Electronic Supplementary Information

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

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## Characterization

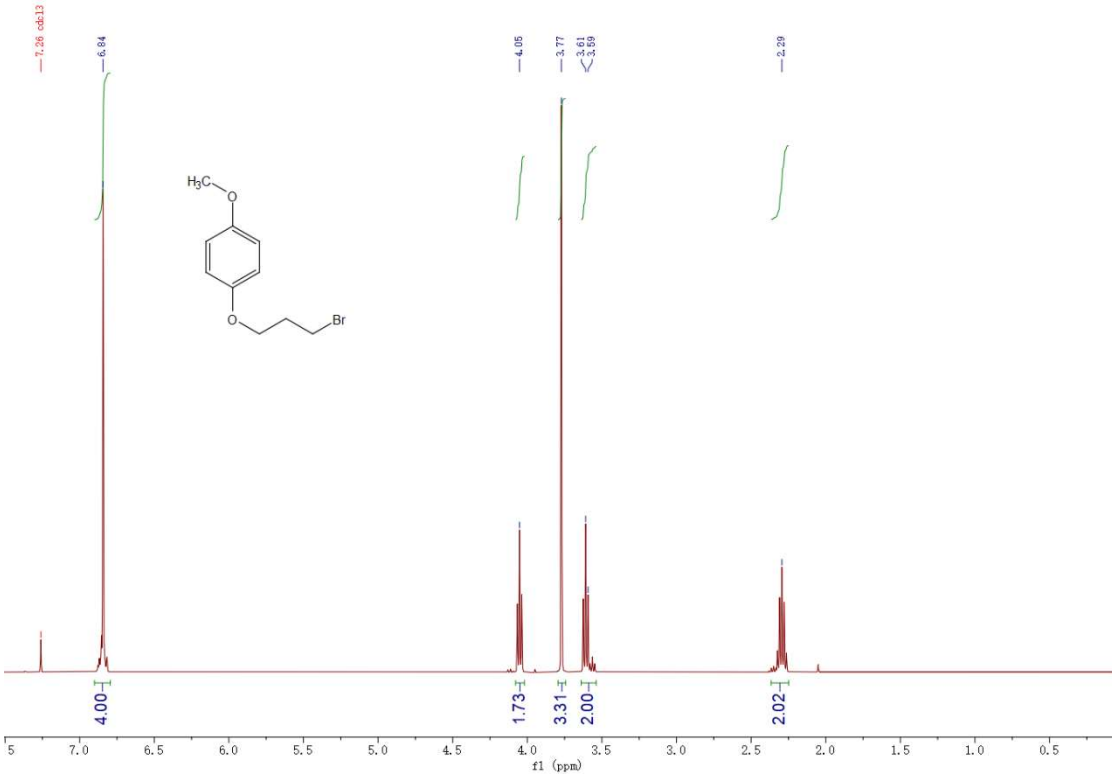


Figure S1. $^{1}$H NMR of M1.

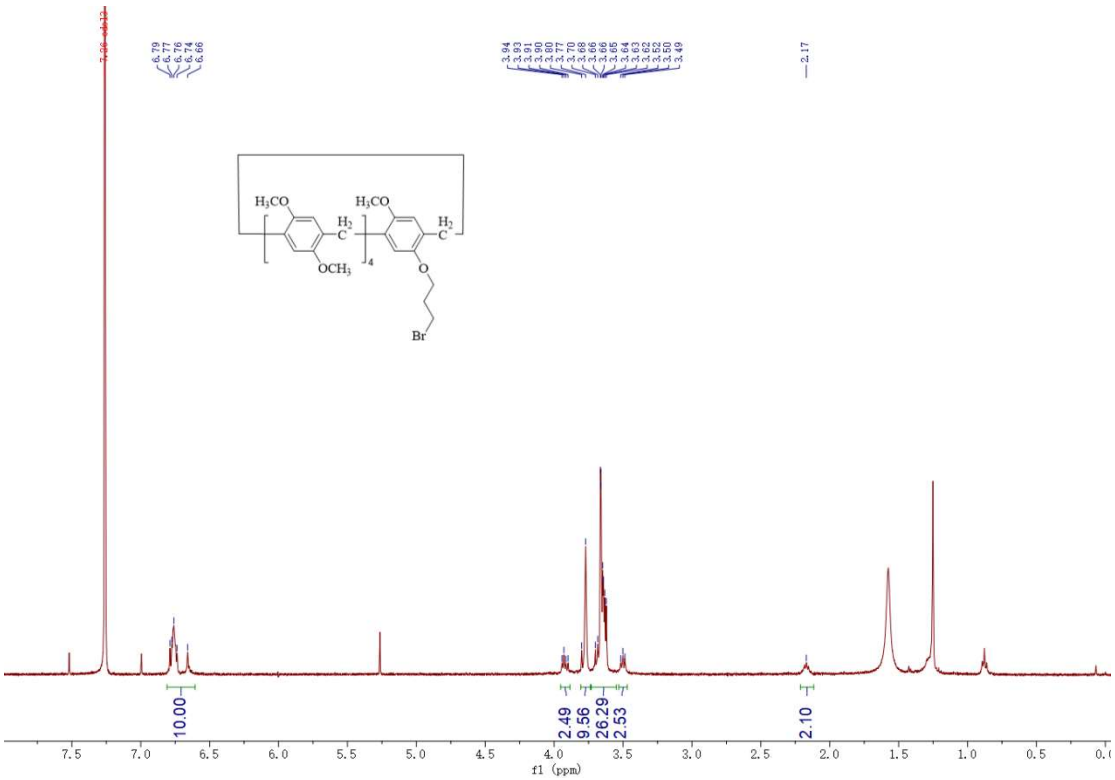


Figure S2. $^{1}$H NMR of P1.

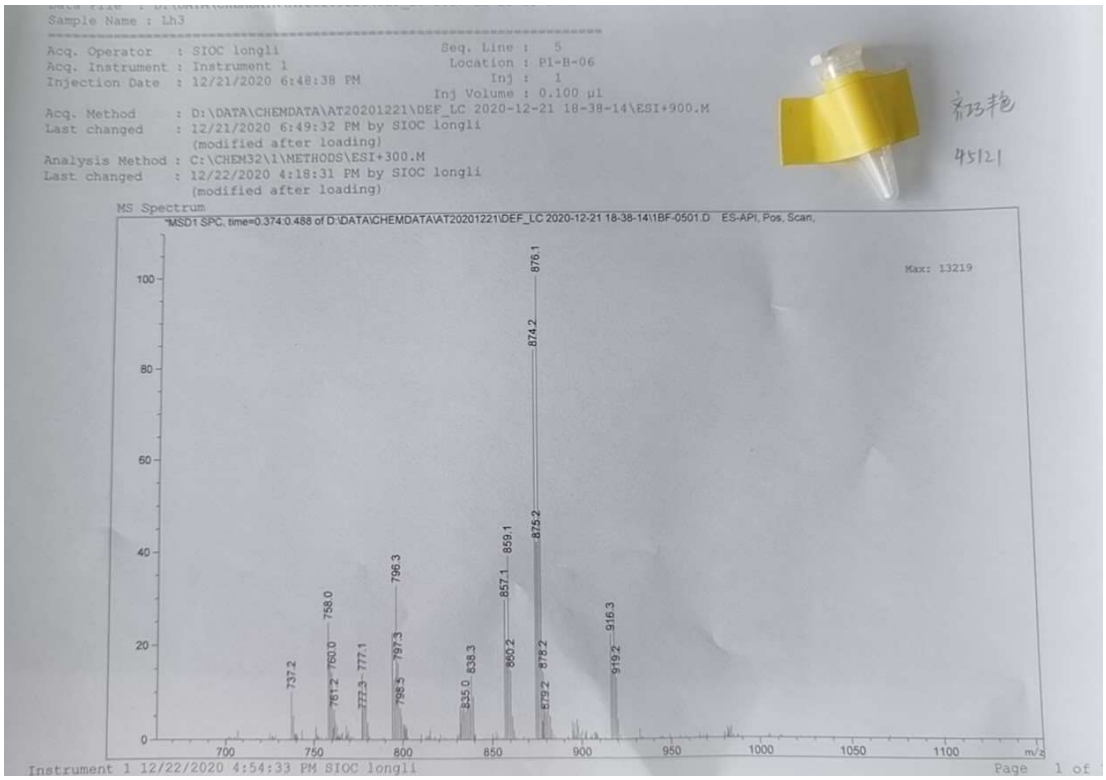


Figure S3. MS of P1.

National Center for Organic Mass Spectrometry in Shanghai
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High Resolution ESI-MS REPORT

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E210027

Sample Serial Number: Lh3

Operator: Songw Date: 2021/01/05

Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 874.32

m/z= 869.32-879.32

| m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition |
|---|---|---|---|---|
| 874.3150 | 874.3160 | -1.18 | 19.5 | $C_{47}H_{57}O_{10}NBr$ |
| | 874.3187 | -4.25 | 24.0 | $C_{50}H_{55}O_7N_2Br$ |

Figure S4. HRMS of P1.

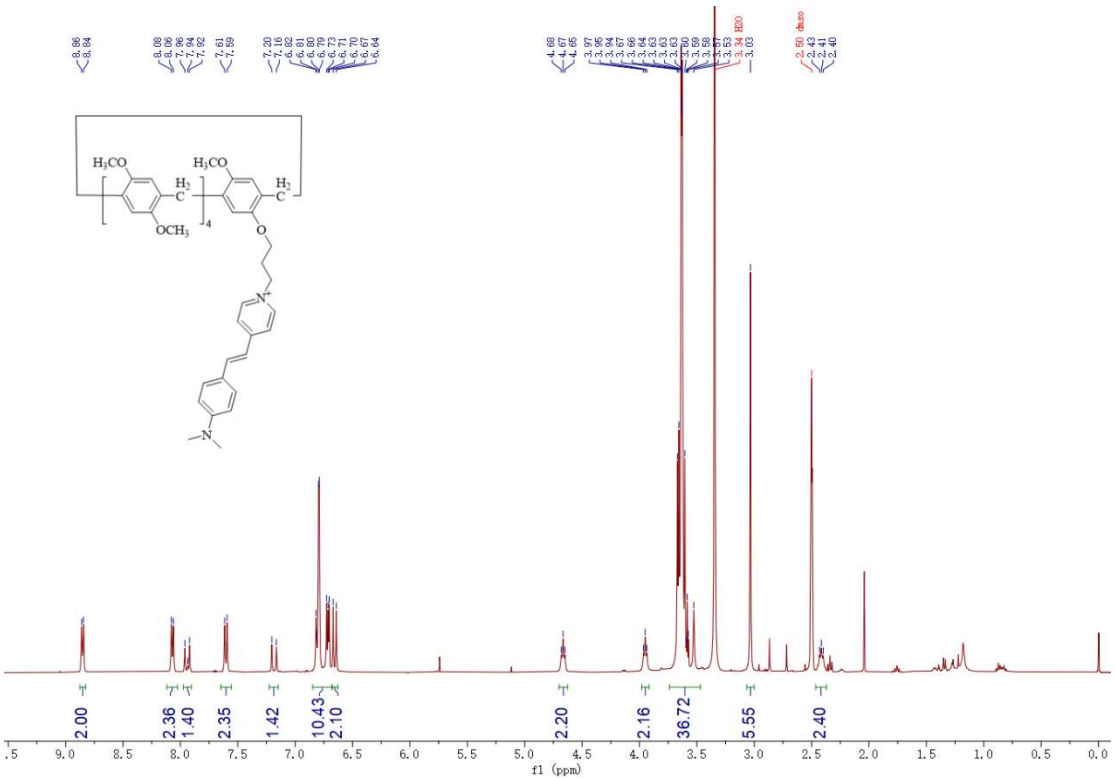



Figure S5. $^{1}$H NMR of PI1.

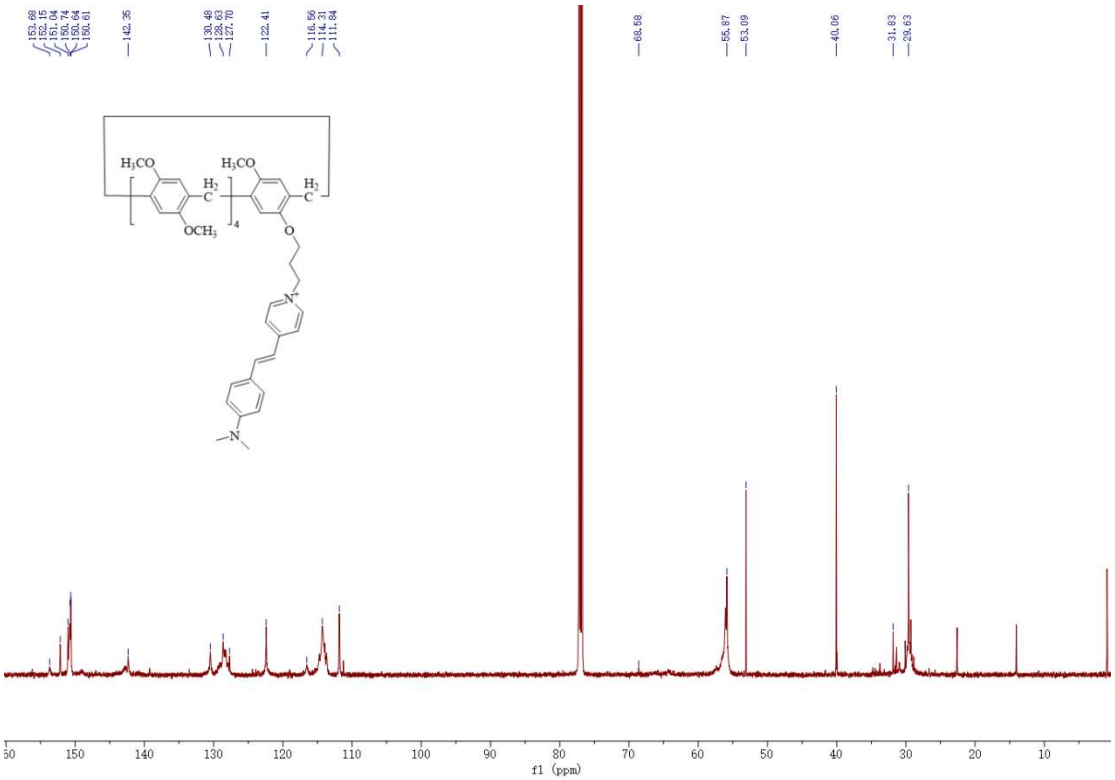



Figure S6. $^{13}$C NMR of PI1.

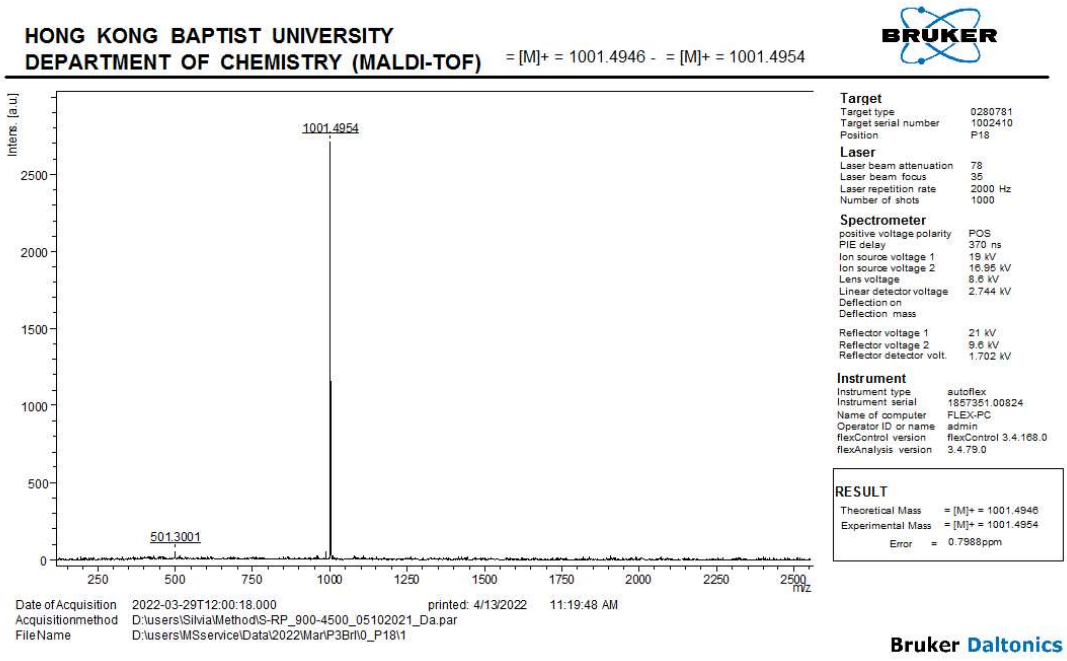



Figure S7. HRMS of PI1.

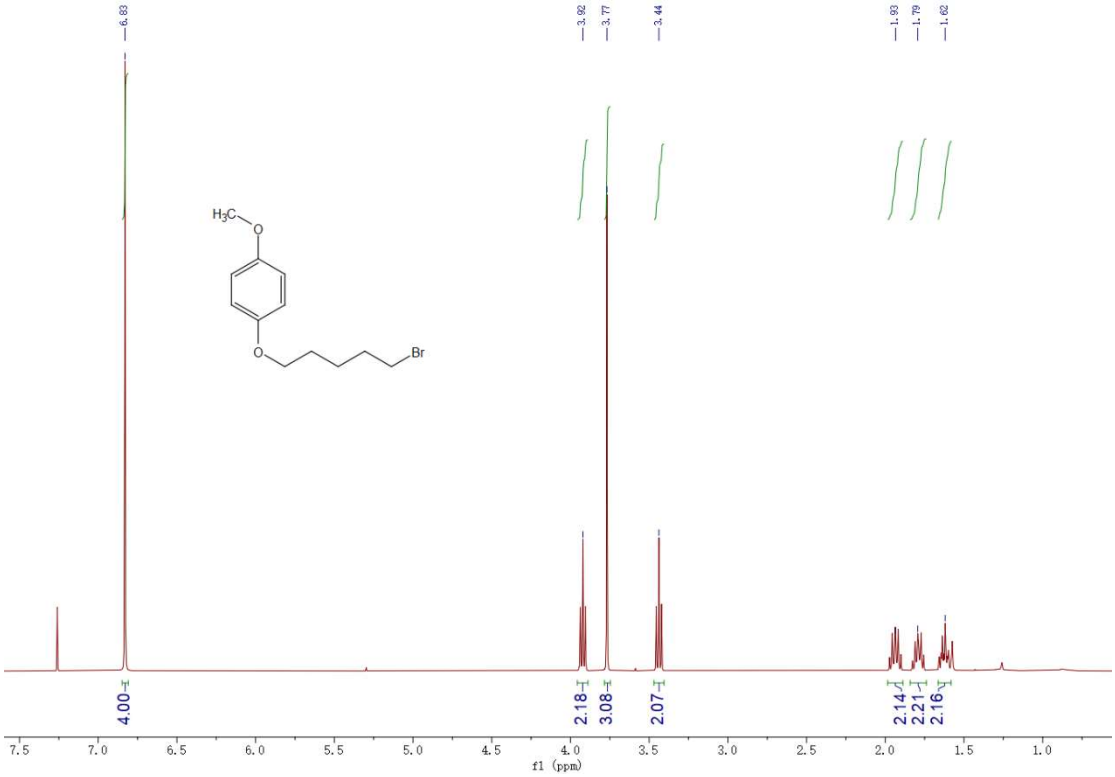



Figure S8. $^{1}$H NMR of M2.

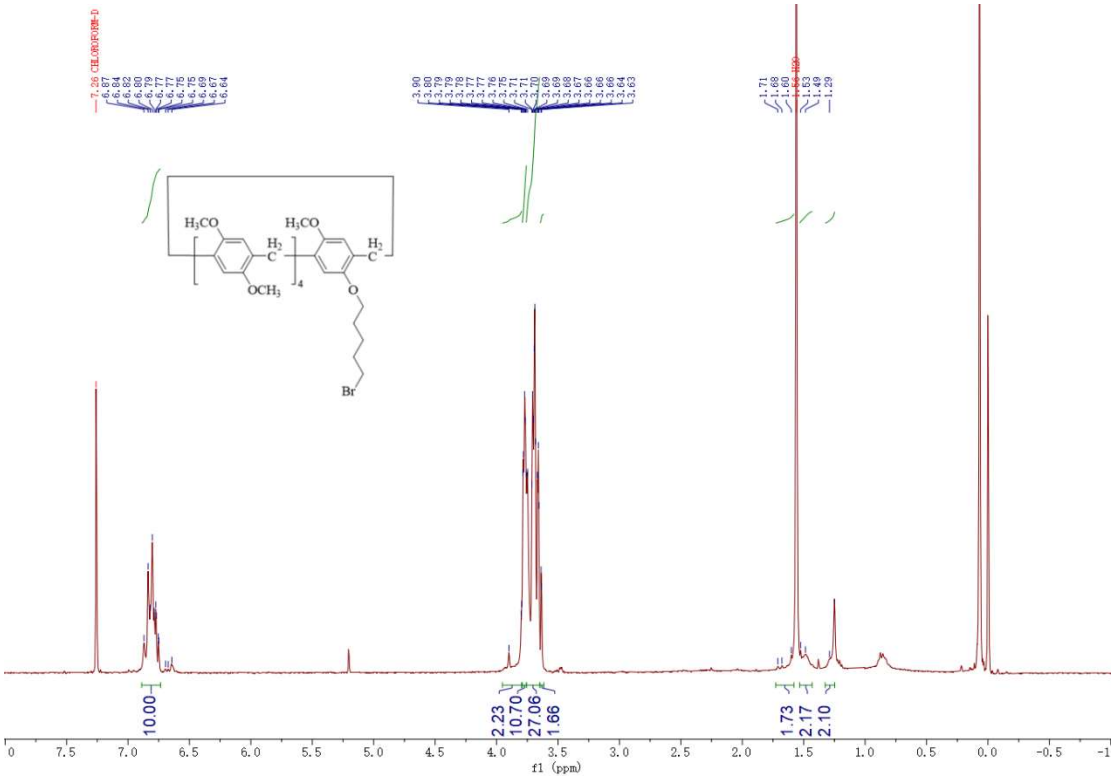



Figure S9. $^{1}$H NMR of P2.

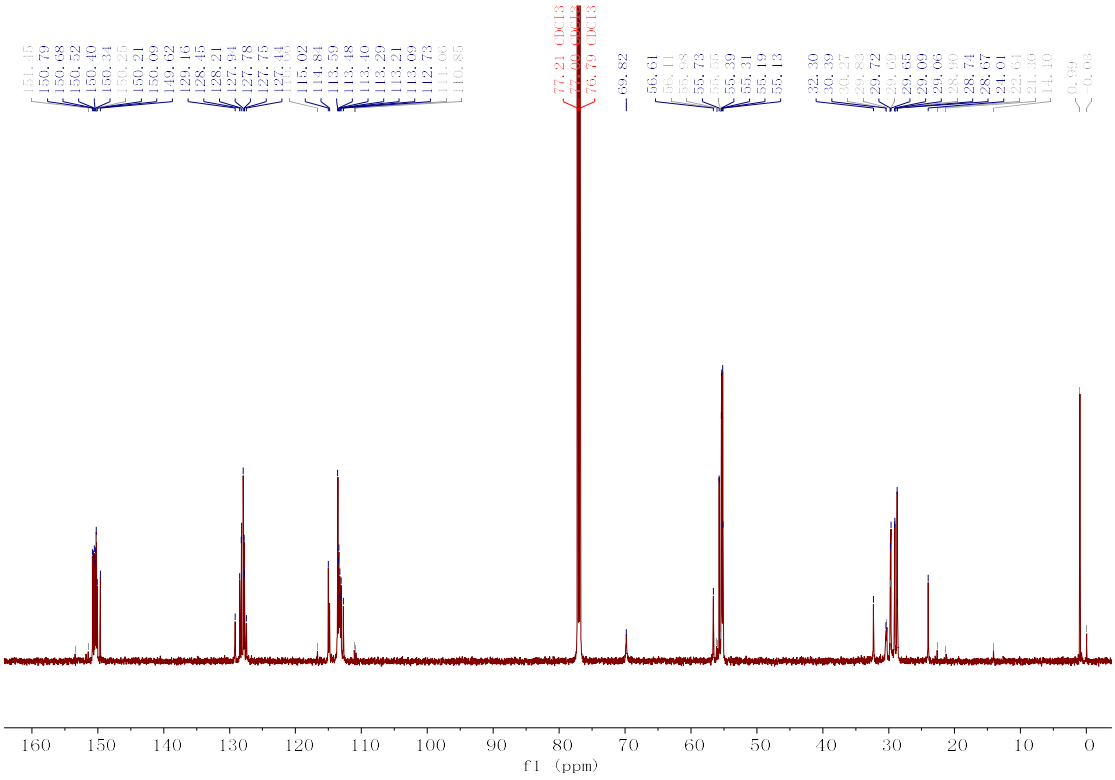



Figure S10. $^{13}$C NMR of P2.

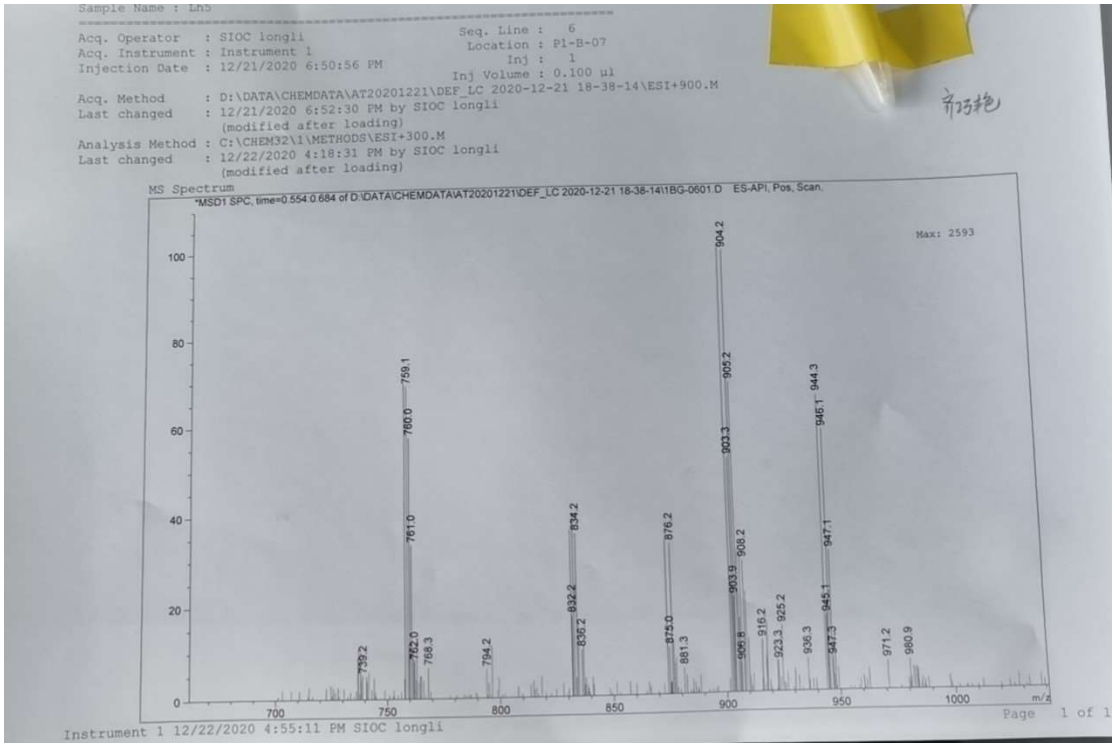
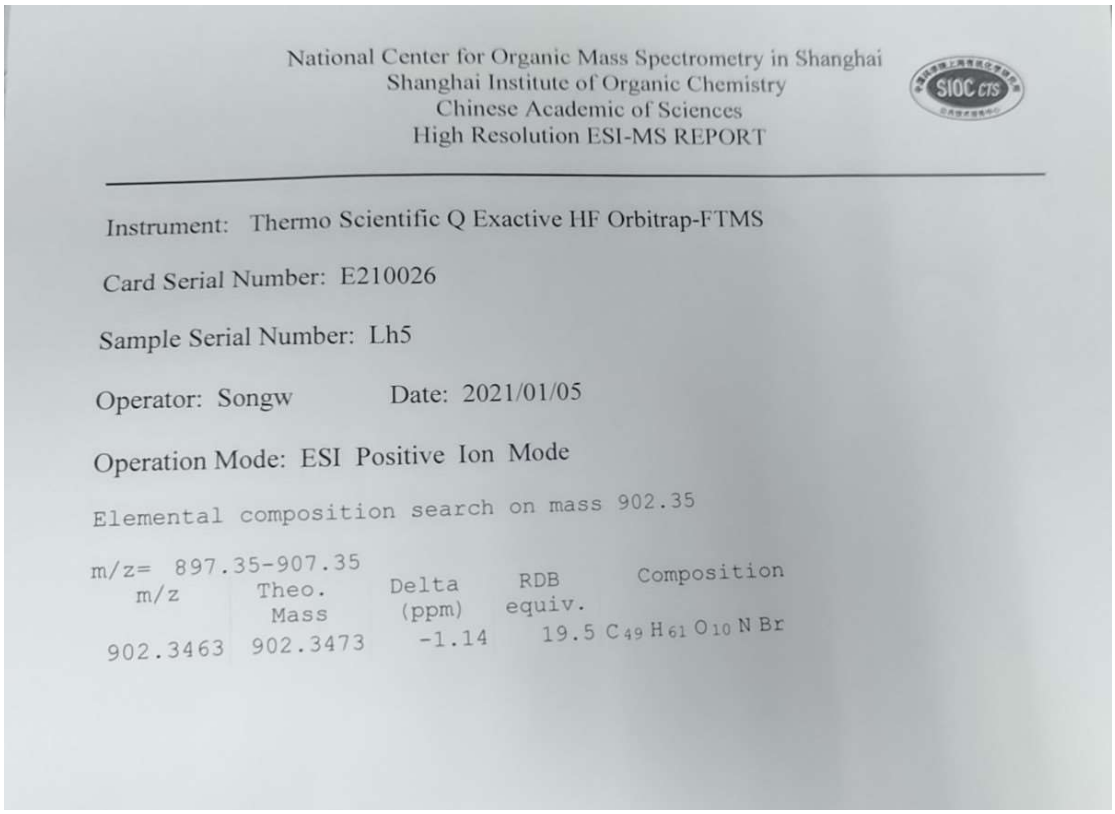



Figure S11. MS of P2.



National Center for Organic Mass Spectrometry in Shanghai
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High Resolution ESI-MS REPORT

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E210026

Sample Serial Number: Lh5

Operator: Songw Date: 2021/01/05

Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 902.35

m/z= 897.35-907.35

| m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition |
|---|---|---|---|---|
| 902.3463 | 902.3473 | -1.14 | 19.5 | $C_{49}H_{61}O_{10}NBr$ |

Figure S12. HRMS of P2.

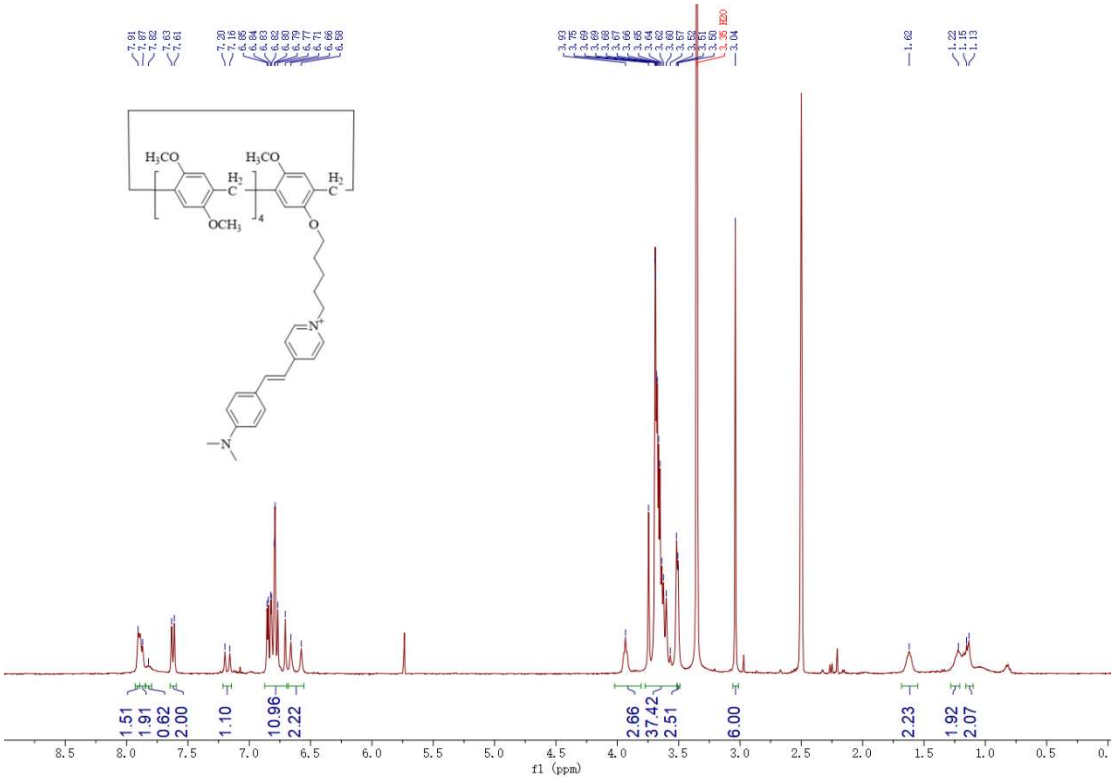


Figure S13. $^{1}$H NMR of PI2.

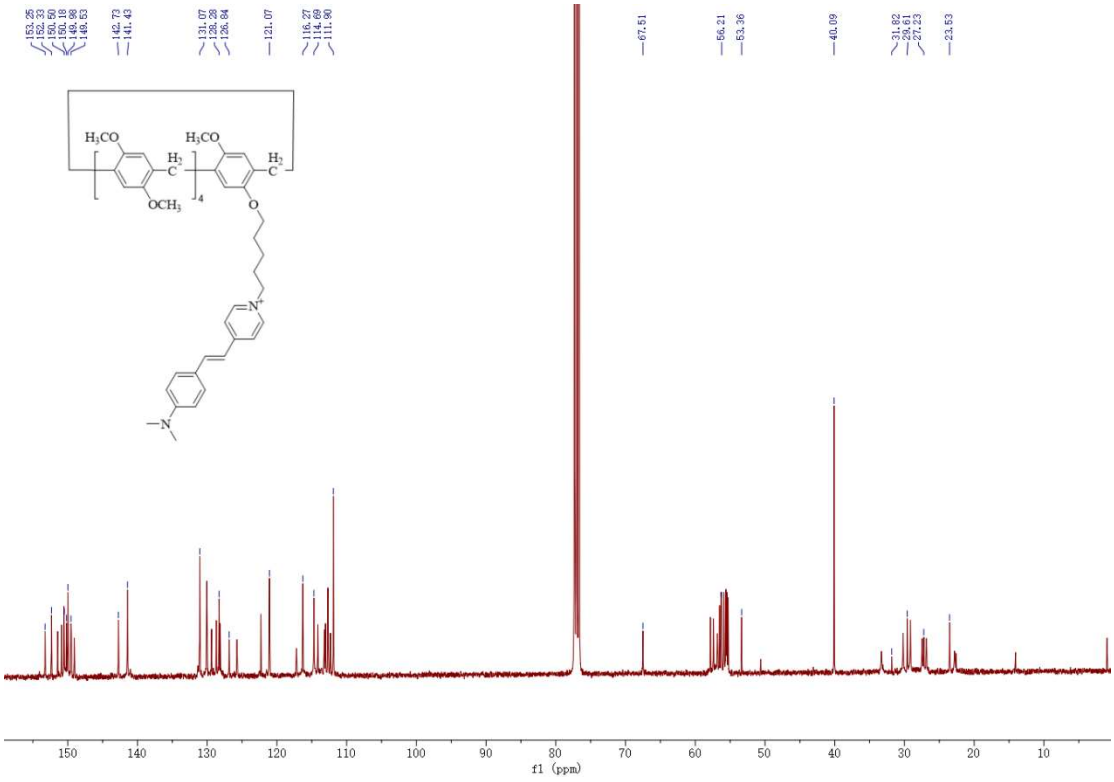


Figure S14. $^{13}$C NMR of PI2.

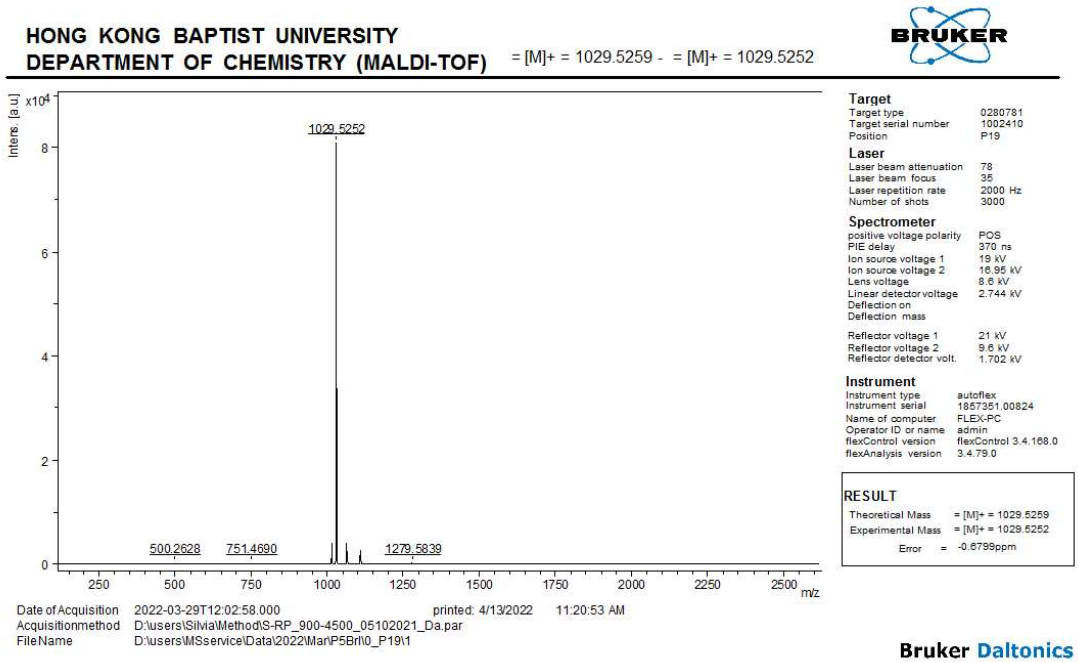


Figure S15. HRMS of PI2.

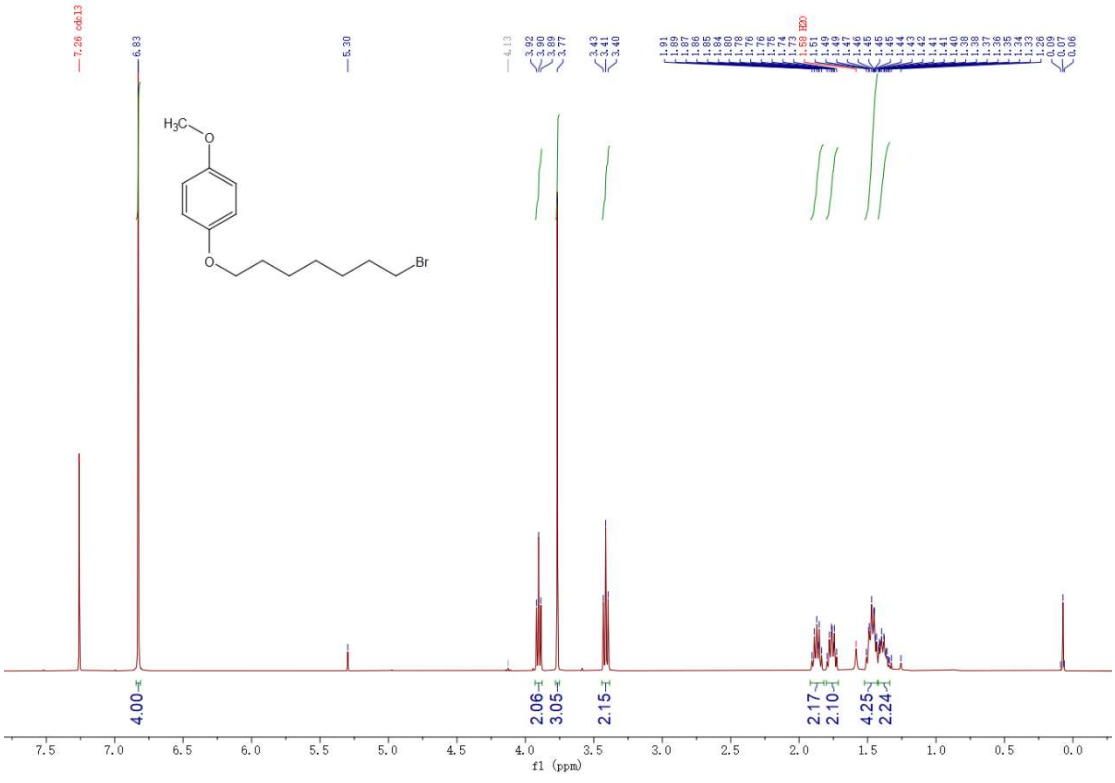


Figure S16. $^{1}$H NMR of M3.

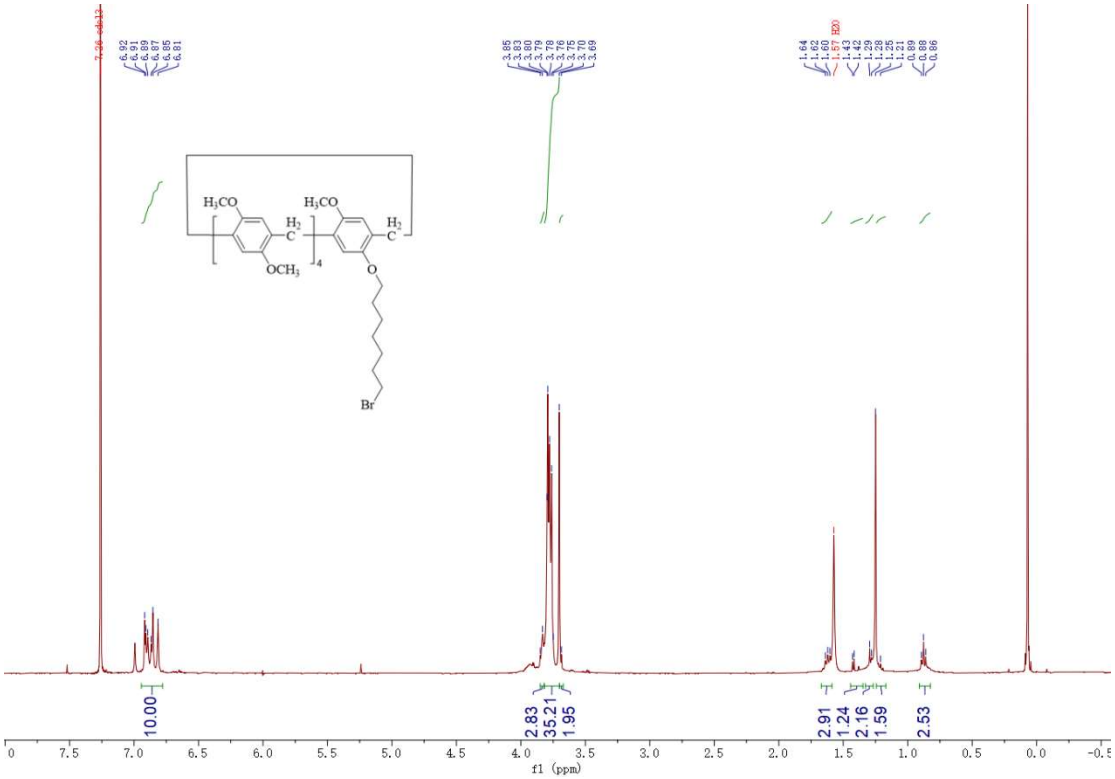


Figure S17. $^{1}$H NMR of P3.

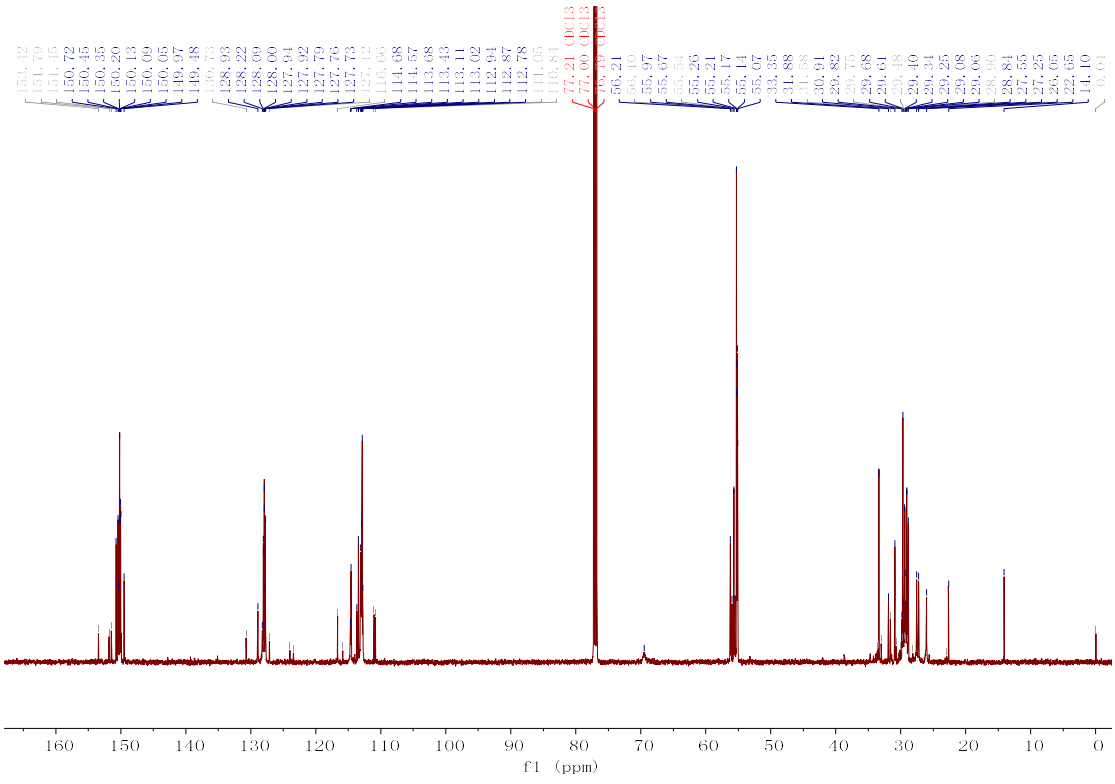


Figure S18. $^{13}$C NMR of P3.

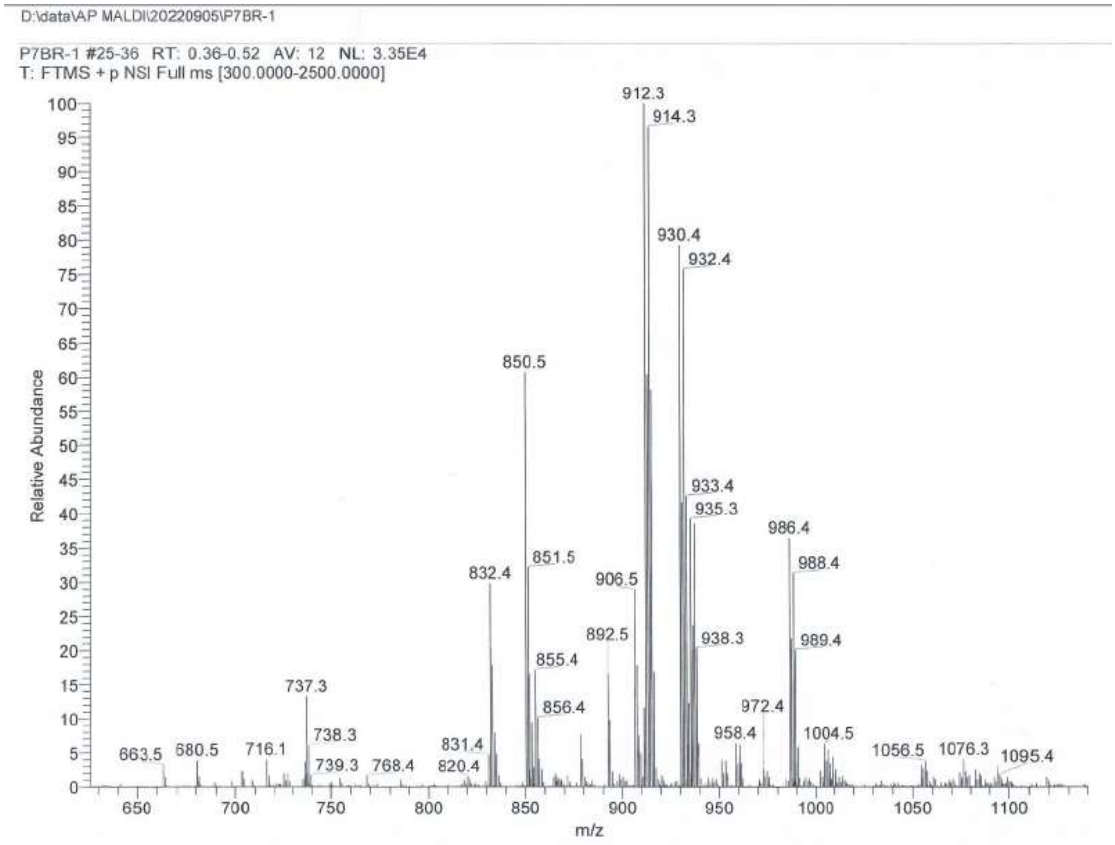


Figure S19. MS of P3.

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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 | $C_{51}H_{61}O_{10}Br$ |

Figure S20. HRMS of P3.

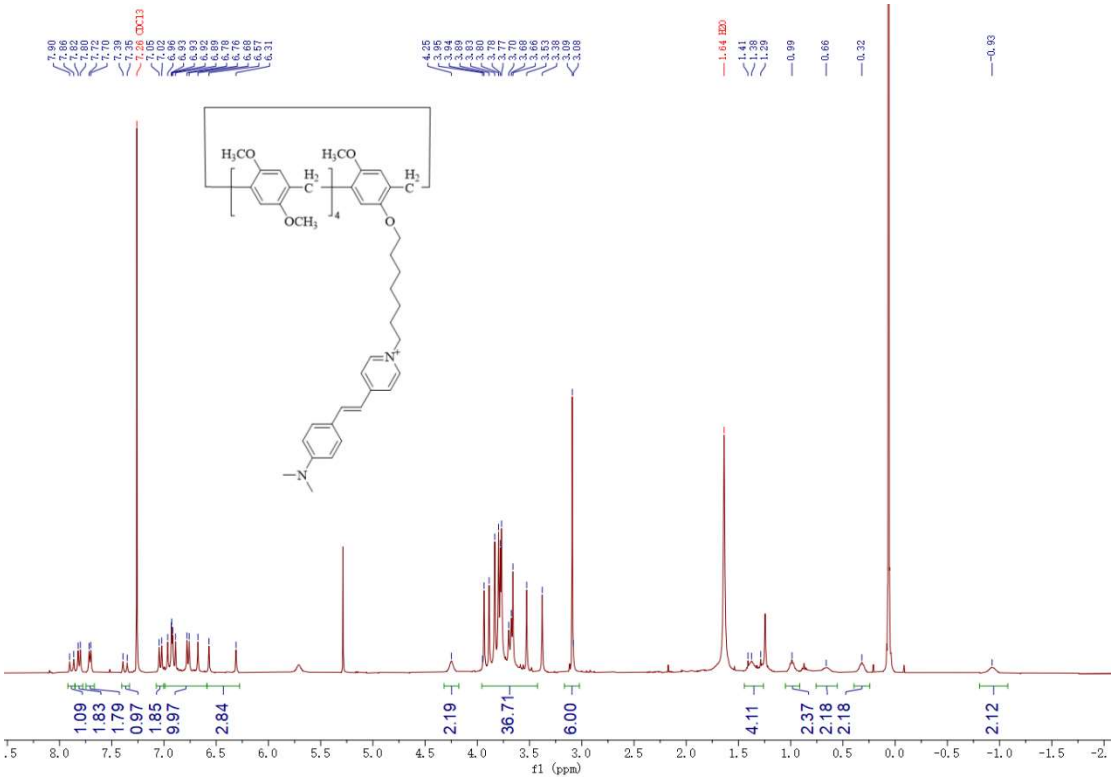


Figure S21. $^{1}$H NMR of PI3.

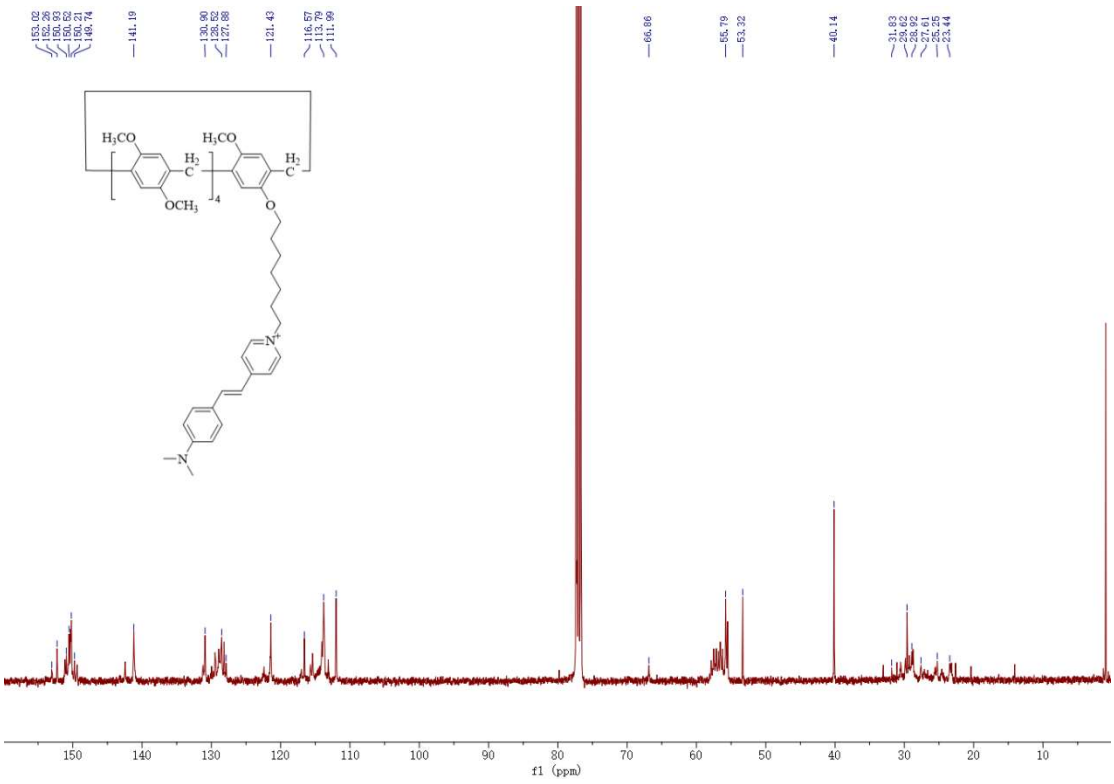


Figure S22. $^{13}$C NMR of PI3.

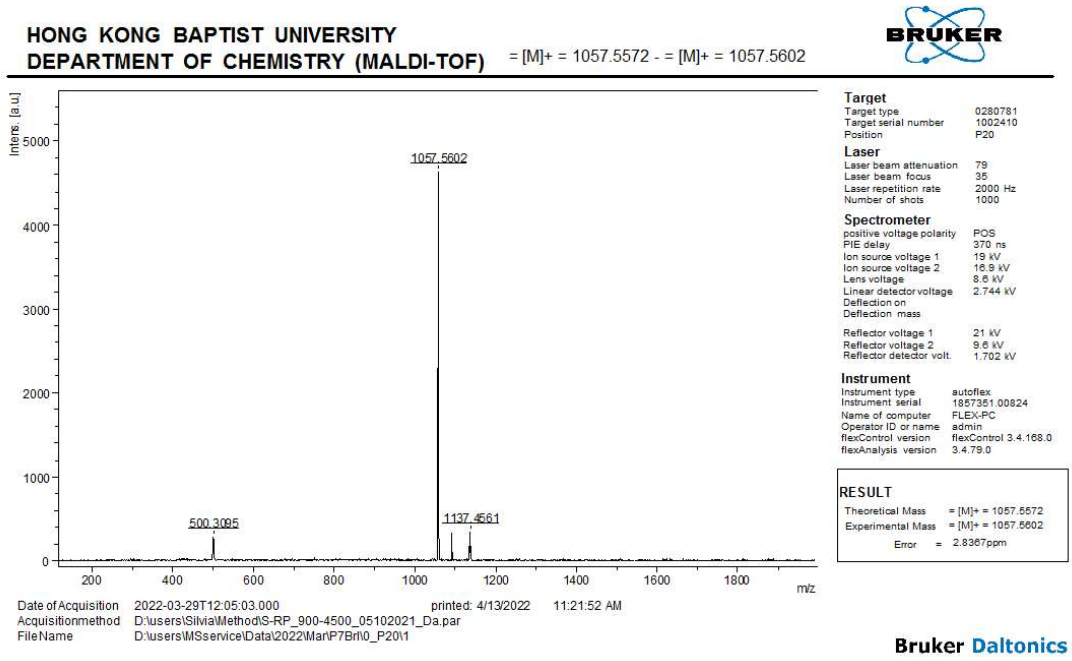


Figure S23. HRMS of PI3.

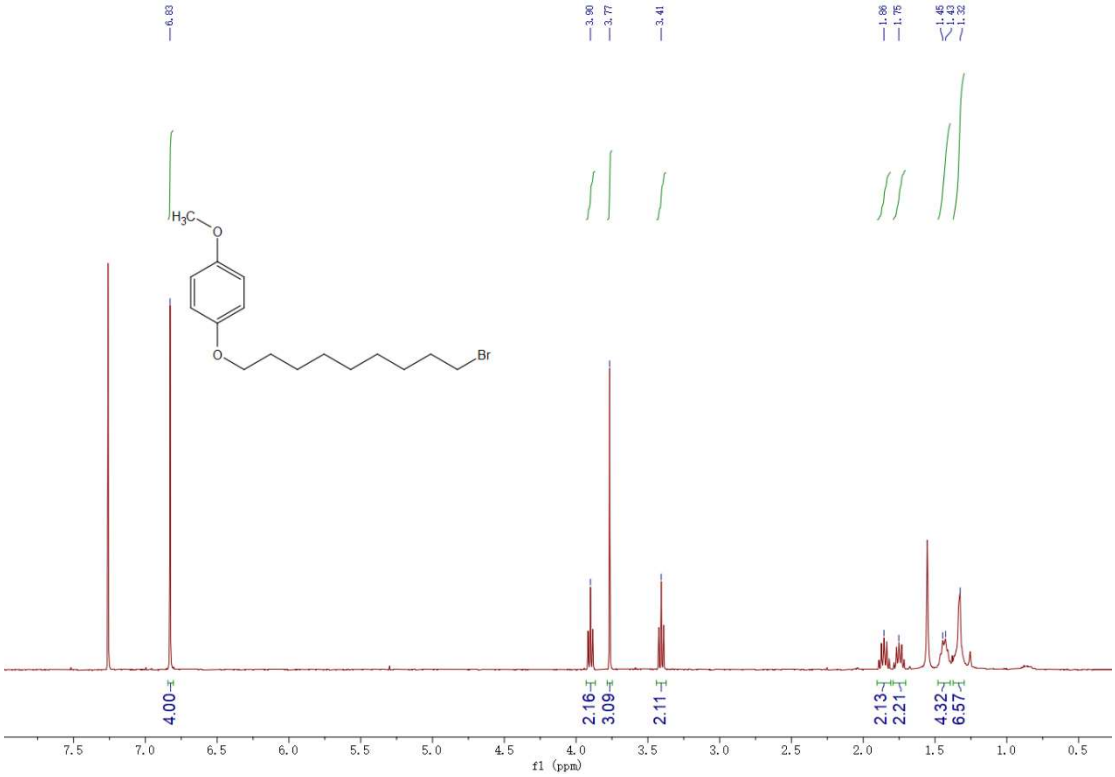


Figure S24. $^{1}$H NMR of M4.

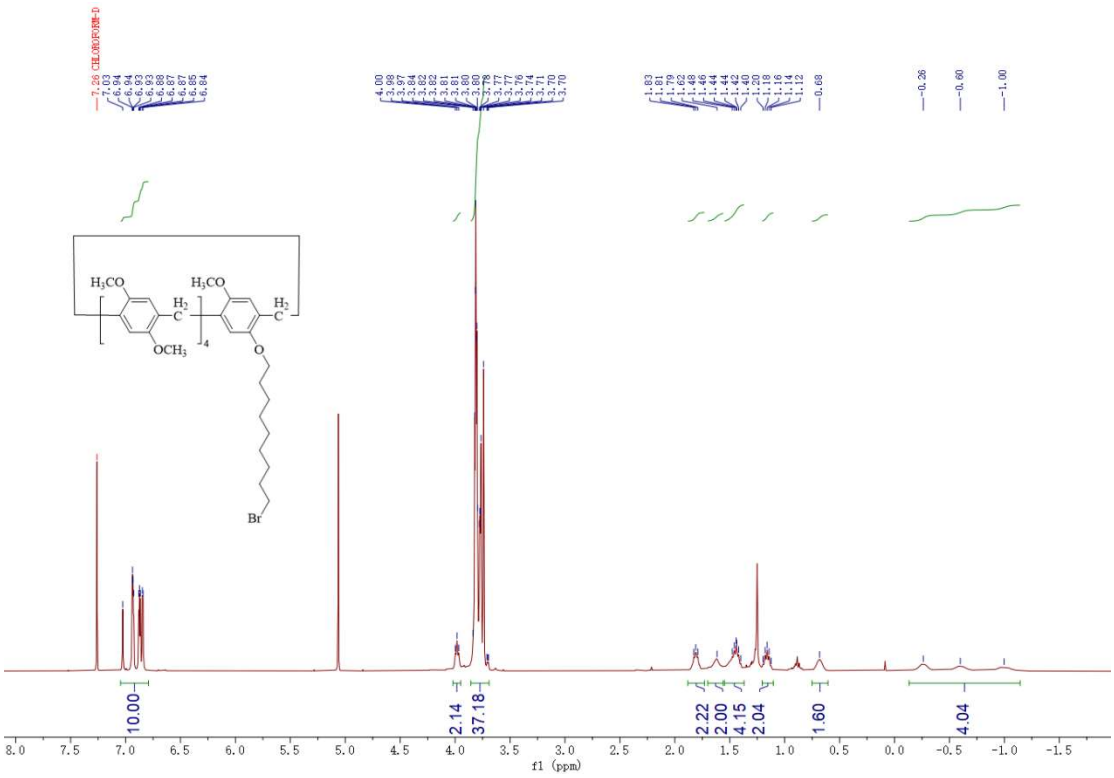


Figure S25. $^{1}$H NMR of P4.

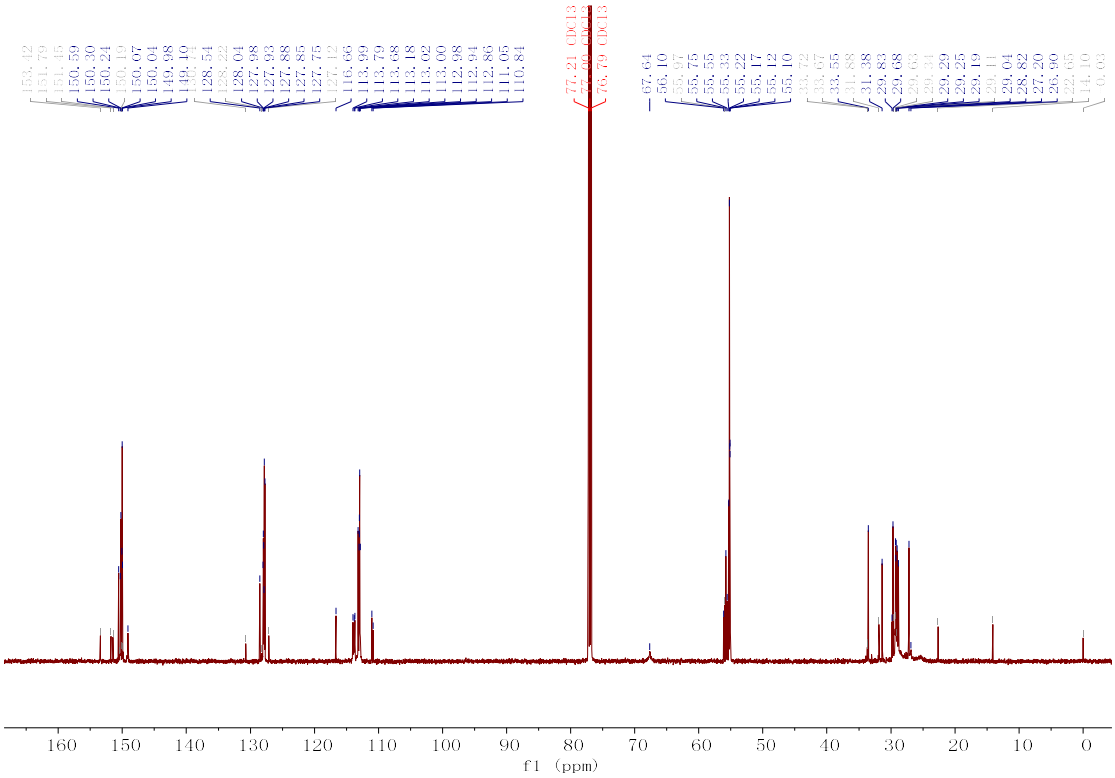


Figure S26. $^{13}$C NMR of P4.

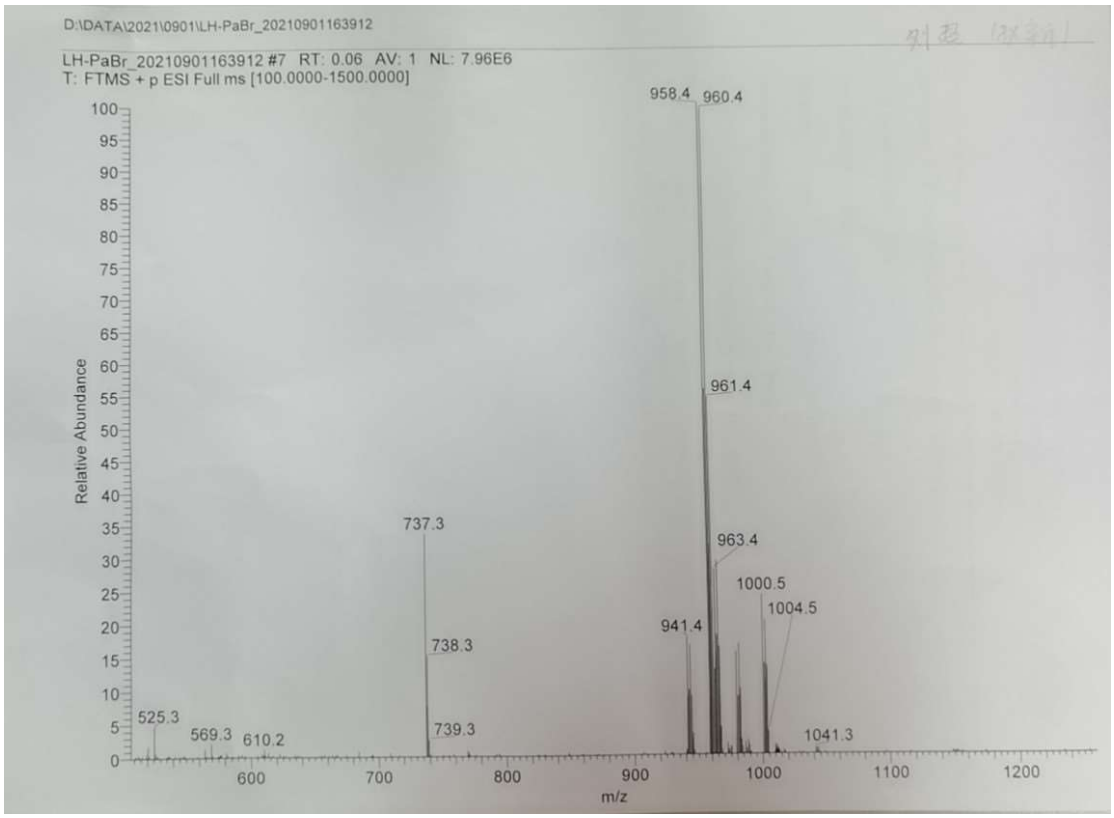


Figure S27. MS of P4.

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High Resolution ESI-MS REPORT

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E212216

Sample Serial Number: LH-PaBr

Operator: Songw Date: 2021/09/01

Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 958.4099

m/z= 953.4099-963.4099

| m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition |
|---|---|---|---|---|
| 958.4099 | 958.4099 | -0.09 | 19.5 | $C_{53}H_{69}O_{10}NBr$ |

Figure S28. HRMS of P4.

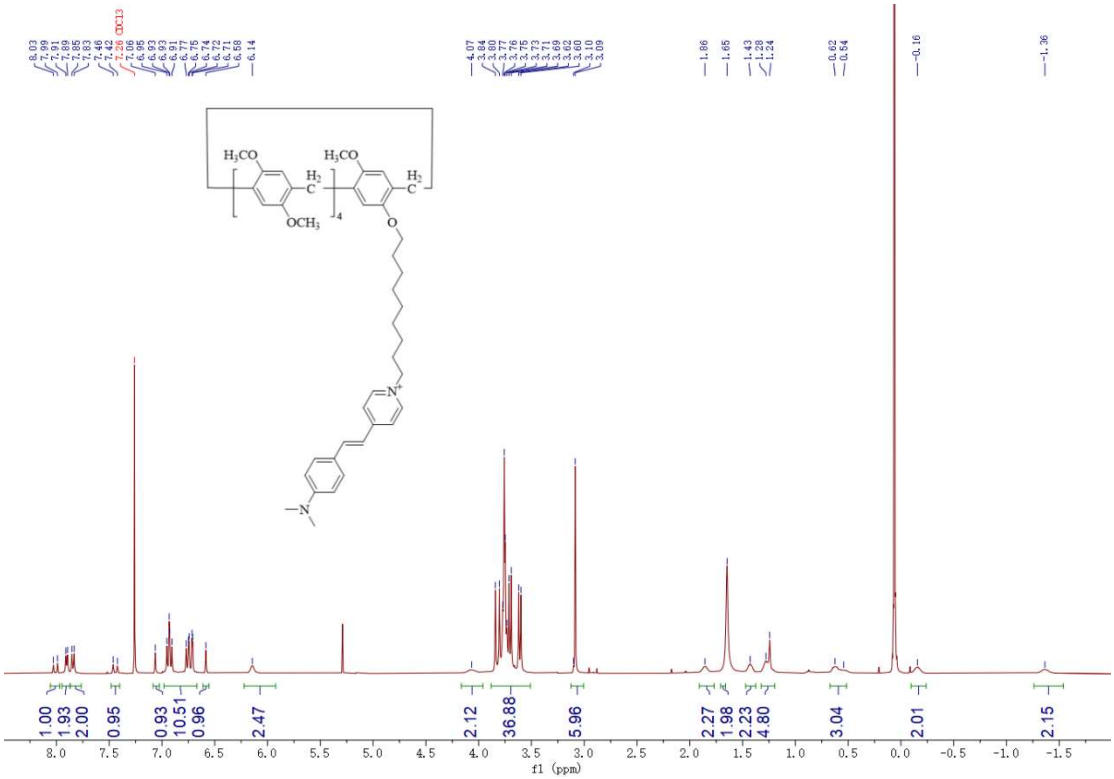


Figure S29. $^{1}$H NMR of PI4.

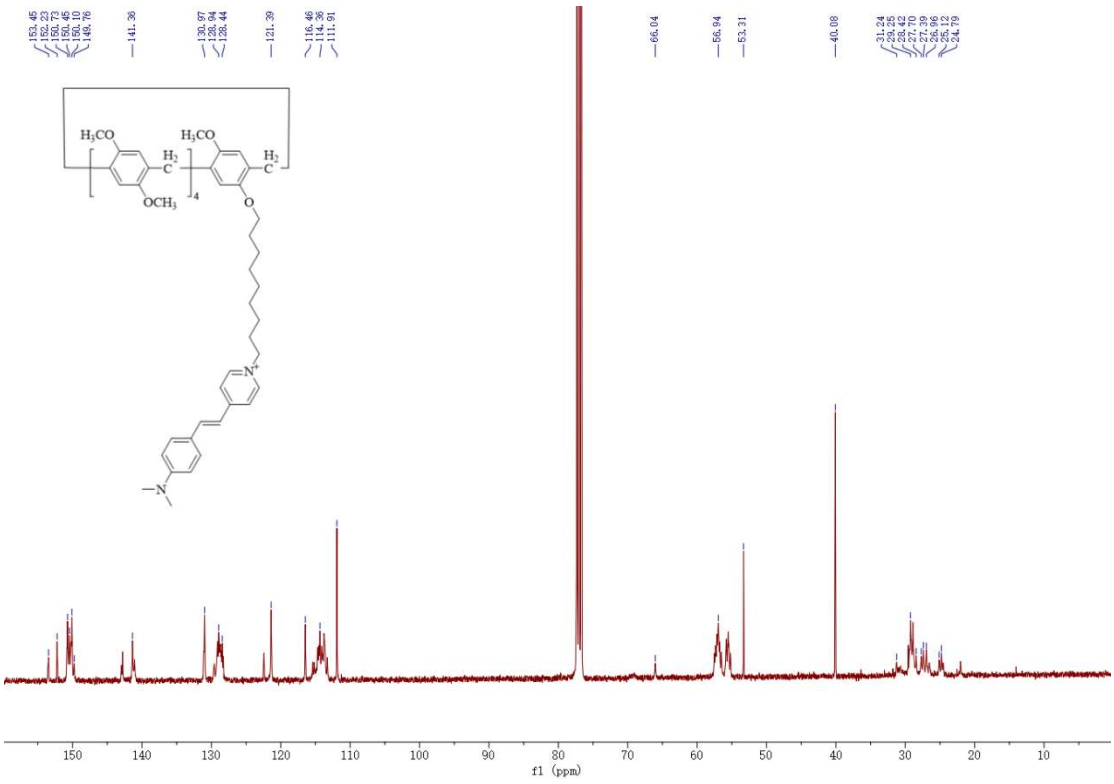


Figure S30. $^{13}$C NMR of PI4.

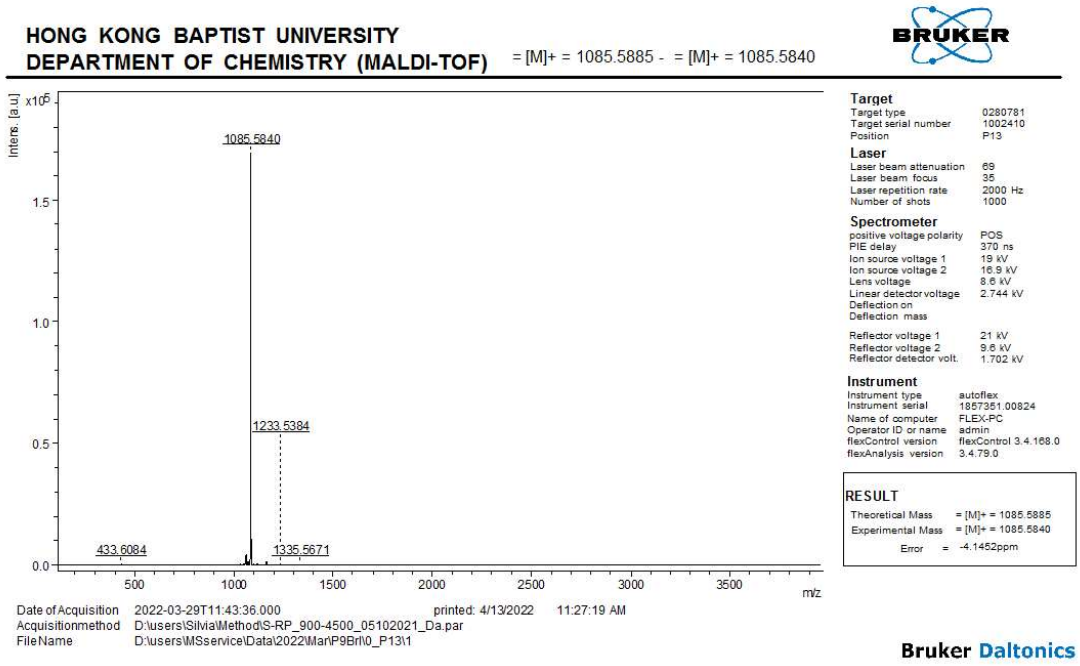


Figure S31. HRMS of PI4.

**Linker length**

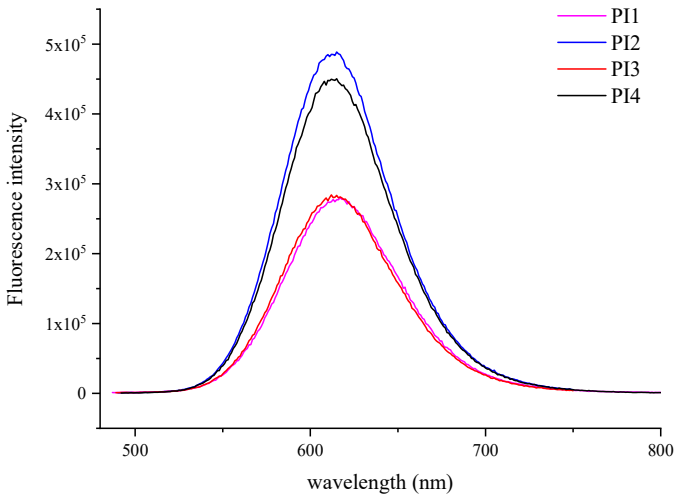


Fig. S32 Fluorescence emission spectra of the monosubstituted pillar[5]arene **PIn** (20 μM) in DMSO at 25°C.

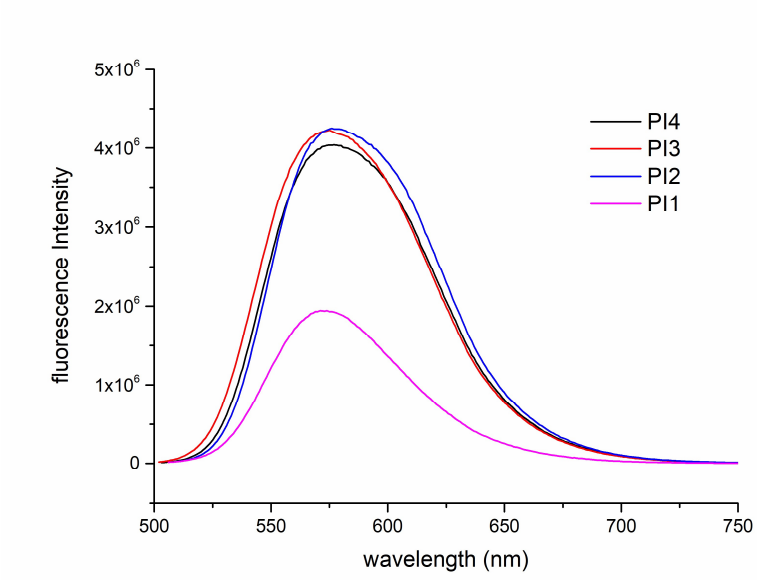


Fig. S33 Fluorescence emission spectra of the monosubstituted pillar[5]arene **PIn** (20 μM) in chloroform at 25°C.

**Solvent**

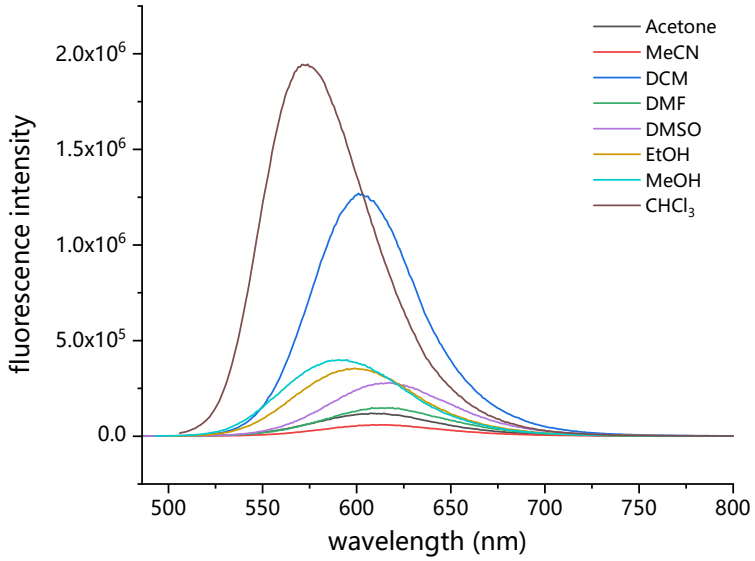


Fig. S34 Fluorescence emission spectra of **PI1** (20 μM) in various solvents.

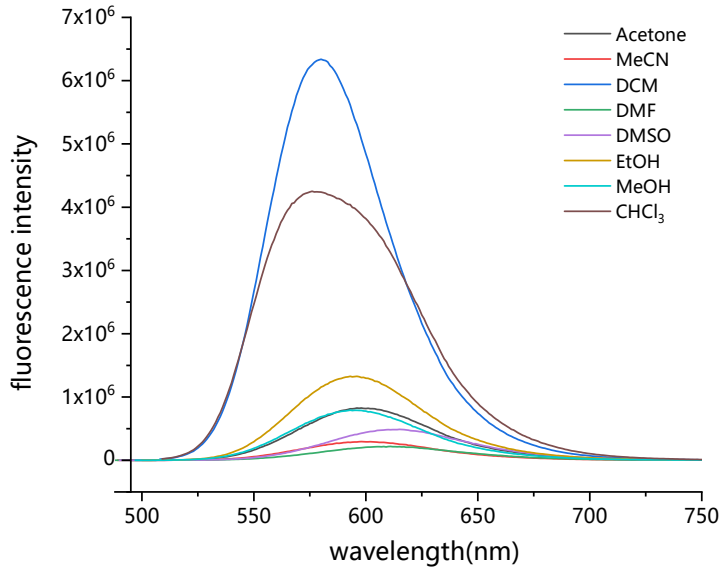


Fig. S35 Fluorescence emission spectra of **PI2** (20 μM) in various solvents.

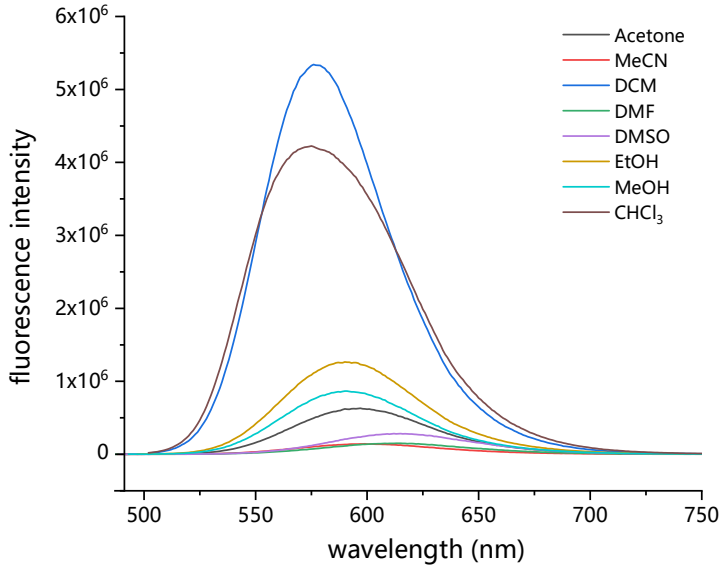


Fig. S36 Fluorescence emission spectra of **PI3** (20 μM) in various solvents.

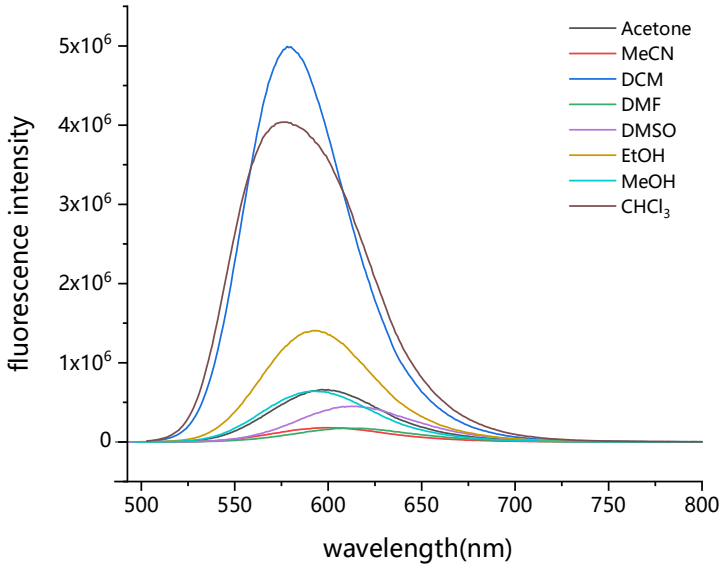


Fig. S37 Fluorescence emission spectra of **PI4** (20 μM) in various solvents.

**Stoke shift and quantum yield**

Table S1. Stoke shifts of **PIn** and **DASP**.

| solvent | Stoke shift ($cm^{-1}$) | | | | |
|---|---|---|---|---|---|
| | **PI4** | **PI3** | **PI2** | **PI1** | **DASP** |
| $CHCl_3$ | 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 ($\phi_F$) is determined with the following equation-1,

$$\emptyset_F = \emptyset_{FR}\left(n^2 \times F \times A_R\right)/\left(n_R^2 \times F_R \times A\right) \quad \text{(equation-1)}$$

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**

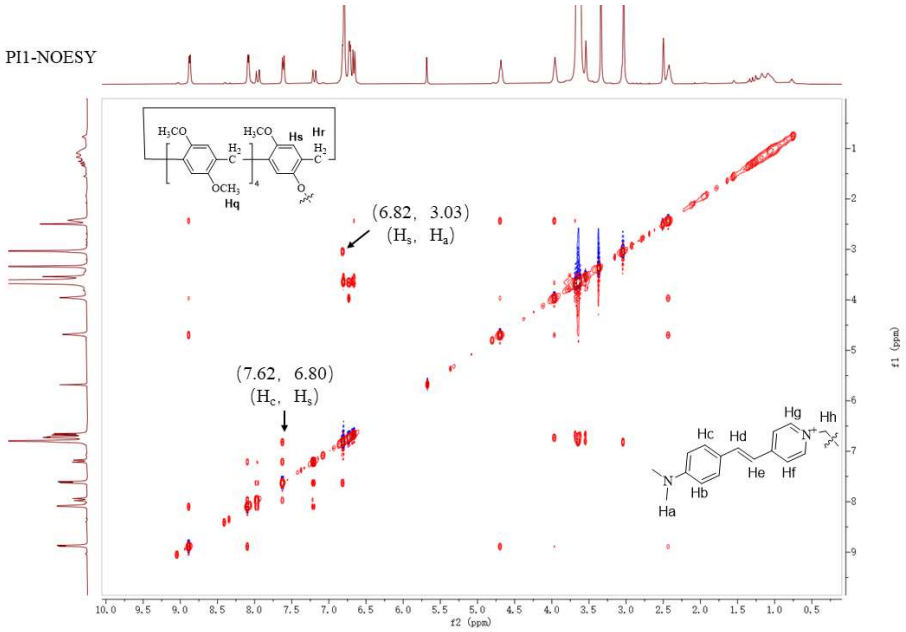


Fig. S38 NOESY spectrum of **PI1** (50 mM, in DMSO)

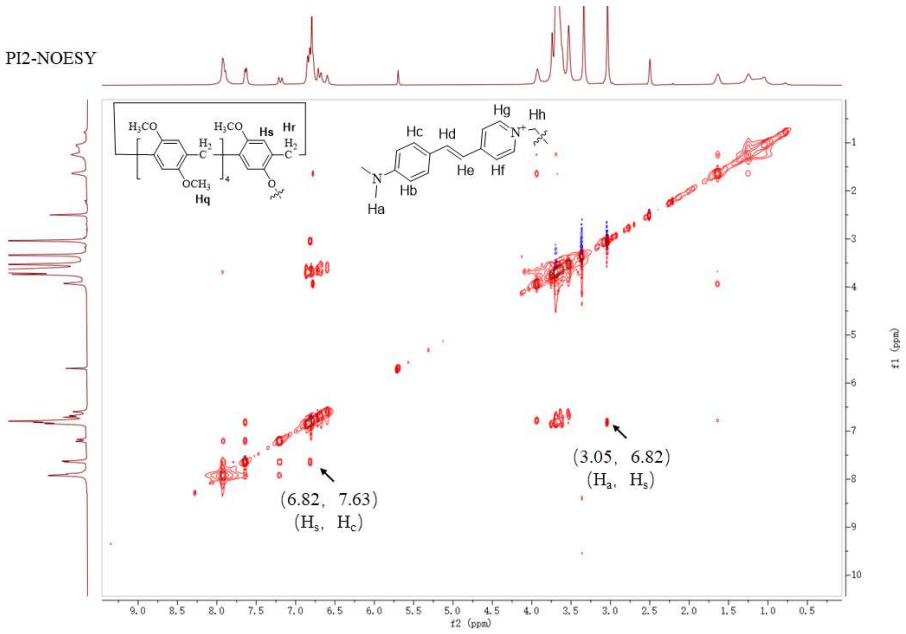


Fig. S39 NOESY spectrum of **PI2** (50 mM, in DMSO)

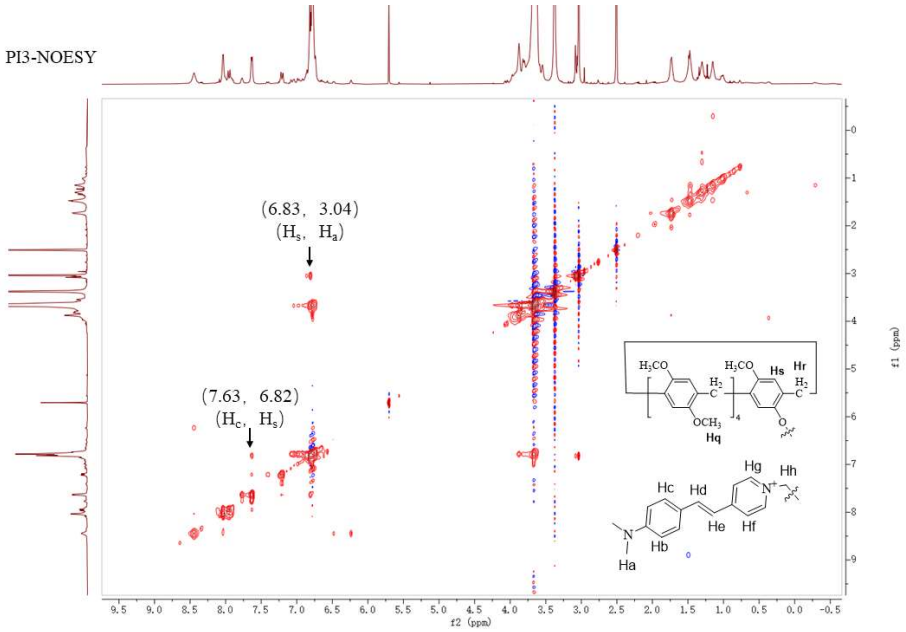


Fig. S40 NOESY spectrum of **PI3** (50 mM, in DMSO)

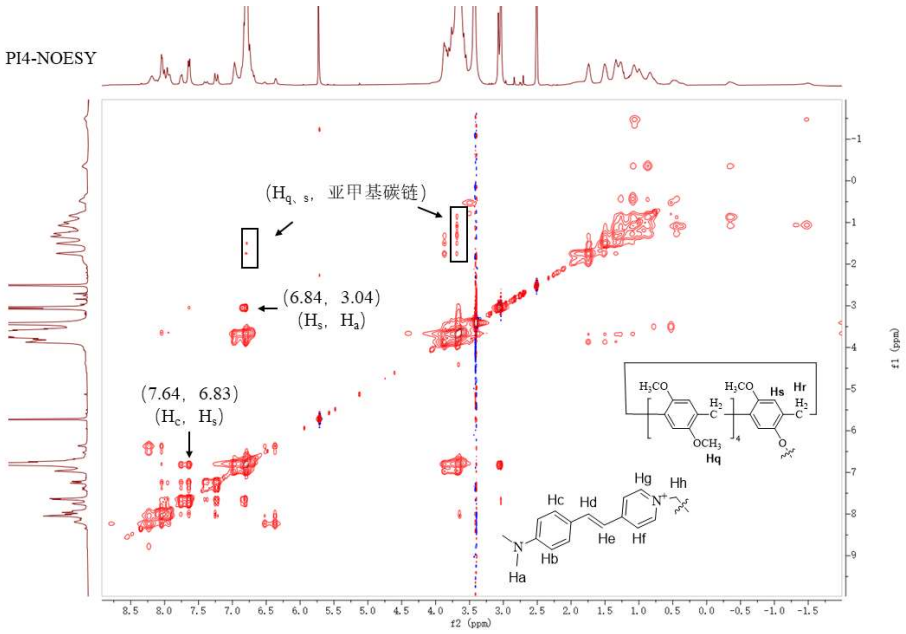


Fig. S41 NOESY spectrum of **PI4** (50 mM, in DMSO)

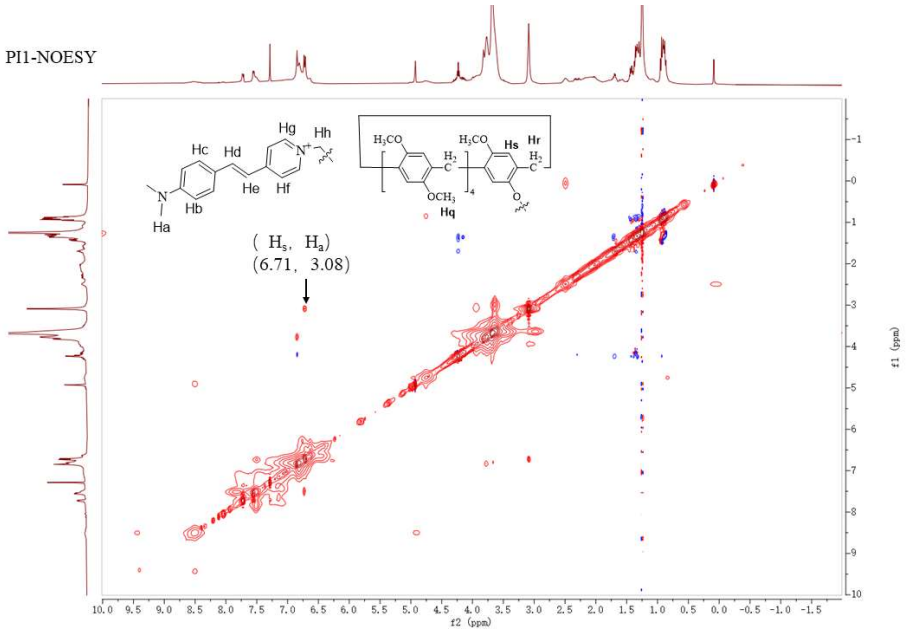


Fig. S42 NOESY spectrum of **PI1** (50 mM, in $CDCl_3$)

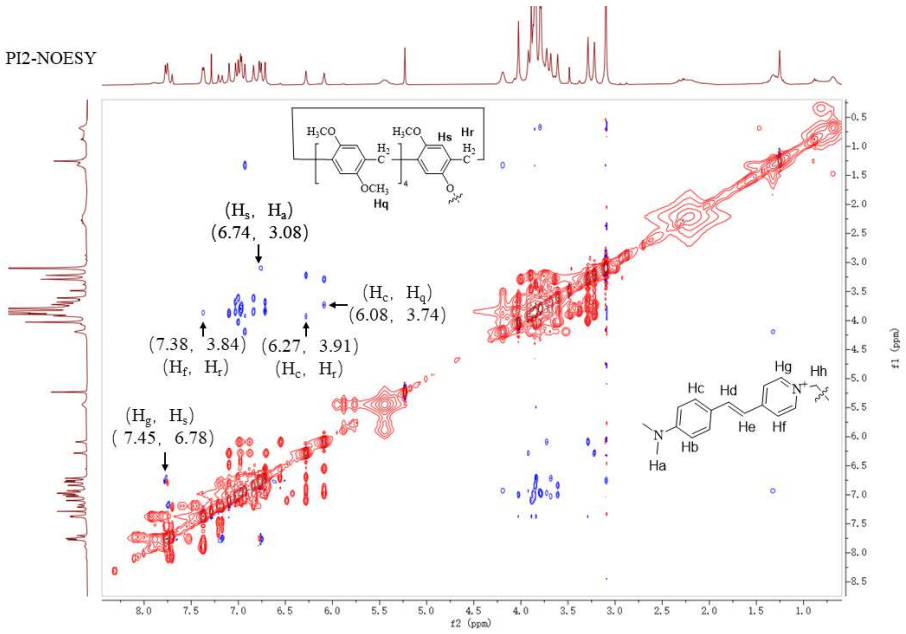


Fig. S43 NOESY spectrum of **PI2** (50 mM, in $CDCl_3$)

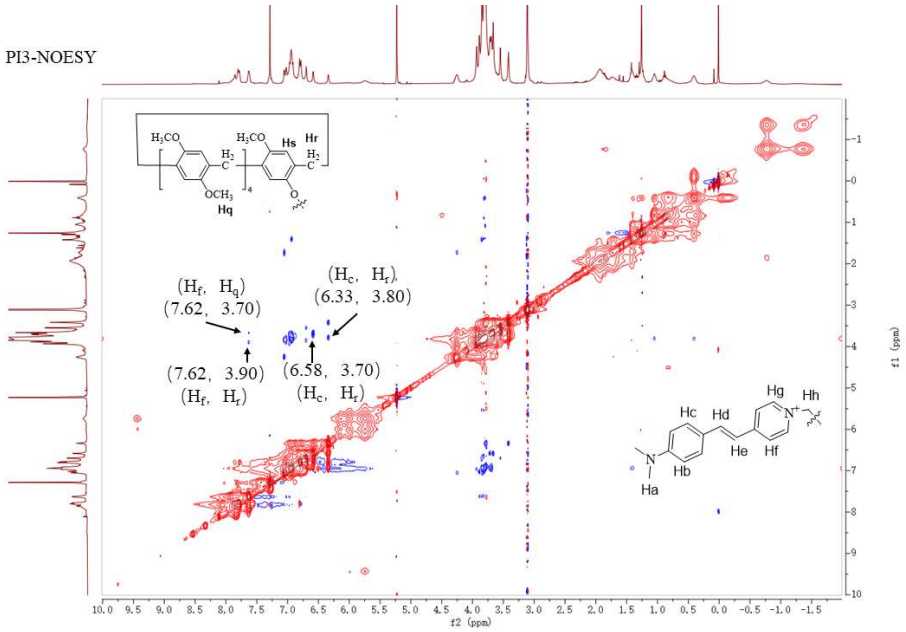


Fig. S44 NOESY spectrum of **PI3** (50 mM, in $CDCl_3$)

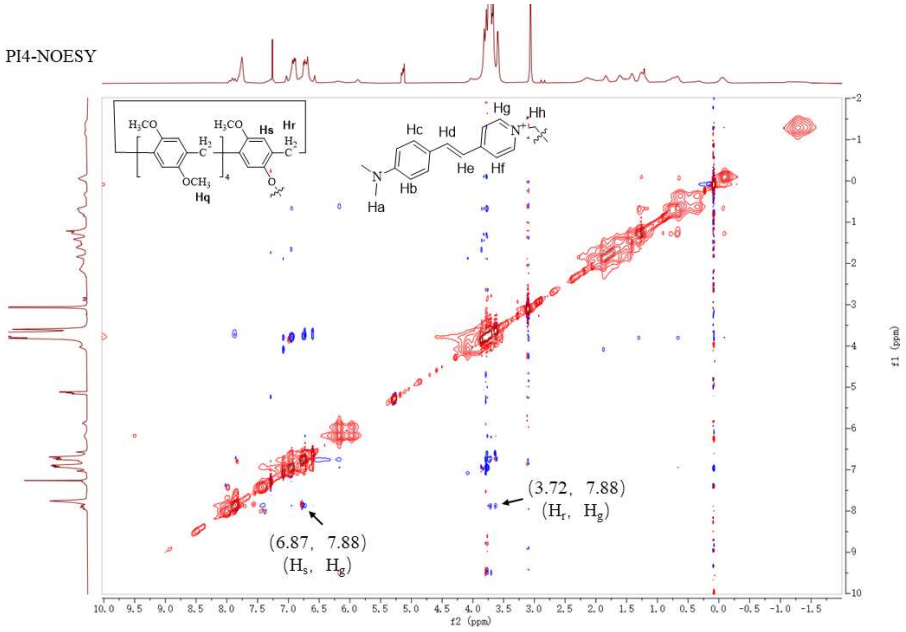


Fig. S45 NOESY spectrum of **PI4** (50 mM, in $CDCl_3$)

**Temperature**

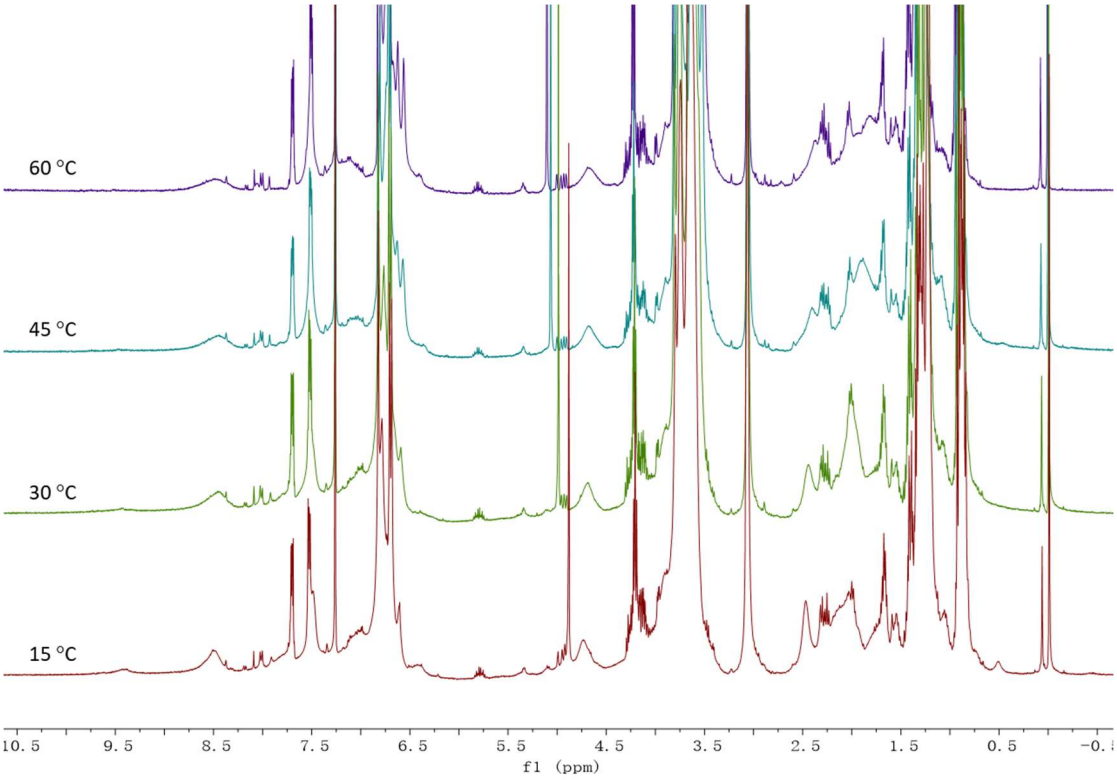


Fig. S46 Partial $^{1}$H NMR spectra of **PI1** at various temperature in $CDCl_3$.

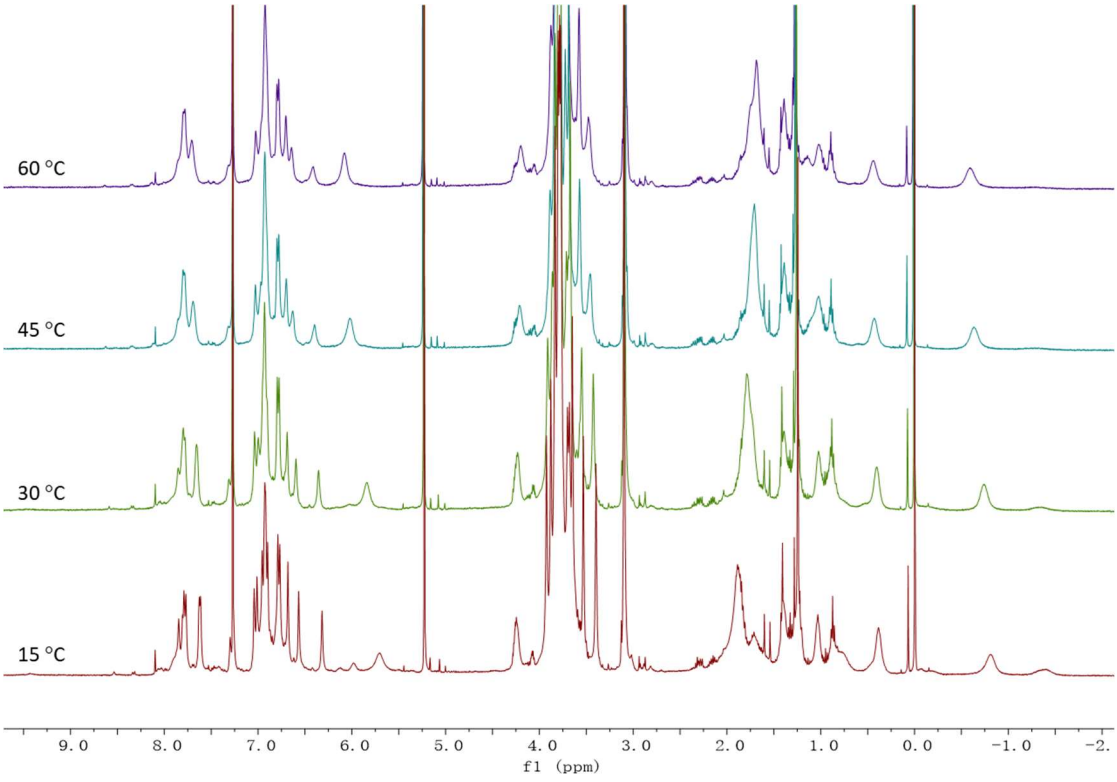


Fig. S47 Partial $^{1}$H NMR spectra of **PI3** at various temperature in $CDCl_3$.

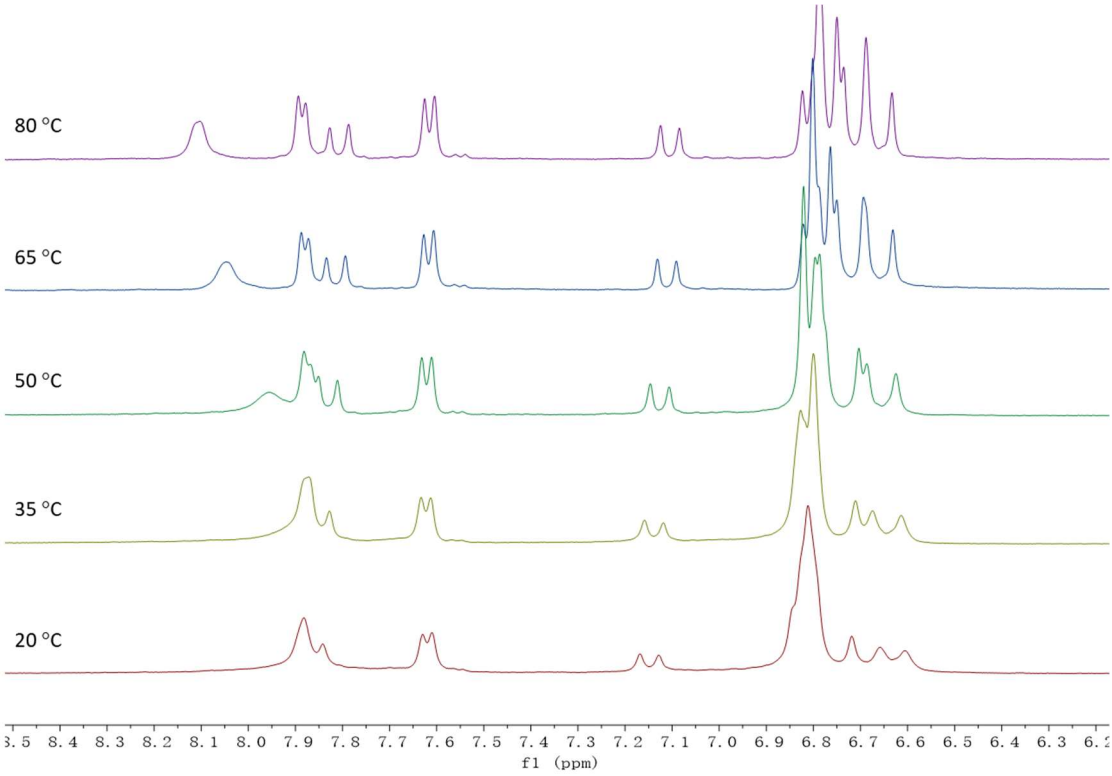


Fig. S48 Partial $^{1}$H NMR spectra of **PI2** at various temperature in DMSO.

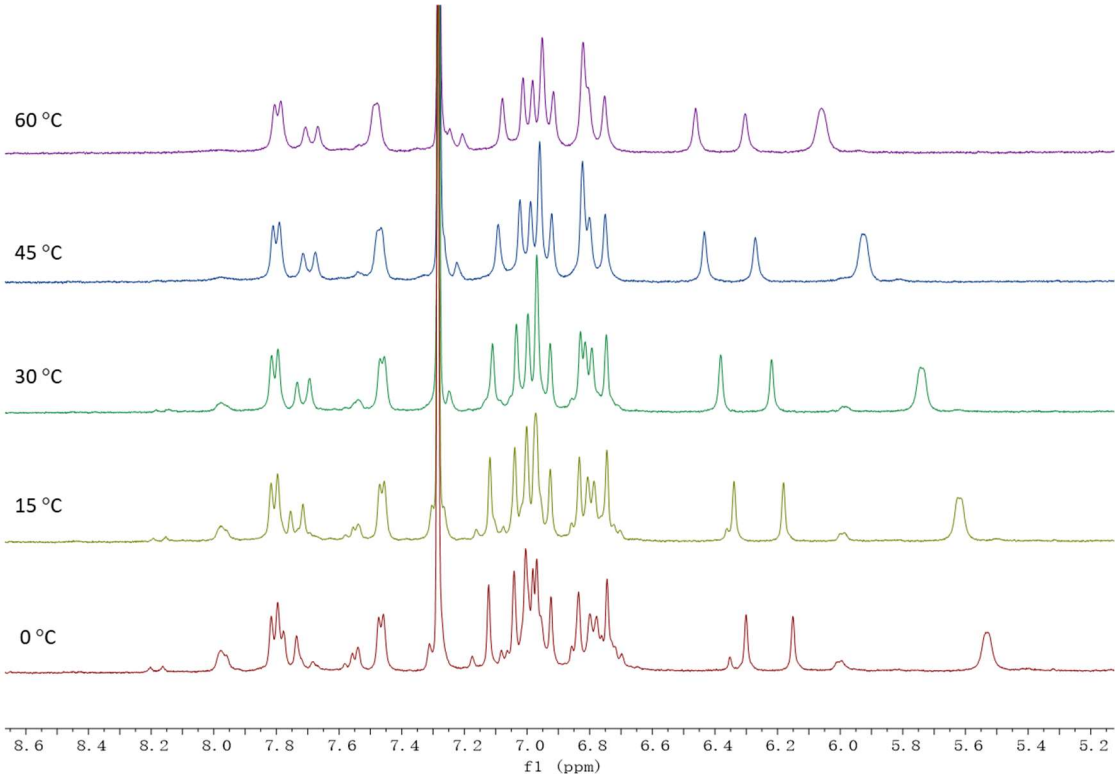


Fig. S49 Partial $^{1}$H NMR spectra of **PI2** at various temperature in CDCl3.

**Temperature**

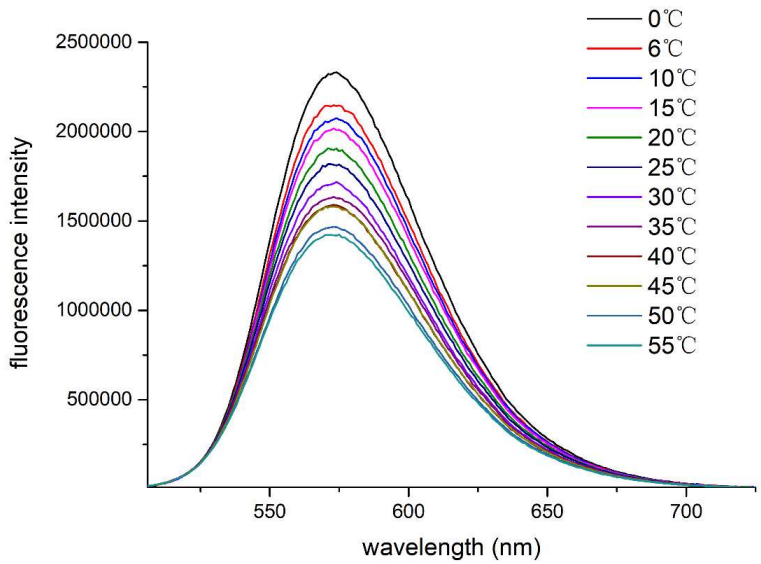


Fig. S50 Fluorescence emission spectra of **PI1** (20 μM) at various temperature in chloroform.

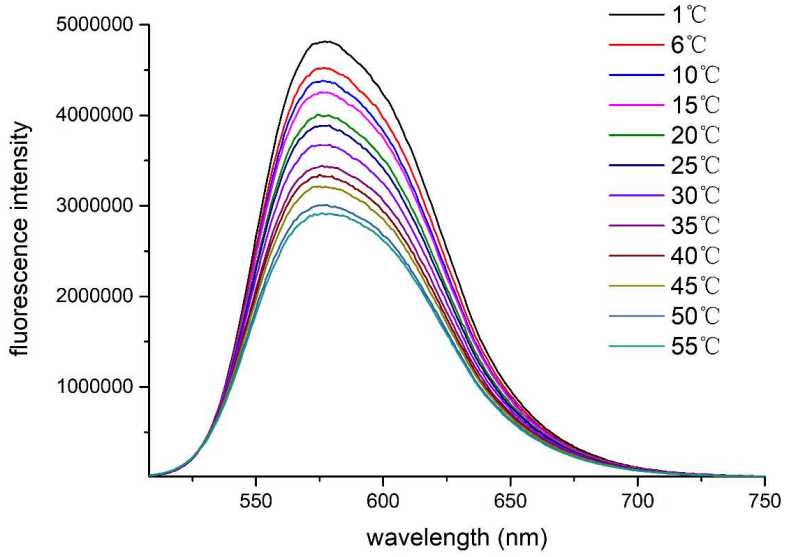


Fig. S51 Fluorescence emission spectra of **PI2** (20 μM) at various temperature in chloroform.

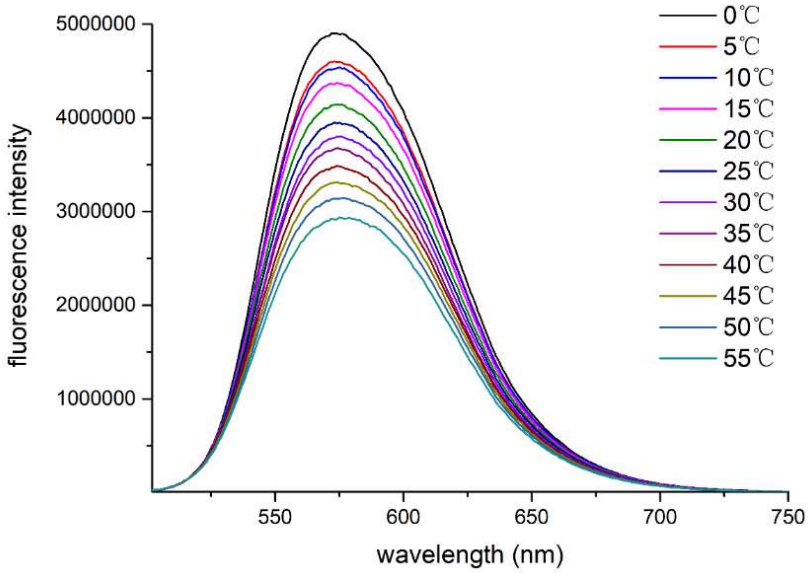


Fig. S52 Fluorescence emission spectra of **PI3** (20 μM) at various temperature in chloroform.

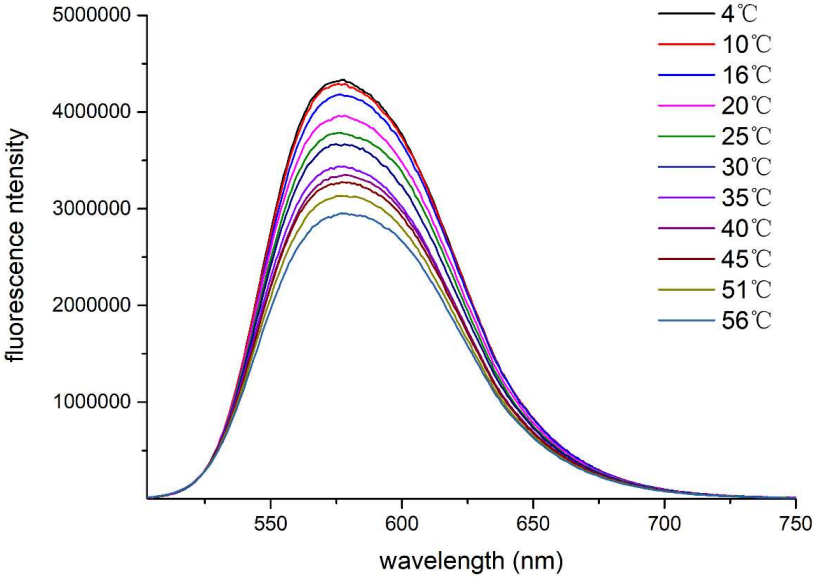


Fig. S53 Fluorescence emission spectra of **PI4** (20 μM) at various temperature in chloroform.

**Concentration**

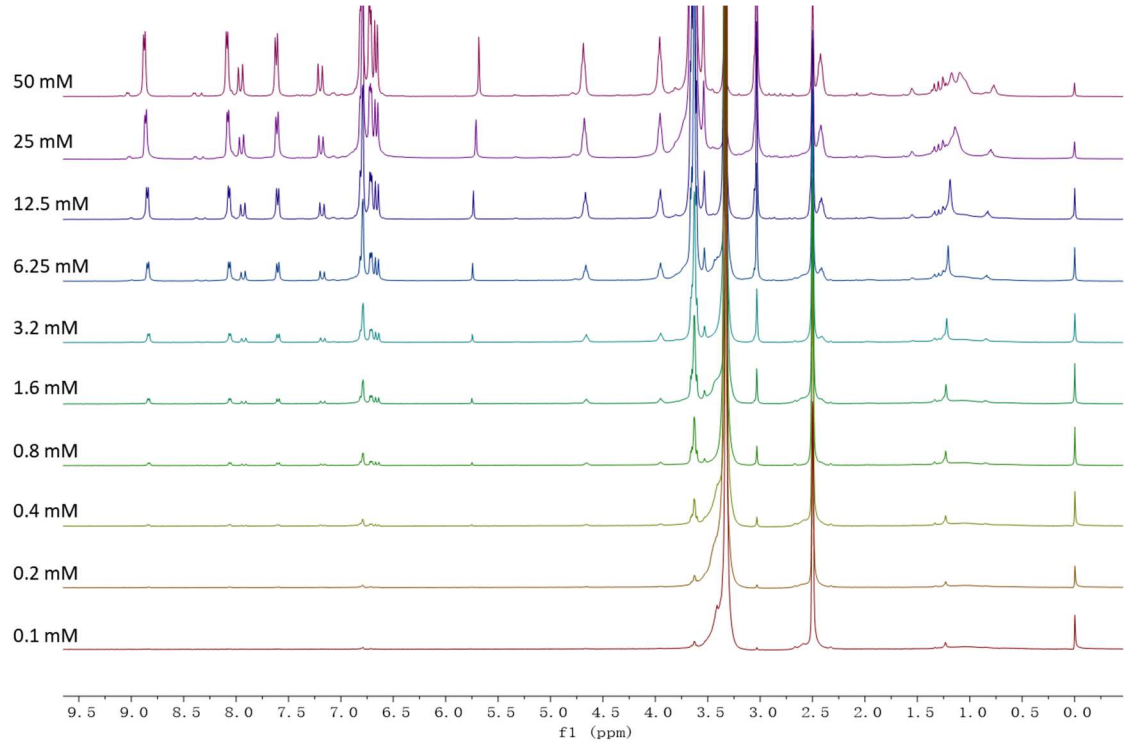


Fig. S54 **PI1** in DMSO at various concentration.

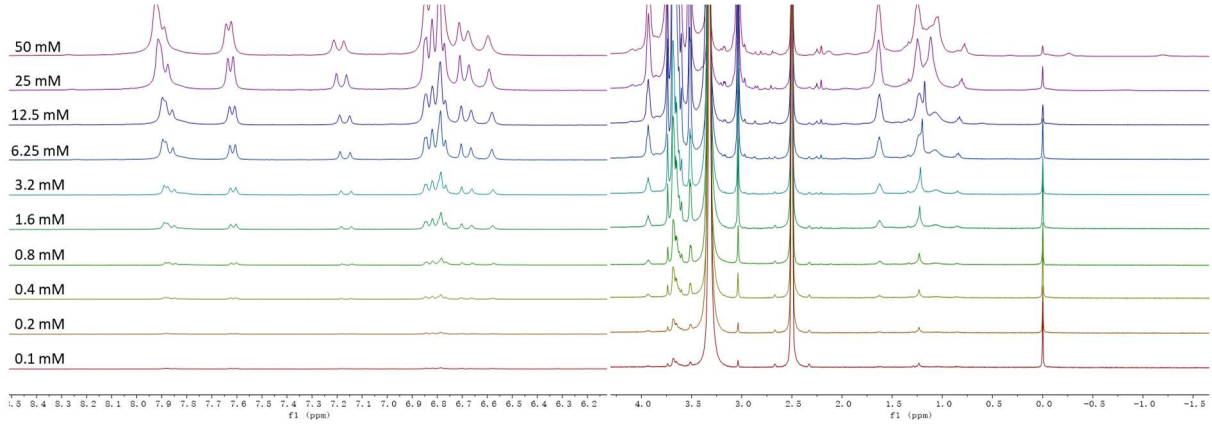


Fig. S55 **PI2** in DMSO at various concentration.

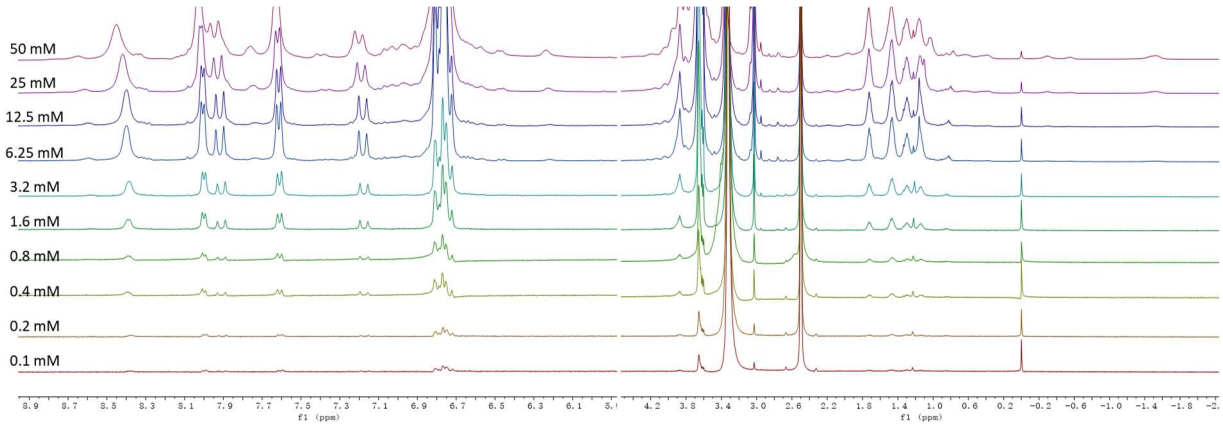


Fig. S56 **PI3** in DMSO at various concentration.

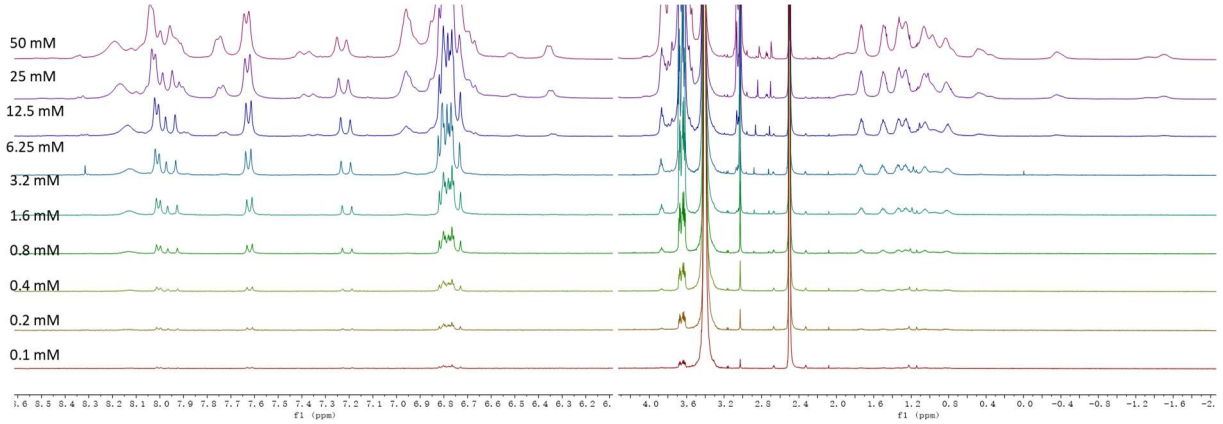


Fig. S57 **PI4** in DMSO at various concentration.

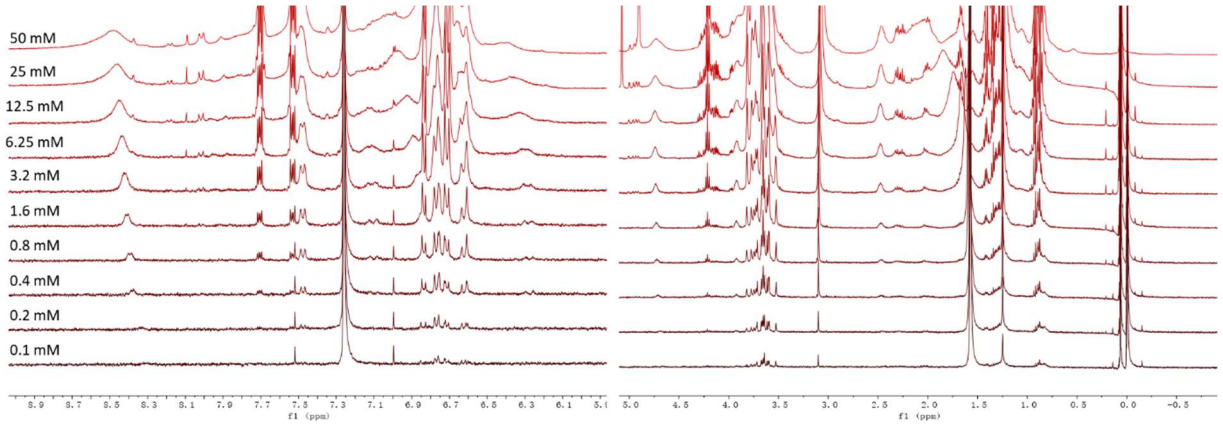


Fig. S58 **PI1** in CDCl3 at various concentration.

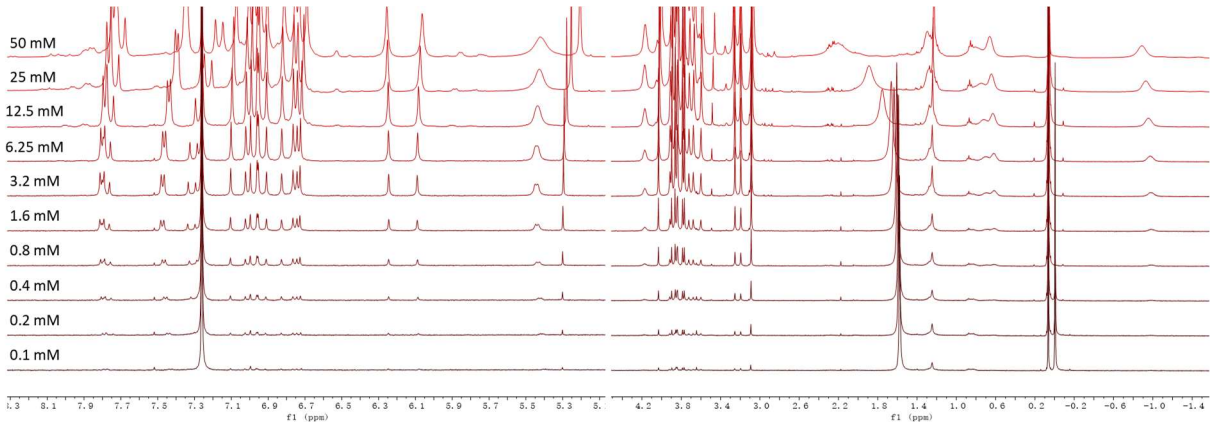


Fig. S59 **PI2** in CDCl3 at various concentration.

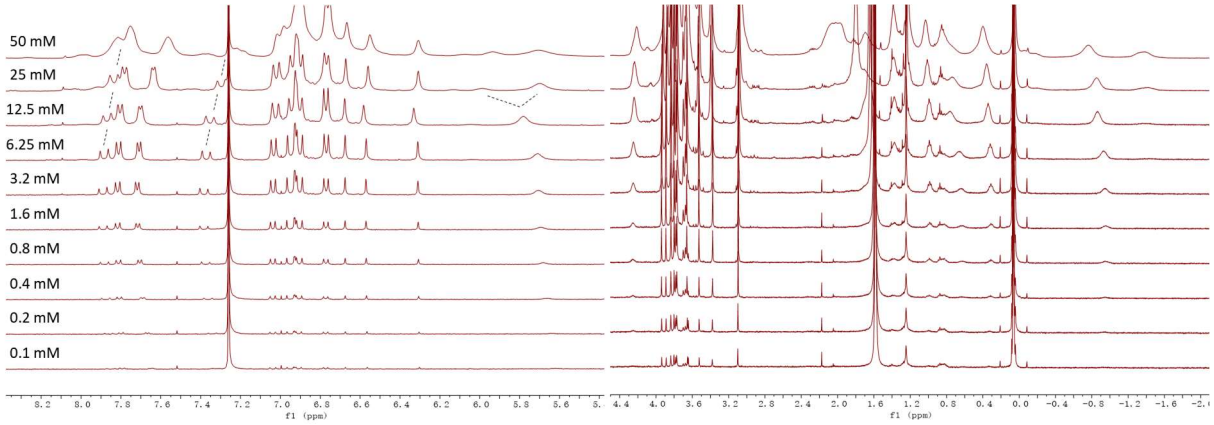


Fig. S60 **PI3** in CDCl3 at various concentration.

## 2D DOSY

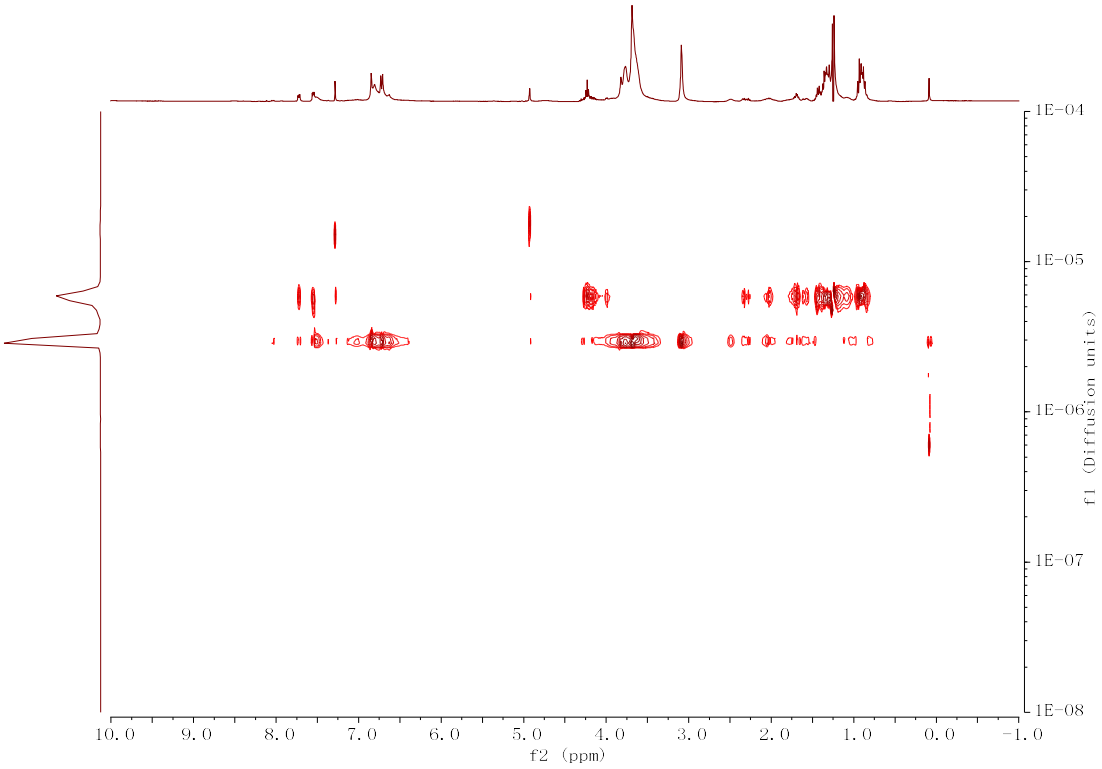


Fig. S61 2D Dosy of **PI1** in $CDCl_3$.

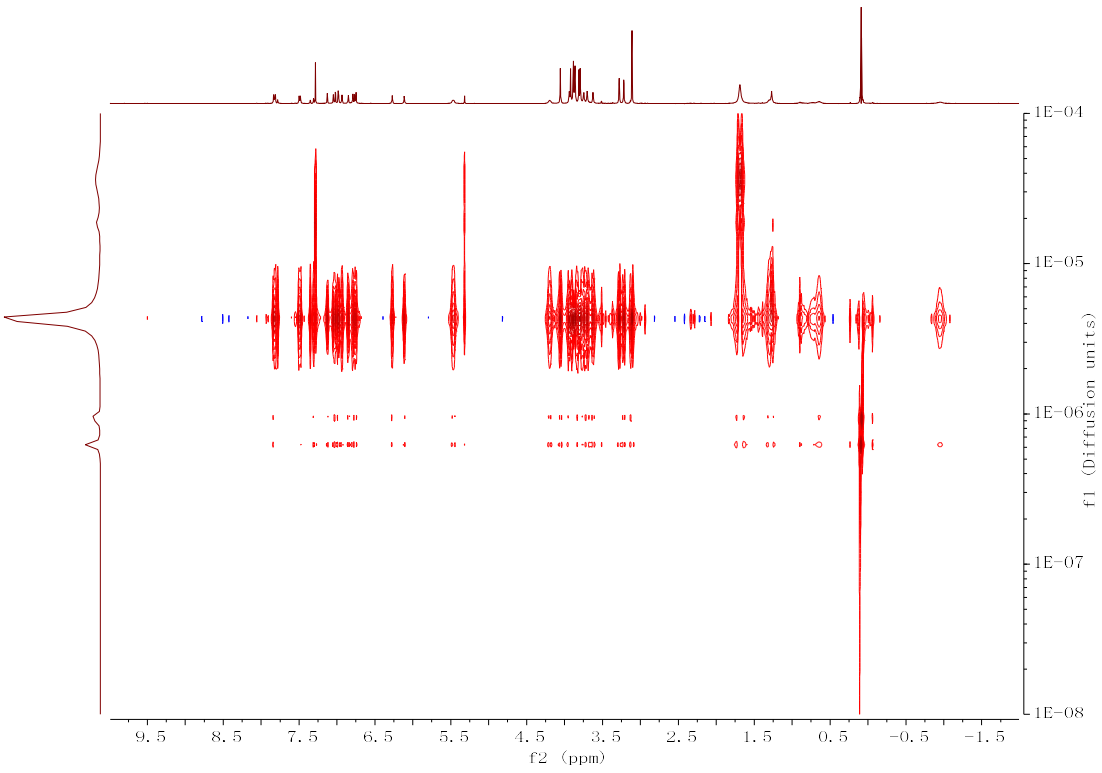


Fig. S62 2D Dosy of **PI2** in $CDCl_3$.

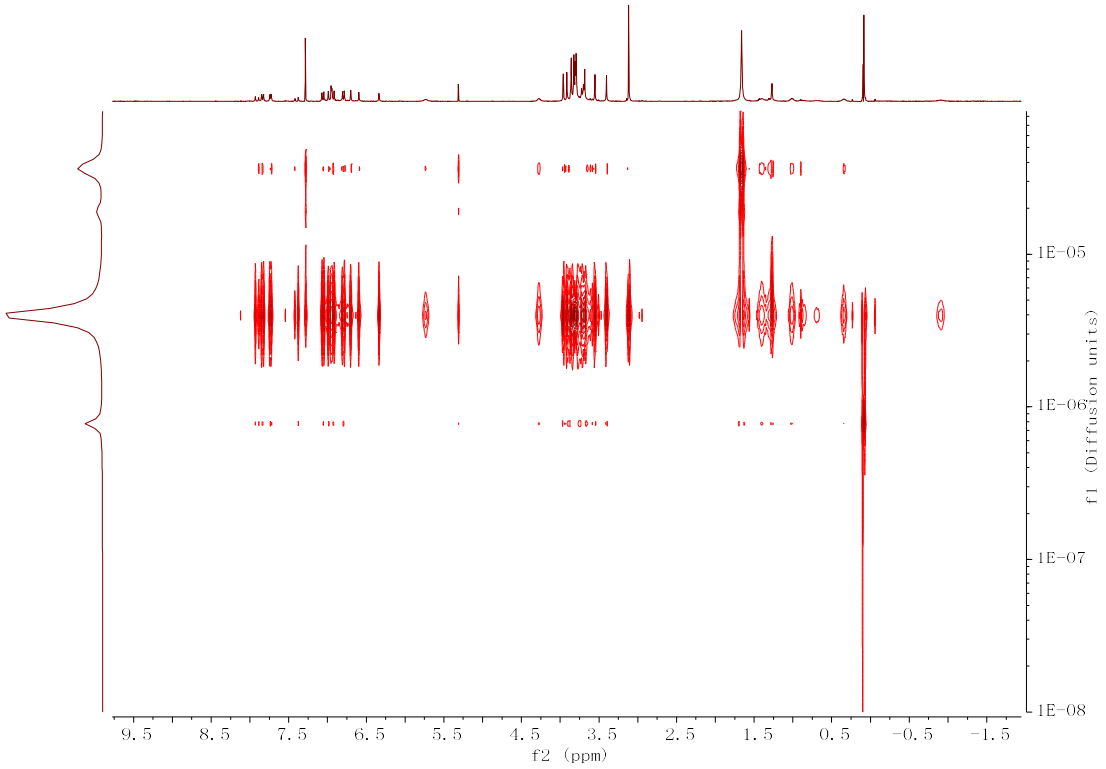


Fig. S63 2D Dosy of **PI3** in $CDCl_3$.

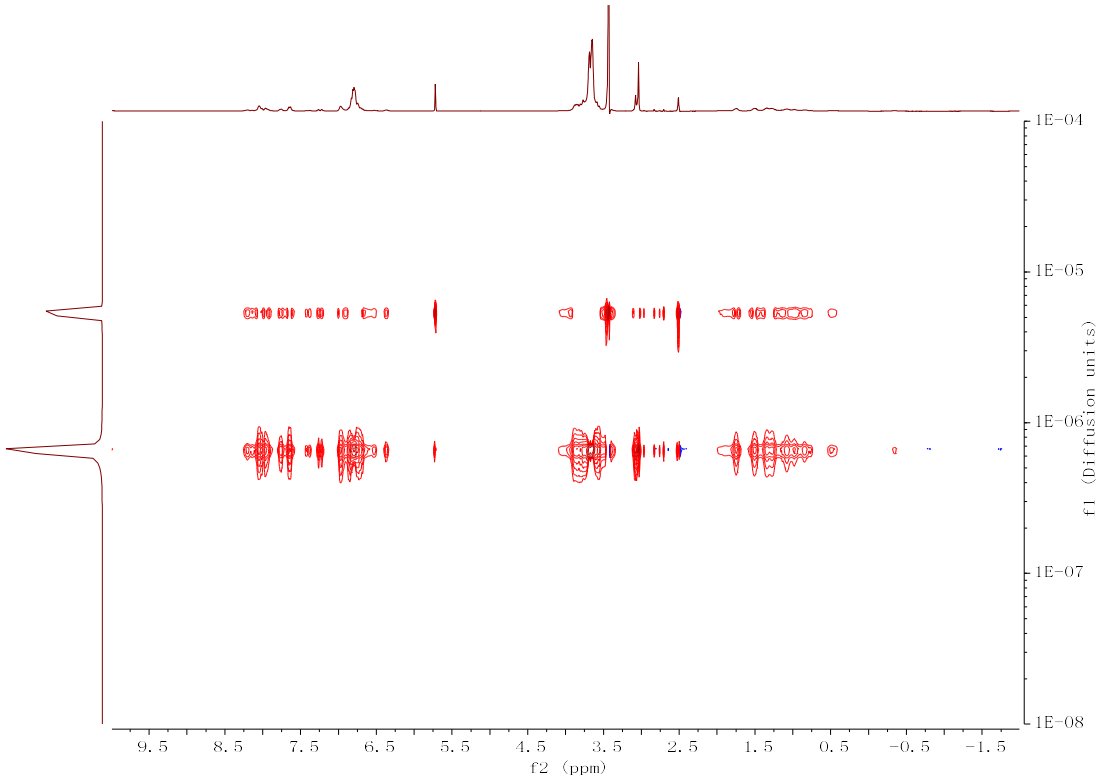


Fig. S64 2D Dosy of **PI4** in DMSO.