

# Bipolar luminescent materials containing pyrimidine terminals: synthesis, photophysical and theoretical study

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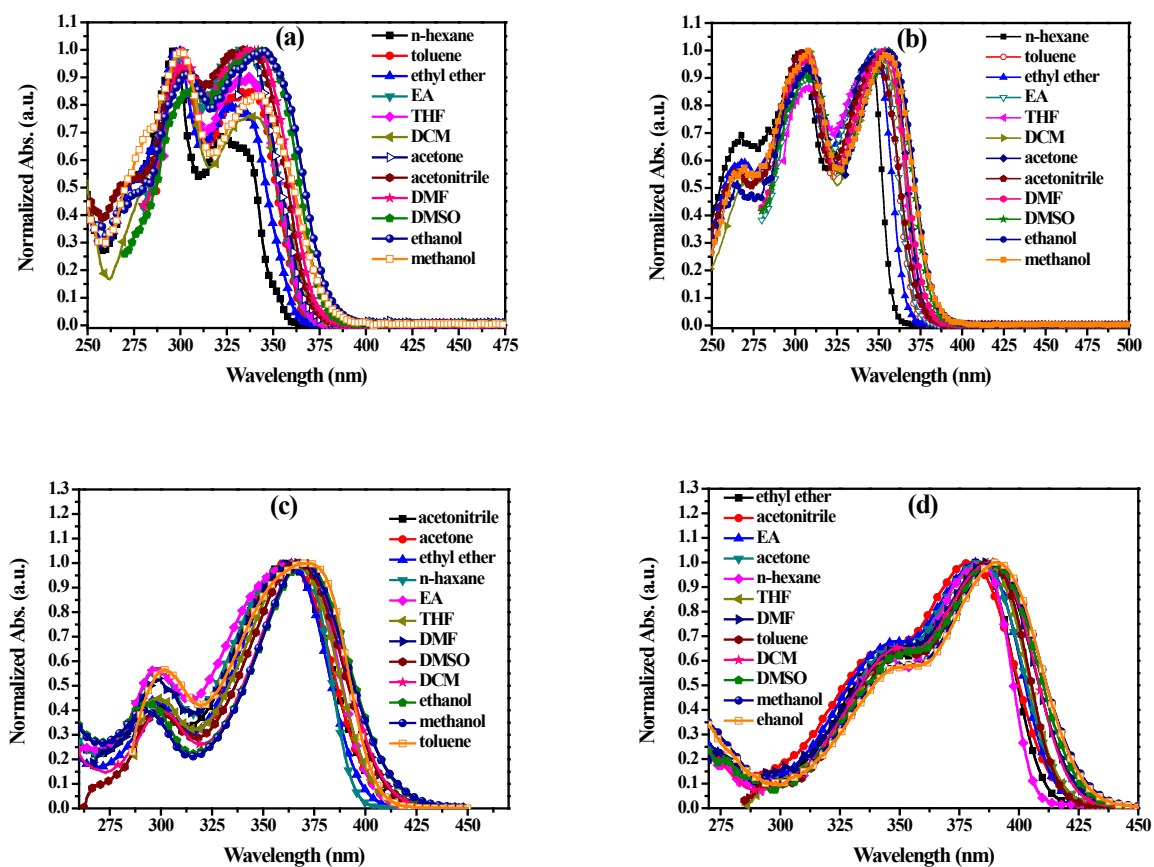
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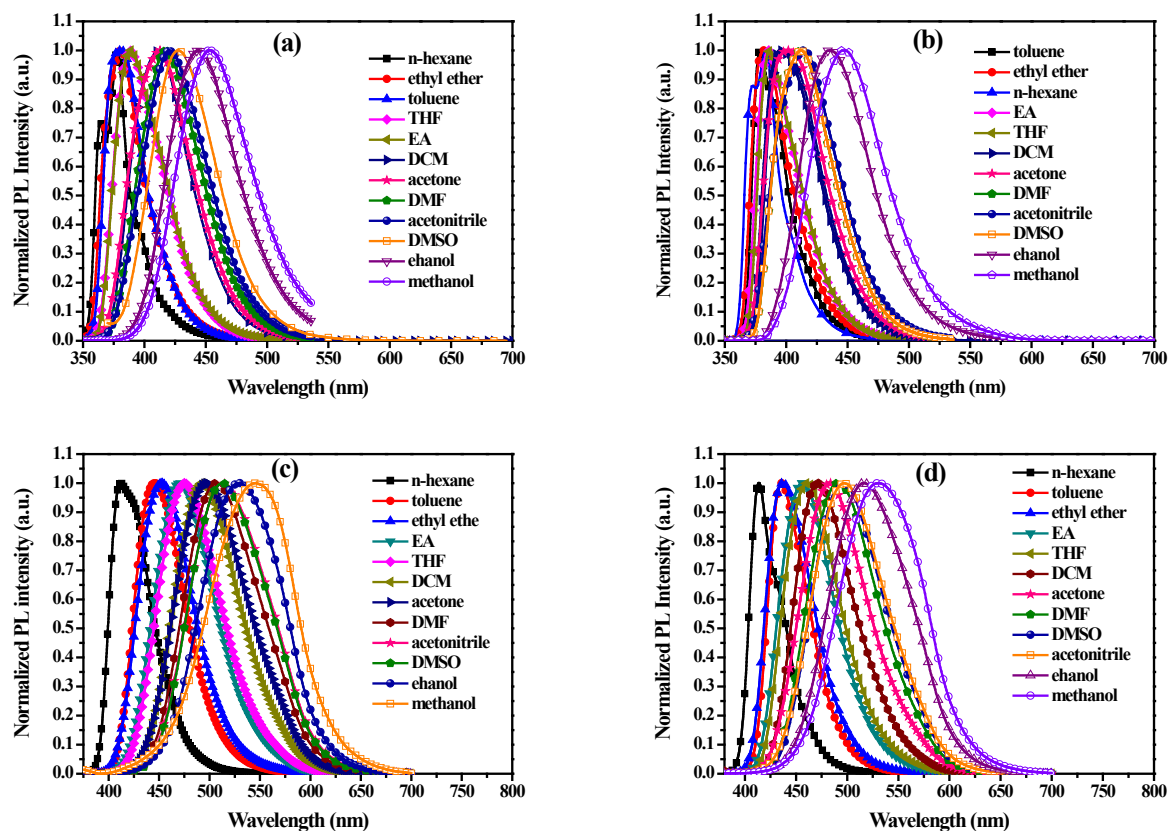
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## 1. Supplementary UV – vis and PL spectra data



**Figure S1** Normalized absorption spectra of PM1 (a), PM2 (b), PM3 (c) and PM4 (d) recorded in different solvents.



**Figure S2** Normalized photoluminescence spectra ( $\lambda_{\text{ex}} = 360\text{nm}$ ) of **PM1** (a), **PM2** (b), **PM3** (c) and **PM4** (d) recorded in different solvents.

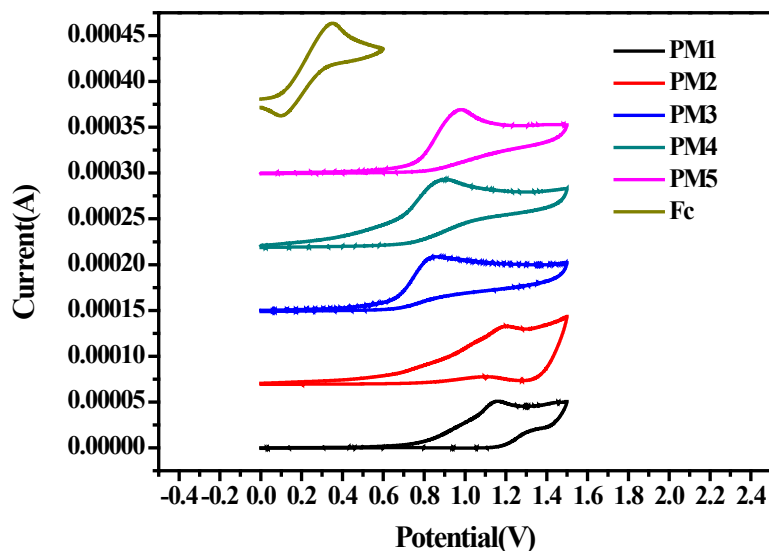
**Table S1** Optical properties of **PM1 – PM5** in solvents of varying polarity

solvent	$\Delta f^a$	$\lambda_{\text{abs, max}}$ (nm)					$\lambda_{\text{em, max}}$ (nm)				
		PM1	PM2	PM3	PM4	PM5	PM1	PM2	PM3	PM4	PM5
<i>n</i> -hexane	-0.0014	322	345	366	385	381	378	383	412	414	416
toluene	0.0132	332	351	372	388	385	381	379	446	436	433
ethyl ether	0.1625	328	347	363	382	378	381	382	453	437	435
EA	0.1996	332	349	366	383	379	389	386	470	456.6	454
THF	0.2096	337	353	366	386	383	388	387	475	461	458
DCM	0.2171	337	353	370	389	384	412	397	487	472	464
acetone	0.2841	338	356	361	383	378	412	402	498	482	475
acetonitrile	0.3046	334	348	360	382	377	420	415	513	497	490
DMF	0.2744	336	355	366	387	384	417	412	507	492	486
DMSO	0.2630	344	355	367	389	387	432	424	513	496	489
ethanol	0.2887	345	356	370	390	384	444	436	529	517	510
methanol	0.3086	343	355	370	391	384	453	448	546	530	522

<sup>a</sup> the orientation polarizability  $\Delta f$  derived from Eq.1.

$$\Delta f = \frac{(\epsilon - 1)}{(2\epsilon + 1)} - \frac{(n^2 - 1)}{(2n^2 + 1)} \quad (\text{Eq. 1})$$

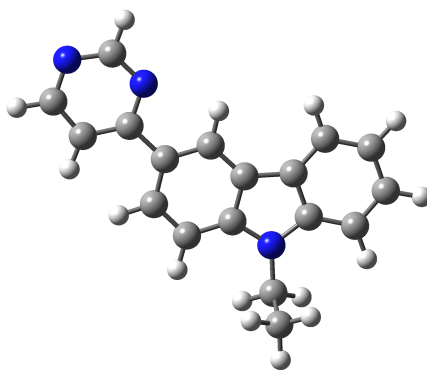
## 2. Cyclic voltammogram of PM1 – PM5 in DCM solution



**Figure S3** Cyclic voltammogram of **PM1 – PM5** in DCM solution

## 3. The optimized ground-state geometries of PM compounds by DFT/B3LYP/6-31G(d)

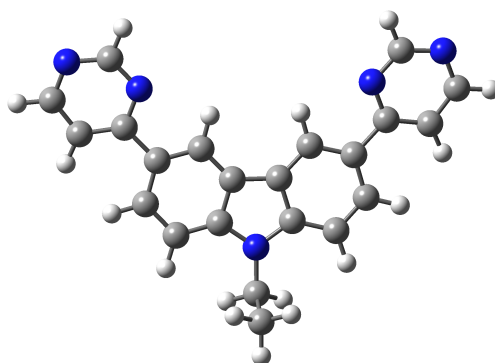
**Table S2** The optimized geometry of **PM1** in ground state at B3LYP/6-31G(d) level



	x	y	z
C	3.32737300	2.99499500	0.09358500
C	4.40256200	2.09756900	-0.02057600
C	4.19335100	0.72505800	-0.14525100
C	2.87281400	0.26748500	-0.15656300
C	1.77595700	1.16040700	-0.03822000
C	2.01360700	2.53329000	0.08533400
H	5.42023400	2.47833300	-0.00917300
H	5.03432400	0.04284500	-0.22666900
H	1.18325300	3.22858800	0.17520800
C	1.00644200	-1.00031400	-0.22099500
C	0.08047300	-2.04775900	-0.28407900
C	-1.27020100	-1.73097200	-0.21408200
C	-1.72663800	-0.39835100	-0.07970000
C	-0.78329800	0.63870400	-0.01326800

C	0.57647200	0.34787800	-0.07995000
H	0.39490300	-3.08240100	-0.38102700
H	-1.98409800	-2.54640000	-0.26316800
H	-1.13880800	1.65766700	0.09135400
N	2.38949500	-1.03541600	-0.28110800
C	3.20777100	-2.23571300	-0.36558600
C	3.58508100	-2.81433800	1.00248000
H	4.10684400	-1.98728200	-0.93952700
H	2.65716200	-2.97442800	-0.95735100
H	4.20046500	-3.71256100	0.87809900
H	4.15325000	-2.08670400	1.59083300
H	2.69005400	-3.08599600	1.57144200
H	3.52512000	4.05858000	0.19061700
C	-3.16835100	-0.06934700	-0.00529600
N	-3.49423600	1.23613400	0.11800000
C	-4.19269500	-1.03125800	-0.05608100
C	-4.78687700	1.54590600	0.18566600
C	-5.50469100	-0.58291200	0.02464800
H	-3.98910900	-2.09102500	-0.15427000
N	-5.83161900	0.71116700	0.14690100
H	-5.02093000	2.60498500	0.28464000
H	-6.33305500	-1.28937400	-0.00994700

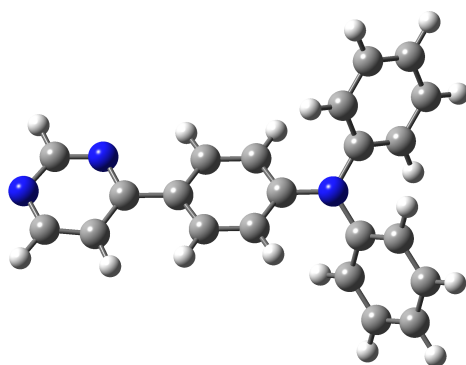
**Table S3** The optimized geometry of **PM2** in ground state at B3LYP/6-31G(d) level



	x	y	z
C	-3.04866000	-0.02137900	-0.07370800
C	-3.42053400	1.34149800	-0.13856200
C	-2.48062400	2.36390200	-0.18941000
C	-1.12753700	2.01103700	-0.18066500
C	-0.72537900	0.65057400	-0.10687700
C	-1.68605300	-0.35555700	-0.05217200
H	-4.47016400	1.61622900	-0.12851100
H	-2.80126100	3.40047200	-0.22551400
H	-1.40602000	-1.40130300	0.00897100
C	1.12753700	2.01103700	-0.18066500
C	2.48062400	2.36390200	-0.18941000
C	3.42053400	1.34149700	-0.13856200
C	3.04866000	-0.02137900	-0.07370800
C	1.68605300	-0.35555700	-0.05217200
C	0.72537900	0.65057400	-0.10687700

H	2.80126100	3.40047200	-0.22551300
H	4.47016400	1.61622900	-0.12851100
H	1.40602000	-1.40130300	0.00897100
N	0.00000000	2.81997700	-0.23807800
C	0.00000000	4.27612000	-0.25648100
C	0.00000000	4.90168900	1.14228800
H	-0.87700900	4.60229400	-0.82522200
H	0.87700900	4.60229400	-0.82522200
H	0.00000000	5.99495100	1.06822100
H	-0.88591400	4.59497600	1.70766600
H	0.88591300	4.59497600	1.70766700
C	-4.05960700	-1.10282300	-0.02110000
N	-3.61142800	-2.34754300	0.24895200
C	-5.43149200	-0.89585400	-0.24500900
C	-4.51097100	-3.32770400	0.30095300
C	-6.27211300	-1.99845200	-0.15727700
H	-5.83752600	0.07812200	-0.49225900
N	-5.83320300	-3.23386800	0.11960700
H	-4.12414200	-4.32199500	0.51909100
H	-7.34382700	-1.89119300	-0.31943500
C	4.05960700	-1.10282300	-0.02110000
N	3.61142800	-2.34754300	0.24895400
C	5.43149100	-0.89585400	-0.24501100
C	4.51097100	-3.32770300	0.30095400
C	6.27211300	-1.99845200	-0.15727800
H	5.83752600	0.07812200	-0.49226200
N	5.83320300	-3.23386800	0.11960700
H	4.12414200	-4.32199400	0.51909400
H	7.34382700	-1.89119300	-0.31943700

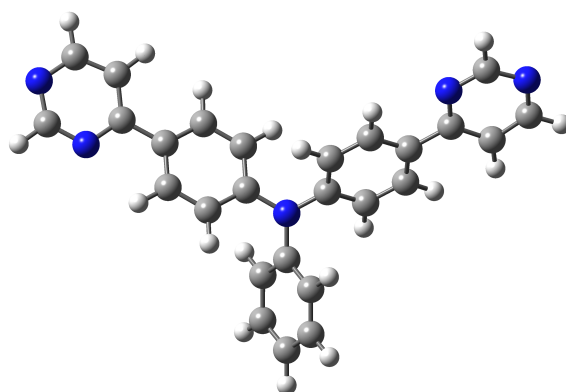
**Table S4** The optimized geometry of **PM3** in ground state at B3LYP/6-31G(d) level



	x	y	z
C	2.71255300	3.46168300	0.93070900
C	2.01435300	2.25551800	0.91390700
C	2.38799600	1.23609700	0.02482100
C	3.47820100	1.44234500	-0.83390700
C	4.18173400	2.64501600	-0.79758500
C	3.80139100	3.66276200	0.07964200
H	2.41066300	4.24218400	1.62407000
H	1.17695300	2.09686500	1.58605300
H	3.76804400	0.65736000	-1.52532100
H	5.02375800	2.79025200	-1.46916300

H	4.34756000	4.60147800	0.10046600
N	1.67833200	-0.00051500	0.00023700
C	0.26768800	-0.01671800	0.01039500
C	-0.43770300	-1.04507500	0.66332700
C	-0.47320100	0.99663600	-0.62774600
C	-1.82584600	-1.06106700	0.66364300
H	0.11024600	-1.82572000	1.17974500
C	-1.85983900	0.97890400	-0.60849200
H	0.04823100	1.79514300	-1.14460500
C	-2.57199800	-0.05292500	0.02899300
H	-2.32739800	-1.86179800	1.19862300
H	-2.42122700	1.76234100	-1.10505400
C	2.41678700	-1.21934300	-0.02952500
C	2.05389000	-2.25238100	-0.90762500
C	3.52560800	-1.39530500	0.81217900
C	2.78052300	-3.44152600	-0.92991100
H	1.20344900	-2.11644600	-1.56830100
C	4.25695200	-2.58108600	0.77042900
H	3.80836700	-0.59975700	1.49433600
C	3.88723300	-3.61242600	-0.09537200
H	2.48720800	-4.23209700	-1.61558400
H	5.11312100	-2.70231600	1.42878000
H	4.45566200	-4.53772100	-0.12085200
C	-4.04965300	-0.04589400	0.01623000
N	-4.65563700	1.07149300	-0.44108500
C	-4.83255800	-1.13314900	0.44219800
C	-5.98703900	1.08586200	-0.45377500
C	-6.21318700	-0.99330300	0.38712900
H	-4.39205400	-2.05996400	0.79122200
N	-6.81957500	0.11624600	-0.05807500
H	-6.45258300	1.99635200	-0.82842200
H	-6.86516000	-1.80447600	0.70848000

**Table S5** The optimized geometry of **PM4** in ground state at B3LYP/6-31G(d) level

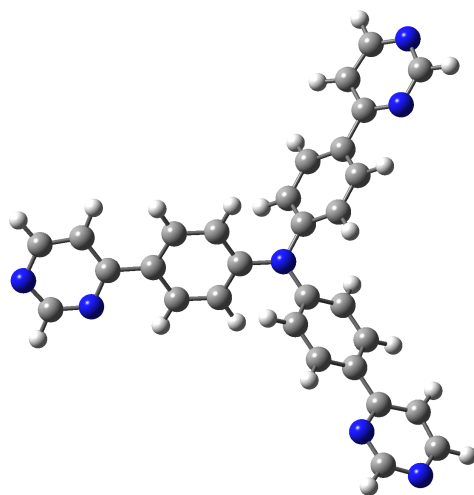


	x	y	z
C	-2.57478200	-1.25253900	0.78024900
C	-1.36967300	-0.56234900	0.77513800
C	-1.22400500	0.61449500	0.01972400
C	-2.32932900	1.08060800	-0.71415300
C	-3.53373000	0.39194700	-0.69077000
C	-3.68397200	-0.79462200	0.04851100

H	-2.65066300	-2.14506400	1.39355200
H	-0.53633300	-0.92657400	1.36656400
H	-2.23453800	1.98456500	-1.30668700
H	-4.38118500	0.75548700	-1.26079300
N	0.00031100	1.32542000	0.01097200
C	1.23944000	0.64181500	0.01791500
C	2.33099900	1.14861000	0.74469500
C	1.41357100	-0.55114500	-0.70697100
C	3.55222100	0.48730800	0.73677100
H	2.21262500	2.05909900	1.32248600
C	2.63341100	-1.21210900	-0.69688000
H	0.58728200	-0.95103700	-1.28539100
C	3.73400600	-0.70653800	0.01795300
H	4.36247200	0.90179900	1.32857700
H	2.76141100	-2.12941400	-1.26038000
C	-0.01564300	2.75372700	-0.00279600
C	0.78771700	3.46166900	-0.90844300
C	-0.83483100	3.46125800	0.88878800
C	0.77568300	4.85552200	-0.91276500
H	1.41600400	2.91494500	-1.60472000
C	-0.85400300	4.85486400	0.86556400
H	-1.45295800	2.91460000	1.59410400
C	-0.04694800	5.55922500	-0.03045000
H	1.40229300	5.39213100	-1.62008200
H	-1.49409600	5.39104900	1.56097700
H	-0.05963500	6.64529200	-0.04165500
C	5.02315200	-1.43185500	-0.00605700
N	5.02447900	-2.66062000	-0.56588700
C	6.21863400	-0.90310400	0.50952000
C	6.18024100	-3.32168500	-0.59147200
C	7.35840200	-1.69343600	0.43034900
H	6.27222300	0.08799800	0.94504800
N	7.36393000	-2.91631400	-0.11796200
H	6.15761200	-4.30924800	-1.04973200
H	8.31030100	-1.33301800	0.81779500
C	-4.97941300	-1.50922000	0.03841900
N	-6.02542400	-0.87355400	-0.53173000
C	-5.15841800	-2.79452200	0.57735600
C	-7.19606700	-1.50813800	-0.54375500
C	-6.43072500	-3.34850500	0.51011600
H	-4.34327500	-3.35428800	1.02123900
N	-7.47412900	-2.71896900	-0.04755800
H	-8.02434400	-0.97728100	-1.01061600
H	-6.62498400	-4.34047700	0.91553400

**Table S6** The optimized geometry of **PM5** in ground state at B3LYP/6-31G(d) level





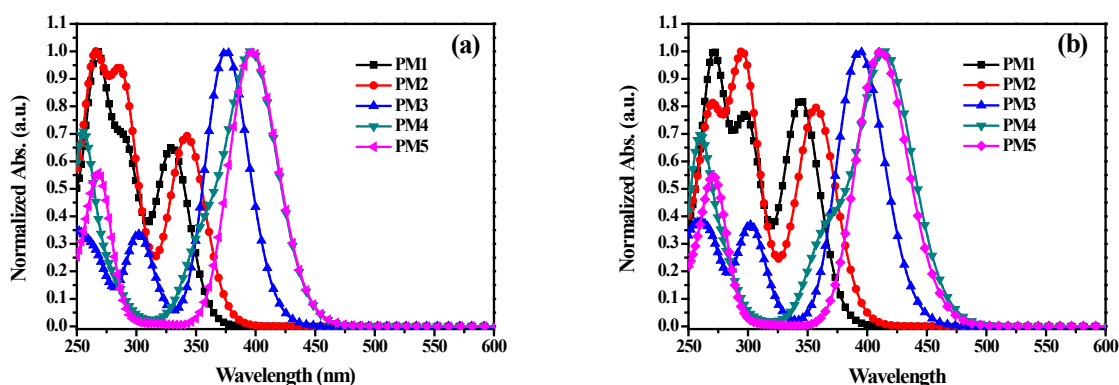
	x	y	z
C	0.29948400	3.60716600	0.81211500
C	0.53903000	2.23885000	0.81168600
C	-0.24010200	1.37987800	0.01898300
C	-1.27186900	1.93224300	-0.75891700
C	-1.51428100	3.29876100	-0.73963500
C	-0.72996000	4.16883400	0.03793300
H	0.91134800	4.23414900	1.45298100
H	1.32724700	1.82720200	1.43322900
H	-1.87849300	1.28377800	-1.38255600
H	-2.31010100	3.72090200	-1.34262700
N	0.00979400	-0.01731500	0.00818900
C	1.34463700	-0.49855500	0.01577900
C	1.70140400	-1.60605300	0.80318100
C	2.33782500	0.12449200	-0.75922100
C	3.00758900	-2.07908100	0.80248900
H	0.95135400	-2.08633600	1.42286600
C	3.64364500	-0.34551500	-0.74172800
H	2.07663800	0.97579600	-1.37939100
C	4.00758300	-1.46183300	0.03181700
H	3.24789700	-2.92298200	1.44176300
H	4.40623500	0.13725300	-1.34227700
C	-1.07329600	-0.93393800	-0.00632000
C	-1.01745400	-2.09285400	-0.79855500
C	-2.22416900	-0.70116300	0.76594000
C	-2.07477500	-2.99371900	-0.80422300
H	-0.14552200	-2.27714400	-1.41737300
C	-3.28231900	-1.59906400	0.74175400
H	-2.28135300	0.18592800	1.38821700
C	-3.22967700	-2.76945400	-0.03566400
H	-2.00165900	-3.86564500	-1.44666200
H	-4.16775200	-1.41595800	1.33981000
C	-4.37231100	-3.71099300	-0.02622000
N	-5.50251100	-3.29523100	0.58333400
C	-4.32473200	-4.99018800	-0.60462600
C	-6.53706000	-4.13389400	0.59438900
C	-5.47239700	-5.77052800	-0.53382600
H	-3.43168600	-5.37690500	-1.08177300
N	-6.59964200	-5.35987600	0.06262600

H	-7.43745100	-3.77824700	1.09272900
H	-5.49131600	-6.76866200	-0.96901700
C	5.40771500	-1.94270000	0.01622700
N	6.32108500	-1.14783500	-0.58017400
C	5.81034800	-3.16647400	0.57600500
C	7.58388000	-1.57099200	-0.59625800
C	7.15887300	-3.49390700	0.50254700
H	5.10768200	-3.84903300	1.03984800
N	8.07143500	-2.70496000	-0.08060700
H	8.30322400	-0.91524200	-1.08422000
H	7.52591500	-4.42869700	0.92380000
C	-1.00741500	5.62323800	0.02035900
N	-2.13451200	6.02329000	-0.60514400
C	-0.16057100	6.57886300	0.60584700
C	-2.39328700	7.32956800	-0.62578800
C	-0.54278800	7.91235600	0.52362600
H	0.76688300	6.30730200	1.09652600
N	-1.66410700	8.31464100	-0.08962700
H	-3.30649500	7.62957200	-1.13726800
H	0.07531200	8.69391400	0.96306300

#### 4. The simulated absorption spectra and detailed data by DFT//B3LYP/6-31G(d)

**Table S7** The absorption spectra calculated by DFT at B3LYP/6-31G(d) in vacuum and solvent (DCM) of **PM1 – PM5**

Molecule	States	Electron transition	Calculated wavelength (nm)	Excitation energy	Main transition configuration	Oscillator strength $f$	Dipole moment (Debye)
<b>PM1</b>	Gas-phase	$S_0$ - $S_1$	330.2	3.76	HOMO→LUMO (0.92)	0.2954	5.1315
		$S_0$ - $S_2$	322.1	3.85	HOMO→LUMO+1 (0.57) HOMO-1→LUMO (0.39)	0.0031	
	DCM	$S_0$ - $S_1$	344.5	3.60	HOMO→LUMO (0.96)	0.4228	
		$S_0$ - $S_2$	325.9	3.80	HOMO→LUMO+1 (0.51) HOMO-1→LUMO (0.45)	0.0033	
<b>PM2</b>	Gas-phase	$S_0$ - $S_1$	342.5	3.62	HOMO→LUMO (0.96)	0.4677	7.7232
		$S_0$ - $S_2$	327.5	3.79	HOMO→LUMO+2 (0.52) HOMO-1→LUMO (0.31) HOMO→LUMO+1 (0.12)	0.0011	
			DCM	$S_0$ - $S_1$	357.3	3.47	
	$S_0$ - $S_2$	331.6	3.74	HOMO→LUMO+2 (0.42) HOMO→LUMO+1 (0.27) HOMO-1→LUMO (0.27)	0.0194		
		DCM	$S_0$ - $S_1$	393.7	3.15	HOMO→LUMO (0.99)	0.7083
	$S_0$ - $S_2$		324.4	3.82	HOMO→LUMO+1 (0.85) HOMO→LUMO+2 (0.10)	0.0109	
DCM			$S_0$ - $S_1$	397.2	3.12	HOMO→LUMO (0.99)	0.7848
	$S_0$ - $S_2$	356.3	3.48	HOMO→LUMO+1 (0.97)	0.2555		
		DCM	$S_0$ - $S_1$	415.2	2.99	HOMO→LUMO (0.99)	0.9041
$S_0$ - $S_2$	367.0		3.38	HOMO→LUMO+1 (0.98)	0.3145		
	<b>PM3</b>	Gas-phase	$S_0$ - $S_1$	375.3	3.30	HOMO→LUMO (0.99)	0.6056
$S_0$ - $S_2$			320.6	3.87	HOMO→LUMO+1 (0.79) HOMO→LUMO+2 (0.09) HOMO→LUMO+3 (0.08)	0.0114	
DCM		$S_0$ - $S_1$	393.7	3.15	HOMO→LUMO (0.99)	0.7083	
		$S_0$ - $S_2$	324.4	3.82	HOMO→LUMO+1 (0.85) HOMO→LUMO+2 (0.10)	0.0109	
<b>PM4</b>	Gas-phase	$S_0$ - $S_1$	397.2	3.12	HOMO→LUMO (0.99)	0.7848	3.7588
		$S_0$ - $S_2$	356.3	3.48	HOMO→LUMO+1 (0.97)	0.2555	
	DCM	$S_0$ - $S_1$	415.2	2.99	HOMO→LUMO (0.99)	0.9041	
		$S_0$ - $S_2$	367.0	3.38	HOMO→LUMO+1 (0.98)	0.3145	
<b>PM5</b>	Gas-phase	$S_0$ - $S_1$	399.1	3.11	HOMO→LUMO (0.99)	0.6520	3.0592
		$S_0$ - $S_2$	395.4	3.14	HOMO→LUMO+1 (0.99)	0.6765	
	DCM	$S_0$ - $S_1$	411.8	3.01	HOMO→LUMO (0.99)	0.7685	
		$S_0$ - $S_2$	410.6	3.02	HOMO→LUMO+1 (0.99)	0.7942	



**Figure S4** The simulated absorption spectra of **PM** compounds in vacuum (a) and DCM (b).

## 5. Characterization: NMR and MS spectra

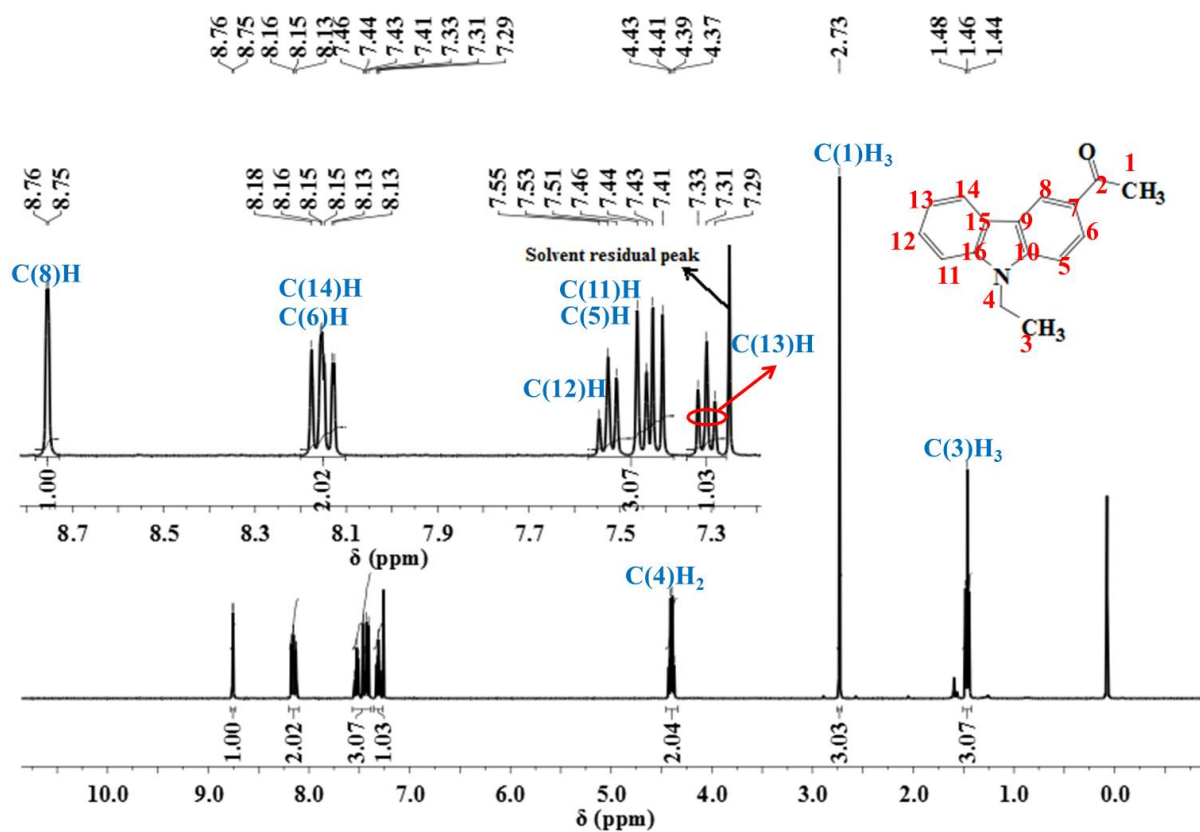


Figure S5  $^1\text{H}$  NMR of A1 in  $\text{CDCl}_3$

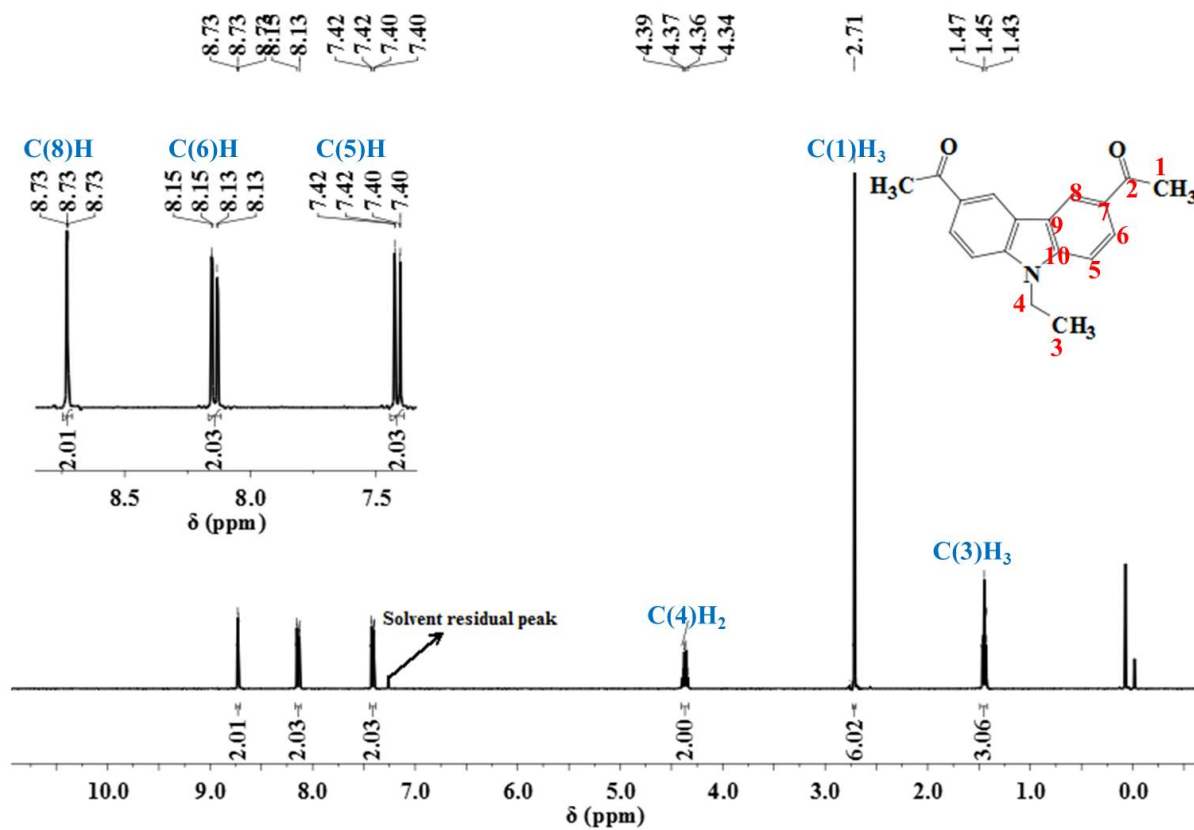


Figure S6  $^{13}\text{C}$  NMR of A1 in  $\text{CDCl}_3$

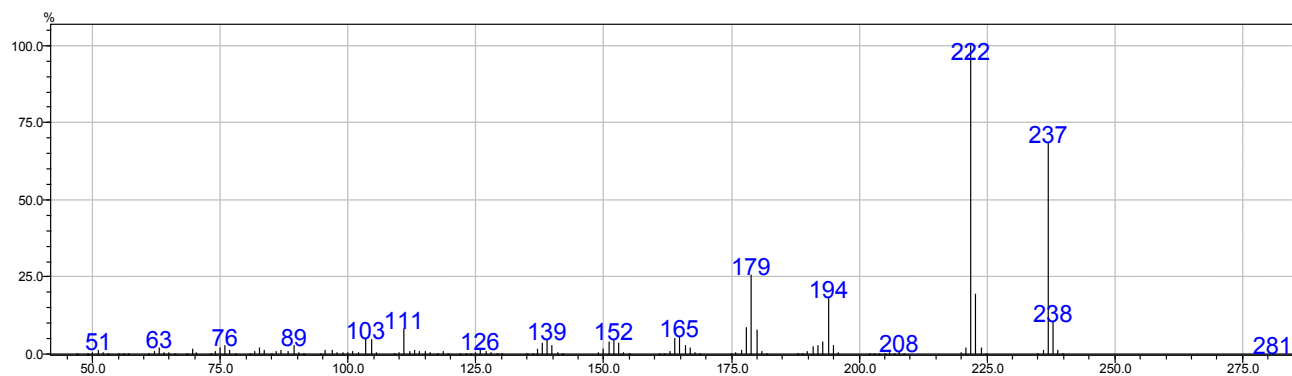


Figure S7 GC-MS spectrum of A1

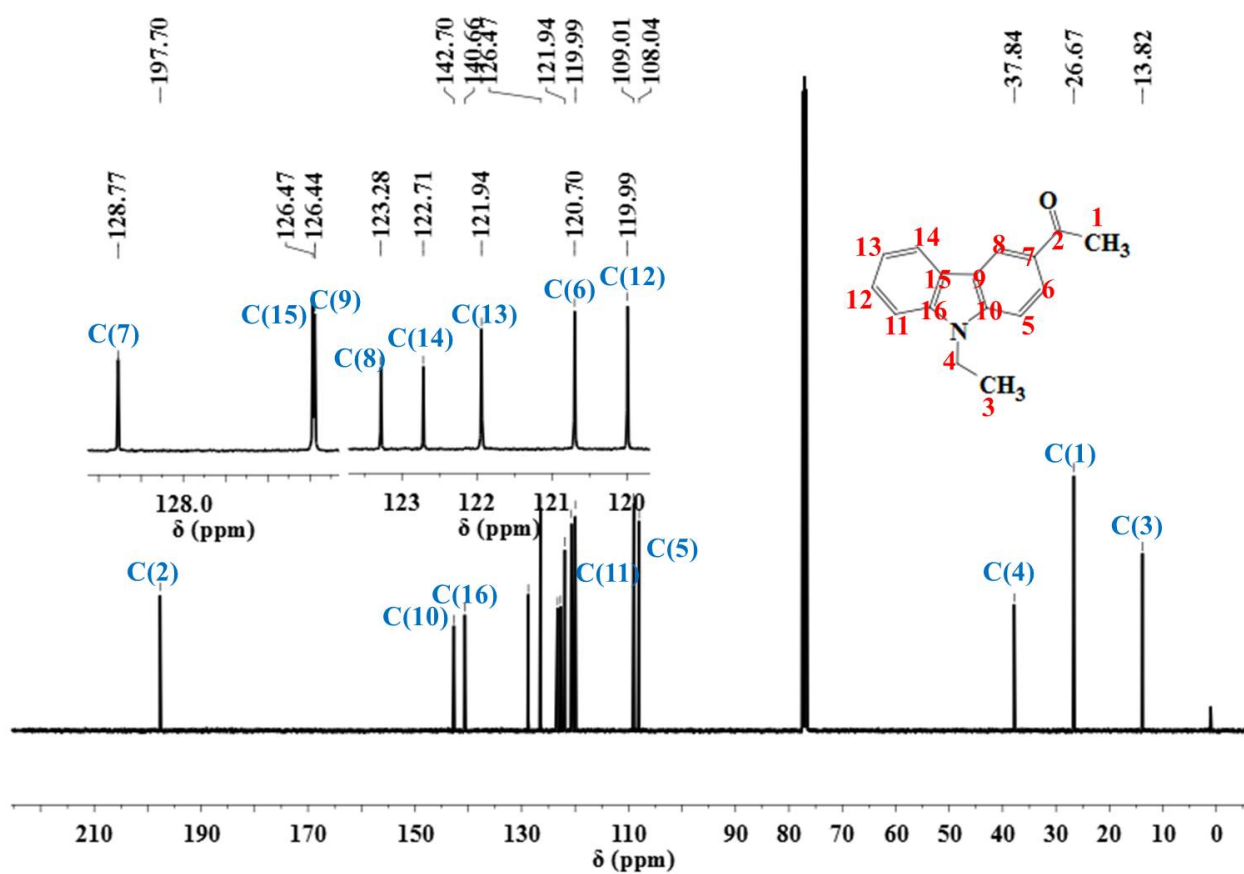


Figure S8  $^{13}\text{C}$  NMR of A2 in  $\text{CDCl}_3$

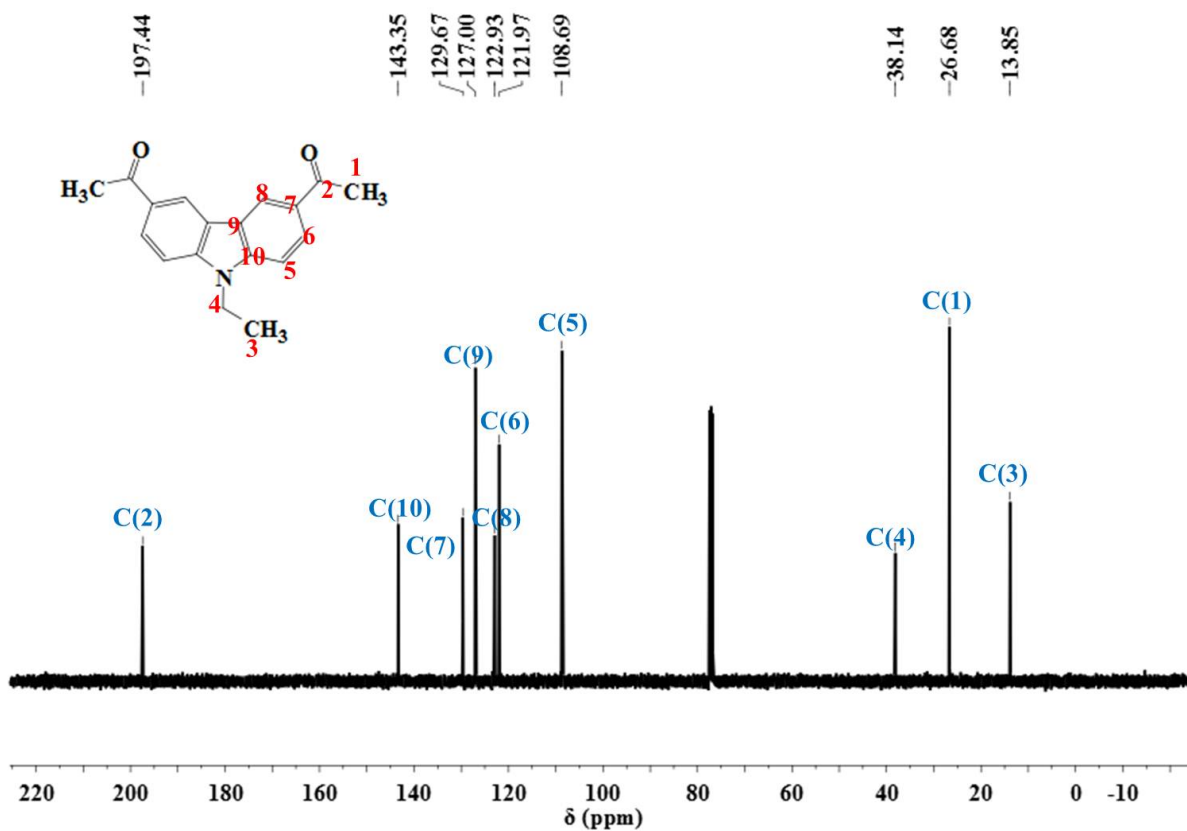


Figure S9 <sup>13</sup>C NMR of A2 in CDCl<sub>3</sub>

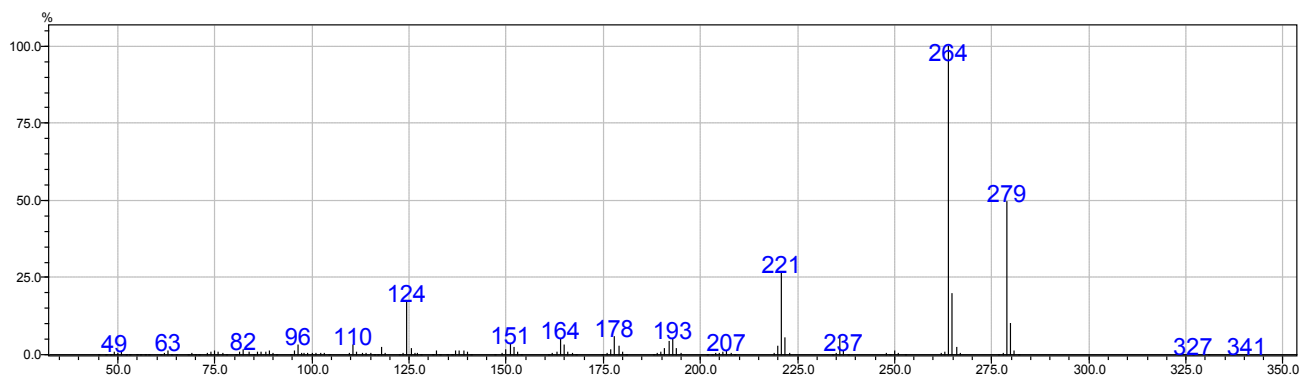
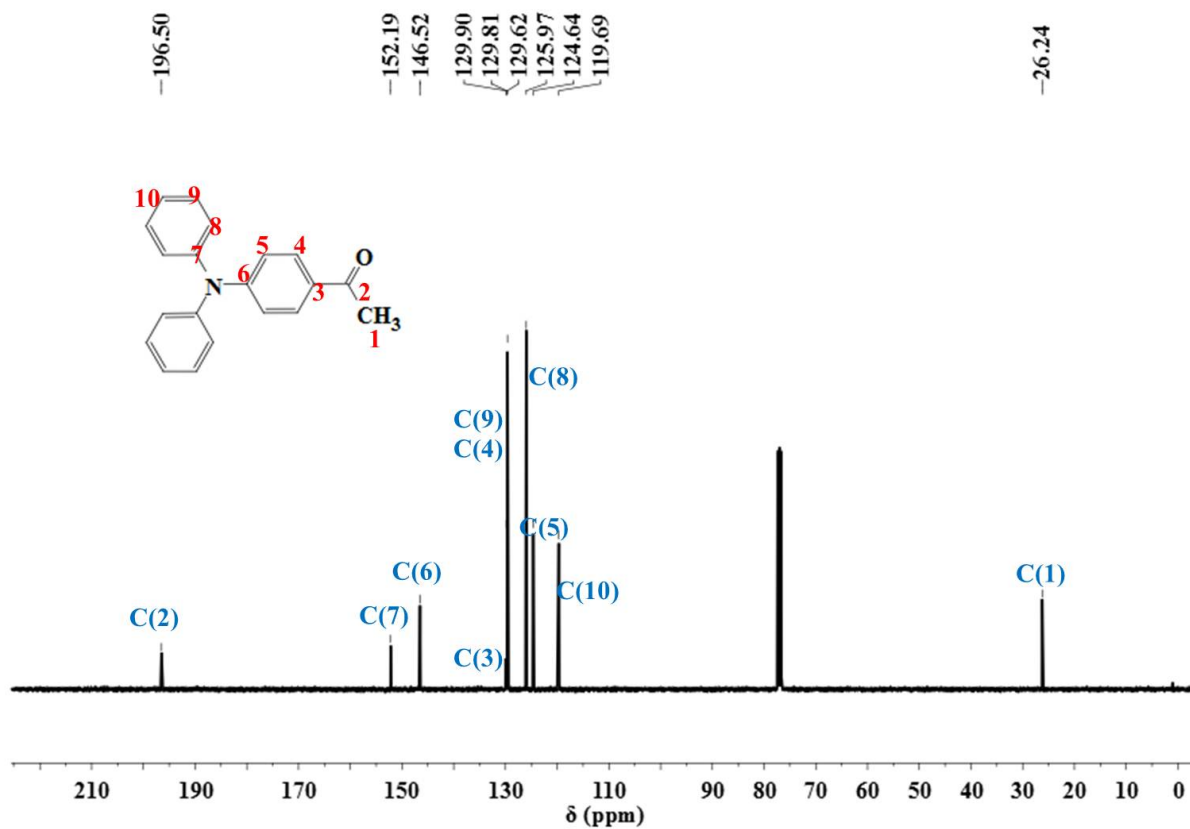
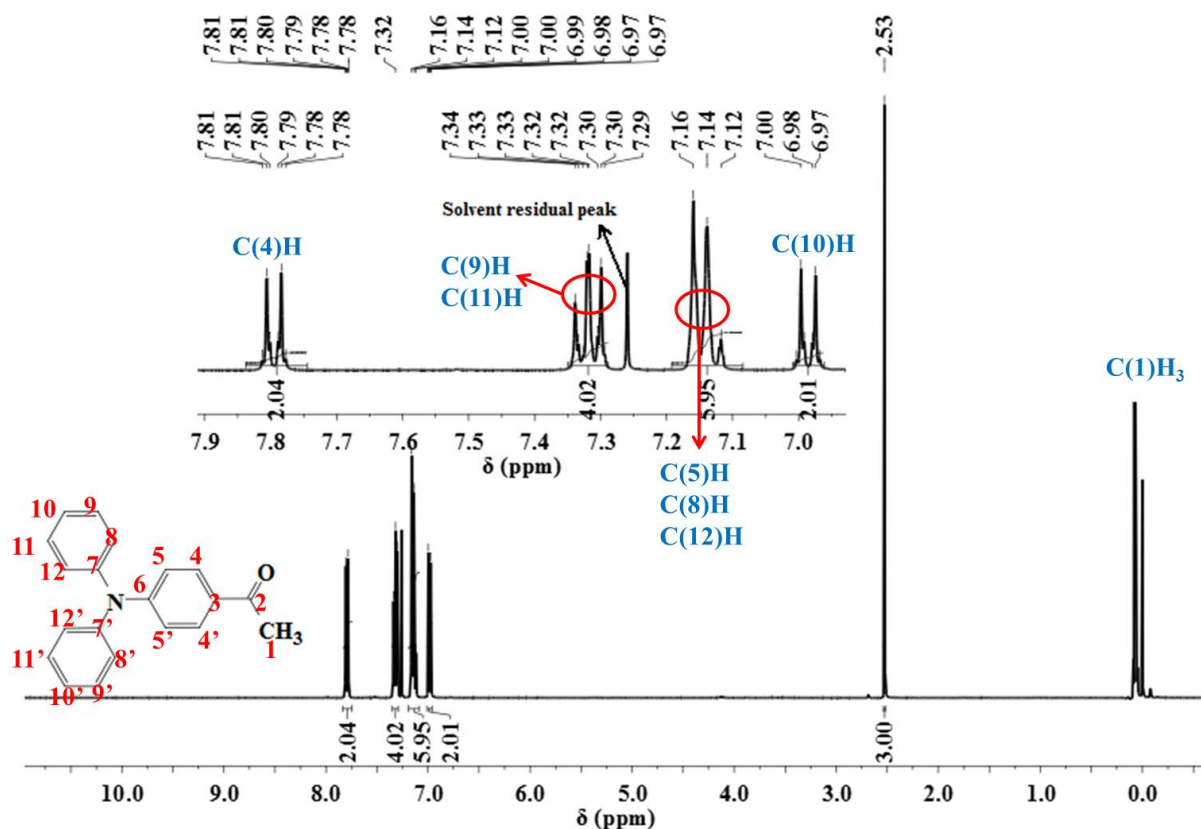


Figure S10 GC-MS spectrum of A2



**Figure S12**  $^{13}\text{C}$  NMR of A3 in  $\text{CDCl}_3$

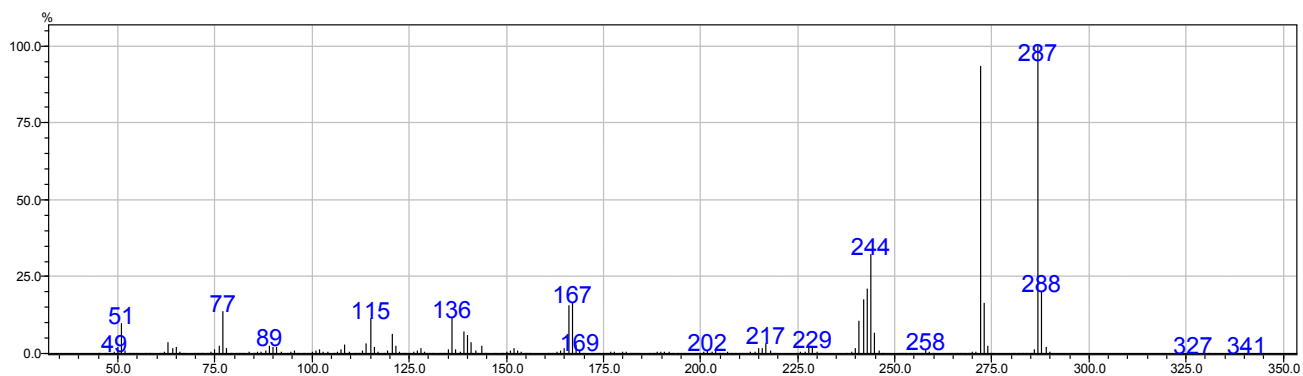


Figure S13 GC-MS spectrum of A3

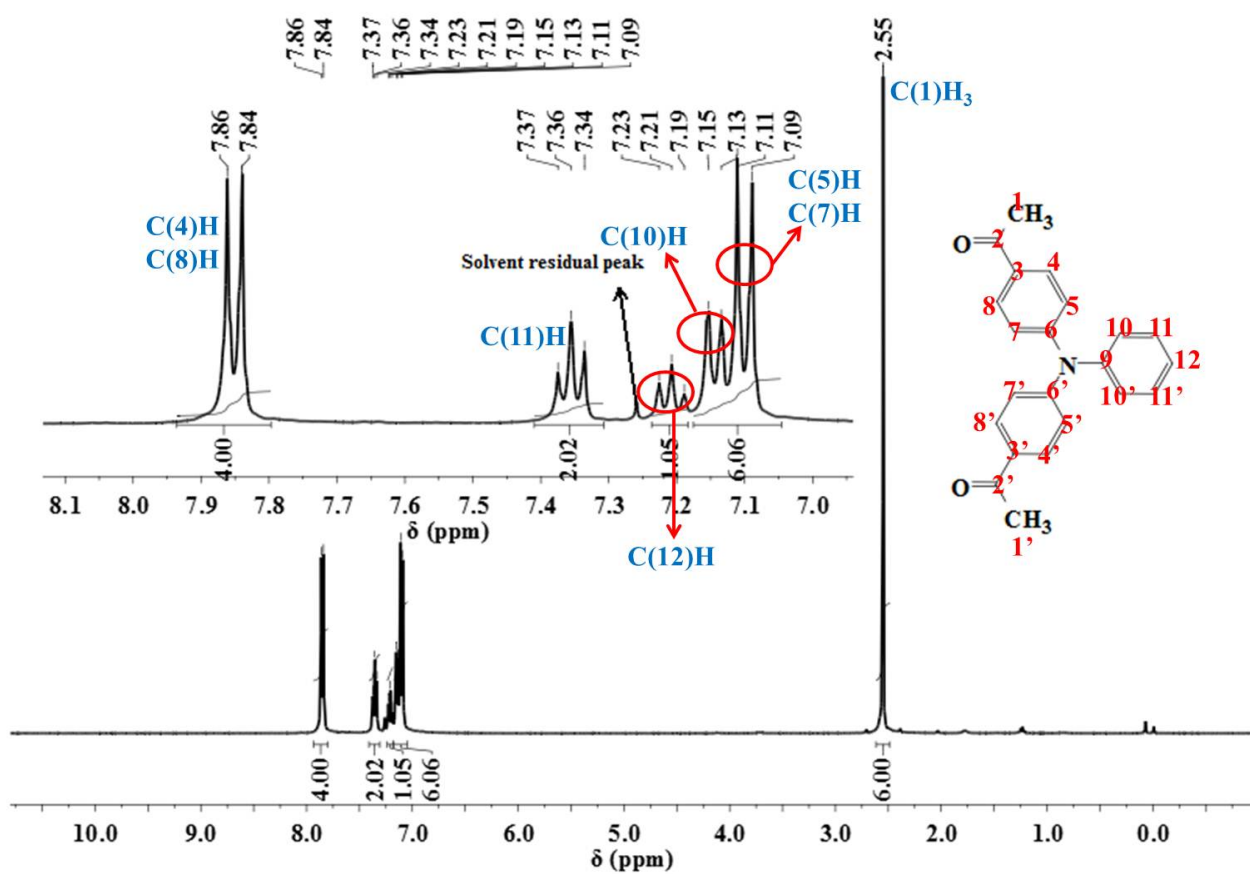


Figure S14 <sup>1</sup>H NMR of A4 in CDCl<sub>3</sub>



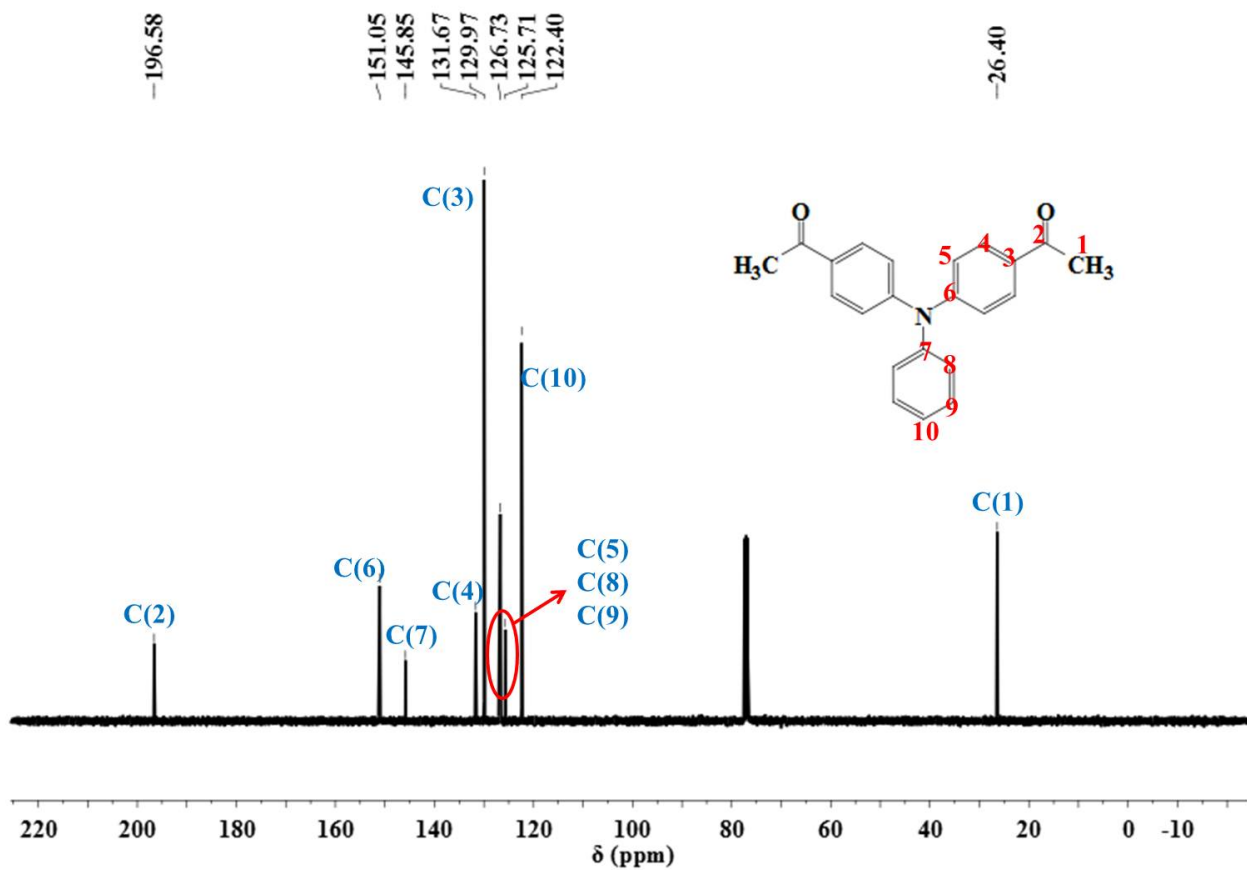


Figure S15  $^{13}\text{C}$  NMR of A4 in  $\text{CDCl}_3$

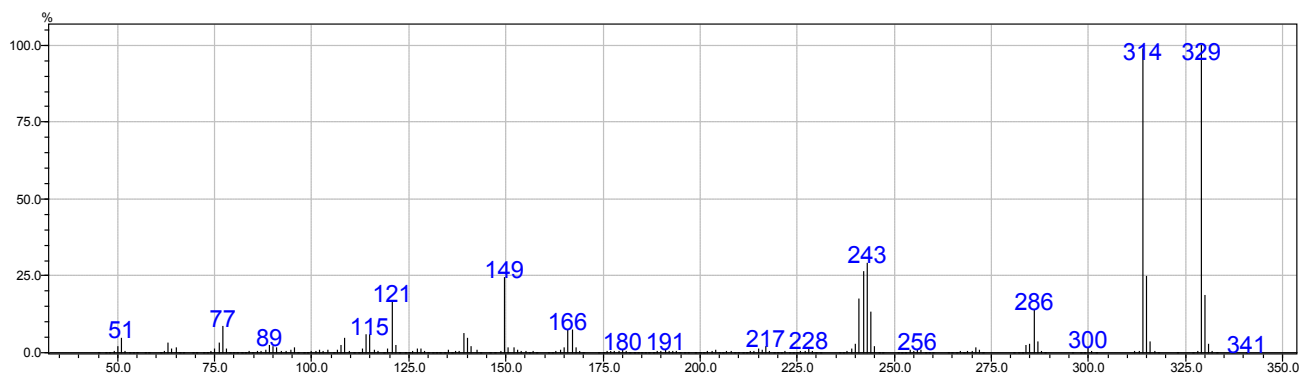
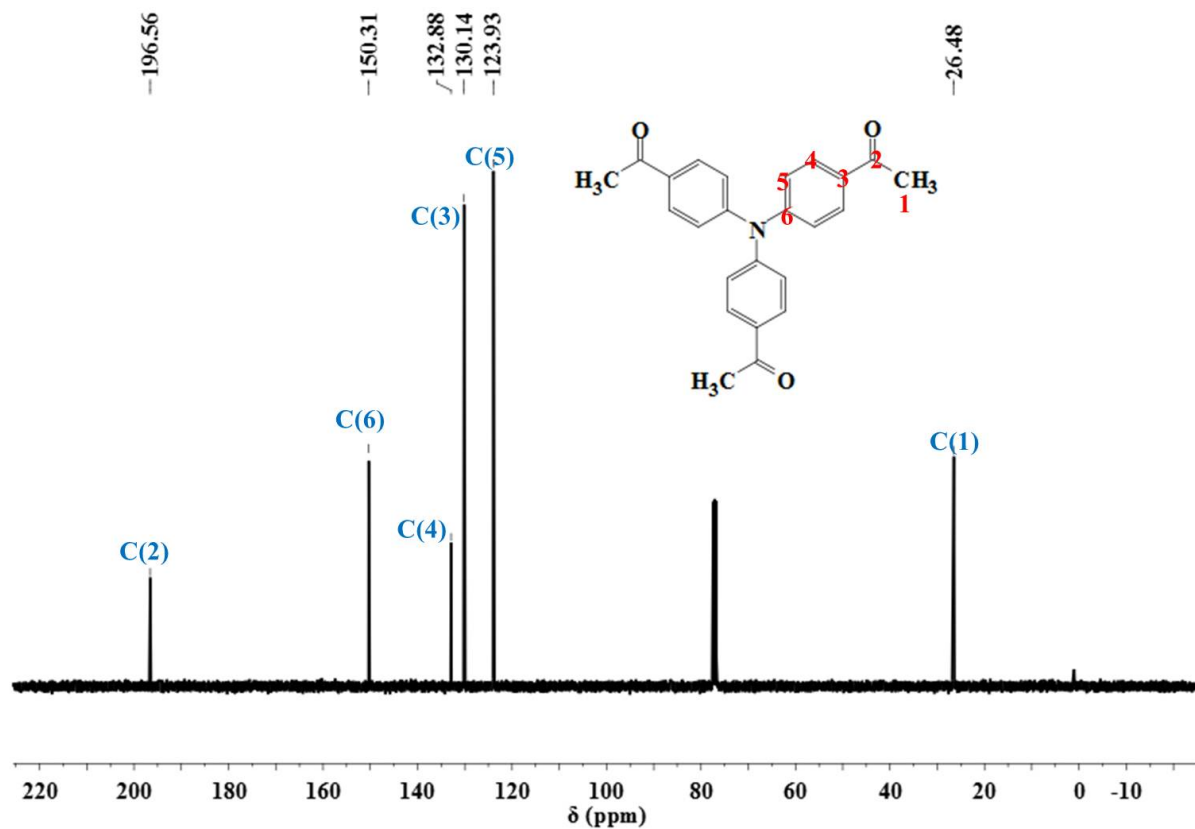
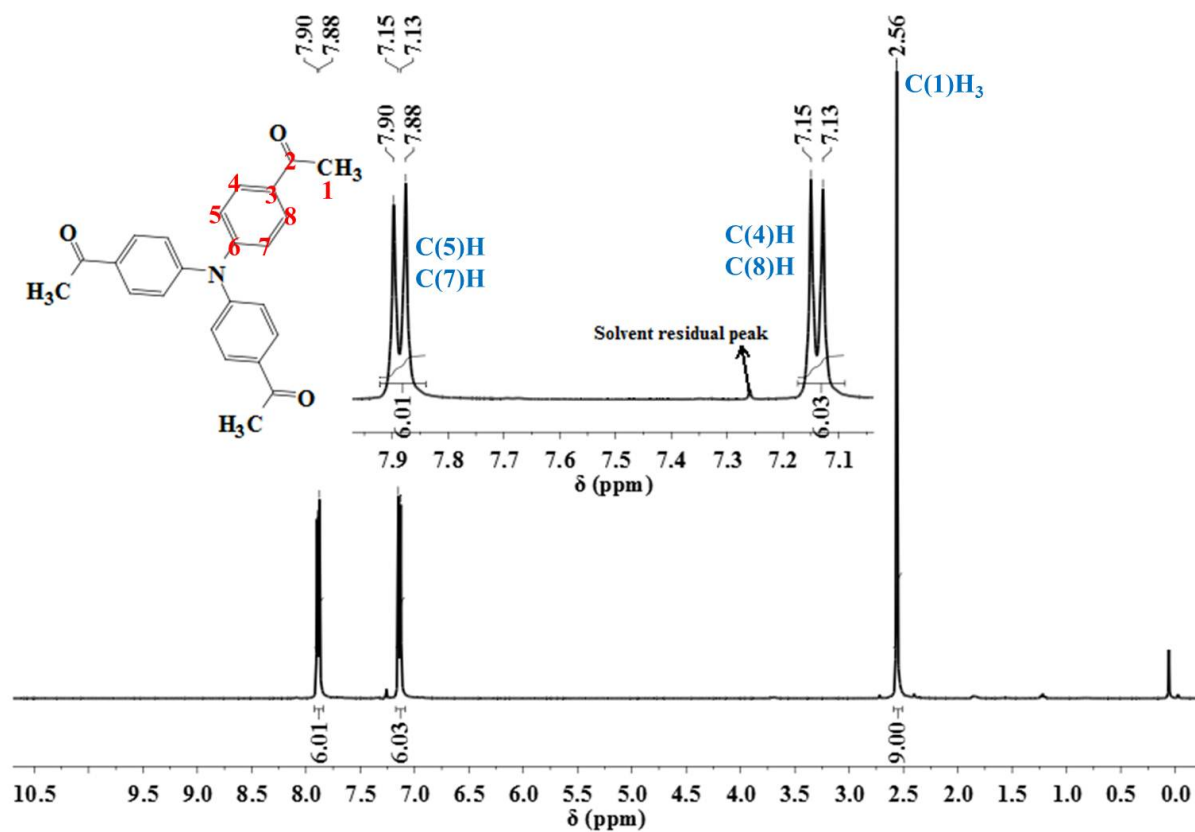


Figure S16 GC-MS spectrum of A4



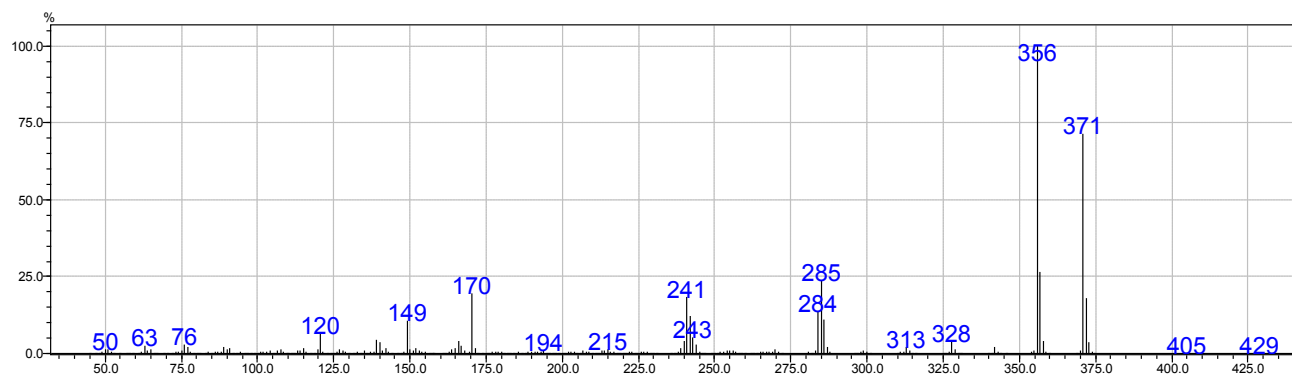


Figure S19 GC-MS spectrum of A5

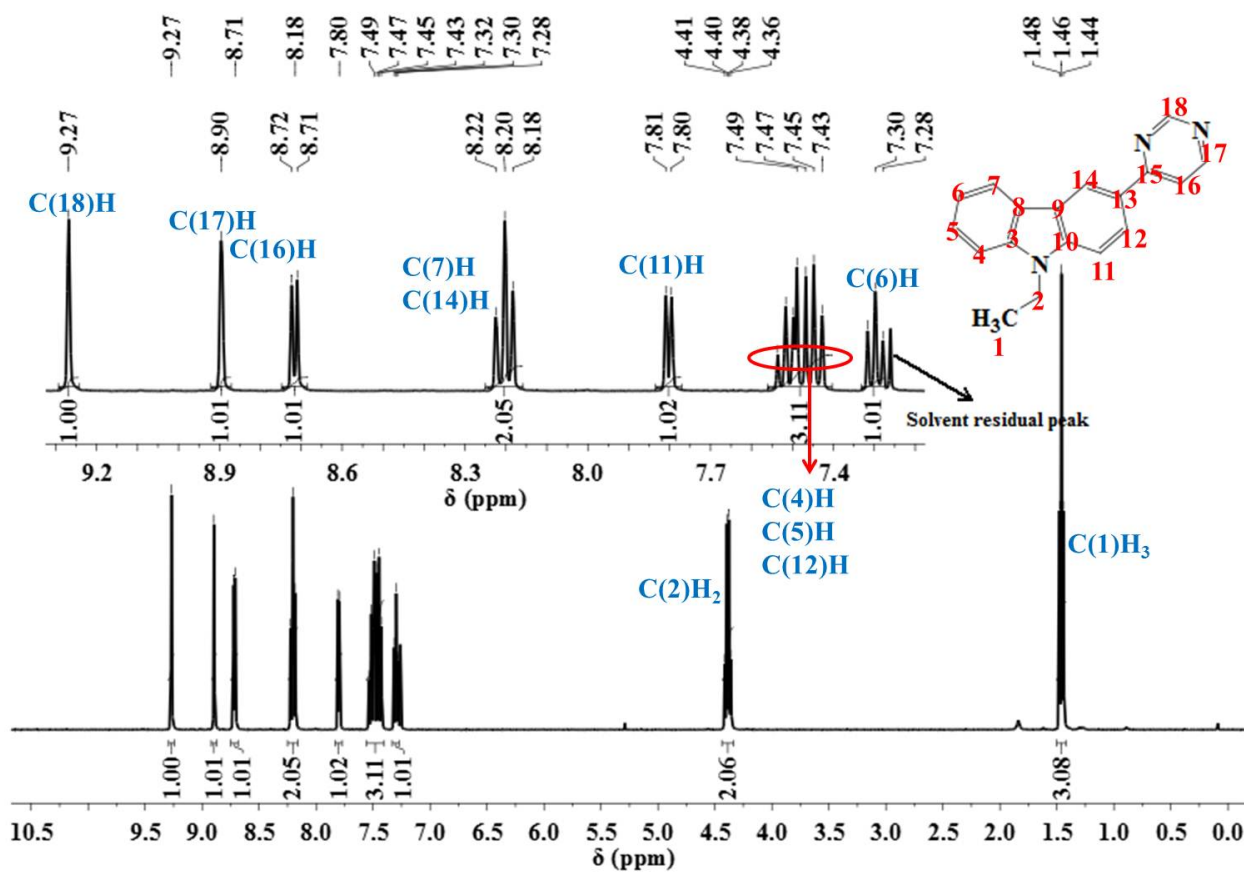
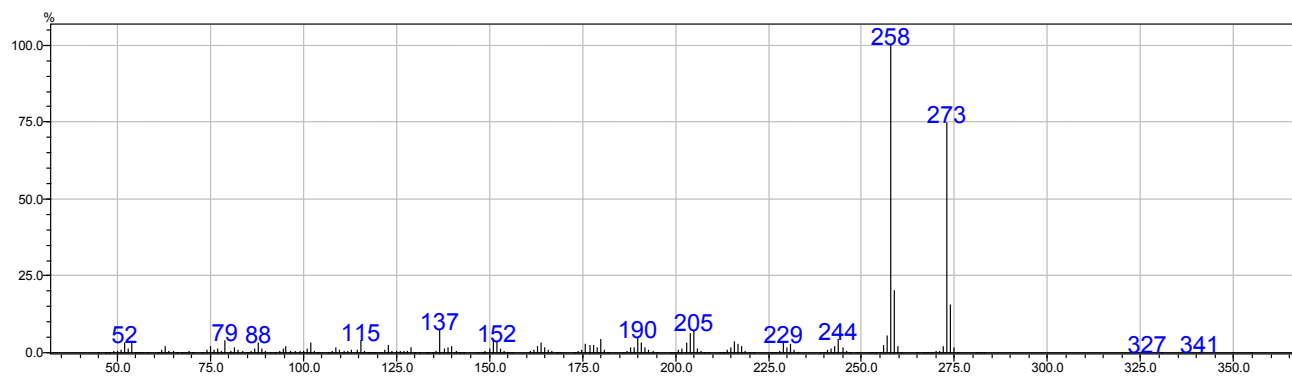
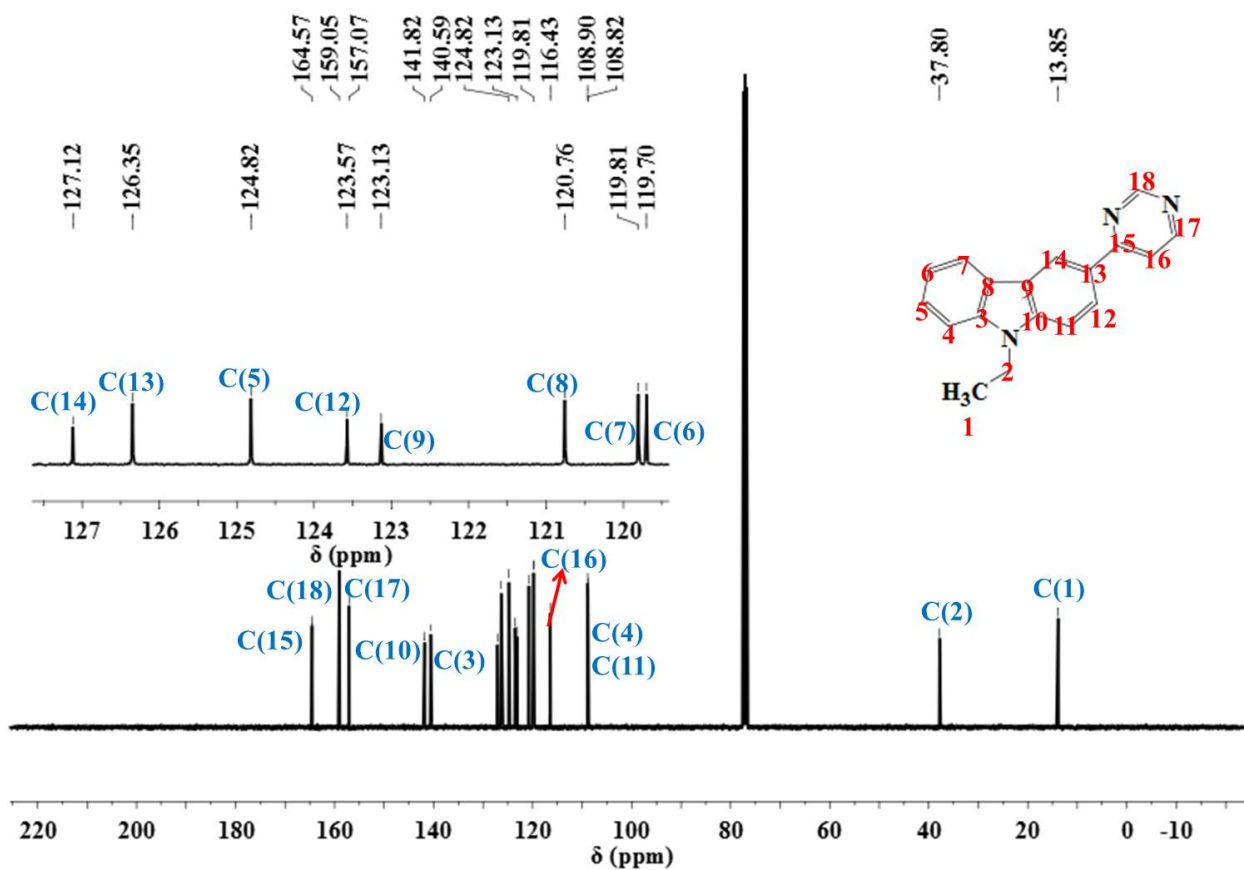
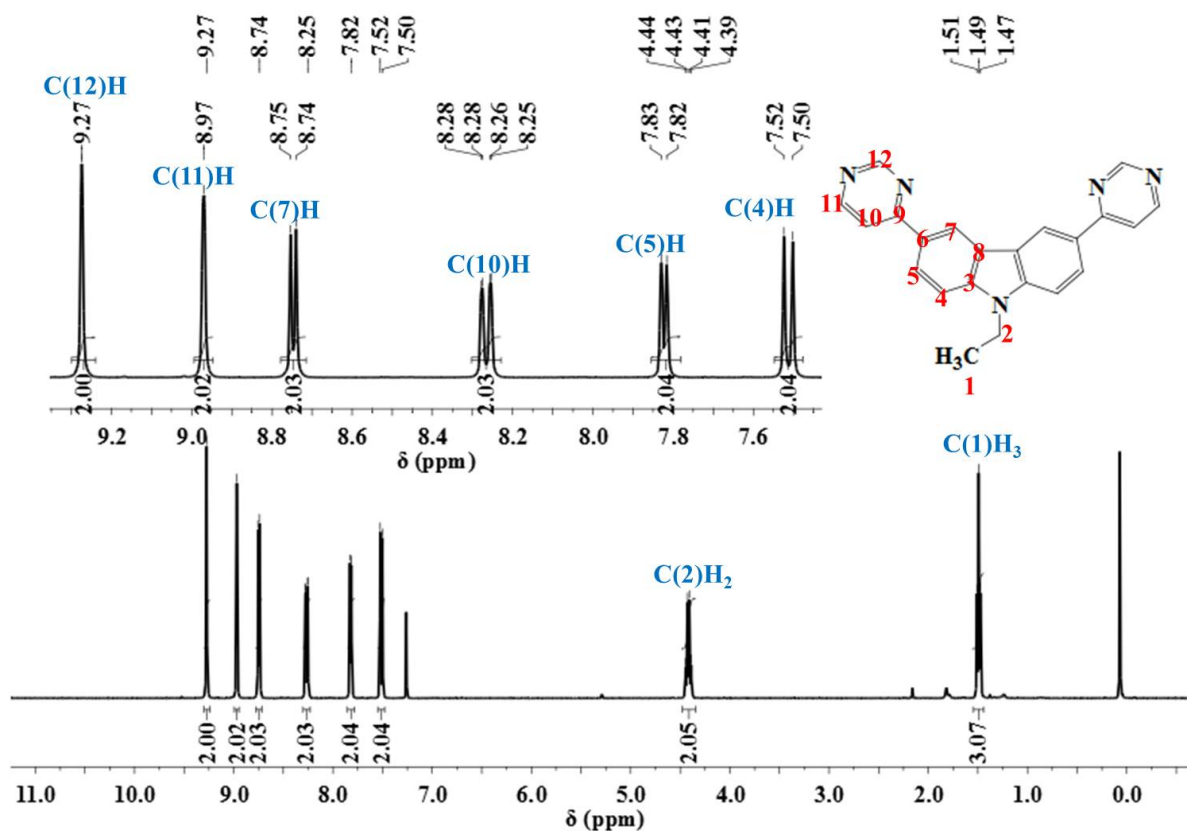
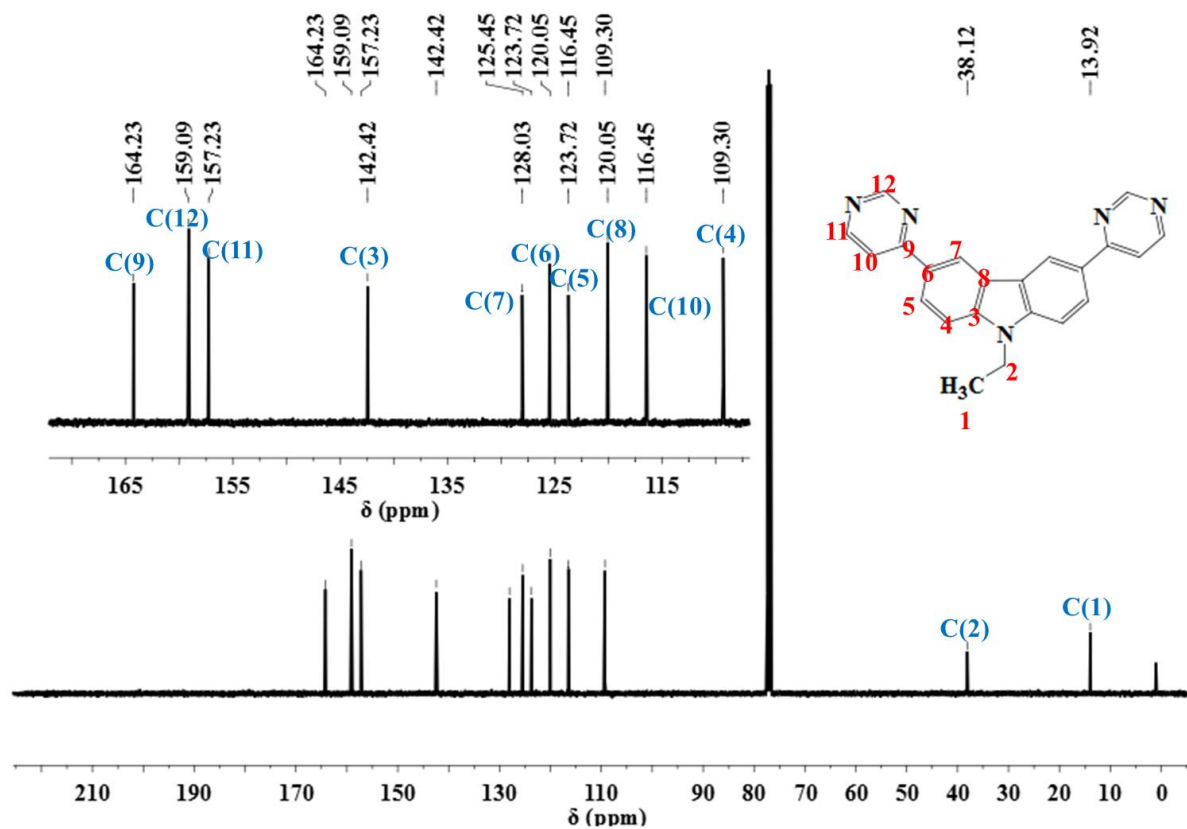


Figure S20  $^1\text{H}$  NMR of PM1 in  $\text{CDCl}_3$





**Figure S23**  $^1\text{H}$  NMR of PM2 in  $\text{CDCl}_3$



**Figure S24**  $^{13}\text{C}$  NMR of PM2 in  $\text{CDCl}_3$

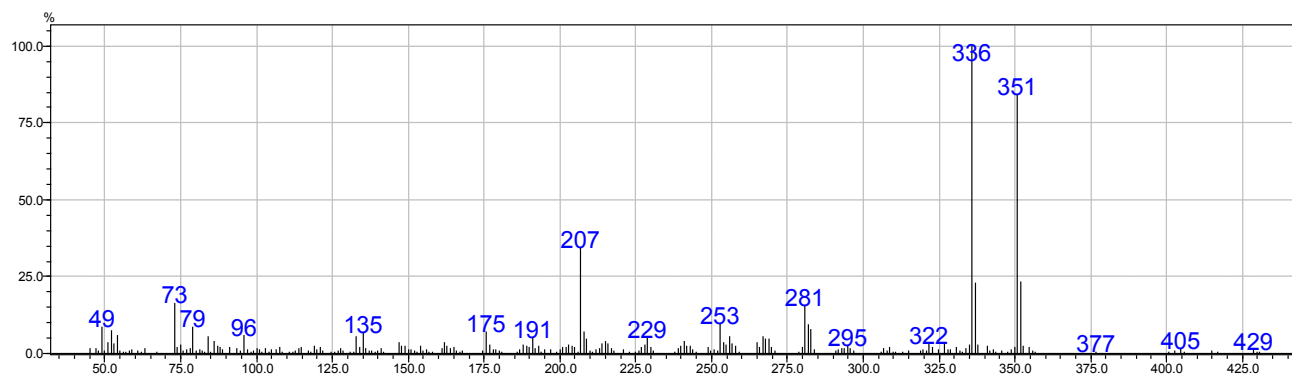


Figure S25 GC-MS spectrum of PM2

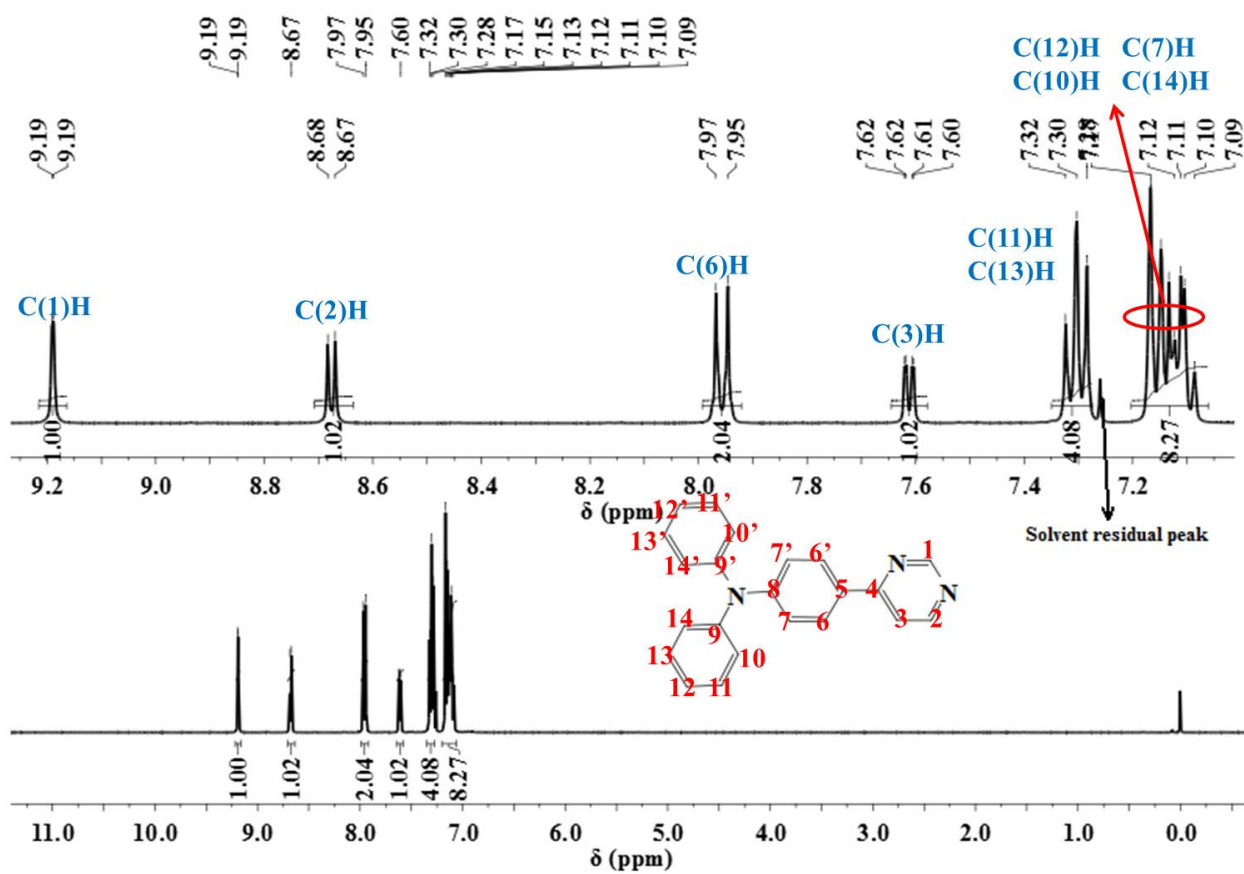


Figure S26  $^1\text{H}$  NMR of PM3 in  $\text{CDCl}_3$

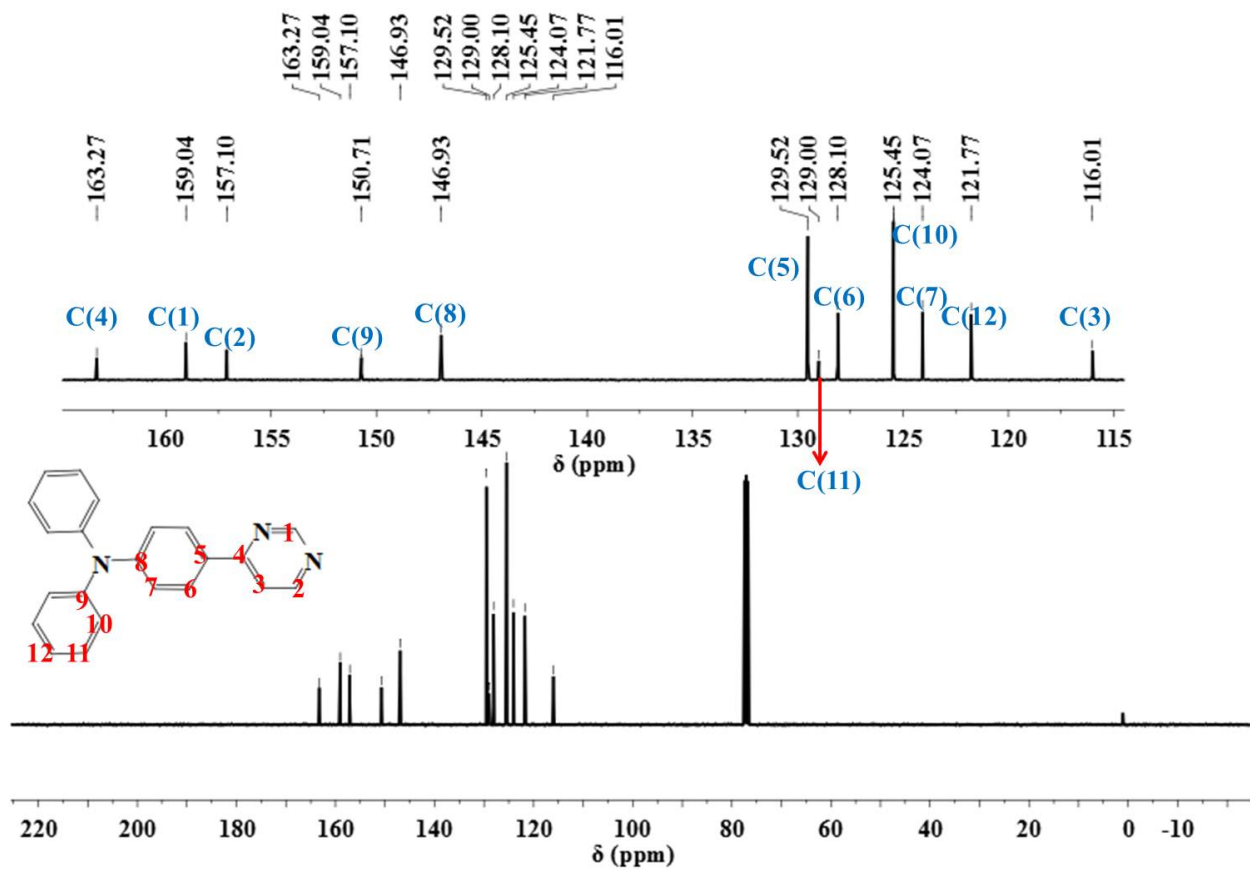


Figure S27 <sup>13</sup>C NMR of PM3 in CDCl<sub>3</sub>

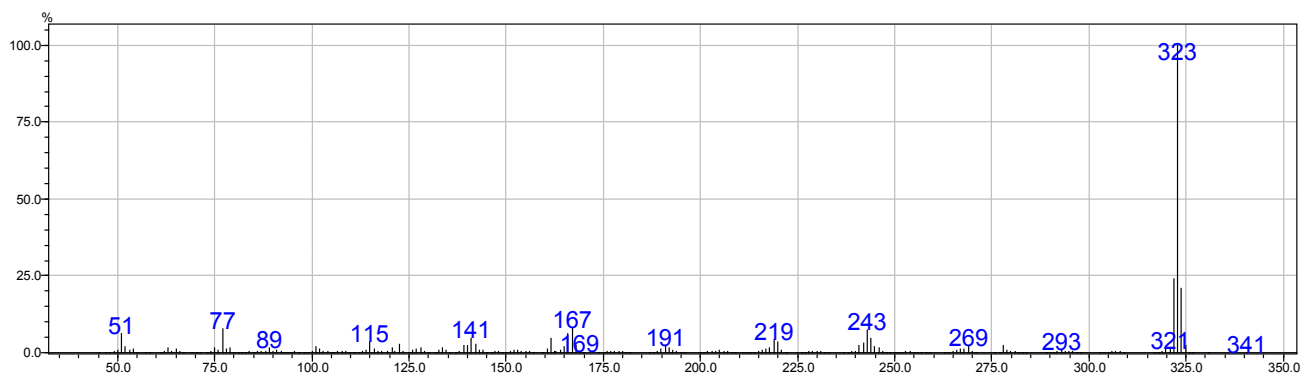
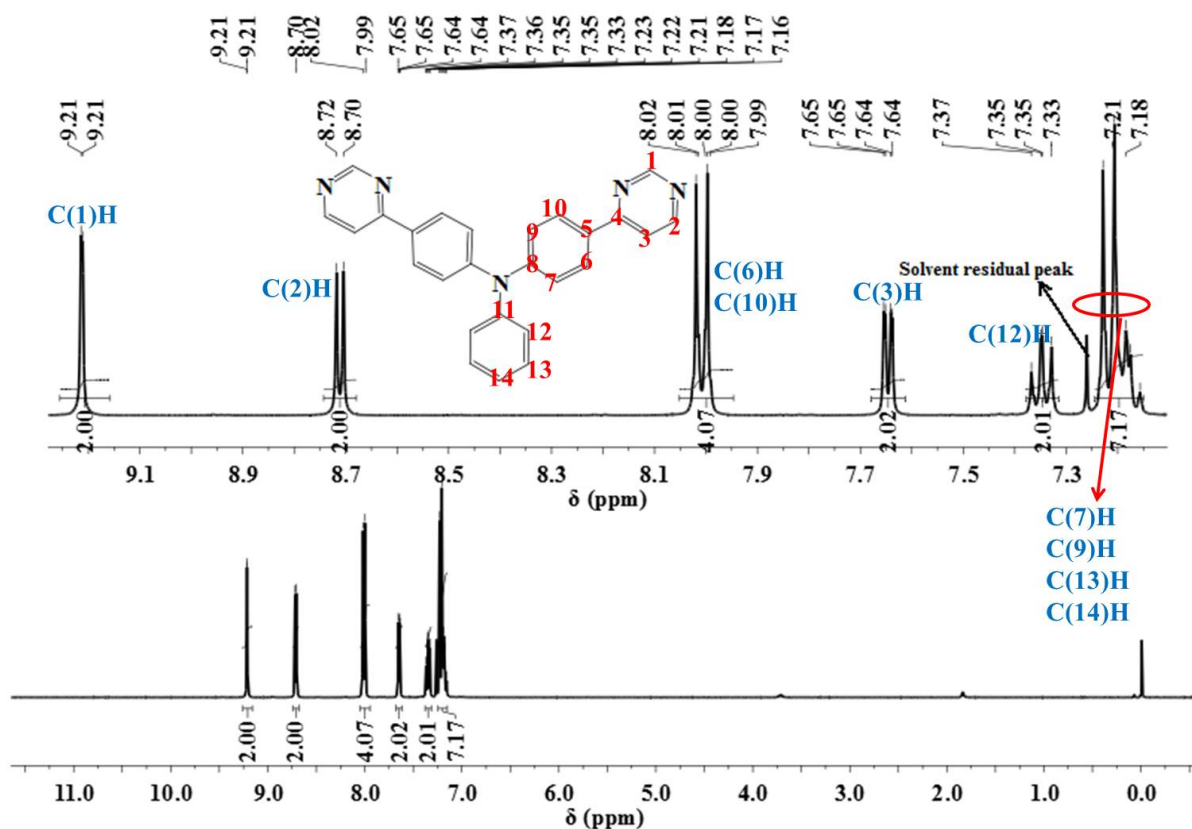
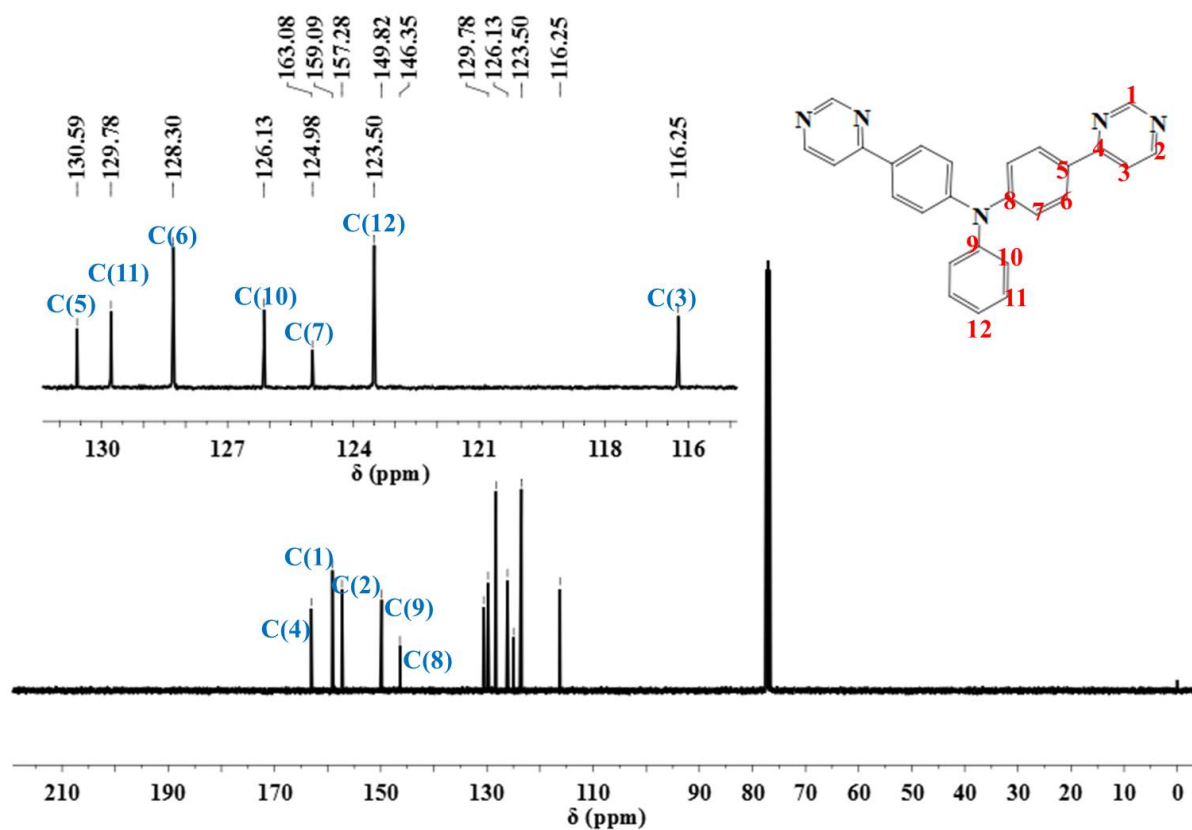


Figure S28 GC-MS spectrum of PM3



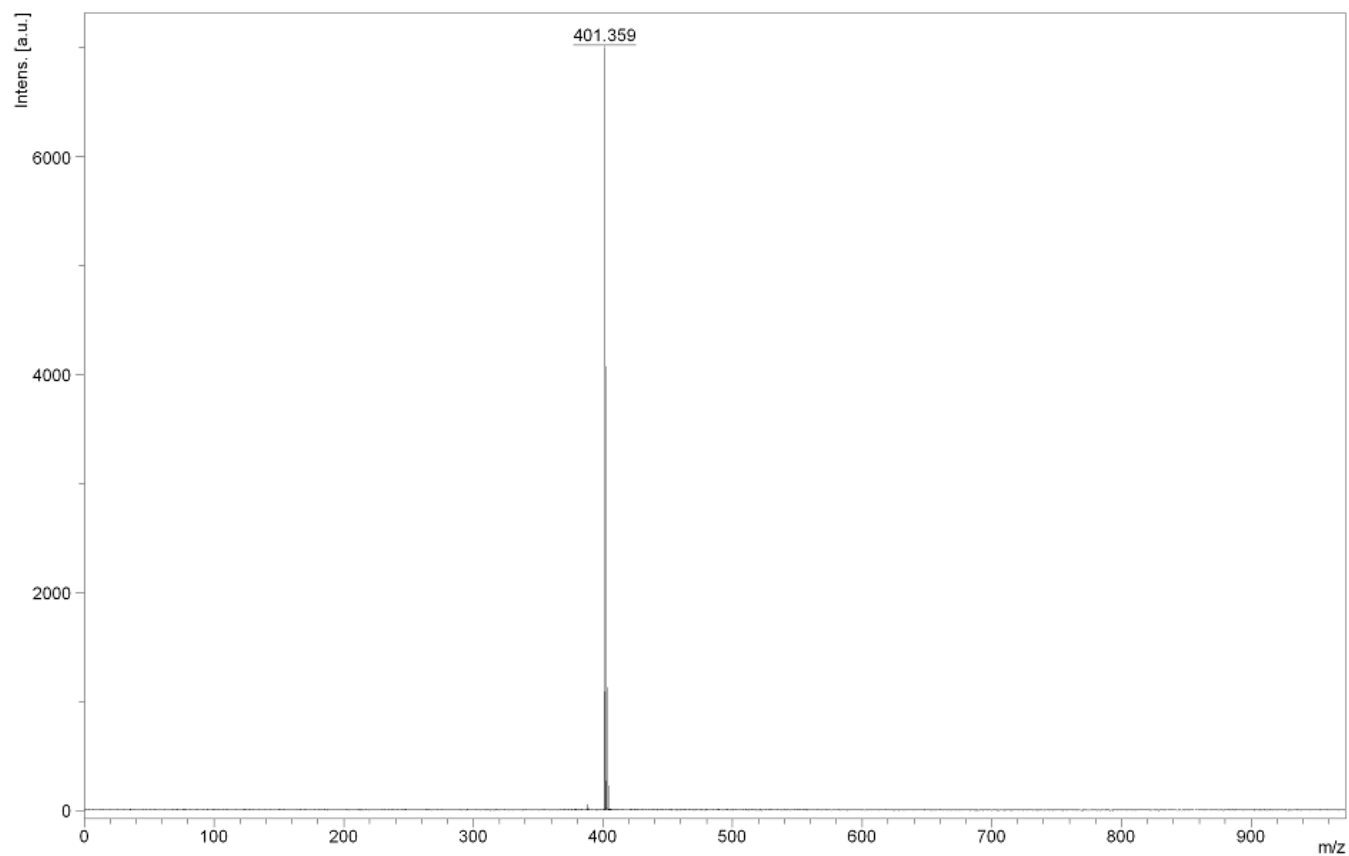
**Figure S29**  $^1\text{H}$  NMR of PM4 in  $\text{CDCl}_3$



**Figure S30**  $^{13}\text{C}$  NMR of PM4 in  $\text{CDCl}_3$



D:\Data\DATA\MQB\WJN\PM4\0\_017\1\1Ref



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**Figure S31** MALDI-TOF-MS spectrum of **PM4**

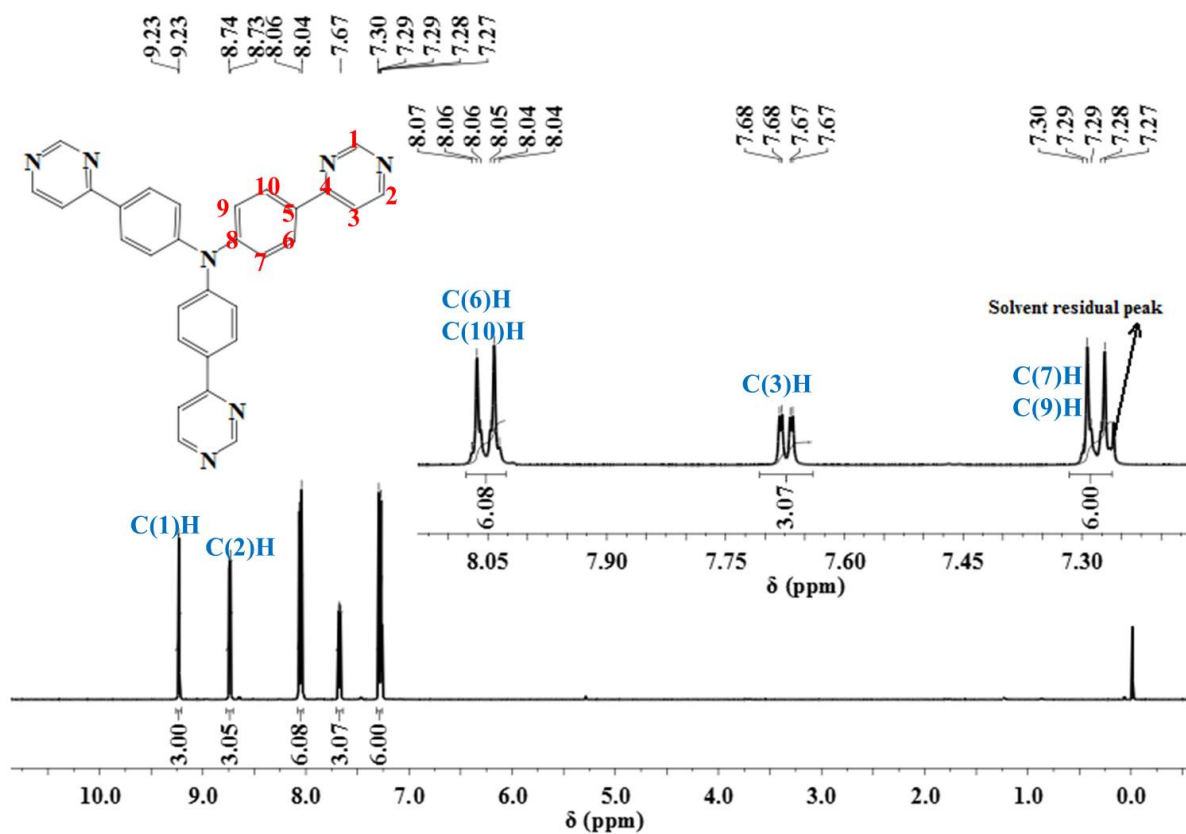


Figure S32 <sup>1</sup>H NMR of PM5 in CDCl<sub>3</sub>

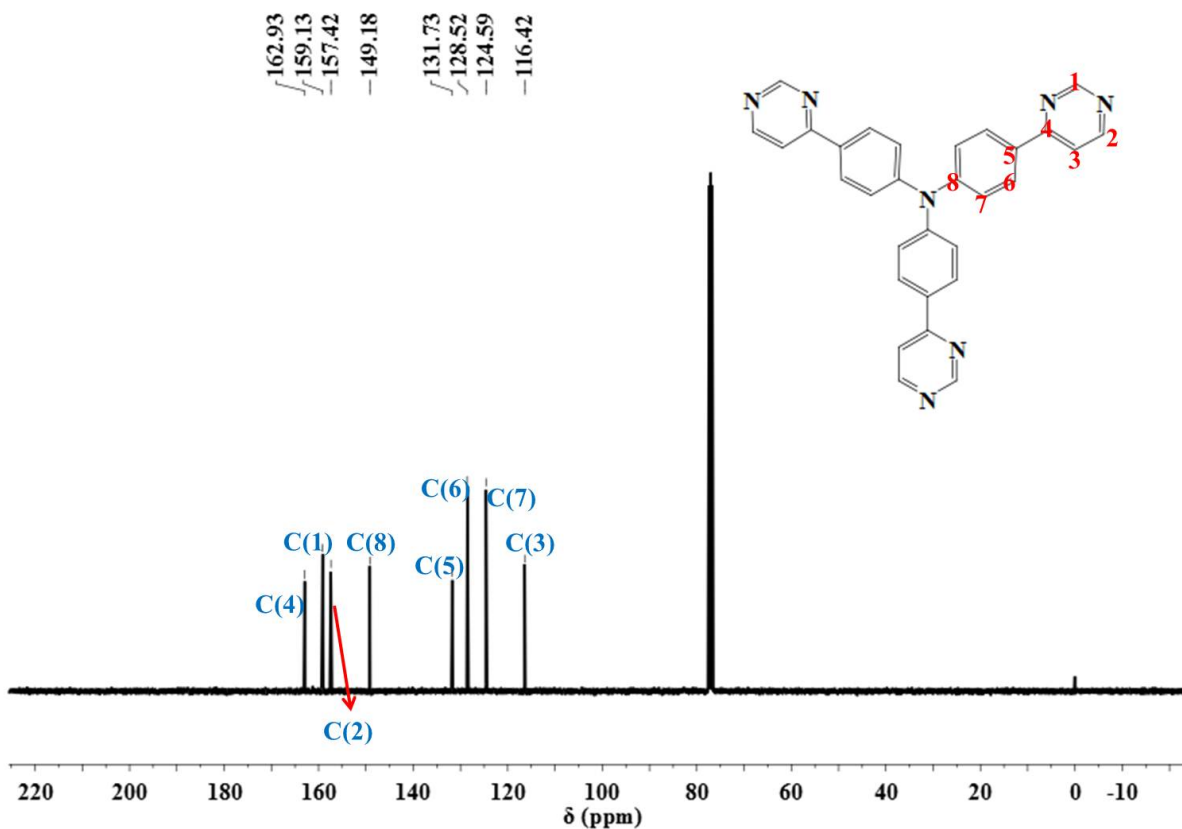
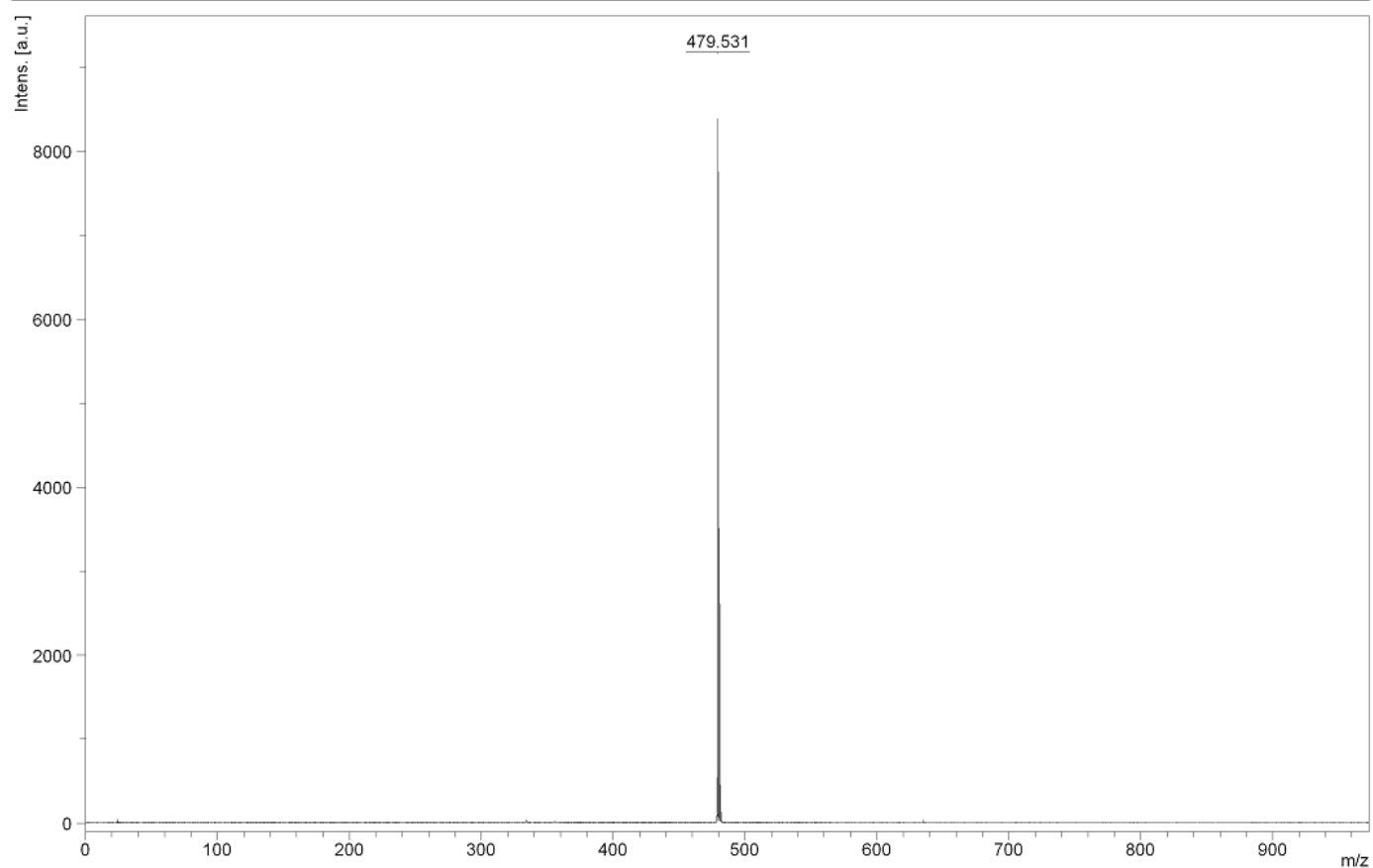


Figure S33 <sup>13</sup>C NMR of PM5 in CDCl<sub>3</sub>

D:\Data\DATA\MQB\WJN\WJN-PM5-2\0\_C13\1\1Ref



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**Figure S34** MALDI-TOF-MS spectrum of **PM5**