Photochromism and Photofluorochromism of Arylvinylene Phenanthridines

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General Information

Reagents and solvents employed are commercially purchased from sigma, SRL, spectrochem, TCI and used as it is. ^{1}H and ^{13}C (Nuclear magnetic resonance) solution state NMR studies are performed in Jeol:400 MHz NMR spectrometer. Agilent Cary 5000 UV-Vis-NIR spectrophotometer with diffuse reflectance and solution state accessory is employed to study the optical properties of the organic compounds synthesized. DFT calculations of the molecular structures (in the gas phase) and the molecular orbital energies were carried out at the B3LYP/6-311G(d) level as implemented in Gaussian 16. The figures were generated with GaussView.

Table S 1 Crystal data and structure refinement for compound **PC_1**

Empirical formula	$C_{33}H_{24}N_2$
Formula weight	448.54
Temperature/K	139.0
Crystal system	triclinic
Space group	P-1
a/Å	9.1336(19)
b/Å	9.519(2)
c/Å	14.327(4)
α/°	95.237(10)
β/°	91.455(10)
γ/°	111.440(8)
Volume/Å^3	1152.3(4)
Z	23
ρ_{calc}g/cm^3	14.867
μ/mm^{-1}	0.866
F(000)	5428.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.294 to 58.384
Index ranges	$-10 \leq h \leq 9$, $-10 \leq k \leq 12$, $-16 \leq l \leq 3$
Reflections collected	1546
Independent reflections	1515 [R_{int} = 0.0981, R_{sigma} = 0.2545]
Data/restraints/parameters	1515/0/141
Goodness-of-fit on F^2	0.920
Final R indexes [I>=2σ (I)]	R_1 = 0.1212, wR_2 = 0.2610
Final R indexes [all data]	R_1 = 0.2309, wR_2 = 0.3684
Largest diff. peak/hole / e Å^{-3}	0.20/-0.22

Table S 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Compound **PC_1**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
N_{001}	386(12)	2417(9)	4703(13)	39(2)
N_{002}	6977(10)	5271(8)	487(10)	30(2)
C_{003}	1032(14)	2375(12)	5545(15)	36(3)
C_{004}	-2327(12)	1914(10)	5247(12)	28(2)
C_{005}	-1216(14)	2419(12)	4589(15)	38(3)
C_{006}	-1610(13)	2878(11)	3706(14)	33(3)
C_{007}	1932(13)	1408(11)	5624(15)	35(3)
C_{008}	1484(12)	2837(10)	3920(12)	23(2)
C_{009}	927(13)	3237(12)	6372(14)	33(3)
C_{00A}	2305(15)	2144(12)	2464(16)	41(3)
C_{00B}	-3838(12)	1828(10)	5088(13)	28(2)

C_{00C}	3505(15)	3548(12)	2502(16)	42(3)
C_{00D}	2577(14)	1319(12)	6488(16)	38(3)
C_{00E}	1263(13)	1765(11)	3150(12)	29(2)
C_{00F}	6035(13)	3893(11)	310(13)	31(2)
C_{00G}	1563(13)	3064(12)	7269(14)	37(3)
C_{00H}	8203(13)	5877(11)	-38(13)	32(2)
C_{00I}	6085(12)	2913(11)	-528(13)	29(2)
C_{00J}	2603(15)	4218(12)	3995(15)	40(3)
C_{00K}	7305(14)	3583(12)	-1110(15)	37(3)
C_{00L}	3709(14)	4607(12)	3289(14)	35(3)
C_{00M}	4673(15)	4049(13)	1757(15)	40(3)
C_{00N}	2449(15)	2157(12)	7300(16)	44(3)
C_{00O}	4808(14)	3253(12)	987(14)	36(3)
C_{00P}	8436(13)	5067(11)	-847(14)	37(3)
C_{00Q}	-3177(14)	2784(12)	3593(15)	42(3)
C_{00R}	-4268(14)	2288(11)	4248(14)	36(3)
C_{00S}	5033(15)	1439(12)	-762(15)	41(3)
C_{00T}	9206(16)	7394(13)	265(17)	50(3)
C_{00U}	5164(15)	579(13)	-1523(16)	43(3)
C_{00V}	9751(14)	5806(12)	-1360(15)	41(3)
C_{00W}	7391(15)	2655(12)	-1950(16)	44(3)
C_{00X}	10751(18)	7286(14)	-1110(20)	57(4)
C_{00Y}	6385(15)	1224(13)	-2166(17)	49(3)
C_{00Z}	10503(19)	8085(17)	-290(20)	66(4)

Table **S 3** Bond Lengths for Compound **PC_1**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
N_{001}	C_{003}	1.34(3)	C_{00D}	C_{00N}	1.38(2)
N_{001}	C_{005}	1.469(17)	C_{00F}	C_{00I}	1.465(18)
N_{001}	C_{008}	1.507(18)	C_{00F}	C_{00O}	1.494(18)
N_{002}	C_{00F}	1.276(13)	C_{00G}	C_{00N}	1.385(17)
N_{002}	C_{00H}	1.342(15)	C_{00H}	C_{00P}	1.398(19)
C_{003}	C_{007}	1.450(18)	C_{00H}	C_{00T}	1.418(17)
C_{003}	C_{009}	1.40(2)	C_{00I}	C_{00K}	1.403(18)
C_{004}	C_{005}	1.388(19)	C_{00I}	C_{00S}	1.384(16)
C_{004}	C_{00B}	1.365(16)	C_{00J}	C_{00L}	1.424(19)
C_{005}	C_{006}	1.45(3)	C_{00K}	C_{00P}	1.421(16)
C_{006}	C_{00Q}	1.405(18)	C_{00K}	C_{00W}	1.45(2)
C_{007}	C_{00D}	1.38(3)	C_{00M}	C_{00O}	1.31(2)
C_{008}	C_{00E}	1.390(17)	C_{00P}	C_{00V}	1.413(17)
C_{008}	C_{00J}	1.331(15)	C_{00Q}	C_{00R}	1.37(2)
C_{009}	C_{00G}	1.44(3)	C_{00S}	C_{00U}	1.34(2)
C_{00A}	C_{00C}	1.379(16)	C_{00T}	C_{00Z}	1.43(2)

C_{00A}	C_{00E}	1.36(2)	C_{00U}	C_{00Y}	1.46(2)
C_{00B}	C_{00R}	1.41(3)	C_{00V}	C_{00X}	1.378(18)
C_{00C}	C_{00L}	1.40(2)	C_{00W}	C_{00Y}	1.337(17)
C_{00C}	C_{00M}	1.51(2)	C_{00X}	C_{00Z}	1.41(3)

Table S 4 Bond Angles for Compound $\mathbf{PC_1}$

Bond Angles for Compound $\mathbf{PC_1}$

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C_{003}	N_{001}	C_{005}	121.8(14)	N_{002}	C_{00H}	C_{00P}	121.5(10)
C_{003}	N_{001}	C_{008}	116.9(10)	N_{002}	C_{00H}	C_{00T}	115.9(12)
C_{005}	N_{001}	C_{008}	119.8(15)	C_{00P}	C_{00H}	C_{00T}	122.6(12)
C_{00F}	N_{002}	C_{00H}	121.6(11)	C_{00K}	C_{00I}	C_{00F}	114.7(9)
N_{001}	C_{003}	C_{007}	119.0(14)	C_{00S}	C_{00I}	C_{00F}	124.6(11)
N_{001}	C_{003}	C_{009}	124.3(11)	C_{00S}	C_{00I}	C_{00K}	120.7(13)
C_{009}	C_{003}	C_{007}	116.6(18)	C_{008}	C_{00J}	C_{00L}	119.3(13)
C_{00B}	C_{004}	C_{005}	121.0(16)	C_{00I}	C_{00K}	C_{00P}	120.7(13)
C_{004}	C_{005}	N_{001}	122.5(17)	C_{00I}	C_{00K}	C_{00W}	116.5(10)
C_{004}	C_{005}	C_{006}	121.6(12)	C_{00P}	C_{00K}	C_{00W}	122.7(12)
C_{006}	C_{005}	N_{001}	115.7(13)	C_{00C}	C_{00L}	C_{00J}	118.3(11)
C_{00Q}	C_{006}	C_{005}	114.5(14)	C_{00O}	C_{00M}	C_{00C}	128.2(11)
C_{00D}	C_{007}	C_{003}	120.1(14)	C_{00D}	C_{00N}	C_{00G}	119.4(19)
C_{00E}	C_{008}	N_{001}	118.2(8)	C_{00M}	C_{00O}	C_{00F}	122.6(10)
C_{00J}	C_{008}	N_{001}	118.5(12)	C_{00H}	C_{00P}	C_{00K}	117.6(11)
C_{00J}	C_{008}	C_{00E}	123.4(12)	C_{00H}	C_{00P}	C_{00V}	117.4(10)
C_{003}	C_{009}	C_{00G}	121.5(11)	C_{00V}	C_{00P}	C_{00K}	124.9(13)
C_{00E}	C_{00A}	C_{00C}	122.4(15)	C_{00R}	C_{00Q}	C_{006}	123.7(19)
C_{004}	C_{00B}	C_{00R}	119.4(12)	C_{00Q}	C_{00R}	C_{00B}	119.8(12)
C_{00A}	C_{00C}	C_{00L}	119.2(14)	C_{00U}	C_{00S}	C_{00I}	122.0(12)
C_{00A}	C_{00C}	C_{00M}	124.9(15)	C_{00H}	C_{00T}	C_{00Z}	117.4(15)
C_{00L}	C_{00C}	C_{00M}	115.9(11)	C_{00S}	C_{00U}	C_{00Y}	119.8(12)
C_{007}	C_{00D}	C_{00N}	122.8(12)	C_{00X}	C_{00V}	C_{00P}	122.6(15)
C_{00A}	C_{00E}	C_{008}	117.3(10)	C_{00Y}	C_{00W}	C_{00K}	122.6(14)
N_{002}	C_{00F}	C_{00I}	123.3(11)	C_{00V}	C_{00X}	C_{00Z}	119.2(15)
N_{002}	C_{00F}	C_{00O}	118.3(12)	C_{00W}	C_{00Y}	C_{00U}	118.3(16)
C_{00I}	C_{00F}	C_{00O}	118.4(9)	C_{00X}	C_{00Z}	C_{00T}	120.8(14)
C_{00N}	C_{00G}	C_{009}	119.2(15)				

Table S5. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for F1_a.

Atom	*x*	*y*	*z*	U(eq)
H_{004}	-2031	1623	5818	34
H_{006}	-868	3215	3244	40
H_{007}	2078	836	5080	42

H_{009}	426	3949	6341	39
H_{00A}	2201	1416	1942	49
H_{00B}	-4594	1463	5538	34
H_{00D}	3133	653	6525	46
H_{00E}	420	806	3102	35
H_{00G}	1376	3567	7831	44
H_{00J}	2662	4937	4514	48
H_{00L}	4563	5559	3350	43
H_{00M}	5403	5067	1858	48
H_{00N}	2963	2111	7875	53
H_{00O}	4097	2230	856	43
H_{00Q}	-3498	3080	3031	51
H_{00R}	-5310	2255	4136	43
H_{00S}	4191	1025	-369	50
H_{00T}	9022	7930	813	60
H_{00U}	4464	-449	-1645	51
H_{00V}	9952	5261	-1899	49
H_{00W}	8194	3079	-2364	52
H_{00X}	11597	7763	-1485	69
H_{00Y}	6464	643	-2724	59
H_{00Z}	11208	9094	-99	79

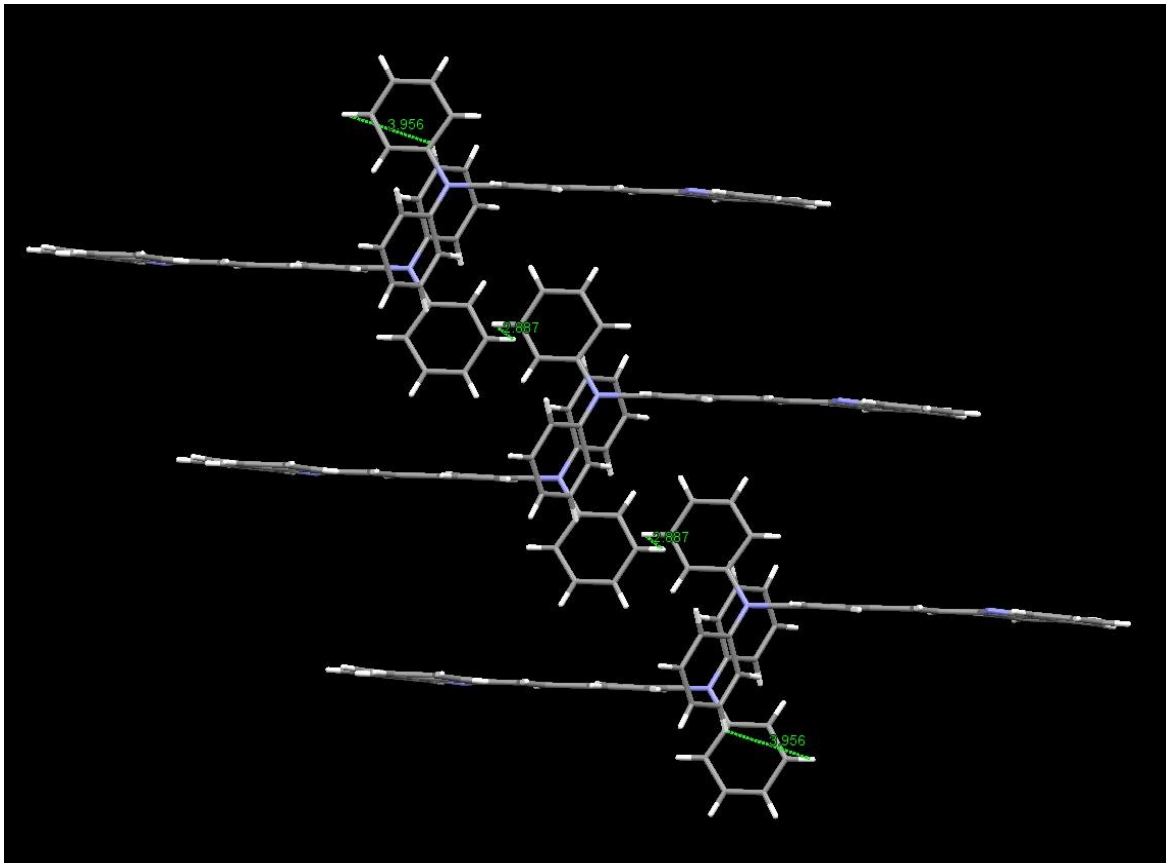


Fig. S 1 Crystal structure packing diagram of compound PC_1

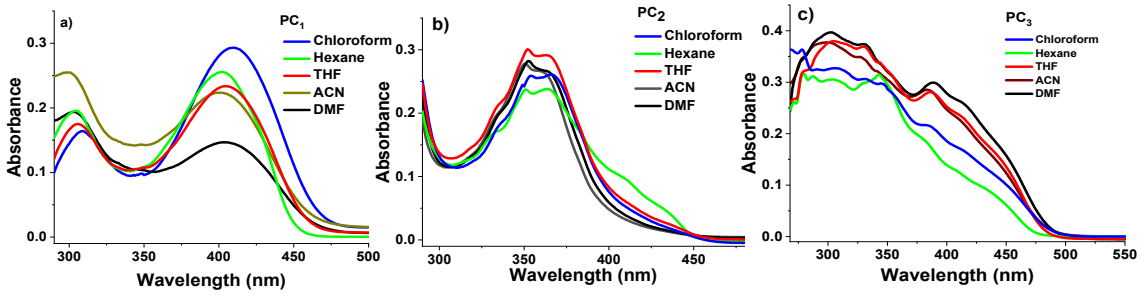


Fig. S 2 UV-vis Absorption spectra of PC_1, PC_2, and PC_3

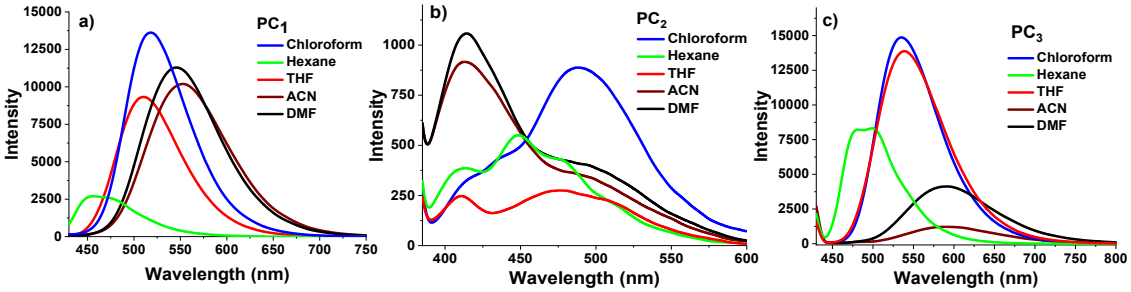


Fig. S 3 Emission spectra of PC_1, PC_2, and PC_3

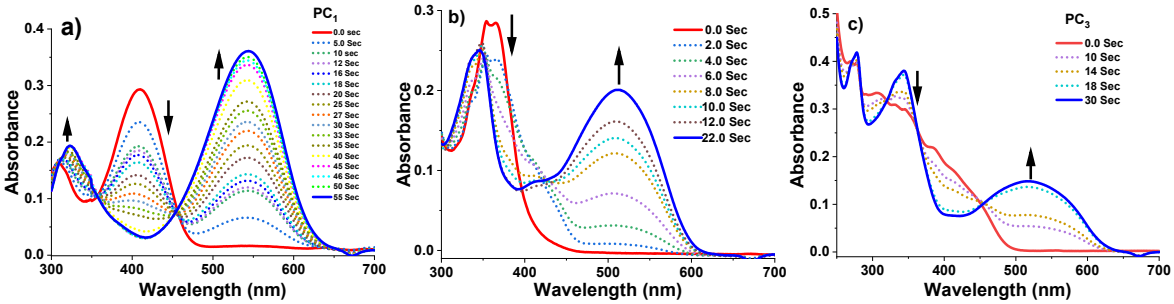


Fig. S 4 Absorption spectra recorded for PC_1–PC_3 after irradiation at 254 nm ($CHCl_3$ $1*10^{-5}$)

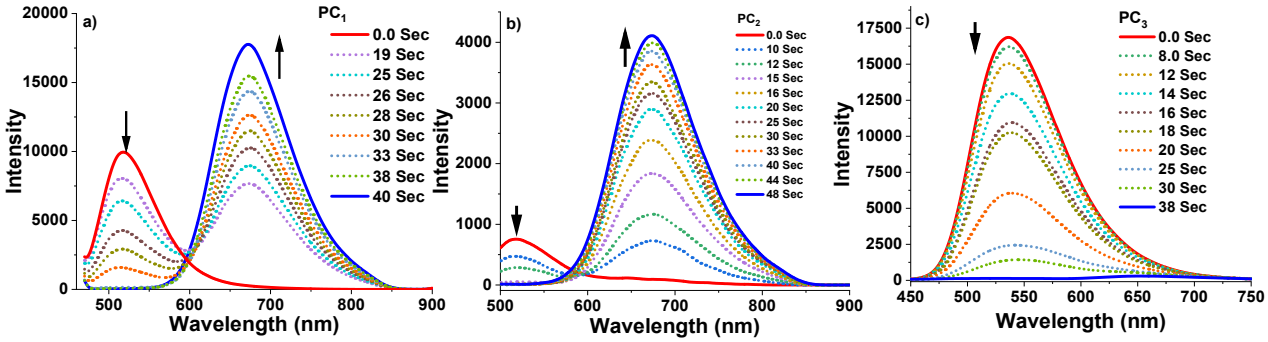


Fig. S 5 Emission spectra recorded for PC_1–PC_3 after irradiation at 254 nm ($CHCl_3$ $1*10^{-6}$)

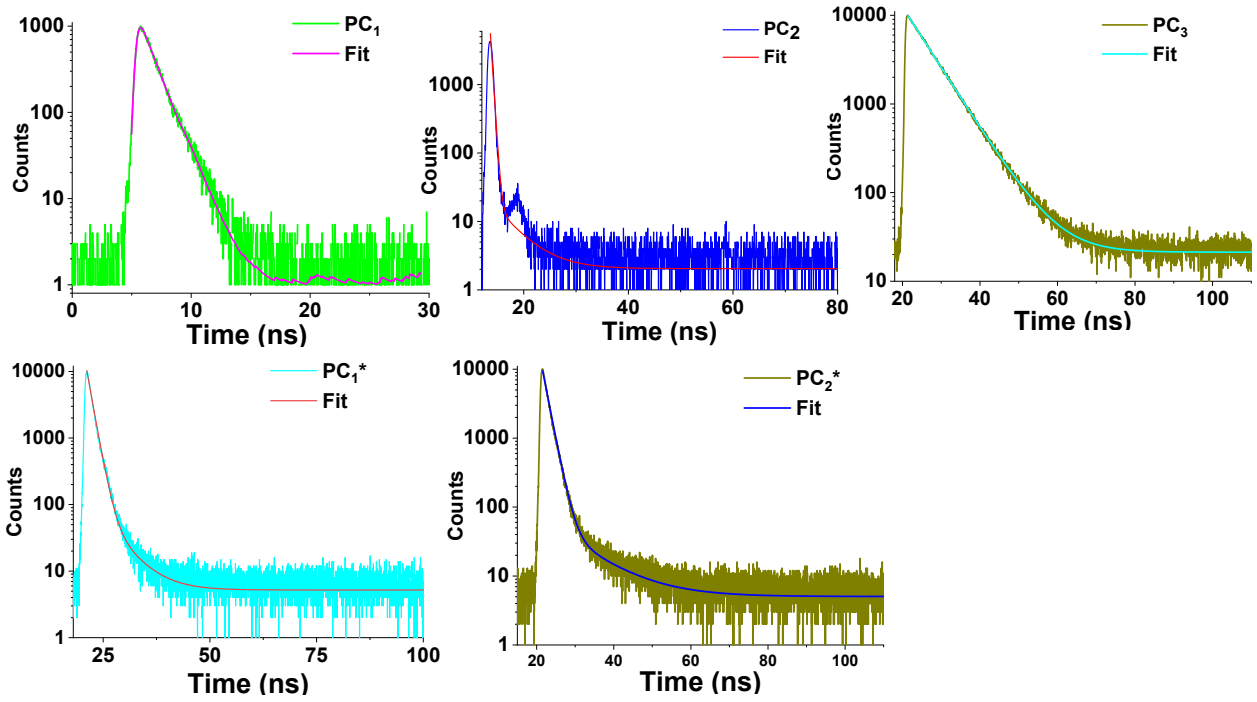


Fig. S 6 Fluorescence life-time decay and Residuals of fit to single and double-exponential function of PC_1-PC_3 and their photo-transformed products (PC_1^*-PC_2^*).

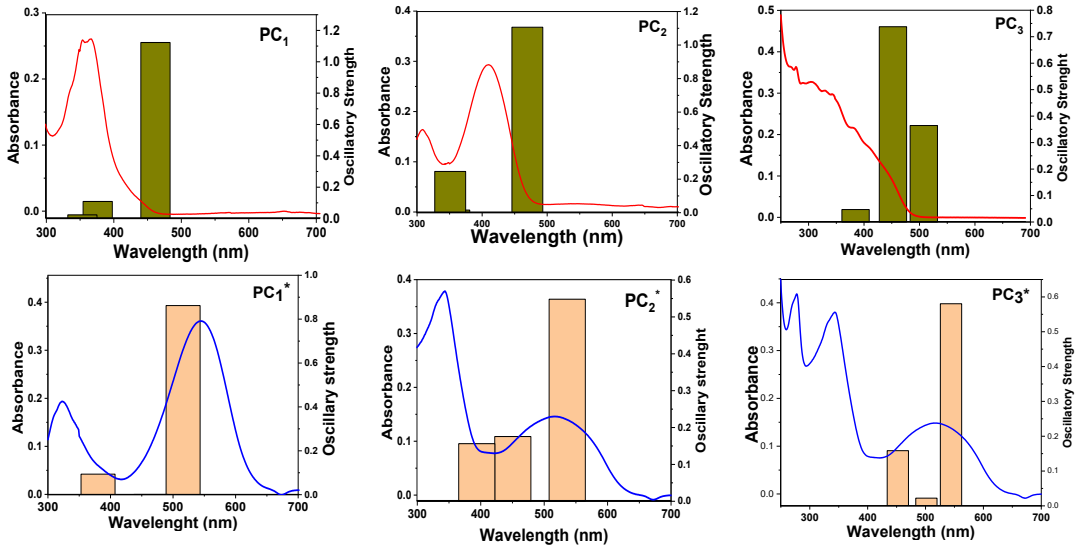
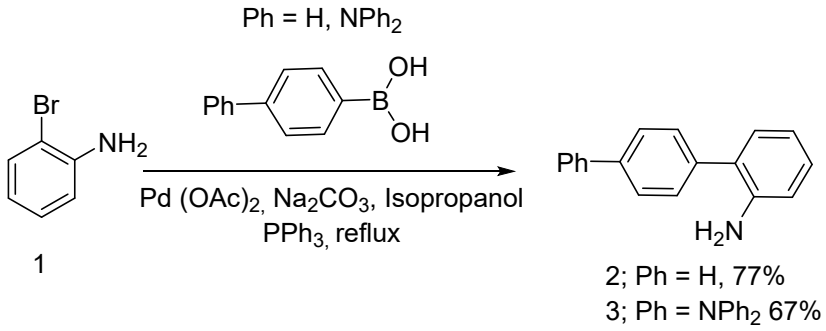


Fig. S 7 Comparison of calculated (dark yellow lines) and experimental (red lines) absorption spectra of PC_1–PC_3, along with photoexcited systems (PC_1^*–PC_3^*) showing calculated (orange lines) and experimental (blue lines) absorption spectra

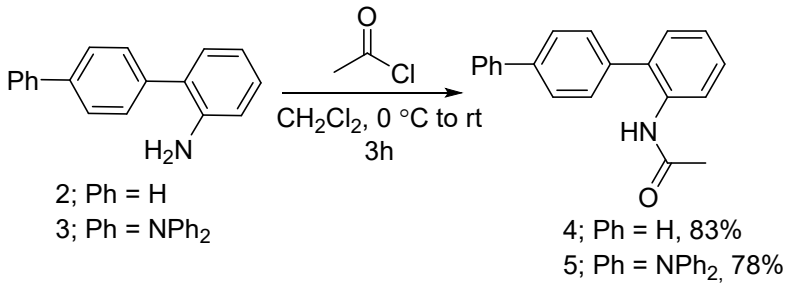
Experimental Section

General procedure for suzuki coupling reaction



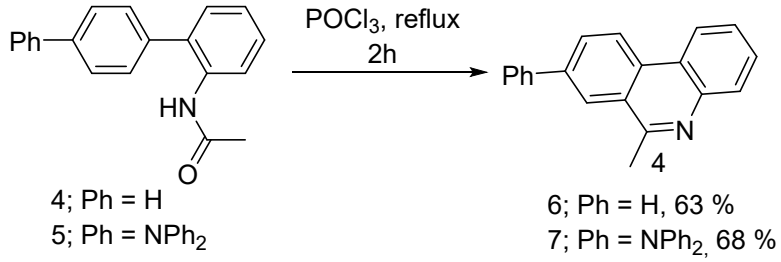
To a 50 mL round-bottom flask equipped with a magnetic stirrer were added 2-bromobenzene (**1**) (1.0 mmol), phenylboronic acid / triphenylamine boronic acid (2.0 mmol), palladium acetate (0.01 mmol), and triphenylphosphine (0.06 mmol). A degassed mixture of isopropanol (10 mL), aqueous Na_2CO_3 (2 N, 3 mL), was added to the reaction flask. The resulting mixture was heated to reflux at 70 °C under a nitrogen atmosphere and stirred overnight. After cooling to room temperature, the mixture was extracted with dichloromethane (3 × 20 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 30:1) to afford the desired product [1,1'-biphenyl]-2-amine (**2**)/ N4',N4'-diphenyl-[1,1'-biphenyl]-2,4'-diamine **(3**) as white crystals

General procedure for acylation reaction



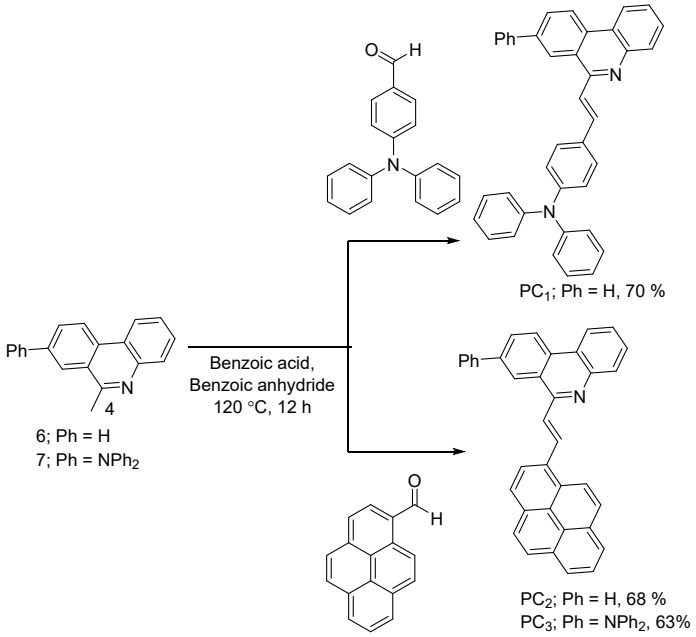
Acetyl chloride (0.62 mmol), Triethyl amine (0.65 mmol) and [1,1'-biphenyl]-2-amine (**2**)/ N4',N4'-diphenyl-[1,1'-biphenyl]-2,4'-diamine **(3**) (0.59 mmol), were added into a flask of Dichloromethane at 0 °C (5 ml) and the resulting solution was stirred room temperature for 3 h. The crude product was extracted with dichloro-methane and the organic layer was concentrated under vacuum, to give N-([1,1'-biphenyl]-2-yl)acetamide (**4**) / N-(4'-(diphenylamino)-[1,1'-biphenyl]-2-yl)acetamide (**5**) as a white solid.

General procedure for cyclization reaction



A mixture of N-([1,1'-biphenyl]-2-yl)acetamide (**4**) / N-(4'-(diphenylamino)-[1,1'-biphenyl]-2-yl)acetamide (**5**) (20 mmol) and phosphorus oxychloride (12.44 g, ~81 mmol) was stirred under reflux at 120 °C for 3 h. After completion, the reaction mixture was concentrated under reduced pressure to remove excess phosphorus oxychloride. The residue was carefully diluted with aqueous NaOH solution (2 M). The resulting precipitate was collected by filtration, washed thoroughly with water, and dried to afford the product 6-methylphenanthridine **(6)** /6-methyl-N, N-diphenylphenanthridin-3-amine **(7)** as a white / orange solid.

General procedure for the Knoevenagel condensation



6-methylphenanthridine **(6)**/6-methyl-N, N-diphenylphenanthridin-3-amine **(7)** (1 mmol) Aromatic aldehyde (8 mmol), Benzoic acid (0.2 mmol), Benzoic Anhydride (2.0 mmol), were added into a flask resulting mixture was stirred under reflux at 120 ^{o}C for 12 h, after completion of reaction, the reaction mixture was treated with aq 1 M NaOH (20 ml). the reaction mixture was diluted with water extracted with dichloromethane, the organic layer was concentrated under vacuum and purified by column chromatography (DCM/pet ether 20:80),) to afford the desired product (E)-4-(2-(phenanthridin-6-yl) vinyl)-N, N-diphenylaniline (**PC$_1$**)/ (E)-6-(2-

(pyren-1-yl) vinyl) phenanthridine **(PC_2)**/ (E)-N, N-diphenyl-6-(2-(pyren-1-yl) vinyl) phenanthridin-8-amine **(PC_3)** as a orange solid.

Spectral Data

N4',N4'-diphenyl-[1,1'-biphenyl]-2,4'-diamine **(3):** White solid (67%), m/z calcd for $C_{24}H_{20}N_2$ ([M+H]): 337.1699; found m/z: 337.1700; ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.37 (d, *J* = 8.6 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.18 (dt, *J* = 9.0, 1.8 Hz, 8H), 7.08 (td, *J* = 7.3, 1.2 Hz, 2H), 6.86 (td, *J* = 7.4, 1.2 Hz, 1H), 6.79 (dd, *J* = 7.6, 0.9 Hz, 1H). {1H}^{13}C NMR (101 MHz, $CDCl_3$) δ 147.84, 147.02, 143.72, 133.51, 130.57, 129.94, 129.45, 128.38, 127.46, 124.63, 123.87, 123.13, 118.83, 115.75.

N-([1,1'-biphenyl]-2-yl) acetamide **(4):** White solid (83%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.3 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.43 – 7.37 (m, 3H), 7.19 (d, *J* = 7.4 Hz, 1H), 2.02 (s, 3H). {H}^{13}C NMR (101 MHz, $CDCl_3$) δ 168.34, 138.26, 134.77, 130.14, 129.32, 129.17, 128.52, 128.06, 124.45, 121.75, 24.66.

N-(4'-(diphenylamino)-[1,1'-biphenyl]-2-yl) acetamide **(5):** White solid (78%); m/z calcd for $C_{26}H_{22}N_2O$ ([M+H]): 379.1805; found m/z: 370.1813; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.3 Hz, 1H), 7.32 – 7.25 (m, 6H), 7.21 – 7.18 (m, 3H), 7.15 – 7.10 (m, 6H), 7.07 – 7.03 (m, 2H), 2.05 (s, 3H). {H}^{13}C NMR (101 MHz, $CDCl_3$) δ 147.80, 147.48, 134.83, 131.32, 130.17, 130.01, 129.51, 128.18, 125.00, 124.45, 123.58, 123.02, 121.71, 29.75.

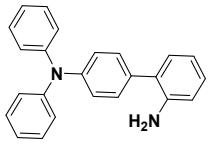
6-methylphenanthridine **(6):** light yellow solid (63%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.4 Hz, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 8.22 (d, *J* = 6.2 Hz, 1H), 8.09 (d, *J* = 6.3 Hz, 1H), 7.84 (t, *J* = 7.0 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.65 – 7.59 (m, 1H), 3.05 (s, 3H).

6-methyl-N,N-diphenylphenanthridin-8-amine **(7)** : Orange solid (68%), m/z calcd for $C_{26}H_{22}N_2$ ([M+H]): 361.1699; found m/z: 361.1728; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 – 8.42 (m, 2H), 7.81 – 7.71 (m, 4H), 7.41 – 7.34 (m, 5H), 7.23 – 7.18 (m, 6H), 3.10 (s, 3H).

(E)-4-(2-(phenanthridin-6-yl) vinyl)-N, N-diphenylaniline **(PC_1).** Orange solid yield (70 %), m/z calcd for $C_{33}H_{24}N_2$ ([M+H]): 449.2012; found m/z: 449.1999; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.3 Hz, 1H), 8.55 (d, *J* = 8.2 Hz, 1H), 8.47 (d, *J* = 8.2 Hz, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 8.06 (d, *J* = 15.4 Hz, 1H), 7.94 (d, *J* = 15.5 Hz, 1H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.73 (q, *J* = 6.5 Hz, 2H), 7.62 (t, *J* = 8.4 Hz, 3H), 7.29 (q, *J* = 8.4 Hz, 4H), 7.17 (d, *J* = 7.8 Hz, 4H), 7.13 – 7.05 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.21, 148.54, 147.46, 144.13, 136.84, 133.33, 130.74, 130.48, 129.99, 129.48, 128.91, 128.67, 127.38, 126.45, 125.75, 125.42, 125.03, 123.87, 123.53, 122.86, 122.56, 122.04, 121.13.

(E)-6-(2-(pyren-1-yl) vinyl) phenanthridine **(PC_2).** Orange solid (68%), m/z calcd for $C_{31}H_{19}N$ ([M+H]): 406.1590; found m/z: 406.1592; ^1H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, *J* = 15.2 Hz, 1H), 8.73 (d, *J* = 9.5 Hz, 2H), 8.64 – 8.54 (m, 3H), 8.36 – 8.31 (m, 2H), 8.27 – 8.18 (m, 4H), 8.11 (s, 2H), 8.03 (t, *J* = 7.5 Hz, 1H), 7.93 – 7.88 (m, 1H), 7.83 – 7.75 (m, 2H), 7.71 – 7.65 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.10, 133.30, 131.71, 131.49, 130.51, 130.27, 128.92, 127.98, 127.84, 127.47, 126.67, 126.15, 125.74, 125.53, 125.16, 124.22, 123.42, 122.56, 122.04.

(E)-N, N-diphenyl-6-(2-(pyren-1-yl) vinyl) phenanthridin-8-amine **(PC_3).** Orange solid (63%), m/z calcd for $C_{43}H_{28}N_2$ ([M+H]): 573.2325; found m/z: 573.2318**;** ^1H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, *J* = 15.3 Hz, 1H), 8.67 (d, *J* = 9.3 Hz, 1H), 8.55 (d, *J* = 9.1 Hz, 1H), 8.49 (d, *J* = 8.2 Hz, 1H), 8.35 – 8.28 (m, 2H), 8.22 – 8.15 (m, 5H), 8.08 (d, *J* = 3.5 Hz, 2H), 8.02 (t, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 15.3 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.66 (ddd, *J* = 8.2, 4.2, 1.8 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 4H), 7.23 (d, *J* = 7.4 Hz, 4H), 7.10 (t, *J* = 7.4 Hz, 2H)**.**^{13}C NMR (101 MHz, $CDCl_3$) δ 154.33, 147.41, 131.79, 131.56, 131.35, 131.07, 129.95, 129.71, 129.51, 128.64, 128.29, 128.07, 127.93, 127.51, 126.94, 126.67, 126.18, 125.59, 125.45, 125.16, 124.96, 124.83, 124.32, 124.13, 123.87, 123.81, 123.56, 121.70, 117.89.



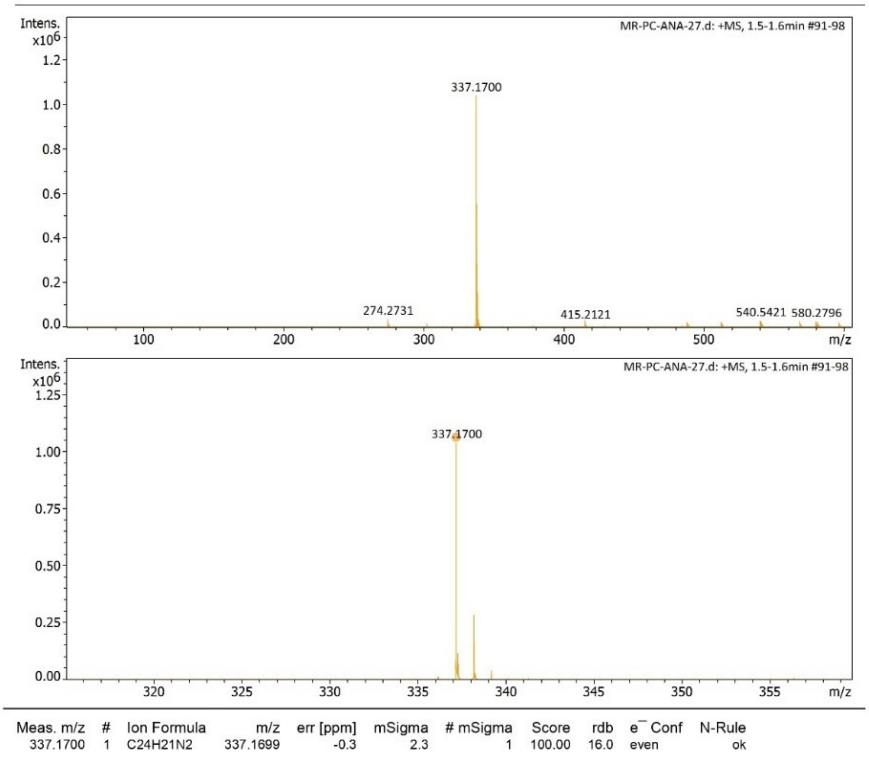


Fig. S 8 HRMS of compound **3**

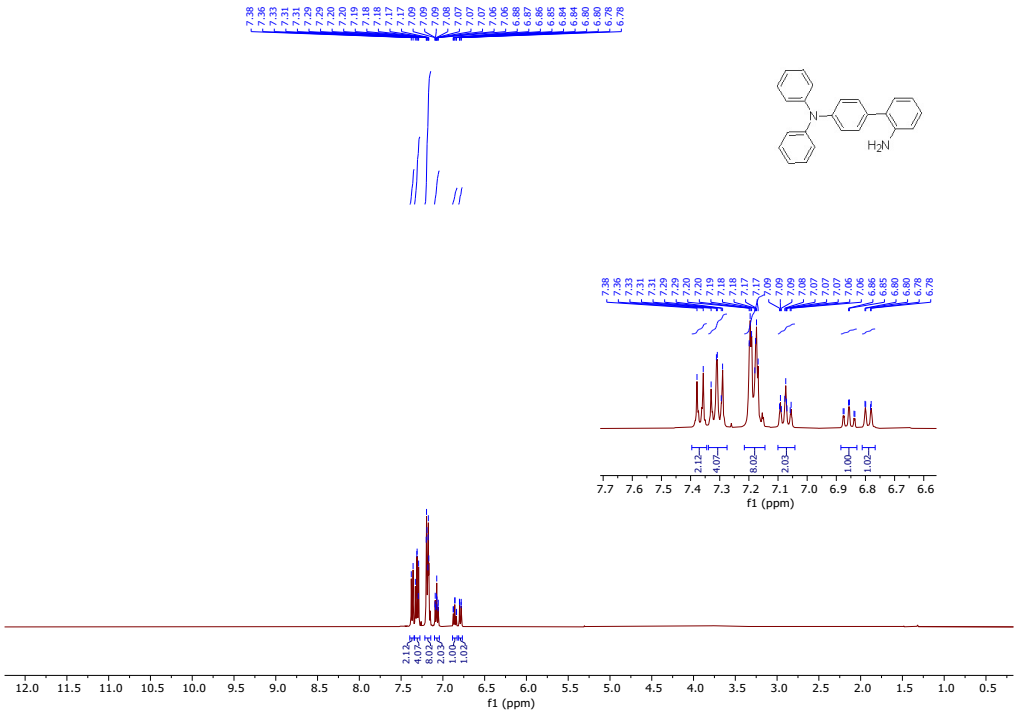


Fig. S 9 ^{1}H NMR spectrum of compound **3** (400 MHz, $CDCl_3$)

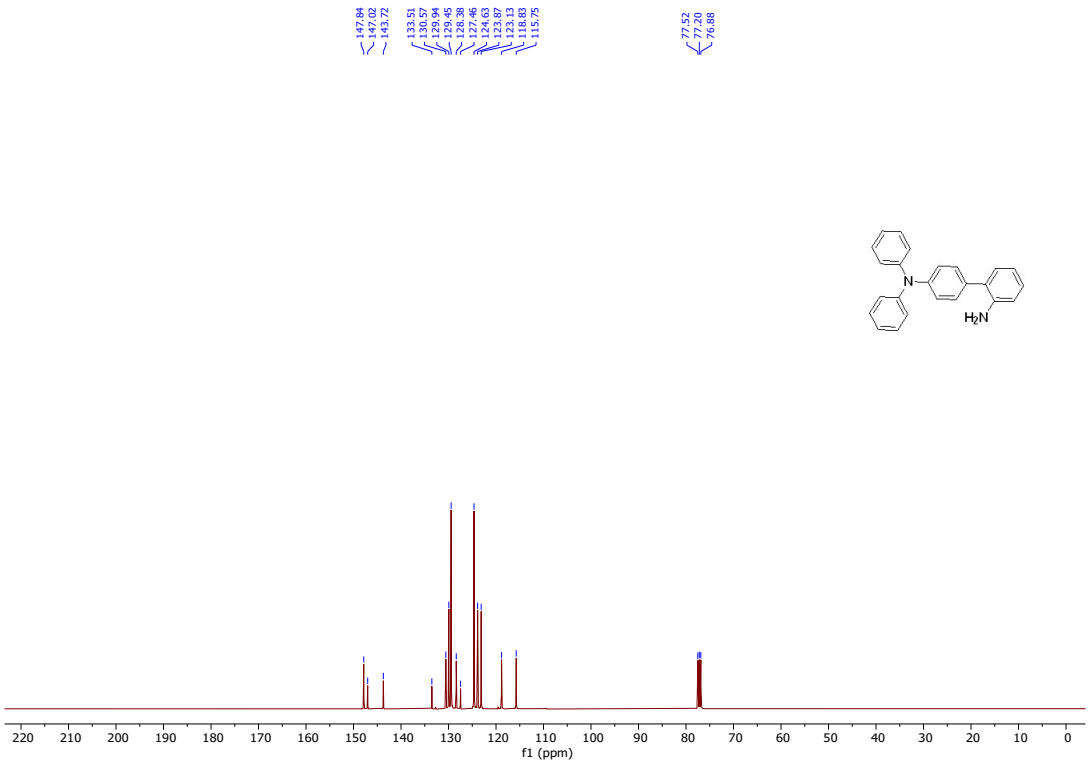


Fig. S 10 {1H}^{13}C NMR spectrum of compound **3** (101 MHz, $CDCl_3$)

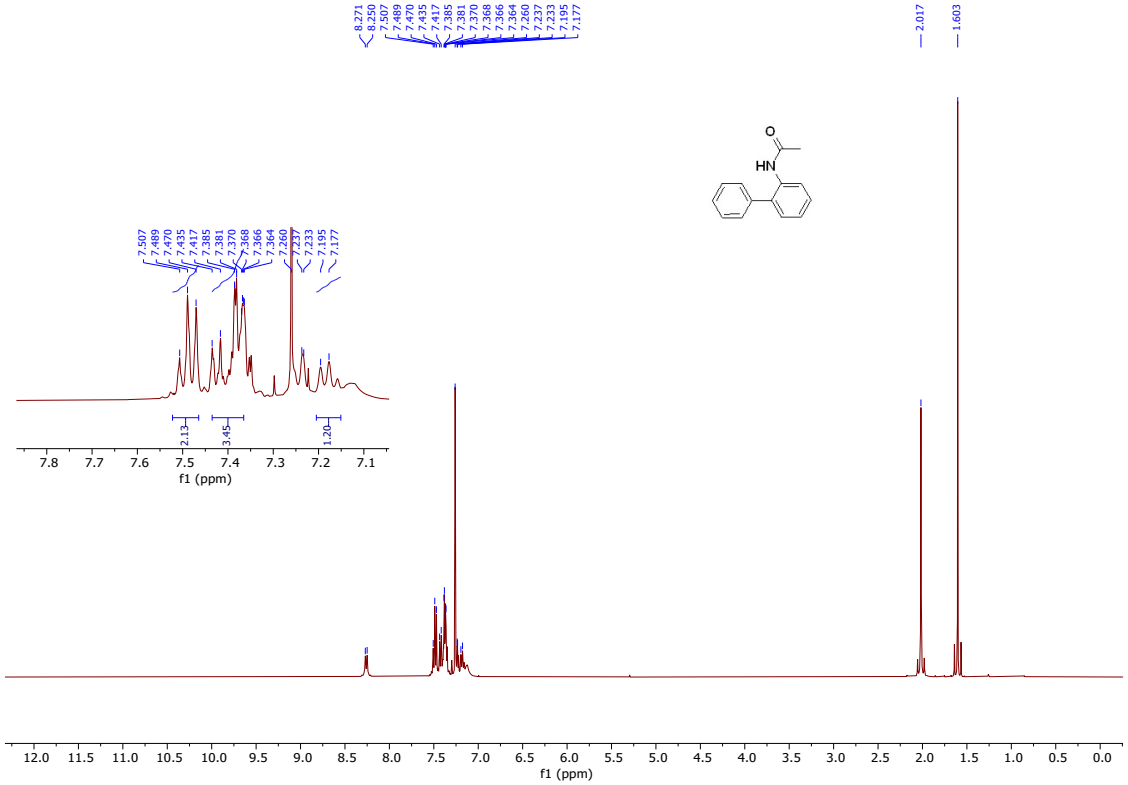


Fig. S 11 ^{1}H NMR spectrum of compound **4** (400 MHz, $CDCl_3$)

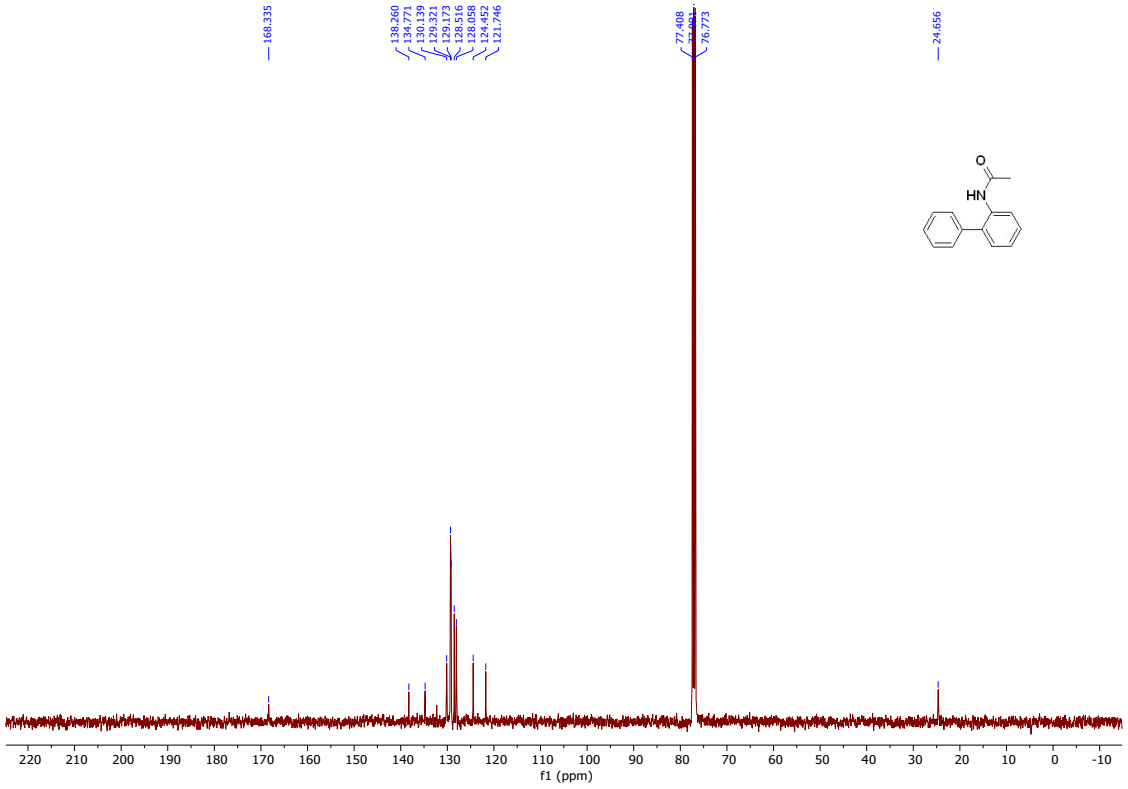


Fig. S 12 {1H}^{13}C NMR spectrum of compound **4** (101 MHz, $CDCl_3$)

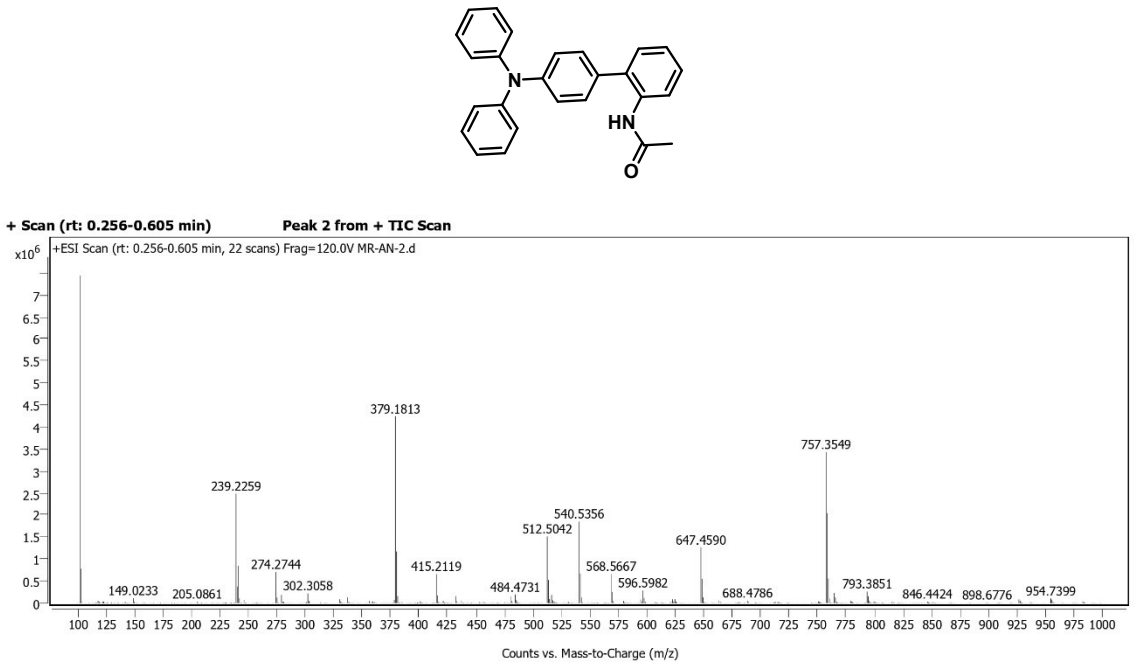


Fig. S 13 HRMS of compound **5**

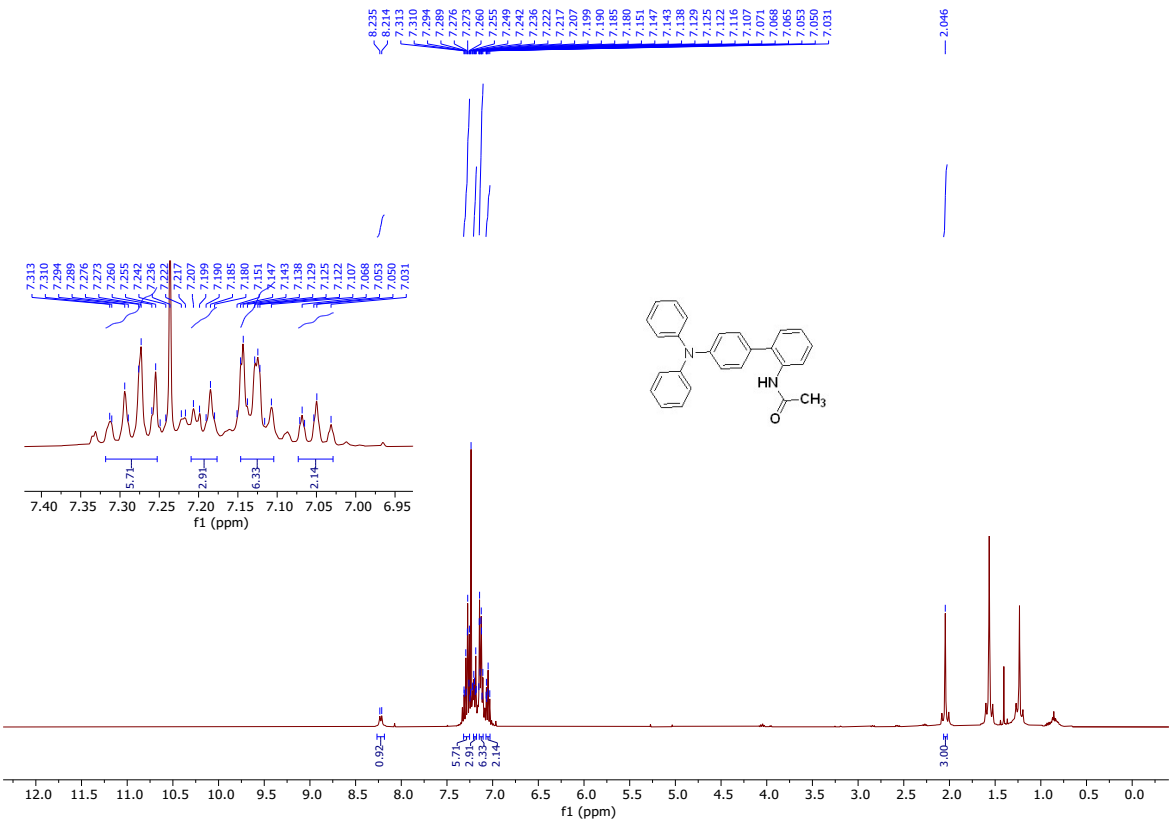


Fig. S 14 ^{1}H NMR spectrum of compound **5** (400 MHz, $CDCl_3$)

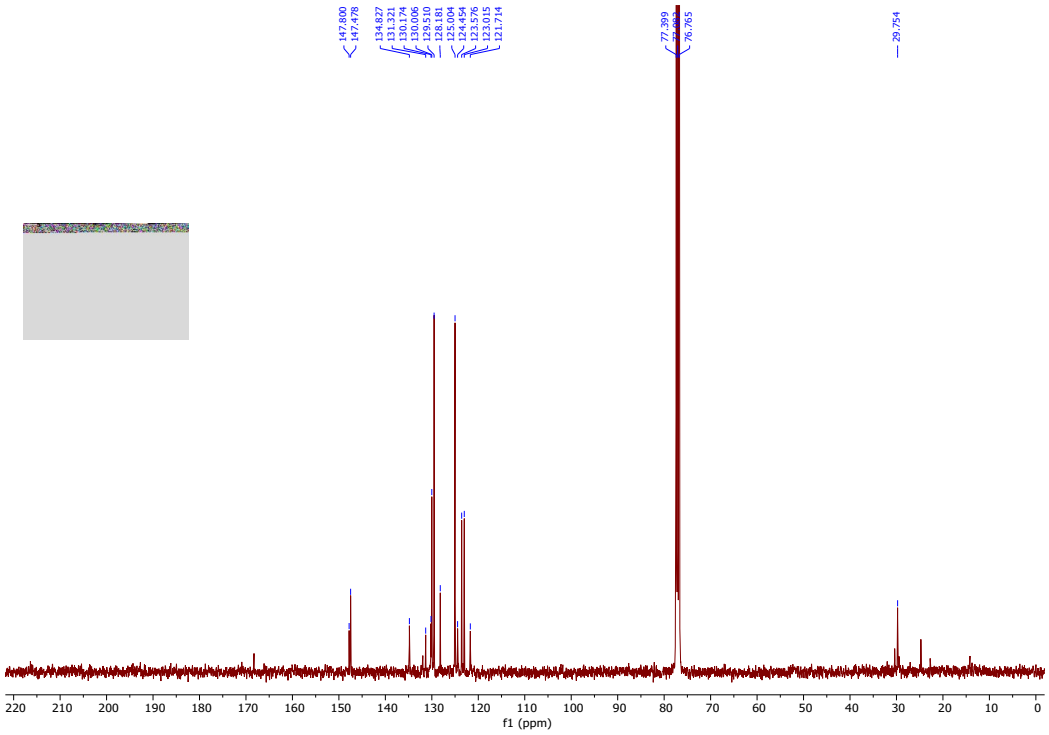


Fig. S 15 {1H}^{13}C NMR spectrum of compound **5** (101 MHz, $CDCl_3$)

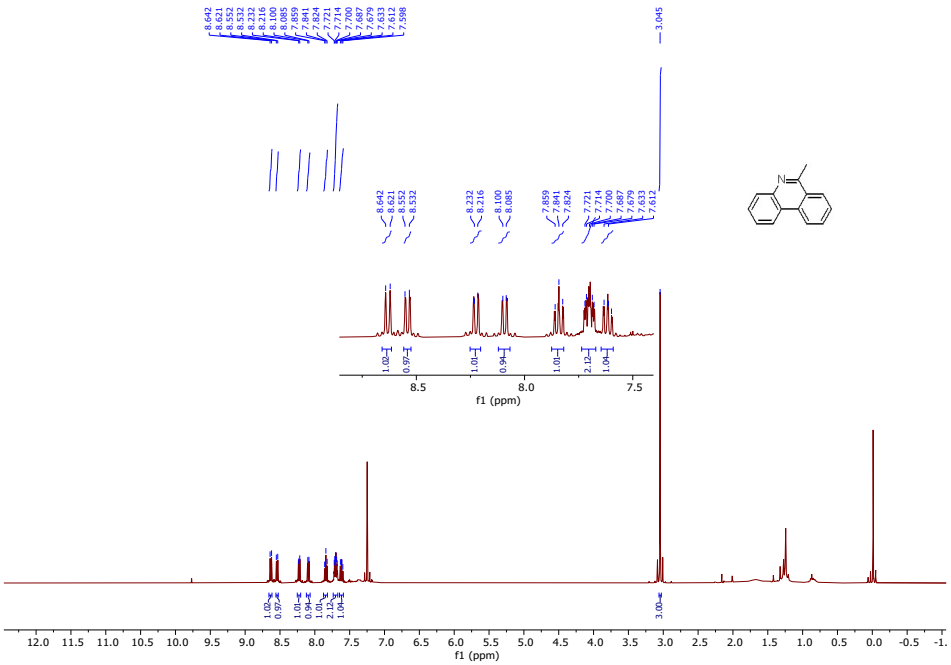
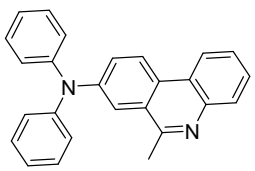


Fig. S 16 ^{1}H NMR spectrum of compound **6** (400 MHz, $CDCl_3$)



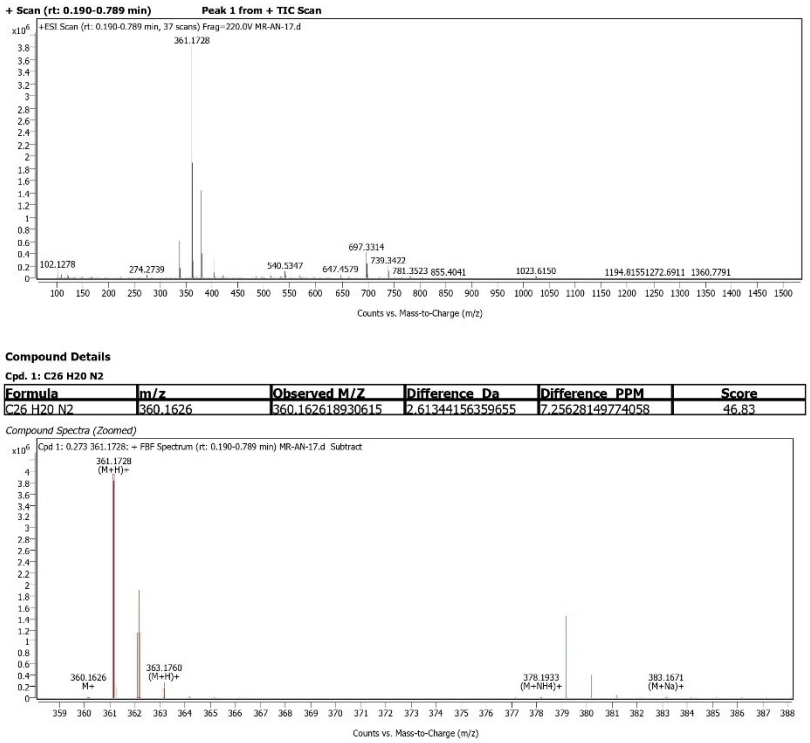


Fig. S 17 HRMS of compound **7**

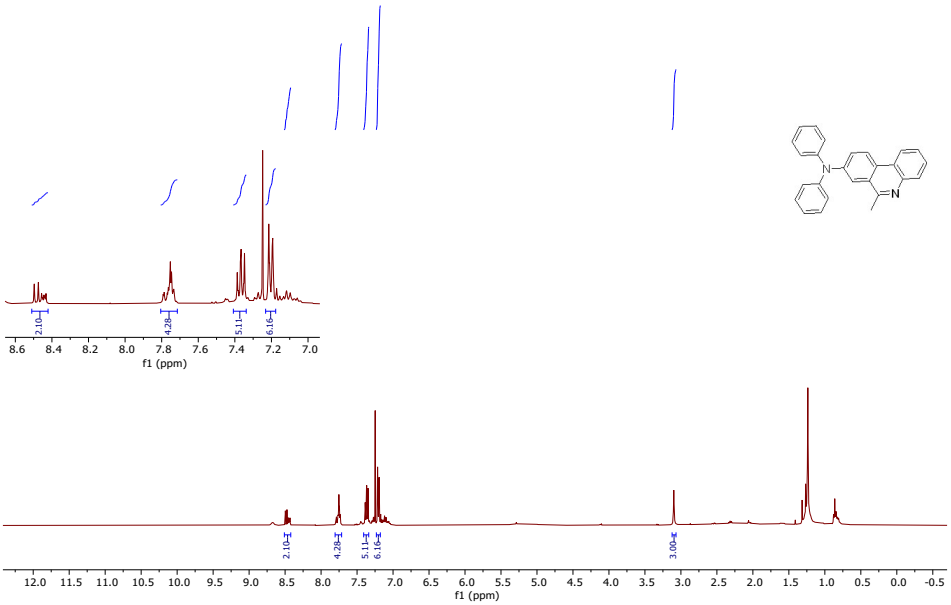


Fig. S 18 ^{1}H NMR spectrum of compound **7** (400 MHz, $CDCl_3$)

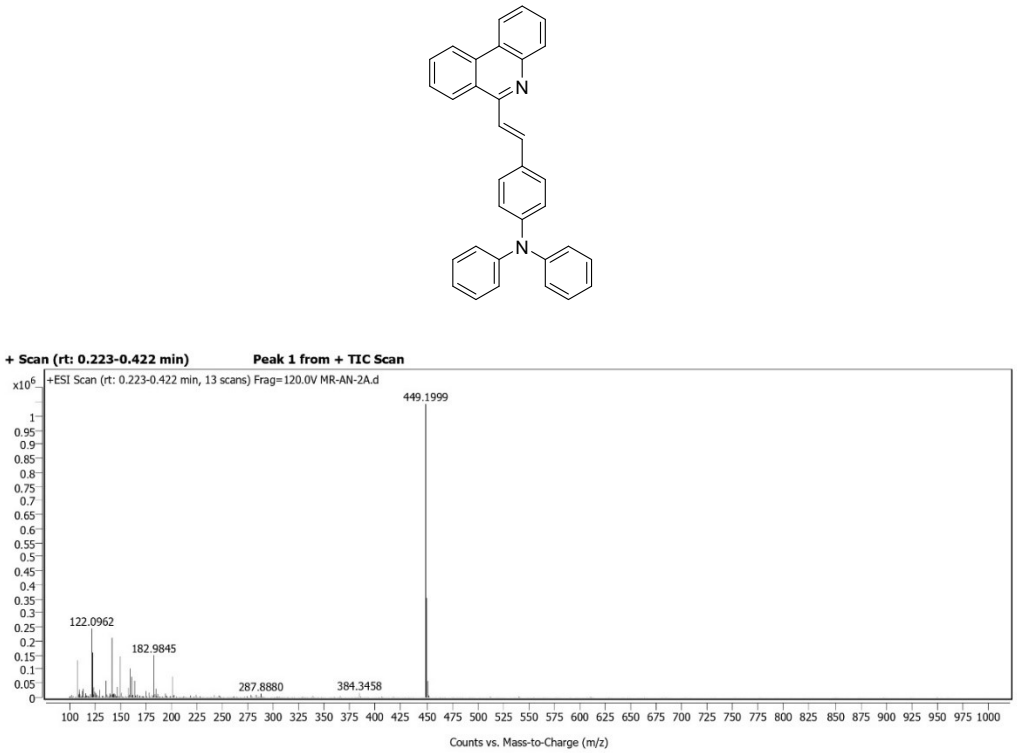


Fig. S 19 HRMS of compound **PC_1**

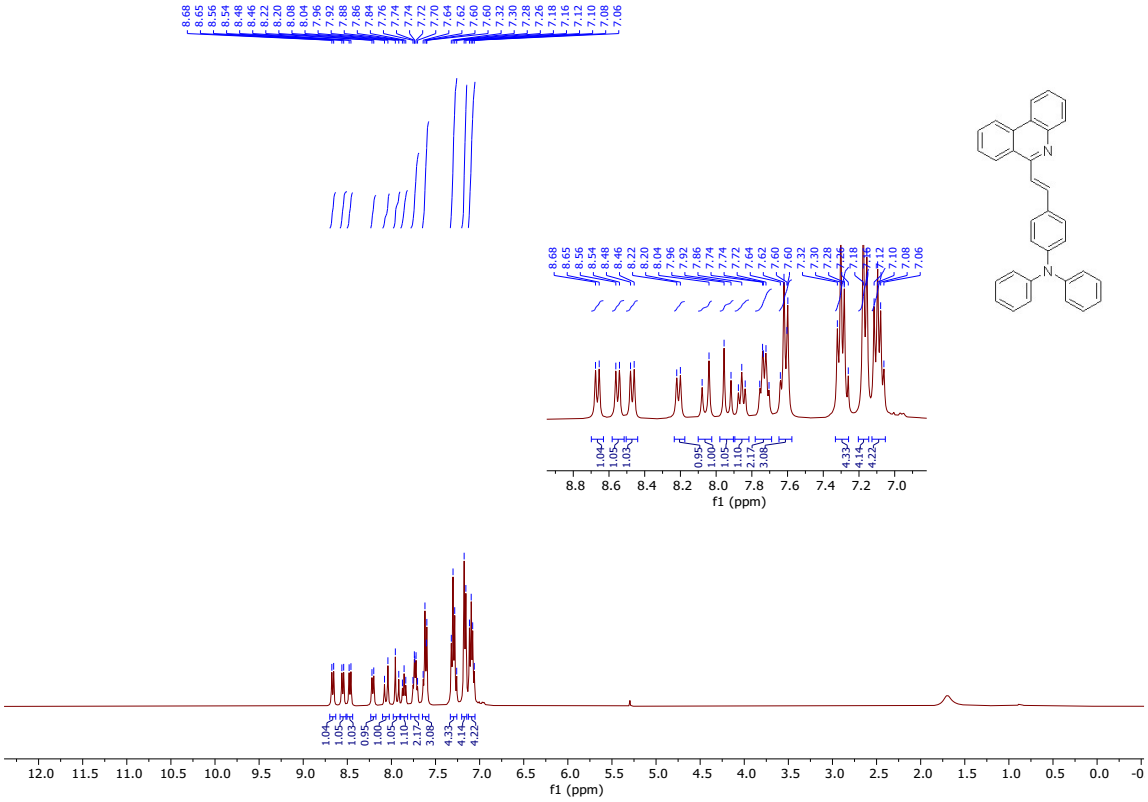


Fig. S 20 ^{1}H NMR spectrum of compound **PC_1** (400 MHz, $CDCl_3$)

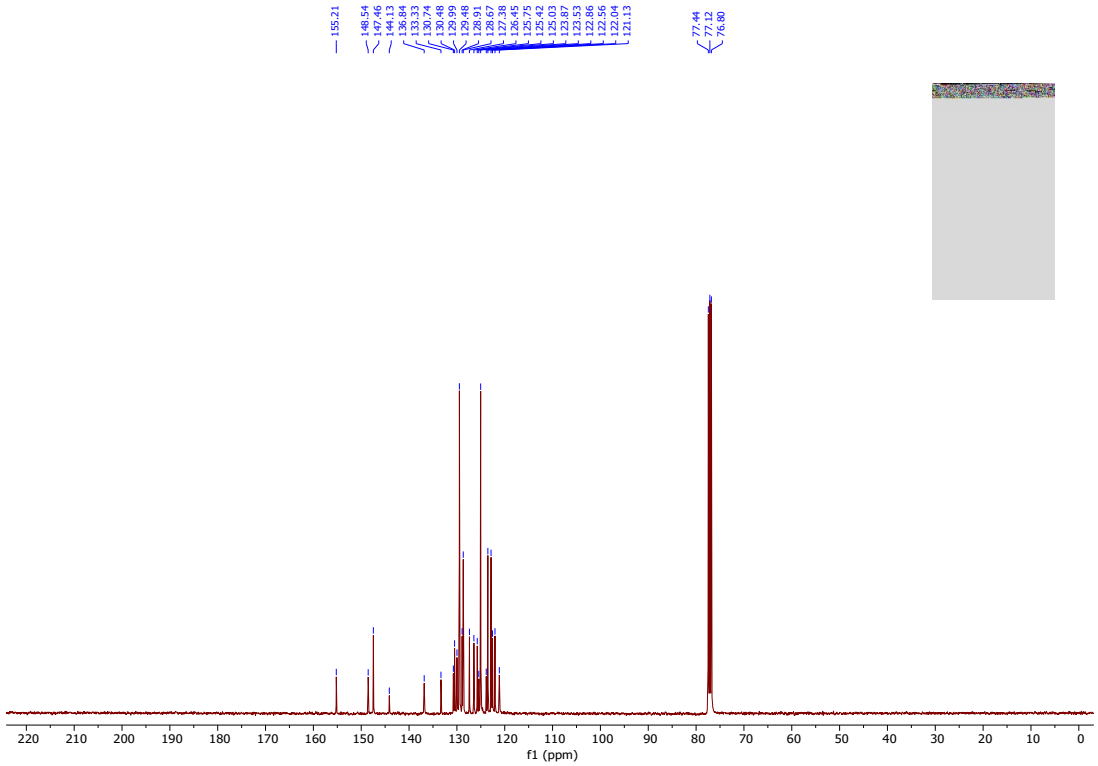
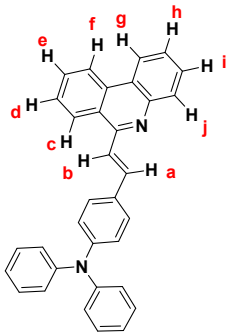


Fig. S 21 {1H}^{13}C NMR spectrum of compound **PC$_1$** (101 MHz, $CDCl_3$)



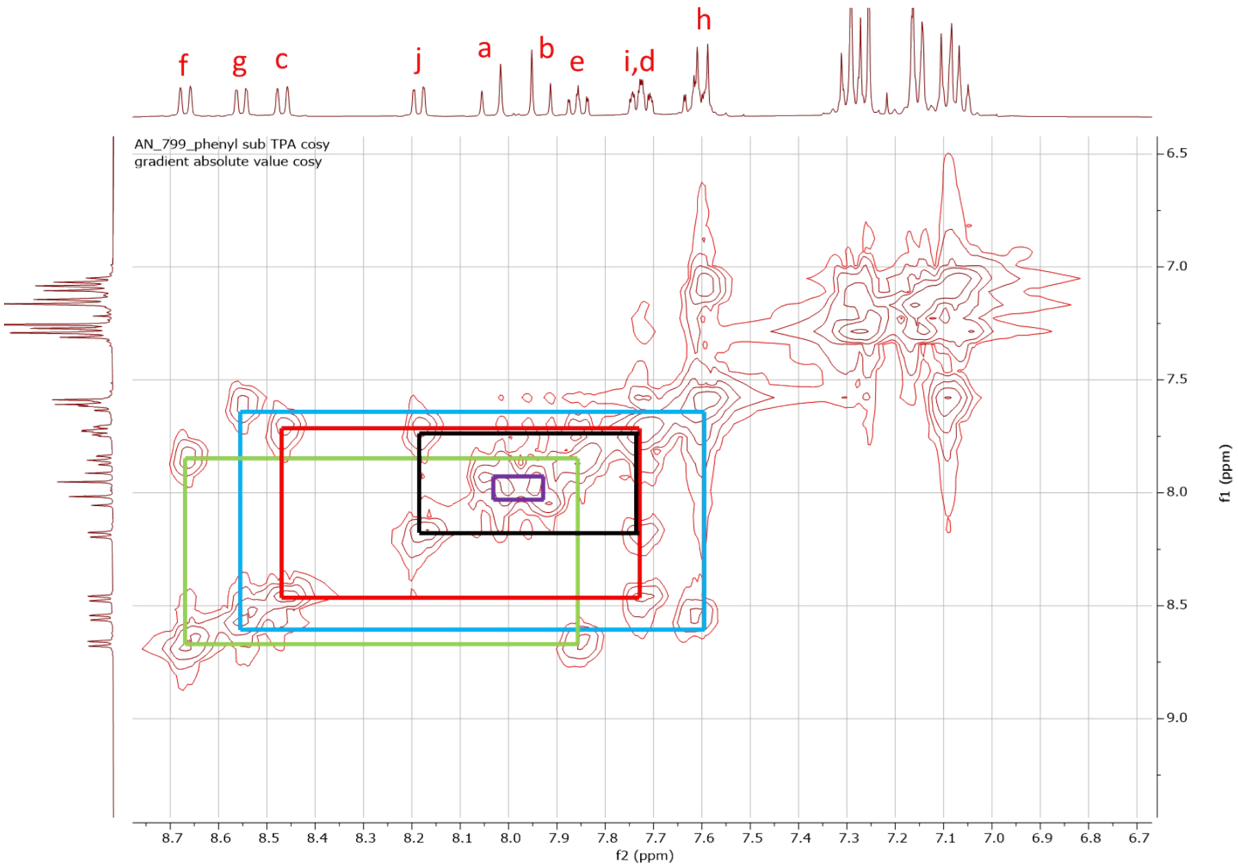


Fig. S 22 ^{1}H-^{1}H, COSY NMR spectrum of compound **PC$_1$** before irradiation of light (400 MHz, $CDCl_3$)

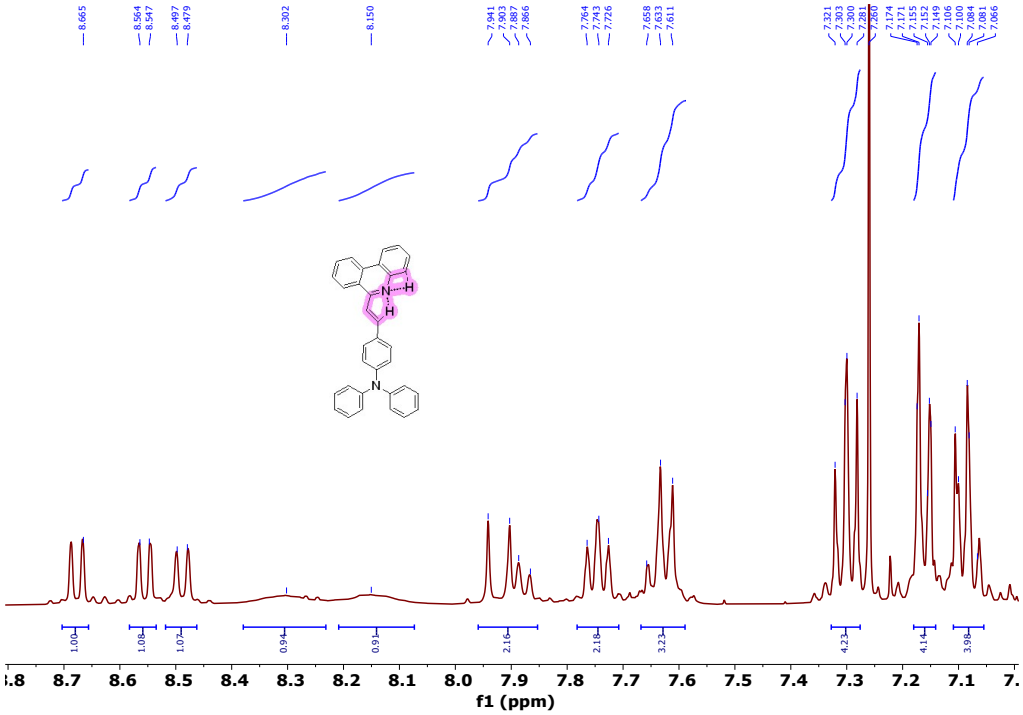
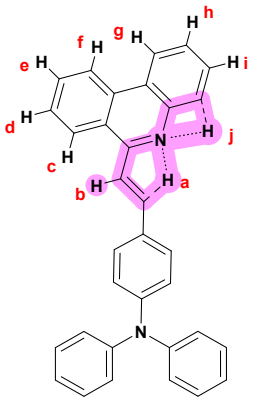


Fig. S 23 ^{1}H NMR spectrum of compound $\mathbf{PC_1}^*$ after irradiation of light (400 MHz, $CDCl_3$)



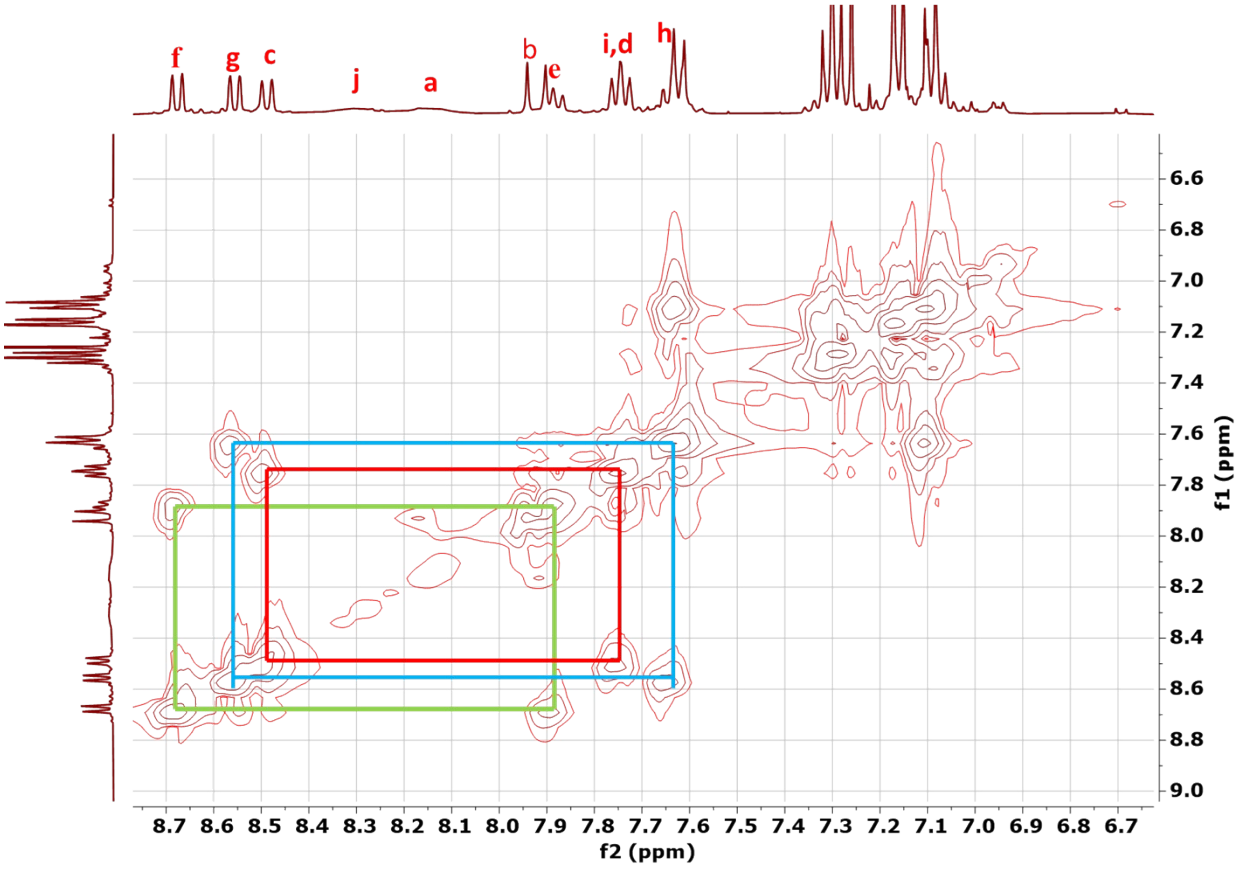


Fig. S 24 ^{1}H-^{1}H, COSY NMR spectrum of compound **PC$_1$***after irradiation of light (400 MHz, $CDCl_3$)

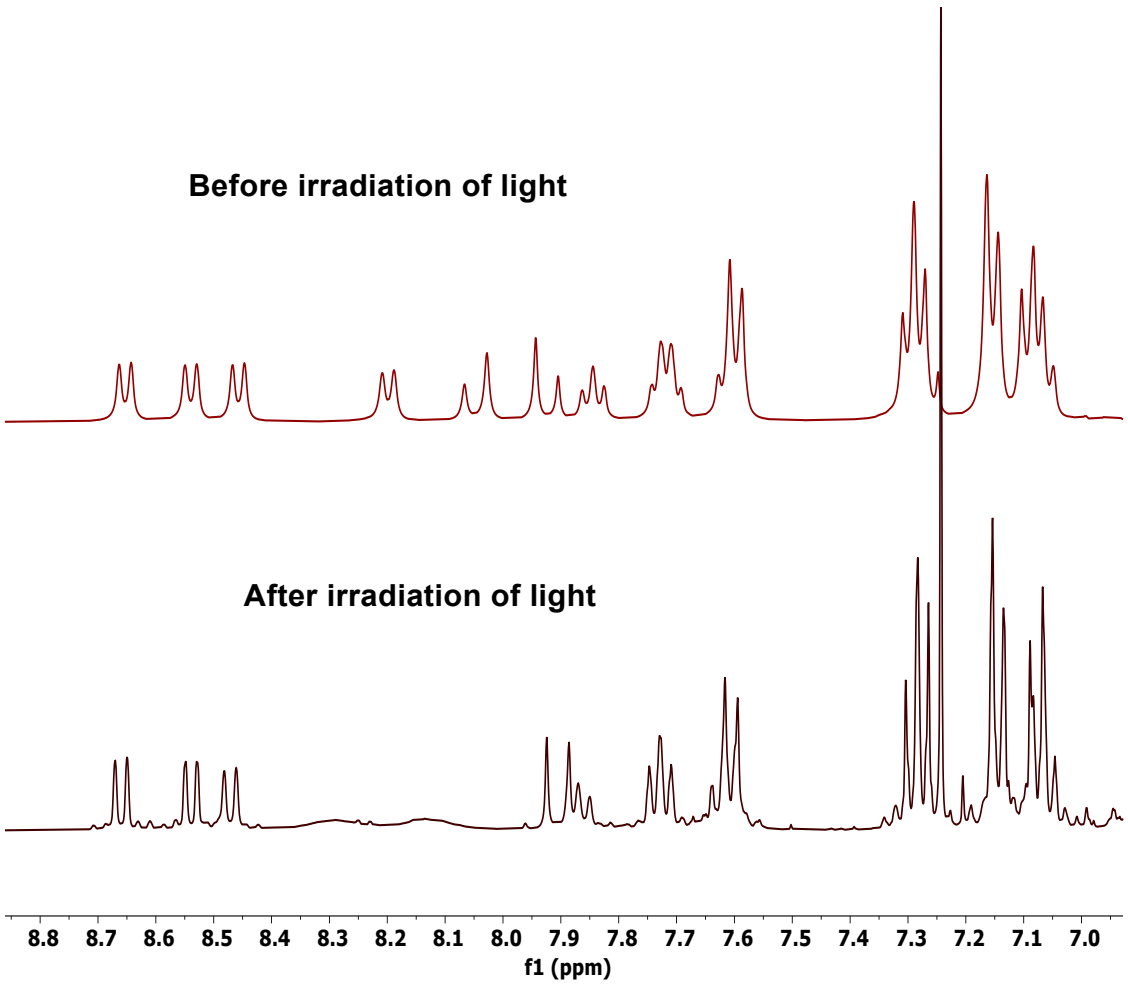


Fig. S 25 ^{1}H NMR spectra of compound before **(PC_1)** and after **(PC_1^*)** irradiation of light

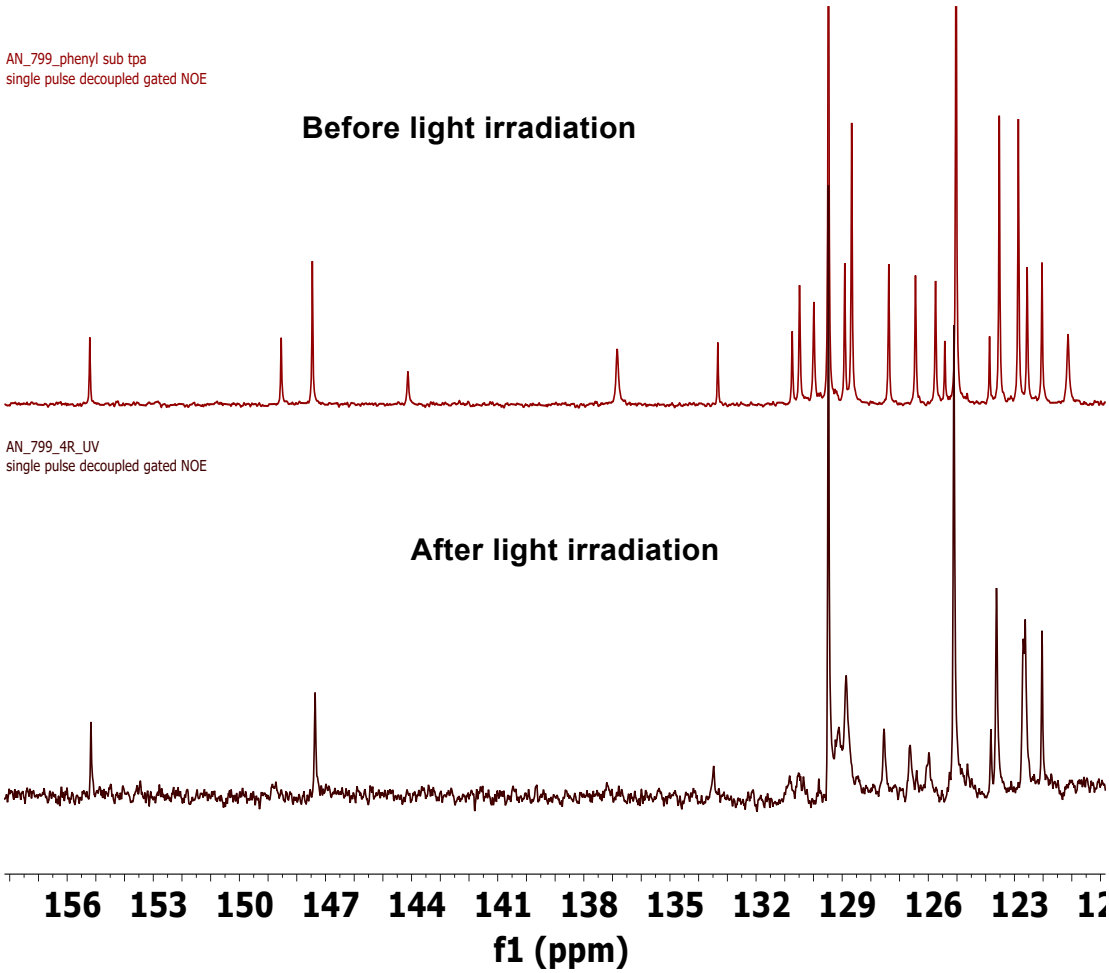


Fig. S 26 {1H}^{13}C NMR spectrum of compound before (**PC_1**) and after (**PC_1^***) light irradiation (101 MHz, $CDCl_3$)

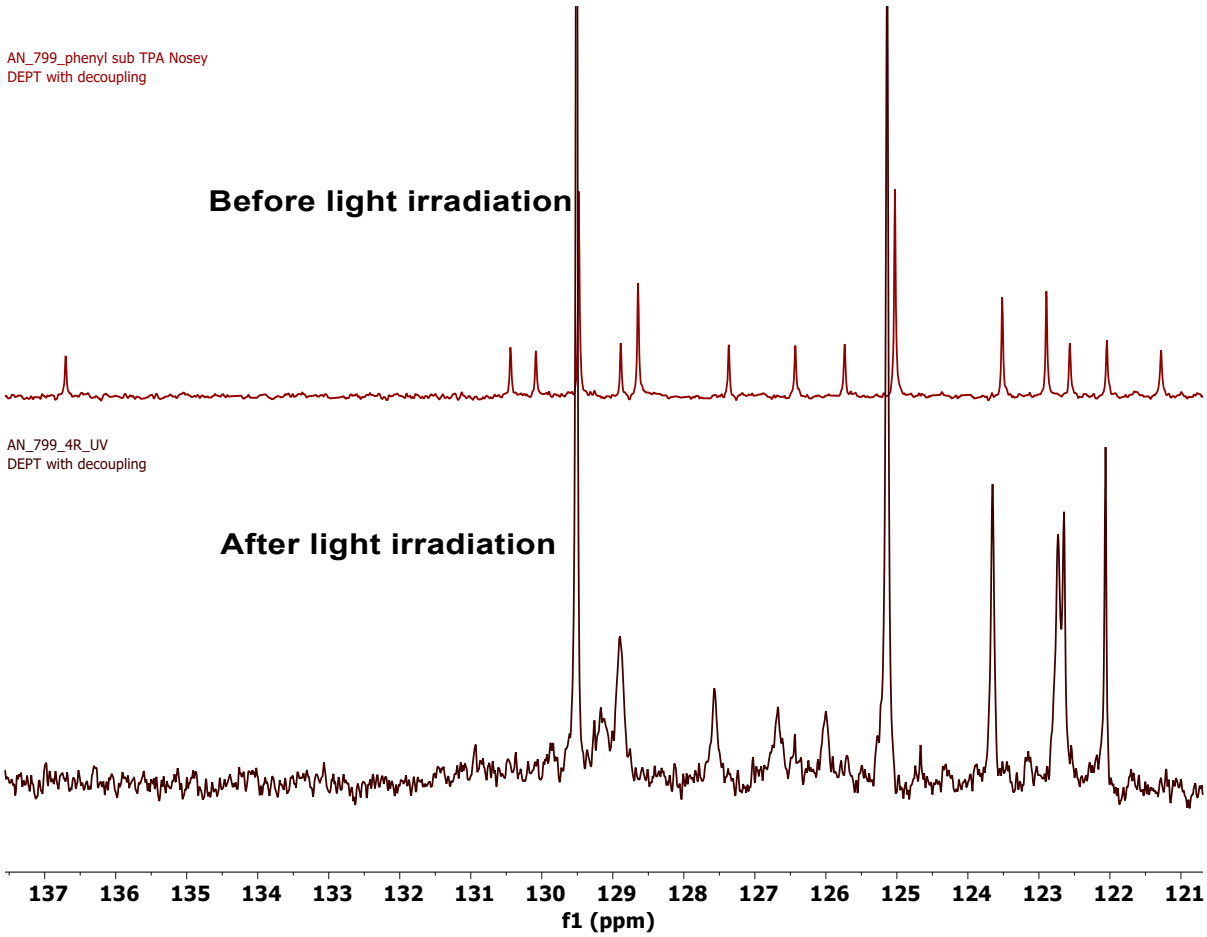


Fig. S 27 ^{13}C DEPT-135 NMR spectrum of compound before (**PC_1**) and after (**PC_1^***) irradiation of light (101 MHz)

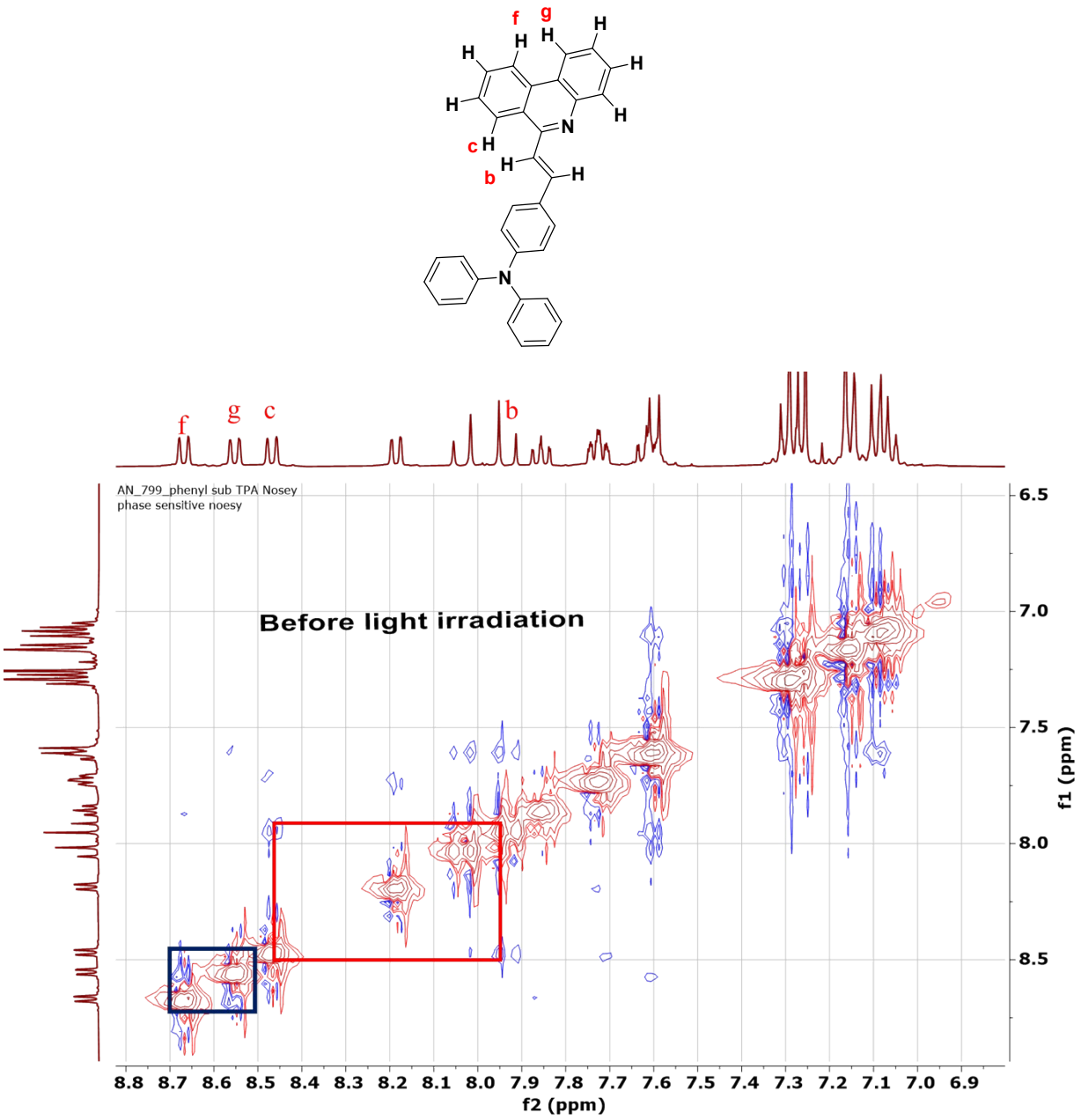


Fig. S 28 ^{1}H-^{1}H, NOSEY NMR spectrum of compound **PC$_1$** (400 MHz, $CDCl_3$)

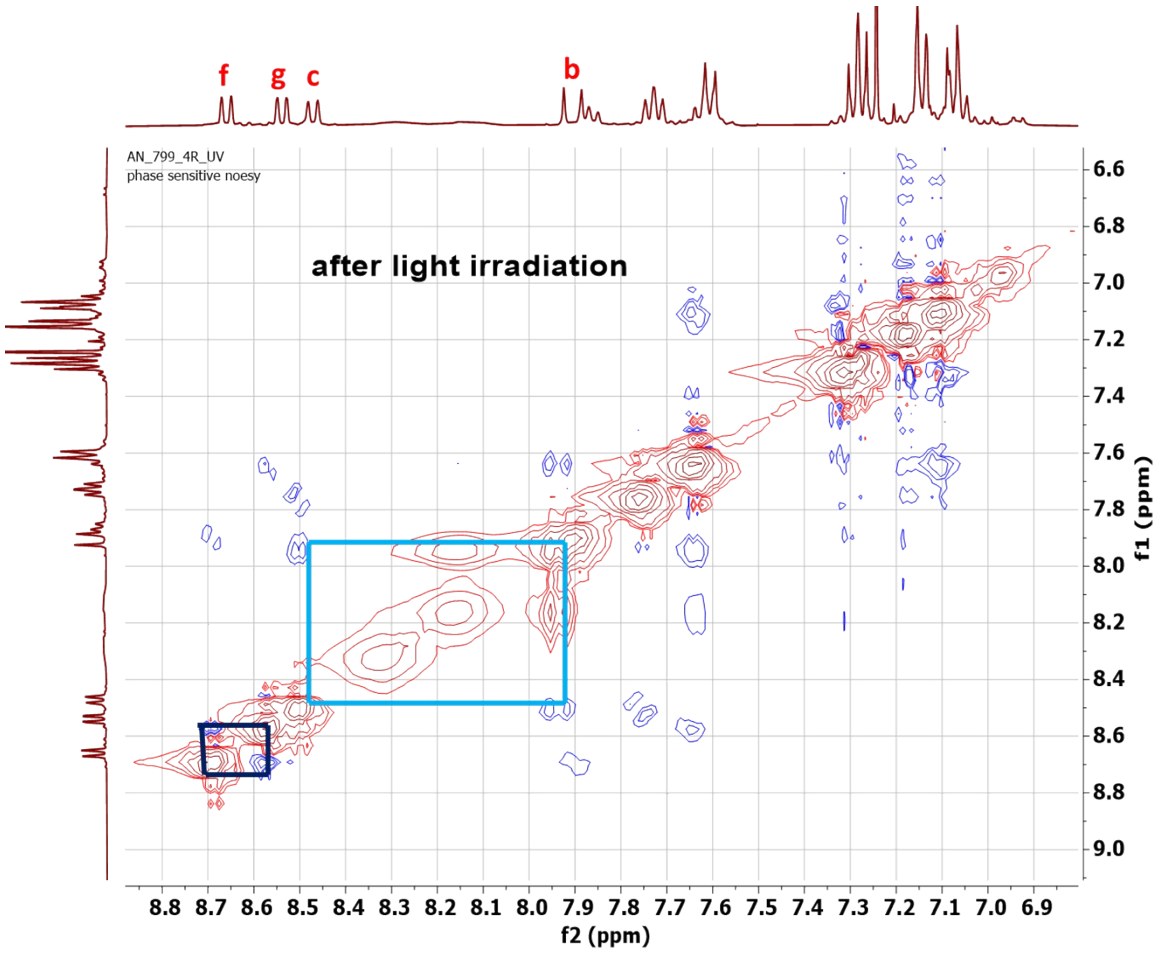
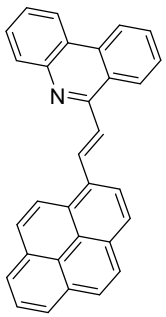


Fig. S 29 ^{1}H-^{1}H, NOSEY NMR spectrum of compound **PC$_1$*** (400 MHz, $CDCl_3$)



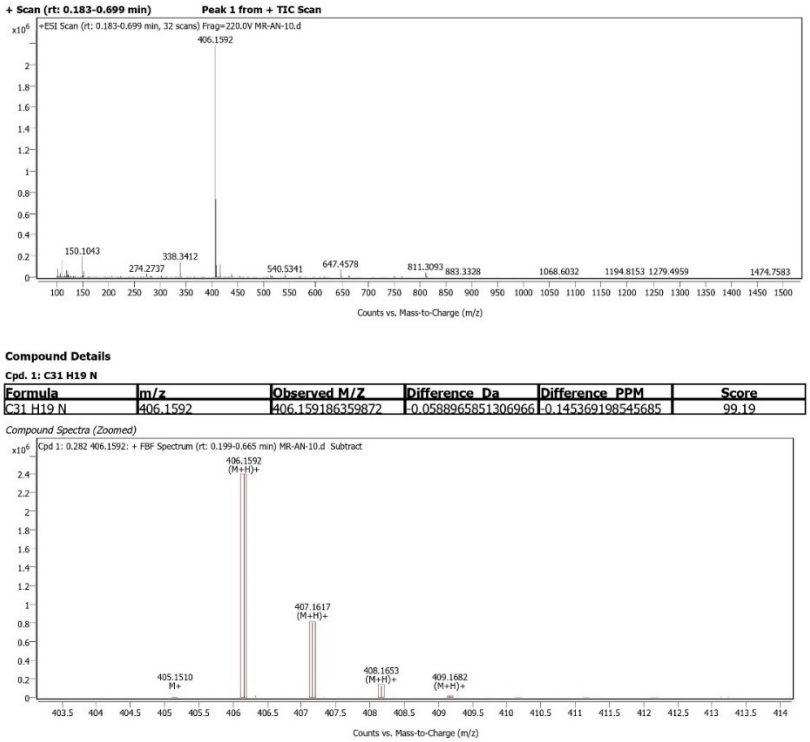


Fig. S 30 HRMS of compound **PC_2**

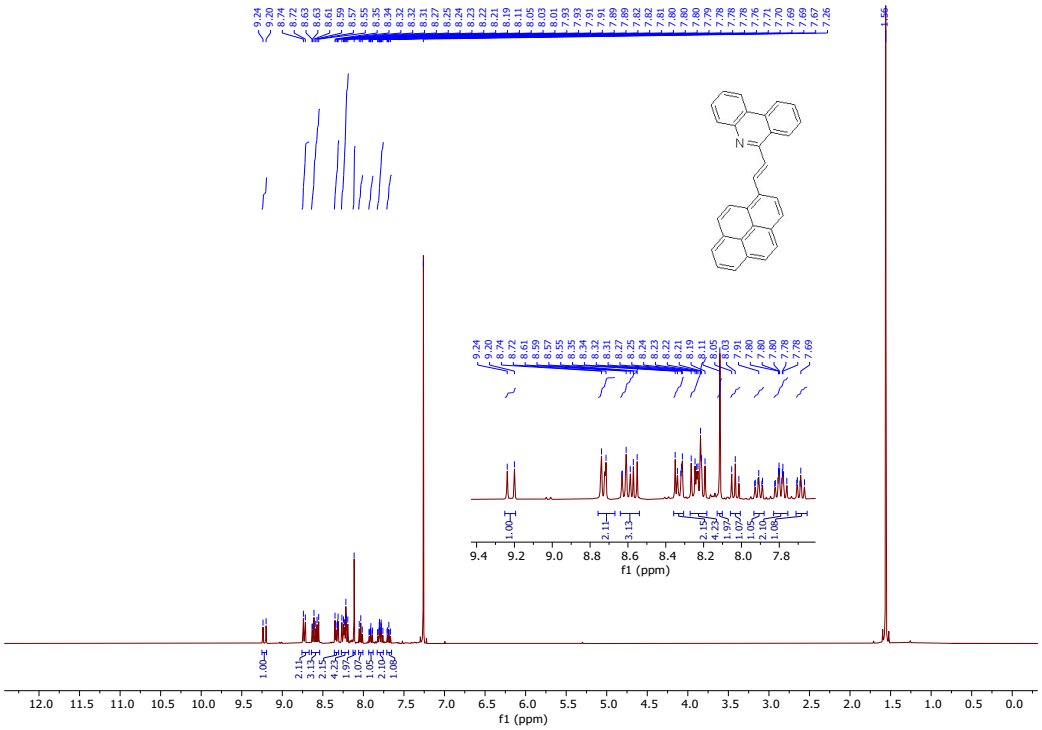


Fig. S 31 ^{1}H NMR spectrum of Compound **PC_2** (400 MHz, $CDCl_3$)

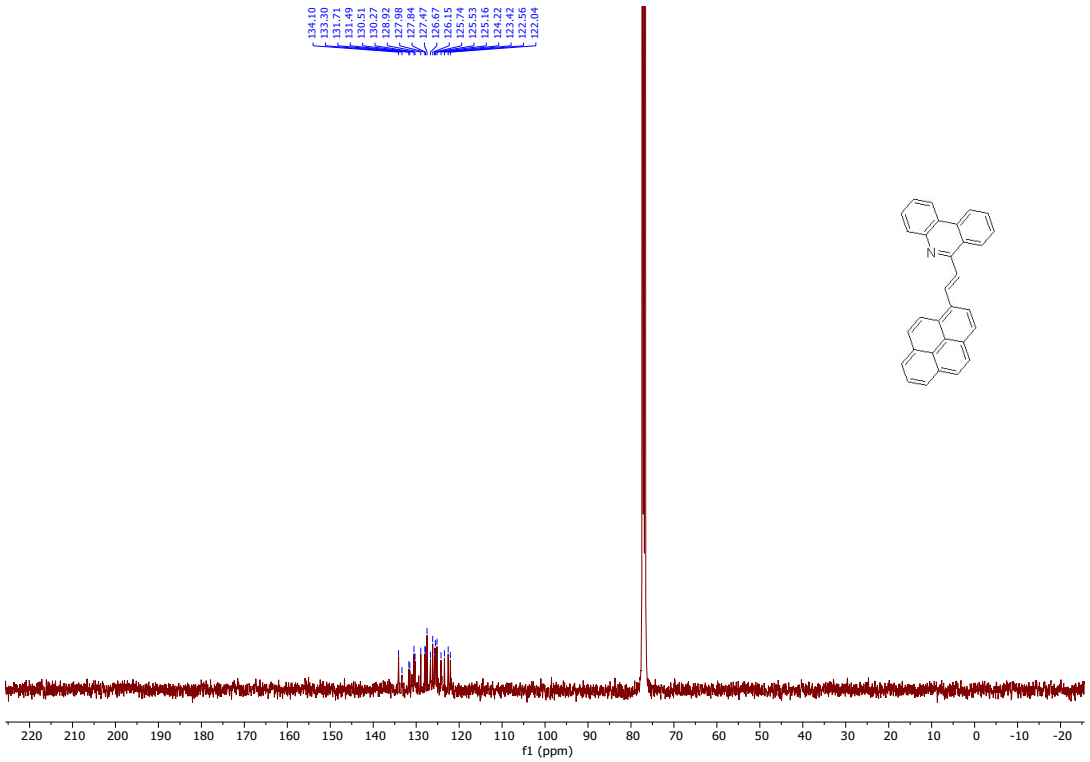


Fig. S 32 {1H}^{13}C NMR spectrum of Compound **PC_2** (101 MHz, $CDCl_3$)

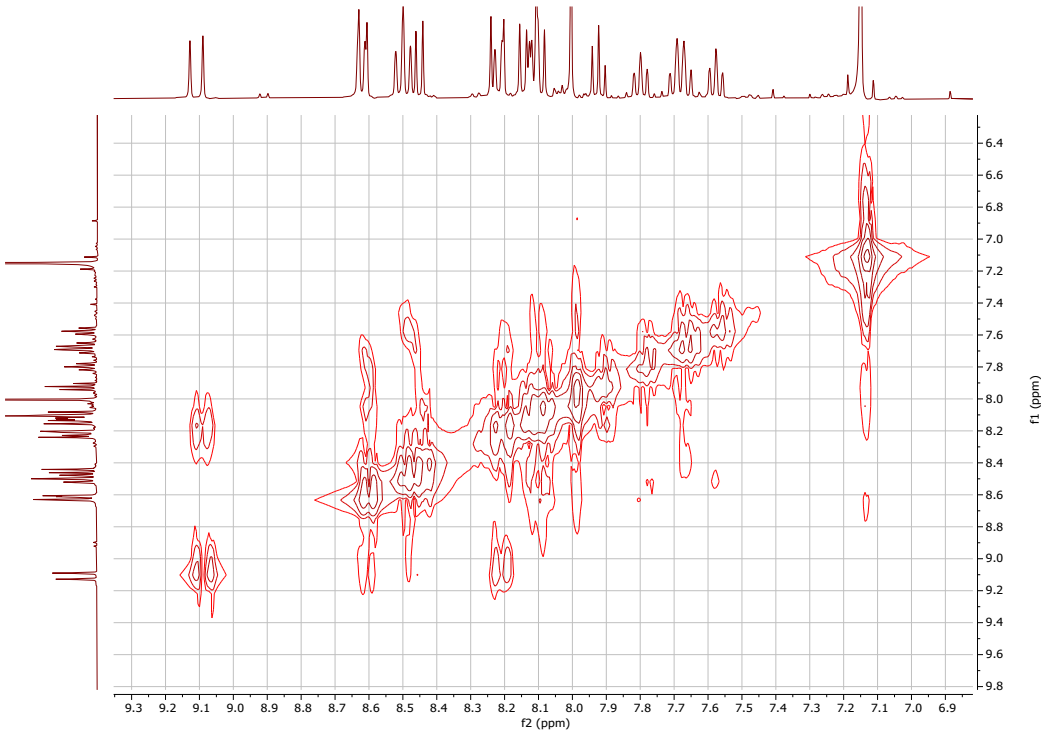
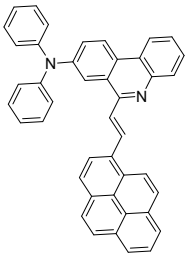
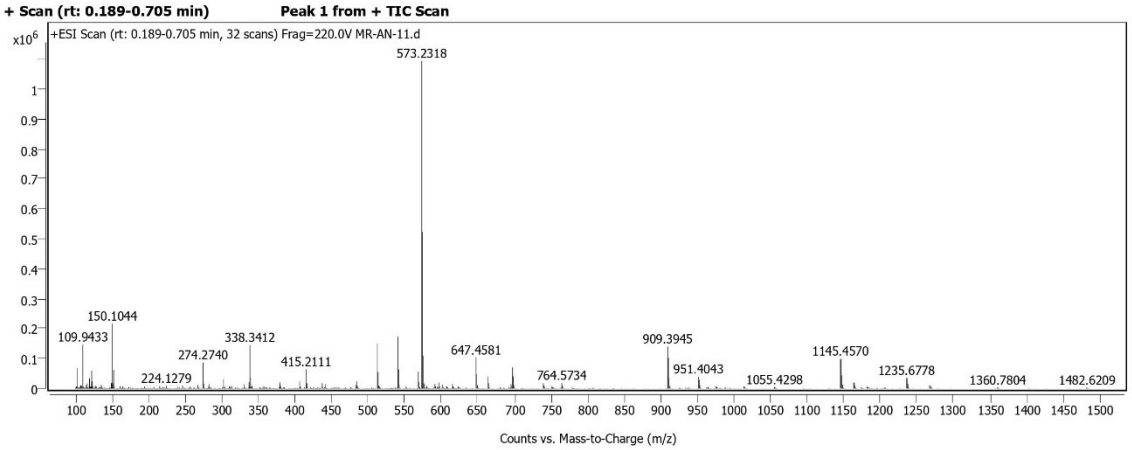
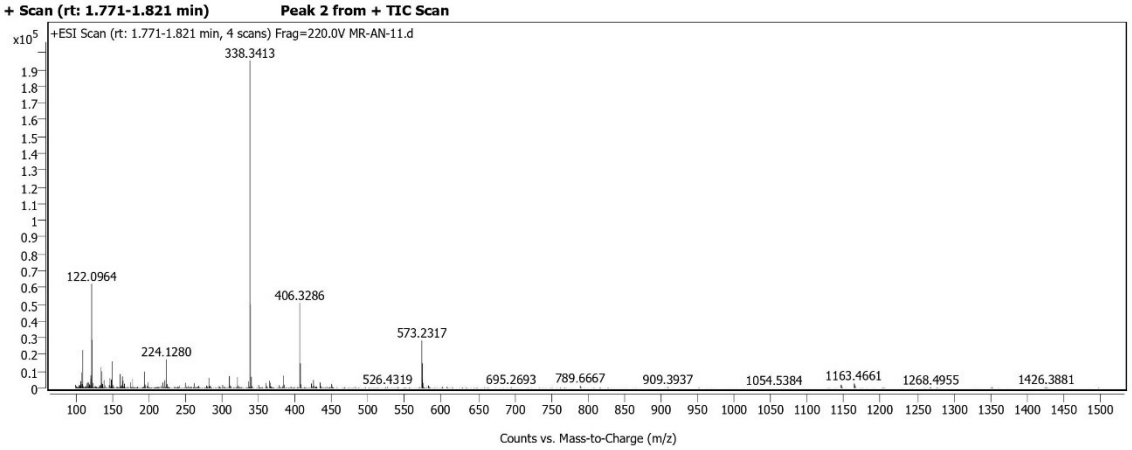


Fig. S 33 ^{1}H-^{1}H, COSY NMR spectrum of compound **PC_2** (400 MHz, $CDCl_3$)







Compound Details

Cpd. 1: C43 H28 N2

Formula	m/z	Observed M/Z	Difference Da	Difference PPM	Score
C43 H28 N2	573.2318	573.23178626202	-0.696034600537132	-1.21636471278645	98.88

Fig. S 34 HRMS of compound **PC_3**

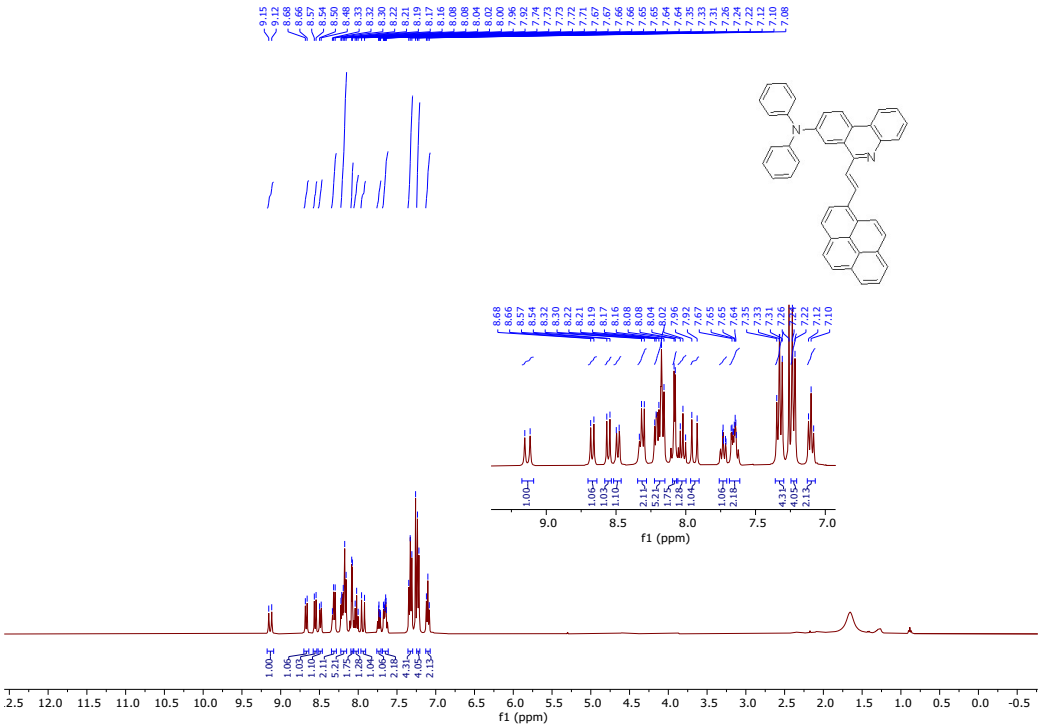


Fig. S 35 ^{1}H NMR spectrum of Compound **PC$_3$** (400 MHz, $CDCl_3$)

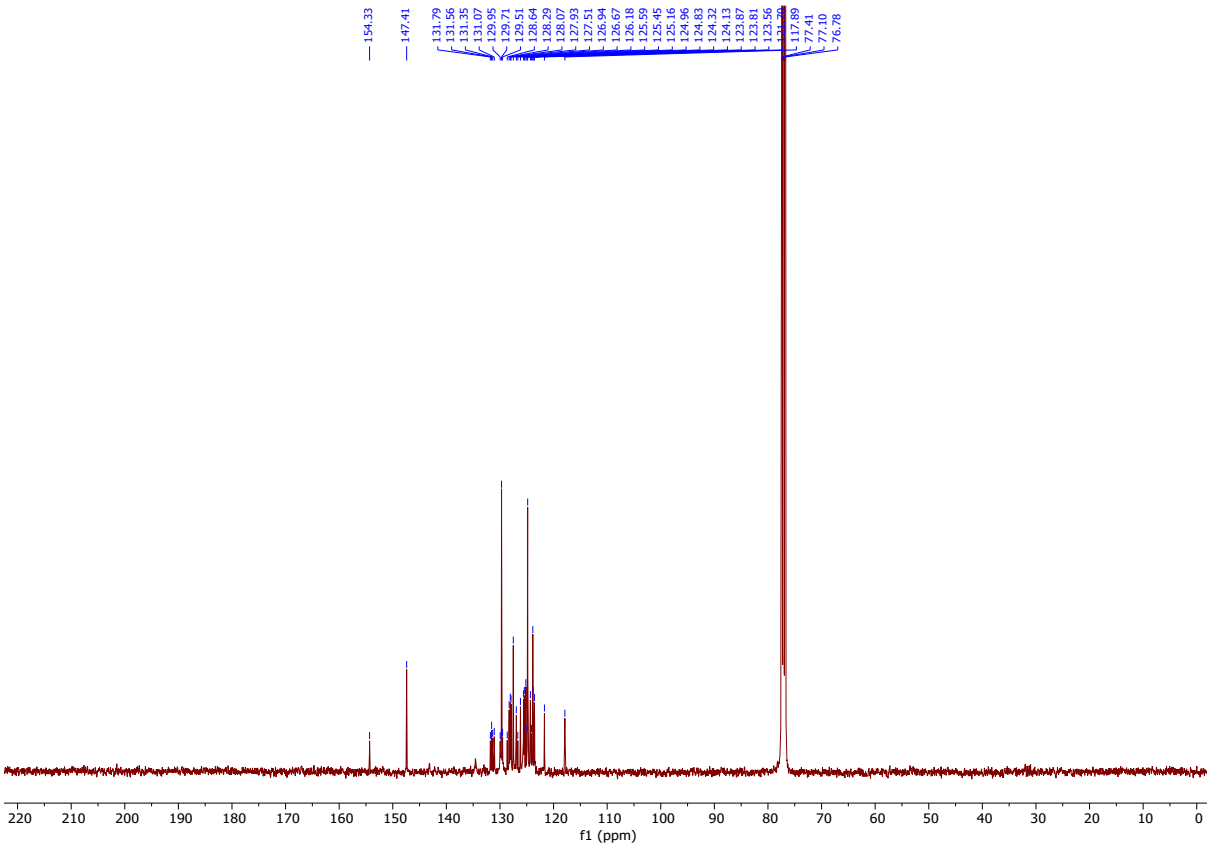


Fig. S 36 {1H}^{13}C NMR spectrum of Compound **PC$_3$** (101 MHz, $CDCl_3$)

Kinetic studies: The kinetic studies of **PC_1-PC_3** were done in chloroform solvent at 300 K. The absorbance versus time has plotted, which displayed first order kinetics with the rate constants ranging from $3.49*10^{-2}$ to $12.5*10^{-2}$ sec^{-1} for the colouring state and $10*10^{-2}$ to $13.99*10^{-2}$ min^{-1}.

Table S 6 The quantum efficiency, rate constants and half-life values for the colouring and bleaching states of **PC_1- PC_3**.

Compound	Quantum efficiency (φ)	k (hv) in sec^{-1}	$t_{1/2}$ (hv) in sec	k (Δ) in min^{-1}	$t_{1/2}$ (Δ) in min
PC_1	16%	$3.49*10^{-2}$	20	$10.09*10^{-2}$	7
PC_2	27%	$6.02*10^{-2}$	11	$76.20*10^{-2}$	1
PC_3	21%	$12.50*10^{-2}$	6	$13.99*10^{-2}$	5

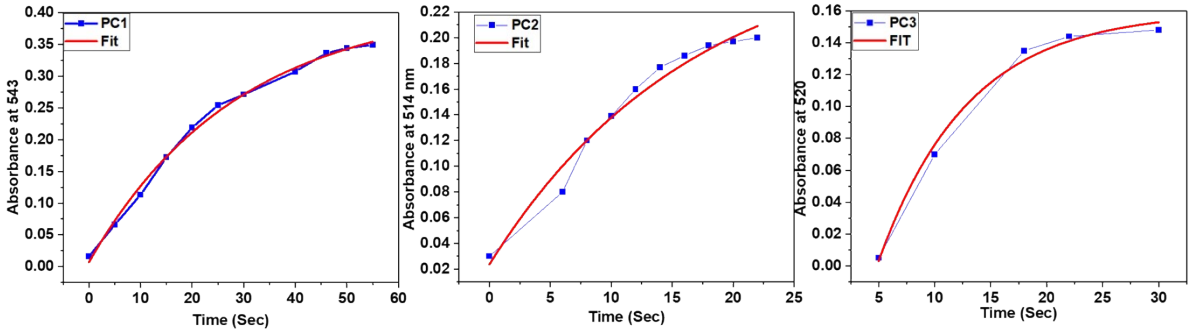


Fig. S 37 Photochromic changes from **PC_1-PC_3** to **PC_1-PC_3***, the increase in the absorbance at 300K versus time in seconds.

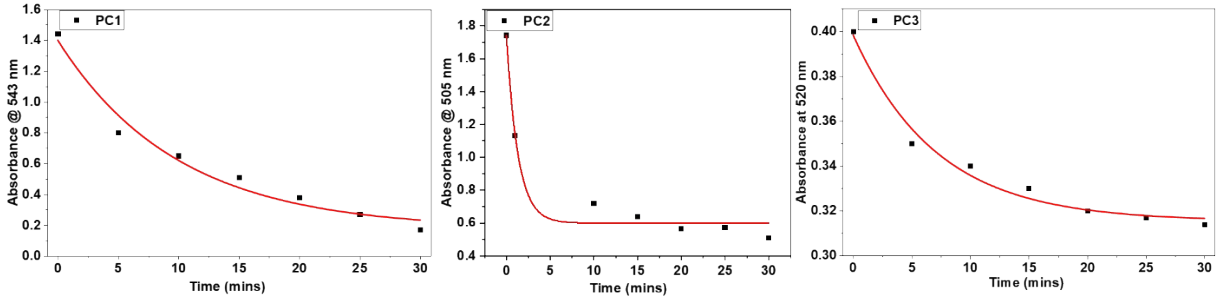
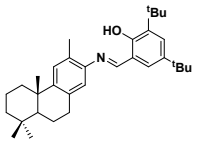
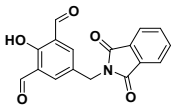
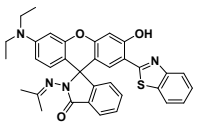
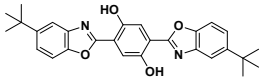
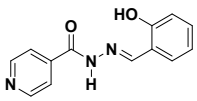
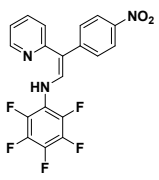
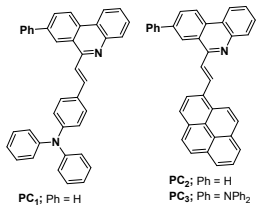


Fig. S 38 Thermal changes from **PC_1-PC_3*** to **PC_1-PC_3**, the decrease in the absorbance at 300K versus time in minutes.

Table S 7 Comparison of the stability, fatigue and resistance of the reported ESIPT based photochromic systems with our systems.

Compound	Spectral shifts	Light source	Irradiation time	Recover time	Stability/No. of cycles	Photofluorochromism	Reference
	New peak at 469 nm	UV light	120 sec	5400 sec	5 cycles	No	**Ref 1** *Nat. Commun.,* **2021,** *12(1),* 1773(1-9).
	New peak at 428 nm	UV light	1200 sec	600 sec	10 cycles	Yes(change)	**Ref 2** *Angew. Chem. Int. Ed.* **2023**, *62,* e202301765(1-10).
	New peak at 595 nm	365 nm (UV light)	5 min	5 min	-	Yes (quenching)	**Ref 3** *Mater. Chem. Front.,* **2019**, *3*, 620-625.
	New peak at 590 nm	365 nm (UV light)	5 min	5 min	8 cycles	Yes (quenching)	**Ref 4** *J. Am. Chem. Soc*., **2006**, *128*, 14542-14547.
	New peak at 500 nm	UV light	-	-	5 cycles	Yes (quenching)	**Ref 5** *Dyes Pigm*., **2022**, *202* 110295(1-6).
	New peak around 500-600 nm	405 nm	-	-	6-12 cycles	No	**Ref 6** *J. Am. Chem. Soc.* **2025***, 147,* 2421−2431.

	Bathoc hromic shift of 324 to 546 nm	254 nm	60 sec	30 mins	5 cycles	Yes (Fluore scence change, fluoresc ence turn off and turn off)	**Our work**

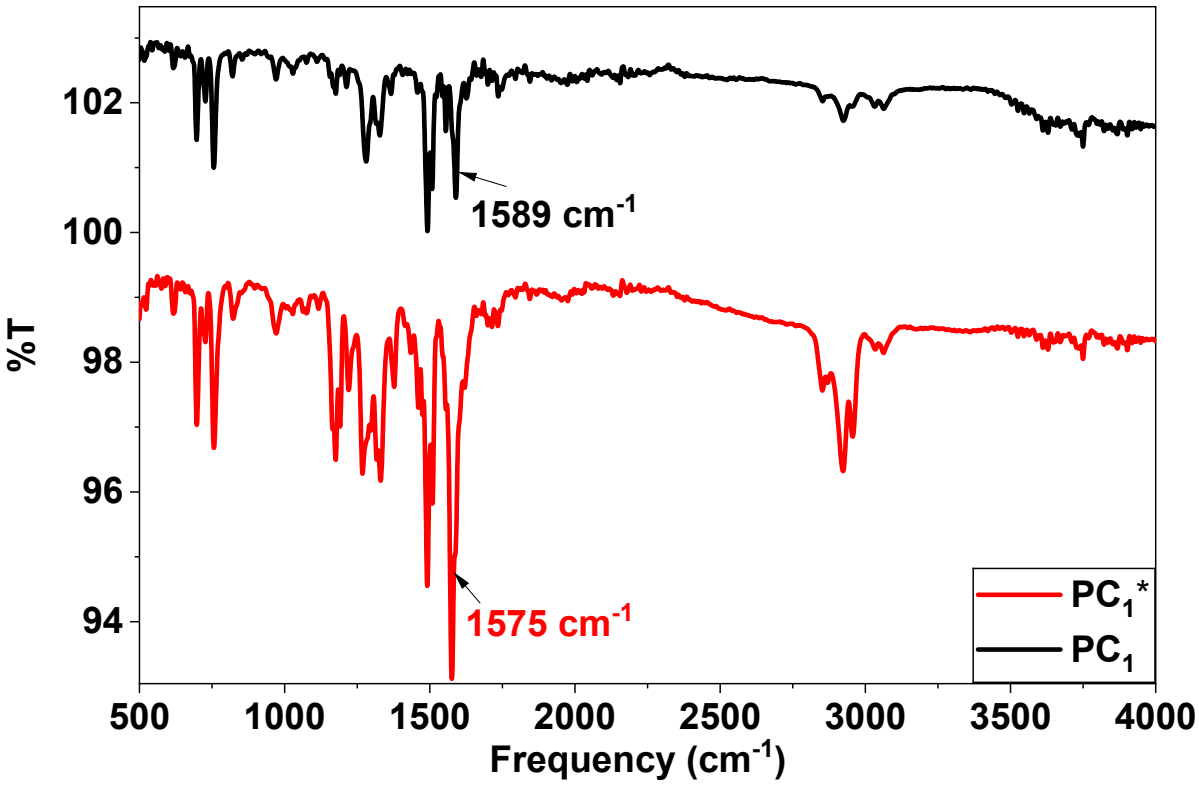


Fig. S 39 FT-IR spectra of **PC$_1$** and **PC$_1$***.

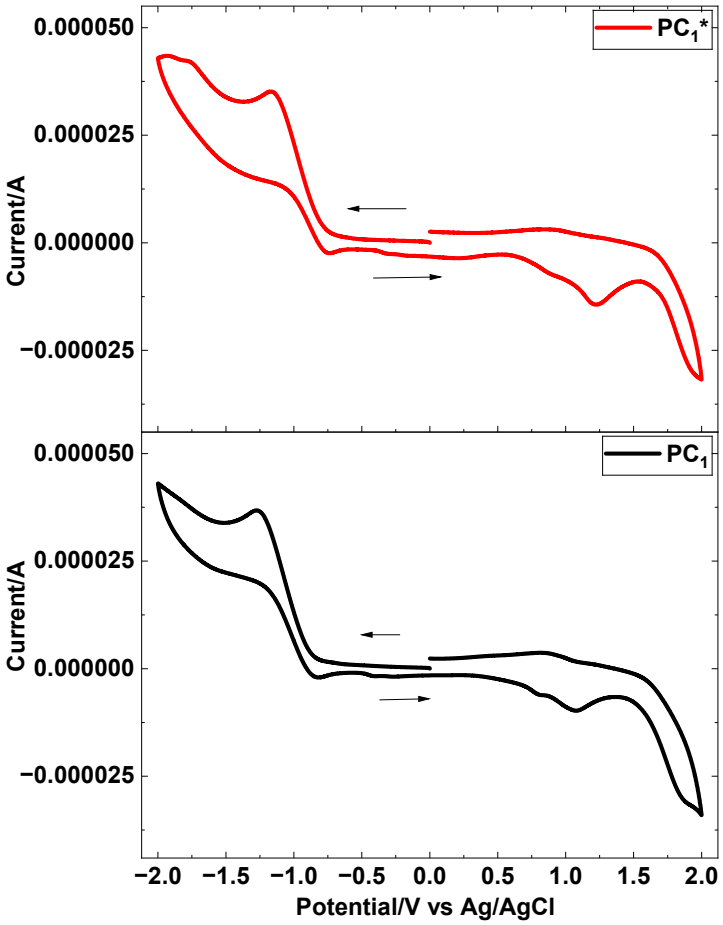


Fig. S 40 Cyclic voltammetry of **PC_1** and **PC_1*** taken in 10^{-5} M solution in $CHCl_3$ at 50 mV/s scan rate.

References:

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3. X. Liu, A. Li, W. Xu, Z. Ma, and X. Jia, *Mater. Chem. Front.,* 2019, **3**, 620-625.
4. S.J. Lim, J. Seo, and S.Y. Park, *J. Am. Chem. Soc*., 2006, **128**, 14542-14547.
5. Y. Li, H. Li, W. Jin, X. Xu, H. Liu, Y. Ding, G. Wang, T. Zhang, Q. Peng, J. He, and Q. Hu, *Dyes Pigm*., 2022, **202**, 110295(1-6).

6. B. Mravec, S. Budzak, M. Medved', L.F. Pasteka, P. Lazar, E. Prochazkova, A. Ruzicka, J. Kozisek, K. Vegso, M. Bodik, and P. Siffalovic, *J. Am. Chem. Soc.* 2025*,* **147***,* 2421−2431.