1 General methods

Synthetic route of F-PzPh, CF_3-PzPh and OCH_3-PzPh refers to previous work[1]. H-PzPh was purchased from Adamas-beta company and used without further purification. 9H-Xanthen-9-one was purchased from Aladdin Company and purified by column chromatography (petroleum ether: dichloromethane = 1:1) to obtain the white powder. Other reagents used for the synthesis or measurements were commercially available without further purification. Water used in tests was ultrapure. 1,4-dioxane was dried with 4 Å molecular sieves and further distilled for the related experiments. ^{1}H NMR spectra were measured on a Bruker AV-400 spectrometer. The UV-Vis absorption spectra of solution were obtained on a Cary 60 (Agilent Technologies) spectrophotometer. The UV-Vis absorption spectra of solid powder were obtained by the Shimadzu-2600 spectrophotometer. Fluorescence, phosphorescence and lifetime of delayed emission spectra were recorded on an Agilent Cary Eclipse spectrophotometer. Photoluminescence spectra were record on HORIBA FluoroMax-4 spectrometer. Delayed emission spectra and time-decay curves from 77K to room-temperature were recorded on EDINBURGH FLS-1000. Absolute PL quantum yields were determined with a spectrometer C11347-11 (Hamamatsu, Japan). Powder X-ray diffraction (XRD) was performed on a D/max2550V. Density functional theory calculations were carried out on the G09 program at B3LYP/6-31G*.

2 Synthesis of target compounds

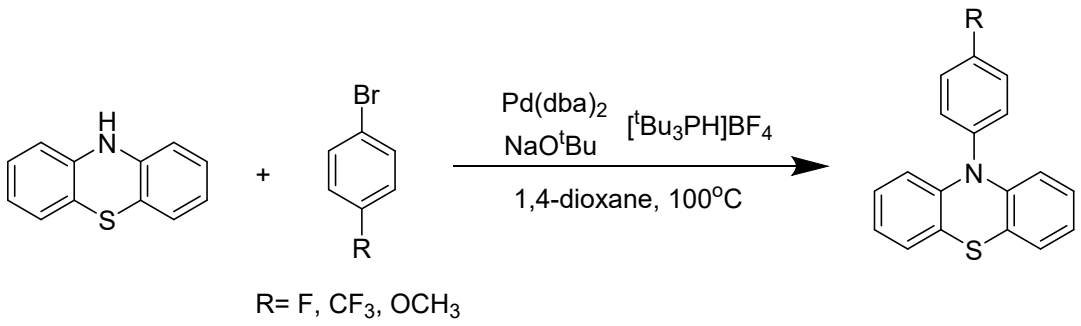


Figure S1 Synthetic route of target compounds.

F-PzPh: 10H-phenothiazine (362 mg, 1.815 mmol), 1-bromo-4-fluorobenzene (289 mg, 1.65 mmol), $Pd(dba)_2$ (48 mg, 6 mol%), tri-tert-butylphosphane tetrafluoroborate (25 mg, 6 mol%) and sodium tert-butoxide (182.5 mg, 1.9 mmol) were dissolved in dry 1,4-dioxane (5 mL). The solution was degassed with nitrogen for 5 min. Then, the reaction mixture was stirred at 100℃ (oil bath temperature) for 7 h. After cooling to room temp deionized water (30 mL), and dichloromethane (30 mL) were successively added. The aqueous phase was extracted with dichloromethane (3 × 5 mL). The combined organic phases were dried with anhydrous magnesium sulfate and the solvents were removed in vacuo. The residue was purified by silica gel column chromatography (petroleum ether: ethyl acetate = 30: 1) to give compound F-PzPh (464 mg, 96%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.36-7.39 (m, 2H), 7.25-7.31 (m, 2H), 7.00-7.02 (d, 2H), 6.80-6.86 (m, 4H), 6.15-6.17 (d, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm): 163.3, 160.9, 144.3, 136.8, 133.0, 132.9, 126.9, 126.8, 122.6, 120.2, 117.9, 117.7, 115.8. HRMS (ESI+), m/z: [M^+], calc. for $C_{18}H_{12}FNS$, 293.0669. Found, 293.0662.

CF_3-PzPh: 10H-phenothiazine (151 mg, 0.758 mmol), 1-bromo-4-(trifluoromethyl)benzene (204 mg, 0.909 mmol), $Pd(dba)_2$ (26 mg, 6 mol%), tri-tert-butylphosphane tetrafluoroborate (13 mg, 6

mol%) and sodium tert-butoxide (145 mg, 1.52 mmol) were dissolved in dry 1,4-dioxane (5 mL). The solution was degassed with nitrogen for 5 min. Then, the reaction mixture was stirred at 100℃ (oil bath temperature) for 5 h. After cooling to room temp deionized water (30 mL), and dichloromethane (30 mL) were successively added. The aqueous phase was extracted with dichloromethane (3 × 5 mL). The combined organic phases were dried with anhydrous magnesium sulfate and the solvents were removed in vacuo. The residue was purified by silica gel column chromatography (petroleum ether) to give compound CF_3-PzPh (250 mg, 96%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.65-7.71 (d, 2H), 7.31-7.36 (d, 2H), 7.20-7.24 (q, 4H), 6.96-7.10 (m, 4H), 6.65-6.70 (d, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.19, 141.67, 126.76, 126.30, 126.26, 126.08, 125.38, 123.50, 123.30, 119.65. HRMS (ESI+), m/z: [M^+], calc. for $C_{19}H_{12}F_3NS$, 343.0637. Found 343.0629.

OCH_3-PzPh: 10H-phenothiazine (177 mg, 0.89 mmol), 1-bromo-4-methoxybenzene (166 mg, 0.89 mmol), $Pd(dba)_2$ (28 mg, 6 mol%), tri-tert-butylphosphane tetrafluoroborate (15 mg, 6 mol%) and sodium tert-butoxide (100 mg, 1.02 mmol) were dissolved in dry 1,4-dioxane (5 mL). The solution was degassed with nitrogen for 5 min. Then, the reaction mixture was stirred at 100℃ (oil bath temperature) for 4 h. After cooling to room temp deionized water (30 mL), and dichloromethane (30 mL) were successively added. The aqueous phase was extracted with dichloromethane (3 × 5 mL). The combined organic phases were dried with anhydrous magnesium sulfate and the solvents were removed in vacuo. The residue was purified by silica gel column chromatography (petroleum ether: ethyl acetate = 80: 1) to give compound OCH_3-PzPh (243 mg, 90%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.29-7.31 (d, 2H), 7.09-7.11 (d, 2H), 6.97-6.99 (d, 2H), 6.77-6.83 (m, 4H), 6.17-6.20 (d, 2H), 3.89 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm): 159.3, 144.7, 133.4, 132.3, 126.9, 126.7, 122.3, 119.7, 115.9, 115.7, 55.6. HRMS (ESI+), m/z: [M^+], calc. for $C_{19}H_{15}NOS$, 305.0869. Found, 305.0862.

3 Characterization of H-PzPh, F-PzPh, CF_3-PzPh, OCH_3-PzPh and 9H-Xanthen-9-one

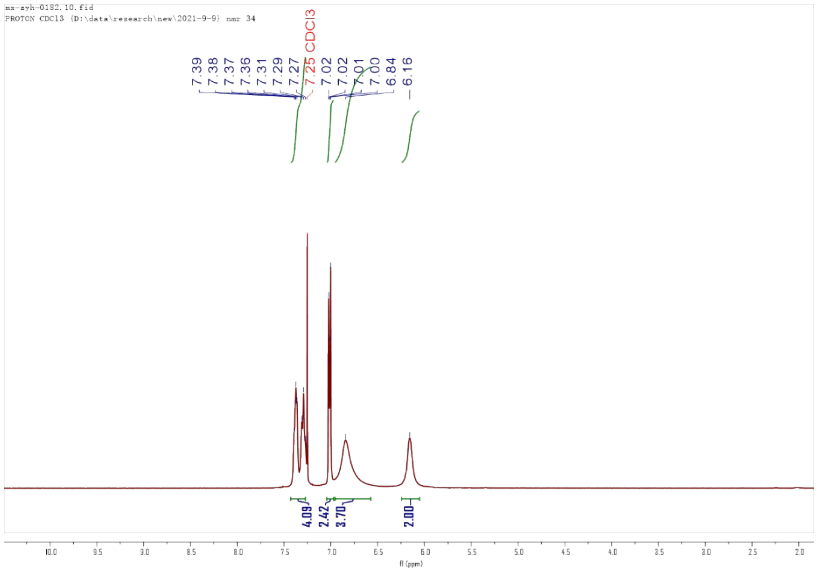


Figure S2 ^{1}H-NMR spectrum (400 MHz) of **F-PzPh** in $CDCl_3$.

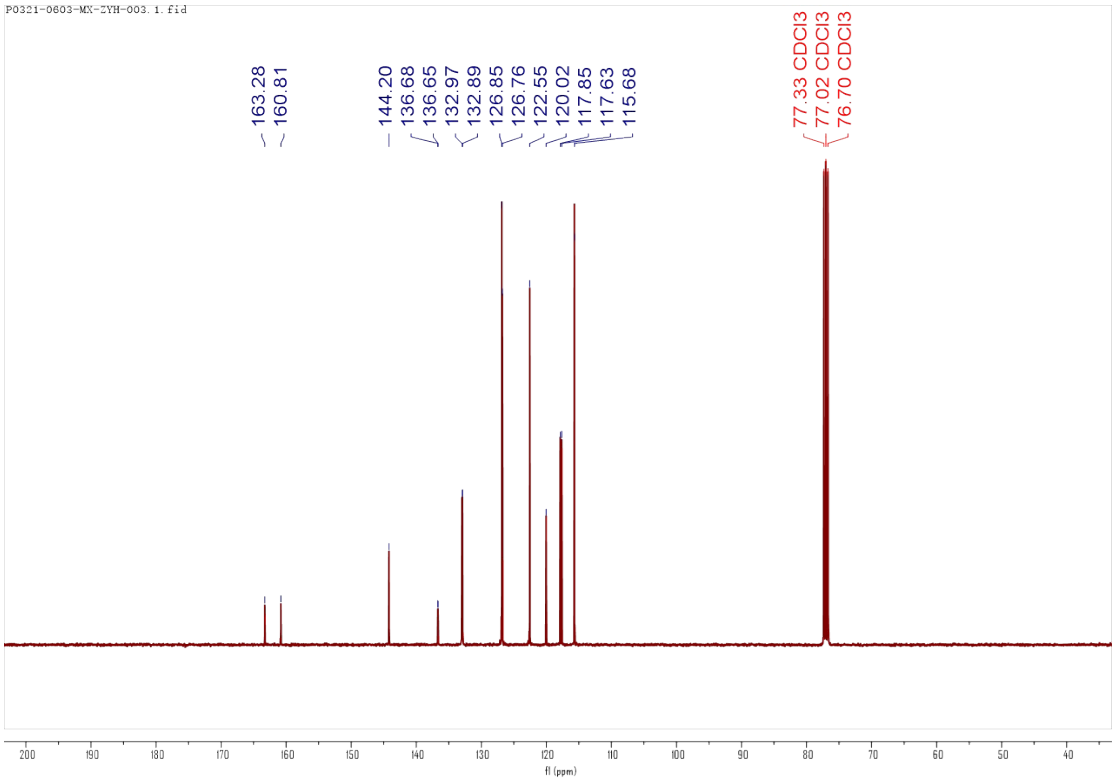


Figure S3 ^{13}C-NMR spectrum of **F-PzPh** in $CDCl_3$.

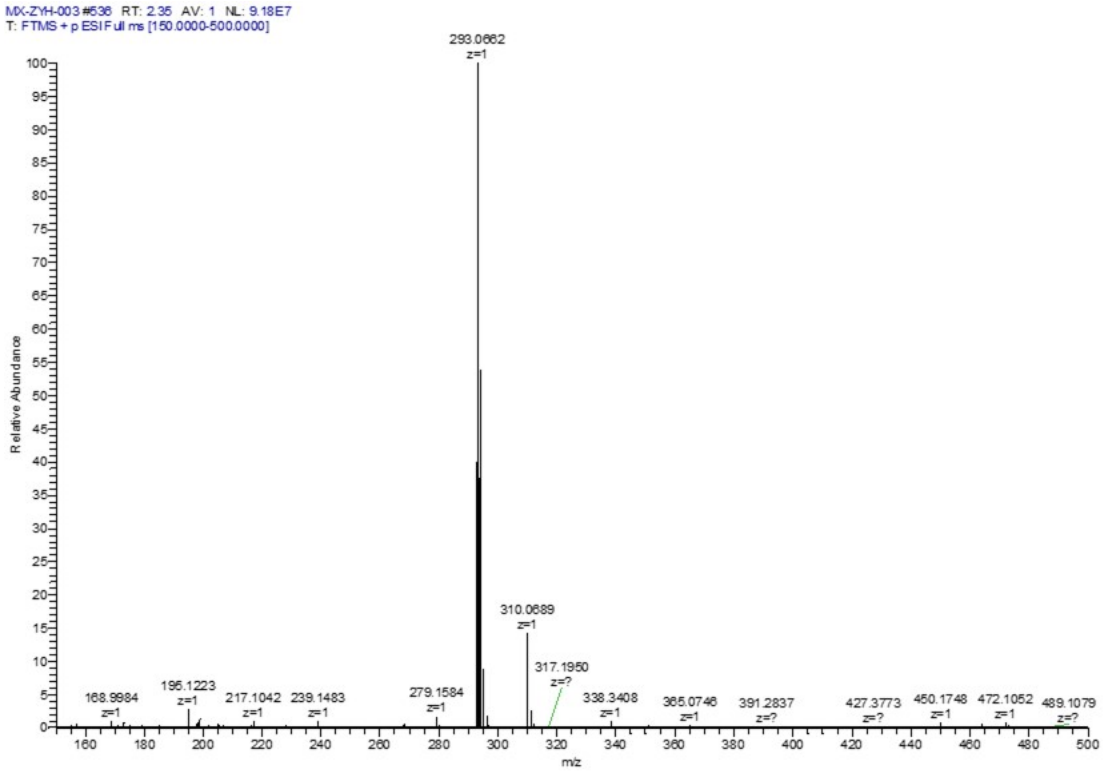


Figure S4 HRMS spectrum of **F-PzPh.**

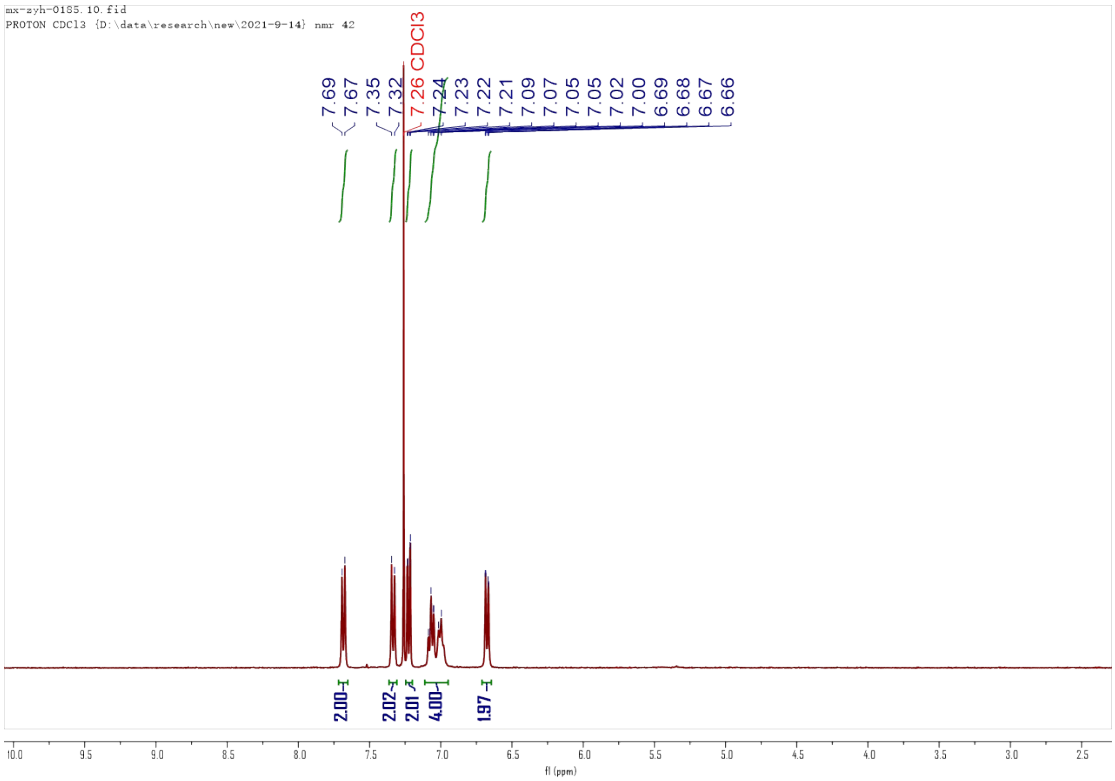


Figure S5 ^{1}H-NMR spectrum (400 MHz) of **CF_3-PzPh** in $CDCl_3$.

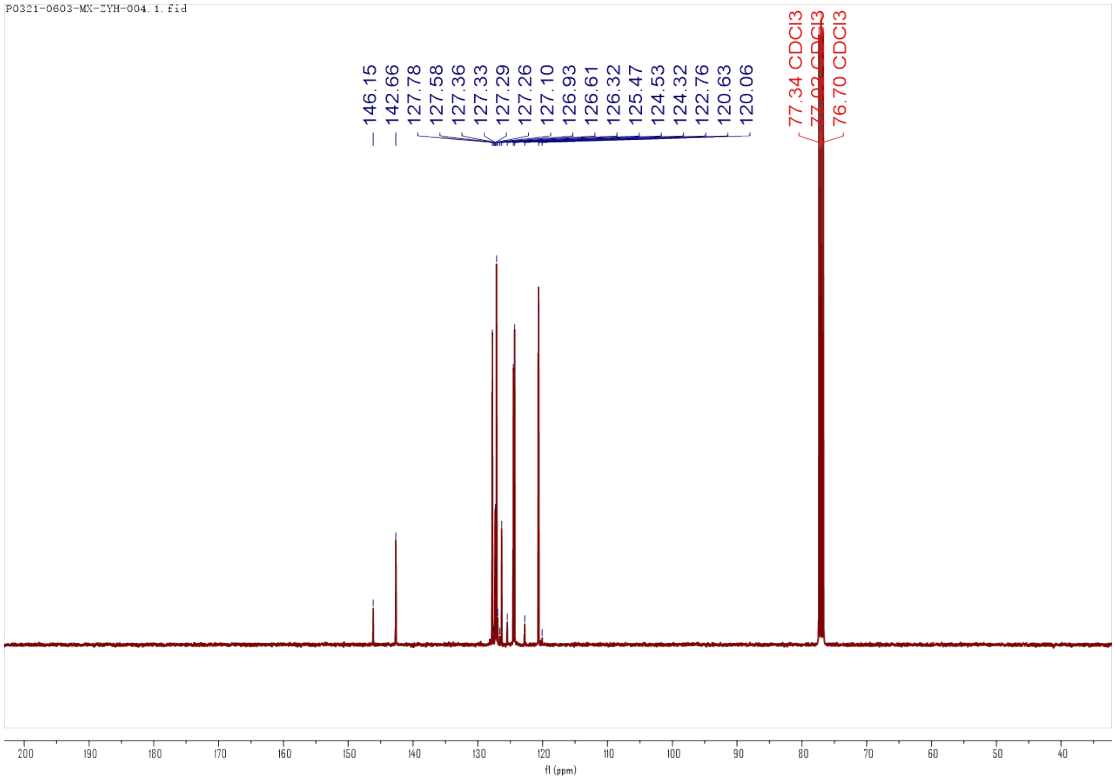


Figure S6 ^{13}C-NMR spectrum of **CF_3-PzPh** in $CDCl_3$.

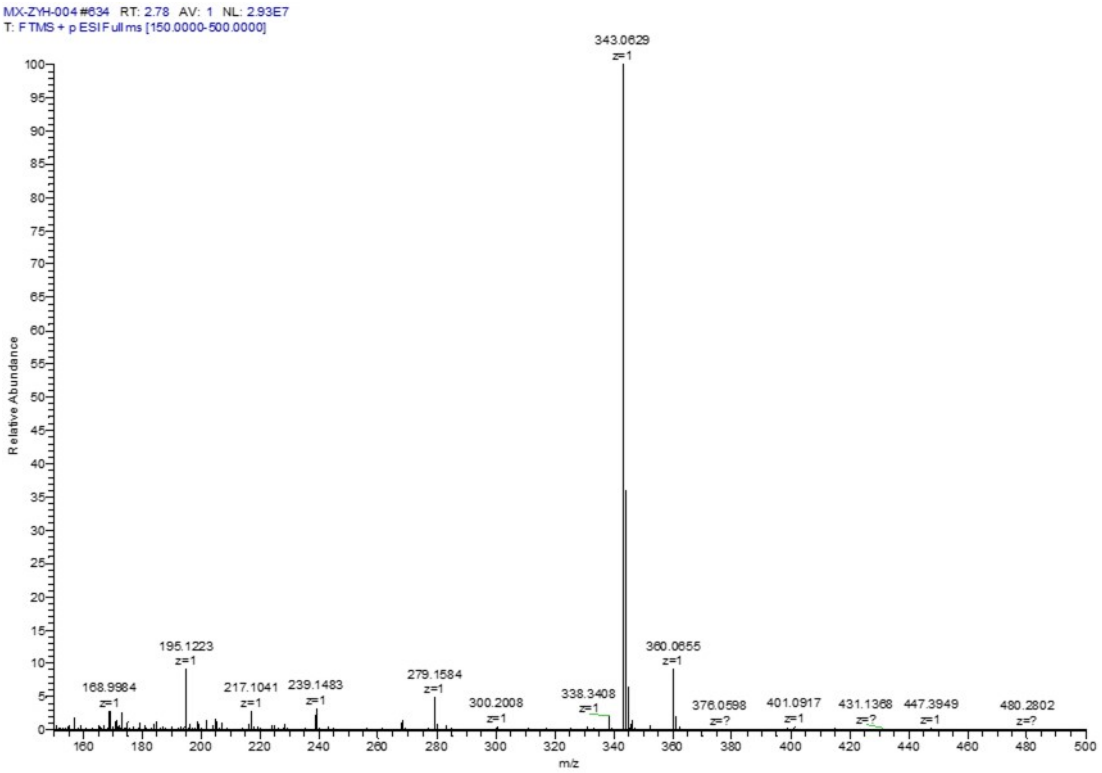


Figure S7 HRMS spectrum of **CF_3-PzPh.**

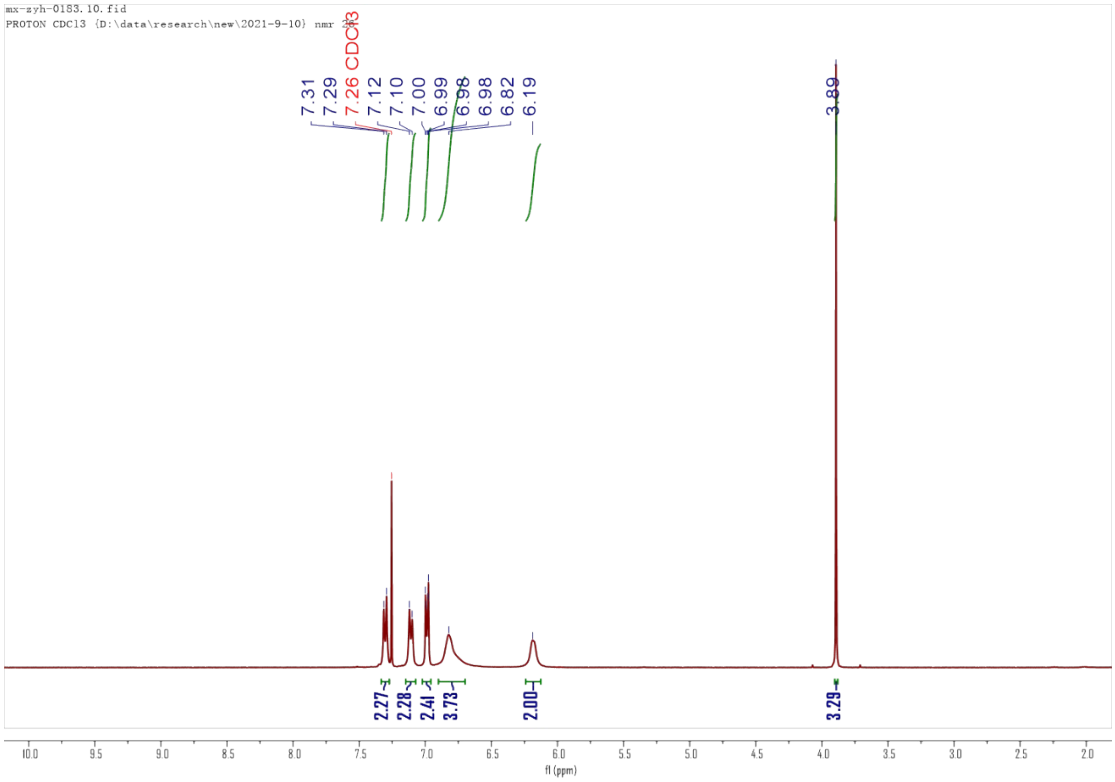


Figure S8 ^{1}H-NMR spectrum (400 MHz) of **OH_3-PzPh** in $CDCl_3$.

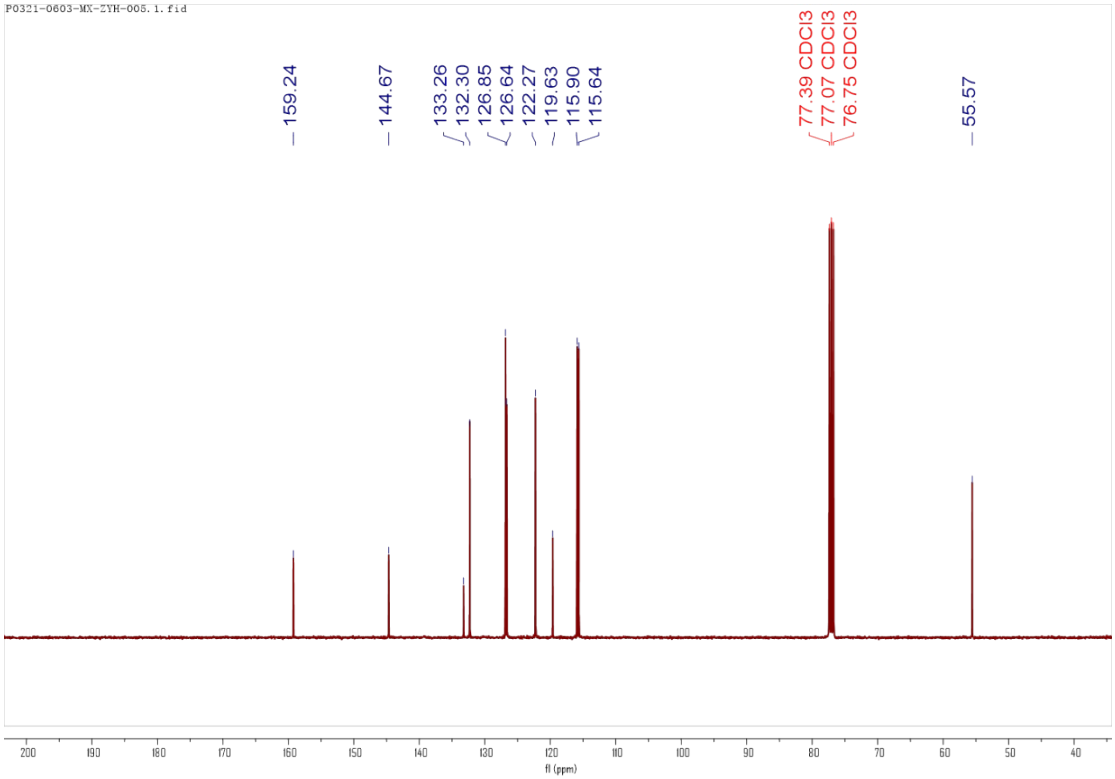


Figure S9 ^{13}C-NMR spectrum of **OH_3-PzPh** in $CDCl_3$.

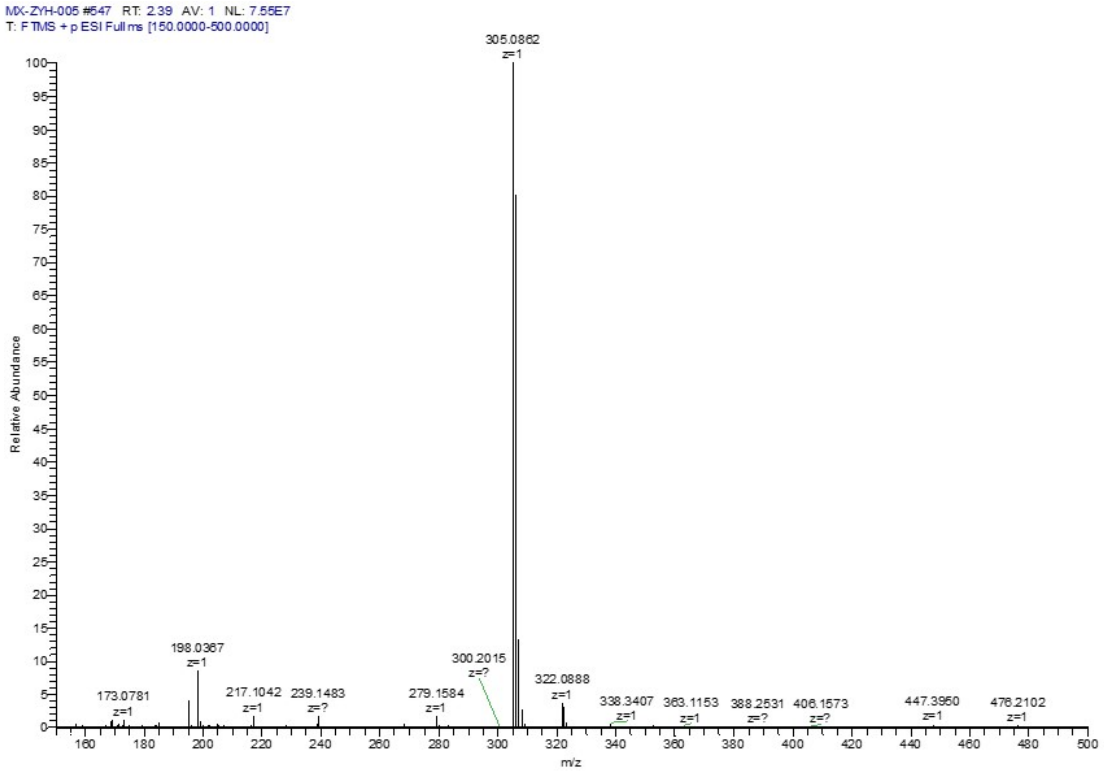


Figure S10 HRMS spectrum of **OH_3-PzPh.**

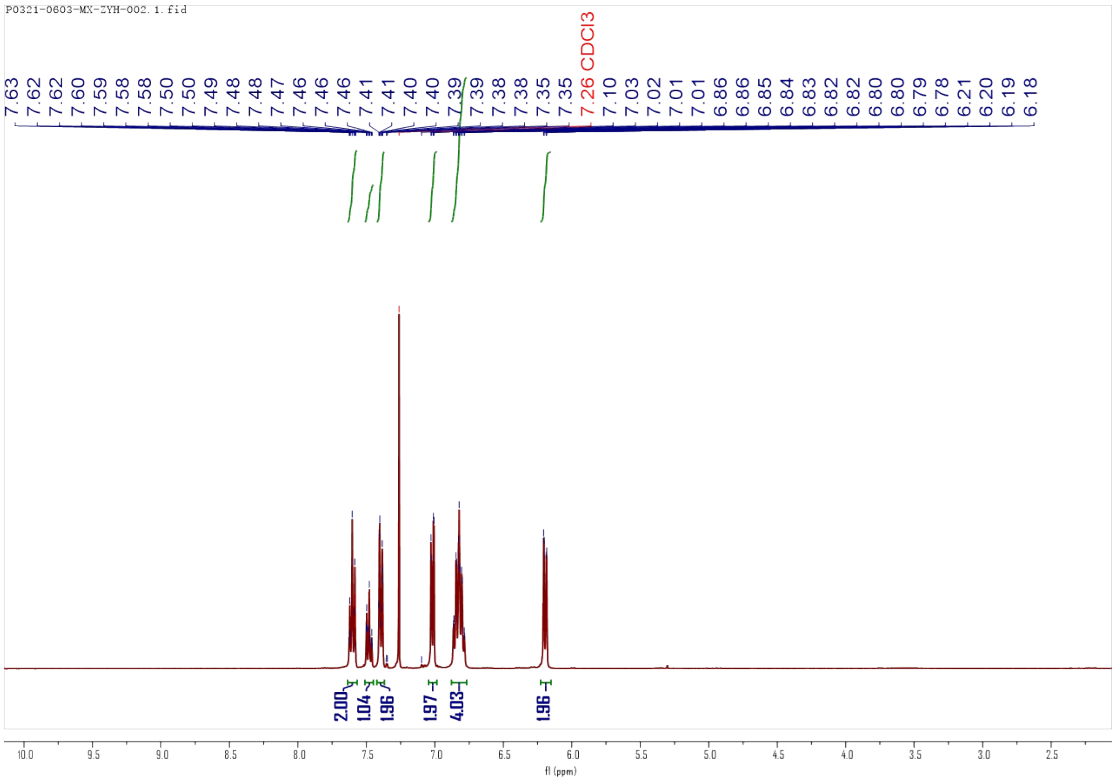


Figure S11 ^{1}H-NMR spectrum (400 MHz) of **H-PzPh** in $CDCl_3$.

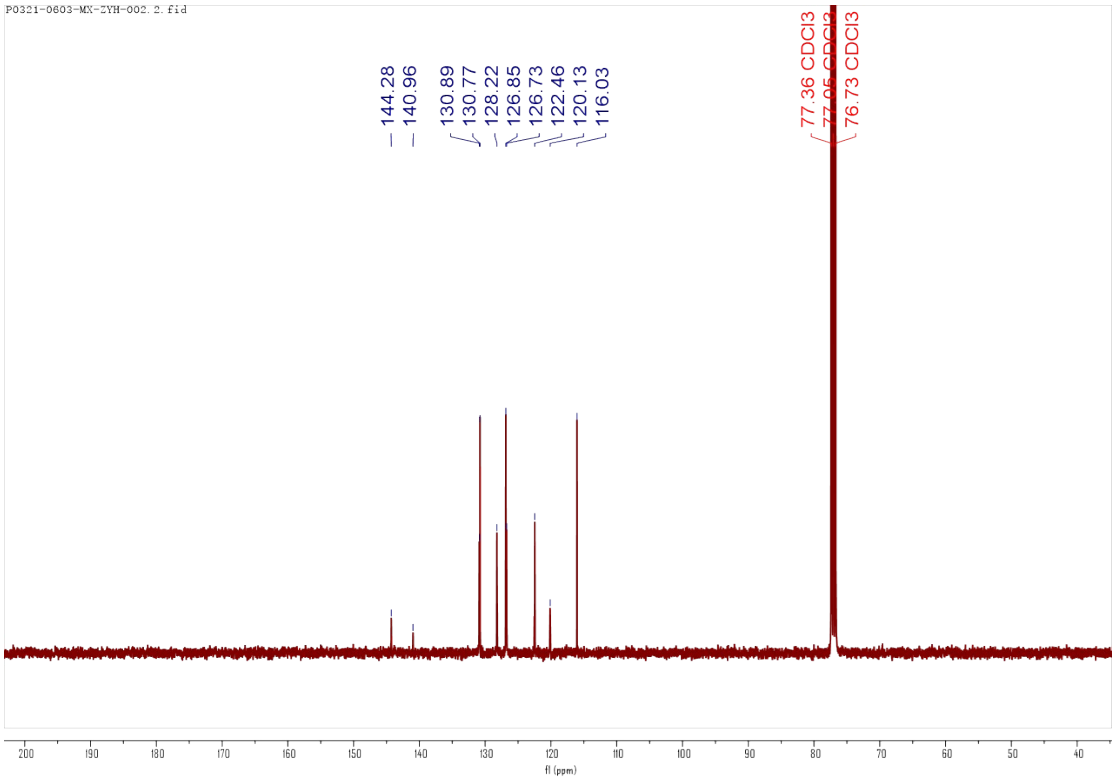


Figure S12 ^{13}C-NMR spectrum of **H-PzPh** in $CDCl_3$.

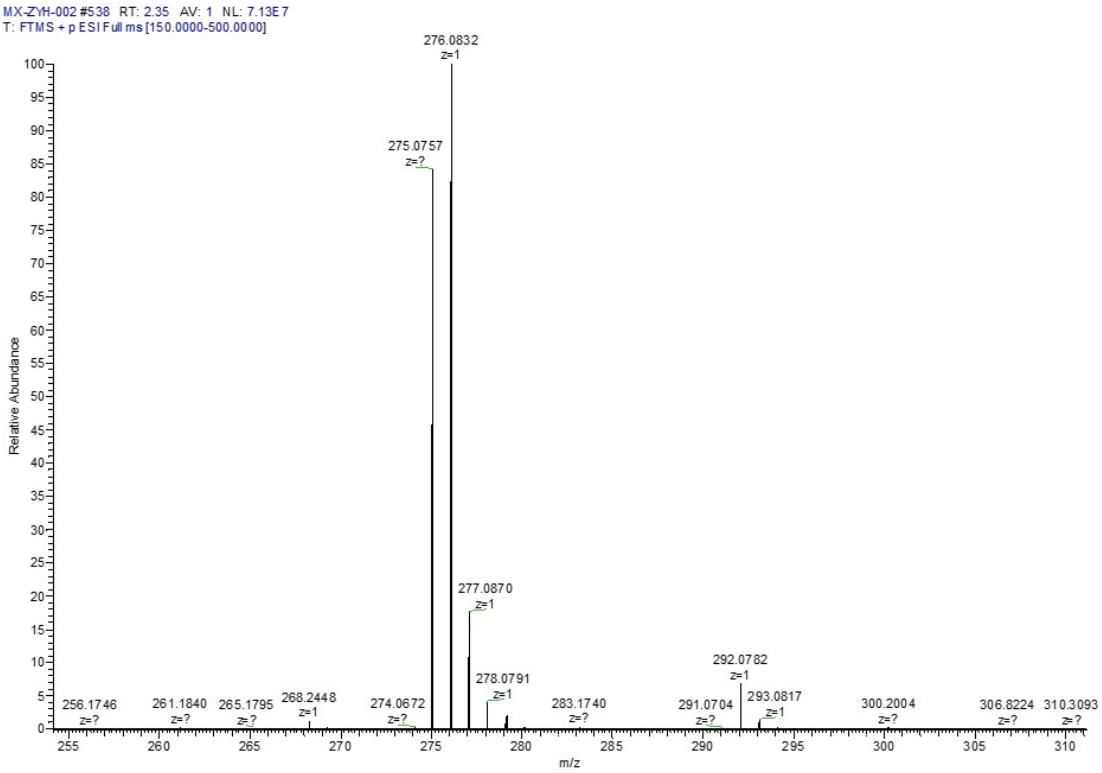


Figure S13 HRMS spectrum of **H-PzPh.**

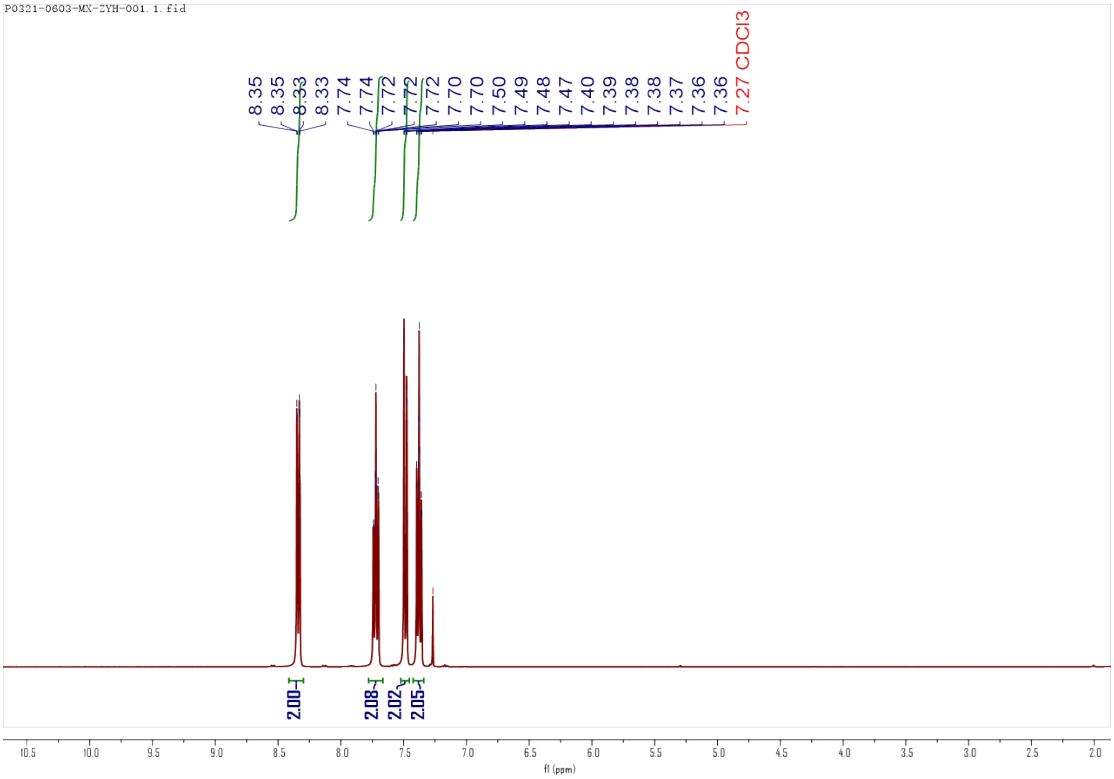


Figure S14 ^{1}H-NMR spectrum (400 MHz) of **9H-Xanthen-9-one** in $CDCl_3$.

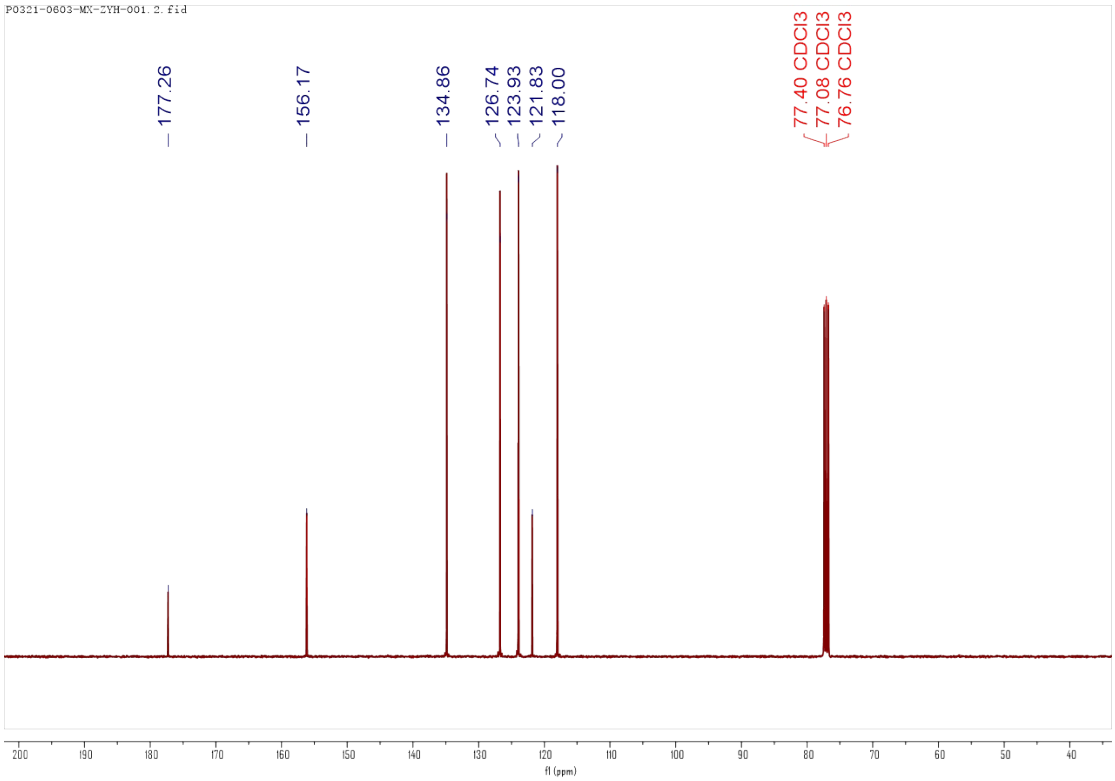


Figure S15 ^{13}C-NMR spectrum of **9H-Xanthen-9-one** in $CDCl_3$.

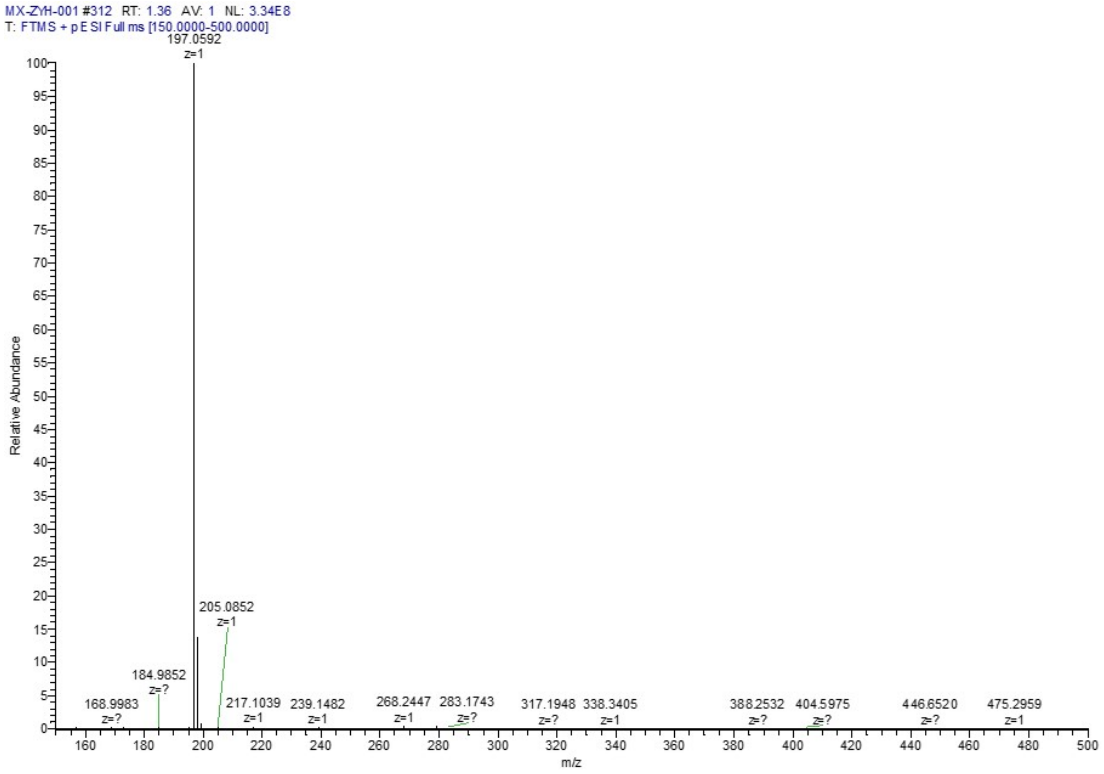


Figure S16 HRMS spectrum of **9H-Xanthen-9-one.**

4 Photophysical spectra

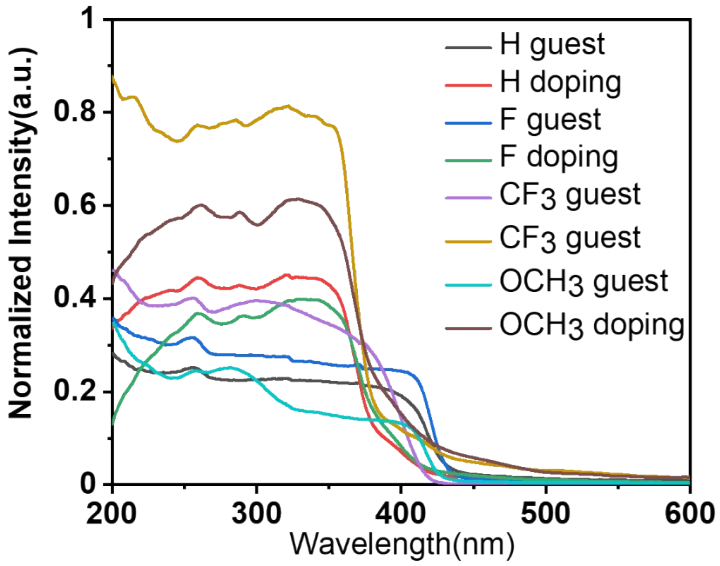


Figure S17 Absorption spectra of different guest powder and different doping systems powder.

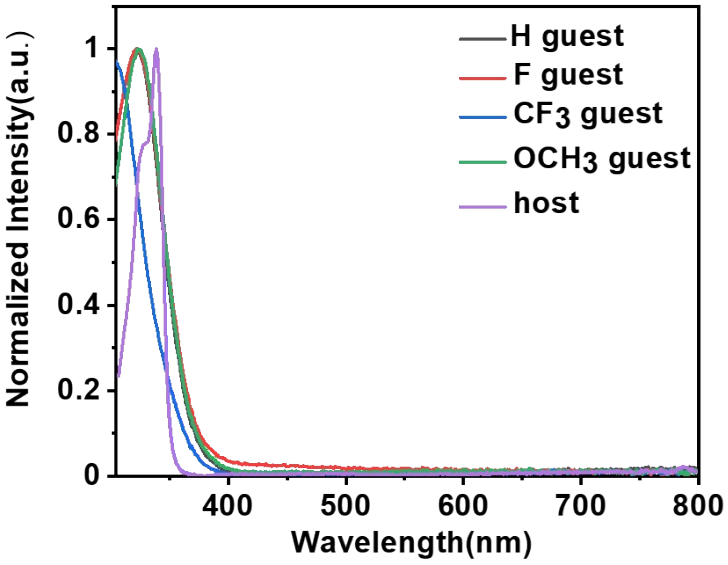


Figure S18 Normalized absorption spectra of different guests and host in toluene (C = 1×10^{-5} M).

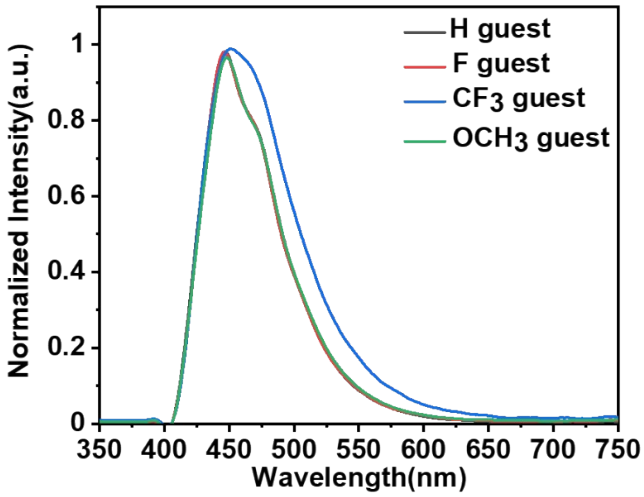


Figure S19 Normalized photoluminescence spectra of different guests in toluene (C = 1×10^{-5} M). Excitation wavelength: 330 nm.

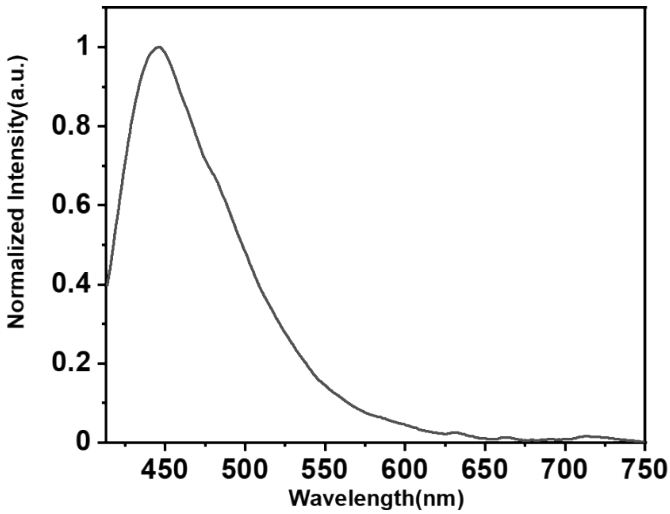


Figure S20 Normalized photoluminescence spectra of host powder. Excitation wavelength: 330 nm

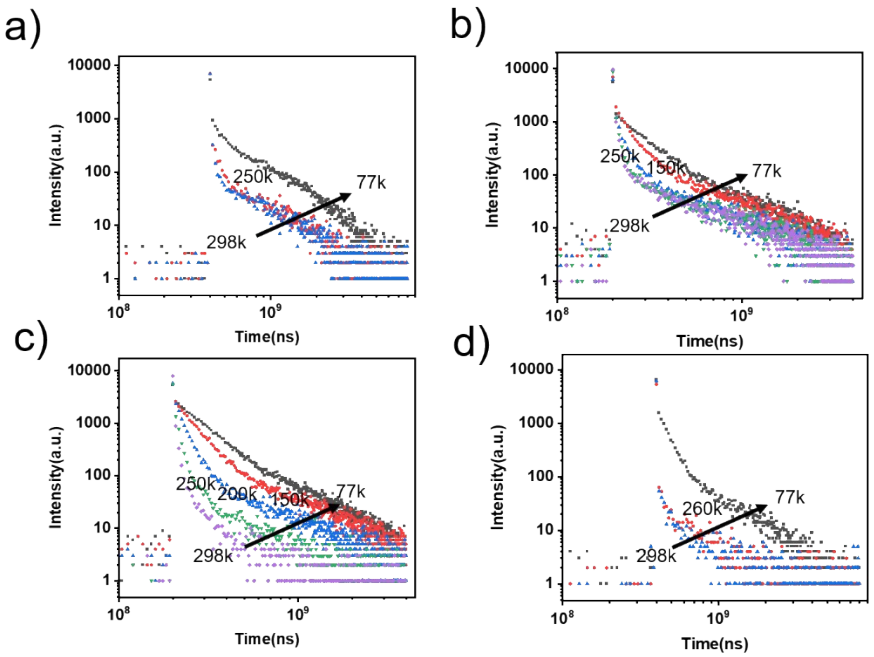


Figure S21 Emission decay profiles of a) H-doping powder (535nm), b) F-doping powder (530nm), c) CF_3-doping powder (520nm) and d) OCH_3-doping powder (540nm) from 298K to 77K.

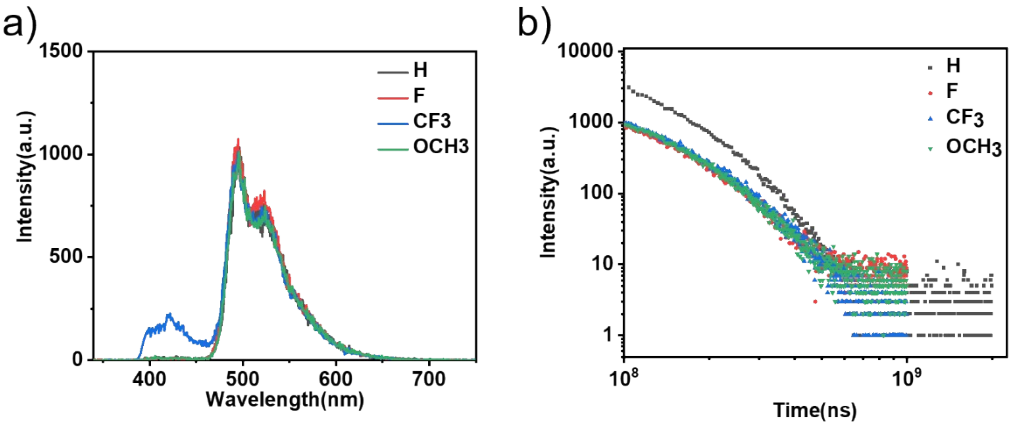


Figure S22 a) Gated-emission spectra (delay time=0.1 ms) of different guests in toluene at 77K. Excitation wavelength: 330 nm. b) Emission decay profiles of different guests in toluene at 77K.

5 Others

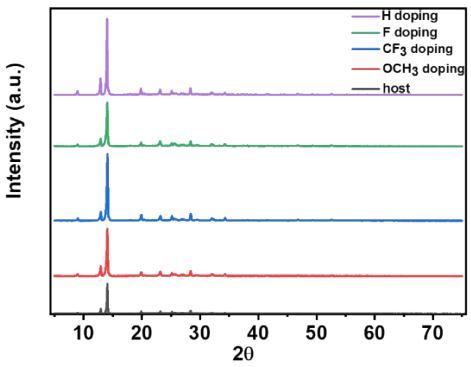


Figure S23 XRD patterns of different doping systems (1 mol%) and host powder.

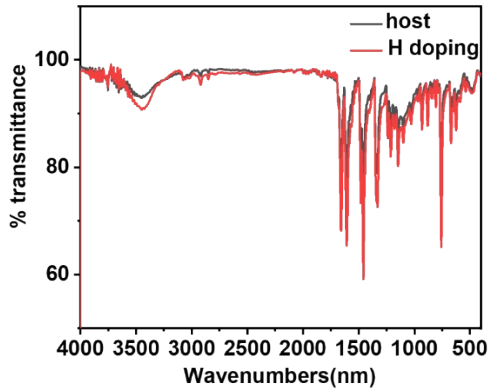
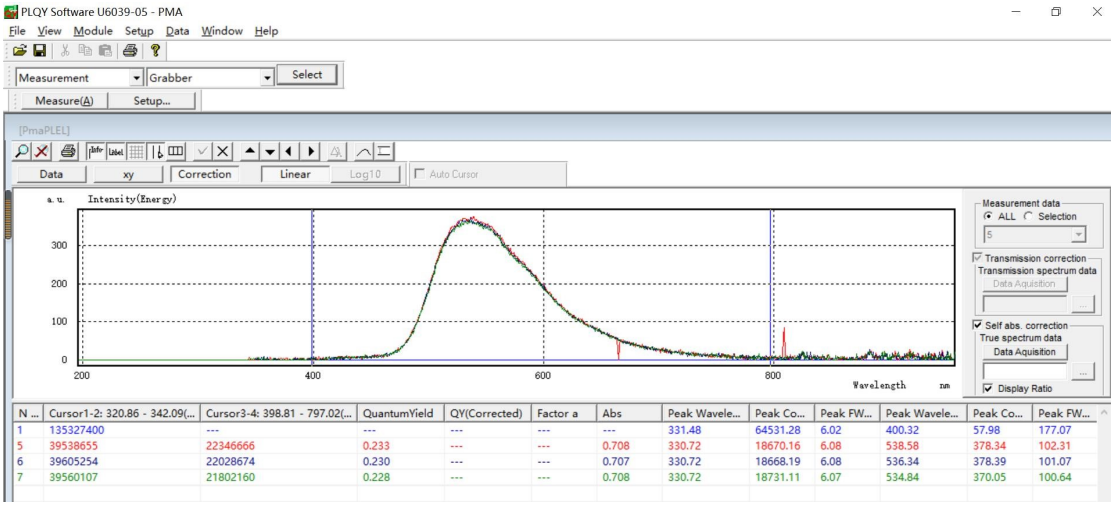
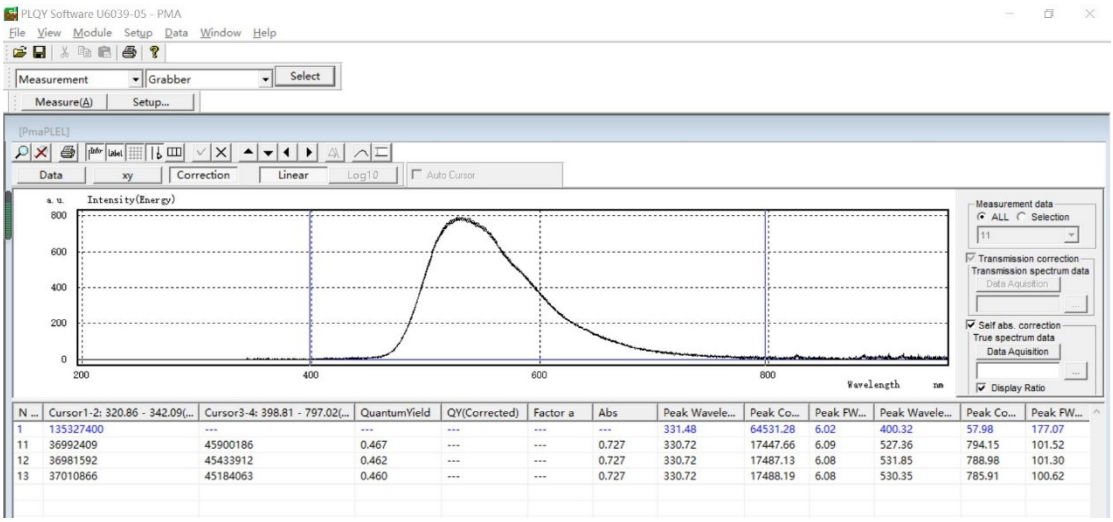


Figure S24 The FT-IR spectra of host powder and H-doping system (1 mol%) (KBr tablet).



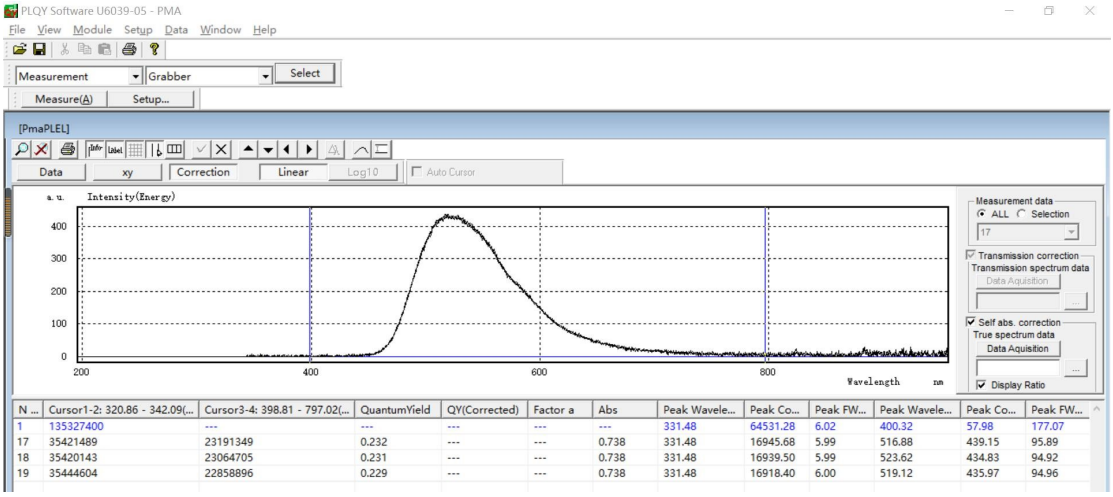
N ...	Cursor1-2: 320.86 - 342.09(...	Cursor3-4: 398.81 - 797.02(...	QuantumYield	QY(Corrected)	Factor a	Abs	Peak Wavele...	Peak Co...	Peak FW...	Peak Wavele...	Peak Co...	Peak FW...
1	135327400	---	---	---	---	---	331.48	64531.28	6.02	400.32	57.98	177.07
5	39538655	22346666	0.233	---	---	0.708	330.72	18670.16	6.08	538.58	378.34	102.31
6	39605254	22028674	0.230	---	---	0.707	330.72	18668.19	6.08	536.34	378.39	101.07
7	39560107	21802160	0.228	---	---	0.708	330.72	18731.11	6.07	534.84	370.05	100.64

Figure S25 The quantum yield of H-PzPh doping system.



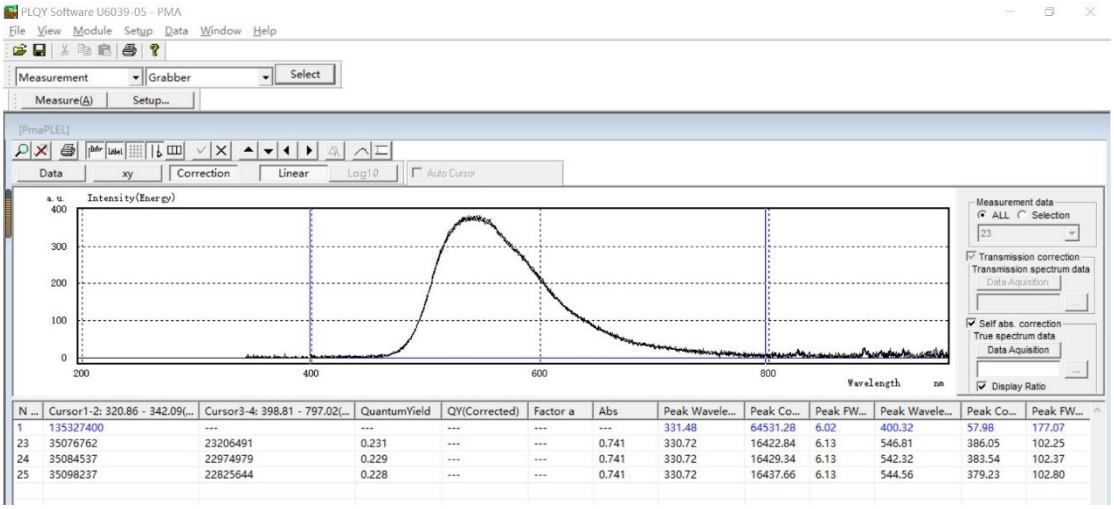
N ...	Cursor1-2: 320.86 - 342.09(...	Cursor3-4: 398.81 - 797.02(...	QuantumYield	QY(Corrected)	Factor a	Abs	Peak Wavele...	Peak Co...	Peak FW...	Peak Wavele...	Peak Co...	Peak FW...
1	135327400	---	---	---	---	---	331.48	64531.28	6.02	400.32	57.98	177.07
11	36992409	45900186	0.467	---	---	0.727	330.72	17447.66	6.09	527.36	794.15	101.52
12	36981592	45433912	0.462	---	---	0.727	330.72	17487.13	6.08	531.85	788.98	101.30
13	37010866	45184063	0.460	---	---	0.727	330.72	17488.19	6.08	530.35	785.91	100.62

Figure S26 The quantum yield of F-PzPh doping system.



N ...	Cursor1-2: 320.86 - 342.09(...	Cursor3-4: 398.81 - 797.02(...	QuantumYield	QY(Corrected)	Factor a	Abs	Peak Wavele...	Peak Co...	Peak FW...	Peak Wavele...	Peak Co...	Peak FW...
1	135327400	---	---	---	---	---	331.48	64531.28	6.02	400.32	57.98	177.07
17	35421489	23191349	0.232	---	---	0.738	331.48	16945.68	5.99	516.88	439.15	95.89
18	35420143	23064705	0.231	---	---	0.738	331.48	16939.50	5.99	523.62	434.83	94.92
19	35444604	22858896	0.229	---	---	0.738	331.48	16918.40	6.00	519.12	435.97	94.96

Figure S27 The quantum yield of CF_3-PzPh doping system.



N ...	Cursor1-2: 320.86 - 342.09(...	Cursor3-4: 398.81 - 797.02(...	QuantumYield	QY(Corrected)	Factor a	Abs	Peak Wavele...	Peak Co...	Peak FW...	Peak Wavele...	Peak Co...	Peak FW...
1	135327400	---	---	---	---	---	331.48	64531.28	6.02	400.32	57.98	177.07
23	35076762	23206491	0.231	---	---	0.741	330.72	16422.84	6.13	546.81	386.05	102.25
24	35084537	22974979	0.229	---	---	0.741	330.72	16429.34	6.13	542.32	383.54	102.37
25	35098237	22825644	0.228	---	---	0.741	330.72	16437.66	6.13	544.56	379.23	102.80

Figure S28 The quantum yield of OCH_3-PzPh doping system.

6 Reference

[1]. Mayer, L.; May, L.; Müller, T. J. J., The interplay of conformations and electronic properties in N-aryl phenothiazines. *Organic Chemistry Frontiers* **2020,** *7* (10), 1206-1217.