Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

for

Synthesis and Properties of a New Class of π-expanded diketopyrrolopyrrole analog and Its Conjugated Polymers

Yazhou Wang, Yuchun Xu, Mahesh Kumar Ravva, Yaping Yu, Mingfei Xiao, Xiang Xue, Xinru Yang, Yongming Chen, Zhengke Li, Wan Yue

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1. Materials and methods

3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione were prepared according to the literature.[S1] All other reagents and solvents were obtained from commercial suppliers and purified and dried according to standard procedures.[S2] Column chromatography was performed on silica gel (General-Regent, 200-300 mesh). Solvents for spectroscopic studies were of spectroscopic grade and used as received. Absorption spectra were measured with Alilent Technologies (Cary 5000/6000i) Cary Win UV-Vis spectrophotometer in a 1-cm quartz cell. Average molecular weights (Mw, Mn) were determined by Gel permeation chromatography (GPC) against polystyrene standards. Chlorobenzene was used as eluent at 80 ^{o}C with a flow rate of 1ml/min. For cyclic voltammetry, a standard commercial electrochemical analyzer (Shanghai Chenhua instrument co. LTD., CHI520E) with a three-electrode single-compartment cell was used. Dichloromethane (HPLC grade) was dried over calcium hydride under argon and degassed before using.

The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) was purchased from Shanghai Macklin Biochemical Co., Ltd, the measurements were carried out in dichloromethane with ferrocene (Fc) as an internal standard for the calibration of the potential. Ag/AgCl reference electrode was used. A glassy carbon electrode and a Pt wire were used as working and auxiliary electrodes, respectively. Cyclic voltammograms of polymers by dropping-cast measured in acetonitrile in the presence of 0.1 M n-Bu4NPF6 as supporting electrolyte at a scan rate of 0.1 V/s. The values are given regarding Fc/Fc^{+}, which has been used as internal standard for calibration of the Ag/AgCl reference electrode. For P1, P2 and P3, polymer was drop casting on working electrode.

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, CD_2Cl_2 or 1,1,2,2-tetrachloroethane-d_2 with a Bruker Avance III spectrometer. High Resolution Matrix-assisted laser desorption/ionization time-of-flight (MALDI TOF) mass spectra were recorded on a Bruker Daltronik (solariX) mass spectrometer. Thermogravimetric analysis (TGA) measurements were conducted on a Netzsch STA 449F3 apparatus at a heating rate of 10 ℃/min under a nitrogen atmosphere.

Computational details: All geometry optimizations of π-expanded diketopyrrolopyrrole analog and oligomers were optimized using ωB97XD/6-31G(d,p)

level of theory. Long alkyl side-chains were replaced with methyl groups to reduce computational cost. Various conformations of oligomers were generated by altering the torsional angles between donor-acceptor units. The stable conformations of oligomers were identified using relative conformational energies. Electronic and optical properties were evaluated for stable oligomer conformations with the tuned ωB97XD functional (OT- ωB97XD). The range separation parameter ω was optimized using IP-tuning procedure. Excited state calculations were carried out at TD-OT-ωB97XD/6-31G(d,p) within self-consistent reaction field (SCRF) framework (chlorobenzene is used as solvent). Furthermore, we have also performed Nucleus Independent Chemical Shifts (NICS) calculations to get insights on the π-electron delocalization in these heterocyclic systems at GAIO-B3LYP/6-311g(d,p) level of theory. We have used $NICS(1)_{zz}$ procedure, suggested by Schleyer et al. and Bachrach and co-workers, the absolute magnetic shielding is evaluated at 1 Å above the geometric center of the ring. All calculations were performed using Gaussian 16 suite of programs.

2. Optimized geometry and NICS calculation.

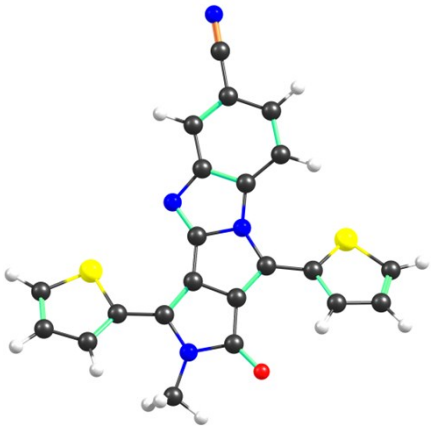
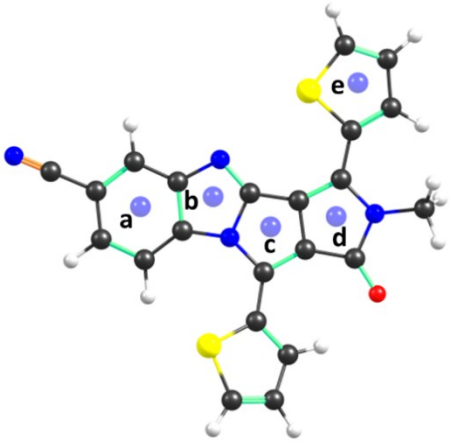


Figure S1: optimized geometry of π-expanded diketopyrrolopyrrole analog as determined at ωB97XD/6-31g(d,p) level of theory.

NICS(1)ZZ calculations:



Ring Center	$NICS(1)_{ZZ}$
a	-24.95
b	- 14.28
c	2.95
d	9.41
e	-21.39

Figure S2: Calculated NICS (1) $_{ZZ}$ aromaticity index (in PPM) at the rings center and 1Å above.

3. Cyclic voltammetry of compounds.

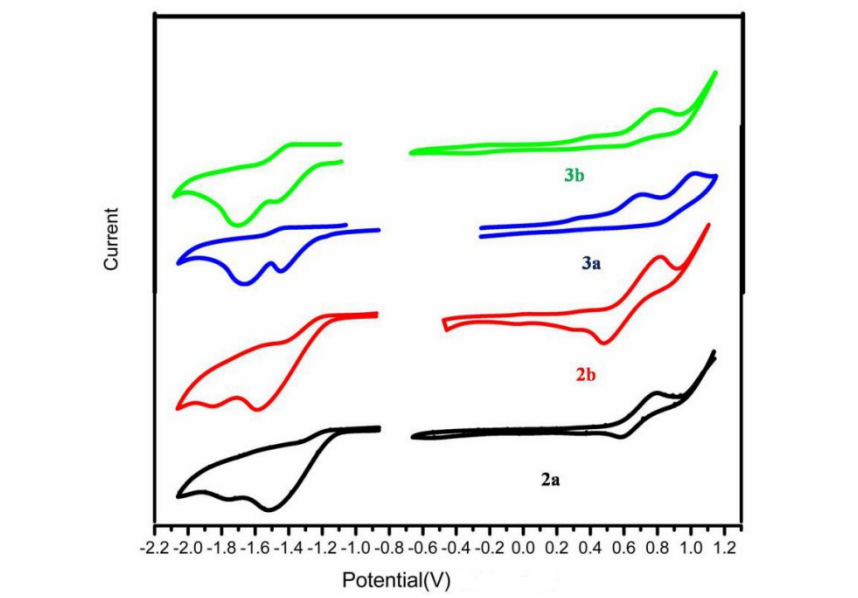


Figure S3. Cyclic voltammograms of compounds **2a** (black), **2b** (red), **3a** (blue), and **3b** (green) measured in dichloromethane in the presence of 0.1 M n-Bu_4NPF_6 as supporting electrolyte at a scan rate of 0.1 V/s. The values are given with regard to Fc/Fc^+, which has been used as internal standard for calibration of the Ag/AgCl reference electrode.

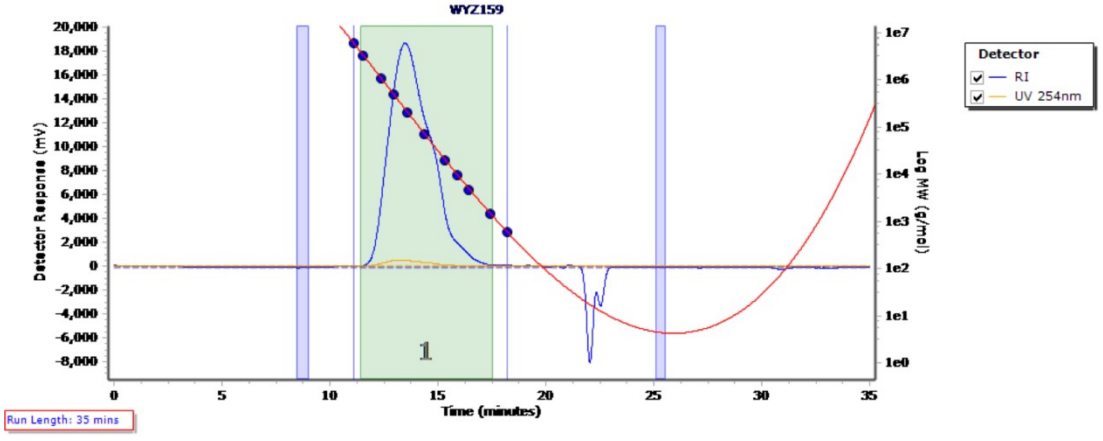
4. Summary of the Optical and electronic properties of compounds

Table S1. Optical and electronic properties of compounds **2a**, **2b**, **3a**, and **3b**.

Comp.	λ_{max} [nm] [a]	ε [$M^{-1}cm^{-1}$] [a]	E_{1r} [V][b]	E_{1o} [V][b]	EA [eV] [c]	IP [eV][d]	E_g [eV] [e]	E_g [eV] [f]	LUMO [eV] [g]	HOMO [eV] [g]
2a	544	32229	-1.13	0.61	3.67	5.41	1.74	2.18	-	-
2b	542	30853	-1.16	0.59	3.64	5.39	1.75	2.18	-	-
3a	563/607	28255/18020	- 1.21	0.26	3.59	5.06	1.47	1.95	-1.33	-7.23
3b	562/604	28540/17818	- 1.22	0.24	3.58	5.04	1.46	1.95	-1.33	-7.23

[a] Measured in dilute chlorobenzene solution. [b] CV measurements of the thin films with the onset energy value for oxidation and reduction peak (in V *vs*. Fc/Fc^+). [c]EA (eV) estimated by the onset potential of reduction peak calculated according to EA (eV) = 4.80 + E_{1r}). [d]HOMO levels were estimated from the onset potential of oxidation peak using the equation, E_{HOMO} (eV) = – (4.8 – E_{ox}). [e]Eg= E_{LUMO}-E_{HOMO} eV. [f] Calculated by the onset of absorption solution spectra according to E_g = ($1240/\lambda_{onset}$). [g] DFT calculated values.

5. GPC data of polymers

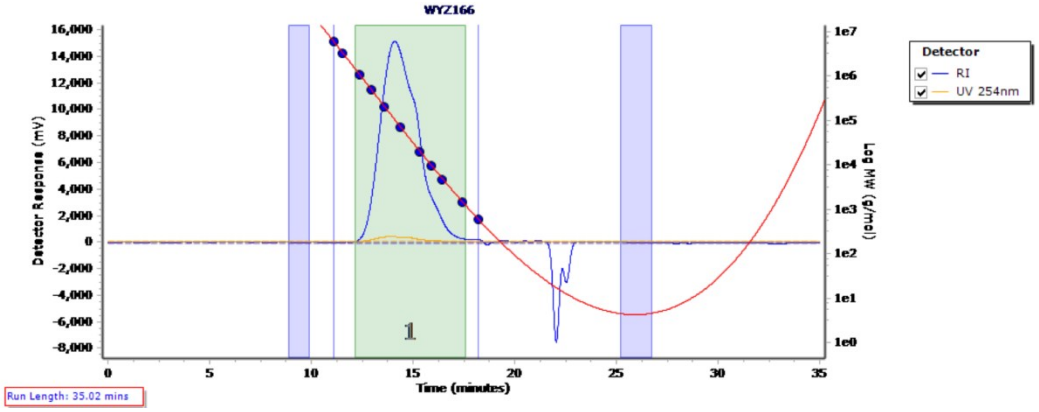


Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	235168	52002	274542	660121	1143887	599883	5.279

Figure S4: GPC data of **P1**.

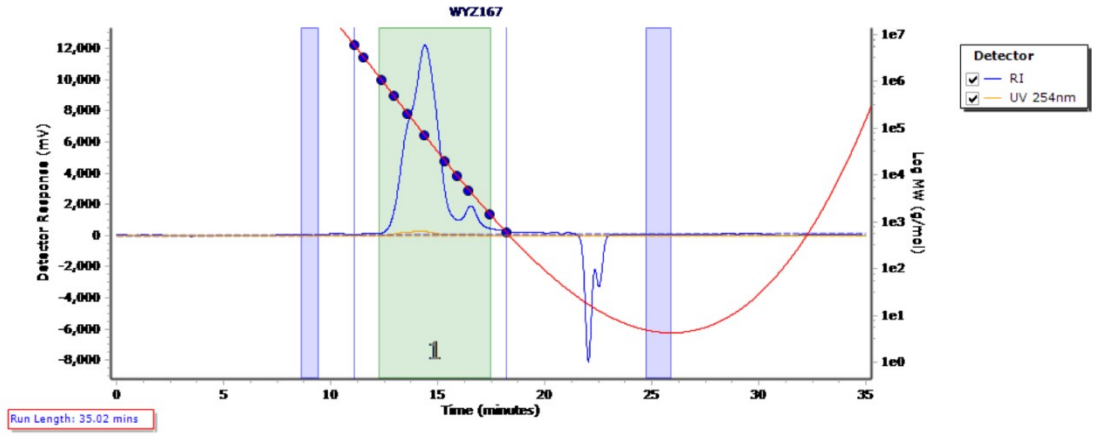
Chromatogram



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	102361	29237	115416	262258	438359	239317	3.948

Figure S5: GPC data of **P2**.



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	67715	25687	107051	226717	379236	207361	4.168

Figure S6: GPC data of **P3**.

6. TGA of polymers.

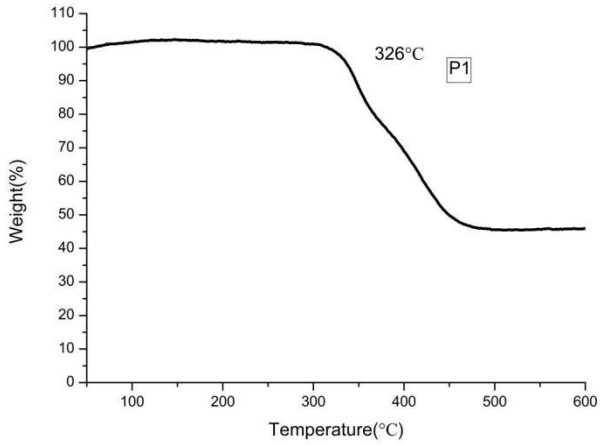


Figure S7. Thermal gravimetric analysis (TGA) curve of **P1**.

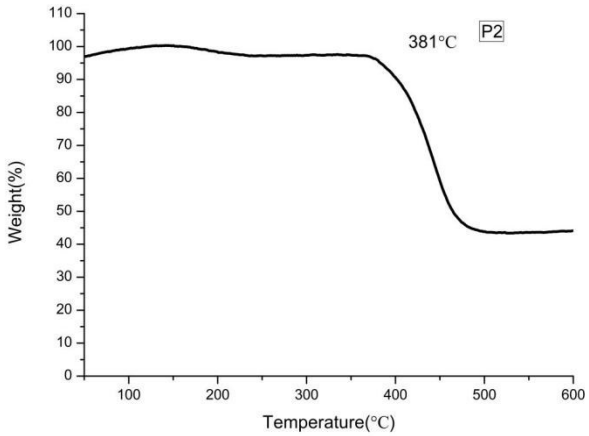


Figure S8. Thermal gravimetric analysis (TGA) curve of **P2.**

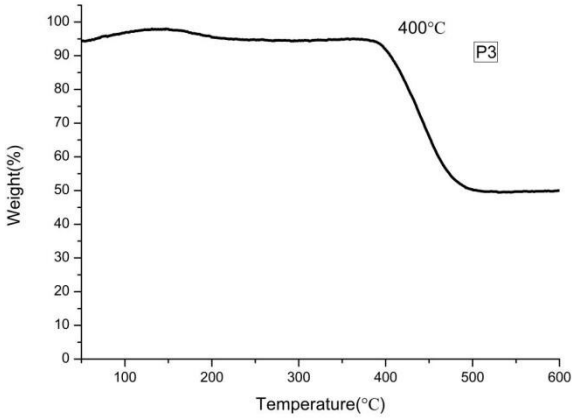
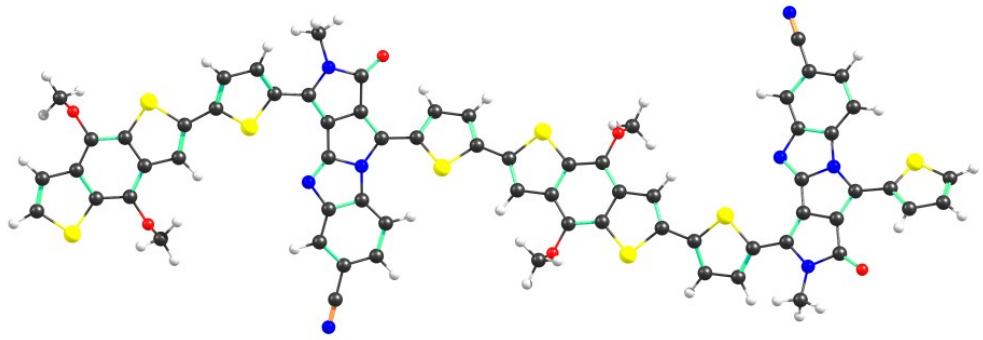
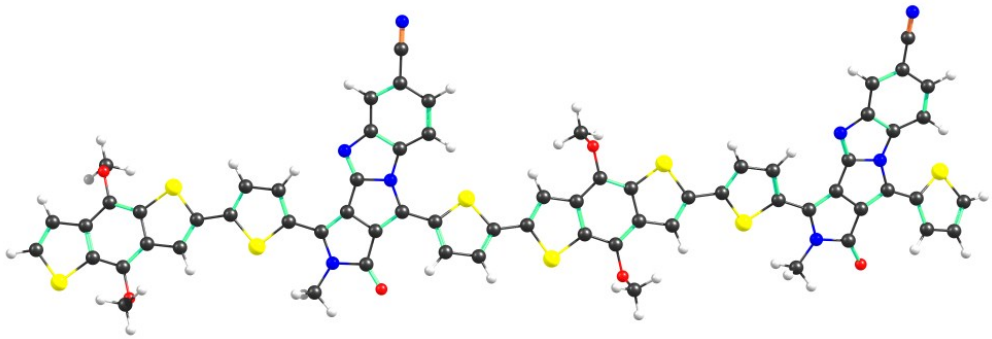


Figure S9. Thermal gravimetric analysis (TGA) curve of **P3**.

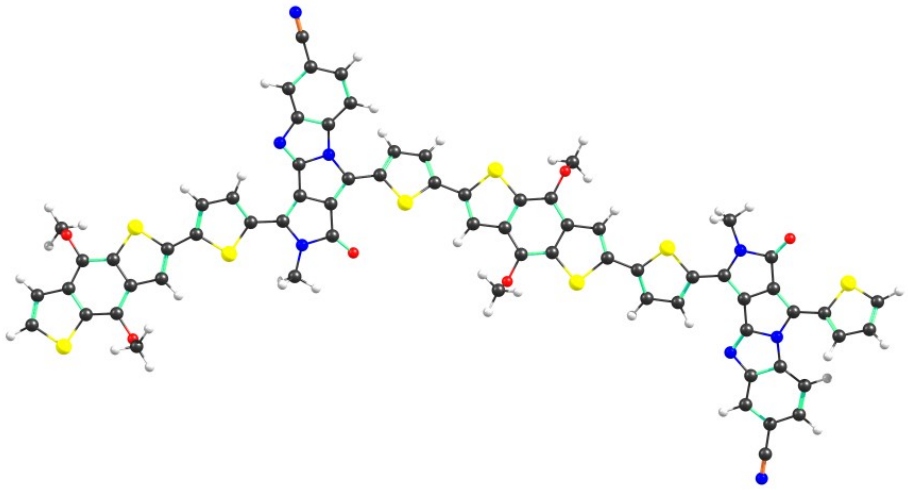
7. Computational details of the oligomer



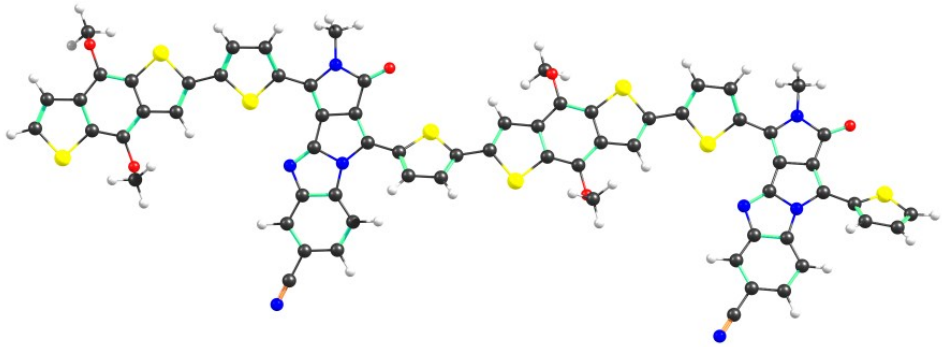
P1-*conf-1* (3.79 kcal/mol)



P1-*conf-2* (0.00 kcal/mol)

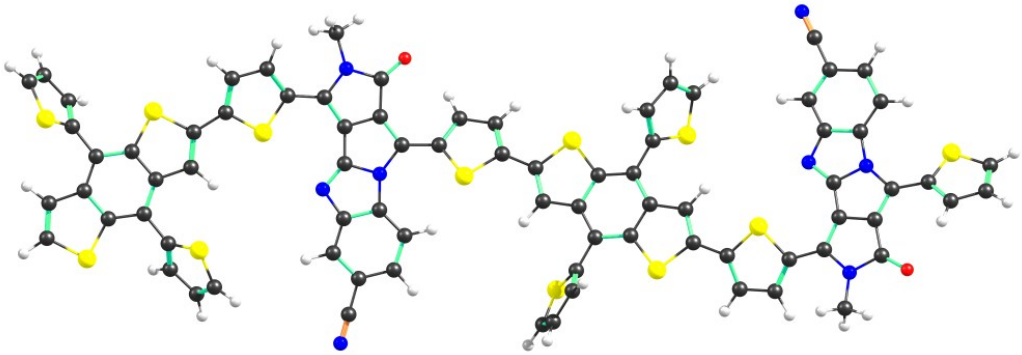


P1-*conf-3* (0.12 kcal/mol)

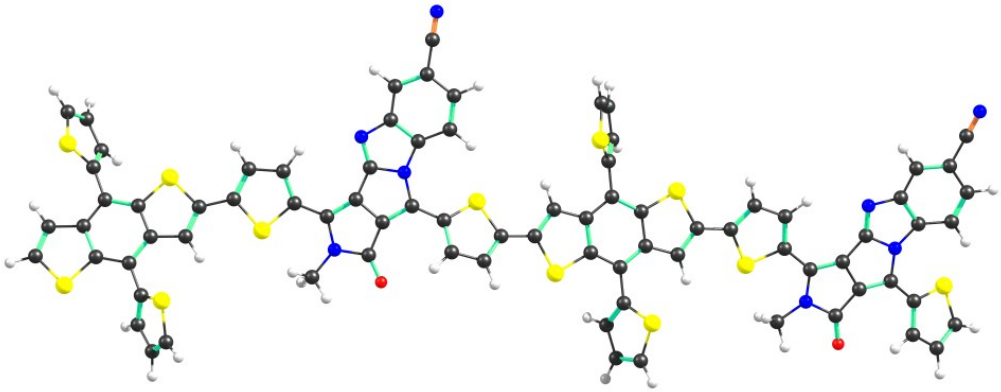


P1-*conf-4* (4.14 kcal/mol)

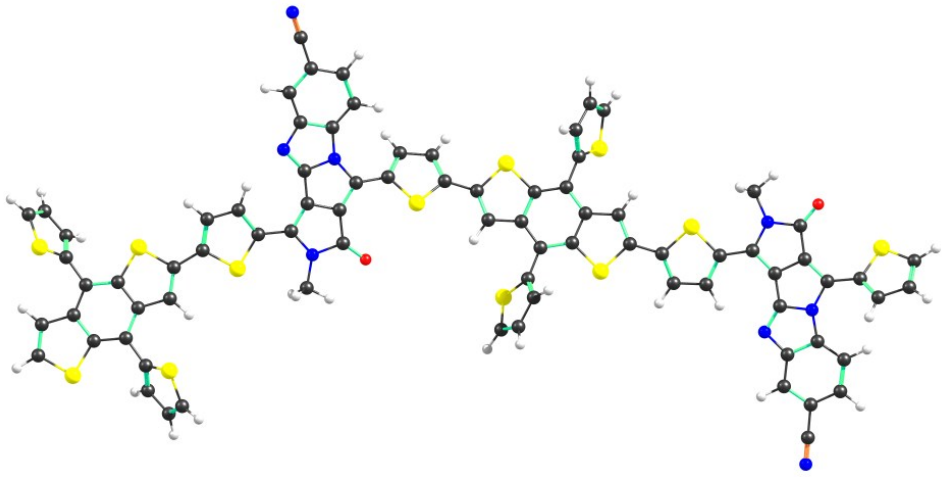
Figure S10: Optimized geometries of various conformations of P1 as determined at ωB97XD/6-31g(d,p) level of theory. Relative conformational energies (kcal/mol) are given in parenthesis.



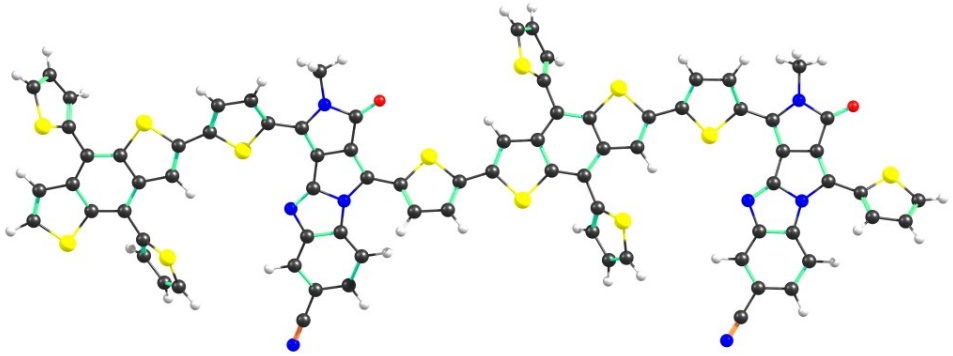
P2-*conf-1* (2.54 kcal/mol)



P2-*conf-2* (0.00 kcal/mol)

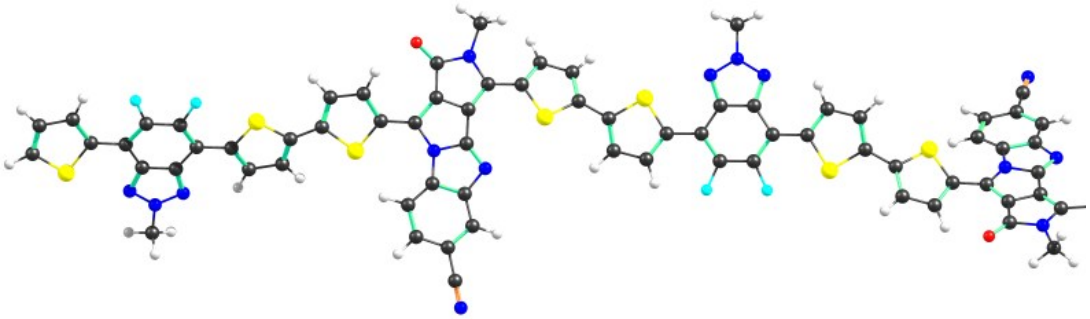


P2-*conf-3* (0.00 kcal/mol)

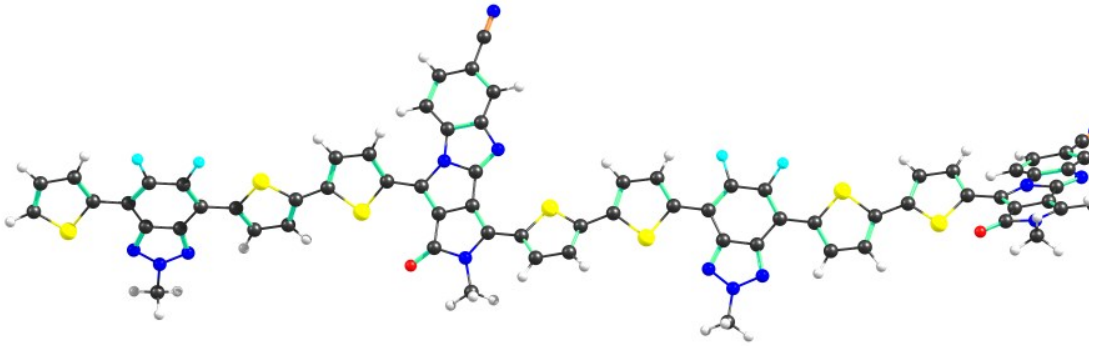


P2-*conf-4* (0.00 kcal/mol)

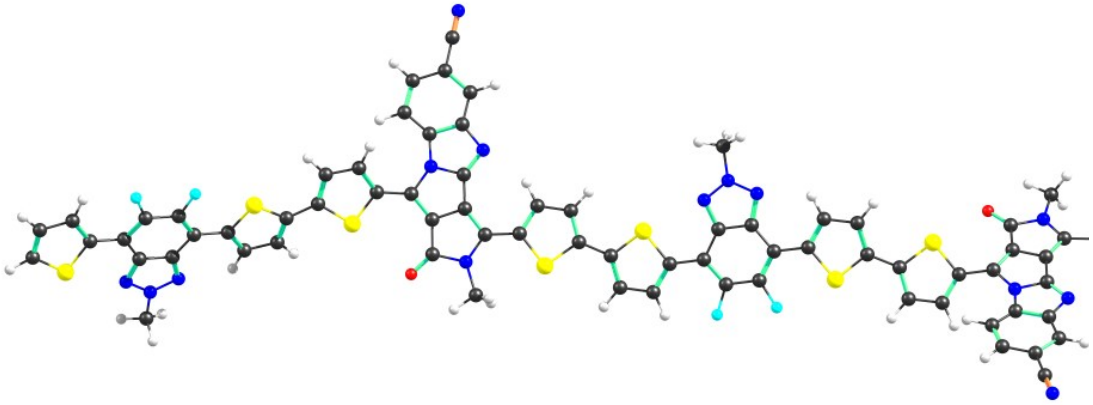
Figure S11: Optimized geometries of various conformations of P2 as determined at ωB97XD/6-31g(d,p) level of theory. Relative conformational energies (kcal/mol) are given in parenthesis.



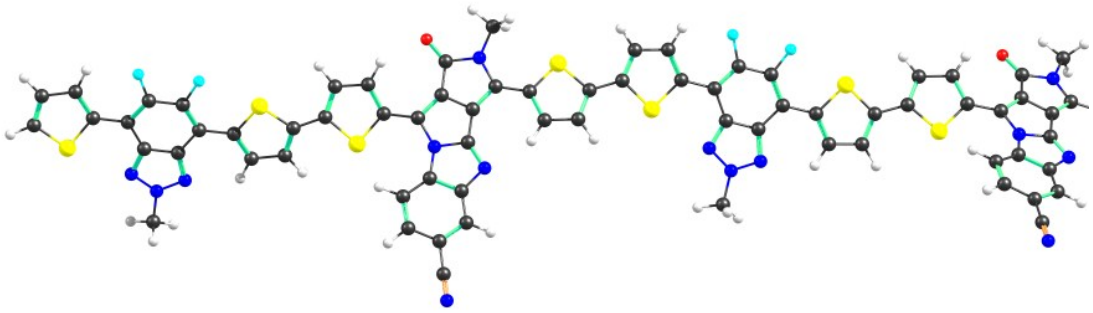
P3-*conf-1* (0.00 kcal/mol)



P3-*conf-2* (0.00 kcal/mol)



P3-*conf-3* (0.00 kcal/mol)



P3-*conf-4* (0.00 kcal/mol)

Figure S12: Optimized geometries of various conformations of P3 as determined at ωB97XD/6-31g(d,p) level of theory. Relative conformational energies (kcal/mol) are given in parenthesis.

8. CV of polymers.

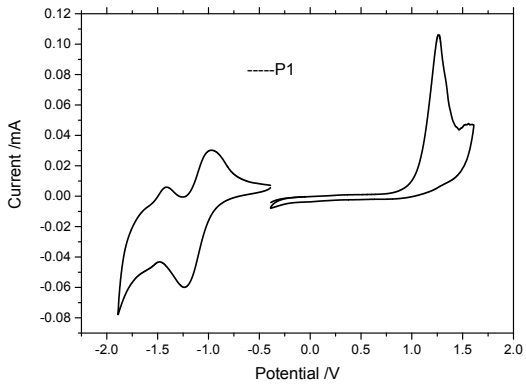


Figure S13: CV of **P1**.

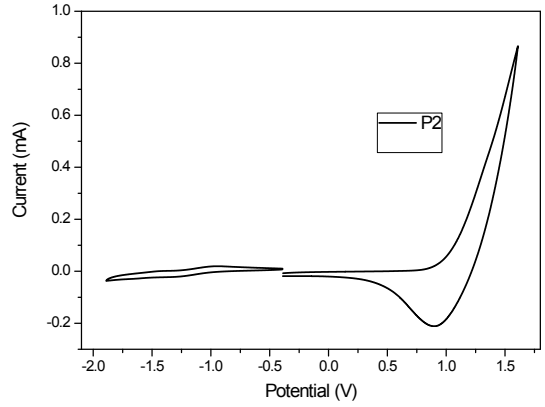


Figure S14: CV of **P2**.

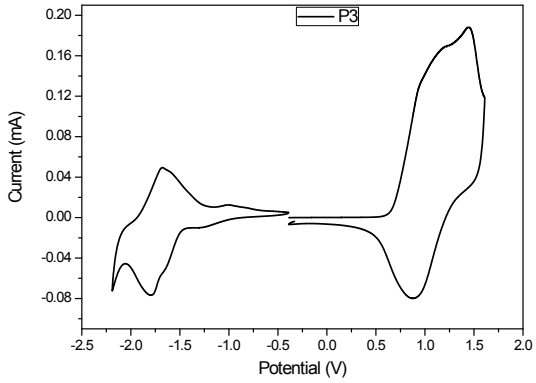
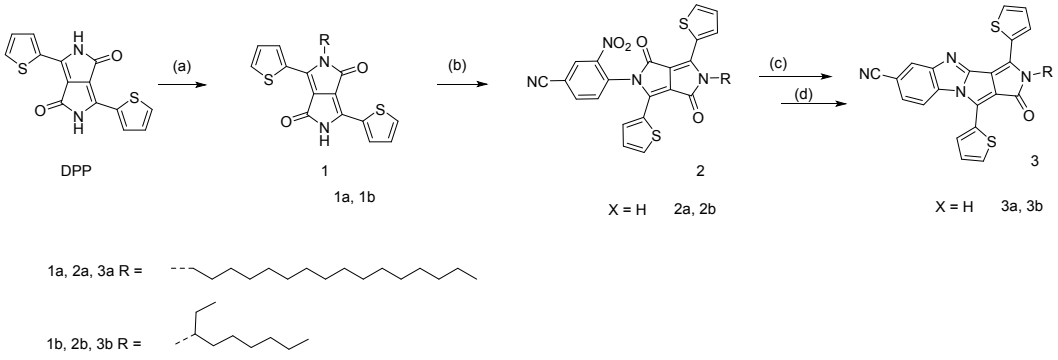


Figure S15: CV of **P3**.

9. Synthesis and characterization



Compound **1a**, **1b**, **1c** have been synthesized according to the literature. [S1]

Compound **1a**

3,6-di(thiophen-2-yl)-4,5-dihydropyrrolo[3,4-c]pyrrol-1(2H)-one (3.0 g, 9.99 mmol), potassium tert-butoxide (2.9 g, 25.84 mmol) was mixed in a N_2 atmosphere, DMF (50 ml) and 1-bromohexadecane (4.6 ml, 14.99 mmol) were added and reacted at room

temperature for 4 hours. DMF was removed under vacuum. The residue was purified by silica gel column chromatography to give 1.57 g (30 %) compound **1a.**
^{1}H NMR [CD_2Cl_2, 400MHz, 300K]: δ 8.74 (dd, J=3.6, 0.8Hz, 1H), 8.23 (dd, J = 4.0, 0.8 Hz, 1H), 7.95 (s, 1H), 7.63 (dd, J = 5.0, 1.1 Hz, 1H), 7.57 (dd, J = 5.2, 1.2 Hz, 1H), 7.23 (dd, J = 5.2, 4.0 Hz, 1H), 7.19 (dd, 4.8, 4.0Hz 1H), 3.9 (t, J=7.6 Hz, 2H), 2.16-2.04 (m, 2H), 1.98-1.89 (m, 2H), 1.64 (dd, J = 15.4, 7.9 Hz, 2H), 1.46 (s, 23H), 0.79 (t, J = 4.3 Hz, 3H). ^{13}C NMR [126 MHz, $CDCl_3$, 300K]: δ 161.99, 161.48, 140.79, 136.19, 135.75, 132.15, 131.20, 130.84, 129.86, 129.31, 128.82, 108.07, 42.40, 32.08, 30.10, 29.97, 29.85, 29.72, 29.68, 29.52, 29.39, 27.02, 22.77, 14.28.

Compound 1**b**
3,6-di(thiophen-2-yl)-4,5-dihydropyrrolo[3,4-c]pyrrol-1(2H)-one (3.0 g, 9.99 mmol), potassium tert-butoxide (2.9 g, 25.84 mmol) was mixed in a N_2 atmosphere. DMF (40 ml) and 2-Ethylhexyl bromide (2.67 ml, 14.99 mmol) were added and reacted at room temperature for 5 hours. DMF was removed under vacuum. The residue was purified by silica gel column chromatography to give 1.65 g (40 %) compound **1b.**
^{1}H NMR [CD_2Cl_2, 400 MHz, 300 K]: δ: 10.10 (s, 1H), 8.79 (d, J = 3.5 Hz, 1H), 8.24 (d, J = 3.5 Hz, 1H), 7.60 (d, J = 4.8 Hz, 1H), 7.54 (d, J = 4.8 Hz, 1H), 7.19 (t, J = 4.4 Hz, 1H), 7.13 (t, J=4.4 Hz, 1H), 3.98-3.83 (m, 2H), 1.97 (d, J = 19.3 Hz, 1H), 1.86-1.61 (m, 2H), 1.38-1.08 (m, 13H), 0.94-0.62 (m, 9H). ^{13}C NMR [101 MHz, CD_2Cl_2, 300K]: δ 163.05, 161.83, 141.34, 136.73, 135.81, 132.15, 131.53, 131.44, 130.36, 129.22, 128.60, 108.59, 46.09, 39.54, 30.57, 28.75, 23.87, 23.48, 14.21, 10.62.

Compound 2**a**
A mixture of 1**a** (1.00g, 1.91 mmol), 4-Fluoro-3-nitrobenzonitrile (0.63 g， 3.79 mmol) and K_2CO_3 (1.05 g, 7.60 mmol) in DMF (30 ml) was stirred at 80^{o}C for 6 h. After the reaction solution was cooled down to room temperature, K_2CO_3 was removed by filtration and the solvent was removed under vacuum. The residue was purified by column chromatography to afford 1.20 g **2a** (yield: 47 %). ^{1}H NMR [CD_2Cl_2, 400MHz, 300K]: δ 8.69 (dd, J = 3.9, 1.1 Hz, 1H), 8.39 (dd, J = 3.9, 1.1 Hz, 1H), 8.37 (d, J = 1.8 Hz, 1H), 7.93 (dd, J = 8.2, 1.9 Hz, 1H), 7.68 (dd, J = 5.0, 1.1 Hz, 1H), 7.55 (d, J = 8.2 Hz, 1H), 7.42 (dd, J = 5.0, 1.1 Hz, 1H), 7.21 (dd, J = 5.0, 4.0 Hz, 1H), 7.09 (dd, J = 5.0, 3.9 Hz, 1H), 4.02 (t, J= 8 Hz, 2H), 1.68 (dt, J = 15.5, 7.6 Hz, 2H), 1.39-1.32 (m, 2H), 1.24-1.14 (m, 24H), 0.79 (t, J = 6.8 Hz, 3H). ^{13}C NMR [101 MHz, CD_2Cl_2, 300 K]: δ 161.69, 159.87, 147.74, 143.07, 137.25, 136.62, 136.51, 134.90, 134.27, 133.62, 132.75, 131.70, 129.79, 129.67, 129.14, 128.90, 116.48, 114.63, 111.41, 105.88, 42.81, 32.34, 30.17, 30.11, 30.07, 29.99, 29.94, 29.77, 29.63, 27.23, 23.11, 14.29. HRMS (MALDI TOF, neg. mode, $CHCl_3$): m/z: calculated for $C_{37}H_{42}N_4O_4S_2$: 670.2624 [M], found: 670.2722.
CV (CH_2Cl_2, 0.1 M TBAHFP, *vs*. Fc/Fc^+): E^{1r} (X/X^-) = –1.13 V, E^{1o}(X/X^+) = 0.61 V.
UV-Vis ($CHCl_3$): max/nm (ε) = 544 (32230 M^{-1} cm^{-1})

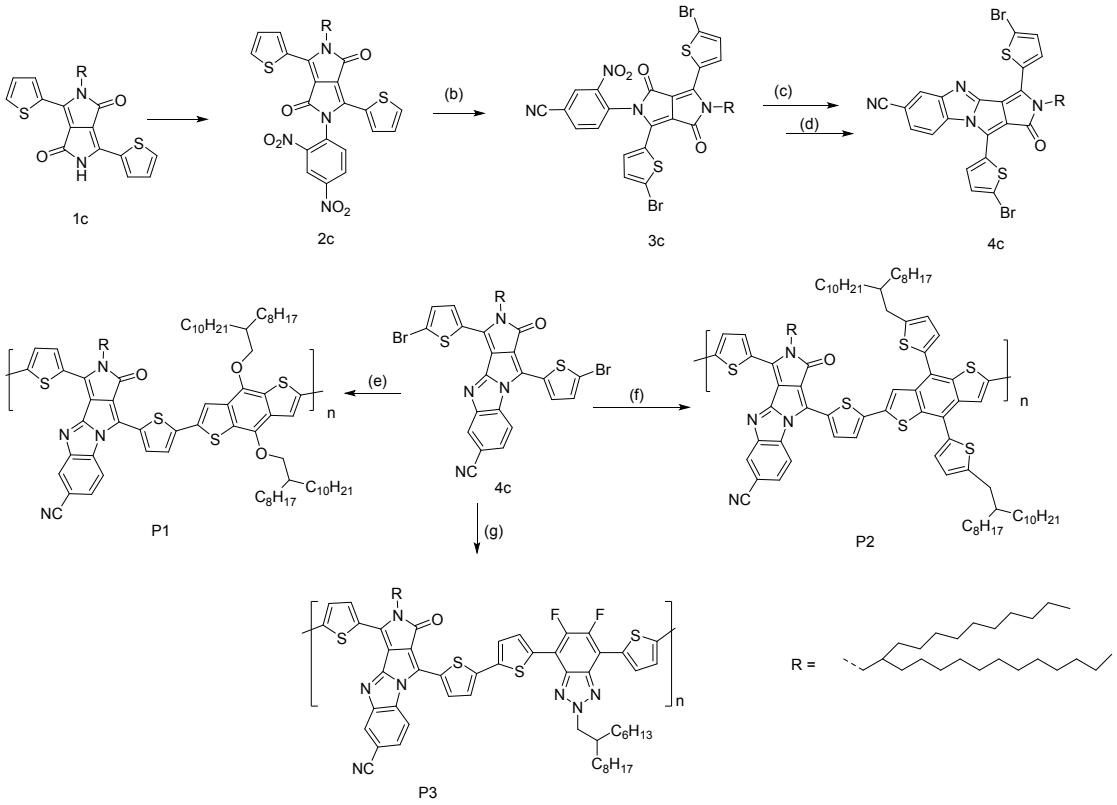
Compound 2**b**
A mixture of 1**b** (1.00 g, 2.50mmol), 4-fluoro-3-nitrobenzonitrile (0.83 g, 5 mmol) and

K_2CO_3(1.00 g, 7.24 mmol) in DMF (20 ml) was stirred at 80°C for 6 h. After the reaction solution was cooled down to room temperature, K_2CO_3 was removed by filtration and the solvent was removed under vacuum. The residue was purified by column chromatography to afford 1.40 g **2b** (yield: 50 %). ^{1}HNMR[CD_2Cl_2, 400MHz, 300K]: δ 8.68-8.61 (m, 1H）, 1H), 8.39 (d, J = 3.6 Hz, 1H), 8.36 (d, J = 1.6 Hz, 1H), 7.96-7.89 (m, 1H), 7.66 (d, J = 5.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 5.0 Hz, 1H), 7.18 (dd, J=9.2, 4.4 Hz, 1H), 7.07 (dd, J = 8.7, 4.0 Hz, 1H), 4.04-3.90 (m, 2H), 1.87-1.70 (m, 1H), 1.38-1.09 (m, 10H), 0.88-0.73 (m, 7H). ^{13}C NMR [101 MHz, CD_2Cl_2, 300K]: δ 159.84, 137.23, 136.42, 134.99, 134.24, 133.56, 132.62, 131.74, 129.76, 129.68, 128.91, 128.88, 116.47, 114.59, 54.38, 54.11, 53.84, 53.57, 53.30, 46.31, 39.43, 30.57, 30.48, 28.73, 28.67, 23.83, 23.45, 14.19, 10.55, 1.16.
HRMS (MALDI TOF, neg. mode, $CHCl_3$): m/z: calculated for $C_{29}H_{26}N_4O_4S_2$: 558.1395 [M] , found: 558.1467.
CV (CH_2Cl_2, 0.1 M TBAHFP, *vs*. Fc/Fc^+): E^{1r} (X/X^-) = –1.16 V, E^{1o}(X/X^+) = 0.59 V.
UV-Vis ($CHCl_3$): max/nm (ε) = 542 (30853 M^{-1} cm^{-1})

Compound **3a**
A mixture of compound **2a** (0.50 g, 0.75 mmol), and $SnCl_2$•$2H_2O$ (1.68 g, 7.45 mmol) in ethyl acetate (20 mL) was heated at 78°C for 1 h under argon. After the mixture was cooled down to room temperature, the pH is made slightly basic (pH 7-8) by addition of 10 % aqueous sodium bicarbonate before extracting with ethyl acetate. The organic phase was collected and dried over magnesium sulfate, the solvent was removed under vacuum to get the crude product, which was washed with methanol (20 mL) and dried under vacuum to get the desired intermediate product, which was used for the next step without further purification. The crude intermediate product from previous step (0.48 g) and DABCO (1.25 g, 11.14 mmol) were dissolved in anhydrous methylbenzene (20 mL) while heating to 120°C for 10 min. Titanium tetrachloride (1.23 mL, 11.19 mmol) was added quickly to the reaction mixture and the solution was kept at 120 °C for 10 h. The hot reaction was dropped quickly in to 50 mL water, extracted with a small amount of ethyl acetate, and the organic phase was passed through a neutral aluminum oxide column using dichloromethane as eluent. The solvent was removed under vacuum and the residue was washed with 2 mL methanol to obtain the pure compound 3**a** as a violet solid. The total yield of the two steps from compound 2**a** to 3**a** is 25 %（117 mg）. ^{1}H NMR [$CDCl_3$, 400 MHz, 300 K]: δ 8.91 (d, *J* = 3.2 Hz, 1H), 8.15 (d, *J* = 3.2 Hz, 1H), 8.00-7.96(m, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.70 (d, *J* = 4.7 Hz, 1H), 7.65 (d, *J* = 4.8 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.36 (d, *J* = 9.2 Hz, 1H), 7.25 (t, *J* = 4.0 Hz, 1H), 3.95 (t, *J* = 7.6 Hz, 2H), 1.76-1.62 (m, 2H), 1.42-1.1 (m, 26H), 0.80 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR [101 MHz, $CDCl_3$, 300 K] δ (ppm): 163.09, 136.99, 133.18, 131.05, 129.66, 128.73, 126.08, 124.64, 119.58, 119.17, 112.82, 107.00, 103.77, 42.44, 32.07, 30.09, 29.84, 29.81, 29.78, 29.70, 29.65, 29.51, 29.36, 26.97, 22.84, 14.27, 1.17. HRMS (MALDI TOF, neg. mode, $CHCl_3$): m/z: calculated for $C_{37}H_{42}N_4OS_2$ 622.2800 [M] found: 622.2871.
CV (CH_2Cl_2, 0.1 M TBAHFP, *vs*. Fc/Fc^+): E^{1r} (X/X^-) = –1.21 V, E^{1o}(X/X^+) = 0.26 V.
UV-vis ($CHCl_3$): max/nm (ε) = 563/607 (28255/18020M^{-1} cm^{-1})

Compound **3b**

A mixture of compound **2b** (0.50 g, 0.92 mmol), and $SnCl_2 \bullet 2H_2O$ (2.07 g, 9.17 mmol) in ethyl acetate (15 mL) was heated at 78°C for 1 h under argon. After the solution was cooled down to room temperature, the pH is made slightly basic (pH 7-8) by addition of 10 % aqueous sodium bicarbonate before extracting with ethyl acetate. The organic phase was collected and dried over magnesium sulfate, and the solvent was removed under reduced pressure to get the crude product, which was washed with methanol (20 mL) and dried under vacuum to get the desired intermediate product, which was used for the next step without further purification. The crude intermediate product from previous step (0.49 mg) and DABCO (1.54 mg, 13.73 mmol) were dissolved in anhydrous methylbenzene (18 mL) while heating to 120°C for 10 min. Titanium tetrachloride (1.51 mL, 13.74 mmol) was added quickly to the reaction mixture and the solution was kept at 120 °C for 10 h. The hot reaction was dropped quickly in to 50 mL water, extracted with a small amount of ethyl acetate, and the organic phase was passed through a neutral aluminum oxide column using dichloromethane as eluent. The solvent was removed under vacuum and the residue was washed with 2 mL methanol to obtain the pure compound 3b as a violet solid. The total yield of the two steps from compound 2**b** to 3**b** is 36 % (169 mg). ^{1}H NMR [$CDCl_3$, 400 MHz, 300 K]: δ 8.89 (d, J = 3.7 Hz, 1H), 8.16(d, J = 3.6 Hz, 1H), 7.99 (s, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.70 (d, J = 4.9 Hz, 1H), 7.65 (d, J = 4.9 Hz, 1H), 7.42-7.38 (m, 1H), 7.37 (d, J = 4.3 Hz, 1H), 7.26 (t, J=4.4 Hz, 1H), 4.00-3.83 (m, 2H), 1.89-1.73 (m, 1H), 1.38-1.19(m, 9H), 0.90-0.72 (m, 6H). ^{13}C NMR [101 MHz, $CDCl_3$, 300 K]: δ 163.45, 136.97, 133.24, 132.95, 132.51, 131.05, 129.84, 129.50, 128.74, 126.13, 124.64, 119.57, 119.02, 112.85, 107.04, 60.53, 46.14, 39.30, 30.36, 28.46, 23.70, 23.20, 14.17, 10.62. HRMS (MALDI TOF, neg. mode, $CHCl_3$): m/z: calculated for $C_{29}H_{26}N_4OS_2$: 510.1548, [M], found: 510.1620.
CV (CH_2Cl_2, 0.1 M TBAHFP, *vs*. Fc/Fc^+): E^{1r} (X/X^-) = –1.22 V, E^{1o}(X/X^+) = 0.24 V.
UV-Vis ($CHCl_3$): max/nm (ε) = 562/604 (28540/17818M^{-1} cm^{-1})



Compound **1c**

3,6-di(thiophen-2-yl)-4,5-dihydropyrrolo[3,4-c]pyrrol-1(2H)-one (3.00 g, 9.99 mmol), potassium carbonate (1.38 g, 9.99 mmol) was mixed in a N_2 atmosphere. DMF (40 ml) and 11-(bromomethyl)tricosane (4.17 g, 9.99 mmol) were added and reacted at room temperature for 15 min hours. DMF was removed under vacuum. The residue was purified by silica gel column chromatography to give 2.55 g (yield: 40%) compound **1c.**

^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 9.53 (s, 1H), 8.86 (d, *J* = 3.8 Hz, 1H), 7.74 (d, *J* = 5.0 Hz, 1H), 7.69 (d, *J* = 4.9 Hz, 1H), 7.34 (dd, J=4.0 Hz, 1H), 7.24 (dd, J=, 1H), 4.05 (d, *J* = 7.7 Hz, 2H), 1.99-1.85 (m, 1H), 1.47-1.02 (m, 42H).[1] ^{13}C NMR [101 MHz, CD_2Cl_2, 300K]: δ 162.64, 161.40, 140.86, 136.36, 135.25, 131.74, 131.14, 130.91, 129.97, 128.78, 128.15, 108.65, 108.20, 46.10, 37.75, 31.91, 31.16, 29.95, 29.68, 29.67, 29.65, 29.63, 29.52, 29.35, 29.34, 26.18, 22.67, 13.86. HRMS (MALDI TOF, neg. mode, $CHCl_3$): m/z: calculated $C_{38}H_{56}N_2O_2S_2$: 636.3783 $[M]^-$, found: 635.37154.

Compound **2c**

A mixture of **1c** (1.59 g, 2.50mmol), 4-fluoro-3-nitrobenzonitrile (0.83 g, 5 mmol) and K_2CO_3(1.00 g, 7.24 mmol) in DMF (20 ml) was stirred at 80°C for 6 h. After the reaction solution was cooled down to room temperature, K_2CO_3 was removed by filtration and the solvent was removed under reduced pressure. The residue was purified by column chromatography to afford 1.04 g 2**c** (yield: 53 %). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ 8.48 (d, *J* = 0.6 Hz, 1H), 8.43 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.89

(d, *J* = 1.5 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.55 (d, *J* = 4.8 Hz, 1H), 7.21 (dd, J=, 1H), 7.13 (dd, J=, 1H), 4.65 (d, *J* = 0.7 Hz, 2H), 1.93-1.85 (m, 1H), 1.52 – 1.16 (m, 54H). ^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ 158.90, 136.46, 134.91, 133.71, 133.25, 132.74, 132.68, 132.19, 129.36, 129.30, 129.23, 128.43, 115.97, 114.01, 113.94, 113.36, 37.85, 31.92, 31.50, 31.48, 30.01, 29.69, 29.66, 29.64, 29.35, 26.89, 22.69, 14.11.
HRMS (MALDI TOF, neg. mode, $CHCl_3$): m/z: calculated for $C_{45}H_{58}N_4O_4S_2$: 783.3933, [M] found: 783.3992.

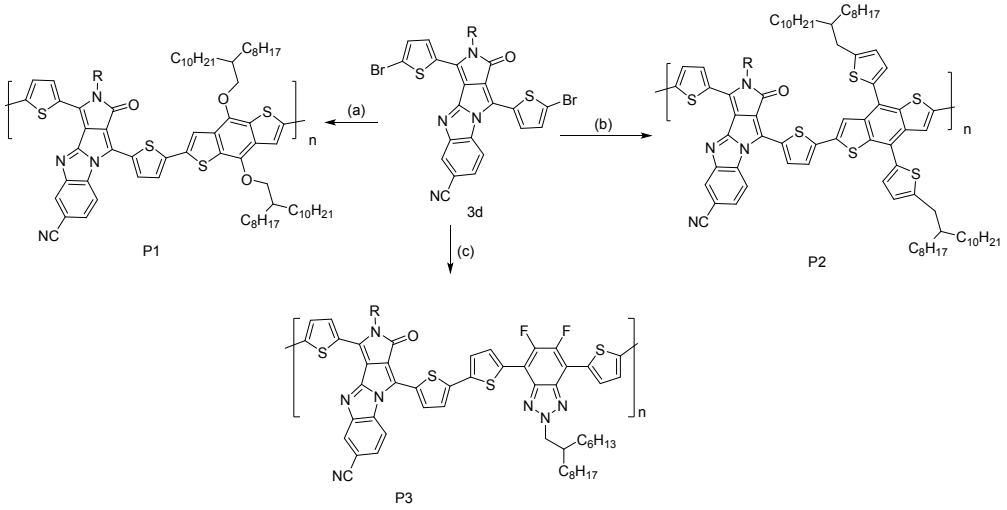
Compound **3c**

A mixture of **2c** (0.78 g, 1.00mmol) was taken in $CHCl_3$, N-bromosuccinimide (2.01mmol) was added slowly portion wise for over 10 minutes at 0℃. The reaction mixture was stirred at the same temperature for 1 hour and kept at room temperature for 48 hours. Completion of the reaction was confirmed by TLC. Water was added, extracted with CH_2Cl_2 (3 x 50 ml), washed with brine. The combined organic layers were collected and dried over anhydrous $MgSO_4$ and the solvent was removed under vacuum. The reside was purified by column chromatography to afford 3**c** (yield: 70 %, 0.66 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 4.0 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.21 (d, *J* = 4.0 Hz, 1H), 7.12 (d, *J* = 4.1 Hz, 1H), 3.97 (t, *J* = 6.4 Hz, 2H), 1.97-1.84 (m, 1H), 1.27 (m, *J* = 26.4 Hz, 52H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.46, 159.31, 147.40, 141.88, 136.78, 136.45, 135.59, 135.16, 133.87, 132.84, 131.73, 130.47, 130.42, 129.52, 120.84, 120.02, 115.83, 114.81, 110.80, 105.92, 46.65, 37.79, 31.93, 31.12, 29.99, 29.70, 29.65, 29.58, 29.36, 26.16, 26.13, 22.70, 14.13. HRMS (MALDI TOF, neg. mode, $CHCl_3$): m/z: calculated for $C_{45}H_{56}Br_2N_4O_4S_2$: 938.2110, $[M]^+$, found: 939.2209.

Compound **4c**

A mixture of compound **3c** (0.50 g, 0.57 mmol), and $SnCl_2$•$2H_2O$ (1.29 g, 5.7 mmol) in ethyl acetate (10 mL) was heated at 78^{o}C for 1 h under argon. After the solution was cooled down to room temperature, the pH is made slightly basic (pH 7-8) by addition of 10 % aqueous sodium bicarbonate before extracting with ethyl acetate. The organic phase was collected and dried over magnesium sulfate, and the solvent was removed under reduced pressure to get the crude product, which was washed with methanol (10 mL) and dried under vacuum to get the desired intermediate product, which was used for the next step without further purification. The crude intermediate product from previous step (0.49 g) and DABCO (0.96 g, 8.55 mmol) were dissolved in anhydrous methylbenzene (10 mL) while heating to 120^{o}C for 10 min. Titanium tetrachloride (0.94 mL, 8.55 mmol) was added quickly to the reaction mixture and the solution was kept at 120 ^{o}C for 10 h. The hot reaction was dropped quickly in to 50 mL water, extracted with a small amount of ethyl acetate, and the organic phase was passed through a neutral aluminum oxide column using dichloromethane as eluent. The solvent was removed under vacuum and the residue was washed with 2 mL methanol to obtain the pure compound **3d** as a violet solid. The total yield of the two steps from compound **3c** to **4c** is 35 % (147 mg). ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K) δ 8.62 (d, *J* = 4.1 Hz, 1H), 7.89

(d, *J* = 4.0 Hz, 1H), 7.86 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.27 (d, *J* = 4.0 Hz, 1H), 7.20 (d, *J* = 4.0 Hz, 1H), 3.71 (d, *J* = 7.8 Hz, 2H), 1.77 (m, 1H), 1.28 – 1.02 (m, 49H). ^{13}C NMR (101 MHz, CD_2Cl_2, 300 K): δ 162.65, 140.94, 136.81, 133.22, 132.66, 132.10, 131.61, 131.15, 130.05, 129.73, 126.03, 124.40, 120.73, 112.55, 106.94, 103.86, 46.27, 37.79, 31.92, 31.90, 31.09, 26.10, 22.66, 13.86. HRMS (MALDI TOF, neg. mode, $CHCl_3$): m/z: calculated for $C_{45}H_{56}Br_2N_4OS_2$: 892.2242, [M], found: 892.2255.



Synthesis of **P1**

To a microwave vial was added **3d** (50.00 mg, 0.056 mmol, 1 equiv.) and 4,8-bis(nonadecan-9-yloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (62.10 mg, 0.056 mmol, 1 equiv), $Pd_2(dba)_3$ (1.00 mg) and P(o-tol)$_3$ (2.00 mg). The tube was sealed and flushed with Argon, and then degassed toluene (0.5 mL) was added. The mixture was thoroughly degassed under argon, and then the argon inlet was removed. The tube was stirred at 80 ℃ for 48 h. After cooling to RT, the polymer was precipitated into methanol, and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, hexane, dichloromethane, chloroform. The chloroform solution was concentrated and precipitated into methanol. The precipitates were filtered and dried under vacuum to afford **P1** as a dark blue solid (55 mg，65 %)，Mn = 52.0 kDa，Mw = 274.5 kDa，PDI = 5.28. ^{1}H NMR (1,1,2,2-tetrachloroethane-d_2, 373K, 400 MHz), δ (ppm)：9.42-7.92 (broad), 7.92-6.9 (broad), 4.70-3.40 (broad), 2.2-0.52 (broad).

Synthesis of **P2**

To a microwave vial was added **3d** (50.00 mg, 0.056 mmol, 1 equiv.) and (4,8-bis(5-(nonadecan-9-yl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis (trimethyl--stannane) (61.51 mg, 0.056mmol, 1 equiv), $Pd_2(dba)_3$ (1.00 mg) and P(o-tol)$_3$ (2.00 mg). The tube was sealed and flushed with Argon, and then degassed toluene (0.5 mL)

was added. The mixture was thoroughly degassed under Argon, and then the argon inlet was removed. The tube was stirred at 80 °C for 48 h. After cooling to RT, the polymer was precipitated into methanol, and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, hexane, dichloromethane, chloroform. The chloroform solution was concentrated and precipitated into methanol. The precipitates were filtered and dried under vacuum to afford **P2** as a dark blue solid (57 mg，62 %)，Mn =29.2 kDa，Mw = 115.4 kDa，PDI = 3.95. ^{1}H NMR (1,1,2,2-tetrachloroethane-d_2, 373K, 400 MHz), δ (ppm)：9.07 (broad), 8.07 (broad), 7.88-6.42 (broad), 3.35-2.75 (broad), 2.16-0.16 (broad).

Synthesis of **P3**

To a microwave vial was added **3d** (50.00 mg, 0.056 mmol, 1 equiv.) and 2-(2-hexyldecyl)-4,7-bis(5-(trimethylstannyl)thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (48.69 mg, 0.056 mmol, 1 equiv), $Pd_2(dba)_3$ (1.50 mg) and P(o-Tol)$_3$ (1.84 mg). The tube was sealed and flushed with Argon, and then degassed methylbenzene (1 mL) was added. The mixture was thoroughly degassed under Argon, and then the argon inlet was removed. The tube was stirred at 80 ℃ for 2 h. After cooling to RT, the polymer was precipitated into methanol, and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, hexane, dichloromethane, chloroform and chlorobenzene. The chlorobenzene solution was concentrated and precipitated into methanol. The precipitates were filtered and dried under vacuum to afford **P3** as a dark blue solid (29 mg，40 %)，Mn =25.69 kDa，Mw = 107.05 kDa，PDI= 4.17. ^{1}H NMR (1,1,2,2-tetrachloroethane-d_2, 373K, 400 MHz), ^{1}H NMR (1,1,2,2-tetrachloroethane-d_2, 393K, 400 MHz), δ (ppm)：7.95 (broad), 7.46 (broad), 4.71 (broad), 3.83 (broad), 2.71-0.49 (broad).

10. ^{1}H NMR and ^{13}C NMR spectra.

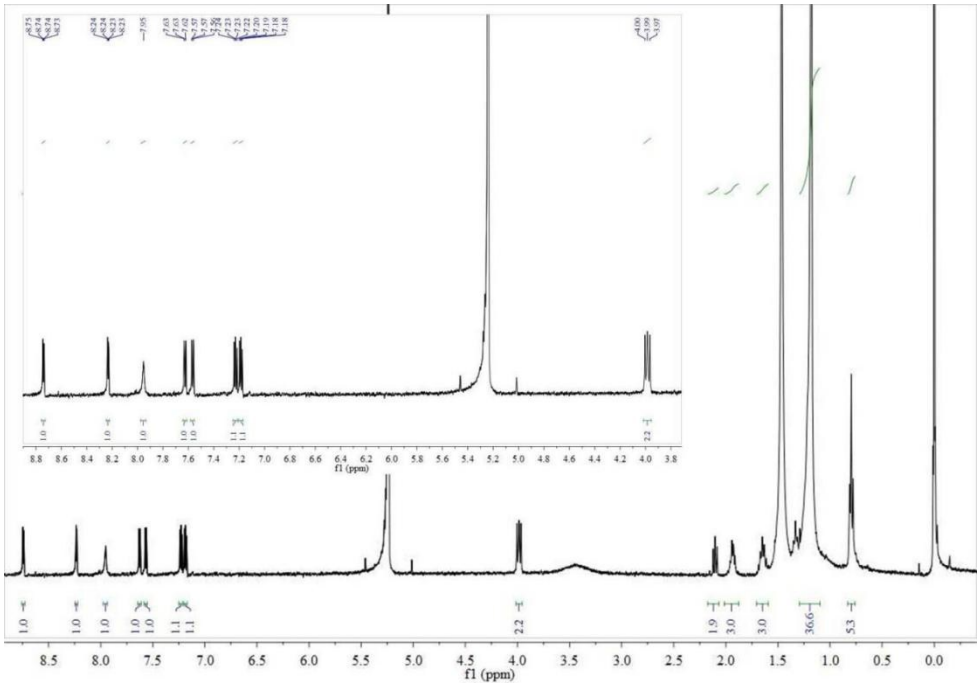


Figure S16：^{1}H NMR spectrum of compound **1a** (CD_2Cl_2, 400 MHz, 300 K)

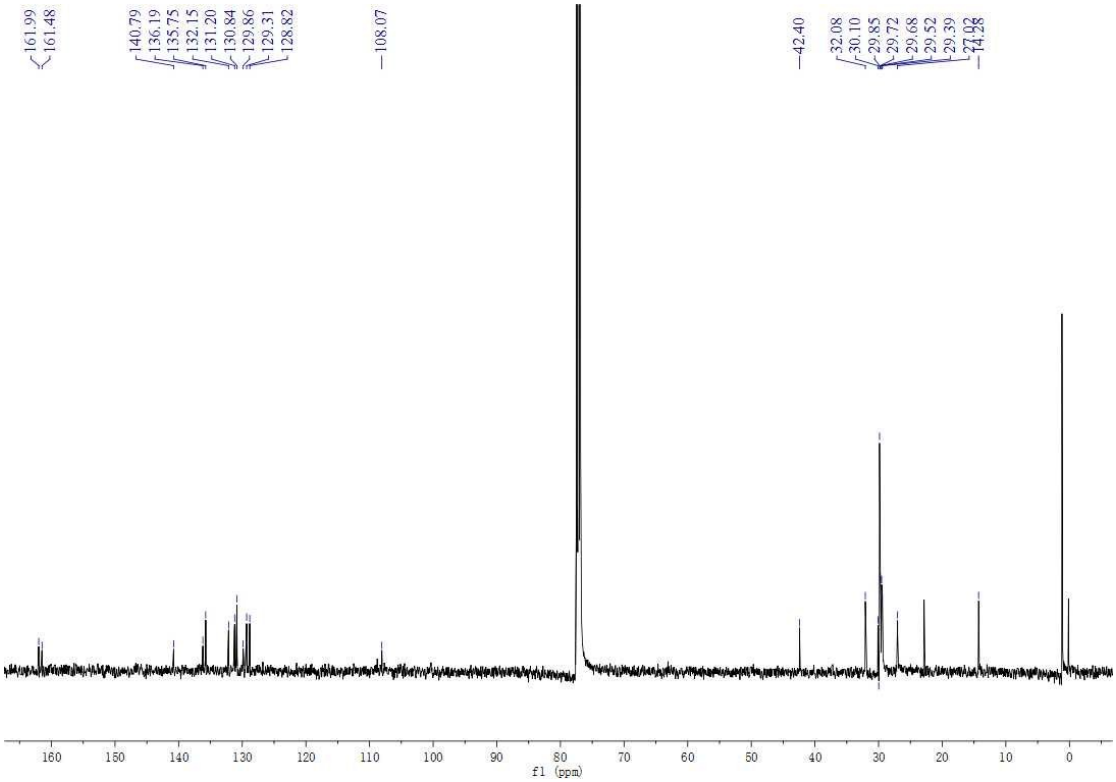


Figure S17: ^{13}C NMR spectrum of compound **1a** (100 MHz, $CDCl_3$, 300K)

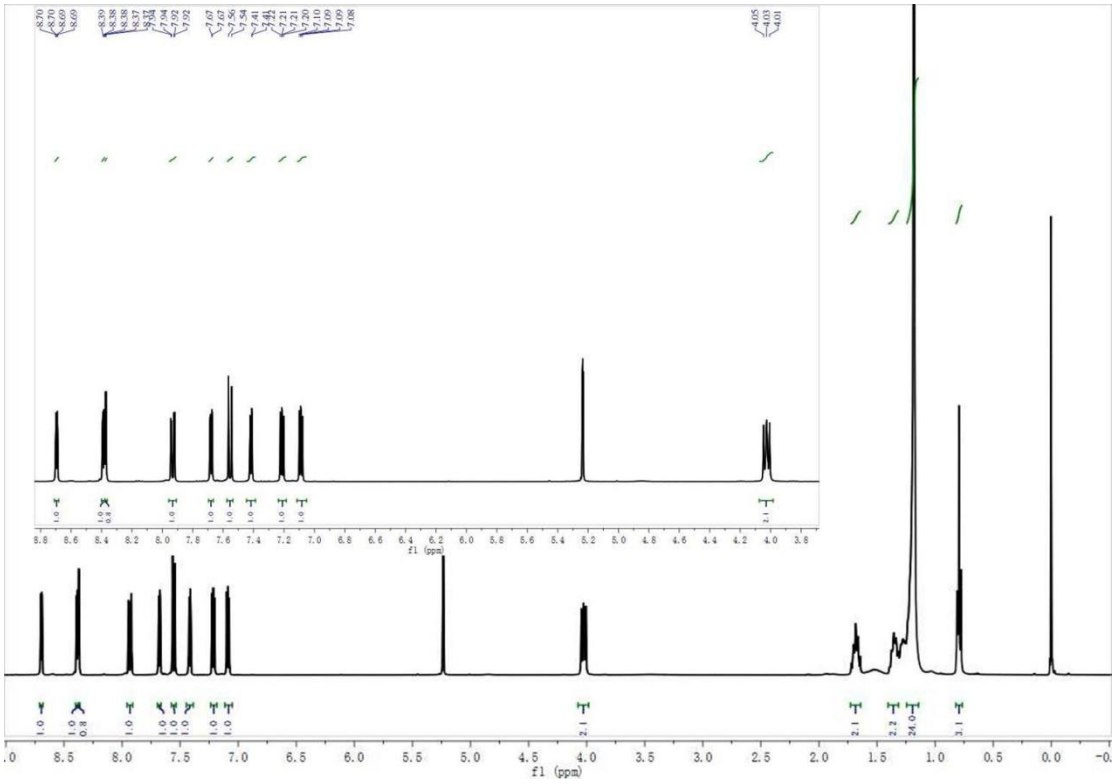


Figure S18：^{1}H NMR spectrum of compound 1**b** (CD_2Cl_2, 400 MHz, 300 K)

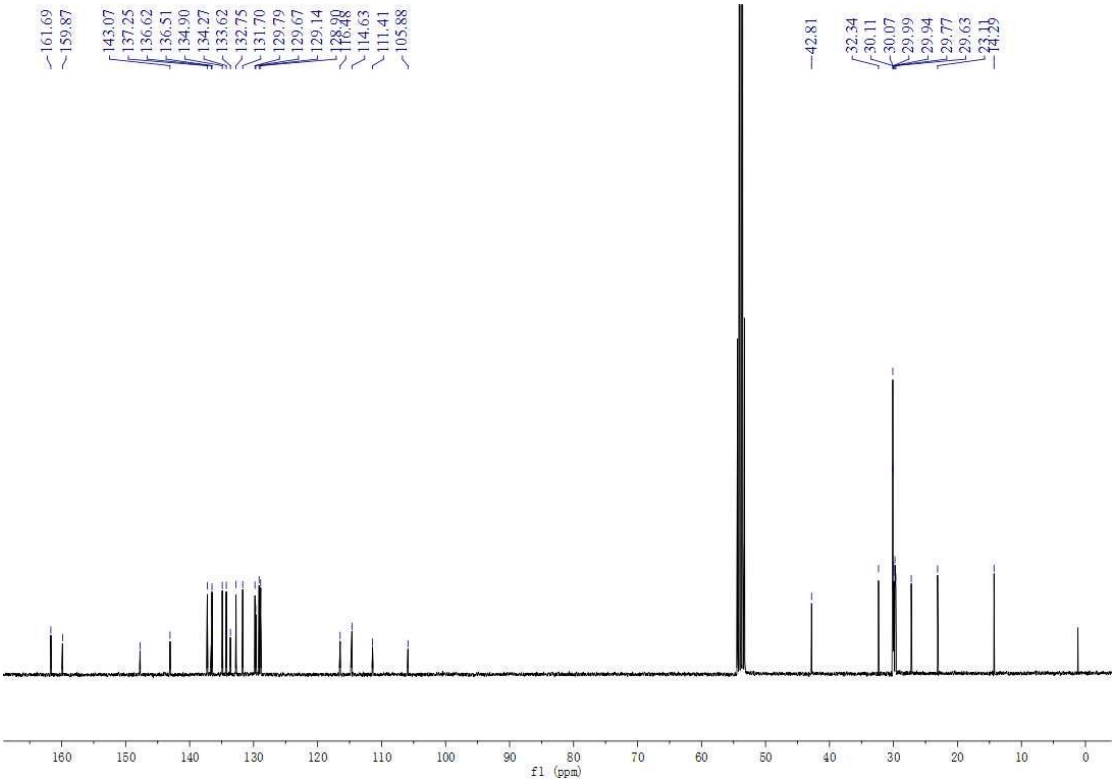


Figure S19: ^{13}C NMR spectrum of compound 1**b** (100 MHz, CD_2Cl_2, 300 K)

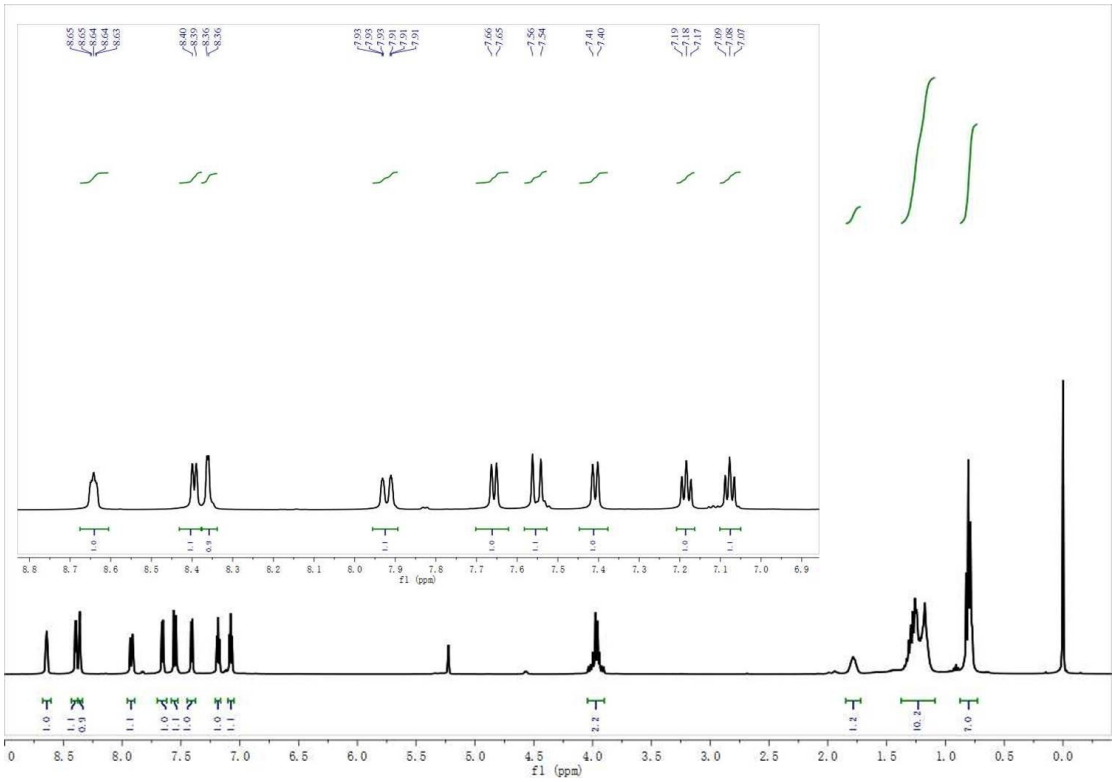


Figure S20：^{1}H NMR spectrum of compound **2a** (CD_2Cl_2, 400 MHz, 300 K)

Figure S21: ^{13}C NMR spectrum of compound **2a** (101 MHz, CD_2Cl_2, 300 K)

Figure S22：^{1}H NMR spectrum of compound **2b** (CD_2Cl_2, 400 MHz, 300 K)

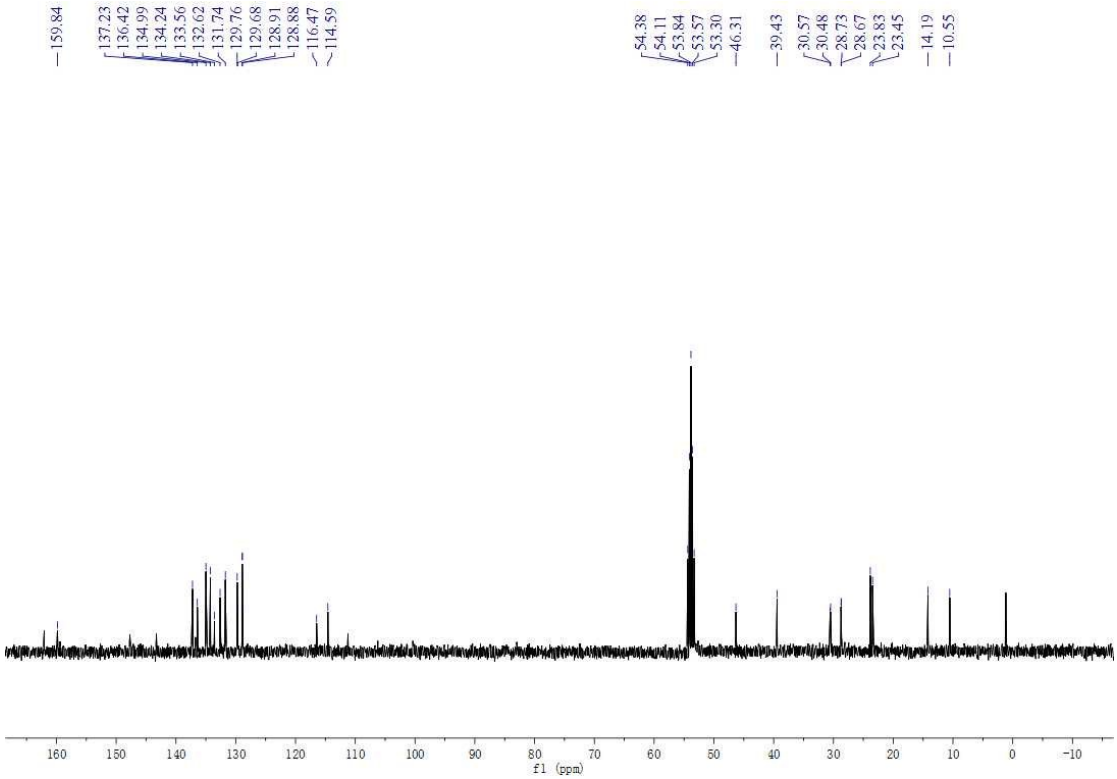


Figure S23: ^{13}C NMR spectrum of compound **2b** (100 MHz, CD_2Cl_2, 300 K)

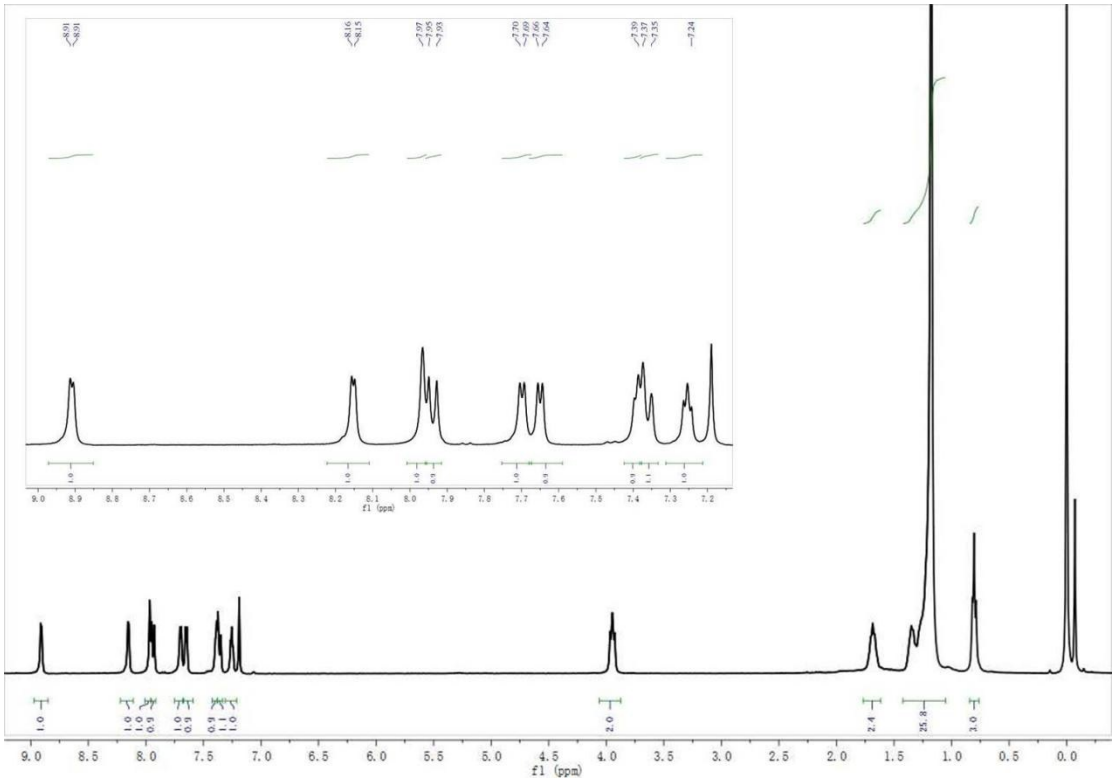


Figure S24：^{1}H NMR spectrum of compound **3a** ($CDCl_3$, 400 MHz, 300 K)

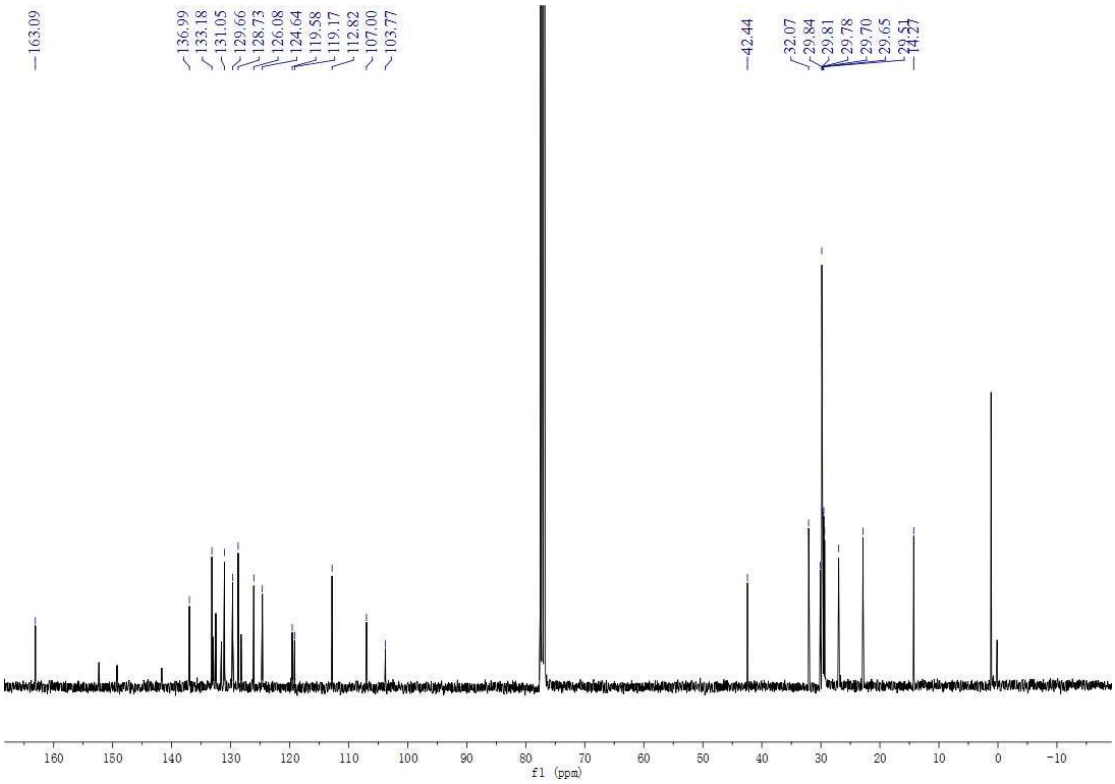


Figure S25: ^{13}C NMR spectrum of compound **3a** (101 MHz, $CDCl_3$, 300 K)

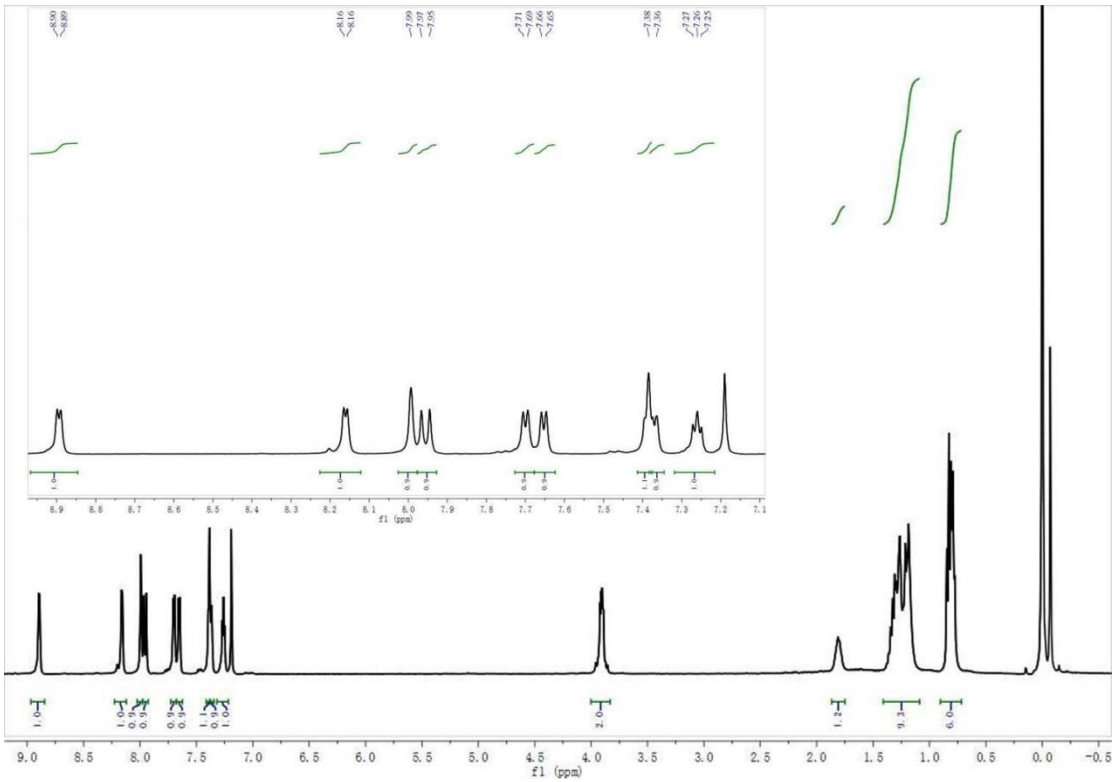


Figure S26：^{1}H NMR spectrum of compound **3b** ($CDCl_3$, 400 MHz, 300 K)

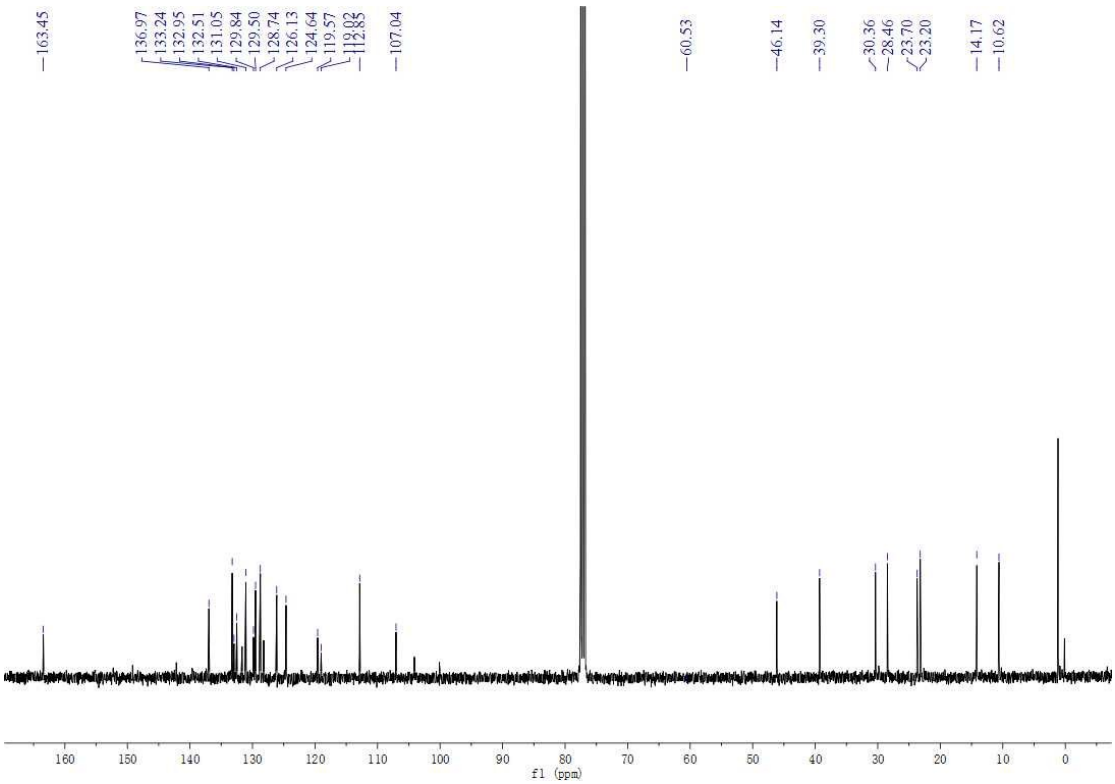


Figure S27: ^{13}C NMR spectrum of compound **3b** (100 MHz, $CDCl_3$, 300 K)

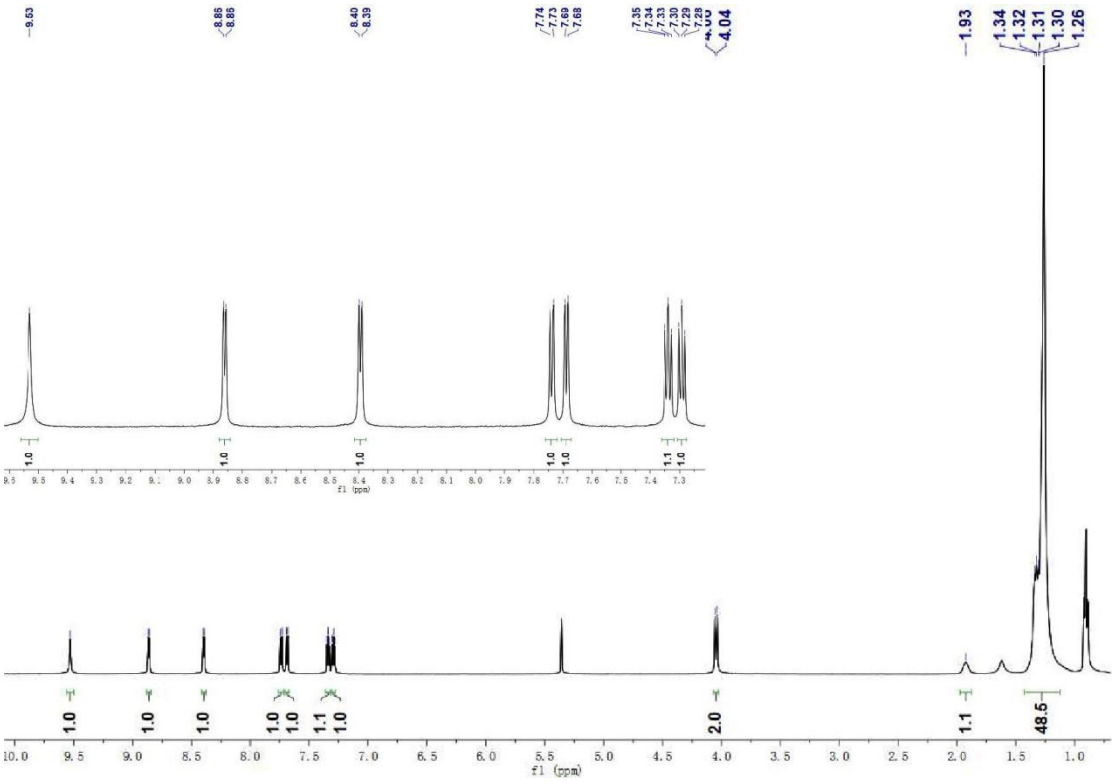


Figure S28：^{1}H NMR spectrum of compound **1c** (CD_2Cl_2, 400 MHz, 300 K)

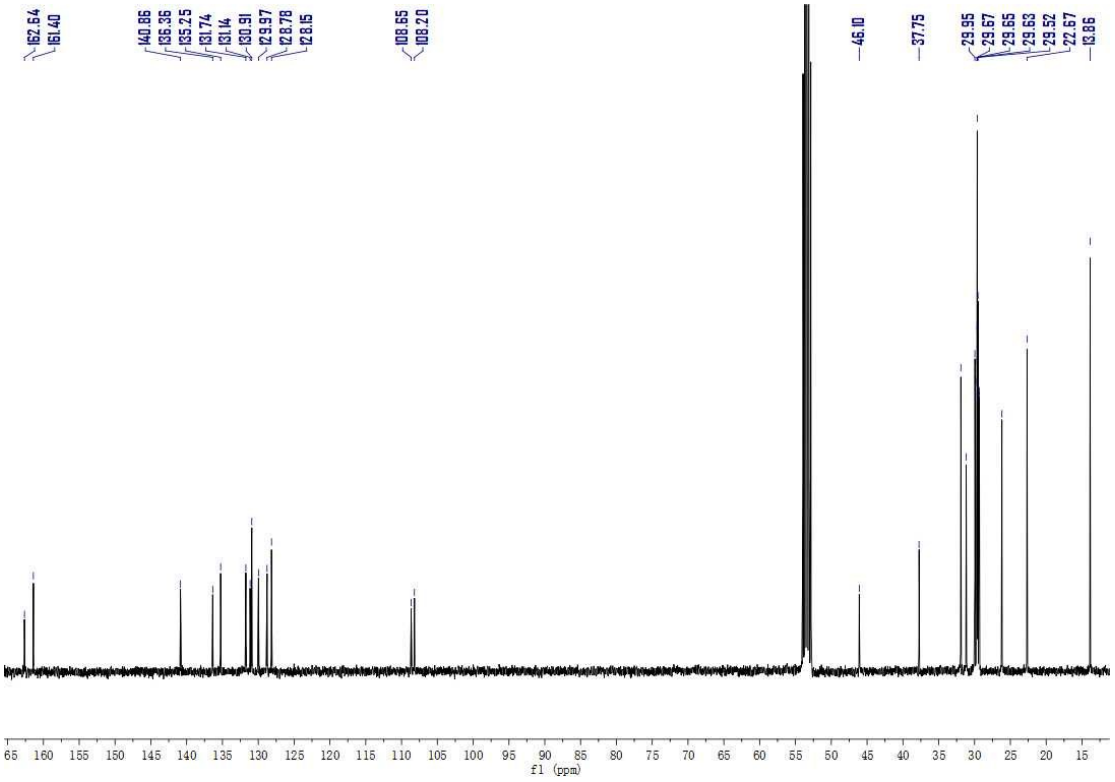


Figure S29: ^{13}C NMR spectrum of compound **1c** (101 MHz, CD_2Cl_2, 300 K)

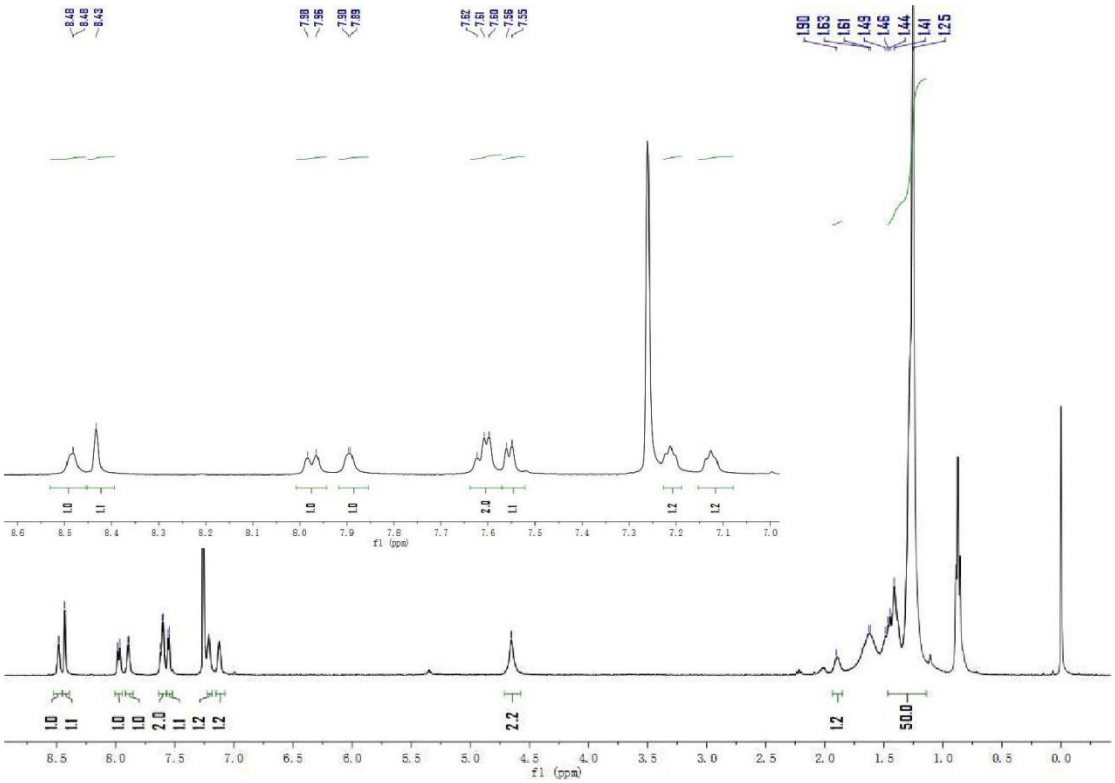


Figure S30：^{1}H NMR spectrum of compound **2c** ($CDCl_3$, 400 MHz, 300 K)

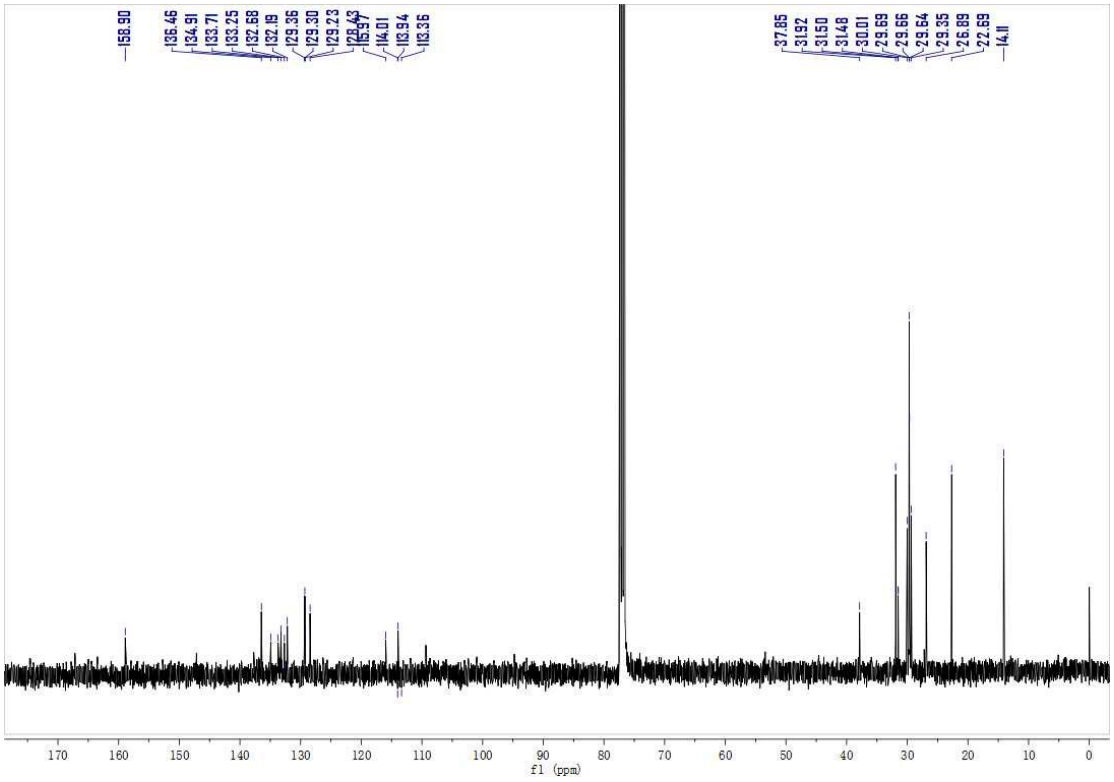


Figure S31: ^{13}C NMR spectrum of compound **2c** (100 MHz, $CDCl_3$, 300 K)

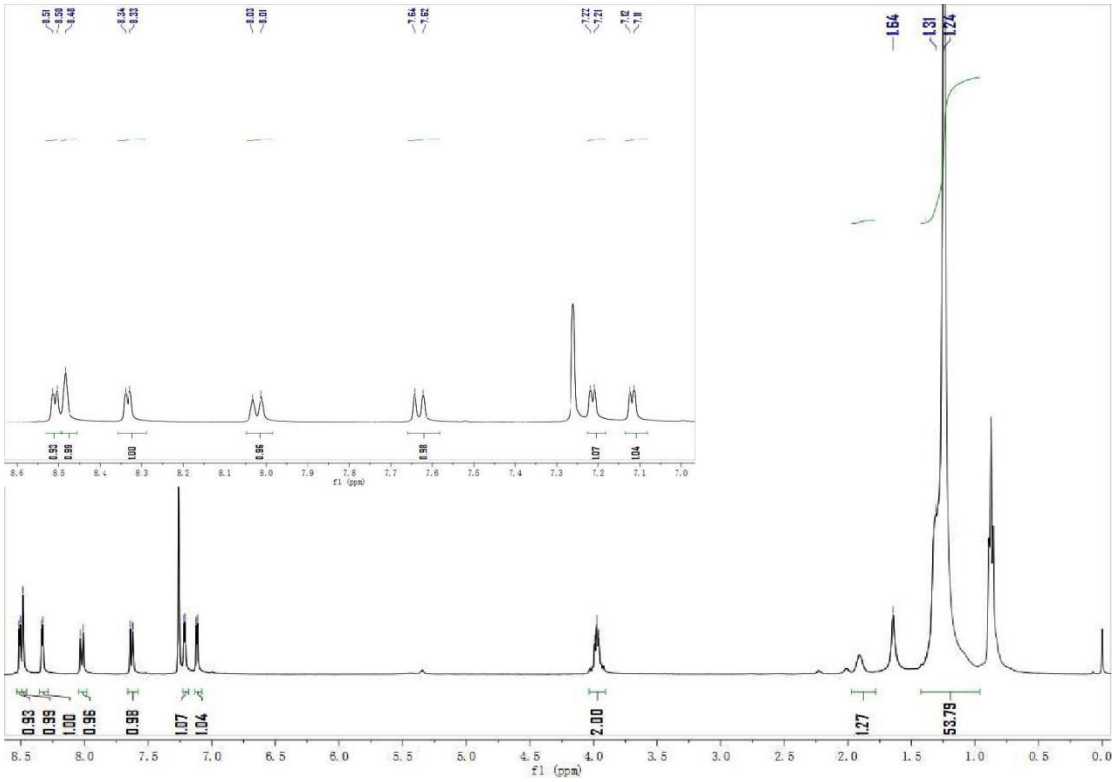


Figure S32：^{1}H NMR spectrum of compound **3c** ($CDCl_3$, 400 MHz, 300 K)

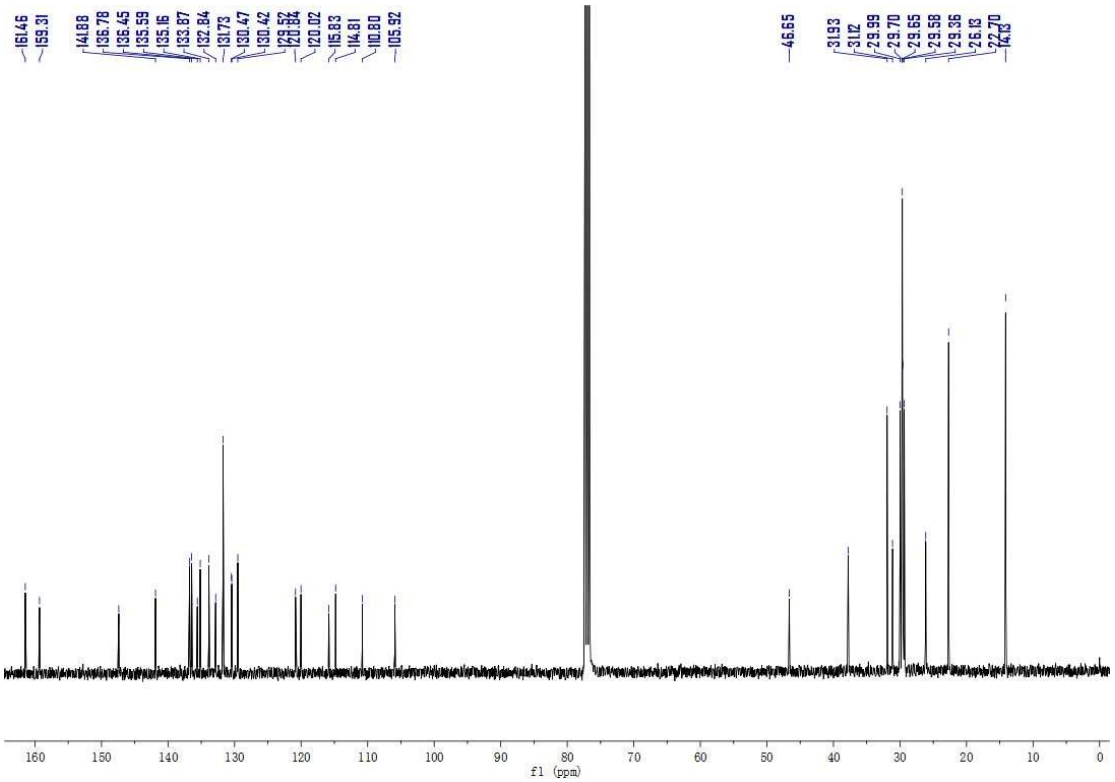


Figure S33: ^{13}C NMR spectrum of compound **3c** (101 MHz, $CDCl_3$, 300 K)

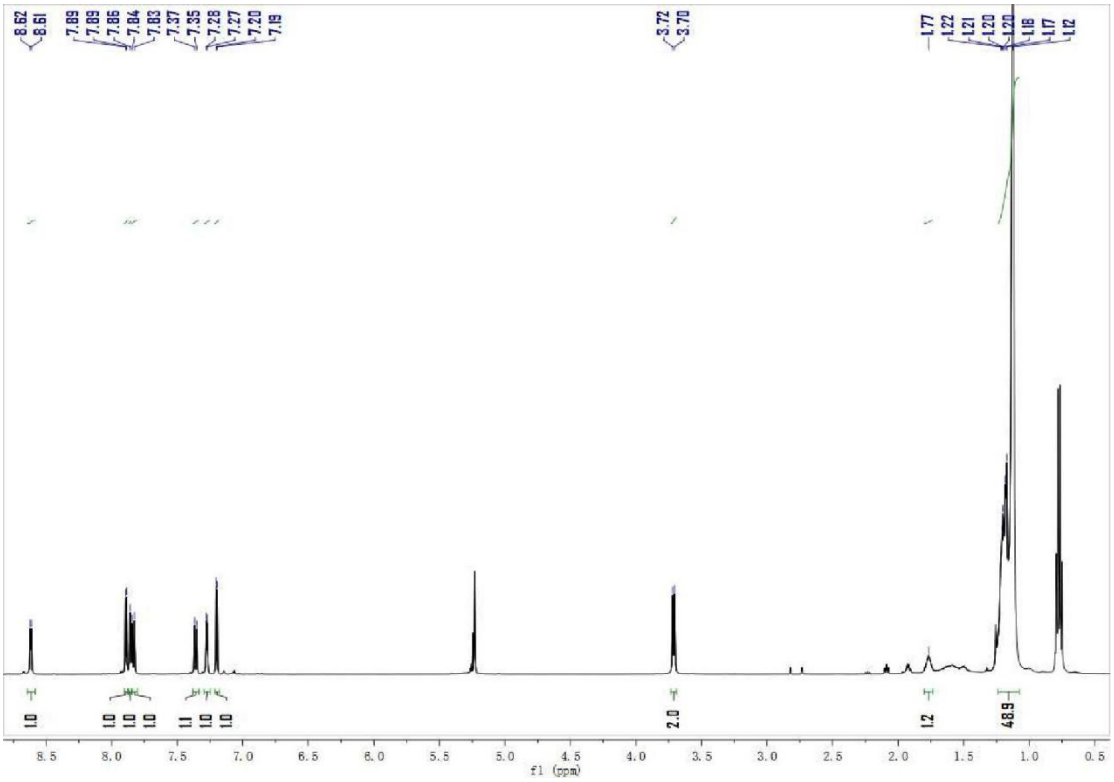


Figure S34：^{1}H NMR spectrum of compound **4c** (CD_2Cl_2, 500 MHz, 300 K)

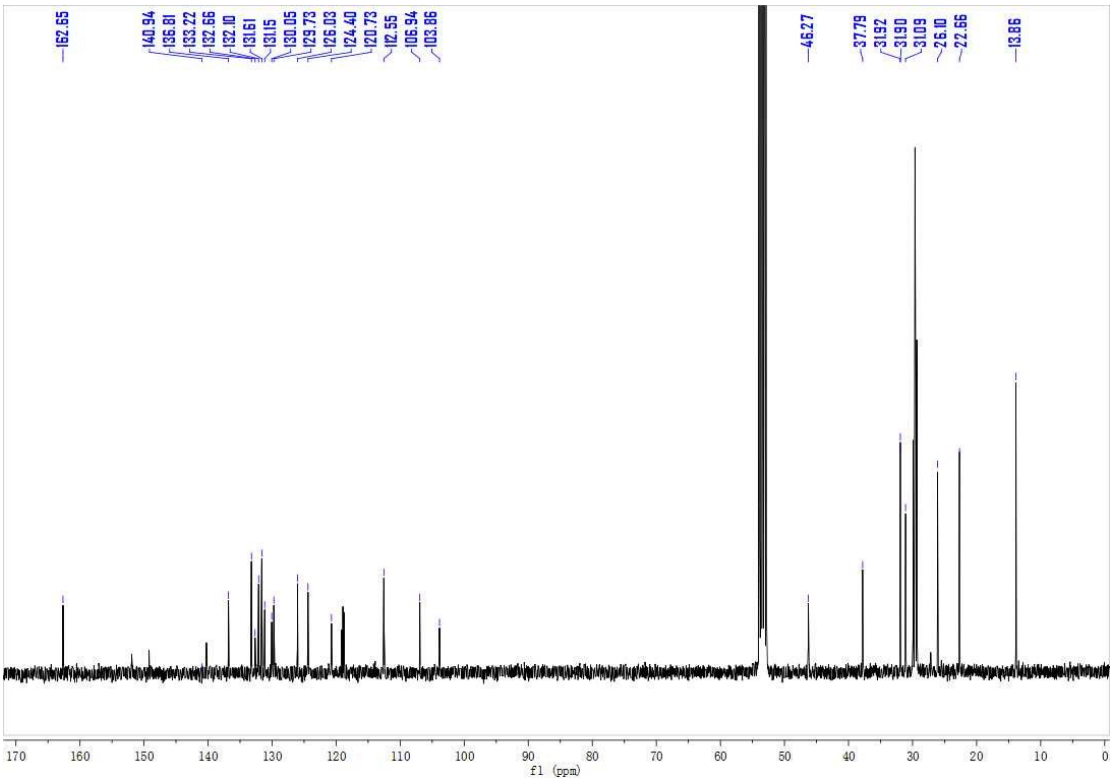


Figure S35: ^{13}C NMR spectrum of compound **4c** (125 MHz, CD_2Cl_2, 300 K)

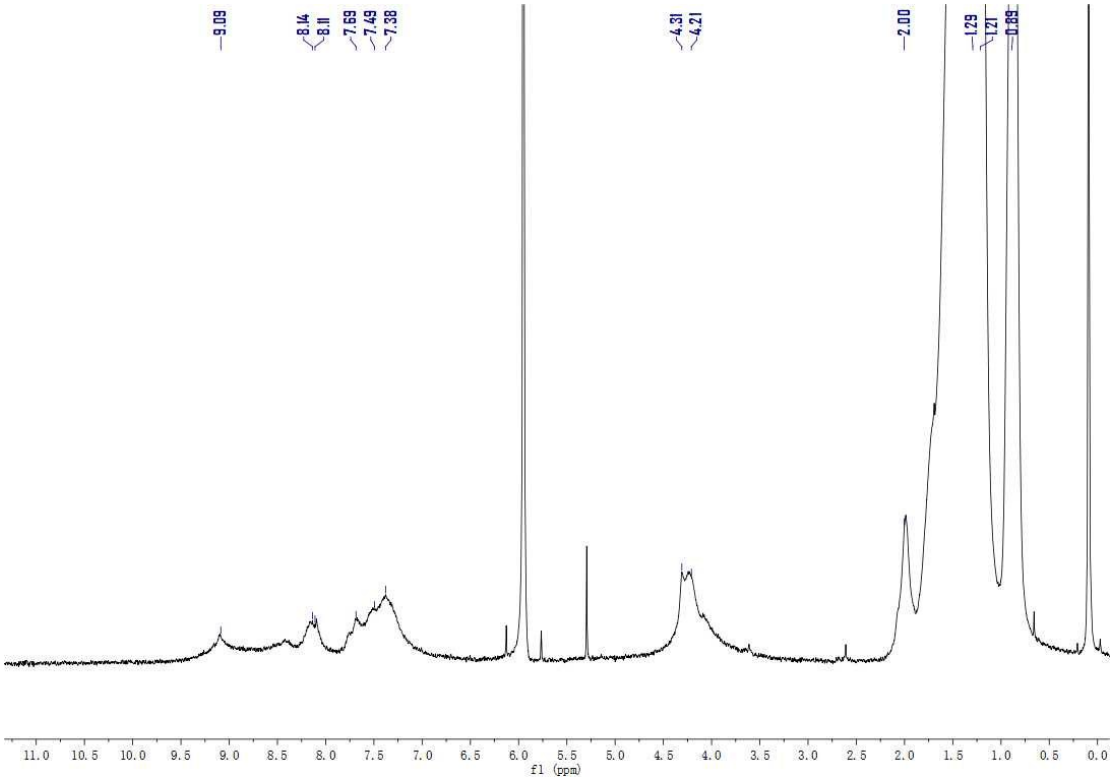


Figure S36：^{1}H NMR spectrum of **P1** (1,1,2,2-tetrachloroethane-d2, 400 MHz, 373 K)

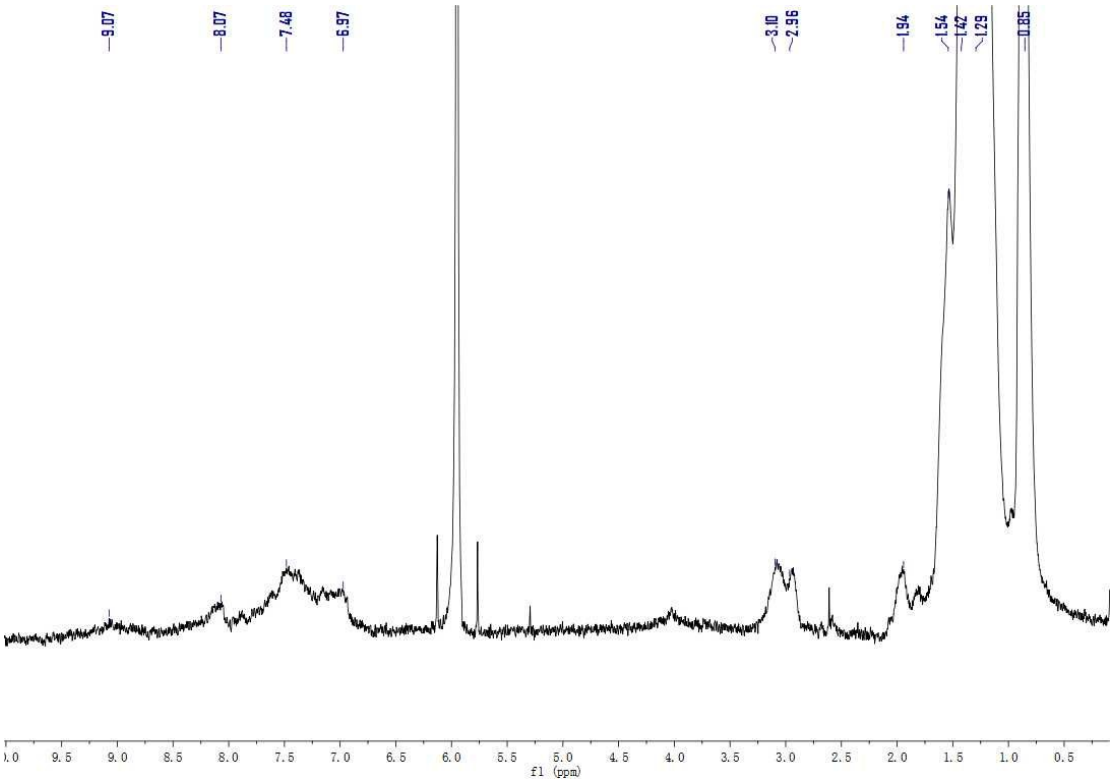


Figure S37：^{1}H NMR spectrum of **P2** (1,1,2,2-tetrachloroethane-d2, 400 MHz, 373 K)

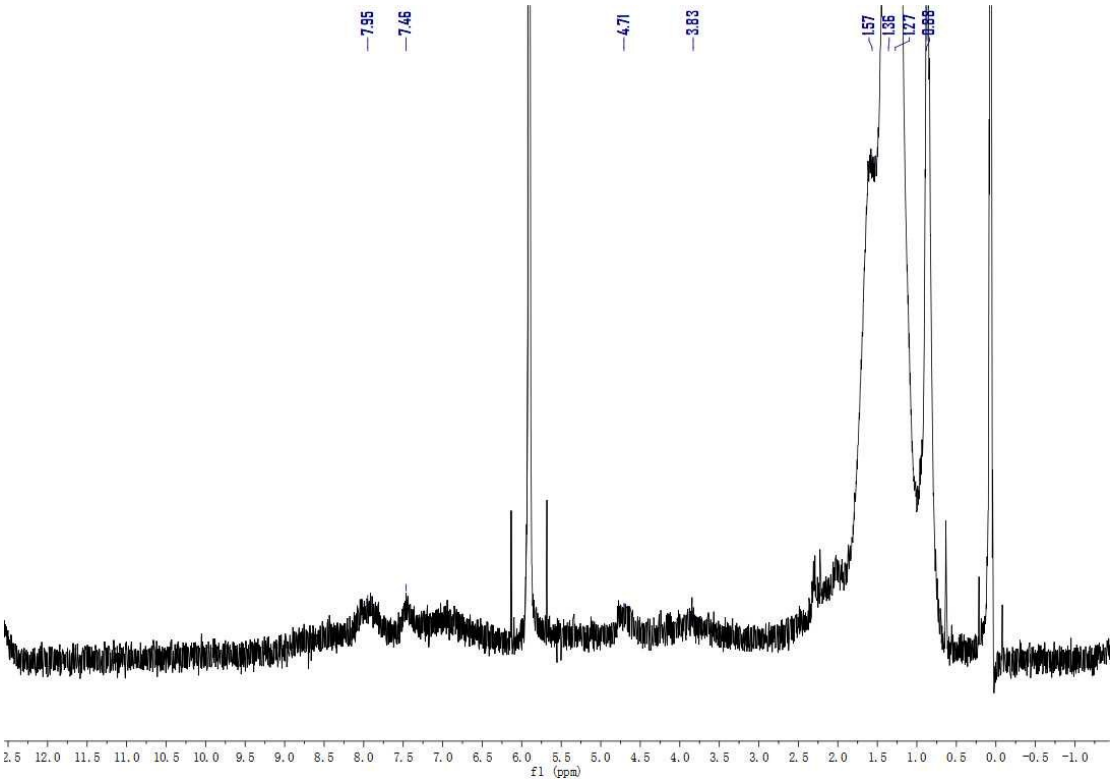


Figure S38：^{1}H NMR spectrum of **P3** (1,1,2,2-tetrachloroethane-d2, 400 MHz, 393 K)

Reference

[S1]. M. Kirkus, R. A. J. Janssen, S. C. J. Meskers, *J. Phys. Chem. A* **2013**, *117*, 4828-4837.