

One-step rapid synthesis of π -conjugated large oligomers *via* C–H activation coupling

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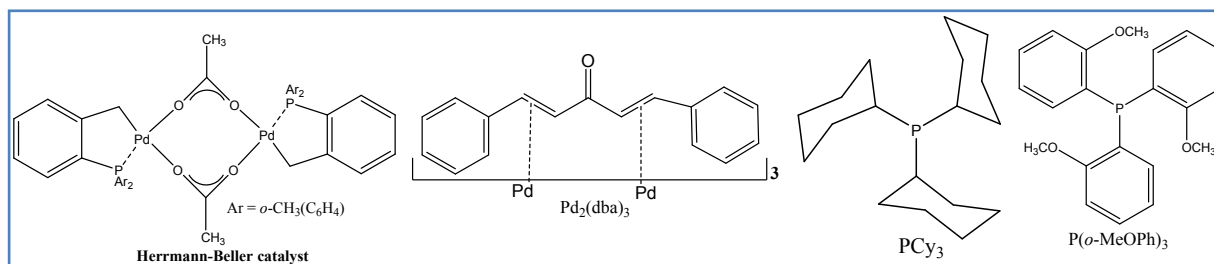
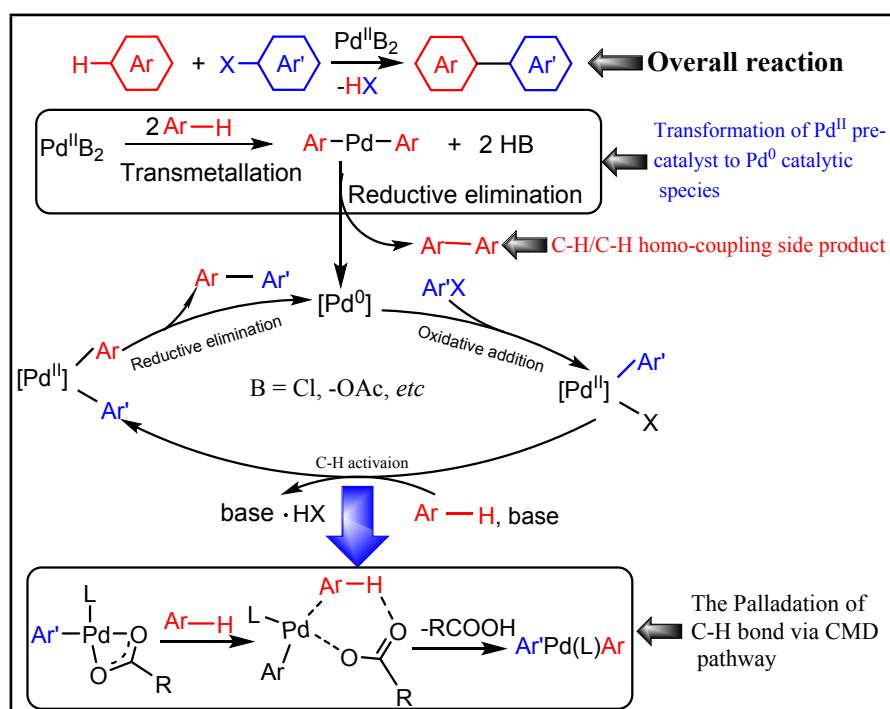


Fig. S1 The molecular structures of Herr Pd, Pd₂(dba)₃, PCy₃ and P(o-MeOPh)₃.



Scheme S1 The Pd-catalyzed DA reaction, the reduction of Pd^{II} pre-catalyst to Pd⁰ catalytic species, the catalytic cycle of the DA coupling, and the palladation of C-H bond.

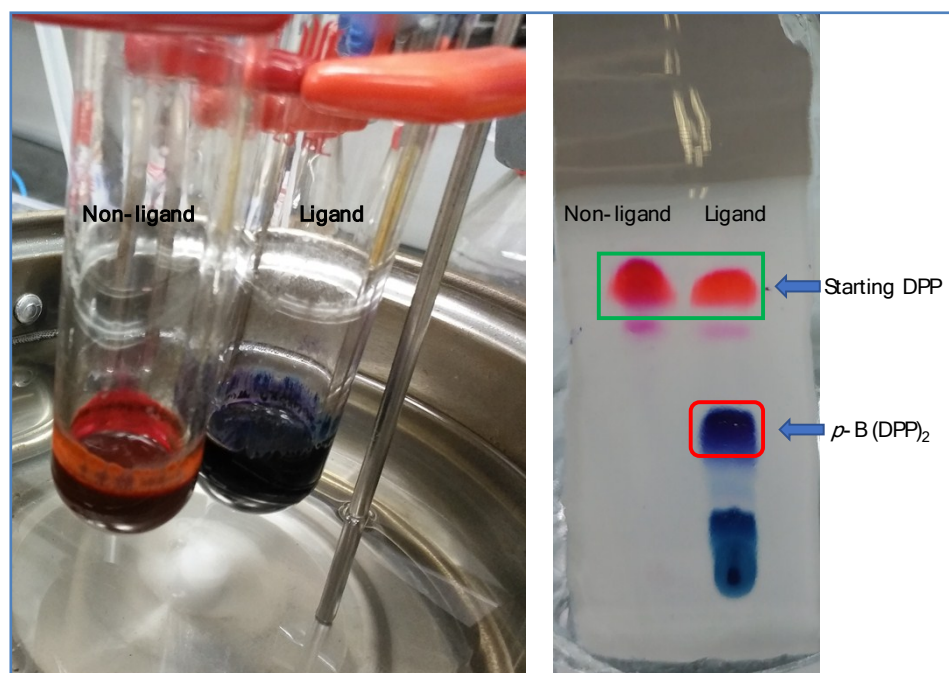


Fig. S2 The reaction between DPP and *p*-dibromobenzene with and without ligand P(*o*-MeOPh)₃ using toluene as reaction medium (entries 10 and 11 in Table 1). Digital photos of (a) The reaction mixtures after reacting for 12 h and cooling to room temperature. (b) The TLC analysis of both reaction mixtures, using CH₂Cl₂ : hexane (2:1, v/v) as eluent, and the spots marked with green and red frame are the reactant DPP and target product *p*-B(DPP)₂, respectively.

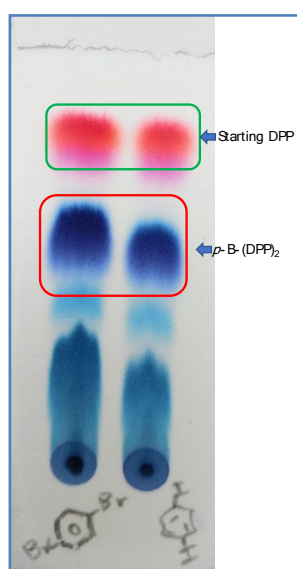


Fig. S3 The TLC analysis of the reactions between DPP and *p*-dibromobenzene (left) or *p*-diiodobenzene (right). (see Entries 12 and 13 in Table 1). The spots marked with green and red frame are the reactant DPP and target product *p*-B(DPP)₂, respectively.

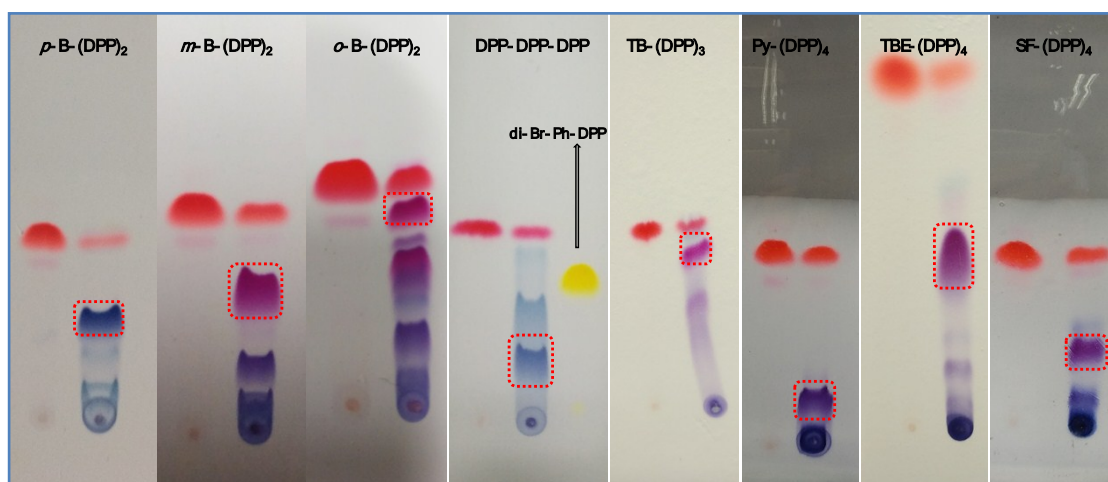


Fig. S4 Digital photos of TLC analysis of the synthetic reactions for the eight oligomers. From left to right are respectively *p*-B-(DPP)₂, *m*-B-(DPP)₂, *o*-B-(DPP)₂, DPP-DPP-DPP, TB-(DPP)₃, Py-(DPP)₄, TBE-(DPP)₄ and SF-(DPP)₄. For all the TLC plates, the spots on the left are the starting DPP, and the spots marked with red dotted frames are the target oligomers.

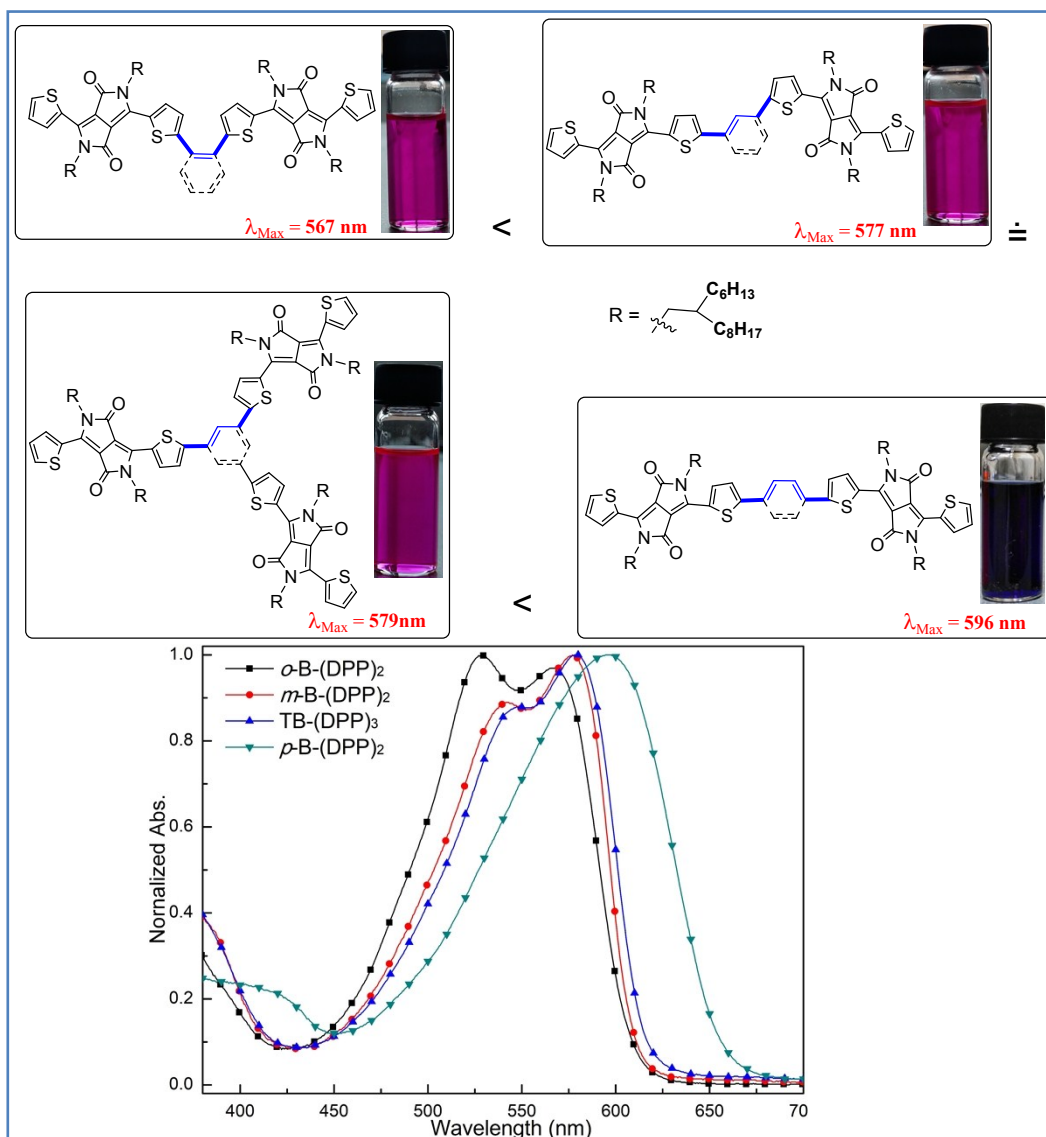


Fig. S5 The shortest pathways of π -electron delocalization (marked with blue color) of the phenyl-cored DPP-based oligomers $o\text{-B}-(\text{DPP})_2$, $m\text{-B}-(\text{DPP})_2$, $p\text{-B}-(\text{DPP})_2$ and $\text{TB}-(\text{DPP})_3$, and the corresponding normalized Uv-vis spectra (below).

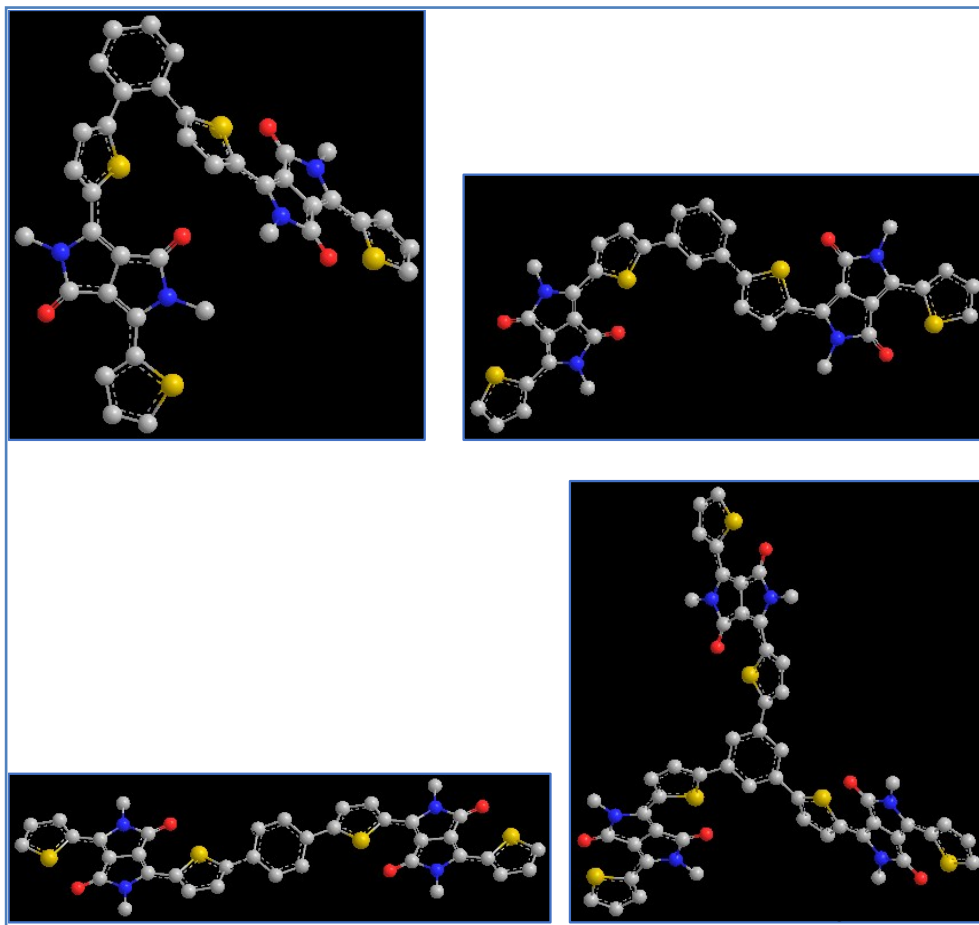


Fig. S6 DFT optimized geometries of phenyl-cored DPP-based oligomers, *o*-B-(DPP)₂, *m*-B-(DPP)₂, *p*-B-(DPP)₂ and TB-(DPP)₃ (the alkyl chains replaced by methyl groups).

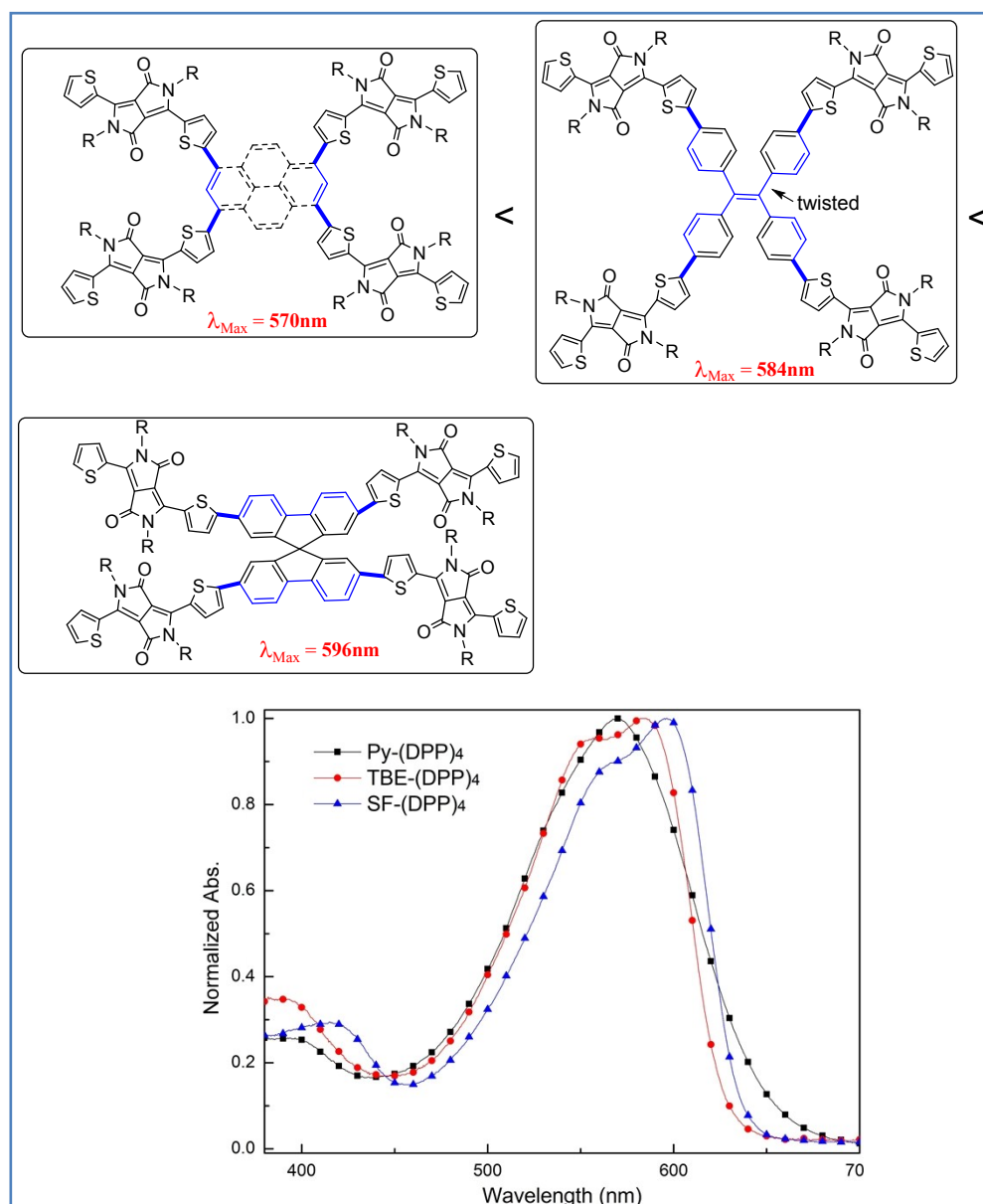


Fig. S7 The shortest pathways of π -electron delocalization (marked with blue color) of the **Py-**, **TBE-** and **SF-(DPP)₄** oligomers, and the corresponding normalized Uv-vis spectra (below).

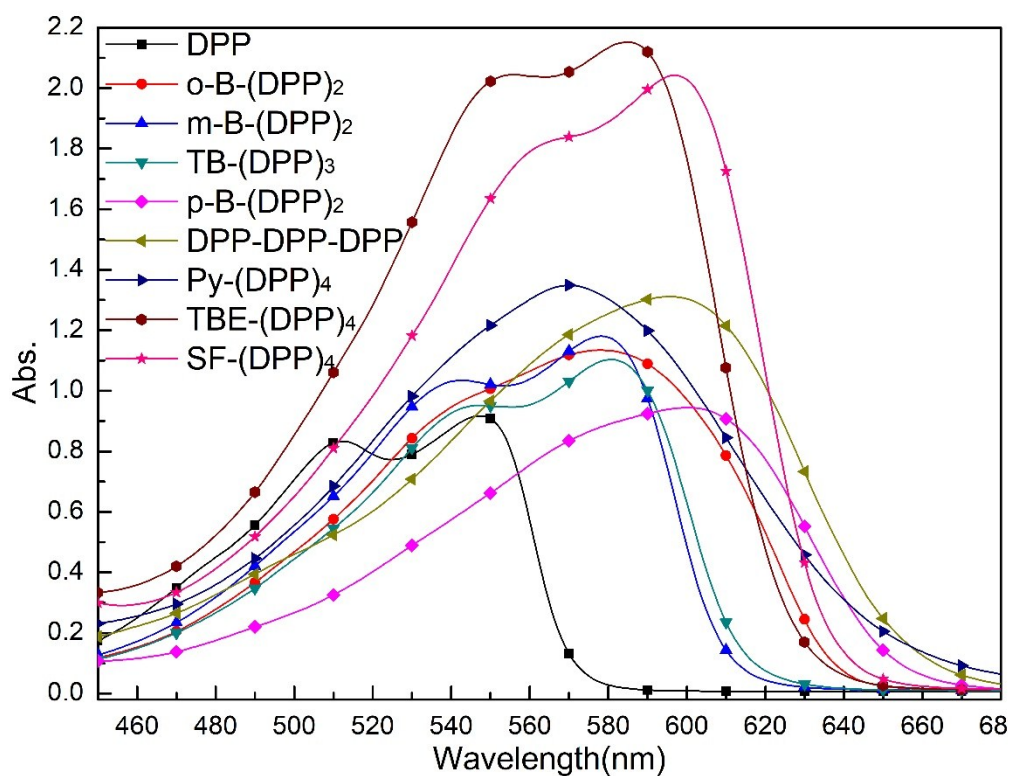
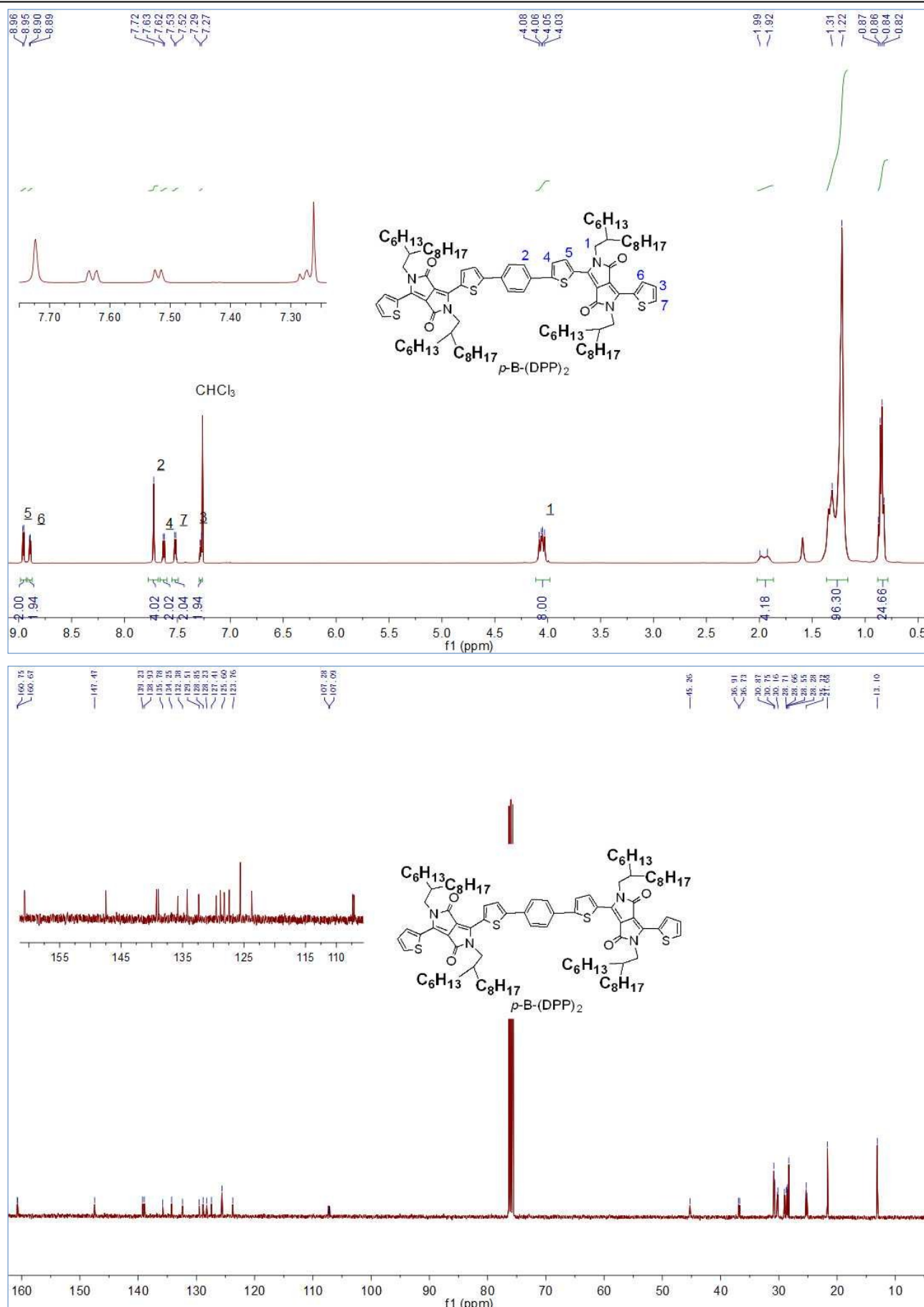
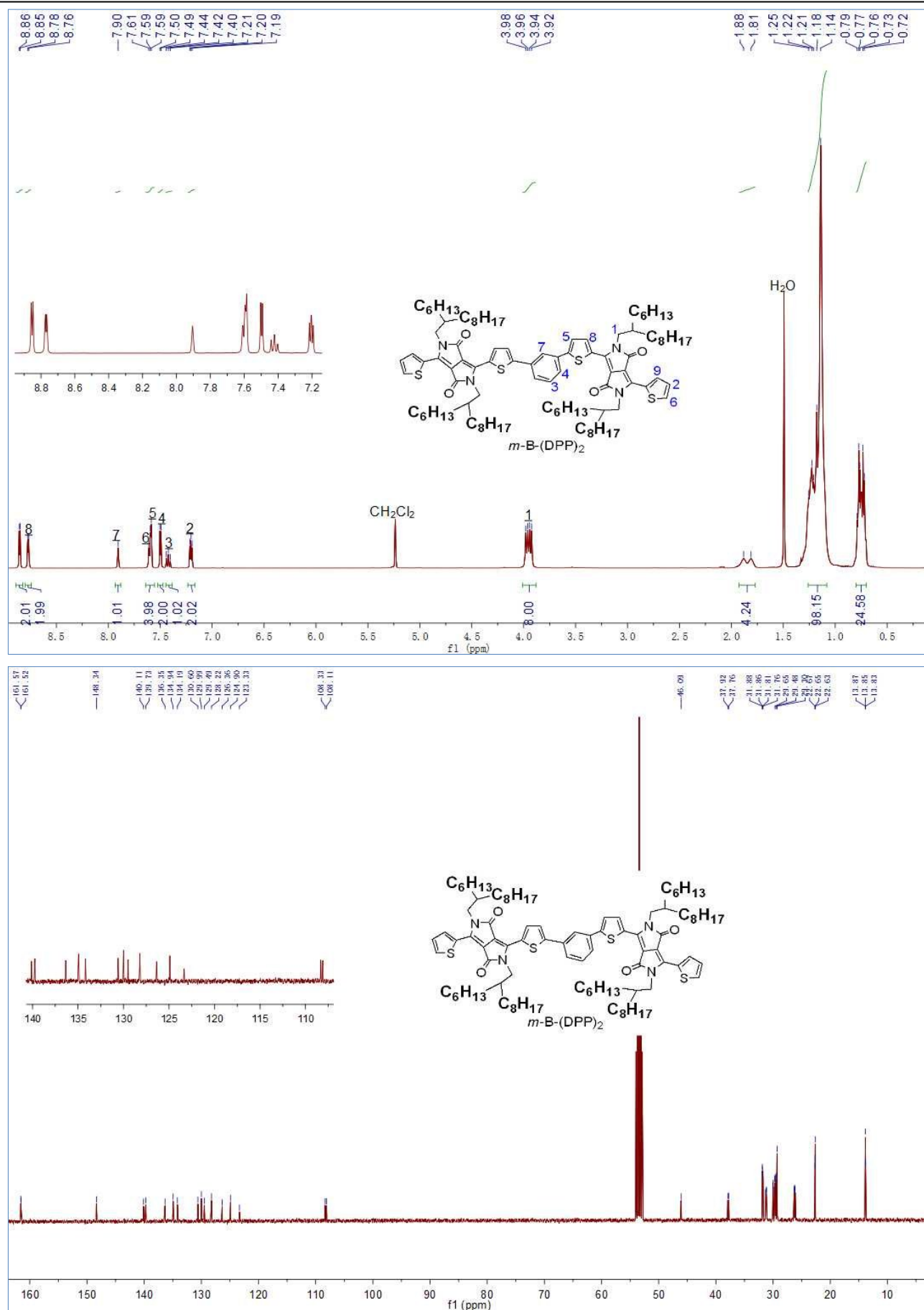


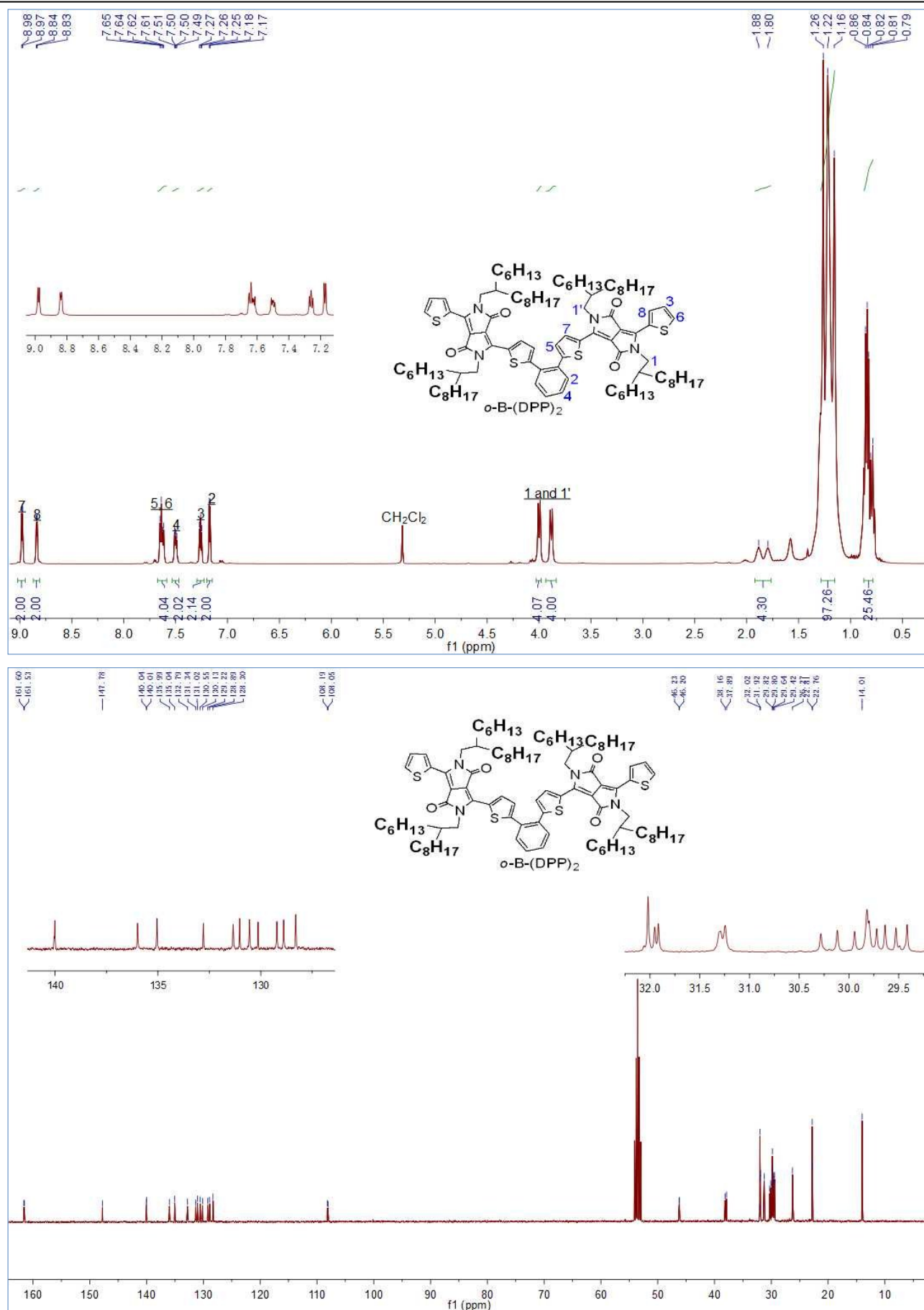
Fig. S8 The Uv-vis spectra of the starting DPP, oligomers *o*-B-(DPP)₂, *m*-B-(DPP)₂, TB-(DPP)₃, *p*-B-(DPP)₂, Py-(DPP)₄, TBE-(DPP)₄ and SF-(DPP)₄ in CHCl₃ at concentrations of 4.54, 2.54, 2.03, 1.55, 2.16, 1.89, 1.07, 1.69 and 1.27×10^{-5} mol/L.

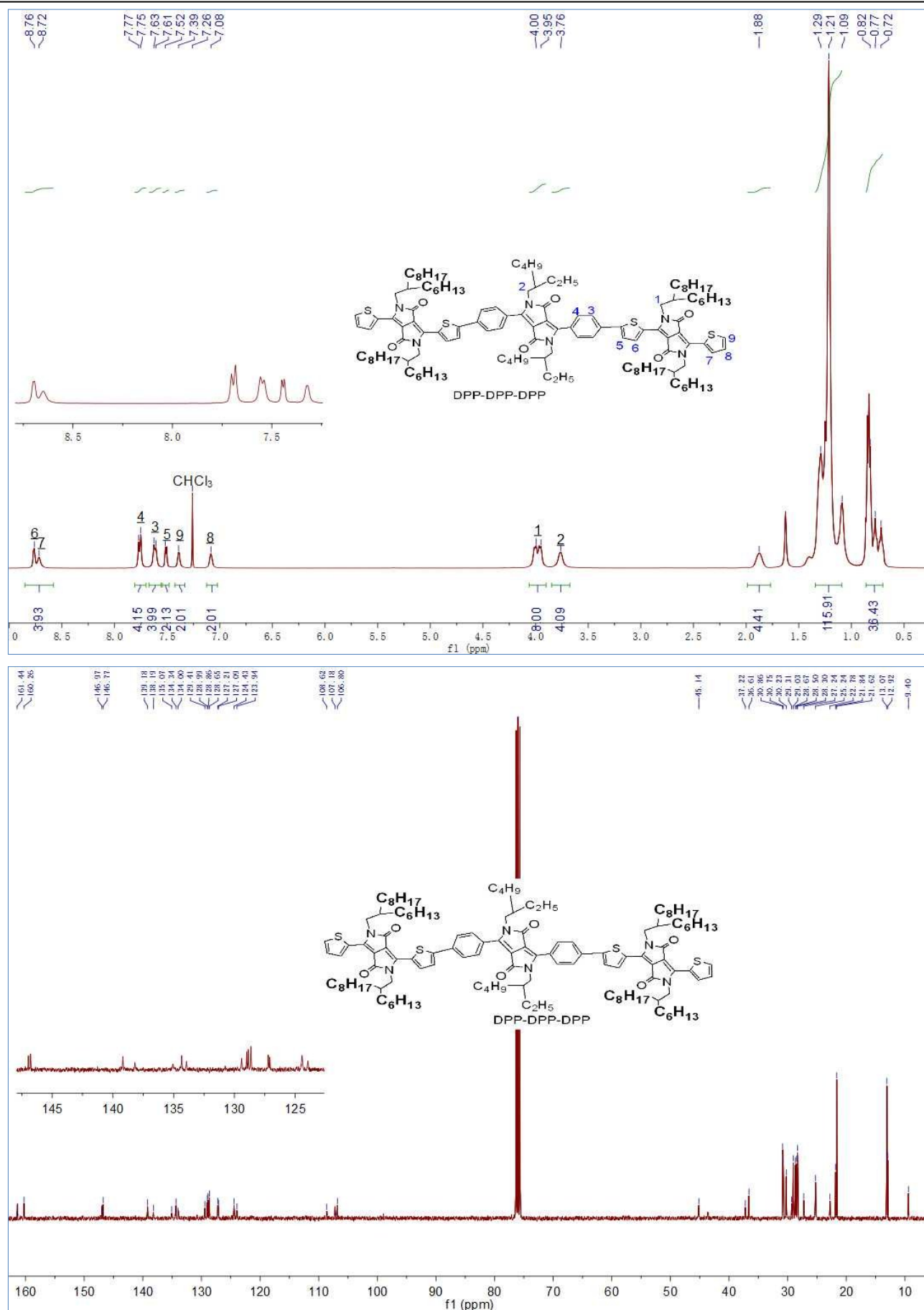
Table S1 The extinction coefficients of the DPP materials at λ_{max} s ($\times 10^4$ M⁻¹ cm⁻¹).

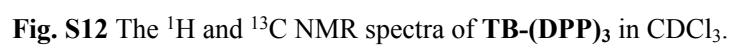
DPP	<i>o</i> -B-(DPP) ₂	<i>m</i> -B-(DPP) ₂	<i>p</i> -B-(DPP) ₂	TB-(DPP) ₃	DPP-DPP-DPP	Py-(DPP) ₄	TBE-(DPP) ₄	SF-(DPP) ₄
2.02	4.47	5.82	4.38	6.94	7.12	12.61	12.74	14.08

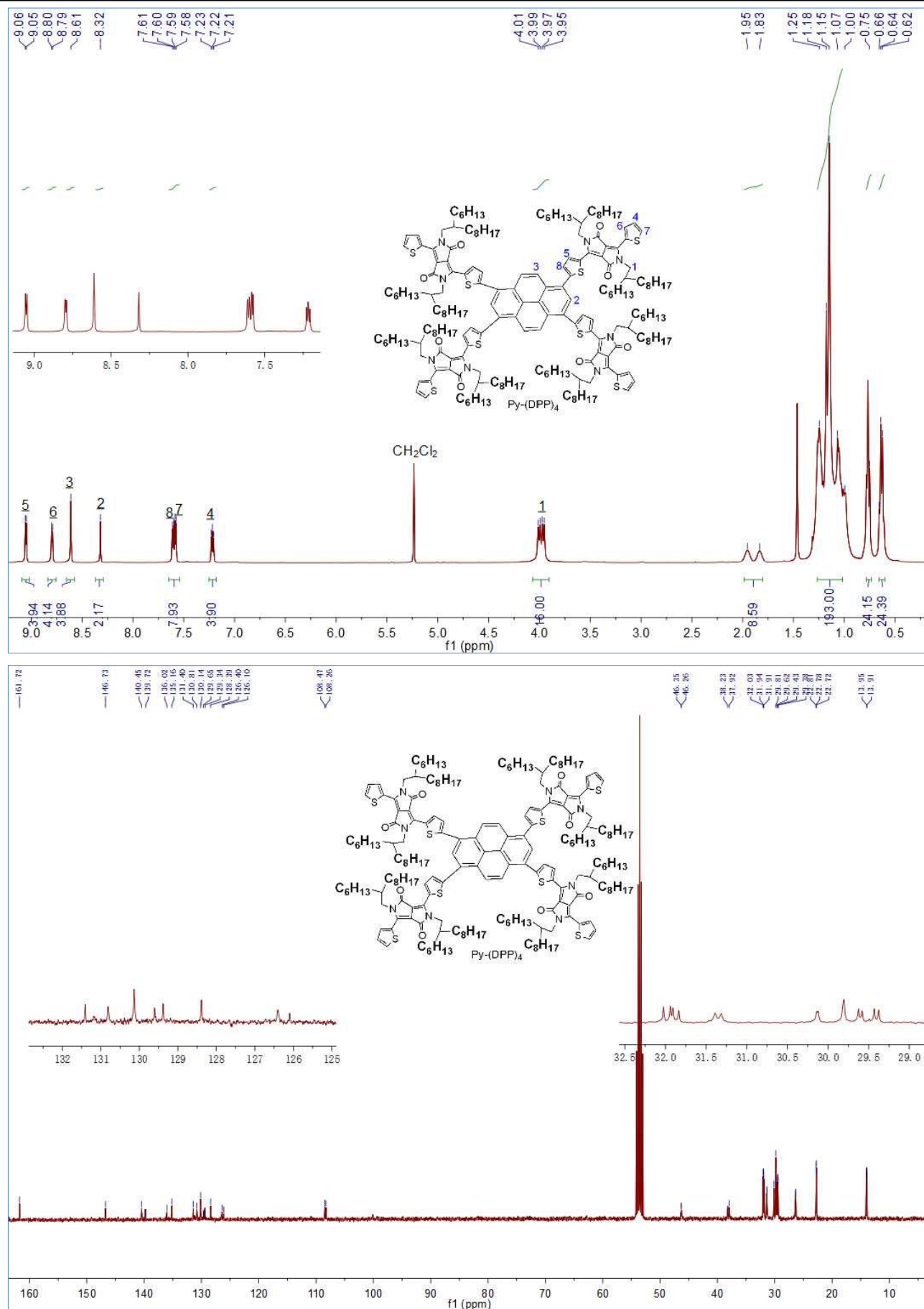
**Fig. S8** The ^1H and ^{13}C NMR spectra of $p\text{-B-(DPP)}_2$ in CDCl_3 .

**Fig. S9** The ^1H and ^{13}C NMR spectra of *m*-B-(DPP) $_2$ in CD_2Cl_2 .

**Fig. S10** The ^1H and ^{13}C NMR spectra of *o*-B-(DPP) $_2$ in CD_2Cl_2 .

**Fig. S11** The ^1H and ^{13}C NMR spectra of DPP-DPP-DPP in CDCl_3 .





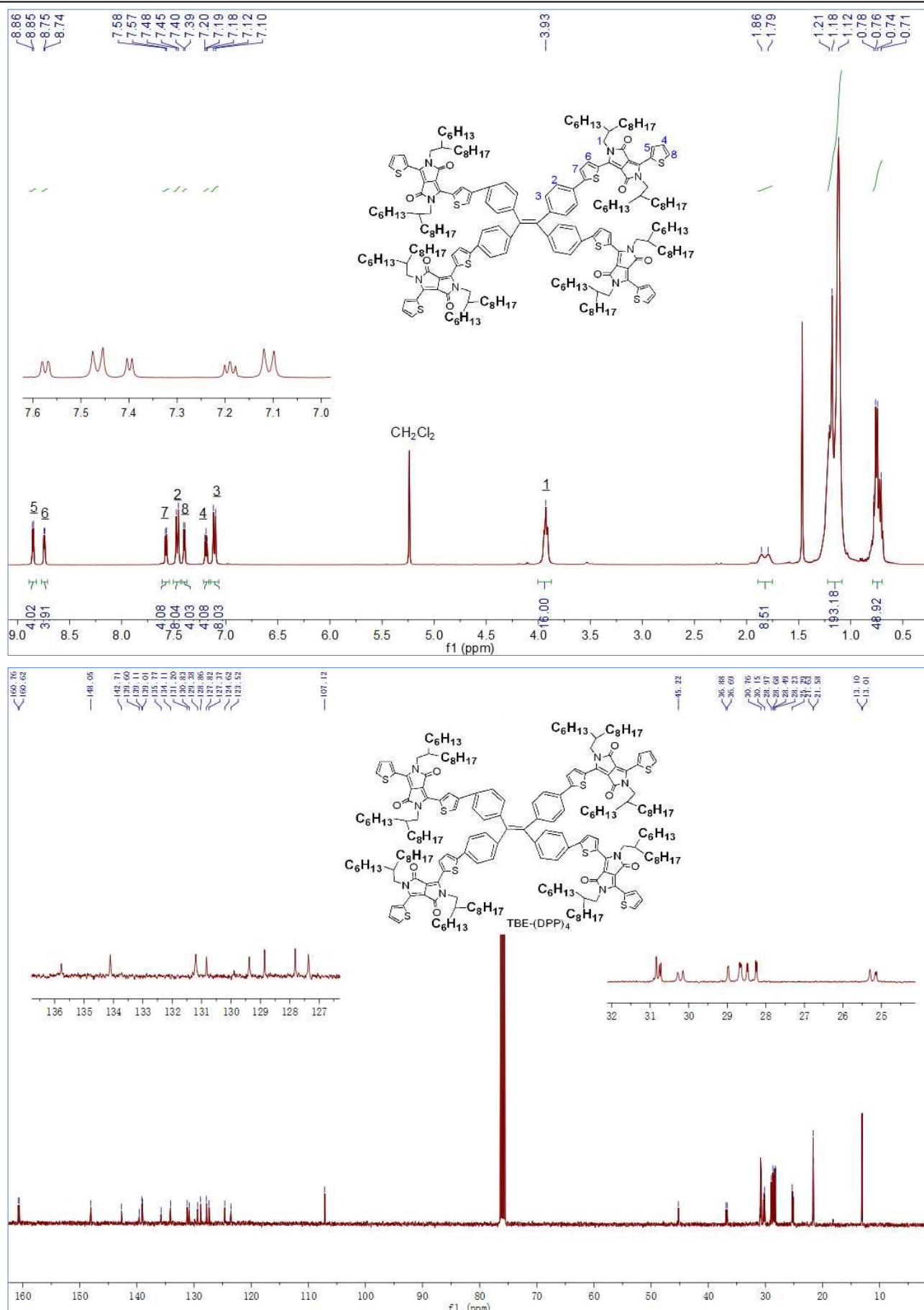


Fig. S14 The ¹H and ¹³C NMR spectra of TBE-(DPP)₄ in CD₂Cl₂ and in CDCl₃, respectively.



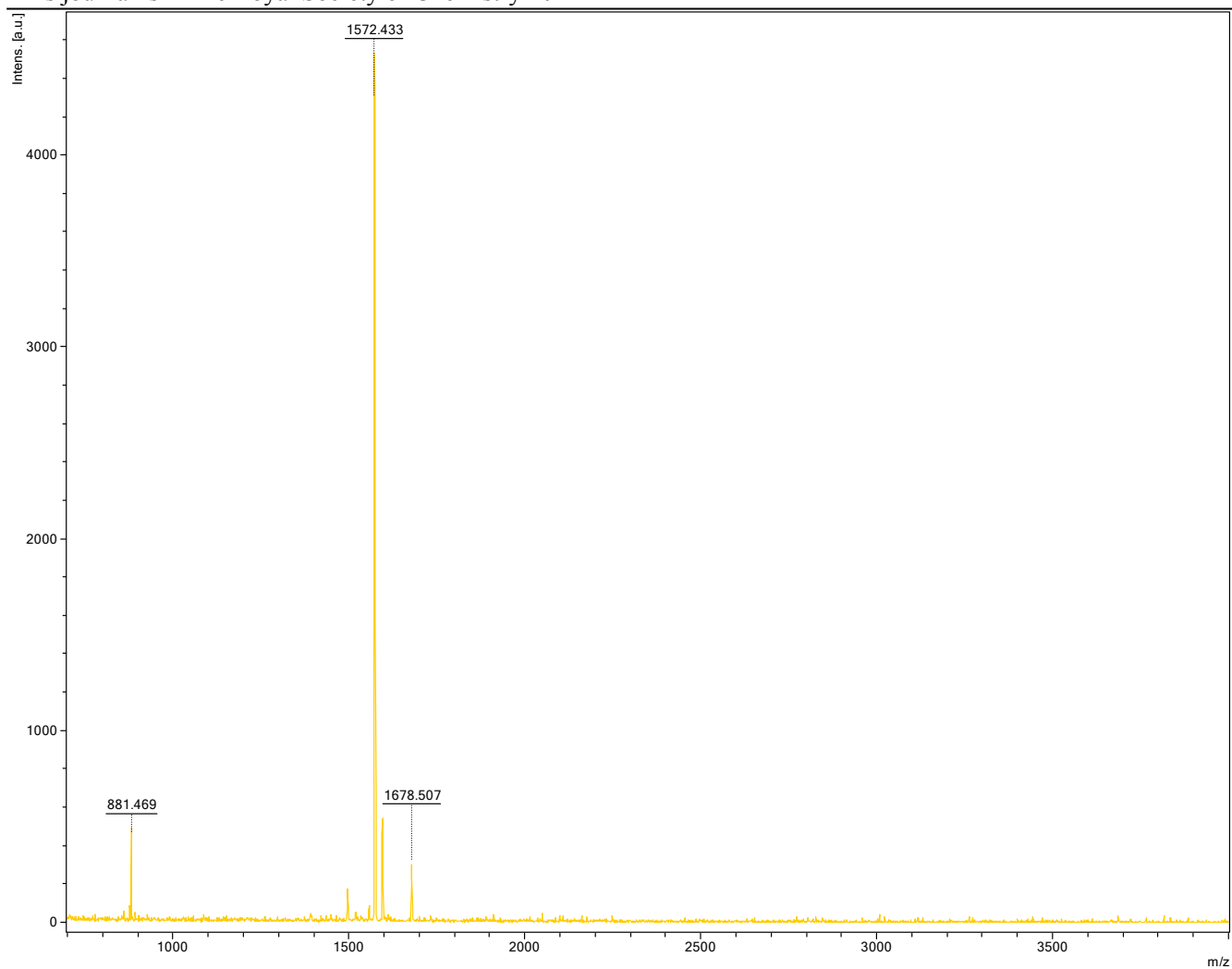


Fig. S16 The MALDI-TOF MS spectrum of *p*-**B-(DPP)₂**, calcd. 1572.51, found 1572.43.

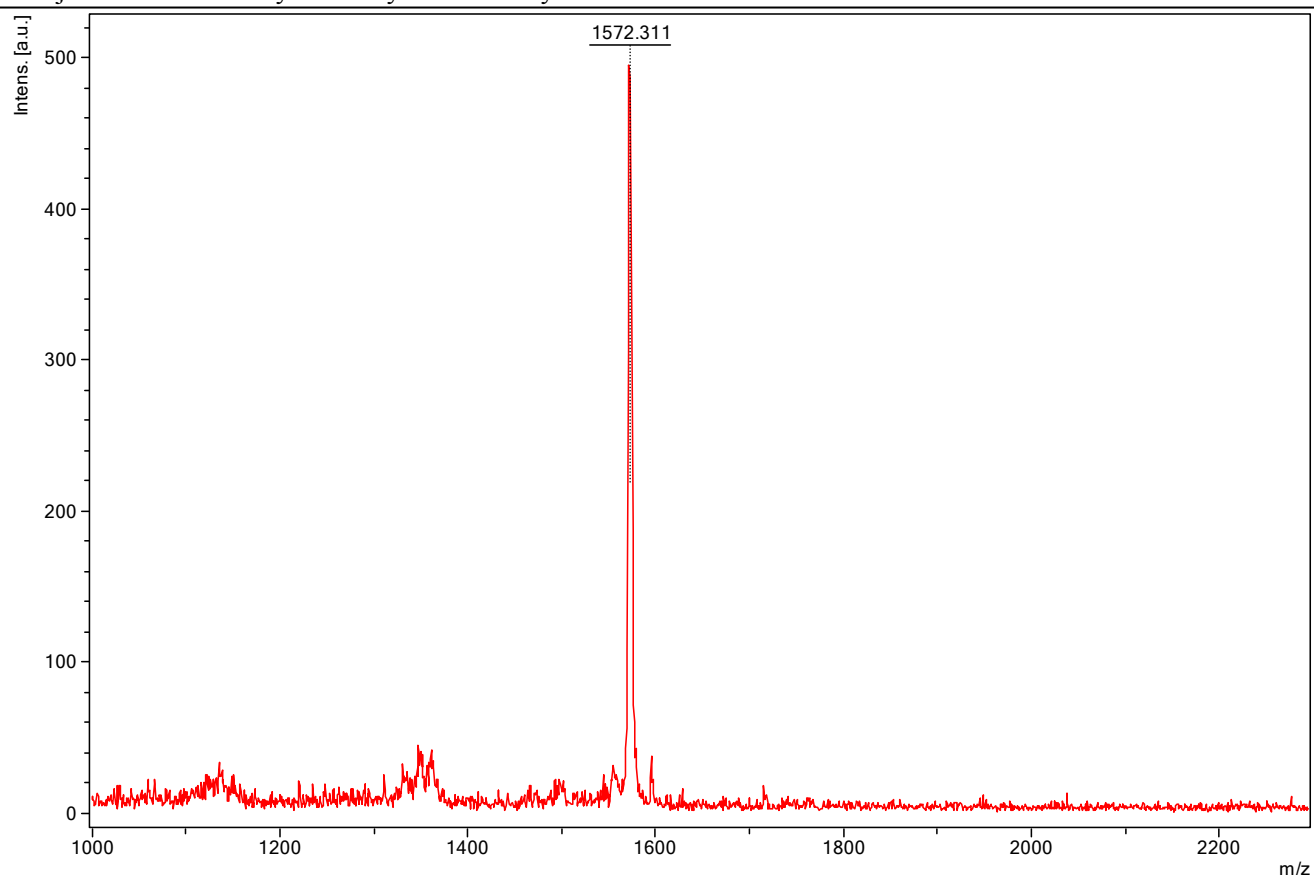


Fig. S17 The MALDI-TOF MS spectrum of *m*-B-(DPP)₂, calcd. 1572.51, found 1572.31.

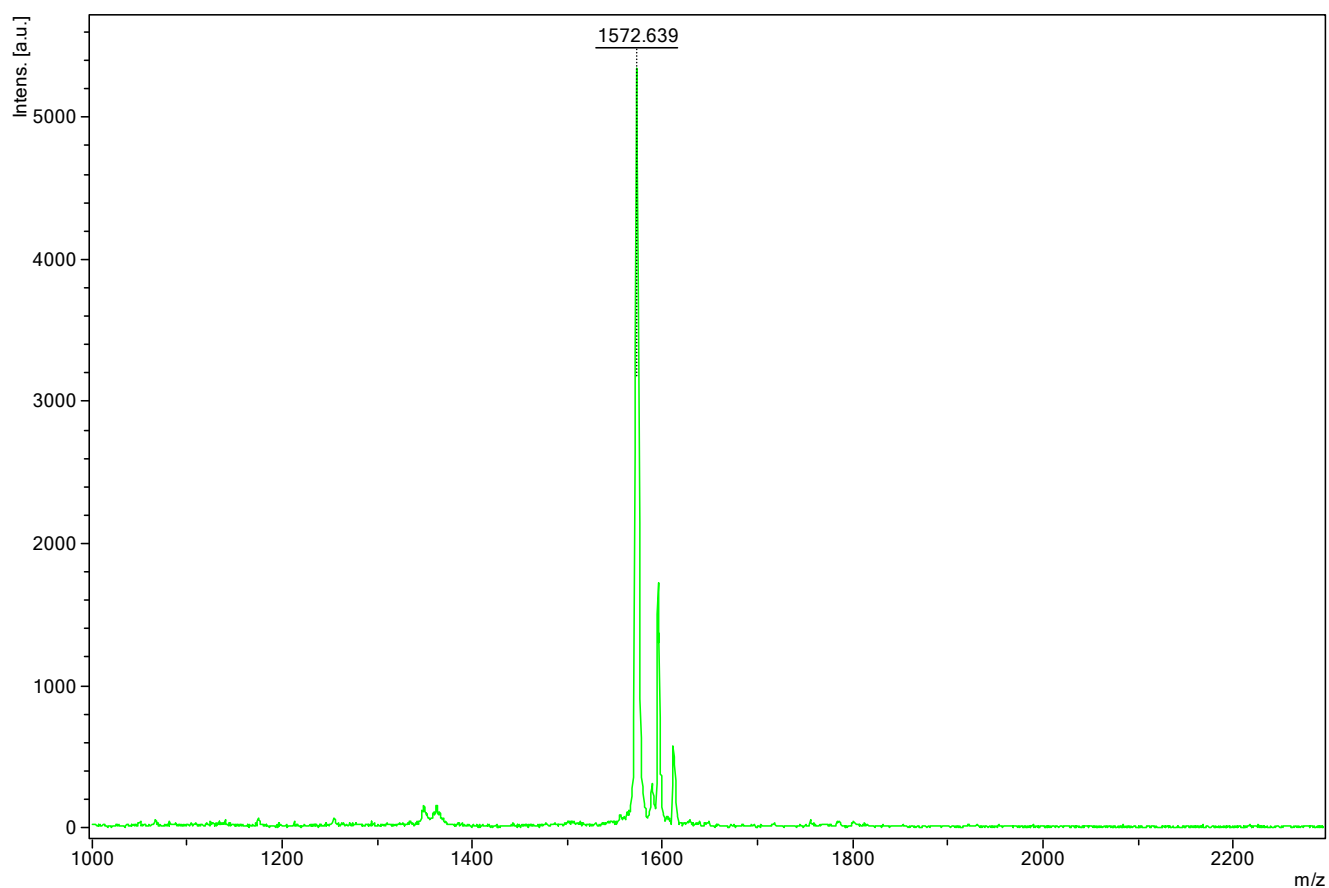


Fig. S18 The MALDI-TOF MS spectrum of *o*-B-(DPP)₂, calcd. 1572.51, found 1572.64.

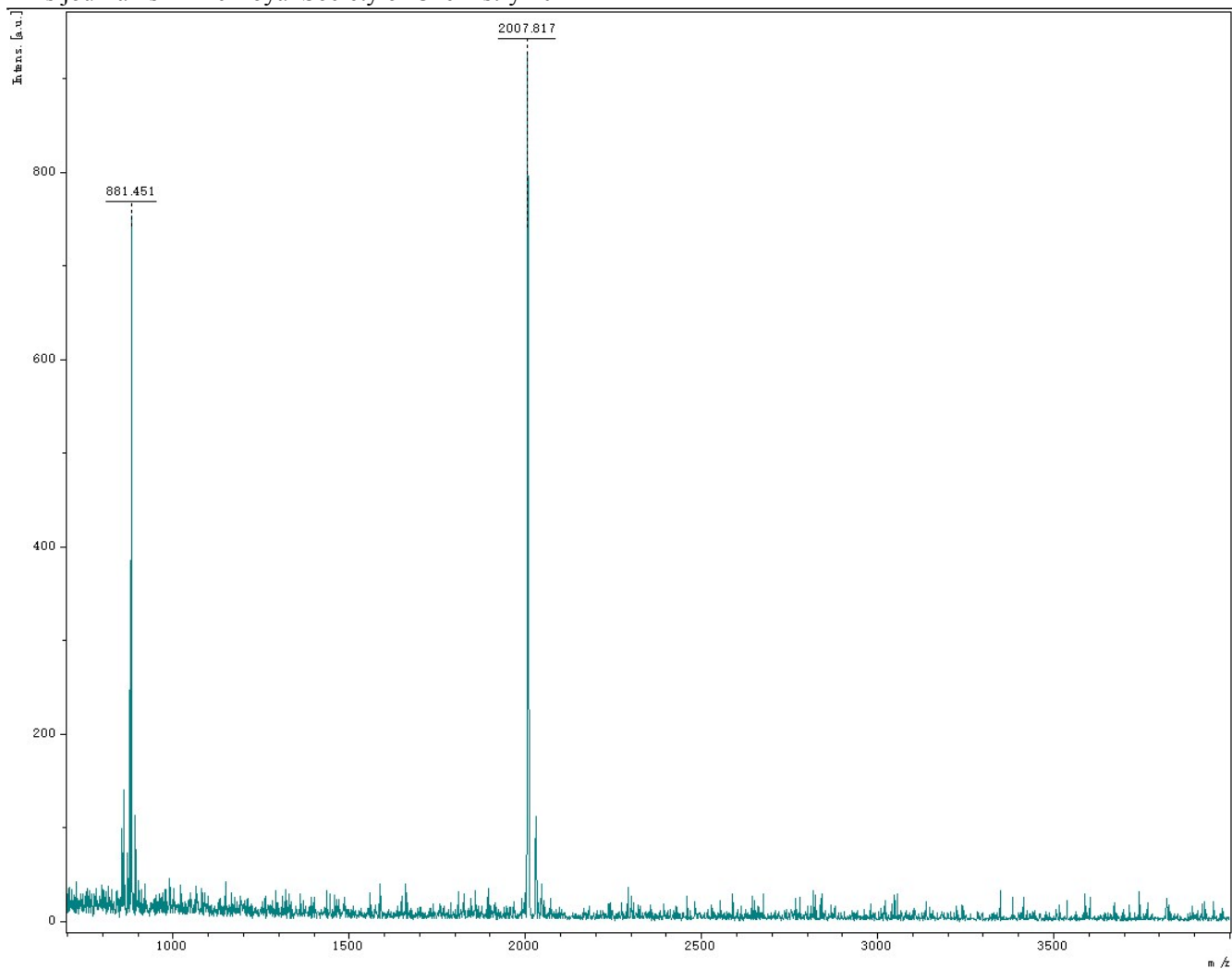


Fig. S19 The MALDI-TOF MS spectrum of **DPP-DPP-DPP**, calcd. 2007.13, found 2007.82.

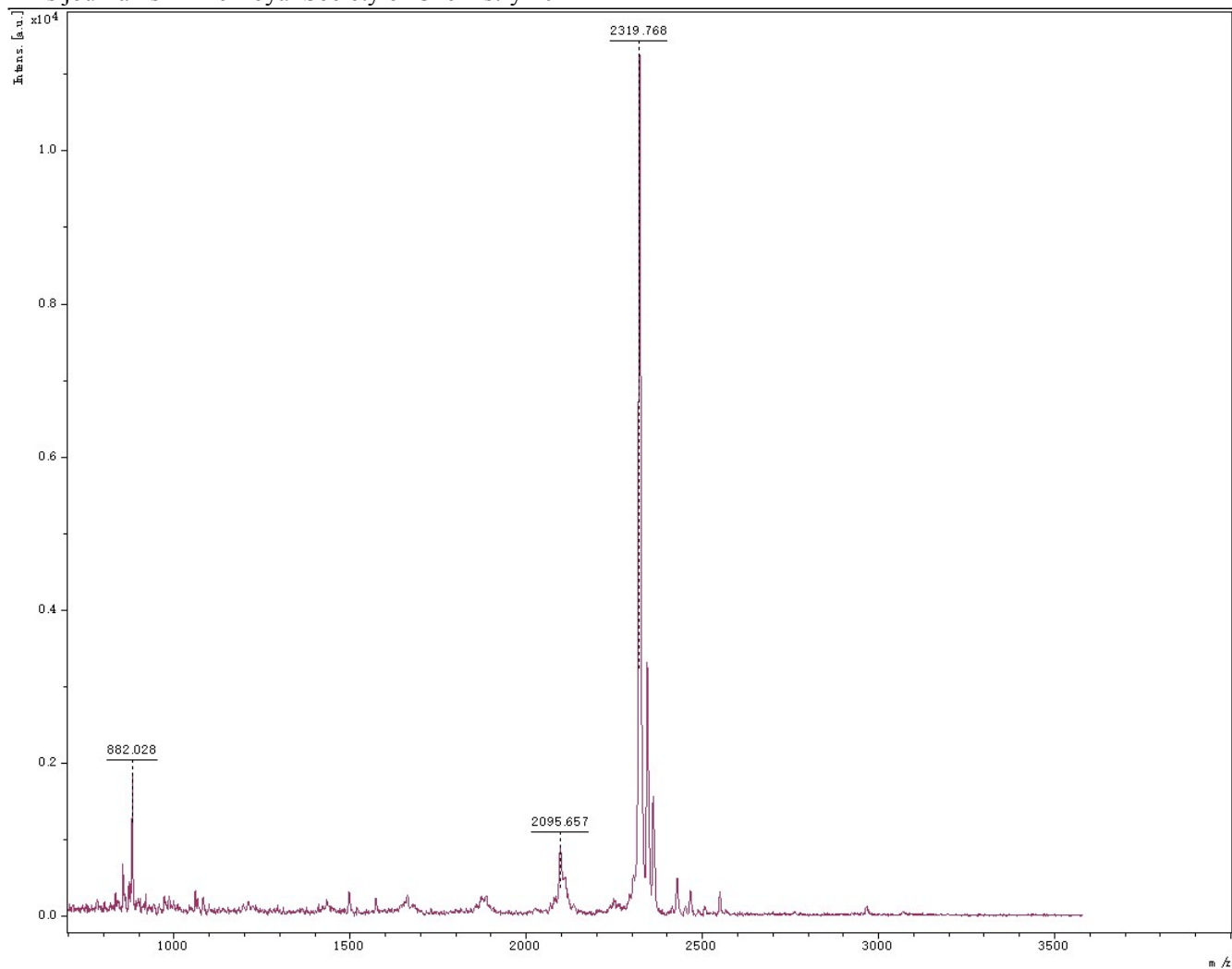


Fig. S20 The MALDI-TOF MS spectrum of **TB-(DPP)₃**, calcd. 2319.71, found 2319.77.

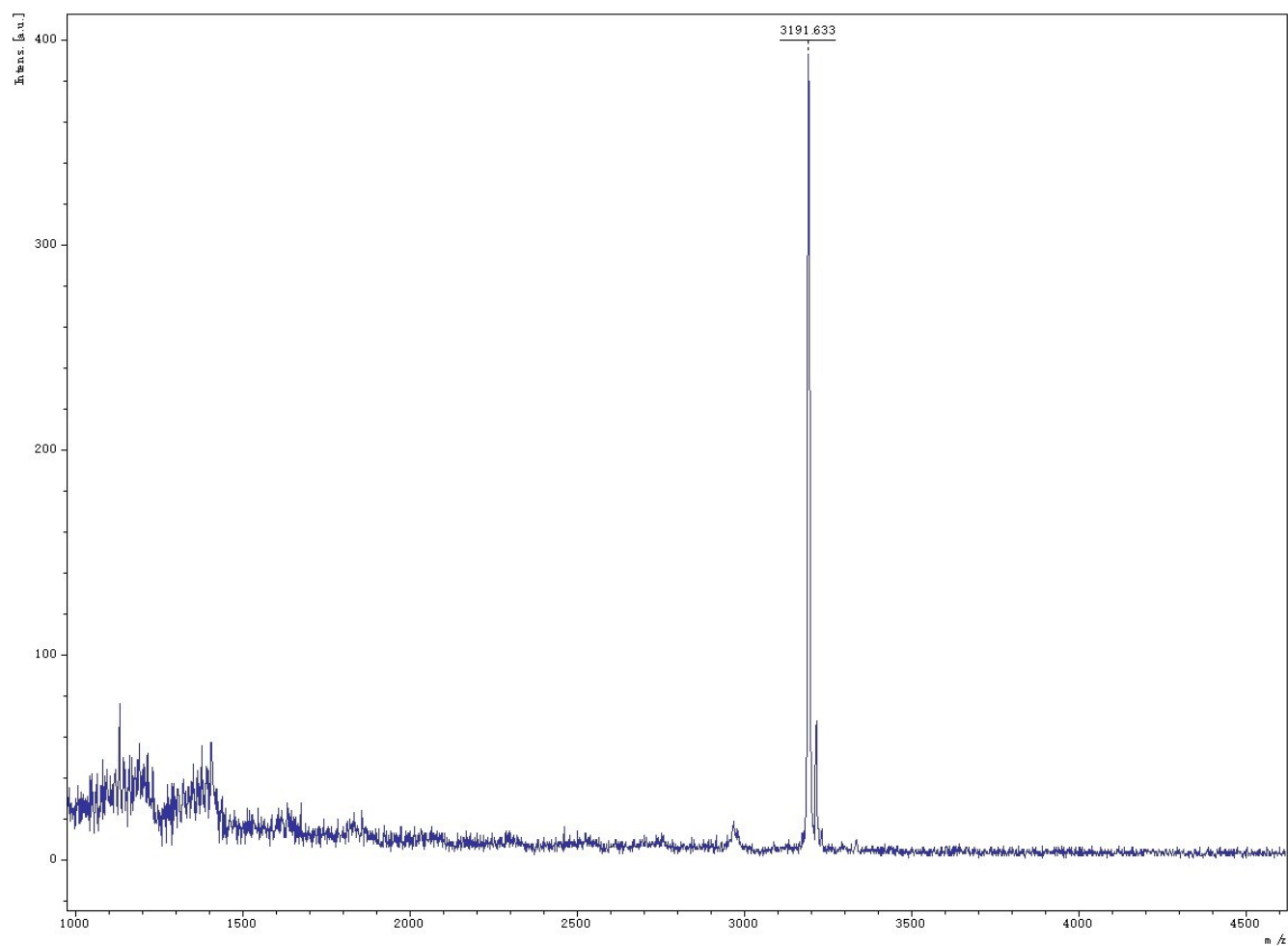


Fig. S21 The MALDI-TOF MS spectrum of **Py-(DPP)₄**, calcd. 3191.05, found 3191.63.

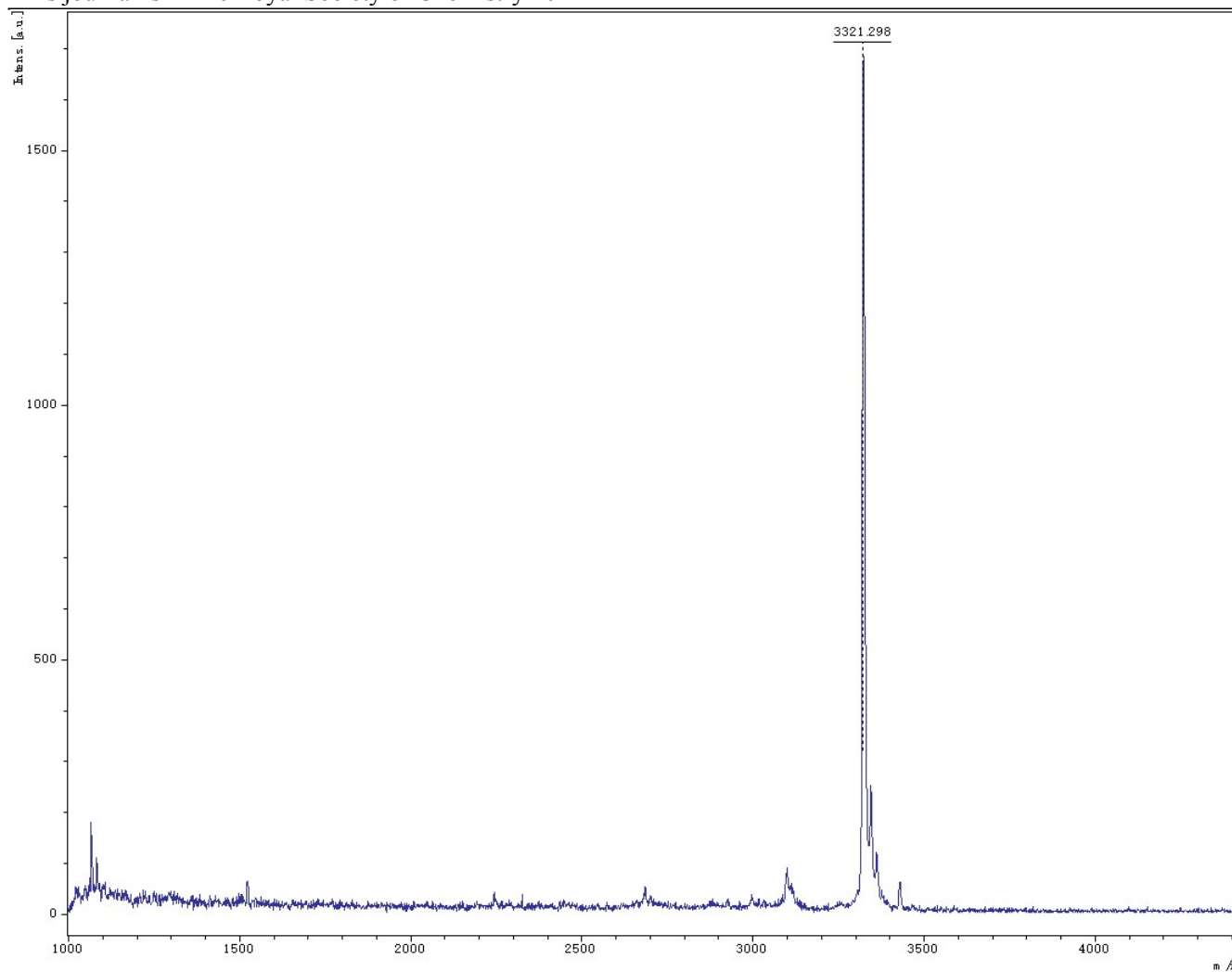


Fig. S22 The MALDI-TOF MS spectrum of **TBE-(DPP)₄**, calcd. 3321.34, found 3321.30.

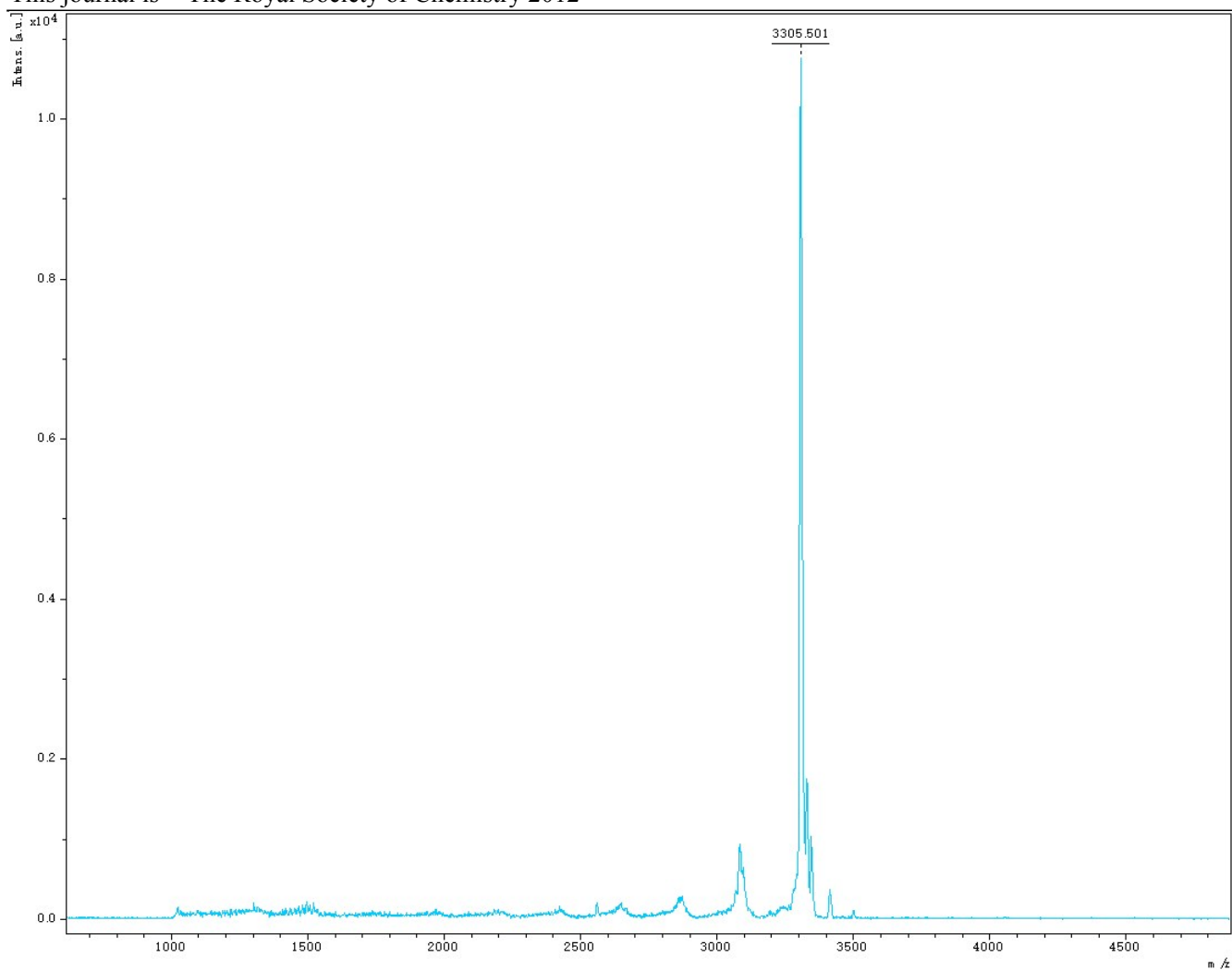


Fig. S23 The MALDI-TOF MS spectrum of **SF-(DPP)₄**, calcd. 3305.20, found 3305.50.