Electronic Supplementary Information

Substituting non-conjugating ester group on benzothiadiazole side chain in donor-acceptor polymer improves the solar cell performance

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MATERIALS AND METHODS

Chemicals and Solvents. $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, benzoyl peroxide, NBS, 4,5-dimethyl-1,2-phenylenediamine and 2-(tributylstannyl)thiophene were purchased form Sigma-Aldrich and used as such. HBr was bought from Alfa Aeser and Bromine from Loba Chemi. Et_3N, DCM, CCl_4, NaOH were purchased from Rankem, India Ltd. All donor units D1, D2, D3, and D4 (Figure 2, literature article) and $PC_{71}BM$ were procured from Lumtech Corporation, Taiwan. CH_3COOH, CH_3COONa, toluene were bought from Merck India Ltd. Thionyl chloride was bought form Spectrochem India Pvt. Ltd. All solvents were purified by standard laboratory purification technique.[1]

Measurements and characterizations. ^{1}H and ^{13}C-NMR spectra were recorded using $CDCl_3$ as reference solvent by a Varian AS 400 MHz, Bruker 600 MHz or Bruker 300 MHz spectrometer. Absorbance spectra of synthesized polymers both in solution and film (drop coated from chlorobenzene on a pre cleaned glass slide and dried on a hot plate upto 100 °C for 1 hour) were recored using a Perkin–Elmer Lambda-35 UV-visible spectrophotometer. Mass fragmental patterns of monomers were analysed from a Micromass Q-TOF ESI-MS instrument (model HAB273) or an Agilent MALDI-TOF mass spectrometer. Gel permeation chromatography (GPC) measurements were carried out on a Waters 515 chromatograh with THF as eluent and polystyrene as standard. Thermal stabilities of all synthesized polymers under nitrogen atmosphere have been analysed by thermogravimetric analysis (TGA) in a Netzch (STA 449, Jupiter) instrument at a heating rate of 10 °C/minute. CH instrument (model 700D) was used to determine oxidation potential of polymer film coated on a glassy

carbon working electrode with platinum wire as a counter and Ag/Ag$^+$ (0.01M AgNO$_3$) as a reference electrode. Electrochemistry was carried out in a solution of tetra-n-butyl ammonium hexafluorophosphate (0.1M) in acetonitrile under argon atmosphere and with ferrocene/ferrocenium ion (Fc/Fc$^+$) as the internal standard. Using the formula $E_{HOMO} = -$ e($_{onset}E^{ox}$ - E$_{1/2}$(Ferrocene)+4.8) with E$_{1/2}$ of ferrocene determined from voltammogram (as ($E_{cathodic}$ + E_{anodic})/2),[2] the highest occupied molecular orbital (HOMO) energy levels of the polymers was estimated from oxidation potential. LUMO^{opt} was calculated from absorption onset using the fromula E$_{LUMO(opt)}$ = E$_{HOMO}$ + bandgap (where band gap = 1240/ λ$_{onset\ film\ (UV-visible)}$). Keithley 2400 sourcemeter was used to determine both dark and light current for fabricated solar cells. Newport solar simulator (Oriel-sol-3A) and Newport oriel IQE-200 instrument were used to provide source for solar spectrum (air mass 1.5, irradiation 100 mW/cm^2) and and external quantum efficiency respectively. A surface profilometer (Veeco dektak-150) was used to measure thickness of active layer and PEDOT:PSS film. Cathode was deposited via VINCI technology thermal evaporator (model-Meca 200). Novascan digital ozone system and spin-150-sps spin coater was usd for UV-ozone treatment and spin coating respectively. Bruker-Innova SPN atomic force microscopy (AFM) was used to investigate impact of ester group on morphology of polymer-PC$_{71}$BM blend (active layer of fabricated solar cells). Thin film X-ray diffraction pattern were determined with a Rigaku TTRAX-III diffroctomer.

FABRICATION OF POLYMER SOLAR CELLS

Device configuration Glass/ITO/PEDOT:PSS/Active Layer (copolymer and PC$_{71}$BM)/ LiF/Al were taken as standard to fabricated polymer solar cell for all synthesized methyl acetate substituted polymers and their results have been compared with their methyl counterpart. Process of device fabrication starts with use of Zn dust and dilutes HCl (1:1) to pattern ITO (serves as anode) coated glass slides. Later it was cleaned with help of a sonicator, using detergent solution in Mili-Q water (15 minute), followed by Mili-Q water, acetone, and isopropyl alcohol for 10 minutes each. The cleaned substrates were dried under argon and treated in a UV-ozone chamber for 20 min. Pattered ITO coated glass were taken to spin-coat ~200 μL of PEDOT:PSS (filtered with 0.45 μm PTFE filters) above it, at 3000 rpm for 60 s followed by annealing at 150 °C for 30 minutes to get a thickness of ~40 nm. Before spin

coating the active layer, appropriate ratio of polymer: PC$_{71}$BM were dissolved in chlorobenzene (concentration 12 mg/ 400 μL) and stirred for 24 hours inside the glove box, it was then filtered through 0.45 μm PTFE filter and spin-coated at 1000-2500 rpm for 60 s, to produce a thickness of blend films varied from 80 to 110 nm. Later LiF 1 nm and Al (80 nm) was evaporated using a thermal evaporator one after another respectively, to serve the top most electrode cathode. The active area of all the devices was 6 mm^2 (0.06 cm^2). Simulated air mass (AM) 1.5 solar irradiation (100 mW cm^{-2}) was used to test the fabricated solar cells inside the glove box. EQE measurements have been carried out outside the glove box in ambient conditions.

THIN FILM X-RAY DIFFRACTION PATTERNS
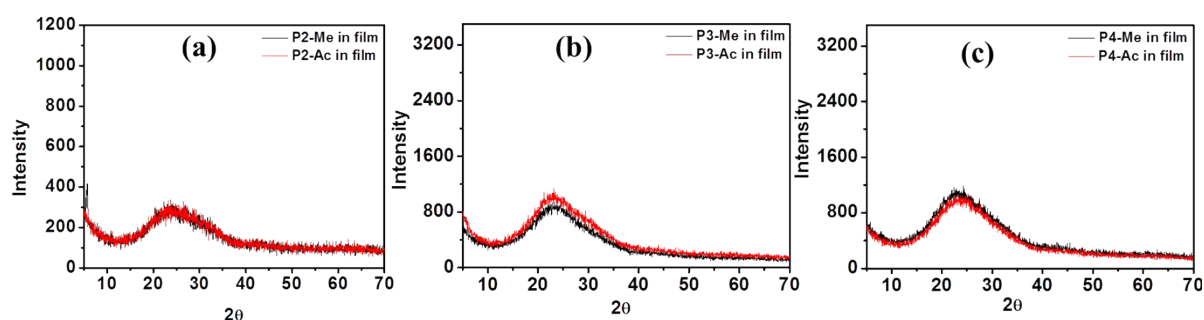
Fig. S1 Thin film X-ray diffraction patterns confirming better π-π stacking in ester functionalized polymers with low dihedral angle along conjugation main chain (a) P2-Me and P2-Ac (b) P3-Me and P3-Ac (c) P4-Me and P4-Ac.
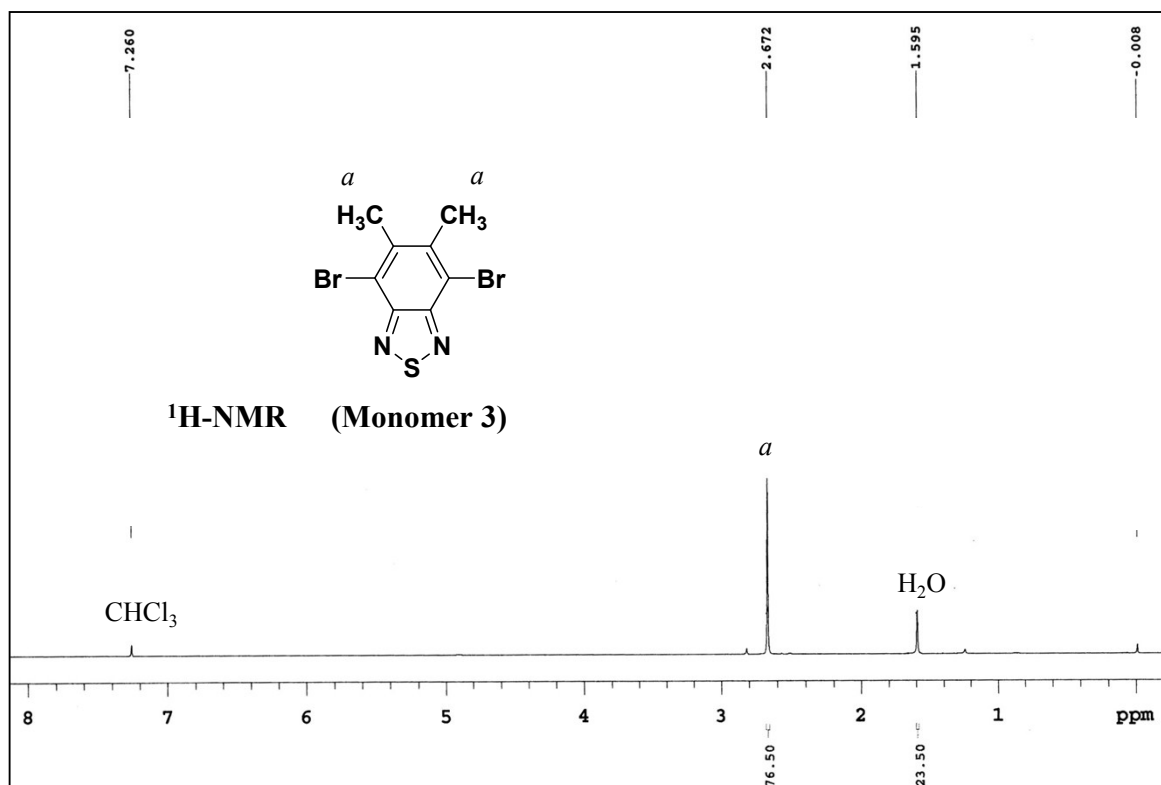
Fig. S2 ^{1}H NMR spectrum of Monomer 3.
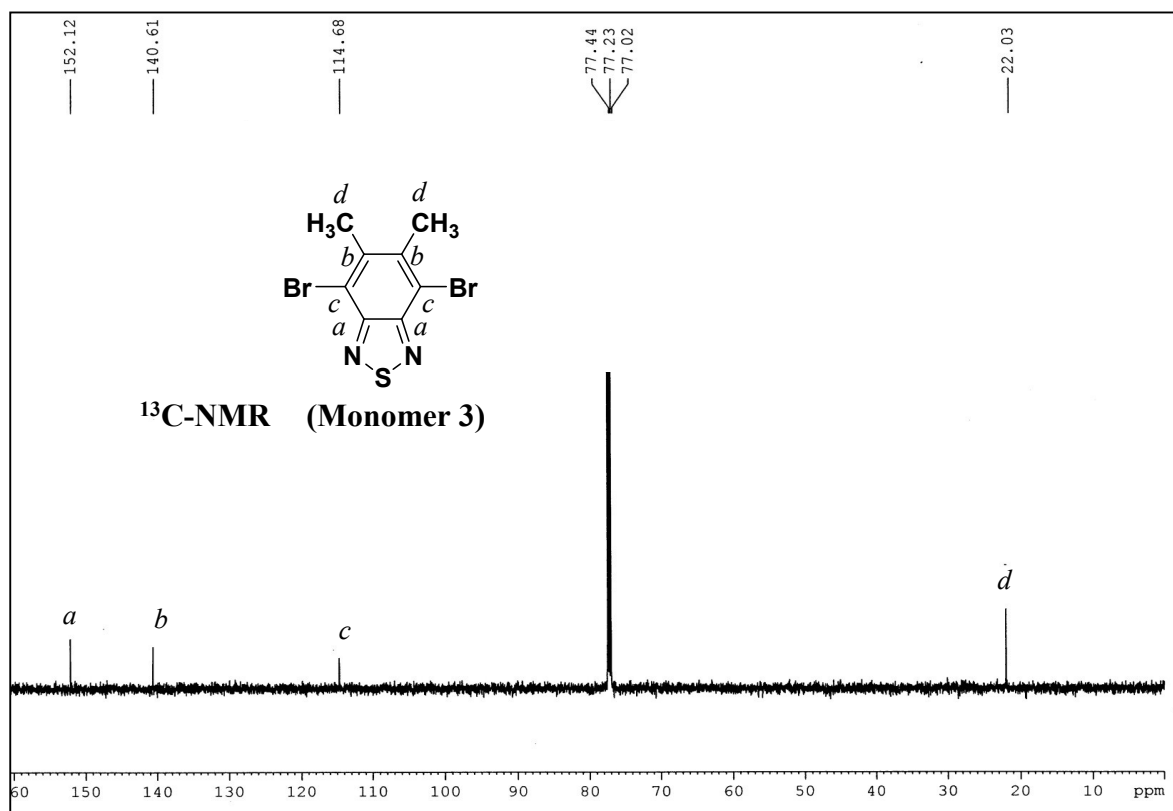
Fig. S3 ^{13}C-NMR of Monomer 3.
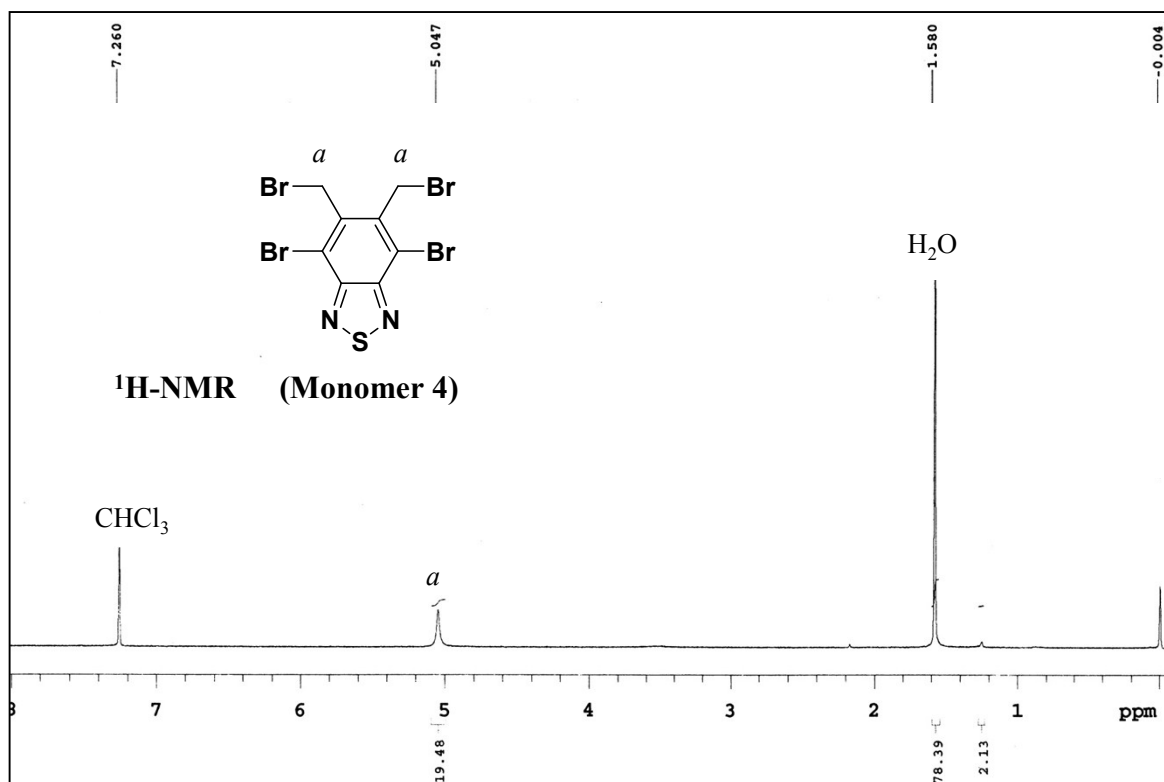
Fig. S4 ^{1}H NMR spectrum of Monomer 4.
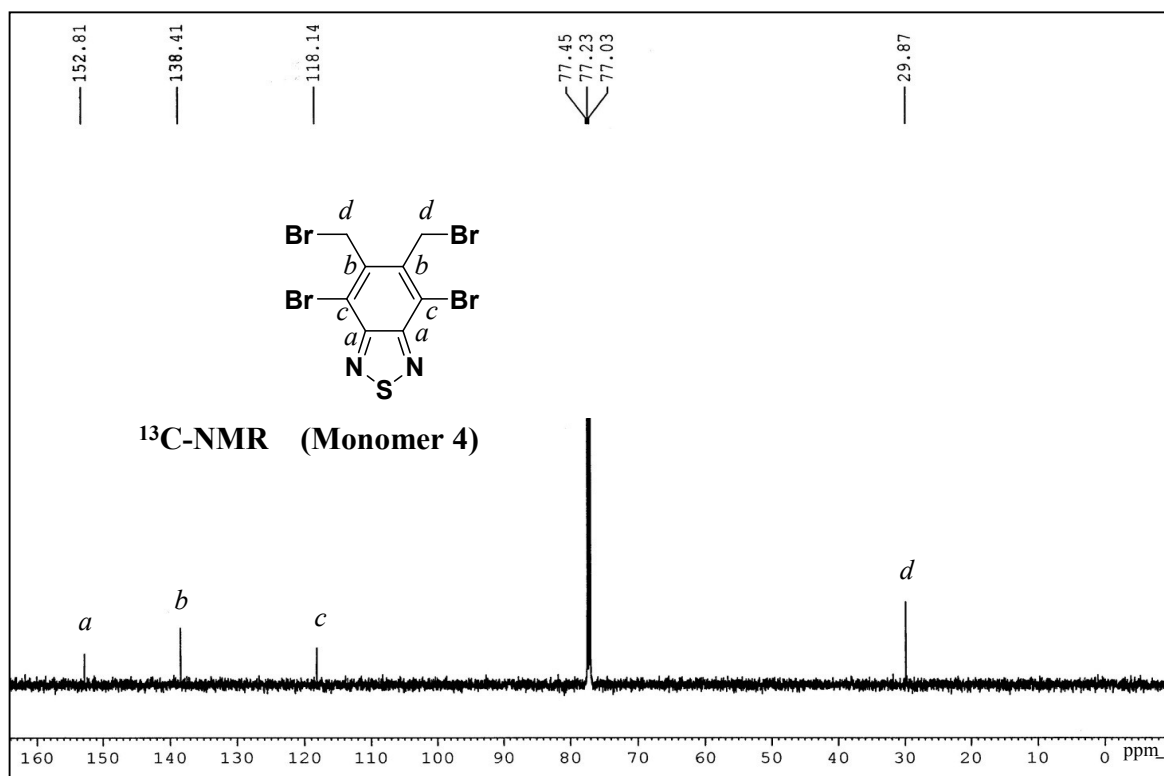
Fig. S5 ^{13}C-NMR of Monomer 4.
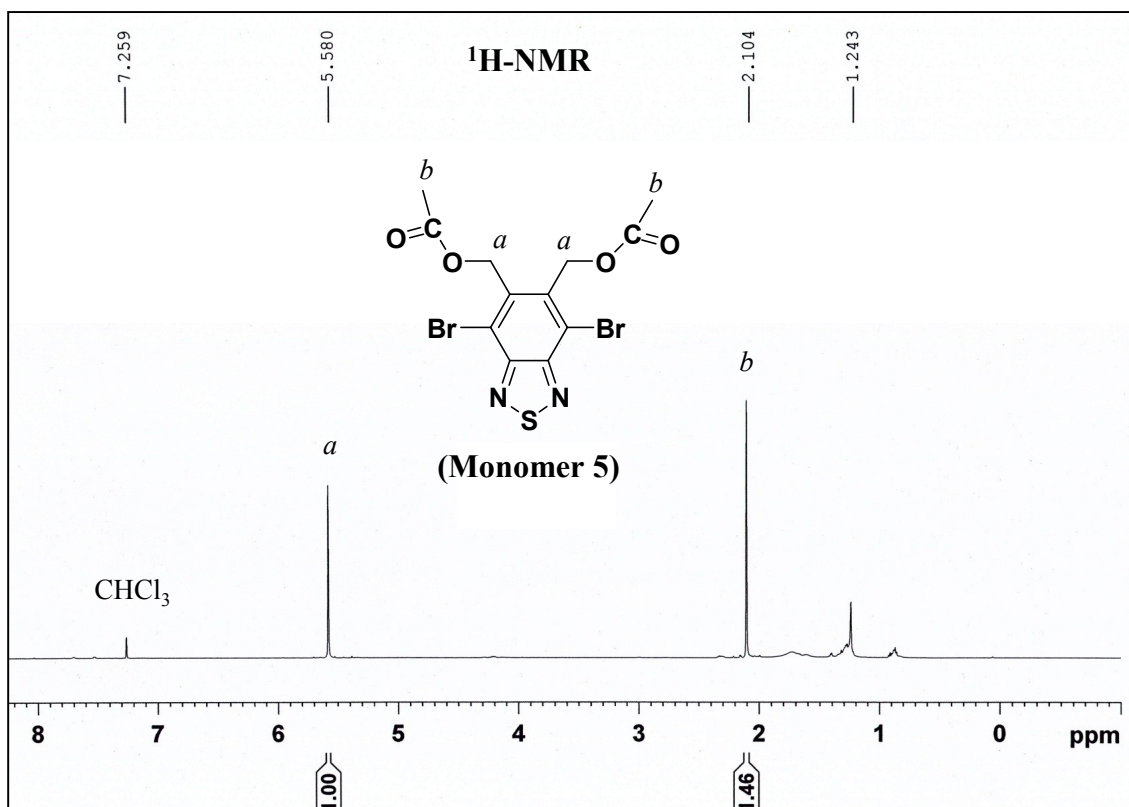
Fig. S6 ¹H NMR spectrum of Monomer 5.
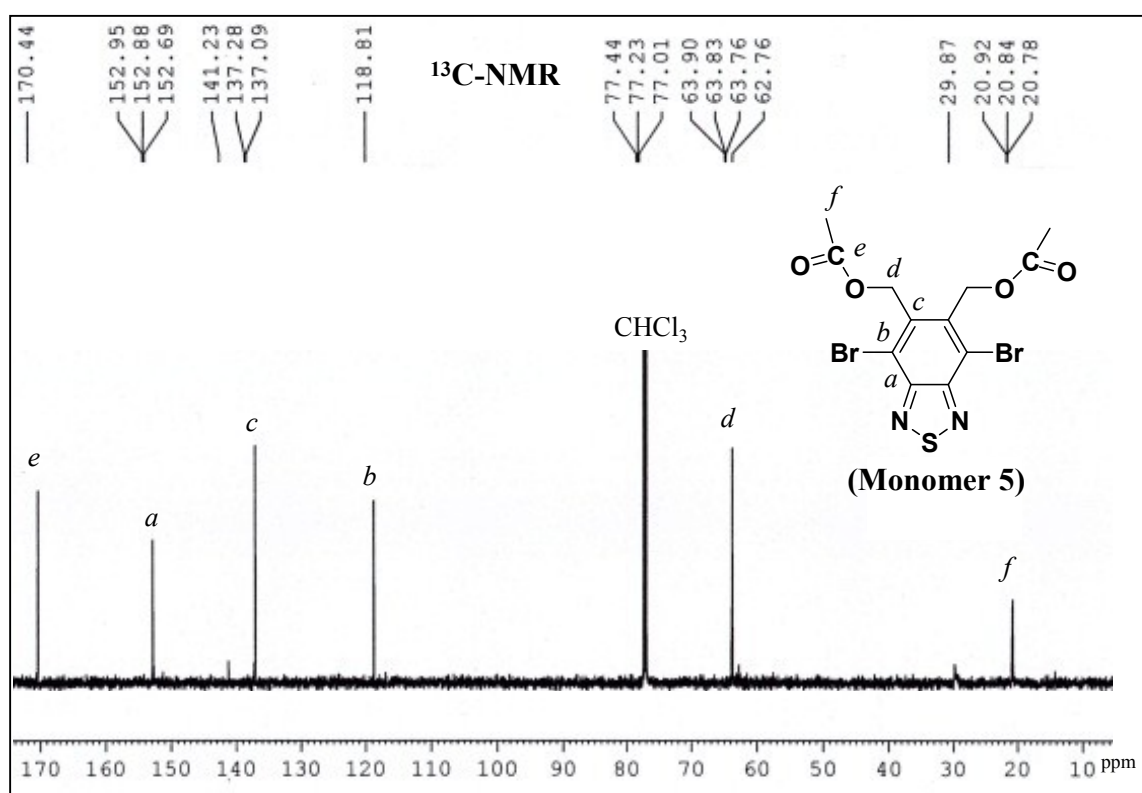
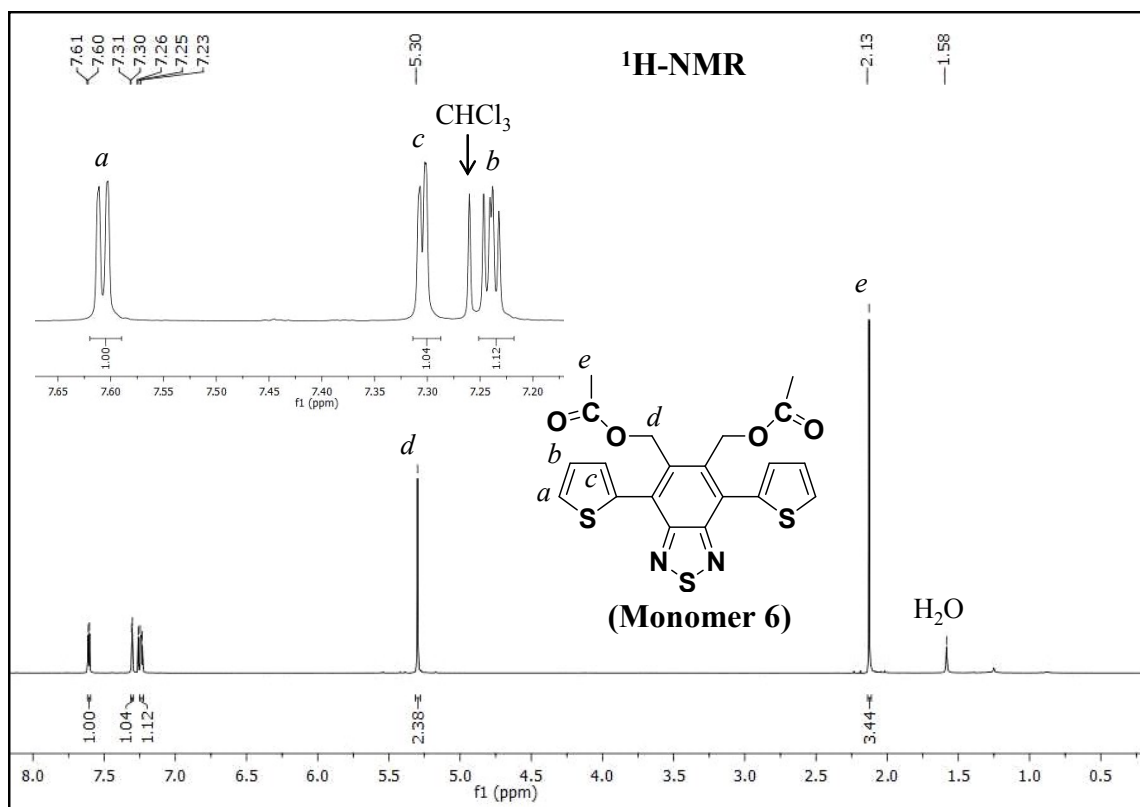**Fig. S7** ¹³C-NMR of Monomer 5.

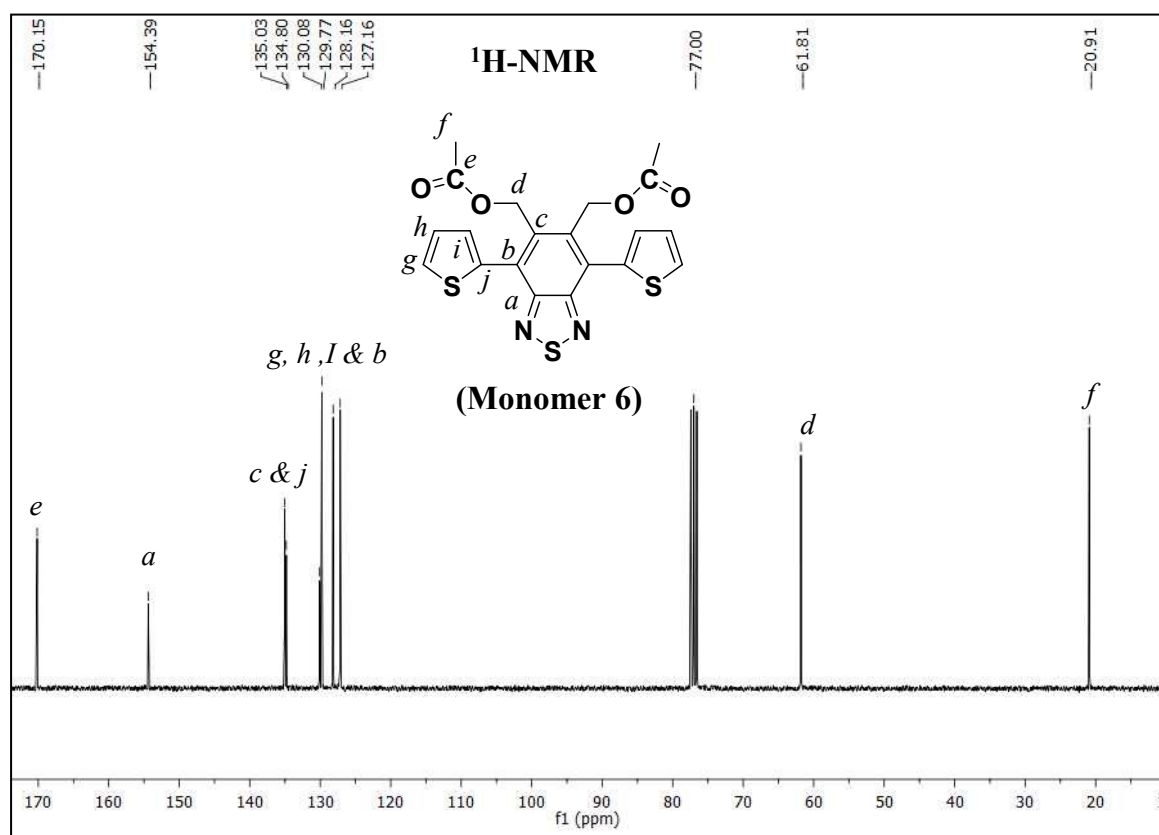**Fig. S8** ^{1}H NMR spectrum of Monomer 6.
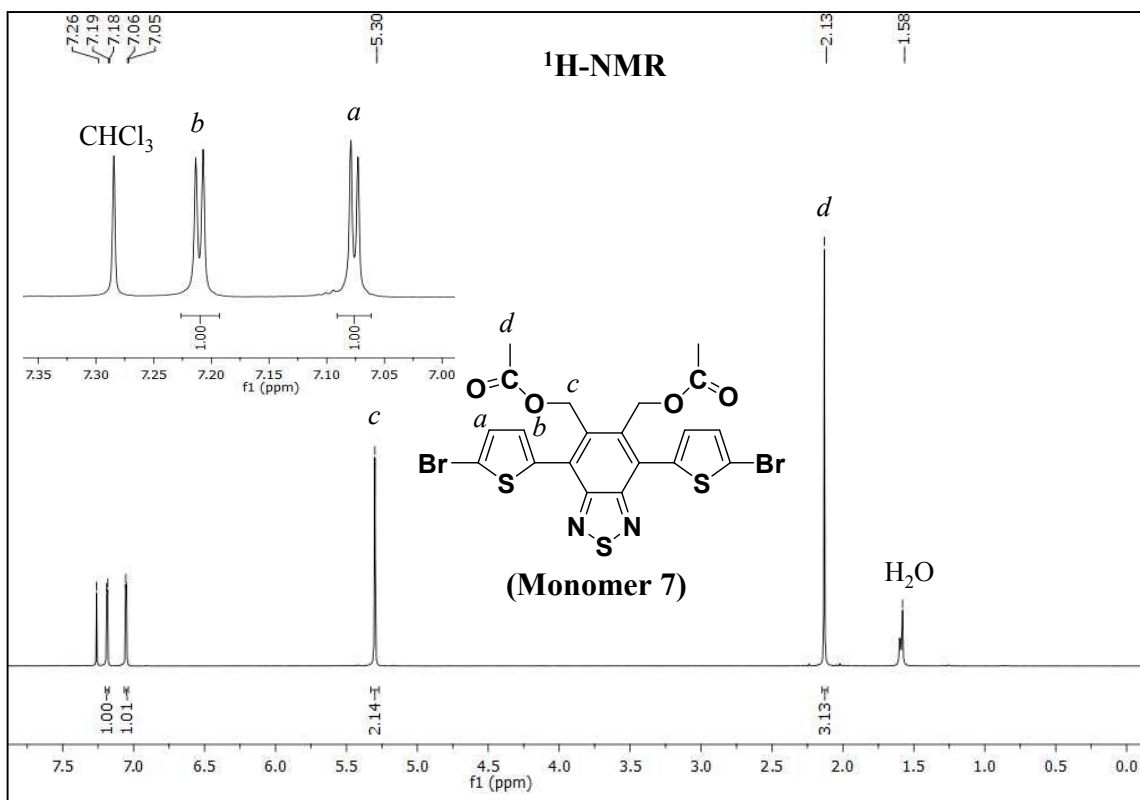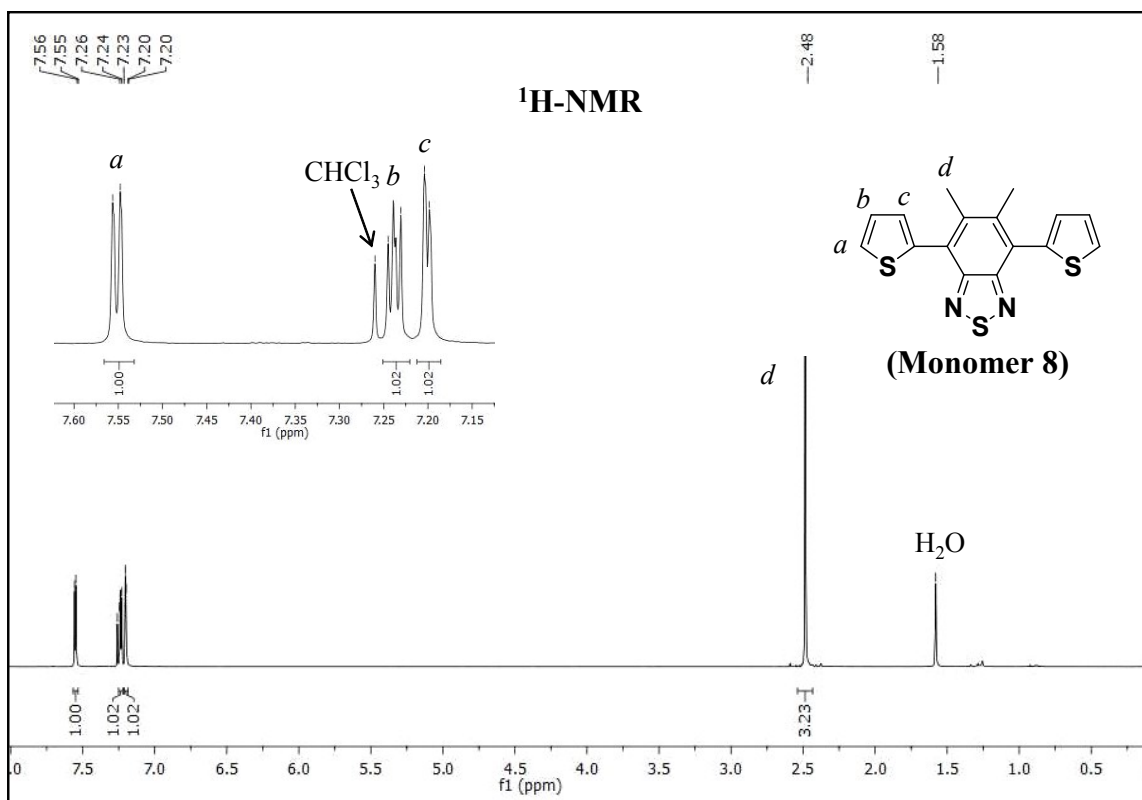

Fig. S9 ^{13}C-NMR of Monomer 6.

Fig. S10 ¹H NMR spectrum of Monomer 7.
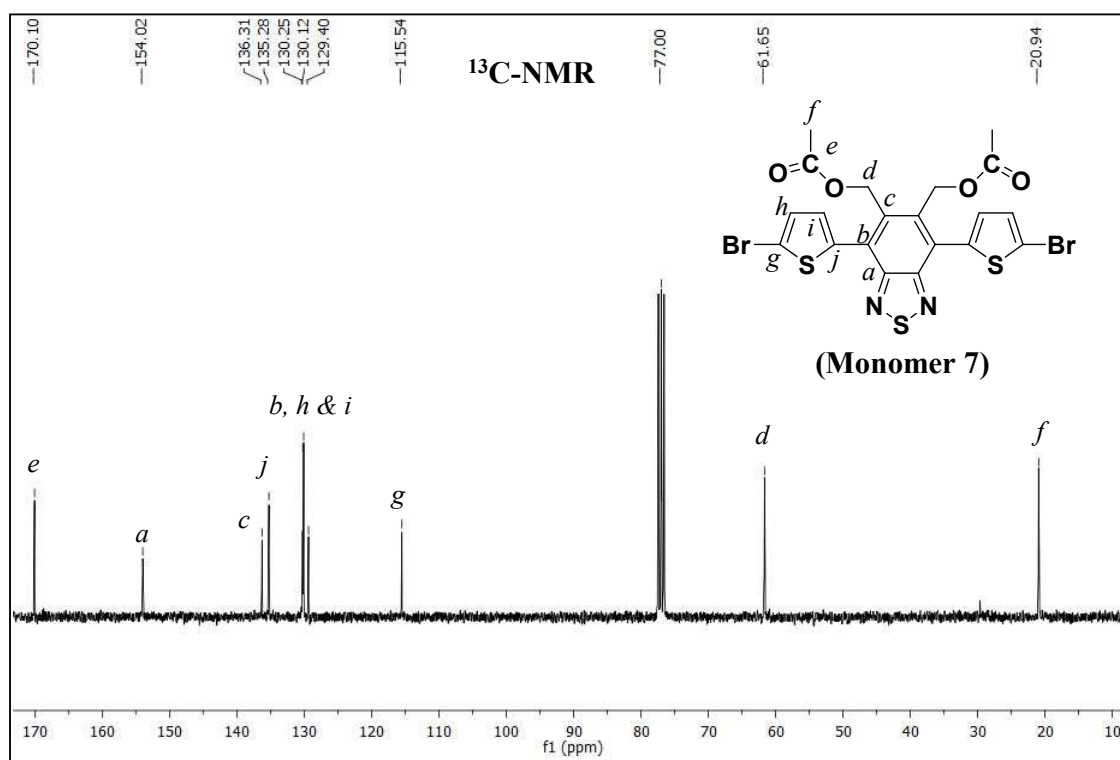
Fig. S11 ¹³C-NMR of Monomer 7.

Fig. S12 ¹H NMR spectrum of Monomer 8.
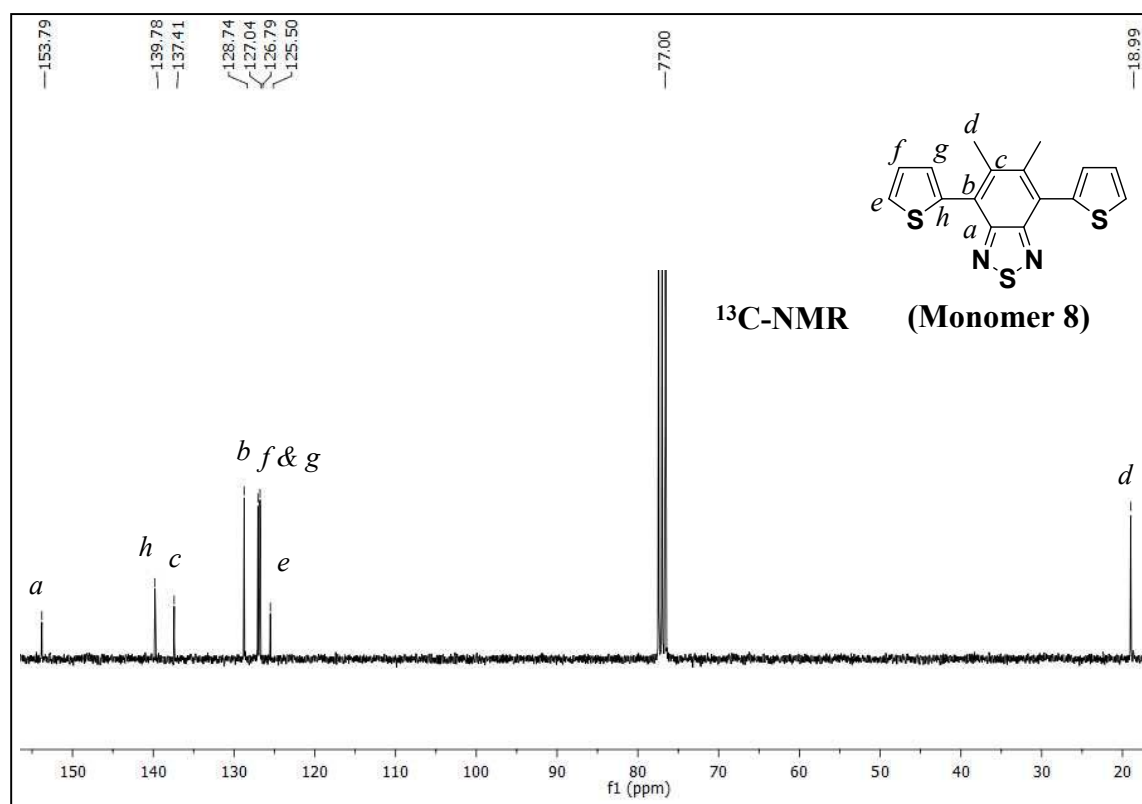
Fig. S13 ¹³C-NMR of Monomer 8.
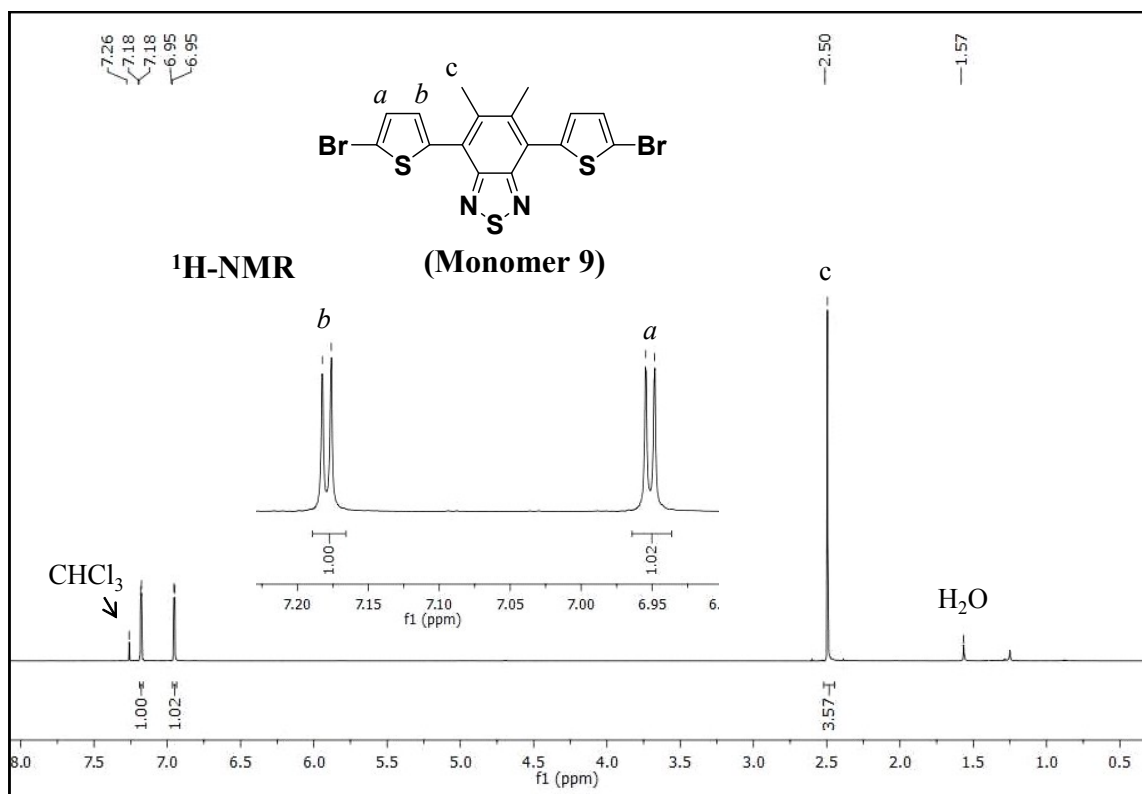
Fig. S14 ^{1}H NMR spectra of Monomer 9.
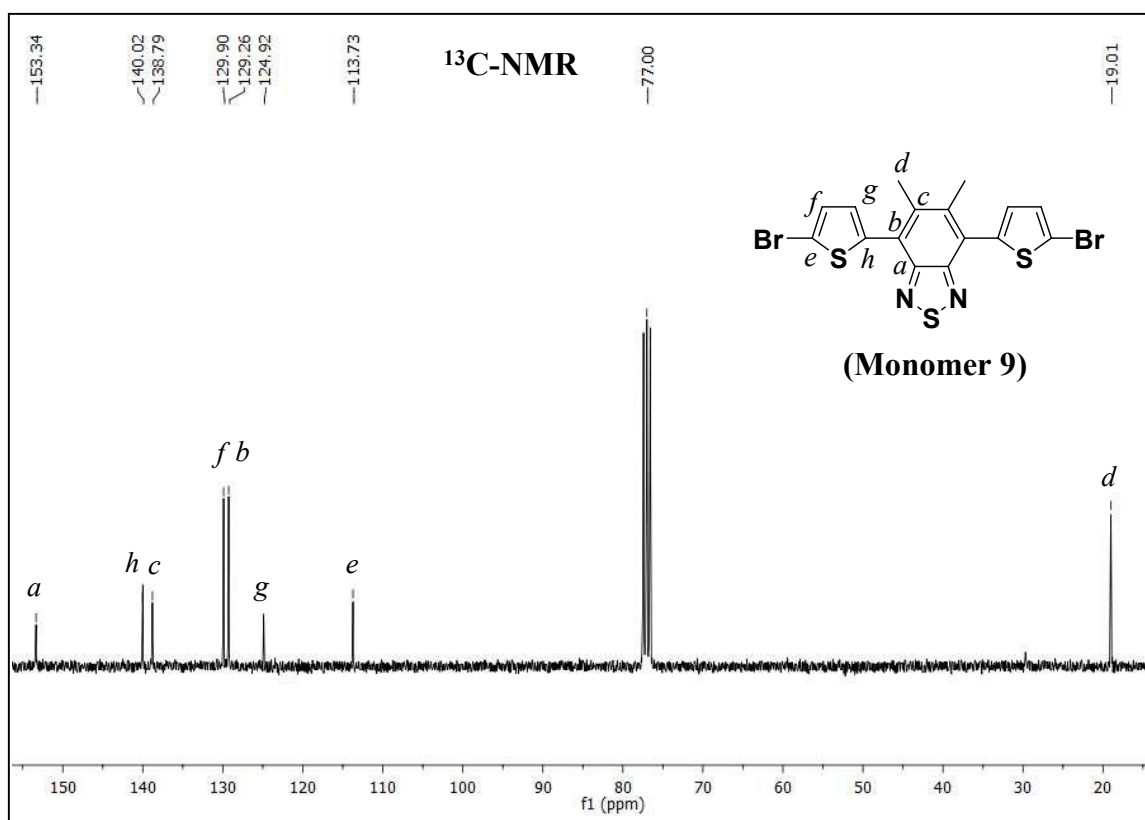
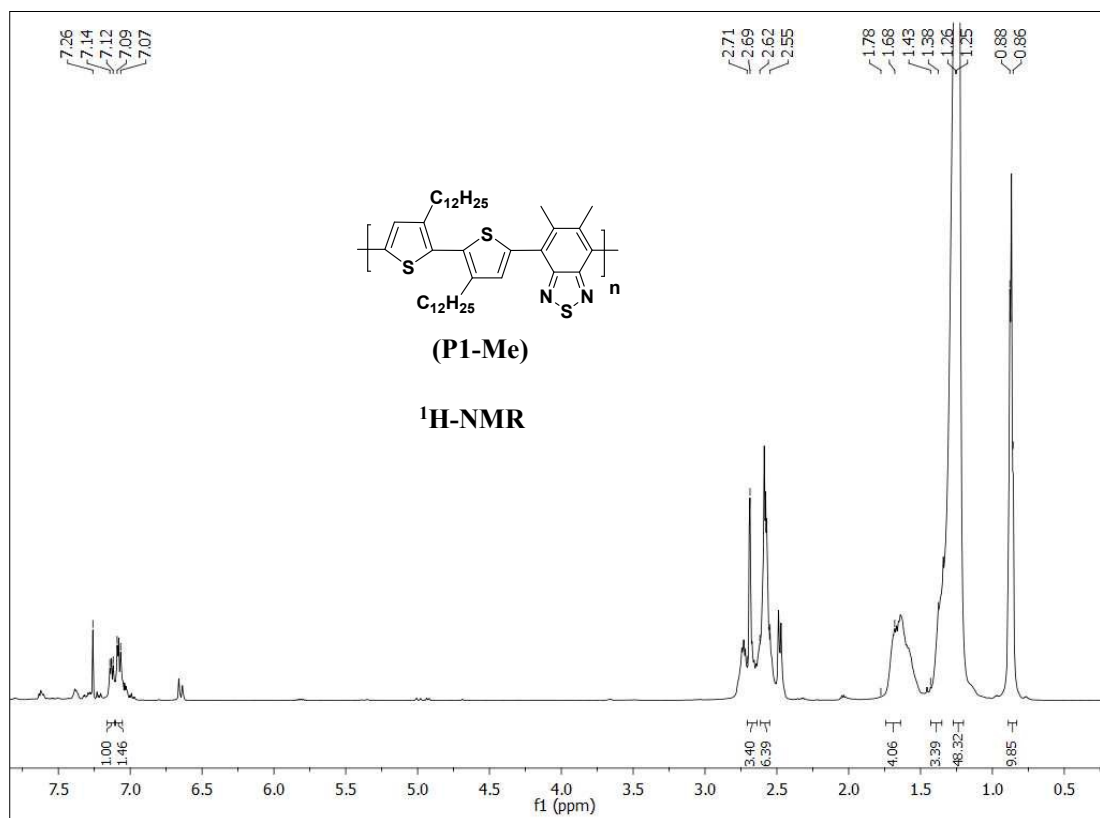**Fig. S15** ^{13}C-NMR of Monomer 9.

Fig. S16 ^{1}H NMR spectrum of Polymer P1-Me.
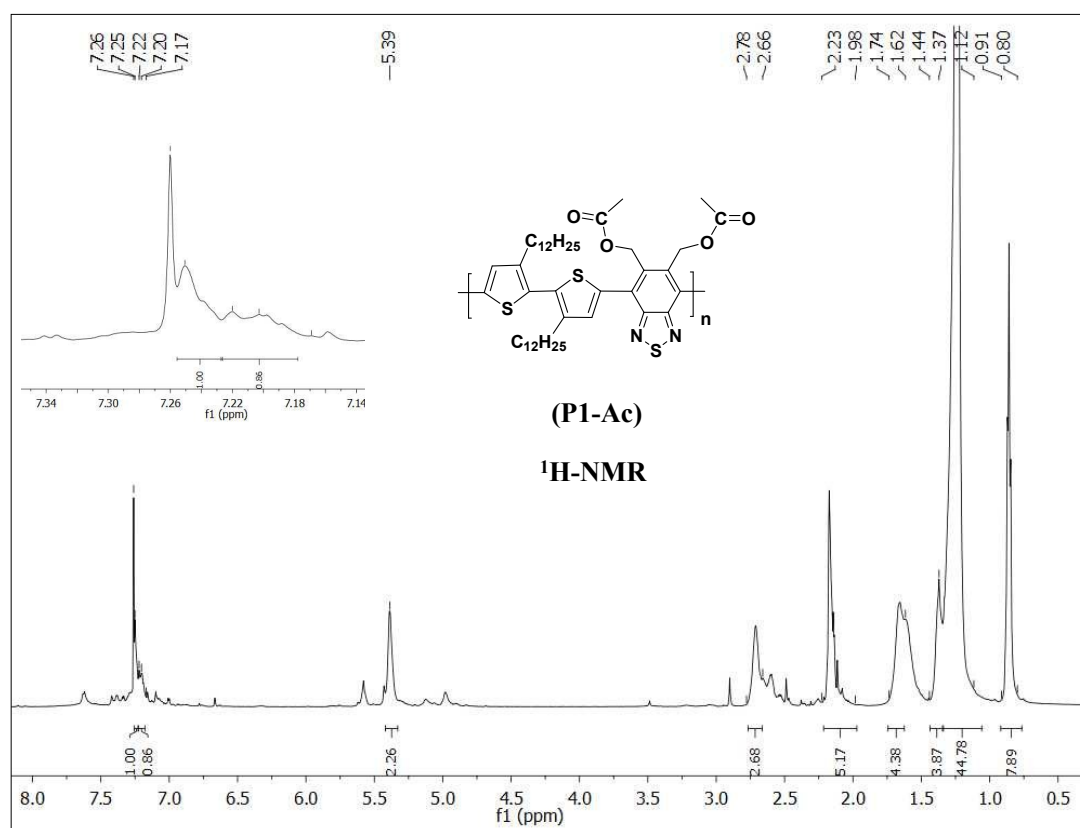

Fig. S17 ^{1}H NMR spectra of Polymer P1-Ac.
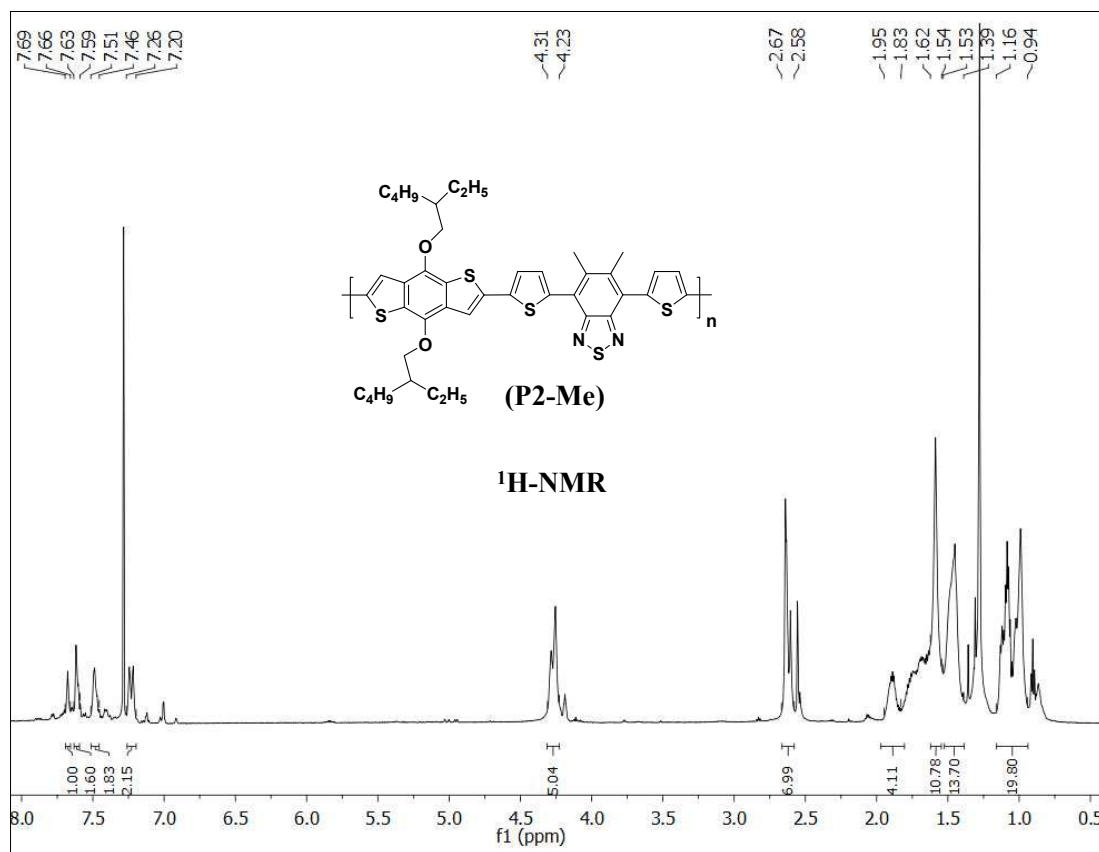
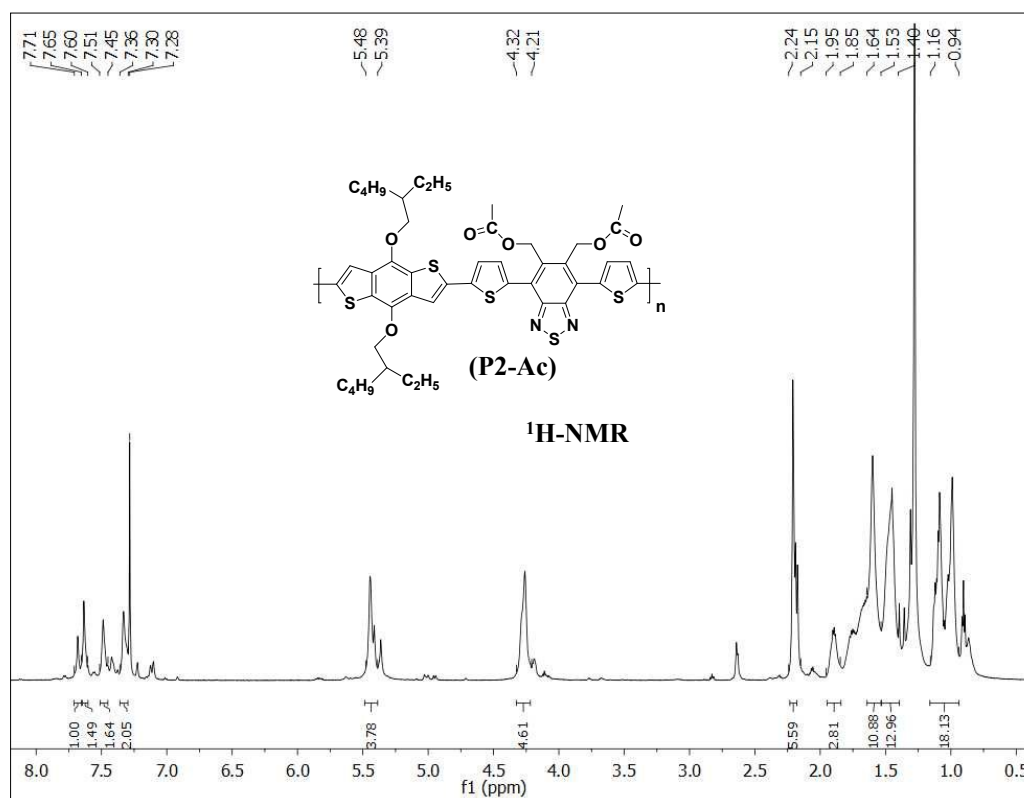**Fig. S18** ^{1}H NMR spectrum of Polymer P2-Me.

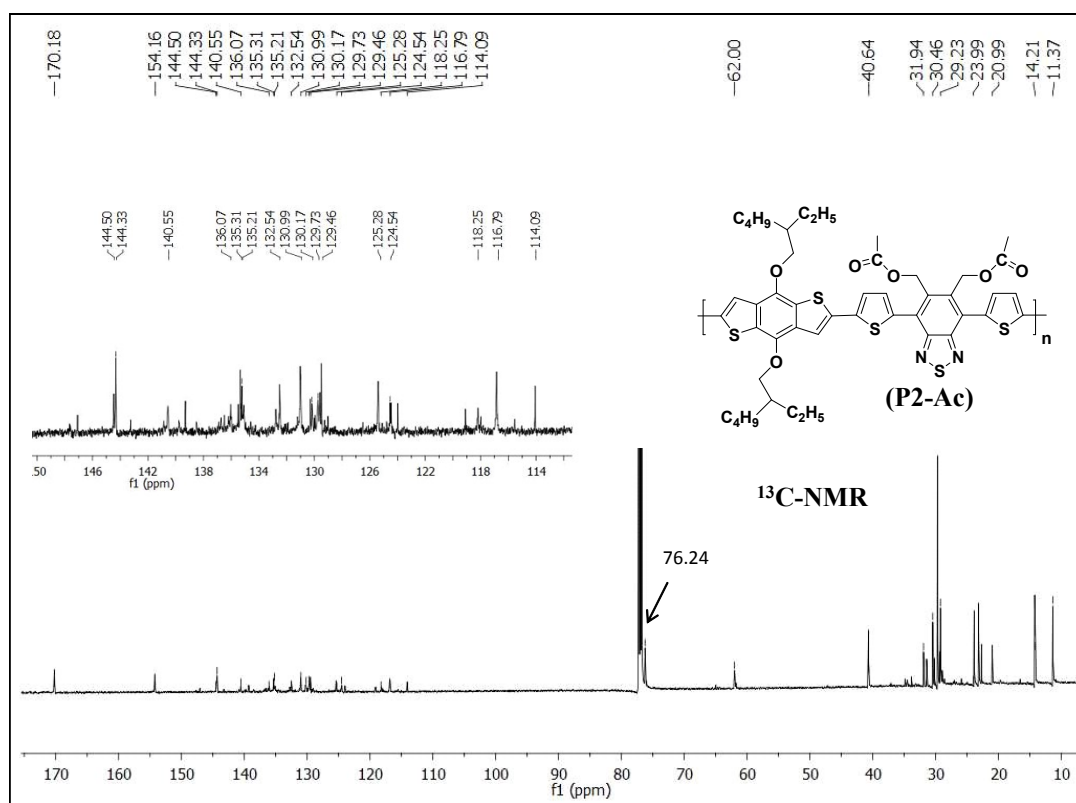**Fig. S19** ^{1}H NMR spectrum of Polymer P2-Ac.

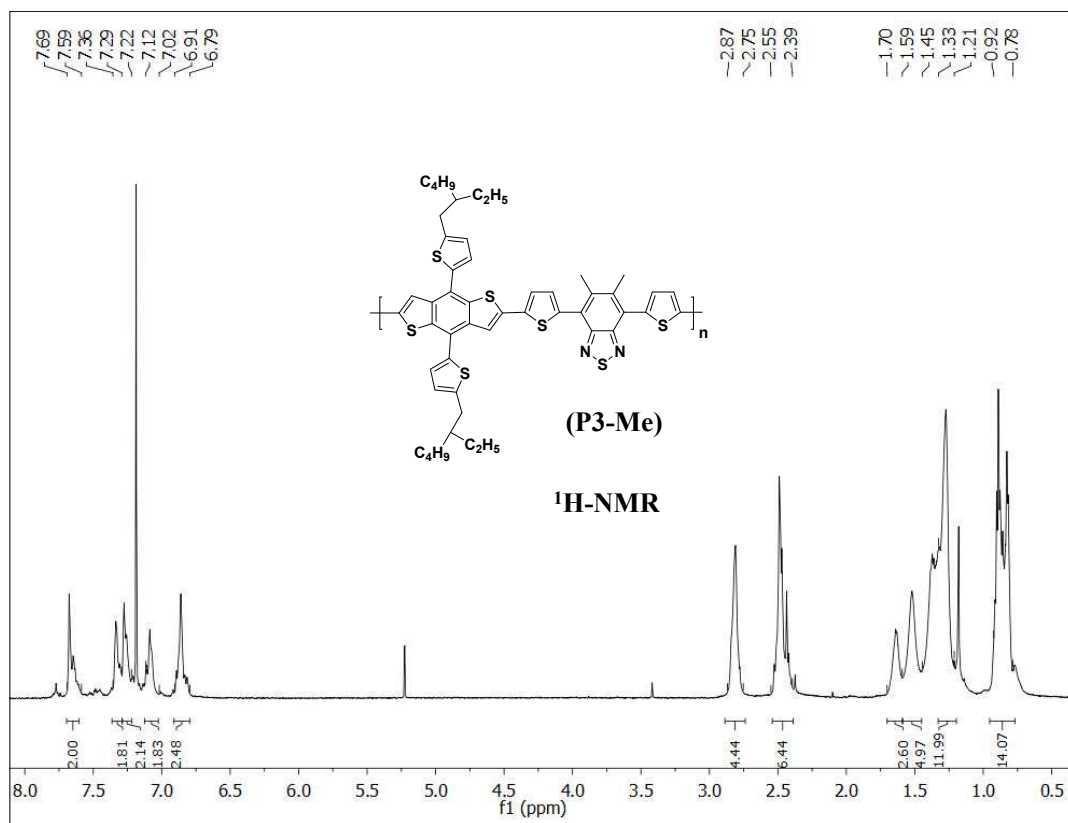**Fig. S20** ^{13}C NMR spectra of Polymer P2-Ac.

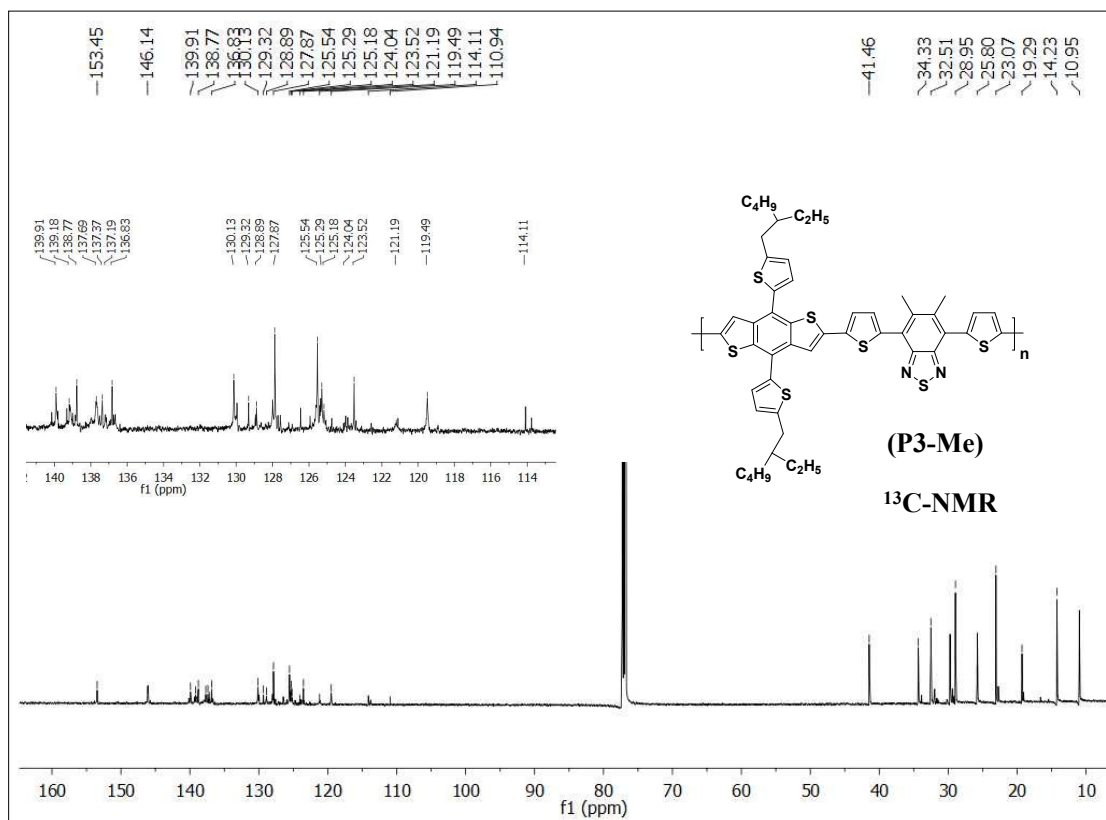**Fig. S21** ^{1}H-NMR spectrum of Polymer P3-Me.

Fig. S22 ^{13}C NMR spectra of Polymer P3-Me.
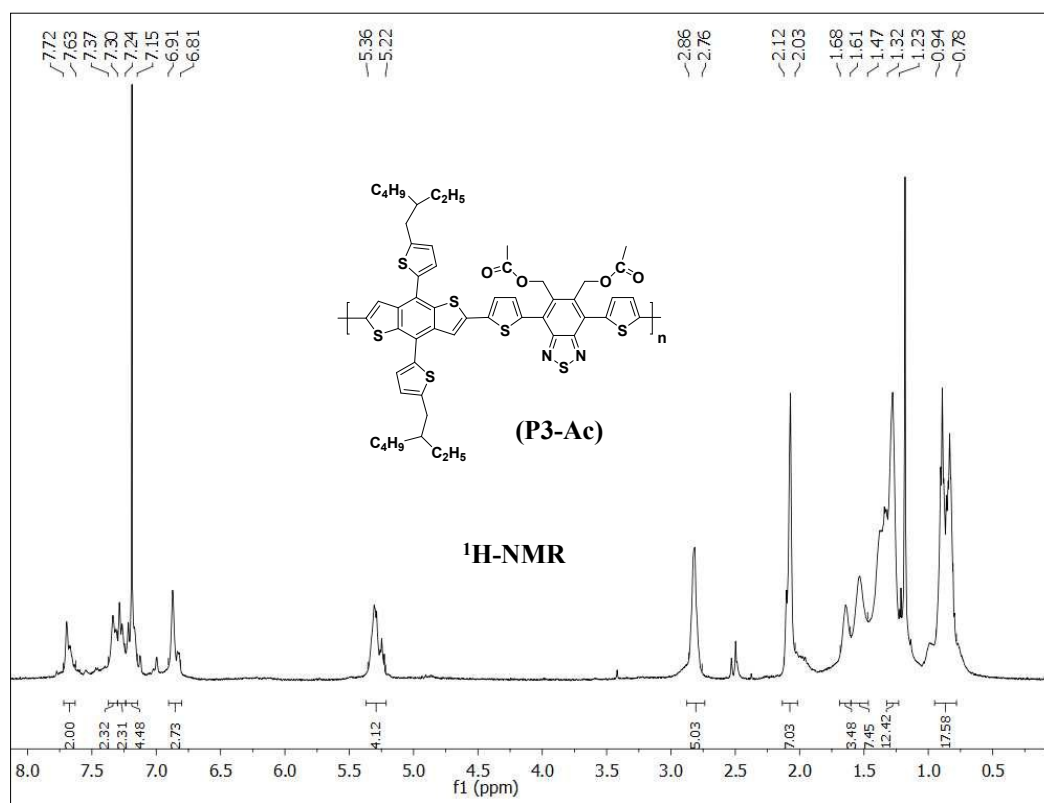
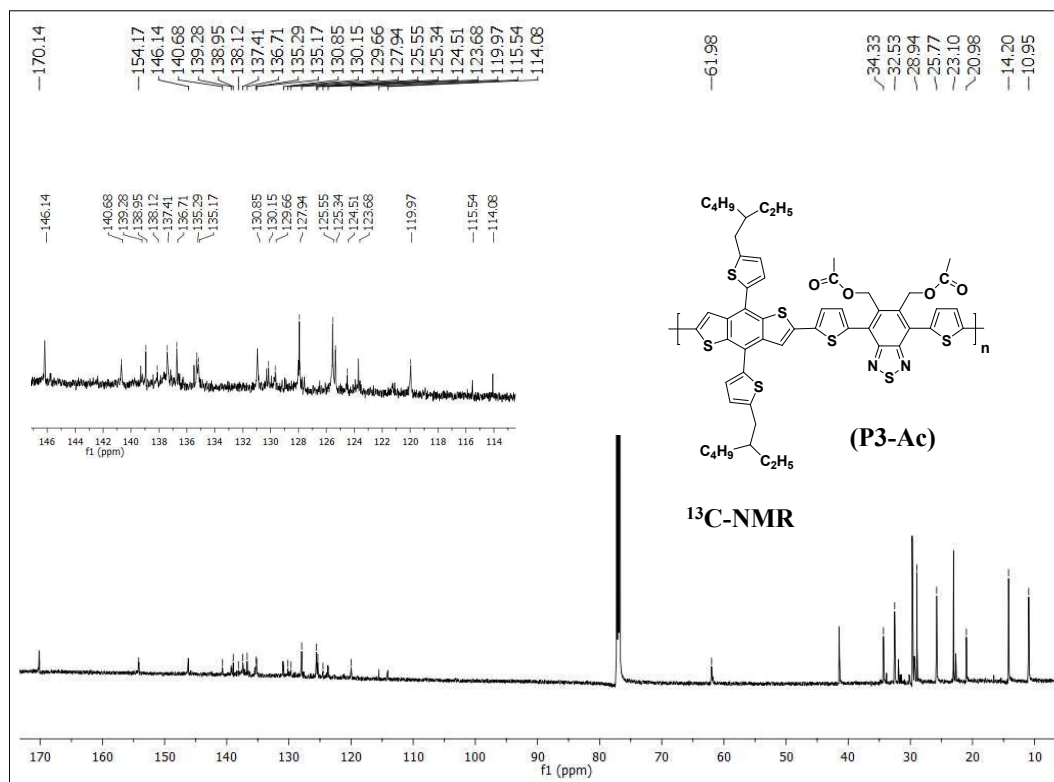**Fig. S23** ^{1}H NMR spectrum of Polymer P3-Ac.

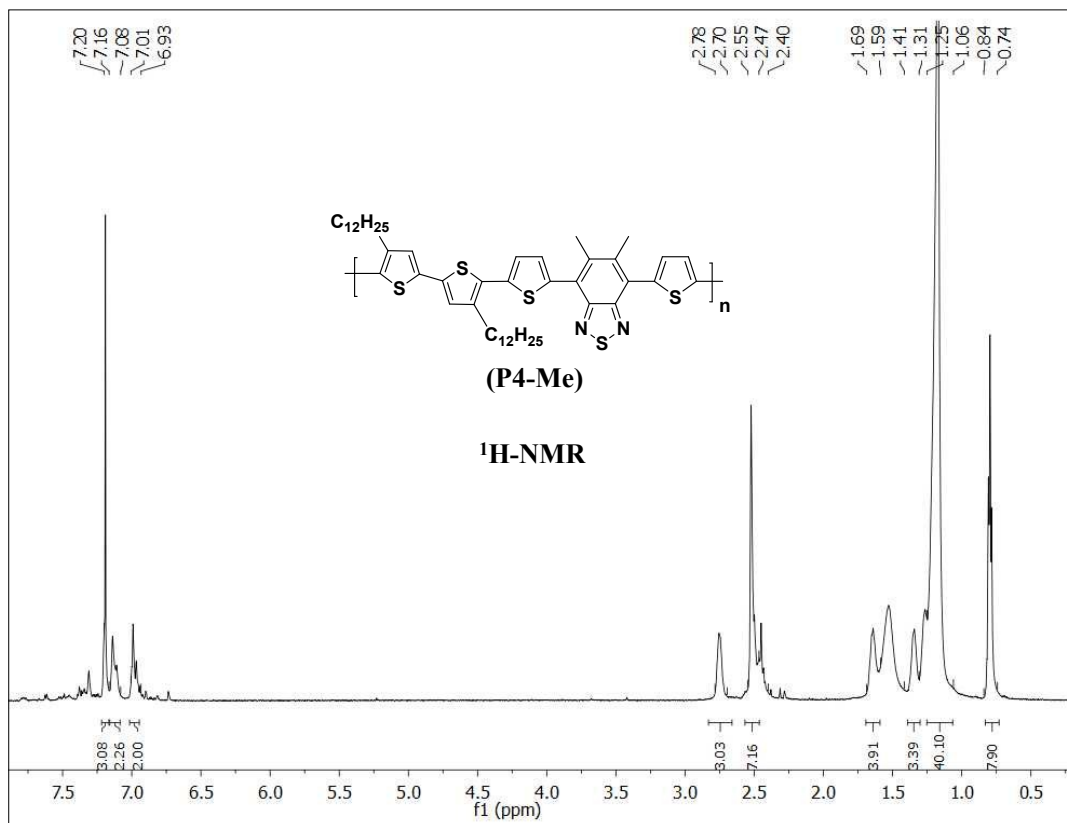**Fig. S24** ^{13}C NMR spectra of Polymer P3-Ac.

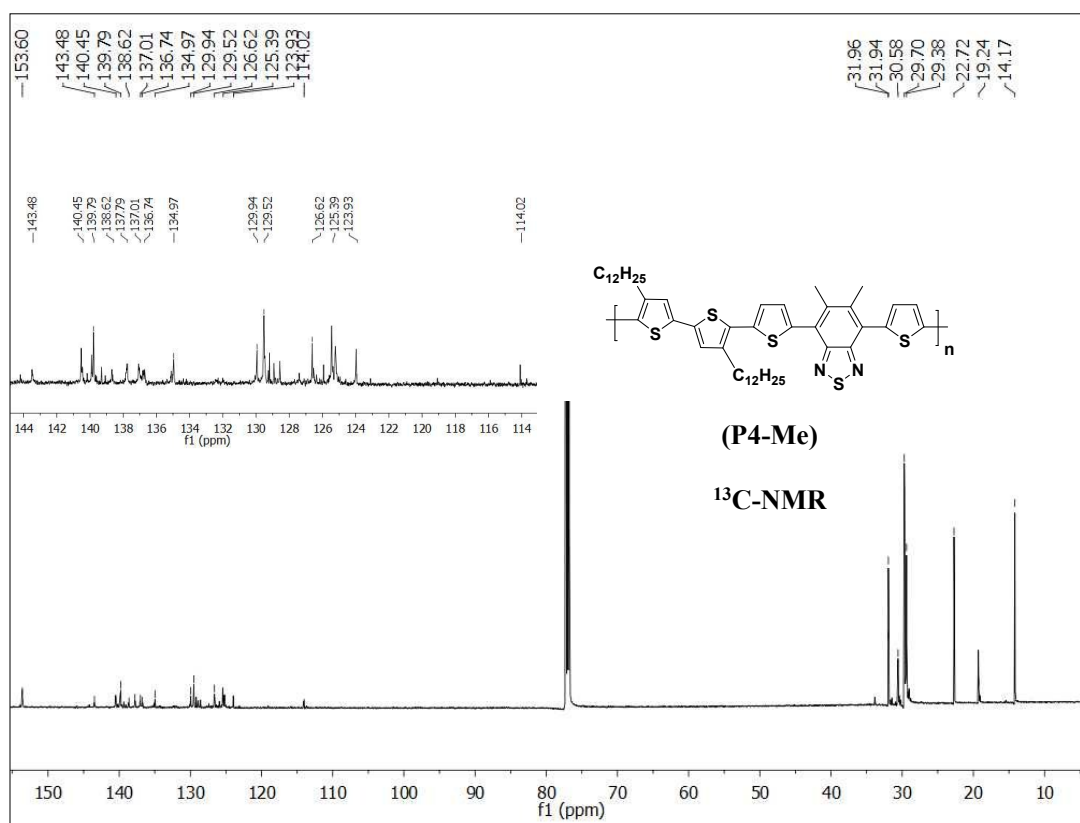**Fig. S25** ^{1}H-NMR spectrum of Polymer P4-Me.

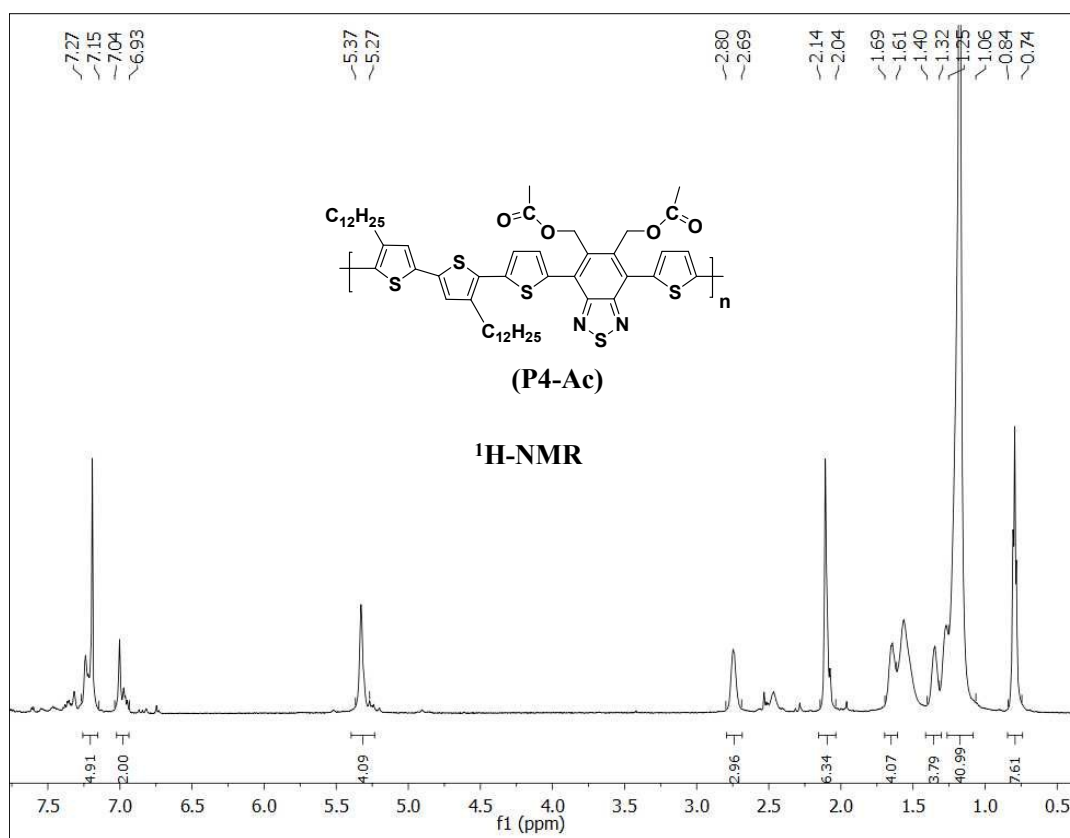**Fig. S26** ^{13}C NMR spectra of Polymer P4-Me.

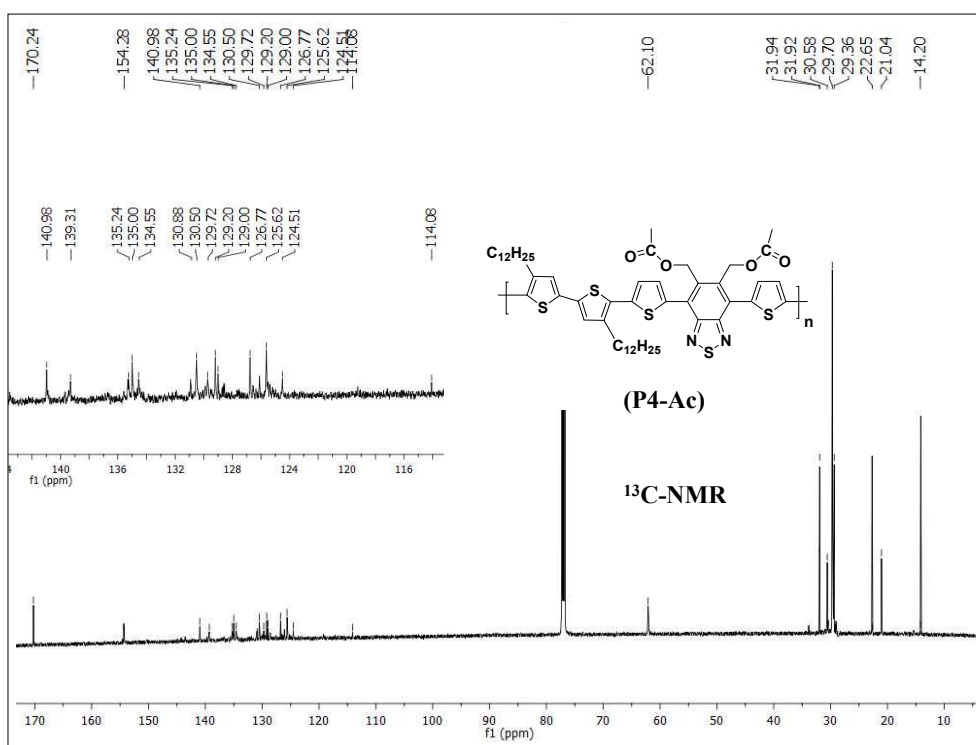**Fig. S27** ^{1}H-NMR spectrum of Polymer P4-Ac.
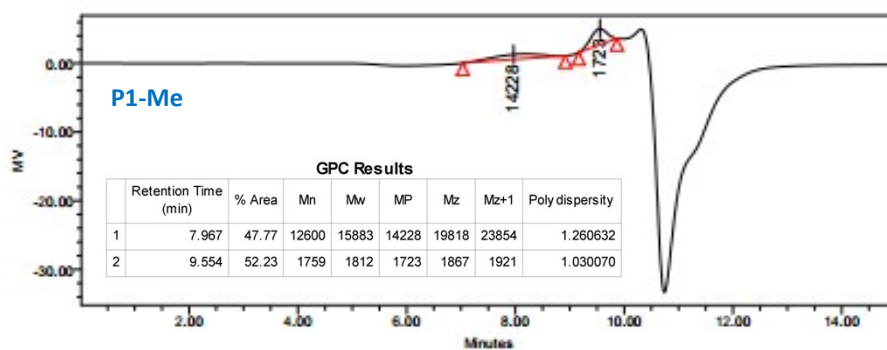

Fig. S28 ^{13}C NMR spectra of Polymer P4-Ac.

Fig. S29 GPC data of Polymer P1-Me.
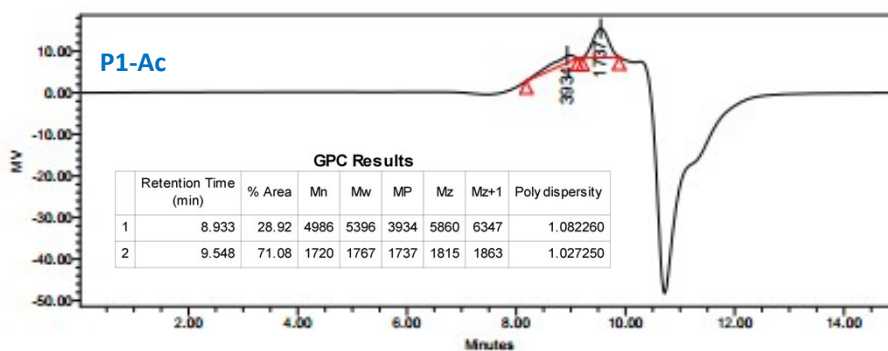
Fig. S30 GPC data of Polymer P1-Ac.

GPC Results

	Retention Time (min)	% Area	Mn	Mw	MP	Mz	Mz+1	Poly dispersity
1	8.033	92.27	11850	15300	13021	19484	23673	1.291088
2	9.377	7.73	2220	2257	2180	2295	2333	1.016723
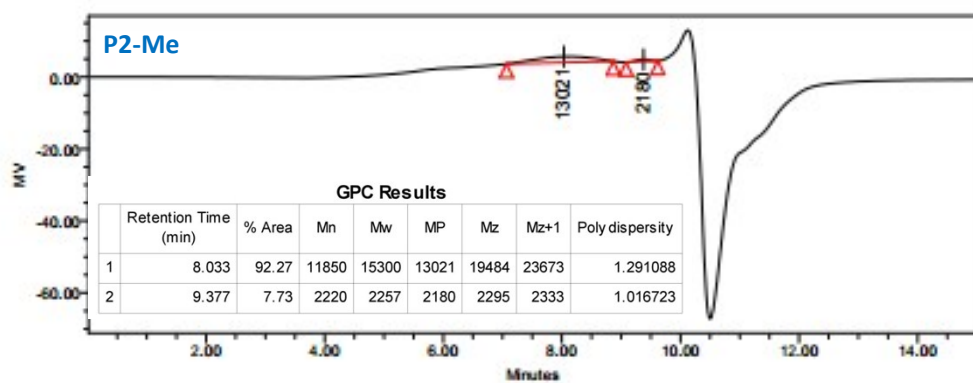
Fig. S31 GPC data of Polymer P2-Me.

GPC Results

	Retention Time (min)	% Area	Mn	Mw	MP	Mz	Mz+1	Poly dispersity
1	8.117	6.33	11581	11959	11655	12344	12725	1.032666
2	9.267	93.67	2496	2539	2525	2583	2626	1.017137
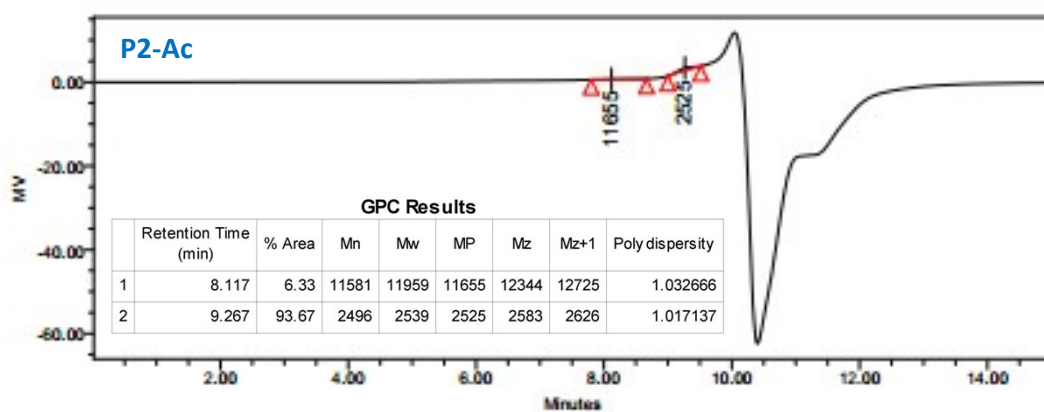
Fig. S32 GPC data of Polymer P2-Ac.

GPC Results

	Retention Time (min)	% Area	Mn	Mw	MP	Mz	Mz+1	Poly dispersity
1	8.100	94.50	11142	13924	11916	17151	20313	1.249770
2	9.333	5.50	2293	2321	2311	2349	2378	1.011979
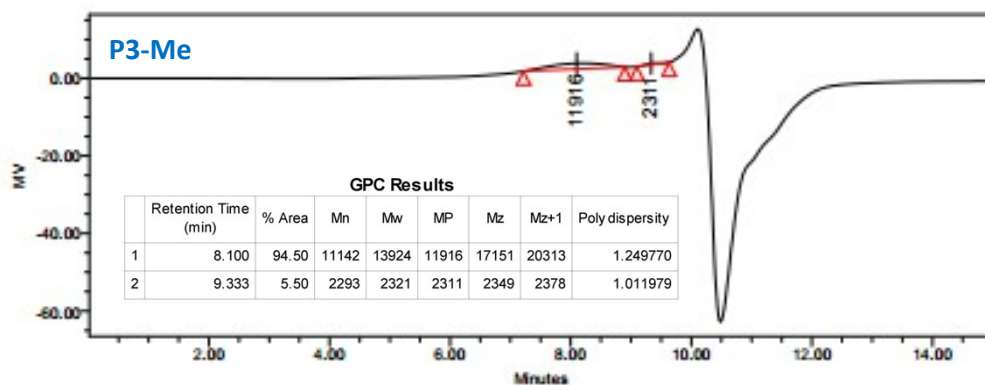
Fig. S33 GPC data of Polymer P3-Me.
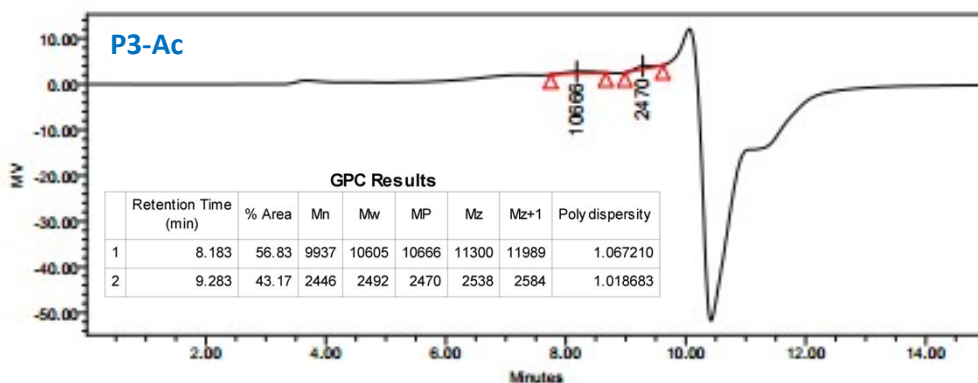
Fig. S34 GPC data of Polymer P3-Ac.

P3-Ac GPC Results:

	Retention Time (min)	% Area	Mn	Mw	MP	Mz	Mz+1	Poly dispersity
1	8.183	56.83	9937	10605	10666	11300	11989	1.067210
2	9.283	43.17	2446	2492	2470	2538	2584	1.018683
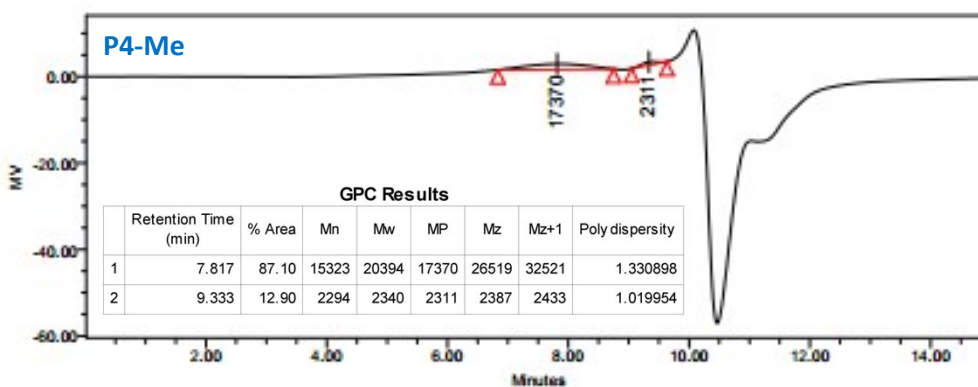
Fig. S35 GPC data of Polymer P4-Me.

P4-Me GPC Results:

	Retention Time (min)	% Area	Mn	Mw	MP	Mz	Mz+1	Poly dispersity
1	7.817	87.10	15323	20394	17370	26519	32521	1.330898
2	9.333	12.90	2294	2340	2311	2387	2433	1.019954

Fig. S36 GPC data of Polymer P4-Ac.

P4-Ac GPC Results:

	Retention Time (min)	% Area	Mn	Mw	MP	Mz	Mz+1	Poly dispersity
1	7.900	89.11	14008	18199	15554	23142	27944	1.299165
2	9.333	10.89	2301	2352	2311	2404	2456	1.022244

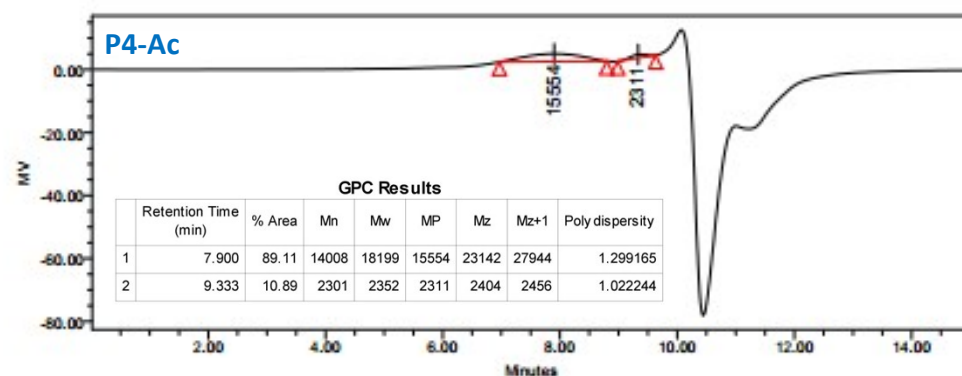## References

1. W. L. F. Armarego, D. D. Perrin, Purification of laboratory chemicals, Butterworth-Heinemann: Burlington, MA, 2002.

2. J. Liu, Q. Zhou, Y. Cheng, Y. Geng, L. Wang, D. Ma, X. Jing, F. Wang, *Adv. Funct. Mater.*, 2006, **16**, 957-965.