Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Novel ethynyl-pyrene substituted phenothiazine based metal free organic dyes in DSSC with 12 % conversion efficiency

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58. **Table S4**. Theoretically calculated HOMO, LUMO and energy gap of the dyes without pyrene moiety

Scheme S1. Synthetic procedure of the starting materials

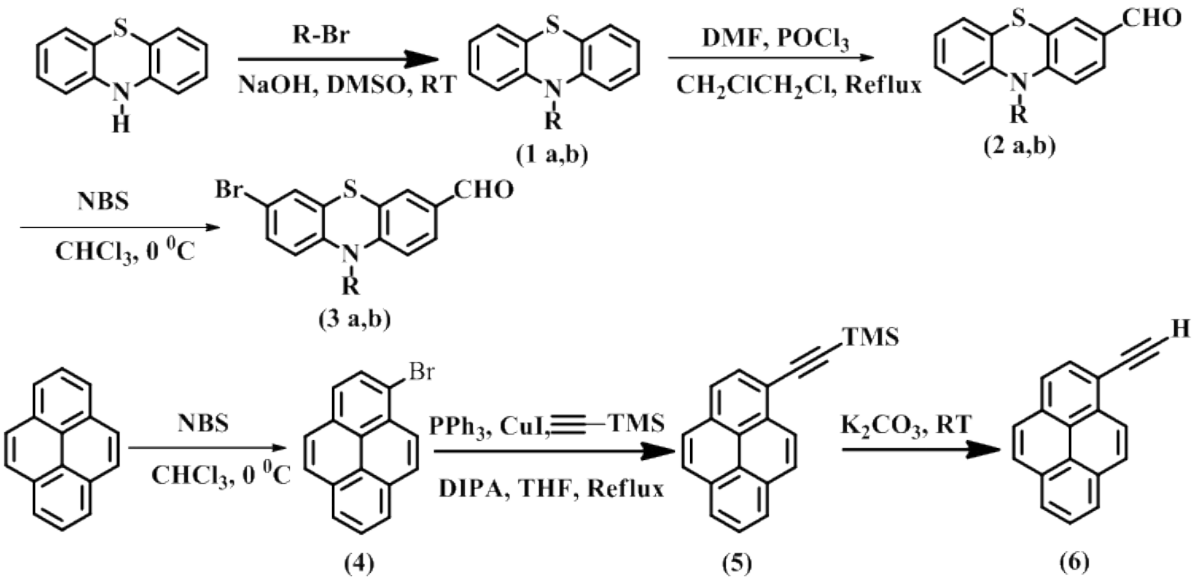


Table S1. The calculated maximum wavelength (λ_{max} in nm), oscillator strength (*f*) and the major contributions of percentage transitions of the dyes (λ_{max} is the maximum wavelength measured experimentally).

Dyes	λ_{max} (nm)	λ_{exp} (nm)	Oscillator strength(*f*)	Major contributions
Dye 1	423	438	1.4787	HOMO-1 to LUMO (34%), HOMO to LUMO (44%)
Dye 2	423	438	1.4787	HOMO-1 to LUMO (34%), HOMO to LUMO (44%)
Dye 3	467	472	1.4563	HOMO-1 to LUMO (41%), HOMO to LUMO (43%)
Dye 4	467	473	1.4557	HOMO-1 to LUMO (40%), HOMO to LUMO (44%)
Dye 5	426	474	1.1976	HOMO-1 to LUMO (36%), HOMO to LUMO (44%)
Dye 6	425	474	1.2149	HOMO-1 to LUMO (36%), HOMO to LUMO (44%)

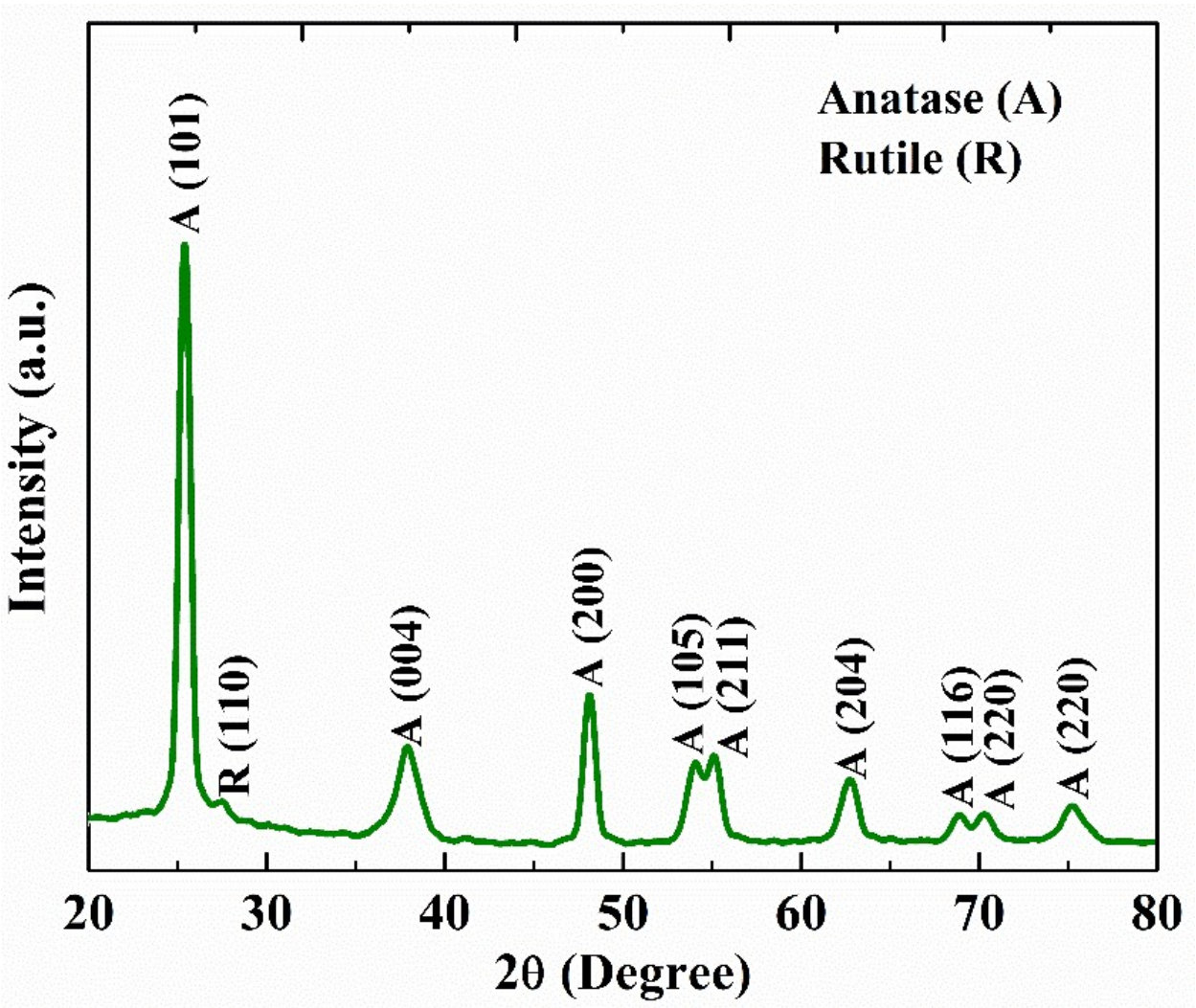


Figure S1. Powder X-ray diffraction of TiO_2

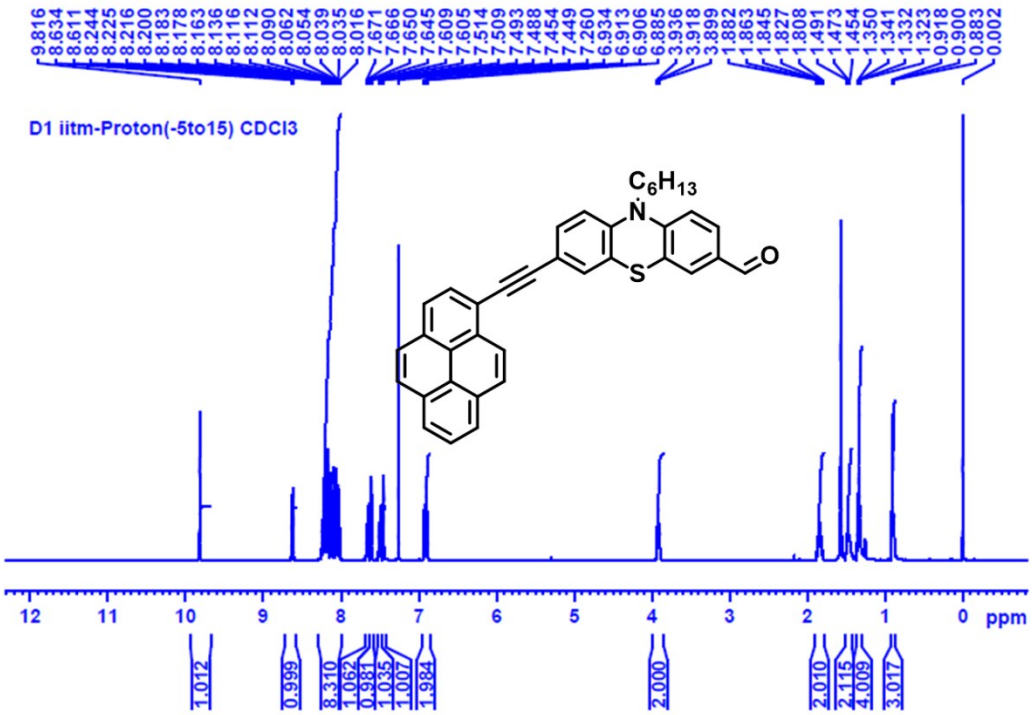


Figure S2. ^{1}H NMR spectrum of donor **1**

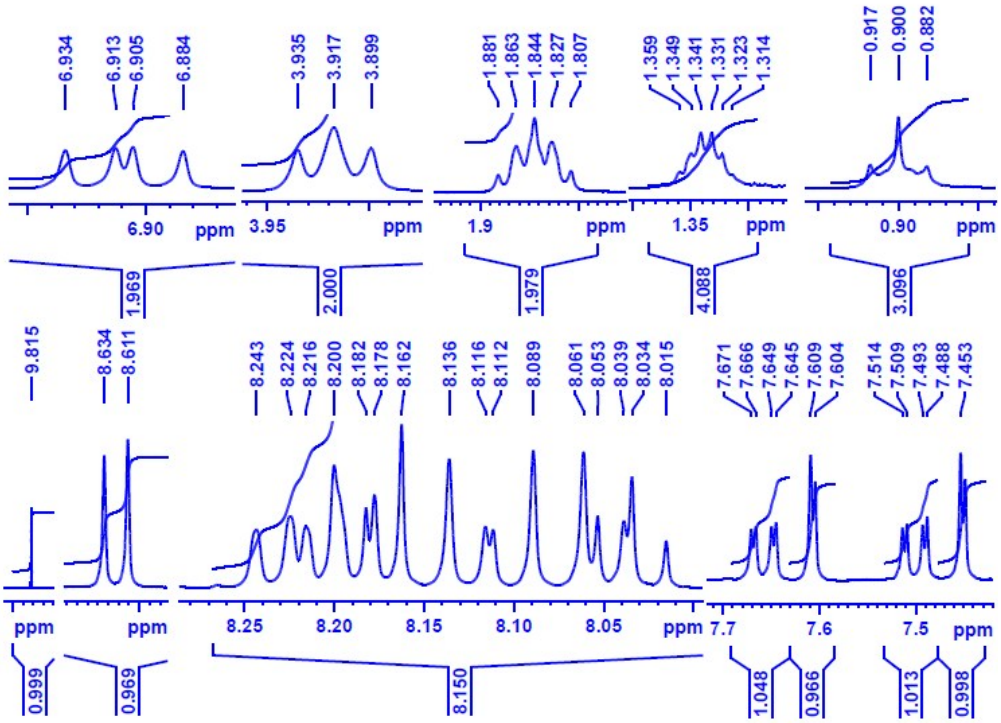


Figure S3. Expanded ^{1}H NMR spectrum of donor **1**

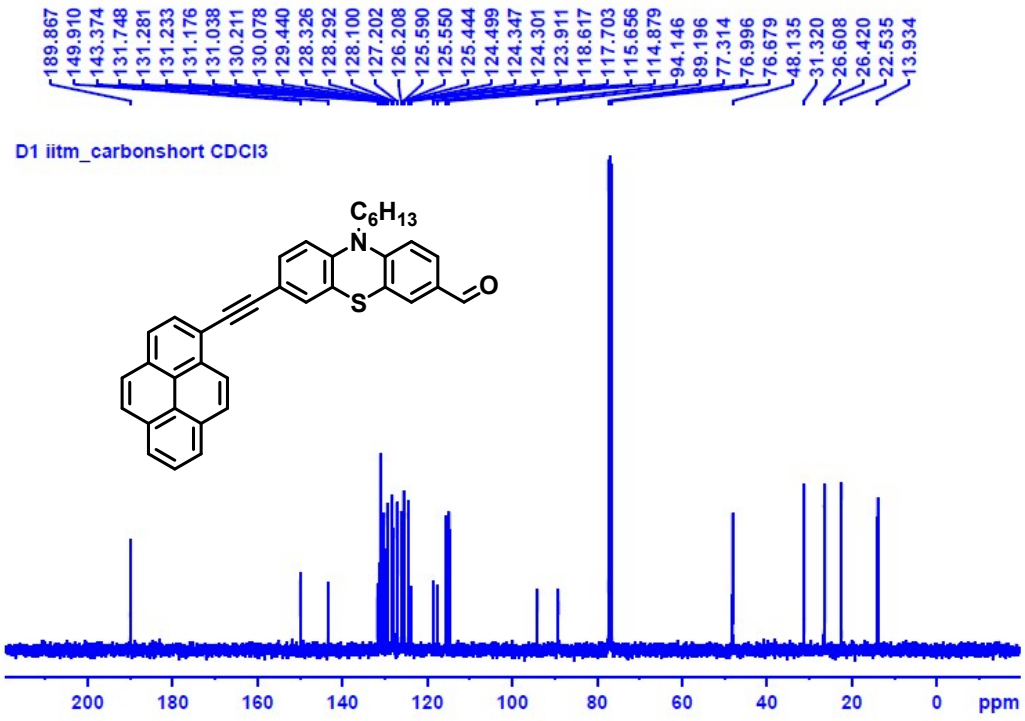


Figure S4. ^{13}C NMR spectrum of donor **1**

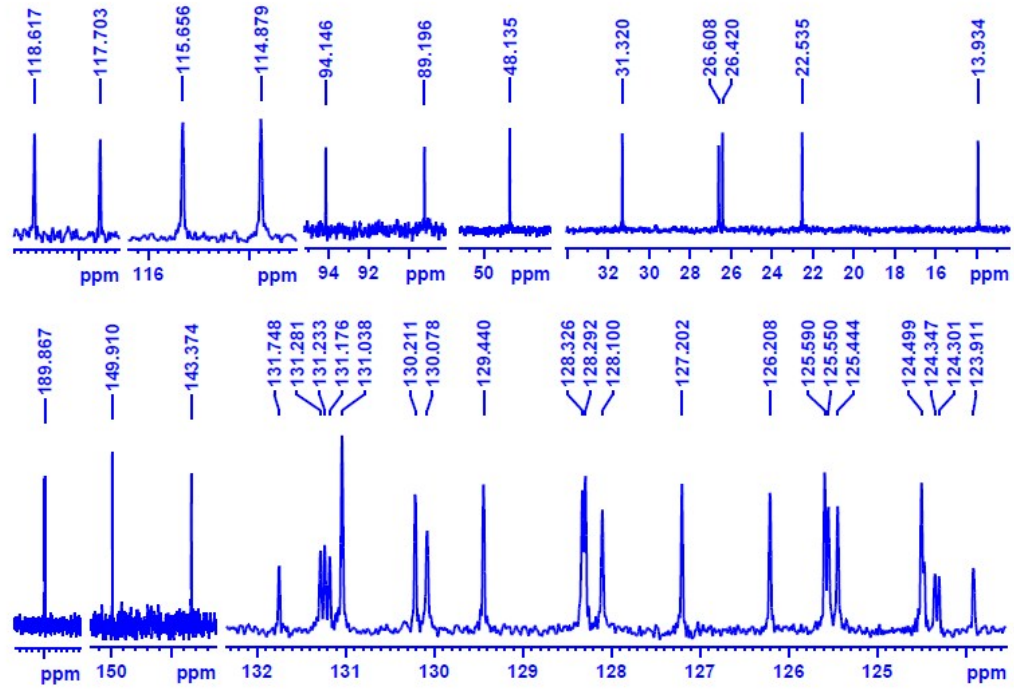


Figure S5. Expanded ^{13}C NMR spectrum of donor **1**

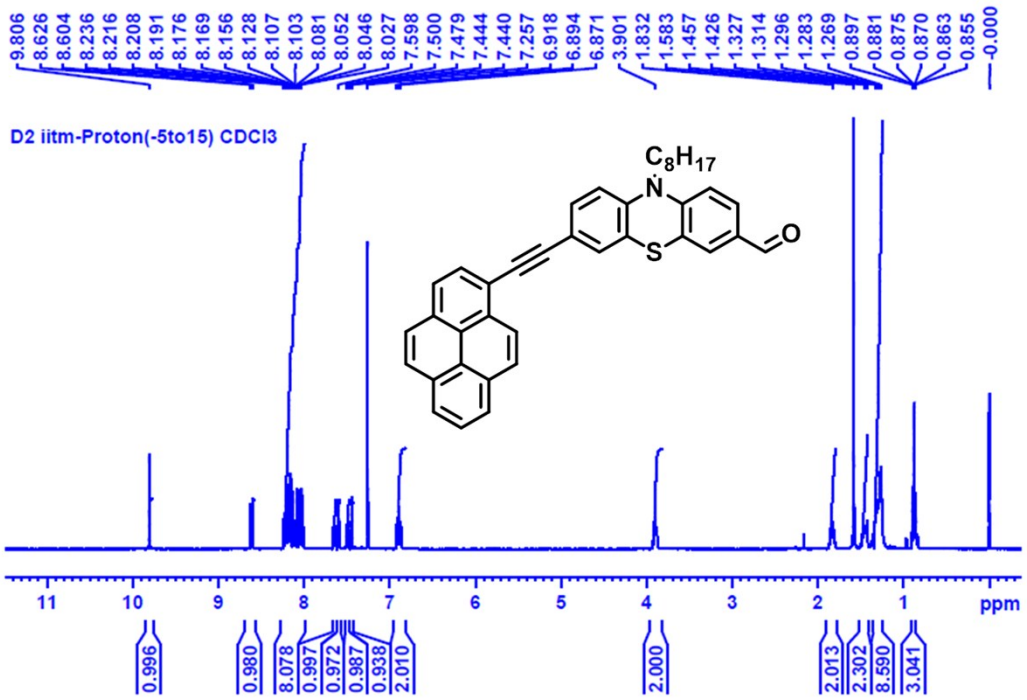


Figure S6. ^{1}H NMR spectrum of donor **2**

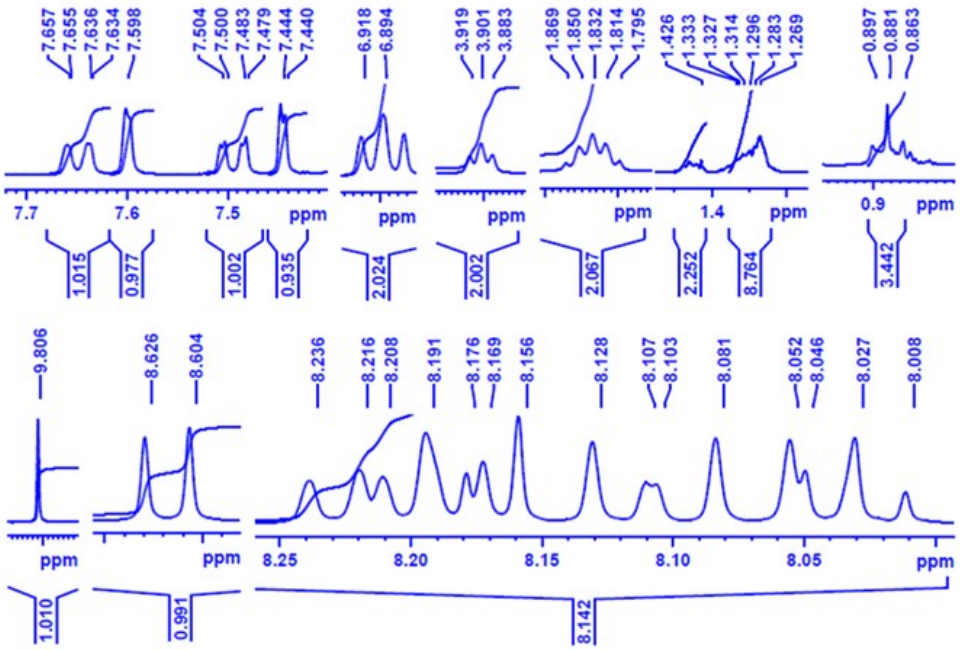


Figure S7. Expanded ^{1}H NMR spectrum of donor **2**

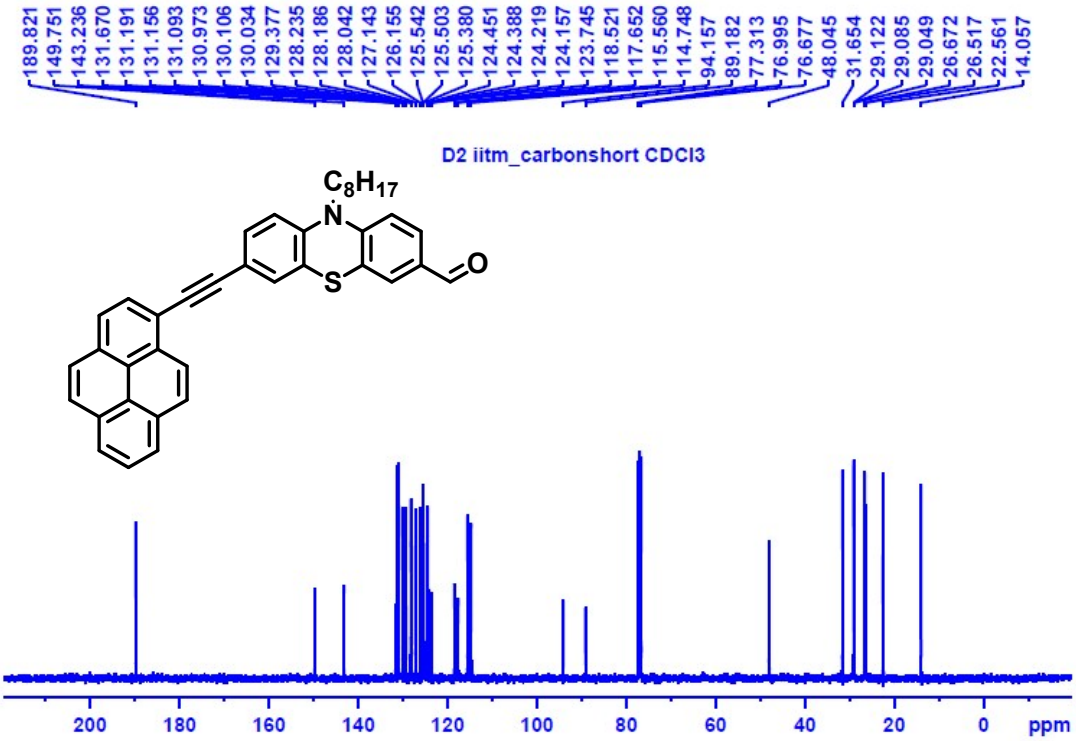


Figure S8. ^{13}C NMR spectrum of donor **2**

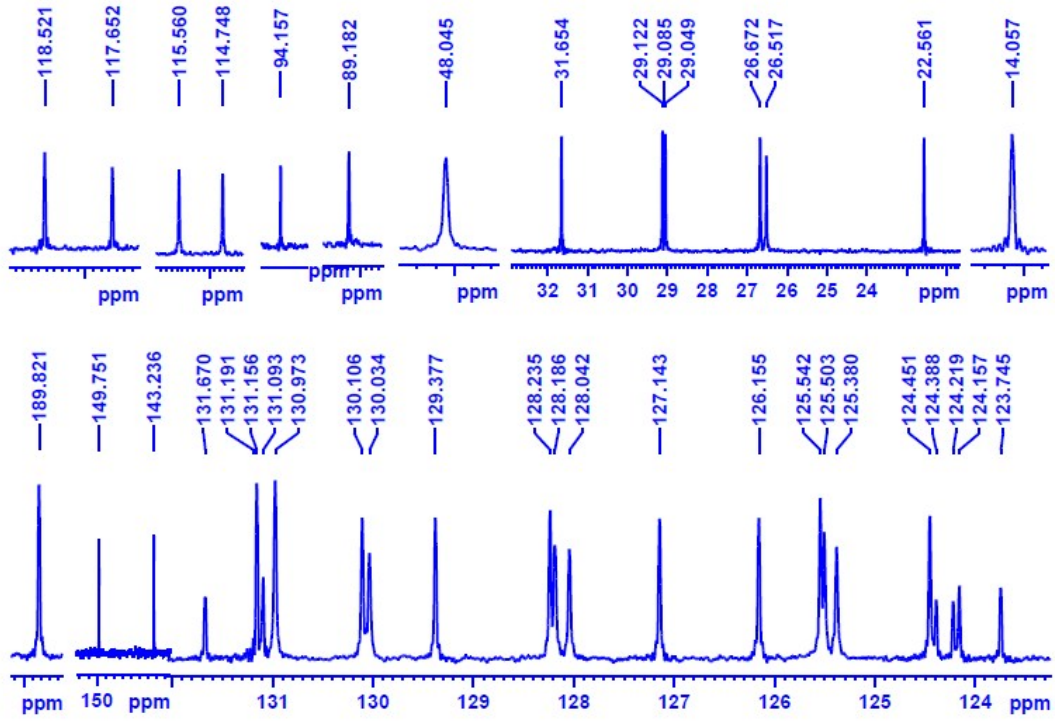


Figure S9. Expanded ^{13}C NMR spectrum of donor **2**

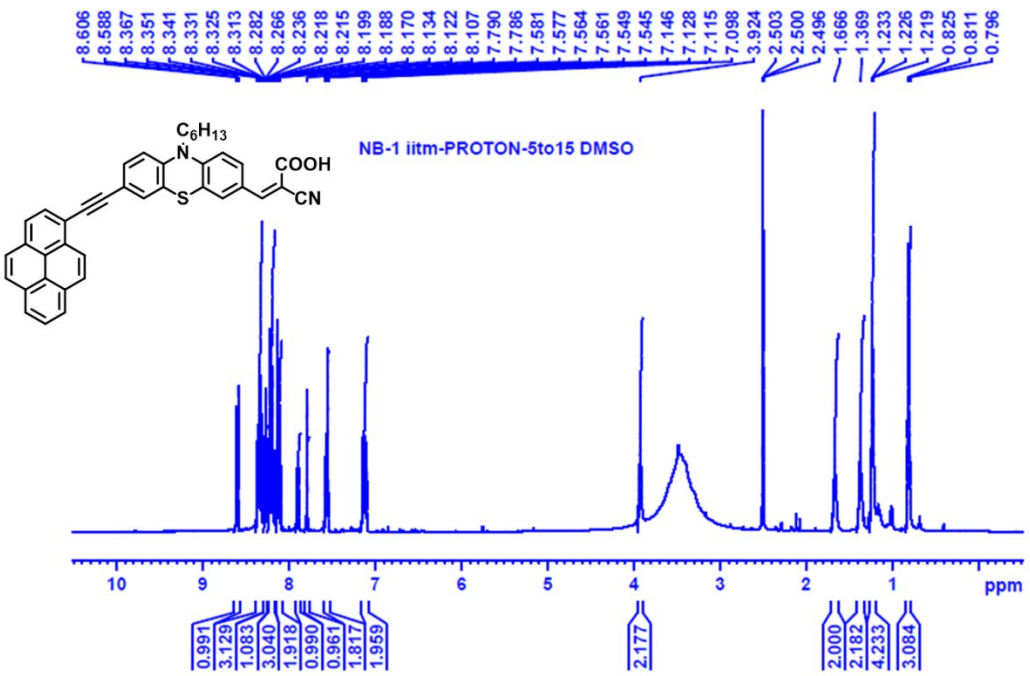


Figure S10. ^{1}H NMR spectrum of dye **1**

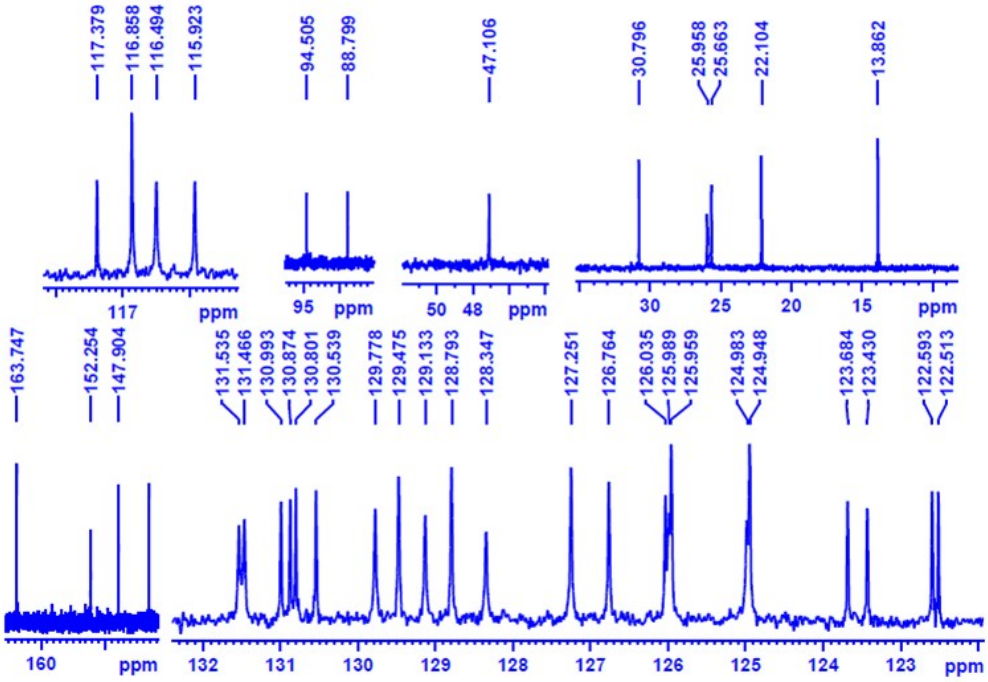


Figure S11. Expanded of ^{1}H NMR of dye **1**

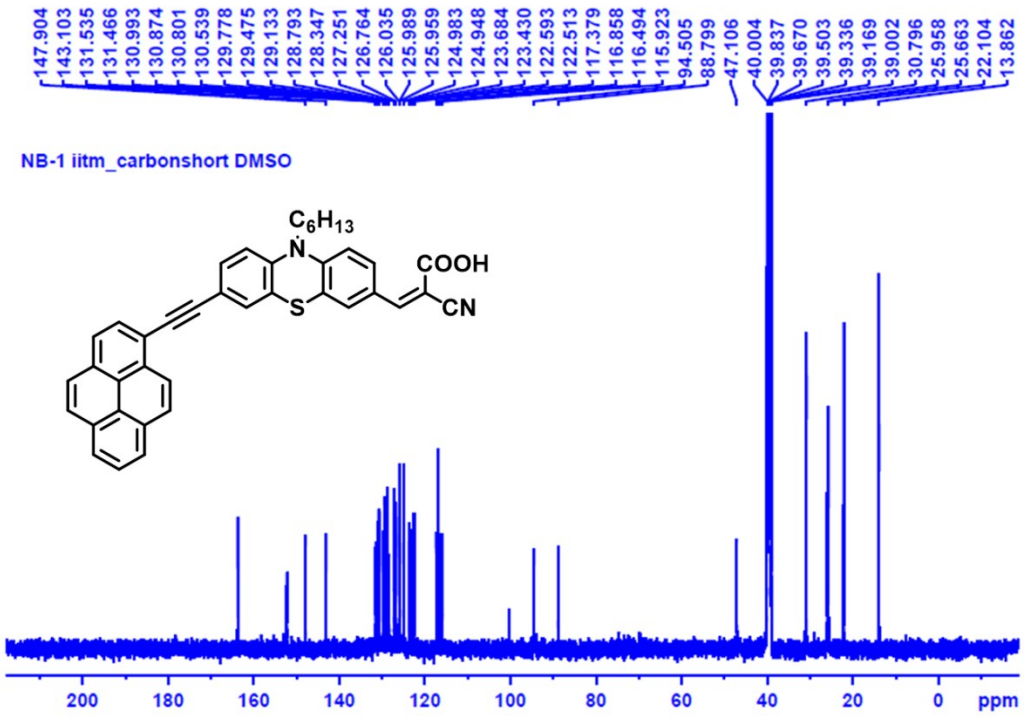


Figure S12. ^{13}C NMR spectrum of dye **1**

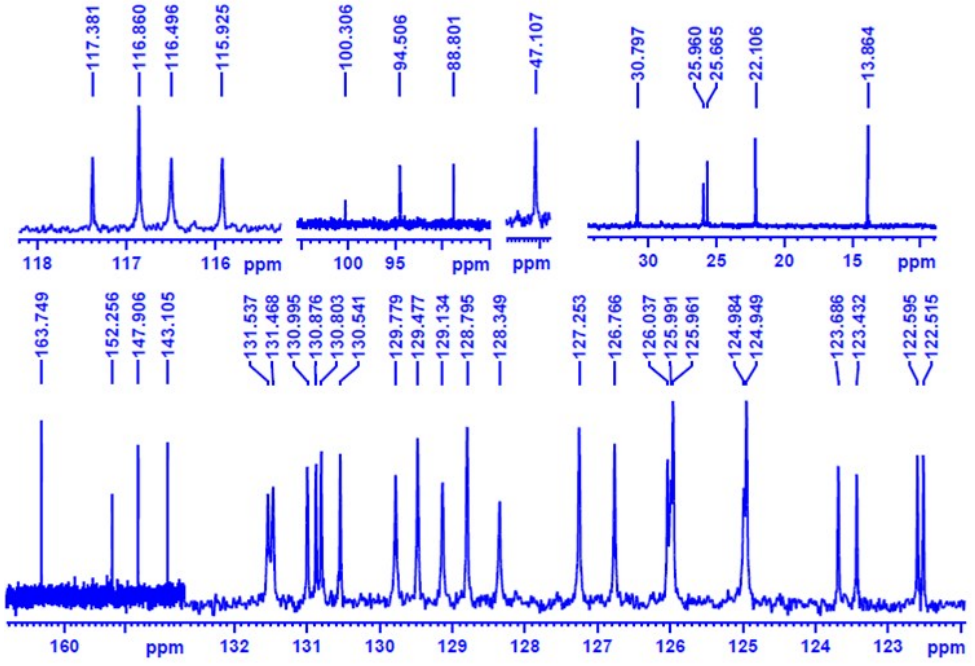


Figure S13. Expanded of ^{13}C NMR spectrum of dye **1**

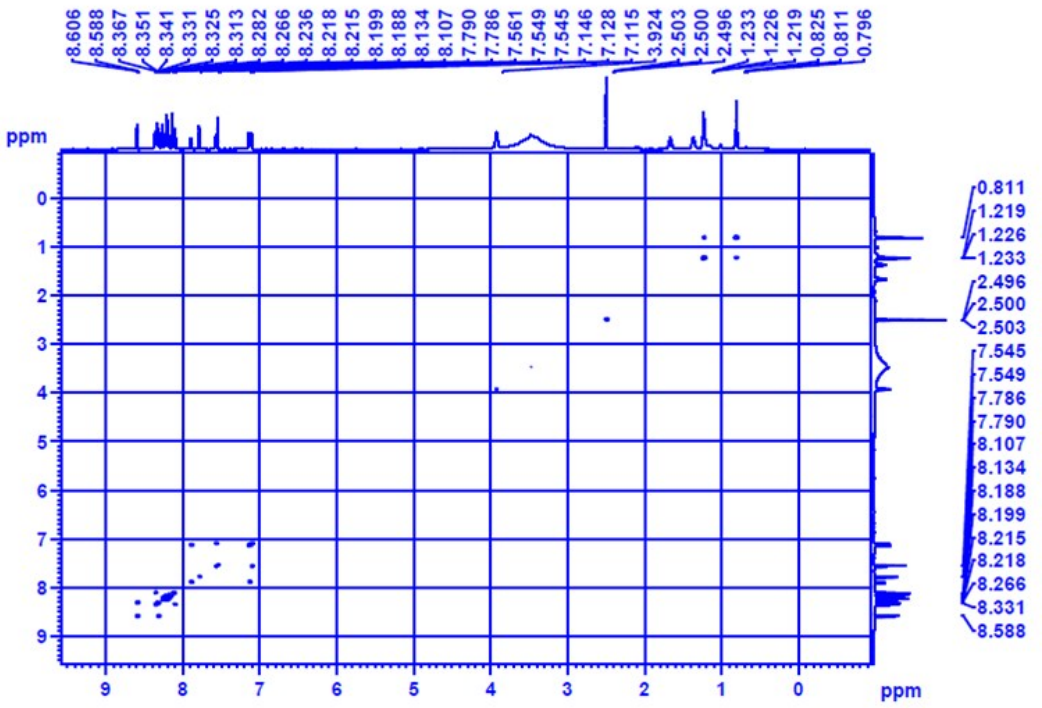


Figure S14. COSY NMR spectrum of dye **1**

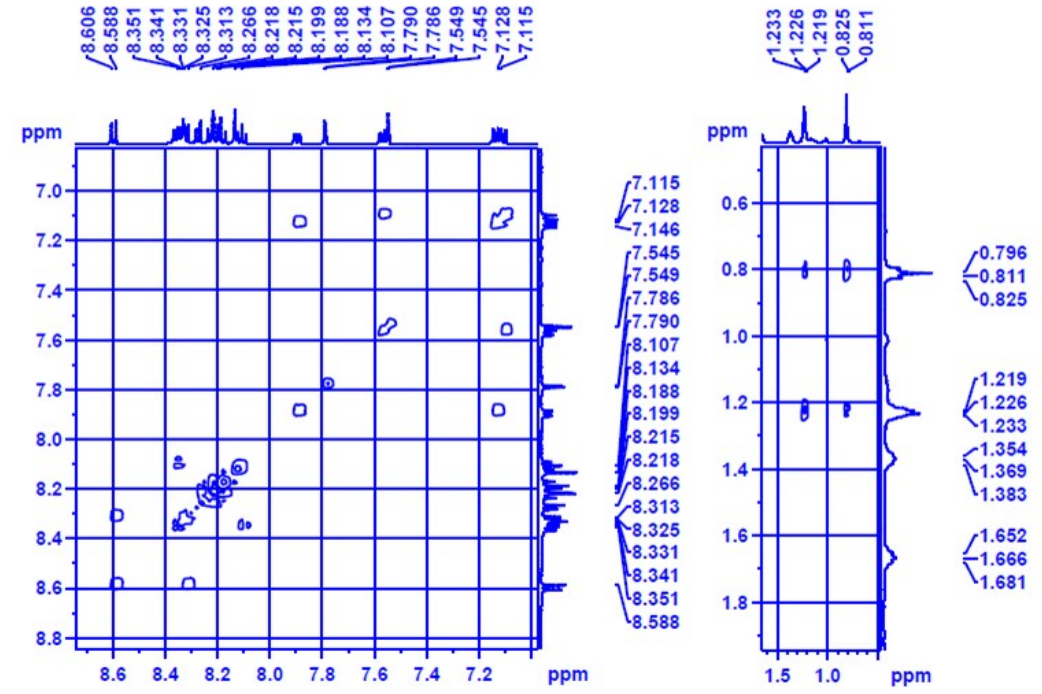


Figure S15. Expanded of COSY NMR spectrum of dye **1**

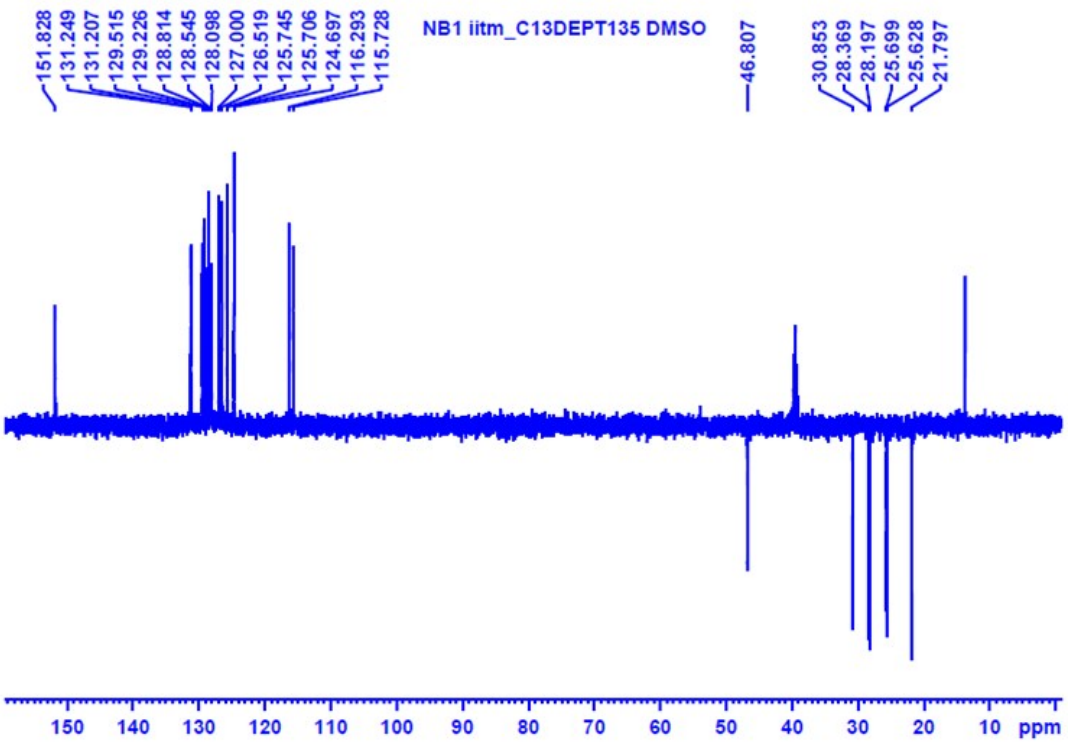


Figure S16. DEPT NMR spectrum of dye **1**

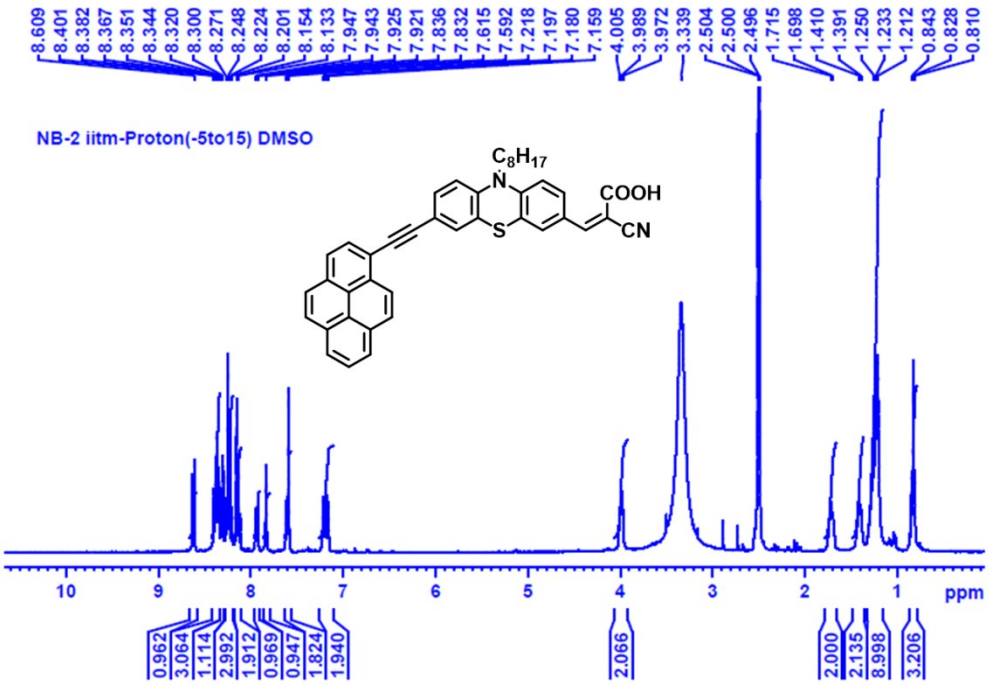


Figure S17. ^{1}H NMR spectrum of dye **2**

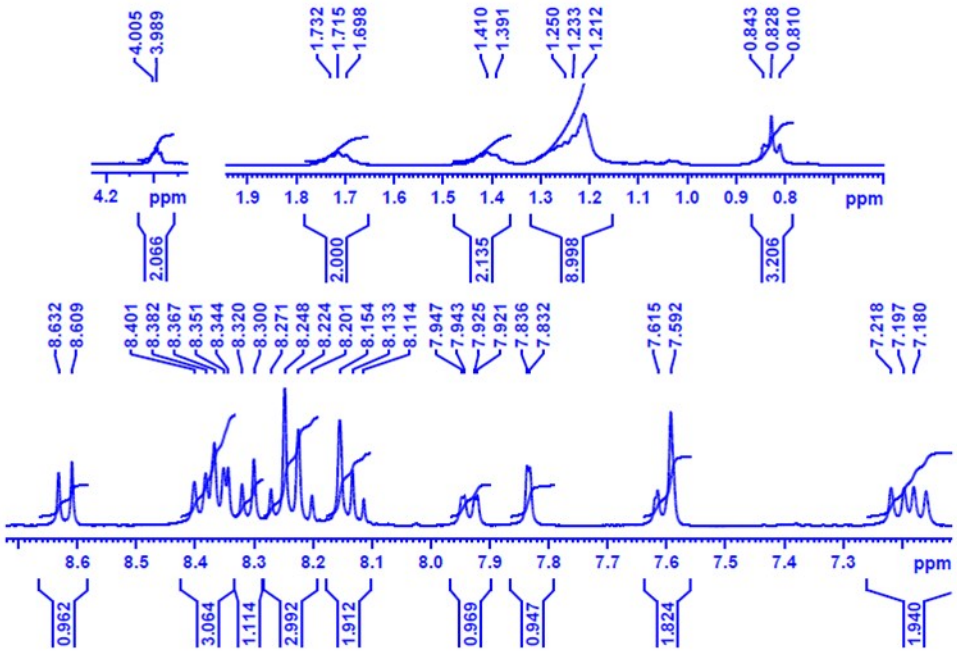


Figure S18. Expanded of ^{1}H NMR spectrum of dye **2**

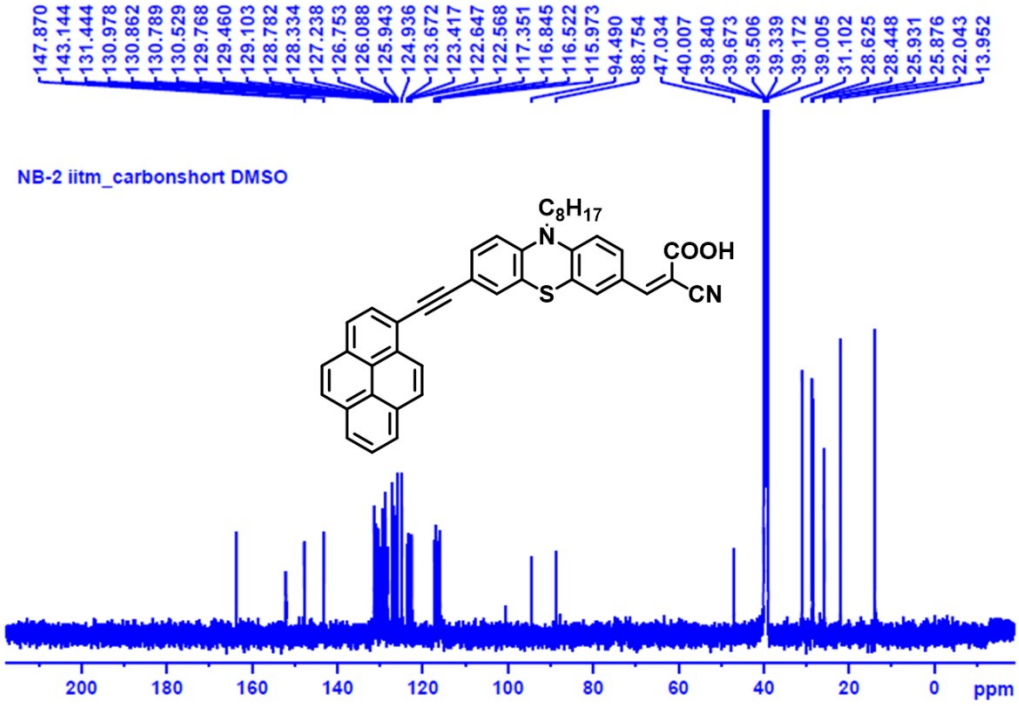


Figure S19. ^{13}C NMR spectrum of dye **2**

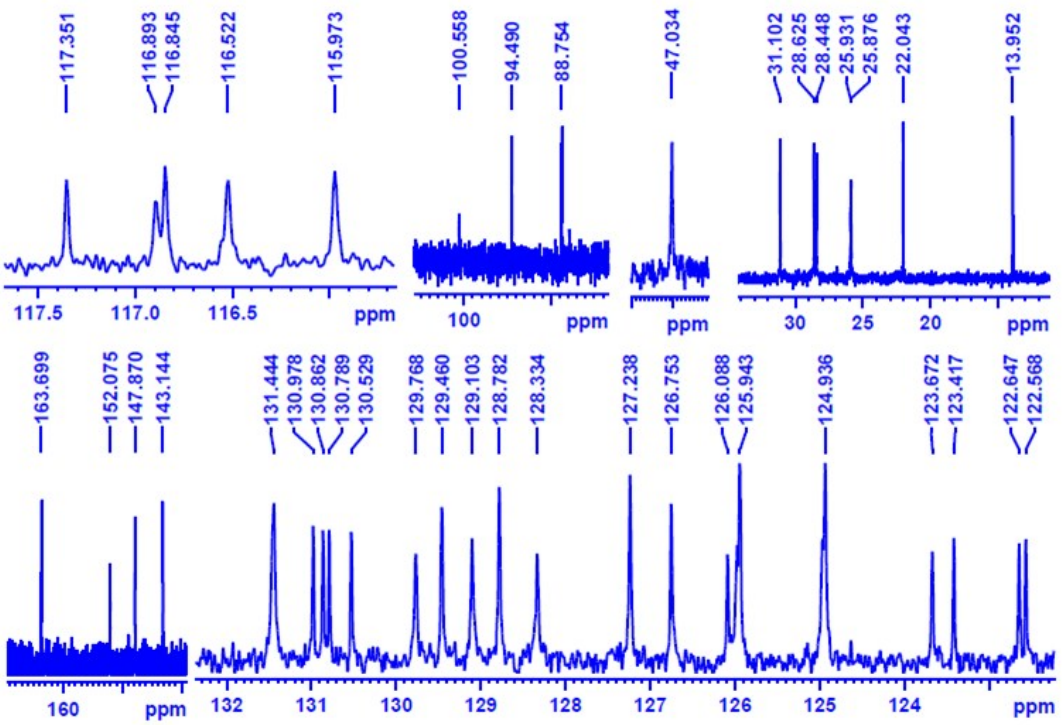


Figure S20. Expanded of ^{13}C NMR spectrum of dye **2**

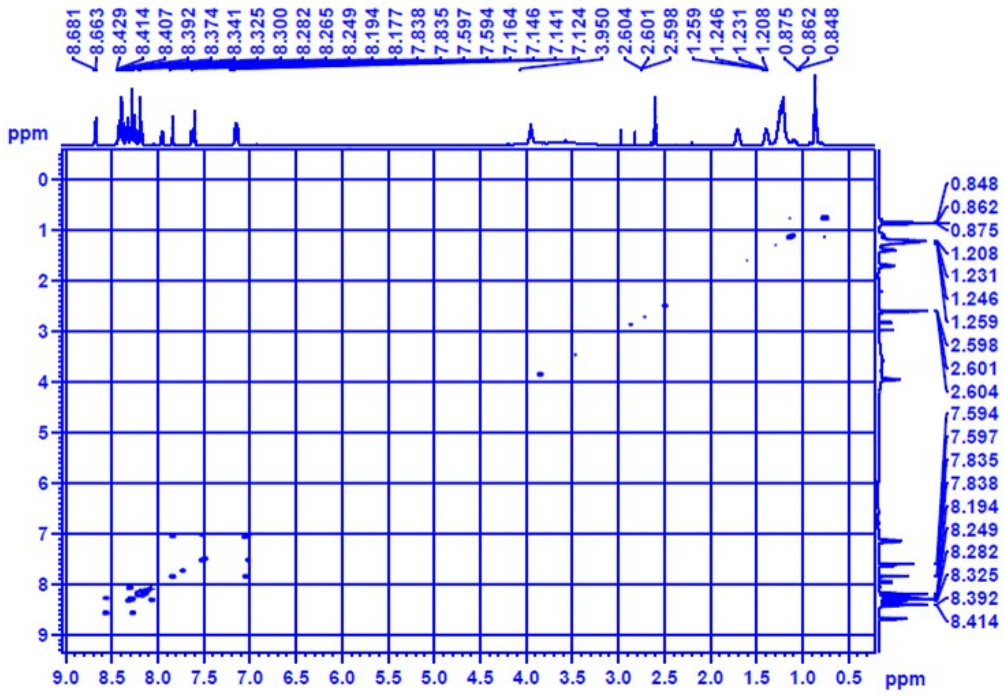


Figure S21. COSY NMR spectrum of dye **2**

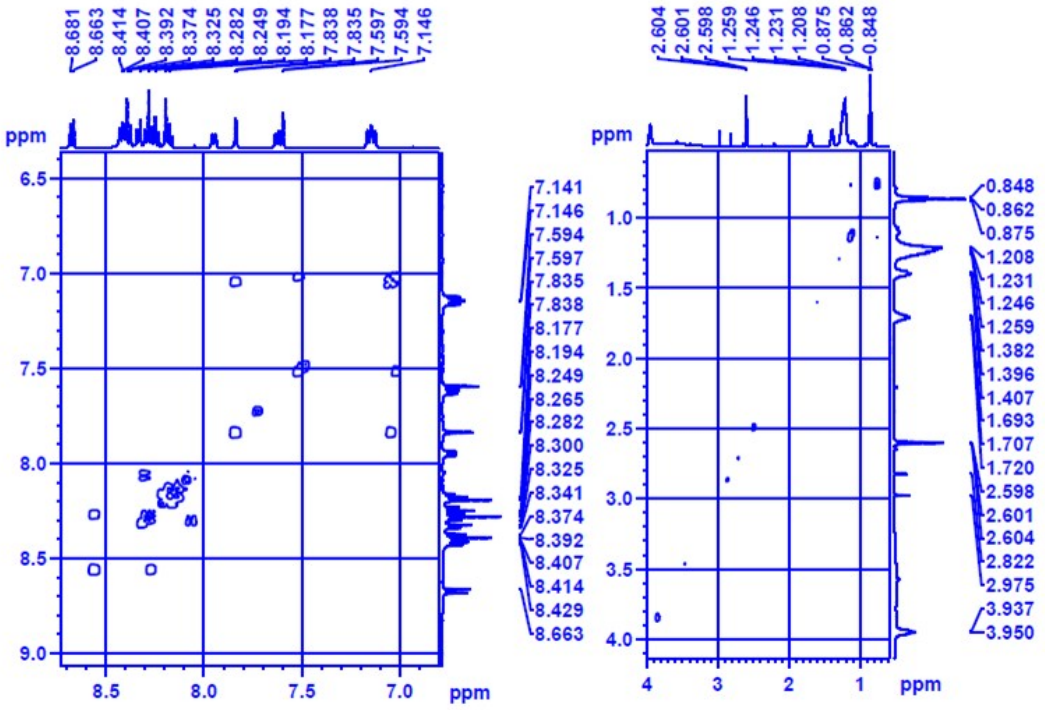


Figure S22. Expanded of COSY NMR spectrum of dye **2**

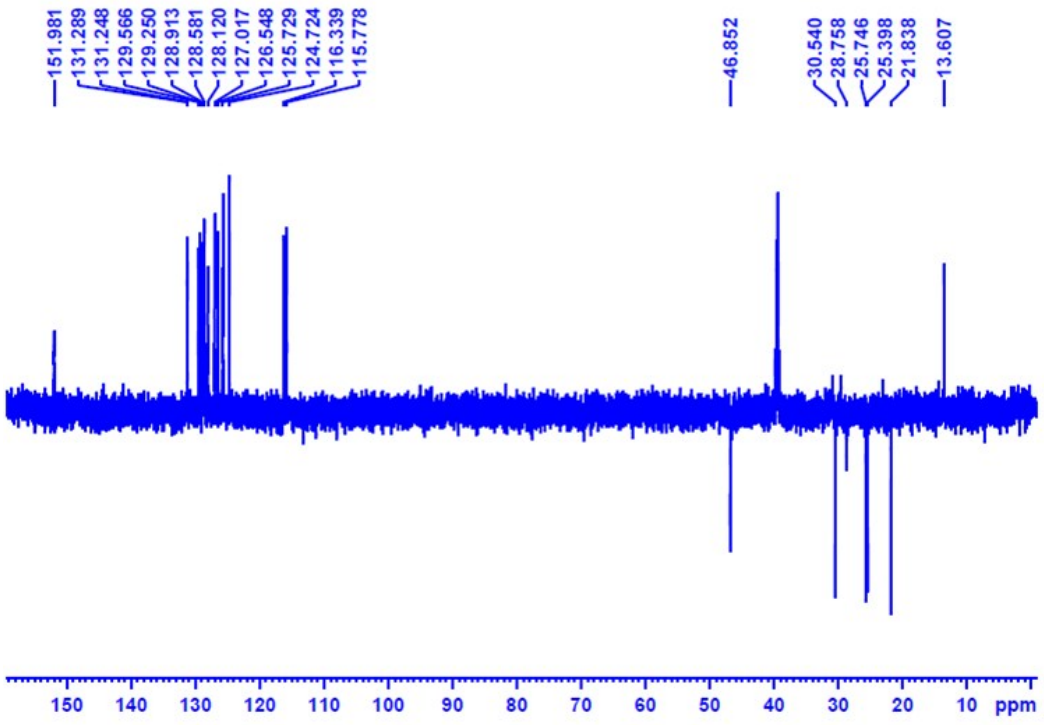


Figure S23. DEPT NMR spectrum of dye **2**

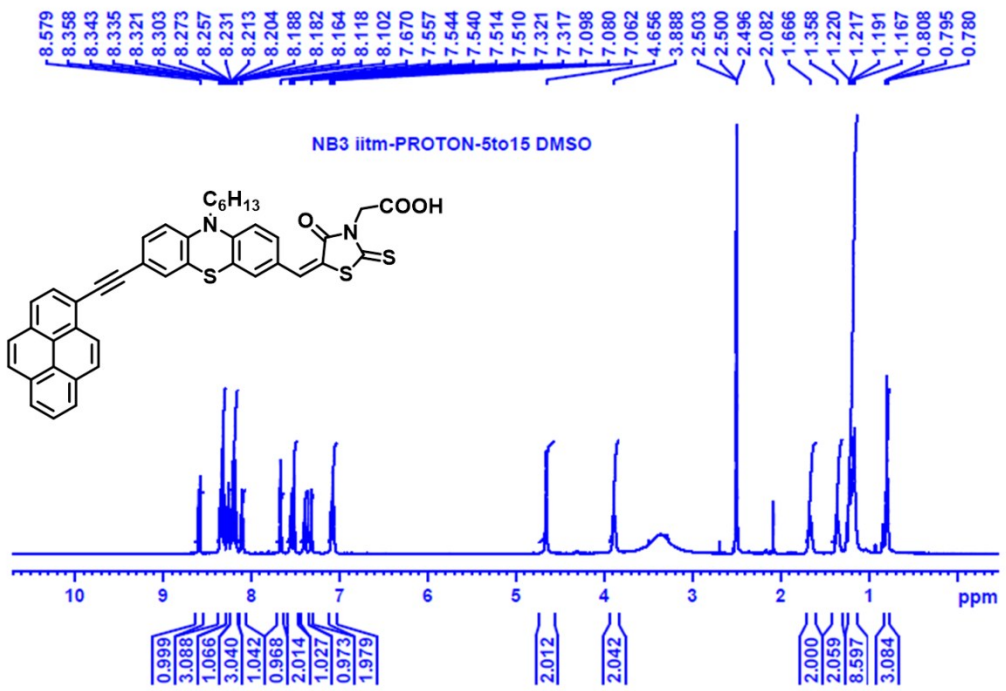


Figure S24. ^{1}H NMR spectrum of dye **3**

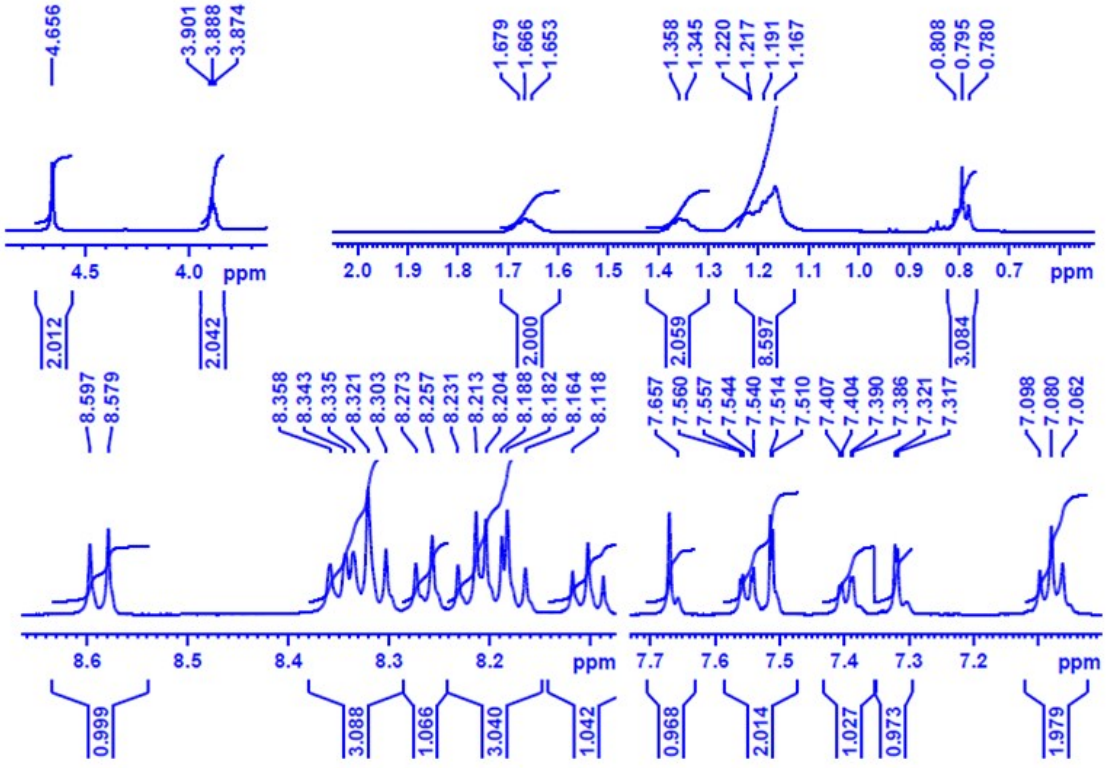


Figure S25. Expanded of ^{1}H NMR spectrum of dye **3**

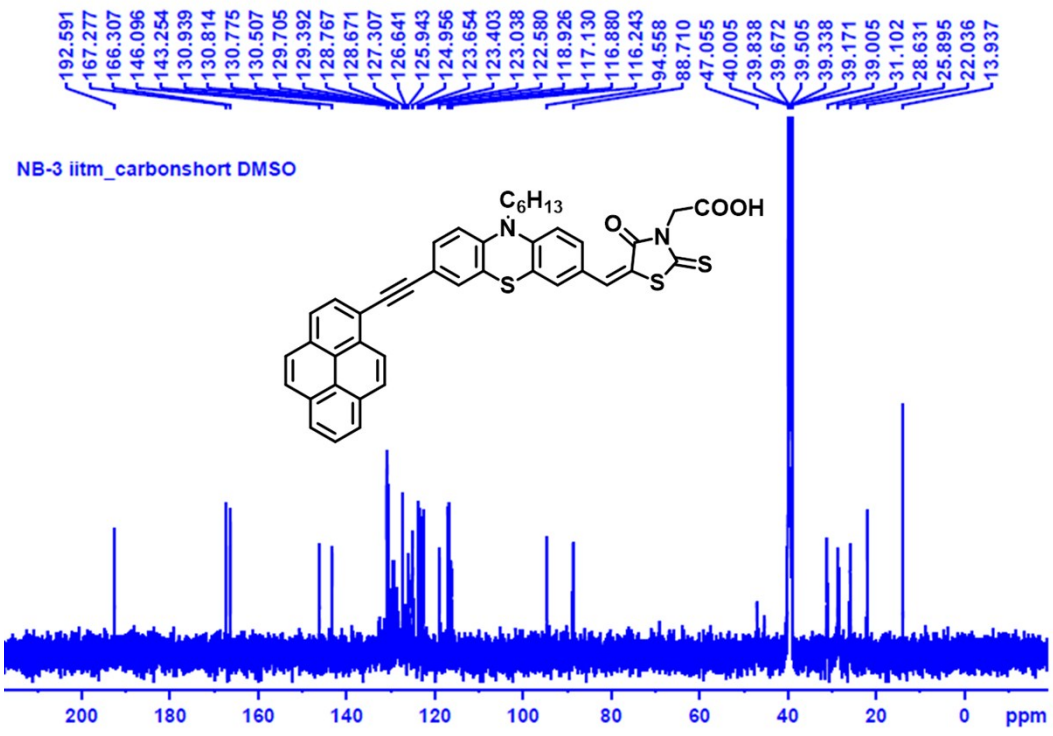


Figure S26. ^{13}C NMR spectrum of dye **3**

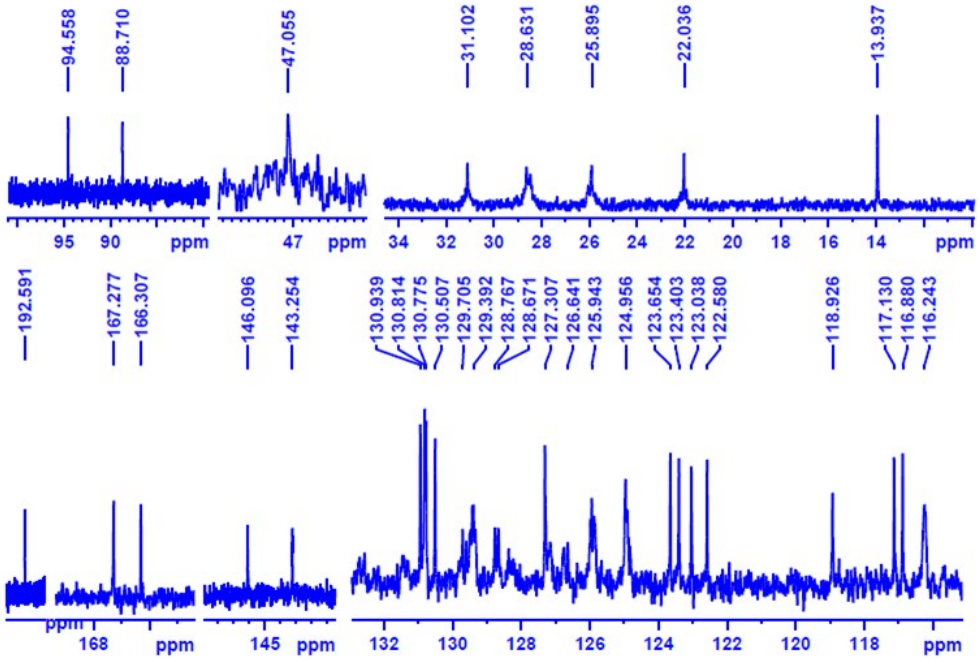


Figure S27. Expanded of ^{13}C NMR spectrum of dye **3**

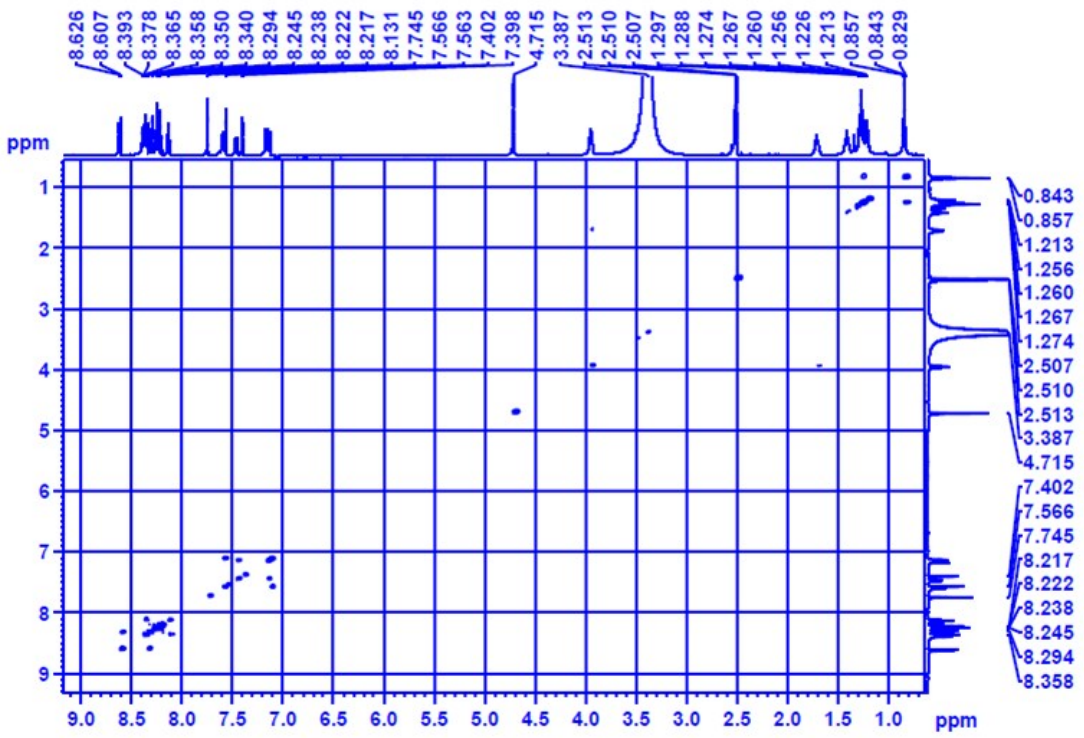


Figure S28. COSY NMR spectrum of dye **3**

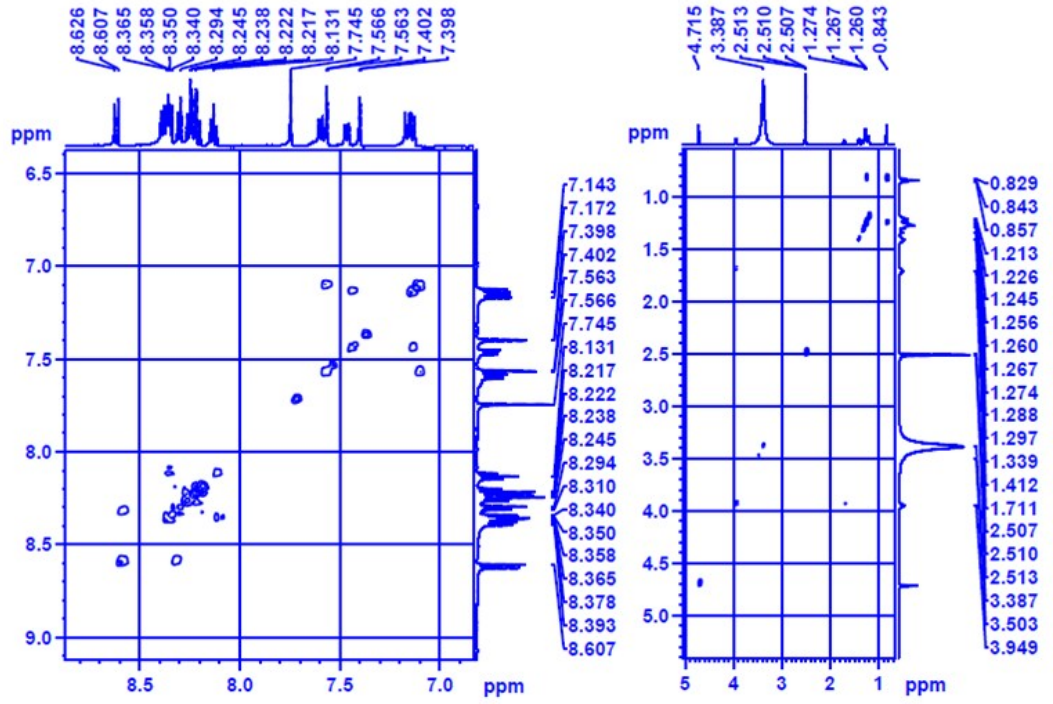


Figure S29. Expanded of COSY NMR spectrum of dye **3**

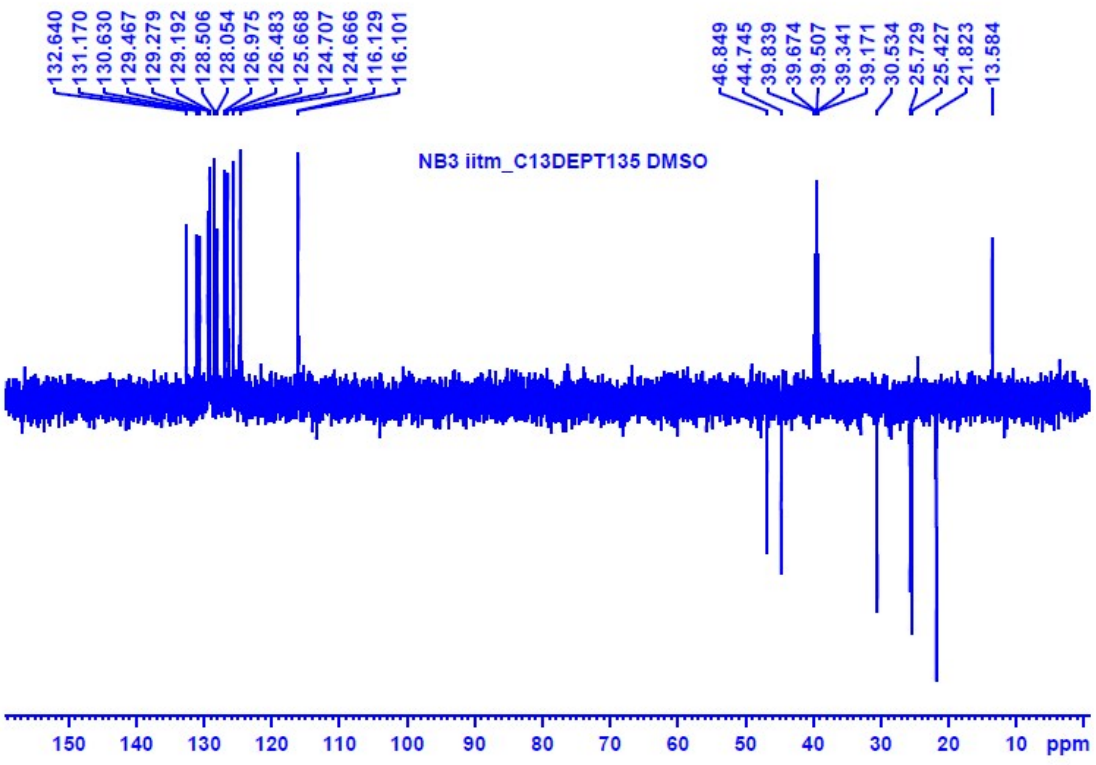


Figure S30. Expanded of COSY NMR spectrum of dye **3**

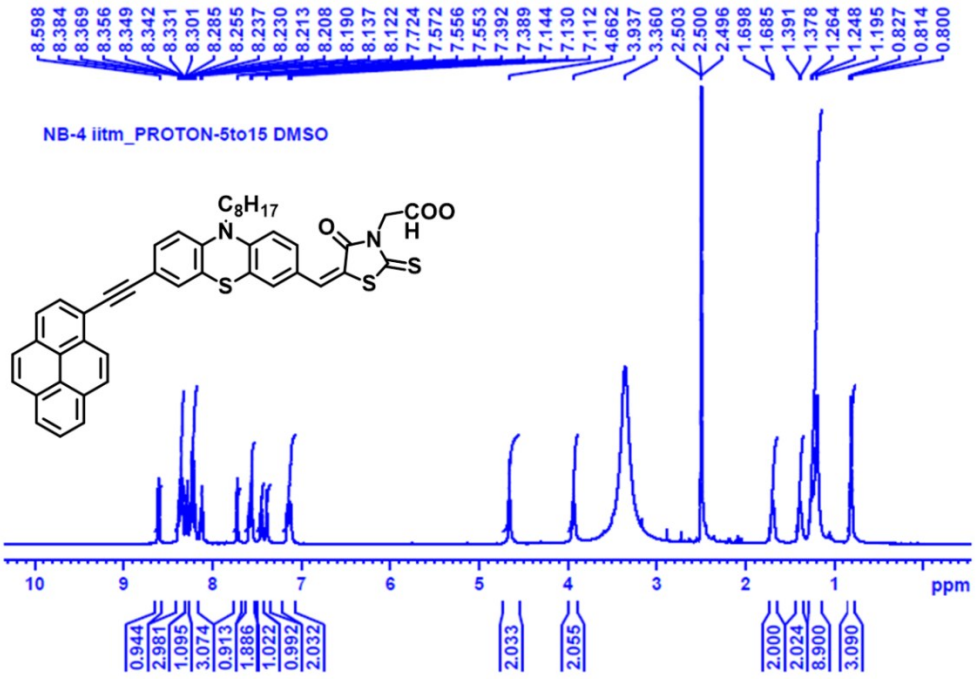


Figure S31. ^{1}H NMR spectrum of dye **4**

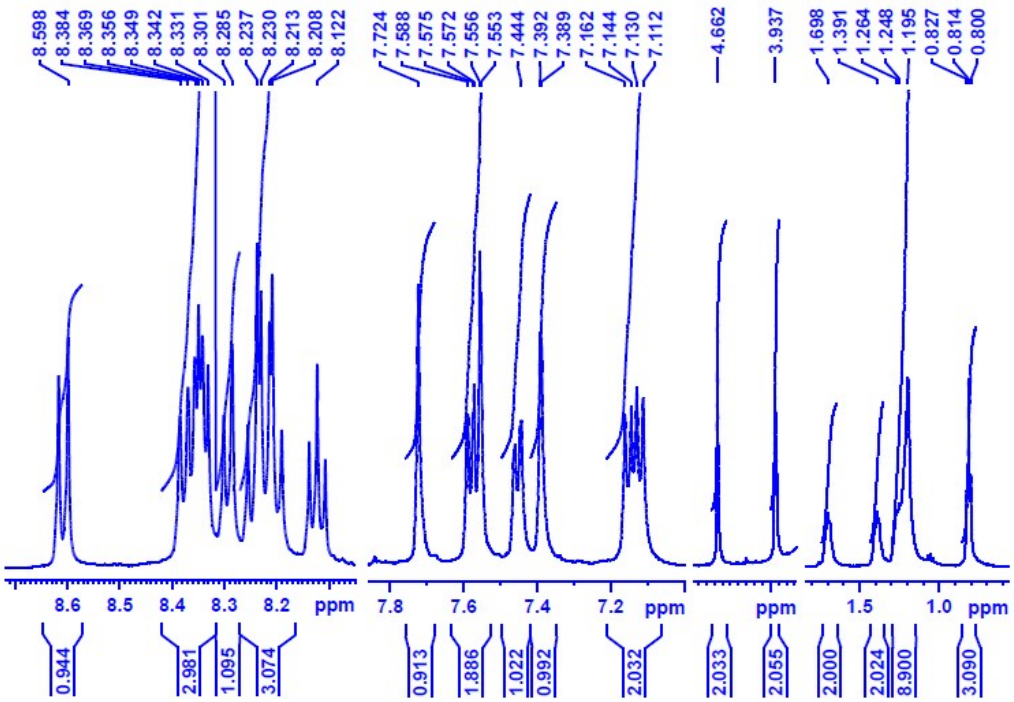


Figure S32. Expanded of ^{1}H NMR spectrum of dye **4**

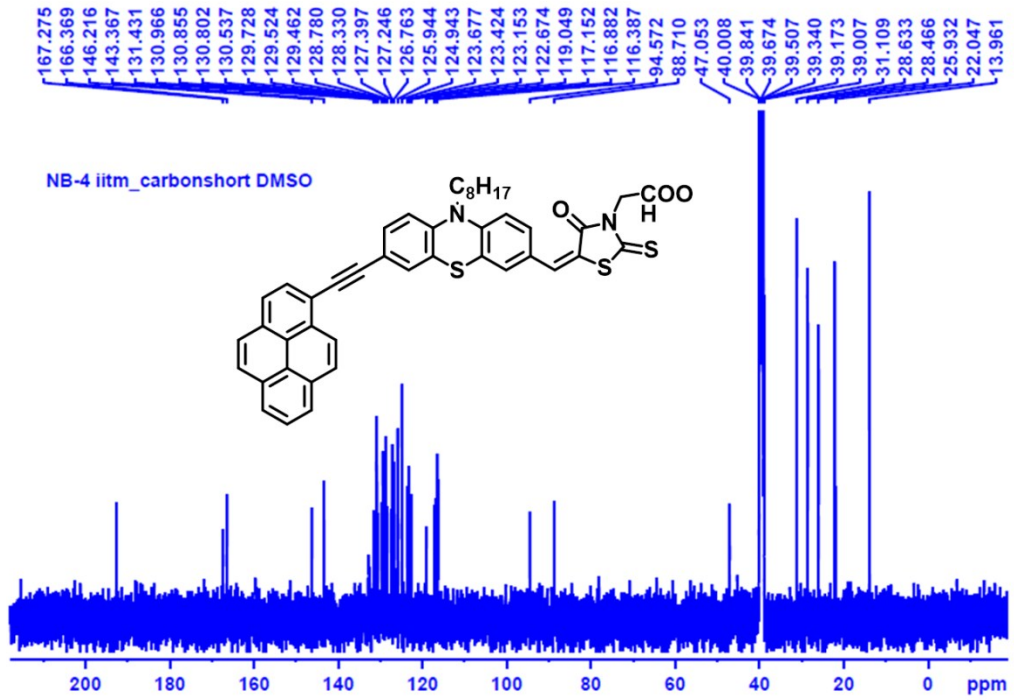


Figure S33. ^{13}C NMR spectrum of dye **4**

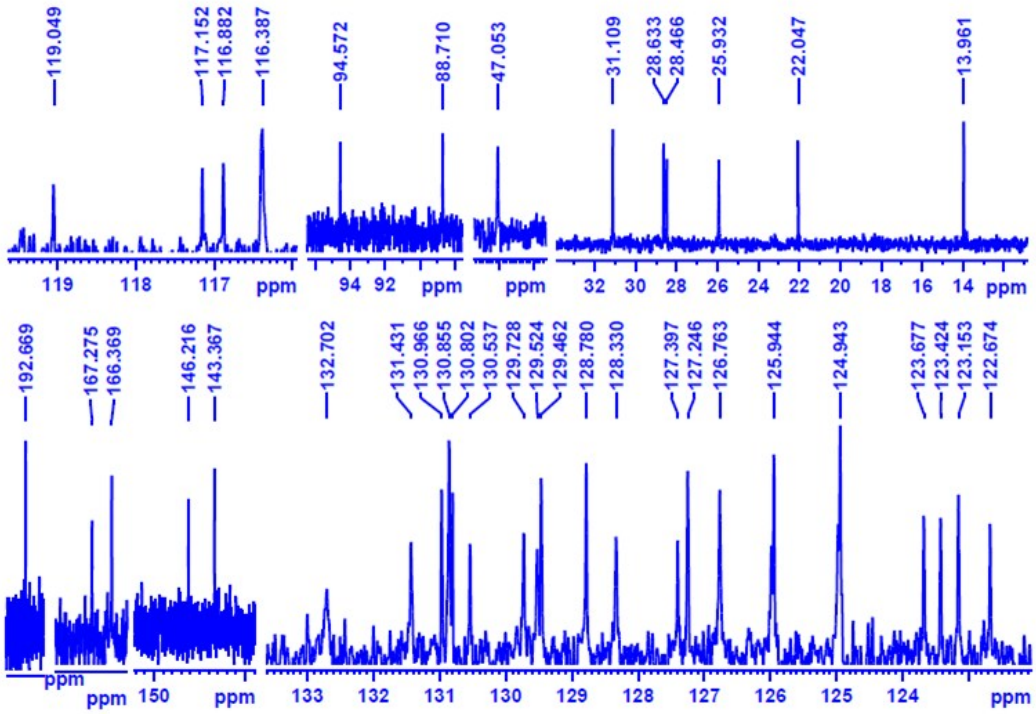


Figure S34. Expanded of ^{13}C NMR spectrum of dye **4**

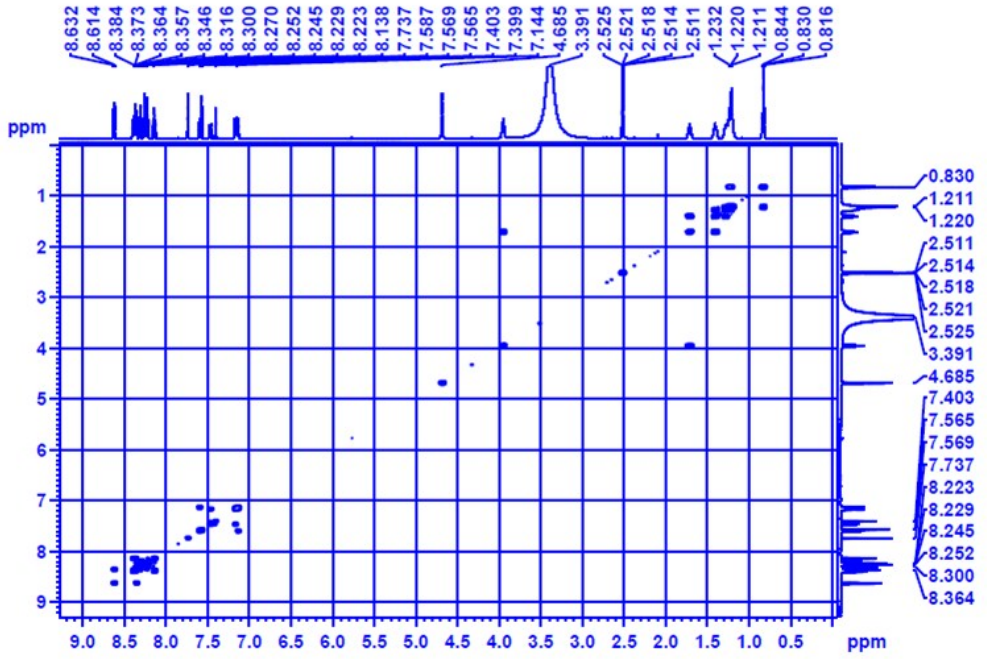


Figure S35. COSY NMR spectrum of dye **4**

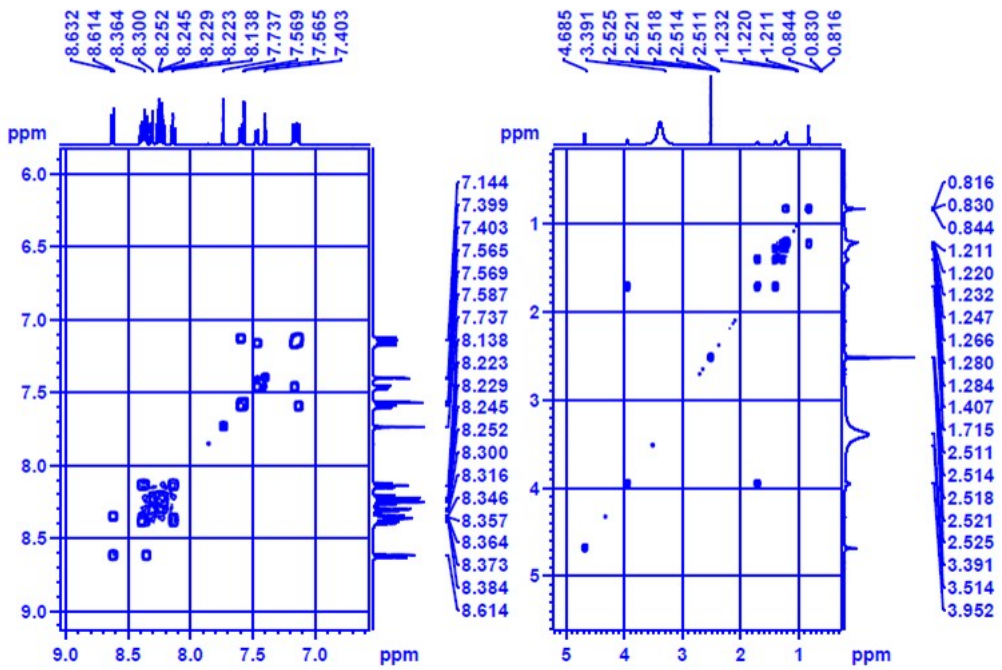


Figure S36. Expanded of COSY NMR spectrum of dye **4**

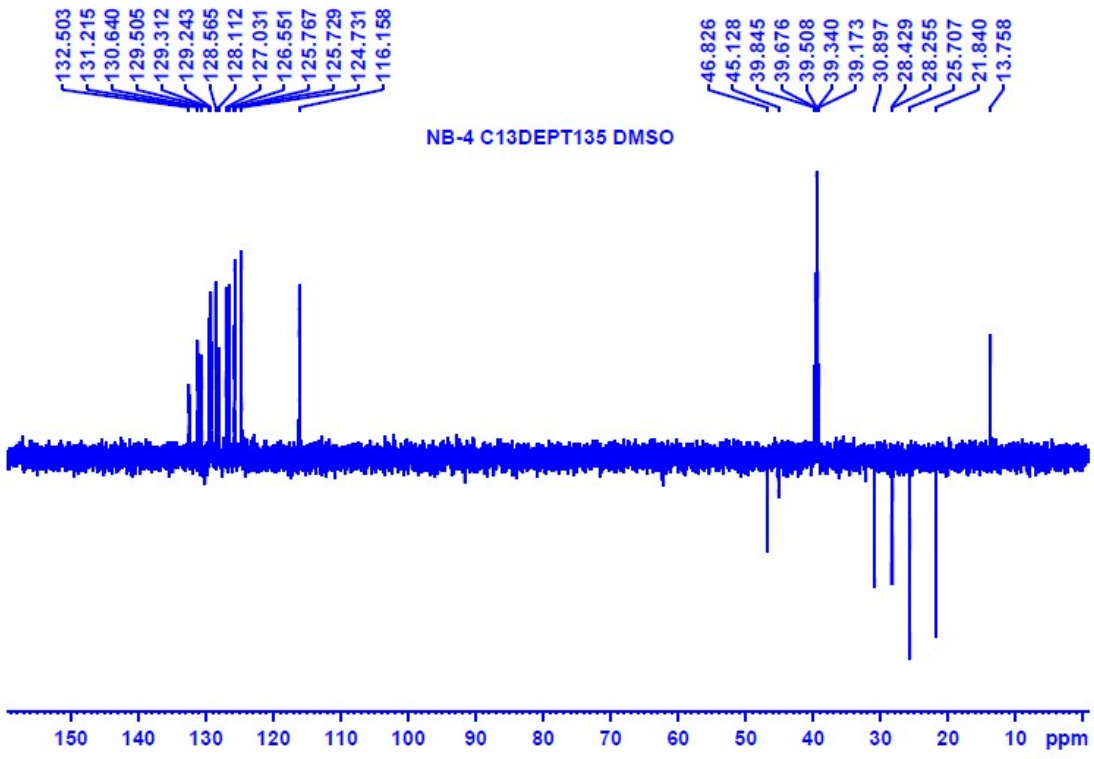


Figure S37. DEPT NMR spectrum of dye **4**

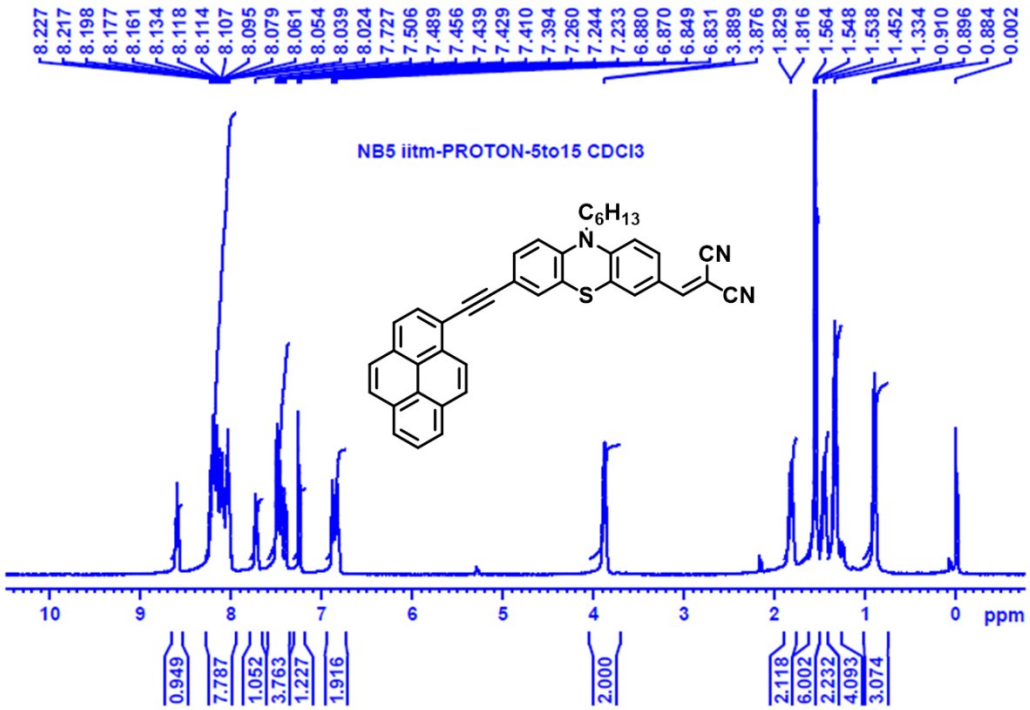


Figure S38. [1]H NMR spectrum of dye **5**

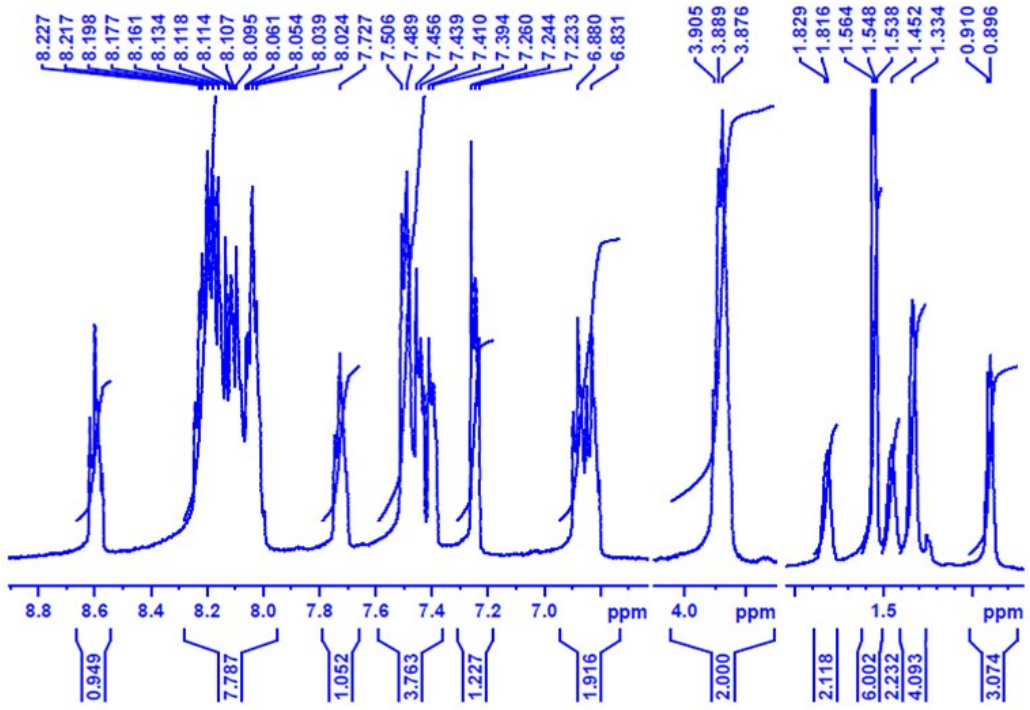


Figure S39. Expanded [1]H NMR spectrum of dye **5**

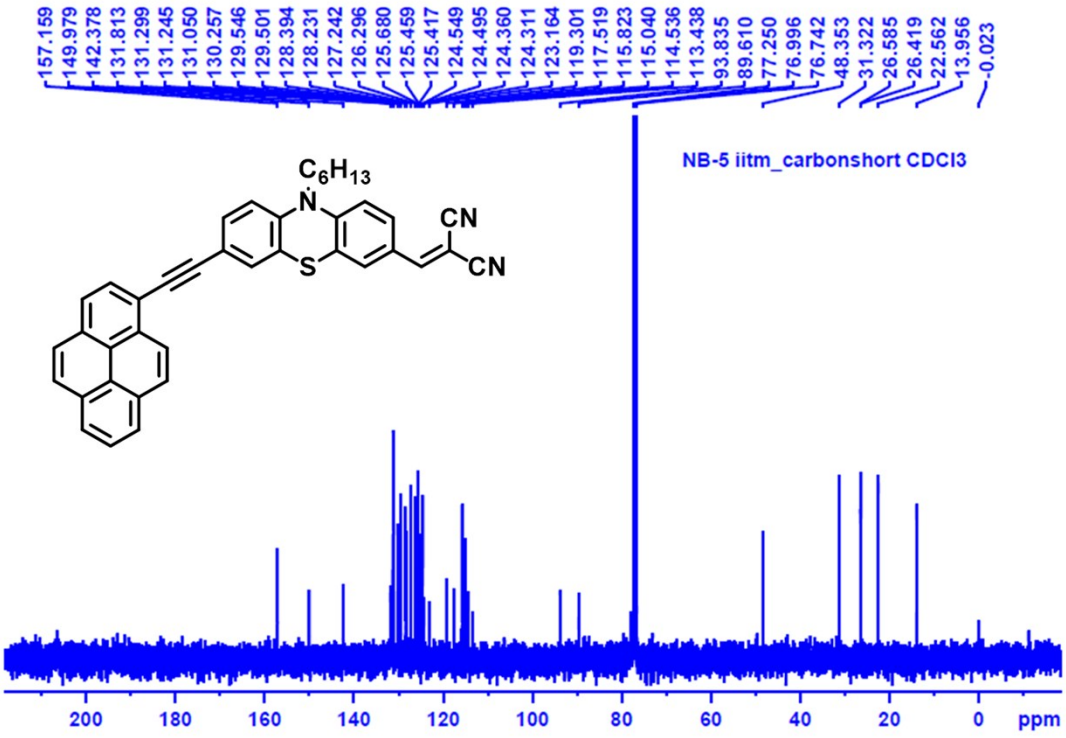


Figure S40. ^{13}C NMR spectrum of dye **5**

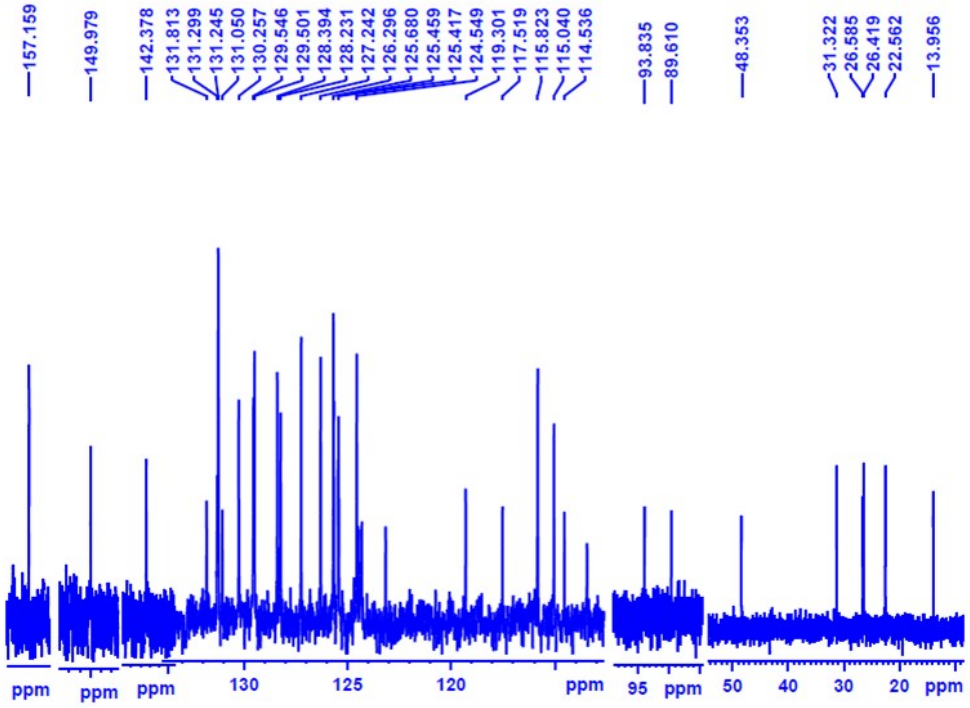


Figure S41. Expanded of ^{13}C NMR spectrum of dye **5**

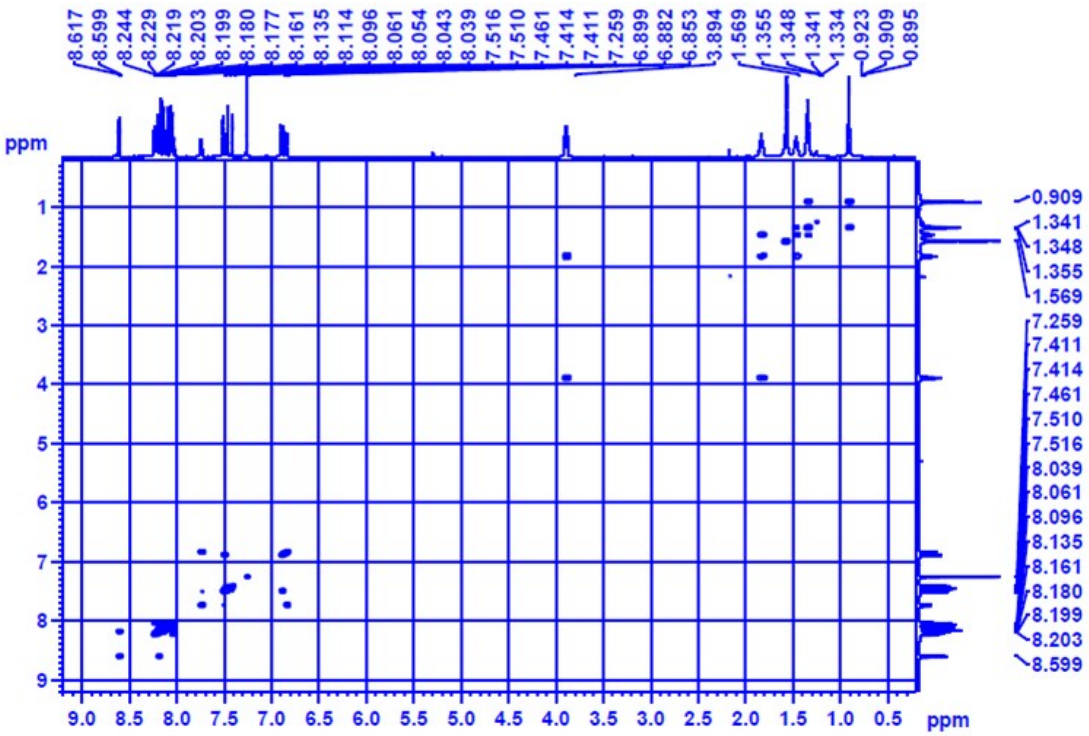


Figure S42. COSY NMR spectrum of dye **5**

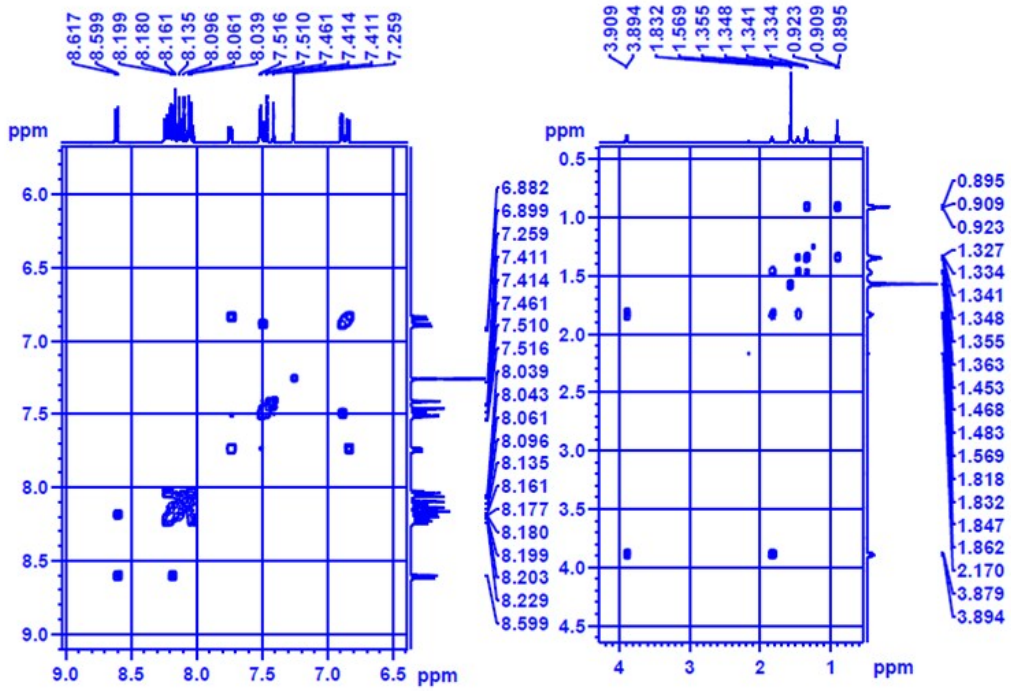


Figure S43. Expanded of COSY NMR spectrum of dye **5**

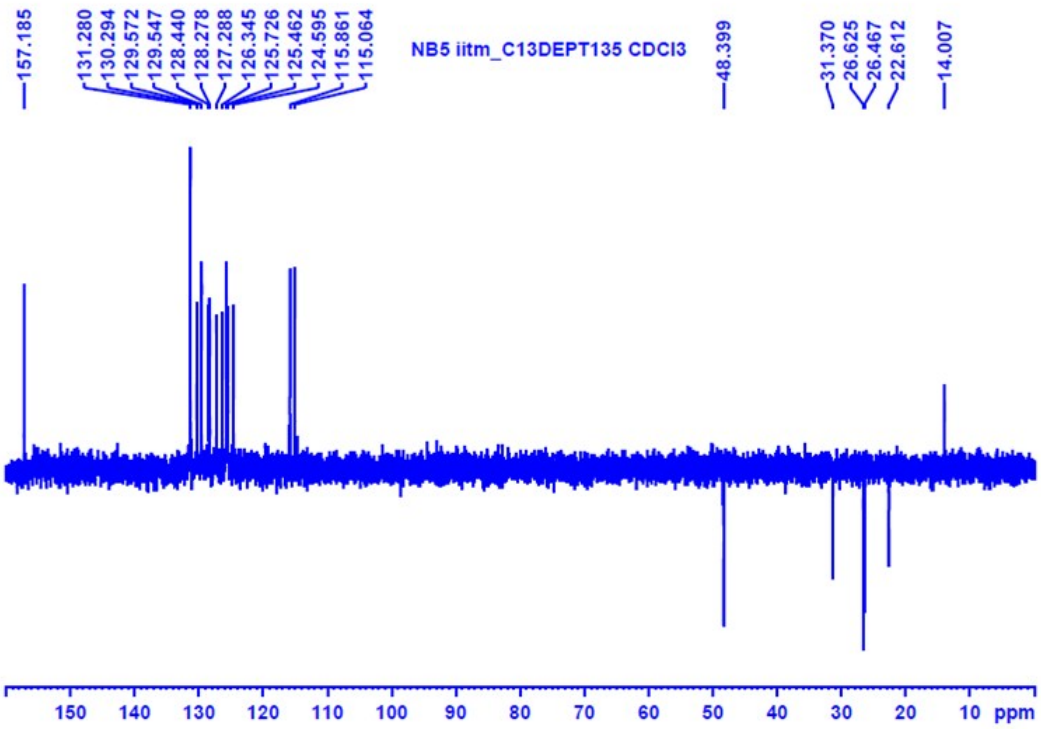


Figure S44. DEPT NMR spectrum of dye **5**

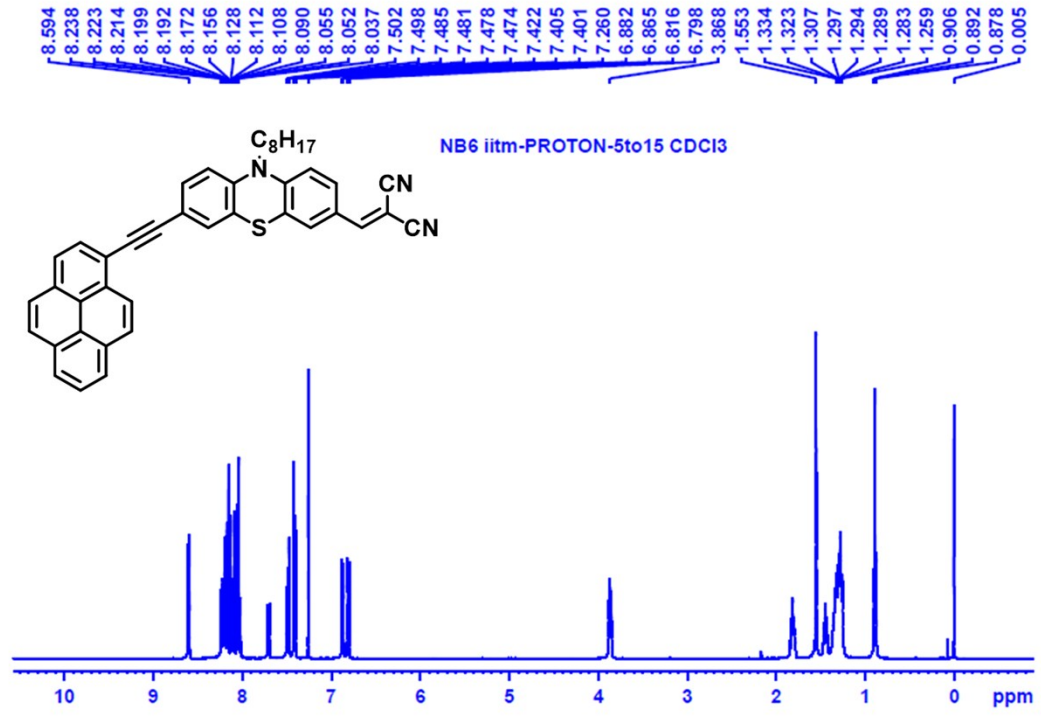


Figure S45. ^{1}H NMR spectrum of dye **6**

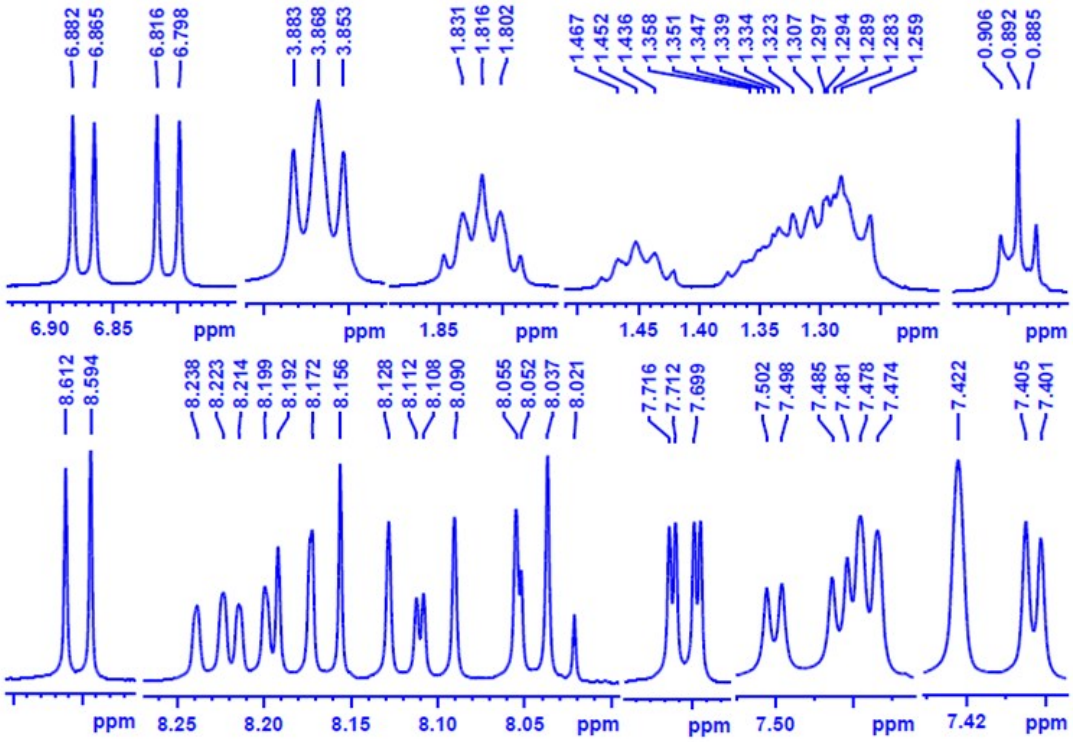


Figure S46. Expanded of ^{1}H NMR spectrum of dye **6**

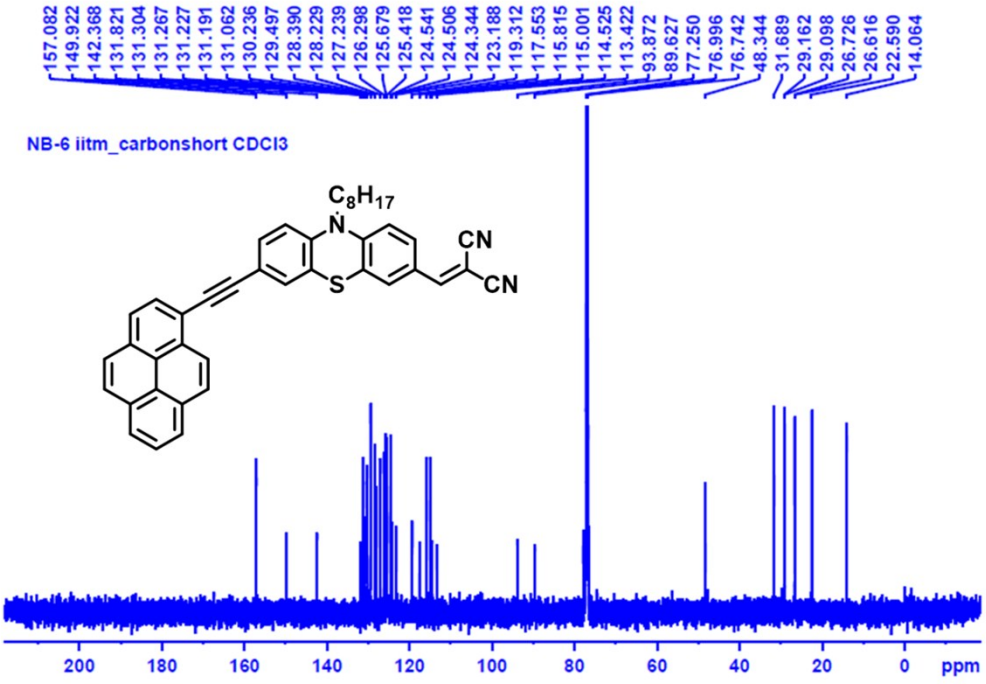


Figure S47. ^{13}C NMR spectrum of dye **6**

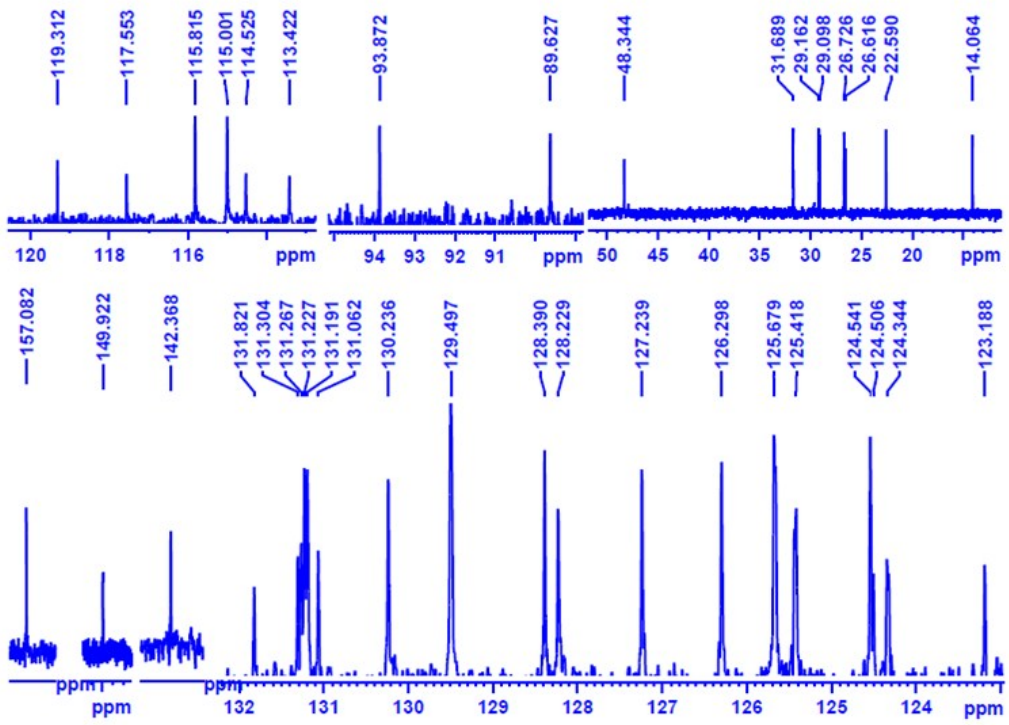


Figure S48. Expanded of ^{13}C NMR spectrum of dye **6**

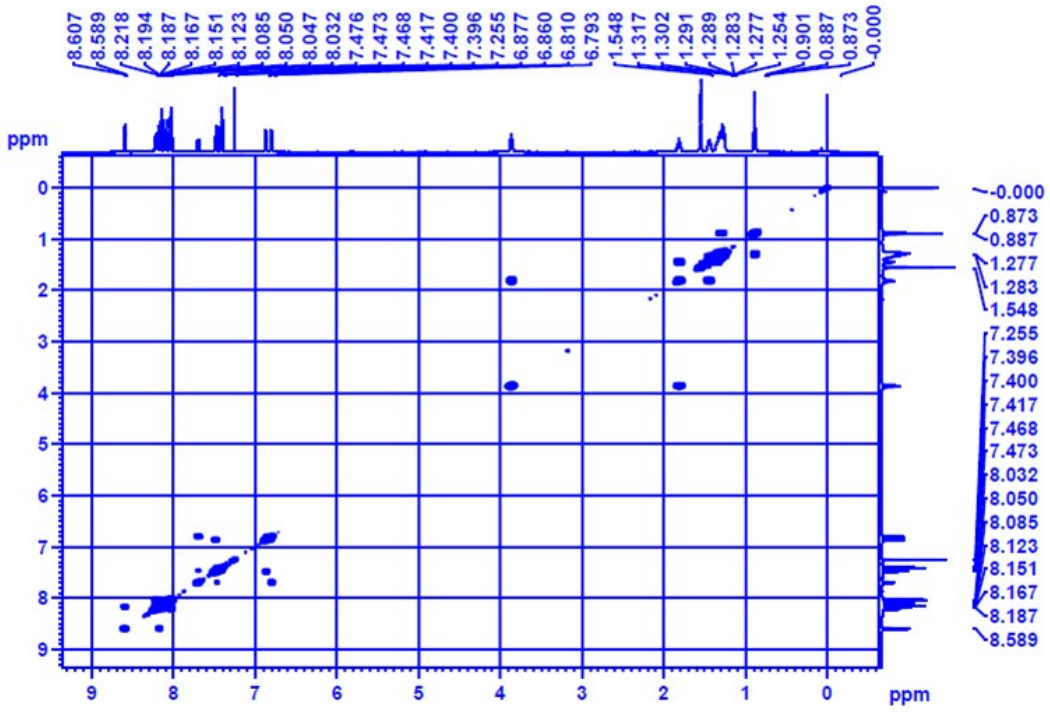


Figure S49. COSY NMR spectrum of dye **6**

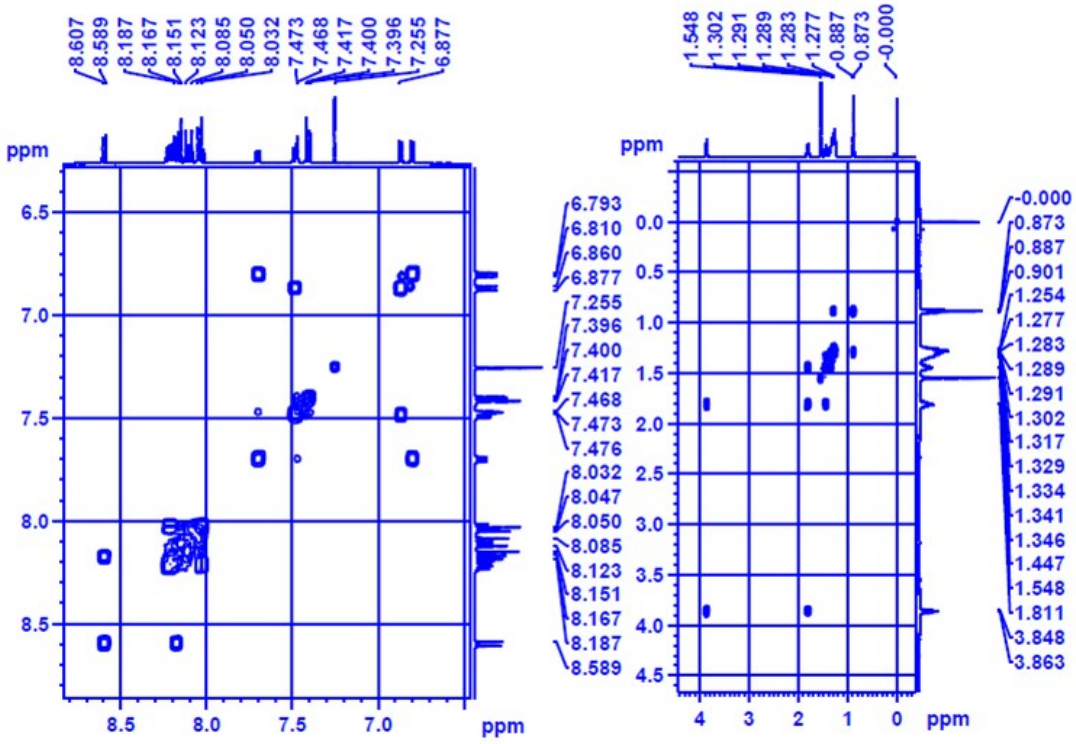


Figure S50. Expanded of COSY NMR spectrum of dye **6**

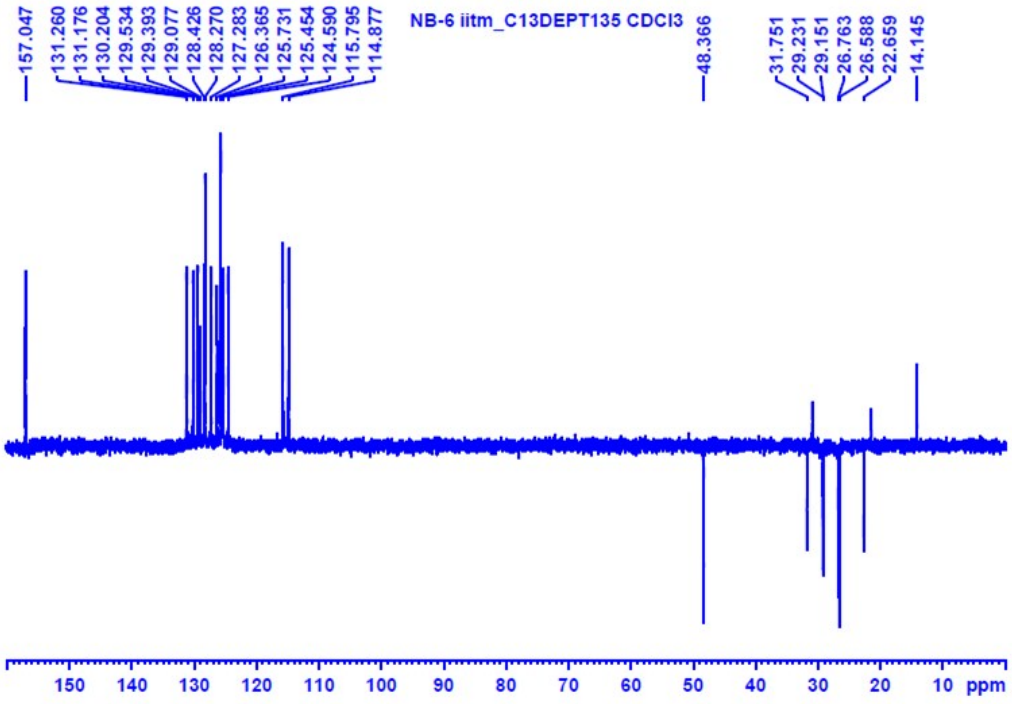


Figure S51. DEPT NMR spectrum of dye **6**

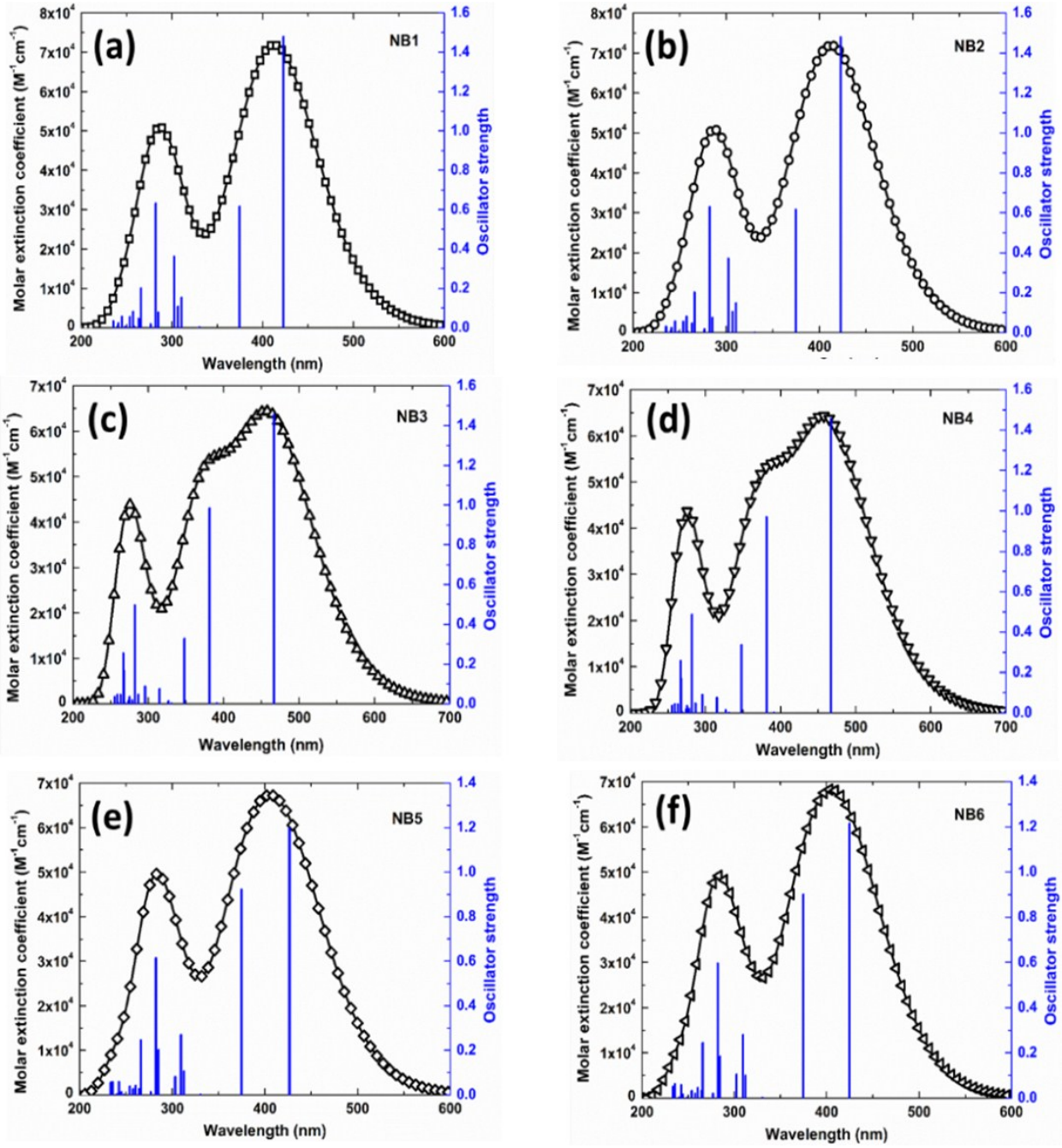


Figure S52. The simulated absorption spectra of the dyes **1-6** (a - f) in acetonitrile solvent.

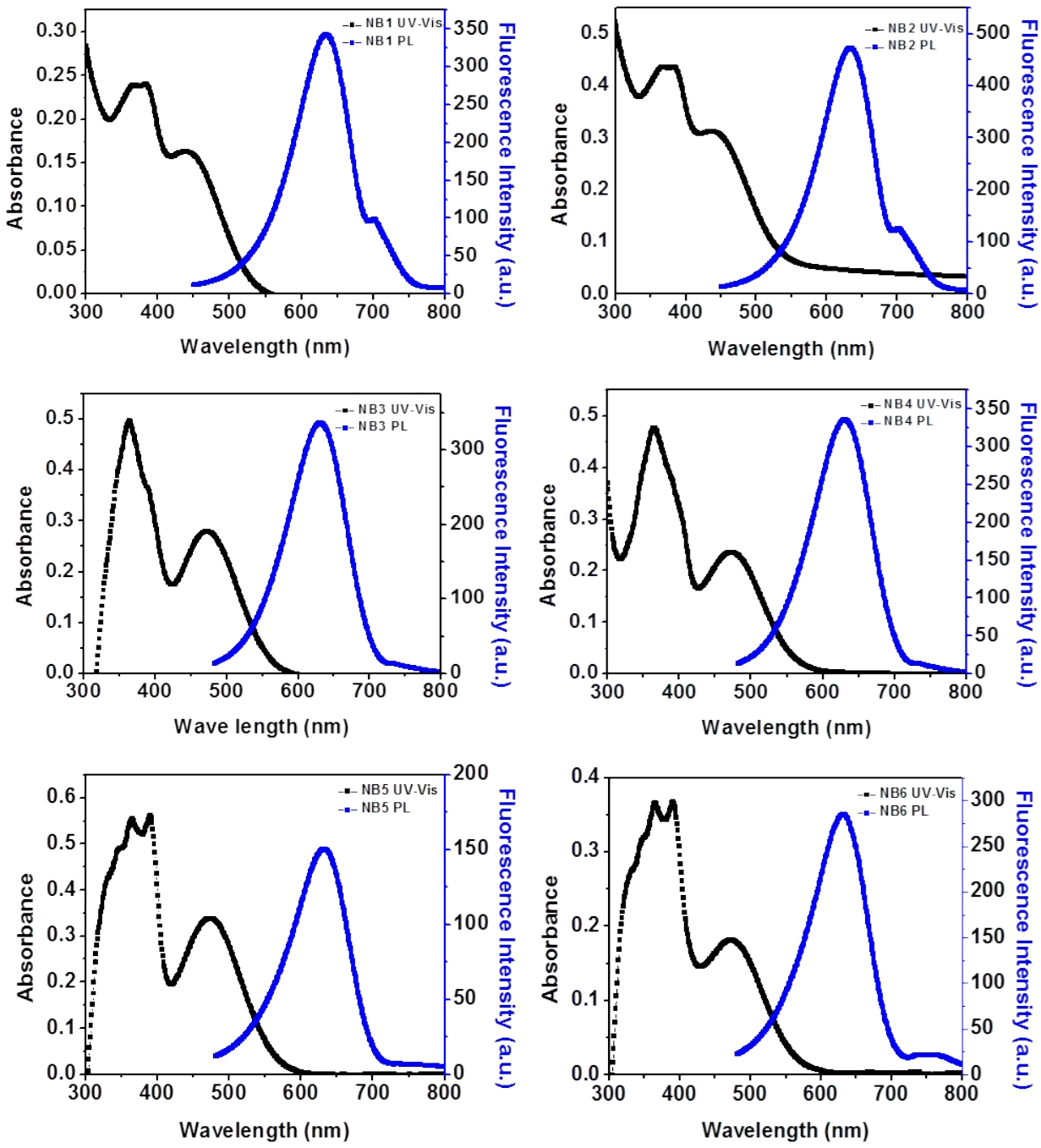


Figure S53. Absorption and emission spectra of the dyes **1**-**6** (a – f) in acetonitrile

Table S2.The DFT calculated dihedral angle of the dyes

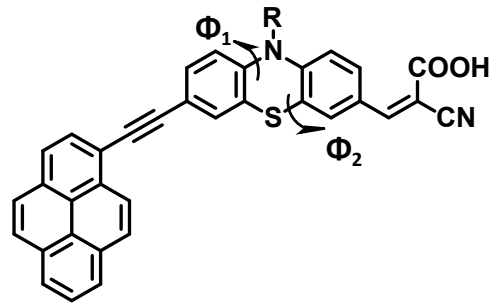
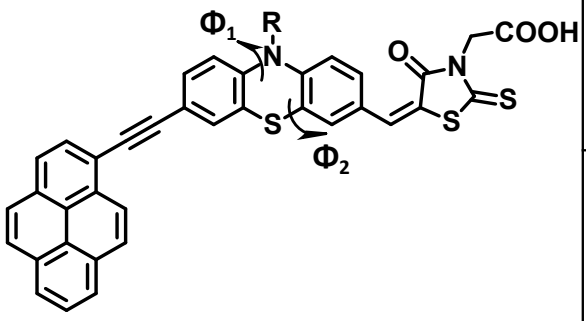
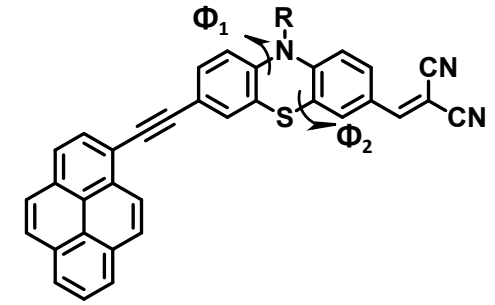
	Dye	Dihedral angle φ
	NB1 = R = C_6H_{13}	$\varphi_1 = 147^0$, $\varphi_2 = 143^0$
	NB2 = R = C_8H_{17}	$\varphi_1 = 148^0$, $\varphi_2 = 143^0$
	NB3 = R = C_6H_{13}	$\varphi_1 = 148^0$, $\varphi_2 = 144^0$
	NB4 = R = C_8H_{17}	$\varphi_1 = 148^0$, $\varphi_2 = 144^0$
	NB5 = R = C_6H_{13}	$\varphi_1 = 147^0$, $\varphi_2 = 143^0$
	NB6 = R = C_8H_{17}	$\varphi_1 = 147^0$, $\varphi_2 = 143^0$

Table S3. Frontier molecular orbitals of the dyes without pyrene obtained using B3LYP/6-31G* level of theory.

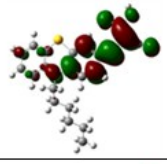
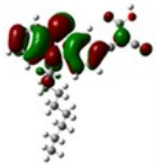
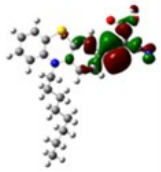
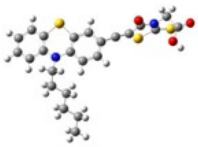
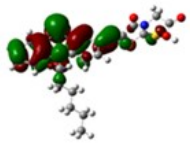
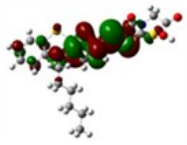
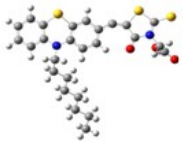
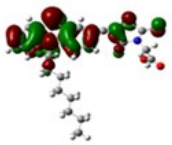
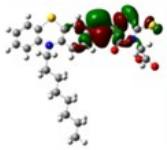
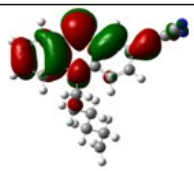
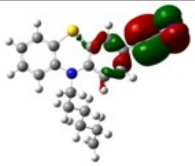
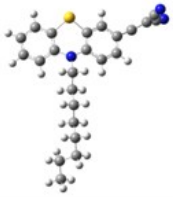
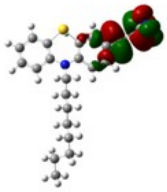
Compound	Optimized structure	HOMO	LUMO
PTC6CNCOOH			
PTC8CNCOOH			
PTC6RhCOOH			
PTC8RhCOOH			
PTC6CN2			
PTC8CN2			

Table S4. Theoretically calculated HOMO, LUMO and energy gap of the dyes without pyrene moiety

Compound	HOMO (eV)	LUMO (eV)	Energy gap (eV)
$PTC_6CNCOOH$	-5.44	-2.57	2.87
$PTC_8CNCOOH$	-5.44	-2.57	2.87
$PTC_6RhCOOH$	-5.63	-3.08	2.55
$PTC_8RhCOOH$	-5.41	-2.91	2.50
PTC_6CN2	-5.77	-3.17	2.60
PTC_8CN2	-5.79	-3.18	2.61