

## Electronic Supplementary Information (ESI)

# **Novel naphtho[1,2-*b*:5,6-*b'*]dithiophene core inear donor- $\pi$ -acceptor conjugated small molecules with thiophene-bridged bithiazole acceptor: Design, synthesis, and their application in bulk heterojunction organic solar cells**

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S2

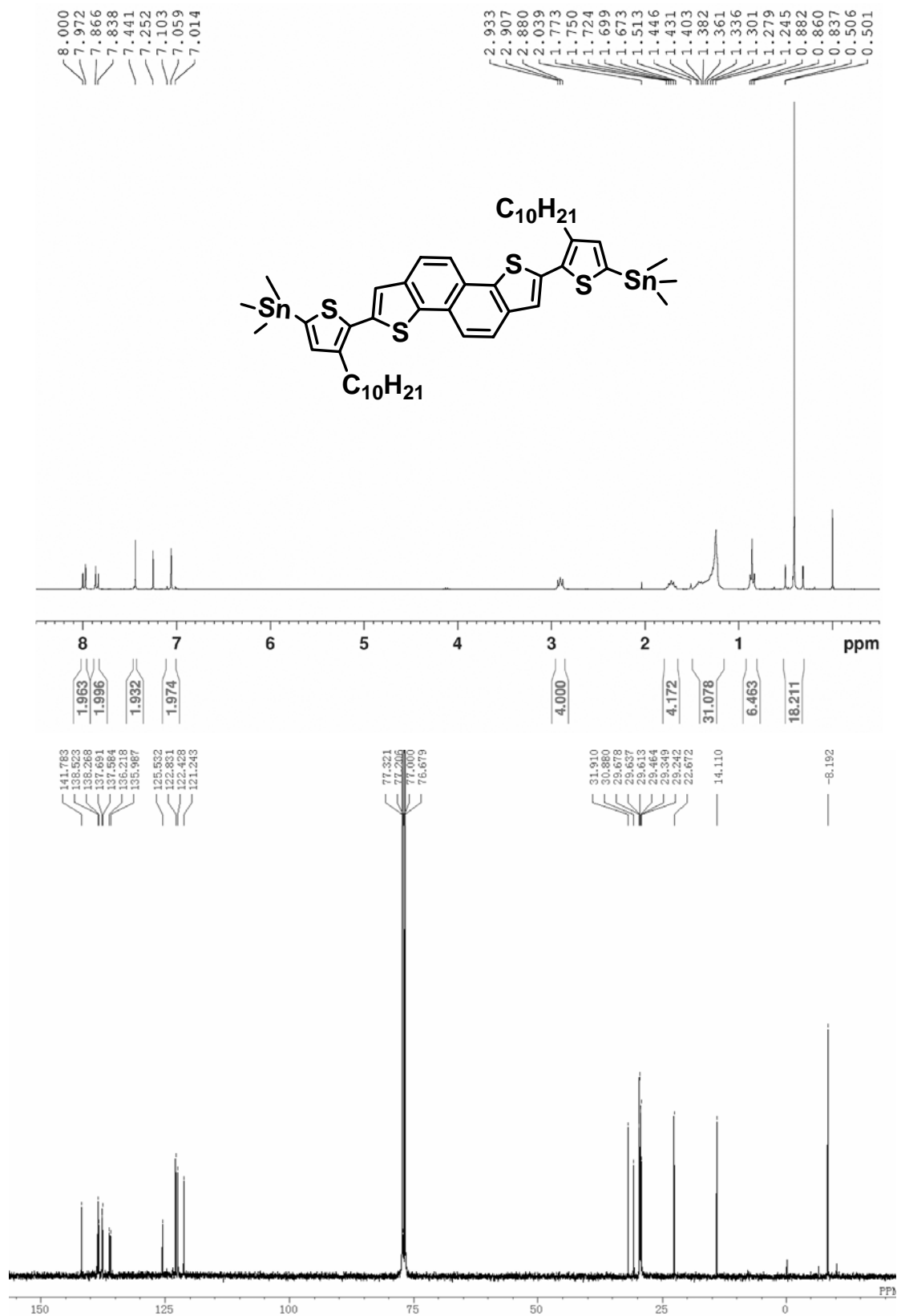


Fig. S1  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of compound **10** in  $\text{CDCl}_3$

S3

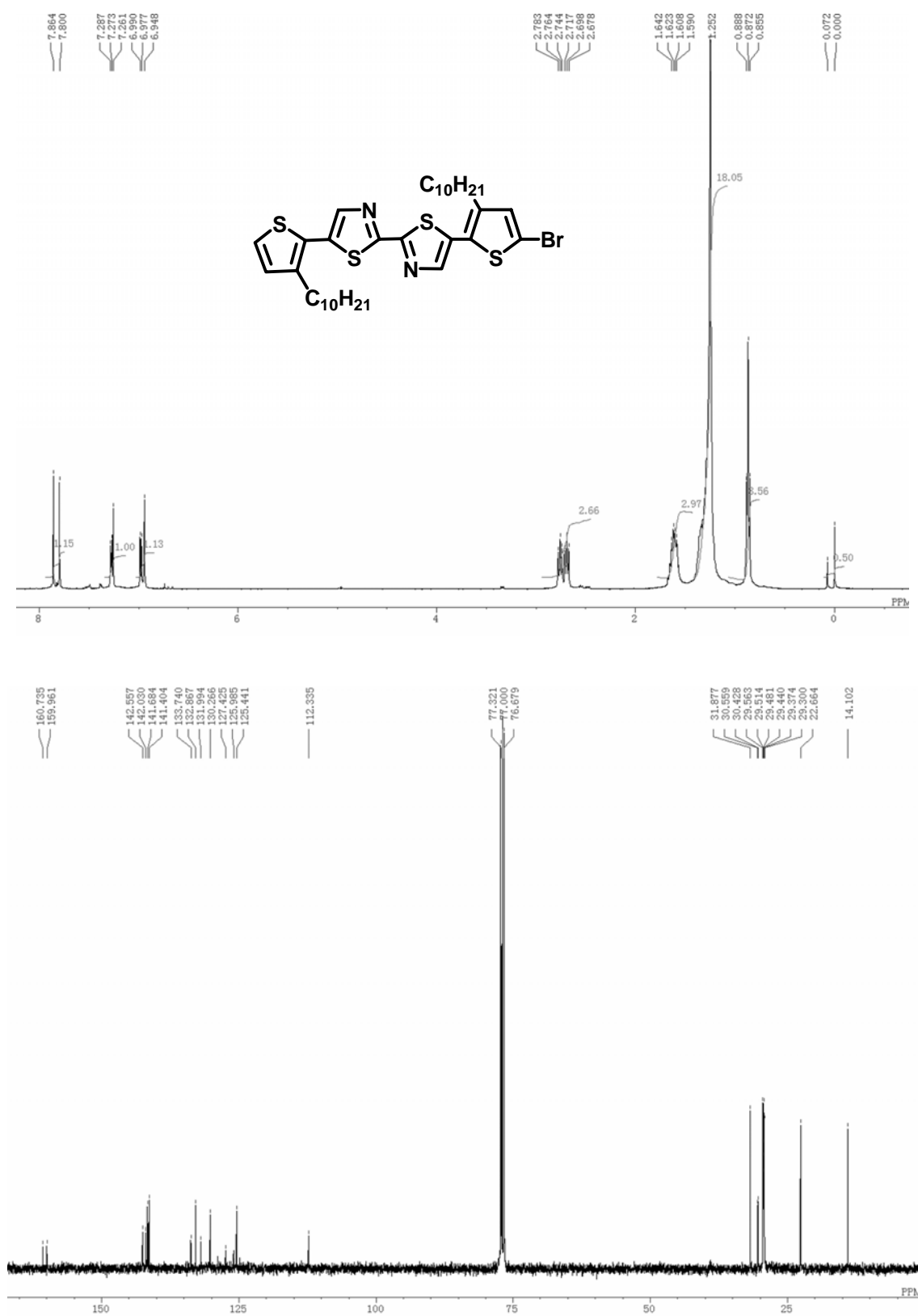


Fig. S2. <sup>1</sup>H-NMR and <sup>13</sup>C NMR spectra of compound **15** in CDCl<sub>3</sub>

S4

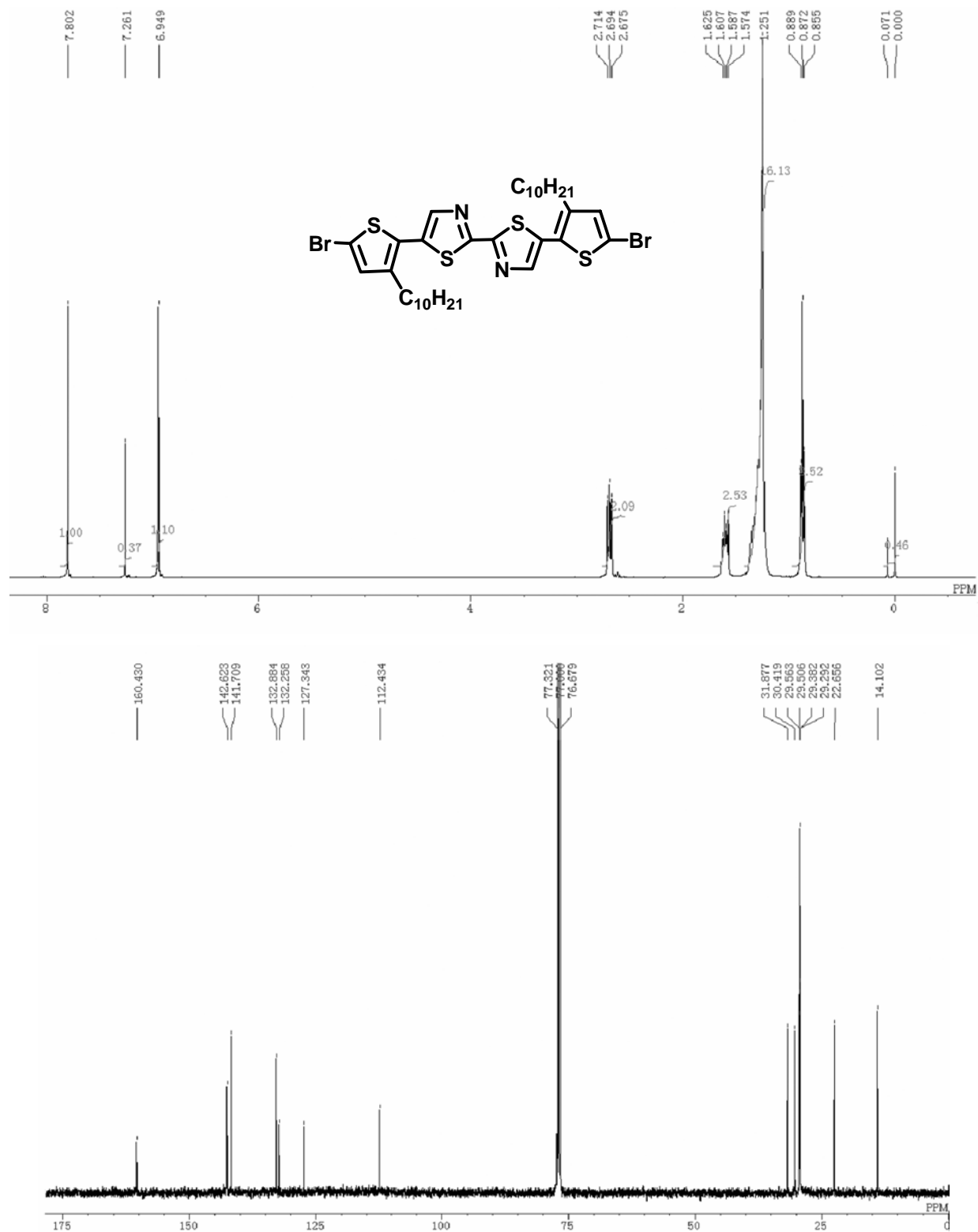


Fig. S3. <sup>1</sup>H-NMR and <sup>13</sup>C NMR spectra of compound 16 in CDCl<sub>3</sub>

S5

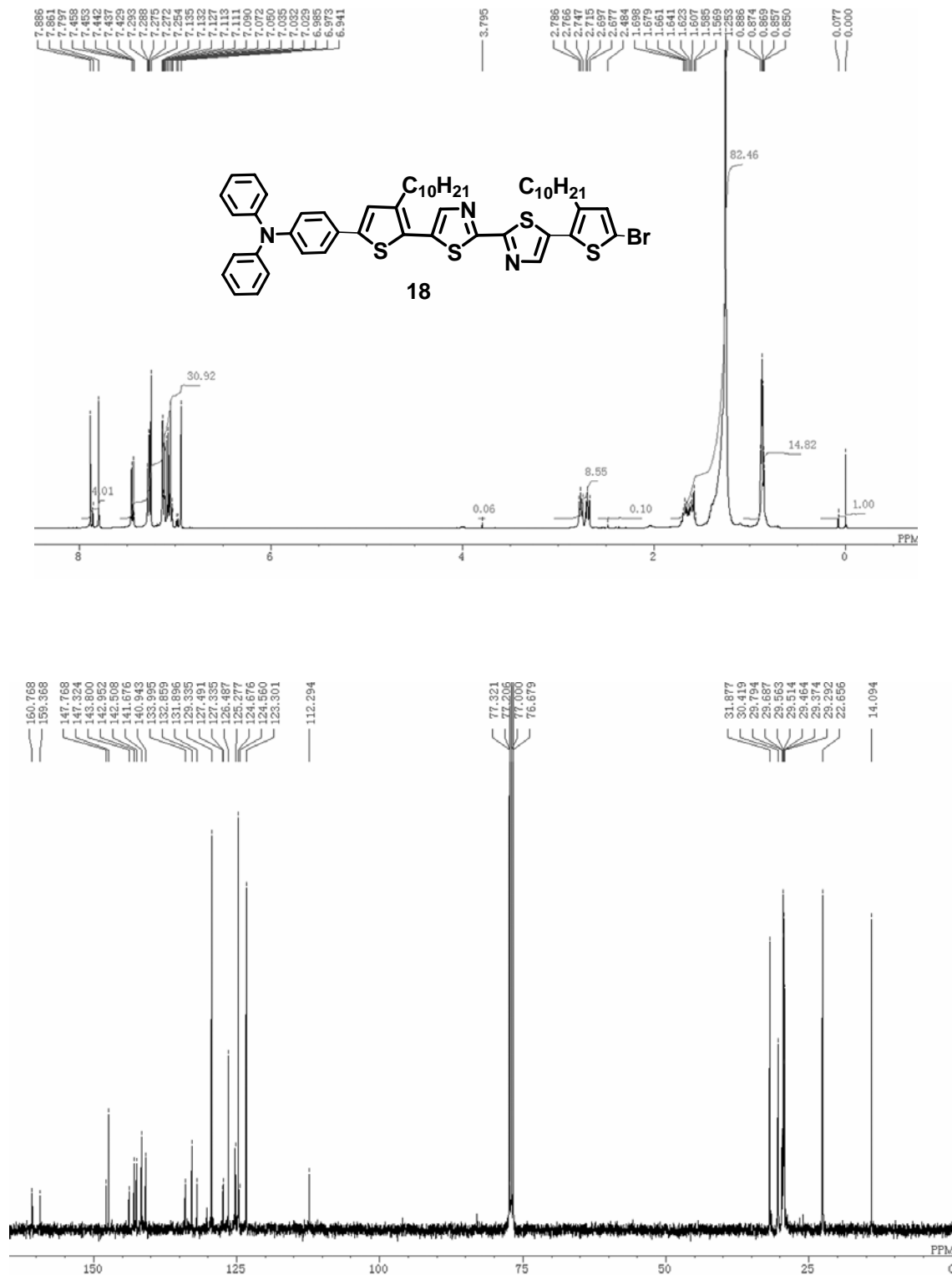
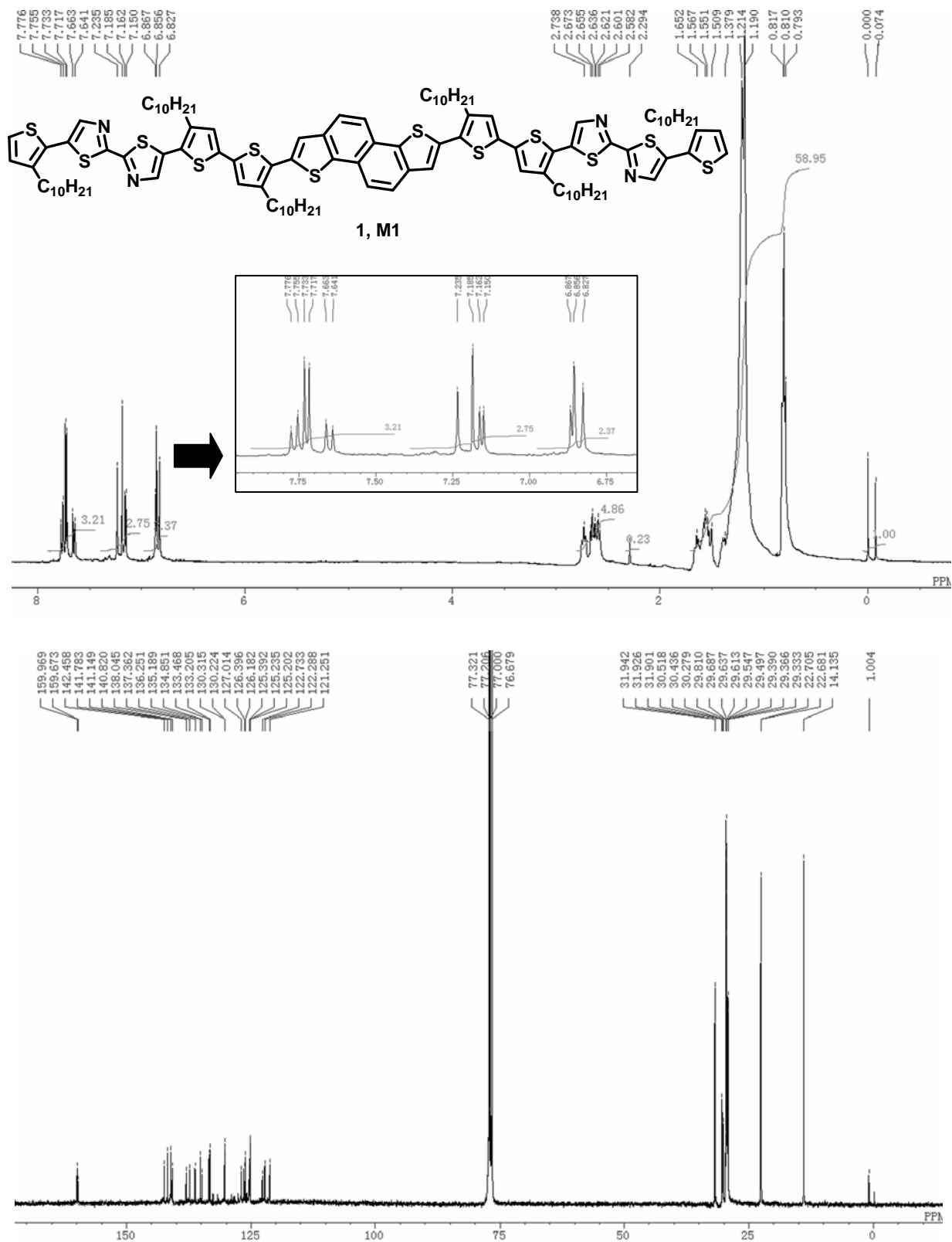


Fig. S4. <sup>1</sup>H-NMR and <sup>13</sup>C NMR spectra of compound **18** in CDCl<sub>3</sub>



**Fig. S5.** <sup>1</sup>H-NMR and <sup>13</sup>C NMR spectra of compound M3 (1) in CDCl<sub>3</sub>

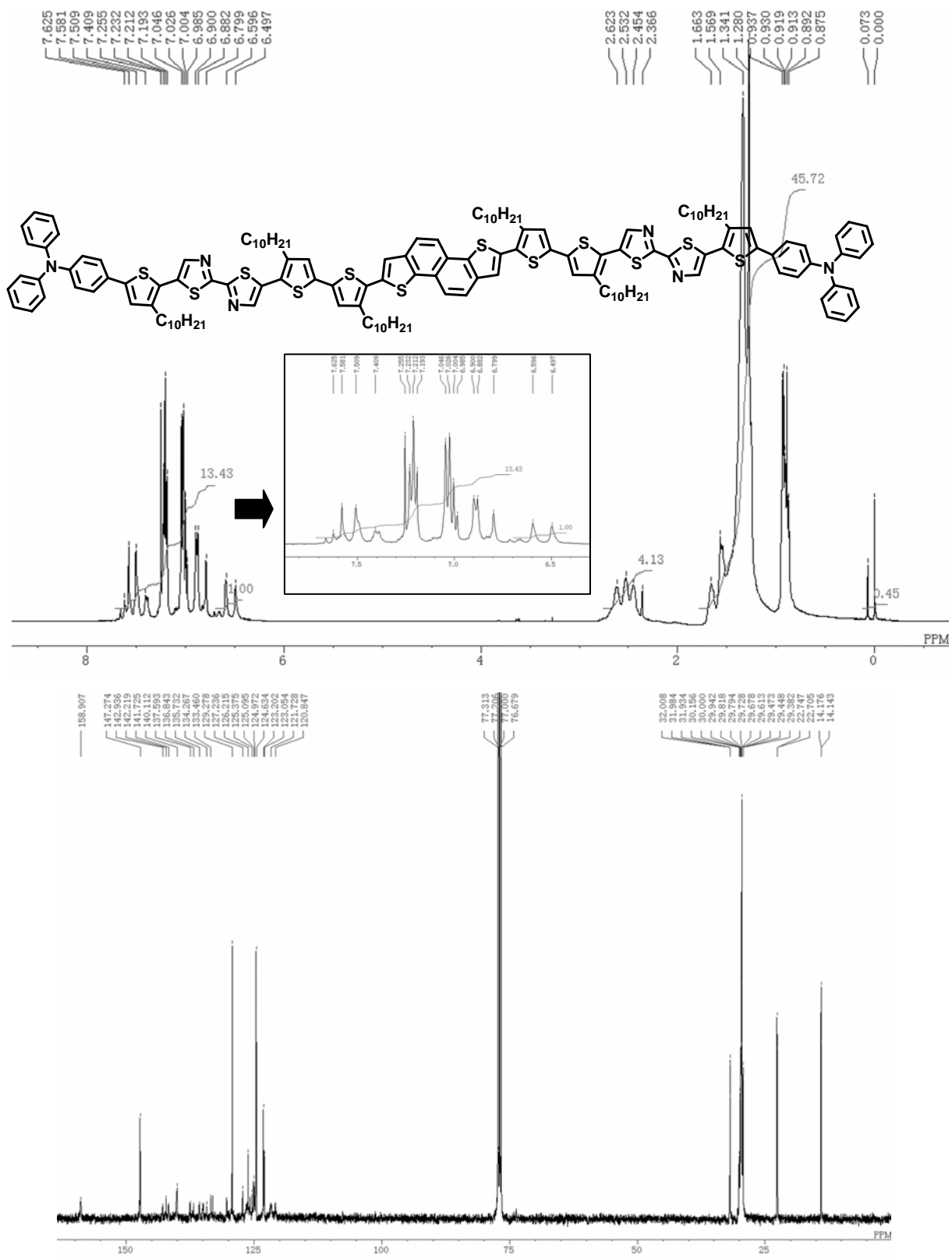
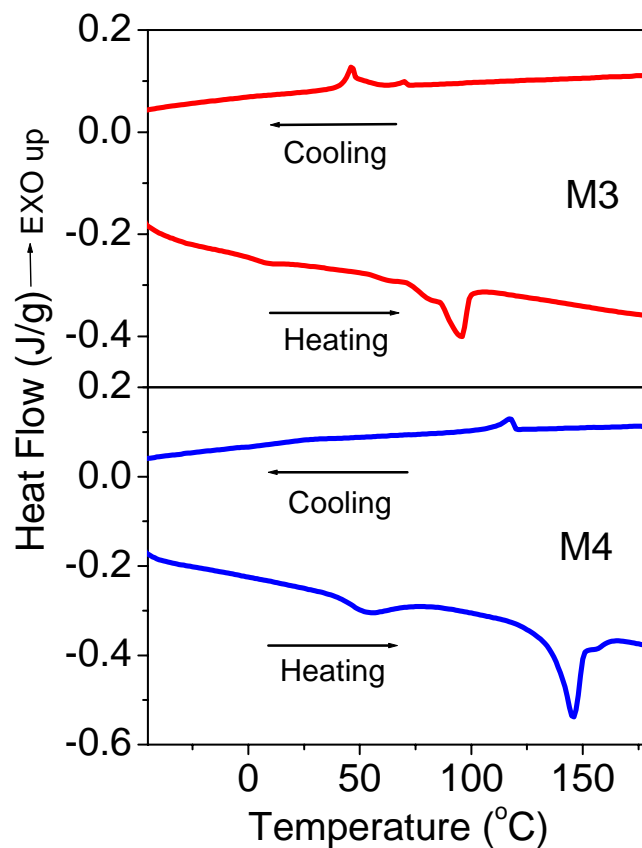
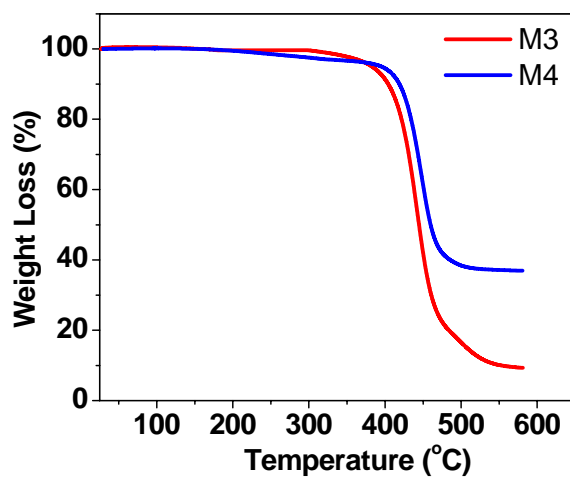


Fig. S6. <sup>1</sup>H-NMR and <sup>13</sup>C NMR spectra of compound M4 (2) in CDCl<sub>3</sub>

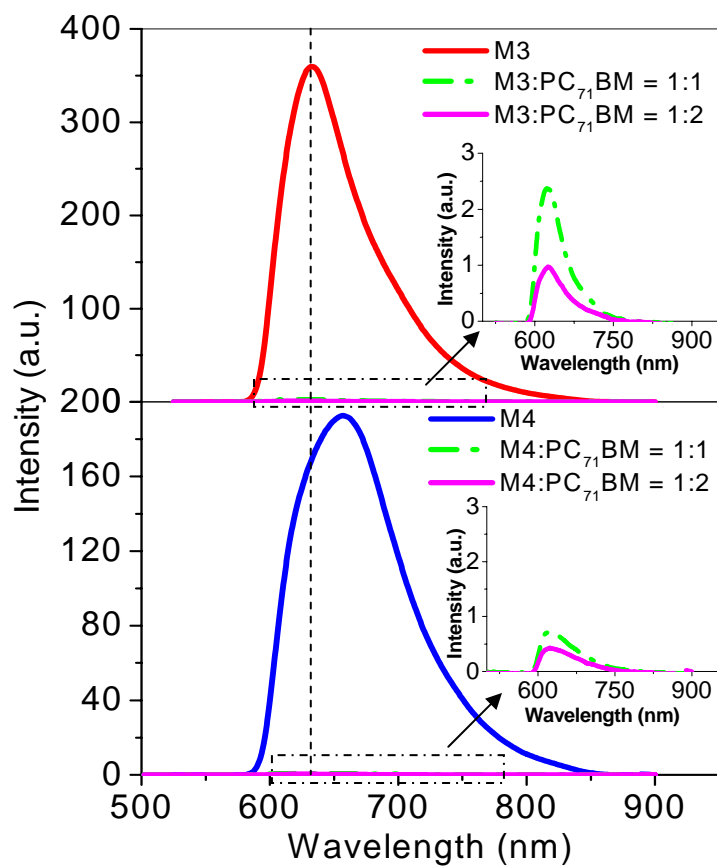


**Fig. S7.** DSC traces of the small molecules at a scanning rate of 10°C/min in the second heating and cooling cycle.



**Fig. S8.** TGA curves of the small molecules with a heating rate of 10°C/min under a nitrogen atmosphere.





**Fig. S9.** PL spectra of small molecules and small molecules/PC<sub>71</sub>BM-blended thin film.