Appendix A

Supplementary information for Chapter 2. NMR spectra, HRMS isotopic pattern matching, IR spectra, X-ray crystallographic data, microscopy images of gels, photophysical spectra and supplementary cyclic voltammograms.

A.1. NMR spectra of ligands and complexes

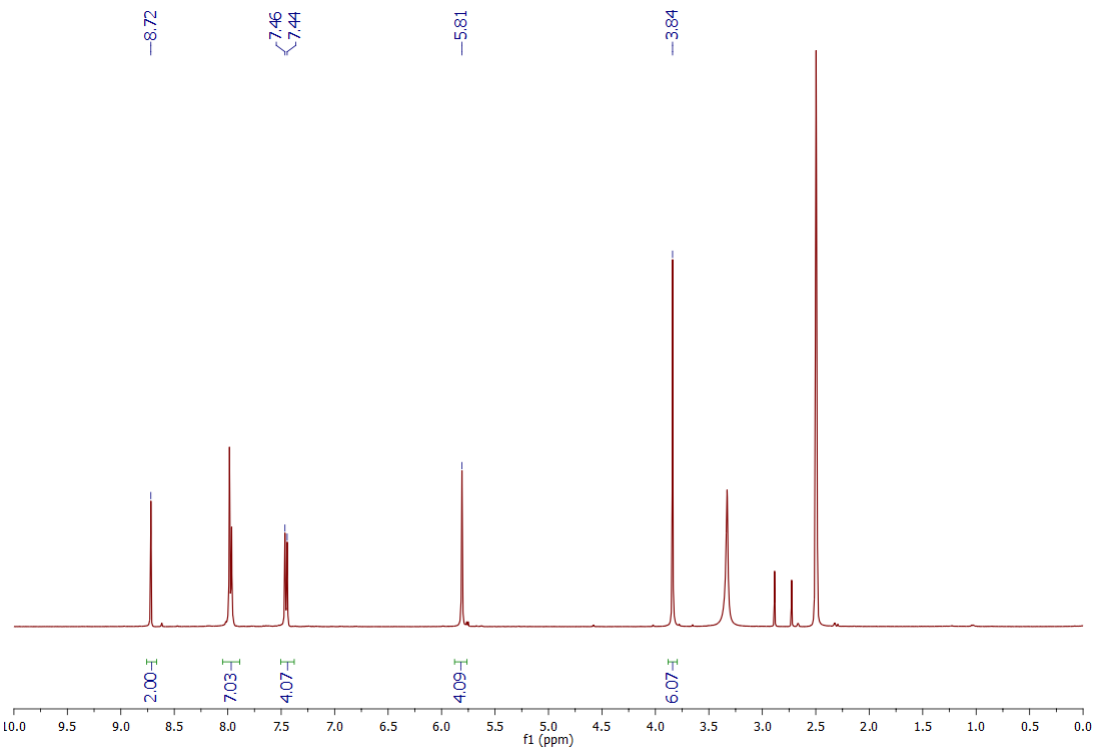

Figure A.1 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of ligand **88**.

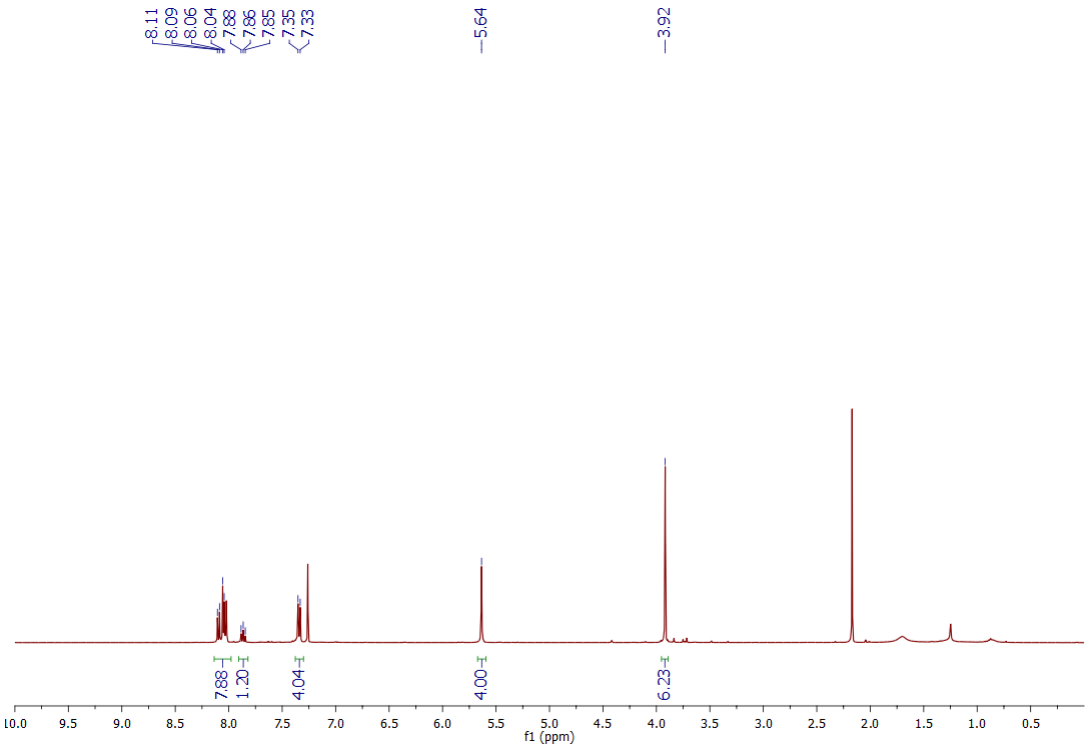

Figure A.2 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ligand **88**.

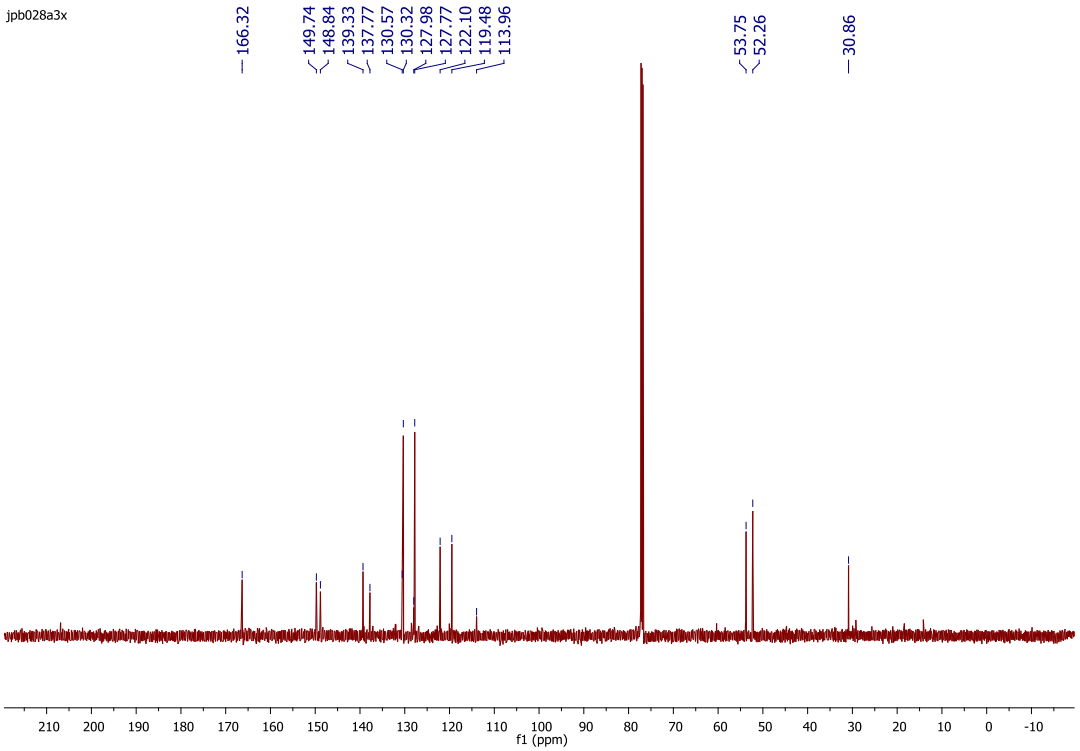

Figure A.3 ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of ligand **88**.

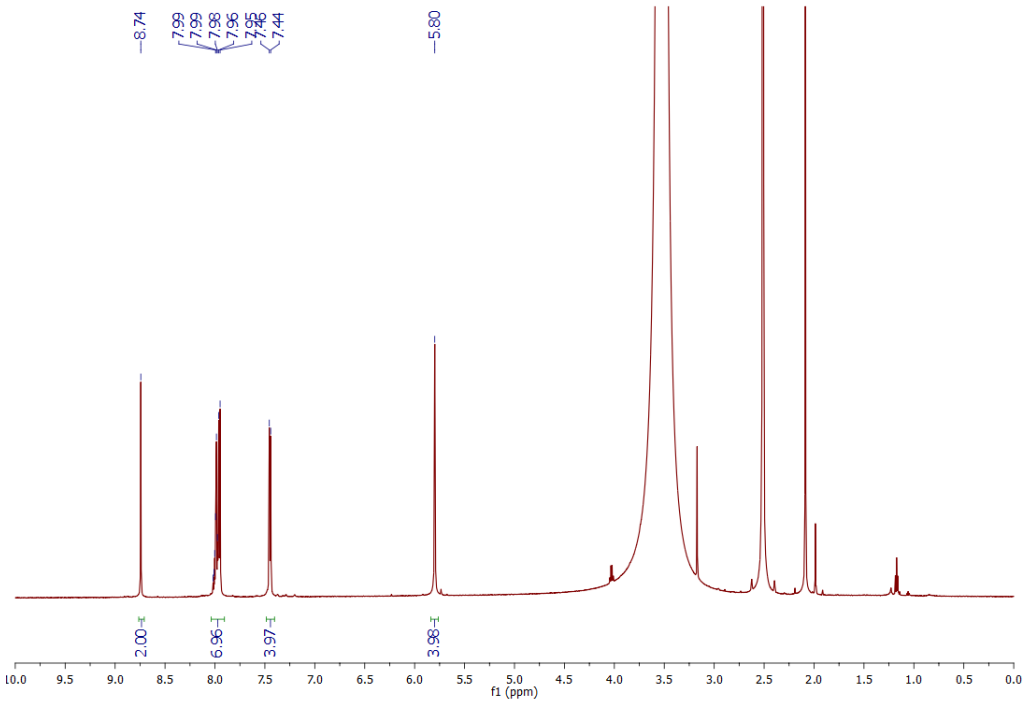

Figure A.4 ^{1}H NMR (600 MHz, DMSO-d_6) spectrum of ligand **89**.

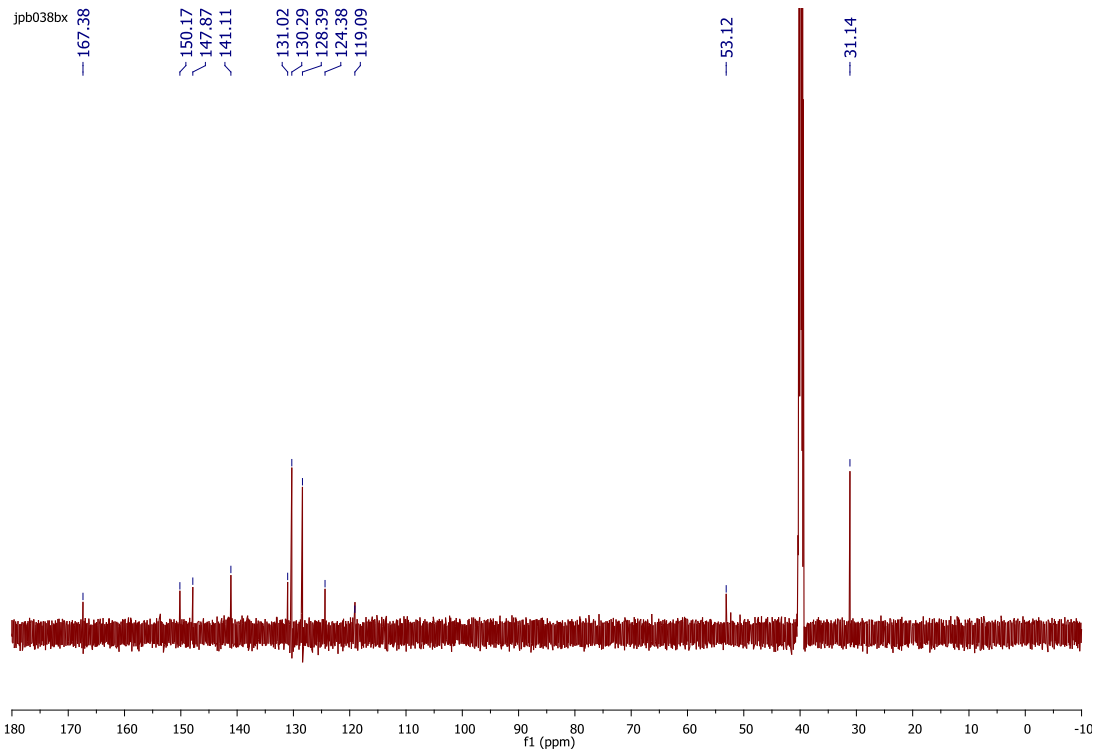

Figure A.5 ^{13}C NMR (150 MHz, DMSO-d_6) spectrum of ligand **89**.

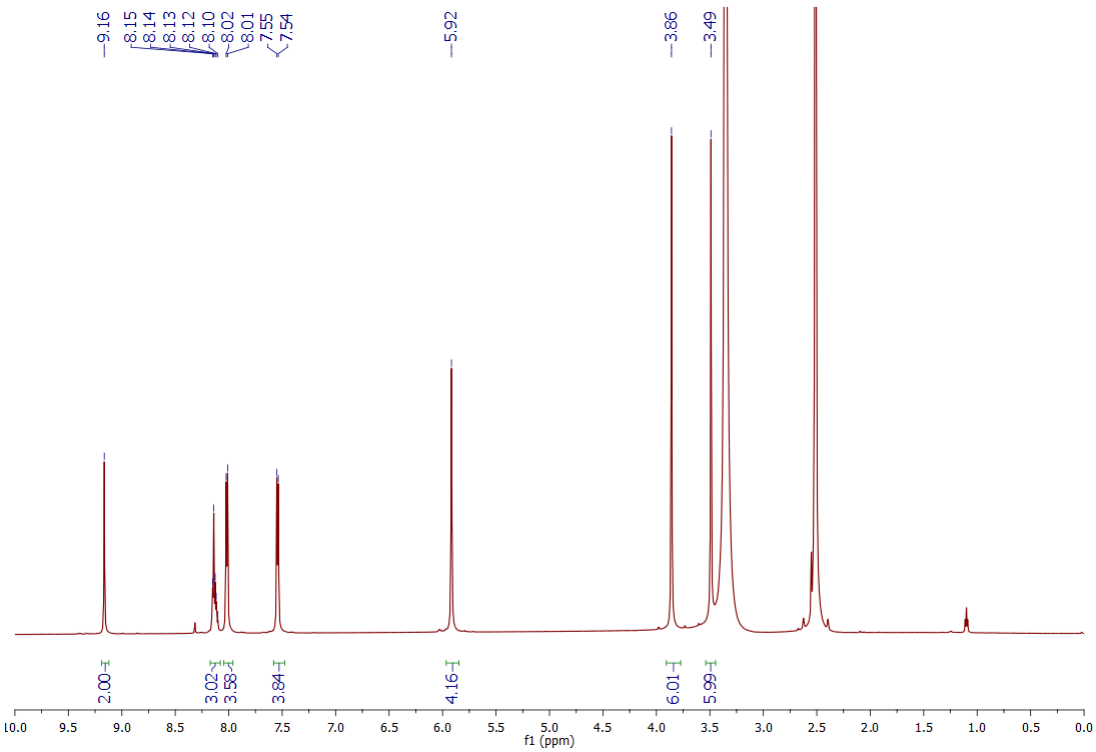

Figure A.6 ^{1}H NMR (600 MHz, DMSO-d_6) spectrum of [Ru·(**88**)Cl_2(DMSO)].

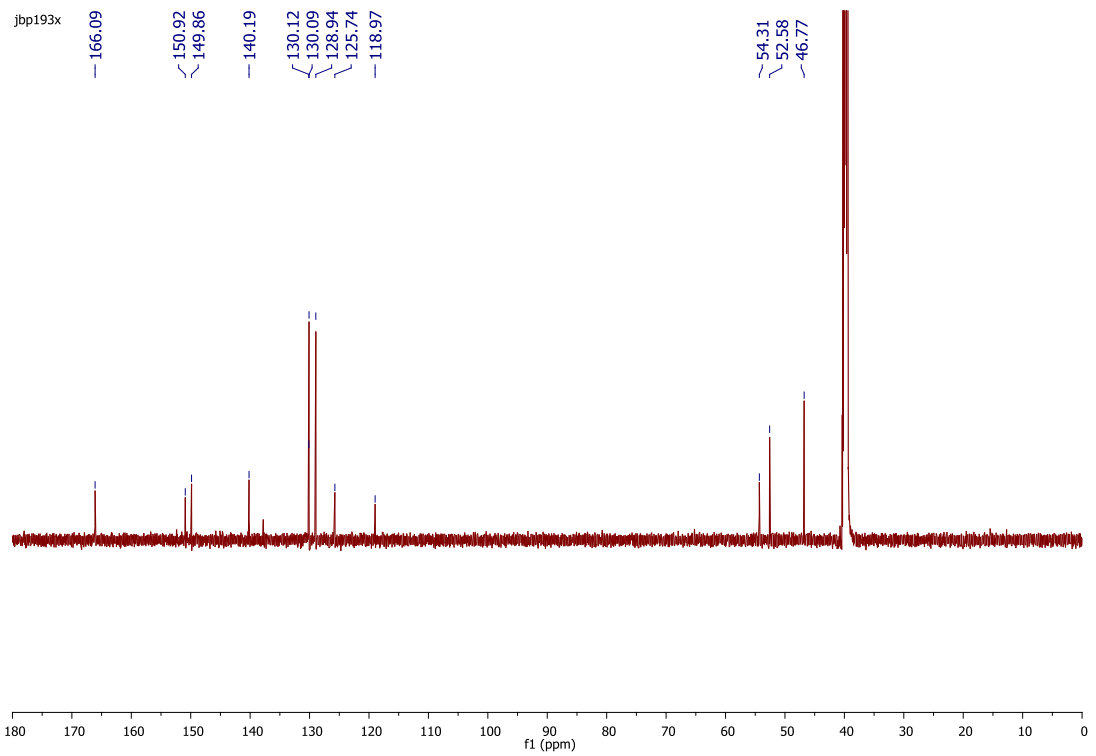

Figure A.7 ^{13}C NMR (150 MHz, DMSO-d_6) spectrum of [Ru·(**88**)Cl_2(DMSO)].

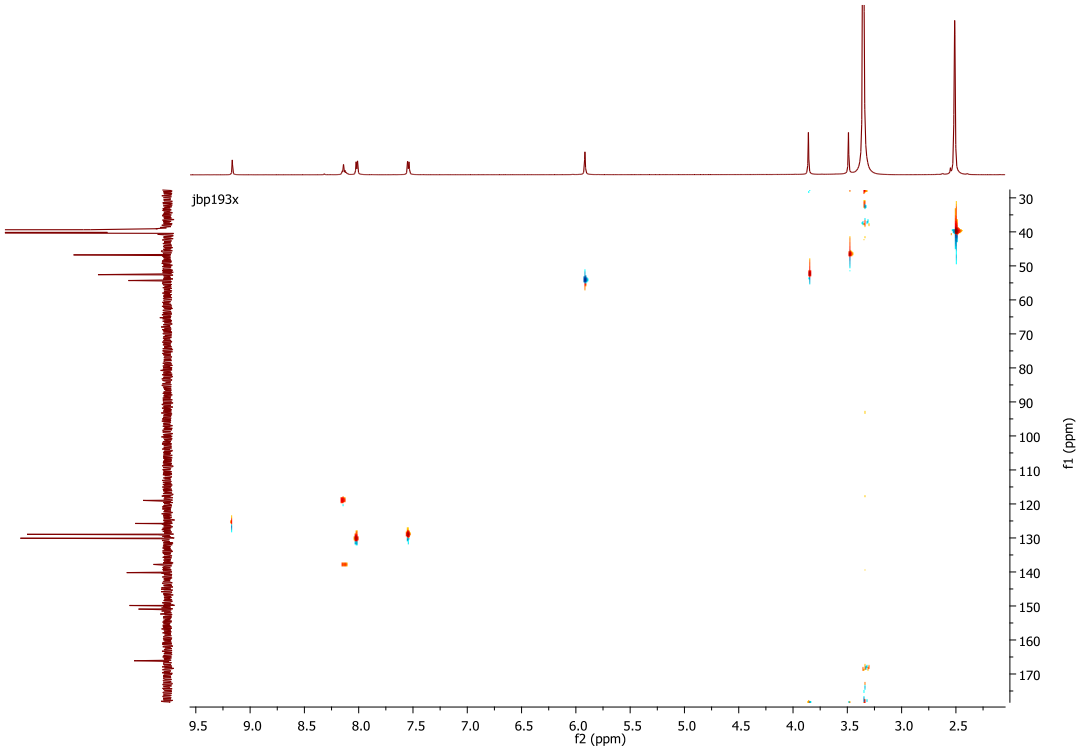

Figure A.8 HSQC (600 MHz, DMSO-d_6) of [Ru·(**88**)Cl_2(DMSO)].

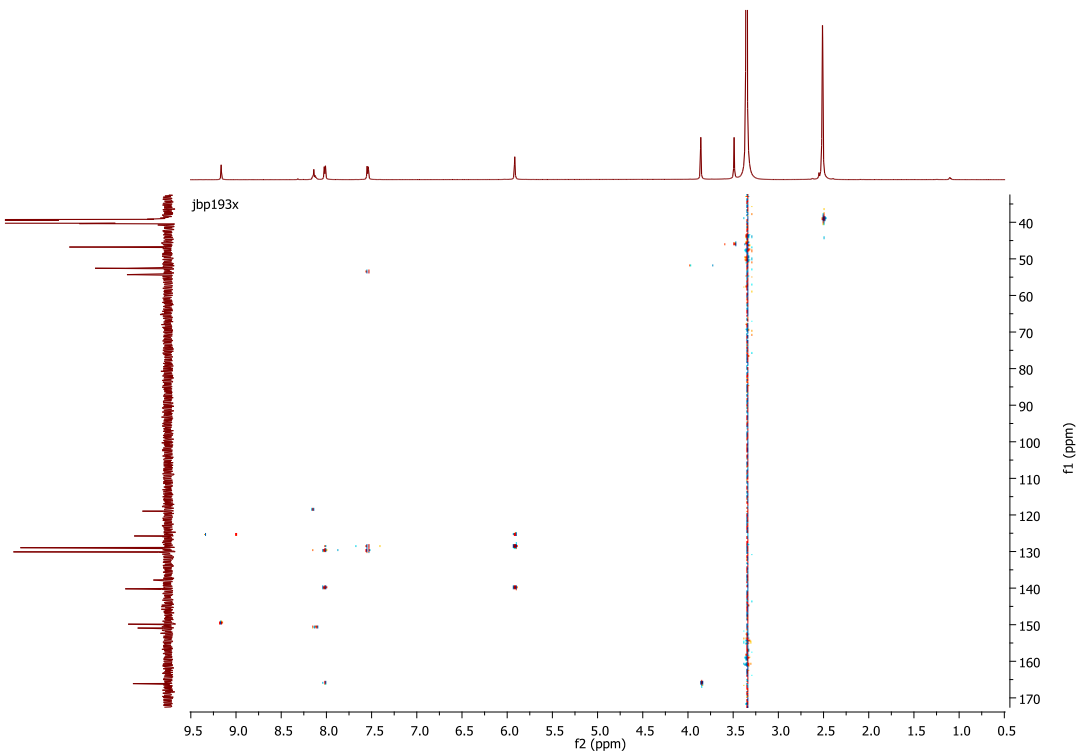

Figure A.9 HMBC (600 MHz, DMSO-d_6) of [Ru·(**88**)Cl_2(DMSO)].

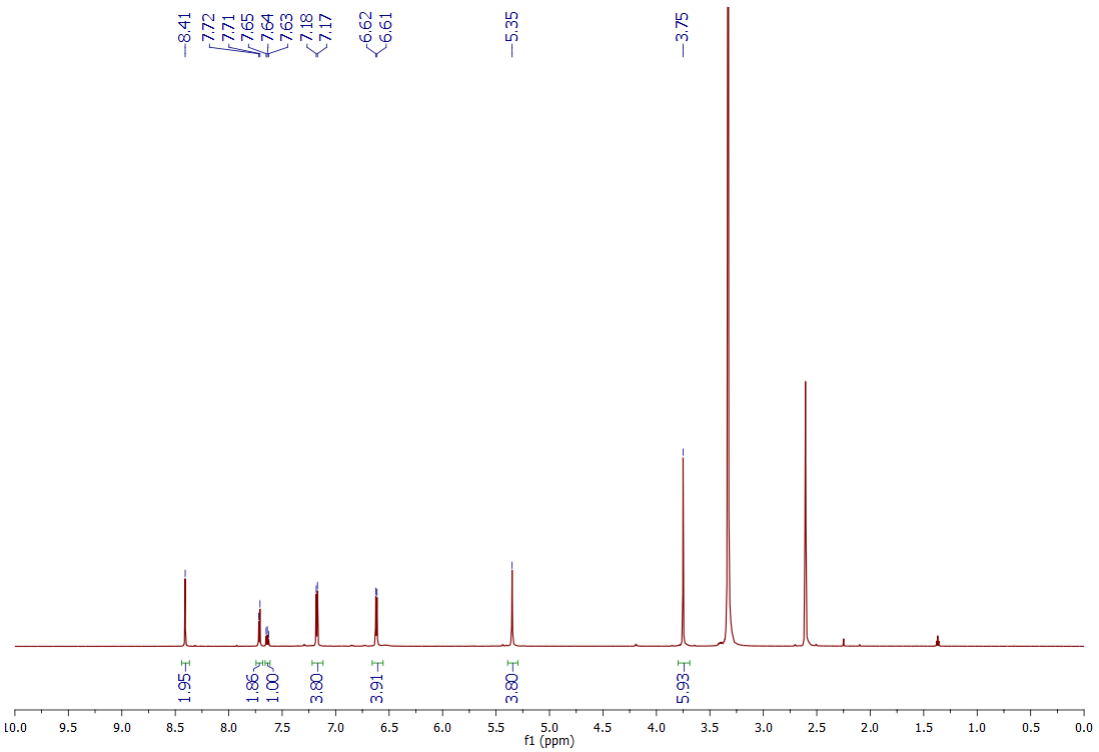

Figure A.10 ^{1}H NMR (600 MHz, DMSO-d_6) spectrum of [Ru·(**88**)$_2$](PF$_6$)$_2$.

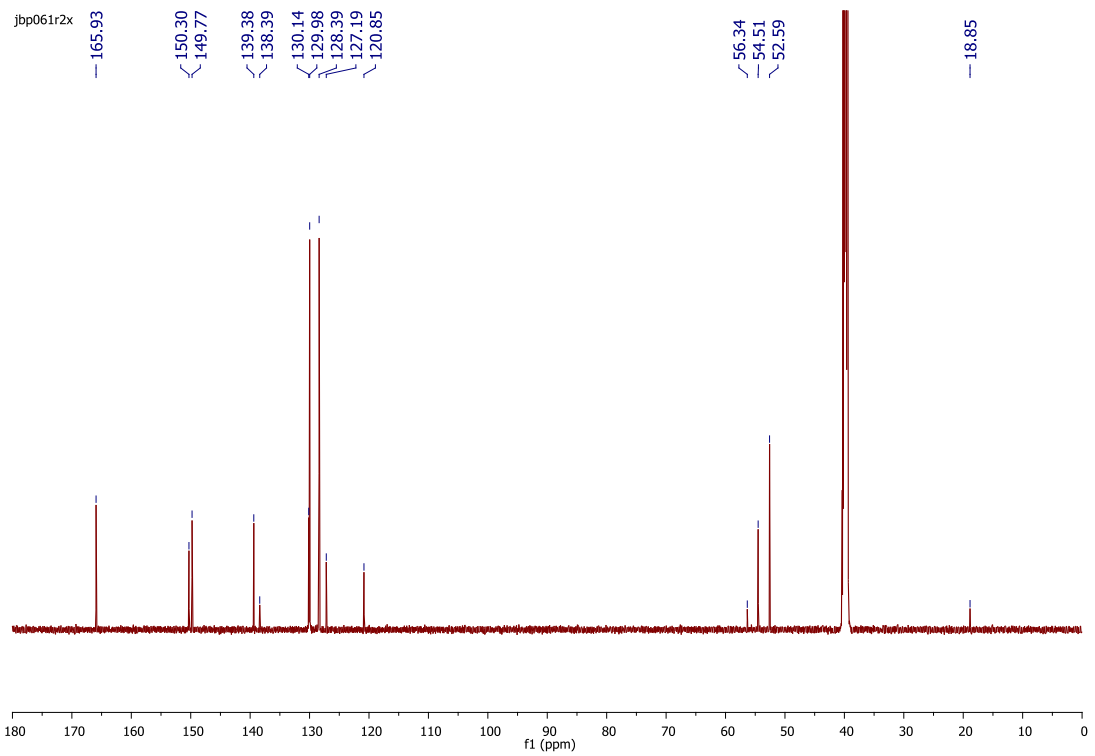

Figure A.11 ^{13}C NMR (150 MHz, DMSO-d_6) spectrum of [Ru·(**88**)$_2$](PF$_6$)$_2$.

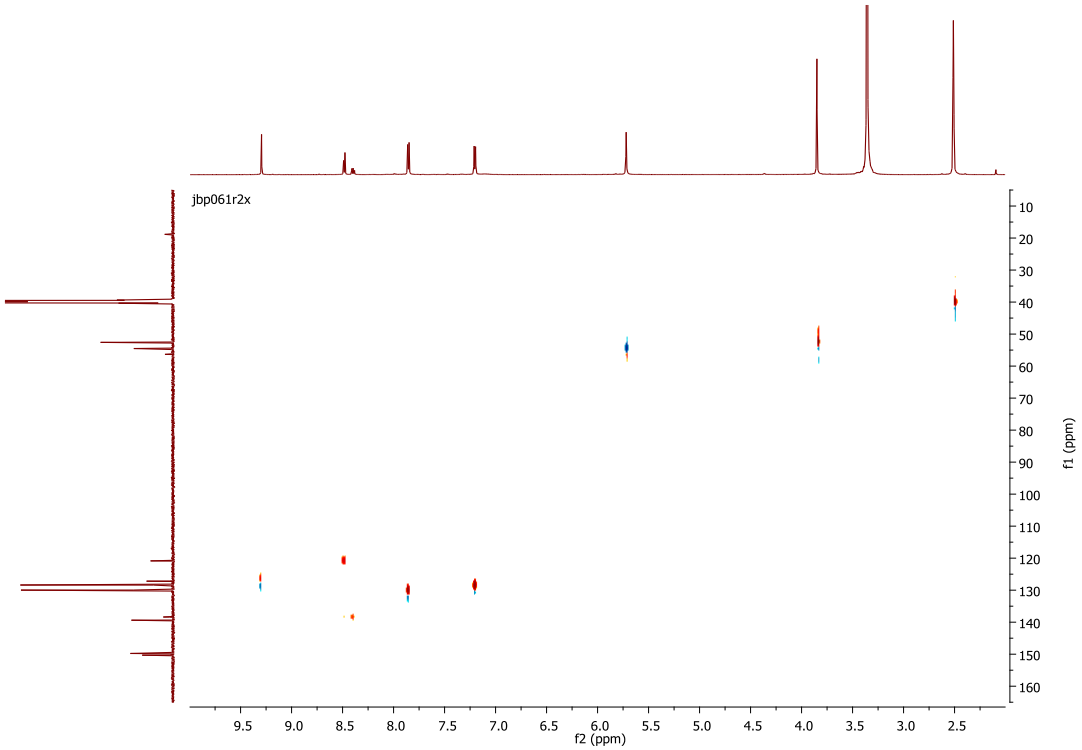

Figure A.12 HSQC (DMSO-d_6) of [Ru·(**88**)$_2$](PF$_6$)$_2$.

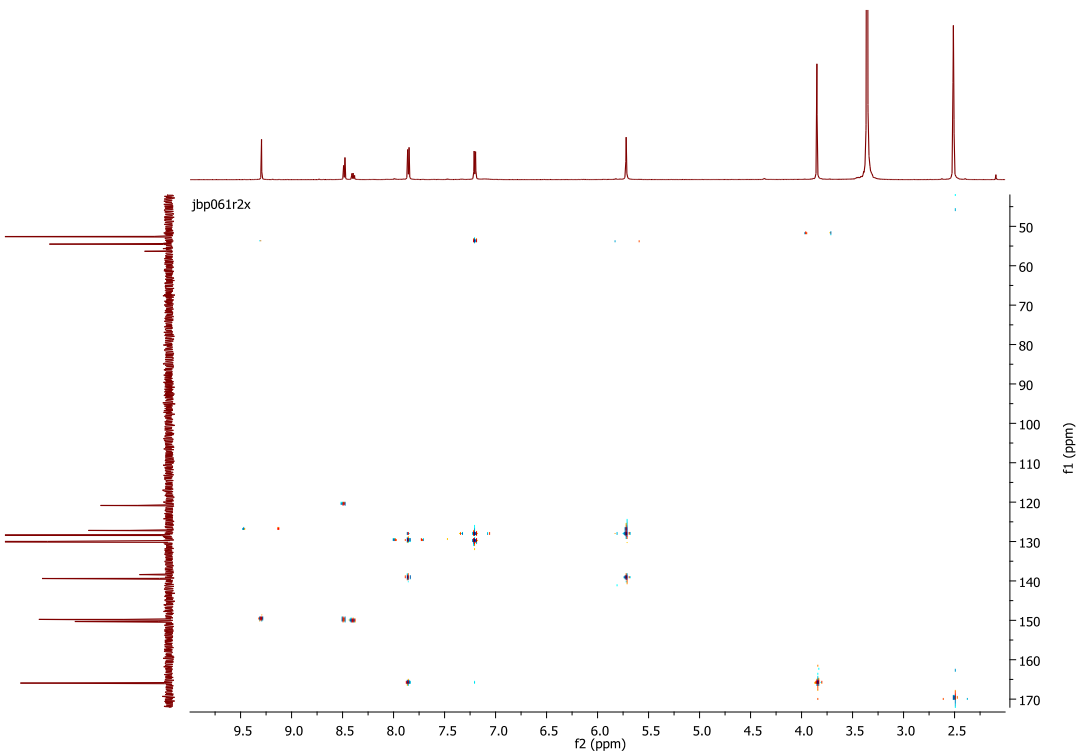

Figure A.13 HMBC (DMSO-d_6) of [Ru·(**88**)$_2$](PF$_6$)$_2$.

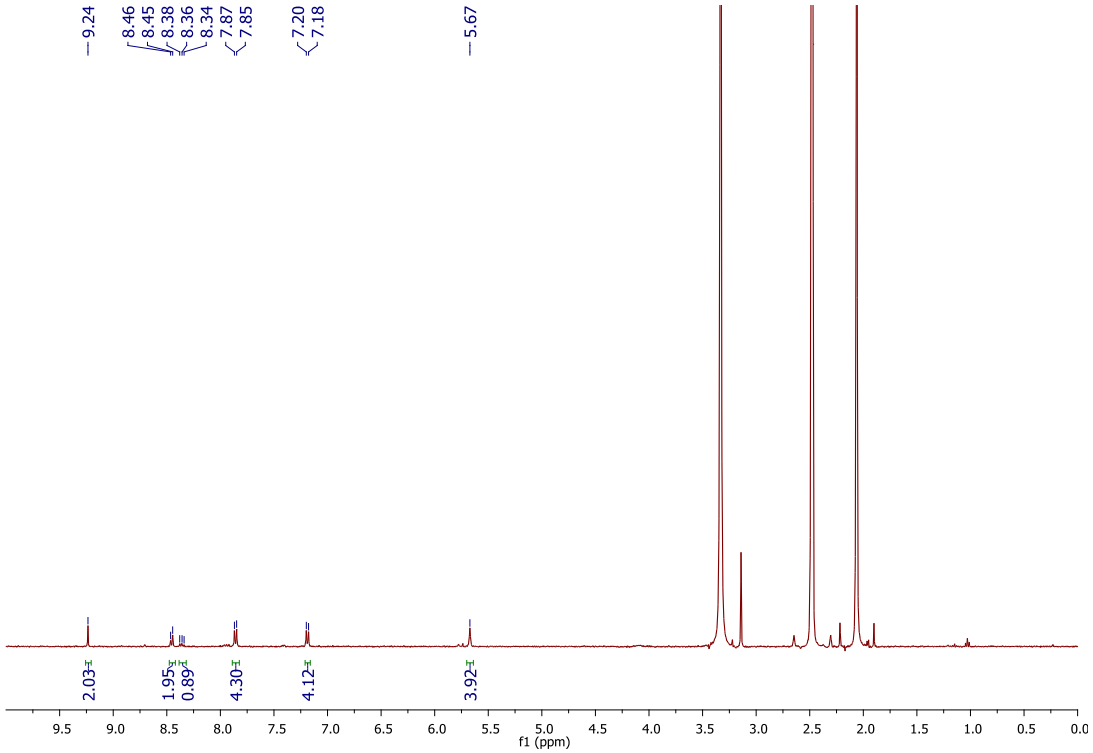

Figure A.14 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of [Ru·(**89**)$_2$](PF$_6$)$_2$.

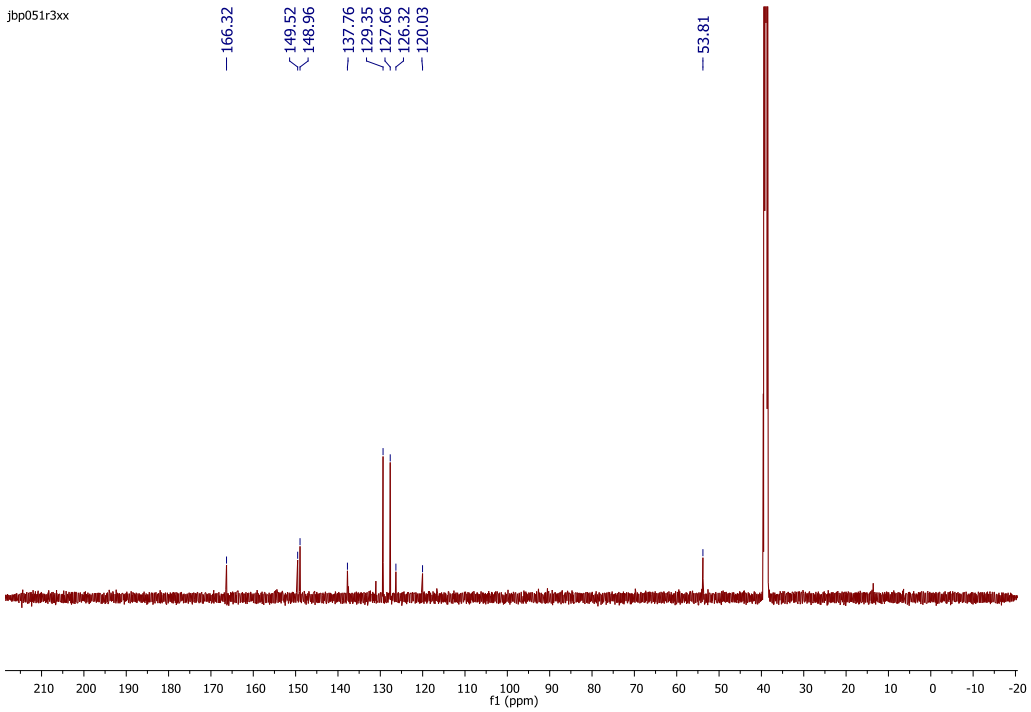

Figure A.15 ^{13}C NMR (150 MHz, DMSO-d_6) spectrum of [Ru·(**89**)$_2$](PF$_6$)$_2$.

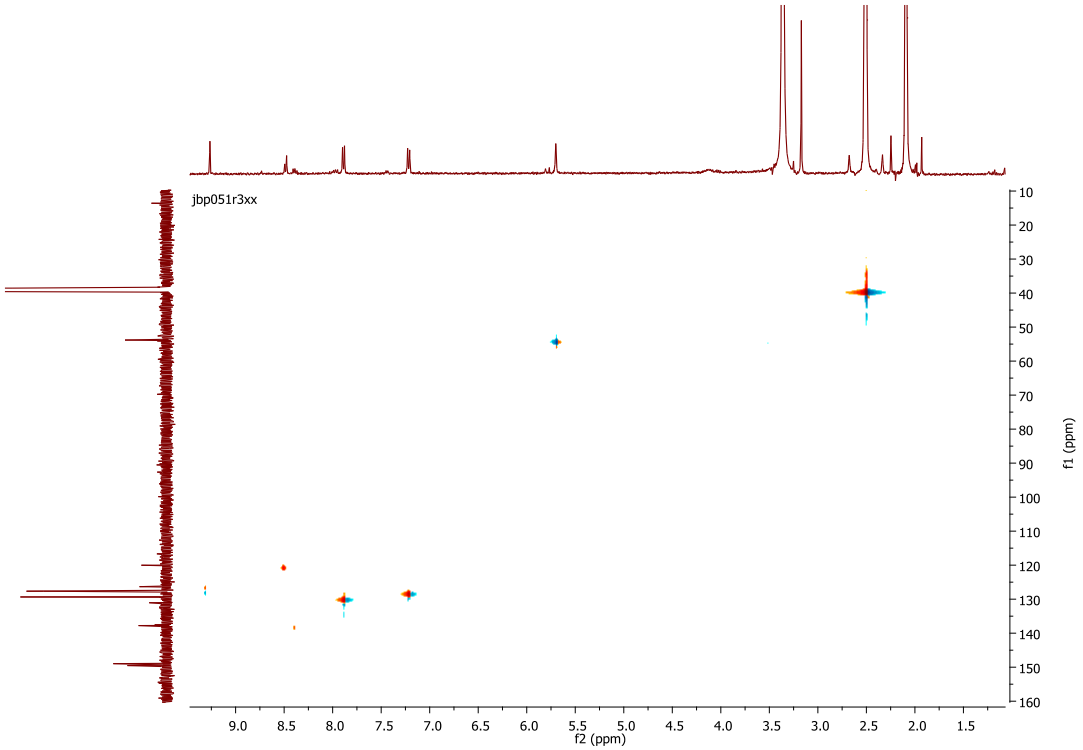

Figure A.16 HSQC (DMSO-d_6) of [Ru·(**89**)$_2$](PF$_6$)$_2$.

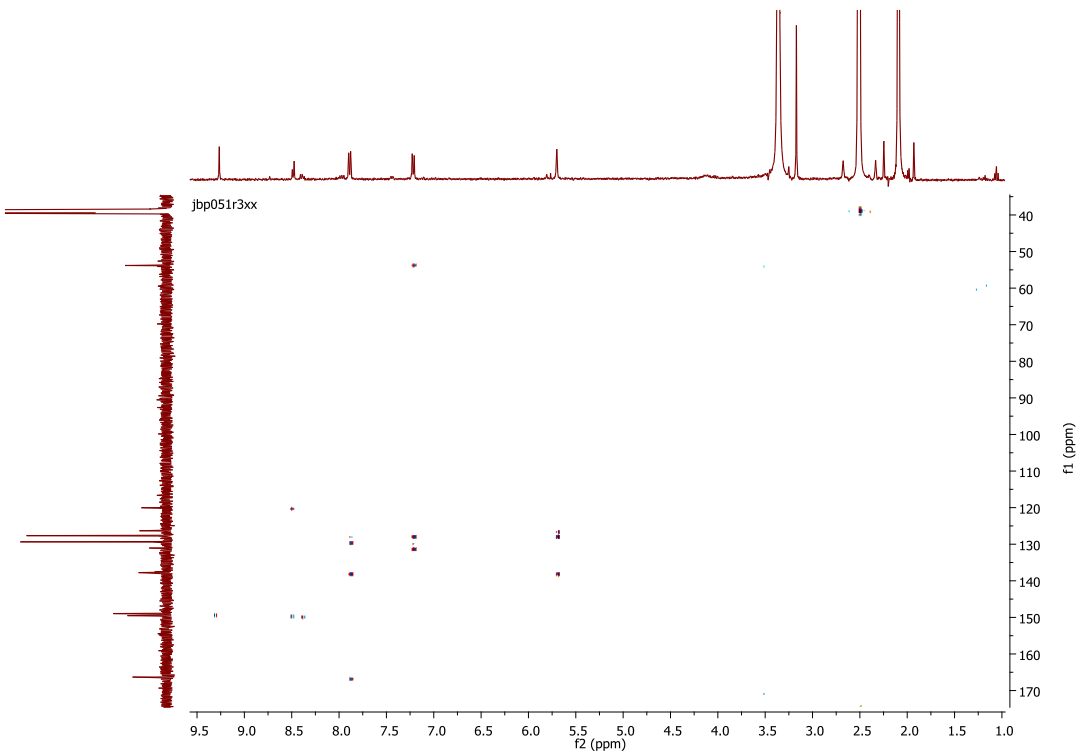

Figure A.17 HMBC (DMSO-d_6) of [Ru·(**89**)$_2$](PF$_6$)$_2$.

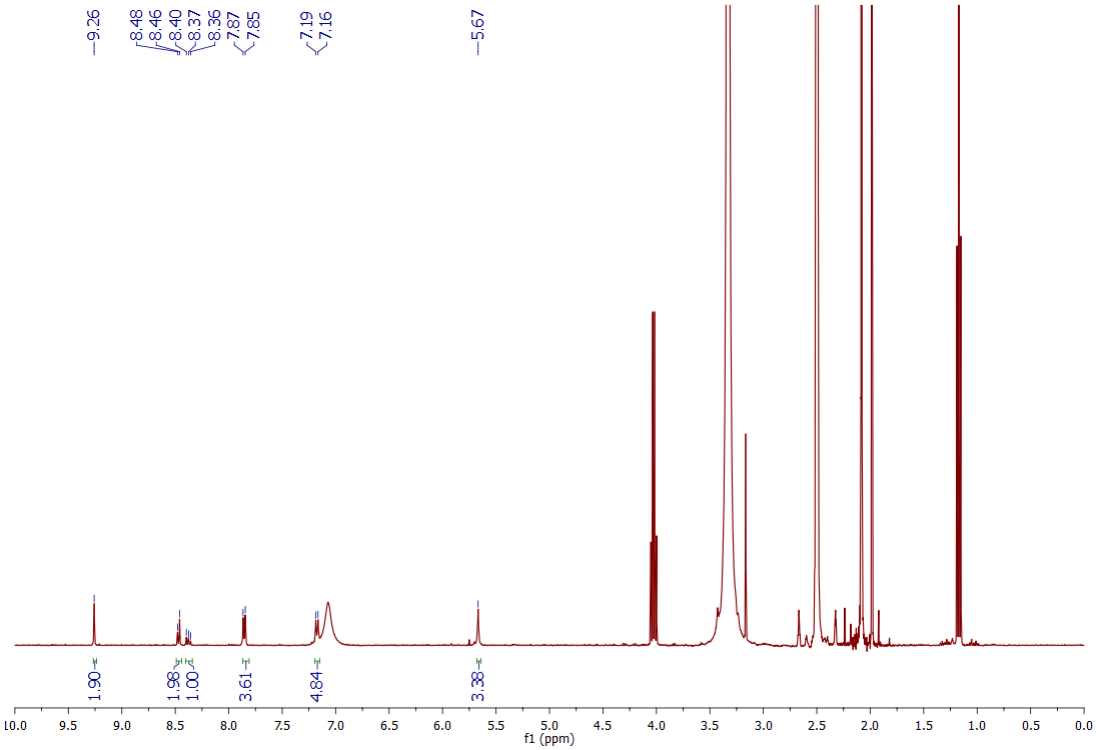

Figure A.18 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of dried gel containing $[Ru\cdot(\mathbf{89})_2]^{2+}$.

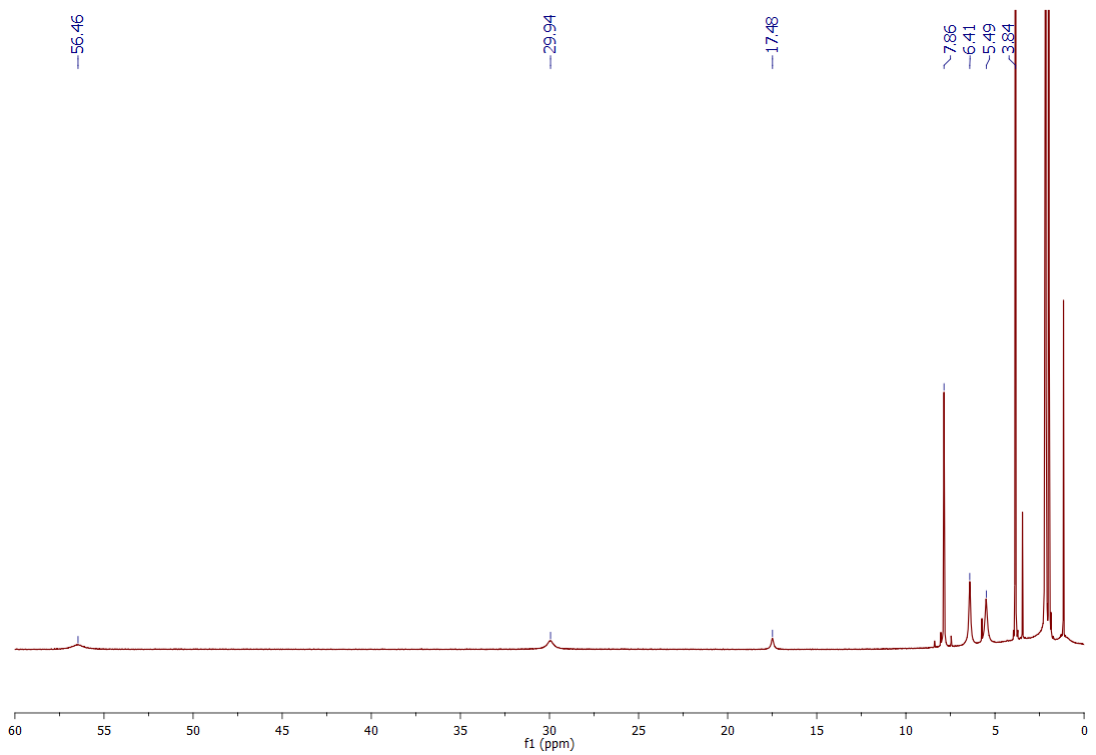

Figure A.19 ^{1}H NMR (600 MHz, CD_3CN) spectrum of paramagnetic complex $[Ni\cdot(\mathbf{88})_2](PF_6)_2$

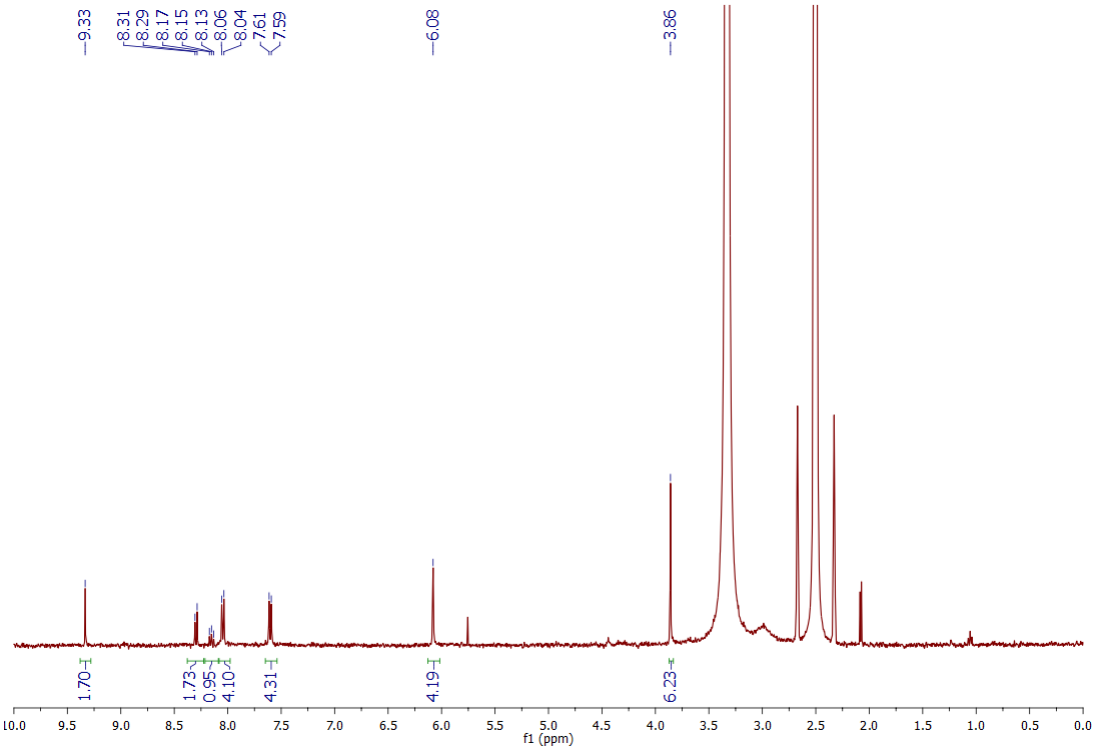

Figure A.20 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of [Ir·(**88**)Cl_3].

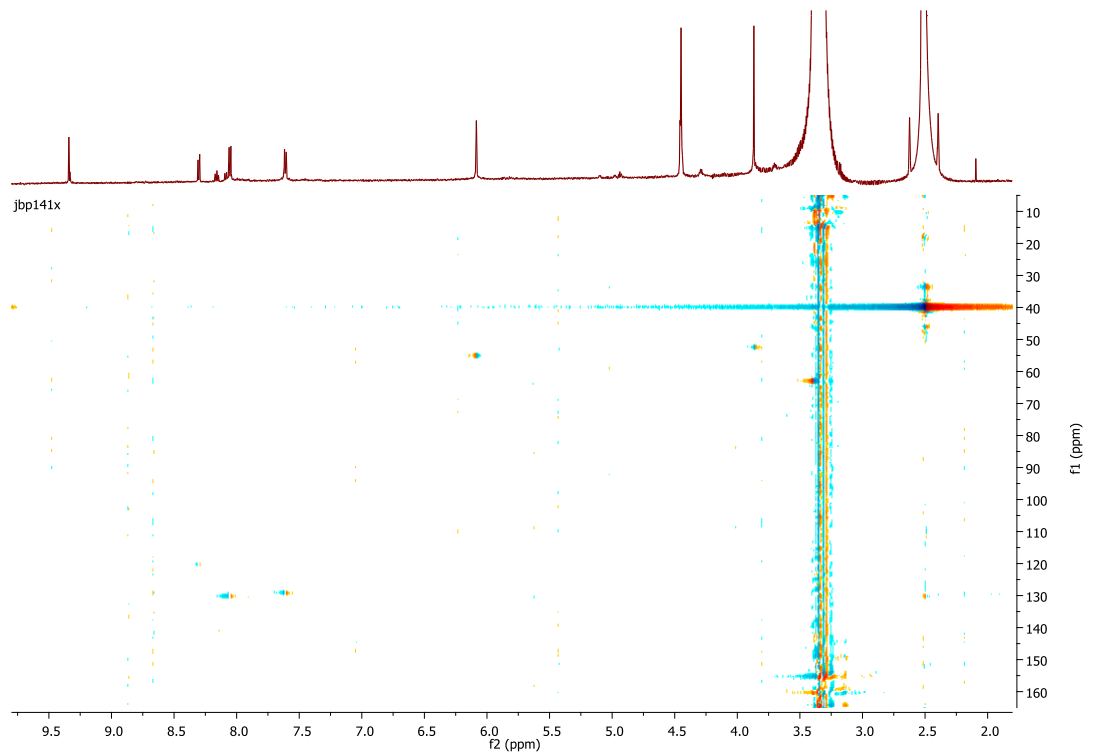

Figure A.21 HSQC (DMSO-d_6) of [Ir·(**88**)Cl_3].

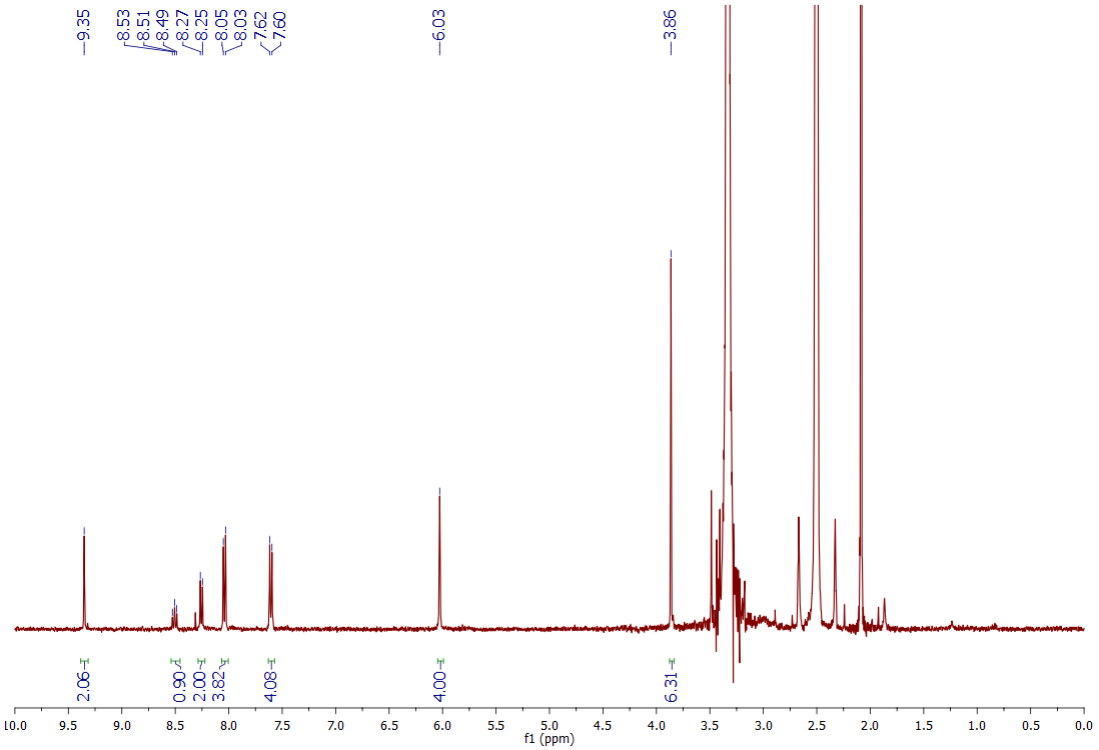

Figure A.22 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of [Pt·(**88**)Cl]Cl.

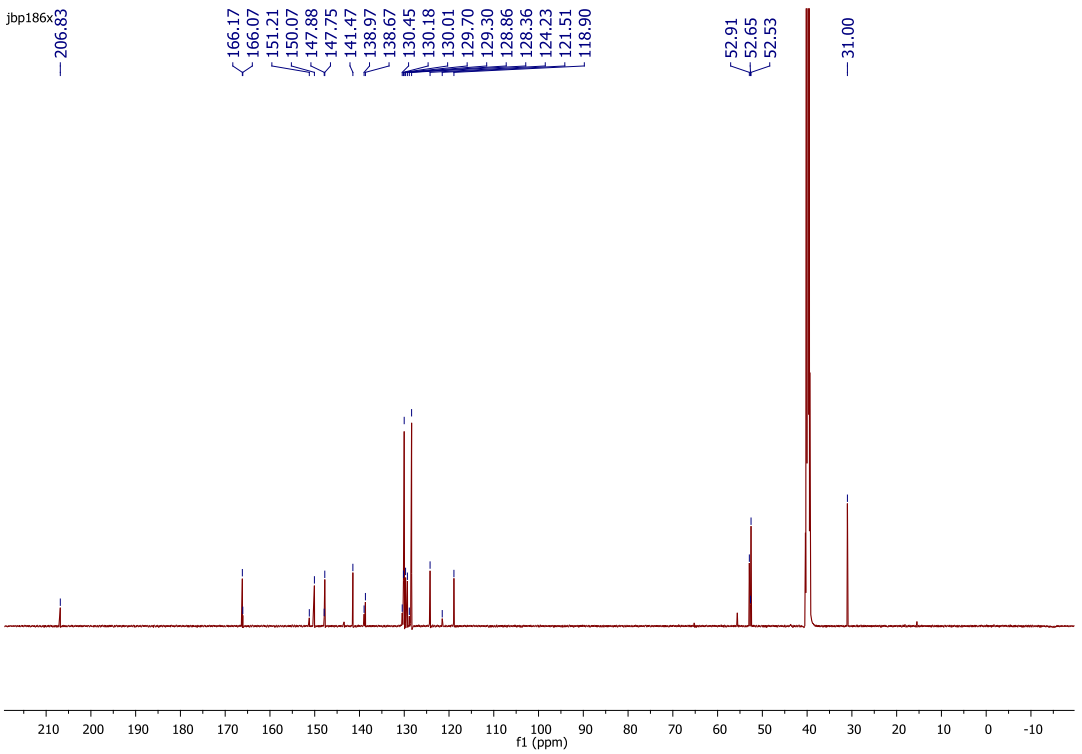

Figure A.23 ^{13}C NMR (150 MHz, DMSO-d_6) spectrum of [Pt·(**88**)Cl]Cl.

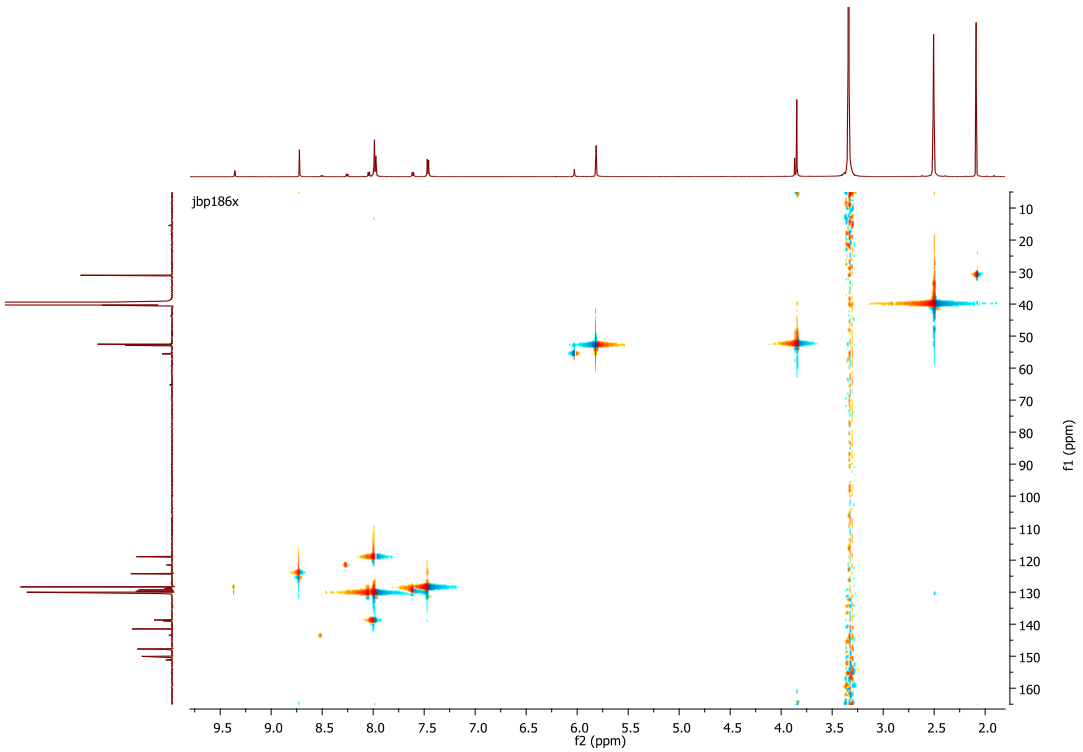

Figure A.24 HSQC (DMSO-d_6) of [Pt·(**88**)Cl]Cl.

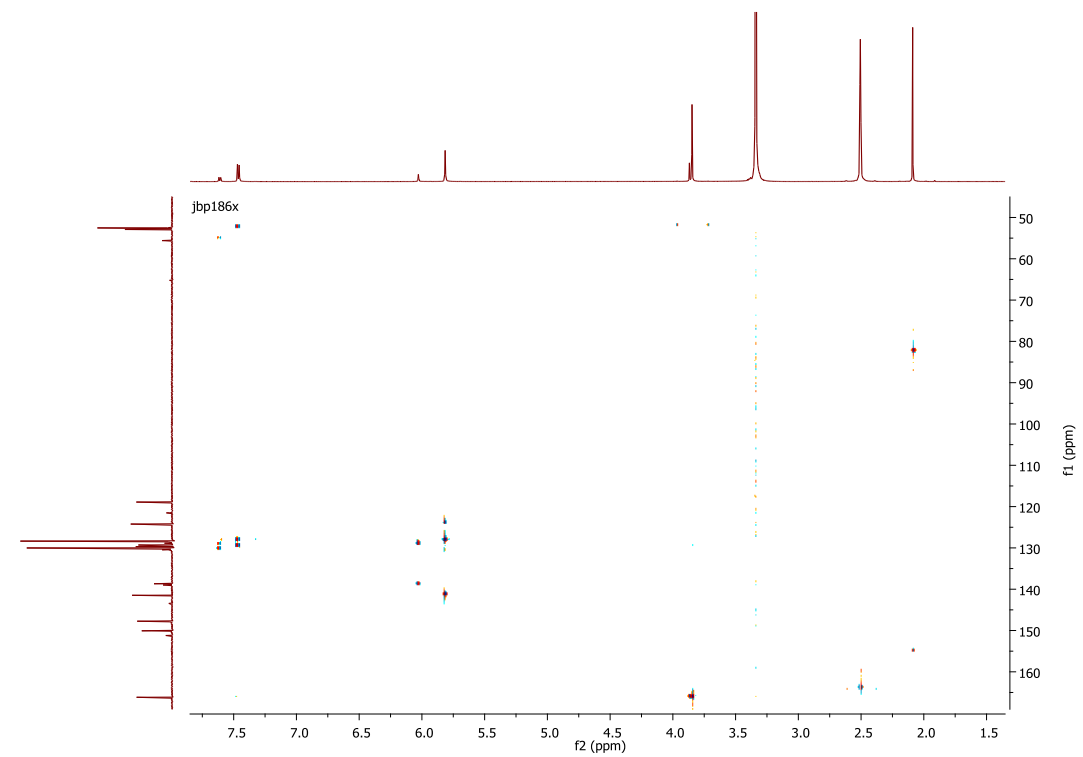

Figure A.25 HMBC (DMSO-d_6) of [Pt·(**88**)Cl]Cl.

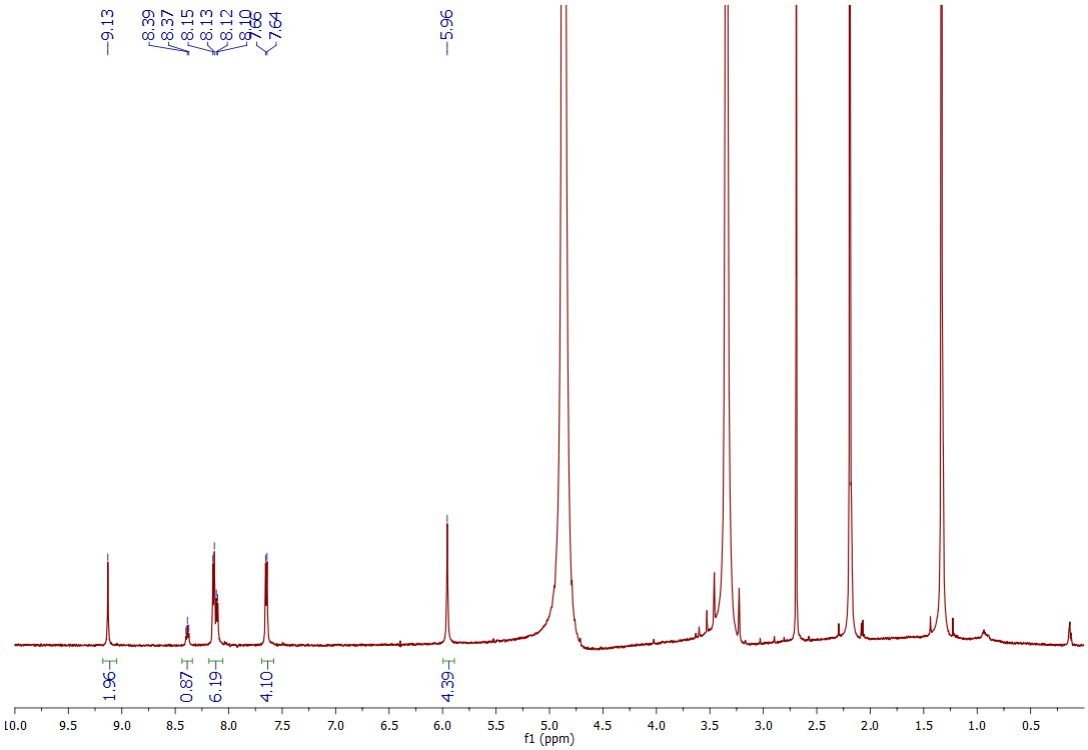

Figure A.26 ^{1}H NMR (600 MHz, CD_3OD) spectrum of [Pt·(**89**)Cl]Cl.

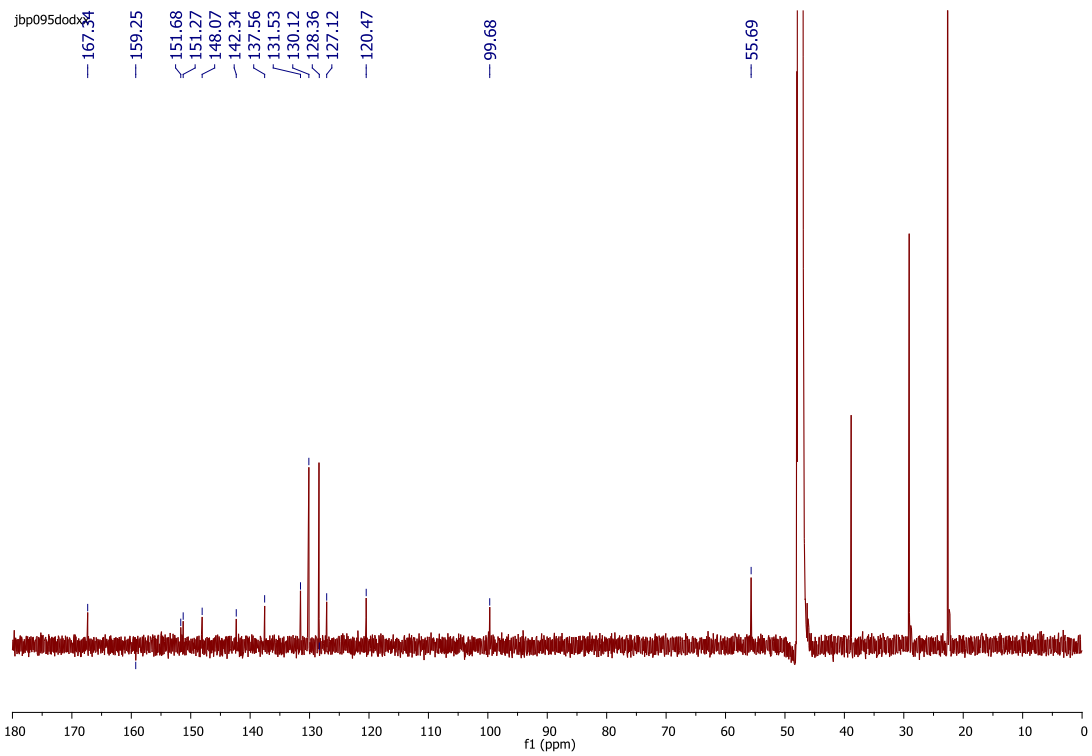

Figure A.27 ^{1}H NMR (150 MHz, CD_3OD) spectrum of [Pt·(**89**)Cl]Cl.

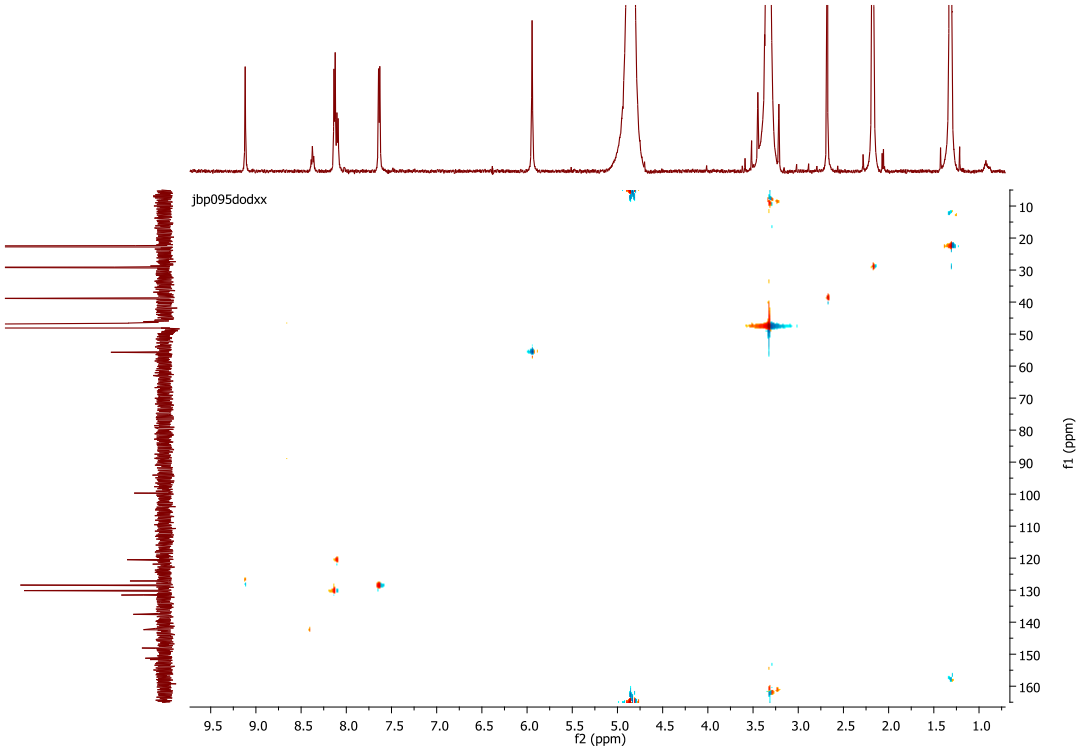

Figure A.28 HSQC (CD_3OD) of [Pt·(**89**)Cl]Cl.

A.2. Mass spectrometry of complexes

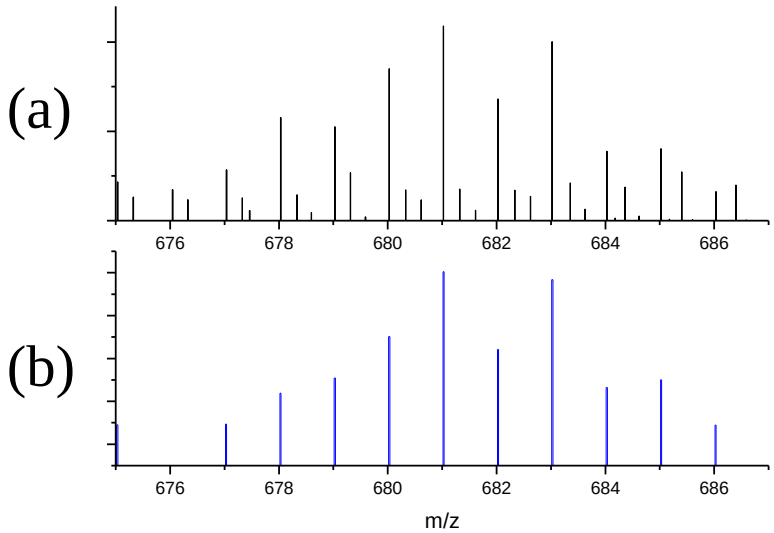

Figure A.29 (a) Experimental and **(b)** calculated HRMS isotopic pattern distribution for [Ru·(**88**)Cl_2(DMSO)]. HRMS (*m/z*) (MALDI+): Calculated for $C_{27}H_{23}N_7O_4Cl_2Ru^+$ *m/z* = 681.0232 $[M-(DMSO)]^+$. Found *m/z* = 681.0213.

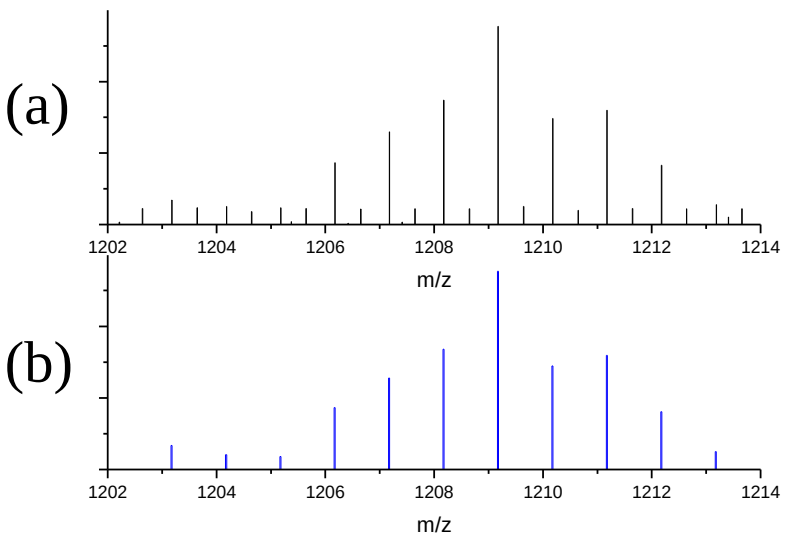

Figure A.30 (a) Calculated and **(b)** theoretical HRMS isotopic pattern distribution for gel of $[Ru\cdot(\mathbf{89})_2]^{2+}$.Calculated for $C_{50}H_{38}N_{14}O_8RuPF_6^+$ $[M-Cl]^+$ *m/z* = 1209.1682. Found *m/z* = 1209.1732.

A.3. Infrared spectra

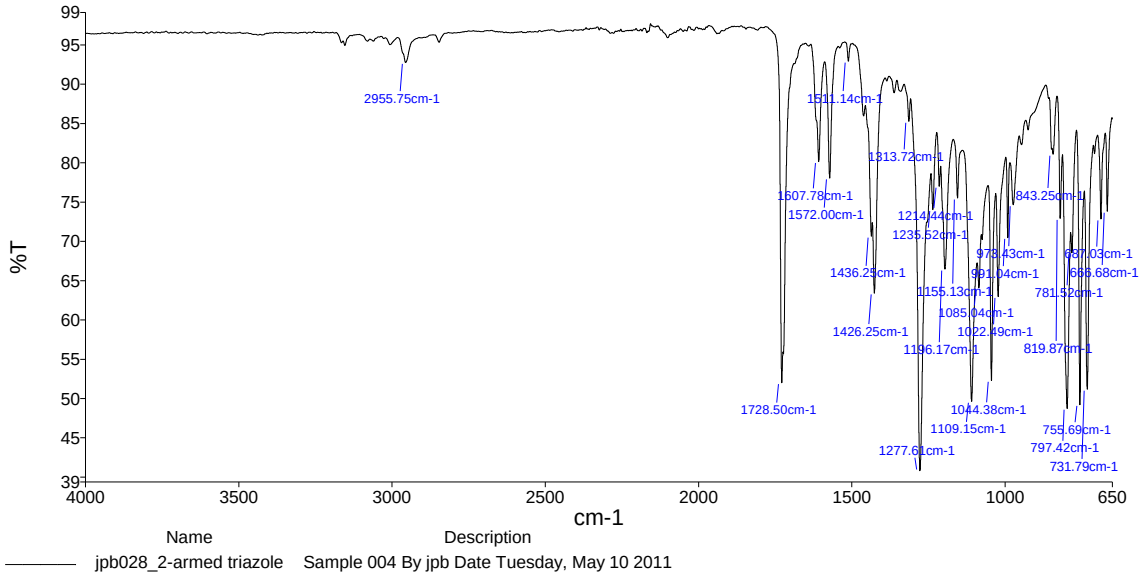

Figure A.31 IR spectrum of ligand **88**.

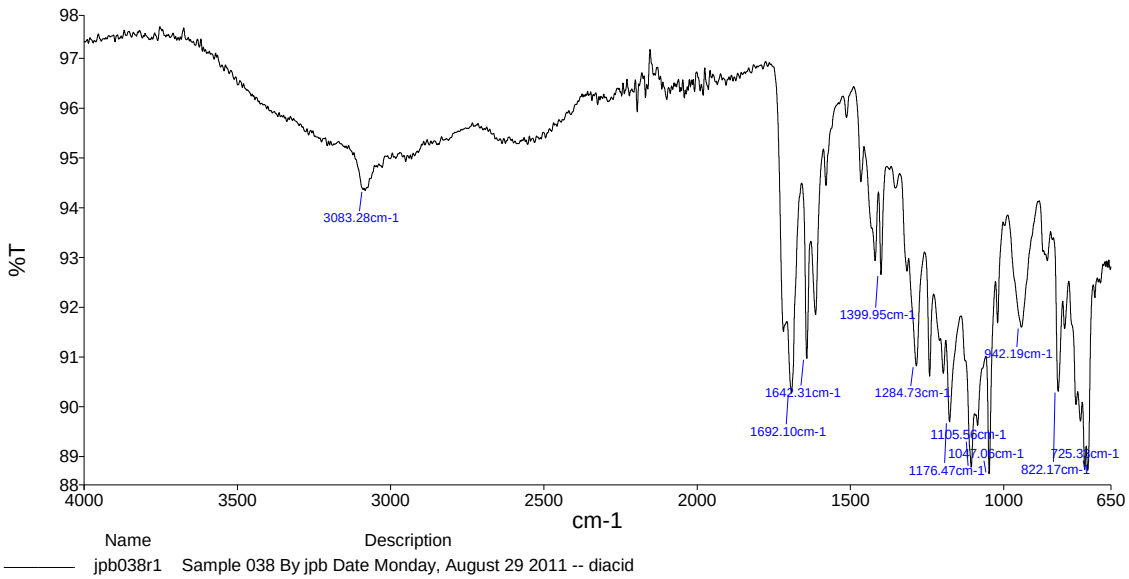

Figure A.32 IR spectrum of ligand **89**.

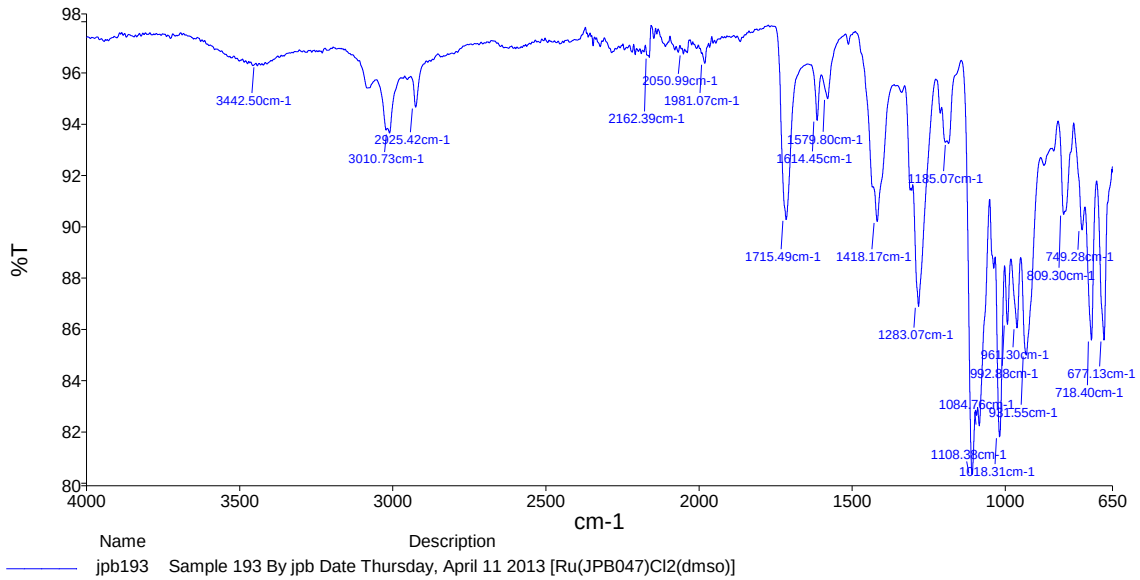

Figure A.33 IR spectrum of complex [Ru·(**88**)Cl_2(DMSO)].

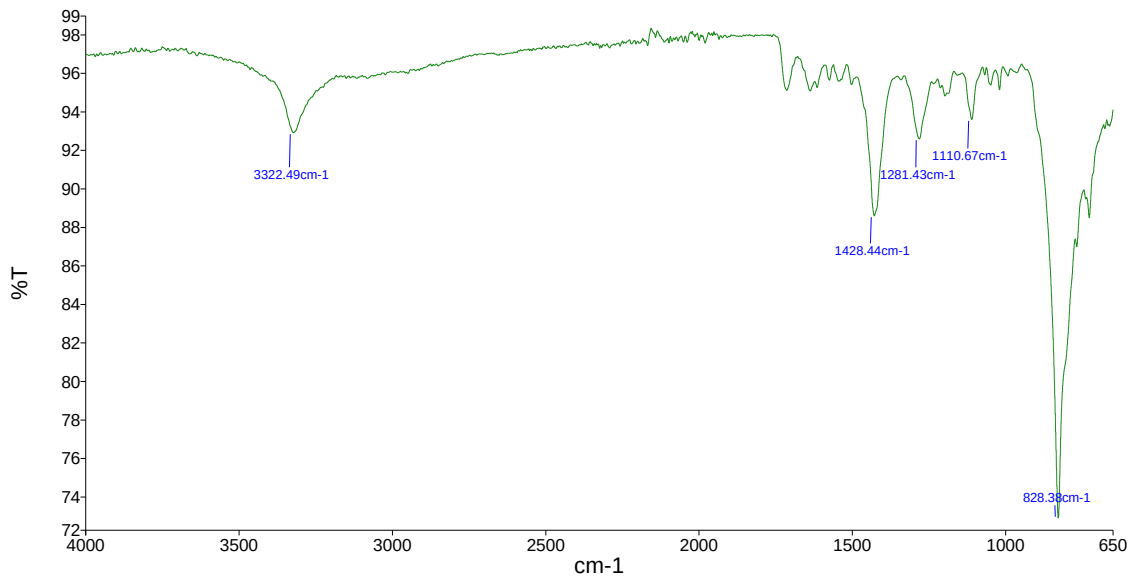

Figure A.34 IR spectrum of complex [Ru·(**88**)$_2$](PF_6)$_2$.

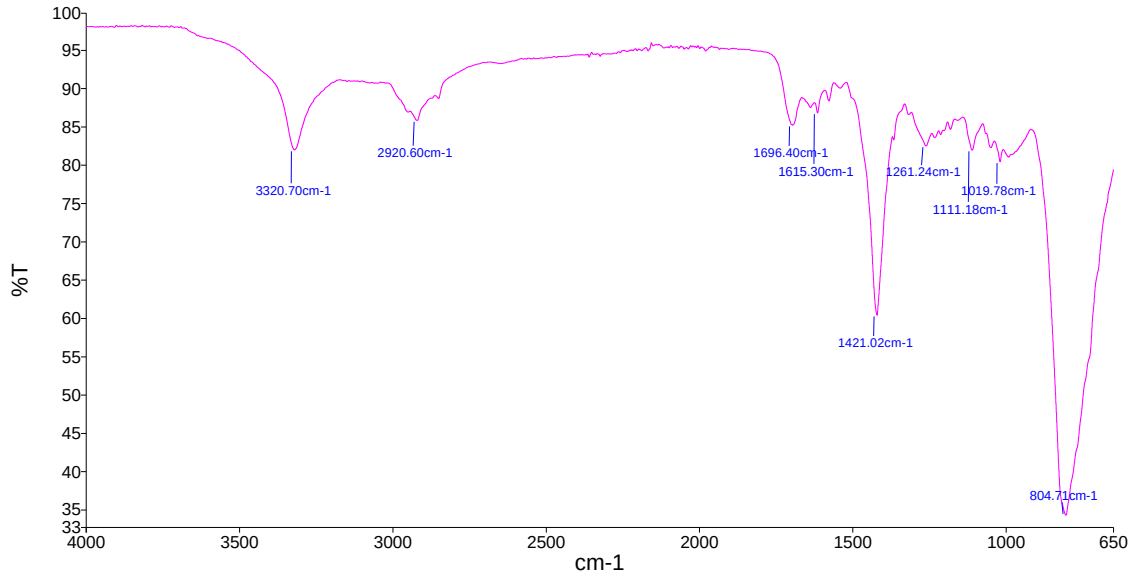

Figure A.35 IR spectrum of complex $[Ru{\cdot}(\mathbf{89})_2](PF_6)_2$.

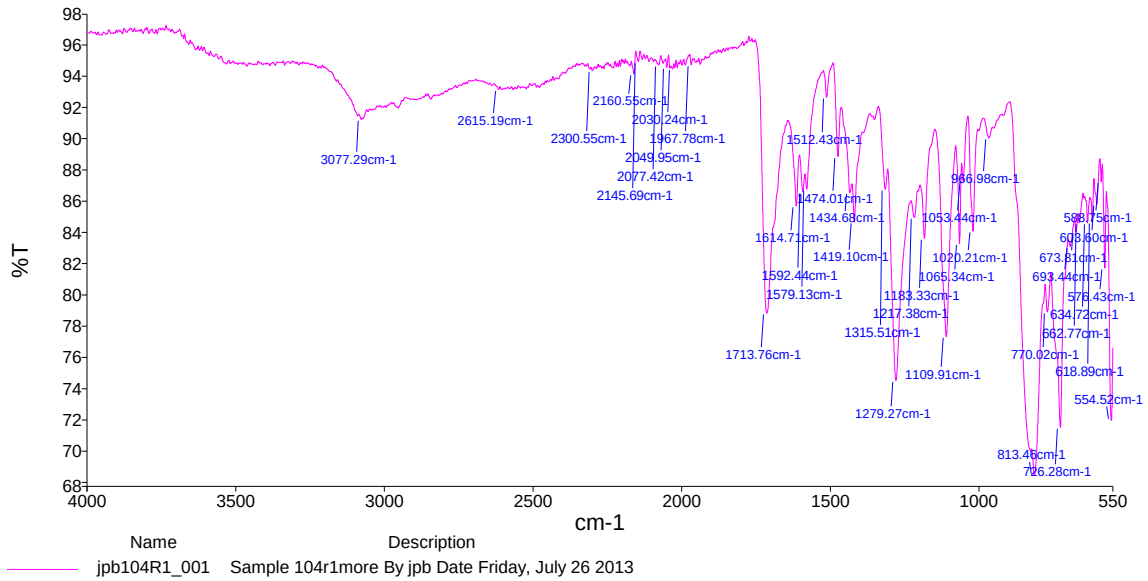

Figure A.36 IR spectrum of complex $[Ni{\cdot}(\mathbf{88})_2](PF_6)_2$.

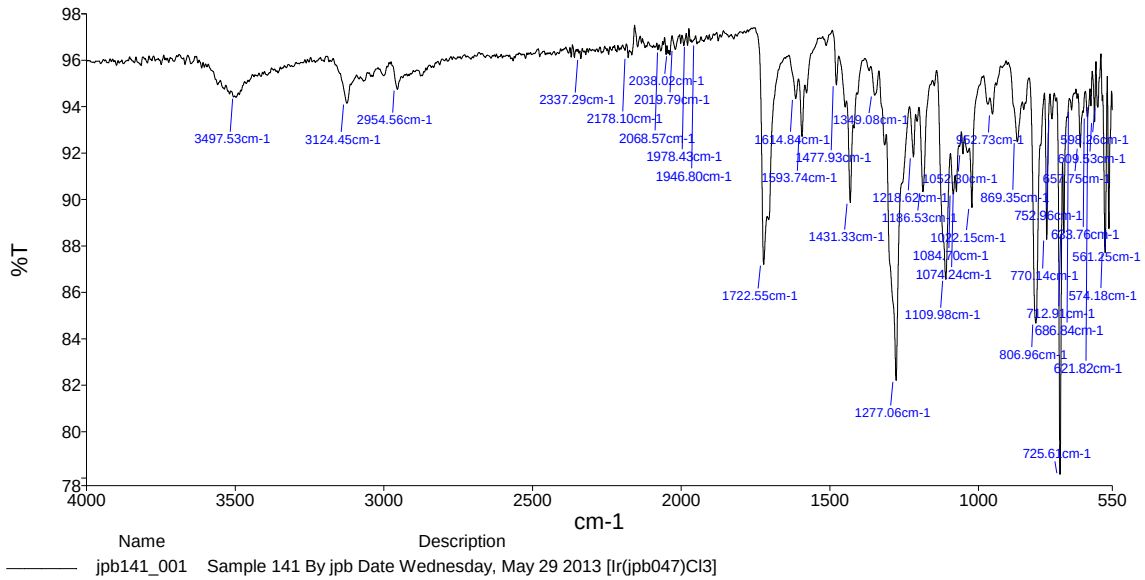

Figure A.37 IR spectrum of complex [Ir·(**88**)Cl_3].

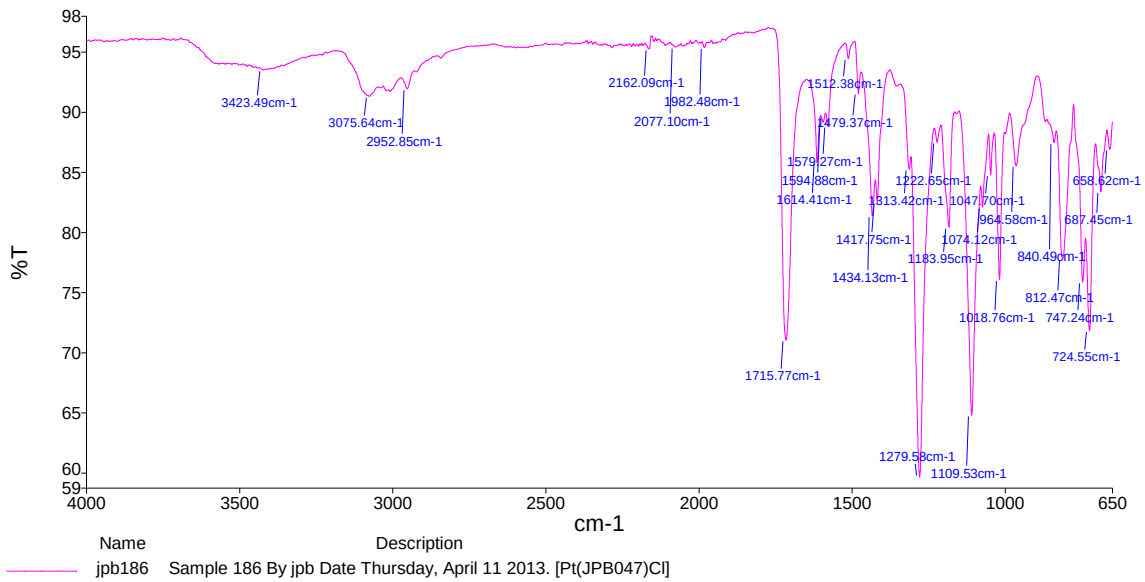

Figure A.38 IR spectrum of complex [Pt·(**88**)Cl]Cl.

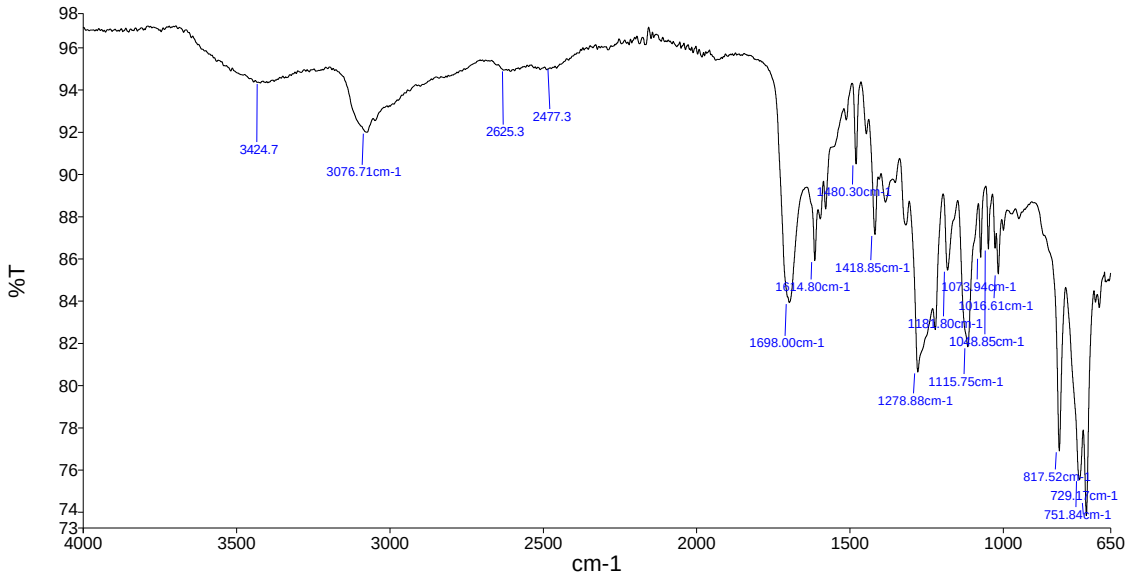

Figure A.39 IR spectrum of complex [Pt·(**89**)Cl]Cl.

A.4. X-Ray and refinement details

Special refinement details for the crystal structures:

88: The structure contained no solvent and no disorder. All non-H atoms were made anisotropic

[Ru·(89)$_2$](PF$_6$)Cl·CH$_3$CN·0.5H$_2$O·1.25EtOH·0.5Et$_2$O: The structure contained a half occupancy Et$_2$O, a half occupancy CH$_3$CN, a full occupancy ethanol where the methyl group was disordered over two sites (0.75:0.25), a half occupancy CH$_3$CN which shares the same site with a 0.25 occupancy water, and finally there is also a 0.25 occupancy ethanol giving a total solvent count of CH$_3$CN·0.5H$_2$O·1.25EtOH·0.5Et$_2$O. The main residue also contains disorder in one of the carboxylic acid arms where the COOH group is split over 2 sites (0.6:0.4). The atoms were best modelled isotropic and split as attempts to model these as anisotropic/split or anisotropic/non-split gave unsatisfactory refinements.

[Ni·(88)$_2$](PF$_6$)Cl:CH$_3$CN·H$_2$O: The structure contained one full occupancy CH$_3$CN and one full occupancy H$_2$O. One of the ester arms in the main residue was disordered over two sites (0.6:0.4) and again it was best to model the groups as spilt and isotropic rather than anisotropic.

[Ir·(88)Cl$_3$]·0.25HOCH$_2$CH$_2$OH·0.25H$_2$O: The structure contains 0.25 ethylene glycol and 0.25 water molecules. Both were refined as isotropic. One of the ester arms in the main

residue was disordered over two sites (0.5:0.5) and again it was best to model the groups as spilt and isotropic rather than anisotropic.

Ligand 88

```
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  Cell:          a=6.3501(13)   b=12.965(3)    c=14.859(3)
                 alpha=92.45(3  beta=101.17(3  gamma=100.30(3)
                            )              )
  Temperatur     108 K
e:
                     Calculated                      Reported
  Volume             1177.0(5)                       1176.9(4)
  Space group        P -1                            P-1
  Hall group         -P 1                            ?
  Moiety formula     C27 H23 N7 O4                   ?
  Sum formula        C27 H23 N7 O4                   C27 H23 N7 O4
  Mr                 509.52                          509.52
  Dx,g cm-3          1.438                           1.438
  Z                  2                               2
  Mu (mm-1)          0.101                           0.101
  F000               532.0                           532.0
  F000'              532.22
  h,k,lmax           7,15,17                         7,15,17
  Nref               4154                            3981
  Tmin,Tmax          0.982,0.990                     0.801,1.000
  Tmin'              0.941
  Correction method= MULTI-SCAN
  Data completeness= 0.958       Theta(max)= 25.000
  R(reflections)= 0.0639( 3614)     wR2(reflections)= 0.1304( 3981)
  S = 1.214             Npar= 345
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Alert level B

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full Low 0.958

Alert level G

PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.03000 Deg.

0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
0 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
1 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

0 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

PLATON version of 30/05/2011; check.def file version of 24/05/2011

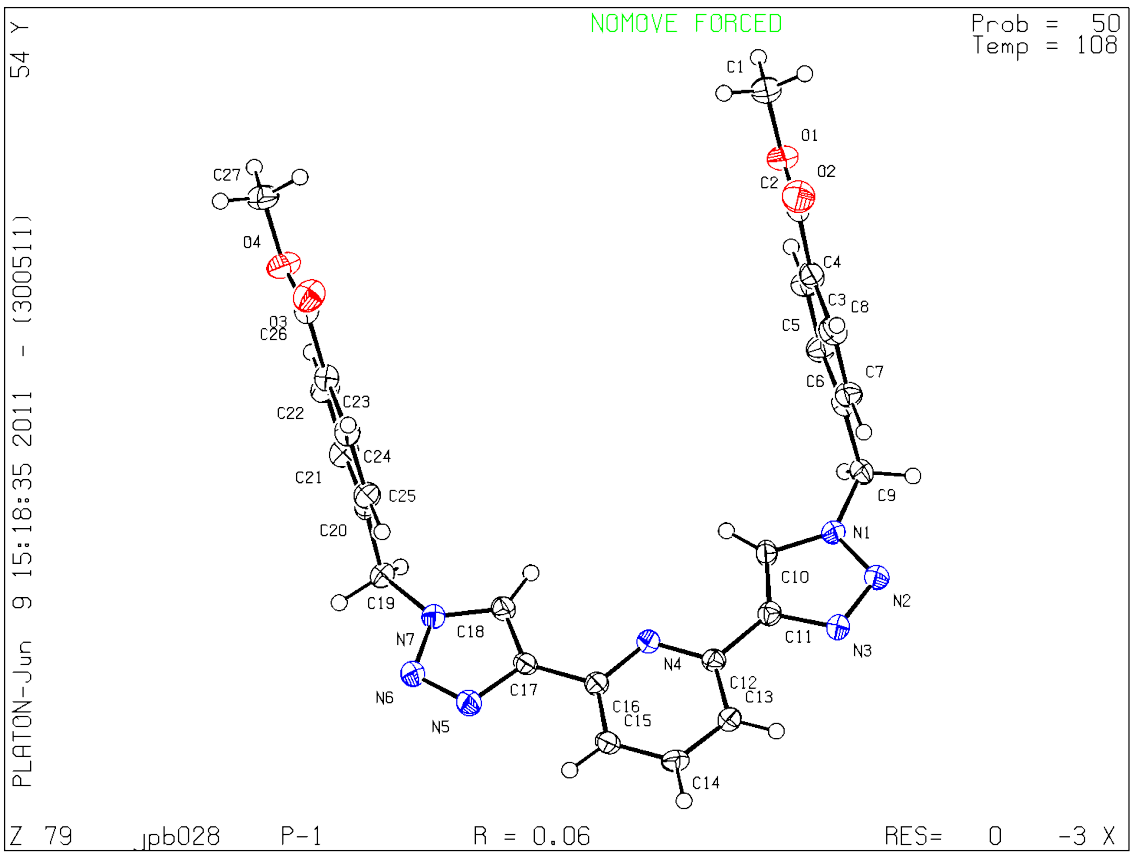

Figure A.40 Ellipsoid plot of the X-ray crystal structure of ligand **88**.

Ru(II) complex $[Ru\cdot(89)_2]PF_6Cl$

```
  Bond precision:      C-C = 0.0083 A              Wavelength=0.71073
  Cell:          a=12.235(2)     b=17.491(4)     c=17.627(4)
                 alpha=105.76(   beta=105.52(    gamma=93.49(3)
               3)              3)
  Temperatur
e:               108 K

                      Calculated                  Reported
  Volume              3461.6(15)                  3461.4(12)
  Space group         P -1                        P-1
```

Hall group	-P 1	?
Moiety formula	2(C50 H38 N14 O8 Ru), 2(F6 P), C4 H10 O, 2(C2 H6 O), C2 H4 N O0	?
Sum formula	C113 H109 Cl2 F12 N30 O20.50 P2 Ru2	C56.50 H54.50 Cl F6 N15 O10.25 P Ru
Mr	2778.29	1389.14
Dx,g cm-3	1.333	1.333
Z	1	2
Mu (mm-1)	0.367	0.367
F000	1421.0	1421.0
F000'	1419.68	
h,k,lmax	14,20,20	14,20,20
Nref	12192	11674
Tmin,Tmax	0.857,0.922	0.659,1.000
Tmin'	0.857	

Correction method= MULTI-SCAN

Data completeness= 0.958 Theta(max)= 25.000

R(reflections)= 0.0705(11286) wR2(reflections)= 0.2138(11674)

S = 1.103 Npar= 873

Alert level B

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full Low 0.958
PLAT201_ALERT_2_B Isotropic non-H Atoms in Main Residue(s) 3
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 4.1 Ratio
PLAT230_ALERT_2_B Hirshfeld Test Diff for O41 -- C41 .. 9.3 su
PLAT230_ALERT_2_B Hirshfeld Test Diff for C41 -- C42 .. 10.0 su
PLAT420_ALERT_2_B D-H Without Acceptor >O111 - >H11X ... ?

Alert level C

PLAT077_ALERT_4_C Unitcell contains non-integer number of atoms .. ?
PLAT202_ALERT_3_C Isotropic non-H Atoms in Anion/Solvent 1
PLAT214_ALERT_2_C Atom C200 (Anion/Solvent) ADP max/min Ratio 4.3 oblat
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 4.5 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for C42 -- C43 .. 5.8 su
PLAT234_ALERT_4_C Large Hirshfeld Difference C2 -- C3 .. 0.16 Ang.
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of P1
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C91
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0083 Ang
PLAT413_ALERT_2_C Short Inter XH3 .. XHn H3 .. H20B .. 2.14 Ang.
PLAT414_ALERT_2_C Short Intra D-H..H-X H7 .. H2X .. 1.97 Ang.
PLAT480_ALERT_4_C Long H...A H-Bond Reported H11X .. O100 .. 2.62 Ang.
PLAT721_ALERT_1_C Bond Calc 0.93000, Rep 0.91570 Dev... 0.01 Ang.
O500 -H50X 1.555 1.555 # 119
PLAT772_ALERT_2_C Suspect O-H Bond in CIF: O200 -- H201 .. 1.35 Ang.

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 3
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF ?
PLAT007_ALERT_5_G Note: Number of Unrefined Donor-H Atoms 12
PLAT045_ALERT_1_G Calculated and Reported Z Differ by ..... 0.50 Ratio
PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large. 0.13
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 9.93
PLAT152_ALERT_1_G The Supplied and Calc. Volume s.u. Differ by ... 3 Units
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.03000 Deg.
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C111

PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of C80
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 4 %
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..... 44 %
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 2

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4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
14 ALERT type 2 Indicator that the structure model may be wrong or deficient
6 ALERT type 3 Indicator that the structure quality may be low
7 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

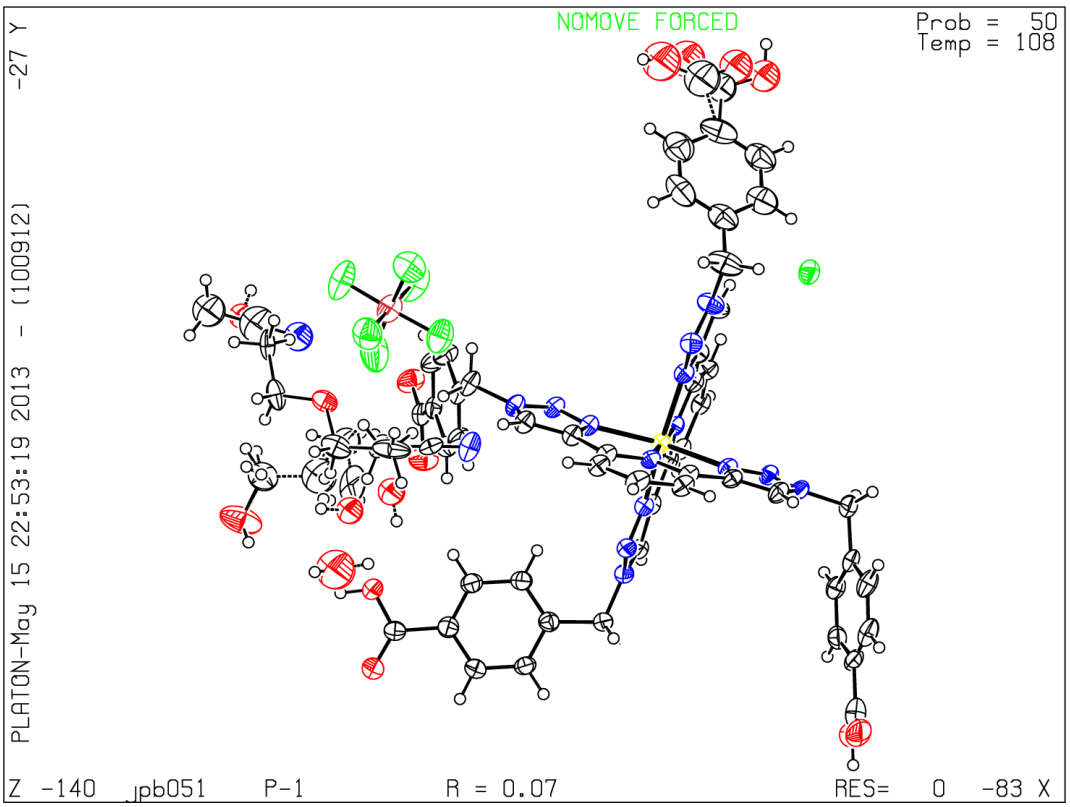

Figure A.41 Ellipsoid plot of the X-ray crystal structure of [Ru·(**89**)$_2$]PF$_6$Cl

Ru(II) complex of $[Ru\cdot(88)_2]^{2+}$

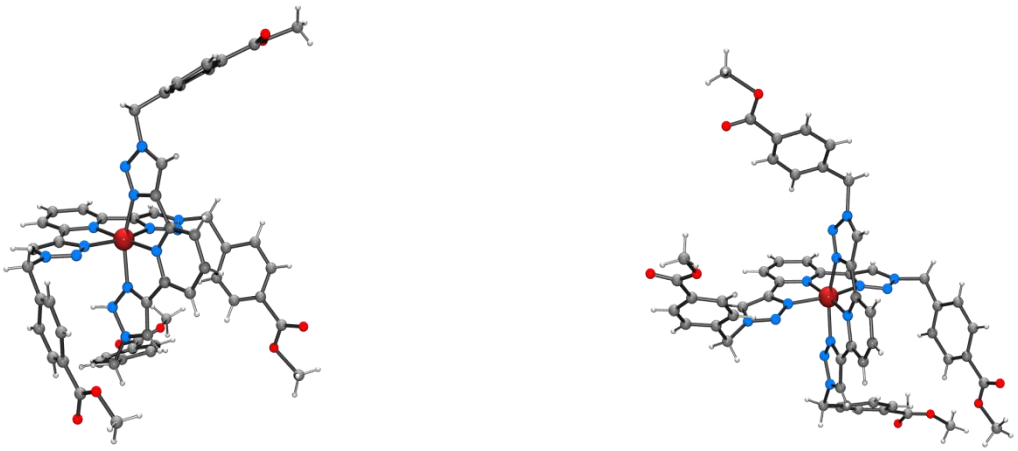

Figure A.42 Ball and stick models of the two independent molecules in the unit cell of $[Ru\cdot(\mathbf{88})_2]^{2+}$. Data could not be refined sufficiently for detailed analysis, but the distorted octahedral geometry is clear and analogous to the geometry of $[Ru\cdot(\mathbf{89})_2]PF_6Cl$.

Ru(II) complex $[Ru\cdot(88)Cl_2(DMSO)]$

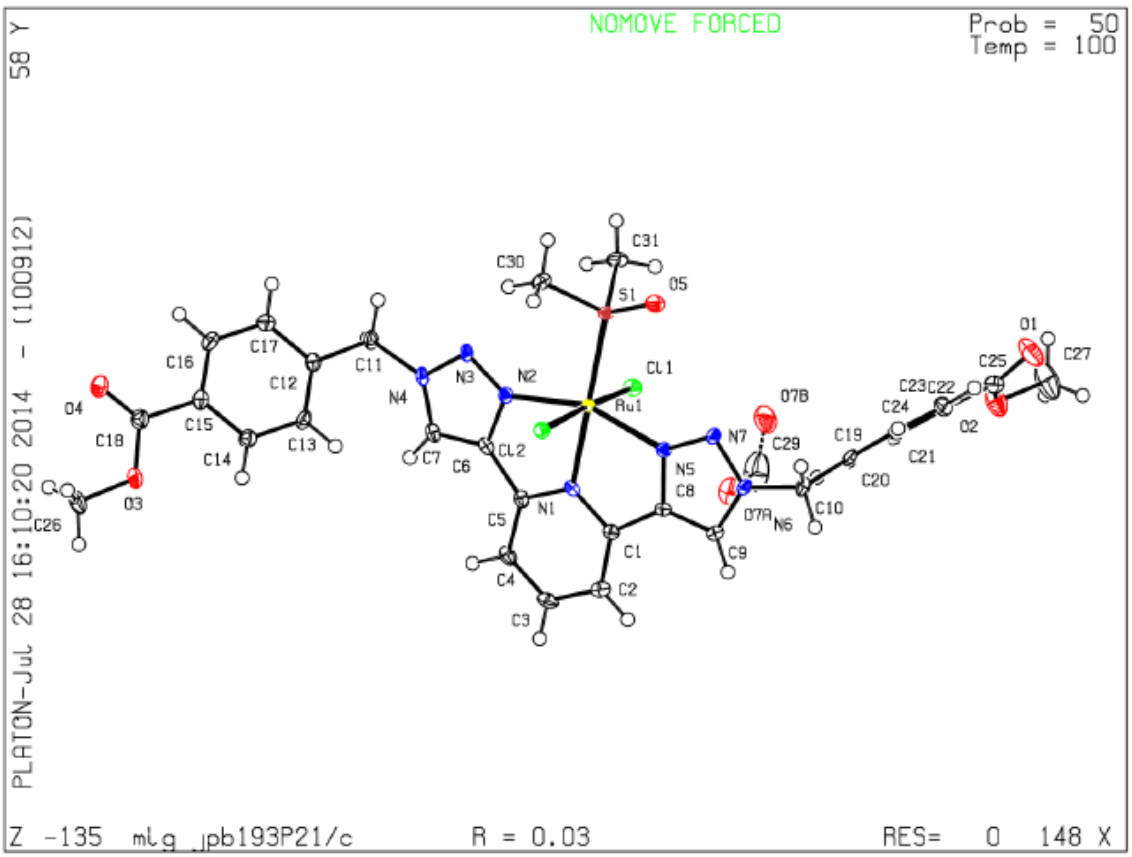

Figure A.43 Ellipsoid plot of the X-ray crystal structure of $[Ru\cdot(\mathbf{89})Cl_2(DMSO)]$.

Ni(II) complex [Ni·(88)$_2$]PF$_6$Cl

```
Bond precision:      C-C = 0.0045 A              Wavelength=1.54178
Cell:          a=14.4083(10)   b=14.8238(11)   c=16.2001(12)
               alpha=108.541(3)  beta=91.506(3)  gamma=115.862(3)
Temperature:   108 K
                    Calculated                    Reported
Volume              2896.2(4)                     2896.2(4)
Space group         P -1                          P-1
Hall group          -P 1                          ?
Moiety formula      C54 H46 N14 Ni O8, F6 P, C2 H3 N, Cl, H2 O   ?
Sum formula         C56 H51 Cl F6 N15 Ni O9 P     C56 H51 Cl F6 N15 Ni O9 P
Mr                  1317.23                       1317.25
Dx,g cm-3           1.510                         1.510
Z                   2                             2
Mu (mm-1)           1.952                         1.952
F000                1356.0                        1356.0
F000'               1355.74
h,k,lmax            16,17,18                      16,16,18
Nref                9473                          8995
Tmin,Tmax           0.558,0.761                   0.558,0.753
Tmin'               0.472
Correction method= MULTI-SCAN
Data completeness= 0.950       Theta(max)= 63.490
R(reflections)= 0.0497( 8484)     wR2(reflections)= 0.1274( 8995)
S = 1.039             Npar= 801
```

Alert level B

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full Low 0.950
PLAT201_ALERT_2_B Isotropic non-H Atoms in Main Residue(s) 4
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 4.3 Ratio

Alert level C

THETM01_ALERT_3_C The value of sine(theta_max)/wavelength is less than 0.590
Calculated sin(theta_max)/wavelength = 0.5804
PLAT220_ALERT_2_C Large Non-Solvent O Ueq(max)/Ueq(min) ... 3.3 Ratio
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 4.7 Ratio
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C42
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of P1
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C100
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor 3.4

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF ? Do !
PLAT007_ALERT_5_G Note: Number of Unrefined Donor-H Atoms 2
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.00300 Deg.
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) P1 -- F6 .. 6.0 su
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 5 %
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 15

```
       N44 -NI1 -N4  -C16    23.80  1.10   1.555   1.555   1.555   1.555
And 3 other PLAT710 Alerts
More ...
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #       226
         C66  -C63  -C166    1.555   1.555   1.555          32.90 Deg.
```

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4 ALERT type 3 Indicator that the structure quality may be low
8 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

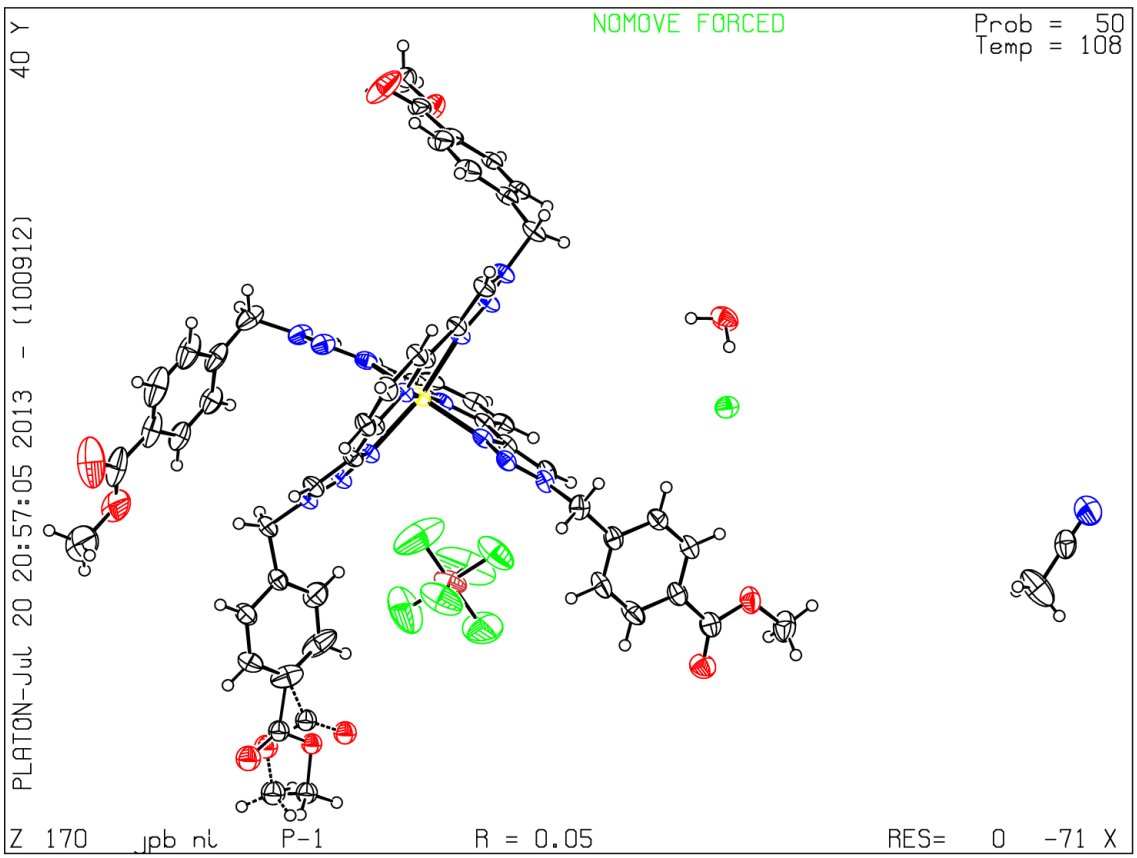

Figure A.44 Ellipsoid plot of the X-ray crystal structure of [Ni·(**88**)$_2$]PF_6Cl

Ir(III) complex [Ir·1Cl$_3$]

```
Bond precision:      C-C = 0.0135 A                Wavelength=1.54178
Cell:          a=15.4149(18)   b=14.1809(19)   c=15.627(2)
               alpha=90        beta=105.781(
                                9)             gamma=90
```

Temperatur e:	100 K	
	Calculated	Reported
Volume	3287.3(7)	3287.2(7)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	?
Moiety formula	4(C27 H23 Cl3 Ir N7 O4), C2 H8 O3	?
Sum formula	C110 H100 Cl12 Ir4 N28 O19	C27.50 H25 Cl3 Ir N7 O4.75
Mr	3312.46	828.10
Dx,g cm-3	1.673	1.673
Z	1	4
Mu (mm-1)	10.497	10.497
F000	1620.0	1620.0
F000'	1609.06	
h,k,lmax	18,16,18	18,16,18
Nref	5756	5490
Tmin,Tmax	0.720,0.900	0.498,0.753
Tmin'	0.626	

Correction method= MULTI-SCAN

Data completeness= 0.954 Theta(max)= 66.160

R(reflections)= 0.0470(4690) wR2(reflections)= 0.1304(5490)

S = 1.072 Npar= 400

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full Low 0.954

Alert level C

PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density 3.81
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) ... 3.1 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C22 -- C23 .. 0.24 Ang.
PLAT241_ALERT_2_C Check High Ueq as Compared to Neighbors for C24
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C2
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C20
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0135 Ang.

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 7
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF ? Do !
PLAT007_ALERT_5_G Note: Number of Unrefined Donor-H Atoms 5
PLAT045_ALERT_1_G Calculated and Reported Z Differ by ..... 0.25 Ratio
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 10.77
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for O4
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C126
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of C100
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 10 %
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..... 100 %
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 19
CL2 -IR1 -N4 -C16 32.00 3.00 1.555 1.555 1.555 1.555

PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 24
CL2 -IR1 -N4 -C12 -145.00 2.00 1.555 1.555 1.555 1.555
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 114
C26 -C23 -C126 1.555 1.555 1.555 25.80 Deg.
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... ! Info
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 5

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6 ALERT type 4 Improvement, methodology, query or suggestion
3 ALERT type 5 Informative message, check

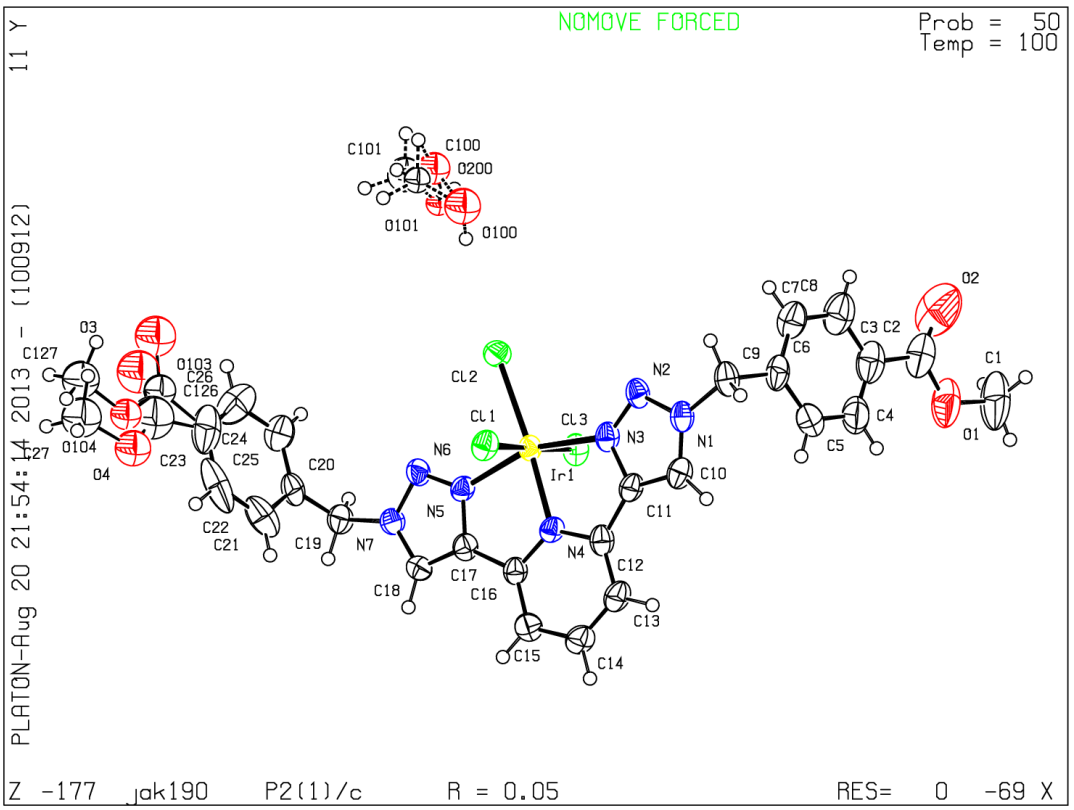

Figure A.45 Ellipsoid plot of the X-ray crystal structure of [Ir·(**88**)Cl_3]

A.5. Spectroscopy

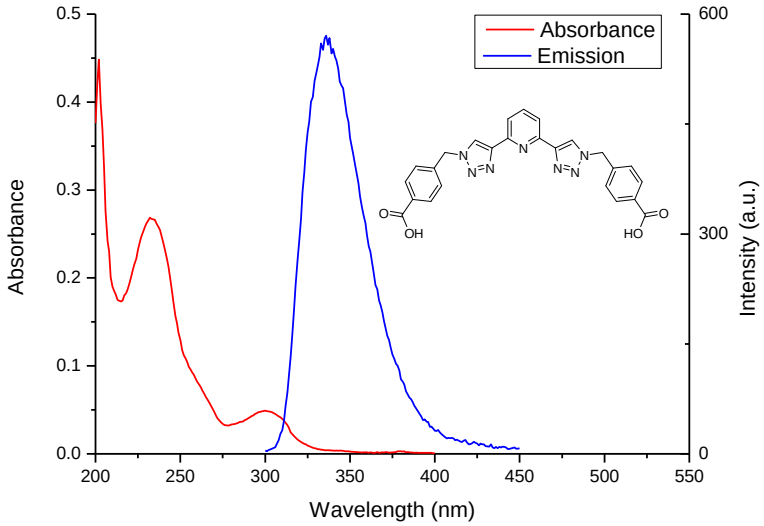

Figure A.46 UV-Vis absorbance (red) and emission (blue) spectra for ligand **89** in CH_3CN.

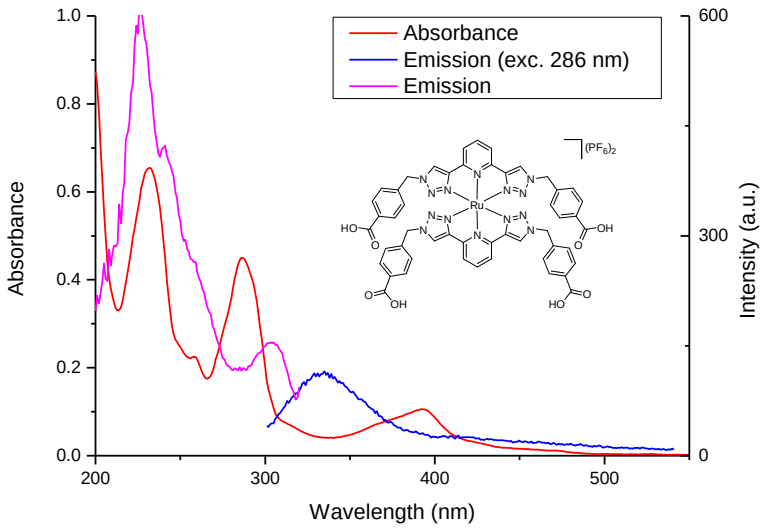

Figure A.47 UV-Vis absorbance (red), emission (blue) and excitation (magenta) spectra for $[Ru\cdot(\mathbf{89})_2](PF_6)_2$ in CH_3CN.

A.6. Electrochemistry

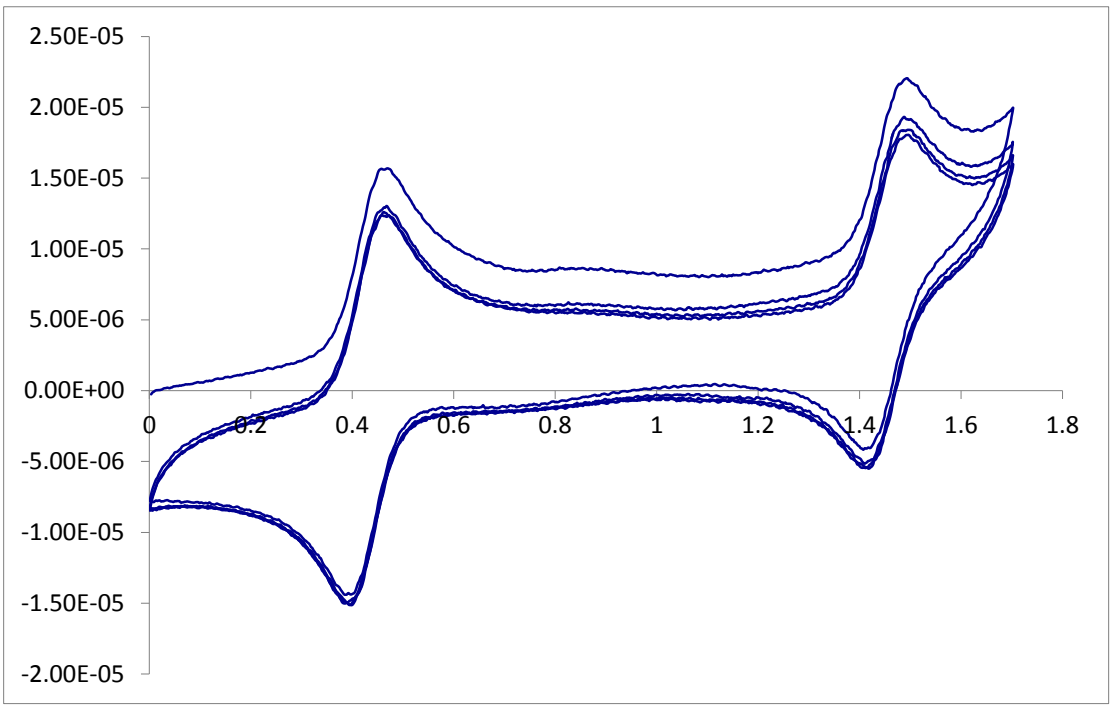

Figure A.48 CV of $[Ru\cdot(\mathbf{89})_2](PF_6)_2$ in CH_3CN. $E_{1/2}$ = +1.43 V (ΔE_p = 60 mV), referenced to Fc^+/Fc, $E_{1/2}$ = +0.41 V (ΔE_p = 72 mV)

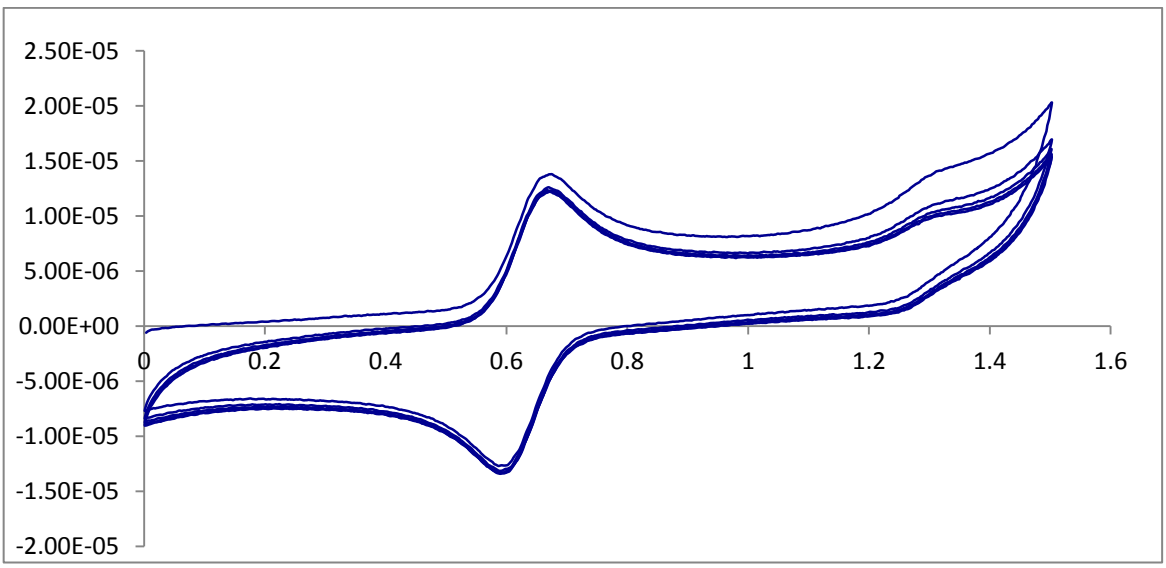

Figure A.49 CV of $[Ru\cdot(\mathbf{88})Cl_2(DMSO)]$ in CH_3NO_2. $E_{1/2}$ = +0.75 V (ΔEp = 58 mV), referenced to $Ru(bpy)_3^{2+/3+}$, $E_{1/2}$ = 1.39 V (ΔEp = 55 mV)