

Electronic Supplementary Information (ESI)

**Palladium-Catalyzed Carbene Coupling Polymerization:
Synthesis of *E*-Poly(arylene vinylene)s**

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1) General

All the reactions were performed under nitrogen atmosphere in oven-dried reaction flasks. Solvents were distilled under nitrogen atmosphere prior to use. For chromatography, 200-300 mesh silica gel (Qingdao, China) was used. Chemicals were purchased from Energy Chemical. Unless otherwise noted, commercially available reagents were used as received.

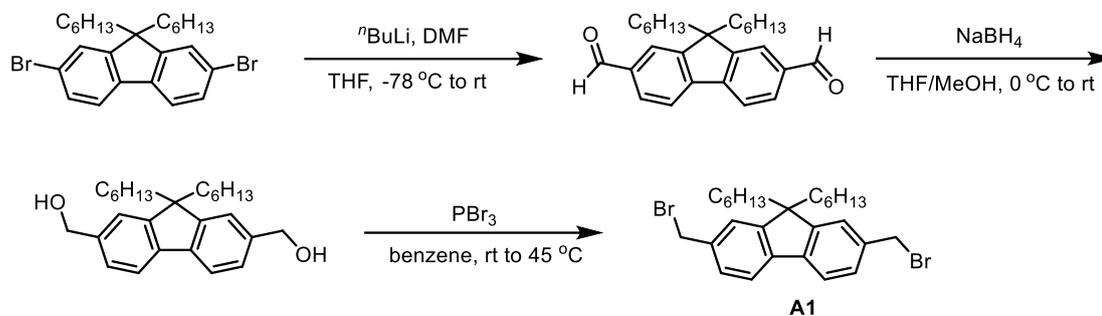
^1H NMR spectra were recorded on Bruker ARX 400 (400 MHz), ^{13}C NMR spectra were recorded on Bruker ARX 400 (100 MHz) or Bruker ARX 500 (125 MHz), ^{19}F NMR spectra were recorded on Bruker-500 MHz NMR. The data for NMR spectra were reported as following: chemical shifts (δ) were reported in ppm using tetramethylsilane (TMS) as the internal standard, and coupling constants (J) are in Hertz (Hz). Size exclusion chromatography (SEC) for the analysis of Molecular weights (M_n) and polydispersity (M_w/M_n) of the polymers was carried out with Waters 515 GPC instrument using THF as an eluent at a flow rate of 1.0 mL/min at 35 °C. The GPC calibration curve was obtained with linear polystyrene standards.

Absorption spectra were performed on PerkinElmer Lambda 750 UV-vis spectrometer. Fluorescence spectra were recorded on F7000. Thermal gravimetric analysis (TGA) was conducted on a Q600-SDT thermogravimetric analyzer at a heating rate of 10 °C/min under a nitrogen atmosphere of 100 mL/min. Differential scanning calorimetry (DSC) was performed on a Q2000 differential scanning calorimeter at a heating rate of 10 °C/min under a nitrogen atmosphere of 50 mL/min. Data of the endothermic thermograms were recorded from the third scan and analyzed with a TA Universal Analysis software. Infrared spectra were recorded on a Thermo Nicolet iS5 spectrometer and were reported in terms of frequency of absorption (cm^{-1}) at 25 °C. HRMS were obtained on Bruker APEX IV FTMS and ThermoFisher Q exactive hybrid quadrupole-orbitrap GC-MS/MS system. Atomic force microscopies (AFM) were performed with Cypher S microscope (Asylum Research, Oxford Instruments) at tapping mode under ambient conditions using silicon cantilever (AC240TS-R3) with a resonant frequency around 70 kHz. ICP analysis was performed on PerkinElmer NexION 350X Inductively Coupled Plasma Mass Spectrometry.

2) Synthesis and characterization of the monomers

2.1 Synthesis and characterization of A1

The procedures were carried out according to literature procedures with slight modifications.^{1,2}



A 200 mL round-bottom flask equipped with a stir bar was charged with commercially available 2,7-dibromo-9,9'-dihexylfluorene (5.02 g, 10.2 mmol) and the flask was evacuated and refilled with N₂ three times. Anhydrous THF (75 mL) was added into the flask, and the solution was cooled to -78 °C. Using a syringe, *n*BuLi (2.5 M hexanes, 12 mL, 30 mmol) was slowly added. The reaction became cloudy and was stirred at -78 °C for 1 h. Anhydrous DMF (4.6 mL, 60 mmol) in a solution of anhydrous THF (15 mL) was added via syringe. The reaction was allowed to warm to room temperature and stirred for 20 h. The reaction was quenched with 50 mL 1 M HCl and extracted with diethyl ether. The combined organics were washed with water and dried over Na₂SO₄. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography with hexanes/ethyl acetate to afford the 9,9'-dihexyl-9H-fluorene-2,7-dicarbaldehyde as white solid in 70% yield.

To a stirred solution of 9,9'-dihexyl-9H-fluorene-2,7-dicarbaldehyde (2.73 g, 7 mmol) in a 3:1 THF/MeOH mixture (64 mL), NaBH₄ (2.12 g, 56 mmol) was added at 0 °C, and then the reaction mixture was allowed to warm to room temperature for 4 h. The reaction was quenched with aqueous NH₄Cl solution, and the aqueous layer was extracted with ethyl acetate. The organic layer was then dried over anhydrous Na₂SO₄, and solvents were evaporated to give a crude mixture, the residue was used in the next step without further purification.

The obtained residue was dissolved in 30 mL benzene, PBr₃ (1.7 mL, 18 mmol) was slowly added at room temperature, then the reaction mixture was heated to 45 °C for 6 h. The reaction was quenched with water and extracted with dichloromethane. The organic layer was dried over anhydrous Na₂SO₄, and solvents were evaporated to give a crude mixture, which was purified by flash column chromatography with hexanes/ethyl acetate to afford the compound **A1** as a white solid (1.5 g, 48%). 2,7-Bis(bromomethyl)-9,9-dihexyl-9H-fluorene (**A1**) were confirmed by comparing their ¹H and ¹³C NMR spectra with literatures.²

A1: m.p. 44-45 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.65-7.63 (m, 2H), 7.37-7.35 (m, 4H), 4.60 (s, 4H), 1.97-1.93 (m, 4H), 1.16-1.01 (m, 12H), 0.77 (t, *J* = 7.0 Hz, 6H),

0.68-0.57 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.6, 140.7, 136.9, 128.0, 123.6, 120.0, 55.1, 40.1, 34.4, 31.3, 29.5, 23.6, 22.5, 14.0; HRMS (ESI, m/z): calcd for $\text{C}_{27}\text{H}_{40}\text{Br}_2\text{N}$ [$\text{M}+\text{NH}_4$] $^+$: **536.1528**, found 536.1527.

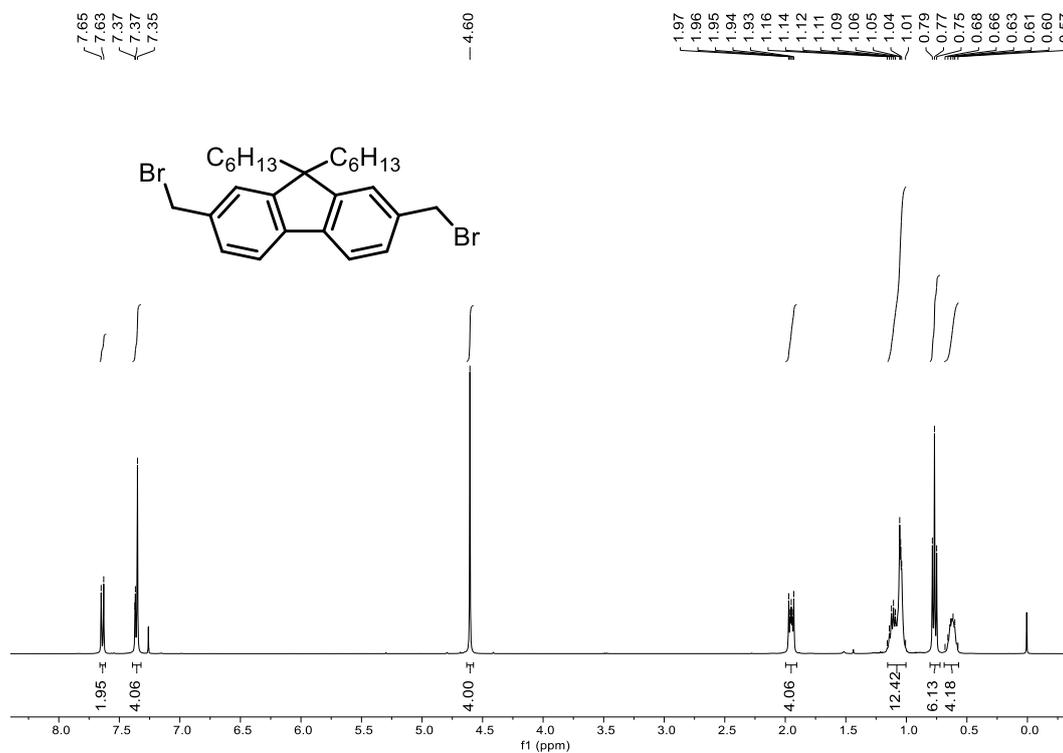


Figure S1. ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of **A1**

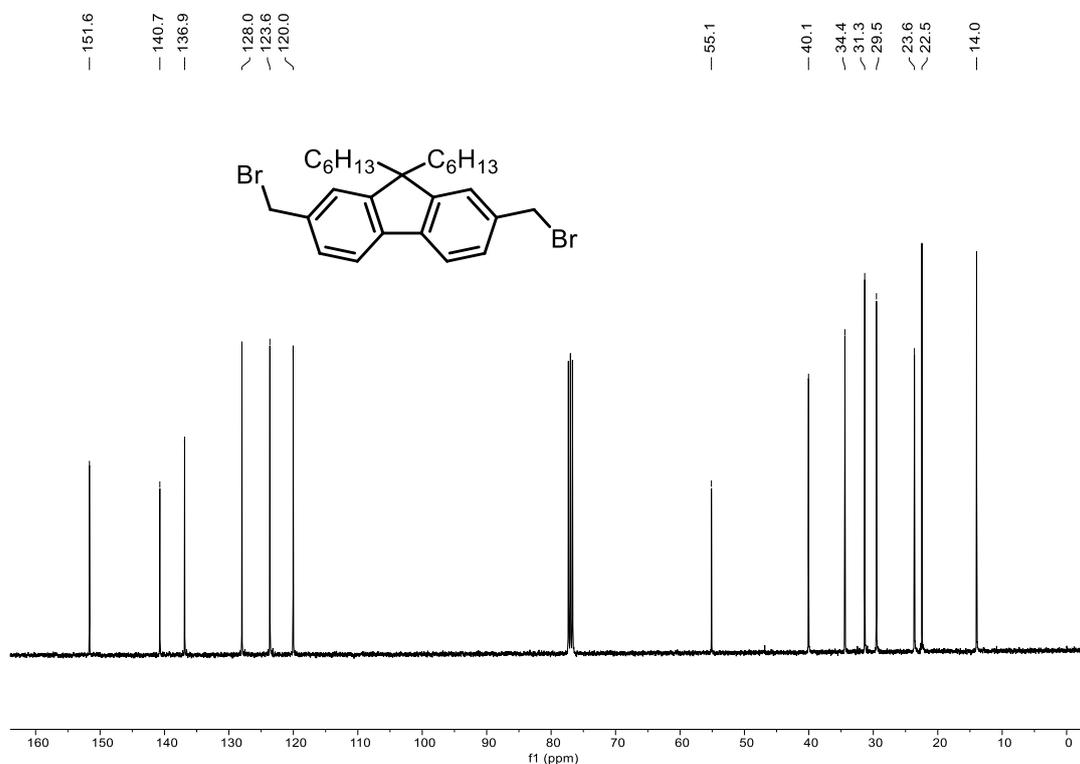
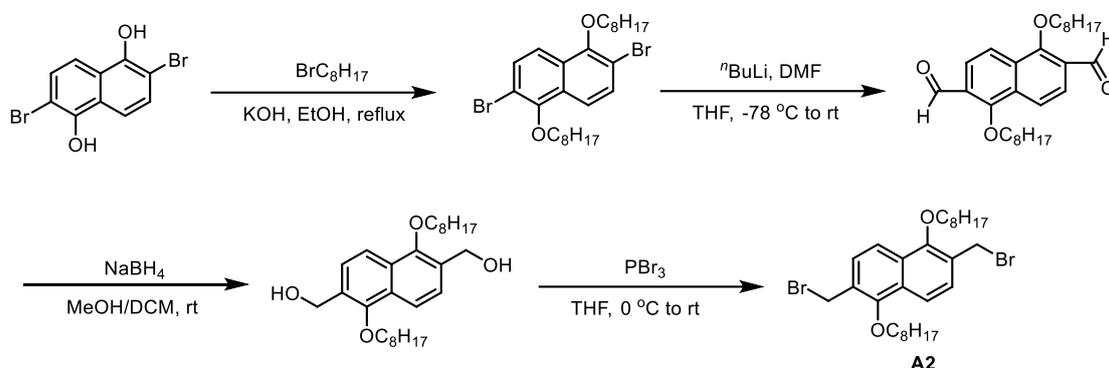


Figure S2. ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$) of **A1**

2.2 Synthesis and characterization of A2

The procedures were carried out according to the literature procedures with slight modifications.³



A solution of commercially available 2,6-dibromo-1,5-dihydroxynaphthalene (5.0 g, 15.7 mmol) and KOH (2.6 g, 47 mmol) in anhydrous ethanol (100 mL) was heated to reflux. Octyl bromide (8.2 mL, 47 mmol) was added slowly, and the solution was refluxed for 12 h. The reaction mixture was cooled and filtered. The solid was then stirred in water (200 mL) for 1 h, filtered, and dried under vacuum, which was purified by flash column chromatography with hexanes/ethyl acetate to afford the 2,6-dibromo-1,5-bis(octyloxy)naphthalene as a yellow solid in 50% yield.

2,6-dibromo-1,5-bis(octyloxy)naphthalene (2.17 g, 4 mmol) was dissolved in anhydrous THF (60 mL) and stirred under a nitrogen atmosphere. The mixture was cooled to $-78\text{ }^\circ\text{C}$ and $n\text{-BuLi}$ (2.5 M hexanes, 4.8 mL, 12 mmol) was added dropwise over a period of 10 minutes and stirred for additional 2 hours. After this period, anhydrous DMF (1.85 mL, 24 mmol) was added all at once to the mixture. The solution was then allowed to warm to room temperature and stirred for 3 h. The solvent was evaporated and extracted with dilute aqueous HCl and ether. The organic layers were combined, dried with Na_2SO_4 , filtered and evaporated. The crude residue was purified by flash column chromatography with hexanes/ethyl acetate to afford the 1,5-bis(octyloxy)naphthalene-2,6-dicarbaldehyde as a yellow solid in 58% yield.

Under a nitrogen atmosphere, NaBH_4 (212 mg, 5.6 mmol) were added to a mixture of methanol (30 mL) and DCM (30 mL) and the suspension was stirred for 5 minutes. 1,5-Bis(octyloxy)naphthalene-2,6-dicarbaldehyde (987 mg, 2.24 mmol) was added to the former mixture and was stirred for 3h at room temperature. After this time, the mixture was extracted with saturated NaHCO_3 solution and DCM, dried over Na_2SO_4 , and then evaporated. The crude compound was purified by column chromatography using ethyl acetate/DCM to give (1,5-bis(octyloxy)naphthalene-2,6-diyl)dimethanol as a white solid in 88% yield.

(1,5-Bis(octyloxy)naphthalene-2,6-diyl)dimethanol (843 mg, 1.91 mmol) was dissolved in anhydrous THF (55 mL) under a nitrogen atmosphere. The mixture was then cooled to $0\text{ }^\circ\text{C}$ and PBr_3 (0.54 mL, 5.74 mmol) was added for 10 minutes. The mixture was allowed to warm to room temperature and stirred overnight. The mixture was extracted with water and DCM. The organic layers were combined, washed with

water, dried with Na_2SO_4 , filtered and evaporated. The crude compound was purified by column chromatography using hexanes/DCM to give 2,6-bis(bromomethyl)-1,5-bis(octyloxy)naphthalene (**A2**) as a white solid in 76% yield. **A2** were confirmed by comparing their ^1H and ^{13}C NMR spectra with those reported in the literature.³

A2: m.p. 90-91 °C, ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 8.7$ Hz, 2H), 7.49 (d, $J = 8.7$ Hz, 2H), 4.74 (s, 4H), 4.10 (t, $J = 6.6$ Hz, 4H), 2.00-1.93 (m, 4H), 1.65-1.56 (m, 4H), 1.47-1.32 (m, 16H), 0.92-0.89 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.9, 129.9, 128.4, 127.4, 119.2, 75.5, 31.8, 30.4, 29.5, 29.3, 28.2, 26.1, 22.7, 14.1; HRMS (ESI, m/z): calcd for $\text{C}_{28}\text{H}_{46}\text{Br}_2\text{NO}_2$ [$\text{M}+\text{NH}_4$] $^+$: 586.1895, found 586.1897.

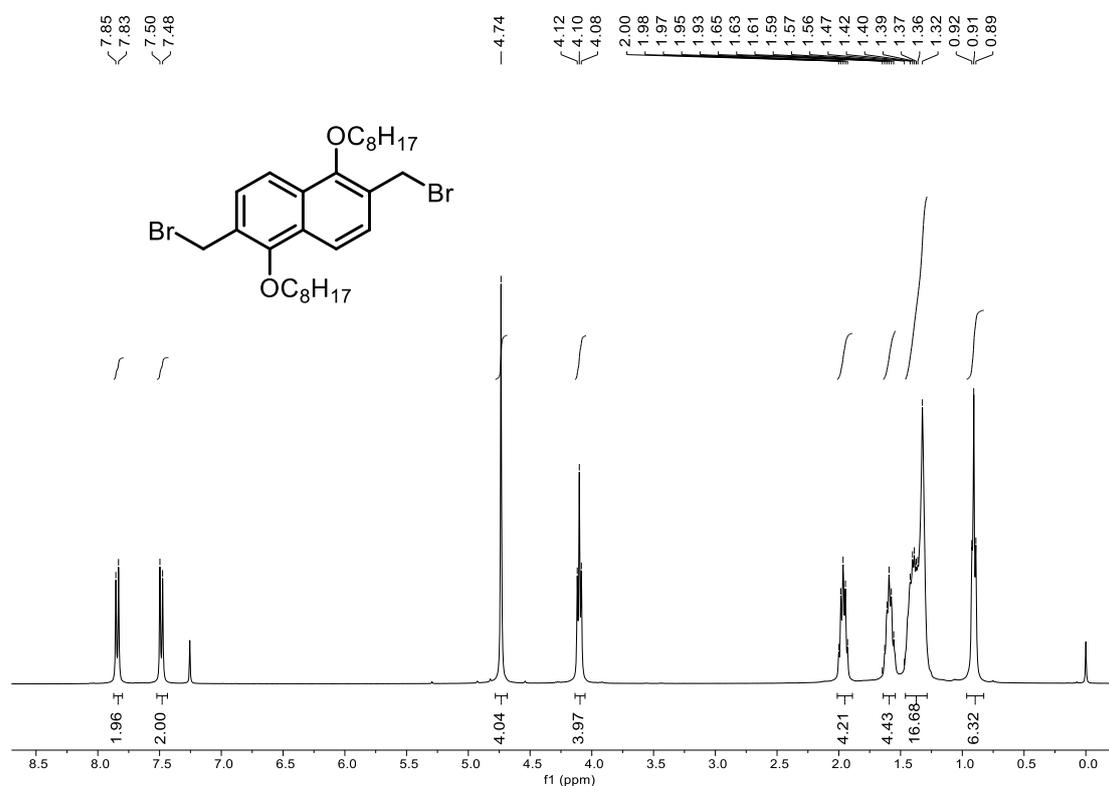


Figure S3. ^1H NMR (400 MHz, CDCl_3 , 25 °C) of **A2**

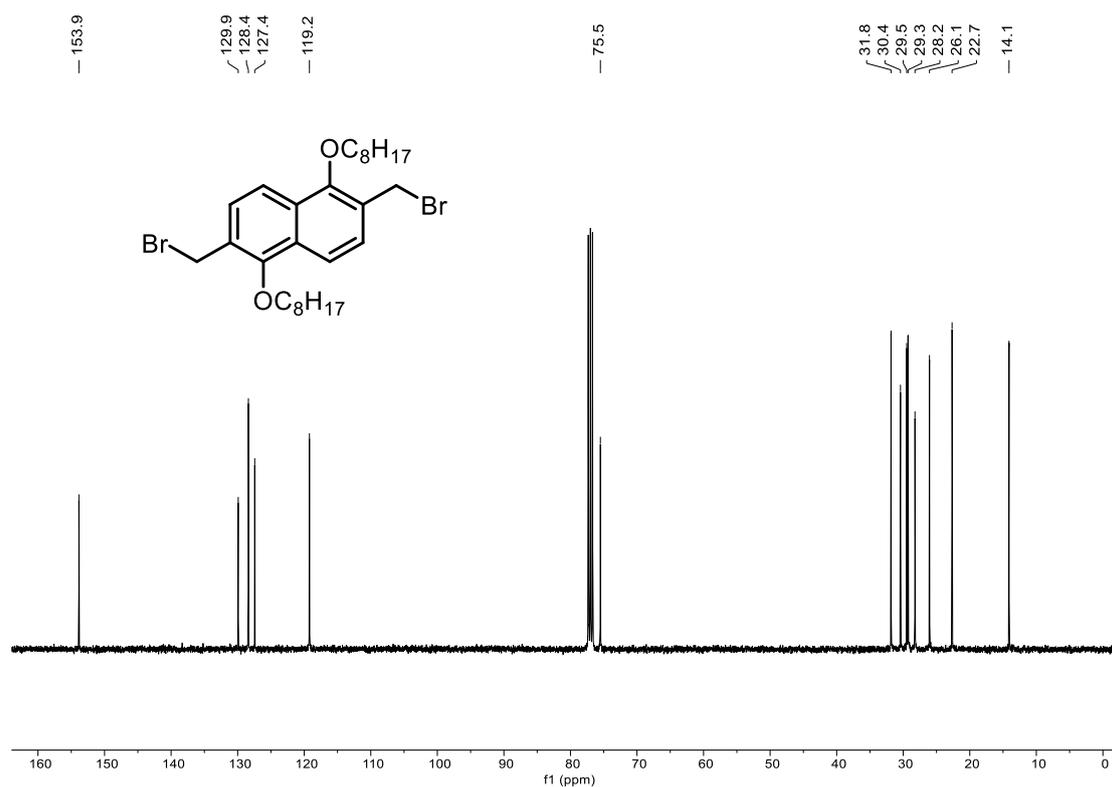
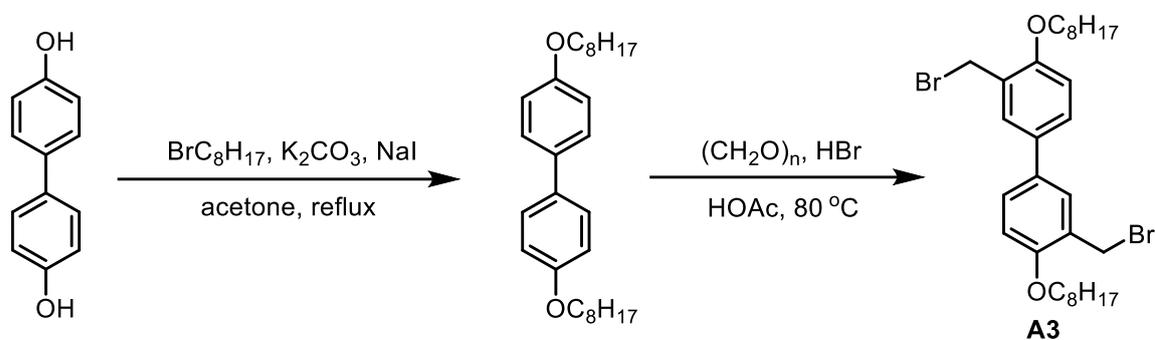


Figure S4. ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$) of **A2**

2.3 Synthesis and characterization of **A3**



The procedures were carried out according to a literature procedure with slight modifications.⁴

Anhydrous potassium carbonate (16.6 g, 120 mmol), 1-bromooctane (8.6 mL, 50 mmol), and a catalytic amount of sodium iodide (1 mmol, 150 mg) were added to a solution of 4,4'-dihydroxy-1,1'-biphenyl (3.7 g, 20 mmol) in 50 mL acetone. The mixture was refluxed for 48 h. After, it was poured into ice water. The product was filtered, washed with water, and dried. After recrystallization from acetone, 4,4'-bis(octyloxy)-1,1'-biphenyl was obtained as white solid in 88% yield.

To a suspension of 4,4'-dioctyloxy-1,1'-biphenyl (4.1 g, 10 mmol) and paraformaldehyde (1.5 g, 50 mmol) in 60 mL of acetic acid, 14 mL of 31% HBr in

one portion was added at 80 °C under nitrogen atmosphere. The reaction mixture became clear immediately. The reaction was stirred for 4 h at 80 °C. It was then cooled to room temperature. The solid product was filtered and washed with water. The organic layer was dissolved in dichloromethane, neutralized with aqueous sodium bicarbonate solution, and dried. The solvent was evaporated and recrystallized from acetone/hexane, 3,3'-bis(bromomethyl)-4,4'-bis(octyloxy)-1,1'-biphenyl (**A3**) was obtained as white solid in 50% yield. **A3** were confirmed by comparing their ¹H and ¹³C NMR spectra with literatures.⁴

A3: m.p. 89-90 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, *J* = 2.4 Hz, 2H), 7.44 (dd, *J* = 8.5, 2.4 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 4.62 (s, 4H), 4.06 (t, *J* = 6.4 Hz, 4H), 2.00-1.93 (m, 4H), 1.59-1.50 (m, 4H), 1.35-1.31 (m, 16H), 0.95-0.85 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 156.2, 132.7, 129.1, 128.2, 126.5, 112.1, 68.4, 31.8, 29.3, 29.2, 29.1, 26.1, 22.7, 14.1; HRMS (ESI, *m/z*): calcd for C₃₀H₄₈Br₂NO₂ [M+NH₄]⁺: **612.2052**, found 612.2048.

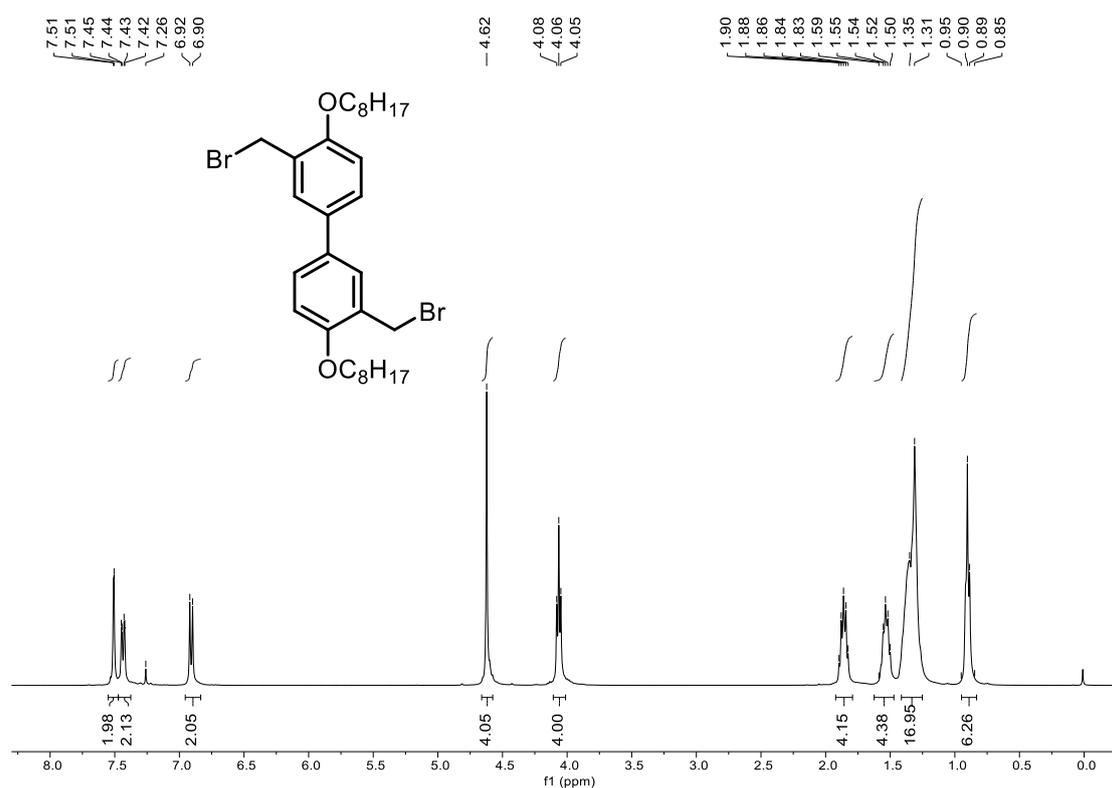


Figure S5. ¹H NMR (400 MHz, CDCl₃, 25 °C) of **A3**

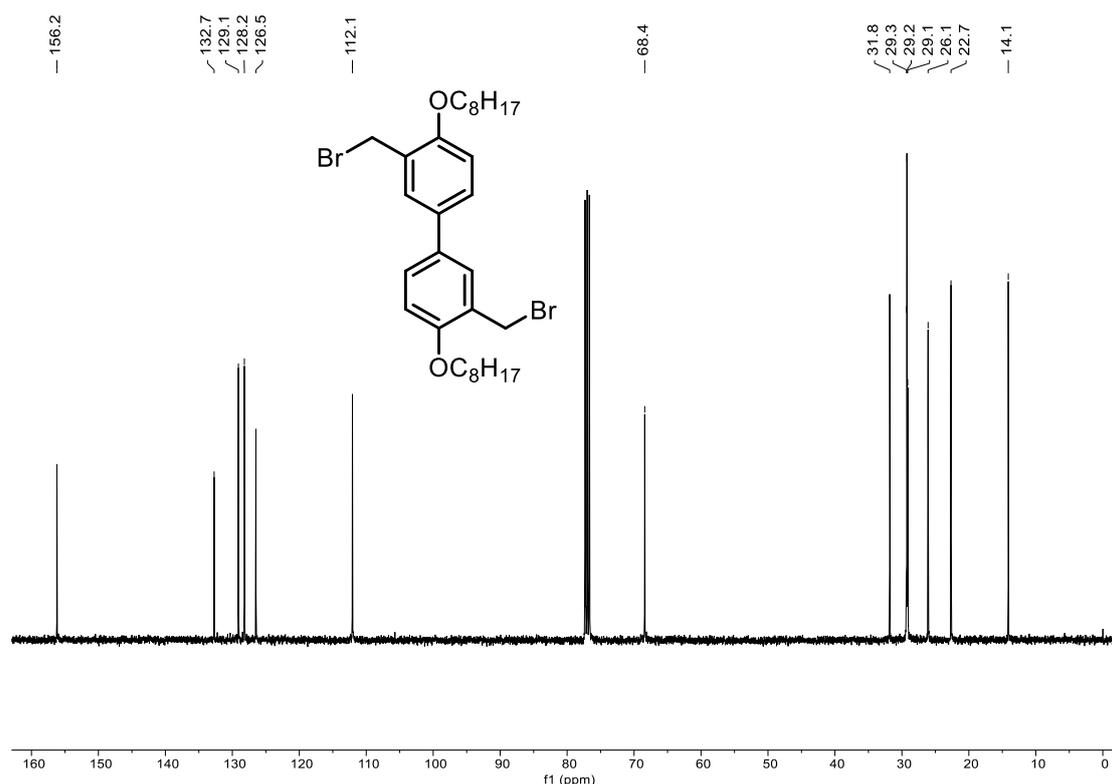
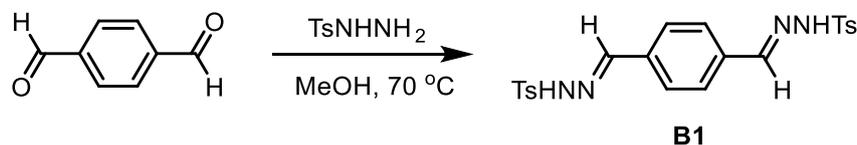


Figure S6. ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$) of **A3**

2.4 Synthesis and characterization of **B1**



A mixture of terephthalaldehyde (670 mg, 5 mmol) and TsNHNH_2 (1.86 g, 10 mmol) in MeOH (10 mL) was heated to 70 $^\circ\text{C}$ until the dialdehyde compound disappeared. The *N*-tosylhydrazones precipitated during the reaction. The precipitate was washed twice with MeOH, *N',N''*-((1*Z*,1'*Z*)-1,4-phenylenebis(methaneylylidene)) bis(4-methylbenzenesulfonylhydrazide) (**B1**) was obtained as white solid in 94% yield.

B1: m.p. 233-234 $^\circ\text{C}$, ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 11.54 (s, 2H), 7.89 (s, 2H), 7.76 (d, $J = 8.2$ Hz, 4H), 7.56 (s, 4H), 7.40 (d, $J = 8.0$ Hz, 4H), 2.35 (s, 6H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 146.1, 143.5, 136.1, 135.0, 129.7, 127.2, 127.1, 21.0.; HRMS (ESI, m/z): calcd for $\text{C}_{22}\text{H}_{23}\text{N}_4\text{O}_4\text{S}_2$ $[\text{M}+\text{H}]^+$: 471.1161, found 471.1155.

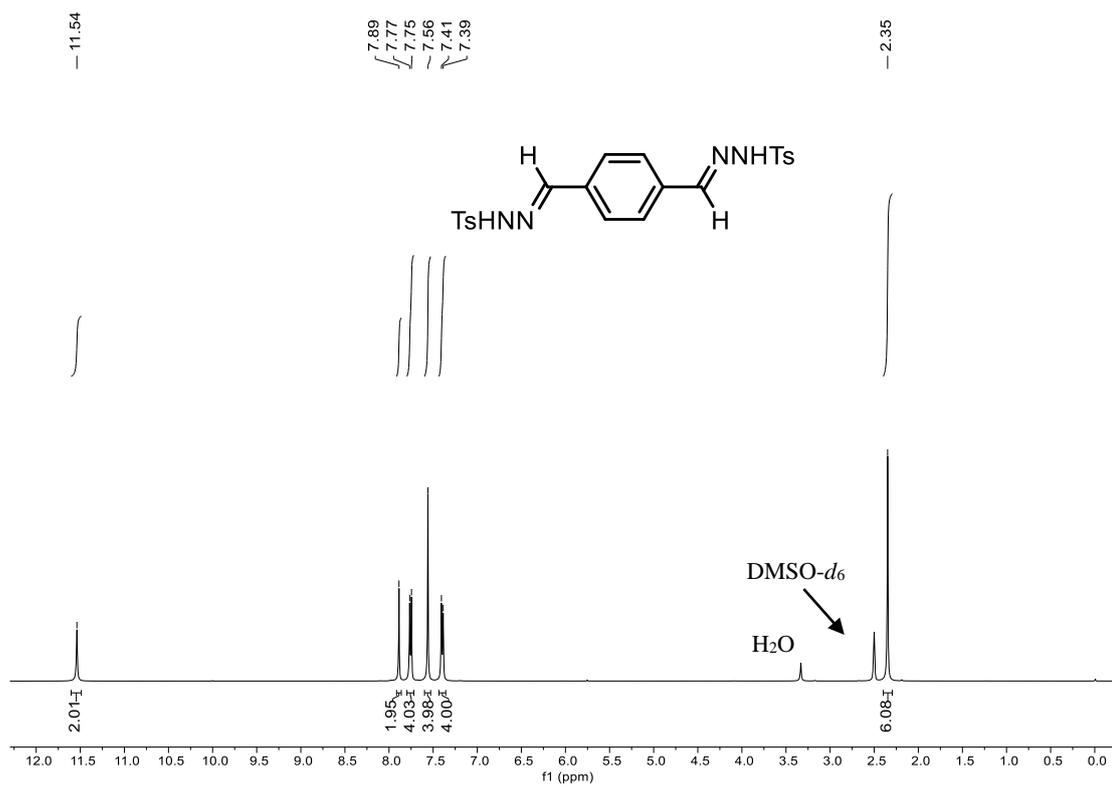


Figure S7. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$) of B1

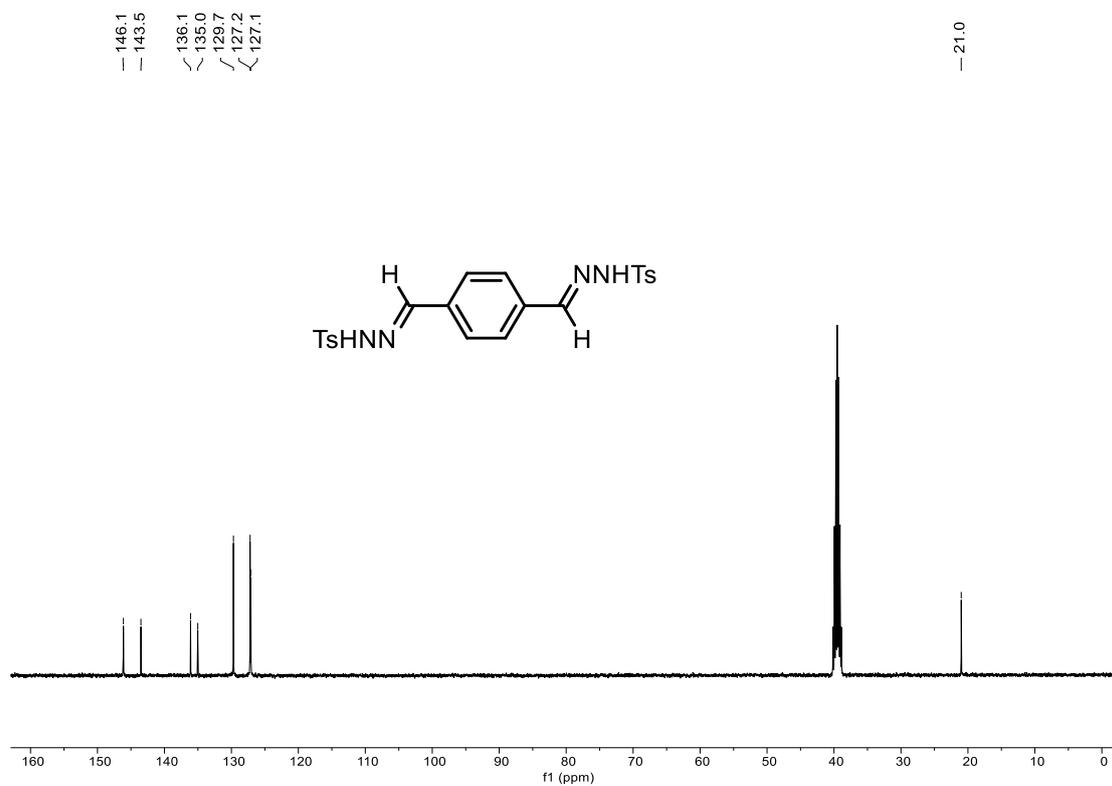
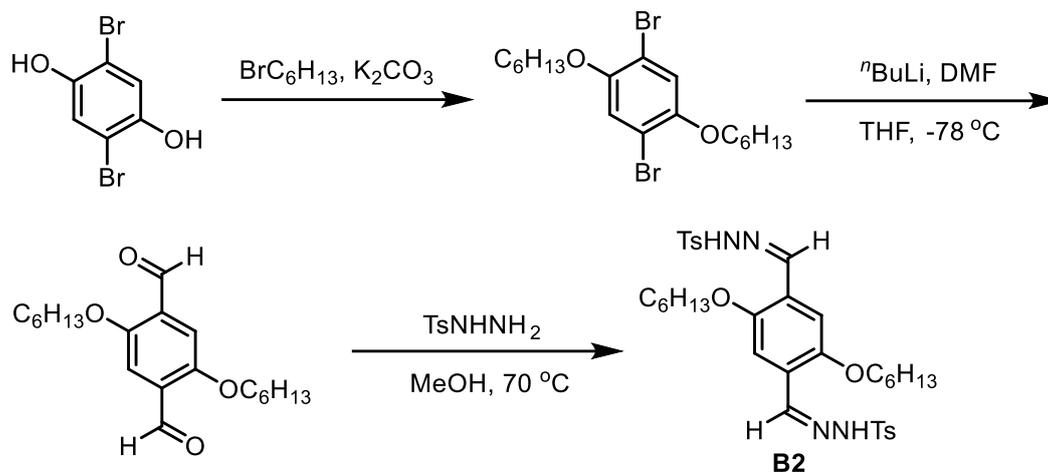


Figure S8. $^{13}\text{C NMR}$ (100 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$) of B1

2.5 Synthesis and characterization of **B2**



Anhydrous potassium carbonate (11.06 g, 80 mmol), 1-bromohexane (11.2 mL, 80 mmol) were added to a solution of 2,5-dibromobenzene-1,5-diol (5.36 g, 20 mmol) in 54 mL DMF. The mixture was heated to $110\text{ }^\circ\text{C}$ for 48 h. The reaction mixture was then poured into 270 mL of H_2O and the solid collected and recrystallized using EtOH to give 1,4-dibromo-2,5-bis(hexyloxy)benzene as white solid in 80% yield.⁵

1,4-dibromo-2,5-bis(hexyloxy)benzene (4.36 g, 10 mmol) was dissolved in anhydrous THF (40 mL) and stirred under a nitrogen atmosphere. The mixture was cooled to $-78\text{ }^\circ\text{C}$ and $n\text{BuLi}$ (2.5 M hexanes, 9.6 mL, 24 mmol) was added dropwise over a period of 10 minutes and stirred for additional 1 h. After this period, anhydrous DMF (2.3 mL, 30 mmol) was added all at once to the mixture. The solution was then allowed to warm to room temperature slowly and stirred for 8 hours. The reaction was quenched with H_2O and extracted with EA. The organic phase was collected and dried by Na_2SO_4 . Then the crude product was purified by a silica column with PE/EA as the eluent to afford 2,5-bis(hexyloxy)terephthalaldehyde as yellow solid in 40% yield.⁶ This compound was further reacted with *p*-toluenesulfonyl hydrazide with the same procedure as **B1** to afford **B2** in 90% yield as a yellow solid.

B2: m.p. $190\text{--}191\text{ }^\circ\text{C}$, $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 11.49 (s, 2H), 8.14 (s, 2H), 7.74 (d, $J = 7.9\text{ Hz}$, 4H), 7.38 (d, $J = 8.0\text{ Hz}$, 4H), 7.13 (s, 2H), 3.92 (s, 4H), 2.34 (s, 6H), 1.72–1.65 (m, 4H), 1.44–1.37 (m, 4H), 1.31–1.28 (m, 8H), 0.89–0.86 (m, 6H); $^{13}\text{C NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ 150.9, 143.5, 141.6, 136.0, 129.6, 127.3, 124.6, 108.7, 68.5, 31.0, 28.6, 25.1, 22.1, 21.0, 13.9; HRMS (ESI, m/z): calcd for $\text{C}_{34}\text{H}_{47}\text{N}_4\text{O}_6\text{S}_2$ $[\text{M}+\text{H}]^+$: 671.2937, found 671.2932.

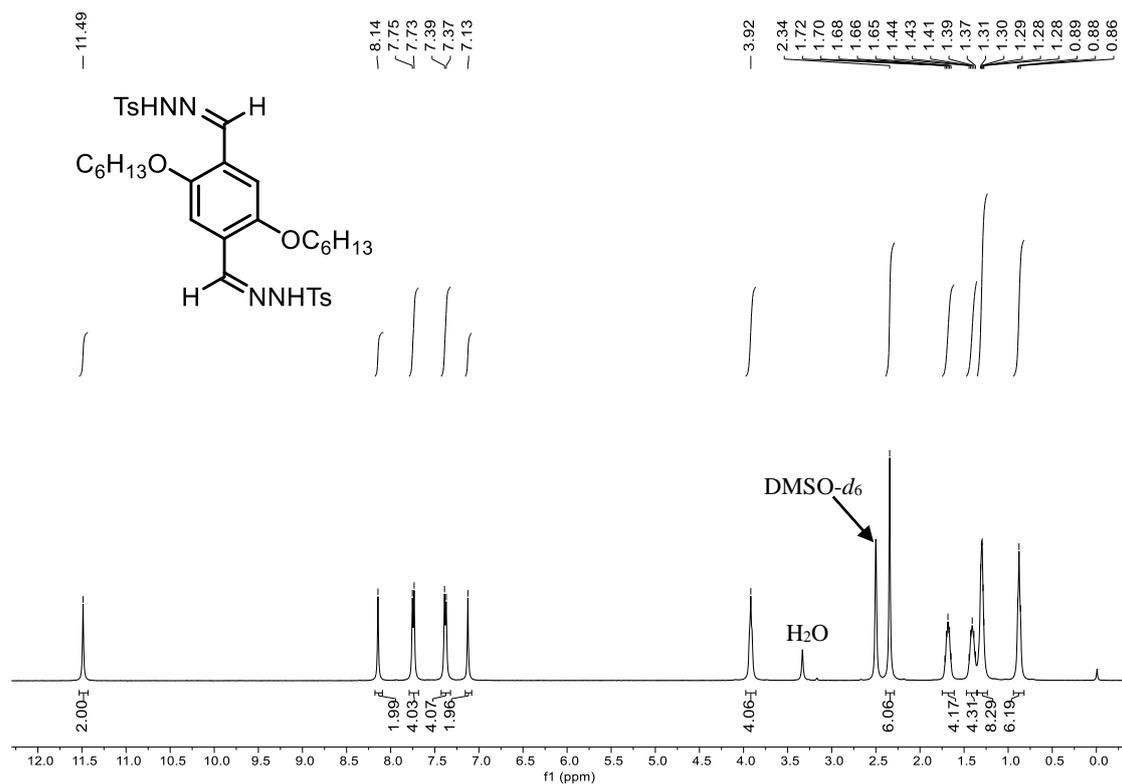


Figure S9. ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C) of B2

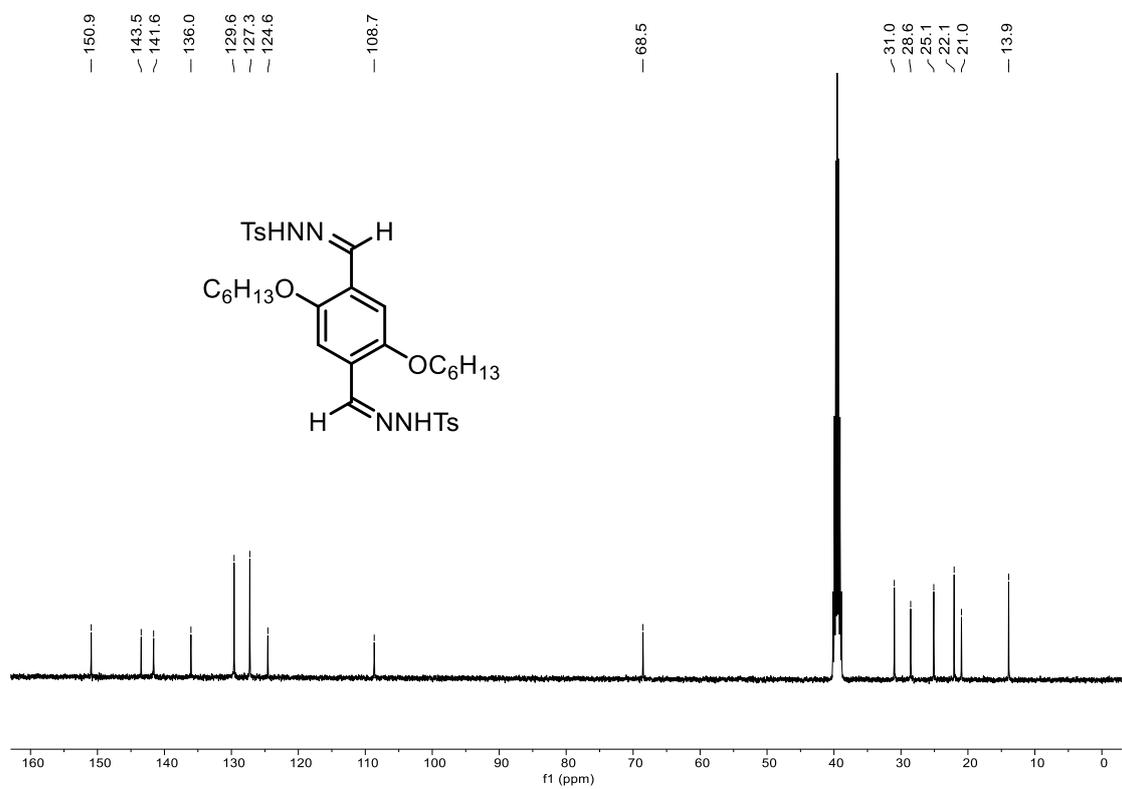
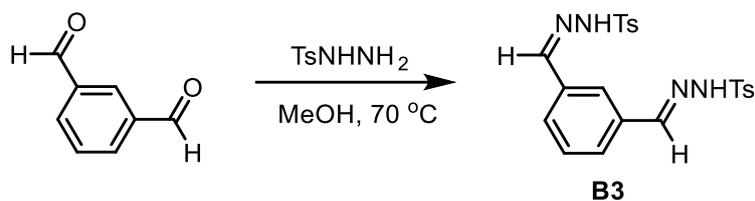


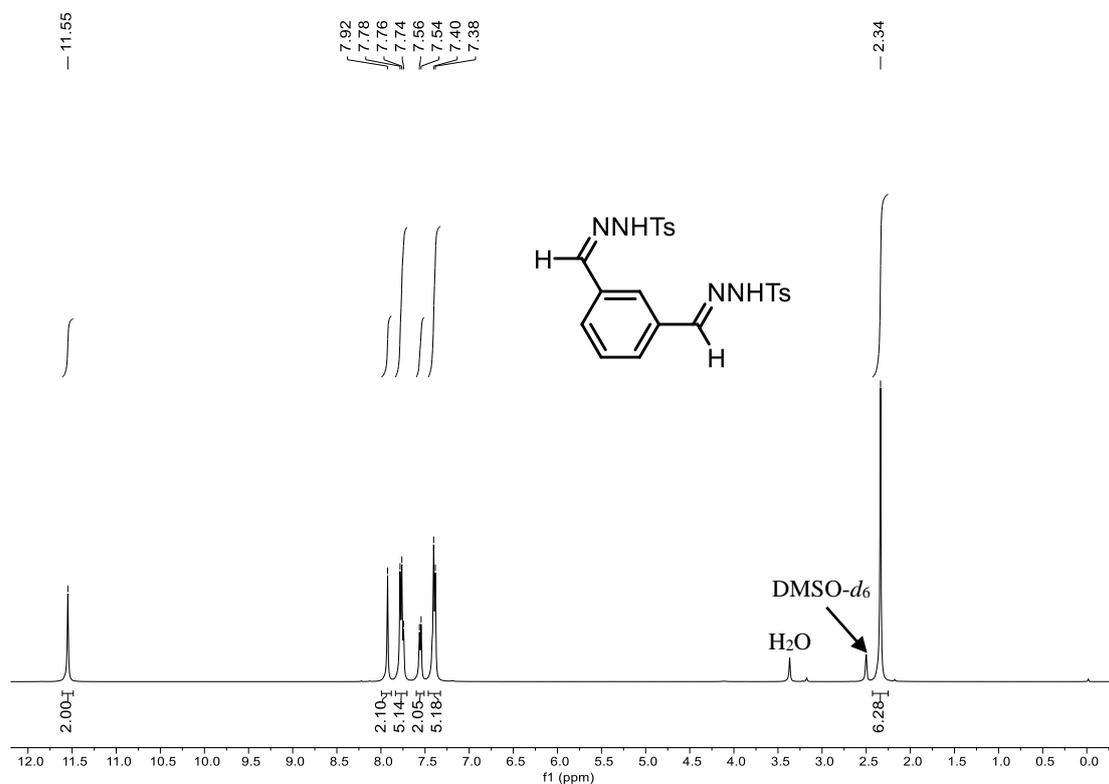
Figure S10. ¹³C NMR (100 MHz, DMSO-*d*₆, 25 °C) of B2

2.6 Synthesis and characterization of B3



A mixture of *m*-phthalaldehyde (670 mg, 5 mmol) and TsNHNH₂ (1.86 g, 10 mmol) in MeOH (10 mL) was heated to 70 °C until the dialdehyde compound disappeared. The *N*-tosylhydrazones precipitated during the reaction. The precipitate was washed twice with MeOH, *N',N'''*-((1*Z*,1'*Z*)-1,3-phenylenebis(methaneylylidene))bis(4-methylbenzenesulfonylhydrazide) (**B3**) was obtained as white solid in 65% yield.

B3: m.p. 175-176 °C, ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.55 (s, 2H), 7.92 (s, 2H), 7.78-7.74 (m, 5H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.40-7.38 (m, 5H), 2.34 (s, 6H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 146.3, 143.5, 136.1, 134.2, 129.7, 129.3, 128.3, 127.2, 124.5, 21.0; HRMS (ESI, *m/z*): calcd for C₂₂H₂₃N₄O₄S₂ [M+H]⁺: 471.1161, found 471.1151.



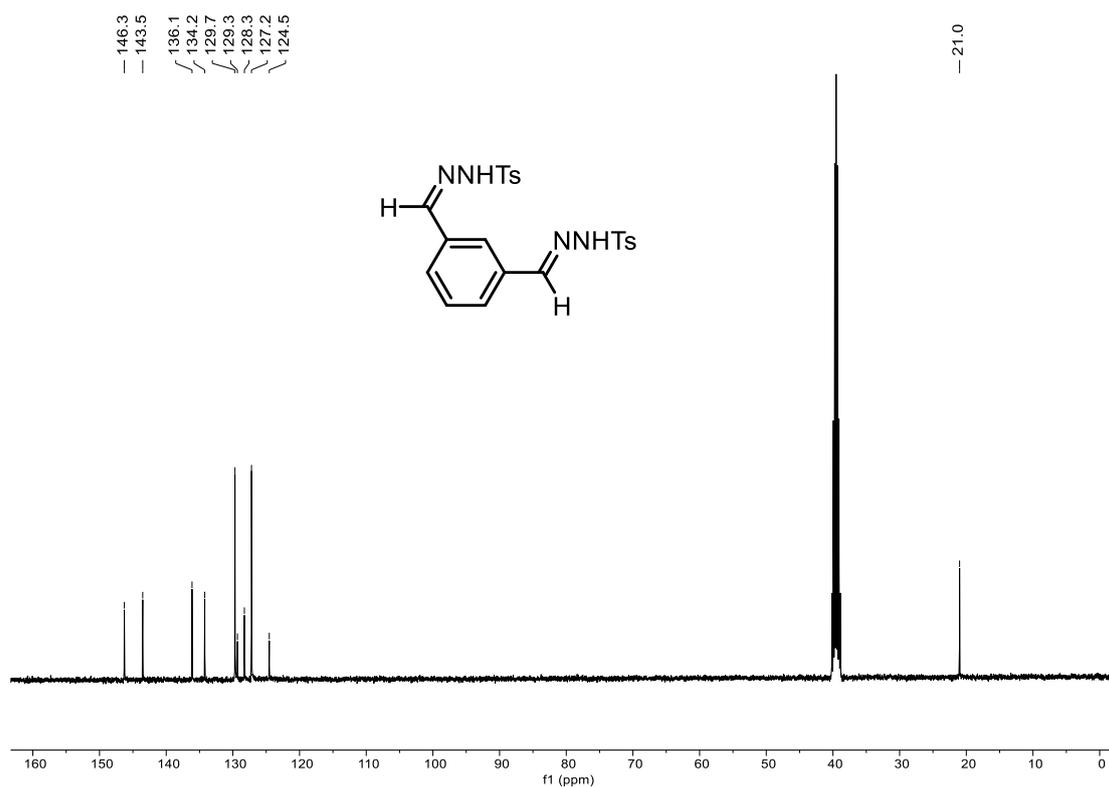
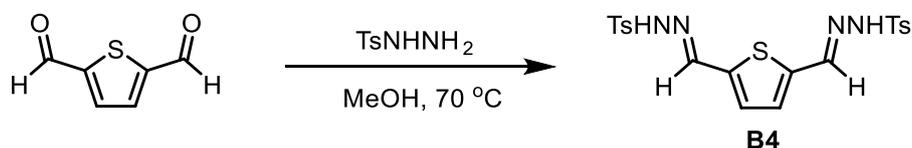


Figure S12. ¹³C NMR (100 MHz, DMSO-*d*₆, 25 °C) of **B3**

2.7 Synthesis and characterization of **B4**



A mixture of terephthalaldehyde (700 mg, 5 mmol) and TsNHNH₂ (1.86 g, 10 mmol) in MeOH (10 mL) was heated to 70 °C until the dialdehyde compound disappeared. The *N*-tosylhydrazones precipitated during the reaction. The precipitate was washed twice with MeOH, *N',N'''*-((1*Z*,1'*E*)-thiophene-2,5-diylbis(methaneylylidene))bis(4-methylbenzenesulfonylhydrazide) (**B4**) was obtained as yellow solid in 80% yield. **B4** were confirmed by comparing their ¹H and ¹³C NMR spectra with literatures.⁷

B4: m.p. 205-206 °C, ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.55 (s, 2H), 8.01 (s, 2H), 7.75 (d, *J* = 7.9 Hz, 4H), 7.42 (d, *J* = 7.9 Hz, 4H), 7.27 (s, 2H), 2.36 (s, 6H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 143.6, 141.6, 139.9, 135.9, 131.0, 129.7, 127.2, 21.0; HRMS (ESI, *m/z*): calcd for C₂₀H₂₁N₄O₄S₃ [M+H]⁺: 477.0725, found 477.0712.

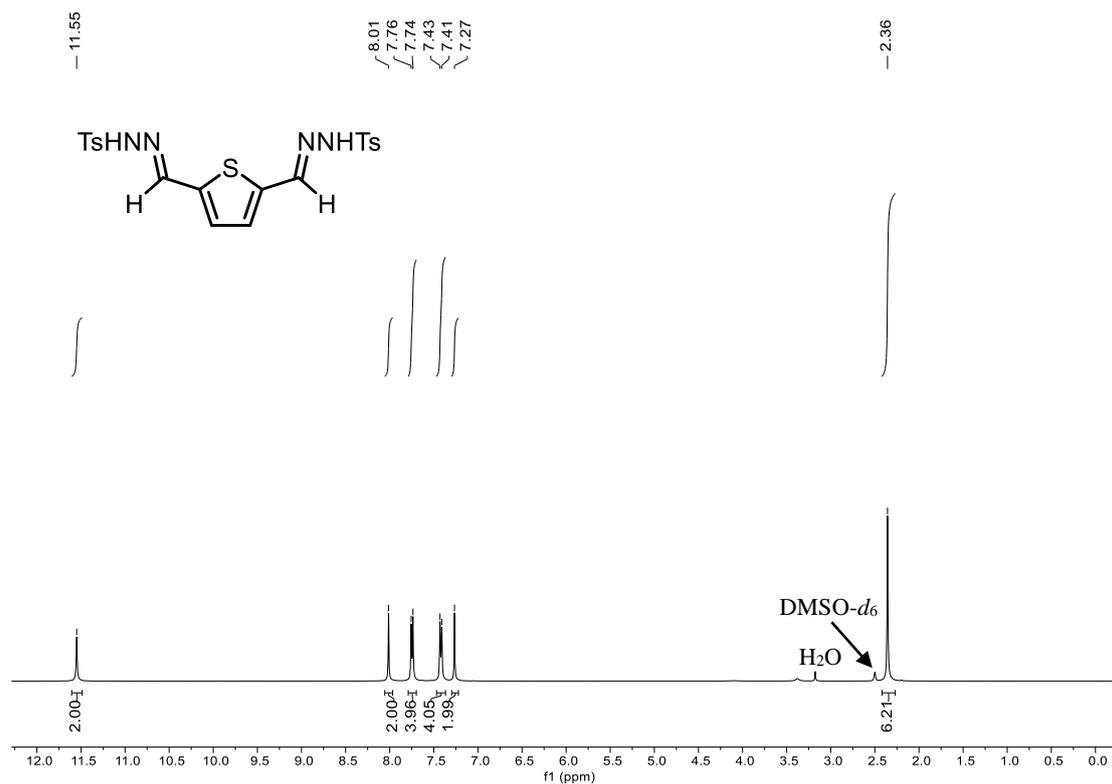


Figure S13. ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C) of **B4**

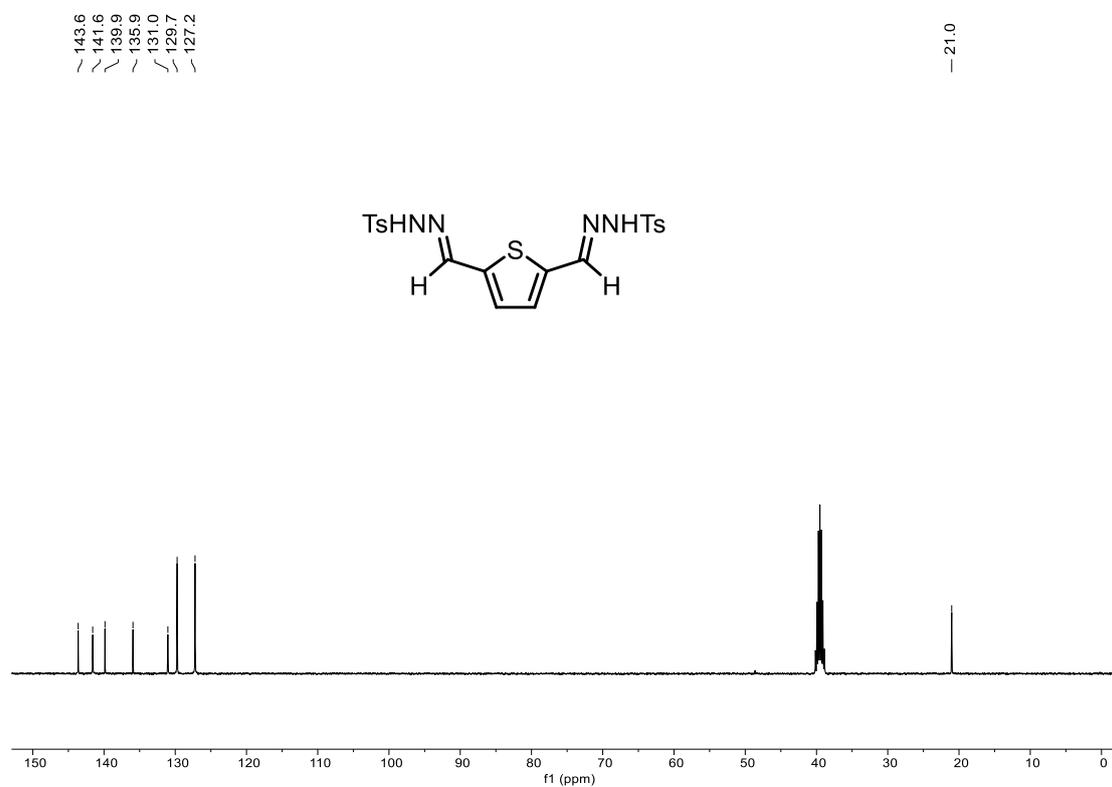
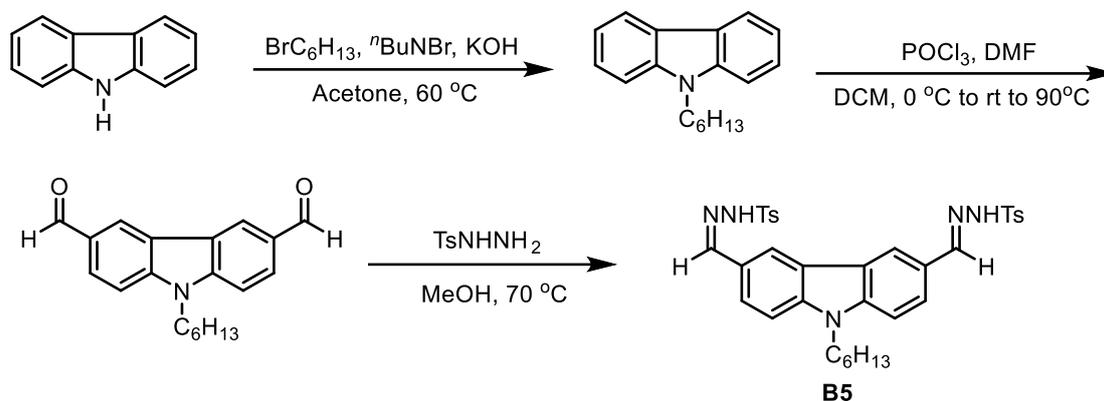


Figure S14. ¹³C NMR (100 MHz, DMSO-*d*₆, 25 °C) of **B4**

2.8 Synthesis and characterization of **B5**



A round-bottom flask equipped with a stir bar was charged with carbazole (3.34 g, 20 mmol) and 50 mL acetone. Then, 1-bromohexane (28 mmol, 3.93 mL), tetrabutylammonium bromide (0.58 g, 1.8 mmol) and potassium hydroxide (1.68 g, 30 mmol) were added into the flask, and the reaction mixture was stirred at $60\text{ }^\circ\text{C}$ for 4 h. After reaction, it was cooled to room temperature. The mixture was diluted with DCM. The organic layer was washed with brine, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by silica gel column chromatography with hexanes to afford 9-hexyl-9H-carbazole in 93% isolated yield.⁸

Phosphoryl chloride (16 mL, 0.17 mol) was added dropwise to DMF (22 mL, 0.28 mol) for 1 h at $0\text{ }^\circ\text{C}$. The mixture was stirred and then 9-hexyl-9H-carbazole (2.51 g, 10 mmol) in dichloromethane (12.5 mL) was added over 0.5 h at room temperature. After standing for 48 h at $90\text{ }^\circ\text{C}$, the mixture was poured into water, stirred overnight, and neutralized with sodium hydroxide. The solution was extracted three times with chloroform and dried with Na_2SO_4 . The solvent was removed under reduced pressure. Then the crude product was purified by a silica column with PE/EA as the eluent to afford 9-hexyl-9H-carbazole-3,6-dicarbaldehyde as yellow solid in 45% yield.⁹ This compound was further reacted with *p*-toluenesulfonyl hydrazide with the same procedure as **B1** to afford **B5** in 66% yield as a light red solid.

B5: m.p. $159\text{--}161\text{ }^\circ\text{C}$, ${}^1\text{H}$ NMR (400 MHz, $\text{DMSO-}d_6$) δ 11.31 (s, 2H), 8.35 (s, 2H), 8.08 (s, 2H), 7.82 (d, $J = 7.9\text{ Hz}$, 4H), 7.73 (d, $J = 8.6\text{ Hz}$, 2H), 7.62 (d, $J = 8.6\text{ Hz}$, 2H), 7.40 (d, $J = 7.9\text{ Hz}$, 4H), 4.36 (t, $J = 7.0\text{ Hz}$, 2H), 2.33 (s, 6H), 1.72–1.69 (m, 2H), 1.21–1.15 (m, 6H), 0.78–0.74 (m, 3H); ${}^{13}\text{C}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 148.2, 143.3, 141.4, 136.3, 129.6, 127.3, 125.3, 124.2, 122.0, 120.5, 110.2, 42.5, 30.9, 28.5, 26.0, 22.0, 21.0, 13.8; HRMS (ESI, m/z): calcd for $\text{C}_{34}\text{H}_{38}\text{N}_5\text{O}_4\text{S}_2$ $[\text{M}+\text{H}]^+$: 644.2365, found 644.2357.

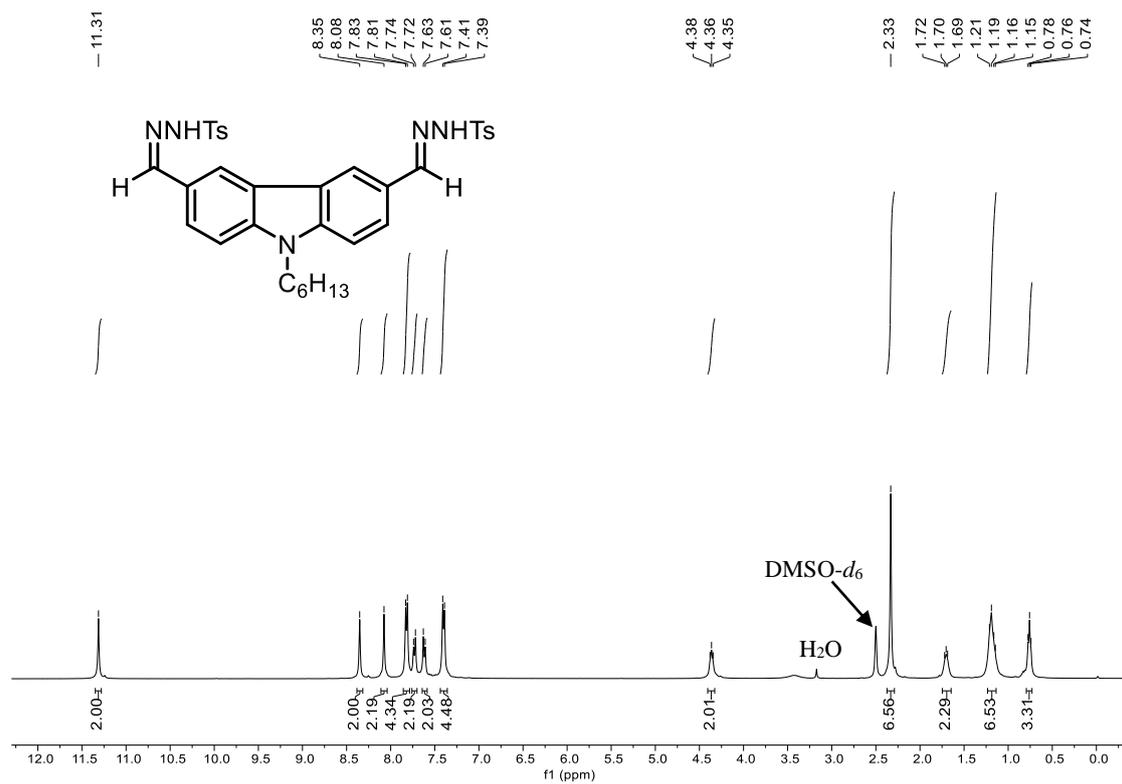


Figure S15. ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C) of **B5**

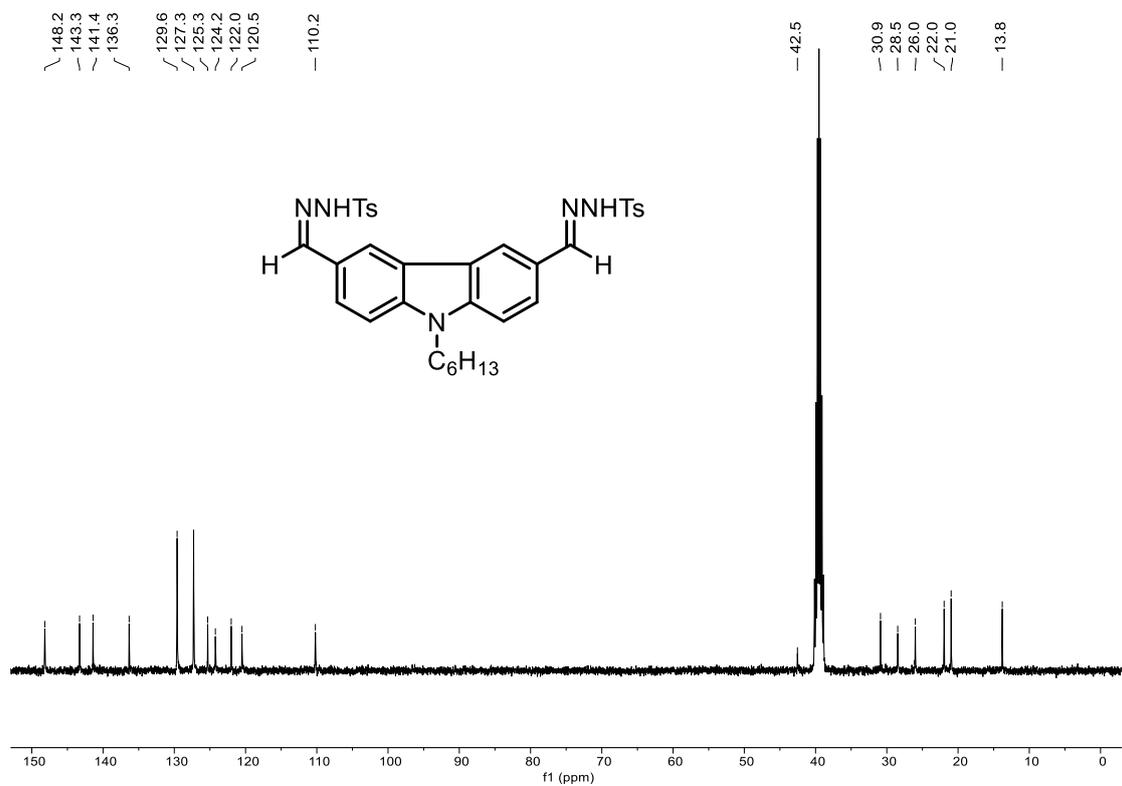
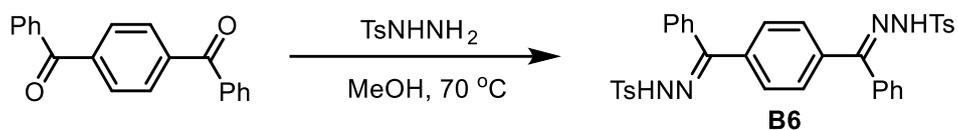


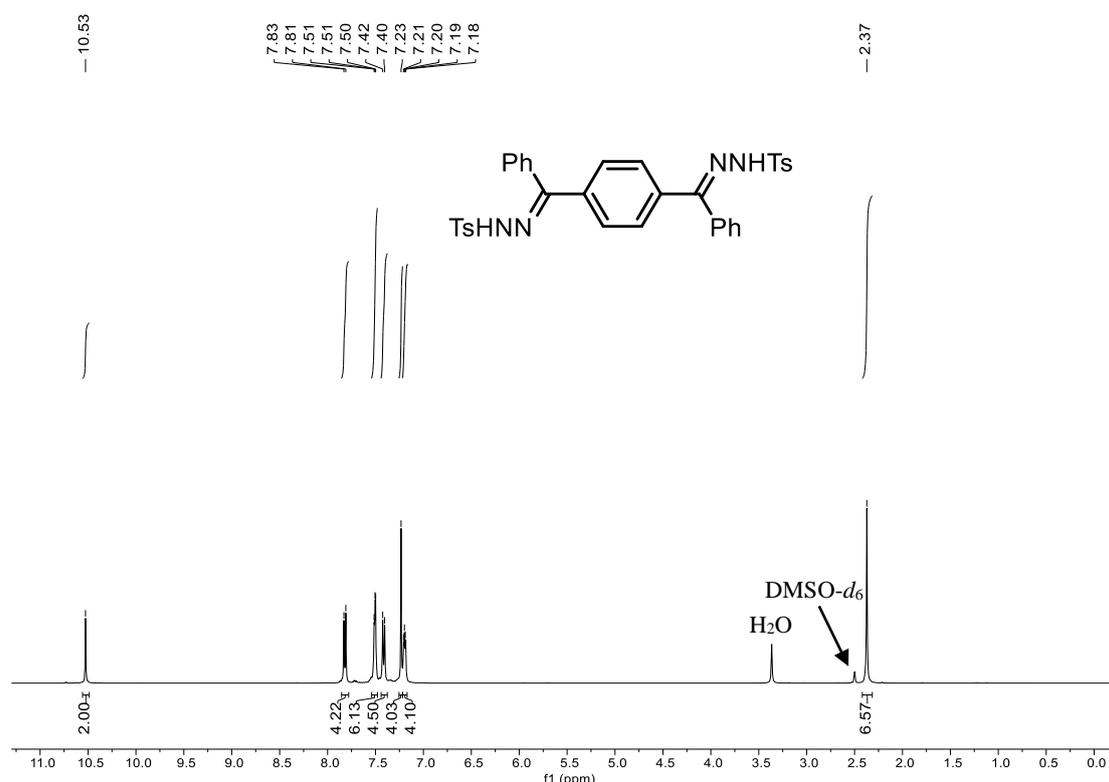
Figure S16. ¹³C NMR (100 MHz, DMSO-*d*₆, 25 °C) of **B5**

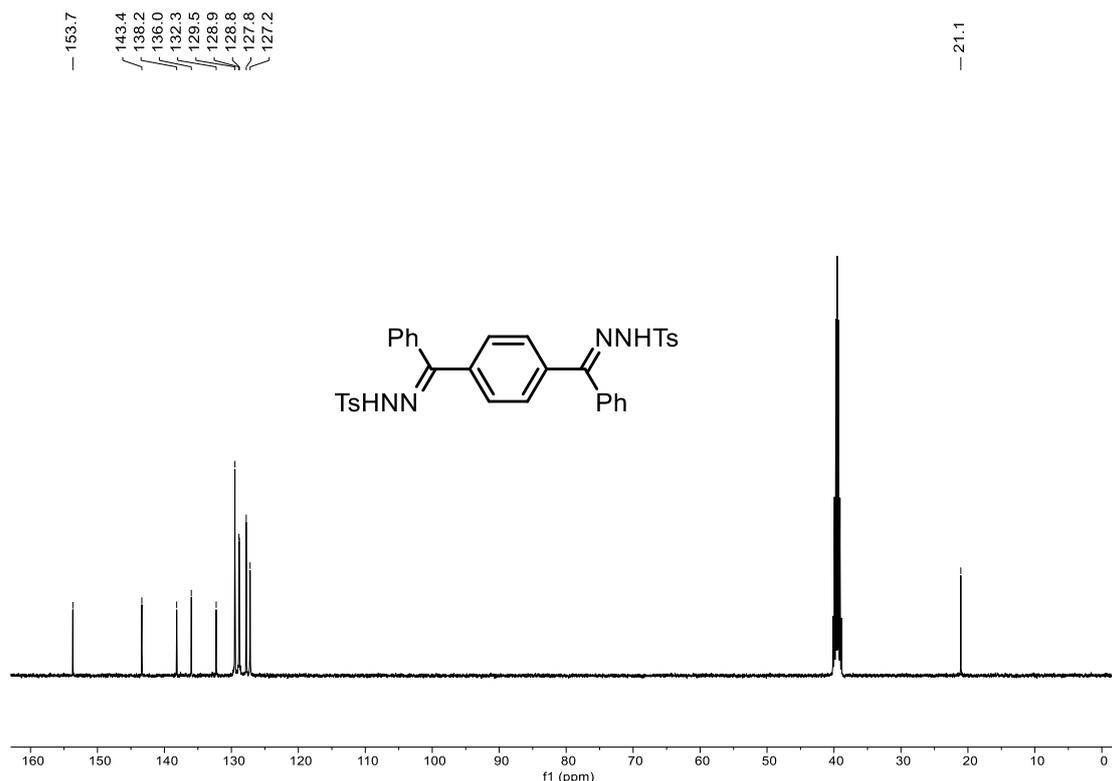
2.9 Synthesis and characterization of **B6**



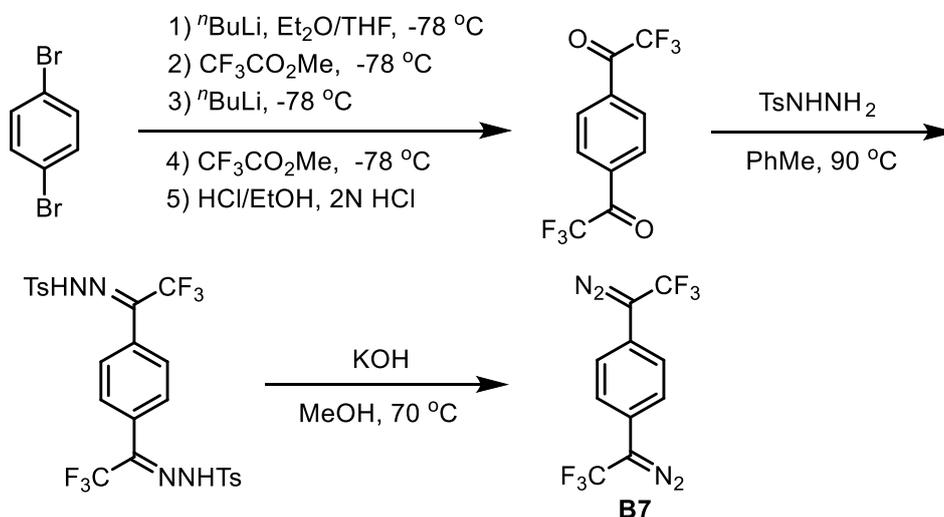
A mixture of 1,4-phenylenebis(phenylmethanone) (1.43 g, 5 mmol) and TsNHNH₂ (1.86 g, 10 mmol) in MeOH (10 mL) was heated to 70 °C until the carbonyl compound disappeared. The *N*-tosylhydrazones precipitated during the reaction. The precipitate was washed twice with MeOH, *N',N'''*-((1*Z*,1'*Z*)-1,4-phenylenebis(phenylmethanylylidene))bis(4-methylbenzenesulfonylhydrazide) (**B6**) was obtained as yellow solid in 63% yield.

B6: m.p. 249-251 °C, ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.53 (s, 2H), 7.82 (d, *J* = 8.0 Hz, 4H), 7.51-7.50 (m, 6H), 7.41 (d, *J* = 8.0 Hz, 4H), 7.23 (s, 4H), 7.23-7.18 (m, 4H), 2.37 (s, 6H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 153.7, 143.4, 138.2, 136.0, 132.3, 129.5, 128.9, 128.8, 127.8, 127.2, 21.1; HRMS (ESI, *m/z*): calcd for C₃₄H₃₁N₄O₄S₂ [M+H]⁺: **623.1787**, found 623.1781.





2.10 Synthesis and characterization of **B7**



Into a Et_2O (44 ml) and THF (44 ml) solution of 1,4-dibromobenzene (4.72 g, 20 mmol) was slowly added $n\text{BuLi}$ (8 mL of a 2.50 M hexane solution, 20 mmol) at $-78\text{ }^\circ\text{C}$ over 10 min. Methyl trifluoroacetate (2.56 g, 20 mmol) was slowly added at $-78\text{ }^\circ\text{C}$ during 10 min. A colorless solution was obtained. After 30 min, $n\text{BuLi}$ (9.6 mL of a 2.50 M hexane solution, 24 mmol) was slowly added to the above solution at $-78\text{ }^\circ\text{C}$ over 10 min. Methyl trifluoroacetate (3.84 g, 30 mmol) was added over a period of 10 min. After an additional 10 min, the solution was hydrolyzed with precooled ($-78\text{ }^\circ\text{C}$) concentrated HCl (3.3 ml) dissolved in ethanol (1.7 ml). The

solution was then poured in 2 N HCl (100 ml), phase separated and dried with Na₂SO₄. Then the crude product was purified by a silica column with PE/EA as the eluent to afford product in 61% yield.¹⁰

A mixture of (1.43 g, 5 mmol) and TsNHNH₂ (1.86 g, 10 mmol) in PhMe (10 mL) was heated to 90 °C until the carbonyl compound disappeared. The *N*-tosylhydrazones precipitated during the reaction. The precipitate was washed twice with MeOH, *N,N'*-(1,4-phenylenebis(2,2,2-trifluoroethan-1-yl-1-ylidene))bis(4-methylbenzene sulfonohydrazide) was obtained as white solid in 63% yield.

N,N'-(1,4-phenylenebis(2,2,2-trifluoroethan-1-yl-1-ylidene))bis(4-methylbenzene sulfonohydrazide) was dissolved in a 0.4 M solution of potassium hydroxide (561 mg, 5.00 mmol, 2.00 equiv) in MeOH (25.0 mL). A condenser was attached and the reaction mixture was stirred at 70 °C for 1 h. Then, the reaction was cooled to room temperature and diluted with water. The crude product was extracted with DCM, dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude was purified by silica gel chromatography using pentane as eluent to afford 1,4-bis(1-diazo-2,2,2-trifluoroethyl)benzene (**B7**) as a red solid in 16% yield.

B7: m.p. 42-43 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.12 (s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 125.4 (q, *J* = 270 Hz), 123.2, 121.1; ¹⁹F NMR (470 MHz, CDCl₃) δ -57.42; IR (film): 2074 (C=N₂), 1519, 1350, 1324, 1108, 958 cm⁻¹.

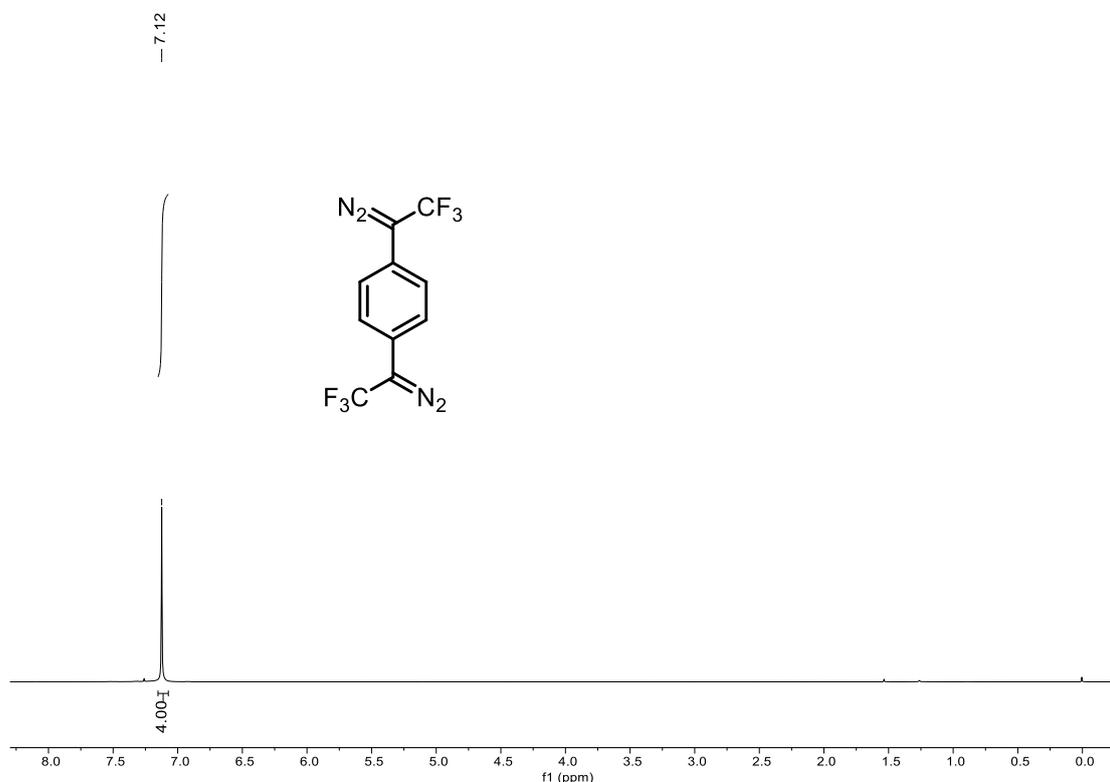
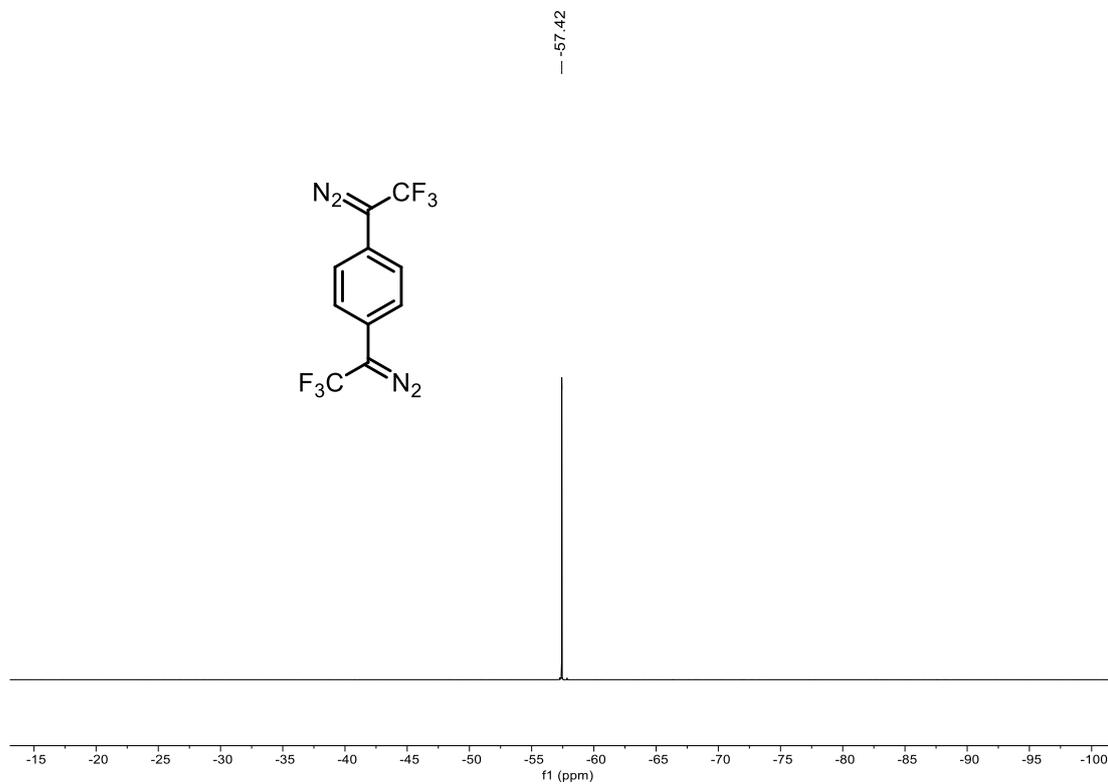
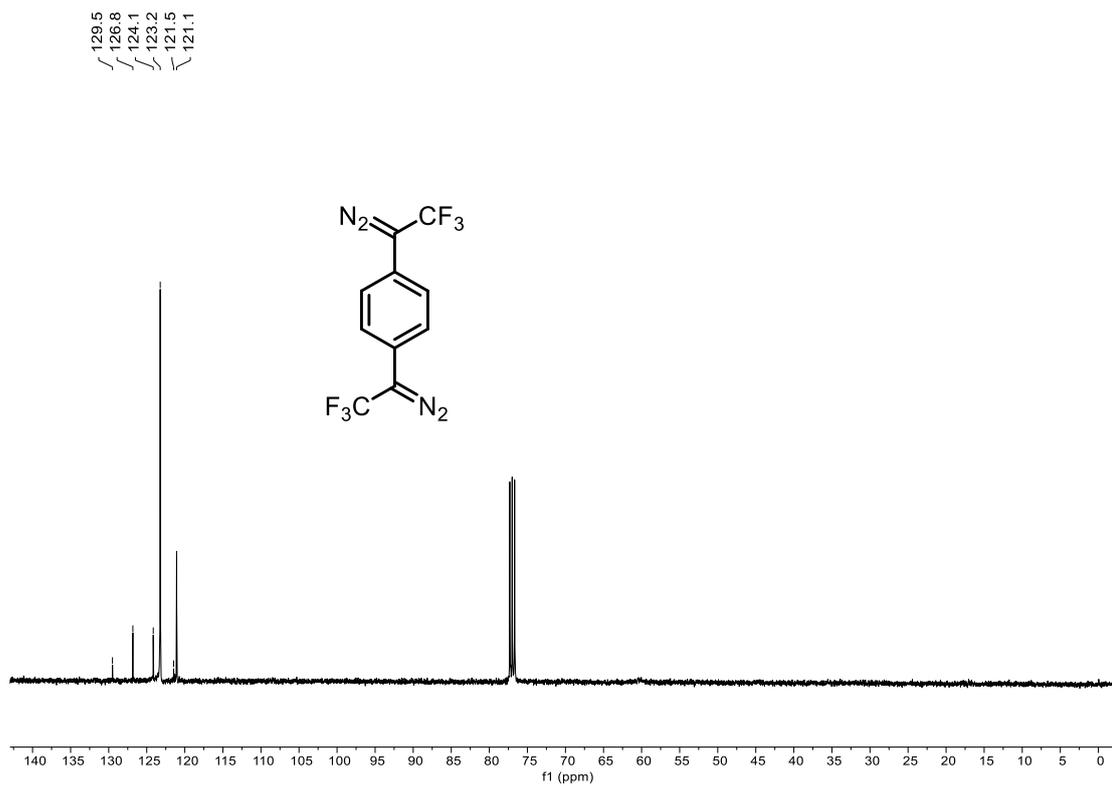


Figure S19. ¹H NMR (400 MHz, CDCl₃, 25 °C) of **B7**



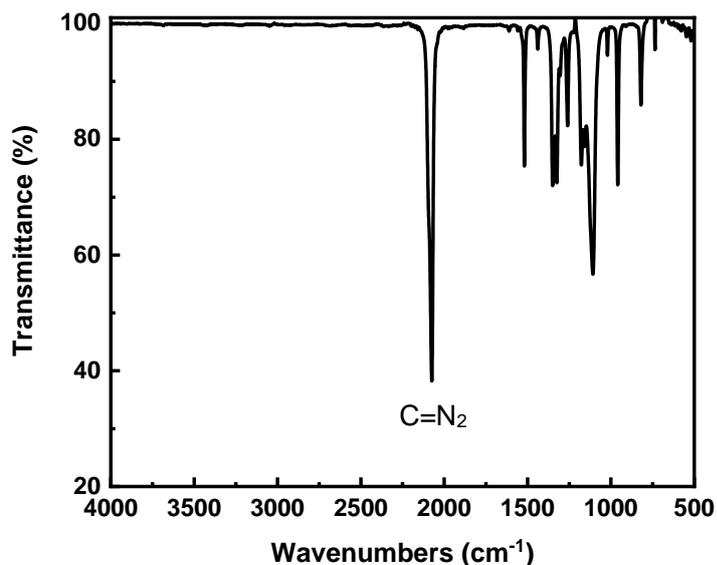
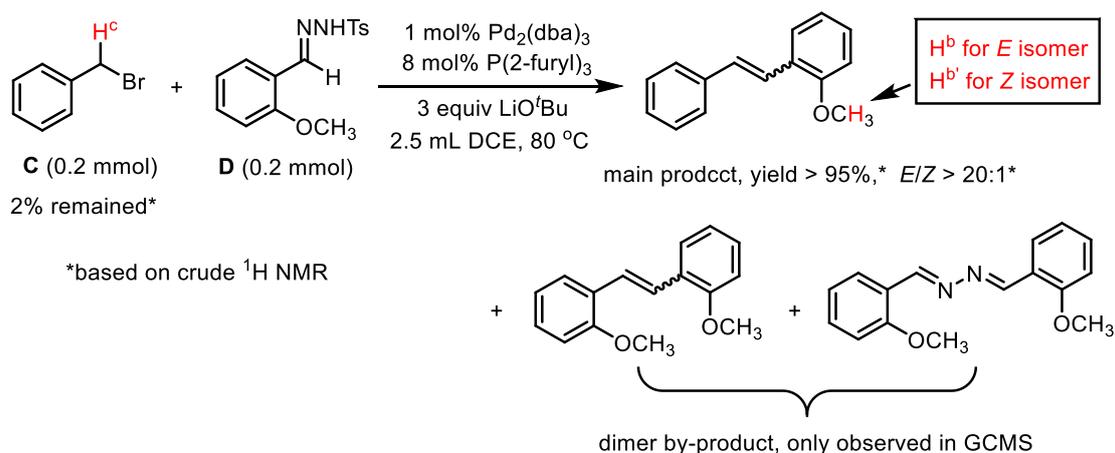


Figure S22. IR spectrum of **B7**

3) Model reaction



$\text{Pd}_2(\text{dba})_3$ (0.002 mmol, 1 mol%), $\text{P}(2\text{-furyl})_3$ (0.016 mmol, 8 mol%), LiO^tBu (0.6 mmol, 3 equiv), benzyl bromide **C** (0.2 mmol) and *(Z)*-*N'*-(2-methoxybenzylidene)-4-methylbenzenesulfonylhydrazide **D** (0.2 mmol) was placed in a 10 mL Schlenk tube, the reaction flask was then degassed and charged with N_2 three times, and dry DCE (2.5 mL) was added by syringe. The reaction was heated at $80 \text{ }^\circ\text{C}$ with stirring for 6 h. Then the reaction mixture was cooled to room temperature, filtered through a short plug of silica gel (washed with CHCl_3). Solvent was then removed in vacuo to provide a crude mixture, then crude NMR and GCMS were tested. From crude ^1H NMR, main product (yield > 95%, *E/Z* > 20:1) was obtained, and 2% of benzyl bromide remained using 0.1 mmol $\text{CHCl}_2\text{CHCl}_2$ as the internal standard. Dimer byproduct could only be observed by GCMS.

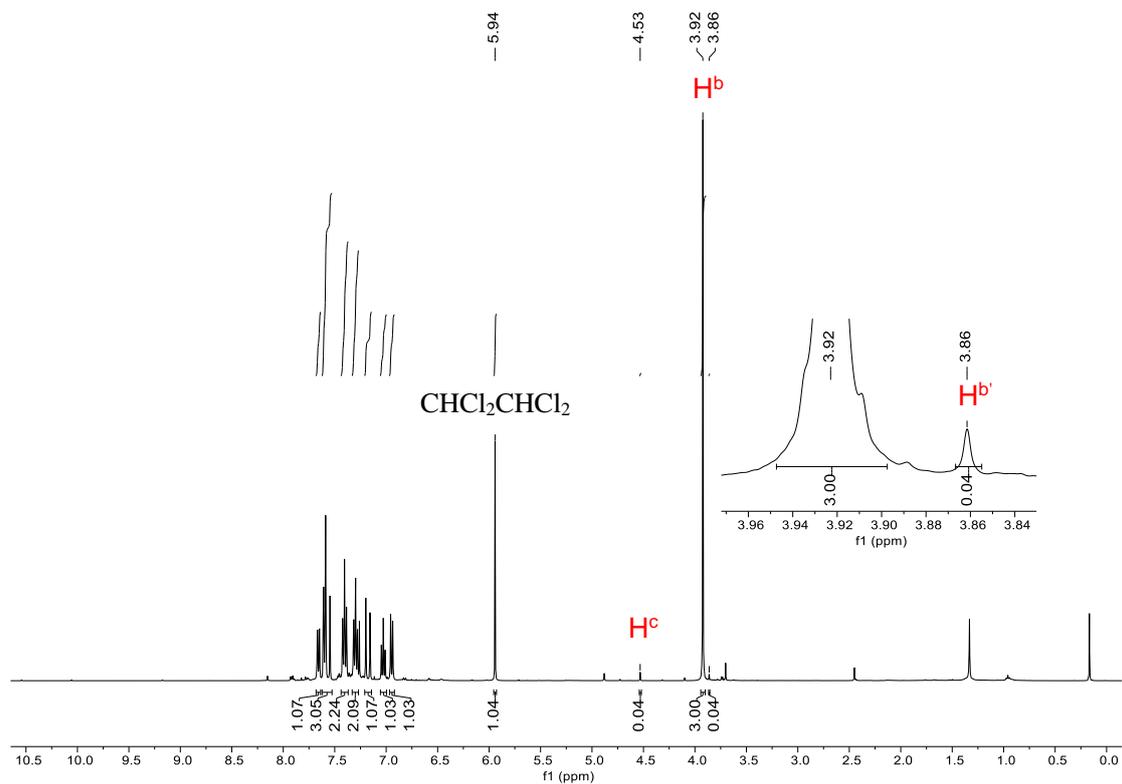
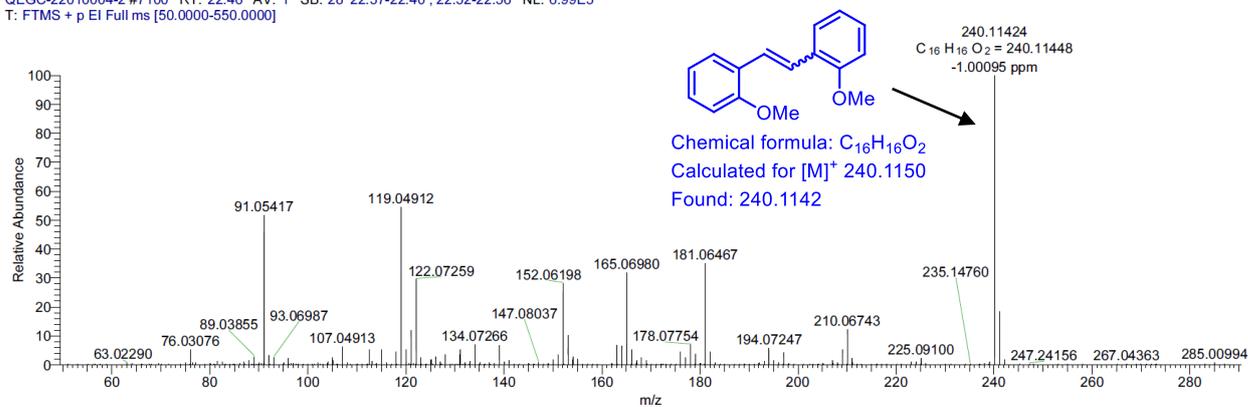


Figure S23. Crude ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of model reaction, 0.1 mmol $\text{CHCl}_2\text{CHCl}_2$ as the internal standard.

QEGC-22010004-2 #7100 RT: 22.46 AV: 1 SB: 28 22.37-22.40 , 22.52-22.56 NL: 6.99E5
T: FTMS + p EI Full ms [50.0000-550.0000]



QEGC-22010004-2 #8172 RT: 25.18 AV: 1 SB: 32 25.10-25.14 , 25.24-25.28 NL: 2.61E5
T: FTMS + p EI Full ms [50.0000-550.0000]

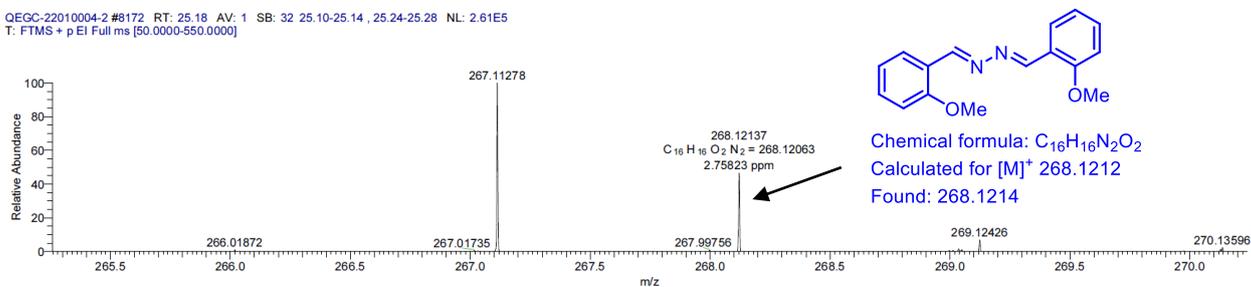
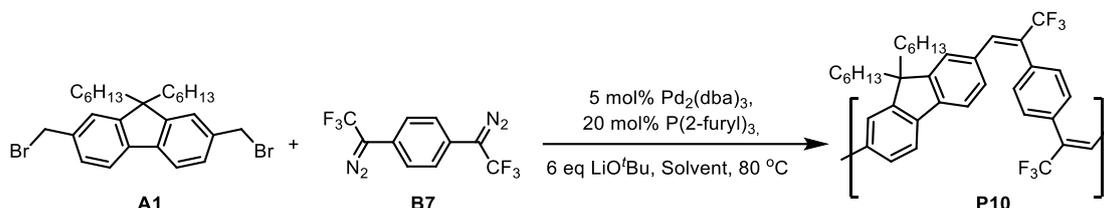


Figure S24. HRMS analysis of the model reaction

4) Optimization of the reaction conditions to synthesis **P10**

Table S1. Optimization of the reaction conditions to synthesis **P10**

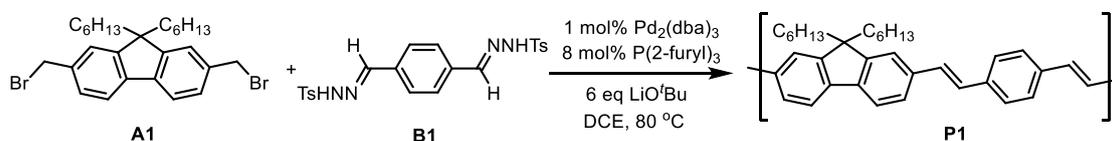


Entry	A1	B7	Solvent	<i>M_n</i> (kDa) ^a	<i>M_w</i> / <i>M_n</i> ^a	Yield(%) ^b
1	0.2 mmol	0.2 mmol	1 mL PhMe	5.6	1.64	80
2 ^c	0.2 mmol	0.2 mmol	1 mL PhMe	4.3	1.44	33
3	0.2 mmol	0.21 mmol	1 mL PhMe	6.2	1.74	86
4	0.2 mmol	0.22 mmol	1 mL PhMe	6.1	2.32	99
5	0.3 mmol	0.315 mmol	1 mL PhMe	10.9	3.32	76

^aThe *M_n* and *M_w*/*M_n* values were determined by SEC with reference to polystyrene standards; ^bIsolated yield, after precipitation with MeOH; ^c2.5 mol% Pd₂(dba)₃, 10 mol% P(2-furyl)₃.

5) Synthesis and characterization of polymers

5.1 General procedure for polymerization



Typical procedure: Pd₂(dba)₃ (1.83 mg, 0.002 mmol, 1 mol%), P(2-furyl)₃ (3.72mg, 0.016 mmol, 8 mol%), LiO^tBu (96 mg, 1.2 mmol, 6 eq), **A1** (104.08 mg, 0.2 mmol), **B1** (94.11 mg, 0.2 mmol) was placed in a 10 mL Schlenk tube, the reaction flask was then degassed and charged with N₂ three times, and dry DCE (2.5 mL) was added by syringe. The reaction was heated at 80 °C with stirring for 6 h, TLC check indicated the complete disappearance of the monomers. Then the reaction mixture was cooled to room temperature, HCl solution (1 N) and water was added. The mixture was extracted three times with CHCl₃. The organic layer was dried over anhydrous Na₂SO₄ and was evaporated under reduced pressure. Then the crude product was filtered through a filtered membrane (0.22 μm). The filtrate was evaporated and precipitated in methanol. The precipitation process was repeated for two times. The precipitate was filtered and dried in *vacuo* to afford the yield, and collected polymer was characterized with ¹H NMR, ¹³C NMR, SEC, TGA, DSC, FT-IR measurements.

5.2 Characterization of polymers

P1. 99% yield; SEC: *M_n* = 17.4 kg/mol, *M_w*/*M_n* = 3.26; ¹H NMR (400 MHz, CDCl₃) δ 7.89-7.41 (m, 9H), 7.34-6.99 (m, 5H), 2.25-1.73 (m, 4H), 1.09-1.06 (m,

12H), 0.84-0.58 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.6, 140.7, 136.7, 129.1, 127.7, 126.8, 125.7, 120.9, 120.5, 119.9, 55.0, 40.4, 31.4, 29.7, 23.7, 22.6, 14.0; IR (film): 3030, 2924, 2853, 1465, 1214, 961(*E*-vinylene), 822, 751 cm^{-1} .

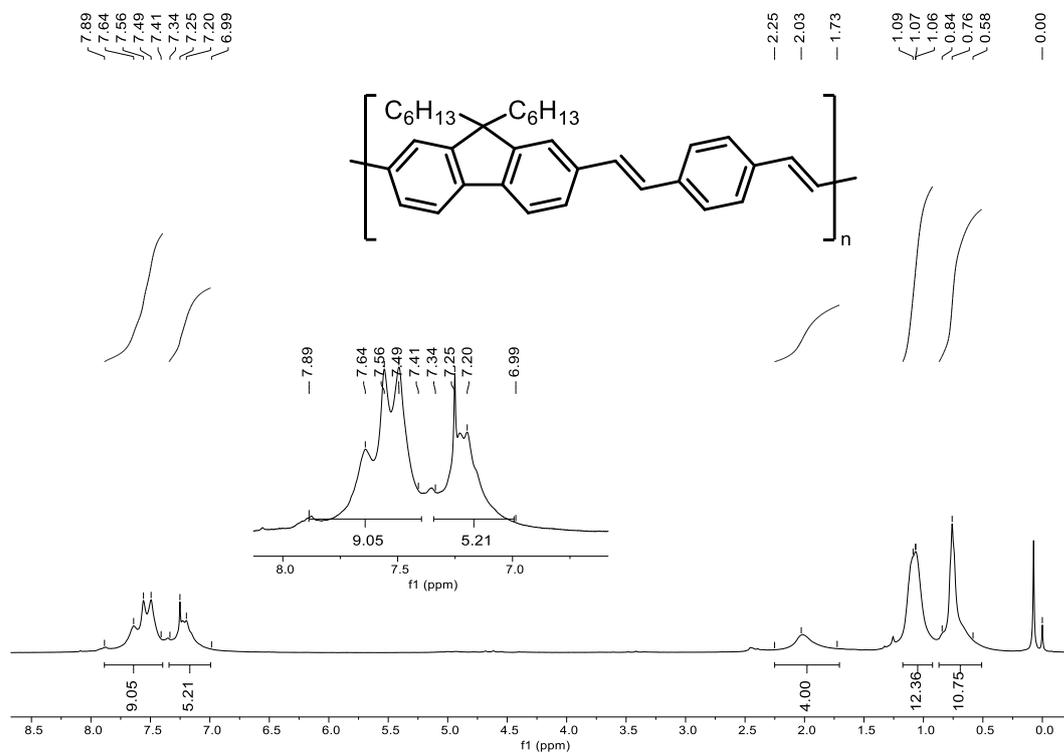


Figure S25. ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of P1

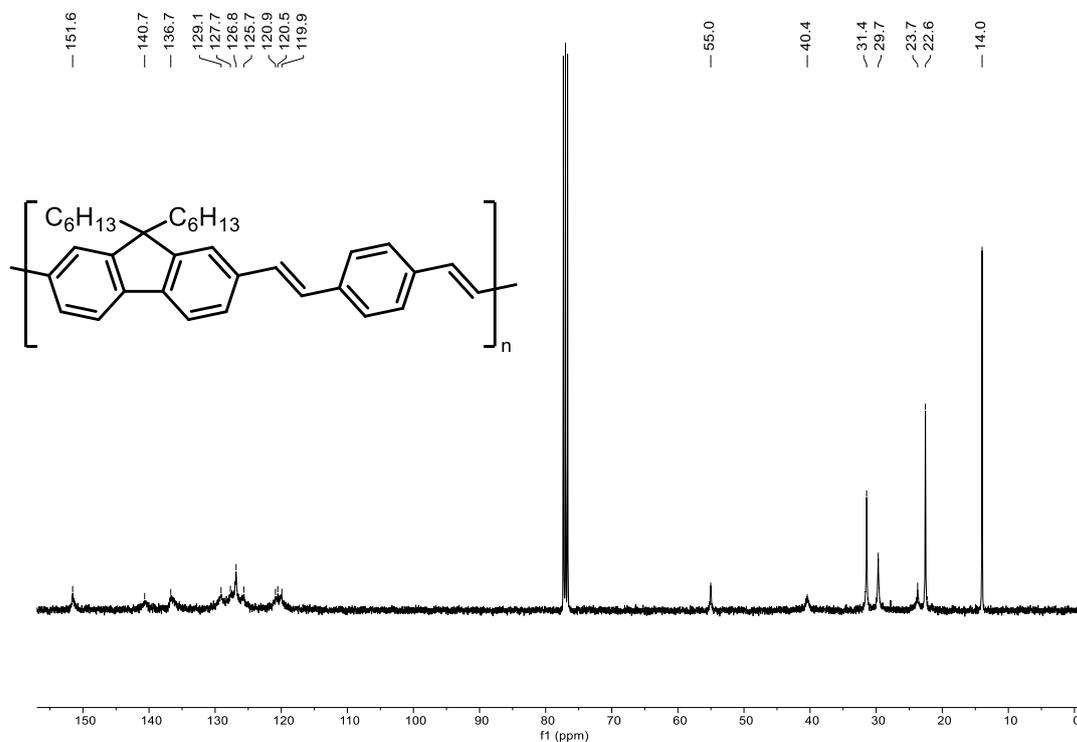


Figure S26. ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$) of P1

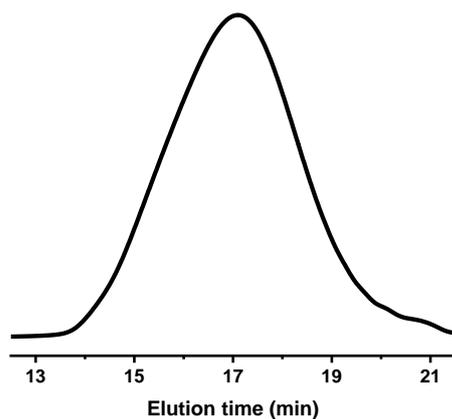


Figure S27. SEC trace of P1

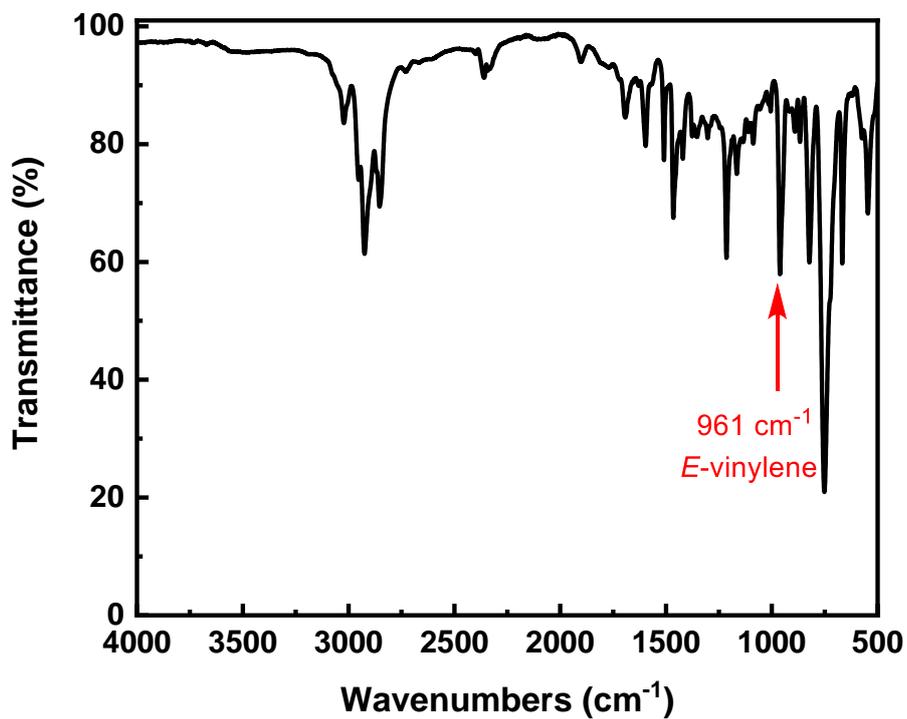


Figure S28. IR spectrum of P1

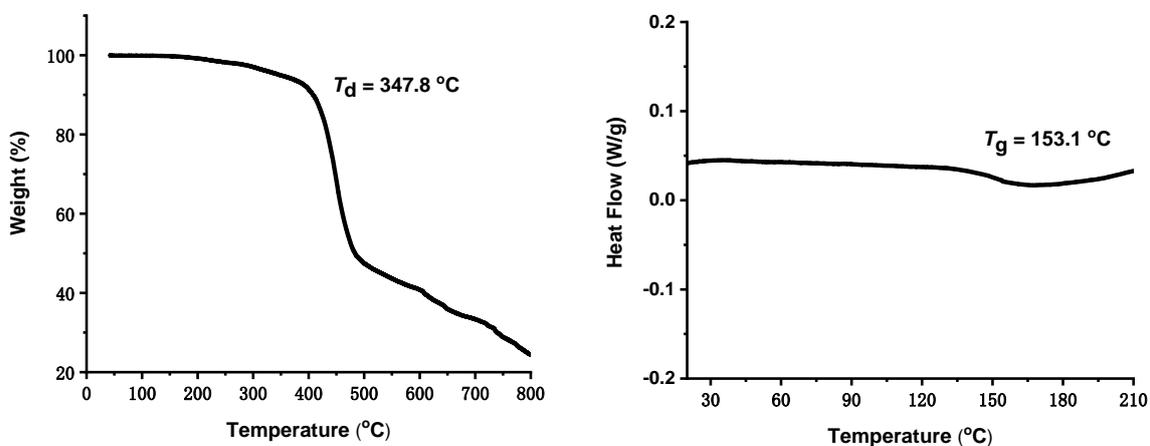


Figure S29. TGA and DSC thermograms of P1

P2. 99% yield; SEC: $M_n = 18.7$ kg/mol, $M_w/M_n = 2.80$; ^1H NMR (400 MHz, CDCl_3) δ 7.77-7.49 (m, 8H), 7.41-7.20 (m, 4H), 4.12 (m, 4H), 3.57 (m, 0.11H), 2.12-1.93 (m, 8H), 1.70-1.51 (m, 4H), 1.51-1.33 (m, 8H), 1.20-1.01 (m, 12H), 1.01-0.89 (m, 6H), 0.83-0.59 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.5, 151.1, 140.5, 136.9, 129.4, 127.0, 125.5, 122.7, 120.8, 119.8, 110.5, 69.5, 54.9, 40.5, 31.6, 31.5, 29.8, 29.5, 26.0, 23.7, 22.7, 22.6, 14.1, 14.0; IR (film): 3018, 2926, 2855, 1466, 1213, 964 (*E*-vinylene), 751 cm^{-1} .

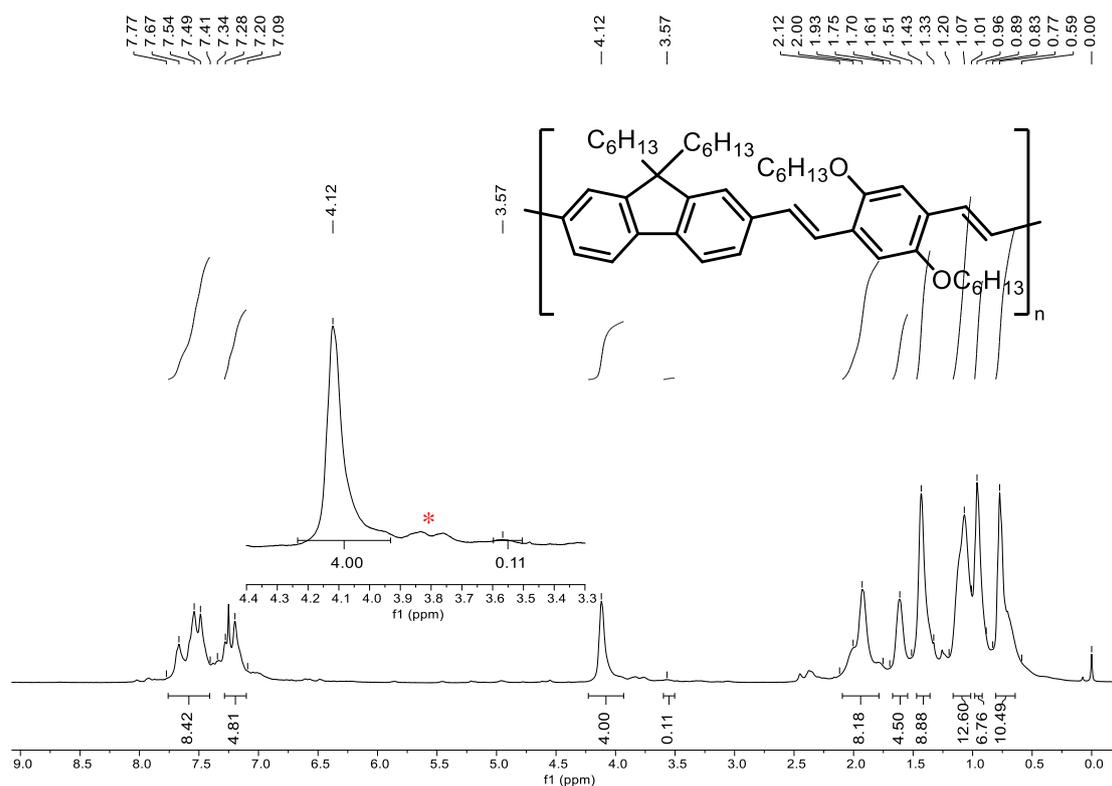


Figure S30. ^1H NMR (400 MHz, CDCl_3 , 25 °C) of **P2** (un-assigned peak * might be caused by polymer end or dimerization side reaction)

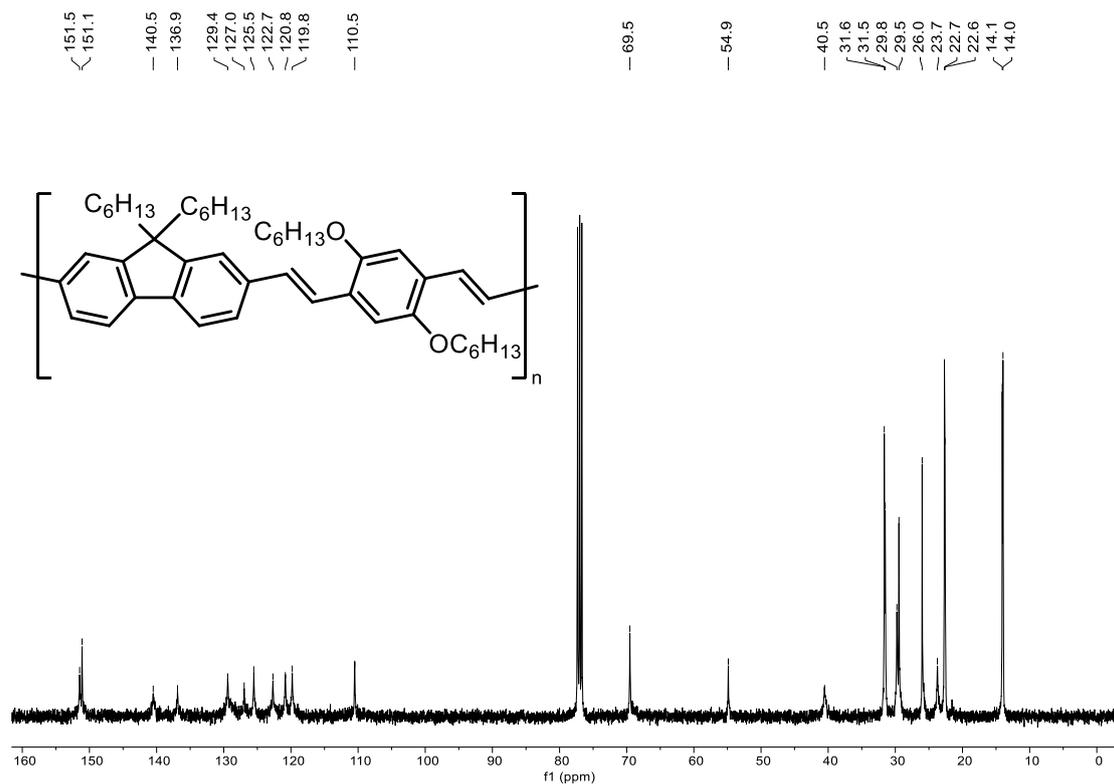


Figure S31. ¹³C NMR (100 MHz, CDCl₃, 25 °C) of **P2**

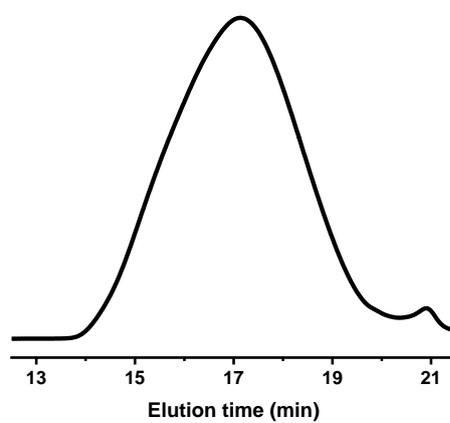


Figure S32. SEC trace of **P2**

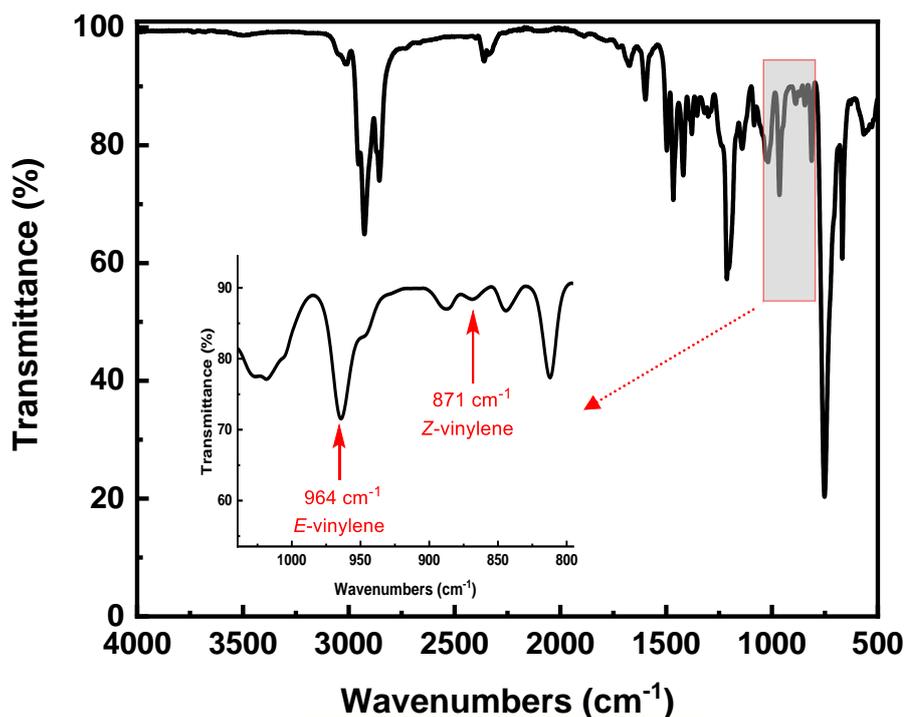


Figure S33. IR spectrum of P2

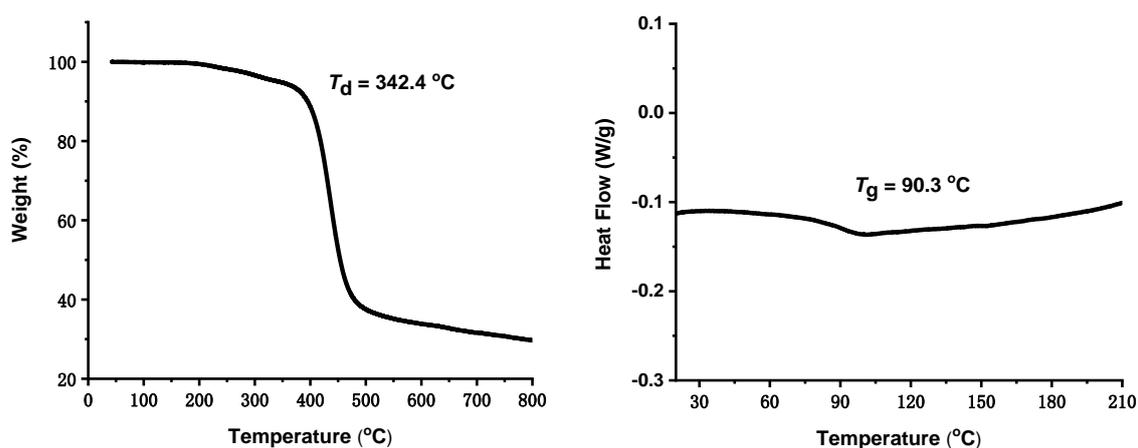
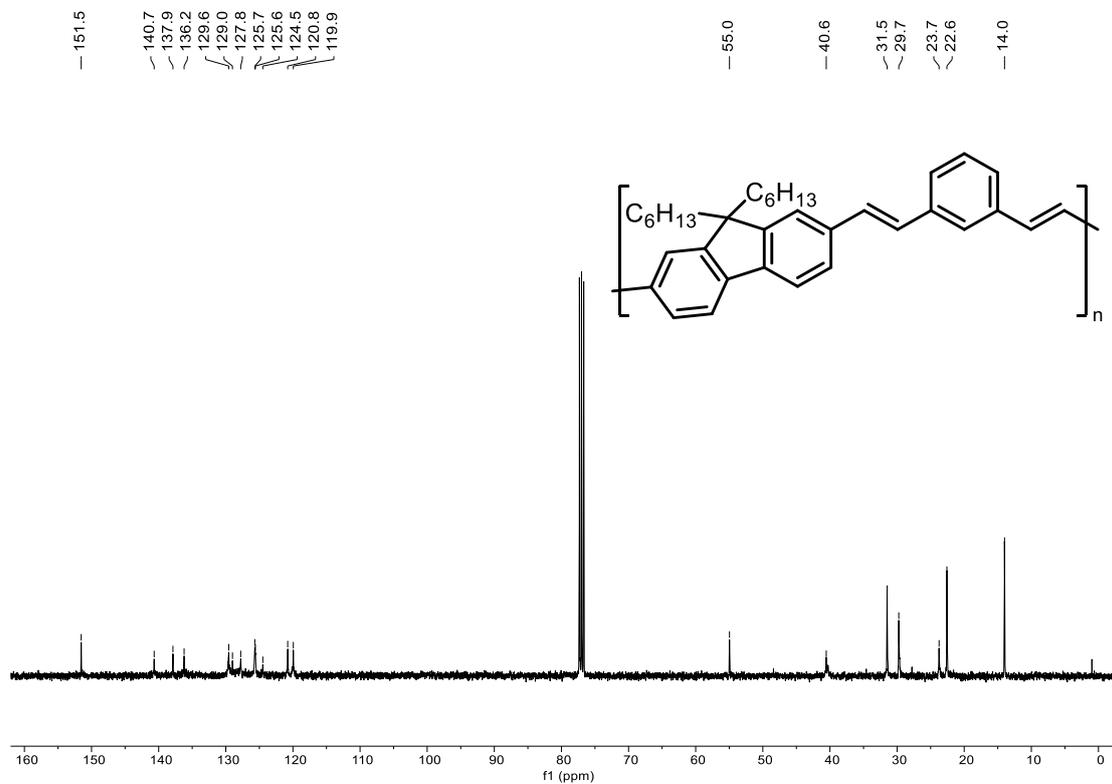
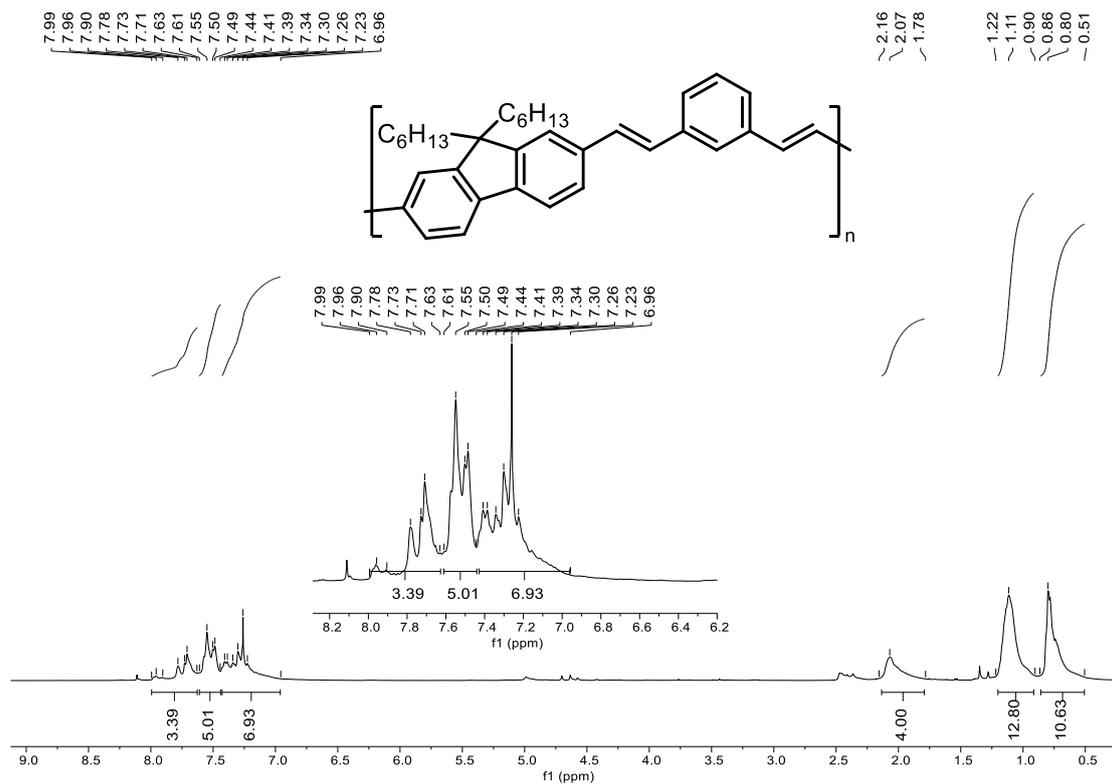


Figure S34. TGA and DSC thermograms of P2

P3 96% yield; SEC: $M_n = 8.1$ kg/mol, $M_w/M_n = 2.24$; ^1H NMR (400 MHz, CDCl_3) δ 7.99-7.63 (m, 3H), 7.61-7.44 (m, 5H), 7.41-6.96 (m, 6H), 2.16-1.78 (m, 4H), 1.22-0.90 (m, 12H), 0.86-0.51 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.5, 140.7, 137.9, 136.2, 129.6, 129.0, 127.8, 125.7, 125.6, 124.5, 120.8, 119.9, 55.0, 40.6, 31.5, 29.7, 23.7, 22.6, 14.0; IR (film): 3024, 2957, 2926, 2857, 1468, 1263, 1048, 1014, 960 (*E*-vinylene), 800, 755 cm^{-1} .



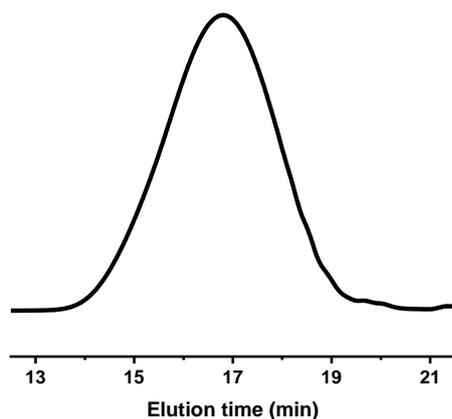


Figure S37. SEC trace of P3

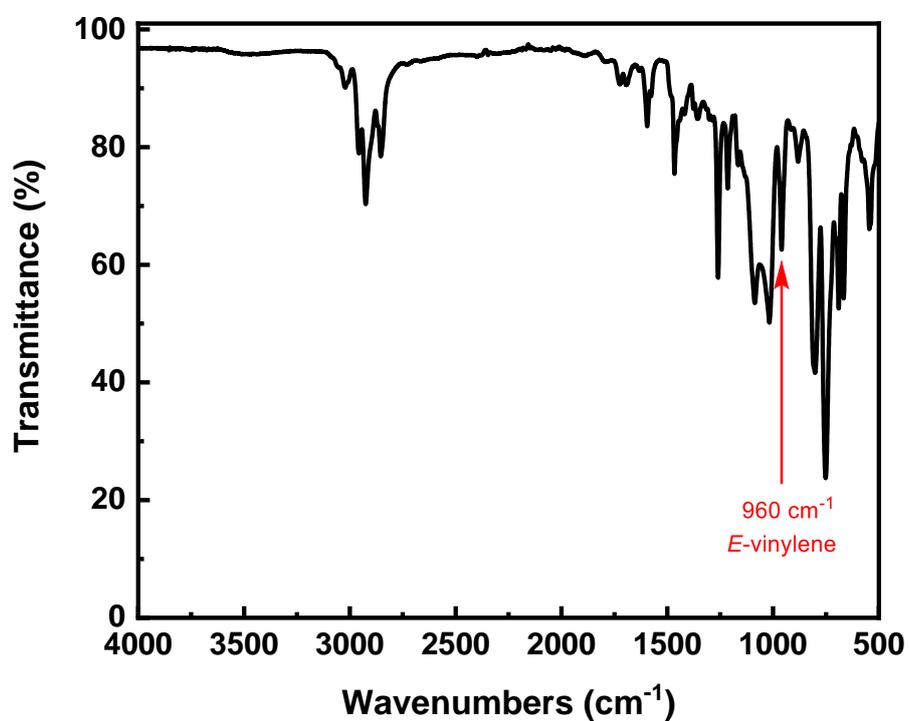


Figure S38. IR spectrum of P3

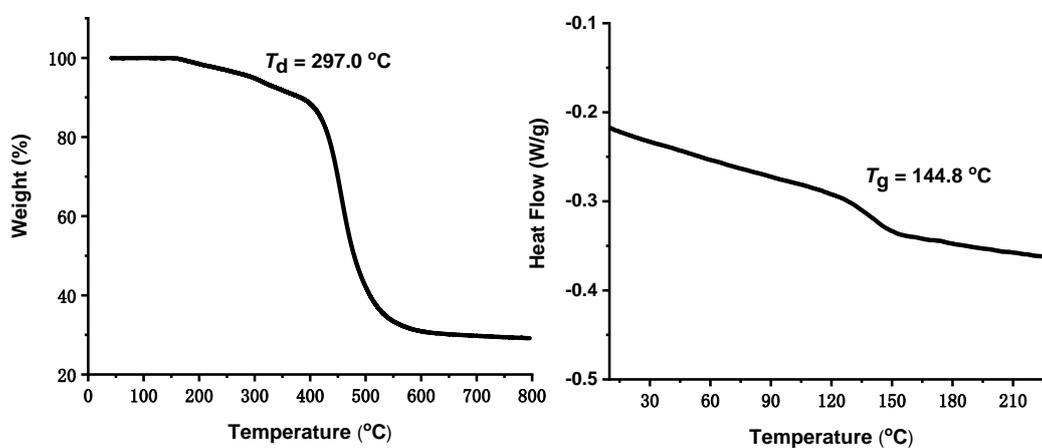


Figure S39. TGA and DSC thermograms of P3

P4. 81% yield; SEC: $M_n = 7.2$ kg/mol, $M_w/M_n = 4.55$; ^1H NMR (400 MHz, CDCl_3) δ 8.00-7.55 (m, 2H), 7.55-7.06 (m, 7H), 7.06-6.75 (m, 3H), **6.72-6.60 (m, 0.45H)**, 2.08-1.66 (m, 4H), 1.20-0.85 (m, 12H), 0.83-0.41 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.7, 140.4, 134.6, 133.9, 129.6, 128.5, 125.6, 120.5, 112.0, 55.0, 40.4, 31.5, 29.7, 23.7, 22.6, 14.0; IR (film): 3026, 2958, 2924, 2853, 1466, 1259, 1087, 1019, 943, 798, 752 cm^{-1} .

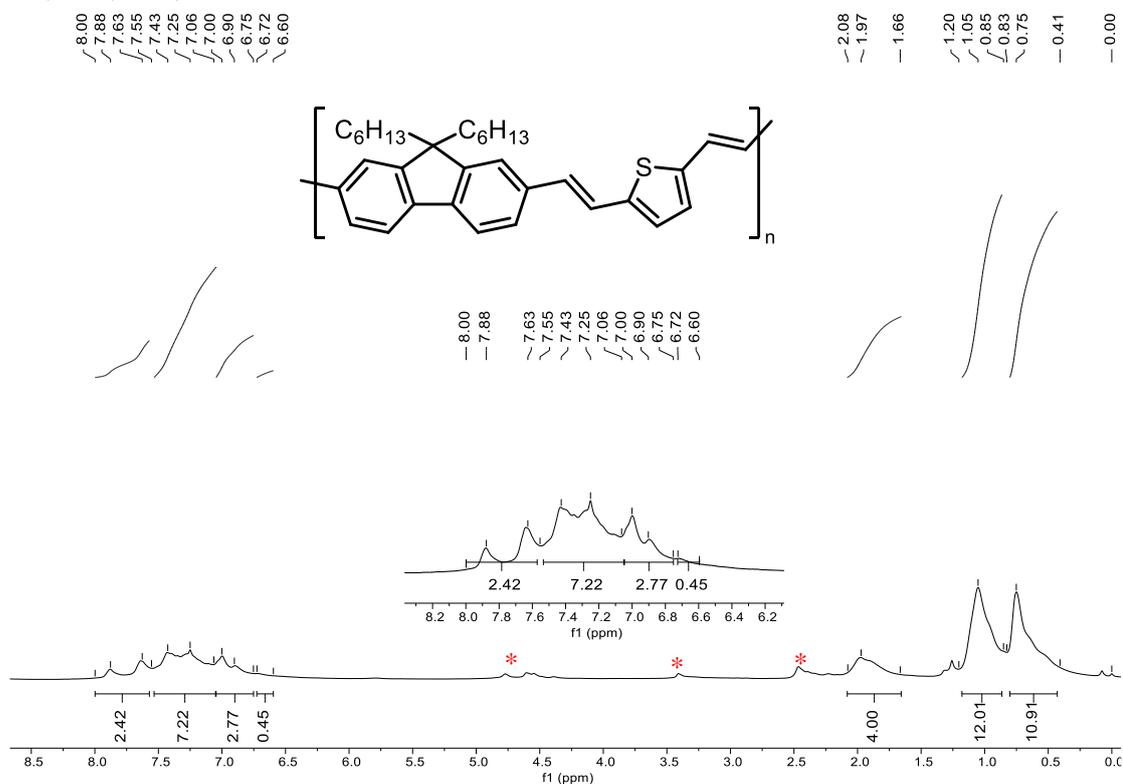


Figure S40. ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of **P4** (some un-assigned peaks * might be caused by polymer end or dimerization side reaction)

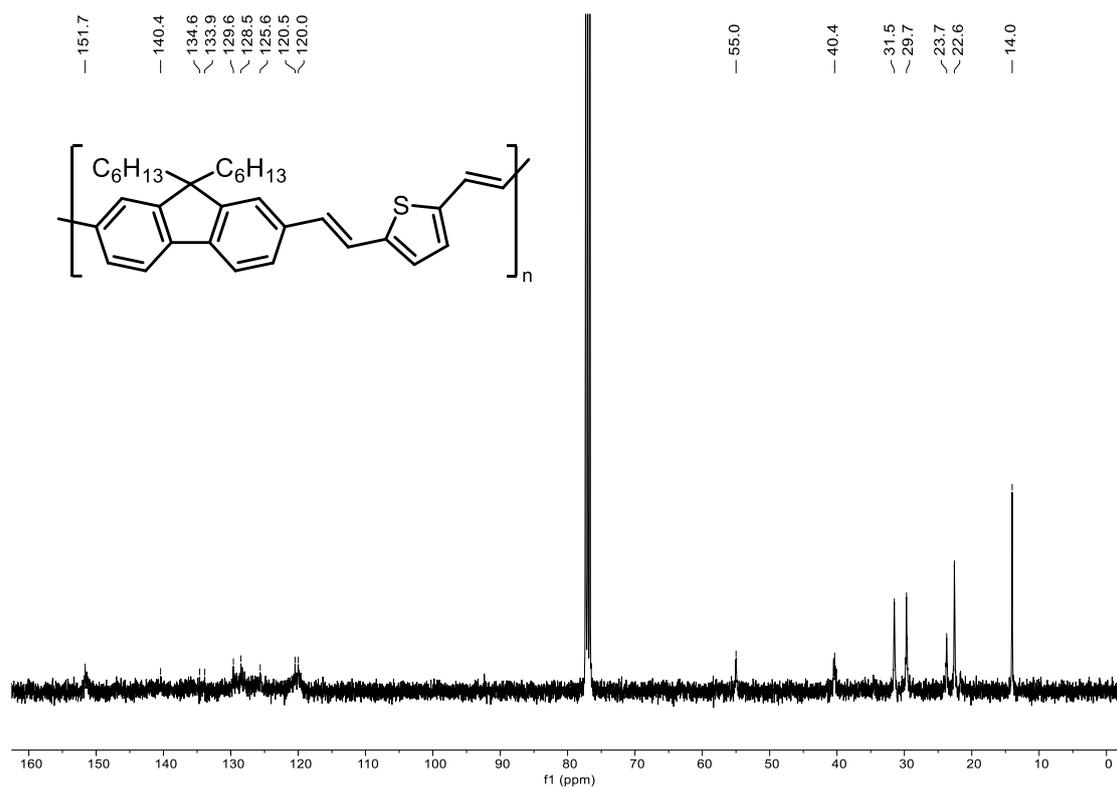


Figure S41. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) of **P4**

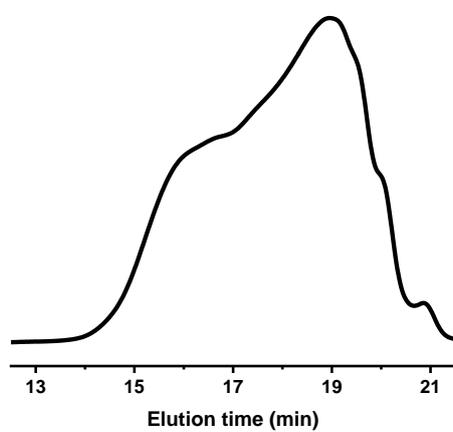


Figure S42. SEC trace of **P4**

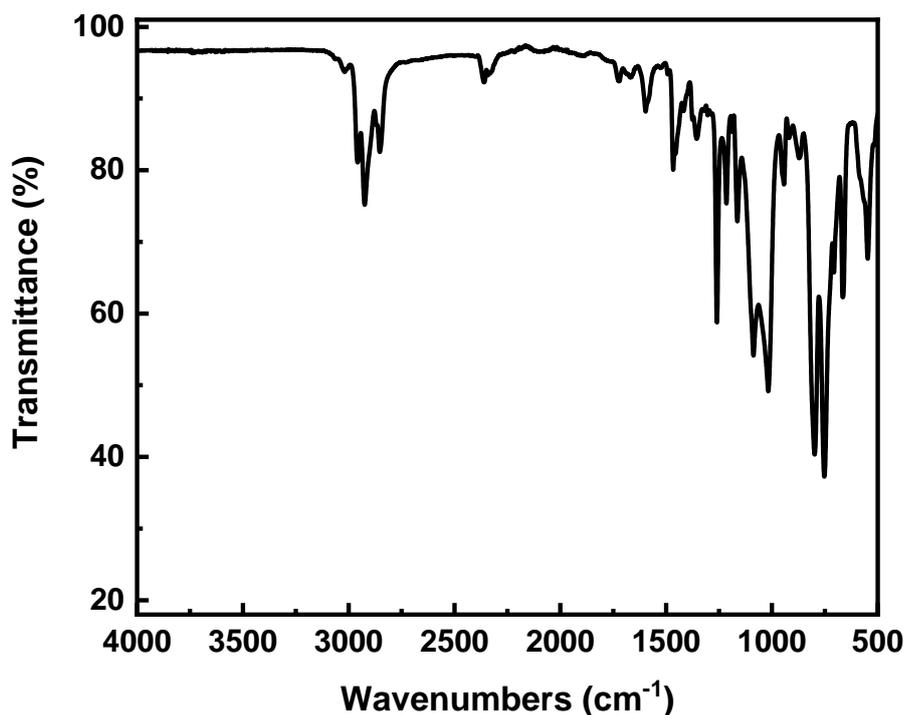


Figure S43. IR spectrum of **P4**

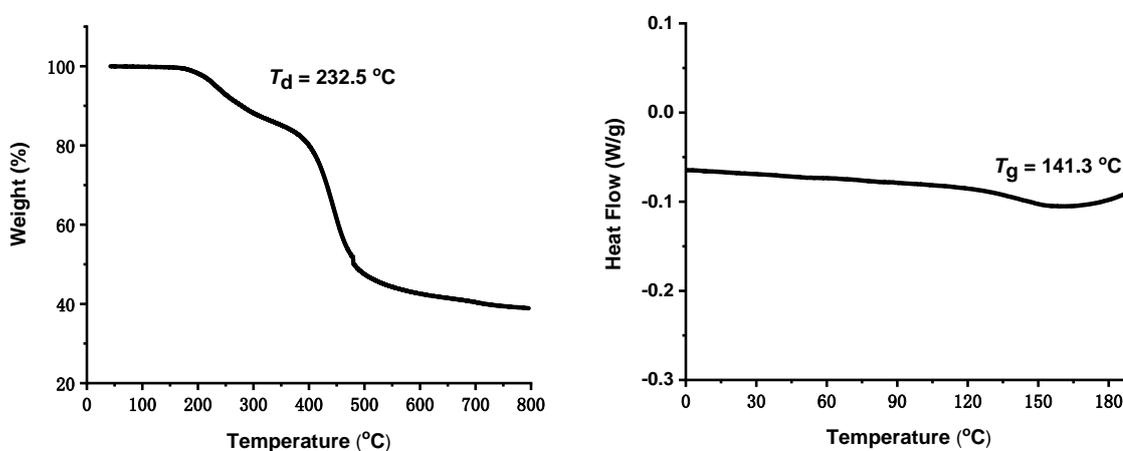


Figure S44. TGA and DSC thermograms of **P4**

P5. 99% yield; SEC: $M_n = 5.5$ kg/mol, $M_w/M_n = 1.73$; ^1H NMR (400 MHz, CDCl_3) δ 8.37-8.11 (m, 1H), 8.11-7.82 (m, 2H), 7.82-7.43 (m, 6H), 7.43-7.02 (m, 7H), 4.37-3.96 (m, 2H), 2.20-1.60 (m, 6H), 1.44-1.19 (m, 6H), 1.19-1.02 (m, 5H), 1.02-0.68 (m, 14H), 0.68-0.34 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.4, 143.9, 142.2, 140.5, 136.7, 134.1, 129.5, 128.4, 125.3, 123.0, 120.4, 119.8, 118.4, 109.0, 54.9, 43.2, 40.4, 31.4, 29.6, 28.8, 27.8, 26.8, 23.7, 22.5, 21.5, 13.9, 13.9; IR (film): 3026, 2956, 2925, 2853, 1596, 1351, 1260, 1088, 960, 801, 753 cm^{-1} .

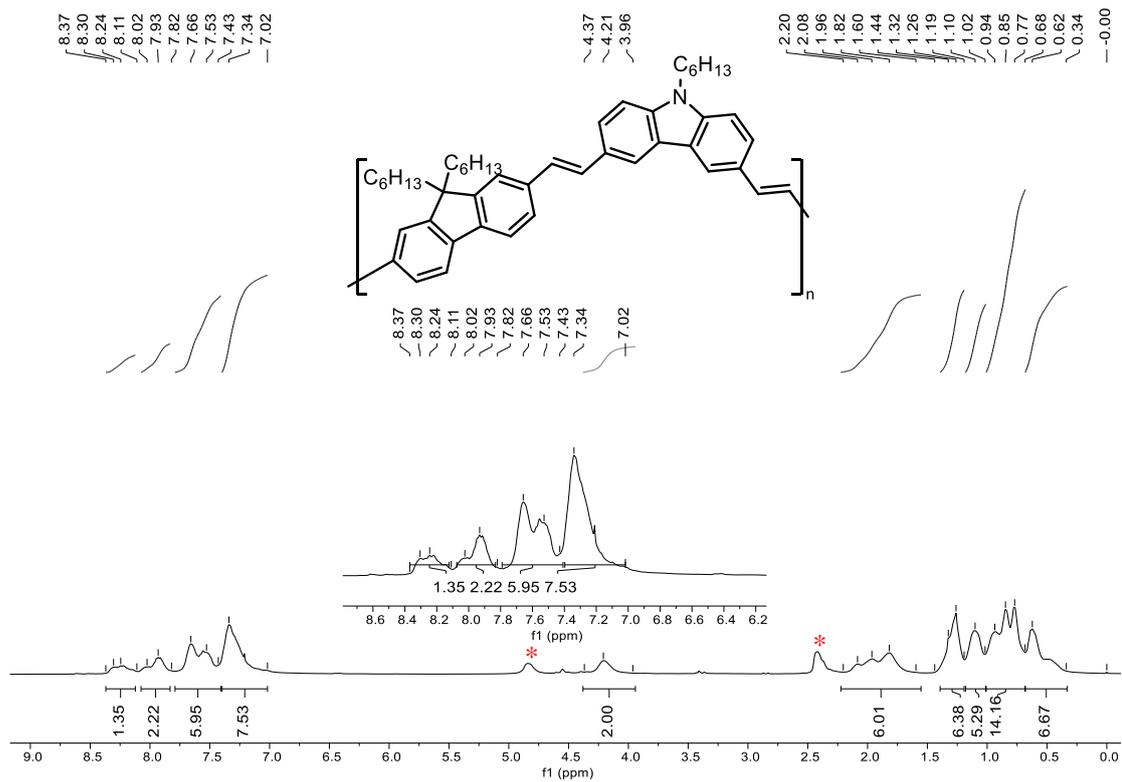


Figure S45. ¹H NMR (400 MHz, CDCl₃, 25 °C) of **P5** (some unassigned peaks * might be caused by polymer end or dimerization side reaction)

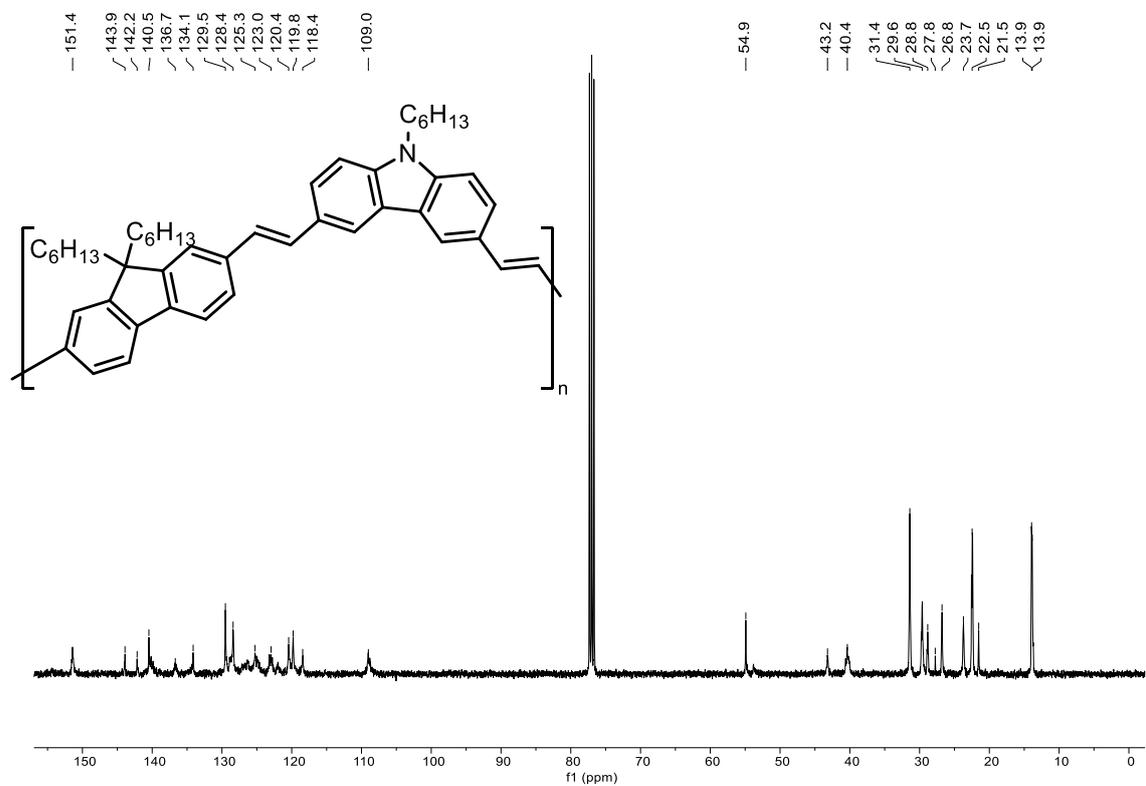


Figure S46. ¹³C NMR (100 MHz, CDCl₃, 25 °C) of **P5**

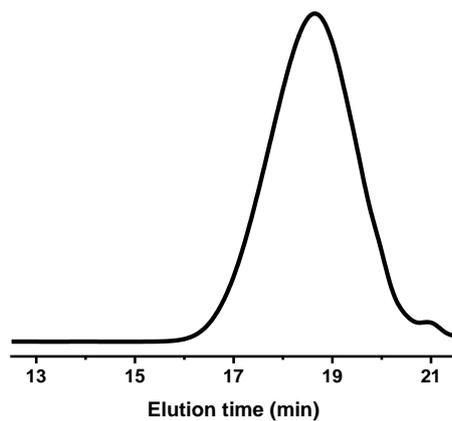


Figure S47. SEC trace of P5

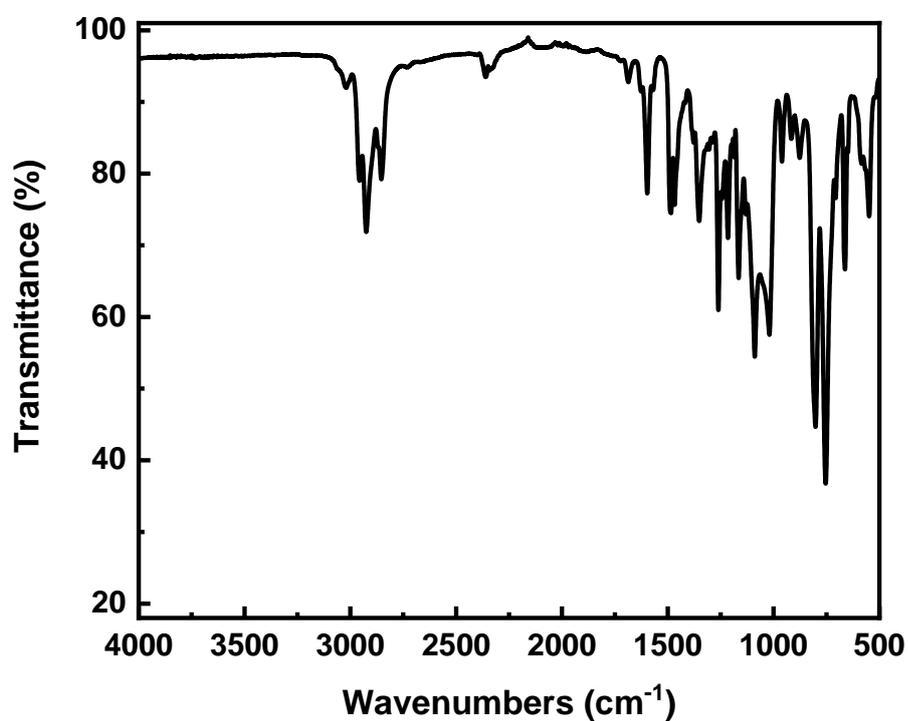


Figure S48. IR spectrum of P5

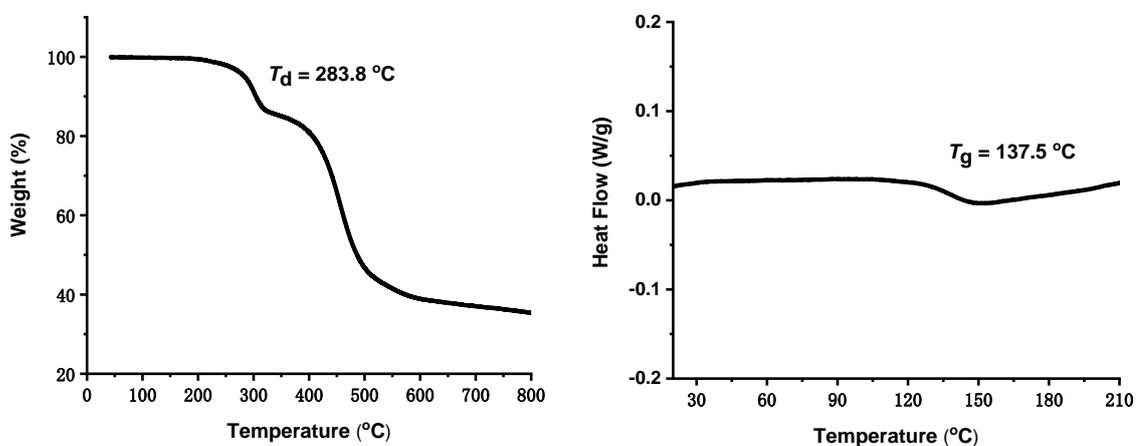


Figure S49. TGA and DSC thermograms of P5

P6. 90% yield; SEC: $M_n = 9.1$ kg/mol, $M_w/M_n = 2.00$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.91-7.44 (m, 1H), 7.44-6.90 (m, 20H), 6.84-6.65 (m, 1H), 1.86-1.32 (m, 4H), 1.23-0.88 (m, 12H), 0.88-0.60 (m, 6H), 0.60-0.21 (m, 4H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 150.5, 143.5, 142.2, 141.4, 140.6, 139.5, 136.1, 130.3, 129.9, 129.2, 128.7, 128.1, 127.5, 127.2, 123.3, 119.2, 54.2, 40.0, 31.6, 29.7, 23.6, 22.6, 14.1; IR (film): 3021, 2926, 2855, 1465, 1214, 748 cm^{-1} .

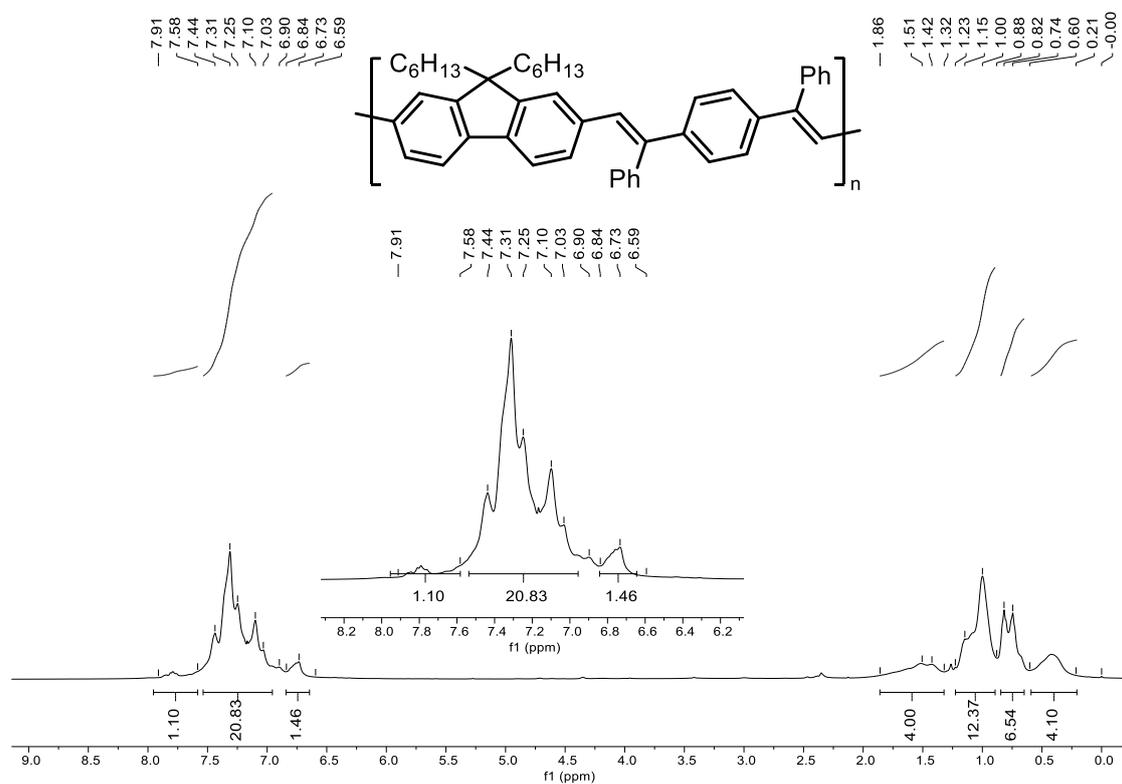


Figure S50. $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of **P6**

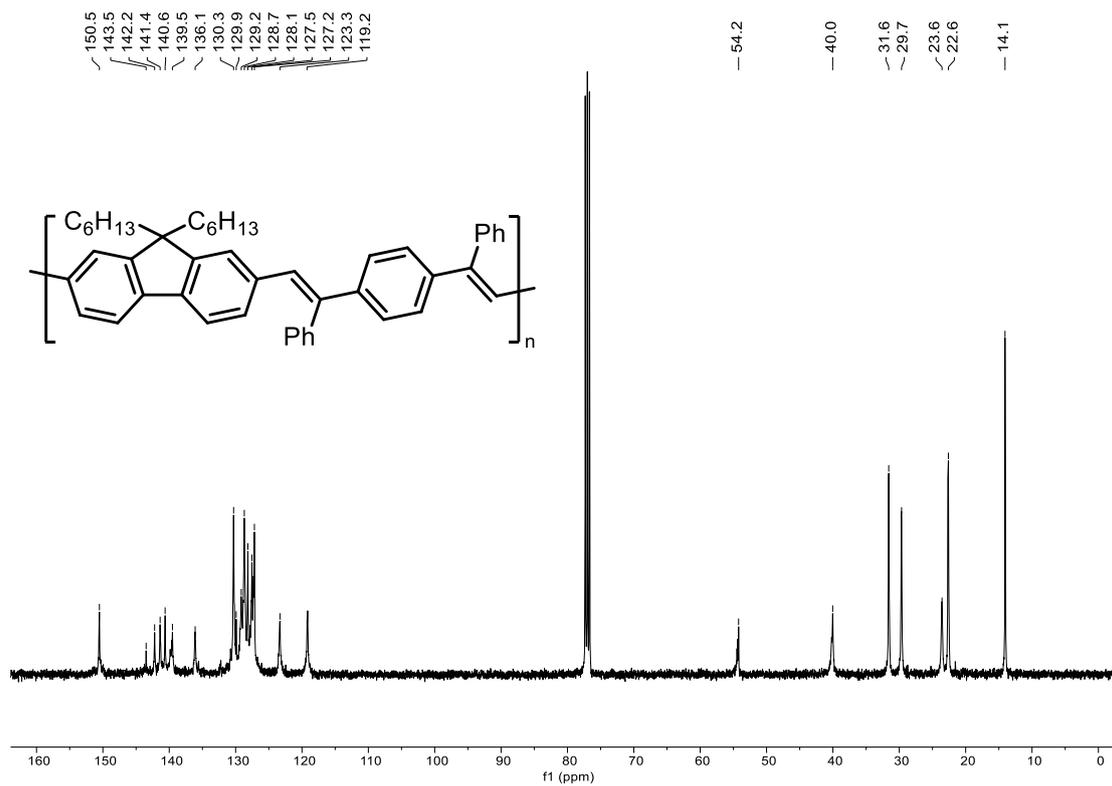


Figure S51. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) of **P6**

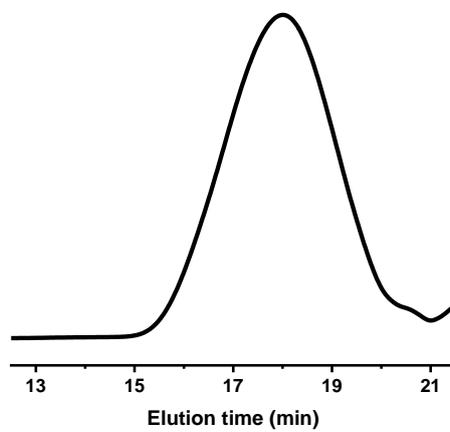


Figure S52. SEC trace of **P6**

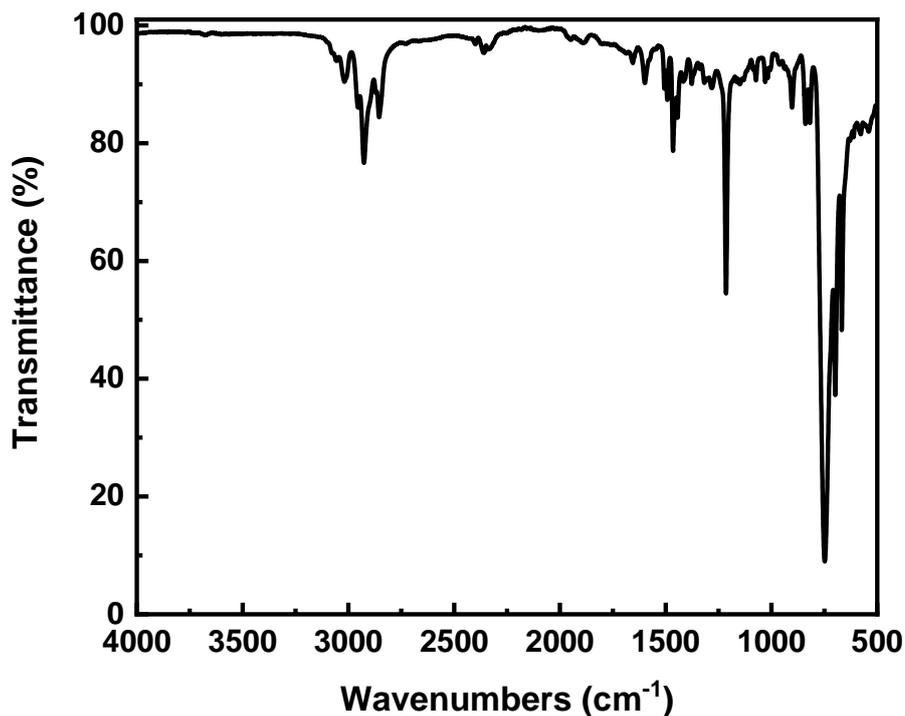


Figure S53. IR spectrum of **P6**

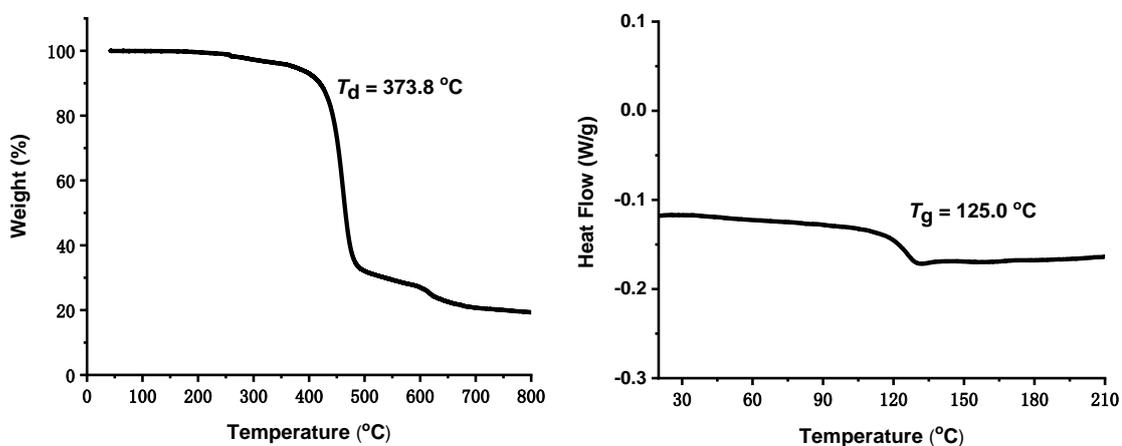
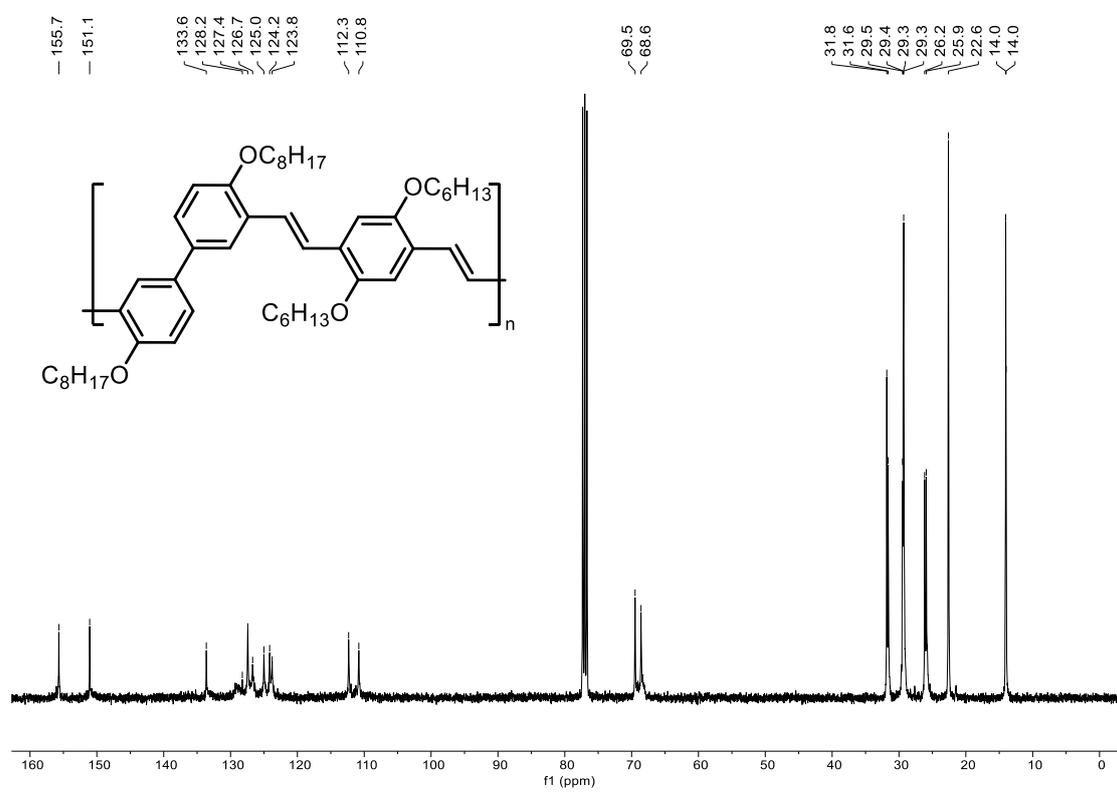
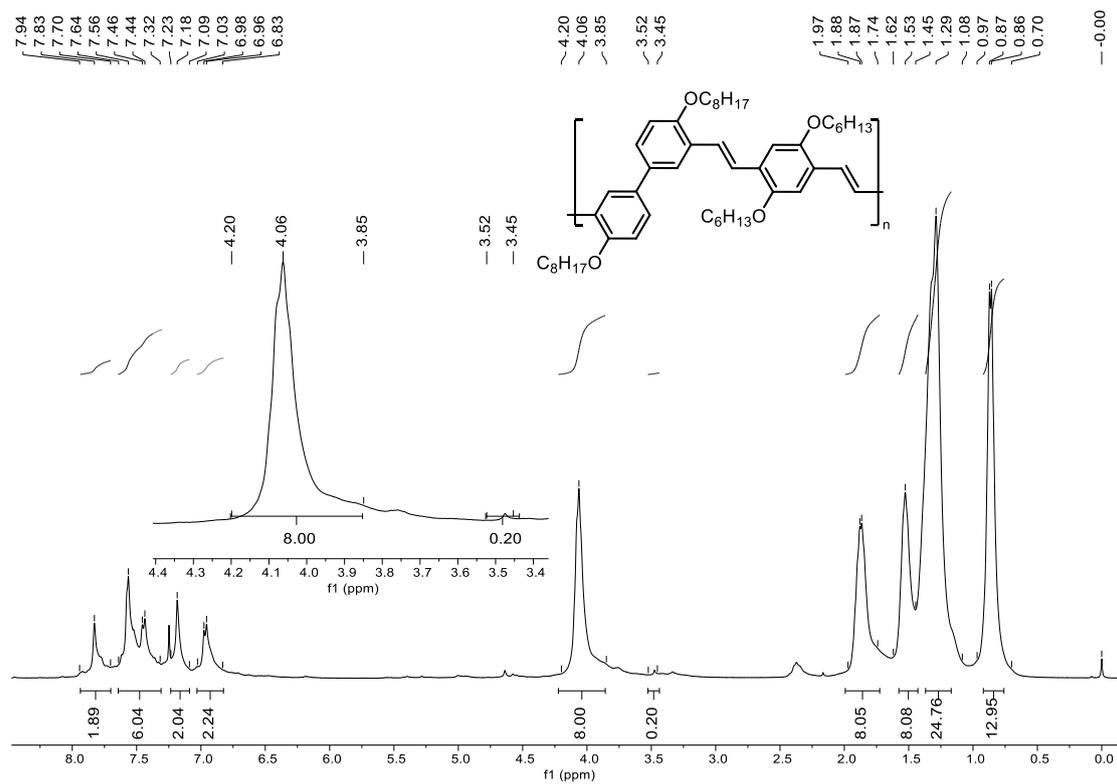


Figure S54. TGA and DSC thermograms of **P6**

P7. 99% yield; SEC: $M_n = 13.8$ kg/mol, $M_w/M_n = 3.50$; ^1H NMR (400 MHz, CDCl_3) δ 7.94-7.70 (m, 2H), 7.64-7.32 (m, 6H), 7.23-7.09 (m, 2H), 7.03-6.83 (m, 2H), 4.20-3.85 (m, 8H), 3.52-3.45 (m, 0.2H), 1.97-1.74 (m, 8H), 1.62-1.45 (m, 8H), 1.45-1.08 (m, 24H), 0.97-0.70 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.7, 151.7, 133.6, 128.2, 127.4, 126.7, 125.0, 124.2, 123.8, 112.3, 110.8, 69.5, 68.6, 31.8, 31.6, 29.5, 29.4, 29.3, 29.3, 26.2, 25.9, 22.6, 14.0, 14.0; IR (film): 3018, 2925, 2855, 1494, 1242, 1214, 1017, 973, 800, 752 cm^{-1} .



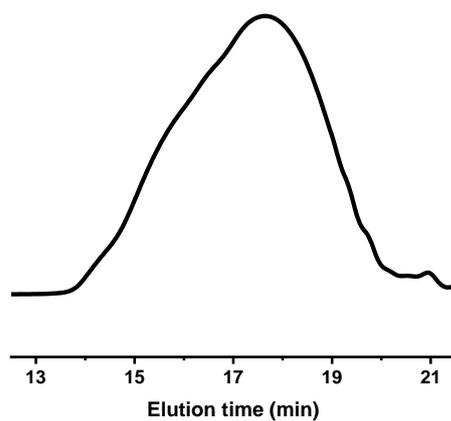


Figure S57. SEC trace of P7

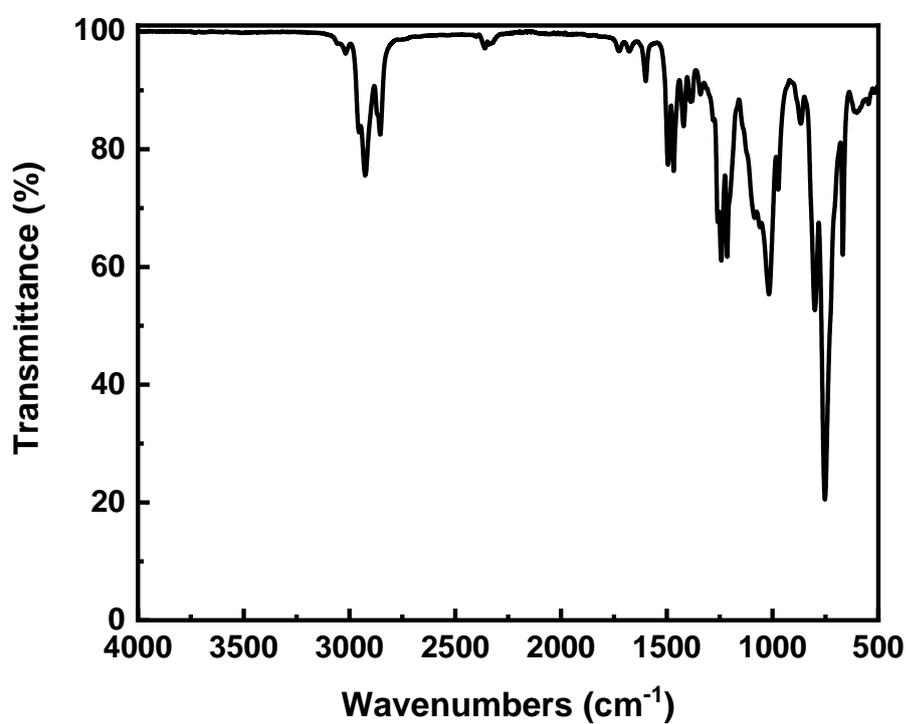


Figure S58. IR spectrum of P7

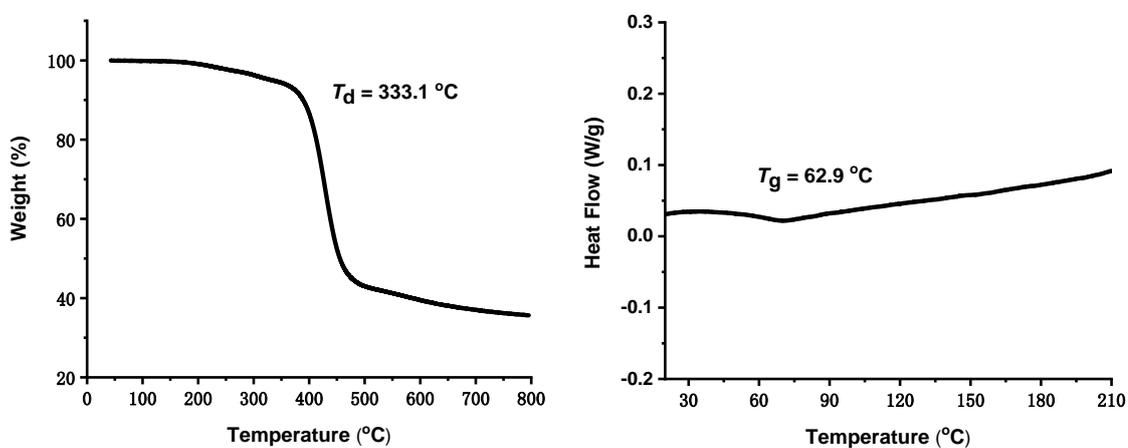


Figure S59. TGA and DSC thermograms of P7

P8. 99% yield; SEC: $M_n = 21.7$ kg/mol, $M_w/M_n = 4.69$; ^1H NMR (400 MHz, CDCl_3) δ 8.06-7.76 (m, 4H), 7.73-7.48 (m, 3H), 7.41-7.09 (m, 3H), 4.40-3.78 (m, 8H), **3.54-3.40 (m, 0.33H)**, 2.11-1.78 (m, 8H), 1.78-1.60 (m, 8H), 1.60-1.31 (m, 24H), 1.04-0.73 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.1, 151.1, 129.4, 127.5, 126.9, 123.8, 123.0, 118.6, 110.2, 75.7, 69.5, 31.9, 31.7, 30.6, 29.7, 29.5, 29.3, 26.4, 26.0, 22.7, 14.1, 14.0; IR (film): 3021, 2926, 2855, 1347, 1213, 1030, 973 (*E*-vinylene), 749 cm^{-1} .

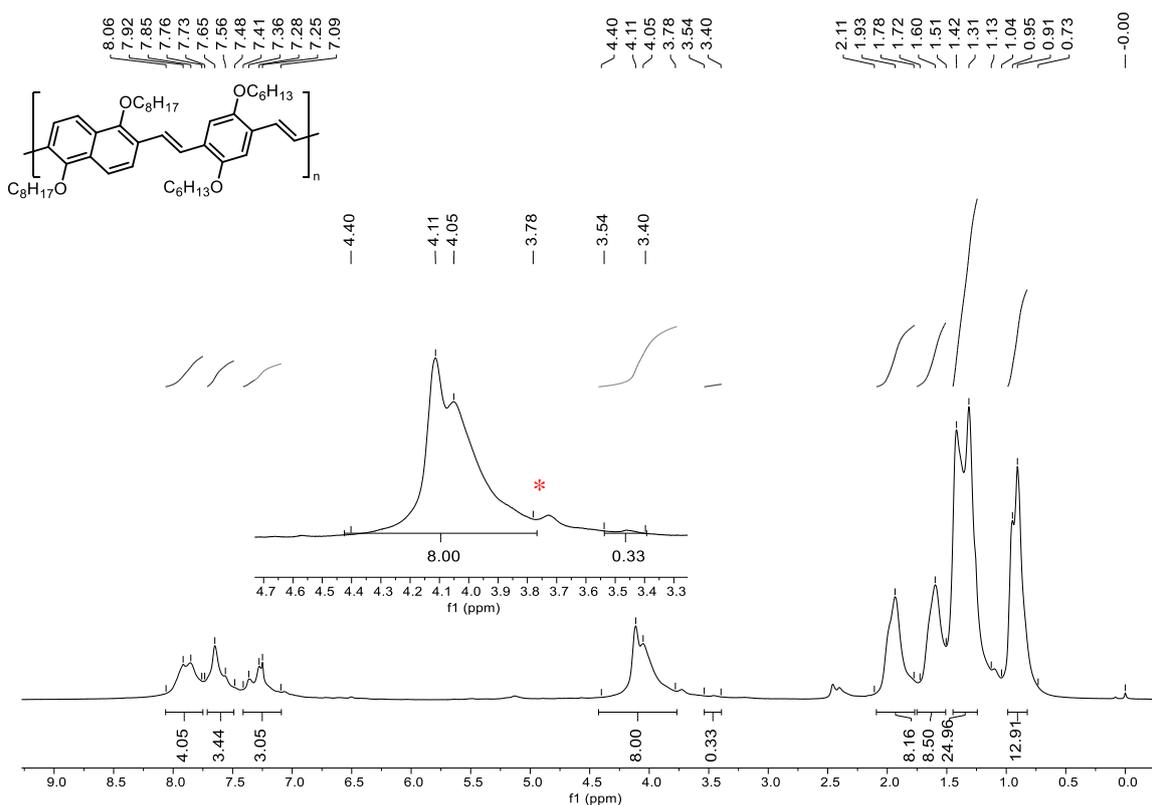


Figure S60. ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of **P8** (unassigned peak * might be caused by polymer end or dimerization side reaction)

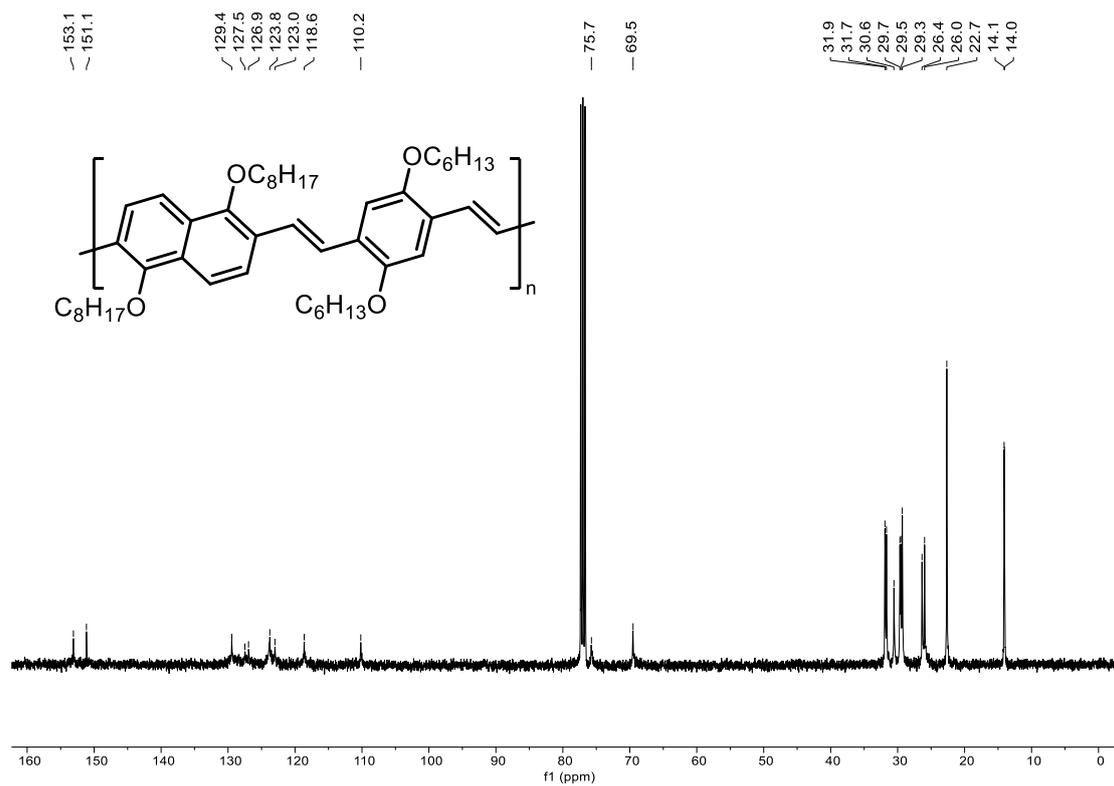


Figure S61. ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) of **P8**

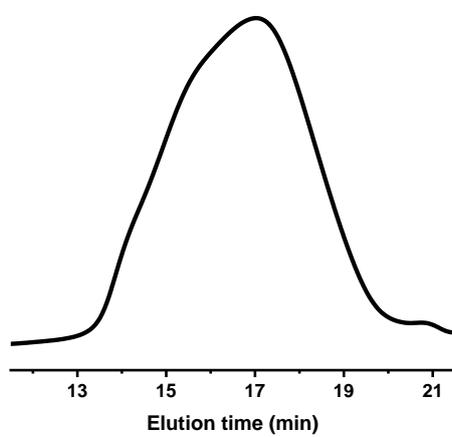


Figure S62. SEC trace of **P8**

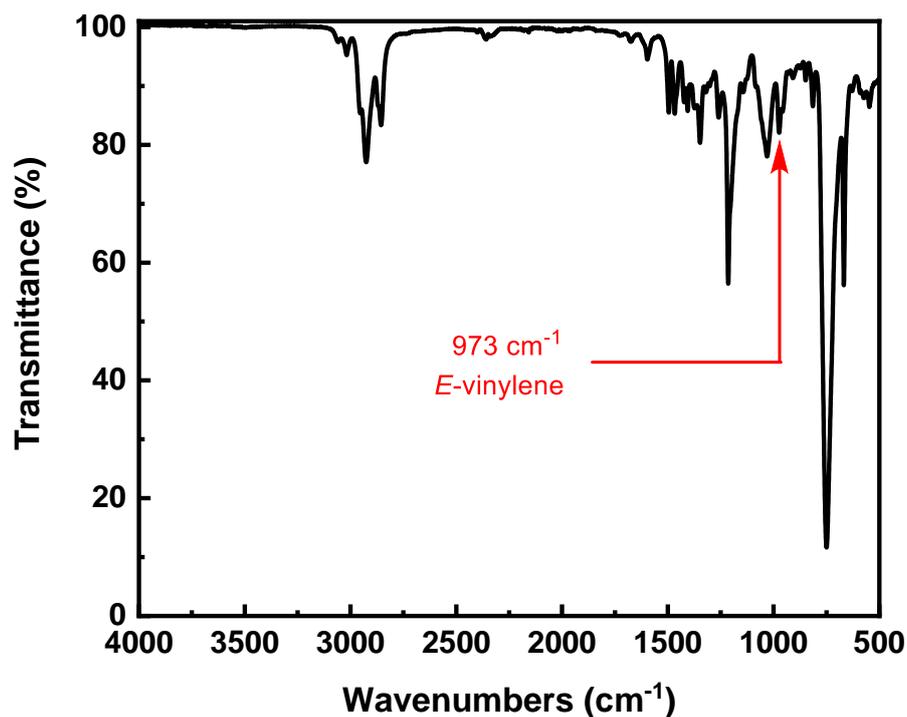


Figure S63. IR spectrum of **P8**

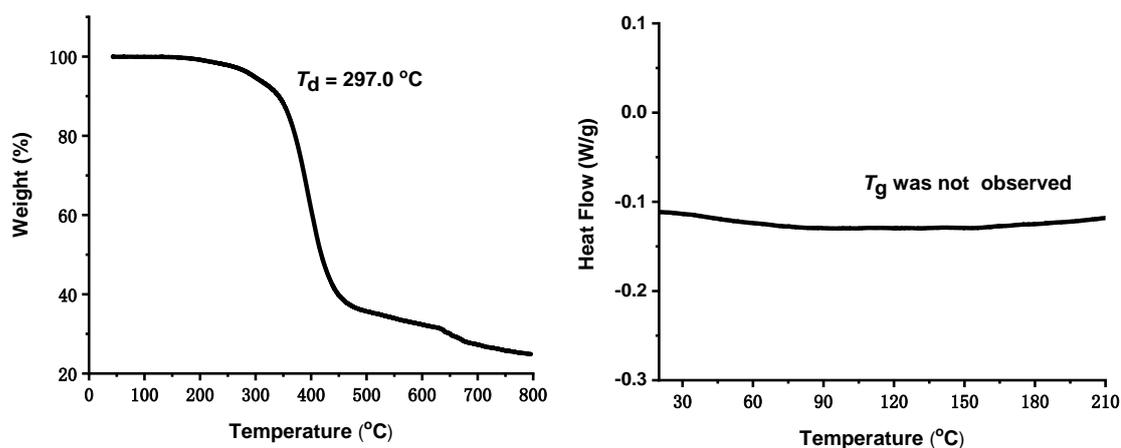


Figure S64. TGA and DSC thermograms of **P8**

P9. 95% yield; SEC: $M_n = 6.4\text{ kg/mol}$, $M_w/M_n = 1.75$; ¹H NMR (400 MHz, CDCl₃) δ 7.68-7.41 (m, 4H), 7.41-7.31 (m, 2H), 7.25-7.02 (m, 4H), 4.20-3.89 (m, 4H), 3.62-3.52 (m, 0.17H), 1.99-1.74 (m, 4H), 1.66-1.47 (m, 4H), 1.45-1.31 (m, 8H), 1.03-0.70 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 150.1, 137.3, 128.1, 127.9, 125.9, 124.3, 123.2, 122.8, 109.8, 68.6, 30.6, 28.5, 24.9, 21.6, 13.0; IR (film): 3018, 2926, 2856, 1497, 1260, 1203, 1018, 965, 801, 753 cm⁻¹.

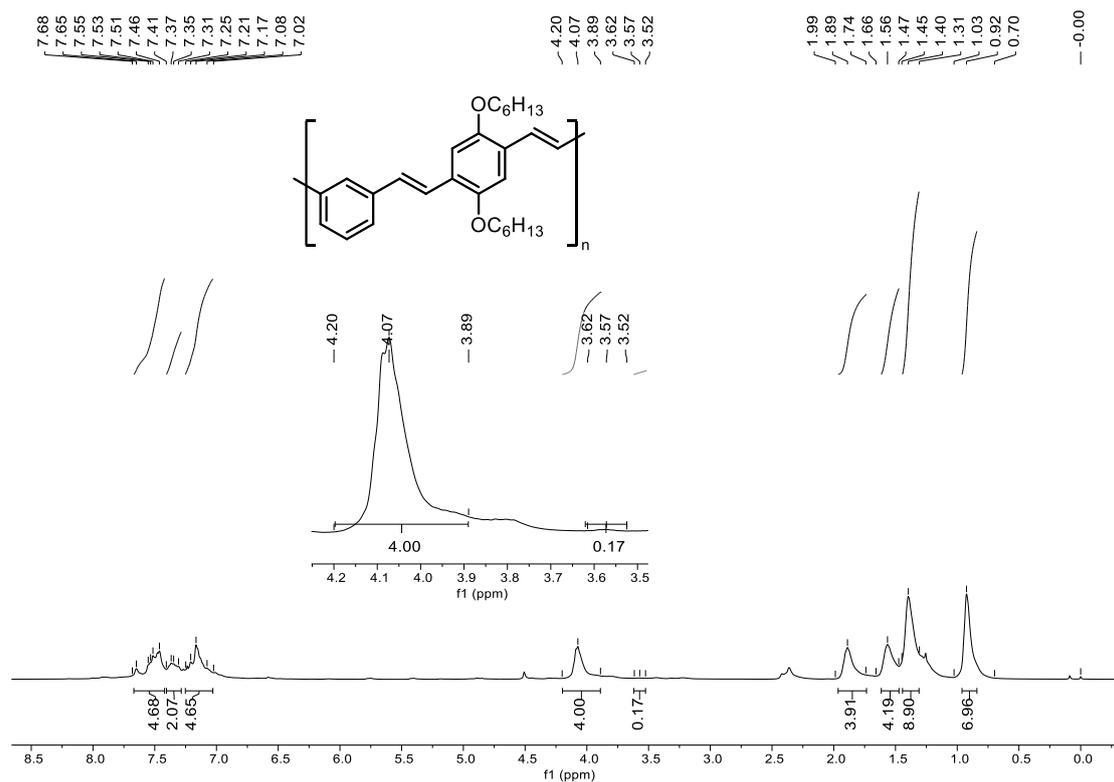


Figure S65. ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of **P9**



Figure S66. ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$) of **P9**

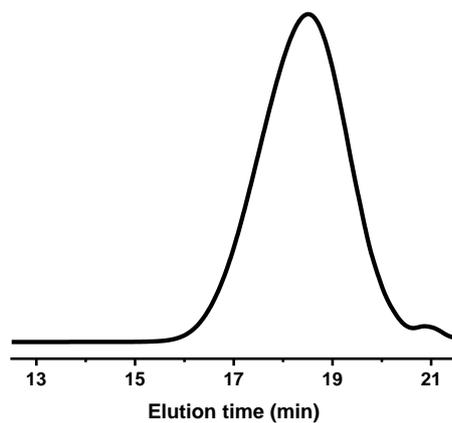


Figure S67. SEC trace of P9

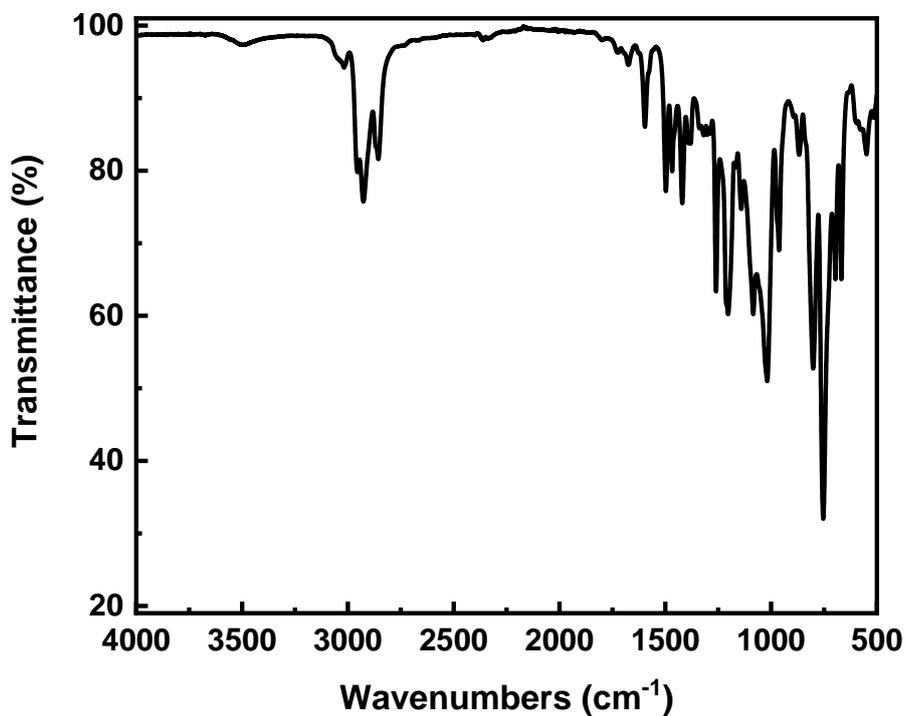


Figure S68. IR spectrum of P9

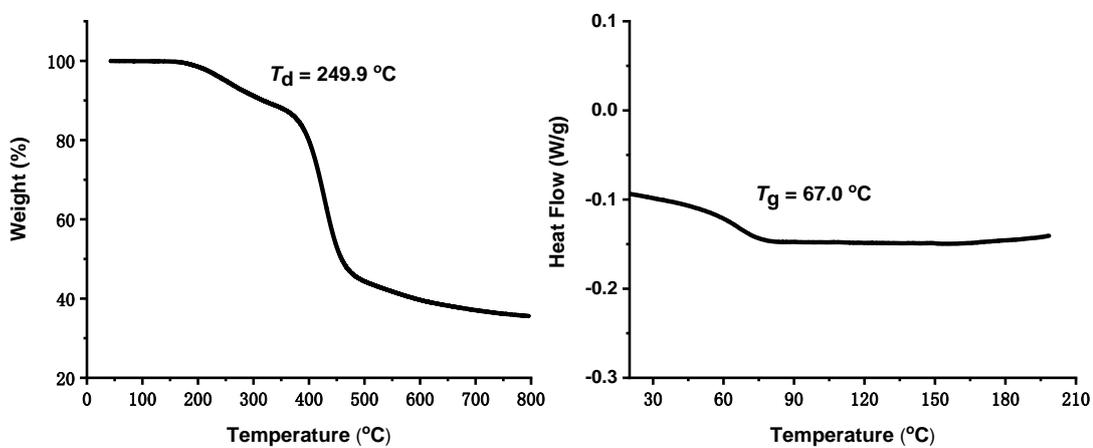


Figure S69. TGA and DSC thermograms of P9

P10. 76% yield; SEC: $M_n = 10.8$ kg/mol, $M_w/M_n = 3.32$; ^1H NMR (400 MHz, CDCl_3) δ 7.71-7.10 (m, 8H), 7.10-6.88 (m, 2H), 6.84-6.56 (m, 2H), 1.87-1.25 (m, 4H), 1.17-0.75 (m, 12H), 0.75-0.48 (m, 6H), 0.48-0.22 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.5, 141.4, 134.0, 132.4, 130.6, 129.9, 129.0, 128.4, 123.8 (q, $J = 270$ Hz) 123.7, 120.0, 54.8, 39.2, 31.4, 29.3, 23.6, 22.5, 13.9; ^{19}F NMR (470 MHz, CDCl_3) δ -65.87 - -64.29 (m, 3F), -56.04 - -55.61 (m, 0.22F); IR (film): 3021, 2927, 2856, 1467, 1260, 1215, 1150, 1113, 1018, 751 cm^{-1} .

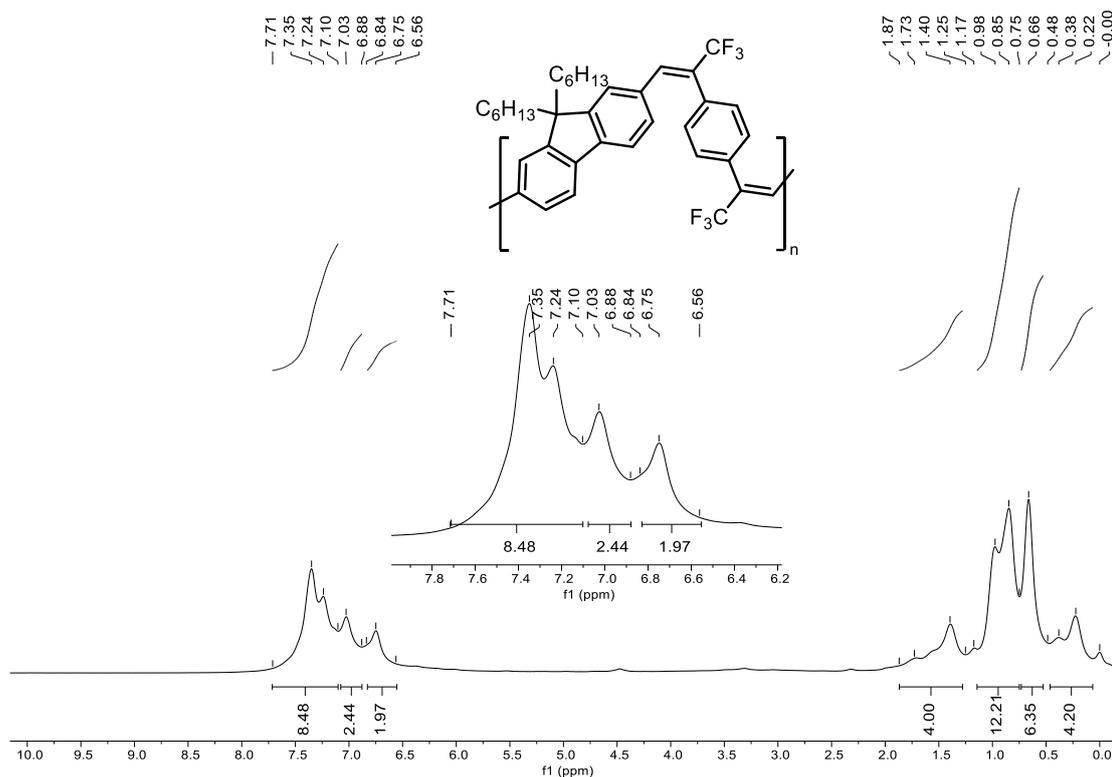


Figure S70. ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of **P10**

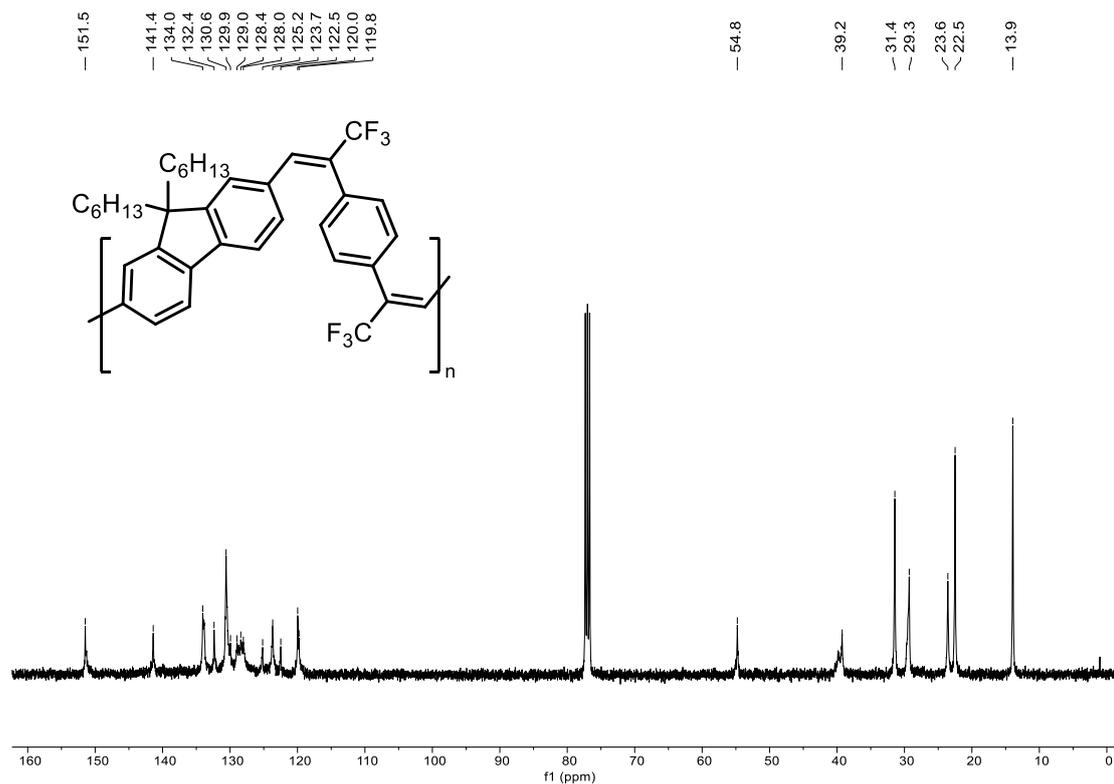


Figure S71. ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) of P10

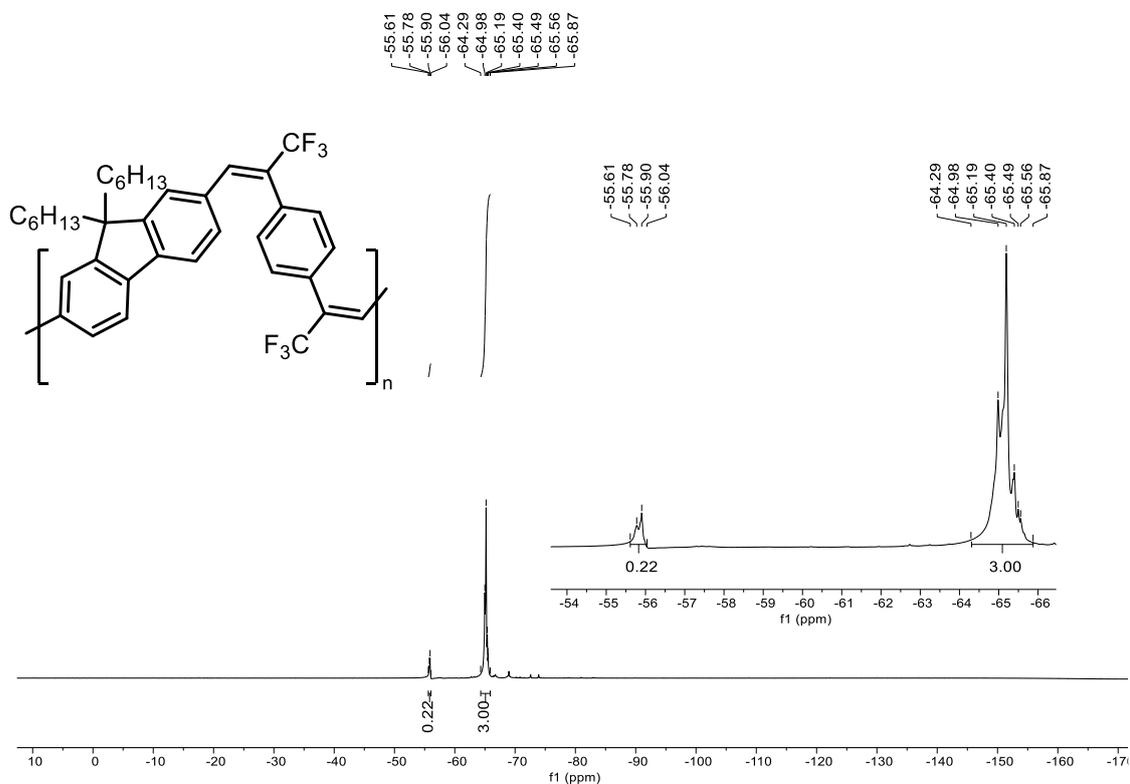


Figure S72. ^{19}F NMR (470 MHz, CDCl_3 , 25 °C) of P10

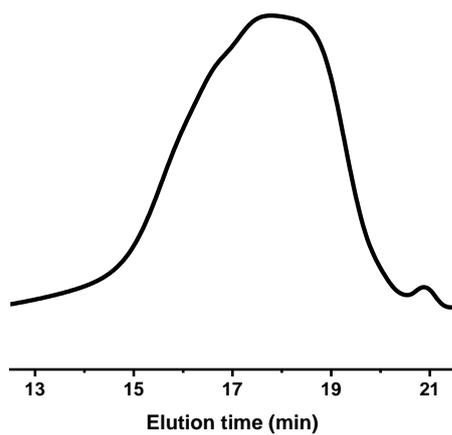


Figure S73. SEC trace of P10

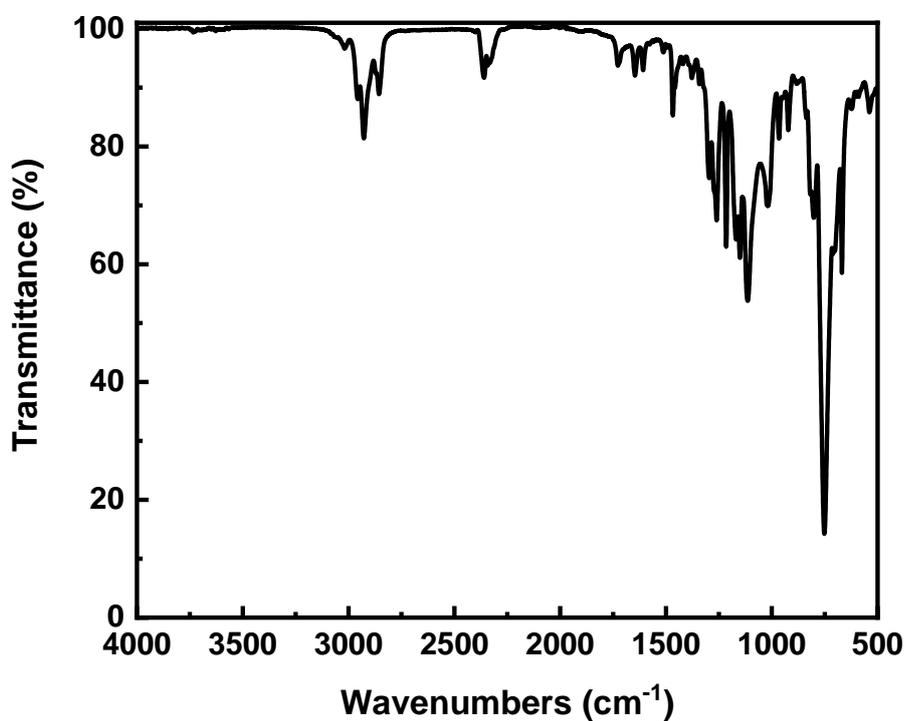


Figure S74. IR spectrum of P10

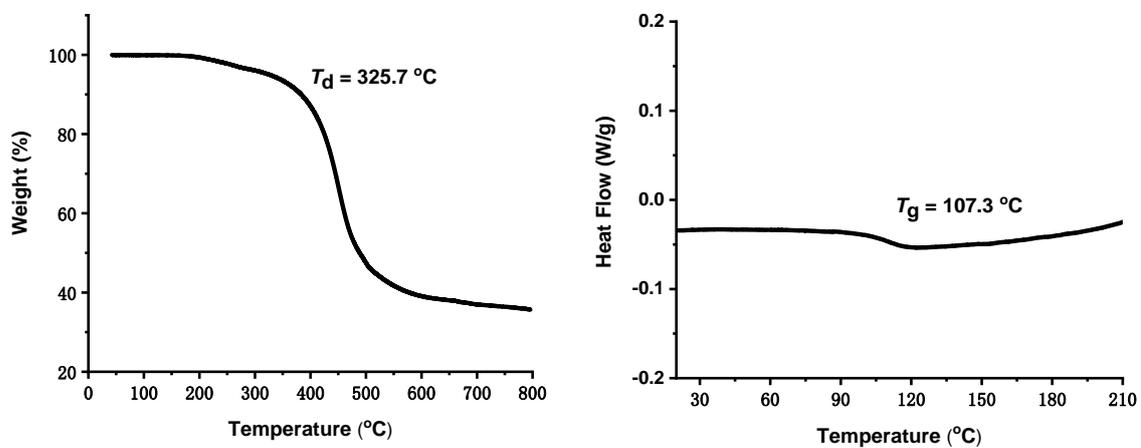


Figure S75. TGA and DSC thermograms of P10

P11. 75% yield; SEC: $M_n = 7.7$ kg/mol, $M_w/M_n = 2.53$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.98-7.40 (m, 5H), 7.40-7.12 (m, 4H), 6.86-6.71 (m, 1H), 4.18-3.78 (m, 4H), 3.46-3.40 (m, 0.31H), 2.05-1.71 (m, 4H), 1.71-1.02 (m, 20H), 0.98-0.69 (m, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 156.0, 133.4, 130.5, 129.7, 129.1, 128.5, 128.3, 126.7, 124.0, 123.7 (q, $J = 270$ Hz), 117.7, 31.7, 30.4, 29.4, 29.2, 29.1, 26.1, 22.6, 14.0; $^{19}\text{F NMR}$ (470 MHz, CDCl_3) δ -65.22 - -64.35 (m, 3F), -56.54 - -56.27 (m, 0.23F); IR (film): 2963, 2926, 2856, 1360, 1277, 1260, 1161, 1112, 1019, 959, 800, 755 cm^{-1} .

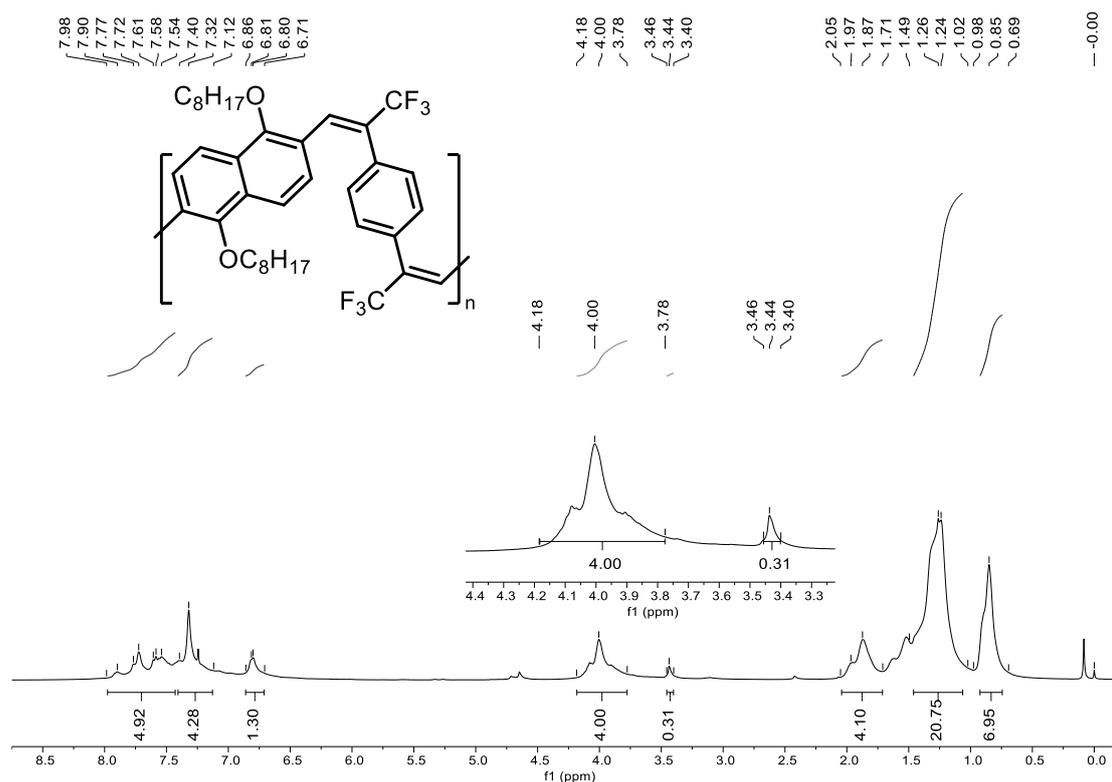


Figure S76. $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of **P11**

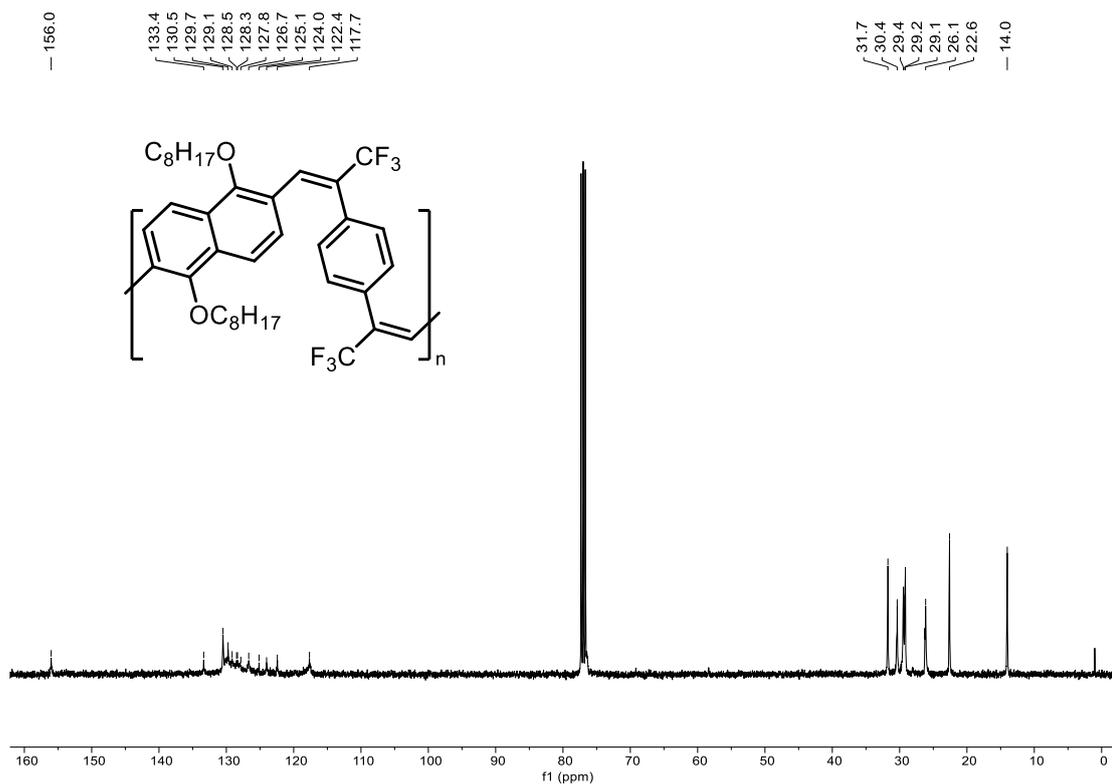


Figure S77. ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) of P11

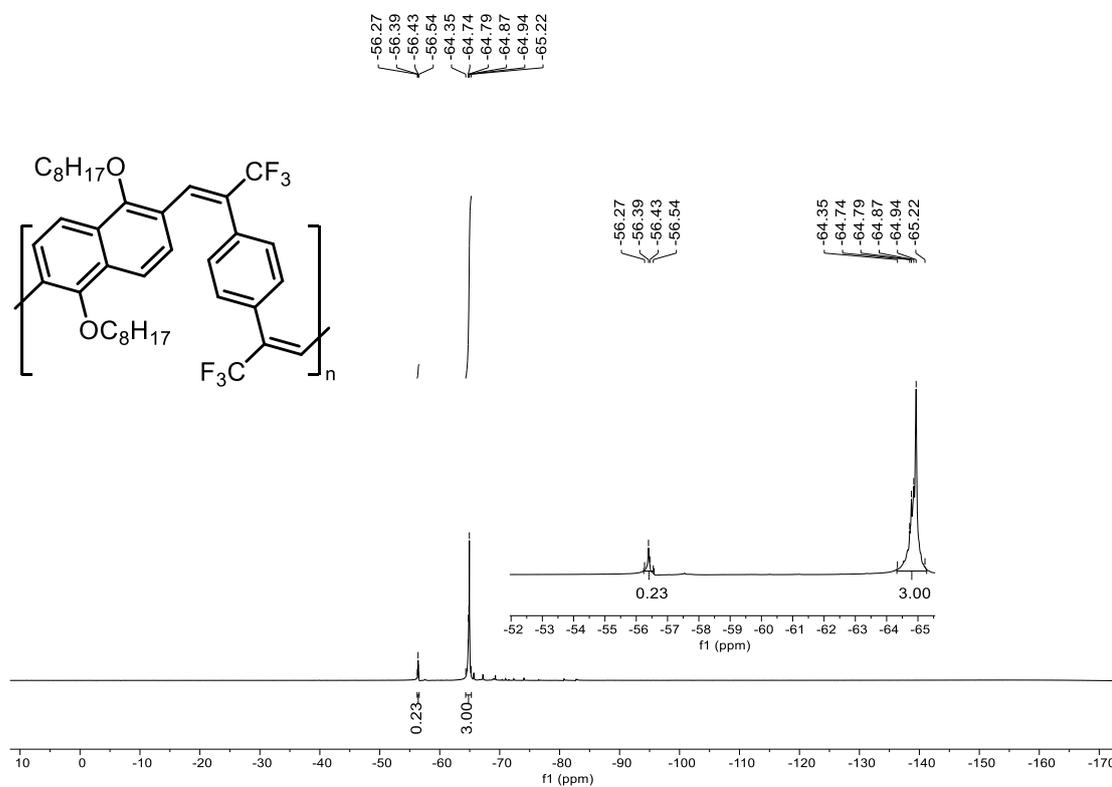


Figure S78. ^{19}F NMR (470 MHz, CDCl_3 , 25 °C) of P11

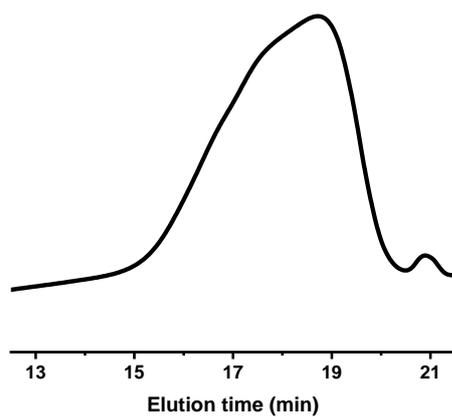


Figure S79. SEC trace of P11

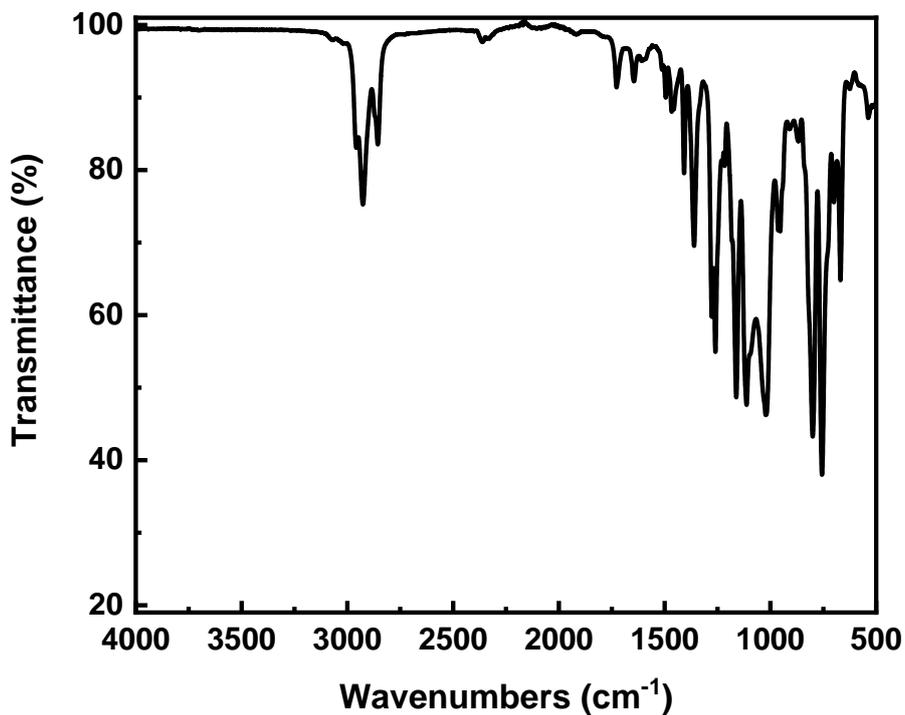


Figure S80. IR spectrum of P11

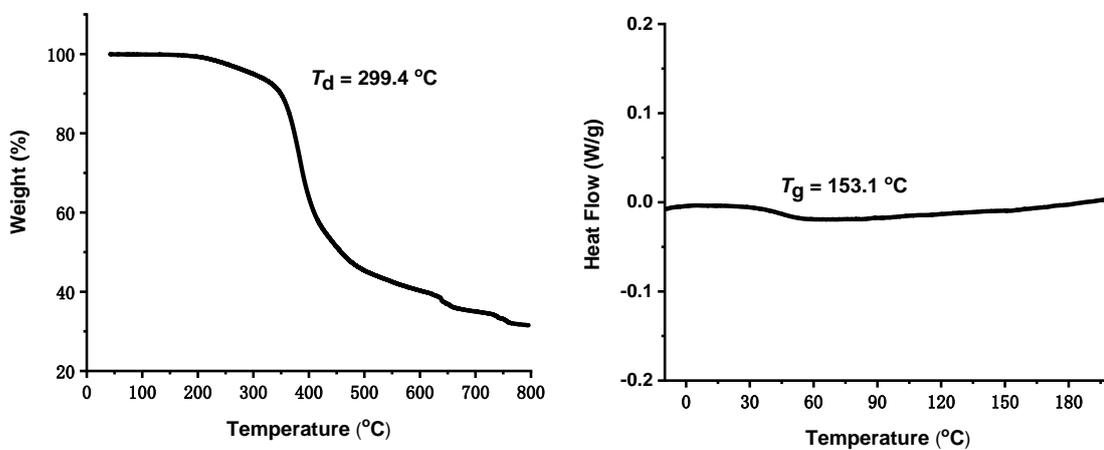


Figure S81. TGA and DSC thermograms of P11

P12. 70% yield; SEC: $M_n = 4.8$ kg/mol, $M_w/M_n = 1.85$; ^1H NMR (400 MHz, CDCl_3) δ 7.84-7.51 (m, 1H), 7.51-7.02 (m, 6H), 7.02-6.36 (m, 5H), 4.14-3.68 (m, 4H), **3.41 (m, 0.33H)**, 1.99-1.60 (m, 4H), 1.55-1.08 (m, 20H), 0.98-0.71 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.8, 156.1, 133.6, 132.3, 130.6, 129.1, 128.6, 128.2, 126.2, 123.8 (q, $J = 270$ Hz), 112.0, 68.7, 31.8, 29.3, 29.2, 26.1, 22.6, 14.1; ^{19}F NMR (470 MHz, CDCl_3) δ -65.33 - -64.13 (m, 3F), -56.67 - -55.87 (m, 0.26F); IR (film): 2926, 2855, 1606, 1489, 1468, 1288, 1249, 1159, 1113, 973, 807 cm^{-1} .

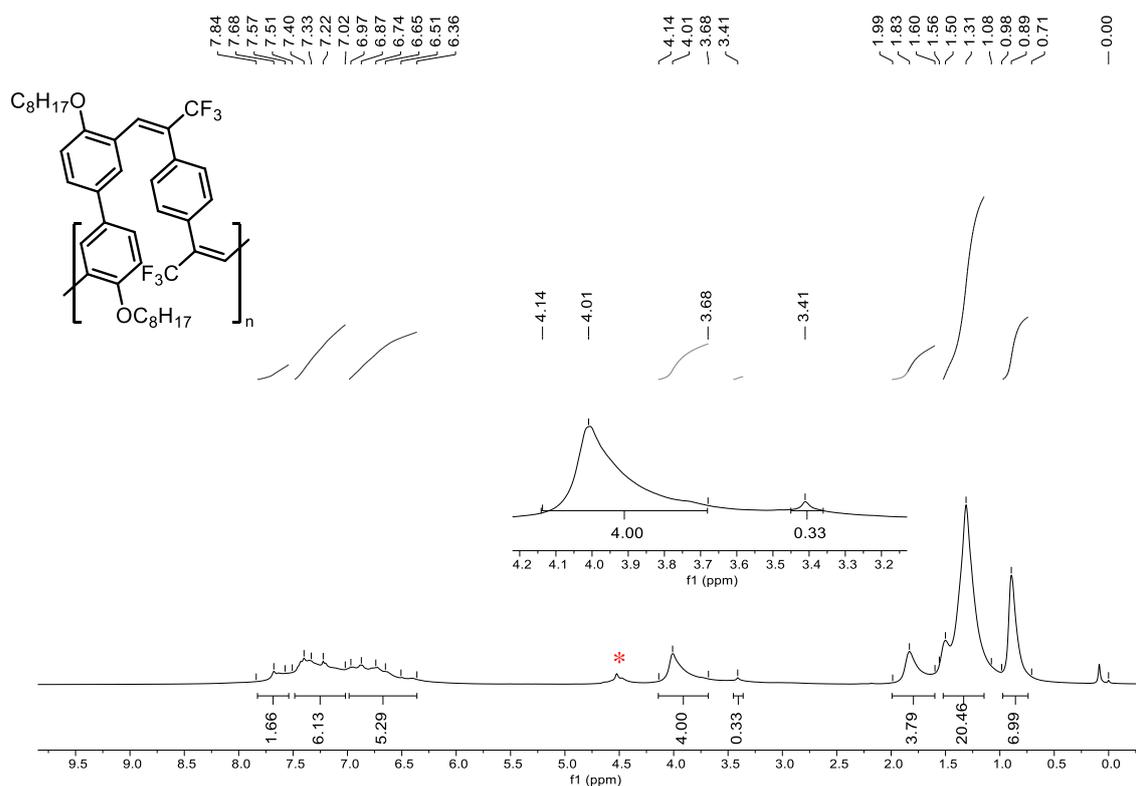


Figure S82. ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of **P12** (unassigned peak * might be caused by polymer end or dimerization side reaction)

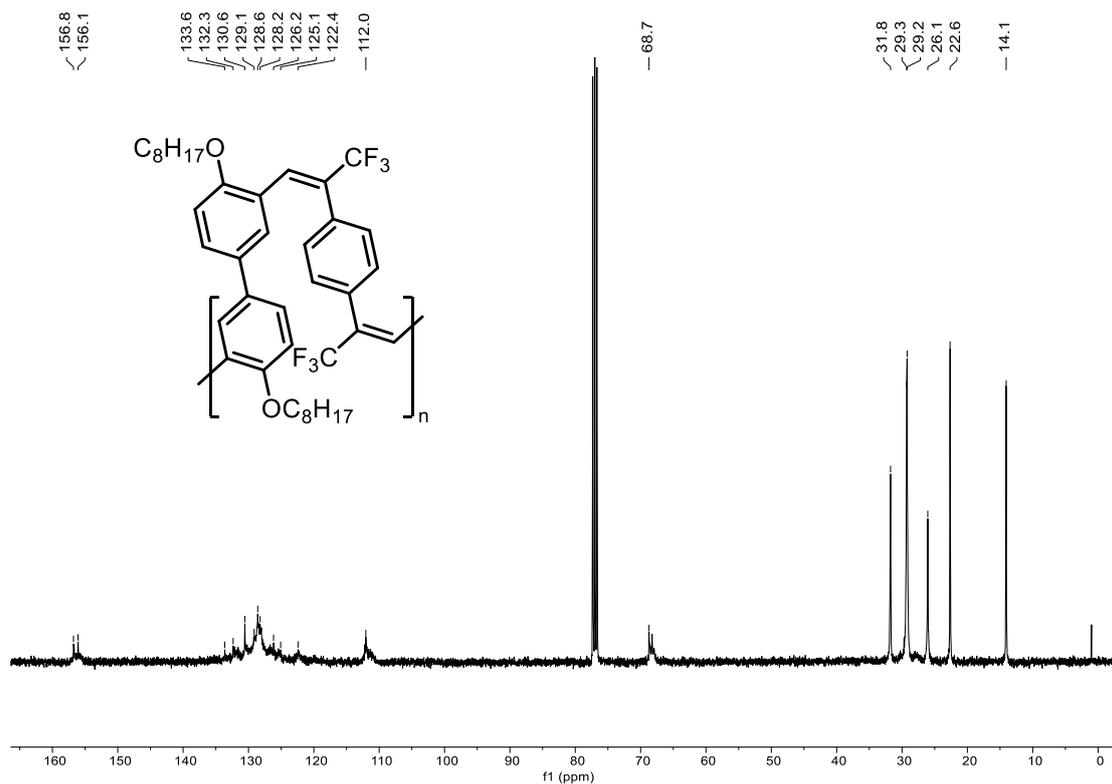


Figure S83. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) of **P12**

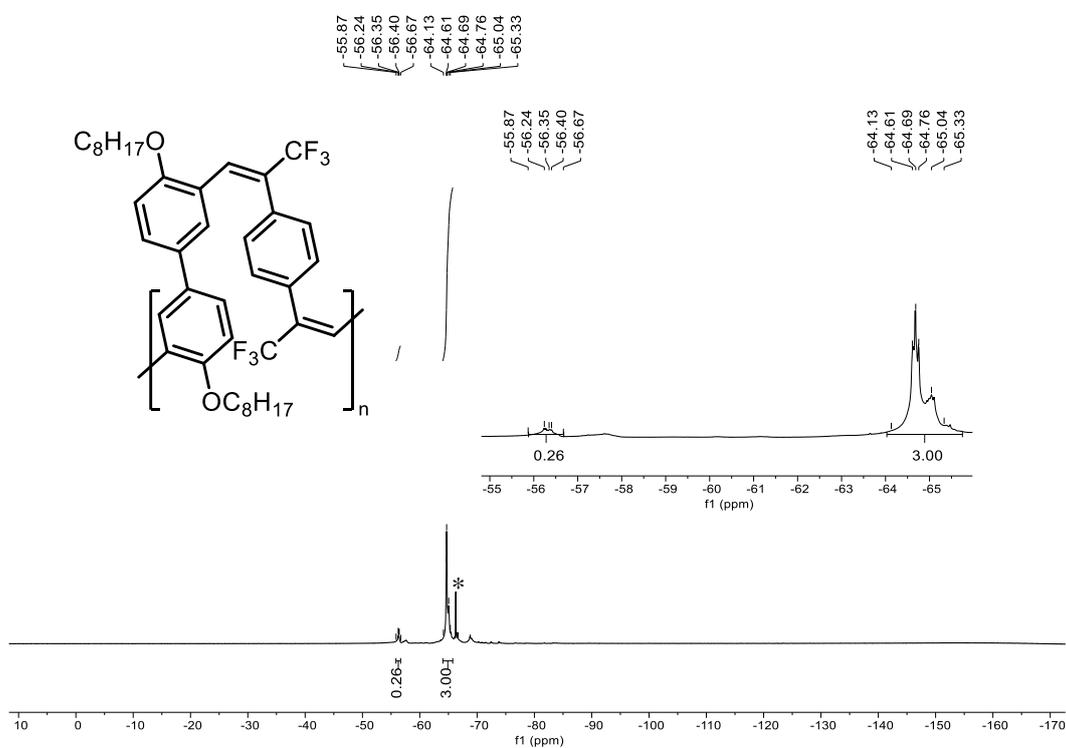


Figure S84. ^{19}F NMR (470 MHz, $CDCl_3$, 25 °C) of **P12** (un-assigned peak * may be caused by polymer end or dimerization side reaction)

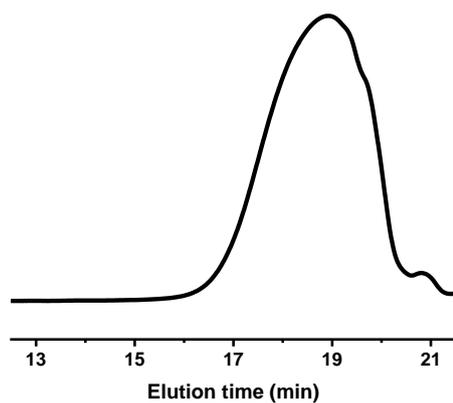


Figure S85. SEC trace of P12

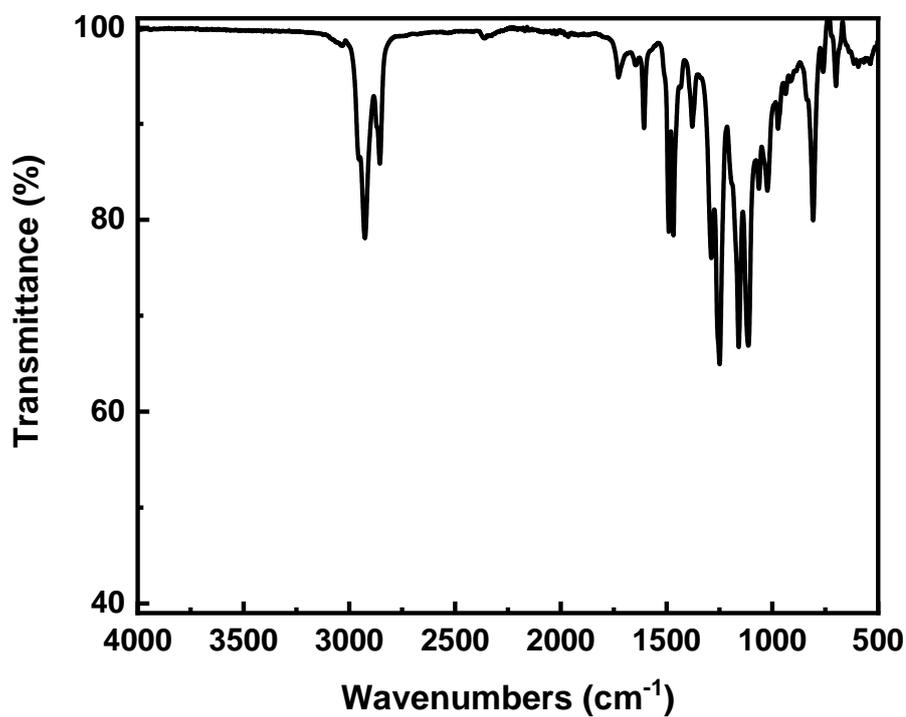


Figure S86. IR spectrum of P12

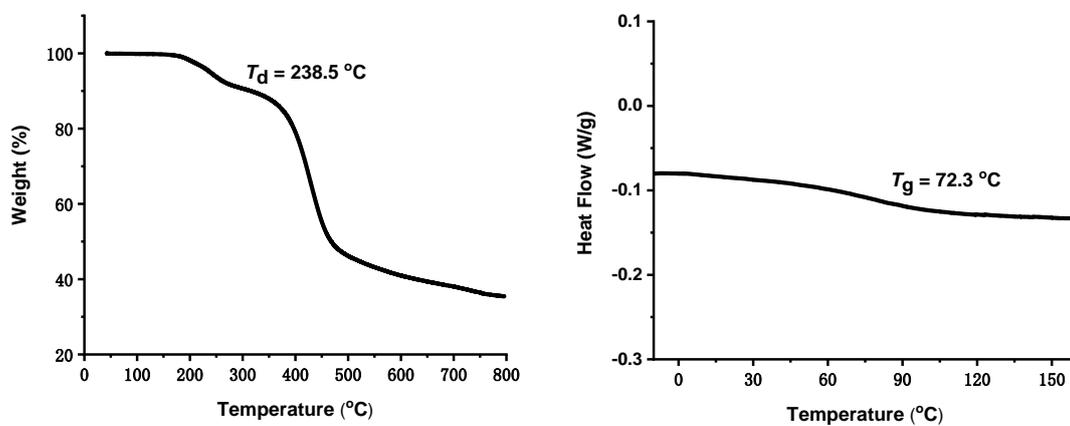


Figure S87. TGA and DSC thermograms of P12

6) Photophysical properties of the polymers

Table S2. Optical properties of the polymers

Polymer ^a	λ_{\max} absorption (nm)	λ_{\max} emission (nm)	λ_{exc} (nm)
P1	428, 451	472, 500	365
P2	448	503, 534	365
P3	379, 403	420, 443	365
P4	431	515, 544	365
P5	312, 373	448, 472	365
P6	393	471	365
P7	399	462, 489	365
P8	452	511, 543	365
P9	326, 396	453, 478	365
P10	342	471	342
P11	328	465	328
P12	271	476	300

^aUV-vis and emission spectra for polymers in CHCl₃ (10⁻⁵ M) at 25 °C.

Thin film fabrication: The thin films of the polymer were deposited on the glass substrates by spin-coating the solutions (3.0 ~ 10.0 mg/mL in chloroform) at 500 ~ 800 rpm for 60 s, and then 3000 rpm for 3 s, followed by annealing at 120 °C for 10 min.

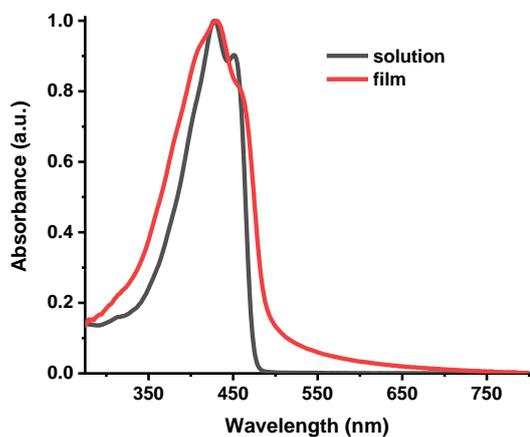


Figure S88. UV-vis spectra for P1

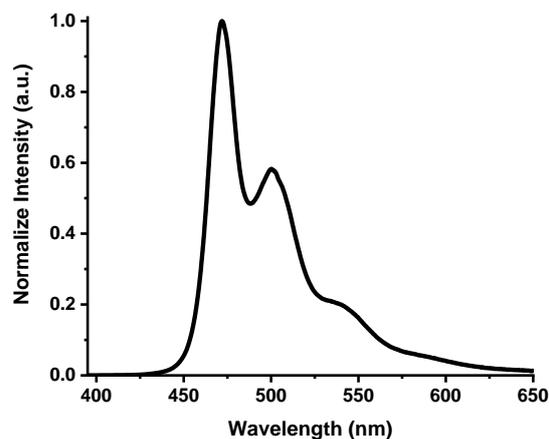


Figure S89. Emission spectra for P1

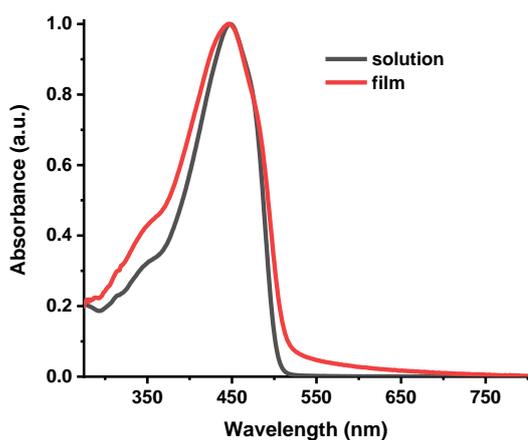


Figure S90. UV-vis spectra for P2

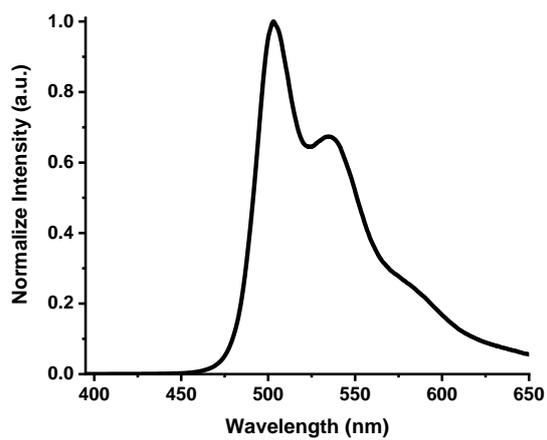


Figure S91. Emission spectra for P2

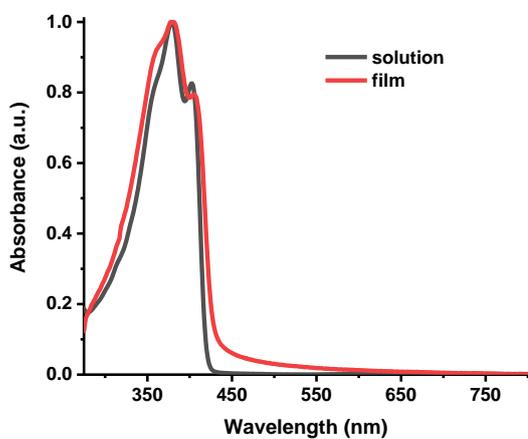


Figure S92. UV-vis spectra for P3

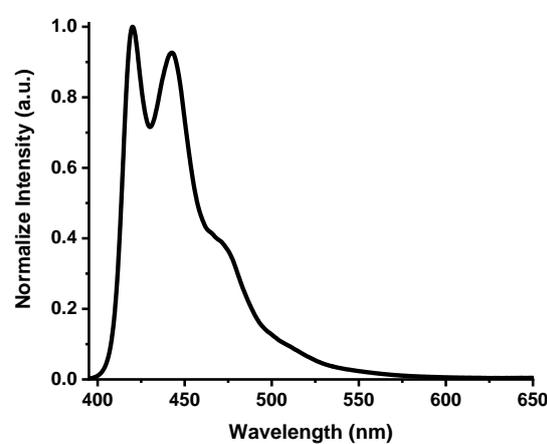


Figure S93. Emission spectra for P3

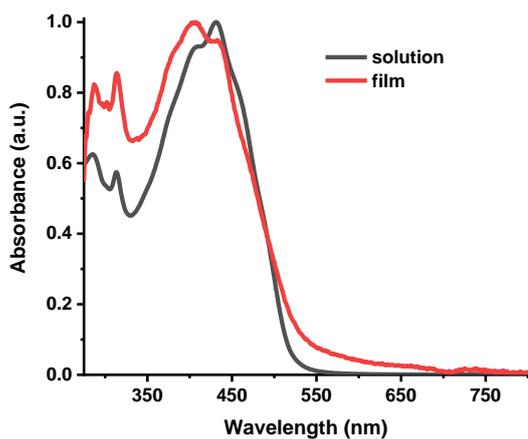


Figure S94. UV-vis spectra for P4

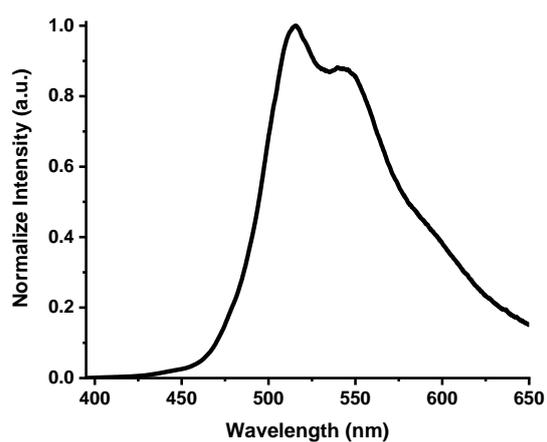


Figure S95. Emission spectra for P4

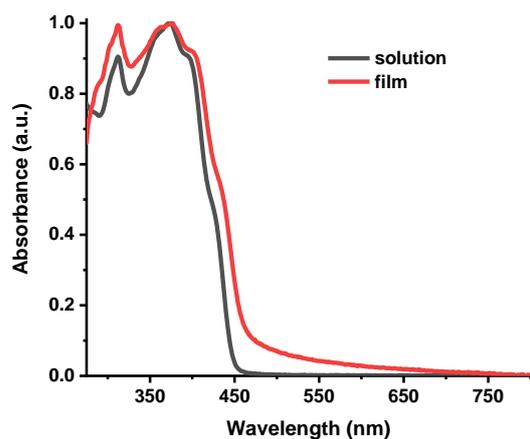


Figure S96. UV-vis spectra for P5

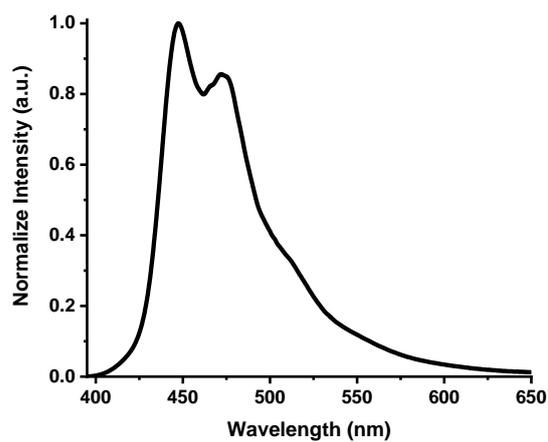


Figure S97. Emission spectra for P5

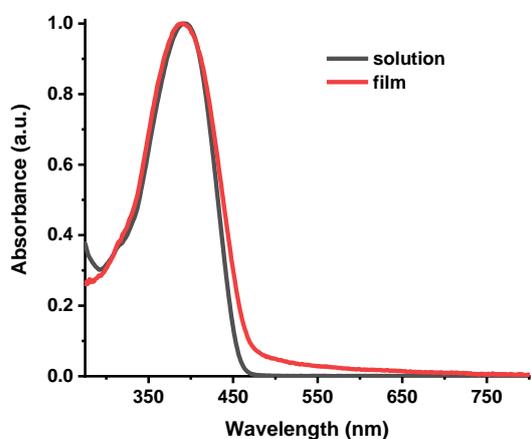


Figure S98. UV-vis spectra for P6

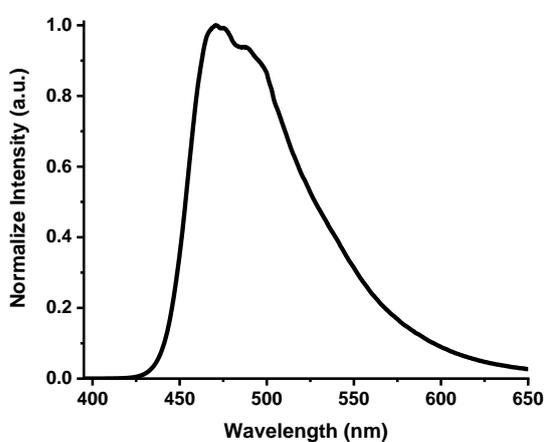


Figure S99. Emission spectra for P6

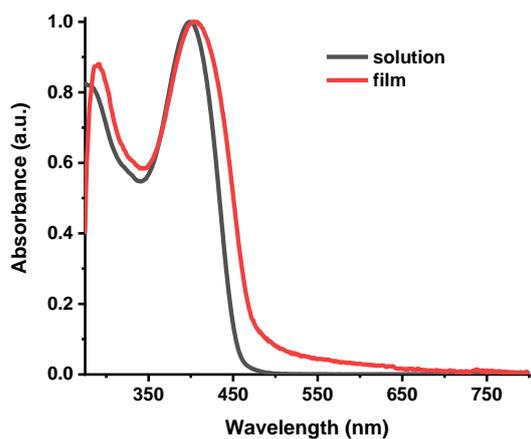


Figure S100. UV-vis spectra for P7

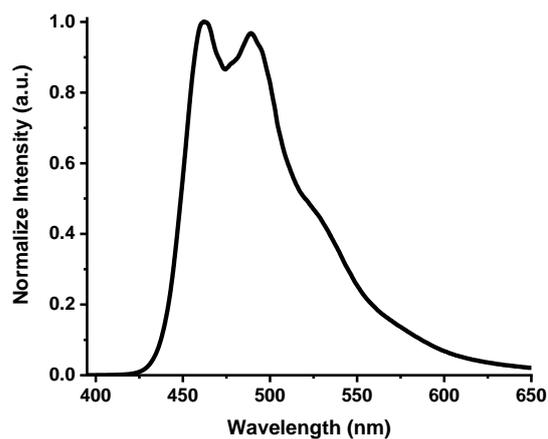


Figure S101. Emission spectra for P7

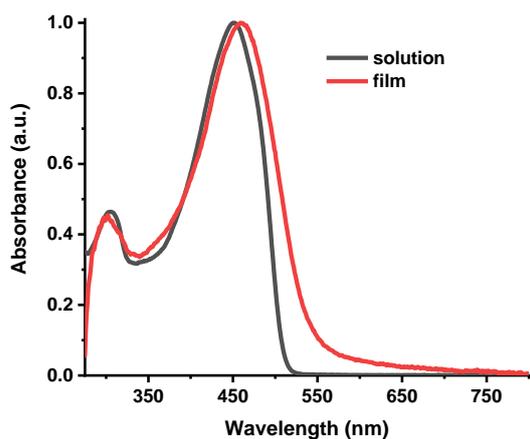


Figure S102. UV-vis spectra for P8

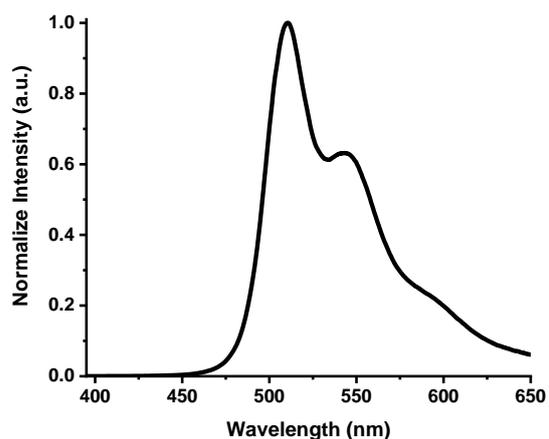


Figure S103. Emission spectra for P8

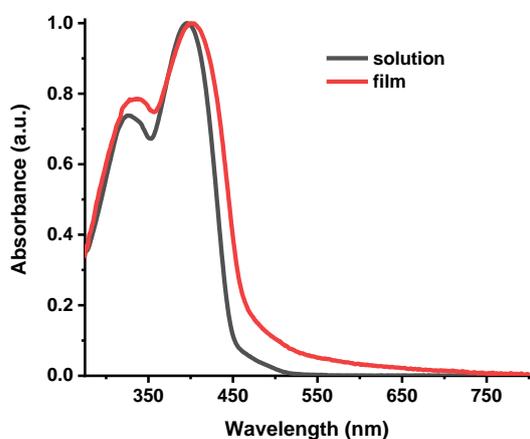


Figure S104. UV-vis spectra for P9

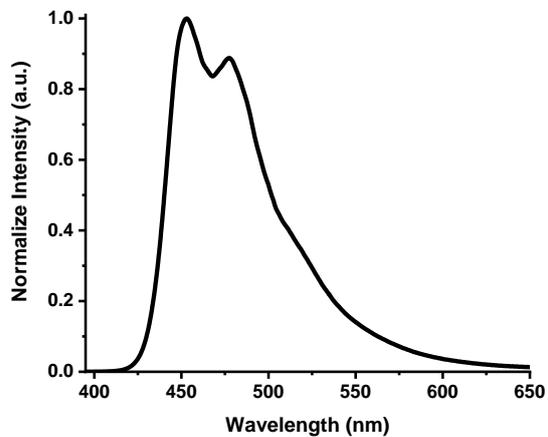


Figure S105. Emission spectra for P9

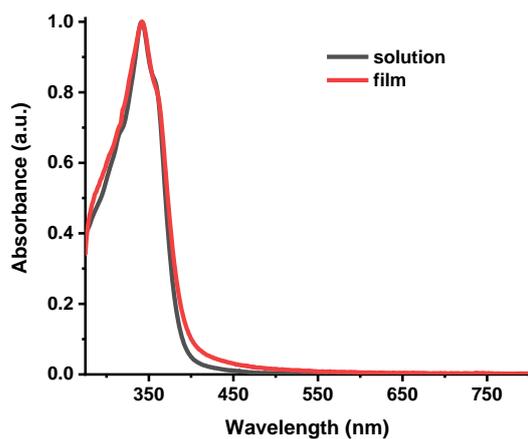


Figure S106. UV-vis spectra for P10

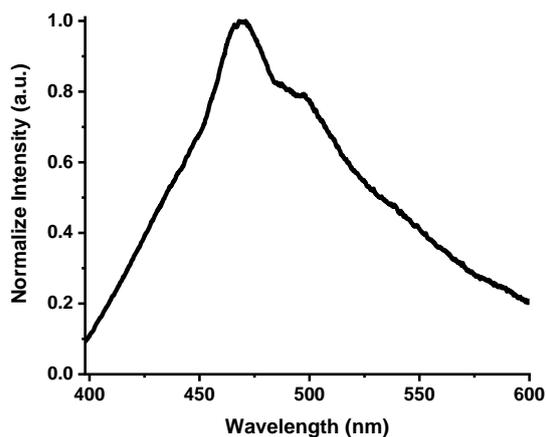


Figure S107. Emission spectra for P10

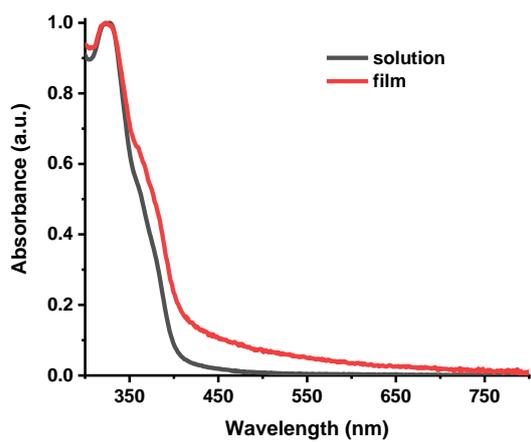


Figure S108. UV-vis spectra for P11

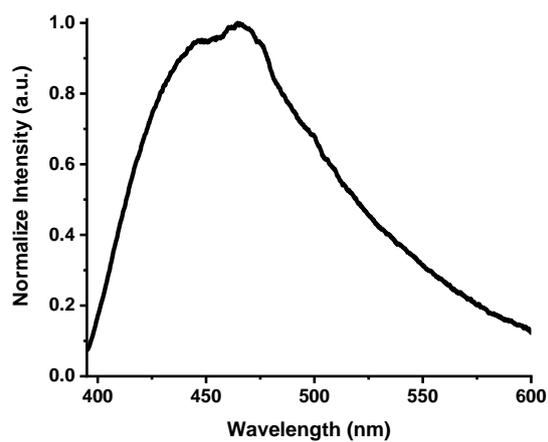


Figure S109. Emission spectra for P11

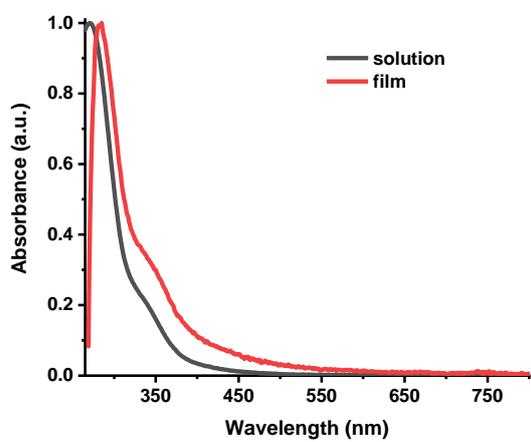


Figure S110. UV-vis spectra for P12

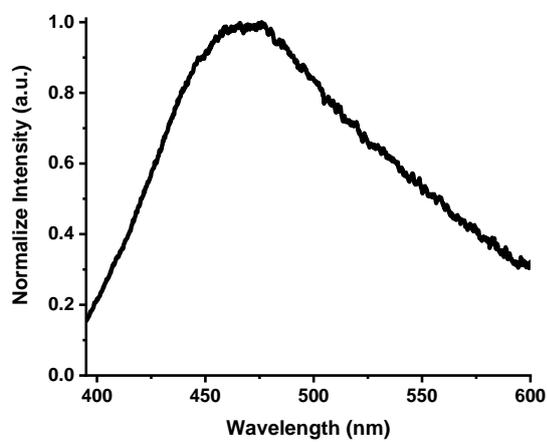
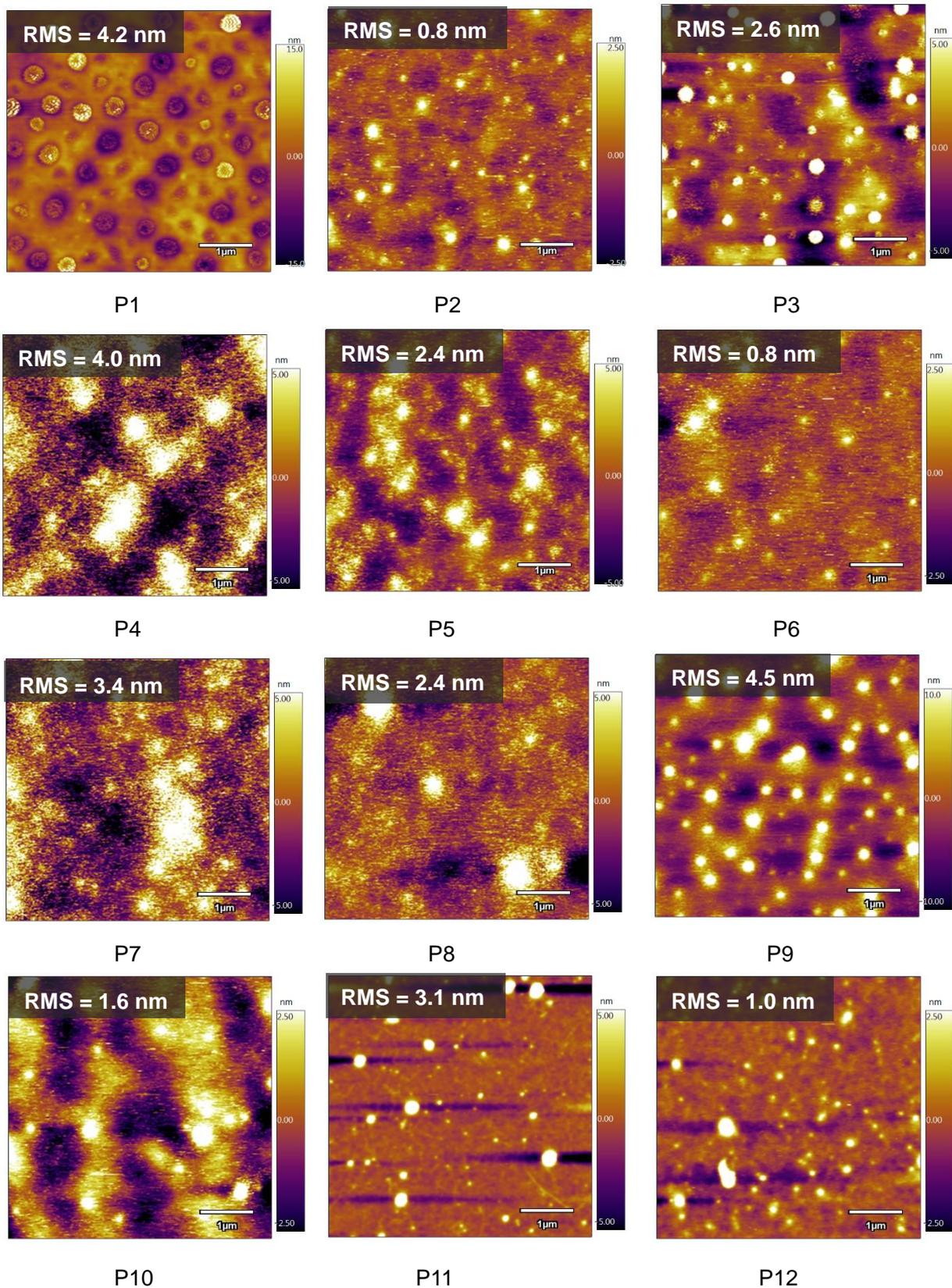


Figure S111. Emission spectra for P12

7) The morphologies of the polymers

The morphologies of the polymer products were analyzed by Atomic Force Microscope (AFM).



8) ICP analysis of the P1

As an example, metal residue in P1 was analyzed by Inductively Coupled Plasma Mass Spectrometry. The concentration of palladium is 0.11%, and the concentration of lithium is 4.5 ppm.

9) References

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