

Electronic Supplementary Information

Side-chain engineering of wide-bandgap copolymers based on two different electron-deficient units for high-performance polymer solar cells

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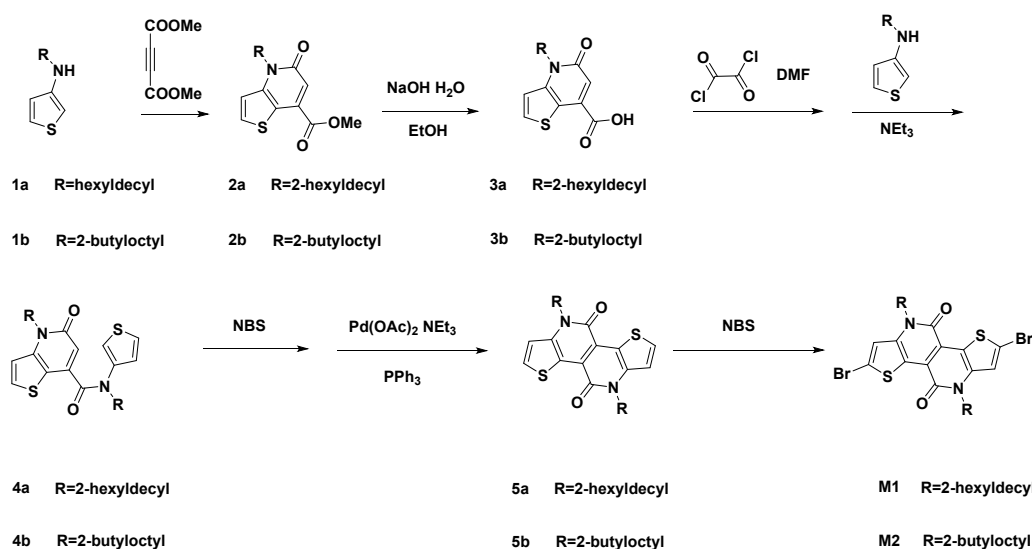
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1. Materials and instruments

L8-BO was purchased from Nanjing Zhiyan Technology Co., Ltd. Compound M3 was purchased from SunaTech Inc. The other reagents were purchased from Adamas-Beta Ltd., Sigma-Aldrich Inc., J&K Scientific Ltd., and Aladdin-Reagent Inc etc. All commercial reagents were used without any further treatment. UV-vis absorption spectra were obtained on a Lambda 365 spectrophotometer. ^1H NMR (400 MHz) spectra were obtained using a Bruker AVANCE-400 spectrometer. Elemental analyses were carried out using a Vario EL-Cube elemental analyzer. Tapping-mode atomic force microscopy (AFM) images of the active layers were acquired using the Dimensional Icon AFM. The film thickness was measured by using a Bruker Dektak XT Surface Profiler. Cyclic voltammetry was performed in a tetra-*n*-butylammonium hexafluorophosphate (0.1 M) acetonitrile solution at a scan rate of 100 mV s^{-1} on a CHI 604E electrochemical workstation with a three-electrode system. Polymers were deposited onto the Pt plate electrode by immersing the electrode in appropriate solutions followed by drying in the atmosphere. Pt wire and Ag/AgNO₃ were used as counter and reference electrodes, respectively. The molecular weight and polydispersity index (D) were obtained by gel permeation chromatography (GPC) at room temperature using an Agilent 1260 Infinity II instrument with chloroform as eluent.

2. Synthesis



Scheme S1. The synthesis route of M1 and M2.

The synthesis of compounds M1 and M2 was according to the previous literature.^[S1]

Synthesis of compound 2a. To a solution of compound 1a (4.8 g, 14.8 mmol) in THF (25 mL) was added dimethyl acetylenedicarboxylate (3.16 g, 22.2 mmol), followed by refluxing for 28 h. After being cooled to room temperature, the mixture was poured into water and extracted with Et₂O. The combined organic phase was washed by brine and dried over anhydrous MgSO₄. After removal of solvent, the residue was purified by silica gel chromatography with petroleum ether/CH₂Cl₂ (8:1, v/v) as an eluent to obtain a yellow oil (2.4 g, 50%). ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 5.6 Hz, 1H), 7.27 (s, 1H), 7.06 (d, *J* = 5.6 Hz, 1H), 4.35-4.13 (m, 2H), 4.00 (s, 3H), 2.02-1.90 (m, 1H), 1.49-1.14 (m, 24H), 0.97-0.75 (m, 6H).

Synthesis of compound 2b. Compound 2b was synthesized according to the same procedure as that for 2a. Compound 2b was isolated as a yellow oil in 53% yield. ¹H NMR (600 MHz, CDCl₃) δ 7.68 (d, *J* = 5.6 Hz, 1H), 7.25 (s, 1H), 7.04 (d, *J* = 5.6 Hz, 1H), 4.16 (s, 2H), 3.98 (s, 3H), 2.00-1.93 (m, 1H), 1.48-1.11 (m, 16H), 0.94-0.72 (m,

6H).

Synthesis of compound 3a. To a solution of compound 2a (1.4 g, 3.23 mmol) in ethanol (35 mL) and water (4 mL) was added NaOH (0.16 g, 3.4 mmol), followed by stirred for 12 h at room temperature. HCl (1 M) was added to the resulting mixture which was then extracted with CH₂Cl₂. The combined organic phase was washed by brine, dried over anhydrous MgSO₄. After removal of the solvent, compound 3a was successfully obtained as a brown oil without any purification (1.25 g, 92%). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 5.6 Hz, 1H), 7.56 (s, 1H), 7.13 (d, *J* = 5.6 Hz, 1H), 4.34 (s, 2H), 2.13-1.98 (m, 1H), 1.66-1.10 (m, 24H), 0.92-0.74 (m, 6H).

Synthesis of compound 3b. Compound 3b was synthesized according to the same procedure as that for 3a. Compound 3b was isolated as a brown oil in 90% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 5.6 Hz, 1H), 7.57 (s, 1H), 7.15 (d, *J* = 5.6 Hz, 1H), 4.35 (s, 2H), 2.13-1.96 (m, 1H), 1.56-1.14 (m, 16H), 0.87 (m, 6H).

Synthesis of compound 4a. To a solution of compound 3a (1.5 g, 3.6 mmol) in CHCl₃ (10 mL) were added oxalyl chloride (1.8 g, 14.3 mmol) and 2 drops of DMF. The mixture was stirred at room temperature for 5 h. The solvent was removed under vacuum to obtain chloride, which was used in next step without purification. To the solution of compound 1a (1.7 g, 5.4 mmol) and triethylamine (0.6 mL) in dry CH₂Cl₂ (10 mL) was slowly added a solution of chloride in CH₂Cl₂ (8 mL) at 0 °C. The mixture was stirred at room temperature overnight. Then, the mixture was poured into water and extracted with CH₂Cl₂. The combined organic phase was washed with water and dried with MgSO₄. After the evaporation of solvent, the residue was purified by column

chromatography with petroleum ether/ethyl acetate (8:1, v/v) as eluent to obtain a brown oil (2.08 g, 77%). ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 5.2 Hz, 1H), 7.20-7.14 (m, 1H), 6.98 (d, *J* = 5.6 Hz, 1H), 6.91-6.77 (m, 2H), 6.15 (s, 1H), 4.16-3.99 (m, 2H), 3.82 (d, *J* = 7.4 Hz, 2H), 1.89-1.83 (m, 2H), 1.43-1.09 (m, 48H), 0.94-0.82 (m, 12H).

Synthesis of compound 4b. Compound 4b was synthesized according to the same procedure as that for 4a. Compound 4b was isolated as a brown oil in 70% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 6.0 Hz, 1H), 7.19-7.14 (m, 1H), 6.98 (d, *J* = 5.4 Hz, 1H), 6.92-6.76 (m, 2H), 6.16 (s, 1H), 4.11-3.98 (m, 2H), 3.83 (d, *J* = 7.3 Hz, 2H), 1.92-1.84 (m, 2H), 1.44-1.11 (m, 32H), 0.97-0.78 (m, 12H).

Synthesis of compound 5a. To a solution of compound 4a (1.7 g, 2.39 mmol) in CHCl₃ (15 mL) was added NBS (0.43 g, 2.39 mmol), and the reaction mixture was stirred for 24 h at room temperature in the dark. Then, the mixture was poured into water and extracted with CH₂Cl₂. The combined organic phase was washed with brine and dried with MgSO₄. After the evaporation of solvent, the residue was purified by column chromatography with petroleum ether/ethyl acetate (8:1, v/v) as eluent to obtain a yellow oil. To a solution of the oil in dry CH₃CN (30 mL) were added PPh₃ (0.13 g, 0.0478 mmol), Pd(OAc)₂ (0.06 g, 0.0239 mmol) and dry NEt₃ (0.49 g, 4.78 mmol), successively. The mixture was refluxed for 8 h under nitrogen. After being cooled to room temperature, the mixture was poured into water and extracted with CH₂Cl₂. The combined organic phase was washed with water and dried with MgSO₄. After the evaporation of solvent, the residue was purified by column chromatography with petroleum ether/CH₂Cl₂ (2:1, v/v) as eluent to obtain a green solid (1.1 g, 65%). ¹H

NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 5.4 Hz, 2H), 7.20 (d, J = 5.4 Hz, 2H), 4.37 (s, 4H), 2.19-2.01 (m, 2H), 1.59 (s, 8H), 1.50-1.12 (m, 40H), 1.01-0.75 (m, 12H).

Synthesis of compound 5b. Compound 5b was synthesized according to the same procedure as that for 5a. Compound 5b was isolated as a green solid in 68% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 5.6 Hz, 2H), 7.21 (d, J = 5.6 Hz, 2H), 4.39 (s, 4H), 2.20-2.10 (m, 2H), 1.59 (s, 4H), 1.54-1.15 (m, 28H), 0.94-0.81 (m, 12H).

Synthesis of compound M1. To a solution of compound 5a (0.2 g, 0.265 mmol) in CHCl₃ (15 mL) was added NBS (0.71 g, 4 mmol), and the reaction mixture was stirred for 24 h at room temperature in the dark. Then, the mixture was poured into water and extracted with CH₂Cl₂. The combined organic phase was washed with water and dried with MgSO₄. After the evaporation of solvent, the residue was purified by column chromatography with petroleum ether/CH₂Cl₂ (3:1, v/v) as eluent to obtain a yellow solid (0.23 g, 85%). ¹H NMR (400 MHz, CDCl₃) δ 7.18 (s, 2H), 4.28 (d, J = 5.2 Hz, 4H), 2.14-2.05 (m, 2H), 1.59 (s, 8H), 1.48-1.19 (m, 40H), 0.98-0.82 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 159.42, 139.44, 121.75, 121.16, 118.45, 117.17, 50.34, 36.98, 31.87, 31.79, 31.36, 31.33, 29.97, 29.65, 29.52, 29.30, 26.38, 22.68, 22.65, 14.15, 14.10. HRMS (MALDI) m/z : calcd for C₄₄H₆₈Br₂N₂O₂S₂, 878.3083; found, 878.3085.

Synthesis of compound M2. Compound M2 was synthesized according to the same procedure as that for M1. Yellow solid of M2 was isolated in 78% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.18 (s, 2H), 4.27 (d, J = 5.2 Hz, 4H), 2.13-2.02 (m, 2H), 1.58 (s, 4H), 1.49-1.18 (m, 28H), 0.92-0.81 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 159.39, 139.42, 121.71, 121.13, 118.44, 117.13, 50.32, 36.98, 31.77, 31.29, 31.05, 29.62, 28.57,

26.35, 23.05, 22.63, 14.08, 14.05. HRMS (MALDI) m/z : calcd for $C_{36}H_{52}Br_2N_2O_2S_2$, 766.1831; found, 766.1835.

Synthesis of P1. Compound M1 (0.1 g, 0.113 mmol) and compound M3 (0.0985 g, 0.113 mmol) were added to a 25 mL two-neck flask with 12 mL of toluene. After bubbling the solution mixture with N_2 for 20 min, $Pd_2(dba)_3$ (0.0052 g, 0.0565 mmol) and $P(o-tol)_3$ (0.0128 g, 0.0418 mmol) were added quickly. Then, the solution was bubbled with N_2 for another 10 min. The degassed solution mixture was heated to 100 °C for 10 h under the protection of N_2 . After cooling to room temperature, the crude product was precipitated with 50 mL of methanol. The copolymer was collected by filtration and Soxhlet-extracted with methanol, acetone, n-hexane and dichloromethane, successively. The final dichloromethane solution was precipitated again with methanol, and the precipitate was filtered. Then the copolymer (P1) was dried under vacuum at 50 °C to yield a black solid (0.098 g, 68%, $M_n = 87.8$ kDa, $D = 3.42$). Elemental analysis calcd (%) $C_{74}H_{107}F_2N_5O_2S_4$: C 70.27%, H 8.53%, N 5.54%; found: C 70.51%, H 8.48%, N 5.47%.

Synthesis of P3. Compound M2 (0.1 g, 0.130 mmol) and compound M3 (0.1058 g, 0.130 mmol) were added to a 25 mL two-neck flask with 12 mL of toluene. After bubbling the solution mixture with N_2 for 20 min, $Pd_2(dba)_3$ (0.006 g, 0.0065 mmol) and $P(o-tol)_3$ (0.0146 g, 0.0481 mmol) were added quickly. Then, the solution was bubbled with N_2 for another 10 min. The degassed solution mixture was heated to 60 °C for 4 h under the protection of N_2 . After cooling to room temperature, the crude product was precipitated with 50 mL of methanol. The copolymer was collected by

filtration and Soxhlet-extracted with methanol, acetone, n-hexane and dichloromethane, successively. The final dichloromethane solution was precipitated again with methanol, and the precipitate was filtered. Then the copolymer (P3) was dried under vacuum at 50 °C to yield a black solid (0.11 g, 73%, $M_n = 131.5$ kDa, $D = 3.62$). Elemental analysis (%) calcd $C_{66}H_{91}F_2N_5O_2S_4$: C 68.77%, H 7.96%, N 6.08%; found: C 69.63%, H 7.96%, N 6.06%.

3. Device fabrication and characterization

PSCs were fabricated with a traditional device configuration of ITO/PEDOT:PSS/active layer/PDIN/Ag. ITO glass was cleaned with detergent, deionized water, acetone, and isopropanol with ultrasonication for 15 min respectively, then dried in an oven overnight, and then performed UV- O_3 treatment for 15 min before using. To obtain PEDOT:PSS thin films on ITO, the filtered PEDOT:PSS solution (BaytronPVPAl4083 from HC Starck) was spun at 3500 rpm onto a clean ITO substrate, followed by baking at 140 °C for 15 min in air. Subsequently, The PEDOT:PSS coated ITO glass substrate was then transferred into an N_2 -filled glove box for further processing. A blend solution of donor and L8-BO with the total concentration of 18 mg mL^{-1} was prepared by dissolving the materials in chloroform, and then was spin-coated at 2600 rpm for 30 s onto the PEDOT:PSS layer to form an active layer (~100 nm). The active layer was then annealed at 70 °C for 3 min. A PDIN layer was then spin-coated (3000 rpm, 30 s) by using a PDIN-methanol solution (2.0 mg mL^{-1} and 0.3% v/v CH_3COOH) to afford a buffer layer with a thickness of ca.10 nm. Finally, 100 nm of Ag layer was deposited on the active layer through a shadow

mask by thermal evaporation at a pressure of 1.0×10^{-4} Pa. The device has an active area of 5 mm^2 . Device characterization was performed using an Oriel sol3A simulator (Newport) and an NREL-certified silicon reference cell under an irradiance of 1.5 G (100 mW cm^{-2}). J - V curves were measured using a Keithley 2440 source meter. EQE spectra were measured on a Newport EQE measurement system.

4. SCLC measurements

Hole- and electron-mobilities were measured using the space charge limited current (SCLC) method. Hole-only devices were fabricated with an architecture of ITO/PEDOT:PSS/active layer/Ag, while electron-only devices were fabricated with an architecture of ITO/ZnO/active layer/Ca/Al. The active layers were prepared by using the same method as that used for the best-performance solar cells. Device area was fixed at 4 mm^2 . The current density (J) was measured by a Keithley 2440 source measurement unit. The SCLC hole/electron mobilities were calculated according to the following equation:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3}$$

Where ε_0 is the permittivity of free space ($8.85 \times 10^{-12} \text{ F m}^{-1}$), ε_r is the dielectric constant of the active layer (3 in this work), μ is the carrier mobility, V is the voltage drop across the device ($V = V_a - V_b$, where V_a is the applied voltage to the device, and V_b is the built-in voltage due to the difference in the work function of two electrodes), and L is the active layer thickness. In this work, the active layer thicknesses are about 106 nm for hole-only devices and 103 nm for electron-only devices.

5. GIWAXS measurements

All samples for GIWAXS measurement were prepared on the PEDOT:PSS-coated Si substrates. The 2D GIWAXS patterns were acquired using a XEUSS 3.0 SAXS/WAXS system at Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences (FJIRSM, Fuzhou). The wavelength of the X-ray beam is 1.54 Å, and the incident angle was set as 0.2°. Scattered X-rays were detected by using a Dectris Pilatus 1M photon counting detector. The coherence length was estimated by the Scherrer equation: $CL = 2\pi k / \text{FWHM}$, where FWHM is the full width at half-maximum of the peak and k is a shape factor (0.9 was used here).

Table S1. Summarized parameters of the ordered structures based on pure and blend films.

Samples	π - π stacking		Lamellar stacking	
	d_π (Å) ^a	CL (Å) (FWHM (Å ⁻¹)) ^b	d_l (Å) ^c	CL (Å) (FWHM (Å ⁻¹)) ^b
P1	3.70	17.24 (0.33)	20.87	92.70 (0.06)
P3 ^d	3.63	12.97 (0.44)	19.27	62.48 (0.09)
P3 ^e	3.63	12.56 (0.45)	19.25	56.55 (0.10)
P1:L8-BO	3.65	16.20 (0.35)	20.47	81.95 (0.07)
P3:L8-BO	3.63	17.56 (0.32)	18.70	53.35 (0.11)

^a d_π was calculated from the (010) diffraction peak along the q_z axis; ^bCL was estimated from the Scherrer equation ($CL = 2\pi K / \text{FWHM}$, $K = 0.9$), in which k is the Scherrer factor and FWHM is the full-width at the half-maximum of the peak; ^c d_l was calculated from the (100) diffraction peak along the q_{xy} axis; ^d $M_n = 131.5$ kDa; ^e $M_n = 75.8$ kDa.

Table S2. Photovoltaic parameters of PSCs based on P3:L8-BO under the illumination of AM 1.5G (100 mW cm⁻²).^a

D/A (w/w)	CN (vol %)	Annealing Temperature (°C)	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE _{max} (%)
1:1	0.3	90 °C, 5 min	0.76	19.34	71.75	10.59
1:1.2	0.3	90 °C, 5 min	0.74	20.52	73.30	11.18
1:1.5	0.3	90 °C, 5 min	0.75	19.12	74.20	10.61
1:1.2	0.3	w/o	0.75	19.43	74.49	10.85
1:1.2	0.3	90 °C, 3 min	0.75	20.46	73.48	11.27
1:1.2	0.3	90 °C, 10 min	0.74	20.17	73.02	10.92
1:1.2	0.3	70 °C, 3 min	0.74	21.64	73.04	11.77
1:1.2	0.3	110 °C, 3 min	0.73	21.13	71.64	11.02
1:1.2	0	70 °C, 3 min	0.75	20.23	70.40	10.70
1:1.2	0.5	70 °C, 3 min	0.74	22.80	74.30	12.56
1:1.2 ^b	0.5	70 °C, 3 min	0.74	21.89	73.97	12.05

^a Blend films based on P3 with high molecular weight (131.5 kDa); ^b Blend films based on P3 with low molecular weight P3 (75.8 kDa).

Table S3. Photovoltaic parameters of PSCs based on J71:L8-BO under the illumination of AM 1.5G (100 mW cm⁻²).

Active Layer	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
J71:L8-BO	0.849	20.86	46.31	8.20 (7.89 ± 0.31)

Table S4. Charge carrier mobilities of blend films based on P3 with low molecular weight (75.8 kDa).

Active Layer	μ_h (cm ² V ⁻¹ s ⁻¹)	μ_e (cm ² V ⁻¹ s ⁻¹)	μ_h/μ_e
P3:L8-BO	5.02 (4.85 ± 0.12) × 10 ⁻⁴	3.51 (3.26 ± 0.23) × 10 ⁻⁴	1.43

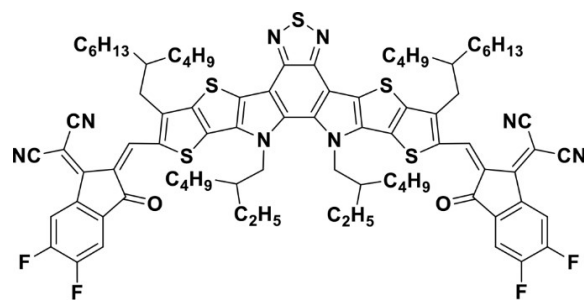


Fig. S1 Molecular structure of L8-BO.

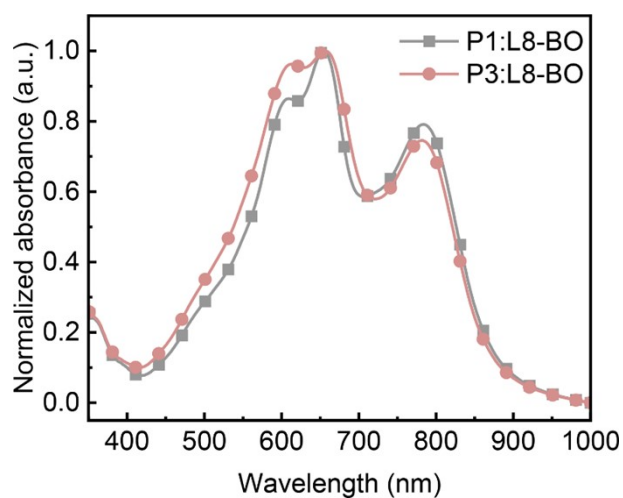


Fig. S2 Normalized UV-vis absorption spectra of P1:L8-BO and P3:L8-BO blend films.

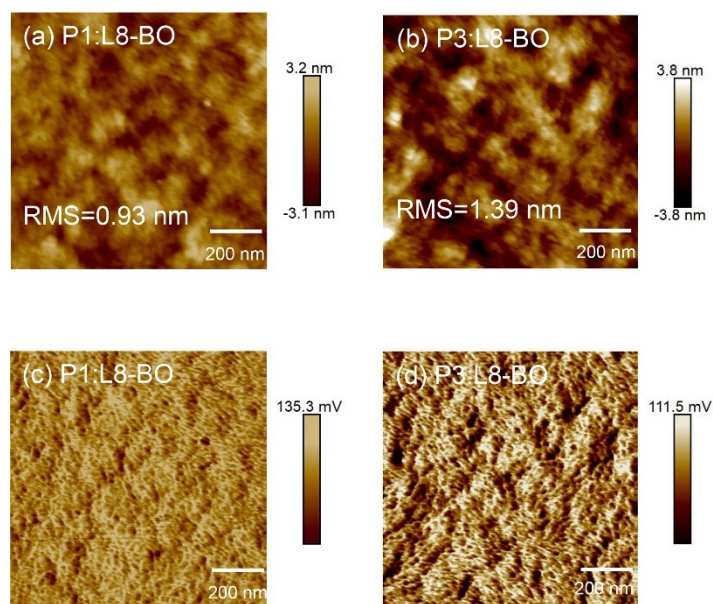


Fig. S3 AFM height (a, b) and phase (c, d) images of P1:L8-BO and P3:L8-BO blend films ($1\mu\text{m} \times 1\mu\text{m}$).

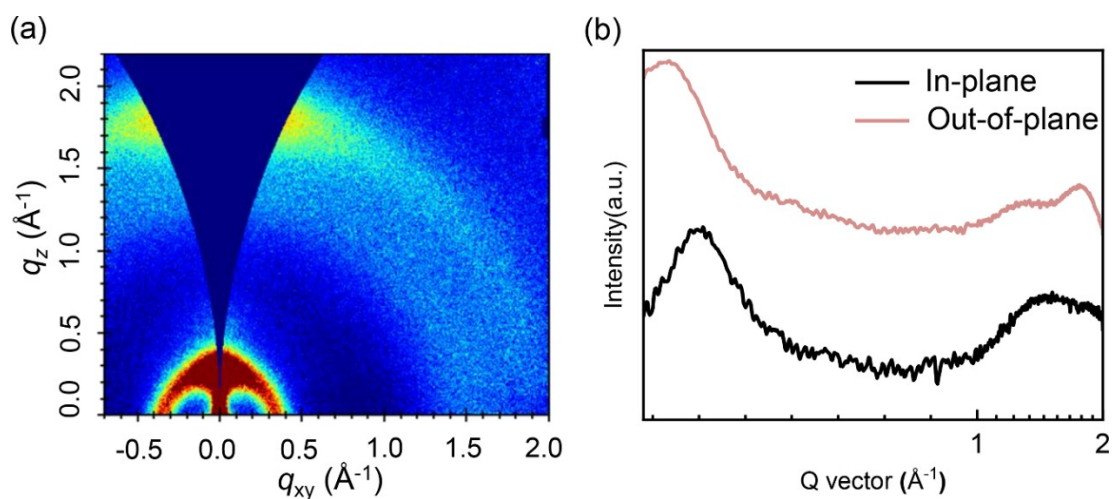
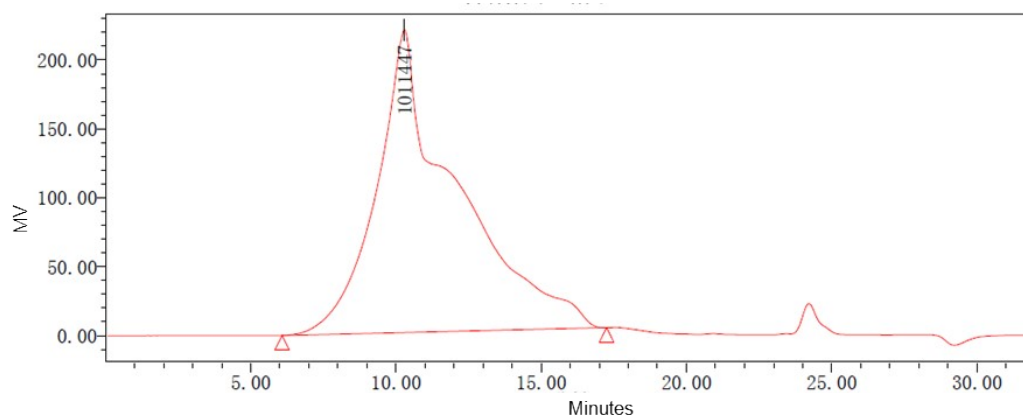
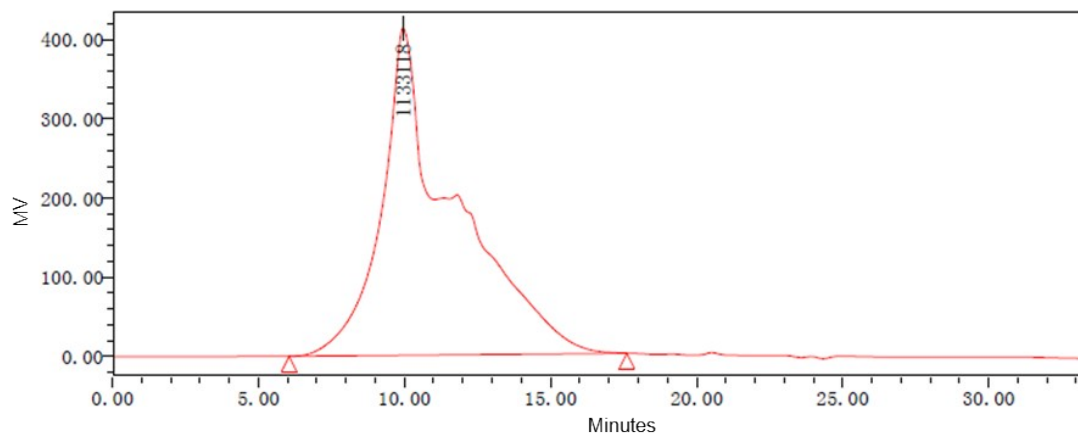


Fig. S4 2D GIWAXS pattern of P3 with low molecular weight (75.8 kDa) in pure film (a), and corresponding 1D line-cuts in the in-plane and out-of-plane directions (b).



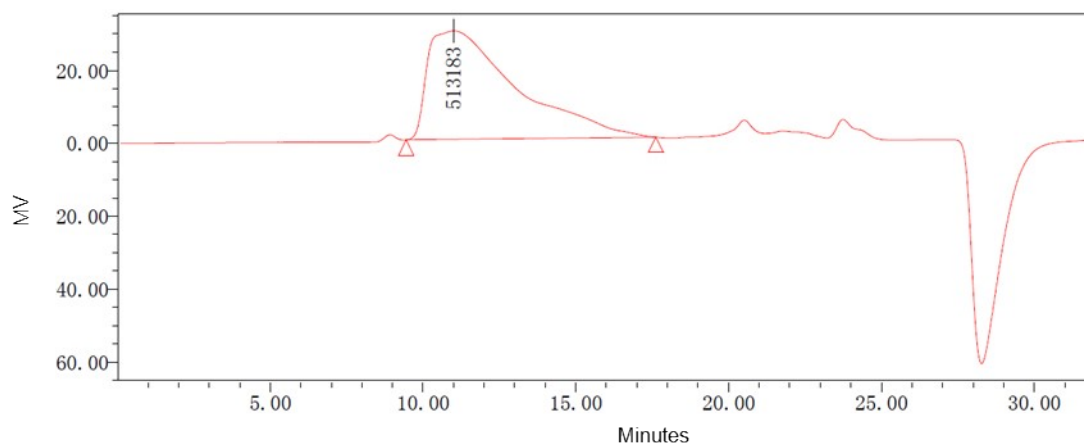
	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1		87825	300131	1011447	564293	712304	3.417378

Fig. S5 GPC data of P1 measured using chloroform as eluent at room temperature.



	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1		131490	476230	1133118	791604	922782	3.621789

Fig. S6 GPC data of the high molecular weight P3 measured using chloroform as eluent at room temperature.



	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1		75757	202438	513183	335147	414662	2.672207

Fig. S7 GPC data of the low molecular weight P3 measured using chloroform as eluent at room temperature.

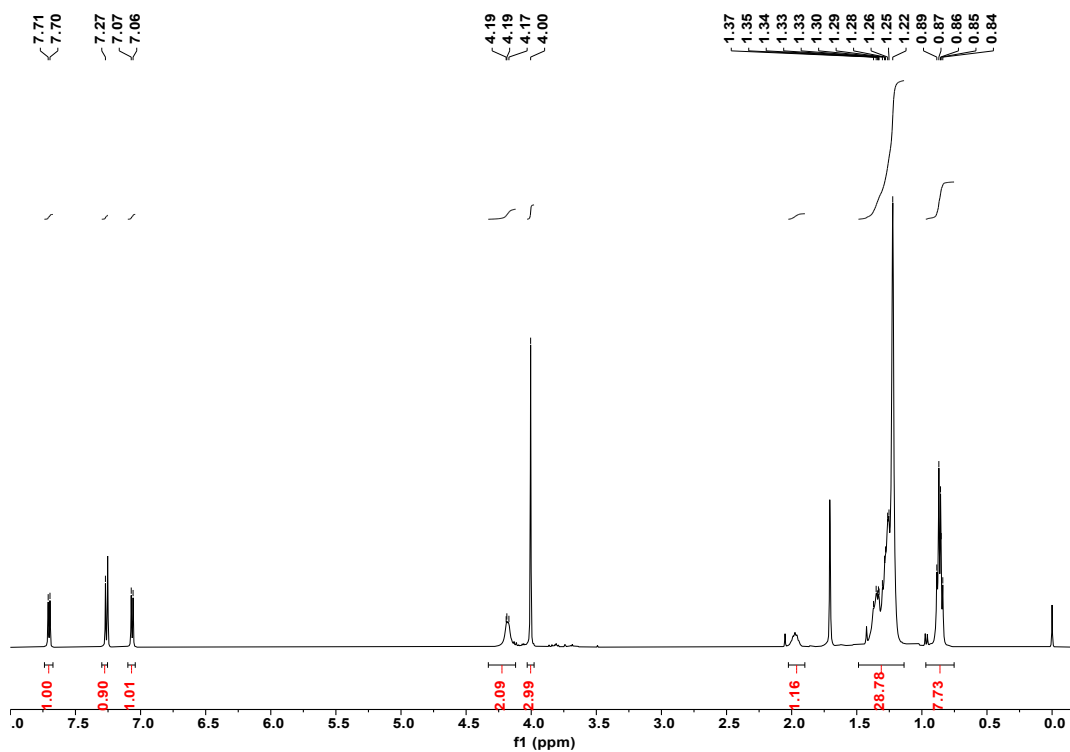


Fig. S8 ^1H NMR spectrum of compound 2a in CDCl_3 .

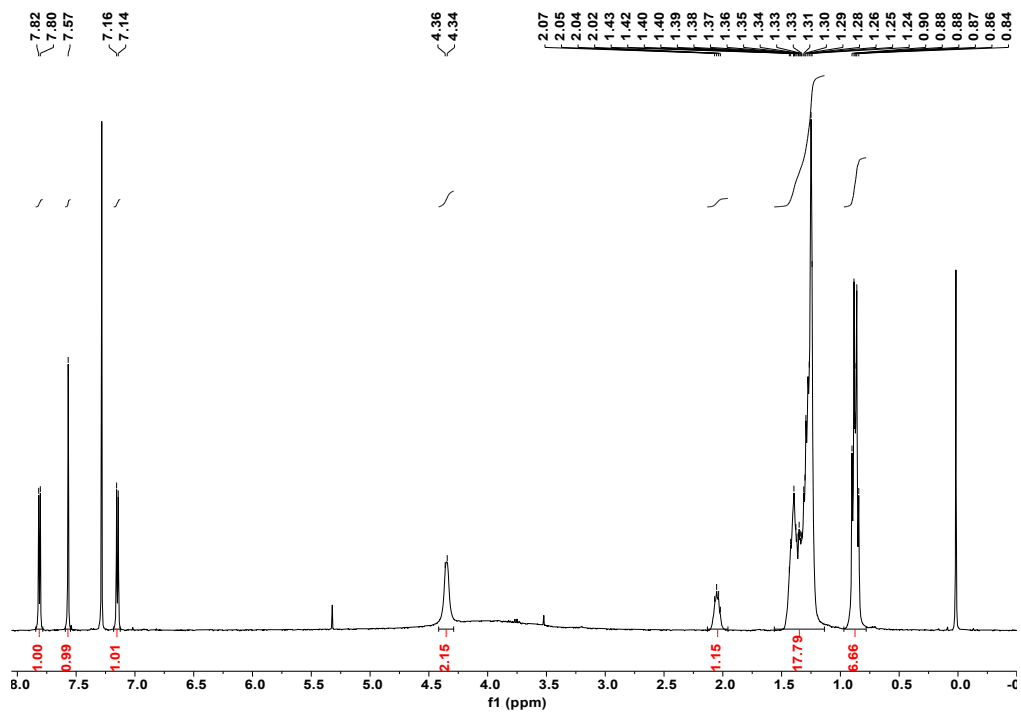


Fig. S9 ^1H NMR spectrum of compound 2b in CDCl_3 .

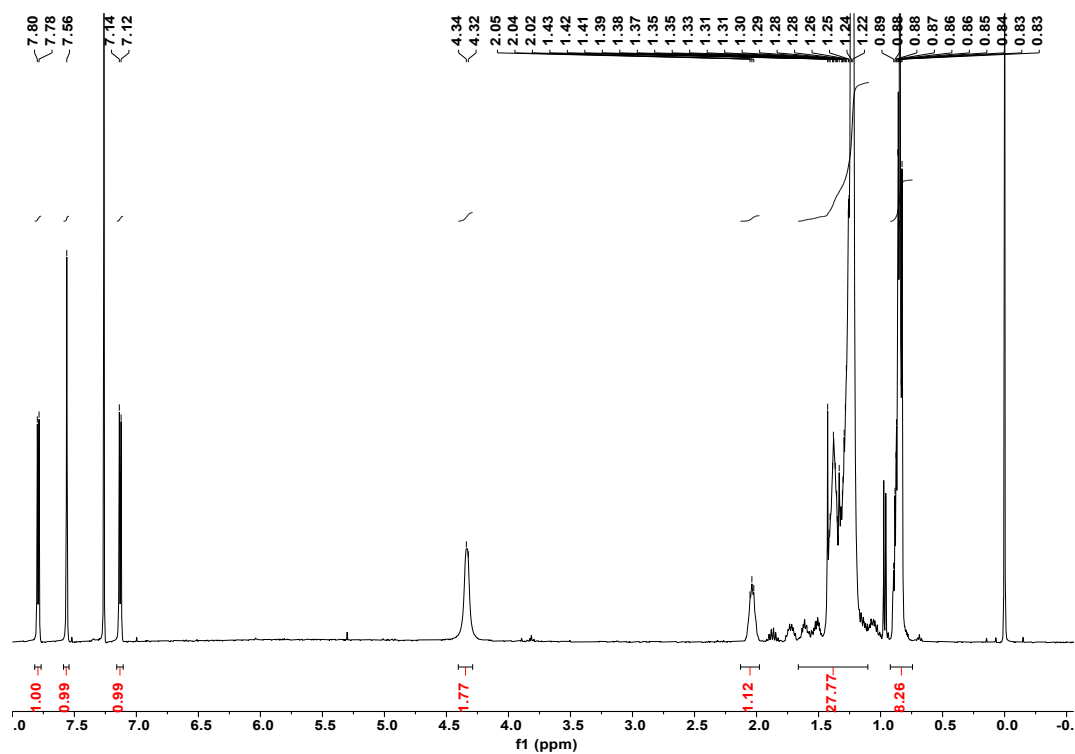


Fig. S10 ^1H NMR spectrum of compound 3a in CDCl_3 .

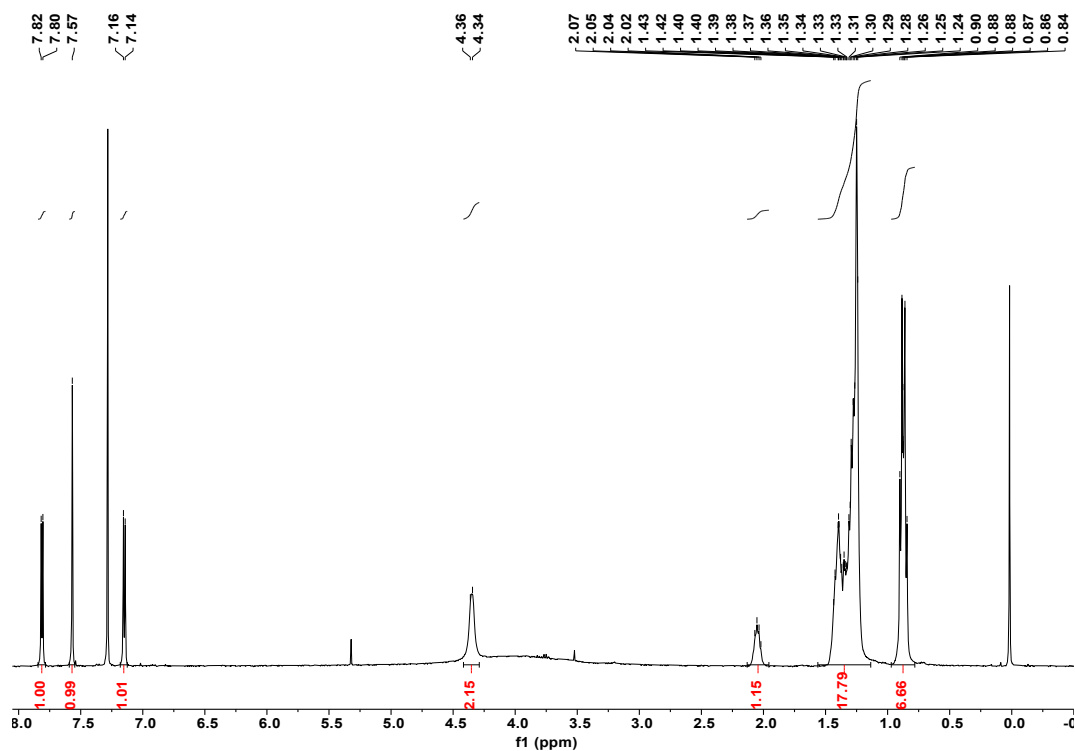


Fig. S11 ^1H NMR spectrum of compound 3b in CDCl_3 .

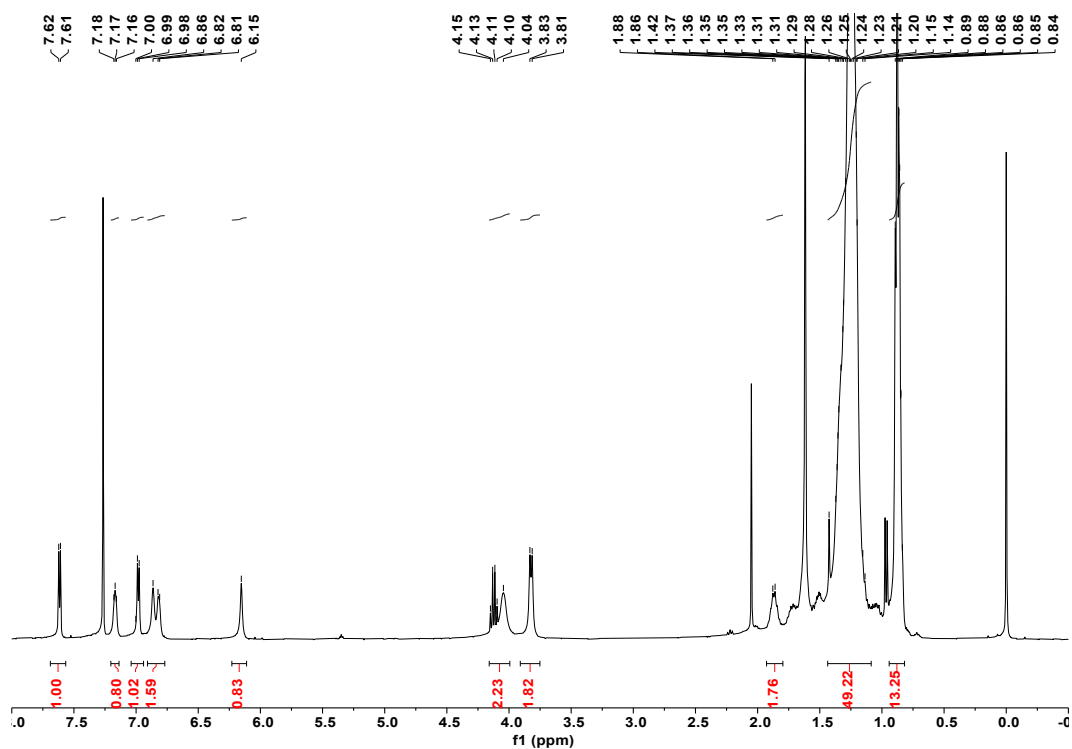


Fig. S12 ^1H NMR spectrum of compound 4a in CDCl_3 .

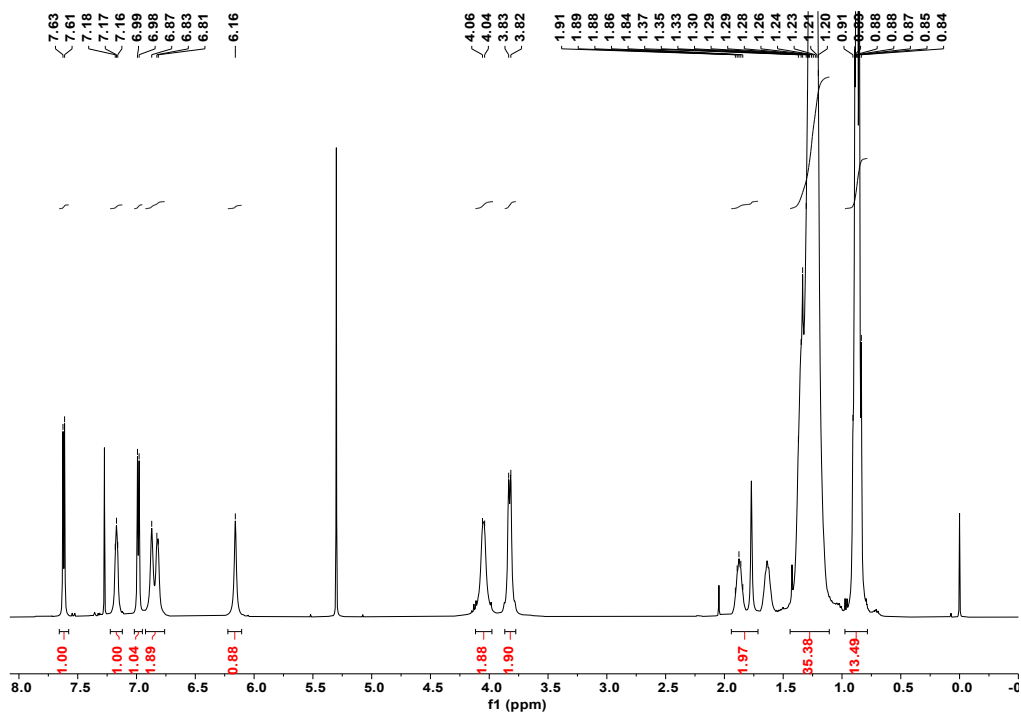


Fig. S13 ^1H NMR spectrum of compound 4b in CDCl_3 .

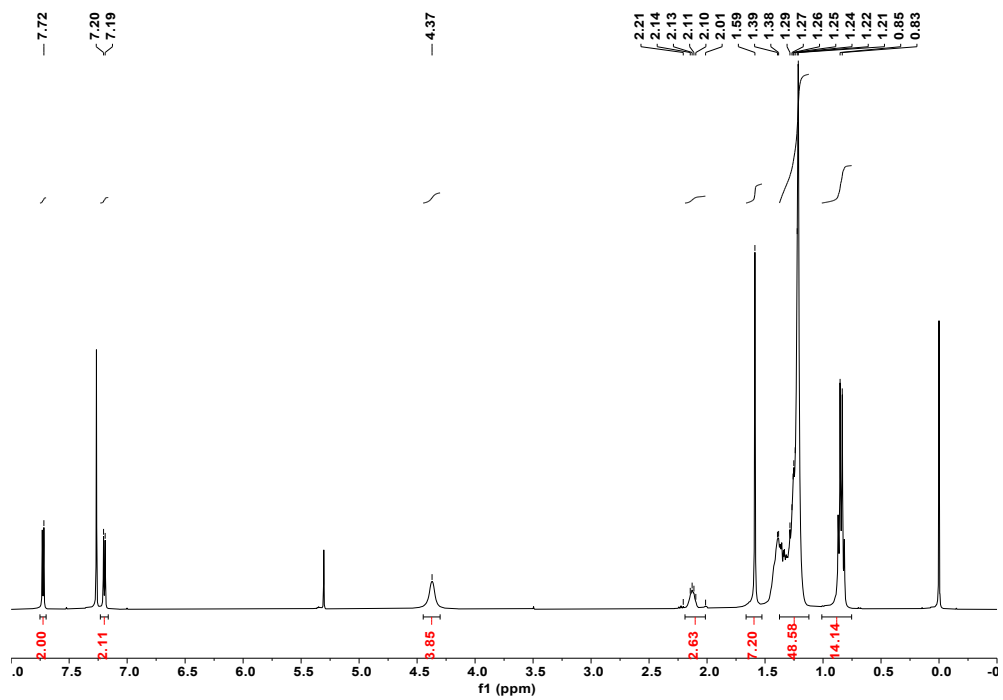


Fig. S14 ^1H NMR spectrum of compound 5a in CDCl_3 .

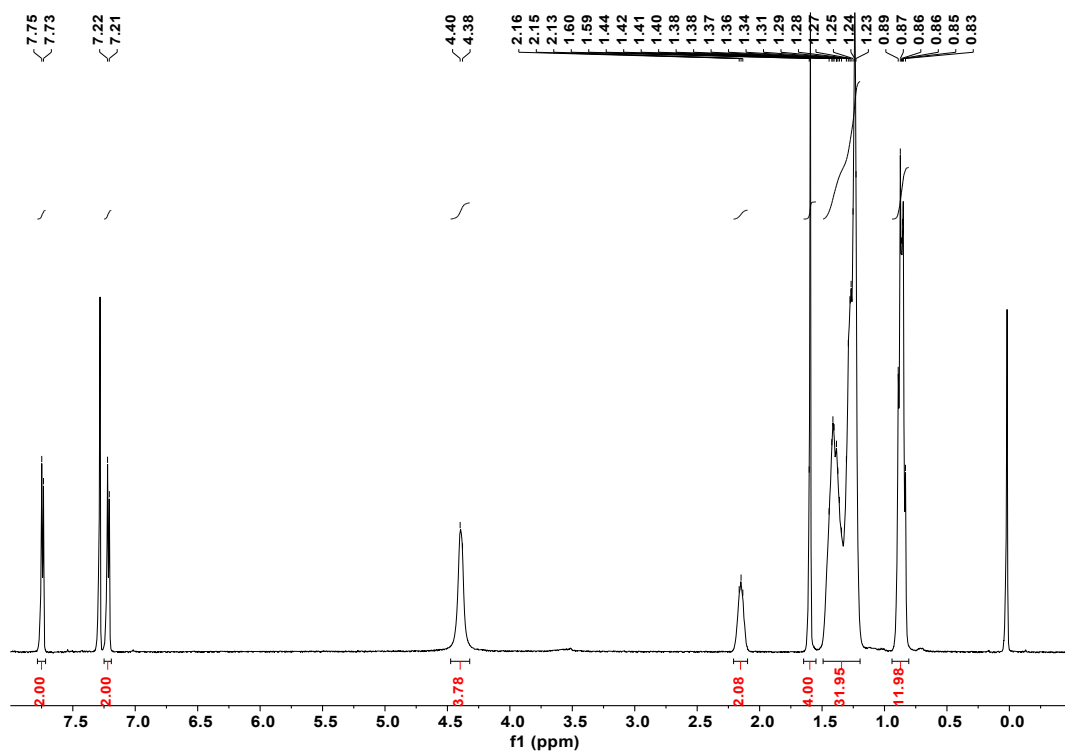


Fig. S15 ^1H NMR spectrum of compound 5b in CDCl_3 .

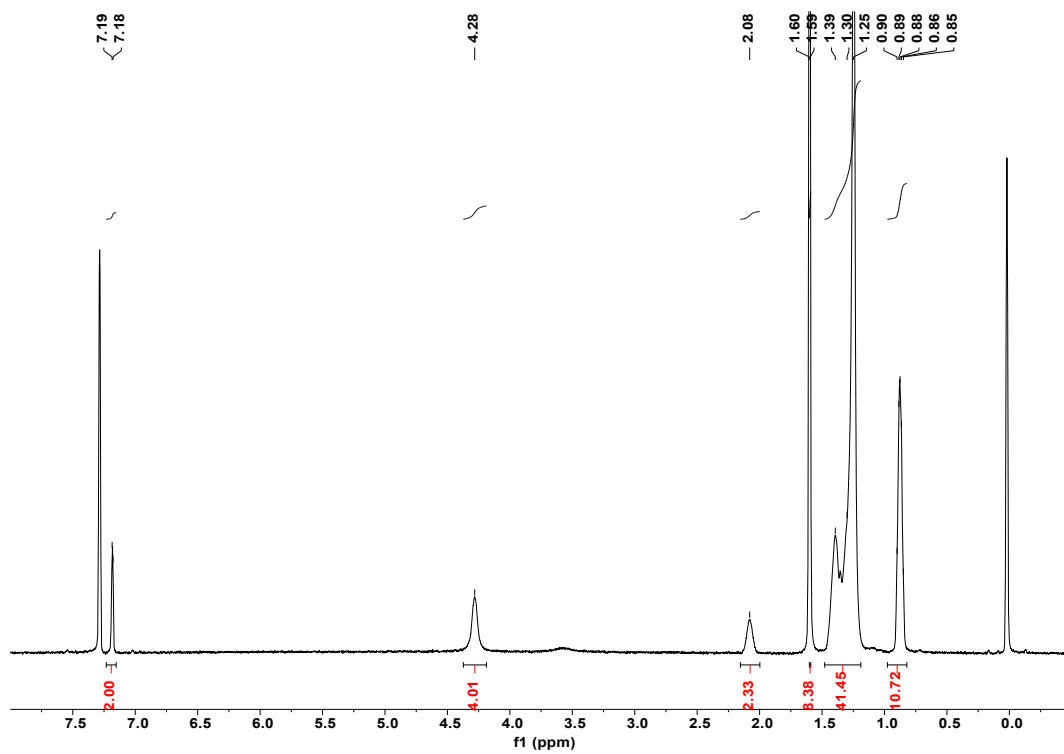


Fig. S16 ^1H NMR spectrum of compound M1 in CDCl_3 .

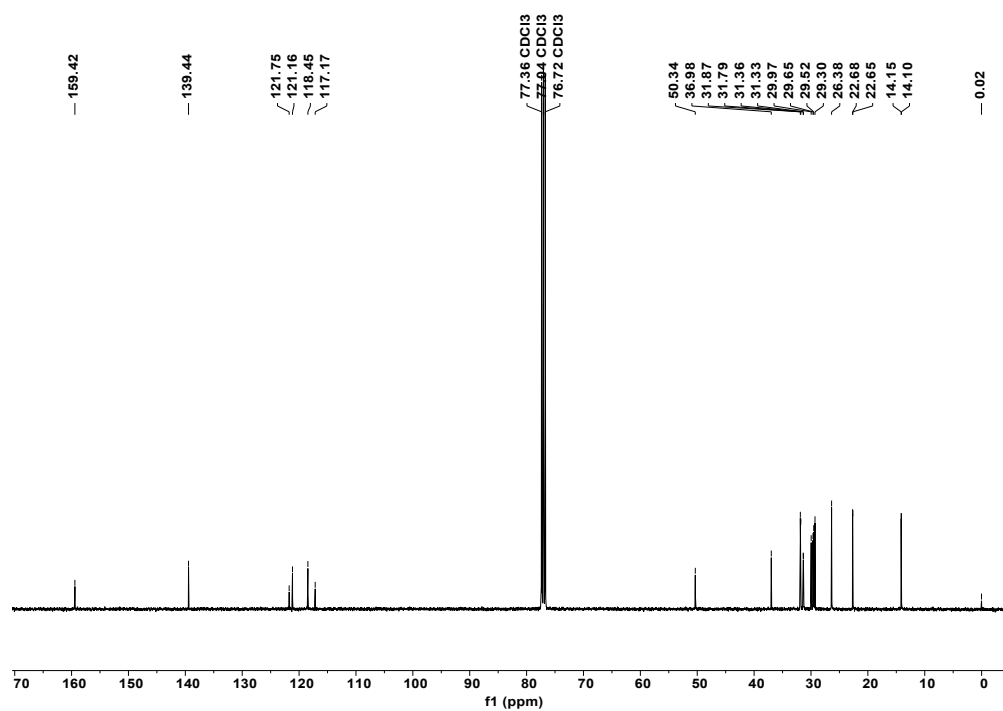


Fig. S17 ^{13}C NMR spectrum of compound M1 in CDCl_3 .

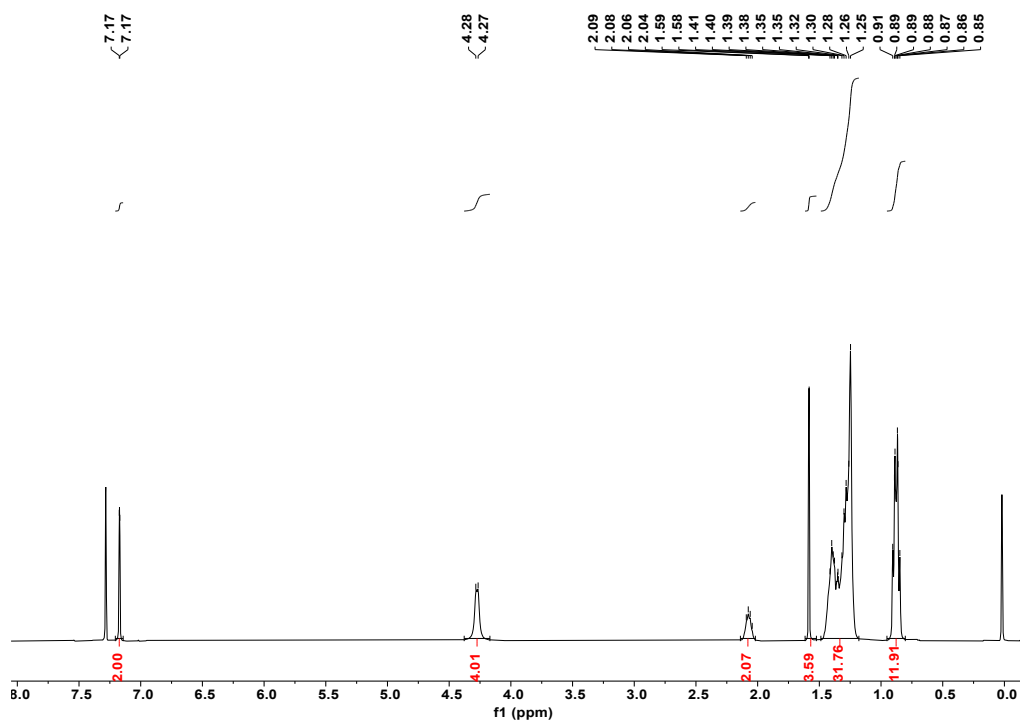


Fig. S18 ^1H NMR spectrum of compound M2 in CDCl_3 .

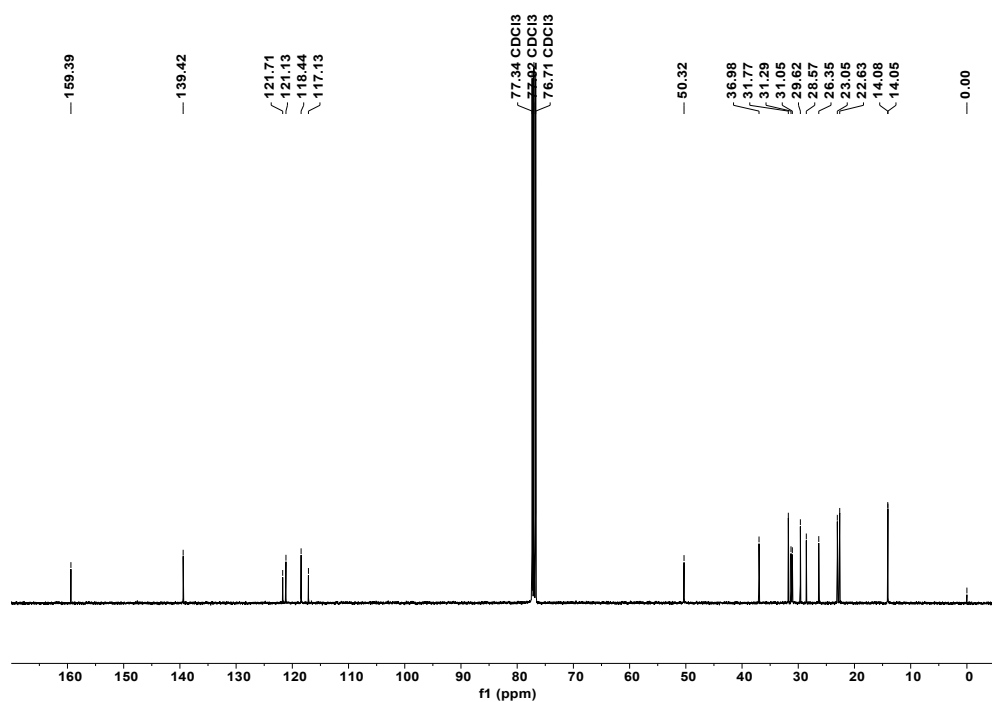


Fig. S19 ^{13}C NMR spectrum of compound M2 in CDCl_3 .

References

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