Supporting Information

Pyrenoimidazole fused phenanthridine derivatives with intense red excimer fluorescence in solid-state

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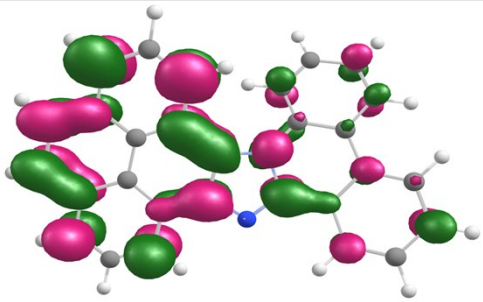
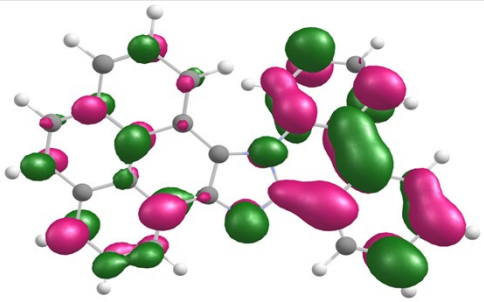
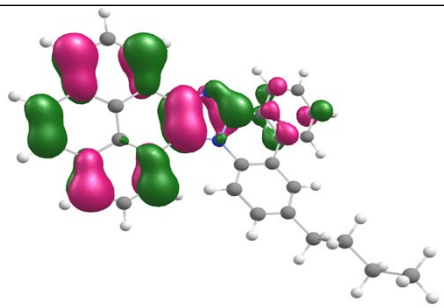
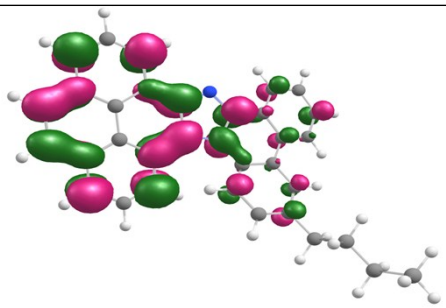
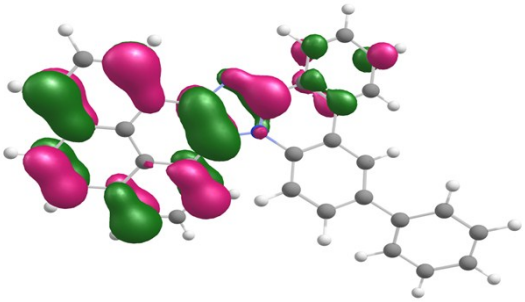
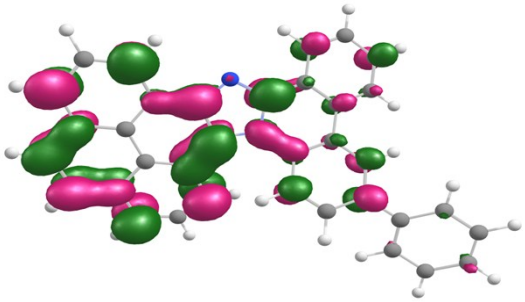
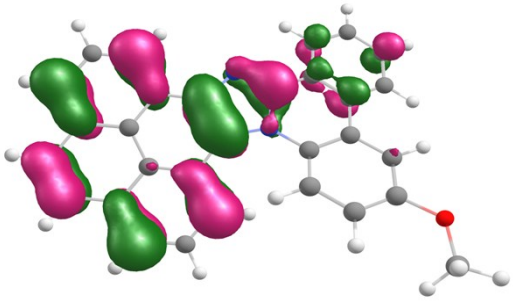
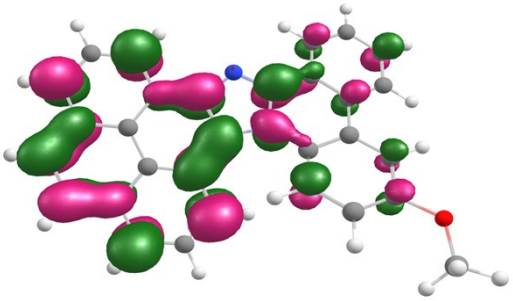
Table S1 Photophysical properties of the compounds **5a-5f** in different solvents

Solvent	Absorption	Fluorescence	Stoke's Shift (cm^{-1})	Φ_{fl}
5a				
Toluene	392	421	1757	0.66
$CHCl_3$	391	421	1757	0.69
EA	391	418	1651	0.64
THF	390	417	1660	0.74
DCM	392	421	1757	0.68
5b				
Toluene	392	421	1757	0.59
$CHCl_3$	392	421	1757	0.54
EA	391	418	1652	0.58
THF	390	417	1660	0.70
DCM	392	421	1757	0.63
5c				
Toluene	393	422	1748	0.66
$CHCl_3$	391	423	1934	0.63
EA	391	418	1652	0.59
THF	390	420	1831	0.69
DCM	391	423	1934	0.68
5d				
Toluene	394	423	1740	0.54
$CHCl_3$	392	423	1869	0.63
EA	392	418	1587	0.53
THF	391	420	1766	0.64
DCM	392	423	1869	0.67
5e				
Toluene	392	446	3089	0.61
$CHCl_3$	392	420	1701	0.65
EA	390	448	2965	0.64
THF	390	439	2862	0.58
DCM	392	419	1643	0.68
5f				
Toluene	394	428	2016	0.59
$CHCl_3$	392	430	2254	0.56
EA	392	428	2145	0.60
THF	391	433	2640	0.66
DCM	391	436	1757	0.61

Table S2 Fluorescence life time values of **5a-5f** in thin film

Compounds	τ_1	A_1	τ_2	A_2	τ_{avg}	χ^2
5a	1.89	19.97	9.33	80.03	7.84	1.12
5b	2.04	29.05	7.07	70.95	5.61	1.19
5c	2.44	28.61	8.67	71.39	6.89	1.11
5d	1.79	29.80	8.16	70.20	6.26	1.11
5e	2.05	28.26	8.01	71.74	6.32	1.13
5f	1.98	45.20	7.17	54.80	4.82	1.11

Table S3. Optimized geometries of **5a-5f** calculated at B3LYP/6-31G*

HOMO	LUMO
	 **5a**
	 **5b**
	 **5c**
	 **5d**

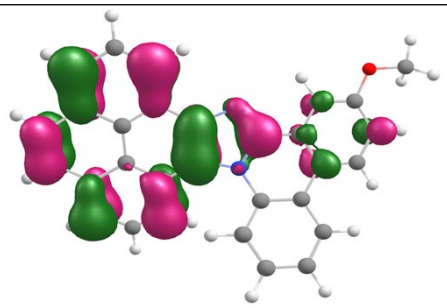
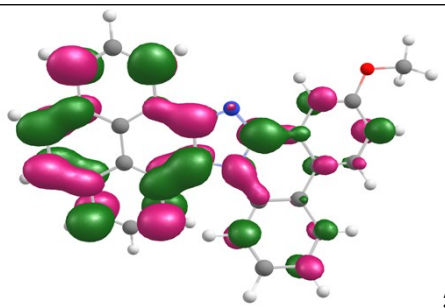
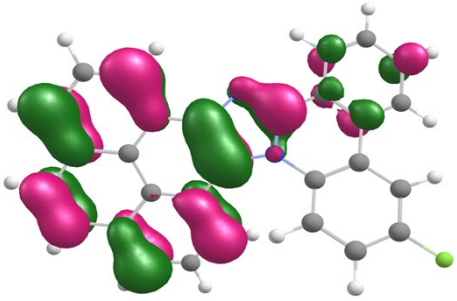
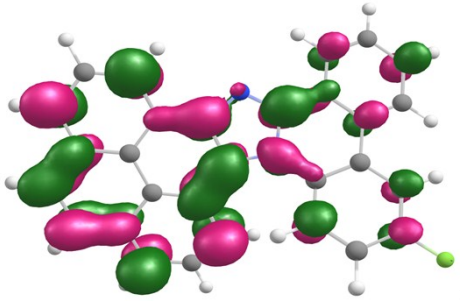
	 **5e**
	 **5f**

Table S4 Selected transitions obtained from TD-DFT calculations

Compound	Wave length (nm)	Osc. Strength	Major contributions
5a	373.71	0.1465	HOMO→LUMO (51%), HOMO→L+1 (37%)
	357.15	0.0849	H-1→LUMO (18%), HOMO→LUMO (27%), HOMO→L+1 (41%)
	320.69	0.226	H-1→LUMO (21%), HOMO→L+2 (25%), HOMO→L+3 (28%)
	309.15	0.2203	H-2→LUMO (12%), H-1→LUMO (30%), HOMO→L+3 (24%)
	300.33	0.1616	H-3→LUMO (10%), H-1→L+1 (59%)
	293.24	0.0942	H-2→LUMO (50%), H-1→L+1 (17%)
	291.03	0.0962	H-2→LUMO (12%), HOMO→L+3 (16%), HOMO→L+4 (51%)
	280.66	0.151	H-3→LUMO (40%), H-1→L+2 (32%)
	249.67	0.1425	H-3→L+1 (11%), H-3→L+2 (21%), H-2→L+2 (28%), HOMO→L+5 (10%)
	248.37	0.1649	H-3→L+2 (35%), H-1→L+3 (14%), H-6→LUMO (6%), H-6→L+1 (3%)

Compound	Wavelength (nm)	Osc. Strength	Major contributions
5b	372.61	0.1457	HOMO→LUMO (49%), HOMO→L+1 (39%)
	357.04	0.0803	H-1→LUMO (20%), HOMO→LUMO (28%), HOMO→L+1 (38%)
	321.71	0.3082	H-1→LUMO (28%), HOMO→L+2 (25%), HOMO→L+3 (19%)

	310.68	0.1707	H-3→LUMO (15%), H-1→LUMO (22%), HOMO→L+3 (35%)
	302.76	0.1545	H-2→LUMO (14%), H-1→L+1 (59%)
	294.39	0.1298	H-2→LUMO (59%), H-1→L+1 (17%)
	289.38	0.0992	HOMO→L+3 (15%), HOMO→L+4 (40%)
	281.86	0.1759	H-3→LUMO (32%), H-1→L+2 (19%), HOMO→L+4 (12%)
	246.01	0.1763	H-3→L+2 (13%), H-2→L+3 (10%), H-1→L+4 (51%)

Compound	**Wavelength (nm)**	**Osc. Strength**	**Major contributions**
5c	375.47	0.1391	HOMO→LUMO (55%), HOMO→L+1 (32%)
	363.09	0.0548	H-1→LUMO (16%), HOMO→LUMO (23%), HOMO→L+1 (48%)
	326.76	0.2536	H-1→LUMO (19%), HOMO→L+2 (36%), HOMO→L+3 (15%)
	320.25	0.357	H-3→LUMO (11%), H-1→LUMO (28%), HOMO→L+3 (38%)
	308.73	0.1537	H-2→LUMO (20%), H-1→L+1 (59%)
	297.53	0.1915	H-2→LUMO (57%), H-1→L+1 (16%)
	286.52	0.2067	H-3→LUMO (24%), H-2→L+1 (16%), H-1→L+2 (22%)
	271.23	0.1092	H-3→L+1 (60%)
	267.51	0.1342	H-3→LUMO (12%), H-2→L+1 (27%)
	258.95	0.1352	H-3→L+2 (46%), H-2→L+3 (17%)

	254.15	0.1465	H-7→LUMO (15%), H-6→LUMO (11%), H-4→L+1 (14%), H-1→L+4 (12%)

Compound	Wavelength (nm)	Osc. Strength	Major contributions
5d	376.88	0.1335	HOMO→LUMO (57%), HOMO→L+1 (32%)
	356.55	0.0637	H-1→LUMO (26%), HOMO→LUMO (21%), HOMO→L+1 (37%)
	327.16	0.2972	H-1→LUMO (40%), HOMO→L+2 (25%)
	310.26	0.1286	H-2→LUMO (17%), H-1→L+1 (55%)
	298.84	0.2885	H-2→LUMO (56%), H-1→L+1 (11%)
	286.37	0.238	H-3→LUMO (28%), H-2→L+1 (16%), H-1→L+2 (24%)
	247.65	0.2582	H-3→L+2 (21%), H-1→L+4 (48%)

Compound	Wavelength (nm)	Osc. Strength	Major contributions
5e	368.84	0.172	HOMO→LUMO (61%), HOMO→L+1 (24%)
	325.67	0.3846	H-1→LUMO (48%), HOMO→L+1 (23%)
	301.50	0.1576	H-3→LUMO (23%), H-1→L+1 (61%)
	292.28	0.4632	H-2→LUMO (46%), HOMO→L+3 (19%)
	260.31	0.3127	H-3→L+1 (34%), H-2→L+2 (11%), H-1→L+3 (11%), HOMO→L+5 (12%)
	248.19	0.0651	H-4→L+1 (18%), H-3→L+3 (13%), H-1→L+4 (19%), HOMO→L+5 (12%)

Compound	Wavelength (nm)	Osc. Strength	Major contributions
5f	386.44	0.1071	HOMO→LUMO (64%), HOMO→L+1 (29%)
	357.90	0.1068	H-1→LUMO (13%), HOMO→LUMO (20%), HOMO→L+1 (51%)
	321.51	0.2396	H-1→LUMO (28%), HOMO→L+2 (27%), HOMO→L+3 (20%)
	303.97	0.2219	H-3→LUMO (17%), H-1→L+1 (39%), HOMO→L+3 (13%)
	295.61	0.1958	H-2→LUMO (63%), H-1→L+1 (12%)
	293.08	0.1137	HOMO→L+3 (19%), HOMO→L+4 (46%)
	282.52	0.1172	H-3→LUMO (38%), H-1→L+2 (39%)
	249.02	0.2419	H-3→L+2 (18%), H-1→L+3 (20%), HOMO→L+5 (14%)

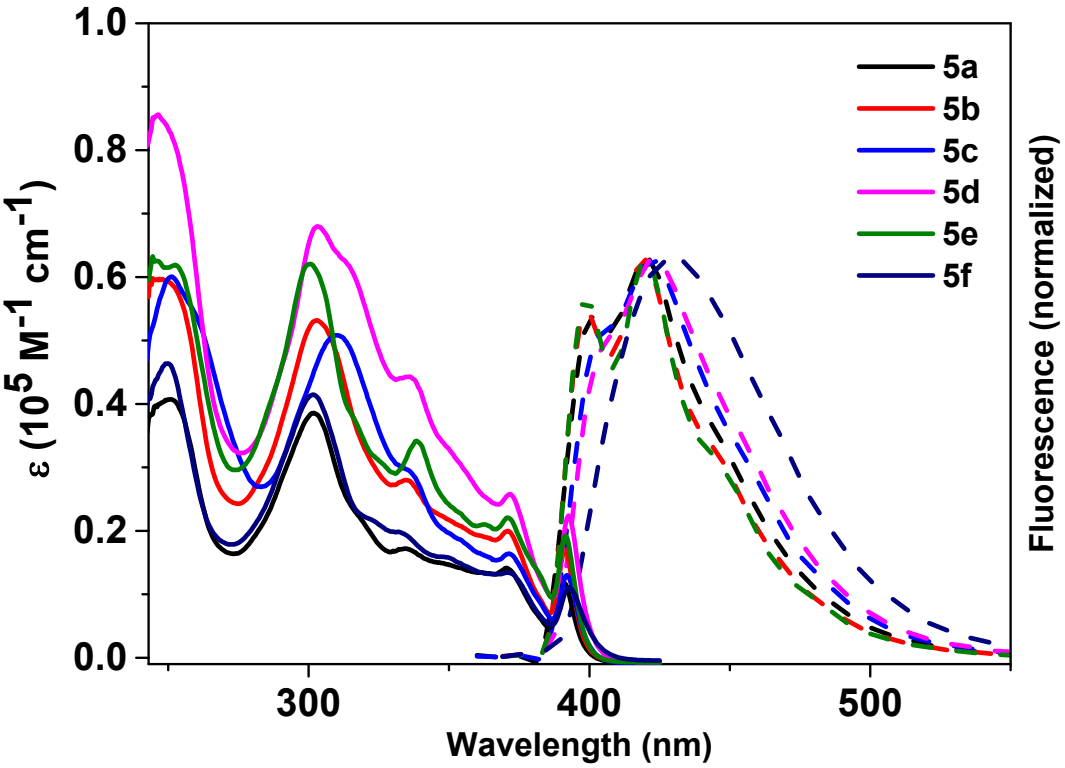


Fig. S1 UV−Visible absorption (solid line) and fluorescence (dotted line) spectra of **PyFP**s in chloroform.

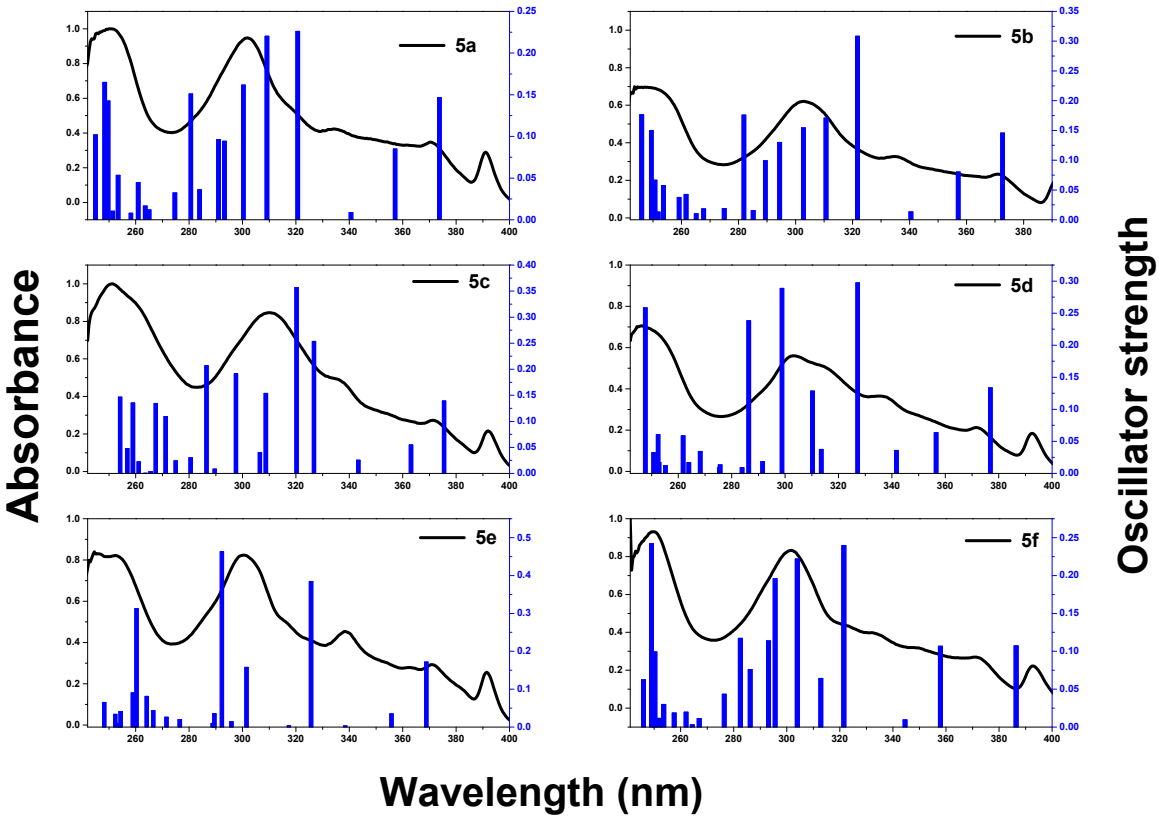
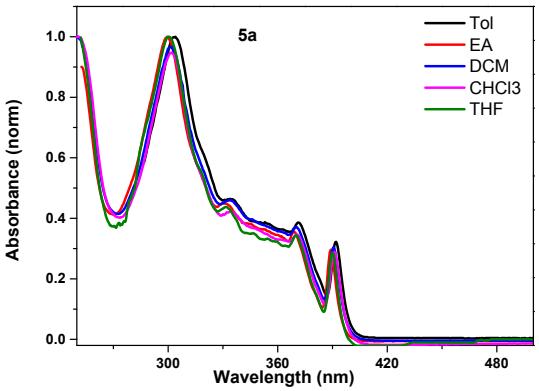
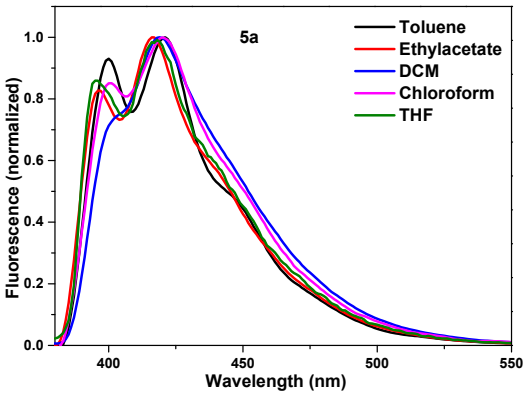
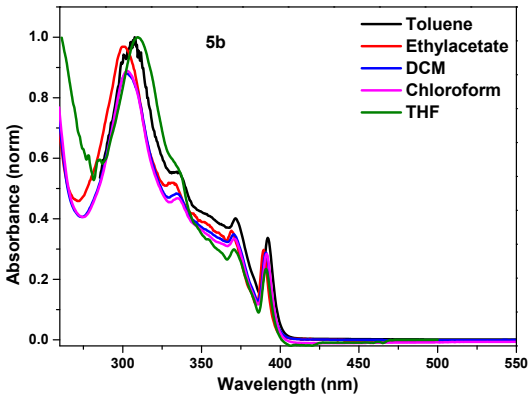
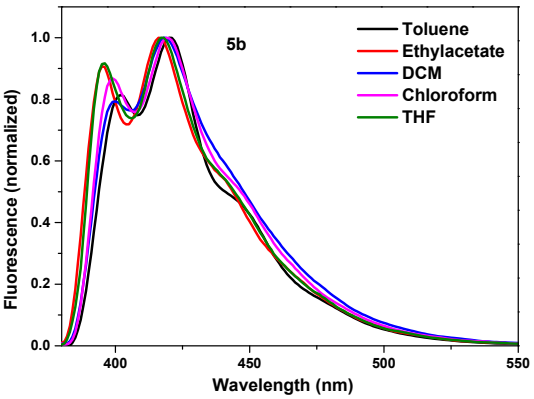


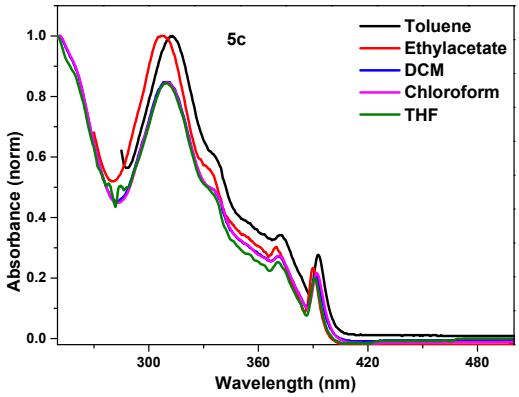
Fig. S2 Calculated (blue) and experimental (black) absorption spectra of **PyFPs 5a-5f** in chloroform. The calculations were carried at B3LYP/6-31G*level of theory.

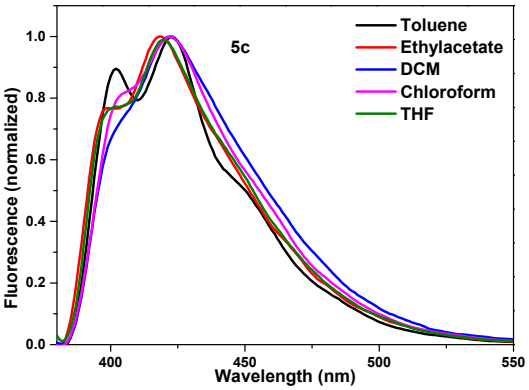

5a
Tol
EA
DCM
CHCl3
THF
Absorbance (norm)
Wavelength (nm)

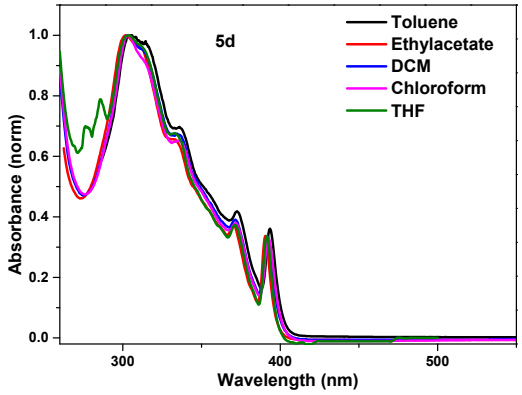

5a
Toluene
Ethylacetate
DCM
Chloroform
THF
Fluorescence (normalized)
Wavelength (nm)

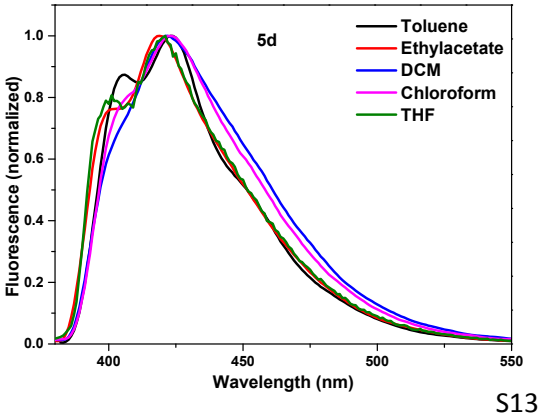

5b
Toluene
Ethylacetate
DCM
Chloroform
THF
Absorbance (norm)
Wavelength (nm)


5b
Toluene
Ethylacetate
DCM
Chloroform
THF
Fluorescence (normalized)
Wavelength (nm)


5c
Toluene
Ethylacetate
DCM
Chloroform
THF
Absorbance (norm)
Wavelength (nm)


5c
Toluene
Ethylacetate
DCM
Chloroform
THF
Fluorescence (normalized)
Wavelength (nm)


5d
Toluene
Ethylacetate
DCM
Chloroform
THF
Absorbance (norm)
Wavelength (nm)


5d
Toluene
Ethylacetate
DCM
Chloroform
THF
Fluorescence (normalized)
Wavelength (nm)

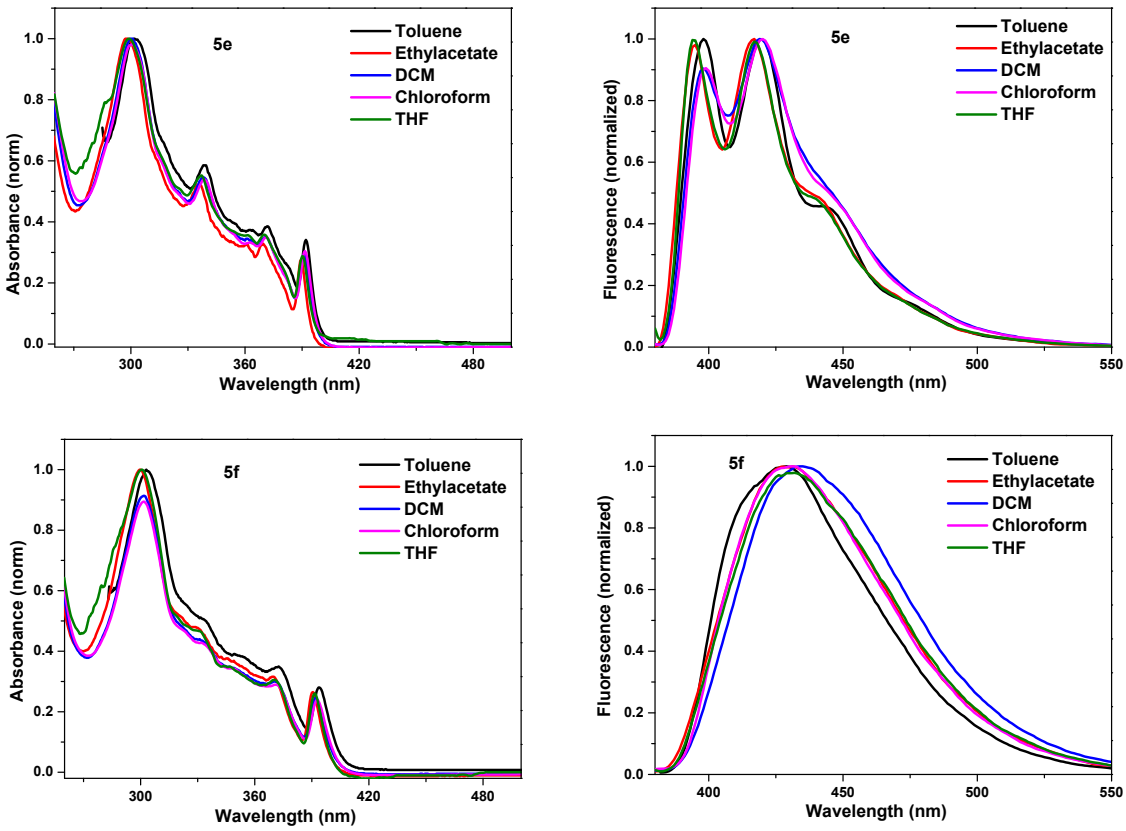


Fig. S3 Absorption and emission spectra of **5a-5f** in different solvents

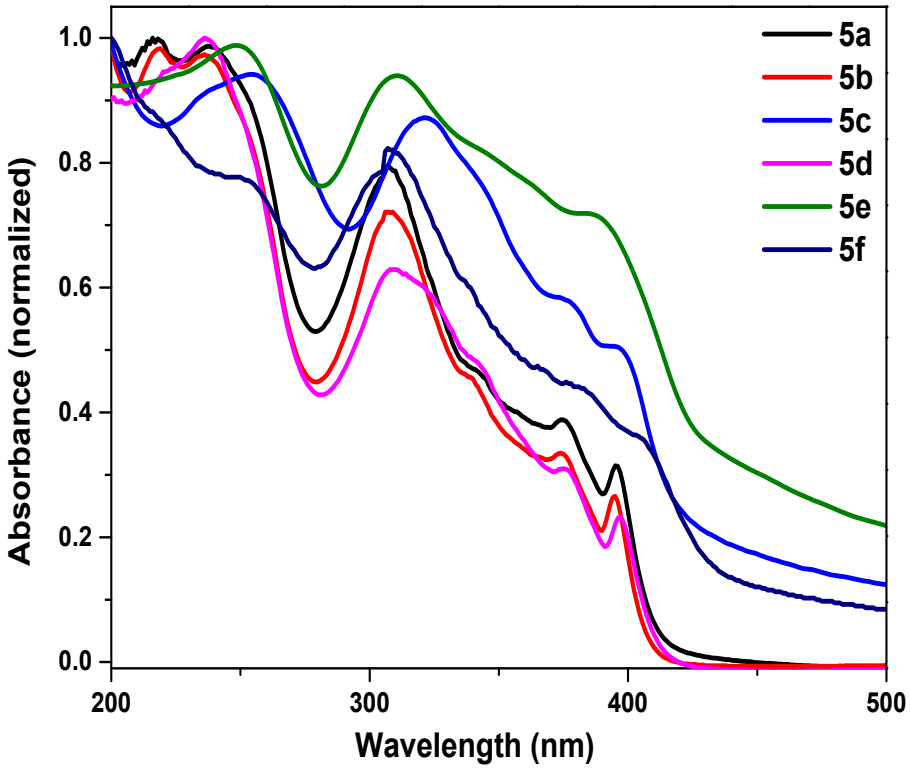


Fig. S4 Absorption spectra of **5a-5f** in thin film.

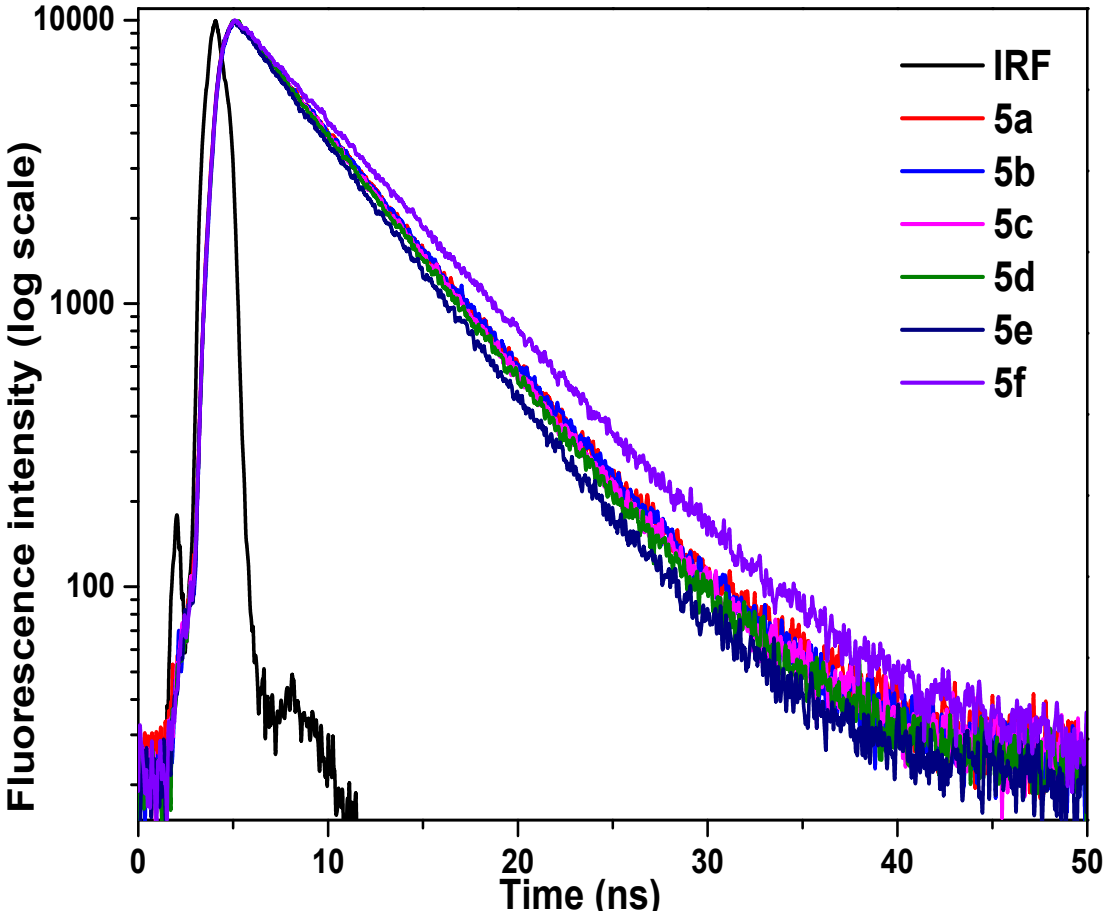


Fig. S5 Fluorescence lifetime decay profiles of **5a–5f** in chloroform. The samples were excited at 371 nm and the decay profiles are monitored at respective λ_{em} .

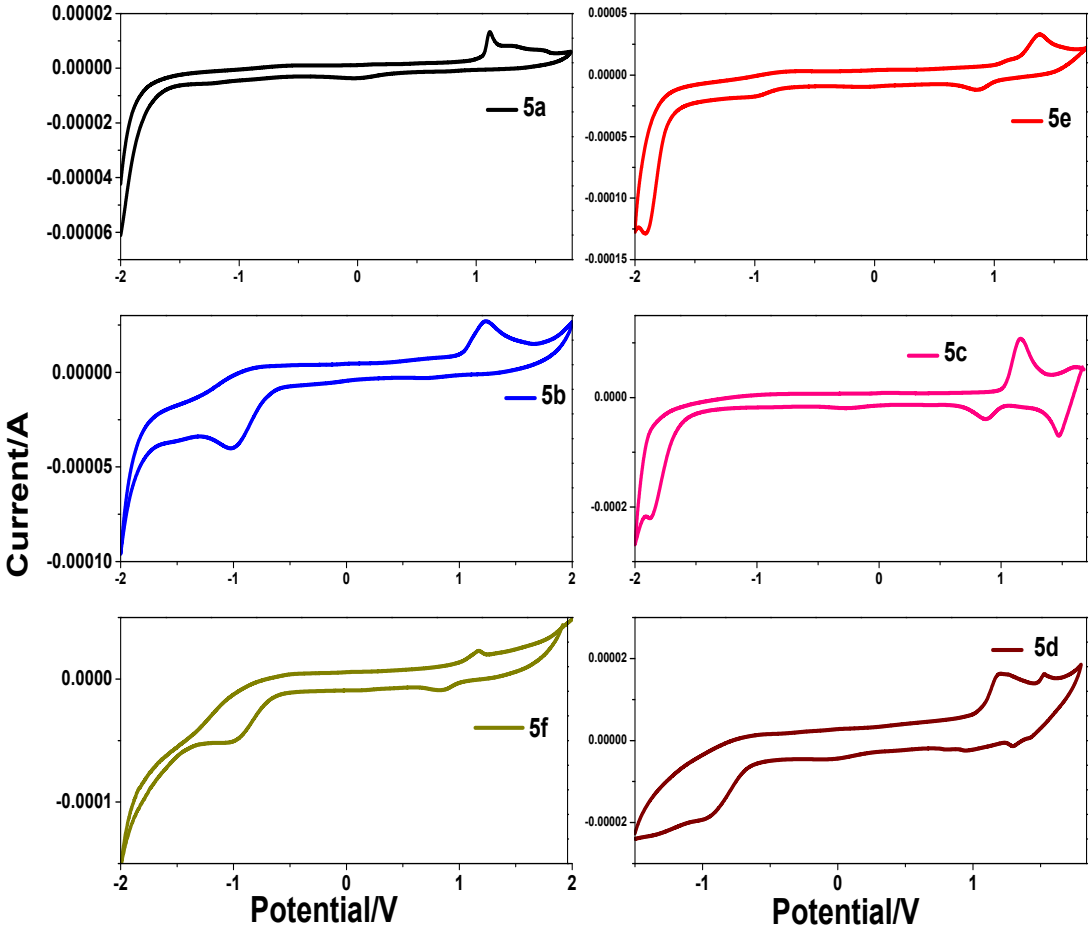


Fig. S6 Cyclic voltammogram of pyrenoimidazoles derivatives **5a-5f** (10^{-3} M solutions, scan rate of 100 mVs^{-1} vs Ag/Ag+) in 0.1 M solution of tetrabutylammonium hexafluorophosphate in acetonitrile solvent.

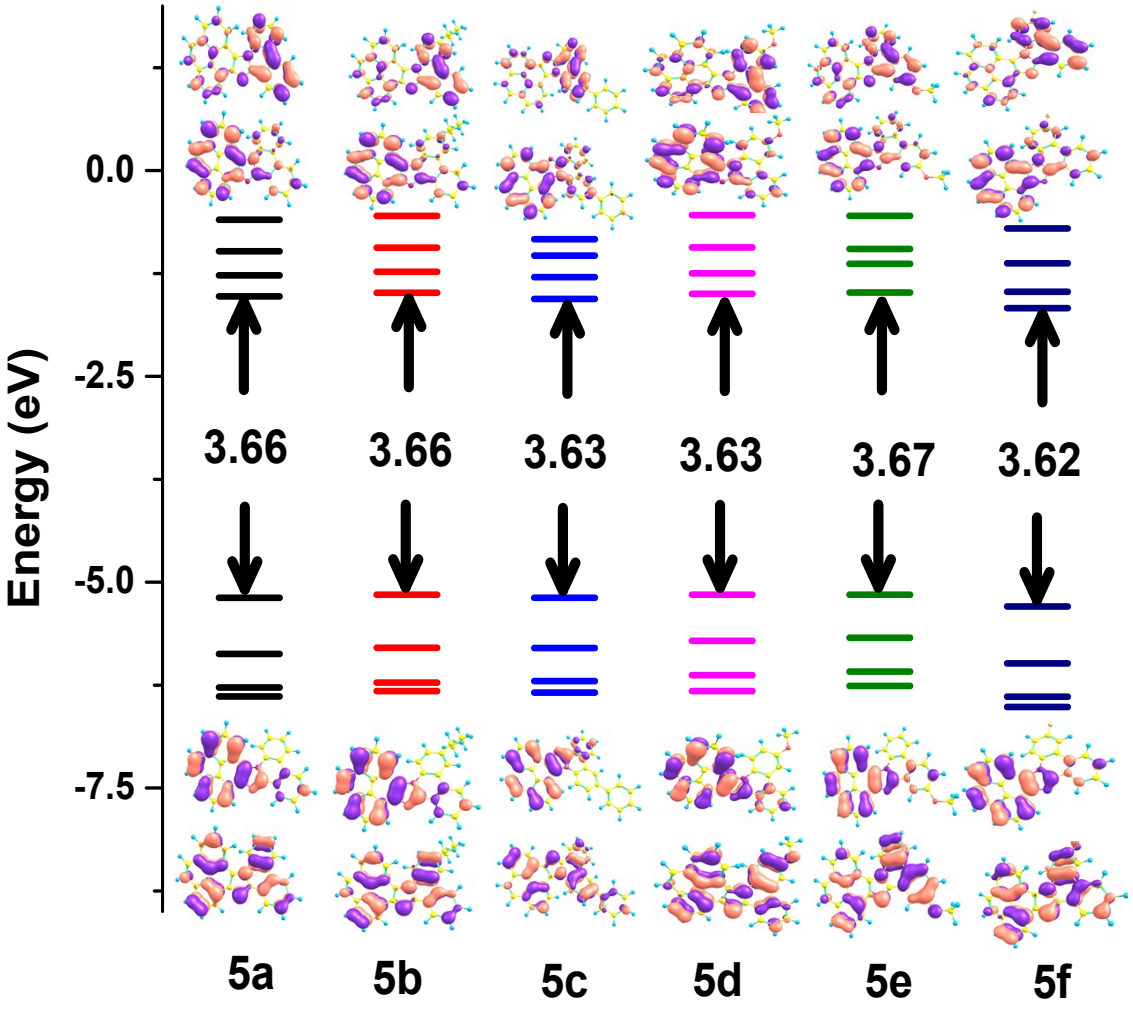


Fig. S7 Molecular energy level diagram and frontier orbitals of **5a-5f** calculated at B3LYP/6-31G* level of theory

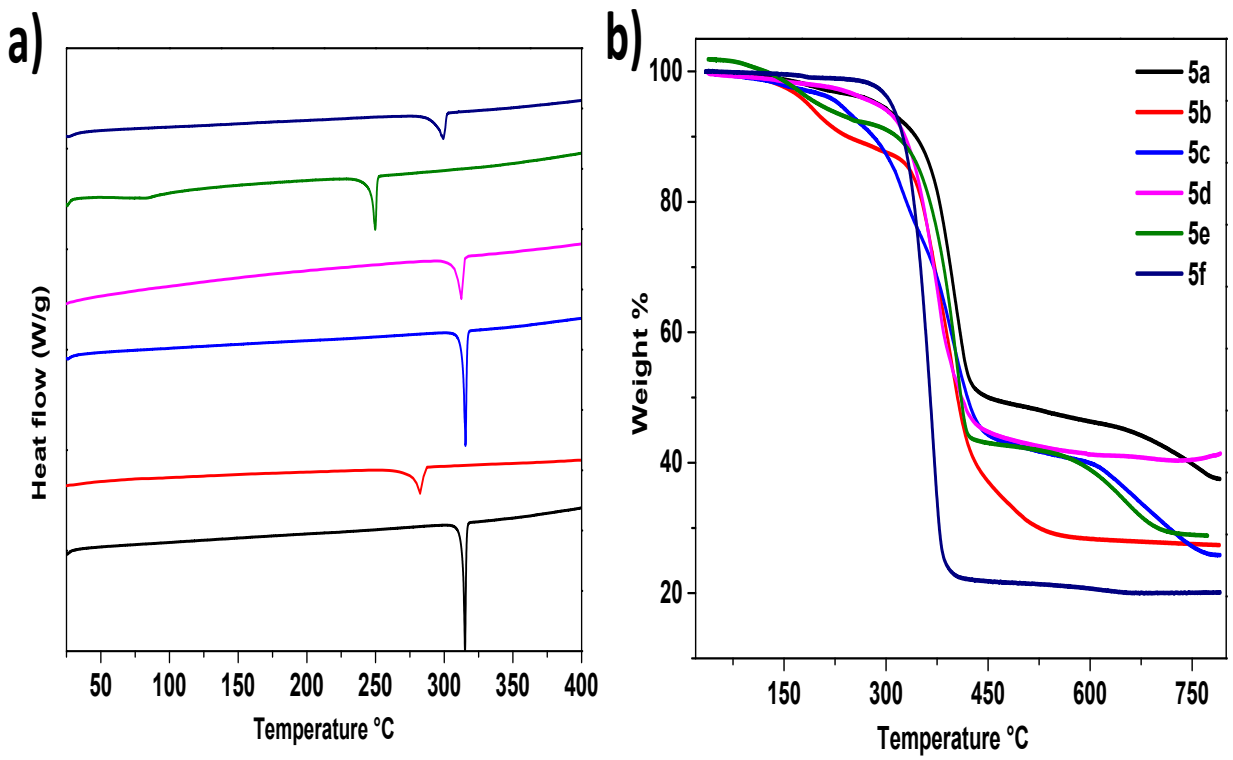
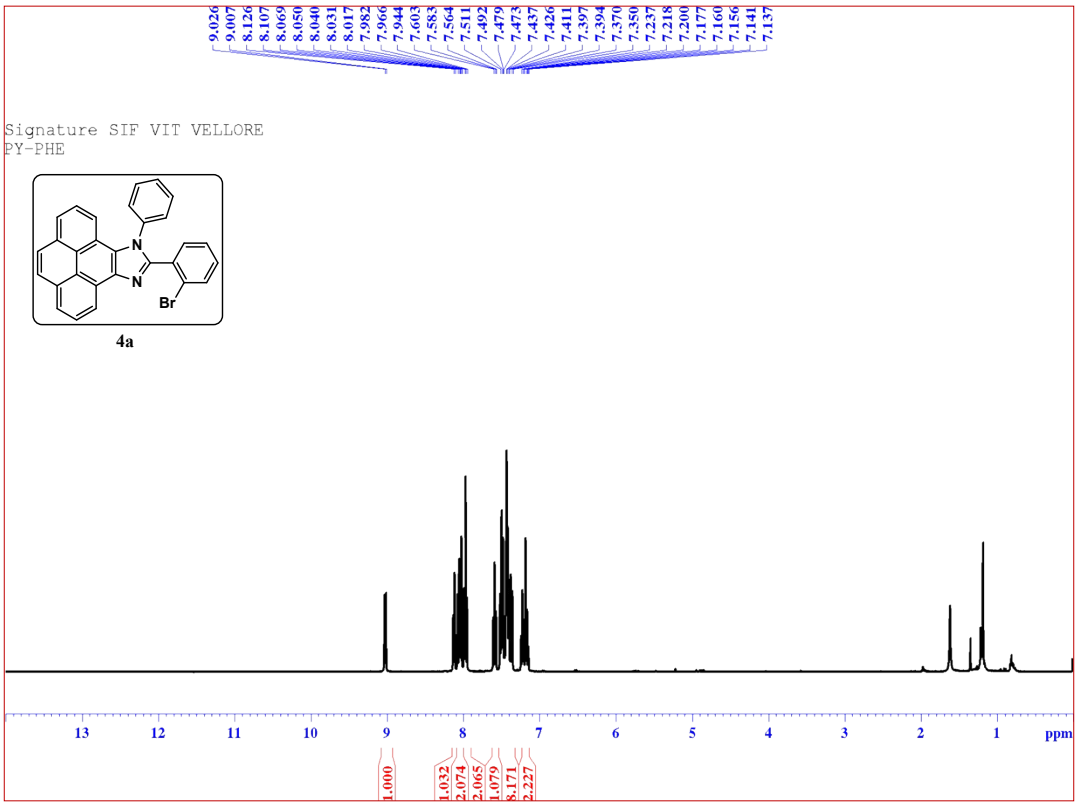
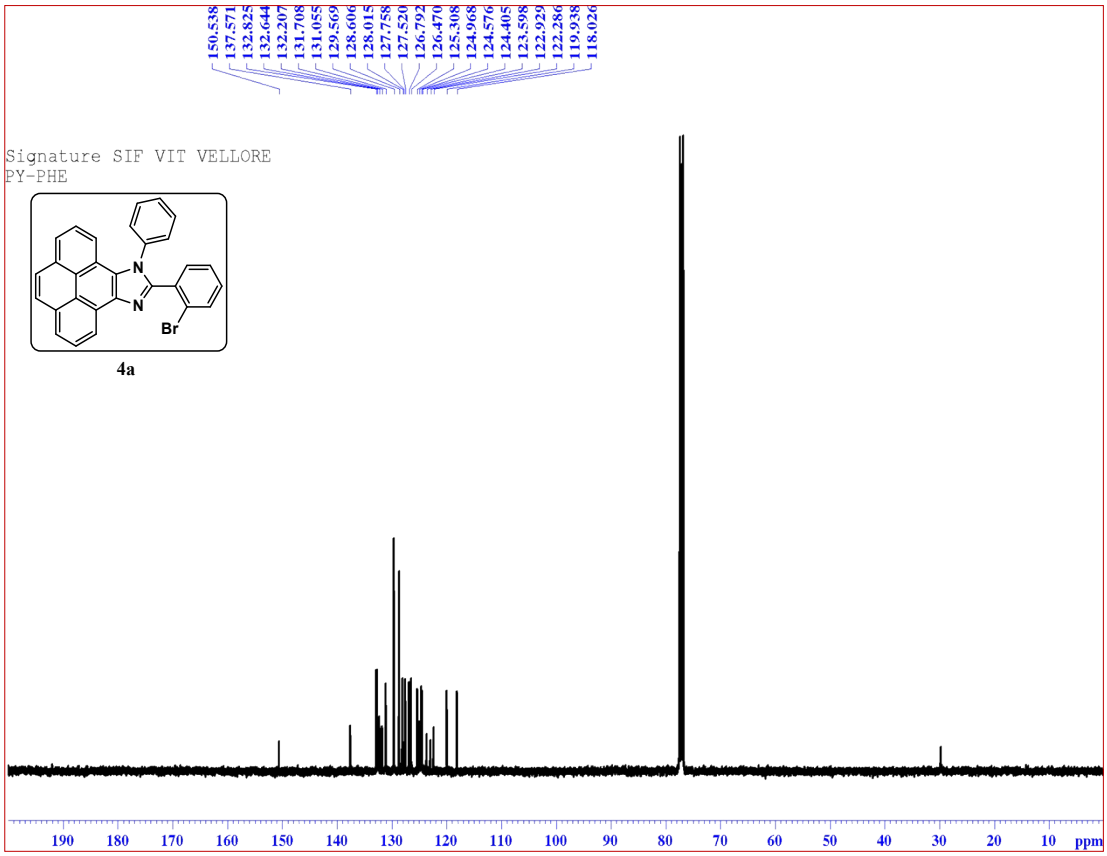


Fig. S8 a) Determined by DSC, scan rate 10 °C min^{-1}, under a N_2 atmosphere. b) TGA curve of **5a-5f** with a heating rate of 10 °C min^{-1} under an inert atmosphere

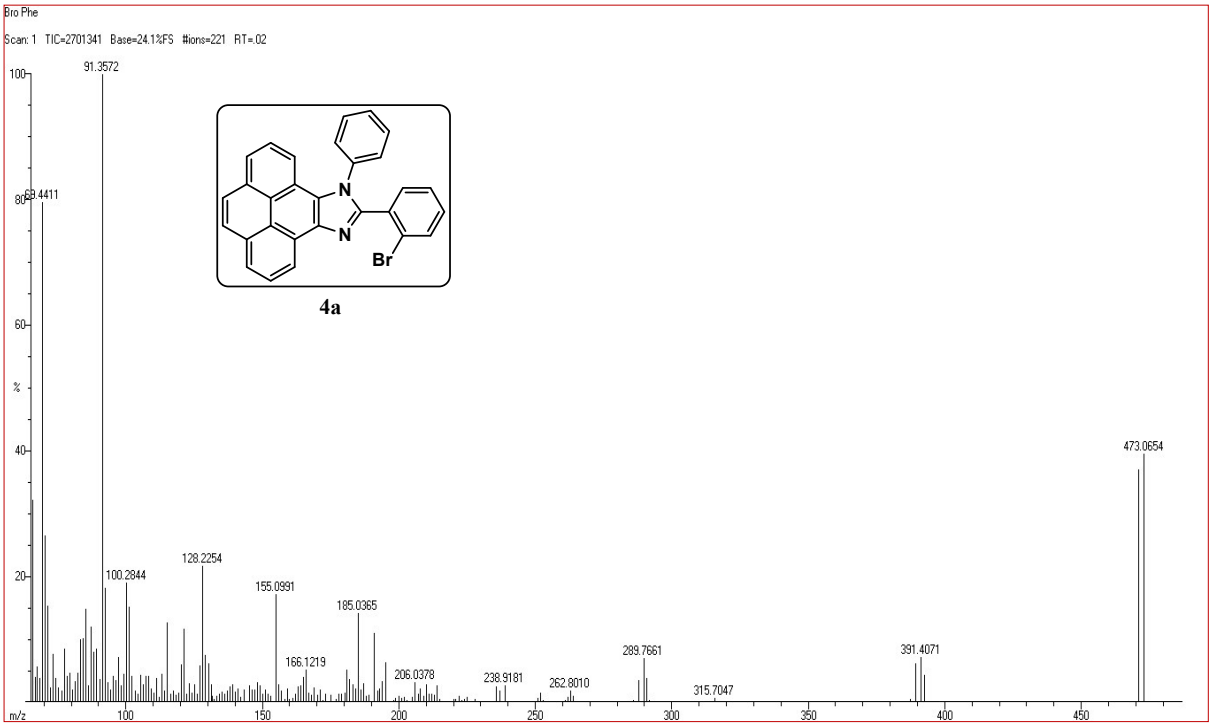
Copies of ^{1}H, ^{13}C, ^{19}F NMR and HRMS of **4a-4f** and **5a-5f**



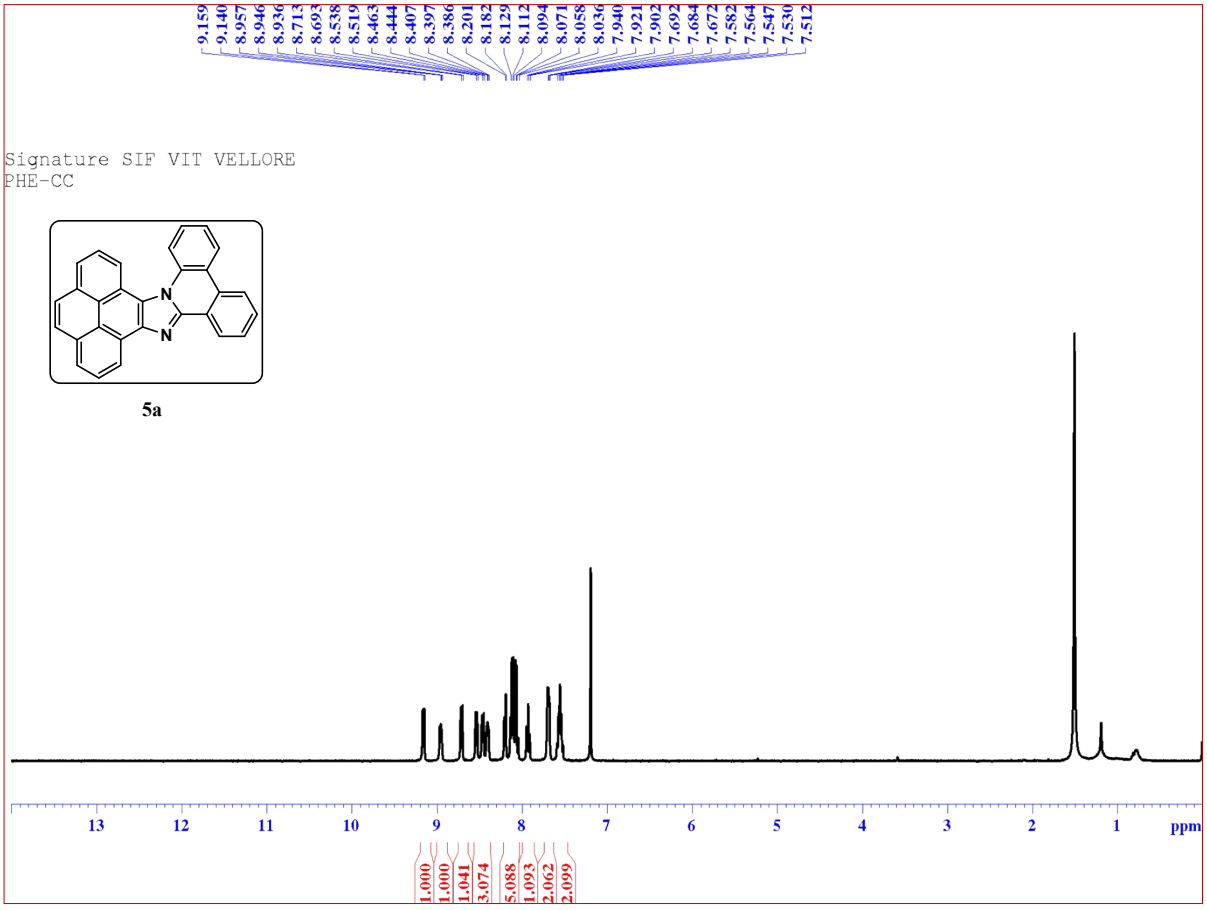
^{1}H NMR spectrum of **4a** in $CDCl_3$



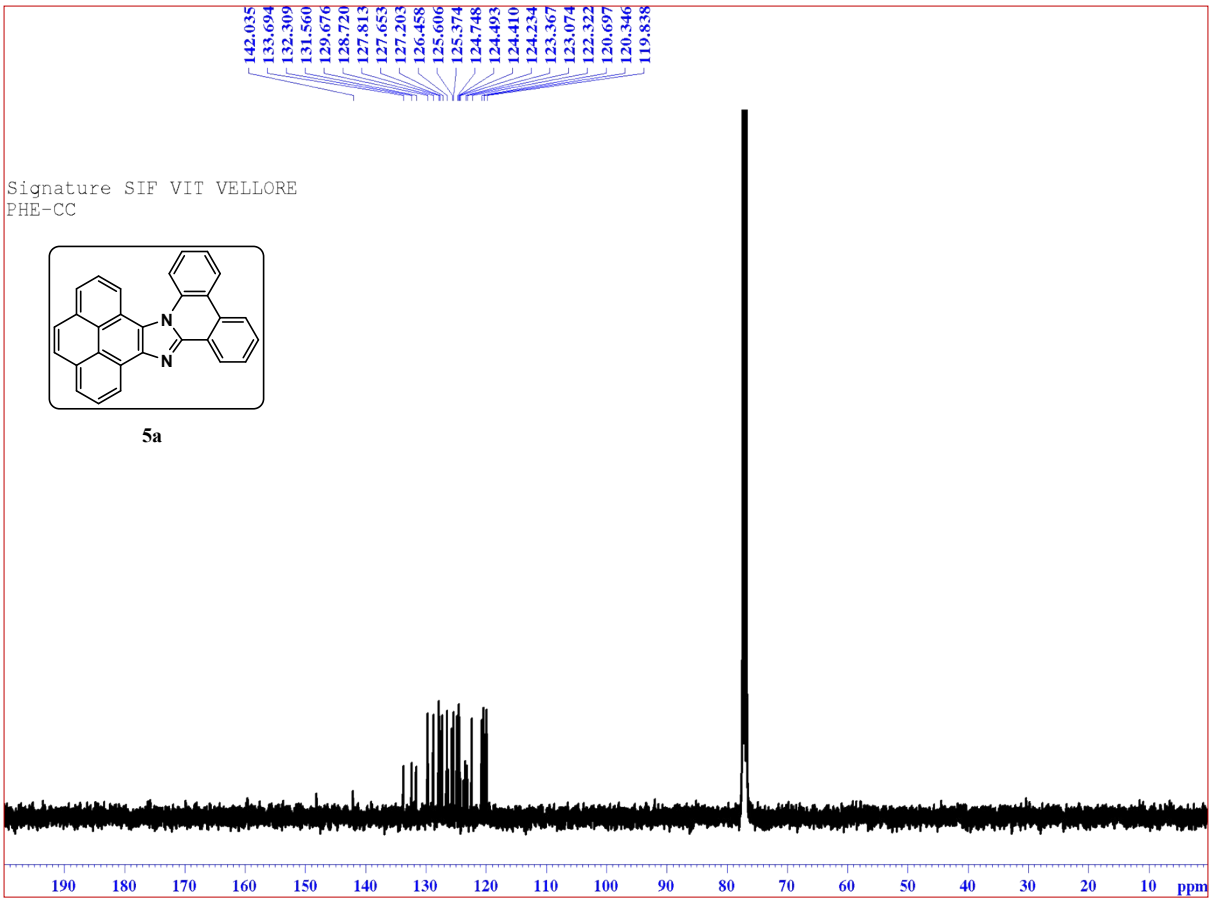
^{13}C NMR spectrum of **4a** in $CDCl_3$



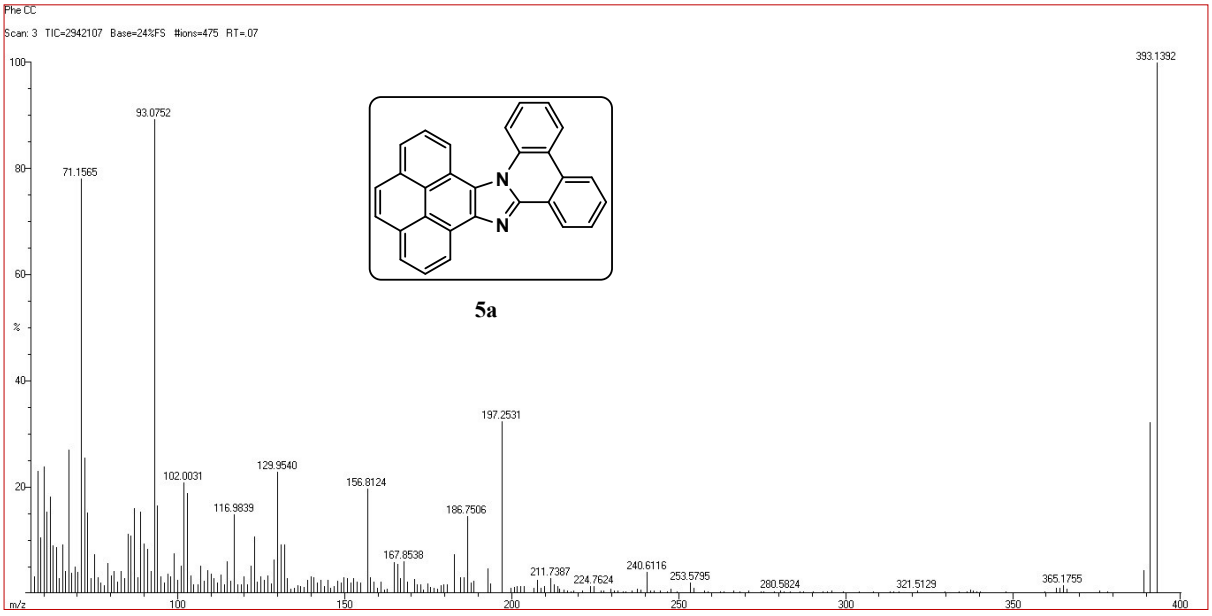
HRMS spectrum of **4a**



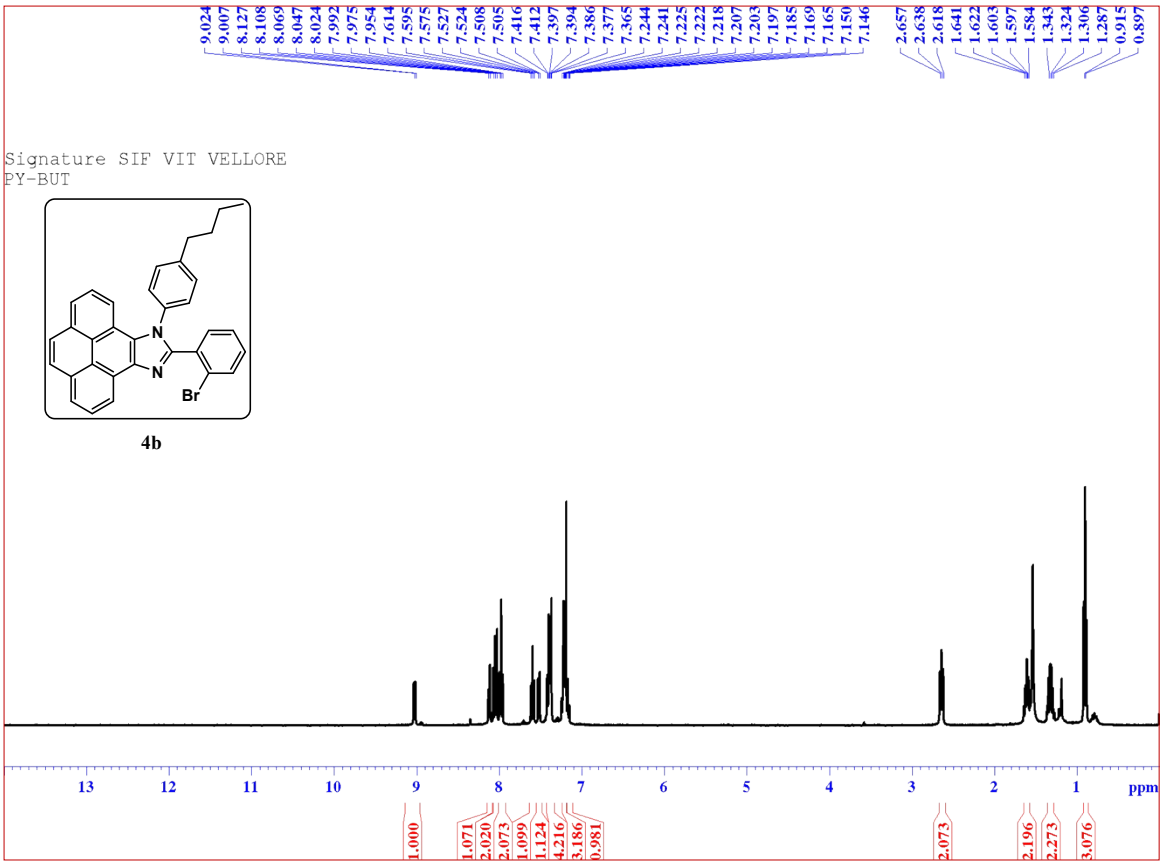
^{1}H NMR spectrum of **5a** in $CDCl_3$



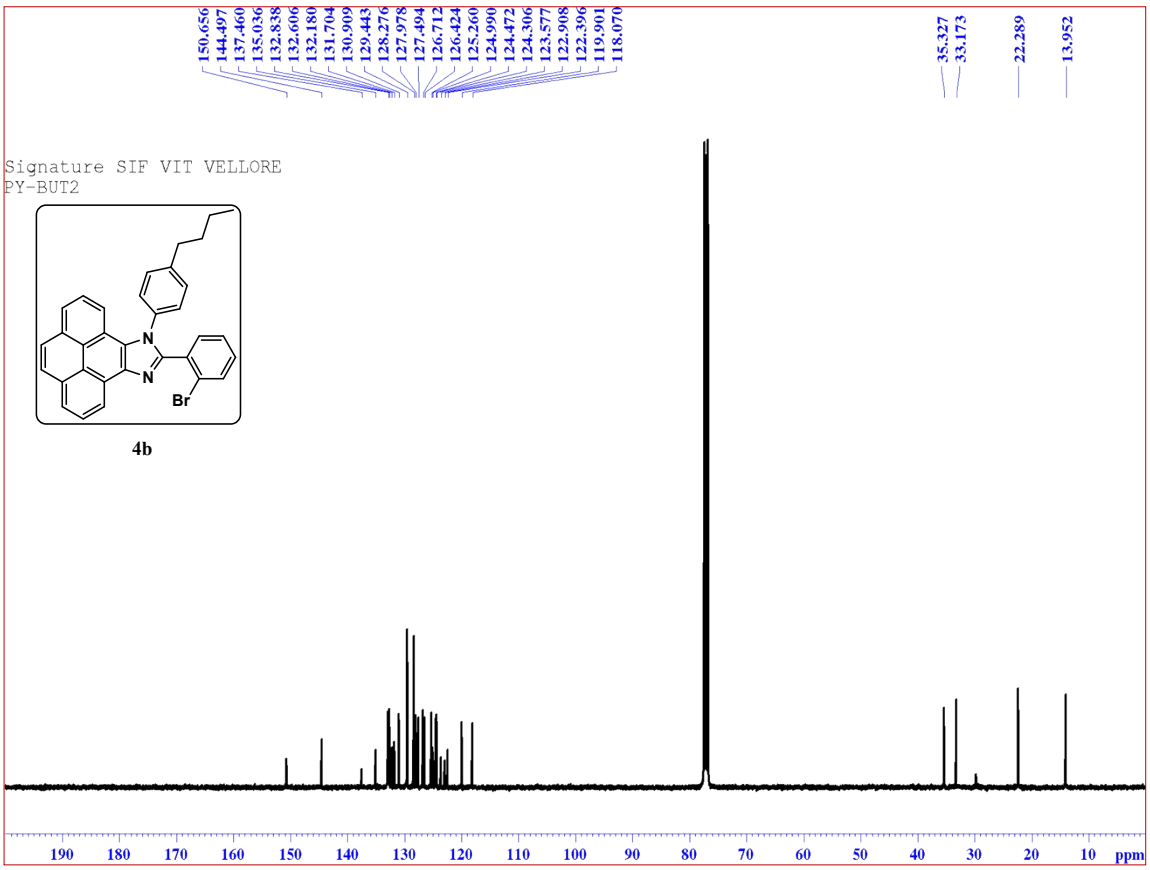
^{13}C NMR spectrum of **5a** in $CDCl_3$



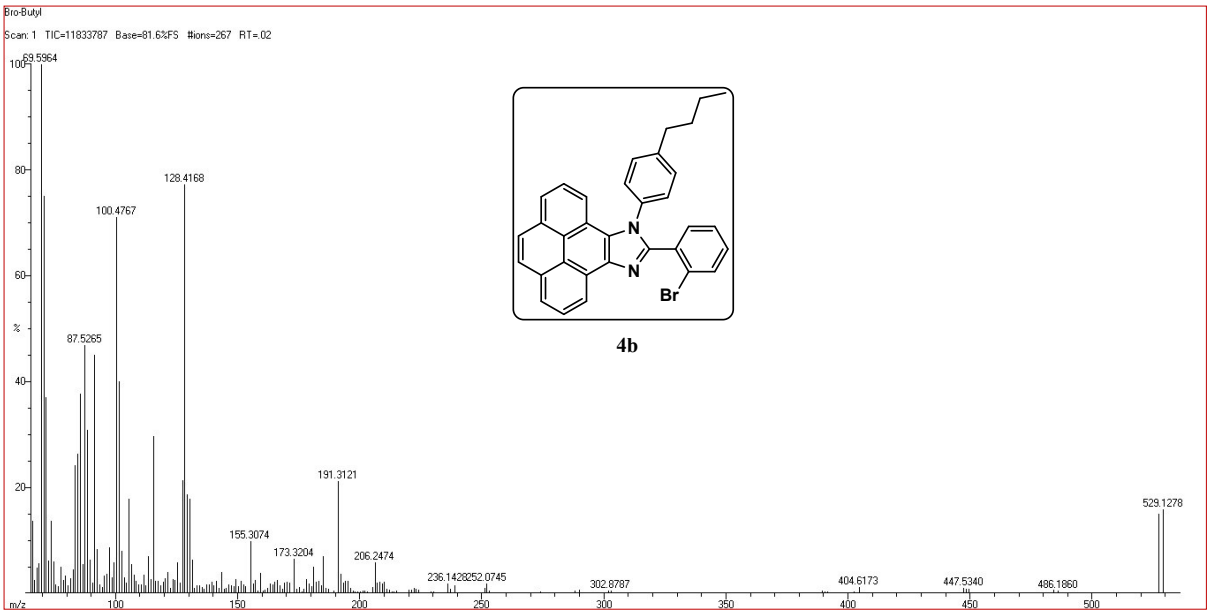
HRMS spectrum of **5a**



^{1}H NMR spectrum of **4b** in $CDCl_3$

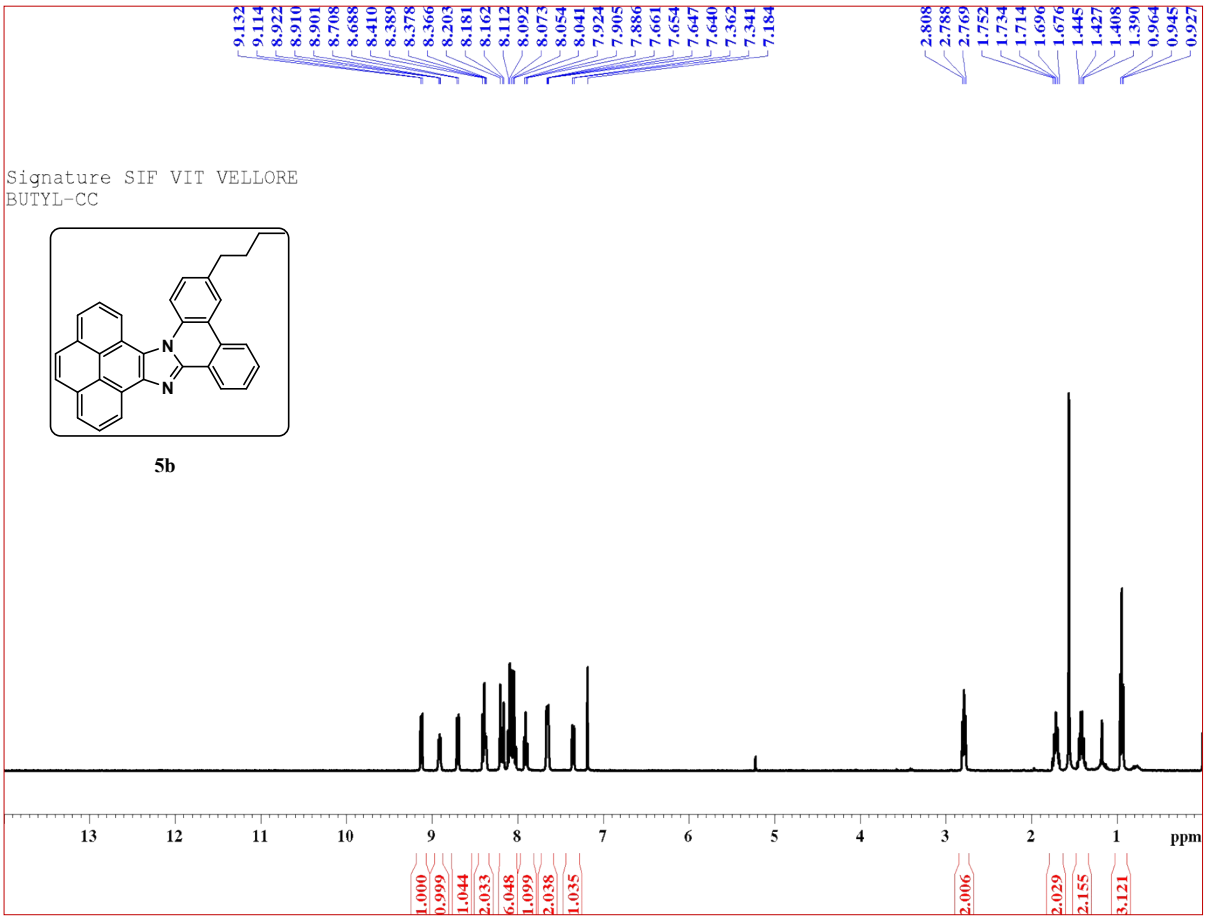


^{13}C NMR spectrum of **4b** in $CDCl_3$



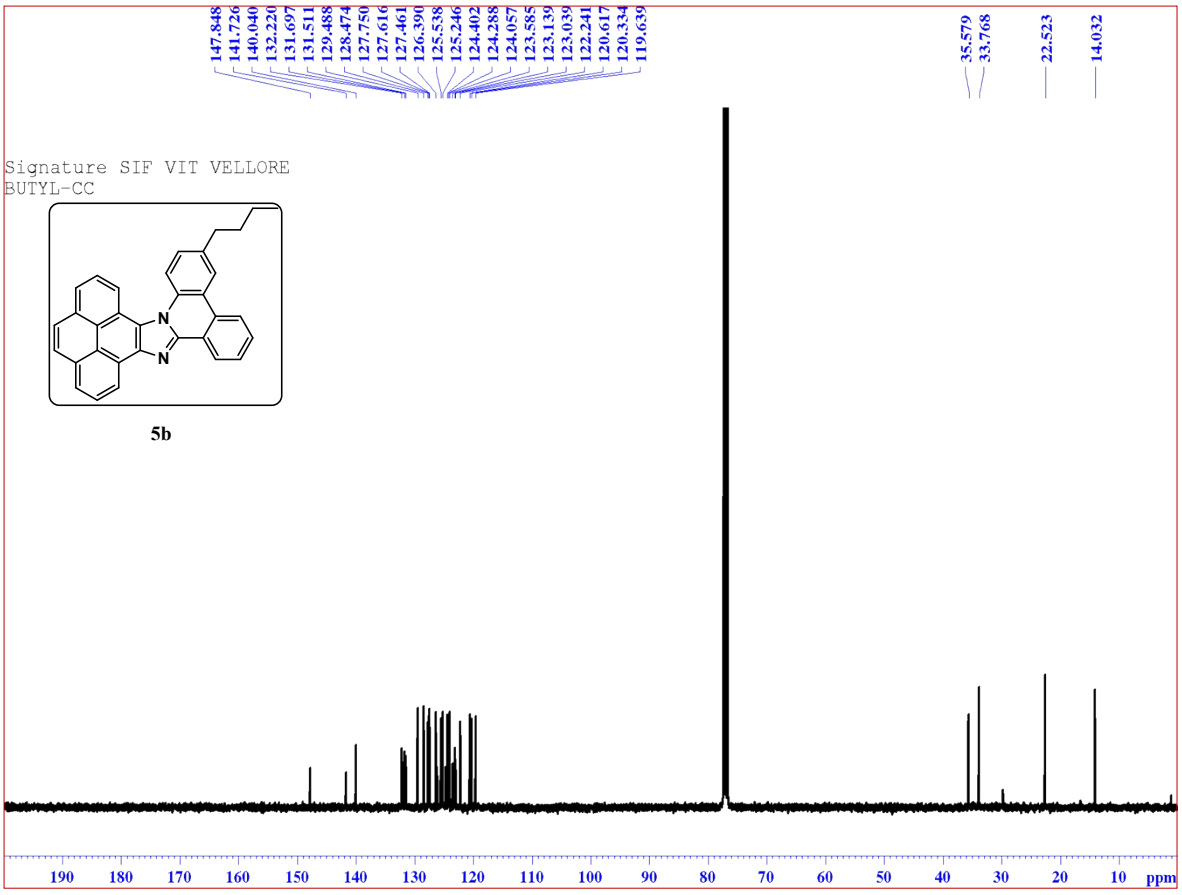
4b

HRMS spectrum of **4b**

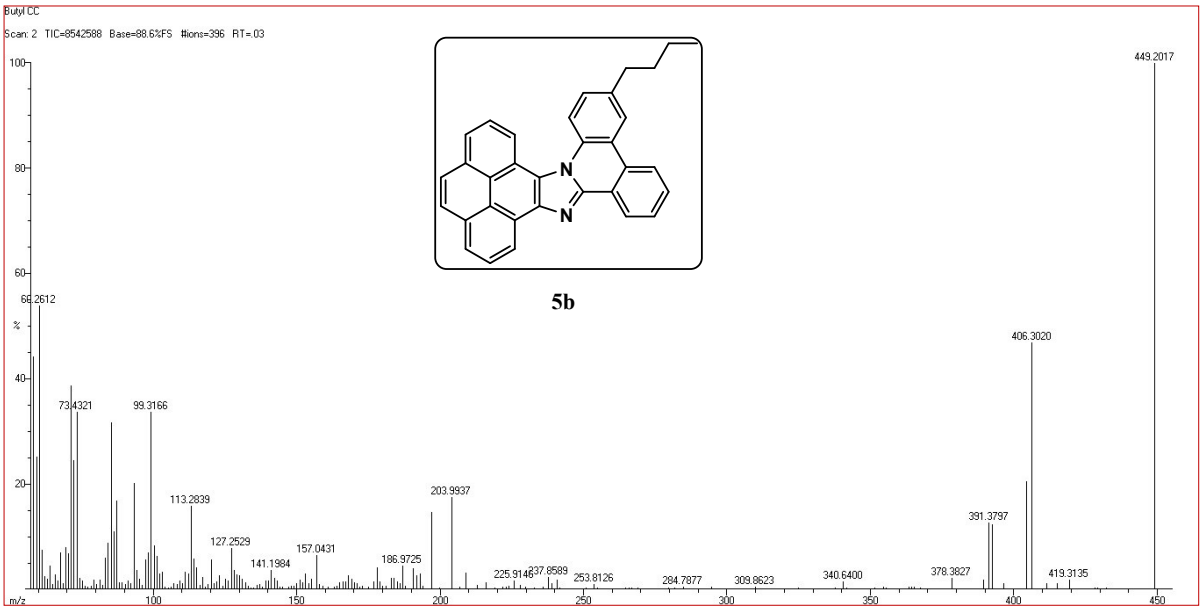


5b

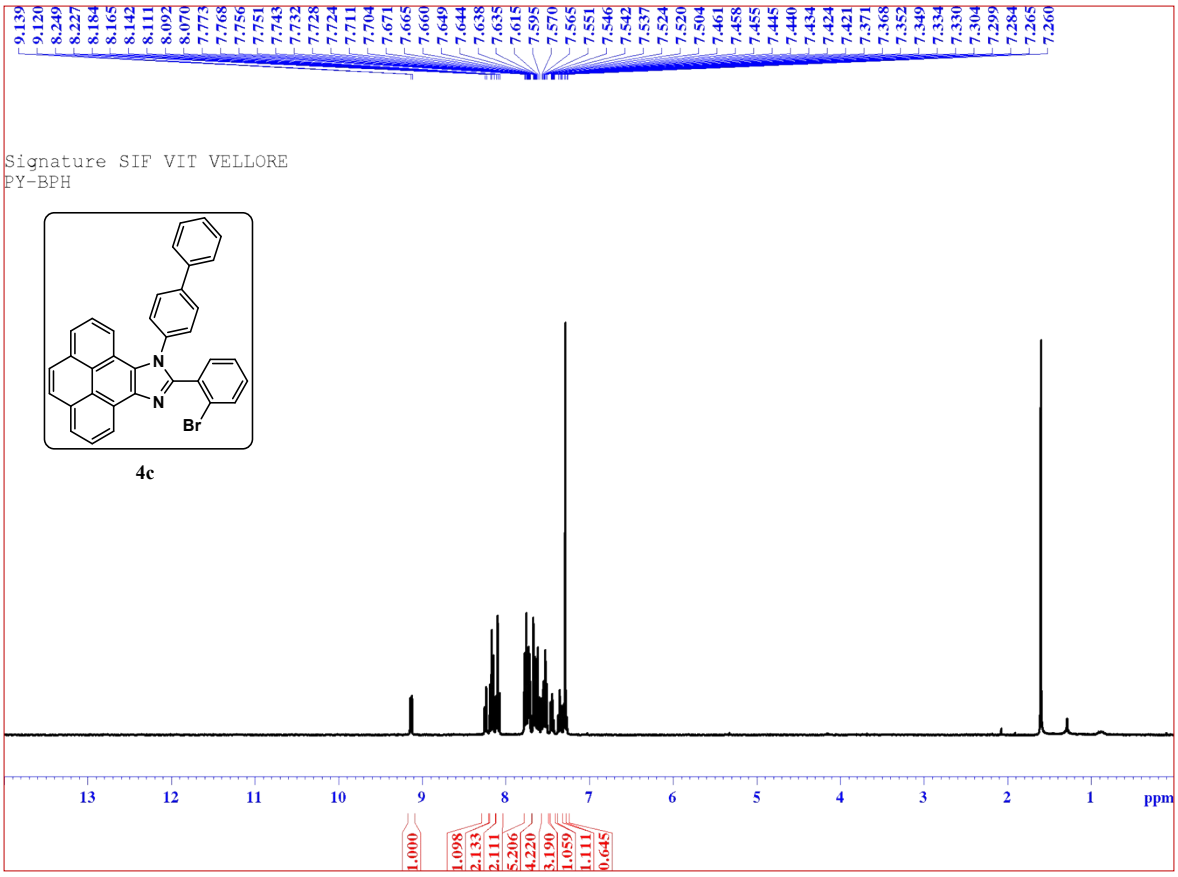
^{1}H NMR spectrum of **5b** in $CDCl_3$



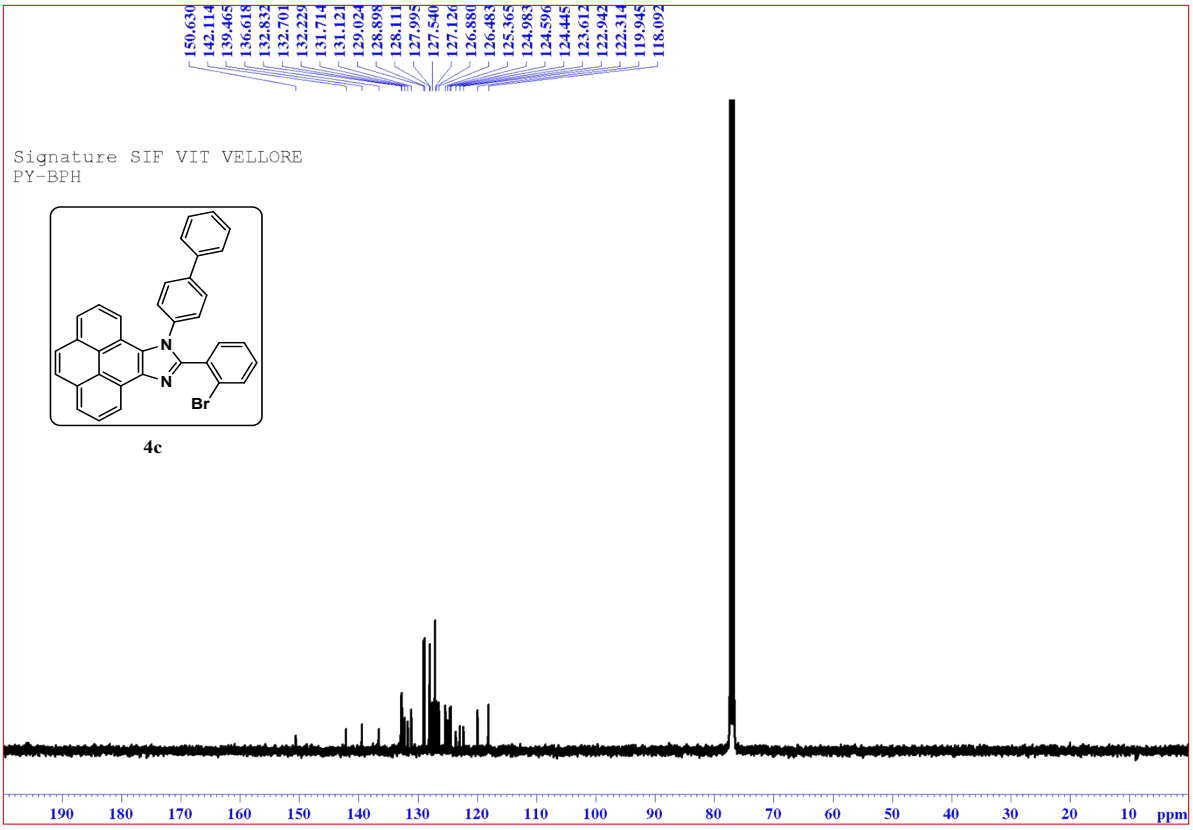
^{13}C NMR spectrum of **5b** in $CDCl_3$



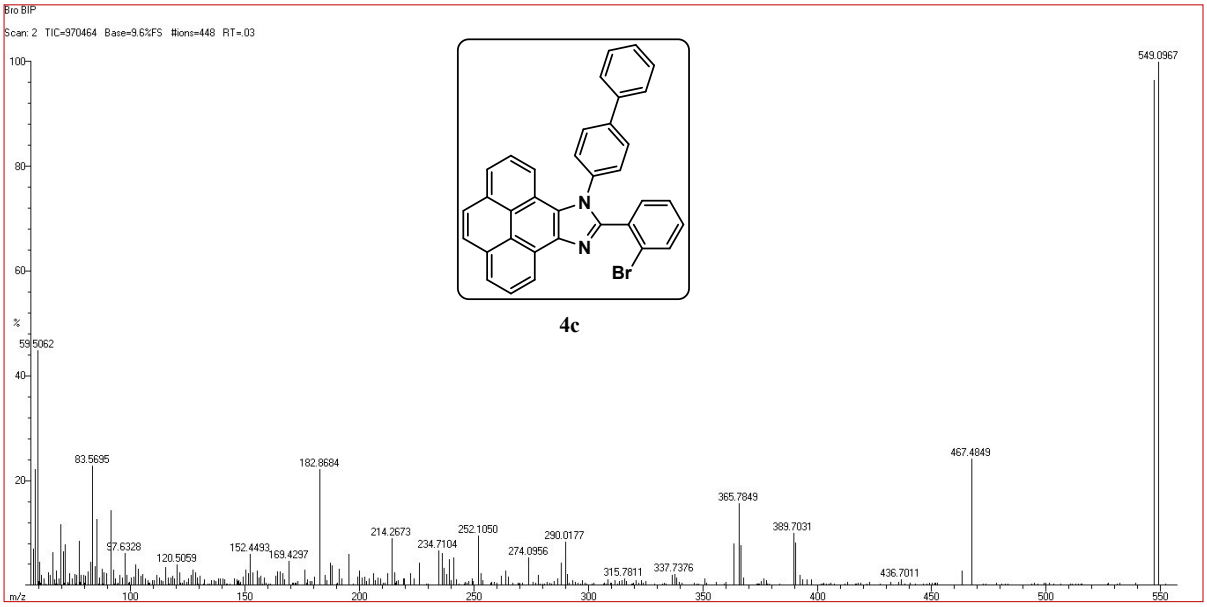
HRMS spectrum of **5b**



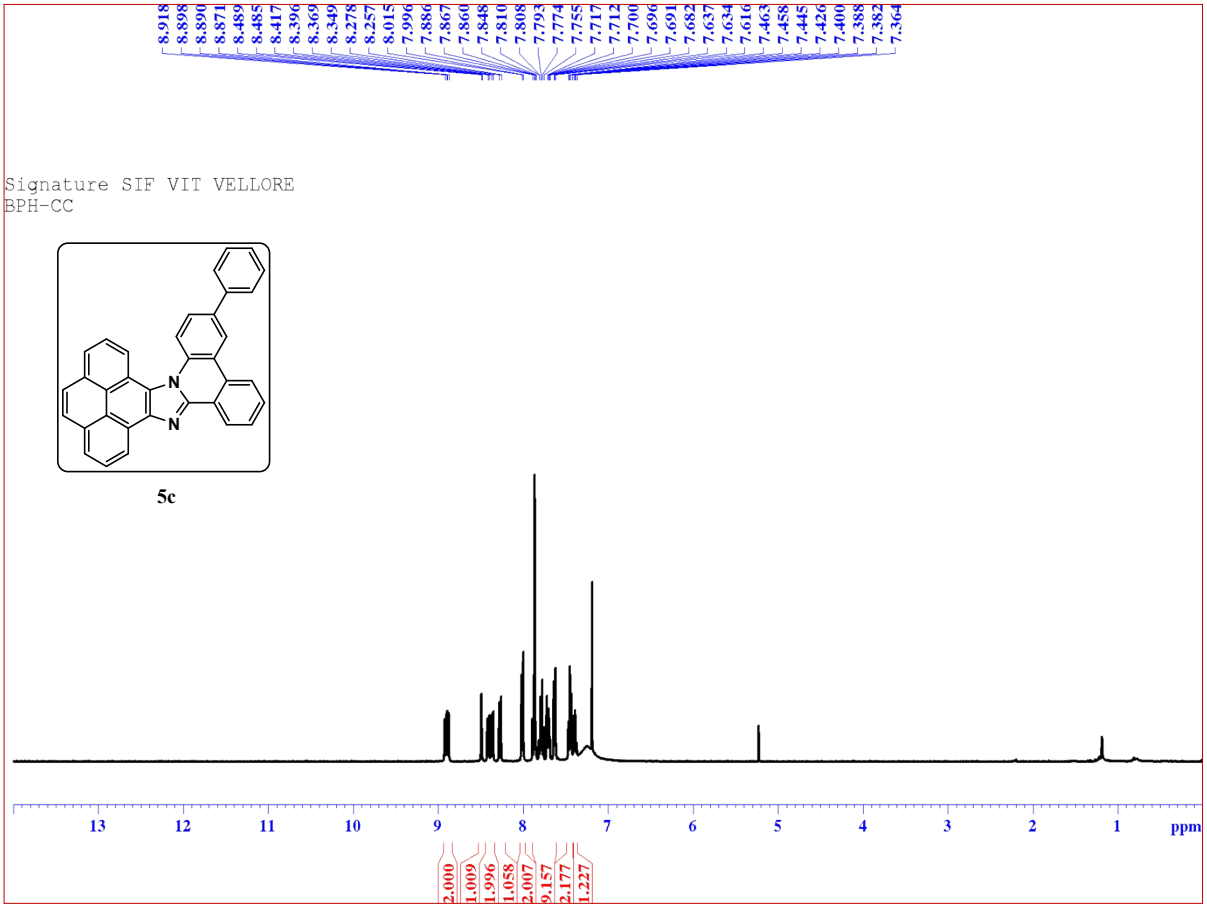
^{1}H NMR spectrum of **4c** in $CDCl_3$



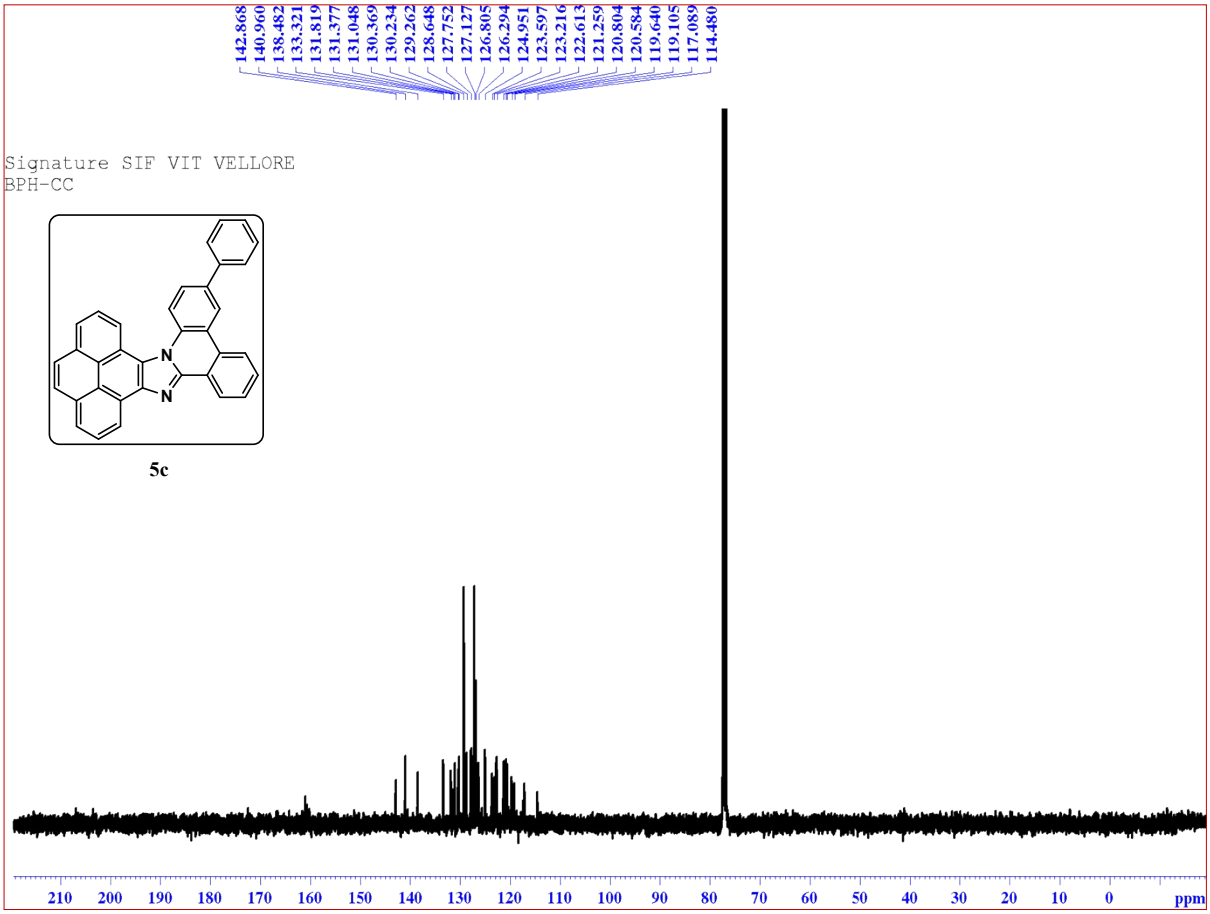
^{13}C NMR spectrum of **4c** in $CDCl_3$



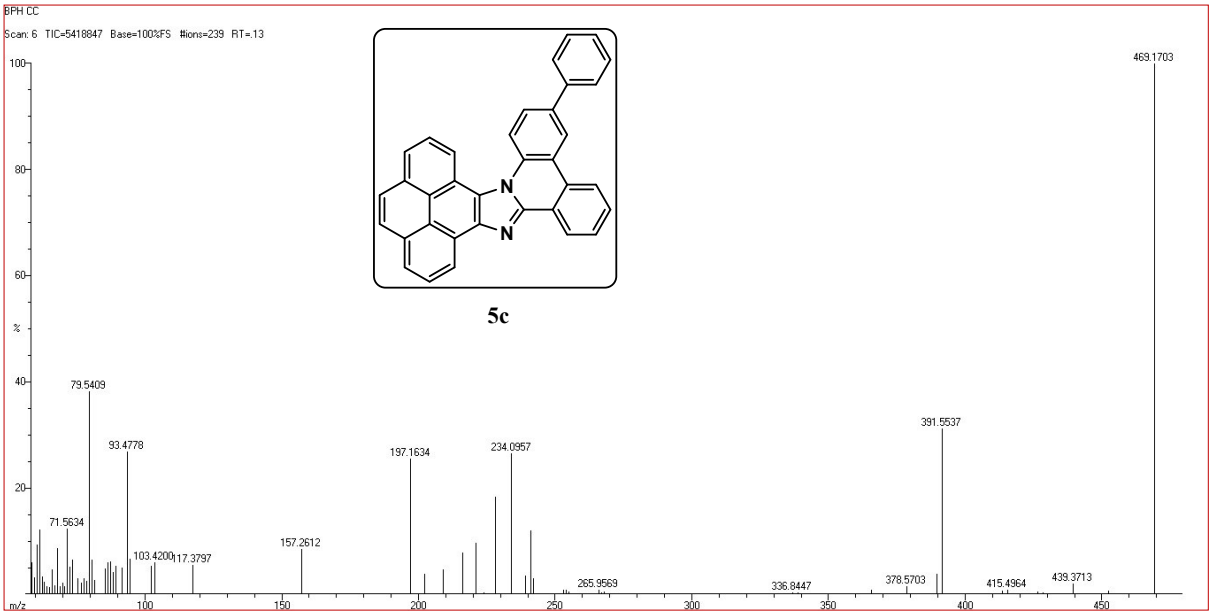
HRMS spectrum of **4c**



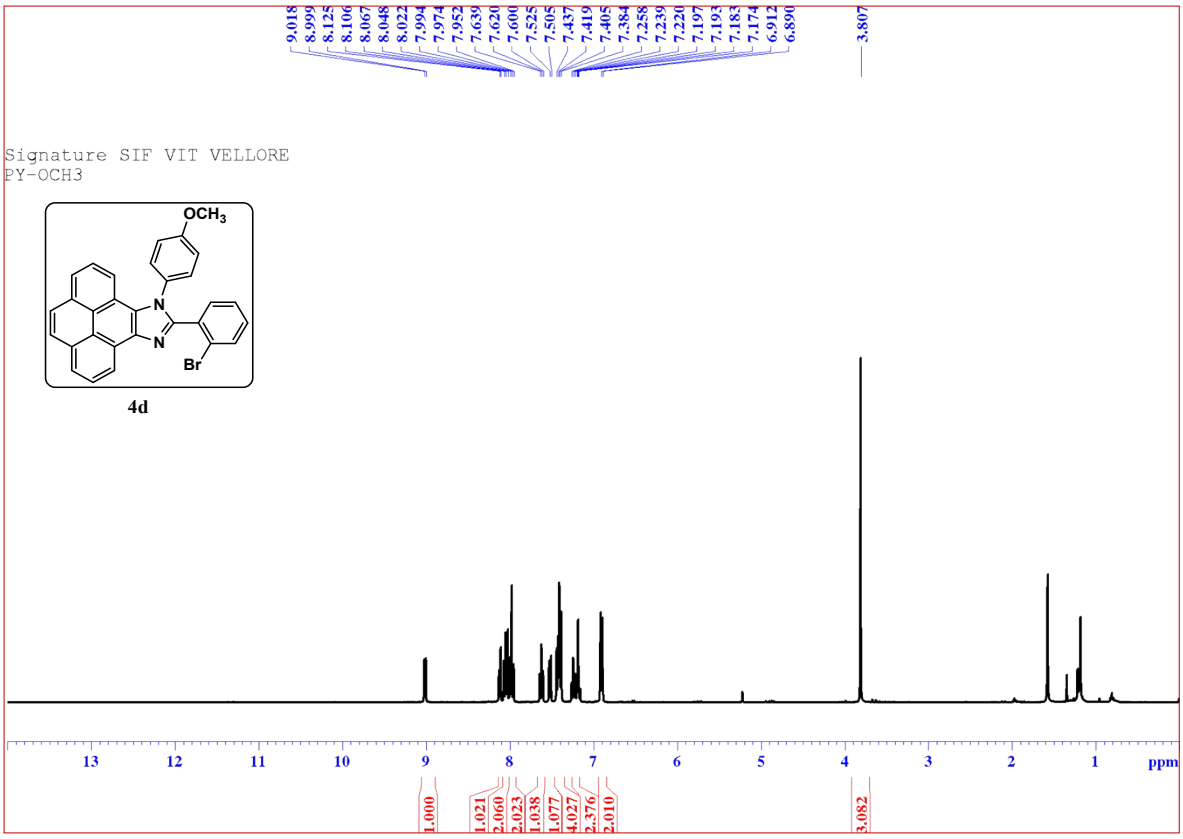
^{1}H NMR spectrum of **5c** in $CDCl_3$



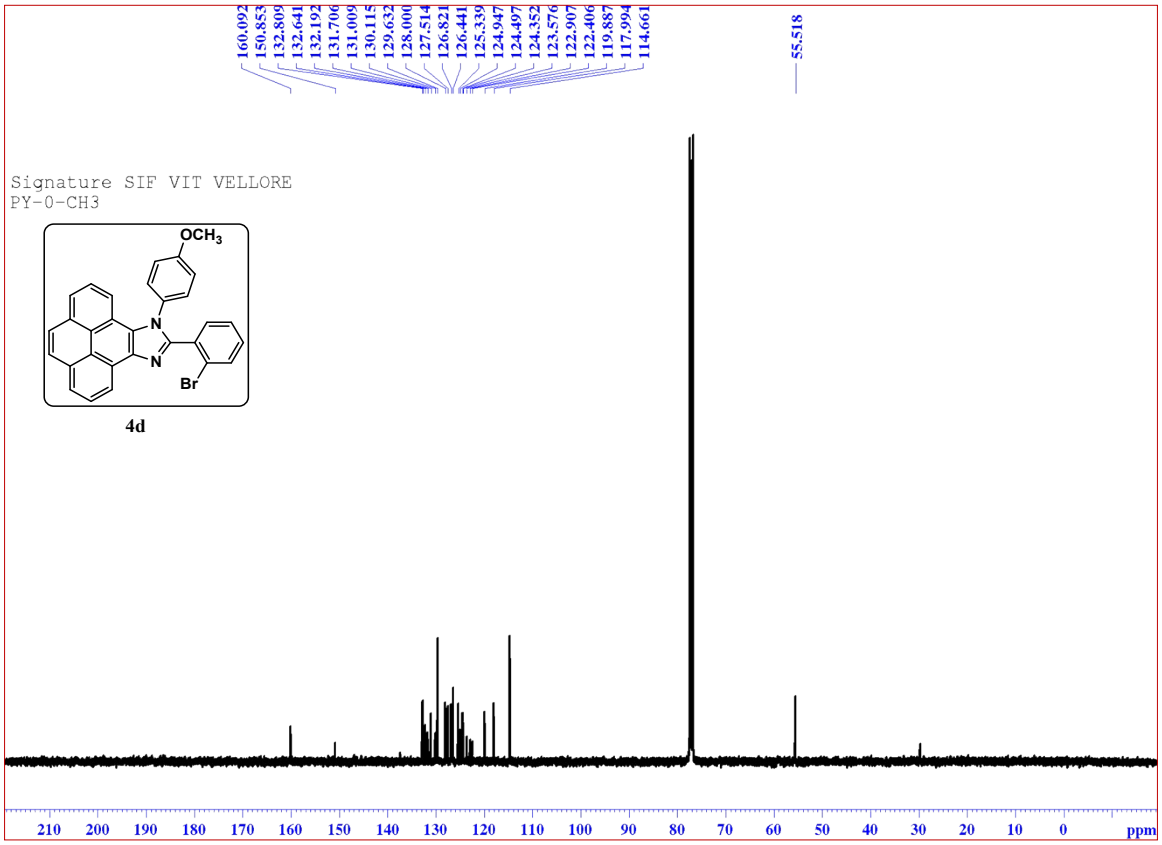
^{13}C NMR spectrum of **5c** in $CDCl_3$



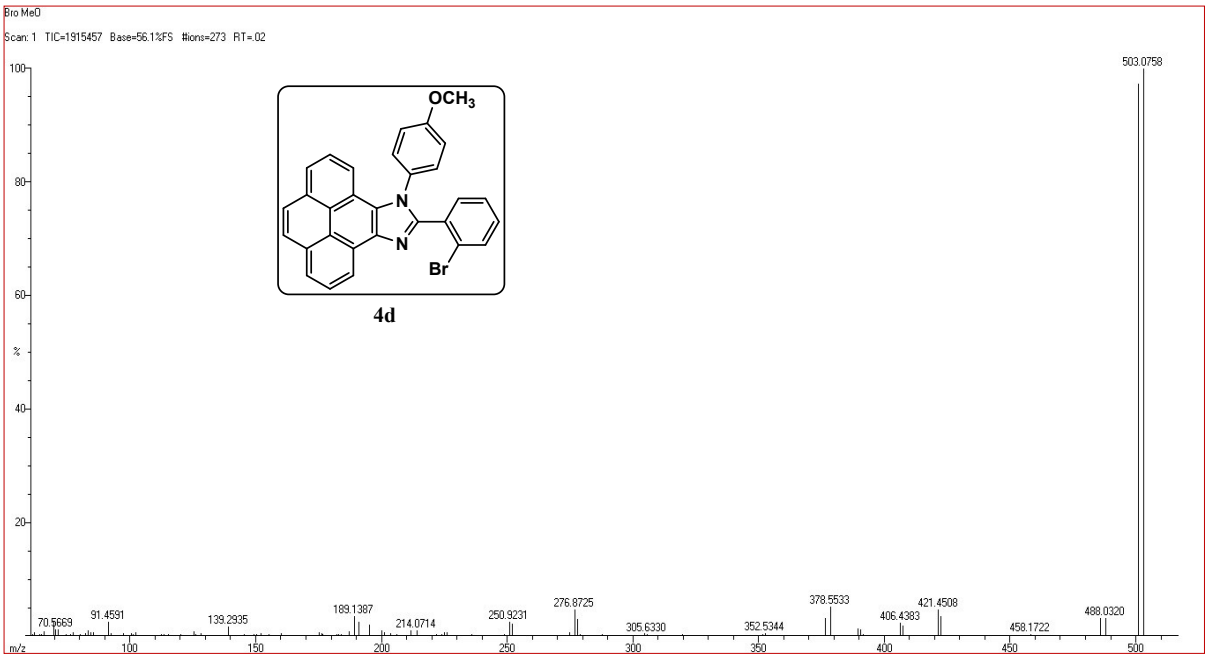
HRMS spectrum of **5c**



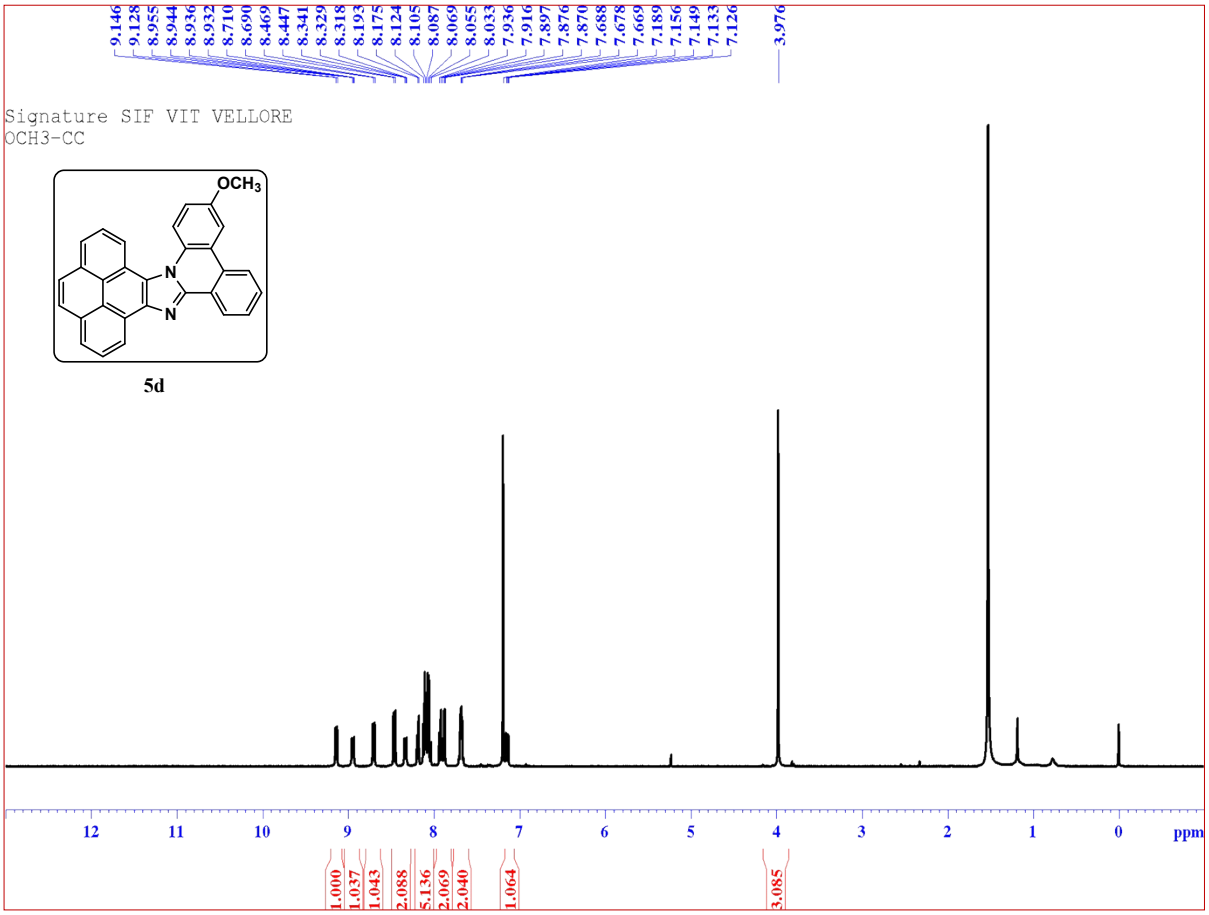
^{1}H NMR spectrum of **4d** in $CDCl_3$



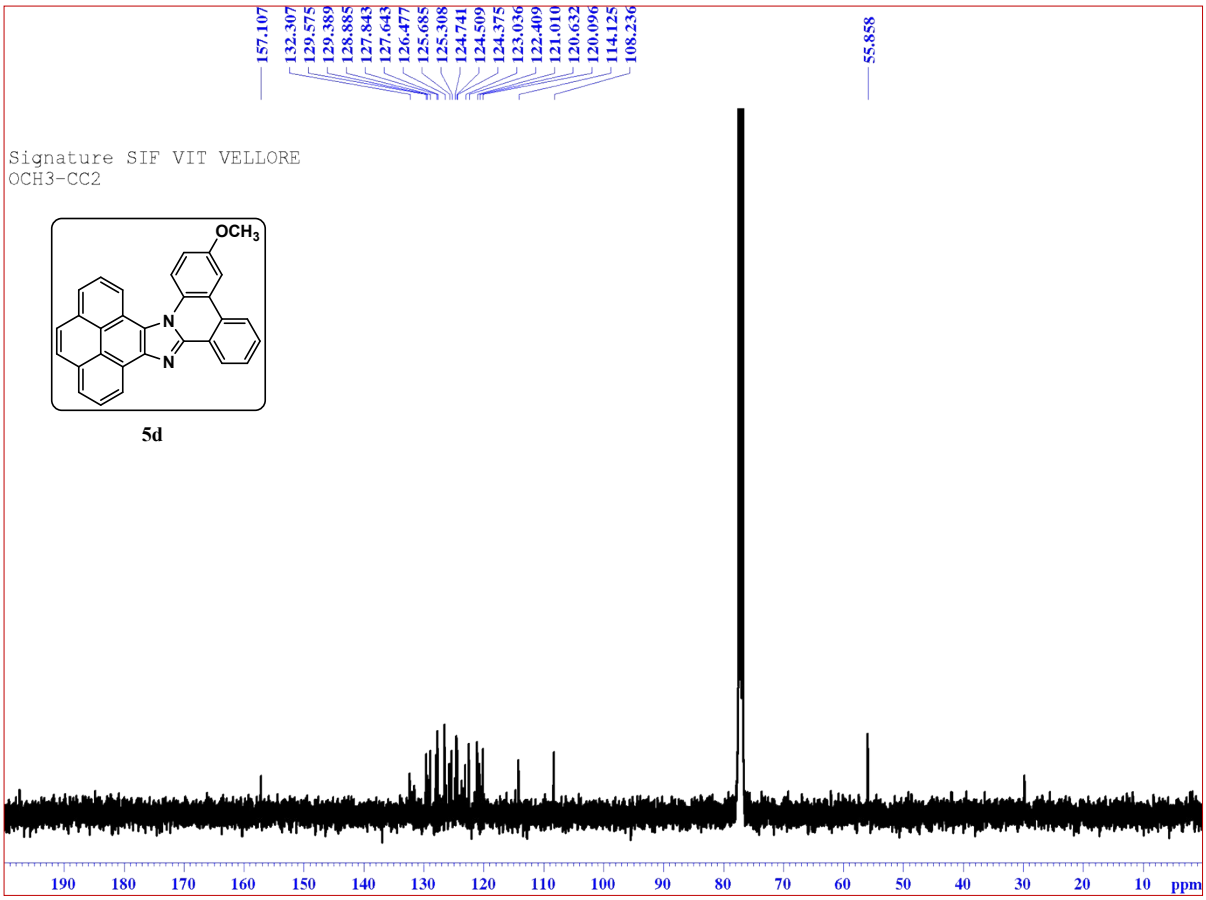
^{13}C NMR spectrum of **4d** in $CDCl_3$



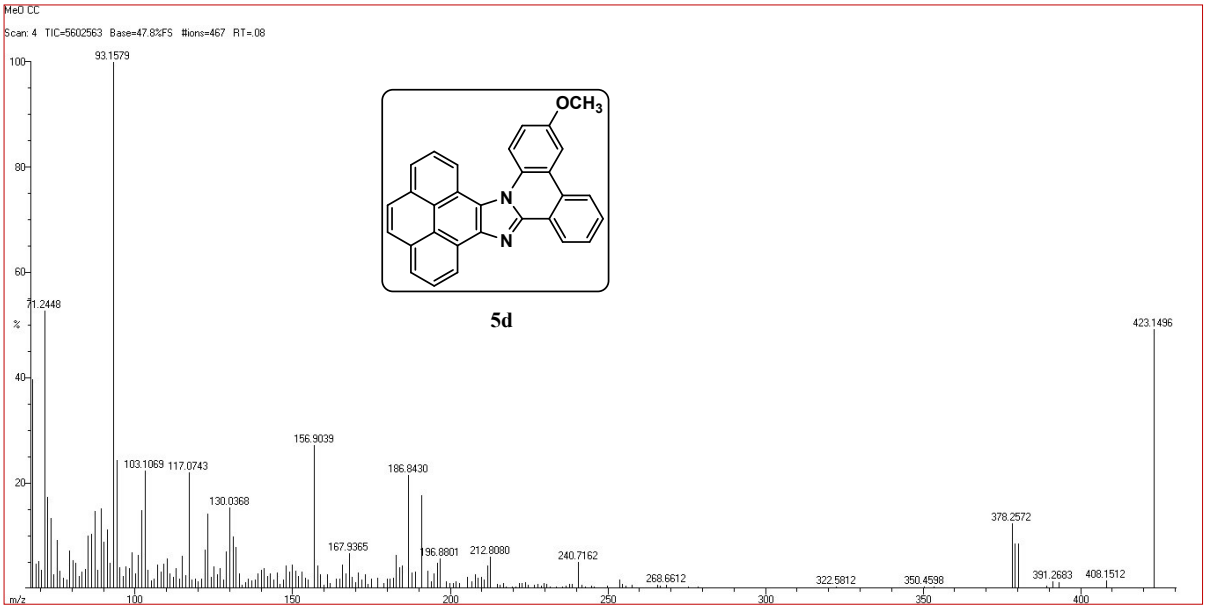
HRMS spectrum of **4d**



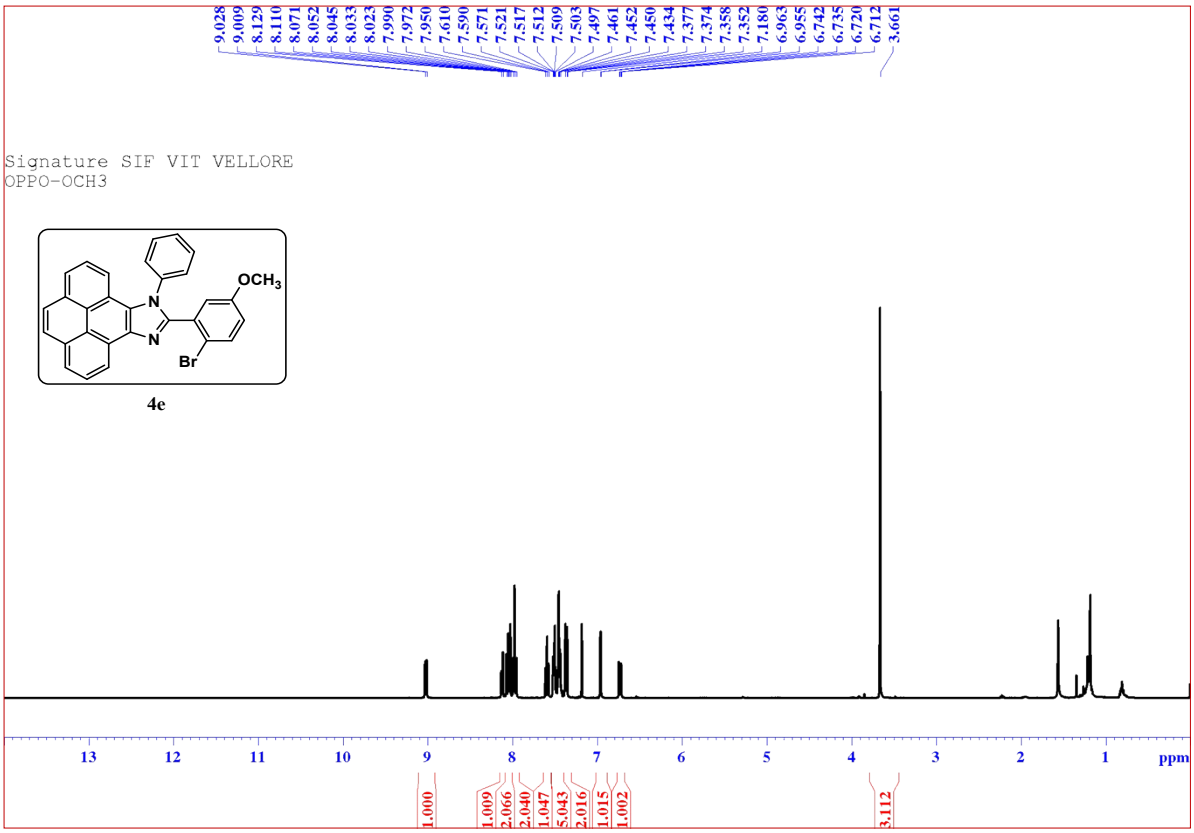
^{1}H NMR spectrum of **5d** in $CDCl_3$



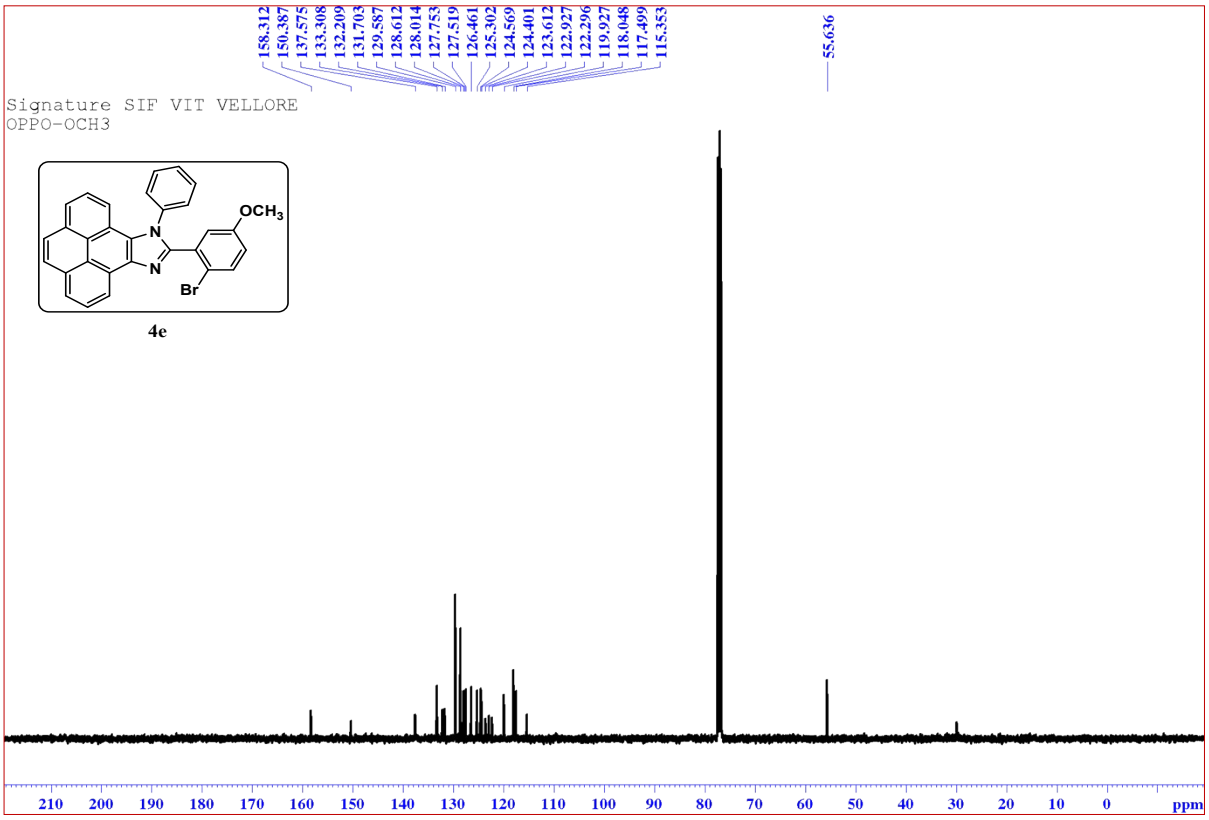
^{13}C NMR spectrum of **5d** in $CDCl_3$



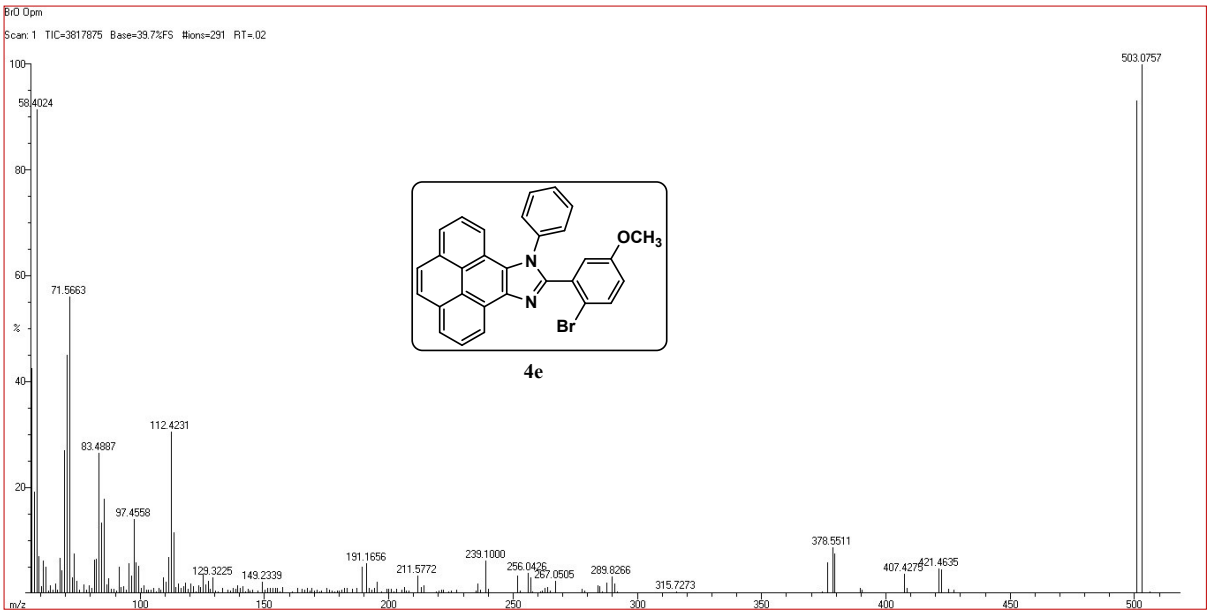
HRMS spectrum of **5d**



^{1}H NMR spectrum of **4e** in $CDCl_3$

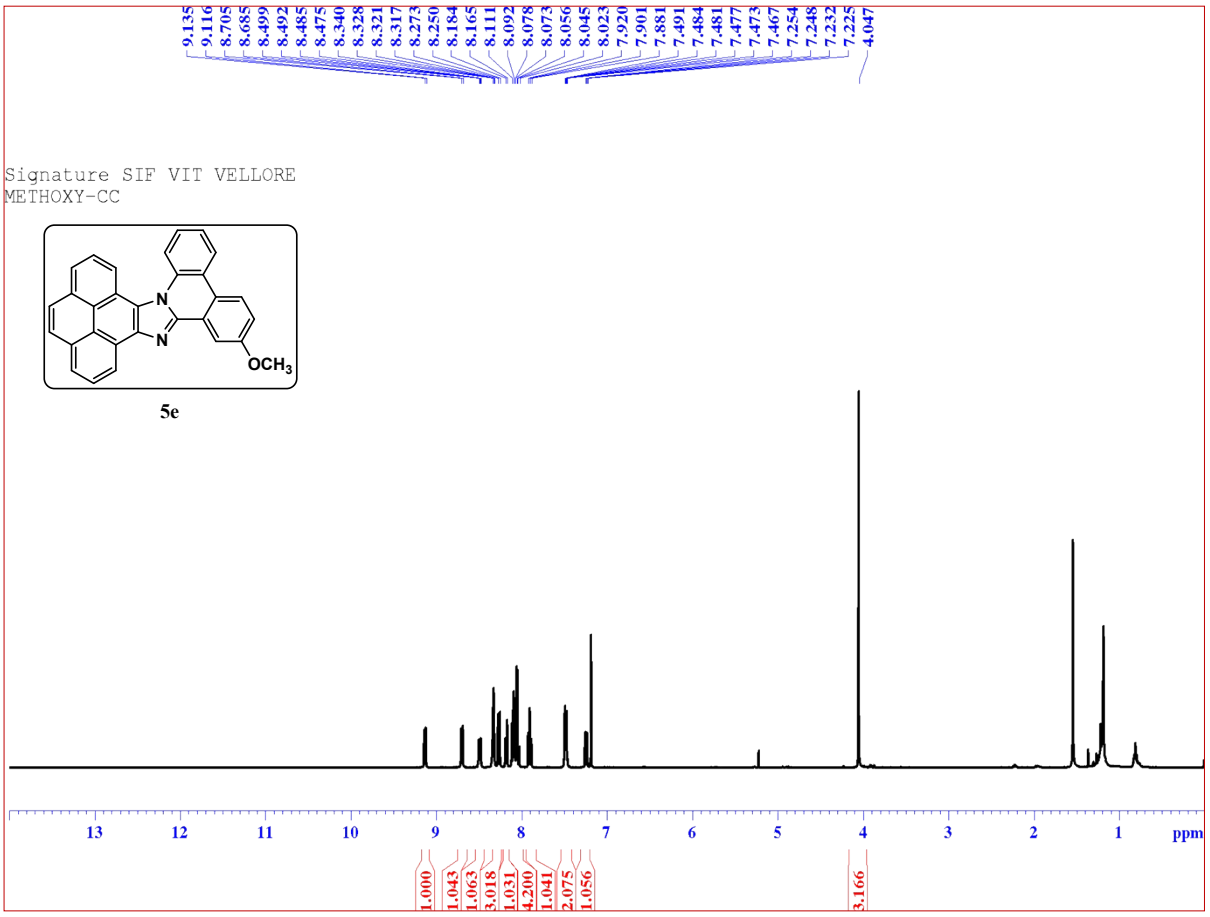


^{13}C NMR spectrum of **4e** in $CDCl_3$



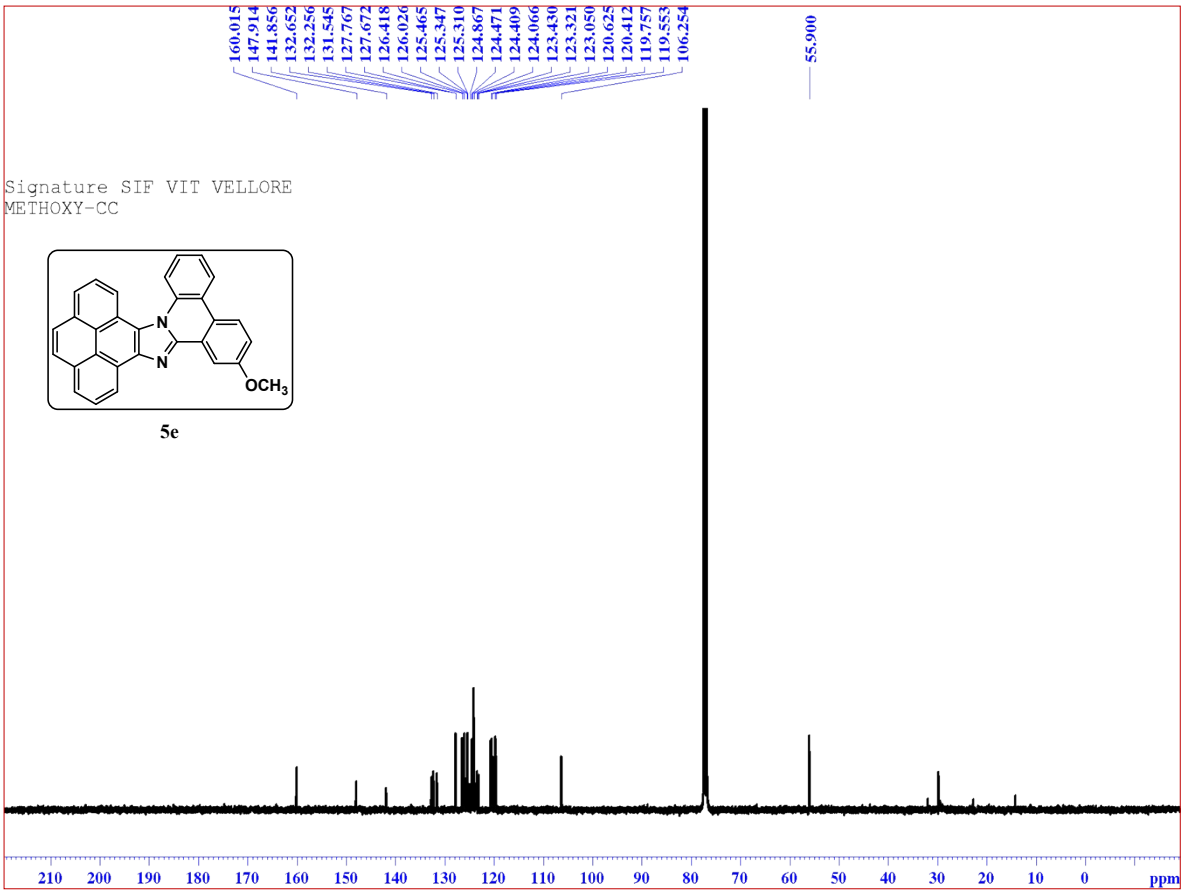
4e

HRMS spectrum of **4e**



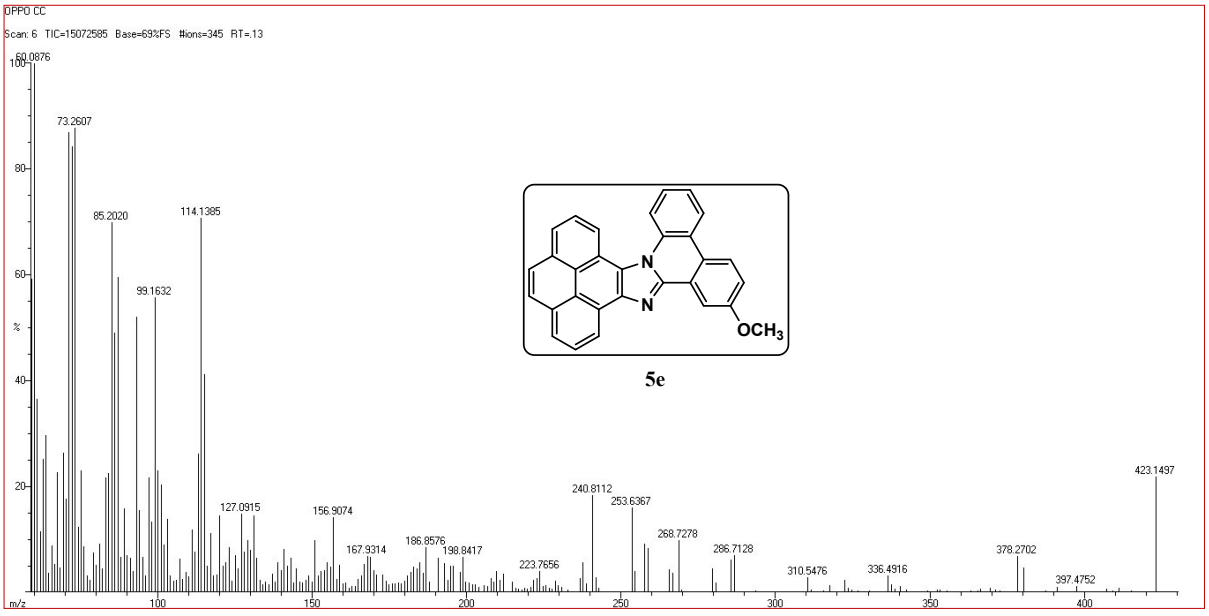
5e

^{1}H NMR spectrum of **5e** in $CDCl_3$



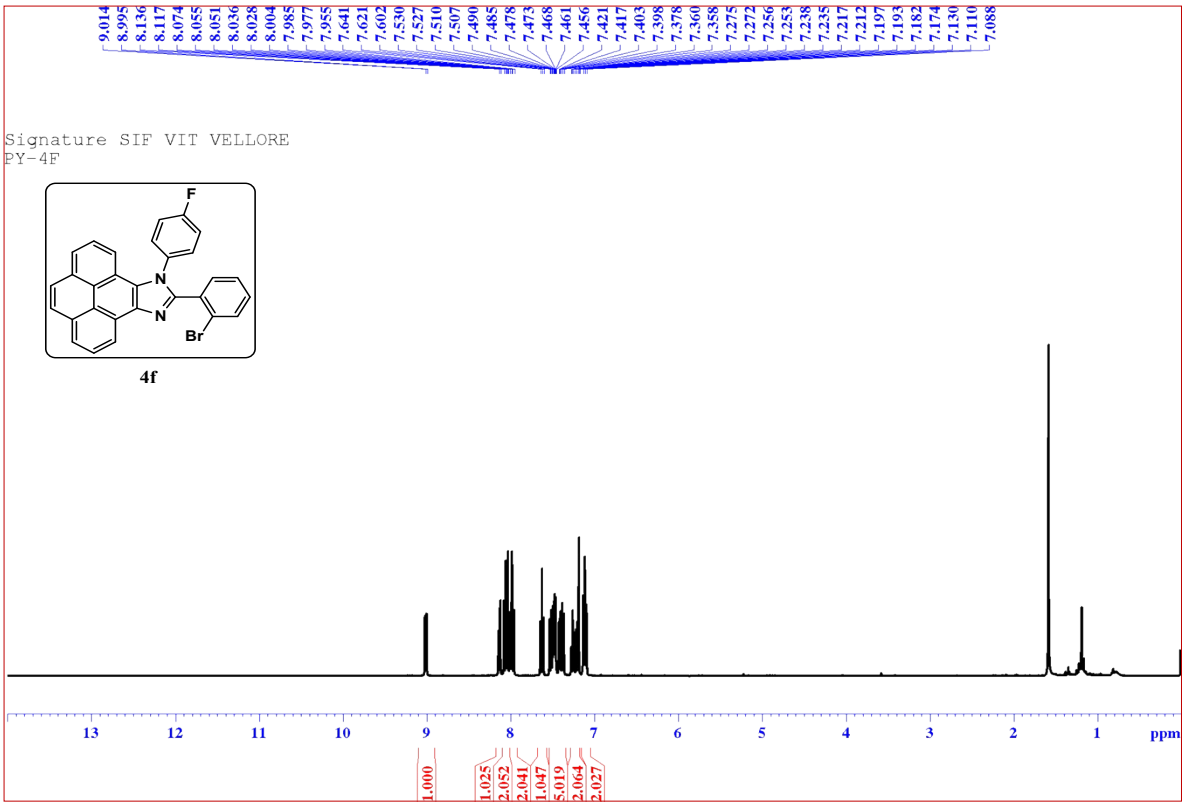
5e

^{13}C NMR spectrum of **5e** in $CDCl_3$

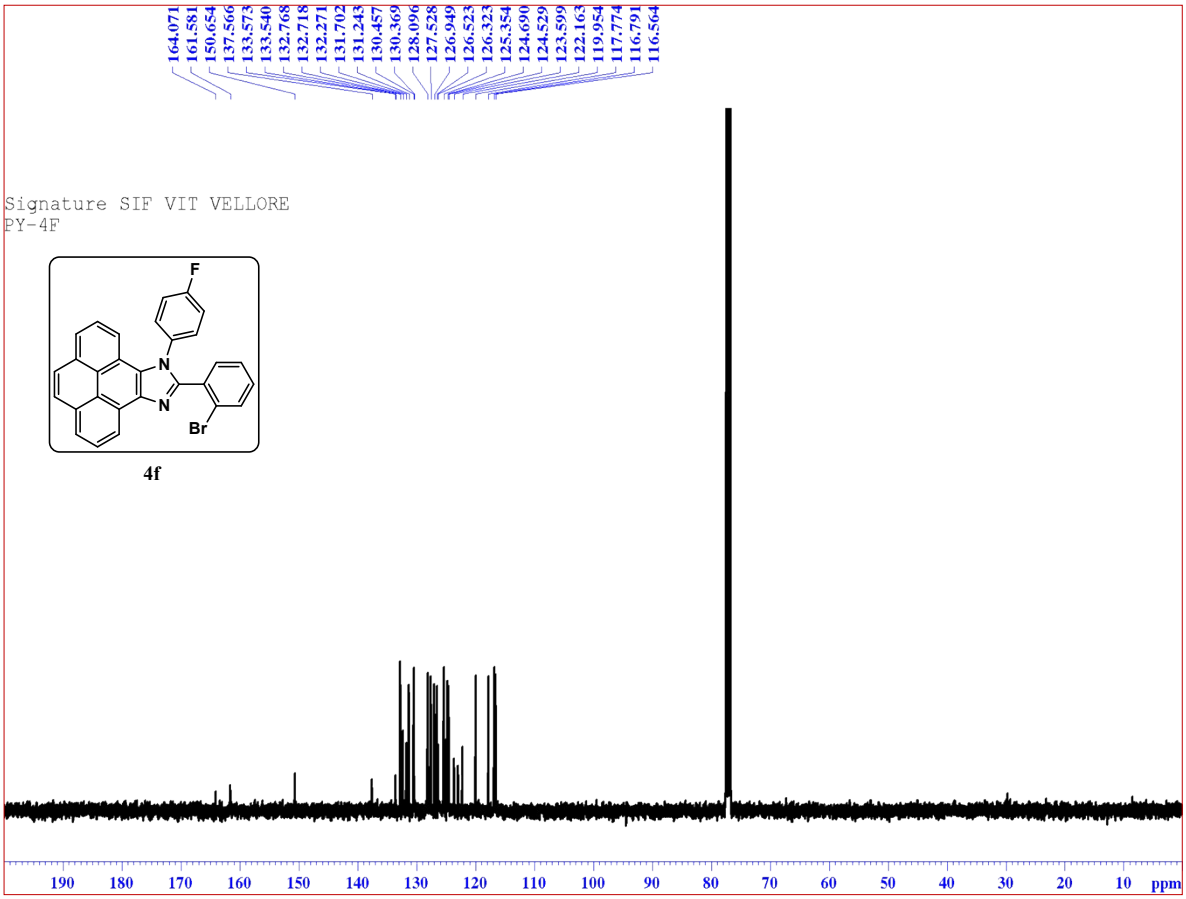


5e

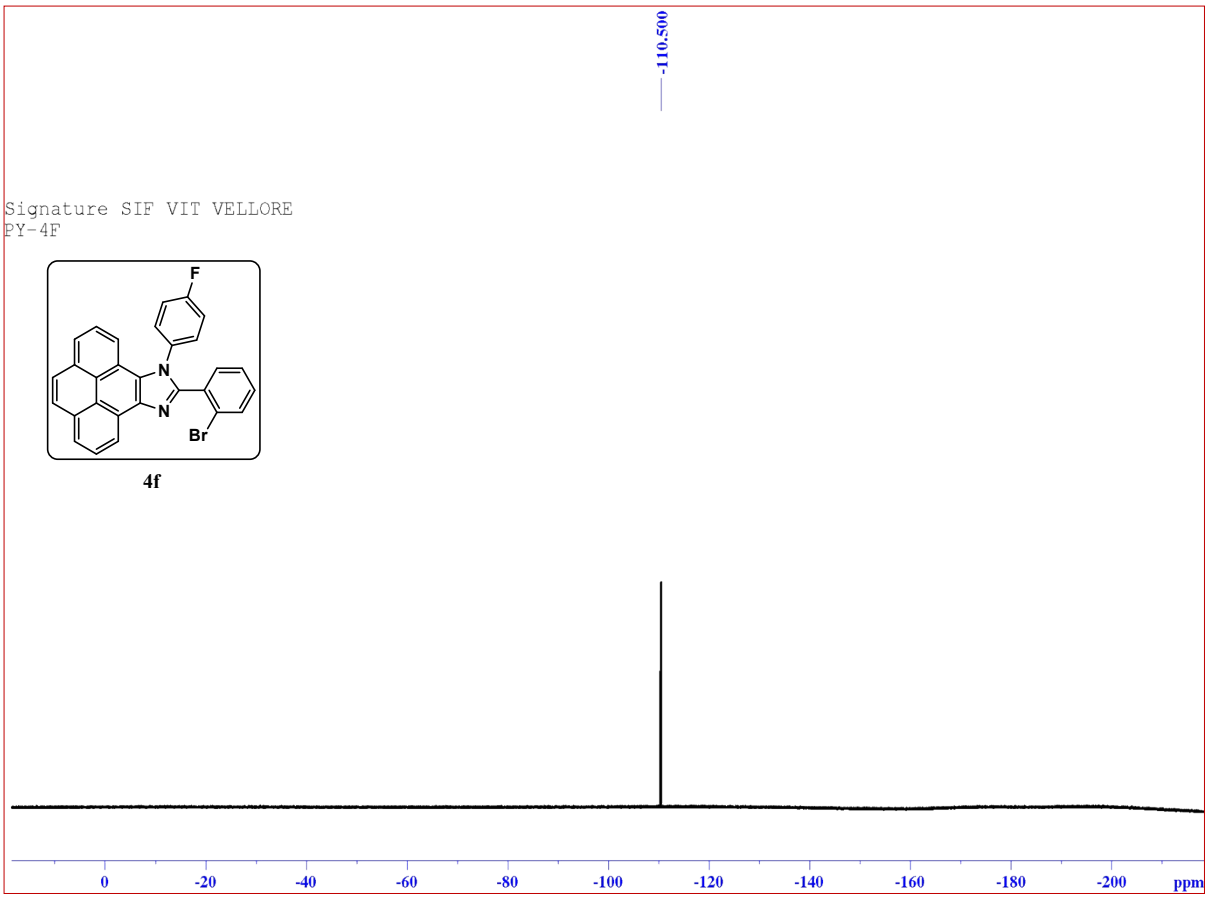
HRMS spectrum of **5e**



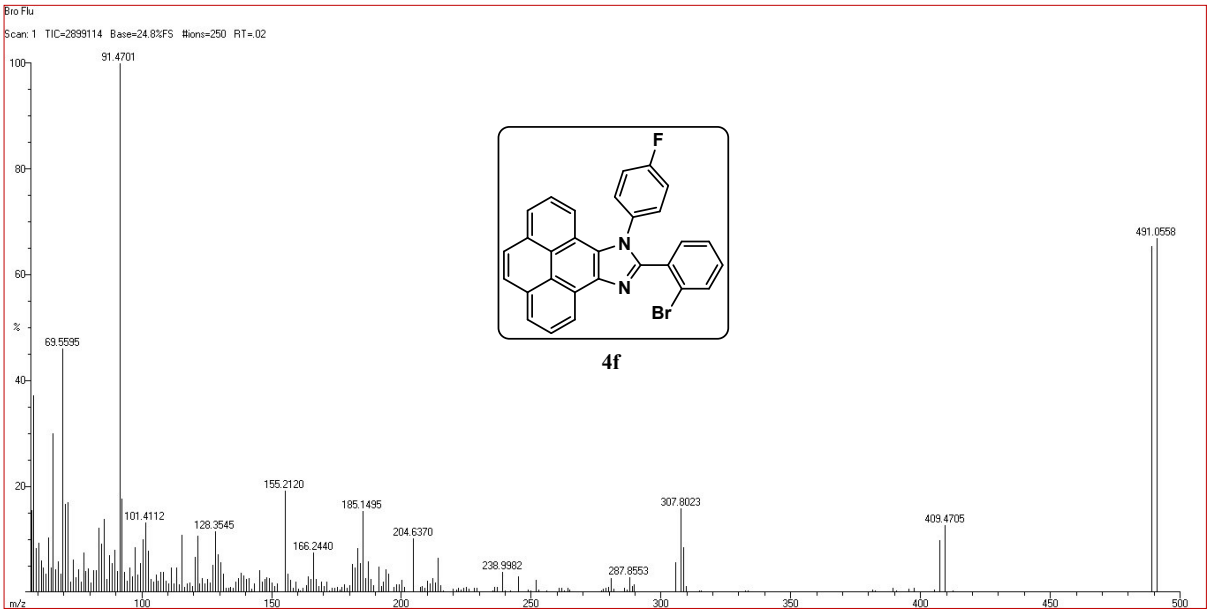
^{1}H NMR spectrum of **4f** in $CDCl_3$



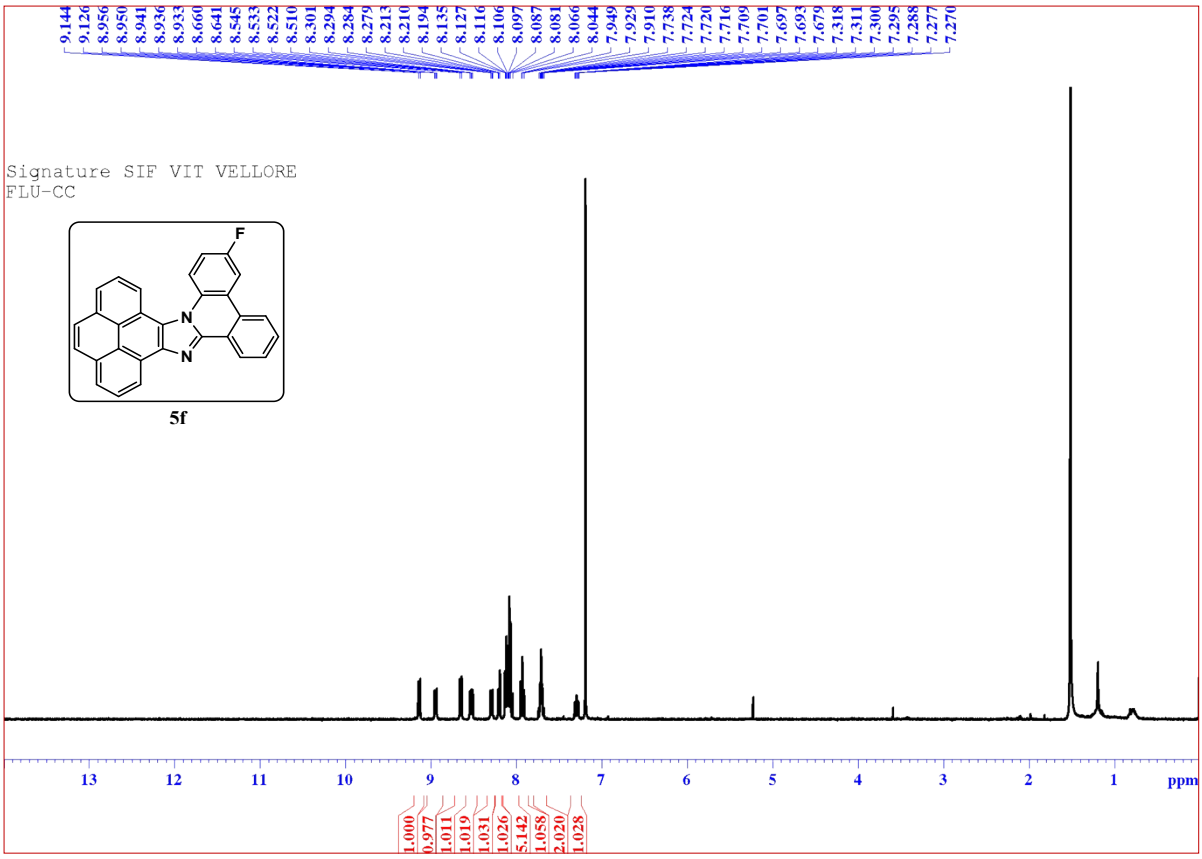
^{13}C NMR spectrum of **4f** in $CDCl_3$



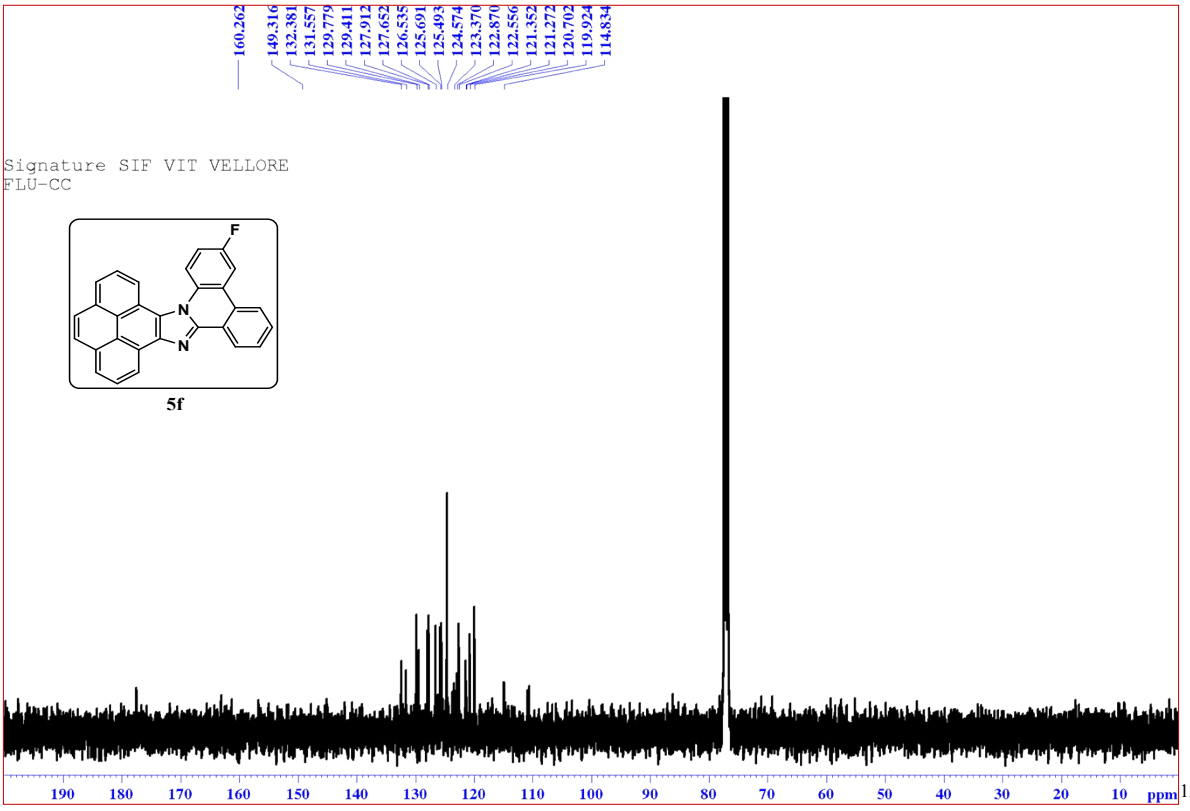
^{19}F NMR spectrum of **4f** in $CDCl_3$



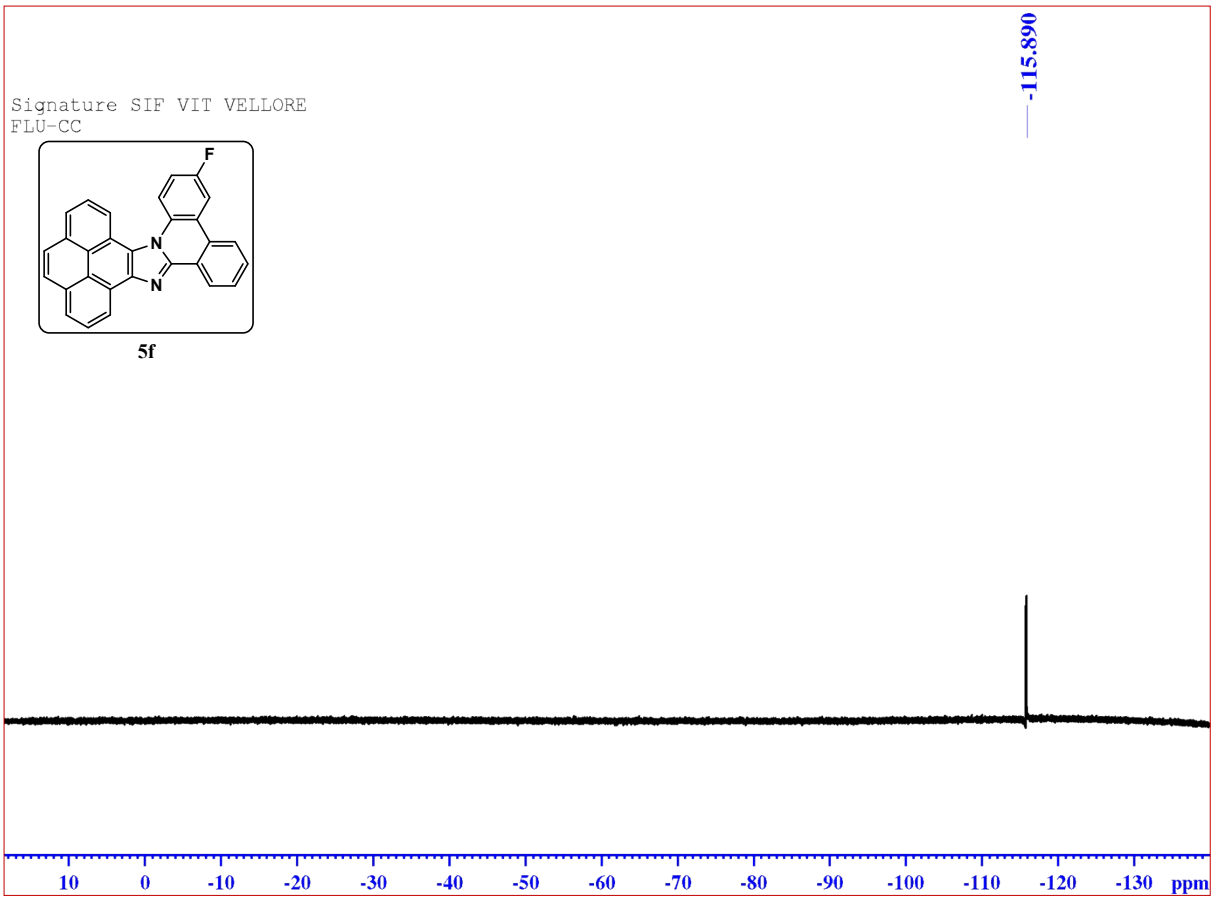
HRMS spectrum of **4f**



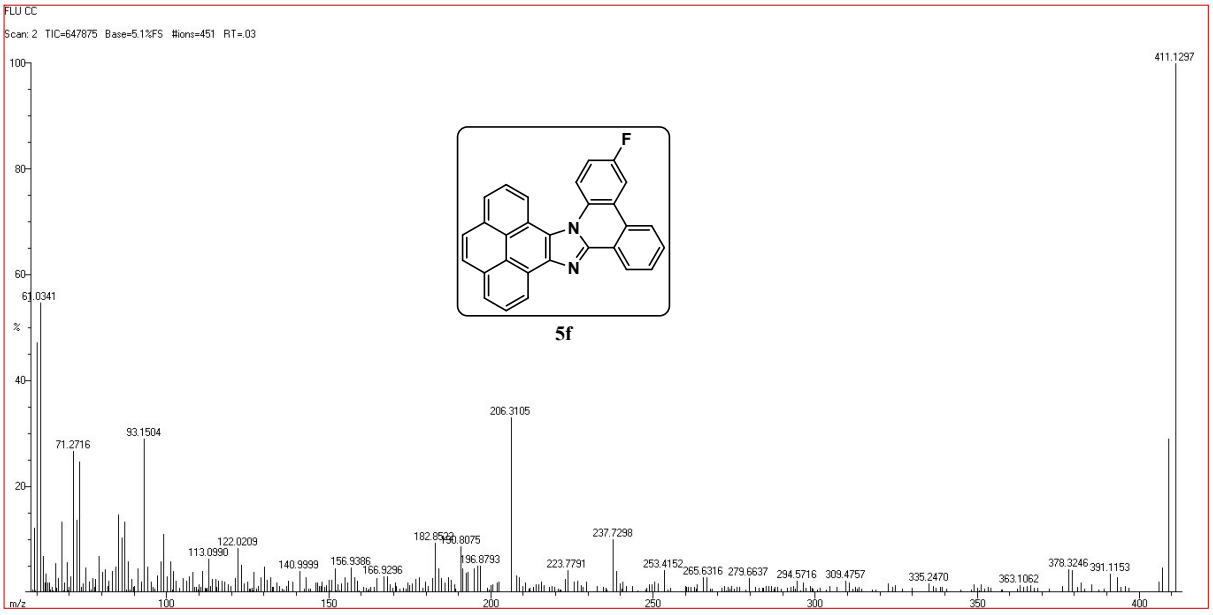
^{1}H NMR spectrum of **5f**



^{13}C NMR spectrum of **5f**



^{19}F NMR spectrum of **5f**



HRMS spectrum of **5f**