Electronic Supplementary Material (ESI) for New Journal of Chemistry

Synthesis and Characterization of Carbene-Pyridyl Anchoring Ru(II) Dyes with Various Binding Functionalities for Photoelectrochemical Cells

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X-ray analysis data of the ester DC109

CCDC 1554935 contains the supplementary crystallographic data for the compound DC109. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal Data and Structure Refinement for DC109.

Identification code	mo_130333lt_0m	
Empirical formula	C28 H30 N8 O4 Ru S2	
Formula weight	707.79	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 19.0058(13) Å	= 90°.
	b = 10.2651(7) Å	= 90.8330(10)°.
	c = 15.6740(11) Å	= 90°.
Volume	3057.6(4) $Å^3$	
Z	4	
Density (calculated)	1.538 Mg/m^3	
Absorption coefficient	0.697 mm^{-1}	
F(000)	1448	
Crystal size	0.25 x 0.12 x 0.10 mm^3	
Theta range for data collection	2.60 to 28.53°.	
Index ranges	-25<=h<=25, -13<=k<=13, -20<=l<=10	
Reflections collected	14275	
Independent reflections	3839 [R(int) = 0.0300]	
Completeness to theta = 28.53°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9486 and 0.7819	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3839 / 3 / 226	
Goodness-of-fit on F^2	1.188	
Final R indices [I>2sigma(I)]	R1 = 0.0395, wR2 = 0.1105	
R indices (all data)	R1 = 0.0416, wR2 = 0.1114	
Largest diff. peak and hole	1.330 and -0.961 $e.Å^{-3}$	

Electrochemical measurement

Cyclic voltammetry (CV) experiments were performed using an electrochemical setup consisting of a conventional single-compartment three-electrode cell, with a glassy carbon electrode as the working electrode, a silver wire ($Ag/AgNO_3$ in acetonitrile) as the reference electrode, a Pt wire as the counter-electrode, and 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. A scan rate of 50 mVs^{-1} was typically used to record the cyclic voltammograms of DC101, DC107, and DC108. After each measurement, ferrocene was added as the internal reference for calibration. Cyclic volatammograms of dyes DC101, DC107, and DC108 were presented in Figure S1.

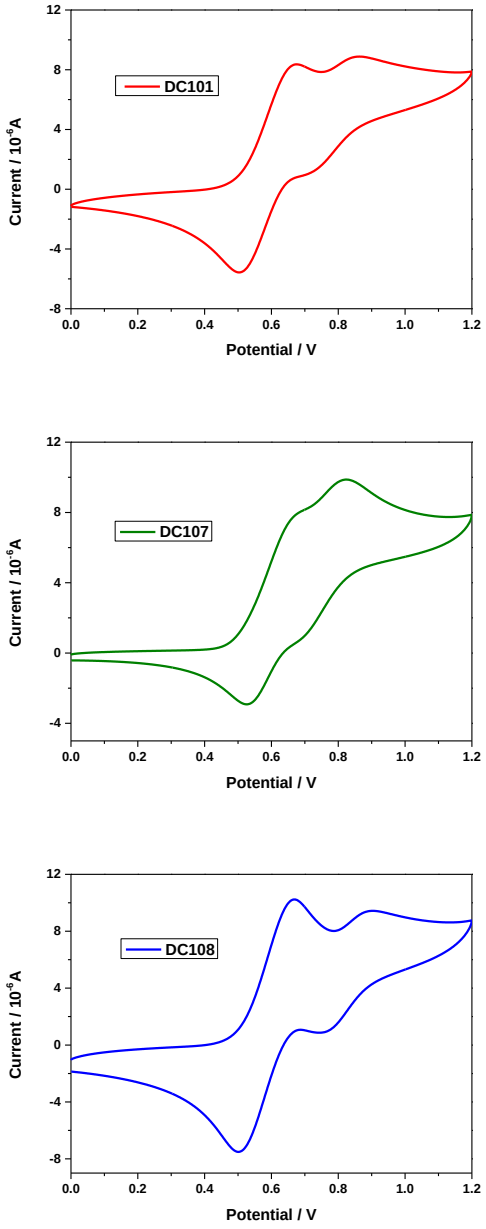


Figure.S1. Cyclic voltammograms of sensitizers DC101, DC107, and DC108

Theoretical calculation for the location of frontier molecular orbitals of dyes DC101, DC107, and DC108

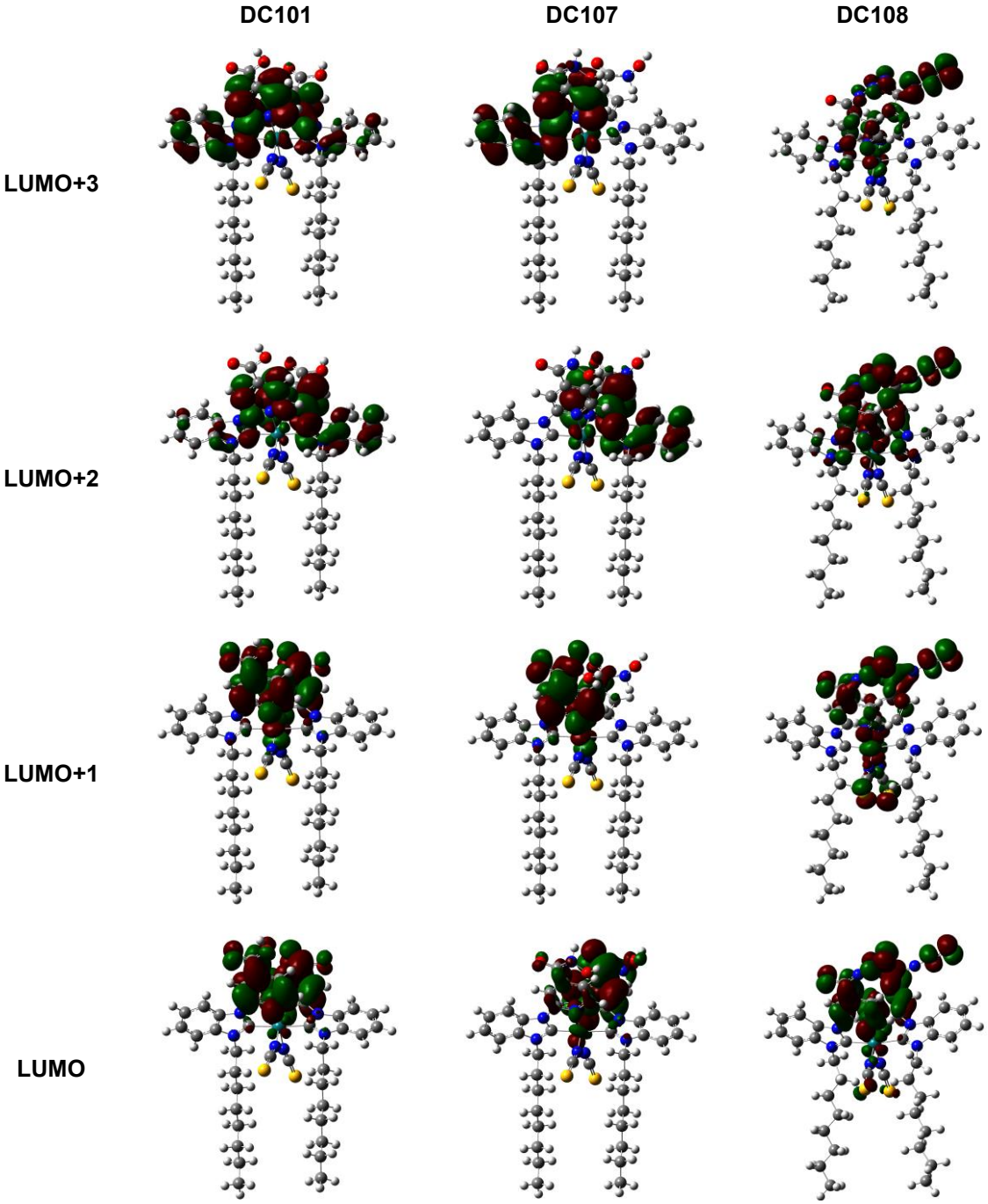


Figure S2: Schematic diagrams of the frontier molecular orbitals (LUMOs) of DC101, DC107, and DC108 calculated at the B3LYP/ LanL2DZ (d,p) level of theory

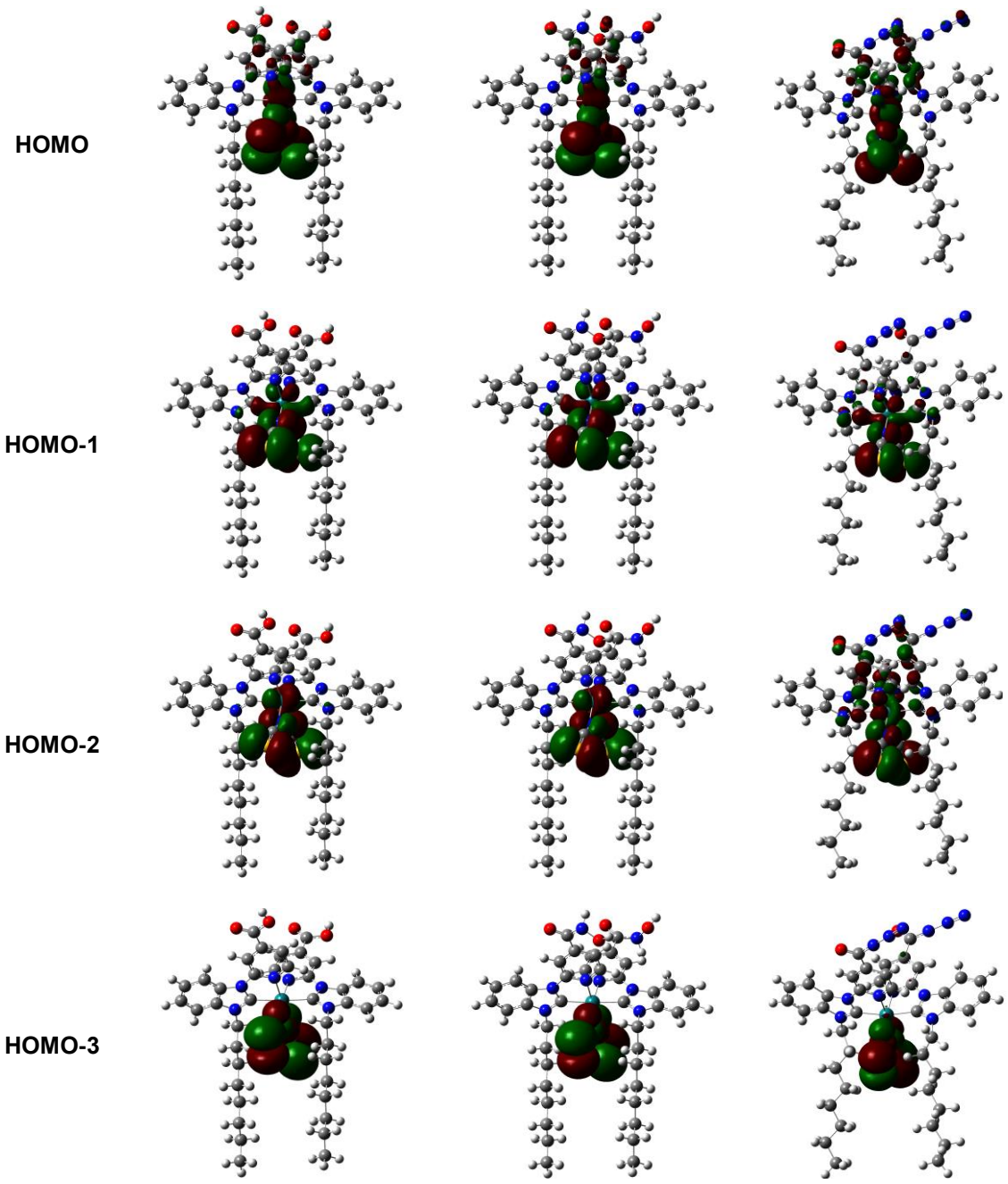


Figure S3: Schematic diagrams of the frontier molecular orbitals (HOMOs) of DC101, DC107, and DC108 calculated at the B3LYP/LanL2DZ (d,p) level of theory.

Table S2. Theoretical calculations of DC dyes

Dye	E_{HOMO} [eV]	E_{LUMO} [eV]	$E_{0\text{-}0}$[a] [eV]
DC101	4.66	2.96	1.70
DC107	4.84	3.07	1.77
DC108	4.73	3.20	1.53

[a]The energy gap, $E_{0\text{-}0} = E_{HOMO}–E_{LUMO}$, the energies obtained were in Hartree units and converted to eV by multiplying with 27.211

Integrated photocurrent (J_{sc}) from IPCE.

The curves of the photocurrent of DC dyes obtained by integrating the area under IPCE curves was presented in Figure. S4 and the corresponding experimental data was provided in Table S3.

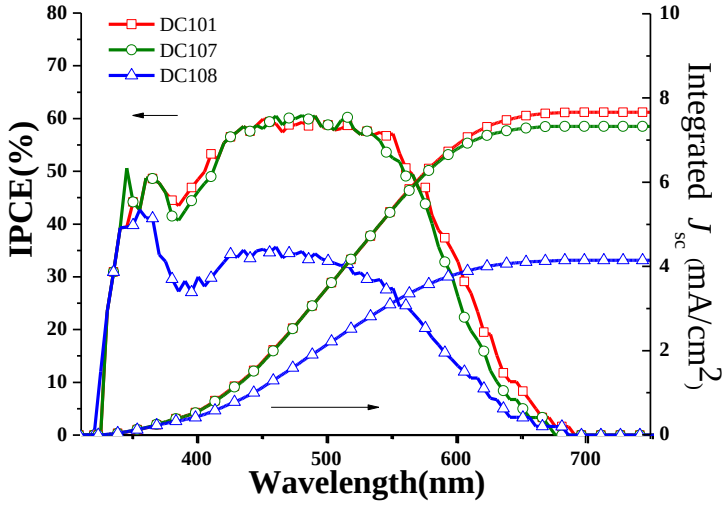


Figure. S4. IPCE spectra and the corresponding integrated J_{sc} of the Dc dyes

Table S3. Performance parameters of the DC dyes

Dyes	Isc (mA)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)	IPCE (%) at 480nm	$J_{sc\ IPCE}$ (mA/cm^2)	Max J_{sc} for 100% IPCE (mA/cm^2)
DC101	1.48	9.26	0.63	0.70	4.06	59.8	7.65	14.46
DC107	1.52	9.50	0.71	0.74	4.97	60.2	7.32	13.71
DC108	0.68	4.26	0.57	0.67	1.62	35.0	4.14	12.76

Electrochemical Impedance Spectroscopy.

The electrochemical impedance spectroscopy (EIS) was employed using an impedance analyzer (IM6ex, Zahner, Germany) at a constant voltage under illumination (100 mW/cm^{-2}) with an ac amplitude of 10 mV and frequency range of 10^2 - 10^5 Hz. Alternative impedance spectra of DSSCs fabricated with **DC101**, **DC107** and **DC108** 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 Figure 4. The Z-VIEW software was utilized for modeling and fitting the EIS data of DSSCs to obtain the various electron transport parameters in DSSCs, including, (1) the charge transfer resistance related to the recombination of electron at the interface (R_k); (2) the electron transport resistance in the photoanode (R_w); (3) the effective rate constant for recombination (k_{eff}); (4) electron lifetime in

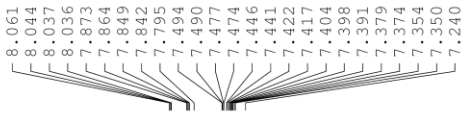
photoanode (τ); (5) electron diffusion length (L_n); and (6) the effective electron diffusion coefficient (D_{eff}) measured at an open-circuit voltage (Voc) under illumination and the data were shown in Table S4.

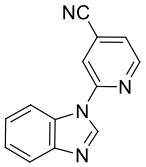
Table S4: Electron transport properties of DSSCs composed of DC dyes

Dyes	R_k	R_w	L(thickness) um	k_{eff}	$\tau(s^{-1})$	Rk/Rw	L_n (um)	Deff(cm^2/s)
DC101	16.62	4.65	15.1	26.1	0.0383	3.574	28.55	2.1E-04
DC107	16.84	8.63	15.1	14.6	0.0685	1.952	21.10	6.5E-05
DC108	22.54	21.64	15.1	26.1	0.0383	1.042	15.41	6.2E-05

^{1}H and ^{13}C NMR spectra of compounds 2-5 and dyes DC101, DC107, and DC108.

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





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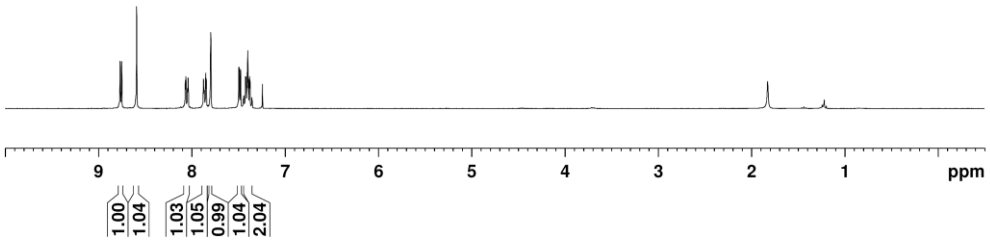

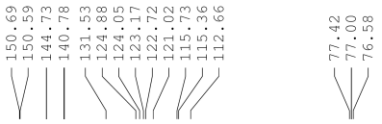


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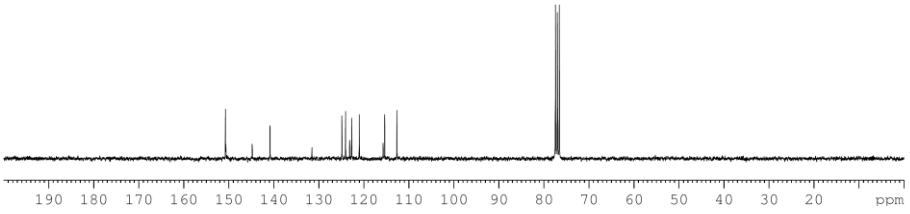
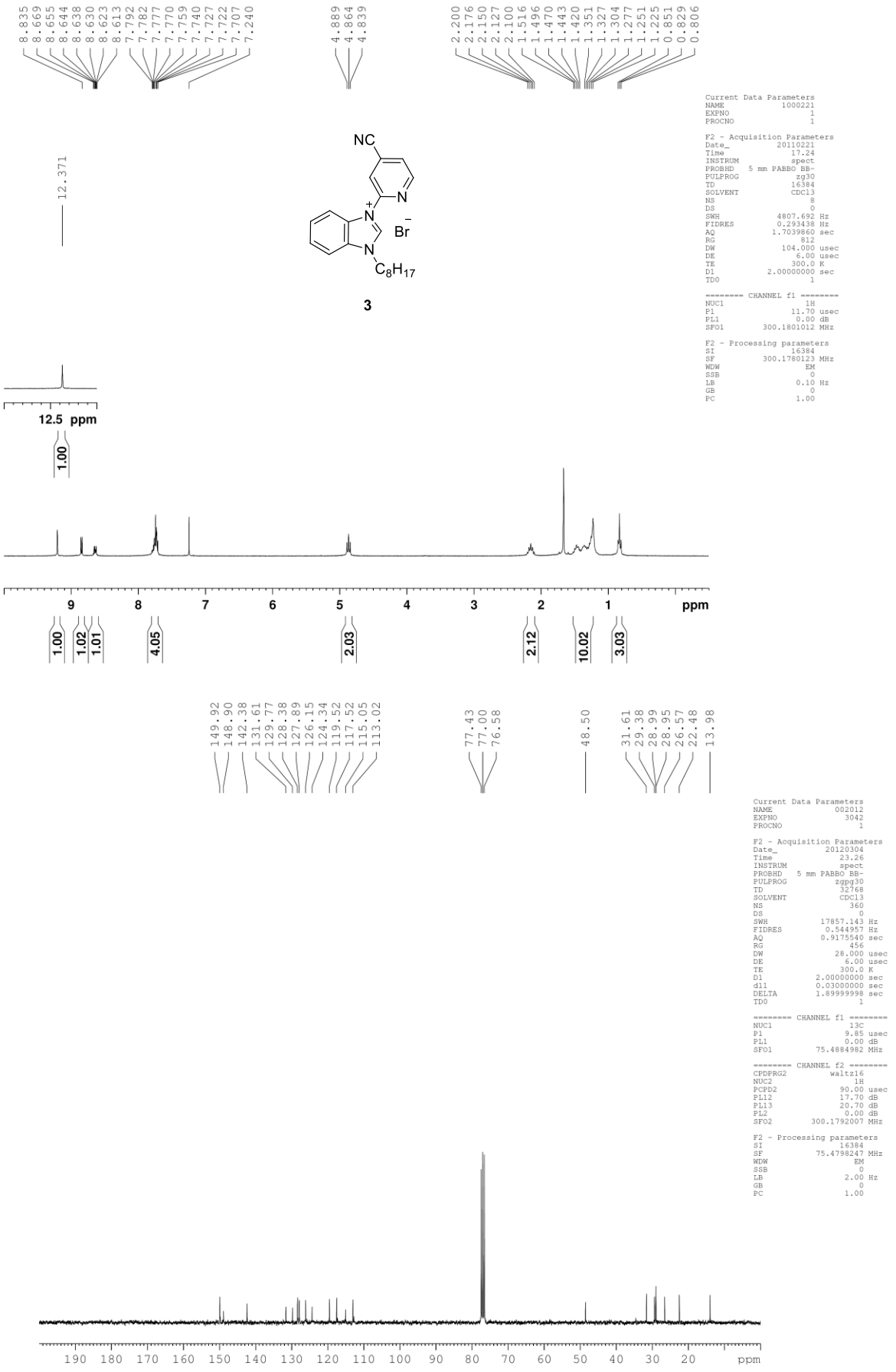
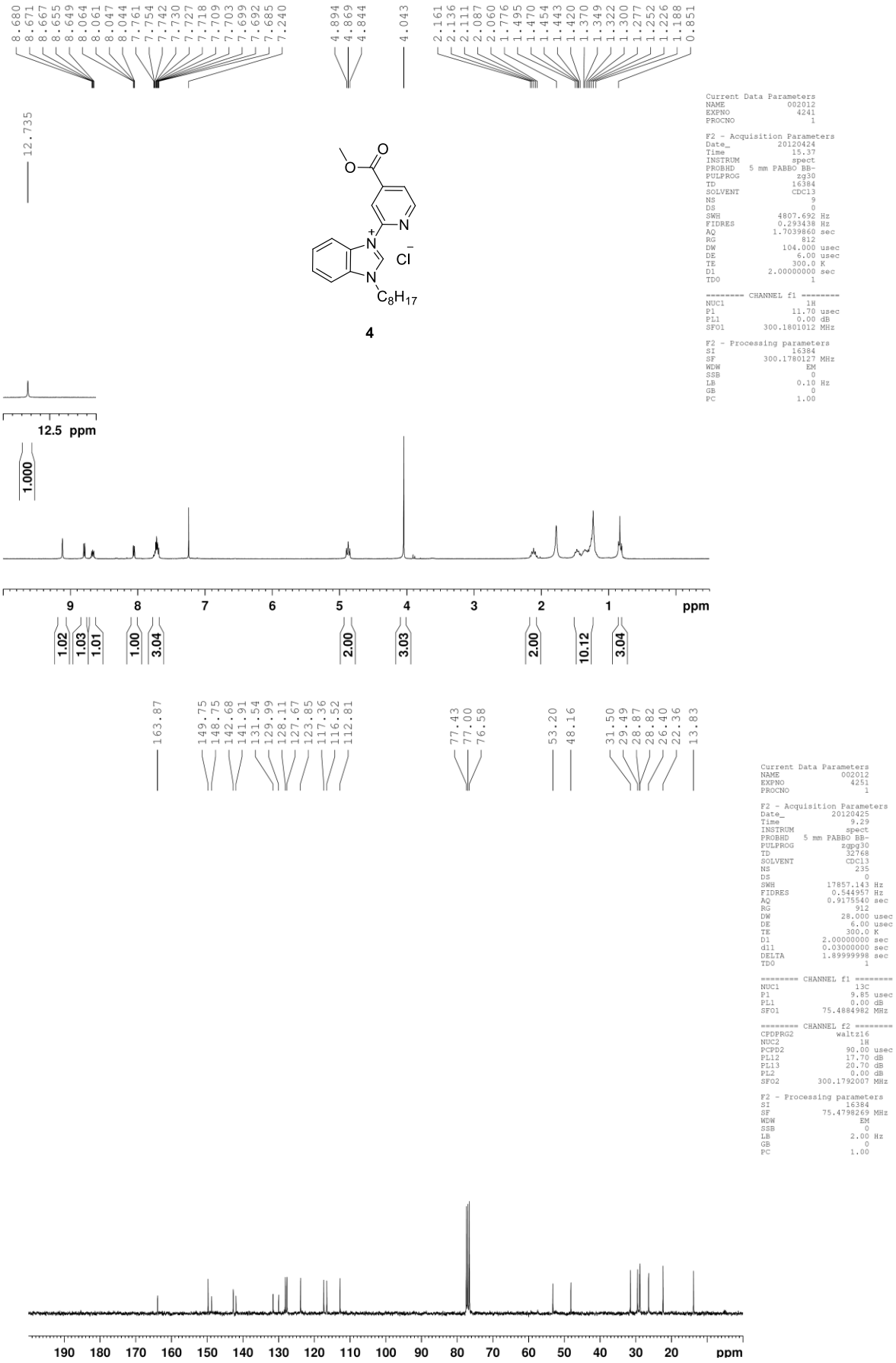


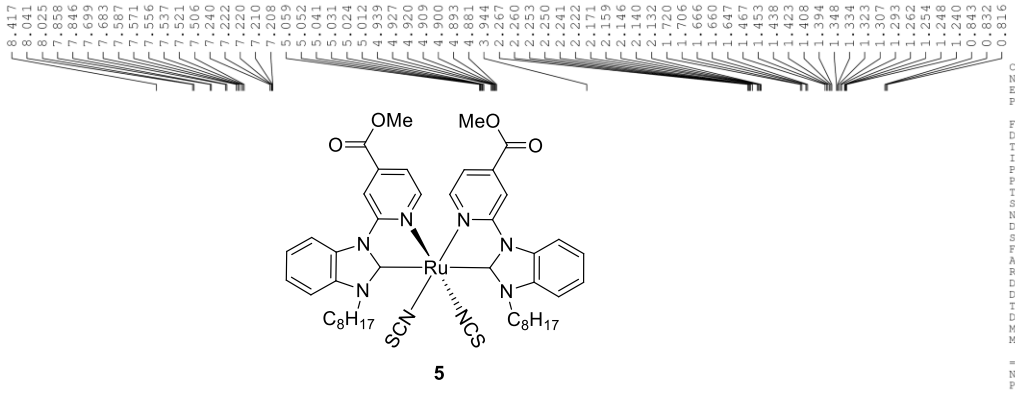
2. ^{1}H and ^{13}C NMR (500 MHz, $CDCl_3$) spectra of compound 3.



3. ^{1}H and ^{13}C NMR (500 MHz, $CDCl_3$) spectra of compound 4.



4. ^{1}H and ^{13}C NMR (500 MHz, $CDCl_3$) spectra of compound 5.



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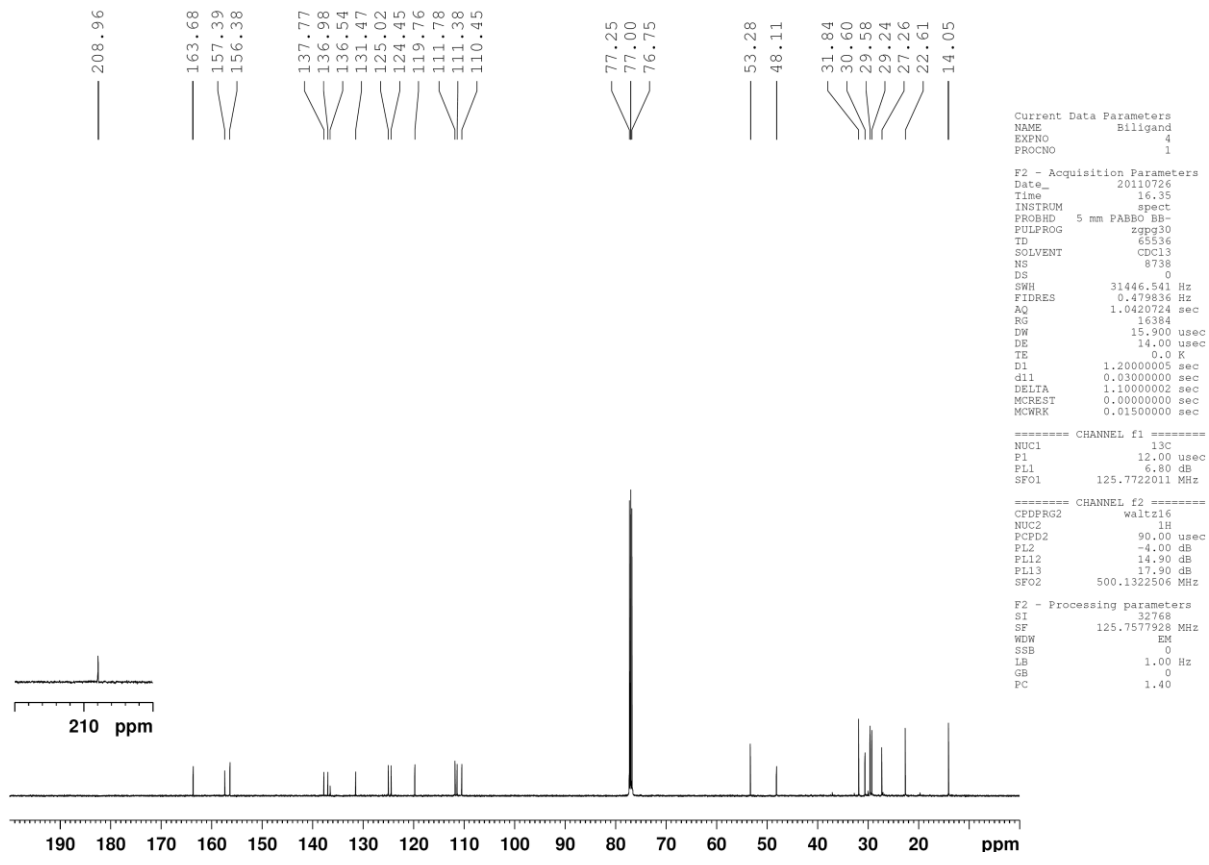
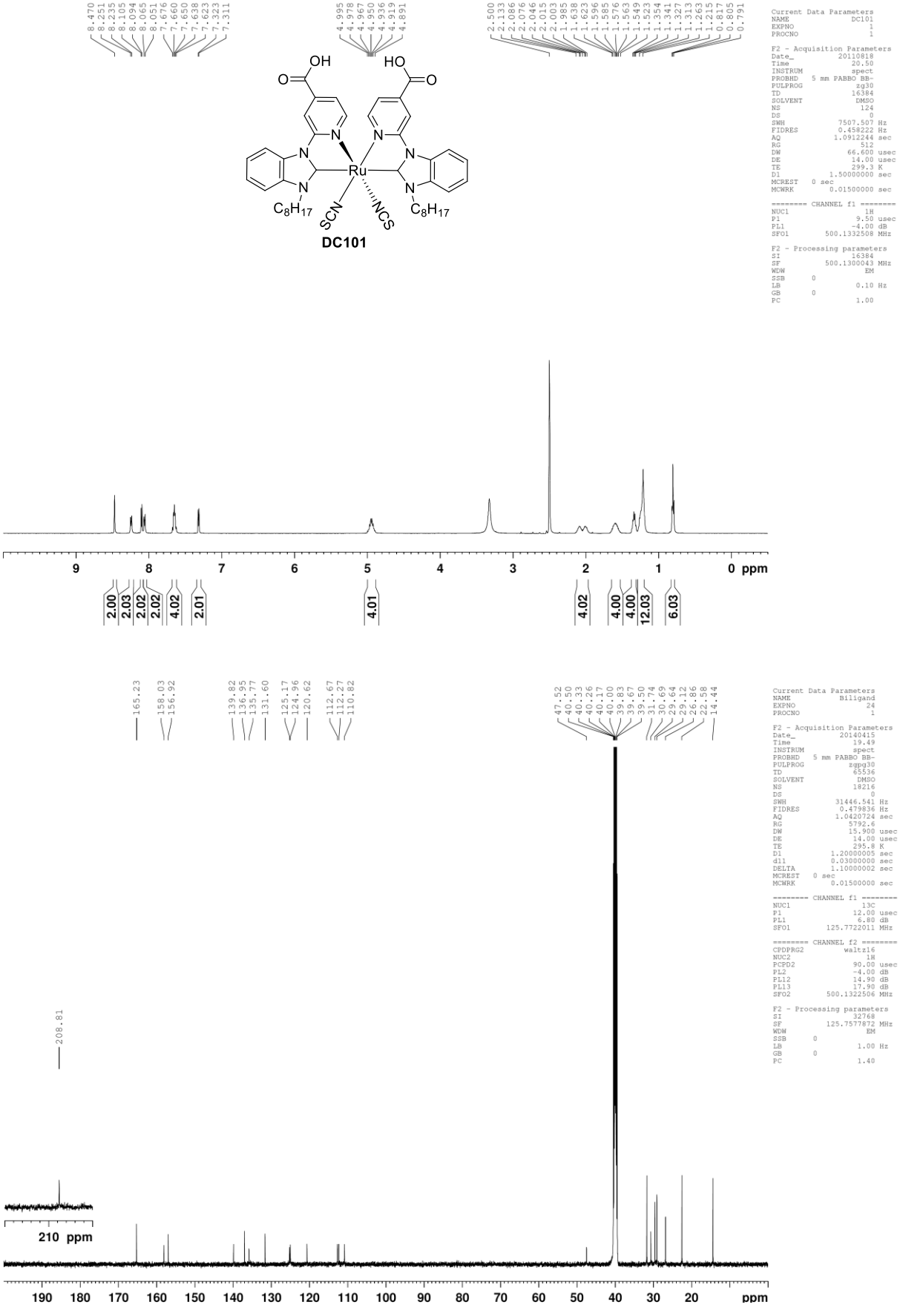
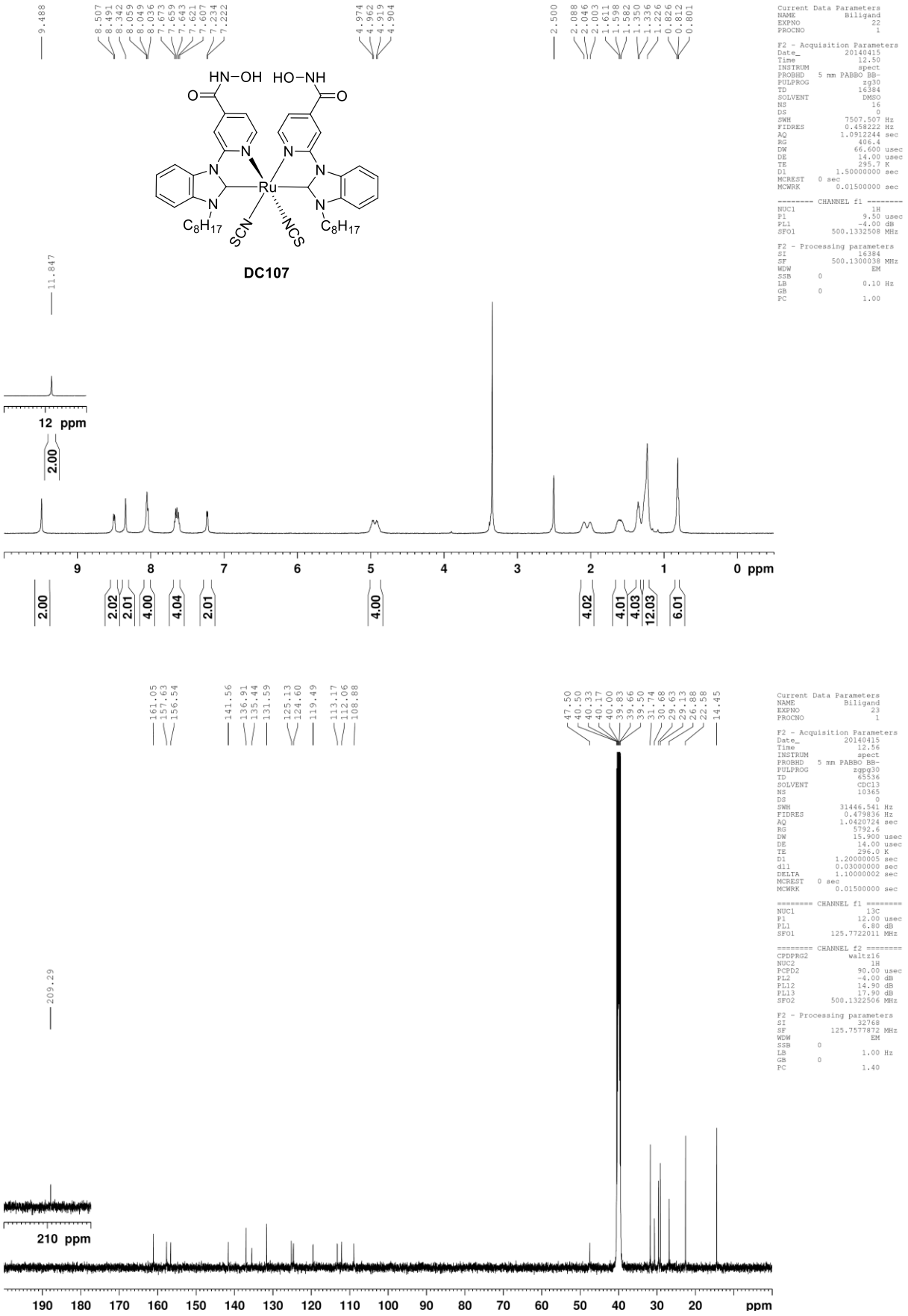


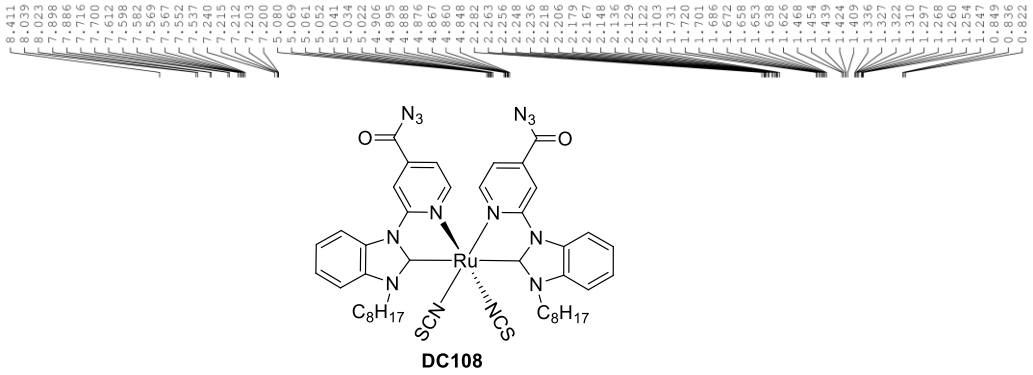
5. ^{1}H and ^{13}C NMR (500 MHz, $CDCl_3$) spectra of DC101.



6. ^{1}H and ^{13}C NMR (500 MHz, $CDCl_3$) spectra of DC107.



7. ^{1}H and ^{13}C NMR (500 MHz, $CDCl_3$) spectra of DC108.



DC108

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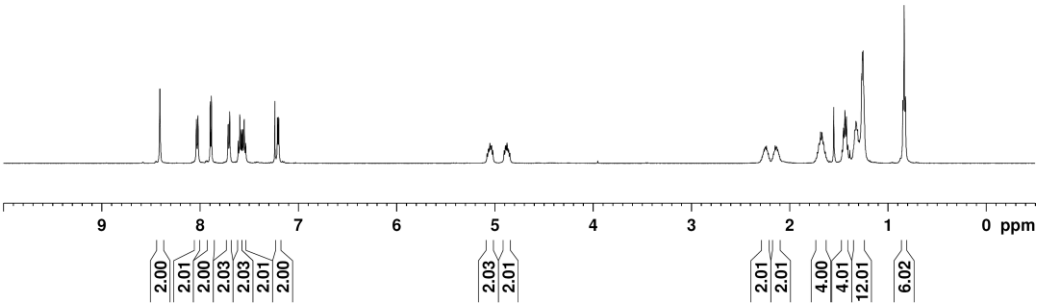


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