Supporting Material

Novel ruthenium complexes bearing bipyridine-based and *N*-heterocyclic carbene-supported pyridine (NCN) ligands: The influence of ligands for catalytic transfer hydrogenation of ketones

Akkharadet Piyasaengthong[a,b],* Luke J. Williams,[a] Dmitri S. Yufit[a], James W. Walton [a,]*

[a]*Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, United Kingdom*

[b] *Bioscience program, Faculty of Science, Kasetsart University, Chatuchak, Bangkok 10900, Thailand*

p.akkharadet@gmail.com; james.walton@durham.ac.uk

Table of Contents

1. NMR and HRMS spectra

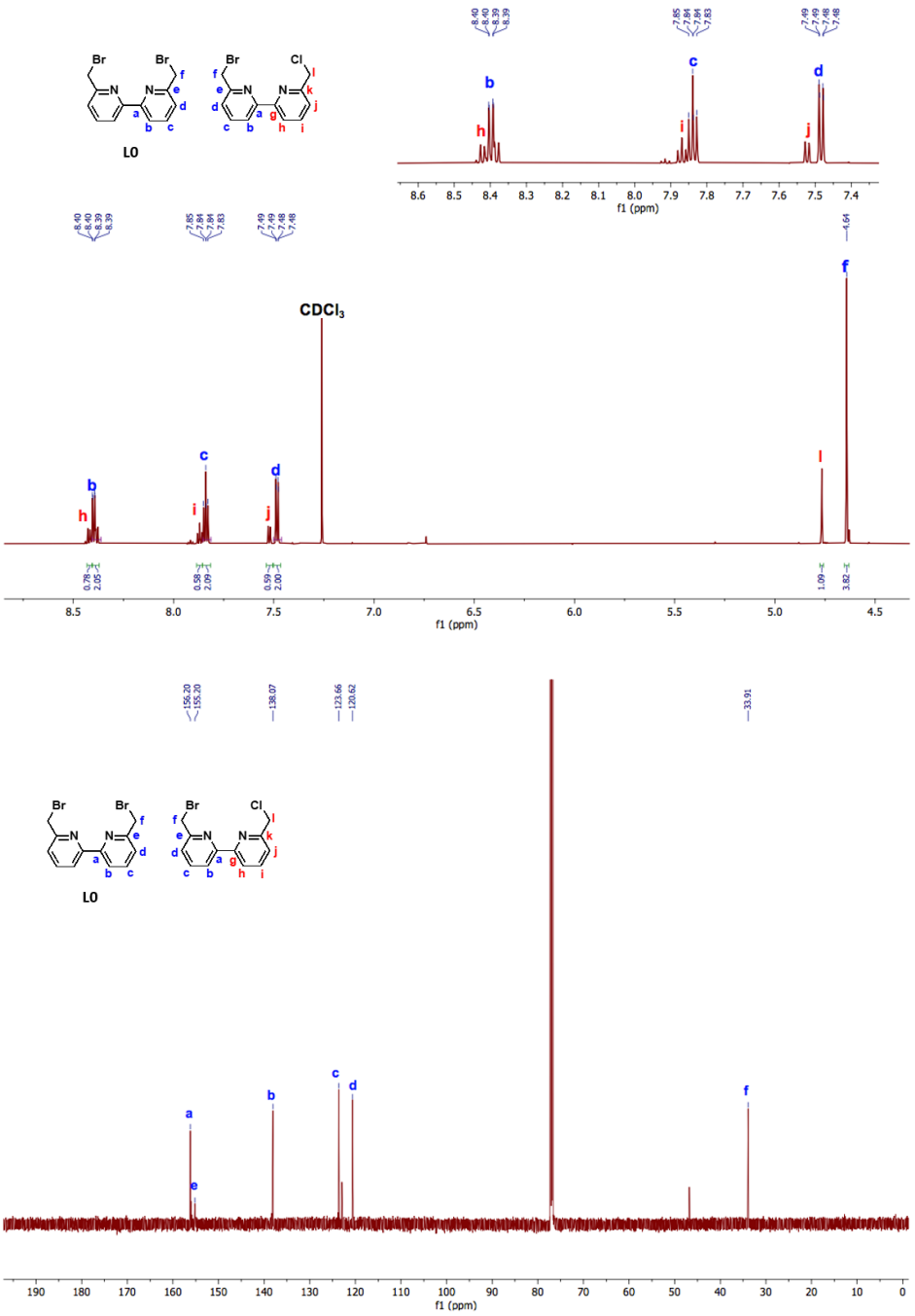


Fig S1. ^{1}H NMR spectrum (upper, Chloroform-*d*, 700 MHz, 298 K) and ^{13}C{^{1}H} NMR spectrum (lower, Chloroform-*d*, 175 MHz, 298 K) of ligand **L0**.

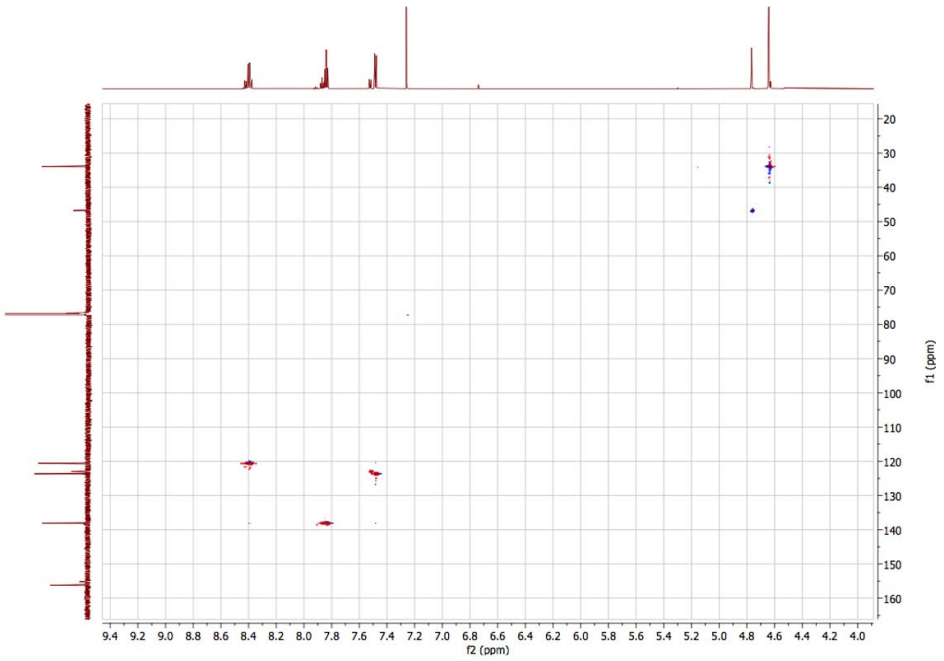
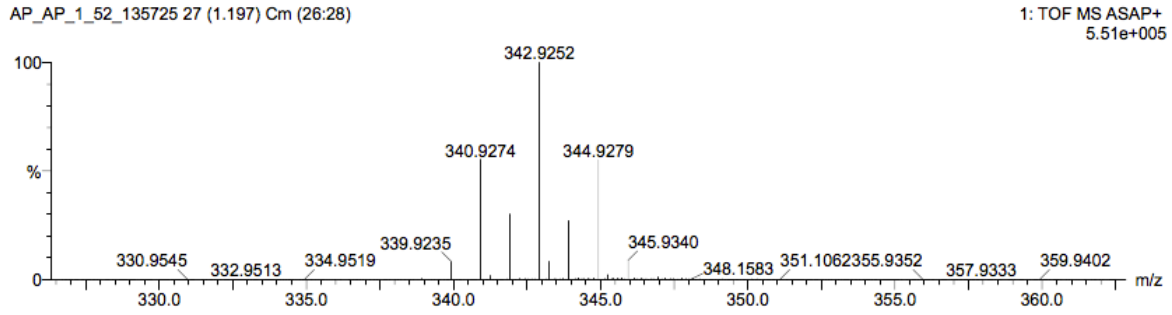


Fig S2. 2D HSQC spectrum (Chloroform-*d*, 700 MHz, 298 K) of ligand **L0**.



Minimum:				-1.5			
Maximum:		5.0	100.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
340.9274	340.9270	0.4	1.2	6.5	295.7	6.8	C11 H11 O5 Co2
	340.9231	4.3	12.6	14.5	295.2	6.2	C11 N5 O5 Co
	340.9289	-1.5	-4.4	7.5	290.9	1.9	C12 H11 N2 Br2
	340.9284	-1.0	-2.9	11.5	295.6	6.6	C12 H7 N4 O Co2

Fig S3. Positive ASAP HRMS spectra of ligand **L0**: *m/z* calculated for $[C_{12}H_{11}{}^{79}Br_2N_2]^+$: 340.9289, found: 340.9274.

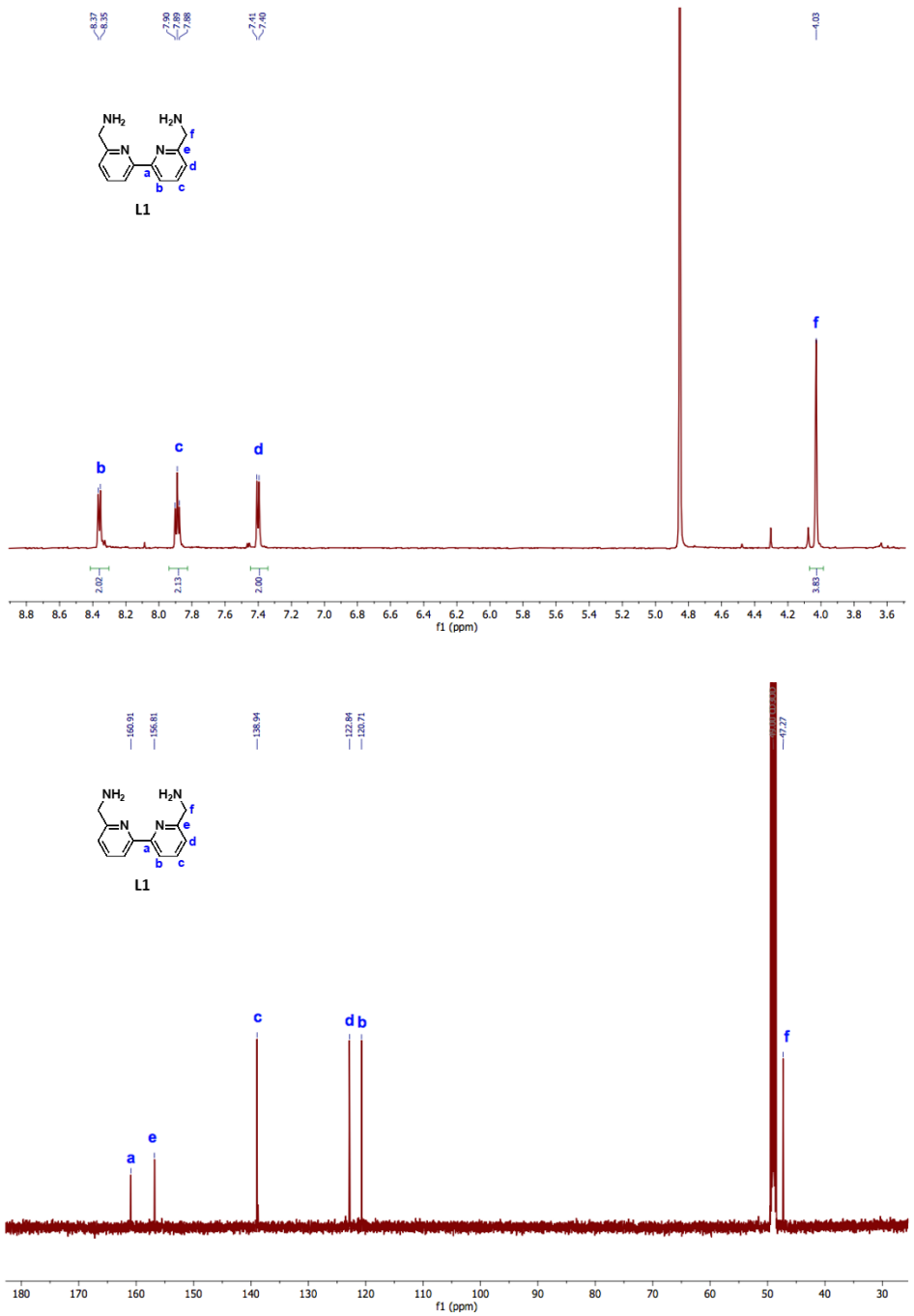


Fig S4. ^{1}H NMR spectrum (upper, Methanol-d_4, 700 MHz, 298 K) and ^{13}C{^{1}H} NMR spectrum (lower, Methanol-d_4, 175 MHz, 298 K) of ligand **L1**.

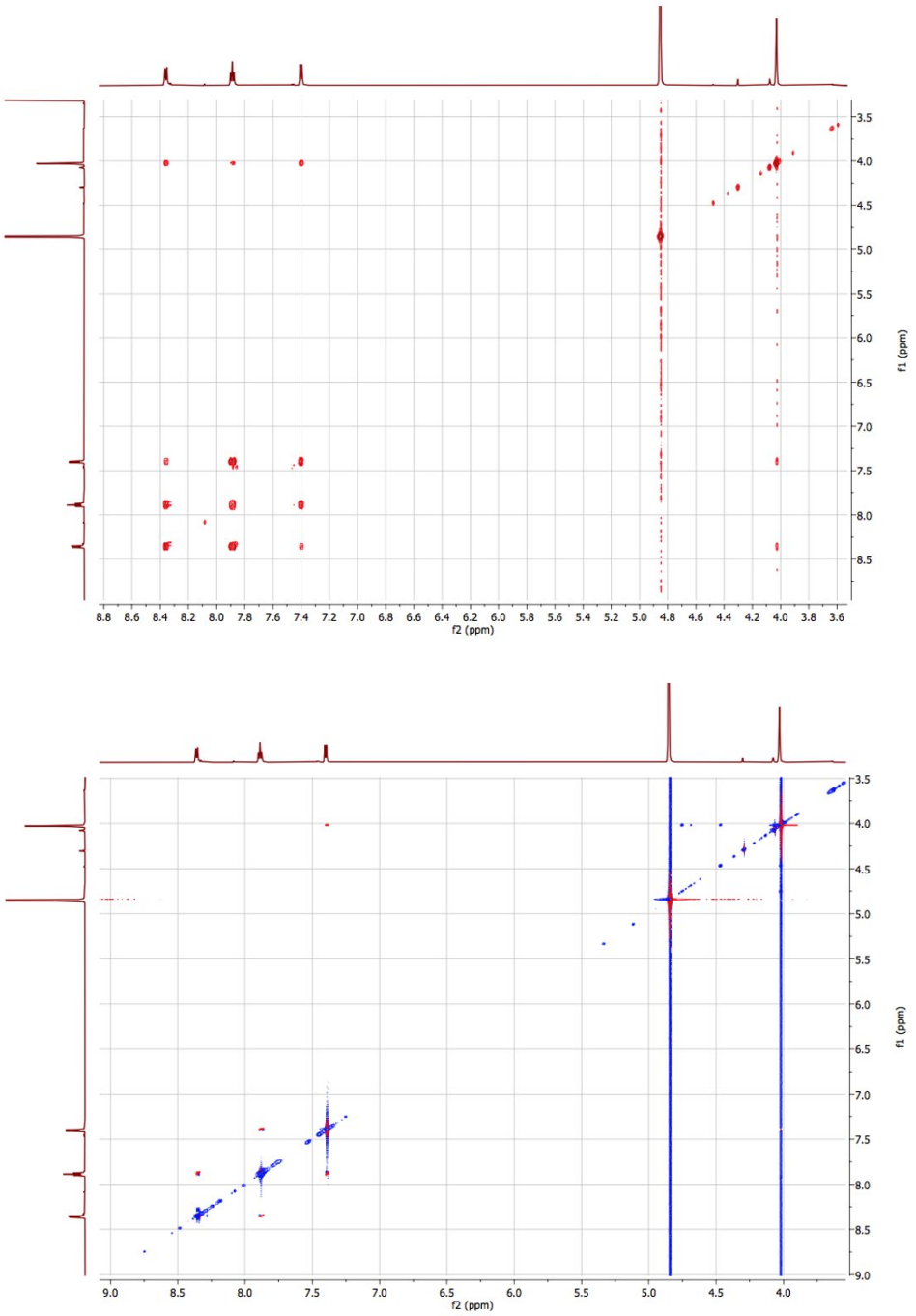


Fig S5. 2D COSY spectrum (upper, Methanol-d_4, 700 MHz, 298 K) and 2D NOESY spectrum (lower, Methanol-d_4, 700 MHz, 298 K) of ligand **L1**.

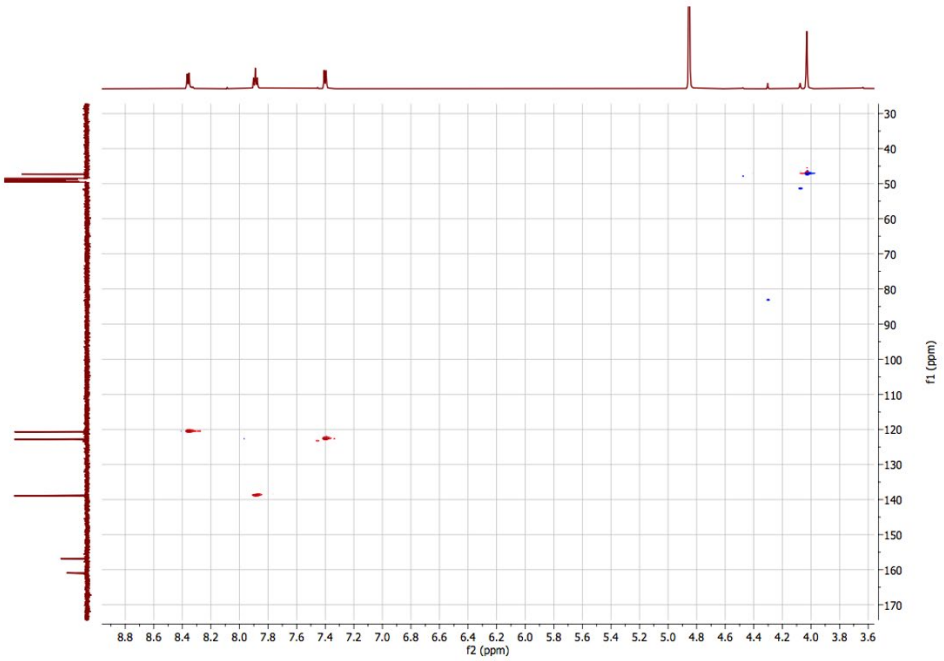
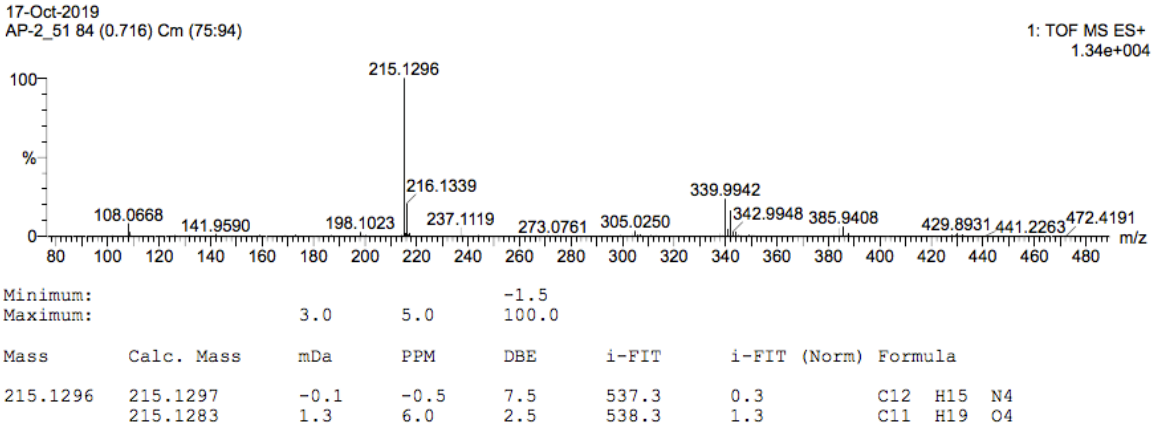


Fig S6. 2D HSQC spectrum (Methanol-d_4, 700 MHz, 298 K) of ligand **L1**.



Minimum:				-1.5			
Maximum:		3.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
215.1296	215.1297	-0.1	-0.5	7.5	537.3	0.3	C12 H15 N4
	215.1283	1.3	6.0	2.5	538.3	1.3	C11 H19 O4

Fig S7. Positive ESI HRMS spectra of ligand **L1**: *m/z* calculated for $[C_{12}H_{15}N_4]^+$: 215.1297, found: 215.1296.

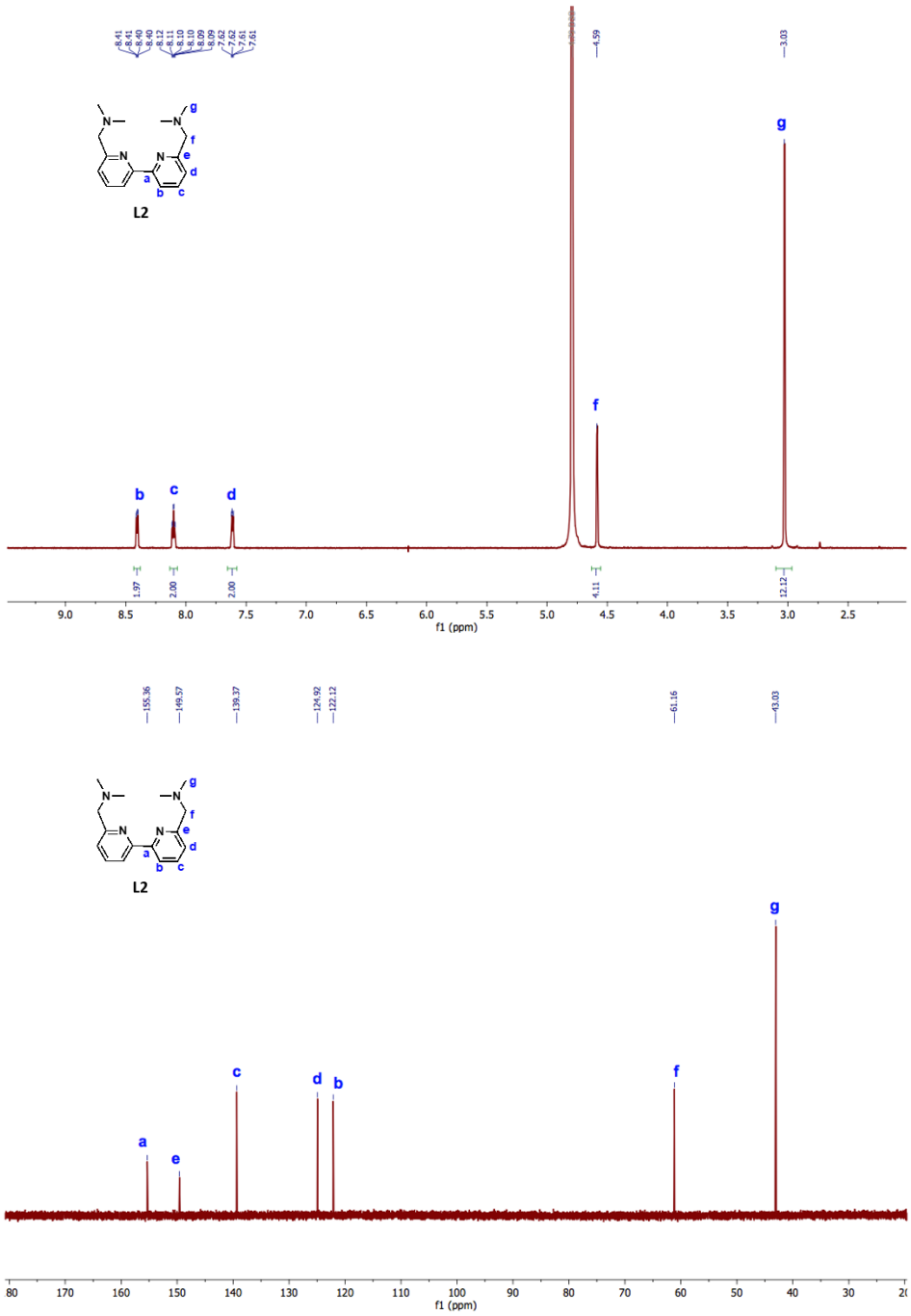


Fig S8. ^{1}H NMR spectrum (upper, Deuterium Oxide, 700 MHz, 298 K) and ^{13}C{^{1}H} NMR spectrum (lower, Deuterium Oxide, 175 MHz, 298 K) of ligand **L2**.

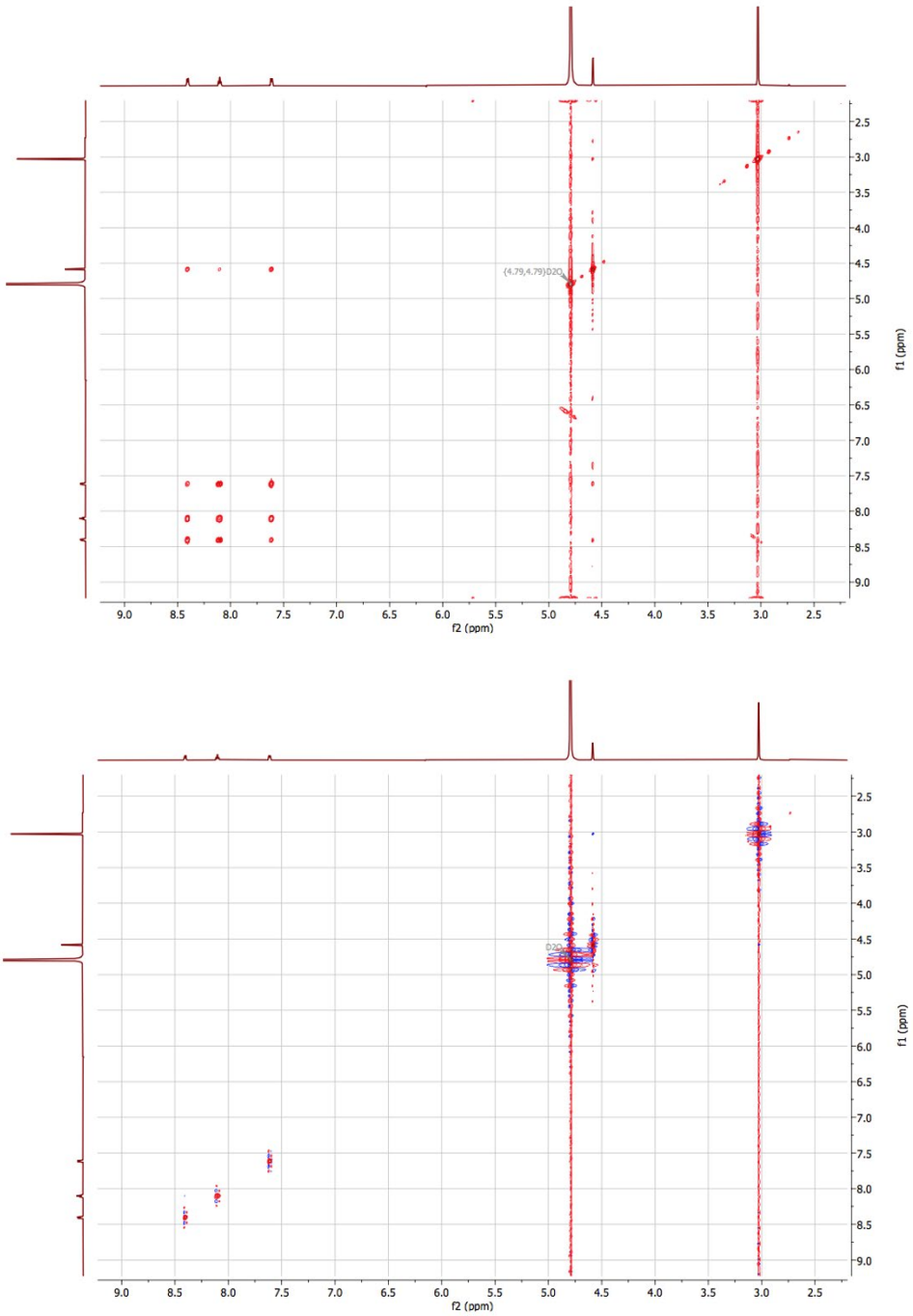


Fig S9. 2D COSY spectrum (upper, Deuterium Oxide, 700 MHz, 298 K) and 2D NOESY spectrum (lower, Deuterium Oxide, 700 MHz, 298 K) of ligand **L2**.

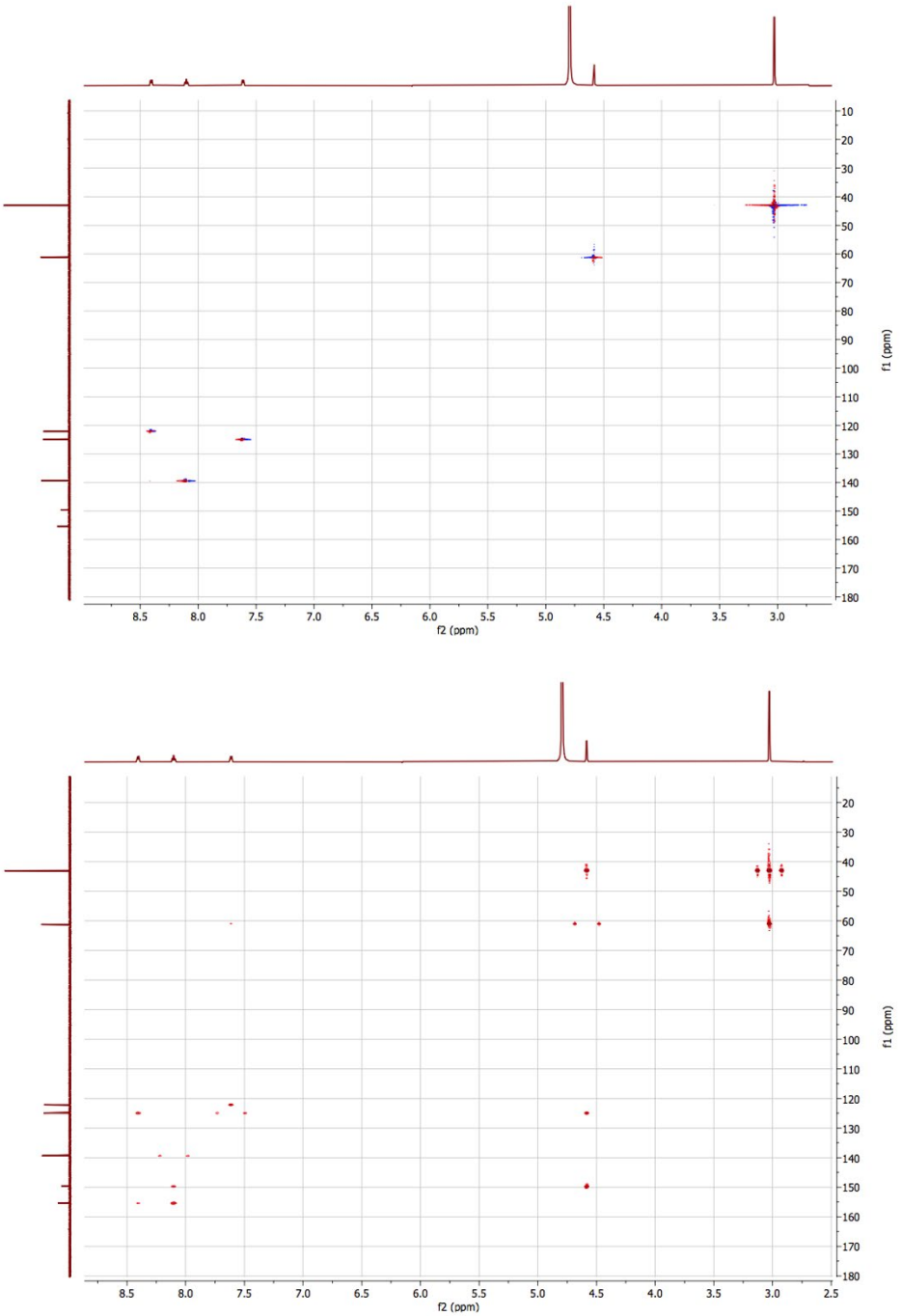
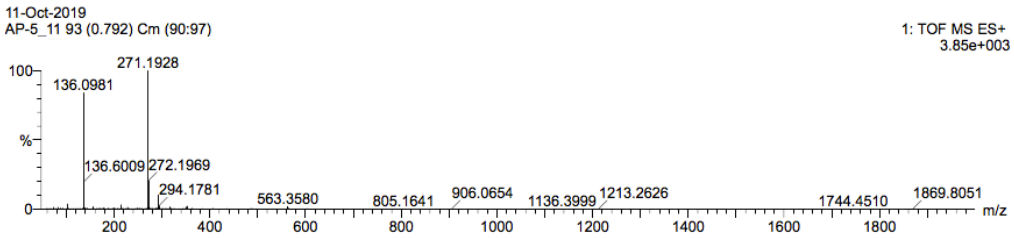


Fig S10. 2D HSQC spectrum (upper, Deuterium Oxide, 700 MHz, 298 K) and 2D HMBC spectrum (lower, Deuterium Oxide, 700 MHz, 298 K) of ligand **L2**.



Minimum:				-1.5			
Maximum:		3.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
271.1928	271.1923	0.5	1.8	7.5	336.4	0.0	C16 H23 N4
	271.1939	-1.1	-4.1	2.5	340.5	4.1	C14 H28 N2 O P
	271.1909	1.9	7.0	2.5	339.9	3.6	C15 H27 O4
	271.1899	2.9	10.7	-1.5	346.0	9.6	C9 H28 N4 O3 P

Fig S11. Positive ESI HRMS spectra of ligand **L2**: m/z calculated for $[C_{16}H_{23}N_4]^+$: 271.1923, found: 271.1928.

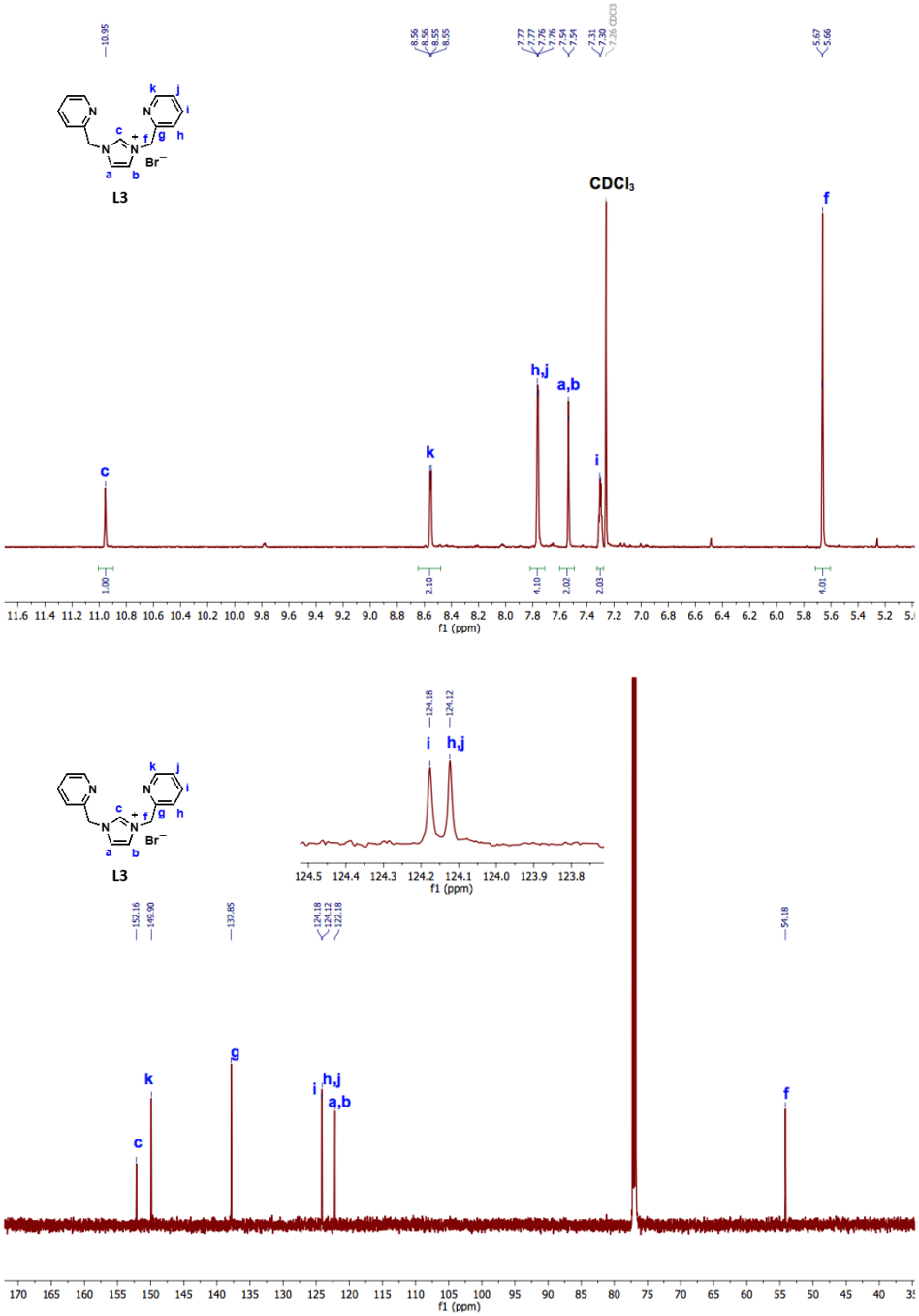


Fig S12. ^{1}H NMR spectrum (upper, Chloroform-*d*, 700 MHz, 298 K) and ^{13}C{^{1}H} NMR spectrum (lower, Chloroform-*d*, 175 MHz, 298 K) of ligand **L3**.

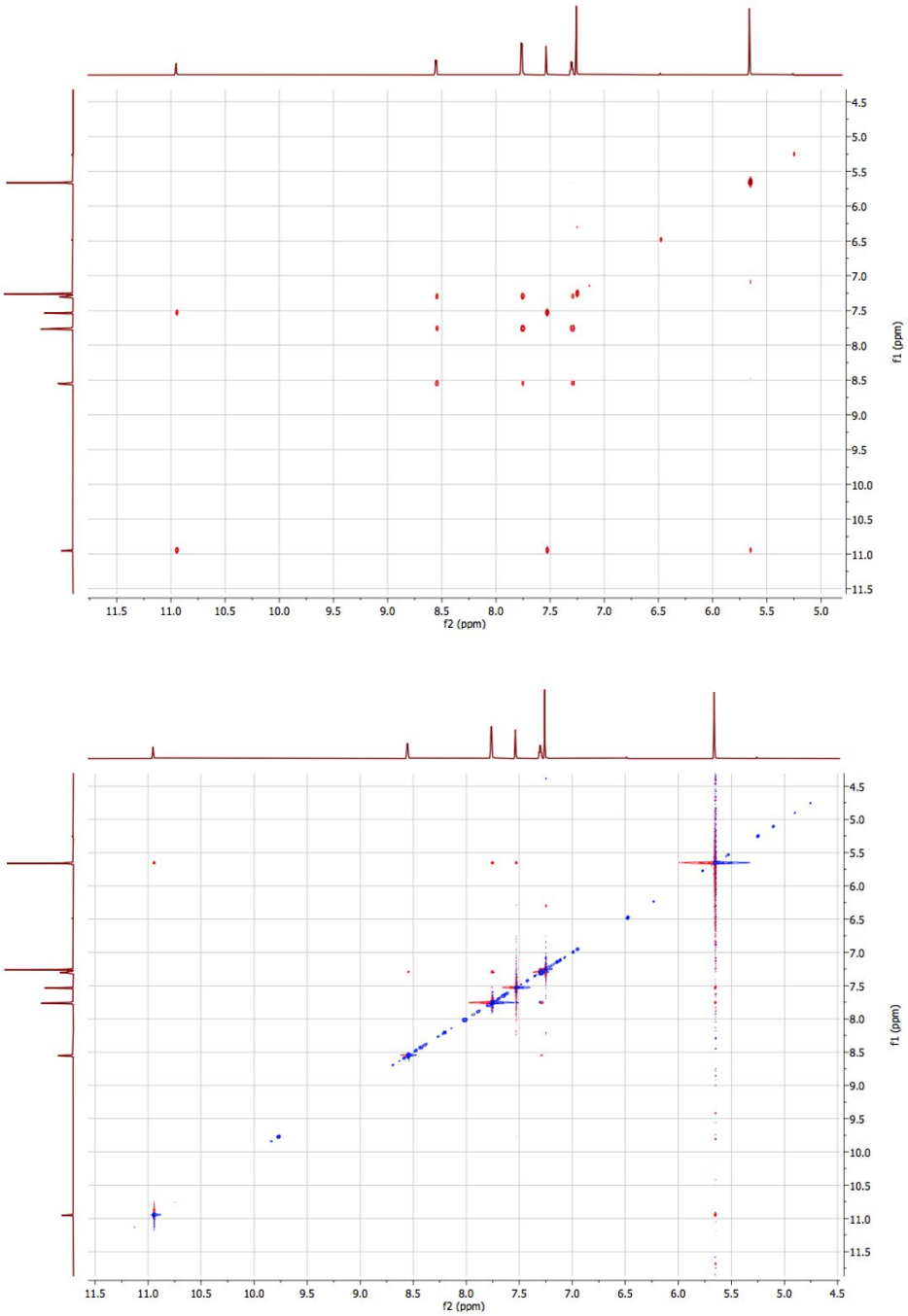


Fig S13. 2D COSY spectrum (upper, Chloroform-*d*, 700 MHz, 298 K) and 2D NOESY spectrum (lower, Chloroform-*d*, 700 MHz, 298 K) of ligand **L3**.

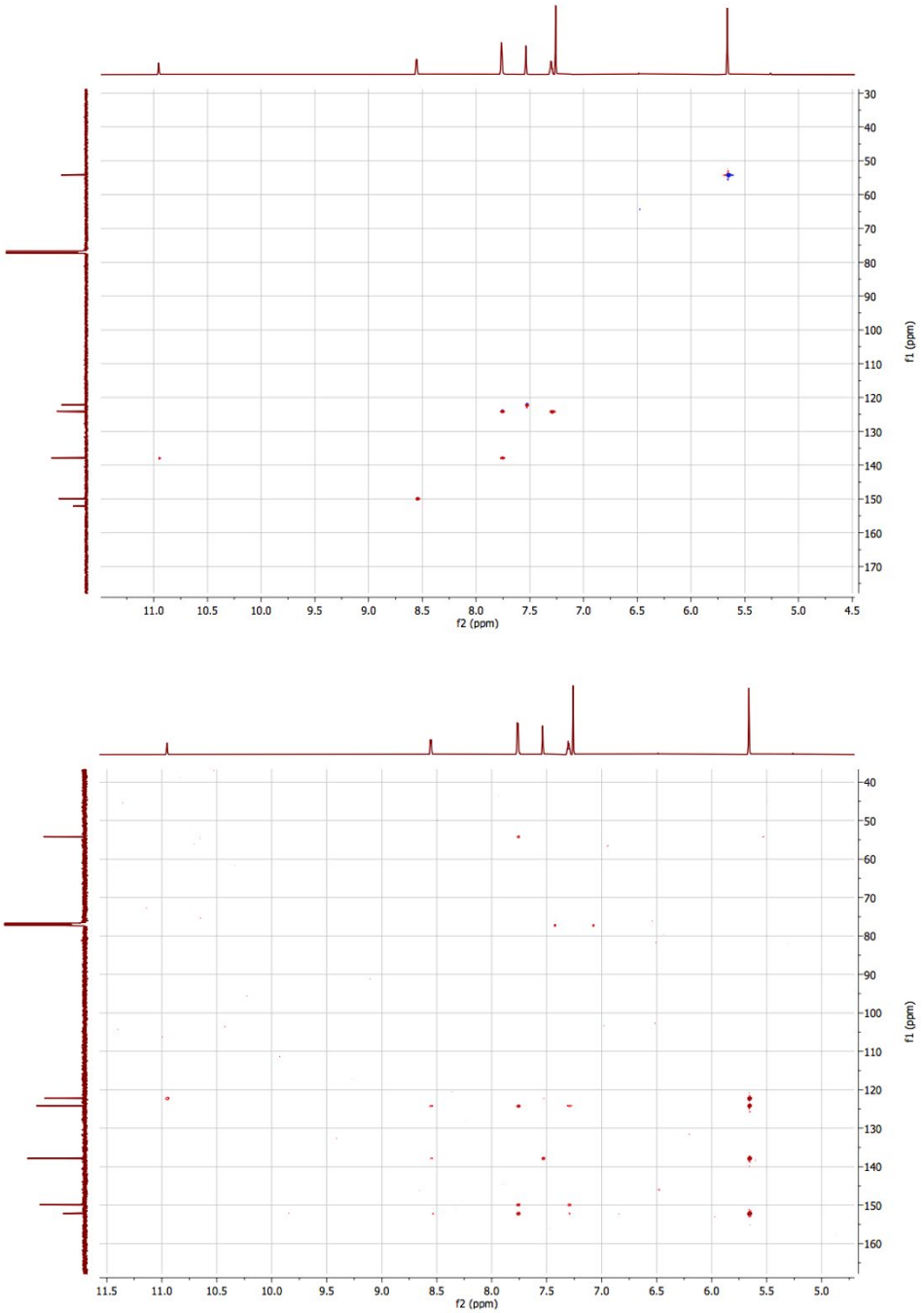
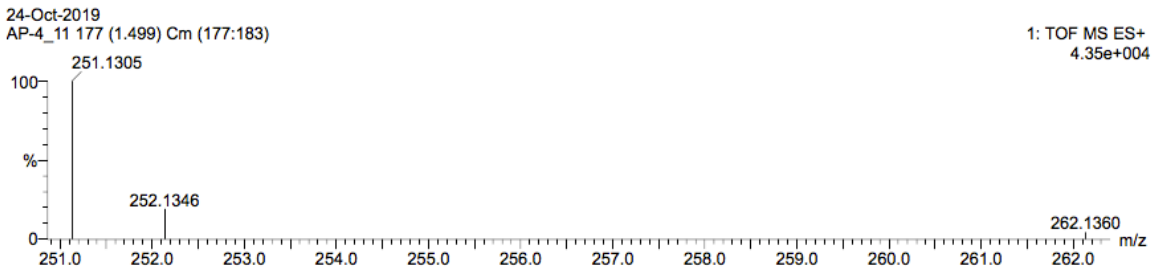


Fig S14. 2D HSQC spectrum (upper, Chloroform-*d*, 700 MHz, 298 K) and 2D HMBC spectrum (lower, Chloroform-*d*, 700 MHz, 298 K) of ligand **L3**.



Minimum:				-1.5			
Maximum:		3.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
251.1305	251.1303	0.2	0.8	1.5	41.4	1.3	C7 H21 N6 P2
	251.1297	0.8	3.2	10.5	42.7	2.5	C15 H15 N4
	251.1313	-0.8	-3.2	5.5	41.6	1.5	C13 H20 N2 O P
	251.1317	-1.2	-4.8	0.5	43.3	3.1	C11 H23 O4 S
	251.1290	1.5	6.0	1.5	45.9	5.8	C7 H19 N6 O2 S
	251.1283	2.2	8.8	5.5	42.5	2.3	C14 H19 O4
	251.1330	-2.5	-10.0	0.5	41.5	1.3	C11 H25 O2 P2
	251.1330	-2.5	-10.0	5.5	44.8	4.7	C12 H19 N4 S

Fig S15. Positive ASAP HRMS spectra of ligand **L3**: *m/z* calculated for $[C_{15}H_{15}N_4]^+$: 251.1297, found: 251.1305.

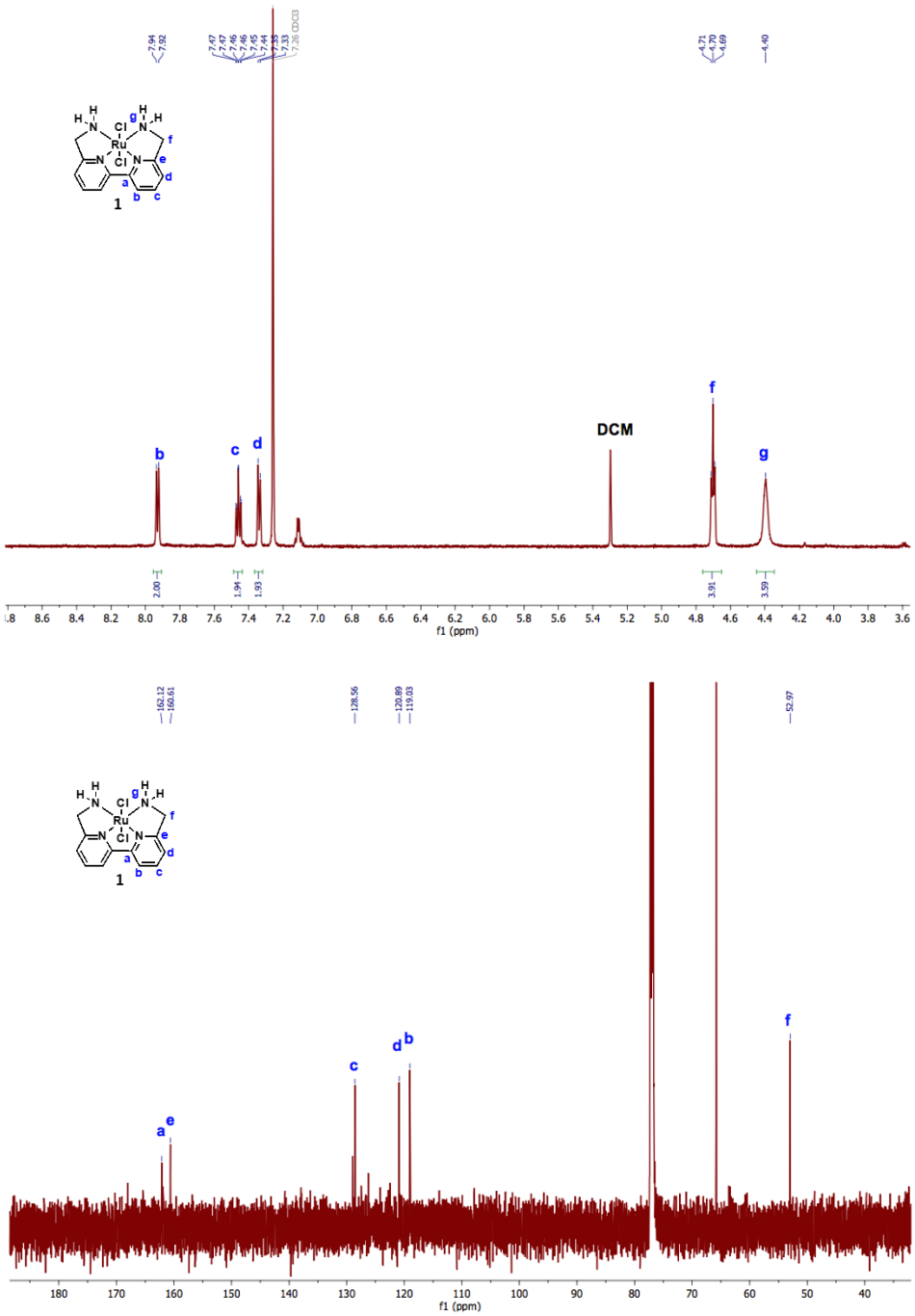


Fig S16. ^{1}H NMR spectrum (upper, Chloroform-*d*, 700 MHz, 298 K) and ^{13}C{^{1}H} NMR spectrum (lower, Chloroform-*d*, 175 MHz, 298 K) of complex **1**.

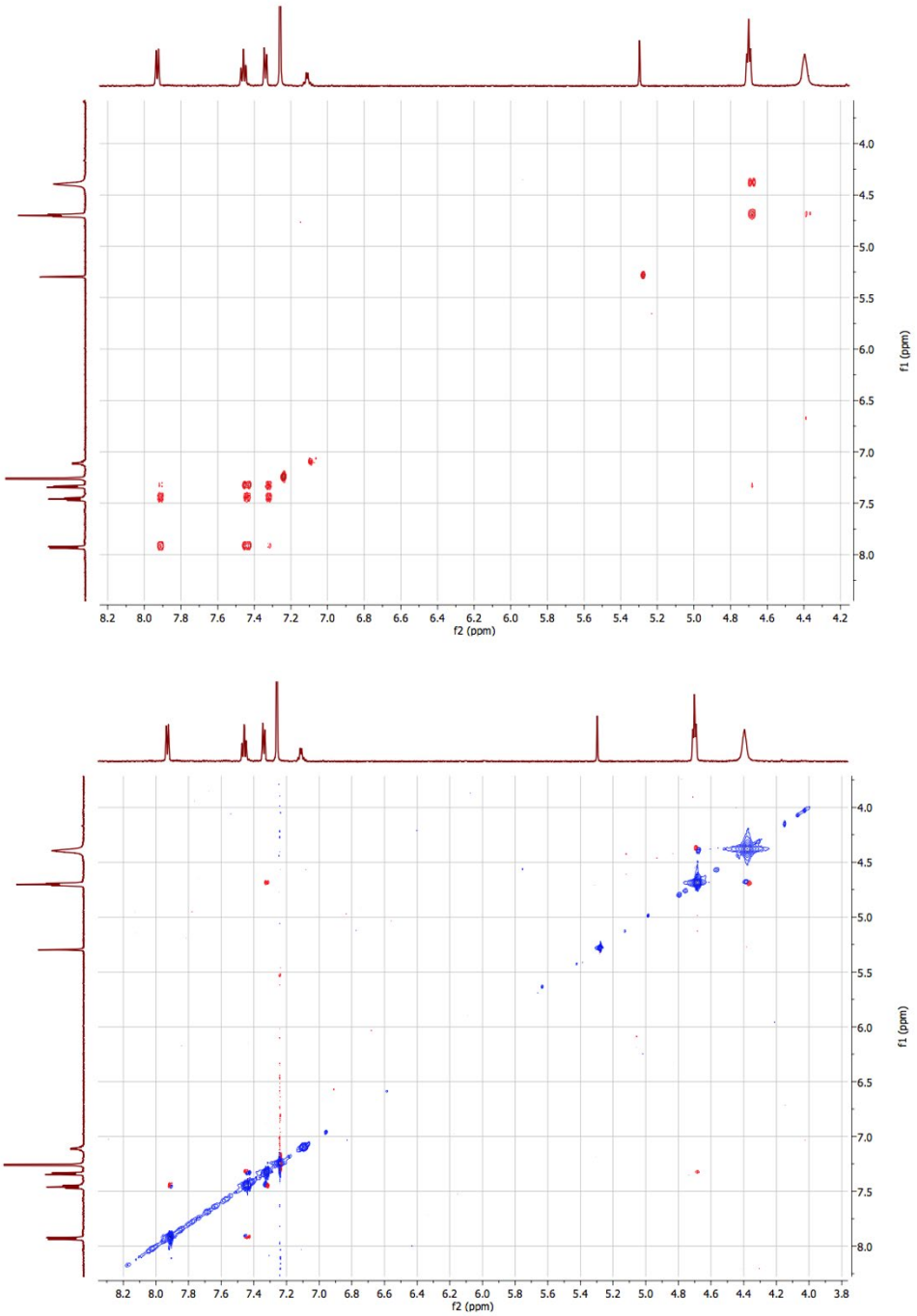


Fig S17. 2D COSY spectrum (upper, Chloroform-*d*, 700 MHz, 298 K) and 2D NOESY spectrum (lower, Chloroform-*d*, 700 MHz, 298 K) of complex **1**.

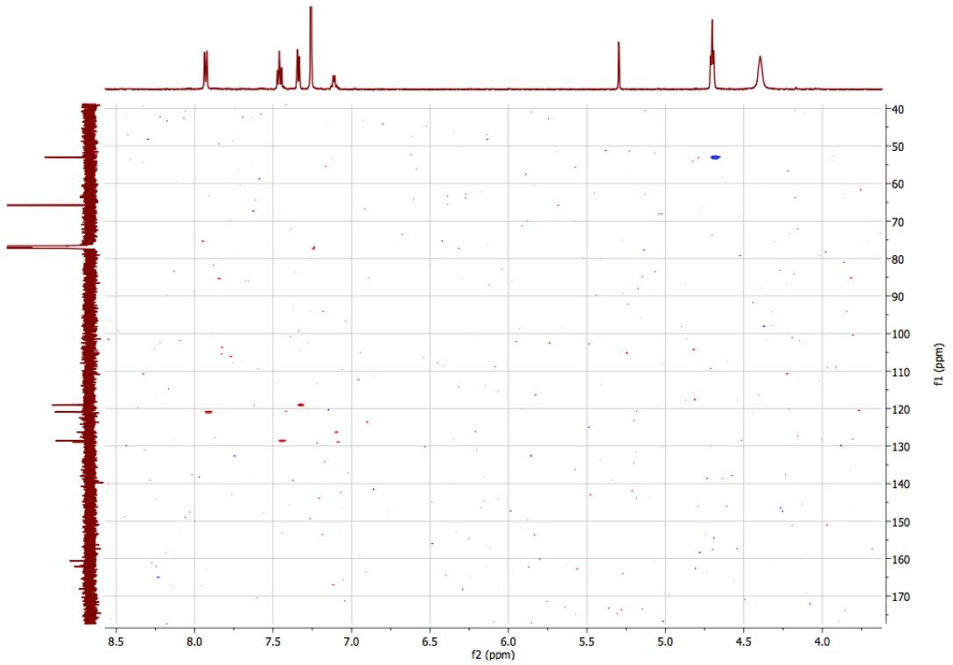
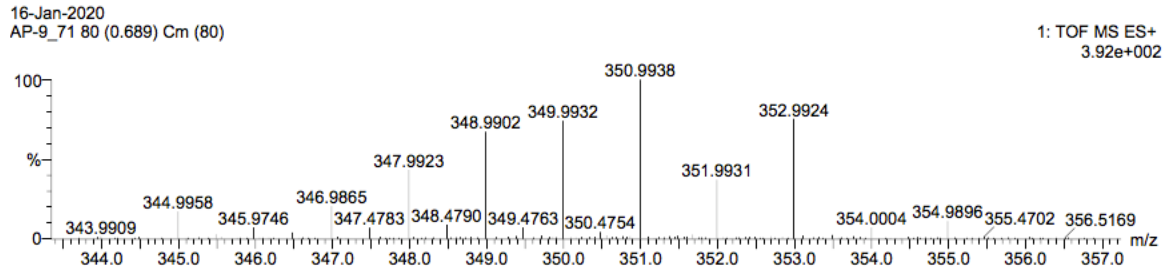


Fig S18. 2D HSQC spectrum (Chloroform-*d*, 700 MHz, 298 K) of complex **1**.



Minimum:				-1.5								
Maximum:		5.0	5.0	100.0								
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula					
344.9958	344.9938	2.0	5.8	8.0	133.3	5.0	C10	H11	N5	O3	96Ru	
	344.9970	-1.2	-3.5	2.5	131.9	3.6	C11	H18	O4	Cl	96Ru	
	345.0001	-4.3	-12.5	2.5	131.7	3.4	C11	H19	N2	Cl2	96Ru	
	344.9951	0.7	2.0	7.5	133.9	5.6	C12	H13	N2	O4	96Ru	
	344.9983	-2.5	-7.2	7.5	132.1	3.9	C12	H14	N4	Cl	96Ru	

Fig S19. Positive ESI HRMS spectra of complex **1**: *m/z* calculated for $[C_{12}H_{14}N_4{}^{35}Cl^{96}Ru]^+$: 344.9983, found: 344.9958.

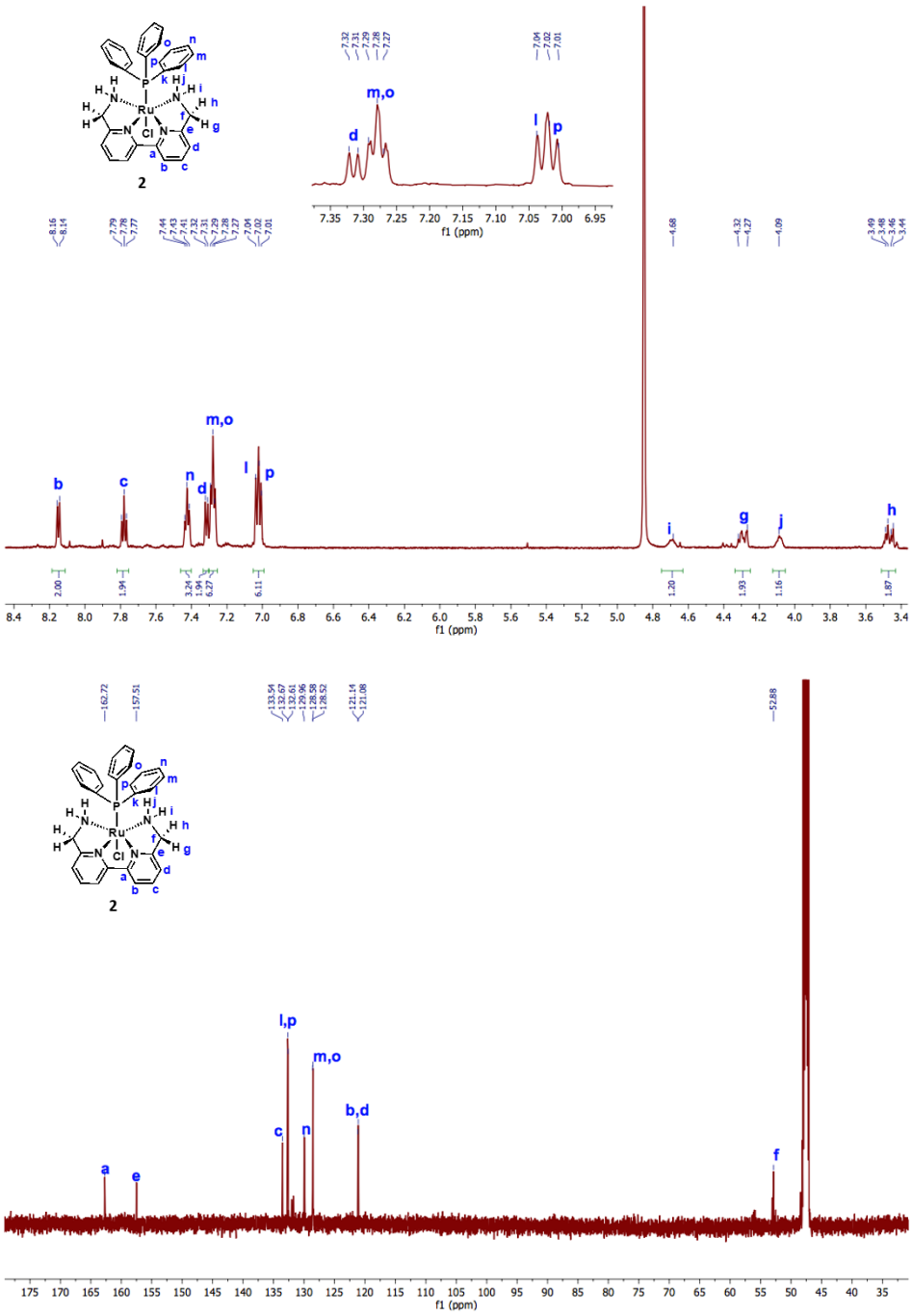


Fig S20. ^{1}H NMR spectrum (upper, Methanol-d_4, 700 MHz, 298 K) and ^{13}C{^{1}H} NMR spectrum (lower, Methanol-d_4, 175 MHz, 298 K) of complex **2**.

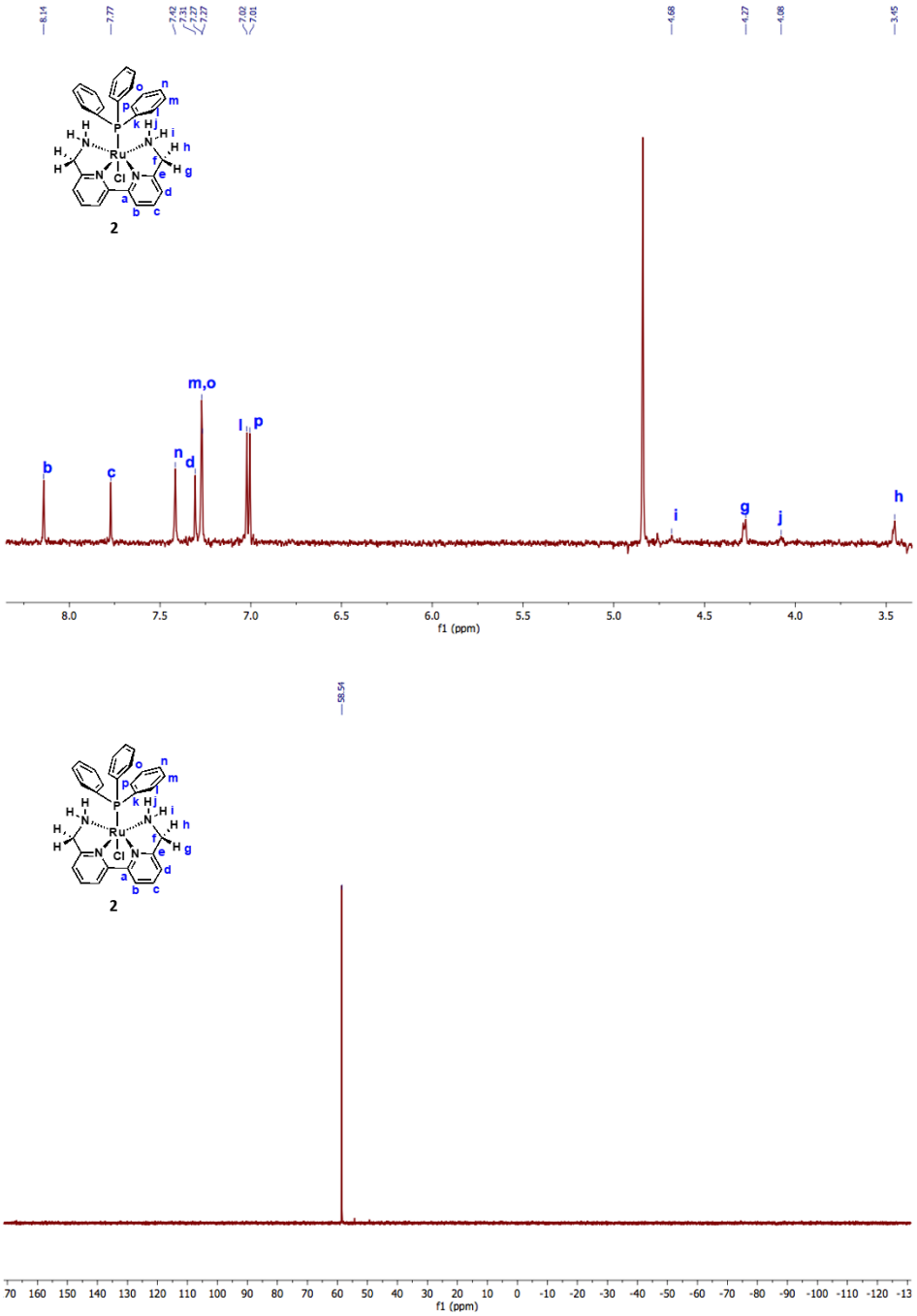


Fig S21. PSYCHE spectrum (upper, Methanol-d_4, 700 MHz, 298 K) and ^{31}P NMR spectrum (lower, DMSO-d_6, 700 MHz, 298 K) of complex **2**.

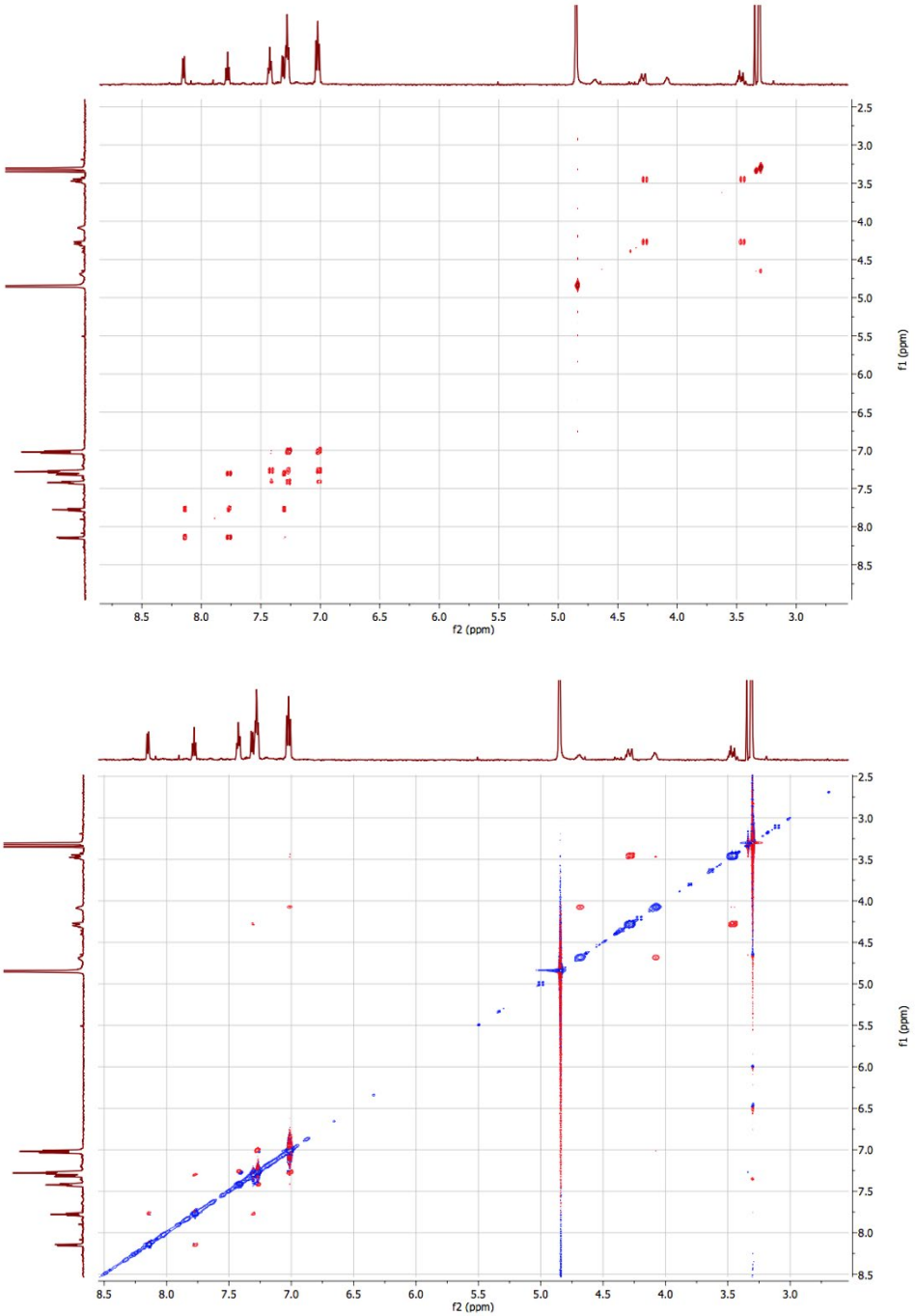


Fig S22. 2D COSY spectrum (upper, Methanol-d_4, 700 MHz, 298 K) and 2D NOESY spectrum (lower, Methanol-d_4, 700 MHz, 298 K) of complex **2**.

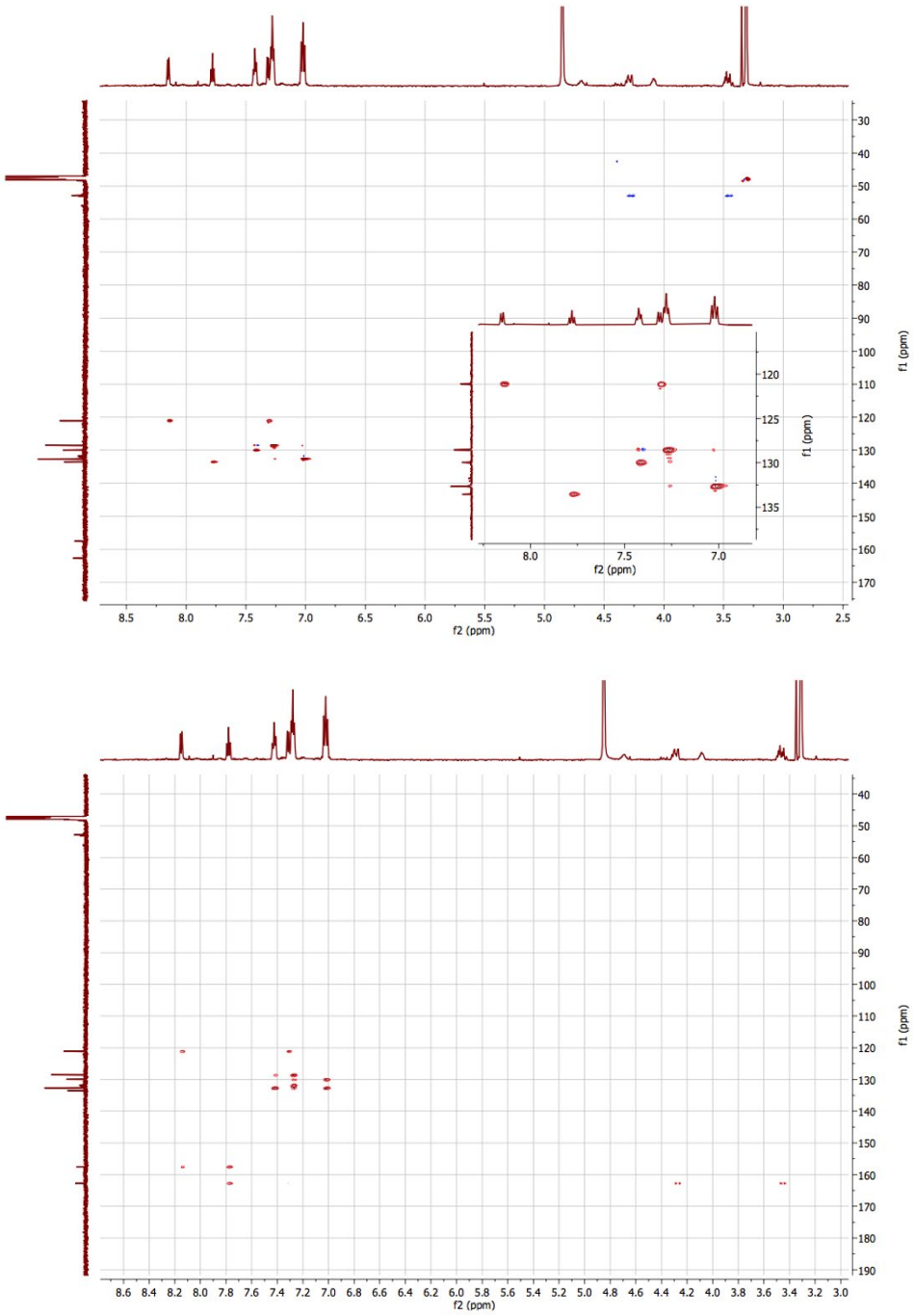


Fig S23. 2D HSQC spectrum (upper, Methanol-d_4, 700 MHz, 298 K) and 2D HMBC spectrum (lower, Methanol-d_4, 700 MHz, 298 K) of complex **2**.

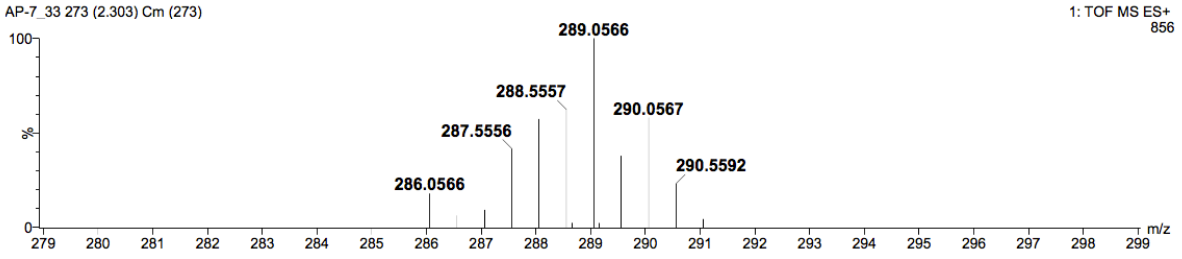


Fig S24. Positive ESI HRMS spectra of complex **2**: *m/z* calculated for $[C_{30}H_{29}N_4P^{96}Ru]^{2+}$: 286.0591, found: 286.0566.

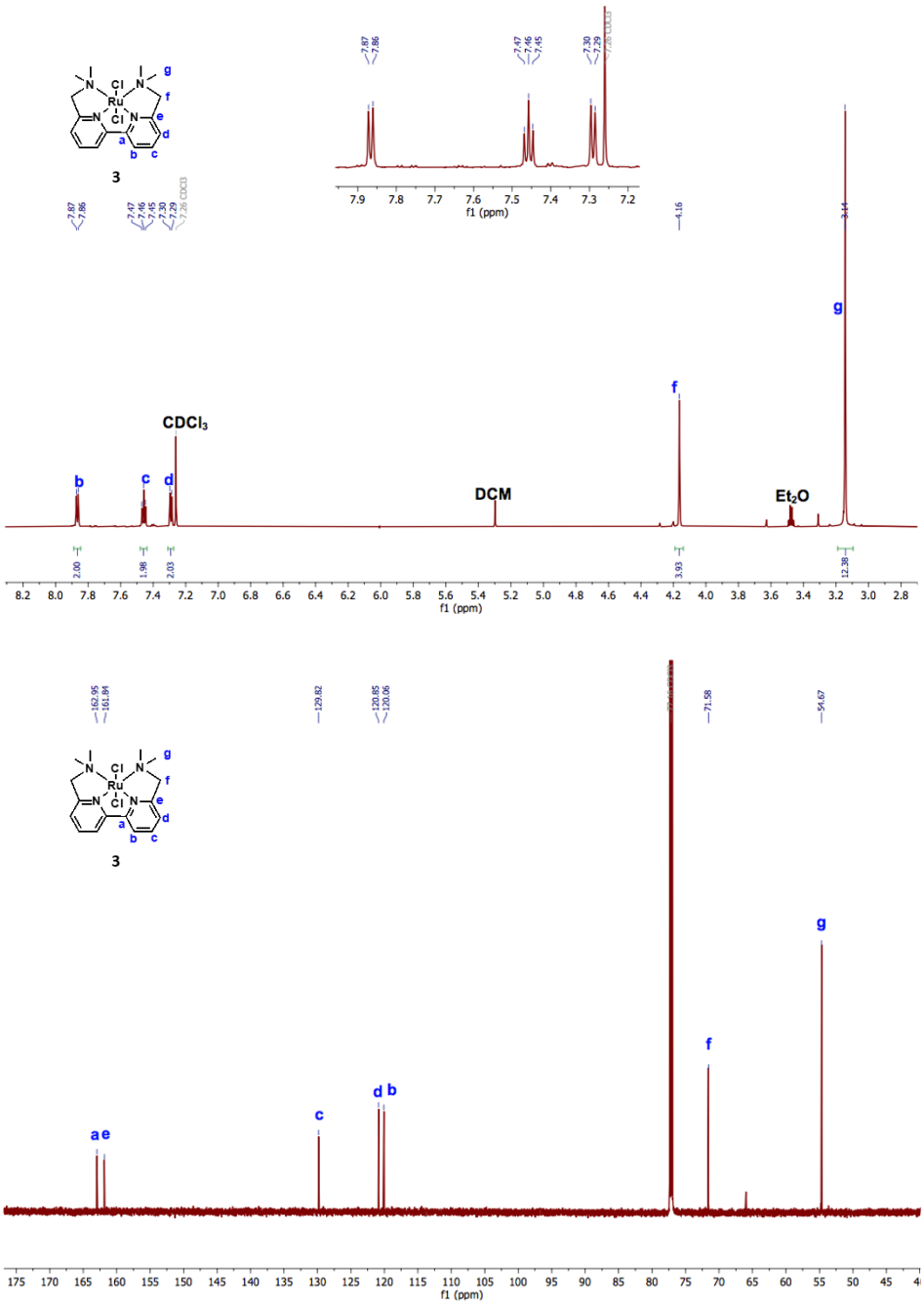


Fig S25. ^{1}H NMR spectrum (upper, Chloroform-*d*, 700 MHz, 298 K) and ^{13}C{^{1}H} NMR spectrum (lower, Chloroform-*d*, 175 MHz, 298 K) of complex **3**.

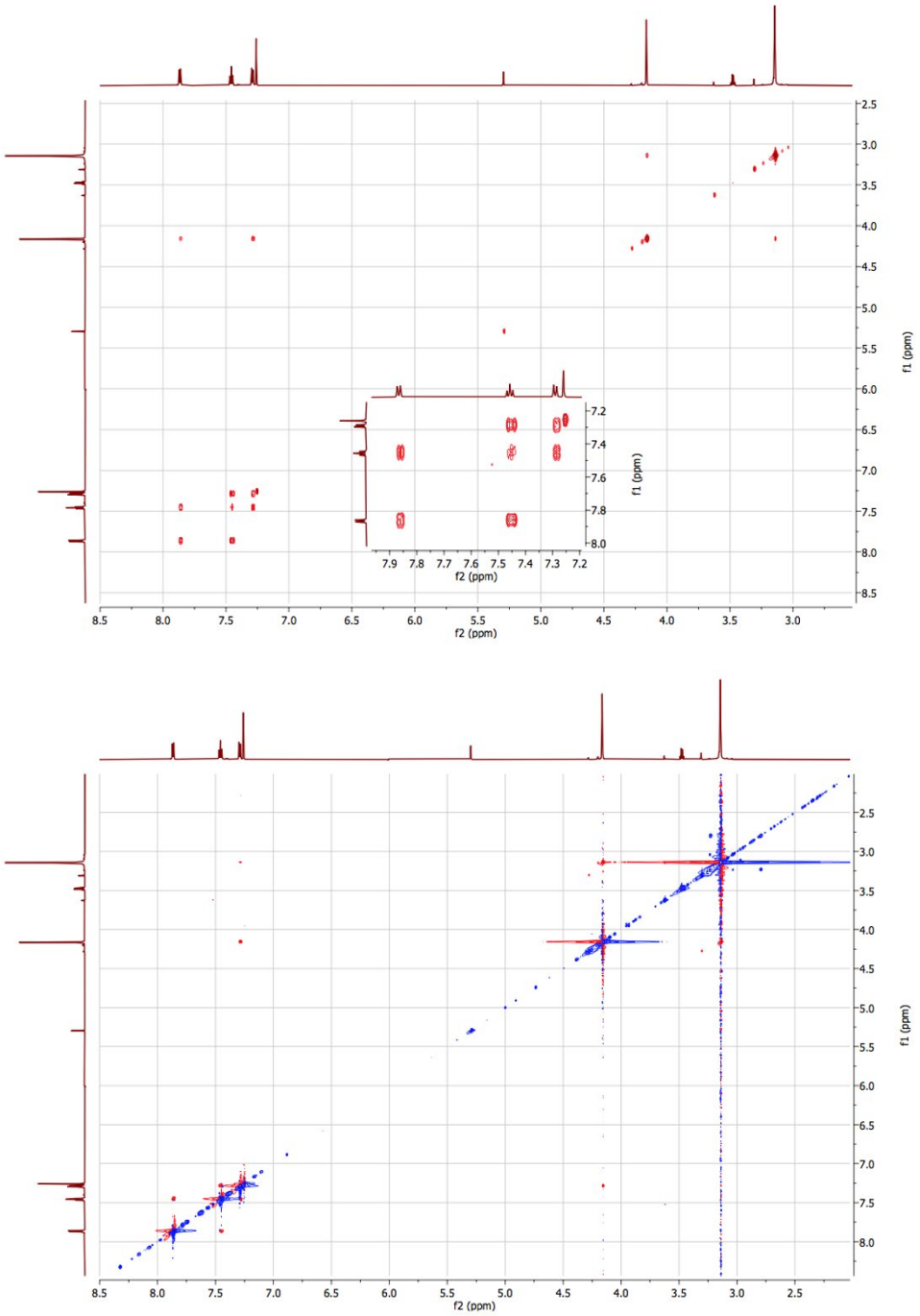


Fig S26. 2D COSY spectrum (upper, Chloroform-*d*, 700 MHz, 298 K) and 2D NOESY spectrum (lower, Chloroform-*d*, 700 MHz, 298 K) of complex **3**.

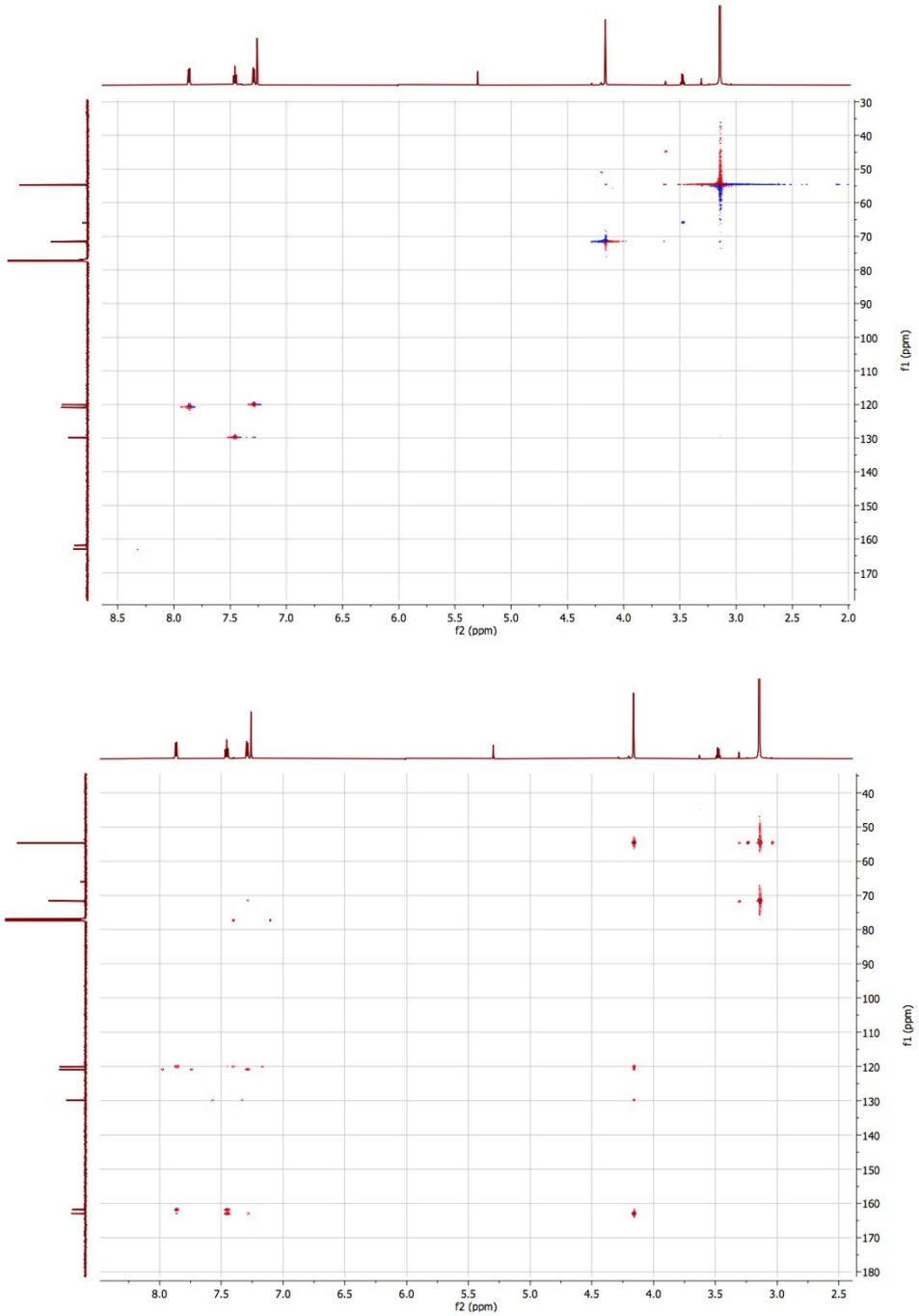
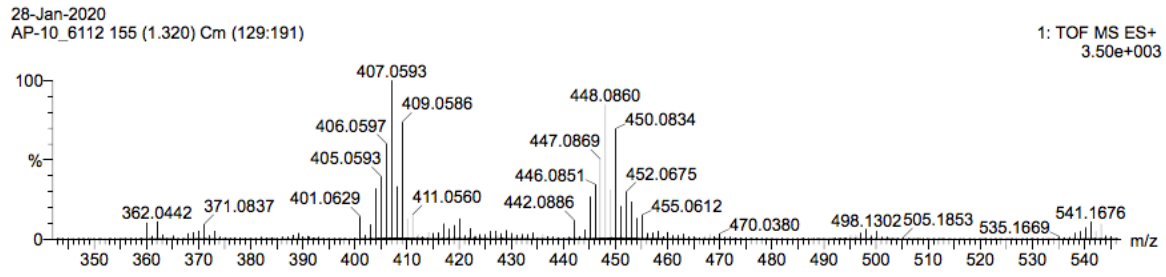


Fig S27. 2D HSQC spectrum (upper, Chloroform-*d*, 700 MHz, 298 K) and 2D HMBC spectrum (lower, Chloroform-*d*, 700 MHz, 298 K) of complex **3**.



Minimum:				-1.5			
Maximum:		3.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
401.0629	401.0626	0.3	0.7	14.5	393.3	1.3	C14 H10 N10 O3 Cl
	401.0634	-0.5	-1.2	18.5	400.1	8.2	C19 H9 N6 O5
	401.0618	1.1	2.7	11.5	400.6	8.6	C21 H21 O2 96Ru
	401.0641	-1.2	-3.0	-0.5	393.3	1.3	C5 H22 N10 O3 Cl 96Ru
	401.0612	1.7	4.2	9.5	393.1	1.1	C13 H14 N6 O7 Cl
	401.0648	-1.9	-4.7	23.5	400.4	8.4	C20 H5 N10 O
	401.0609	2.0	5.0	7.5	394.0	2.0	C16 H22 N4 Cl 96Ru
	401.0609	2.0	5.0	-0.5	398.4	6.4	C5 H21 N8 O7 96Ru

Fig S28. Positive ESI HRMS spectra of complex **3**: *m/z* calculated for $[C_{16}H_{22}N_4{}^{35}Cl^{96}Ru]^+$: 401.0609, found: 401.0629

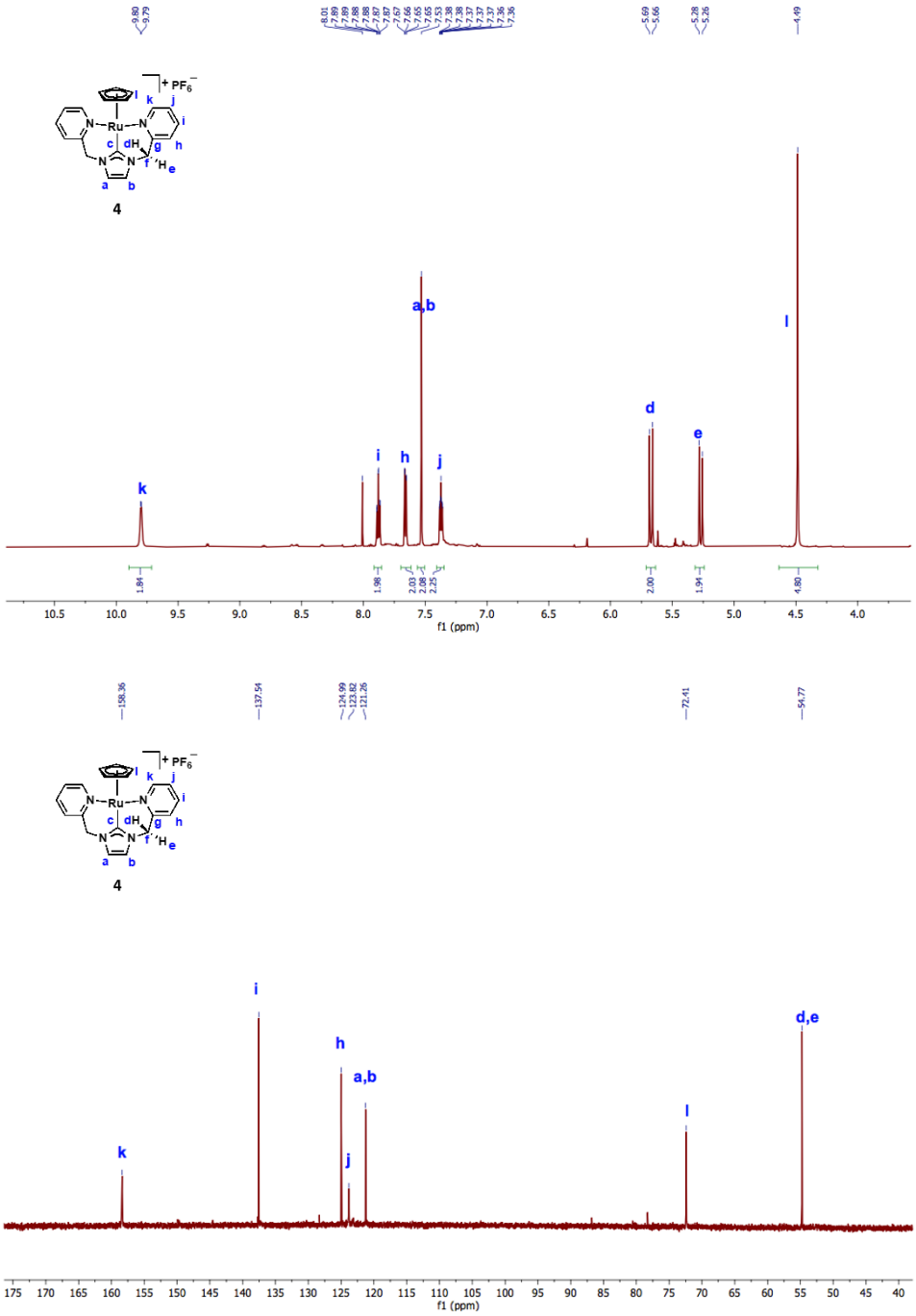


Fig S29. ^{1}H NMR spectrum (upper, Acetone-d_6, 700 MHz, 298 K) and ^{13}C{^{1}H} NMR spectrum (lower, Acetone-d_6, 175 MHz, 298 K) of complex **4**.

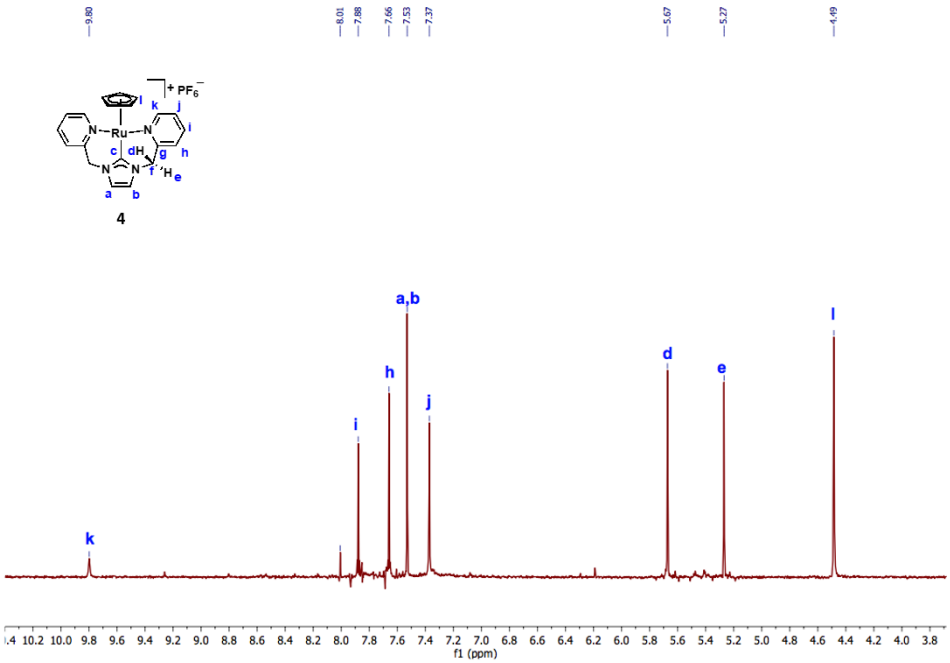


Fig S30. PSYCHE spectrum (Acetone-d_6, 700 MHz, 298 K) of complex **4**.

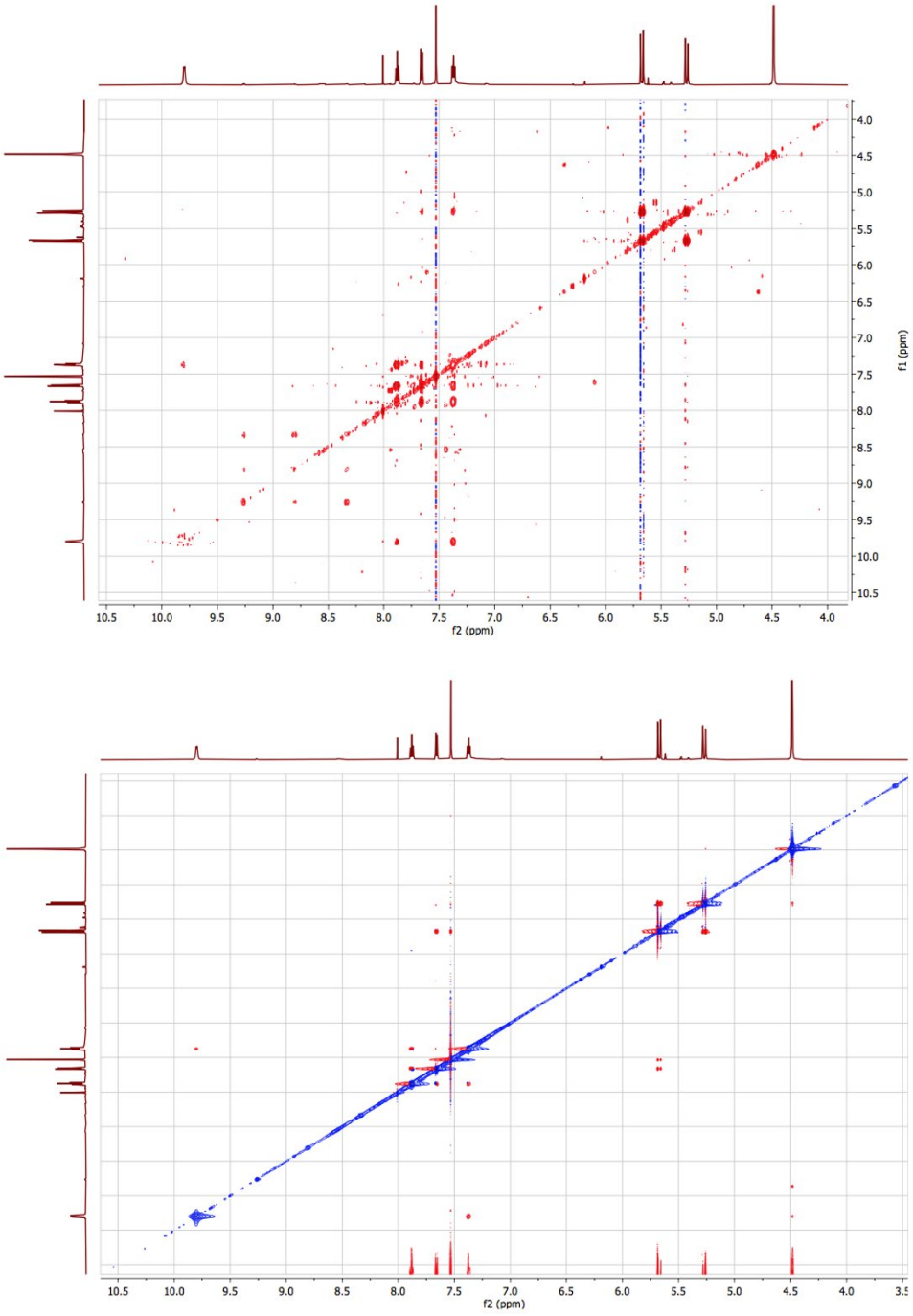


Fig S31. 2D COSY spectrum (upper, Acetone-d_6, 700 MHz, 298 K) and 2D NOESY spectrum (lower, Acetone-d_6, 700 MHz, 298 K) of complex **4**.

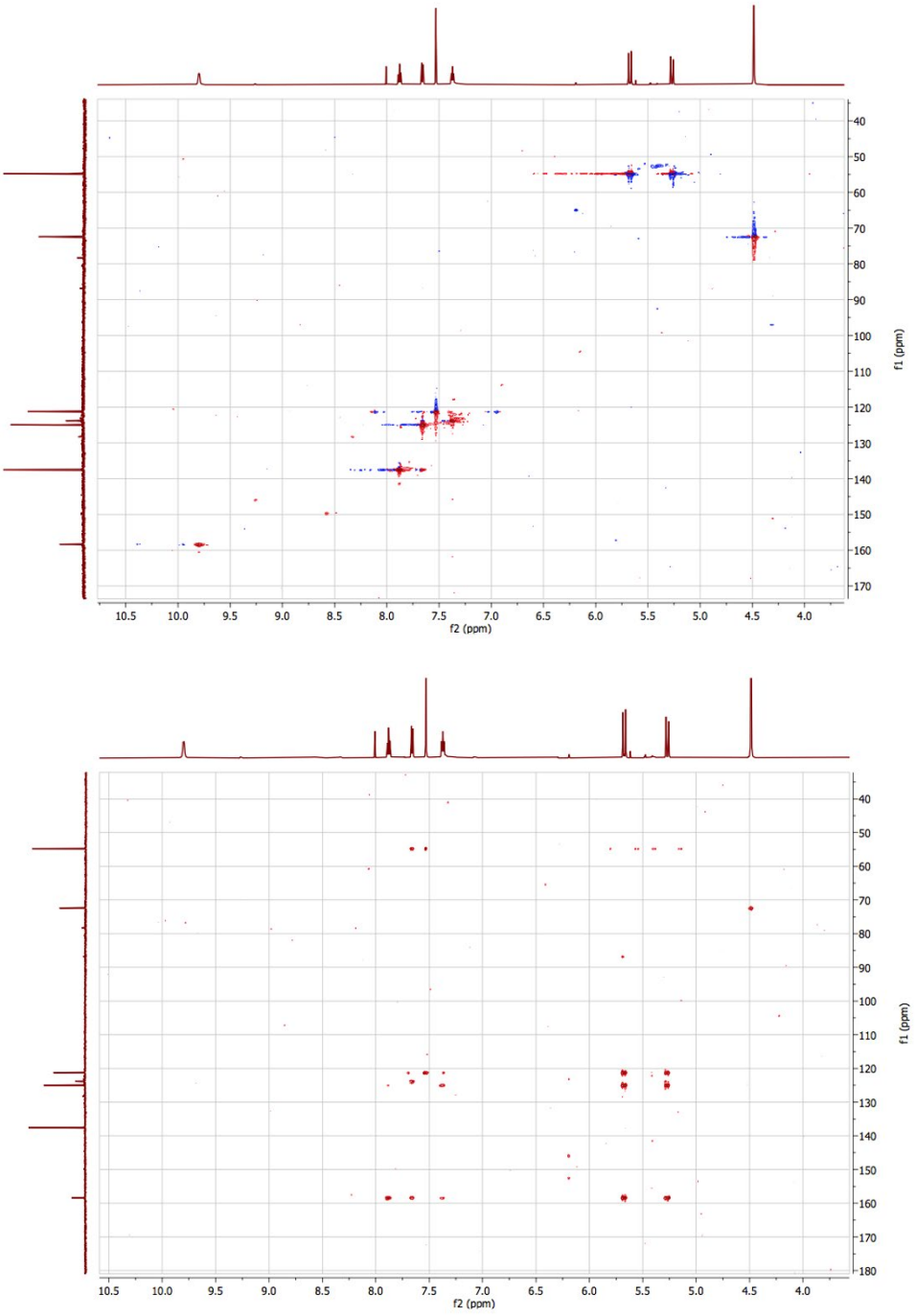
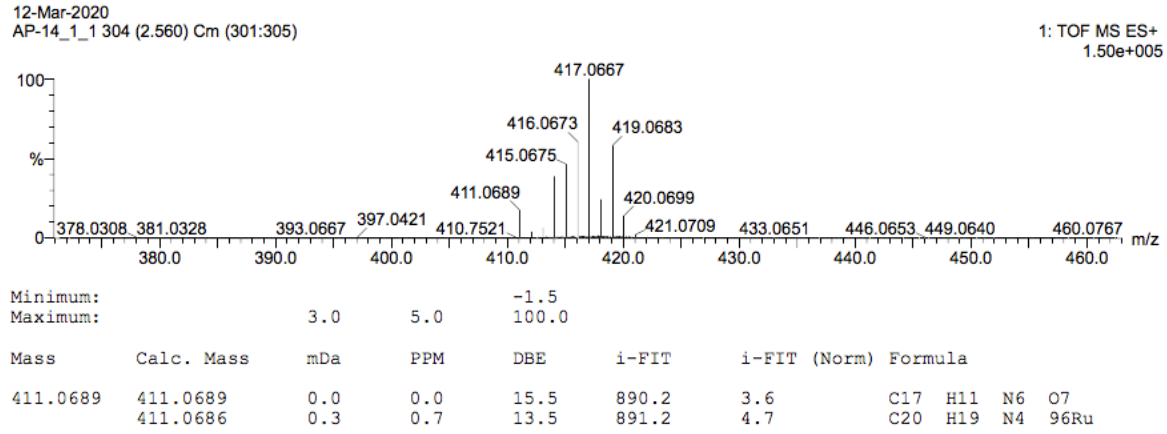


Fig S32. 2D HSQC spectrum (upper, Acetone-d_6, 700 MHz, 298 K) and 2D HMBC spectrum (lower, Acetone-d_6, 700 MHz, 298 K) of complex **4**.



Minimum:				-1.5			
Maximum:		3.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
411.0689	411.0689	0.0	0.0	15.5	890.2	3.6	C17 H11 N6 O7
	411.0686	0.3	0.7	13.5	891.2	4.7	C20 H19 N4 96Ru

Fig S33. Positive ESI HRMS spectra of complex **4**: *m/z* calculated for $[C_{20}H_{19}N_4{}^{96}Ru]^+$: 411.0686, found: 411.0689

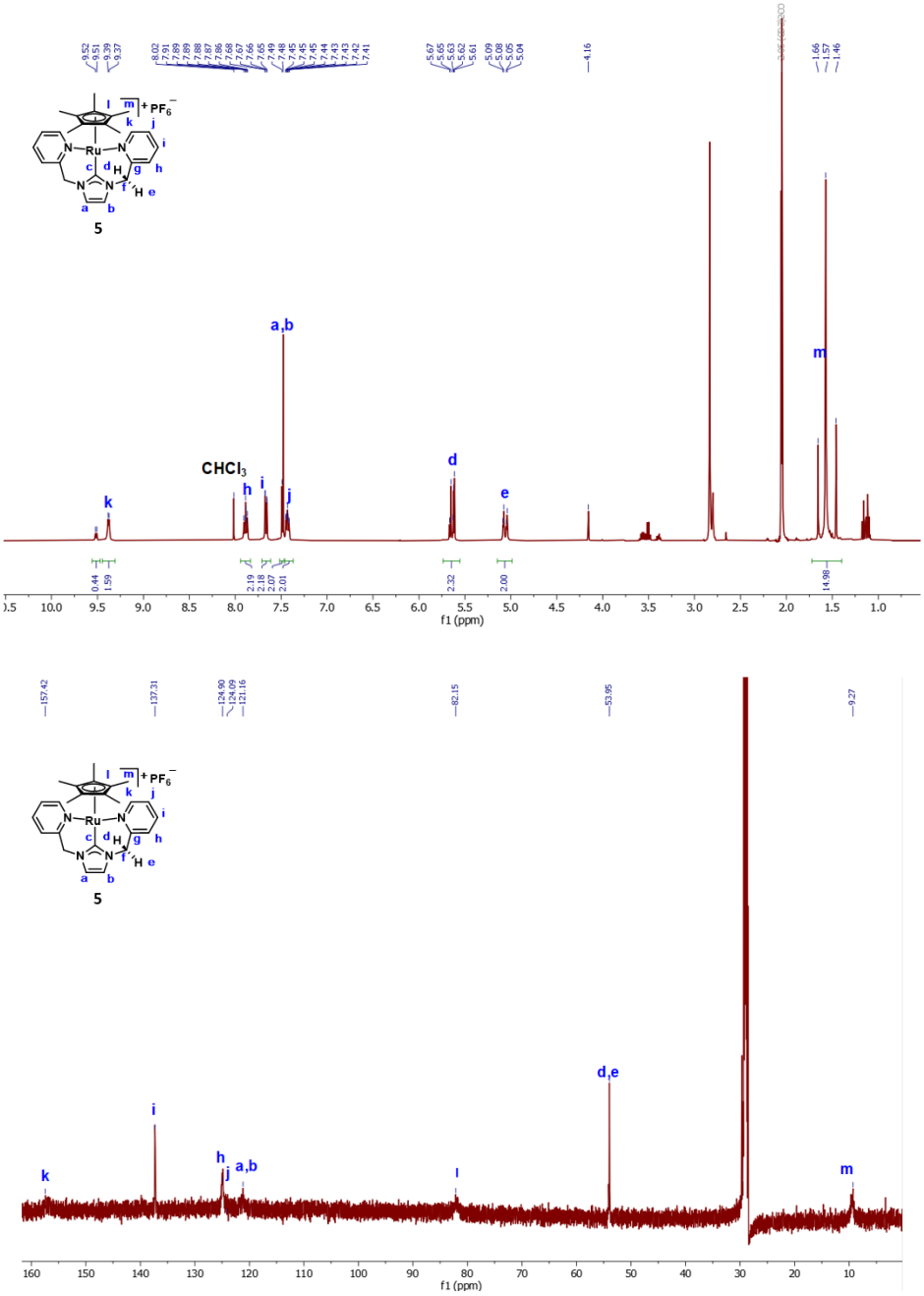


Fig S34. ^{1}H NMR spectrum (upper, Acetone-d_6, 700 MHz, 298 K) and ^{13}C{^{1}H} NMR spectrum (lower, Acetone-d_6, 175 MHz, 298 K) of complex **5**.

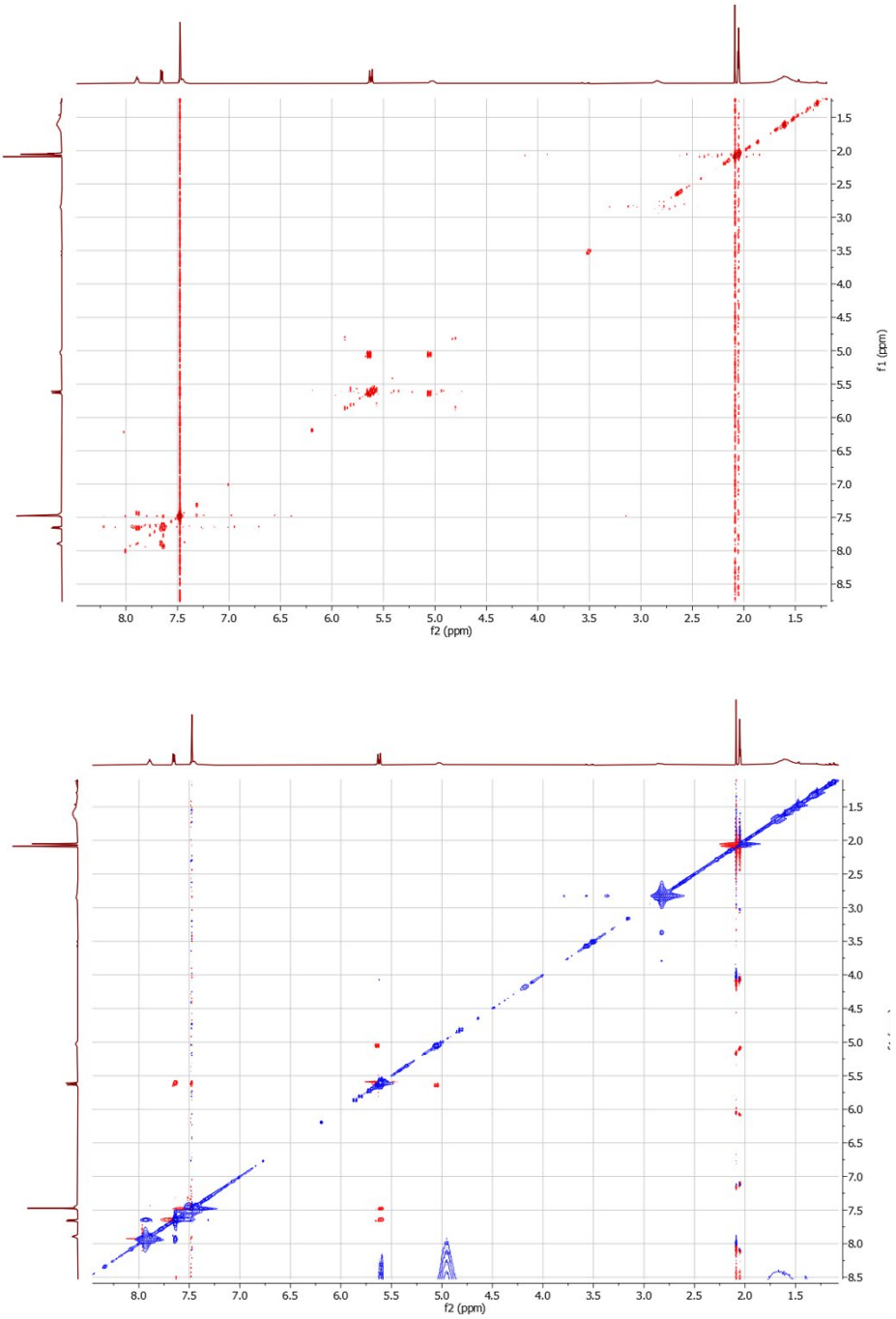


Fig S35. 2D COSY spectrum (upper, Acetone-d_6, 700 MHz, 298 K) and 2D NOESY spectrum (lower, Acetone-d_6, 700 MHz, 298 K) of complex **5**.

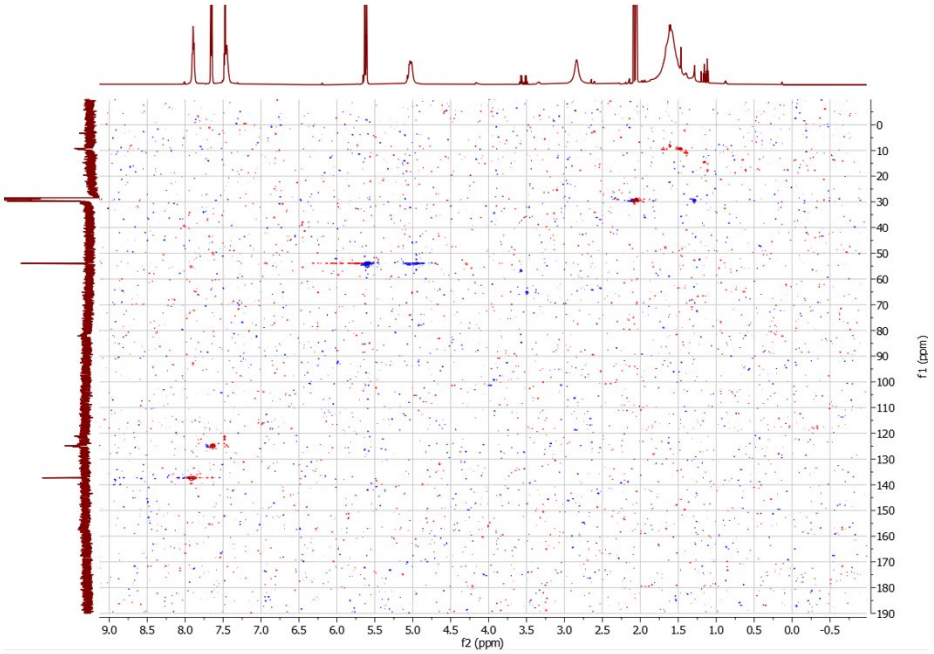
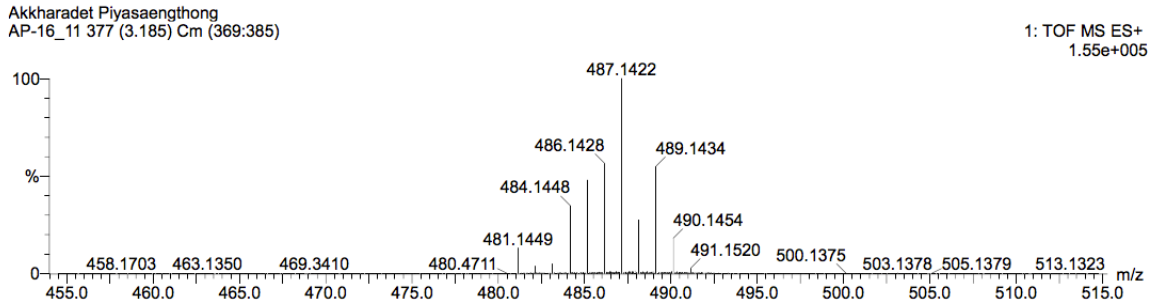


Fig S36. 2D HSQC spectrum (Acetone-d_6, 700 MHz, 298 K) of complex **5**.



Minimum:				-1.5			
Maximum:		3.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
481.1449	481.1428	2.1	4.4	9.5	480.7	1.5	C20 H29 N6 O2 96Ru
	481.1440	0.9	1.9	23.5	480.7	1.5	C33 H21 O4
	481.1453	-0.4	-0.8	28.5	480.8	1.6	C34 H17 N4
	481.1455	-0.6	-1.2	8.5	480.9	1.7	C24 H33 O4 96Ru
	481.1468	-1.9	-3.9	13.5	481.0	1.8	C25 H29 N4 96Ru

Fig S37. Positive ESI HRMS spectra of complex **5**: *m/z* calculated for $[C_{25}H_{19}N_4Ru]^+$: 481.1468, found: 481.1449.

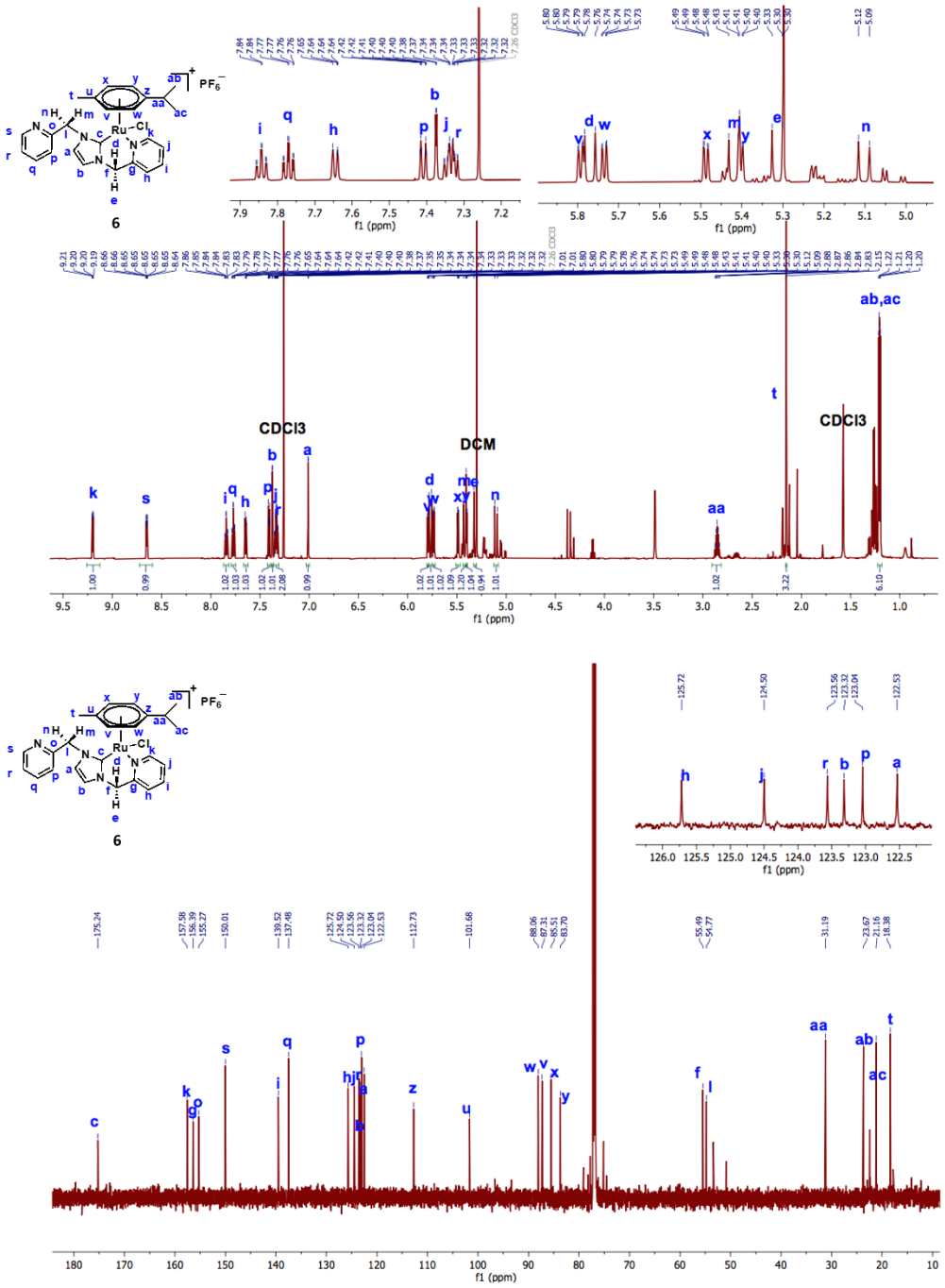


Fig S38. ^{1}H NMR spectrum (upper, Chloroform-*d*, 700 MHz, 298 K) and ^{13}C{^{1}H} NMR spectrum (lower, Chloroform-*d*, 175 MHz, 298 K) of complex **6**.

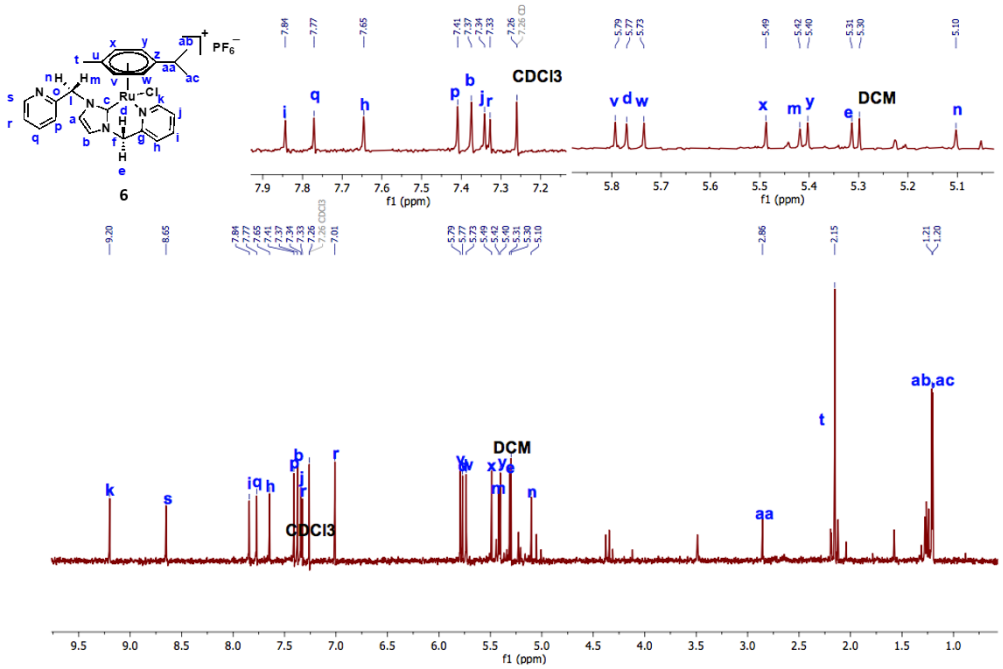


Fig S39. PSYCHE spectrum (Chloroform-*d*, 700 MHz, 298 K) of complex **6**.

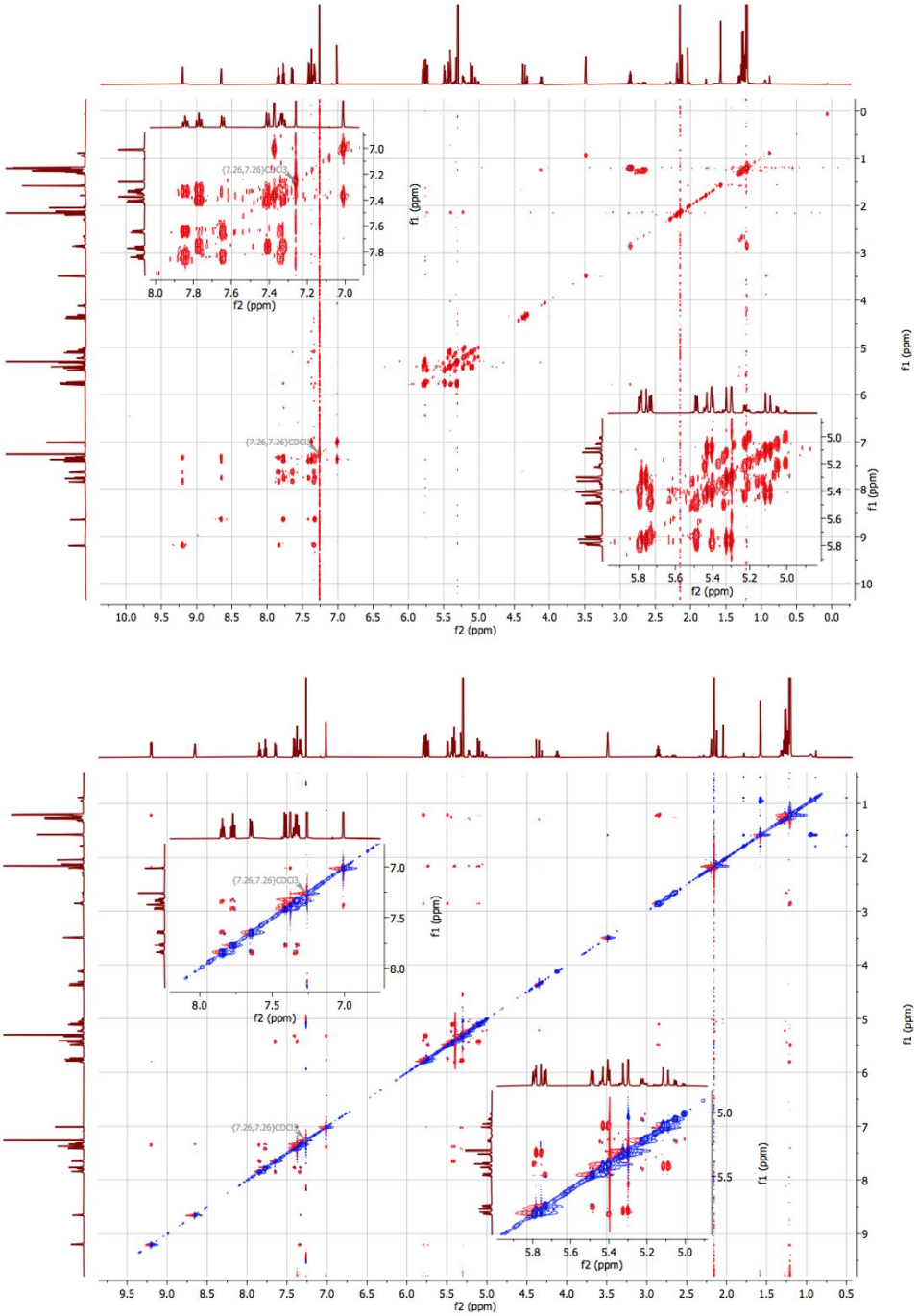


Fig S40. 2D COSY spectrum (upper, Chloroform-*d*, 700 MHz, 298 K) and 2D NOESY spectrum (lower, Chloroform-*d*, 700 MHz, 298 K) of complex **6**.

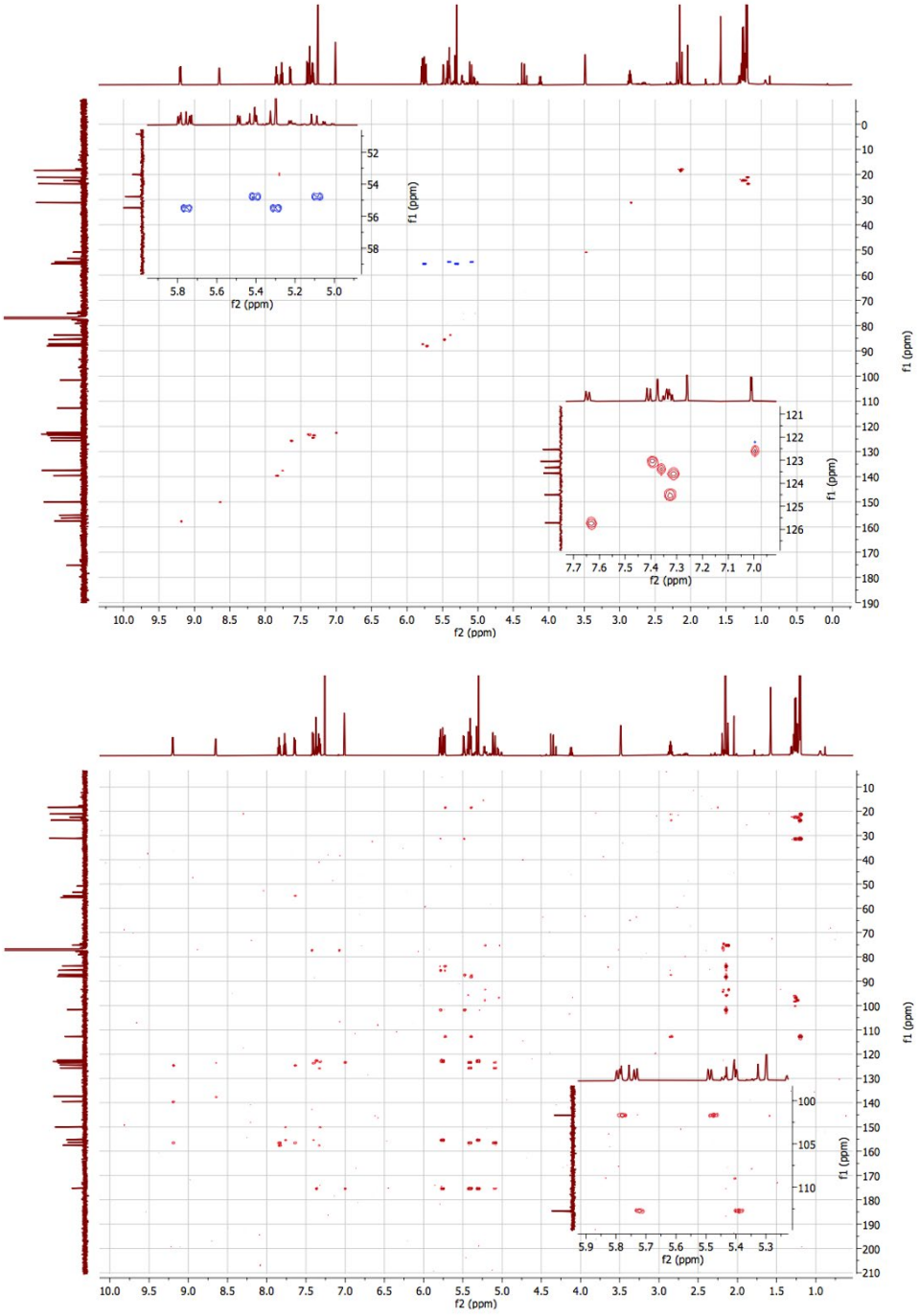
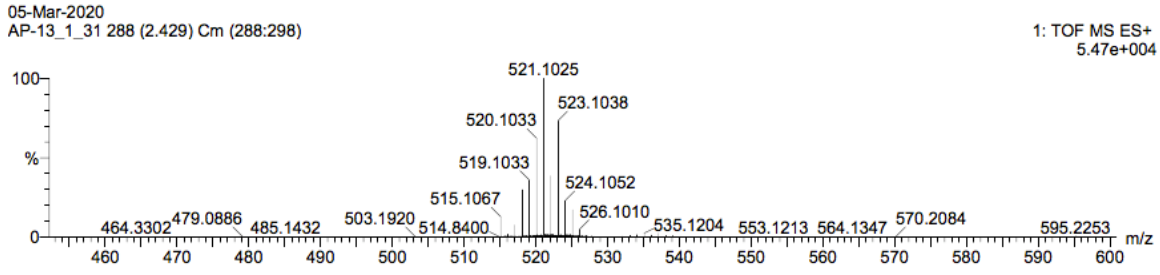


Fig S41. 2D HSQC spectrum (upper, Chloroform-*d*, 700 MHz, 298 K) and 2D HMBC spectrum (lower, Chloroform-*d*, 700 MHz, 298 K) of complex **6**.



Minimum:				-1.5							
Maximum:		3.0	5.0	100.0							
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula				
515.1067	515.1065	0.2	0.4	8.5	704.3	1.7	C24	H32	O4	Cl	96Ru
	515.1063	0.4	0.8	28.5	704.4	1.7	C34	H16	N4	Cl	
	515.1072	-0.5	-1.0	32.5	709.8	7.1	C39	H15	O2		
	515.1060	0.7	1.4	18.5	709.2	6.5	C26	H23	N6	96Ru	
	515.1078	-1.1	-2.1	13.5	704.4	1.7	C25	H28	N4	Cl	96Ru
	515.1082	-1.5	-2.9	15.5	704.0	1.3	C22	H20	N6	O7	Cl
	515.1050	1.7	3.3	23.5	704.5	1.8	C33	H20	O4	Cl	
	515.1047	2.0	3.9	13.5	709.0	6.3	C25	H27	N2	O4	96Ru
	515.1087	-2.0	-3.9	17.5	709.8	7.1	C30	H27	O2	96Ru	
	515.1045	2.2	4.3	33.5	709.3	6.6	C35	H11	N6		

Fig S42. Positive ESI HRMS spectra of complex **6**: *m/z* calculated for $[C_{25}H_{28}N_4{}^{35}Cl{}^{96}Ru]^+$: 515.1078, found: 515.1067.

2. Single-crystal X-Ray crystallography

Table S1 Crystal data and structure refinement.

Compound	**2**	**5**	**L0**	**L1**
Empirical formula	$C_{32}H_{36}Cl_2N_4O_{2.5}PRu$	$C_{26}H_{31}Cl_2F_6N_4PRu$	$C_{12}H_{10}Br_2N_2$	$C_{12}H_{19}Cl_3N_4O$
Formula weight	719.59	716.49	342.04	341.66
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C2/c	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	19.9245(9)	12.6371(4)	12.0100(4)	11.2416(11)
b/Å	11.0559(5)	14.0622(5)	4.4177(2)	6.6518(7)
c/Å	30.7401(14)	16.8293(6)	10.9527(4)	21.523(2)
α/°	90	90	90	90
β/°	107.531(2)	94.3000(10)	94.1004(14)	104.610(3)
γ/°	90	90	90	90
Volume/Å^3	6457.0(5)	2982.24(18)	579.63(4)	1557.4(3)
Z	8	4	2	4
ρ_{calc}g/cm^3	1.480	1.596	1.960	1.457
μ/mm^{-1}	0.738	0.820	6.964	0.589
F(000)	2952.0	1448.0	332.0	712.0
Reflections collected	55339	44067	8661	30404
Independent refl., R_{int}	9406, 0.0522	8700, 0.0501	1609, 0.0268	4131, 0.0804
Data/restraints/parameters	9406/8/396	8700/114/457	1609/0/73	4131/7/261
Goodness-of-fit on F^2	1.071	1.075	1.126	1.101
Final R_1 [≥2σ (I)]	0.0404	0.0662	0.0201	0.0675
Final wR_2 [all data]	0.1024	0.1721	0.0520	0.1684
Largest diff. peak/hole /e Å^{-3}	1.01/-1.57	1.54/-1.14	1.14/-0.30	0.98/-0.60

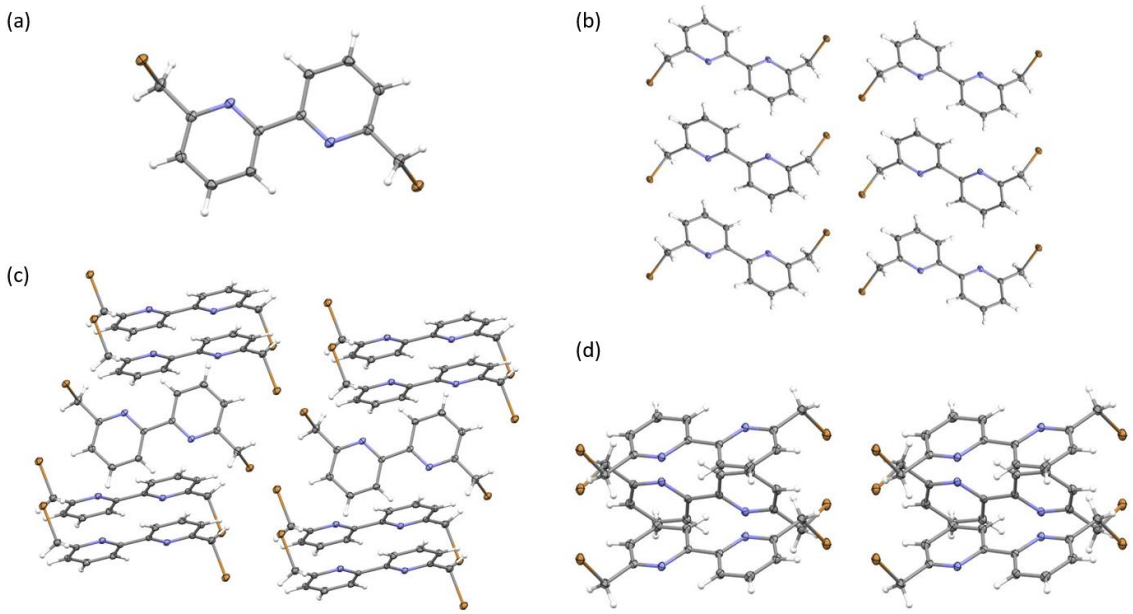


Fig S43. Molecular and packing structures of **L0** with thermal ellipsoids shown at 50% probability.

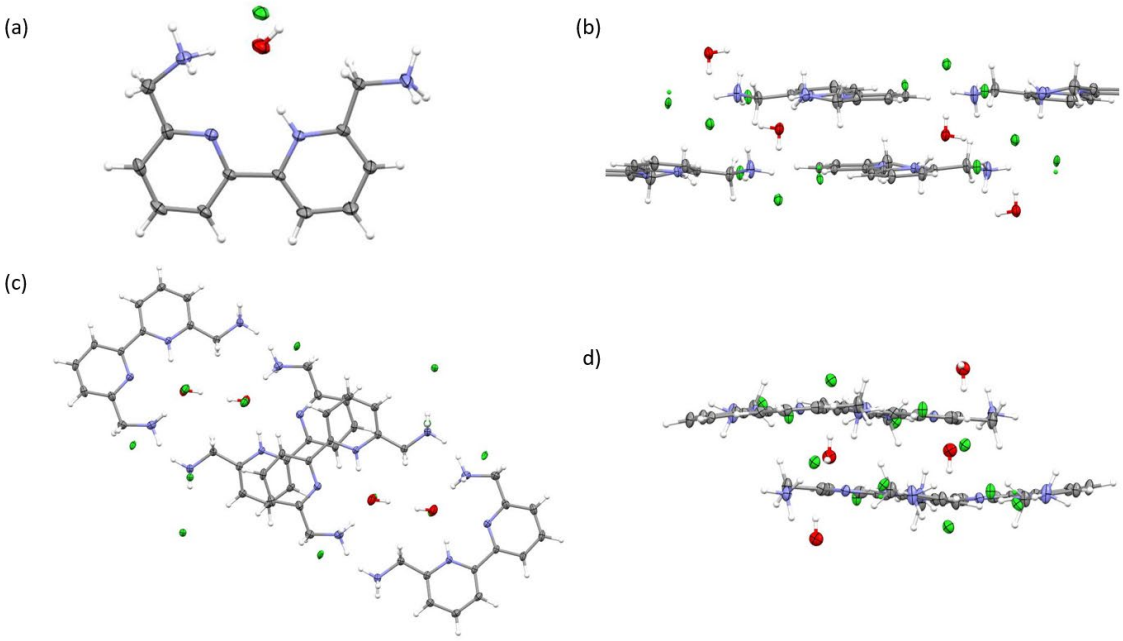


Fig S44. Molecular and packing structures of **L1** with thermal ellipsoids shown at 50% probability.

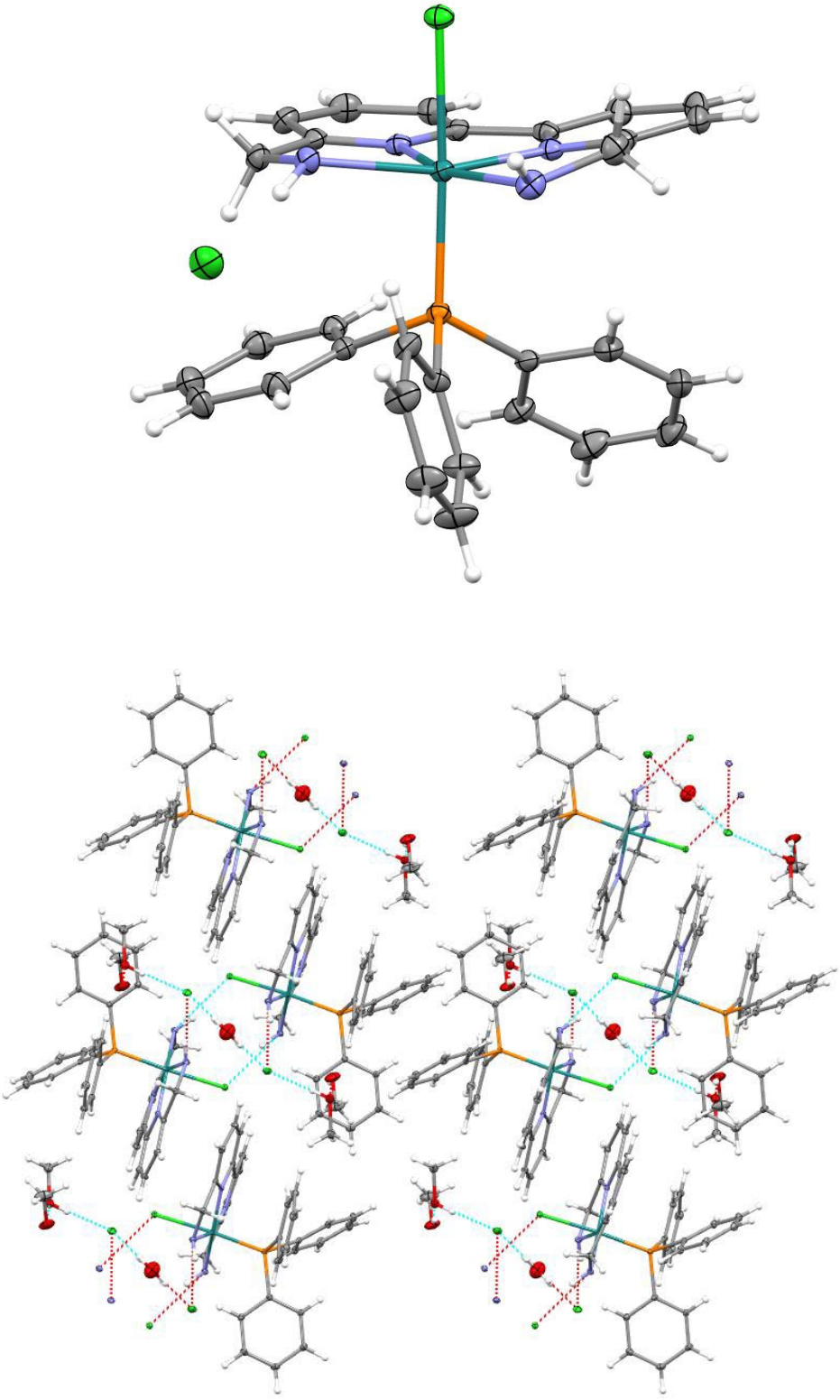


Fig S45. Molecular and packing structures of **2** with thermal ellipsoids shown at 50% probability.

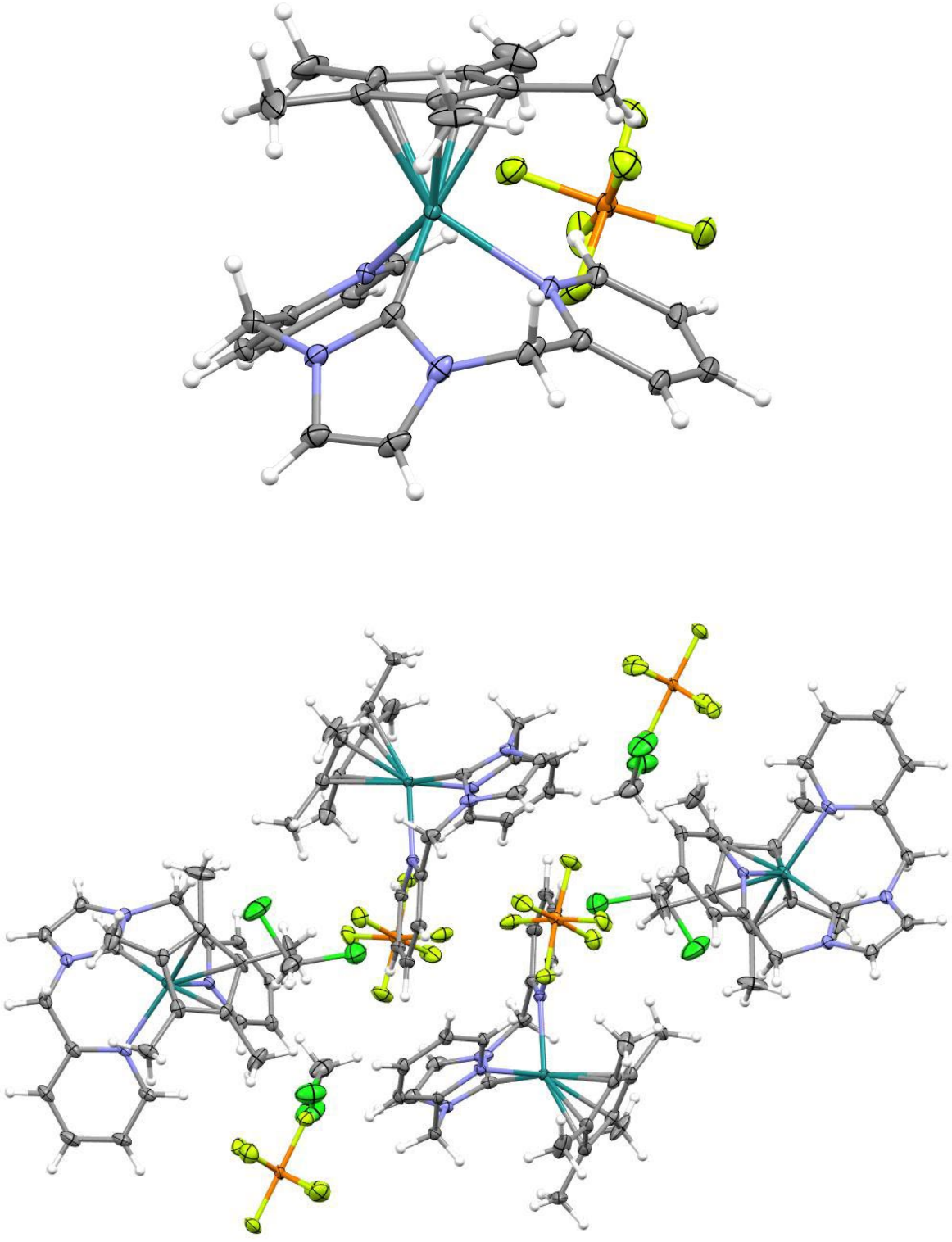


Fig S46. Molecular and packing structures of **5** with thermal ellipsoids shown at 20% probability.

3. Typical procedure for transfer hydrogenation of ketones

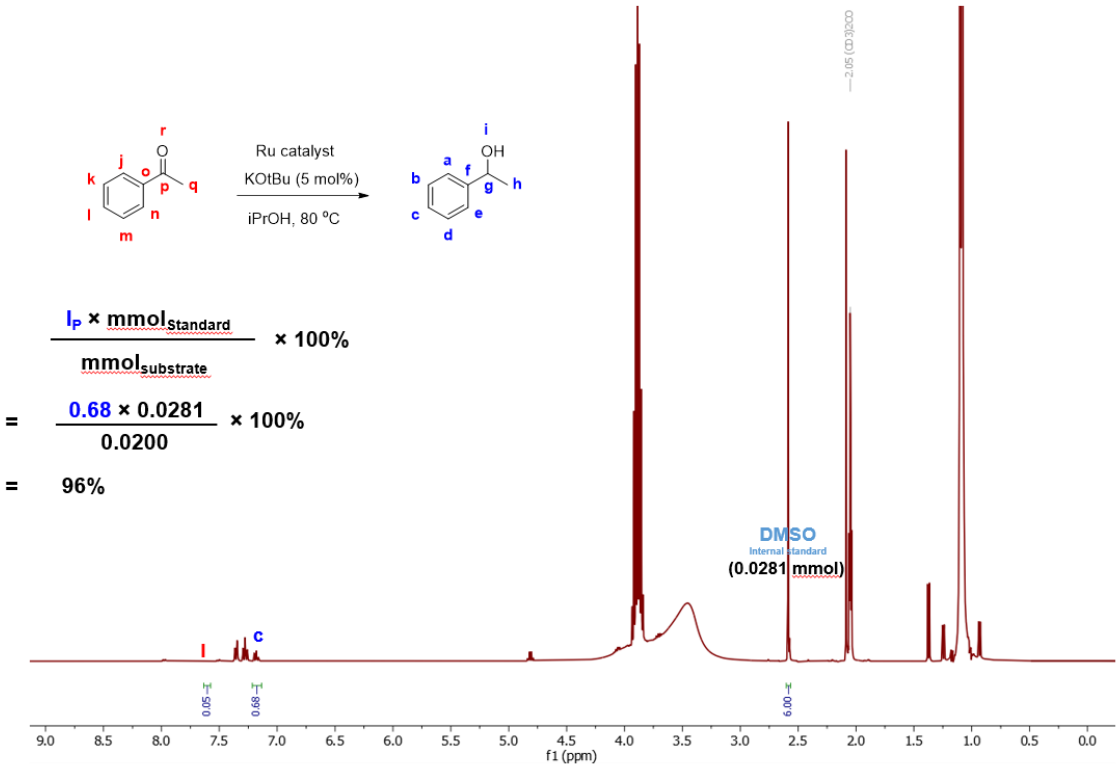


Fig S47. Demonstrate the calculated percent conversion by NMR spectroscopy.

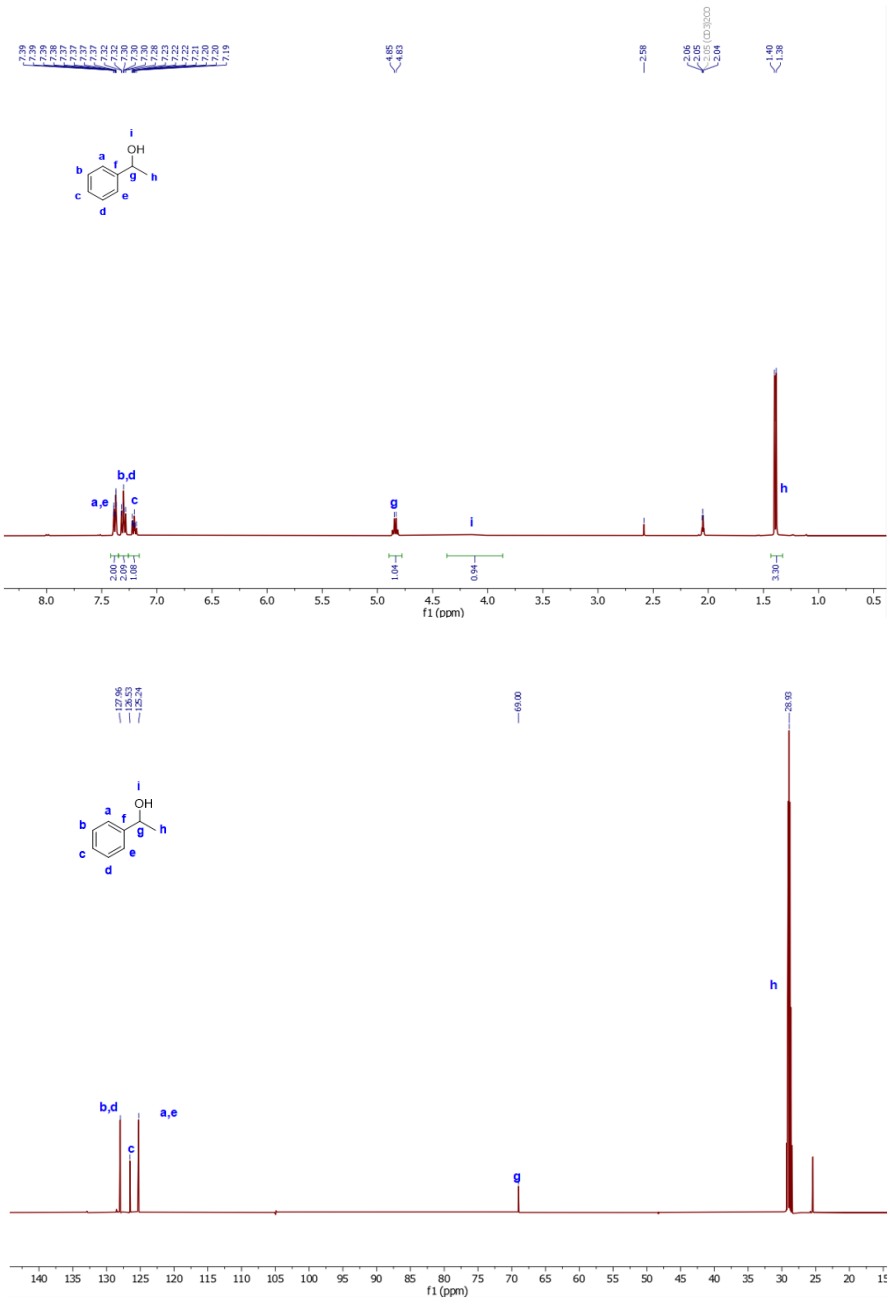


Fig S48. ^{1}H NMR spectrum (upper, Acetone-d_6, 600 MHz, 298 K) and ^{13}C{^{1}H} NMR spectrum (lower, Acetone-d_6, 151 MHz, 298 K) of 1-phenylethanol.

4. Kinetic analysis

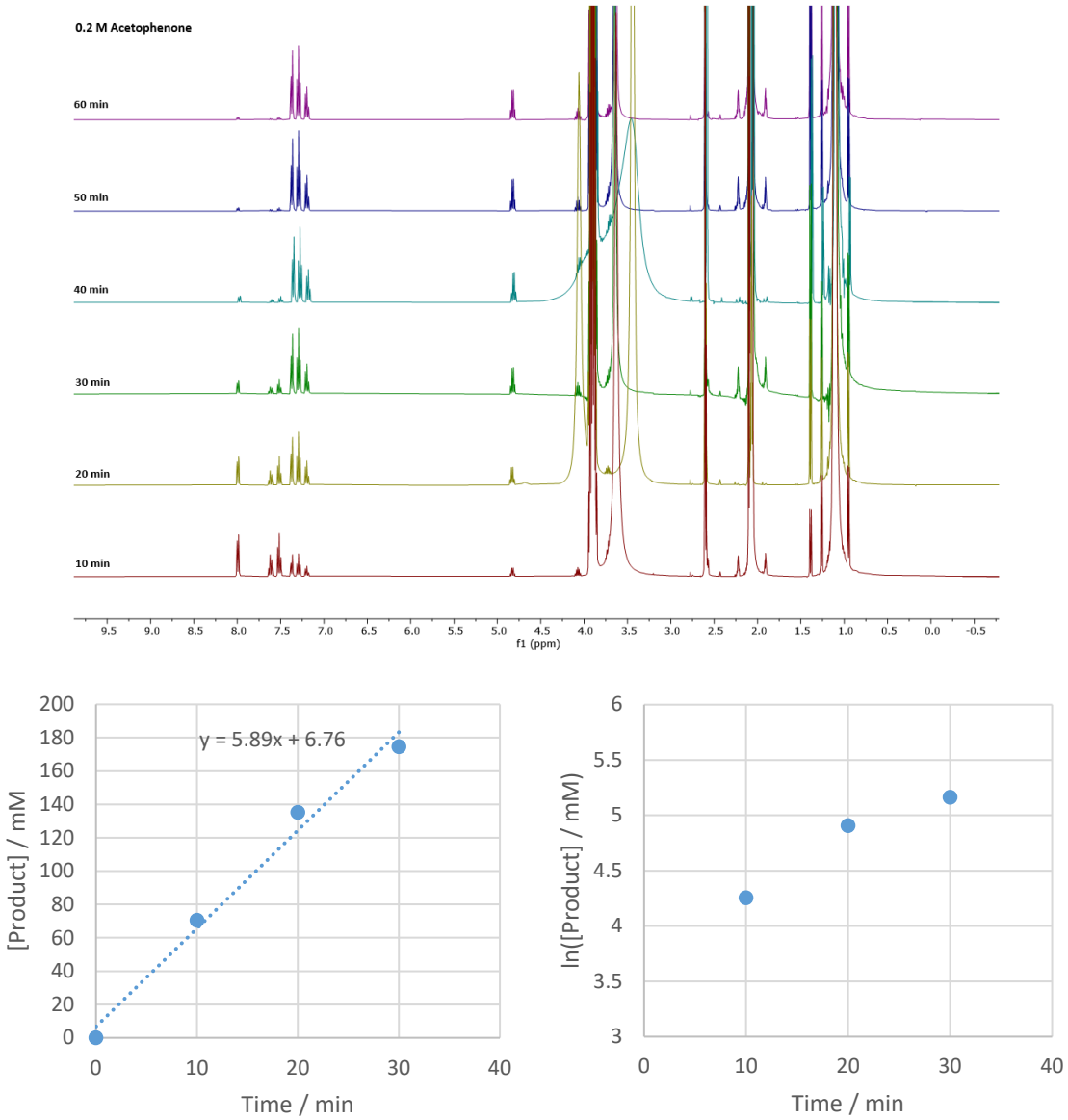


Fig S49. *Upper* Stacked ^{1}H NMR spectrums (Acetone-d_6, 400 MHz, 298 K) of acetophenone TH catalysed by **1** with condition: [Ru] = 2.0 mM, [*i*PrOH] = 13.1 M, [acetophenone]$_0$ = 0.2 M, 80 °C. *Lower* Kinetic data plots, showing a reaction first order in acetophenone.

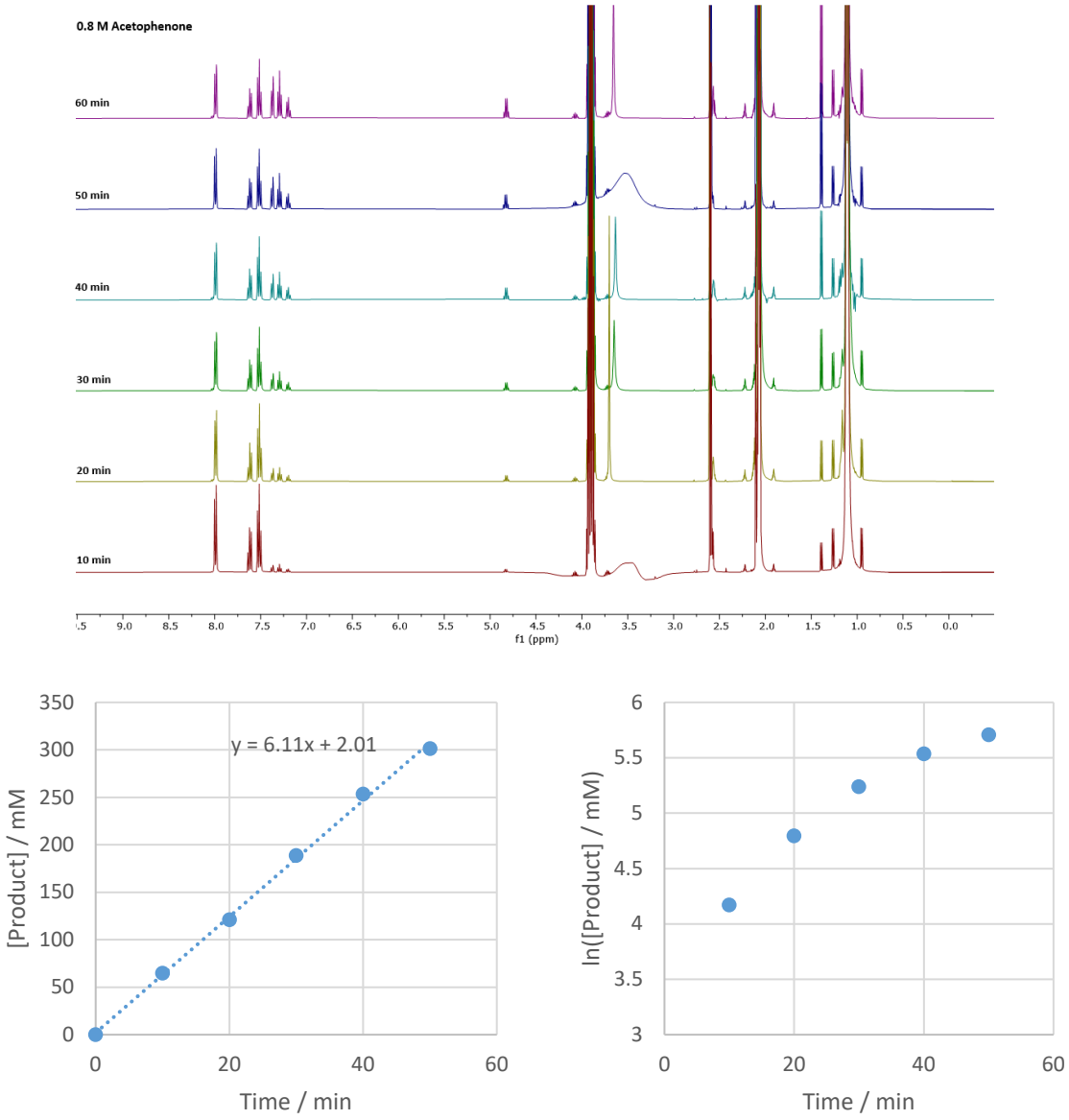


Fig S50. *Upper* Stacked ^{1}H NMR spectrums (Acetone-d_6, 400 MHz, 298 K) of acetophenone TH catalysed by **1** with condition: [Ru] = 2.0 mM, [*i*PrOH] = 13.1 M, [acetophenone]$_0$ = 0.8 M, 80 °C. *Lower* Kinetic data plots, showing a reaction first order in acetophenone.

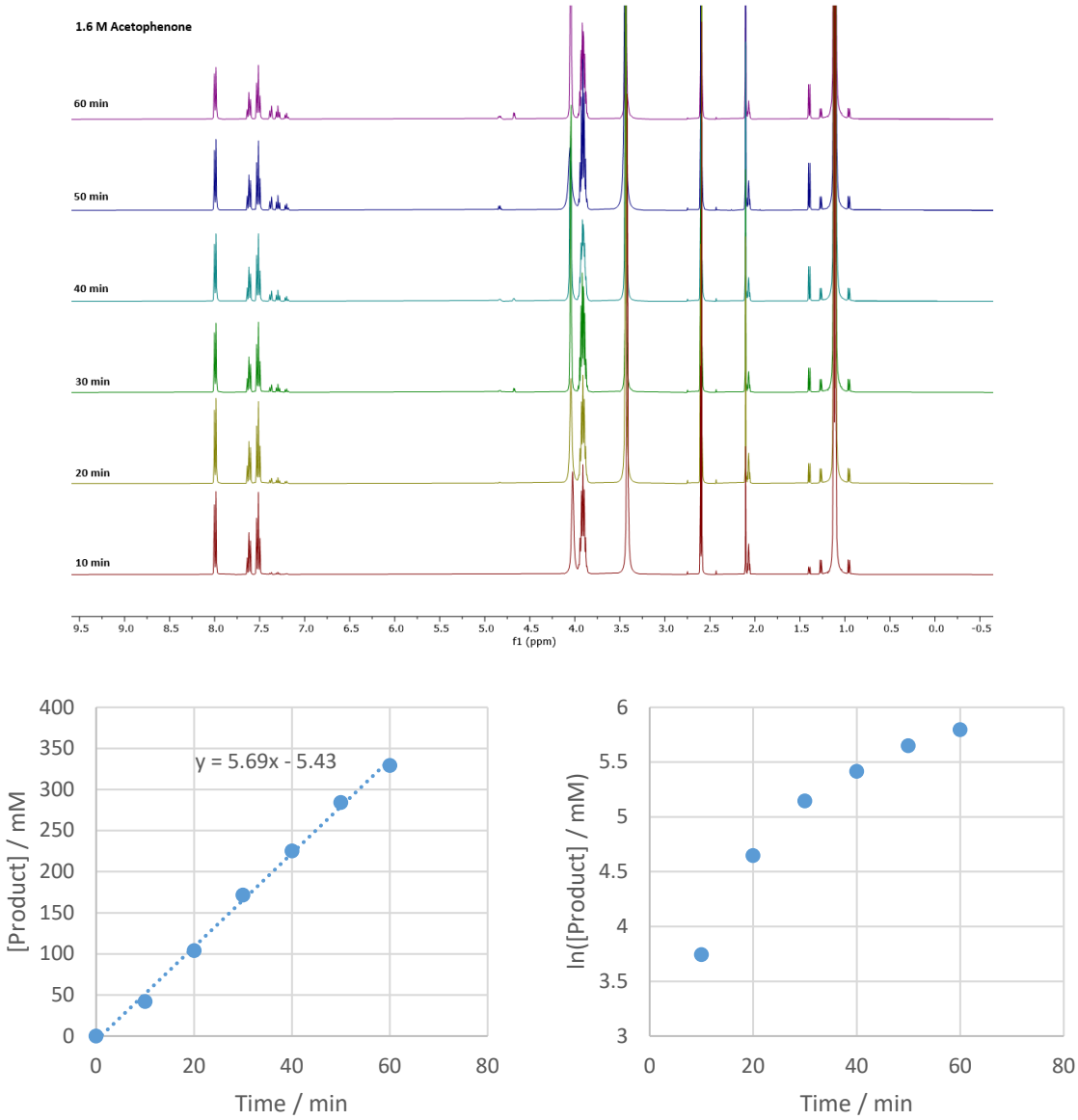


Fig S51. *Upper* Stacked ^{1}H NMR spectrums (Acetone-d_6, 400 MHz, 298 K) of acetophenone TH catalysed by **1** with condition: [Ru] = 2.0 mM, [*i*PrOH] = 13.1 M, [acetophenone]$_0$ = 1.6 M, 80 °C. *Lower* Kinetic data plots, showing a reaction first order in acetophenone.

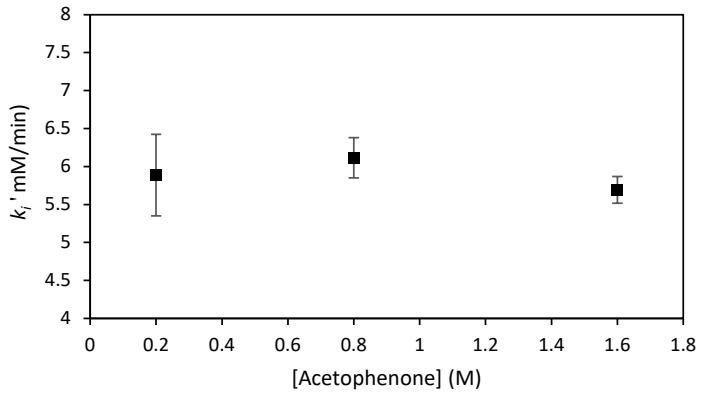


Fig S52 Kinetic analytical dependence of acetophenone on the initial rates (k_i) of Acetophenone TH catalysed by **1** with conditions: [Ru] = 2.0 mM, [*i*PrOH] = 13.1 M, $[acetophenone]_0$ = 0.2-1.6 M, 80 °C

5. Eyring analysis

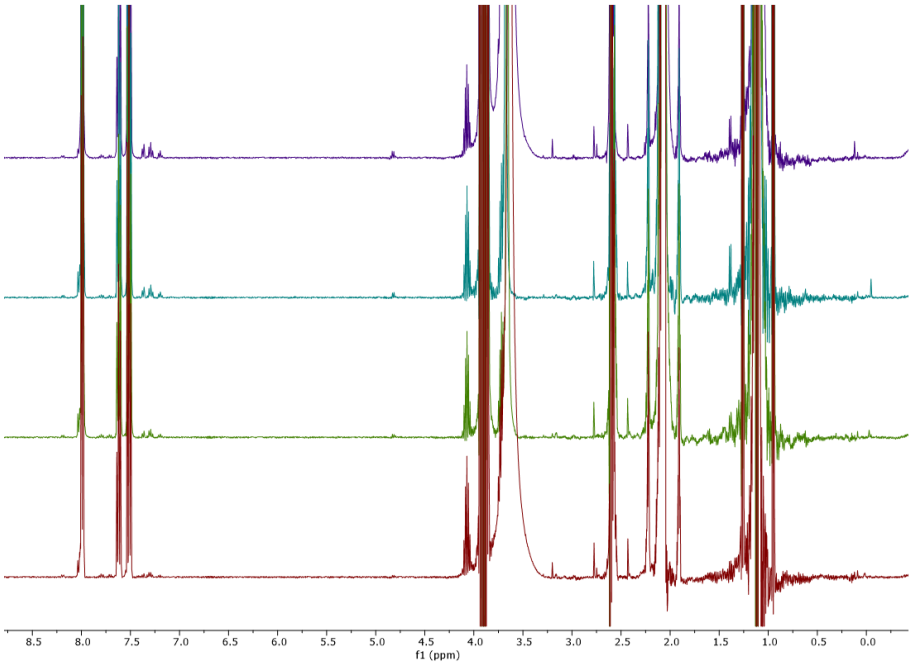


Fig S53. Stacked ^{1}H NMR spectrums (Acetone-d_6, 400 MHz, 298 K) of acetophenone TH catalysed by **1** with condition: Ru:KO*t*Bu:acetophenone = 1:5:100 at temperatures 50 °C. From *bottom* to *top* 5 min, 10 min, 15 min, 20 min.

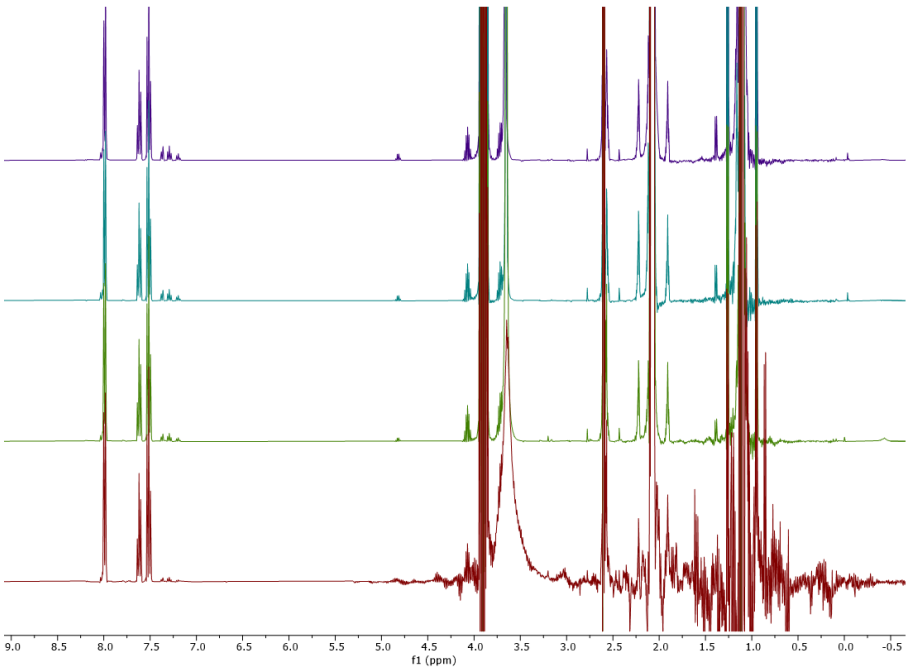


Fig S54. Stacked ^{1}H NMR spectrums (Acetone-d_6, 400 MHz, 298 K) of acetophenone TH catalysed by **1** with condition: Ru:KO*t*Bu:acetophenone = 1:5:100 at temperatures 60 °C. From *bottom* to *top* 5 min, 10 min, 15 min, 20 min.

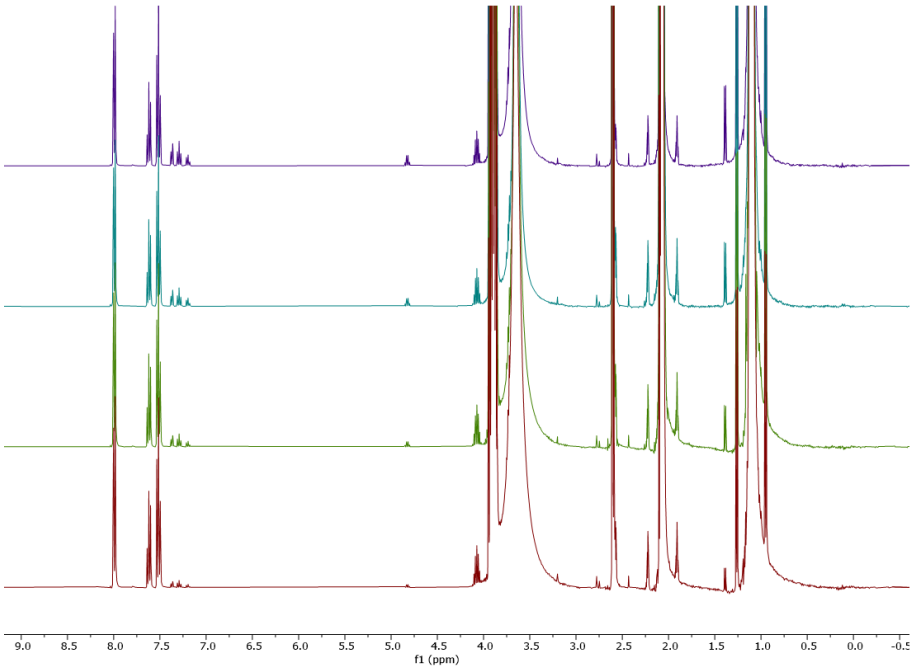


Fig S55. Stacked ^{1}H NMR spectrums (Acetone-d_6, 400 MHz, 298 K) of acetophenone TH catalysed by with condition: Ru:KO*t*Bu:acetophenone = 1:5:100 at temperatures 70 °C. From *bottom* to *top* 5 min, 10 min, 15 min, 20 min.

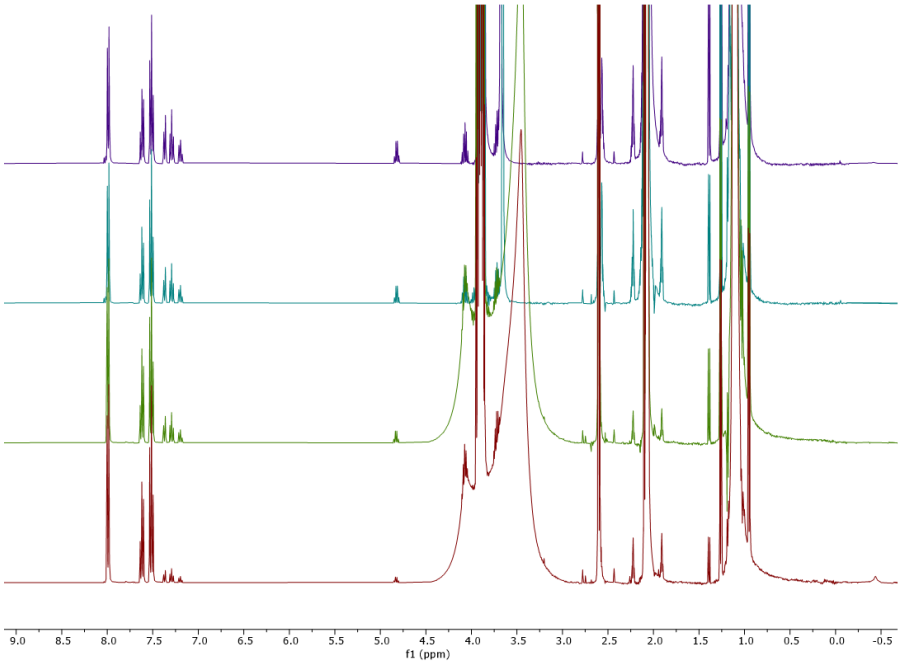


Fig S56. Stacked ^{1}H NMR spectrums (Acetone-d_6, 400 MHz, 298 K) of acetophenone TH catalysed by **1** with condition: Ru:KO*t*Bu:acetophenone = 1:5:100 at temperatures 80 °C. From *bottom* to *top* 5 min, 10 min, 15 min, 20 min.

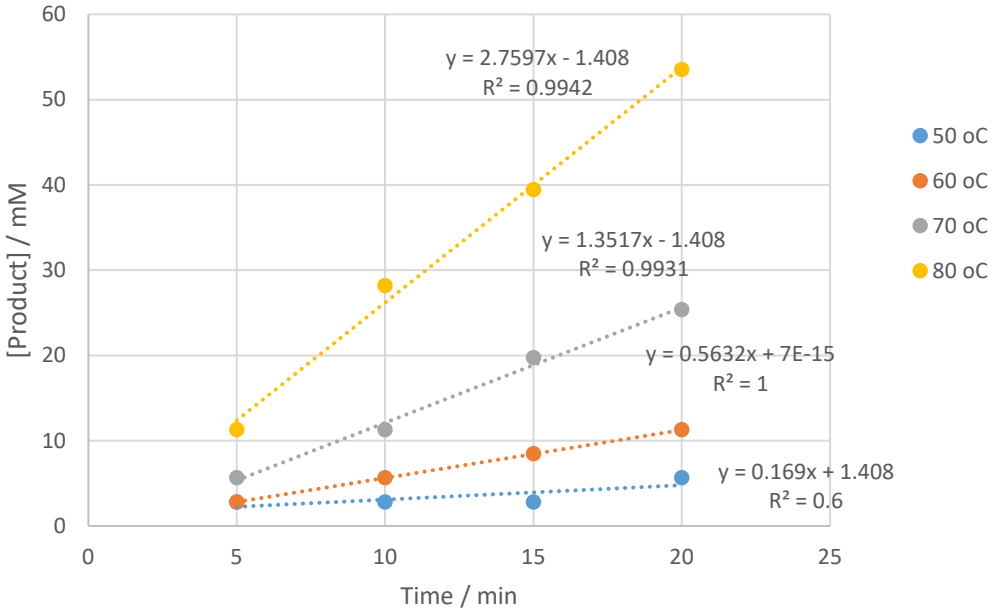


Fig S57. Summary of kinetic data for Eyring analysis.

Table S2 Eyring analysis of catalytic transfer hydrogenation of acetophenone in 2-propanol.

Time(min)	1-phenylethanol (mM)[a]			
	50 °C	60 °C	70 °C	80 °C
5	2.82	2.82	5.63	11.26
10	2.82	5.63	11.26	28.16
15	2.82	8.45	19.71	39.42
20	5.63	11.26	25.34	53.50
Initial rate (k) (mM/min)	0.17	0.56	1.35	2.76
ln(k/T)	-7.56	-6.38	-5.54	-4.85
1/T ($K^{-1} \times 10^{-3}$)	3.09	3.00	2.91	2.83

Reaction conditions: Ru:KO*t*Bu:acetophenone = 1:5:100 at temperatures 50-80 °C. [a]Determined by ^{1}H NMR spectroscopy using dimethyl sulfoxide as internal standard, conversions correspond to yields.

According to Eyring equation: $\ln\frac{k}{T} = \frac{-\Delta H^{\ddagger}}{R} \cdot \frac{1}{T} + \ln\frac{K_B}{h} + \frac{\Delta S^{\ddagger}}{R}$

Eyring plot between ln(k/T) and 1/T obtains a straight linear with negative slope ($\frac{-\Delta H^{\ddagger}}{R}$) and a y-intercept ($\ln\frac{K_B}{h} + \frac{\Delta S^{\ddagger}}{R}$). See main text.

Slope: $(\frac{-\Delta H^{\ddagger}}{R})$ = -10.2

$\Delta H^{\ddagger}$ = 85.3 kJ mol^{-1}

y-intercept $(\ln\frac{K_B}{h} + \frac{\Delta S^{\ddagger}}{R})$ = 24.3

$\Delta S^{\ddagger}$ = 4.2 J mol^{-1} K^{-1}

At 80 °C $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$

$\Delta G^{\ddagger} = 85.3 - (353)(0.0042)$

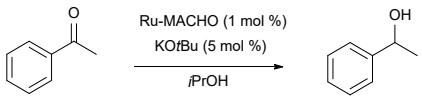
$\Delta G^{\ddagger} = 83.8$ kJ mol^{-1}

6. Catalytic activity of Ru-MACHO in TH of acetophenone

Procedure

Ru-MACHO catalyst (1 mol%) and base (5 mol%) were added into a microwave vial with a magnetic stirring bar. After replacing atmosphere with nitrogen gas four times, 2.5 mL of degassed anhydrous 2-propanol were added and stirred for 30 min. Acetophenone (0.05 mmol) was added into the solution and stirred with/without heat. DI water (0.5 ml) was added to stop the reaction. DMSO (0.05 mL, 0.704 mmol) was added as the internal standard. Around 0.1 mL of the reaction mixture was dissolved in acetone-d_6 to obtain a NMR sample.

Table S4 Catalytic activity of Ru-MACHO in TH of acetophenone.

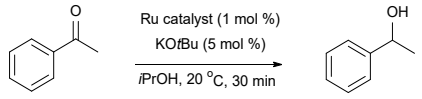


Entry	Cat.	Base	Ketone/base/cat. (mol %)	Temp. (°C)	Time (h)	Conv. (%)[a]
1	Ru-MACHO	KO*t*Bu	100/5/1	80	1	92
2	Ru-MACHO	KO*t*Bu	100/5/1	80	3	96
3	Ru-MACHO	KO*t*Bu	100/5/1	80	5	97
4	Ru-MACHO	KO*t*Bu	100/5/1	80	16	98
5	Ru-MACHO	KO*t*Bu	100/10/1	80	1	89
6	Ru-MACHO	NaOH	100/10/1	80	1	91
7	Ru-MACHO	KOH	100/10/1	80	1	88
8	Ru-MACHO	KO*t*Bu	100/5/1	60	1	93
9	Ru-MACHO	KO*t*Bu	100/5/1	40	1	90
10	Ru-MACHO	KO*t*Bu	100/5/1	20	0.02	28
11	Ru-MACHO	KO*t*Bu	100/5/0.5	20	0.08	79
12	Ru-MACHO	KO*t*Bu	100/5/2.5	20	0.20	82
13	Ru-MACHO	KO*t*Bu	100/5/5	20	0.25	85
14	Ru-MACHO	KO*t*Bu	100/5/5	20	0.50	89
15	Ru-MACHO	KO*t*Bu	100/5/5	20	1	90

Reaction conditions: acetophenone (0.5 mmol), base, Ru catalyst, and 2-propanol (2.5 mL). [a]Determined by ^{1}H NMR spectroscopy using dimethyl sulfoxide as internal standard, conversions correspond to yields.

7. Catalytic activity of complexes 1-6 in TH of acetophenone

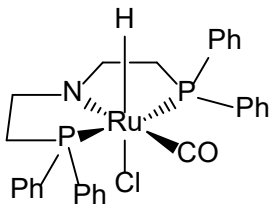
Table S5 Catalytic activity of complexes **1**-**6** in TH of acetophenone at 20 °C.



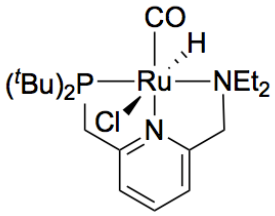
Entry	Cat.	Base	Ketone/base/cat. (mol %)	Temp. (°C)	Time (h)	Conv. (%)[a]
1	**1**	KO*t*Bu	100/5/1	20	0.5	0
2	**2**	KO*t*Bu	100/5/1	20	0.5	0
3	**3**	KO*t*Bu	100/5/1	20	0.5	0
4	**4**	KO*t*Bu	100/5/1	20	0.5	0
5	**5**	KO*t*Bu	100/5/1	20	0.5	0
6	**6**	KO*t*Bu	100/5/1	20	0.5	0
7	Milstein catalyst	KO*t*Bu	100/5/1	20	0.5	0

Reaction conditions: acetophenone (0.5 mmol), base, Ru catalyst, and 2-propanol (2.5 mL). [a]Determined by ^{1}H NMR spectroscopy using dimethyl sulfoxide as internal standard, conversions correspond to yields.

8. Structures of catalysts and Transfer Hydrogenation Mechanism

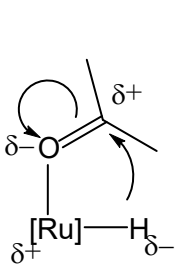


RuMACHO

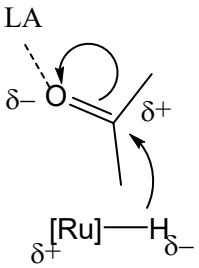


Milstein Catalyst

Figure S58 *left*: RuMACHO ({Bis[2-(diphenylphosphino)ethyl]amine} carboynlchlorohydridoruthenium(II)); *right*: Milstein catalyst [2-(Di-tert-butylphosphinomethyl)-6-(diethylaminomethyl)pyridine] carbonylchlorohydridoruthenium(II)



Inner-sphere
hydride transfer



Inner-sphere
hydride transfer

Figure S59 Hydride transfer step in Inner sphere (IT, *left*) and outer sphere (OT, *right*) Ru-catalysed transfer hydrogenation. LA = Lewis acid or other electrophilic group. Each process can be ligand assisted, whereby polarisation of the ketone is enhanced by ligand coordinated to the [Ru] centre. See article reference 35 for more details.

9. IR Spectra of complexes 1-6

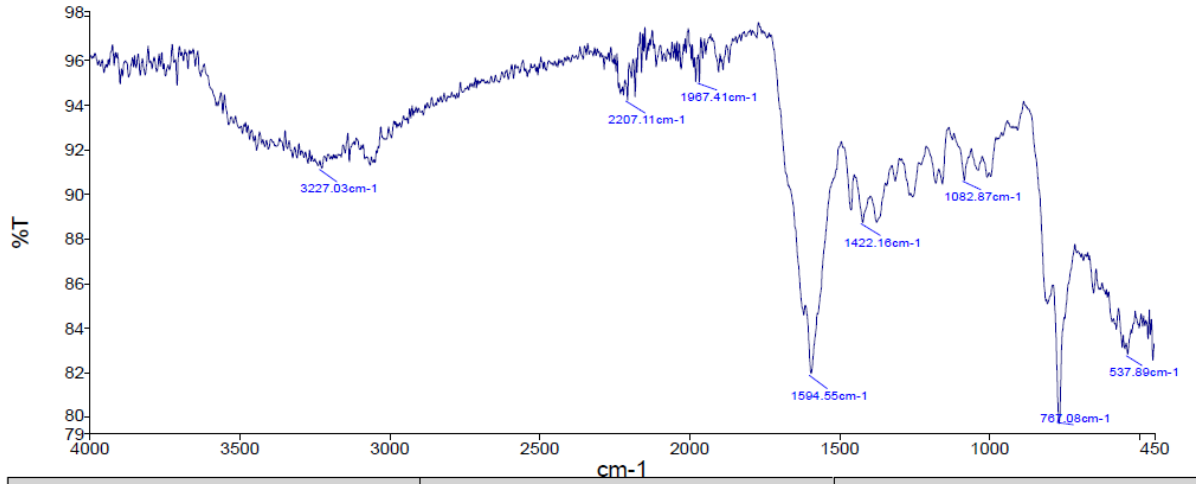


Fig S60 IR spectrum of complex **1.**

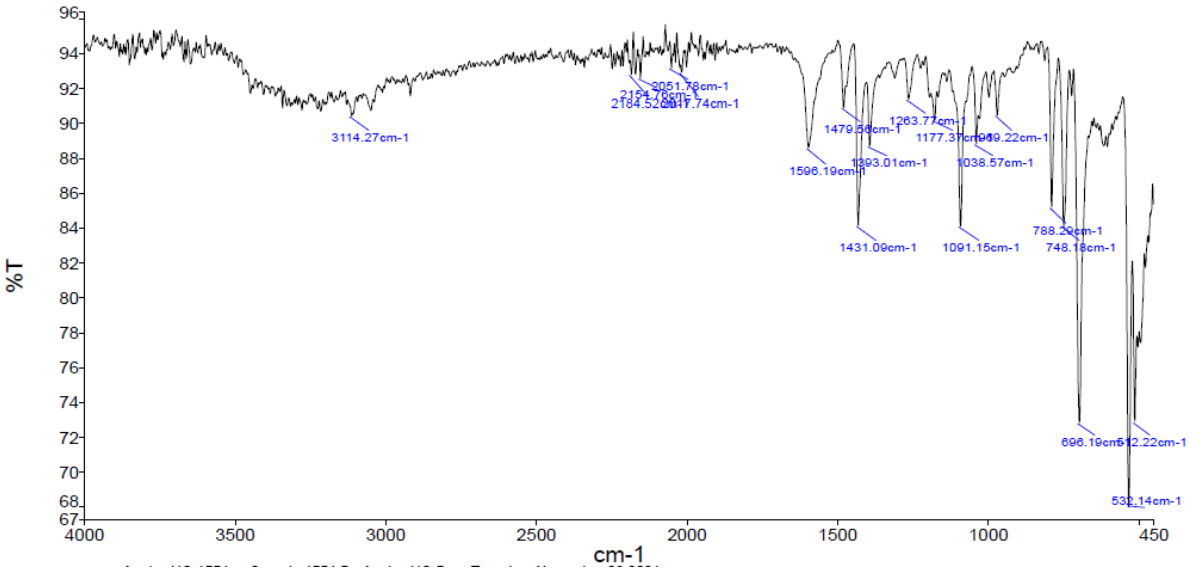


Fig S61 IR spectrum of complex **2.**

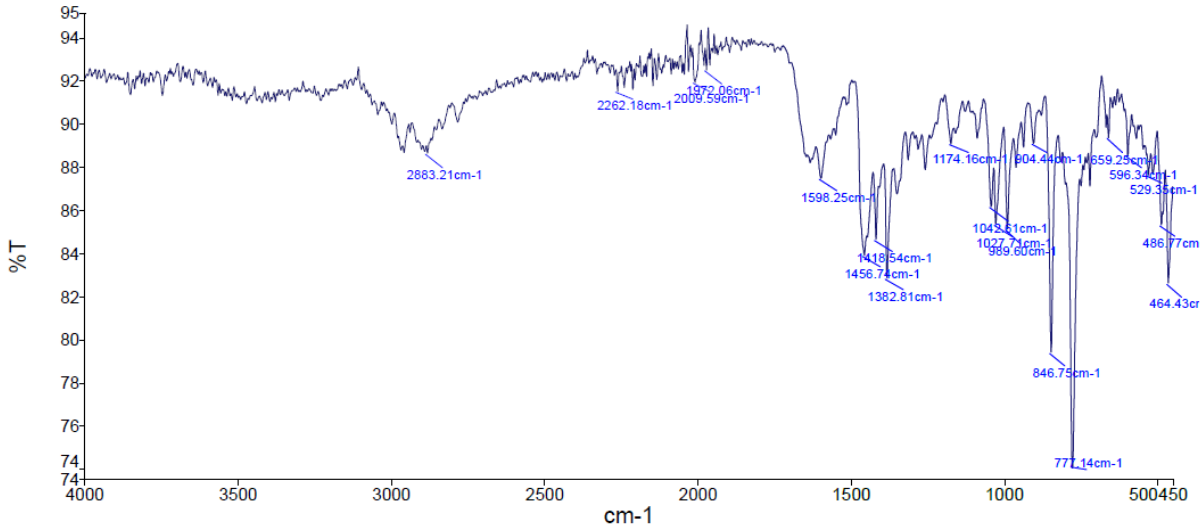


Fig S62 IR spectrum of complex **3.**

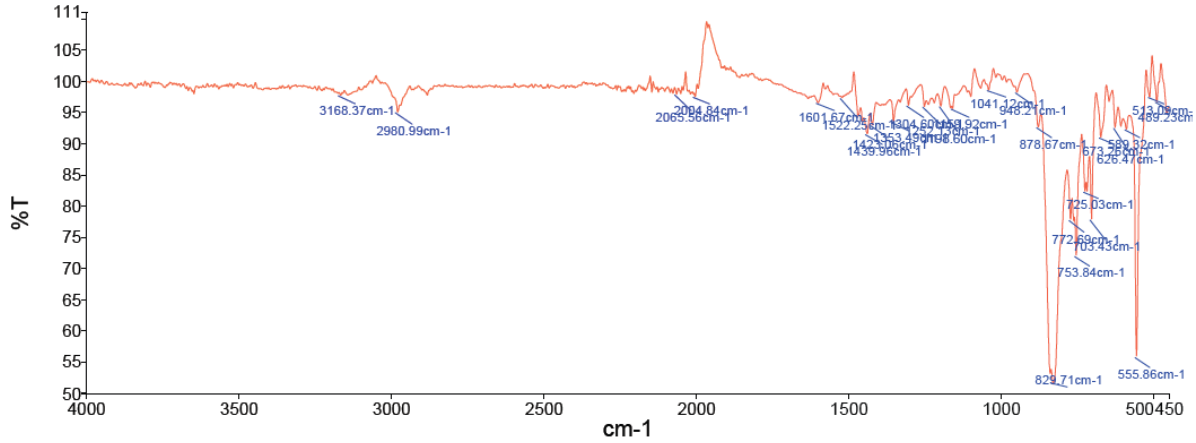


Fig S63 IR spectrum of complex **4.**

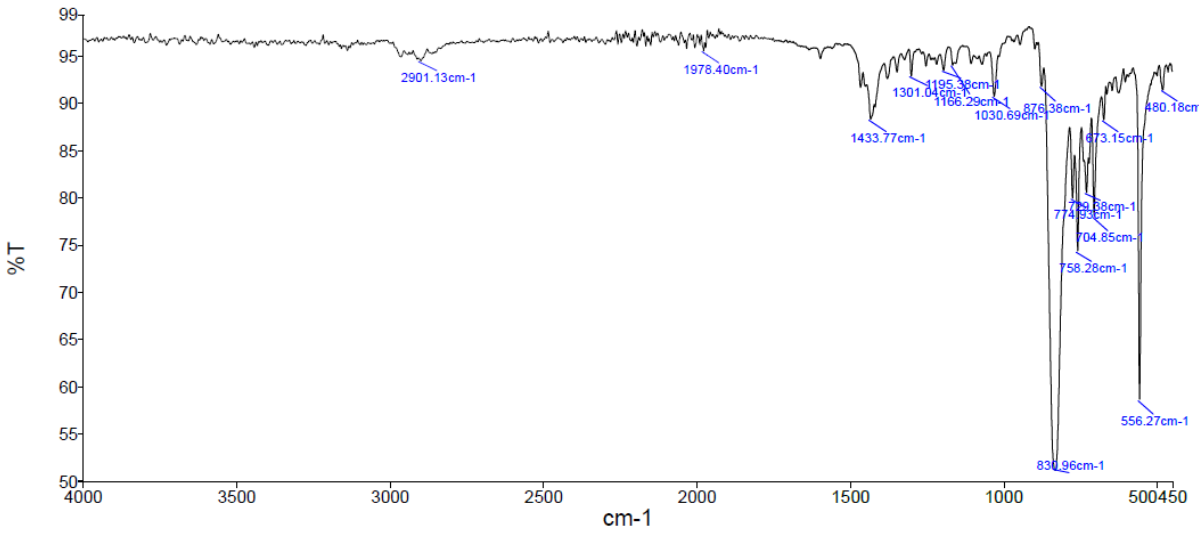


Fig S64 IR spectrum of complex **5.**

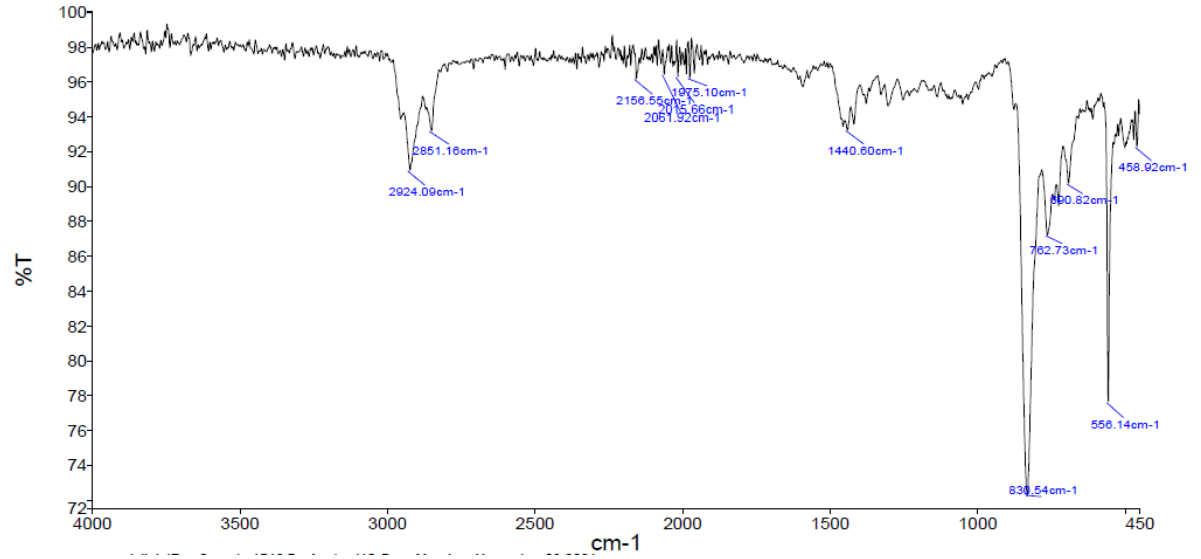


Fig S65 IR spectrum of complex **6.**