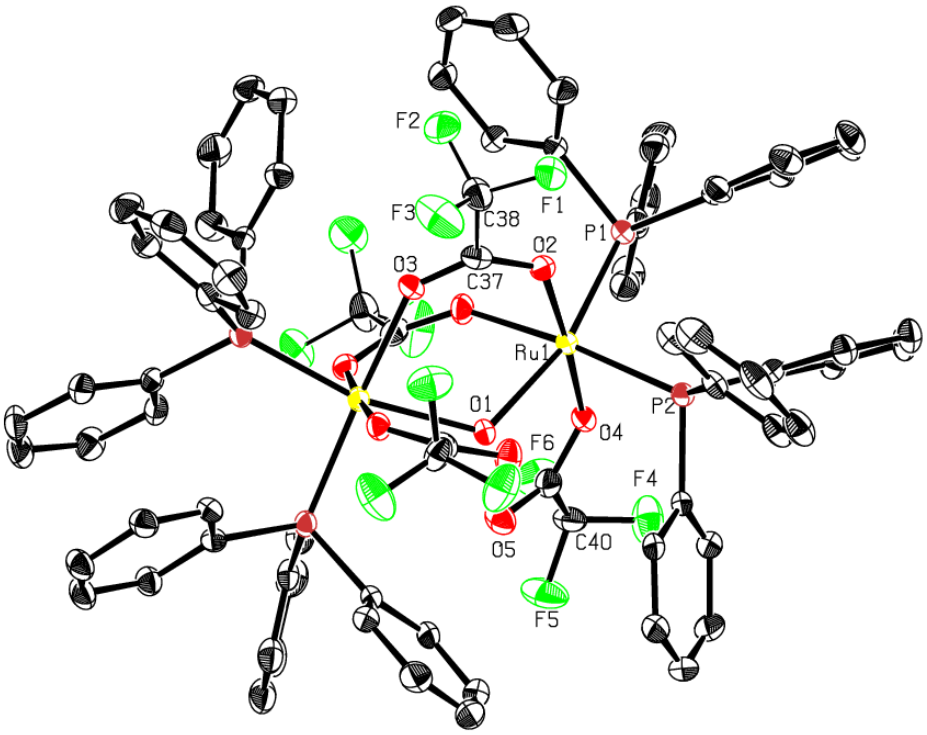


Figure S1.1. ORTEP style drawing of **1a** with ellipsoids at 50% probability level. All hydrogen atoms were omitted for clarity, hydrogens on O1 could be located in the difference Fourier maps.

A clear yellow-brown fragment-like specimen of $C_{40}H_{31}F_6O_{4.50}P_2Ru$, approximate dimensions 0.105 mm x 0.211 mm x 0.345 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Duo IMS system equipped with a Helios optic monochromator and a Mo IMS microsource (λ = 0.71073 Å).

A total of 4799 frames were collected. The total exposure time was 12.88 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 281355 reflections to a maximum θ angle of 25.02° (0.84 Å resolution), of which 7083 were independent (average redundancy 39.723, completeness = 99.9%, R_{int} = 6.86%, R_{sig} = 1.67%) and 6223 (87.86%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.9960(14) Å, b = 30.198(4) Å, c = 44.214(5) Å, volume = 16017.(3) Å^3, are based upon the refinement of the XYZ-centroids of 9475 reflections above 20 σ(I) with 4.566° < 2θ < 51.34°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.913. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8360 and 0.9460.

The final anisotropic full-matrix least-squares refinement on F^2 with 523 variables converged at R1 = 6.74%, for the observed data and wR2 = 17.08% for all data. The goodness-of-fit was 1.068. The largest peak in the final difference electron density synthesis was 6.577 e^-/Å^3 and the largest hole was -1.270 e^-/Å^3 with an RMS deviation of 0.138 e^-/Å^3. On the basis of the final model, the calculated density was 1.428 g/cm^3 and F(000), 6960 e^-.

Table 1.1.1. Sample and crystal data for **1a**.

CCDC number	1892673	
Chemical formula	$C_{40}H_{31}F_6O_{4.50}P_2Ru$	
Formula weight	860.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.105 x 0.211 x 0.345 mm	
Crystal habit	clear yellow-brown fragment	
Crystal system	orthorhombic	
Space group	I b c a	
Unit cell dimensions	a = 11.9960(14) Å	α = 90°
	b = 30.198(4) Å	β = 90°
	c = 44.214(5) Å	γ = 90°
Volume	16017.(3) $Å^3$	
Z	16	
Density (calculated)	1.428 g/cm^3	
Absorption coefficient	0.539 mm^{-1}	
F(000)	6960	

Table 1.1.2. Data collection and structure refinement for **1a**.

Diffractometer	Bruker D8 Venture Duo IMS
Radiation source	IMS microsource, Mo
Theta range for data collection	2.05 to 25.02°
Index ranges	-14<=h<=14, -35<=k<=35, -52<=l<=52
Reflections collected	281355
Independent reflections	7083 [R(int) = 0.0686]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9460 and 0.8360
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7083 / 128 / 523
Goodness-of-fit on F^2	1.068
Δ/σ_{max}	0.001
Final R indices	6223 data; I>2σ(I) R1 = 0.0674, wR2 = 0.1604
	all data R1 = 0.0765, wR2 = 0.1708
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0677P)^2+286.9807P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	6.577 and -1.270 $eÅ^{-3}$
R.M.S. deviation from mean	0.138 $eÅ^{-3}$

1.2 Crystallographic data for complex 1b.

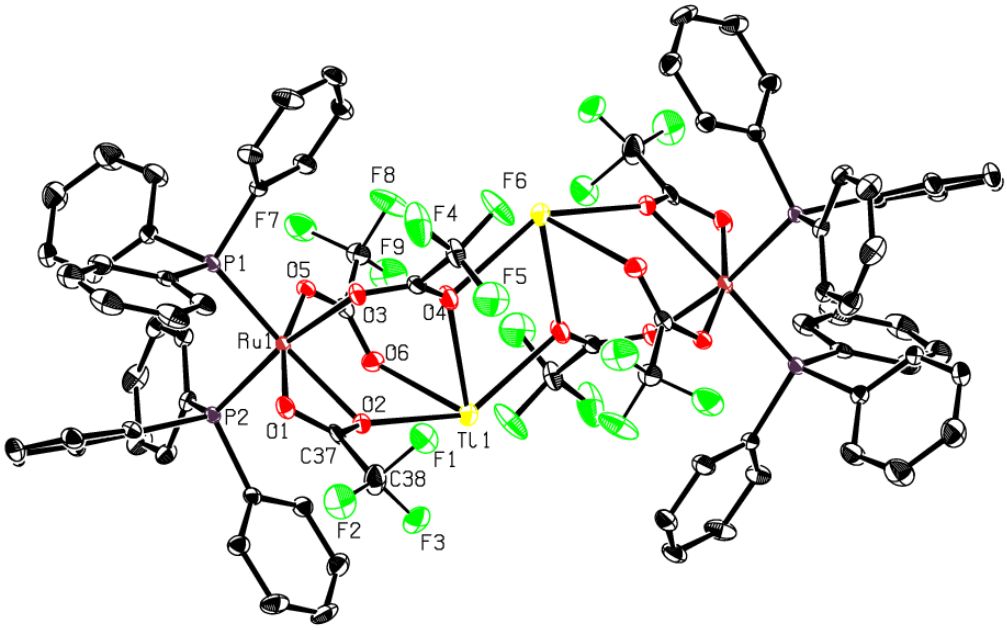


Figure S1.2. ORTEP style drawing of **1b** with ellipsoids at 50% probability level. Hydrogen atoms were omitted for clarity.

A clear yellow-brown fragment-like specimen of $C_{84}H_{60}F_{18}O_{12}P_4Ru_2Tl_2$, approximate dimensions 0.133 mm x 0.149 mm x 0.192 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture system equipped with a Helios optic monochromator and a Mo TXS rotating anode (λ = 0.71073 Å).

A total of 2140 frames were collected. The total exposure time was 2.77 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 139817 reflections to a maximum θ angle of 25.68° (0.82 Å resolution), of which 8182 were independent (average redundancy 17.088, completeness = 99.9%, R_{int} = 5.10%, R_{sig} = 1.71%) and 7387 (90.28%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.7843(9) Å, b = 16.6625(13) Å, c = 24.1130(19) Å, β = 96.281(3)°, volume = 4306.9(6) $Å^3$, are based upon the refinement of the XYZ-centroids of 288 reflections above 20 σ(I) with 4.403° < 2θ < 47.02°. The ratio of minimum to maximum apparent transmission was 0.894. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6663 and 0.7453.

The structure was solved and refined using the Bruker SHELXTL Software Package in conjunction with SHELXLE, using the space group P 1 21/n 1, with Z = 2 for the formula unit, $C_{84}H_{60}F_{18}O_{12}P_4Ru_2Tl_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 606 variables converged at R1 = 1.97%, for the observed data and wR2 = 4.69% for all data. The goodness-of-fit was 1.059. The largest peak in the final difference electron density synthesis was 1.263 $e^-/Å^3$ and the largest hole was -0.822 $e^-/Å^3$ with an RMS deviation of 0.075 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.803 g/cm^3 and F(000), 2264 e^-.

Table 1.2.1. Sample and crystal data for **1b**.

CCDC number	1892671	
Chemical formula	$C_{84}H_{60}F_{18}O_{12}P_4Ru_2Tl_2$	
Formula weight	2338.10	
Wavelength	0.71073 Å	
Crystal size	0.133 x 0.149 x 0.192 mm	
Crystal habit	clear yellow-brown fragment	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 10.7843(9) Å	α = 90°
	b = 16.6625(13) Å	β = 96.281(3)°
	c = 24.1130(19) Å	γ = 90°
Volume	4306.9(6) $Å^3$	
Z	2	
Density (calculated)	1.803 g/cm^3	
Absorption coefficient	4.246 mm^{-1}	
F(000)	2264	

Table 1.2.2. Data collection and structure refinement for **1b**.

Diffractometer	Bruker D8 Venture
Radiation source	TXS rotating anode, Mo
Theta range for data collection	2.26 to 25.68°
Index ranges	-13<=h<=13, -20<=k<=20, -29<=l<=29
Reflections collected	139817
Independent reflections	8182 [R(int) = 0.0510]
Coverage of independent reflections	99.9%
Max. and min. transmission	0.7453 and 0.6663
Structure solution technique	direct methods
Structure solution program	SHELXT (Sheldrick, 2015)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL2014 (Sheldrick, 2014), SHELXLE (Huebschle, 2011)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	8182 / 66 / 606
Goodness-of-fit on F^2	1.059
Δ/σ_{max}	0.009
Final R indices	7387 data; I>2σ(I) R1 = 0.0197, wR2 = 0.0458
	all data R1 = 0.0240, wR2 = 0.0469
Weighting scheme	$W=1/[\Sigma^2(F_o^2)+(0.0232P)^2+4.2704P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.263 and -0.822 $eÅ^{-3}$
R.M.S. deviation from mean	0.075 $eÅ^{-3}$

1.3 Crystallographic data for complex 2.

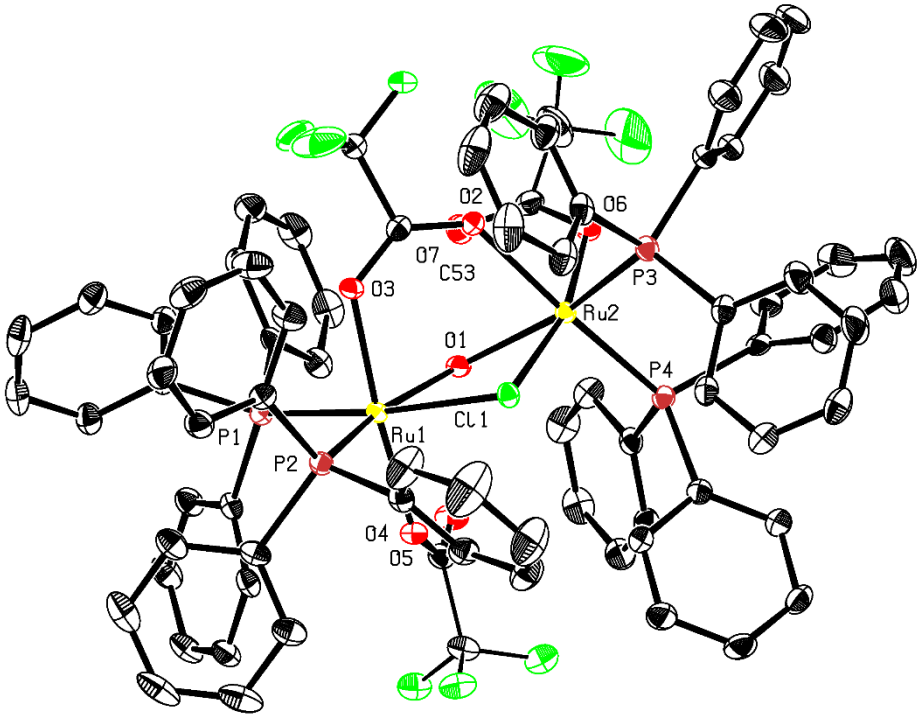


Figure S1.3. ORTEP style drawing of dinuclear complex **2** with ellipsoids at 50% probability level. All hydrogen atoms were omitted for clarity, hydrogens on O1 could be located in the difference Fourier maps.

A clear intense orange fragment-like specimen of $C_{79}H_{64}Cl_3F_9O_7P_4Ru_2$, approximate dimensions 0.054 mm x 0.139 mm x 0.287 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Kappa Apex II system equipped with a Triumph monochromator monochromator and a Mo fine-focus sealed tube (λ = 0.71073 Å).

A total of 2886 frames were collected. The total exposure time was 8.02 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 77986 reflections to a maximum θ angle of 25.45° (0.83 Å resolution), of which 14180 were independent (average redundancy 5.500, completeness = 98.7%, R_{int} = 5.69%, R_{sig} = 4.42%) and 11518 (81.23%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.819(3) Å, b = 39.501(10) Å, c = 14.479(4) Å, β = 100.849(14)°, volume = 7762.(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 115 reflections above 20 σ(I) with 11.51° < 2θ < 46.70°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.929. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8360 and 0.9660.

The final anisotropic full-matrix least-squares refinement on F^2 with 1057 variables converged at R1 = 3.24%, for the observed data and wR2 = 7.30% for all data. The goodness-of-fit was 1.016. The largest peak in the final difference electron density synthesis was 0.517 $e^-/Å^3$ and the largest hole was -0.817 $e^-/Å^3$ with an RMS deviation of 0.070 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.479 g/cm^3 and F(000), 3496 e^-.

Table 1.3.1. Sample and crystal data for **2**.

CCDC number	1892670	
Chemical formula	$C_{79}H_{64}Cl_3F_9O_7P_4Ru_2$	
Formula weight	1728.67	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.054 x 0.139 x 0.287 mm	
Crystal habit	clear intense orange fragment	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 13.819(3) Å	α = 90°
	b = 39.501(10) Å	β = 100.849(14)°
	c = 14.479(4) Å	γ = 90°
Volume	7762.(3) $Å^3$	
Z	4	
Density (calculated)	1.479 g/cm^3	
Absorption coefficient	0.649 mm^{-1}	
F(000)	3496	

Table 1.3.2. Data collection and structure refinement for **2**.

Diffractometer	Bruker D8 Kappa Apex II	
Radiation source	fine-focus sealed tube, Mo	
Theta range for data collection	1.59 to 25.45°	
Index ranges	-16<=h<=10, -47<=k<=47, -16<=l<=17	
Reflections collected	77986	
Independent reflections	14180 [R(int) = 0.0569]	
Coverage of independent reflections	98.7%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9660 and 0.8360	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	14180 / 259 / 1057	
Goodness-of-fit on F^2	1.016	
Δ/σ_{max}	0.002	
Final R indices	11518 data; I>2σ(I)	R1 = 0.0324, wR2 = 0.0683
	all data	R1 = 0.0466, wR2 = 0.0730
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0276P)^2+6.4943P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.517 and -0.817 $eÅ^{-3}$	
R.M.S. deviation from mean	0.070 $eÅ^{-3}$	

1.4 Crystallographic data for complex 3.

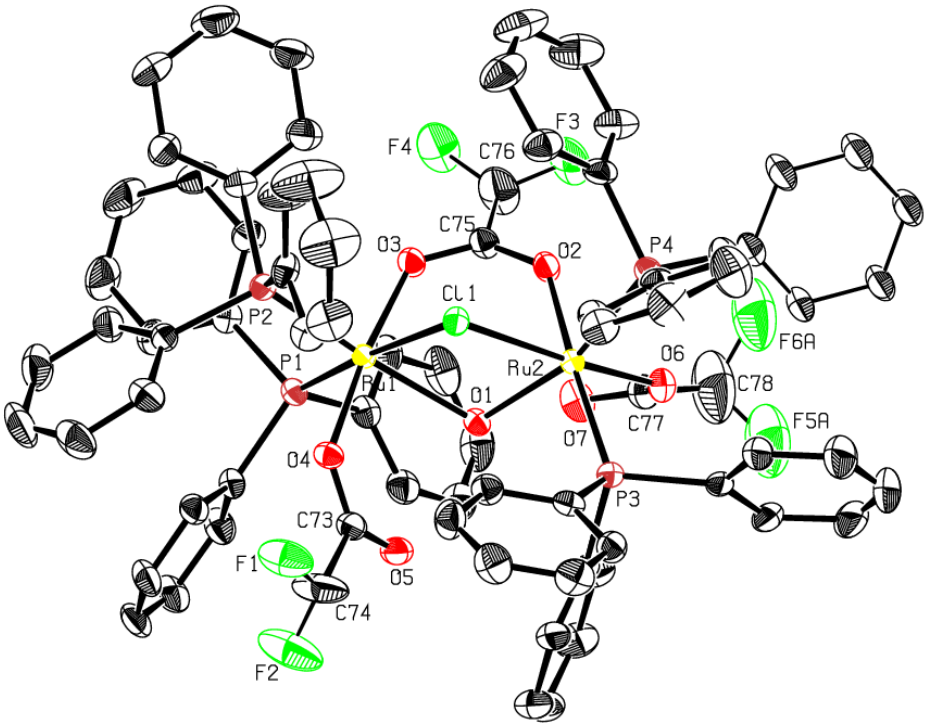


Figure S1.4. ORTEP style drawing of dinuclear complex **3** with ellipsoids at 50% probability level. All hydrogen atoms were omitted for clarity, hydrogens on O1 could be located in the difference Fourier maps.

A specimen of $C_{79}H_{67}Cl_3F_6O_7P_4Ru_2$, approximate dimensions 0.088 mm x 0.172 mm x 0.649 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture system equipped with a Helios optic monochromator and a Mo TXS rotating anode (λ = 0.71073 Å).

A total of 2525 frames were collected. The total exposure time was 3.31 hours. The integration of the data using a monoclinic unit cell yielded a total of 129404 reflections to a maximum θ angle of 25.03° (0.84 Å resolution), of which 13519 were independent (average redundancy 9.572, completeness = 99.9%, R_{int} = 12.91%, R_{sig} = 6.41%) and 10421 (77.08%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.639(7) Å, b = 39.50(2) Å, c = 14.472(8) Å, β = 100.941(16)°, volume = 7655.(7) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6780 and 0.9450.

The final anisotropic full-matrix least-squares refinement on F^2 with 1030 variables converged at R1 = 4.58%, for the observed data and wR2 = 11.01% for all data. The goodness-of-fit was 1.008. The largest peak in the final difference electron density synthesis was 1.034 $e^-/Å^3$ and the largest hole was -0.630 $e^-/Å^3$ with an RMS deviation of 0.089 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.453 g/cm^3 and F(000), 3400 e^-.

Table 1.4.1. Sample and crystal data for **3**.

CCDC number	1892675	
Chemical formula	$C_{79}H_{67}Cl_3F_6O_7P_4Ru_2$	
Formula weight	1674.69	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.088 x 0.172 x 0.649 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 13.639(7) Å	α = 90°
	b = 39.50(2) Å	β = 100.941(16)°
	c = 14.472(8) Å	γ = 90°
Volume	7655.(7) $Å^3$	
Z	4	
Density (calculated)	1.453 g/cm^3	
Absorption coefficient	0.650 mm^{-1}	
F(000)	3400	

Table 1.4.2. Data collection and structure refinement for **3**.

Diffractometer	Bruker D8 Venture	
Radiation source	TXS rotating anode, Mo	
Theta range for data collection	2.17 to 25.03°	
Index ranges	-13<=h<=16, -47<=k<=47, -17<=l<=17	
Reflections collected	129404	
Independent reflections	13519 [R(int) = 0.1291]	
Max. and min. transmission	0.9450 and 0.6780	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	13519 / 424 / 1030	
Goodness-of-fit on F^2	1.008	
Δ/σ_{max}	0.002	
Final R indices	10421 data; I>2σ(I)	R1 = 0.0458, wR2 = 0.1006
	all data	R1 = 0.0687, wR2 = 0.1101
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0402P)^2+15.8467P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.034 and -0.630 $eÅ^{-3}$	
R.M.S. deviation from mean	0.089 $eÅ^{-3}$	

1.5 Crystallographic data for complex 4.

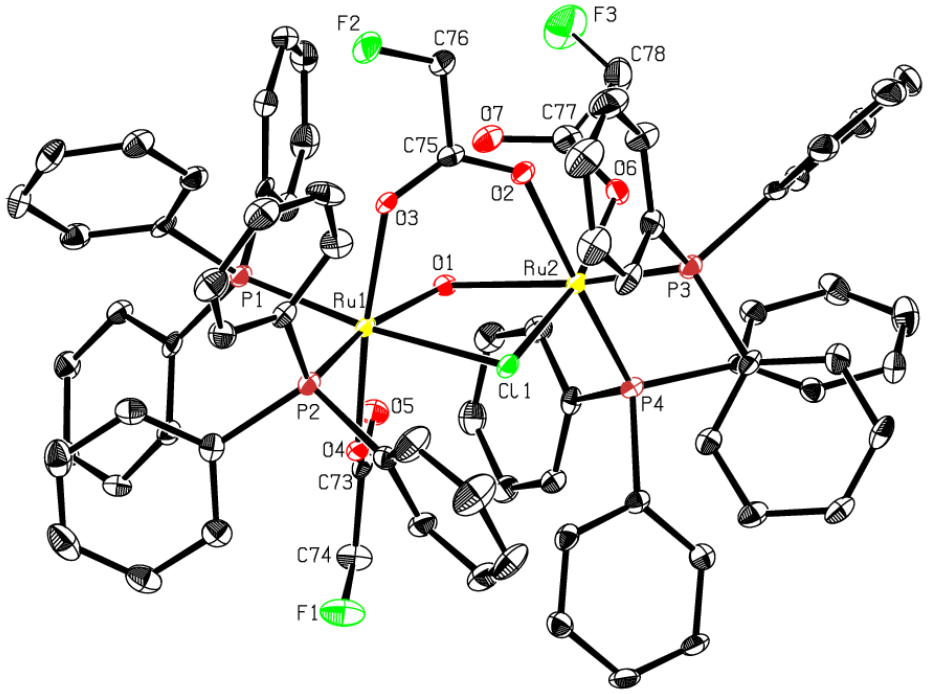


Figure S1.5. ORTEP style drawing of dinuclear complex **4** with ellipsoids at 50% probability level. All hydrogen atoms were omitted for clarity, hydrogens on O1 could be located in the difference Fourier maps.

A clear yellow fragment-like specimen of $C_{80}H_{72}Cl_5F_3O_7P_4Ru_2$, approximate dimensions 0.103 mm x 0.172 mm x 0.272 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Kappa Apex II system equipped with a Triumph monochromator monochromator and a Mo fine-focus sealed tube (λ = 0.71073 Å).

A total of 4757 frames were collected. The total exposure time was 13.21 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 76154 reflections to a maximum θ angle of 25.03° (0.84 Å resolution), of which 13286 were independent (average redundancy 5.732, completeness = 100.0%, R_{int} = 9.67%, R_{sig} = 7.75%) and 9354 (70.40%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.584(3) Å, b = 39.646(9) Å, c = 14.247(3) Å, β = 100.978(13)°, volume = 7532.(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9587 reflections above 20 σ(I) with 4.604° < 2θ < 50.74°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.862. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8270 and 0.9290.

The final anisotropic full-matrix least-squares refinement on F^2 with 965 variables converged at R1 = 4.86%, for the observed data and wR2 = 12.49% for all data. The goodness-of-fit was 1.025. The largest peak in the final difference electron density synthesis was 1.444 $e^-/Å^3$ and the largest hole was -1.629 $e^-/Å^3$ with an RMS deviation of 0.113 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.504 g/cm^3 and F(000), 3472 e^-.

Table 1.5.1. Sample and crystal data for **4**.

CCDC number	1892672	
Chemical formula	$C_{80}H_{72}Cl_5F_3O_7P_4Ru_2$	
Formula weight	1705.64	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.103 x 0.172 x 0.272 mm	
Crystal habit	clear yellow fragment	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 13.584(3) Å	α = 90°
	b = 39.646(9) Å	β = 100.978(13)°
	c = 14.247(3) Å	γ = 90°
Volume	7532.(3) $Å^3$	
Z	4	
Density (calculated)	1.504 g/cm^3	
Absorption coefficient	0.725 mm^{-1}	
F(000)	3472	

Table 1.5.2. Data collection and structure refinement for **4**.

Diffractometer	Bruker D8 Kappa Apex II
Radiation source	fine-focus sealed tube, Mo
Theta range for data collection	1.03 to 25.03°
Index ranges	-16<=h<=16, -47<=k<=46, -16<=l<=16
Reflections collected	76154
Independent reflections	13286 [R(int) = 0.0967]
Coverage of independent reflections	100.0%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9290 and 0.8270
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	13286 / 104 / 965
Goodness-of-fit on F^2	1.025
Δ/σ_{max}	0.001
Final R indices	9354 data; I>2σ(I) R1 = 0.0486, wR2 = 0.1102
	all data R1 = 0.0832, wR2 = 0.1249
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0569P)^2+10.9304P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.444 and -1.629 $eÅ^{-3}$
R.M.S. deviation from mean	0.113 $eÅ^{-3}$

1.6 Crystallographic data for complex 6.

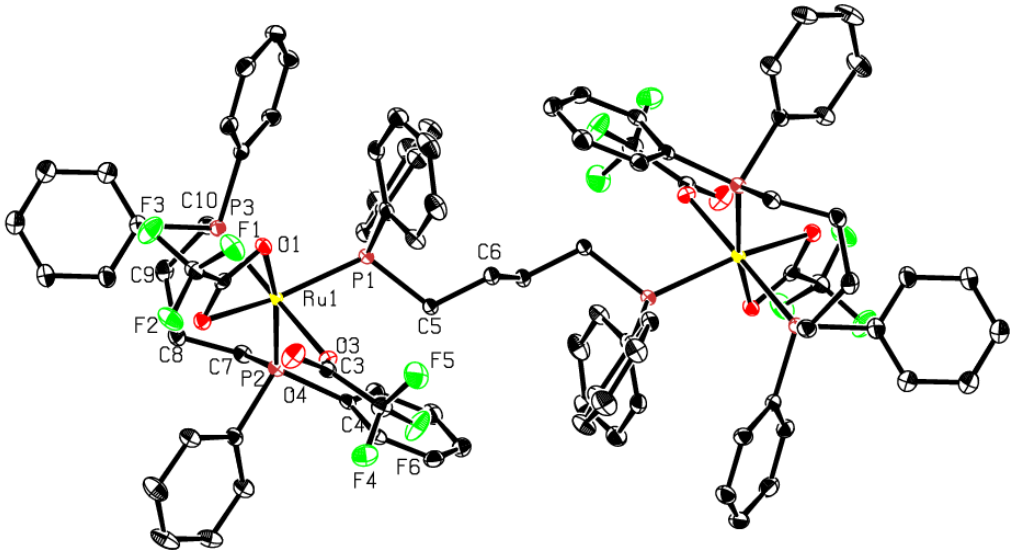


Figure S1.6. ORTEP style drawing of **6** with ellipsoids at 50% probability level. Hydrogen atoms were omitted for clarity.

A clear yellow fragment-like specimen of $C_{92}H_{84}F_{12}O_8P_6Ru_2$, approximate dimensions 0.039 mm x 0.092 mm x 0.187 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Duo IMS system equipped with a Helios optic monochromator and a Mo IMS microsource (λ = 0.71073 Å).

A total of 2009 frames were collected. The total exposure time was 15.39 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 61100 reflections to a maximum θ angle of 25.03° (0.84 Å resolution), of which 7762 were independent (average redundancy 7.872, completeness = 100.0%, R_{int} = 3.87%, R_{sig} = 1.96%) and 7147 (92.08%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.8399(6) Å, b = 11.0183(6) Å, c = 21.0415(12) Å, α = 95.630(2)°, β = 101.051(2)°, γ = 114.300(2)°, volume = 2203.6(2) Å^3, are based upon the refinement of the XYZ-centroids of 9388 reflections above 20 σ(I) with 4.445° < 2θ < 51.33°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.953. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9070 and 0.9800.

The structure was solved and refined using the Bruker SHELXTL Software Package in conjunction with SHELXLE, using the space group P -1, with Z = 1 for the formula unit, $C_{92}H_{84}F_{12}O_8P_6Ru_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 542 variables converged at R1 = 3.37%, for the observed data and wR2 = 6.85% for all data. The goodness-of-fit was 1.069. The largest peak in the final difference electron density synthesis was 1.211 e^-/Å^3 and the largest hole was -1.314 e^-/Å^3 with an RMS deviation of 0.071 e^-/Å^3. On the basis of the final model, the calculated density was 1.457 g/cm^3 and F(000), 986 e^-.

Table 1.6.1. Sample and crystal data for **6**.

CCDC number	1892669	
Chemical formula	$C_{92}H_{84}F_{12}O_8P_6Ru_2$	
Formula weight	1933.55	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.039 x 0.092 x 0.187 mm	
Crystal habit	clear yellow fragment	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.8399(6) Å	α = 95.630(2)°
	b = 11.0183(6) Å	β = 101.051(2)°
	c = 21.0415(12) Å	γ = 114.300(2)°
Volume	2203.6(2) $Å^3$	
Z	1	
Density (calculated)	1.457 g/cm^3	
Absorption coefficient	0.532 mm^{-1}	
F(000)	986	

Table 1.6.2. Data collection and structure refinement for **6**.

Diffractometer	Bruker D8 Venture Duo IMS
Radiation source	IMS microsource, Mo
Theta range for data collection	2.01 to 25.03°
Index ranges	-12<=h<=12, -13<=k<=12, -25<=l<=25
Reflections collected	61100
Independent reflections	7762 [R(int) = 0.0387]
Coverage of independent reflections	100.0%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9800 and 0.9070
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7762 / 66 / 542
Goodness-of-fit on F^2	1.069
Δ/σ_{max}	0.001
Final R indices	7147 data; I>2σ(I) R1 = 0.0337, wR2 = 0.0670
	all data R1 = 0.0373, wR2 = 0.0685
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0060P)^2+5.8589P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.211 and -1.314 $eÅ^{-3}$
R.M.S. deviation from mean	0.071 $eÅ^{-3}$

1.7 Crystallographic data for complex 7.

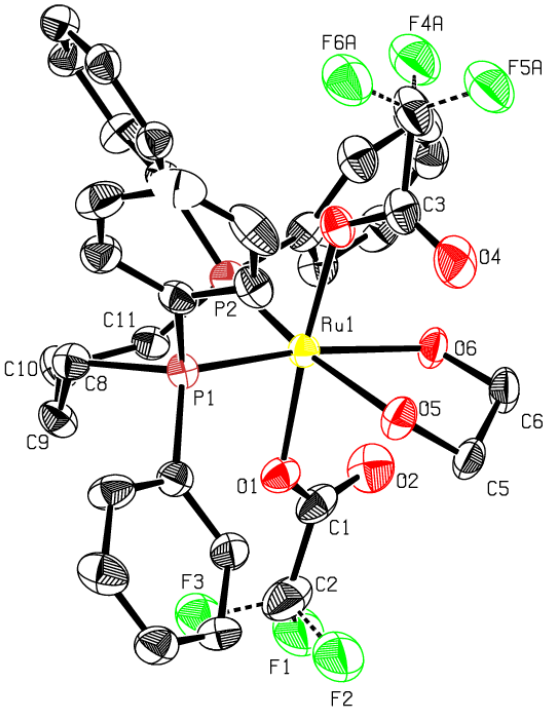


Figure S1.7. ORTEP style drawing of **7** with ellipsoids at 50% probability level. All hydrogen atoms were omitted for clarity, hydrogens on O5 and O6 could be located in the difference Fourier maps.

A yellow fragment-like specimen of $C_{34}H_{34}F_6O_6P_2Ru$, approximate dimensions 0.180 mm x 0.310 mm x 0.430 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Duo IMS system equipped with a Helios optic monochromator and a Mo IMS microsource (λ = 0.71073 Å).

A total of 947 frames were collected. The total exposure time was 2.18 hours. The integration of the data using an orthorhombic unit cell yielded a total of 40954 reflections to a maximum θ angle of 25.02° (0.84 Å resolution), of which 5799 were independent (average redundancy 7.062, completeness = 100.0%, R_{int} = 10.98%, R_{sig} = 6.52%) and 4938 (85.15%) were greater than $2\sigma(F^2)$. The final cell constants of a = 18.484(6) Å, b = 10.708(3) Å, c = 17.311(6) Å, volume = 3426.3(18) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7740 and 0.8950.

The structure was solved and refined using the Bruker SHELXTL Software Package in conjunction with SHELXLE, using the space group P n a 21, with Z = 4 for the formula unit, $C_{34}H_{32}F_6O_6P_2Ru$. The final anisotropic full-matrix least-squares refinement on F^2 with 498 variables converged at R1 = 4.29%, for the observed data and wR2 = 11.27% for all data. The goodness-of-fit was 1.076. The largest peak in the final difference electron density synthesis was 0.739 $e^-/Å^3$ and the largest hole was -0.732 $e^-/Å^3$ with an RMS deviation of 0.091 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.577 g/cm^3 and F(000), 1648 e^-.

Table 1.7.1. Sample and crystal data for **7**.

CCDC number	1892668	
Chemical formula	$C_{34}H_{34}F_6O_6P_2Ru$	
Formula weight	813.60	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.180 x 0.310 x 0.430 mm	
Crystal habit	yellow fragment	
Crystal system	orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 18.484(6) Å	α = 90°
	b = 10.708(3) Å	β = 90°
	c = 17.311(6) Å	γ = 90°
Volume	3426.3(18) $Å^3$	
Z	4	
Density (calculated)	1.577 g/cm^3	
Absorption coefficient	0.628 mm^{-1}	
F(000)	1648	

Table 1.7.2. Data collection and structure refinement for **7**.

Diffractometer	Bruker D8 Venture Duo IMS	
Radiation source	IMS microsource, Mo	
Theta range for data collection	2.20 to 25.02°	
Index ranges	-22<=h<=22, -12<=k<=12, -20<=l<=18	
Reflections collected	40954	
Independent reflections	5799 [R(int) = 0.1098]	
Max. and min. transmission	0.8950 and 0.7740	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5799 / 79 / 498	
Goodness-of-fit on F^2	1.076	
Final R indices	4938 data; I>2σ(I)	R1 = 0.0429, wR2 = 0.0977
	all data	R1 = 0.0595, wR2 = 0.1127
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0295P)^2+7.2904P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.0(0)	
Largest diff. peak and hole	0.739 and -0.732 $eÅ^{-3}$	
R.M.S. deviation from mean	0.091 $eÅ^{-3}$	

1.8 Crystallographic data for complex 8.

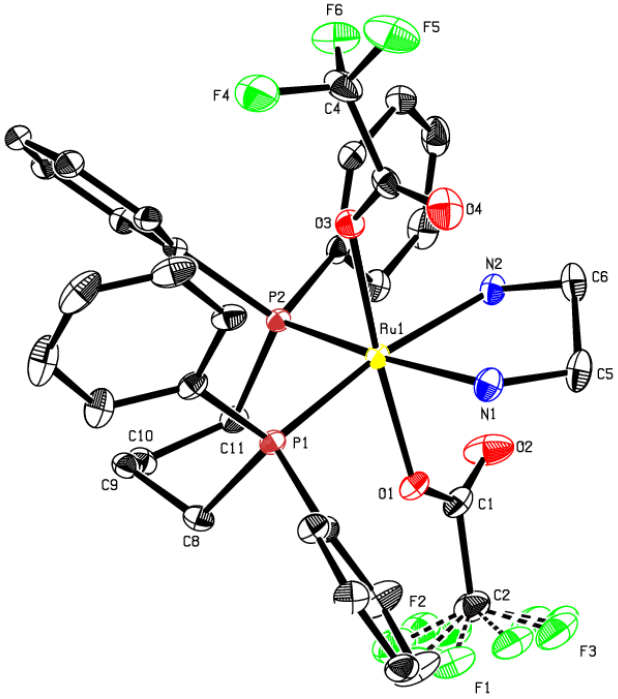


Figure S1.8. ORTEP style drawing of **8** with ellipsoids at 50% probability level. All hydrogen atoms were omitted for clarity, hydrogens on N1 and N2 could be located in the difference Fourier maps.

A clear yellow fragment-like specimen of $C_{34}H_{36}F_6N_2O_4P_2Ru$, approximate dimensions 0.065 mm x 0.074 mm x 0.227 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture system equipped with a Helios optic monochromator and a Mo TXS rotating anode (λ = 0.71073 Å).

A total of 2600 frames were collected. The total exposure time was 6.77 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 68362 reflections to a maximum θ angle of 25.03° (0.84 Å resolution), of which 6045 were independent (average redundancy 11.309, completeness = 99.9%, R_{int} = 3.16%, R_{sig} = 1.32%) and 5566 (92.08%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.6493(8) Å, b = 10.9413(8) Å, c = 17.1095(13) Å, α = 72.020(3)°, β = 77.186(3)°, γ = 65.201(3)°, volume = 1711.5(2) Å^3, are based upon the refinement of the XYZ-centroids of 9866 reflections above 20 σ(I) with 4.719° < 2θ < 51.48°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.960. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8710 and 0.9600.

The structure was solved and refined using the Bruker SHELXTL Software Package in conjunction with SHELXLE, using the space group P -1, with Z = 2 for the formula unit, $C_{34}H_{36}F_6N_2O_4P_2Ru$. The final anisotropic full-matrix least-squares refinement on F^2 with 511 variables converged at R1 = 2.37%, for the observed data and wR2 = 5.67% for all data. The goodness-of-fit was 1.053. The largest peak in the final difference electron density synthesis was 0.611 $e^-/Å^3$ and the largest hole was -0.656 $e^-/Å^3$ with an RMS deviation of 0.060 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.579 g/cm^3 and F(000), 828 e^-.

Table 1.8.1. Sample and crystal data for **8**.

CCDC number	1892674	
Chemical formula	$C_{34}H_{36}F_6N_2O_4P_2Ru$	
Formula weight	813.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.065 x 0.074 x 0.227 mm	
Crystal habit	clear yellow fragment	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.6493(8) Å	α = 72.020(3)°
	b = 10.9413(8) Å	β = 77.186(3)°
	c = 17.1095(13) Å	γ = 65.201(3)°
Volume	1711.5(2) $Å^3$	
Z	2	
Density (calculated)	1.579 g/cm^3	
Absorption coefficient	0.625 mm^{-1}	
F(000)	828	

Table 1.8.2. Data collection and structure refinement for **8**.

Diffractometer	Bruker D8 Venture
Radiation source	TXS rotating anode, Mo
Theta range for data collection	2.35 to 25.03°
Index ranges	-12<=h<=12, -13<=k<=13, -20<=l<=20
Reflections collected	68362
Independent reflections	6045 [R(int) = 0.0316]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9600 and 0.8710
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6045 / 118 / 511
Goodness-of-fit on F^2	1.053
Δ/σ_{max}	0.009
Final R indices	5566 data; R1 = 0.0237, wR2 = 0.0548 I>2σ(I)
	all data R1 = 0.0270, wR2 = 0.0567
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0201P)^2+2.3716P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.611 and -0.656 $eÅ^{-3}$
R.M.S. deviation from mean	0.060 $eÅ^{-3}$

2. NMR spectra

2.1 NMR spectra of complex 1.

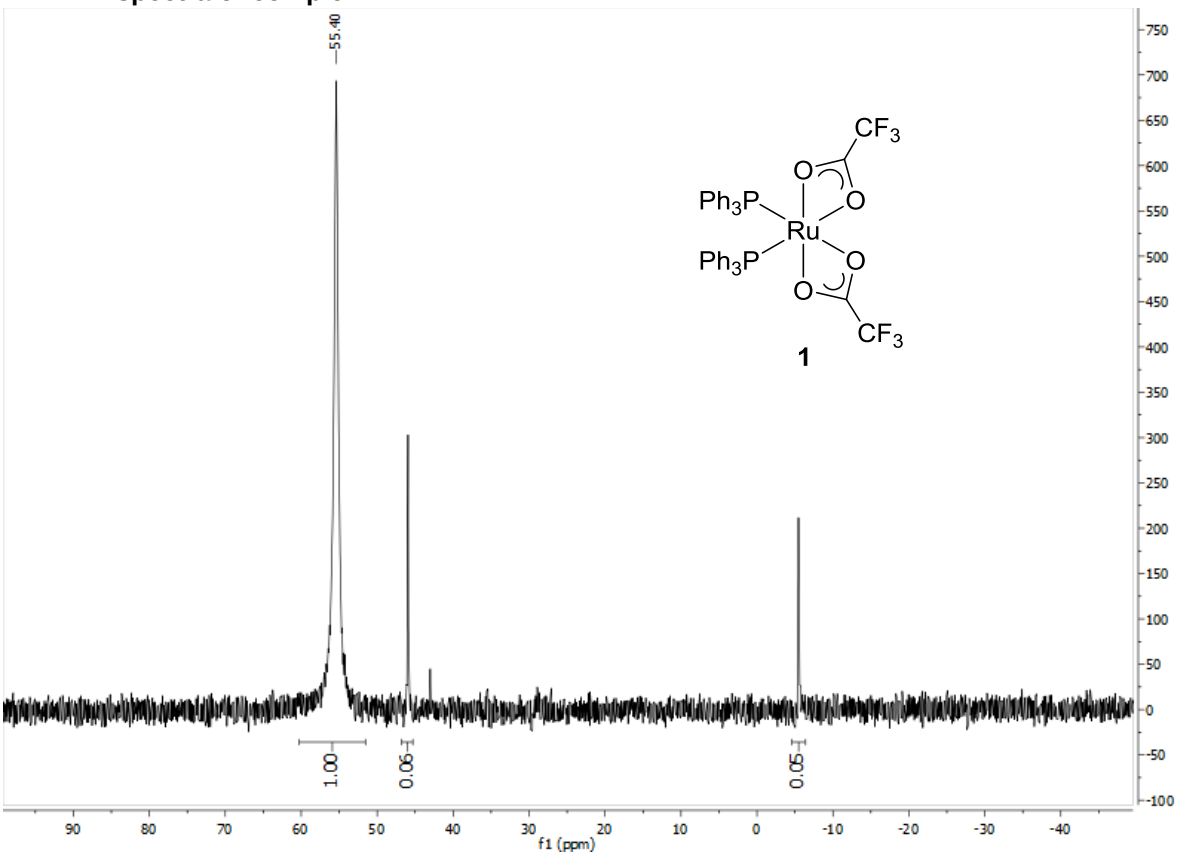


Figure S2.1.1.$^{31}P\{^{1}H\}$ NMR spectrum of **1** in CD_2Cl_2.

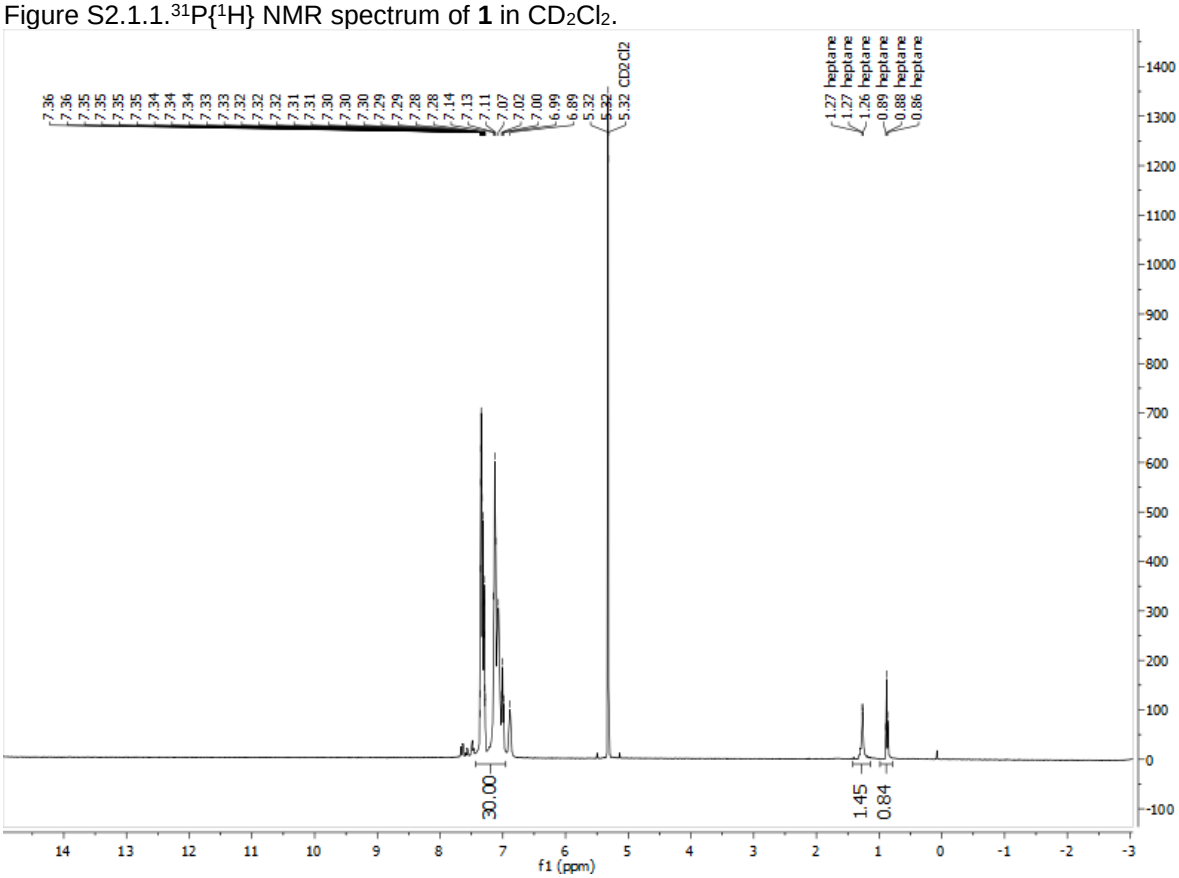


Figure S2.1.2.^{1}H NMR spectrum of **1** in CD_2Cl_2.

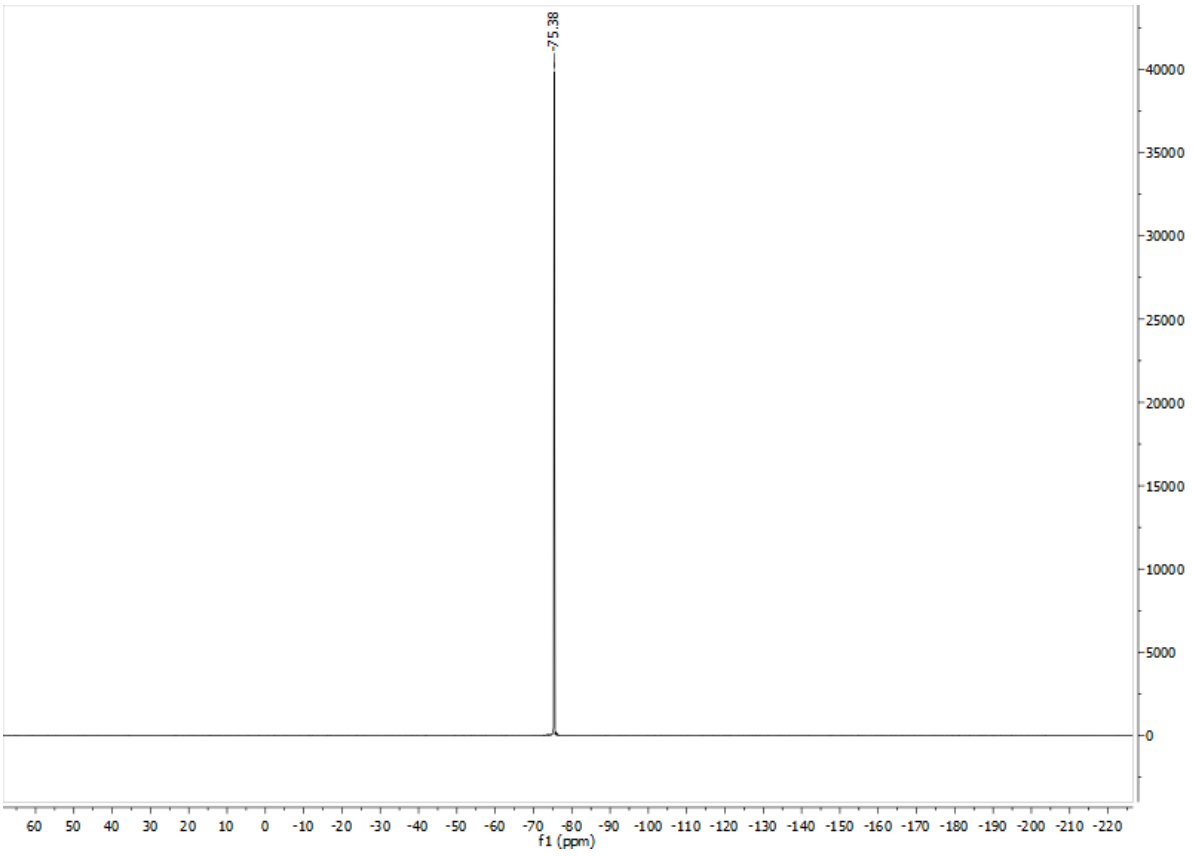


Figure S2.1.3.$^{19}F\{^{1}H\}$ NMR spectrum of **1** in CD_2Cl_2.

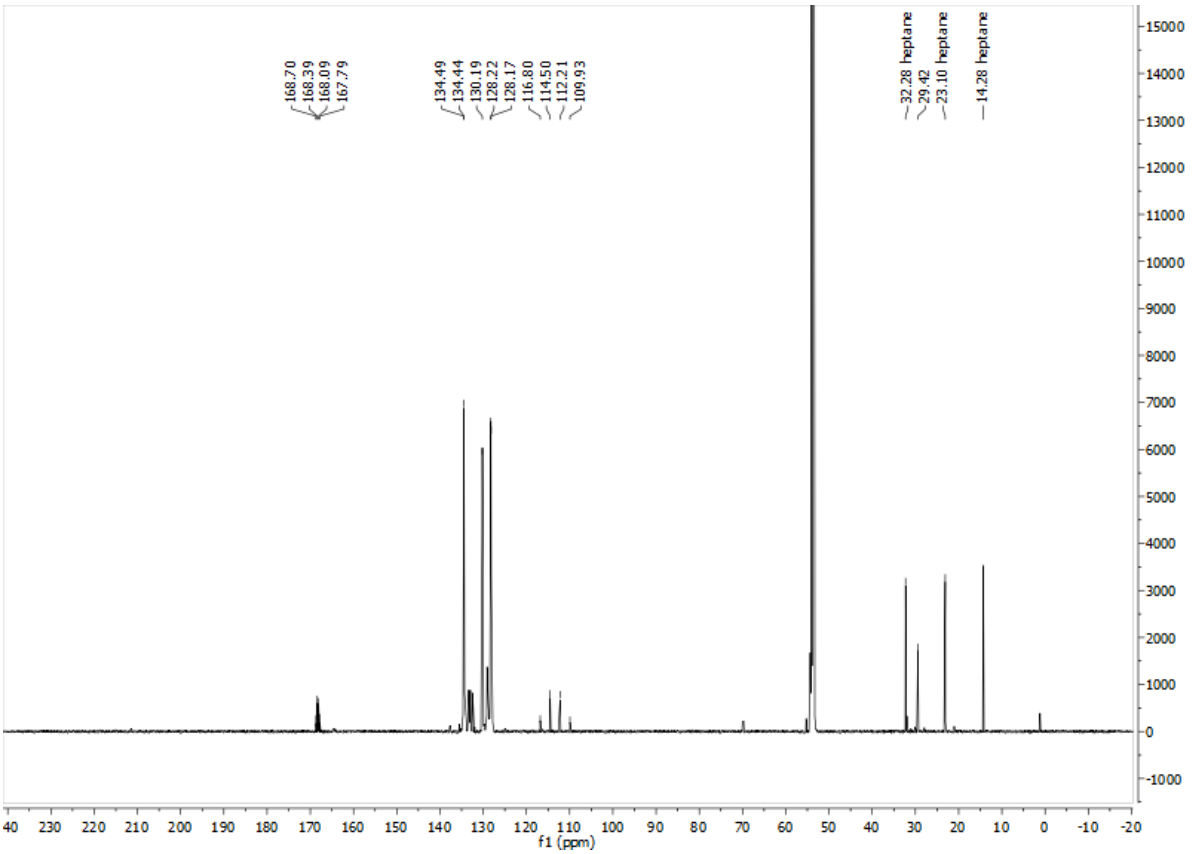
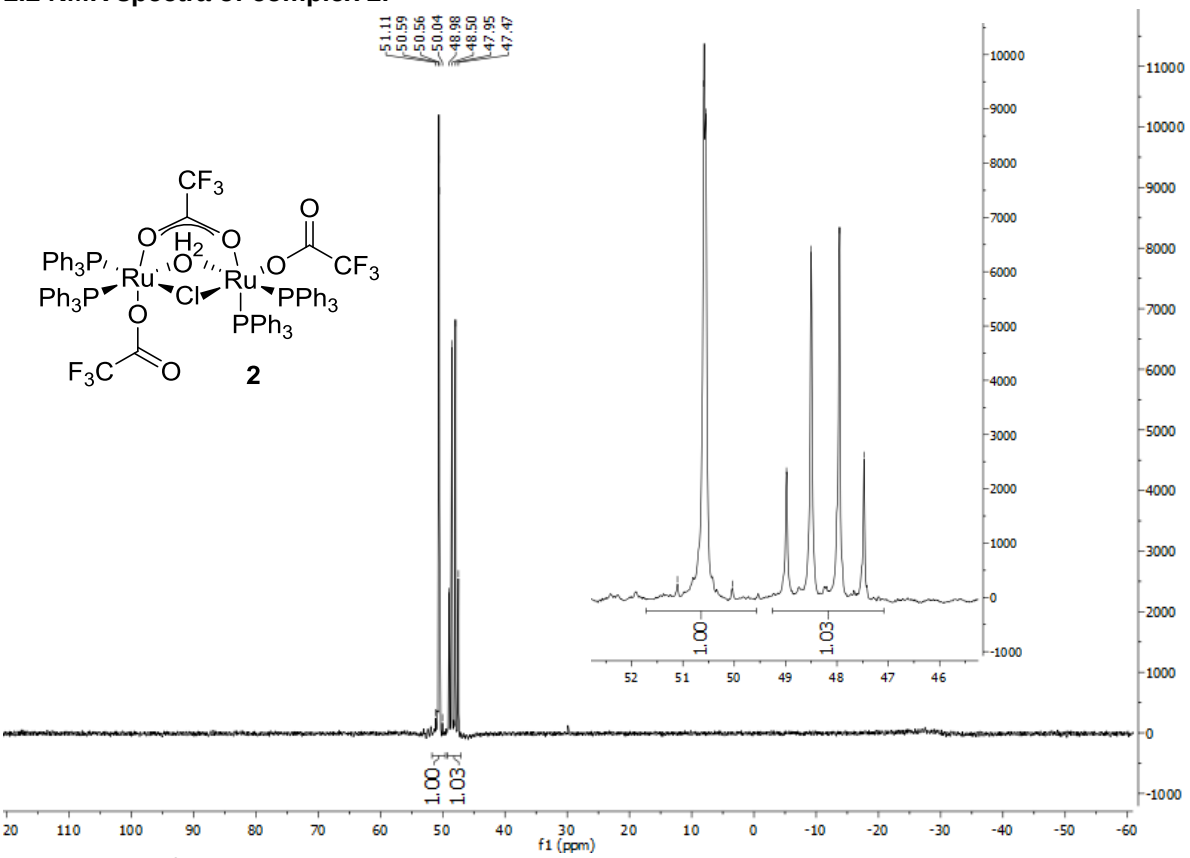


Figure S2.1.4.$^{13}C\{^{1}H\}$ NMR spectrum of **1** in CD_2Cl_2.

2.2 NMR spectra of complex 2.



2

Figure S2.2.1.$^{31}P\{^{1}H\}$ NMR spectrum of **2** in CD_2Cl_2.

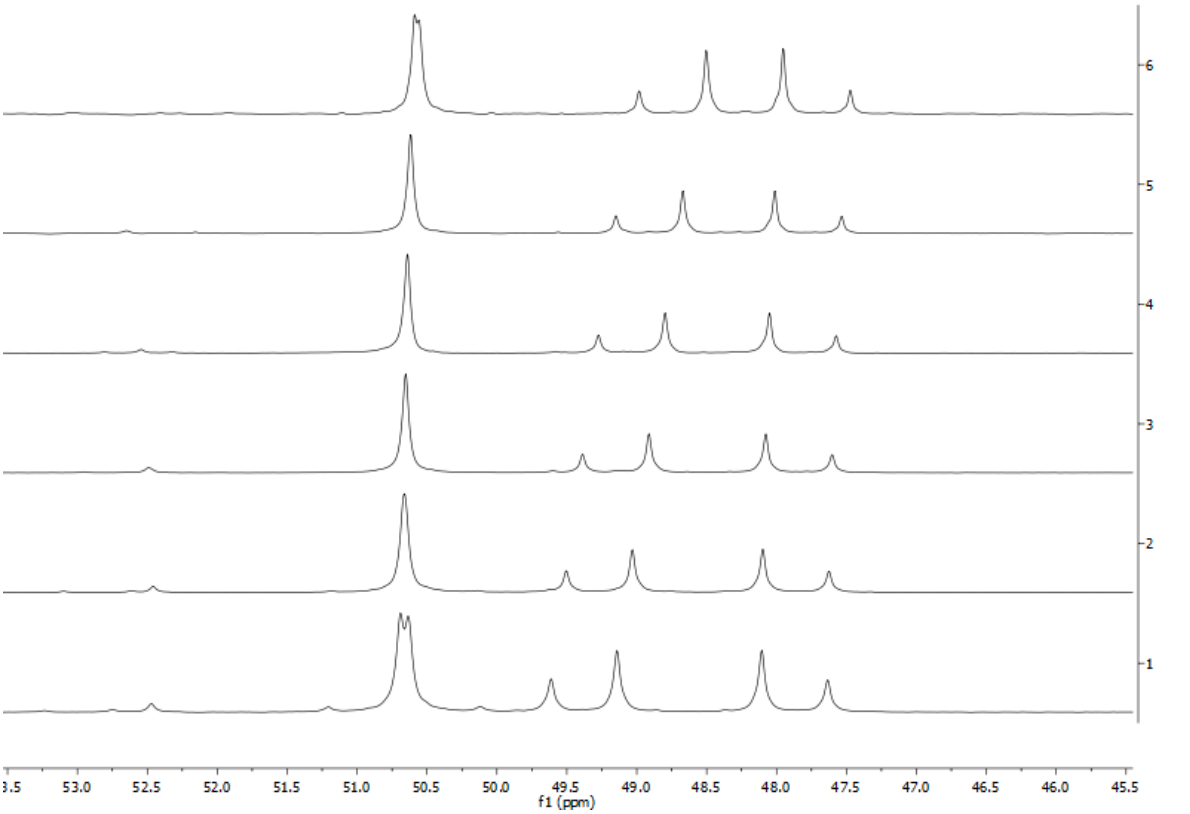


Figure S2.2.2.$^{31}P\{^{1}H\}$ VT-NMR spectra of **2** in CD_2Cl_2. (1) T = -80°C; (2) T = -60°C; (3) T = -40°C; (4) T = -20°C; (5) T = 0°C; (6) T = 20°C.

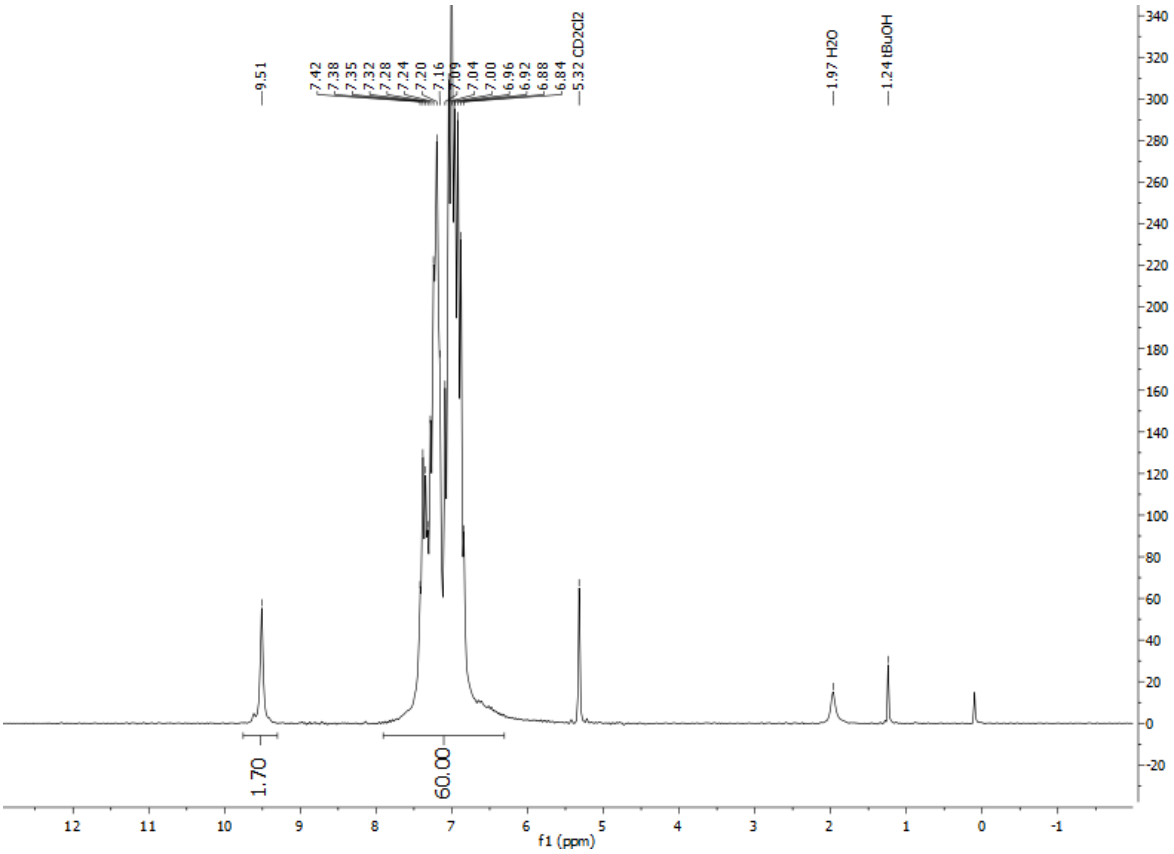


Figure S2.2.3.^{1}H NMR spectrum of **2** in CD_2Cl_2.

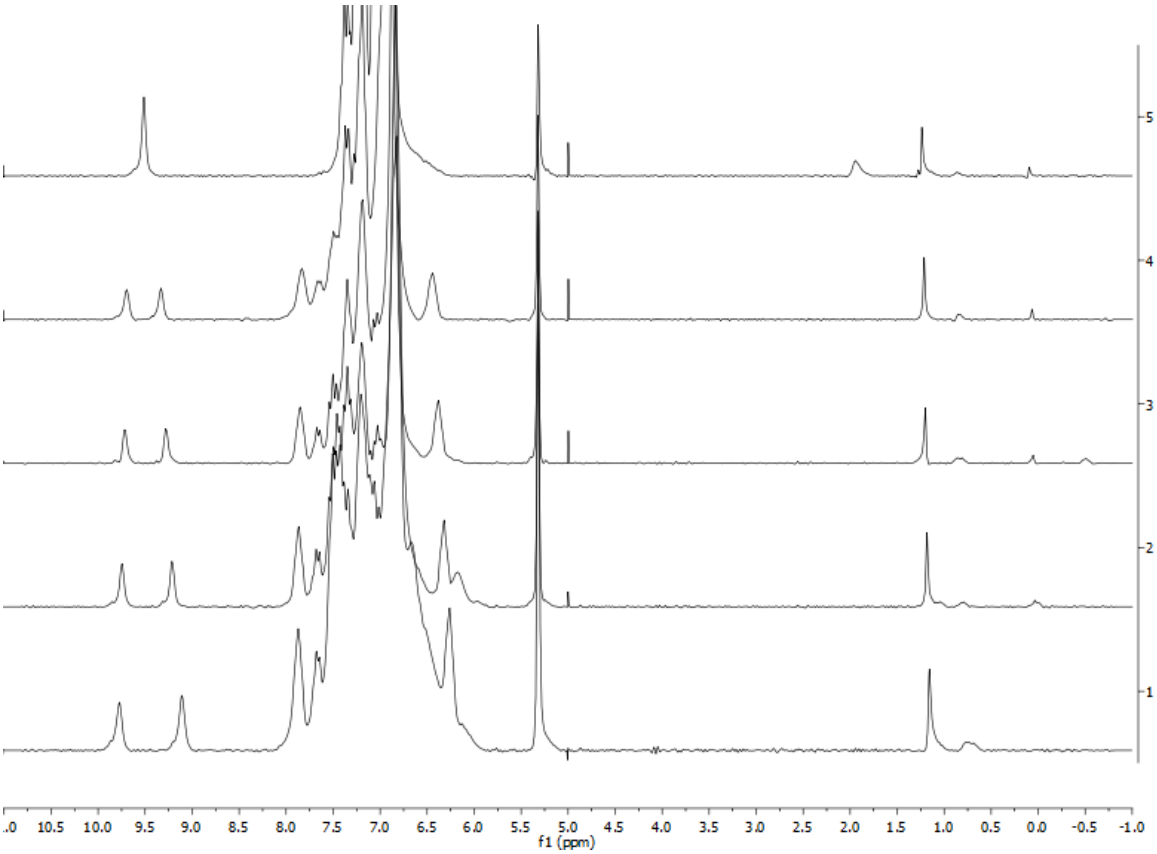


Figure S2.2.4.^{1}H VT-NMR spectra of **2** in CD_2Cl_2. (1) T = -80°C; (2) T = -60°C; (3) T = -40°C; (4) T = -20°C; (5) T = 20°C.

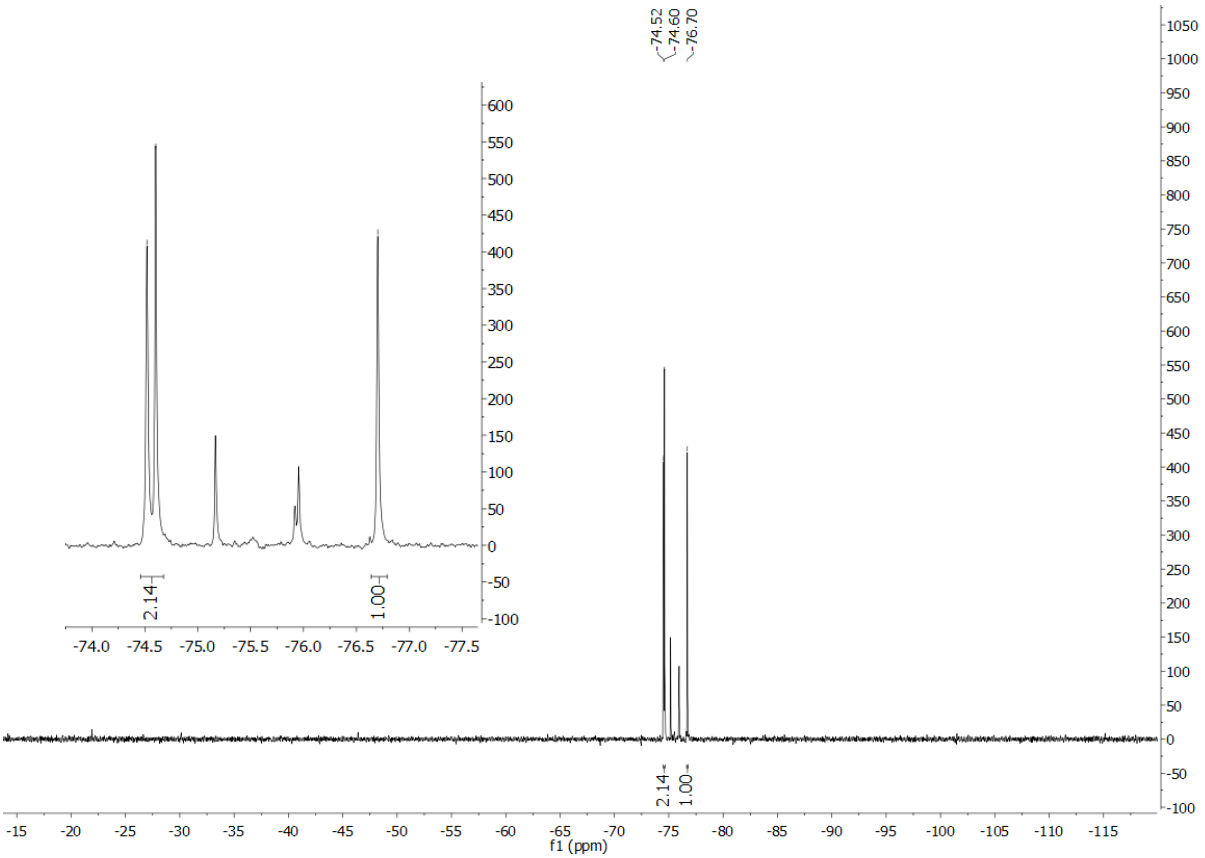


Figure S2.2.5. $^{19}F\{^{1}H\}$ NMR spectrum of **2** in CD_2Cl_2.

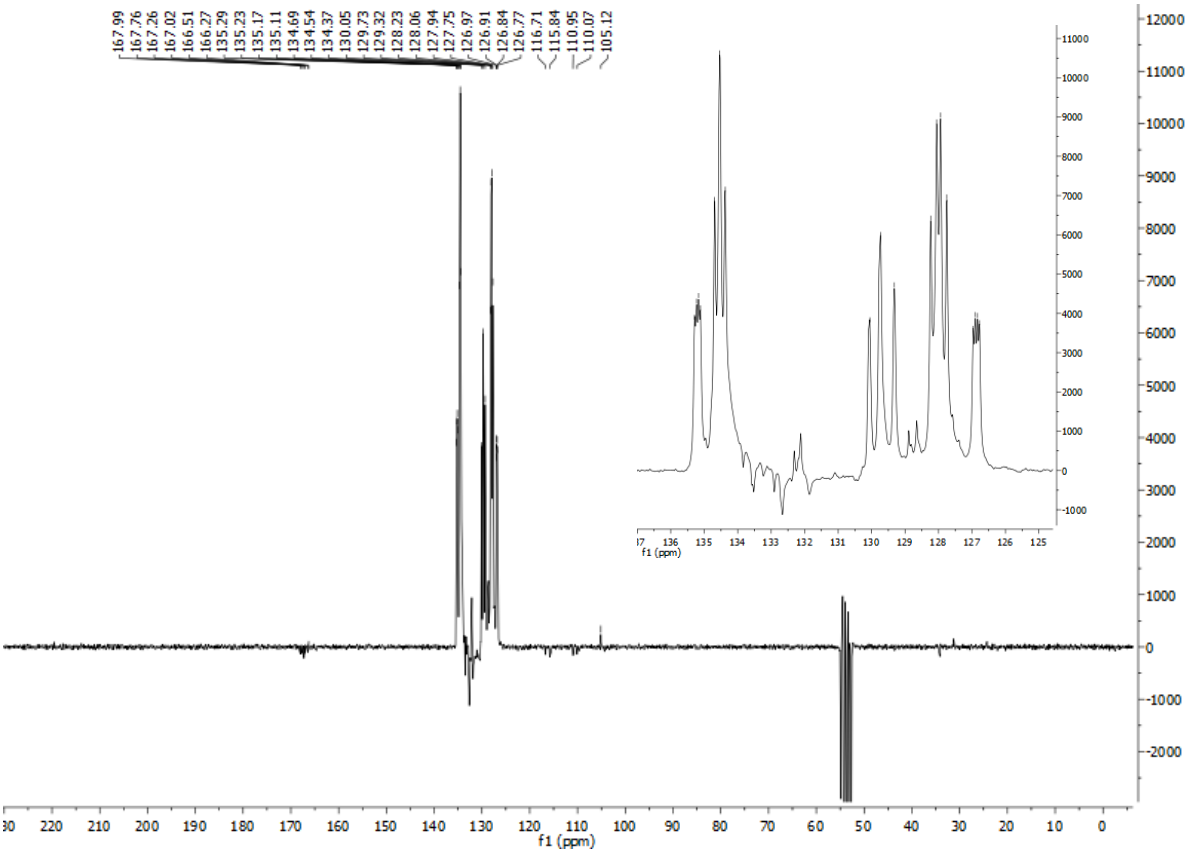


Figure S2.2.6. $^{13}C\{^{1}H\}$ DEPT NMR spectrum of **2** in CD_2Cl_2.

2.3 NMR spectra of complex 3.

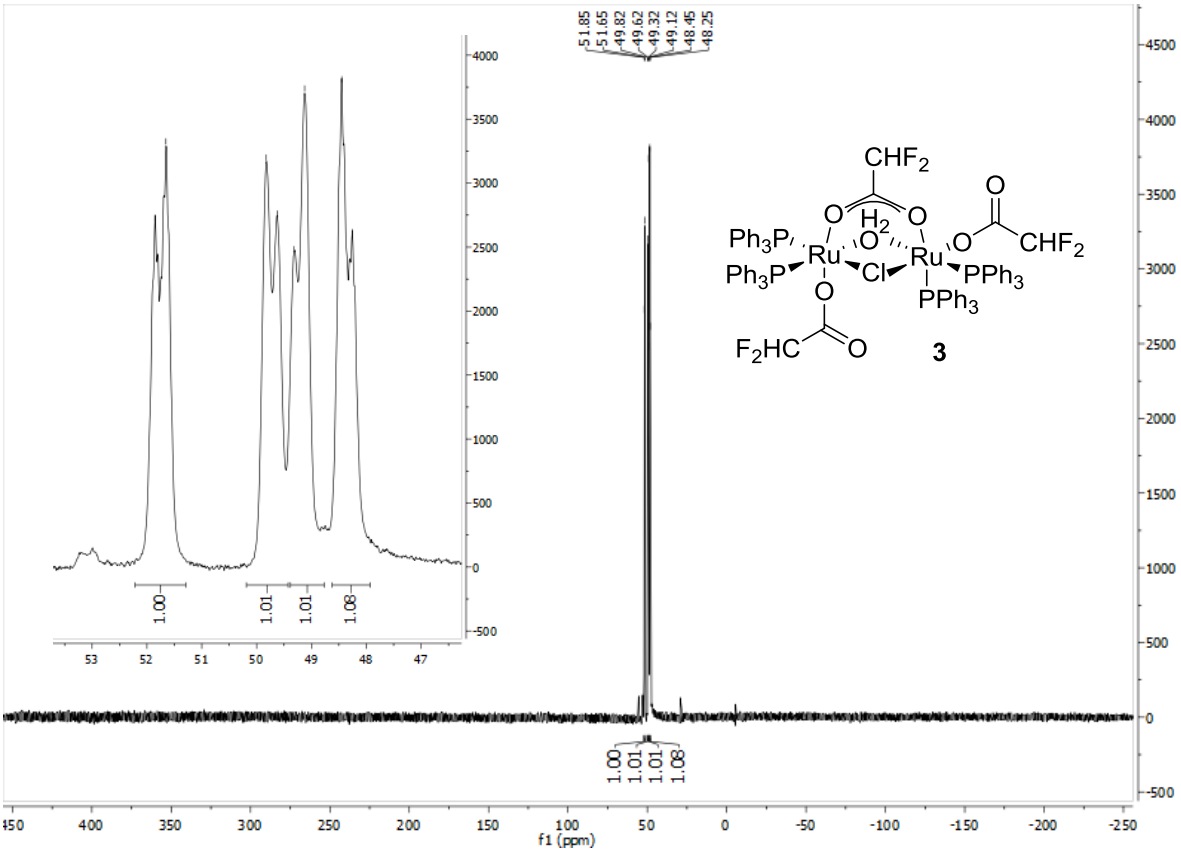


Figure S2.3.1.$^{31}P\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

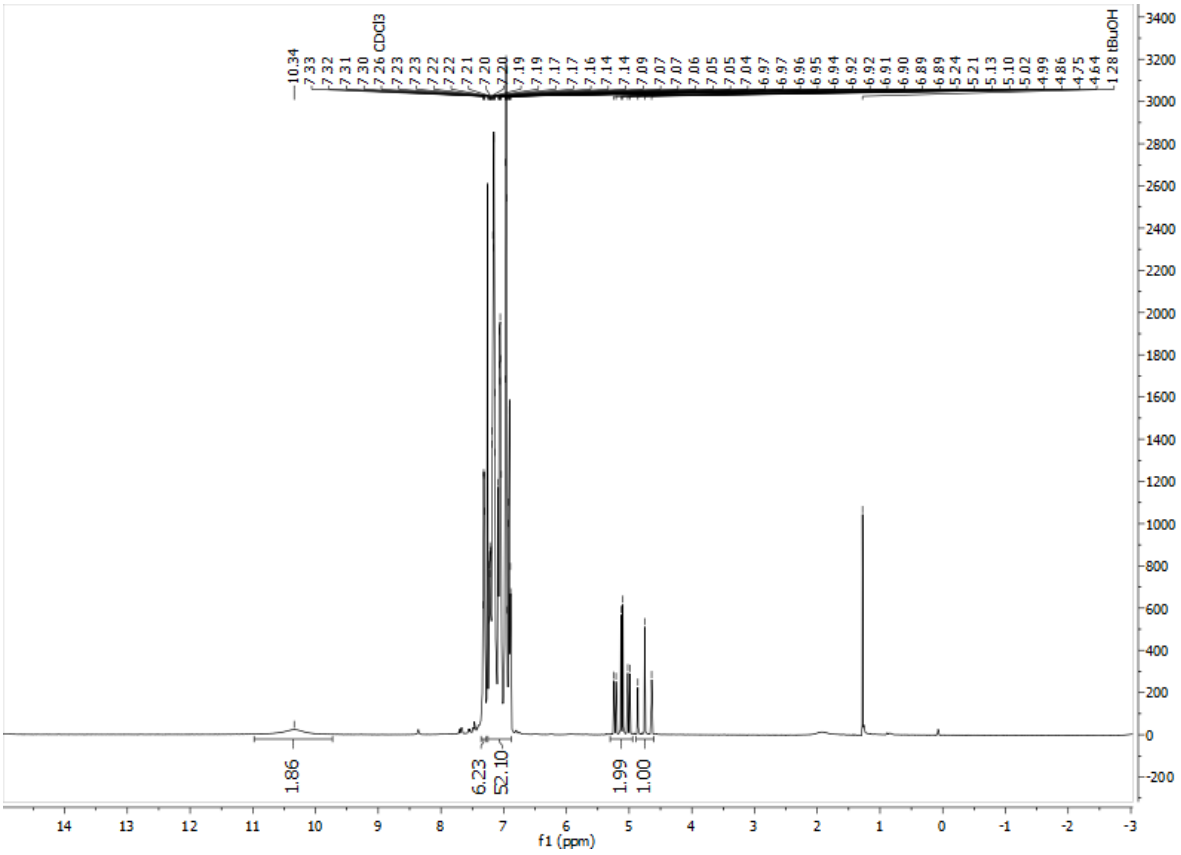


Figure S2.3.2.^{1}H NMR spectrum of **3** in $CDCl_3$.

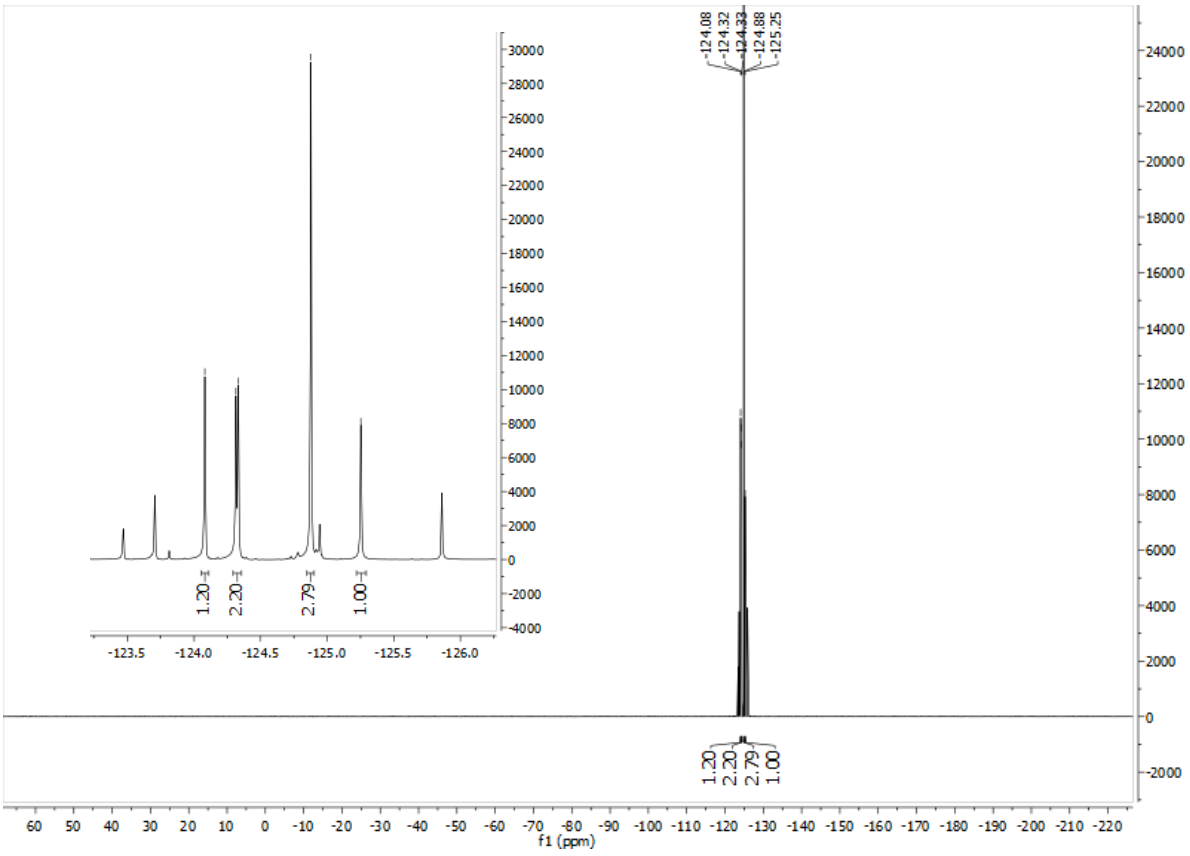


Figure S2.3.3.$^{19}F\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

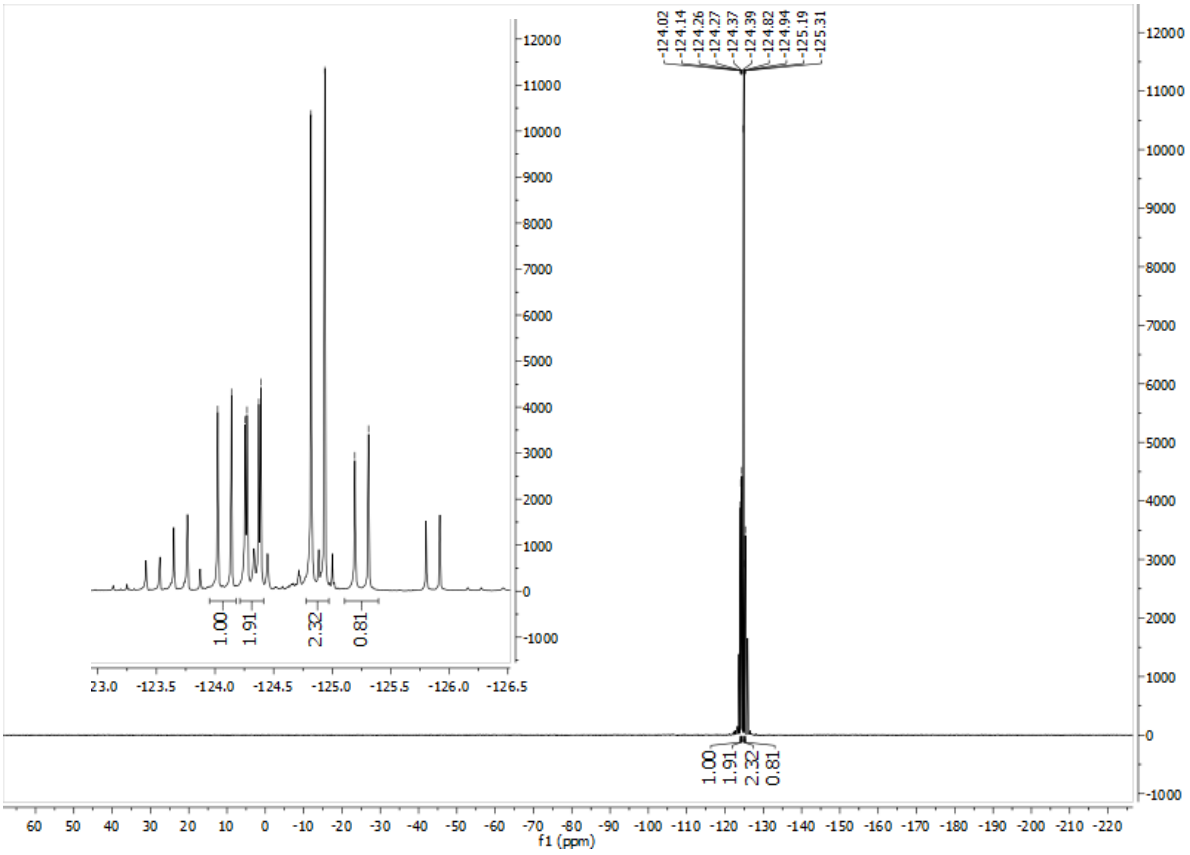


Figure S2.3.4.^{19}F NMR spectrum of **3** in $CDCl_3$.

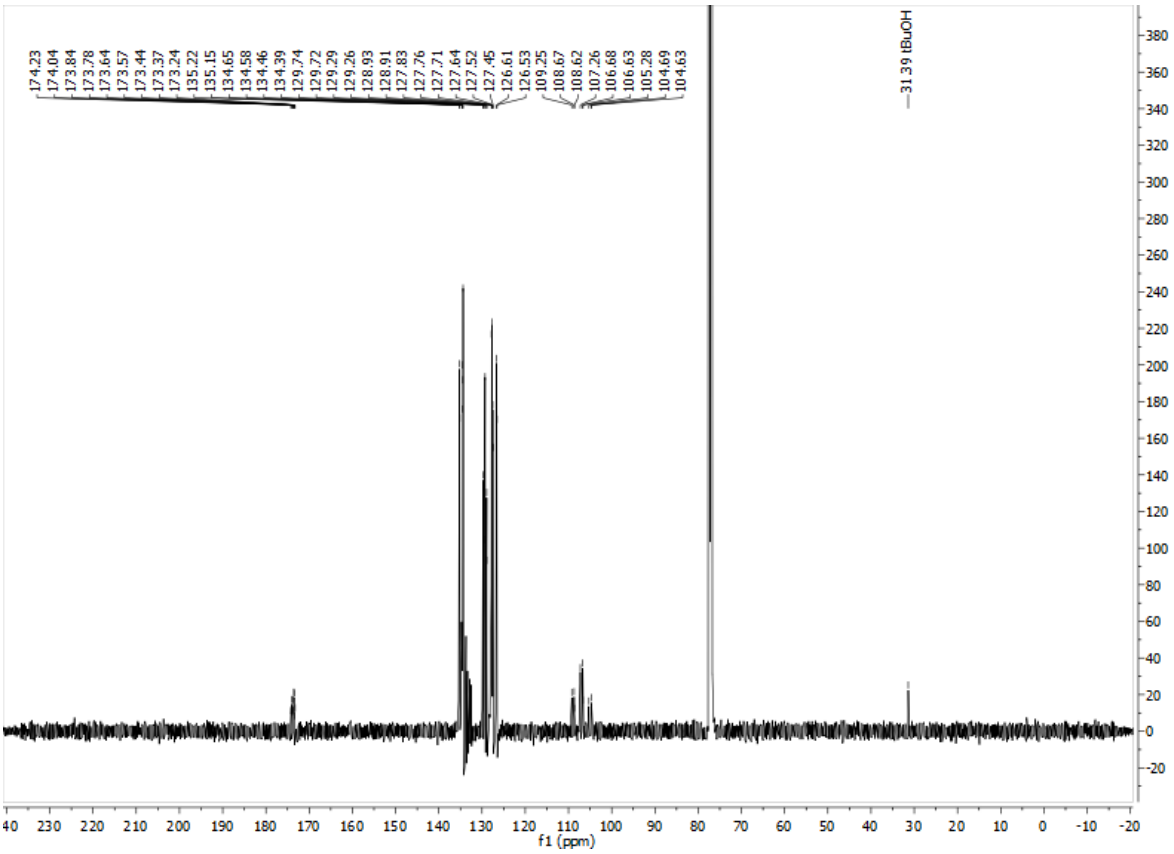
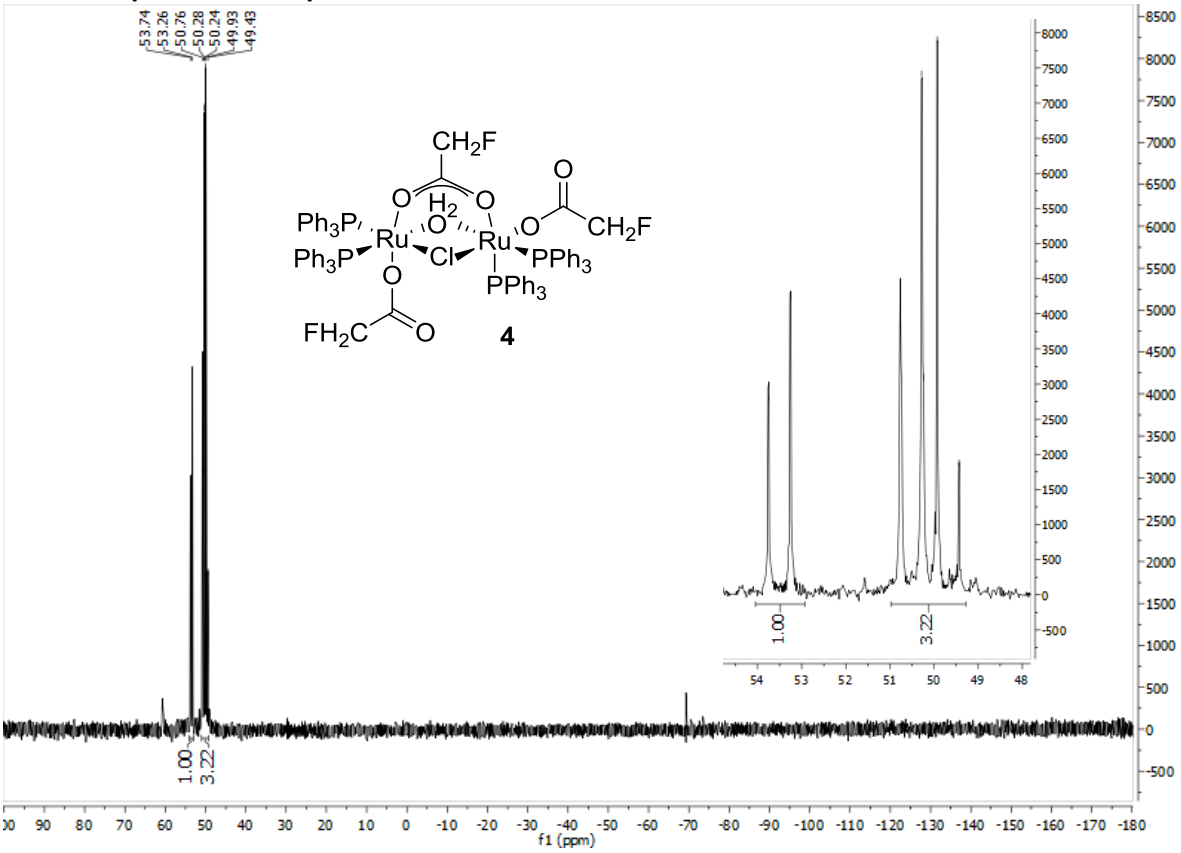


Figure S2.3.5. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

2.4 NMR spectra of complex 4.



4

Figure S2.4.1.$^{31}P\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$.

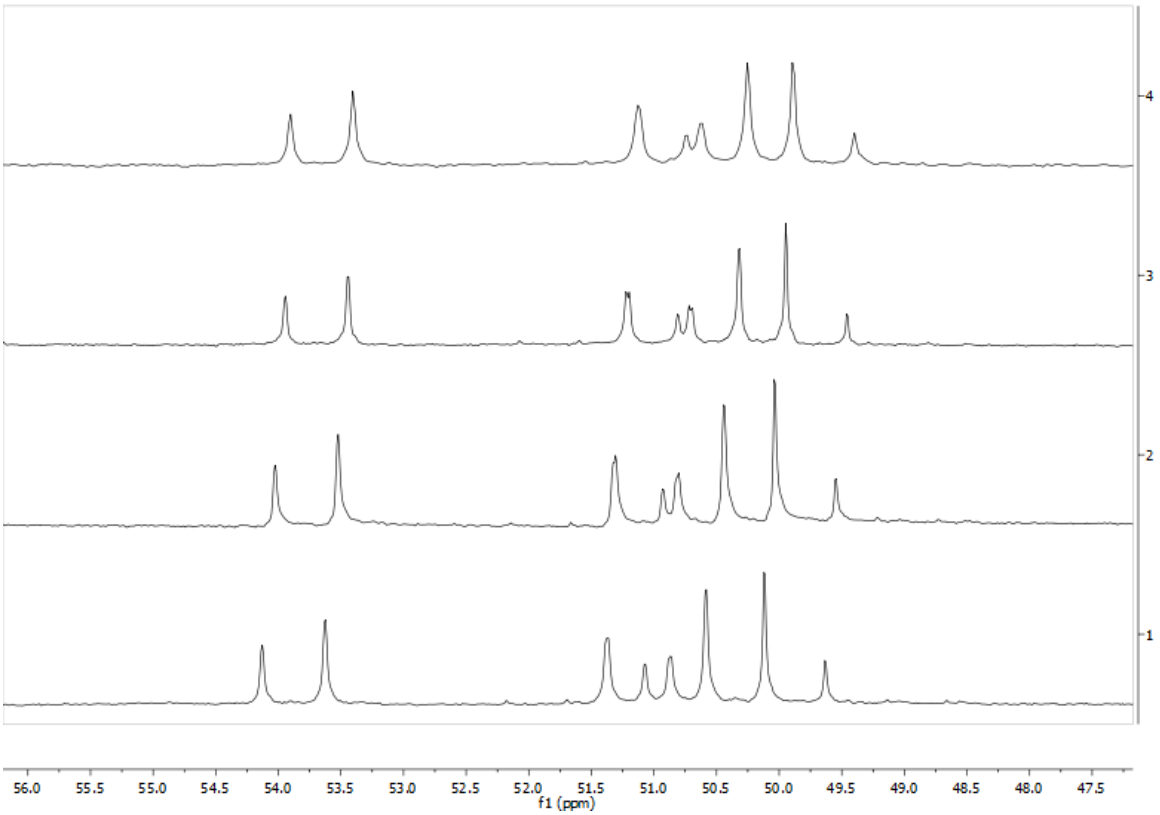


Figure S2.4.2.$^{31}P\{^{1}H\}$ VT-NMR spectra of **4** in CD_2Cl_2. (1) T = -40°C; (2) T = -20°C; (3) T = 0°C; (4) T = 10°C.

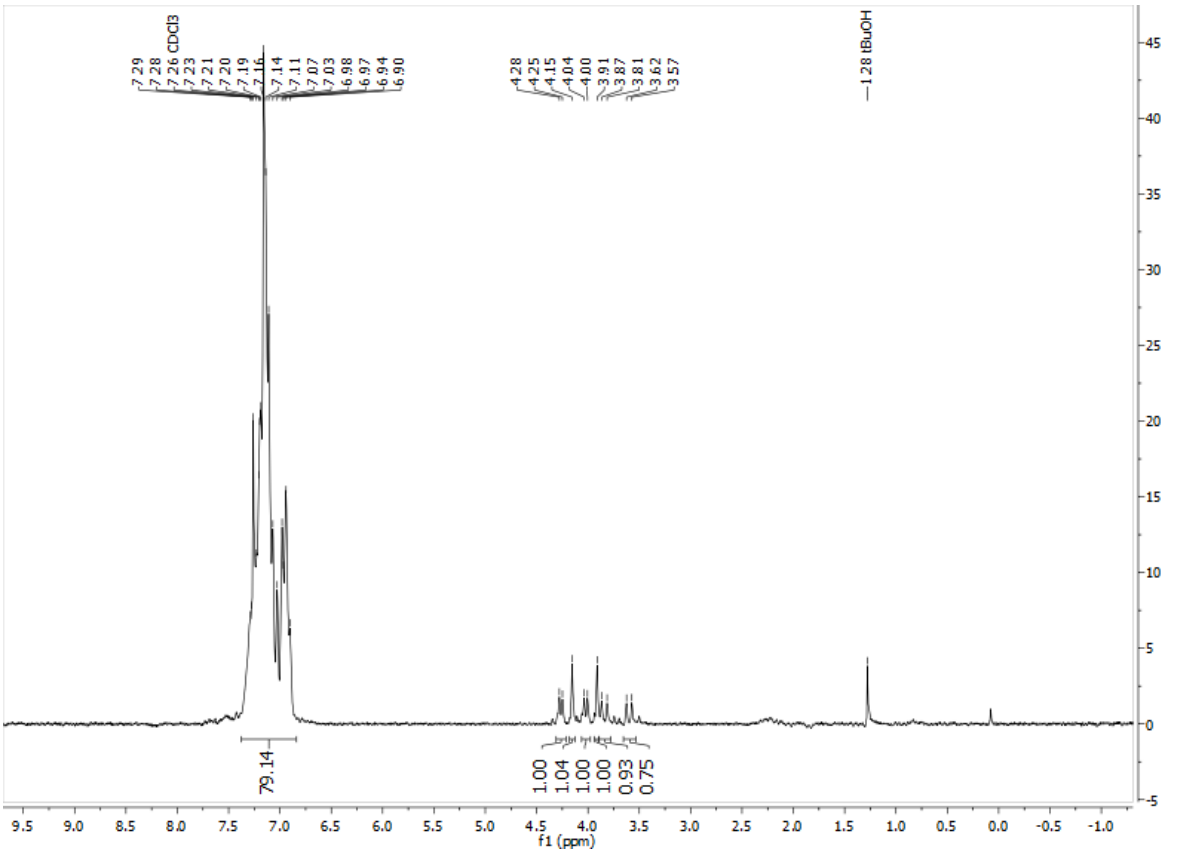


Figure S2.4.3.^{1}H NMR spectrum of **4** in $CDCl_3$.

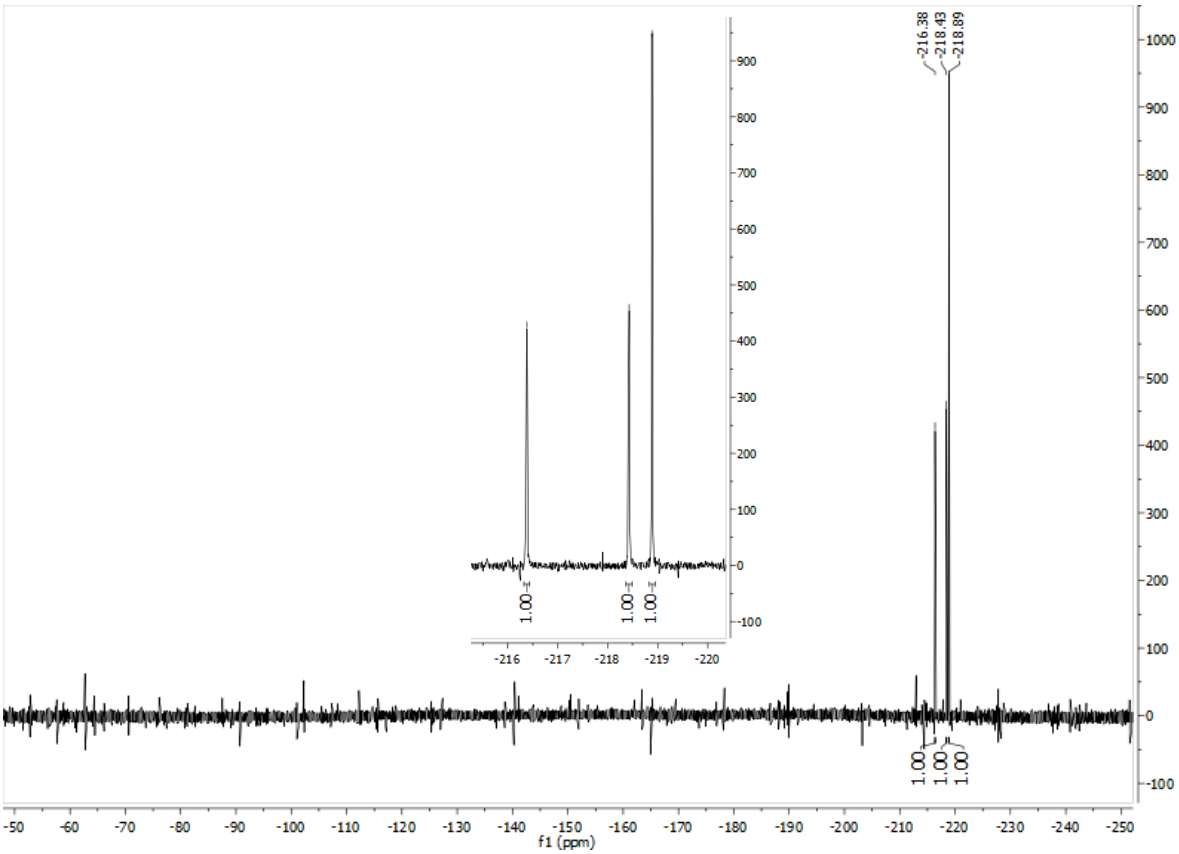


Figure S2.4.4.^{19}F{^{1}H} NMR spectrum of **4** in CD_2Cl_2.

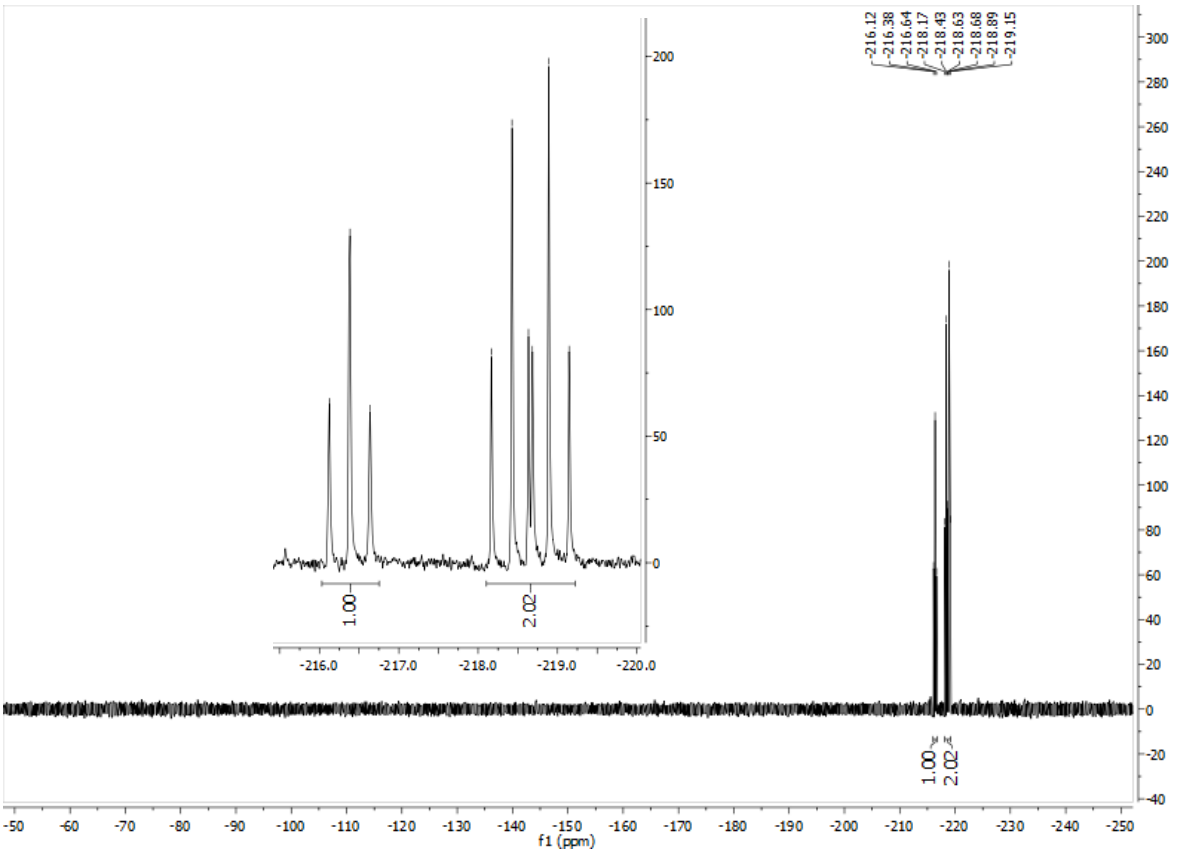


Figure S2.4.5.^{19}F NMR spectrum of **4** in CD_2Cl_2.

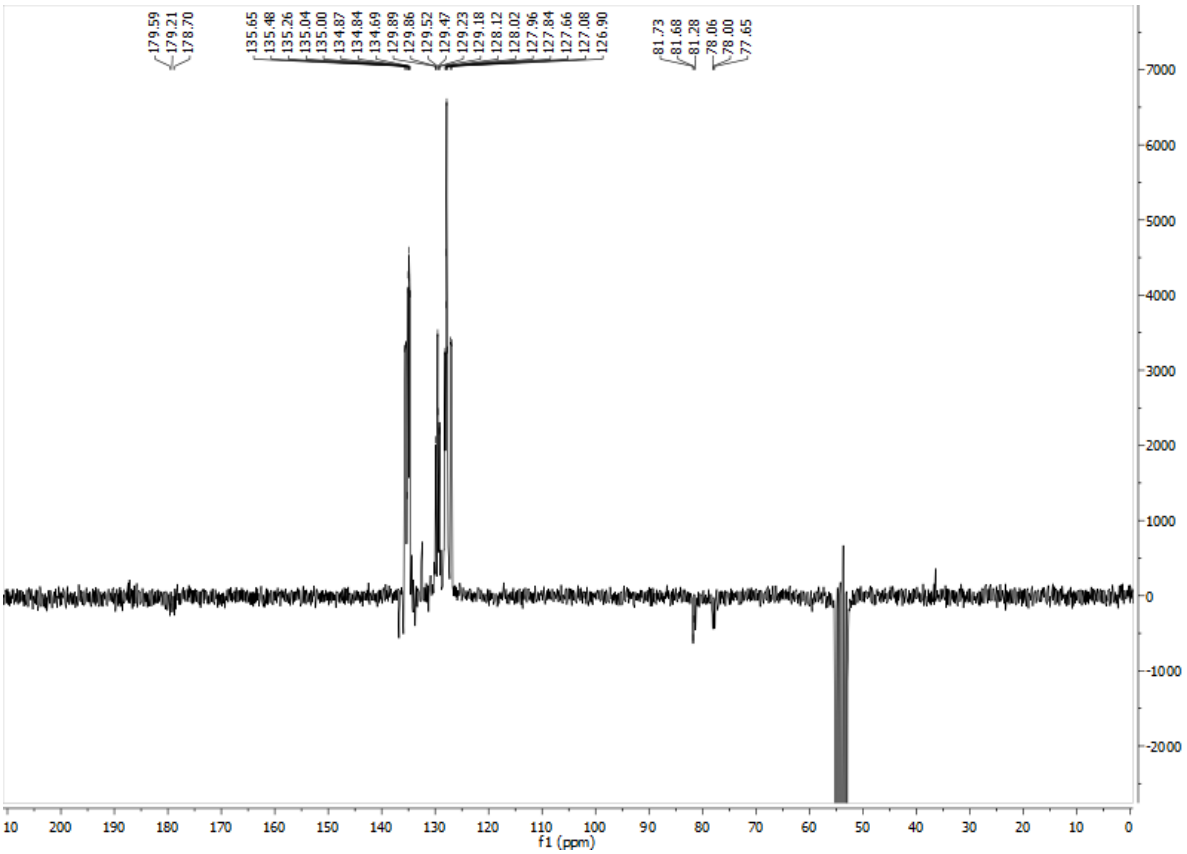


Figure S2.4.6.^{13}C{^{1}H} DEPT NMR spectrum of **4** in $CDCl_3$.

2.5 NMR spectra of complex 7.

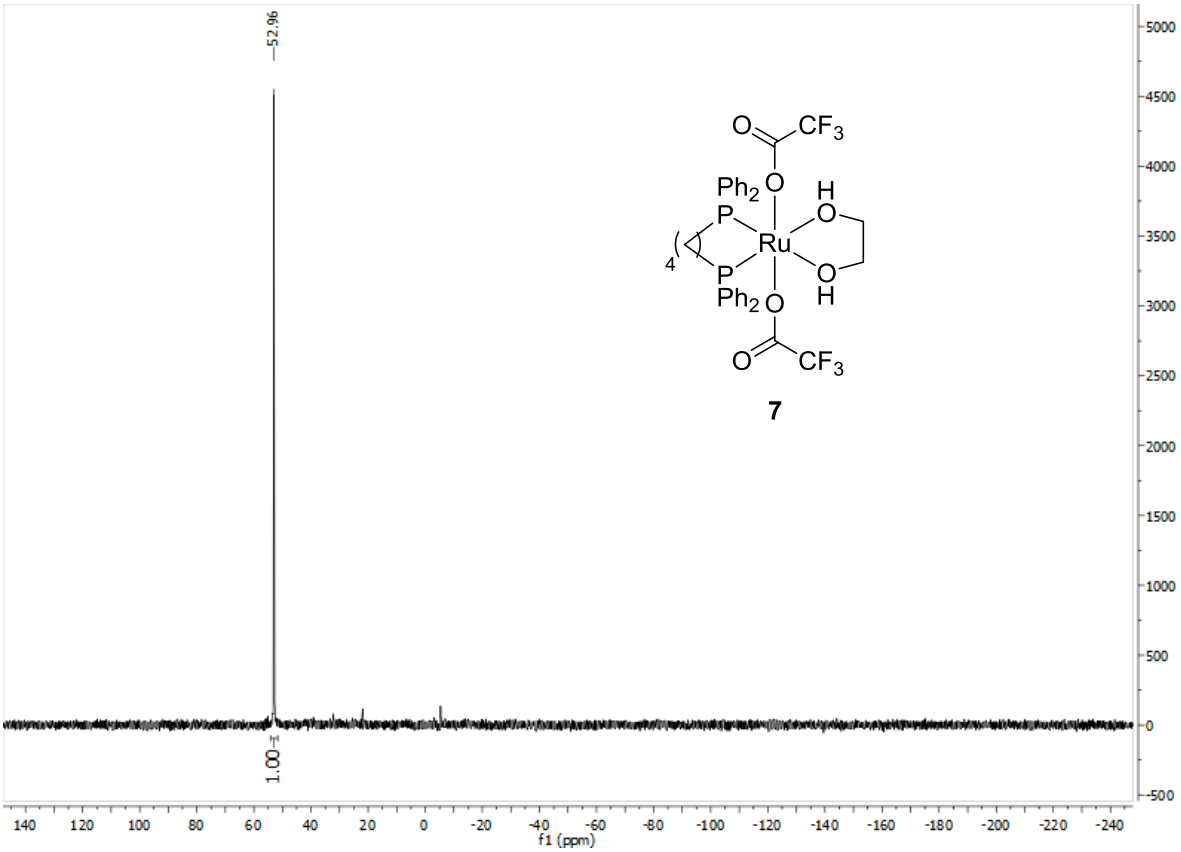


Figure S2.5.1.$^{31}P\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$.

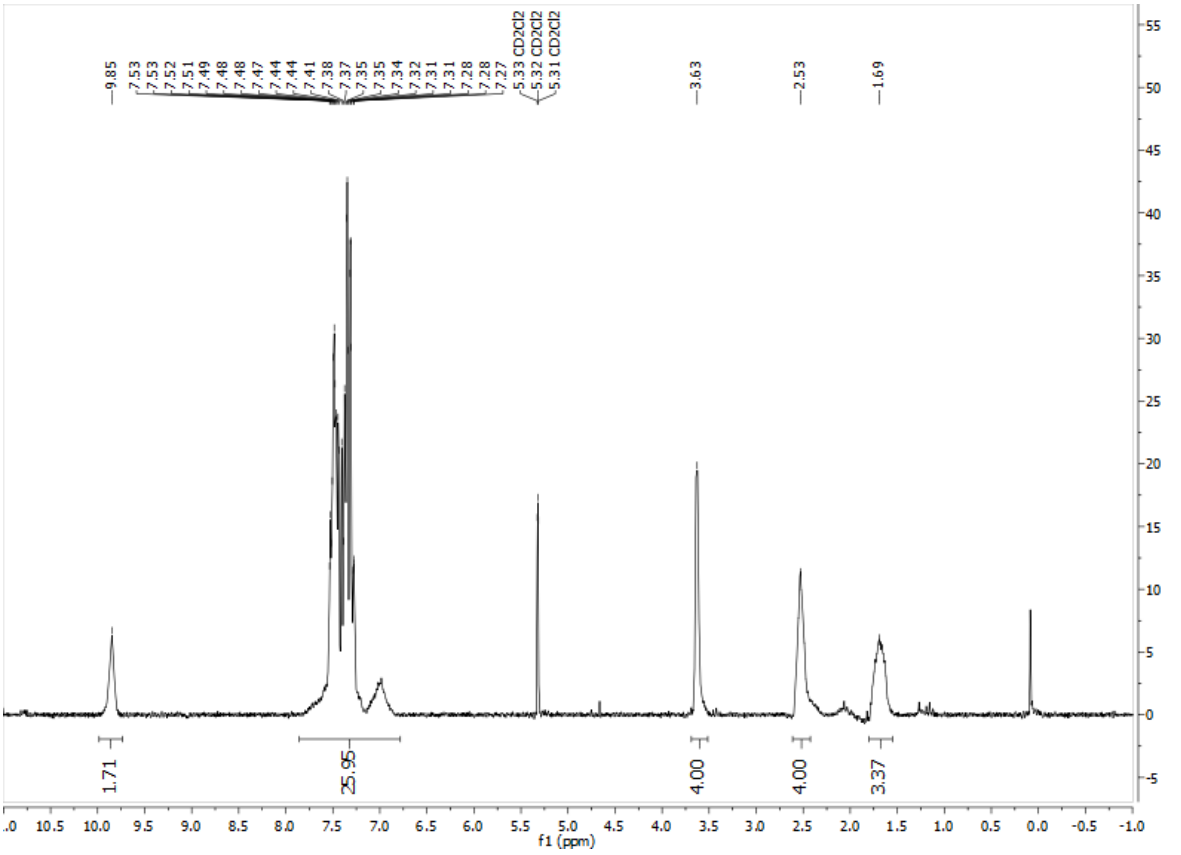


Figure S2.5.2.^{1}H NMR spectrum of **7** in CD_2Cl_2.

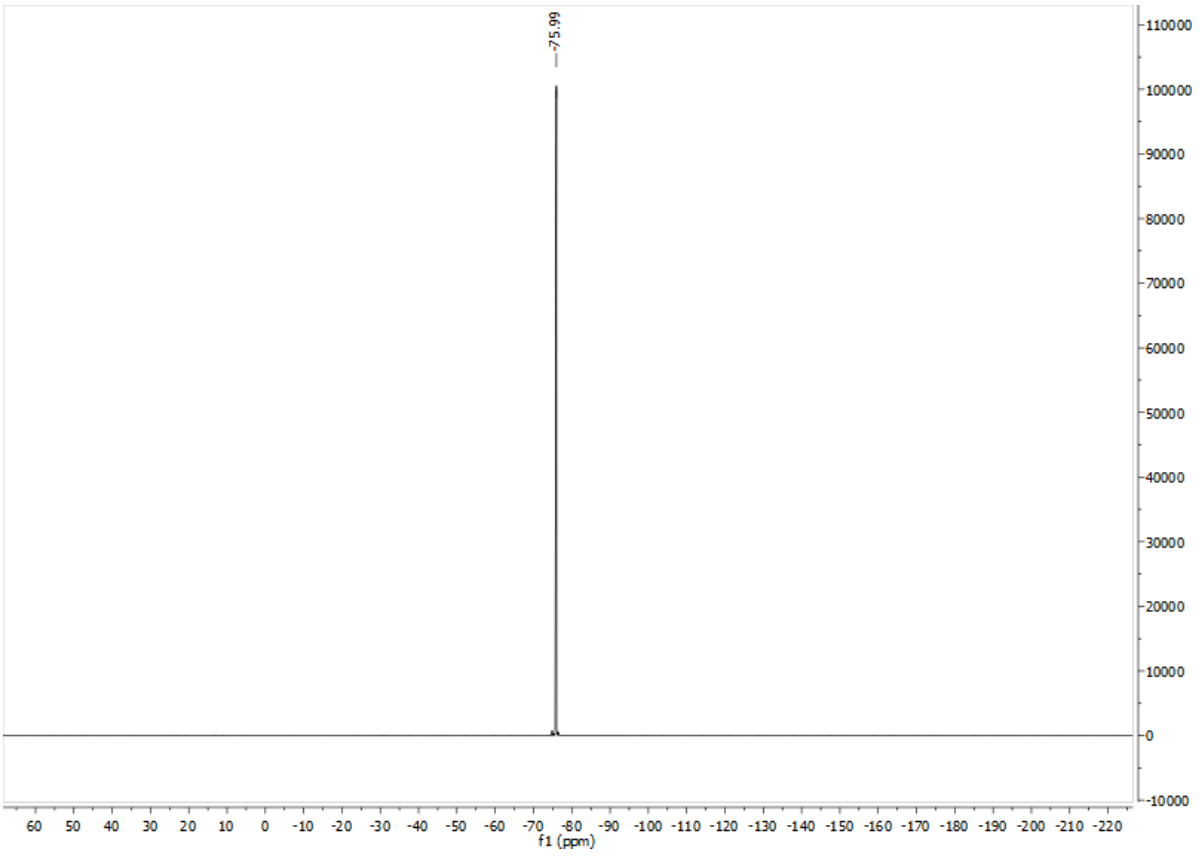


Figure S2.5.3.$^{19}F\{^{1}H\}$ NMR spectrum of **7** in CD_2Cl_2.

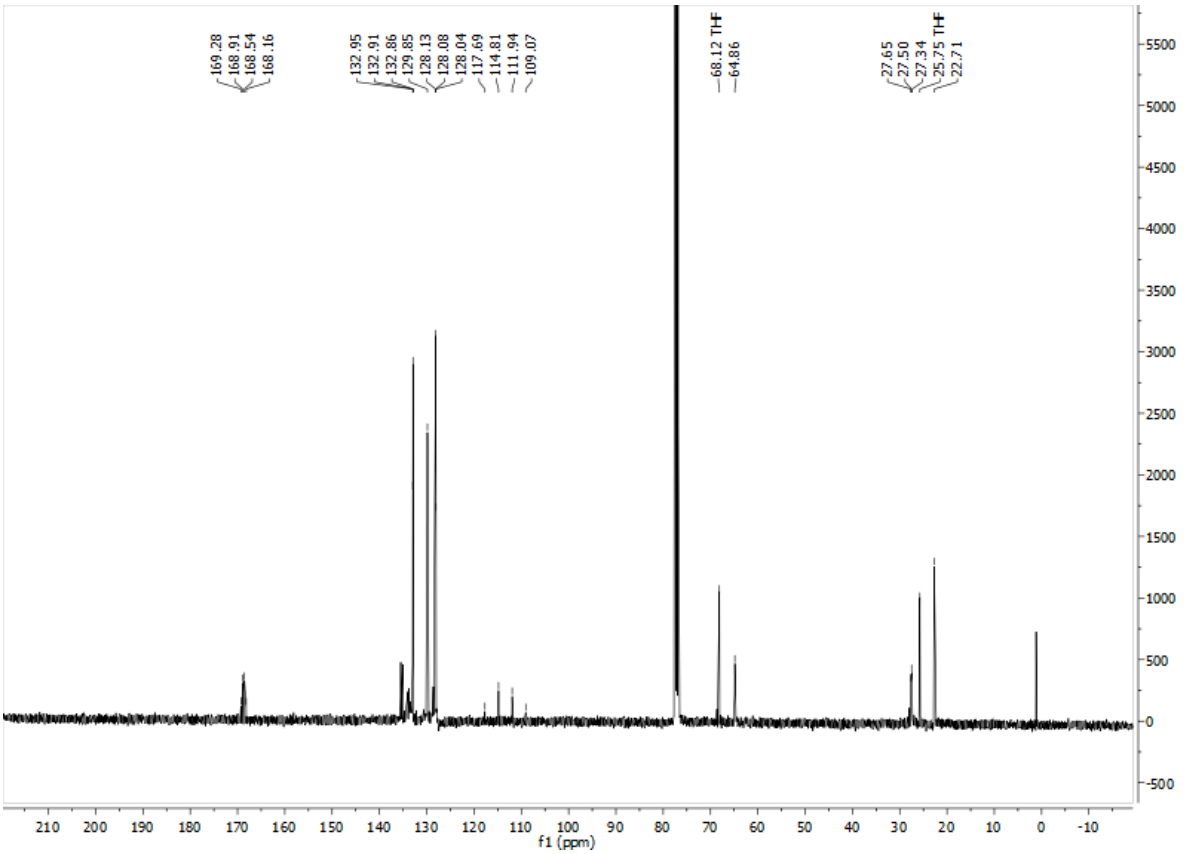
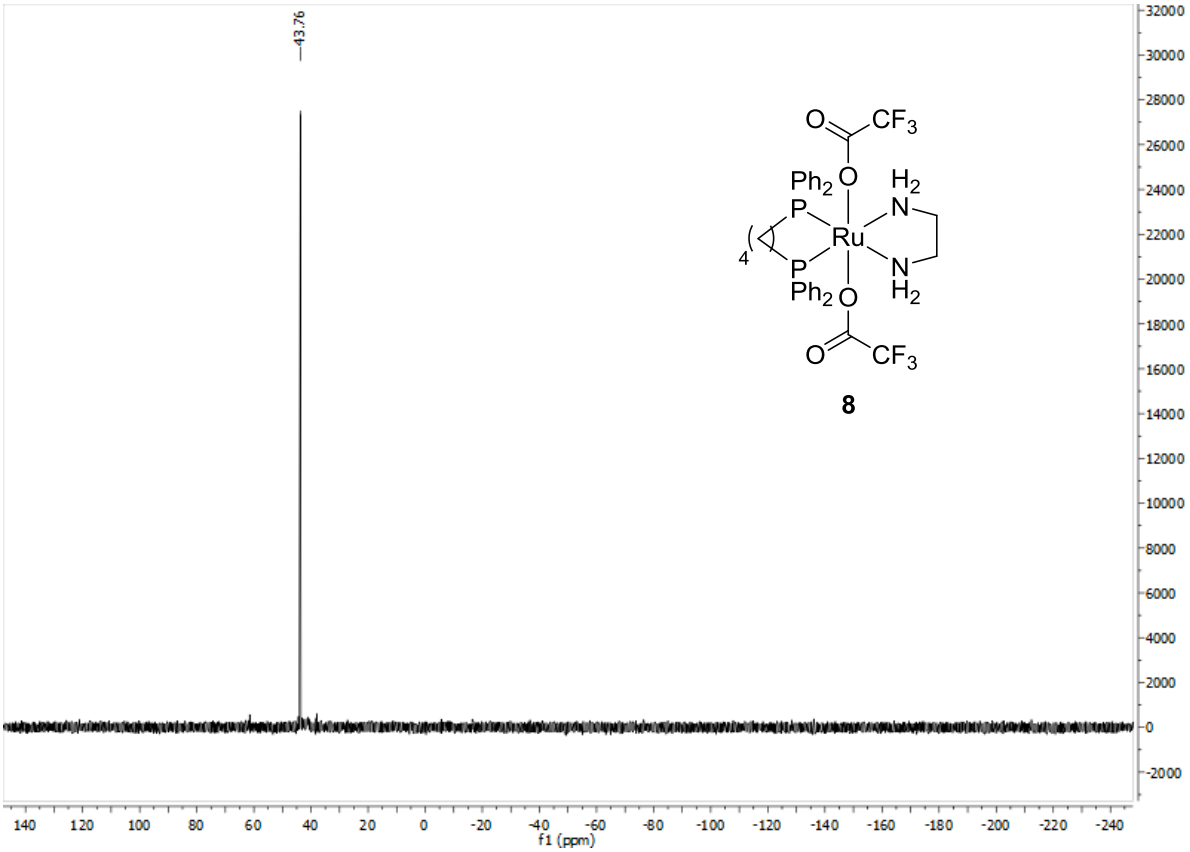


Figure S2.5.4.$^{13}C\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$.

2.6 NMR spectra of complex 8.



8

Figure S2.6.1.$^{31}P\{^{1}H\}$ NMR spectrum of **8** in CD_2Cl_2.

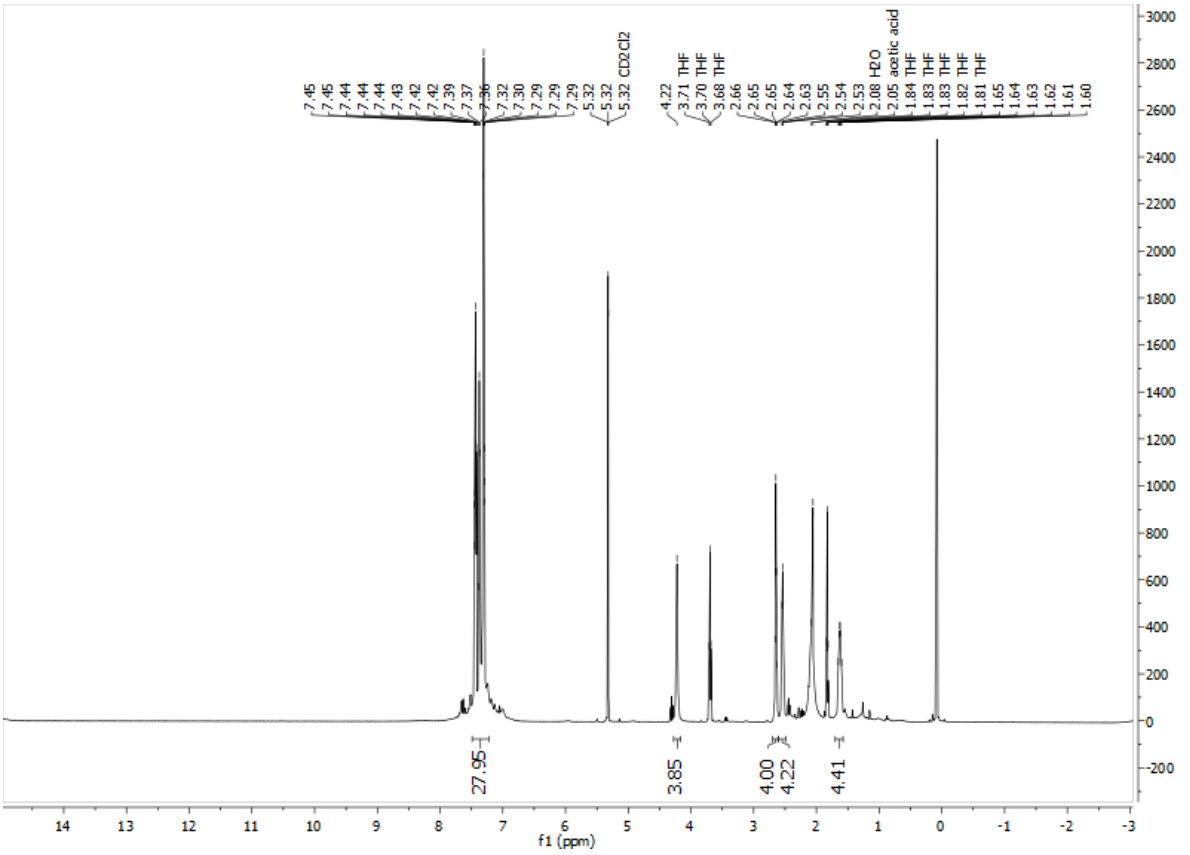


Figure S2.6.2.^{1}H NMR spectrum of **8** in CD_2Cl_2.

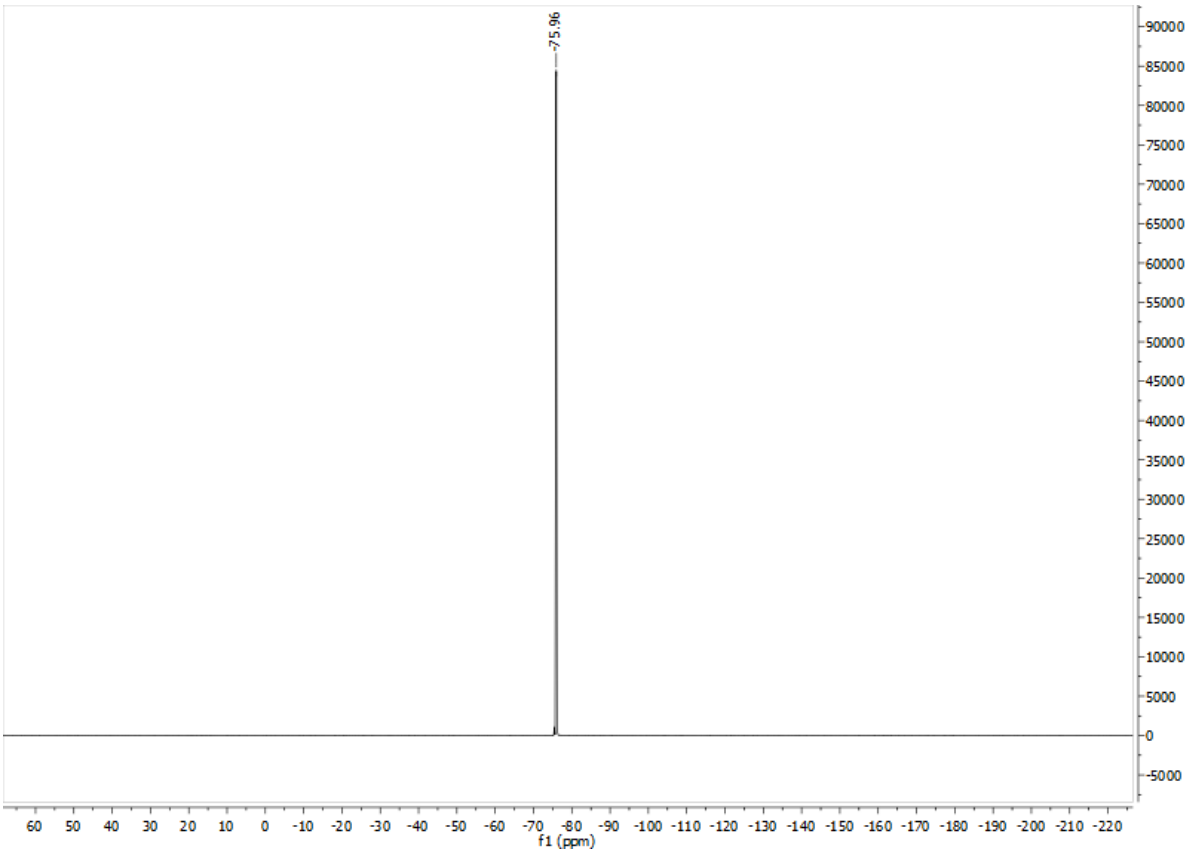


Figure S2.6.3.$^{19}F\{^{1}H\}$ NMR spectrum of **8** in CD_2Cl_2.

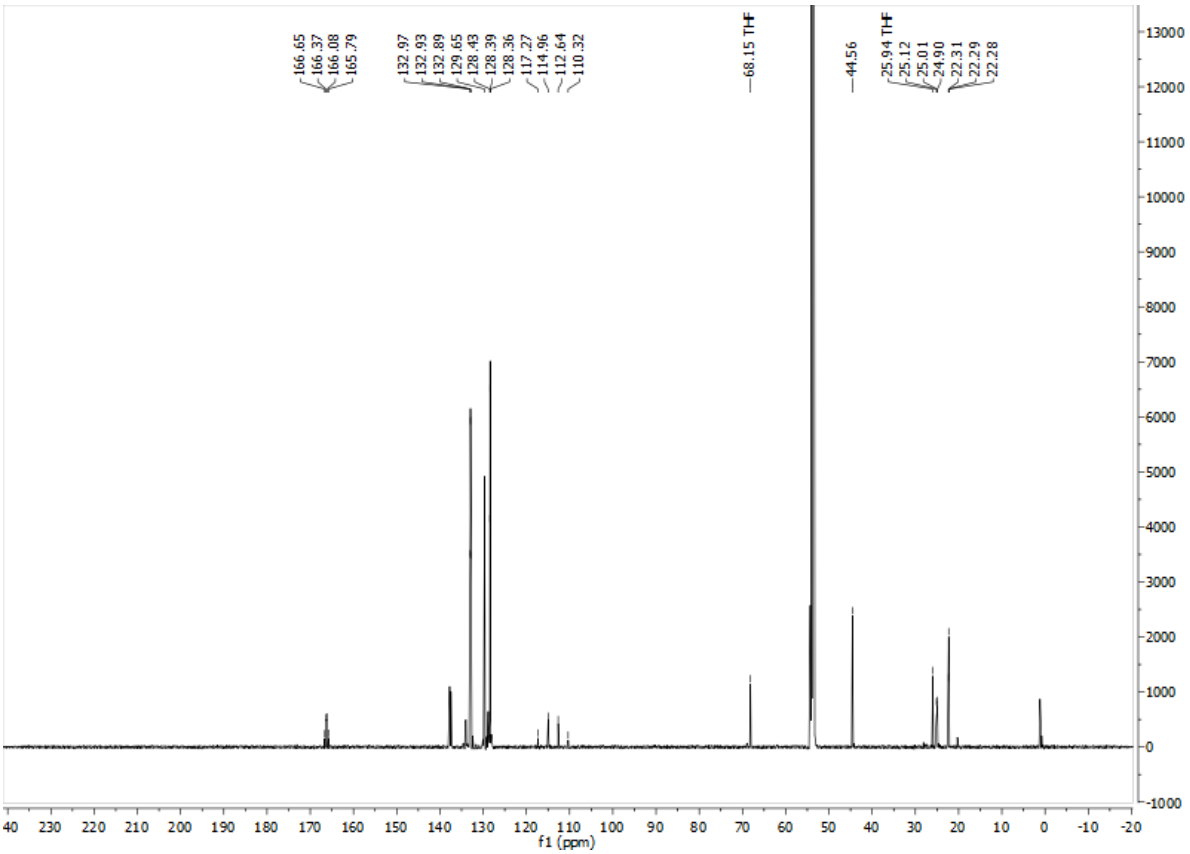


Figure S2.6.4.$^{13}C\{^{1}H\}$ NMR spectrum of **8** in CD_2Cl_2.

3. Catalytic transfer hydrogenation of ketones

3.1 Transfer hydrogenation of acetophenone

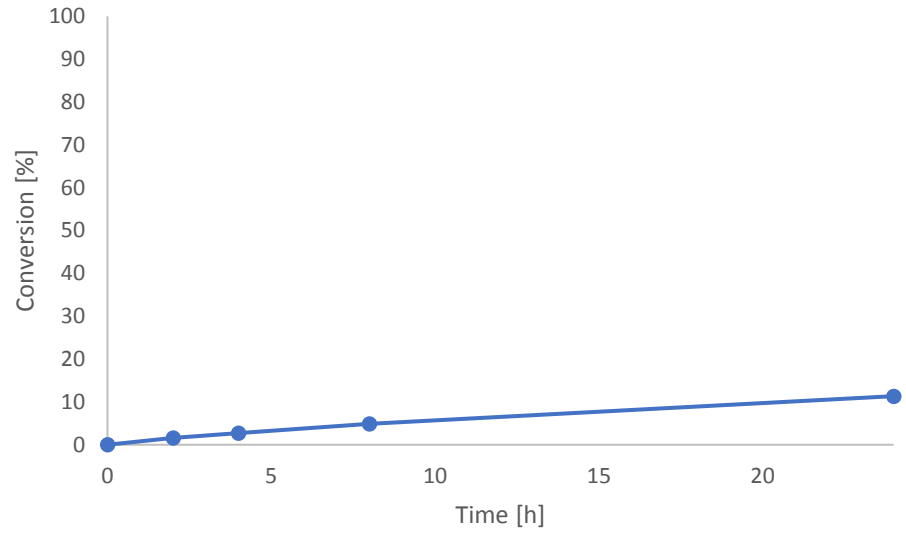


Figure S3.1.1. Transfer hydrogenation of acetophenone in ^{i}PrOH with 2 mol% NaO^{i}Pr without catalyst.

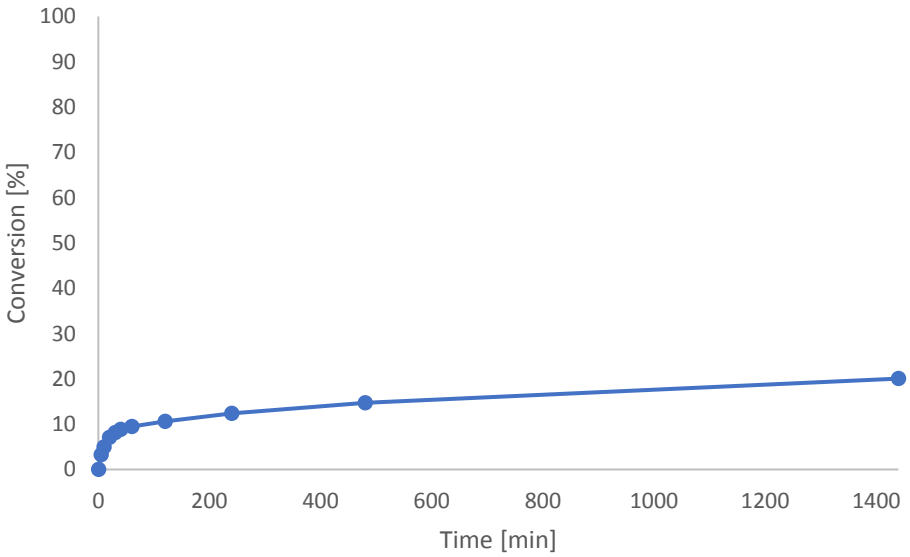


Figure S3.1.2. Transfer hydrogenation of acetophenone in ^{i}PrOH with 2 mol% NaO^{i}Pr and 0.1 mol% **1**.

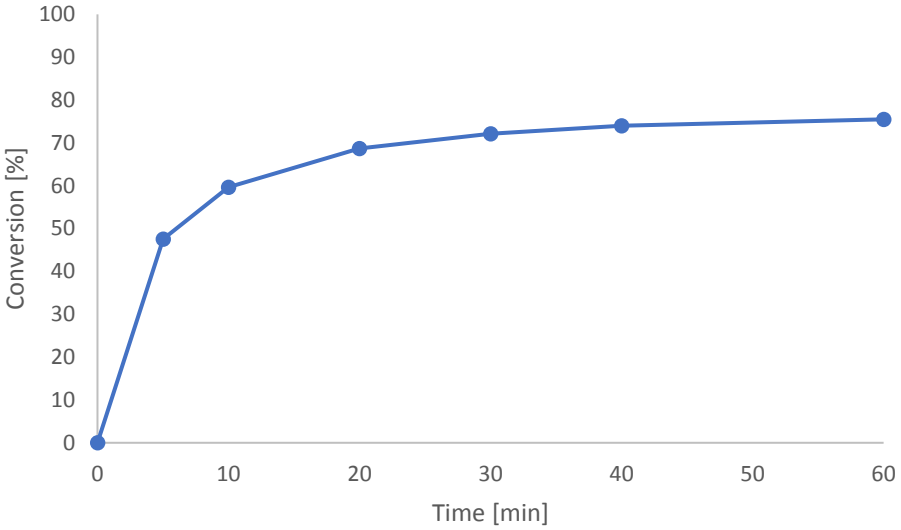


Figure S3.1.3. Transfer hydrogenation of acetophenone in ^{i}PrOH with 2 mol% NaO^{i}Pr and 0.1 mol% **7**.

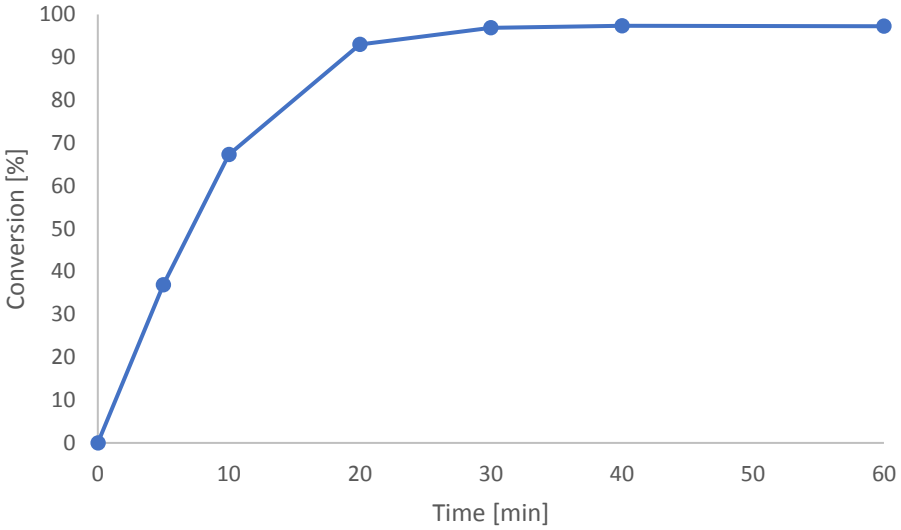


Figure S3.1.4. Transfer hydrogenation of acetophenone in ^{i}PrOH with 2 mol% NaO^{i}Pr and 0.1 mol% **8**.

3.2 Transfer hydrogenation of benzophenone

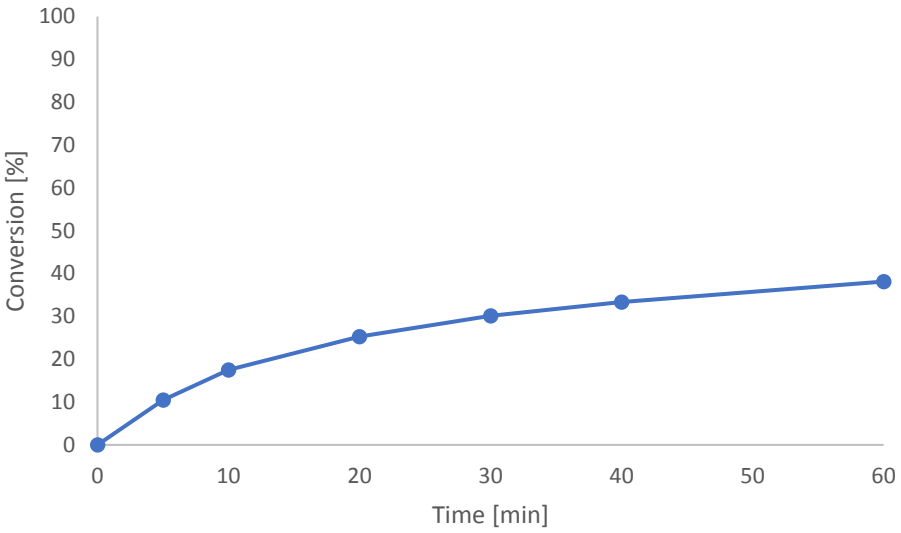


Figure S3.2.1. Transfer hydrogenation of benzophenone in ^{i}PrOH with 2 mol% NaO^{i}Pr and 0.1 mol% **7**.

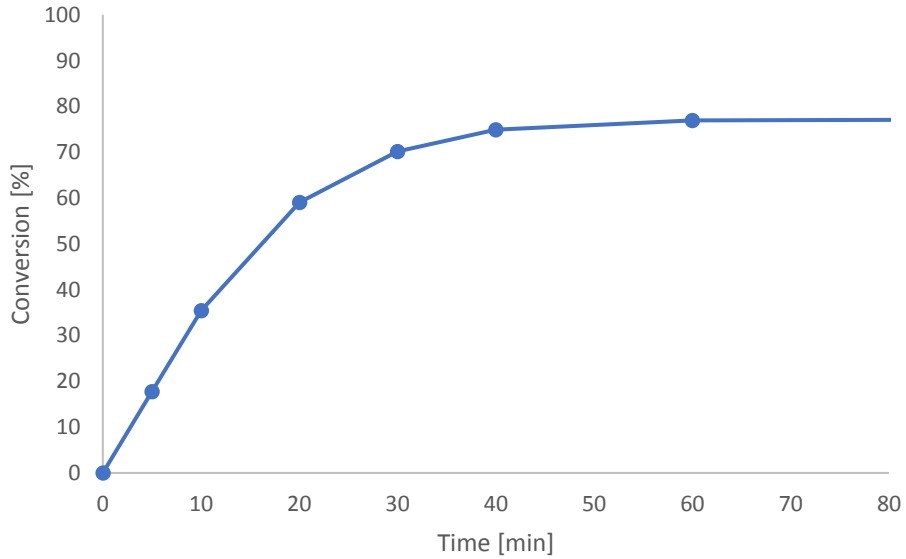


Figure S3.2.2. Transfer hydrogenation of benzophenone in ^{i}PrOH with 2 mol% NaO^{i}Pr and 0.1 mol% **8**.

3.3 Transfer hydrogenation of cyclohexanone

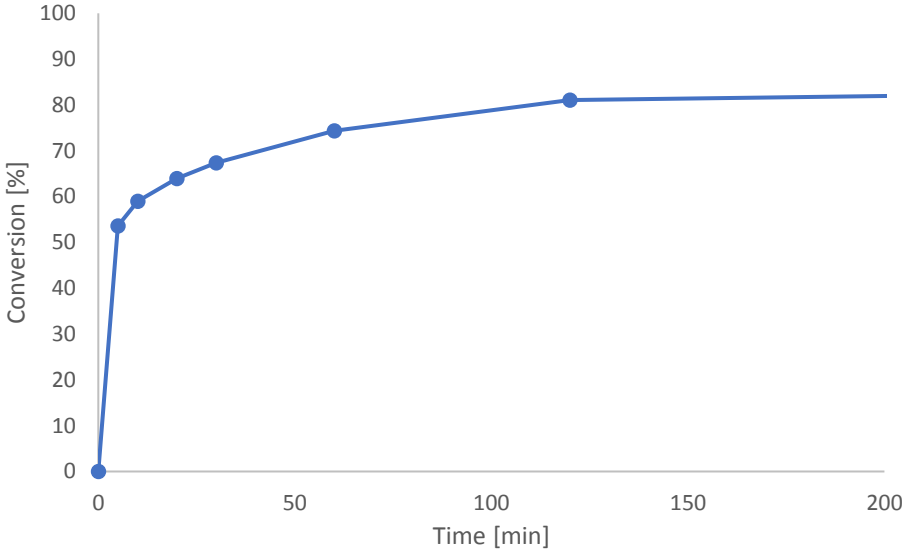


Figure S3.3.1. Transfer hydrogenation of cyclohexanone in ^{i}PrOH with 2 mol% NaO^{i}Pr and 0.03 mol% **7**.

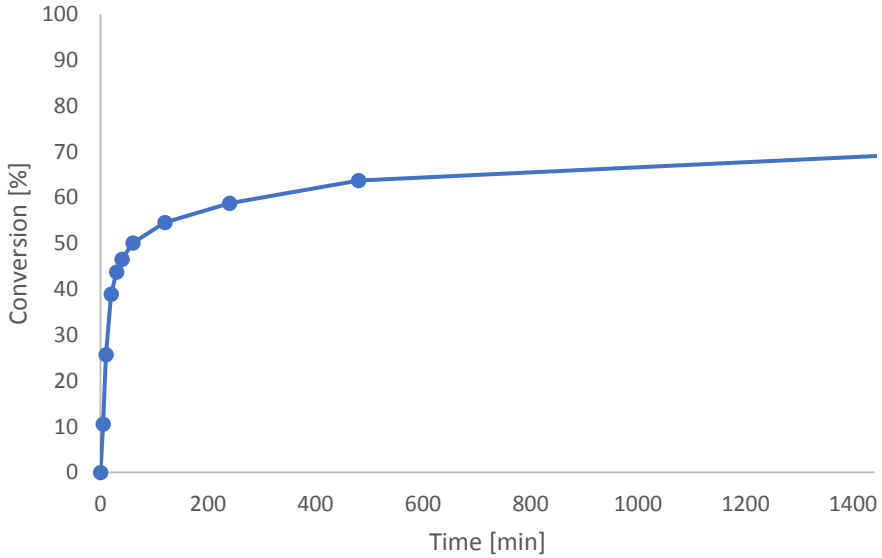


Figure S3.3.2. Transfer hydrogenation of cyclohexanone in ^{i}PrOH with 2 mol% NaO^{i}Pr and 0.03 mol% **8**.