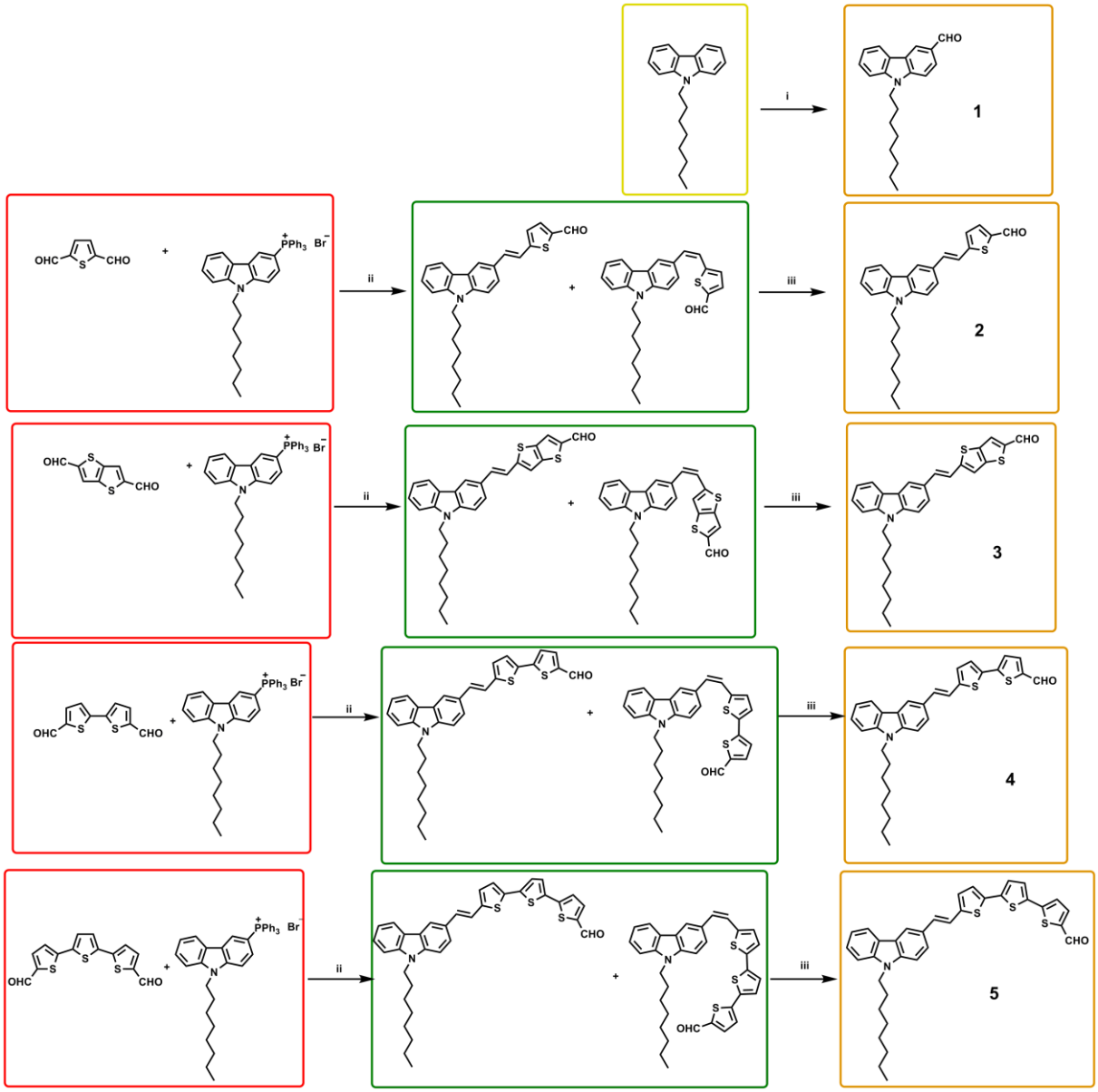
Electronic Supplementary Material (ESI) for RSC Advances.

Systematic elongation of thienyl linkers and their effect on optical and electrochemical properties in Carbazole-BODIPY donor-acceptor systems

Alina Brzeczek, Katarzyna Piwowar, Wojciech Domagala, Mikołaj M. Mikołajczyk, Krzysztof Walczak, Pawel Wagner

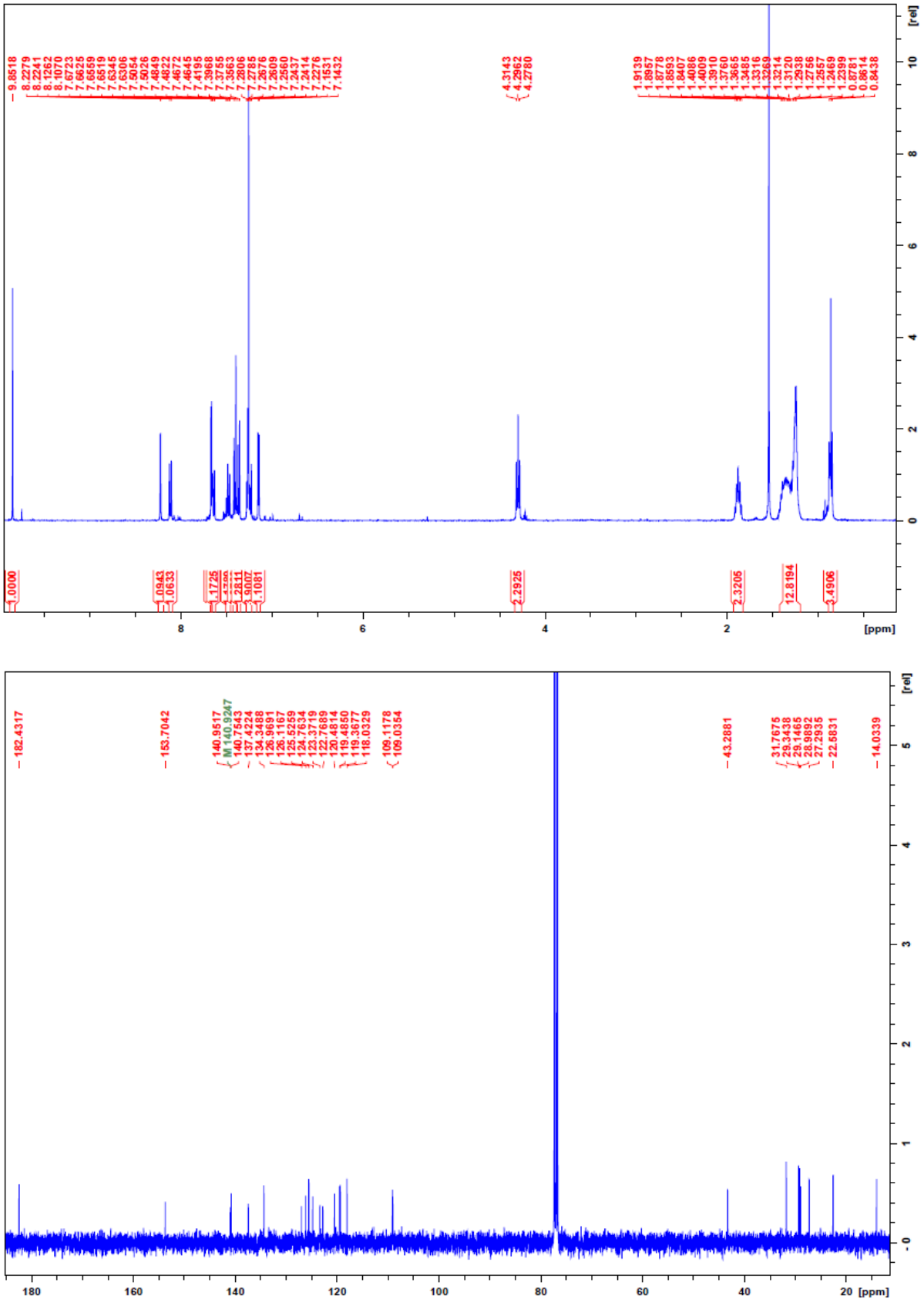
Electronic Supporting Information



Scheme SI.1. Synthetic route for the preparation of aldehydes 2–5. Reagents and conditions: (i) $POCl_3$, DMF, (ii)18-Crown-6, K_2CO_3, CH_2Cl_2, reflux, 1,5h; (iii) TFA, CH_2Cl_2, H_2O, r.t., 0,5h.

Figure SI.1 ^{1}H and ^{13}C NMR spectra of aldehydes **2**, **3**, **4**, **5**.

2



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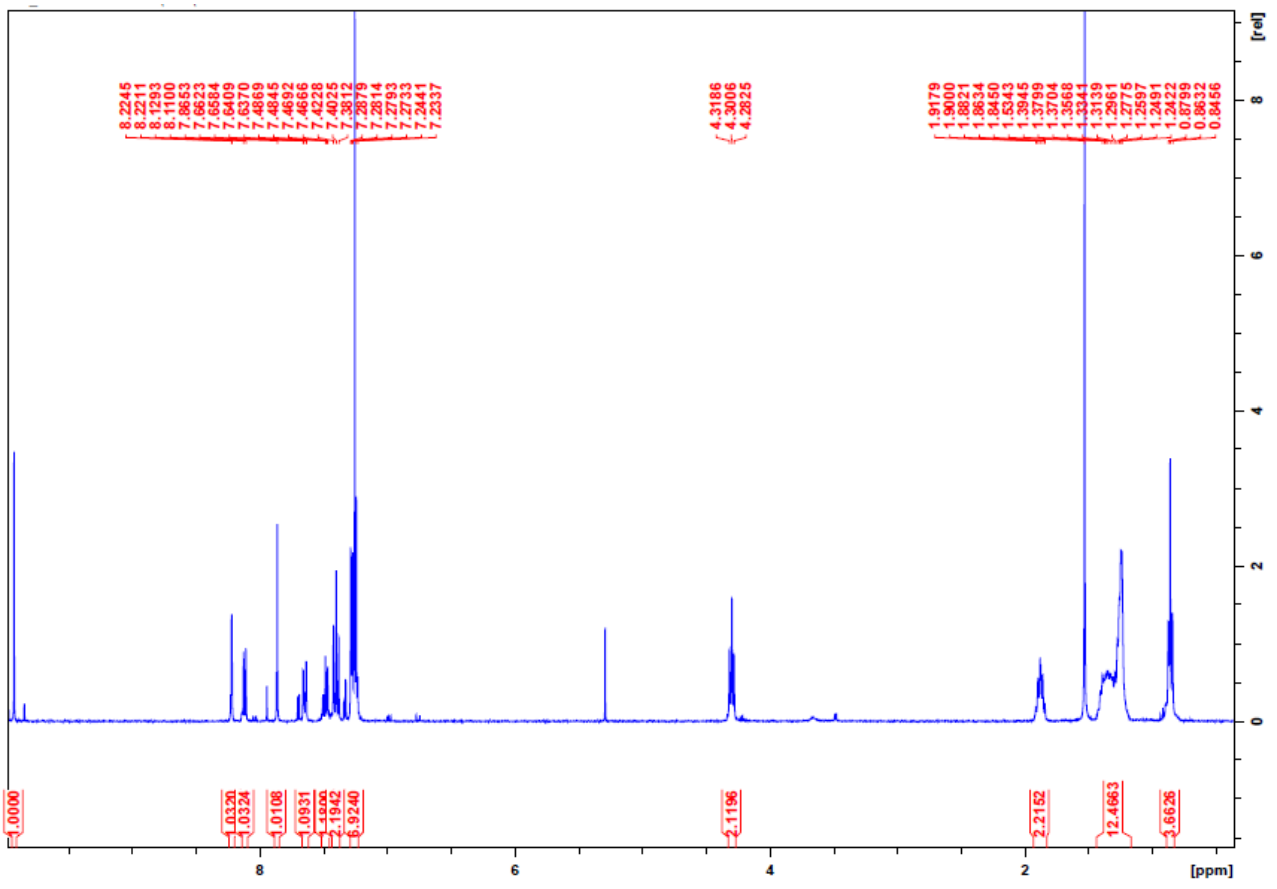
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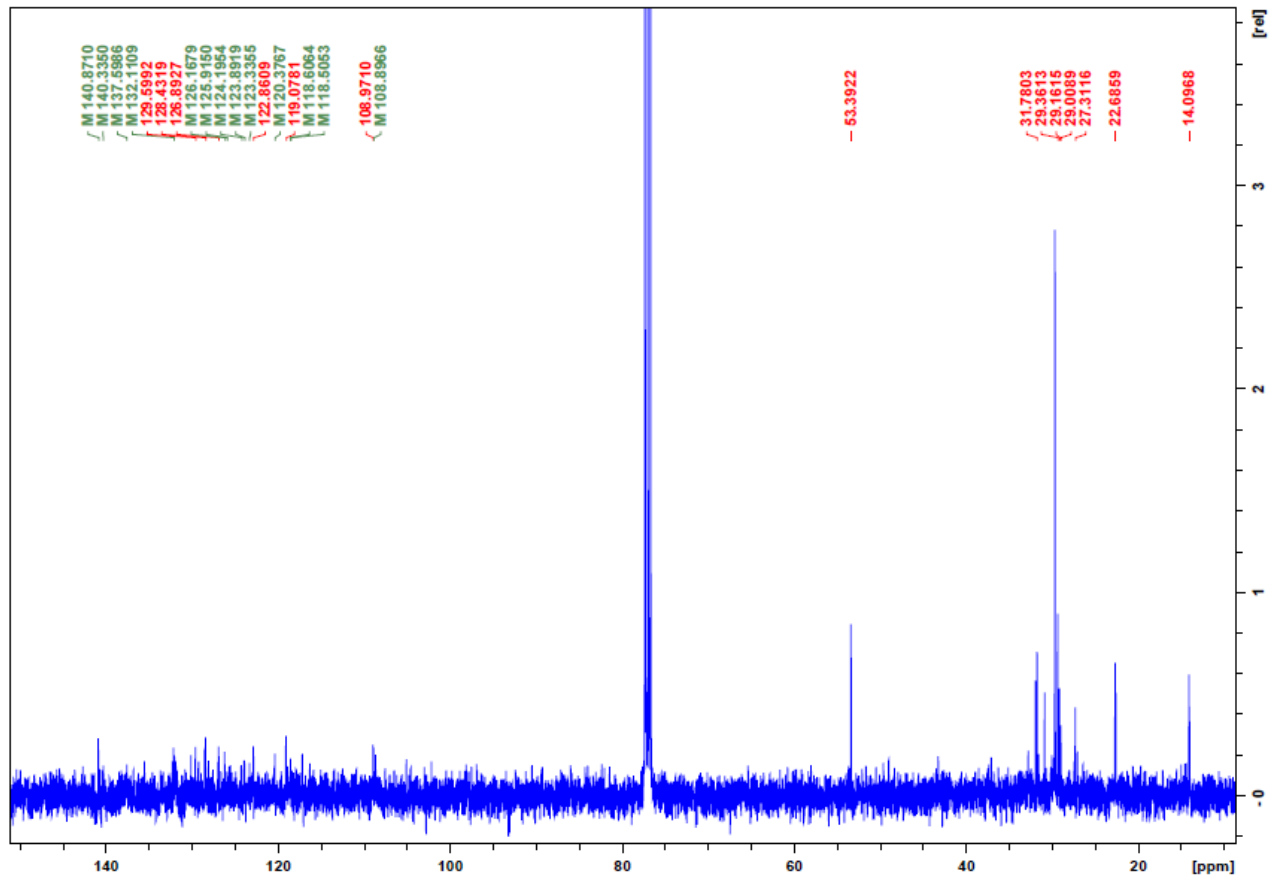
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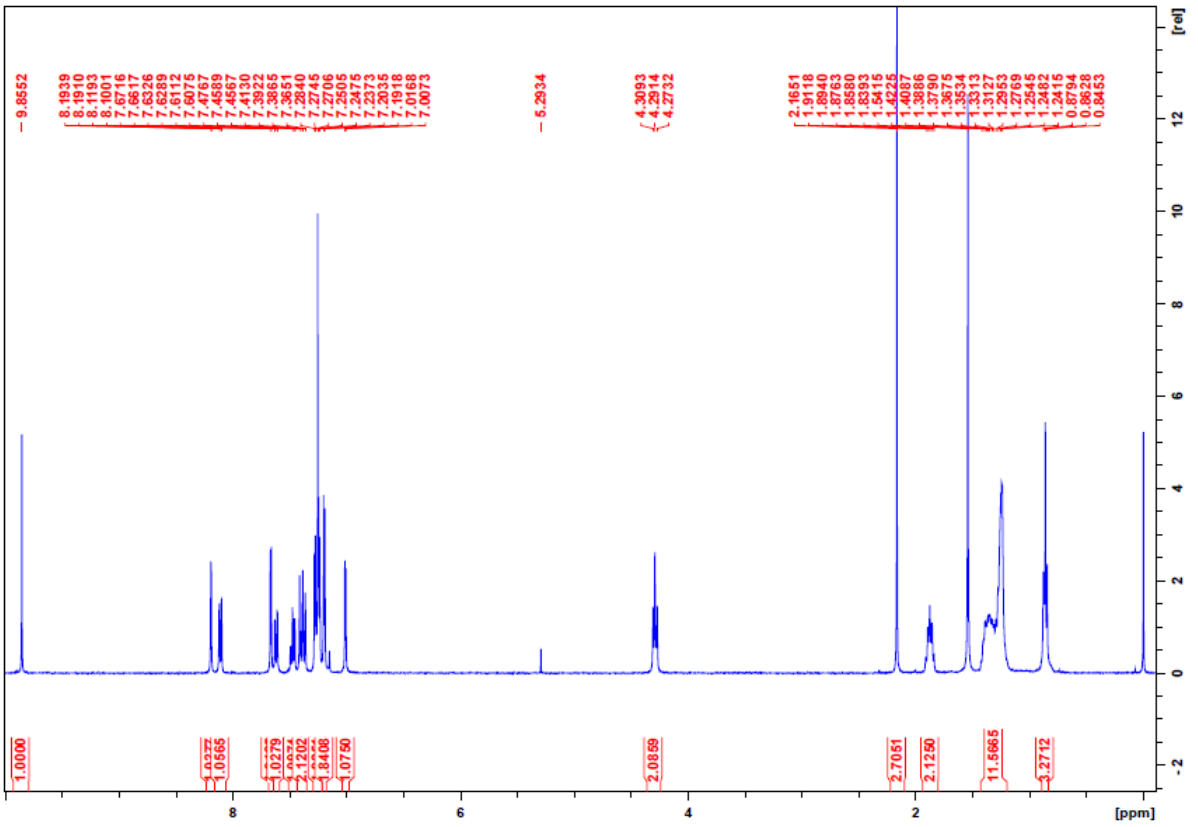
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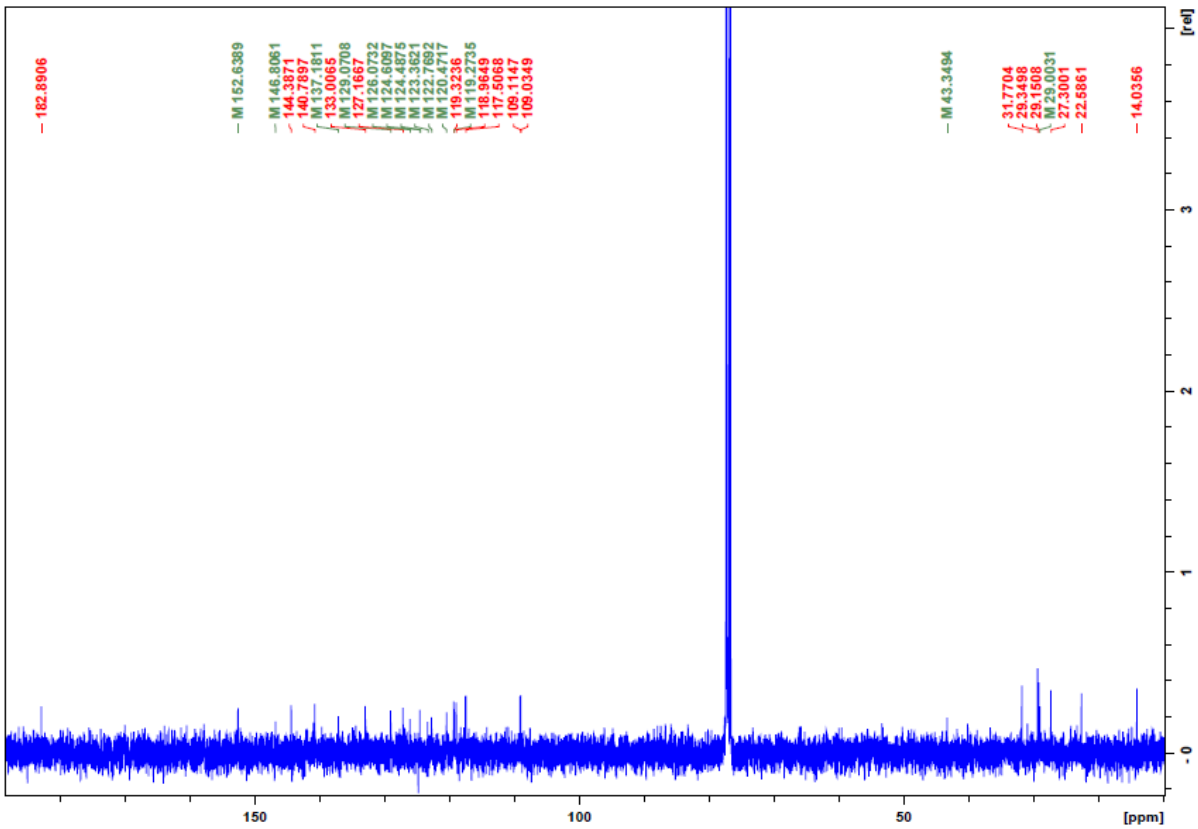
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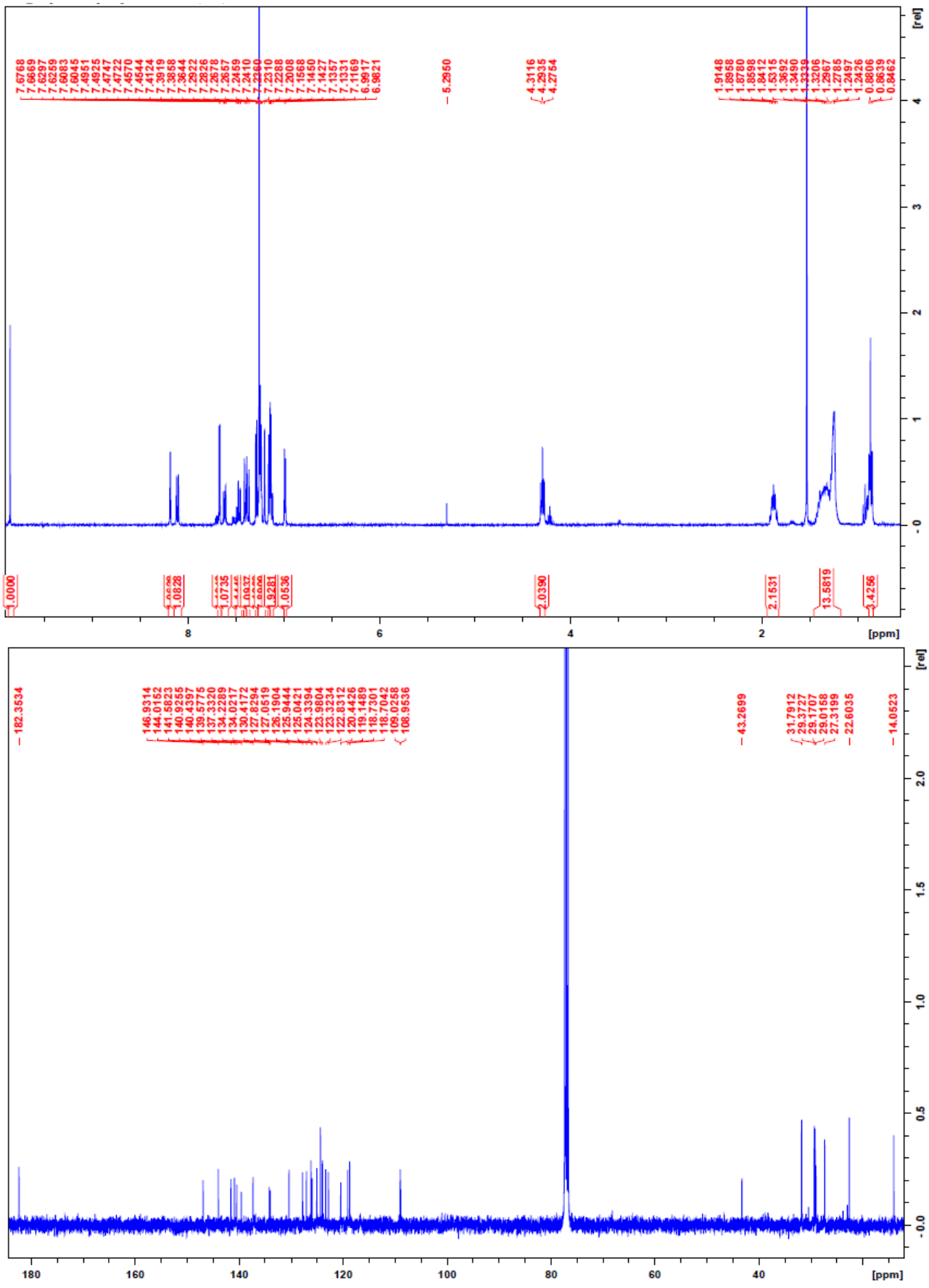
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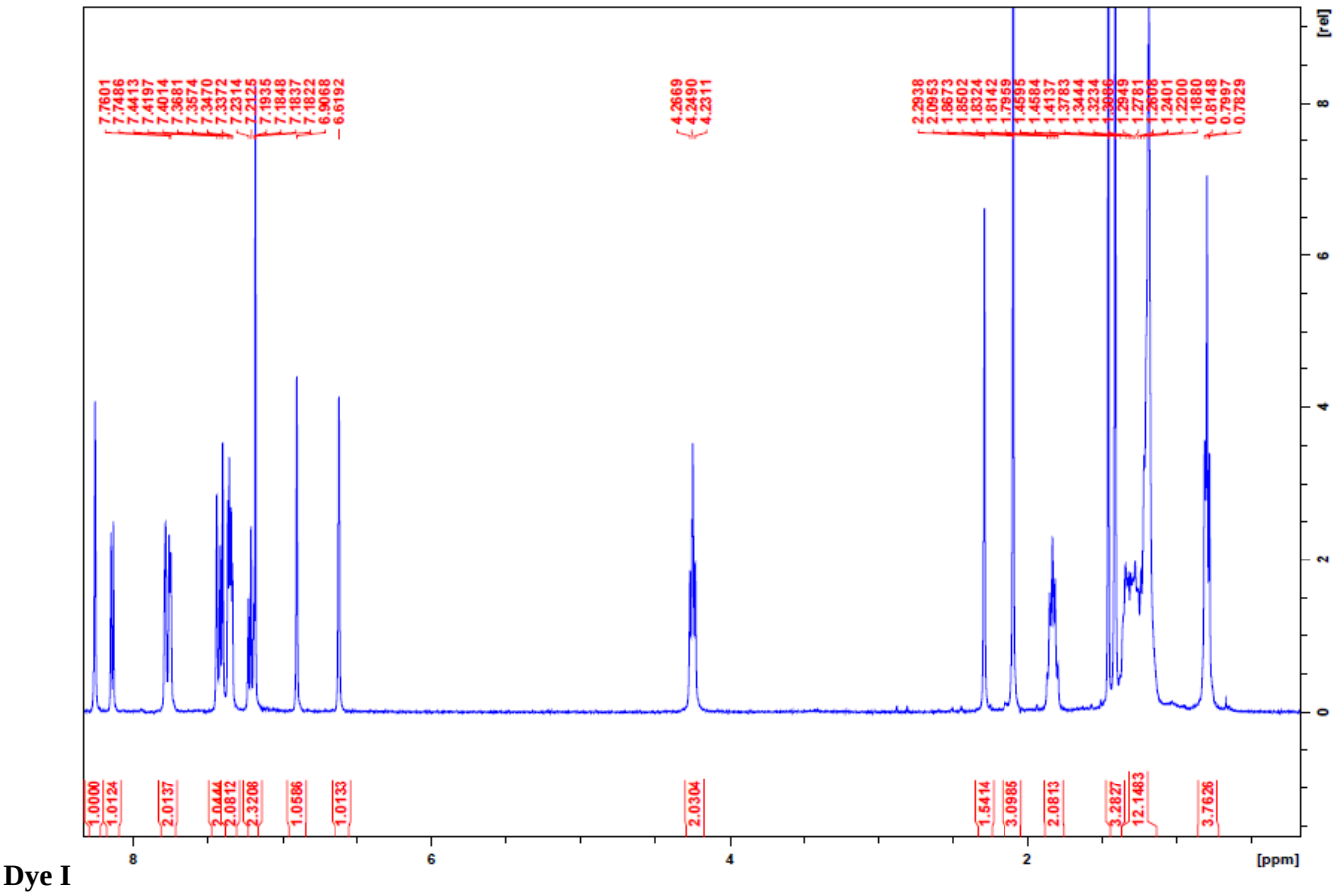
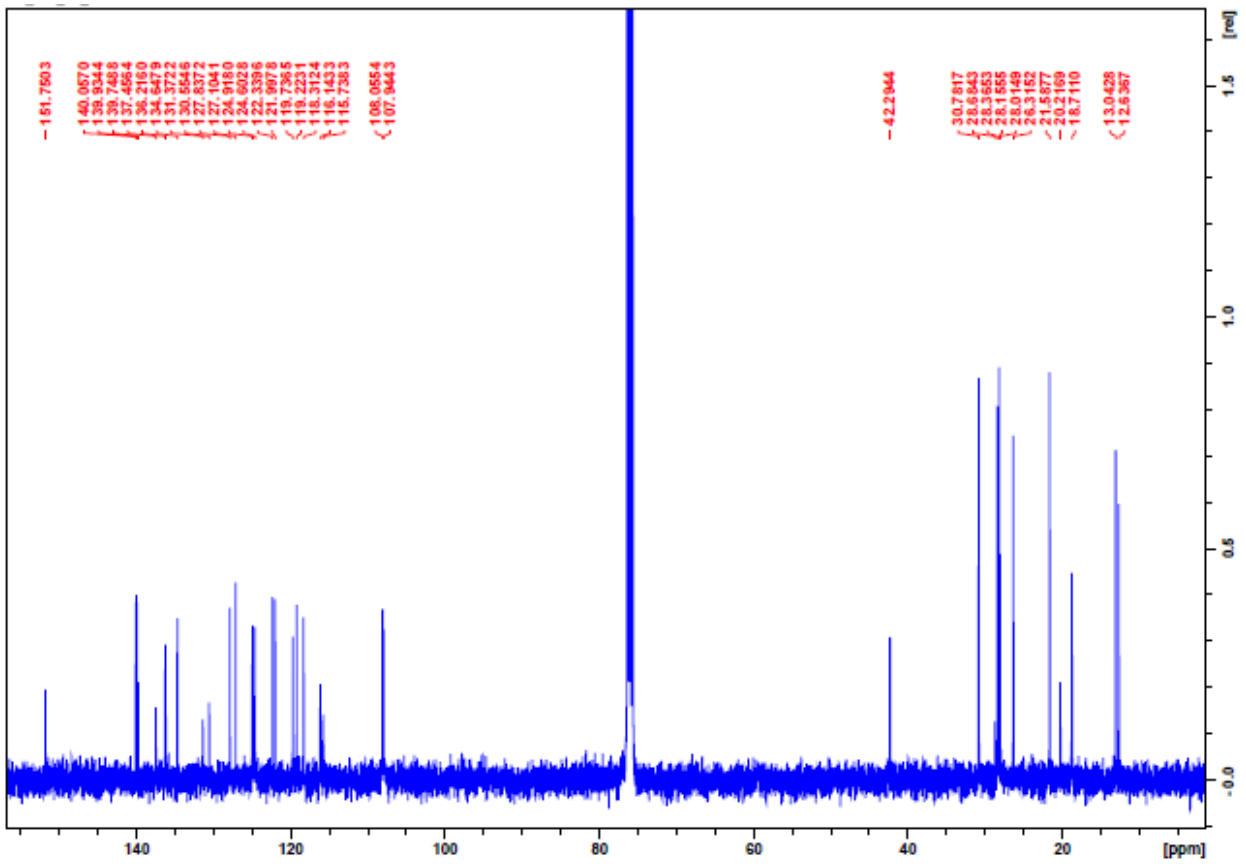
Figure SI.2 ^{1}H and ^{13}C NMR spectra of dyes **I**, **II**, **III**, **IV**, **V**.

Dye I





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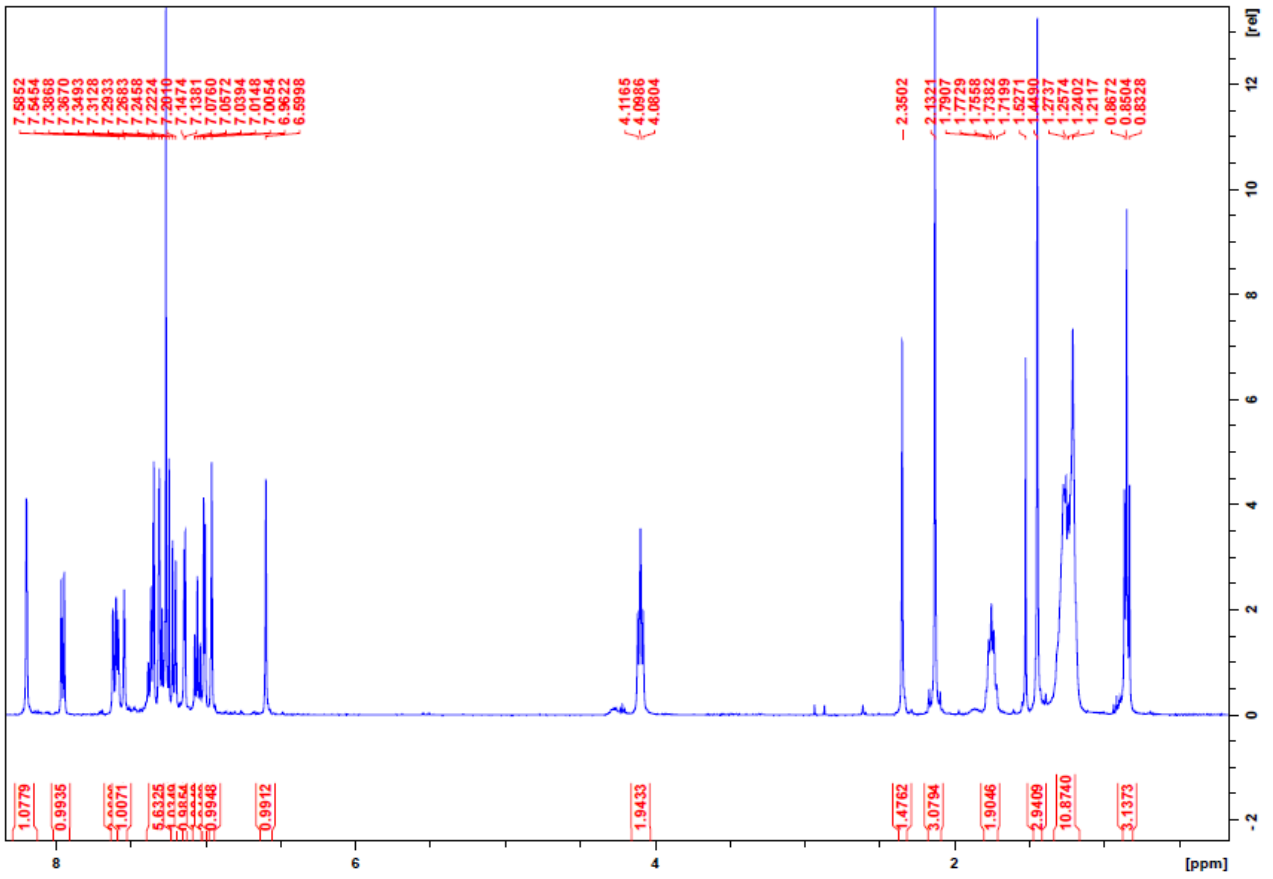
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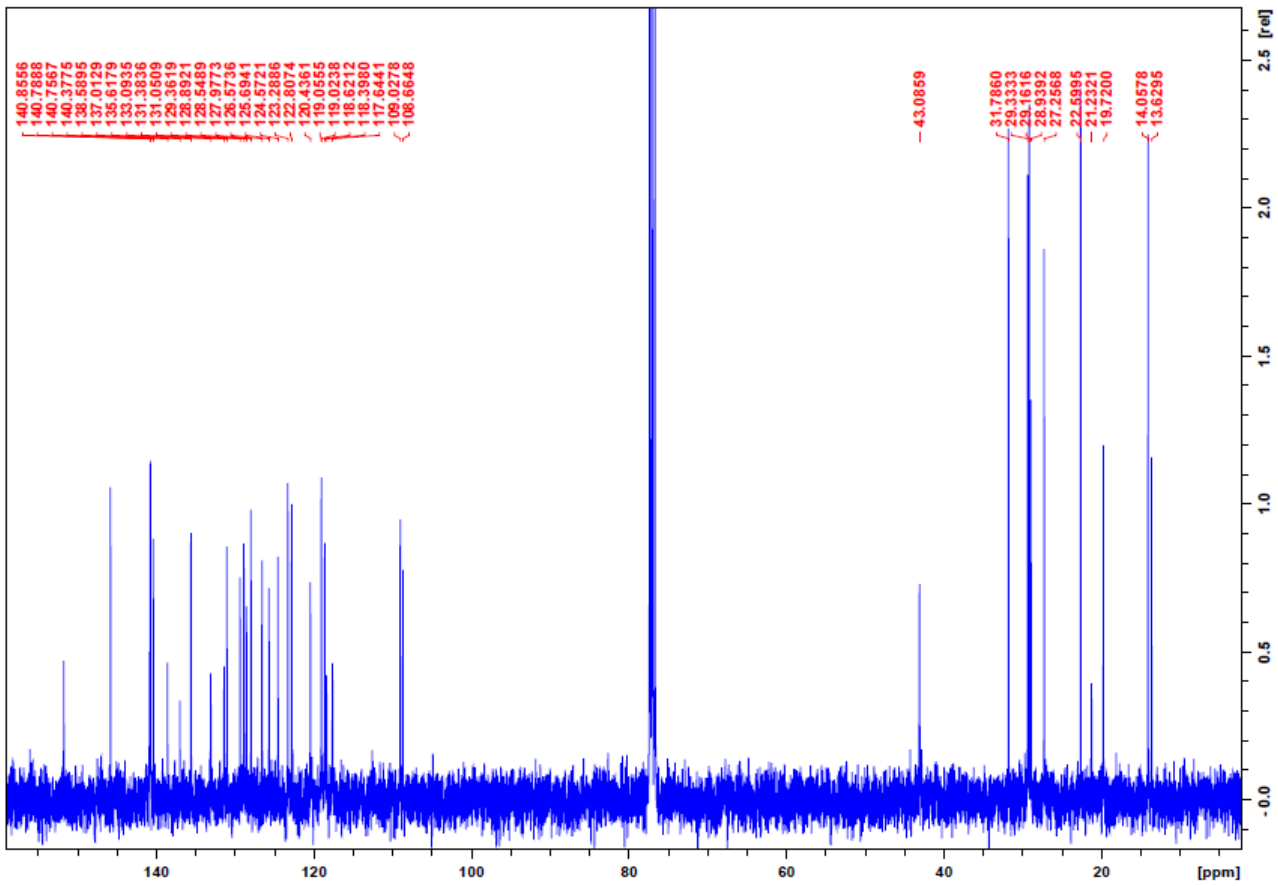
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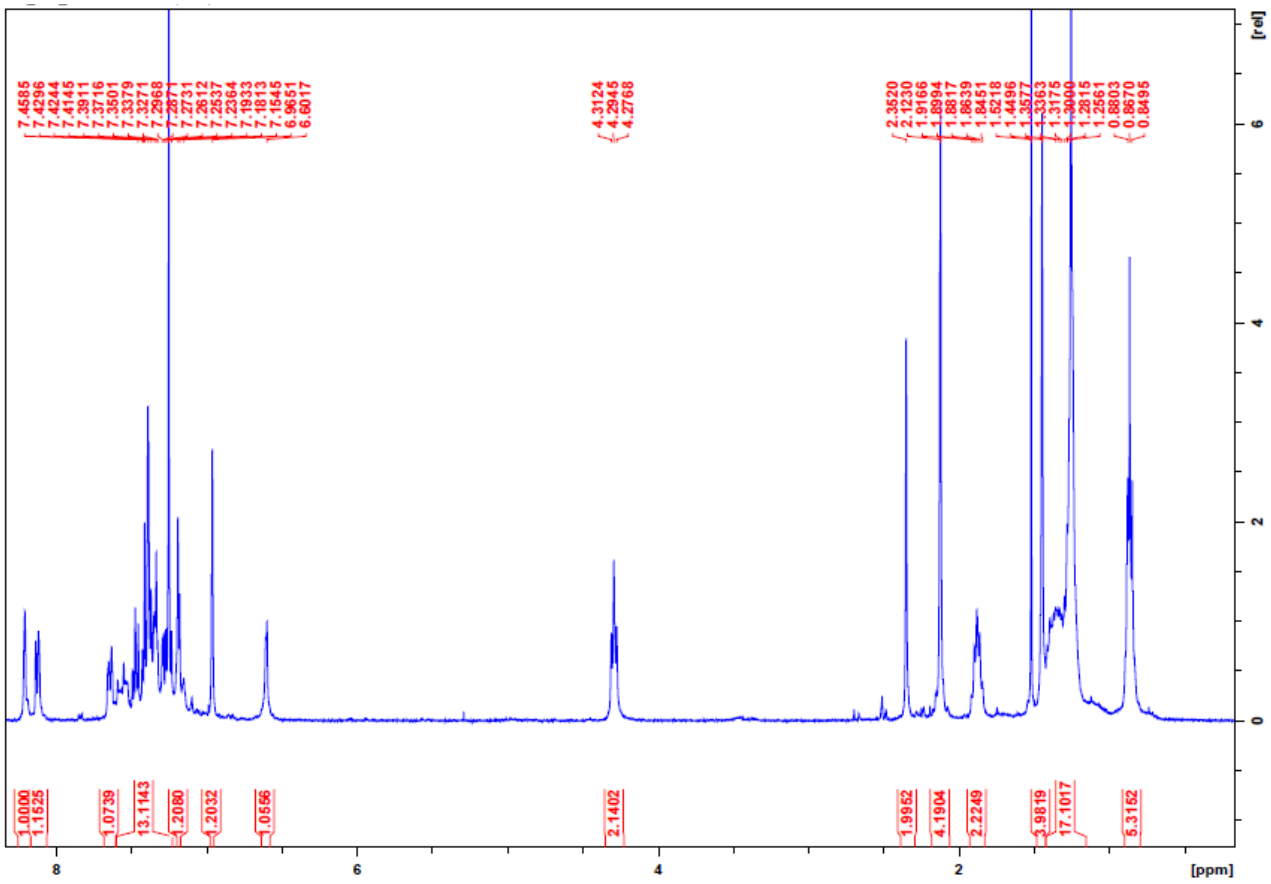
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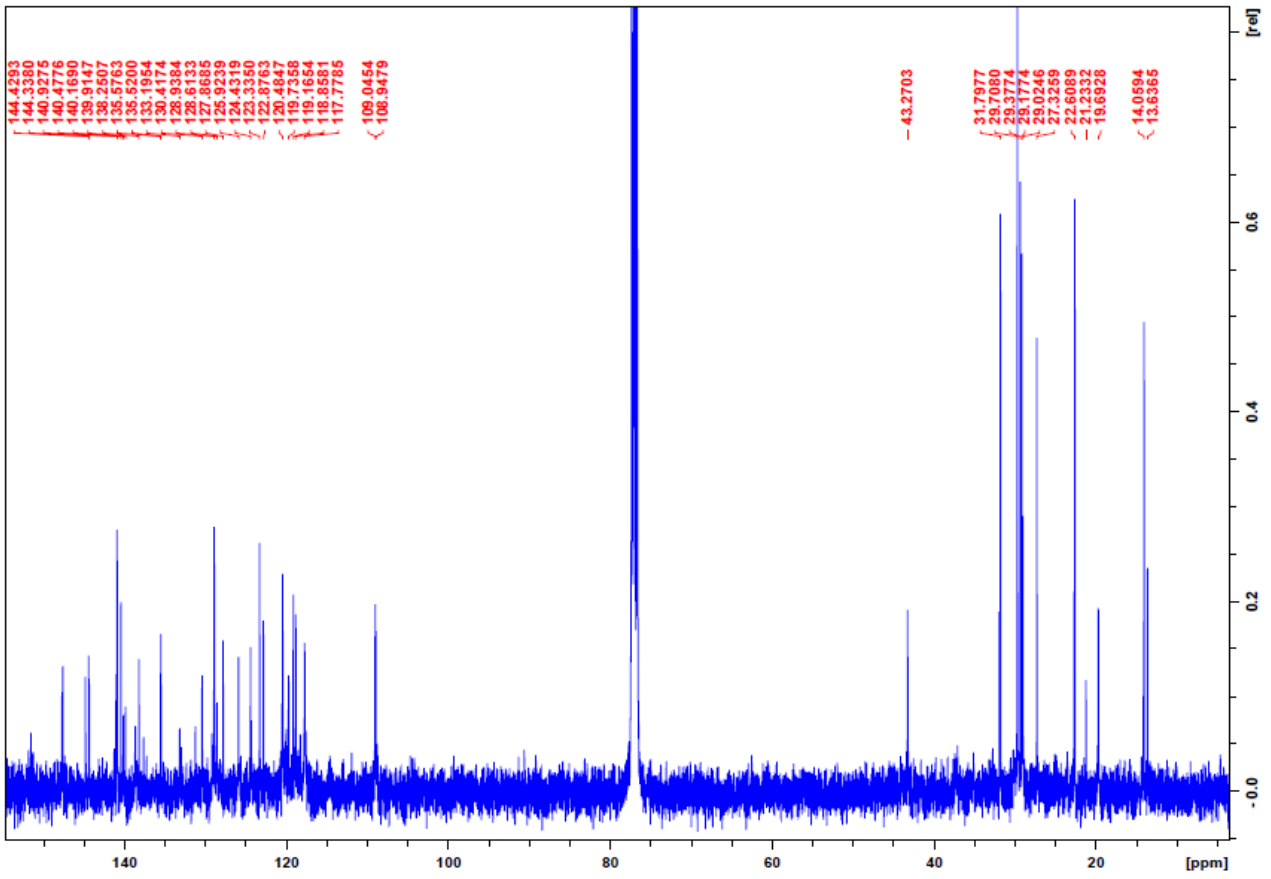
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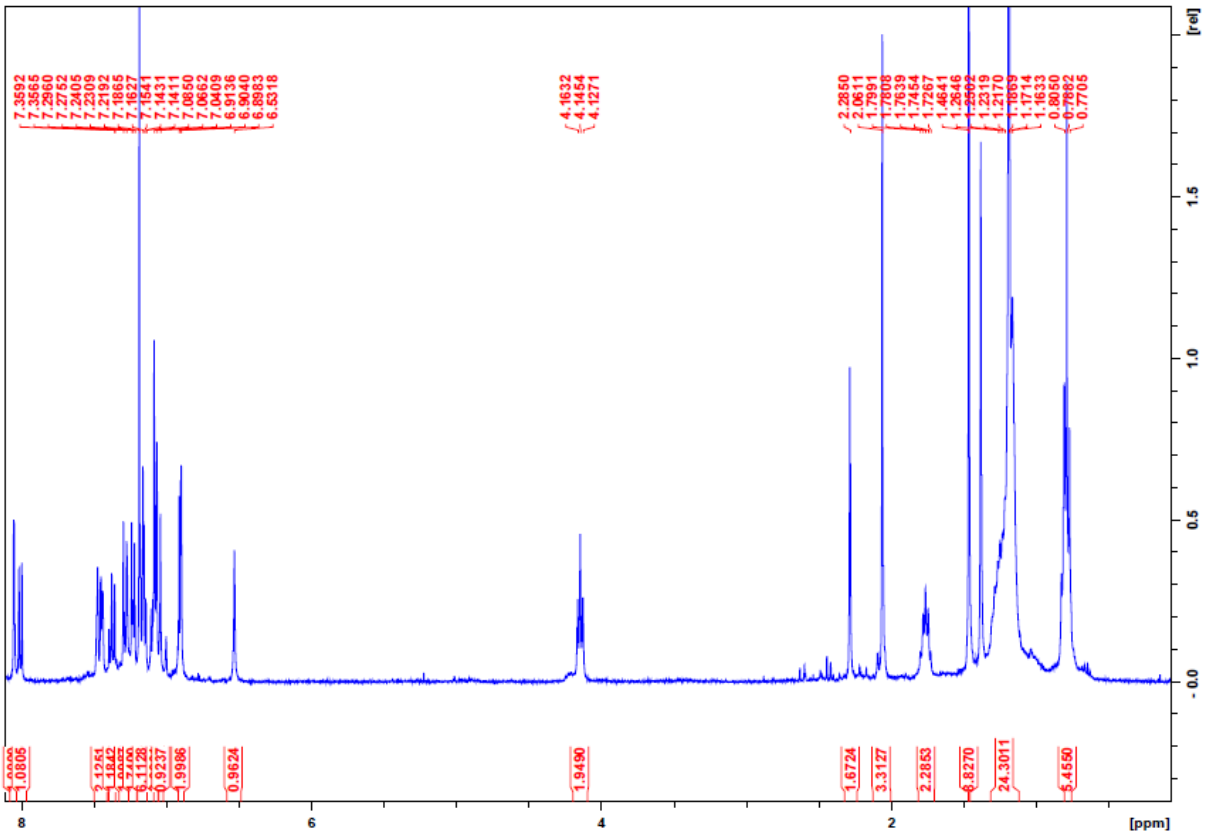
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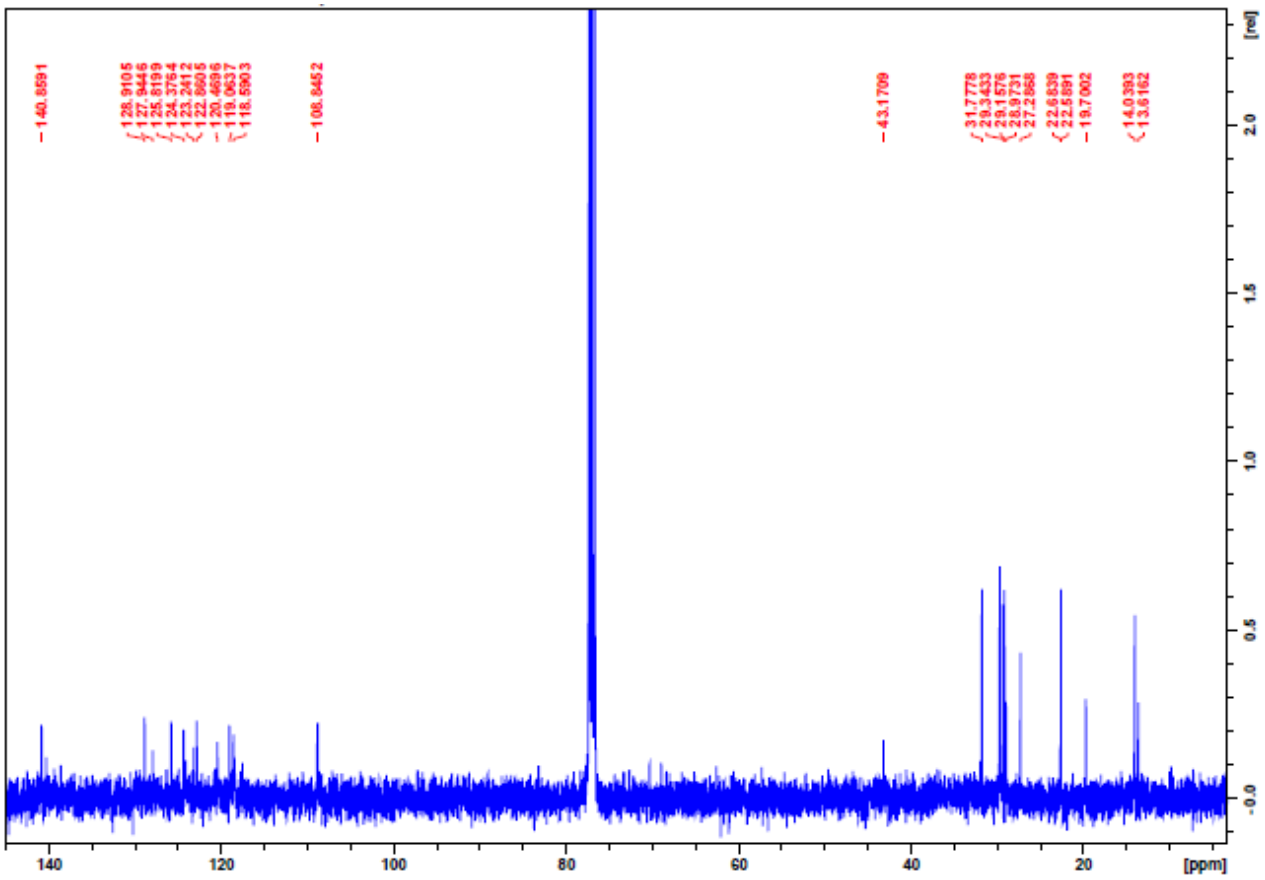
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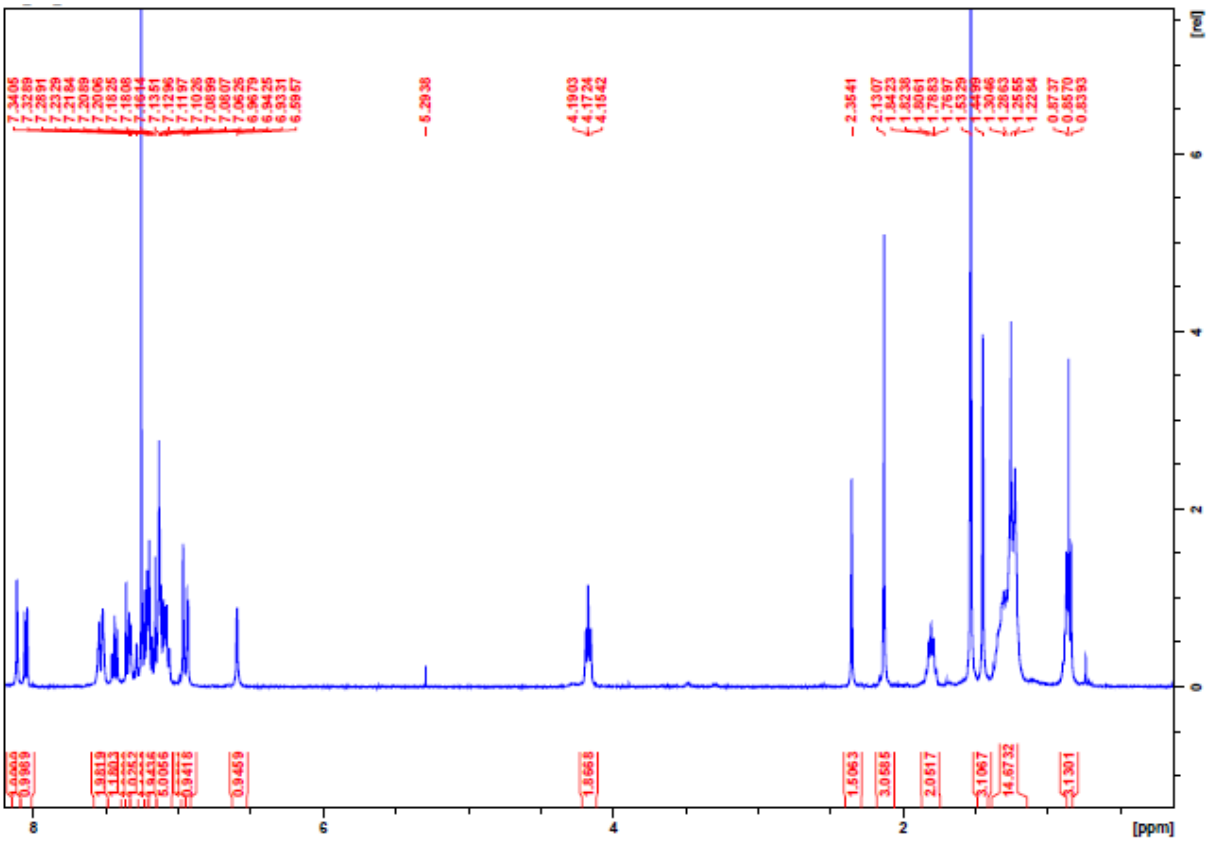
DYE V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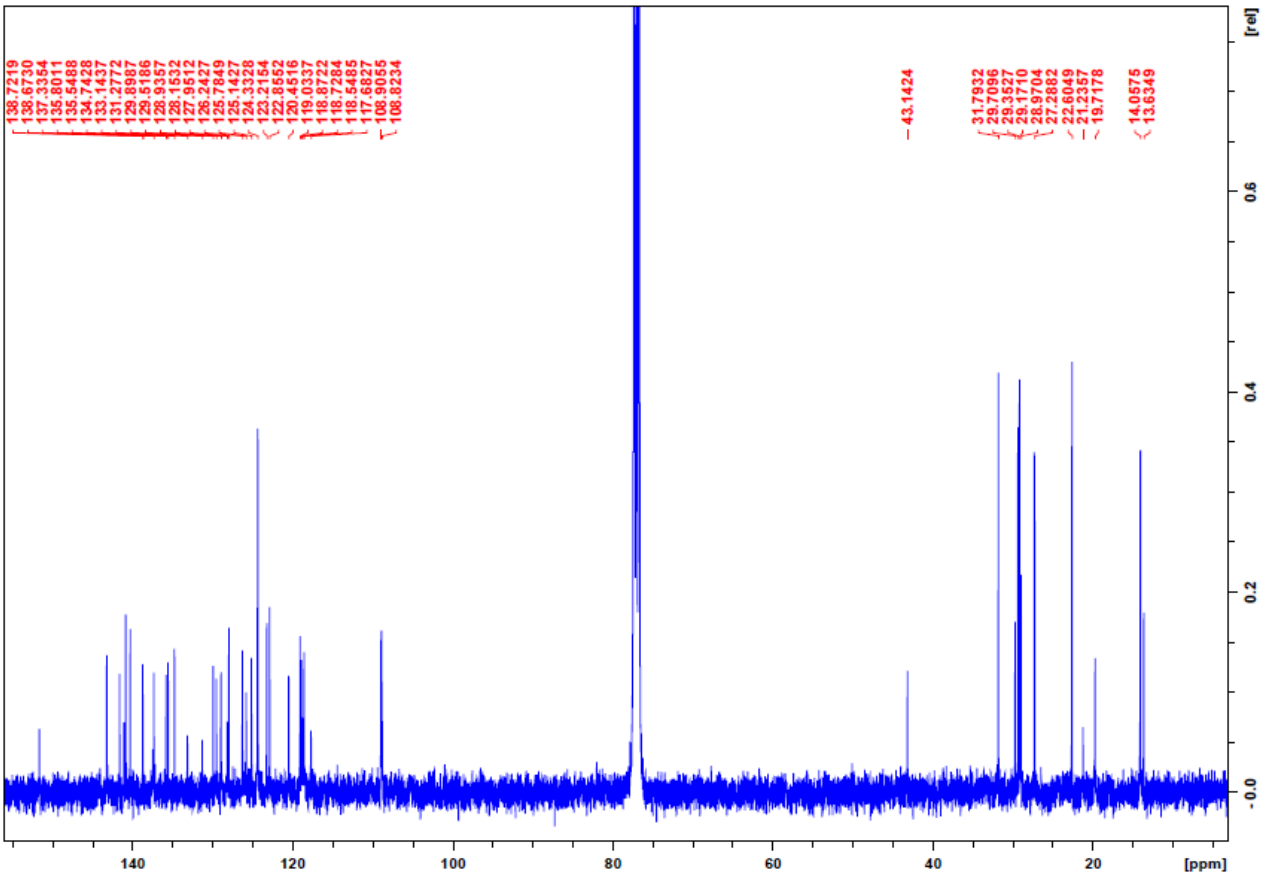
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Table SI.1. Formal potentials and peak-to-peak separation parameter of redox pairs of dyes **I** to **V** computed from cyclic voltammograms presented in figure 8. Due to close overlap of redox peaks of dyes **II** to **V** in the positive potentials' segment, meaningful determination of experimental formal potentials of redox pairs involved is unfeasible.

Dye	E_0' [V]	$\Delta E'_{pp}$ [mV]	E_0'' [V]	$\Delta E''_{pp}$ [mV]	E_0''' [V]	$\Delta E'''_{pp}$ [mV]
I	-1.52	88	0.22	77	0.47	77
II	-1.57	143	-	-	-	-
III	-1.39	113	-	-	-	-
IV	-1.31	80	-	-	-	-
V	-1.66	132	-	-	-	-

Table SI.2. Conjugation ratio expressing the number of atoms contributing their atomic orbitals to a given molecular orbital, to the total number of atoms in a molecule, set against ionization potentials and electron affinities of all investigated dyes.

Dye	Conjugation ratio for:		IP [eV]	EA [eV]
	HOMO	LUMO		
I	0.867	0.474	5.24	3.65
II	0.760	0.438	5.28	3.67
III	0.893	0.408	5.22	3.76
IV	0.793	0.379	5.27	3.84
V	0.698	0.515	5.32	3.53

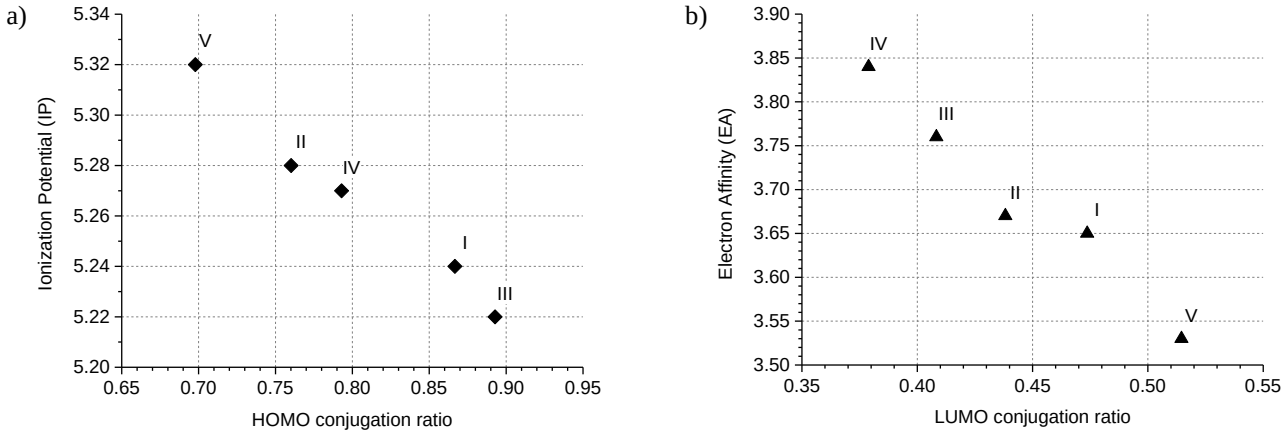
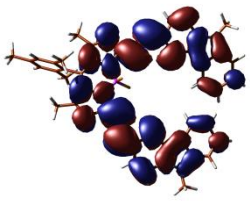
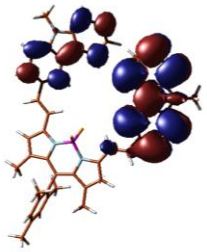
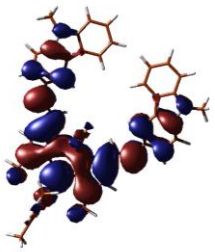
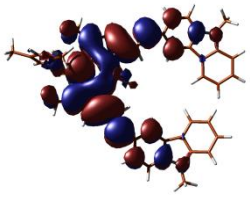
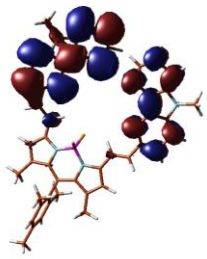
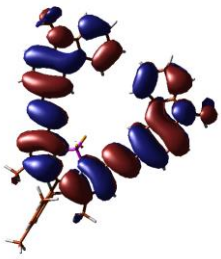
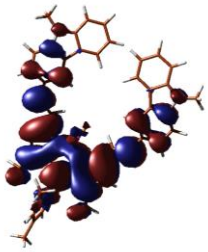
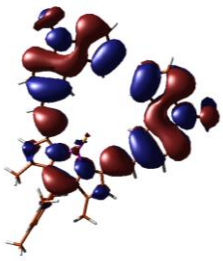
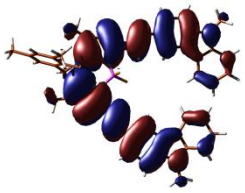
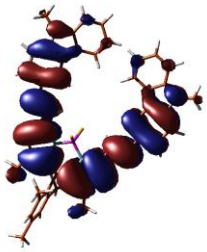
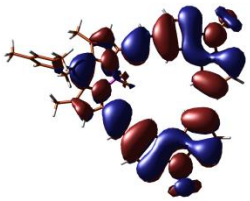


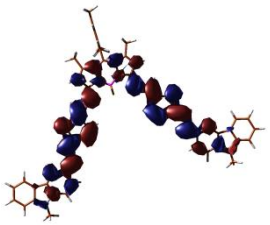
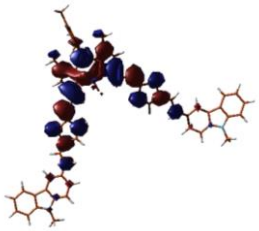
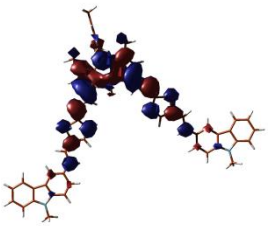
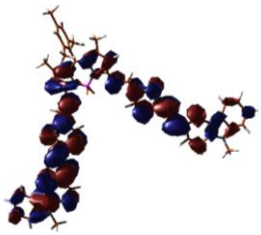
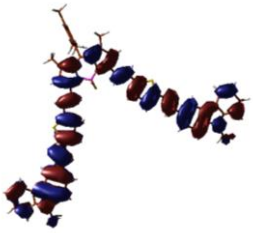
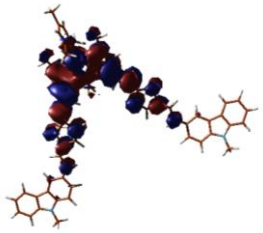
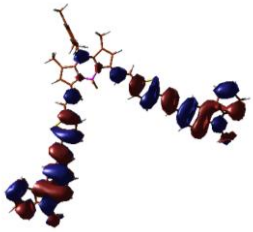
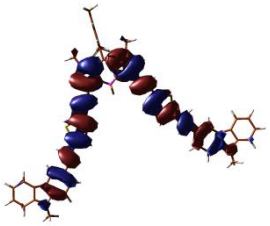
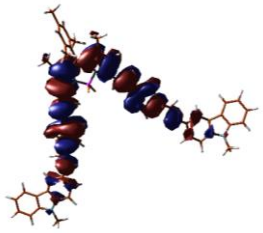
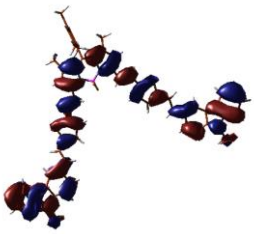
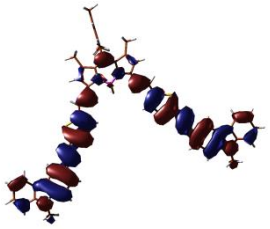
Figure SI.3. Correlation plots of characteristic electron transfer energies with conjugation ratio of given frontier molecular orbitals for dyes **I** through **V**: a) Ionization Potential vs HOMO, b) Electron Affinity vs LUMO.

Figure SI.4 Contours of selected molecular orbitals of neutral and singly charged states of dye: a) **I**, b) **II**, c) **III**, d) **IV**, e) **V**

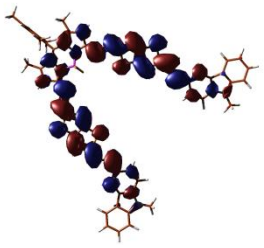
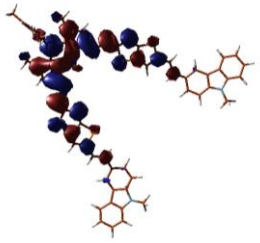
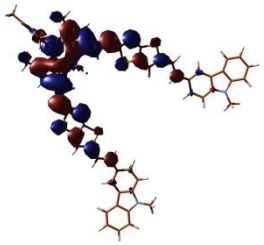
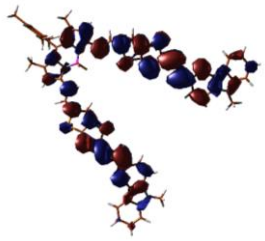
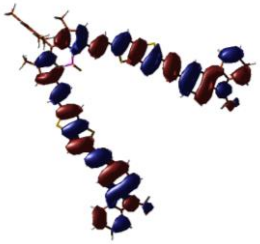
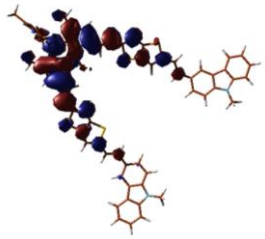
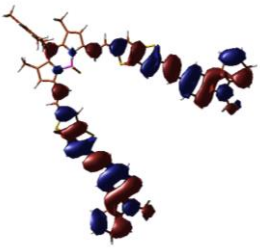
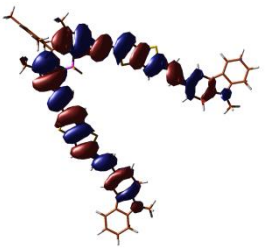
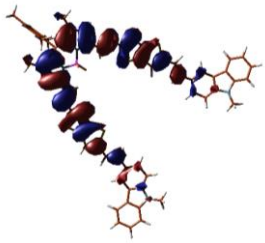
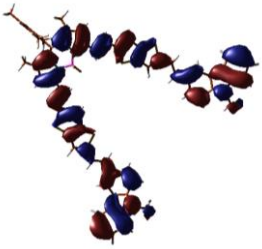
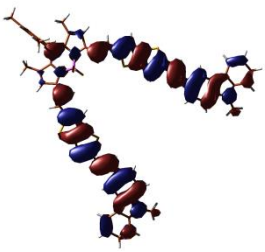
a) Dye **I**

	Radical cation			Neutral molecule			Radical anion		
	No.		E [a.u.]	No.		E [a.u.]	No.		E [a.u.]
LUMO+1				199		0.01043	200		0.09437
LUMO	198		-0.15530	198		-0.05472	199		0.09284
SOMO	197		-0.30694				198		-0.05713
HOMO	196		-0.32188	197		-0.20403	197		-0.11075
HOMO-1				196		-0.23464			

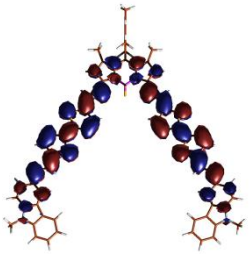
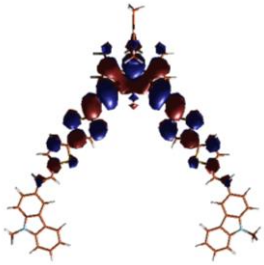
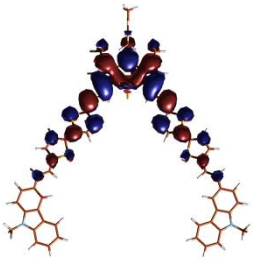
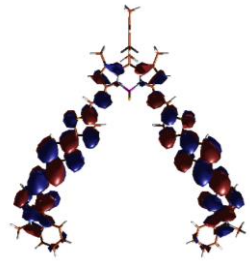
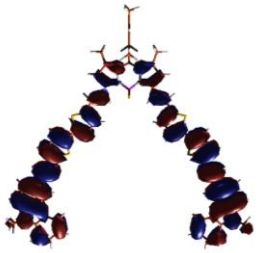
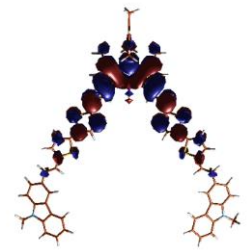
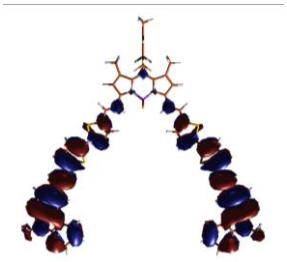
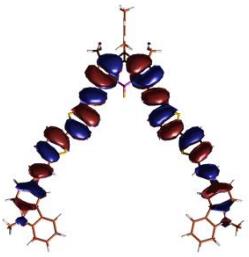
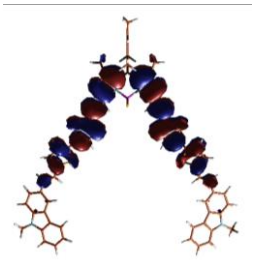
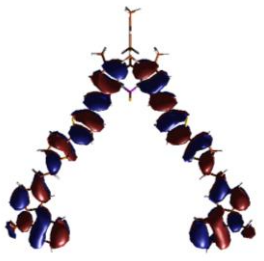
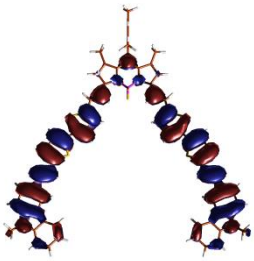
b) Dye **II**

	Radical cation			Neutral molecule			Radical anion		
	No.		E [a.u.]	No.		E [a.u.]	No.		E [a.u.]
LUMO+1				255		-0.02092			
LUMO	254		-0.15140	254		-0.06417	255		0.05728
SOMO	253		-0.28329				254		-0.07056
HOMO	252		-0.28963	253		-0.19975	253		-0.11698
HOMO-1	251		-0.31187	252		-0.22050			

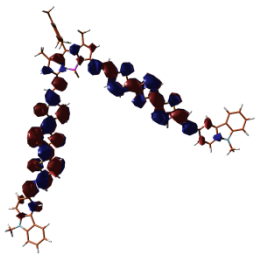
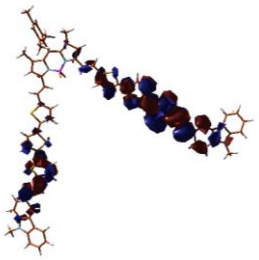
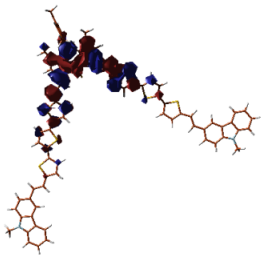
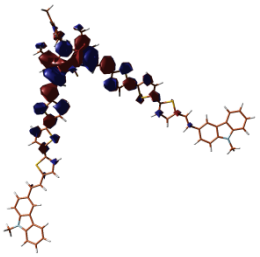
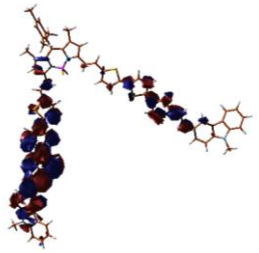
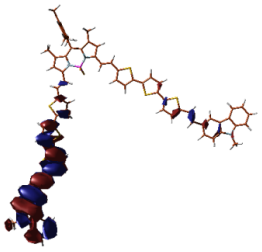
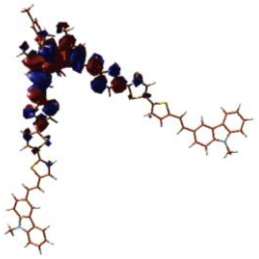
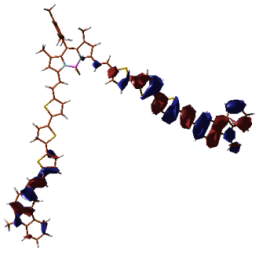
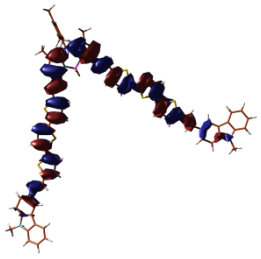
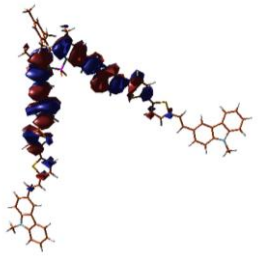
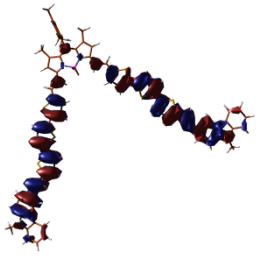
c) Dye **III**

	Radical cation			Neutral molecule			Radical anion		
	No.		E [a.u.]	No.		E [a.u.]	No.		E [a.u.]
LUMO+1				283		-0.02717	284		0.05144
LUMO	282		-0.15271	282		-0.06706	283		0.04698
SOMO	281		-0.28077				282		-0.07360
HOMO	280		-0.28525	281		-0.20144	281		-0.11993
HOMO-1	279		-0.30743	280		-0.21933			

d) Dye **IV**

	Radical cation			Neutral molecule			Radical anion		
	No.		E [a.u.]	No.		E [a.u.]	No.		E [a.u.]
LUMO+1				297		-0.02965	298		0.04298
LUMO	296		-0.15138	296		-0.06739	297		0.04025
SOMO	295		-0.27412				296		-0.07414
HOMO	294		-0.27685	295		-0.20055	295		-0.12023
HOMO-1	293		-0.29971	294		-0.21556			

e) Dye **V**

	Radical cation			Neutral molecule			Radical anion		
	No.		E [a.u.]	No.		E [a.u.]	No.		E [a.u.]
LUMO+1				339		-0.03648	340		0.02703
LUMO	338		-0.15304	338		-0.06985	339		0.02509
SOMO	337		-0.26489				338		-0.07712
HOMO	336		-0.26651	337		-0.20240	337		-0.12305
HOMO-1	335		-0.29100	336		-0.21377			