Room Temperature, Deep-Red/NIR-Emissive, C_3-Symmetric (n,π-conjugated) Columnar Liquid Crystals: C_{3h}-Tris(keto-hydrazone)s

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[c] *Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039,* ***India.***

* Corresponding author : yelamaggad@cens.res.in; yelamaggad@gmail.com

Supporting Information

Contents

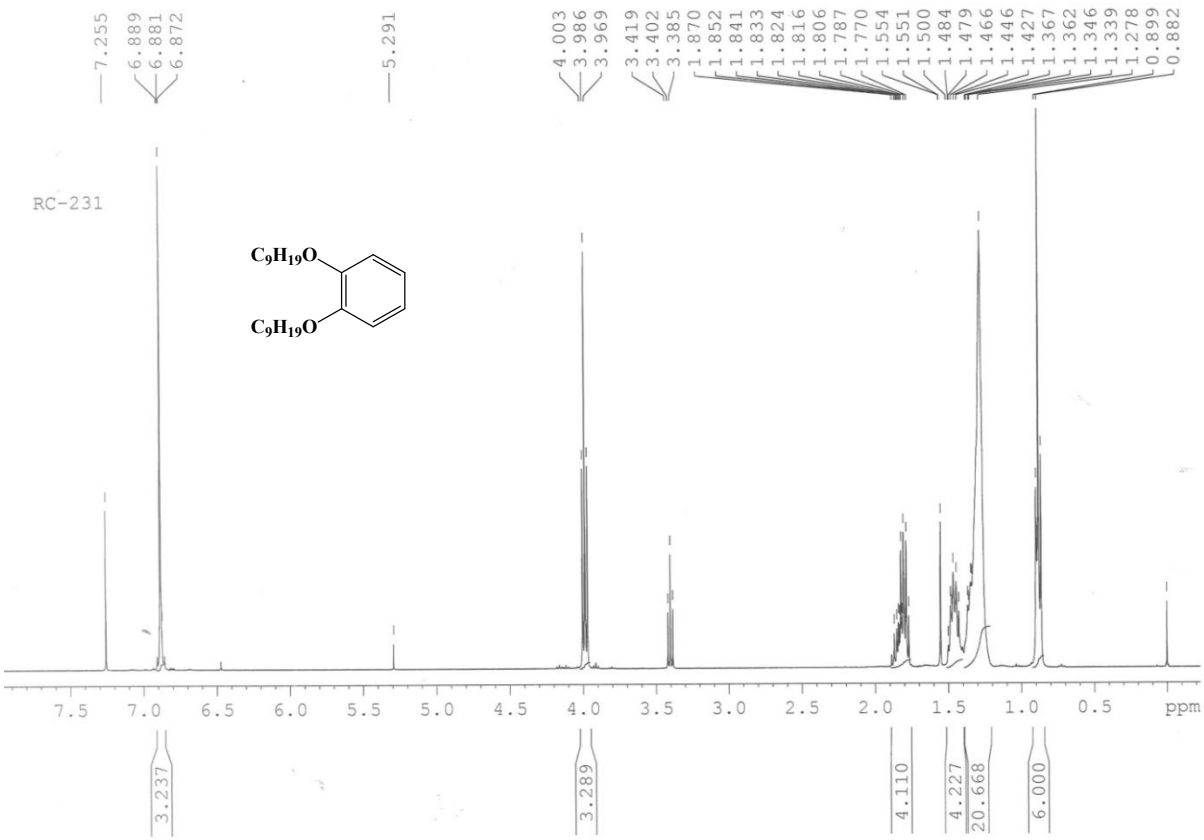


Figure S1. [1]H NMR spectrum of compound **1d** (400MHz; $CDCl_3$)

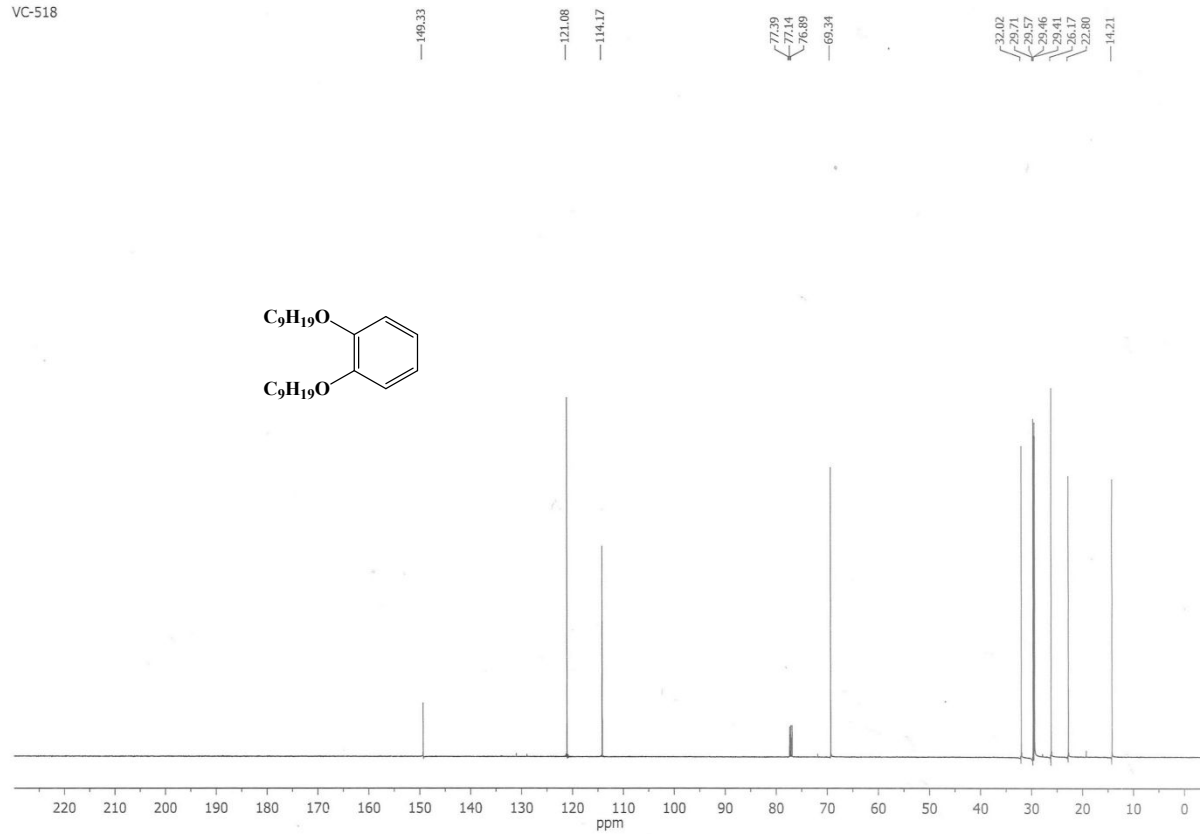


Figure S2. [13]C NMR spectrum of compound **1d** (100MHz; $CDCl_3$)

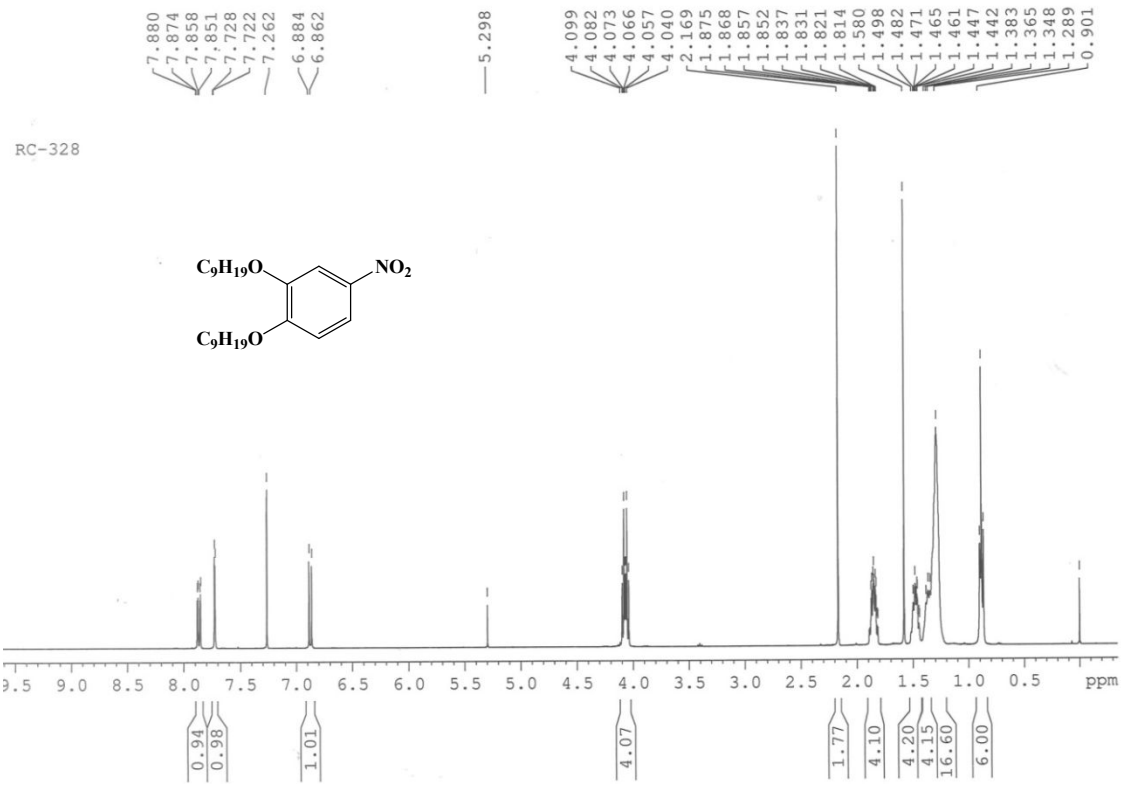


Figure S3. ^{1}H NMR spectrum of compound **2d** (400MHz; $CDCl_3$)

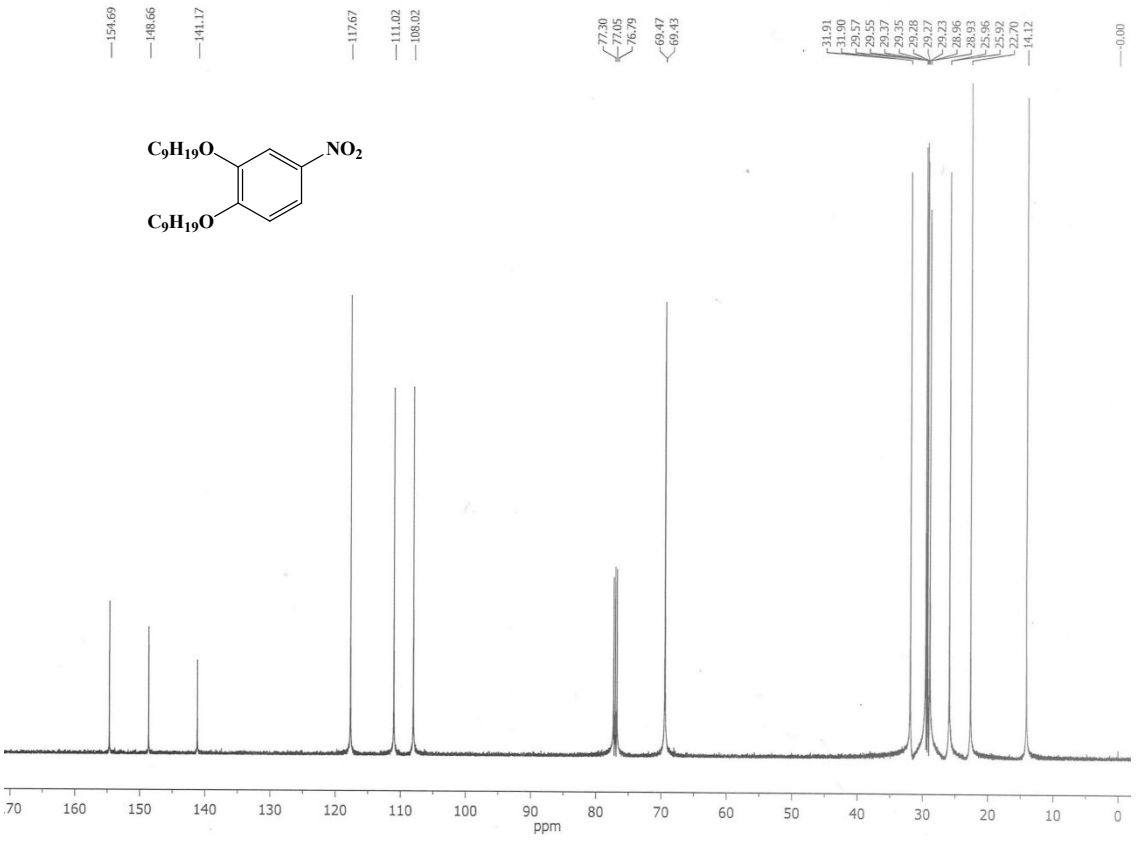


Figure S4. ^{13}C NMR spectrum of compound **2d** (100MHz; $CDCl_3$)

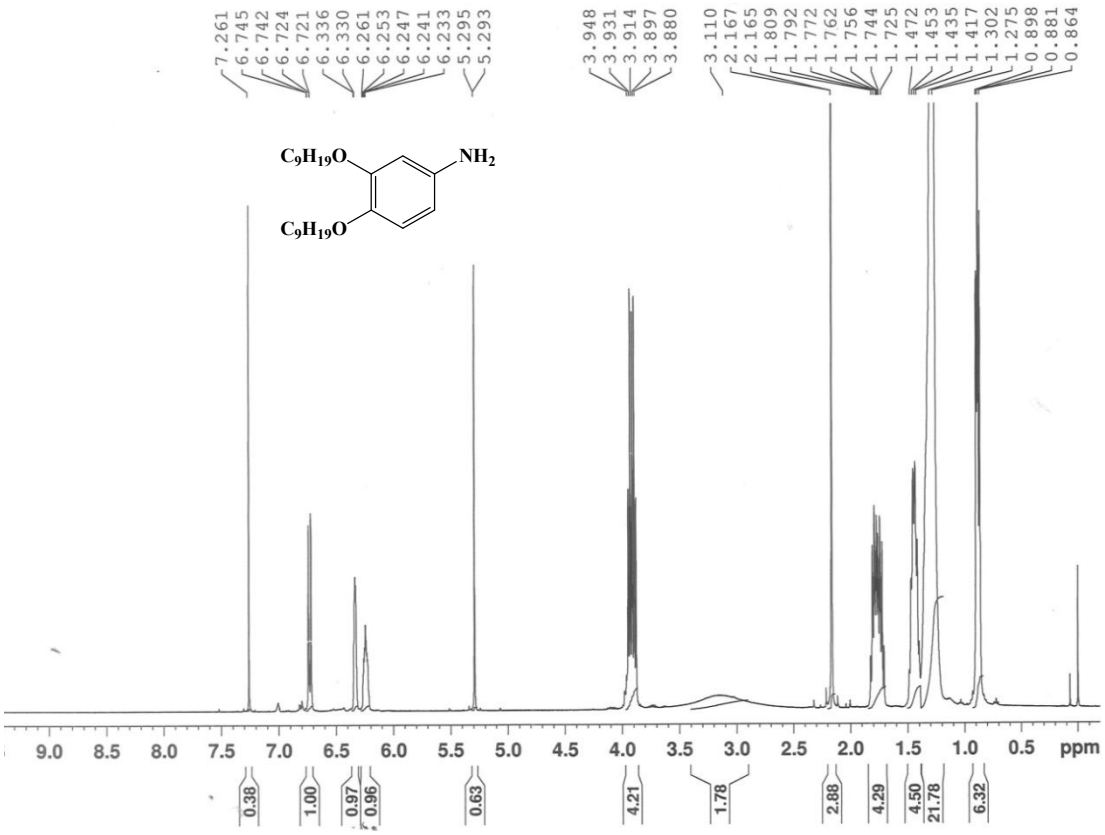


Figure S5. [1]H NMR spectrum of compound **3d** (400MHz; $CDCl_3$)

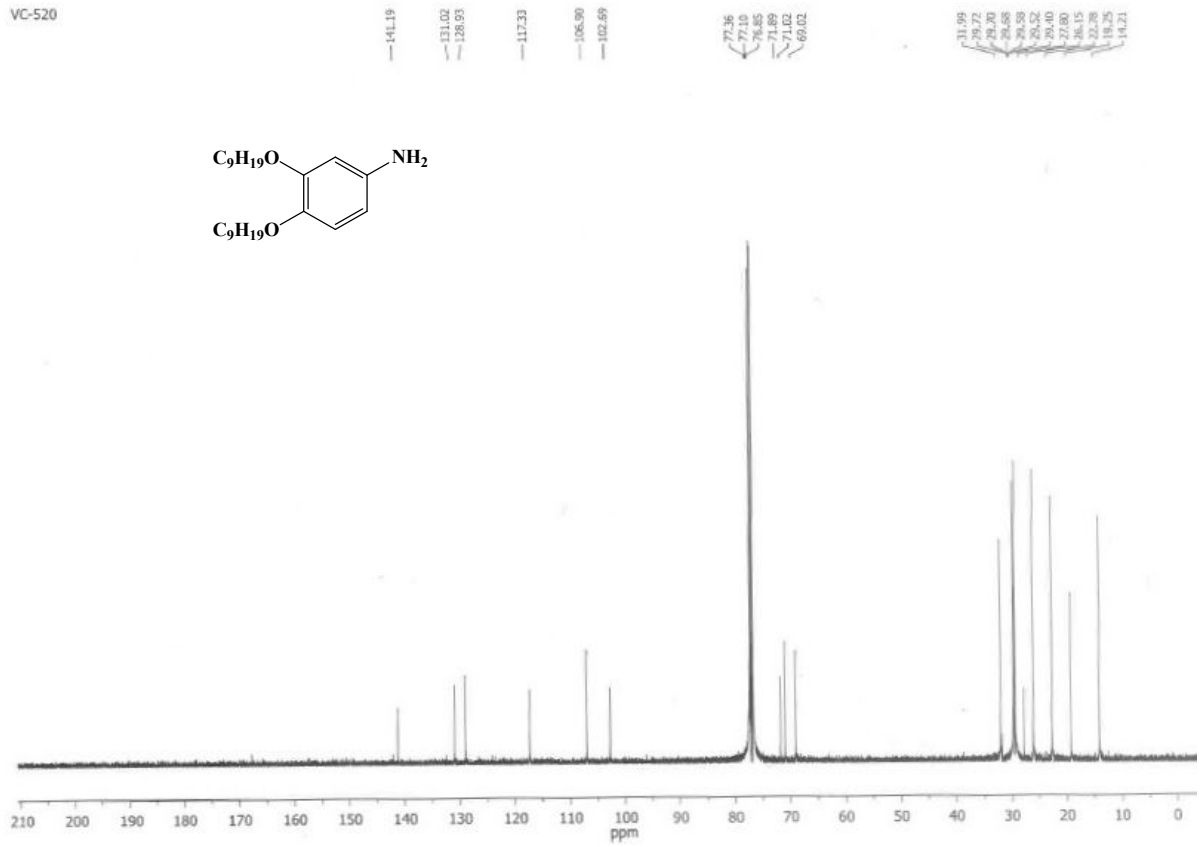


Figure S6. ^{13}C NMR spectrum of compound **3d** (100MHz; $CDCl_3$)

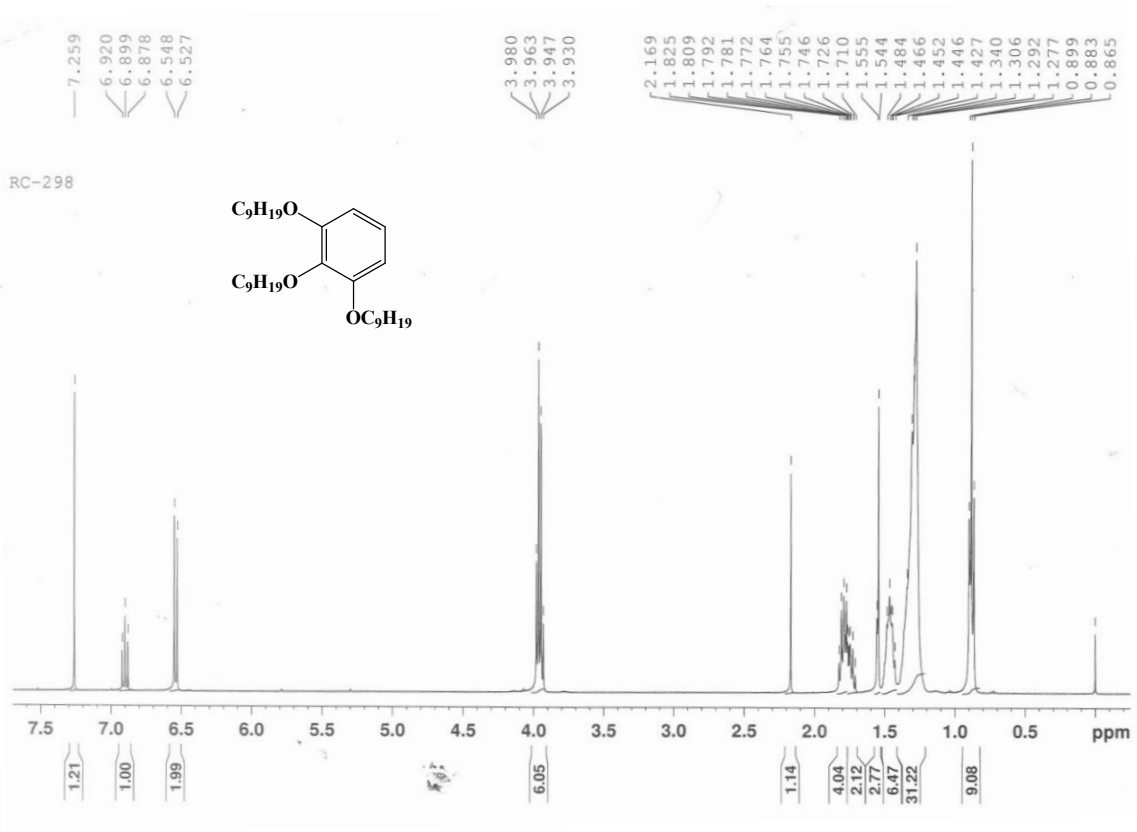


Figure S7. ^{1}H NMR spectrum of compound **4d** (400MHz; $CDCl_3$)

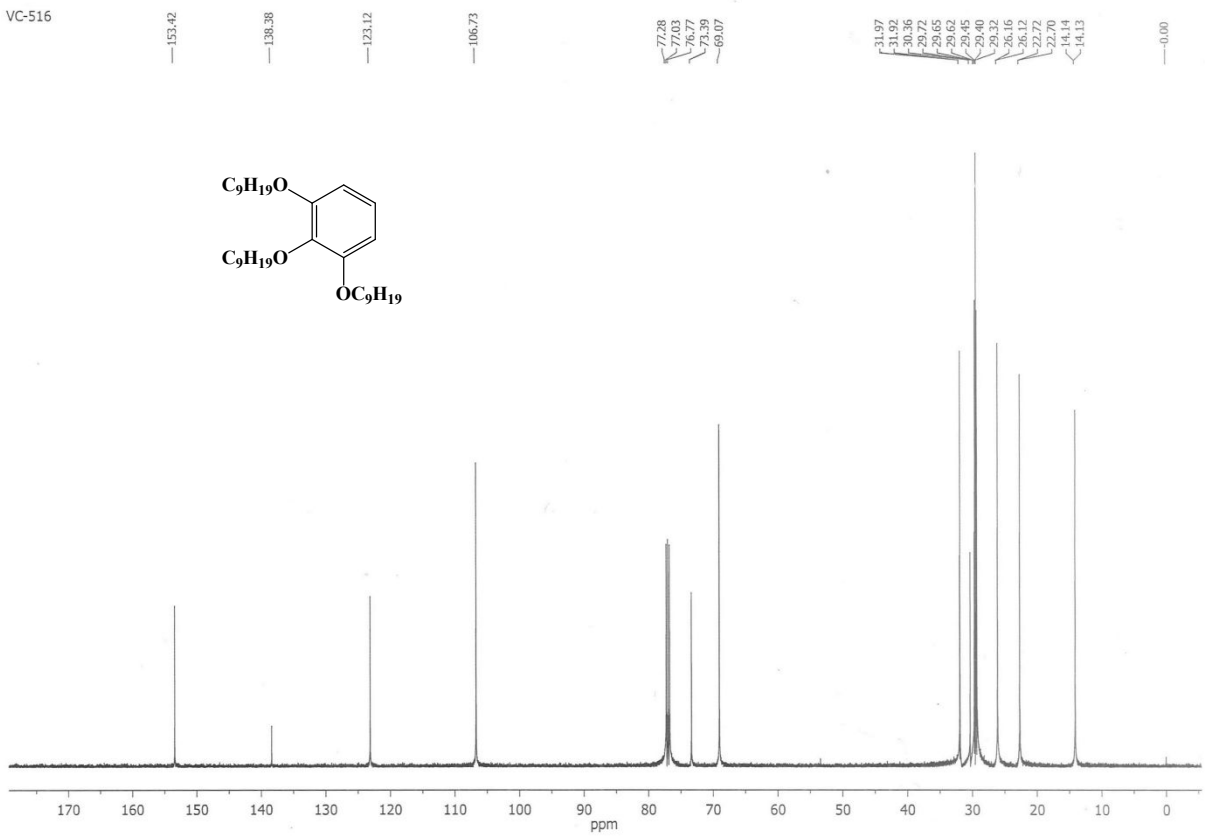


Figure S8. ^{13}C NMR spectrum of compound **4d** (100MHz; $CDCl_3$)

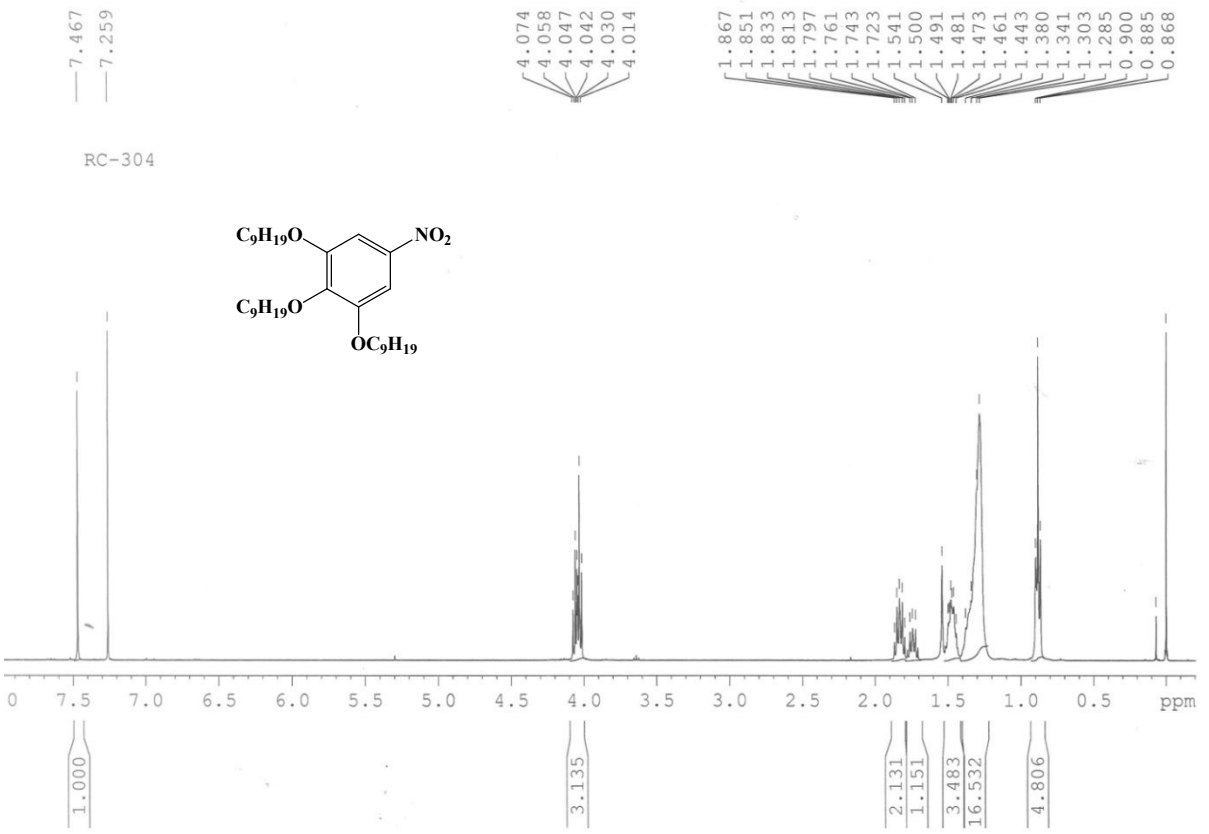


Figure S9. ^{1}H NMR spectrum of compound **5d** (400MHz; $CDCl_3$)

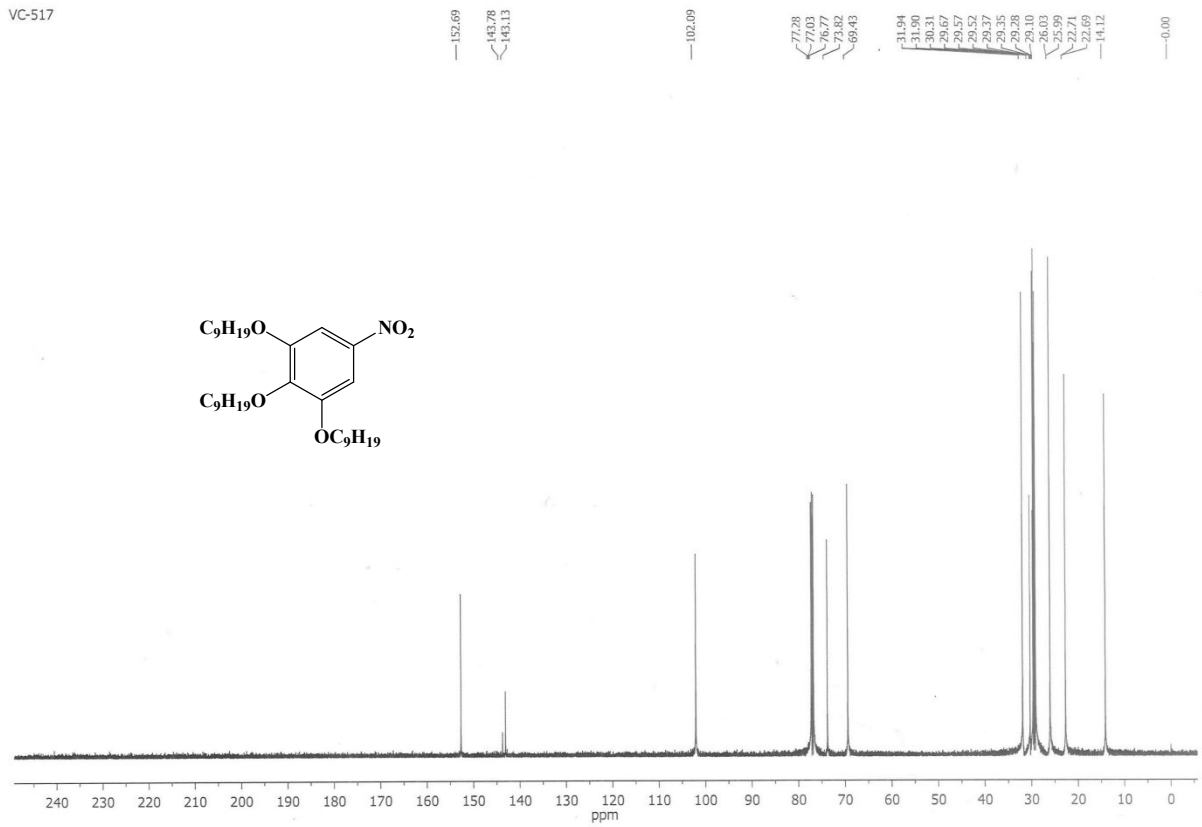


Figure S10. ^{13}C NMR spectrum of compound **5d** (100MHz; $CDCl_3$)

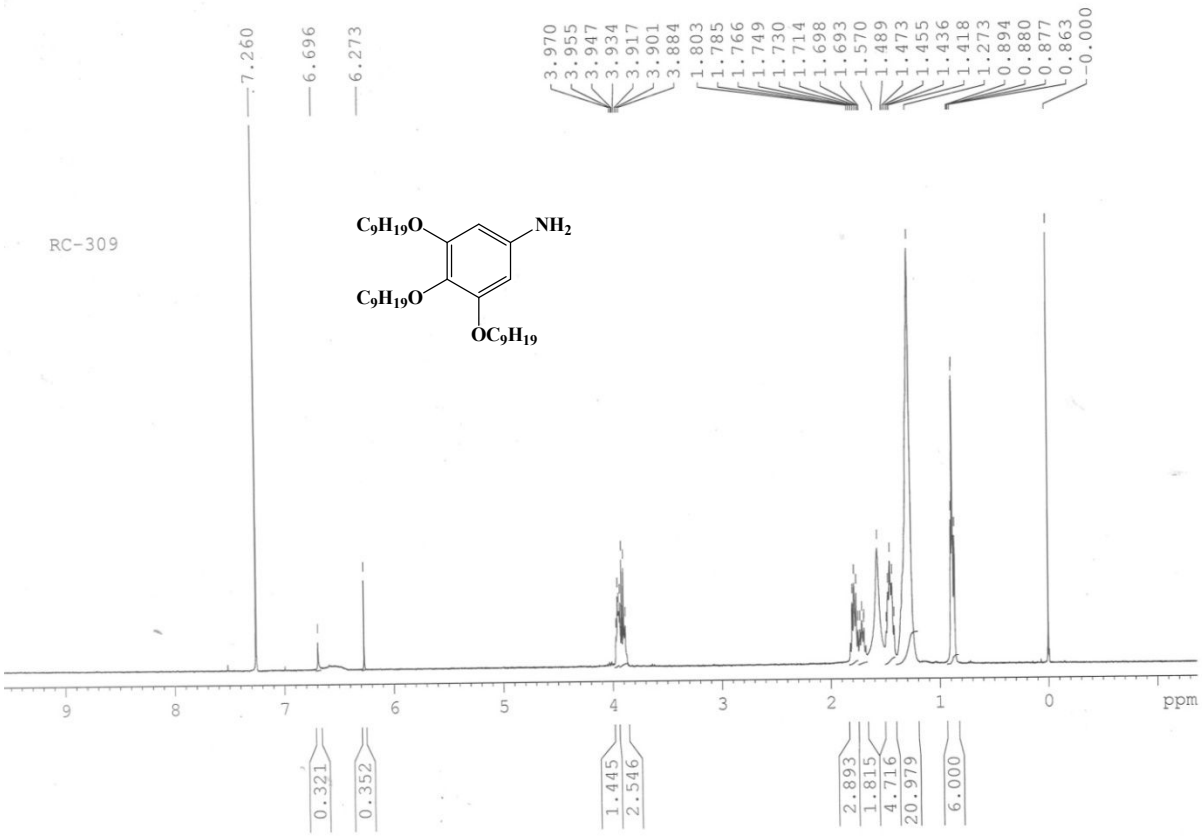


Figure S11. [1]H NMR spectrum of compound **6d** (400MHz; $CDCl_3$)

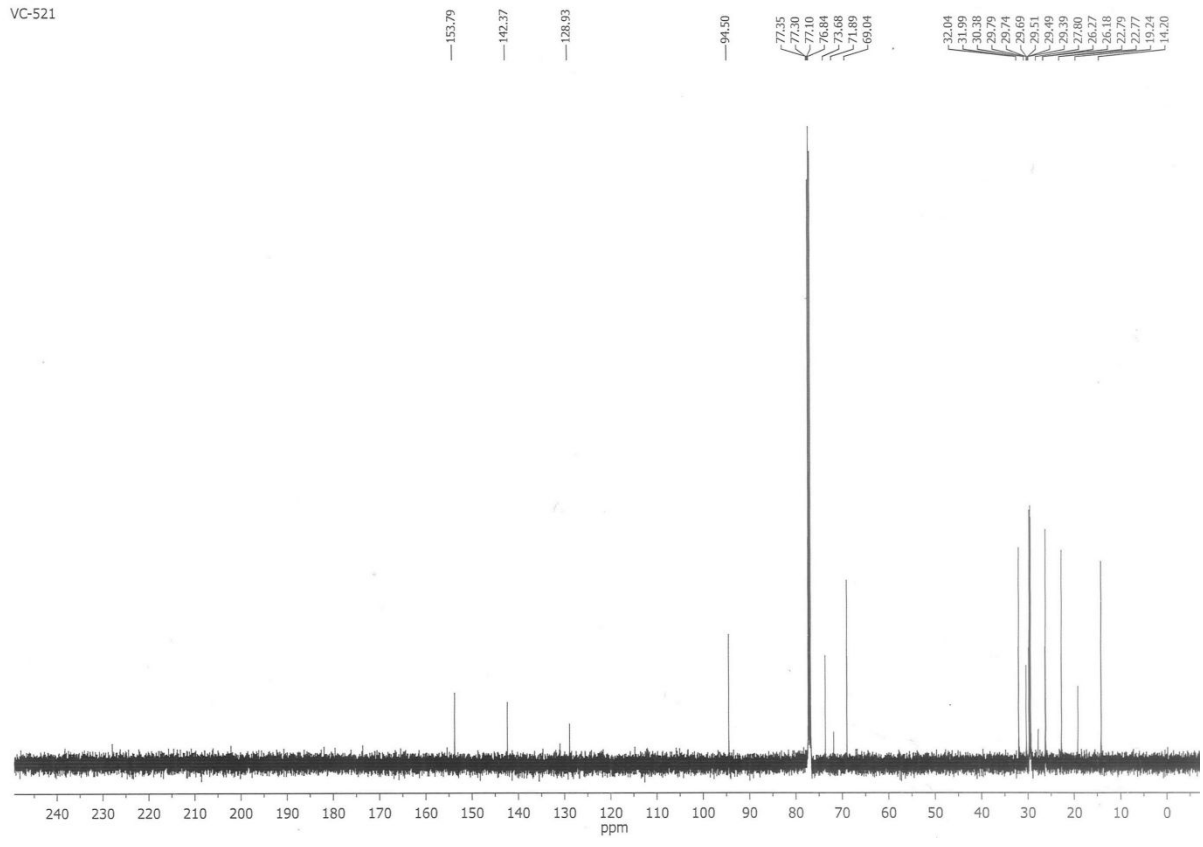


Figure S12. ^{13}C NMR spectrum of compound **6d** (100MHz; $CDCl_3$)

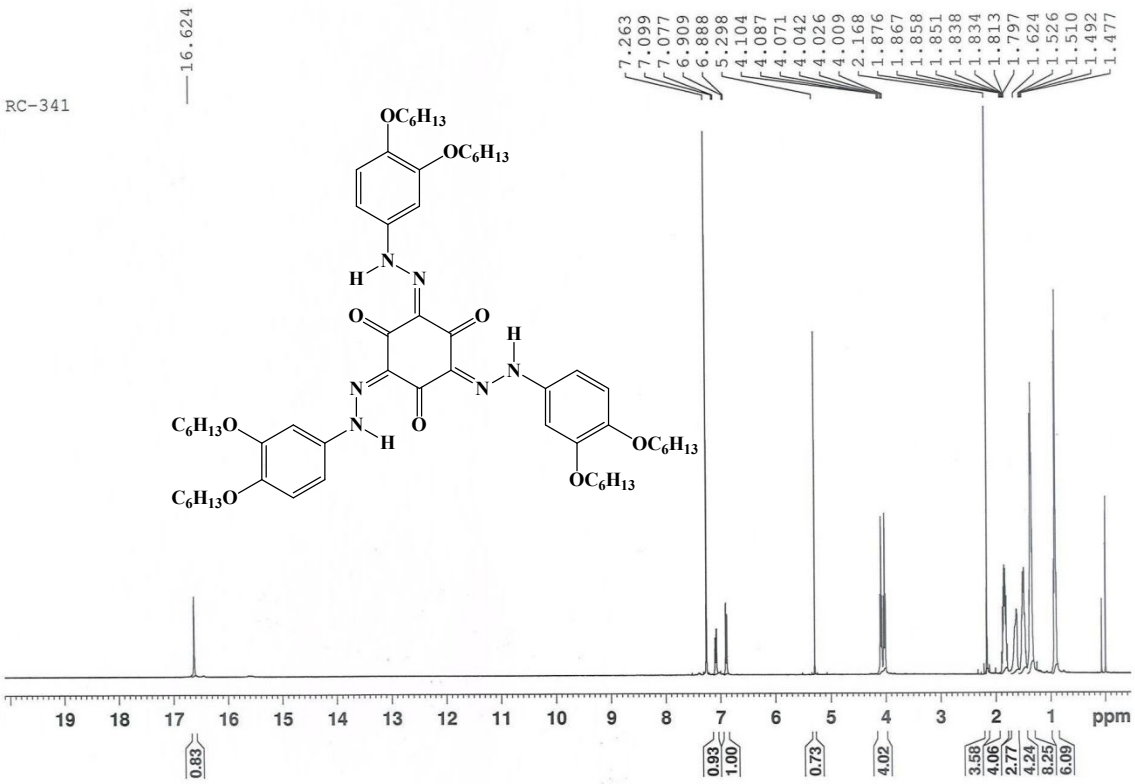


Figure S13. ^{1}H NMR spectrum of compound **THN(6)6** (400MHz; $CDCl_3$)

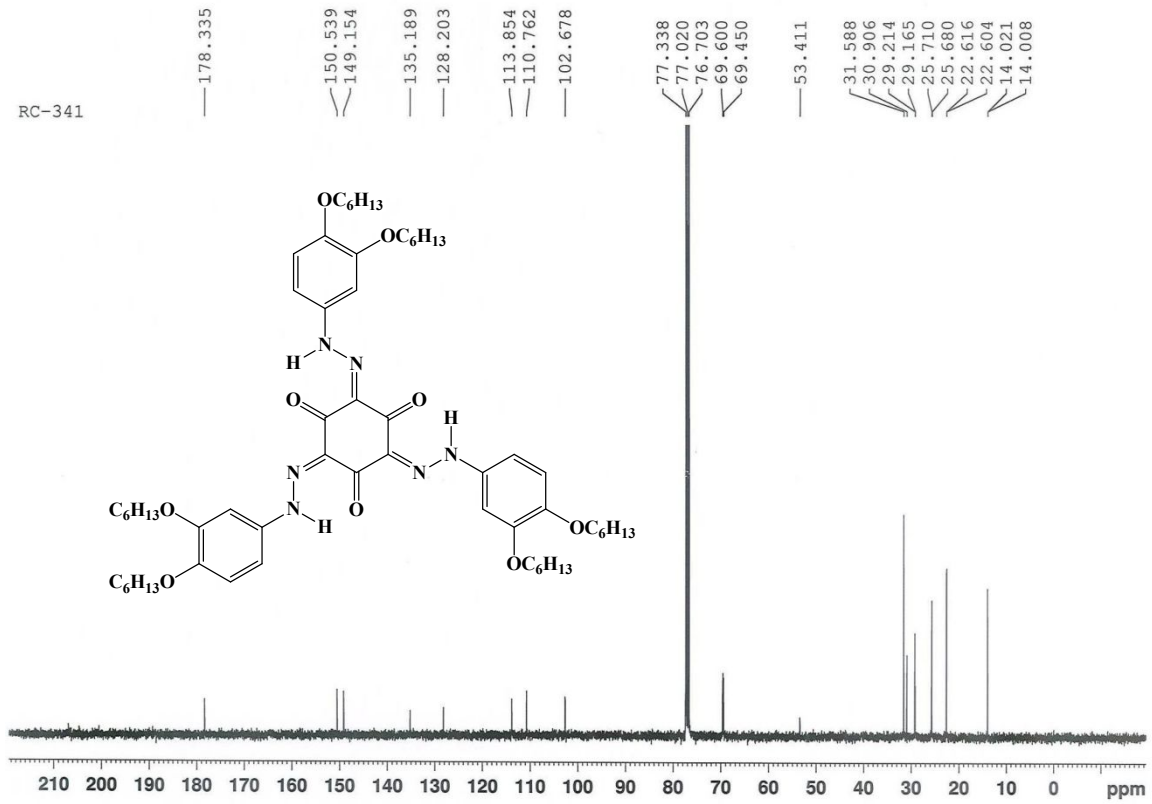


Figure S14. ^{13}C NMR spectrum of compound **THN(6)6** (100MHz; $CDCl_3$)

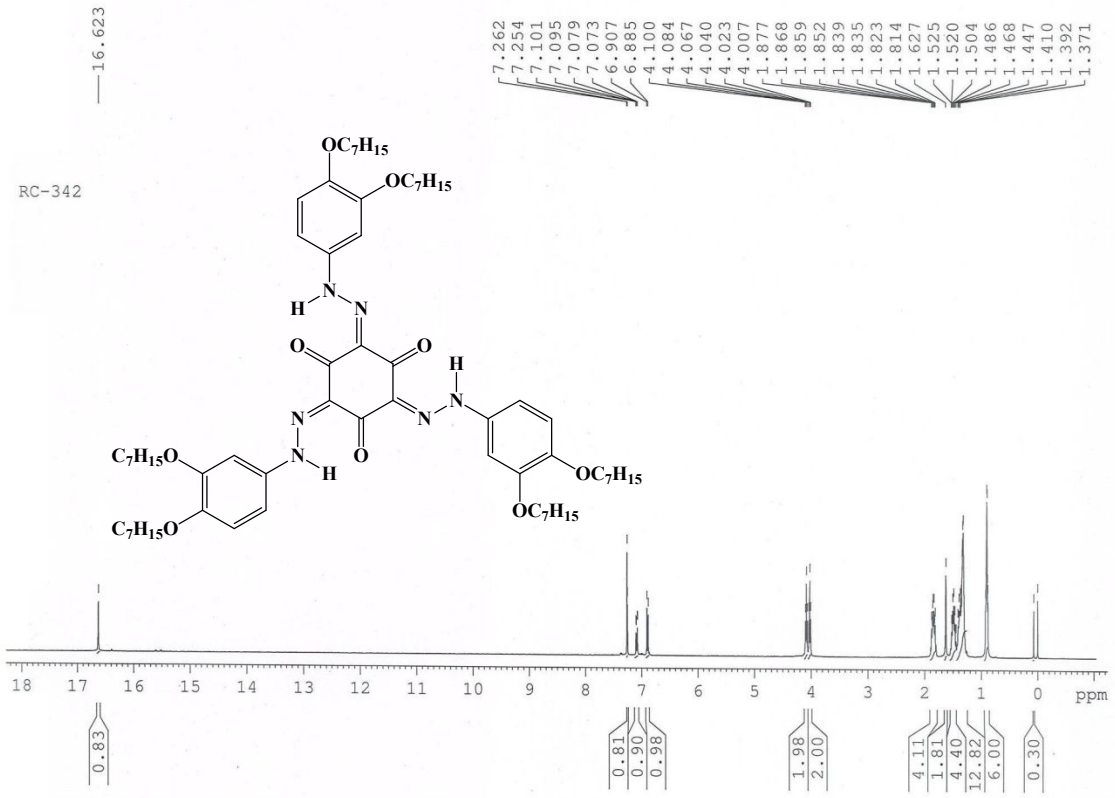


Figure S15. ^{1}H NMR spectrum of compound **THN(6)7** (400MHz; $CDCl_3$)

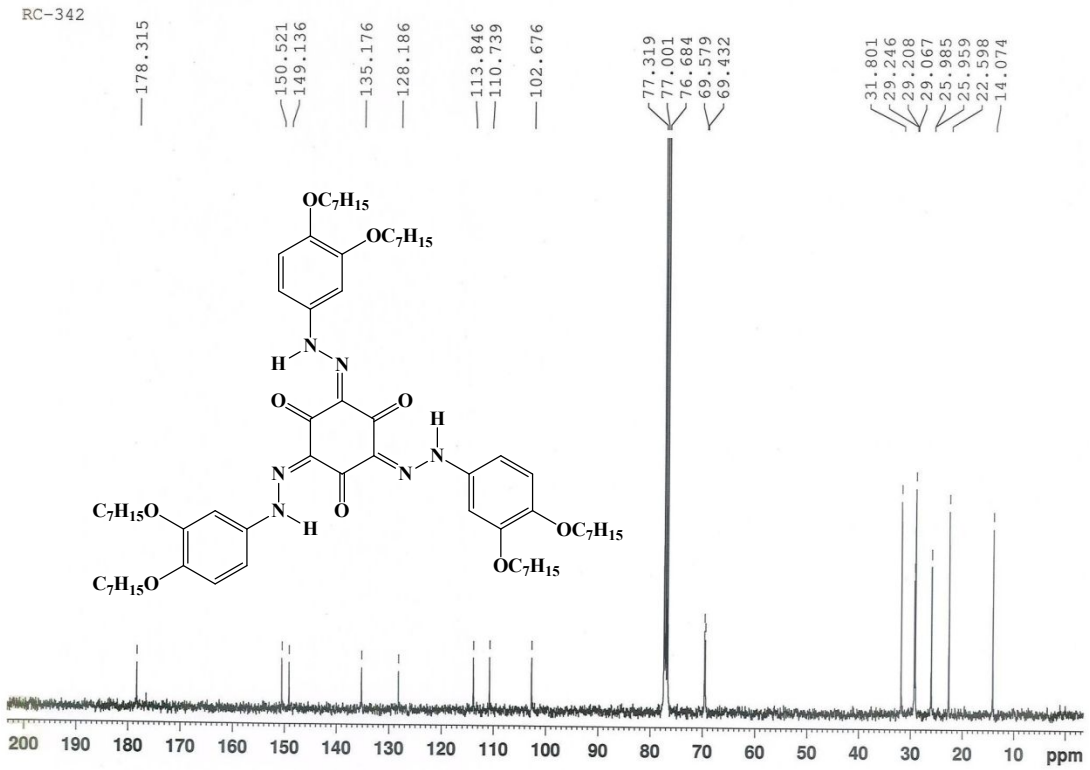


Figure S16. ^{13}C NMR spectrum of compound **THN(6)7** (100MHz; $CDCl_3$)

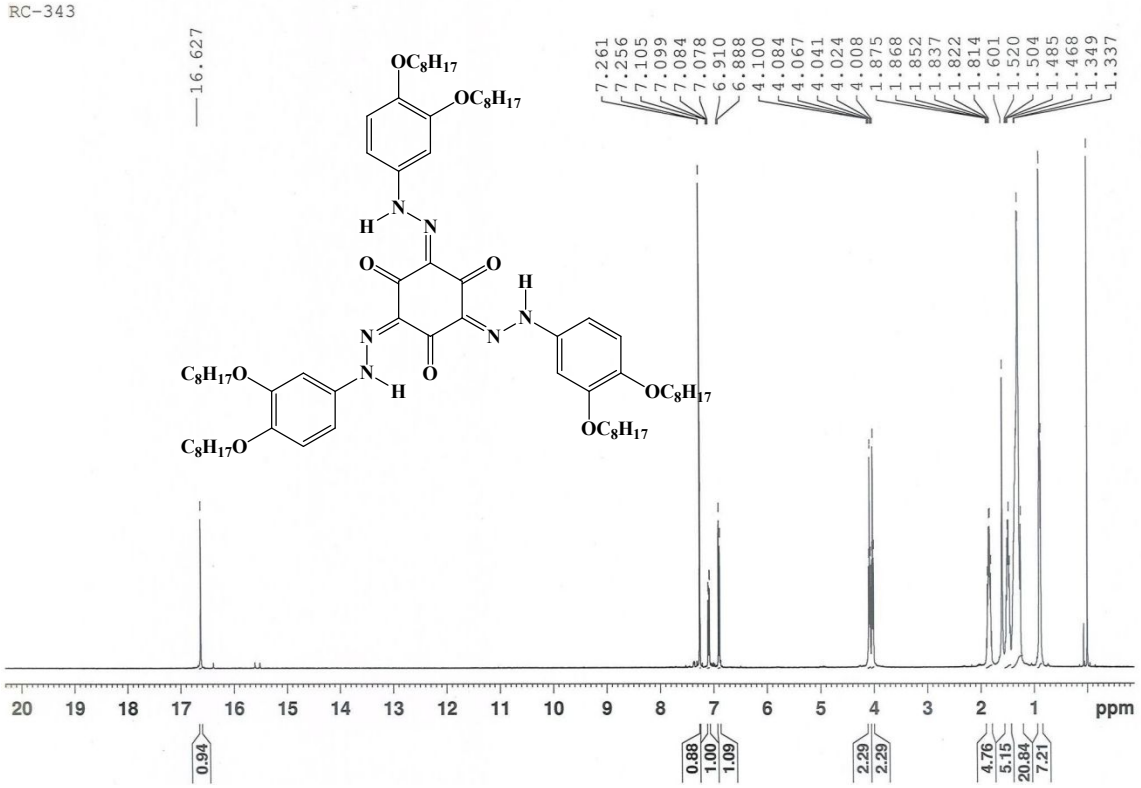


Figure S17. ^{1}H NMR spectrum of compound **THN(6)8** (400MHz; $CDCl_3$)

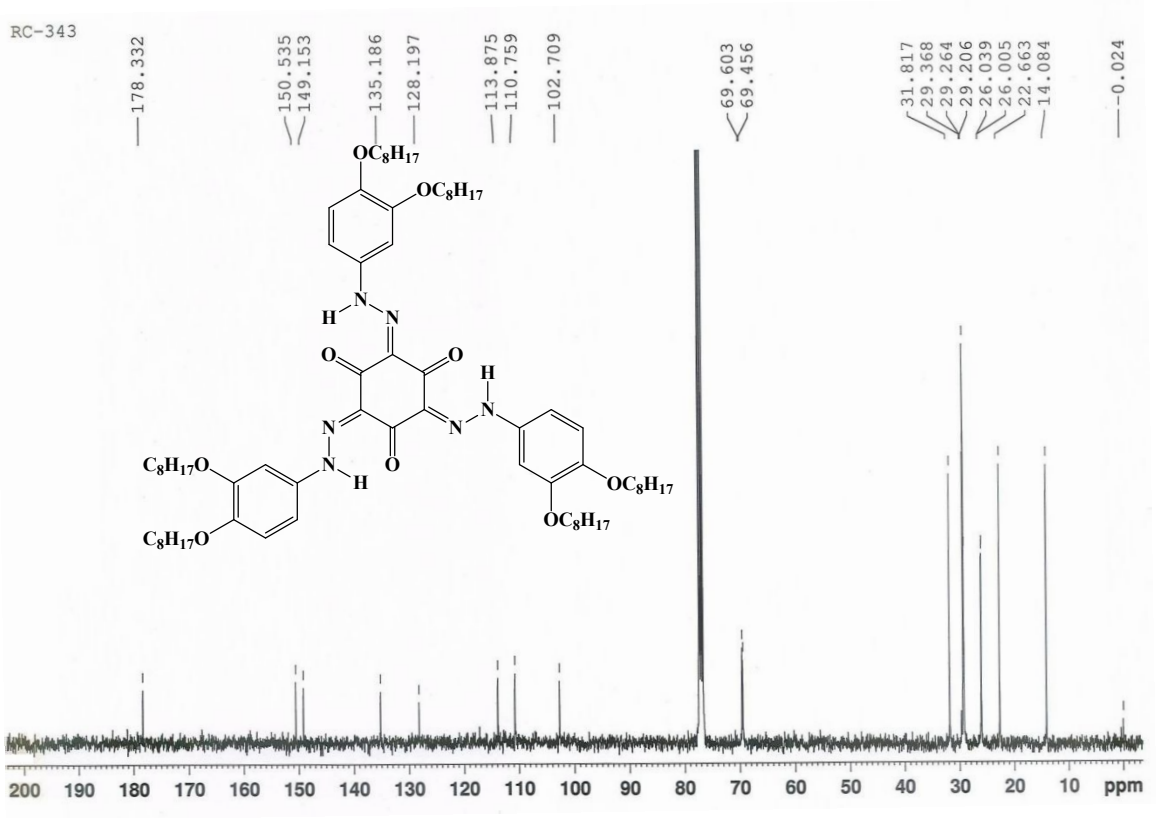


Figure S18. ^{13}C NMR spectrum of compound **THN(6)8** (100MHz; $CDCl_3$)

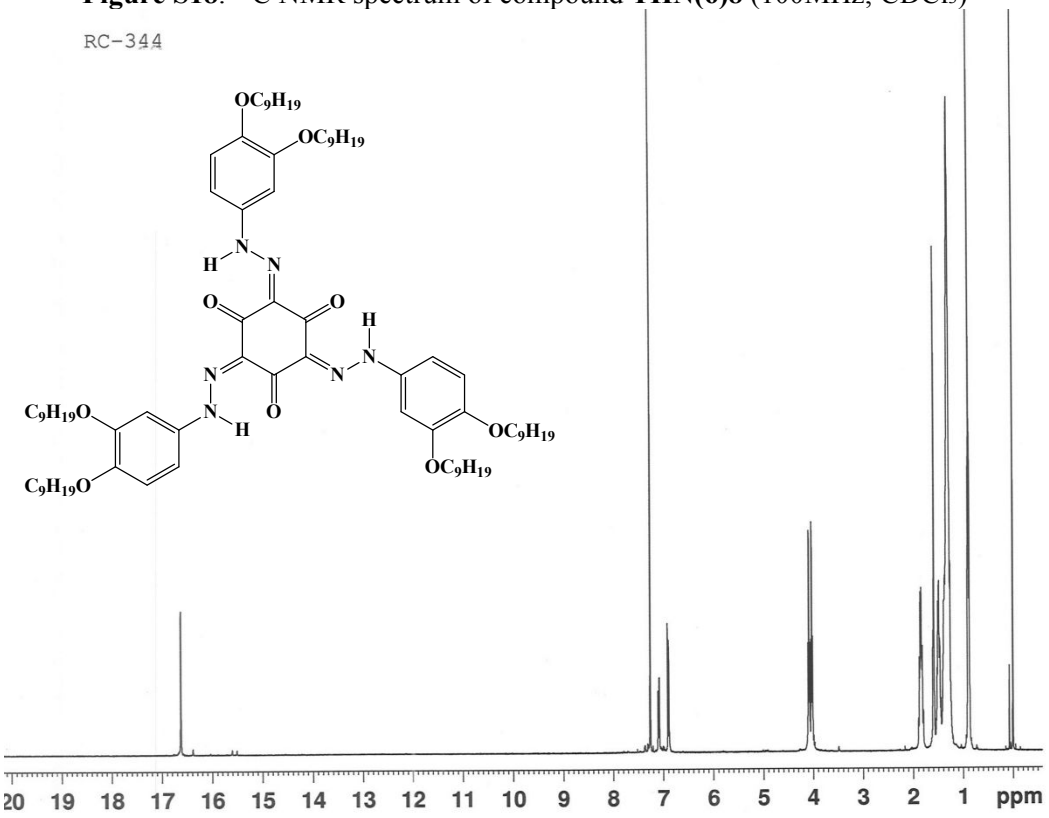


Figure S19. ^{1}H NMR spectrum of compound **THN(6)9** (400MHz; $CDCl_3$)

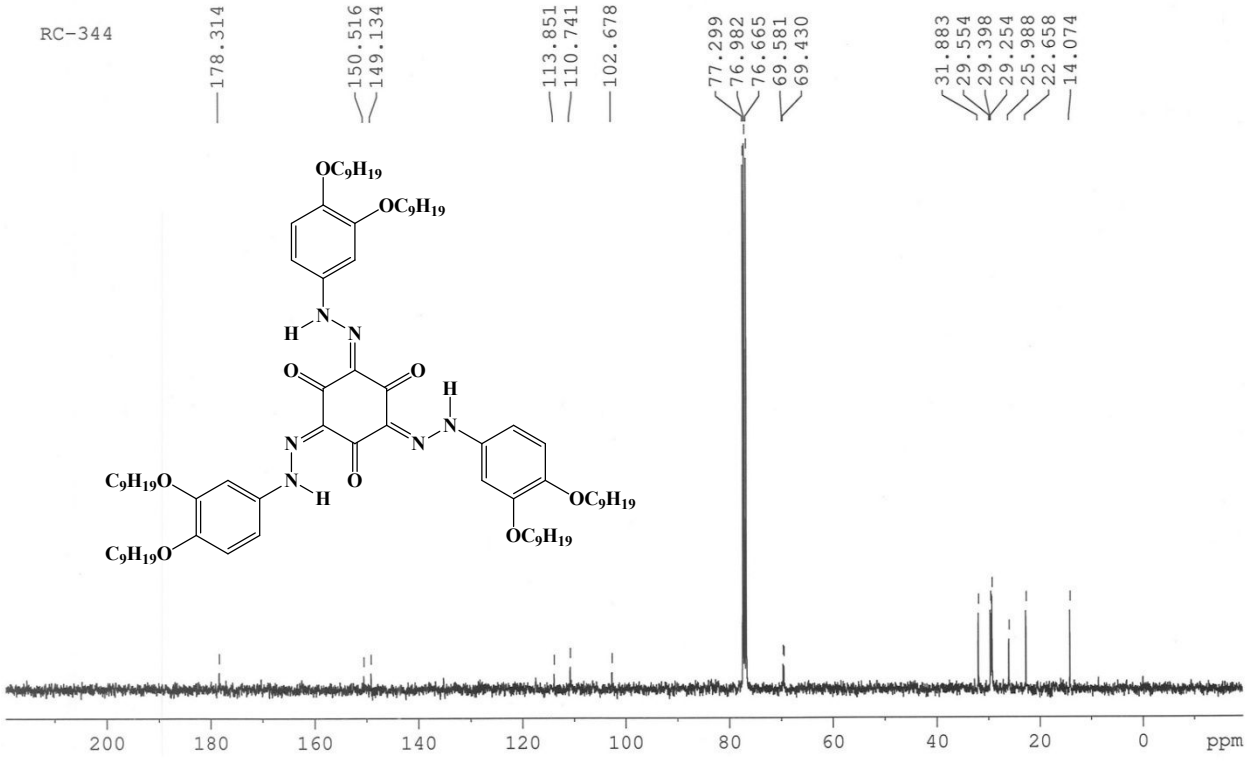


Figure S20. ^{13}C NMR spectrum of compound **THN(6)9** (100MHz; $CDCl_3$)

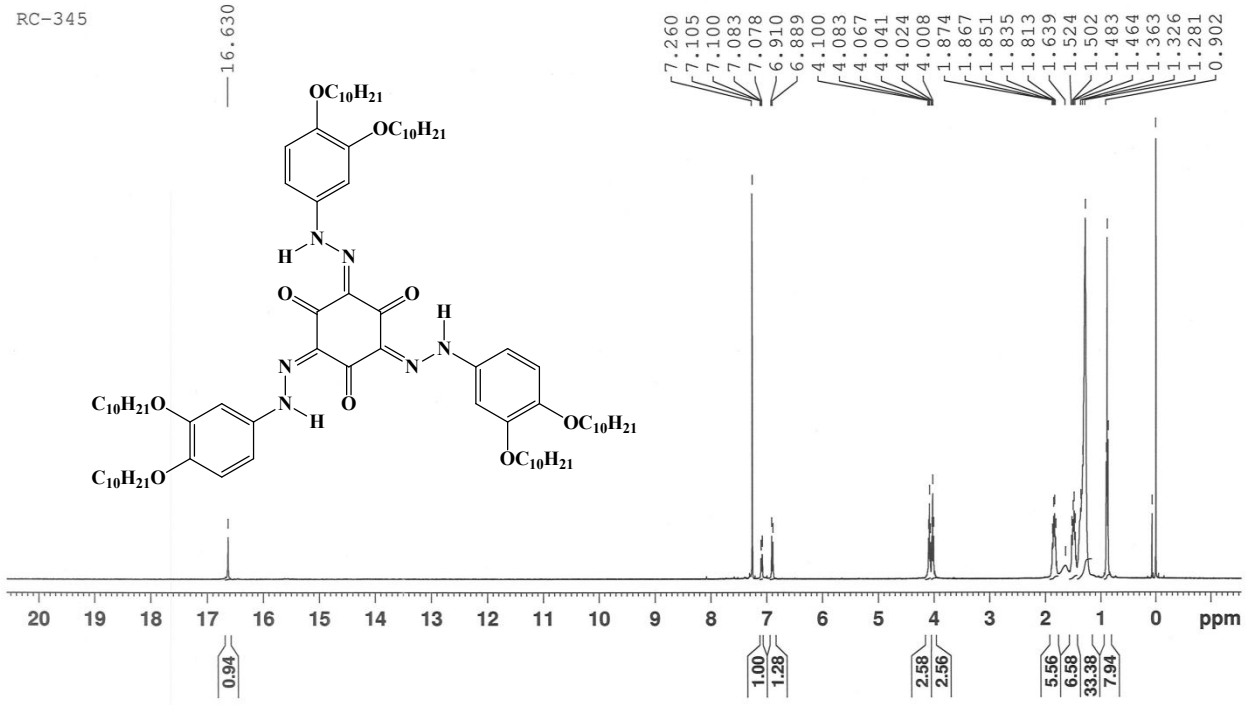


Figure S21. ^{1}H NMR spectrum of compound **THN(6)10** (400MHz; $CDCl_3$)

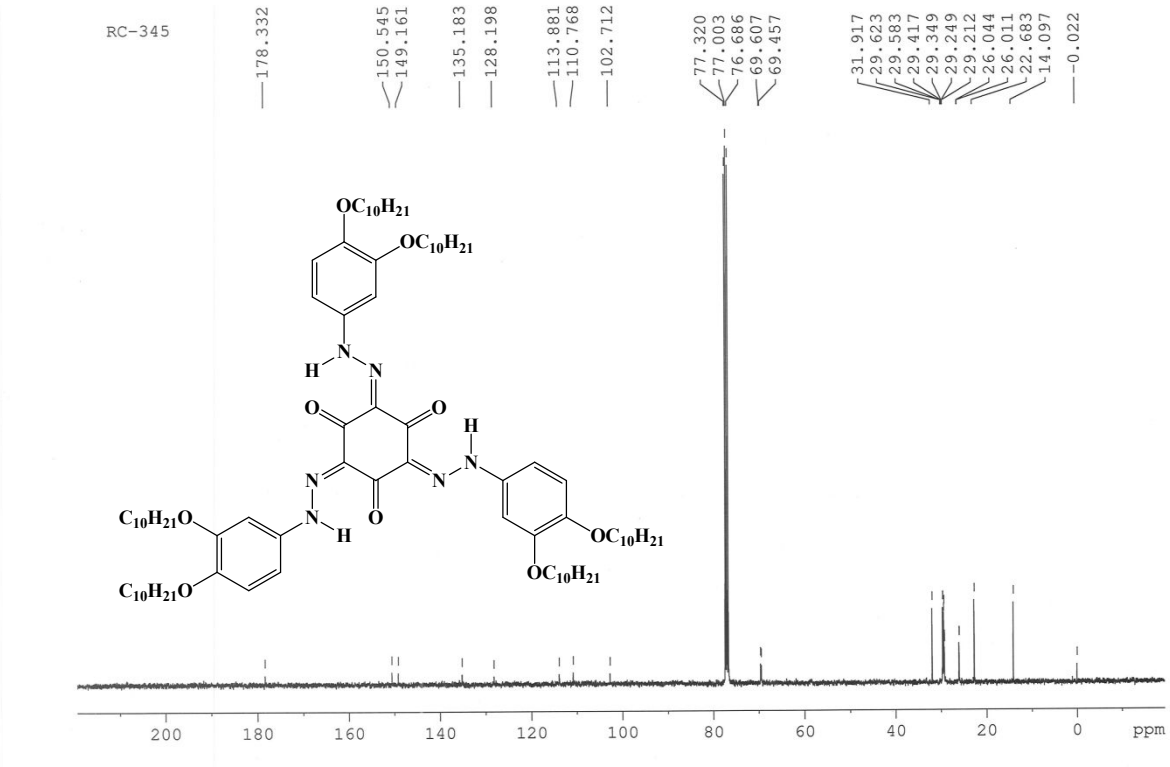


Figure S22. ^{13}C NMR spectrum of compound **THN(6)10** (100MHz; $CDCl_3$)

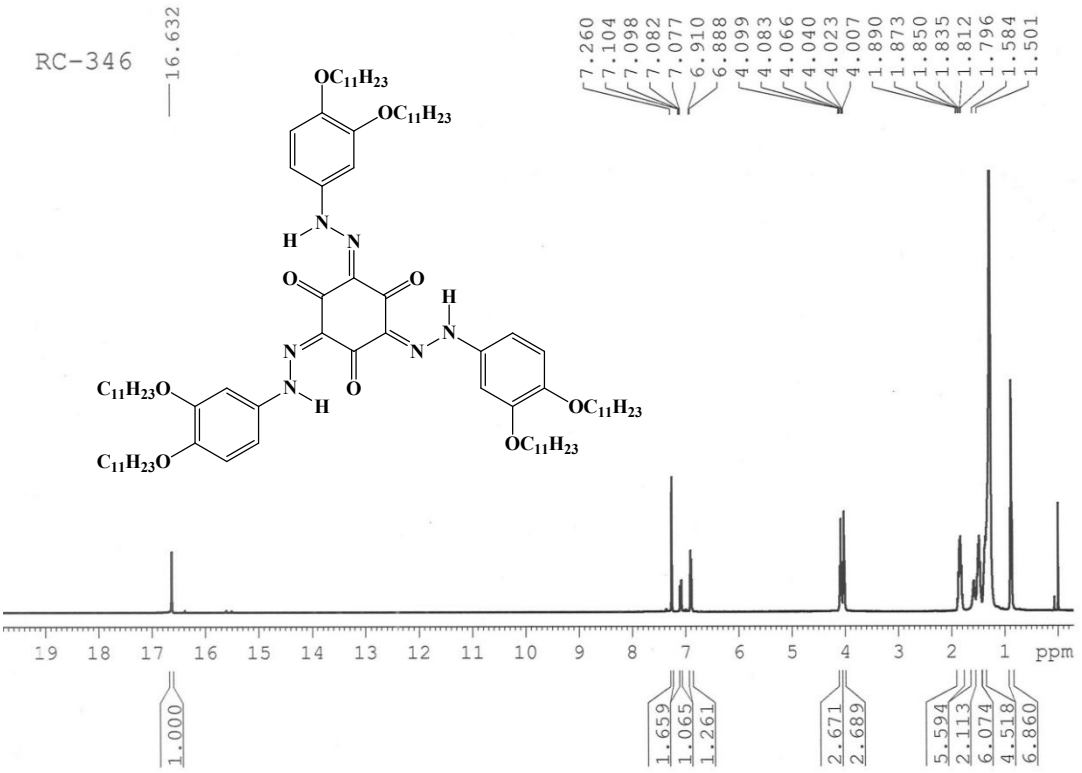


Figure S23. ^{1}H NMR spectrum of compound **THN(6)11** (400MHz; $CDCl_3$)

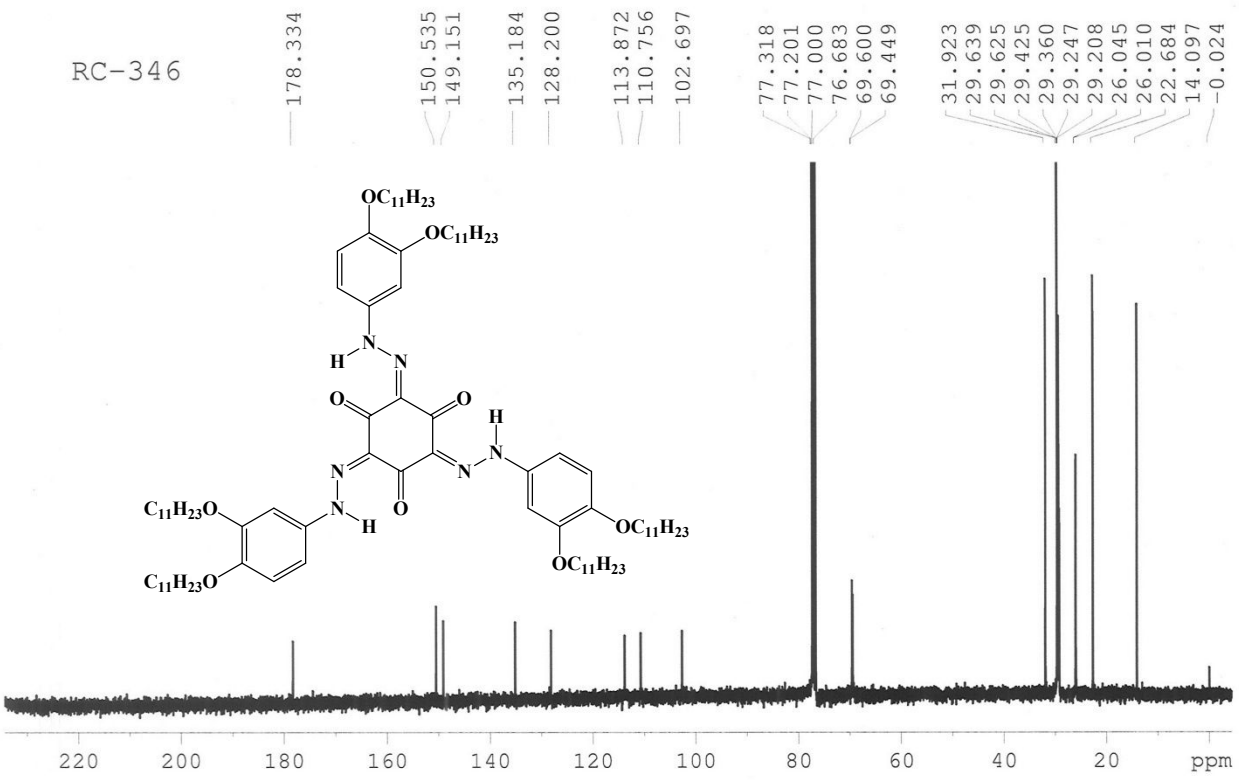


Figure S24. ^{13}C NMR spectrum of compound **THN(6)11** (100MHz; $CDCl_3$)

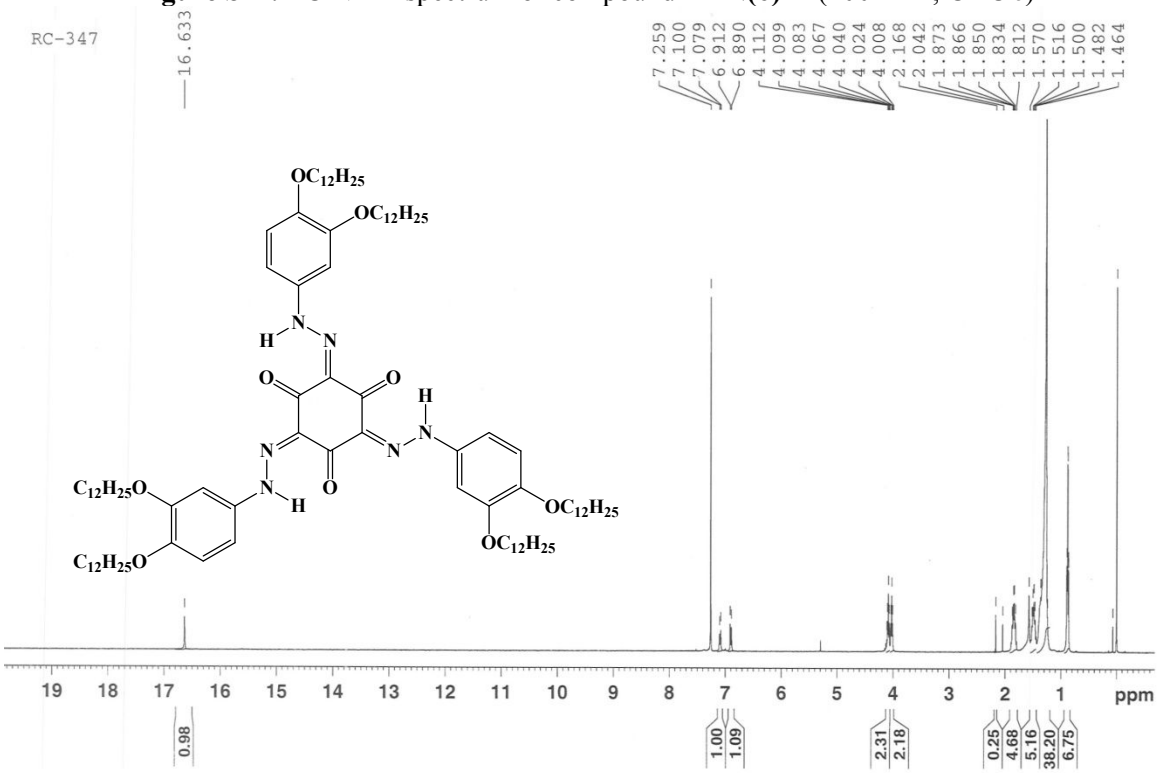


Figure S25. ^{1}H NMR spectrum of compound **THN(6)12** (400MHz; $CDCl_3$)

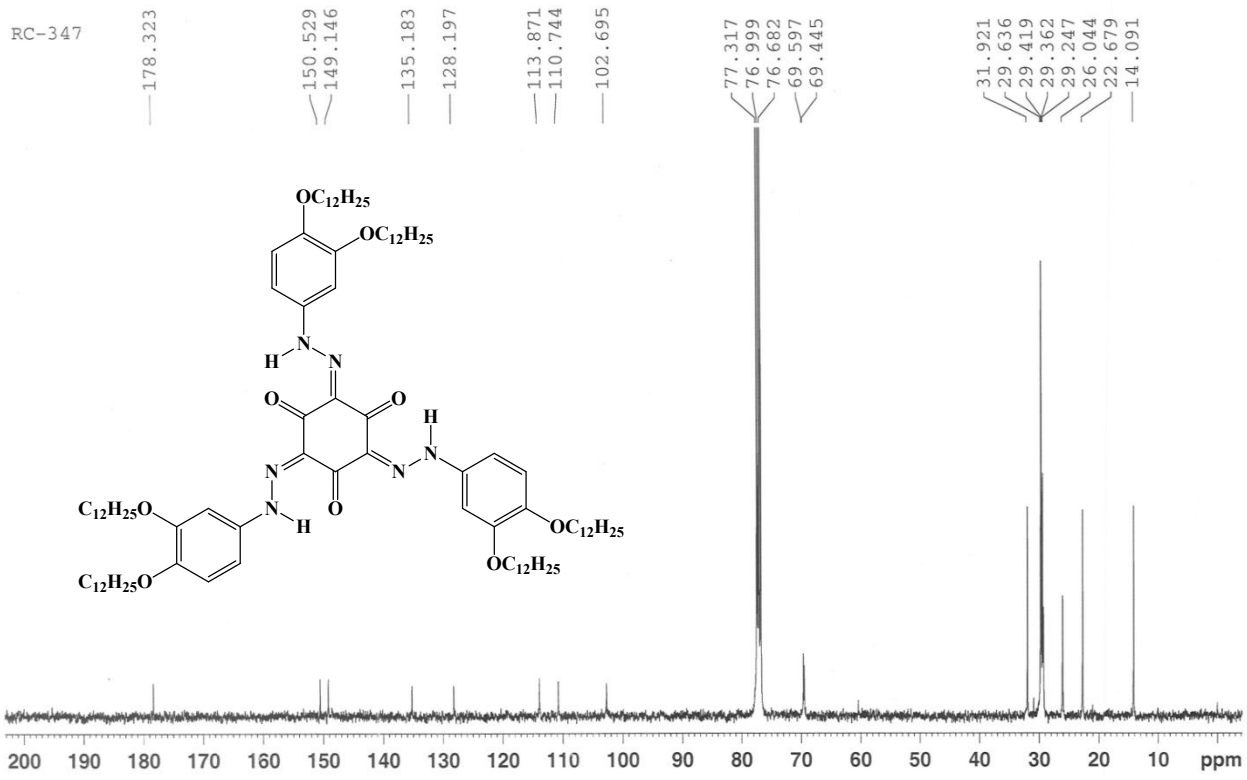


Figure S26. ^{13}C NMR spectrum of compound **THN(6)12** (100MHz; $CDCl_3$)

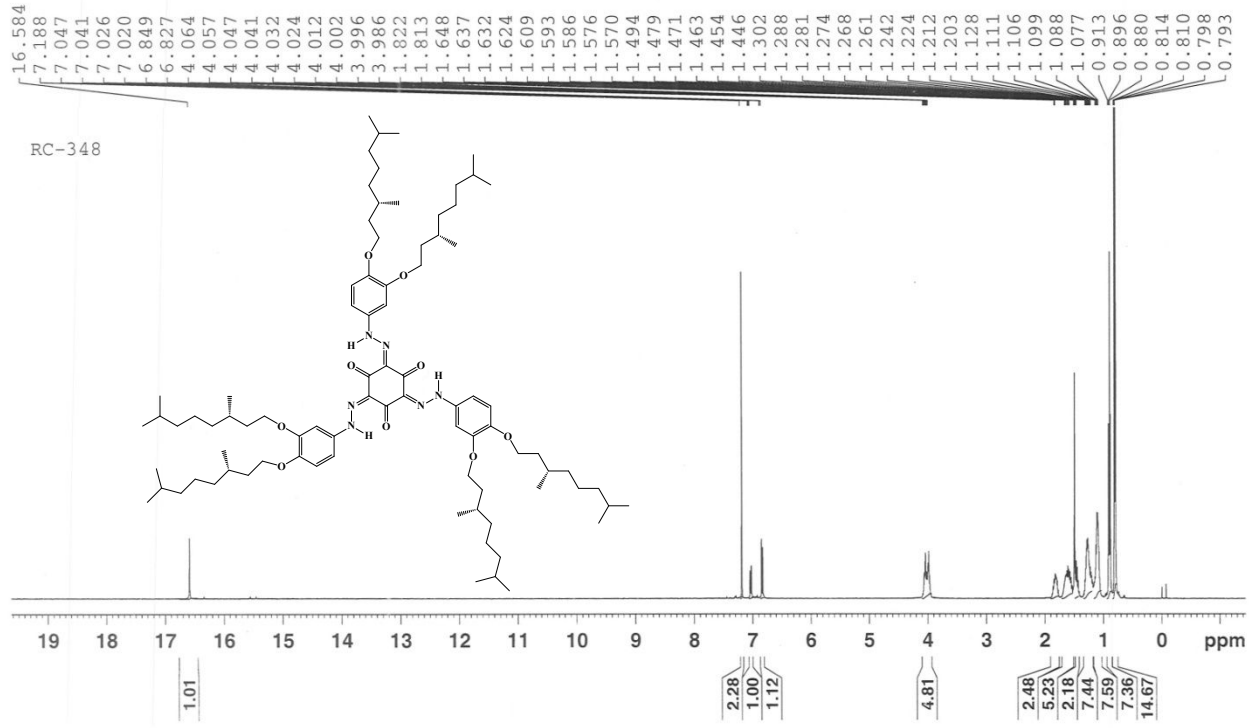


Figure S27. ^{1}H NMR spectrum of compound **THN(6)10B** (400 MHz; $CDCl_3$)

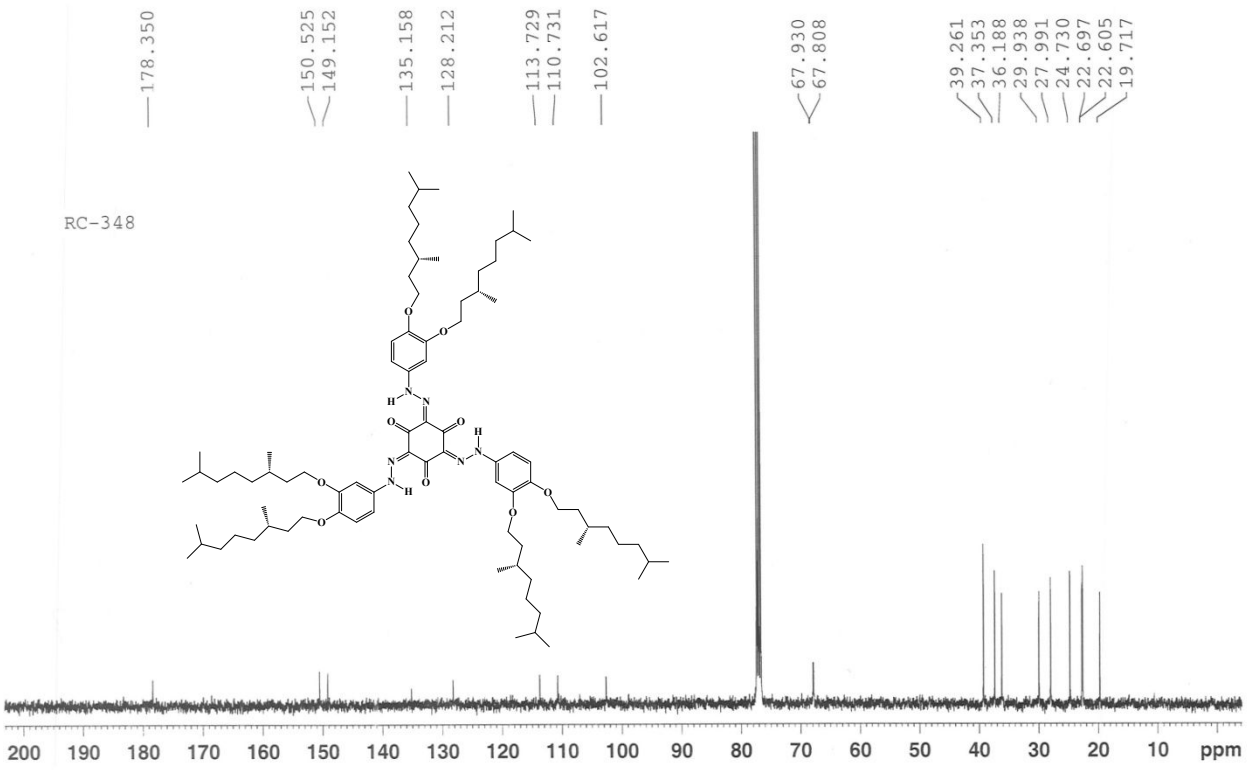


Figure S28. ^{13}C NMR spectrum of compound **THN(6)10B** (100 MHz; $CDCl_3$)

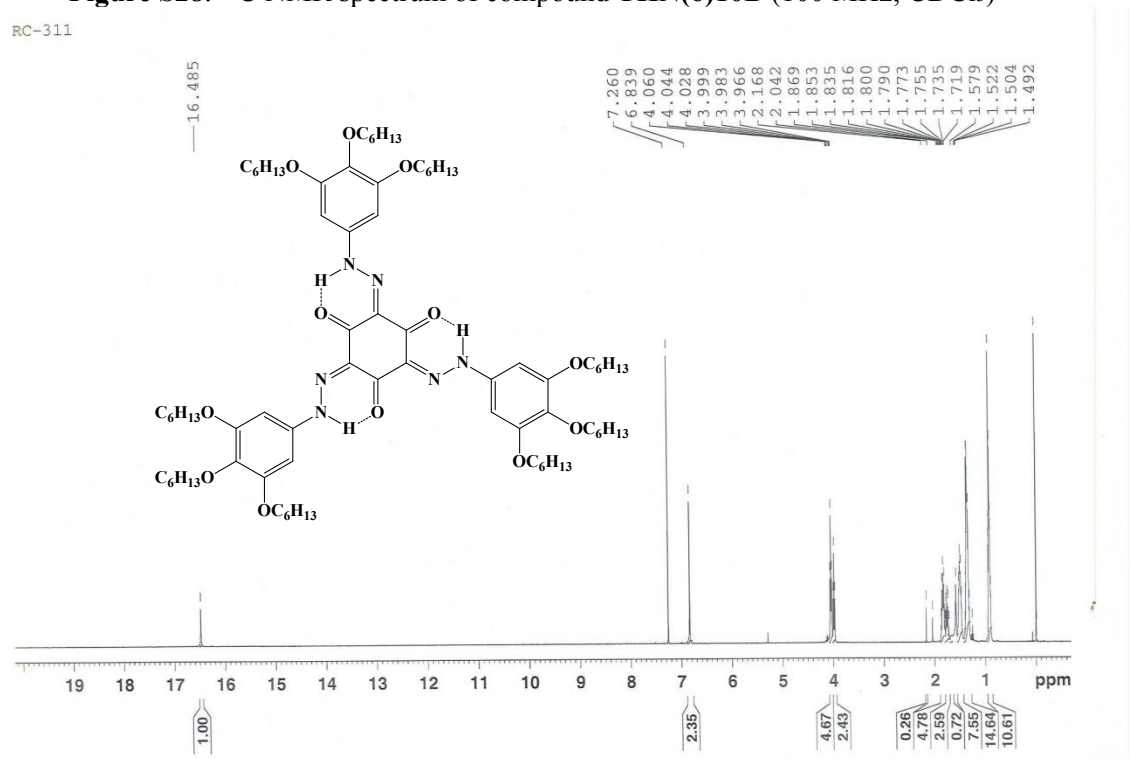


Figure S29. ^{1}H NMR spectrum of compound **THN(9)6** (400MHz; $CDCl_3$)

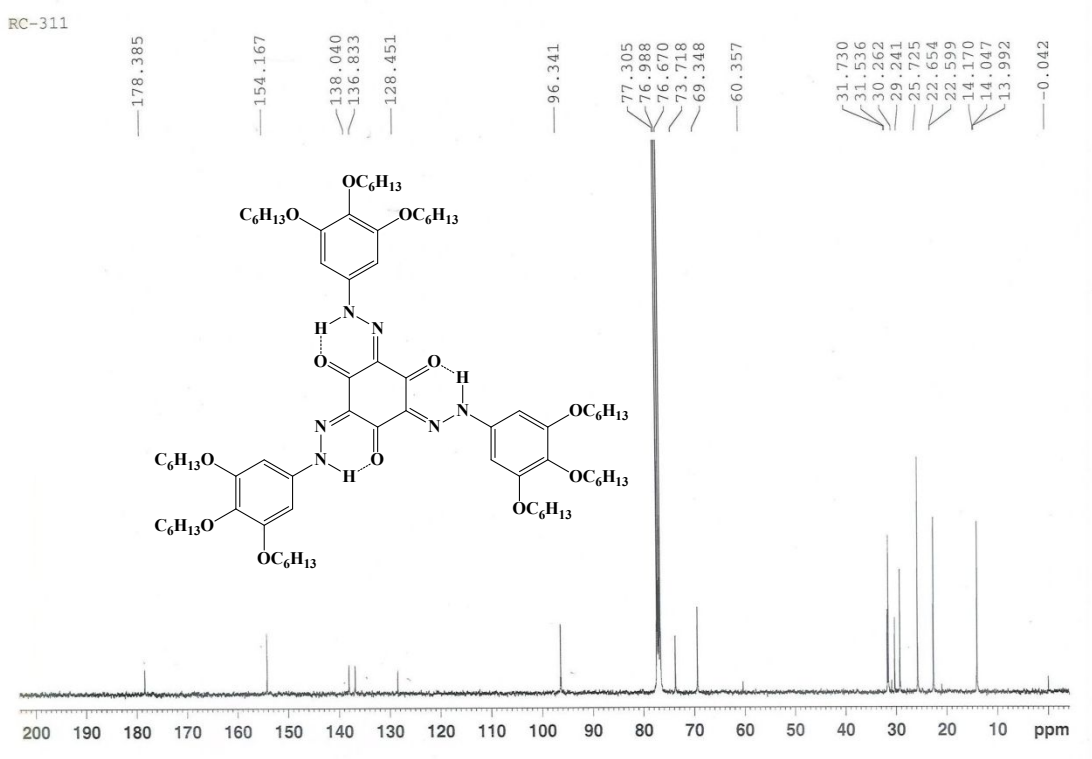


Figure S30. ^{13}C NMR spectrum of compound **THN(9)6** (100MHz; $CDCl_3$)

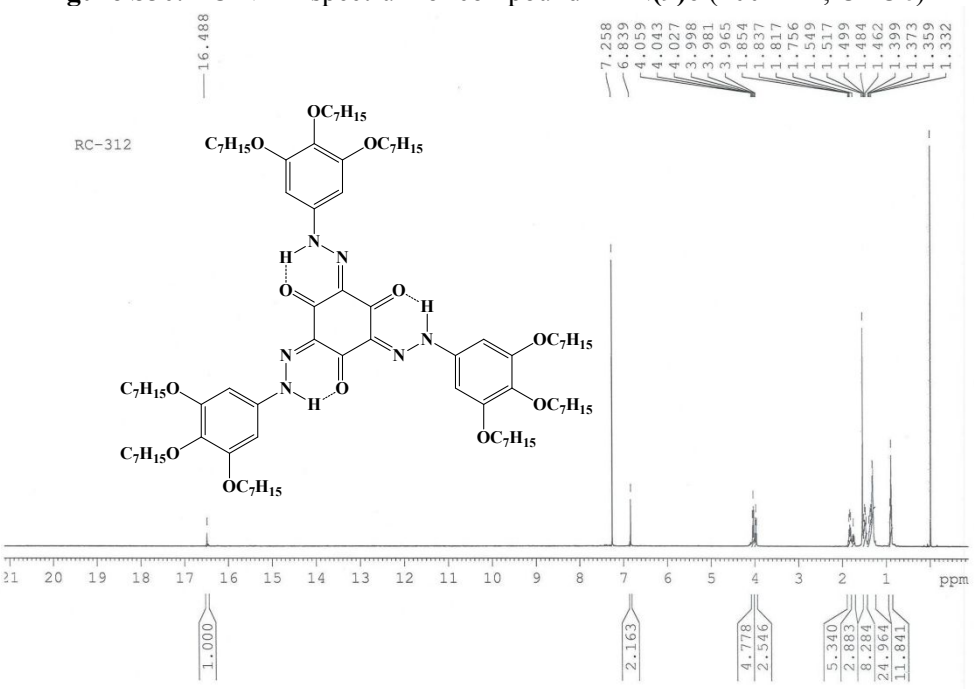


Figure S31. ^{1}H NMR spectrum of compound **THN(9)7** (400MHz; $CDCl_3$)

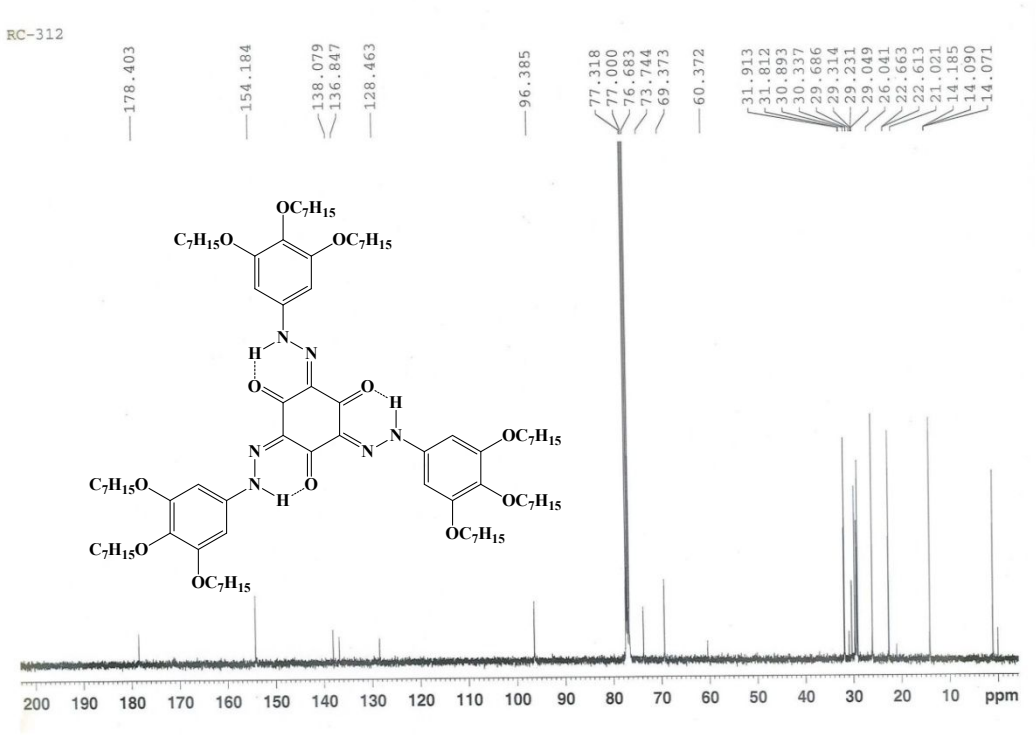


Figure S32. ^{13}C NMR spectrum of compound **THN(9)7** (100MHz; $CDCl_3$)

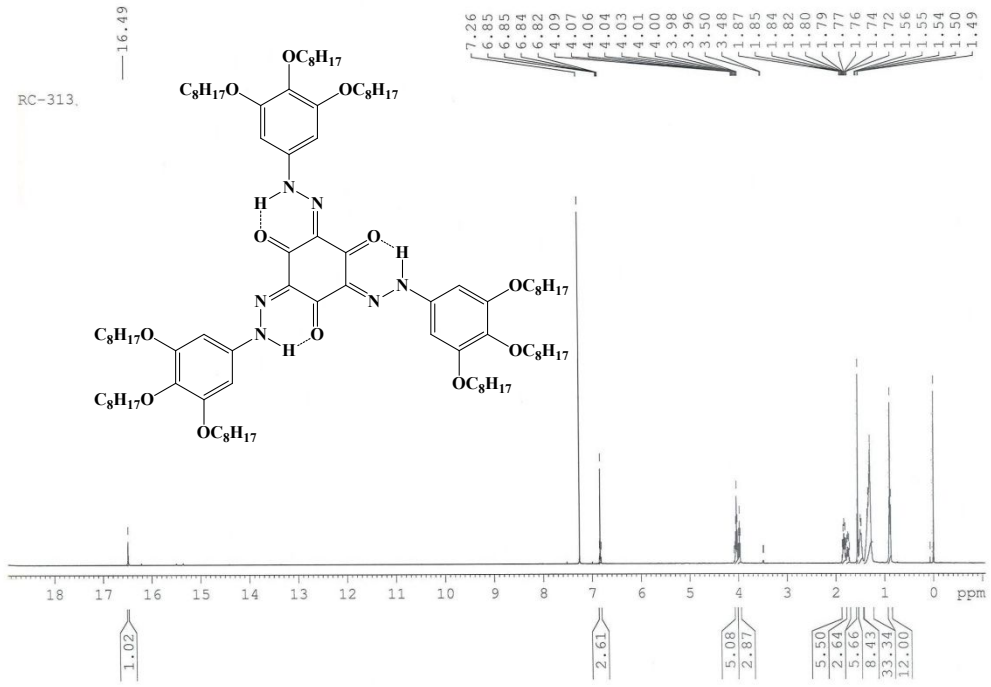


Figure S33. ^{1}H NMR spectrum of compound **THN(9)8** (400MHz; $CDCl_3$)

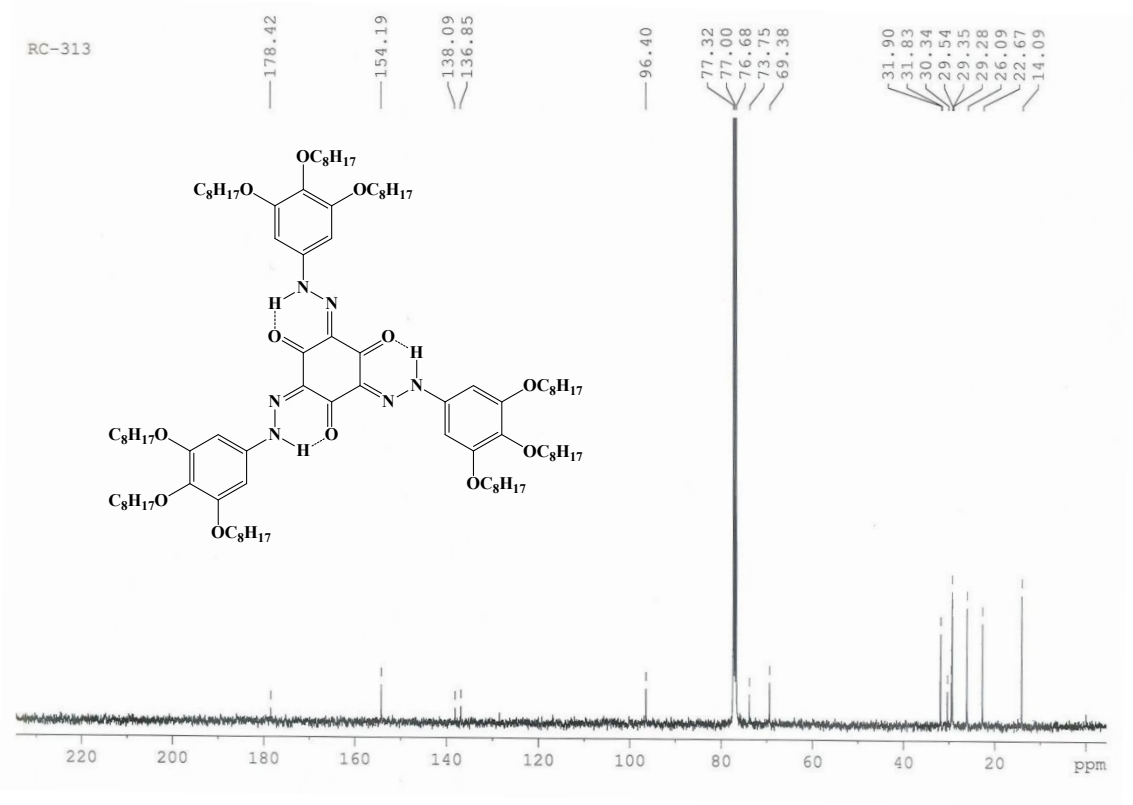


Figure S34. ^{13}C NMR spectrum of compound **THN(9)8** (100MHz; $CDCl_3$)

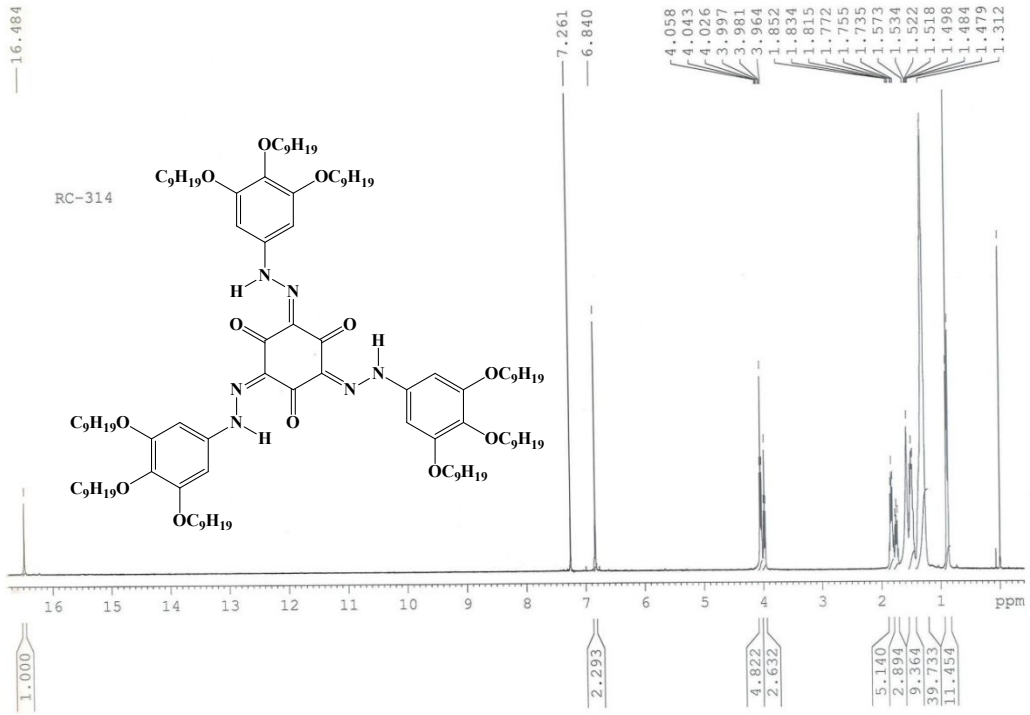


Figure S35. ^{1}H NMR spectrum of compound **THN(9)9** (400MHz; $CDCl_3$)

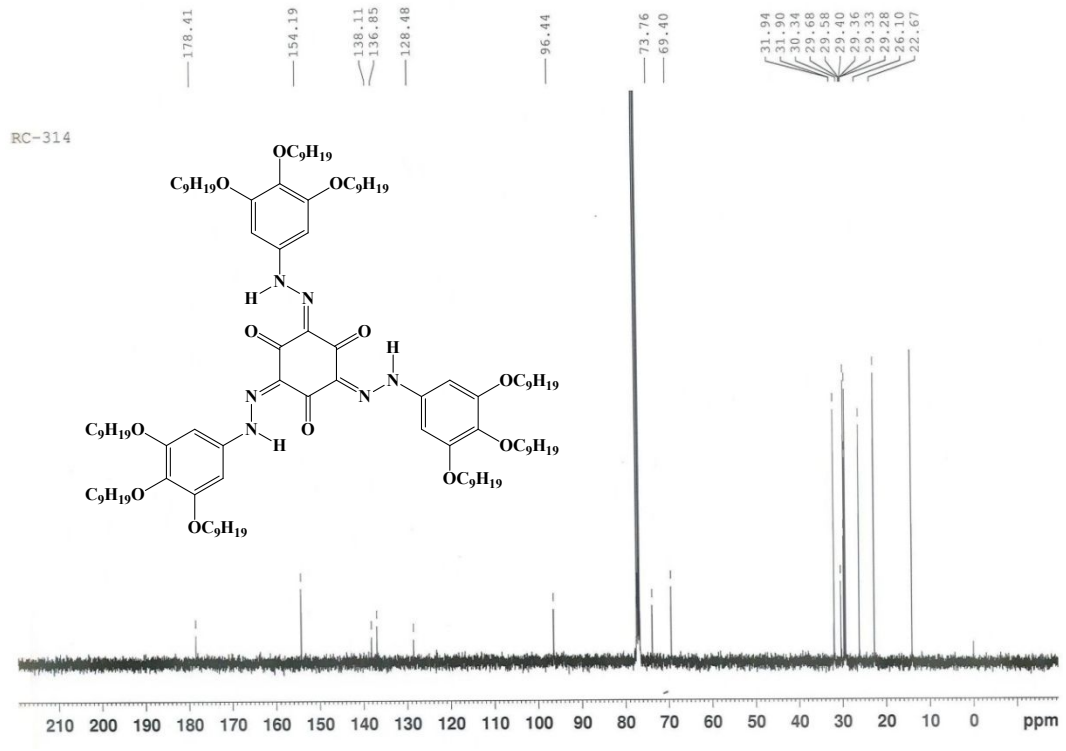


Figure S36. ^{13}C NMR spectrum of compound **THN(9)9** (100MHz; $CDCl_3$)

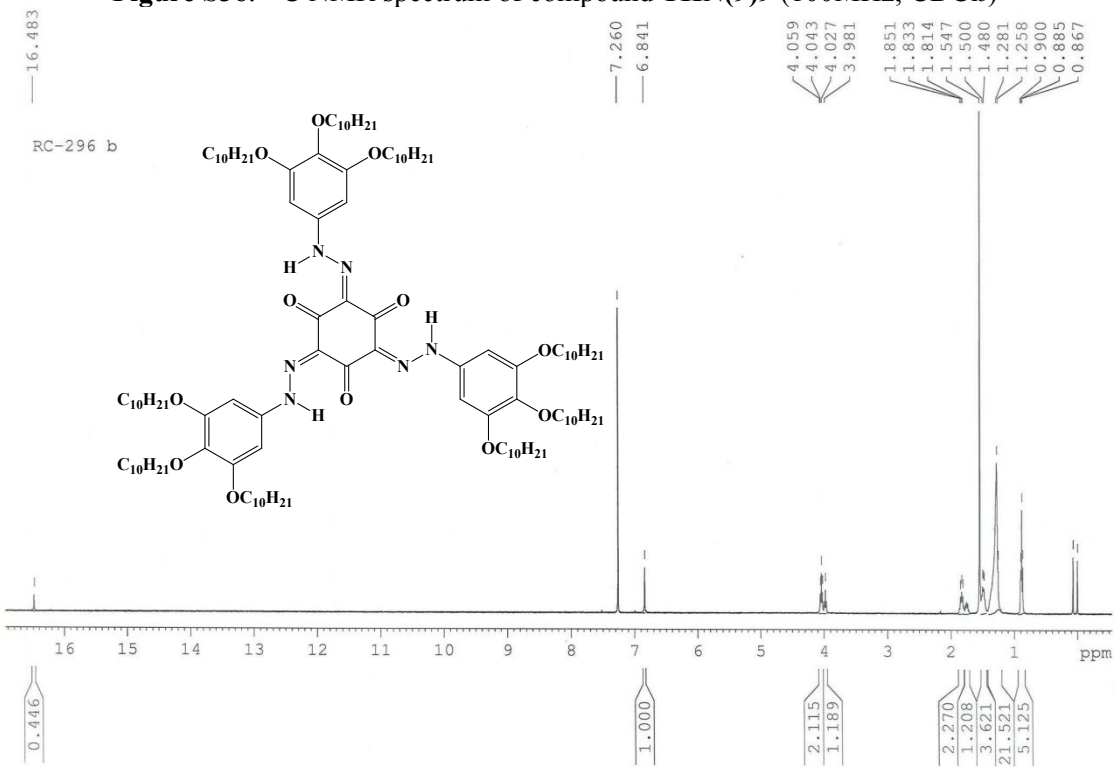


Figure S37. ^{1}H NMR spectrum of compound **THN(9)10** (400MHz; $CDCl_3$)

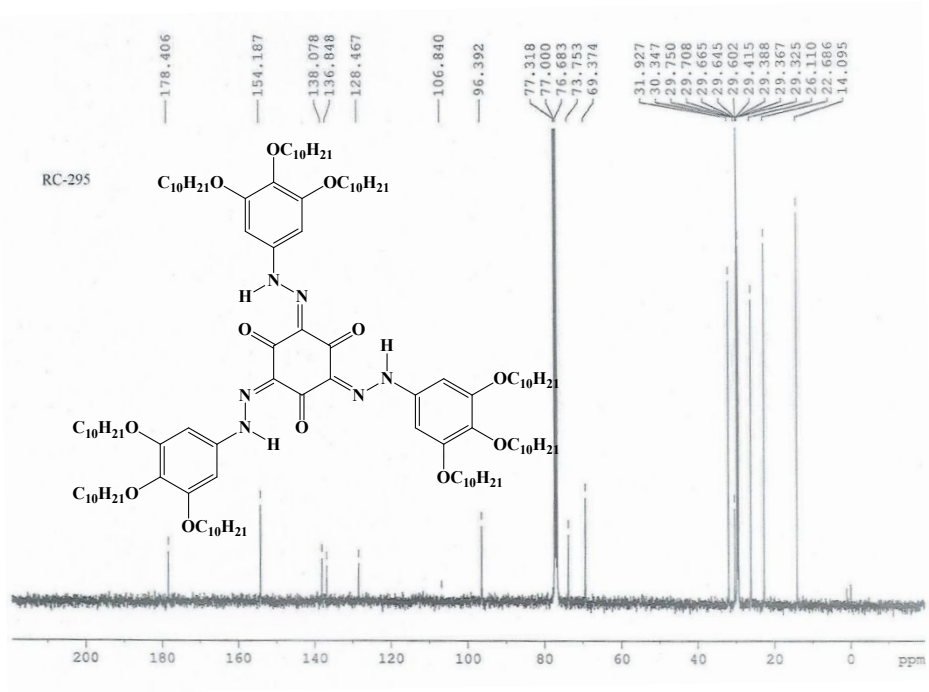


Figure S38. ^{13}C NMR spectrum of compound **THN(9)10** (100MHz; $CDCl_3$)

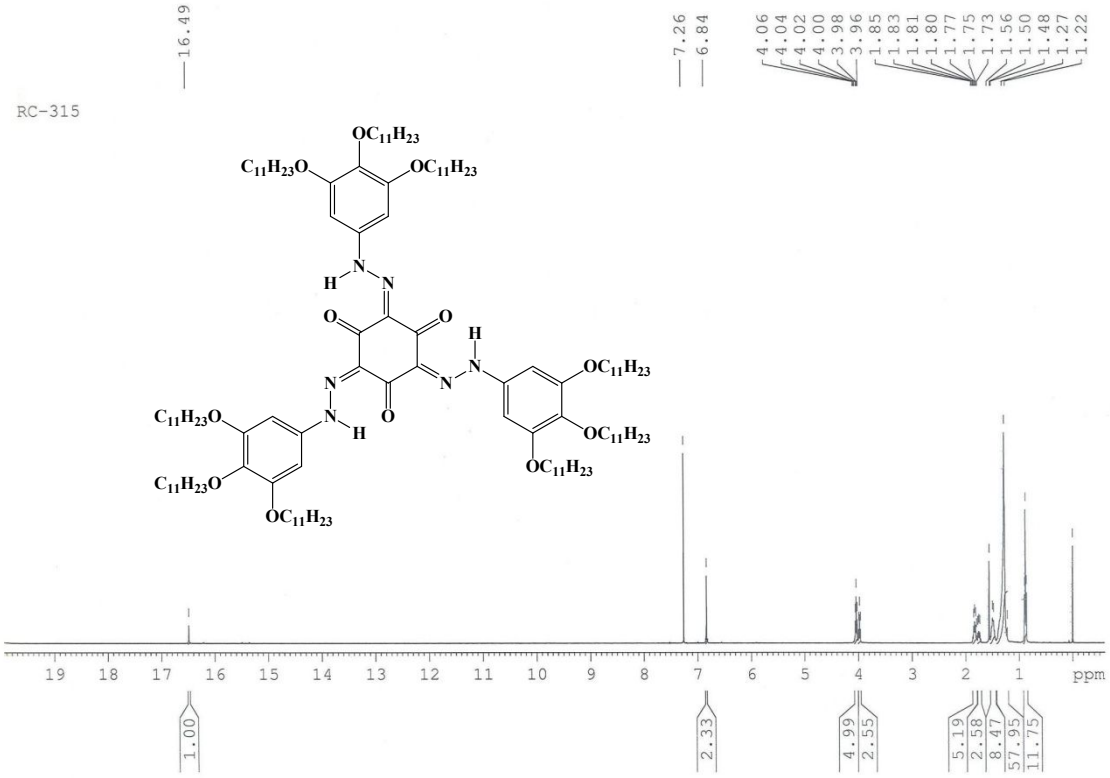


Figure S39. ^{1}H NMR spectrum of compound **THN(9)11** (400MHz; $CDCl_3$)

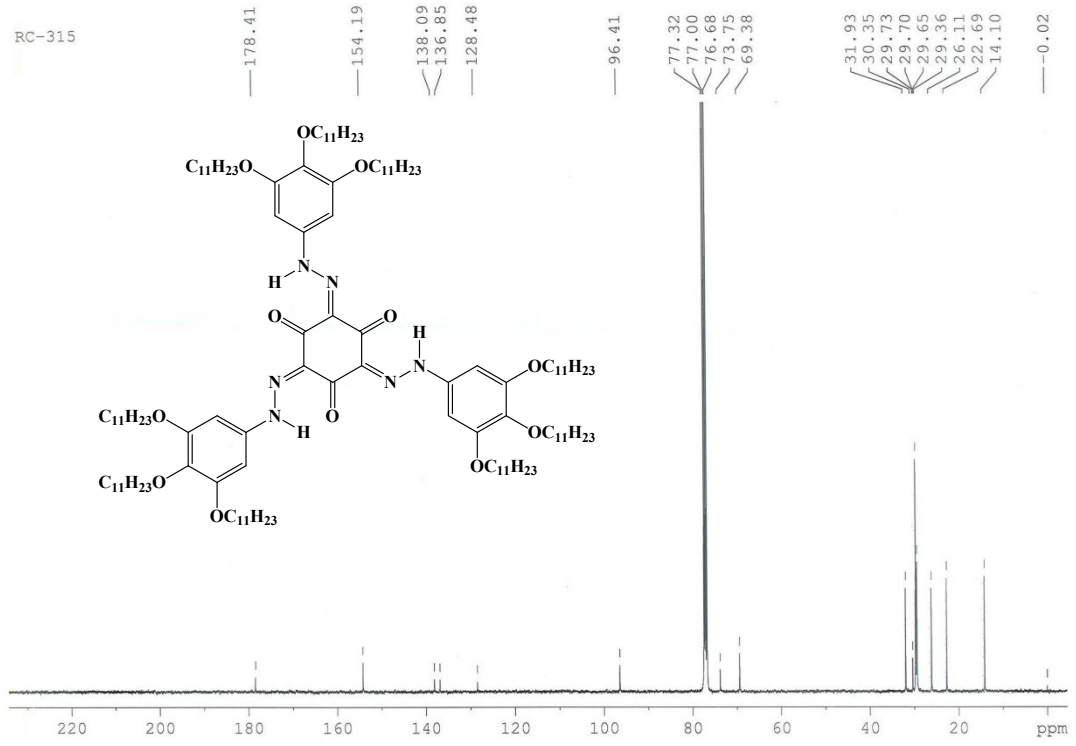


Figure S40. ^{13}C NMR spectrum of compound **THN(9)11** (100MHz; $CDCl_3$)

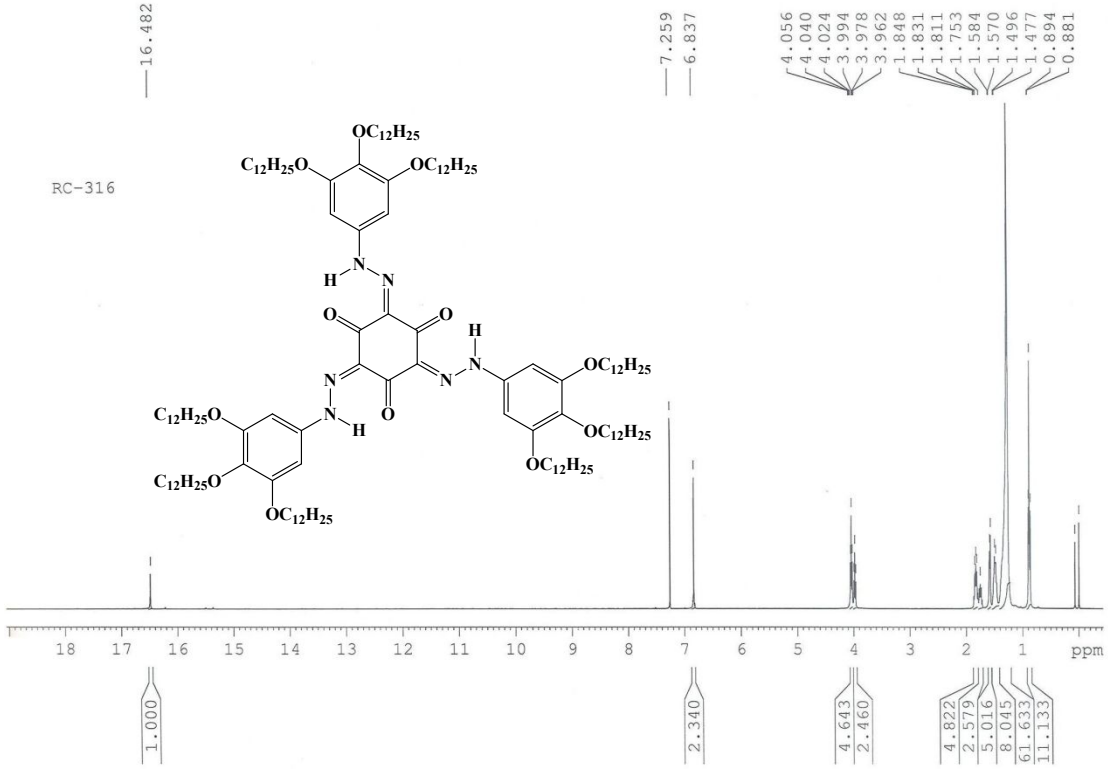


Figure S41. ^{1}H NMR spectrum of compound **THN(9)12** (400MHz; $CDCl_3$)

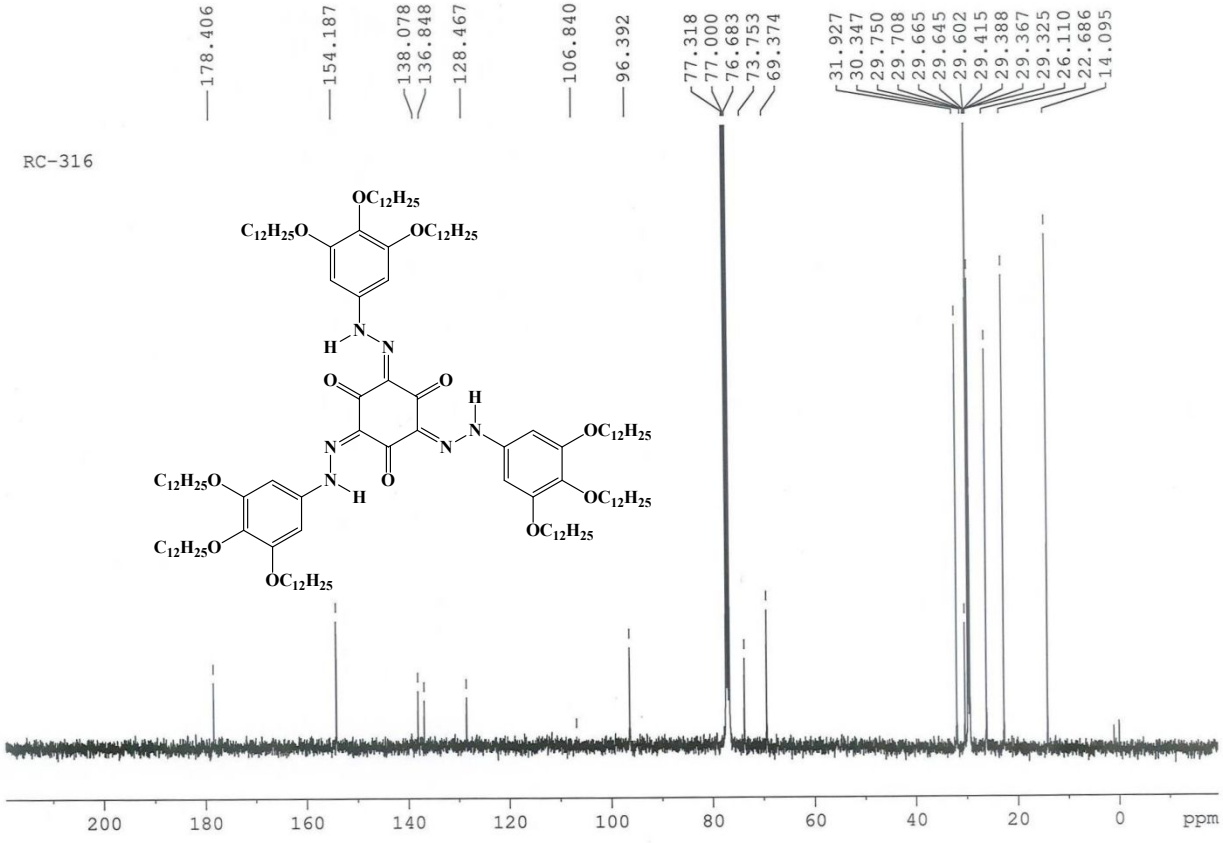


Figure S42. ^{13}C NMR spectrum of compound **THN(9)12** (100MHz; $CDCl_3$)

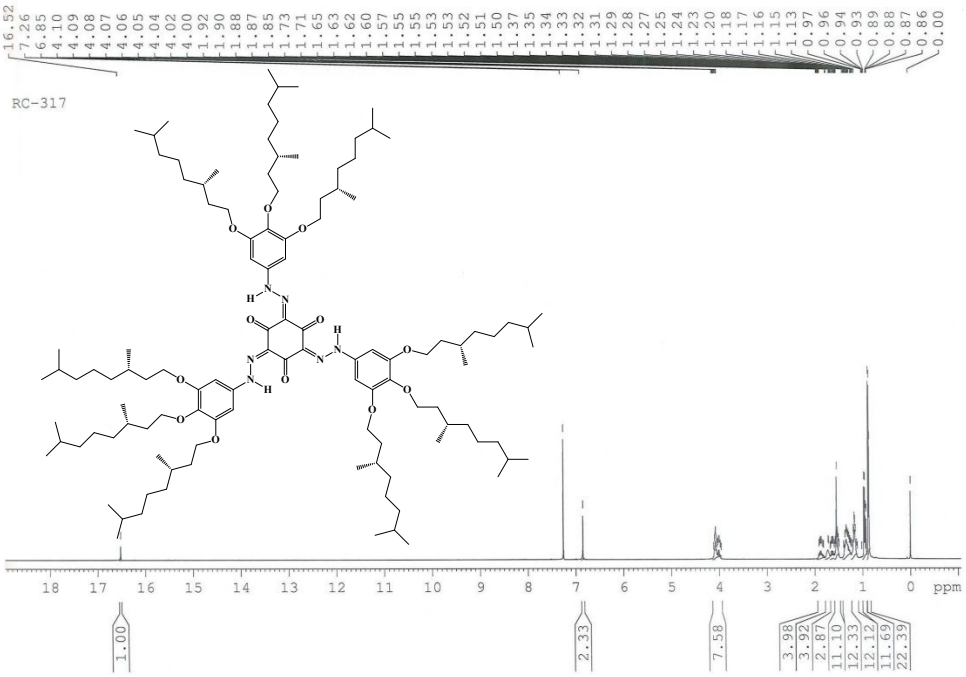


Figure S43. ^{1}H NMR spectrum of compound **THN(9)10B** (400 MHz; $CDCl_3$)

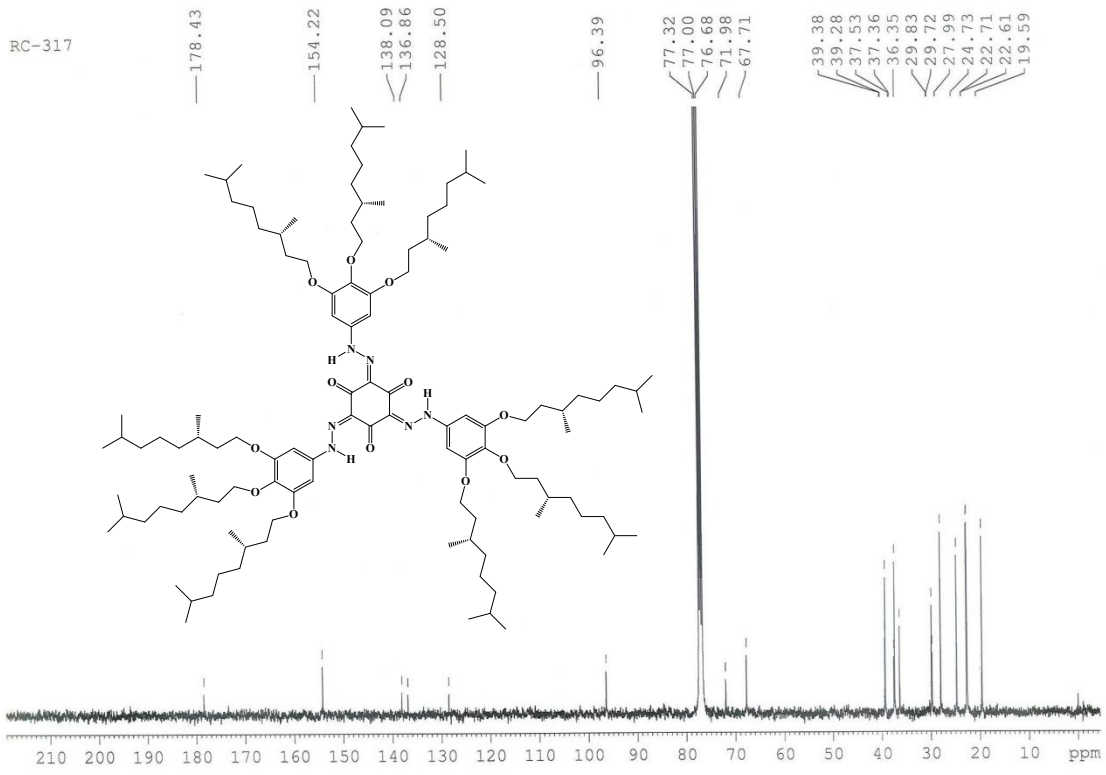
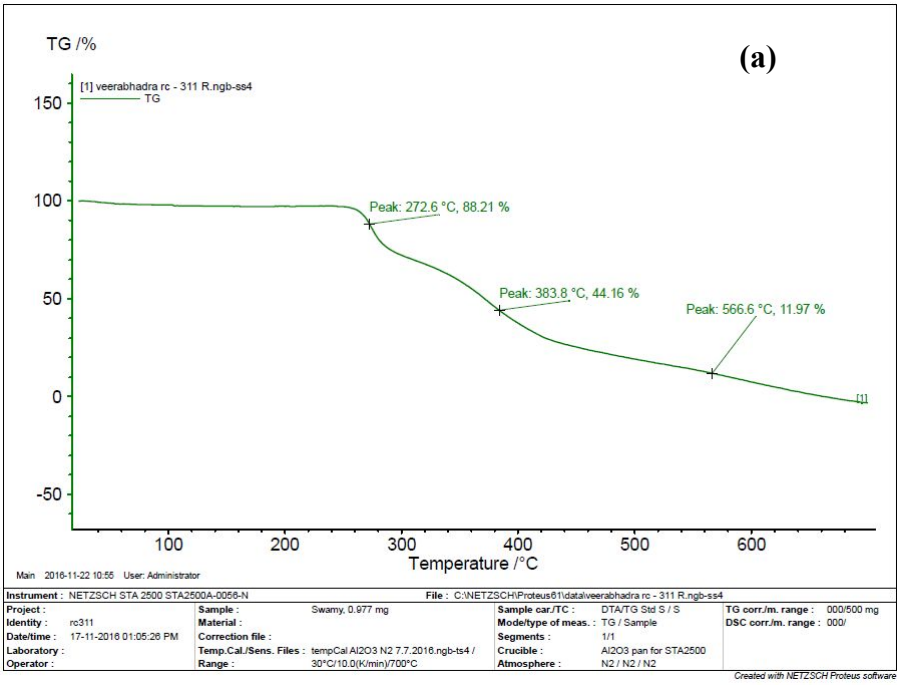


Figure S44. ^{13}C NMR spectrum of compound **THN(9)10B** (100 MHz; $CDCl_3$)



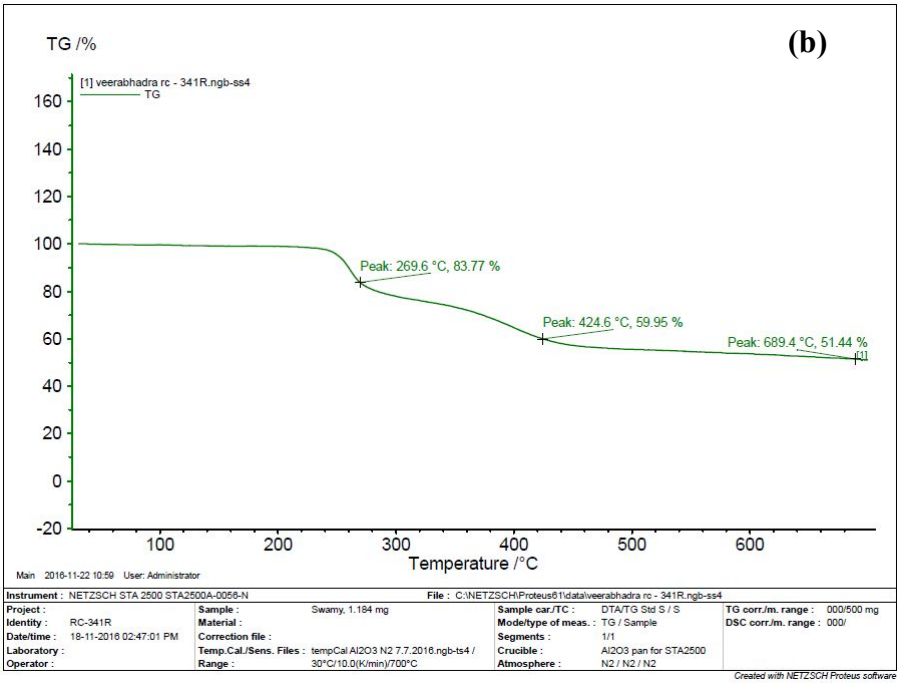
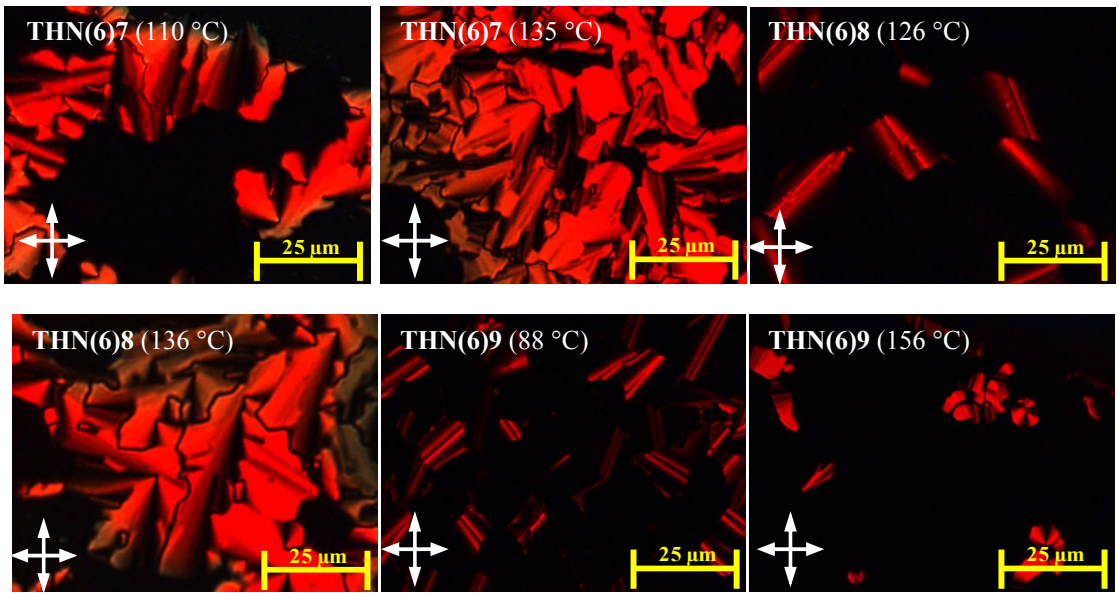
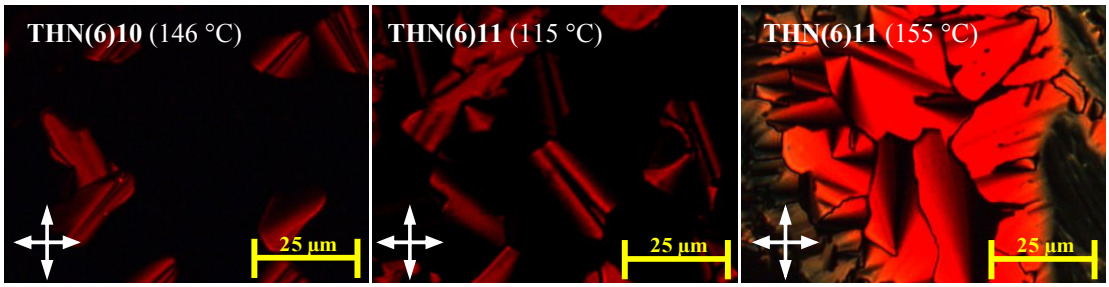
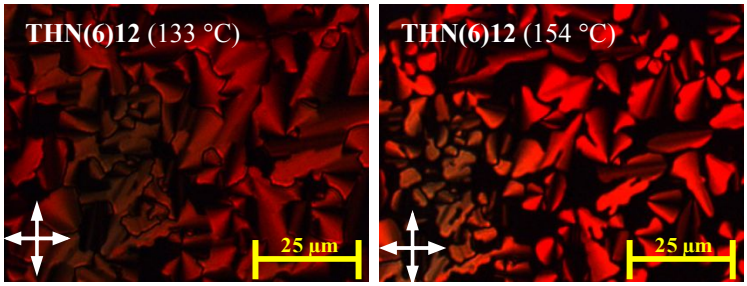
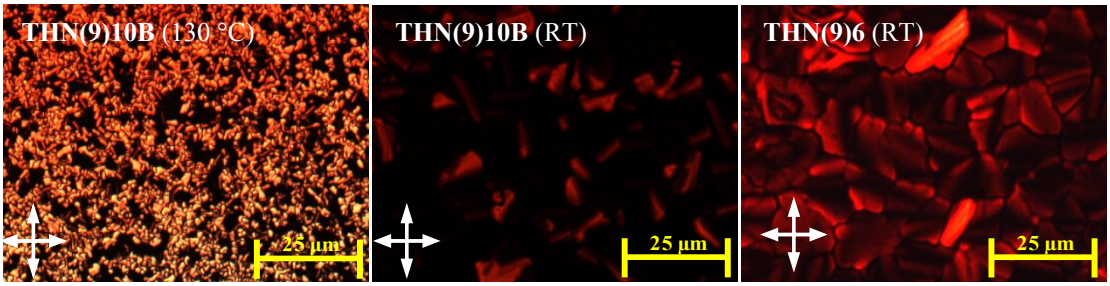


Figure S45. TGA graphs of compounds **THN(6)6** (a) and **THN(9)6** (b)

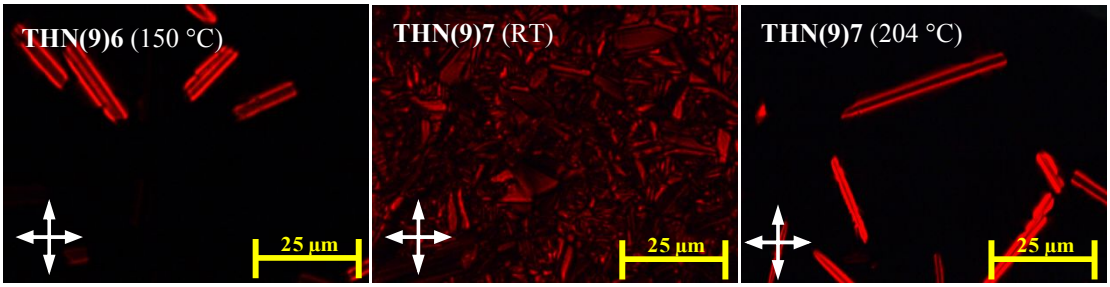


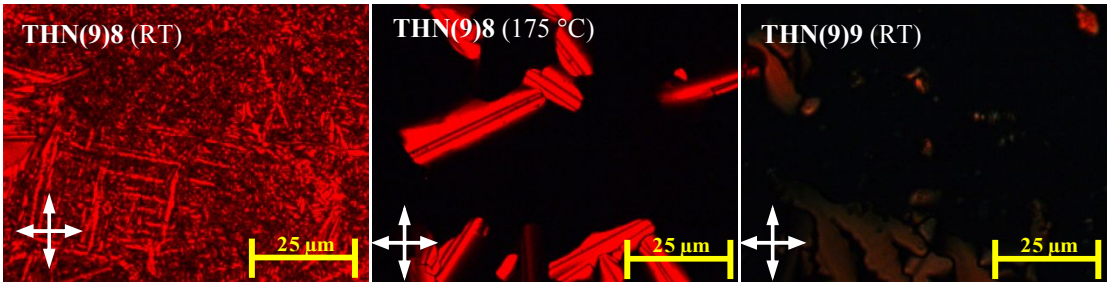

THN(6)10 (146 °C)
25 µm
THN(6)11 (115 °C)
25 µm
THN(6)11 (155 °C)
25 µm


THN(6)12 (133 °C)
25 µm
THN(6)12 (154 °C)
25 µm


THN(9)10B (130 °C)
25 µm
THN(9)10B (RT)
25 µm
THN(9)6 (RT)
25 µm

Continued.....


THN(9)6 (150 °C)
25 µm
THN(9)7 (RT)
25 µm
THN(9)7 (204 °C)
25 µm


THN(9)8 (RT)
25 µm
THN(9)8 (175 °C)
25 µm
THN(9)9 (RT)
25 µm

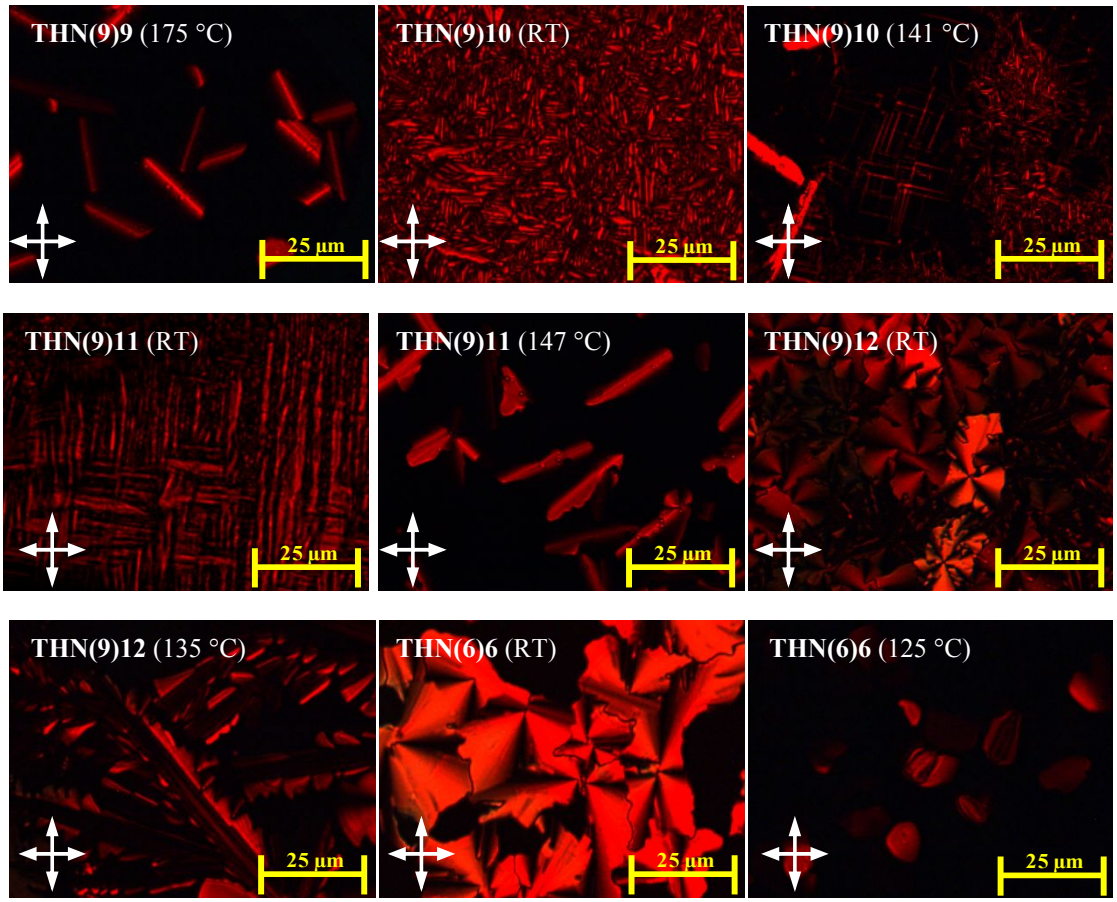


Figure S46. Photomicrographs of the optical textures observed for the Col phase exhibited by discogens of **THN(6)n** and **THN(9)n** series. RT = Room temperature (23-25 °C)

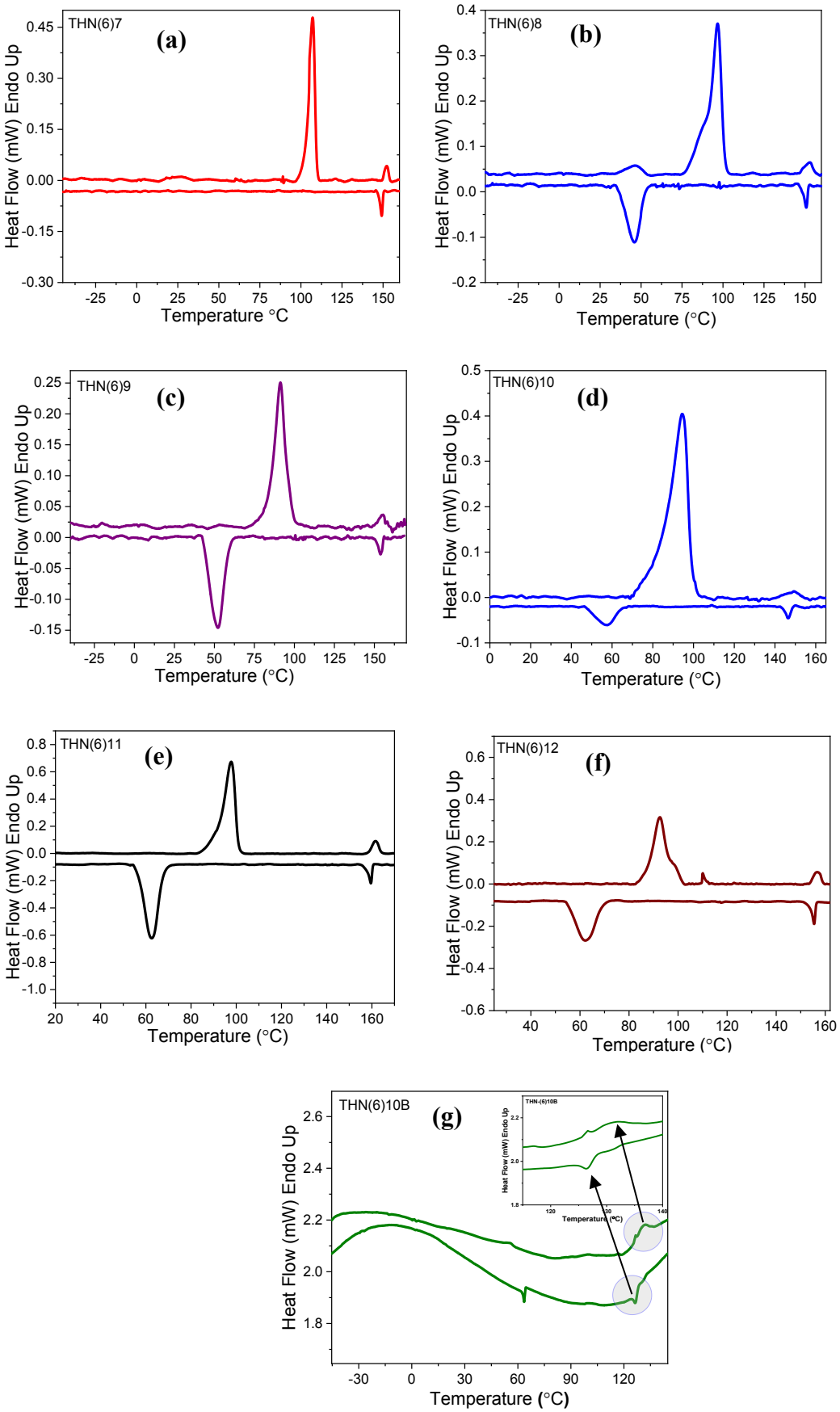


Figure S47. DSC thermograms obtained for discotics belonging to **THN(6)n** series during first heating (top trace) and subsequent cooling (bottom curve) cycles at a rate of 5°C/min.

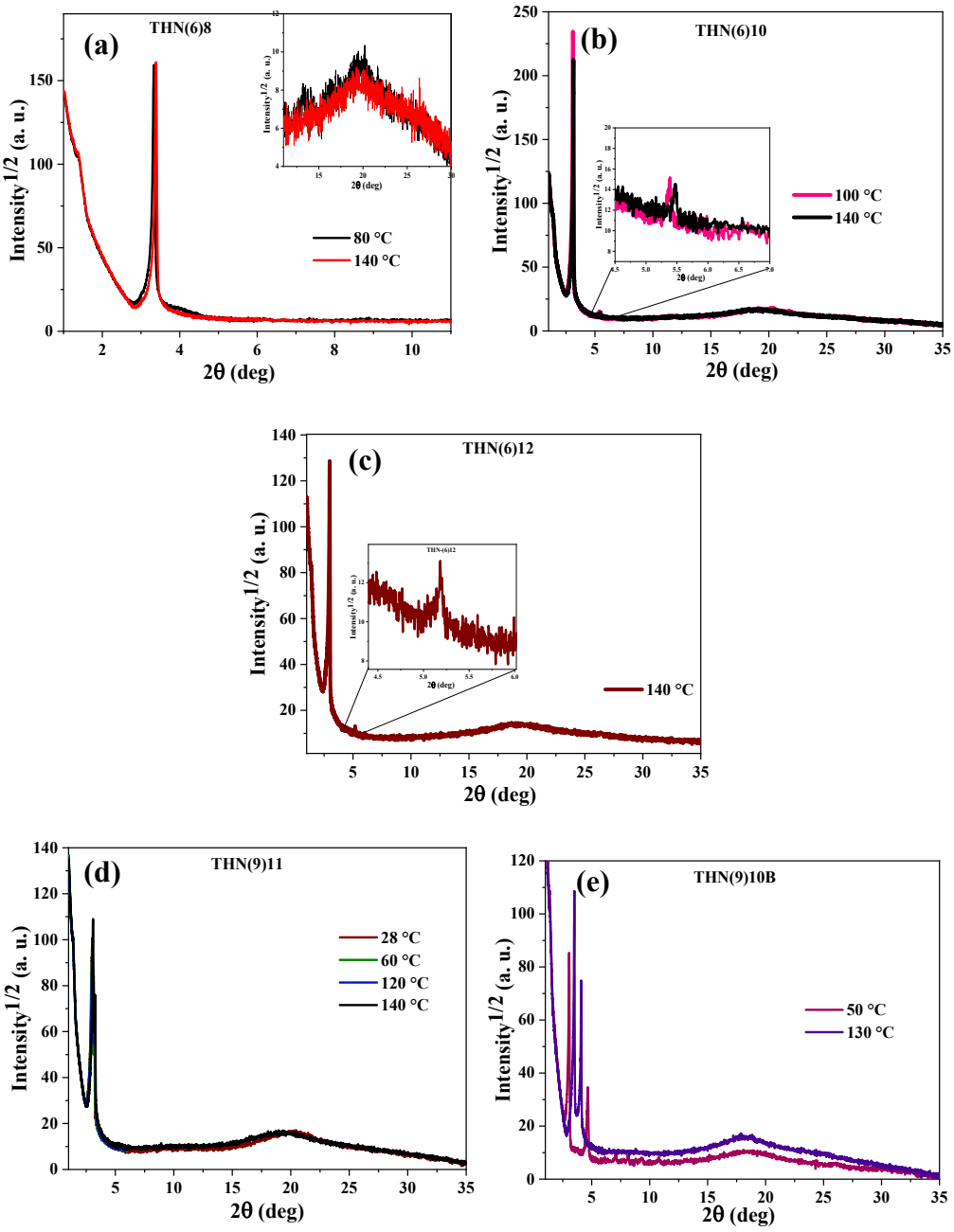


Figure S48. The 1D intensity *vs* 2θ profiles obtained for the Col phase of discogens **THN(6)8** (a), **THN(6)10**(b), **THN(6)12**(c), **THN(9)11**(d) &**THN(9)10B**(e).

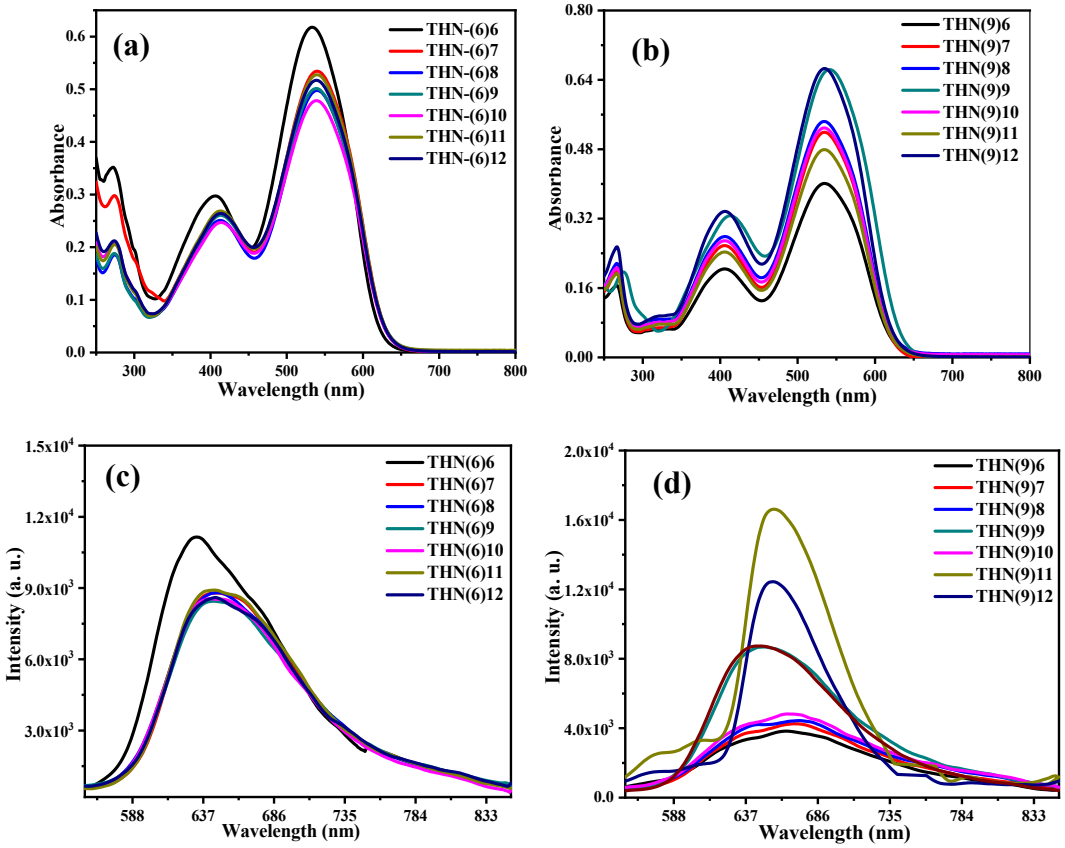
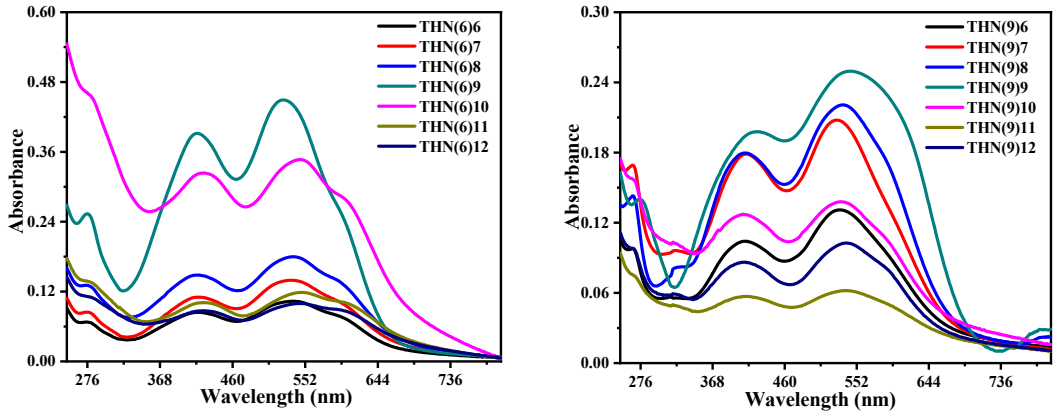


Figure S49. UV-Vis (a) & (b) and emission (c) & (d) spectra of discotic LCs belonging to **THN(6)n** and **THN(9)n** series in the dichloromethane (DCM) solution.



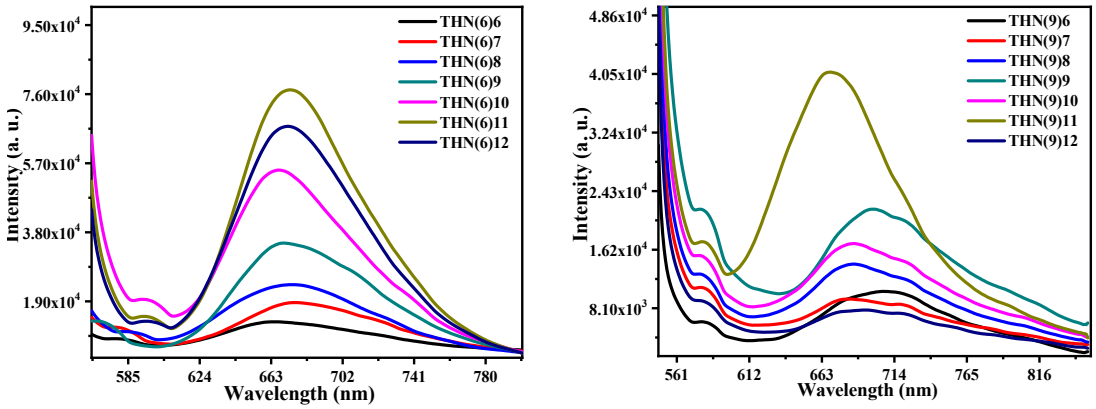


Figure S50. Solid state (thin film) absorption and emission spectra of **TNH(6)n** and **TNH(9)n** series of discotics.

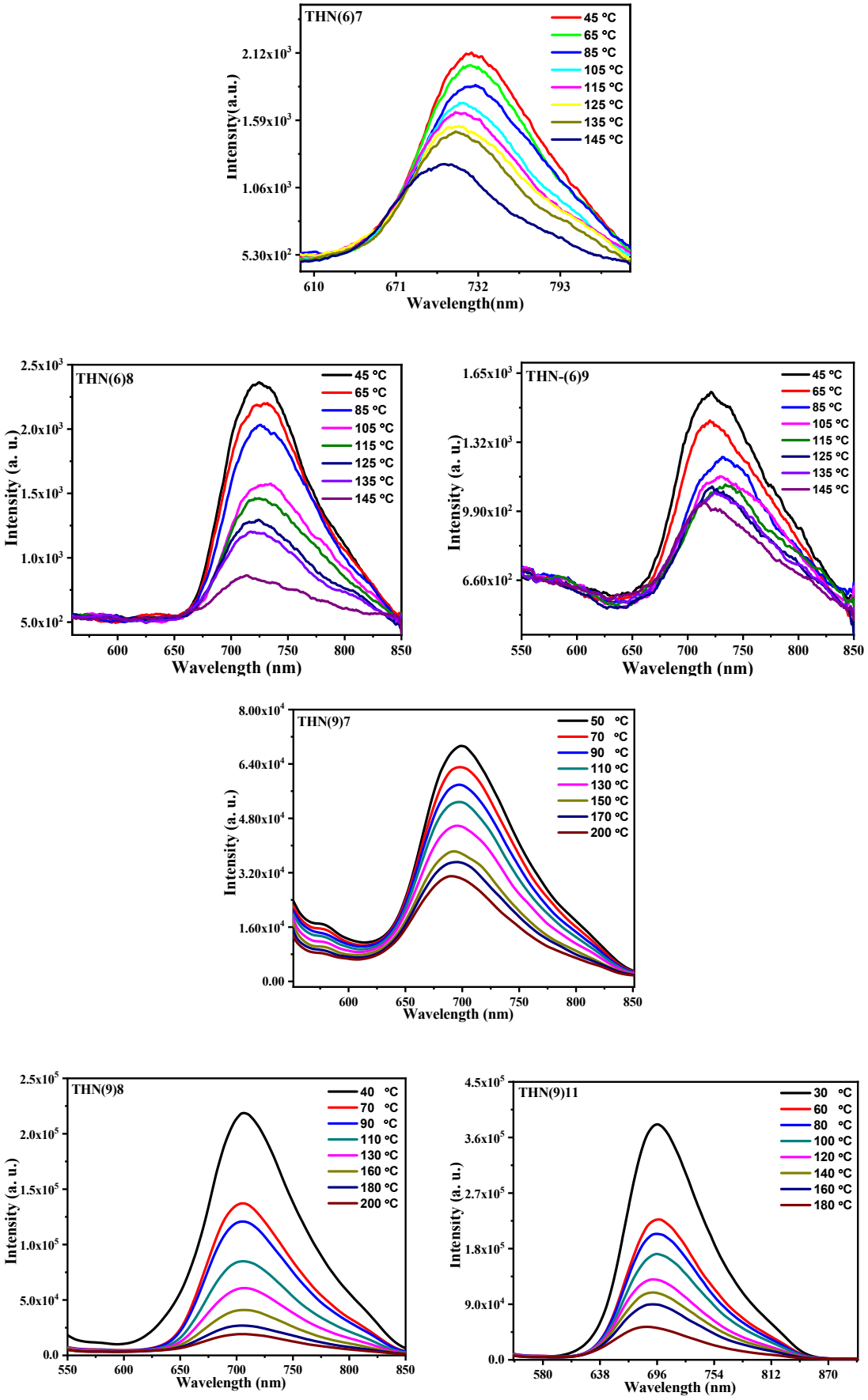


Figure S51. The emission spectra recorded as function of temperature for the Col phase of several representative discotics chosen from **TNH(6)n** and **TNH(9)n** series.

Table S1. Quantum yield of **THN(6)6** and **THN(9)6** discotics

Discotics	Quantum yield (%)
THN(6)6	4.5
THN(9)6	9.8
Relative quantum yield technique adopted, **Rhodamine-B** dissolved in water was used as internal standard. The excitation wavelength of Rhodamine-B is 545 nm and emission wavelength is 586 nm. 0.2 μM, 0.4 μM, 0.6 μM and 0.8 μM solutions of Rhodamine-B has been used. The quantum yield of Rhodamine-B is 31%.	

To determine the efficiency of emission, the quantum yield was calculated for all the samples. Relative quantum yield technique was used for the determination of quantum yield. Rhodamine-B dissolved in water was used as an internal standard. After dissolving the known amounts of compounds, **THN(6)6** and **THN(9)6**, in DCM with different concentration, absorption and emission spectra were recorded. A plot consisting of emission *vs* absorption intensity was obtained as shown in Fig. S41. The slope (gradient) obtained from this plot was used for the calculation of relative quantum yield using the formula given below.

$$\Phi_x = \Phi_{std}\,[Grad_x/Grad_{std}][\eta^2_x/\,\eta^2_{std}]$$

Φ_x– Quantum yield of the unknown sample (LC)

Φ_{std}- Quantum yield of the standard (Rhodamine B)

$Grad_x$ – slope/gradient obtained for the plot of unknown sample (LC)

$Grad_{std}$ – slope/gradient obtained for the plot of Standard sample

η^2_x – refractive index of the solvent used for standard

η^2_{std} – refractive index of the solvent used for unknown (LC)

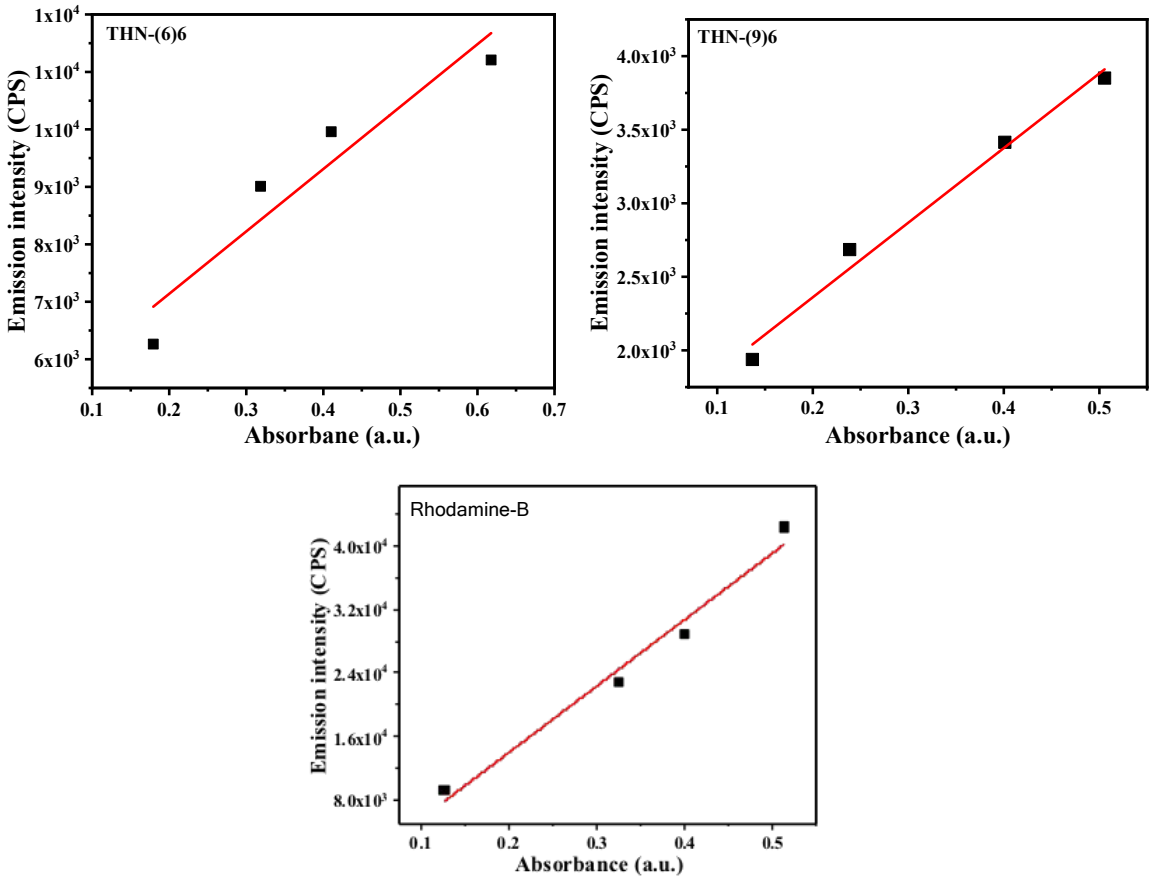


Figure S52. Plots of integrated fluorescence intensity *vs* the absorbance of compounds **THN(6)6**, and **THN(9)6** at 0.2 μM, 0.4 μM, 0.6 μM and 0.8 μM concentration in dichloromethane (DCM) and the same obtained for Rhodamine B dissolved in water at same concentrations.

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