Effect of *Cis-trans* Configurational Difference on the Performance of Pyridylimine-based Ruthenium Sensitizers

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X-ray Crystallography of IP102 ester (5a).

A suitable deep purple crystal of compound **5a** having dimensions 0.12 x 0.06 x 0.01 mm^3 was selected for X-ray crystallographic analysis. The intensity data was collected on a Bruker Kappa Apex II CCD diffractometer which was equipped with a normal focus, 3-kW sealed tube X-ray source. The X-ray intensity data were measured and collected at 100 K through a refinement of 6330 reflections to a maximum resolution of 0.75 Å via a series of 0.5° ω and ϕ scans. The absorption correction ($T_{min/max}$ = 0.3955 /0.9486) was carried out using the SADABS V2008 program.[S1] The frames were integrated with the Bruker Apex II software. The structure was solved utilizing direct methods and the refinement was performed using the Bruker *SHELXTL* version 6.14 software package.[S2] Data analysis showed no sample decomposition.

Table S1. Crystal data and structure refinement for IP102 ester (5a).

Identification code	120809lt	
Empirical formula	C30 H26 N6 O4 Ru S2	
Formula weight	699.76	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 10.337(6) Å	a= 90°.
	b = 34.87(2) Å	b= 101.049(13)°.
	c = 8.498(5) Å	g = 90°.
Volume	3006(3) Å3	
Z	4	
Density (calculated)	1.546 Mg/m^3	
Absorption coefficient	0.707 mm^{-1}	
F(000)	1424	
Crystal size	0.12 x 0.06 x 0.01 mm^3	
Theta range for data collection	2.01 to 26.88°.	
Index ranges	-13<=h<=12, -44<=k<=43, -10<=l<=4	

Reflections collected	24541
Independent reflections	6330 [R(int) = 0.2549]
Completeness to theta = 26.88°	97.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9486 and 0.3955
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6330 / 0 / 392
Goodness-of-fit on F2	0.947
Final R indices [I>2sigma(I)]	R1 = 0.0964, wR2 = 0.1756
R indices (all data)	R1 = 0.2477, wR2 = 0.2377
Largest diff. peak and hole	0.970 and -0.601 e.$Å^{-3}$

X-ray Crystallography of IP104 ester (5b).

A deep green compound **5b** crystal with dimensions 0.38 x 0.18 x 0.14 mm^3 was chosen for X-ray crystallographic analysis. The intensity data were obtained at 296 K through a refinement of 9440 reflections to a maximum resolution of 0.8 Å via a series of 0.5° ω and ϕ scans. The absorption correction ($T_{min/max}$ = 0.7733 /0.9067), the refinement and the structure was carried out and solved according to the method described for compound **5a**.

Table S2. Crystal data and structure refinement for IP104 ester (5b).

Identification code	13ja13	
Empirical formula	C37 H32 Cl2 N6 O4 Ru S2	
Formula weight	860.78	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.1605(4) Å	a= 90°.
	b = 12.2206(4) Å	b= 93.388(2)°.
	c = 25.5273(8) Å	g = 90°.
Volume	3786.9(2) $Å^3$	
Z	4	
Density (calculated)	1.510 Mg/m^3	
Absorption coefficient	0.713 mm^{-1}	
F(000)	1752	
Crystal size	0.38 x 0.18 x 0.14 mm^3	

Theta range for data collection	1.60 to 28.42°.
Index ranges	-16<=h<=16, -16<=k<=16, -32<=l<=34
Reflections collected	54131
Independent reflections	9440 [R(int) = 0.0298]
Completeness to theta = 28.42°	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.905 and 0.857
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9440 / 0 / 473
Goodness-of-fit on F2	1.015
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.1118
R indices (all data)	R1 = 0.0578, wR2 = 0.1245
Largest diff. peak and hole	0.718 and -0.944 e.$Å^{-3}$

Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as deposition No's CCDC 1821991-1821992. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Theoretical calculation for the location of HOMOs and LUMOs

Frontier molecular orbitals of the HOMO and LUMO for the dyes IP102 and IP104 were calculated using the Gaussian software package.

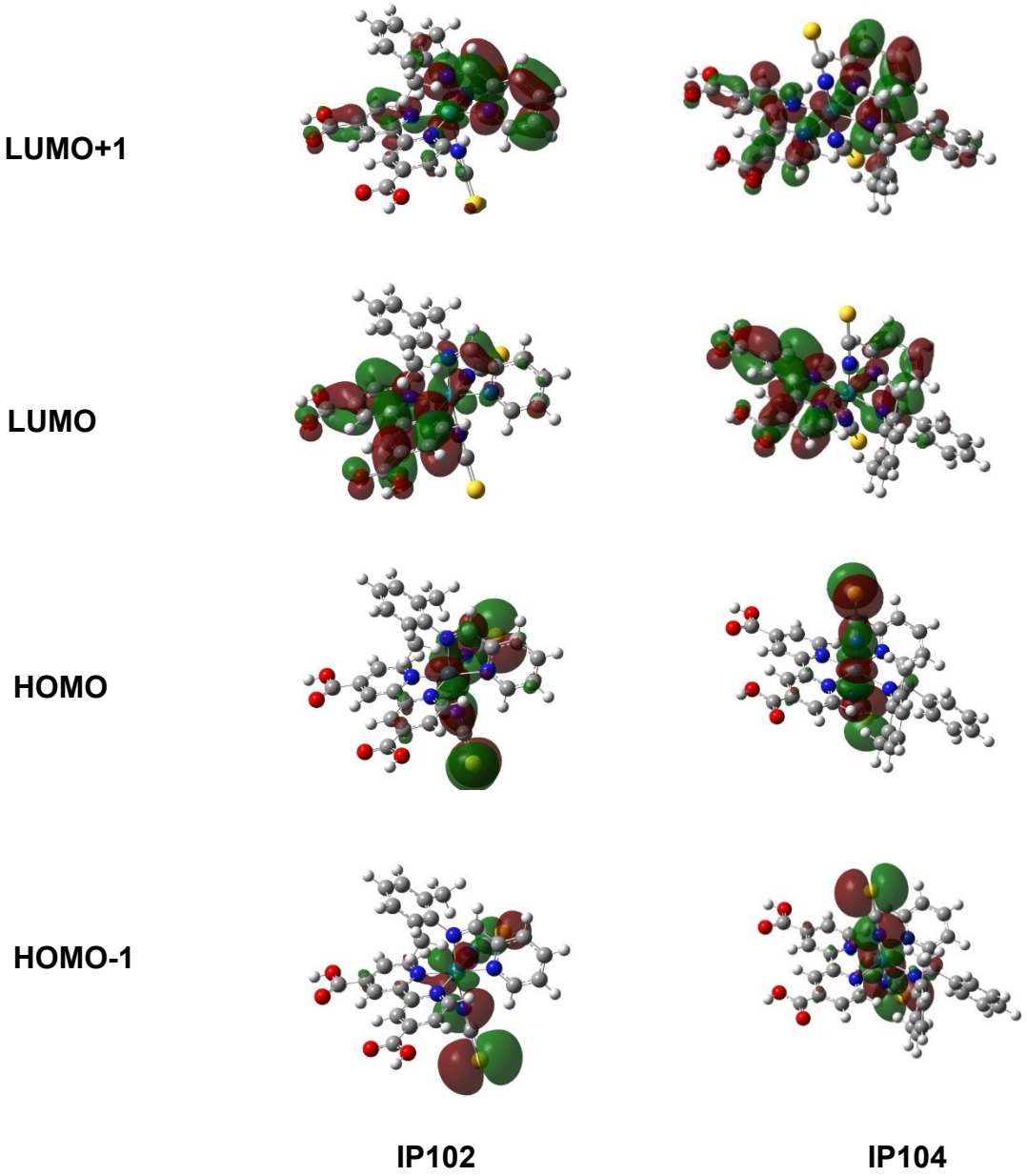


Figure S1. Graphical representation of the frontier orbitals of IP102 and IP104.

EIS measurements:

The electron transport properties were studied by electrochemical impedance spectroscopy (EIS) with an impedance analyzer (IM6ex, Zahner, Germany) under illumination condition of 100 mW/cm^{-2} with an ac amplitude of 10 mV and frequency range of 10^{-1}-10^{5} Hz. Alternative impedance spectra of DSSCs fabricated with IP102, IP104 and N719 were measured at a forward bias of 0.70 V in dark conditions. The Nyquist plots measured under dark and illumination conditions were shown in Fig. S2 and Fig. 5 (manuscript), respectively. Modeling and fitting the EIS data of DSSCs was carried out using the ZView software to obtain the electron transport parameters of cells.

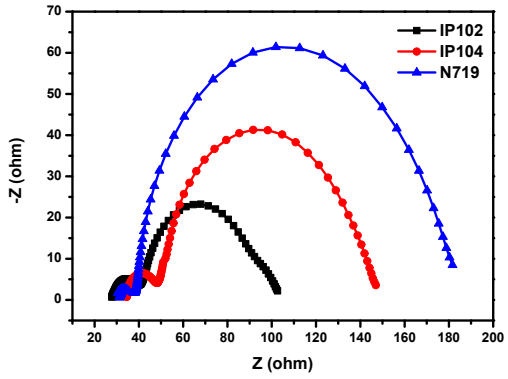


Figure S2. ESI (Nyquist plots) of DSSCs measured under dark conditions.

The equivalent circuit used for model the data was as follows:

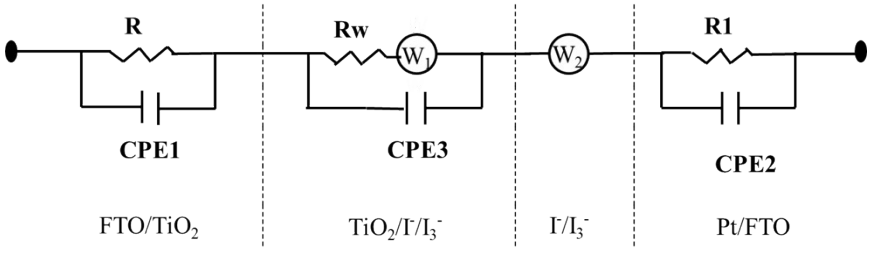


Figure S3. Equivalent circuit for modeling the EIS data.

The rate constant of recombination of electron in the film (k_{eff}) was estimated from the peak frequency ω_{max} of the central arc.

The electron life time (τ) in the working electrode was inverse of the k_{eff}.

The charge transfer resistance including recombination of electrons at TiO_2/ electrolyte interface (R_k) is the diameter of the central arc.

Effective electron diffusion coefficient (D_{eff}) was determined from the equation:

$$D_{eff} = \left(\frac{R_k}{R_w}\right) L^2 k_{eff}$$

R_k/R_w was estimated from the central arc and L is the thickness of the film.

Electron transport resistance in semiconductor film (R_w) was determined from the equation:

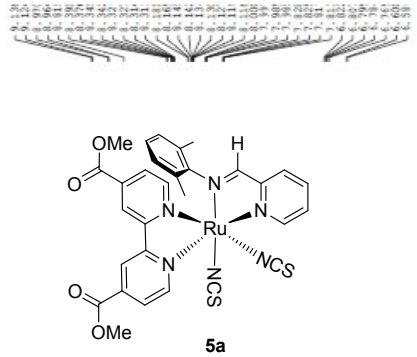
$$R_w = R_k + L^2 \times k_{eff}/D_{eff}$$

The electron diffusion length L_n was calculated from the equation:

$$L_n = L\sqrt{\tau/\tau_d} = L\sqrt{\frac{\tau}{1/k}}; \quad k = \frac{1}{\tau_d}$$

^{1}H and ^{13}C NMR spectra of IP102 and IP104

1. ^{1}H and ^{13}C NMR (500MHz) spectra of compound 5a.



5a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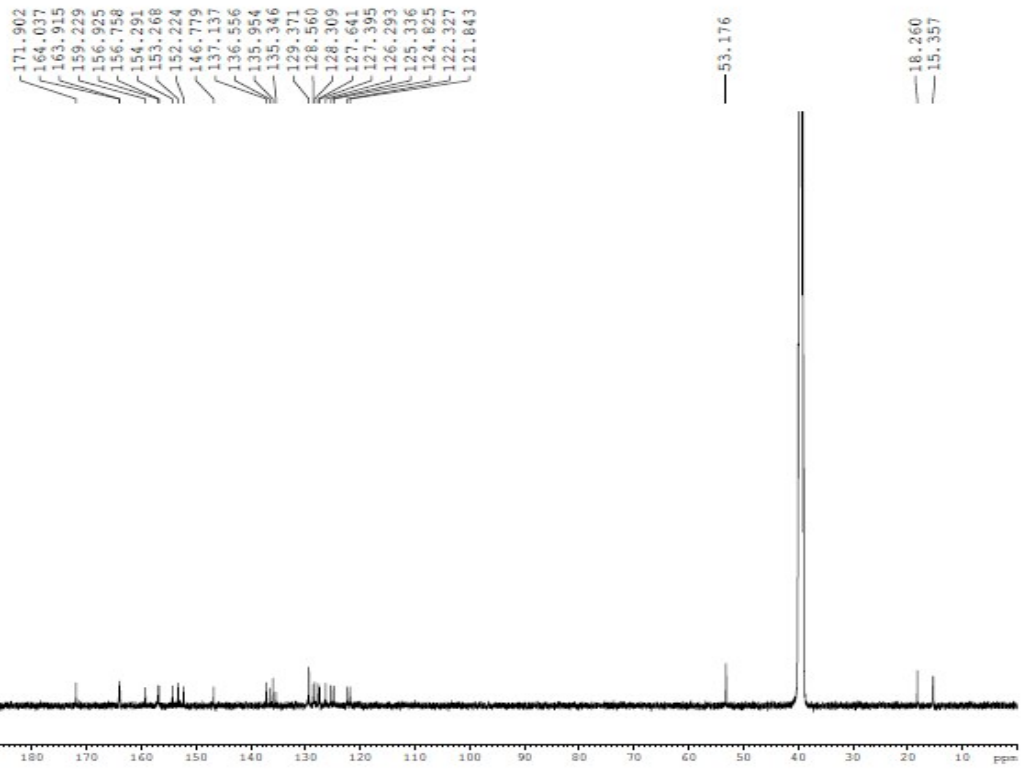
Current Data Parameters
NAME       IP102-H-1010725
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20120725
Time                 17.03
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  16384
SOLVENT              CDCl3
NS                      32
DS                       0
SWH             7507.507 Hz
FIDRES          0.458222 Hz
AQ              1.0912244 sec
RG                     362
DW                66.600 usec
DE                14.00 usec
TE                301.2 K
D1              1.50000000 sec
MCREST    0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.50 usec
PL1                 -4.00 dB
SFO1          500.1332508 MHz

F2 - Processing parameters
SI                    16384
SF          500.1300047 MHz
WDW                     EM
SSB                  0
LB                   0.10 Hz
GB                   0
PC                   1.00
```



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Current Data Parameters
NAME       IP102-Ester-C13
EXPNO                    4
PROCNO                   1

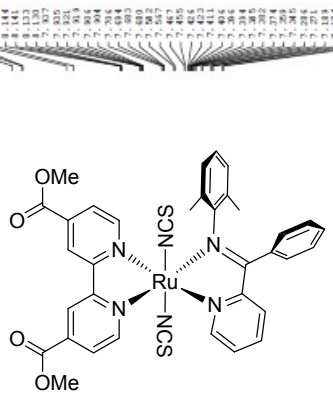
F2 - Acquisition Parameters
Date_              20121105
Time                 18.01
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                  65536
SOLVENT              CDCl3
NS                   30000
DS                       0
SWH            31446.541 Hz
FIDRES          0.479834 Hz
AQ              1.0420724 sec
RG                  5792.6
DW                15.900 usec
DE                14.00 usec
TE                295.8 K
D1              1.20000005 sec
d11             0.03000000 sec
DELTA           1.10000002 sec
MCREST    0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                   12.00 usec
PL1                   6.80 dB
SFO1          125.7722011 MHz

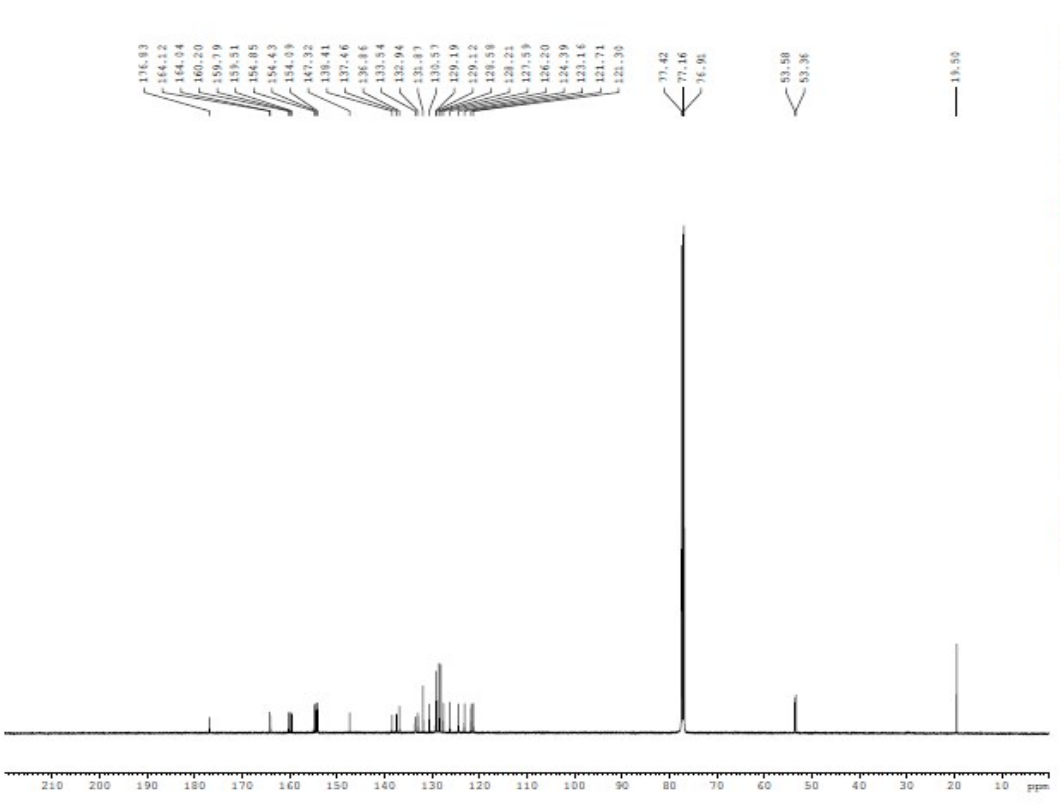
======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2                90.00 usec
PL2                  -4.00 dB
PL12                 14.90 dB
PL13                 17.90 dB
SFO2          500.1322506 MHz

F2 - Processing parameters
SI                    32768
SF          125.7578460 MHz
WDW                     EM
SSB                  0
LB                    1.00 Hz
GB                   0
PC                   1.40
```

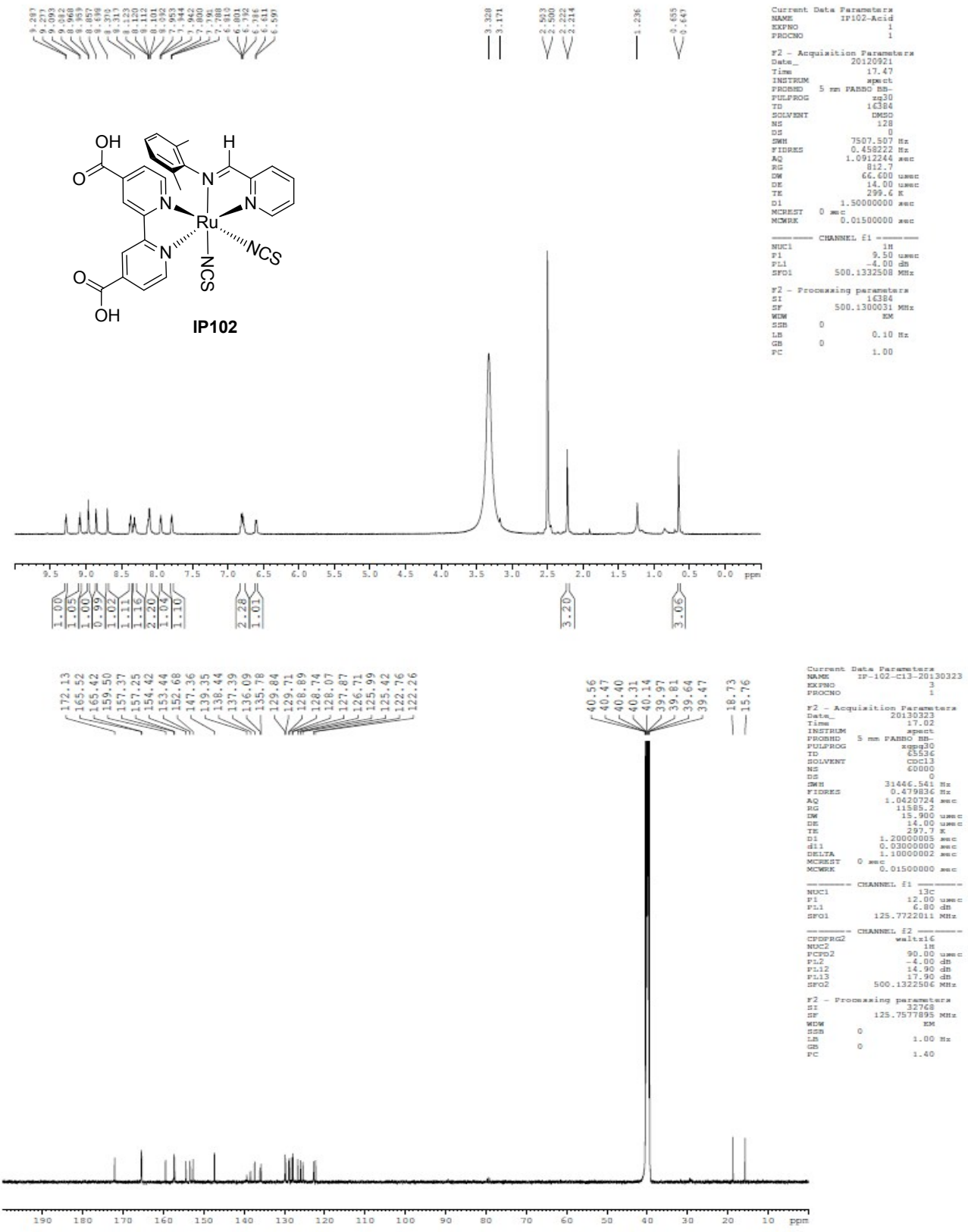
2.^{1}H and ^{13}C NMR (500MHz) spectra of compound 5b



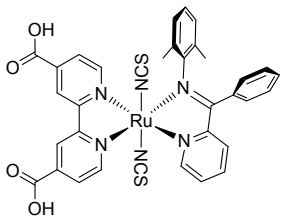
5b



3.^{1}H and ^{13}C NMR (500MHz) spectra of IP102



4.^{1}H and ^{13}C NMR (500MHz) spectra of IP104



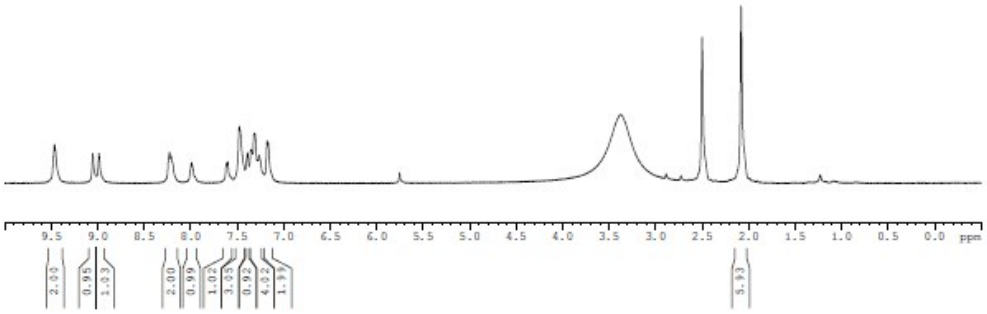
IP104

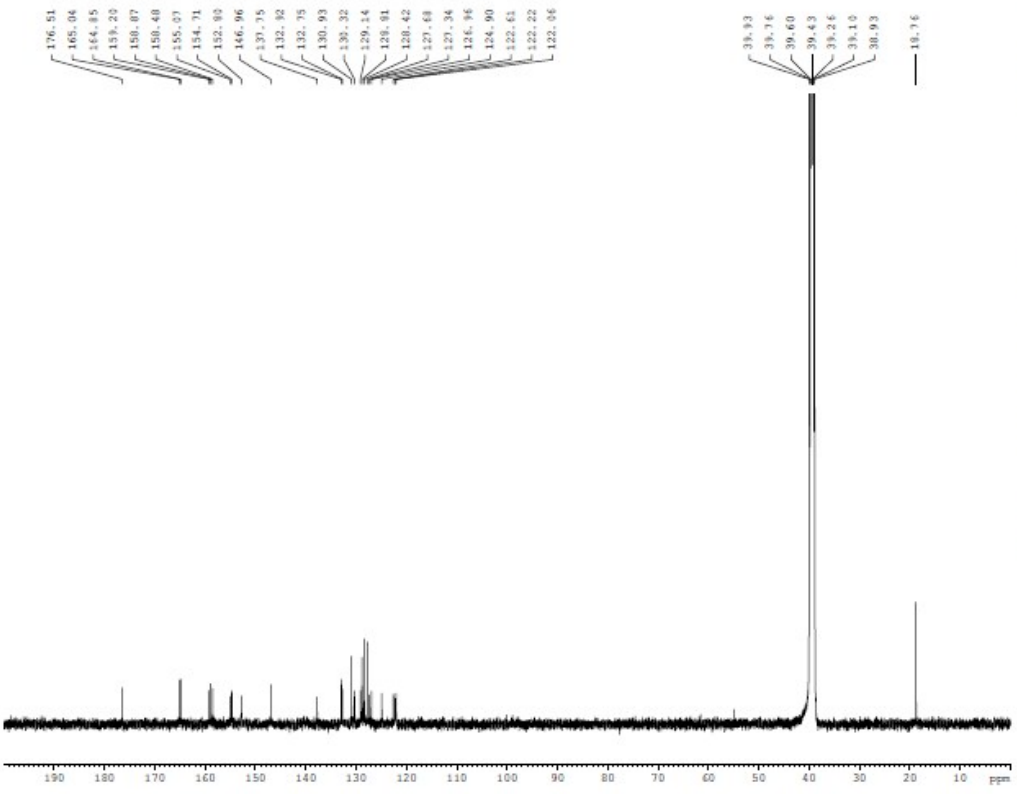
```
Current Data Parameters
NAME        IP104-H1-20130327
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_              20130327
Time                 20.08
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  16384
SOLVENT              DMSO
NS                     32
DS                      0
SWH               7507.507 Hz
FIDRES            0.458222 Hz
AQ                1.0912244 sec
RG                    322.5
DW                   66.600 usec
DE                   14.00 usec
TE                   296.3 K
D1                1.50000000 sec
MCREST    0 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.50 usec
PL1                 -4.00 dB
SFO1          500.1332508 MHz

F2 - Processing parameters
SI                    16384
SF              500.1300018 MHz
WDW                     EM
SSB       0
LB                    0.10 Hz
GB        0
PC                    1.00
```



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Current Data Parameters
NAME        IP104-H1-20130327
EXPNO                       3
PROCNO                      1

F2 - Acquisition Parameters
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Time                 20.20
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT              DMSO
NS                     30000
DS                      0
SWH              31446.541 Hz
FIDRES            0.479836 Hz
AQ                1.0420724 sec
RG                    13004
DW                   15.900 usec
DE                   14.00 usec
TE                   296.6 K
D1                1.20000005 sec
d11               0.03000000 sec
DELTA             1.10000002 sec
MCREST    0 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   12.00 usec
PL1                   6.80 dB
SFO1          125.7722011 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2                90.00 usec
PL2                  -4.00 dB
PL12                 14.90 dB
PL13                 17.90 dB
SFO2          500.1322506 MHz

F2 - Processing parameters
SI                    32768
SF              125.7578569 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

REFERENCES

(S1) Sheldrick, G. M. *SADABS*, version 2008/1; University of Göttingen: Göttingen, Germany, 2008.
(S2) Sheldrick, G. M. *SHELXTL*, version 6.14; Bruker AXS GmbH: Karlsruhe, Germany, 2000.