Tandem transfer hydrogenation-epoxidation of ketone substrates catalysed by alkene-tethered Ru(II)-NHC complexes

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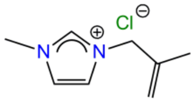
Supporting Information

1. Synthesis, characterization, and NMR spectra of [H(**L1**-**L6**)]Cl

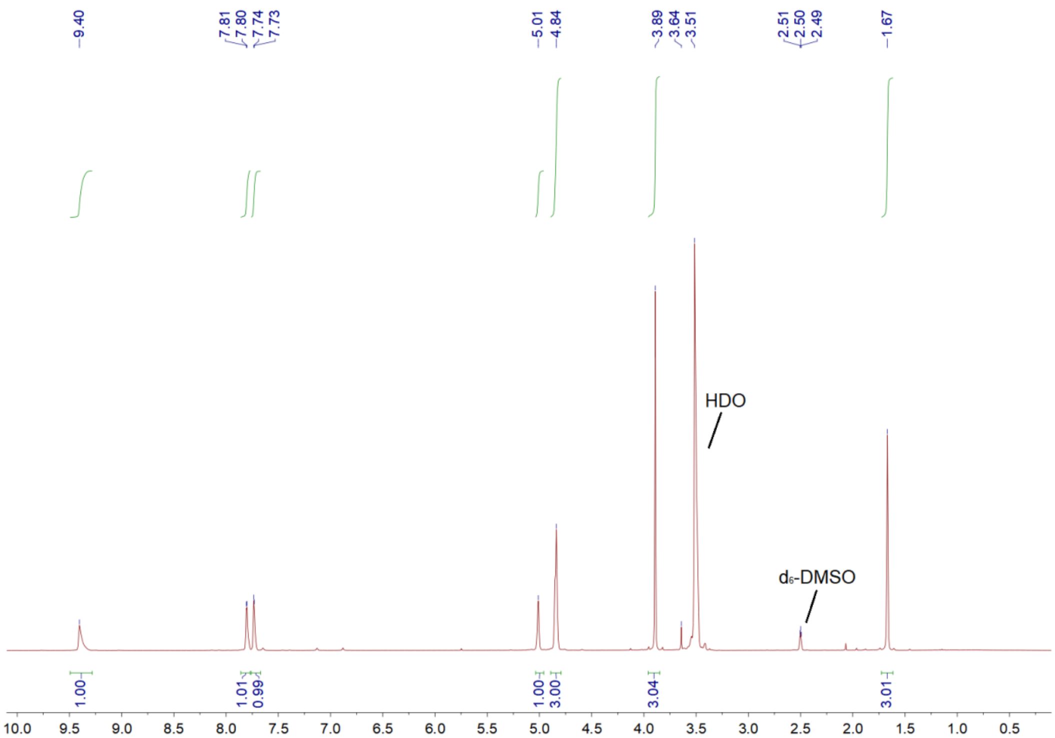
General synthesis of imidazolium salts: To an acetonitrile (20 mL) solution of the respective *N*-alkyl imidazole (42 mmol, [H**L1**]Cl, [H**L2**]Cl) was added 1-chloro-2-methylpropene (1 equivalent), and the resulting mixture heated under reflux overnight. After cooling, the reaction mixture was concentrated *in vacuo*, and washed with a 1:1 v/v Et_2O/Et_2OAc mixture (3 × 15 mL). The resulting oil/solid was concentrated in vacuo to give the respective ligands [H(**L1**-**L6**)]Cl.

[H**L1**]Cl: Yield: 94%. ^{1}H NMR ($(CD_3)_2SO$): δ_H = 1.67 (s, 3H, CH_3), 3.89 (s, 3H, NCH_3), 4.84 (s, 3H, =CH + NCH_2), 5.01 (s, 1H, =CH), 7.74 (d, $^{3}J_{HH}$ = 2 Hz, 1H, NCH), 7.81 (d, $^{3}J_{HH}$ = 2 Hz, 1H, NCH), 9.40 (s, 1H, NCHN). ^{13}C{^{1}H} NMR ($(CD_3)_2SO$): δ_C = 19.5 (s, CH_3), 35.9 (s, NCH_3), 54.0 (s, NCH_2), 114.9 (s, =CH_2), 122.6 (s, NCH), 123.9 (s, NCH), 137.0 (s, CCH_2), 139.5 (s, NCN).

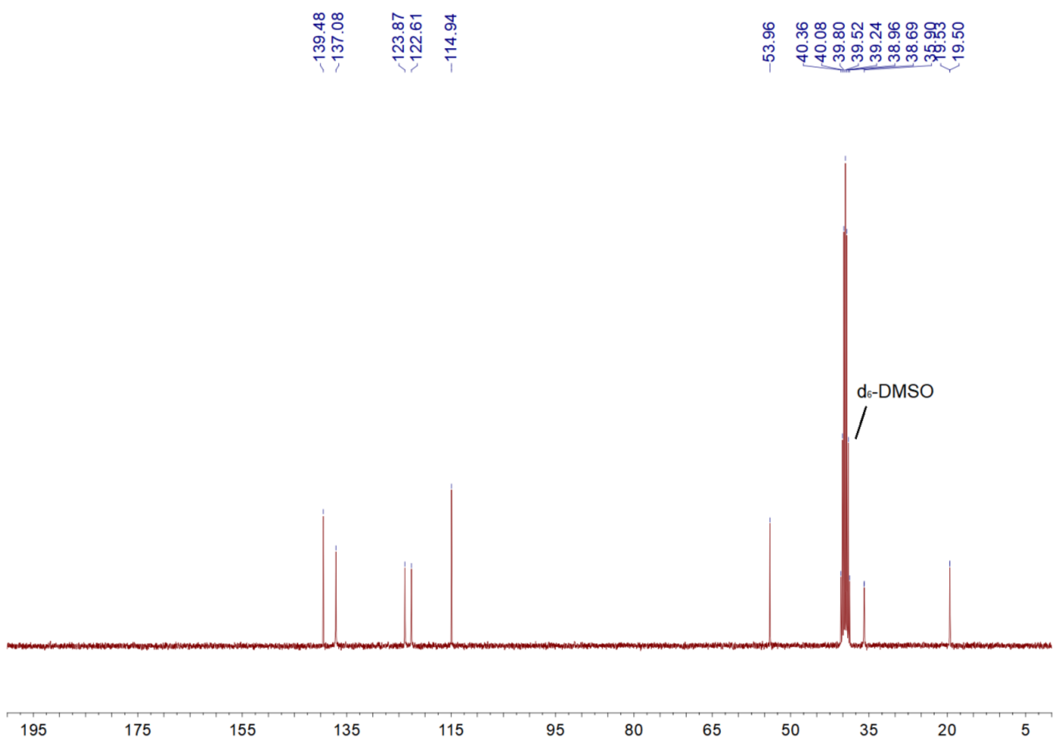
^{1}H-NMR



[H**L1**]Cl

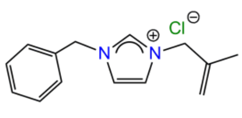


^{13}C-NMR

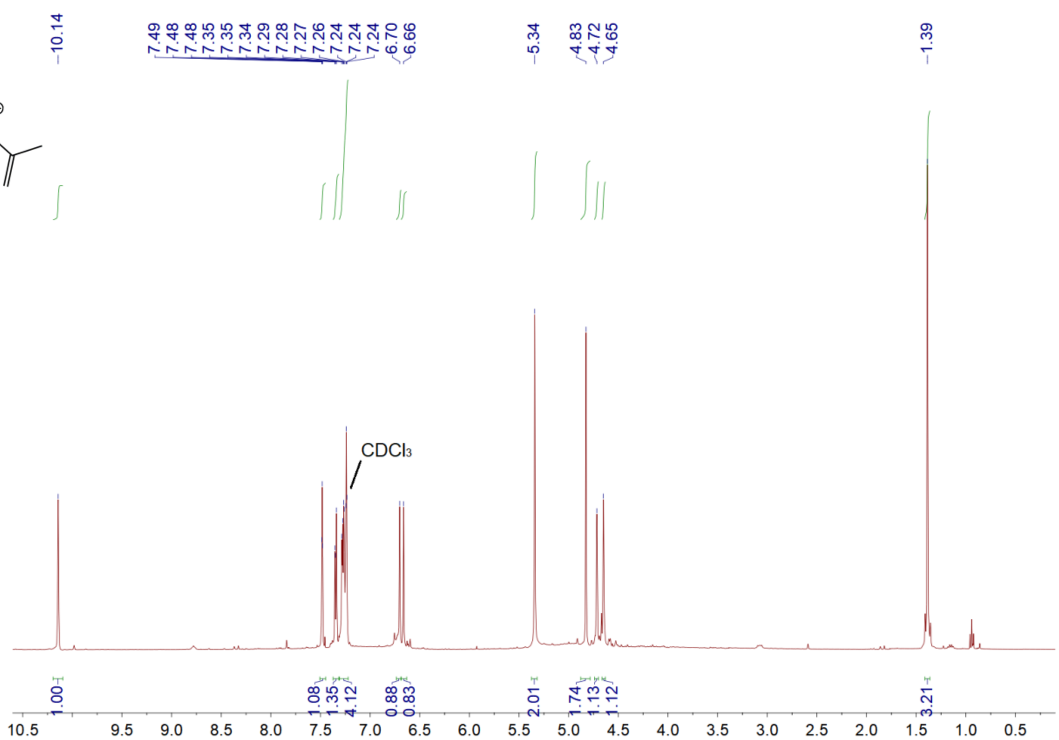


[H**L2**]Cl: Yield: 91%. [1]H NMR ($CDCl_3$): δ_H = 1.39 (s, 3H, CH_3), 4.65 (s, 1H, $=CH_2$), 4.72 (s, 1H, $=CH_2$), 4.83 (s, 2H, CH_2), 5.34 (s, 2H, CH_2), 6.66 (s, 1H, NCH), 6.70 (s, 1H, NCH), 7.26 (m, 4H, C_6H_5), 7.49 (m, 1H, C_6*H_5*), 10.14 (s, 1H, NCHN). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C = 18.5 (s, CH_3), 51.6 (s, CH_2), 53.9 (s, CH_2), 115.5 (s, $=CH_2$), 121.4 (s, NCH), 121.4 (s, NCH), 132.6 (s, C_6H_5), 135.1 (s, C_6H_5), 135.7 (s, *ipso* C_6H_5), 136.0 (s, CCH_2), 136.9 (s, NCN).

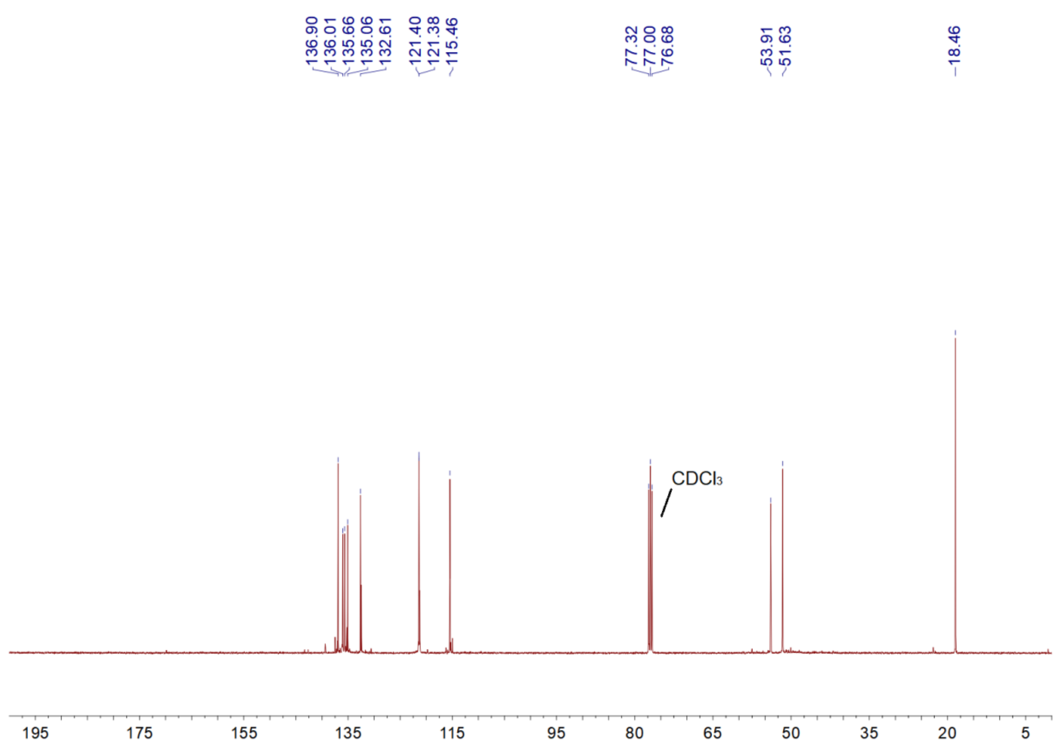
[1]H-NMR



[H**L2**]Cl

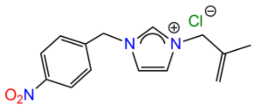


[13]C-NMR

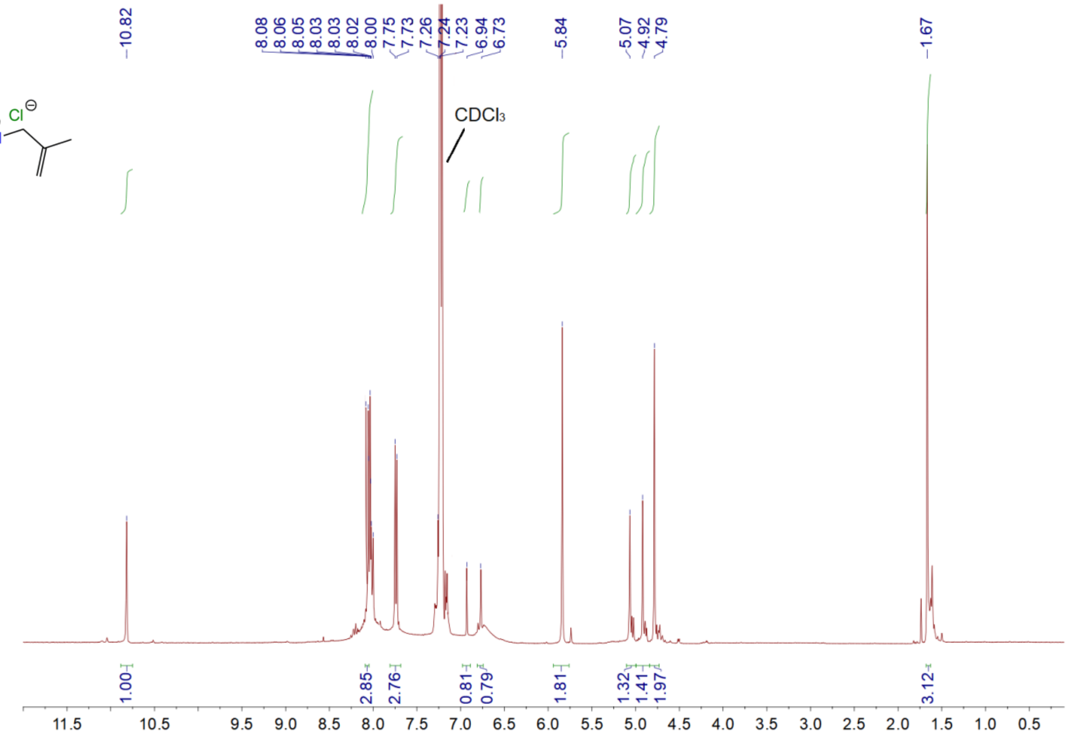


[H**L3**]Cl: Yield: 67%. [1]H NMR ($CDCl_3$): δ_H = 1.67 (s, 3H, CH_3), 4.79 (s, 2H, CH_2), 4.92 (s, 1H, =CH), 5.07 (s, 1H, =CH), 5.84 (s, 2H, CH_2), 6.74 (s, 1H, NCH), 6.94 (s, 1H, NCH), 7.74 (d, $^3J_{HH}$ = 6 Hz, 2H, C_6H_4), 8.05 (m, 2H, C_6H_4), 10.82 (s, 1H, NCHN). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C = 19.5 (s, CH_3), 51.9 (s, CH_2), 53.6 (s, CH_2), 117.4 (s, =CH_2), 122.0 (s, NCH), 122.3 (s, NCH), 129.1 (s, C_6H_4), 129.5 (s, C_6H_4), 129.9 (s, *ipso* C_6H_4), 137.4 (s, CCH_2), 143.4 (s, NCN).

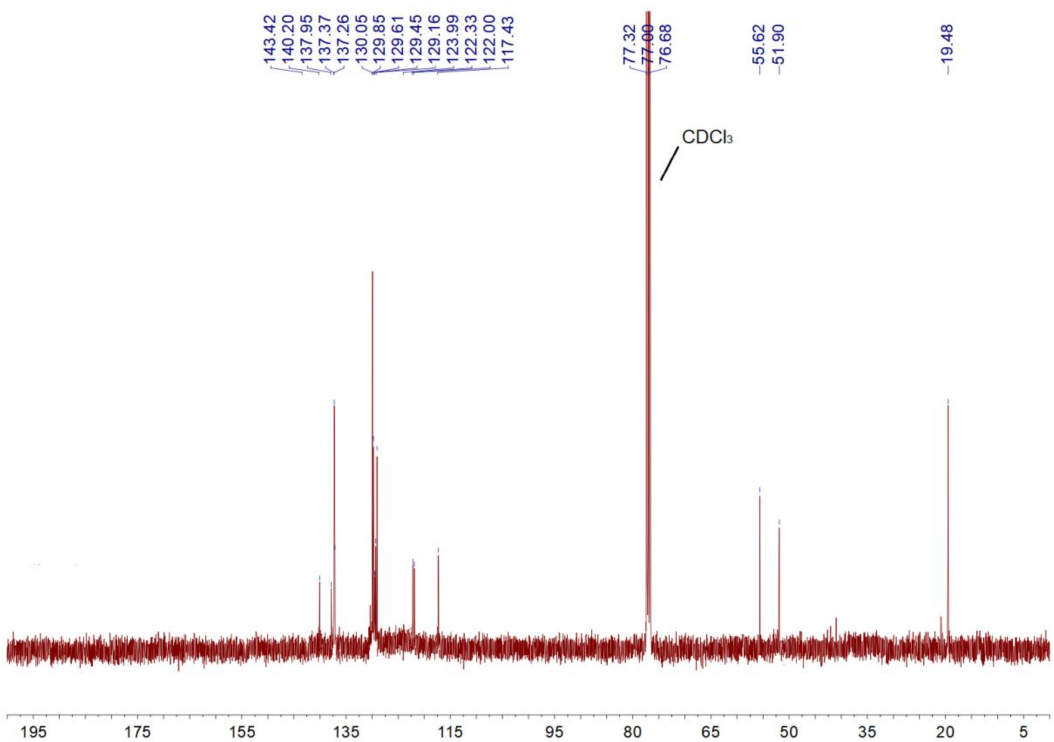
[1]H-NMR



[H**L3**]Cl

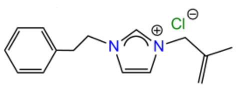


[13]C-NMR

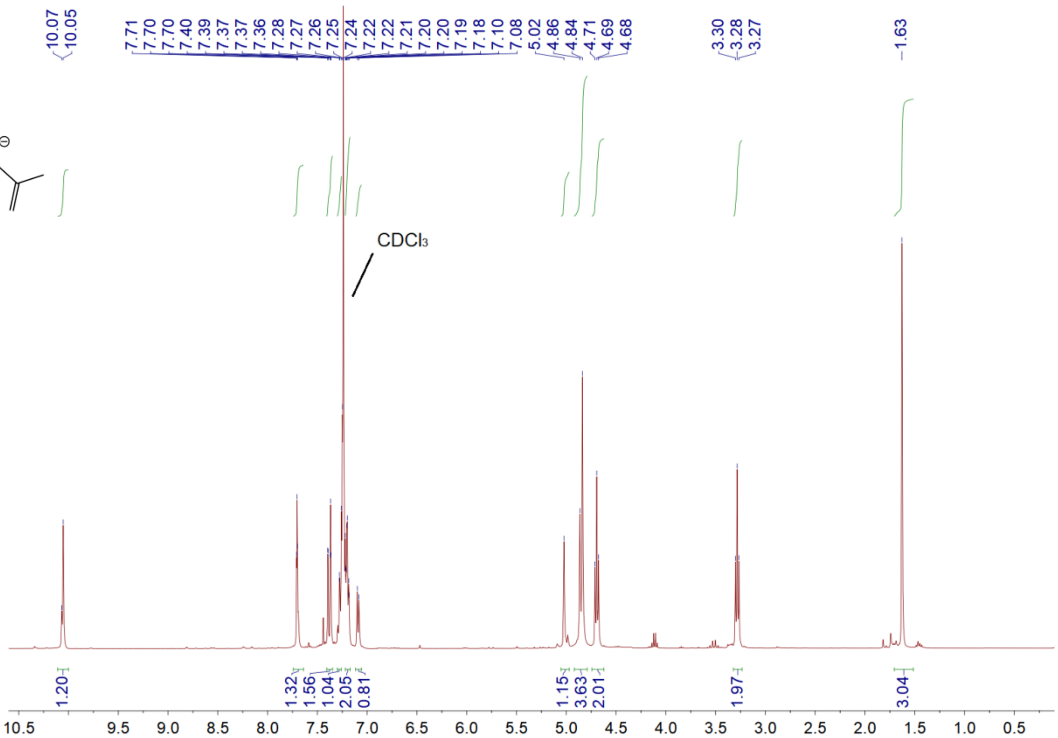


[H**L4**]Cl: Yield: 86%. [1]H NMR ($CDCl_3$): δ_H = 1.63 (s, 3H, CH_3), 1.97 (t, $^3J_{HH}$ = 8 Hz, 2H, CH_2), 4.69 (t, $^3J_{HH}$ = 8 Hz, 2H, CH_2), 4.84 (m, 4H, =CH_2 + CH_2), 5.02 (s, 1H, =CH_2), 7.09 (d, $^3J_{HH}$ = 8 Hz, 1H, NCH), 7.18-7.28 (m, 3H, NCH + C_6H_5), 7.37 (m, 1H, C_6H_5), 7.40 (m, 1H, C_6H_5), 7.70 (m, 1H, C_6H_5), 10.06 (s, 1H, NCHN). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C = 19.1 (s, CH_3), 35.8 (s, CH_2), 50.4 (s, CH_2), 54.8 (s, CH_2), 116.4 (s, =CH_2), 121.5 (s, NCH), 122.5 (s, NCH), 126.5 (s, C_6H_5), 128.3 (s, C_6H_5), 128.4 (s, C_6H_5), 135.3 (s, *ipso* C_6H_5), 136.4 (s, CCH_2), 137.4 (s, NCN).

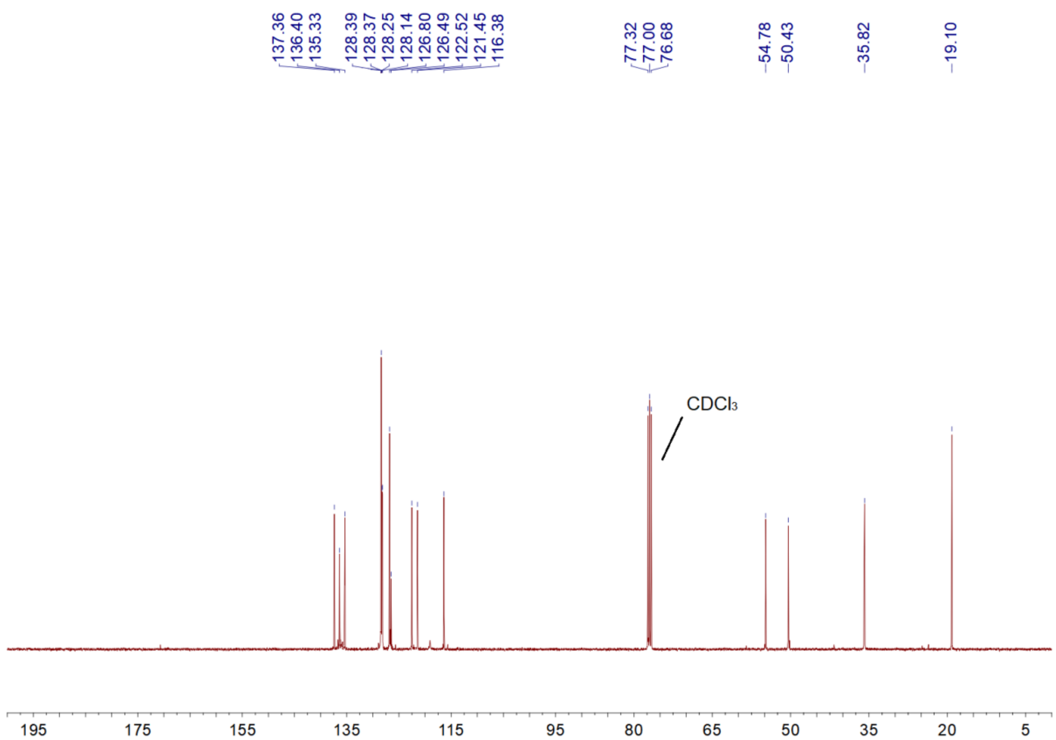
^{1}H-NMR



[H**L4**]Cl

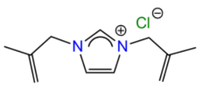


^{13}C-NMR

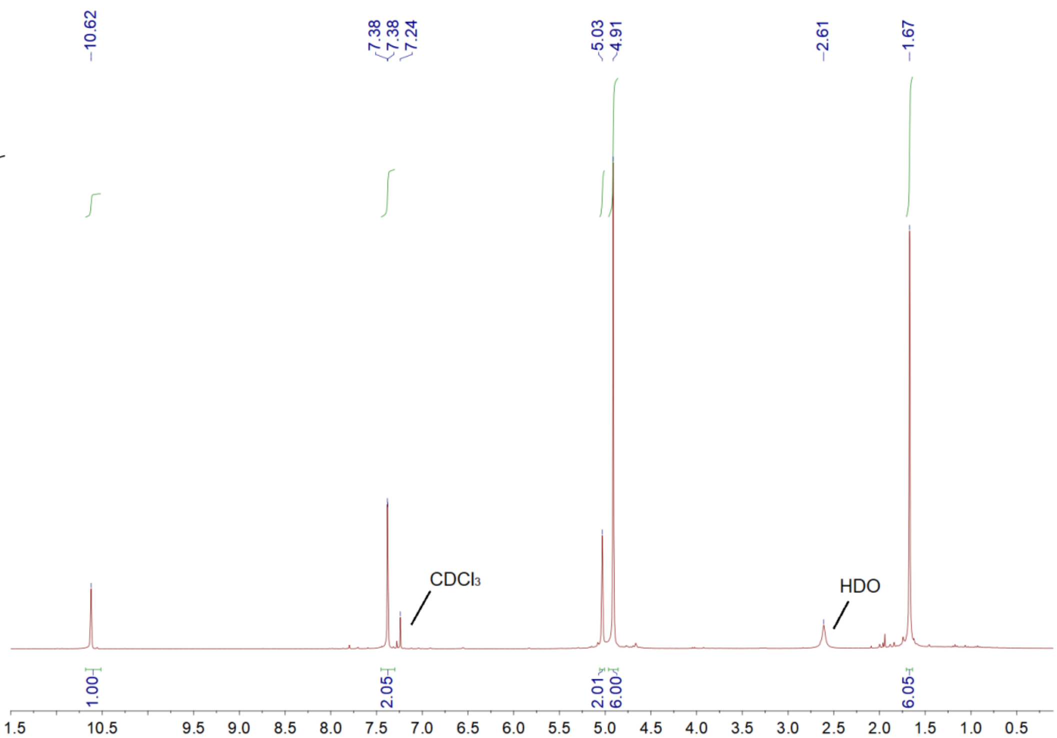


[H**L5**]Cl: Yield: 88%. ^{1}H NMR ($CDCl_3$): δ_H = 1.67 (s, 6H, CH_3), 4.91 (s, 6H, CH_2 + =CH_2), 5.03 (s, 2H, =CH_2), 7.38 (s, 2H, NCH), 10.62 (s, 1H, NCH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ_C = 19.5 (s, CH_3), 19.6 (s, CH_3), 55.4 (s, CH_2), 116.9 (s, =CH_2), 122.0 (s, NCH), 137.9 (s, $C(CH_3)_2$), 138.3 (s, NCN).

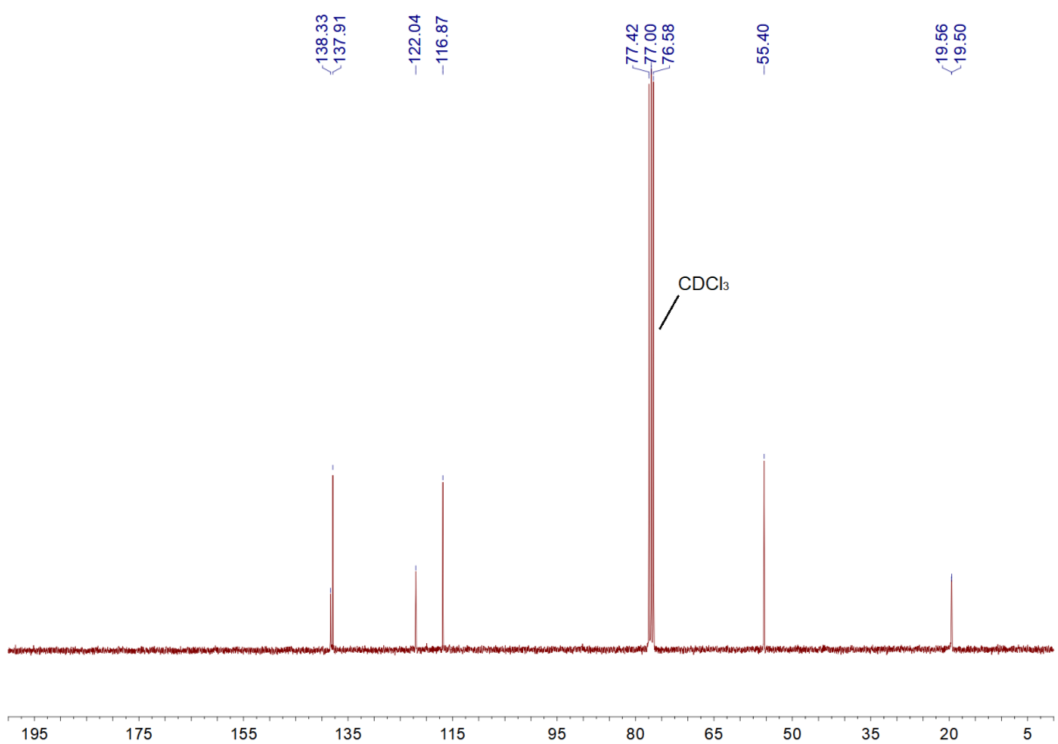
^{1}H-NMR



[H**L5**]Cl

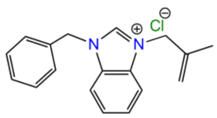


^{13}C-NMR

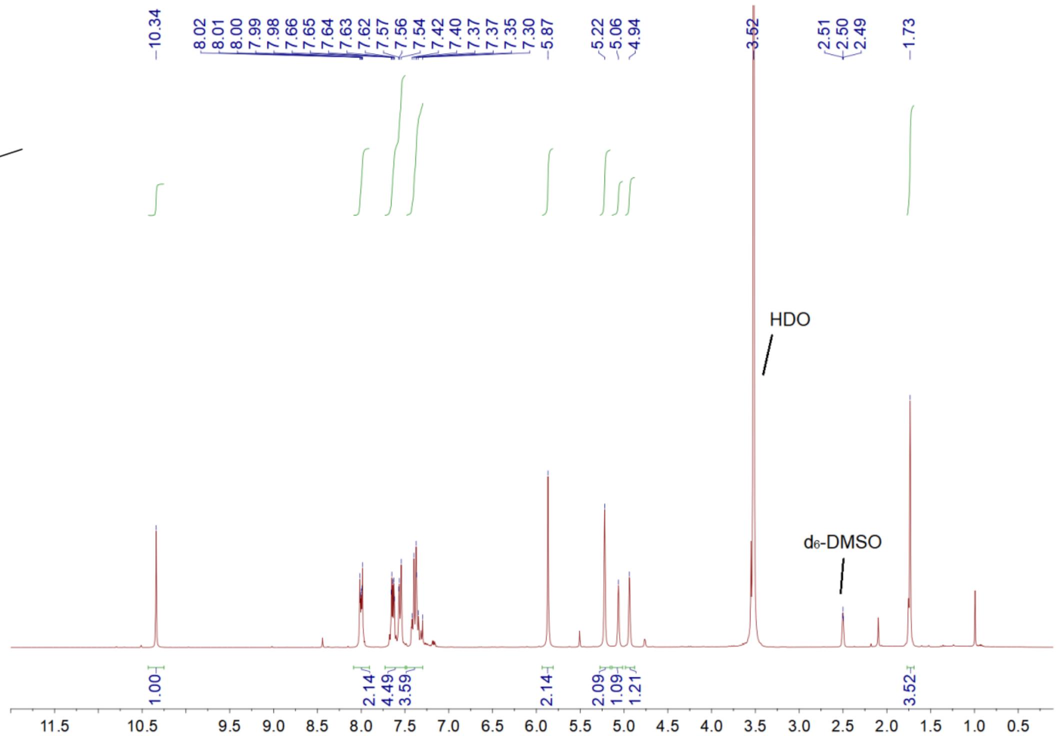


[H**L6**]Cl: Yield: 92%. ^{1}H NMR ($(CD_3)_2SO$): δ_H = 1.73 (s, 3H, CH_3), 4.94 (s, 1H, $=CH_2$), 5.06 (s, 1H, $=CH_2$), 5.22 (s, 2H, NCH_2), 5.87 (s, 2H, NCH_2), 7.30-7.42 (m, 3H, C_6H_4), 7.54-7.66 (m, 4H, C_6H_4 + C_6H_5), 8.00 (m, 2H, C_6H_5), 10.34 (s, 1H, NCHN). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$): δ_C = 19.8 (s, CH_3), 47.8 (s, CH_2), 51.5 (s, CH_2), 110.8 (s, C_6H_4), 119.6 (s, $=CH_2$), 121.8 (s, NCH), 122.6 (s, NCH), 127.5 (s, C_6H_5), 127.8 (s, C_6H_5), 128.8 (s, C_6H_5), 133.7 (s, C_6H_4), 137.0 (s, *ipso* C_6H_5), 143.6 (s, CCH_2), 144.3 (s, NCN).

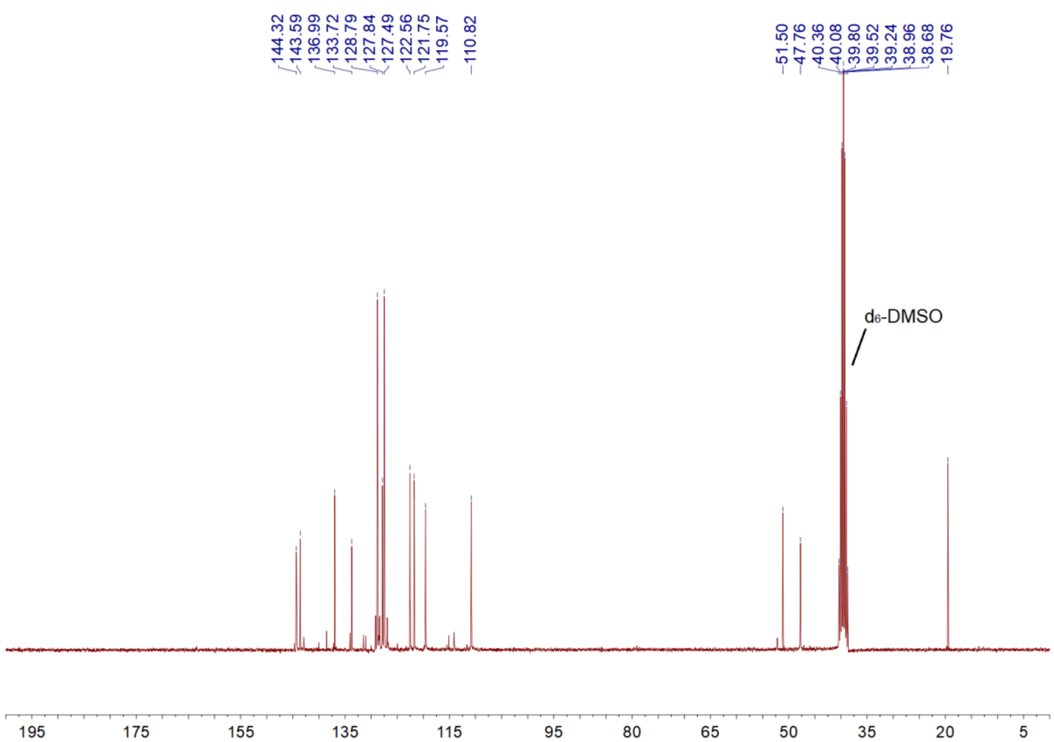
^{1}H-NMR



[H**L6**]Cl



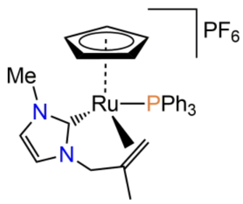
^{13}C-NMR

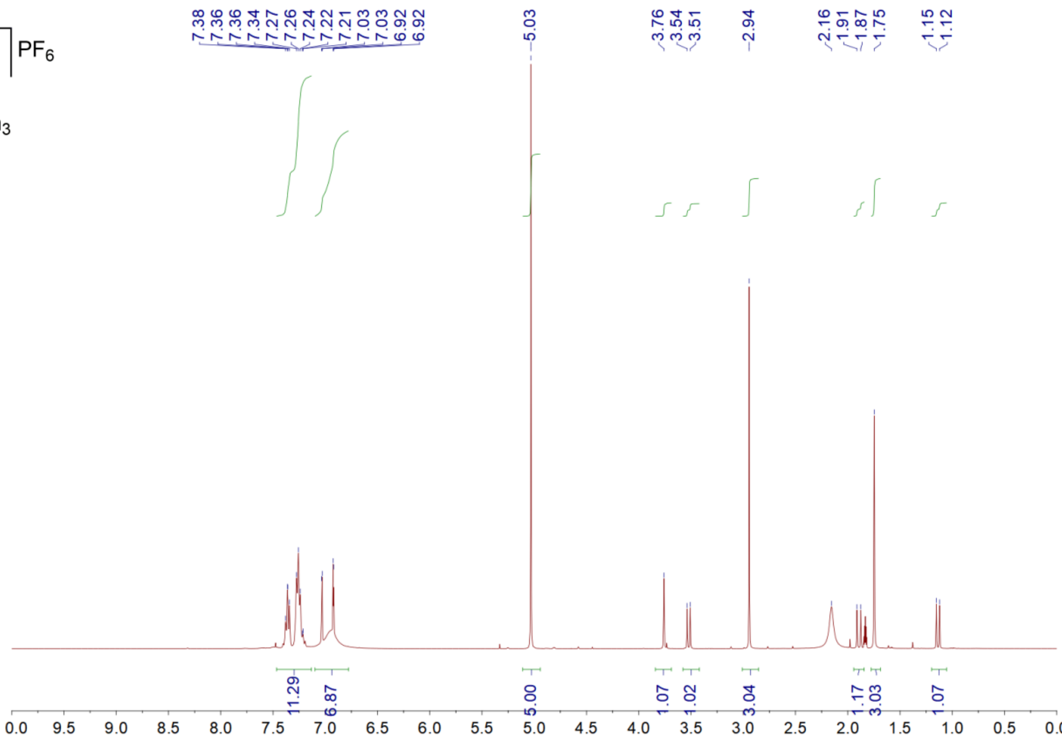


2. ^{1}H-, ^{13}C-, ^{31}P-NMR spectra of **1-9**

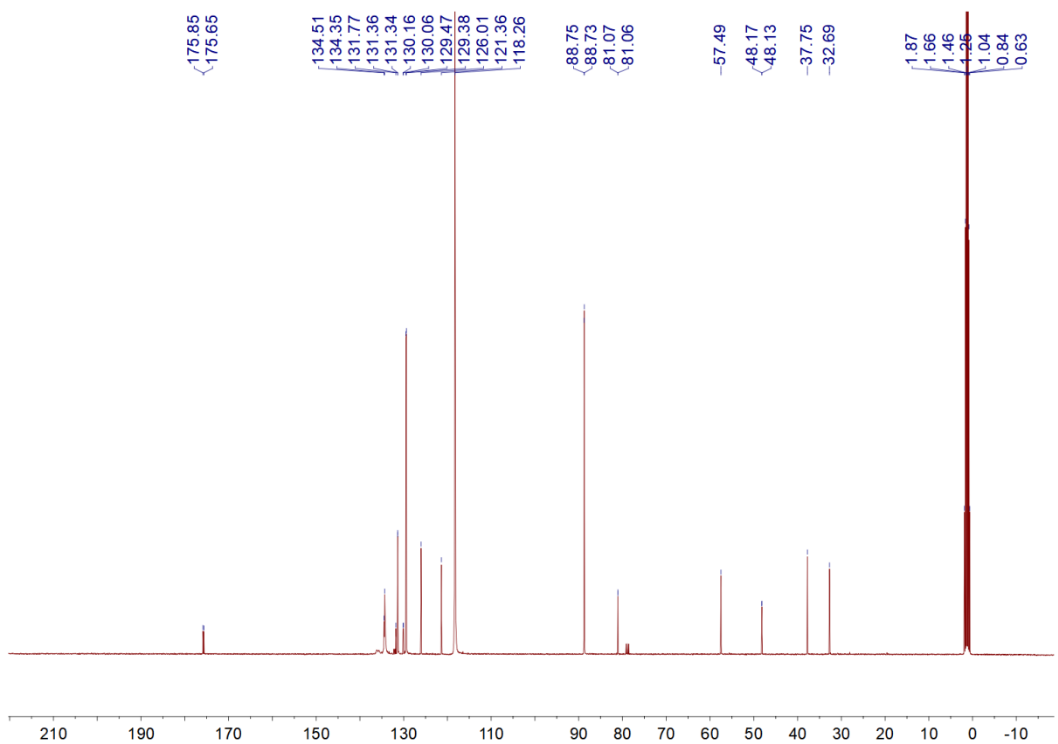
<u>Complex **1**</u>

^{1}H-NMR

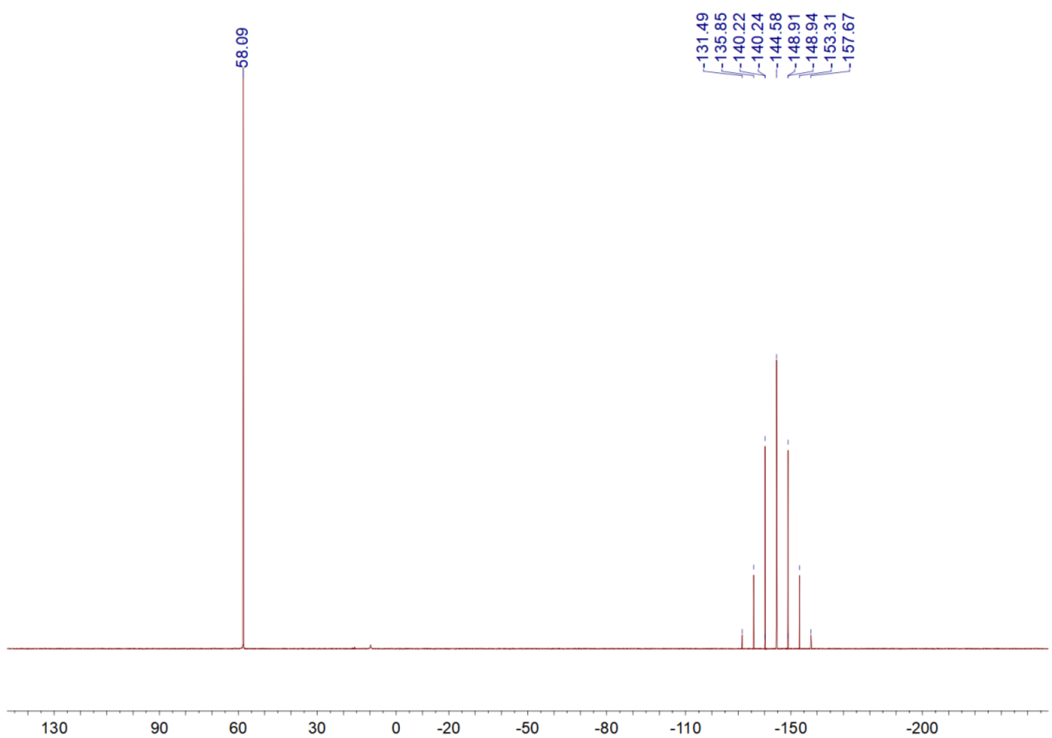




^{13}C-NMR

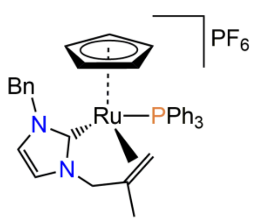


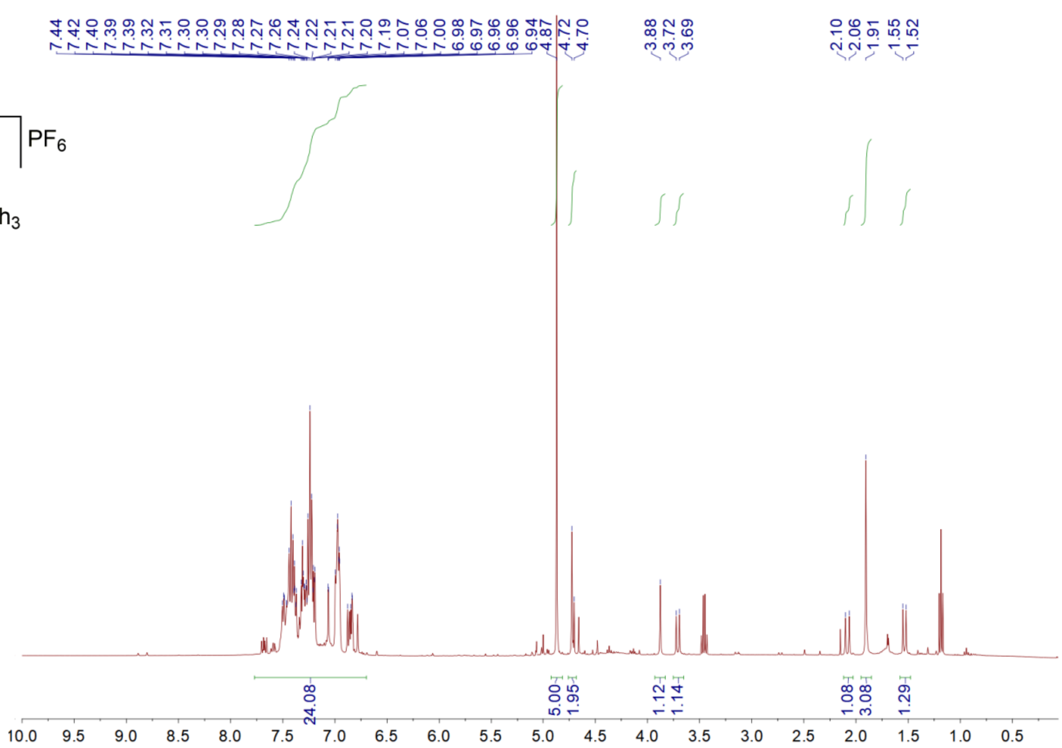
^{31}P-NMR



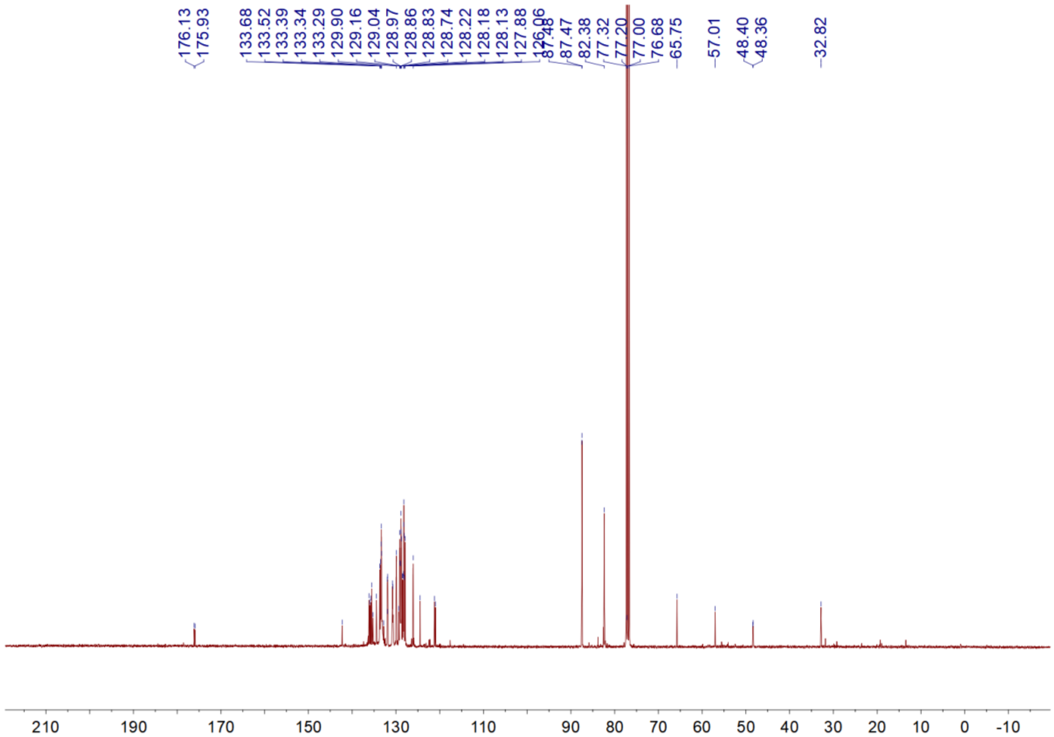
Complex **2**

^{1}H-NMR





^{13}C-NMR



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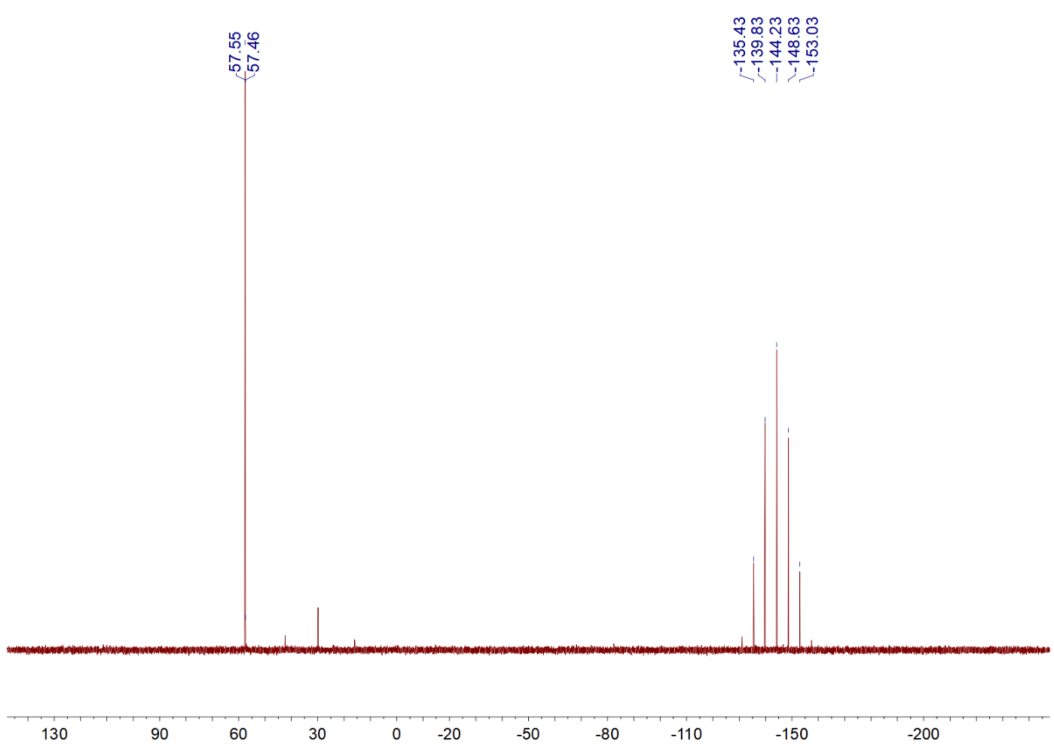
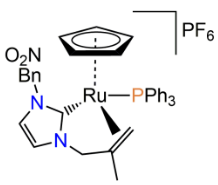
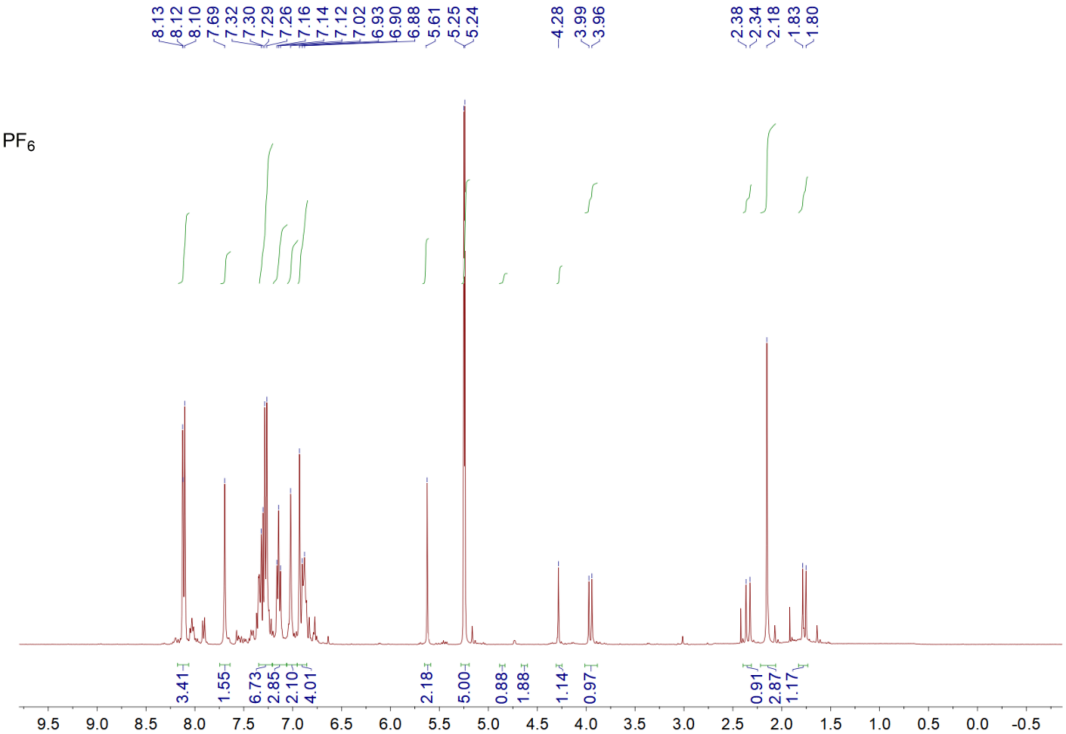


Complex **3**

^{1}H-NMR





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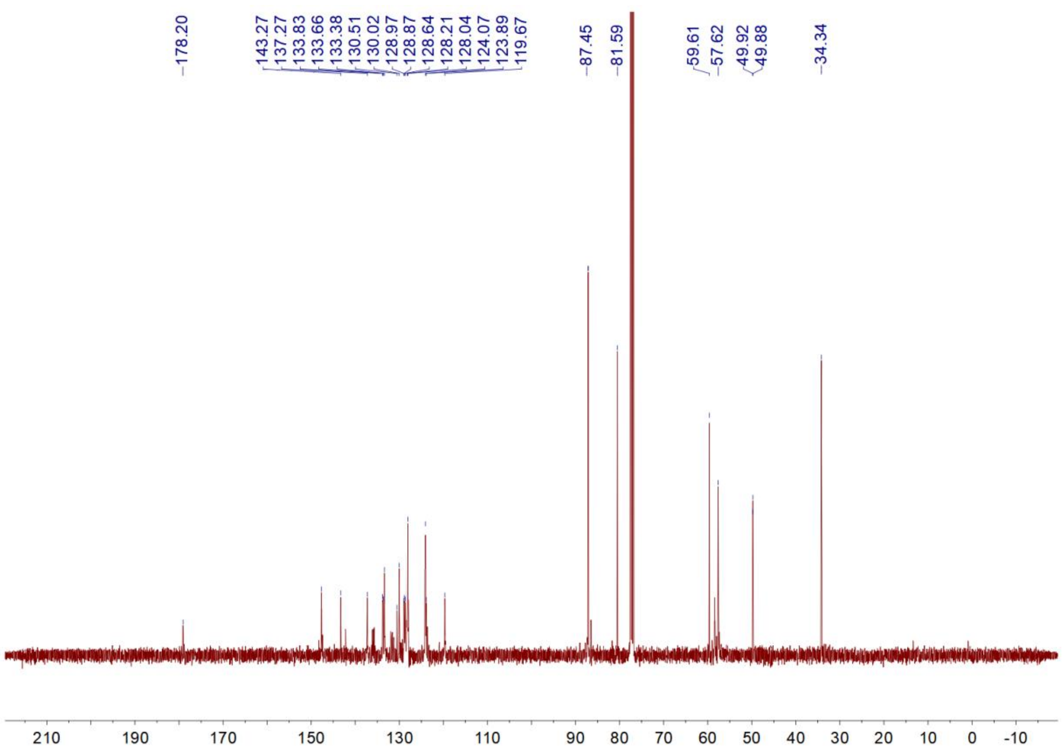

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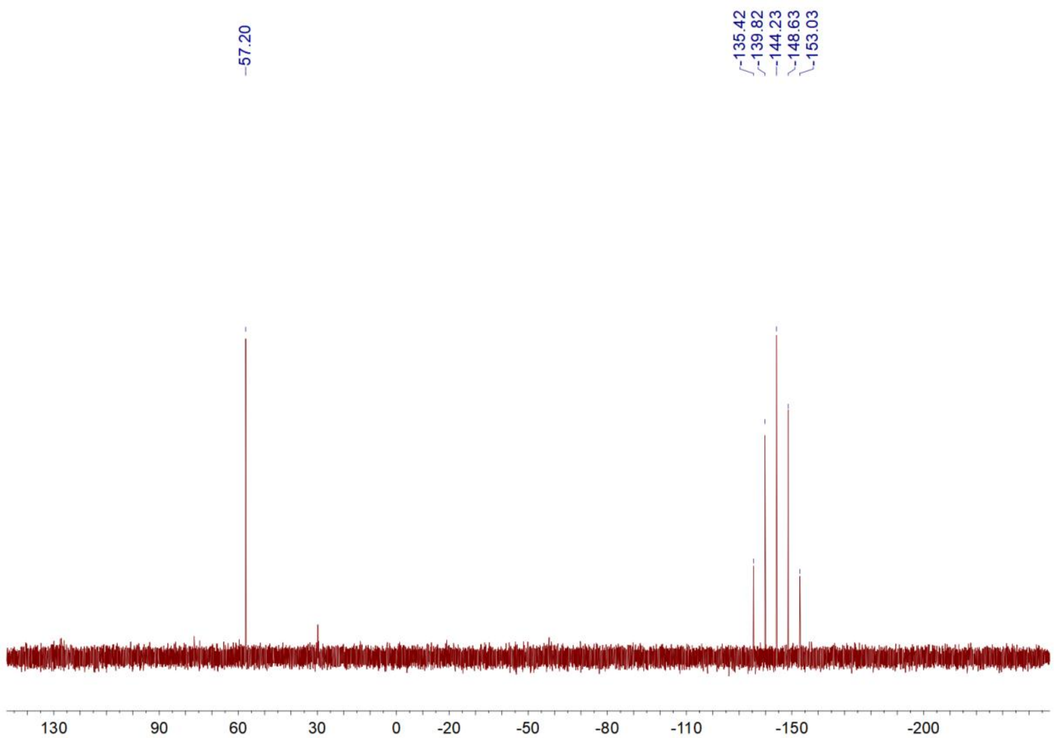
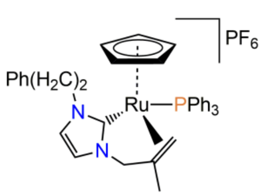
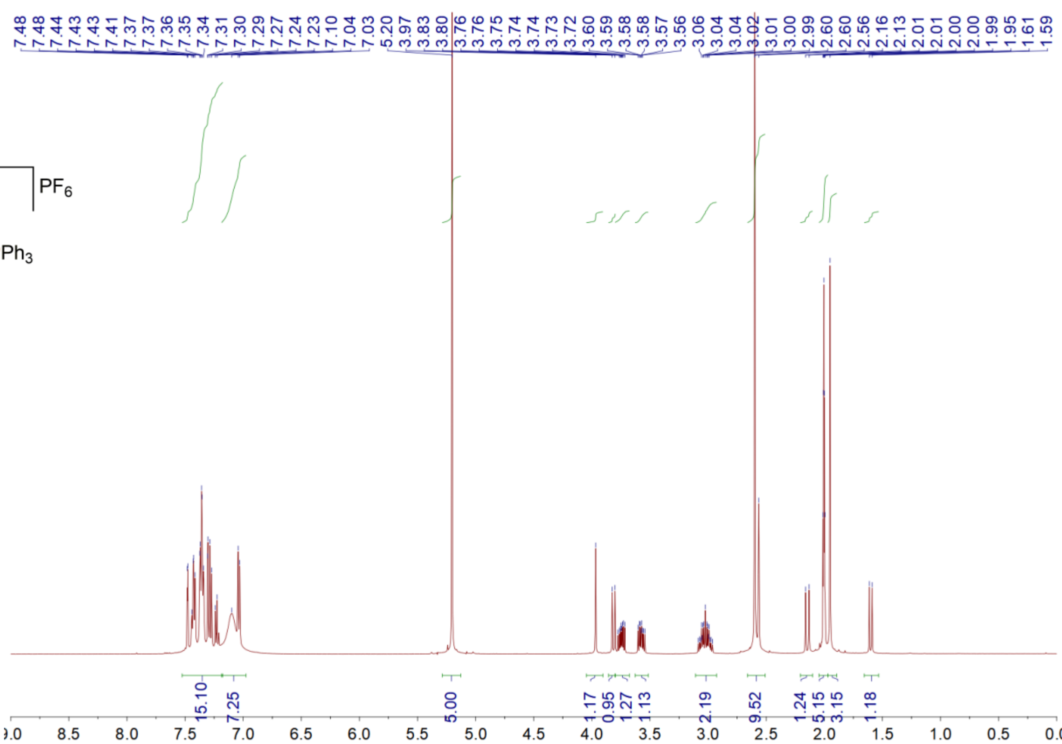


Complex **4**

^{1}H-NMR





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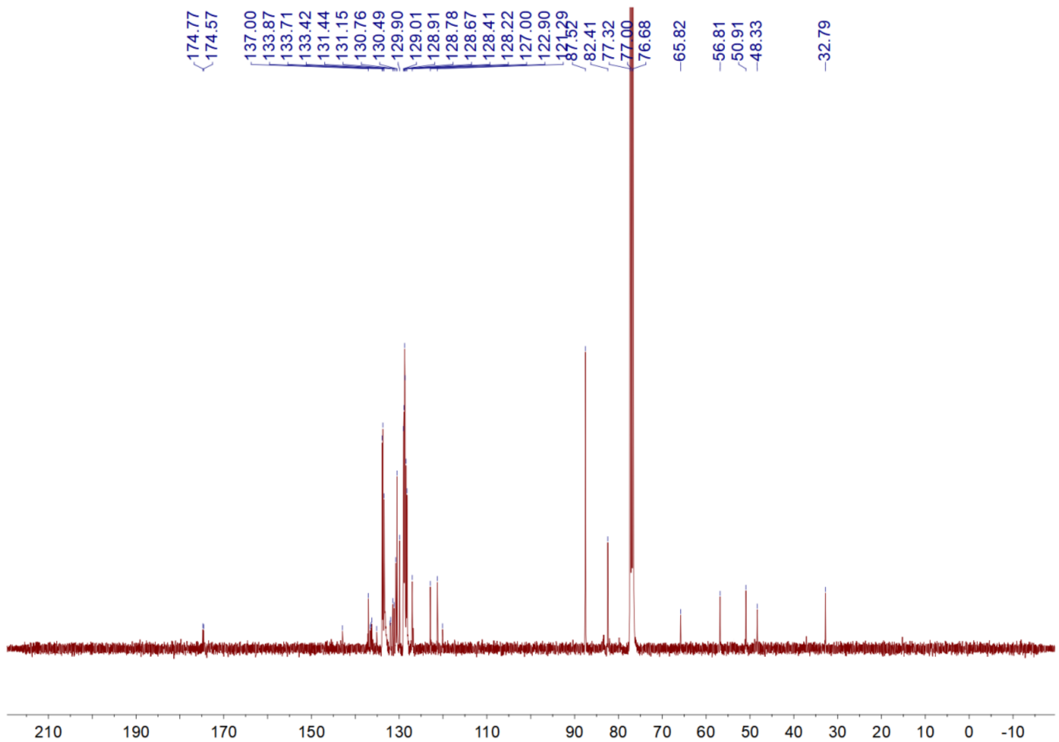

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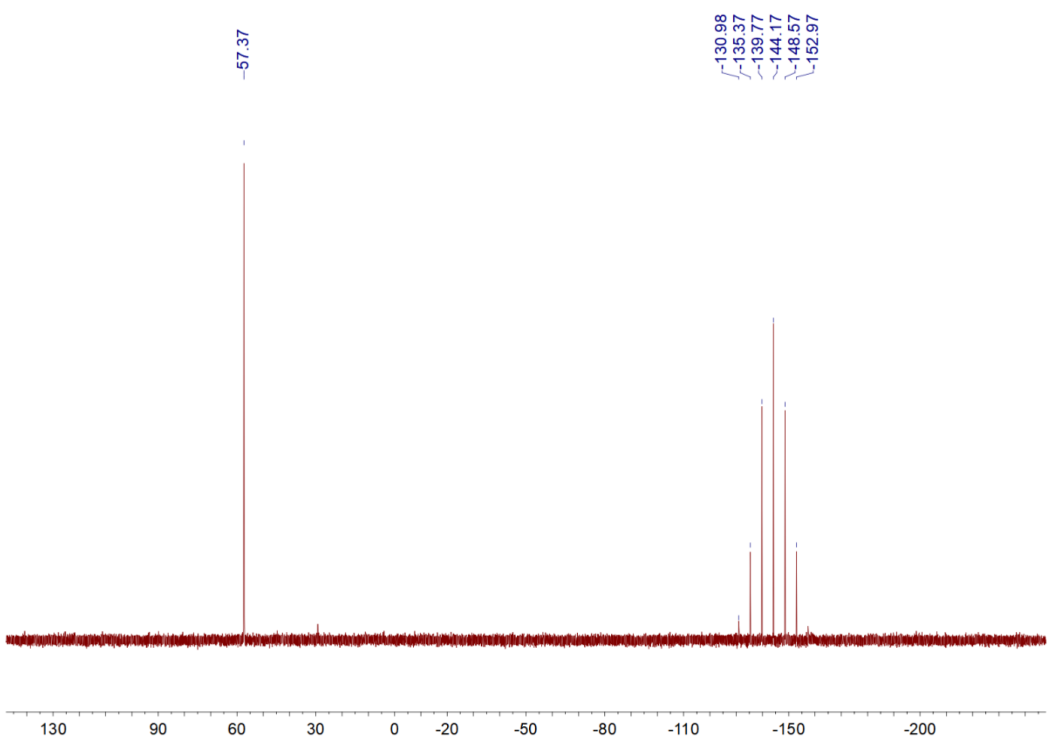
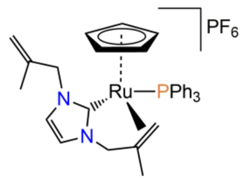
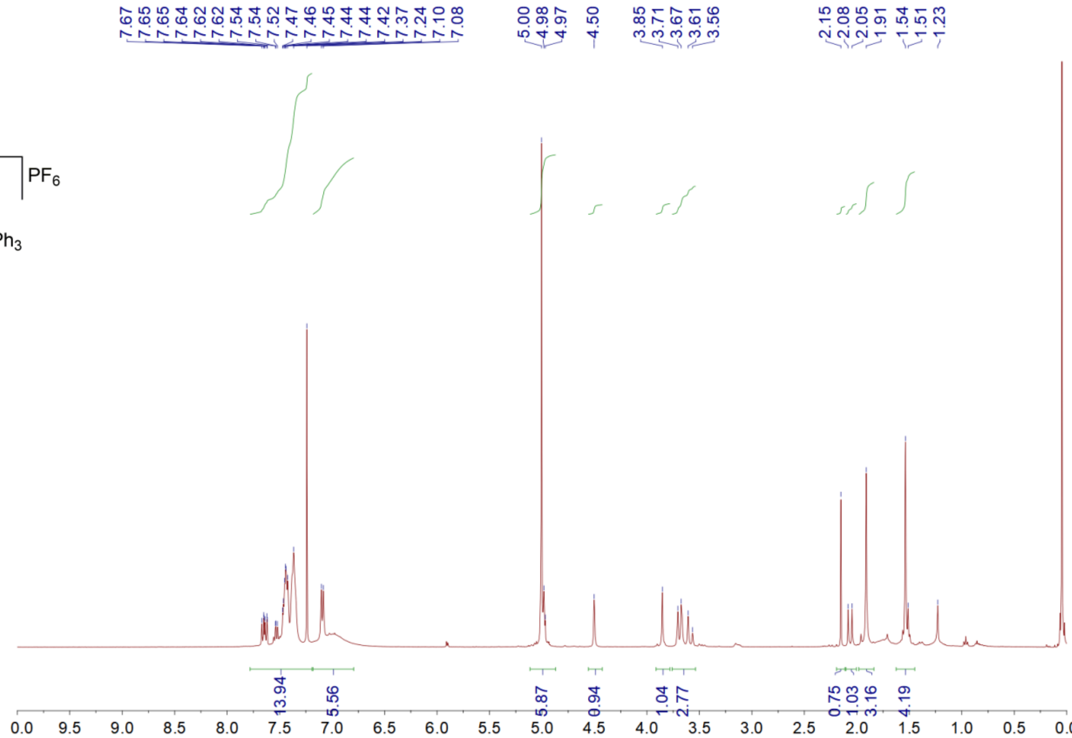


Complex **5**

^{1}H-NMR





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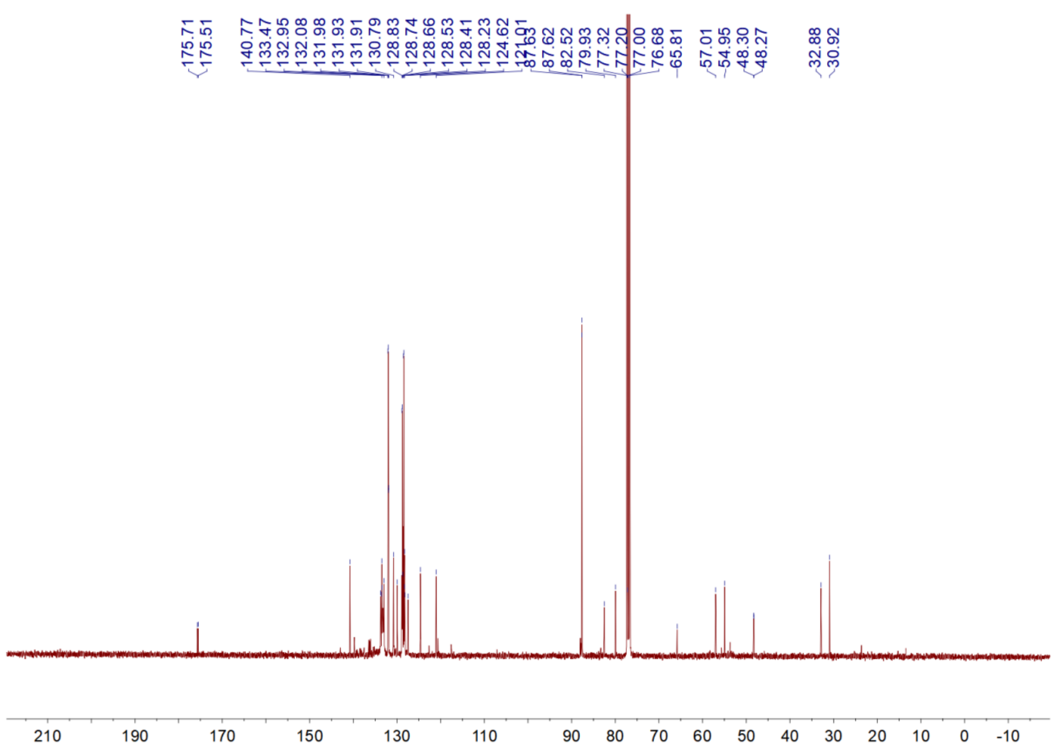

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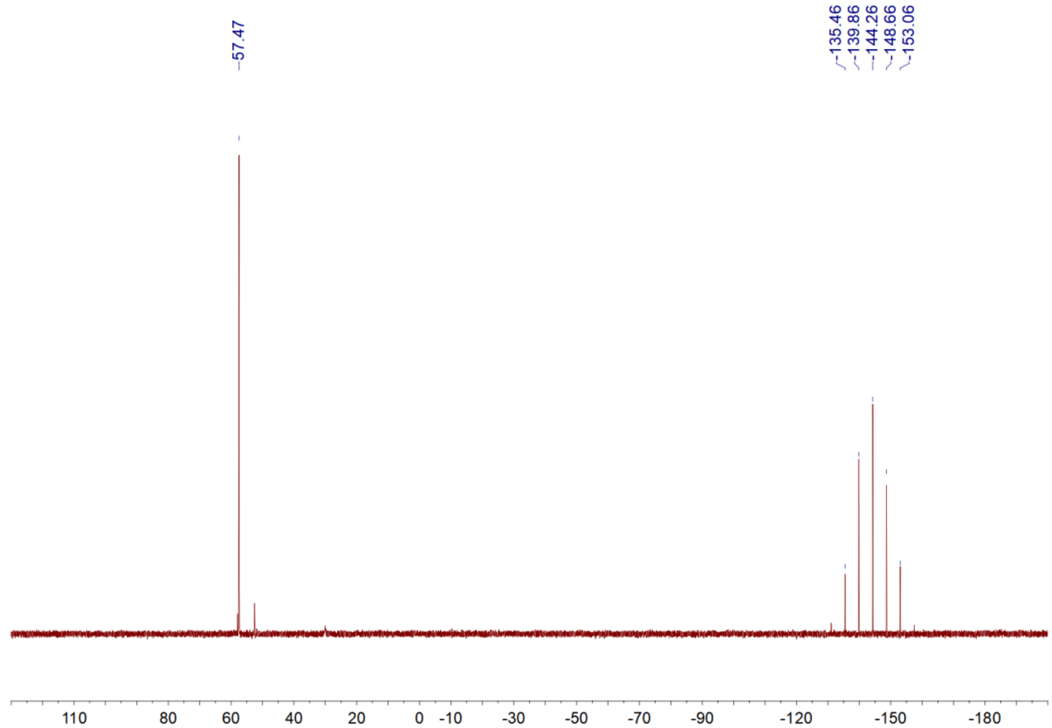
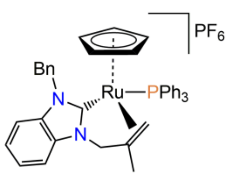
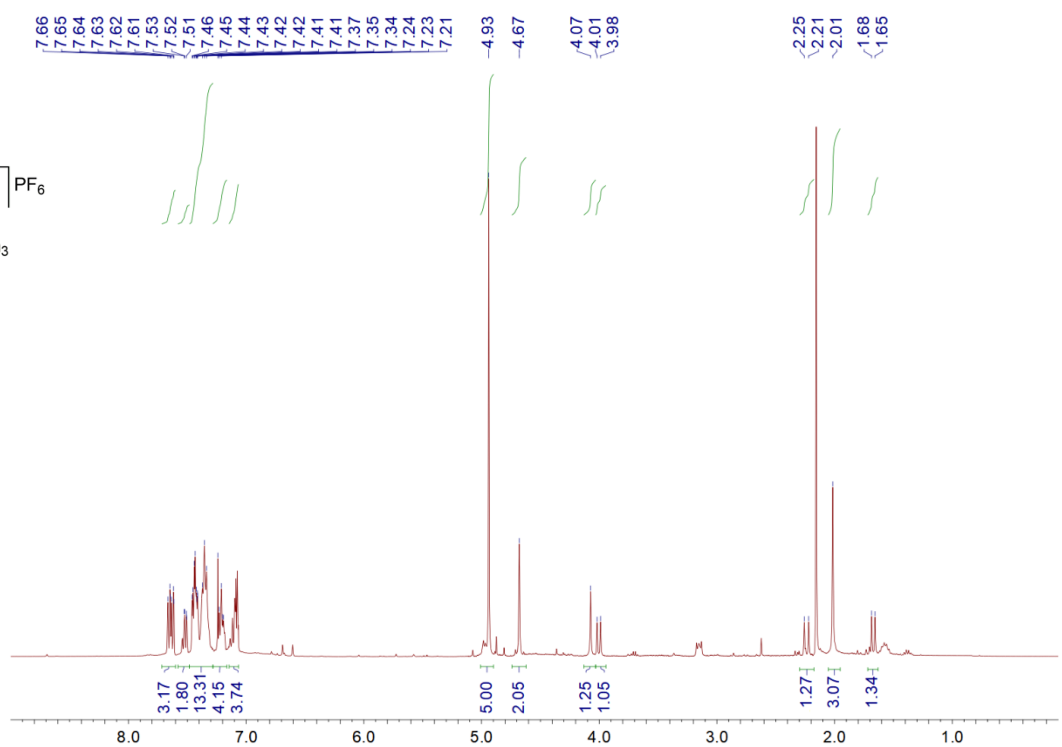


Complex **6**

^{1}H-NMR





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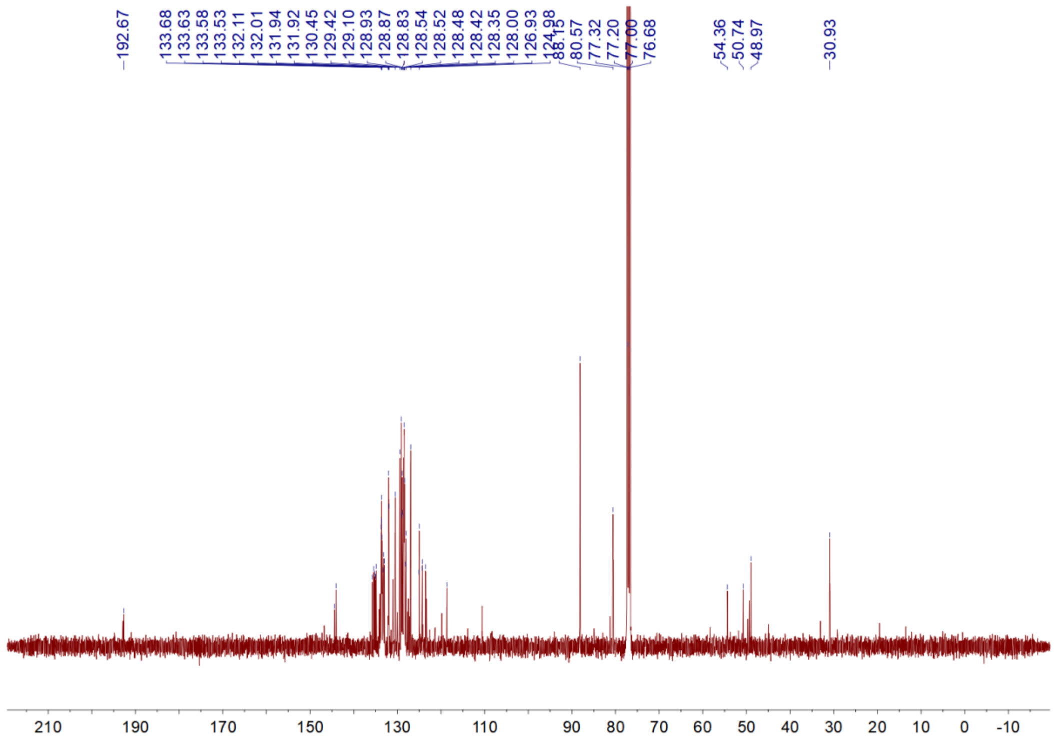

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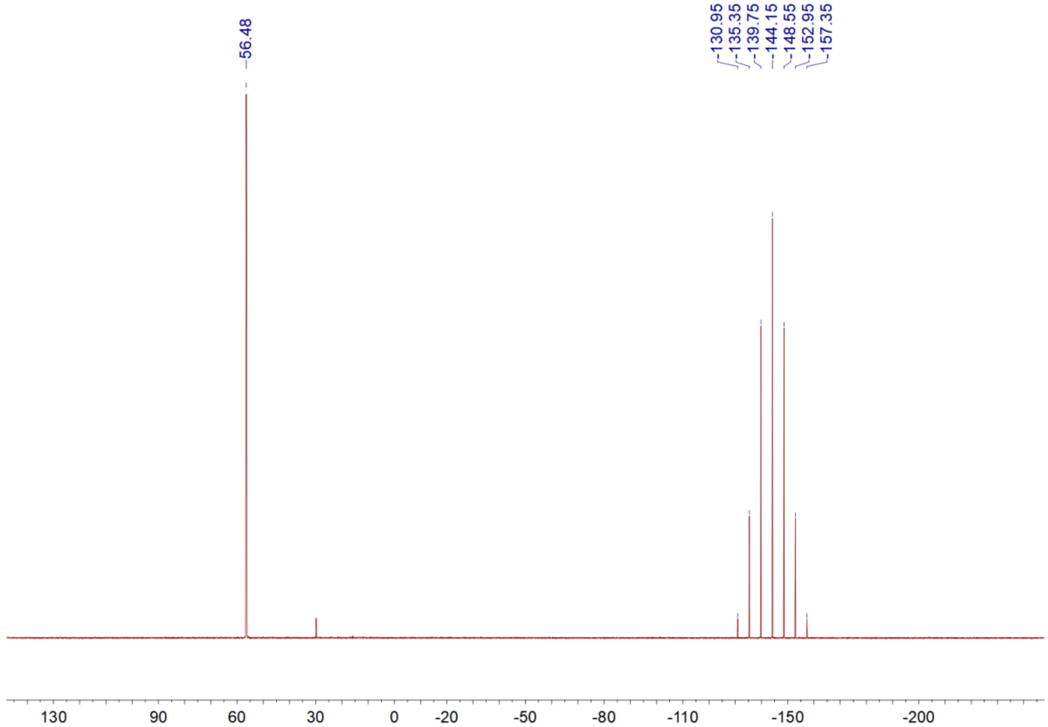
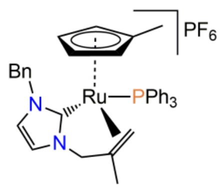
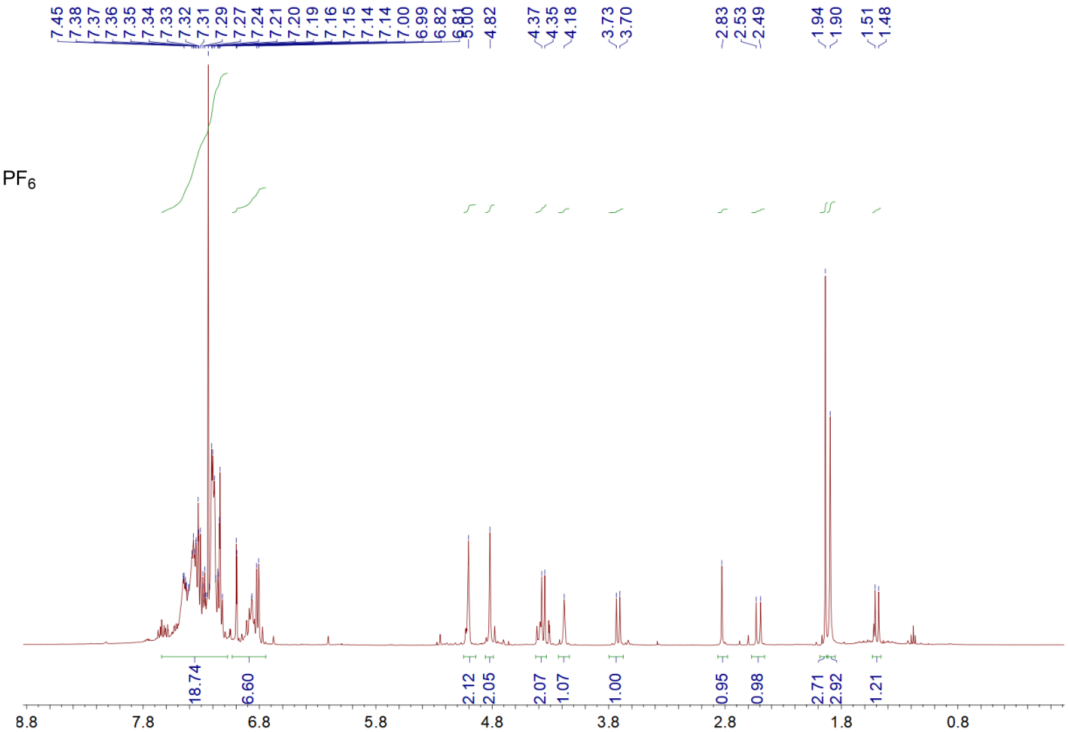


Complex **7**

^{1}H-NMR





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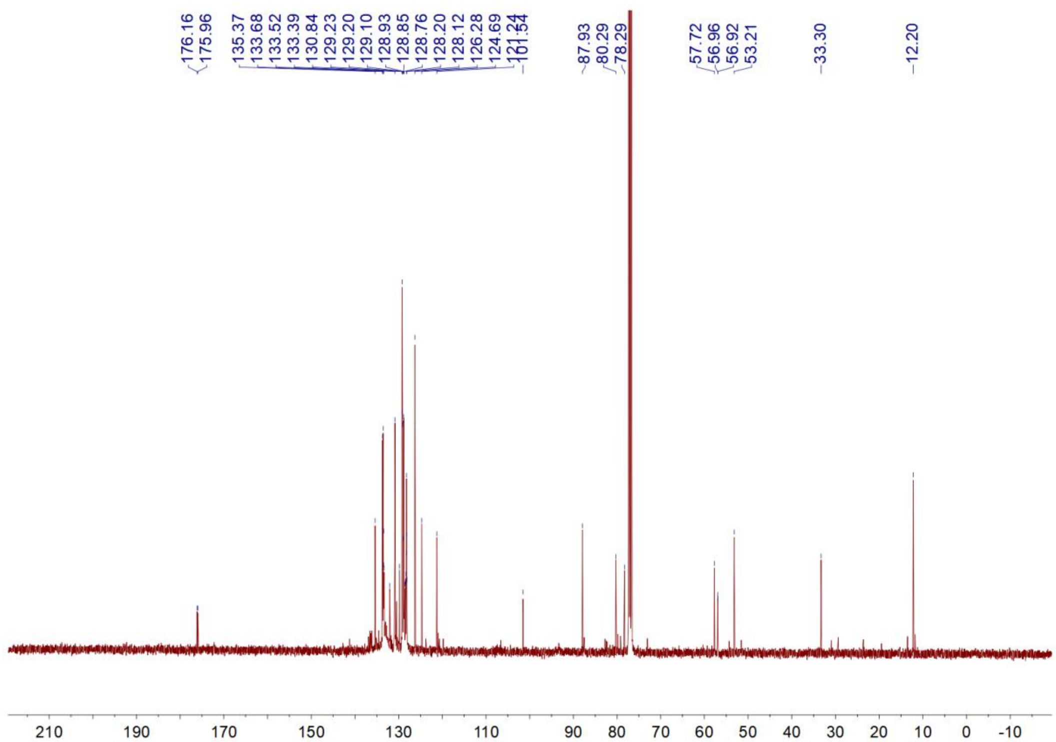

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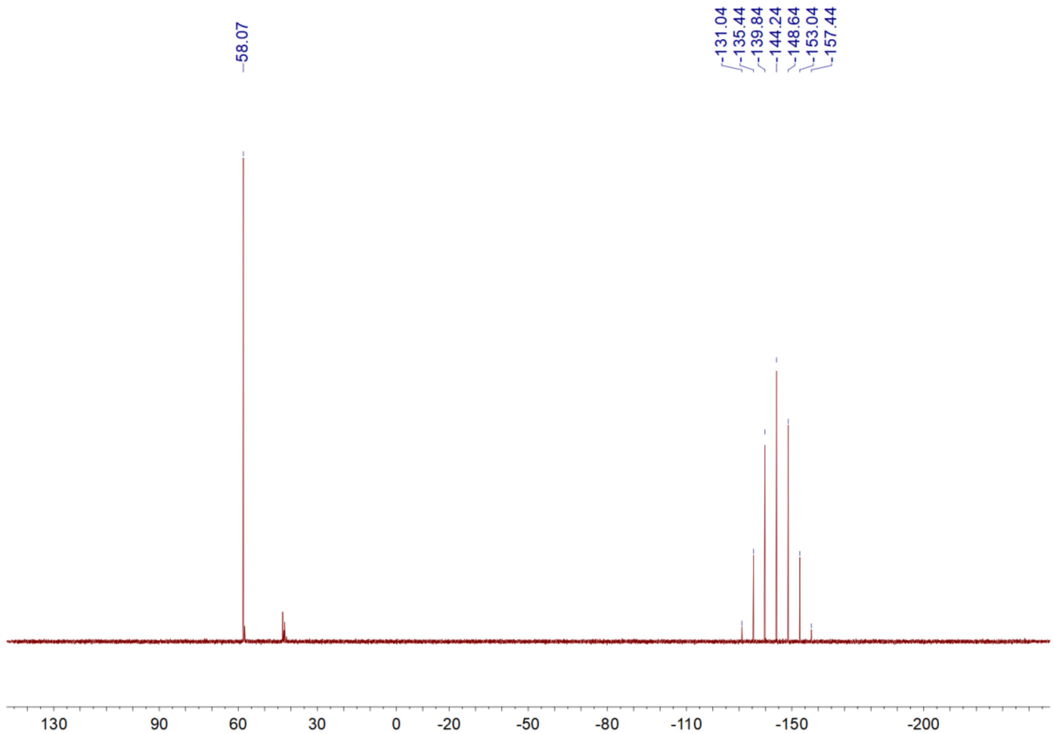
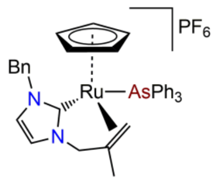
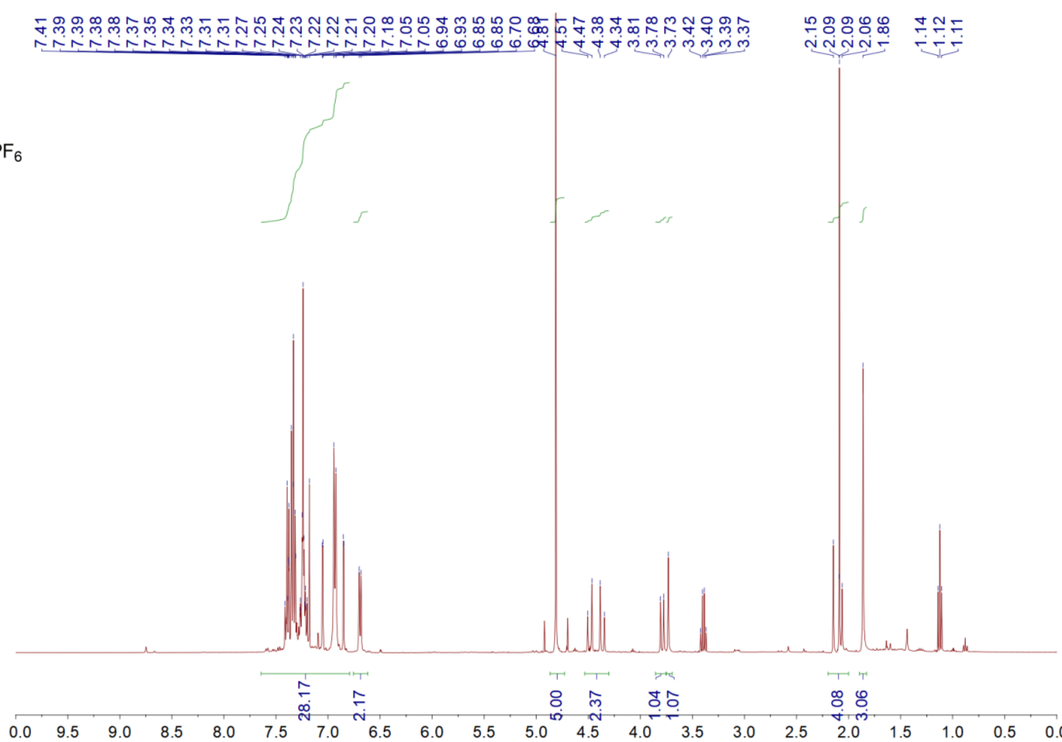


Complex **8**

^{1}H-NMR





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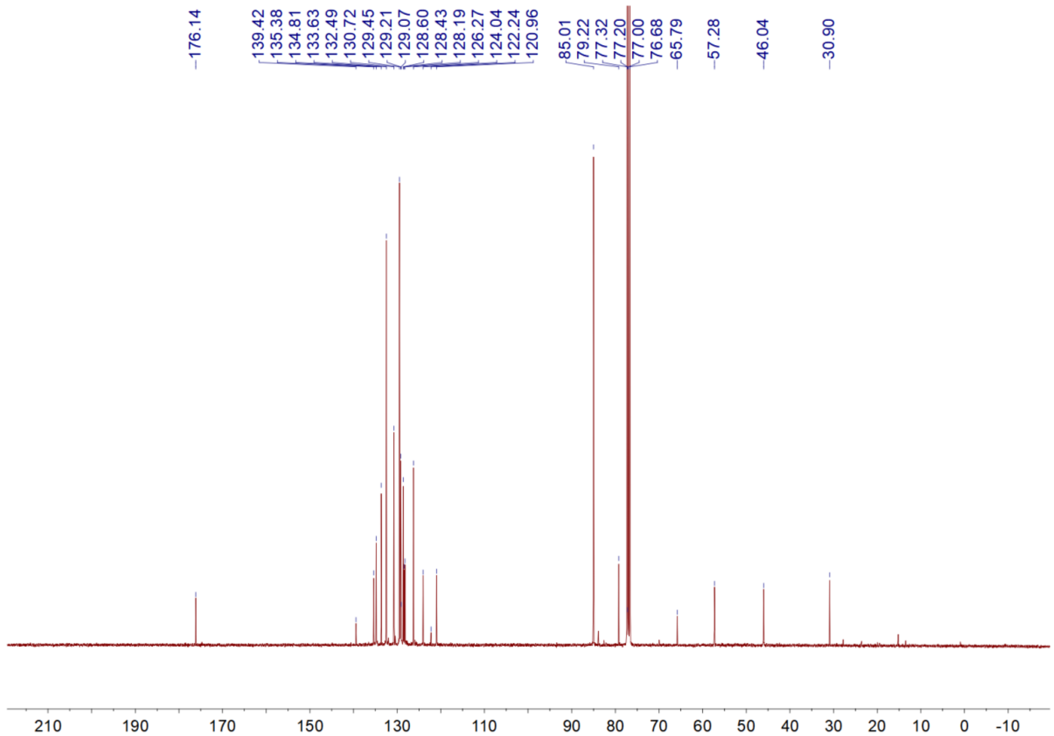

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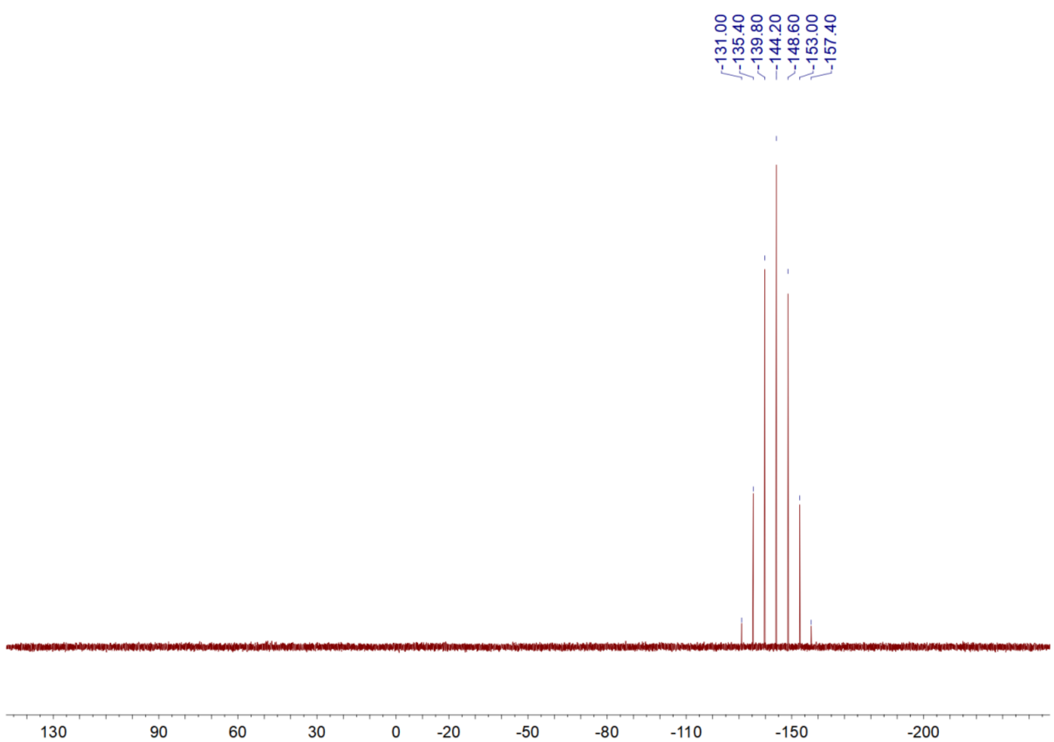
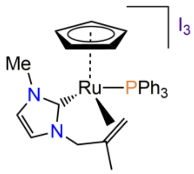
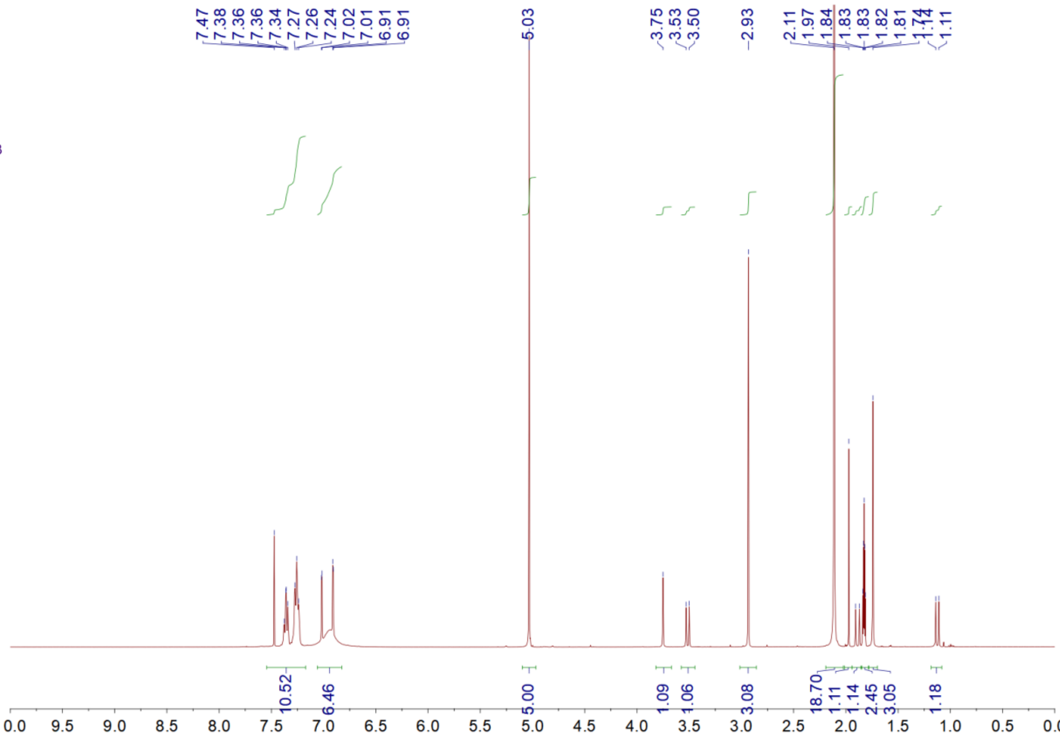


Complex **9**

^{1}H-NMR





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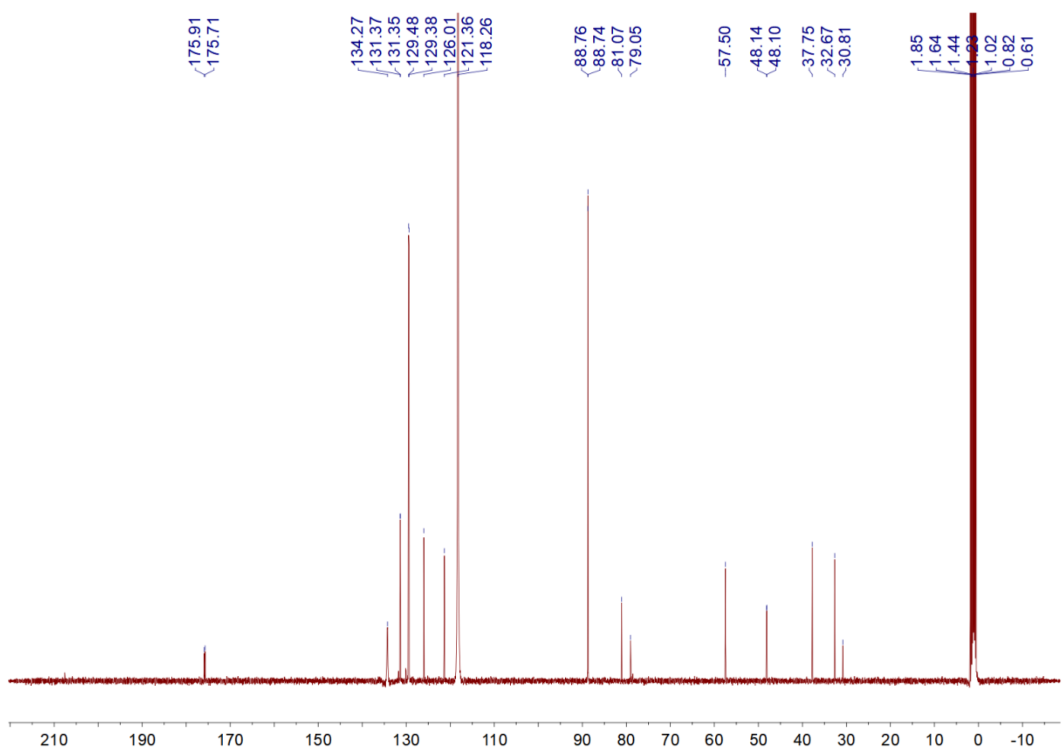
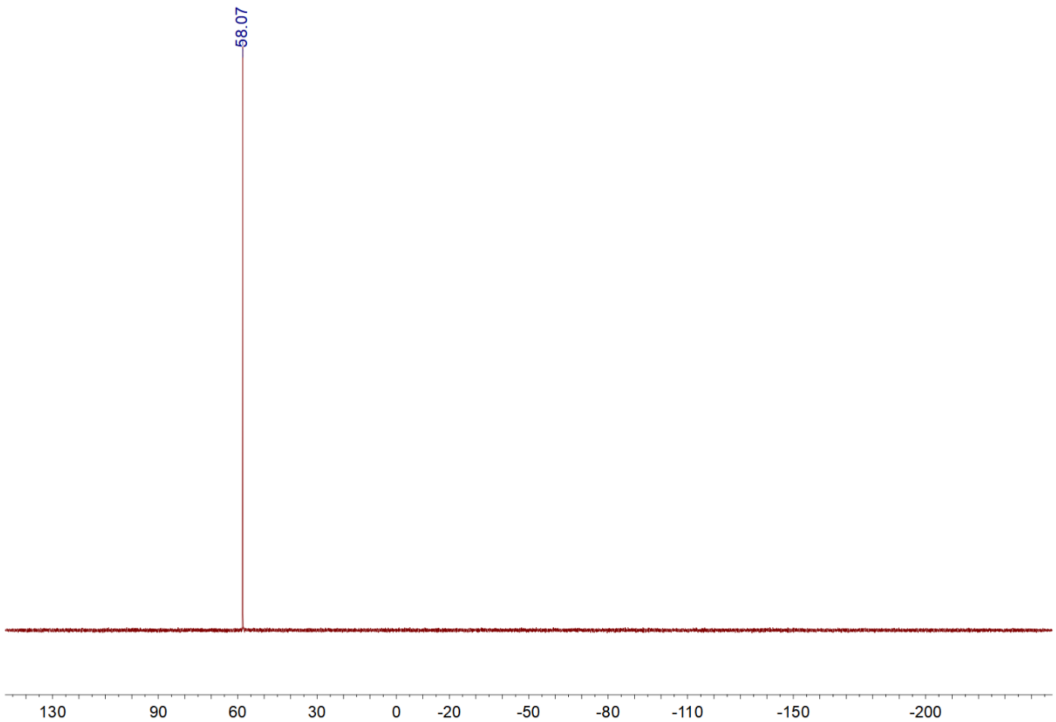
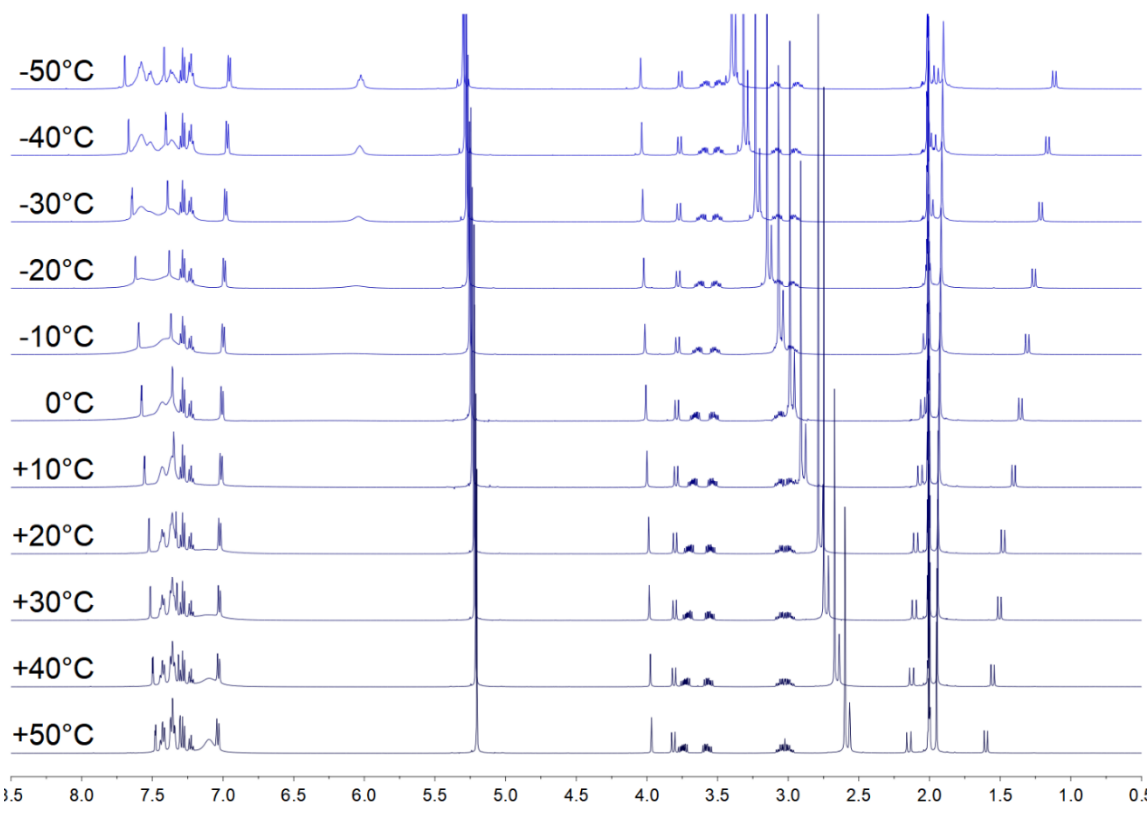


^{31}P-NMR



3. Variable temperature ^{1}H-NMR (400 MHz) spectra (complex **4**). [Solvent = $(CD_3)_2CO$.]



4. Crystal data and structure refinement for [H**L5**]Cl, **P2**,**P3**,**1**,**2**,**4**,**5**,**8** (**Tables S1**,**S2**, **S3**)

Table S1

Complex	[H**L5**]Cl	P2	P3	1
Emp. formula	$C_{14.7}H_{24}N_{2.7}O_{0.7}Cl_{1.3}$	$C_{43}H_{39}Cl_3P_2Ru$	$C_{42}H_{37}Cl_3As_2Ru$	$C_{31}H_{32}N_2F_6P_2Ru$
Form. wt. (g.mol^{-1})	295.64	740.17	898.97	709.59
Crystal system	orthorhombic	triclinic	triclinic	monoclinic
Space group	*Pbcn*	*P-1*	*P-1*	*P2₁/c*
Crystal descr.	colourless blade	yellow block	orange block	yellow plate
a (Å)	16.1278(8)	9.8196(2)	9.931(7)	16.2788(2)
b (Å)	12.2682(5)	14.155(3)	14.018(1)	9.1026(9)
c (Å)	12.5817(6)	14.978(3)	14.536(1)	19.875(2)
α (°)	90	73.264(8)	102.99(2)	90
β (°)	90	71.924(7)	104.958(2)	96.086(3)
γ (°)	90	78.353(7)	98.90(2)	90
Volume (Å^3)	2489.4(2)	1880.8(6)	1856.0(2)	2928.5(5)
Z	6	2	2	4
Abs. coeff. (m.mm^{-1})	0.280	0.600	2.438	0.708
F(000)	953.5	760.0	900.0	1440.0
Independent refl.	2565	7775	9240	6046
Completeness (%)	99.9	99.2	99.6	99.6
Data/Restr/Para	2565/0/138	7775/0/443	9240/0/433	6046/0/381
Goodness of fit on F^2	1.034	0.963	1.037	1.045
Final R$_1$ indexes	0.0376	0.0318	0.0264	0.0307
wR$_2$ indices (all data)	0.1331	0.1153	0.0524	0.0666
Largest diffr. peak and hole (e.Å^{-3})	0.31/-0.32	1.25/-0.97	0.47/-0.63	1.83/-1.02

Table S2

Complex	2	4	5	8
Emp. formula	$C_{38}H_{38}N_2F_6P_2Cl_2Ru$	$C_{38}H_{38}N_2F_6P_2Ru$	$C_{34}H_{36}N_2F_6P_2Ru$	$C_{150}H_{148}N_8F_{24}P_4As_4Cl_4Ru$
Form. wt. g.mol^{-1})	870.61	799.71	749.66	3488.51
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	*P2₁/n*	*P-1*	*C2/c*	*P2₁*
Crystal descr.	yellow block	yellow needle	yellow block	yellow block
a (Å)	13.8600(6)	11.0881(7)	18.0319(9)	9.910(2)
b (Å)	13.9831(7)	13.1574(8)	13.2824(6)	24.910(5)
c (Å)	18.9389(9)	14.6115(8)	29.0663(1)	15.236(3)
α (°)	90	113.867(2)	90	90
β (°)	93.545(2)	95.538(2)	99.842(2)	108.51(3)
γ (°)	90	111.568(2)	90	90
Volume (Å^3)	3663.4(3)	1735.89(2)	6859.1(6)	3566.6(1)
Z	4	2	8	1
Abs. coeff. (m.mm^{-1})	0.723	0.607	0.609	1.542
F(000)	1768.0	816.0	3056.0	1753.0
Independent refl.	7590	7167	7046	14652
Completeness (%)	99.7	99.9	99.8	99.7
Data/Restr/Para	7590/0/461	7167/0/443	7046/0/408	14652/1/905
Goodness of fit on F^2	1.535	1.096	1.132	0.843
Final R$_1$ indexes	0.0532	0.0367	0.0351	0.0289
wR$_2$ indices (all data)	0.1895	0.1288	0.0842	0.0637
Largest diffr. peak and hole (e.Å^{-3})	1.98/-1.82	1.08/-0.87	0.73/-0.80	0.63/-0.54

Table S3

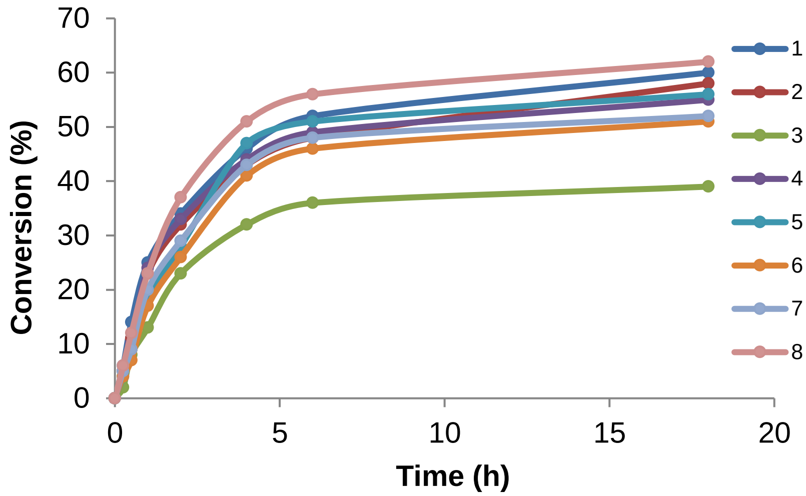
Complex	9
Emp. formula	$C_{15.5}H_{16}NP_{0.5}I_{1.5}Ru_{0.5}$
Form. weight (g.mol^{-1})	472.66
Crystal system	triclinic
Space group	*P-1*
Crystal descr.	yellow block
a (Å)	9.4358(2)
b (Å)	9.7889(2)
c (Å)	18.948(4)
α (°)	91.365(6)
β (°)	94.352(6)
γ (°)	114.451(5)
Volume (Å^3)	1585.6(5)
Z	4
Abs. coeff. (m.mm^{-1})	3.488
F(000)	900.0
Independent refl.	6706
Completeness (%)	98.4
Data/Restr/Para	6706/0/348
Goodness of fit on F^2	1.047
Final R$_1$ indexes	0.0218
wR$_2$ indices (all data)	0.0467
Largest diffr. peak and hole (e.Å^{-3})	1.31/-1.27

5. **Table S4:** Selected bond lengths and angles for [H**L5**]Cl, **P2**,**P3**,**1**,**2**,**4**,**5**,**8**,**9**

Description	[H**L5**]Cl	**P2**	**P3**	**1**	**2**	**4**	**5**	**8**	**9**
Ru1-C2	-	-	-	2.033(2)	2.042(4)	2.040(3)	2.038(3)	2.035(4)	2.033(3)
Ru1-Cg[a]	-	1.844(3)	1.813(4)	1.899(3)	1.894(3)	1.892(4)	1.889(6)	1.874(6)	1.907(7)
Ru-E1[b]	-	2.3222(7)	2.4229(2)	2.3262(6)	2.2993(1)	2.3135(7)	2.3168(6)	2.4190(7)	2.3155(8)
Ru1-C2-N1	-	-	-	120.23(2)	119.90(3)	119.95(2)	119.60(2)	119.7(3)	120.81(2)
C2-Ru1-E1[b]	-	-	-	87.32(7)	88.98(1)	86.84(7)	87.19(7)	85.92(1)	87.51(7)
E1-Ru1-Ca[b,c]	-	-	-	93.99(7)	95.33(1)	95.34(7)	96.08(8)	94.50(9)	93.14(7)
C2-Ru1-Ca[c]	-	-	-	89.65(1)	89.58(1)	89.71(1)	89.66(1)	89.38(2)	89.38(1)
C2-N1-C4	125.22(1)			130.7(2)	118.0(3)	129.6(2)	118.4(2)	118.8(3)	117.6(2)
C2-N2-C8	126.14(2)	-	-	126.30(2)	127.00(3)	125.8(2)	126.4(2)	125.5(3)	126.1(2)
C2-N1-C4-C5	104.65(2)	-	-	28.3(3)	26.6(5)	24.7(3)	27.5(3)	-22.6(7)	-26.8(3)
C2-N2-C8-C9	-68.92(2)	-	-	-	-91.4(5)	-104.4(3)	-99.9(3)	100.9(7)	-

[a] Cg = centroid of arene/cyclopentadienyl moiety. [b] E = P (1-7), As (8). [c] Average position between two carbon atoms belonging to the alkene moiety.

6. Time-resolved conversion profiles in the transfer hydrogenation-epoxidation catalysis



General conditions: 4'-bromophenylphenacylbromide (BPAB, 0.6 mmol), iPrOH (4 mL), KO^{t}Bu (1.2 eq.), [Ru] (2 mol%), 110 °C. Determined by ^{1}H-NMR, based on the average of at least two runs.

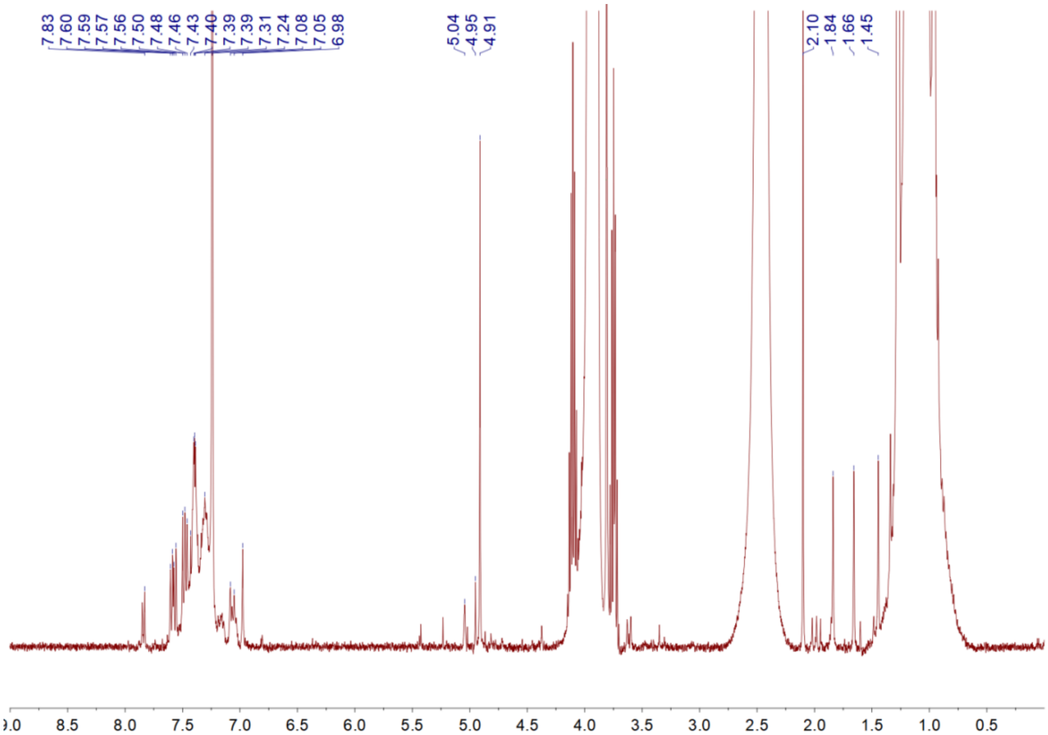
7. Optimization of transfer hydrogenation-epoxidation conditions (**Table S5**)

Table S5: Optimization of transfer hydrogenation-epoxidation conditions.

Entry	Complex	Temp (ºC)	Base	Conversion[a] (%) 2h	6h	18h	Selectivity[b] (%)
1	**-**	110	-	0	1	2	0:0:100
2	**-**	110	KO^{t}Bu	0	2	3	0:0:100
3	**1**	110	KOH	19	31	38	49:51:0
4	**1**[c]	110	KOH	20	36	41	90:3:7
5	**1** (3 mol%)	110	KO^{t}Bu	37	55	63	29:71:0
6	**1** (1 mol%)	110	KO^{t}Bu	21	37	43	47:53:0
7	**1**	110	KOH	26	44	49	43:57:0
8	**1**	25	KOH	7	8	9	89:11:0

General conditions: 4'-bromophenylphenacylbromide (BPAB, 0.6 mmol), iPrOH (4 mL), base (1.2 eq.), [Ru] (2 mol%), 110 °C. [a] Determined by ^{1}H-NMR, based on the average of at least two runs. [b] Selectivity (A:E:O) = alcohol:epoxide:other, after 18 hours. [c] Two equivalents of base used.

8. ^{1}H-NMR spectrum of catalysis reaction mixture



General conditions: 4'-bromophenylphenacylbromide (BPAB, 0.6 mmol), ^{i}PrOH (4 mL), KO^{t}Bu (1.2 eq.), [**1**] (2 mol%), anisole (0.6 mmol), 110 °C. Aliquot taken after 6 hours reaction time analysed using $CDCl_3$.