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## Supporting Information

### Non-fullerene acceptor fibrils enable efficient ternary organic solar cells with 16.6% efficiency

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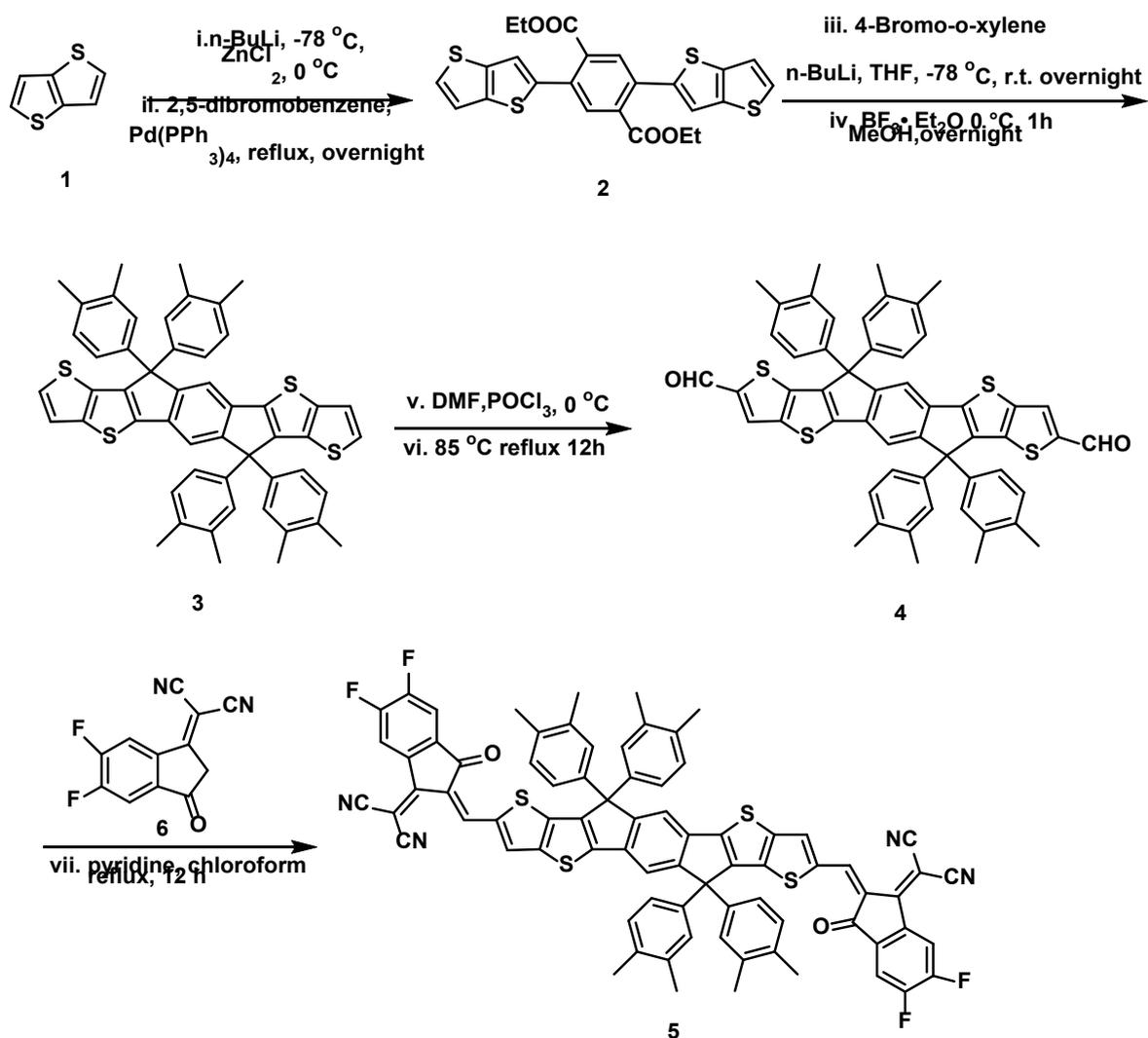
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### Experimental Section

**Materials:** PBDB-T-2F was purchased from Solarmer Materials (Beijing) Inc. BTP-4F was purchased from eFlex PV Technology (Shenzhen) Co., Ltd. ZnO precursor solution was synthesized according to a previous literature report [1], All air and water-sensitive reactions were carried out under nitrogen. Tetrahydrofuran (THF) was dried by sodium and then freshly distilled before use, the rest of the chemicals and solvents were used directly without further purification. 2-(5,6-Difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (6) was bought from Zhi-Yan (China).

**Synthetic procedures:** The non-fullerene small molecular acceptor IDMIC-4F was synthesized with the procedure shown in **Scheme S1**. Column chromatography was carried out with 300-400 nm mesh silica.



**Scheme S1.** Synthesis routes for non-fullerene acceptor IDMIC-4F.

**Synthesis of diethyl 2,5-bis(thieno[3,2-b]thiophen-2-yl)terephthalate (2)** : Into a solution of thieno[3,2-b]thiophene (4.6 g, 32.8 mmol, 1 eq) in dry THF (100 mL) was added 2.5 M solution of *n*-butyllithium in hexane (19.2 mL, 47 mmol, 1.43 eq) dropwise at  $-78\text{ }^\circ\text{C}$  under argon atmosphere. After being stirred for 30 mins at  $-78\text{ }^\circ\text{C}$ , the resulting solution was warmed to  $-35\text{ }^\circ\text{C}$  and stirred for another 15 min. Then anhydrous zinc chloride (6.4 g, 47 mmol, 1.43 eq) in dry THF (70 mL) was added to the mixture. The mixture was stirred for 1 h at  $0\text{ }^\circ\text{C}$  and then the cooling bath was removed. Diethyl 2,5-dibromoterephthalate (5 g, 13.2 mmol, 0.4 eq) and  $\text{Pd}(\text{PPh}_3)_4$  (650 mg, 0.65 mmol, 0.002 eq) were added directly under argon atmosphere. The reaction mixture was refluxed overnight at  $80\text{ }^\circ\text{C}$ . Upon completion, the reaction mixture was filtered, extracted with ethyl acetate and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The product was purified by silica gel column using a mixture of hexane/DCM (5/2, v/v) as the eluent to afford a light yellow solid (8.9 g, 54.4%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (s, 2H), 7.41 (d,  $J = 5.2\text{ Hz}$ , 2H), 7.31-7.27 (m, 4H), 4.25 (q,

$J = 7.1$  Hz, 4H), 1.13 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.43 (s), 142.04 (s), 139.97 (s), 139.41 (s), 134.13 (s), 133.81 (s), 132.08 (s), 127.40 (s), 119.41 (s), 119.33 – 119.32 (m), 61.80 (s), 13.83 (s).

**Synthesis of Compound 3:** To a solution of 4-Bromo-1,2-dimethylbenzene (1.11g, 6 mmol, 1 eq) in dry THF (40 mL) at  $-78$  °C was added 2.5 M solution of n-butyllithium in hexane (2.5 mL, 6 mmol, 1 eq) and the mixture was kept at  $-78$  °C for 1 h. A solution of compound 2 (500 mg, 1 mmol, 0.17 eq) in dry THF (30 mL) was then added slowly. After this addition, the mixture was stirred at room temperature overnight and then poured into water and extracted with ethyl acetate. The combined organic phase was dried over  $\text{Na}_2\text{SO}_4$ . After removing the solvent, the crude product was charged into single-neck flask. To a solution of the crude product in dichloromethane (30 mL) at  $0$  °C was added boron trifluoride etherate (1.5 mL) under argon atmosphere. After stirring for 45 min, 30 mL of methanol was added and stirred overnight. After removing the solvent, the resulting crude compound was purified by silica gel column using a mixture of hexane/DCM (10/1, v/v) as the eluent to give a yellow powdery solid (200 mg, 25.2%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (s, 2H), 7.12 (d,  $J = 8.4$  Hz, 2H), 7.05 (s, 4H), 7.04-6.99 (m, 8H), 6.99 (s, 2H), 2.21 (s, 12H), 2.18 (s, 12H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.17 (s), 146.07 (s), 143.24 (s), 141.62 (s), 140.64 (s), 136.72 (s), 136.59 (s), 136.12 (s), 135.29 (s), 129.69 (s), 129.43 (s), 129.31 (d,  $J = 28.2$  Hz), 129.20 (s), 125.59 (s), 120.31 (s), 62.97 (s), 19.92-19.87 (m), 19.36 (s), 19.35 (s).

**Synthesis of Compound 4:** A 100 mL three-necked round bottom flask equipped with mechanical stirrer were charged with N, N-dimethylformamide (9 mL, 21.42 mmol, 34 eq) and phosphorus oxychloride (6 mL, 2.015 mmol, 3.2 eq), the reaction was cooled to  $0$  °C and stirred for 30 mins. Compound 3 (500 mg, 0.63 mmol, 1 eq) was dissolved in anhydrous 1,2-dichloroethane (40 mL) and cooled to  $0$  °C. The compound 3 solution was transferred to a three-necked flask by a double-ended needle and maintained at  $0$  °C for one hour. The reaction mixture was refluxed overnight at  $85$  °C. Upon completion, the reaction mixture was slowly poured into 100 mL of saturated sodium carbonate ice water solution and extracted with dichloromethane. The combined organic phase was dried over  $\text{Na}_2\text{SO}_4$ . The product was purified by silica gel column using a mixture of hexane/DCM (5/2, v/v) as the eluent to give an orange-yellow powdery solid (468 mg, 87.3%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.90 (s, 2H), 7.96 (s, 2H), 7.09 – 6.98 (m, 14H), 2.24 (s, 12H), 2.20 (s, 12H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  139.51 (s), 136.45 (d,  $J = 135.9$  Hz), 129.97 (s), 129.11 (s), 125.40 (s), 19.98 (s), 19.35 (s).

**Synthesis of Compound 5 (IDMIC-4F):** Compound 4 (100 mg, 0.12 mmol, 1 eq), 2-(5,6-Difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (**6**) (140 mg, 0.7 mmol, 5.83 eq), pyridine (0.5 mL) and chloroform (30 mL) were dissolved in a round bottom flask under nitrogen. The mixture was stirred at 80 °C overnight, and then poured into methanol and filtered after cooling to room temperature. After removing the solvent, the product was purified by silica gel column using a mixture of hexane/DCM (10/1, v/v) as the eluent to afford the title compound IDMIC-4F (120 mg, 83.3%) as purple black solid.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.86 (s, 2H), 8.68 (d,  $J = 7.5$  Hz, 2H), 8.19 (s, 2H), 7.90 (d,  $J = 7.1$  Hz, 2H), 7.77-7.64 (m, 4H), 7.13-7.02 (m, 8H), 2.23 (d,  $J = 5.4$  Hz, 24H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.68 (s), 149.18 (s), 139.33 (s), 137.03 - 136.87 (m), 136.06 (s), 130.09 (s), 129.06 - 128.90 (m), 125.32 (s), 118.68 (s), 114.16 (s), 112.73 - 112.57 (m), 63.14 (s), 29.58 (s), 19.97 - 19.82 (m).

**Solar Cell Fabrication and Characterization:** All solar cells were fabricated with an inverted structure. Pre-patterned ITO-glass substrates (resistance *ca.* 15  $\Omega$  per square) were cleaned by sequential sonication in deionized water, ethanol, and isopropyl alcohol for 10 minutes each before drying at 100 °C on a hotplate. They were subsequently treated with ultraviolet/ozone for 15 min. The ZnO precursor solution was spin-coated on top of the cleaned ITO substrates, then annealed at 200 °C for 30 min in air creating films with a thickness of *ca.* 30 nm. Next, the active layer was deposited on top of the ZnO layer by spin-coating from 16 mg/mL solution of PBDB-T-2F:BTP-4F:IDMIC-4F in chloroform (with 0.5 vol.% 1-chloronaphthalene (CN) additive) to obtain films of *ca.* 130 nm thick, in a nitrogen-filled glovebox. The weight ratio of PBDB-T-2F to electron acceptors (i.e., BTP-4F and IDMIC-4F) is fixed at 1:1.2. Finally, 10 nm  $\text{MoO}_3$  and 100 nm Ag were thermally evaporated onto the photoactive layer under high vacuum through a shadow mask as hole transport layer and anode, respectively. The size of the photoactive area defined by the overlap of the anode and cathode is 4 mm<sup>2</sup>. Device current density-voltage (J-V) measurements were performed under AM 1.5G (100 mW cm<sup>-2</sup>) using a Newport 3A solar simulator (Newport, USA) in air at room temperature after the light intensity was calibrated using a standard silicon

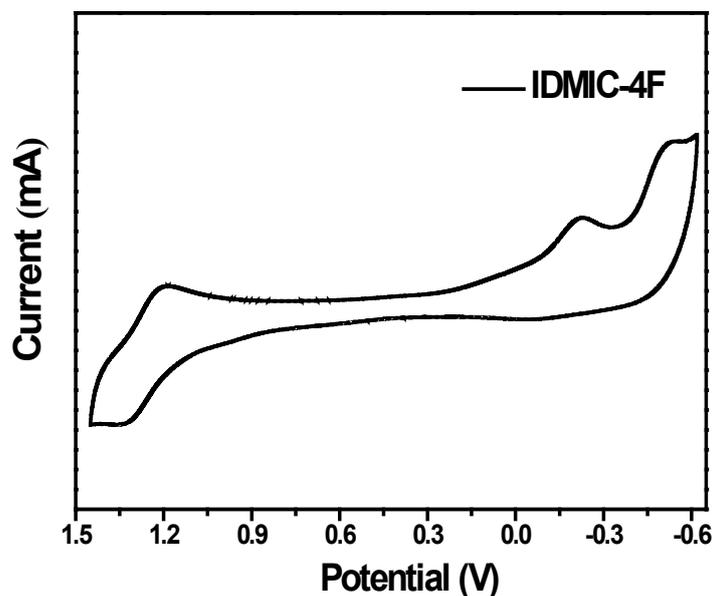
reference cell certified by the National Renewable Energy Laboratory (NREL, USA). J-V characteristics were measured using software developed by Ossila Ltd. (UK) together with a source meter unit (2612B, Keithley, USA). An aperture mask was placed over the device to define an accurate illumination area of 2.2 mm<sup>2</sup> for each pixel. External quantum efficiency (EQE) was measured with an EQE system (Zolix, China) equipped with a standard Si diode.

**UV-Vis absorption, PL, cyclic voltammetry and NMR:** Film absorption spectra were measured using a UV-Visible spectrophotometer (HITACHI, Japan). Photoluminescence (PL) measurement was using a PL microscopic spectrometer (Flex One, Zolix, China) with a 532 nm CW laser as the excitation source. Cyclic voltammetry was carried out in the solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile, working electrode was glassy carbon electrode and the counter electrode was platinum electrode. Saturated calomel electrode was used as the reference electrode, the Fc/Fc<sup>+</sup> redox couple was used as an internal standard. NMR spectra were measured in CDCl<sub>3</sub> solvent using a BRUKER DRX500 spectrometer with the tetramethylsilane (TMS) as internal standard.

**Film thickness and charge carrier mobility:** Film thickness was measured using a spectroscopic ellipsometer (J. A. Woollam, USA) and was fitted with Cauchy model using Complete Ease software. The space charge-limited current (SCLC) method based the Mott-Gurney equation:  $J = \frac{9}{8} \epsilon_r \epsilon_0 \mu \frac{V^2}{L^3}$  was used to study the electron and hole mobilities, where devices with structures of ITO/ZnO/Active layer/Ca/Ag and ITO/PEDOT:PSS/Active layer/MoO<sub>3</sub>/Ag were fabricated with thickness of 130 nm, respectively.

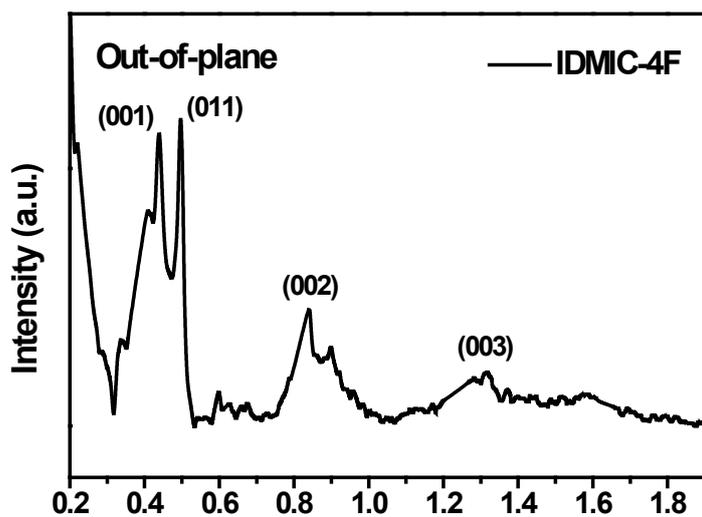
**TEM, GIWAXS and GISAXS:** The morphologies of the active layers were characterized by transmission electron microscopy (TEM) (JEOL, Japan). Synchrotron grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were conducted at beamline I07 of Diamond Light Source in the UK. All GIWAXS data was processed, corrected and analysed using the GIXSGUI Matlab toolbox [2]. Synchrotron grazing-incidence small-angle X-ray scattering (GISAXS) measurements were conducted using the beamline BL16B1 at the Shanghai Synchrotron Radiation Facility in China.

### Cyclic voltammogram of IDMIC-4F



**Figure S1** Cyclic voltammogram of IDMIC-4F, performed in anhydrous  $\text{CH}_3\text{CN}$  solution with  $\text{Ag}/\text{AgCl}$  as the reference electrode and ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox couple as the internal reference.

### 1D profile of 2D GIWAXS pattern of IDMIC-4F



**Figure S2** 1D out-of-plane profile of 2D GIWAXS pattern of a neat IDMIC-4F film.

The TEM image of PBDB-T-2F:IDMIC-4F binary blend

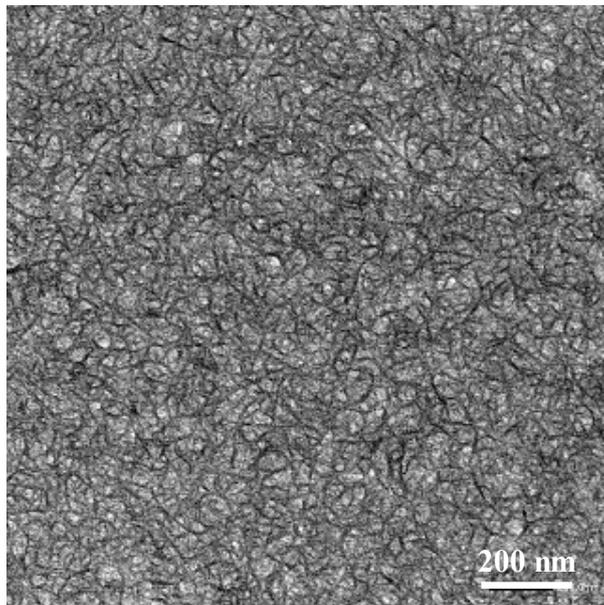


Figure S3 TEM images of PBDB-T-2F:IDMIC-4F binary blend

The AFM images of BTP-4F and BTP-4F:IDMIC-4F blend film

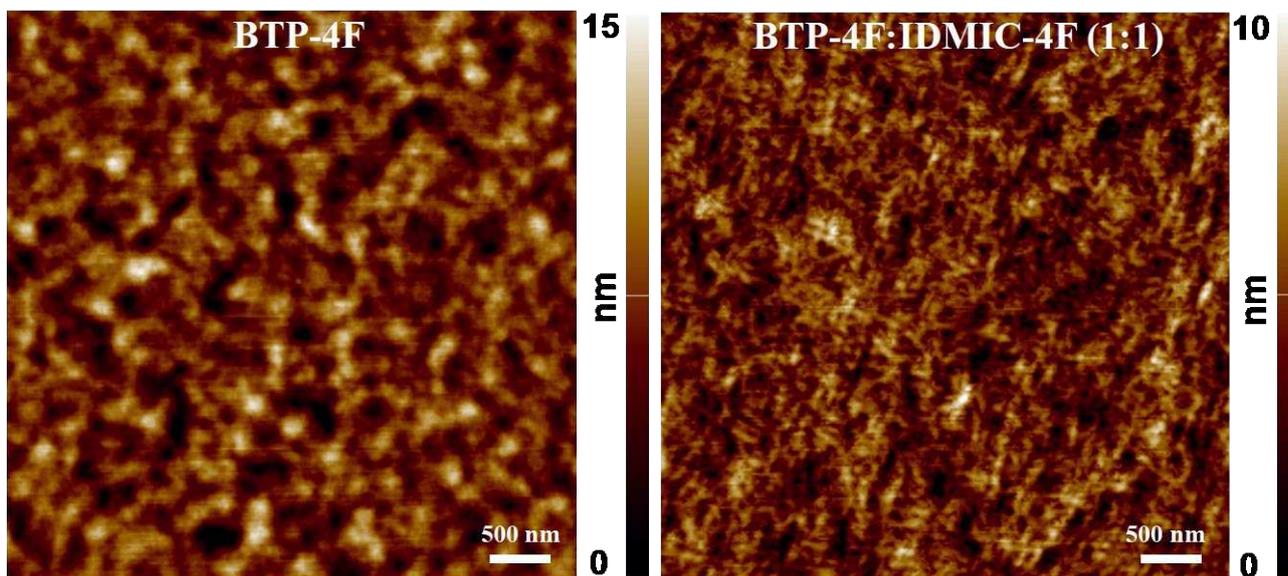


Figure S4 AFM images of BTP-4F and BTP-4F:IDMIC-4F blend film.

## PL spectra of BTP-4F and BTP-4F:IDMIC-4F (10 wt%) films

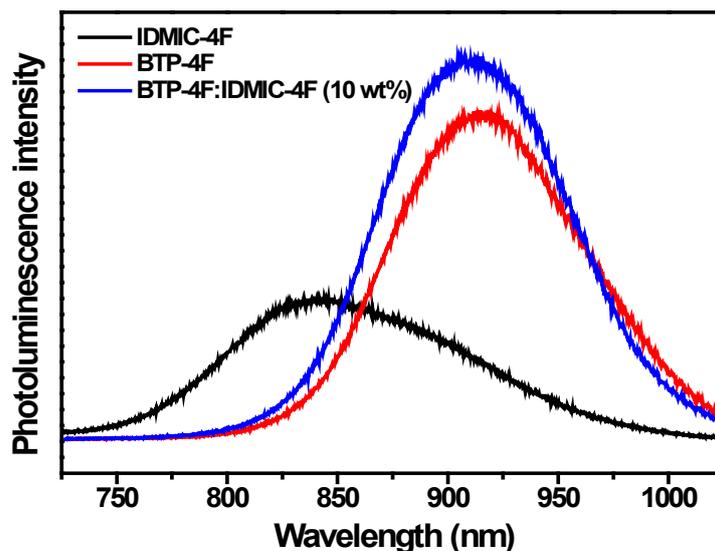


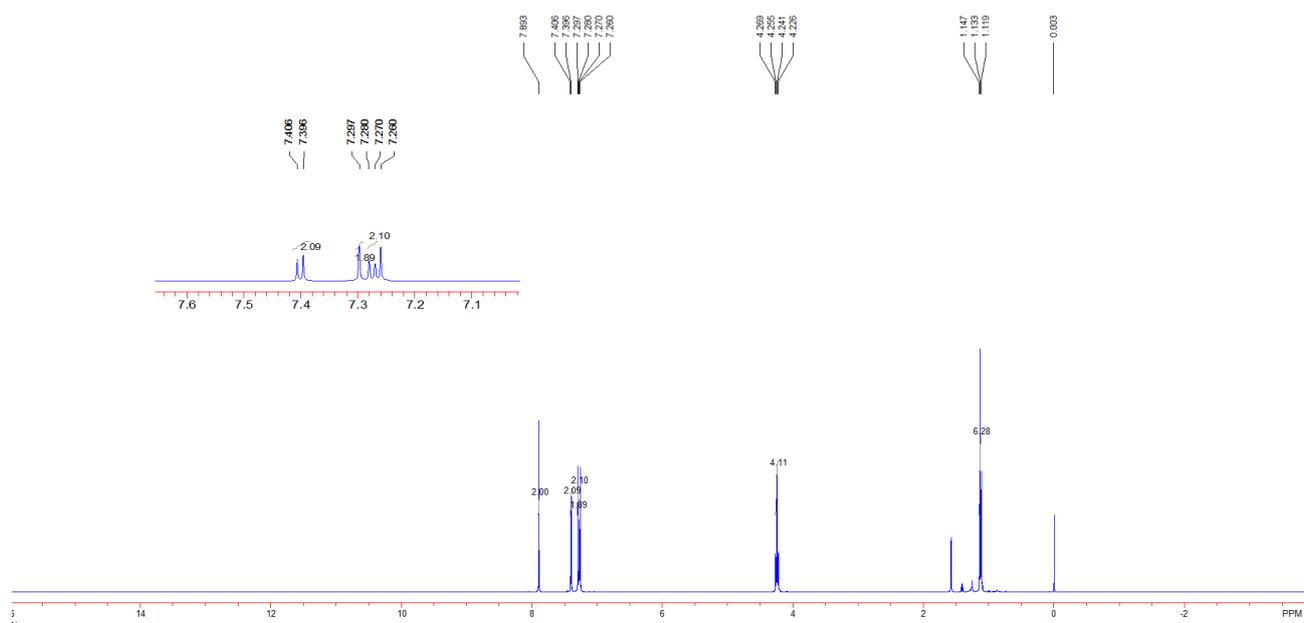
Figure S5 PL spectra of BTP-4F and BTP-4F:IDMIC-4F (10 wt%) films

## GISAXS modeling

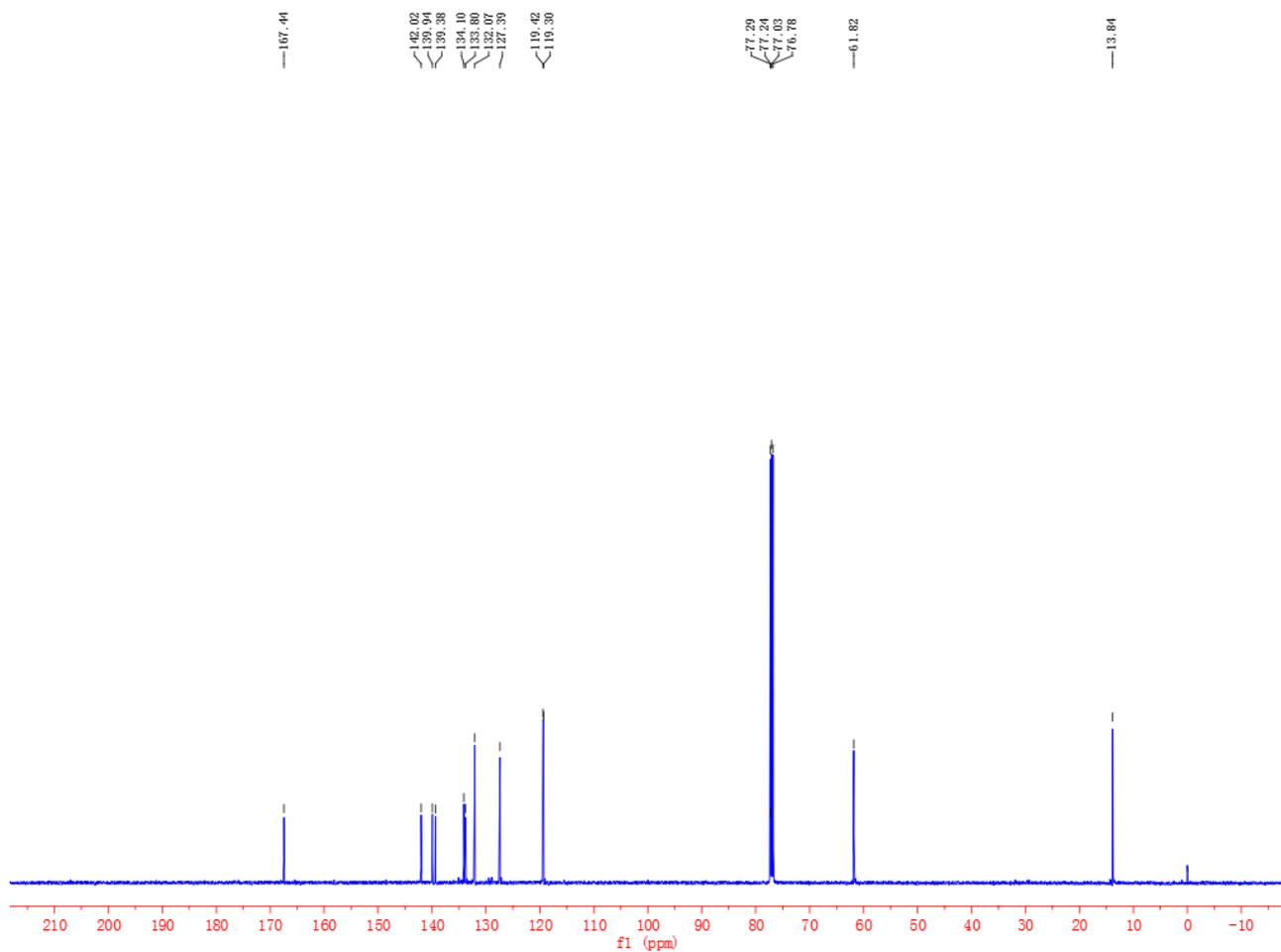
In order to unveil the nanoscale phase separation information in the binary and ternary blend films, 1D GISAXS profiles are fitted on the basis of the model expressed in Equation 1. The first term of the Debye-Anderson-Brumberger (DAB) model is used for simulating the scattering of the polymer domain, in which  $\xi$  is the average correlation length of the polymer domain, and  $q$  is the scattering wave vector,  $A_1$  is an independent fitting parameter [3,4]. The second term of the equation refers to the occupation of fractal-like structure of the non-fullerene acceptor.  $P(q, R)$  and  $S(q, R)$  are form factor and fractal structure factor, respectively, the correlation length of the fractal-like structure is represented by  $\eta$ . The average domain size of acceptor phase can be characterized by the Guinier radius ( $R_g$ ,  $R_g = \sqrt{\frac{D(D+1)}{2}}\eta$ ) [5].

$$I(q) = \frac{A_1}{[1+(q\xi)^2]^2} + A_2(P(q, R))S(q, R, \eta, D) + B \quad (1)$$

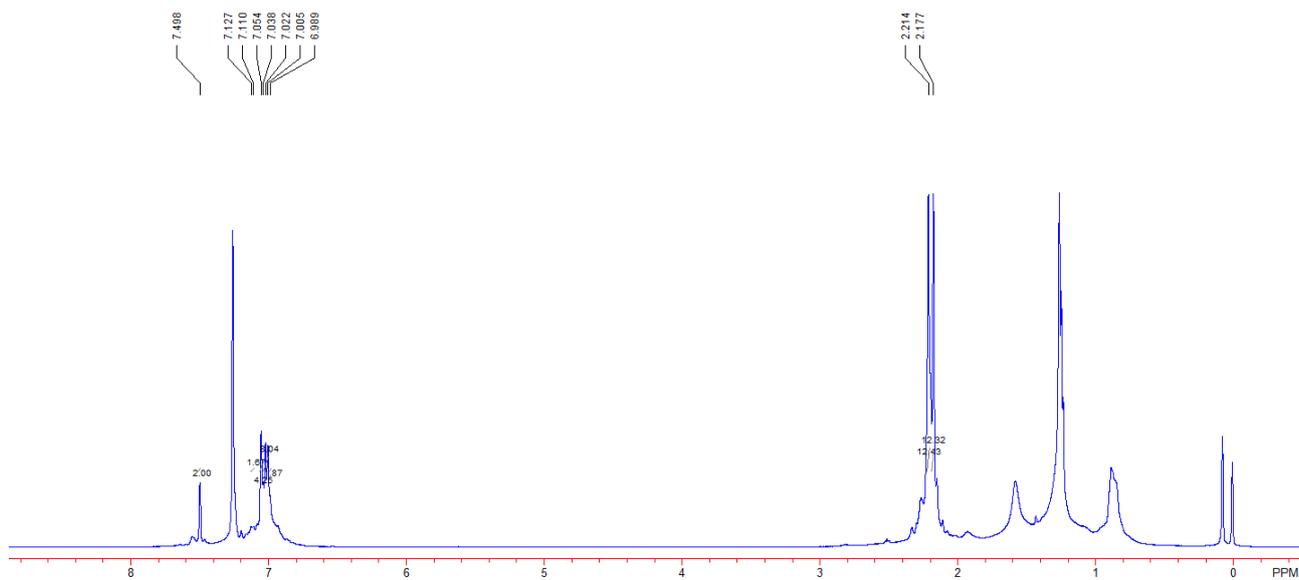
$$S(q) = 1 + \frac{\sin[(D-1) \tan^{-1}(q\eta)]b \pm \sqrt{b^2 - 4ac}}{(qR)^D} \frac{D\Gamma(D-1)}{[1 + \frac{1}{(q\eta)^2}]^{(D-1)/2}} \quad (2)$$



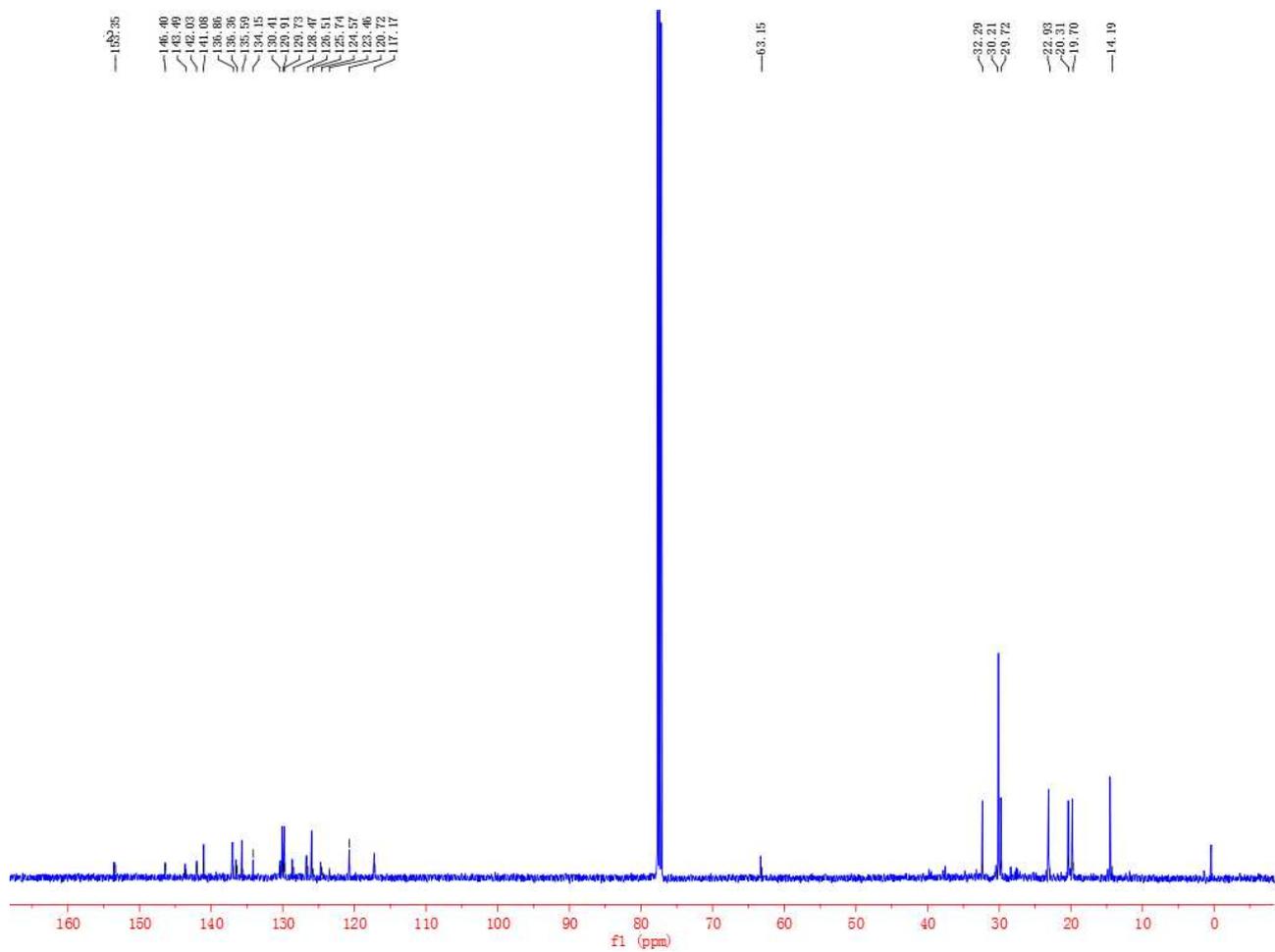
**Figure S6**  $^1\text{H}$  NMR spectrum of compound 2 in  $\text{CDCl}_3$



**Figure S7**  $^{13}\text{C}$  NMR spectrum of compound 2 in  $\text{CDCl}_3$



**Figure S8**  $^1\text{H}$  NMR spectrum of compound 3 in  $\text{CDCl}_3$



**Figure S9**  $^{13}\text{C}$  NMR spectrum of compound 3 in  $\text{CDCl}_3$

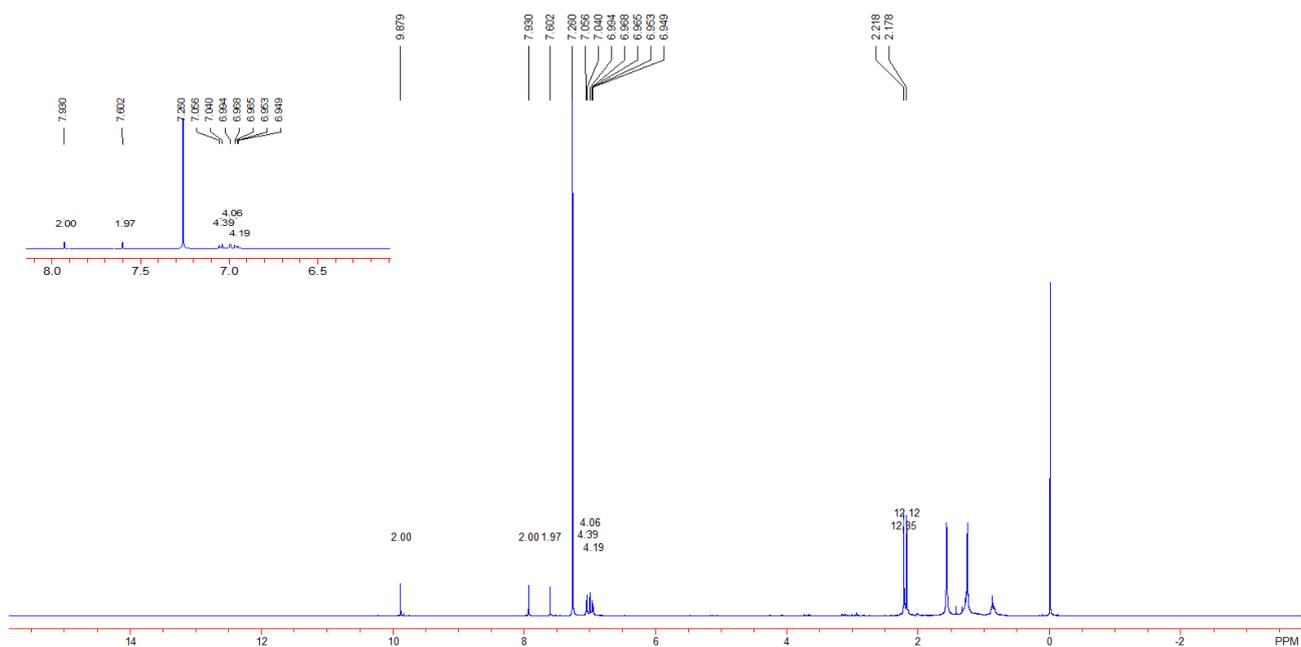


Figure S10  $^1\text{H}$  NMR spectrum of compound 4 in  $\text{CDCl}_3$

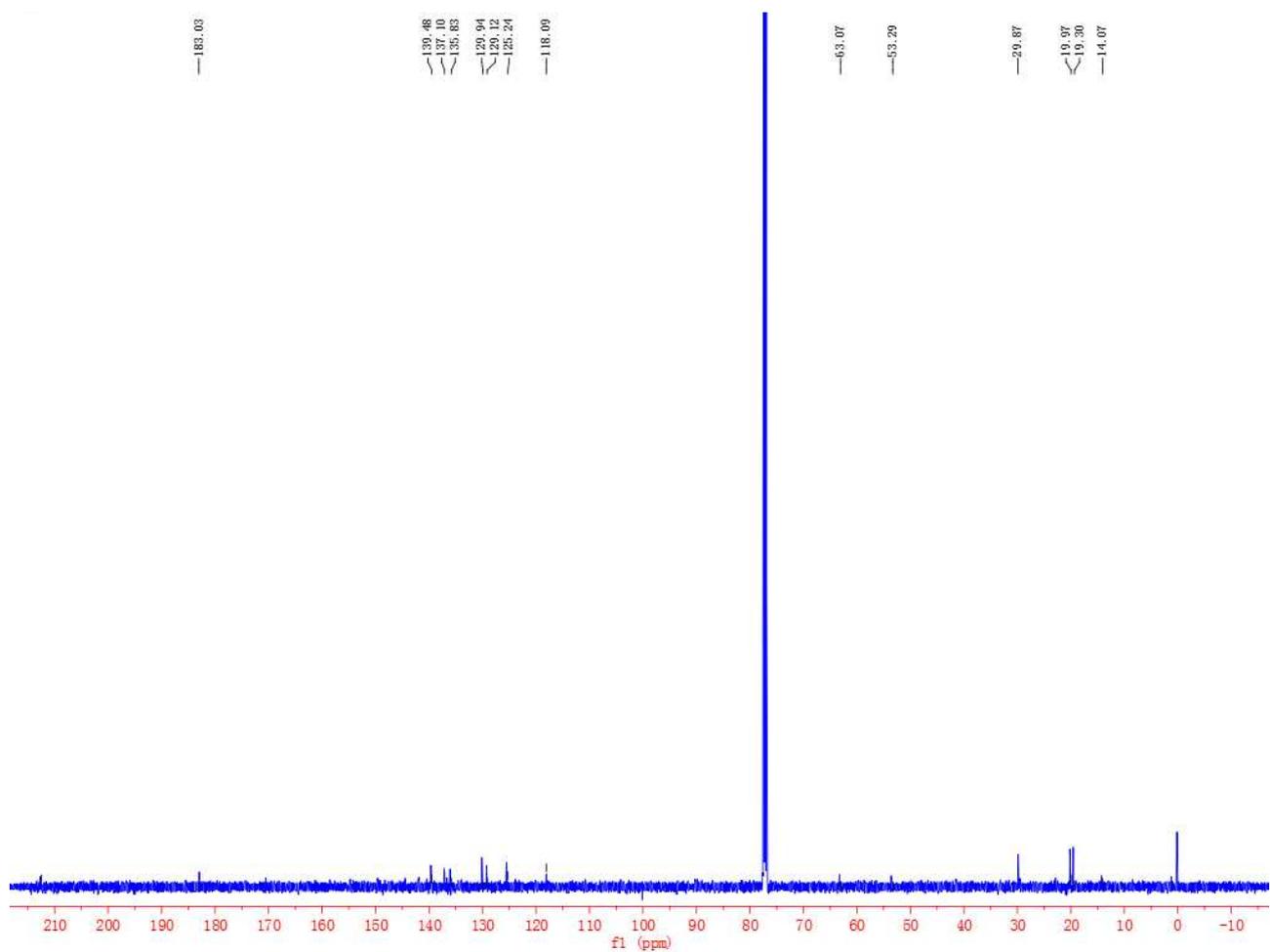


Figure S11  $^{13}\text{C}$  NMR spectrum of compound 4 in  $\text{CDCl}_3$

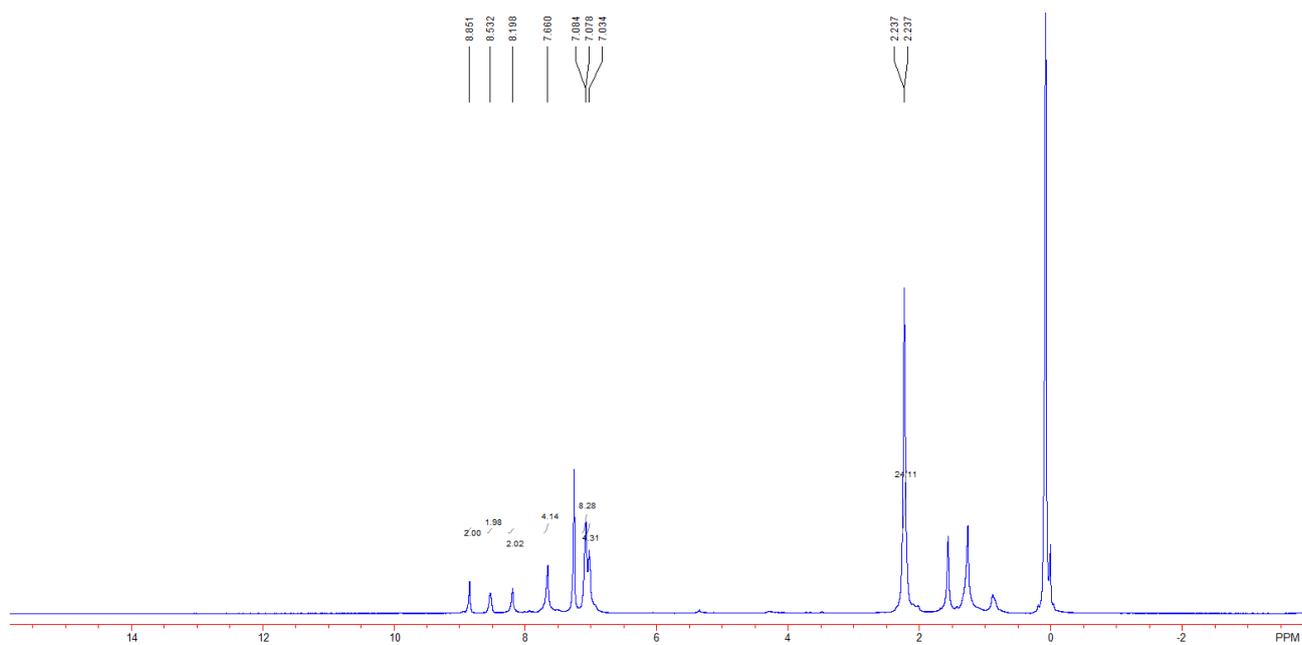


Figure S12  $^1\text{H}$  NMR spectrum of compound 5 in  $\text{CDCl}_3$

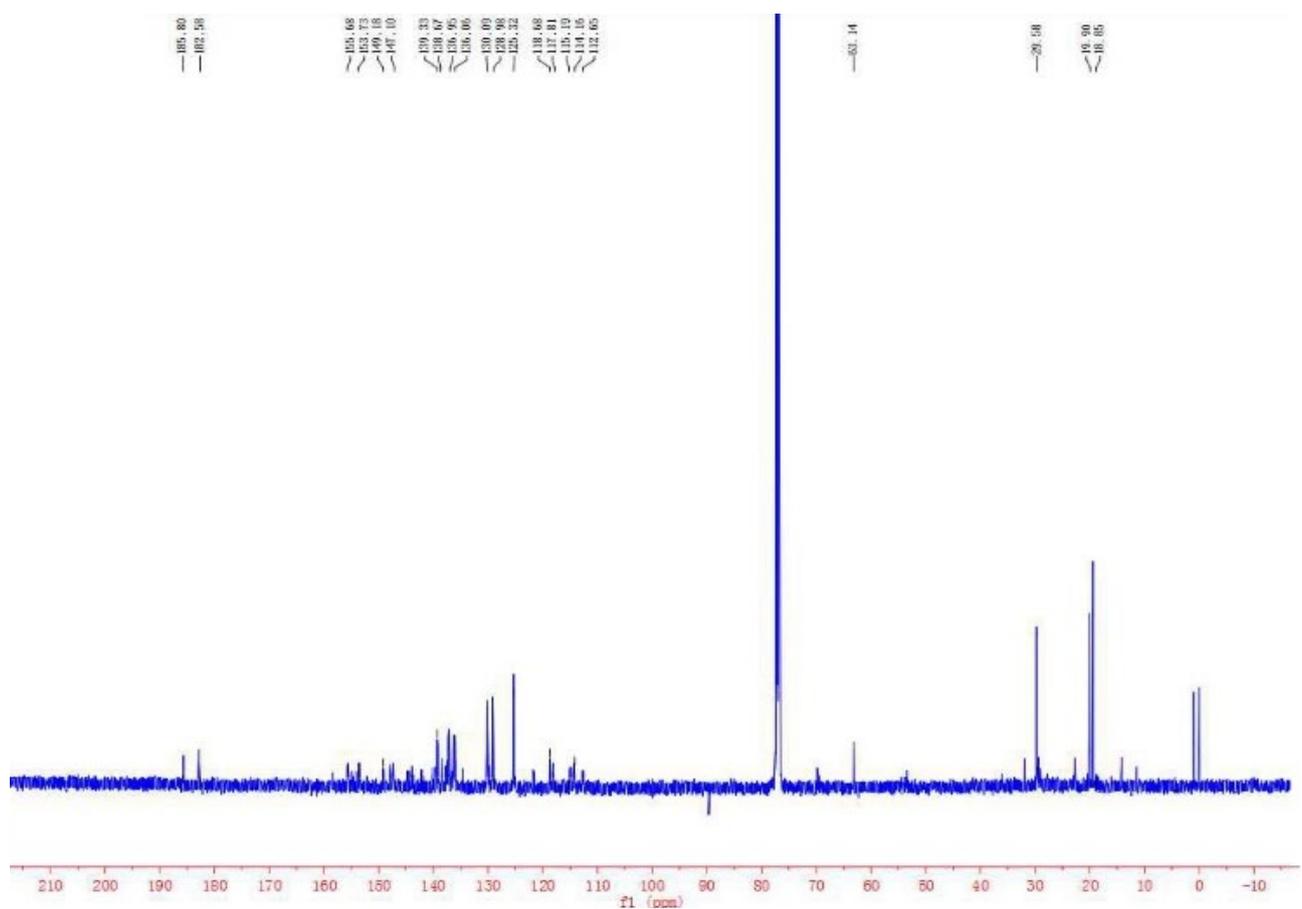


Figure S13  $^{13}\text{C}$  NMR spectrum of compound 5 in  $\text{CDCl}_3$

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