SUPPORTING INFORMATION

Photoejection-recapture of Ca^{2+} Cation studied by time resolved spectroscopy and TDDFT calculations: the case study of Azacrown –Iridium (III) complex.

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Figure S1. Job Plot: JOB plot obtained at 375 nm from the absorption spectra of **1 i**n CH_3CN (28µM) upon successive addition of calcium perchlorate solution from 0 to 0.29 M. Fitting results indicates a molar ratio 1:1.

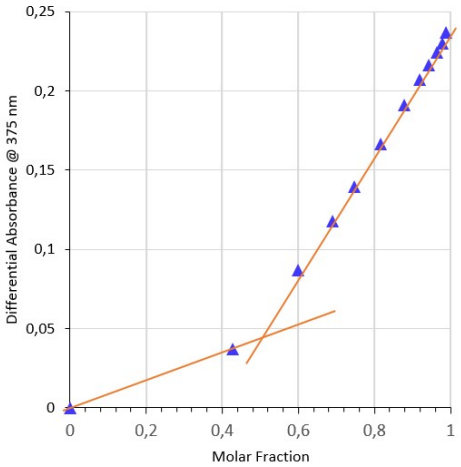


Figure S2. Molecule 1: Energies of the S_n and T_n states (n=1..6) in eV at the S_0 geometry. Selected spin-orbit coupling matrix elements $\langle S_n|\hat{H}_{SO}|T_k\rangle$ are given (cm^{-1}) ($\langle S_1|\hat{H}_{SO}|T_k\rangle$ in red, $\langle S_2|\hat{H}_{SO}|T_k\rangle$ in dark blue). The variation of the electronic density upon excitation for the transitions $S_n \longleftarrow S_0$ and $T_n \longleftarrow S_0$ is also provided along with the norm of the CT dipole moment (blue: loss of electronic density, red: gain of electronic density).

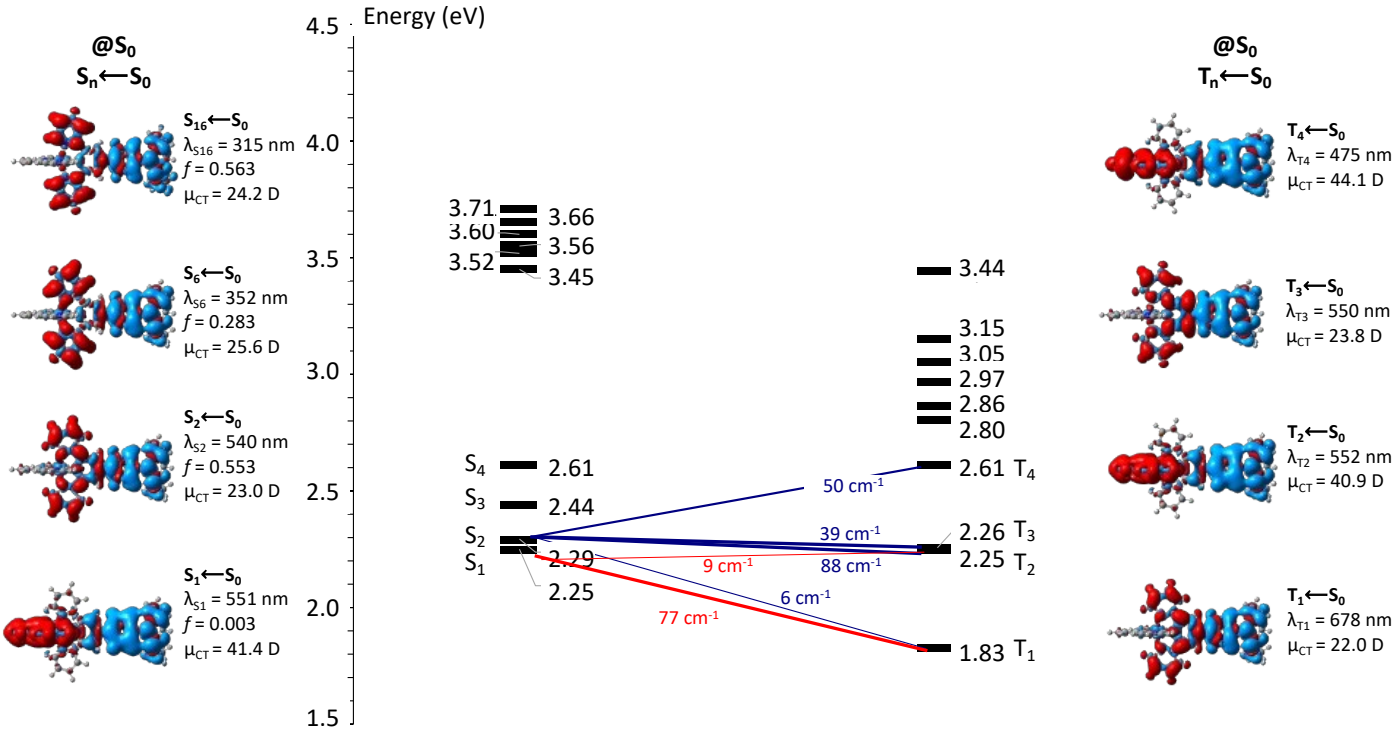


Figure S3. Molecule 1-Ca^{2+}: Energies of the S_n and T_n states (n=1..6) in eV at the S_0 geometry. Selected spin-orbit coupling matrix elements $\langle S_n|\hat{H}_{SO}|T_k\rangle$ are given (cm^{-1}) ($\langle S_1|\hat{H}_{SO}|T_k\rangle$ in red, $\langle S_2|\hat{H}_{SO}|T_k\rangle$ in dark blue). The variation of the electronic density upon excitation for the transitions $S_n \longleftarrow S_0$ and $T_n \longleftarrow S_0$ is also provided along with the norm of the CT dipole moment (blue: loss of electronic density, red: gain of electronic density).

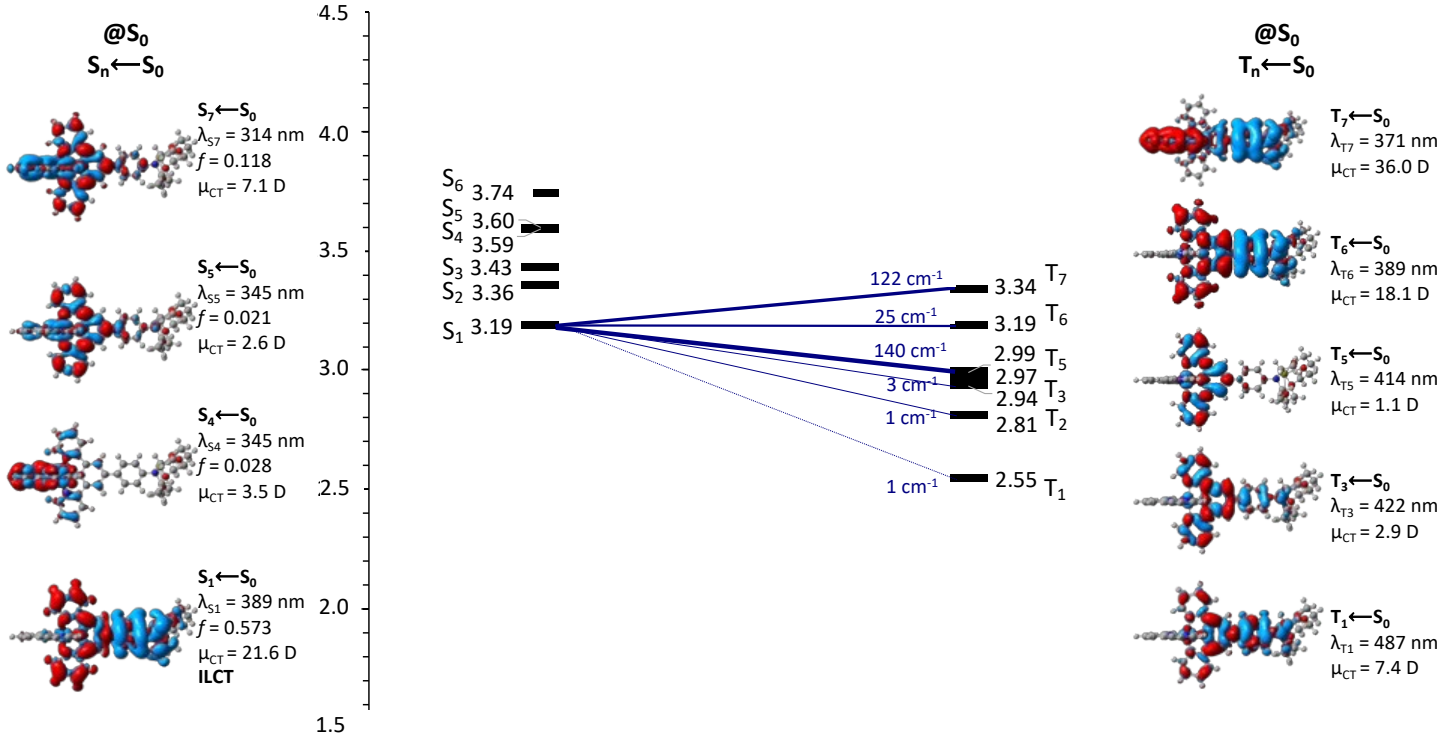
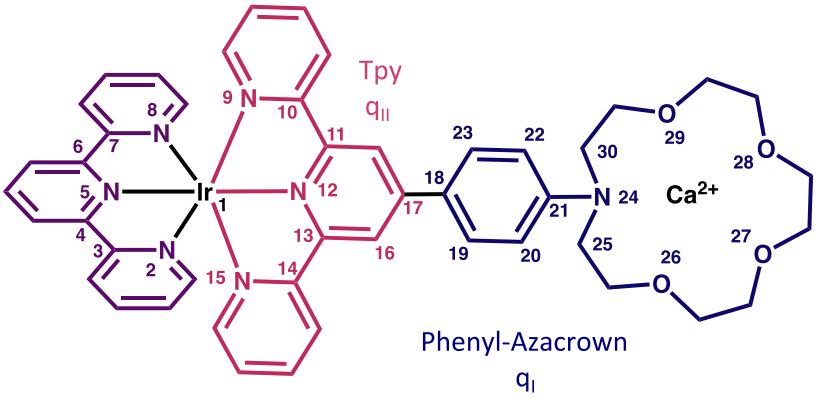


Table S1: 1-Ca^{2+} complex: Main distances (in Å) of Ca^{2+} inside the azacrown. $\langle d_O \rangle$ is the average distance between Ca^{2+} and the oxygens. The distances are defined in Figure S3.

	d_{14}	d_{15}	d_{16}	d_{17}	d_{18}	$\langle d_O \rangle$
$S_{0,opt}$	2.764	2.399	2.458	2.449	2.396	2.425
$S_{1,opt}$	3.853	2.524	2.410	2.472	2.504	2.478

Figure S4: Definition of the structural parameters and of the different regions used to calculate the variation of Natural Population Analysis (NPA) charges: I = phenyl-azacrown (blue); II = 2,2':6',2"-terpyridine (=tpy) (pink); III = tpy (purple)



d_1 : Ir-2
d_2 : Ir-5
d_3 : Ir-8
d_4 : Ir-9
d_5 : Ir-12
d_6 : Ir-15

d_7 : 3-4
d_8 : 6-7
d_9 : 10-11
d_{10} : 13-14
d_{11} : 19-20
d_{12} : 17-18
d_{13} : 21-24

d_{14} : Ca^{2+}-24
d_{15} : Ca^{2+}-26
d_{16} : Ca^{2+}-27
d_{17} : Ca^{2+}-28
d_{18} : Ca^{2+}-29

ϕ_1: 2-3-4-5
ϕ_2: 5-6-7-8
ϕ_3: 9-10-11-12
ϕ_4: 12-13-14-15
ϕ_5: 16-17-18-19
ϕ_6: 20-21-24-25

Table S2. Molecule 1: Absorption wavelengths (nm) calculated for the first 6 excited states with their corresponding oscillator strength (f), electronic excitation assignments and charge transfer parameters: D in Å, q in |e| and μ_{CT} in D. The variations of NPA charges upon the corresponding excitation are also given according to the regions defined above.

1									
State	λ	f	Electronic excitation	Δq_I	Δq_{II}	Δq_{III}	Δq_{Ir}	μCT	DCT
$S_1 \leftarrow S_0$	551	0.002	HOMO → LUMO	-0.796	0.865	-0.011	0.003	41.4	4.956
$S_2 \leftarrow S_0$	540	0.552	HOMO → LUMO+1	-0.633	0.068	0.621	0.004	23.0	6.236
$S_3 \leftarrow S_0$	507	0.000	HOMO → LUMO+3	-0.742	0.073	0.700	-0.003	24.64	4.523
$S_4 \leftarrow S_0$	475	0.000	HOMO → LUMO+2	-0.803	0.887	-0.019	-0.004	43.75	6.619
$S_5 \leftarrow S_0$	359	0.000	HOMO → LUMO+4	-0.794	0.405	0.456	-0.006	34.36	5.468
$S_6 \leftarrow S_0$	352	0.283	HOMO → LUMO+6	-0.676	0.034	0.708	-0.005	25.59	5.046

Table S3. 1-Ca^{2+} complex: Absorption wavelengths (nm) calculated for the first 6 excited states with their corresponding oscillator strength (f), electronic excitation assignments and charge transfer parameters: D in Å, q in |e| and μ_{CT} in D. The variations of "Natural Population Analysis" (NPA) charges upon the corresponding excitation are also given according to the regions defined above.

1 –Ca^{2+}									
State	λ	f	Electronic excitation	Δq_I	Δq_{II}	Δq_{III}	Δq_{Ir}	μCT	DCT
$S_1 \leftarrow S_0$	389	0.573	HOMO → LUMO	-0.611	-0.585	-0.043	-0.010	21.6	4.608
$S_2 \leftarrow S_0$	369	0.000	HOMO → LUMO+1	-0.682	0.098	-0.823	-0.036	36.8	5.855
$S_3 \leftarrow S_0$	361	0.001	HOMO → LUMO+2	-0.584	0.604	0.011	-0.025	18.46	4.097
$S_4 \leftarrow S_0$	345	0.028	HOMO-1 → LUMO+1	-0.010	-0.143	0.272	-0.118	3.49	1.123
$S_5 \leftarrow S_0$	345	0.020	HOMO-1 → LUMO	-0.036	0.327	-0.172	-0.118	2.56	0.807
$S_6 \leftarrow S_0$	331	0.000	HOMO → LUMO+3	-0.717	-0.105	0.861	-0.033	40.46	6.291

Figure S5. 1-Ca^{2+} complex: Variation of the electronic density upon excitation for the transitions $S_n \longleftarrow S_0$ (n=1 to 15)

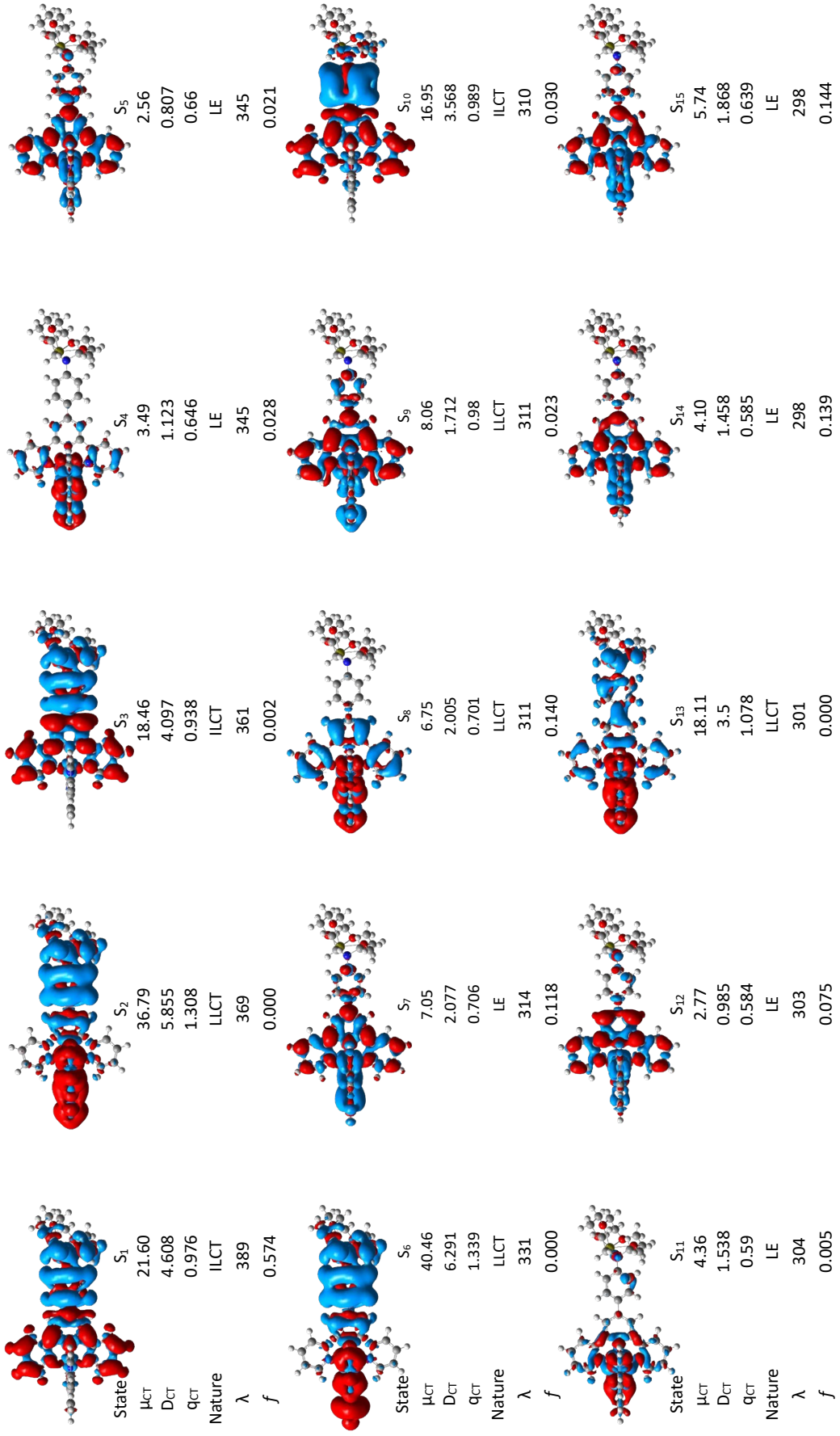


Figure S6 ^{1}H NMR spectrum of compound **4** ($CDCl_3$, 400 MHz)

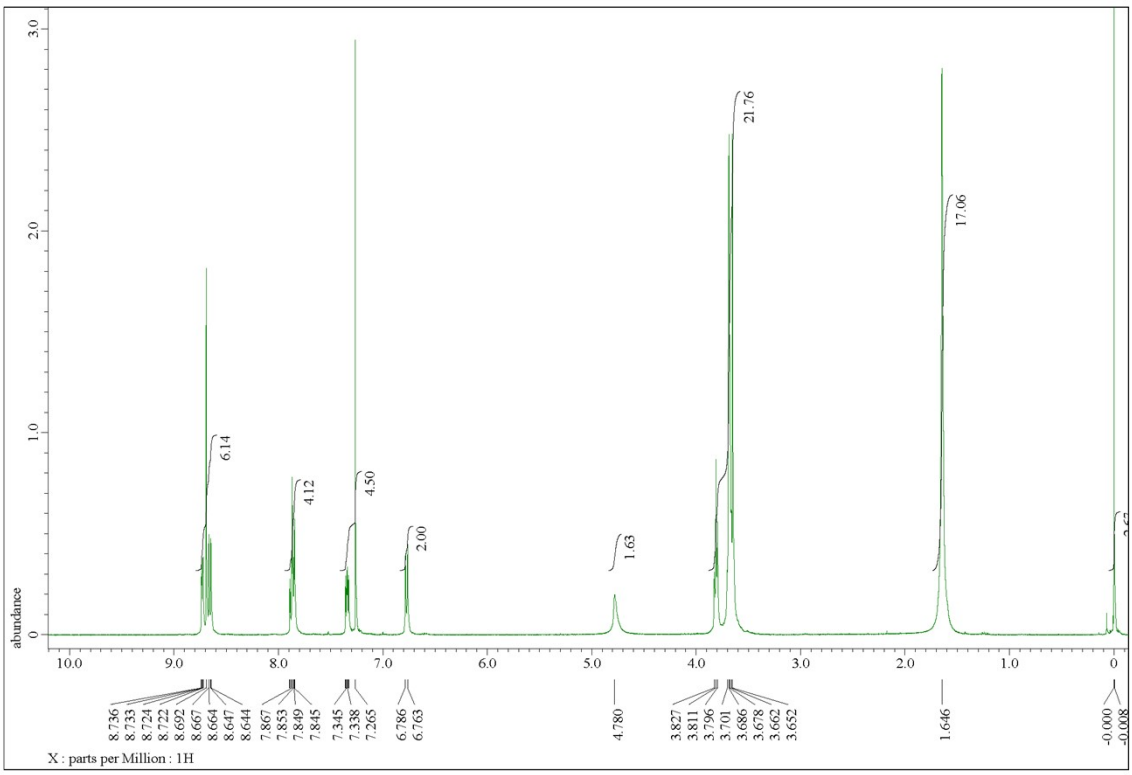


Figure S7 ^{13}C NMR spectrum of compound **4** ($CDCl_3$, 100 MHz)

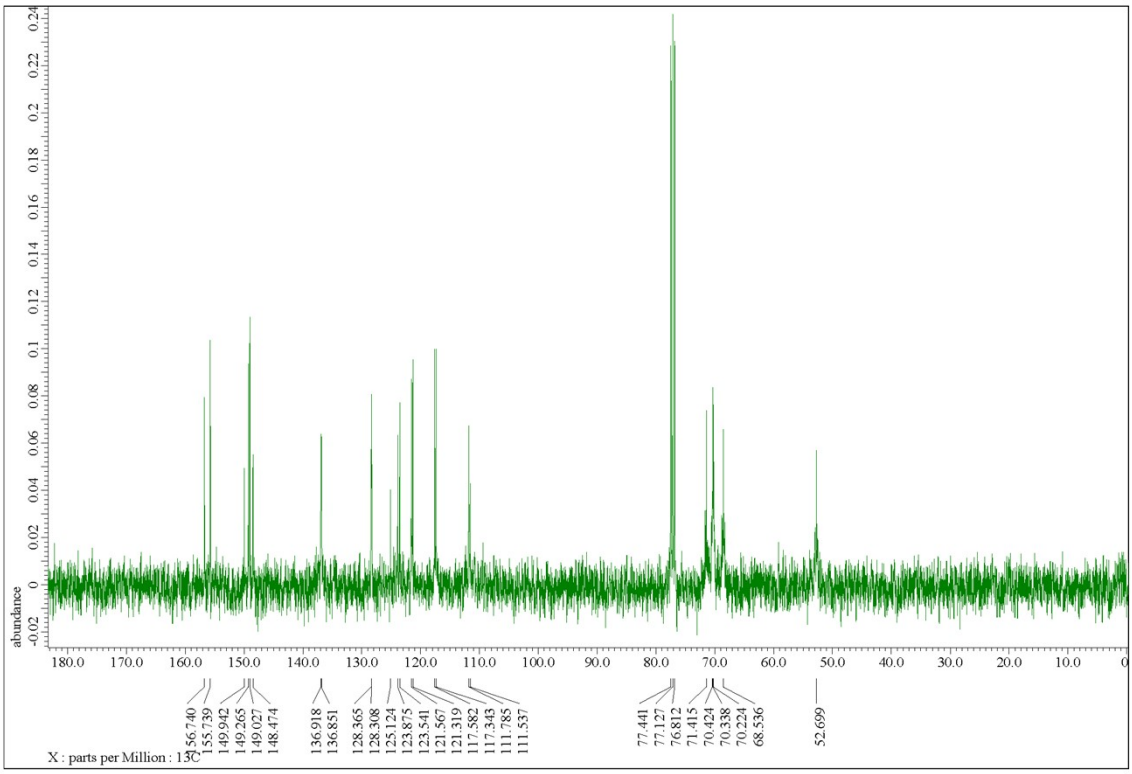


Figure S8 ^{1}H NMR spectrum of compound **5** (DMS0-d_6, 80 °C, 400 MHz)

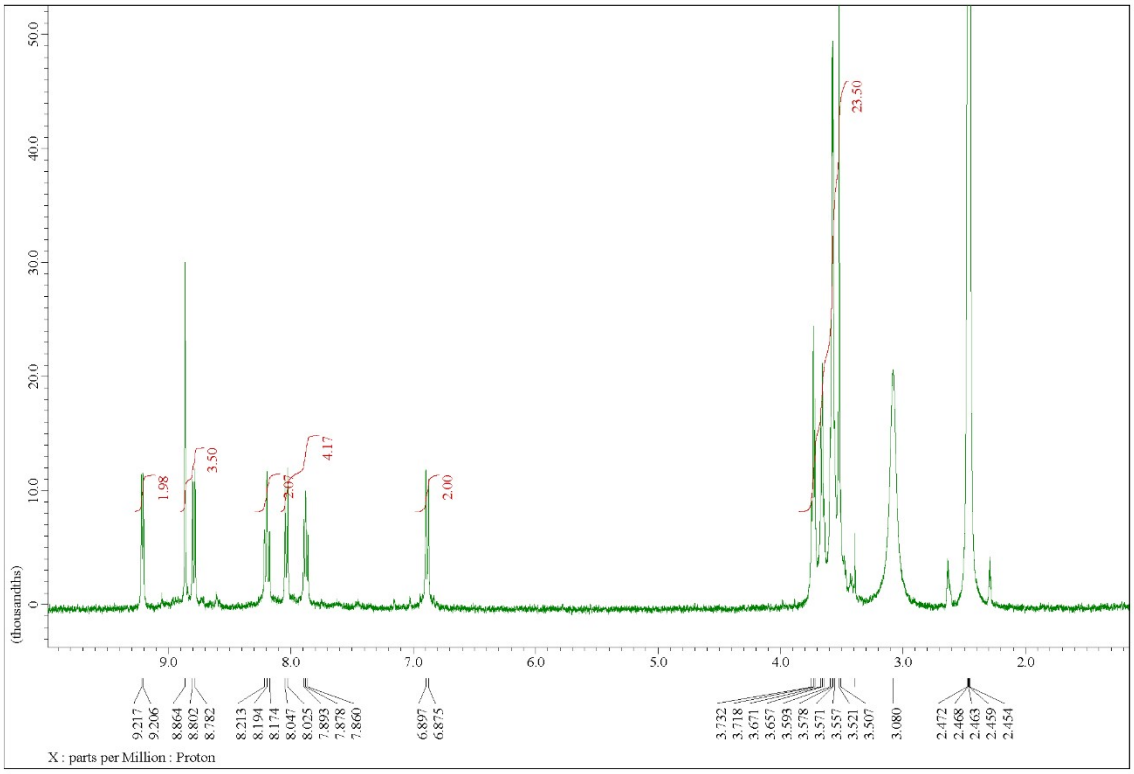


Figure S9 ^{13}C NMR spectrum of compound **5** (DMS0-d_6, 80 °C, 100 MHz)

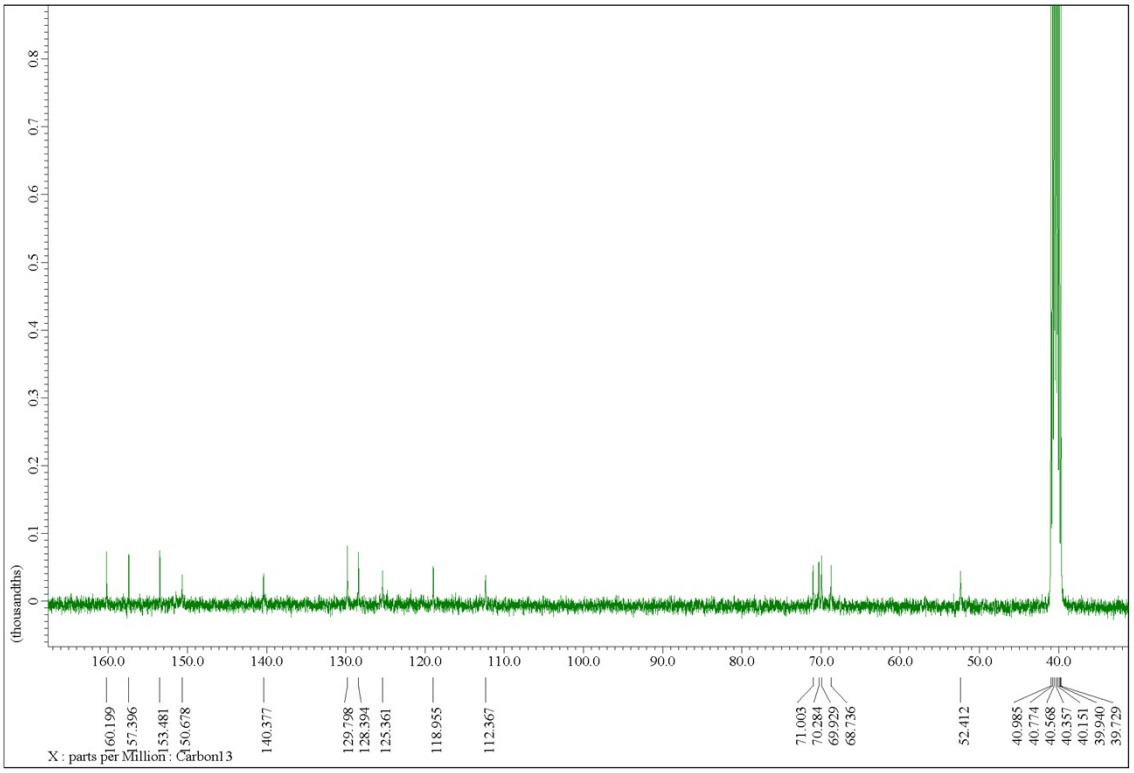


Figure S10 ^{1}H NMR spectrum of compound **1** (Acetone-d6, 400 MHz)