

## Electronic Supplementary Information

### Effect on the conformation of monosubstituted pillar[5]arene: Solvent, temperature, concentration, and length of linker

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# Characterization

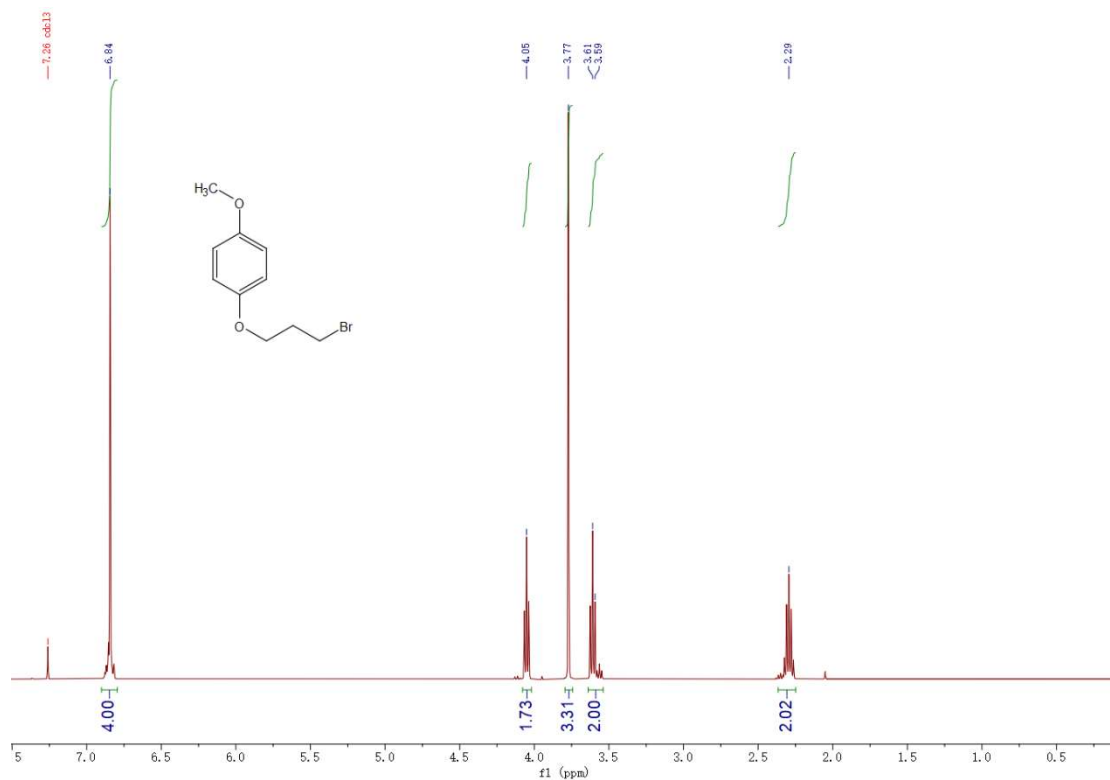


Figure S1. <sup>1</sup>H NMR of M1.

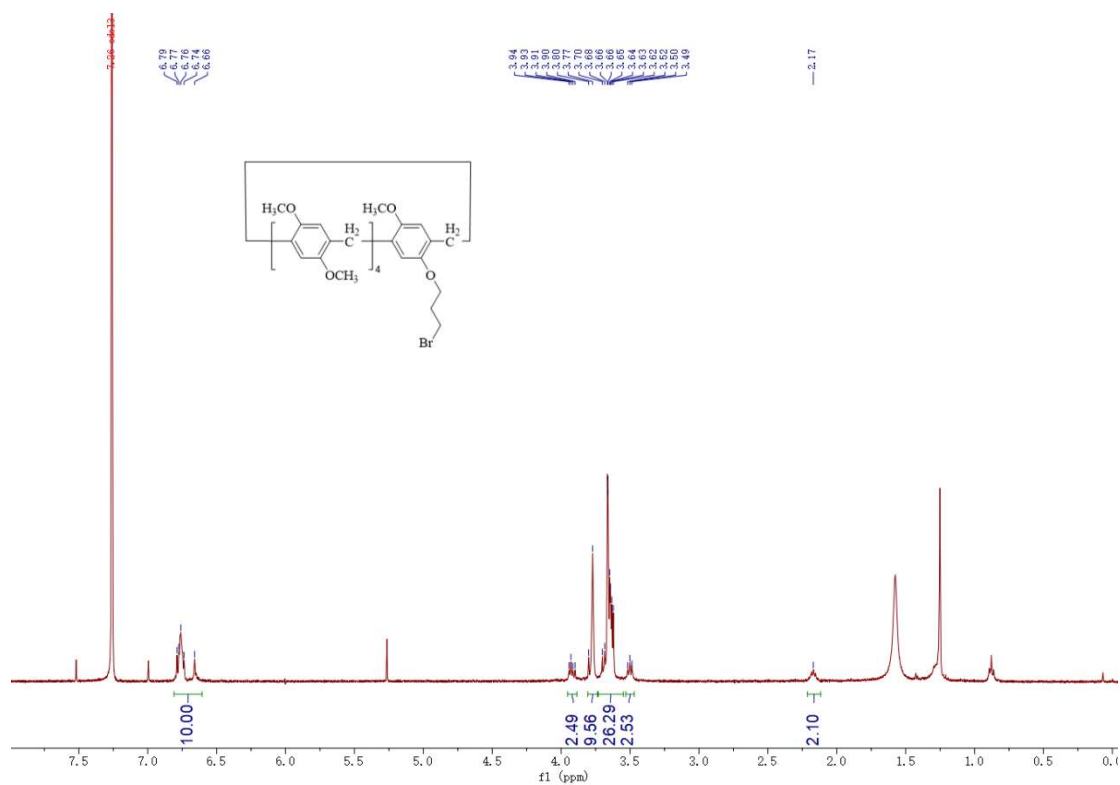


Figure S2. <sup>1</sup>H NMR of P1.

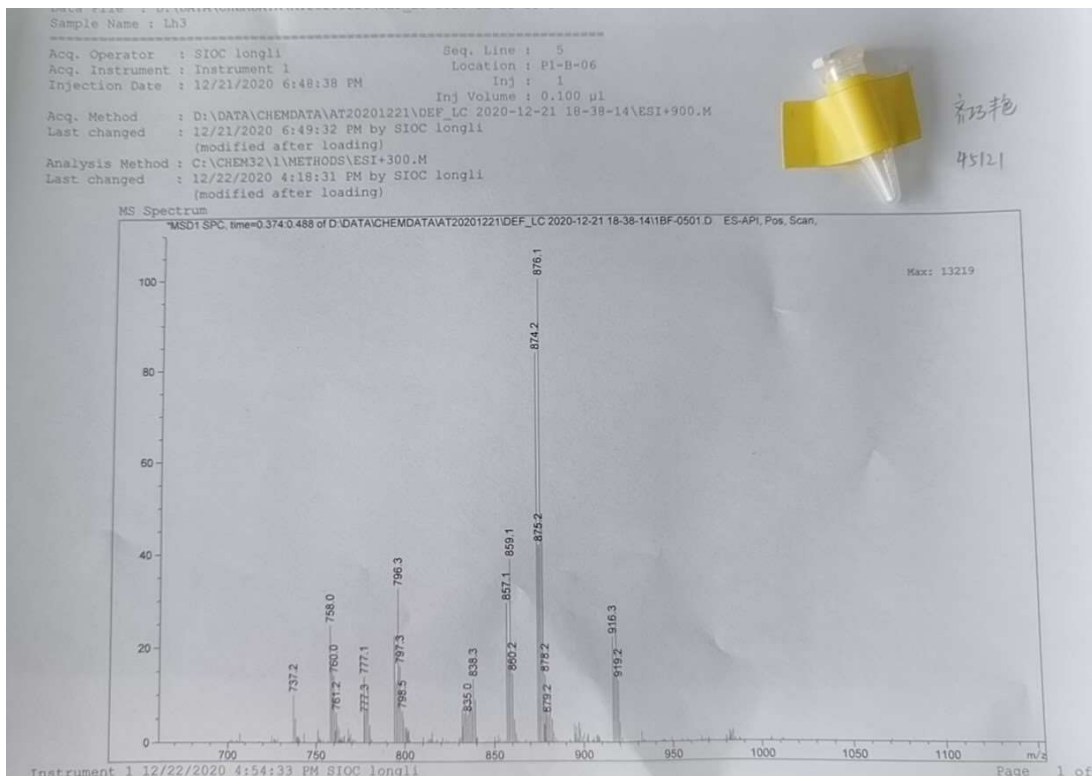


Figure S3. MS of P1.

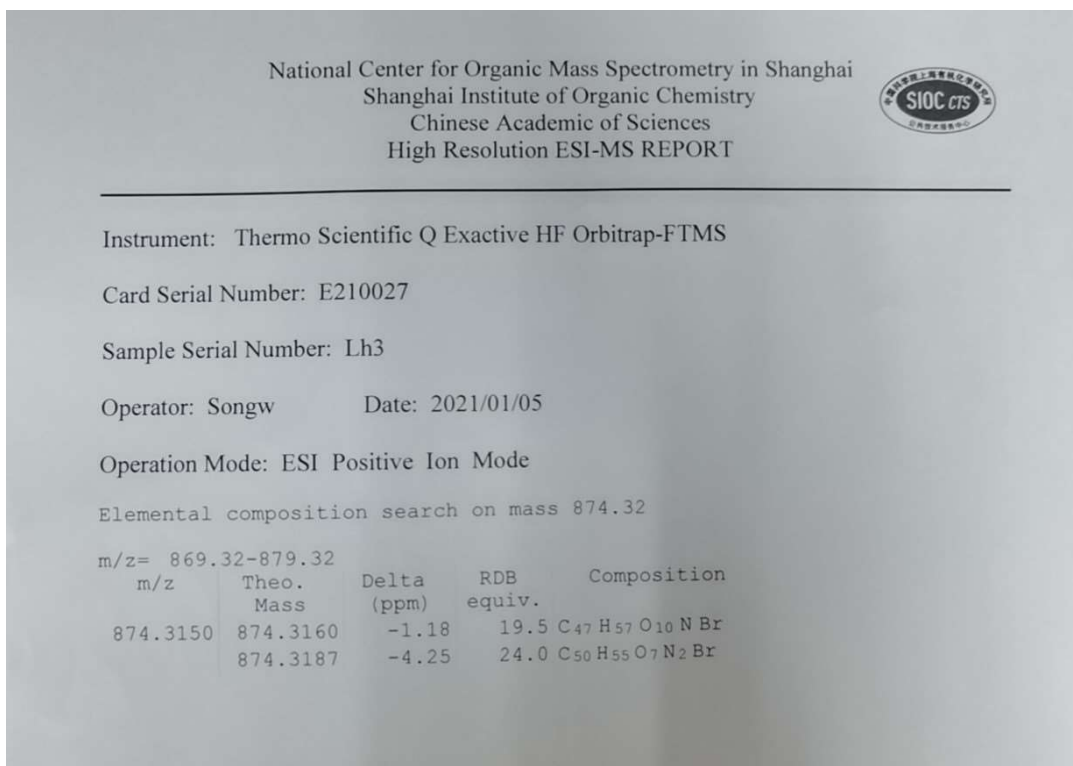


Figure S4. HRMS of P1.

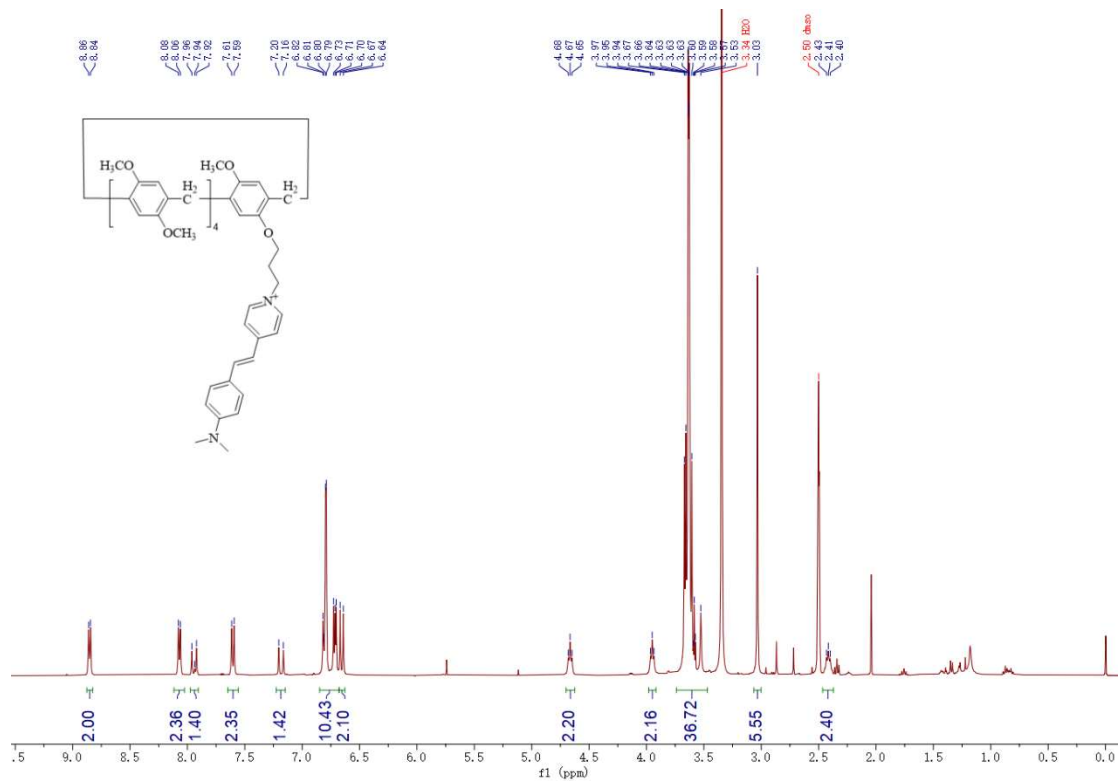


Figure S5. <sup>1</sup>H NMR of PI1.

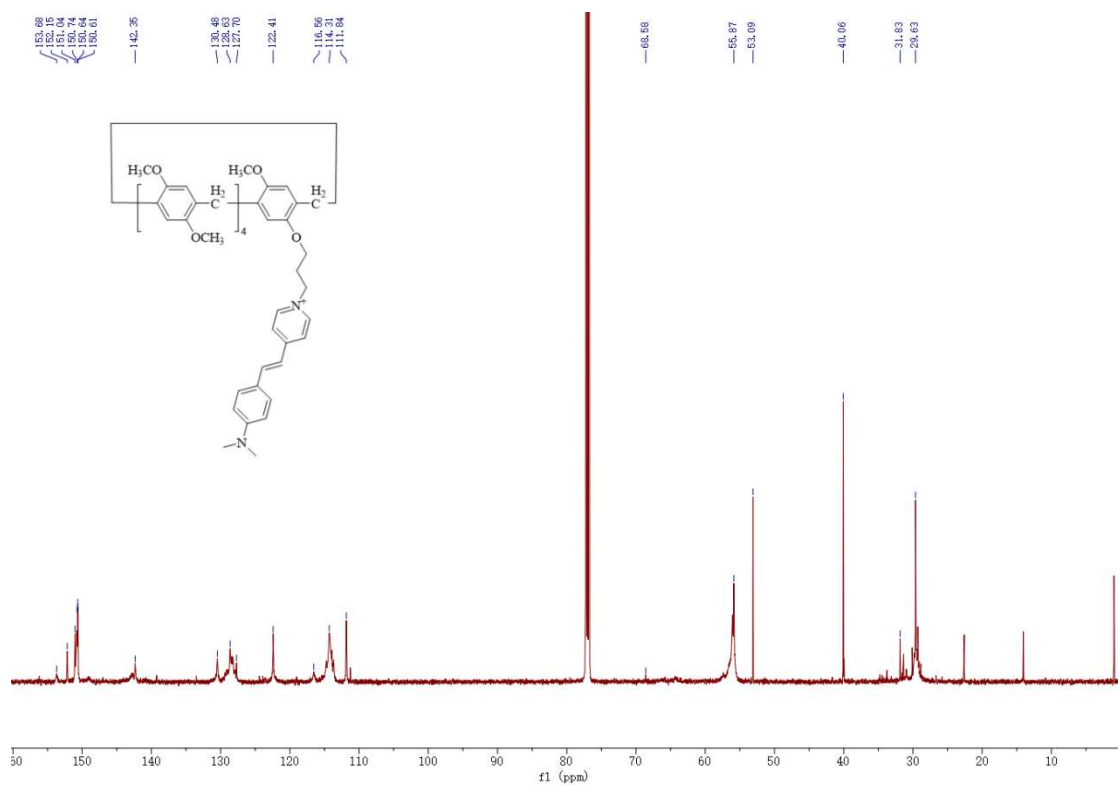
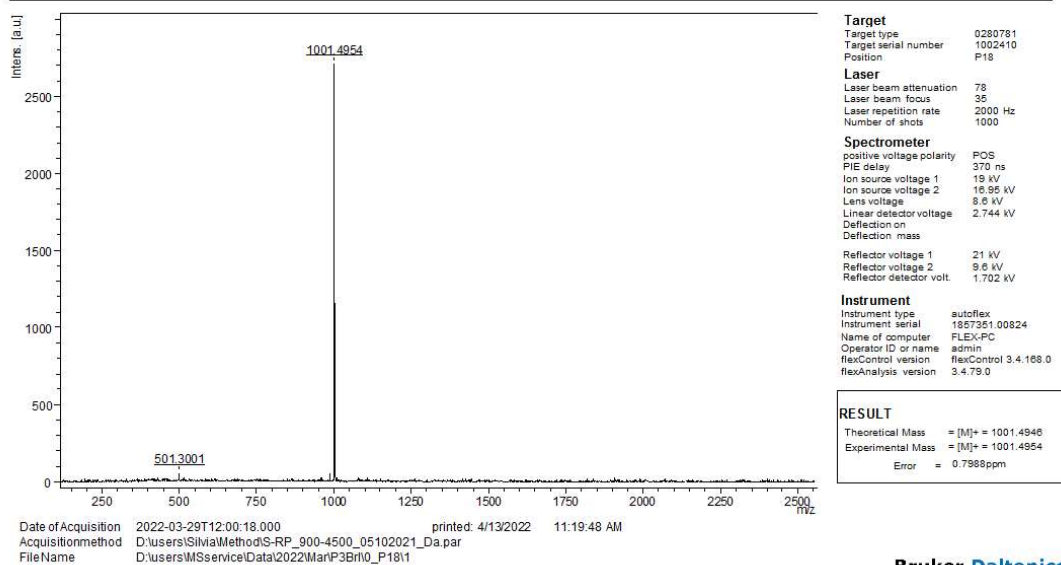


Figure S6. <sup>13</sup>C NMR of PI1.



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Figure S7. HRMS of PI1.

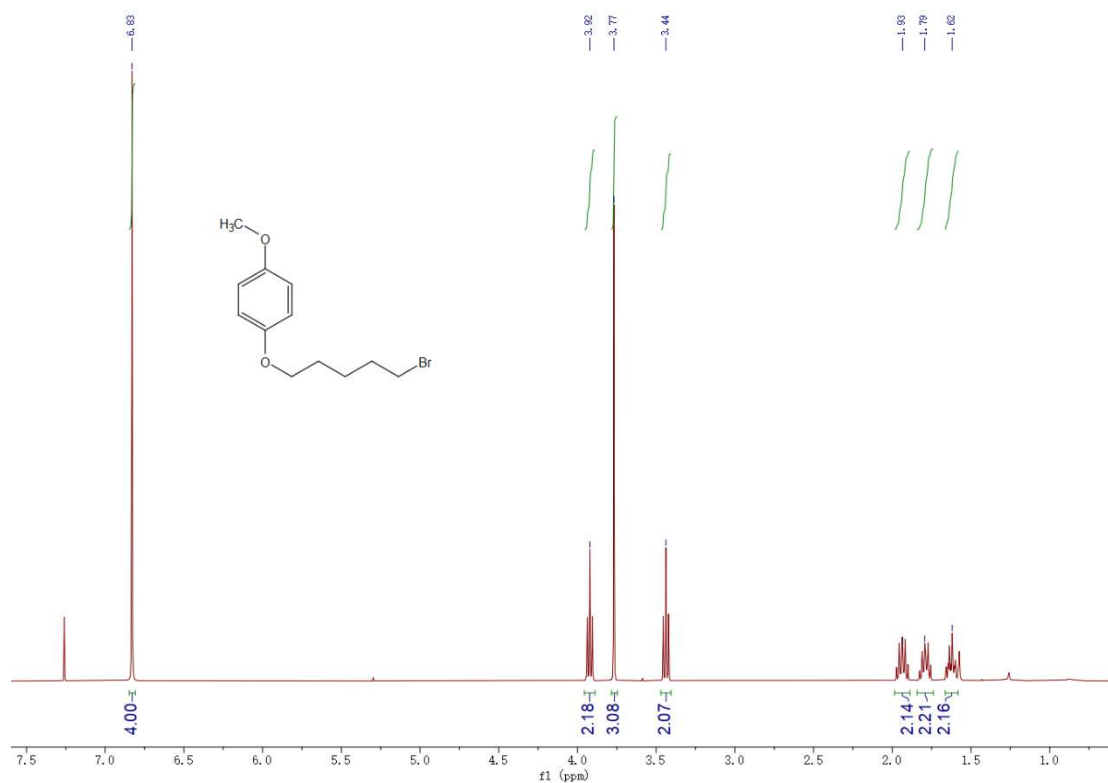


Figure S8. <sup>1</sup>H NMR of M2.

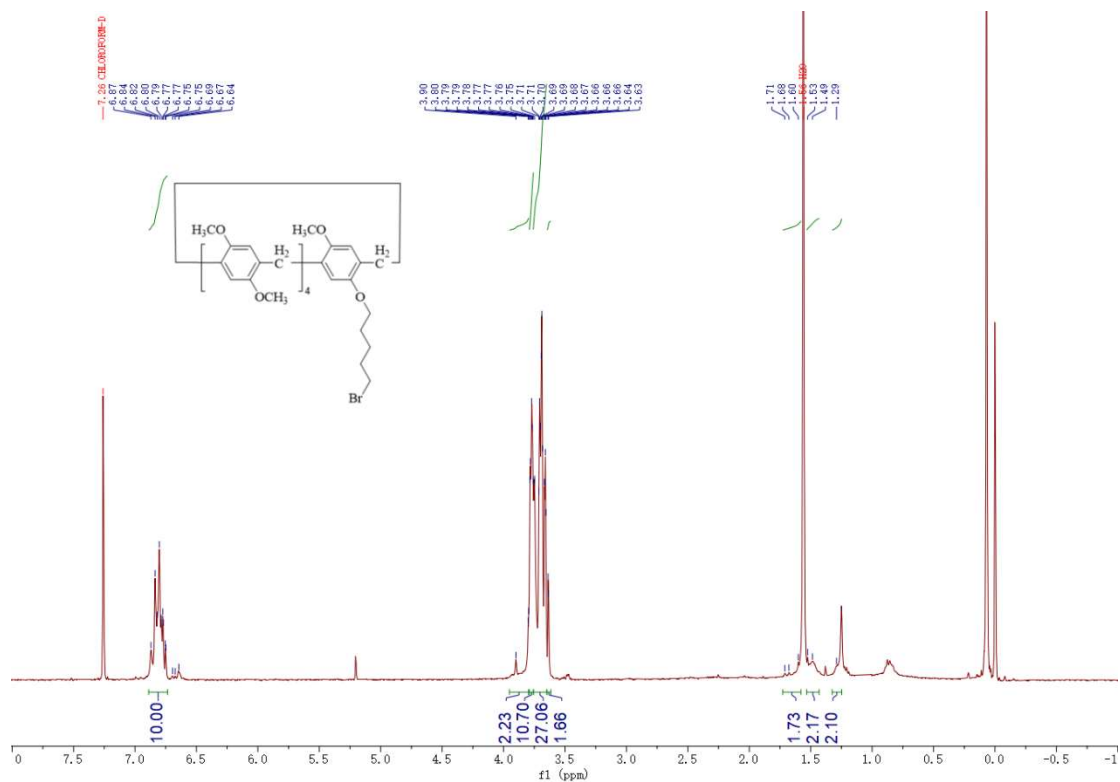


Figure S9. <sup>1</sup>H NMR of P2.

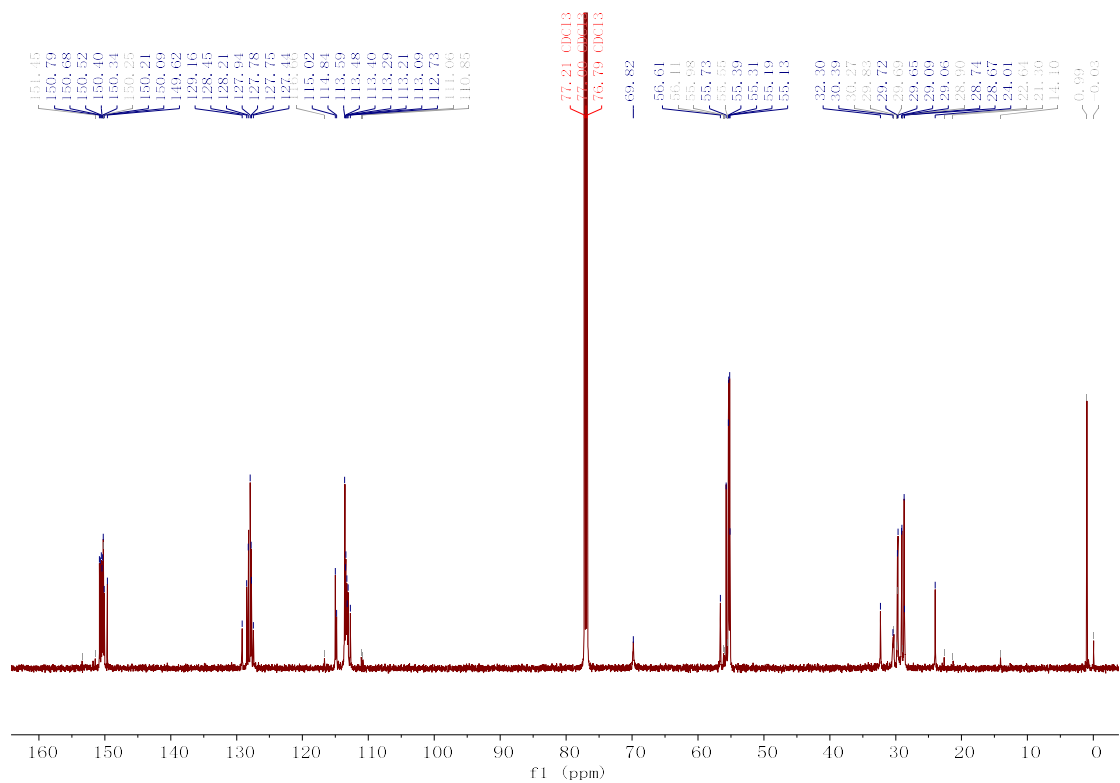
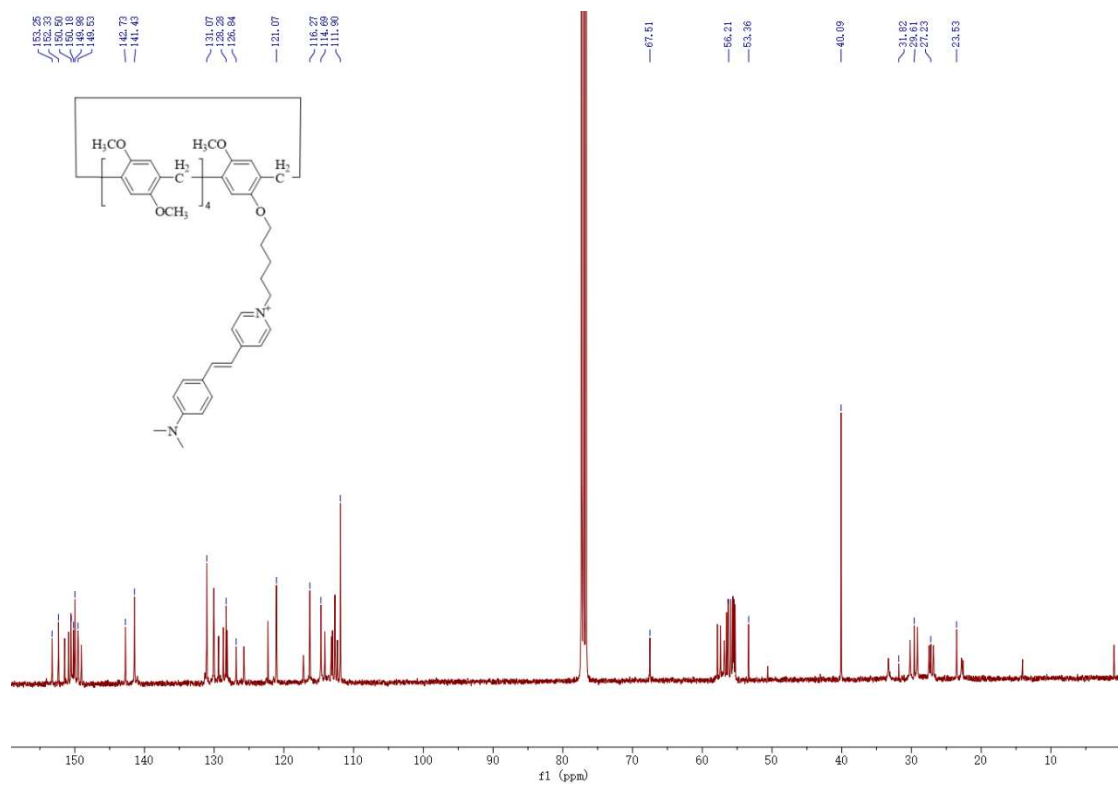
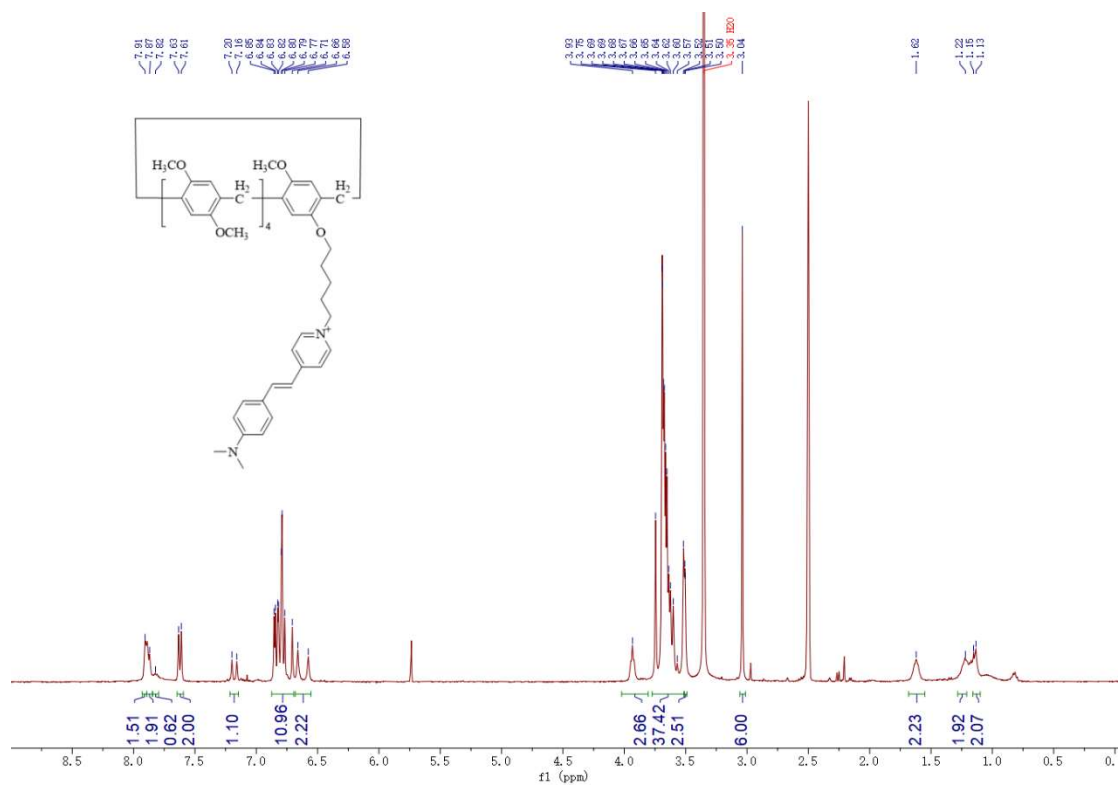
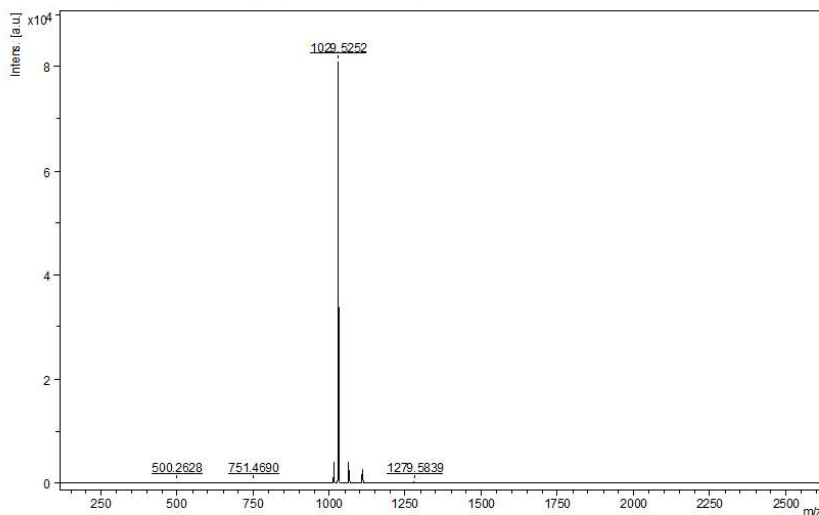


Figure S10. <sup>13</sup>C NMR of P2.









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Target serial number 1002410  
Position P19

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Laser beam focus 35  
Laser repetition rate 2000 Hz  
Number of shots 3000

**Spectrometer**  
positive voltage polarity POS  
PIE delay 370 ns  
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Ion source voltage 2 10.95 kV  
Lens voltage 8.6 kV  
Linear detector voltage 2.744 kV  
Deflection on  
Deflection mass

Reflector voltage 1 21 kV  
Reflector voltage 2 9.6 kV  
Reflector detector volt. 1.702 kV

**Instrument**  
Instrument type autoflex  
Instrument serial 1857351.00824  
Name of computer FLEX-PC  
Operator ID or name admin  
flexControl version flexControl 3.4.108.0  
flexAnalysis version 3.4.79.0

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FileName D:\users\MSservice\Data\2022\Mar\P5BrI0\_P191

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Figure S15. HRMS of PI2.

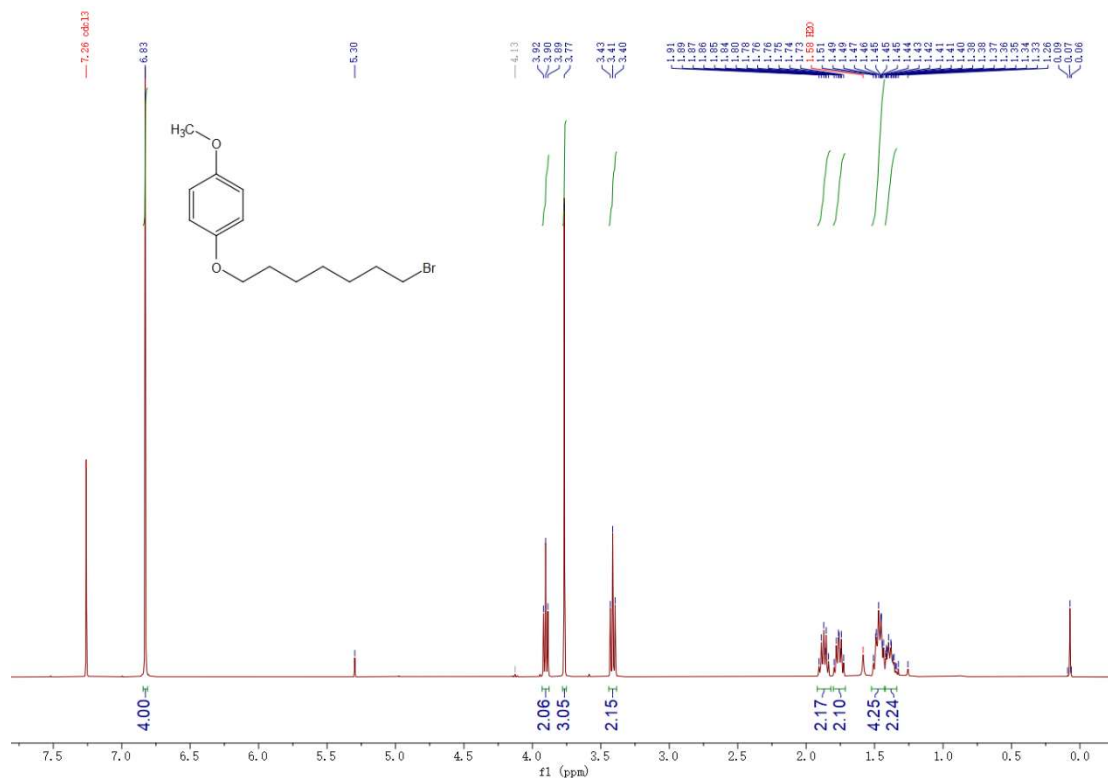
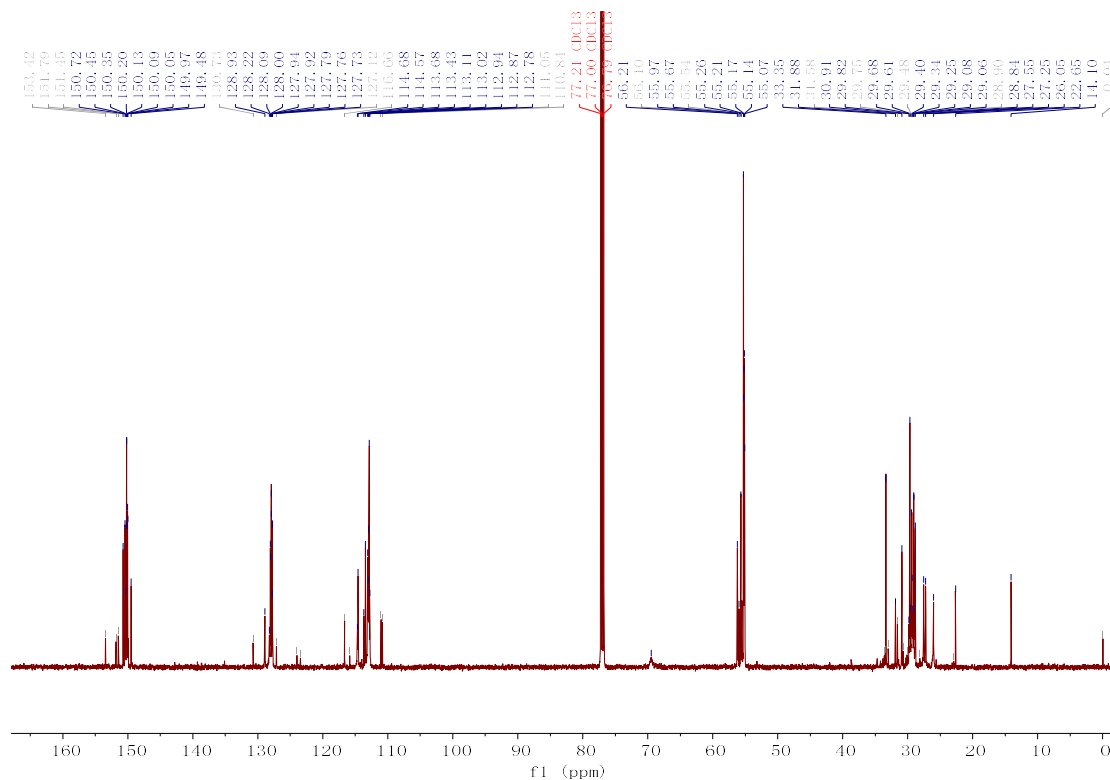
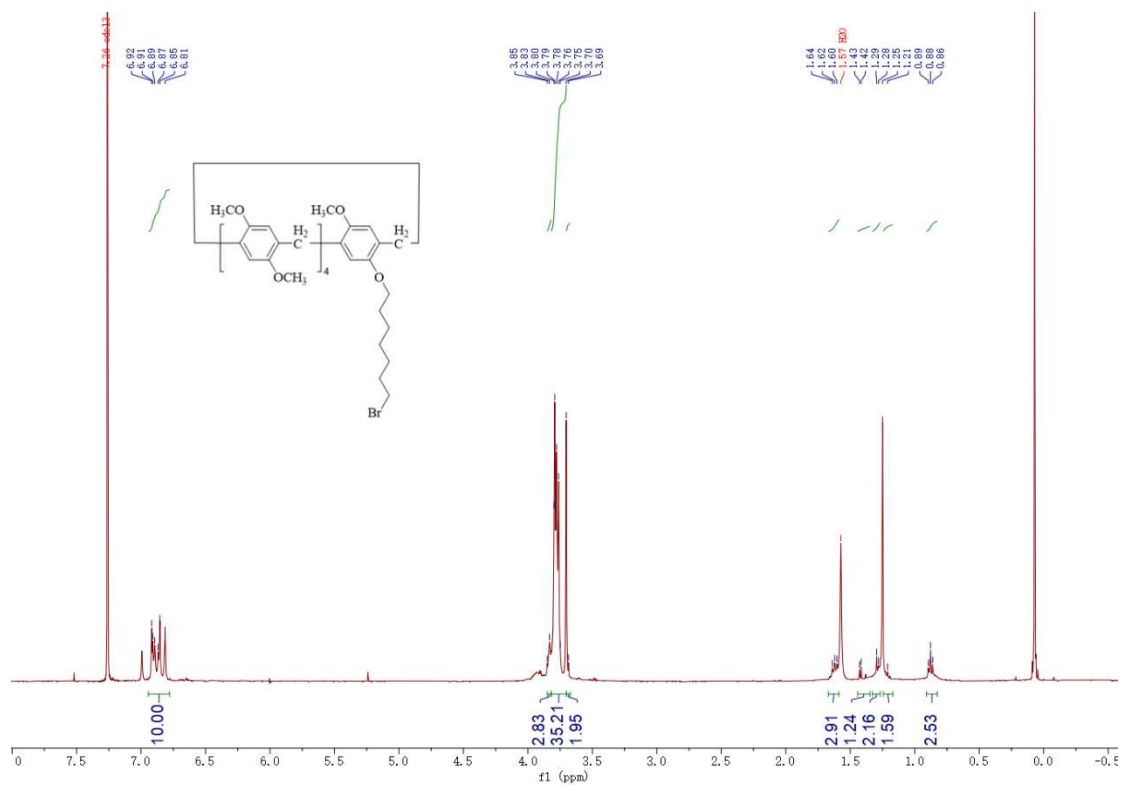


Figure S16. <sup>1</sup>H NMR of M3.



D:\data\AP MALDI\20220905\P7BR-1

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T: FTMS + p NSI Full ms [300.0000-2500.0000]

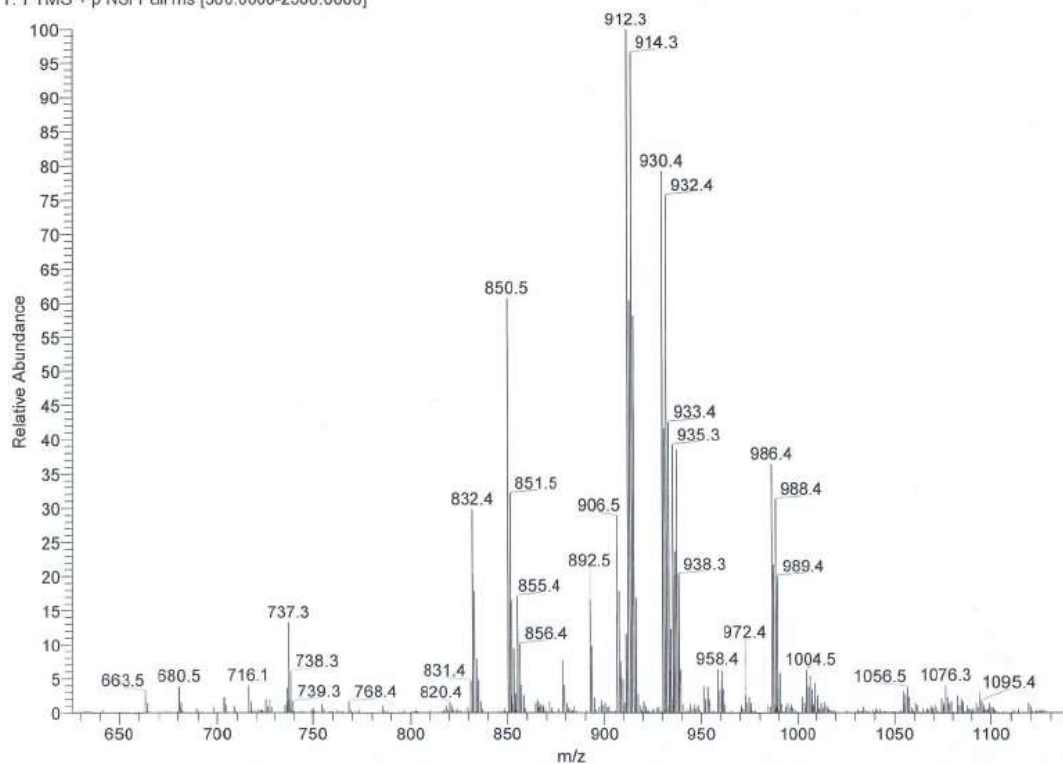


Figure S19. MS of P3.

National Center for Organic Mass Spectrometry in Shanghai  
Shanghai Institute of Organic Chemistry  
Chinese Academic of Sciences  
High Resolution AP-MALDI-MS REPORT



Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E221704

Sample Serial Number: P7Br

Operator: Songw Date: 2022/09/06

Operation Mode: AP-MALDI Positive Ion Mode

Elemental composition search on mass 912.3420

m/z= 907.3420-917.3420

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
912.3420	912.3443	-2.48	21.0	C <sub>51</sub> H <sub>61</sub> O <sub>10</sub> Br

Figure S20. HRMS of P3.

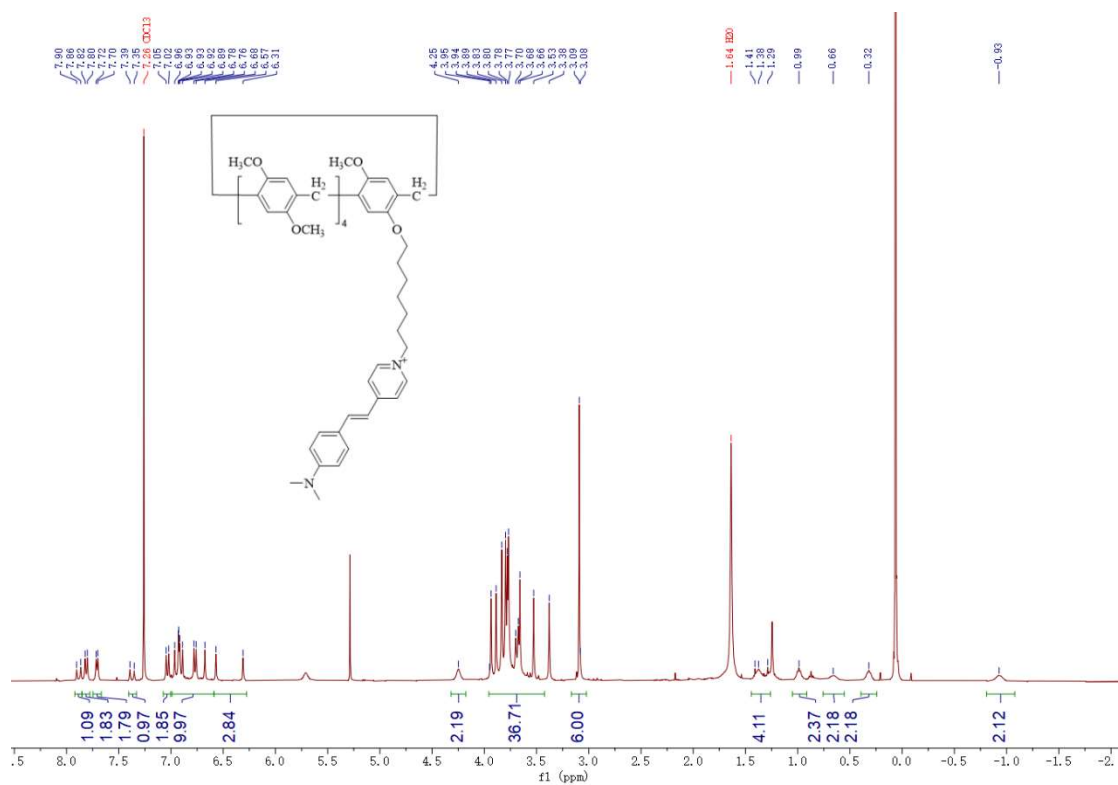


Figure S21. <sup>1</sup>H NMR of PI3.

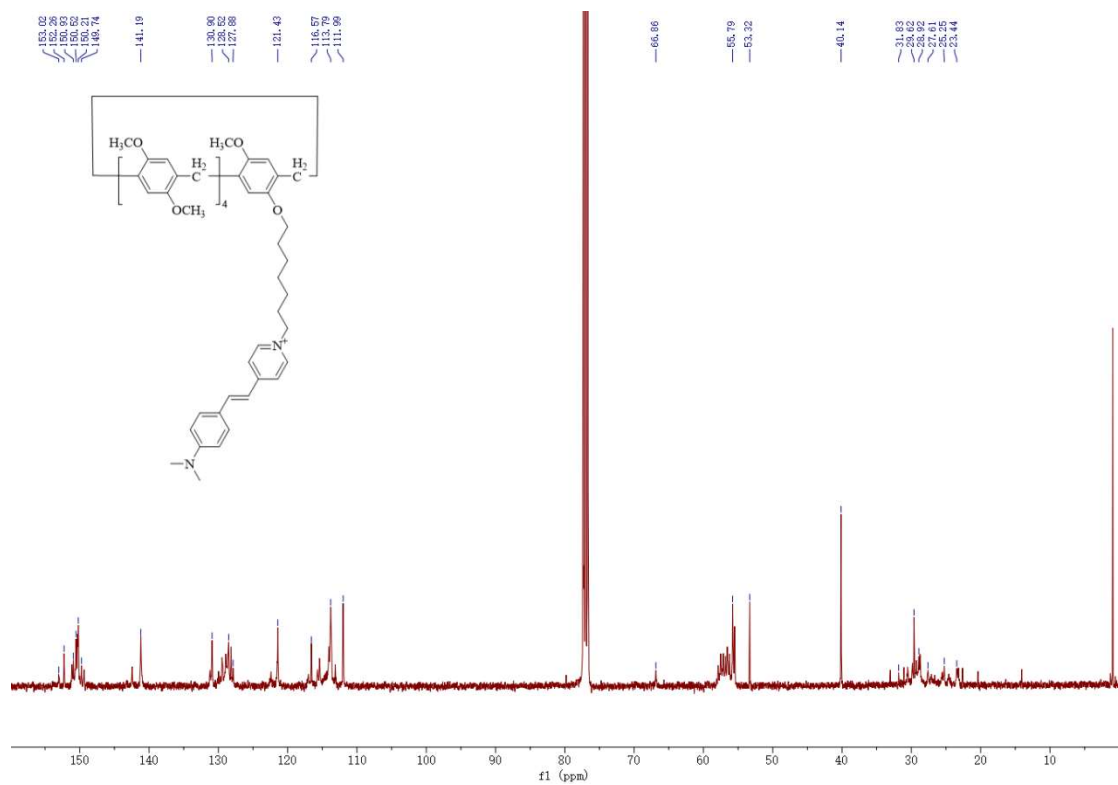
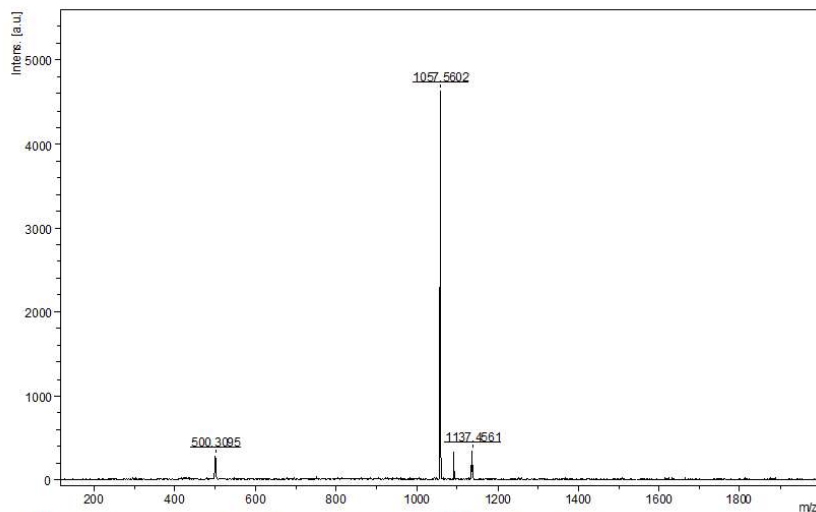


Figure S22. <sup>13</sup>C NMR of PI3.



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Target serial number 1002410  
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Laser beam focus 35  
Laser repetition rate 2000 Hz  
Number of shots 1000

**Spectrometer**  
positive voltage polarity POS  
PIE delay 370 ns  
ion source voltage 1 19 kV  
ion source voltage 2 15.9 kV  
Lens voltage 8.6 kV  
Linear detector voltage 2.744 kV  
Deflection on Deflection mass  
Reflector voltage 1 21 kV  
Reflector voltage 2 9.6 kV  
Reflector detector volt. 1.702 kV

**Instrument**  
Instrument type autoflex  
Instrument serial 1857351.00824  
Name of computer FLEX-PC  
Operator ID or name admin  
flexControl version flexControl 3.4.168.0  
flexAnalysis version 3.4.79.0

**RESULT**  
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FileName D:\users\MSservice\Data\2022\Mar\P7Br\0\_P20\1

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Figure S23. HRMS of PI3.

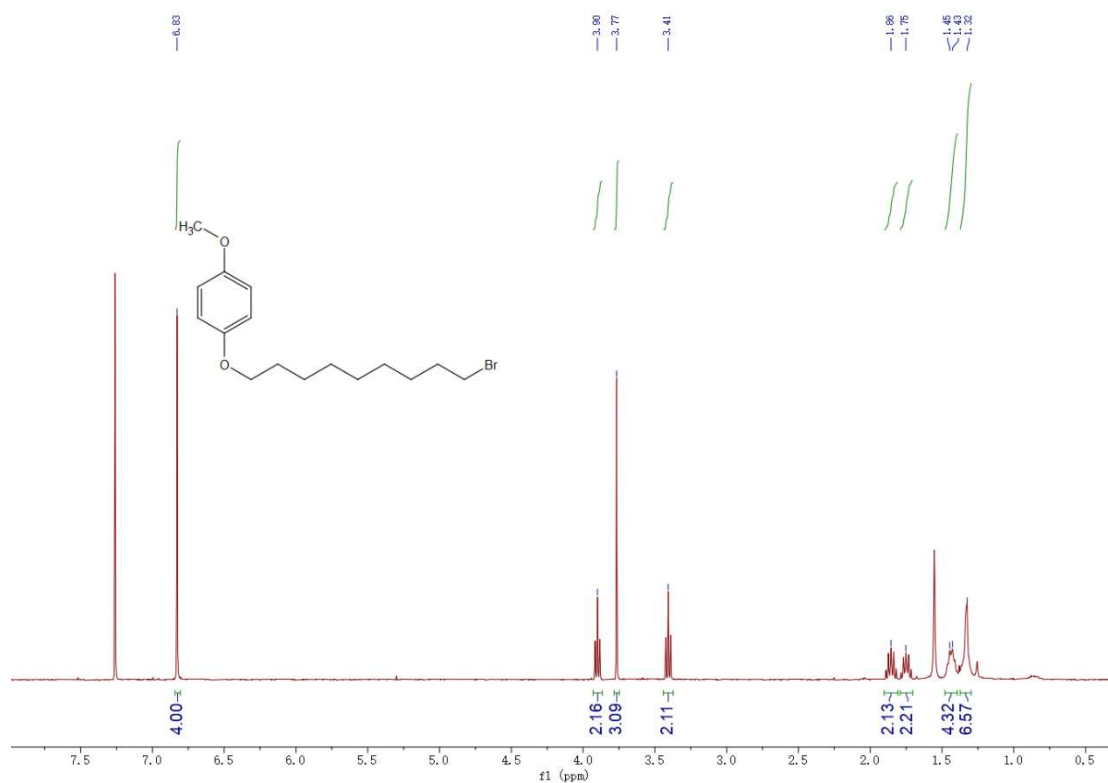


Figure S24. <sup>1</sup>H NMR of M4.

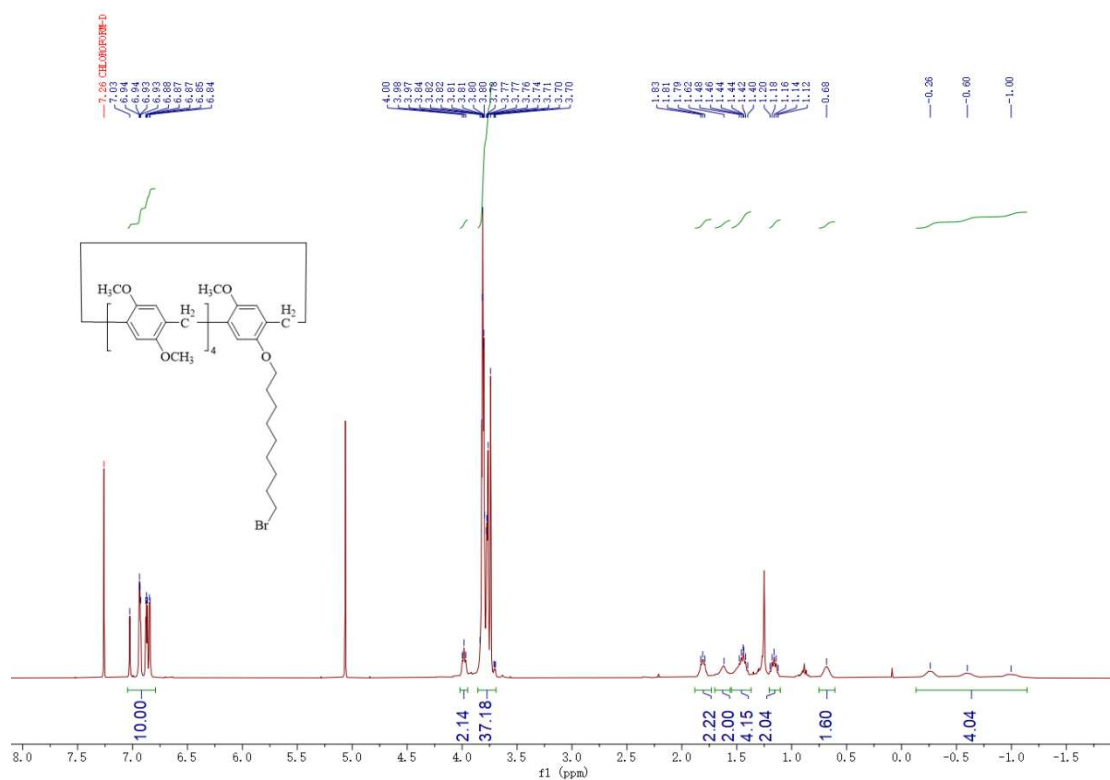


Figure S25. <sup>1</sup>H NMR of P4.

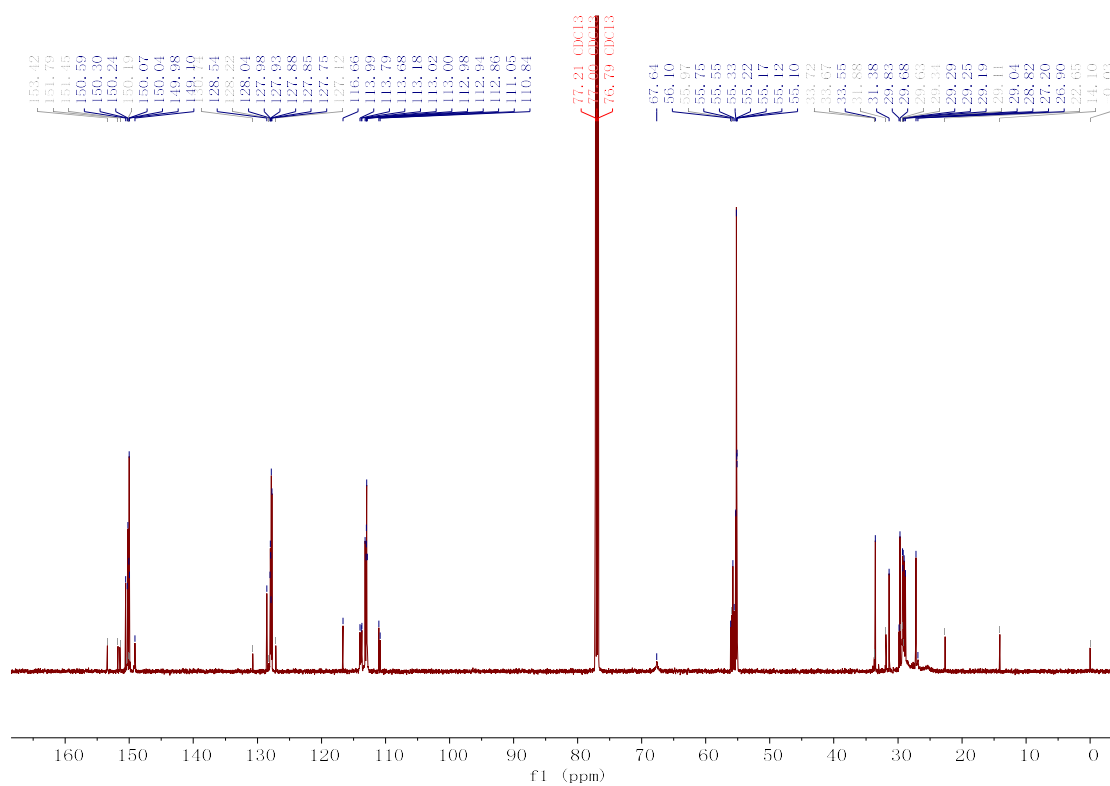


Figure S26. <sup>13</sup>C NMR of P4.

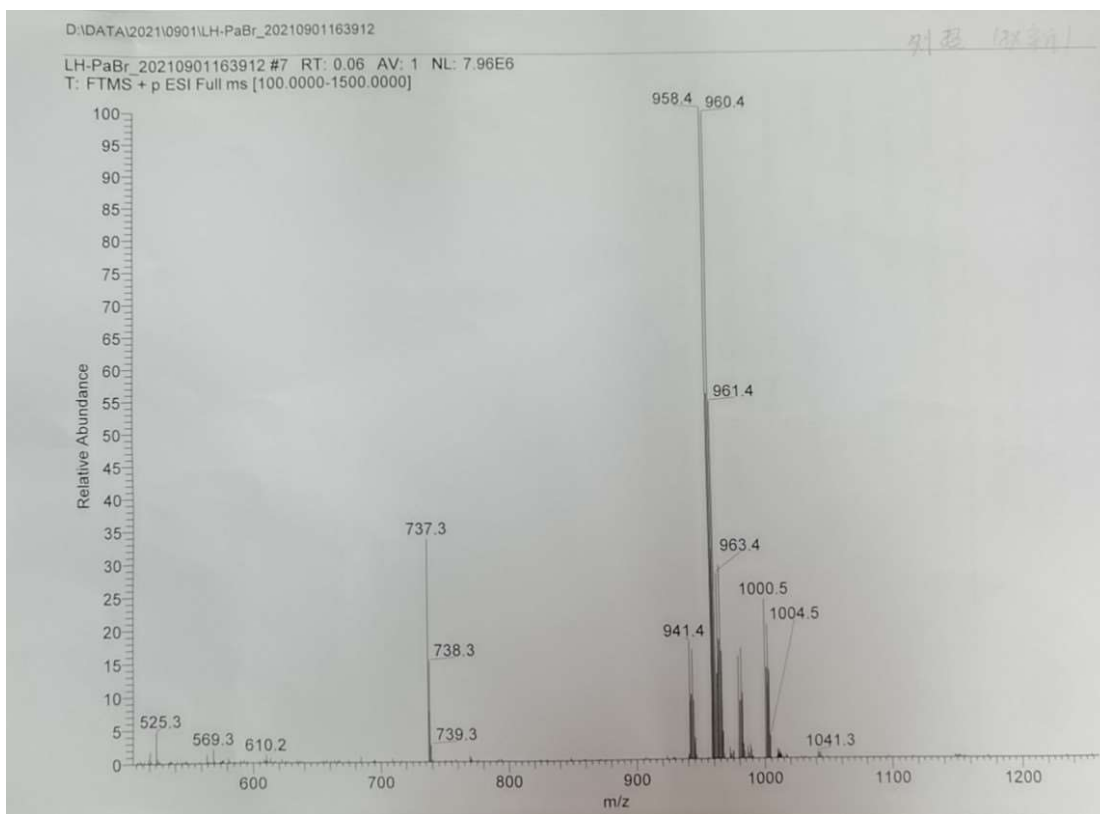


Figure S27. MS of P4.

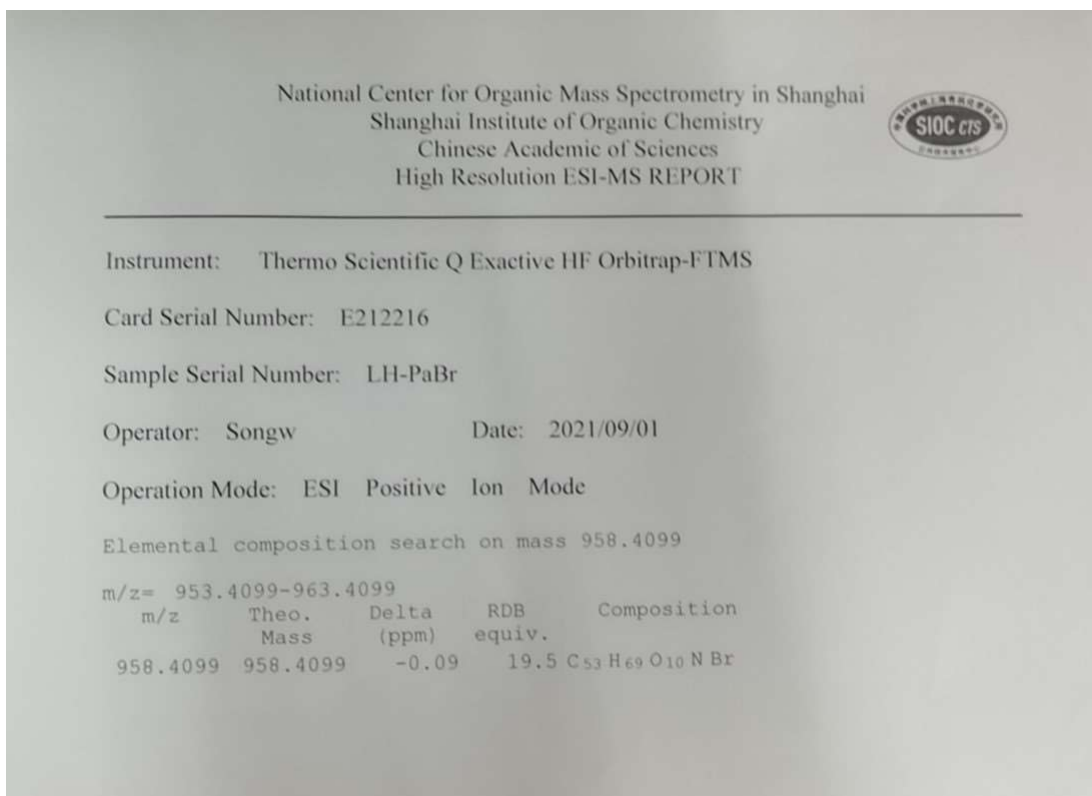


Figure S28. HRMS of P4.

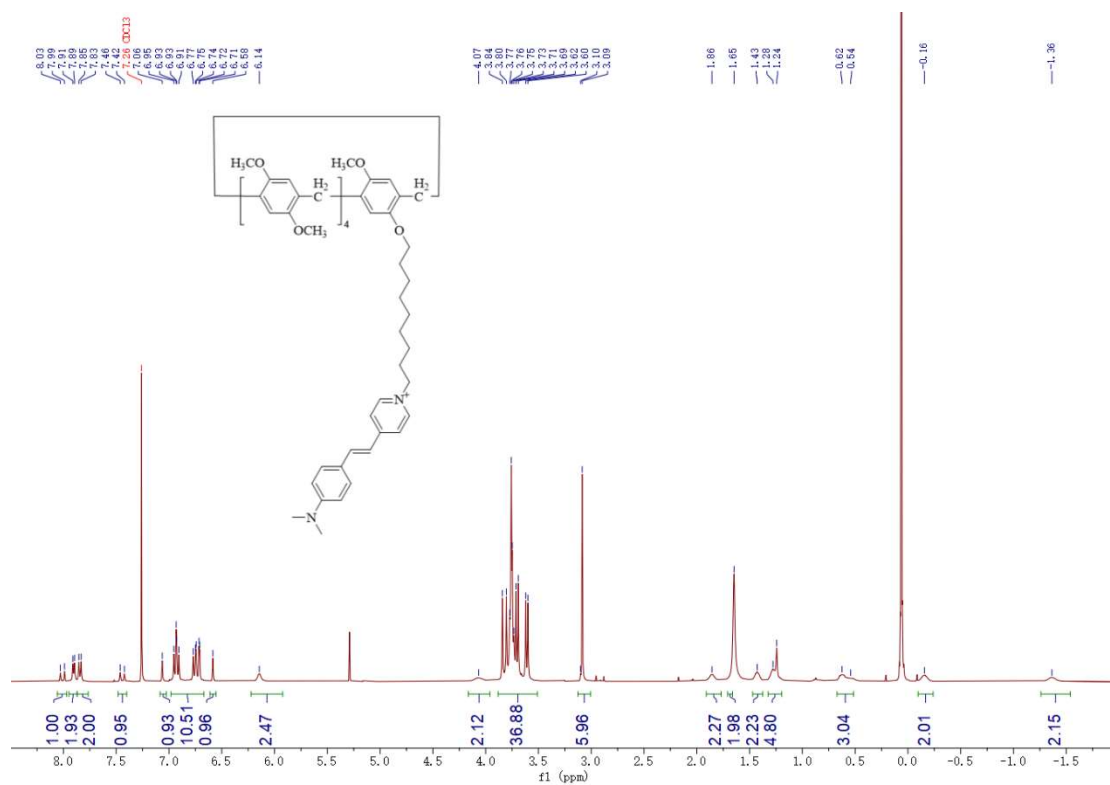


Figure S29. <sup>1</sup>H NMR of PI4.

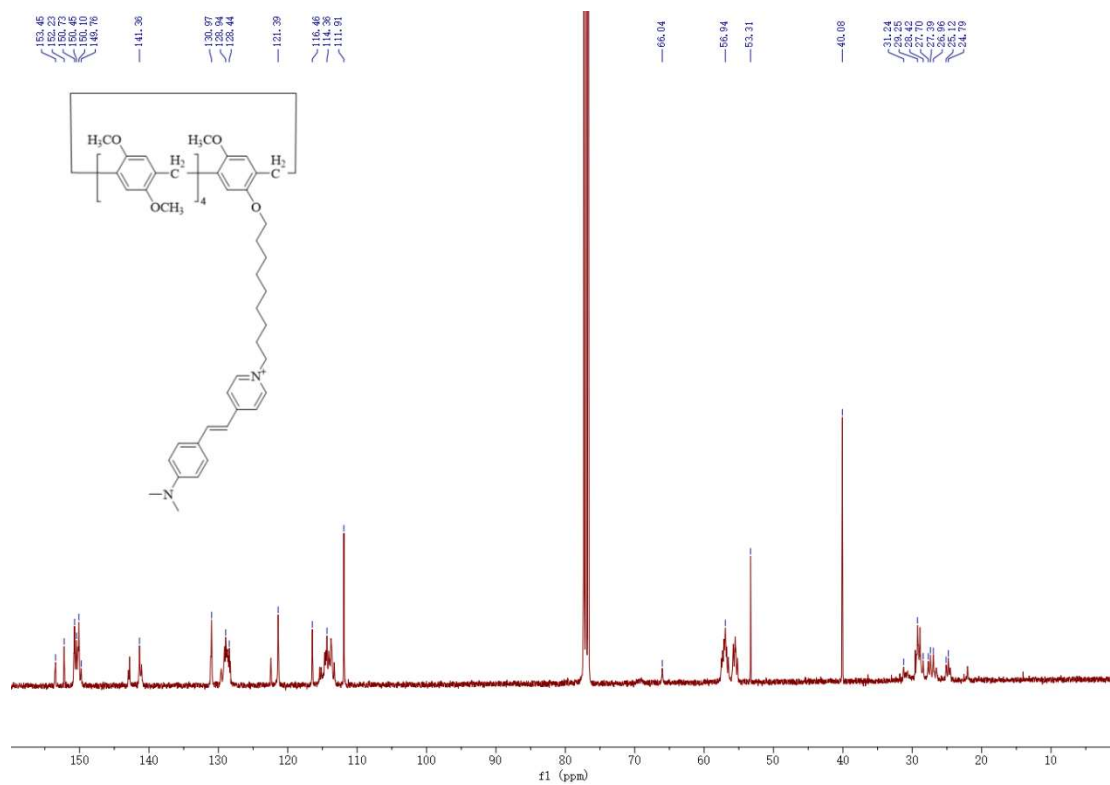
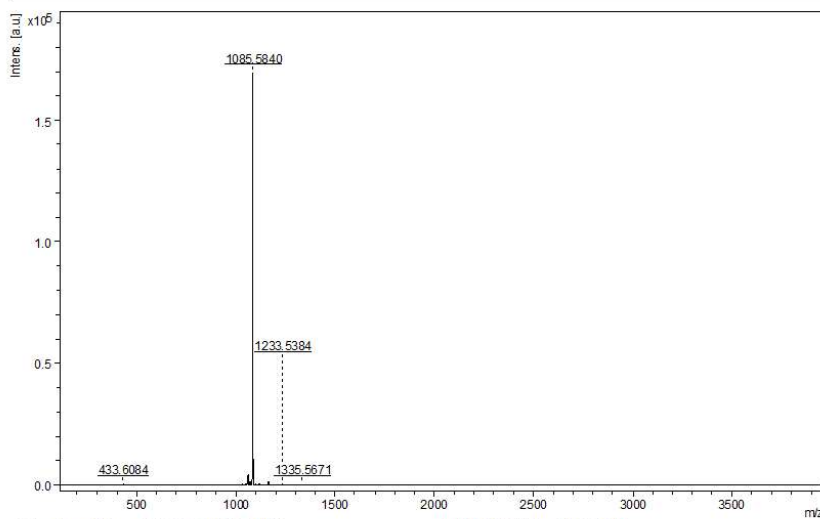


Figure S30. <sup>13</sup>C NMR of PI4.





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Laser beam focus 35  
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Number of shots 1000

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PIE delay 370 ns  
Ion source voltage 1 19 kV  
Ion source voltage 2 18.9 kV  
Lens voltage 8.6 kV  
Linear detector voltage 2.744 kV  
Deflection on  
Deflection mass  
Reflector voltage 1 21 kV  
Reflector voltage 2 9.6 kV  
Reflector detector volt. 1.702 kV

**Instrument**  
Instrument type autoflex  
Instrument serial 1857351.00824  
Name of computer FLEX-PC  
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Figure S31. HRMS of PI4.

## Linker length

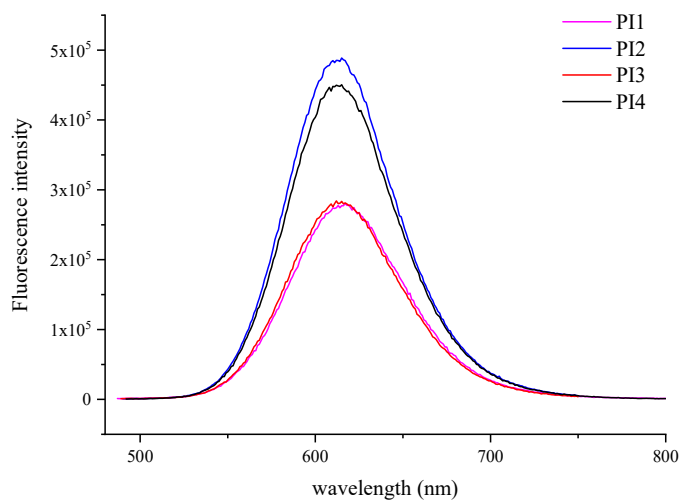


Fig. S32 Fluorescence emission spectra of the monosubstituted pillar[5]arene **PIn** ( $20 \mu\text{M}$ ) in DMSO at  $25^\circ\text{C}$ .

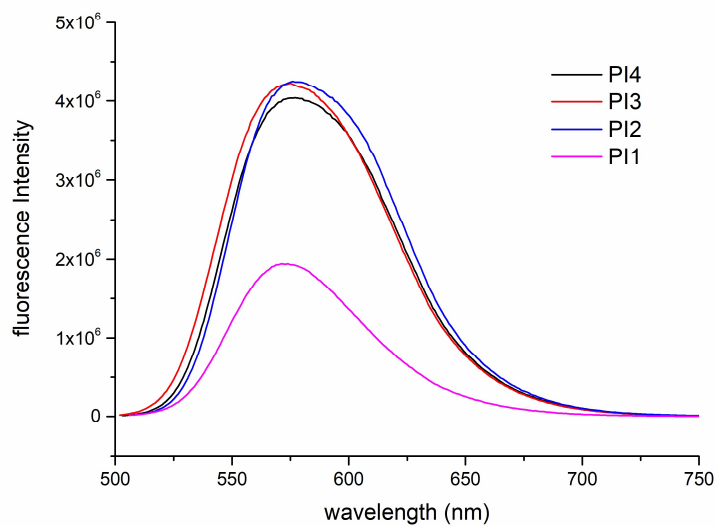


Fig. S33 Fluorescence emission spectra of the monosubstituted pillar[5]arene **PIn** ( $20 \mu\text{M}$ ) in chloroform at  $25^\circ\text{C}$ .

## Solvent

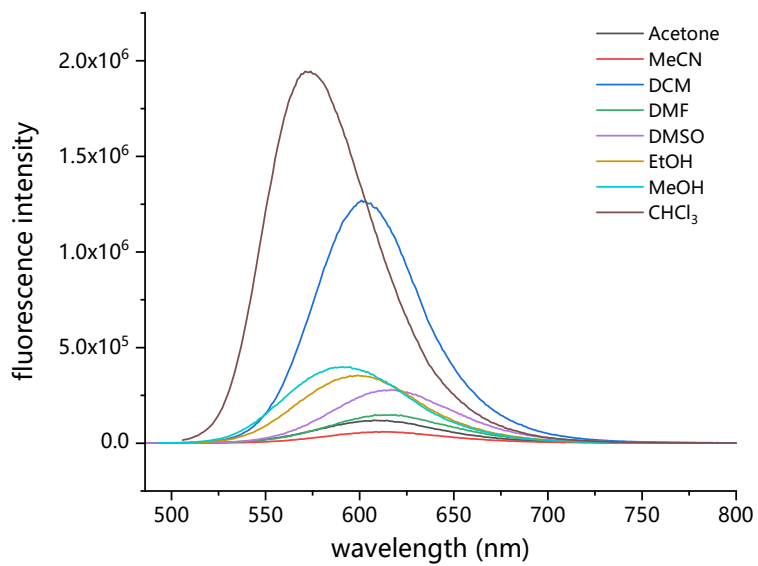


Fig. S34 Fluorescence emission spectra of **PI1** (20 μM) in various solvents.

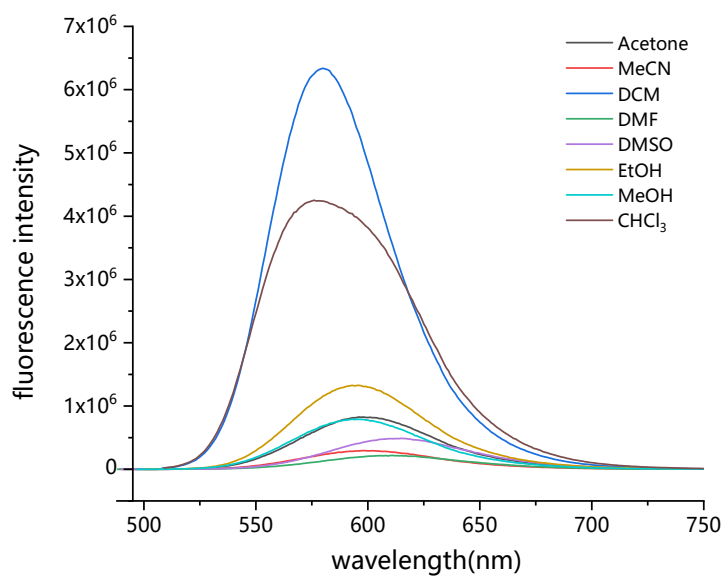


Fig. S35 Fluorescence emission spectra of **PI2** (20 μM) in various solvents.

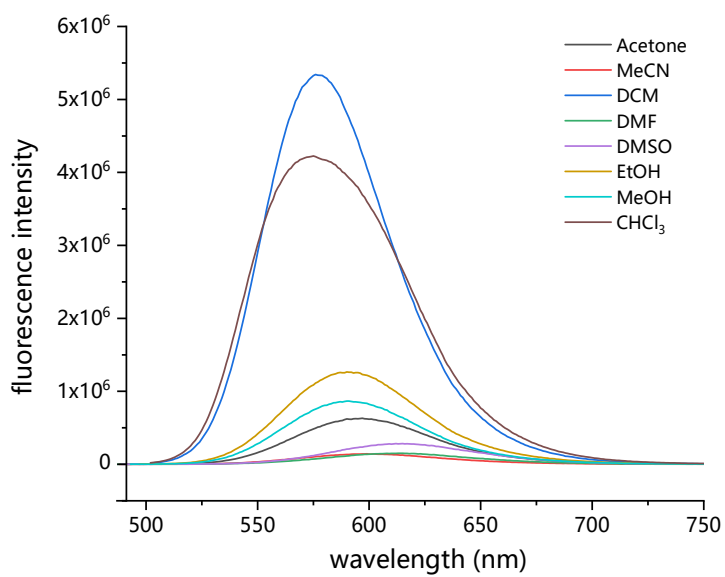


Fig. S36 Fluorescence emission spectra of **PI3** (20 μM) in various solvents.

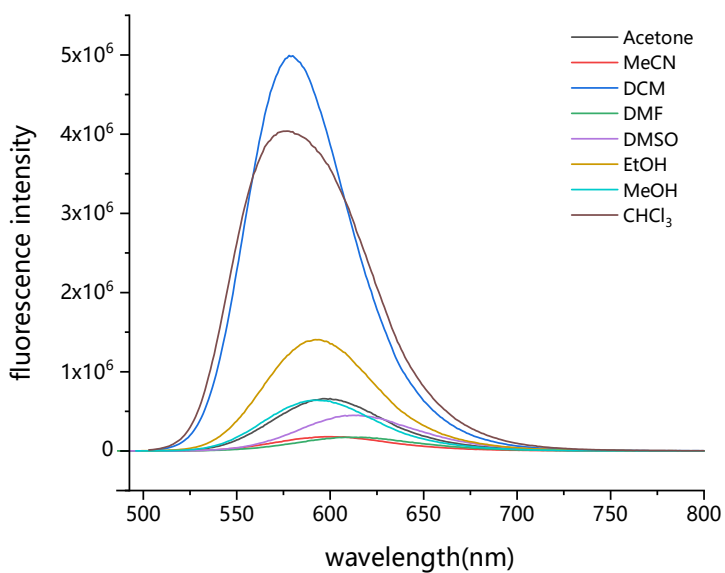


Fig. S37 Fluorescence emission spectra of **PI4** (20 μM) in various solvents.

## Stoke shift and quantum yield

Table S1. Stoke shifts of **PI**n and **DASP**.

solvent	Stoke shift (cm <sup>-1</sup> )				
	<b>PI4</b>	<b>PI3</b>	<b>PI2</b>	<b>PI1</b>	<b>DASP</b>
CHCl <sub>3</sub>	119048	120482	126582	128205	153846
DCM	120457	120482	121951	129890	133333
EtOH	97087	97087	94340	94340	99010
MeOH	83458	83458	84340	89286	94340
Acetone	75470	75470	80090	78740	81301
DMSO	71188	72464	74074	75429	78740
DMF	74758	74942	75188	76336	79365
MeCN	72645	72645	74034	75188	80000

The fluorescence quantum yield ( $\phi$ ) is determined with the following equation-1,

$$\phi_F = \phi_{FR} (n^2 \times F \times A_R) / (n_R^2 \times F_R \times A) \quad (\text{equation-1})$$

Where  $\phi_{FR}$  is the fluorescence quantum yield of the reference compound (luciferin in ethanol).  $F$  and  $F_R$  are the integrated values of the fluorescence spectra for the sample and reference,  $A$  and  $A_R$  are the absorbance at the excitation wavelength, and  $n$  and  $n_R$  are the refractive indexes of the solvents.

# NOESY

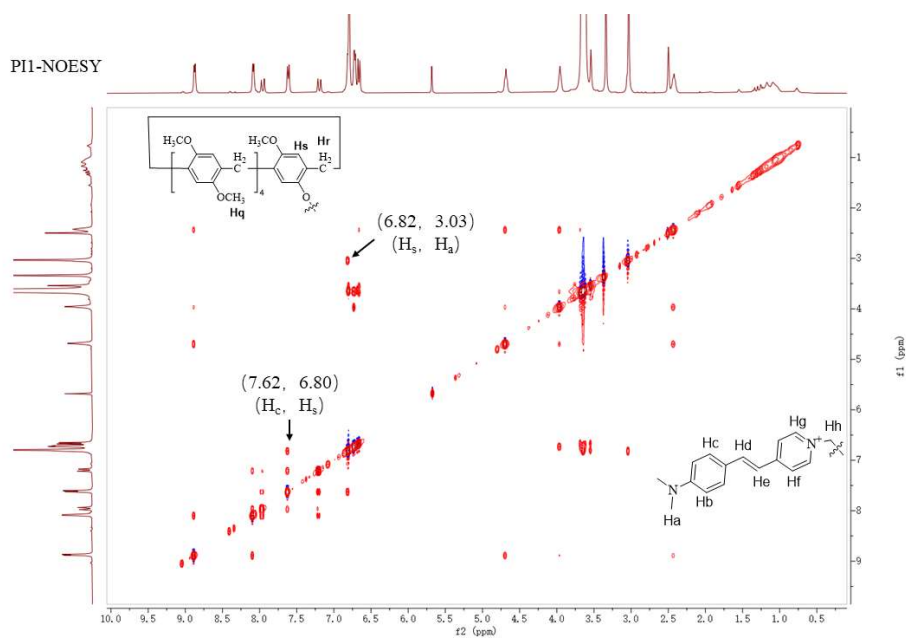


Fig. S38 NOESY spectrum of **PI1** (50 mM, in DMSO)

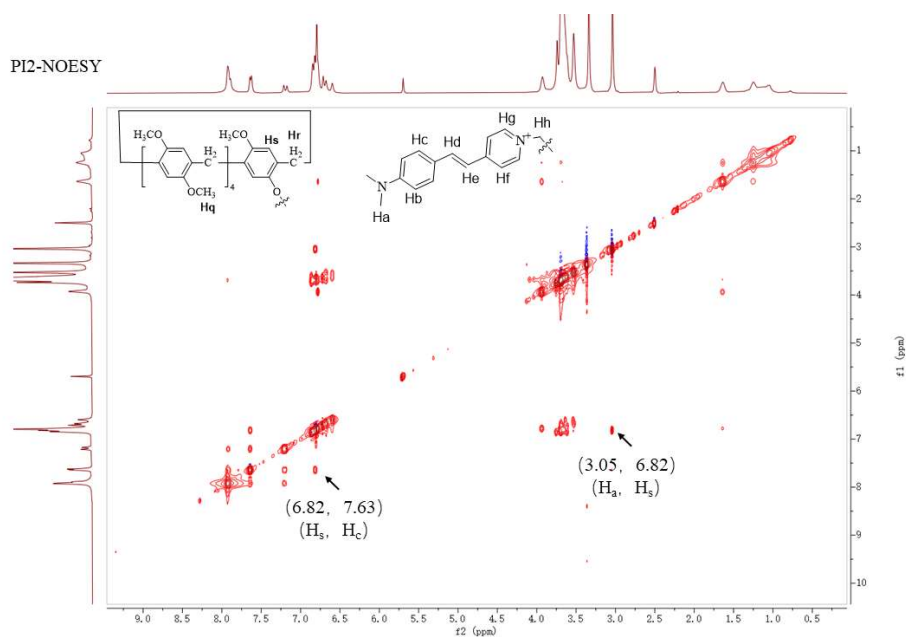


Fig. S39 NOESY spectrum of **PI2** (50 mM, in DMSO)

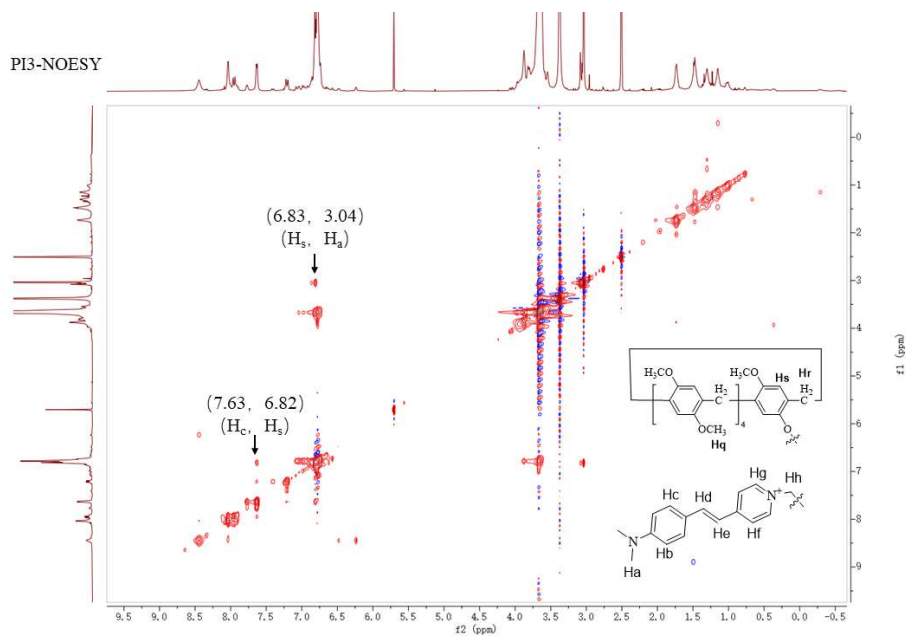


Fig. S40 NOESY spectrum of **PI3** (50 mM, in DMSO)

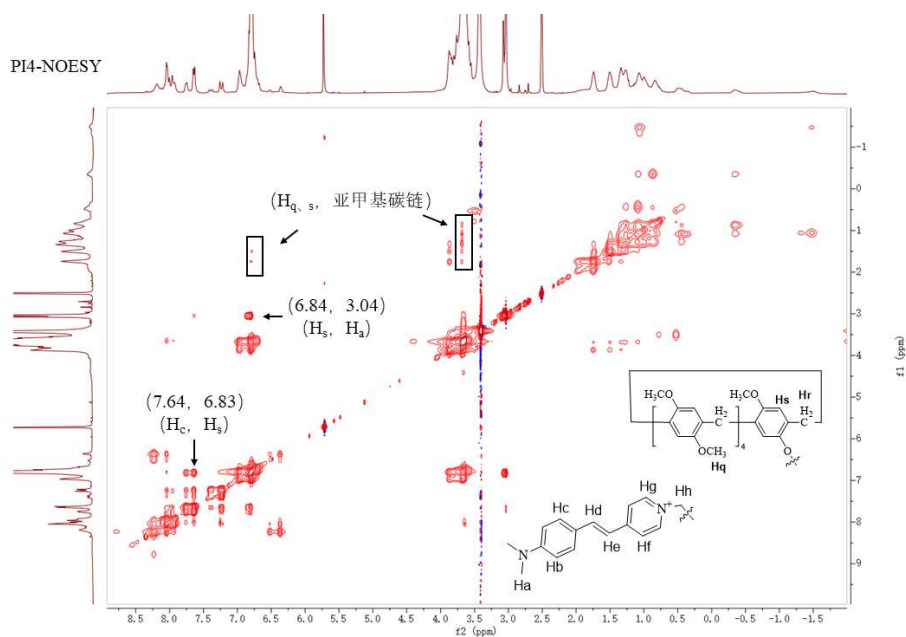


Fig. S41 NOESY spectrum of **PI4** (50 mM, in DMSO)

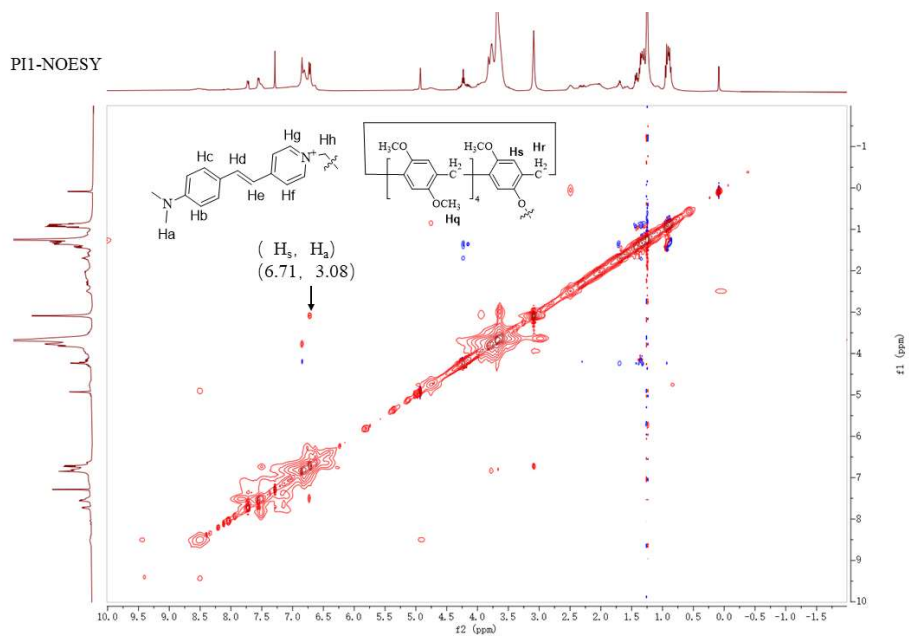


Fig. S42 NOESY spectrum of **PI1** (50 mM, in CDCl<sub>3</sub>)

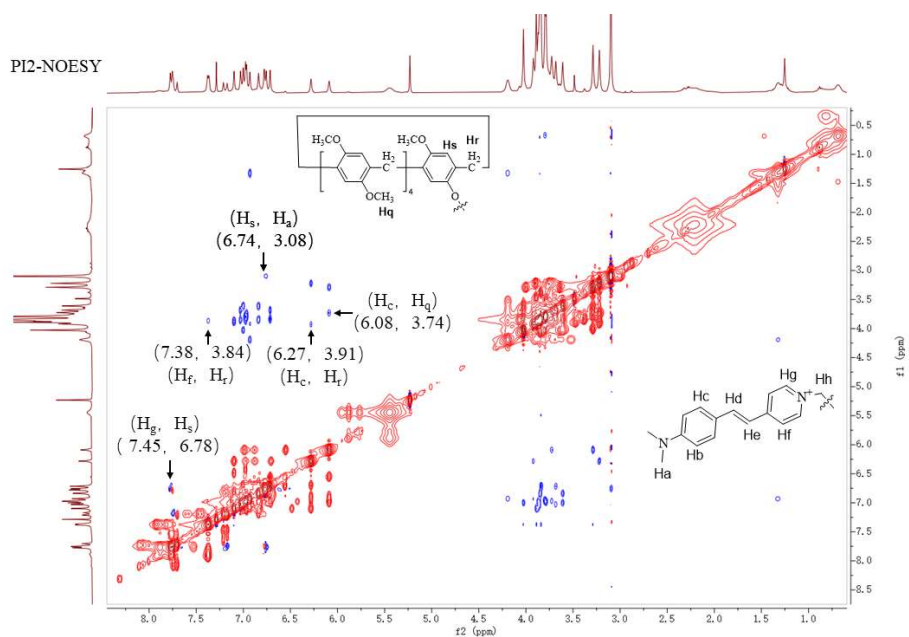


Fig. S43 NOESY spectrum of **PI2** (50 mM, in CDCl<sub>3</sub>)



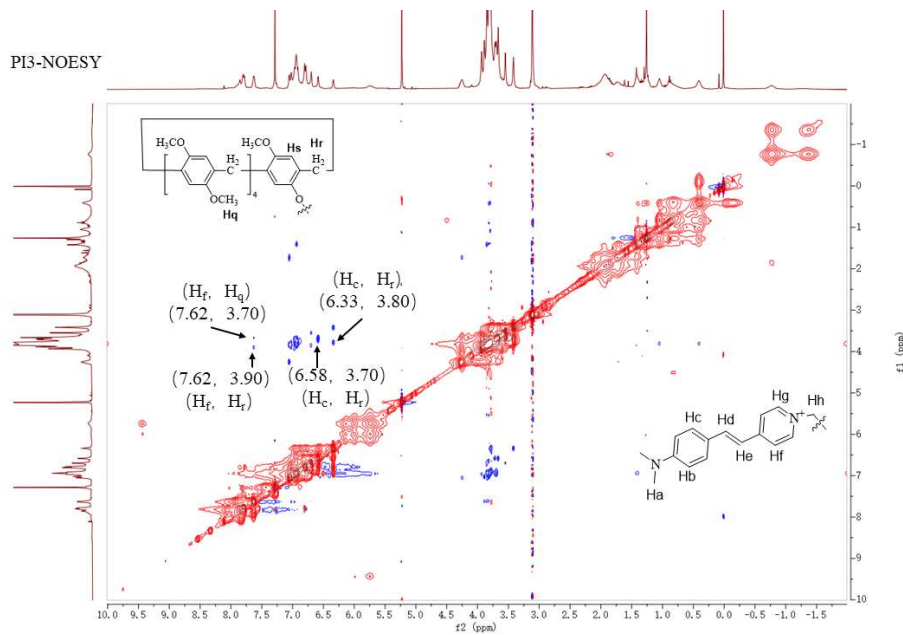


Fig. S44 NOESY spectrum of **PI3** (50 mM, in  $CDCl_3$ )

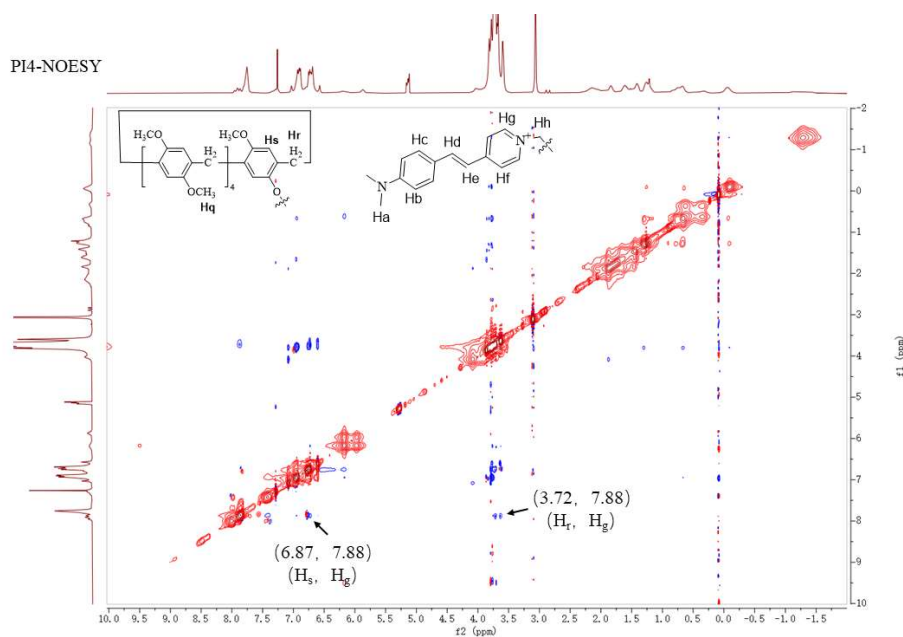


Fig. S45 NOESY spectrum of **PI4** (50 mM, in  $CDCl_3$ )

## Temperature

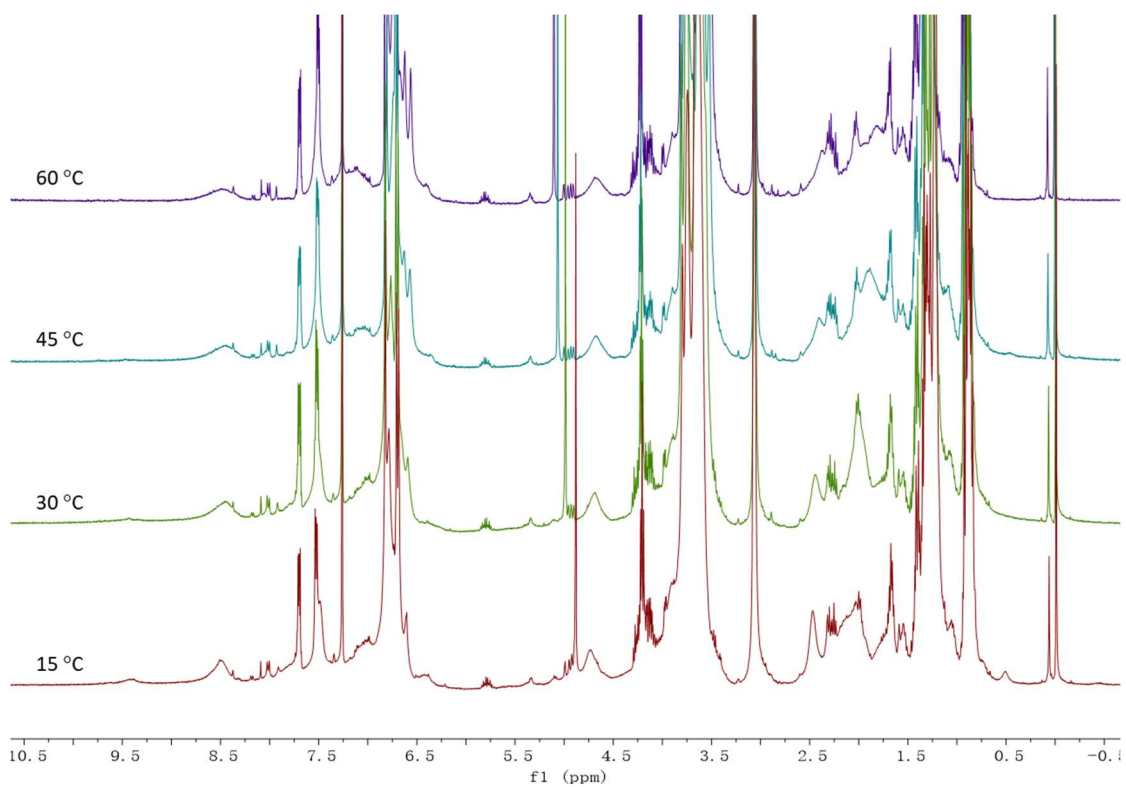


Fig. S46 Partial  $^1\text{H}$  NMR spectra of **PI1** at various temperature in  $\text{CDCl}_3$ .

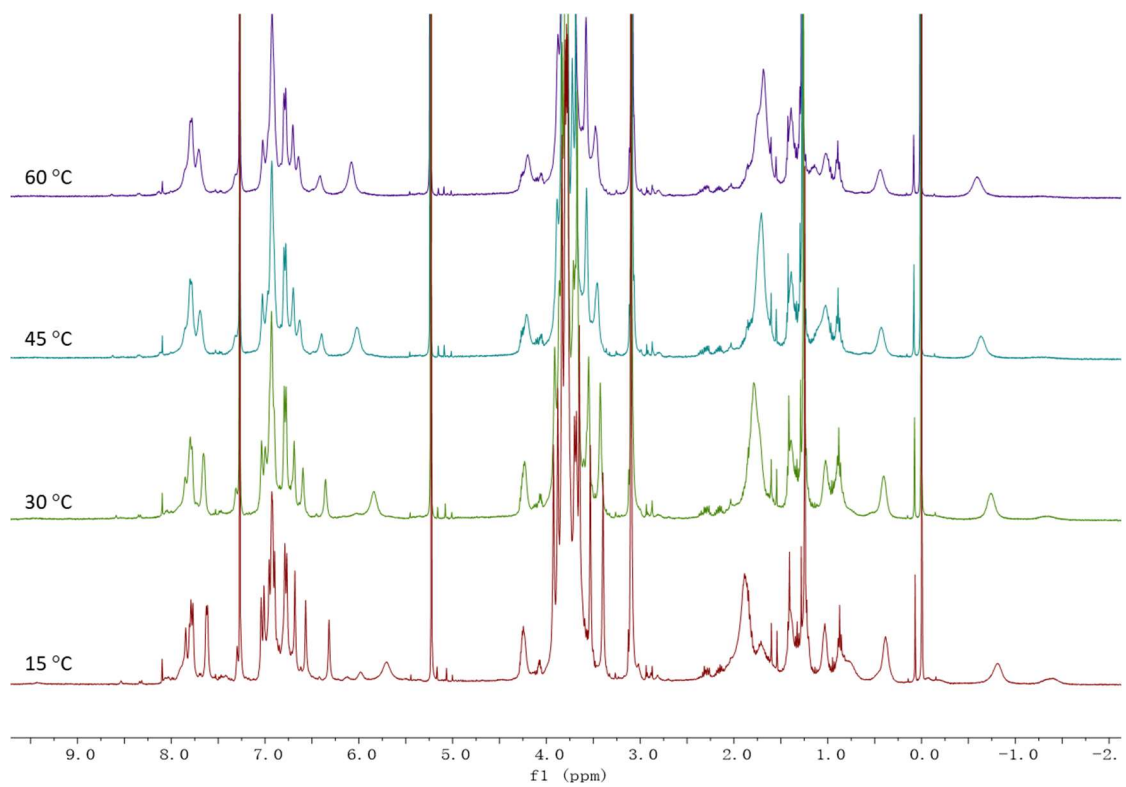


Fig. S47 Partial  $^1\text{H}$  NMR spectra of **PI3** at various temperature in  $\text{CDCl}_3$ .

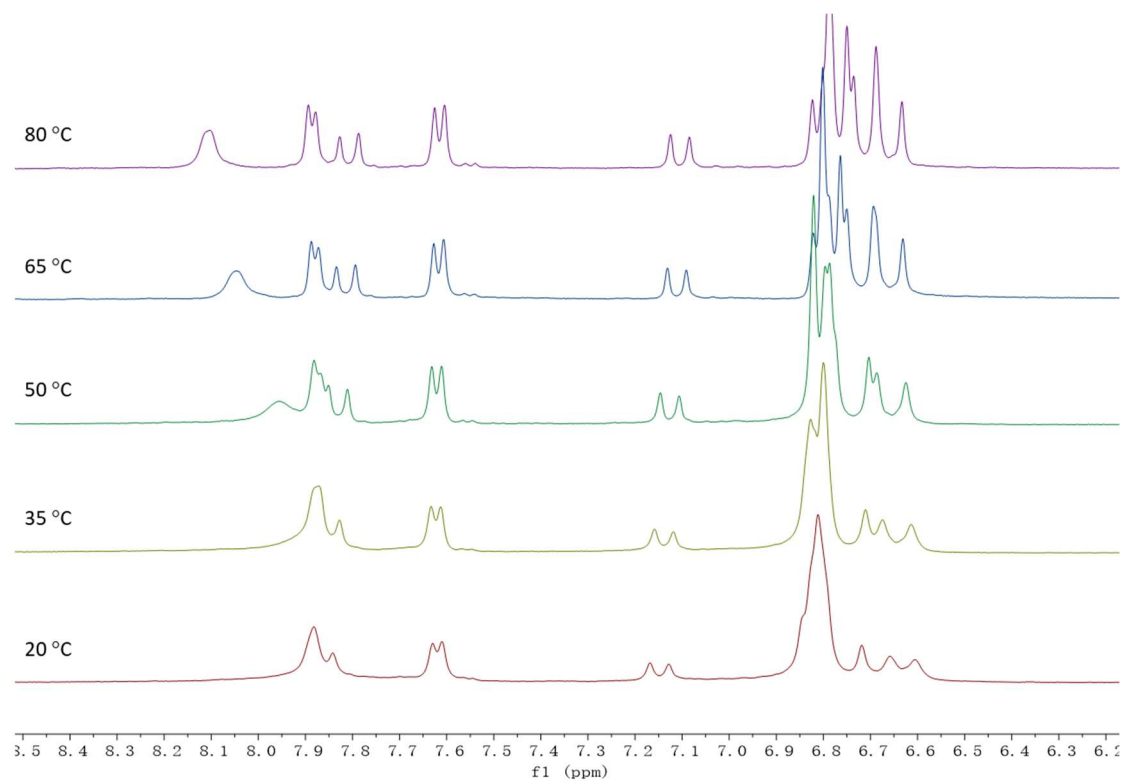


Fig. S48 Partial  $^1\text{H}$  NMR spectra of **PI2** at various temperature in DMSO.

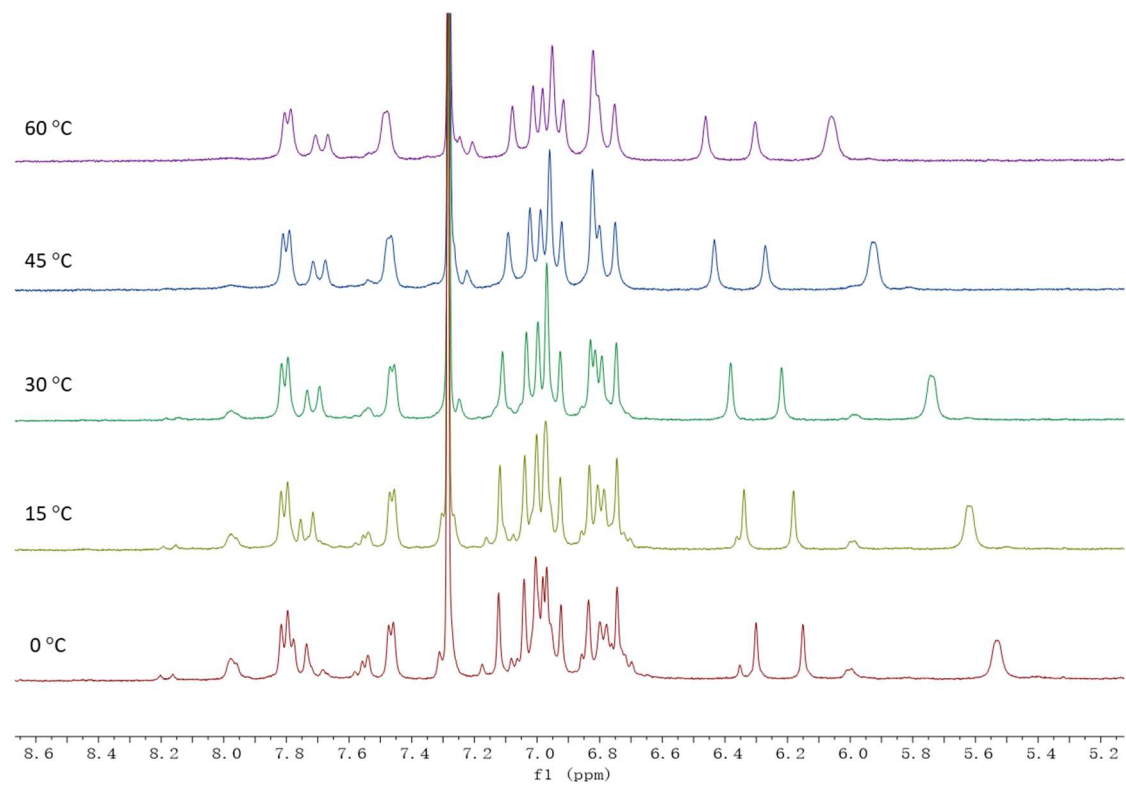


Fig. S49 Partial  $^1\text{H}$  NMR spectra of **PI2** at various temperature in  $\text{CDCl}_3$ .

## Temperature

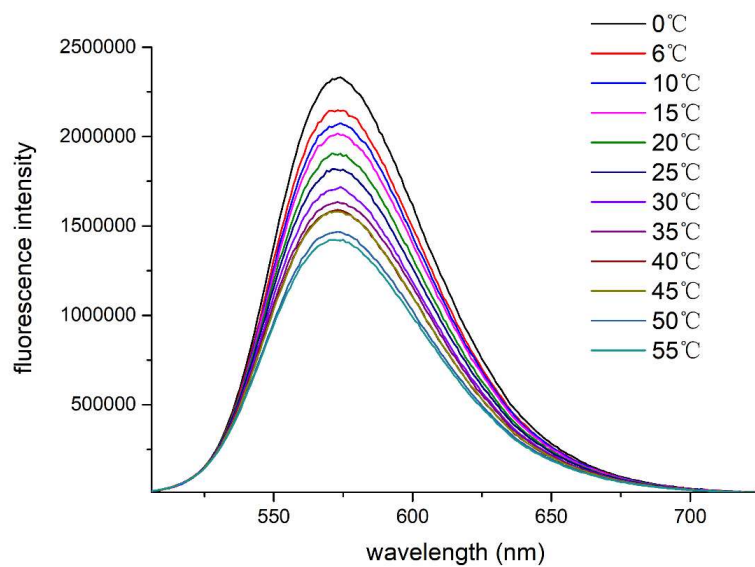


Fig. S50 Fluorescence emission spectra of **PI1** (20 μM) at various temperature in chloroform.

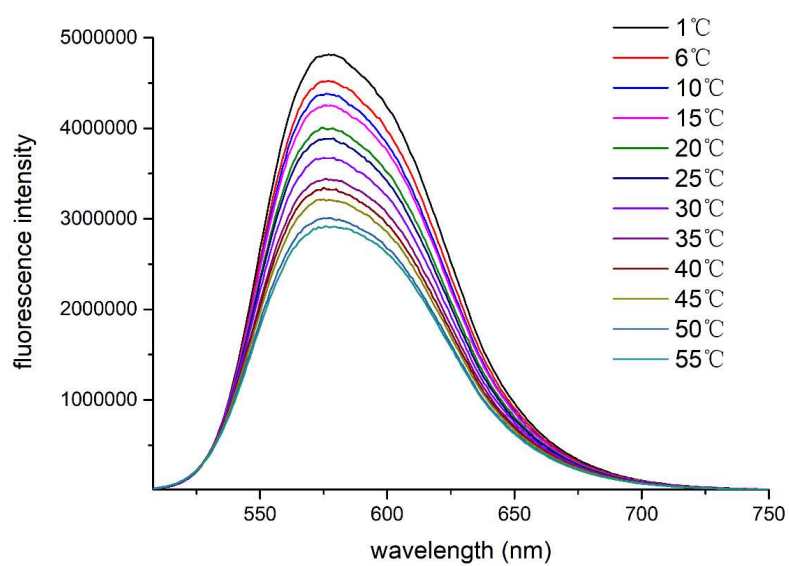


Fig. S51 Fluorescence emission spectra of **PI2** (20 μM) at various temperature in chloroform.

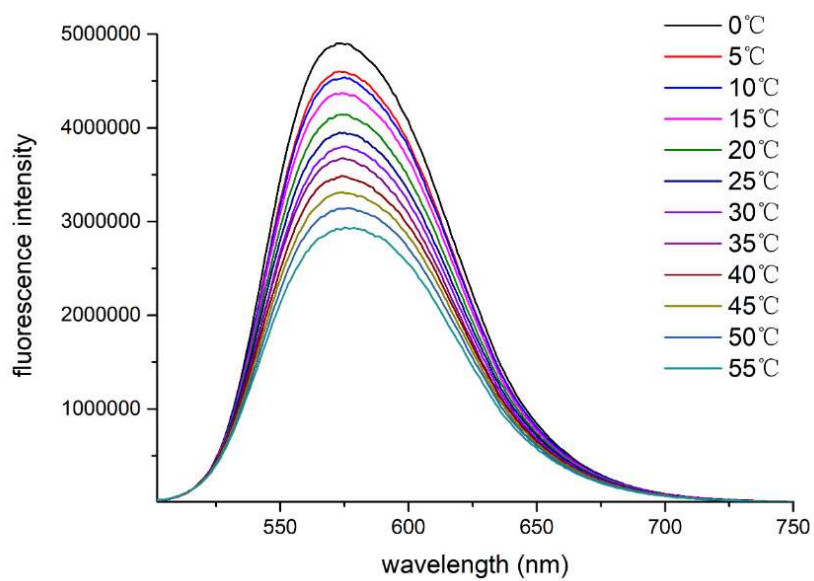


Fig. S52 Fluorescence emission spectra of **PI3** (20 μM) at various temperature in chloroform.

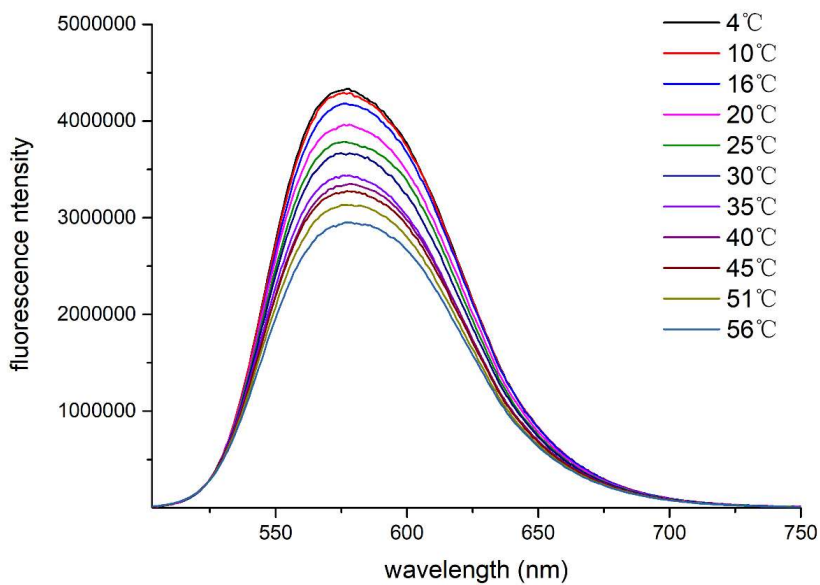


Fig. S53 Fluorescence emission spectra of **PI4** (20 μM) at various temperature in chloroform.

## Concentration

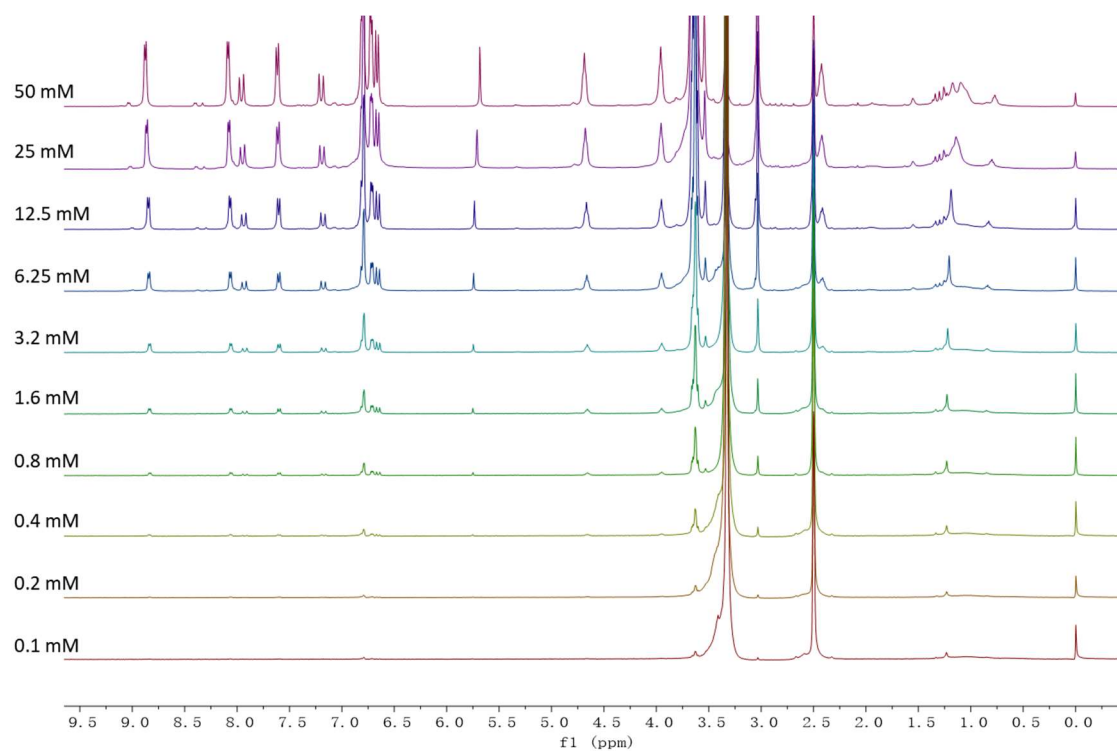


Fig. S54 **PI1** in DMSO at various concentration.

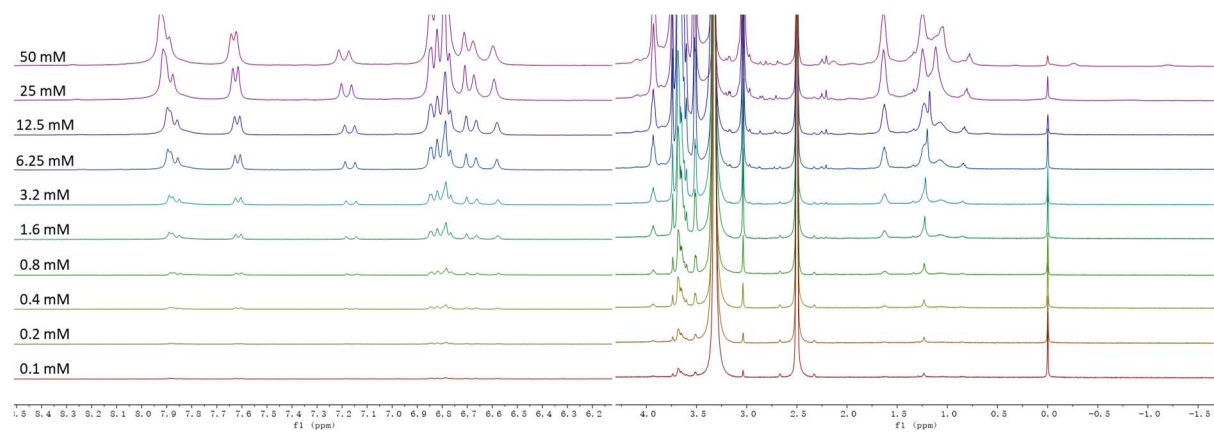


Fig. S55 **PI2** in DMSO at various concentration.

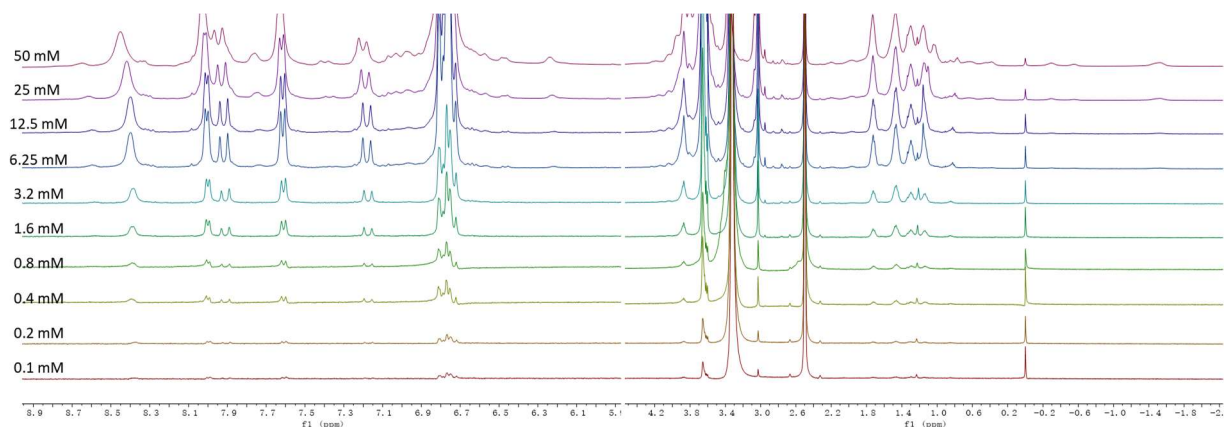


Fig. S56 **PI3** in DMSO at various concentration.

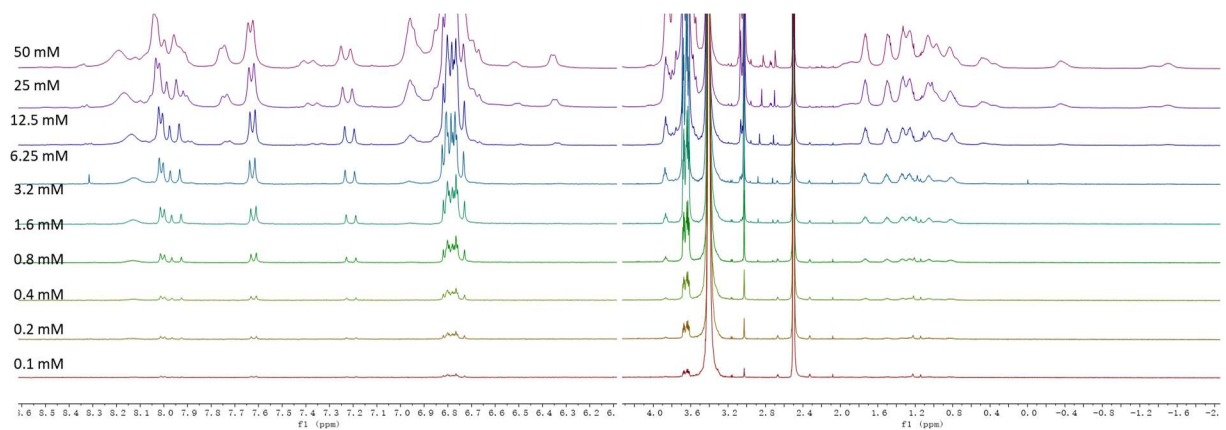


Fig. S57 **PI4** in DMSO at various concentration.

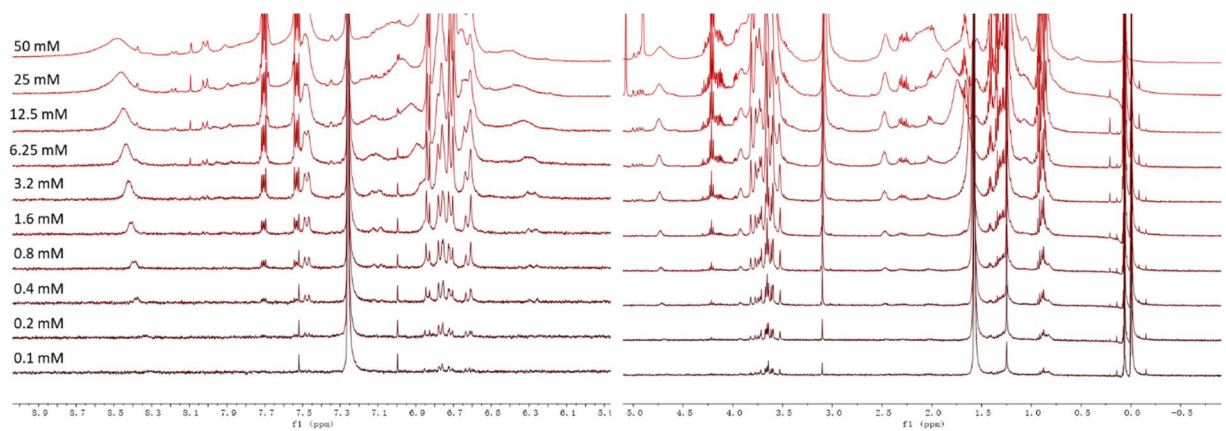


Fig. S58 **PI1** in CDCl<sub>3</sub> at various concentration.

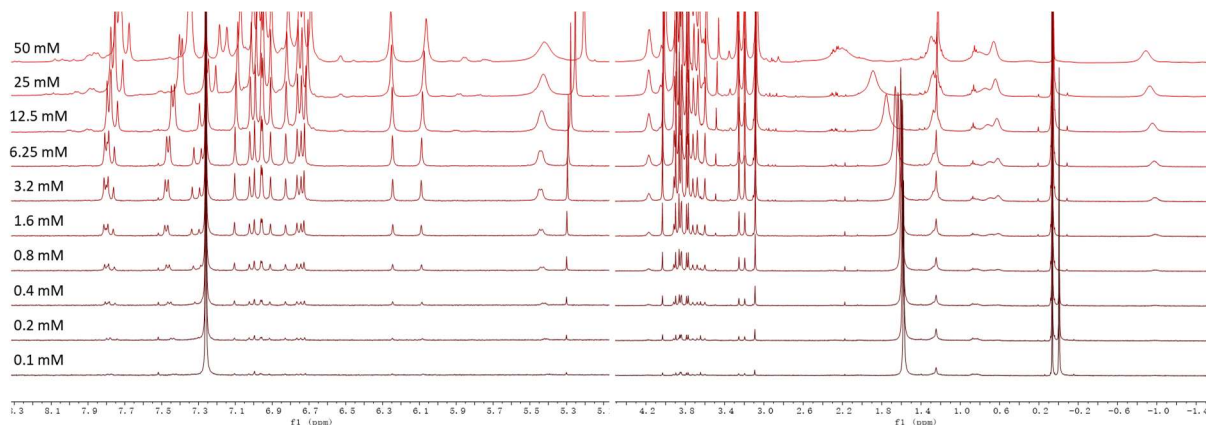


Fig. S59 **PI2** in CDCl<sub>3</sub> at various concentration.

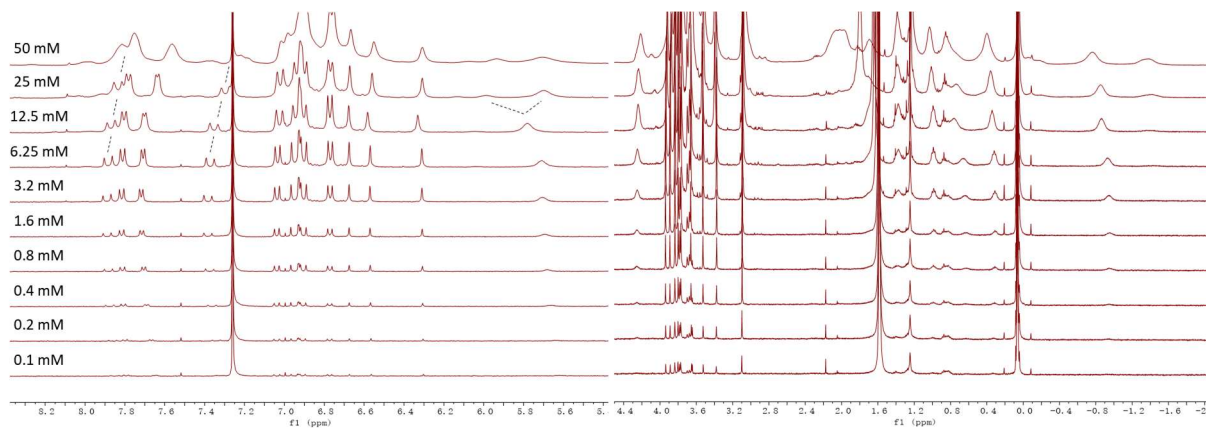


Fig. S60 **PI3** in CDCl<sub>3</sub> at various concentration.



## 2D DOSY

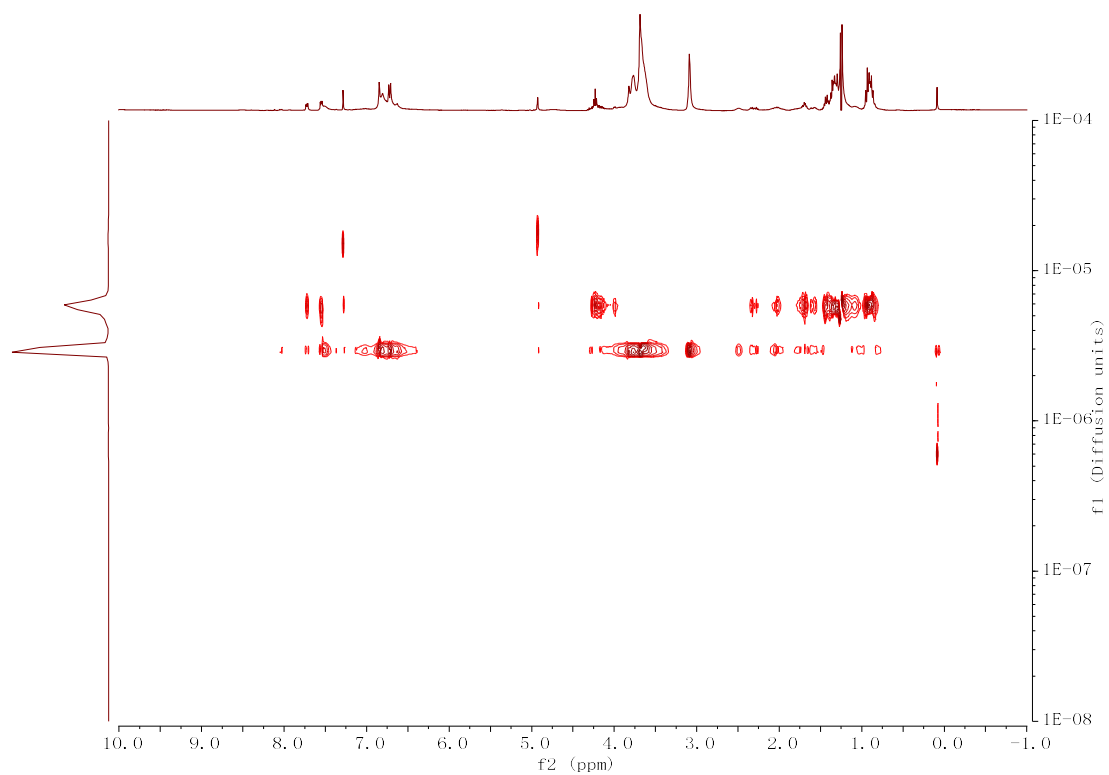


Fig. S61 2D Dosl of **PI1** in CDCl<sub>3</sub>.

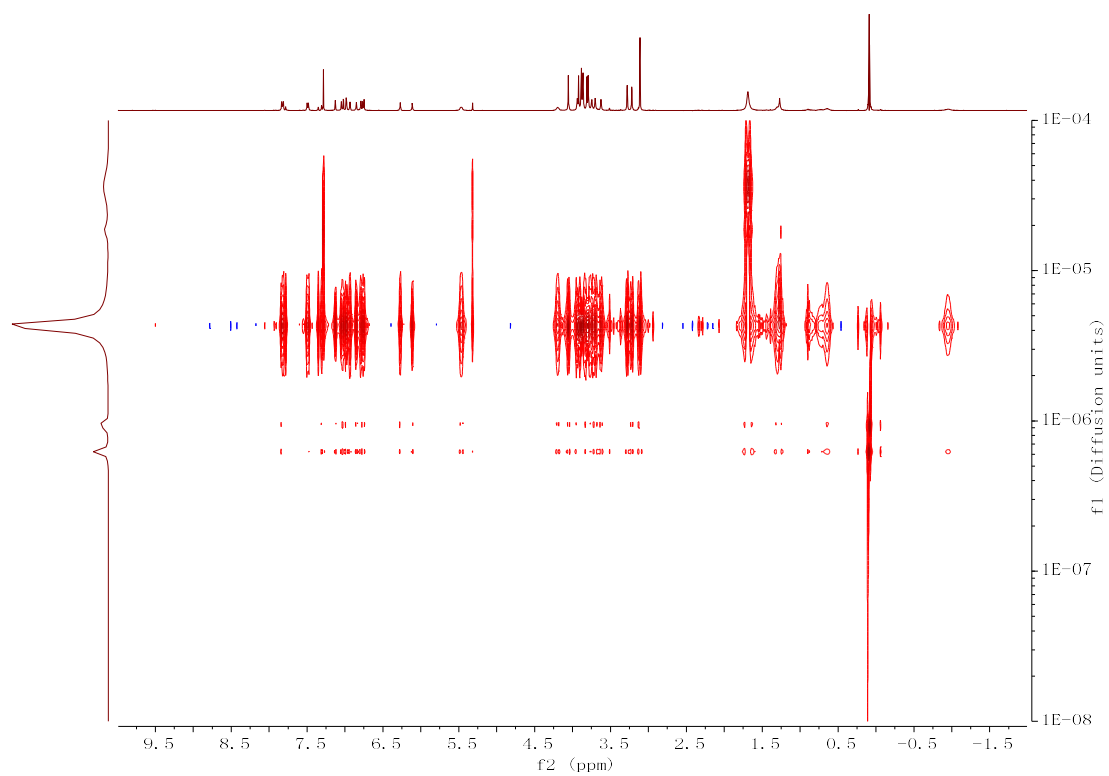


Fig. S62 2D Dosl of **PI2** in CDCl<sub>3</sub>.

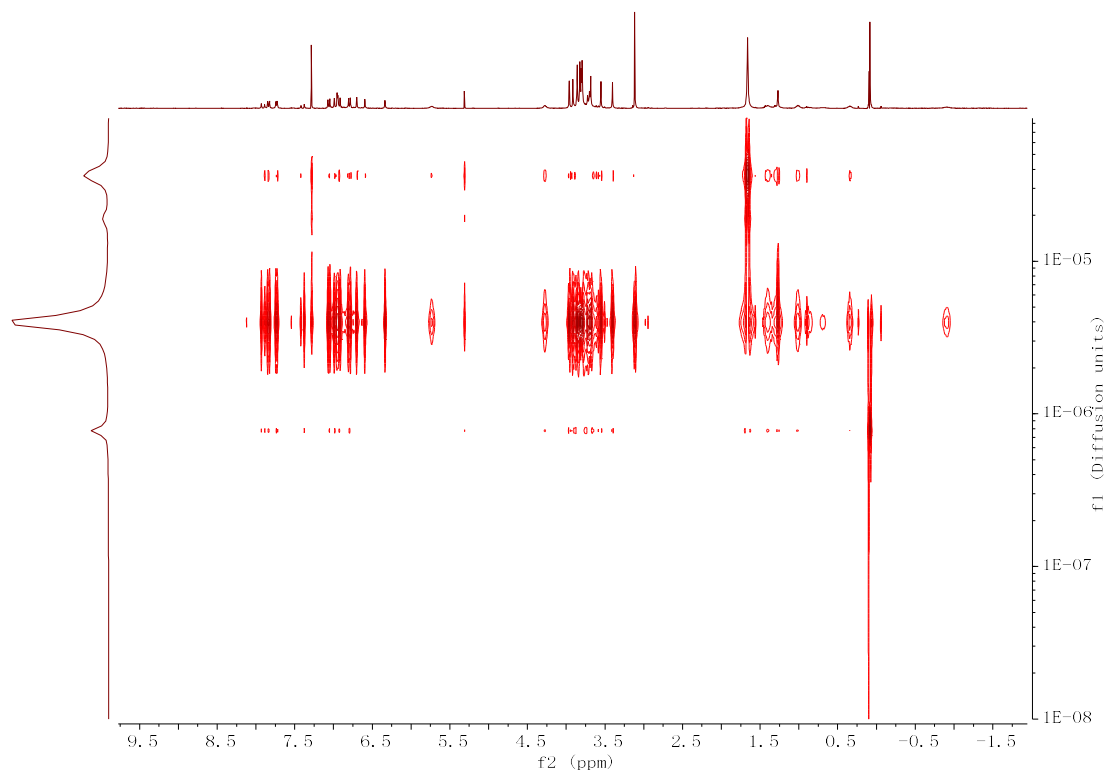


Fig. S63 2D Dosy of **PI3** in  $\text{CDCl}_3$ .

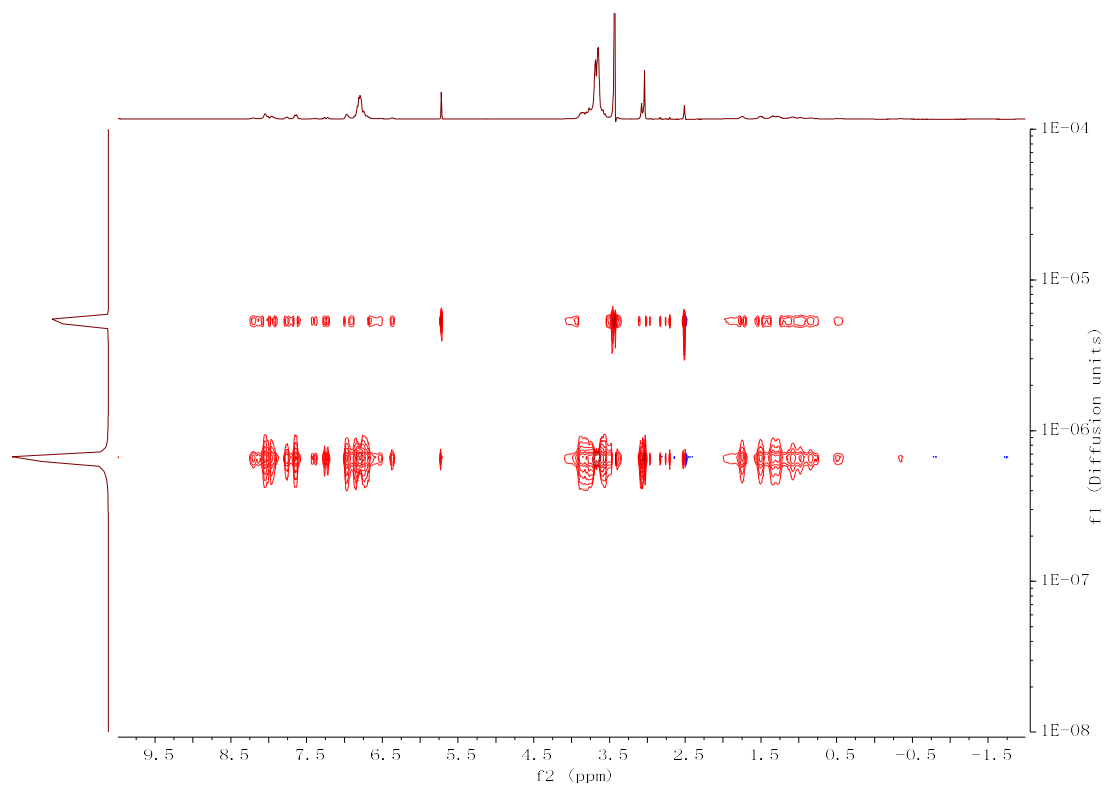


Fig. S64 2D Dosy of **PI4** in DMSO.