Supporting Information for

Ruthenium Catalyzed Dehydrogenation of Alcohols and Mechanistic Study

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General Information and Materials. All reactions were performed under Argon gas atmosphere using chemicals of high purity purchased from sigma Aldrich, TCI chemicals and Alfa Aesar.

Instrumentation. ^{1}H NMR (300, 400 and 500 MHz), ^{13}C NMR (100 MHz) and ^{31}P NMR (161.97 MHz) spectra are recorded at 298 K using DMSO-d_6, $CDCl_3$ or methanol-d_4 as the solvent on a Bruker Avance 300, 400 and 500 spectrometer. Tetramethylsilane (TMS) is used as an external standard and the chemical shifts in ppm are reported relative to the centre of the singlet at 7.26 ppm for $CDCl_3$, 2.49 ppm for DMSO-d_6 and multiplet at 3.30 ppm for methanol-d_4 in ^{1}H NMR, and to the centre of the triplet at 77.0 ppm for $CDCl_3$ and 39.50 ppm for DMSO-d_6 in ^{13}C NMR. Suitable single crystals of complexes **[Ru]-1, [Ru]-2** and **[Ru]-5** subjected to single-crystal X-ray structural studies using Agilent Technologies Supernova CCD system. Coupling constant (*J*) values are reported in hertz (Hz), and the splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); br. (broad). ESI (positive mode), and high-resolution mass spectra (HRMS) are recorded on a micro TF-Q II mass spectrometer. GC-TCD analysis was performed on a Shimadzu GCMS-QP2010 Ultra and GC-2010 Plus system in EI (electron impact) mode using RT-Msieve 5A column.

Single-crystal X-ray diffraction studies: Single crystal was obtained by diffusion of diethyl ether into methanol solution of the complex **[Ru]-1, [Ru]-2,** and **[Ru]-5** are performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data are collected at 150(2) K using graphite-monochromated Mo Kα radiation ($\lambda\alpha$ = 0.71073 A). The strategy for the data collection evaluated using the CrysAlisPro CCD software. The data are collected using the standard 'phi-omega' scans techniques, and are scaled and reduced using CrysAlisPro RED software. The structures are solved by direct methods using SHELXS-97, and refined using full

matrix least-squares with SHELXL-97, refining on F2.[S1] The positions of all the atoms are obtained by direct methods. All non-hydrogen atoms are refined anisotropically. The remaining hydrogen atoms are placed in geometrically constrained positions, and refined with isotropic temperature factors, generally 1.2 Ueq of their parent atoms. The crystal and refinement data are summarized in Tables 1 (in manuscript). Selected bond lengths and bond angles are summarized in Tables S1 and S2. CCDC deposition numbers of the complexes **[Ru]-1**, **[Ru]-2** and **[Ru]-5** are 1872164, 1865341 and 1872151, respectively. These data are freely available at www.ccdc.cam.ac.uk (or can be procured from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Table S1. Selected bond lengths for complexes **[Ru]-1, [Ru]-2 and [Ru]-5**

Bond Length(Å)	[Ru]-1	[Ru]-2	[Ru]-5
Ru1 N1	2.083(4)	2.1033(17)	2.090(3)
Ru1 N2	2.123(4)	2.1926(18)	2.138(3)
Ru1 C7	2.182(6)	-	-
Ru1 C8	2.175(5)	-	-
Ru1 C9	2.192(5)	-	-
Ru1 C10	2.191(5)	2.178(3)	-
Ru1 C11	2.202(6)	2.159(3)	-
Ru1 C12	2.173(5)	2.197(3)	2.172(5)
Ru1 C13	-	2.201(3)	2.168(5)
Ru1 C14	-	2.218(3)	2.139(4)
Ru1 C15	-	2.202(3)	2.159(5)
Ru1 C16	-	-	2.188(5)
Ru1 C17	-	-	2.182(5)
Ru1 Cl1	2.3923(12)	2.4308(6)	2.4007(10)
N1 C5	1.345(6)	1.356(3)	1.348(5)
N1 C1	1.343(6)	1.358(3)	1.340(5)
N2 C6	1.478(6)	1.504(3)	1.490(5
N2 C7	-	1.513(3)	1.479(5)

C1 C2	1.358(8)	1.388(4)	1.387(7)
C2 C3	1.393(8)	1.387(4)	1.365(8)
C3 C4	1.376(7)	1.390(4)	1.373(8)
C4 C5	1.379(7)	1.397(3)	1.372(6)
C5 C6	1.495(7)	1.502(3)	1.484(6)
C7 C8	1.430(9)	1.536(4)	1.506(5)
C8 C9	1.391(8)	-	1.539(6)
C9 C10	1.405(8)	-	1.520(7)
C10 C11	1.380(8)	1.438(6)	-
C11 C12	1.437(10)	1.416(5)	-
C12 C13	-	1.390(5)	1.363(10)
C13 C14	-	1.396(4)	1.406(10)
C14 C15	-	1.362(5)	1.359(9)
C15 C16		-	1.378(8)
C16 C17	-	-	1.354(9)
C7 C12	1.387(10)	-	-
C15 C10	-	1.426(6)	-
C7 C9	-	1.541(4)	-
C9 C11	-	-	1.540(8)
C12 C17	-	-	1.362(10)

Table S2. Selected bond Angles for complexes **[Ru]-1, [Ru]-2 and [Ru]-5**

Bond Angles (deg)	[Ru]-1	[Ru]-2	[Ru]-5
N1-Ru-N2	76.19(14)	77.98(7)	76.42(12)
N1-Ru-Cl	84.23(11)	84.77(5)	85.61(9)
N2-Ru-Cl	84.19(11)	93.48(5)	84.28(9)
N2-Ru-C_t	131.64	130.28	129.06
N2-Ru-C_t	132.12	128.61	133.52
Cl-Ru-C_t	129.34	126.14	129.29
Ru-N1-C5	117.2(3)	115.59(14)	116.5(3)

Ru-N2-C6	109.0(3)	104.55(13)	106.9(2)
Ru-N1-C1	124.7(3)	125.12(15)	124.2(3)
N1-C5-C6	114.4(4)	115.19(18)	114.3(3)
N2-C6-C5	108.0(4)	111.32(18)	109.5(3)
C6-N2 –C7	-	116.07(18)	111.6(3)
C8-C7-C9	-	109.4(2)	-
C8-C7-N2	-	107.73(19)	112.2(3)
C9-C7-N2	-	113.2(2)	-
C9-C8-C7	-	-	113.1(4)
C8-C9-C10	-	-	110.3(5)
C8-C9-C11	-	-	109.8(5)
C10-C9-C11	-	-	110.1(4)

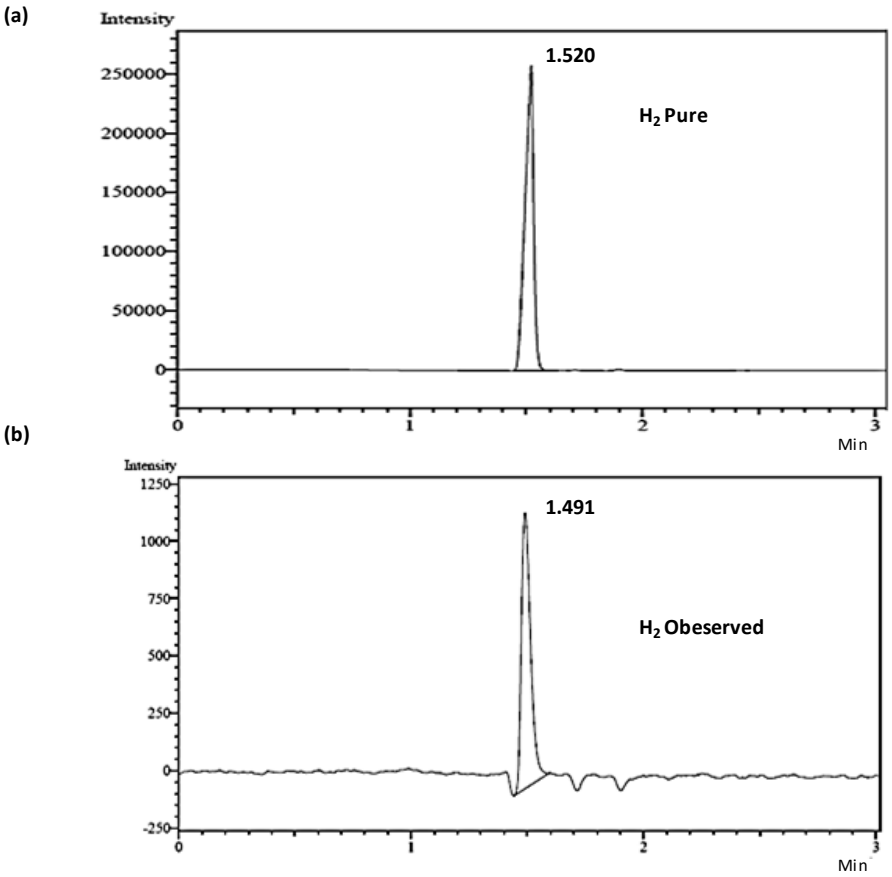
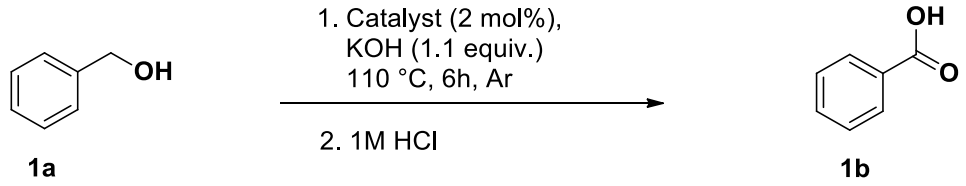


Figure S1. GC-TCD (using Argon as carrier gas) of (a) H_2 gas (Pure sample) (b) evolved gas from the reaction mixture. Reaction condition: **1a** (1 mmol), catalyst (2 mol%), KOH (1.1 equiv.), toluene (2 mL), 110 °C.

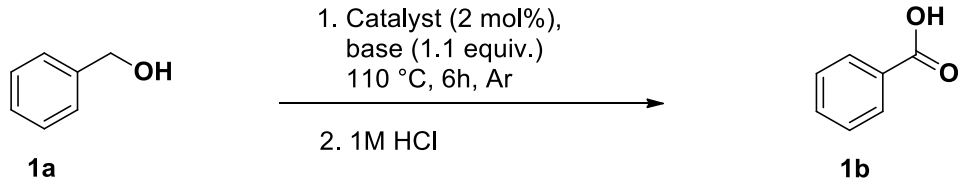
Table S3. Screening of the catalyst for benzyl alcohol dehydrogenation[a]



entry	catalyst	temperature (°C)	conv. (**1b**) (%)[b]
1.	**[{(η^6-C_6H_6)$RuCl_2$}$_2$]**	110	65
2.	**[{(η^6-$C_{10}H_{14}$)$RuCl_2$}$_2$]**	110	17
3.	**[{(η^6-C_6Me_6)$RuCl_2$}$_2$]**	110	22
4.	**[Ru]-1**	110	>99
5.	**[Ru]-6**	110	76
6.	**[Ru]-7**	110	73
7.	**[Ru]-8**	110	77
8.	**[Ru]-9**	110	72
9.	**[Ru]-10**	110	63

[a]Reaction condition: **1a** (1 mmol), catalyst (2 mol%), KOH (1.1 equiv.), toluene (2 mL), 6 h. [b]conv. determined using ^{1}H NMR.

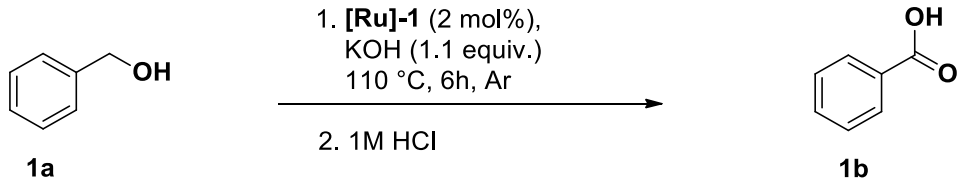
Table S4. Screening of the base for benzyl alcohol dehydrogenation[a]



entry	catalyst	base	conv. (**1b**) (%)
1.	**[Ru]-1**	KOH	>99
2.	**[Ru]-1**	NaOH	62
3.	**[Ru]-1**	K_2CO_3	3
4.	**[Ru]-1**	Na_2CO_3	2
5.	**[Ru]-1**	$NaHCO_3$	<1

[a]Reaction condition: **1a** (1 mmol), catalyst (2 mol%), base (1.1 equiv.), toluene (2 mL), 6 h, 110 °C.

Table S5. Effect of temperature in benzyl alcohol dehydrogenation



entry	catalyst(mmol)	temperature (°C)	isolated yield (1b) (%)	volume of gas (mL)	TOF (h^{-1})
1.	[Ru]-1	110	94.00	48	32.75
2.	[Ru]-1	100	72.25	28	18
3.	[Ru]-1	90	39.41	12	9.5

Reaction condition: **1a** (1 mmol), **[Ru]-1** (2 mol%), KOH (1.1 equiv.), toluene (2 mL), 6 h

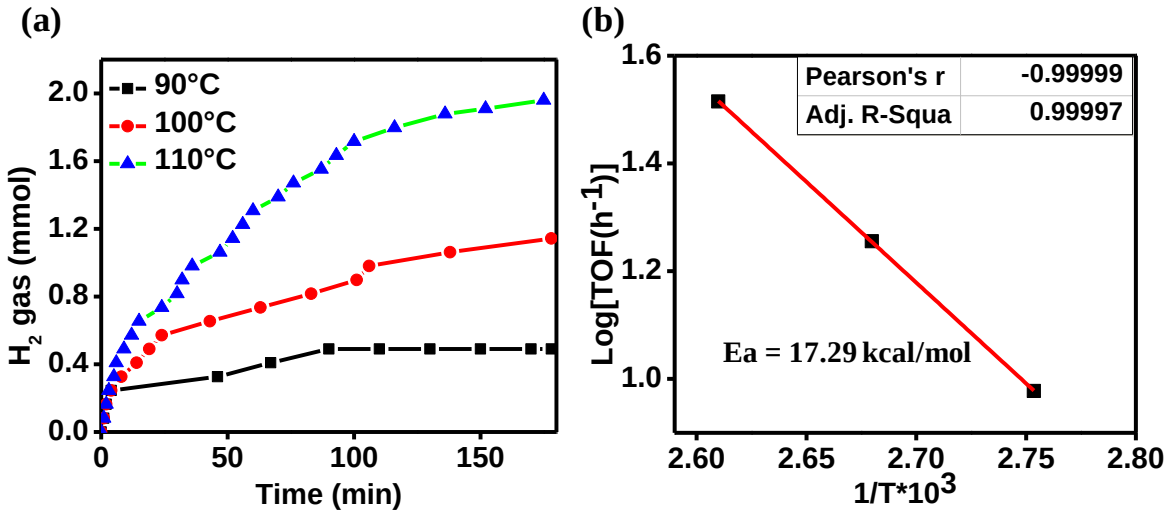
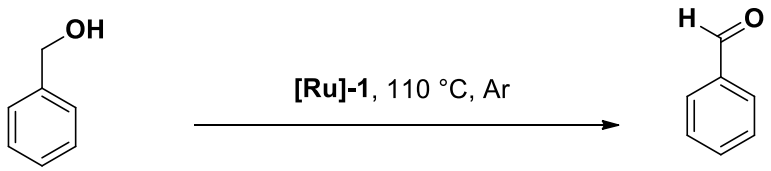


Figure S2. (a) Dehydrogenation of benzyl alcohol (**1a**) over **[Ru]-1** catalyst at various temperatures. (b) Arrhenius plot of TOF values. Reaction condition: **1a** (1 mmol), catalyst (2 mol%), KOH (1.1 equiv.), toluene (2 mL)

Dehydrogenation of benzyl alcohol to benzaldehyde



[Ru]-1 (0.02 mmol), benzyl alcohol (1.0 mmol) and toluene (2 mL) were took in a test-tube charged with a stirring bar and equipped with reflux condenser. The reaction mixture was actively stirred at reflux (oil bath, 110 °C), evolved gas was measured by water displacement method. After the reaction was over, the products were analyzed by ^{1}H NMR spectroscopy. The conversion of benzyl alcohol to benzaldehyde was found 6 %.

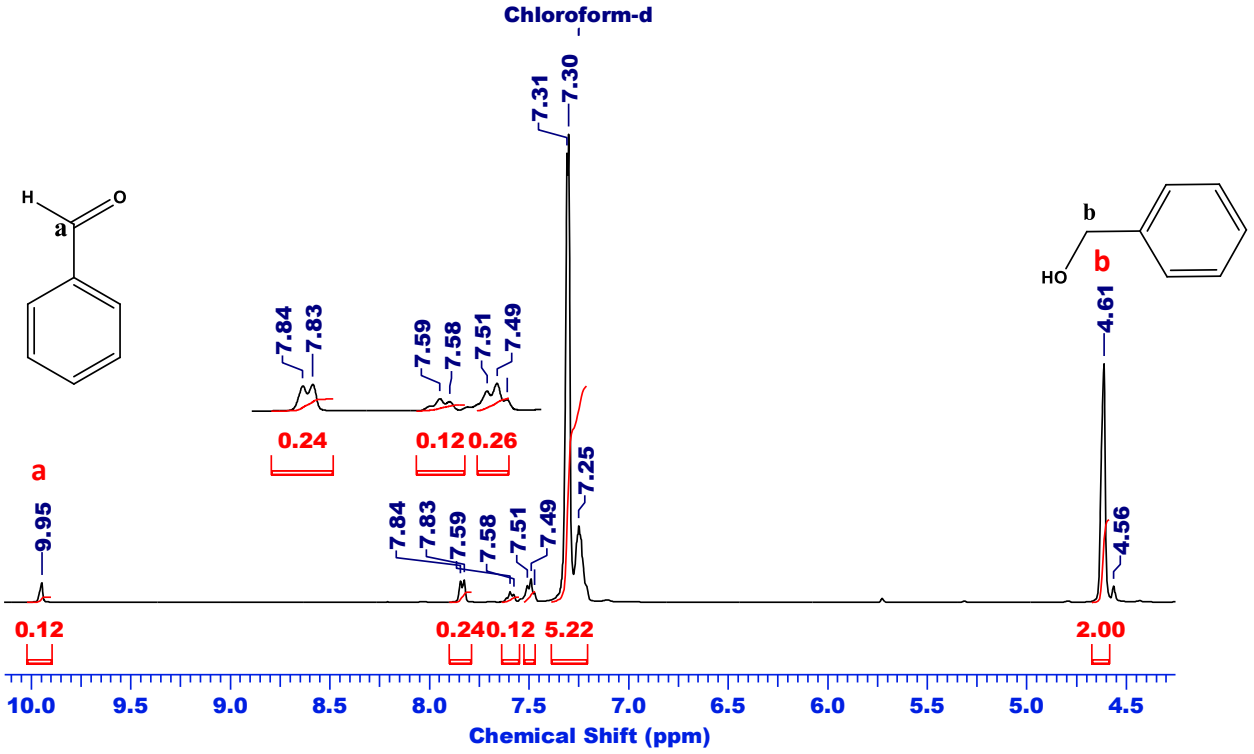
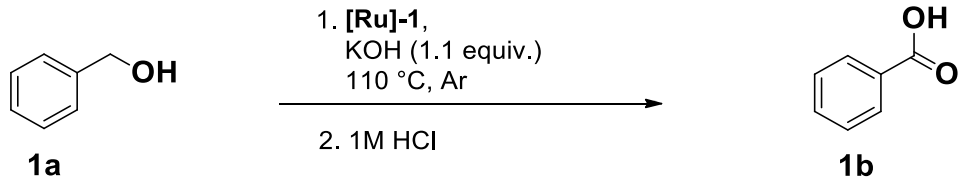


Figure S3. ^{1}H NMR spectra after the reaction of benzyl alcohol in absence of base

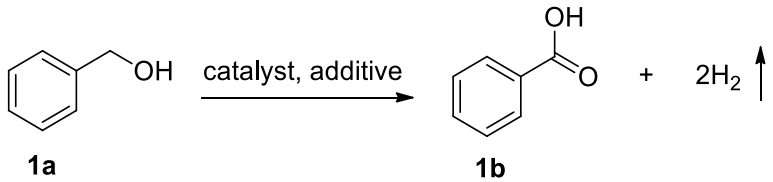
Table S6. Screening of catalyst amount in benzyl alcohol dehydrogenation

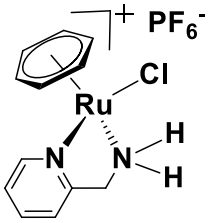
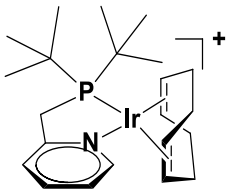


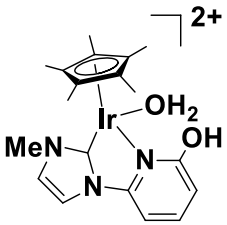
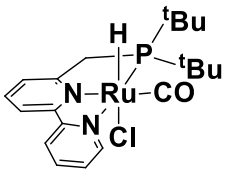
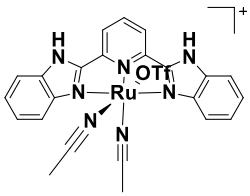
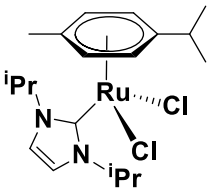
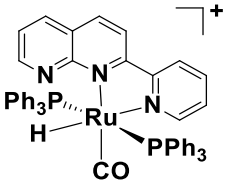
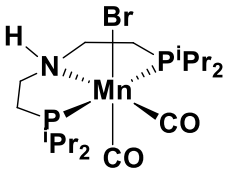
entry	catalyst (mol%)	solvent (mL)	time (h)	temperature (°C)	isolated yield (1b) (%)
1.	**[Ru]-1** (2.0)	toluene (2 mL)	6	110	94
2.	**[Ru]-1** (2.0)	water (2 mL)	6	110	10
2.	**[Ru]-1** (0.5)	toluene (2 mL)	24	110	76
3.	**[Ru]-1** (0.1)	toluene (2 mL)	24	110	62

Reaction condition: **1a** (1 mmol), **[Ru]-1**, KOH (1.1 equiv.), 110 °C.

Table S7. Comparative study for the catalytic dehydrogenation of benzyl alcohols to benzoic acid



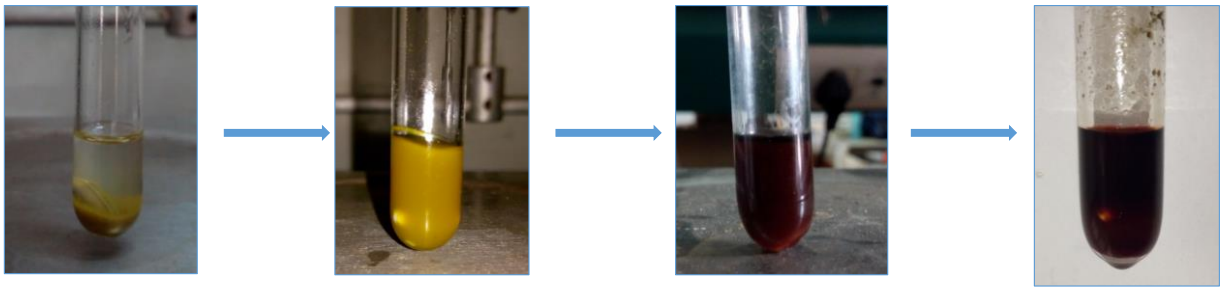
entry	**Cat.**	**cat. (mol%)**	**temp. (°C)**	**t (h)**	**base (equiv.)**	**solvent**	**TON (TOF)**	**Ref.**
1.		**2.0**	110	6	KOH (1.1)	toluene	47 (8 h^{-1})	This work
		0.2	110	9	KOH (1.1)	toluene	400 (44 h^{-1})	This work
		0.1	110	24	KOH (1.1)	toluene	620 (26 h^{-1})	This work
		0.01[a]	110	24	KOH (1.1)	toluene	1378 (57 h^{-1})	This work
2.		**0.2**	120	40	KOH (1.1)	toluene	490[b] (12 h^{-1})	S2

3.		**2.0**	140	20	-	water	40 (2 h^{-1})	S3
4.		**0.2**	reflux	18	NaOH (1.1)	water	455 (25 h^{-1})	S4
5.		**0.2**	150	24	CsOH (1.0)	-	400[c] (17 h^{-1})	S5
6.		**1.0**	110	6	KOH (1.2) [$PCy_3 \cdot HBF_4$]	toluene	79 (13 h^{-1})	S6
7.		**5.0**	110	6	NaOH (18.5)	water	20 (3 h^{-1})	S7
8.		**0.2**	160	16	NaOH (1.1)	water	470 (29 h^{-1})	S8

[a]Reaction with 50 mmol of **1a**. [b]TON 40600 (for gram scale reaction). [c]TON ~10000 (bulk reaction).

Mechanistic investigations

The **[Ru]-3** and the base (KOH) was mixed with toluene in inert atmosphere and stirring for 30 min at room temperature a suspension of catalysts in toluene was formed. Further, upon addition of *p*-methylbenzyl alcohol in the reaction mixture the color changed from yellow to wine red.



[Ru]-3, Toluene

[Ru]-3, Toluene, KOH, Stirring at room-temperature for 30 min

[Ru]-3, Toluene, KOH, p-me benzyl alcohol stirred at room-temperature for 2 min

[Ru]-3, Toluene, KOH, p-me benzyl alcohol heated at 110 °C for 30 min

Figure S4. Visible color change observed during controlled reaction

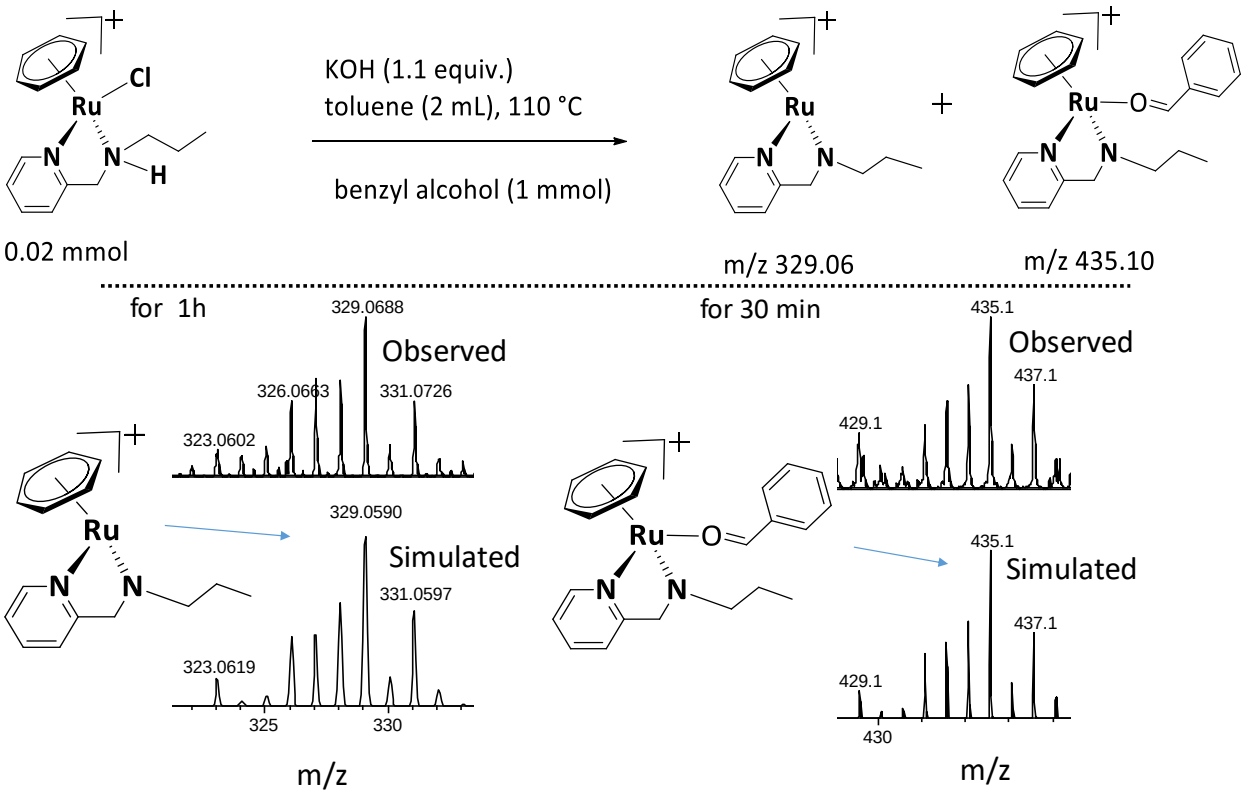


Figure S5. ESI-MS analysis of the reaction mixture after heating at 110 °C in catalytic reaction condition using the **[Ru]-3** (2 mol%), KOH (1.1 equiv.), benzyl alcohol (1 mmol), toluene (2 mL) in 30 min and 1 h.

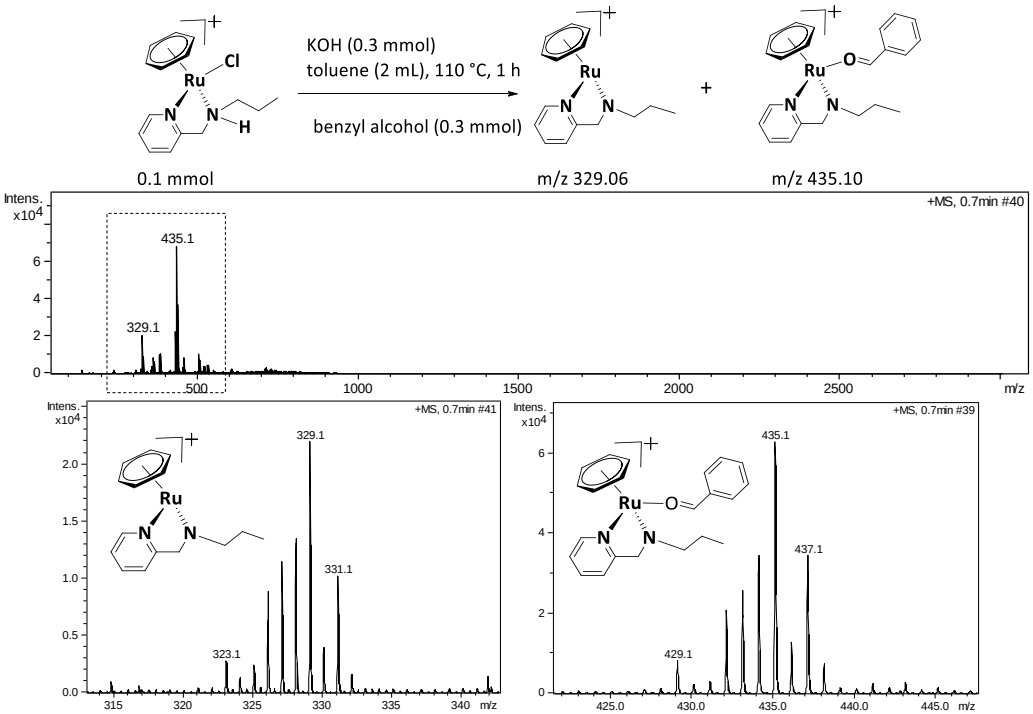


Figure S6. ESI-MS analysis of the reaction aliquot for benzyl alcohol dehydrogenation after heating at 110 °C for 1 h under controlled reaction condition using the catalyst **[Ru]-3** (0.1 mmol), benzyl alcohol (0.3 mmol) and KOH (0.3 mmol) in toluene (2 mL).

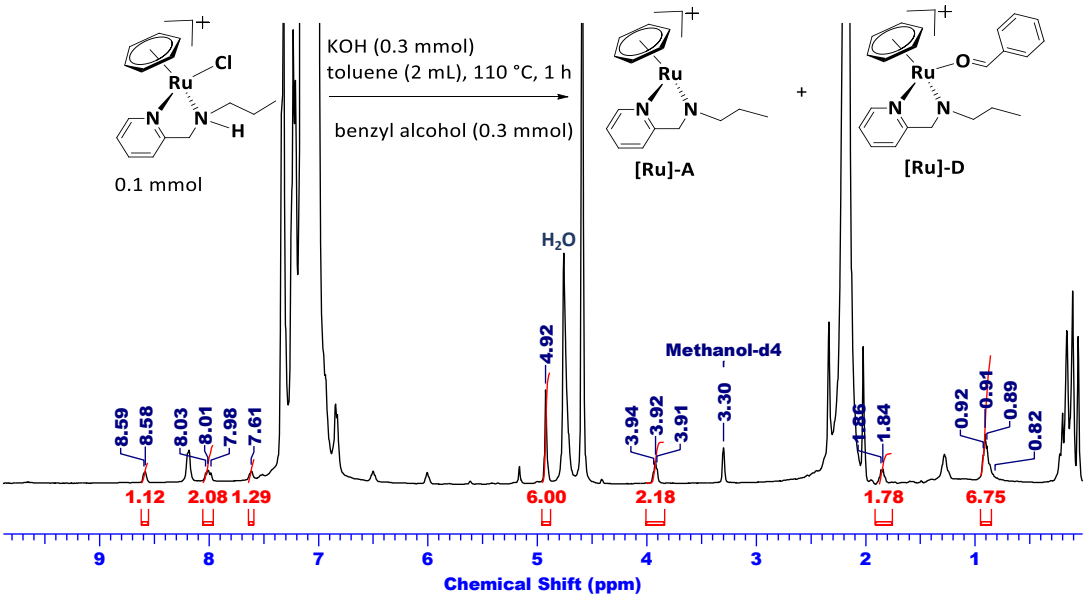
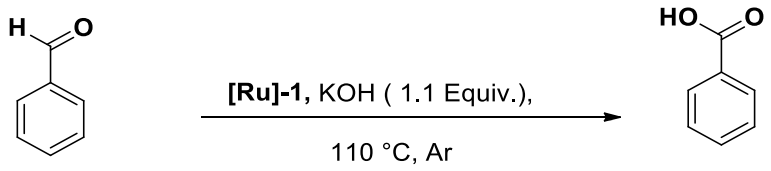


Figure S7. ^{1}H NMR of the reaction aliquot (diluted with methanol-d_4) for benzyl alcohol dehydrogenation after heating at 110 °C for 1 h under controlled reaction condition using the catalyst **[Ru]-3** (0.1 mmol), benzyl alcohol (0.3 mmol) and KOH (0.3 mmol) in toluene (2 mL).

Dehydrogenation of benzaldehyde



Benzaldehyde (1.0 mmol), **[Ru]-1** (2 mol%), and KOH (1.1 mmol) are mixed in dry toluene (2 mL) in two necked test tube equipped with a condenser. The reaction mixture is stirred at 110 °C on an oil bath under Argon atmosphere. The gas evolved is measured by water displacement method. After the reaction was over, the products are analyzed by ^{1}H NMR spectroscopy. The selectivity for benzoic acid and benzyl alcohol are respectively, 92% (89% isolated yield) and 8%.

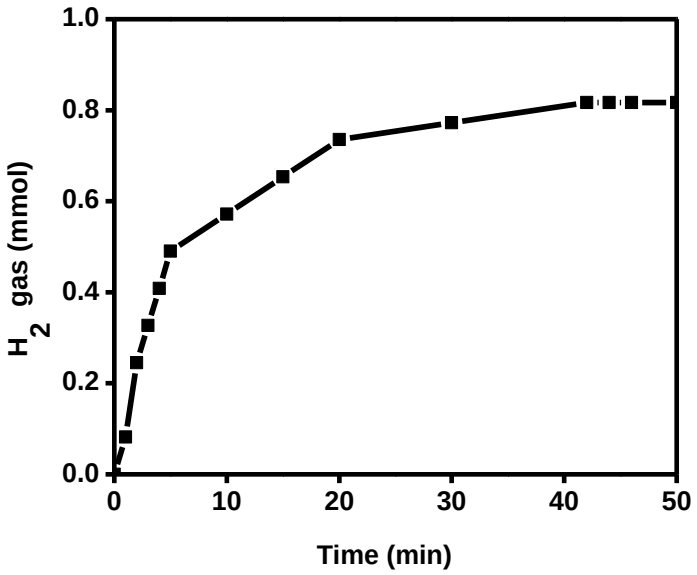


Figure S8. Hydrogen generation from benzaldehyde to benzoic acid using **[Ru]-1** catalyst. Reaction condition: benzaldehyde (1 mmol), **[Ru]-1** (2 mol%), KOH (1.1 equiv.), toluene (2 mL), 1 h, 110 °C

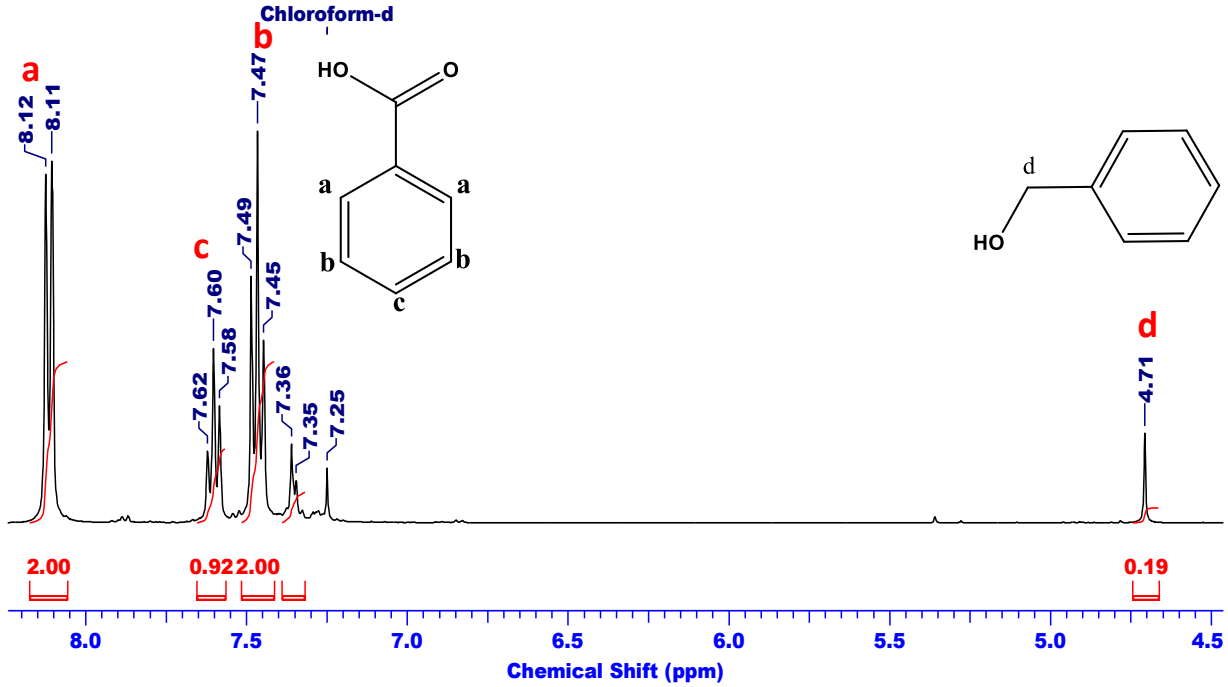
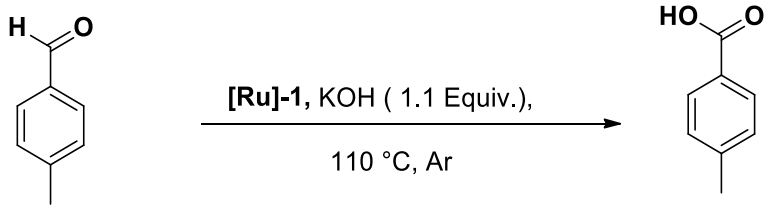


Figure S9. ^{1}H NMR spectra after the reaction of benzaldehyde

Dehydrogenation of *p*-methyl benzaldehyde



p-Methylbenzaldehyde (1.0 mmol), **[Ru]-1** (2 mol%), and KOH (1.1 mmol) are mixed in dry toluene (2 mL) in two necked test tube equipped with a condenser. The reaction mixture is stirred at 110 °C on an oil bath under Argon atmosphere. The gas evolved is measured by water displacement method. The isolated yield of *p*-methyl benzoic acid is 95%.

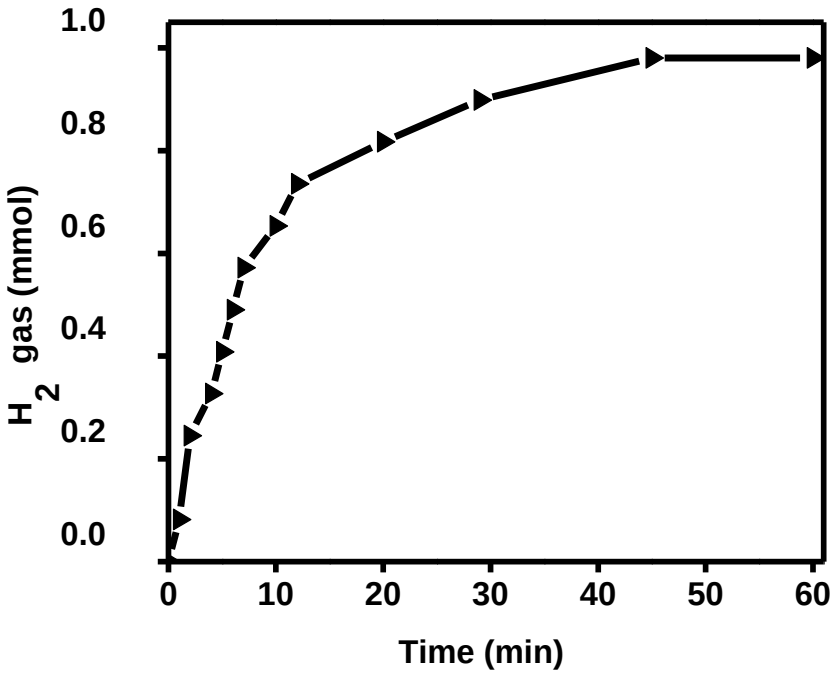
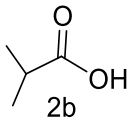


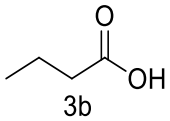
Figure S10. Hydrogen generation from *p*-methyl benzaldehyde to benzoic acid using **[Ru]-1** catalyst. Reaction condition: *p*-methyl benzaldehyde (1 mmol), **[Ru]-1** (2 mol%), KOH (1.1 equiv.), toluene (2 mL), 1 h, 110 °C

Spectral data for dehydrogenation products of alcohols[S2-S8]

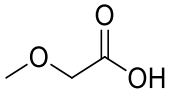
Isobutyric acid (2b): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.17-1.18 (d, 6H, J = 5 Hz), 2.54-2.64 (m, 1H).



Butyric acid (3b): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 2.33-2.36 (t, 2H, *J1*= 10 Hz, *J2*= 5 Hz), 1.64-1.71 (m, 2H), 0.96-0.99 (t, 2H, *J1*= 5 Hz, *J2*= 10 Hz).

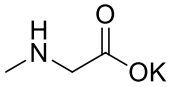


2-methoxyacetic acid (4b): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.09 (s, 2H), 3.48 (s, 3H).



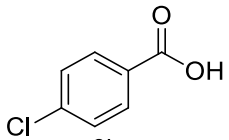
4b

Potassium-2-(methylamino)acetate (5b): ^{1}H NMR (300 MHz, D_2O): δ (ppm) = 3.35 (s, 2H), 2.49 (s, 3H).



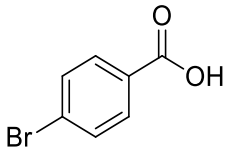
5b

4-chlorobenzoic acid (6b): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.02-8.04 (d, 2H, J = 10 Hz), 7.44-7.45 (d, 2H, J = 5 Hz).



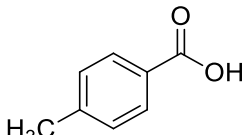
6b

4-bromobenzoic acid (7b): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.96-7.98 (d, 2H, J = 10 Hz), 7.62-7.64 (d, 2H, J = 10 Hz).



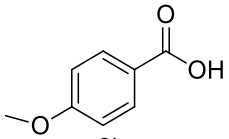
7b

4-methylbenzoic acid (8b): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.00-8.02 (d, 2H, J = 10 Hz), 7.27-7.29 (d, 2H, J = 10 Hz), 2.44(s, 1H).



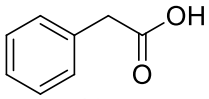
8b

4-methoxybenzoic acid 2-phenylacetic acid (9b): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.06-8.08 (d, 2H, J = 10 Hz), 6.94-6.96 (d, 2H, J = 10 Hz), 3.88 (s, 1H).



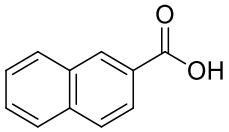
9b

2-phenylacetic acid (10b): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.33-7.36 (m, 2H), 7.27-7.30 (m, 3H), 3.66 (s, 2H).



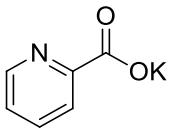
10b

2-naphthoic acid (11b): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.74 (s, 1H), 8.13-8.15 (d, 1H, *J* = 10 Hz), 7.99-8.01 (d, 1H, *J* = 10 Hz), 7.90-7.94 (t, 1H, *J1* = 10 Hz, *J2* = 10 Hz), 7.62-7.65 (t, 1H, *J1* = 10 Hz, *J2* = 5 Hz), 7.56-7.59 (t, 1H, *J1* = 5 Hz, *J2* = 10 Hz).



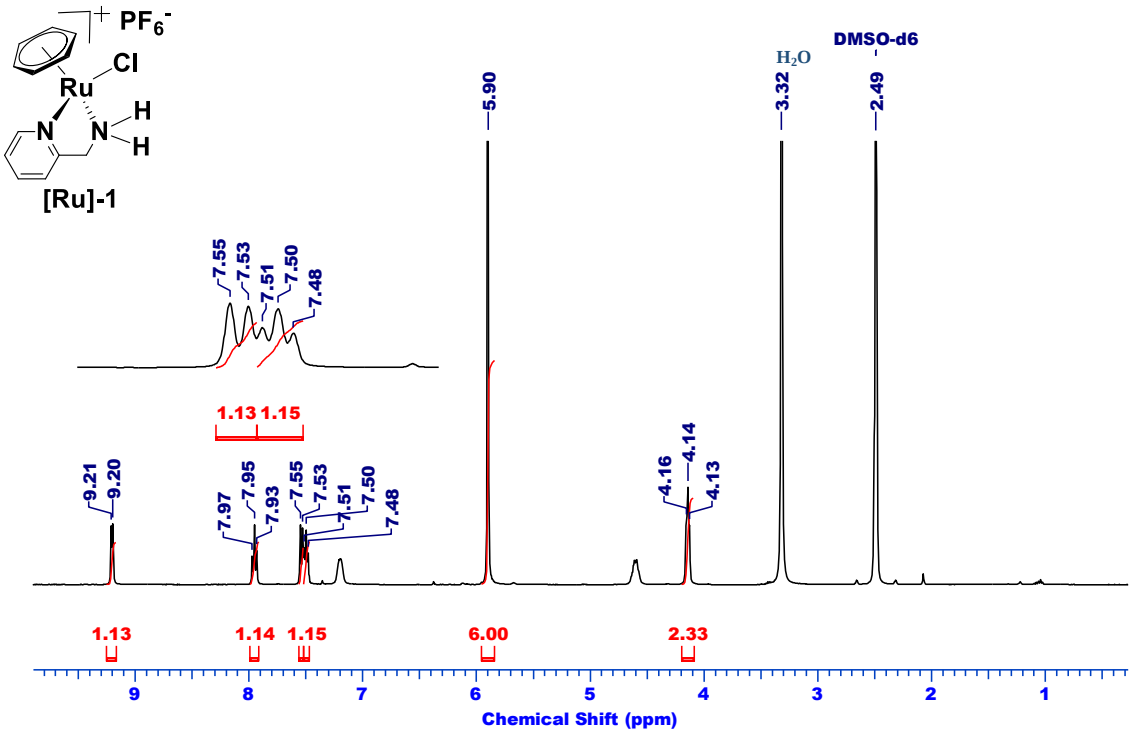
11b

potassium picolinate (12b): ^{1}H NMR (500 MHz, CD_3OD): δ (ppm) = 8.54-8.55 (d, 1H, *J* = 5 Hz), 7.97-7.99 (d, 1H, *J* = 10 Hz), 7.81-7.85 (t, 1H, *J1* = 10 Hz, *J2* = 10 Hz), 7.38-7.40 (t, 1H, *J1* = 5 Hz, *J2* = 5 Hz).

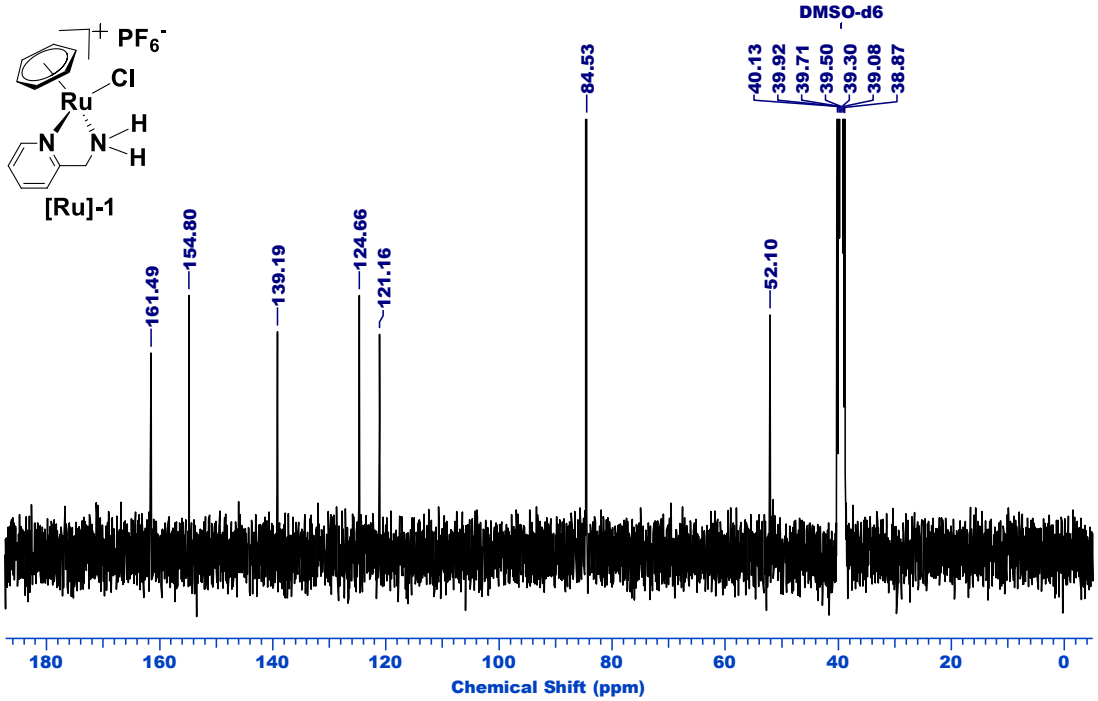


12b

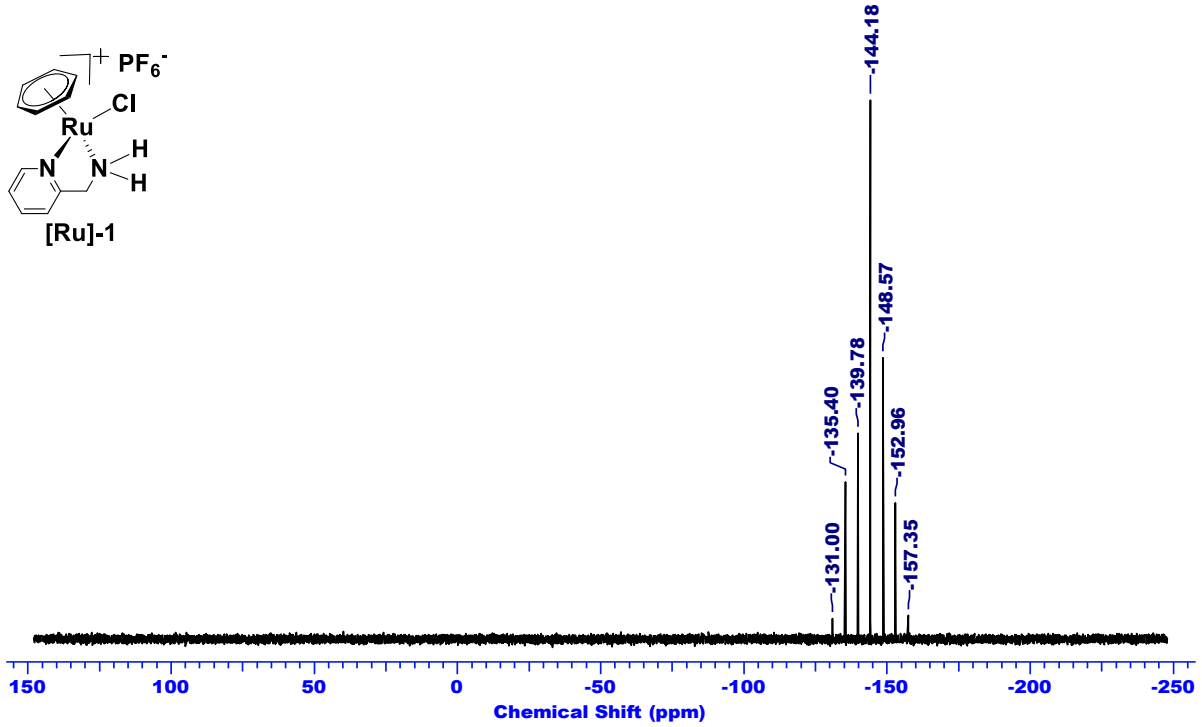
Spectral data for synthesized complexes



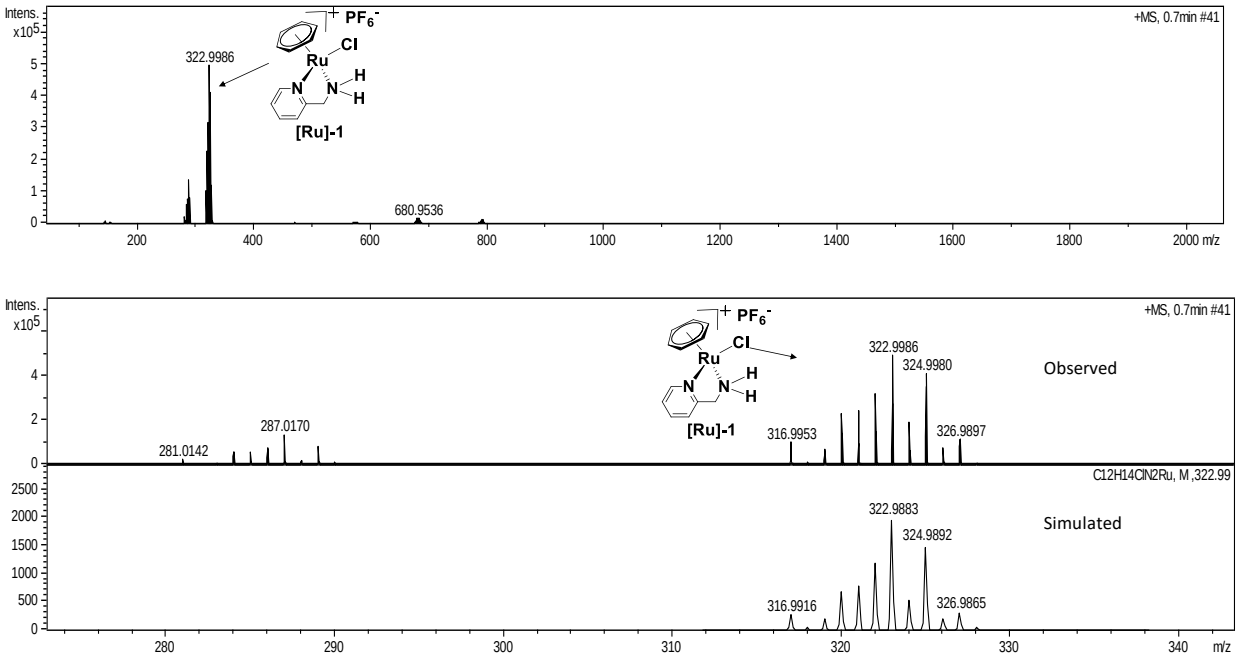
^{1}H NMR spectra of complex **[Ru]-1**



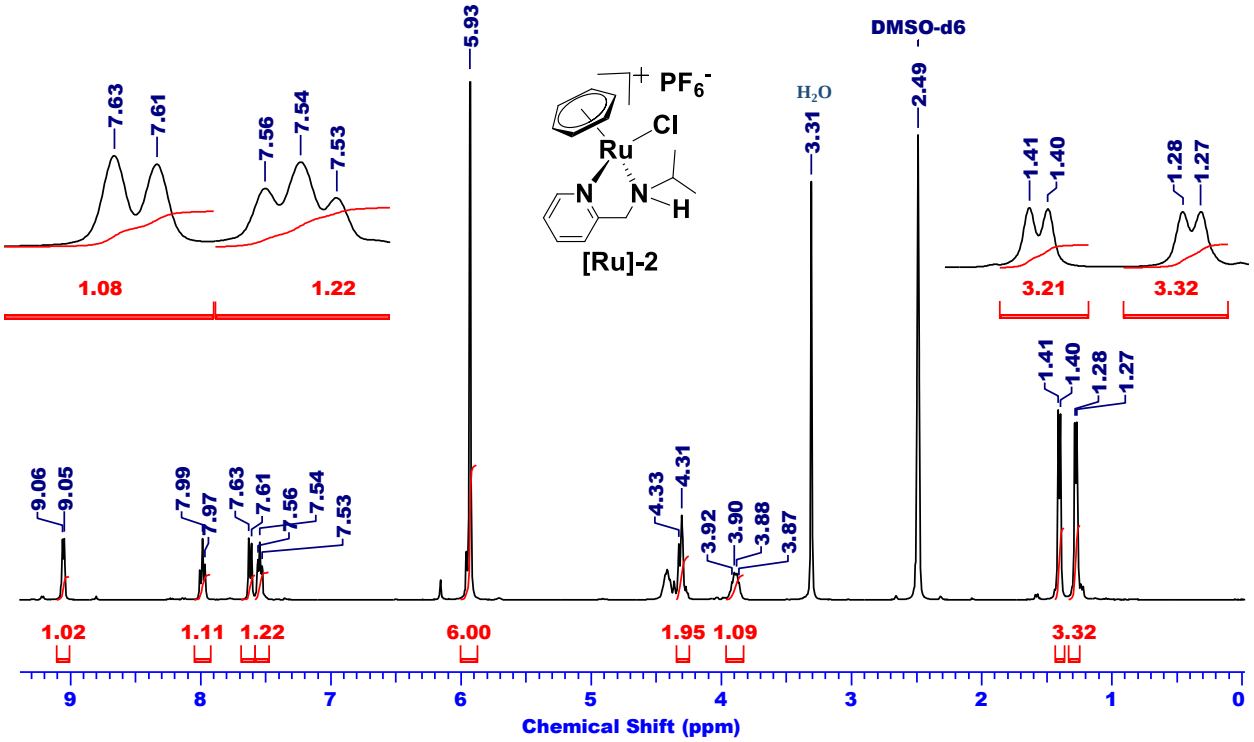
^{13}C NMR spectra of complex **[Ru]-1**



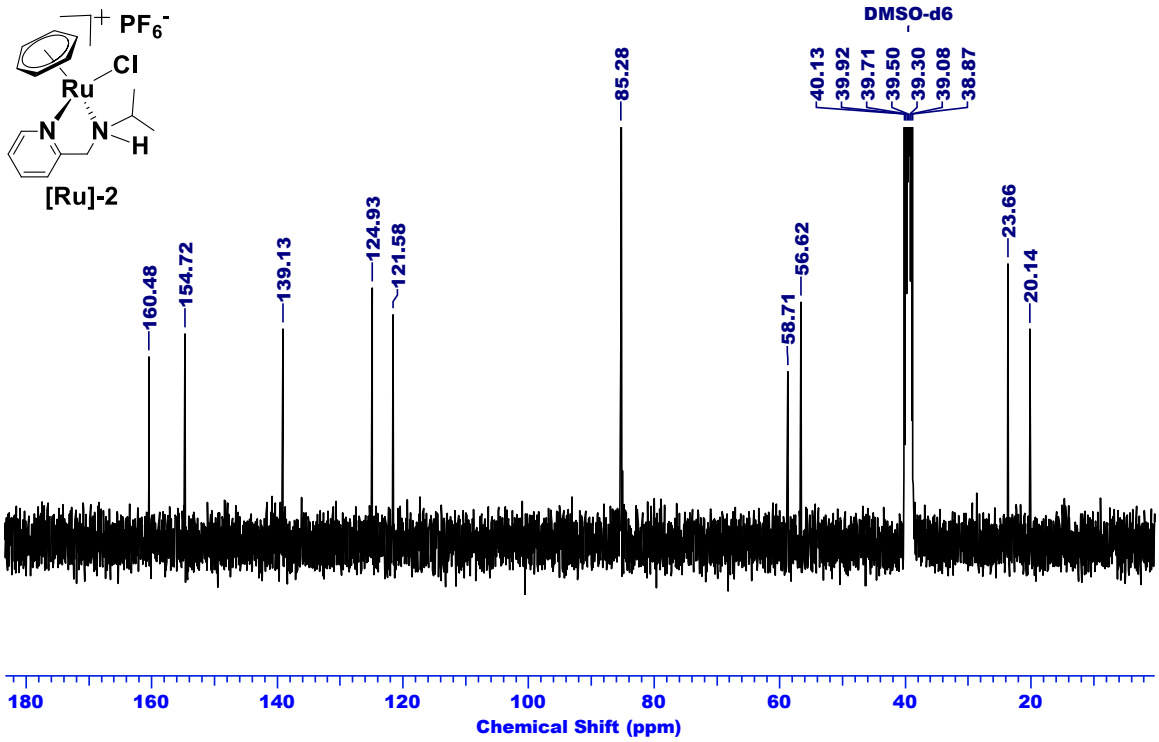
^{31}P NMR spectra of complex **[Ru]-1**



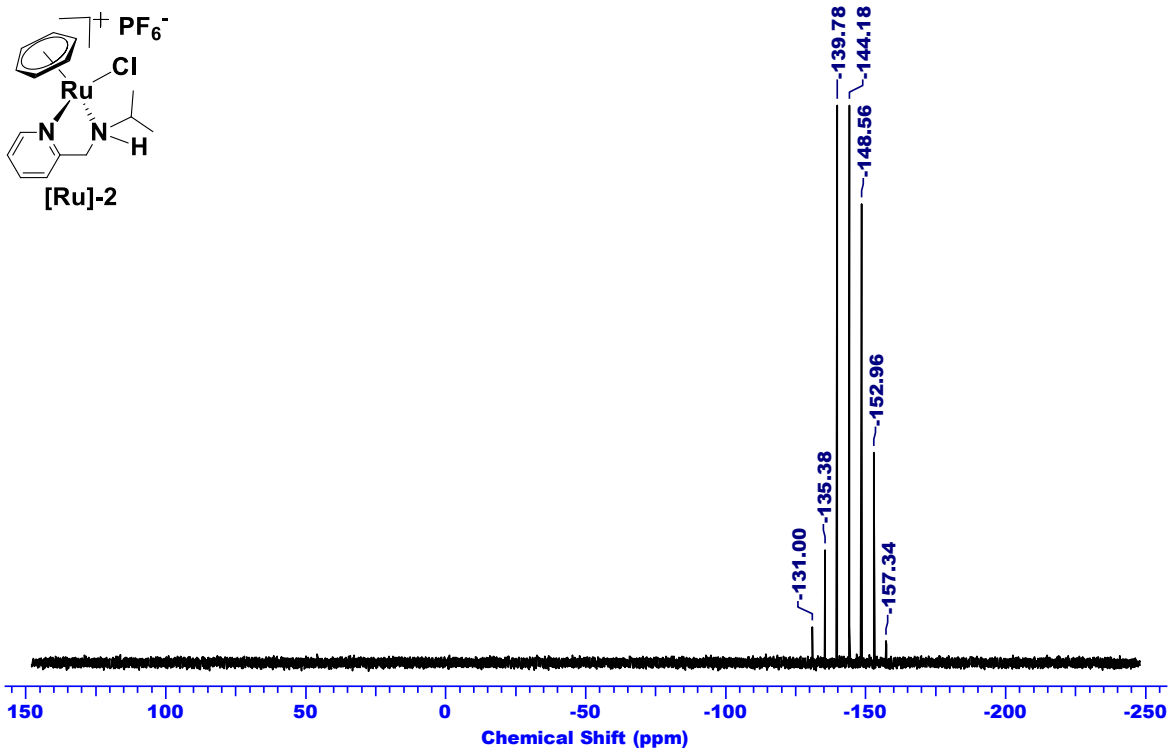
ESI-MS spectra of complex **[Ru]-1**



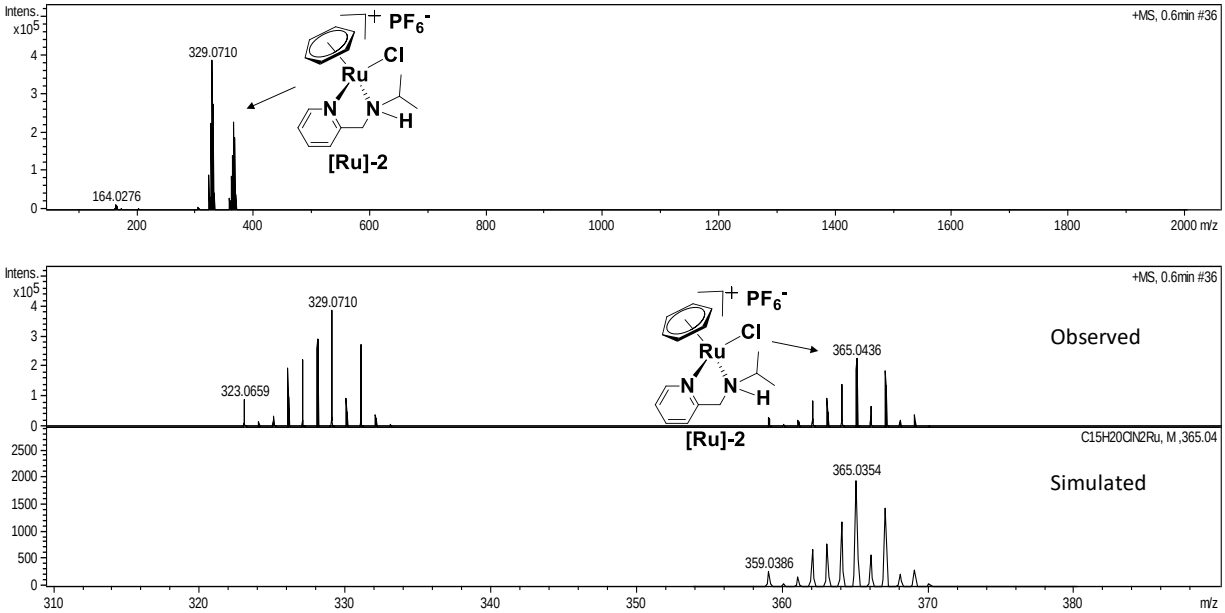
^{1}H NMR spectra of complex **[Ru]-2**



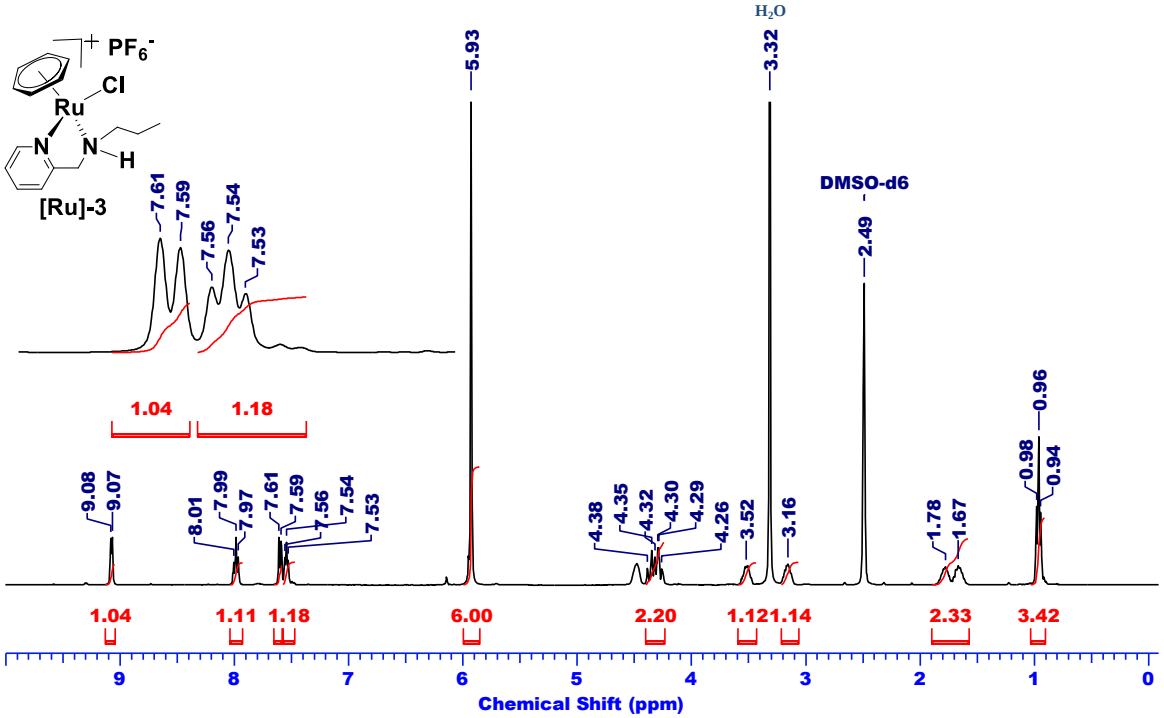
13C NMR spectra of complex **[Ru]-2**



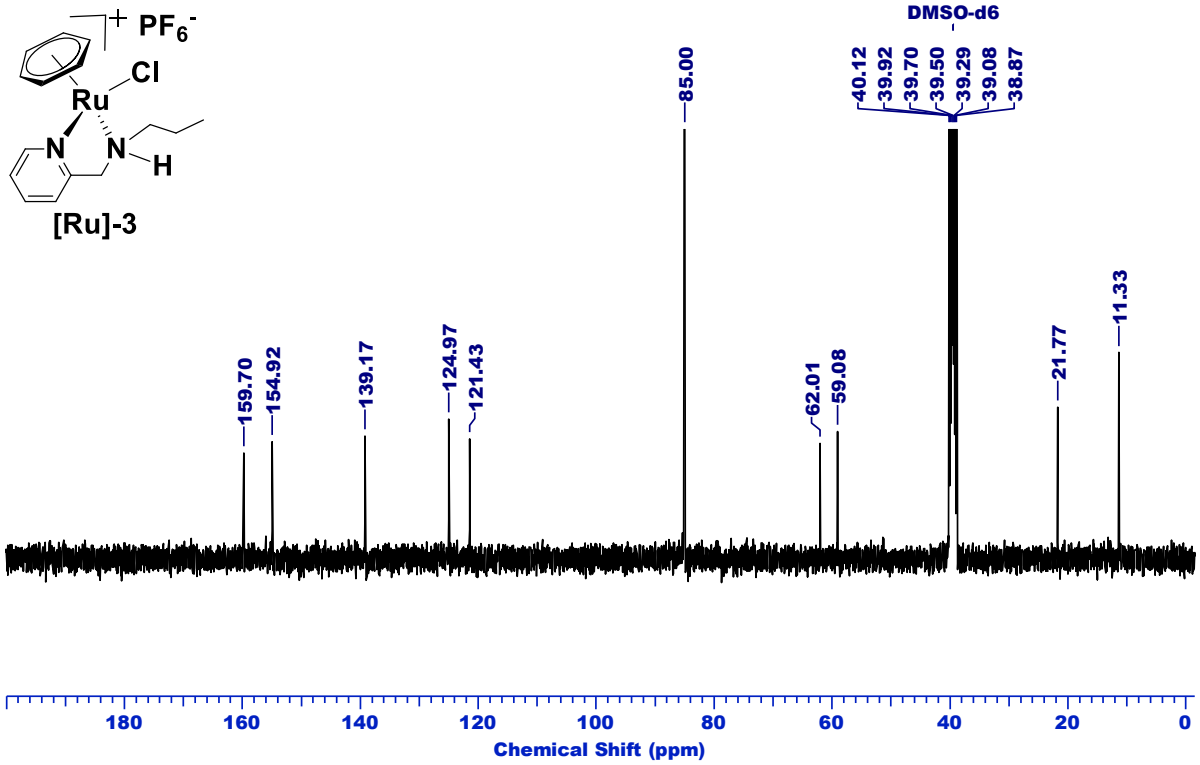
^{31}P NMR spectra of complex **[Ru]-2**



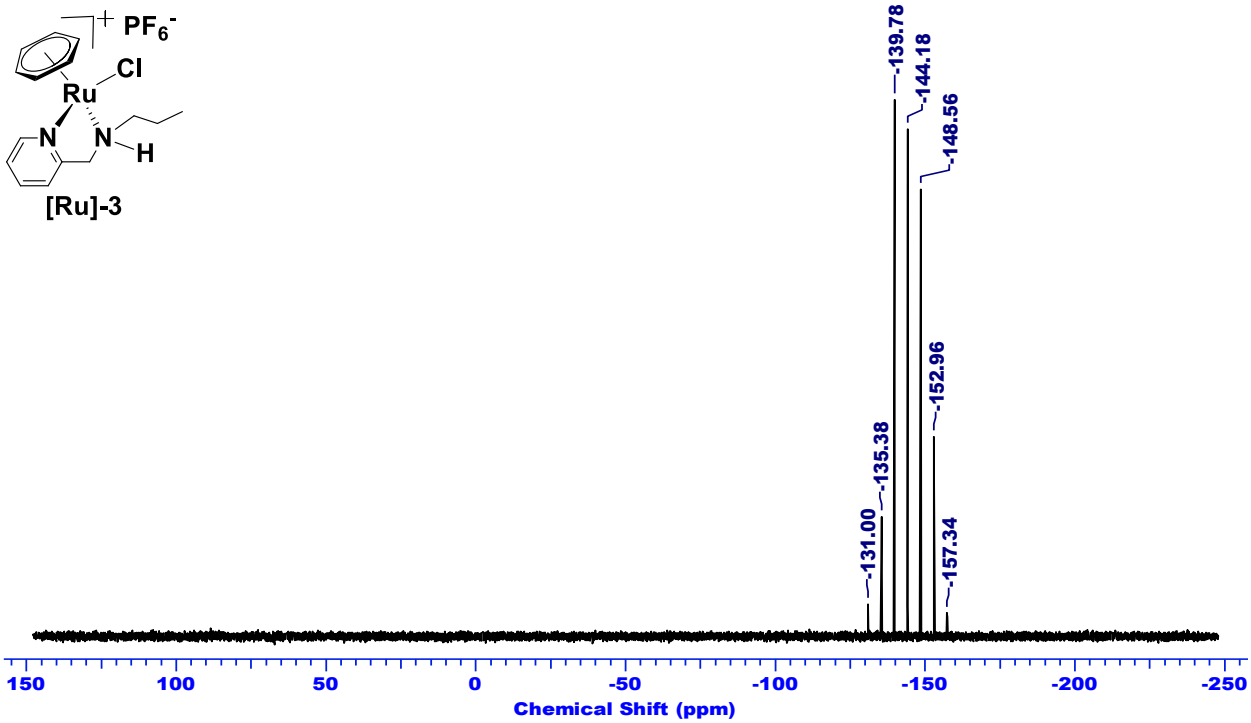
ESI-MS spectra of complex **[Ru]-2**



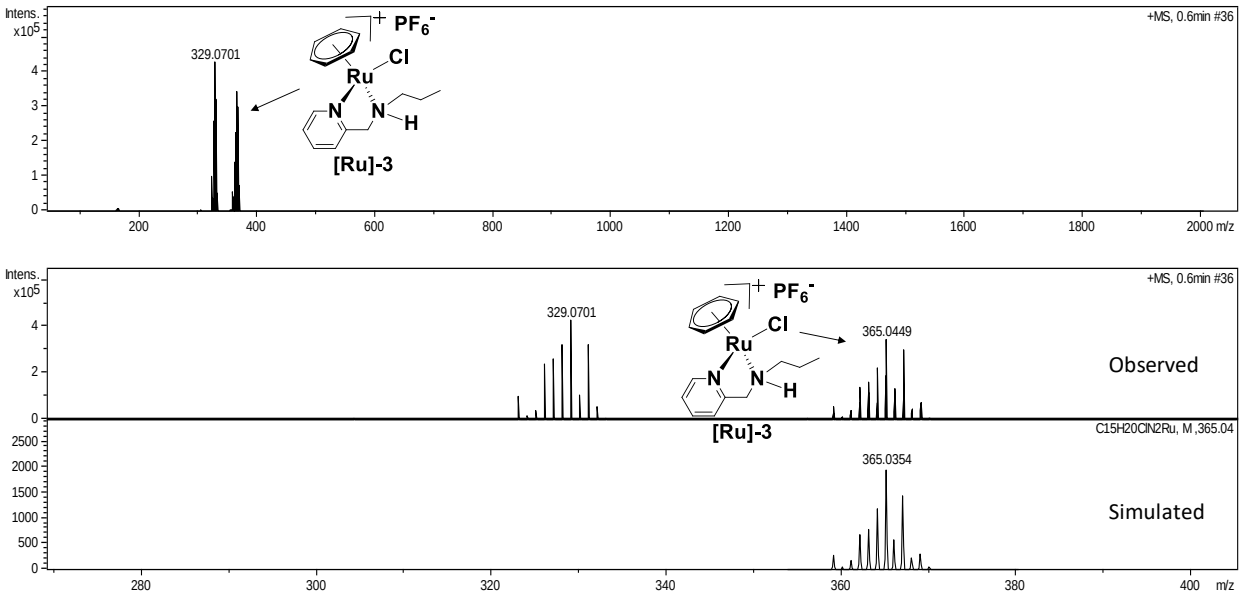
^{1}H NMR spectra of complex **[Ru]-3**



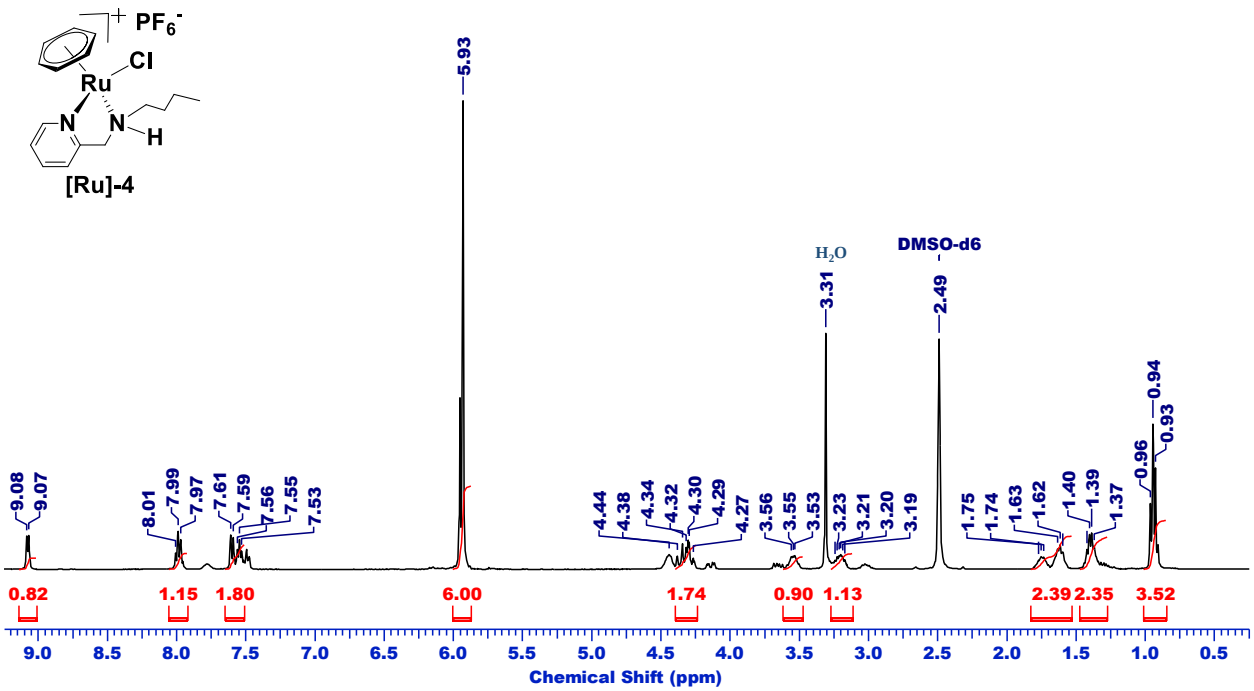
^{13}C NMR spectra of complex **[Ru]-3**



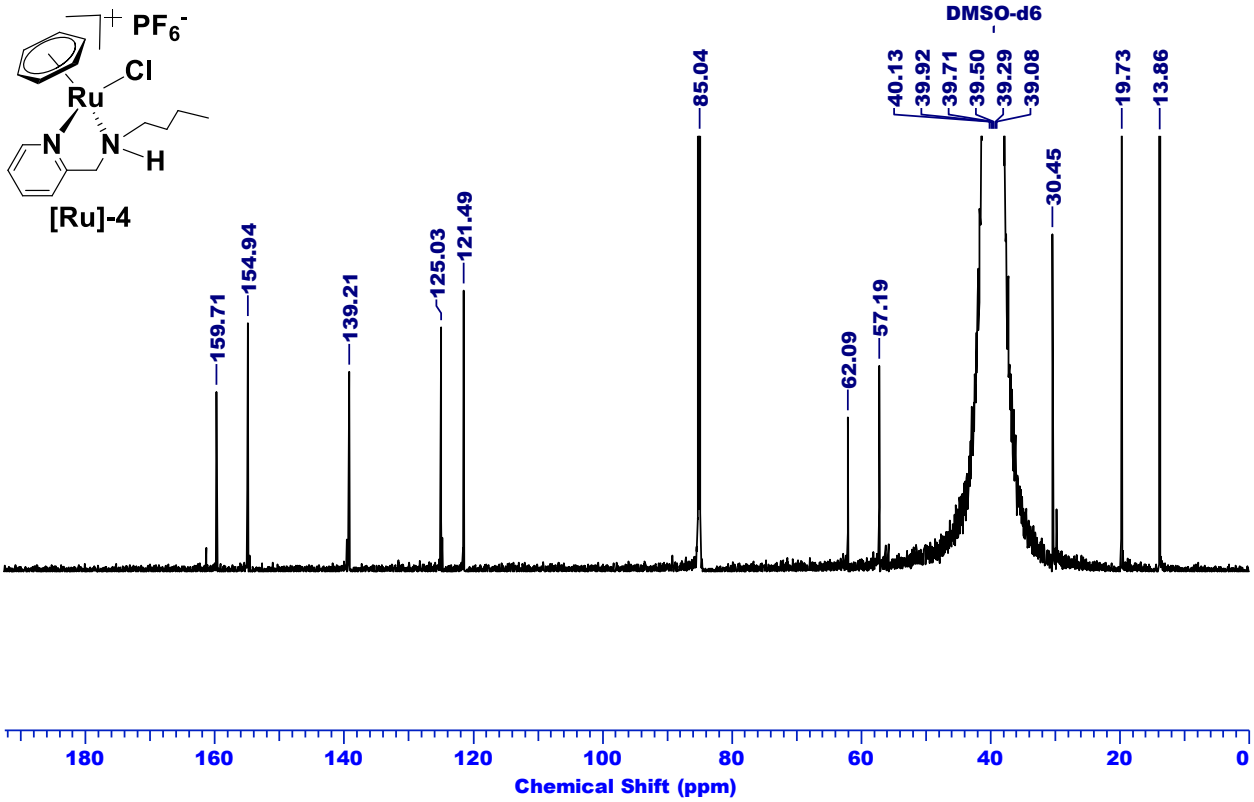
^{31}P NMR spectra of complex **[Ru]-3**



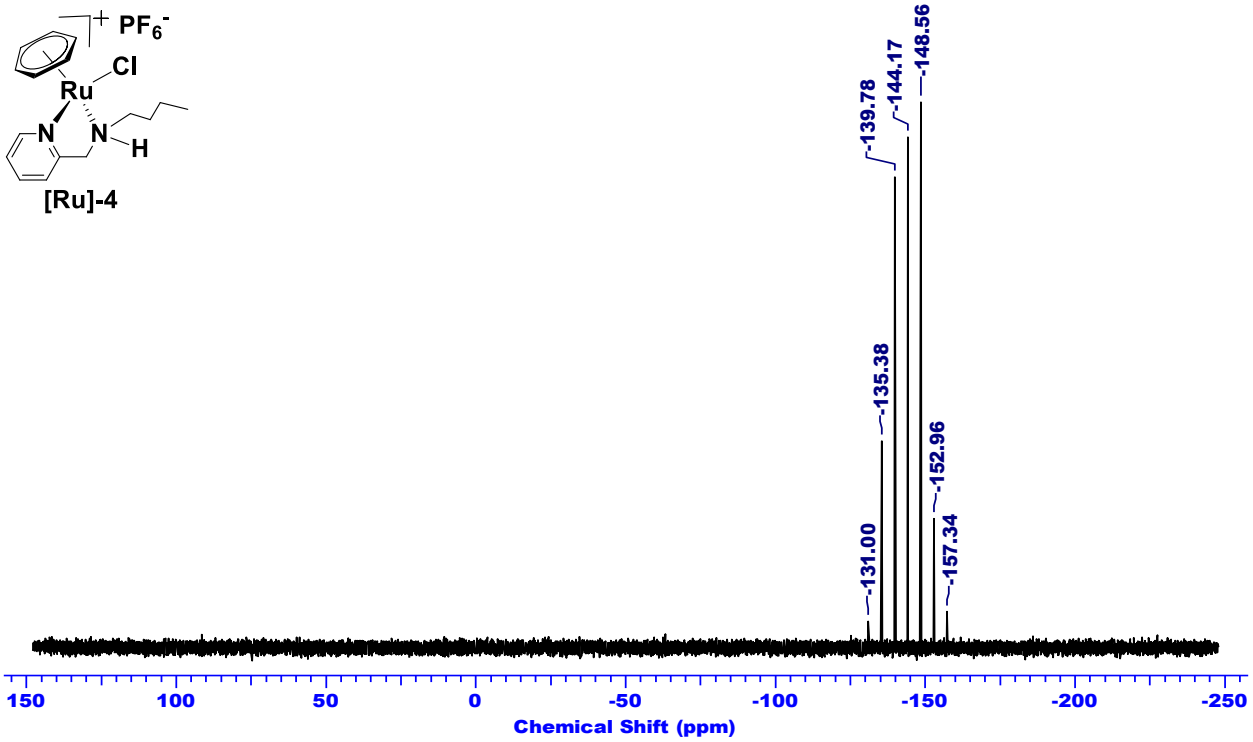
ESI-MS spectra of complex **[Ru]-3**



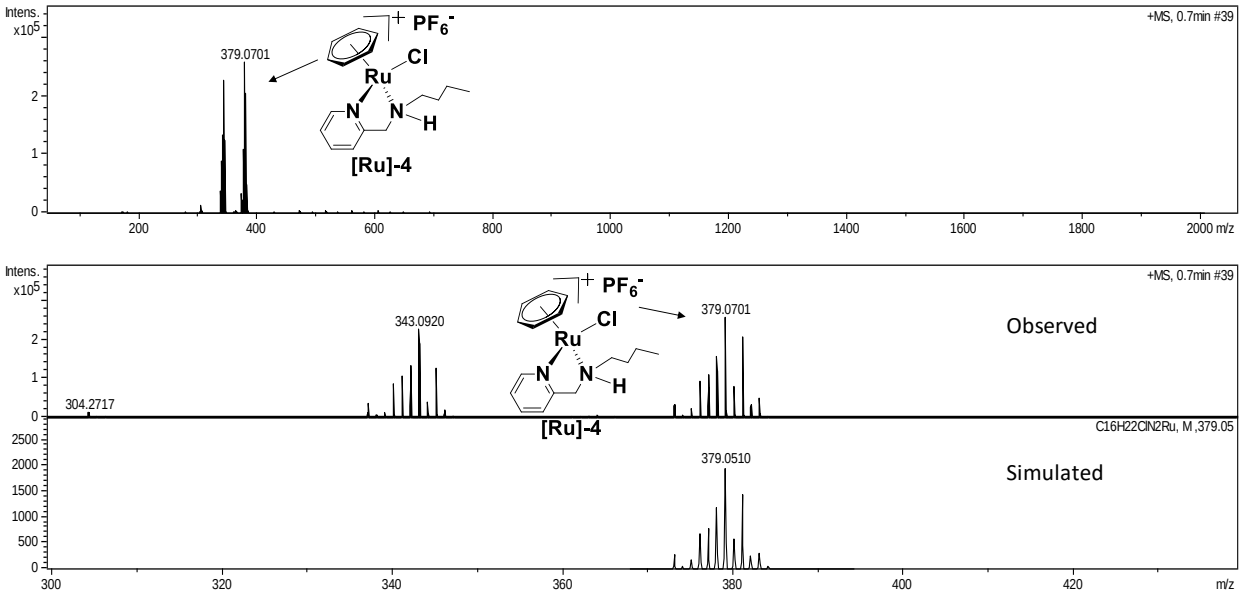
^{1}H NMR spectra of complex **[Ru]-4**



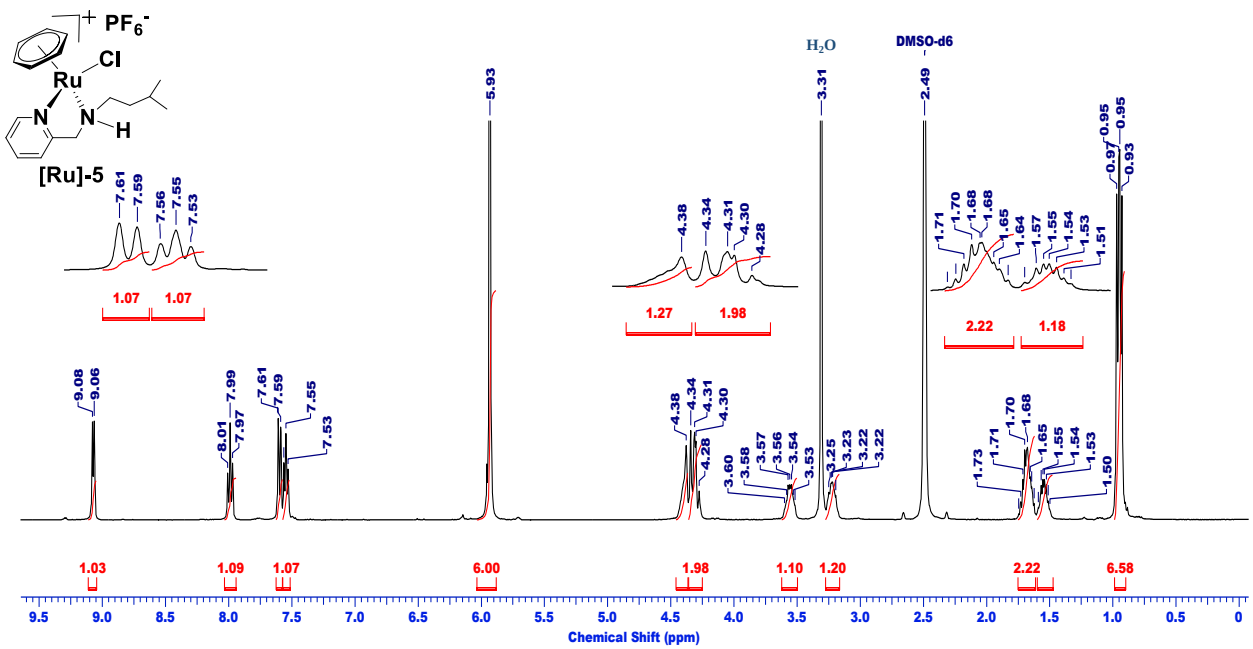
^{13}C NMR spectra of complex **[Ru]-4**



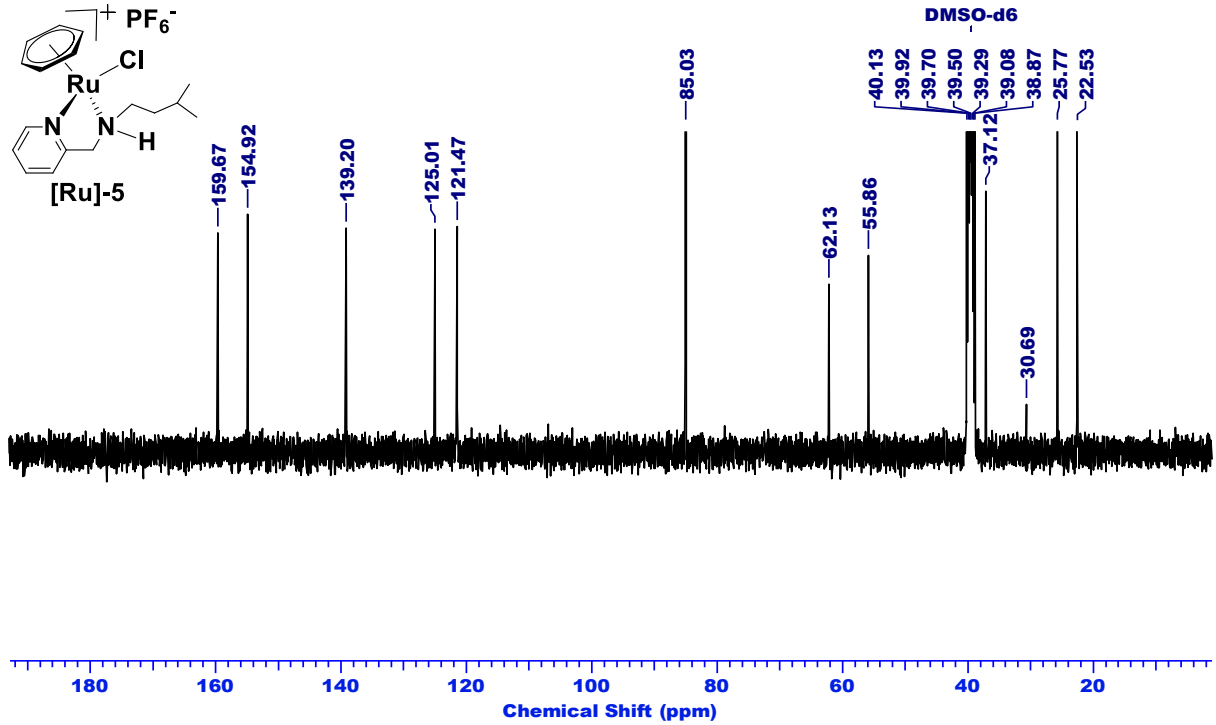
^{31}P NMR spectra of complex **[Ru]-4**



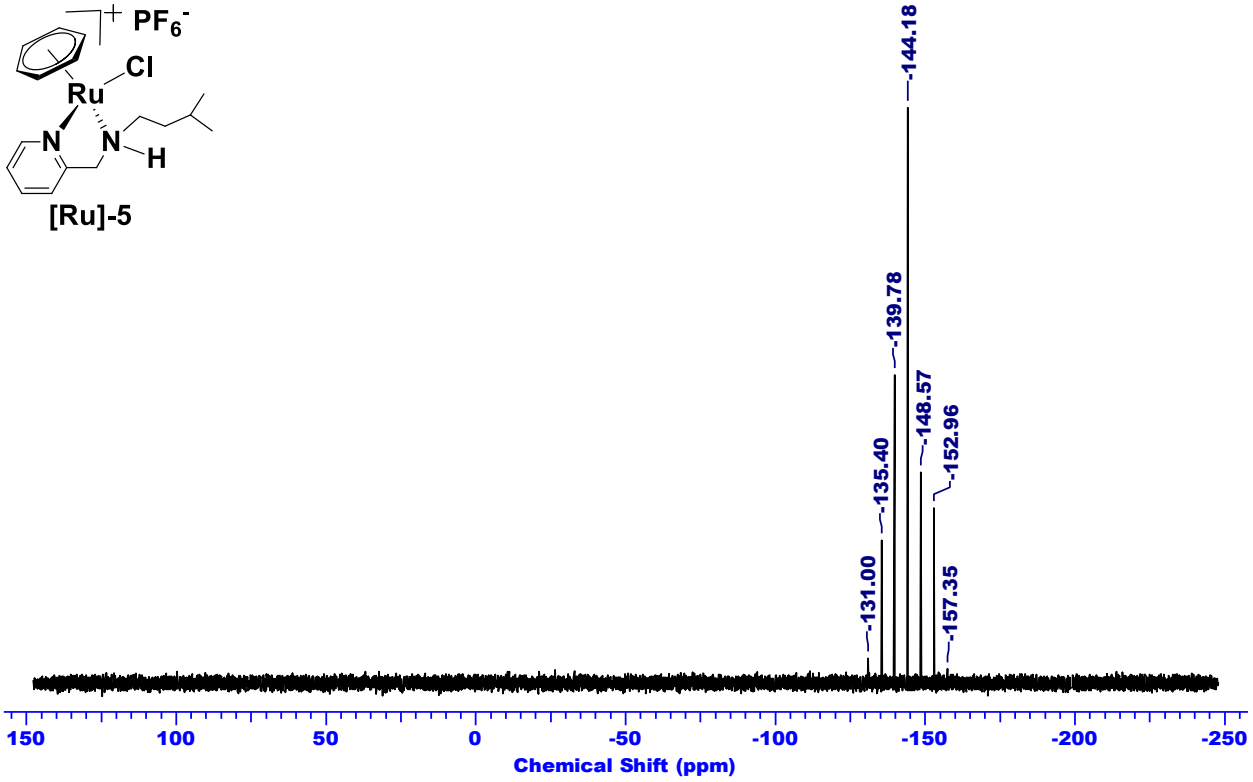
ESI-MS spectra of complex **[Ru]-4**



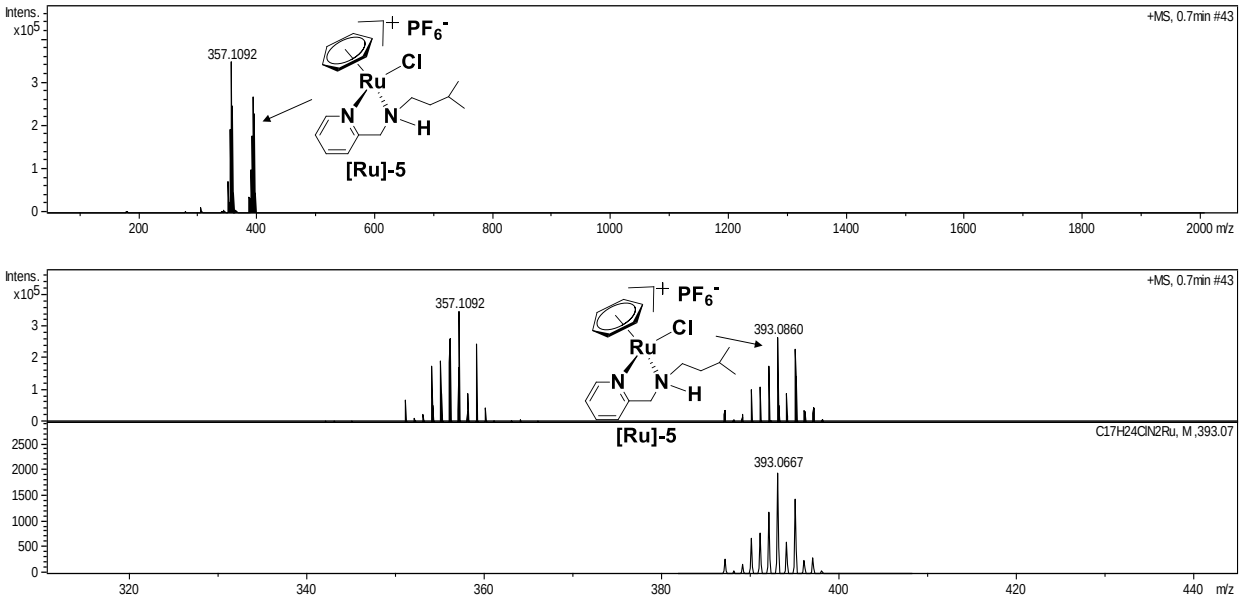
^{1}H NMR spectra of complex **[Ru]-5**



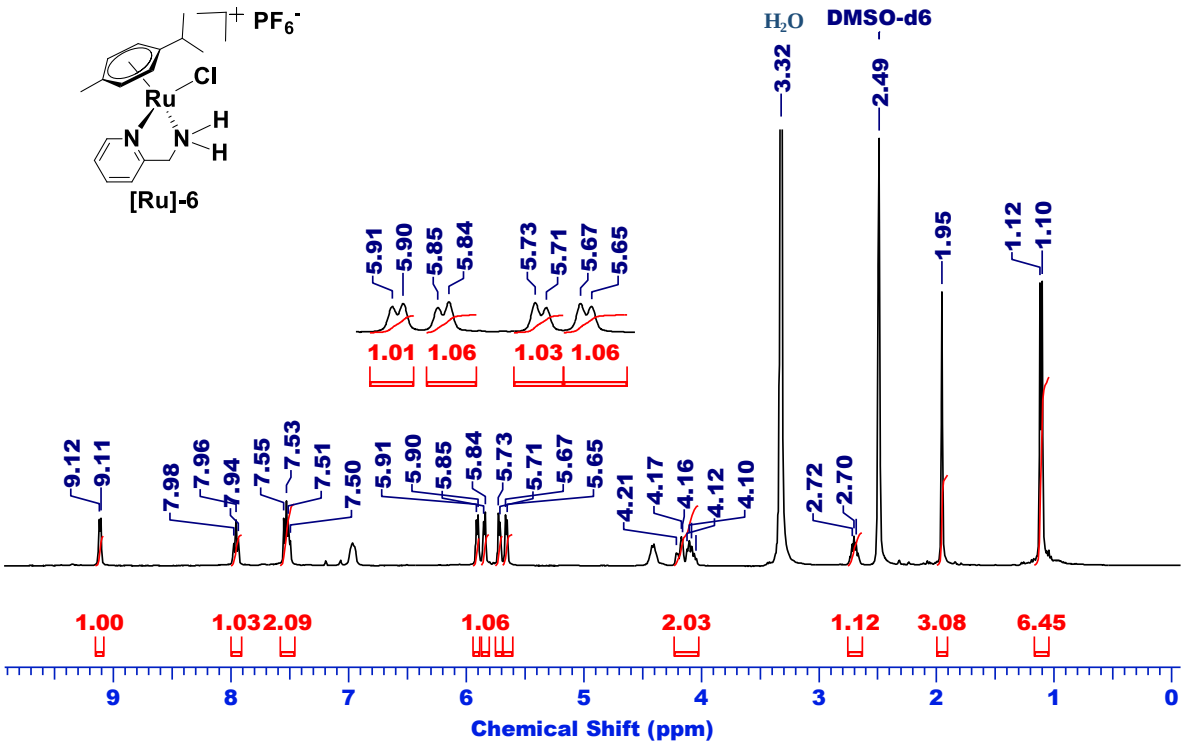
^{13}C NMR spectra of complex **[Ru]-5**



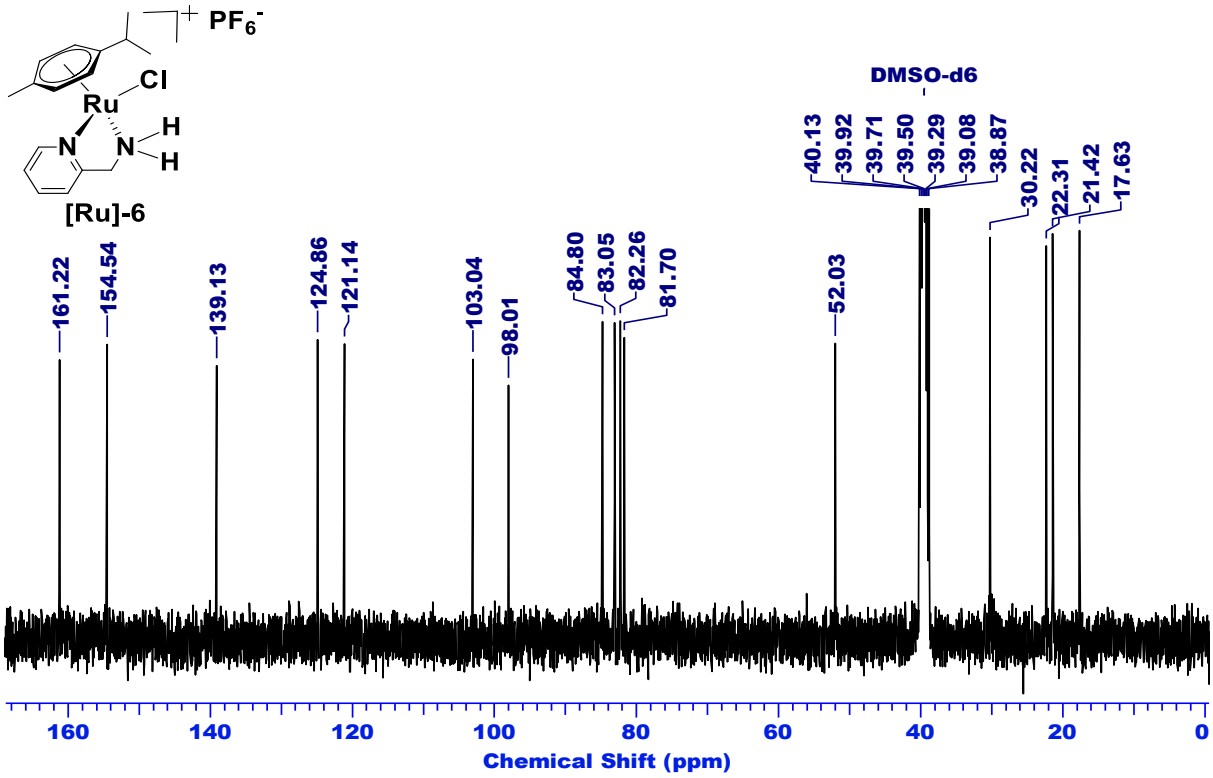
^{31}P NMR spectra of complex **[Ru]-5**



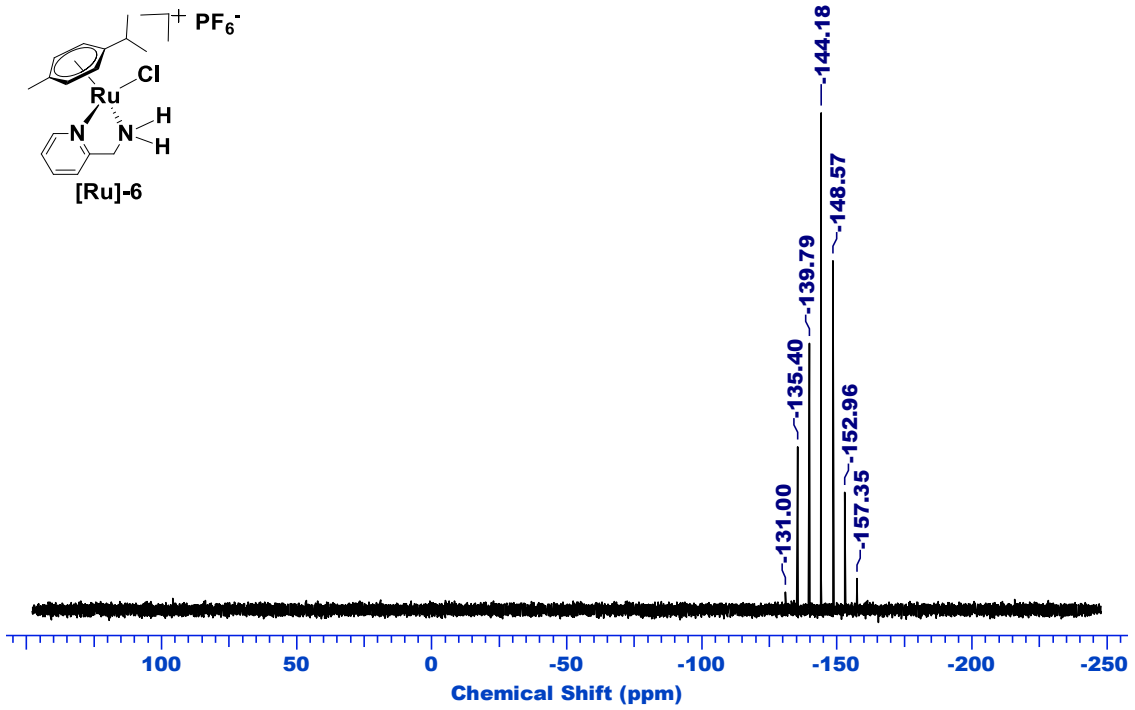
ESI-MS spectra of complex **[Ru]-5**



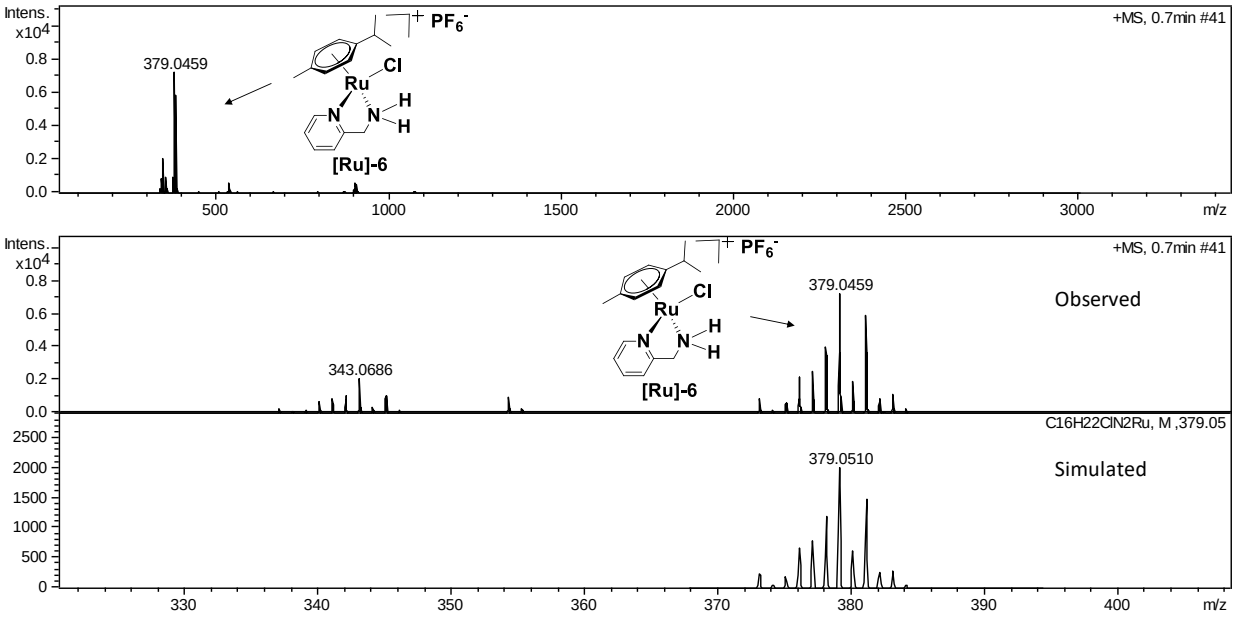
^{1}H NMR spectra of complex **[Ru]-6**



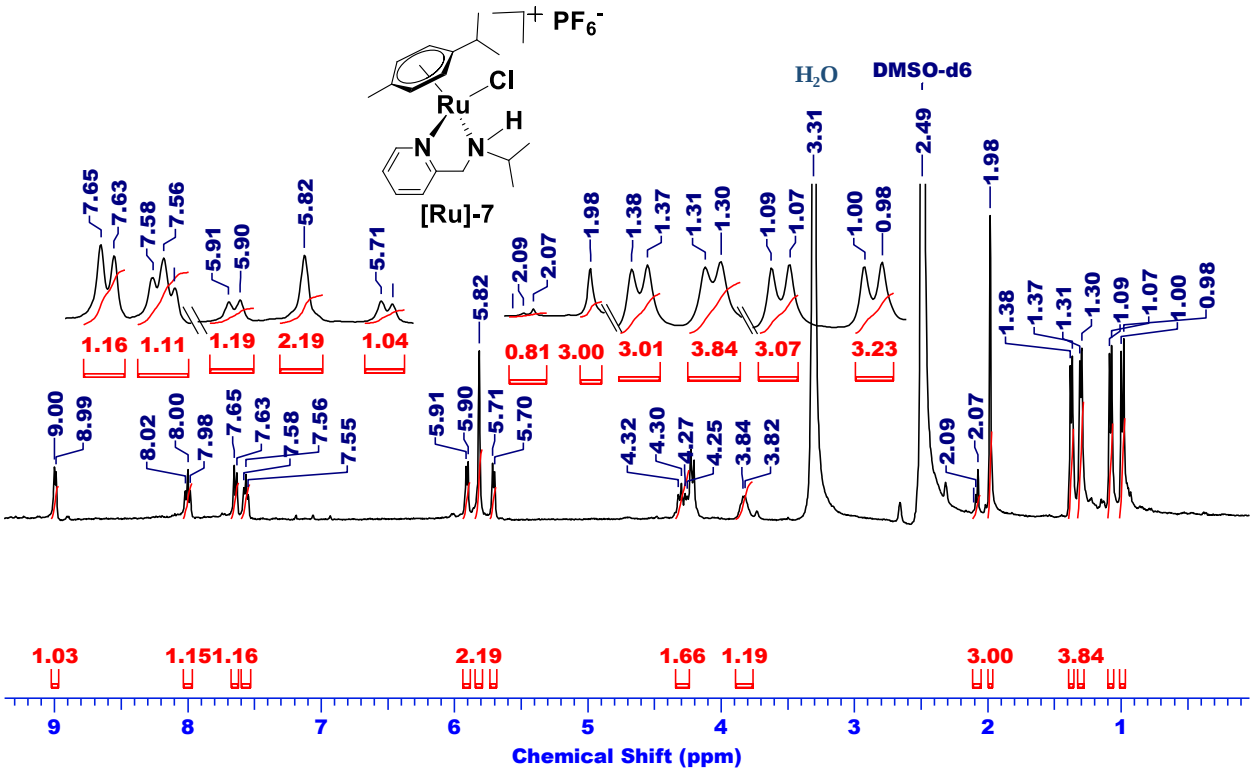
^{13}C NMR spectra of complex **[Ru]-6**



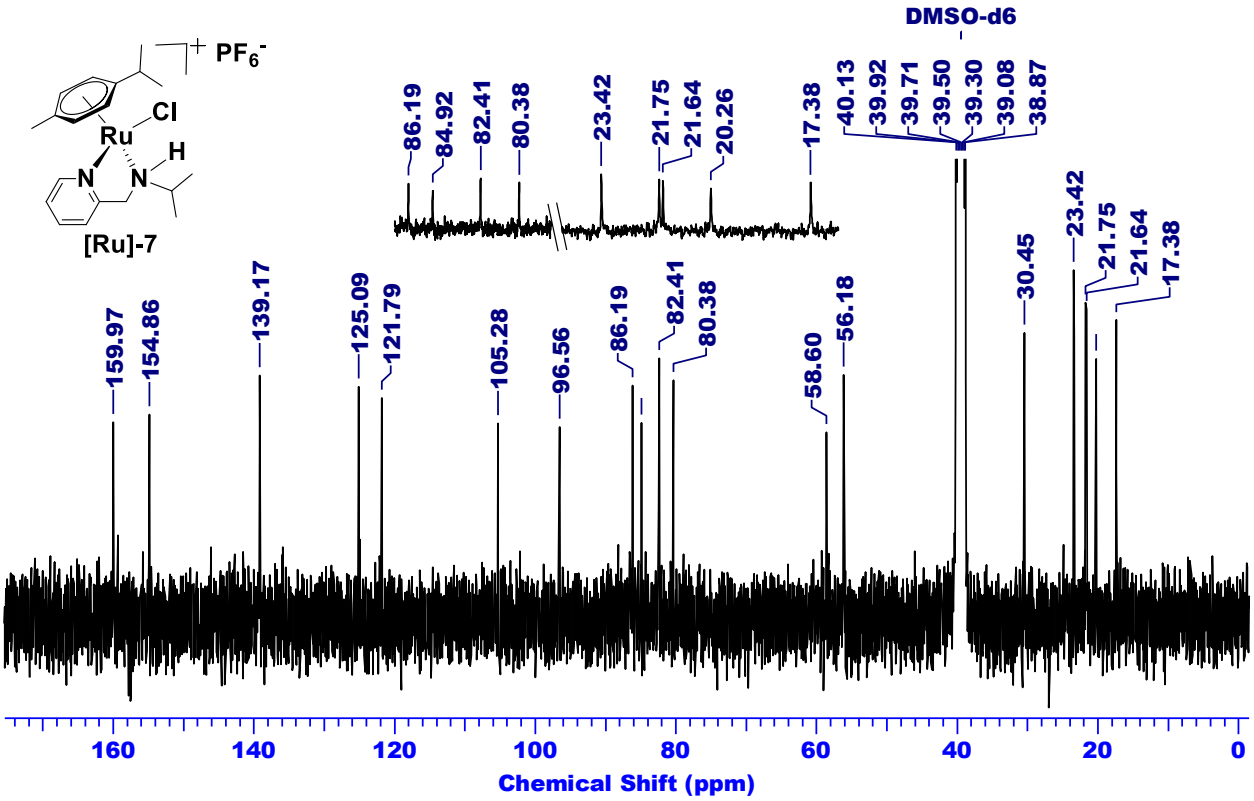
^{31}P NMR spectra of complex **[Ru]-6**



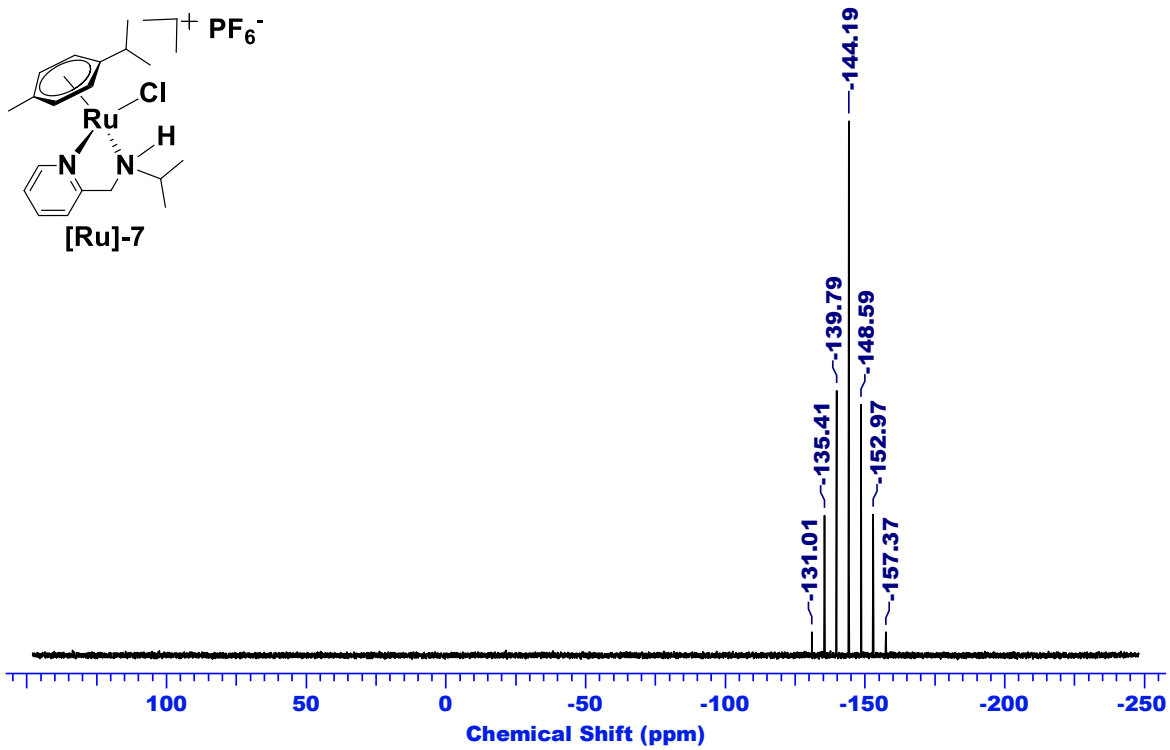
ESI-MS spectra of complex **[Ru]-6**



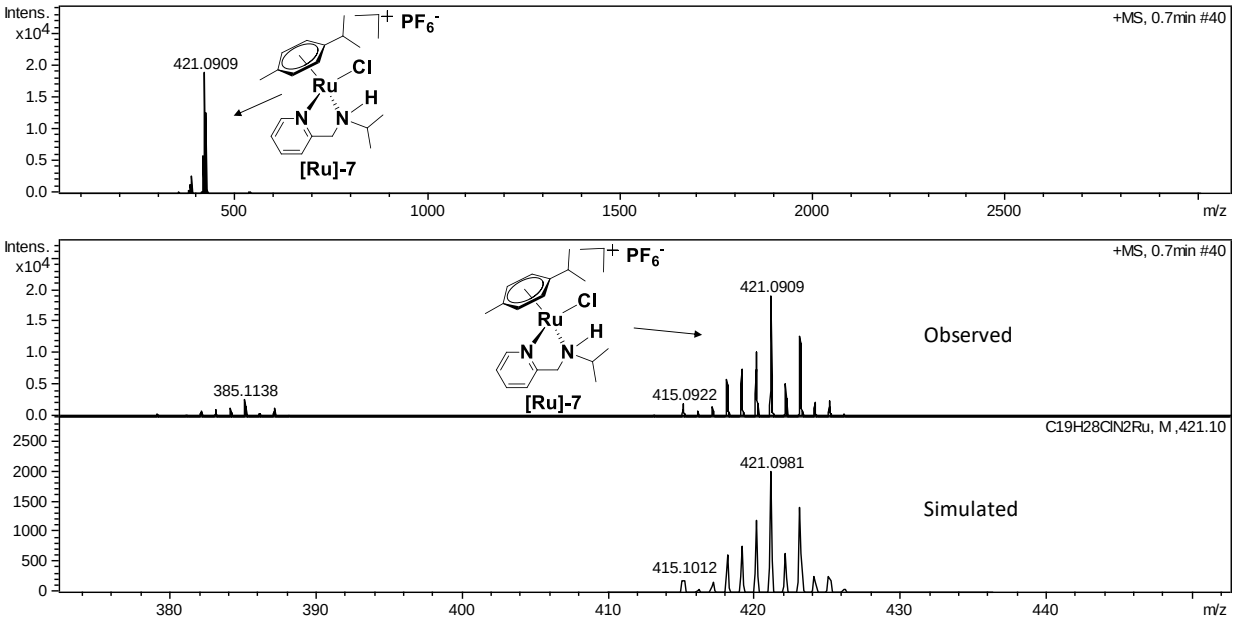
^{1}H NMR spectra of complex **[Ru]-7**



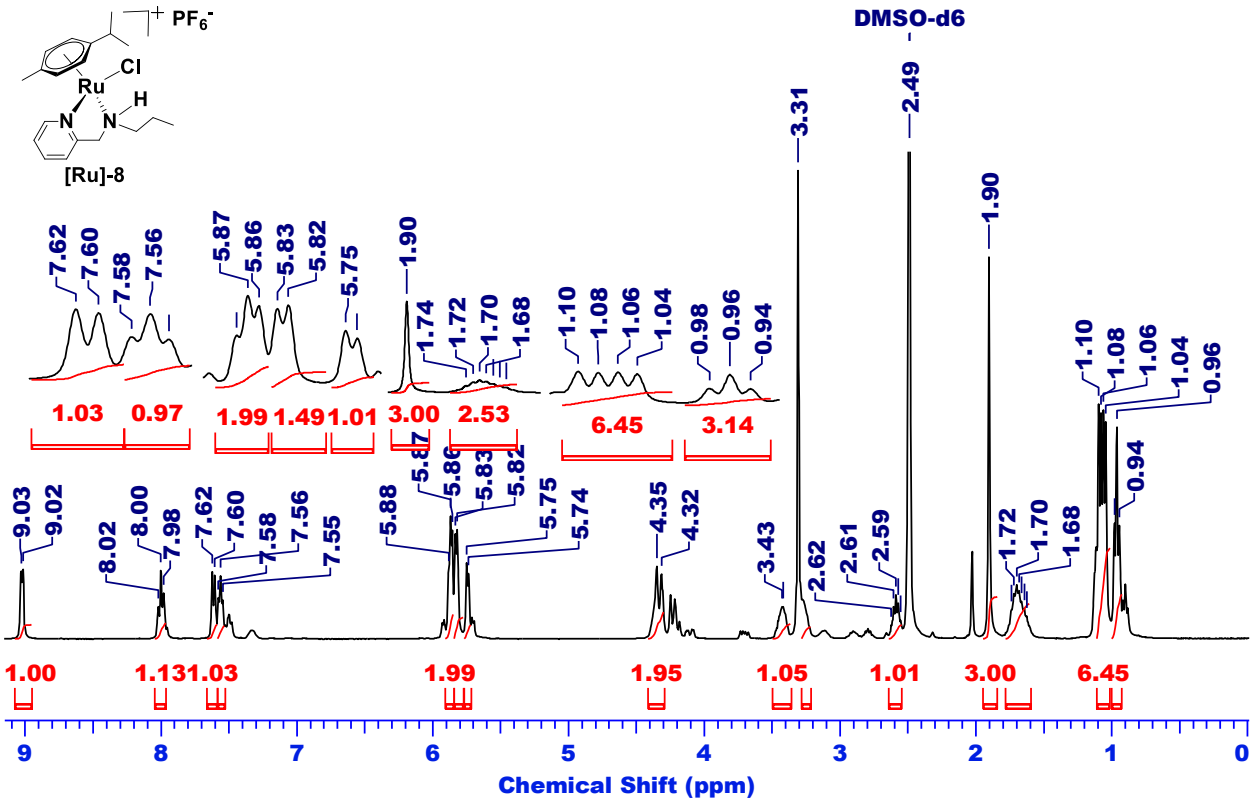
^{13}C NMR spectra of complex **[Ru]-7**



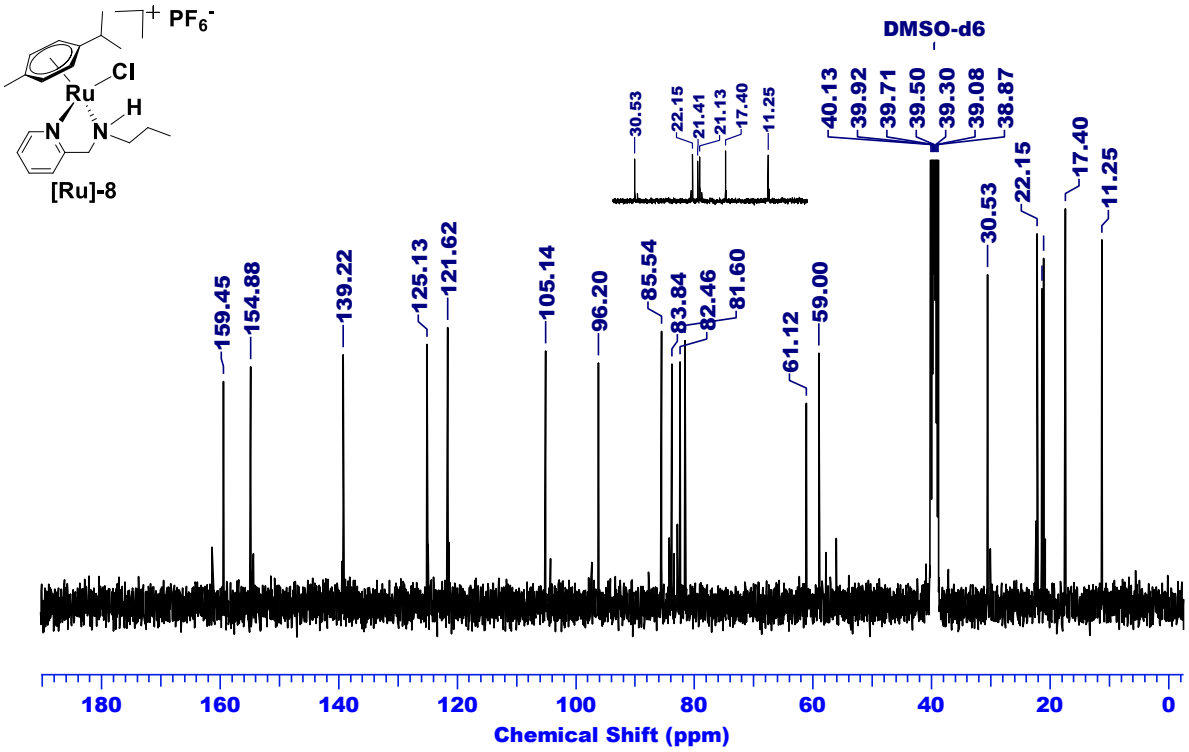
^{31}P NMR spectra of complex **[Ru]-7**



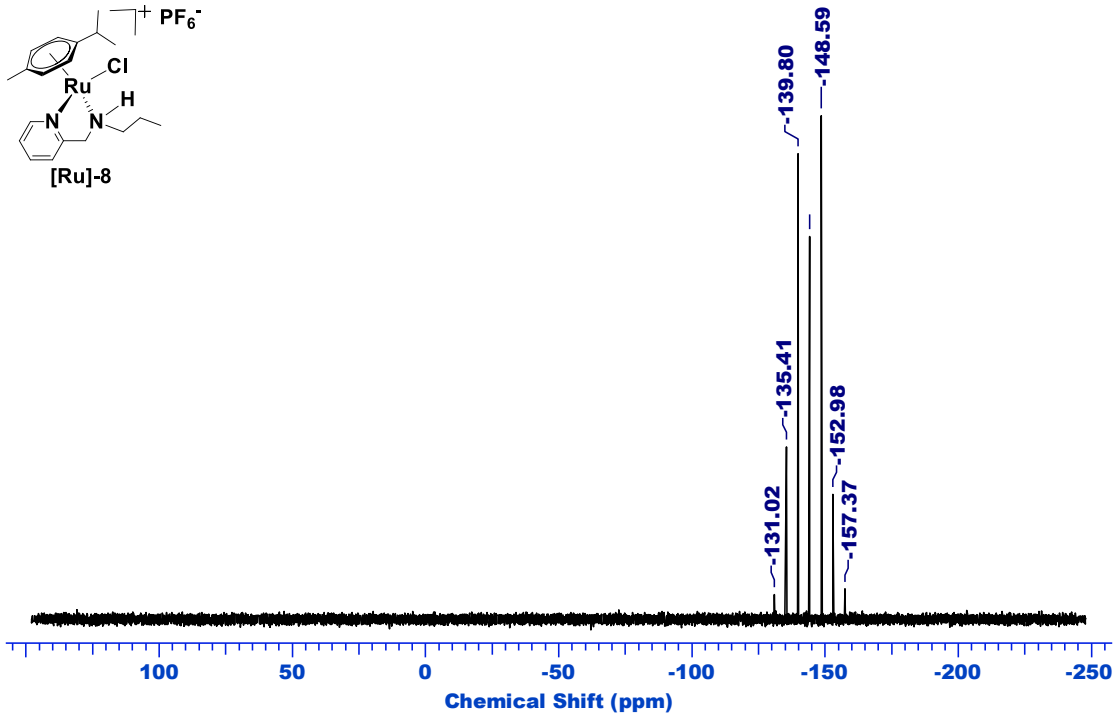
ESI-MS spectra of complex **[Ru]-7**



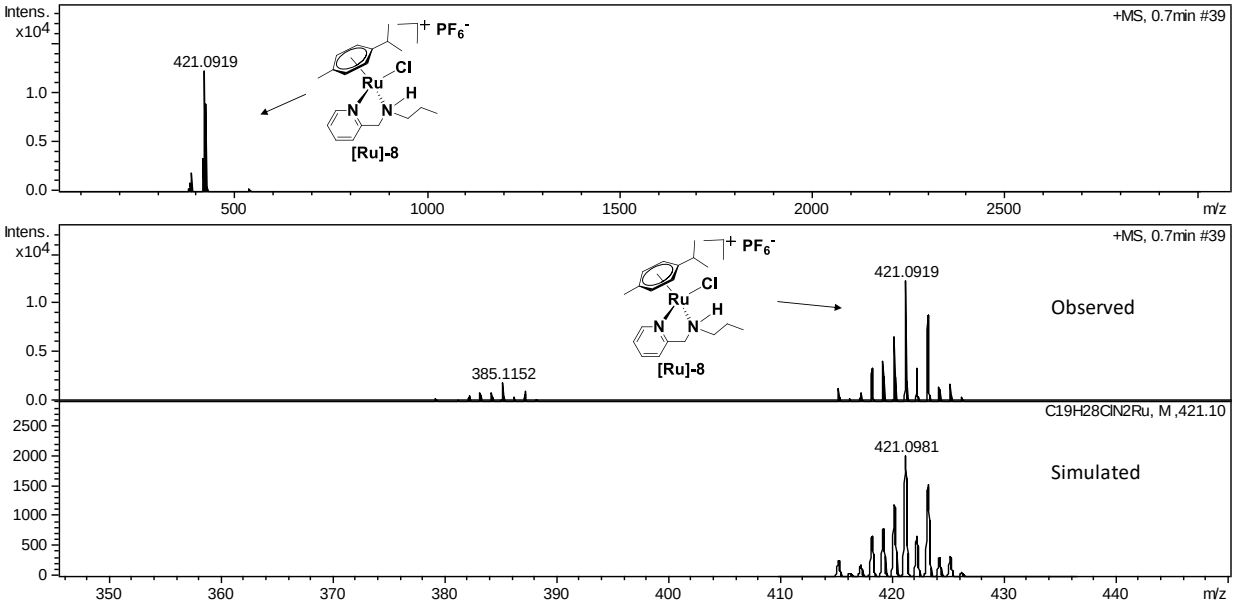
^{1}H NMR spectra of complex **[Ru]-8**



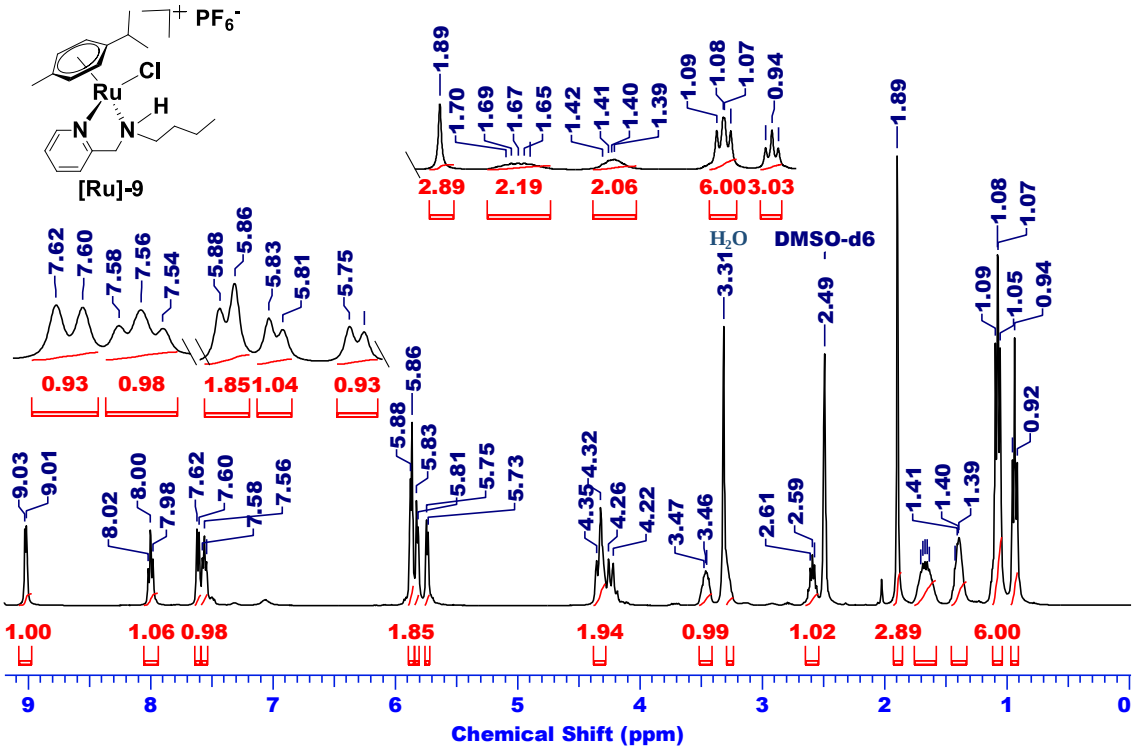
^{13}C NMR spectra of complex **[Ru]-8**



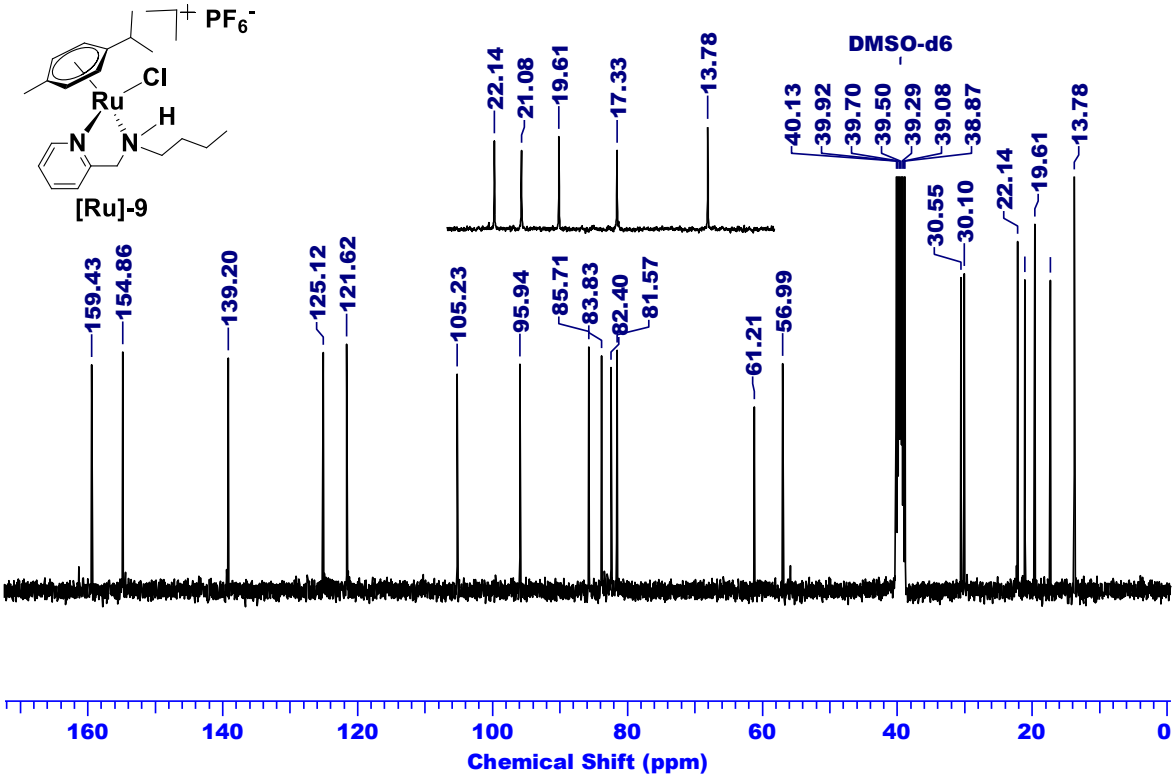
^{31}P NMR spectra of complex **[Ru]-8**



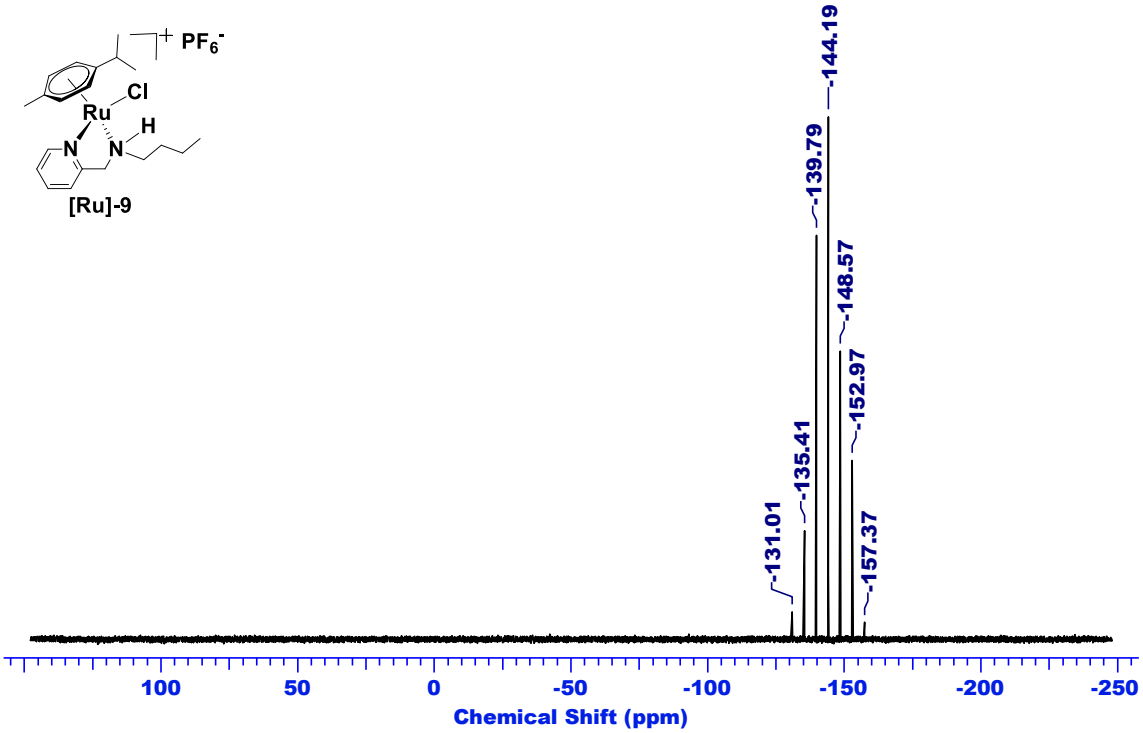
ESI-MS spectra of complex **[Ru]-8**



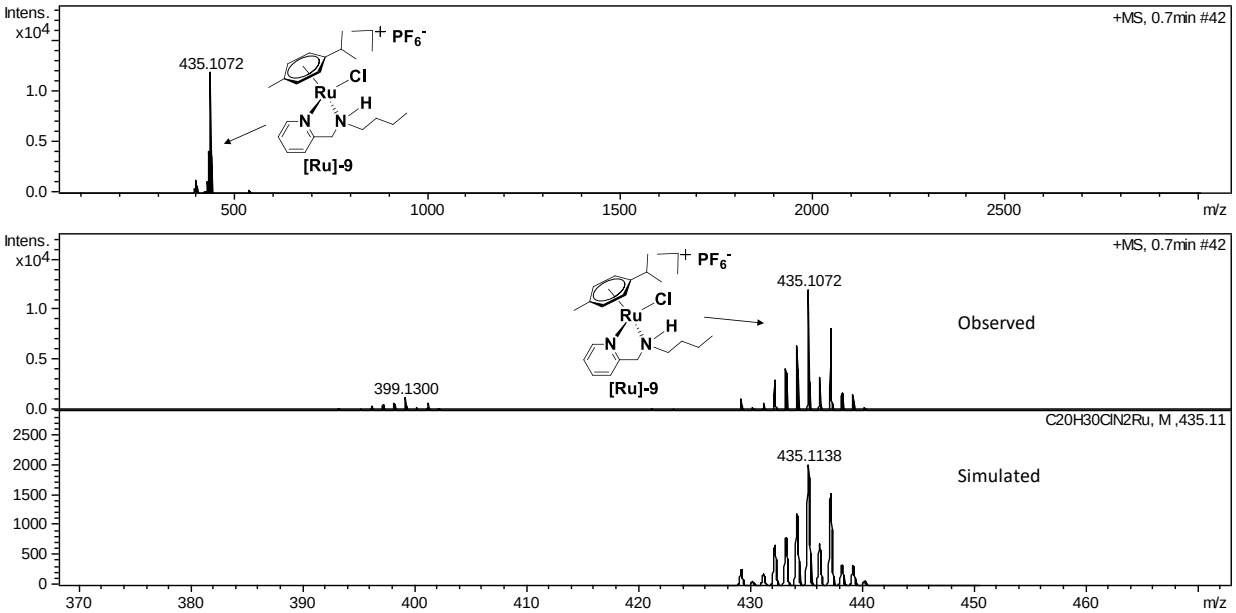
^{1}H NMR spectra of complex **[Ru]-9**



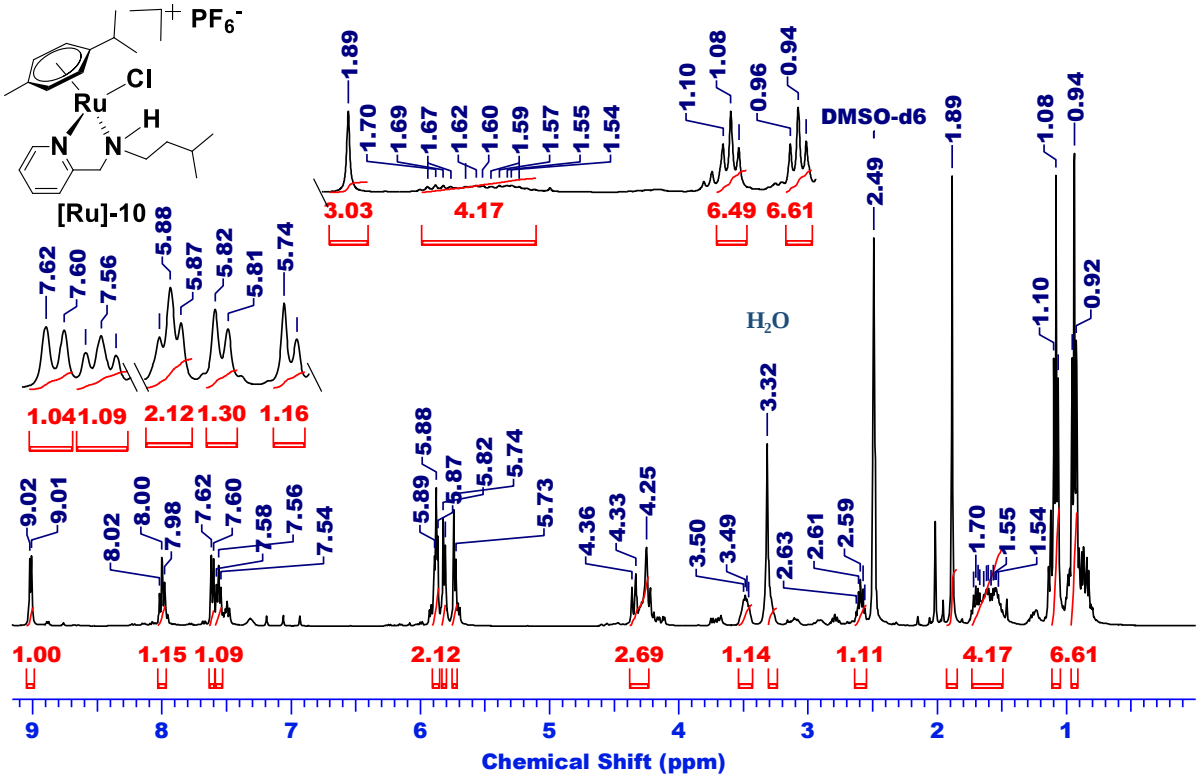
^{13}C NMR spectra of complex **[Ru]-9**



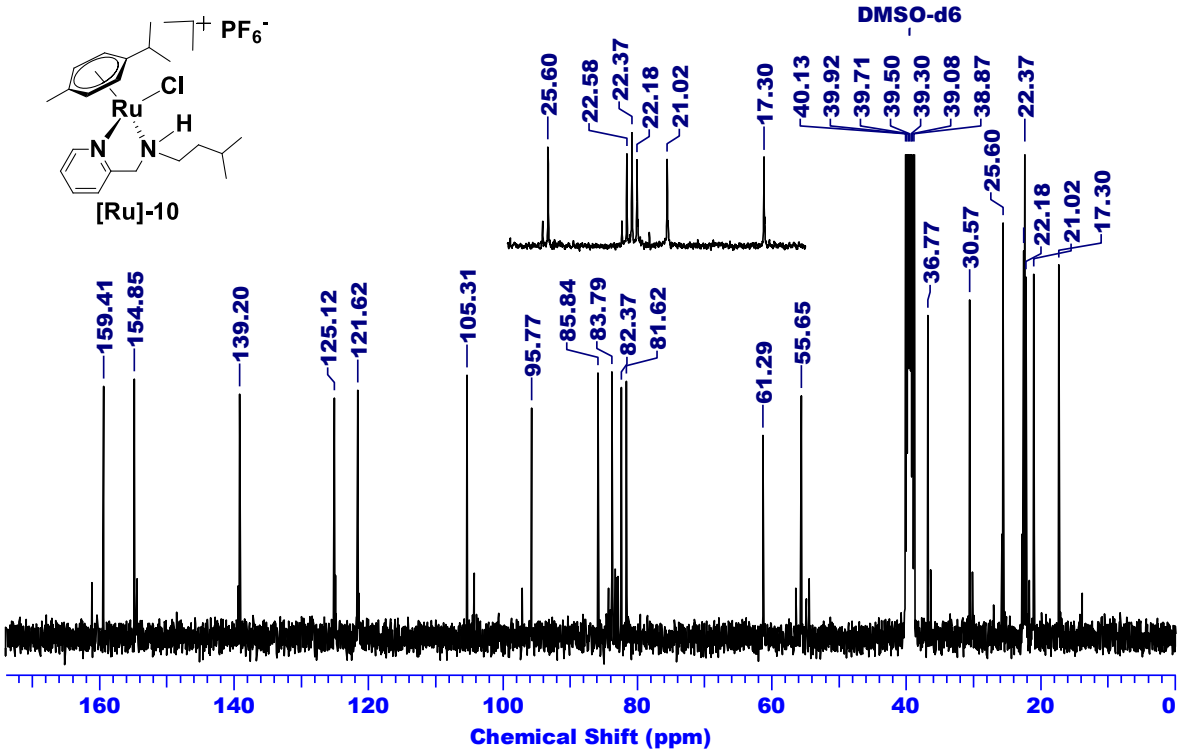
^{31}P NMR spectra of complex **[Ru]-9**



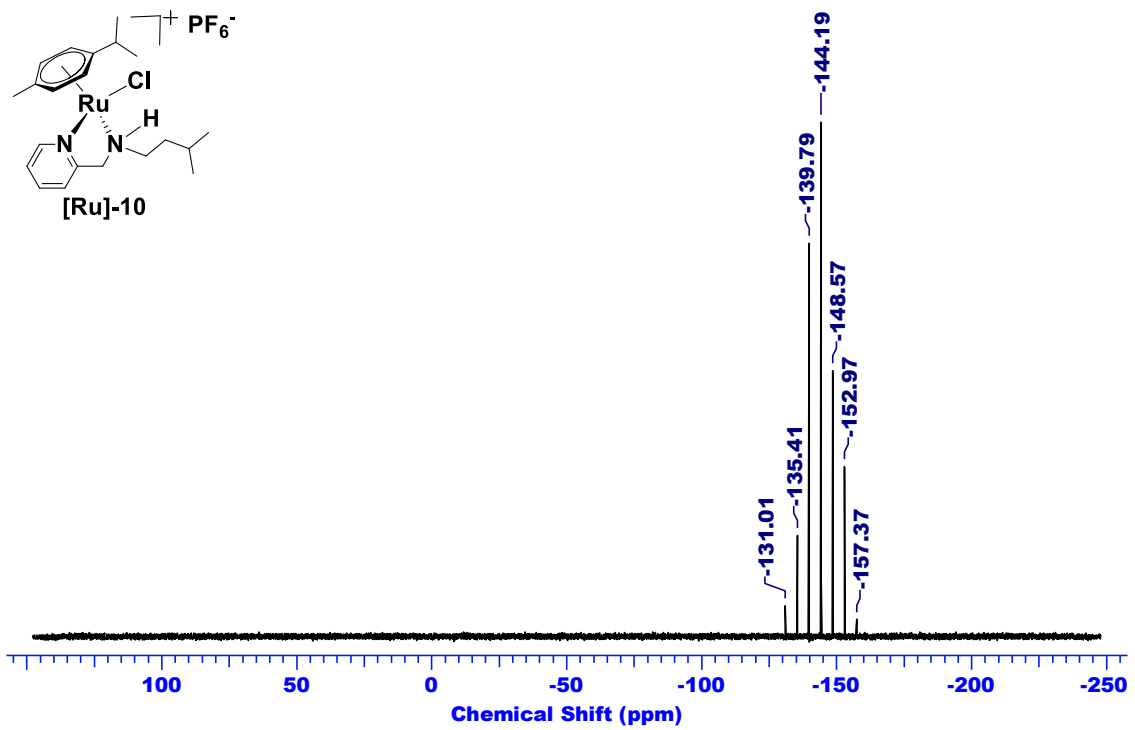
ESI-MS spectra of complex **[Ru]-9**



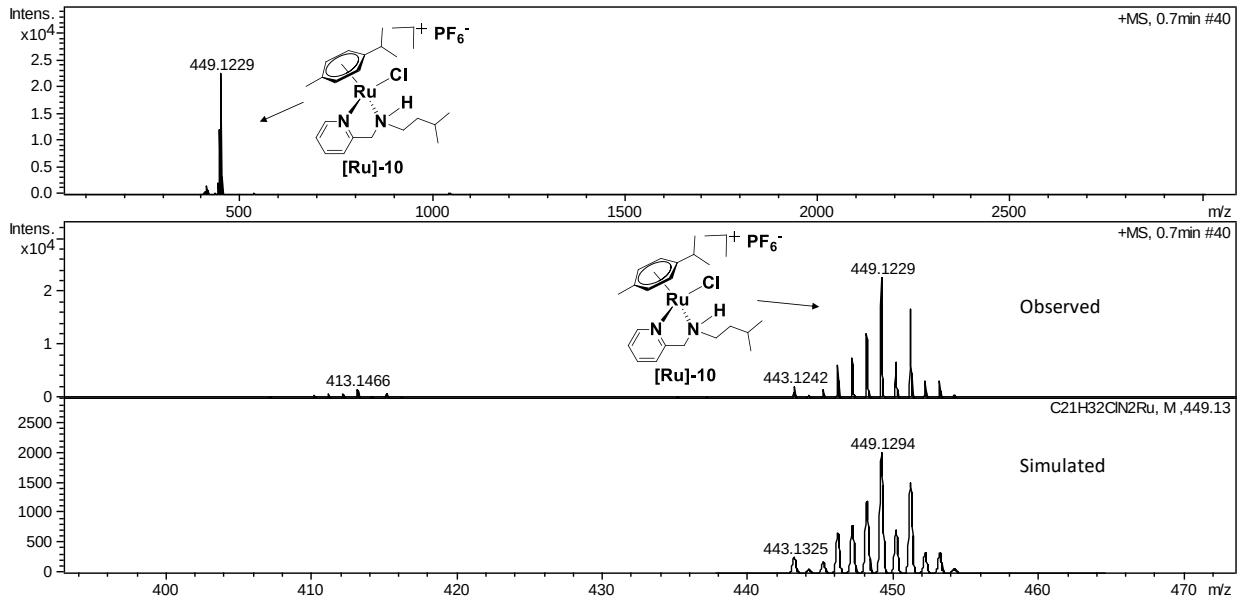
^{1}H NMR spectra of complex **[Ru]-10**



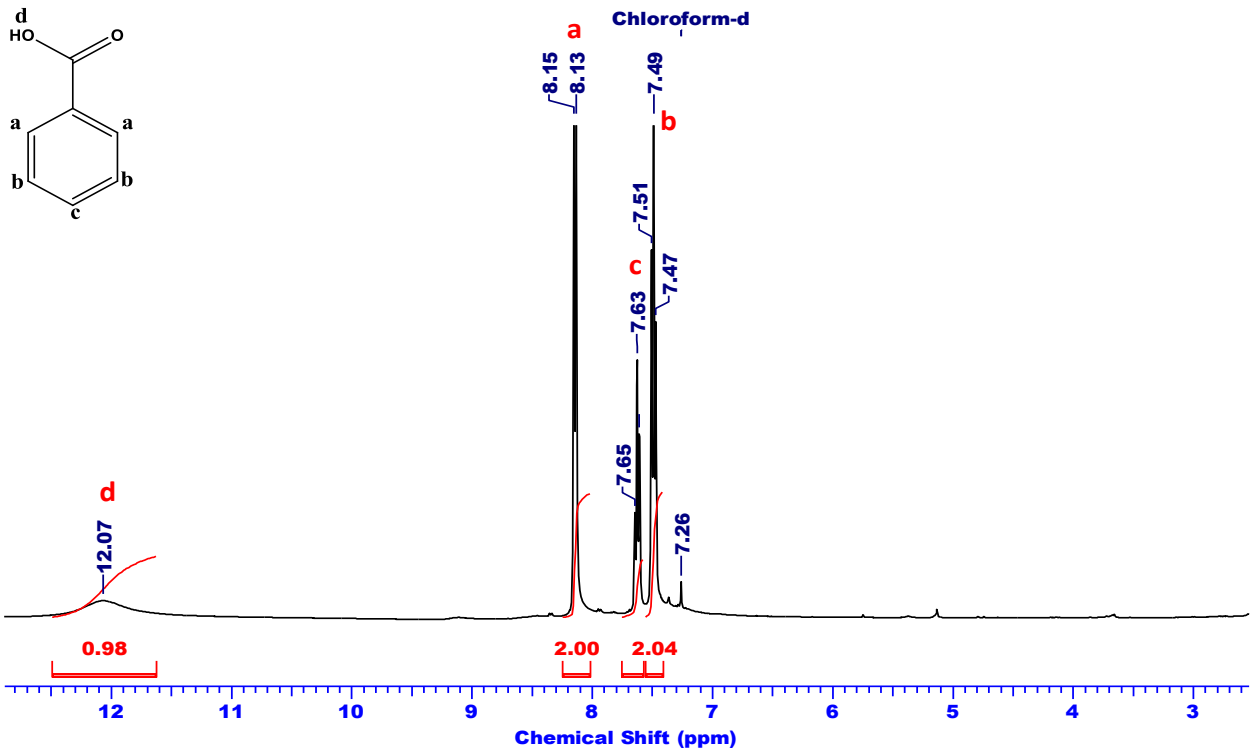
^{13}C NMR spectra of complex **[Ru]-10**



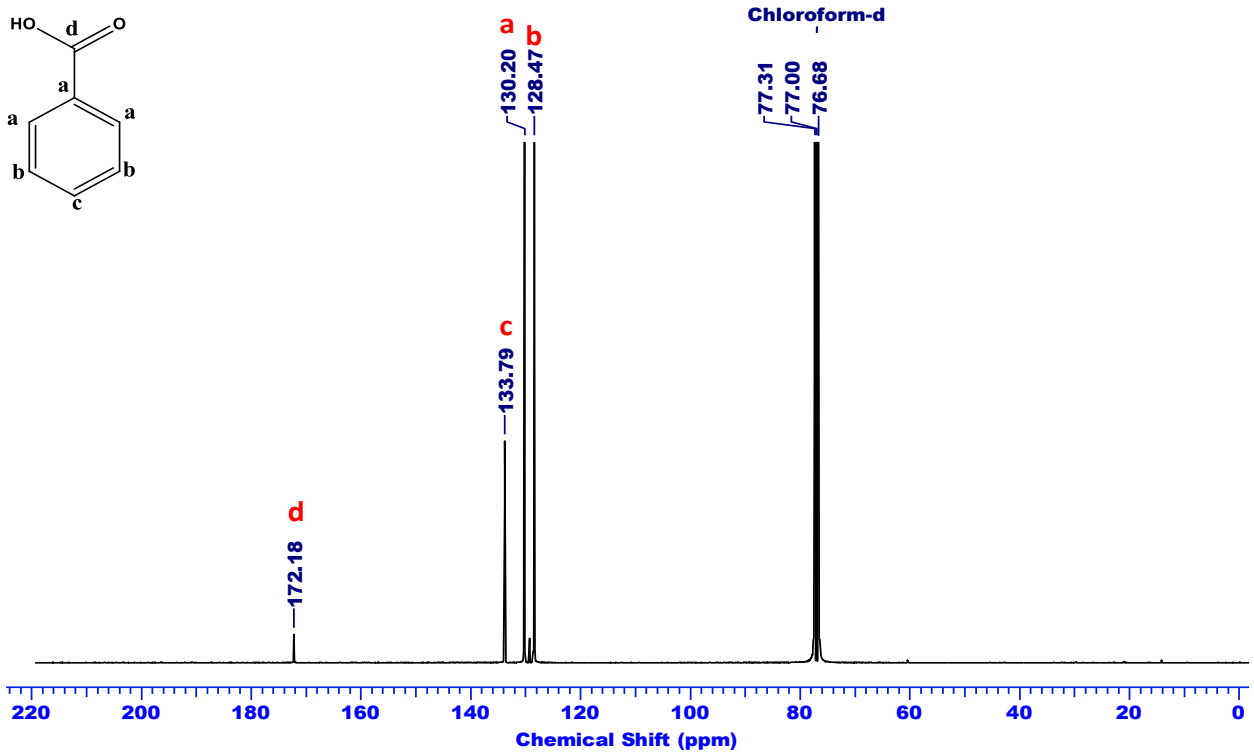
^{31}P NMR spectra of complex **[Ru]-10**



ESI-MS spectra of complex **[Ru]-10**



^{1}H NMR spectra of benzoic acid



^{13}C NMR spectra of benzoic acid

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