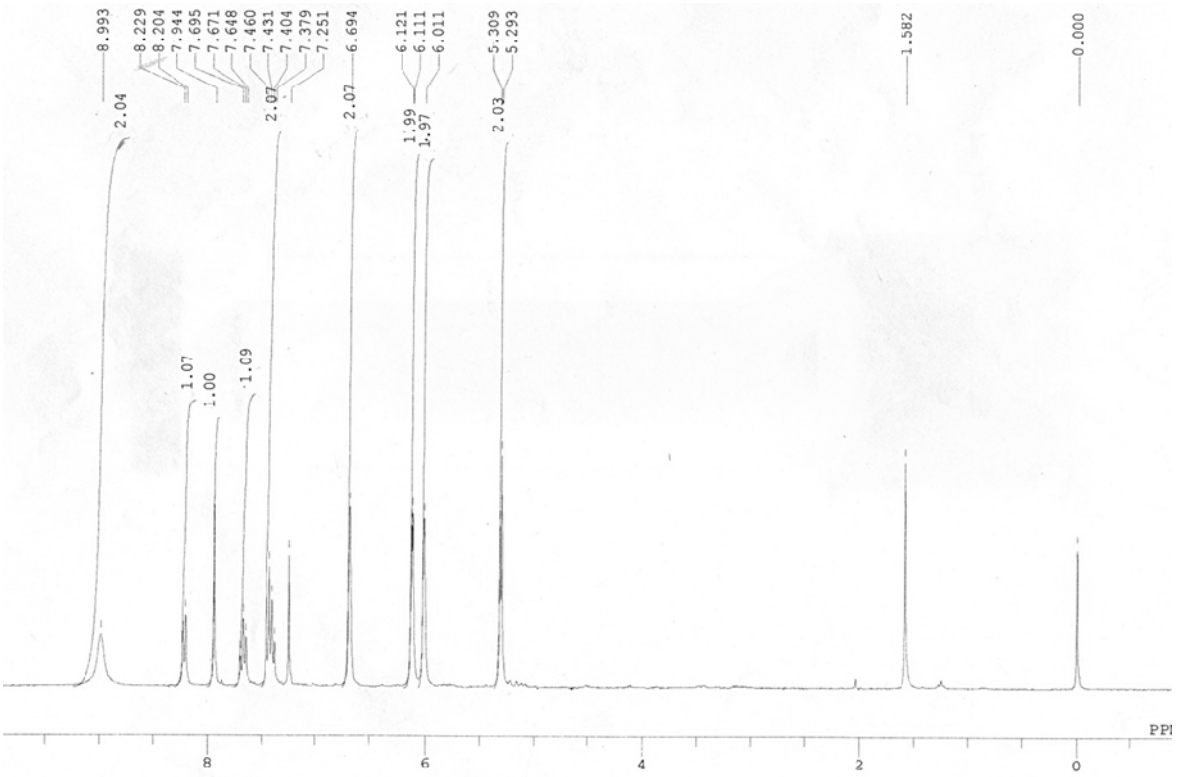
Luminescent N,O-Chelated Chroman-BF_2 Complexes: Structural Variants of BODIPY

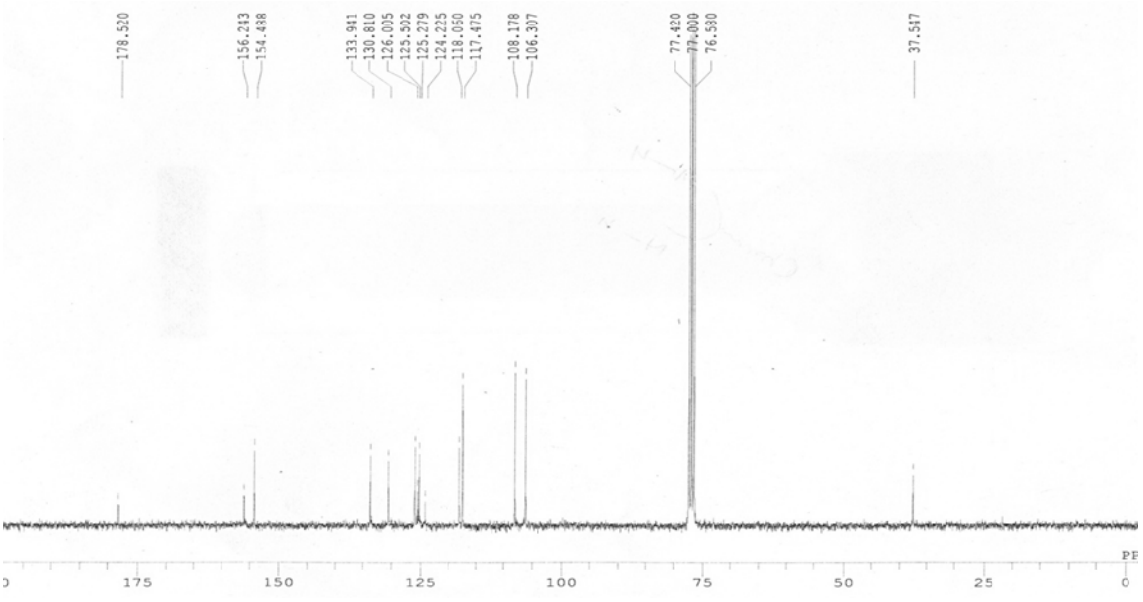
Roop Shikha Singh, Mahendra Yadav, Rakesh Kumar Gupta, Rampal Pandey and Daya Shankar Pandey*

Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi - 221 005 (U. P.) India.

Contents

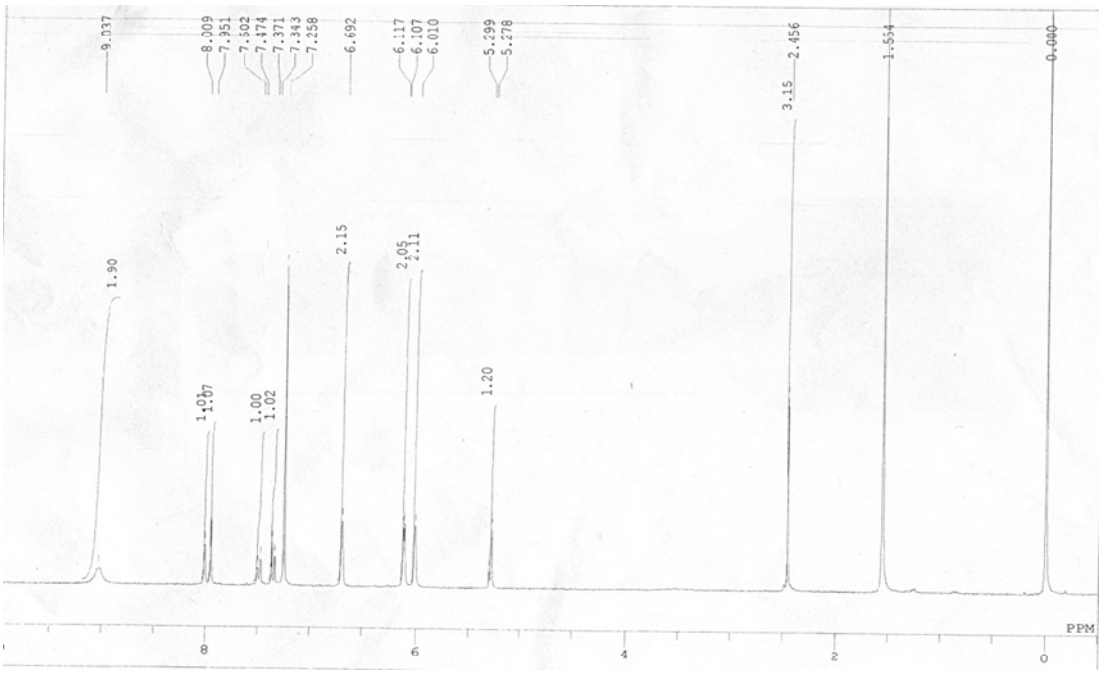


(a)

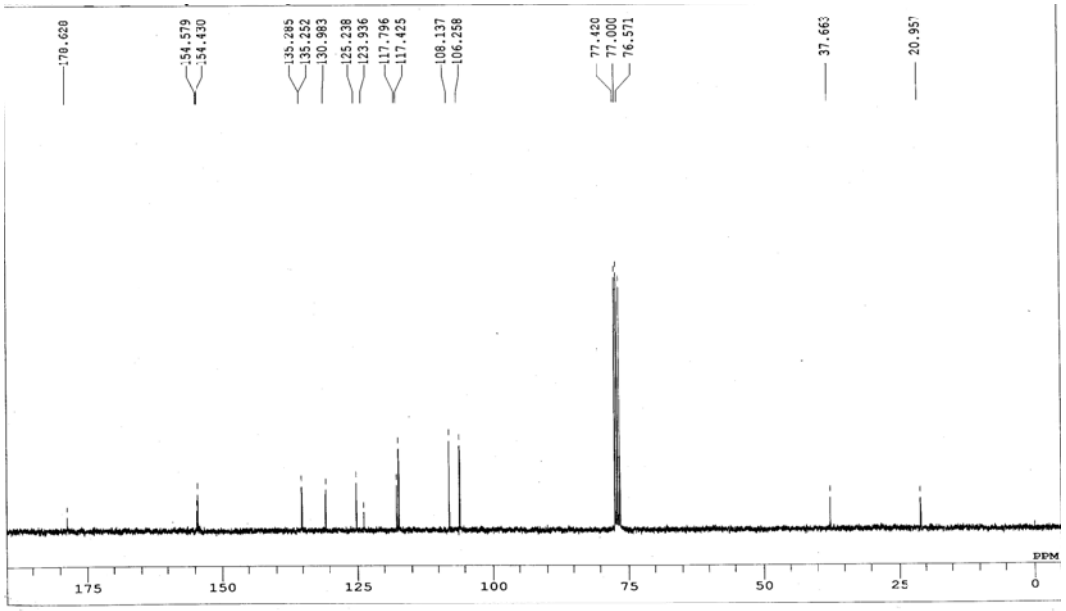


(b)

Figure S1 ^{1}H (a) and ^{13}C (b) NMR spectra of **1**

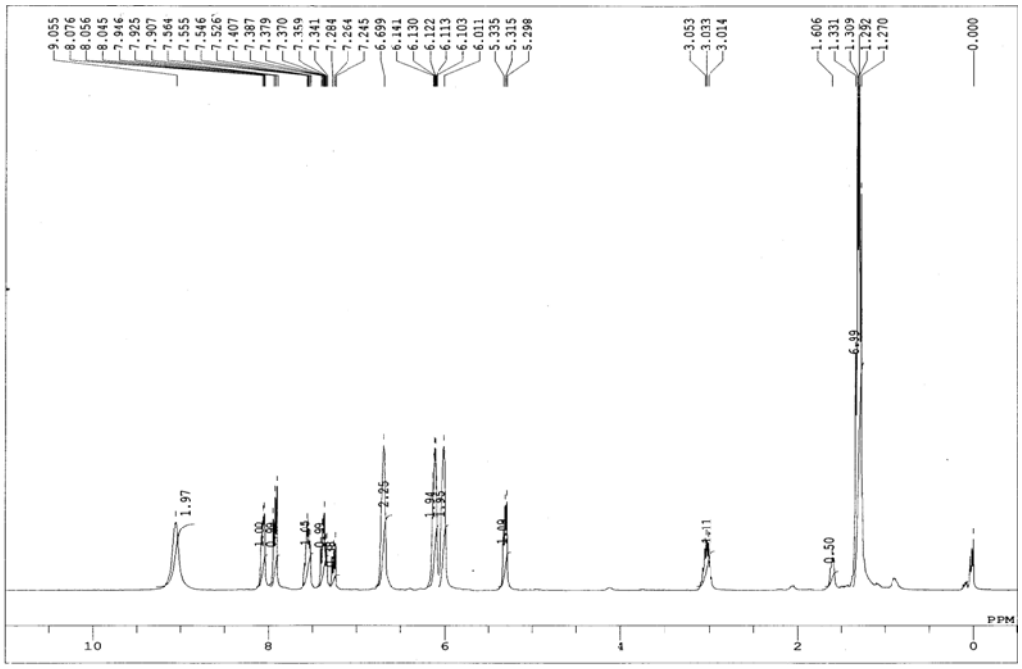


(a)

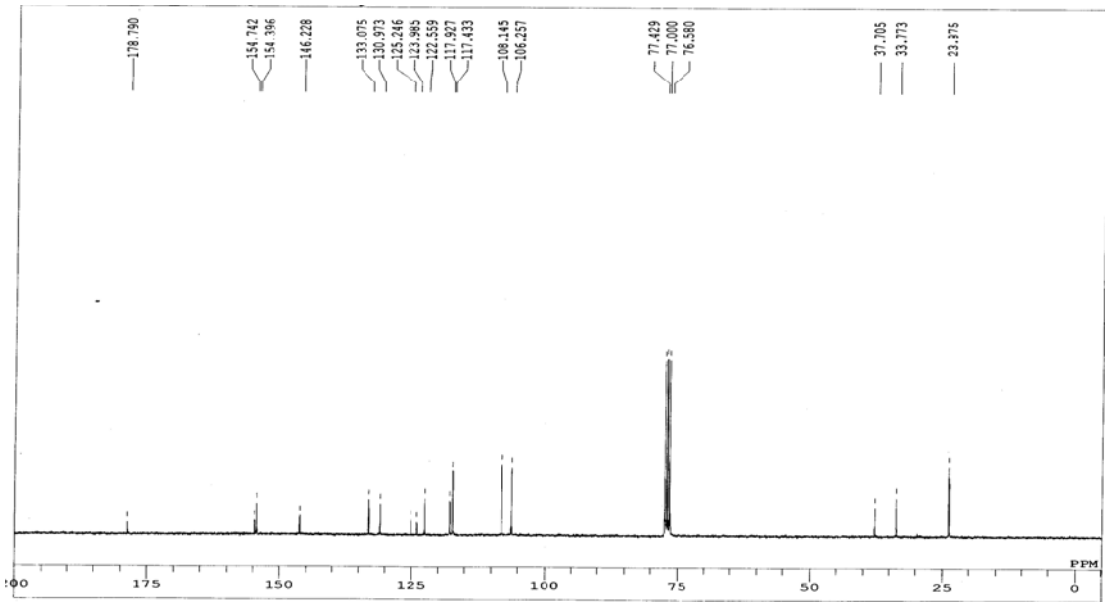


(b)

Figure S2: ^{1}H (a) and ^{13}C (b) NMR spectra of **2**

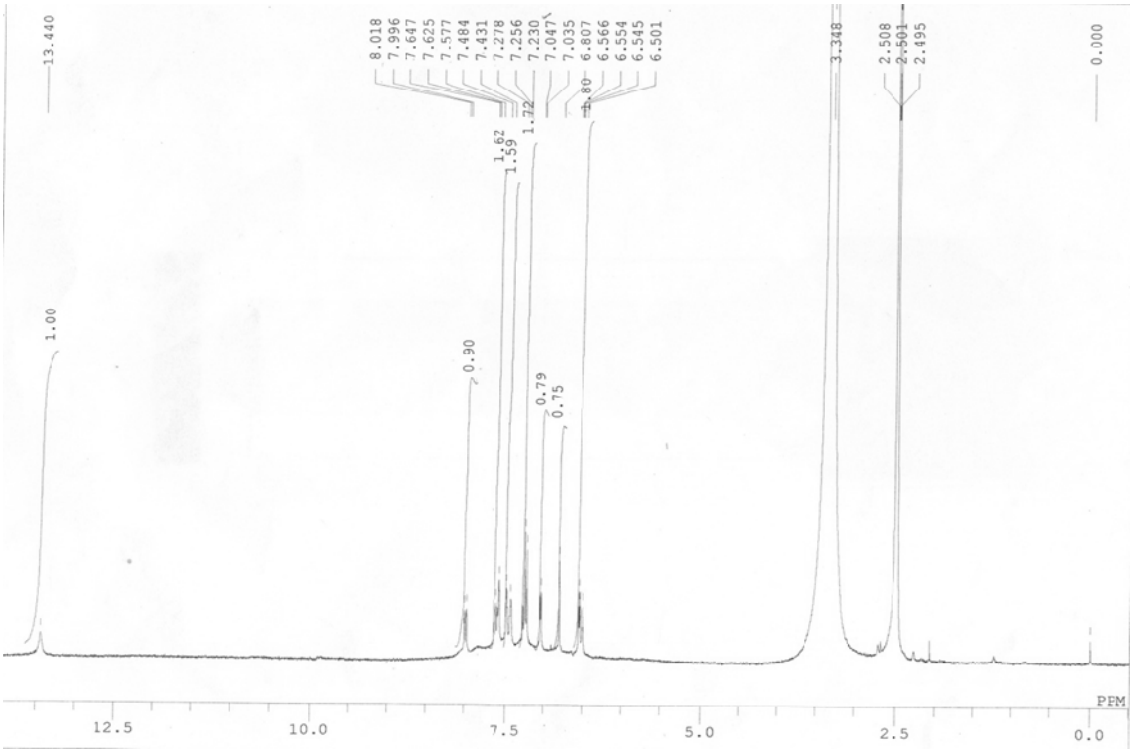


(a)

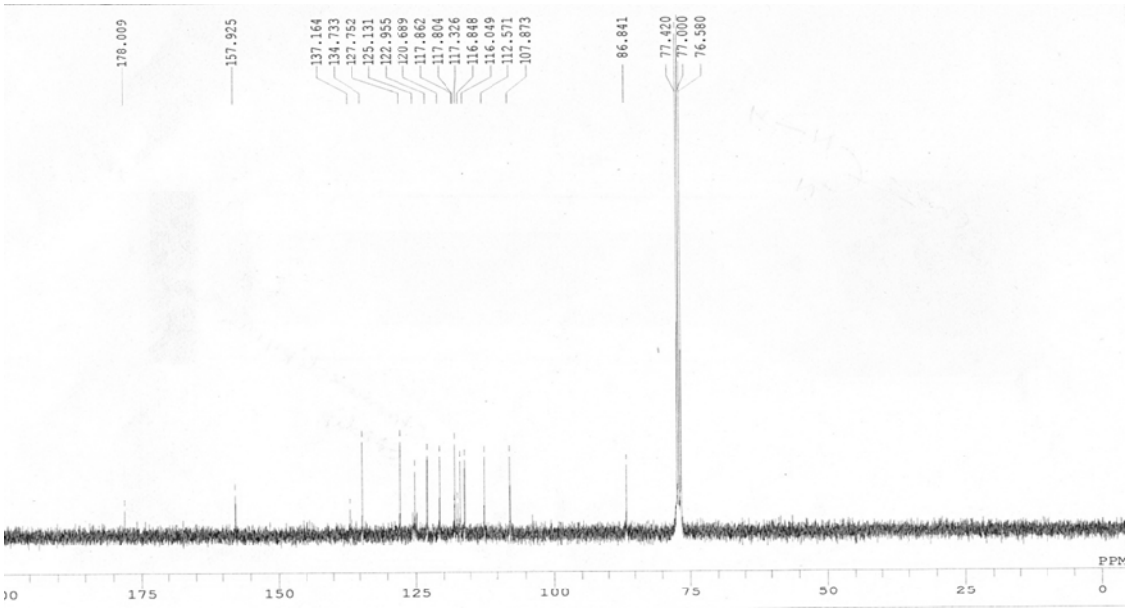


(b)

Figure S3: ^{1}H (a) and ^{13}C (b) NMR spectra of **3**

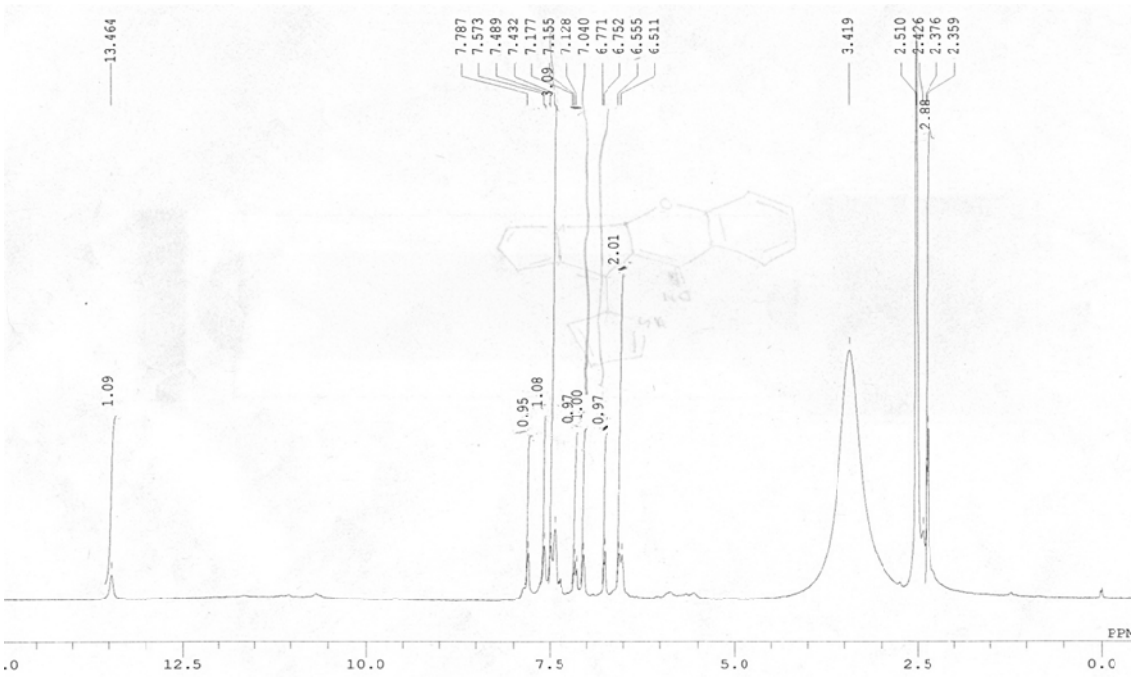


(a)

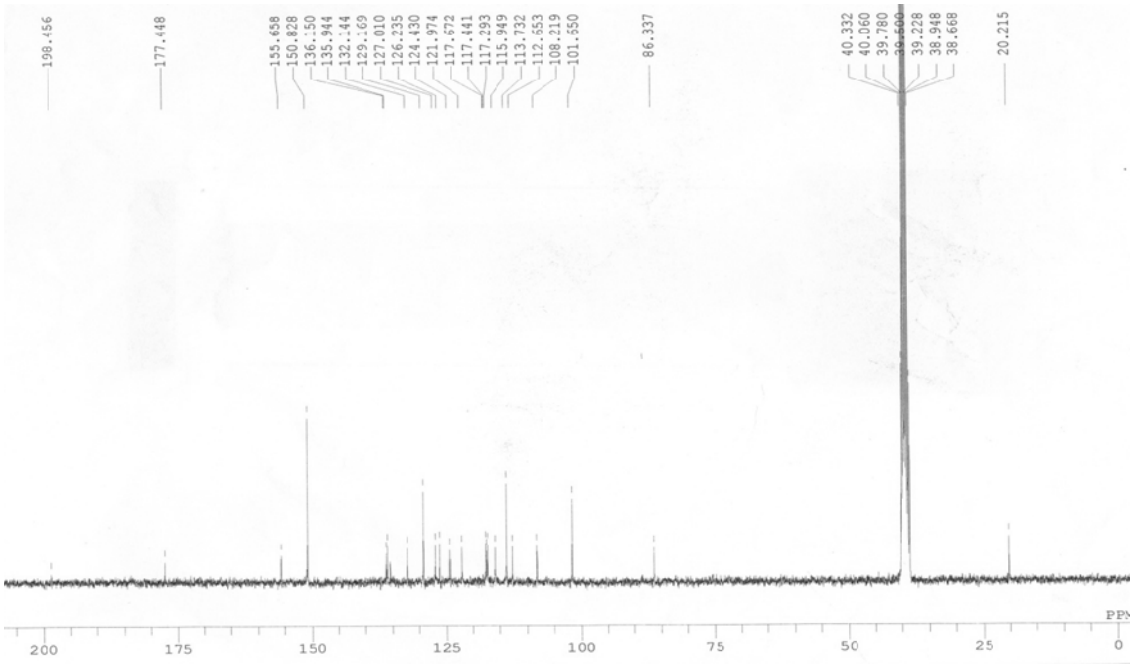


(b)

Figure S4 ^{1}H (a) and ^{13}C (b) NMR spectrum of **4**

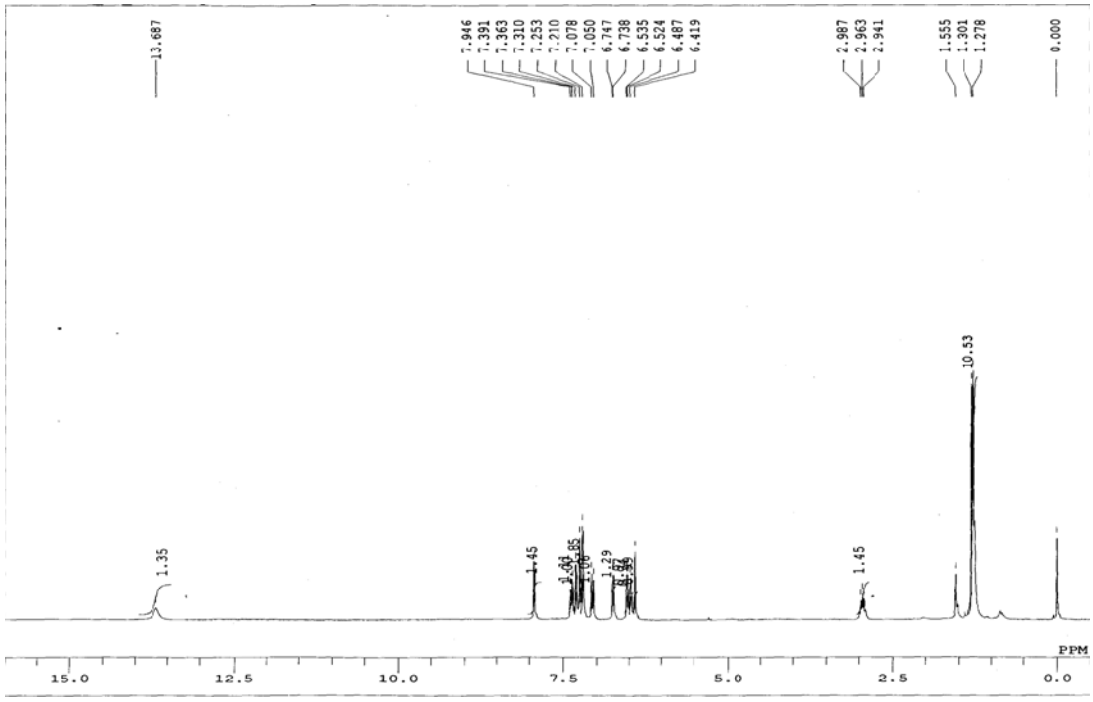


(a)

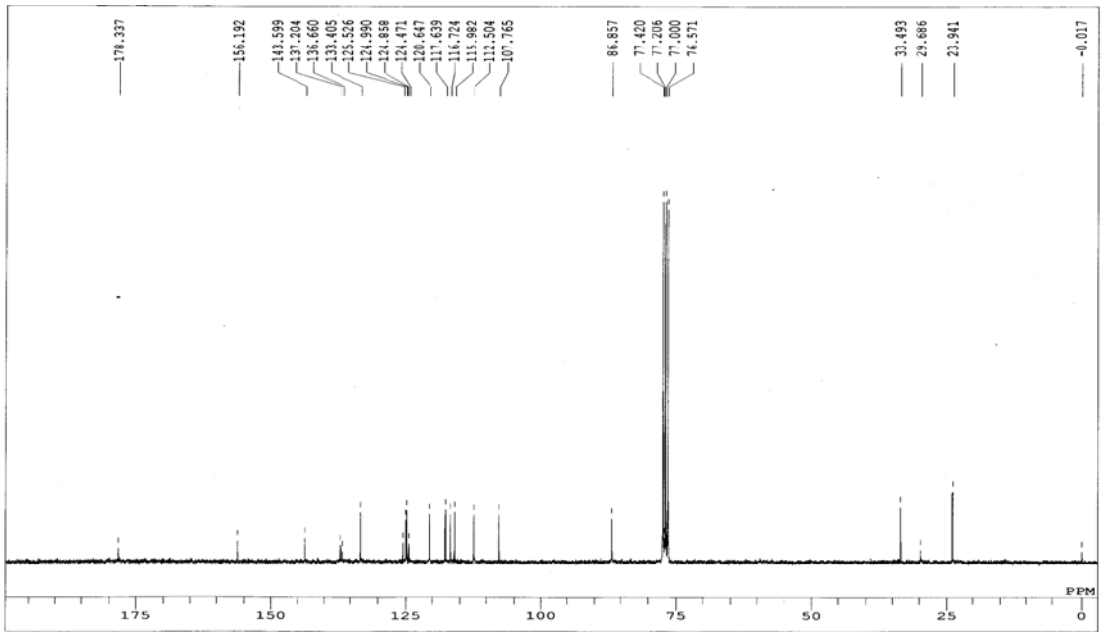


(b)

Figure S5 ^{1}H (a) and ^{13}C (b) NMR spectrum of **5**

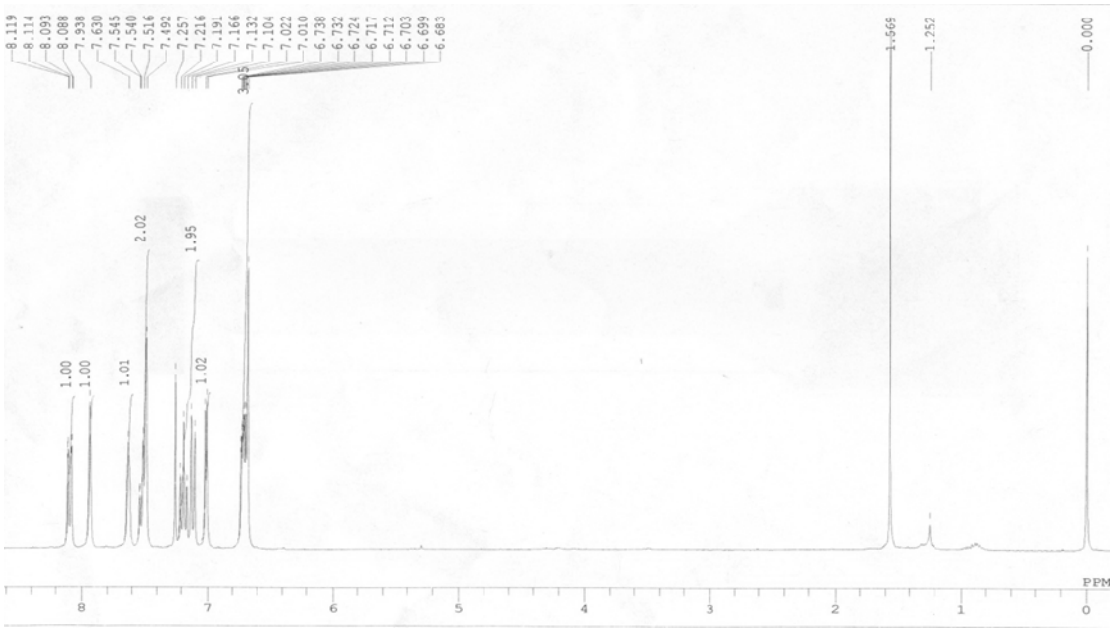


(a)

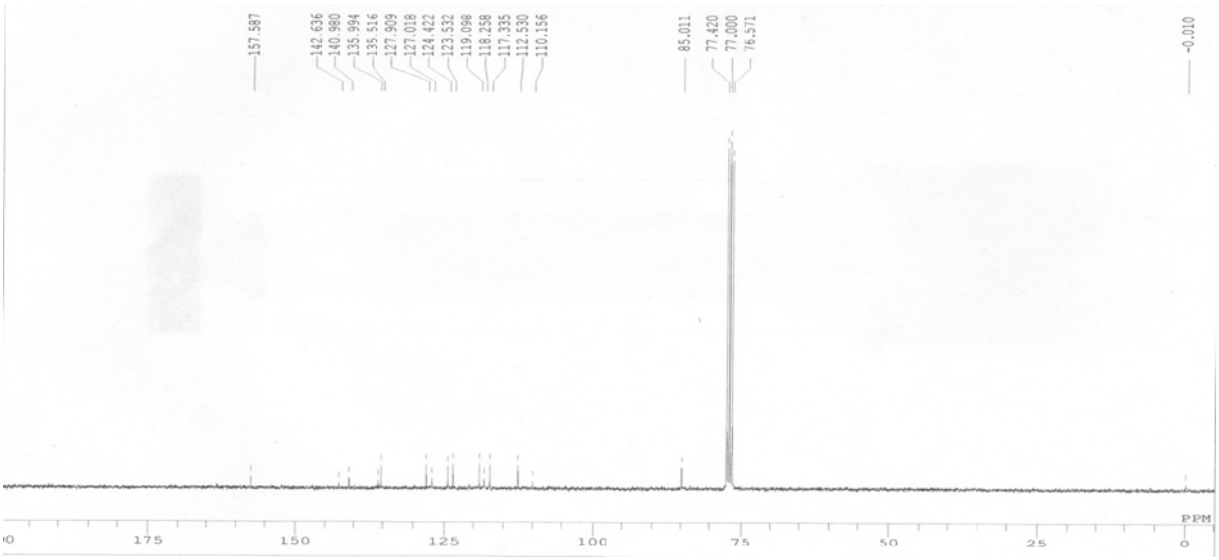


(b)

Figure S6 ^{1}H (a) and ^{13}C (b) NMR spectrum of **6**

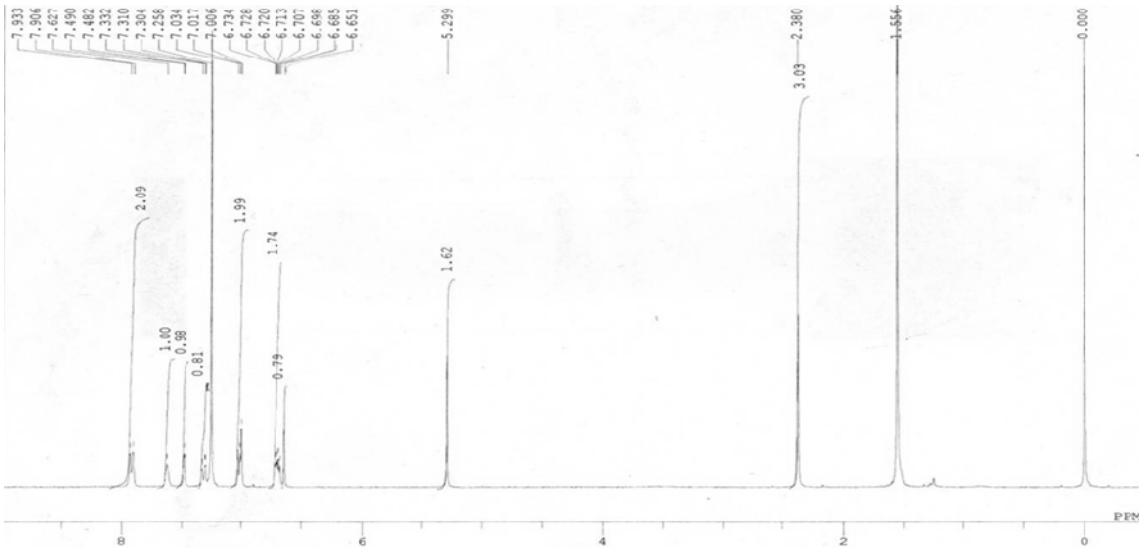


(a)

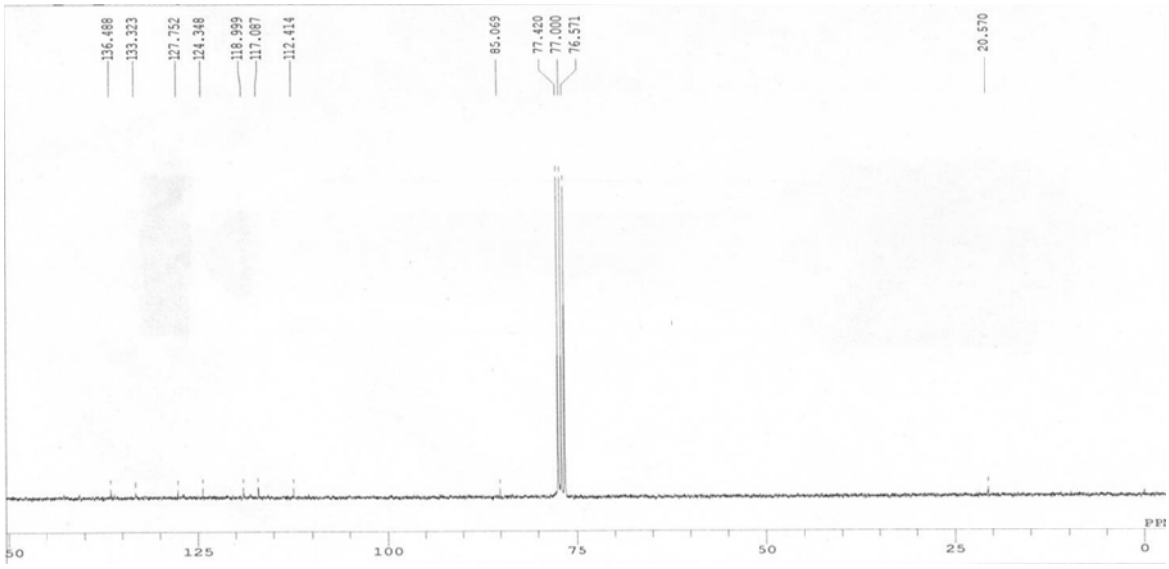


(b)

Figure S7 ^{1}H (a) and ^{13}C (b) NMR spectrum of **7**

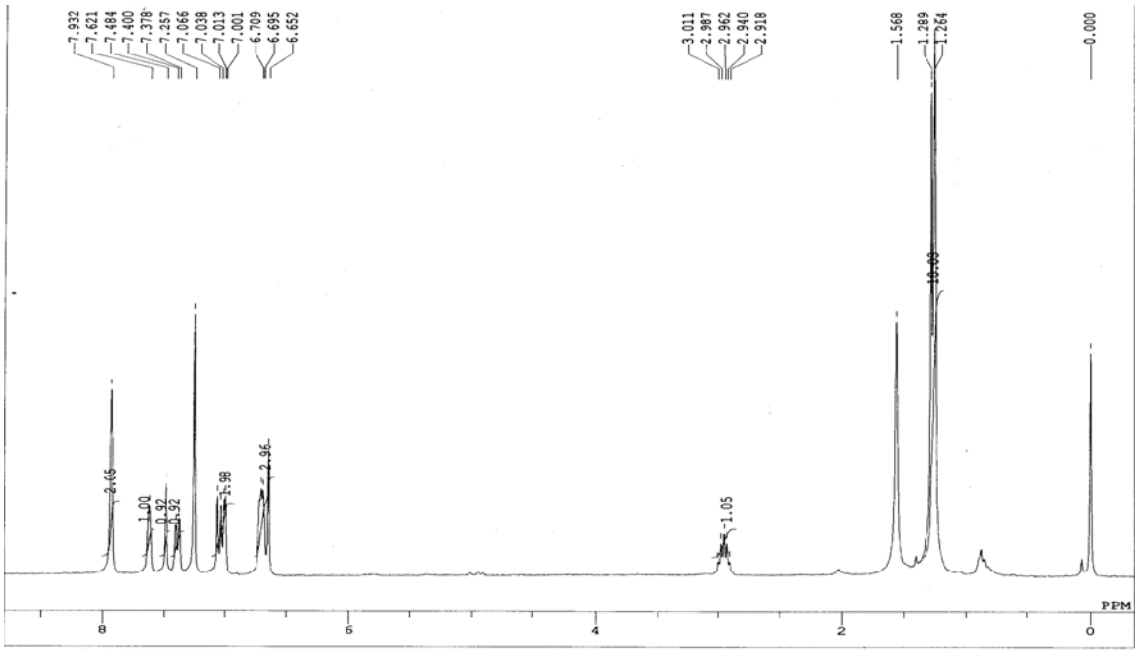


(a)

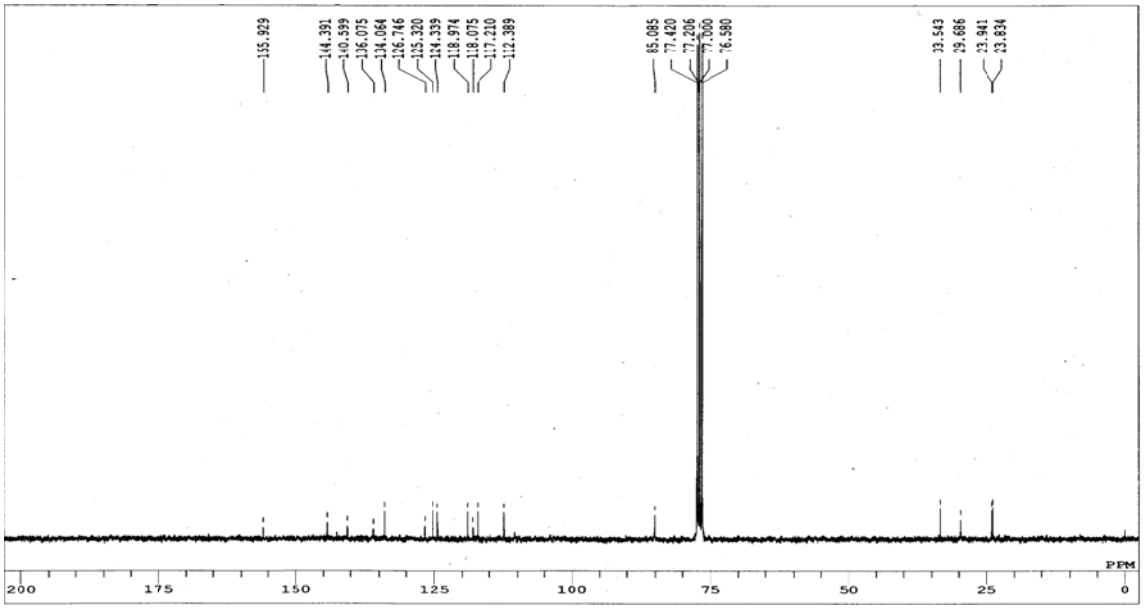


(b)

Figure S8 ^{1}H (a) and ^{13}C (b) NMR spectrum of **8**

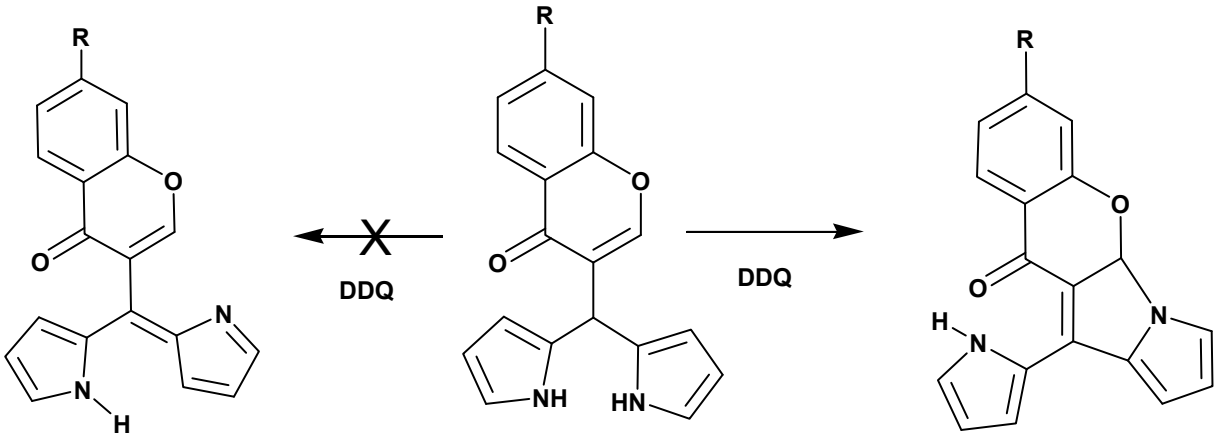


(a)

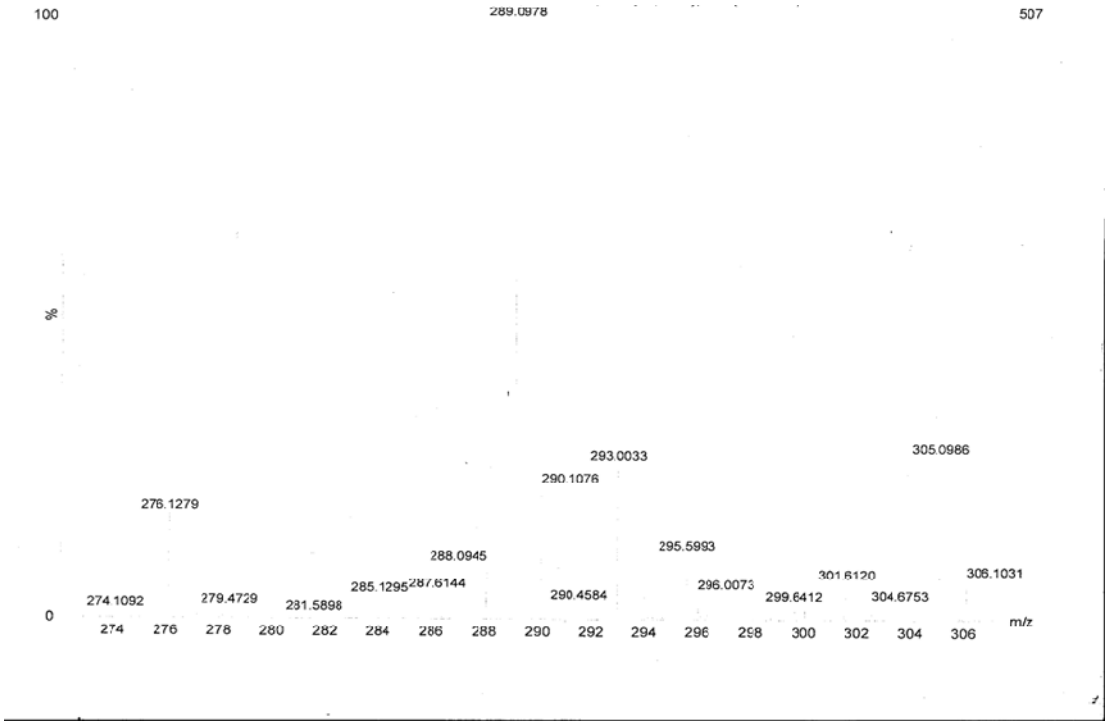


(b)

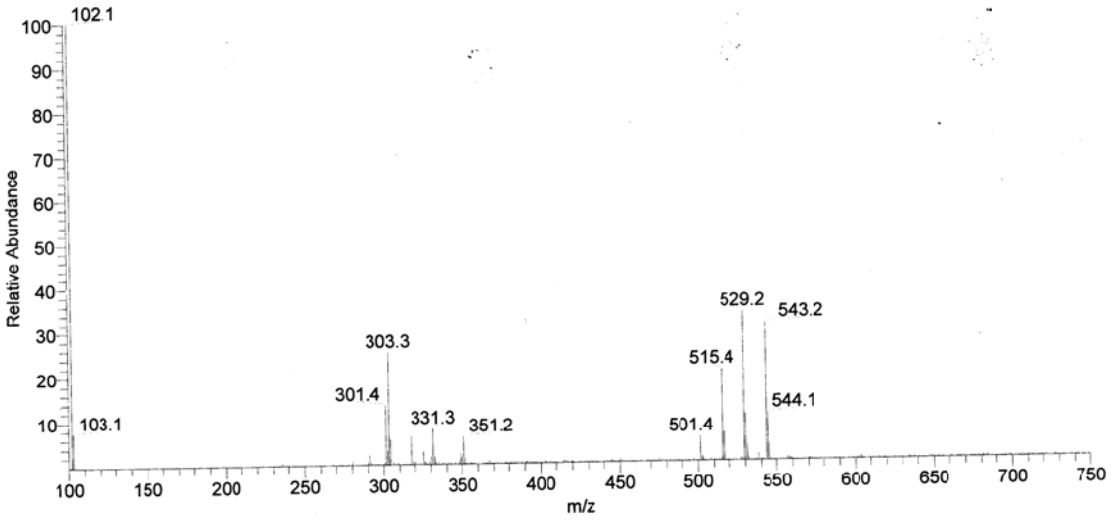
Figure S9 ^{1}H (a) and ^{13}C (b) NMR spectrum of **9**



Scheme S1 Scheme showing formation of chromans **4-6** instead of dipyrromethenes **4′-6′**



(a)



(b)

Figure S10: HRMS data of compound **4** (a) and **8** (b)

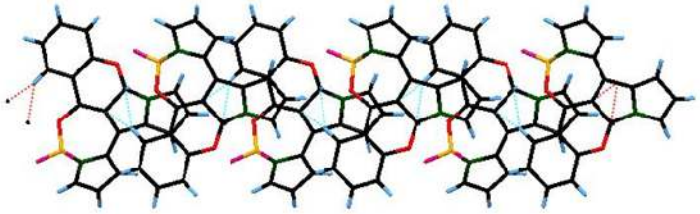


Figure S11 The C-H···π interactions in **7** along crystallographic-'*a*' axis

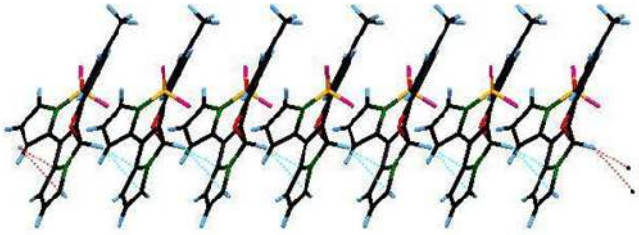


Figure S12 The C-H···π interactions in **8** along crystallographic-'*b*' axis

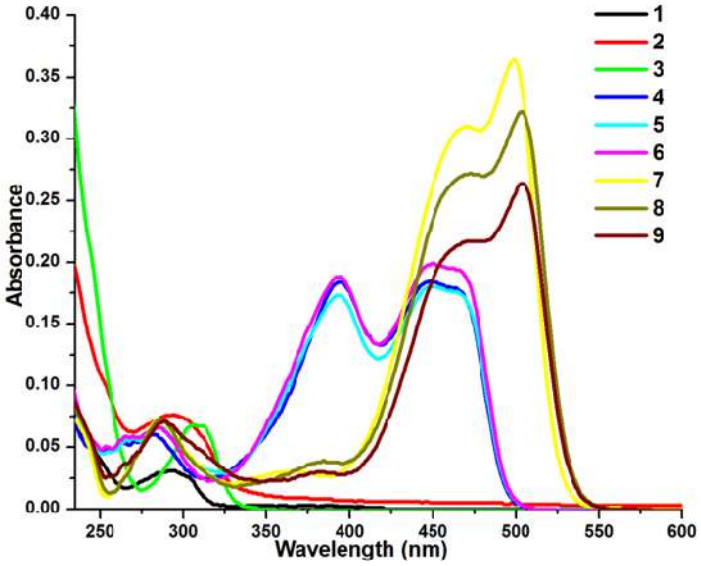


Figure S13 Absorption spectra of **1-9** (c , 10 μM).

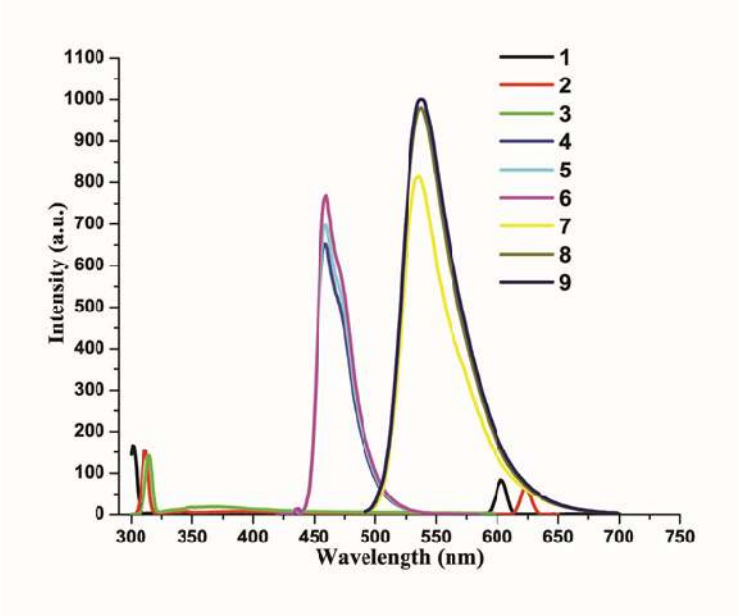


Figure S14 Fluorescence spectra of **1-9** (c, 10 μM)

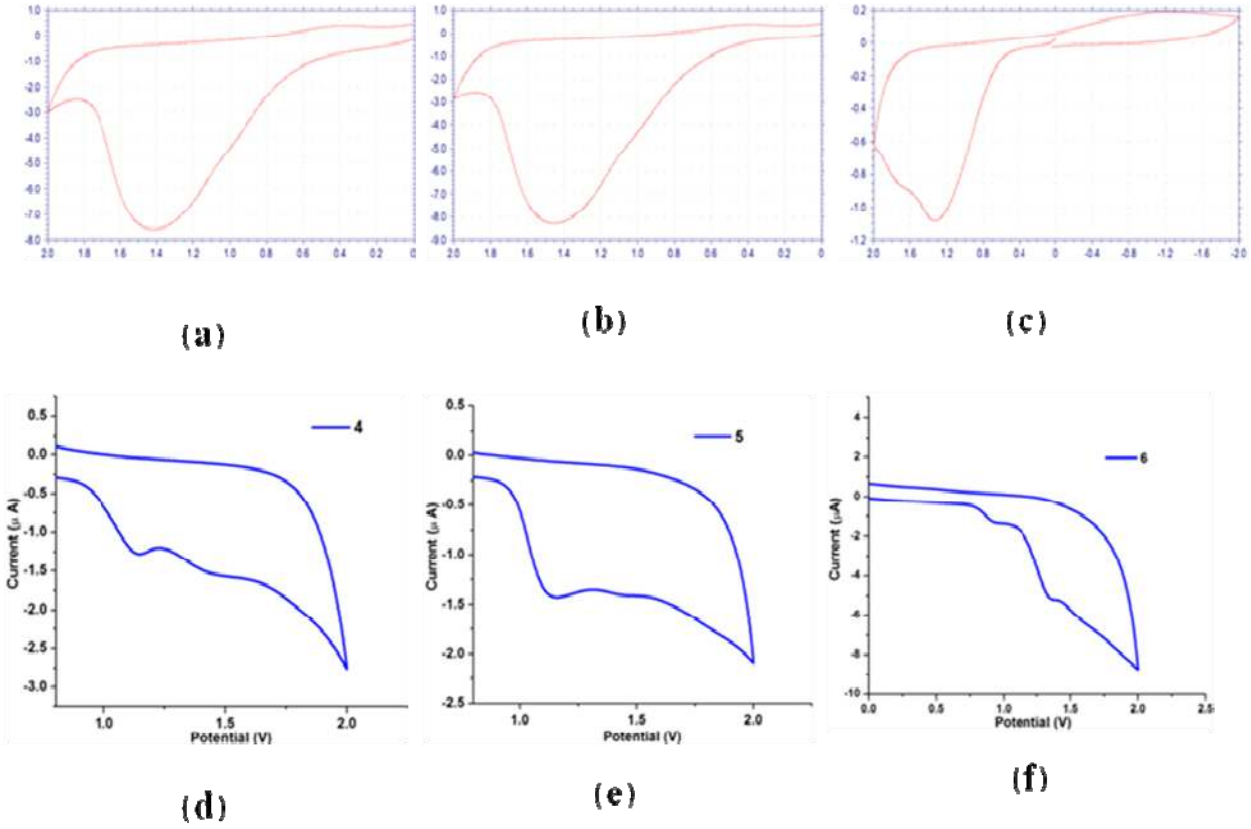
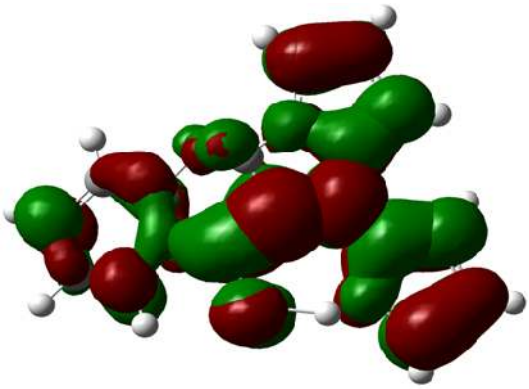
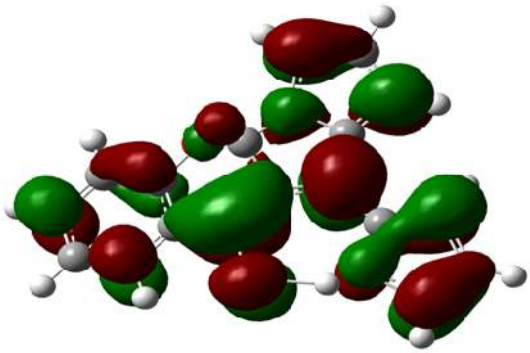


Figure S15 Cyclic voltammograms of ligands **1** (**a**), **2** (**b**), **3**(**c**), **4** (**d**), **5**(**e**), **6**(**f**)

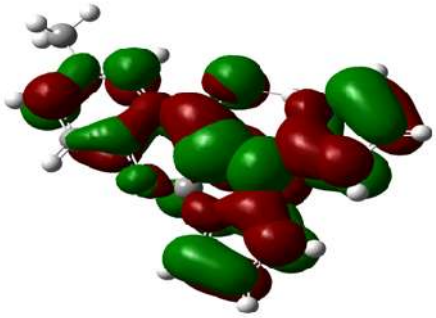


(a)

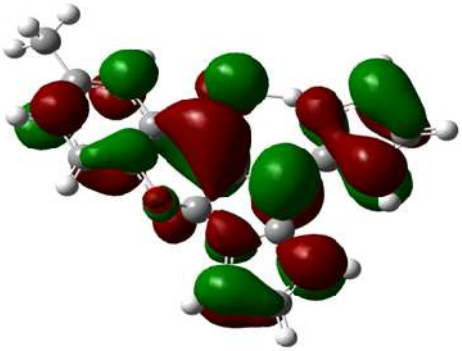


(b)

Figure S16 HOMO (a) and LUMO (b) envelop plots for **4**

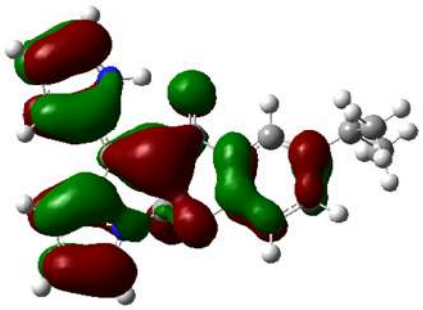


(a)

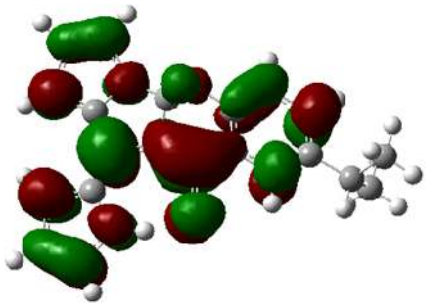


(b)

Figure S17 HOMO (a), LUMO (b) envelop plots for **5**

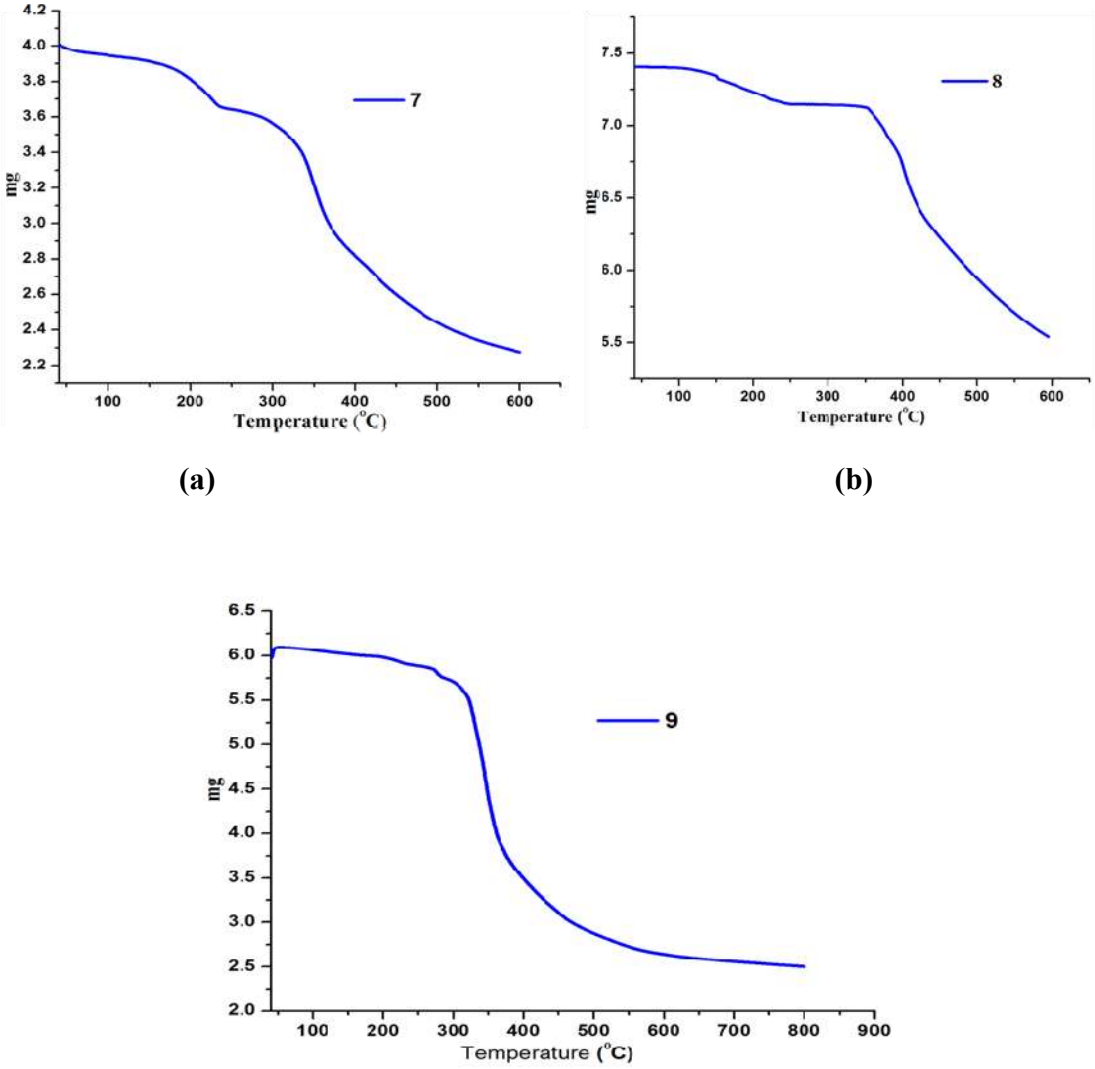


(a)



(b)

Figure S18 HOMO (a), LUMO (b) envelop plots for **6**



(a) **(b)**

(c)

Figure S19 TGA plot of **7** (a), **8** (b), **9** (c)

Table S1. Selected bond distances (a) and Angles (b) in **1, 2, 6** and **7-9**

1		**2**		**6**	
O1 -C9	1.357(3)	O1- C9	1.346(2)	N1-C16	1.3663(2)
N1- C11	1.366(3)	C11- N1	1.371(2)	N1-C11	1.4355(2)
N1- C14	1.374(3)	C14- N1	1.422(3)	C10-C11	1.5128(2)
N2- C18	1.357(4)	N2- C18	1.423(3)	C10-C21	1.4428(2)
N2- C15	1.370(3)	C15- N2	1.379(3)	C10-C14	1.3768(2)
C7- C8	1.438(4)	C8- C7	1.459(2)	C13-C14	1.4600(2)
C8- C9	1.337(4)	C8- C9	1.354(2)	N2-C20	1.346(2)
C10- C15	1.511(4)	C10- C15	1.508(2)	O1-C21	1.2385(12)
C10 -C11	1.515(4)	C10- C11	1.510(2)		
7		**8**		**9**	
B1- F2	1.369(3)	B1 -F2	1.380(3)	B1 -F2	1.376(5)
B1- F1	1.389(3)	B1- F1	1.379(3)	B1- F1	1.373(5)
B1- O1	1.483(3)	B1 –O1	1.487(3)	B1 –O1	1.468(5)
B1- N1	1.542(3)	B1 -N1	1.554(3)	B1 -N1	1.552(5)
N2- C15	1.388(3)	N2 -C9	1.436(3)	N2 –C12	1.442(4)
N2- C8	1.437(3)	N2 -C16	1.383(3)	N2 -C14	1.389(4)
N1- C13	1.396(3)	C1 -C10	1.379(3)	C10 -C11	1.360(4)
O1- C1	1.324(2)	C9 -C10	1.513(3)	C11 -C12	1.507(5)
C1- C9	1.365(3)	C11 -C12	1.393(3)	C20 -C21	1.385(6)
C8- C9	1.512(3)				
C13-C14	1.395(3)				

(a)

1		2		6	
C1 -O1- C9	117.6(2)	O1- C18-C10	125.96(2)	N2-C17-C14	123.54(1)
C8- C9 -O1	125.7(3)	C17-O1-C18	117.67(1)	C11-N1-C13	111.95(1)
C8-C10- C15	114.1(2)	C10- C5- C6	113.48(1)	C7-O2-C11	111.90(1)
C8-C10- C11	114.2(2)	C10- C5- C6	113.96(1)	C10-C14-C13	107.05(1)
C7 -C8- C9	119.3(3)	C11-C10-C18	118.99(2)	C10-C14-C17	130.18(1)
				C11-C10-C21	116.42(1)

7		8		9	
N1-B1-F1	108.19(2)	N1-B1-F1	109.79(2)	N1-B1-F1	107.7(3)
N1-B1-F2	109.4(2)	N1-B1-F2	107.9(2)	N1-B1-F2	109.6(4)
O1-B1-F1	108.9(2)	O1-B1-F1	109.1(2)	O1-B1-F1	106.0(4)
O1-B1-F2	106.92(2)	O1-B1-F2	106.47(2)	O1-B1-F2	108.2(3)
C8-N2-C15	112.73(2)	C9-N2-C16	113.09(2)	C12-N2-C17	137.1(3)
C9-C14-15	106.5(2)	C8-O2-C9	110.67(2)	C7-O2-C12	110.9(3)
C9-C14-C13	127.78(2)	C10-C15-C14	127.95(2)	C11-C13-C14	106.8(3)
C12-C13-C14	129.21(2)	C10-C15-C16	106.4(2)	C11-C13-C18	128.1(3)

(b)

Table S2. Optimized energies for **4-9** and dipyrrins **4′- 6′**

Compound	Energy (kcal mol^{-1})
4	-5.98077×10^5
4′	-5.98063×10^5
5	-6.22751×10^5
5′	-6.22737×10^5
6	-6.72093×10^5
6′	-6.71452×10^5
7	-7.3871×10^5
8	-7.63384×10^5
9	-8.12727×10^5