Electronic Supplementary Information

Spirolactam Capped Cyanine Dyes for Designing NIR Probes to Target Multiple Metal Ions

Chirantan Kar[a], Yutaka Shindo[b], Kotaro Oka[b], Shigeru Nishiyama[c], Koji Suzuki[a] and Daniel Citterio[a]

[a]Department of Applied Chemistry, [b]Department of Biosciences and Informatics and [c]Department of Chemistry, Faculty of Science and Technology Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

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Table S1: Optical properties of IR-NCS and IR-PYR in Methanol.

Probe	λ_{abs} (nm)[a]	λ_{em} (nm)[b]	Stokes shift (nm)	ε_{max} (M^{-1} cm^{-1})	Φ_f[c]
IR-NCS	763	784	21	268800	0.0619
IR-PYR	766	784	18	88000	0.0982

[a] The maximal absorption of the dye; [b] The maximal emission of the dye; [c] Φ_f is the relative fluorescence quantum yield estimated by using ICG (Φ_f = 0.13 in DMSO) as a fluorescence standard.

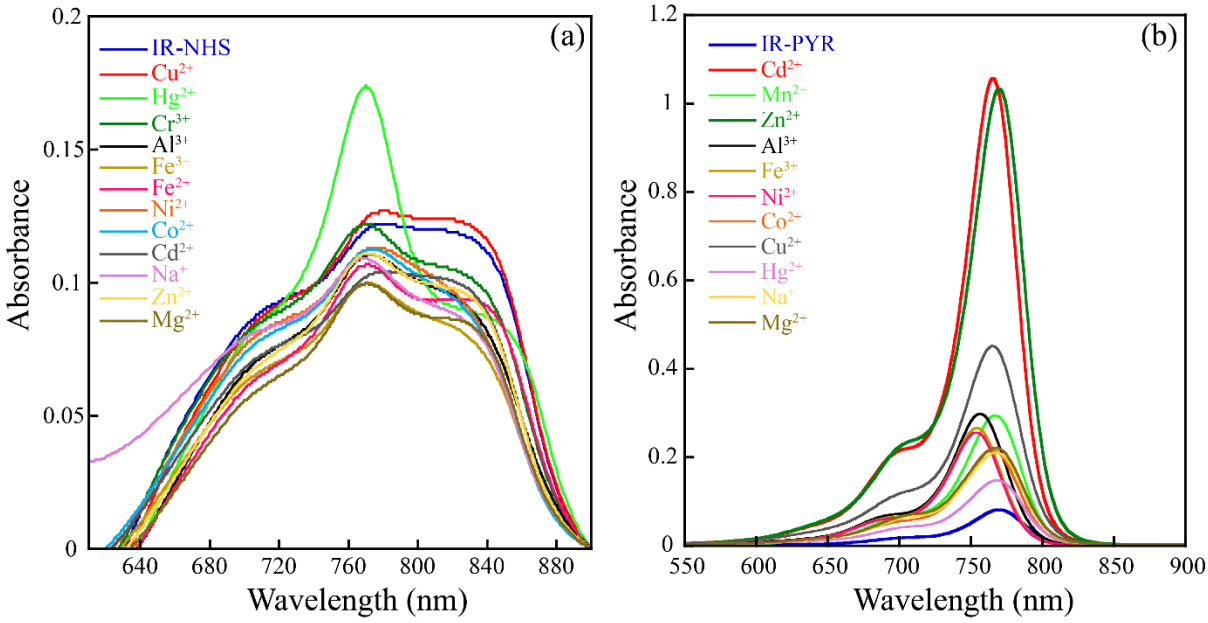


Figure S1: UV/Vis spectra of IR-NCS and IR-PYR in presence of various metal ions.

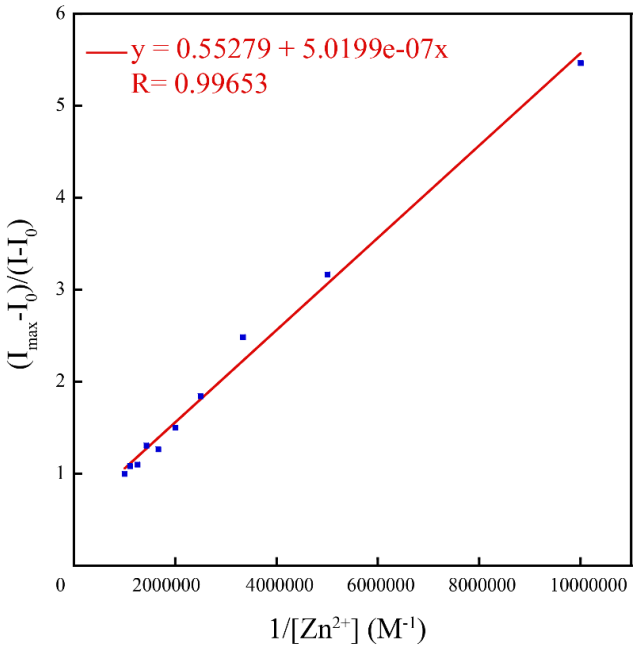


Figure S2: Binding constant for the 1:1 IR-PYR-Zn complex, calculated using Benesi−Hildebrand method.

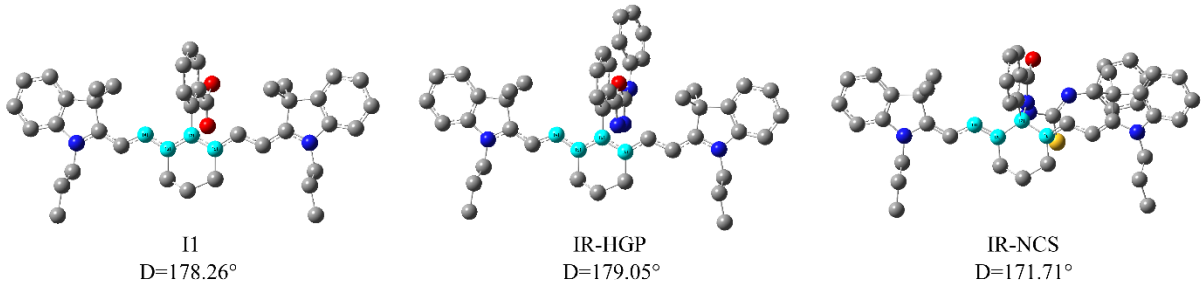


Figure S3: Dihedral angles (between the bonds linking the highlighted atoms) of I1, IR-HGP and IR-NCS.

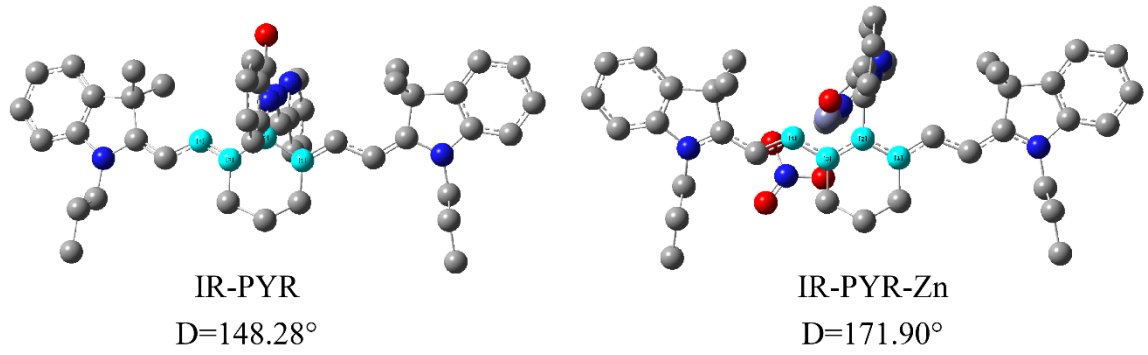


Figure S4: Dihedral angles (between the bonds linking the highlighted atoms) of IR-PYR and IR-PYR-Zn.

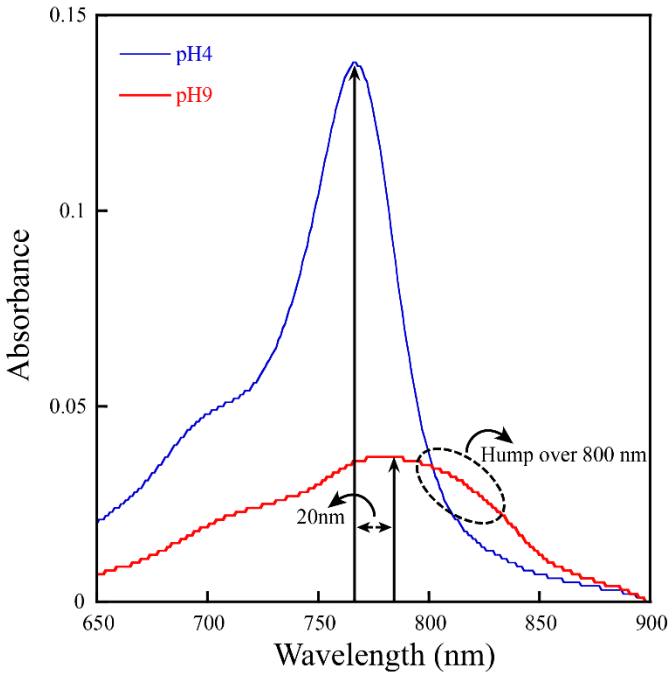


Figure S5: Absorbance spectra of 10 μM IR-NCS in solutions of pH 4 and pH 9.

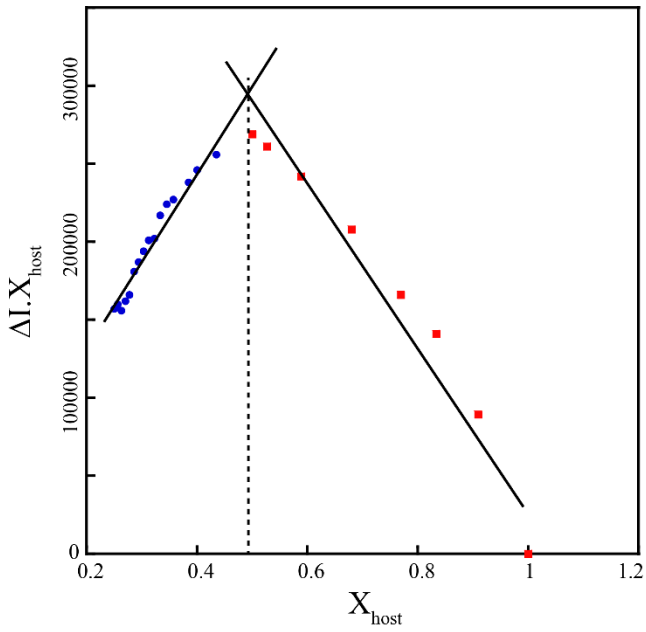


Figure S6: Job's plot diagram for the IR-PYR and Zn^{2+} metal ion complex. X_{host} represent the mole fraction of IR-PYR and ΔI represent the change in fluorescence intensity.

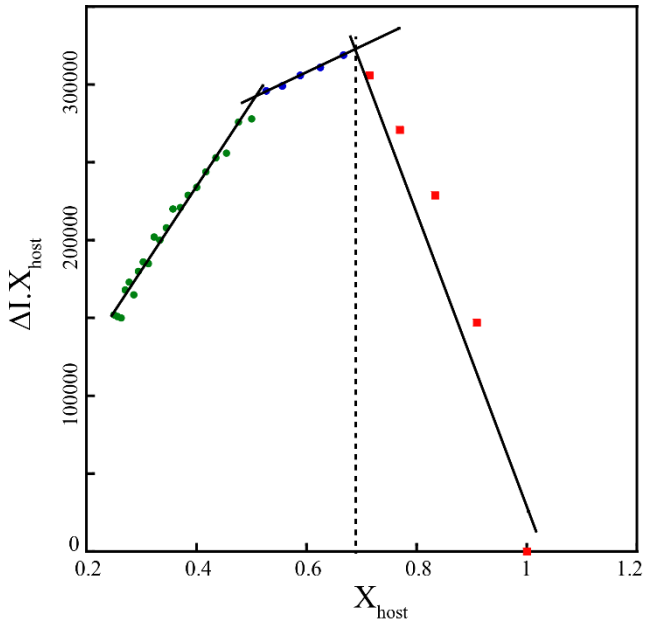


Figure S7: Job's plot diagram for the IR-PYR and Cd^{2+} metal ion complex. X_{host} represent the mole fraction of IR-PYR and ΔI represent the change in fluorescence intensity.

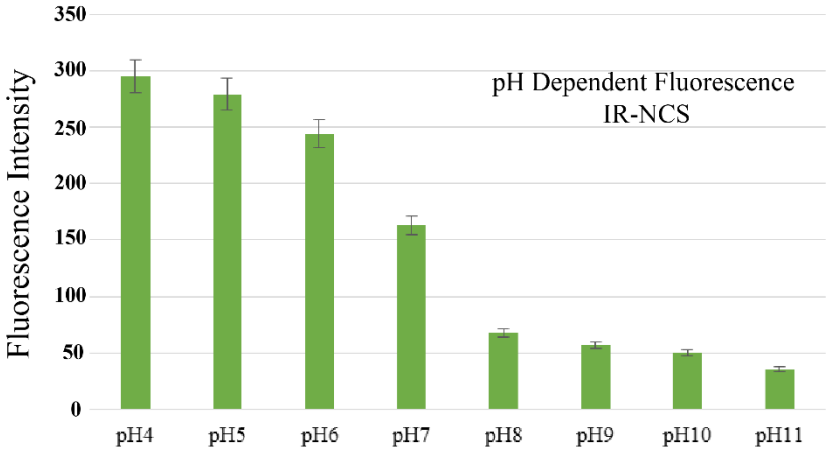


Figure S8: pH dependent fluorescence of IR-NCS.

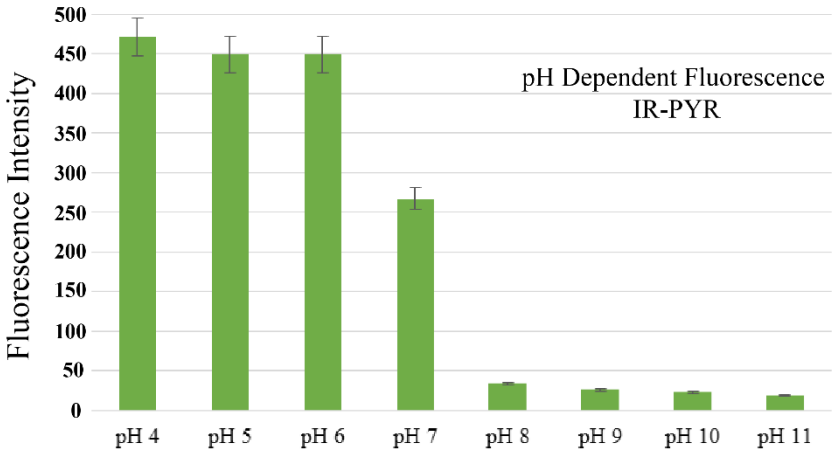
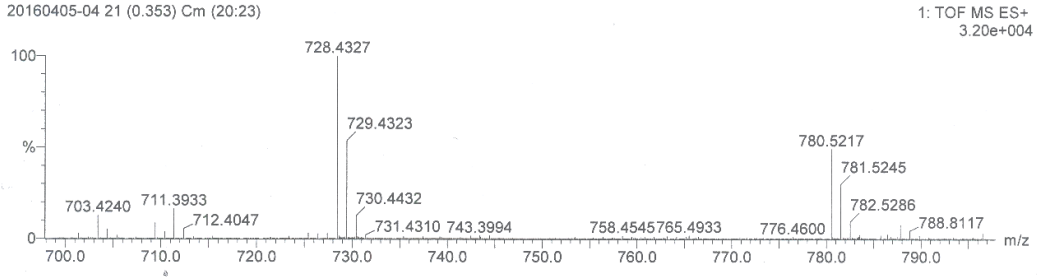


Figure S9: pH dependent fluorescence of IR-PYR

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 49-49 H: 53-54 N: 5-5 O: 1-1
Kar4
20160405-04 21 (0.353) Cm (20:23)



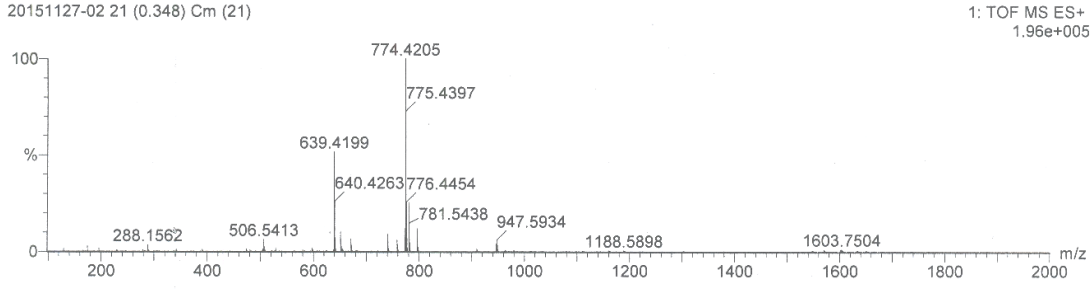
Minimum:				-1.5			
Maximum:		3.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
728.4327	728.4328	-0.1	-0.1	25.5	282.0	0.0	C49 H54 N5 O

Figure S10: Mass spectral data of IR-PYR ($C_{49}H_{54}N_5O$).

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 50-50 H: 55-56 N: 5-5 O: 1-1 S: 1-1
Kar
20151127-02 21 (0.348) Cm (21)



Minimum:				-1.5			
Maximum:		3.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
774.4205	774.4206	-0.1	-0.1	25.5	182.7	0.0	C50 H56 N5 O S

Figure S11: Mass spectral data of IR-NCS ($C_{50}H_{56}N_5OS$).

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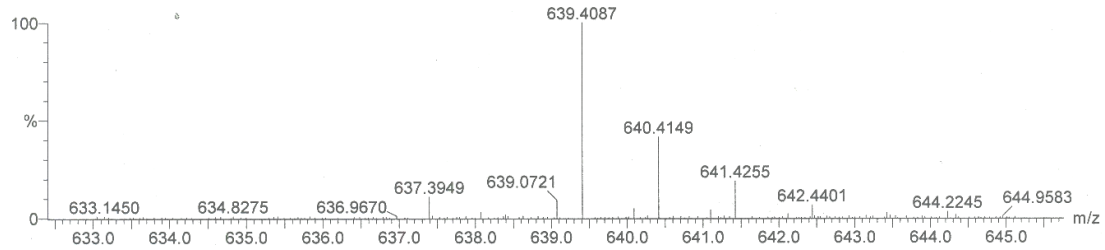
Single Mass Analysis
Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 43-43 H: 50-52 N: 4-4 O: 1-1
Kar2
20151102-05 44 (0.711) Cm (43:46)



Minimum:				-1.5			
Maximum:		3.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
639.4087	639.4063	2.4	3.8	20.5	147.6	0.0	C43 H51 N4 O

Figure S12: Mass spectral data of I2 ($C_{43}H_{51}N_4O$).

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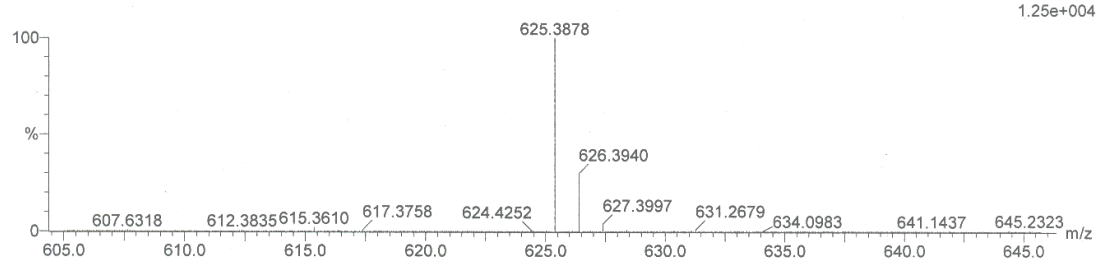
Single Mass Analysis
Tolerance = 500.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 43-43 H: 49-50 N: 2-2 O: 2-2
Kar
20151028-04 66 (1.081) Cm (62:71)



Minimum:				-1.5			
Maximum:		500.0	500.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
625.3878	625.3794	8.4	13.4	20.5	131.5	0.0	C43 H49 N2 O2

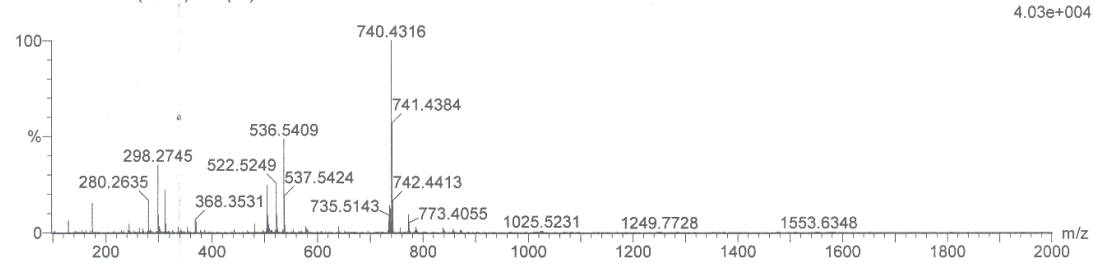
Figure S13: Mass spectral data of I1 ($C_{43}H_{49}N_2O_2$).

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 50-50 H: 53-54 N: 5-5 O: 1-1

Kar Hg complex
20160325-01 28 (0.456) Cm (28)



Minimum:				-1.5			
Maximum:		3.0	500.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
740.4316	740.4328	-1.2	-1.6	26.5	132.3	0.0	C50 H54 N5 O

Figure S14: Mass spectral data of IR-HGP ($C_{50}H_{54}N_5O$).

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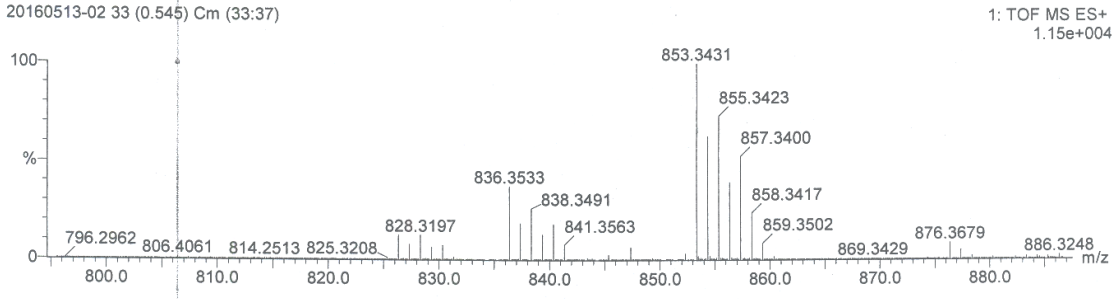
Single Mass Analysis
Tolerance = 300.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 49-49 H: 53-53 N: 6-6 O: 4-4 Zn: 1-1

Kar Zn
20160513-02 33 (0.545) Cm (33:37)



Minimum:				-1.5			
Maximum:		300.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
853.3431	853.3420	1.1	1.3	26.5	192.3	0.0	C49 H53 N6 O4 Zn

Figure S15: Mass spectral data of IR-PYR-Zn complex ($C_{49}H_{53}N_6O_4Zn$).

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 300.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
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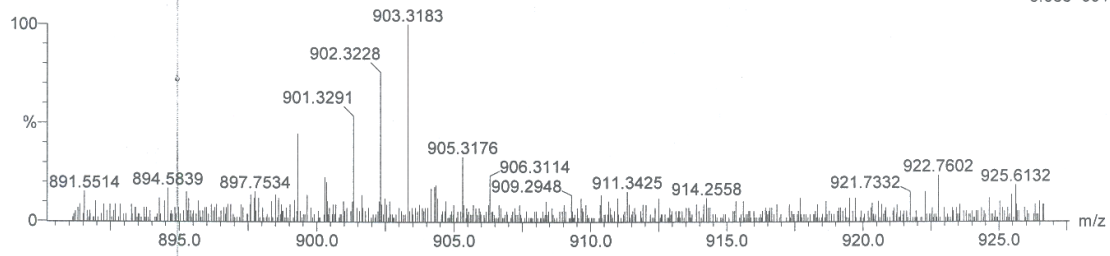
Kar Cd
20170116-09 77 (1.265) Cm (77:82)



Minimum:				-1.5			
Maximum:		300.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
903.3183	903.3162	2.1	2.3	26.5	129.8	0.0	C49 H53 N6 O4 Cd

Figure S16: Mass spectral data of IR-PYR-Cd complex ($C_{49}H_{53}N_6O_4Cd$).

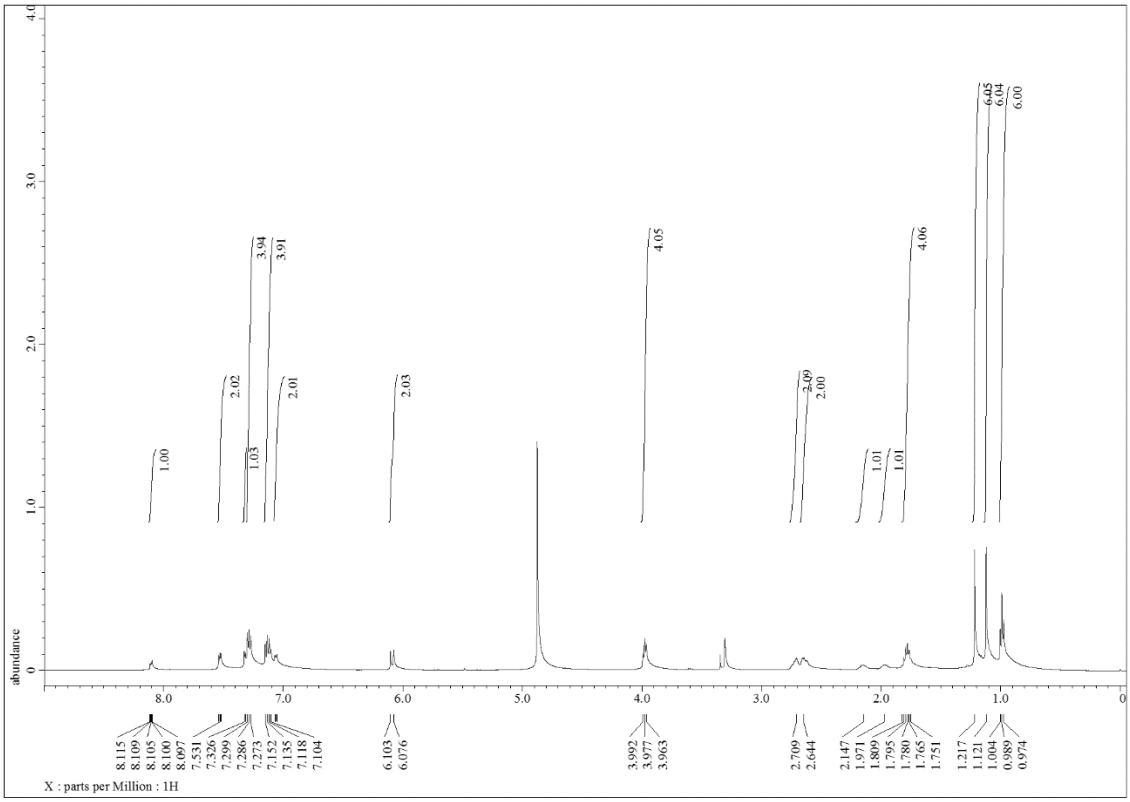


Figure S17: ^{1}H NMR spectra of I1 in MeOH-d_4

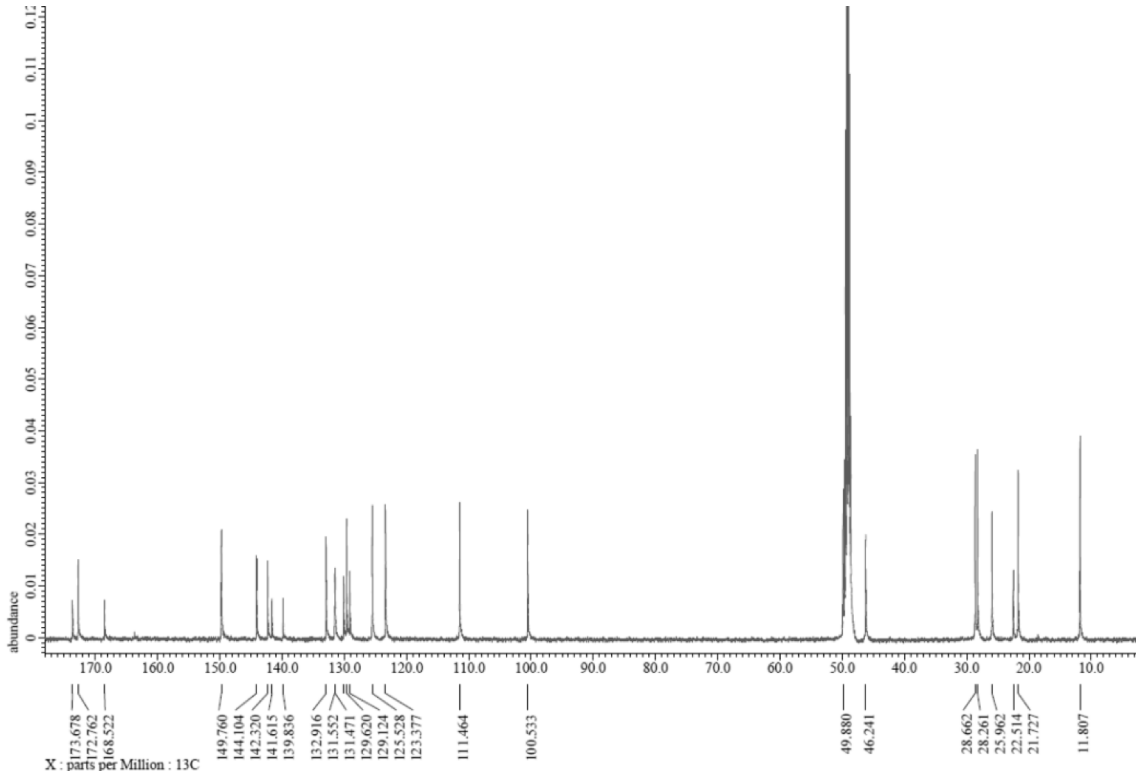


Figure S18: ^{13}C NMR spectra of I1 in MeOH-d_4

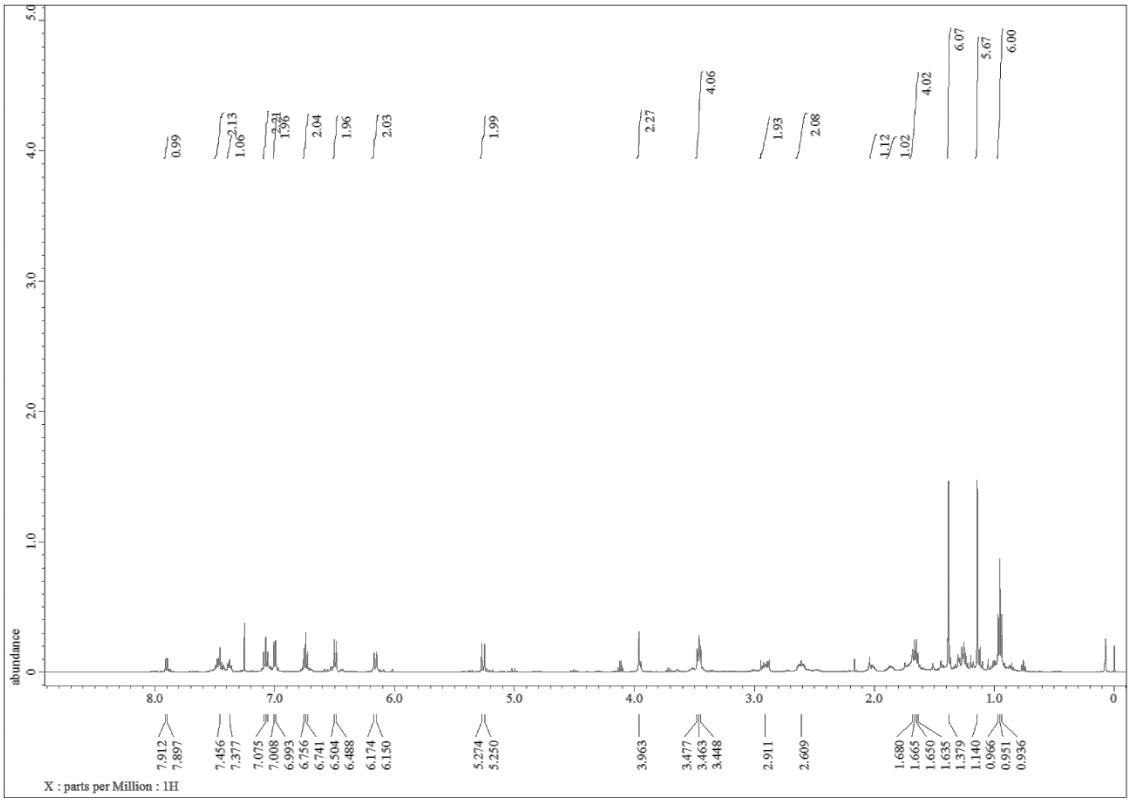


Figure S19: ^{1}H NMR spectra of I2 in $CDCl_3$

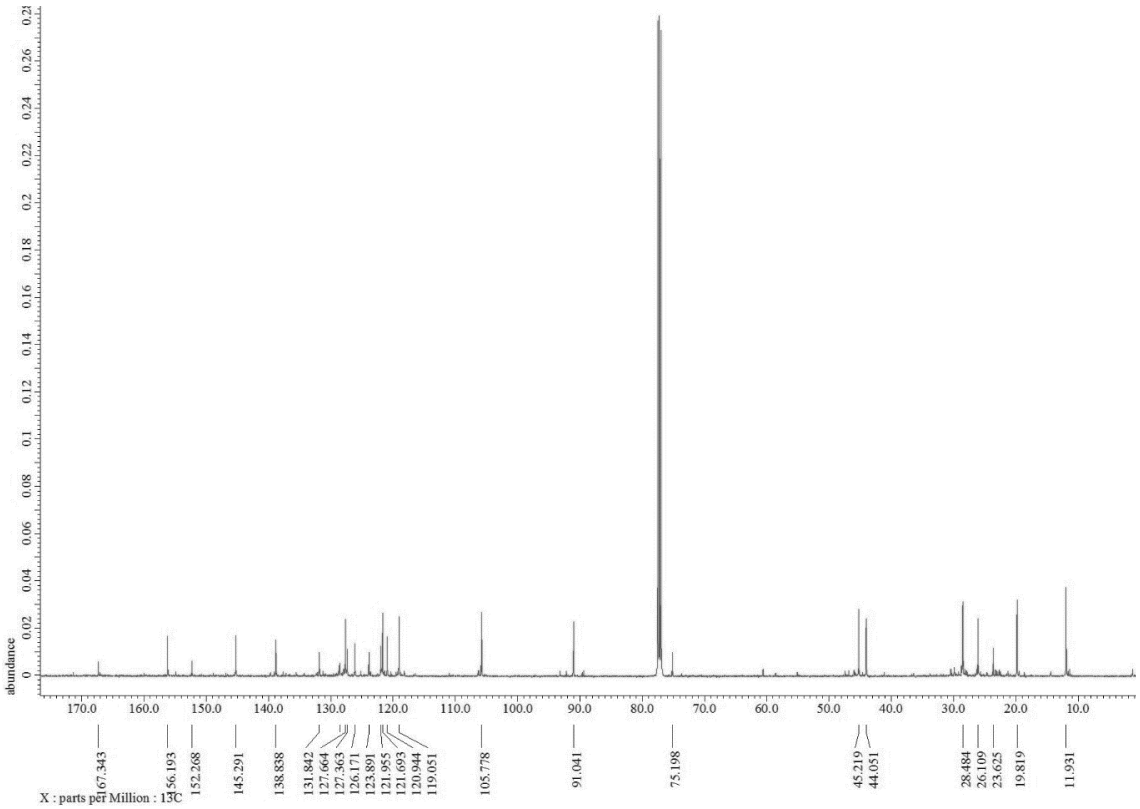


Figure S20: ^{13}C NMR spectra of I2 in $CDCl_3$.

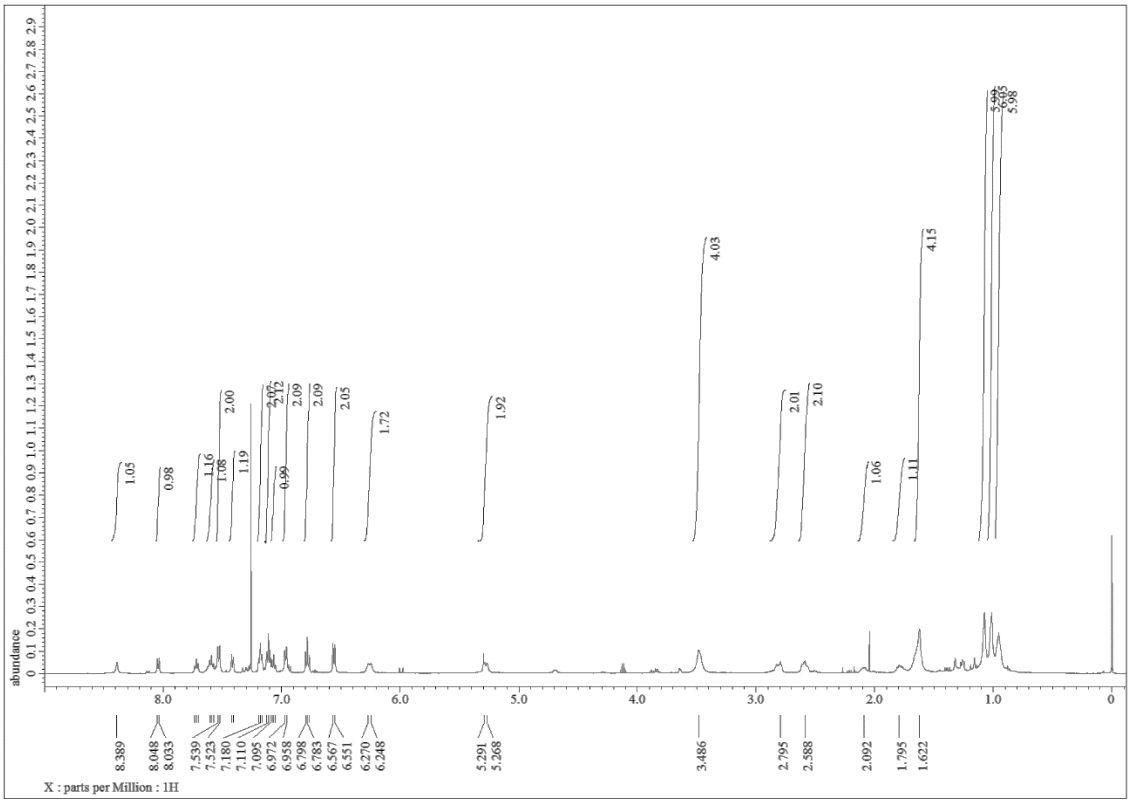


Figure S21: ^{1}H NMR spectra of IR-NCS in $CDCl_3$.

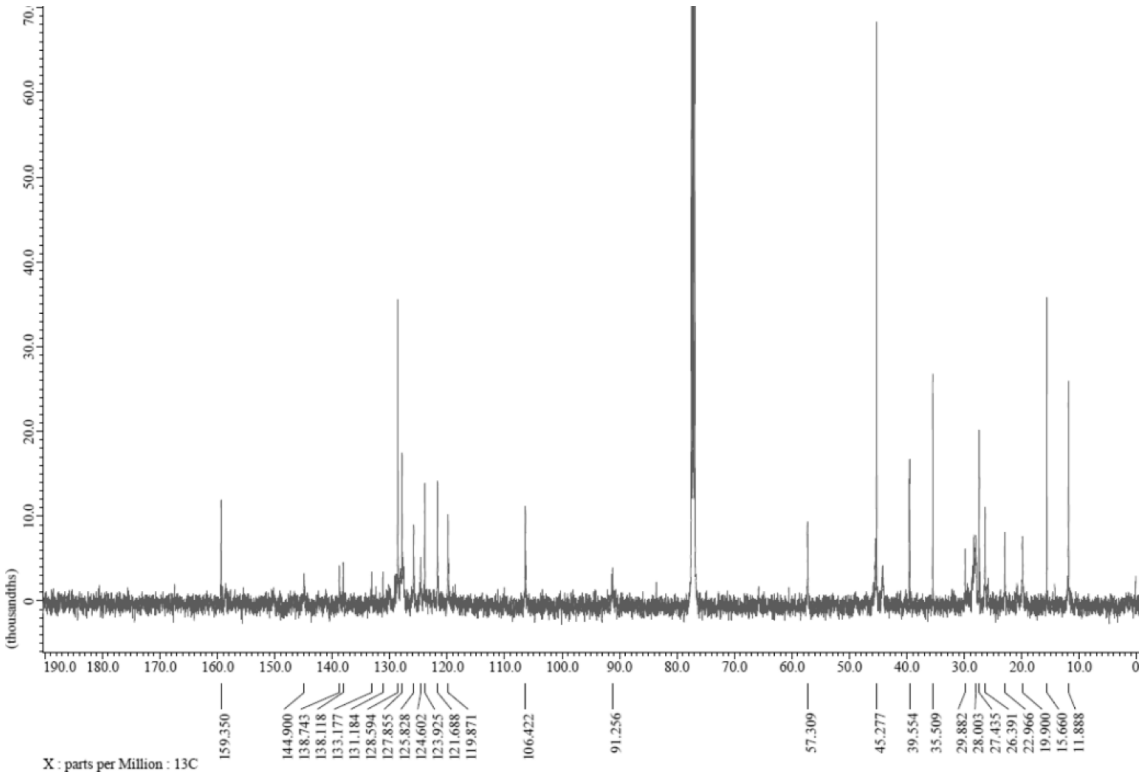


Figure S22: ^{13}C NMR spectra of IR-NCS in $CDCl_3$.

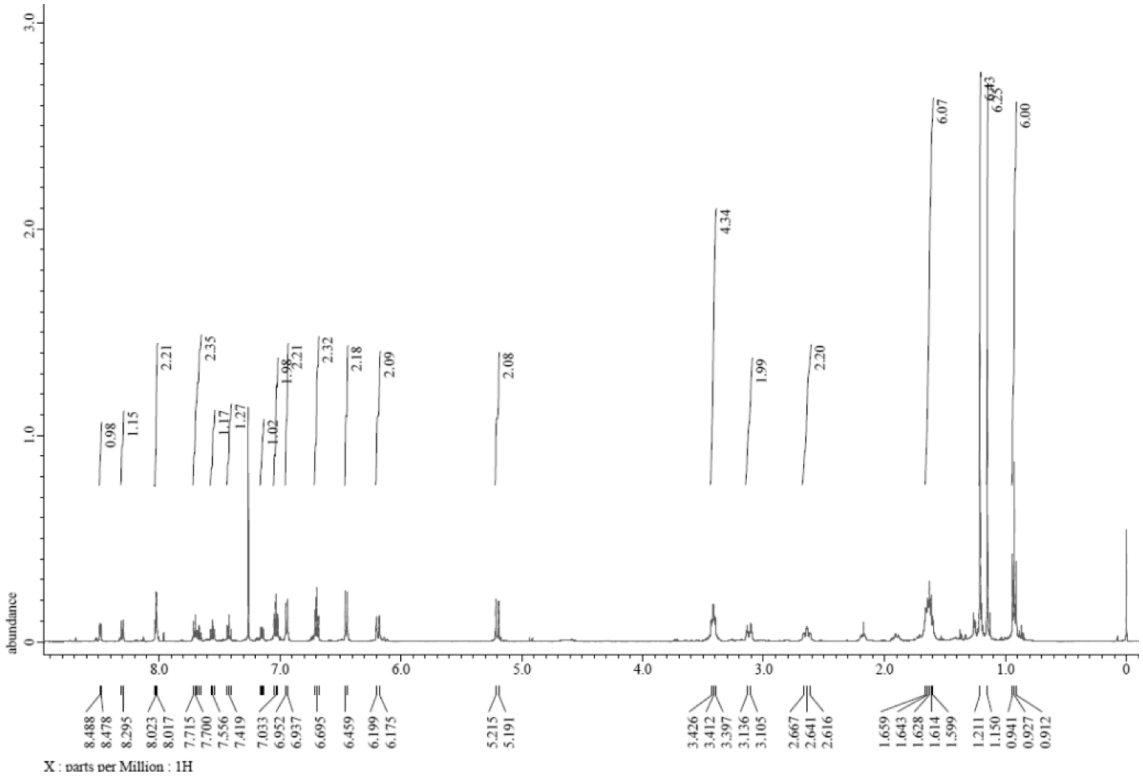


Figure S23: ^{1}H NMR spectra of IR-PYR in $CDCl_3$.

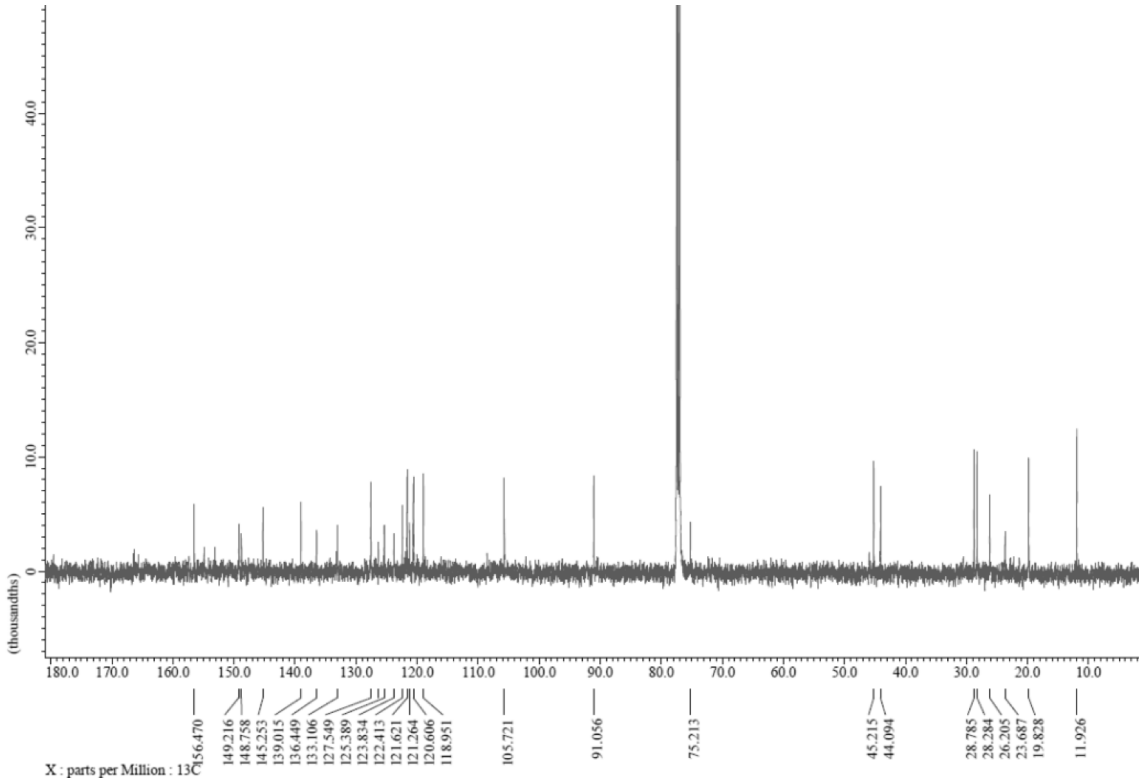


Figure S24: ^{13}C NMR spectra of IR-PYR in $CDCl_3$.