Electronic Supplementary Information (ESI)

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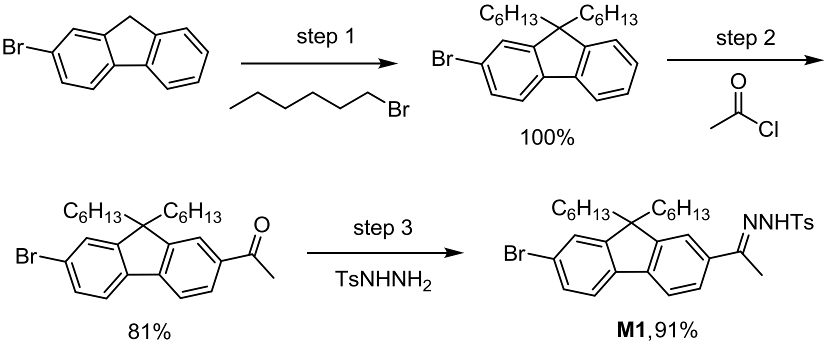
1) General

Dioxane for polymerization was distilled with sodium/benzophenone under nitrogen atmosphere prior to use. All reagents, unless otherwise noted, are commercially available and used without further purification. All polymerization reactions were carried out under nitrogen atmosphere. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz with Brucker ARX 400 spectrometer or 500 MHz with Bruker-500 MHz NMR (AVANCE III). Chemical shifts were reported in ppm using tetramethylsilane as the internal standard. Size exclusion chromatography (SEC) for the analysis of number-average molecular weights M_n and M_w/M_n of the polymers was carried out with Waters 515 GPC instrument using THF as eluent at a flow rate of 1.0 mL/min at 35 ^{o}C. The GPC calibration curve was obtained with linear polystyrene standards. Thermal gravimetric analysis (TGA) was conducted on a Q600-SDT thermogravimetric analyzer at a heating rate of 10 ℃/min under a nitrogen atmosphere of 100 mL/min. Differential scanning calorimetry (DSC) was performed on a Q100 differential scanning calorimeter at a heating rate of 10 ℃/min under a nitrogen atmosphere of 50 mL/min. Data of the endothermic thermograms were recorded from the second scan and analyzed with a TA Universal Analysis software. HRMS data were obtained on Brucker Apex IV FTMS spectrometer and ThermoFisher Q exactive hybrid quadrupole-orbitrap GC-MS/MS system. MALDI-TOF mass spectra were recorded on an AB Sciex-5800 in the reflection mode with a laser (λ = 337 nm) using hydrochinon acid as a matrix. The absorption spectra of polymers were obtained using a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. The emission and excitation spectra of polymers were obtained using a Horiba Scientific FLUOROMAX-4 spectrofluorometer. PE: petroleum ether; EA: ethyl acetate.

2) Preparation of the monomers

Synthesis and characterization of the monomer M1



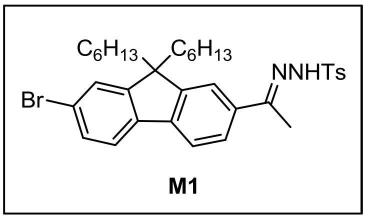
Step 1.[1] Under N_2 atmosphere, 2-bromofluorene (9.76 g, 40 mmol), benzyltriethylammoniumchloride (501.1 mg, 2.2 mmol) in 60 mL of DMSO and 40 mL of aqueous NaOH (50%, w/w) were mixed. 1-Bromohexane (19.810 g, 120 mmol) was added to the mixture using a syringe. The mixture was stirred at 35 ℃ for 5 h. After 80 mL of H_2O was added, the solution was then extracted twice with 100 mL of diethyl ether. The diethyl ether layer was dried over anhydrous Na_2SO_4 and then was evaporated under reduced pressure,

followed by removal of excess 1-bromohexane by distillation under vacuum. The crude product was purified by chromatography on silica gel with petroleum ether to afford 2-bromo-9,9-dihexyl-9*H*-fluorene as a colorless oil in quantitative yield.

Step 2.[2] To a mixture of 2 mL of DCM and $AlCl_3$ (800.04 mg, 6 mmol), which was cooled to approximately 0 °C. Acetyl chloride (429 mg, 5.5 mmol) in 3 mL of DCM was added over a period of 15-20 min. Then, a solution of 2-bromo-9,9-dihexyl-9*H*-fluorene (2.06 g, 5 mmol) in 5 mL of DCM was gradually added to the resulting acetylating complex at 0 °C over a period of 1 h. Then the reaction mixture was stirred at 0 ℃ for an additional 2.5 h. The cooled hydrochloric acid was added carefully, and the solution was then extracted twice with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and then was evaporated under reduced pressure. The crude product was purified by chromatography on silica gel with petroleum ether and ethyl acetate (PE:EA = 50:1) to afford 1-(7-bromo-9,9-dihexyl-9*H*-fluoren-2-yl)ethan-1-one as a yellow oil in 81% yield.

Step 3. A mixture of 1-(7-bromo-9,9-dihexyl-9*H*-fluoren-2-yl)ethan-1-one (1.7971 g, 3.96 mmol) and $TsNHNH_2$ (736.6 mg, 3.96 mmol) in MeOH (4 mL) was heated to 50 ℃ until the carbonyl compound disappeared. The *N*-tosylhydrazones precipitated during the reaction. The precipitate was washed twice with MeOH and the white solid (**M1**, 2.464 g, 91% yield) was obtained and used without further purification.

(Z)-N'-(1-(7-bromo-9,9-dihexyl-9H-fluoren-2-yl)ethylidene)-4-methylbenzenesulfonohydrazide (M1)



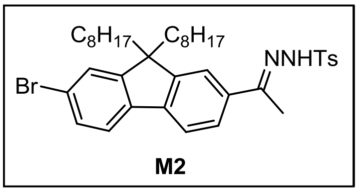
M1

White solid (m.p. = 162-163 °C); ^1H NMR (400 MHz, d_6-DMSO): δ 10.52 (s, 1H), 7.89 (d, J = 8.2 Hz, 2H), 7.79 (dd, J = 12.2, 8.1 Hz, 2H), 7.67 (s, 2H), 7.62 (dd, J = 8.0, 1.3 Hz, 1H), 7.52 (dd, J = 8.1, 1.7 Hz, 1H), 7.41 (d, J = 8.2 Hz, 2H), 2.36 (s, 3H), 2.23 (s, 3H), 2.04-1.92 (m, 4H), 1.08-0.93 (m, 12H), 0.70 (t, J = 7.0 Hz, 6H), 0.46 (m, 4H); ^{13}C NMR (101 MHz, d_6-DMSO): δ 153.8, 153.7, 150.2, 143.7, 141.2, 139.6, 137.2, 136.7, 130.5, 129.7, 128.3, 126.5, 125.9, 122.5, 121.4, 120.6, 120.4, 55.5, 31.3, 29.4, 23.8, 22.4, 21.4, 14.9, 14.2; HRMS (ESI): calcd for $C_{34}H_{44}BrN_2O_2S$ $[M+H]^+$ 623.2301, found 623.2296.

Synthesis and characterization of the monomer M2

The monomer **M2** was prepared following the same procedure as for the preparation of **M1**.

(Z)-N'-(1-(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)ethylidene)-4-methylbenzenesulfonohydrazide (M2)

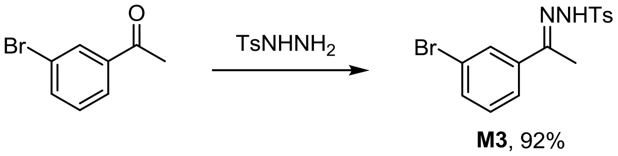


M2

White solid (m.p. = 158-159 °C); ^1H NMR (400 MHz, d_6-DMSO): δ 10.51 (s, 1H), 7.87 (d, J = 8.2 Hz, 2H), 7.76 (dd, J = 12.0, 8.1 Hz, 2H), 7.66-7.59 (m, 3H), 7.49 (dd, J = 8.1, 1.6 Hz, 1H), 7.38 (d, J = 8.2 Hz, 2H), 2.34 (s, 3H), 2.21 (s, 3H), 1.95 (d, J = 9.0 Hz, 4H), 1.14-0.96 (m, 20H), 0.74 (t, J = 7.1 Hz, 6H), 0.46 (m, 4H); ^{13}C NMR (101 MHz, d_6-DMSO): δ 153.7, 153.6, 150.2, 143.6, 141.2, 139.6, 137.2, 136.7, 130.4, 129.7, 128.3, 126.4, 125.8, 122.5, 121.4, 120.6, 120.3, 55.5, 31.6, 29.6, 29.0, 23.7, 22.5, 21.4, 14.8, 14.3. HRMS (ESI):

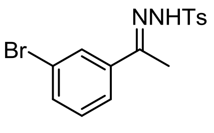
calcd for $C_{38}H_{52}BrN_2O_2S$ $[M+H]^+$ 679.2927, found 679.2926.

Synthesis and characterization of the monomer M3



A mixture of 1-(3-bromophenyl)ethan-1-one (1.99 g, 10 mmol) and $TsNHNH_2$ (1.86 g, 10 mmol) in MeOH (10 mL) was heated to 50 °C until the carbonyl compound disappeared. The *N*-tosylhydrazones precipitated during the reaction. The precipitate was washed twice with MeOH and the white solid (**M3**, 3.3564 g, 92% yield) was obtained and used without further purification.

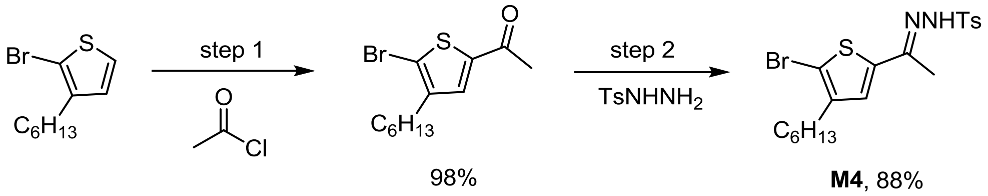
(Z)-N'-(1-(3-bromophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (M3)



M3

White solid (m.p. = 166-167 °C); ^{1}H NMR (400 MHz, d_6-DMSO): δ 10.70 (s, 1H), 7.83 (d, J = 8.2 Hz, 2H), 7.75 (t, J = 1.6 Hz, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.56 (dd, J = 8.0, 1.0 Hz, 1H), 7.42 (d, J = 8.1 Hz, 2H), 7.34 (t, J = 7.9 Hz, 1H), 2.37 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, d_6-DMSO): δ 151.9, 143.9, 140.2, 136.6, 132.5, 131.0, 130.0, 129.0, 128.0, 125.5, 122.3, 21.5, 14.7. HRMS (ESI): calcd for $C_{15}H_{16}BrN_2O_2S$ $[M+H]^+$ 367.0110, found 367.0114.

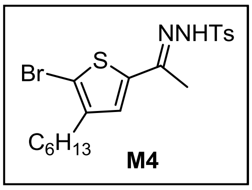
Synthesis and characterization of the monomer M4



Step 1.[3] To a mixture of 10 mL of DCE and $AlCl_3$ (733.4 mg, 5.5 mmol), which was cooled to approximately 0 °C, acetyl chloride (429 mg, 5.5 mmol) in 3 mL of DCE was added over a period of 15-20 min. Then, a solution of 2-bromo-3-hexylthiophene (1.236 g, 5 mmol) in 10 mL of DCE was gradually added to the resulting acetylating complex at 0 °C over a period of 10 min. the reaction mixture was slowly warmed to RT and allowed to stir at RT. After the completion of the reaction (monitored by TLC), the cooled hydrochloric acid was added carefully, and the solution was then extracted twice with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and then was evaporated under reduced pressure. The crude product was purified by chromatography on silica gel with petroleum ether and ethyl acetate (PE:EA = 20:1) to afford 1-(5-bromo-4-hexylthiophen-2-yl)ethan-1-one as a yellow oil in 98% yield.

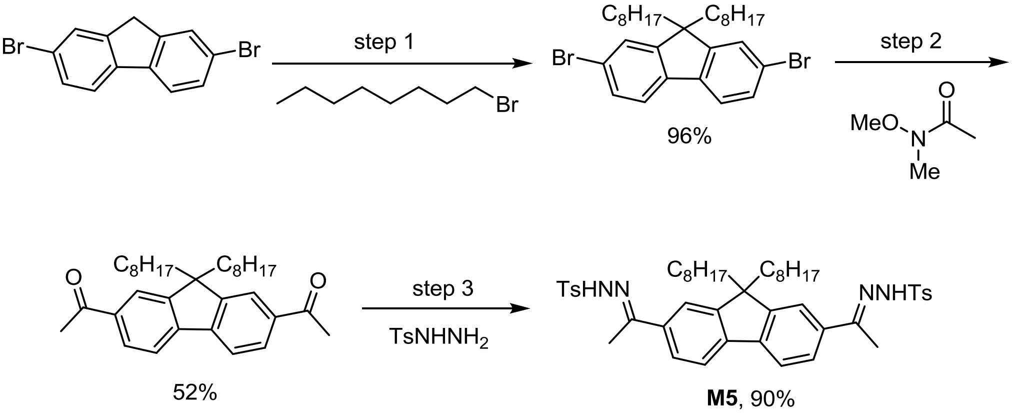
Step 2. A mixture of 1-(5-bromo-4-hexylthiophen-2-yl)ethan-1-one (1.3733 g, 4.77 mmol) and $TsNHNH_2$ (887.2 mg, 4.77 mmol) in MeOH (5 mL) was heated to 50 °C until the carbonyl compound disappeared. Then the solvent was evaporated under reduced pressure and the crude product was purified by chromatography on silica gel with petroleum ether and ethyl acetate (PE:EA = 5:1) to afford the monomer **M4** as a yellow solid in 88%.

(Z)-N'-(1-(5-bromo-4-hexylthiophen-2-yl)ethylidene)-4-methylbenzenesulfonohydrazide (M4)



Yellow solid (m.p. = 117-118 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.3 Hz, 2H), 7.82 (s, 1H), 7.33 (d, J = 8.1 Hz, 2H), 6.86 (s, 1H), 2.48 (t, J = 7.6 Hz, 2H), 2.43 (s, 3H), 2.10 (s, 3H), 1.54-1.48 (m, 2H), 1.32-1.28 (m, 6H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, d_6-DMSO): δ 149.4, 143.9, 142.7, 142.6, 136.4, 129.9, 129.2, 128.1, 111.6, 31.4, 29.4, 28.6, 22.5, 21.5, 14.4, 14.2. HRMS (ESI): calcd for $C_{19}H_{26}BrN_2O_2S_2$ $[M+H]^+$ 457.0613, found 457.0615.

Synthesis and characterization of the monomer M5

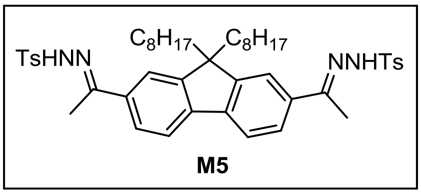


Step 1.[4] To a mixture of 2,7-dibromofluorene (3.24 g, 10 mmol), triethylbenzylammonium chloride (136.7 mg, 0.6 mmol) in 15 mL DMSO and 3.8 mL of aqueous NaOH (50 % w/w), 1-bromooctane (5.7936 g, 5.2 mL) was added. The reaction mixture was warmed to 60 °C and stirred for 2 h at this temperature. 30 mL of H_2O was added and the mixture was then extracted twice with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and then was evaporated under reduced pressure, followed by removal of excess 1-bromooctane by distillation under vacuum. The crude product was recrystallized with ethyl ether to afford 2,7-dibromo-9,9-dioctyl-9*H*-fluorene as a white solid in 96% yield.

Step 2.[5] A solution of *n*-BuLi (2.5 M, 15.4 mmol) was added dropwise under nitrogen to a cooled (-78 °C) solution of 2,7-dibromo-9,9-dioctyl-9*H*-fluorene (3.822 g, 7 mmol) in dry THF (49 mL). The resulting mixture was stirred at -78 °C for 1 h, a solution of *N*-methoxy-*N*-methylacetamide (2.97 ml, 28 mmol) in dry THF (14 ml) was added. The reaction mixture was warmed to the room temperature gradually for 18 h. H_2O was added to quench the reaction, and the mixture was extracted twice with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and then was evaporated under reduced pressure. The crude product was purified by chromatography on silica gel with petroleum ether and ethyl acetate (PE:EA = 5:1) to afford 1,1'-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)bis(ethan-1-one) as a white solid in 52% yield.

Step 3. A mixture of 1,1'-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)bis(ethan-1-one) (2.37 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 and the white solid (**M5**, 3.6510 g, 90% yield) was obtained and used without further purification.

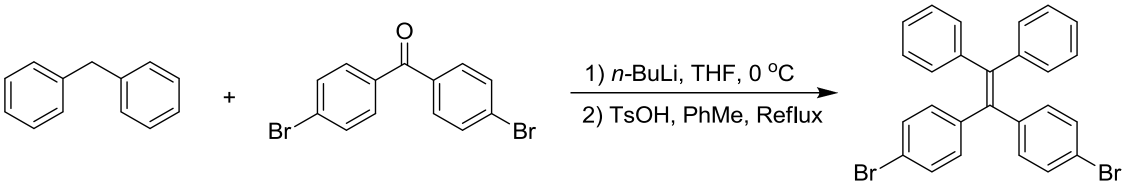
N',N'''-((1E,1'Z)-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(4-methylbenzenesulfonohydrazide) (M5)



M5

White solid (m.p. = 157-158 °C); ^{1}H NMR (400 MHz, d_6-DMSO): δ 10.53 (s, 2H), 7.90 (d, J = 8.0 Hz, 4H), 7.79 (d, J = 8.0 Hz, 2H), 7.71 (s, 2H), 7.62 (d, J = 7.9 Hz, 2H), 7.41 (d, J = 8.0 Hz, 4H), 2.36 (s, 6H), 2.24 (s, 6H), 1.98 (m, 4H), 1.31-1.00 (m, 20H), 0.74 (t, J = 7.0 Hz, 6H), 0.50 (m, 4H); ^{13}C NMR (101 MHz, d_6-DMSO): δ 153.7, 151.1, 143.6, 141.6, 137.1, 136.7, 129.7, 128.3, 125.8, 120.6, 120.5, 55.0, 31.6, 29.8, 29.0, 23.9, 22.5, 21.4, 14.8, 14.3. HRMS (ESI): calcd for $C_{47}H_{63}N_4O_4S_2$ $[M+H]^+$ 811.4285, found 811.4285.

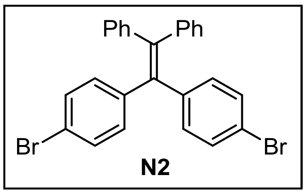
Synthesis and characterization of the monomer N2[6]



N2, 76%

A 2.5 M solution of *n*-BuLi in hexane (24 mmol, 9.6 mL) was added to a solution of diphenylmethane (5.04 g, 30 mmol) in anhydrous tetrahydrofuran (80 mL) at 0 °C under N_2 atmosphere. The solution was stirring for 1 h at this temperature, then bis(*p*-bromophenyl)methanone (6.8 g, 20 mmol) was added. the mixture was slowly warmed to room temperature after 2 h. Then, the reaction was quenched with an aqueous solution of ammonium chloride and the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and then was evaporated under reduced pressure. The crude product was dissolved in toluene (80 mL) with the addition of *p*-toluenesulfonic acid (688 mg, 4 mmol). The mixture was refluxed overnight and cooled to RT. The solution was evaporated and the crude product was purified by chromatography on silica gel with petroleum ether to afford the monomer **N2** as a white solid in 76%.

4,4'-(2,2-diphenylethene-1,1-diyl)bis(bromobenzene) (N2)



N2

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.20 (m, 4H), 7.14-7.10 (m, 6H), 7.02-6.97 (m, 4H), 6.88-6.85 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.0, 142.3, 142.2, 138.4, 133.0, 131.2, 131.0, 128.0, 126.9, 120.7. HRMS (ESI): calcd for $C_{47}H_{63}N_4O_4S_2$ $[M+H]^+$ 811.4285, found 811.4285.

3) General procedures for polymerization

Under N_2 atmosphere, $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 1 mol%), Xphos (9.5 mg, 0.02 mmol, 2 mol%), LiO*t*-Bu (176 mg, 2.2 mmol), *N*-tosylhydrazone **M1** (1 mmol) were successively added to a flame-dried 25 mL Schlenk tube. The reaction tube was degassed three times with N_2 and dry dioxane (6 mL) was added by syringe. The reaction was heated at 90 ^{o}C with stirring for 12 h. Then the reaction mixture was cooled to room temperature, HCl solution (2 N) was added. The mixture was extracted three times with $CHCl_3$. The organic layer was dried over anhydrous Na_2SO_4 and then was evaporated under reduced pressure. The crude product was filtered through a filter membrane (0.22 μm) to remove deactivated catalyst. The filtrate was evaporated and precipitated in methanol or methanol and acetone (3:1) at room temperature. The precipitate was filtered and dried in *vacuo* to afford the yield, then molecular weights (M_n) and molecular weight distributions (M_w/M_n) was measured by gel permeation chromatography (GPC). The precipitate was further purified by preparative recycling GPC to afford the NMR spectrum.

4) ^{1}H and ^{13}C NMR characterization data for the polymers

P1: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 7.8 Hz, 2H), 7.41 (s, 2H), 7.35 (d, J = 8.0 Hz, 2H), 5.58 (s, 2H), 1.95 (m, 4H), 1.16-1.08 (m, 12H), 0.81-0.73 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.0, 150.8, 140.6, 140.4, 127.4, 122.7, 119.3, 113.4, 55.1, 40.2, 31.5, 29.6, 23.8, 22.5, 14.0.

P2: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, J = 7.4 Hz, 2H), 7.42 (s, 2H), 7.35 (d, J = 7.3 Hz, 2H), 5.58 (s, 2H), 1.96 (m, 4H), 1.22-1.09 (m, 20H), 0.83-0.74 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.0, 150.8, 140.6, 140.4, 127.4, 122.7, 119.3, 113.3, 55.1, 40.2, 31.8, 30.0, 29.3, 29.2, 23.9, 22.6, 14.0.

P3: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (s, 1H), 7.15 (s, 3H), 5.34 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.6, 142.2, 128.9, 128.8, 128.7, 115.6.

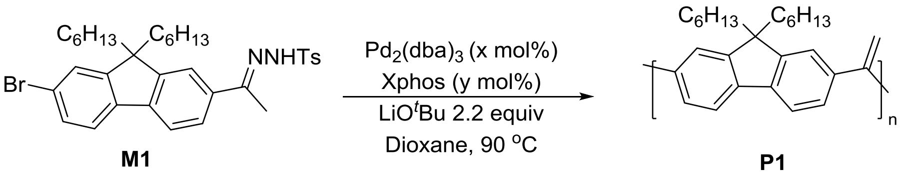
P4: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-6.69 (m, 1H), 5.62 (s, 0.2H), 5.13 (s, 0.2H), 2.34 (s, 2H), 1.40-0.76 (m, 11H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.2, 140.8, 135.6, 129.2, 128.2, 115.9, 31.5, 30.4, 29.5, 29.0, 22.5, 13.9.

P5: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 7.8 Hz, 2H), 7.38-7.35 (m, 8H), 5.54 (d, J = 6.7 Hz, 4H), 1.93 (m, 4H), 1.18-1.05 (m, 20H), 0.80-0.71 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.0, 150.1, 141.1, 140.5, 140.2, 128.0, 127.4, 122.8, 119.3, 113.7, 55.0, 40.1, 31.7, 29.9, 29.2, 29.2, 23.8, 22.5, 14.0.

P6: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.53 (m, 2H), 7.22-6.99 (m, 22H), 5.39 (s, 2H), 1.80 (s, 4H), 1.09-0.93 (m, 20H), 0.71-0.53 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.8, 150.0, 143.6, 143.0, 140.4, 140.1, 139.5, 131.3, 131.3, 131.0, 128.5, 127.8, 127.6, 127.1, 126.5, 122.8, 119.2, 113.3, 54.9, 40.1, 31.7, 29.9, 29.2, 29.1, 23.7, 22.5, 14.0.

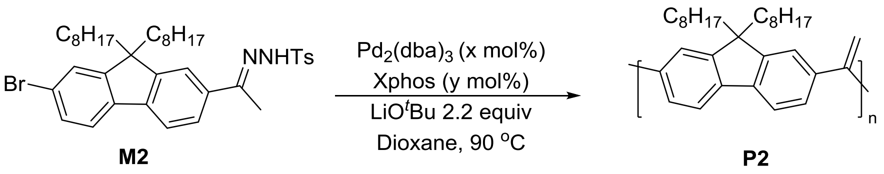
5) Optimization of polymerization

Table S1. Optimization of synthesizing polymer **P1**



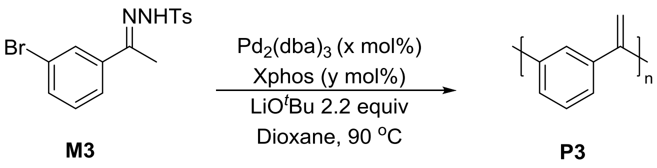
Entry	n (mmol)	Solvent	Pd_2dba_3 /Xphos	Yield	M_n	M_w	PDI	DP
1	0.2 mmol	dioxane (1.5mL)	1mol%/2 mol%	99%	7585	15343	2.02	21
2	0.2 mmol	dioxane (2mL)	1mol%/2 mol%	99%	5088	8063	1.59	14
3	0.2 mmol	dioxane (3mL)	1mol%/2 mol%	89%	4573	7436	1.63	13
4	1 mmol	dioxane (6mL)	1 mol%/2 mol%	82%	28328	88980	3.14	79
5	1 mmol	dioxane (6mL)	2 mol%/4 mol%	88%	20620	44014	2.14	58
6	1 mmol	dioxane (6mL)	5 mol%/10 mol%	76%	17711	34532	1.95	49

Table S2. Optimization of synthesizing polymer **P2**



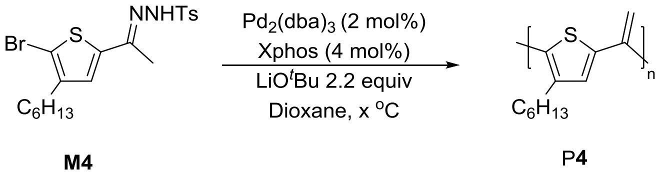
Entry	n (mmol)	Solvent	Pd_2dba_3 /Xphos	Yield	M_n	M_w	PDI	DP
1	1 mmol	dioxane (6mL)	1 mol%/2 mol%	99%	10942	30393	2.78	26

Table S3. Optimization of synthesizing polymer **P3**



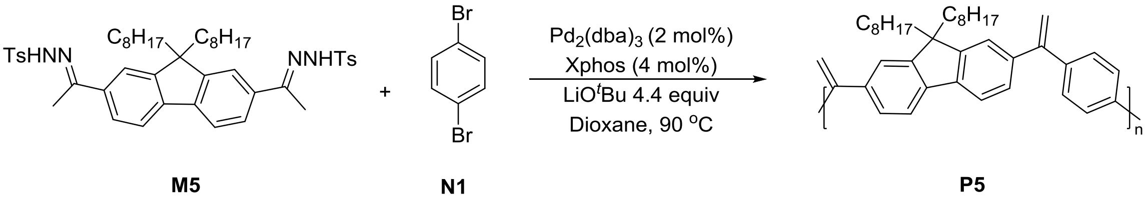
Entry	n (mmol)	Solvent	Pd_2dba_3 /Xphos	Yield	M_n	M_w	PDI	DP
1	1 mmol	dioxane (4mL)	1 mol%/2 mol%	99%	4999	10335	2.07	49
2	1 mmol	dioxane (6mL)	1 mol%/2 mol%	94%	4840	9809	2.03	47
3	2 mmol	dioxane (8mL)	1 mol%/2 mol%	81%	5910	13958	2.36	58

Table S4. Optimization of synthesizing polymer **P4**



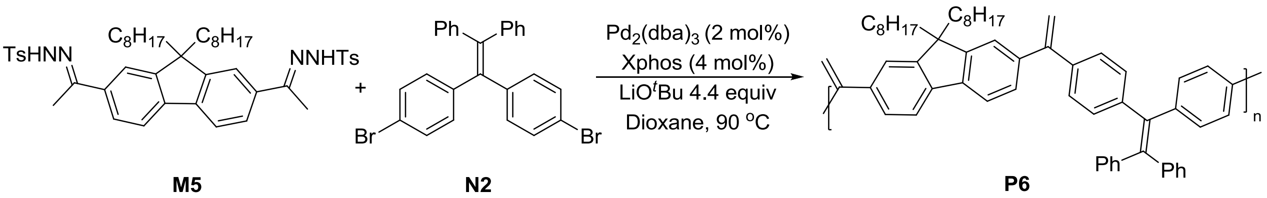
Entry	n (mmol)	Solvent	T(^oC)	Yield	M_n	M_w	PDI	PDI
1	0.5 mmol	dioxane (2mL)	90	99%	7666	29693	3.87	40
2	0.5 mmol	dioxane (2mL)	100	78%	7481	23031	3.08	39
3	1 mmol	dioxane (6mL)	90	98%	5600	14401	2.57	29
4	1 mmol	dioxane (7.5mL)	110	81%	5412	11568	2.14	28

Table S5. Optimization of synthesizing polymer **P5**



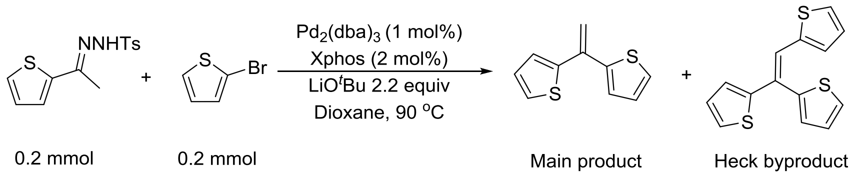
Entry	M5 : N1(mmol)	Solvent	Pd_2dba_3 /Xphos	Yield	M_n	M_w	PDI	DP
1	0.5 : 0.5	dioxane (4mL)	2 mol%/4 mol%	99%	16903	65196	3.86	33

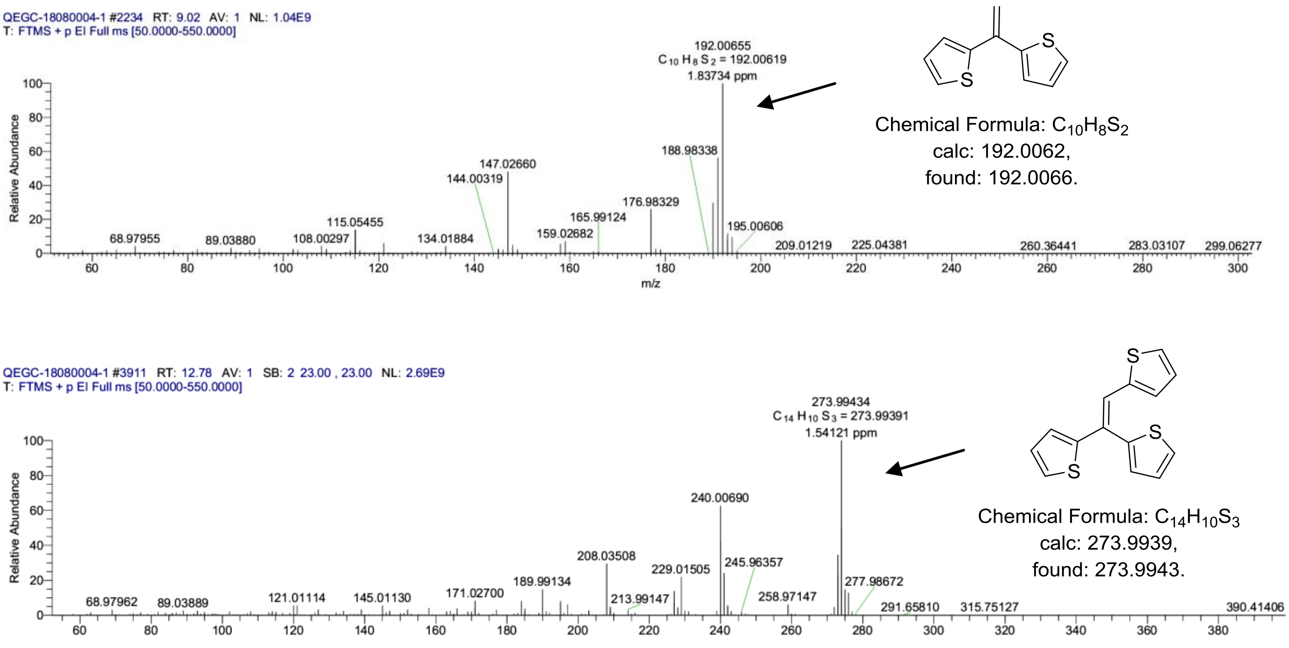
Table S6. Optimization of synthesizing polymer **P6**



Entry	M5 : N2(mmol)	Solvent	Pd_2dba_3 /Xphos	Yield	M_n	M_w	PDI	DP
1	0.3 : 0.3	dioxane (2.4mL)	2 mol%/4 mol%	97%	8292	14445	1.74	11

6) HRMS analysis of the model reaction





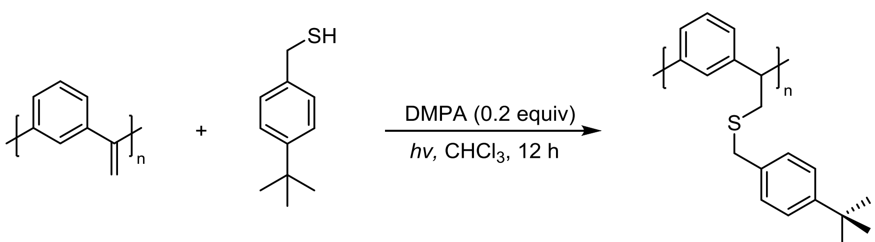
Chemical Formula: $C_{10}H_8S_2$
calc: 192.0062,
found: 192.0066.

Chemical Formula: $C_{14}H_{10}S_3$
calc: 273.9939,
found: 273.9943.

Figure S1. HRMS analysis of the model reaction

7) Post-modification of polymers

Photocuring thiol-*ene post-modification of* ***P3***



P3-PM1, 96%

Polymer **P3** (20.4 mg, 0.2 mmol, M_n = 4.5 kDa, M_w/M_n = 1.89), (4-(tert-butyl)phenyl)methanethiol (180.3 mg, 1.0 mmol), DMPA (10.3 mg, 0.04 mmol), and $CHCl_3$ (2 mL) were added into a 10 ml round-bottom flask. The mixture was stirred under 365 nm UV lamp at room temperature for 12 h and then precipitated into methanol (30 mL). A yellow solid (**P3-PM1**) was obtained in 96% yield after vacuum dryness. M_n = 9.4 kDa, M_w/M_n = 3.25.

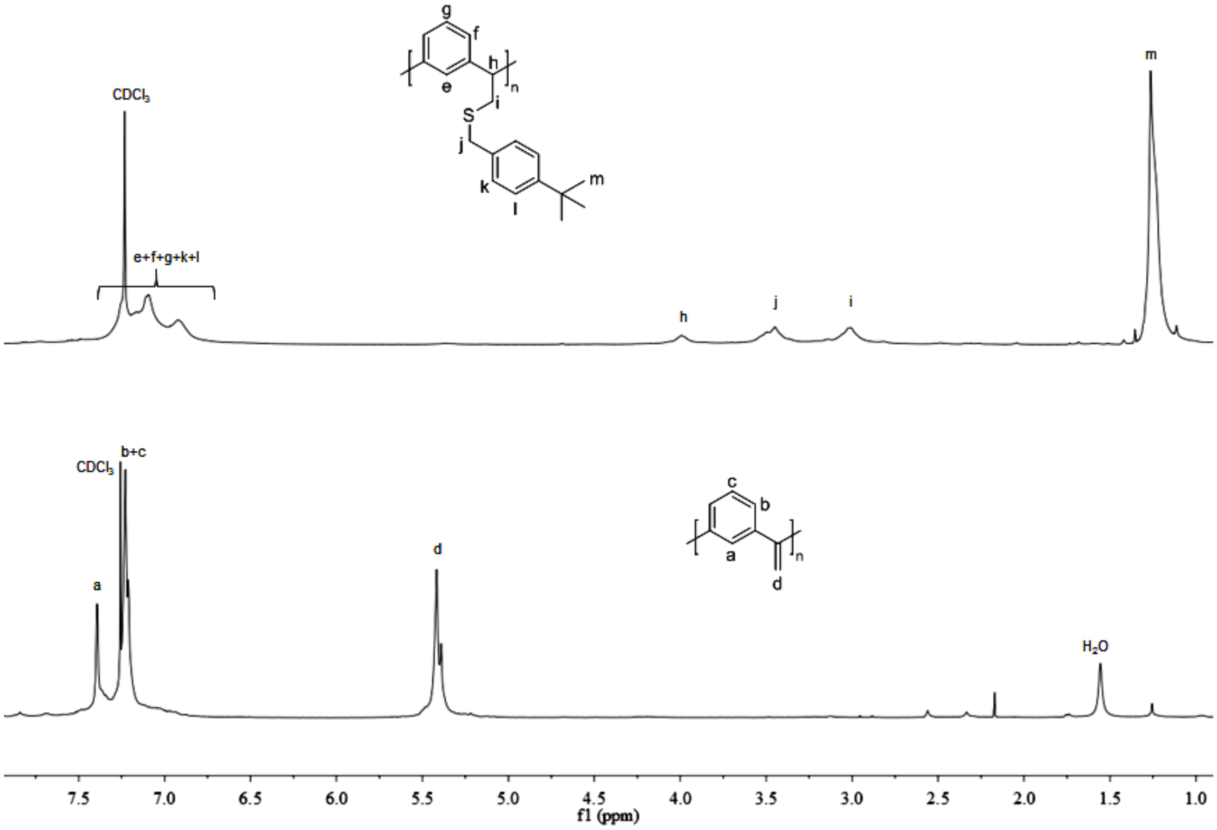


Figure S2. ^{1}H NMR ($CDCl_3$) spectra of **P3** and **P3-PM1** to show complete conversion of the alkenyl groups.

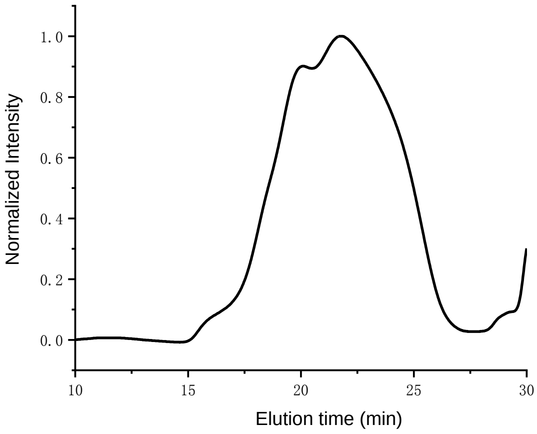
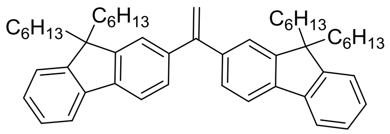


Figure S3. SEC traces of **P3-PM1**.

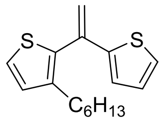
8) Photophysical properties of the polymers

Table S7. Optical properties of polymers

Polymer[a]	λ_{max} *absorption (nm)*	λ_{max} *emission (nm)*	λ_{exc} *(nm)*
P1	334	359, 376, 417, 445	308
P2	332	418, 446	320
P4	304	406, 432	350
P5	327	357, 374	300
P6[b]	324	407, 432	330
DM1	295, 317	352	290
DM2	260	317, 360	260



DM1



DM2

[a]The polymers were prepared as 10 μM solution in $CHCl_3$ and tested at 25 °C. Maximum absorption wavelengths were determined by UV-vis spectroscopy. Maximum emission wavelengths were determined by fluorescence spectroscopy at specific $\lambda_{exc.}$ [b] Prepared as 10 μM solution in THF.

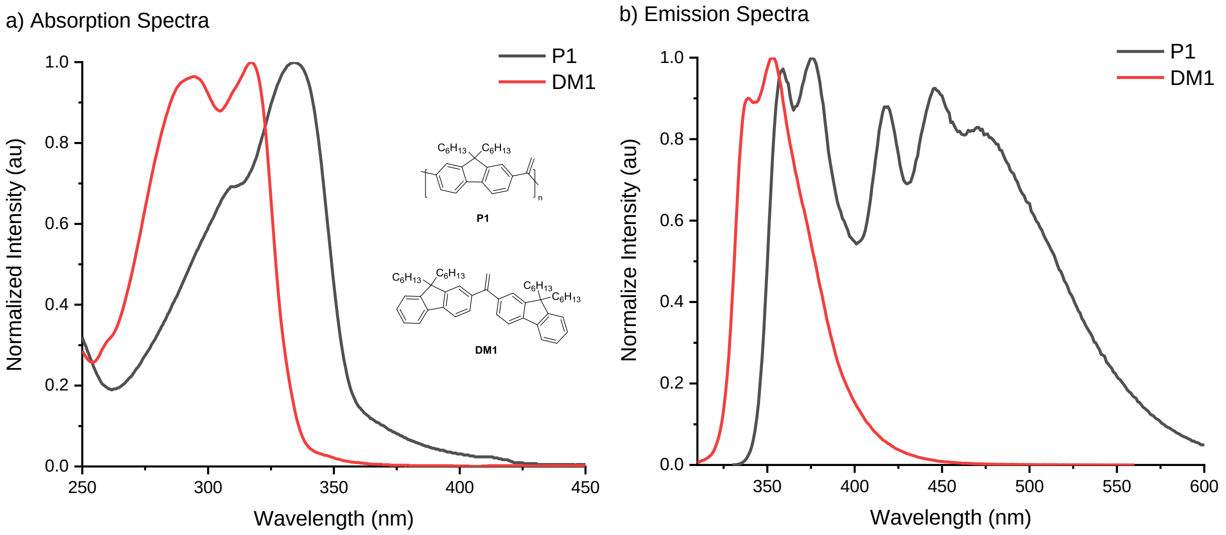


Figure S4. Absorption and emission spectra of **P1 and DM1** as 10 μM solution in $CHCl_3$.

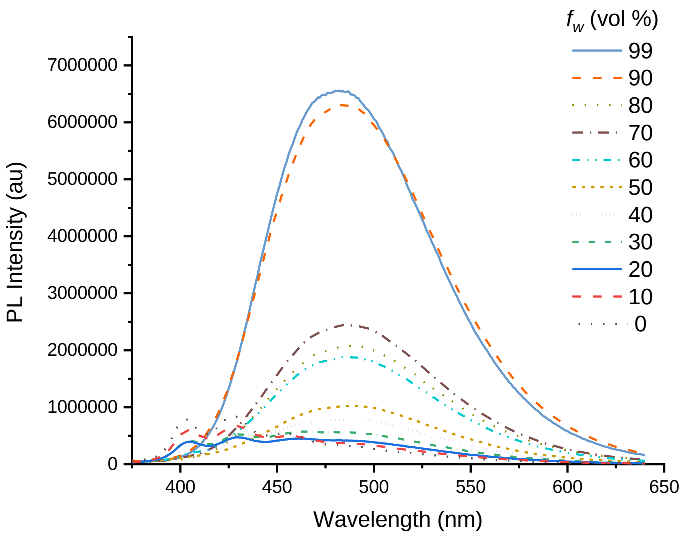


Figure S5. PL spectra of **P6** in THF and THF/water mixtures with different water fractions. Solution concentration: 10 μM; excitation wavelength: 330 nm.

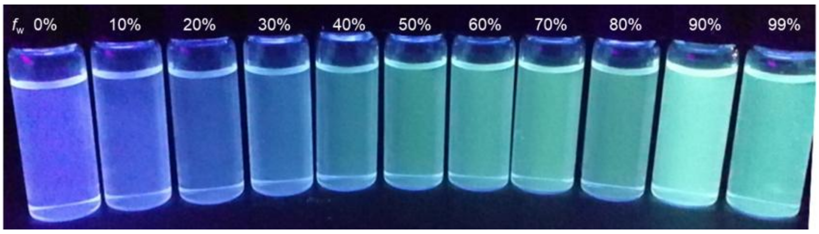
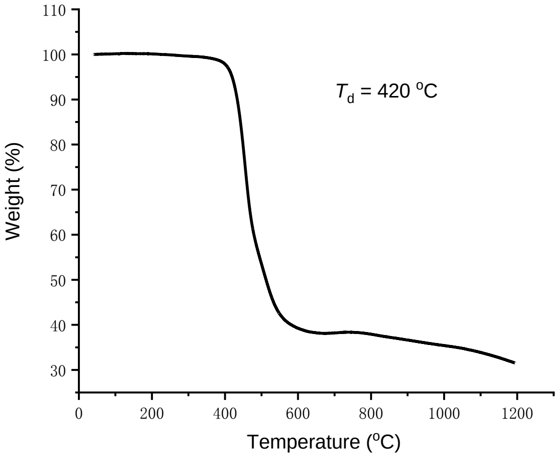


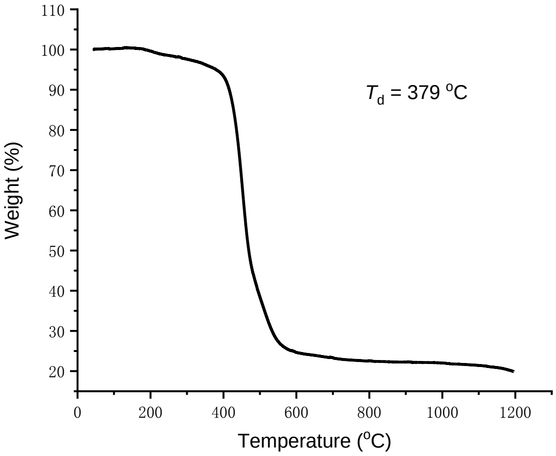
Figure S6. Fluorescent photographs of **P6** in THF and THF/water mixtures with different water fractions (f_w) taken under 365 nm UV irradiation. Solution concentration: 10 μM.

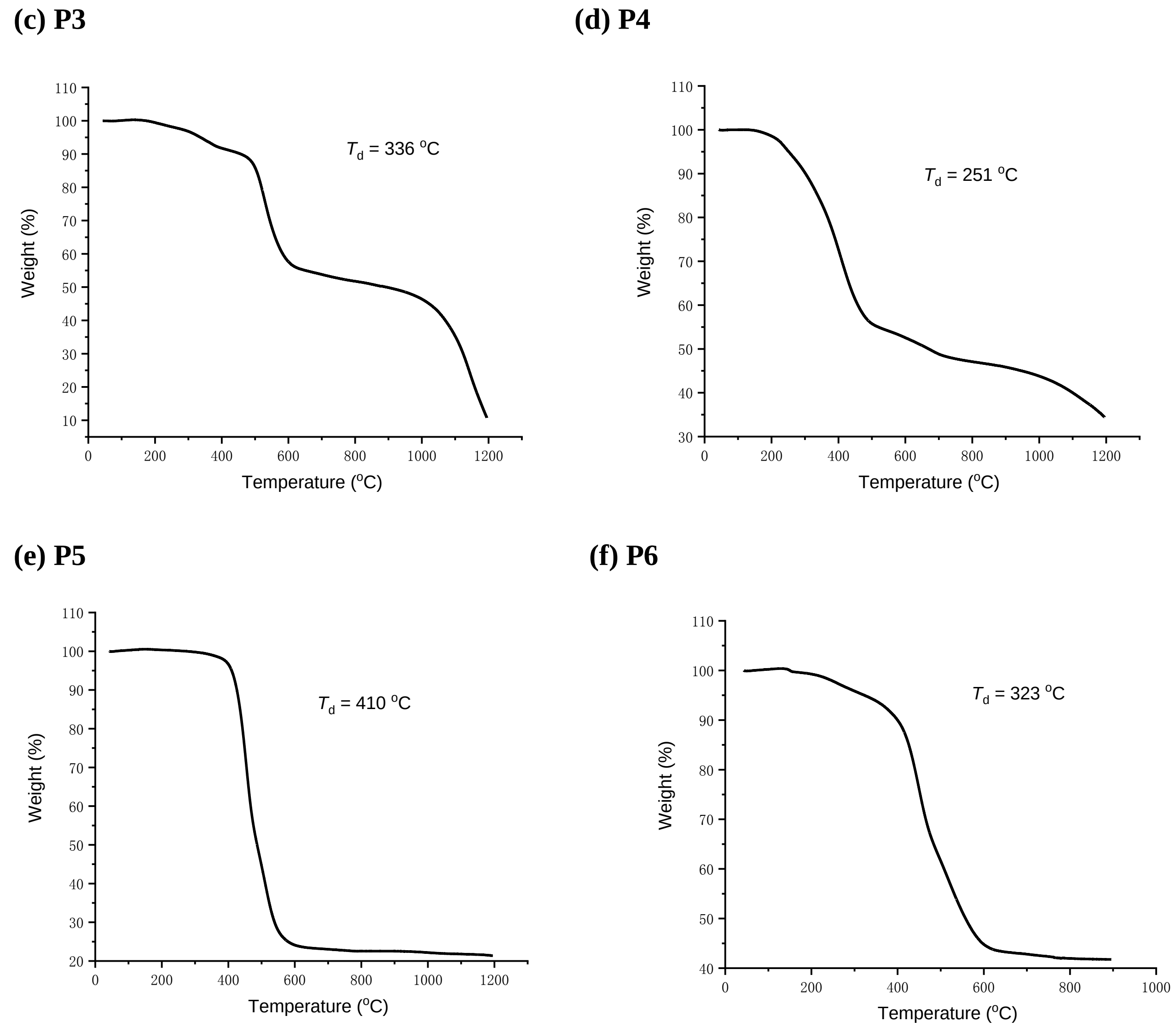
9) TGA and DSC data of polymers

(a) P1



(b) P2



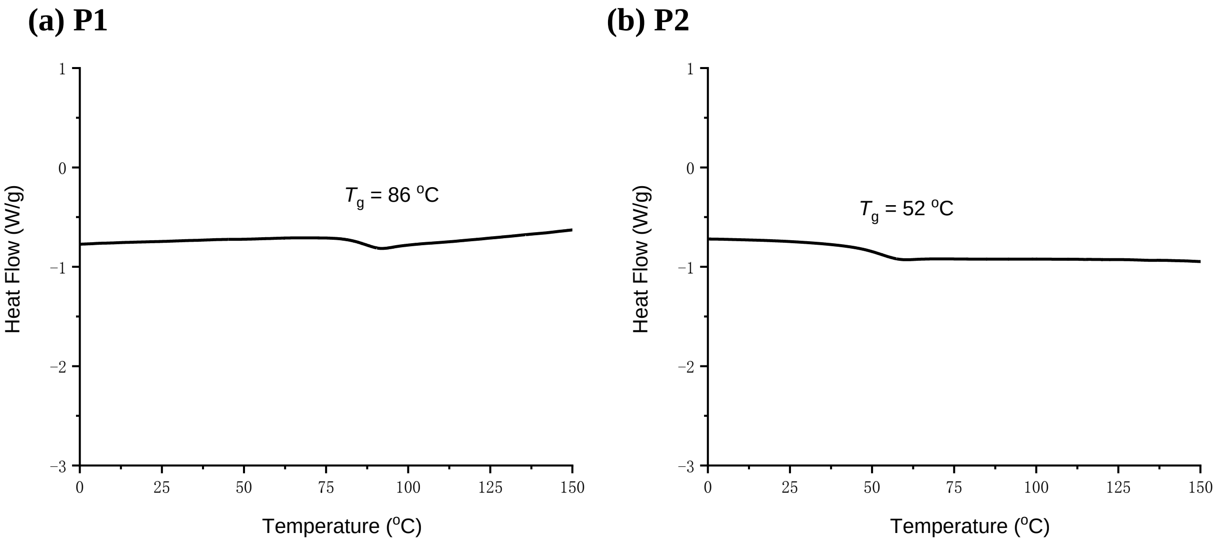

(c) P3

(d) P4

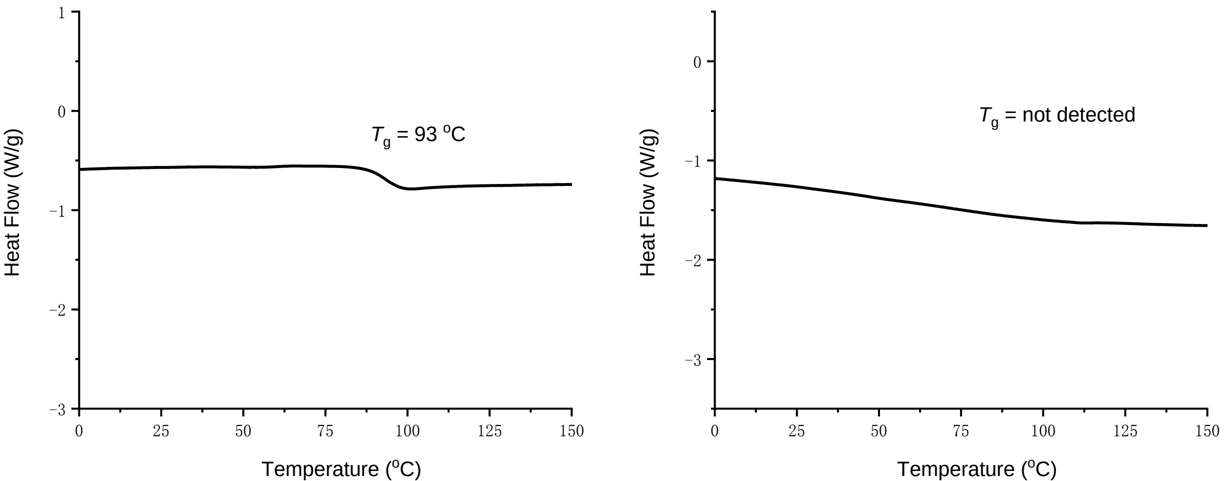
(e) P5

(f) P6

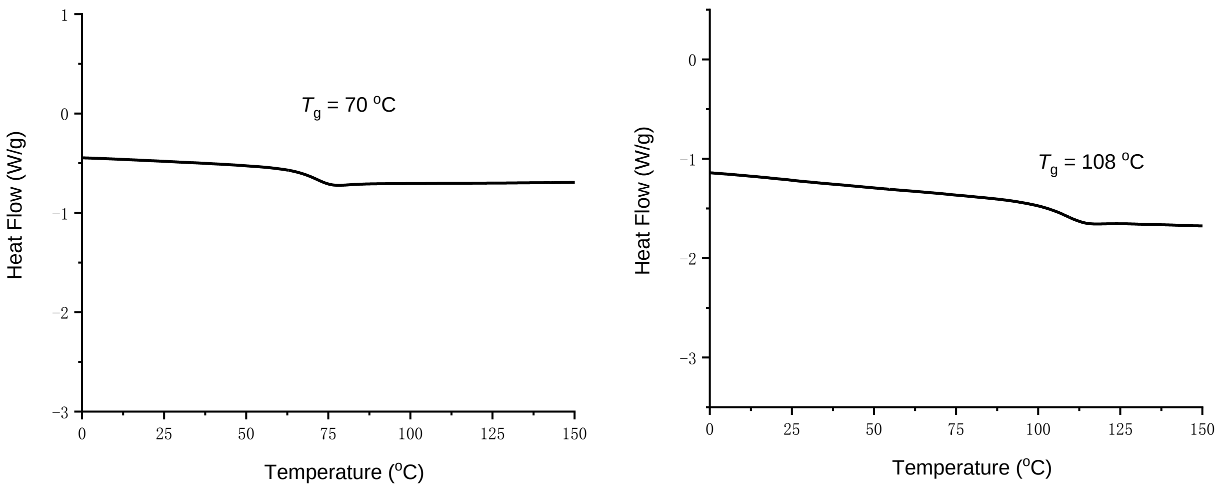
Figure S7. TGA profiles


(a) P1

(b) P2



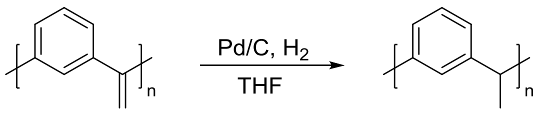
(c) P3 **(d) P4**



(e) P5 **(f) P6**

Figure S8. DSC profiles

10) MALDI-TOF-MS spectrum of P3-PM2.



P3 **P3-PM2**

In a 10 ml round bottle, **P3** (51 mg, 0.5 mmol, M_n = 4.5 kDa, M_w/M_n = 1.89) and 5% w/w of Pd/C (265 mg, 0.25 eq) was added. The mixture was degassed by ‘pump-freeze-thaw’ cycle three times and flushed with hydrogen. Then THF (3 ml) was added and the solution was stirred at RT for 48 h under 1 atm of hydrogen atmosphere. The mixture was filtered through a filter membrane (0.22 μm) to remove Pd/C and the crude product was precipitated in methanol (30 mL). A white solid (**P3-PM2**) (18.6 mg) was obtained after vacuum dryness. M_n = 3.2 kDa, M_w/M_n = 1.40.

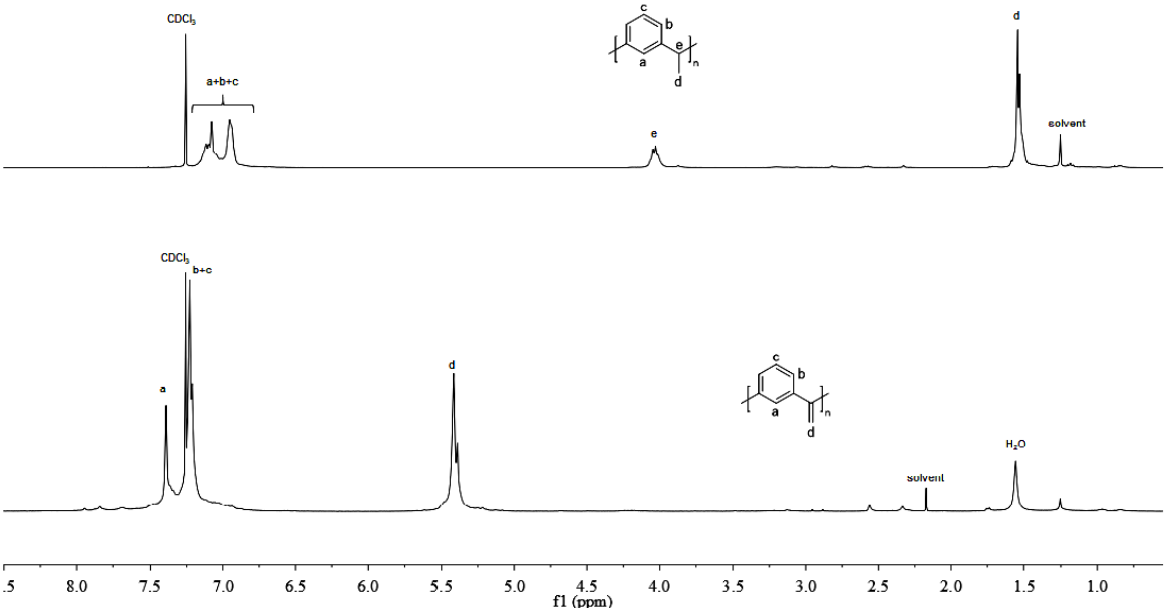


Figure S9. ^{1}H NMR (CDCl$_3$) spectra of **P3** and **P3-PM2** to show complete conversion of alkenyl groups.

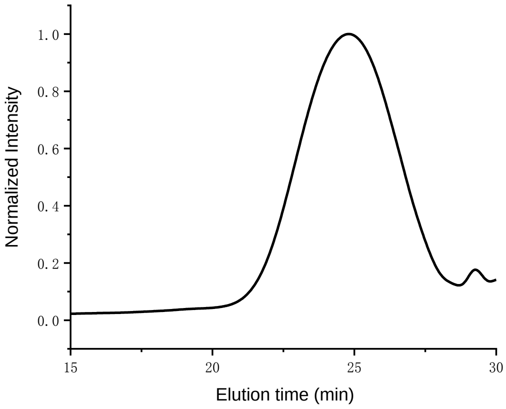


Figure S10. SEC traces of **P3-PM2**.

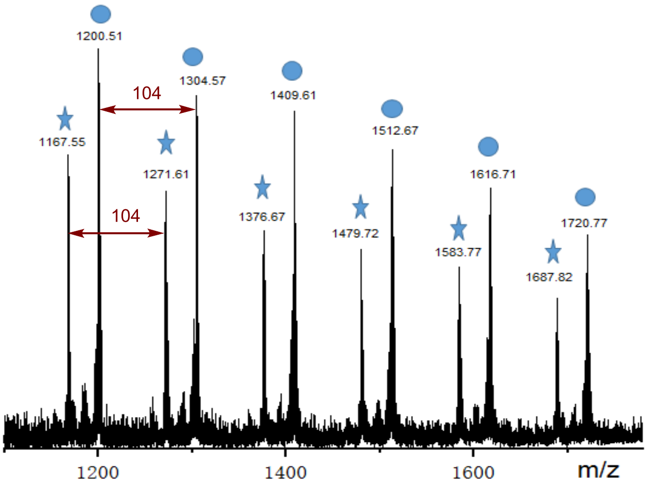
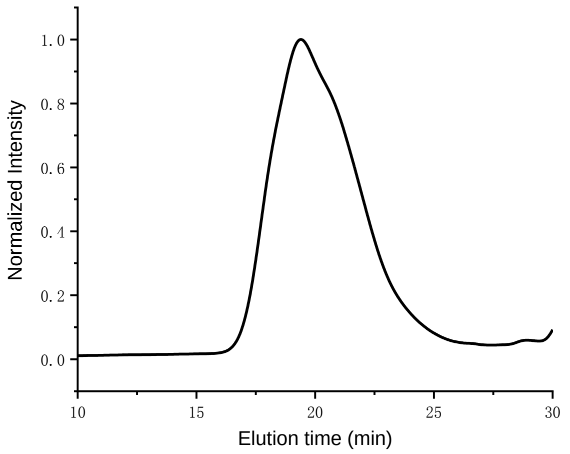


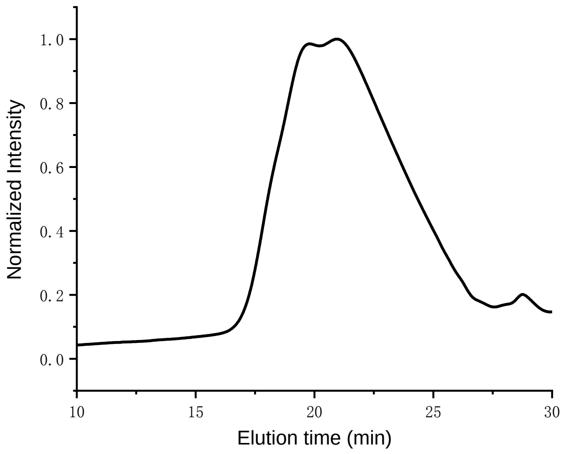
Figure S11. MALDI-TOF-MS spectrum of polymer **P3-PM2.**

11) SEC traces of polymers

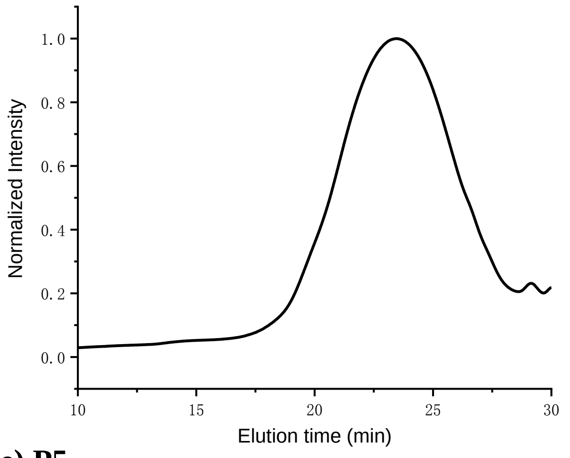
(a) P1



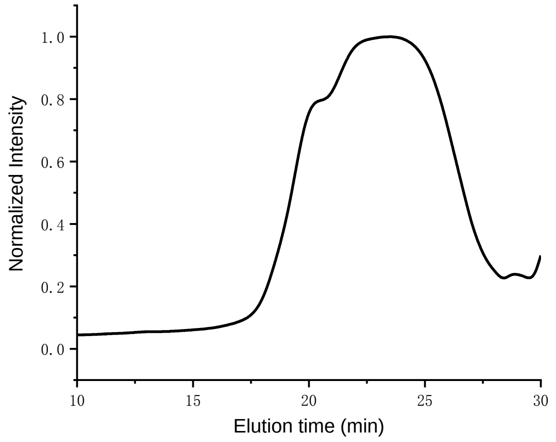
(b) P2



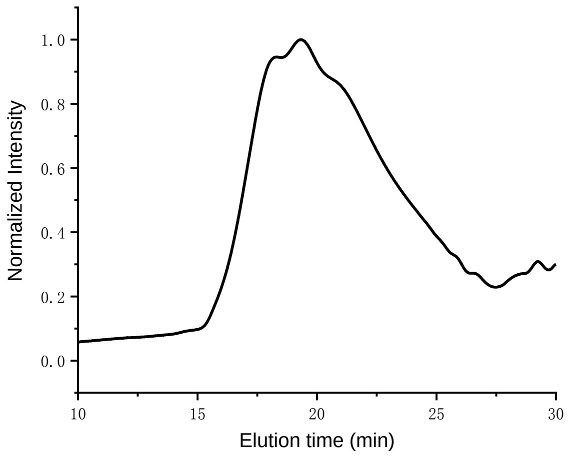
(c) P3



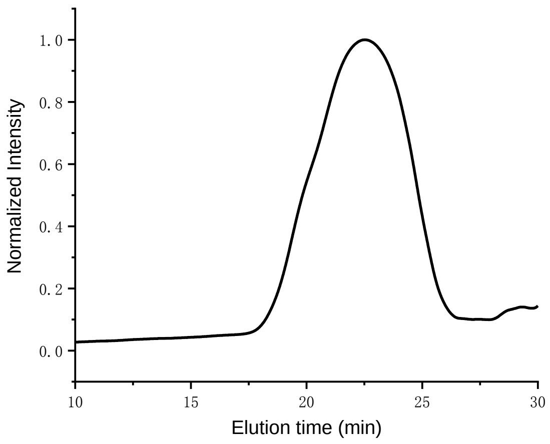
(d) P4



(e) P5

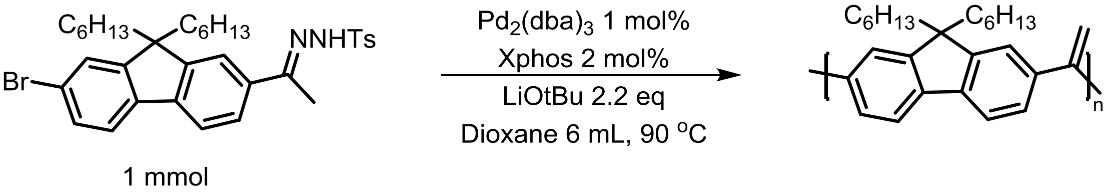


(f) P6

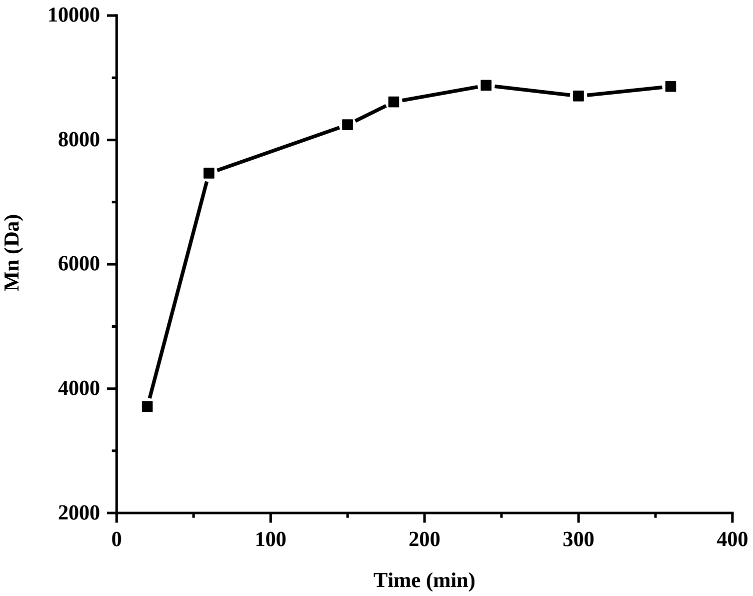


12) The experiment of the relationship between the M_n and reaction time

Procedure: Under N_2 atmosphere, $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 1 mol%), Xphos (9.5 mg, 0.02 mmol, 2 mol%), LiO*t*-Bu (176 mg, 2.2 mmol), *N*-tosylhydrazone **M1** (1 mmol) were successively added to a flame-dried 25 mL Schlenk tube. The reaction tube was degassed three times with N_2 and dry dioxane (6 mL) was added by syringe. The reaction was heated at 90 °C with stirring. 300 μL of the reaction mixture was taken out from the Schlenk tube in different time, which was used to measure molecular weights (M_n) by gel permeation chromatography(GPC).



Entry	Time (min)	Mn (Da)	PDI
1	10	-	-
2	20	3711	1.52
3	60	7465	1.92
4	150	8244	1.99
5	180	8611	2.08
6	240	8877	2.08
7	300	8706	2.00
8	360	8860	2.01



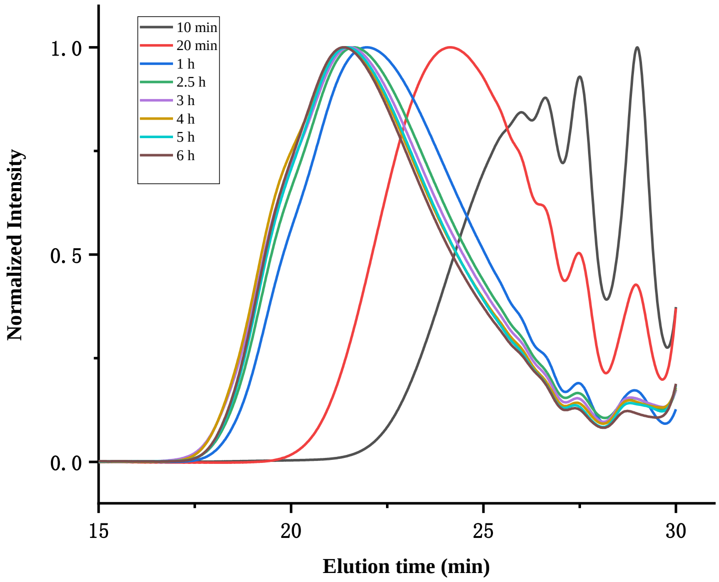
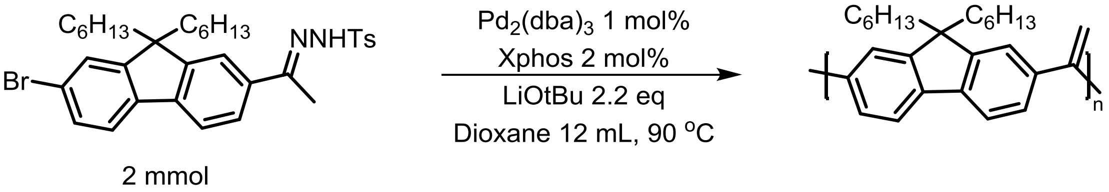


Figure S12. SEC traces of **P1** in different time.

Procedure: Under N_2 atmosphere, $Pd_2(dba)_3$ (18.4 mg, 0.01 mmol, 1 mol%), Xphos (19 mg, 0.02 mmol, 2 mol%), LiO*t*-Bu (352 mg, 2.2 mmol), *N*-tosylhydrazone **M1** (2 mmol) were successively added to a flame-dried 25 mL Schlenk tube. The reaction tube was degassed three times with N_2 and dry dioxane (12 mL) was added by syringe. The reaction was heated at 90 ^{o}C with stirring. 300 μL of the reaction mixture was taken out from the Schlenk tube in different time, which was used to measure molecular weights (M_n) by gel permeation chromatography(GPC).



Entry	Time (min)	Mn (Da)	PDI
1	10	3158	1.39
2	20	5136	1.71
3	30	6331	1.75
4	40	6881	2.30
5	75	7662	2.20
6	105	8015	2.28
7	120	8202	2.11
8	240	8241	1.95
9	300	8448	2.06
10	360	8895	2.14
11	420	9894	2.07
12	480	9935	2.18
13	540	10383	2.25
14	600	10557	2.32
15	660	10896	2.37
16	720	11096	2.46

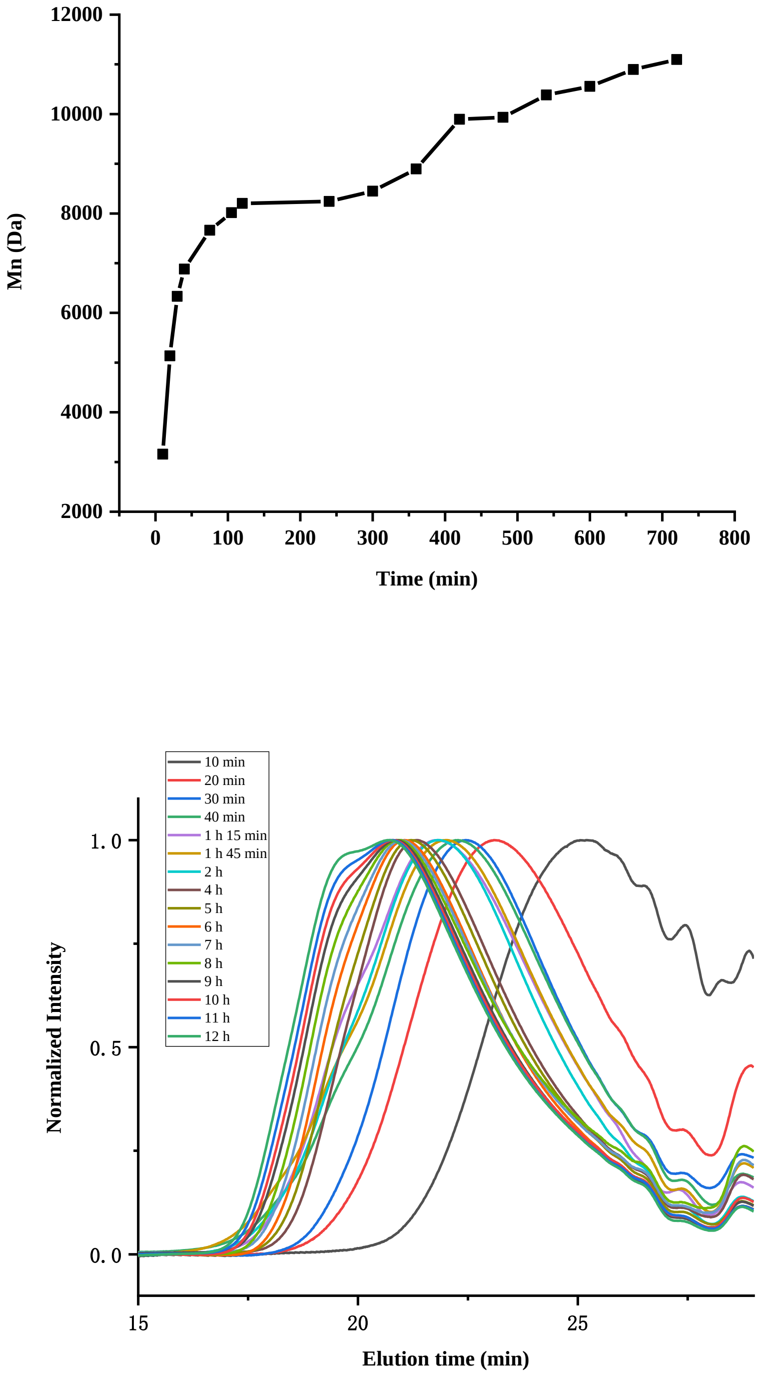
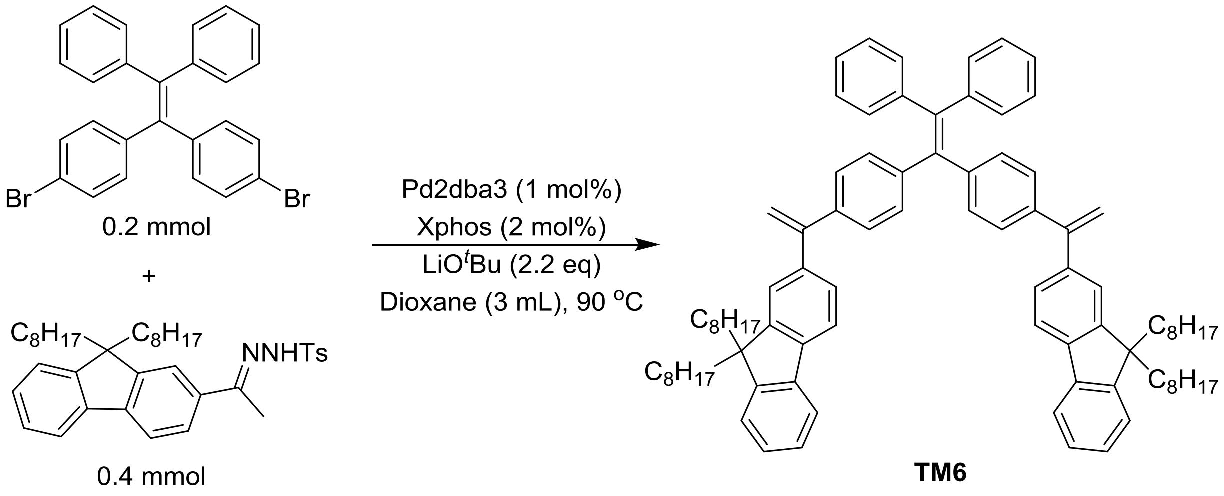


Figure S13. SEC traces of **P1** in different time.

13) Photophysical properties of small molecules



Procedure: Under N_2 atmosphere, $Pd_2(dba)_3$ (1.8 mg, 0.01 mmol, 1 mol%), Xphos (1.9 mg, 0.02 mmol, 2 mol%), LiO*t*-Bu (70.4 mg, 2.2 mmol), TPE (0.2 mmol), *N*-tosylhydrazone (0.4 mmol) were successively added to a flame-dried 10 mL Schlenk tube. The reaction tube was degassed three times with N_2 and dry dioxane (3 mL) was added by syringe. The reaction was heated at 90 ^{o}C with stirring for 2 h. The crude product was purified by chromatography on silica gel with petroleum ether and ethyl acetate (PE:EA = 30:1) to afford **TM6**.

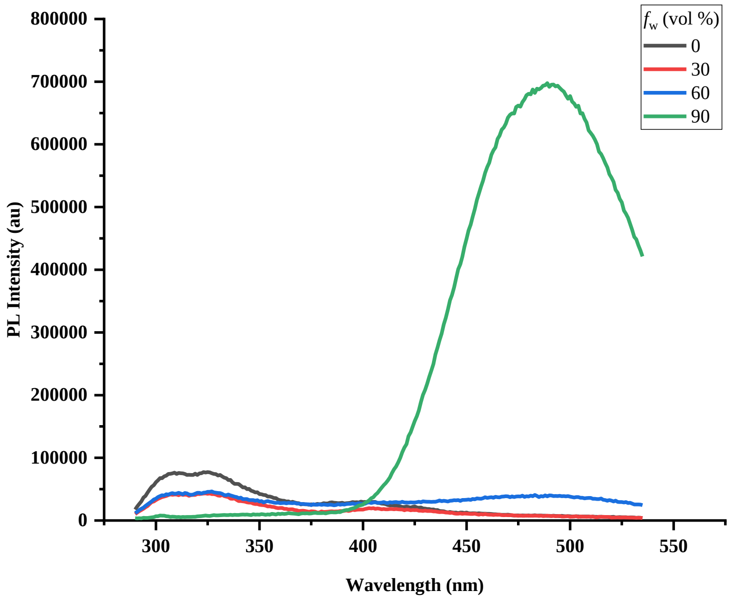


Figure S14. PL spectra of **TM6** in THF and THF/water mixtures with different water fractions. Solution concentration: 10 μM; excitation wavelength: 275 nm.

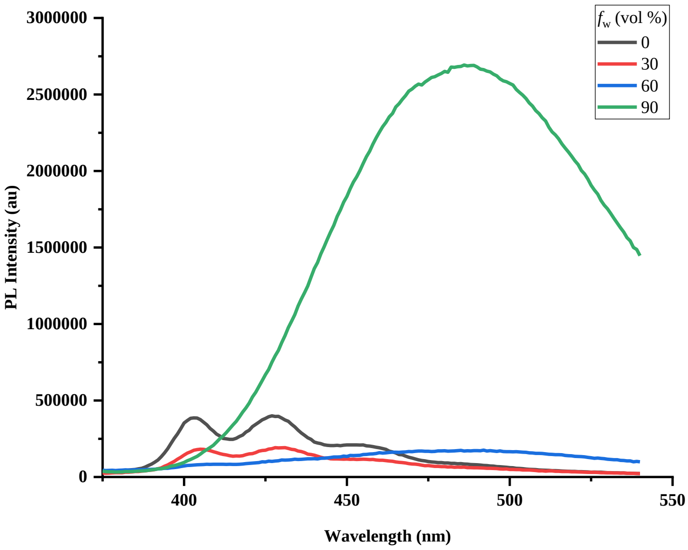


Figure S15. PL spectra of **TM6** in THF and THF/water mixtures with different water fractions. Solution concentration: 10 μM; excitation wavelength: 330 nm.

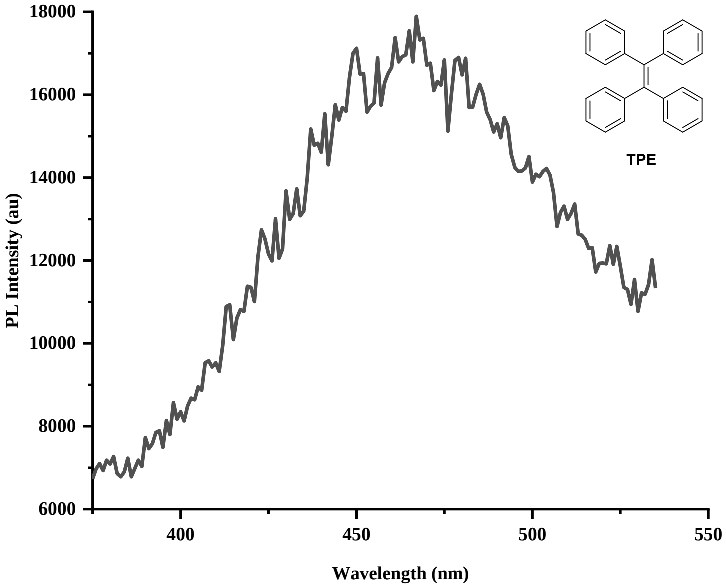


Figure S16. PL spectra of **TPE** in THF/water(10 : 90) mixtures. Solution concentration: 10 μM; excitation wavelength: 275 nm.

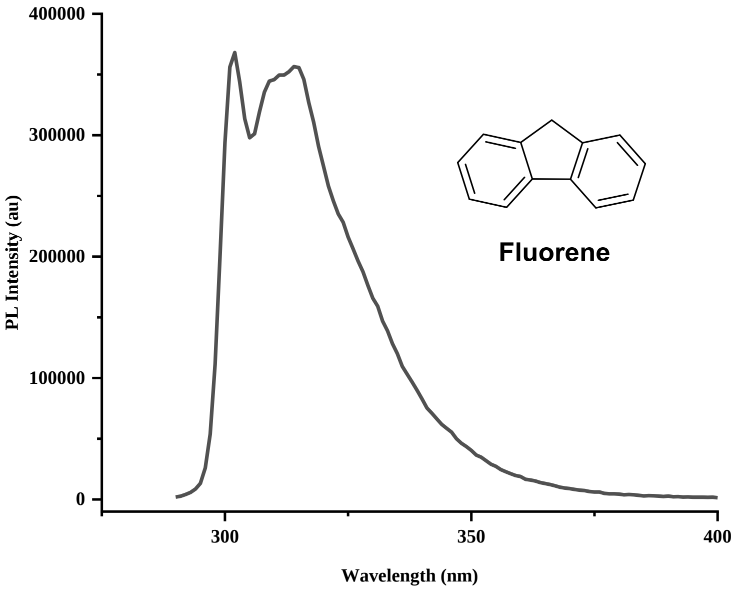


Figure S17. PL spectra of **Fluorene** in THF. Solution concentration: 10 μM; excitation wavelength: 275 nm.

12) References

1 J. Ding, M. Day, G. Robertson, J. Roovers, *Macromolecules* 2002, **35**, 3474-3483.

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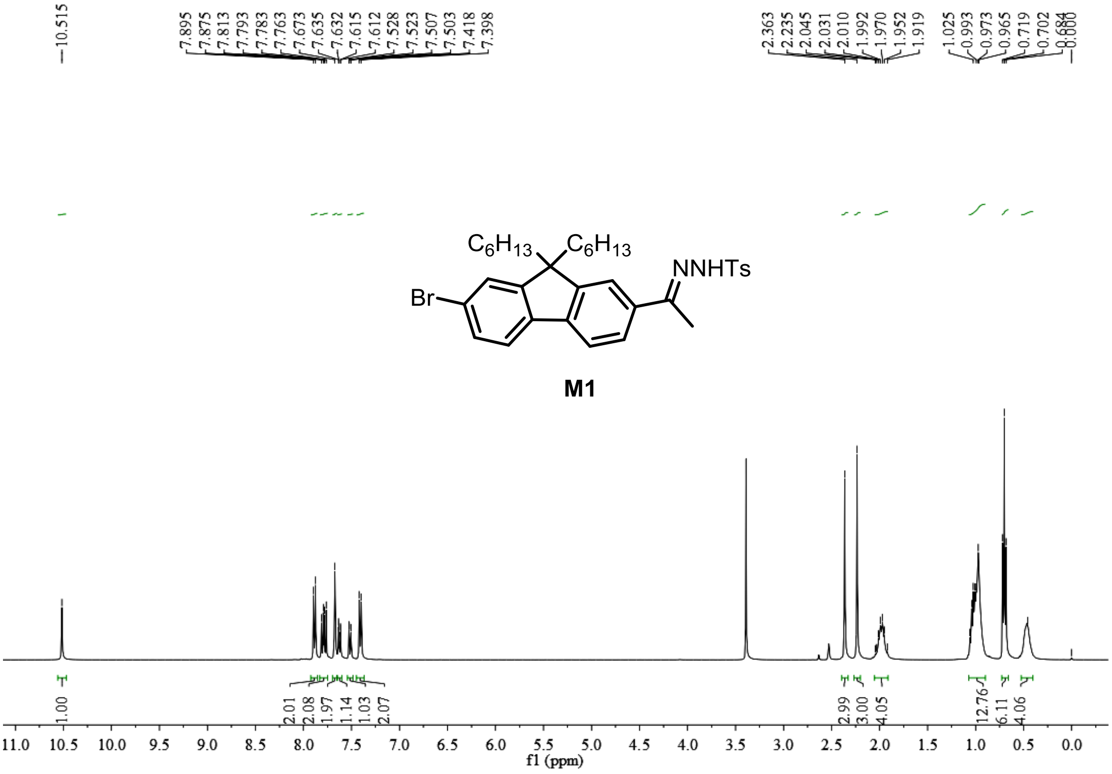
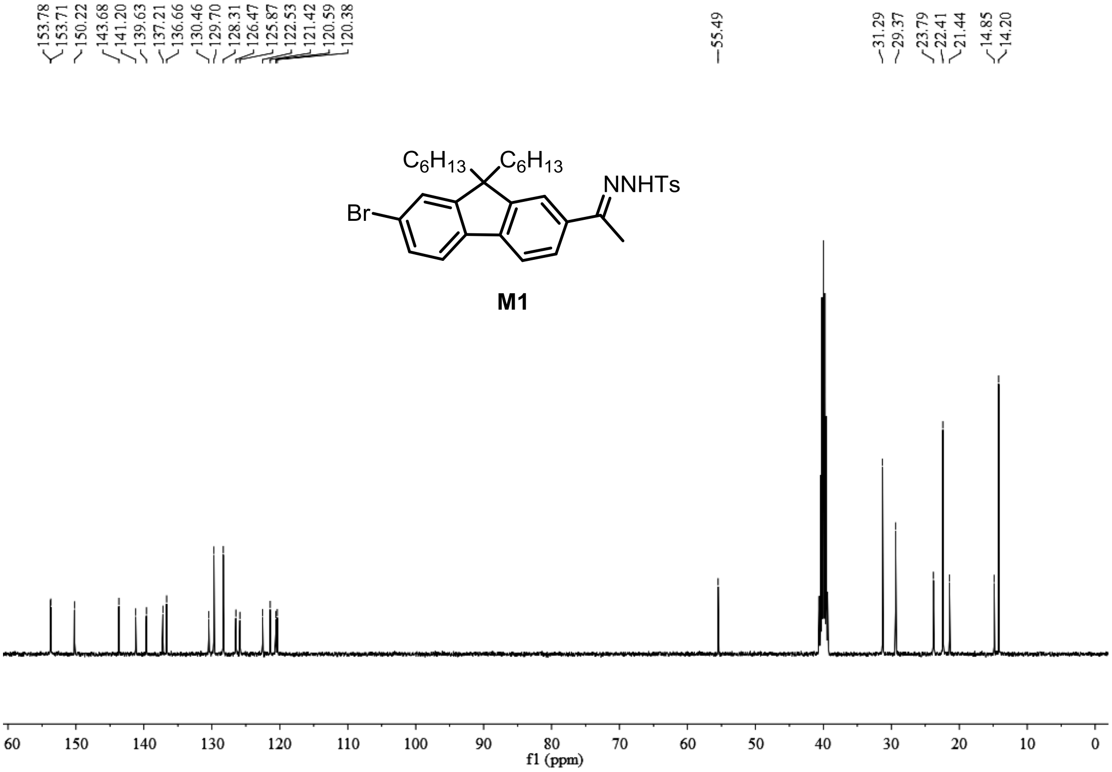
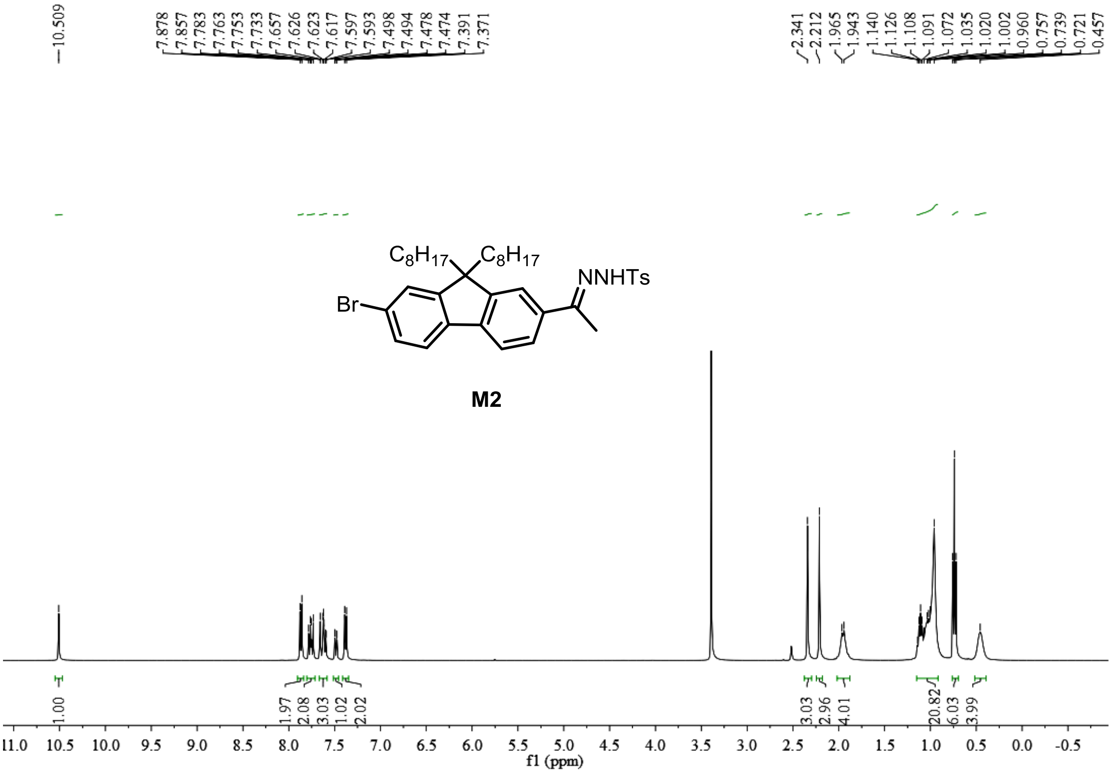
13) ^{1}H, ^{13}C spectra for the monomers and polymers

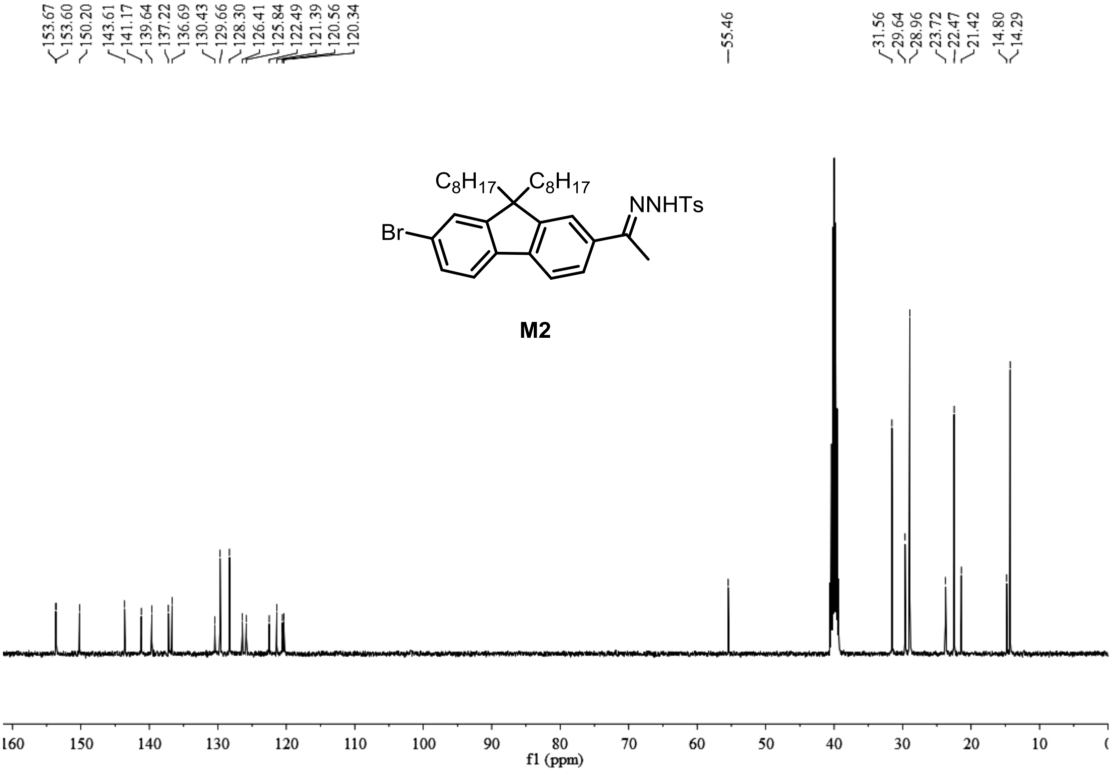
a) ^{1}H, ^{13}C spectra of **M1**



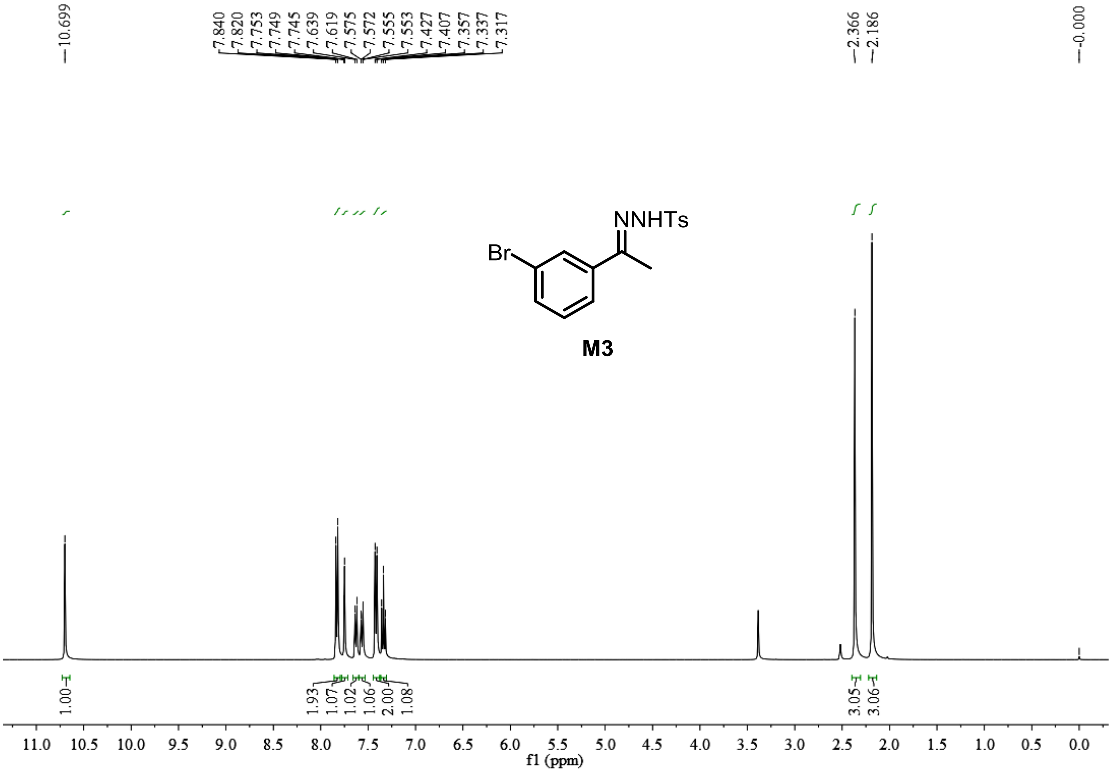


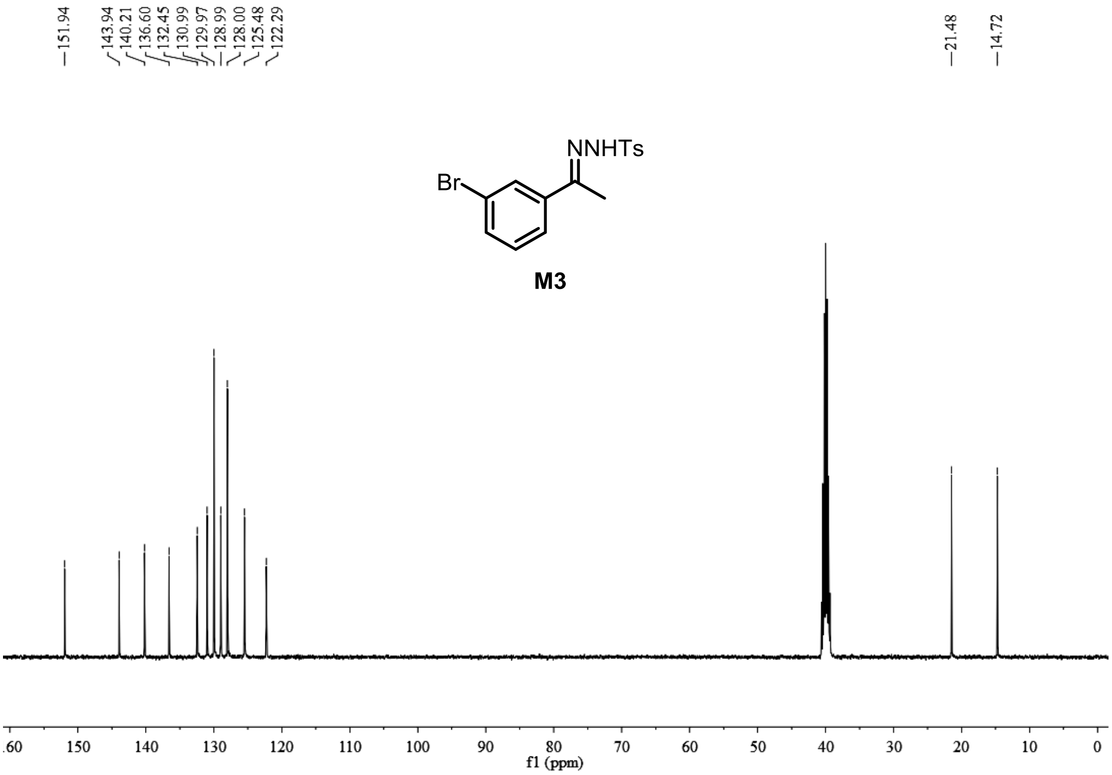
b) ^{1}H, ^{13}C spectra of **M2**



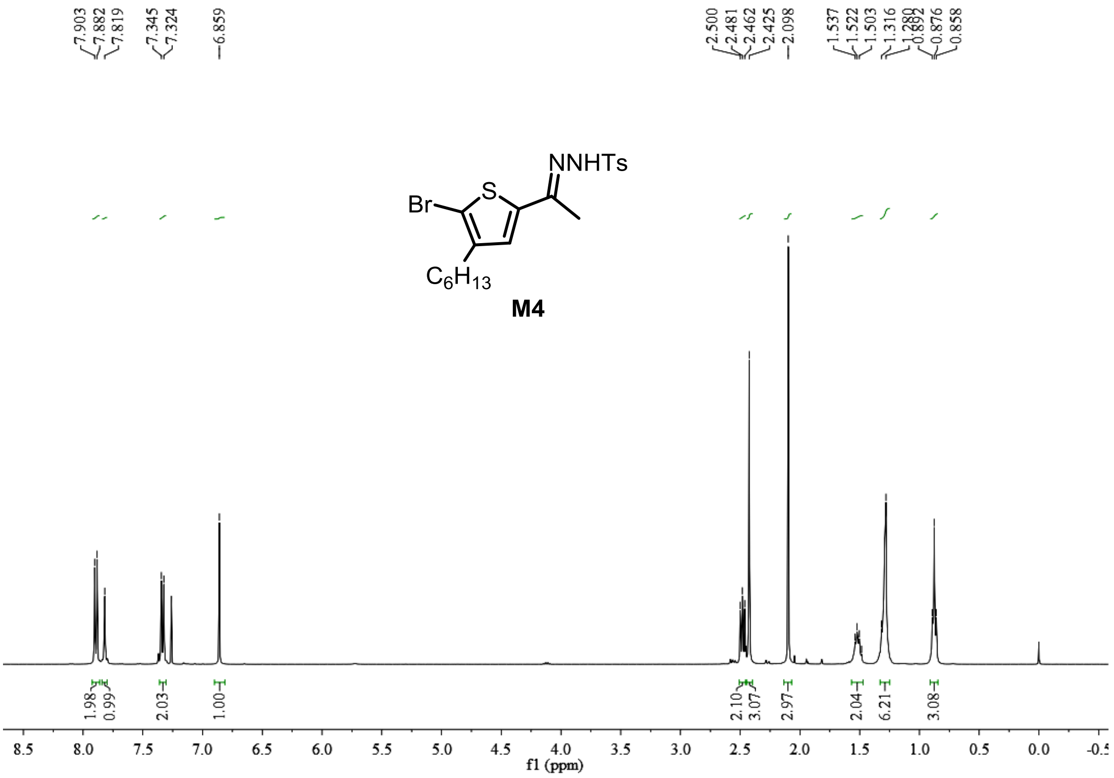


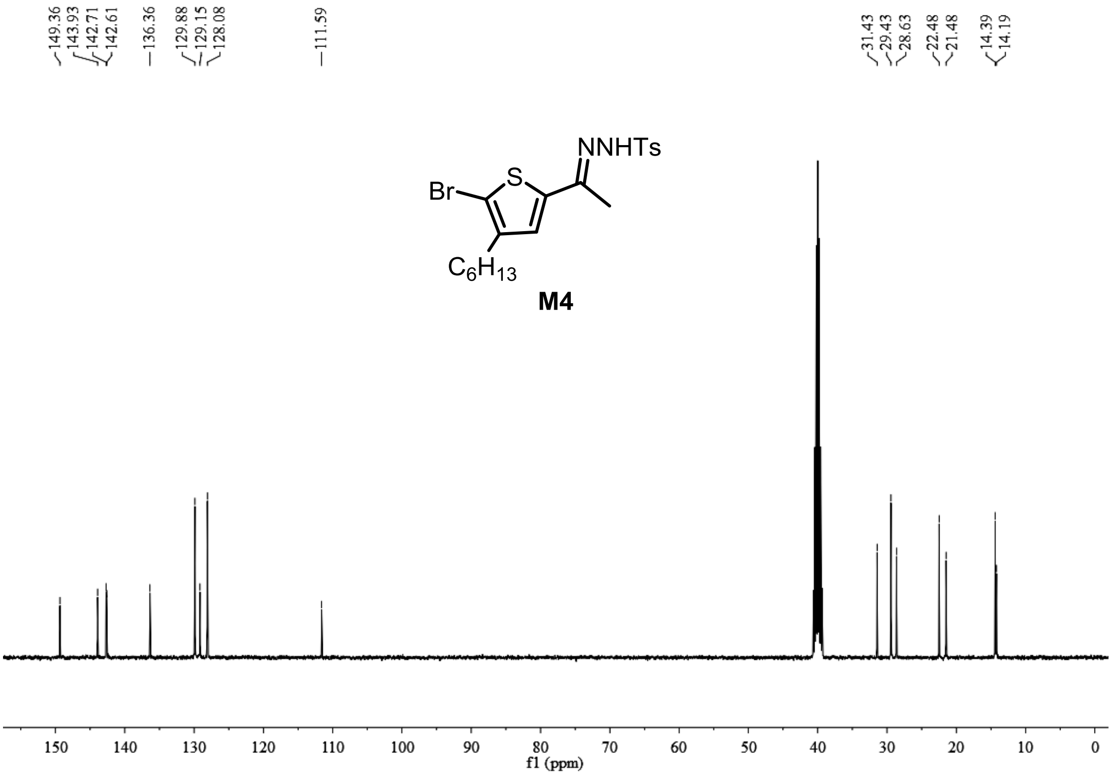
c) ^{1}H, ^{13}C spectra of **M3**



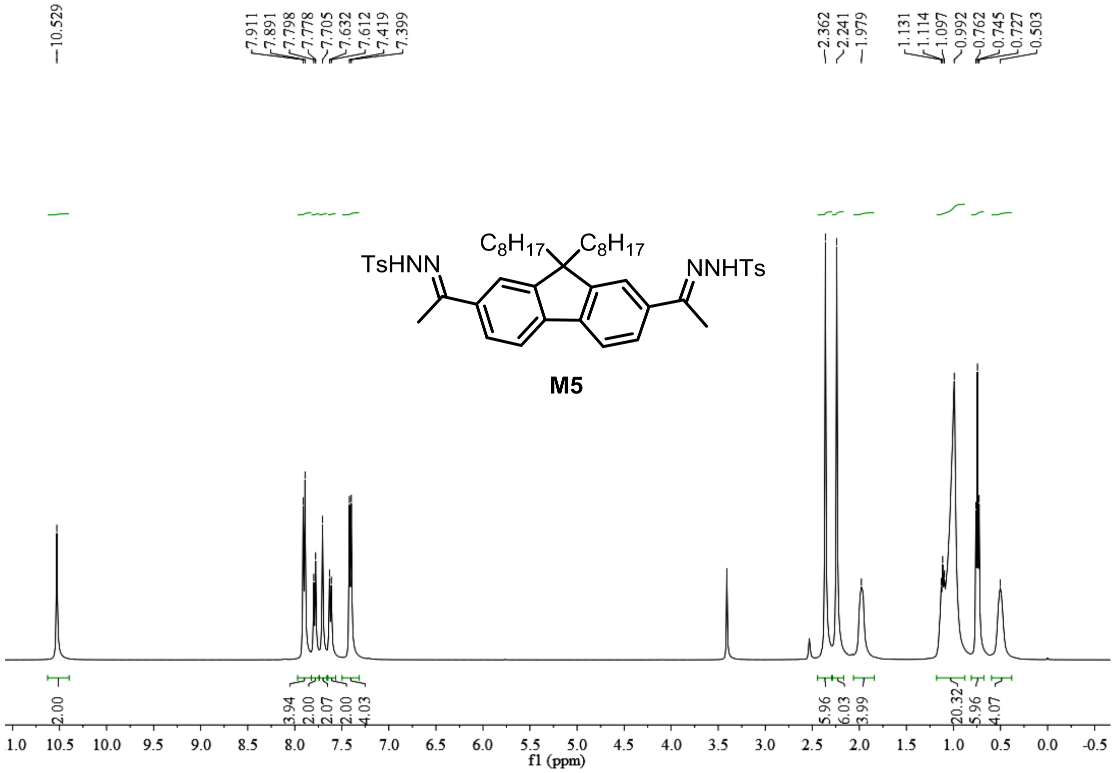


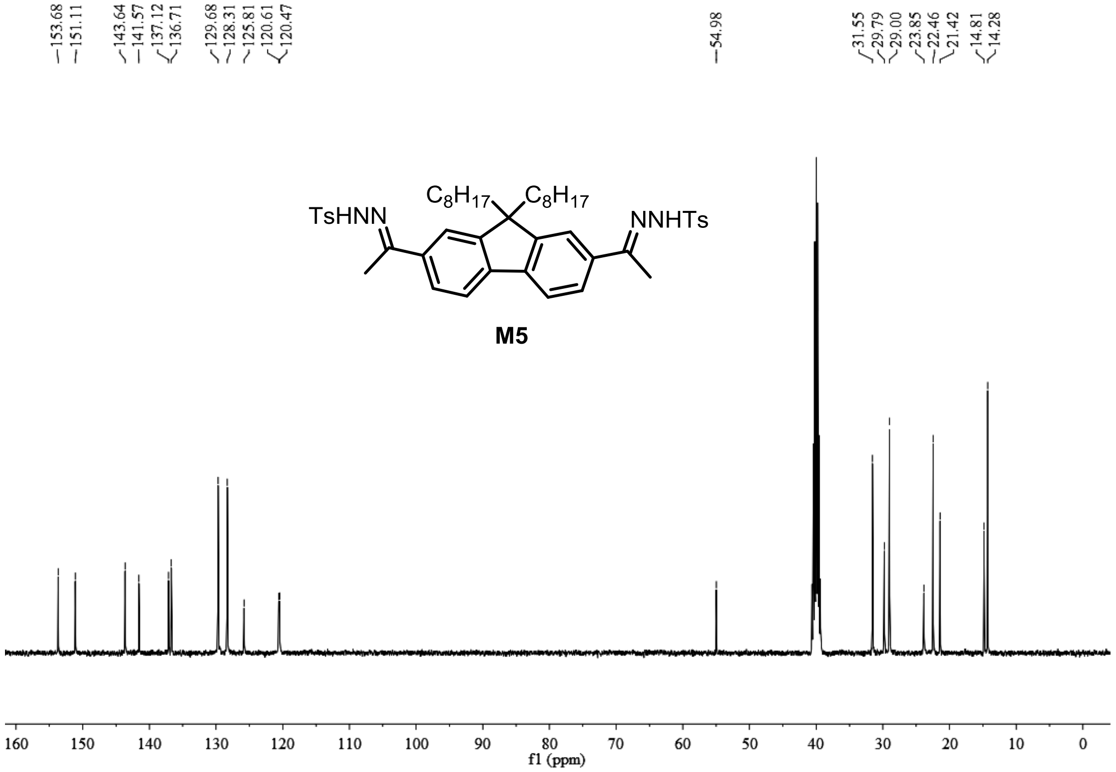
d) ^{1}H, ^{13}C spectra of **M4**



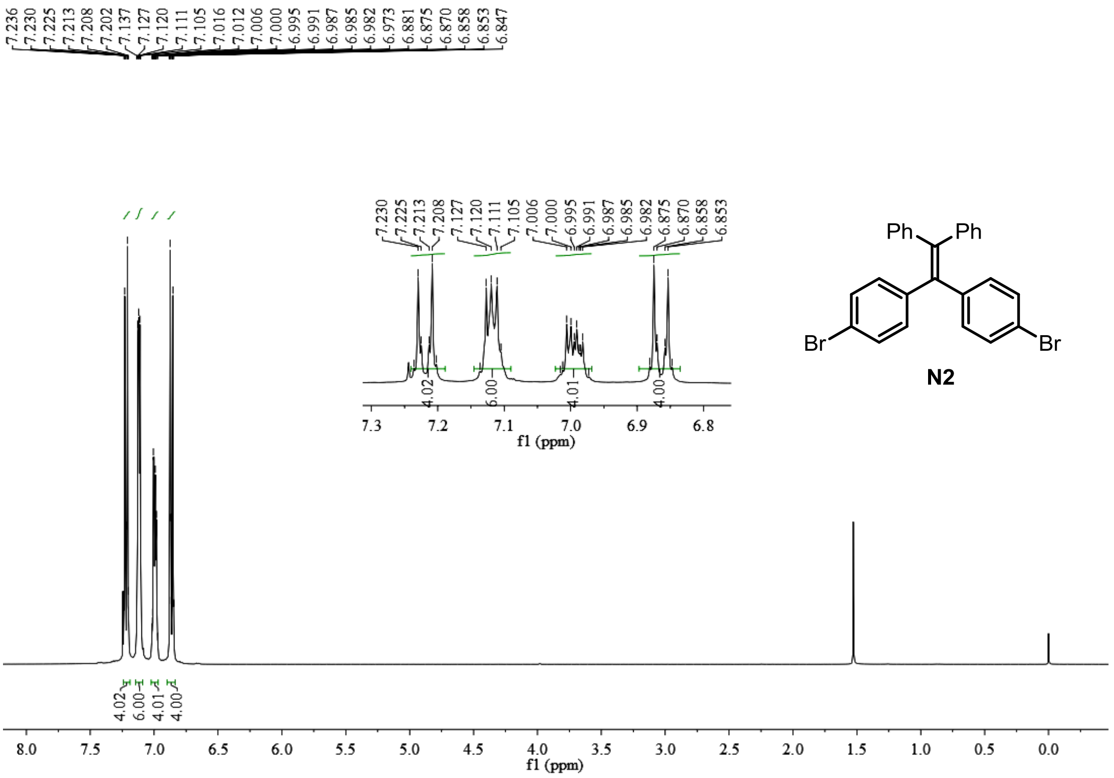


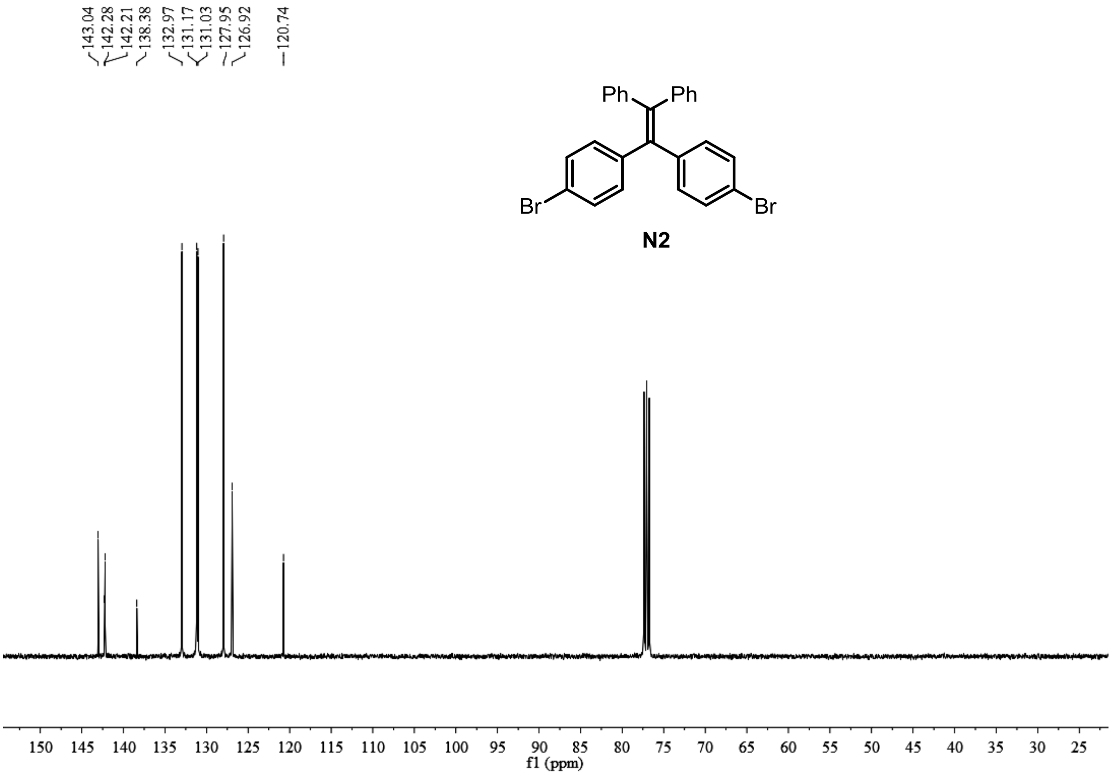
e) ^{1}H, ^{13}C spectra of **M5**



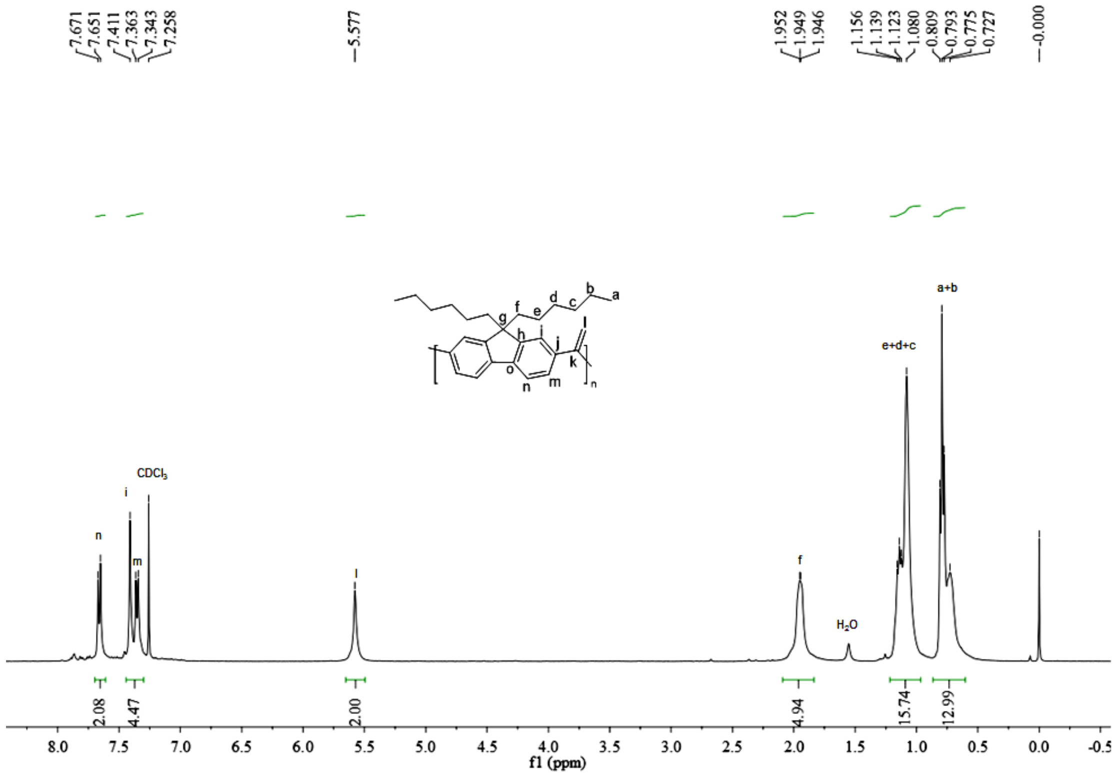


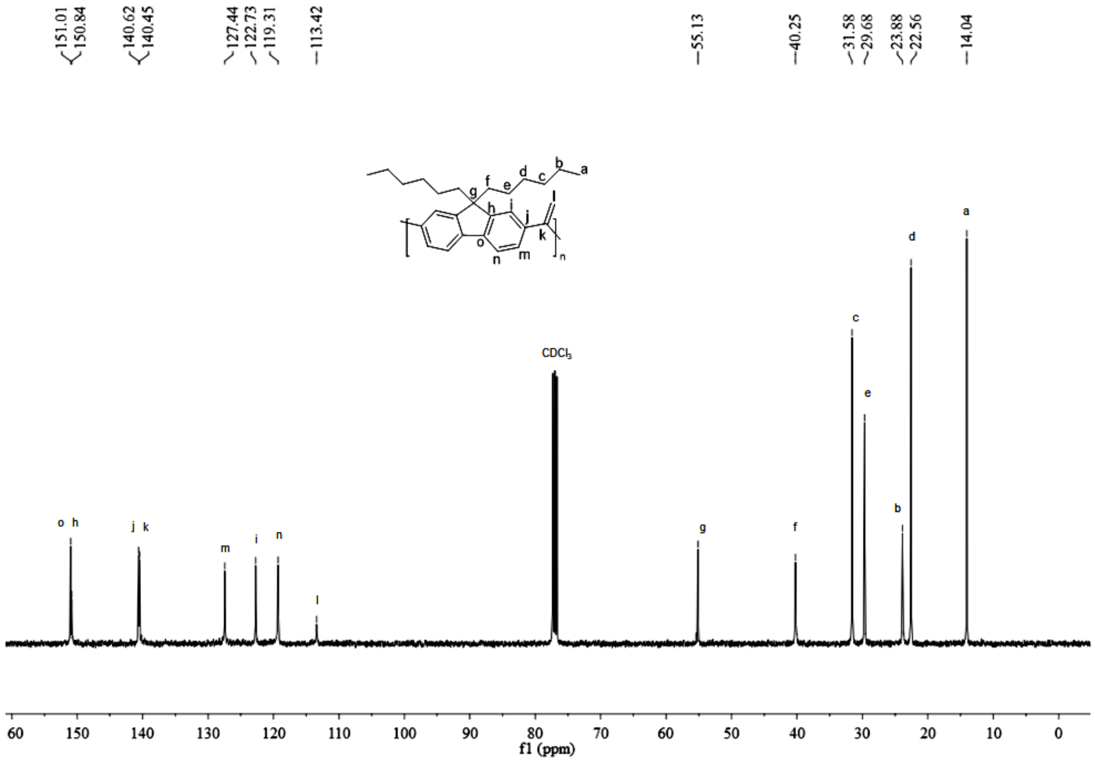
f) ^{1}H, ^{13}C spectra of **N2**



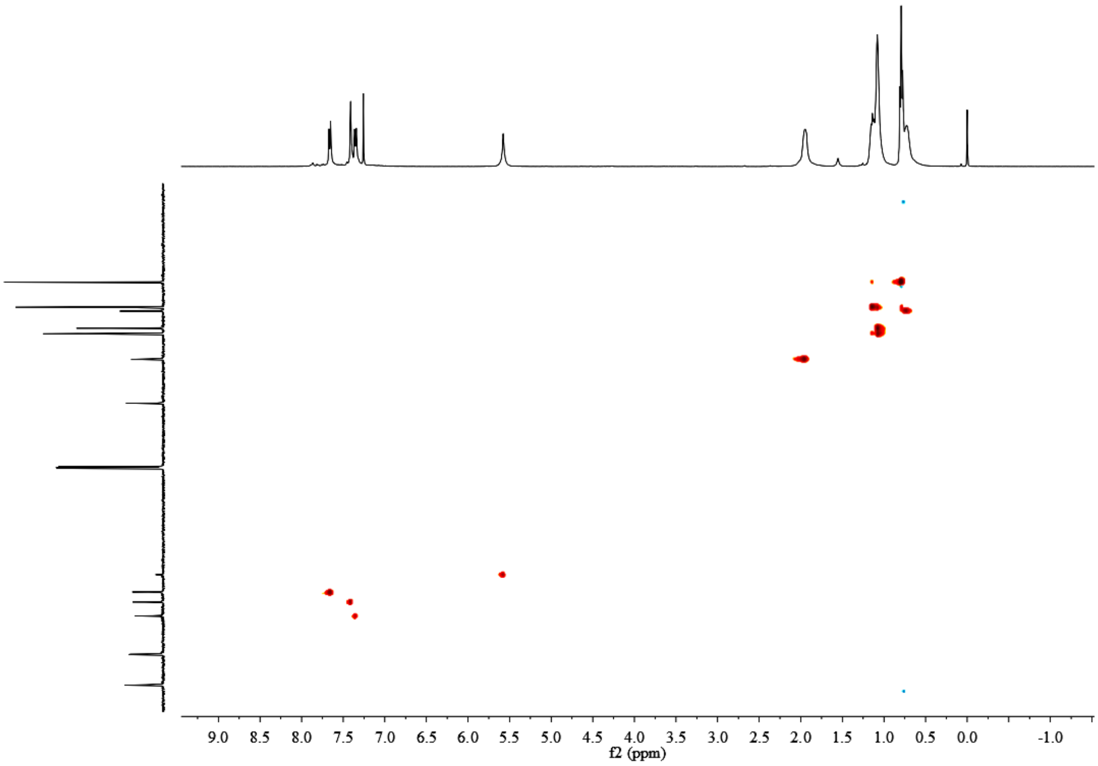


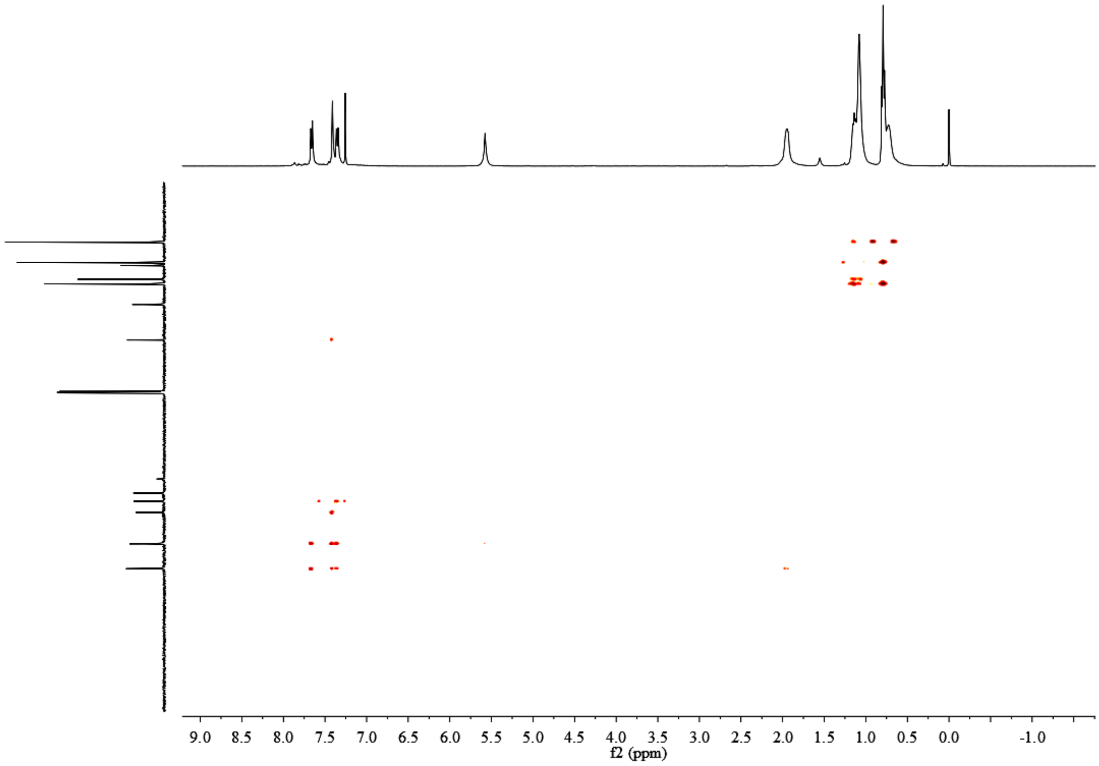
g) ^{1}H, ^{13}C spectra of **P1**



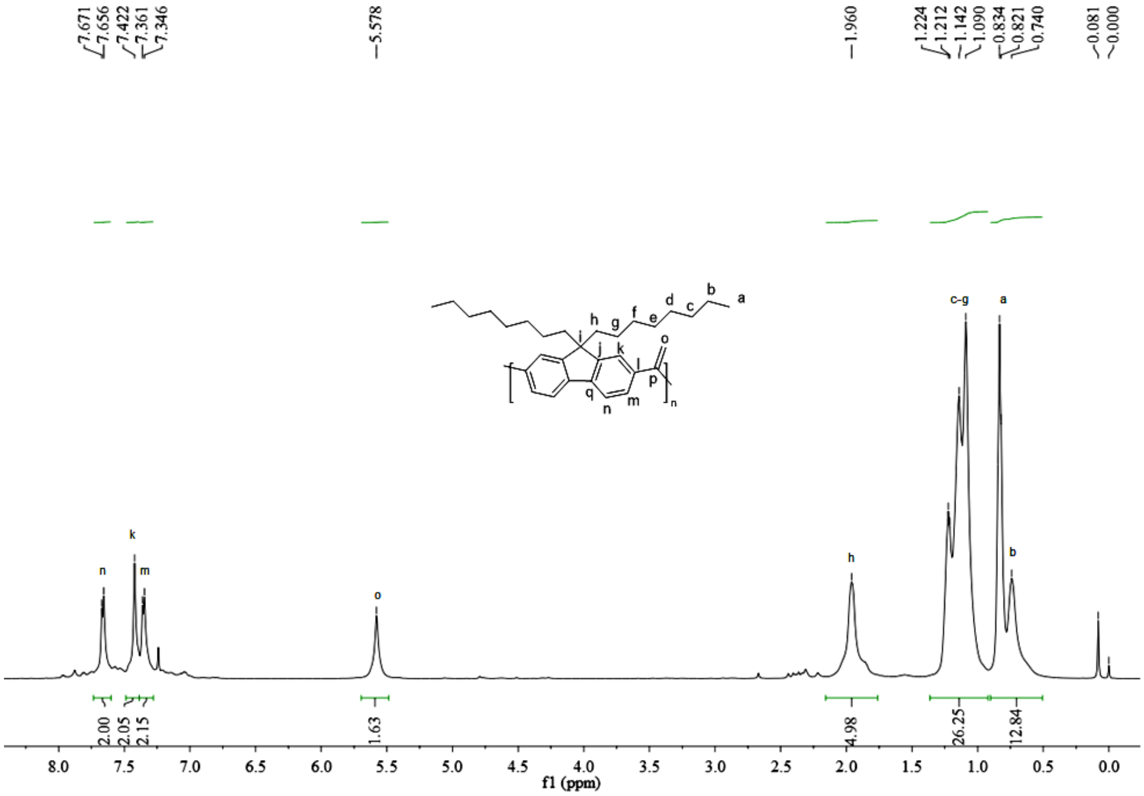


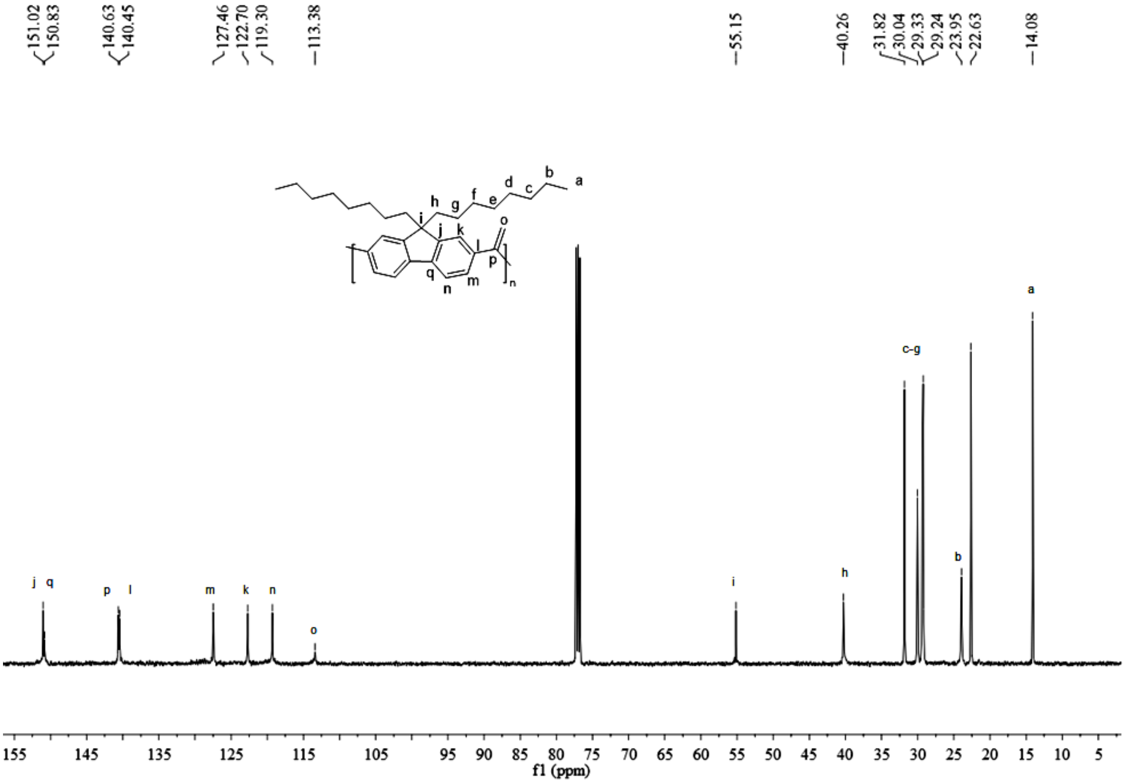
HSQC and HMBC spectrum of **P1**



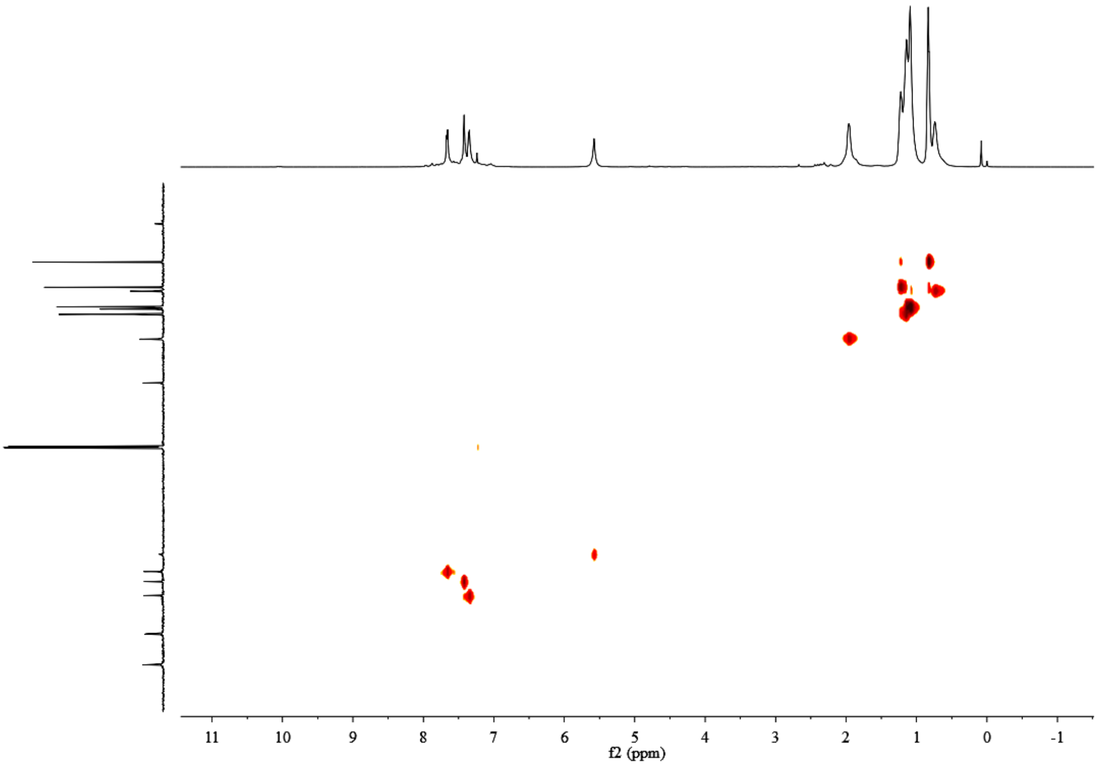


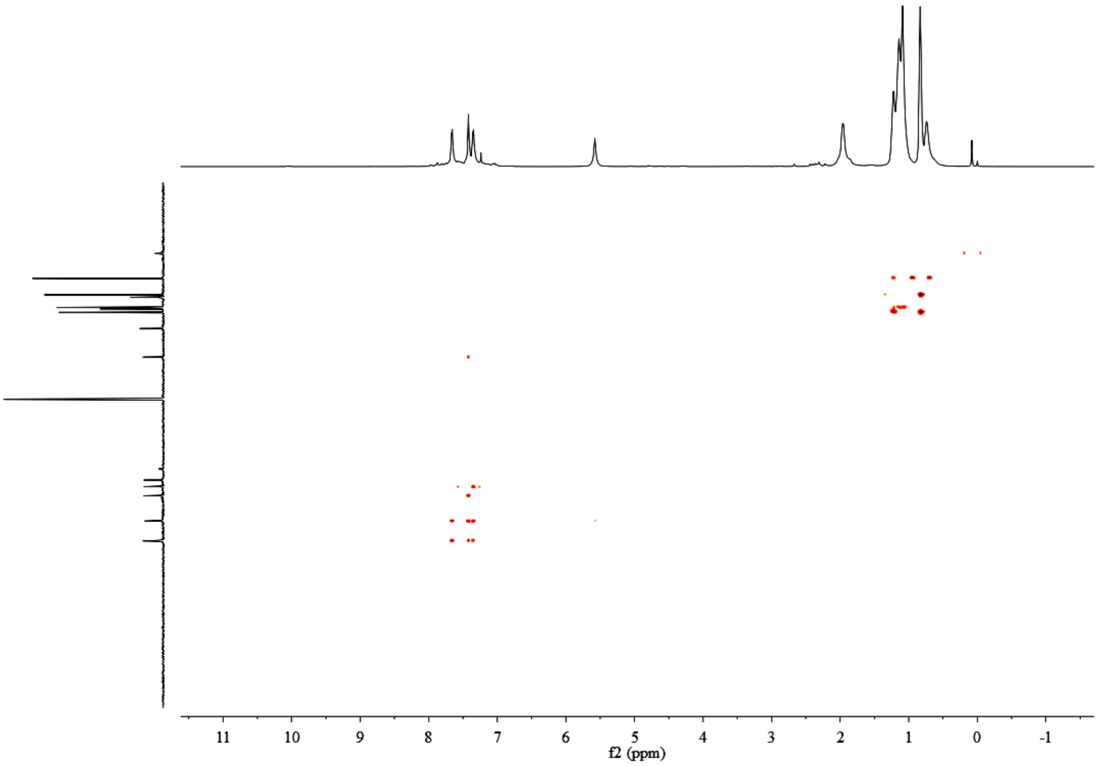
h) ^{1}H, ^{13}C spectra of **P2**



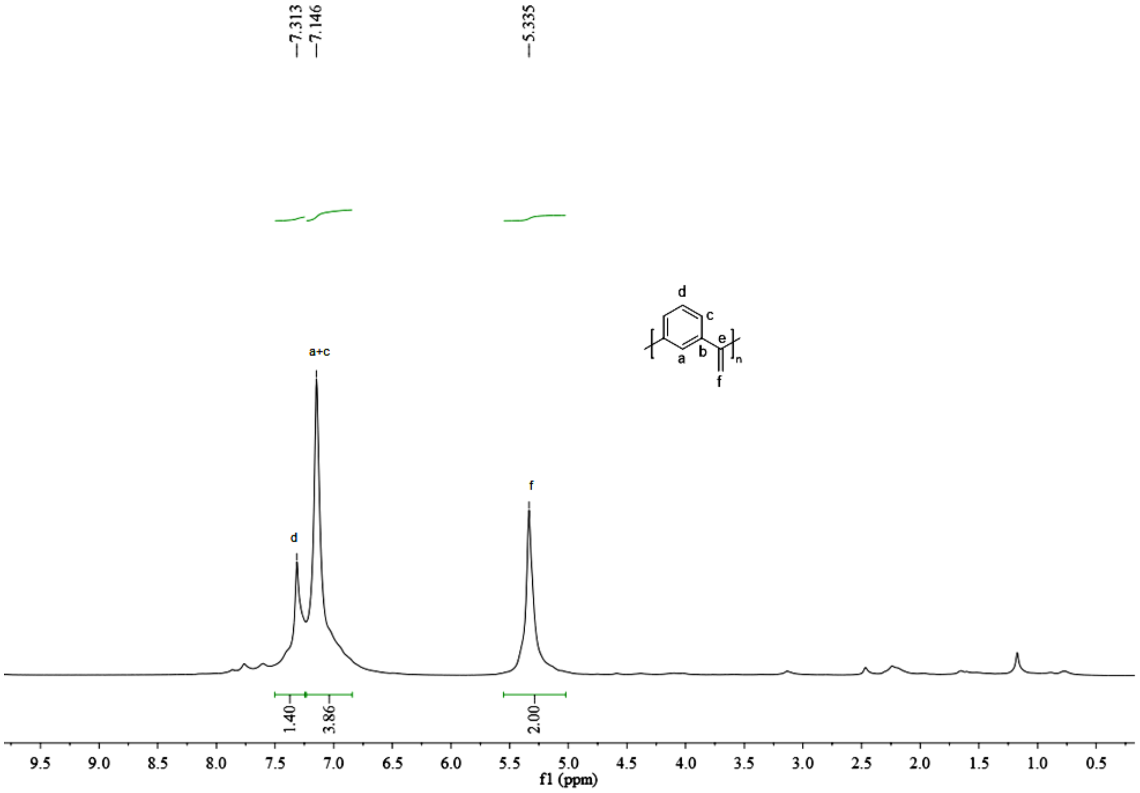


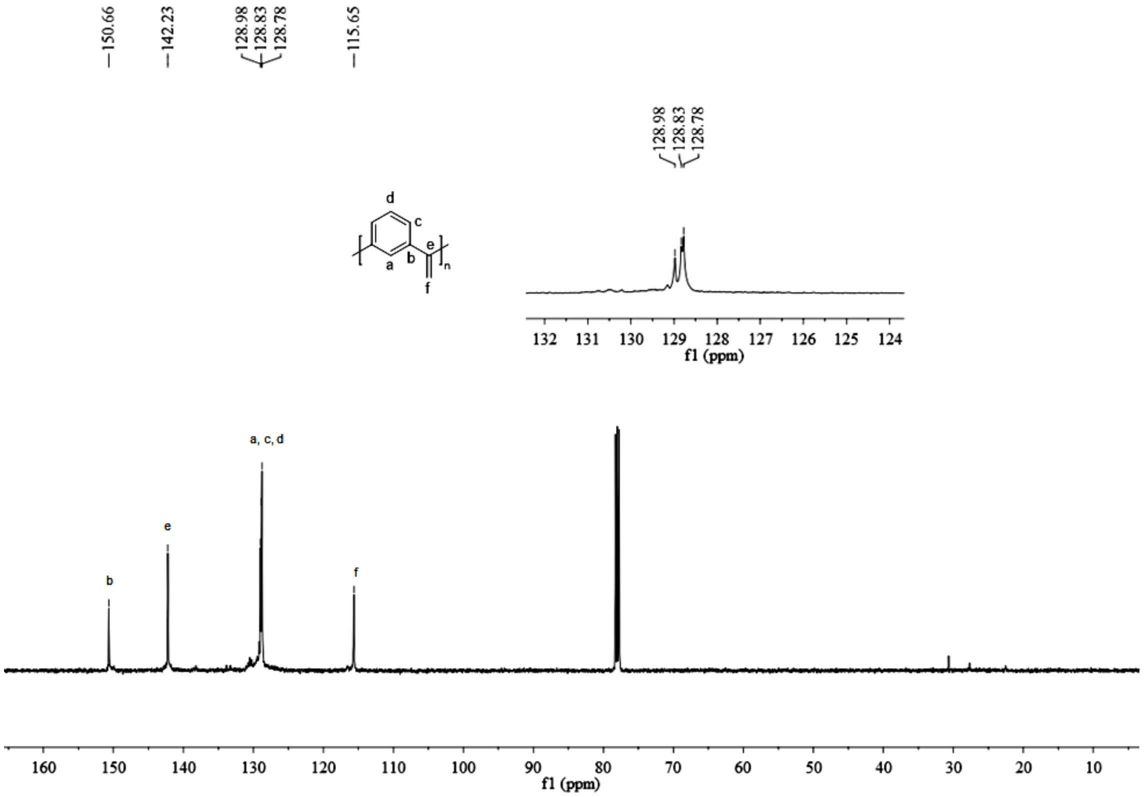
HSQC and HMBC spectrum of **P2**



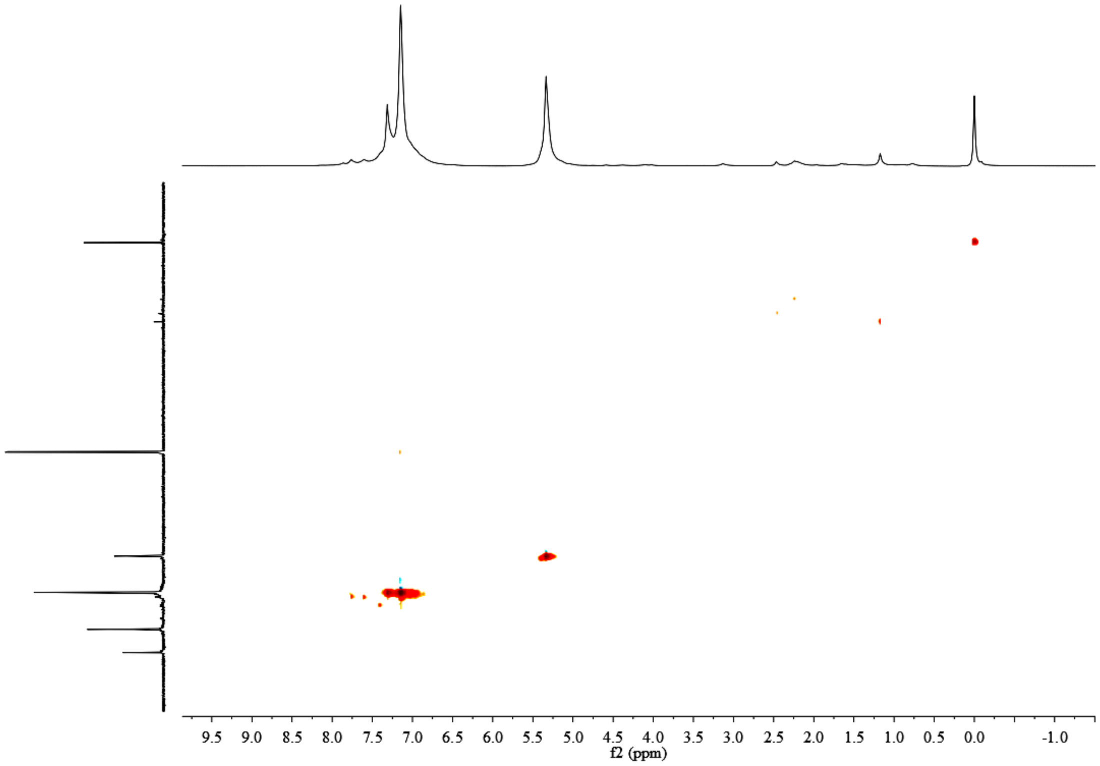


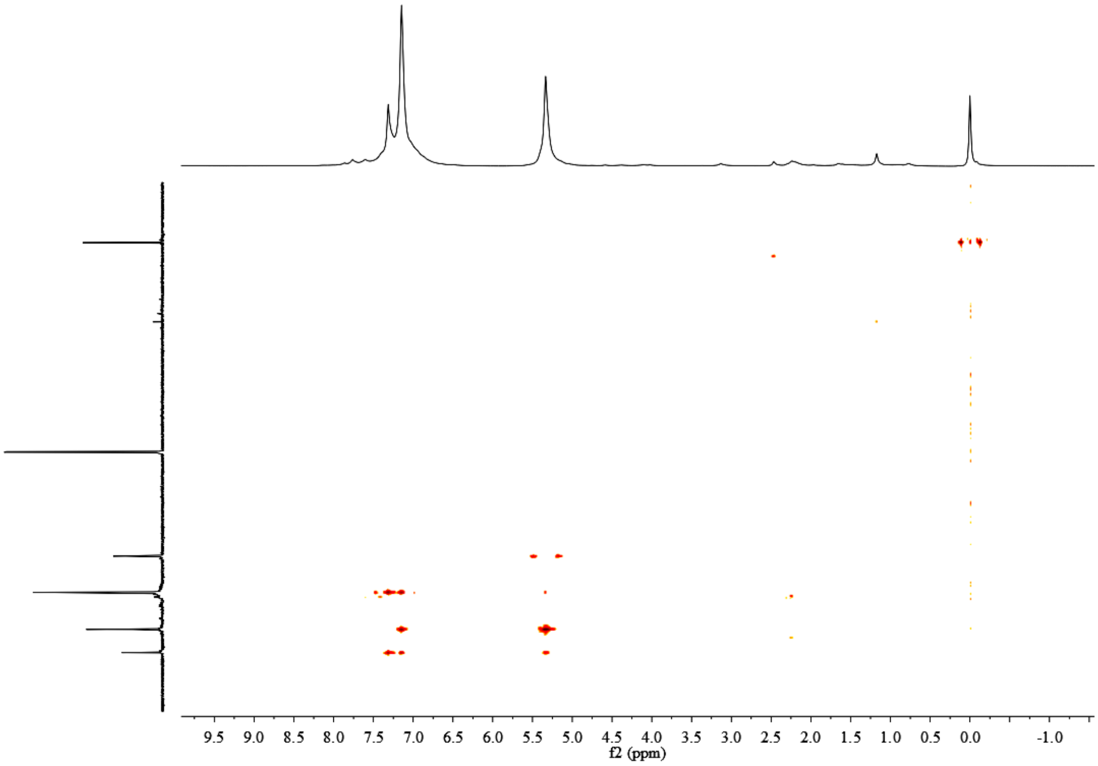
i) ^{1}H, ^{13}C spectra of **P3**



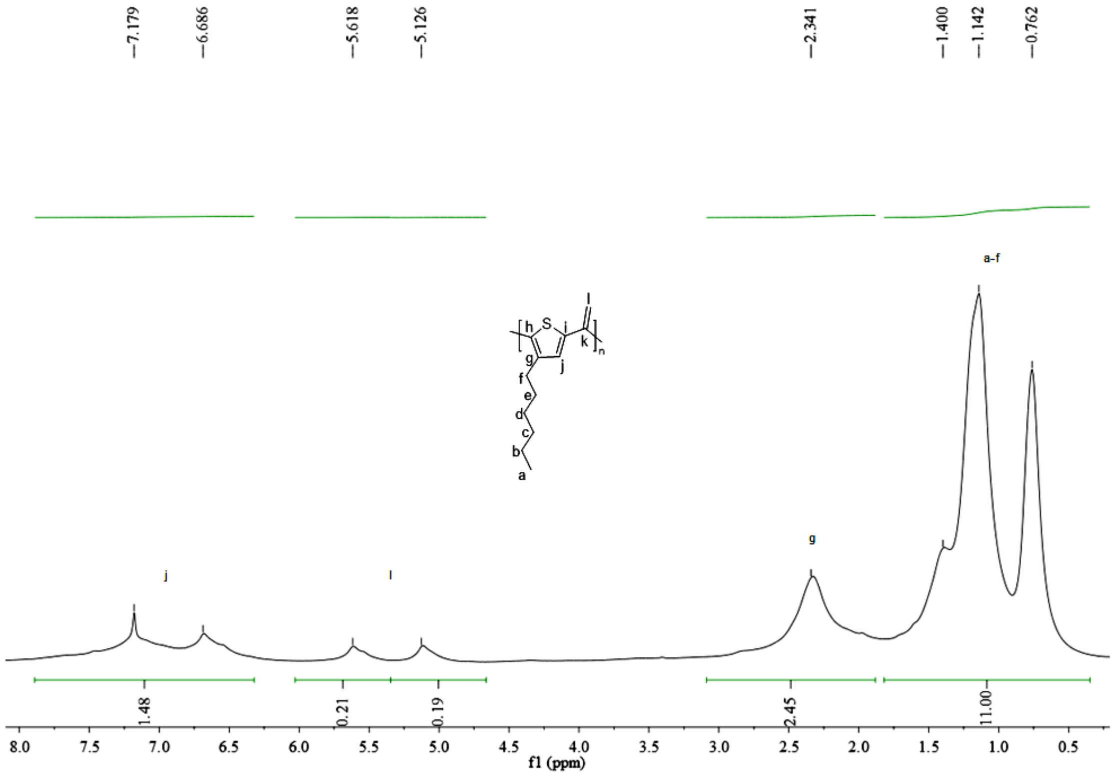


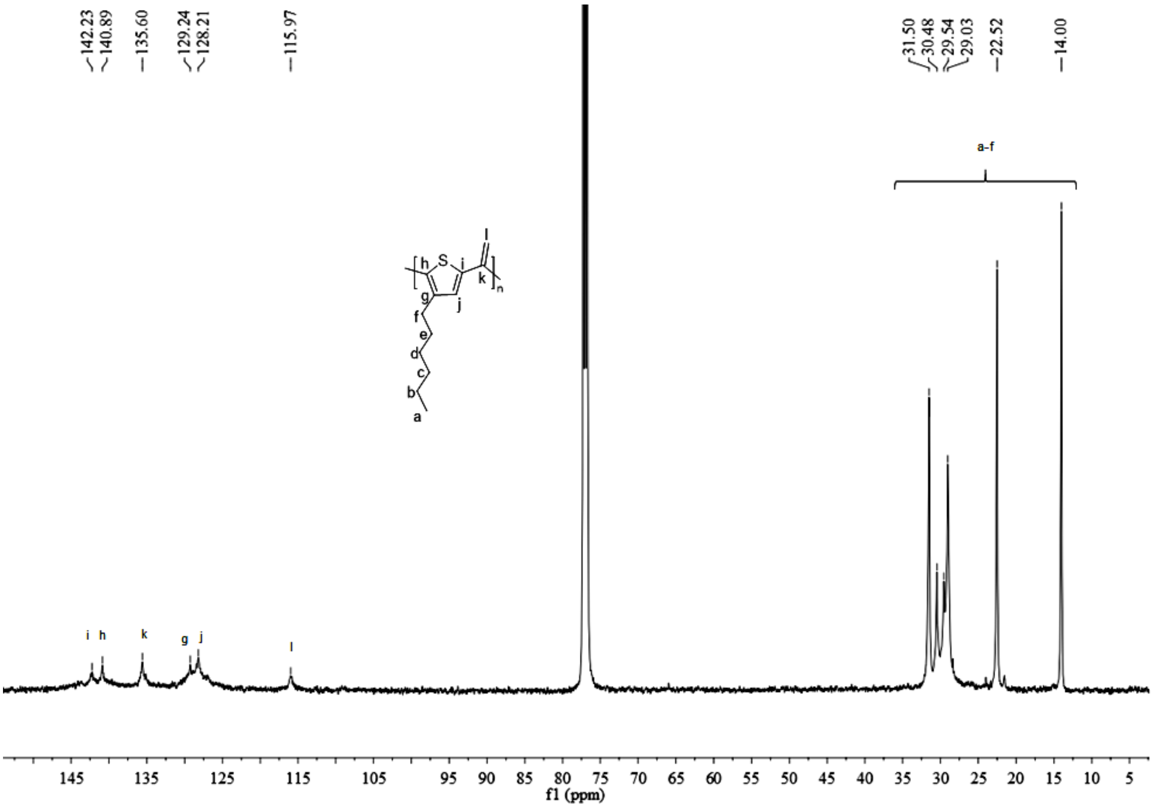
HSQC and HMBC spectrum of **P3**



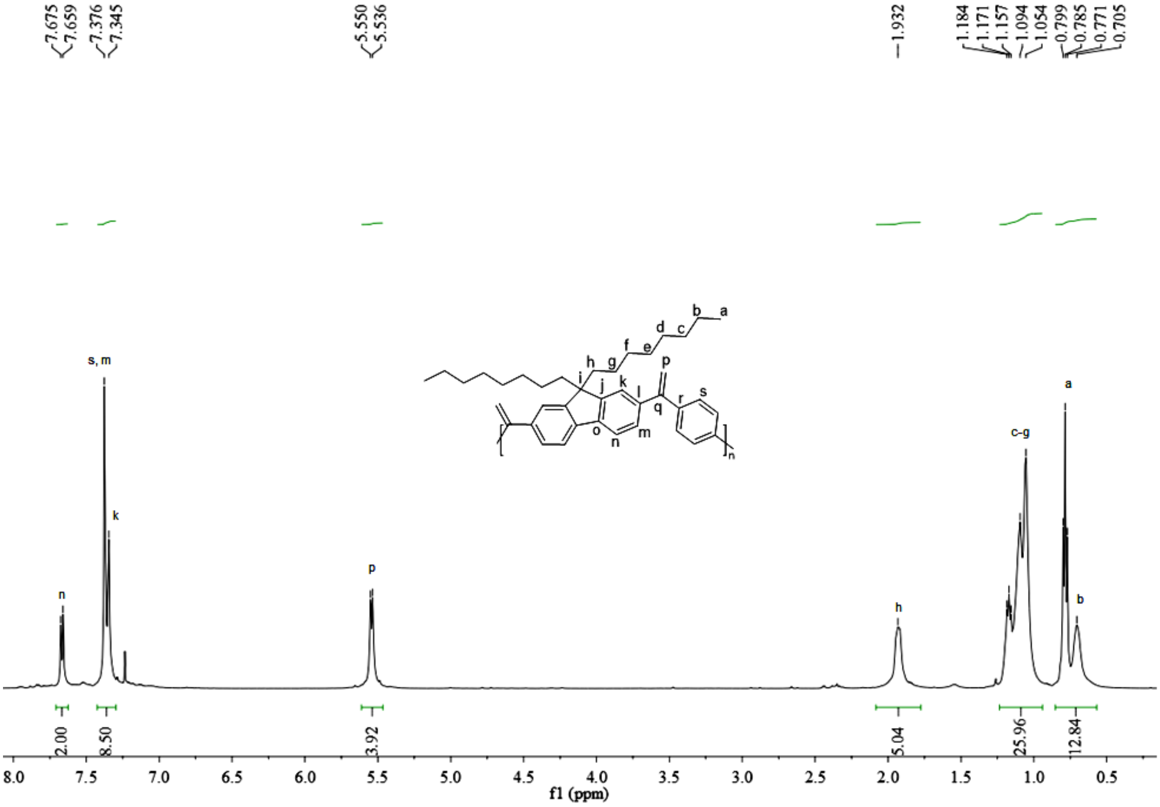


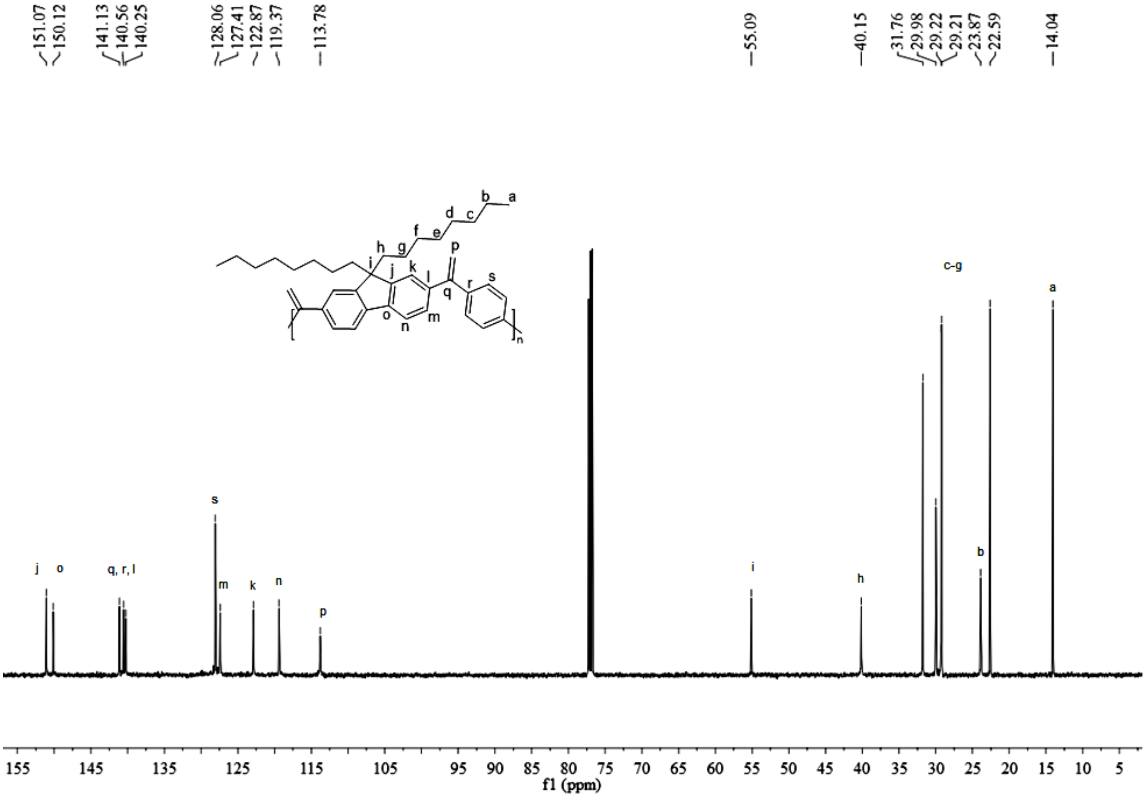
j) ^{1}H, ^{13}C spectra of **P4**



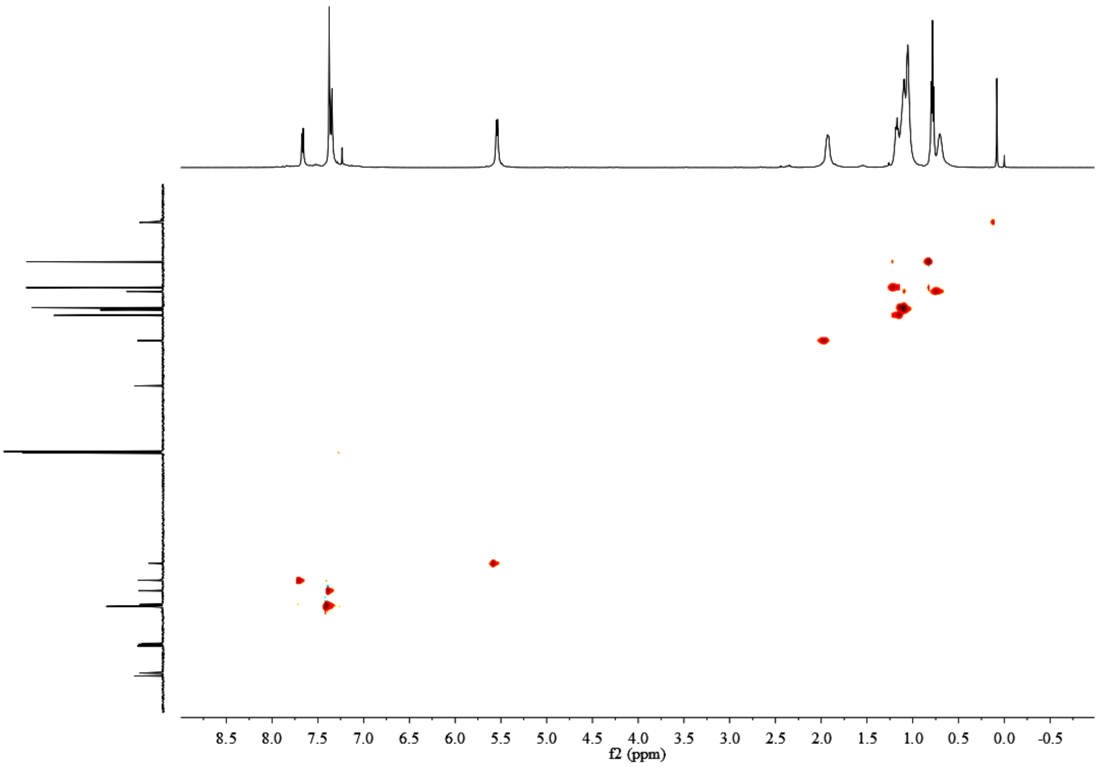


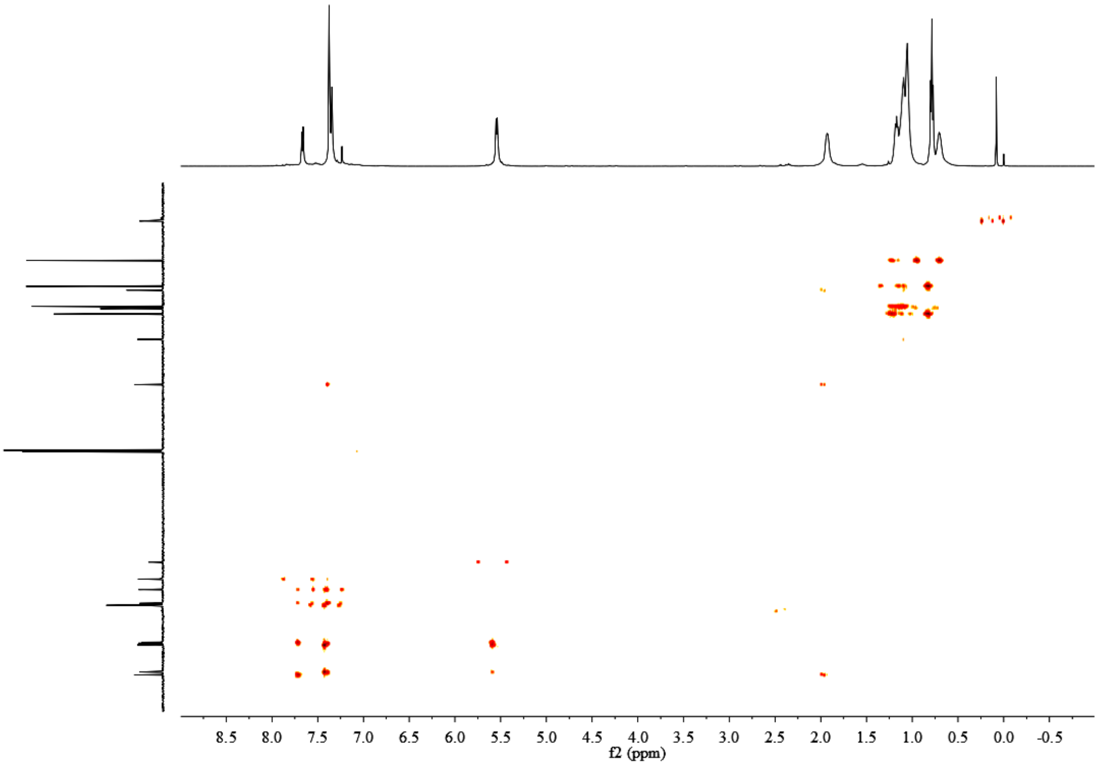
k) ^{1}H, ^{13}C spectra of **P5**





HSQC and HMBC spectrum of **P5**





l) ^{1}H, ^{13}C spectra of **P6**